DISSERTATION

UTILIZING SILICON FOR THE SYNTHESIS OF STEREODEFINED TRI- AND TETRASUBSTITUTED OLEFINS

Submitted by

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ABSTRACT

UTILIZING SILICON FOR THE SYNTHESIS OF STEREODEFINED TRI- AND TETRASUBSTITUTED OLEFINS

Functionalized organosilanes serve an important role as reactive precursors for a number of synthetic transformations. Consequently there is still great use for the development of new methods that allow for facile and efficient generation of organosilicon compounds. Herein, a number of such methods are described.

The stereoselective syntheses of α-silylenones using catalytic $PtCl_2$ are reported. Via alkyne activation, α-hydroxypropargylsilanes are converted to (*Z*)-silylenones through a highly selective silicon migration. A *trans* halosilylation of alkynes is also reported. Both the $PtCl_2$ catalyzed silyl migration the halosilylation reaction proceed through a 1,2-silicon shift onto the activated alkyne intermediate in an anti fashion relative to the activating agent. Both reactions afford excellent yields and selectivity for the product tri- and tetrasubstituted alkenes.

The high yielding Pt catalyzed hydrosilylation reactions of internal alkynes are described with a focus on understanding the factors that govern the regioselectivity of the process. Electronic, steric, and functional group properties all influence the selectivity, an understanding of which allows the selective formation of trisubstituted vinylsilanes, which are synthetically useful compounds for accessing stereodefined alkenes.

Finally, efforts to show the synthetic utility of tri- and tetrasubstituted vinylsilanes for the formation of C–C bonds using Hiyama coupling and halodesilylation reactions are reported. Hiyama couplings of tetraorganosilanes with and without the use of fluoride activators are thoroughly evaluated. Coupling reactions with vinylsiloxanes are also shown. Finally, stereoretentive halodesilylation reactions are explored with the product vinylhalides subsequently subjected to Suzuki cross coupling conditions affording high yields of highly substituted all-carbon alkenes with good retention of alkene geometry.

ACKNOWLEDGEMENTS

There are many people whom I need to acknowledge for making it possible to complete this dissertation. First, I must thank my advisor Dr. Eric Ferreira (the Boss) for his patience and guidance. Without him, I would have never made it this far. He is also one of the kindest guys I have ever met. I would also like to thank the Ferreira group for putting up with me for five years. The Rovis group has also been tremendously helpful, especially in my formative years. A personal shout-out is in order for Paul Allegretti, Eric Newcomb, Nick White, and Oz for being guys with whom I could always commiserate. My doctoral advisory committee (John Wood, Matt Shores, Olve Peersen, Yian Shi, and Nick Fisk) provided thoughtful and engaging discussions about my research.

Throughout my entire life, my family has been tremendously supportive of me. They have always provided me with the tools to succeed and have expected nothing in return. They have allowed me to make mistakes so that I may learn on my own but were always there to pick me up when needed.

Most importantly, I have to thank Holly and the Moose. Every day when I go home I feel as if I have won the game of life. I will leave it at that because, if I start gushing, it may turn into another thesis…

AUTOBIOGRAPHY

Douglas Rooke was born on August 1, 1985 in Seattle, Washington to Donna and Alec Rooke. Within a year, they moved to Shoreline, a suburb immediately north of Seattle. From a very young age, Doug showed tremendous interest in the sciences, often begging his parents to take him to the Pacific Science Center. This affliction was reinforced when he attended The Lakeside School in North Seattle from 7th through 12th grade. At Lakeside, he was very fortunate to have amazing science faculty who focused on engendering a love of research and experimentation. Although Doug enjoyed learning in high school, he rarely enjoyed studying. Instead, he was convinced that football, lacrosse, cross country skiing, playing guitar, and hanging out with his friends were much more valuable uses of his time. Unfortunately, the carefree days of high school came to a close and Doug had to make a decision on where to attend college. Being a prolific procrastinator, he waited until the very last day to make his decision, which ultimately came down to a coin flip between Colby College (tails) and Whitman College (heads).

Tails won, so Doug made the trek across the country to the tiny town of Waterville, Maine. At Colby, Doug was quite happy continuing his old high school habits of not studying until he took sophomore organic chemistry with Professor Jeff Katz. Doug quickly found himself in the library more and more, craving more organic chemistry knowledge. Shortly thereafter, Doug joined Professor Katz's lab where he worked on the synthesis of novel oxacalixarenes. Knowing that he truly loved research, Doug decided to pursue his PhD in organic chemistry at Colorado State University.

In the fall of 2008, Doug joined the lab of Professor Eric Ferreira. Joining a brand new lab was both daunting and exciting at the same time. Ultimately, it proved to be a valuable experience. In June 2013, Doug received his PhD for his work in organosilicon chemistry. In August 2013, Doug will be prolonging his adolescence for a bit longer by attending medical school at the University of Colorado.

DEDICATION

To Holly and the Moose

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Chapter One

Introduction to Silicon in Organic Synthesis

1.1 Brief History of Organosilicon Compounds in Synthesis

As an inexpensive, highly abundant element that also possesses very low toxicity, Si is an attractive choice as a synthetic handle.[1] The unique reactivity displayed by the C–Si bond can be harnessed with numerous transformations for the assembly of complex molecules. Fundamentally, the C–Si bond is relatively strong (~76 kcal/mol), making it generally stable under most conditions, however, due to the Pauling electronegativity differences (C = 2.55, Si = 1.90) the bond is still polarized toward carbon. Silicon also has a profound affinity for fluorine and oxygen. The inherent polarization of C–Si bonds, coupled with the thermodynamically favorable generation of Si–F and Si–O bonds can be exploited in a number of useful transformations such as the Brook rearrangement,[2] the Peterson olefination,[3] the Sakurai reaction,[4] the Tamao-Fleming oxidation,[5] and the Hiyama coupling.[6]

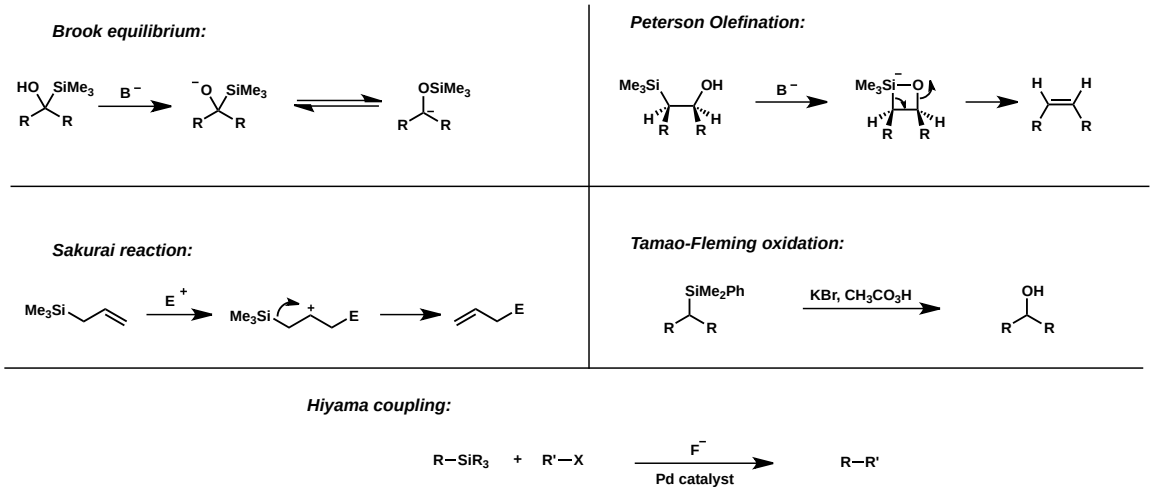

Figure 1.1.1 Common silicon based organic named-reactions

1.2 Vinylsilanes in Organic Synthesis

More specifically, the research described in this thesis will discuss the synthesis and utilization of highly substituted, stereodefined vinylsilane species in the context of cross coupling reactions for the downstream generation of C–C bonds. The synthesis of acyclic tri- and tetrasubstituted alkenes can be a challenging task for synthetic chemists.[7] The regio- and stereospecific addition of a silicon moiety to an alkyne presents an elegant solution to this problem. Herein, we describe three different methods for the stereospecific generation of highly substituted vinylsilanes.

The first is a novel Pt catalyzed, 1,2-silyl migration reaction of α-hydroxypropargylsilanes (**1**). This is a formal *trans* addition of silicon and hydrogen across the substrate alkyne that proceeds in high stereoselectivity and yield for the product α-silylenones (**2**).[8] There have been very few reports in the literature that involve such a silicon migration onto an alkyne, none of which are both catalytic and stereoselective.[9] The scope of this reaction will be shown in Chapter 2. Later, in the same chapter, a similar 1,2-silyl migration reaction is described; however, in this case, a net *trans* halosilylation onto the substrate alkyne (**1**) mediated by an *N*-halosuccinimide is observed.[10] The stereodefined product **3** contains two synthetic handles in the vinylsilane and vinylhalide moieties which can provide orthogonal handles for further divergent transformations.

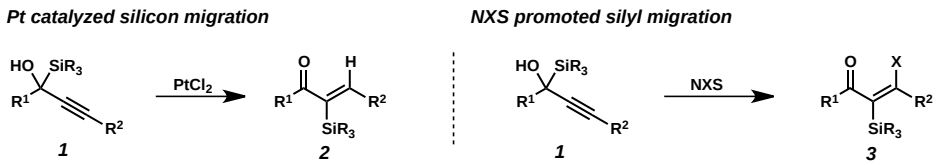

Figure 1.1.2 1,2-silyl migration reactions

A complementary method for the generation of trisubstituted silylalkenes is the catalytic hydrosilylation reaction. In the hydrosilylation reaction, a Si–H species is added across an

alkyne in a *cis* fashon. Such reactions have been the subject of decades of research by the synthetic community as a versatile reaction for the generation of vinylsilanes.[11] Although there are many different hydrosilylation catalysts, this thesis will focus on the Pt-catalyzed variants. While the regioselective Pt-catalyzed hydrosilylations of terminal alkynes are well established, their internal alkyne counterparts have received considerably less attention. We have developed a method that utilizes the polarization of electronically unsymmetrical internal alkynes to afford high regioselection for the Pt-catalyzed hydrosilylation event, which is elucidated in Chapter 3.[12]

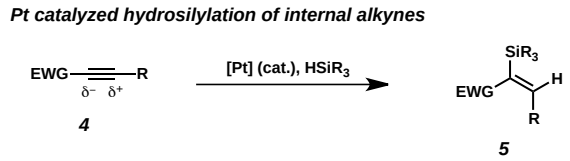

Figure 1.1.3 Internal alkyne hydrosilylation

To demonstrate the synthetic utility of our product vinylsilanes, Hiyama coupling and halodesilylation reactions were performed (Chapter 4). In the past 20 years, the Hiyama coupling has been the subject of a renaissance in the field of cross coupling chemistry. The pioneering work of both Hiyama and Denmark has laid the groundwork for the extension of this methodology for more widespread synthetic use. We have built upon this knowledge by exploring the Si mediated cross coupling reactions of hindered alkenes (**6**) as well as electron deficient alkenes (**7**). Furthermore, progress was made to employ fluoride free silicon activation conditions which would avoid the potentially deleterious effects of a fluoride base.[13]

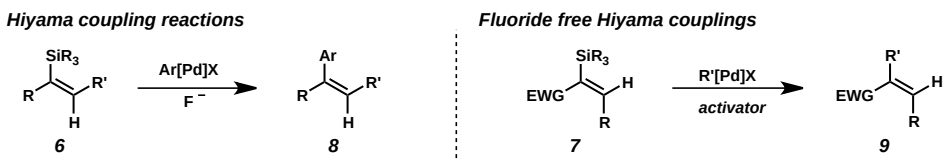

Figure 1.1.4 General Hiyama couplings

Finally, halodesilylation reactions that selectively proceed with stereoretention or inversion are shown. The product vinylhalide can be subsequently employed as an electrophile in cross coupling reactions.

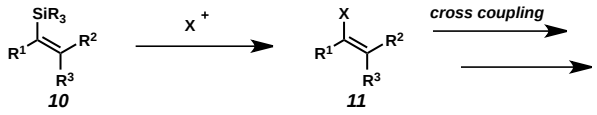

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Figure 1.1.5 Utilization of halodesilylation

CHAPTER ONE NOTES AND REFERENCES

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CHAPTER TWO

$PtCl_2$ Catalyzed and *N*-Halosuccinimide Mediated 1,2-Silyl Migration Reactions

2.1 Introduction

Lewis acid-mediated and catalyzed additions of nucleophiles into alkynes have been widely studied.[14] More commonly called alkyne activation, transformations of this sort have shown great promise for synthetic chemists as a means to rapidly generate molecular complexity.[15] Typically these systems are paired with some sort of tethered nucleophile, such as alkenes, carbonyls, ethers, or strained carbocycles. The nucleophilic species adds to the activated alkyne affording isomerization based products of increased molecular complexity. The use of π-acidic metals, particularly complexes based on gold and platinum, to render an alkyne electrophilic, has recently come to the forefront of catalytic alkyne activation transformations.[16] Electrophilic halogen sources have also been shown to be efficient promoters of alkyne activation reactions. Our group entered this field with the curiosity to probe whether the C–Si bond, with its intrinsic electron rich nature, could act as a nucleophile in a similar reactivity mode to generate metal carbenoid species. Although that goal has yet to be realized, two novel 1,2-silyl migration reactions were discovered and elucidated. Both methods proceed in excellent yields and selectivity and should find use in the synthetic community. Using Pt^{2+} to activate alkynes, we were able to develop a method to produce stereodefined trisubstituted alkenes.[17] From our original report utilizing alkynophilic metals, we were able to extend the methodology to electrophilic *N*-halosuccinimides affording tetrasubstituted alkenes.[18]

2.2 Background

2.2.1 Alkyne activation

Late transition metals such as Au and Pt have been implicated in countless alkyne activation reactions, and this field has blossomed as a result of two decades of intense research.[19] The mechanisms of these isomerization based transformations all begin with rendering an alkyne electrophilic. Recently much of the focus of alkyne activation has focused on utilizing the intrinsic π-Lewis acidity of late transition, noble metals.

The basis of coordination for alkyne π-systems and transition metals is typically discussed in the context of the Dewar-Chatt-Duncanson (DCD) model.[20] In this model, the nature of the bonding between the metal and the alkyne can be described as initial donation of π-bond electron density into an empty [M] orbital creating, a σ-type bond. In the cases of both Au and Pt, the back donation is relatively weak.[21]

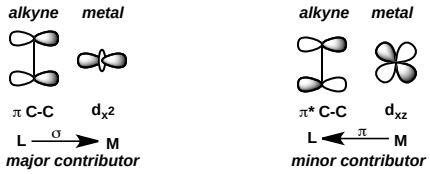
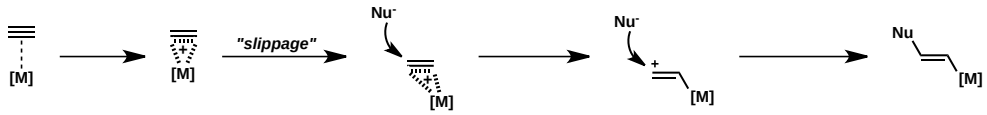


Figure 2.2.1 Transition metal-alkyne ligand orbital interaction diagram

At this point the Lewis acidic metal has rendered the alkyne electrophilic and susceptible to nucleophilic addition. As the nucleophile initiates the attack on the opposite face of the metal coordinated alkyne, the metal slips from an η^2 to an η^1 mode of coordination. Finally, the full trans-based attack is completed with one alkyne carbon is bound to the nucleophile and the other is bound to the metal in full η^1 coordination.



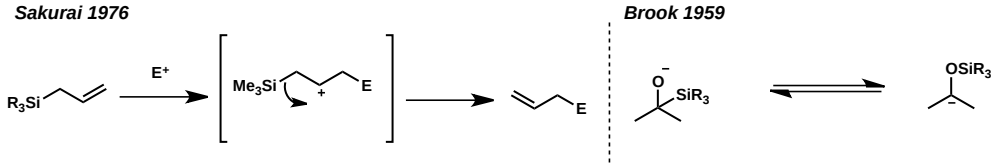
Scheme 2.2.1 Basic mechanistic steps for π-acid catalyzed nucleophilic addition into an alkyne

The utilization of this mechanistic sequence has been extensively and variously applied to many different nucleophilic species for alkyne attack.[16,19] In the Ferreira lab we have focused on enantiospecific enyne cycloisomerizations,[22] furan syntheses,[23] and isoxazole syntheses.[24] My personal contribution to this field has been the expansion of this methodology to utilize the carbon silicon (C–Si) bond as a nucleophilic species for the attack of an π-acid activated alkyne.

2.2.2 Carbon silicon bond nucleophilicity

Compared to many other carbon-metalloid bonds (C–P, C–Al, C–B, C–Sn, etc.), C–Si bonds are frequently robust and stable to many common synthetic condition sets. The intrinsic stability of the C–Si bond, together with the low reactivity and minimal toxicity of silicon, make the development of methods utilizing organosilicon compounds quite attractive.[25] Perhaps the most famous examples of this are demonstrated in the Sakurai reaction and the Brook rearrangement. In the Sakurai reaction, π-electrons from an allylsilane attack an electrophile. This process is driven by the favorability of a β-silyl carbocation stabilized by hyperconjugative donation by the C–Si bond. The ultimate nucleophilicity of the C–Si bond is realized when it is dissociated heterolytically and quenches the carbocation.[26] The concept has even been applied in a few cases to propargylsilanes and carbon-based electrophiles to form allenes.[27] Another well-known organosilicon reaction is the Brook rearrangement, which again relies on the polarizability of the

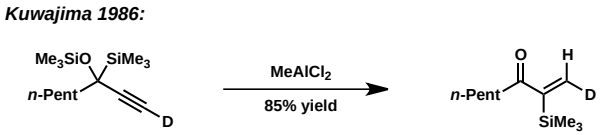
C–Si bond and the increased stability of the O–Si bond.[28] The consequence of the forward Brook rearrangement is the formation of a carbanion where the silicon was once appended.



Scheme 2.2.2 Sakurai and Brook reactions

2.2.3 Silicon Migration

Although there has been, and continues to be, substantial focus on 1,2-silyl migrations as they pertain to allylsilane substrates,[29] there is a dearth of reported instances of 1,2-silyl migrations of propargylsilanes. The first example in the literature was by Kuwajima in 1984, where a TMS-protected α-hydroxypropargylsilane was subjected to a stoichiometric amount of $MeAlCl_2$ to form α-silylenones.[30] More interestingly, they were able to show that the transformation proceeds with the Si group adding into the alkyne in an *anti*-attack relative to the coordinated Lewis acid.

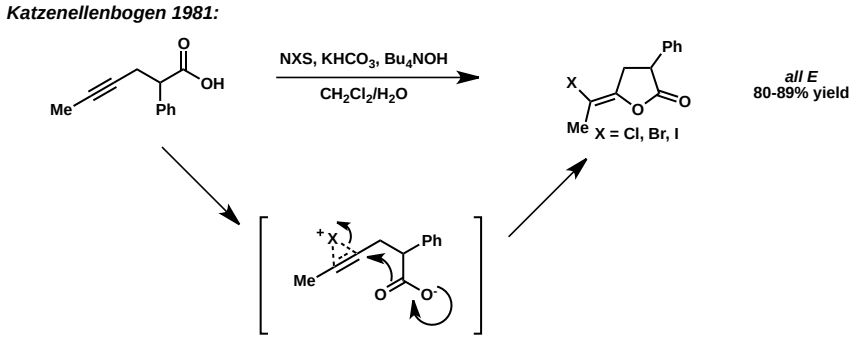


Scheme 2.2.3 First reported silyl migration onto and alkyne

Subsequent to Kuwajima's report, similar observed silicon migrations have been rare and often found as low yielding byproducts of desired transformations.[31]

2.2.4 Alkyne Addition Into a Halogen Electrophile

Electrophilic halogen sources have been widely shown for the activation of alkynes most often in the form of intramolecular cyclizations.[32] Katzenellenbogen reported one of the very first examples of this transformation in 1981. Distal acetylenic carboxylic acids were subjected to base and *N*-halosuccinimides (NXS) to afford halolactonization products. All examples were completely *E*-selective, and they surmised that a discrete halonium ion is formed followed by *anti* carboxylate attack.[33]



Scheme 2.2.4 Early halolactonizations

Subsequently, hundreds of different electrophilic halogen promoted alkyne cyclizations have been reported utilizing an array of nucleophiles, most typically heteroatoms.[34] Similar reactions involving an exogenous nucleophile are few.[35] Acyclic reactions with intramolecular delivery of the nucleophile are non-existent.

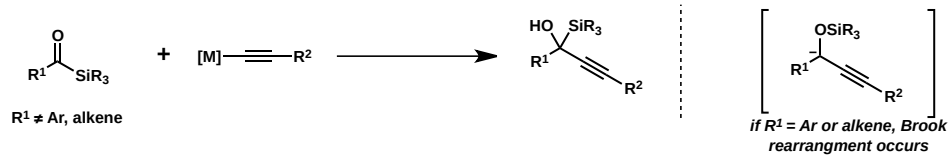
2.2.5 Background Summary

Extensive research has been performed on Lewis acidic alkyne activation with either electrophilic halogen sources or π-acidic metals. However, there has been a dearth of research on the nucleophilic addition of Si species into alkynes. We began our research program to expand alkyne activation methodology to utilize the nucleophilicity of the C–Si bond in our stereoselective syntheses of tri- and tetrasubstituted alkenes. We hypothesized that α-hydroxypropargylsilanes would serve as a set of readily accessible compounds with which alkyne activation could be employed to access new reaction manifolds. Like other systems, α-hydroxypropargylsilanes provide an intramolecular delivery of the nucleophile. The intramolecular attack, however, would come from a 1,2-shift of the silicon group rather than a tethered nucleophile, thus allowing for a new mode a reactivity that would afford stereodefined acyclic alkenes.

2.3 Platinum Catalyzed 1,2-Silyl Migration Reactions

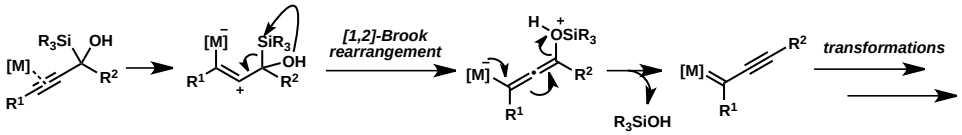
2.3.1 Initial experiments

Our model α-hydroxypropargylsilanes can be easily synthesized by simple Grignard addition of various terminal metal acetylides into acylsilane precursors. This general entry allows for divergent syntheses of a large number of α-hydroxypropargylsilane substrates. These additions generally proceed without incident, with the exception of aryl and vinyl acylsilanes, which promote the Brook rearrangement due to the relative stability of the carbanion.



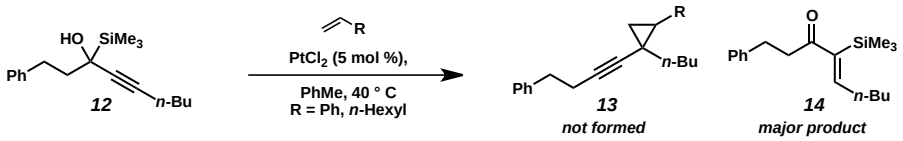
Scheme 2.3.1 Synthesis of α-hydroxypropargylsilanes

Using established protocols by Scheidt and others we were able to access the α-hydroxypropargylsilanes in short order.[36] Initially, we envisioned these substrates could engage in a "pull-push" type of mechanism where an alkynophilic transition metal species coordinated to the alkyne would induce a [1,2]-Brook rearrangement, forming an allene intermediate. The resulting metal anion would then push an electron pair back into the allene, releasing the silanol, and ultimately affording a reactive propargylic metallocarbene.[37]



Scheme 2.3.2 Proposed Metal-Carbene Generation

However, when **12** was subjected to $PtCl_2$ in PhMe at 40 °C in the presence of styrene or 1-octene as a trap for any potentially generated carbene species, no products that could have arisen from carbene generation were observed. Instead both reactions formed the exact same product, which was shortly determined to be α-silylenone **14**.



Scheme 2.3.3 Attempted carbene generation

Intrigued by this unprecedented reactivity, we decided to further investigate this transformation by optimizing and expanding its scope. It was determined that the added olefin has no observable effect on reactivity, and the rearrangement proceeded to afford **14** in 95% yield with or without the presence of added olefin. Analysis of the ^{1}H NMR spectrum showed a product ratio of 6 to 1 favoring the *Z*-isomer. The stereochemical assignments by NMR matched those of known compounds in the literature.[38] Enone **14** was further reduced to vinylsilane **15** and *NOE* studies confirmed the conjectured selectivity of the rearrangement.

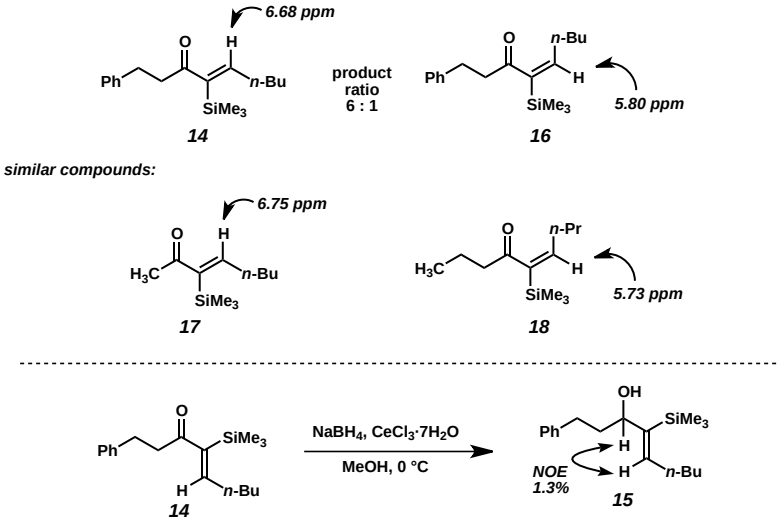
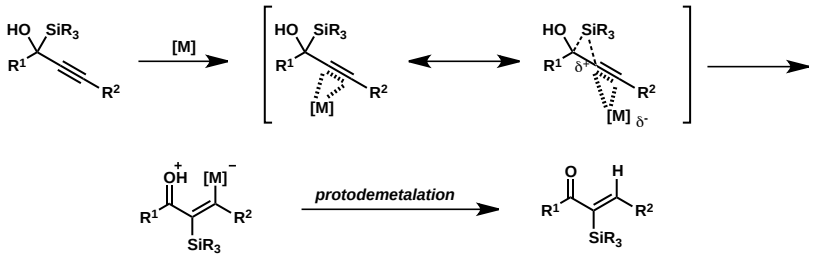


Figure 2.3.1 Determination of alkene stereochemistry

The mechanism for this transformation is likely akin to other alkynophilic metal rearrangements.[19] First, the [Pt] coordinates to the alkyne with η^2 hapticity. As the C-Si bond begins to donate into the alkyne *anti* to the coordinated metal, the metal begins to slip toward an η^1 mode. A 1,2-silyl migration then occurs, facilitated by the donation of electron density into the developing carbocation by the alcohol oxygen's lone pairs. This results in an α,β-unsaturated oxocarbenium metalloanion species that can perhaps undergo an intramolecular proton transfer, thus affording the product enone.



Scheme 2.3.4 Proposed mechanism

Although the conditions of $PtCl_2$ and toluene at 50 °C resulted in excellent yields for the rearrangement, the *Z*-selectivity of only 6 to 1 required improvement. In a solvent screen of DCM, DCE, THF, MeCN, and DMF, only DCE at elevated temperature (50 °C) showed any, albeit very little, formation of enone **14**, whereas the reactions involving the other solvents only resulted in recovered starting material.

A number of different known alkynophilic metals were also screened. Aside from both Au and Pt species, all other metals did not effect the desired rearrangement to the α-silylenone. Au(I) and Au(III) chlorides effected complete consumption of starting material (Table 2.3.1, Entries 8 and 9); however the major products of these reactions were the protodesilylated enones and the final product ratios were almost 1:1 *Z/E*. Using a cationic Au complex afforded excellent selectivity (>19:1 α/β) but only in 76% isolated yield (Table 2.3.1, Entry 10) of **14**. Returning to $PtCl_2$, it was found that running the reaction at lower temperature did not effect any conversion to product. Instead, surprisingly, upon increasing the reaction temperature to 80 °C the product ratio dramatically increased to >19:1 (Table 2.3.1, Entry 13). The best way to account for this observation is that the increase in temperature likely increases the reaction rate of the 1,2-silyl migration process significantly, more than the increase in rate for the background $PtCl_2$ catalyzed

product alkene isomerization. Indeed, upon resubjecting **14** to the reaction conditions, noticeable olefin isomerization did occur over time.

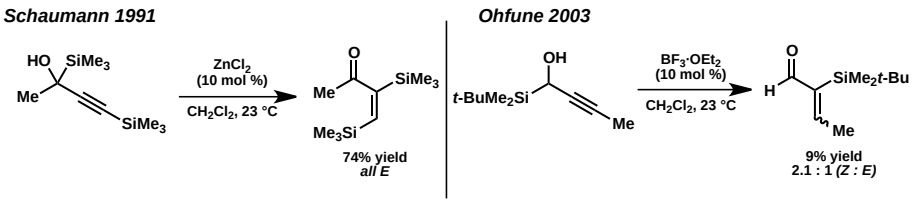
Table 2.3.1 Metal catalyst screen

Entry	Catalyst (5 mol %)	Solvent, temp (°C)	Time (h)	Conv. (%)[a]	Isomer Ratio (*Z* : *E*)[a]
1	$RuCl_3$	$PhCH_3$, 70	72	< 5	--
2	$IrCl_3$	$PhCH_3$, 70	72	< 5	--
3	$RhCl_3$	$PhCH_3$, 70	72	< 5	--
4	CuI	$PhCH_3$, 70	48	0	--
5	$PdCl_2$	$PhCH_3$, 70	48	< 5	--
6	$CpRu(CH_3CN)_3PF_6$	$PhCH_3$, 50	36	< 5	--
7	$(Ph_3P)_3RuCl_2$	$PhCH_3$, 50	36	< 5	--
8	AuCl	$PhCH_3$, 50	5	100	1.7 : 1[b]
9	$AuCl_3$	$PhCH_3$, 50	5	100	1 : 1.7[b]
10	Au complex[c]	$PhCH_3$, 40	1	100 (76[d])	>19 : 1
11	$PtCl_2$	$PhCH_3$, 35	48	0	--
12	$PtCl_2$	$PhCH_3$, 50	3.5	100 (95[d])	6 : 1
13	$PtCl_2$	$PhCH_3$, 80	2	100 (99[d])	> 19 : 1
14	$ZnCl_2$	CH_2Cl_2, 23	4	0	--
15	$ZnCl_2$	$PhCH_3$, 50	4	0	--

a) Measured by ^1H NMR b) Significant quantities of protodesilylated enones were observed
c) Au complex: Chloro[2-(di-*tert*-butylphosphino)-biphenyl]gold(I) (5 mol %) + $AgSbF_6$ (20 mol %)
d) isolated yield

While the observed excellent *Z*-selectivity of this transformation is unprecedented, there is precedent for this metal-induced alkyne activation and subsequent silyl group shift. In 1991, Ernst Schaumann's group discovered similar reactivity using zinc chloride. The salient difference is that they observed only (*E*)-enones.[39] The acetylenic TMS group also seems to be a requirement for the $ZnCl_2$ mediated rearrangement, since subjecting **12** to the zinc catalyst results in no conversion (Table 2.3.1, Entries 14 and 15). In a 2003 report on their studies of α-silylcarbocations, Ohfune and co-workers also observed a [1,2]-silyl group shift in trace yield

and selectivity using a catalytic amount of BF_3•Et_2O.[40] Also, **12** was subjected to TFA at 80 °C with only starting material recovered, suggesting that Brønsted acids do not promote the 1,2-silyl migration.

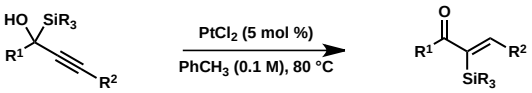


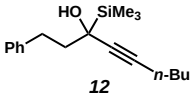
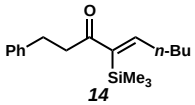
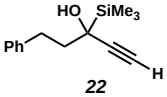
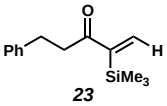
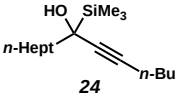
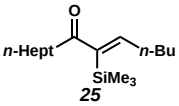
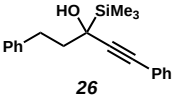
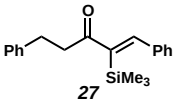
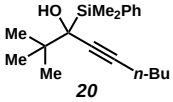
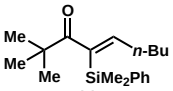
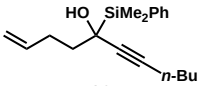
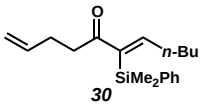
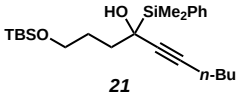
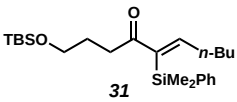
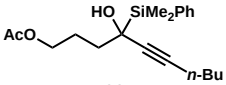
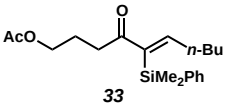
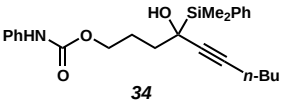
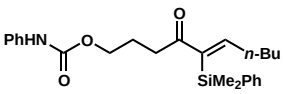
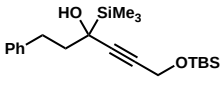
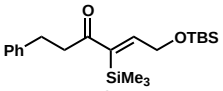
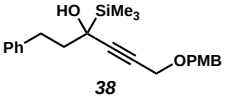
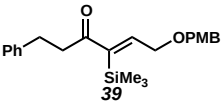
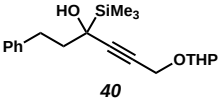
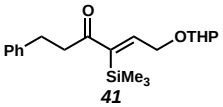
Scheme 2.3.5 Silyl Migration Precedents

2.3.2 Scope of $PtCl_2$ Catalyzed 1,2-Silyl Migration Reaction

With the platinum catalyzed 1,2-silyl migration method fully optimized ($PtCl_2$, PhMe, 80 °C), a number of different α-hydroxypropargylsilane subtrates were successfully isomerized to the corresponding (*Z*)-α-silylenones. Even hindered substrate **20** was tolerated, although significantly longer reaction times were required (Table 2.3.2, Entry 5). The isomerizations were found to be highly functional group tolerant. The reaction with distal TBS protected alcohol **21** proceeded in both high yield and selectivity (Table 2.3.2, Entry 7). Intrigued by this result, other, more potentially nucleophilic distal species, were screened. Acetates, carbamates and olefins are all known species that can act as nucleophiles for activated alkynes, but were not found to interfere with the silyl migration reaction (Table 2.3.2**,** Entries 6, 7, and 9). Even terminal alkynes were found to be highly tolerated by this reaction (Table 2.3.2, Entry 2).

Table 2.3.2 Substrate scope of $PtCl_2$ catalyzed rearrangement



Entry	Substrate	Product	Time (h)	Yield (%)[a]	Isomer Ratio (*Z* : *E*)[a]
1	 **12**	 **14**	1.5	99	10 : 1
2[b]			1.5	99	>19 : 1
3	 **22**	 **23**	1.5	99	N/A
4	 **24**	 **25**	1.5	98	>19 : 1
5[b]			1.5	99	>19 : 1
6	 **26**	 **27**	1.5	98	>19 : 1
7	 **20**	 **28**	20.5	87	>19 : 1
8	 **29**	 **30**	1.5	80	>19 : 1
9	 **21**	 **31**	1.5	93	10 : 1
10	 **32**	 **33**	1.5	93	11 : 1
11	 **34**	 **35**	1.5	93	>19 : 1
12	 **36**	 **37**	1.5	76	>19 : 1
13	 **38**	 **39**	0.2	83	>19 : 1
14[c]	 **40**	 **41**	0.75	89	>19 : 1

a) measured by ^1H NMR b) 1 mol % $PtCl_2$ c) 2.5% mol % $PtCl_2$

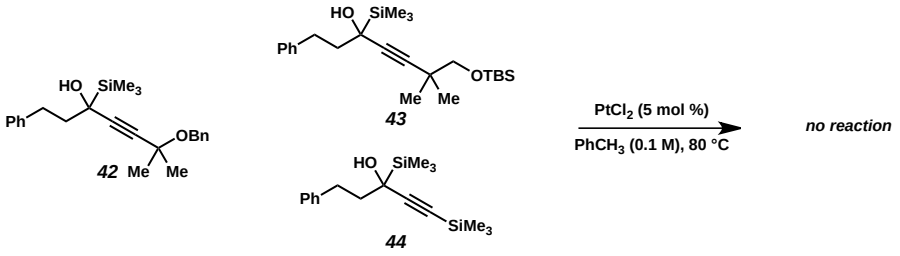
Primary protected propargyl alcohols also undergo platinum catalyzed rearrangements to afford their respective protected allylic alcohols (Table 2.3.2, Entries 9-11) in good yield and excellent selectivity. Of note, reactions forming compounds **39** and **41** (2.5 mol % Pt) are complete after 10 and 45 min respectively, whereas alcohol **36** requires the normal 1.5 h at the same temperature. This could be due to the propargyl ether oxygen coordinating the metal next to the alkyne in a way that would accelerate alkyne activation, resulting in the relatively fast formation of enones **39** and **41**. This effect could be suppressed by the bulky TBS group in the case of alcohol **36**.

2.3.3 Low Catalyst Loading

Although all of the reactions listed in Table 2.3.2 were run with 5 mol % $PtCl_2$, it is important to note that catalyst loading can be dropped significantly. Substrates **12** and **24** were subjected to only 1 mol % $PtCl_2$, and for both 1,2-silicon migration reactions there was no observable drop in yield and selectivity. Also, the reactions proceeded in roughly the same amount of time as with 5 mol % [Pt].

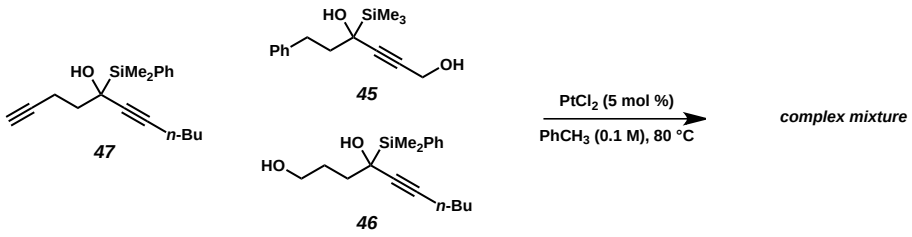
2.3.4 Failed Pt Catalyzed 1,2-Silicon Migrations

As apparent in the above table, all substrates contain a propargyl methylene group opposite the silane moiety. Hindered alkynes **42** and **43** only provided recovered starting material when subjected to our prescribed conditions. Notably, acetylenic TMS substrate **44**, similar to Schaumann's example (*vide supra*) was completely unreactive. Likely, the alkyne is too hindered for [Pt] coordination.



Scheme 2.3.6 Failed hindered alkyne substrates

Primary alcohol substrates **45** and **46** as well as terminal acetylene substrate **47** were completely consumed under the reaction conditions; however, all three resulted in complex mixtures. Likely, in the case of the diol substrates, the additional nucleophile can be reactive with either a reaction intermediate or the enone product, causing numerous side reactions. Likewise, with the terminal alkyne decomposition pathways could arise from further $PtCl_2$ alkyne activation.

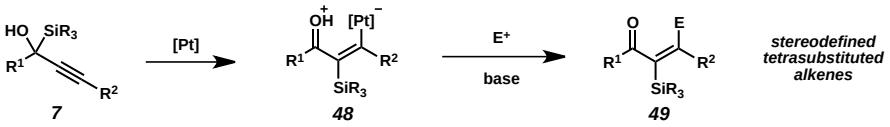


Scheme 2.3.7 Failed reactions arising from side reaction decomposition

2.4 *N*-Halosuccinimide Mediated 1,2-Silicon Migration Reactions

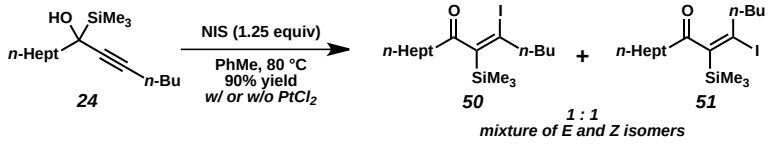
2.4.1 Initial Experiments

While the aforementioned trisubstituted vinylsilanes arise from the protodemetalation of a vinyl Pt species (**48**), we were curious if other electrophiles could be captured as well. This would provide entry into the syntheses of stereodefined tetrasubstituted olefins.



Scheme 2.4.1 Possible utilization of the vinyl platinum intermediate

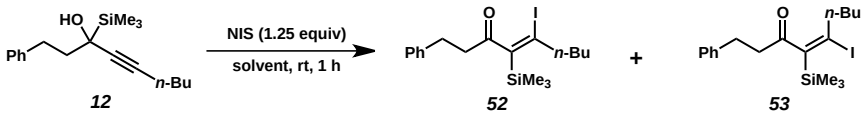
Perhaps serendipitously, for reasons that will later become apparent, the very first electrophile we chose to employ was *N*-iodosuccinimide (NIS). To our surprise, upon subjecting **24** to our previously prescribed conditions for the $PtCl_2$ catalyzed rearrangement with NIS added (5 mol % $PtCl_2$, 1.1 equiv NIS, PhMe, 80 °C), starting material was consumed within 1 h. Since the same reaction without NIS took 1.5 hours (*vide supra*) we hypothesized that the NIS may be an activator as well. To test this, the reaction was run again without the $PtCl_2$ catalyst. Again, starting material was consumed in less than 1 h. For both reactions, *E/Z* selectivity was negligible (1:1), but the transformation was high yielding for a preliminary result (90%).



Scheme 2.4.2 NIS mediated silyl migration

Using a similar substrate (**12**), it was found that cooling the reaction mixture to room temperature still effected the transformation within an hour with an increase in selectivity to 5:1 *E*/Z. At this point I employed my undergraduate assistant Zach Menard, to perform a reaction screen of a number of solvents at room temperature to find out if selectivity could be improved simply with a judicious choice of solvent.

Table 2.4.1 Solvent screen of the halosilylation reaction



entry	solvent	conversion (%)[a]	selectivity (*E*/*Z*)[a]
1	PhMe	100	5 : 1
2	THF	100	10 : 1
3	MeOH	< 50	10 : 1
4	CH_2Cl_2	100	15 : 1
5	Et_2O	100	9 : 1
6	DMF	100	N/A (complex mixture)
7	CH_3CN	100	2.8 : 1
8	DMSO	100	N/A[b]
9	EtOAc	100	15 :1

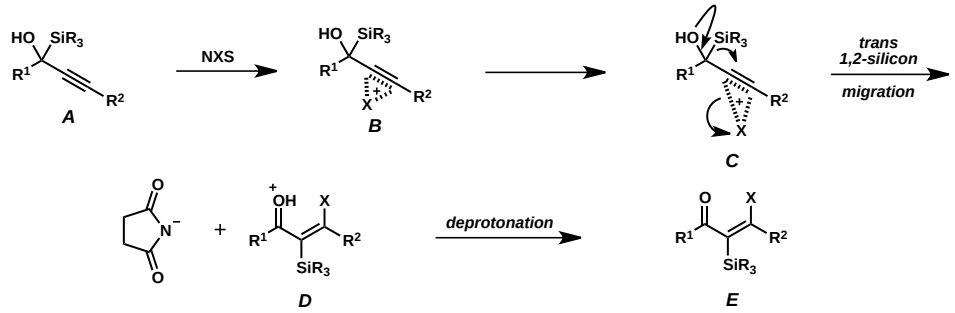
a) Measured by ^{1}H NMR of the crude reaction mixture b) Product was the ynone arising from silyl iodide elimination

Running the reaction in DMF gave a complex mixture (Table 2.4.1**,** entry 6). Using DMSO gave excellent conversion to the ynone presumably arising from elimination of silyl iodide (Table 2.4.1**,** entry 8). All other solvents afforded modest to excellent conversion to the product tetrasubstituted alkene. Toluene gave improved selectivity (Table 2.4.1, entry 1, 5:1 *E/Z*) over the similar reactions at 80 °C. MeCN was tolerated but afforded only 2.8:1 selectivity for **52**. Although THF, Et_2O, EtOAc, and CH_2Cl_2 all facilitated clean conversion and high selectivity for the (*E*)-alkene, CH_2Cl_2 was chosen as the ideal solvent for further reactions due to the practical workup it allows.

2.4.2 Mechanistic Discussion

Mechanistic insights of the NXS mediated 1,2-silicon migration can be gleaned from the aforementioned $PtCl_2$ catalzed trans selective silyl migration reaction as well as established work utilizing electrophilic halogen mediated alkyne activation (vide supra). We hypothesize that the electrophilic halogen provided by the NXS reagent reacts with the α-hydroxypropargylsilane (**A**)

to form a three-membered halonium ring. This renders the original alkyne carbons in **B** electrophilic. The nucleophilic C-Si bond can donate electon density into the proximal carbon making it more susceptible to nucleophilic attack and essentially distorting the three-membered ring (**C**). At this point the silyl migration event likely occurs, aided by the alcohol oxygen donating election density into the developing carbocation. This transformation is inherently trans, with the silyl migration attacking from the backside of the three-membered halonium ring. The resulting oxocarbenium (**D**) is deprotonated, likely with the anionic succinimide byproduct to afford the product tetrasubstituted alkene.



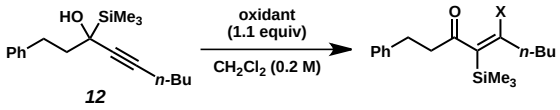
Scheme 2.4.3 Proposed mechanism for NXS mediated 1,2-silyl migration

2.4.3 Electrophile Screen

We investigated a number of electrophiles to evaluate their respective propensities for promoting the 1,2-silicon migration reaction. Using CH_2Cl_2 as a solvent and temperatures up to 50 °C, electrophilic Cl- and F- based reagents (*N*-chlorosuccinimide [NCS], trichlorocyanuric acid, Selectfluor®, and *N*-fluorobenzenesulfonimide) were all unreactive under these conditions, although NCS was found to effect the transformation under a separate set of conditions (*vide infra*). Resembling our results with NIS, we found that NBS accomplished the desired transformation in similarly high yield and selectivity for the β-bromoenone. The transformation proceeded effectively at room temperature for NBS, affording >19:1 selectivity for the (*E*)-

silylenone, whereas the more reactive NIS required lower temperatures (0 °C) to achieve >19:1 selectivity for the β-iodoenone.

Table 2.4.2 Electrophile induced 1,2-silyl migration



12

entry	oxidant	temp (°C)	yield (%)[a,b]	*E* : *Z*[c]
1	*m*-CPBA	50	NR	--
2	NCS	55	NR	--
3	TCCA	50	NR	--
4	Selectfluor	23	NR	--
5	NFSI	50	NR	--
6	NBS	23	91	>19 : 1
7	NIS	23	90	15 : 1
8	NIS	0	90	>19 : 1

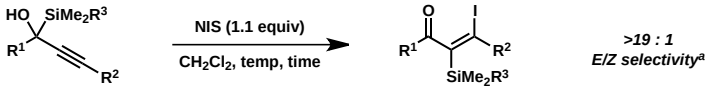
a) Isolated yield b) NR: no reaction c) Selectivity determined by ^{1}H NMR analysis of the crude reaction mixture

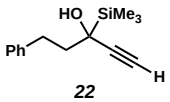
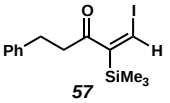
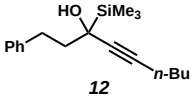
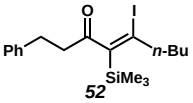
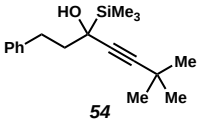
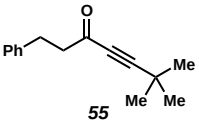
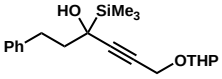
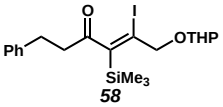
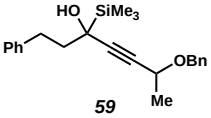
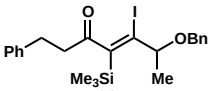
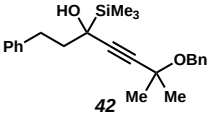
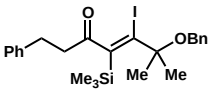
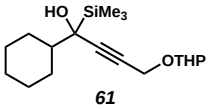
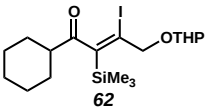
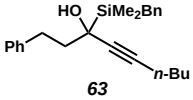
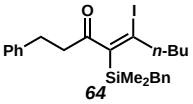
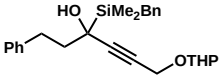
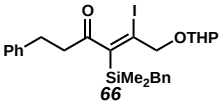
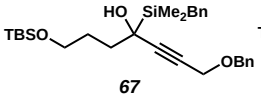
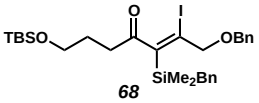
2.4.4 NIS Mediated Silyl Migration Scope

At this point, a postdoctoral research associate in the group, Dr. Nick Barczak, carried out the majority of substrate scope evaluation for this reaction. A number of α-hydroxypropargyl silanes were subjected to NIS in CH_2Cl_2 at room temperature or below. Substrates bearing terminal, unbranched, and even branched propargylic substitution proceeded smoothly. This deviates from the $PtCl_2$ silyl migration reaction, where only substrates with terminal alkynes and unbranched propargyl substitution reacted. Propargylic oxygenation did not hinder reaction progress (Table 2.4.3, entries 4-7, 9-10). Three different silicon species (-$SiMe_3$, -$SiMe_2$Bn, and -$SiMe_2$Ph) were employed, and no discrepancies in reactivity were observed. Almost universally, the reactions proceeded in high yield and with excellent geometrical selectivity (>19:1 *E/Z*). One anomalous substrate, hindered alkyne **54,** was indeed reactive when subjected to NIS; however, the desired α-silyl enone was not formed in any observable amount. Instead,

ynone **55** was formed. Likely, the 1,2-silyl migration reaction occurs but the C-Si bond of the enone species eliminates the iodide, forming alkyne **55**. Notably, the halosilylation of another particularly hindered alkyne (**42**) resulted in the formation of enone **56** with excellent selectivity (>19:1).

Table 2.4.3 NIS promoted 1,2 silyl migration



entry	substrate	product	temperature (°C)	time (h)	yield (%)
1	 ***22***	 ***57***	-10	0.25	90
2	 ***12***	 ***52***	0	0.25	94
3	 ***54***	 ***55***	-10	3	>90[b]
4	 ***40***	 ***58***	0	0.5	95
5	 ***59***	 ***60***	-15	0.5	93
6	 ***42***	 ***56***	-78 → -10	6	63
7	 ***61***	 ***62***	0	0.3	92
8	 ***63***	 ***64***	0	0.25	94
9	 ***65***	 ***66***	0	0.25	92
10	 ***67***	 ***68***	0	0.25	90

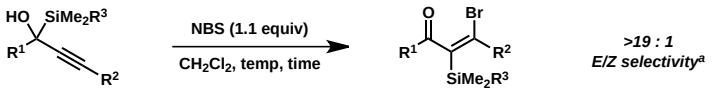
a) Measured by ^{1}H NMR b) Estimated by ^{1}H NMR

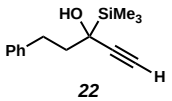
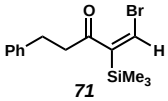
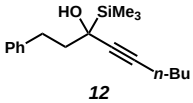
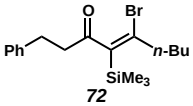
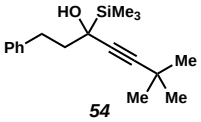
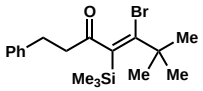
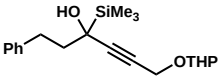
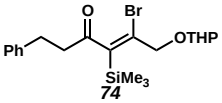
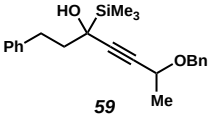
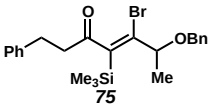
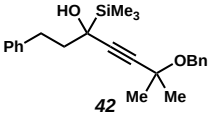
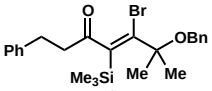
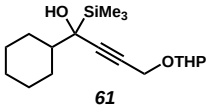
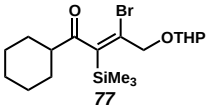
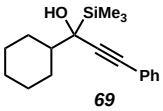
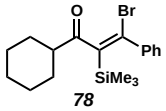
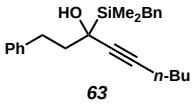
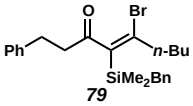
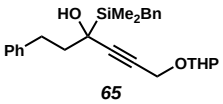
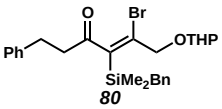
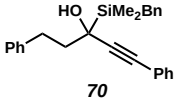
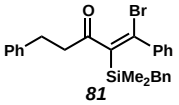
These reactions are remarkably simple to run and workup. No precautions are necessary for the removal of H_2O or air. Upon consumption of starting material addition of hexane or pentane will triturate the succinimide byproducts and any unreacted halosuccinimde. The mixture can simply be filtered through a small pad of Celite. Upon concentration of filtrate, analytically pure (*E*)-silylenones were afforded. These products can be carried on to subsequent cross coupling steps without further purification.

2.4.5 NBS mediated silyl migration scope

A similar evaluation of electrophilic halogen induced 1,2-silyl migration was performed using NBS (Table 2.4.4). Like the similar reactions using NIS, bromosilylation reactions afforded α-silyl-β-bromoenones in high yields and excellent selectivity for the *E*-alkene isomer. Phenyl acetylene substrates **69** and **70** reacted smoothly with little observed formation of ynones arising from elimination of the bromide (Table 2.4.4, entries 8 and 11). Even highly hindered alkyne **54** was found to be a competent reactant for the halosilylation reaction, unlike the similar reaction using NIS (Table 2.4.4, entry 3).

Table 2.4.4 NBS promoted 1,2 silyl migration

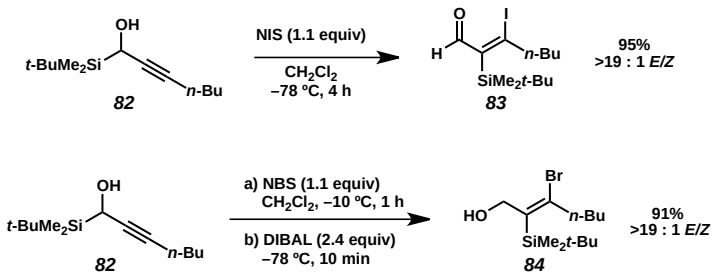


entry	substrate	product	temperature (°C)	time (h)	yield (%)
1	 ***22***	 ***71***	-15	0.25	89[b]
2	 ***12***	 ***72***	0	0.25	91
3	 ***54***	 ***73***	-78 → -10	2.5	75
4	 ***40***	 ***74***	0	0.25	92
5	 ***59***	 ***75***	-15	0.5	89
6	 ***42***	 ***76***	-78 → -10	5	85
7	 ***61***	 ***77***	0	0.3	92
8	 ***69***	 ***78***	-78 → 0	4	94
9	 ***63***	 ***79***	0	0.75	92
10	 ***65***	 ***80***	0	0.25	88
11	 ***70***	 ***81***	-78 → 0	4	80

a) Measured by ^{1}H NMR b) Yield of allylic alcohol after in situ reduction (DIBAL, -78 °C)

2.4.6 Reactions With Secondary α-Hydroxypropargylsilanes

Like their tertiary counterparts, secondary alcohol α-hydroxypropargylsilanes were proficient substrates. To illustrate this, alkyne **82** was subjected to both NIS and NBS (Scheme 2.4.4). Each reaction proceeded effectively to afford only one observable isomer. Iodoenal **83** was isolated in excellent yield, while the related bromide was unstable and therefore subjected to an *in situ* DIBAL reduction, and the resulting alcohol (**84**) was isolated in high yield and selectivity (91% yield, >19:1 *E/Z*).



Scheme 2.4.4 Reactivity of secondary α-hydroxypropargylsilanes

2.4.7 Stereochemical Rationale

Although we were quite certain about the *trans* selectivity of the halosilylation reaction, we still performed a number of NOE experiments in order to support our hypothesis. Silylenones **52** and **66** showed a moderate NOE when allylic protons were selectively irradiated. Trisubstituted alkene **71** showed a small but still relevant NOE when the alkene proton was selectively irraditated.

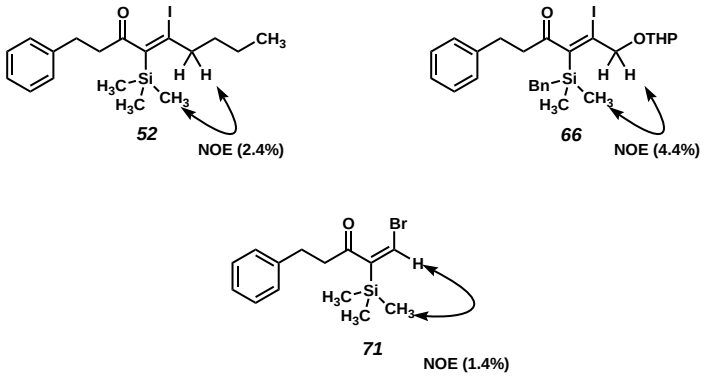


Figure 2.4.1 Confirmation of stereochemistry

2.5 Summary of 1,2-Silyl Migration Reactions

We have developed two novel reaction manifolds in which a 1,2-silicon migration occurs onto an activated alkyne intermediate. In the first reaction studied, an α-hydroxypropargylsilane was subjected to $PtCl_2$ at elevated temperature (80 °C). The Pt coordinated alkyne induced a net *trans*-silyl migration allowing facile access to trisubstituted, stereodefined (*Z*)-alkenes with excellent yields and selectivities. The second reaction described in this chapter utilized the same reactive moiety, the α-hydroxypropargylsilane. For this transformation, an *N*-halosuccinimide induced a net *trans*-halosilylation of the substrate alkyne. Like the Pt catalyzed reaction, these reactions generally proceeded in excellent yields and excellent *E/Z* selectivities. Unlike with $PtCl_2$, the NXS mediated rearrangements proceeded with sterically hindered alkynes. The geometrically defined alkene products, from both the $PtCl_2$ catalyzed and NXS mediated methods, provide an excellent handle for the downstream generation of all carbon tri- and tetrasubstituted olefins. The utility of these product vinylsilanes will be described in detail later in Chapter 4.

2.6 Experimental Section

2.6.1 Materials and Methods

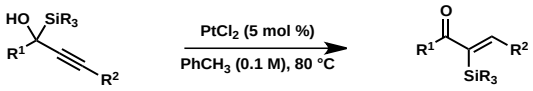
All reactions were performed under an argon atmosphere unless otherwise noted. Tetrahydrofuran, ether, and toluene were purified by passing through activated alumina columns. Chlorotrimethylsilane was freshly distilled from calcium hydride prior to its use in reactions. All other reagents were used as received unless otherwise noted. Commercially available chemicals were purchased from Alfa Aesar (Ward Hill, MA), Sigma-Aldrich (St. Louis, MO), Gelest (Morrisville, PA), Oakwood Products, (West Columbia, SC), Strem (Newburport, MA) and TCI America (Portland, OR). Qualitative TLC analysis was performed on 250 mm thick, 60 Å, glass backed, F254 silica (Silicycle, Quebec City, Canada). Visualization was accomplished with UV light and exposure to either *p*-anisaldehyde or $KMnO_4$ solution followed by heating. Flash chromatography was performed using Silicycle silica gel (230-400 mesh). ^1H NMR spectra were acquired on either a Varian Mercury 300 (at 300 MHz), a Varian Inova 400 (at 400 MHz), or a Varian 400 MR (at 400 MHz) and are reported relative to $SiMe_4$ (δ 0.00). ^{13}C NMR spectra were acquired on either a Varian Inova 400 (at 100 MHz), a Varian Mercury 300 (at 75 MHz), , or a Varian 400 MR (at 100 MHz) and are reported relative to $SiMe_4$ (δ 0.0). All IR spectra were obtained on NaCl plates (film) with either a Nicolet Magna FTIR 760, a Nicolet 380 FTIR, or a Bruker Tensor 27. High resolution mass spectrometry data were acquired by the Colorado State University Central Instrument Facility on an Agilent 6210 TOF LC/MS.

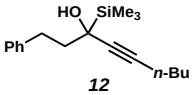
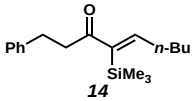
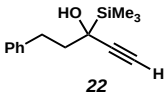
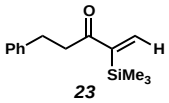
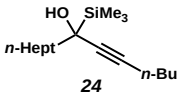
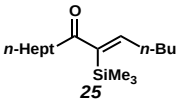
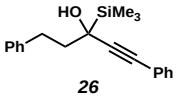
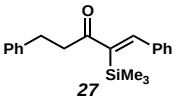
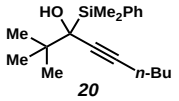
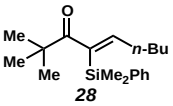
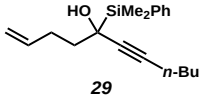
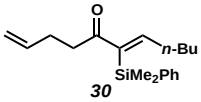
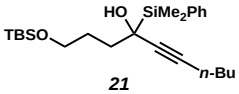
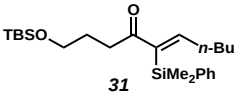
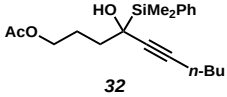
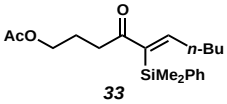
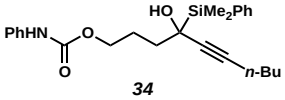
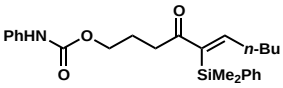
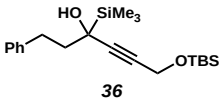
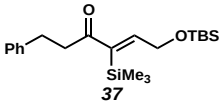
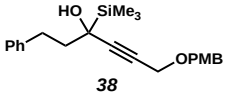
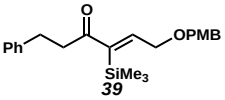
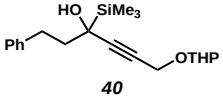
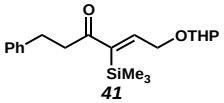
2.6.2 General Procedure for Platinum Catalyzed Rearrangement of α-hydroxypropargylsilanes

To an α-hydroxypropargylsilane in toluene (0.1 M) under argon was added $PtCl_2$ (5 mol %), and the reaction flask was placed in an 80 ℃ oil bath. The mixture was allowed to stir, turning brown, until the starting material was consumed as determined by TLC. The mixture was then diluted with Et_2O (~ 1.5x reaction volume) and filtered through silica gel, further rinsing with Et_2O (~ 3x reaction volume). The solvents were removed via rotary evaporation, and the resulting brown oil was purified by silica gel flash chromatography. If a mixture of enone isomers were present, the enones were generally inseparable and therefore isolated as a mixture.

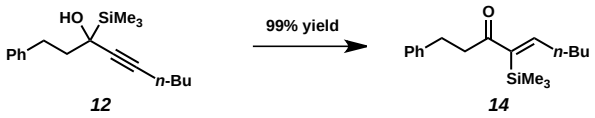
2.6.3 Platinum-Catalyzed Silyl Migrations

Table 2.3.2 (*reproduced*):



Entry	Substrate	Product	Time (h)	Yield (%)[a]	Isomer Ratio (*Z* : *E*)[a]
1	 **12**	 **14**	1.5	99	10 : 1
2[b]			1.5	99	>19 : 1
3	 **22**	 **23**	1.5	99	N/A
4	 **24**	 **25**	1.5	98	>19 : 1
5[b]			1.5	99	>19 : 1
6	 **26**	 **27**	1.5	98	>19 : 1
7	 **20**	 **28**	20.5	87	>19 : 1
8	 **29**	 **30**	1.5	80	>19 : 1
9	 **21**	 **31**	1.5	93	10 : 1
10	 **32**	 **33**	1.5	93	11 : 1
11	 **34**	 **35**	1.5	93	>19 : 1
12	 **36**	 **37**	1.5	76	>19 : 1
13	 **38**	 **39**	0.2	83	>19 : 1
14[c]	 **40**	 **41**	0.75	89	>19 : 1

a) measured by ^{1}H NMR b) 1 mol % $PtCl_2$ c) 2.5% mol % $PtCl_2$

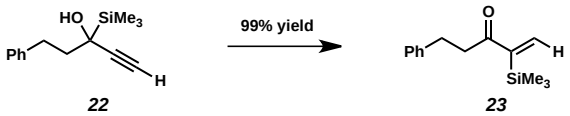


12 *14*

Table 2.3.2, Entry 1: According to the general procedure, α-hydroxypropargylsilane **12** (145 mg, 0.503 mmol) and $PtCl_2$ (6.7 mg, 0.0251 mmol) were stirred in 5.00 mL toluene under argon for 1.5 h. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (7 mL) was added, and the mixture was filtered through a plug of silica gel (1 x 2 cm) washing with more Et_2O (15 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford enone **14** as a colorless oil (145 mg, 99% yield, 10:1 *Z/E*, R_F = 0.55 in 9:1 hexanes/EtOAc).

α-Silylenone 14: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.3 Hz, 2H), 7.20 (app. d, *J* = 7.1 Hz, 3H), 6.68 (t, *J* = 7.2 Hz, 1H), 2.87 (app. s, 4H), 2.23 (q, *J* = 7.2 Hz, 2H), 1.40-1.28 (comp m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 152.7, 145.7, 141.7, 128.6, 126.2, 42.1, 31.7, 31.6, 30.7, 22.6, 14.1, 0.9; IR (film) 2957, 2929, 1664, 1600, 1248, 842 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{18}H_{29}OSi]^+$: 289.1982, found 289.1985.

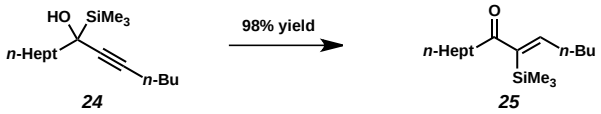
(low catalyst loading): According to the general procedure, α-hydroxypropargylsilane **12** (586 mg, 2.02 mmol) and $PtCl_2$ (5.4 mg, 0.0202 mmol) were stirred in 8.00 mL toluene under argon for 1.5 h. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (15 mL) was added, and the mixture was filtered through a plug of silica gel (3 x 3.5 cm) washing with more Et_2O (30 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford enone **14** as a colorless oil (582 mg, 99% yield, >19:1 *Z/E*).



22 *23*

Table 2.3.2, Entry 3: To α-hydroxypropargylsilane **22** (77.1 mg, 0.332 mmol) in 3.3 mL toluene under argon was added $PtCl_2$ (4.4 mg, 0.0167 mmol), and the reaction flask was placed in an 80 °C oil bath. The mixture was allowed to stir, turning brown, until the starting material was consumed as determined by TLC. The mixture was then diluted with Et_2O (4 mL) and filtered through a plug of SiO_2 (1 x 2 cm), washing with Et_2O (7 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford enone **23** (77.0 mg, R_F = 0.30 in 9:1 hexanes/EtOAc, 99% yield) as a colorless oil.

α-Silylenone 23: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.0 Hz, 2H), 7.20 (app. d, *J* = 7.2 Hz, 3H), 6.44 (app. s, 1H), 6.11 (app. s, 1H), 2.99-2.90 (comp m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.4, 154.1, 141.5, 135.6, 128.6, 128.5, 126.2, 40.4, 30.3, -1.2; IR (film) 3029, 2956, 1667, 1247, 842, 699 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{14}H_{21}OSi]^+$: 233.1356, found 233.1357.



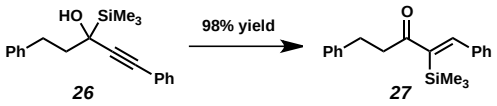
24 *25*

Table 2.3.2, Entry 4: According to the general procedure, α-hydroxypropargylsilane **24** (53.4 mg, 0.189 mmol) and $PtCl_2$ (2.5 mg, 0.00945 mmol) were stirred in 1.89 mL toluene under argon for 1.5 h. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (3 mL) was added, and the mixture was filtered through a plug of silica gel (1 x 2 cm) washing with more Et_2O (6 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash

chromatography (39:1 hexanes/EtOAc eluent) to afford enone **25** a colorless oil (52.3 mg, 98% yield, >19:1 *Z/E*, R_F = 0.55 in 9:1 hexanes/EtOAc).

α-Silylenone 25: ^{1}H NMR (400 MHz, $CDCl_3$,) δ 6.67 (t, *J* = 7.5 Hz, 1H), 2.54 (t, *J* = 7.4 Hz, 2H), 2.26 (q, *J* = 7.3 Hz, 2H), 1.58-1.53 (m, 2H), 1.44-1.31 (comp m, 4H), 0.92, (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 6.7 Hz, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 151.8, 145.9, 40.5, 31.9, 31.7, 29.5, 29.3, 24.7, 22.8, 22.6, 14.2, 14.1, 0.8; IR (film) 2957, 2928, 1665, 1600, 1248, 843 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{17}H_{35}OSi]^+$: 283.2452, found 283.2448.

(low catalyst loading): According to the general procedure, α-hydroxypropargylsilane **24** (172 mg, 0.609 mmol) and $PtCl_2$ (1.6 mg, 0.00609 mmol) were stirred in 2.50 mL toluene under argon for 1.5 h. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (4 mL) was added, and the mixture was filtered through a plug of silica gel (1 x 2 cm) washing with more Et_2O (8 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (39:1 hexanes/EtOAc eluent) to afford enone **25** a colorless oil (172 mg, 99% yield, >19:1 *Z/E*, R_F = 0.55 in 9:1 hexanes/EtOAc).

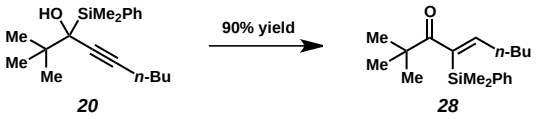


26 *27*

Table 2.3.2, Entry 6: According to the general procedure, α-hydroxypropargylsilane **26** (152 mg, 0.492 mmol) and $PtCl_2$ (6.5 mg, 0.0246 mmol) were stirred in 4.90 mL toluene under argon for 1.5 h. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (7 mL) was added, and the mixture was filtered through a plug of silica gel (1 x 2 cm) washing with Et_2O (15 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford enone **27** as a colorless oil (149 mg, 98%

yield, >19:1 *Z/E*, R_F = 0.49 in 9:1 hexanes/EtOAc).

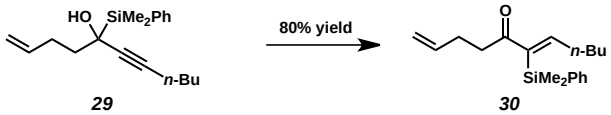
α-Silylenone 27: ^{1}H NMR (400 MHz, $CDCl_3$,) δ 7.74 (s, 1H), 7.35-7.19 (comp m, 9H), 3.06 (t, *J* = 6.7 Hz, 2H), 2.99 (t, *J* = 6.7 Hz, 2H), 0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 148.4, 141.5, 138.0, 128.6, 128.6, 128.5, 128.2, 126.2, 42.1, 30.5, 0.6; IR (film) 3062, 3027, 2954, 1665, 1248, 841, 698 cm^{-1}; HRMS *m/z* calc'd for $(M + Na)^+$ $[C_{20}H_{24}OSi + Na]^+$: 331.1489, found 331.1491.



20 *28*

Table 2.3.2, Entry 7: According to the general procedure, α-hydroxypropargylsilane **20** (142 mg, 0.469 mmol) and $PtCl_2$ (6.2 mg, 0.0234 mmol) were stirred in 4.00 mL toluene under argon for 20.5 h. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (7 mL) was added, and the mixture was filtered through a plug of silica gel (1 x 2 cm) washing with Et_2O (15 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (39:1 hexanes/EtOAc eluent) to afford enone **28** as a colorless oil (124 mg, 87% yield, >19:1 *Z/E*, R_F = 0.56 in 9:1 hexanes/EtOAc).

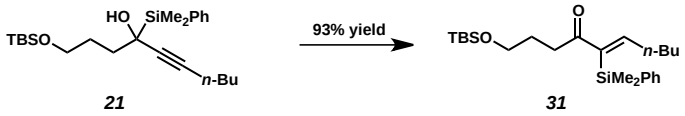
α-Silylenone 28: ^{1}H NMR (400 MHz, $CDCl_3$,) δ 7.61-7.58 (m, 2H), 7.35-7.33 (comp m, 3H), 6.18 (t, *J* = 7.4 Hz, 2H), 1.97 (q, *J* = 7.3 Hz, 2H), 1.16 (app. s, 13H), 0.76 (t, *J* = 7.1 Hz, 3H), 0.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.0, 144.9, 143.9, 138.5, 134.2, 129.2, 127.9, 44.6, 32.3, 31.3, 27.8. 22.5, 14.0, -0.9; IR (film) 2958, 2930, 1672, 1250, 1108, 785, 700 cm^{-1}; HRMS *m/z* calc'd for $(M + Na)^+$ $[C_{19}H_{30}OSi + Na]^+$: 325.1958, found 325.1962.



29 *30*

Table 2.3.2, Entry 8: According to the general procedure, α-hydroxypropargylsilane **29** (57.1 mg, 0.190 mmol) and $PtCl_2$ (2.5 mg, 0.00950 mmol) were stirred in 1.90 mL toluene under argon for 1.5 h. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (4 mL) was added, and the mixture was filtered through a plug of silica gel (1 x 2 cm) washing with Et_2O (8 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford enone **30** as a colorless oil (458 mg, 80% yield, >19:1 *Z/E*, R_F = 0.51 in 9:1 hexanes/EtOAc).

α-Silylenone 30: ^{1}H NMR (400 MHz, $CDCl_3$,) δ 7.54 (t, *J* = 3.4 Hz, 2H), 7.34 (app. t, *J* = 3.0 Hz, 3H), 6.79 (t, *J* = 7.5 Hz, 2H), 5.80 (ddt, *J* = 17.3, 10.7, 6.8 Hz, 1H), 5.02 (d, *J* = 17.3 Hz, 1H), 4.97 (d, *J* = 10.7 Hz, 1H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.31 (app. q, *J* = 7.1 Hz, 2H), 2.02 (q, *J* = 7.5 Hz, 2H), 1.27-1.10 (comp m, 4H), 0.77 (t, *J* = 7.1 Hz, 3H), 0.44 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5, 154.0, 144.2, 133.9, 129.1, 128.0, 115.2, 39.5, 32.0, 31.3, 28.7, 22.5, 14.0, -0.6; IR (film) 2958, 2928, 1683, 1250, 1112, 834, 701 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{19}H_{28}OSi + Na]^+$: 323.1802, found 323.1806.

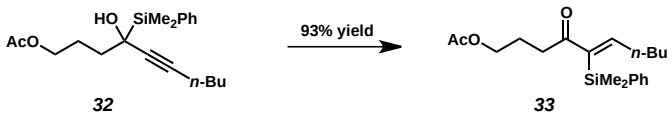


21 *31*

Table 2.3.2, Entry 9: According to the general procedure, α-hydroxypropargylsilane **21** (97.1 mg, 0.232 mmol) and $PtCl_2$ (3.1 mg, 0.0116 mmol) were stirred in 2.30 mL toluene under argon for 1.5 h. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (5 mL) was added, and the mixture was filtered through a plug of silica gel (1 x 2 cm) washing with Et_2O (10

mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford enone **31** as a colorless oil (90.6 mg, 93% yield, 10:1 *Z/E*, R_F = 0.51 in 9:1 hexanes/EtOAc).

α-Silylenone 31: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, *J* = 3.6 Hz, 2H), 7.34-7.30 (comp m, 3H), 6.81 (t, *J* = 7.6 Hz, 1H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H), 2.25 (q, *J* = 7.2 Hz, 2H), 1.77 (quint, *J* = 6.8 Hz, 2H), 1.29-1.10 (comp m, 4H), 0.89 (s, 9H), 0.44 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 153.5, 143.8, 138.9, 133.5, 128.7, 127.6, 62.0, 36.2, 31.5, 30.9, 27.3, 25.7, 22.1, 18.1, 13.6. -1.0, -5.5; IR (film) 2957, 2858, 1666, 1253, 1100, 836 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{24}H_{42}O_2Si_2 + Na]^+$: 441.2616, found 441.2625.

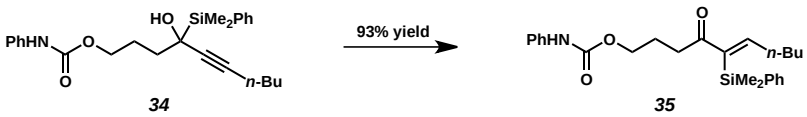


32 *33*

Table 2.3.2, Entry 10: According to the general procedure, α-hydroxypropargylsilane **32** (826 mg, 0.237 mmol) and $PtCl_2$ (3.2 mg, 0.0119 mmol) were stirred in 2.40 mL toluene under argon for 1.5 h. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (5 mL) was added, and the mixture was filtered through a plug of silica gel (1 x 2 cm) washing with Et_2O (10 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford enone **33** as a colorless oil (149 mg, 93% yield, >19:1 *Z/E*, R_F = 0.32 in 9:1 hexanes/EtOAc).

α-Silylenone 33: ^{1}H NMR (400 MHz, $CDCl_3$,) δ 7.55-7.53 (app. q, 2H), 7.34-7.32 (comp m, 3H), 6.80 (t, *J* = 7.5 Hz, 1H), 4.05 (t, *J* = 6.5 Hz, 2H), 2.65 (t, *J* = 7.3 Hz, 2H), 2.01 (app. s, 5H), 1.89 (quint, *J* = 6.9 Hz, 2H), 1.28-1.10 (comp m, 4H), 0.78 (t, *J* = 7.3 Hz, 3H), 0.44 (s, 6H); ^{13}C

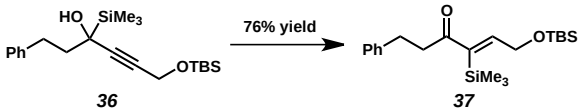
NMR (100 MHz, $CDCl_3$) δ 206.8, 171.0, 154.0, 143.9, 138.9, 133.7, 129.0, 127.8, 63.8, 36.3, 31.7, 31.1, 22.3, 21.0, 13.8, -0.8; IR (film) 2958, 2929, 1742, 1665, 1246, 836, 702 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{20}H_{30}O_3Si + Na]^+$: 369.1856, found 369.1861.



34 *35*

Table 2.3.2, Entry11: According to the general procedure, α-hydroxypropargylsilane **34** (210 mg, 0.517 mmol) and $PtCl_2$ (6.8 mg, 0.0259 mmol) were stirred in 5.20 mL toluene under argon for 1.5 h. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (8 mL) was added, and the mixture was filtered through a plug of silica gel (1 x 2 cm) washing with Et_2O (15 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 → 9:1 hexanes/EtOAc eluent) to afford enone **35** as a colorless oil (195 mg, 93% yield, >19:1 *Z/E*, R_F = 0.37 in 9:1 hexanes/EtOAc).

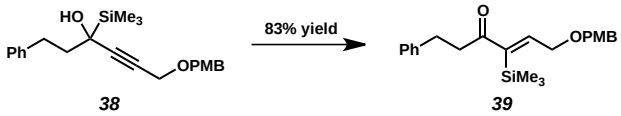
α-Silylenone 35: ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (app. q, *J* = 3.2 Hz, 2H), 7.38-7.28 (comp m, 7H), 7.06 (tt, *J* = 7.3, 1.3 Hz, 1H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.60 (br s, 1H), 4.16 (t, *J* = 6.4 Hz, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.04 (q, *J* = 7.4 Hz, 2H), 1.95 (app. quint, *J* = 6.9 Hz, 2H), 1.28-1.21 (m, 2H), 1.44 (dq, *J* = 14.7, 7.3 Hz, 2H), 0.78 (t, *J* = 7.2 Hz, 3H), 0.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 154.2, 144.1, 138.0, 133.9, 128.0, 123.6, 118.8, 64.7, 36.4, 31.9, 31.2, 23.8, 22.5, 14.0, -0.6; IR (film) 3325, 2957, 1734, 1599, 1540, 1444, 1313, 1219, 1057 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{25}H_{33}NO_3Si + Na]^+$: 446.2122, found 446.2122.



36 *37*

Table 2.3.2, Entry 12: According to the general procedure, α-hydroxypropargylsilane **36** (162 mg, 0.430 mmol) and $PtCl_2$ (5.7 mg, 0.0215 mmol) were stirred in 4.30 mL toluene under argon for 1.5 h. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (7 mL) was added, and the mixture was filtered through a plug of silica gel (1 x 2 cm) washing with Et_2O (15 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford enone **37** as a colorless oil (124 mg, 76% yield, 13:1 *Z/E*, R_F = 0.50 in 9:1 hexanes/EtOAc).

α-Silylenone 37: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.19 (comp m, 5H), 6.74 (t, *J* = 5.2 Hz, 1H), 4.72 (d, *J* = 5.6 Hz, 2H), 2.91 (app. s, 4H), 0.91 (s, 9H), 0.16 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 152.0, 144.6, 141.3, 128.42, 128.39, 126.0, 62.3, 41.5, 30.3, 25.9, 18.3, 0.4, -5.2; IR (film) 3447, 2955, 2930, 2857, 1249, 1086, 700 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{21}H_{36}O_2Si_2 + Na]^+$: 399.2146, found 399.2149.

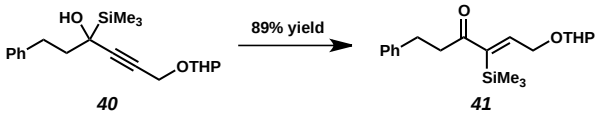


38 *39*

Table 2.3.2, Entry 13: According to the general procedure, α-hydroxypropargylsilane **38** (146 mg, 0.381 mmol) and $PtCl_2$ (5.1 mg, 0.0191 mmol) were stirred in 4.00 mL toluene under argon for 10 min. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (6 mL) was added, and the mixture was filtered through a plug of silica gel (1 x 2 cm) washing with Et_2O (10 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 → 9:1 hexanes/EtOAc eluent) to afford enone **39** as a colorless oil (121

mg, 83% yield, >19:1 *Z/E*, R_F = 0.30 in 9:1 hexanes/EtOAc).

α-Silylenone 39: ^{1}H NMR (400 MHz, $CDCl_3$,) δ 7.26 (app. t, *J* = 7.4 Hz, 5H), 7.17 (app. d, *J* = 5.5 Hz, 3H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.76 (t, *J* = 5.7 Hz, 1H), 4.45 (s, 2H), 4.17 (d, *J* = 5.7 Hz, 2H), 3.79 (s, 3H), 2.89 (app. s, 4H), 0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 159.6, 148.1, 147.1, 141.4, 129.9, 129.7, 128.6, 128.5, 126.2, 114.1, 72.8, 68.7, 55.4, 41.8, 30.3, 0.5; IR (film) 2953, 2837, 1667, 1612, 1514, 1249, 1100, 844 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{23}H_{30}O_3Si + Na]^+$: 405.1856, found 405.1852.



40 *41*

Table 2.3.2, Entry 14: According to the general procedure, α-hydroxypropargylsilane **40** (140 mg, 0.428 mmol) and $PtCl_2$ (2.8 mg, 0.0107 mmol) were stirred in 2.00 mL toluene under argon for 45 min. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (3 mL) was added, and the mixture was filtered through a plug of silica gel (1 x 2 cm) washing with Et_2O (8 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford enone **41** as a colorless oil (125 mg, 89% yield, >19:1 *Z/E*, R_F = 0.39 in 9:1 hexanes/EtOAc).

α-Silylenone 41: ^{1}H NMR (400 MHz, $CDCl_3$,) δ 7.27 (app. t, *J* = 6.8 Hz, 2H), 7.17 (app. t, *J* = 7.9 Hz, 3H), 6.75 (t, *J* = 5.9 Hz, 1H), 4.61 (t, *J* = 3.4 Hz, 1H), 4.41 (dd, *J* = 14.3, 5.5 Hz, 1H), 4.20 (dd, *J* = 14.3, 6.3 Hz, 1H), 3.83 (ddd, *J* = 11.1, 8.1, 3.0 Hz, 1H), 3.50 (dt, *J* = 10.7, 5.1 Hz, 1H), 2.91 (comp m, 4H), 1.85-1.68 (comp m, 2H) 1.62-1.51 (comp m, 4H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 147.9, 147.1, 141.4, 128.6, 128.5, 126.2, 98.6, 66.0, 62.5, 41.9, 30.7, 30.3, 25.5, 19.5, 0.5; IR (film) 2947, 1667, 1249, 1133, 1121, 1033, 844 cm^{-1}; HRMS

(ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{20}H_{30}O_3Si]^+$: 369.1856, found 369.1854.

2.6.4 $PtCl_2$ Catalyzed 1,2-Silyl Migration Optimization

Table 2.3.1 (*reproduced*)

Entry	Catalyst (5 mol %)	Solvent, temp (°C)	Time (h)	Conv. (%)[a]	Isomer Ratio (*Z* : *E*)[a]
1	$RuCl_3$	$PhCH_3$, 70	72	< 5	--
2	$IrCl_3$	$PhCH_3$, 70	72	< 5	--
3	$RhCl_3$	$PhCH_3$, 70	72	< 5	--
4	CuI	$PhCH_3$, 70	48	0	--
5	$PdCl_2$	$PhCH_3$, 70	48	< 5	--
6	$CpRu(CH_3CN)_3PF_6$	$PhCH_3$, 50	36	< 5	--
7	$(Ph_3P)_3RuCl_2$	$PhCH_3$, 50	36	< 5	--
8	AuCl	$PhCH_3$, 50	5	100	1.7 : 1[b]
9	$AuCl_3$	$PhCH_3$, 50	5	100	1 : 1.7[b]
10	Au complex[c]	$PhCH_3$, 40	1	100 (76[d])	>19 : 1
11	$PtCl_2$	$PhCH_3$, 35	48	0	--
12	$PtCl_2$	$PhCH_3$, 50	3.5	100 (95[d])	6 : 1
13	$PtCl_2$	$PhCH_3$, 80	2	100 (99[d])	> 19 : 1
14	$ZnCl_2$	CH_2Cl_2, 23	4	0	--
15	$ZnCl_2$	$PhCH_3$, 50	4	0	--

a) Measured by ^{1}H NMR b) Significant quantities of protodesilylated enones were observed
c) Au complex: Chloro[2-(di-*tert*-butylphosphino)-biphenyl]gold(I) (5 mol %) + $AgSbF_6$ (20 mol %)
d) Isolated yield

General procedure for reaction optimization of transformation 12 → 14.

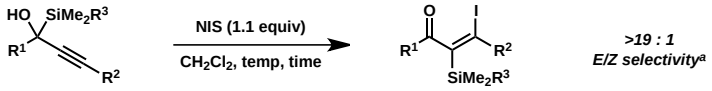
To a solution of α-hydroxypropargylsilane **12** (.0350-0.0701 mmol) in toluene (0.1 M) under argon was added catalyst (5 mol %, plus 20 mol % $AgSbF_6$ for entry 6) as a solid. The resulting mixture was heated to the specified temperature and stirred for the listed time. The mixture was then cooled to room temperature, filtered through a plug of silica gel (1.5 x 0.5 cm) washing with Et_2O (1-2 mL), and the filtrate was concentrated in vacuo. Analysis by ^{1}H NMR was conducted to determine conversion and isomeric ratio. In entries 8 and 11, the crude material was then purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford enone **14** as a colorless oil.

2.6.5 General Procedure for the *N*-Halosuccinimide Induced Silyl Migrations of α-hydroxypropargylsilanes

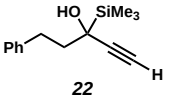
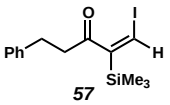
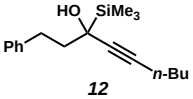
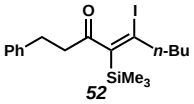
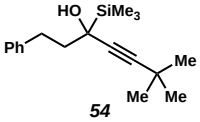
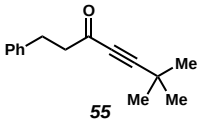
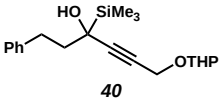
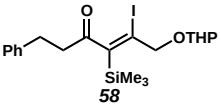
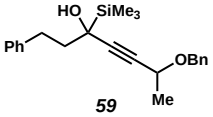
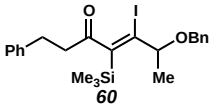
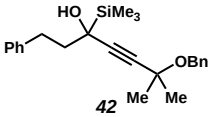
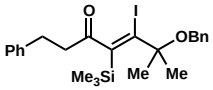
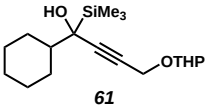
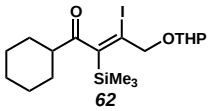
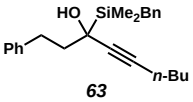
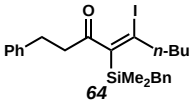
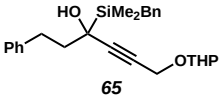
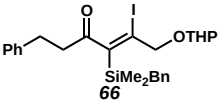
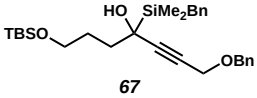
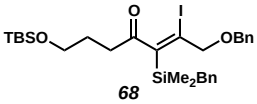
α-Hydroxypropargylsilane (0.300 mmol, 1.00 equiv) was dissolved in 1.50 mL of dry CH_2Cl_2 under Ar. The solution was then cooled to the designated temperature. *N*-halosuccinimide (0.330 mmol, 1.10 equiv) was added quickly in one portion to the reaction mixture. The reaction mixture was monitored by TLC for the disappearance of starting hydroxypropargylsilane. When all starting material was consumed, 10 mL of pentane was added and the reaction mixture was filtered through a small pad of celite to remove the precipitated succinimide. Removal of the solvent in vacuo afforded a pale yellow oil. The product was generally sufficiently pure for subsequent transformations. For characterization, purification by flash column chromatography on dried silica gel (hexanes/EtOAc as eluent) provided the (*E*)-α-silyl-β-haloenones. In all cases, the *E/Z* selectivity was greater than >19:1; only the data for the major isomer is reported.

2.6.6 *N*-Iodosuccinimide Induced Silyl Migrations of α-hydroxypropargylsilanes

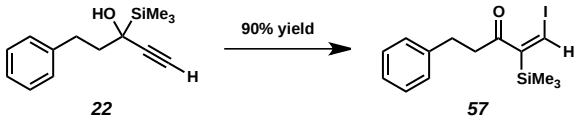
Table 2.4.3 (*reproduced*)**:**



>19 : 1
E/Z selectivity[a]

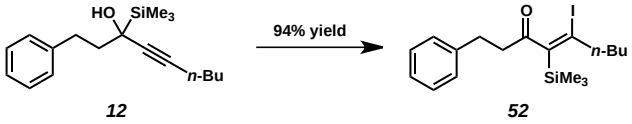
entry	substrate	product	temperature (°C)	time (h)	yield (%)
1	 ***22***	 ***57***	-10	0.25	90
2	 ***12***	 ***52***	0	0.25	94
3	 ***54***	 ***55***	-10	3	>90[b]
4	 ***40***	 ***58***	0	0.5	95
5	 ***59***	 ***60***	-15	0.5	93
6	 ***42***	 ***56***	-78 → -10	6	63
7	 ***61***	 ***62***	0	0.3	92
8	 ***63***	 ***64***	0	0.25	94
9	 ***65***	 ***66***	0	0.25	92
10	 ***67***	 ***68***	0	0.25	90

a) Measured by ^{1}H NMR b) Estimated by ^{1}H NMR



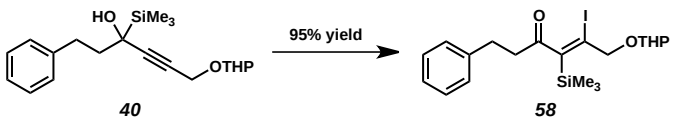
22 *57*

α-Silyl-β-iodoenone 57 (Table 2.4.3, Entry 1): Using substrate **22**,[41] reaction was conducted at –10 ºC for 15 min. Colorless oil (96.7 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.26 (comp m, 5H), 6.65 (s, 1H), 2.98 (app t, *J* = 7.6 Hz, 2H), 2.88 (app t, *J* = 7.2 Hz, 2H), 0.14 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.8, 162.8, 141.1, 128.7, 128.6, 126.3, 86.0, 43.7, 29.2, -1.3; **IR** (film) 3028, 2957, 1689, 1603, 1556, 1496, 1453, 1403, 1354, 1252 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{14}H_{20}BrOSi$ $(M + H)^+$ 313.0442, found 313.0438; **TLC** R_f = 0.42 (19:1 hexanes/EtOAc).



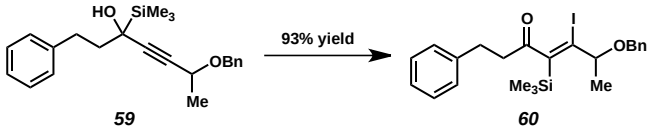
12 *52*

α-Silyl-β-iodoenone 52 (Table 2.4.3, Entry 2): Using substrate **12**, reaction was conducted at 0 ºC for 15 min. Colorless oil (117 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.17 (comp m, 5H), 2.98 (app. t, *J* = 8.0 Hz, 2H), 2.83 (app. t, *J* = 7.2 Hz, 2H), 2.52–2.48 (m, 2H), 1.61–1.54 (m, 2H), 1.36 (app. sextet, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.6 Hz, 3H), 0.20 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.2, 154.4, 141.3, 128.7, 128.6, 126.2, 116.6, 45.0, 44.1, 32.7, 29.5, 21.9, 14.2, 0.5; **IR** (film) 3027, 2957, 2872, 1693, 1587, 1496, 1454, 1406, 1353, 1252, 1212 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{18}H_{28}IOSi$ $(M + H)^+$ 415.0956, found 415.0956; **TLC** R_f = 0.35 (19:1 hexanes/EtOAc).



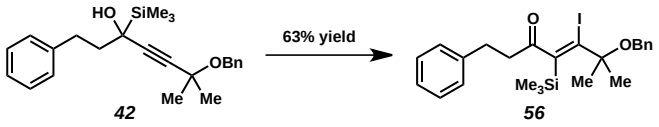
40 *58*

α-Silyl-β-iodoenone 58 (Table 2.4.3, Entry 4): Using substrate **40**, reaction was conducted at 0 ºC for 30 min. Colorless oil (134 mg, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.17 (m, 5H), 4.65 (app. t, *J* = 3.2 Hz, 1H), 4.27 (ABq, *J* = 12.8 Hz, Δν = 39.9 Hz, 2H), 3.92-3.84 (m, 1H), 3.55-3.48 (m, 1H), 2.98 (app. t, *J* = 7.6 Hz, 2H), 2.84 (app. q, *J* = 8.0 Hz, 2H), 1.89-1.66 (m, 2H) 1.62-1.51 (comp m, 4H), 0.23 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.0, 158.7, 141.2, 128.7, 128.6, 126.3, 111.4, 97.5, 72.2, 62.5, 43.8, 31.1, 30.6, 29.3, 25.5, 19.3, 0.4; **IR** (film) 3027, 2947, 2870, 1694, 1589, 1496, 1453, 1404, 1353, 1254, 1201, 1182, 1120, 1076 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{20}H_{33}INO_3Si$ $(M + NH_4)^+$ 490.1274, found 490.1281; **TLC** R_f = 0.43 (9:1 hexanes/EtOAc).



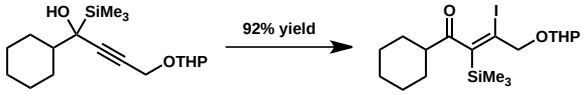
59 *60*

α-Silyl-β-iodoenone 60 (Table 2.4.3, Entry, 5): Reaction was conducted at –15 ºC for 30 min. Colorless oil (137 mg, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41–7.18 (comp m, 10H), 4.56 (d, *J* = 11.2 Hz, 1H), 4.23 (d, *J* = 11.2 Hz, 1H), 3.61 (q, *J* = 6.0 Hz, 1H), 3.02 (app. t, *J* = 8.0 Hz, 2H), 2.89 (br s, 2H), 1.27 (d, *J* = 6.0 Hz, 3H), 0.20 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.6, 157.1, 141.2, 137.7, 128.70, 128.66, 128.6, 128.0, 127.9, 126.3, 124.3, 70.4, 44.2, 29.5, 22.4, 0.7; **IR** (film) 3063, 3028, 2955, 2931, 2896, 1693, 1578, 1496, 1453, 1404, 1369, 1310, 1253, 1202, 1147 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{23}H_{33}INO_2Si$ $(M + NH_4)^+$ 510.1325, found 510.1327; **TLC** R_f = 0.49 (19:1 hexanes/EtOAc).



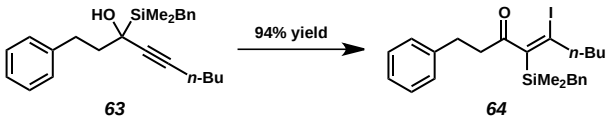
42 *56*

α-Silyl-β-iodoenone 56 (Table 2.4.3, Entry 6): Reaction was conducted at –78 ºC for 4 h, then allowed to warm to –10 ºC and stir for 2 h. Colorless solid (95.7 mg, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.10 (comp m, 10H), 4.54 (app. d, *J* = 5.2 Hz, 2H), 3.10–3.02 (m, 1H), 2.96-2.86 (m, 2H), 2.51-2.41 (m, 1H), 1.57 (s, 3H), 1.50 (s, 3H), 0.1 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.1, 154.9, 141.4, 138.0, 128.9, 128.63, 128.58, 128.5, 128.0, 126.2, 123.2, 82.3, 67.3, 44.0, 29.6, 27.3, 26.3, 2.8; **IR** (film) 3063, 3028, 2947, 1694, 1603, 1570, 1496, 1454, 1387, 1362, 1246, 1209, 1158, 1104 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{24}H_{31}INaO_2Si$ $(M + Na)^+$ 529.1036, found 529.1060; **TLC** R_f = 0.60 (19:1 hexanes/EtOAc).



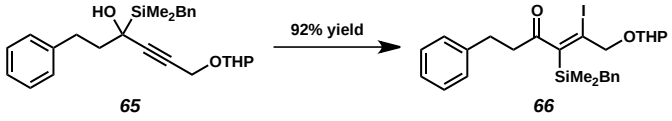
61 *62*

α-Silyl-β-iodoenone 62 (Table 2.4.3, Entry 7): Reaction was conducted at 0 ºC for 20 min. Colorless oil (124 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.69 (app. t, *J* = 4.8 Hz, 1H), 4.28 (ABq, *J* = 17.2 Hz, Δν = 48.3 Hz, 2H), 3.96-3.87 (m, 1H), 3.59-3.49 (m, 1H), 2.69 (m, 1H), 2.05–1.99 (m, 2H), 1.84–1.69 (comp m, 6H), 1.62–1.52 (comp m, 3H), 1.37–1.17 (comp m, 6H), 0.22 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.4, 158.4, 111.9, 97.7, 72.5, 62.5, 49.6, 30.6, 28.2, 26.2, 25.5, 19.3, 0.7; **IR** (film) 2937, 2853, 1683, 1583, 1449, 1385, 1340, 1307, 1253, 1201, 1121, 1076 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{18}H_{35}INO_3Si$ $(M + NH_4)^+$ 468.1431, found 468.1433; **TLC** R_f = 0.50 (9:1 hexanes/EtOAc).



63 *64*

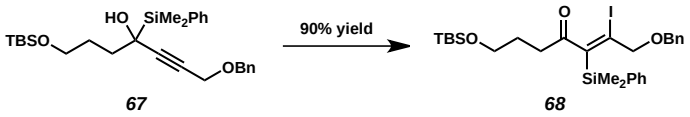
α-Silyl-β-iodoenone 64 (Table 2.4.3, Entry 8): Using substrate **63**, reaction was conducted at 0 ºC for 15 min, utilizing 1.30 g (3.56 mmol) of α-hydroxypropargylsilane. Pale yellow oil (1.64 g, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.26 (m, 2H), 7.23–7.16 (comp m, 5H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 2H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.62 (br t, *J* = 7.0 Hz, 2H), 2.42–2.38 (m, 2H), 2.27 (s, 2H), 1.60–1.52 (m, 2H), 1.35 (app. sextet, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.16 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.2, 152.5, 141.2, 138.1, 128.7, 128.6, 128.53, 128.51, 126.1, 124.9, 117.7, 45.1, 43.7, 32.7, 29.3, 26.3, 22.0, 14.1, -1.5; **IR** (film) 3026, 2955, 2872, 1693, 1587, 1496, 1454, 1406, 1353, 1252, 1212, 1151, 1120, 1076 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{24}H_{32}IOSi$ $(M + H)^+$ 491.1267, found 491.1270; **TLC** R_f = 0.48 (19:1 hexanes/EtOAc).



65 *66*

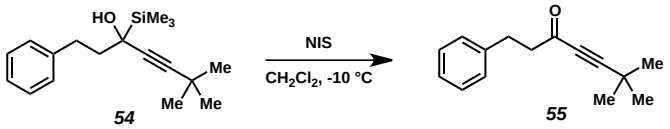
α-Silyl-β-iodoenone 66 (Table 2.4.3, Entry 9): Reaction was conducted at 0 ºC for 15 min. Pale yellow oil (151 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28–7.24 (m, 2H), 7.21–7.13 (comp m, 5H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 2H), 4.64 (t, *J* = 3.2 Hz, 1H), 4.15 (ABq, *J* = 12.8 Hz, Δν = 53.4 Hz, 2H), 3.92-3.84 (m, 1H), 3.55–3.51 (m, 1H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.67-2.48 (br m, 2H), 2.28 (s, 2H), 1.89–1.81 (m, 1H), 1.78–1.68 (comp m, 2H), 1.60–1.52 (comp m, 3H), 0.17 (s, 3H), 0.15 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.0, 156.7, 141.0, 137.9, 128.7, 128.62, 128.58, 128.5, 126.2, 125.0, 112.2, 97.7, 72.4, 62.5, 43.2, 30.5, 29.1, 25.5, 19.2, -1.6; **IR** (film) 3025, 2944, 1693, 1588, 1493, 1452, 1402, 1353, 1254,

1202, 1153, 1120, 1076 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{26}H_{37}INO_3Si$ $(M + NH_4)^+$ 566.1587, found 566.1588; **TLC** R_f = 0.74 (3:1 hexanes/EtOAc).



67 *68*

α-Silyl-β-iodoenone 68 (Table 2.4.3, Entry 10): Reaction was conducted at –10 ºC for 20 min. Pale yellow oil (164 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.42–7.36 (comp m, 6H), 7.30–7.26 (m, 2H), 7.23–7.21 (m, 1H), 4.06 (s, 2H), 3.98 (s, 2H), 3.66 (t, *J* = 6.0 Hz, 2H), 2.71 (t, *J* = 7.2 Hz, 2H), 1.85 (app. quint, *J* = 6.7 Hz, 2H), 0.89 (s, 9H), 0.43 (s, 6H), 0.05 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.9, 157.4, 137.5, 136.4, 133.9, 130.1, 128.5, 128.4, 128.1, 127.9, 112.7, 75.5, 71.8, 62.1, 38.4, 26.3, 26.1, 18.4, -1.0, -5.1; **IR** (film) 2955, 2929, 2857, 1693, 1587, 1471, 1428, 1405, 1360, 1309, 1254, 1181, 1100 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{28}H_{42}IO_3Si_2$ $(M + H)^+$ 609.1717, found 609.1717; **TLC** R_f = 0.28 (19:1 hexanes/EtOAc).



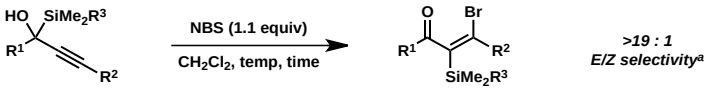
54 *55*

Ynone 55 (Table 2.4.3, Entry 3): α-Hydroxypropargylsilane **54** (0.300 mmol, 86.6 mg, 1.00 equiv) was dissolved in 1.50 mL of dry CH_2Cl_2 under Ar. The solution was then cooled to –10 ºC in an ice/NaCl bath. *N*-iodosuccinimide (0.330 mmol, 74.2 mg, 1.10 equiv) was added quickly in one portion to the reaction mixture. The reaction mixture was monitored by TLC for the disappearance of starting hydroxypropargylsilane. After 3 h, when all starting material was consumed, 10 mL of pentane was added and the reaction mixture was filtered through a small

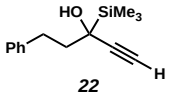
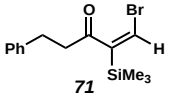
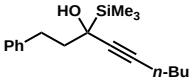
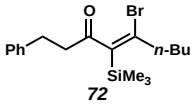
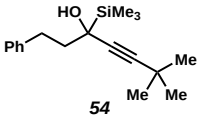
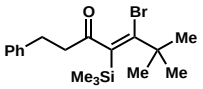
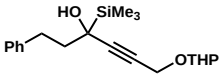
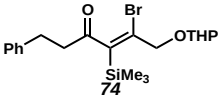
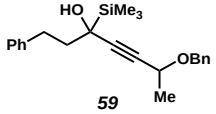
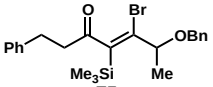
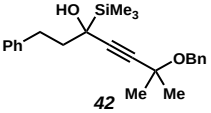
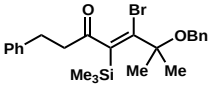
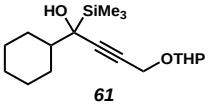
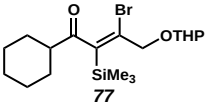
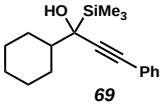
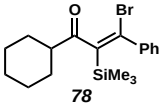
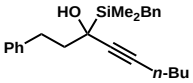
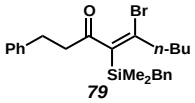
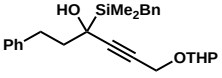
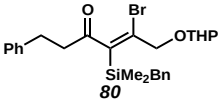
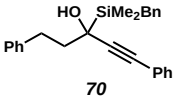
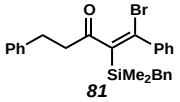
plug of silica gel to remove the insoluble material. Removal of the solvent in vacuo afforded a pale yellow oil, which was determined as ynone **55**.

2.6.7 *N*-Bromosuccinimide Induced Silyl Migrations of α-hydroxypropargylsilanes

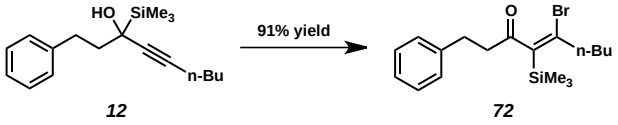
Table 2.4.4 (*reproduced*)



>19 : 1
E/Z selectivity[a]

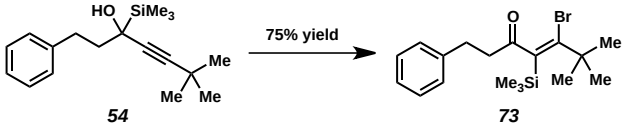
entry	substrate	product	temperature (°C)	time (h)	yield (%)
1	 ***22***	 ***71***	-15	0.25	89[b]
2	 ***12***	 ***72***	0	0.25	91
3	 ***54***	 ***73***	-78 → -10	2.5	75
4	 ***40***	 ***74***	0	0.25	92
5	 ***59***	 ***75***	-15	0.5	89
6	 ***42***	 ***76***	-78 → -10	5	85
7	 ***61***	 ***77***	0	0.3	92
8	 ***69***	 ***78***	-78 → 0	4	94
9	 ***63***	 ***79***	0	0.75	92
10	 ***65***	 ***80***	0	0.25	88
11	 ***70***	 ***81***	-78 → 0	4	80

a) Measured by ^{1}H NMR b) Yield of allylic alcohol after in situ reduction (DIBAL, -78 °C)



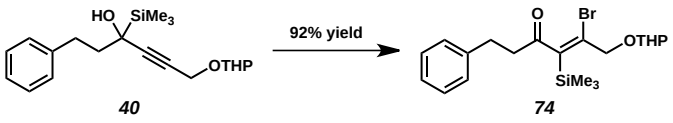
12 *72*

α-Silyl-β-bromoenone 72 (Table 2.4.4, Entry 2): Using substrate **12**,**Error! Bookmark not defined.** reaction was conducted at 0 ºC for 15 min. Pale yellow oil (100 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.17 (m, 5H), 2.96 (app t, *J* = 8.0 Hz, 2H), 2.85 (app t, *J* = 8.0 Hz, 2H), 2.53–2.49 (m, 2H), 1.67–1.59 (m, 2H), 1.37 (app sextet, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.6 Hz, 3H), 0.20 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.2, 146.6, 141.3, 135.1, 128.62, 128.60, 126.58, 45.0, 41.2, 31.3, 29.4, 22.2, 14.1, 0.1; **IR** (film) 3063, 3028, 2957, 2873, 1695, 1601, 1496, 1454, 1407, 1354, 1252, 1213, 1134 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{18}H_{27}BrNaOSi$ $(M + Na)^+$ 389.0912, found 389.0914; **TLC** R_f = 0.35 (19:1 hexanes/EtOAc).



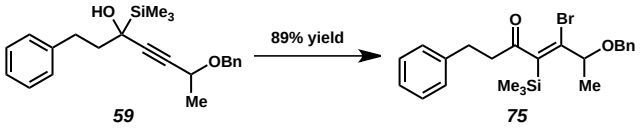
54 *73*

α-Silyl-β-bromoenone 54 (Table 2.4.4, Entry 3): Reaction was conducted at –78 ºC for 1 h followed by –10 ºC for 1.5 h. Pale yellow oil (82.6 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.17 (comp m, 5H), 3.15 (br s, 1H), 2.98 (app t, *J* = 8.0 Hz, 2H), 2.54 (br s, 1H), 1.34 (s, 9H), 0.30 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.7, 148.8, 145.1, 141.4, 128.63, 128.60, 126.2, 45.3, 42.5, 31.2, 29.6, 3.2; **IR** (film) 3063, 3027, 2966, 2866, 1695, 1603, 1562, 1496, 1454, 1408, 1362, 1249, 1204, 1101, 1074 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{18}H_{27}BrNaOSi$ $(M + Na)^+$ 389.0912, found 389.0911; **TLC** R_f = 0.44 (19:1 hexanes/EtOAc).



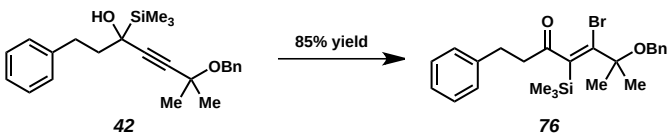
40 *74*

α-Silyl-β-bromoenone 74 (Table 2.4.4, Entry 4): Using substrate **40**, reaction was conducted at 0 ºC for 15 min. Pale yellow oil (117 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.17 (comp m, 5H), 4.68 (app t, *J* = 3.2 Hz, 1H), 4.32 (ABq, *J* = 12.8 Hz, Δν = 38.5 Hz, 2H), 3.91–3.86 (m, 1H), 3.56–3.51 (m, 1H), 2.97 (app t, *J* = 7.6 Hz, 2H), 2.89 (app t, *J* = 7.6 Hz, 2H), 1.89–1.56 (comp m, 6H), 0.23 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.9, 188.5, 151.4, 141.1, 129.6, 128.64, 128.61; 126.2, 97.8, 70.1, 62.4, 44.6, 30.5, 29.3, 25.5, 19.3, 0.1; **IR** (film) 3063, 3027, 2949, 1697, 1603, 1496, 1453, 1406, 1353, 1254, 1201, 1122 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{20}H_{33}BrNO_3Si$ $(M + NH_4)^+$ 442.1413, found 442.1405; **TLC** R_f = 0.43 (9:1 hexanes/EtOAc).



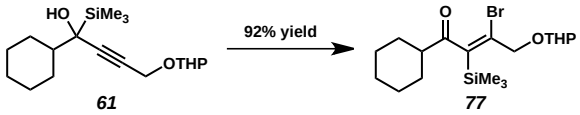
59 *75*

α-Silyl-β-bromoenone 75 (Table 2.4.4, Entry 5): Reaction was conducted at –15 ºC for 30 min. Pale yellow oil (118 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.19 (comp m, 10H), 4.57 (d, *J* = 11.2 Hz, 1H), 4.31 (d, *J* = 11.2 Hz, 1H), 4.24 (q, *J* = 6.2 Hz, 1H), 3.02 (app t, *J* = 6.8 Hz, 2H), 2.93–2.88 (m, 2H), 1.40 (d, *J* = 6.2 Hz, 3H), 0.22 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.6, 194.9, 149.9, 141.1, 137.8, 128.7, 128.6, 128.0, 127.9, 126.3, 76.2, 70.4, 45.0, 29.4, 21.2, 0.4; **IR** (film) 3030, 2955, 2896, 1696, 1591, 1496, 1453, 1406, 1370, 1355, 1320, 1254, 1202, 1150 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{23}H_{33}BrNO_2Si$ $(M + NH_4)^+$ 462.1467, found 462.1467; **TLC** R_f = 0.42 (19:1 hexanes/EtOAc).



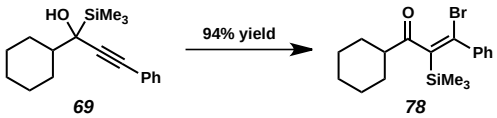
42 *76*

α-Silyl-β-bromoenone 76 (Table 2.4.4, Entry 6): Reaction was conducted at –78 ºC for 4 h, then warmed to –10 ºC for 1 h. colorless oil (117 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.17 (comp m, 10H), 4.59 (s, 2H), 3.08 (br s, 1H), 2.96 (t, *J* = 8.0 Hz, 2H), 2.59 (br s, 1H), 1.60 (s, 6H), 0.01 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.9, 147.0, 141.4, 138.9, 137.8, 128.9, 128.44, 128.41, 128.3, 127.8, 82.2, 66.6, 44.8, 29.5, 25.6, 2.3; **IR** (film) 3063, 3029, 2945, 1698, 1586, 1496, 1454, 1388, 1362, 1246, 1163, 1108, 1026 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{24}H_{31}BrNaO_2Si$ $(M + Na)^+$ 481.1174, found 483.1160; **TLC** R_f = 0.59 (19:1 hexanes/EtOAc).



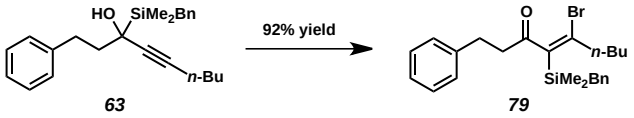
61 *77*

α-Silyl-β-bromoenone 77 (Table 2.4.4, Entry 7): Reaction was conducted at 0 ºC for 20 min. Colorless oil (111 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.69 (app t, *J* = 4.0 Hz, 1H), 4.36 (ABq, *J* = 12.8 Hz, Δν = 43.3 Hz, 2H), 3.95-3.88 (m, 1H), 3.58-3.51 (m, 1H), 2.63 (tt, *J* = 11.6, 3.6 Hz, 1H), 2.00–1.97 (m, 2H), 1.91–1.52 (comp m, 9H), 1.38–1.11 (comp m, 5H), 0.24 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.8, 151.1, 129.9, 97.9, 70.3, 62.5, 50.4, 30.5, 28.3, 26.2, 26.1, 25.5, 19.3, 0.5; **IR** (film) 2933, 2855, 1674, 1450, 1343, 1241, 1159, 1122, 1031 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{18}H_{35}BrNO_3Si$ $(M + NH_4)^+$ 420.1570, found 420.1549; **TLC** R_f = 0.50 (9:1 hexanes/EtOAc).



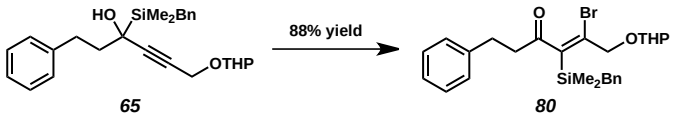
69 *78*

α-Silyl-β-bromoenone 78 (Table 2.4.4, Entry 8): Reaction was conducted at –78 ºC for 2 h, then warmed to 0 ºC for 2 h. Colorless solid (103 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (br s, 5H), 2.67 (tt, *J* = 11.6, 3.6 Hz, 1H), 2.11 (app. d, *J* = 12.1 Hz, 2H), 1.86 (dt, *J* = 12.5, 3.2 Hz, 2H), 1.71 (app. d, *J* = 12.1 Hz, 1H), 1.49–1.16 (comp m, 5H), 0.10 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.9, 149.9, 141.7, 129.3, 128.9, 128.6, 128.3, 50.7, 28.5, 26.2, 26.1, 0.4; **IR** (film) 3058, 2932, 2854, 1685, 1611, 1583, 1486, 1445, 1409, 1361, 1307, 1250, 1209, 1147, 1114, 1071 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{18}H_{26}BrOSi$ $(M + H)^+$ 365.0936, found 365.0913; **TLC** R_f = 0.45 (19:1 hexanes/EtOAc).



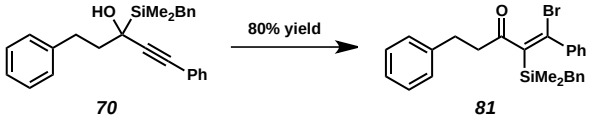
63 *79*

α-Silyl-β-bromoenone 79 (Table 2.4.4, Entry 9): Using substrate **63**, reaction was conducted at 0 ºC for 45 min. Colorless oil (122 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.15 (comp m, 7H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 6.8 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.39–2.35 (m, 2H), 2.26 (s, 2H), 1.62–1.54 (m, 2H), 1.33 (app sextet, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.14 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.2, 144.8, 141.2, 138.2, 136.2, 128.7, 128.60, 128.55, 128.5, 126.1, 124.9, 44.6, 41.3, 31.2, 29.3, 26.1, 22.2, 14.1, -1.8; **IR** (film) 3060, 2958, 2872, 1693, 1587, 1496, 1454, 1406, 1355, 1252, 1212, 1151, 1120, 1076 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{24}H_{32}BrOSi$ $(M + H)^+$ 443.1406, found 443.1392; **TLC** R_f = 0.43 (19:1 hexanes/EtOAc).



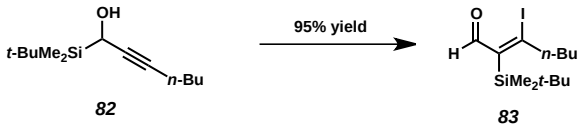
65 *80*

α-Silyl-β-bromoenone 80 (Table 2.4.4, Entry 10): Reaction was conducted at 0 ºC for 45 min. Colorless oil (132 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27–7.12 (comp m, 7H), 7.05 (t, *J* = 6.4 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 2H), 4.64 (app t, *J* = 3.5 Hz, 1H), 4.17 (ABq, *J* = 12.9 Hz, Δν = 54.8 Hz, 2H), 3.93-3.83 (m, 1H), 3.58-3.49 (m, 1H), 2.87 (app t, *J* = 7.8 Hz, 2H), 2.64–2.57 (m, 2H), 2.27 (s, 2H), 1.89–1.51 (comp m, 6H), 0.16 (s, 3H), 0.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.9, 149.5, 141.0, 138.0, 130.4, 128.7, 128.62, 128.60, 128.5, 126.2, 125.0, 97.9, 70.3, 62.4, 44.1, 30.5, 29.1, 26.1, 25.5, 19.3, -1.9; **IR** (film) 3061, 3026, 2949, 1695, 1600, 1494, 1453, 1403, 1354, 1257, 1203, 1125 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{26}H_{37}BrNO_3Si$ $(M + NH_4)^+$ 518.1726, found 518.1726; **TLC** R_f = 0.73 (3:1 hexanes/EtOAc).



70 *81*

α-Silyl-β-bromoenone 81 (Table 2.4.4, Entry 11): Reaction was conducted at –78 ºC for 2 h, then warmed to 0 ºC for 2 h. Colorless oil (111 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.16 (comp m, 12H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.4 Hz, 2H), 3.00 (app t, *J* = 8.4 Hz, 2H), 2.95 (app t, *J* = 6.3 Hz, 2H), 1.99 (s, 2H), -0.22 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.1, 148.7, 141.2, 141.1, 138.3, 129.3, 128.7, 128.62, 128.60, 128.5, 128.4, 126.3, 124.8, 98.7, 44.7, 29.5, 25.7, -2.3; **IR** (film) 2932, 2854, 1686, 1610, 1583, 1486, 1444, 1249, 1209, 1147, 1114, 1071 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{26}H_{28}BrOSi$ $(M + H)^+$ 463.1093, found 463.1108; **TLC** R_f = 0.48 (19:1 hexanes/EtOAc).



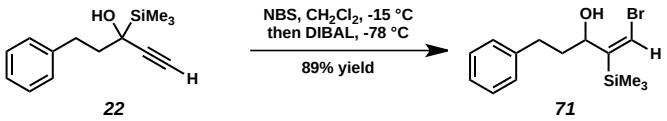
82 *83*

α-Silyl-β-iodoenal 83: Using substrate **82**,[42] reaction was conducted at –78 ºC for 4 h. The product is not stable to silica gel flash chromatography. Pale yellow oil (101 mg, 95% yield) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 2.84–2.81 (m, 2H), 1.72–1.64 (m, 2H), 1.43 (app sextet, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.94 (s, 9H), 0.22 (s, 6H); **^{13}C NMR** (100 MHz, 400 MHz, $CDCl_3$) δ 203.3, 143.0, 138.6, 47.5, 32.7, 27.2, 22.1, 18.6, 14.1, -2.4; **IR** (film) 2957, 2859, 2715, 1686, 1555, 1467, 1391, 1363, 1252, 1209, 1137, 1081 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{13}H_{26}IOSi$ 353.0798, found 353.0797; **TLC** R_f = 0.36 (4:1 hexanes/EtOAc).

2.6.8 *N*-Halosuccinimide-induced silyl migration/DIBAL reduction of α-hydroxypropargylsilanes

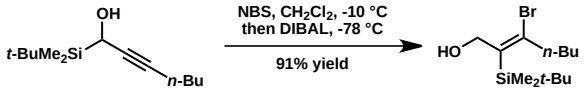
α-Hydroxypropargylsilane (0.400 mmol, 1.00 equiv) was dissolved in 2.0 mL of dry CH_2Cl_2 under Ar. The solution was cooled to the designated temperature. *N*-Halosuccinimide (0.440 mmol, 1.10 equiv) was added quickly in one portion to the reaction mixture. The reaction mixture was monitored by TLC for the disappearance of starting α-hydroxypropargylsilane. When all starting material was consumed, the reaction mixture was cooled to –78 ºC and DIBAL (1.02 mL, 0.98 M in toluene, 2.5 equiv) was added dropwise via syringe. The reaction mixture stirred for 10 minutes, after which time TLC indicated consumption of enone. A saturated solution of Rochelle's salt (10 mL) was added to the reaction mixture, followed by 20 mL of CH_2Cl_2. The mixture was warmed to room temperature and stirred form 3 h. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (1 x 15 mL) and then dried over Na_2SO_4. Filtration and removal

of the solvent in vacuo afforded a pale yellow oil. Purification was accomplished by flash column chromatography on silica gel (hexanes/EtOAc as eluent).



22 *71*

Alcohol 71 (Table 2.4.4, Entry 1): The 1,2-silyl migration was performed at –15 ºC for 1 h. Colorless oil (112 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.18 (m, 5H), 6.33 (s, 1H), 4.73 (app. t, *J* = 6.7 Hz, 1H), 2.93–2.85 (m, 1H), 2.75–2.67 (m, 1H), 1.90 (app. q, *J* = 7.2 Hz, 2H), 1.76 (br s, 1H), 0.19 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.3, 141.7, 128.7, 128.5, 126.1, 112.4, 75.9, 37.7, 32.5, 0.3; **IR** (film) 3471, 3065, 3027, 2954, 1560, 1496, 1454, 1409, 1377, 1248, 1052 cm^{-1}; **HRMS** (DART) *m/z* calc'd for $C_{14}H_{25}BrNOSi$ $(M + NH_4)^+$ 332.0868, found 332.0858; **TLC** R_f = 0.53 (9:1 hexanes/EtOAc).

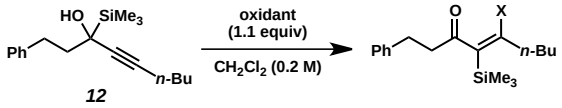


82 *84*

Alcohol 84: Using substrate **82**,[42] the silyl migration was performed at –10 ºC for 1 h. Colorless oil (112 mg, 91% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 4.21 (s, 2H), 2.60–2.55 (m, 2H), 1.97 (br s, 1H), 1.67–1.59 (m, 2H), 1.36 (app. sextet, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.92 (s, 9H), 0.25 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 144.9, 135.3, 67.0, 42.8, 32.0, 26.9, 22.4, 18.6, 14.1, -3.1; **IR** (film) 3436, 2957, 2858, 2592, 1495, 1465, 1390, 1362, 1254, 1213, 1125, 1062 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{13}H_{28}BrOSi$ $(M + H)^+$ 307.1093, found 307.1091; **TLC** R_f = 0.29 (9:1 hexanes/EtOAc)

2.6.9 Oxidant Screen

Table 2.4.2 (*reproduced*)



12

entry	oxidant	temp (°C)	yield (%)[a,b]	*E* : *Z*[c]
1	*m*-CPBA	50	NR	--
2	NCS	55	NR	--
3	TCCA	50	NR	--
4	Selectfluor	23	NR	--
5	NFSI	50	NR	--
6	NBS	23	91	>19 : 1
7	NIS	23	90	15 : 1
8	NIS	0	90	>19 : 1

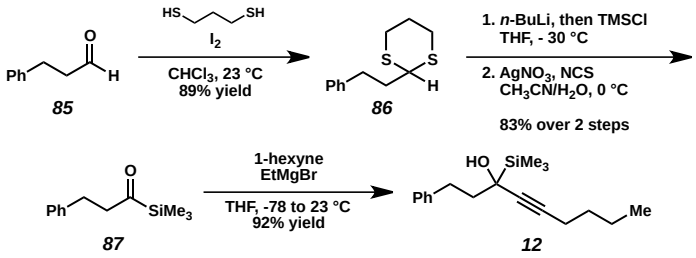
a) Isolated yield b) NR: no reaction c) Selectivity determined by ^{1}H NMR analysis of the crude reaction mixture

Representative Procedure. In a 2-dram vial, α-Hydroxypropargylsilane (0.300 mmol, 1.00 equiv) was dissolved in 1.50 mL of dry CH_2Cl_2. At room temperature, the indicated oxidant (0.330 mmol, 1.10 equiv) was added quickly in one portion to the reaction mixture. The reaction mixture was then sealed under a stream of argon and heated at the designated temperature for 5 h. After this time, TLC and ^{1}H NMR analysis of the crude reaction mixture indicated either no change or production of enones **52** or **72**.

2.6.10 Substrate Synthesis

General procedure for alkyne addition into acylsilanes. A flame dried flask was charged with an alkyne (1.5 equiv) and THF (0.5 M). The solution was cooled to 0 ˚C and EtMgBr (3.0 M in Et_2O, 1.5 equiv) was added dropwise. The solution was allowed to warm to room temperature while stirring for 45 min. The deprotonated alkyne solution was then cooled to -78 ˚C. In a

separate flame dried flask, the acylsilane was dissolved in THF (~1.0 M) and added dropwise to the reaction mixture via syringe. The reaction mixture was allowed to warm slowly up to 23 °C until the acylsilane was consumed as judged by TLC analysis, at which point it was cooled to -78˚ C and quenched with saturated aqueous ammonium chloride. The mixture was allowed to warm to room temperature, and THF was removed via rotary evaporation. The mixture was then extracted with Et_2O (2 x 20-50 mL), and the combined organic layers were washed with brine, and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography to afford the α-hydroxypropargylsilane.



Dithiane 86: Thioketalization was conducted according to the procedure of Firouzabadi and coworkers.[43] To a solution of hydrocinnamaldehyde (**85**, 2.64 mL, 20.0 mmol) and 1,3-propanedithiol (2.20 mL, 22.0 mmol) in $CHCl_3$ (100 mL) at 23 °C under argon was added I_2 (508 mg, 2.00 mmol) as a solid. The reaction was stirred for 1.5 h, at which point it was quenched with aq. $Na_2S_2O_3$ (90 mL, 0.1 M). The phases were separated, and the aqueous layer was extracted with $CHCl_3$ (100 mL). The combined organic phases were washed with aq. NaOH (10% w/v, 100 mL), brine (2 x 100 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the residue was purified by flash chromatography (3:1 hexanes/CH_2Cl_2 eluent) to afford **86** (3.99 g, 89% yield, R_F = 0.60 in 1:1 hexanes/CH_2Cl_2) as a pale yellow oil.

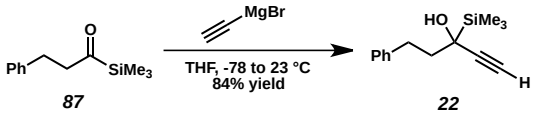
To a solution of **86** (4.46 g, 19.9 mmol) in 45.0 mL THF at –30 °C under argon was added *n*-BuLi (9.55 mL, 2.5 M in hexanes, 23.9 mmol) dropwise. The resulting red/brown solution was allowed to stir for 2 h, and then it was cooled to –78 °C, and TMSCl (3.02 mL, 23.9 mmol) was added. The reaction was stirred for 1 h at –78 °C and then quenched with sat. aq. NH_4Cl (25 mL). The mixture was extracted with Et_2O (2 x 100 mL), and the combined organic layers were washed with brine (100 mL) and dried over $MgSO_4$. The solution was concentrated in vacuo, and the crude dithiane (R_F = 0.67 in 1:1 hexanes/CH_2Cl_2) was taken immediately to the next step.

Acylsilane 87: Dithiane hydrolysis was conducted according to the procedure of Corey and Erickson.[44] To a solution of $AgNO_3$ (4.22 g, 27.0 mmol), and NCS (4.06 g, 30.4 mmol) in CH_3CN:H_2O (4:1, 60 mL) at 0 °C in an Erlenmeyer flask was added a portion of the crude dithiane (2.00 g, 6.75 mmol) in 5 mL THF. Immediately, a white precipitate formed. The mixture was stirred for 5 min and then quenched with sat. aq. Na_2SO_3 (7 mL), sat. aq. Na_2CO_3 (7 mL), and brine (7 mL) in 1 min increments while stirring. CH_2Cl_2/hexanes (1:2, 100 mL) were added to the reaction mixture, stirred 5 min, and the organic layer was decanted into a separatory funnel, taking care to leave the precipitate in the Erlenmeyer flask. The extraction process was repeated, and the combined organic layers were washed with water (100 mL), then brine (100 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford acylsilane **87** (1.20 g, 83% yield over 2 steps, R_F = 0.38 in 9:1 hexanes/EtOAc).

α-Hydroxypropargylsilane 12: According to the general procedure, 1-hexyne (0.280 mL, 2.44 mmol) in 5.0 mL THF was deprotonated by EtMgBr (0.830 mL, 2.49 mmol). To the alkynyl Grignard was added **87** (343 mg, 1.66 mmol) in 8.30 mL THF dropwise. The reaction was

stirred until completion as judged by TLC (9:1 hexanes/EtOAc). Purification by flash chromatography (9:1 hexanes/EtOAc eluent) afforded **12** as a colorless oil (394 mg, 82% yield, R_F = 0.30 in 9:1 hexanes/EtOAc).

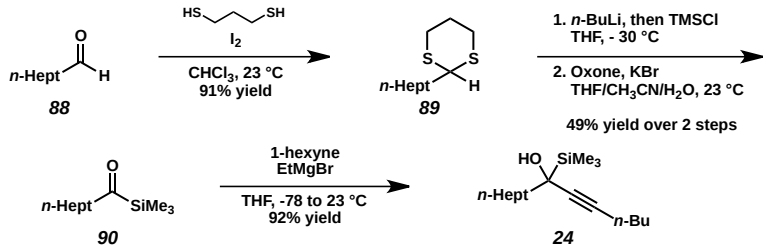
α-Hydroxypropargylsilane 12: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.23 (comp m, 4H), 7.18 (t, *J* = 7.2 Hz, 1H), 2.91 (t, *J* = 8.4, 2H), 2.28 (t, *J* = 6.4 Hz, 2H), 1.98-1.77 (m, 2H), 1.55-1.40 (m, 4H), 0.93 (t, *J* = 6.4 Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 128.8, 128.6, 126.0, 88.7, 82.4, 65.0, 40.0, 31.4, 30.5, 22.1, 18.9, 13.8, -4.1; IR (film) 3456, 3027, 2958, 2862, 1455, 1247, 1023 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M - OH)^+$ $[C_{18}H_{28}OSi - OH]^+$: 271.1877, found 271.1877.



α-Hydroxypropargylsilane 87: To a solution of acylsilane **22** (476 mg, 2.31 mmol) in 7.0 mL THF at -78 °C was added a solution of ethynylmagnesium bromide (5.99 mL, 0.5 M in THF, 3.00 mmol) dropwise via syringe. The reaction mixture was allowed to warm slowly to 23 °C until the acylsilane was consumed as judged by TLC analysis, at which point it was cooled to -78 °C and quenched with sat. aq. NH_4Cl (5 mL). The mixture was allowed to warm to room temperature, and THF was removed by rotary evaporation. The mixture was then extracted with Et_2O (2 x 30 mL), and the combined organic layers were washed with brine (40 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford α-hydroxypropargylsilane **22** (453 mg, R_F = 0.20 in 9:1 hexanes/EtOAc, 84% yield) as a colorless oil.

α-Hydroxypropargylsilane 22: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.22 (m, 4H), 7.18 (t, *J* =

7.0 Hz, 1H), 2.92 (app. ddd, *J* = 10.1, 6.6, 3.0 Hz, 2H) 2.68 (s, 1H), 2.01-1.81 (comp m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 128.7, 128.6, 126.0, 86.5, 76.0, 64.7, 39.5, 30.3, -4.3; IR (film) 3553, 3308, 2956, 1249, 842, 702 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{14}H_{21}OSi]^+$: 233.1356, found 233.1353.



Dithiane 89: Thioketalization was conducted according to the procedure of Firouzabadi and coworkers.[43] To a solution of octanal (**88**, 7.80 mL, 50.0 mmol) and 1,3-propanedithiol (5.52 mL, 55.0 mmol) in $CHCl_3$ (200 mL) at 23 °C under argon was added I_2 (1.27 g, 5.00 mmol) as a solid. The reaction was stirred for 1.5 h, at which point it was quenched with sat. aq. $Na_2S_2O_3$ (10 mL). Water (100 mL) was added, the phases were separated, and the aqueous layer was extracted with $CHCl_3$ (100 mL). The combined organic phases were washed with aq. NaOH (10% w/v, 100 mL), brine (200 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the residue was purified by flash chromatography (3:1 hexanes/CH_2Cl_2 eluent) to afford **89** (9.89 g, 91% yield, R_F = 0.70 in 1:1 hexanes/CH_2Cl_2) as a pale yellow oil.

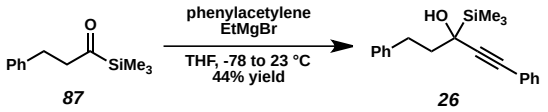
To a solution of **89** (1.56 g, 7.14 mmol) in 35.0 mL THF at –30 °C under argon was added *n*-BuLi (3.43 mL, 2.5 M in hexanes, 8.57 mmol) dropwise. The resulting red/brown solution was allowed to stir for 2 h, and then it was cooled to –78 °C, and TMSCl (1.10 mL, 8.57 mmol) was added. The reaction was stirred for 1 h at –78 °C and then quenched with sat. aq. NH_4Cl (4 mL). The mixture was extracted with Et_2O (2 x 40 mL), and the combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The solution was concentrated in

vacuo, and the crude dithiane (R_F = 0.79 in 1:1 hexanes/CH_2Cl_2) was taken immediately to the next step.

AcylSilane 90: Dithiane hydrolysis was conducted according to the procedure of Desai and coworkers.[45] A portion of the crude product (860 mg, 2.96 mmol) was added to a solution of KBr (704 mg, 5.92 mmol) in THF:CH_3CN:H_2O (1:2:1, 14.8 mL). Oxone (1.82 g, 5.92 mmol) in water was then added to the reaction mixture, and the solution was stirred for 1 h at 23 °C. The mixture was then extracted with Et_2O (2 x 25 mL), and the combined organic layers were washed with water (30 mL), then brine (30 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the residue was purified by column chromatography (19:1 hexanes/EtOAc eluent) to afford acylsilane **90** (310 mg, 49% yield over two steps, R_F = 0.36 in 9:1 hexanes/EtOAc).

α-Hydroxypropargylsilane 24: According to the general procedure, 1-hexyne (0.141 mL, 1.25 mmol) in 5.0 mL THF was deprotonated by EtMgBr (0.416 mL, 1.25 mmol). To the alkynyl Grignard was added **90** (209 mg, 1.04 mmol) in 2.0 mL THF dropwise. The reaction was stirred until completion as judged by TLC (9:1 hexanes/EtOAc). Purification by flash chromatography (15:1 hexanes/EtOAc eluent) afforded **24** as a colorless oil (271 mg, 92% yield, R_F = 0.48 in 9:1 hexanes/EtOAc).

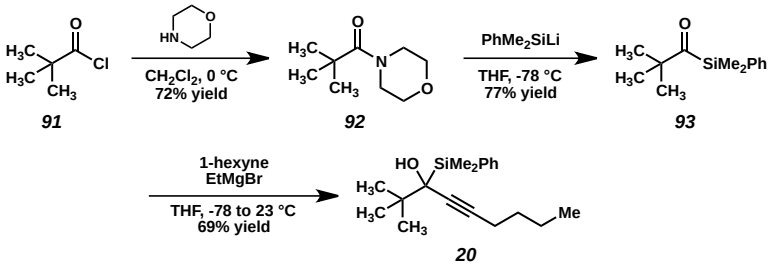
α-Hydroxypropargylsilane 24: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (t, *J* = 7.0 Hz, 2H), 1.61-1.29 (comp m, 16H), 0.91 (t, *J* = 7.3, 3H), 0.89 (t, *J* = 7.6 Hz, 3H), 0.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 88.0, 82.8, 65.0, 37.9, 32.1, 31.3, 30.1, 29.5, 23.8, 22.9, 22.1, 18.8, 14.3, 13.8, -4.0; IR (film) 3602, 3460, 2957, 2858, 1466, 1247 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $[M - OH]^+$ ($C_{17}H_{34}OSi$ - OH): 265.2346, found 265.2348.



87 26

α-Hydroxypropargylsilane 26: According to the general procedure, phenylacetylene (0.371 mL, 3.38 mmol) in 5.0 mL THF was deprotonated by EtMgBr (1.01 mL, 3.38 mmol). To the alkynyl Grignard was added **87** (466 mg, 2.26 mmol) in 2.0 mL THF dropwise. The reaction was stirred until completion as judged by TLC (9:1 hexanes/EtOAc). Purification by flash chromatography (9:1 hexanes/EtOAc eluent) afforded **26** as a colorless oil (307 mg, 44% yield, R_F = 0.43 in 9:1 hexanes/EtOAc).

α-Hydroxypropargylsilane 26: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.34-7.32 (comp m, 7H), 7.22 (t, *J* = 7.6 Hz, 1H), 3.05-3.00 (m, 2 H), 2.12-1.95 (m, 2H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 131.2, 128.3, 128.1, 128.0, 127.7, 125.5, 91.2, 87.8, 64.7, 39.2, 30.2, -4.6; IR (film) 3553, 3447, 3026, 2954, 1599, 1489, 1248 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M - OH_2)^+$ $[C_{20}H_{24}OSi - H_2O]^+$: 291.1564, found 291.1563.



91 92 93 20

Acylsilane **93** was synthesized according to the procedure of Scheidt et al.[46]

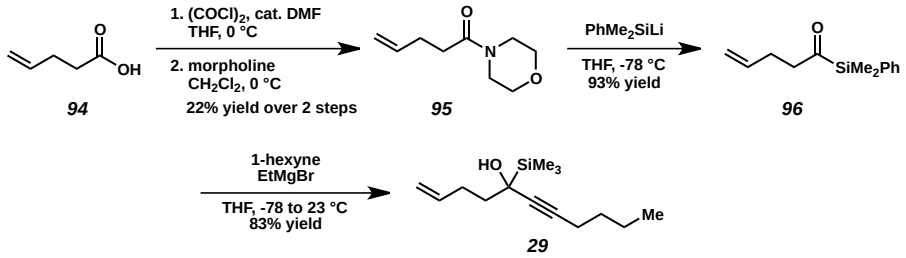
Amide 92: To a solution of trimethylacetyl chloride (2.00 mL, 16.2 mmol) in 24.0 mL CH_2Cl_2 at 0 °C under argon was added morpholine (4.08 mL, 46.8 mmol) dropwise. The resulting mixture was stirred for 30 min, and then it was diluted with EtOAc (100 mL) and washed sequentially with 1.0 M aq. HCl (2 x 30 mL), sat. aq. $NaHCO_3$ (40 mL), and brine (50 mL). The organic

layer was dried over Na_2SO_4 and concentrated in vacuo to afford amide **92** (1.80 g, 72% crude yield, R_F = 0.07 in 9:1 hexanes/EtOAc) as a white solid.

Acylsilane 93: To a solution of **92** (1.61 g, 9.39 mmol) in 14.0 mL THF at –78 °C under argon was added a solution of $PhMe_2SiLi$ (14.1 mL, 1.0 M in THF, 14.1 mmol) dropwise slowly. The resulting mixture was stirred for 2 h, then quenched with sat. aq. NH_4Cl (14 mL) slowly at –78 °C. The mixture was warmed to room temperature, extracted with Et_2O (2 x 40 mL), and the combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by flash chromatography (9:1 hexanes/EtOAc eluent) afforded **93** (1.59 g, 77% yield, R_F = 0.48 in 9:1 hexanes/EtOAc) as a colorless oil.

α-Hydroxypropargylsilane 20: To a flame dried round bottom flask, 1-hexyne (0.392 mL, 3.48 mmol) in 10.0 mL THF was cooled in an ice water bath. To that solution, EtMgBr (1.16 mL, 3.48 mmol) was added dropwise. Subsequently, the solution was allowed to stir at room temperature for 30 min. The alkynyl Grignard was cooled back down in an ice water bath and **93** (512 mg, 2.32 mmol) in 2.0 mL THF was added dropwise. The reaction was stirred until completion (5 min) as judged by TLC (9:1 hexanes/EtOAc). Purification by flash chromatography (9:1 hexanes/EtOAc eluent) afforded **20** as a colorless oil (486 mg, 69% yield, R_F = 0.49 in 9:1 hexanes/EtOAc).

α-Hydroxypropargylsilane 20: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.8 Hz, 2H), 7.35 (app. s, 3H), 2.27 (t, *J* = 7.0 Hz, 2H), 1.54-1.34 (comp m, 4H), 0.98-0.94 (app. d, *J* = 7.2 Hz, 12H), 0.51 (s, 3H), 0.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 135.0, 129.3, 127.7, 89.5, 83.1, 72.5, 39.4, 31.2, 26.9, 22.2, 18.9, 13.8, -1.9, -2.2; IR (film) 3595, 2958, 2933, 1479, 1247, 1111, 834 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{19}H_{30}OSi + Na]^+$: 325.1958, found 325.1962.



Acylsilane **96** was synthesized according to the procedure of Scheidt et al.[46]

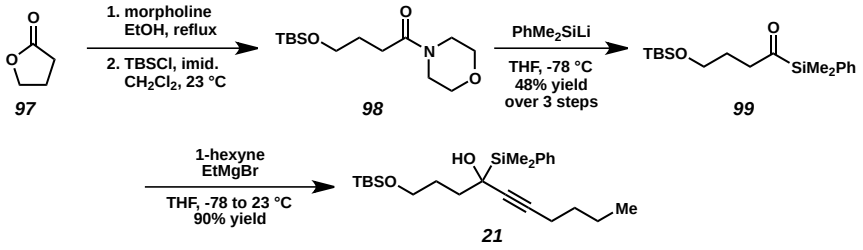
Amide 95: To a solution of 4-pentenoic acid (0.512 mL, 5.00 mmol) in 25.0 mL THF at 0 °C under argon was added $(COCl)_2$ (2.18 mL, 25.0 mmol), followed by DMF (10 μl). The mixture was stirred at 0 °C for 5 min, then allowed to warm to 23 °C and stirred 1 h. The volatile materials were removed by rotary evaporation, and the residue was concentrated from PhH (3 x 10 mL) and taken immediately to the next reaction.

To a solution of the crude acid chloride in 25.0 mL CH_2Cl_2 at 0 °C was added morpholine (1.30 mL, 15.0 mmol) dropwise. The resulting mixture was stirred for 30 min, and then it was diluted with EtOAc (30 mL) and washed sequentially with 1.0 M aq. HCl (2 x 10 mL), sat. aq. $NaHCO_3$ (20 mL), and brine (30 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. Purification by flash chromatography afforded **95** (183 mg, 22% yield over 2 steps, R_F = 0.06 in 9:1 hexanes/EtOAc) as a colorless oil.

Acylsilane 96: To a solution of **95** (104 mg, 0.615 mmol) in 6.2 mL THF at –78 °C under argon was added a solution of $PhMe_2SiLi$ (1.23 mL, 1.0 M in THF, 1.23 mmol) dropwise slowly. The resulting mixture was stirred for 1.5 h, then quenched with sat. aq. NH_4Cl (2 mL) slowly at –78 °C. The mixture was warmed to room temperature, extracted with Et_2O (2 x 20 mL), and the combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by flash chromatography (9:1 hexanes/EtOAc eluent) afforded **96** (125 mg, 93% yield, R_F = 0.35 in 9:1 hexanes/EtOAc) as a colorless oil.

α-Hydroxypropargylsilane 29: According to the general procedure, 1-hexyne (0.112 mL, 0.995 mmol) in 2.0 mL THF was deprotonated by EtMgBr (0.331 mL, 0.995 mmol). To the alkynyl Grignard was added **96** (145 mg, 0.483 mmol) in 2.0 mL THF dropwise. The reaction was stirred until completion as judged by TLC (9:1 hexanes/EtOAc). Purification by flash chromatography (19:1 hexanes/EtOAc eluent) afforded **29** as a colorless oil (165 mg, 83% yield, R_F = 0.44 in 9:1 hexanes/EtOAc).

α-Hydroxypropargylsilane 29: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (app. d, *J* = 6.2 Hz, 2H), 7.37 (app. q, *J* = 6.9 Hz, 3H), 5.85 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.03 (d, *J* = 17.0 Hz, 1H), 4.94 (d, *J* = 10.2 Hz, 1H), 2.40-2.24 (comp m, 2H), 2.26 (t, *J* = 6.9 Hz, 2H), 1.74-1.71 (m, 2H), 1.59-1.57 (m, 2H), 1.40 (app. q, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.44 (s, 3H), 0.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 134.9, 129.6, 127.8, 114.8, 89.1, 82.2, 64.8, 37.0, 31.2, 28.5, 22.1, 18.8, 13.7, -5.6, -5.7; IR (film) 3451, 2959, 2933, 1248, 1113, 832, 803, 702 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{19}H_{28}OSi + Na]^+$: 323.1802, found 323.1806.



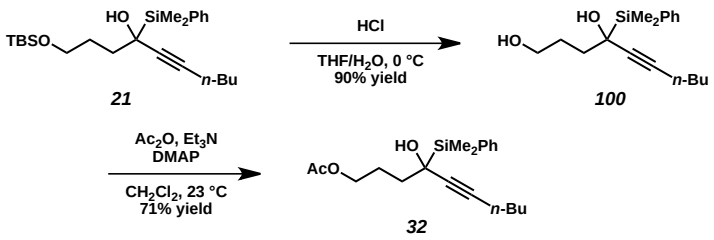
Acylsilane **99** was synthesized according to the procedure of Scheidt et al.[46]

Acyl silane 99: A mixture of γ-butyrolactone (**97**, 3.07 mL, 40.0 mmol) and morpholine (3.49 mL, 40.0 mmol) was heated to 85 °C and stirred overnight. The mixture was then cooled to room temperature, and dissolved in CH_2Cl_2 (80.0 mL). To this solution was added TBSCl (6.63 g, 44.0 mmol) and imidazole (3.00 g, 43.4 mmol), and the resulting mixture was stirred

overnight. The reaction was then quenched with sat. aq. $NaHCO_3$ (30 mL), and it was extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude amide (**98,** R_F = 0.25 in 2:1 hexanes/EtOAc) was dissolved in THF (100 mL) under argon, and cooled to –78 °C. A solution of $PhMe_2SiLi$ (60.0 mL, 1.0 M in THF, 60.0 mmol) was added dropwise slowly. The resulting mixture was stirred for 2 h at –78 °C, then quenched with sat. aq. NH_4Cl (60 mL) slowly at –78 °C. The mixture was warmed to room temperature, extracted with Et_2O (2 x 200 mL), and the combined organic layers were washed with brine (300 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by flash chromatography (9:1 hexanes/EtOAc eluent) afforded **99** (6.42 g, 48% over 3 steps, R_F = 0.51 in 9:1 hexanes/EtOAc) as a colorless oil.

α-Hydroxypropargylsilane 21: According to the general procedure, 1-hexyne (0.200 mL, 1.80 mmol) in 1.0 mL THF was deprotonated by EtMgBr (0.600 mL, 1.80 mmol). To the alkynyl Grignard was added **99** (403 mg, 1.20 mmol) in 1.0 mL THF dropwise. The reaction was stirred until completion as judged by TLC (9:1 hexanes/EtOAc). Purification by flash chromatography (9:1 hexanes/EtOAc eluent) afforded **21** as a colorless oil (452 mg, 90% yield, R_F = 0.33 in 9:1 hexanes/EtOAc).

α-Hydroxypropargylsilane 21: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (app. dd, *J* = 7.3, 1.5 Hz, 2H), 7.36 (app. q, *J* = 6.9 Hz, 3H), 3.68 (dt, *J* = 10.4, 5.4 Hz, 1H), 3.59 (ddd, *J* = 10.1, 7.1, 5.1 Hz, 1H), 2.24 (t, *J* = 6.9 Hz, 2H), 1.88-1.57 (comp m, 4H), 1.51-1.35 (comp m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.88 (s, 9H), 0.43 (s, 6H), 0.040 (s, 3H), 0.035 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 134.9, 129.5, 127.7, 88.3, 82.7, 64.0, 63.6, 34.7, 31.2, 27.5, 26.1 22.1, 18.9, 18.5, 13.8, -5.15, -5.18, -5.57, -5.64; IR (film) 3387, 2956, 2930, 2858, 1253, 1111, 835 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{24}H_{42}O_2Si_2 + Na]^+$: 441.2616, found 441.2614.

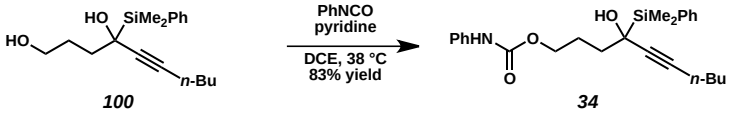


Diol 100: To a solution of **21** (186 mg, 0.450 mmol) in THF (6.0 mL) at 0 °C was added HCl (0.490 mL, 12.1 M) dropwise. The reaction was quenched after 10 min with sat. aq. $NaHCO_3$ (3 mL). The THF was removed in vacuo, and the residue was extracted with Et_2O (2 x 20 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified using flash chromatography (19:1 CH_2Cl_2/MeOH eluent) to afford **100** as a white solid (124 mg, 90% yield, R_F = 0.31 in 2:1 hexanes/EtOAc)

α-Hydroxypropargylsilane 32: To a solution of **100** (124 mg, 0.407 mmol) in 4.0 mL CH_2Cl_2 was added Ac_2O (0.460 mL, 0.488 mmol), Et_3N (0.113 mL, 0.814 mmol) and DMAP (5.0 mg, 0.0407 mmol) sequentially. The mixture was stirred at room temperature for 1 h, monitoring by TLC (4:1 hexanes/EtOAc). The reaction was then quenched with sat. aq. $NaHCO_3$ (1 mL). It was then extracted with Et_2O (2 x 20 mL), and the combined organic layers were washed with brine (30 mL) before being dried over magnesium sulfate and concentrated in vacuo. The residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford **32** as a colorless oil (100 mg, 71% yield, R_F = 0.13 in 9:1 hexanes/EtOAc).

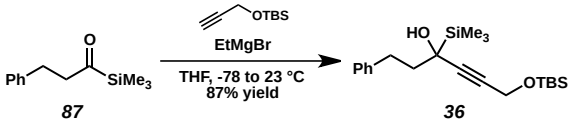
α-Hydroxypropargylsilane 32: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 5.9 Hz, 2H), 7.39 (app. q, *J* = 7.4 Hz, 3H), 4.06 (t, *J* = 6.1 Hz, 2H), 2.24 (t, *J* = 7.0 Hz, 2H), 2.02 (s, 3H), 1.92-1.83 (m, 2H), 1.47 (tt, *J* = 7.5, 6.5 Hz, 2 H), 1.40 (tt, *J* = 7.2, 7.6 Hz, 2H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 135.4, 134.7, 129.5, 127.7, 89.0, 81.9, 64.8, 64.1, 33.9, 31.0, 21.9, 21.0, 18.6, 13.6, -5.8, -5.9; IR (film) 3485, 2958, 2932, 1741, 1247, 833,

702 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{20}H_{30}O_3Si + Na]^+$: 369.1856, found: 369.1857.



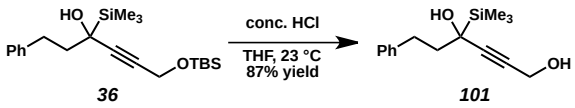
α-Hydroxypropargylsilane 34: To a solution of **100** (321 mg, 1.05 mmol) in 5.0 mL DCE under argon at room temperature was added phenyl isocyanate (0.126 mL, 1.16 mmol) and pyridine (0.0930 mL, 1.16 mmol). Subsequently, the solution was heated to 38 °C and stirred for 2 h, monitoring by TLC (3:1 hexanes/EtOAc). The reaction was quenched with water and the product was extracted with ether (2 x 30 mL), and the combined organic layers were washed with brine and dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford **34** as a colorless oil (353 mg, 83% yield, R_F = 0.17 in 9:1 hexanes/EtOAc).

α-Hydroxypropargylsilane 34: ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 2H), 7.38-7.34 (comp m, 5H), 7.30 (app. t, *J* = 7.3 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.56 (br s, 1H), 4.17 (t, *J* = 6.4 Hz, 2H), 2.25 (t, *J* = 7.0 Hz, 2H), 1.94-1.84 (m, 2H), 1.73-1.60 (m, 2H), 1.52-1.36 (comp m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.45 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 132.1, 134.5, 133.9, 126.9, 122.5, 117.7, 88.3, 81.0, 64.7, 63.4, 33.1, 30.1, 22.7, 17.8, 12.8, -6.6, -6.7; IR (film) 3398, 3323, 2958, 2932, 1710, 1600, 1540, 1444, 1314 cm^{-1}; HRMS *m/z* calc'd for $(M+ Na)^+$ $[C_{25}H_{33}NO_3Si + Na]^+$: 446.2122, found 446.2122.



α-Hydroxypropargylsilane 36: According to the general procedure, *tert*-butyldimethyl(2-propynyloxy)silane (1.37 g, 8.04 mmol) in 10 mL THF was deprotonated by EtMgBr (2.67 mL, 8.01 mmol). To the alkynyl Grignard was added **87** (706 mg, 1.87 mmol) in 15 mL THF dropwise. The reaction was stirred until completion as judged by TLC (9:1 hexanes/EtOAc). Purification by flash chromatography (9:1 hexanes/EtOAc eluent) afforded **36** as a colorless oil (1.12 g, 87% yield, R_F = 0.36 in 9:1 hexanes/EtOAc).

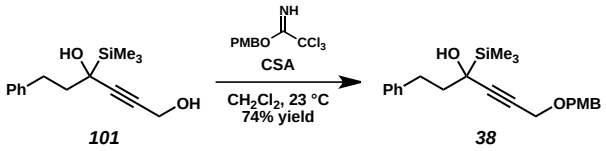
α-Hydroxypropargylsilane 36: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (comp m, 4H), 7.17 (t, *J* = 7.2 Hz, 1H), 4.40 (s, 2H), 2.93 (t, *J* = 5.6 Hz, 1H), 2.90 (t, *J* = 5.6 Hz, 1H), 2.00-1.81 (m, 2H), 0.93 (s, 9H), 0.12 (s, 6H), 0.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 128.8, 128.6, 126.0, 94.6, 87.0, 64.8, 52.1, 39.6, 30.5, 26.0, 18.5, -4.1, -4.9; IR (film) 3447, 2954, 2857, 1248, 1086 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{21}H_{36}O_2Si_2 + Na]^+$: 399.2146, found 399.2149.



α-Hydroxypropargylsilane 101: A solution of silyl ether **36** (1.10 g, 2.98 mmol) and HCl (1.5 mL, 12.1 M) in THF (24.0 mL) was stirred at room temperature. The reaction was complete in 5 min as monitored by TLC (9:1 hexanes/EtOAc). To the reaction mixture was added saturated aq. $NaHCO_3$ until bubbling ceased. The mixture was then extracted with Et_2O (3 x 40 mL), and the combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The solution was concentrated in vacuo, and the residue was purified using column chromatography

(2:1 hexanes/EtOAc eluent) affording **101** as a white solid (680 mg, 87 % yield, R_F = 0.36 in 2:1 hexanes/EtOAc).

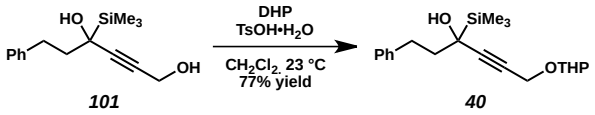
α-Hydroxypropargylsilane 101: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.22 (m, 3H), 7.18 (app. t, *J* = 7.1 Hz, 2H), 4.34 (d, *J* = 5.2 Hz, 2H), 2.96-2.83 (comp m, 2H), 2.00-1.82 (comp m, 2 H), 0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 128.7, 128.6, 126.0, 88.3, 86.6, 64.6, 51.5, 39.4, 30.4, -4.2; IR (film) 3360, 2953, 1497, 1455, 1249, 1020, 840 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{15}H_{22}O_2Si + Na]^+$: 285.1281, found 285.1280.



α-Hydroxypropargylsilane 38: To a solution of diol **101** (239 mg, 0.910 mmol) and *p*-methoxybenzyltrichloroacetimidate (321 mg, 1.14 mmol) in CH_2Cl_2 (4.5 mL) at 23 °C under argon was added CSA (21.0 mg, 0.0904 mmol), and the solution was allowed to stir overnight. The reaction was then quenched with sat. aq. $NaHCO_3$ (10 mL), and the mixture was extracted with Et_2O (2 x 30 mL). The organic layers were washed with brine and dried over magnesium sulfate. The solution was concentrated in vacuo, and the residue was purified using flash chromatography (9:1 → 5:1 hexanes/EtOAc eluent) to afford **38** as a white solid (259 mg, 74% yield, R_F = 0.09 in 9:1 hexanes/EtOAc).

α-Hydroxypropargylsilane 38: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.25 (comp m, 6H), 7.20 (app. t, *J* = 7.1 Hz, 1H), 6.90 (app. d, *J* = 8.7 Hz, 2H), 4.58 (s, 2H), 4.28 (s, 2H), 3.81 (s, 3H), 3.01-2.88 (m, 2H), 2.05-1.86 (comp m, 2H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5,

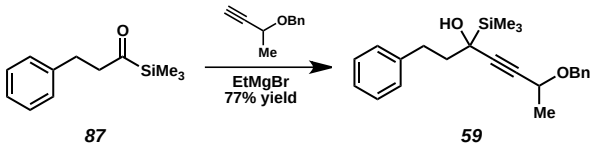
142.5, 129.9, 129.7, 128.7, 128.6, 126.0, 114.0, 89.1, 84.3, 71.0, 64.8, 57.4, 55.4, 39.4, 30.5, -4.1; IR (film) 3444, 2954, 2911, 1612, 1514, 1249, 841 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{23}H_{30}O_3Si + Na]^+$: 405.1856, found 405.1866.



101 ***40***

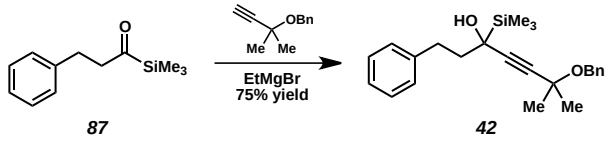
α-Hydroxypropargylsilane 40: To a solution of diol **101** (256 mg, 1.01 mmol) in CH_2Cl_2 (9.0 mL) was added DHP (0.0940 mL, 1.14 mmol) and $TsOH•H_2O$ (96.0 mg, 0.520 mmol). The mixture was stirred at 23 °C for 30 min and was then quenched with sat. aq. $NaHCO_3$ (10 mL). The mixture was extracted with Et_2O (2 x 30 mL), and the combined organic layers were washed with brine (30 mL) and dried over magnesium sulfate. The solution was concentrated in vacuo, and the residue was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford **40** as a colorless oil (270 mg, 77% yield, R_F = 0.31 in 9:1 hexanes/EtOAc).

α-Hydroxypropargylsilane 40: ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.23 (comp m, 4H), 7.19 (tt, *J* = 7.1, 1.5 Hz, 1H), 4.89 (app. s, 1H), 4.39 (s, 2H), 3.87 (ddd, *J* = 11.3, 8.6, 2.9 Hz, 1H), 3.57-3.52 (m, 1H), 2.98-2.84 (comp m, 2H), 1.98-1.72 (comp m, 2H), 1.65-1.52 (comp m, 4H), 0.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 128.8, 128.7, 128.6, 126.0, 96.5, 88.5, 84.3, 64.8, 62.3, 54.5, 39.6, 39.5, 30.5, 30.5, 25.6, 19.4, -4.2; IR (film) 3435, 2947, 1247, 1022, 841, 701 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{20}H_{30}O_3Si + Na]^+$: 369.1856, found 369.1855.



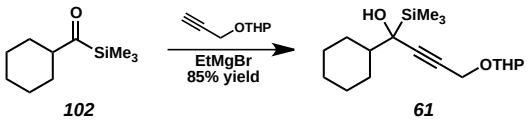
87 *59*

α-Hydroxypropargylsilane 59: A flame-dried flask was charged with ((but-3-yn-2-yloxy)methyl)benzene (0.580 g, 3.62 mmol) in 7.00 mL of dry THF. The solution was cooled to 0 ºC and EtMgBr (1.20 mL, 3.0 M in Et_2O, 3.60 mmol) was added dropwise. The solution was warmed to room temperature and stirred for 45 min. The reaction mixture was then cooled to –78 ºC. A solution of acylsilane **87** (494 mg, 2.40 mmol) in 4.00 mL of dry THF was slowly added dropwise. The reaction mixture was stirred for 30 min at –78 ºC, then warmed slowly to room temperature. Upon consumption of acylsilane, as judged by TLC, the mixture was cooled to –78 ºC and quenched with saturated aqueous ammonium chloride (10 mL). The mixture was allowed to warm to room temperature, and THF was removed via rotary evaporation. The mixture was then extracted with Et_2O (2 x 50 mL), and the combined organic layers were washed with brine (20 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography to afford the α-hydroxypropargylsilane **59** (1.01 g, 77% yield) as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.16 (comp m, 10H), 4.80 (d, *J* = 11.6 Hz, 1H), 4.51 (d, *J* = 11.6 Hz, 1H), 4.32 (q, *J* = 6.7 Hz, 1H), 2.99–2.86 (m, 2H), 2.03–1.95 (m, 1H), 1.90–1.82 (m, 1H), 1.49 (d, *J* = 6.7 Hz, 3H), 0.15 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.5, 138.1, 128.7, 128.63, 128.58, 128.1, 127.9, 126.0, 88.1, 87.7, 70.7, 64.9, 64.7, 39.7, 39.6, 30.6, 22.74, 22.72, -4.1; **IR** (film) 3450, 3028, 2954, 2862, 2216, 1947, 1872, 1721, 1603, 1496, 1454, 1370, 1327, 1248, 1149, 1093 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{23}H_{34}NO_2Si$ $(M + NH_4)^+$ 384.2359, found 384.2353; **TLC** R_f = 0.39 (9:1 hexanes/EtOAc).



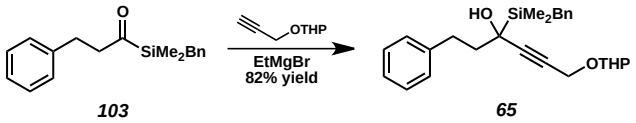
87 *42*

α-Hydroxypropargylsilane 42: A flame-dried flask was charged with (((2-methylbut-3-yn-2-yl)oxy)methyl)benzene (0.910 g, 5.22 mmol) in 10.0 mL of dry THF. The solution was cooled to 0 ºC and EtMgBr (1.75 mL, 3.0 M in Et_2O, 5.25 mmol) was added dropwise. The solution was warmed to room temperature and stirred for 45 min. The reaction mixture was then cooled to –78 ºC. A solution of acylsilane **87** (720 mg, 3.50 mmol) in 5 mL of dry THF was slowly added dropwise. The reaction mixture was stirred for 30 min at –78 ºC, then warmed slowly to room temperature. Upon consumption of acylsilane, as judged by TLC, the mixture was cooled to –78 ºC and quenched with saturated aqueous ammonium chloride (10 mL). The mixture was allowed to warm to room temperature, and THF was removed via rotary evaporation. The mixture was then extracted with Et_2O (2 x 50 mL), and the combined organic layers were washed with brine (20 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography to afford the α-hydroxypropargylsilane **42** (1.60 g, 75% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.18 (comp m, 10H), 4.68 (s, 2H), 2.99–2.85 (m, 2H), 2.00 (ddd, *J* = 13.8, 9.6, 6.0 Hz, 1H), 1.86 (ddd, *J* = 13.8, 9.6, 6.0 Hz, 1H), 1.60 (s, 6H), 0.16 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.5, 139.2, 128.7, 128.6, 128.5, 127.8, 127.5, 126.0, 90.5, 86.8, 71.1, 66.7, 64.7, 39.6, 30.6, 29.5, 29.4, -4.1; **IR** (film) 3451, 3029, 2954, 2862, 2211, 1947, 1872, 1721, 1601, 1496, 1454, 1370, 1327, 1248, 1149, 1093 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{24}H_{32}NaO_2Si$ $(M + H)^+$ 403.2069, found 403.2072; **TLC** R_f = 0.48 (9:1 hexanes/EtOAc).



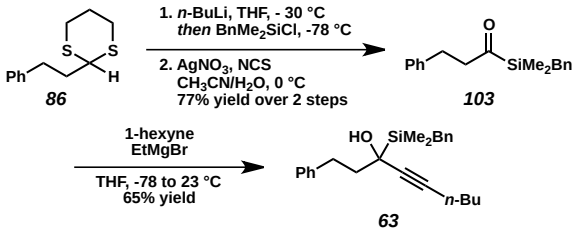
102 *61*

α-Hydroxypropargylsilane 61: A flame-dried flask was charged with 2-(prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran (0.420 g, 3.00 mmol) in 6.00 mL of dry THF. The solution was cooled to 0 ºC and EtMgBr (1.00 mL, 3.0 M in Et_2O, 3.00 mmol) was added dropwise. The solution was warmed to room temperature and stirred for 45 min. The reaction mixture was then cooled to –78 ºC. A solution of acylsilane **102**[47] (369 mg, 2.00 mmol) in 3.00 mL of dry THF was slowly added dropwise. The reaction mixture was stirred for 30 min at –78 ºC, then warmed slowly to room temperature. Upon consumption of acylsilane, as judged by TLC, the mixture was cooled to –78 ºC and quenched with saturated aqueous ammonium chloride (10 mL). The mixture was allowed to warm to room temperature, and THF was removed via rotary evaporation. The mixture was then extracted with Et_2O (2 x 30 mL), and the combined organic layers were washed with brine (20 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography to afford the α-hydroxypropargylsilane **61** (0.827 g, 85% yield) as a viscous, pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.88 (app. q, *J* = 4.0 Hz, 1H), 4.33 (ABq, *J* = 15.8 Hz, Δν = 10.2 Hz, 2H), 3.88-3.82 (m, 1H), 3.56-3.49 (m, 1H), 1.96–1.52 (comp m, 11H), 1.31–1.09 (comp m, 6H), 0.16 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 96.4, 88.3, 84.5, 68.5, 62.40, 62.37, 54.4, 45.4, 30.5, 28.87, 28.86, 27.3, 26.58, 26.57, 26.5, 26.4, 25.6, 19.5, 19.4, -2.6; **IR** (film) 3446, 2956, 2219, 1677, 1450, 1345, 1247, 1201, 1183, 1118, 1021 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{18}H_{31}O_2Si$ $(M - H_2O)^+$ 307.2088, found 307.2086; **TLC** R_f = 0.71 (3:1 hexanes/EtOAc).



103 *65*

α-Hydroxypropargylsilane 65. A flame-dried flask was charged 2-(prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran (1.05 g, 7.50 mmol) in 15.0 mL of dry THF. The solution was cooled to 0 ºC and EtMgBr (2.50 mL, 3.0 M in Et_2O, 7.50 mmol) was added dropwise. The solution was warmed to room temperature and stirred for 45 min. The reaction mixture was then cooled to –78 ºC. A solution of acylsilane **103** (1.41 g, 5.00 mmol) in 6.00 mL of dry THF was slowly added dropwise. The reaction mixture was stirred for 30 min at –78 ºC, then warmed slowly to room temperature. Upon consumption of acylsilane, as judged by TLC, the mixture was cooled to –78 ºC and quenched with saturated aqueous ammonium chloride (10 mL). The mixture was allowed to warm to room temperature, and THF was removed via rotary evaporation. The mixture was then extracted with Et_2O (2 x 50 mL), and the combined organic layers were washed with brine (50 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography to afford the α-hydroxypropargylsilane **65** as a colorless solid (1.73 g, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.18 (comp m, 7H), 7.11–7.05 (comp m, 3H), 4.92 (app. t, *J* = 3.2 Hz, 1H), 4.41 (s, 2H), 3.89 (app. t, *J* = 11.2 Hz, 1H), 3.57 (app. dt, *J* = 11.6, 4.0 Hz, 1H), 2.98–2.86 (comp m, 2H), 2.29 (ABq, *J* = 13.6 Hz, Δν = 12.6 Hz, 2H), 1.99 (ddd, *J* = 13.8, 9.6, 6.0 Hz, 1H), 1.90–1.75 (comp m, 3H), 1.68-1.54 (comp m, 4H), 0.101 (s, 3H), 0.096 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.4, 139.4, 128.7, 128.6, 128.50, 128.48; 96.6, 88.3, 84.9, 64.7, 62.3, 54.5, 39.8, 39.7, 30.5, 30.3, 25.5, 22.6, 19.3, -5.9, -6.2; **IR** (film) 3426, 3063, 3027, 2967, 2865, 2211, 1712, 1603, 1496, 1454, 1362, 1247, 1204, 1022 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{26}H_{34}NaO_3Si$ $(M + Na)^+$ 445.2175, found 445.2173; **TLC** R_f = 0.72 (3:1 hexanes/EtOAc).



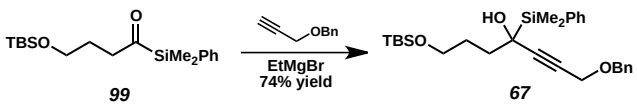
Acylsilane 103: To a solution of **86** (7.81 g, 34.8 mmol) in 80.0 mL THF at –30 °C under argon was added *n*-BuLi (15.3 mL, 2.5 M in hexanes, 38.3 mmol) dropwise. The resulting red/brown solution was allowed to stir for 2 h, and then it was cooled to –78 °C, and $BnMe_2SiCl$ (6.95 mL, 38.2 mmol) was added. The reaction was stirred for 3 h at –78 °C and then quenched with sat. aq. NH_4Cl (30 mL). The mixture was extracted with Et_2O (2 x 100 mL), and the combined organic layers were washed with brine (100 mL) and dried over $MgSO_4$. The solution was concentrated in vacuo, and the residue was purified by flash chromatography (5:1 hexanes/CH_2Cl_2 eluent) to afford the silylated dithiane product (11.7 g, 90% yield, R_F = 0.69 in 1:1 hexanes/CH_2Cl_2).

Dithiane hydrolysis was conducted according to the procedure of Corey and Erickson.[48] To a solution of $AgNO_3$ (6.86 g, 42.0 mmol), and NCS (6.44 g, 48.0 mmol) in CH_3CN:H_2O (4:1, 100 mL) at 0 °C in an Erlenmeyer flask was added a portion of the crude dithiane (4.00 g, 10.7 mmol) in 7 mL THF. Immediately, a white precipitate formed. The mixture was stirred for 5 min and then quenched with sat. aq. Na_2SO_3 (11 mL), sat. aq. Na_2CO_3 (11 mL), and brine (11 mL) in 1 min increments while stirring. CH_2Cl_2/hexanes (1:2, 200 mL) were added to the reaction mixture, stirred 5 min, and the organic layer was decanted into a separatory funnel, taking care to leave the precipitate in the Erlenmeyer flask. The extraction process was repeated, and the combined organic layers were washed with water (200 mL), then brine (200 mL), dried

over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford acylsilane **103** (2.60 g, 86% yield, R_F = 0.40 in 9:1 hexanes/EtOAc).

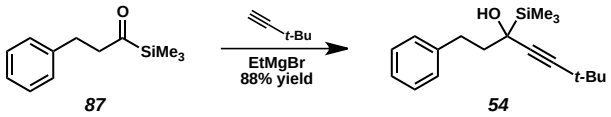
α-Hydroxypropargyl silane 63: According to the general procedure, hexyne (0.900 mL, 8.00 mmol) in 25.0 mL THF was deprotonated by EtMgBr (2.66 mL, 8.00 mmol). To the alkynyl Grignard was added **103** (1.50 g, 5.31 mmol) in 5.0 mL THF dropwise. The reaction was stirred until completion as judged by TLC (9:1 hexanes/EtOAc). Purification by flash chromatography (9:1 hexanes/EtOAc eluent) afforded **63** (1.25 g, 65% yield, R_F = 0.35 in 9:1 hexanes/EtOAc) as a colorless oil.

α-Hydroxypropargyl silane 63: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.16 (comp m, 7H), 7.08-7.04 (comp m, 3H), 2.90 (t, *J* = 8.2 Hz, 2H), 2.30 (t, *J* = 6.6 Hz, 2 H), 2.27 (app. d, *J* = 4.5 Hz, 2H), 1.98-1.76 (m, 2H), 1.56-1.45 (m, 2H), 1.44 (s, 2H), 0.94 (t, *J* = 7.1 Hz, 3H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 139.8, 128.8, 128.6, 128.5, 126.0, 124.4, 89.3, 82.2, 64.9, 40.2, 31.3, 30.3, 22.7, 22.2, 18.9, 13.8, -5.8, -6.2; IR (film) 3556, 3452, 2957, 2931, 1600, 1493, 1247 cm^{-1}; HRMS (ESI$^-$) *m/z* calc'd for $(M - H)^-$ $[C_{24}H_{31}OSi - H]^-$: 363.2144, found 363.2161.



Propargyl alcohol 67: According to the general procedure, benzylprotected propargyl alcohol (304 mg, 2.08 mmol) in 2.08 mL THF was deprotonated by EtMgBr (0.520 mL, 1.56 mmol). To the alkynyl Grignard was added **99** (350 mg, 1.04 mmol) in 1 mL THF dropwise. The reaction was stirred until completion as judged by TLC (9:1 hexanes/EtOAc). Purification by flash

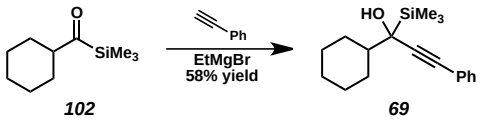
chromatography (9:1 hexanes/EtOAc eluent) afforded α-hydroxypropargylsilane **67** (0.359 g, 74% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.39-7.30 (comp m, 8H), 4.56 (s, 2H), 4.26 (s, 2H), 3.72 (app dt, *J* = 10.2, 5.2 Hz, 1H), 3.58 (ddd, *J* = 10.2, 7.7, 4.3 Hz, 1H), 1.94-1.63 (comp m, 6H), 0.89 (s, 9H), 0.48 (s, 6H), 0.052 (s, 3H), 0.045 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.8, 135.7, 134.9, 129.6, 128.5, 128.2, 127.9, 127.8, 89.8, 83.6, 71.3, 63.7, 63.5, 57.8, 34.8, 27.7, 26.1, 18.5, -5.17, -5.23, -5.6, -5.9; **IR** (film) 3364, 2955, 2857, 1471, 1251, 1099 cm^{-1}; **HRMS** (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{28}H_{42}NaO_3Si_2]^+$: 505.2570, found 505.2562; **TLC** R_f = 0.30 (9:1 hexanes/EtOAc).



87 ***54***

α-Hydroxypropargylsilane 54: A flame-dried flask was charged with *tert*-butylacetylene (630 µl, 5.10 mmol) in 10.0 mL of dry THF. The solution was cooled to 0 ºC and EtMgBr (1.70 mL, 3.0 M in Et_2O, 5.10 mmol) was added dropwise. The solution was warmed to room temperature and stirred for 45 min. The reaction mixture was then cooled to –78 ºC. A solution of acylsilane **87** (701 mg, 3.40 mmol) in 4.00 mL of dry THF was slowly added dropwise. The reaction mixture was stirred for 30 min at –78 ºC, then warmed slowly to room temperature. Upon consumption of acylsilane, as judged by TLC, the mixture was cooled to –78 ºC and quenched with saturated aqueous ammonium chloride (10 mL). The mixture was allowed to warm to room temperature, and THF was removed via rotary evaporation. The mixture was then extracted with Et_2O (2 x 50 mL), and the combined organic layers were washed with brine (20 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography to afford the α-hydroxypropargylsilane **54** (0.863 g, 88% yield) as a

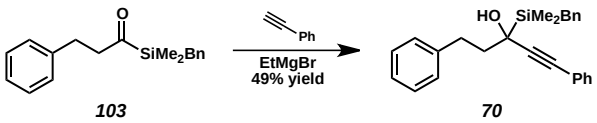
colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.15 (m, 5H), 2.89 (app. t, *J* = 8.2 Hz, 2H), 1.96–1.90 (m, 1H), 1.84–1.76 (m, 1H), 1.24 (s, 9H), 0.11 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.9, 128.7, 128.6, 125.9, 97.3, 80.7, 64.7, 39.8, 31.4, 30.5, 27.8; **IR** (film) 3447, 3064, 3027, 2967, 2865, 2212, 1941, 1713, 1603, 1496, 1475, 1454, 1362, 1247 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{18}H_{29}OSi$ $(M + H)^+$ 289.1988, found 289.1986; **TLC** R_f = 0.61 (9:1 hexanes/EtOAc).



102 ***69***

α-Hydroxypropargylsilane 69: A flame-dried flask was charged with phenylacetylene (460 µl, 4.20 mmol) in 9.00 mL of dry THF. The solution was cooled to 0 ºC and EtMgBr (1.40 mL, 3.0 M in Et_2O, 4.20 mmol) was added dropwise. The solution was warmed to room temperature and stirred for 45 min. The reaction mixture was then cooled to –78 ºC. A solution of acylsilane **102**[47] (515 mg, 2.80 mmol) in 5.00 mL of dry THF was slowly added dropwise. The reaction mixture was stirred for 30 min at –78 ºC, then warmed slowly to room temperature. Upon consumption of acylsilane, as judged by TLC, the mixture was cooled to –78 ºC and quenched with saturated aqueous ammonium chloride (10 mL). The mixture was allowed to warm to room temperature, and THF was removed via rotary evaporation. The mixture was then extracted with Et_2O (2 x 30 mL), and the combined organic layers were washed with brine (20 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography to afford the α-hydroxypropargylsilane **69** (465 mg, 58% yield) as a viscous, yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.32–7.28 (comp m, 3H), 2.03–2.00 (m, 1H), 1.83–1.64 (comp m, 5H), 1.39-1.15 (comp m, 5H), 0.22 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 131.6, 128.4, 127.9, 123.7, 91.6, 88.5, 68.9, 45.6, 29.0, 27.4, 26.7, 26.6,

26.4, -2.4; **IR** (film) 3434, 2931, 2854, 2202, 1703, 1598, 1489, 1450, 1248, 1069 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{18}H_{25}Si$ $(M - H_2O)^+$ 269.4766, found 269.4764; **TLC** R_f = 0.58 (9:1 hexanes/EtOAc).



103 ***70***

α-Hydroxypropargylsilane 70: A flame-dried flask was charged with phenylacetylene (0.823 mL, 7.50 mmol) in 15.0 mL of dry THF. The solution was cooled to 0 ºC and EtMgBr (2.50 mL, 3.0 M in Et_2O, 7.50 mmol) was added dropwise. The solution was warmed to room temperature and stirred for 45 min. The reaction mixture was then cooled to –78 ºC. A solution of acylsilane **103** (1.41 g, 5.00 mmol) in 6.00 mL of dry THF was slowly added dropwise. The reaction was warmed and cooled according the general procedure. The mixture was then extracted with Et_2O (2 x 50 mL), and the combined organic layers were washed with brine (20 M), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography to afford the α-hydroxypropargylsilane **70** (0.942 g, 49% yield) as a viscous, yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.47–7.44 (m, 2H), 7.36–7.20 (comp m, 11H), 3.03–2.97 (comp m, 2H), 2.39 (ABq, *J* = 13.6 Hz, Δν = 12.6 Hz, 2H), 2.06 (ddd, *J* = 13.8, 9.6, 6.0 Hz, 1H), 1.95 (ddd, *J* = 13.8, 9.6, 6.0 Hz, 1H), 1.63 (s, 1H), 0.152 (s, 3H), 0.148 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 142.5, 139.4, 131.7, 128.8, 128.7. 128.6, 128.5, 128.3, 126.1, 124.5, 123.3, 91.4, 88.8, 65.2, 39.9, 31.1, 30.5, 22.7, -5.8, -6.1; **IR** (film) 3436, 3061, 3026, 2957, 2204, 1946, 1857, 1703, 1599, 1492, 1453, 1407, 1250, 1206, 1156 cm^{-1}; **HRMS** (ESI) *m/z* calc'd for $C_{26}H_{28}NaOSi$ $(M + Na)^+$ 407.1807, found 407.1816; **TLC** R_f = 0.43 (9:1 hexanes/EtOAc).

CHAPTER TWO NOTES AND REFERENCES

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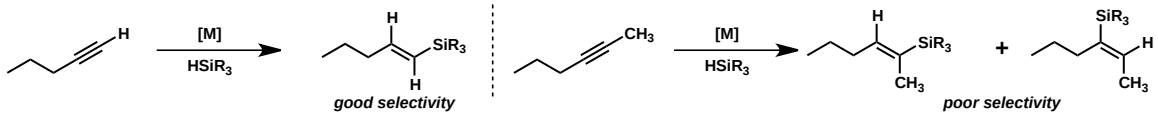
CHAPTER THREE

The Regioselective Hydrosilylations of Internal Alkynes

3.1 Introduction

The metal catalyzed hydrosilylation reaction of alkenes and alkynes is a well-studied transformation.[49] Silylolefins can serve as useful precursors for Tamao-Fleming oxidations, nucleophilic additions,[50] Hiyama couplings,[51] and halodesilylation reactions.[52] The widespread synthetic use of vinylsilanes rests upon the ability for their syntheses to be facile with high regio- and stereocontrol. Because of this need, an overwhelming majority of research on alkyne hydrosilylation has focused on the anti-Markovnikov addition of a silane across a terminal alkyne. Conversely, internal alkynes have received considerably less attention, which can be partially attributed to the difficulty of differentiating the carbons of disubstituted alkynes.



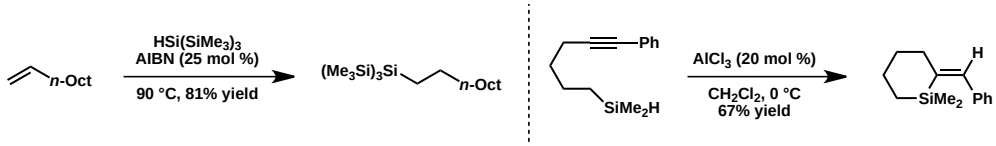
Scheme 3.1.1 Hydrosilylations of terminal and internal alkynes

Our entry into the field of metal catalyzed hydrosilylations began with our desire to obtain (*E*)-α-silylenones, the geometric isomers of the products of our platinum catalyzed 1,2-silyl migration reaction of α-hydroxypropargylsilanes.[53] To our delight, the polarized internal alkyne substrates afforded excellent regio- and stereoselectivity and spawned a new direction for our research program.

3.2 Background

3.2.1 Hydrosilylation Background

There are many different methods reported to afford hydrosilylation products. However, selectivity of Si–H addition limits these methods' further synthetic utility. Radically induced hydrosilylation requires a silane that can easily undergo homolytic cleavage of the Si–H bond.[54] The intermediate of the radical silane addition to the alkyne can interconvert to the thermodynamically stable species and propagate to afford the silyl alkene. Due to thermodynamic control of these reactions, the steric bulk of alkyne substituents generally control selectivity. Lewis acids like $AlCl_3$ catalyze the trans addition of hydrosilane across an alkyne.[55]

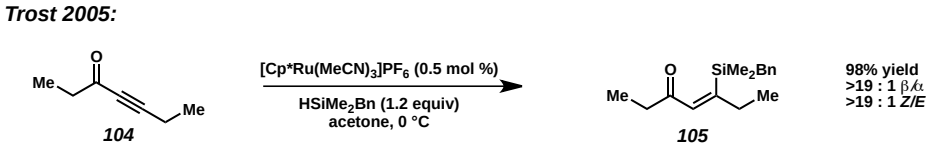


Scheme 3.2.1 Non-transition metal catalyzed hydrosilylations

However, strong Lewis acids can also catalyze the isomerization of the alkene. Early transition metal complexes such as titanocene[56] and organoyttrium compounds[57] have been shown to catalyze the *cis*-addtition of a silane across an alkyne. Due to issues surrounding regioselectivity and functional group tolerance, the abovementioned methods of hydrosilylation have received little attention in the context of synthetic utility. Conversely, late transition metals have been the subject of intense research for decades in regards to hydrosilylation.

3.2.2 Late Transition Metal Hydrosilylations of Internal Alkynes

The hydrosilylation chemistry catalyzed by late transition metals is both diverse and well documented. Two separate mechanisms are cited for the observed regioselectivity of the hydrosilylation. Late transition metal catalysts such as Rh, Ir, and Ru proceed via the Crabtree-Ojima mechanism that can form a metallocarbene species which can account for possible *E/Z* isomerization, but nonetheless, substrate scope and selectivities remain low.[58] Accordingly, Trost and Ball have shown that $CpRu(MeCN)_3PF_6$ catalyzes an exclusively trans addition of silane with excellent selectivity and for a wide variety of substrate internal alkynes.[59] Pt catalyzed hydrosilylations generally proceed though the standard Chalk-Harrod mechanism which provides complementary *cis*- addition products.

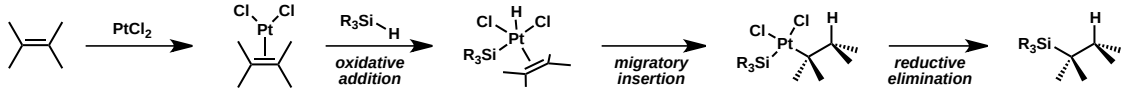


Scheme 3.2.2 [Ru] catalyzed *trans*-selective hydrosilylation

3.2.3 Chalk-Harrod Mechanism

Platinum and palladium catalysts are widely used for hydrosilylation reactions and generally give products arising from the syn addition of silane across an alkyne. In 1957, Speier was the first to report platinum catalyzed hydrosilylations using H_2PtCl_6.[60] This catalyst, known as Speier's Catalyst, is today one of the most commonly used hydrosilylation catalysts in an industrial setting. The selectivity of addition is largely attributed to the Chalk-Harrod mechanism for Pt hydrosilylation.[61] In studies of hydrosilylations using Pt(II) catalysts, they proposed a mechanism wherein Pt(II) coordinates to an olefin (later applied to alkynes) and then is oxidatively inserted into the Si–H bond. The resulting Pt(IV) complex can undergo migratory

insertion across an olefin or alkyne delivering a hydride to one of the two carbons. The resulting C–Pt–Si complex can then undergo reductive elimination to afford *cis* hydrosilylation products.



Scheme 3.2.3 Originally proposed mechanism by Chalk and Harrod

The Chalk-Harrod mechanism has been widely accepted by the synthetic community for decades and can generally be applied to platinum hydrosilylation reactions. However, a number of phenomena are still unexplained by this mechanism. First, the other widely used catalyst is Karstedt's catalyst, a Pt(0)divinyldisiloxane complex, which gives rise to the possibility of a similar catalytic system that invokes Pt(II) and Pt(0) oxidation states.[62] Second, it has been shown that the common platinum catalysts, such as $Pt(cod)Cl_2$, are not the active catalysts but instead are precatalysts that must undergo an induction period. Roy and Taylor have studied this induction period in depth and have concluded that the classical Chalk-Harrod mechanism can proceed through both Pt(II) to Pt(IV) and Pt(0) to Pt(II) catalytic cycles.[63] As long as the Chalk-Harrod mechanism holds, we can assume that the hydride is delivered during the migratory insertion step and is thus playing a significant role in determining the regioselectivity and stereoselectivity of the net hydrosilylation.

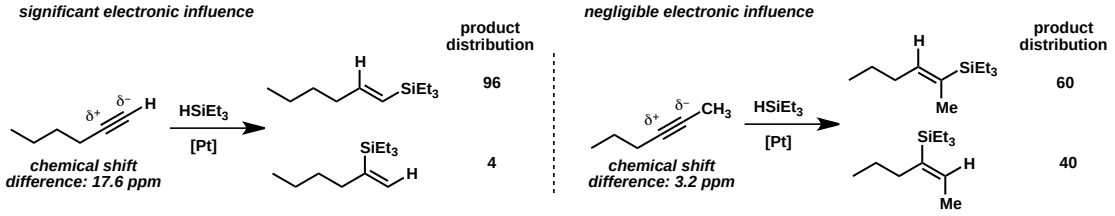
3.2.4 Recent Internal Alkyne Hydrosilylation Regioselectivity

Today, regioselective hydrosilylation on internal alkynes remains difficult, and research efforts have often focused on exploiting sterics dictated by both the substrate and catalyst system. Markó and co-workers have performed extensive work on the hydrosilylation of alkynes using bulky Pt/NHC catalysts developed in their lab. Although focused on terminal alkynes, a number

of internal alkynes were also investigated.[64] In 2011, Cook developed an active catalytic system for the hydrosilylation of propargylic alcohols.[65] Predictably, terminal alkynes showed excellent selectivity, and internal alkynes were unselective unless significant steric bulk was employed to influence the addition. There have been a few isolated exampled where the alkyne electronic influence has been observed, often in substrate syntheses or specialized cases.[66]

3.2.5 Alkyne Electronic Influence

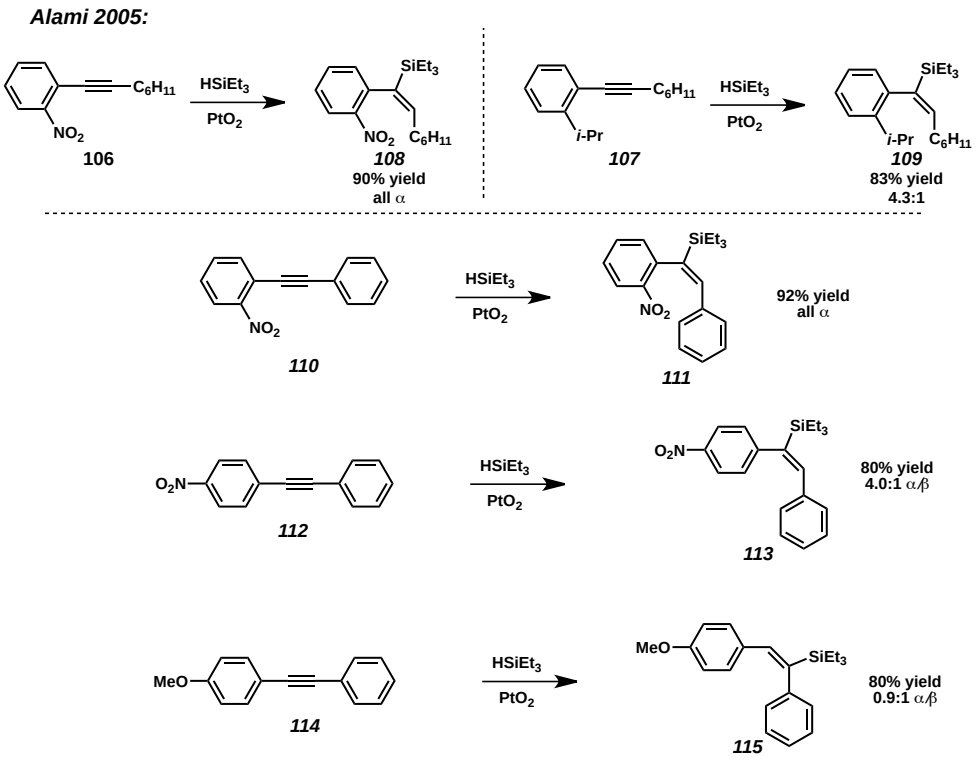
Electronically influenced alkyne hydrosilylation is not a new concept. In 1980, Tsipis hypothesized that the polarization of an alkyne would direct the hydride addition to the more electropositive carbon.[67] Up until this point, since most hydrosilylation centered around terminal alkynes and alkenes, sterics were thought to be the single most contributing factor affecting regioselectivity. Tsipis made the correlation that the magnitude of difference in ^{13}C chemical shifts for terminal alkynes is rather large (~15-20 ppm).[68] However, for internal alkynes, the difference in alkyne chemical shifts is markedly less, at around ~3-5 ppm. These data could serve as predictors for which carbon has the lowest lying LUMO. He posited that the regioselectivity of hydrosilylation could be affected by alkyne polarization, along with sterics.



Scheme 3.2.4 Tsipis's observation of alkyne polarization influence

Alami, with a specific case of *ortho*-substituted arylacetylenes, showed one of most salient first examples of highly selective internal alkyne hydrosilylation using PtO_2 in 2005.[69] Interestingly,

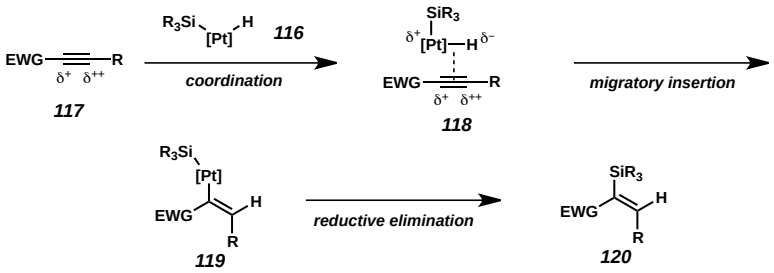
it was found that almost any substituent, from -NO_2 (**106**) to -*i*-Pr (**107**), induced selectivity for the α-silyl regioisomer. This effect manifests even for cases involving diarylacetylenes – the silicon species will preferentially add to the side of the alkyne with an *ortho*-substituted aryl group.



Scheme 3.2.5 Hydrosilylations of aryl acetylenes

Perhaps more telling of absolute electronic effects of silane additon would be Alami's focus on *para* substituted diarylacetylenes.[70] Both sides of diarylactetylenes **112** and **114** should have the same steric hindrance, and the *para* substituent should exert negligible coordinating effect. Therefore, any addition selectivity should be a consequence of alkyne polarization. In comparing the hydrosilylations of **112** and **114**, it is apparent that the electron withdrawing *para*-nitrophenyl (**112**) induces α-silyl selectivity whereas the electron donating *para*-methoxyphenyl (**114**) reverses selectivity to give, predominantly, the β-silyl isomer.

These data integrate well into Tsipis's original hypothesis that the silylplatinum hydride **116** will undergo migratory insertion across an alkyne **117**, preferentially delivering the hydride to the most electropositive carbon. The Chalk-Harrod mechanism for Pt catalyzed hydrosilylations can easily be applied to this concept, and selectivity distributions for α and β isomers of vinylsilane **119** will ultimately be governed by the polarization of the alkyne.



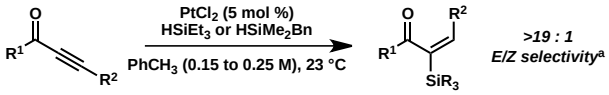
Scheme 3.2.6 Electronic influence applied to the Chalk-Harrod mechanism

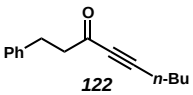
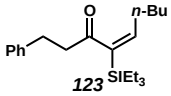
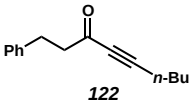
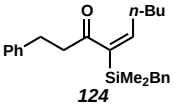
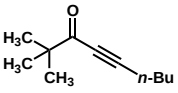
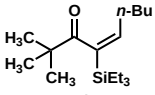
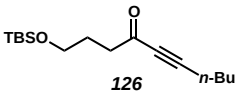
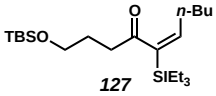
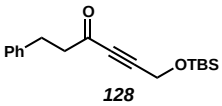
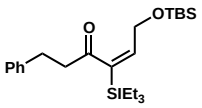
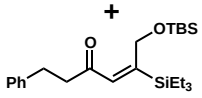
3.3 Our Work

3.3.1 Hydrosilylations of Ynones

As previously mentioned, we entered the field of hydrosilylation to selectively make (*E*)-silylenones as a complement to our 1,2-silicon migration method that affords (*Z*)-silylenones (Chapter 2). We envisioned that the highly polarized ynone substrates would induce high selectivity for the desired α-silyl regioisomer. To our delight, treatment of various ynones and trialkylsilanes with catalytic $PtCl_2$ proceeded under mild conditions and generally excellent yields and selectivity (Table 3.3.1). Even the hydrosilylation of highly hindered pivaloyl alkyne **120** afforded >19:1 regioselectivity for the α-silylenone, albeit in modest yield.

Table 3.3.1 Pt Catalyzed Hydrosilylations of Ynones



entry	Substrate	Product	time (h)	yield (%)[a]	α : β[b]
1	 **122**	 **123**	1.5	98	>19 : 1
2	 **122**	 **124**	1.5	99	>19 : 1
3	 **121**	 **125**	9	65	>19 : 1
4	 **126**	 **127**	2	92	>19 : 1
5	 **128**	 **129** +  **130**	2	87	2 : 1

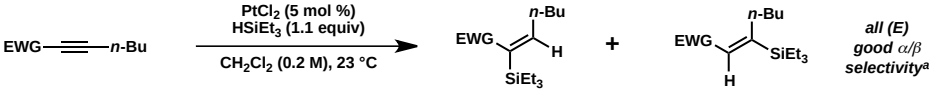
a) Isolated yield b) Measured by ^{1}H NMR

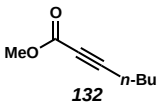
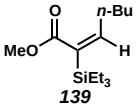
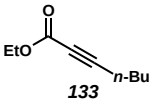
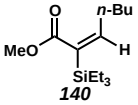
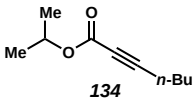
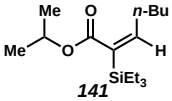
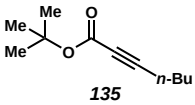
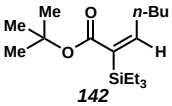
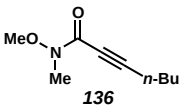
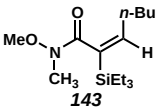
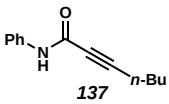
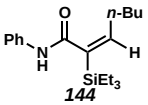
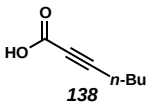
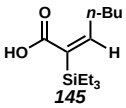
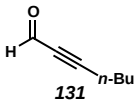
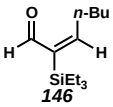
One of the abovementioned substrates, the hydrosilylation of propargyl silyl ether **128** showed only slight preference for the α-silyl regioisomer. We originally attributed this to the –OTBS group coordinating to the silylplatinum intermediate (**118)**, the inductive electronic influence of the –OTBS group, or some combination of these effects. Nonetheless, our interest was piqued, and we sought to elucidate this method as a useful, facile means to access stereodefined trisubstituted olefins.

3.3.2 Varying the sp^2 Electron Withdrawing Substituent

Based on the high levels of regioselectivity observed in the hydrosilylations of ynones, we anticipated that other carbonyl based electron-withdrawing groups such as esters and amides would induce analogous selectivity with similar reactivity. To probe this hypothesis, a number of alkynes were subjected to conditions similar to our hydrosilylations of ynones, with the salient difference being that CH_2Cl_2 was found to be nominally better than $PhCH_3$. All substrates, with the exception of aldehyde **131**, reacted efficiently, and the resulting products were isolated in high yields. Also notably, in all cases the hydrosilylations proceeded with selectivity favoring the α-silyl isomer. Linear esters (**132** and **133**) provided >19:1 and 16:1 α/β selectivity, respectively, showing excellent differentiation over the *n*-butyl group. Branched esters **134** and **135** were unsurprisingly less regioselective, likely due to increased steric bulk, affording still respectable 9.3:1 and 7.5:1 α/β selectivities. Weinreb (**136**) and phenyl (**137**) amides also demonstrated high selectivity. Even a carboxylic acid (**138**) was tolerated under the reaction conditions. The hydrosilylation of aldehyde **131** was the only outlier, affording only 58% yield in the best case and with varying regioselectivity (3.1-5.8:1). This can likely be attributed to the differential carbonyl hydrosilylation of the product vinylsilanes. The differences in observed regioselectivity could be explained by differences in reaction rates for the carbonyl hydrosilylation of α and β-isomers.

Table 3.3.2 Electron-withdrawing group analysis



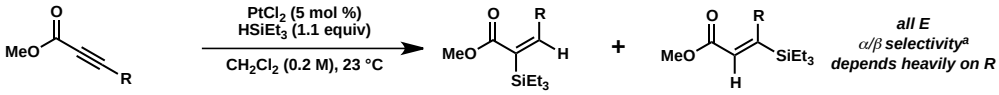
entry	substrate	major product	time (h)	yield (%)	α : β[a]
1	 ***132***	 ***139***	3	95	>19 : 1
2	 ***133***	 ***140***	3	93	16 : 1
3	 ***134***	 ***141***	3	93	9.3 : 1
4	 ***135***	 ***142***	7	95	7.5 : 1
5	 ***136***	 ***143***	5	89	>19 : 1
6	 ***137***	 ***144***	24	80	12 : 1
7	 ***138***	 ***145***	5.5	95	13 : 1
8	 ***131***	 ***146***	3	58[b]	3.1-5.8 : 1

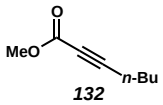
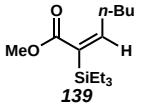
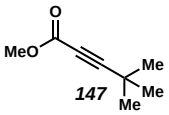
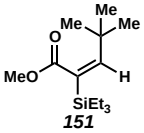
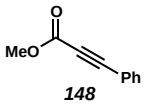
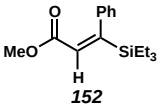
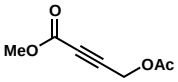
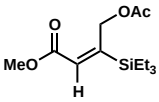
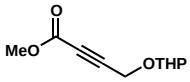
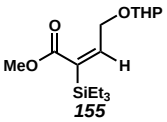
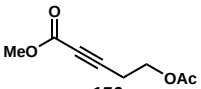
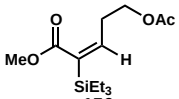
a) Determined by ^{1}H NMR spectroscopy. b) Best isolated yield
EWG = electron-withdrawing group

We also evaluated a number of methyl ynoate substrates by varying the opposite side of the alkyne and observing differences in regioselectivity of addition as well as reactivity (Table 3.3.3). Increasing the size of the R group for alkyne **147** severely retarded the rate of reaction, yet still resulted in a 96% yield and >19:1 α/β selectivity (Table 3.3.3, Entry 2). More interestingly, substituents opposite of the methyl ester that affected the alkyne's polarization

showed dramatically reduced hydrosilylation selectivity. Upon treatment of phenyl substituted methyl ynoate **148** with $PtCl_2$ and $HSiEt_3$, the major product was the β-silyl regioisomer (1:3.5 α/β). Introducing oxygenation at the propargyl postion similarly eroded selectivity, which was also observed with ynone **128**. The reaction with propargyl acetate **149** also resulted in slight inversion of selectivity, affording a 1:1.1 α/β mixture of isomers arising from an inductive electron withdrawing effect of the acetate, or coordination of the acetate to either the platinum or the silicon (*vide infra*). Diminished inductive effects can be observed in the hydrosilylation of homopropargyl acetate **150.** We envisioned that an additional methylene spacer between the alkyne and the acetate group (**150**) would decrease the inductive electronic effect of the acetate as well as reduce the possibility of coordination to the silylplatinum intermediate. This indeed further increased the reaction selectivity, favoring the α isomer 5.2:1.

Table 3.3.3 Effect of methyl ynoate alkyne substituents

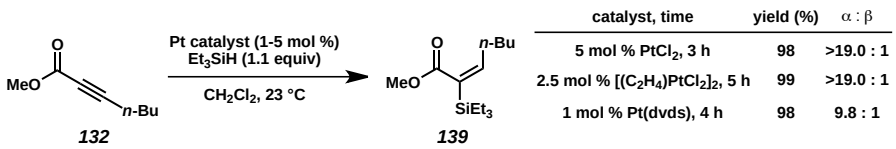


entry	substrate	major product	time (h)	yield (%)	α : β[a]
1	 **132**	 **139**	3	95	>19 : 1
2	 **147**	 **151**	150	96	>19 : 1
3	 **148**	 **152**	11	90	1 : 3.5
4	 **149**	 **153**	7	97	1 : 1.1
5	 **154**	 **155**	12	92	3.5 : 1
6	 **150**	 **156**	3	88	5.2 : 1

a) Determined by ^{1}H NMR spectroscopy.

3.3.3 Catalyst Evaluation

We have identified three commercially available Pt catalysts that can be used for our hydrosilylation reactions. We tested these catalysts on substrate **132** in a series of similar condition sets with reasonable amounts of catalyst loadings.

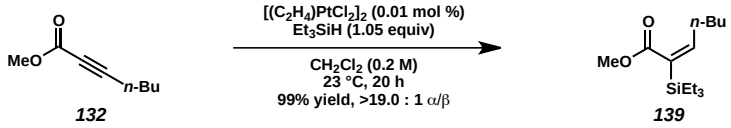


Scheme 3.2.7 Catalyst evaluation

Reactions with both the $PtCl_2$ (5 mol%) and Zeise's dimer [{$(C_2H_4)PtCl_2$}$_2$] (5 mol % Pt) were virtually identical and showed exquisite selectivity for the α-isomer. Karstedt's catalyst [Pt(dvds)] (1 mol %)[71] was competent in the hydrosilylation, showing similarly high yields for enoate **139** but with somewhat diminished selectivity (9.8:1 α/β).

3.3.4 Catalyst loading

The hydrosilylation of internal alkynes can be performed with remarkably low catalyst loadings. The high solubility and activity of [{$(C_2H_4)PtCl_2$}$_2$] in CH_2Cl_2 made it an ideal choice for good catalyst turnover. For example, the hydrosilylation of alkyne **132** using 0.01 mol %[72] catalyst effected the transformation to vinylsilane **139** in high yield and regioselectivity.



Scheme 3.2.8 High turnover for internal alkyne hydrosilylation

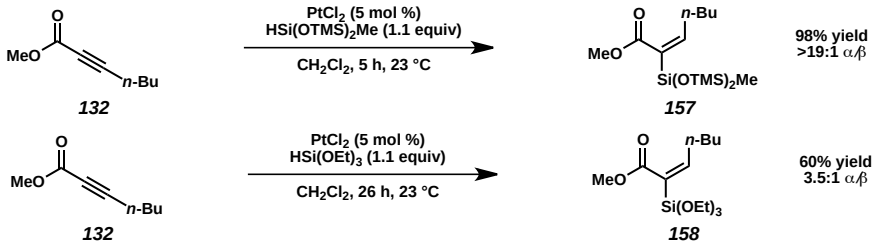
3.3.5 Evaluating Different Silanes

After evaluating the effects of carbonyl based electron-withdrawing group as well as the different alkyne substituents, we felt it prudent to investigate different silanes as a third possible arm of substrate control. Simple, vinyltrialkylsilanes are inherently useful for due to their high stability; however, often a more activated silicon species is generally necessary for synthetic

utility. Reactions such as Tamao-Fleming oxidations allow for vinylsilanes to serve as stable, masked carbonyls that can be unveiled later in a synthesis. These C–Si bond oxidations require halogen-, oxygen-, or aryl- substituted silicon species.[73] Another important utilization of the C–Si bond, the Hiyama coupling,[74] requires a pentacoordinate silicon intermediate. If mild activation conditions are necessary to access such a species, the vinylsilicon must contain oxygenation, halogenation or some carbon based leaving group. Consequently, methods for the selective installation of the aforementioned silicon groups would find use in the synthetic community for the implementation of both Tamao-Fleming and Hiyama coupling reactions.

3.3.6 First Attempts at Oxygenated Silanes

In an extension of our hydrosilylation methodology, two of the first silanes (without oxygen substitution) we tried was triethoxysilane ($HSi(OEt)_3$) and heptamethyltrisiloxane ($HSi(OTMS)_2Me$), as both are inexpensive commodity chemicals often used on an industrial scale and have previously been shown in the Pt catalyzed hydrosilylations of aliphatic terminal alkynes.[75]



Scheme 3.2.9 Initial oxygenated silane additions

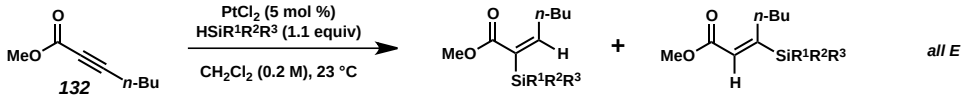
The formation of vinylsilane **157** proceeded in excellent yield and selectivity, much like the aforementioned additions using $HSiEt_3$. The use of $HSi(OEt)_3$ resulted in diminished yield and selectivity. More interestingly, the reaction required 26 h to consume all of the starting material.

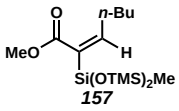
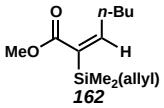
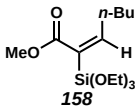
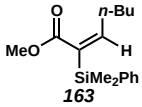
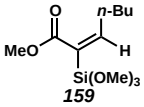
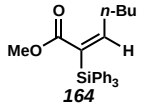
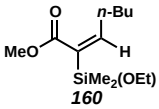
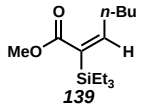
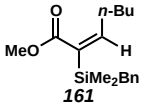
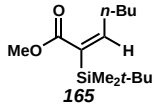
After careful analysis of conditions, it was found that this reaction was significantly more effective under an atmosphere of argon (6 h, 86% yield, 6.4:1 α/β).[63]

3.3.7 Scope of Silanes

With a reliable set of conditions in hand, a number of different commercially availible silanes were added across methyl heptynoate (**132**). All reactions proceeded in in good to excellent yield. The regioselectivity of addition was found to be heavily dependent on silane substituents.

Table 3.3.4 Methyl ynoate silane evaluation



entry	major product	time (h)	yield (%)	α : β[a]	entry	major product	time (h)	yield (%)	α : β[a]
1	 **157**	5	98	>19 : 1	6	 **162**	12	90	10.4 : 1
2	 **158**	8	86	6.4 : 1	7	 **163**	2	95	10.2 : 1
3	 **159**	6.5	81	1.6 : 1	8	 **164**	23	94	6.0 : 1
4	 **160**	2	81	10.3 : 1	9	 **139**	3	94	>19 : 1
5	 **161**	16	98	17.8 : 1	10	 **165**	45	74	10 : 1

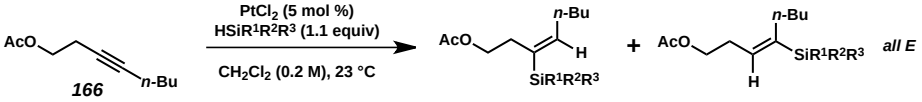
a) Determined by ^{1}H NMR spectroscopy.

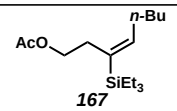
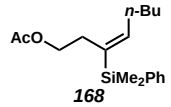
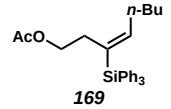
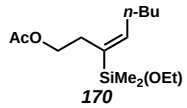
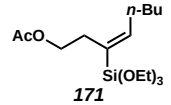
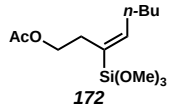
One interesting observation is the difference in selectivity between the hydrosilylation with $HSi(OEt)_3$, which afforded good selectivity for **158**, and the reaction with the similar $HSi(OMe)_3$ (**159**), which showed little preference for the α isomer (1.6:1 α/β), but with comparable yields.

Benzyl- and allyl-silanes reacted with high yields and selectivities (**161** and **162,** respectively). Phenyldimethyl- and triphenylvinylsilanes were formed in very high yields. The triphenylsilyl derivative (**164)** was produced in diminished but still good selectivity (6.0:1). The electron withdrawing nature of the three phenyl rings may lessen the H-Pt-Si intermediate's sensitivity to any alkyne polarization. Even highly hindered *t*-butyldimethylsilane added preferentially to the α-carbon (**165,** 74% yield, 10:1 α/β).

To further evaluate the regioselective influence of various silane reagents, we tested six different silanes with a significantly less selective system. The hydrosilylation of homopropargyl acetate **166** with triethylsilane gives only 3.8:1 selectivity for vinylsilane **167.** In a stark contrast to the hydrosilylations of methyl heptynoate (**132**), where regioselectivity seemed highly dependent on silane substitution, all six different silanes effected a relatively similar regioselective outcome.

Table 3.3.5 Silane regioselectivity with homopropargyl acetate **166**



entry	major product	time (h)	yield (%)	α : β[a]
1	 **167**	5.5	90	3.8 : 1
2	 **168**	1.5	93	3.1 : 1
3	 **169**	16	98	4.5 : 1
4	 **170**	2.5	94	3.9 : 1
5	 **171**	4	87	4.2 : 1
6	 **172**	4.5	88	3.2 : 1

a) Determined by ^{1}H NMR spectroscopy.

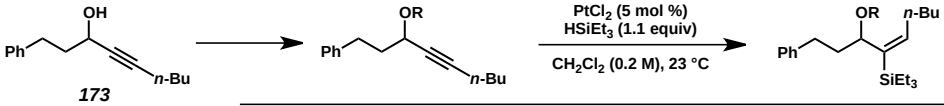
3.4 Oxygen Coordination

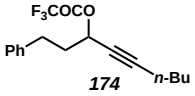
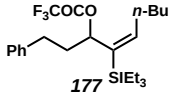
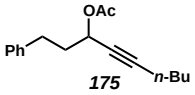
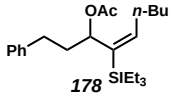
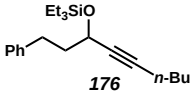
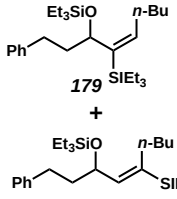
3.4.1 Propargylic Oxygenation

In our earliest studies of ynone internal alkyne hydrosilylation,[53] it was noticed that propargylic oxygenation, products akin to **128,** had a pronounced effect on alkyne regioselectivity. More noticeably, the hydrosilylation of propargyl acetate **149** afforded a reversal of regioselectivity, favoring the β-silyl product relative to the methyl ester. Because of the apparent influence of propargylic oxygenation, we sought to investigate whether these functionalities could steer regioselectivity over aliphatic moieties. Indeed, propargylic oxygen based electron withdrawing

groups effected noticeable differentiation of alkyne carbons. Hydrosilylations of primary and secondary propargyl triflouroacetates showed exceptionally high preference for the α-silyl regioisomer. As can be expected, when the electron-withdrawing nature of the substituent is decreased, the regioselectivity of addition is lessened. To illustrate this, secondary propargyl alcohol **173** was protected as a trifluoroacetate (**174**), an acetate (**175**), and a triethylsilyl group (**176**) and subjected to identical hydrosilylation conditions. Table 3.4.1 shows the progression of decreasing selectivity as electronic influence decreases.

Table 3.4.1 Differential alkyne polarization analysis



entry	Substrate	Product	time (h)	yield (%)	α : β[a]
1			12	95	>19 : 1
2			16	97	7.1 : 1
3			16	98	1.0 : 1

decreasing alkyne polarization

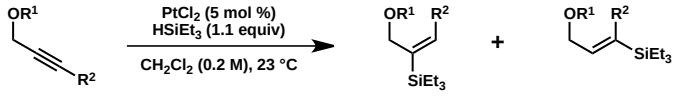
[a] Measured by ^{1}H NMR

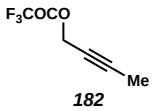
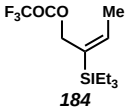
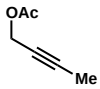
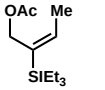
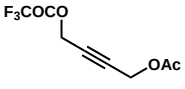
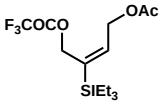
3.4.2 Small Propargyl Alcohol Substrates

Often highly functionalized, small substrates have great use as upstream synthetic precursors and it is necessary to have facile access to such compounds. However, small substrate alkynes can show little differentiation between carbons, thus diminishing hydrosilylation regioselectivity. We felt these systems would be an excellent application for our polarized alkyne hydrosilylation

method. To demonstrate this, we subjected acetate protected 2-butyn-1-ol **181** to our hydrosilylation conditions which only afforded modest selectivity (3.7:1) for the α-silyl isomer. Using the more electron withdrawing trifluoroacetate group (**182**), selectivity was greatly increased to a more synthetically useful 17:1 α/β ratio of isomers. To directly compare the influence of the two different propargyl acetates, protected diol **183** was evaluated (entry 3) and the catalyst system was able to effectively differentiate both alkyne carbons (3.8:1 α/β), favoring silyl addition on the carbon proximal to the more electron deficient trifluoroacetate. This result also serves as evidence that coordination is not a significant contributor to regioselection, as the acetate should exert stronger coordinative influence than the trifluoroacetate and would therefore favor the observed minor product.

Table 3.4.2 Evaluation of small substrates with propargyl oxygenation

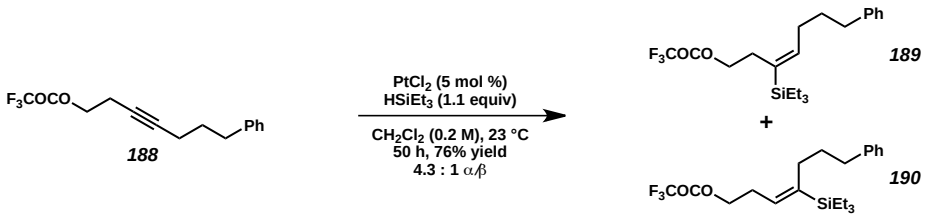


entry	Substrate	Major Product	time (h)	yield (%)	α : β[a]
1	 *182*	 *184*	8	89	17 : 1
2	 *185*	 *186*	10	90	7.1 : 1
3	 *183*	 *187*	60	69	3.8 : 1

[a] Measured by ^{1}H NMR

Fascinated by the strong inductive influence afforded by the propargyl trifluoroacetate, a homopropargyl system was tested (scheme 3.4.1). Notably, both sides of the alkyne have –CH_2CH_2R groups, and while the respective "R" groups are different, the relative steric

encumbrance about both alkyne carbons should be very similar. Nevertheless, the strong inductive effect provides significant influence, affording 4.3:1 α/β selectivity.



Scheme 3.4.1 Homopropargyl trifluoroacetate hydrosilylation

3.5 Evaluation of Selectivity Determinants

3.5.1 Introduction to Selectivity Studies

There are three possible factors that may play a role in the overall regioselectivity of the hydrosilylation event. Alkyne polarization likely plays a major role, but sterics (Tables 3.4.1 and 3.4.2) as well as coordination (Table 3.3.1, entry 5) may also be influential. This section aims to address these potential factors.

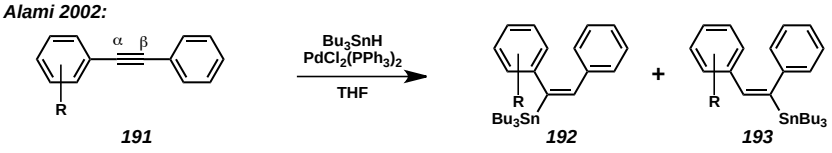
3.5.2 Electronic Effects

The aforementioned data strongly implicates that the most salient driving force for alkyne hydrosilylation regioselectivity is the polarization of the alkyne. We have shown that introducing groups of varying electron withdrawing natures can differentially influence the selectivity of addition. In all cases, we believe this reaction proceeds through the standard Chalk-Harrod mechanism (Scheme 3.2.3), where the hydride preferentially adds to the more electropositive carbon on the platinum coordinated alkyne.

A few isolated examples have employed ^{13}C chemical shift data to differentiate alkyne carbons and explain hydrosilylation regioselectivity. Tsipis's seminal report, which hypothesized an

electronic effect influencing selectivity, also discussed such ^{13}C NMR data in the evaluation of a number of aliphatic alkynes.[67] Others have looked into ^{13}C data to explain the high regioselectivity for the hydrosilylation of terminal alkynes.[76] Alami and co-workers correlated ^{13}C NMR data as a means to explain why the hydrostannylations of *ortho*-substituted diaryl acetylenes are more selective than their *para*-substituted counterparts (Table 3.5.1).[77]

Table 3.5.1 Alami's correlation between ^{13}C data and regioselectivity



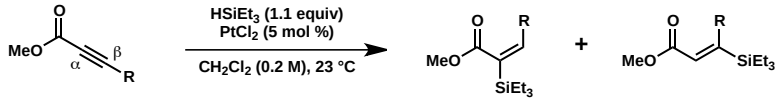
entry	R	^{13}C chemical shifts $\delta(C_\alpha)$	$\delta(C_\beta)$	$\Delta\delta_{C\beta-C\alpha}$	*192* : *193*
1	*p*-CHO	88.5	93.3	4.8	5.7 : 1
2	*o*-CHO	84.9	96.3	11.4	>19 : 1
3	*p*-Me	89.6	88.7	-0.9	1.0 : 1
4	*o*-Me	88.6	93.6	5.0	13.3 : 1
5	*p*-OMe	89.4	88.1	-1.3	0.7 : 1
6	*o*-OMe	85.7	93.4	7.7	9 : 1

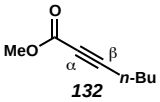
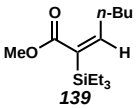
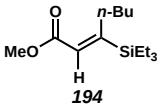
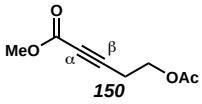
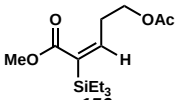
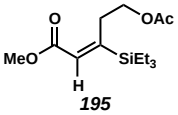
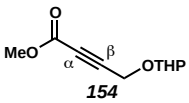
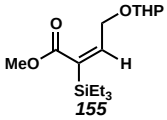
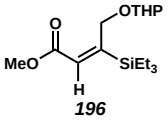
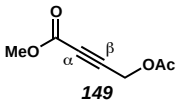
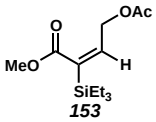
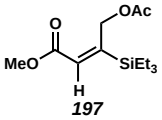
The results reported by Alami show that the substrates with *ortho* substituted phenyl diarylacetlenes have an increased difference between α and β ^{13}C chemical shifts. Correspondingly, α-silyl selectivity was high. Conversely, the chemical shift difference for the respective *para* substituted phenyl diarylacetylenes was relatively small, and the overall regioselectivity was diminished. In all cases, a larger magnitude between α and β ^{13}C chemical shifts resulted in greater selectivity, and we were eager to extend and expand this concept to our substrate controlled hydrosilylation methodology.

3.5.3 Evaluation of ^{13}C Data for Methyl Ynoate Substrates

As illustrated in Table 3.5.2, the hydrosilylations of select methyl ynoate substrates afforded sequentially decreasing regioselectivities even though the four respective substituents are of relatively similar size. An evaluation of alkyne ^{13}C chemical shifts for each compound clearly shows that each group exerts a noticeably different inductive effect.

Table 3.5.2 Methyl ynoate hydrosilylation regioselectivity correlated to ^{13}C NMR data



entry	substrate	^{13}C chemical shifts $\delta(C_\alpha)$	$\delta(C_\beta)$	$\Delta\delta_{C\beta-C\alpha}$	α-isomer	β-isomer	α : β[a]
1	 ***132***	73.0	90.1	17.1	 ***139***	 ***194***	>19 : 1
2	 ***150***	74.0	85.0	11.0	 ***156***	 ***195***	5.2 : 1
3	 ***154***	77.4	84.2	6.8	 ***155***	 ***196***	3.5 : 1
4	 ***149***	81.6	78.0	-3.6	 ***153***	 ***197***	0.9 : 1

a) Determined by ^1H NMR spectroscopy.

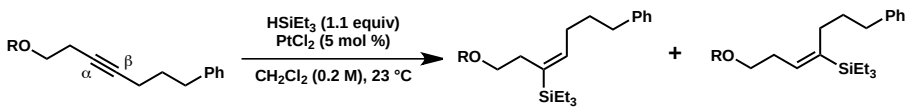
The hydrosilylation of methyl heptynoate (**132**, entry 1) produces enoate **139** with high regioselectivity; this corresponds with a high difference in alkyne carbon chemical shifts (Δ = 17.1 ppm). Homopropargyl acetate **150** shows markedly less α-selectivity, and accordingly the alkyne carbons are less differentiated (11.0 pm). On the other end of the spectrum, a propargyl acetate (**149**) seemingly exerts a stronger electronic influence than the methyl ester, showing a slight preference for the β-silyl regioisomer and a negative difference between $\delta(C\beta)$ and $\delta(C\alpha)$. Overall, the magnitude and direction of the difference between alkyne carbon chemical shifts

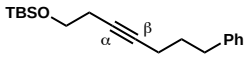
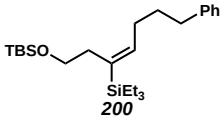
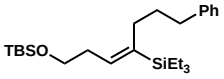
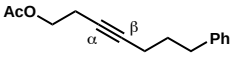
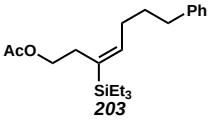
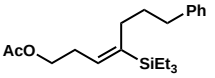
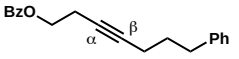
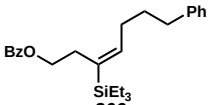
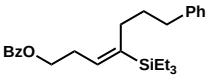
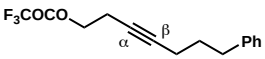
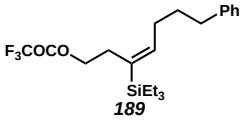
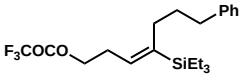
corresponds to observed regioselectivity of hydrosilylation, suggesting this concept may be applied broadly to other substrates.

3.5.4 Evaluation of ^{13}C Data for Protected Homopropargyl Alcohols

We were curious to find out if the ^{13}C NMR chemical shift difference could be used to evaluate the hydrosilylations of alkynes bearing very similar substituents, hopefully observing modest differences in selectivity that still correlate with the given trend. To test this hypothesis, homopropargylic alcohol **198** was protected with four different common protecting groups, three of which are esters of differing electronic properties. Hydrosilylations were then carried out on these substrates.

Table 3.5.3 Evaluating small differences in ^{13}C data



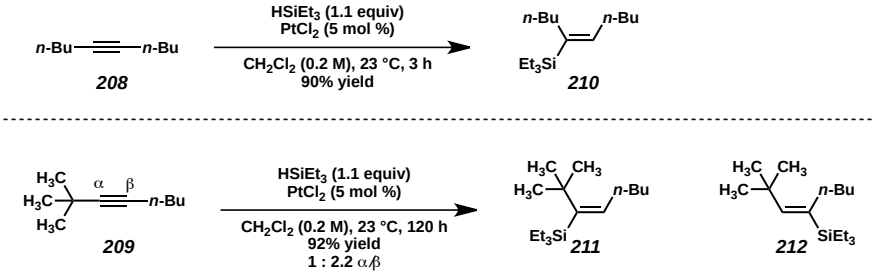
entry	substrate	^{13}C chemical shifts $\delta(C_\alpha)$	$\delta(C_\beta)$	$\Delta\delta_{C\beta-C\alpha}$	α-isomer	β-isomer	α : β[a]
1	 ***199***	77.8	81.3	3.5	 ***200***	 ***201***	1.4 : 1
2	 ***202***	76.5	81.8	5.3	 ***203***	 ***204***	2.5 : 1
3	 ***205***	76.5	82.0	5.5	 ***206***	 ***207***	2.7 : 1
4	 ***188***	74.7	83.0	8.3	 ***189***	 ***190***	4.3 : 1

a) determined by ^{1}H NMR spectroscopy.

As the data in Table **3.5.3** clearly shows, even small changes in inductive effects (best highlighted by entries 2 and 3) can be indicated by variations in Δ(δCβ-δCα) and ultimately correlated to differential regioselectivity. This may allow for reasonable predictability for future alkyne hydrosilylation reactions.

3.5.5 Steric Influence

To evaluate the influence of steric hindrance on hydrosilylation regioselectivity, we turned to all aliphatic alkyne substituents to remove any significant electronic or coordinative effects. First we subjected 5-decyne (**208**) to our hydrosilylation conditions. The reaction proceeded in 3 h, not unlike the aforementioned methyl heptynoate substrate (**132)**. The reaction time for *tert*-butyl alkyne **209** was substantially longer (120 h), reflecting the difficulty of coordination of silyl-platinum-hydride complex **116** to the alkyne as well as the migratory insertion step.



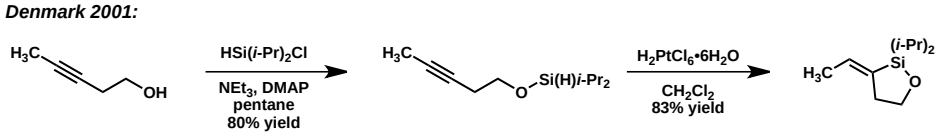
Scheme 3.5.1 Hydrosilylation of aliphatic internal alkynes

Interestingly, even though one side of alkyne **209** is significantly more hindered than the other, only a 1:2.2 α/β ratio of regioisomers is observed. This suggests that sterics may not be as significant an influence on regioselectivity as the overall polarization of the alkyne. This premise is also applied in the hydrosilylations of ynoates **132-135** in Table 3.3.2. As the ester substituents increased in size, regioselectivity measurably decreased, albeit only slightly.

3.6 Coordination Effects

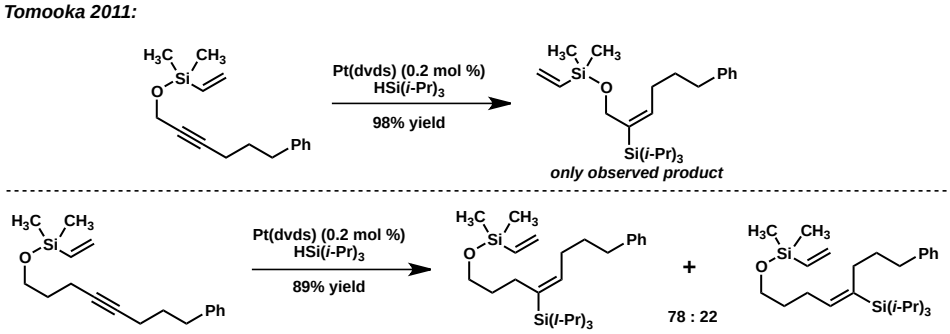
3.6.1 Coordination Effects Background

Establishing a protocol that addresses coordination-directed hydrosilylation is crucial if one would like to predict the regioselective outcome of the reaction. Previously, many others have described directed intramolecular hydrosilylations using tethered silanes.[78]



Scheme 3.6.1 An example of Denmark's tethered hydrosilylations

More recently, Tomooka and co-workers employed a tethered, cleavable dimethylvinyl silyl directing group for the platinum catalyzed hydrosilylation of alkynes. When the directing group was proximal, exquisite levels of regioselectivity were observed, however, as the distance between the alkyne and the directing group increased, the overall selectivity decreased accordingly.



Scheme 3.6.2 Tomooka's recently described directed hydrosilylation

3.6.2 Our Evaluation of Coordination Effects of Propargylic and Homopropargylic Oxygenation

The hydrosilylations of a number of previously described substrates with propargylic oxygenation (for example: **128, 149, 154**) displayed significantly diminished regioselectivity. We hypothesized that the proximal oxygen could coordinate either the platinum or silicon of intermediate **213** and direct silicon addition toward the side of said group.

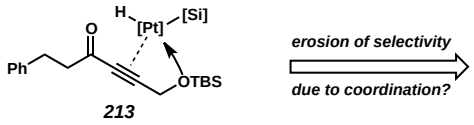
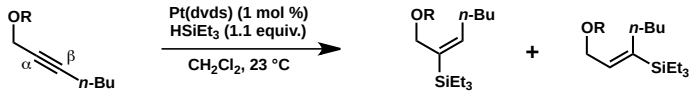
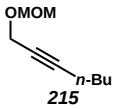
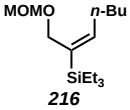
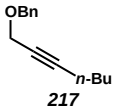
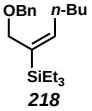
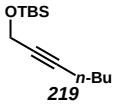
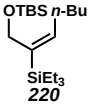


Figure 3.6.1 Previous result leading to hypothesis

To more quantitatively evaluate any potential effects of coordination on hydrosilylation regioselectivity, propargylic alcohol **214** was protected with groups of varying coordinative properties yet similar inductive effects. These substrates were then subjected to hydrosilylation conditions using Pt(dvds).[79]

Table 3.6.1 Coordinative effects of protected propargyl alcohols



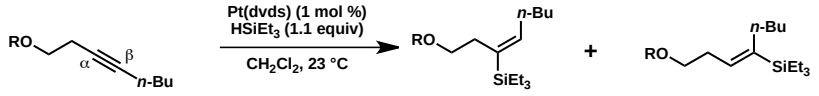
entry	substrate	major product	time (h)	yield (%)	$\alpha : \beta^a$	$\Delta(\delta C_\beta - \delta C_\alpha)$
1	 **215**	 **216**	16	73	2.8 : 1	11.7
2	 **217**	 **218**	16	96	3.2 : 1	11.5
3	 **219**	 **220**	16	78	2.7 : 1	8.2

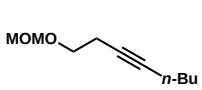
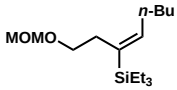
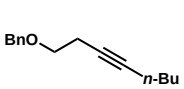
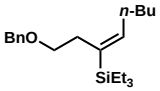
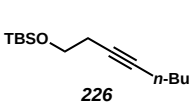
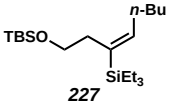
a) Measured by ^{1}H NMR

Of the three protected propargyl alcohols, the methoxymethyl group in entry 1 would likely demonstrate the greatest coordination and thus the highest selectivity. However, we actually observe almost identical α/β product ratios when comparing entry 1 and entry 3, with the latter substrate containing a significantly less coordinating TBS ether.

To further study the possibility of oxygen coordination influence of regioselectivity, an identical study was carried out with homopropargylic alcohol **221**.

Table 3.6.2 Coordinative effects of protected homopropargylic alcohols



entry	substrate	major product	time (h)	yield (%)	α : β[a]	Δ(δC$_\beta$–δC$_\alpha$)
1			16	93	2.1 : 1	4.9
	222	***223***				
2			16	98	2.0 : 1	4.8
	224	***225***				
3			16	95	1.9 : 1	4.6
	226	***227***				

a) Measured by ^{1}H NMR

The above table perhaps best illustrates the lack of influence that coordinating groups have on hydrosilylation regioselectivity. All three entries have essentially identical observed product ratios even though all substrates have different coordinative properties. Notably, the relevant ^{13}C data tabulated in Tables 3.6.1 and 3.6.2 reflects the hypothesis that the observed regioslectivity chiefly arises from inductive electronic effects.

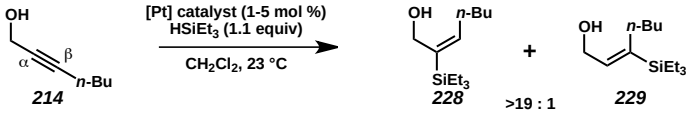
Curiously, the parent propargylic alcohol **214** showed significantly increased selectivity over their protected counterparts, as will be described below.

3.7 Hydrosilylations of Propargyl Alcohols

3.7.1 Influence of Free Alcohols

For almost every hydrosilylation reaction we have performed, $PtCl_2$ is always the first precatalyst attempted. Some substrates, however, afford much lower yields than typically observed for hydrosilylations when $PtCl_2$ is employed. HCl, a potential byproduct of Pt(II) salt catalyst induction period, can promote the decomposition of the product alcohols, likely through ionization pathways. When $PtCl_2$ is used for the hydrosilylation of propargyl alcohol **214**, low yields resulted, even after exhaustive efforts to observe the reactions progress. To identify an ideal set of conditions for propargyl alcohol hydrosilylations, three [Pt] catalysts were screened under identical conditions.

Table 3.7.1 Catalyst evaluation

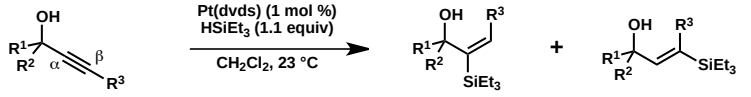


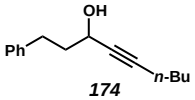
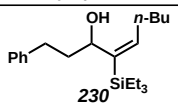
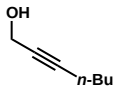
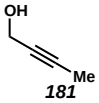
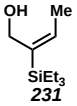
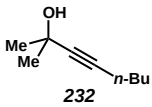
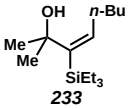
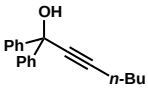
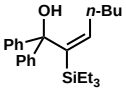
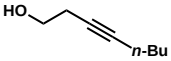
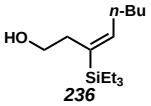
entry	catalyst	time (h)	yield (%)	α : β
1	$PtCl_2$ (5 mol %)	6	45	>19 : 1
2	$[\{(C_2H_4)PtCl_2\}_2]$ (2.5 mol %)	4	47	>19 : 1
3	Pt(dvds)[a]	5	92	>19 : 1

a) dvds = divinyltetramethyldisiloxane

Since both $PtCl_2$ and Zeise's dimer precatalyst have the potential to generate acidic species such as silyl chlorides and HCl, similarly low yields were observed. The Pt(0) catalyst Pt(dvds)[80] was able to circumvent the problem of acid generation affording excellent yield and selectivity (92% yield, >19:1 α/β) of the vinylsilanes. This observation is different from that of the catalyst evaluation for methyl heptynoate (**132**, Table 3.2.7), in which Pt(dvds) afforded diminished selectivity compared to the Pt(II) based salts. A number of propargyl alcohol substrates were evaluated.

Table 3.7.2 Propargylic alcohol substrates



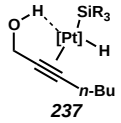
entry	substrate	major product	time (h)	yield (%)	α : β[a]
1	 ***174***	 ***230***	3	86	>19 : 1
2	 ***214***	 ***228***	5	92	>19 : 1
3	 ***181***	 ***231***	24	97	3.3 : 1
4	 ***232***	 ***233***	24	88	3.2 : 1
5	 ***234***	 ***235***	24	81	9.2 : 1
6	 ***221***	 ***236***	6	97	3.0 : 1

a) determined by ^{1}H NMR spectoscopy

Excellent selectivity was observed for the hydrosilylation of primary and secondary propargyl alcohols **214** and **174**; however, 2-butyn-1-ol **181** was significantly less selective. Sterics could potentially play a role with the relatively small methyl alkyne substituent.[66] Although highly hindered alkyne **232** unsurprisingly showed modest selectivity, similarly hindered, yet highly polarized alkyne **234** showed a high isomeric ratio (9.2:1 α/β).

We were intrigued about the unexpectedly high regioselectivity observed in the hydrosilylation of **214**. One could surmise that is the alcohol may participate in a favorable hydrogen bond

interaction with the silyl platinum intermediate (**237)** thus acting as a directing group for the addition process.



237

Figure 3.7.1 Possible H–bond coordination of intermediate **237**

3.8 Conclusion

In summary, the hydrosilylation of internal alkynes, once thought to be highly unselective, can be harnessed using substrate control. We have demonstrated the hydrosilylations of numerous internal alkynes using mild conditions and simple, stable Pt catalysts. In many cases, these reactions proceed in high yield and selectivity. To further elucidate selectivity controls, the effects of electronics, steric hindrance, and coordination were comprehensively evaluated. Notably, it was found that alkyne polarization afforded the greatest influence over the regioselectivity of silane additon. This electronic effect can be reasonably quantified using ^{13}C NMR data. A greater magnitude between alkyne carbon chemical shifts correlates to greater observed regioselctivity of silane addition.[81] The effects of sterics are measurable but significantly less influential. Coordination by proximal oxygen was originally thought to direct selectivity, but after evaluation of numerous substrates, it can be determined that the inductive effect of the oxygen group probably affects overall regioselectivity more than coordination from oxygen. This expansion of hydrosilylation methodology will hopefully serve the synthetic community with its ability to generate synthetically useful stereodefined trisubstituted alkenes. Our own efforts toward the utilization of our product vinylsilanes are outlined in Chapter 4.

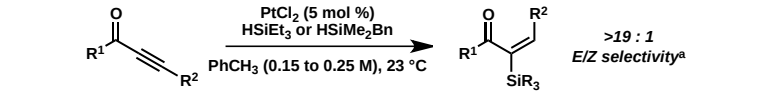
3.9 Experimental Section

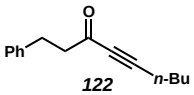
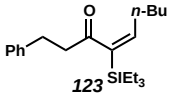
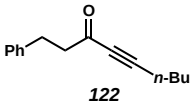
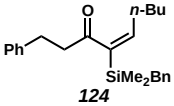
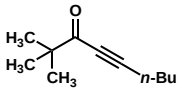
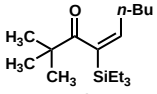
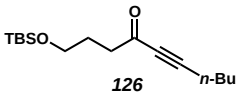
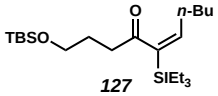
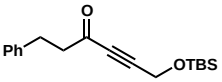
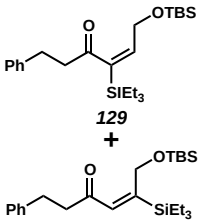
3.9.1 Materials and Methods

All reactions were performed under an argon atmosphere unless otherwise noted. Tetrahydrofuran, ether, and toluene were purified by passing through activated alumina columns. Chlorotrimethylsilane was freshly distilled from calcium hydride prior to its use in reactions. All other reagents were used as received unless otherwise noted. Commercially available chemicals were purchased from Alfa Aesar (Ward Hill, MA), Sigma-Aldrich (St. Louis, MO), Gelest (Morrisville, PA), Oakwood Products, (West Columbia, SC), Strem (Newburport, MA) and TCI America (Portland, OR). Qualitative TLC analysis was performed on 250 mm thick, 60 Å, glass backed, F254 silica (Silicycle, Quebec City, Canada). Visualization was accomplished with UV light and exposure to either *p*-anisaldehyde or $KMnO_4$ stain solutions followed by heating. Flash chromatography was performed using Silicycle silica gel (230-400 mesh). ^1H NMR spectra were acquired on either a Varian Mercury 300 (at 300 MHz), a Varian Inova 400 (at 400 MHz), or a Varian 400 MR (at 400 MHz) and are reported relative to $SiMe_4$ (δ 0.00). ^{13}C NMR spectra were acquired on either a Varian Inova 400 (at 100 MHz), a Varian Mercury 300 (at 75 MHz), or a Varian 400 MR (at 100 MHz) and are reported relative to $SiMe_4$ (δ 0.0). All IR spectra were obtained on NaCl plates (film) with a Bruker Tensor 27. High resolution mass spectrometry data were acquired by the Colorado State University Central Instrument Facility on an Agilent 6210 TOF LC/MS.

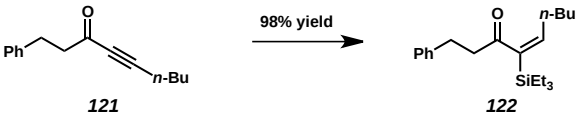
3.9.2 Hydrosilylations of Ynones

Table 3.3.1 (*reproduced*)



entry	Substrate	Product	time (h)	yield (%)[a]	α : β[b]
1	 122	 123	1.5	98	>19 : 1
2	 122	 124	1.5	99	>19 : 1
3	 121	 125	9	65	>19 : 1
4	 126	 127	2	92	>19 : 1
5	 128	 129 + 130	2	87	2 : 1

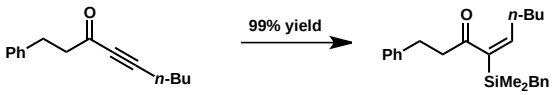
a) Isolated yield b) Measured by ^{1}H NMR



121 122

Table 3.3.1, Entry 1. To a solution of 1-phenylnon-4-yn-3-one (**121**, 163 mg, 0.762 mmol) in toluene (4.00 mL) at 23 °C under argon was added triethylsilane (0.134 mL, 0.838 mmol). To the reaction vessel was then added $PtCl_2$ (10.0 mg, 0.0381 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (2 h), as judged by TLC (9:1 hexanes/EtOAc), the mixture was filtered through a plug of silica gel (1 x 2 cm) and subsequently washed with Et_2O (25 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford enone **122** (246 mg, 98% yield, >19:1 *Z/E*, R_F = 0.53 in 9:1 hexanes/EtOAc) as a colorless oil.

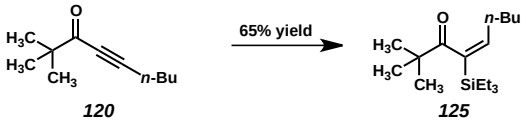
α-Silylenone 122: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22-7.07 (comp m, 5H), 5.67 (t, *J* = 7.3 Hz, 1H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 1.89 (q, *J* = 7.2 Hz, 2H), 1.30-1.10 (m, 2H), 0.84 (t, *J* = 7.8 Hz, 9H), 0.78 (t, *J* = 7.1 Hz, 3H), 0.50 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.4, 143.6, 141.9, 140.5, 138.2, 125.4, 125.3, 122.8, 42.9, 28.4, 28.3, 26.3, 19.1, 10.8, 4.0, 0.0; IR (film) 2956, 2875, 1685, 1455, 1006, 699 cm^{-1}; HRMS (ESI^{+}) *m/z* calc'd for $(M + Na)^{+}$ $[C_{21}H_{34}OSi + Na]^{+}$: 353.2271, found 353.2270.



123 *124*

Table 3.3.1, Entry 2. To a solution of 1-phenylnon-4-yn-3-one (**123**, 179 mg, 0.838 mmol) in 4.00 mL toluene at 23 °C under argon was added benzyldimethylsilane (0.146 mL, 0.922 mmol). To the reaction vessel was then added $PtCl_2$ (11.1 mg, 0.0419 mmol) and the mixture was allowed to stir for 1.5 hours. Upon completion, as judged by TLC (9:1 hexanes/EtOAc), the mixture was filtered through a plug of silica gel (1 x 2 cm) and subsequently washed with Et_2O (15 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/EtOAc eluent) to afford enone **124** (304 mg, 99% yield, >19:1 *Z/E*, R_F = 0.55 in 9:1 hexanes/EtOAc) as a colorless oil.

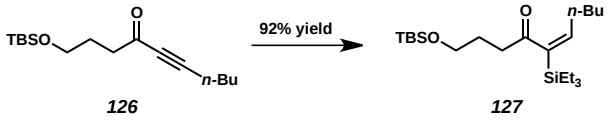
α-Silylenone 124: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.17 (comp m, 7H), 7.09-6.97 (comp m, 3H), 5.71 (t, *J* = 7.3 Hz, 1H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.71 (app. t, *J* = 7.6 Hz, 2H), 2.16 (s, 2H), 1.97 (q, *J* = 7.3 Hz, 2H) 1.33-1.19 (comp m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 146.2, 144.4, 141.4, 139.3, 128.7, 128.6, 128.3, 126.2, 124.4, 46.3, 31.7, 31.4, 29.6, 25.7, 14.0, -3.3; IR (film) 3026, 2958, 1684, 1601, 1494, 835 cm^{-1}; HRMS (ESI^{+}) *m/z* calc'd for $(M + H)^{+}$ $[C_{24}H_{33}OSi]^{+}$: 365.2295, found 365.2302.



120 *125*

Table 3.3.1, Entry 3. To a solution of **120** (88.9 mg, 0.535 mmol) in 2.20 mL toluene at 23 °C under argon was added triethylsilane (94.0 μl, 0.589 mmol). To the reaction vessel was then added $PtCl_2$ (7.1 mg, 0.0268 mmol) and the mixture was allowed to stir at 23 °C. Upon completion (9 h), as judged by TLC (9:1 hexanes/EtOAc), the mixture was filtered through a plug of silica gel (1 x 2 cm) and subsequently washed with Et_2O (15 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/EtOAc eluent) to afford enone **125** (98.5 mg, 65% yield, >19:1 *Z/E*, R_F = 0.52 in 9:1 hexanes/EtOAc) as a colorless oil.

α-Silylenone 125: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 (t, *J* = 7.1 Hz, 1H), 1.98 (q, *J* = 7.3 Hz, 2H), 1.40-1.26 (comp m, 4H), 1.14 (s, 9H), 0.95 (t, *J* = 7.8 Hz, 9H), 0.87 (t, *J* = 7.1 Hz, 3H), 0.62 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 219.2, 144.4, 142.3, 43.7, 33.4, 31.5, 27.6, 22.5, 14.4, 7.3, 3.9; IR (film) 2957, 2876, 1673, 1082, 1005, 717 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{17}H_{35}OSi]^+$: 283.2452, found 283.2454.

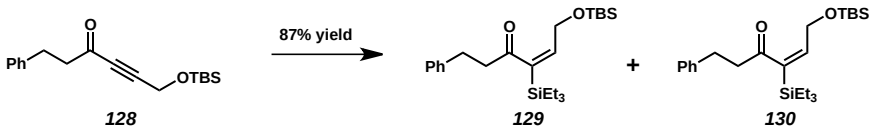


126 *127*

Table 3.3.1, Entry 4. To a solution of **126** (91.2 mg, 0.323 mmol) in 2.00 mL toluene at 23 °C under argon was added triethylsilane (61.6 μl, 0.387 mmol). To the reaction vessel was then added $PtCl_2$ (4.2 mg, 0.0162 mmol) and the mixture was allowed to stir at 23 °C. Upon completion (2 h), as judged by TLC (9:1 hexanes/EtOAc), the mixture was filtered through a plug of silica gel (1 x 2 cm) and subsequently washed with Et_2O (10 mL). The filtrate was

concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/EtOAc eluent) to afford enone **127** (118 mg, 92% yield, >19:1 *Z/E*, R_F = 0.30 in 9:1 hexanes/EtOAc) as a colorless oil.

α-Silylenone 127: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.75 (t, *J* = 7.2 Hz, 1H), 3.63 (t, *J* = 6.1 Hz, 2H), 2.54 (t, *J* = 7.4 Hz, 2H), 2.06 (q, *J* = 7.2 Hz, 2H), 1.79 (app. dq, *J* = 14.0, 6.7 Hz, 2H), 1.40-1.26 (comp m, 4H), 0.93 (t, *J* = 7.8 Hz, 9H), 0.88 (s, 6H), 0.61 (q, *J* = 7.8 Hz, 6H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.4, 145.4, 143.4, 62.3, 40.7, 31.6, 31.5, 26.6, 26.0, 22.4, 14.0, 7.3, 3.3, -5.3; IR (film) 2956, 2876, 1686, 1099, 836, 720 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{22}H_{47}O_2Si_2]^+$: 399.3109, found 399.3102.



128 *129* *130*

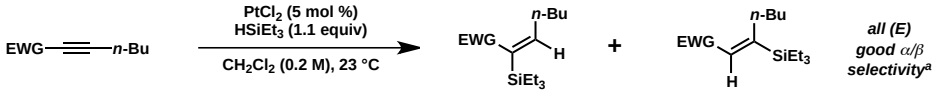
Table 3.3.1, Entry 5. To a solution of **128** (167 mg, 0.550 mmol) in toluene (2.75 mL) was added triethylsilane (96.4 μl, 0.605 mmol) under an argon atmosphere. To the reaction vessel was then added $PtCl_2$ (7.3 mg, 0.0275 mmol) and the mixture was allowed to stir at 23 °C. Upon completion (2 h), as judged by TLC (9:1 hexanes/EtOAc), the mixture was filtered through a plug of silica gel (1 x 2 cm) and subsequently washed with Et_2O (10 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/EtOAc) to afford a mixture of **129** and **130** (200 mg, 87% total yield, 2:1 α:β, R_F = 0.45 in 9:1 hexanes/EtOAc) as a colorless oil. **129** was further purified by flash chromatography for characterization purposes.

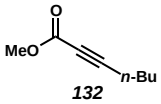
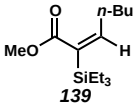
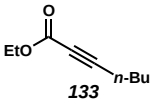
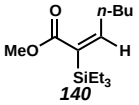
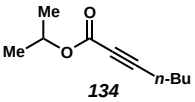
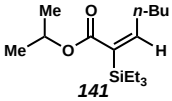
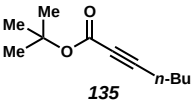
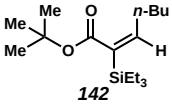
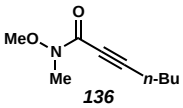
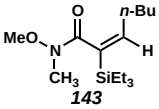
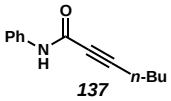
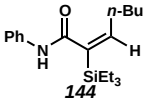
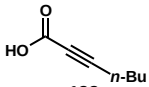
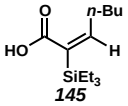
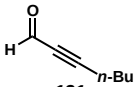
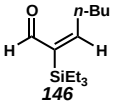
α-Silylenone 129: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.21 (comp m, 2H), 7.16 (app. d, *J* = 8.2 Hz, 3H), 5.82 (t, *J* = 5.1 Hz, 1H), 4.12 (d, *J* = 5.1 Hz, 2H), 2.90-2.85 (m, 2H), 2.75 (app. ddd, *J* =

8.4, 6.9, 1.6 Hz, 2H), 0.89 (t, *J* = 7.8 Hz, 9H), 0.84 (s, 9H), 0.57 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.2, 142.9, 141.5, 128.6, 128.4, 126.2, 62.6, 45.8, 29.6, 26.3, 26.1, 15.8, 7.3, 3.9, 3.2, 2.5, -5.1; IR (film) 2958, 2876, 1673, 1460, 1082, 718 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{24}H_{42}O_2Si_2 + Na]^+$: 441.2616, found 441.2623.

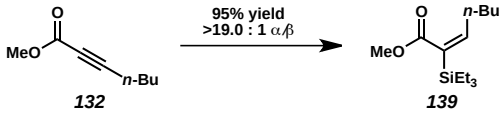
3.9.3 Hydrosilylations of Ynoates and Ynamides

Table 3.3.2 (*reproduced*)



entry	substrate	major product	time (h)	yield (%)	α : β[a]
1	 **132**	 **139**	3	95	>19 : 1
2	 **133**	 **140**	3	93	16 : 1
3	 **134**	 **141**	3	93	9.3 : 1
4	 **135**	 **142**	7	95	7.5 : 1
5	 **136**	 **143**	5	89	>19 : 1
6	 **137**	 **144**	24	80	12 : 1
7	 **138**	 **145**	5.5	95	13 : 1
8	 **131**	 **146**	3	58[b]	3.1-5.8 : 1

a) Determined by ^{1}H NMR spectroscopy. b) Best isolated yield.
EWG = electron-withdrawing group

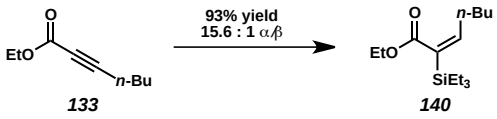


132 **139**

Table 3.3.2, Entry 1. To a solution of methyl hept-2-ynoate (**132**, 75.9 mg, 0.541 mmol) and Et_3SiH (94.8 µl, 0.595 mmol) in CH_2Cl_2 (2.70 mL) at 23 °C under argon was $PtCl_2$ (7.2 mg,

0.0271 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (3 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (9 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford enoate **139** (133 mg, 95% yield, >19.0:1 $\alpha\beta$, R_F = 0.37 in 19:1 hexanes/Et_2O) as a colorless oil.

α-Silylenoate 139: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (t, *J* = 7.2 Hz, 1H), 3.71 (s 3H), 2.32 (q, *J* = 7.26, 2H), 1.45-1.25 (comp m, 4H), 0.98-0.88 (comp m, 12H), 0.64 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 151.9, 133.1, 51.2, 31.7, 31.4, 22.4, 14.1, 7.3, 3.3; IR (film) 2956, 2876, 1718, 1606, 1197, 1006 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{14}H_{28}O_2Si]^+$: 256.1856, found 256.1859.



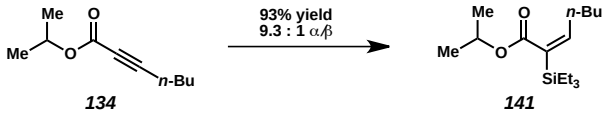
133 *140*

Table 3.3.2, Entry 2. To a solution of ethyl hept-2-ynoate (**133**, 70.0 mg, 0.454 mmol) and Et_3SiH (79.5 μl, 0.499 mmol) in CH_2Cl_2 (2.27 mL) at 23 °C under air was added $PtCl_2$ (6.0 mg, 0.0227 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (3 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes (3 mL), filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (9 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 39:1 hexanes/Et_2O eluent) to afford enoate **140** (115 mg, 93% yield, 15.6:1 $\alpha\beta$, R_F = 0.49 in 19:1 hexanes/Et_2O) as a colorless oil.

α-Silylenoate 140: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (t, *J* = 7.2 Hz, 1H), 4.16 (q, *J* = 7.1 Hz,

2H), 2.32 (q, *J* = 7.3 Hz, 2H), 1.43-1.24 (comp m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.8 Hz, 9H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.63 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 151.7, 133.3, 60.0, 31.5, 22.4, 14.5, 14.0, 7.3, 3.3; IR (film) 2957, 2876, 1715, 1606, 1461, 1190 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{30}O_2Si]^+$: 271.2095, found 271.2095.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 6.06 ppm, β: 5.97 ppm). ^{1}H and ^{13}C data for α isomer only.



134 141

Table 3.3.2, Entry 3: To a solution of isopropyl hept-2-ynoate (**134**, 70.0 mg, 0.416 mmol) and Et_3SiH (72.9 μL, 0.458 mmol) in CH_2Cl_2 (2.25 mL) at 23 °C under air was added $PtCl_2$ (5.5 mg, 0.0208 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (3 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes (3 mL), filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (9 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 39:1 hexanes/Et_2O eluent) to afford enoate **141** (114 mg, 93% yield, 9.3:1 α/β, R_F = 0.50 in 19:1 hexanes/Et_2O) as a colorless oil.

α-Silylenoate 141: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (t, *J* = 7.2 Hz, 1H), 5.06 (septet, *J* = 6.3 Hz, 1H), 2.34 (q, *J* = 7.3 Hz, 2H), 1.43-1.28 (comp m, 4H), 1.26 (d, *J* = 6.3 Hz, 6H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.63 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 151.1, 133.7, 67.4, 31.4, 22.5, 22.1, 14.0, 7.4, 3.3; IR (film) 2957, 2876, 1710, 1465, 1197, 1109 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{16}H_{32}O_2Si]^+$: 285.2250, found 285.2251.

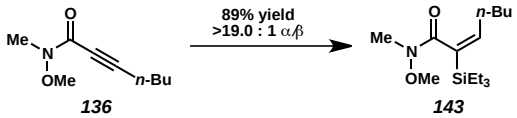
Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 6.04 ppm, β: 5.93 ppm (s)). ^{1}H and ^{13}C data for α isomer only.

135 *142*

Table 3.3.2, Entry 4. To a solution of *tert*-butyl hept-2-ynoate (**135**, 58.9 mg, 0.323 mmol) and Et_3SiH (56.5 μL, 0.355 mmol) in CH_2Cl_2 (1.61 mL) at 23 °C under argon was added $PtCl_2$ (4.3 mg, 0.0162 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (7 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (8 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford enoate **142** (91.9 mg, 95% yield, 7.5:1 $\alpha\beta$, R_F = 0.40 in 19:1 hexanes/Et_2O) as a colorless oil.

α-Silylenone 142: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (t, *J* = 7.2 Hz, 1H), 2.32, (q, *J* = 7.2 Hz, 2H), 1.49 (s, 9H), 1.44-1.30, (comp m, 4H), 0.95-0.88 (comp m, 12H), 0.64 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 150.0, 134.8, 80.3, 31.5, 31.3, 28.5, 28.4, 22.5, 14.1, 7.4, 3.3; IR (film) 2957, 2876, 1710, 1606, 1158, 1006 cm^{-1}; LRMS (EI^+) *m/z* calc'd for $(M - SiEt_3)^+$ $[C_{11}H_{19}O_2]^+$: 183, found 183.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 5.97 ppm, β: 6.88 ppm (s)). ^{1}H data for α isomer only; ^{13}C data for both isomers.



136 *143*

Table 3.3.2, Entry 5. To a solution of *N*-methoxy-*N*-methylhept-2-ynamide (**136**, 90.0 mg, 0.532 mmol) and Et_3SiH (93.2 μl, 0.585 mmol) in CH_2Cl_2 (2.70 mL) at 23 °C under argon was added $PtCl_2$ (7.1 mg, 0.0266 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (19 h), as judged by TLC (5:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (9 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (5:1 hexanes/Et_2O eluent) to afford amide **143** (135 mg, 89% yield, >19.0:1 α/β, R_F = 0.24 in 5:1 hexanes/Et_2O) as a colorless oil.

Amide 143: ^1H NMR (300 MHz, $CDCl_3$) δ 5.83 (t, *J* = 6.8 Hz, 1H), 3.78 (s, 1H), 3.53 (s, 2H), 3.20 (s, 3H), 2.16 (q, *J* = 7.3 Hz, 2H), 1.43-1.28 (comp m, 4H), 0.94 (t, *J* = 7.8 Hz, 9H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.63 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 145.3, 144.2, 137.1, 61.1, 36.0, 32.5, 32.0, 22.6, 14.1, 7.3, 5.9, 3.7, 3.3; IR (film) 2957, 2876, 1650, 1369, 1018 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{32}NO_2Si]^+$: 286.2197, found 286.2195.

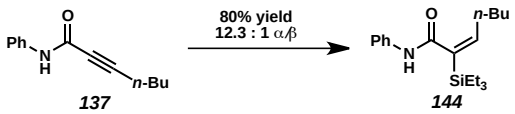
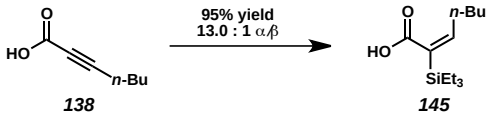


Table 3.3.2, Entry 6. To a solution of *N*-phenylhept-2-ynamide (**137**, 150 mg, 0.745 mmol) and Et_3SiH (130 μl, 0.819 mmol) in CH_2Cl_2 (3.72 mL) at 23 °C under argon was added $PtCl_2$ (9.9 mg, 0.0373 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (23 h), as judged by TLC (5:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (10 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford amide **144** (189 mg, 80% yield, 12.3:1 α/β, R_F = 0.26 in 5:1 hexanes/Et_2O) as a

white solid.

Amide 144: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.90 (br s, 1H), 5.94 (t, *J* = 7.2 Hz, 1H), 2.29 (q, *J* = 7.2 Hz, 2H), 1.47–1.29 (comp m, 4H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.70 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 146.0, 138.9, 138.1, 129.2, 124.3, 119.9, 31.7, 31.5, 22.5, 14.1, 7.4, 3.2; IR (film) 3271, 2955, 2875, 1644, 1596, 1018 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{32}NOSi]^+$: 318.2248, found 318.2250.

Note: Isolated as pure α isomer. Isomeric ratio determined by integration of vinylic protons (α: 5.94 ppm, β: 6.02 ppm (s)). ^{1}H and ^{13}C data for α isomer only.

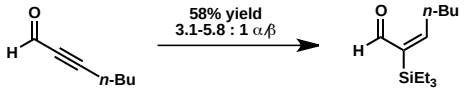


138 *145*

Table 3.3.2, Entry 7. To a solution of hept-2-ynoic acid (**138**, 80.0 mg, 0.634 mmol) and Et_3SiH (111 μl, 0.697 mmol) in CH_2Cl_2 (3.17 mL) at 23 °C under argon was added $PtCl_2$ (8.4 mg, 0.0317 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (8 h), as judged by TLC (5:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (9 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford acid **145** (147 mg, 95% yield, 13.0:1 *αβ*, R_F = 0.46 in 5:1 hexanes/Et_2O) as a colorless oil.

α-Silyl acid 145: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.17 (t, *J* = 7.2 Hz, 1H), 2.42 (q, *J* = 7.2 Hz, 2H), 1.46-1.27 (comp m, 4 H), 0.99-0.89 (comp m, 12H), 0.68 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.6, 176.7, 153.8, 132.2, 35.1, 31.7, 31.5, 30.5, 26.7, 22.7, 22.5, 14.2,

14.1, 7.3, 5.9, 3.2, 2.7; IR (film) 2958, 2877, 2736, 2631, 1682, 1254 cm^{-1}; HRMS (ESI^-) *m/z* calc'd for $(M - H)^-$ $[C_{13}H_{25}O_2Si]^-$: 241.1629, found 241.1633. *Note*: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 6.17 ppm, β: 6.01 ppm (s)). ^1H data for α isomer only; ^{13}C data for both isomers.



131 *146*

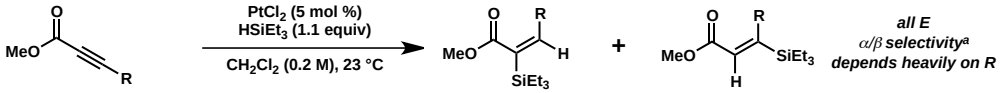
Table 3.3.2, Entry 8. To a solution of alkyne **146** (50.0 mg, 0.454 mmol) and Et_3SiH (79.5 μL, 0.499 mmol) in CH_2Cl_2 (2.27 mL) at 23 °C under air was added $PtCl_2$ (6.0 mg, 0.0227 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (3 h), as judged by TLC (>19:1 hexanes/Et_2O eluent), the mixture was diluted with hexanes (3 mL) and NEt_3 (0.5 mL) then filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (7 mL, with approx. 1% NEt_3). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (39:1 hexanes/Et_2O with 1% Et_3N eluent) to afford enal **146** as a colorless oil (59.1 mg, 58% yield, 3.1:1 α/β, R_F = 0.20 in 19:1 hexanes/Et_2O).

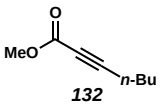
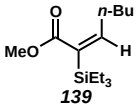
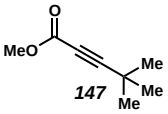
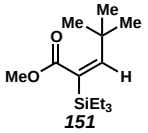
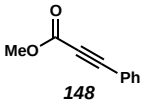
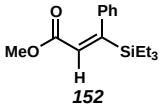
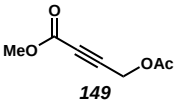
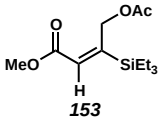
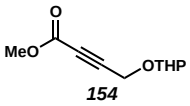
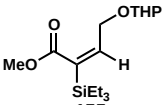
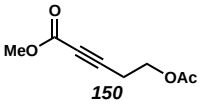
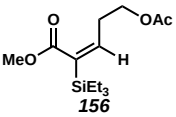
α-Silylenal 146: ^1H NMR (400 MHz, C_6D_6) δ 10.36 (s, 1H), 6.65 (t, *J* = 7.8 Hz, 1H), 2.28 (q, *J* = 7.4 Hz, 2H), 1.23-1.18 (comp m, 4H), 1.12-1.07 (comp m, 12H), 0.91-0.85 (comp m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 161.4, 140.4, 31.7, 28.7, 22.4, 13.9, 7.7, 3.4; IR (film) 2957, 2877, 1670, 1594, 1239, 1005 cm^{-1}; HRMS ($DART^+$) *m/z* calc'd for $(M + H)^+$ $[C_{13}H_{27}OSi]^+$: 227.1831, found 227.1826.

Note: Isolated as pure α isomer. Isomeric ratio determined by integration of vinylic protons (α: 6.65 ppm, β: 6.28 ppm (d)). ^1H and ^{13}C data for α isomer only.

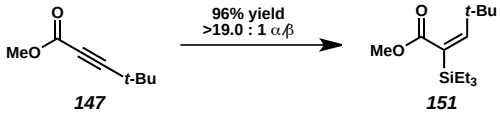
3.9.4 Hydrosilylations of Methyl Ynoates

Table 3.3.3 (*reproduced*)



entry	substrate	major product	time (h)	yield (%)	α : β[a]
1	 **132**	 **139**	3	95	>19 : 1
2	 **147**	 **151**	150	96	>19 : 1
3	 **148**	 **152**	11	90	1 : 3.5
4	 **149**	 **153**	7	97	1 : 1.1
5	 **154**	 **155**	12	92	3.5 : 1
6	 **150**	 **156**	3	88	5.2 : 1

a) Determined by ^{1}H NMR spectroscopy.

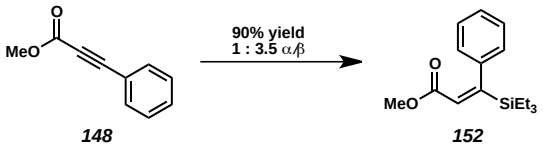


147 **151**

Table 3.3.3, Entry 2. To a solution of methyl 4,4-dimethylpent-2-ynoate (**147**, 65.4 mg, 0.467 mmol) and Et_3SiH (81.8 μl, 0.514 mmol) in CH_2Cl_2 (2.33 mL) at 23 °C under argon was added $PtCl_2$ (6.2 mg, 0.0233 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (5 d), as judged by TLC (19:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (9 mL). The filtrate

was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford enoate **151** (123 mg, 96% yield, >19.0:1 $\alpha\beta$, R_F = 0.43 in 19:1 hexanes/Et_2O) as a colorless oil.

α-Silylenoate 151: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 (s, 1H), 3.68 (s, 3H), 1.07 (s, 9H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.61 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 153.8, 129.9, 51.1, 36.4, 29.6, 7.2, 3.2; IR (film) 2956, 2878, 1717, 1608, 1193, 1018 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{14}H_{28}O_2Si]^+$: 256.1860, found 256.1859.



148 *152*

Table 3.3.3, Entry 3. To a solution of methyl 3-phenylpropiolate (**148**, 63.7 mg, 0.397 mmol) and Et_3SiH (69.6 μl, 0.437 mmol) in CH_2Cl_2 (1.98 mL) at 23 °C under argon was added $PtCl_2$ (5.3 mg, 0.0199 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (11 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (9 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford enoate **152** as a mixture of α- and β-silyl isomers (98.5 mg, 90% yield, 1:3.5 $\alpha\beta$, R_F = 0.43 in 19:1 hexanes/Et_2O) as a colorless oil.

β-Silylenoate 152: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 1H), 7.29-7.21 (comp m, 5H), 3.69 (s, 3H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.74 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 153.9, 142.5, 136.8, 135.8, 135.6, 128.6, 128.5, 128.3, 128.2, 128.0, 51.8, 51.6, 7.6, 7.3, 4.6. 3.2; IR (film) 2954, 2877, 1712, 1210, 1021 cm^{-1}; LRMS (EI$^+$) *m/z* calc'd for $(M - C_2H_5)^+$ $[C_{16}H_{24}O_2Si - C_2H_5]^+$: 247, found 247.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 8.19 ppm, β: 6.80 ppm). ^{1}H data for β isomer only; ^{13}C data for both isomers.

α-Silylenoate: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.29-7.21 (comp m, 5H), 3.78 (s, 3H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.54 (q, *J* = 7.9 Hz, 6H).

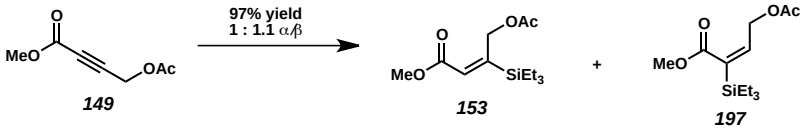
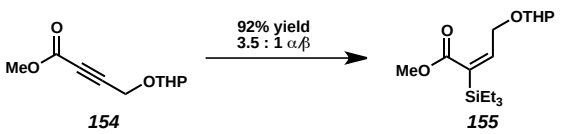


Table 3.3.3, Entry 4. To a solution of methyl 4-acetoxybut-2-ynoate (**149**, 52.9 mg, 0.339 mmol) and Et_3SiH (59.4 μl, 0.373 mmol) in CH_2Cl_2 (1.70 mL) at 23 °C under air was added $PtCl_2$ (4.5 mg, 0.0169 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (7 h), as judged by TLC (9:1 hexanes/EtOAc), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (8 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford enoate **153** as a mixture of α- and β-silyl isomers (90.2 mg, 97% yield, 1:1.1 *α/β*, R_F = 0.38 in 9:1 hexanes/EtOAc) as a colorless oil.

β-Silylenoate 153: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (s, 1H), 5.33 (s, 2H), 3.73 (s, 3H), 2.09 (s, 3H), 0.96-0.90 (comp m, 9H), 0.73-0.64 (comp m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.4, 165.4, 157.8, 148.0, 134.8, 128.5, 66.3, 64.3, 51.5, 21.1, 21.0, 7.4, 7.3, 3.5, 3.1; IR (film) 2956, 2877, 1748, 1718, 1229, 1040 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{13}H_{25}O_4Si]^+$: 273.1517, found 273.1516.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 6.21 ppm, β: 6.06 ppm). ^{1}H data for β isomer only; ^{13}C data for both isomers.

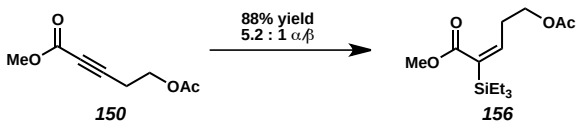


154 *155*

Table 3.3.3, Entry 5. To a solution of alkyne **154** (75.0 mg, 0.378 mmol) and Et_3SiH (66.3 μl, 0.416 mmol) in CH_2Cl_2 (1.89 mL) at 23 °C under air was added $PtCl_2$ (4.3 mg, 0.0189 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (6 h), as judged by TLC (2:1 hexanes/EtOAc), the mixture was diluted with hexanes (3 mL), filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (9 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 → 9:1 hexanes/EtOAc eluent) to afford enoate **155** (109 mg, 92% yield, 3.5:1 *αβ*, R_F = 0.78 in 2:1 hexanes/EtOAc) as a colorless oil.

α-Silylenoate 155: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (t, *J* = 4.8 Hz, 1H), 5.02 (app. d, *J* = 16.2 Hz, 1H), 4.57 (dd, *J* = 16.0, 4.5 Hz, 1H), 4.38 (dd, *J* = 16.1, 5.0 Hz, 1H), 3.87-3.82 (m, 1H), 3.69 (s, 3H), 3.49-3.47 (m, 1H), 1.85-1.52 (comp m, 6H), 0.92 (t, *J* = 7.8 Hz, 9H), 0.66 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 151.6, 132.8, 98.9, 67.5, 62.6, 51.3, 30.8, 25.5, 19.8, 7.3, 3.2; IR (film) 2395, 2876, 1716, 1608, 1202, 1035 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{16}H_{30}NaO_4Si]^+$: 337.1811, found 337.1818.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 6.34 ppm, β: 5.96 ppm (s)). ^{1}H and ^{13}C data for α isomer only.



150 *156*

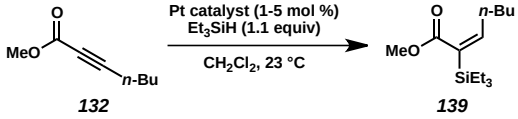
Table 3.3.3, Entry 6. To a solution of methyl 5-acetoxypent-2-ynoate (**150**, 56.8 mg, 0.334 mmol) and Et_3SiH (58.5 μl, 0.367 mmol) in CH_2Cl_2 (1.67 mL) at 23 °C under air was added

$PtCl_2$ (4.4 mg, 0.0167 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (3 h), as judged by TLC (4:1 hexanes/Et_2O), the mixture was diluted with hexanes (3 mL), filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (8 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (9:1 to 3:1 hexanes/Et_2O eluent) to afford enoate **156** as a mixture of α- and β-silyl isomers (83.9 mg, 88% yield, 5.2:1 α/β, R_F = 0.20 in 9:1 hexanes/Et_2O) as a colorless oil.

α-Silylenoate 156: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (t, *J* = 7.1 Hz, 1H), 4.12 (t, *J* = 6.6 Hz, 2H), 3.68 (s, 3H), 2.64 (q, *J* = 6.8 Hz, 2H), 2.00 (s, 3H), 0.89 (t, *J* = 7.8 Hz, 9H), 0.61 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.9, 165.2, 159.1, 146.3, 136.3, 130.1, 63.2, 51.2, 31.2, 30.5, 20.9, 7.2, 3.1, 2.5; IR (film) 2956, 1717, 1610, 1433, 1236, 1019 cm^{-1}; HRMS ($APCI^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{14}H_{30}NO_4Si]^+$: 304.1939, found 304.1944.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 6.06 ppm, β: 6.09 ppm (s)). ^{1}H data for α isomer only; ^{13}C data for both isomers.

3.9.5 Catalyst Evaluation



132 139

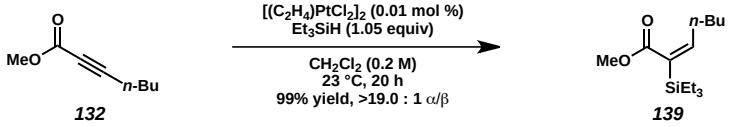
catalyst, time	yield (%)	α : β
5 mol % $PtCl_2$, 3 h	98	>19.0 : 1
2.5 mol % $[(C_2H_4)PtCl_2]_2$, 5 h	99	>19.0 : 1
1 mol % Pt(dvds), 4 h	98	9.8 : 1

To a solution of methyl hept-2-ynoate (**132**, 120 mg, 0.850 mmol) and Et_3SiH (149 μl, 0.935 mmol) in CH_2Cl_2 (4.30 mL) at 23 °C under argon was added $[(C_2H_4)PtCl_2]_2$ (12.4 mg, 0.0212 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (3 h), as judged by TLC (19:1 hexanes/Et_2O eluent), the mixture was diluted with hexanes (6 mL), filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (9 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash

chromatography (19:1 hexanes/Et_2O eluent) to afford enoate **139** as a colorless oil (217 mg, 99% yield, 9.8:1 $\alpha\beta$, R_F = 0.37 in 19:1 hexanes/Et_2O).

To a solution of methyl hept-2-ynoate (**132**, 50.0 mg, 0.357 mmol) and Pt(dvds) (23.2 mg, 3 wt% Pt in PDMS, 0.00357 mmol) in CH_2Cl_2 (11.78 mL) at 23 °C under air was added Et_3SiH (62.5 μl, 0.392 mmol). The resulting mixture was allowed to stir at 23 °C. Upon completion (4 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes (3 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with hexanes (7 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/Et_2O eluent) to afford vinylsilane **139** (89.5 mg, 98% yield, 9.8:1 $\alpha\beta$, R_F = 0.37 in 19:1 hexanes/Et_2O eluent).

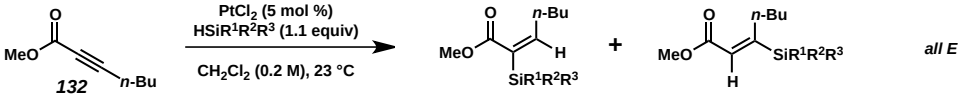
Low Catalyst Loading

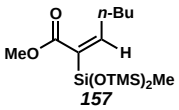
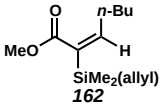
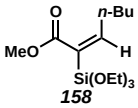
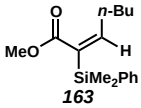
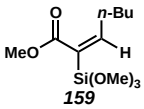
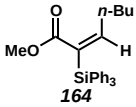
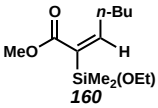
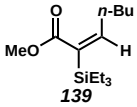
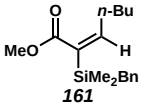
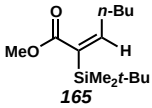


To a solution of methyl hept-2-ynoate (**132**, 0.932 g, 6.65 mmol) and Et_3SiH (1.11 mL, 6.98 mmol) in CH_2Cl_2 (6.65 mL) at 23 °C under argon was added $[(C_2H_4)PtCl_2]_2$ (0.4 mg, 0.000665 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (20 h), as judged by TLC (19:1 hexanes/Et_2O eluent), the mixture was diluted with hexanes (10 mL) and filtered through a plug of silica gel (2 x 4 cm), and the plug was subsequently washed with Et_2O (75 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford enoate **139** (1.73 g, 99% yield, >19.0:1 $\alpha\beta$, R_F = 0.37 in 19:1 hexanes/Et_2O) as a colorless oil.

3.9.6 Evaluation of Different Silanes

Table 3.3.4 (reproduced)



entry	major product	time (h)	yield (%)	α : β[a]	entry	major product	time (h)	yield (%)	α : β[a]
1	 **157**	5	98	>19 : 1	6	 **162**	12	90	10.4 : 1
2	 **158**	8	86	6.4 : 1	7	 **163**	2	95	10.2 : 1
3	 **159**	6.5	81	1.6 : 1	8	 **164**	23	94	6.0 : 1
4	 **160**	2	81	10.3 : 1	9	 **139**	3	94	>19 : 1
5	 **161**	16	98	17.8 : 1	10	 **165**	45	74	10 : 1

a) Determined by ^{1}H NMR spectroscopy.

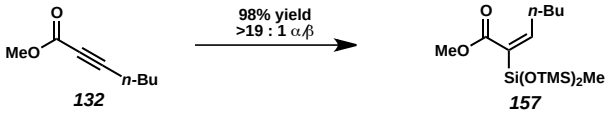


Table 3.3.4, Entry 1: To a solution of alkyne **132** (0.500 g, 3.57 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (1.07 mL, 3.92 mmol) in CH_2Cl_2 (17.8 mL) was added Pt(dvds) (0.174 mL, 0.0178 mmol, 2 wt % Pt in xylenes) under ambient atmosphere. The reaction mixture was allowed to stir at room temperature for 4 h, at which point the reaction mixture was filtered through a plug of silica gel (2 x 4 cm) washing with Et_2O (50 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100 % hexanes → 19:1 hexanes/Et_2O eluent) to afford vinylsilane **157** (1.26 g, 98% yield, R_F = 0.52 in

19:1 hexanes/Et_2O) as a pale yellow oil.

Vinylsilane 157: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (t, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 2.43 (q, *J* = 7.3 Hz, 2H), 1.46-1.31 (comp m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.18 (s, 3H), 0.10 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 156.1, 133.5, 51.0, 31.2, 31.2, 22.5, 14.0, 1.9, 0.3; IR (film) 2959, 1721, 1609, 1258, 1200, 1075 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{35}O_4Si_3]^+$: 363.1838, found 363.1846.

132 *158*

Table 3.3.4, Entry 2: To a solution of alkyne **132** (50.0 mg, 0.356 mmol) and triethoxysilane (72.4 μl, 0.392 mmol) in CH_2Cl_2 (1.78 mL) was added $PtCl_2$ (4.7 mg, 0.0178 mmol) under an argon atmosphere. The reaction mixture was allowed to stir at room temperature for 8 h, at which point the reaction mixture was filtered through a plug of silica gel (0.5 x 1 cm) washing with Et_2O (10 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford vinylsilane **158** (93.3 mg, 86% yield, 6.4:1 α/β, R_F = 0.35 in 9:1 hexanes/Et_2O for the α-isomer, R_F = 0.43 in 9:1 hexanes/Et_2O for the β-isomer) as a colorless oil.

α-isomer 158: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (t, *J* = 7.2 Hz, 1H), 3.84 (q, *J* = 7.0 Hz, 6H), 3.73 (s, 3H), 2.46 (q, *J* = 7.2 Hz, 2H), 1.43 (quint, *J* = 7.4 Hz, 2H), 1.33 (sextet, *J* = 7.4 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 9H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 160.5, 127.5, 59.3, 51.7, 31.8, 31.4, 22.9, 18.6, 14.3; IR (film) 2975, 1720, 1609, 1434, 1391, 1206, 788 cm^{-1}; LRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{14}H_{29}O_5Si]^+$: 305.2, found 305.2.

β-isomer 158β: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (s, 1H), 3.84 (q, *J* = 7.1 Hz, 6H), 3.72 (s,

3H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.50-1.33 (comp m, 2H) 1.25 (t, *J* = 7.0 Hz, 9H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 157.2, 130.1, 59.2, 51.5, 31.9, 31.1, 23.6, 18.6, 14.4; IR (film) 2976, 1727, 1434, 1082, 963, 783 cm^{-1}; LRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{14}H_{29}O_5Si]^+$: 305.2, found 305.2.

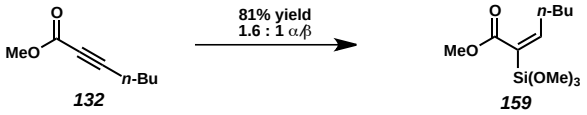
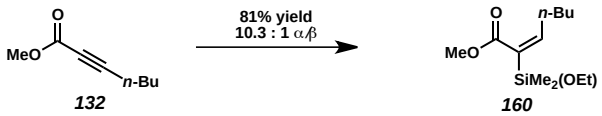


Table 3.3.4, Entry 3: To a solution of alkyne **132** (50.0 mg, 0.356 mmol) and trimethoxysilane (50.5 μl, 0.392 mmol) in CH_2Cl_2 (1.78 mL) was added $PtCl_2$ (4.7 mg, 0.0178 mmol) under an argon atmosphere. The reaction mixture was allowed to stir at room temperature for 6.5 h, at which point the reaction mixture was filtered through a plug of silica gel (0.5 x 1 cm) washing with Et_2O (10 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford vinylsilane **159** (88.6 mg, 81% yield, 1.6:1 α/β, R_F = 0.30 in 9:1 hexanes/EtOAc for the α-isomer, R_F = 0.46 in 9:1 hexanes/Et_2O for the β-isomer) as a colorless oil.

α-isomer 159: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (t, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 3.58 (s, 9H), 1.48-1.41 (m, 2H), 1.34 (sextet, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 161.2, 125.5, 51.4, 50.9, 31.3, 22.4, 13.8; IR (film) 2954, 2844, 1721, 1608, 1207, cm^{-1}; LRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{11}H_{22}O_5Si]^+$: 263.1, found 263.1.

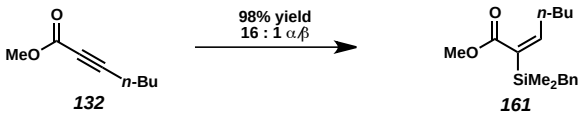
β-isomer 159β: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28 (s, 1H), 3.73 (s, 3H), 3.59 (s, 9H), 2.66 (t, *J* = 7.8 Hz, 2H), 1.49-1.34 (comp m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 155.4, 130.4, 51.4, 51.1, 31.6, 30.8, 23.4, 14.2; IR (film) 2954, 2844, 1727, 1194, 1089, 813 cm^{-1}; LRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{11}H_{22}O_5Si]^+$: 263.1, found 263.1.



132 *160*

Table 3.3.4, Entry 4: To a solution of alkyne **132** (50.0 mg, 0.356 mmol) and ethoxydimethylsilane (53.9 μl, 0.392 mmol) in CH_2Cl_2 (1.78 mL) was added $PtCl_2$ (4.7 mg, 0.0178 mmol) under an argon atmosphere. The reaction mixture was allowed to stir at room temperature for 2 h, at which point the reaction mixture was filtered through a plug of silica gel (0.5 x 1 cm), washing with Et_2O (10 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford vinylsilane **160** (70.6 mg, 81% yield, 10.3:1 α/β, R_F = 0.52 in 9:1 hexanes/Et_2O) as a colorless oil.

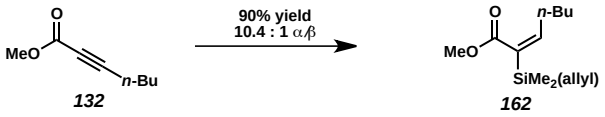
Vinylsilane 160: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (t, *J* = 7.2 Hz, 1H), 3.73 (s, 3H), 3.69 (q, *J* = 7.0 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.44 (quint, *J* = 7.4 Hz, 2H), 1.34 (sextet, *J* = 7.4 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 155.1, 134.1, 59.0, 51.4, 31.6, 31.4, 22.7, 18.7, 14.2, -1.4; IR (film) 2960, 1719, 1252, 1199, 835 cm^{-1}; XRMS (XXX^+) *m/z* calc'd for $(M + H)^+$ $[XXX]^+$: XX, found XXXX.



132 *161*

Table 3.3.4, Entry 5: To a solution of alkyne **132** (0.500 g, 3.57 mmol) and benzyldimethylsilane (0.621 mL, 3.92 mmol) in CH_2Cl_2 (17.8 mL) was added $PtCl_2$ (47.4 mg, 0.178 mmol) under an ambient atmosphere. The reaction mixture was allowed to stir at room temperature for 16 h, at which point Et_2O (10 mL) was added and the mixture was filtered through a plug of silica (2 x 3 cm), washing with additional Et_2O (30 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **161** (1.02 g, 98% yield, 17.8:1 α/β, R_F = 0.53 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 161: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 6.9 Hz, 2H), 6.06 (t, *J* = 7.2 Hz, 1H), 3.73 (s, 3H), 2.34 (q, *J* = 7.3 Hz, 2H), 2.23 (s, 2H), 1.40-1.24 (comp m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 153.9, 139.7, 133.7, 128.5, 128.4, 128.3, 128.2, 124.2, 51.2, 31.6, 31.2, 25.7, 22.5, 14.0, -3.4; IR (film) 2958, 1717, 1601, 1493, 1199 cm^{-1}; HRMS (DART$^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{17}H_{30}NO_2Si]^+$: 308.2046, found 308.2040.



132 *162*

Table 3.3.4, Entry 6: To a solution of alkyne **132** (90.0 mg, 0.642 mmol) and allyldimethylsilane (100 μl, 0.706 mmol) in CH_2Cl_2 (3.21 mL) was added $PtCl_2$ (8.5 mg, 0.0321 mmol) under ambient atmosphere. The reaction mixture was allowed to stir at room temperature for 12 h, at which point Et_2O (4 mL) was added and the mixture was filtered through a plug of

silica (0.5 x 2 cm), washing with additional Et_2O (5 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **162** (138 mg, 90% yield, 10.4:1 α/β, R_F = 0.41 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 162: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (t, *J* = 7.1 Hz, 1H), 5.74 (ddt, *J* = 16.3, 10.5, 8.1 Hz, 1H), 4.86-4.82 (comp m, 2H), 3.72 (s, 3H), 2.36 (q, *J* = 7.2 Hz, 2H), 1.65 (d, *J* = 8.0 Hz, 2H), 1.44-1.28 (comp m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 153.7, 134.9, 134.5, 113.9, 51.5, 31.9, 31.7, 23.6, 22.8, 14.4, -3.1; IR (film) 2958, 1718, 1433, 1250, 1199 cm^{-1}; HRMS (DART$^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{13}H_{28}NO_2Si]^+$: 258.1889, found 258.1884.

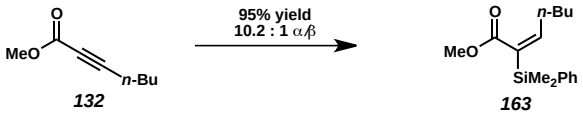
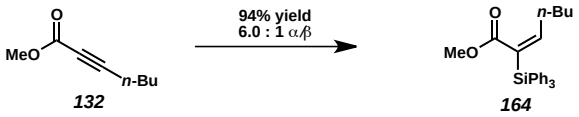


Table 3.3.4, Entry 7: To a solution of alkyne **132** (50.0 mg, 0.356 mmol) and phenyldimethylsilane (60.1 μl, 0.392 mmol) in CH_2Cl_2 (1.78 mL) was added $PtCl_2$ (4.7 mg, 0.0178 mmol) under an argon atmosphere. The reaction mixture was allowed to stir at room temperature for 2 h, at which point the reaction mixture was filtered through a plug of silica gel (0.5 x 1 cm) washing with Et_2O (10 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford vinylsilane **163** (93.1 mg, 95% yield, 10.2:1 α/β, R_F = 0.29 in 19:1 hexanes/Et_2O) as a clear oil.

Vinylsilane 163: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (comp m, 2H), 7.37-7.34 (comp m, 3H), 6.20 (t, *J* = 7.2 Hz, 1H), 3.65 (s, 3H), 2.39 (q, *J* = 7.3 Hz, 2H), 1.43-1.27 (comp m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 155.4, 138.1,

134.60, 134.58, 129.7, 128.3, 51.6, 32.2, 31.7, 23.0, 14.5, -1.9; IR (film) 2957, 1717, 1606, 1200, 835 cm^{-1}; HRMS ($APCI^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{16}H_{28}NO_2Si]^+$: 294.1889, found 294.1888.



132 *164*

Table 3.3.4, Entry 8: To a solution of alkyne **132** (50 mg, 0.356 mmol) and triphenylsilane (103 mg, 0.392 mmol) in CH_2Cl_2 (1.78 mL) was added $PtCl_2$ (4.7 mg, 0.0178 mmol) under an argon atmosphere. The reaction mixture was allowed to stir at room temperature for 23 h, at which point the reaction mixture was filtered through a plug of silica gel (0.5 x 1 cm) washing with Et_2O (10 mL) the solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford vinylsilane **164** (134 mg, 94% yield, 6.0:1 α/β, R_F = 0.26 in 19:1 hexanes/Et_2O) as a clear oil.

α-isomer 164: ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (app d, *J* = 8.0, 6H), 7.45-7.36 (comp m, 9H), 6.32 (t, *J* = 7.3 Hz, 1H), 3.48 (s, 3H), 2.47 (q, *J* = 7.3 Hz, 2H), 1.44-1.28 (comp m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 158.9, 136.6, 134.1, 131.7, 130.0, 128.2, 51.5, 32.3, 31.5, 22.9, 14.3; IR (film) 2955, 1715, 1485, 1203, 1109 cm^{-1}; HRMS ($APCI^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{26}H_{32}NO_2Si]^+$: 418.2202, found 418.2183.

β-isomer 164β: ^1H NMR (400 MHz, $CDCl_3$) δ 7.58-7.56 (m, 6H), 7.48-7.38 (comp m, 9H), 6.23 (s, 1H), 3.72 (s, 3H), 2.75 (app t, *J* = 7.5 Hz, 2H), 1.42-1.11 (comp m, 4H), 0.67 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165-9, 161.6, 136.7, 133.0, 130.2, 128.3, 51.3, 32.2, 32.0, 23.3, 13.9; IR (film) 3070, 2956, 1721, 1485, 1714, 700 cm^{-1}; LRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{26}H_{29}O_2Si]^+$: 401.2, found 401.2.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 6.32 ppm, β: 6.23 ppm (s)).

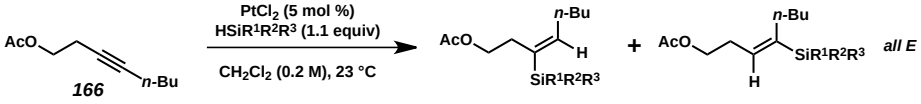
132 *165*

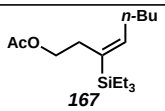
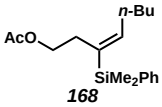
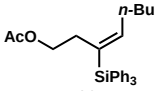
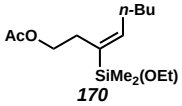
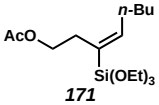
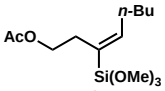
Table 3.3.4, Entry 10: To a solution of alkyne **132** (50 mg, 0.356 mmol) and *t*-butyldimethylsilane (64.9 μl, 0.392 mmol) in CH_2Cl_2 (1.78 mL) was added $PtCl_2$ (4.7 mg, 0.0178 mmol) under an argon atmosphere. The reaction mixture was allowed to stir at room temperature for 23 h, at which point the reaction mixture was filtered through a plug of silica gel (0.5 x 1 cm), washing with Et_2O (10 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **165** (67.2 mg, 74% yield, 6.0:1 α/β, R_F = 0.56 in 19:1 hexanes/Et_2O) as a clear oil.

Vinylsilane 165: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (t, *J* = 7.2, 1H), 3.71 (s, 3H), 2.26 (q, *J* = 7.3 Hz, 2H), 1.45-1.28 (comp m, 4H), 0.94-0.89 (comp m, 12H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 151.2, 134.8, 51.5, 32.2, 31.7, 27.1, 22.8, 17.8, 14.4, -5.3; IR (film) 2957, 1718, 1604, 1465, 1200, 835 cm^{-1}; HRMS (APCI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{14}H_{29}OSi]^+$: 257.1937, found 257.1917.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 6.07 ppm, β: 6.01 ppm (s)).

Table 3.3.5 (*reproduced*)



entry	major product	time (h)	yield (%)	α : β[a]
1	 ***167***	5.5	90	3.8 : 1
2	 ***168***	1.5	93	3.1 : 1
3	 ***169***	16	98	4.5 : 1
4	 ***170***	2.5	94	3.9 : 1
5	 ***171***	4	87	4.2 : 1
6	 ***172***	4.5	88	3.2 : 1

a) Determined by ^{1}H NMR spectroscopy.

Table 3.3.5, Entry 1: To a solution of alkyne **166** (50.0 mg, 0.297 mmol) and triethylsilane (52.0 μl, 0.327 mmol) in CH_2Cl_2 (1.48 mL) was added $PtCl_2$ (3.9 mg, 0.0148 mmol) under an argon atmosphere. The reaction mixture was allowed to stir at room temperature for 5.5 h, at which point the reaction mixture was filtered through a plug of silica gel (0.5 x 1 cm), washing with Et_2O (10 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **167** (76.3

mg, 90% yield, 3.8:1 α/β, R_F = 0.38 in 19:1 hexanes/Et_2O) as a clear oil.

Vinylsilane 167: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (t, *J* = 7.0 Hz, 1H), 3.95 (app. t, *J* = 8.0 Hz, 2H), 2.44 (dd, *J* = 8.3, 7.6 Hz, 2H), 2.17 (q, *J* = 7.1 Hz, 2H), 2.05 (s, 3H), 1.39-1.33 (comp m, 4H), 0.92 (t, *J* = 7.8 Hz, 9H), 0.60 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 146.0, 132.1, 64.2, 32.3, 29.4, 28.9, 22.9, 21.5, 14.5, 7.8, 3.4; IR (film) 2956, 1745, 1464, 1239, 1031, 718 cm^{-1}; HRMS (DART$^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{16}H_{36}NO_2Si]^+$: 302.2515, found 302.2518.

Note: Isomeric ratio determined by integration of vinylic protons (α: 5.81 ppm, β: 5.62 ppm (t)).

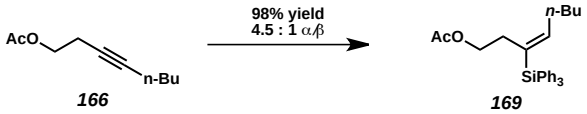
166 ***168***

Table 3.3.5, Entry 2: To a solution of alkyne **166** (50.0 mg, 0.297 mmol) and phenyldimethylsilane (51.2 μl, 0.327 mmol) in CH_2Cl_2 (1.48 mL) was added $PtCl_2$ (3.9 mg, 0.0148 mmol) under an argon atmosphere. The reaction mixture was allowed to stir at room temperature for 1.5 h, at which point the reaction mixture was filtered through a plug of silica gel (0.5 x 1 cm), washing with Et_2O (10 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **168** (97.4 mg, 93% yield, 3.1:1 α/β, R_F = 0.53 in 9:1 hexanes/EtOAc) as a clear oil.

Vinylsilane 168: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.35-7.32 (comp m, 3H), 5.96 (t, *J* = 7.0 Hz, 1H), 3.86 (app. t, *J* = 7.8 Hz, 2H), 2.45 (t, *J* = 7.6 Hz, 2H), 2.18 (q, *J* = 7.1 Hz, 2H), 1.97 (s, 3H), 1.39-1.31 (comp m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H) 0.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 146.4, 138.9, 134.2, 133.6, 129.2, 128.0, 64.0, 32.0, 29.1, 29.0, 22.8, 21.3, 14.3, -2.5; IR (film) 2958, 1743, 1241, 1110, 1033, 818 cm^{-1}; HRMS (APCI$^+$) *m/z* calc'd

for $(M + NH_4)^+$ $[C_{18}H_{32}NO_2Si]^+$: 322.2202, found 322.2191.

Note: Isomeric ratio determined by integration of vinylic protons (α: 5.96 ppm, β: 5.76 ppm (t)).

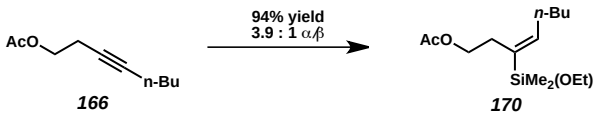


166 ***169***

Table 3.3.5, Entry 3: To a solution of alkyne **166** (52.0 mg, 0.298 mmol) and triphenylsilane (85.2 mg, 0.327 mmol) in CH_2Cl_2 (1.49 mL) was added $PtCl_2$ (4.0 mg, 0.0149 mmol) under an argon atmosphere. The reaction mixture was allowed to stir at room temperature for 16 h, at which point the reaction mixture was filtered through a plug of silica gel (0.5 x 1 cm), washing with Et_2O (10 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **169** (131 mg, 98% yield, 4.5:1 α/β, R_F = 0.47 in 9:1 hexanes/EtOAc) as a white solid.

Vinylsilane 169: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 6H), 7.43-7.35 (comp m, 9H), 6.13 (t, *J* = 7.0 Hz, 1H), 3.75 (t, *J* = 7.6 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.29 (q, *J* = 7.1 Hz, 2H), 1.86 (s, 3H), 1.40-1.32 (comp m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 151.4, 136.8, 134.8, 130.0, 128.3, 64.3, 32.1, 29.7, 23.1, 21.4, 14.5; IR (film) 3069, 2957, 1741, 1428, 1240, 702 cm^{-1}; HRMS ($APCI^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{28}H_{36}NO_2Si]^+$: 446.2515, found 446.2508.

Note: Isolated as a mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 6.13 ppm, β: 5.92 ppm (t)).



166 170

Table 3.3.5, Entry 4: To a solution of alkyne **166** (50.0 mg, 0.297 mmol) and dimethylethoxysilane (45.0 μl, 0.327 mmol) in CH_2Cl_2 (1.48 mL) was added $PtCl_2$ (3.9 mg, 0.0148 mmol) under an argon atmosphere. The reaction mixture was allowed to stir at room temperature for 2.5 h, at which point the reaction mixture was filtered through a plug of silica gel (0.5 x 1 cm), washing with Et_2O (10 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **170** (76.0 mg, 89% yield, 3.9:1 α/β, R_F = 0.31 in 9:1 hexanes/EtOAc) as a clear oil.

Vinylsilane 170: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (t, *J* = 6.9 Hz, 1H), 4.01 (t, *J* = 7.8 Hz 2H), 3.63 (q, *J* = 7.0 Hz, 2H), 2.50 (t, *J* = 7.8 Hz, 2H), 2.17 (q, *J* = 7.1 Hz, 2H), 2.05 (s, 3H), 1.40-1.32 (comp m, 4H), 1.19 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H), 0.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 146.3, 134.3, 64.2, 58.8, 32.0, 28.8, 28.7, 22.9, 21.5, 18.9, 14.5, -1.6; IR (film) XXX cm^{-1}; HRMS (APCI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{14}H_{28}O_3Si]^+$: 273.1808, found 273.1800.

Note: Isolated as a mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 5.98 ppm, β: 5.80 ppm (t)).

166 171

Table 3.3.5, Entry 5: To a solution of alkyne **166** (59.0 mg, 0.351 mmol) and triethoxysilane (71.2 μl, 0.386 mmol) in CH_2Cl_2 (1.76 mL) was added $PtCl_2$ (4.7 mg, 0.0175 mmol) under an argon atmosphere. The reaction mixture was allowed to stir at room temperature for 4 h, at

which point the reaction mixture was filtered through a plug of silica gel (0.5 x 1 cm), washing with Et_2O (10 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **171** (102 mg, 87% yield, 4.2:1 α/β, R_F = 0.24 in 9:1 hexanes/Et_2O) as a clear oil.

Vinylsilane 171: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (t, *J* = 7.0 Hz, 1H), 4.06 (t, *J* = 7.6 Hz, 2H), 3.81 (q, *J* = 7.6 Hz, 6H), 2.47 (t, *J* = 7.3 Hz, 2H), 2.17 (q, *J* = 7.2 Hz, 2H), 2.03 (s, 3H), 1.43-1.29 (comp m, 4H), 1.22 (t, *J* = 7.1, 9H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 149.4, 127.9, 64.1, 58.9, 31.8, 28.81, 28.77, 22.9, 21.5, 18.6, 14.4; IR (film) 2974, 1744, 1618, 1388, 1242, 959, 781 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{16}H_{32}NaO_5Si]^+$: 355.1917, found 355.1906.

Note: Isomeric ratio determined by integration of vinylic protons (α: 6.22 ppm, β: 6.05 ppm (t)).

Table 3.3.5, Entry 6: To a solution of alkyne **166** (73.1 mg, 0.435 mmol) and trimethoxysilane (61.9 μl, 0.479 mmol) in CH_2Cl_2 (2.18 mL) was added $PtCl_2$ (5.8 mg, 0.0217 mmol) under an argon atmosphere. The reaction mixture was allowed to stir at room temperature for 4.5 h, at which point the reaction mixture was filtered through a plug of silica gel (0.5 x 1 cm), washing with Et_2O (10 mL). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **172** (111 mg, 88% yield, 3.2:1 α/β, R_F = 0.31 in 9:1 hexanes/EtOAc) as a colorless oil.

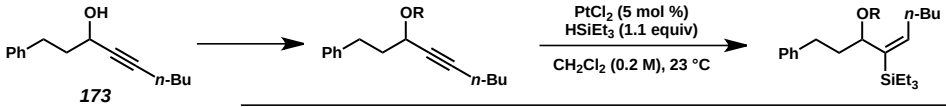
Vinylsilane 172: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (t, *J* = 7.1 Hz, 1H), 4.06 (t, *J* = 7.5 Hz, 2H), 3.57 (s, 9H), 2.48 (t, *J* = 7.5 Hz, 2H), 2.29 (q, *J* = 7.1 Hz, 2H), 2.03 (s, 3H), 1.42-1.30

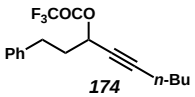
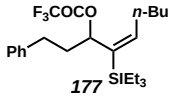
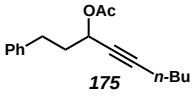
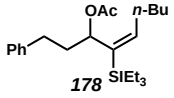
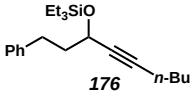
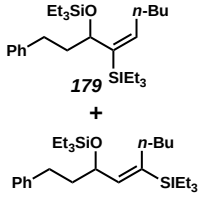
(comp m, 4H), 0.92 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 150.1, 126.8, 64.1, 51.1, 31.8, 28.8, 21.7, 22.9, 21.5, 14.4; IR (film) 2958, 2842, 1744, 1617, 1243, 811 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{13}H_{26}O_5SiNa]^+$: 313.1447, found 313.1446.

Note: Isomeric ratio determined by integration of vinylic protons (α: 6.21 ppm, β: 6.04ppm (t)).

3.9.7 Propargylic Oxygenation Analysis

Table 3.4.1 (*reproduced*)



entry	Substrate	Product	time (h)	yield (%)	α : β[a]
1			12	95	>19 : 1
2			16	97	7.1 : 1
3			16	98	1.0 : 1

decreasing alkyne polarization

[a] Measured by ^{1}H NMR

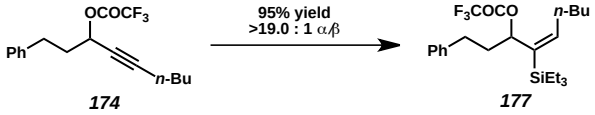
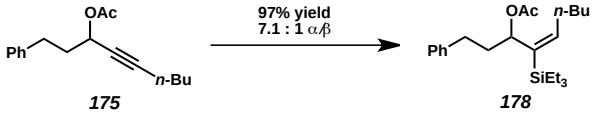


Table 3.4.1, Entry 1. To a solution of propargylic trifluoroacetate **174** (34.0 mg, 0.109 mmol) and Et_3SiH (19.1 μl, 0.119 mmol) in CH_2Cl_2 (0.545 mL) at 23 °C under argon was added $PtCl_2$ (1.5 mg, 0.00544 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (24 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (8 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **177** (46.7 mg, 95% yield, >19.0:1 $\alpha\beta$, R_F = 0.74 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 177: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.3 Hz, 2H), 7.21 (t, *J* = 7.4 Hz,

1H), 7.15 (d, *J* = 6.8 Hz, 2H), 5.89-5.83 (comp m, 2H), 2.74-2.52 (comp m, 2H), 2.27-2.00 (comp m, 3H), 1.84 (dddd, *J* = 14.3, 9.7, 7.1, 4.7 Hz, 1H), 1.37-1.23 (comp m, 4H), 0.92-0.87 (comp m, 12H), 0.63 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 140.6, 134.5, 128.7, 128.5, 126.4, 79.7, 36.7, 32.1, 31.7, 29.4, 22.5, 14.1, 7.4, 3.9; IR (film) 2957, 2876, 1782, 1220, 1154 cm^{-1}; HRMS (DART$^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{23}H_{39}F_3NO_2Si]^+$: 446.2702, found 446.2701.



175 *178*

Table 3.4.1, Entry 2. To a solution of alkyne **175** (68.8 mg, 0.266 mmol) and Et_3SiH (46.6 μl, 0.279 mmol) in CH_2Cl_2 (1.33 mL) at 23 °C under argon was added $PtCl_2$ (3.5 mg, 0.0133 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (18 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (8 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **178** (86.0 mg, 97% yield, 7.1:1 $\alpha\beta$, R_F = 0.23 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 178: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.3 Hz, 2H), 7.21-7.16 (m, 3H), 5.82 (dd, *J* = 9.8, 4.1 Hz, 1H), 5.75 (t, *J* = 7.0 Hz, 1H), 2.70-2.52 (comp m, 2H), 2.24-2.01 (comp m, 3H), 2.04 (s, 3H), 1.73 (dddd, *J* = 13.9, 10.2, 6.4, 4.8 Hz, 1H), 1.41-1.25 (comp m, 4H), 0.94-0.88 (comp m, 12H), 0.64 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 144.6, 141.7, 136.6, 128.5, 126.0, 74.8, 37.3, 32.5, 31.8, 29.3, 22.6, 21.5. 14.1, 7.5, 4.1; IR (film) 2955, 2874, 1740, 1456, 1235, 1020 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{23}H_{42}NO_2Si]^+$:

392.2979, found 392.2977.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 5.75 ppm, β: 5.59 ppm (d)). ^{1}H and ^{13}C data for α isomer only.

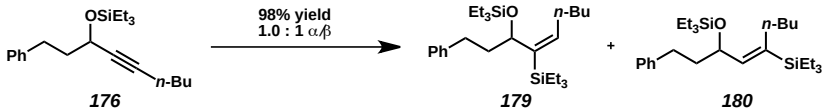
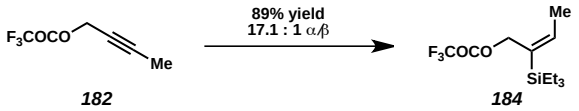


Table 3.4.1, Entry 3. To a solution of alkyne **176** (63.2 mg, 0.191 mmol) and Et_3SiH (33.4 μl, 0.210 mmol) in CH_2Cl_2 (0.955 mL) at 23 °C under argon was added $PtCl_2$ (2.5 mg, 0.00956 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (18 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (8 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (39:1 hexanes/Et_2O eluent) to afford α–vinylsilane **179** (42.8 mg, R_F = 0.82 in 19:1 hexanes/Et_2O) and β–vinylsilane **180** (41.3 mg, R_F = 0.58 in 19:1 hexanes/Et_2O) (98% total yield, 1.0:1 α/β) as colorless oils.

α-Vinylsilane 179: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (app. t, *J* = 7.4 Hz, 2 H), 7.17 (app. t, *J* = 7.5 Hz, 3H), 5.66 (t, *J* = 6.9 Hz, 1H), 4.69 (t, *J* = 6.8 Hz, 2H), 2.60 (td, *J* = 12.8, 5.2 Hz, 1H), 2.48 (td, *J* = 12.8, 5.1 Hz, 1H), 2.25-2.03 (comp m, 2H), 1.93-1.69 (comp m, 2H), 1.39-1.30 (comp m, 4H), 0.98-0.89 (comp m, 21H), 0.69-0.49 (comp m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 141.6, 141.1, 128.7, 128.6, 126.0, 73.0, 40.1, 32.9, 32.3, 29.6, 22.9, 14.4, 7.9, 7.3, 7.2, 6.8, 5.4, 4.7; IR (film) 2955, 2876, 1415, 1083, 1005 cm^{-1}; LRMS (EI^+) *m/z* calc'd for $(M - SiEt_3)^+$ $[C_{21}H_{35}OSi - SiEt_3]^+$: 331, found 331.

β-Vinylsilane 180: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.16 (comp m, 5H), 5.72 (d, *J* = 8.1 Hz, 1H), 4.54 (td, *J* = 8.0, 4.4 Hz, 2H), 2.81-2.60 (comp m, 2H), 2.12-1.96 (m, 2H), 1.86 (dddd, *J* =

13.3, 10.6, 8.0, 5.2 Hz, 1H), 1.74-1.65 (m, 1H), 1.34-1.18 (comp m, 4H), 0.99-0.88 (comp m, 21H), 0.63-0.56 (comp m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 142.7, 137.3, 128.6, 128.4, 125.8, 68.5, 40.7, 32.8, 32.1, 30.5, 23.5, 14.1, 7.6, 7.1, 5.3, 3.3.

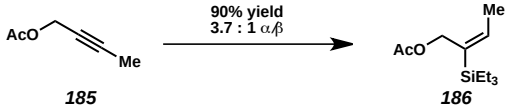


182 *184*

Alkene 184: To a solution of alkyne **182** (71.3 mg, 0.429 mmol) and Et_3SiH (75.2 μl, 0.472 mmol) in CH_2Cl_2 (2.36 mL) at 23 °C under argon was added $PtCl_2$ (5.7 mg, 0.0215 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (20 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (9 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **184** (108 mg, 89% yield, 17.1:1 $\alpha\beta$, R_F = 0.50 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 184: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (q, *J* = 6.8 Hz, 1H), 5.00 (s, 1H), 1.85 (d, *J* = 6.7 Hz, 3H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.64 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 131.6, 66.5, 15.3, 7.5, 3.2; IR (film) 2957, 2879, 1786, 1222, 1168, 1004 cm^{-1}; LRMS (EI^+) *m/z* calc'd for $(M - C_8H_{11}F_2O_2)^+$ $[C_4H_{10}FSi]^+$: 105, found 105.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 6.18 ppm, β: 5.80 ppm (t)). ^{1}H and ^{13}C data for α isomer only.

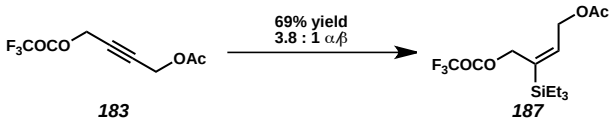


185 *186*

Alkene 186. To a solution of alkyne **185** (54.7 mg, 0.488 mmol) and Et_3SiH (85.5 μl, 0.537 mmol) in CH_2Cl_2 (2.44 mL) at 23 °C under argon was added $PtCl_2$ (6.5 mg, 0.0244 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (20 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (9 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **186** (109 mg, 98% yield, 3.7:1 α/β, R_F = 0.27 in 19:1 hexanes/Et_2O) isolated as an inseparable mixture of α- and β-silyl isomers as a colorless oil.

Vinylsilane 186: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (q, *J* = 6.7 Hz, 1H), 4.72 (s, 2H), 2.05 (s, 3H), 1.78 (d, *J* = 6.7 Hz, 3H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.61 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 140.6, 133.6, 63.0, 21.2, 15.0, 7.5, 3.3; IR (film) 2955, 2877, 1743, 1618, 1228 cm^{-1}; LRMS (EI$^+$) *m/z* calc'd for $(M - C_6H_{11})^+$ $[C_6H_{13}O_2Si]^+$: 145, found 145.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 6.03 ppm, β: 5.77 ppm (t)). ^{1}H and ^{13}C data for α isomer only.



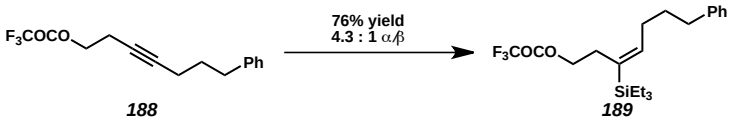
183 *187*

Alkene 187: To a solution of alkyne **183** (29.8 mg, 0.133 mmol) and Et_3SiH (23.3 μl, 0.146 mmol) in CH_2Cl_2 (0.65 mL) at 23 °C under argon was added $PtCl_2$ (1.8 mg, 0.00665 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (24 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (9 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford

vinylsilane **187** (31.1 mg, 69% yield, 3.8:1 $\alpha\beta$, R_F = 0.19 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 187: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (t, *J* = 6.0 Hz, 1H), 4.92 (s, 2H), 4.68 (d, *J* = 6.0 Hz, 2H), 2.01 (s, 3H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.59 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 141.0, 135.2, 66.2, 61.1, 21.0, 7.3, 3.0; IR (film) 2958, 2879, 1787, 1747, 1227, 1153 cm^{-1}; LRMS (EI^+) *m/z* calc'd for $(M - C_{10}H_{13}F_2O_4)^+$ $[C_4H_{10}FSi]^+$: 105, found 105.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 5.99 ppm, β: 5.94 ppm (t)). ^{1}H and ^{13}C data for α isomer only.



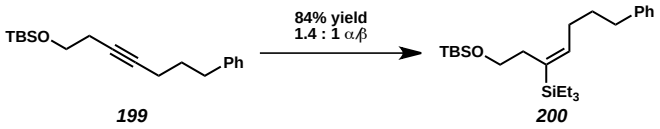
188 ***189***

Vinylsilane 189: To a solution of alkyne **188** (35.7 mg, 0.126 mmol) and Et_3SiH (22.1 μl, 0.138 mmol) in CH_2Cl_2 (0.630 mL) at 23 °C under argon was added $PtCl_2$ (1.7 mg, 0.00660 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (20 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **189** (44.0 mg, 87% yield, 4.3:1 $\alpha\beta$, R_F = 0.50 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 189: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.21-7.17 (comp m, 3H), 5.91 (t, *J* = 7.0 Hz, 1H), 4.19 (app. t, *J* = 8.0 Hz, 2H), 2.64 (app. t, *J* = 7.7 Hz, 2H), 2.52 (t, *J* = 7.9 Hz, 2H), 2.21 (q, *J* = 7.3 Hz, 2H), 1.73 (quint, *J* = 7.6 Hz, 2H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.61 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 142.3, 131.2, 128.54, 128.49,

126.0, 67.1, 35.6, 31.4, 28.6, 28.4, 7.5, 3.1; IR (film) 2955, 2877, 1786, 1607, 1222, 1152 cm^{-1}; HRMS (DART$^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{21}H_{35}F_3NO_2Si]^+$: 418.2389, found 418.2384.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 5.91 ppm, β: 5.61 ppm (t)). ^1H and ^{13}C data for α isomer only.



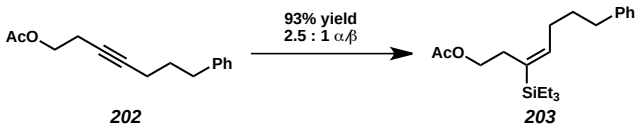
199 ***200***

Alkene 200: To a solution of alkyne **199** (84.6 mg, 0.280 mmol) and Et_3SiH (49.0 μl, 0.308 mmol) in CH_2Cl_2 (1.40 mL) at 23 °C under air was added $PtCl_2$ (3.7 mg, 0.0140 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (12 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes (2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/Et_2O eluent) to afford vinylsilane **200** as an inseparable mixture of α- and β-silyl isomers (98.9 mg, 84% yield, 1.4:1 *αβ*, R_F = 0.74 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 200: ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.7 Hz, 2H), 7.20-7.18 (comp m, 3H), 5.81 (t, *J* = 6.9 Hz, 1H), 3.50-3.46 (m, 2H), 2.66-2.61 (m, 2H), 2.33 (q, *J* = 6.9 Hz, 2H), 2.21 (q, *J* = 7.1 Hz, 2H), 1.72 (quint, *J* = 7.6 Hz, 2H), 0.95-0.90 (comp m, 18H), 0.60 (q, *J* = 7.9 Hz, 6H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 142.6, 139.3, 138.1, 133.4, 128.55, 128.51, 128.44, 128.39, 125.85, 125.79, 63.1, 62.8, 36.6, 35.8, 33.9, 32.4, 32.0, 31.8, 30.1, 28.6, 26.2, 26.1, 18.6, 7.61, 7.59, 3.3, 3.2, -5.0 -5.1; IR (film) 2954, 2875, 1462, 1254, 1094, 1006 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{25}H_{47}OSi_2]^+$: 419.3160, found 419.3148.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic

protons (α: 5.81 ppm, β: 5.73 ppm (t)). ^{1}H data for α isomer only; ^{13}C data for both isomers.

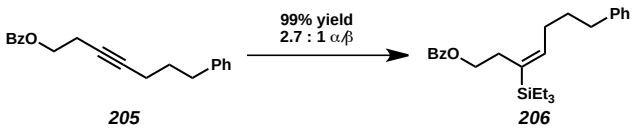


202 *203*

Alkene 203: To a solution of alkyne **202** (59.6 mg, 0.259 mmol) and Et_3SiH (45.3 μl, 0.285 mmol) in CH_2Cl_2 (1.25 mL) at 23 °C under air was added $PtCl_2$ (3.4 mg, 0.0129 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (12 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes (2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/Et_2O eluent) to afford vinylsilane **203** as an inseparable mixture of α- and β-silyl isomers (83.6 mg, 93% yield, 2.5:1 *αβ*, R_F = 0.22 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 203: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.20-7.17 (comp m, 3H), 5.86 (t, *J* = 6.9 Hz, 1H), 3.94 (app. t, *J* = 8.0 Hz, 2H), 2.63 (q, *J* = 7.4 Hz, 2H), 2.43 (t, *J* = 7.3 Hz, 2H), 2.22 (q, *J* = 7.3 Hz, 2H), 2.04 (s, 3H), 1.73 (quint, *J* = 7.6 Hz, 2H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.61 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 144.9, 142.5, 140.9, 136.2, 132.6, 128.52, 128.49, 128.43, 128.40, 125.8, 64.0, 63.8, 36.5, 35.7, 31.9, 31.6, 29.9, 29.1, 28.5, 28.1, 21.1, 7.5, 3.2, 3.1; IR (film) 2953, 1743, 1496, 1240, 1031 cm^{-1}; HRMS (ESI^{+}) *m/z* calc'd for $(M + H)^{+}$ $[C_{21}H_{35}O_2Si]^{+}$: 347.2401, found 347.2408.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 5.86 ppm, β: 5.65 ppm (t)). ^{1}H data for α isomer only; ^{13}C data for both isomers.



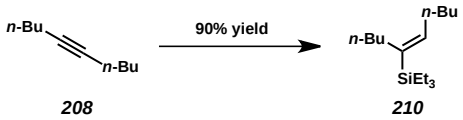
205 *206*

Vinylsilane 206: To a solution of alkyne **205** (60.0 mg, 0.205 mmol) and Et_3SiH (35.9 μl, 0.226 mmol) in CH_2Cl_2 (1.02 mL) at 23 °C under air was added $PtCl_2$ (2.7 mg, 0.0102 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (12 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes (2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/Et_2O eluent) to afford vinylsilane **206** as an inseparable mixture of α- and β-silyl isomers (83.2 mg, 99% yield, 2.7:1 α/β, R_F = 0.29 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 206: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.19-7.17 (comp m, 3H), 5.91 (t, *J* = 6.9 Hz, 1H), 4.21 (app. t, *J* = 8.0 Hz, 2H), 2.67-2.56 (comp m, 4H), 2.29 (q, *J* = 7.3 Hz, 2H), 1.75 (quint, *J* = 7.6 Hz, 2H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 145.1, 142.5, 141.0, 136.4, 132.9, 132.5, 130.6, 129.7, 128.5, 128.4, 125.8, 64.5, 64.1, 36.5, 35.7, 32.0, 31.7, 29.9, 29.3, 28.5, 28.2, 7.6, 3.1; IR (film) 2953, 2874, 1720, 1273, 1110 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{26}H_{37}O_2Si]^+$: 409.2557, found 409.2545.

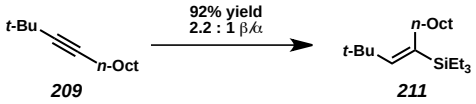
Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinylic protons (α: 5.91 ppm, β: 5.76 ppm (t)). ^{1}H data for α isomer only; ^{13}C data for both isomers.

3.9.8 Evaluation of Sterics



208 *210*

Vinylsilane 210: To a solution of 5-decyne (**208**, 50.0 mg, 0.362 mmol) and Et_3SiH (63.4 μl, 0.398 mmol) in CH_2Cl_2 (1.81 mL) at 23 °C under air was added $PtCl_2$ (4.8 mg, 0.0181 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (3 h), as judged by TLC (100% hexanes eluent), the mixture was diluted with hexanes (3 mL), filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with hexanes (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 → 9:1 hexanes/EtOAc eluent) to afford vinylsilane **210**[82] (82.8 mg, 90% yield, R_F = 0.85 in 100% hexanes eluent) as a colorless oil.



209 *211*

Vinylsilane 211: To a solution of alkyne **209** (75.9 mg, 0.391 mmol) and Et_3SiH (68.5 μl, 0.430 mmol) in CH_2Cl_2 (1.96 mL) at 23 °C under argon was added $PtCl_2$ (5.2 mg, 0.0196 mmol), and the resulting mixture was allowed to stir at 23 °C for 5 days. The mixture was diluted with hexanes (2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with hexanes (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (100% hexanes eluent) to afford vinylsilane **211** (91.2 mg, 92% yield, 1:2.2 α/β, R_F = 0.87 in 100% hexanes) as a colorless oil.

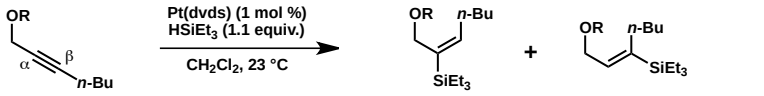
Vinylsilane 211: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57 (s, 1H), 2.18 (t, *J* = 7.5 Hz, 2H), 1.32-1.27 (comp m, 12H), 1.12 (s, 9H), 0.93-0.87 (comp m, 12H), 0.55 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 150.4, 144.9, 144.4, 136.5, 35.1, 32.1, 32.0, 31.7, 31.6, 31.2, 30.75, 30.66, 30.4, 29.7, 29.64, 29.62, 29.52, 29.46, 22.9, 14.3, 7.9, 7.6, 5.8, 3.7; IR (film) 2955, 1464, 1236, 1006, 720 cm^{-1}; LRMS (EI^+) *m/z* calc'd for $(M - C_2H_5)^+$ $[C_{20}H_{42}Si]^+$: 281, found 281.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of allylic protons (α: 2.29 ppm (q), β: 2.18 ppm). ^1H data for β isomer only; ^{13}C data for both isomers.

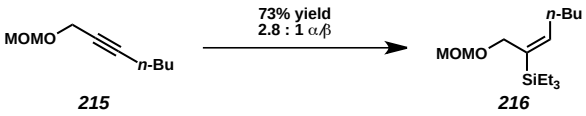
3.9.9 Evaluation of Oxygen Coordination

Table 3.6.1 (*reproduced*)



entry	substrate	major product	time (h)	yield (%)	α : β[a]	Δ(δC$_\beta$−δC$_\alpha$)
1	OMOM, n-Bu (215)	MOMO, n-Bu, SiEt$_3$ (216)	16	73	2.8 : 1	11.7
2	OBn, n-Bu (217)	OBn, n-Bu, SiEt$_3$ (218)	16	96	3.2 : 1	11.5
3	OTBS, n-Bu (219)	OTBS, n-Bu, SiEt$_3$ (220)	16	78	2.7 : 1	8.2

a) Measured by ^1H NMR



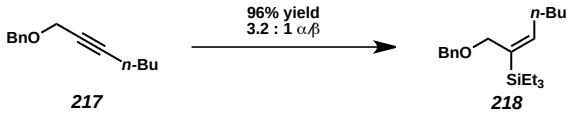
215 216

Table 3.6.1, Entry 1: To a solution of methoxymethyl ether **215** (50.0 mg, 0.320 mmol) and Et_3SiH (56.1 μl, 0.352 mmol) in CH_2Cl_2 (1.60 mL) at 23 °C under air was added Pt(dvds) (20.8 mg, 3.0 wt % Pt, 0.00320 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (16 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes

(2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/Et_2O eluent) to afford vinylsilane **216** (63.3 mg, 73% yield, 2.8:1 $\alpha\beta$, R_F = 0.45 in 1:1 hexanes/CH_2Cl_2) as a colorless oil.

Vinylsilane 216: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (t, *J* = 7.0 Hz, 1H), 4.59 (s, 2H), 4.16 (s, 2H), 3.38 (s, 3H), 2.17 (q, *J* = 7.1 Hz, 2H), 1.40-1.25 (comp m, 4H), 0.91 (app. q, *J* = 7.8 Hz, 12H), 0.61 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 134.2, 95.9, 65.9, 55.4, 31.9, 28.8, 22.5, 14.1, 7.6, 3.4; IR (film) 2956, 2876, 1613, 1460, 1260, 1046 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{33}O_2Si]^+$: 273.2244, found 273.2240.

Note: Isolated as pure α isomer. Isomeric ratio determined by integration of vinyl protons (α: 5.88 ppm, β: 5.81 ppm (t)). ^{1}H and ^{13}C data for α isomer only.



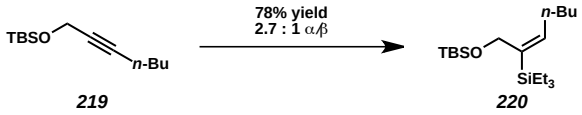
217 *218*

Table 3.6.1, Entry 2: To a solution of benzyl ether **217** (50.0 mg, 0.247 mmol) and Et_3SiH (43.3 μl, 0.263 mmol) in CH_2Cl_2 (1.25 mL) at 23 °C under air was added Pt(dvds) (16.1 mg, 3.0 wt % Pt, 0.00247 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (16 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes (2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/Et_2O eluent) to afford vinylsilane **218** (75.9 mg, 96% yield, 3.2:1 $\alpha\beta$, R_F = 0.48 in 3:1 hexanes/CH_2Cl_2) as a colorless oil.

Vinylsilane 218: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (app. d, *J* = 4.5 Hz, 3H), 7.35-7.27 (m,

2H), 5.89 (t, *J* = 7.0 Hz, 1H), 4.49 (s, 2H), 4.14 (s, 2H), 2.16 (q, *J* = 7.1 Hz, 2H), 1.42-1.28 (comp m, 4H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.91 (t, *J* = 7.1 Hz, 3H), 0.65 (q, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 139.0, 134.9, 128.4, 127.8, 127.5, 72.5, 68.8, 31.9, 28.9, 22.5, 14.1, 7.6, 3.4; IR (film) 2957, 1613, 1455, 1261, 1097 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{20}H_{38}NOSi]^+$: 336.2717, found 336.2724.

Note: Isolated as pure α isomer. Isomeric ratio determined by integration of benzylic protons (α: 4.49 ppm, β: 4.45 ppm (s)). ^{1}H and ^{13}C data for α isomer only.



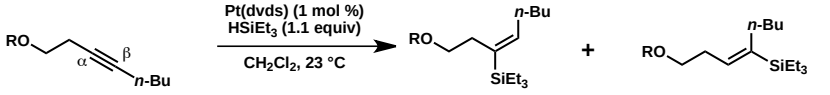
219 *220*

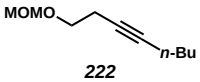
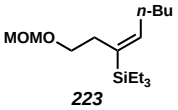
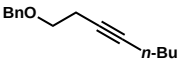
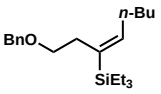
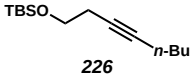
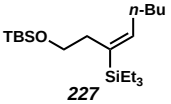
Table 3.6.1, Entry 3: To a solution of silyl ether **219** (54.2 mg, 0.239 mmol) and Et_3SiH (41.9 μl, 0.263 mmol) in CH_2Cl_2 (1.19 mL) at 23 °C under air was added Pt(dvds) (15.5 mg, 3.0 wt % Pt, 0.00239 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (16 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes (2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes eluent) to afford vinylsilane **220** (64.0 mg, 78% yield, 2.7:1 *αβ*, R_F = 0.71 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 220: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 (t, *J* = 7.0 Hz, 1H), 4.28 (s, 2H), 2.11 (q, *J* = 7.0 Hz, 2H), 1.40-1.21 (comp m, 4H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.91 (s, 9H), 0.62 (q, *J* = 7.9 Hz, 6H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 137.9, 62.4, 32.1, 28.8, 26.3, 22.7, 18.7, 14.3, 7.8, 3.8, -5.2; IR (film) 2958, 1613, 1463, 1252, 1085, 1005 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{43}OSi_2]^+$: 343.2852, found 343.2847.

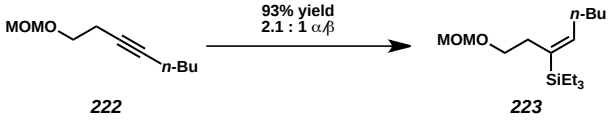
Note: Isolated as pure α isomer. Isomeric ratio determined by integration of vinyl protons (α: 5.69 ppm, β: 5.78 ppm (t)). ^{1}H and ^{13}C data for α isomer only.

Table 3.6.2 (*reproduced*)



entry	substrate	major product	time (h)	yield (%)	α : β[a]	Δ(δC$_\beta$–δC$_\alpha$)
1			16	93	2.1 : 1	4.9
	222	***223***				
2			16	98	2.0 : 1	4.8
	224	***225***				
3			16	95	1.9 : 1	4.6
	226	***227***				

a) Measured by ^{1}H NMR

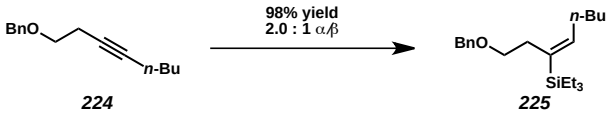


222 ***223***

Table 3.6.2, Entry 1: To a solution of methoxymethyl ether **222** (50.0 mg, 0.294 mmol) and Et_3SiH (51.4 μl, 0.323 mmol) in CH_2Cl_2 (1.47 mL) at 23 °C under air was added Pt(dvds) (19.1 mg, 3.0 wt % Pt, 0.00294 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (16 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes (2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/Et_2O eluent) to afford vinylsilane **223** (78.5 mg, 93% yield, 2.1:1 *αβ*, R_F = 0.36 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 223: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (t, *J* = 6.9 Hz, 1H), 4.61 (s, 2H), 3.42-3.37 (m, 2H), 3.36 (s, 3H), 2.43 (q, *J* = 6.9 Hz, 2H), 2.14 (q, *J* = 7.0 Hz, 2H), 1.40-1.21 (comp m, 4H), 0.90 (app. t, *J* = 7.9 Hz, 12H), 0.58 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 140.4, 136.9, 132.5, 96.4, 67.7, 67.3, 55.2, 32.5, 32.0, 30.4, 30.1, 29.2, 28.5, 23.3, 22.6, 14.7, 7.5, 3.3, 3.2; IR (film) 2957, 1610, 1464, 1267, 1110 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{16}H_{35}O_2Si]^+$: 287.2401, found 287.2396.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinyl protons (α: 5.78 ppm, β: 5.69 ppm (t)). ^{1}H data for α isomer only; ^{13}C data for both isomers.



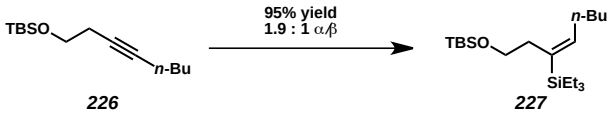
224 *225*

Table 3.6.2, Entry 2: To a solution of benzyl ether **224** (50.0 mg, 0.231 mmol) and Et_3SiH (40.5 μl, 0.254 mmol) in CH_2Cl_2 (1.15 mL) at 23 °C under argon was added Pt(dvds) (15.0 mg, 3.0 wt % Pt, 0.00231 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (16 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes (2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/Et_2O eluent) to afford vinylsilane **225** (75.5 mg, 98% yield, 2.0:1 *αβ*, R_F = 0.47 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 225: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (app. d, *J* = 4.5 Hz, 3H), 7.33-7.27 (m, 2H), 5.76 (t, *J* = 6.9 Hz, 1H), 4.53 (s, 2H), 3.36 (t, *J* = 8.2 Hz, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 2.14 (q, *J* = 7.1 Hz, 2H), 1.37-1.26 (comp m, 4H), 0.95-0.89 (comp m, 12H), 0.57 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 140.2, 138.7, 137.0, 132.6, 128.5, 127.8, 127.6, 73.0, 72.9,

70.3, 69.8, 32.5, 32.0, 30.4, 30.1, 29.3, 28.5, 23.4, 22.6, 14.2, 7.6, 3.3; IR (film) 2957, 1610, 1456, 1261, 1101 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{21}H_{37}OSi]^+$: 333.2608, found 333.2609.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinyl protons (α: 5.76 ppm, β: 5.69 ppm (t)). ^1H data for α isomer only; ^{13}C data for both isomers.



226 *227*

Table 3.6.2, Entry 3: To a solution of silyl ether **226** (50.0 mg, 0.208 mmol) and Et_3SiH (36.4 μl, 0.229 mmol) in CH_2Cl_2 (1.04 mL) at 23 °C under air was added Pt(dvds) (13.5 mg, 3.0 wt % Pt, 0.00208 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (16 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes (2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/Et_2O eluent) to afford vinylsilane **227** (70.8 mg, 95% yield, 1.9:1 *αβ*, R_F = 0.86 in 19:1 hexanes/Et_2O) as a colorless oil.

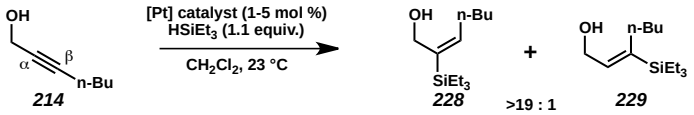
Vinylsilane 226: ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (t, *J* = 6.9 Hz, 1H), 3.46 (app. t, *J* = 8.0 Hz, 2H), 2.35 (dd, *J* = 11.7, 4.5 Hz, 2H), 2.14 (q, *J* = 7.0 Hz, 2H), 1.38-1.22 (comp m, 4H), 0.90 (app. t, *J* = 7.8 Hz, 21H), 0.57 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 139.8, 137.5, 132.5, 63.2, 62.9, 33.9, 32.6, 32.4, 32.1, 30.1, 28.7, 26.2, 26.1, 23.4, 22.6, 18.6, 18.5, 14.22, 14.19, 7.6, 3.3, 3.2, -5.0, -5.1; IR (film) 2958, 1610, 1463, 1256, 1098, 1007 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{48}NOSi_2]^+$: 372.3274, found 372.3271.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinyl

protons (α: 5.76 ppm, β: 5.68 ppm (t)). ^{1}H data for α isomer only; ^{13}C data for both isomers.

3.9.10 Hydrosilylations of Propargyl Alcohols

Catalyst evaluation for the hydrosilylation of propargyl alcohol 214:



entry	catalyst	time (h)	yield (%)	α:β
1	$PtCl_2$ (5 mol %)	6	45	>19 : 1
2	$[\{(C_2H_4)PtCl_2\}_2]$ (2.5 mol %)	4	47	>19 : 1
3	Pt(dvds)[a]	5	92	>19 : 1

a) dvds = divinyltetramethyldisiloxane

To a solution of hept-2-yn-1-ol (**214**, 29.1 mg, 0.259 mmol) and Et_3SiH (45.4 μl, 0.285 mmol) in CH_2Cl_2 (1.29 mL) at 23 °C under argon was added $PtCl_2$ (3.4 mg, 0.0129 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (6 h), as judged by TLC (9:1 hexanes/EtOAc), the mixture was filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (8 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford vinylsilane **228** (28.4 mg, 48% yield, >19.0:1 *α*/*β*, R_F = 0.39 in 4:1 hexanes/Et_2O) as a colorless oil.

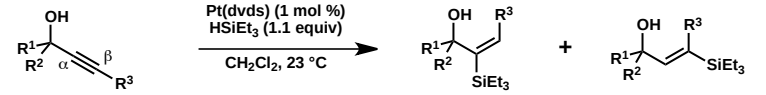
Vinylsilane 228: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (t, *J* = 7.1Hz, 2H), 4.23 (s, 2H), 2.19 (q, *J* = 7.1 Hz, 2H), 1.41-1.26 (comp m, 4H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.62 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 137.2, 60.8, 32.0, 28.6, 22.5, 14.1, 7.6, 3.4; IR (film) 3357, 2955, 1611, 1460, 1005 cm^{-1}; HRMS ($DART^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{13}H_{32}NOSi]^+$: 246.2248, found 246.2247.

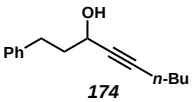
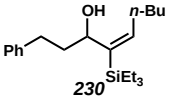
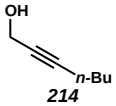
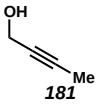
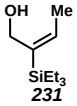
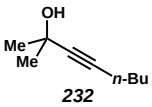
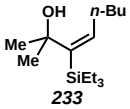
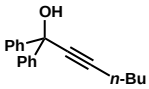
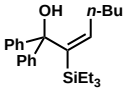
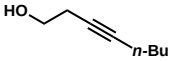
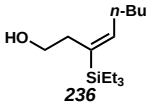
To a solution of hept-2-yn-1-ol (**214**, 45.7 mg, 0.407 mmol) and Et_3SiH (92.0 μl, 0.578 mmol) in

CH_2Cl_2 (2.62 mL) was added $[(C_2H_4)PtCl_2]_2$ (11.9 mg, 0.0203 mmol) at 23 °C under air. The resulting mixture was allowed to stir at 23 °C. Upon completion (4 h), as judged by TLC (4:1 hexanes/Et_2O), the mixture was diluted with hexanes (5 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (10 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (9:1 → 4:1 hexanes/Et_2O eluent) to afford vinylsilane **228** (43.3 mg, 47% yield, >19:1 α/β, R_F = 0.39 in 4:1 hexanes/Et_2O eluent).

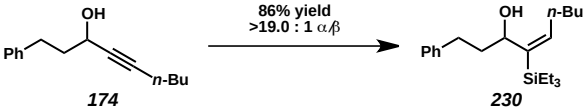
To a solution of hept-2-yn-1-ol (**214**, 58.9 mg, 0.525 mmol) and Pt(dvds) (34.1 mg, 3 wt% Pt in PDMS, 0.00525 mmol) in CH_2Cl_2 (2.62 mL) at 23 °C under air was added Et_3SiH (92.0 μl, 0.578 mmol). The resulting mixture was allowed to stir at 23 °C. Upon completion (5 h), as judged by TLC (4:1 hexanes/Et_2O), the mixture was diluted with hexanes (5 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (10 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (9:1 → 4:1 hexanes/Et_2O eluent) to afford vinylsilane **228** (111 mg, 92% yield, >19.0:1 α/β, R_F = 0.39 in 4:1 hexanes/Et_2O eluent).

Table 3.7.2 (*reproduced*)



entry	substrate	major product	time (h)	yield (%)	α : β[a]
1	 ***174***	 ***230***	3	86	>19 : 1
2	 ***214***	 ***228***	5	92	>19 : 1
3	 ***181***	 ***231***	24	97	3.3 : 1
4	 ***232***	 ***233***	24	88	3.2 : 1
5	 ***234***	 ***235***	24	81	9.2 : 1
6	 ***221***	 ***236***	6	97	3.0 : 1

a) determined by ^{1}H NMR spectoscopy

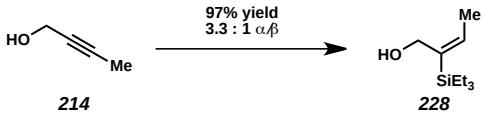


174 ***230***

Table 3.7.2, Entry 1: To a solution of propargylic alcohol **174** (75.0 mg, 0.430 mmol) and Et_3SiH (75.4 μl, 0.473 mmol) in CH_2Cl_2 (2.15 mL) at 23 °C under argon was added Pt(dvds) (27.9 mg, 3 wt% Pt in PDMS, 0.00430 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (3 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes (2 mL), filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (8 mL). The filtrate was concentrated in vacuo, and the residue was purified

by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **230** (107 mg, 86% yield, >19.0:1 $\alpha\beta$, R_F = 0.55 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 230: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (app. t, *J* = 7.3 Hz, 2H), 7.22-7.17 (comp m, 3H), 5.67 (t, *J* = 7.0 Hz, 1H), 4.62 (app. d, *J* = 9.2 Hz, 1H), 2.81 (ddd, *J* = 13.9, 9.5, 4.8 Hz, 1H), 2.64 (ddd, *J* = 13.7, 9.3, 7.3 Hz, 1H), 2.09-1.91 (comp m, 3H), 1.69 (dddd, *J* = 13.8, 9.8, 7.3, 4.1 Hz, 1H), 1.41-1.22 (comp m, 4H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.65 (app. q, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 142.4, 141.5, 128.8, 128.7, 126.1, 74.5, 39.4, 33.0, 32.2, 29.3, 22.8, 14.3, 7.9, 4.5; IR (film) 3488, 2955, 2874, 1603, 1456, 1006 cm^{-1}; HRMS (DART$^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{21}H_{40}NOSi]^+$: 350.2874, found 350.2875.



214 *228*

Table 3.7.2, Entry 3: To a solution of alcohol **214** (50.0 mg, 0.670 mmol) and Et_3SiH (117 μl, 0.737 mmol) in CH_2Cl_2 (3.35 mL) at 23 °C under argon was added Pt(dvds) (43.5 mg, 3.0 wt % Pt, 0.00670 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (24 h), as judged by TLC (4:1 hexanes/Et_2O), the mixture was diluted with hexanes (2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (9:1 → 2:1 hexanes/CH_2Cl_2 eluent) to afford vinylsilane **228** (121 mg, 97 % yield, 3.3:1 $\alpha\beta$, R_F = 0.78 in 1:1 hexanes/CH_2Cl_2) as a colorless oil.

Vinylsilane 228: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (t, *J* = 6.7 Hz, 1H), 4.25 (s, 2H), 1.78 (d, *J* = 6.7 Hz, 3H), 0.92 (t, *J* = 7.7 Hz, 9H), 0.62 (q, *J* = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

139.3, 138.6, 60.5, 14.7, 7.6, 3.4; IR (film) 3346, 2955, 1615, 1237, 1018 cm^{-1}; HRMS ($DART^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{10}H_{26}NOSi]^+$: 204.1778, found 204.1780.

Note: Isolated as pure α isomer. Isomeric ratio determined by integration of vinyl protons (α: 5.97 ppm, β: 5.86 ppm (t)). ^1H and ^{13}C data for α isomer only.

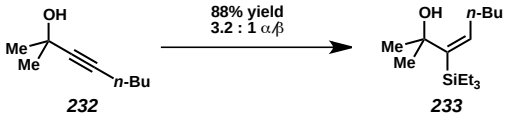
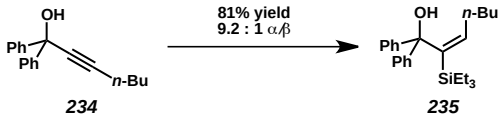


Table 3.7.2, Entry 4: To a solution of alcohol **232** (50.0 mg, 0.509 mmol) and Et_3SiH (89.3 μl, 0.560 mmol) in CH_2Cl_2 (2.54 mL) at 23 °C under argon was added Pt(dvds) (33.0 mg, 3.0 wt % Pt, 0.00509 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (24 h), as judged by TLC (1:1 hexanes/CH_2Cl_2), the mixture was diluted with hexanes (2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (5:1 → 1:1 hexanes/CH_2Cl_2 eluent) to afford vinylsilane **233** (95.7 mg, 88% yield, 3.2:1 *αβ*, R_F = 0.28 in 1:1 hexanes/CH_2Cl_2) as a colorless oil.

Vinylsilane 233: ^1H NMR (400 MHz, $CDCl_3$) δ 5.52 (t, *J* = 7.3 Hz, 1H), 2.17 (q, *J* = 7.2 Hz, 2H), 1.42 (s, 9H), 1.38-1.32 (comp m, 4H), 0.93 (app. t, *J* = 7.9 Hz, 12H), 0.64 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 141.1, 75.7, 32.5, 31.2, 30.7, 22.7, 14.2, 7.9, 5.0; IR (film) 3621, 3491, 2958, 1603, 1461, 1005 cm^{-1}; HRMS ($DART^+$) *m/z* calc'd for $(M - OH)^+$ $[C_{15}H_{31}Si]^+$: 239.2190, found 239.2199.

Note: Isolated as pure α isomer. Isomeric ratio determined by integration of vinyl protons (α: 5.952 ppm, β: 5.72 ppm (s)). ^1H and ^{13}C data for α isomer only.

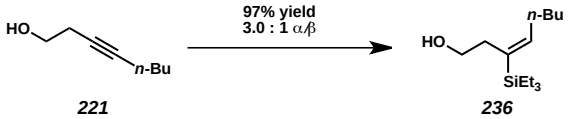


234 *235*

Table 3.7.2, Entry 5: To a solution of alcohol **234** (75.0 mg, 0.337 mmol) and Et_3SiH (59.1 μl, 0.371 mmol) in CH_2Cl_2 (1.68 mL) at 23 °C under argon was added Pt(dvds) (21.9 mg, 3.0 wt % Pt, 0.00337 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (24 h), as judged by TLC (1:1 hexanes/CH_2Cl_2), the mixture was diluted with hexanes (2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (pH 7 buffered silica gel, 9:1 hexanes/CH_2Cl_2 eluent) to afford vinylsilane **235** (92.1 mg, 81% yield, 9.2:1 $\alpha\beta$, R_F = 0.78 in 1:1 hexanes/CH_2Cl_2) as a colorless oil.

Vinylsilane 235: ^{1}H NMR (400 MHz, C_6D_6) δ 7.38 (d, *J* = 7.03 Hz, 2H), 7.19-7.08 (comp m, 3H), 6.04 (t, *J* = 7.2 Hz, 1H), 2.15 (s, 1H), 1.56 (q, *J* = 7.4 Hz, 2H), 1.10-1.02 (comp m, 4H), 1.08 (t, *J* = 7.8 Hz, 9H), 0.85 (q, *J* = 7.8 Hz, 6H), 0.71 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 146.2, 143.4, 128.3, 128.2, 127.4, 84.0, 31.8, 22.8, 14.1, 8.0, 5.4; IR (film) 3062, 2955, 1488, 1237, 1005 cm^{-1}; HRMS (DART$^+$) *m/z* calc'd for $(M - OH)^+$ $[C_{25}H_{35}Si]^+$: 363.2503, found 363.2511.

Note: Isolated as pure α isomer. Isomeric ratio determined by integration of vinyl protons (α: 6.04 ppm, β: 6.56 ppm (s)). ^{1}H and ^{13}C data for α isomer only.



221 *236*

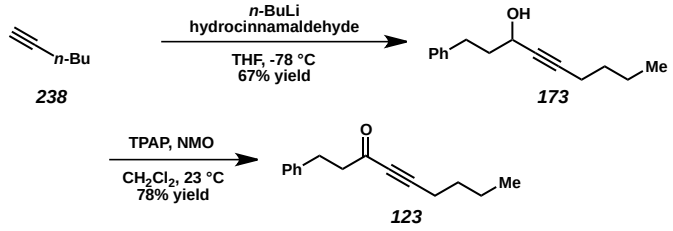
Table 3.7.2, Entry 6: To a solution of alcohol **221** (50.0 mg, 0.396 mmol) and Et_3SiH (69.4 μl, 0.436 mmol) in CH_2Cl_2 (1.98 mL) at 23 °C under argon was added Pt(dvds) (25.7 mg, 3.0 wt %

Pt, 0.00396 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (16 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes (2 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (5 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/Et_2O eluent) to afford vinylsilane **236** (93.5 mg, 97% yield, 3.0:1 α/β, R_F = 0.26 in 9:1 hexanes/EtOAc) as a colorless oil.

Vinylsilane 236: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (t, *J* = 7.0 Hz, 1H), 3.54 (t, *J* = 7.4 Hz, 2H), 2.42 (app. t, *J* = 7.4 Hz, 2H), 2.16 (q, *J* = 7.0 Hz, 2H), 1.38-1.25 (comp m, 4H), 0.91 (app. t, *J* = 7.9 Hz, 12H), 0.59 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 132.5, 62.2, 33.4, 32.1, 28.7, 22.6, 14.2, 7.5, 3.3; IR (film) 3315, 2966, 1610, 1460, 1017 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{14}H_{31}OSi]^+$: 243.2139, found 243.2139.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinyl protons (α: 5.85 ppm, β: 5.66 ppm (t)). ^{1}H and ^{13}C data for α isomer only.

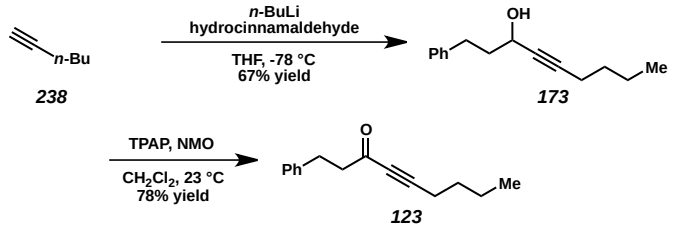
3.9.11 Substrate Syntheses



Propargyl alcohol 173: To a solution of 1-hexyne (**238**, 2.11 mL, 18.8 mmol) in THF (40.0 mL) under an argon atmosphere at -78 °C was added *n*-BuLi (8.15 mL, 2.3 M in hexanes, 18.8 mmol). The solution was allowed to stir for 30 min, then hydrocinnamaldehyde (1.98 mL, 15.0 mmol) was added dropwise. After 1 h at –78 °C, the reaction was quenched with sat. aq. NH_4Cl

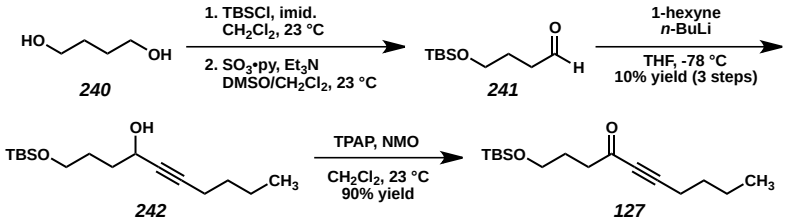
(10 mL) and the product was extracted with Et_2O (2 x 60 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography (19:1 → 9:1 hexanes/EtOAc eluent) to afford **173** (2.17 g, 67% yield, R_F = 0.28 in 9:1 hexanes/EtOAc) as a colorless oil.

Ynone 123: To a solution of **173** (853 mg, 3.94 mmol) in CH_2Cl_2 (17.0 mL) was added NMO (554 mg, 4.73 mmol) and then TPAP (68.5 mg, 0.195 mmol) under an argon atmosphere at 23 °C. The reaction was allowed to stir for 1.5 h, and then the mixture was filtered through a small plug of silica gel (3 x 3.5 cm) washing with Et_2O (30 mL). The solvent was removed in vacuo, and the resulting residue was purified using silica gel flash chromatography (19:1 hexanes/EtOAc eluent) to afford **123** (0.650 g, 78% yield, R_F = 0.47 in 9:1 hexanes/EtOAc) as a colorless oil. Spectroscopic data for **123** matched those reported in the literature.[83]



Propargyl alcohol 239: To a solution of 1-hexyne (**238**, 0.675 mL, 6.00 mmol) in THF (40.0 mL) under an argon atmosphere at -78 °C was added *n*-BuLi (2.60 mL, 2.3 M in hexanes, 6.00 mmol). The solution was allowed to stir for 30 min, and then trimethylacetaldehyde (0.563 mL, 5.00 mmol) was added dropwise. After 1 h at –78 °C, the reaction was quenched with sat. aq. NH_4Cl (5 mL), and the mixture was extracted with Et_2O (2 x 30 mL). The combined organic layers were washed with brine (40 mL), dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography (19:1 hexanes/EtOAc eluent) to afford **239** (702 mg, 83% yield, R_F = 0.34 in 9:1 hexanes/EtOAc) as a colorless oil.

Ynone 120: To a solution of **239** (702 mg, 4.17 mmol) in CH_2Cl_2 (10.0 mL) was added NMO (586 mg, 5.00 mmol) and then TPAP (73.2 mg, 0.209 mmol) under an argon atmosphere at 23 °C. The reaction was allowed to stir for 1.5 h and then the mixture was filtered through a small plug of silica gel (3 x 3.5 cm) washing with Et_2O (30 mL). The solvent was removed in vacuo, and the resulting residue was purified using silica gel flash chromatography (19:1 hexanes/EtOAc eluent) to afford **120** (589 mg, 85% yield, R_F = 0.49 in 9:1 hexanes/EtOAc) as a colorless oil. Spectroscopic data for **120** matched those reported in the literature.[84]



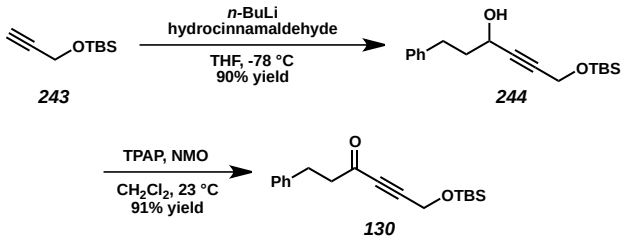
Aldehyde 241: To a solution of **240** (3.35 mL, 25.0 mmol) in CH_2Cl_2 (100 mL) at 23 °C under argon was added TBSCl (754 mg, 5.00 mmol) and imidazole (374 mg, 6.50 mmol), and the resulting mixture was allowed to stir overnight. The reaction was quenched with sat. aq. $NaHCO_3$ (10 mL), the phases were separated, and the aqueous layer was extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude residue was purified using silica gel flash chromatography (4:1 hexanes/EtOAc eluent) to afford the mono-TBS protected butanediol (590 mg, 2.89 mmol), which was then dissolved in DCM (10.0 mL), DMSO (5.0 mL), placed under argon and cooled to 0 °C. In a separate flame-dried flask under argon was added SO_3•pyridine (689 mg, 4.33 mmol) and DMSO (5.0 mL). To the alcohol solution was added Et_3N (1.22 mL, 8.66 mmol) and subsequently, the SO_3•pyridine solution. The reaction mixture was allowed to warm to 23 °C and stirred for 1 h before it was quenched with H_2O (30 mL). The product was extracted with

Et_2O (2 x 30 mL), and the combined organic layers were washed with brine (40 mL), dried over $MgSO_4$, and concentrated in vacuo to afford crude **241**, which was immediately subjected to the next step.

Propargyl alcohol 242: To a solution of 1-hexyne (0.489 mL, 4.35 mmol) in THF (6.0 mL) under an argon atmosphere at -78 °C was added *n*-BuLi (1.89 mL, 2.3 M in hexanes, 4.35 mmol). The solution was allowed to stir for 30 min, then crude **241** (~586 mg, ~2.90 mmol) in THF (2 mL) was added dropwise. After 1 h at –78 °C, the reaction was quenched with sat. aq. NH_4Cl (5 mL), and the mixture was extracted with Et_2O (2 x 20 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography (19:1 hexanes/EtOAc eluent) to afford **242** (141 mg, 10% yield over three steps from **240,** R_F = 0.19 in 9:1 hexanes/EtOAc) as a colorless oil.

Ynone 127: To a solution of **242** (141 mg, 0.495 mmol) in dichloromethane (10.0 mL) at 23 °C was added TPAP (8.6 mg, 0.0247 mmol) and NMO (69.6 mg, 0.594 mmol). The dark green solution was allowed to stir for 1 h, and then filtered through a plug of silica gel (1 x 2 cm) and washed with Et_2O (30 mL). The filtrate was concentrated in vacuo, and the crude material was purified using flash chromatography (39:1 → 19:1 hexanes/EtOAc eluent) to afford **127** (126 mg, 90% yield, R_F = 0.28 in 9:1 hexanes/EtOAc) as a colorless oil.

Ynone 127: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (t, *J* = 6.1 Hz, 2H), 2.61 (t, *J* = 7.3 Hz, 2H), 2.36 (t, *J* = 7.0 Hz, 2H) 1.90-1.83 (m, 2H), 1.60-1.53 (m, 2H), 1.43 (app. dq, *J* = 14.8, 7.3 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 94.6, 81.3, 62.3, 42.4, 30.1, 27.6, 26.3, 22.3, 19.0, 13.9, -5.0; IR (film) 2958, 2859, 1677, 1255, 837 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{16}H_{31}O_2Si]^+$: 283.2088, found 283.2084.



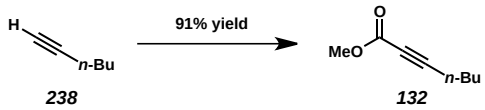
Propargyl alcohol 244: To a solution of **243** (1.02 mL, 5.99 mmol) in THF (15.0 mL) under an argon atmosphere at -78 °C was added *n*-BuLi (2.60 mL, 2.3 M in hexanes, 5.99 mmol). The solution was allowed to stir for 30 min, then hydrocinnamaldehyde (0.661 mL, 5.05 mmol) was added dropwise. After 1 h at –78 °C, the reaction was quenched with sat. aq. NH_4Cl (6 mL), and the mixture was extracted with Et_2O (2 x 30 mL). The combined organic layers were washed with brine (40 mL), dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography (19:1 hexanes/EtOAc eluent) to afford **244** (1.38 g, 90% yield, R_F = 0.08 in 9:1 hexanes/EtOAc) as a colorless oil.

Ynone 130: To a solution of **244** (1.38 g, 4.53 mmol) in dichloromethane (10.0 mL) at 23 °C was added NMO (527 mg, 4.50 mmol) then TPAP (69.9 mg, 0.199 mmol). The dark green solution was allowed to stir for 2 h, and then filtered through a plug of silica gel (3 x 3.5 cm) washing with Et_2O (70 mL). The filtrate was concentrated in vacuo, and the crude residue was purified using silica gel flash chromatography (19:1 hexanes/EtOAc eluent) to afford **130** (1.26 g, 91% yield, R_F = 0.14 in 9:1 hexanes/EtOAc) as a colorless oil.

Ynone 130: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (t, *J* = 6.9 Hz, 2H), 7.22 (app. t, *J* = 6.9 Hz, 3H), 4.48 (s, 2H), 3.01 (t, *J* = 6.8 Hz, 2H), 2.91 (t, *J* = 6.8 Hz, 2H), 0.95 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.3, 140.2, 128.6, 128.4, 126.4, 90.9, 83.8, 51.6, 46.8, 29.8, 25.8, 18.3, -5.1; IR (film) 2931, 2858, 2216, 1681, 1100, 699 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{18}H_{27}O_2Si]^+$: 303.1775, found 303.1772.

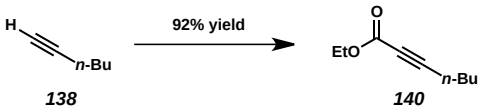
General procedure for the addition of an alkyne nucleophile into an electrophile.

To a solution of alkyne in THF (0.2 M) at -78 ˚C under argon was added *n*-BuLi (1.1 equiv) dropwise. The solution was allowed to stir for 45 min at -78 ˚C. The alkylchloroformate (1.1 equiv) was then added dropwise, and the reaction mixture was allowed to stir for 2 h at -78 ˚C. The reaction was quenched with sat. aq. NH_4Cl and allowed to warm to room temperature. The mixture was extracted with Et_2O two times. The organic layers were then combined and washed with water, then brine, and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography to afford the resulting internal alkyne.



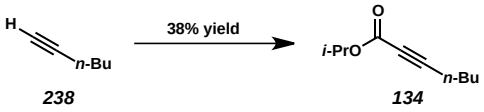
238 *132*

Ester 132: According to the general procedure, to a solution of 1-hexyne (5.63 mL, 50.0 mmol) in THF (100 mL) at -78 ˚C was added *n*-BuLi (20.0 mL, 2.5 M in hexanes, 50.0 mmol). The solution was allowed to stir for 45 min at -78 ˚C. Methylchloroformate (3.85 mL, 50.0 mmol) was then added, and the reaction mixture was allowed to stir for 2 h at -78 ˚C. The reaction was quenched with sat. aq. NH_4Cl (25 mL) and allowed to warm to room temperature. The mixture was extracted with Et_2O (2 x 100 mL). The organic layers were then combined and washed with water (100 mL), then brine (100 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by vacuum distillation (62 °C at 2 mm Hg) to afford ester **132**[85] (6.37 g, 91% yield, R_F = 0.38 in 19:1 hexanes/Et_2O eluent) as a colorless oil.



138 *140*

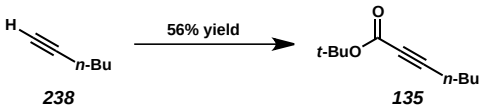
Ester 140: According to the general procedure, to a solution of 1-hexyne (0.563 mL, 5.00 mmol) in THF (20 mL) at -78 ˚C was added *n*-BuLi (2.00 mL, 2.5 M in hexanes, 5.00 mmol). The solution was stirred for 45 min at -78 ˚C. Ethyl chloroformate (0.478 mL, 5.00 mmol) was then added, and the reaction mixture was stirred for 2 h at -78 ˚C. The reaction was quenched with H_2O (20 mL) and allowed to warm to room temperature. The mixture was extracted with Et_2O (2 x 50 mL). The organic layers were then combined and washed with brine (75 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography (hexanes → 19:1 hexanes/Et_2O eluent) to afford ester **140**[86] (0.706 g, 92% yield, R_F = 0.29 in 19:1 hexanes/Et_2O eluent) as a colorless oil.



238 *134*

Ester 134: According to the general procedure, to a solution of 1-hexyne (0.563 mL, 5.00 mmol) in THF (20 mL) at -78 ˚C was added *n*-BuLi (2.00 mL, 2.5 M in hexanes, 5.00 mmol). The solution was stirred for 45 min at -78 ˚C. Isopropyl chloroformate (5.00 mL, 1.0 M in THF, 5.00 mmol) was then added, and the reaction mixture was allowed to stir for 4 h at -78 ˚C. The reaction was quenched with H_2O (20 mL) and allowed to warm to room temperature. The mixture was extracted with Et_2O (2 x 50 mL). The organic layers were then combined and washed with brine (75 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography (hexanes → 19:1

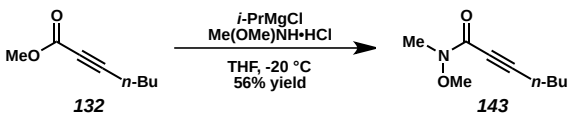
hexanes/Et_2O eluent) to afford ester **134**[87] (0.322 g, 38% yield, R_F = 0.48 in 19:1 hexanes/Et_2O eluent) as a colorless oil.



238 *135*

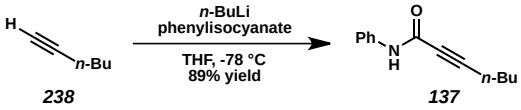
Ester 135: According to the general procedure, to a solution of 1-hexyne (1.12 mL, 10.0 mmol) in THF (33.0 mL) at -78 ˚C was added *n*-BuLi (4.00 mL, 2.5 M in hexanes, 10.0 mmol). The solution was allowed to stir for 45 min at -78 ˚C. Boc_2O (2.18 g, 10.0 mmol in 5.00 mL THF) was then added, and the reaction mixture was allowed to stir for 2 h at -78 ˚C and then allowed to warm to room temperature overnight. The reaction was quenched with saturated aq. NH_4Cl (10 mL), and the mixture was extracted with Et_2O (2 x 100 mL). The organic layers were then combined and washed with water (100 mL), then brine (100 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography (19:1 hexanes/Et_2O) to afford ester **135** (1.02 g, 56% yield, R_F = 0.41 in 19:1 hexanes/Et_2O eluent) as a colorless oil.

Ester 135: ^1H NMR (400 MHz, $CDCl_3$) δ 2.31 (t, *J* = 7.1 Hz, 2H), 1.61-1.39 (comp m, 4H), 1.50 (s, 9H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 87.3, 83.1, 74.7, 29.9, 28.3, 22.2, 18.6, 13.7; IR (film) 2963, 2874, 2235, 1707, 1277 1163 cm^{-1}; HRMS ($APCI^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{11}H_{22}NO_2]^+$: 200.1645, found 200.1642.



132 *143*

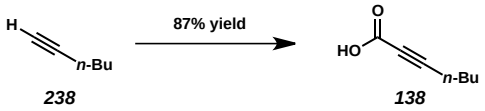
Amide 143: To a flame dried flask containing ester **132** (2.25 mL, 20.0 mmol), Me(OMe)NH•HCl (0.641 g, 6.57 mmol) in THF (8.76 mL) at -20 °C was added *i*-PrMgCl (6.55 mL, 13.1 mmol) dropwise. The solution was allowed to stir for 30 min at -10 °C. The reaction was quenched with sat. aq. NH_4Cl (5 mL) and the mixture was partitioned between Et_2O (50 mL) and H_2O (25 mL). The aqueous layer was extracted with Et_2O (50 mL). The combined organic layers were washed with brine (75 mL) and dried over $MgSO_4$. The filtered solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography (7:3 hexanes/EtOAc eluent) to afford amide **143**[88] (0.414 g, 56% yield, R_F = 0.47 in 2:1 hexanes/EtOAc) as a white solid.



***N*-Phenylamide 137:** To a solution of 1-hexyne (2.25 mL, 20.0 mmol) in THF (40.0 mL) at -78 °C was added *n*-BuLi (8.40 mL, 2.5 M in hexanes, 21.0 mmol) dropwise. The solution was allowed to stir for 45 min at -78 °C. Phenylisocyanate (2.29 mL, 21.0 mmol) was added dropwise, and the solution was allowed to warm to room temperature slowly overnight. The reaction was quenched with methanol (2 mL), and the mixture was partitioned between Et_2O (50 mL) and H_2O (50 mL). The aqueous layer was extracted with Et_2O (50 mL). The combined organic layers were washed with brine (75 mL) and dried over $MgSO_4$. The filtered solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography (9:1 → 7:3 hexanes/EtOAc eluent) to afford amide **137** (3.59 g, 89% yield, R_F = 0.59 in 2:1 hexanes/EtOAc) as a pale yellow oil.

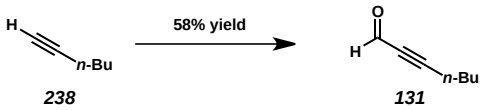
***N*-Phenylamide 137**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.42 (br s, 1H),

7.34 (t, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 2.36 (t, *J* = 7.0 Hz, 2H), 1.60 (quint, *J* = 7.2 Hz, 2H), 1.47 (app. sextet, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 0.95, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 129.5, 125.1, 120.2, 89.0, 76.5, 30.2, 22.4, 18.8, 13.9; IR (film) 3270, 2960, 2934, 2231, 1641, 1598, 1261 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M+H)^+$ $[C_{13}H_{15}NO]^+$: 202.1226, found 202.1232.



238 *138*

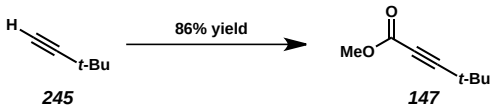
Acid 138: According to the general procedure, to a solution of 1-hexyne (1.68 mL, 15.0 mmol) in THF (15 mL) at -78 ˚C was added *n*-BuLi (6.30 mL, 2.5 M in hexanes, 5.00 mmol). The solution was stirred for 45 min at -78 ˚C. then placed in a 0 °C bath. Carbon dioxide gas (from dry ice, passed through anhydrous $CaSO_4$) was bubbled through the reaction mixture for 30 minutes at 0 °C. The reaction was quenched with sat. aq. NH_4Cl (20 mL) and allowed to warm to room temperature. The mixture was extracted with EtOAc (2 x 75 mL). The organic layers were then combined and washed with brine (100 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo to afford alkynoic acid **138**[89] (1.65 g, 87% yield, R_F = 0.10 in 4:1 hexanes/Et_2O eluent) as a colorless oil that was used without further purification.



238 *131*

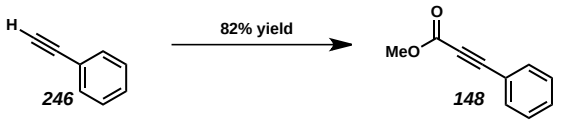
Aldehyde 131: To a solution of 1-hexyne (2.81 mL, 25.0 mmol) in Et_2O (75.0 mL) at -78 °C was added *n*-BuLi (10.0 mL, 2.5 M in hexanes, 25.0 mmol) dropwise. The solution was stirred for 1 h at -78 °C. DMF (2.90 mL, 37.5 mmol) was added dropwise, and the solution was stirred

at -78 °C for 30 min, at which point the bath was removed and allowed to stir for another 30 min at 23 °C. The reaction was quenched with H_2O (40 mL), and the mixture was extracted with Et_2O (2 x 75 mL). The combined organic layers were washed with 10 % aq. $KHSO_4$ (50 mL) then brine (75 mL) and dried over K_2CO_3. The filtered solution was concentrated in vacuo. (CAREFUL! Product volatile.) The resulting oil was purified by flash chromatography (9:1 pentane/Et_2O eluent) to afford aldehyde **131**[90] (1.59 g, 58% yield, R_F = 0.12 in 19:1 hexanes/Et_2O) as a pale yellow oil.

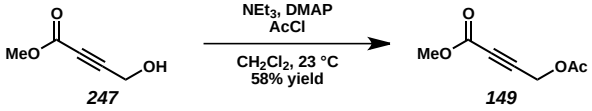


245 *147*

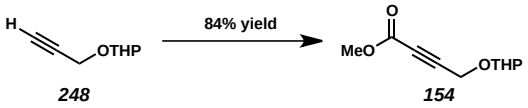
Alkyne 147: According to the general procedure, to a solution of *t*-butylacetylene (0.200 mL, 1.63 mmol) in THF (3.26 mL) at -78 ˚C was added *n*-BuLi (0.684 mL, 2.5 M in hexanes, 1.71 mmol). The solution was stirred for 45 min at -78 ˚C. Methyl chloroformate (0.132 mL, 1.71 mmol) was then added, and the reaction mixture was allowed to warm slowly to 23 °C overnight. The reaction was quenched with H_2O (10 mL), and the mixture was extracted with Et_2O (2 x 30 mL). The organic layers were then combined and washed with brine (40 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford alkyne **147**[91] (196 mg, 86% yield, R_F = 0.38 in 19:1 hexanes/Et_2O eluent) as a pale yellow oil.



Methyl 3-phenylpropiolate 148: According to the general procedure, to a solution of phenylacetylene (0.549 mL, 5.00 mmol) in THF (25.0 mL) at -78 ˚C was added *n*-BuLi (2.20 mL, 2.5 M in hexanes, 5.50 mmol). The solution was allowed to stir for 45 min at -78 ˚C. Methylchloroformate (0.423 mL, 5.50 mmol) was then added, and the reaction mixture was allowed to stir for 2 h at -78 ˚C. The reaction was quenched with sat. aq. NH_4Cl (5 mL) and allowed to warm to room temperature. The mixture was extracted with Et_2O (2 x 50 mL). The organic layers were then combined and washed with water (50 mL), then brine (50 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford methyl 3-phenylpropiolate **148**[92] (0.722 g, 82% yield, R_F = 0.29 in 19:1 hexanes/Et_2O eluent) as a pale yellow oil.

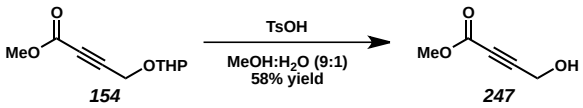


Alkyne 149: To a solution of propargyl alcohol **247** (170 mg, 1.49 mmol) in CH_2Cl_2 (7.44 mL) was added acetyl chloride (175 µl, 2.23 mmol), NEt_3 (0.627 mL, 4.46 mmol), and DMAP (18.3 mg, 0.149 mmol) sequentially at 23 °C under argon. The mixture was stirred for 1.5 h, at which point the reaction was quenched with sat. aq. $NaHCO_3$ (10 mL) and H_2O (10 mL) and extracted with Et_2O (2 x 25 mL). The combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. The solvent was removed in vacuo and the resulting residue was purified by flash chromatography (2:1 hexanes/EtOAc eluent) to afford alkyne **149**[93] (186 mg, 80% yield, R_F = 0.54 in 2:1 hexanes/EtOAc eluent) as a colorless oil.



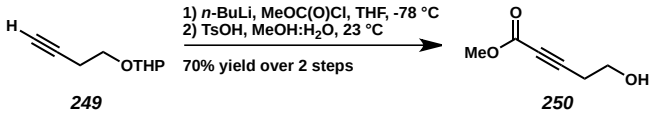
248 *154*

Ester 154: According to the general procedure, to a solution of alkyne **248** (2.64 mL, 18.8 mmol) in THF (60.0 mL) at -78 ˚C was added *n*-BuLi (9.02 mL, 2.5 M in hexanes, 22.6 mmol). The solution was allowed to stir for 45 min at -78 ˚C. Methylchloroformate (1.74 mL, 22.6 mmol) was then added, and the reaction mixture was allowed to stir for 2 h at -78 ˚C. The reaction was quenched with sat. aq. NH_4Cl (5 mL) and allowed to warm to room temperature. The mixture was extracted with Et_2O (2 x 100 mL). The organic layers were then combined and washed with water (100 mL), then brine (150 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography (19:1 → 9:1 hexanes/EtOAc eluent) to afford ester **154**[94] (3.14 g, 84% yield, R_F = 0.10 in 9:1 hexanes/EtOAc eluent) as a colorless oil.



154 *247*

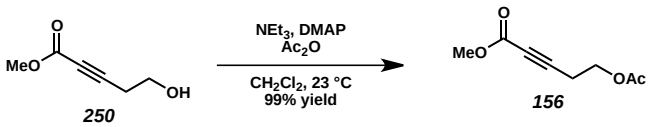
Ester 247: To a solution of **154** (1.51 g, 7.61 mmol) in MeOH:H_2O (9:1, 38.0 mL) at 23 °C was added TsOH·H_2O (0.145 g, 0.761 mmol), and the mixture was allowed to stir for 36 h. The reaction was quenched with sat. aq. $NaHCO_3$, and the majority of the MeOH was removed in vacuo. The mixture was extracted with Et_2O (4 x 40 mL), and the combined organic layers were washed with brine (100 mL) and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography (9:1 → 2:1 hexanes/EtOAc eluent) to afford ester **247** (0.500 g, 58% yield, R_F = 0.37 in 2:1 hexanes/EtOAc) as a white solid. The spectroscopic data was consistent with that previously reported in the literature[95].



249 *250*

Alcohol 250: To a solution of ether **249**[96] (0.455 g, 2.95 mmol) in THF (14.7 mL) at -78 °C under argon was added *n*-BuLi (1.24 mL, 3.10 mmol) dropwise. The solution was allowed to stir for 1.5 h, at which time methylchloroformate (0.239 mL, 3.10 mmol) was added dropwise. The reaction was allowed to stir for 2 h at -78 °C, and then was quenched with 10 mL H_2O and extracted with Et_2O (2 x 100 mL). The combined organic layers were washed with brine (100 mL) and dried over $MgSO_4$. The solvent was removed in vacuo, and the resulting ester (R_F = 0.54 in 2:1 hexanes/EtOAc eluent)[97] was used without further purification. To the crude ester product in MeOH (14.7 mL) at 23 °C was added TsOH•H_2O (28.1 mg, 0.147 mmol), and the mixture was allowed to stir for 1.5 h, at which point the reaction was quenched with 5 % aq. $NaHCO_3$ solution (20 mL). The mixture was extracted with Et_2O (2 x 50 mL), and the combined organic layers were washed with brine (2 x 50 mL) and dried over $MgSO_4$. The solvent was removed in vacuo, and the resulting residue was purified by flash chromatography (2:1 → 1:1 hexanes/EtOAc eluent) to afford homopropargylic alcohol **250** (263 mg, 70% yield over two steps, R_F = 0.17 in 2:1 hexanes/EtOAc) as a colorless oil.

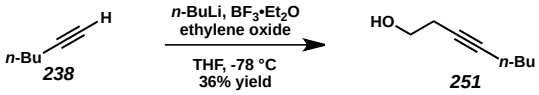
Alcohol 250: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (t, *J* = 6.9 Hz, 2H), 3.73 (s, 3H), 2.57 (app. t, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 87.0, 74.0, 60.0, 52.8, 23.0; IR (film) 3411, 2957, 2242, 1717, 1436, 1078 cm^{-1}; HRMS ($APCI^+$) *m/z* calc'd for $(M + H)^+$ $[C_6H_9O_3]^+$: 129.0546, found 129.0548.



250 *156*

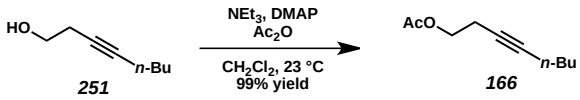
Acetate 156: To a solution of alcohol **250** (170 mg, 1.32 mmol) and Ac_2O (187 μ, 1.99 mmol) in CH_2Cl_2 (6.60 mL) at 0 °C under argon was added NEt_3 (0.549 mL, 3.96 mmol) and DMAP (16.1 mg, 0.0132 mmol), and the mixture was stirred for 5 min, at which time the ice bath was removed. The reaction mixture was allowed to stir at room temperature until starting material was consumed (1 h). The reaction was quenched with sat. aq. $NaHCO_3$ (20 mL) and extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with 1 M HCl (40 mL), then brine (50 mL), and finally dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford acetate **156** (226 mg, 99% yield, R_F = 0.10 in 4:1 hexanes/Et_2O) as a colorless oil.

Acetate 156: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18 (t, *J* = 6.6 Hz, 2H), 3.74 (s, 3H), 2.66 (t, *J* = 6.6 Hz, 2H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 153.9, 85.0, 74.0, 61.0, 52.8, 20.8, 19.3; IR (film) 2958, 2243, 1748, 1717, 1081, 1044 cm^{-1}; HRMS (APCI$^+$) *m/z* calc'd for (M + H)$^+$ $[C_8H_{11}O_4]^+$: 171.0652, found 171.0652.



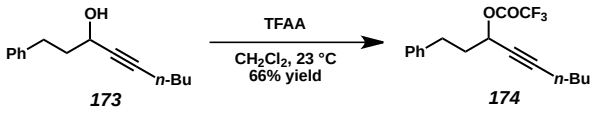
Alcohol 251: To a solution of *n*-butyllithium, (4.09 mL, 9.5 mmol, 2.32 M in hexanes) in THF (10.0 mL) at 0 °C was added 1-hexyne (1.14 mL, 10.0 mmol) dropwise. The mixture was allowed to stir at 0 °C for 30 min and was then cooled to -78 °C and BF_3•Et_2O (1.30 mL, 10.5 mmol) was added dropwise. To this mixture was added excess ethylene oxide in THF (5 mL) dropwise by cold cannula transfer. The reaction was allowed to stir for 1 h at -78 °C at which point H_2O was added (20 mL) and the mixture was extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The solvent was removed in vacuo and the resulting residue was purified by flash chromatography (5:1

Et_2O/hexanes) to afford alcohol **250** (0.429 g, 36% yield, R_F = 0.48 in 2:1 hexanes/EtOAc eluent) as a colorless oil. The compound's spectroscopic data matched that of commercially available material.



251 *166*

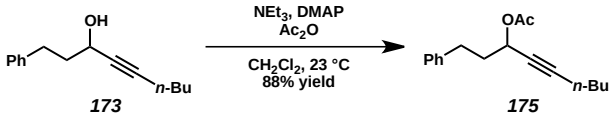
Acetate 166: To a solution of alcohol **251** (0.429 mg, 3.40 mmol) and Ac_2O (0.481 mL, 5.10 mmol) in CH_2Cl_2 (13.6 mL) at 0 °C under argon was added NEt_3 (1.41 mL, 10.2 mmol) and DMAP (41.5 mg, 0.340 mmol), and the mixture was allowed to stir for 5 min, at which time the bath was removed. The reaction mixture was allowed to stir at room temperature until starting material was consumed (1 h). The reaction was quenched with sat. aq. $NaHCO_3$ (20 mL) and extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with 1 M HCl (40 mL), then brine (50 mL), and then dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford homopropargylic acetate **166** (0.584 mg, 99% yield, R_F = 0.27 in 19:1 hexanes/Et_2O) as a colorless oil.



173 *174*

Trifluoroacetate 174: To a solution of alcohol **173** (100 mg, 0.462 mmol) in CH_2Cl_2 (2.31 mL) at 0 °C was added TFAA (0.129 mL, 0.925 mmol), and the mixture was allowed to stir for 5 min. The solvent and remaining TFAA were removed in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford propargylic trifluoroacetate **174** (94.5 mg, 66% yield, R_F = 0.57 in 9:1 hexanes/EtOAc) as a colorless oil.

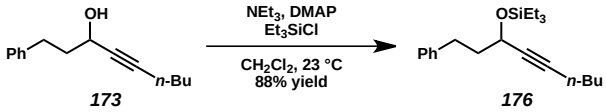
Trifluoroacetate 174: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.3 Hz, 2H), 7.24-7.17 (comp m, 3H), 5.44 (t, *J* = 6.6 Hz, 1H), 2.79 (ddd, *J* = 9.0, 6.7, 2.6 Hz, 2H), 2.25 (td, *J* = 7.0, 2.0 Hz, 2H), 2.22-2.15 (m, 2H), 1.55-1.37 (comp m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 128.8, 128.51, 128.48, 126.5, 89.6, 75.1, 68.8, 36.4, 31.2, 30.4, 22.0, 18.5, 13.7; IR (film) 2936, 2867, 1789, 1223 1150 cm^{-1}; HRMS (DART^{+}) *m/z* calc'd for $(M + NH_4)^{+}$ $[C_{17}H_{23}F_3NO_2]^{+}$: 330.1681, found 330.1684.



Acetate 175: To a solution of alcohol **173** (100 mg, 0.462 mmol) and AcCl (49.0 μl, 0.693 mmol) in CH_2Cl_2 (4.62 mL) at 0 °C under argon was added NEt_3 (0.195 mL, 1.39 mmol) and DMAP (2.8 mg, 0.0231 mmol), and the mixture was allowed to stir for 5 min, at which time the ice bath was removed. The reaction mixture was allowed to stir at room temperature until starting material was consumed (6 h). The reaction was quenched with sat. aq. $NaHCO_3$ (20 mL) and extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with 1 M HCl (40 mL), then brine (50 mL), and then dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford propargylic acetate **175** (105 mg, 88% yield, R_F = 0.46 in 9:1 hexanes/EtOAc) as a colorless oil.

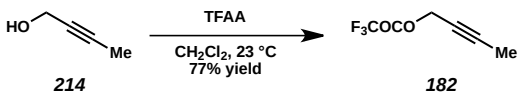
Acetate 175: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 7.21-7.18 (comp m, 3H), 5.38 (t, *J* = 6.5 Hz, 1H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.24 (app td, *J* = 7.0, 2.0 Hz, 2H), 2.12-2.02 (comp m, 2H), 2.07 (s, 3H), 1.59-1.38 (comp m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 141.1, 128.6, 128.5, 128.4, 126.2, 86.8, 77.5, 64.3, 36.8, 31.5, 30.7, 22.0, 21.2, 18.5, 13.7; IR (film) 2931, 1740, 1370, 1231, 1021 cm^{-1}; HRMS (DART^{+}) *m/z* calc'd for (M +

$NH_4)^+$ $[C_{17}H_{26}NO_2]^+$: 276.1958, found 276.1964.



Silyl ether 176: To a solution of alcohol **173** (100 mg, 0.462 mmol) and Et_3SiCl (0.116 mL, 0.693 mmol) in CH_2Cl_2 (4.62 mL) was added NEt_3 (0.195 mL, 1.39 mmol) and DMAP (7.8 mg, 0.231 mmol) at 0 °C. The mixture was allowed to stir for 5 min, at which point the bath was dropped and the mixture was stirred for an additional 3 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL) and the aqueous layer was rinsed with Et_2O (2 x 40 mL). The combined organic layers were washed with HCl (40 mL), then brine (50 mL), and then dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford silyl ether **176** (135 mg, 88% yield, R_F = 0.38 in 19:1 hexanes/Et_2O) as a colorless oil.

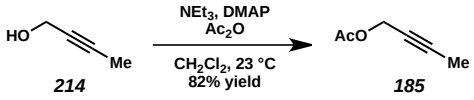
Silyl ether 176: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (app. t, *J* = 7.3 Hz, 2 H), 7.21-7.16 (comp m, 3 H), 4.36 (t, *J* = 6.4 Hz, 2H), 2.76 (dd, *J* = 9.2, 5.9 Hz, 2H), 2.21 (t, *J* = 6.9 Hz, 2H), 1.96 (app. dtd, *J* = 9.9, 6.3, 1.2 Hz, 2H), 1.52-1.39 (comp m, 4H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.65 (qd, *J* = 7.9, 6.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 128.8, 128.7, 126.1, 85.2, 81.8, 62.7, 41.1, 32.0, 31.1, 22.3, 18.8, 13.9, 7.2, 5.2; IR (film) 2956, 2876, 1456, 1090, 1005 cm^{-1}; LRMS (EI^+) *m/z* calc'd for $(M - C_2H_5)^+$ $[C_{21}H_{34}OSi - C_2H_5]^+$: 301, found 301.



Alkyne 182: To a solution of but-2-yn-1-ol (**214**, 0.250 mL, 3.34 mmol) in CH_2Cl_2 (6.68 mL) at 0 °C under argon was added trifluoroacetic anhydride (0.697 mL, 5.01 mmol). The mixture was

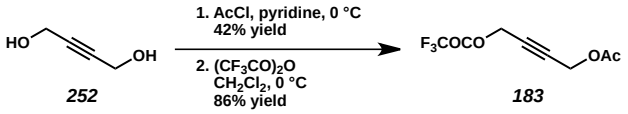
allowed to stir at 0 °C for 15 min, at which point the solvent and excess TFAA were removed in vacuo (CAREFUL! Product volatile). $CHCl_3$ (2 mL) was added and subsequently removed in vacuo. The resulting residue was eluted through a small plug of silica (19:1 Et_2O/pentane eluent) to afford alkyne **182** (0.427 mg, 77% yield, R_F = 0.55 in 19:1 hexanes/Et_2O eluent) as a colorless oil.

Alkyne 214: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 (q, $J_{propargyl}$ = 2.4 Hz, 2H), 1.84 (t, $J_{propargyl}$ = 2.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0 (q, J = 41.7 Hz), 114.6 (q, J = 285.3 Hz), 85.0, 70.8, 56.4, 3.4.



Alkyne 185: To a solution of but-2-yn-1-ol (**214**, 0.500 mL, 6.68 mmol) in CH_2Cl_2 (13.4 mL) was added Ac_2O (0.948 mL, 10.0 mmol), NEt_3 (2.77 mL, 20.0 mmol) and DMAP (81.6 mg, 0.668 mmol) sequentially at 23 °C under argon. The mixture was allowed to stir for 3 h, at which point sat. aq. $NaHCO_3$ (20 mL) was added and the mixture was extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The solvent was removed in vacuo and the resulting residue was purified by flash chromatography (9:1 pentane/Et_2O eluent) to afford alkyne **185** (0.614 g, 82% yield, R_F = 0.26 in 19:1 hexanes/Et_2O eluent) as a colorless oil

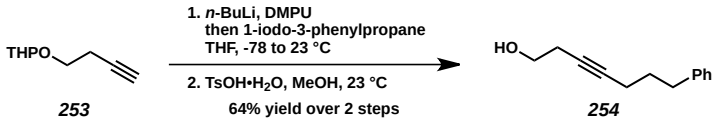
Alkyne 185: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (s, 2H), 1.98 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 82.9, 73.1, 52.6, 20.6, 3.4; IR (film) 2925, 2241, 1750, 1379, 1227 cm^{-1}; HRMS (DART$^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_6H_{12}NO_2]^+$: 130.0863, found 130.0861.



Trifluoroacetate 183: To a solution of 1,4-butynediol (**252**, 4.30 g, 50.0 mmol) in pyridine (20.0 mL) at 0 °C was added AcCl (0.711 mL, 10.0 mmol), and the mixture was allowed to stir for 1.5 h. The reaction was quenched with sat. aq. $NaHCO_3$ (10 mL) and extracted with Et_2O (2 x 75 mL). The combined organic layers were washed with 1M HCl (2 x 20 mL) and brine (40 mL), and the residue was purified by flash chromatography (2:1 hexanes/EtOAc eluent) to afford the monopropargylacetate[98] (534 mg, 42% yield, R_F = 0.29 in 2:1 hexanes/EtOAc) as a colorless oil.

To a solution of the monoacetate (148 mg, 1.48 mmol) in CH_2Cl_2 (5.92 mL) at 0 °C was added TFAA (0.321 mL, 2.31 mmol), and the mixture was allowed to stir for 15 min. The solvent and remaining TFAA were removed in vacuo, and the residue was purified by flash chromatography (5:1 hexanes/EtOAc eluent) to afford trifluoroacetate **183** (223 mg, 86% yield, R_F = 0.65 in 2:1 hexanes/EtOAc) as a colorless oil.

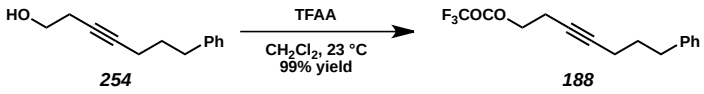
Trifluoroacetate 183: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 (s, 2H), 4.73 (s, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 83.7, 78.4, 55.6, 52.1, 21.0; IR (film) 2952, 1973, 1750, 1341, 1226, 1031 cm^{-1}; LRMS (EI$^+$) *m/z* calc'd for $(M - C_2F_3O_2)^+$ $[C_6H_7O_2]^+$: 111, found 111.



Alkyne 254: To a solution of alkyne **253** (0.522 g, 9.87 mmol) and DMPU (5.00 mL, 41.5 mmol) in THF (49.0 mL) was added *n*-BuLi (3.98 mL, 2.5 M in hexanes, 9.87 mmol) dropwise at -78 °C under argon. The mixture was stirred at -78 °C for 45 min, at which point 1-iodo-3-

phenylpropane (2.56 g, 10.4 mmol) in THF (5.00 mL) was added dropwise, and the mixture was allowed to slowly warm to room temperature overnight. A condenser was attached, the system was flushed with argon then heated to reflux for 2 days. The reaction was quenched with H_2O (20 mL) and extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The solvent was removed in vacuo, and the resulting crude alkyne (1.99 g, R_F = 0.47 in 9:1 hexane/EtOAc eluent) was used without further purification.

To a solution of the crude alkyne (0.748 g, 2.74 mmol) in MeOH (10.9 mL) was added TsOH•H_2O (26.0 mg, 0.137 mmol) at room temperature, and it was allowed to stir for 45 min, at which point the reaction was quenched with sat. aq. $NaHCO_3$ (10 mL) and extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The solvent was removed in vacuo and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford alkyne **254**[99] (0.505 g, 64% yield over two steps, R_F = 0.12 in 9:1 hexane/EtOAc eluent) as a colorless oil.

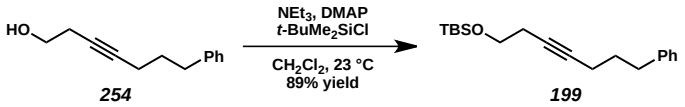


254 *188*

Trifluoroacetate 188: To a solution of alcohol **254** (81.5 mg, 0.433 mmol) in CH_2Cl_2 (0.866 mL) at 0 °C was added TFAA (0.129 mL, 0.925 mmol), and the mixture was allowed to stir for 5 min. The solvent and remaining TFAA were removed in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford propargylic trifluoroacetate **188** (121 mg, 99% yield, R_F = 0.48 in 9:1 hexanes/EtOAc) as a colorless oil.

Trifluoroacetate 188: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.17 (comp m, 5H), 4.42 (t, *J* = 6.9 Hz, 1H), 2.70 (app. t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 6.9, Hz, 2H), 2.16 (t, *J* = 7.0 Hz, 2H), 1.80 (quint, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 128.6, 128.4, 126.0, 82.1, 74.5,

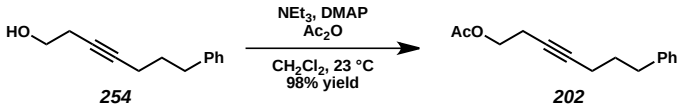
66.2, 34.9, 30.4, 19.2, 18.2; IR (film) 3029, 2941, 1789, 1351, 1223, 1157 cm^{-1}; LRMS (EI^+) *m/z* calc'd for $(M)^+$ $[C_{15}H_{15}F_3O_2Si]^+$: 284, found 284.



254 *199*

Silyl ether 199: To a solution of alcohol **254** (147 mg, 0.781 mmol) and TBSCl (177 mg, 1.17 mmol) in CH_2Cl_2 (3.90 mL) at 0 °C under argon was added NEt_3 (0.325 mL, 2.34 mmol) and DMAP (9.5 mg, 0.0781 mmol), and the mixture was allowed to stir for 5 min, at which time the ice bath was removed. The reaction mixture was allowed to stir at room temperature until starting material was consumed (1 h). The reaction was quenched with sat. aq. $NaHCO_3$ (10 mL) and extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with 1 M HCl (40 mL), then brine (50 mL), and then dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford silyl ether **199** (210 mg, 89% yield, R_F = 0.53 in 9:1 hexanes/EtOAc) as a colorless oil.

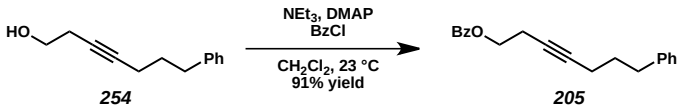
Silyl ether 199: ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 7.20 (app. d, *J* = 7.0 Hz, 3H), 3.72 (t, *J* = 7.3 Hz, 2H), 2.72 (app. t, *J* = 7.6 Hz, 2H), 2.40 (t, *J* = 7.3, 2H), 2.17 (t, *J* = 7.0 Hz, 2H), 1.81 (quint, *J* = 7.4 Hz, 2H), 0.91 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 128.7, 128.4, 125.9, 81.1, 77.6, 62.6, 35.0, 30.7, 26.1, 23.4, 18.4, -5.1; IR (film) 2930, 2858, 1255, 1104, 837 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{31}OSi]^+$: 303.2139, found 303.2125.



254 *202*

Acetate 202: To a solution of alcohol **254** (128 mg, 0.680 mmol) and Ac_2O (96.5 mg, 1.02 mmol) in CH_2Cl_2 (3.40 mL) at 0 °C under argon was added NEt_3 (0.283 mL, 2.04 mmol) and DMAP (8.3 mg, 0.0680 mmol), and the mixture was allowed to stir for 5 min, at which time the bath was removed. The reaction mixture was allowed to stir at room temperature until starting material was consumed (1 h). The reaction was quenched with sat. aq. $NaHCO_3$ (20 mL) and extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with 1 M HCl (40 mL), then brine (50 mL), and then dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford homopropargylic acetate **202** (153 mg, 98% yield, R_F = 0.43 in 9:1 hexanes/EtOAc) as a colorless oil.

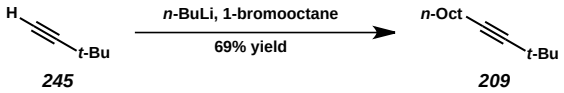
Acetate 202: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.20-7.17 (comp m, 3H), 4.16 (t, *J* = 7.0 Hz, 2H), 2.71 (app. t, *J* = 7.6 Hz, 2H), 2.51 (t, *J* = 7.0 Hz, 2H), 2.17 (t, *J* = 7.0 Hz, 2H), 2.01 (s, 3H), 1.80 (quint, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 141.8, 128.6, 128.4, 126.0, 81.6, 76.3, 63.0, 34.8, 30.6, 21.1, 19.4, 18.3; IR (film) 2941, 1743, 1455, 1239, 1042 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{18}O_2]^+$: 231.1380, found 231.1381.



Benzoate 205: To a solution of alcohol **254** (76.0 mg, 0.404 mmol) and BzCl (51.6 µl, 1.02 mmol) in CH_2Cl_2 (2.02 mL) at 0 °C under argon was added NEt_3 (0.168 mL, 1.21 mmol) and DMAP (4.9 mg, 0.0404 mmol), and the mixture was allowed to stir for 5 min, at which time the ice bath was removed. The reaction mixture was allowed to stir at room temperature until starting material was consumed (1 h). The reaction was quenched with sat. aq. $NaHCO_3$ (20 mL)

and extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with 1 M HCl (40 mL), then brine (50 mL), and then dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford homopropargylic benzoate **254** (121 mg, 91% yield, R_F = 0.36 in 9:1 hexanes/EtOAc) as a colorless oil.

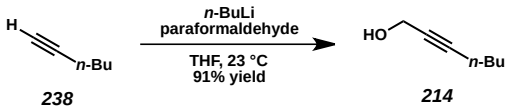
Benzoate 254: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.19-7.15 (comp m, 3H), 4.41 (t, *J* = 6.9 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 6.9 Hz, 2H), 2.17 (t, *J* = 6.9 Hz, 2H), 1.79 (quint, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 141.8, 133.1, 130.2, 129.8, 128.6, 128.5, 129.4, 125.9, 81.8, 76.3, 63.5, 34.8, 30.5, 19.6, 18.3; IR (film) 3027, 2942, 1721, 1453, 1272, 1113 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{21}O_2]^+$: 293.1536, found 293.1530.



Alkyne 209: To a solution of *t*-butylacetylene (300 μl, 2.45 mmol) in THF (12.3 mL) at -78 °C under argon was added *n*-BuLi (0.979 mL, 2.45 mmol) dropwise. The solution was allowed to stir for 45 min, at which time 1-bromooctane (0.423 mL, 2.45 mmol) and Li_2CuCl_4 (0.490 mL, 0.1 M in THF, 0.049 mmol) were added dropwise. The reaction was then heated to reflux and allowed to stir for 3 d before it was quenched with H_2O (20 mL) and extracted with hexanes (2 x 75 mL). The combined organic layers were washed with brine (75 mL) and dried over $NaSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography (hexanes eluent) to afford alkyne **209** (331 mg, 69% yield, R_F = 0.49 in hexanes) as a colorless oil.

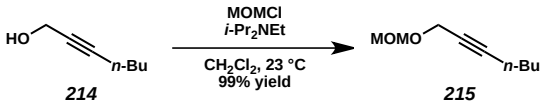
Alkyne 209: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (t, *J* = 7.1 Hz, 2H), 1.50-1.43 (m, 2H), 1.38-

1.28 (comp m, 10 H), 1.19 (s, 9H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 89.1, 78.7, 32.0, 31.6, 30.8, 29.4, 29.3, 28.9, 22.8, 18.8, 14.2; IR (film) 2967, 2928, 2958, 1458, 1266 cm^{-1}; LRMS (EI^+) *m/z* calc'd for $(M)^+$ $[C_{14}H_{26}]^+$: 194, found 194.



238 214

Hept-2-yn-1-ol (214): This compound was prepared according to procedure by Li and O'Doherty. The spectroscopic data matched that which has been previously reported in the literature.[100]

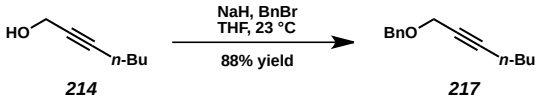


214 215

Methoxymethyl ether 215: To a solution of propargylic alcohol **214** (0.400 g, 3.57 mmol) in CH_2Cl_2 (14.3 mL) at room temperature under argon was added MOMCl (0.298 mL, 3.92 mmol). The mixture was allowed to stir for 2 min, at which time *i*-Pr_2NEt (1.38 mL, 10.7 mmol) was added, and the reaction was allowed to stir overnight. The reaction was quenched with H_2O (10 mL) and extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with 1 M HCl (50 mL), then brine (50 mL), and then dried over $MgSO_4$. The solvent was removed in vacuo, and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford methoxymethyl ether **215** (0.556 g, 99% yield, R_F = 0.69 in 2:1 hexanes/EtOAc) as a colorless oil.

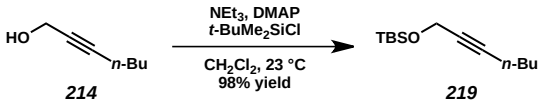
Methoxymethyl ether 215: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (s, 2H), 4.18 (s, 2H), 3.36 (s, 3H), 2.20 (t, J = 7.0 Hz, 2H), 1.52-1.34 (comp m, 4H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 94.7, 87.1, 75.4, 55.6, 54.8, 30.8, 22.0, 18.6, 13.7; IR (film) 2935, 1466, 1377, 1151, 1048 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_9H_{16}O_2]^+$: 157.1221, found 157.1223.



214 *217*

Benzyl ether 217: To a solution of propargylic alcohol **217** (0.400 g, 3.57 mmol) in THF (14.3 mL) at room temperature under argon was added NaH (157 mg, 60% dispersion in mineral oil, 3.92 mmol). The mixture was allowed to stir for 2 min, at which time benzyl bromide (0.466 mL, 3.92 mmol) was added, and the reaction was allowed to stir overnight. The reaction was quenched with H_2O (10 mL) and extracted with Et_2O (2 x 25 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The solvent was removed in vacuo, and the resulting residue was purified by flash chromatography (hexanes → 9:1 hexanes/Et_2O eluent) to afford benzyl ether **217** (0.635 g, 88% yield, R_F = 0.54 in 9:1 hexanes/EtOAc) as a colorless oil. The spectroscopic properties matched that which has been previously reported in the literature.[101]

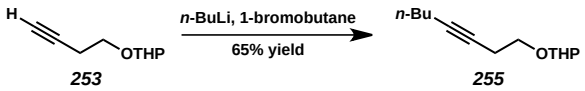


214 *219*

Silyl ether 219: To a solution of propargylic alcohol **214** (150 mg, 1.34 mmol) and TBSCl (.222 g, 1.47 mmol) in CH_2Cl_2 (6.85 mL) at room temperature under argon was added NEt_3 (0.557 mL, 4.02 mmol) and DMAP (16.4 mg, 0.134 mmol). The reaction was quenched with sat. aq. $NaHCO_3$ (10 mL) and extracted with Et_2O (2 x 25 mL). The combined organic layers were washed with 1 M HCl (25 mL), then brine (50 mL), and then dried over $MgSO_4$. The solvent was removed in vacuo, and the resulting residue was purified by flash chromatography (19:1

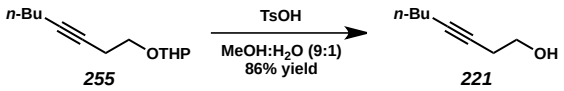
hexanes/Et_2O eluent) to afford silyl ether **219** (0.297 g, 98% yield, R_F = 0.44 in 19:1 hexanes/Et_2O eluent) as a colorless oil. The spectroscopic properties matched that which has been previously reported in the literature.[102]

Alternate route to homopropargyl alcohol 221:

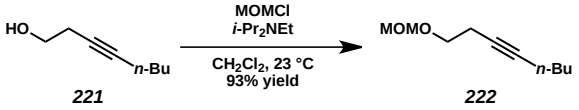


Alkyne 255: To a solution of alkyne **253** (2.00 g, 13.0 mmol) in THF (64.8 mL) under argon was added *n*-BuLi (5.18 mL, 2.5 M in hexanes, 13.0 mmol) dropwise at 0 °C. The solution was allowed to stir for 45 min, at which time *n*-butyl iodide (1.45 mL, 13.0 mmol) was added dropwise. A condenser was then attached, the system was flushed with argon, and the reaction was heated to reflux for 30 h. The reaction was quenched with 10 mL H_2O and extracted with Et_2O (2 x 100 mL). The combined organic layers were washed with brine (100 mL) and dried over $MgSO_4$. The solvent was removed in vacuo, and the resulting residue was purified by flash chromatography (19:1 → 9:1 hexanes/EtOAc eluent) to afford alkyne **255** (1.76 g, 65% yield, R_F = 0.53 in 9:1 hexanes/EtOAc) as a colorless oil.

Alkyne 255: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (t, *J* = 3.5 Hz, 1H), 3.88 (ddd, *J* = 11.2, 8.1, 3.1 Hz, 1H), 3.79 (dt, *J* = 9.5, 7.2 Hz, 1H), 3.55-3.48 (comp m, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.14 (t, *J* = 6.9 Hz, 2H), 1.89-1.78 (m, 1H), 1.74-1.67 (m, 1H), 1.63-1.34 (comp m, 8H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.7, 81.3, 76.8, 66.3, 62.2, 31.2, 30.7, 25.6, 22.0, 20.3, 19.5, 18.5. 13.7; IR (film) 2938, 2873, 1456, 1352, 1122, 1034 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{13}H_{22}O_2]^+$: 211.1698, found 211.1693.



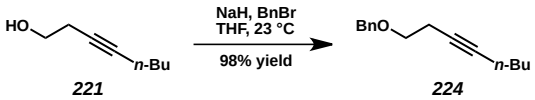
Oct-3-yn-1-ol (221): To a solution of ether **255** (1.09 g, 5.20 mmol) in MeOH (20.8 mL) at 23 °C was added TsOH•H_2O (49.5 mg, 0.260 mmol). The mixture was stirred overnight, at which point 5% aq. $NaHCO_3$ was added (20 mL) and the mixture was extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with brine (75 mL) and dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford oct-3-yn-1-ol (0.566 g, 86% yield, R_F = 0.48 in 2:1 hexanes/EtOAc eluent) as a colorless oil. The spectroscopic properties matched that of commercially available material (Aldrich).



Methoxymethyl ether 222: To a solution of homopropargylic alcohol **221** (80.0 mg, 0.634 mmol) in CH_2Cl_2 (3.12 mL) at room temperature under argon was added MOMCl (72.2 mg, 0.951 mmol). The mixture was allowed to stir for 2 min, at which time *i*-Pr_2NEt (0.331 mL, 1.90 mmol) was added, and the reaction was allowed to stir overnight. The reaction was quenched with H_2O (5 mL) and extracted with Et_2O (2 x 25 mL). The combined organic layers were washed with 1 M HCl (30 mL), then brine (50 mL), and then dried over $MgSO_4$. The solvent was removed in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford methoxymethyl ether **222** (100 mg, 93% yield, R_F = 0.75 in 2:1 hexanes/EtOAc) as a colorless oil.

Methoxymethyl ether 222: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (s, 2H), 3.61 (t, *J* = 6.9 Hz, 2H), 3.37 (s, 3H), 2.45 (t, *J* = 6.9 Hz, 2H), 2.15 (t, *J* = 6.9 Hz, 2H), 1.50-1.34 (comp m, 4H), 0.89 (t, *J*

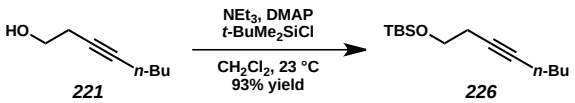
= 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 96.7, 81.8, 76.9, 66.9, 55.5, 31.4, 22.3, 20.6, 18.8, 14.0; IR (film) 2933, 2875, 1466, 1151, 1112, 1029 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{10}H_{19}O_2]^+$: 171.1385, found 171.1380.



221 *224*

Benzyl ether 224: To a solution of homopropargylic alcohol **221** (80.0 mg, 0.624 mmol) in THF (3.12 mL) at room temperature under argon was added NaH (50.4 mg, 60% dispersion in mineral oil, 1.26 mmol). The mixture was allowed to stir for 2 min, at which time BnBr (75.4 μl, 0.634 mmol) was added, and the reaction was allowed to stir overnight. The reaction was quenched with H_2O (5 mL) and extracted with Et_2O (2 x 25 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The solvent was removed in vacuo, and the resulting residue was purified by flash chromatography (hexanes → 19:1 hexanes/Et_2O eluent) to afford homopropargylic benzyl ether **224** (134 mg, 98% yield, R_F = 0.68 in 9:1 hexanes/EtOAc) as a colorless oil.

Benzyl ether 224: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (comp m, 5H), 4.56 (s, 2H), 3.57 (t, *J* = 7.1 Hz, 2H), 2.48 (t, *J* = 7.1 Hz, 2H), 2.16 (t, *J* = 7.0 Hz, 2H), 1.51-1.35 (comp m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 128.8, 128.1, 128.0, 81.8, 77.0, 73.3, 69.4, 31.5, 22.3, 20.6, 18.9, 14.0; IR (film) 2932, 2861, 1454, 1362, 1103 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{21}O]^+$: 217.1584, found 217.1587.

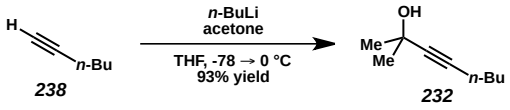


221 *226*

Silyl ether 226: To a solution of homopropargylic alcohol **221** (80.0 mg, 0.634 mmol) in

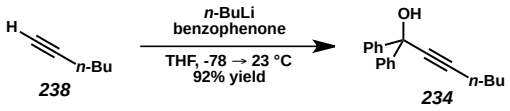
CH_2Cl_2 (3.12 mL) at room temperature under argon was added TBSCl (146 mg, 0.951 mmol). The mixture was allowed to stir for 2 min, at which time NEt_3 (0.264 mL, 1.90 mmol) and DMAP (7.8 mg, 0.0634 mmol) were added, and the reaction was allowed to stir overnight. The reaction was quenched with H_2O (5 mL) and extracted with Et_2O (2 x 25 mL). The combined organic layers were washed with 1 M HCl (30 mL) then brine (50 mL), and then dried over $MgSO_4$. The solvent was removed in vacuo, and the resulting residue was purified by flash chromatography (hexanes eluent) to afford silyl ether **226** (142 mg, 93% yield, R_F = 0.92 in 2:1 hexanes/EtOAc eluent) as a colorless oil.

Silyl ether 226: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (t, *J* = 7.2 Hz, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 2.14 (t, *J* = 7.0 Hz, 2H), 1.49-1.34 (comp m, 4H), 0.92-0.88 (comp m, 9H), 0.07 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.6, 77.0, 62.6, 31.3, 26.1, 23.4, 22.1, 18.6, 18.5, 13.8, -5.1; IR (film) 2931, 2859, 1471, 1255, 1104 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{14}H_{29}OSi]^+$: 241.1987, found 241.1982.



Propargylic alcohol 231: To a solution of 1-hexyne (1.00 mL, 8.89 mmol) in THF (29.6 mL) at -78 °C under argon was added *n*-BuLi (3.73 mL, 2.5 M in hexanes, 9.33 mmol) dropwise. The solution was allowed to stir for 1 h, at which time acetone (0.686 mL, 9.33 mmol) was added dropwise. The reaction was allowed to warm slowly to 0 °C. The reaction was quenched with 10 mL H_2O and extracted with Et_2O (2 x 100 mL). The combined organic layers were washed with brine (100 mL) and dried over $MgSO_4$. The solvent was removed in vacuo, and the resulting residue was purified by flash chromatography (19:1 → 5:1 hexanes/Et_2O eluent) to

afford propargylic alcohol **232** (1.16 g, 93% yield, R_F = 0.28 in 5:1 hexanes/Et_2O) as a colorless oil. The spectroscopic data matched that which has been previously reported in the literature.[103]



Propargylic alcohol 234: To a solution of 1-hexyne (1.00 mL, 8.89 mmol) in THF (29.6 mL) at -78 °C under argon was added *n*-BuLi (3.73 mL, 2.5 M in hexanes, 9.33 mmol) dropwise. The solution was allowed to stir for 1 h, at which time a solution of benzophenone (1.70 g, 9.33 mmol) in 4.00 mL THF was added dropwise. The reaction was allowed to warm slowly to 23 °C. The reaction was quenched with 10 mL H_2O and extracted with Et_2O (2 x 100 mL). The combined organic layers were washed with brine (100 mL) and dried over $MgSO_4$. The solvent was removed in vacuo, and the resulting residue was purified by flash chromatography (19:1 → 5:1 hexanes/Et_2O eluent) to afford propargylic alcohol **234** (2.16 g, 92% yield, R_F = 0.48 in 5:1 hexanes/Et_2O) as a colorless oil. The spectroscopic data matched that which has been previously reported in the literature.[104]

CHAPTER THREE NOTES AND REFERENCES

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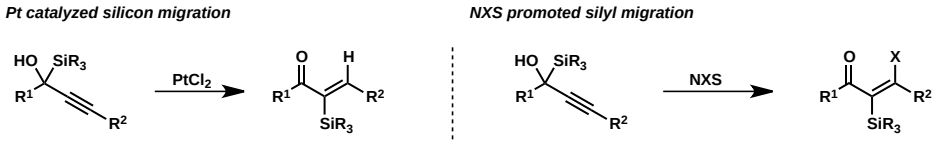
CHAPTER FOUR

The Utilization of Tri- and Tetrasubstituted Vinylsilanes for the Formation of Stereodefined All-Carbon Alkenes

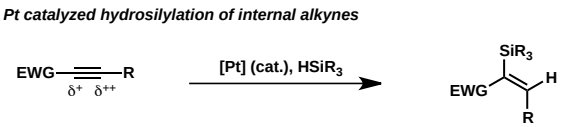
4.1 Introduction

Chapters 2 and 3 of this thesis described our efforts toward the development of three methodologies for the synthesis of vinylsilane species. In the first part of Chapter 2 we demonstrated a novel 1,2-silyl migration reaction of α-hydroxypropargylsilanes to generate *Z*-α-silylenones. Later, we showed a similar silicon migration of α-hydroxypropargylsilanes in the presence of *N*-halosuccinimides to produce (*E*)-α-silyl-β-haloenones. Both reactions proceed with a stereospecific *anti* attack onto the activated alkyne moiety, affording excellent geometric selectivity.



Scheme 4.1.1 Vinylsilanes produced by 1,2-silyl migration

In Chapter 3 we elucidated the selective hydrosilylation of internal alkynes upon finding that alkyne polarization coupled with the right set of conditions can induce high levels of regioselectivity for the *cis* addition of a Si–H species across an alkyne.



Scheme 4.1.2 Regioselective hydrosilylations

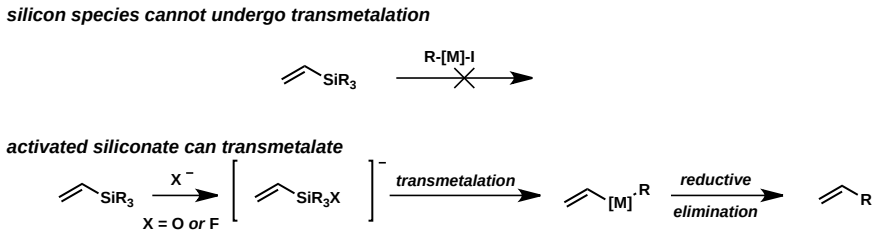
The attractiveness of the three aforementioned reactions is that they provide facile access to tri- and tetrasubstituted vinyl silane products that can provide a synthetic handle for further transformations. There are many different methods that utilize silicon-substituted alkenes.[105] This chapter will focus on exploiting the previously described syntheses of highly substituted stereodefined vinylsilanes into useful cross coupling methodology. We were able to accomplish this through three different methods. The first utilized tetrabutylammonium fluoride promoted Hiyama type coupling reactions. Wanting to depart from the potentially deleterious effects of fluoride, we then explored mild fluoride sources as well as fluoride-free silicon based cross-coupling reactions. Finally, we employed halodesilylation chemistry to produce electrophiles for cross-coupling reactions.

4.2 Hiyama Coupling Background

4.2.1 History and Background

The first transition metal-catalyzed cross-coupling reactions were reported by Corriu[106] and Kumada.[107] Aside from organomagnesium couping reactions, the most prominent early developments in the field focused on organoboron,[108] organozinc,[109] and organotin.[110] It was not until 16 years later when Hiyama published his seminal report that showed the C-Si bond could act as a viable nucleophile for cross-coupling reactions.[111] Silicon has many advantages over some of the other metal organic cross coupling nucleophiles due to its low toxicity and high availability.[112] Tetraorganosilicon compounds are also quite stable, which can prove to be useful for organic synthesis as they can tolerate a wide variety of conditions that other organometallic species cannot. However, due to their inherent stability, the tetraorganosilicon species are incapable of directly undergoing the transmetalation step of a cross coupling reaction. In order

to undergo transmetalation, the silicon must be converted to a significantly more reactive species. Fortunately, silicon has an incredibly high affinity for fluorine and oxygen atoms due to the energetic favorability of Si–O and Si–F bonds. With judicious choice of activating agents, the resulting siliconate species can undergo transmetalation.

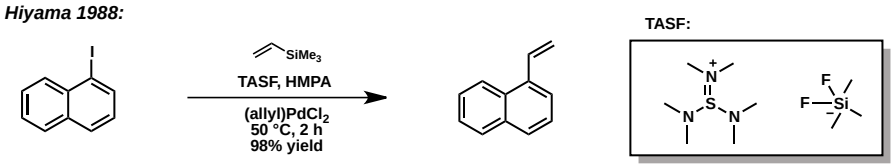


Scheme 4.2.1 Activation is necessary for silicon cross coupling reactions

Consequently, as a result of the desire to pursue Si mediated cross coupling reactions and other transformations such as the Tamao-Fleming oxidation,[113] the expansion of silicon's valency has been studied extensively.[114] In our work with Hiyama type couplings, we employ both an exogenous source of fluoride, as well as an intramolecular delivery of oxygen to produce a pentacoordinate silicon and induce reactivity.

4.2.2 First Silicon Cross-Coupling

The first silicon-based cross coupling reaction involved coupling iodonaphthalene to vinyltrimethylsilane. This employed rather harsh conditions of HMPA, 50 ℃, and a harsh, "naked" source of fluoride, tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF).[111] The fluoride adds to the silicon, creating a pentacoordinate species, which was believed to be the active species for transmetalation.



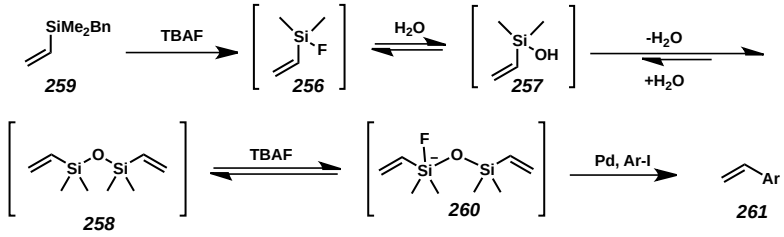
Scheme 4.2.2 First reported silicon based cross coupling

After Hiyama's seminal report, research focus shifted to silicon moieties more apt to undergo nucleophilic addition to create the reactive hypervalent silicon species necessary for transmetalation. Hiyama later found that alkenyl(halo)silanes, alkynyl(halo)silanes, as well as aryl(halo)silanes all can undergo transmetalation with only KF, a weaker fluoride source.[115] A drawback to this is that halosilanes are susceptible to hydrolysis, rendering them less desirable for synthesis.[116] To overcome these issues, a number of alternatives have been explored, including silacyclobutanes, silanols, alkoxysilanes, and polysiloxanes.[117] Mechanistic insight by Denmark and coworkers suggests that a disiloxane may be a reactive intermediate for many of silicon cross-coupling reactions.[118] There is no general consensus in the literature, however, as to whether or not there is a consistently similar intermediate for the transmetalation step.

4.2.3 Fluoride Promoted Tetraorganosilicon Activation

Many of the established silyl groups used in Hiyama coupling were already substituted with a heteroatom, which made for facile activation, but were often not stable enough to be carried through a number of synthetic steps. An ideal vinylsilicon functionality would be stable to most conditions but easily activated for the desired cross coupling reaction.[119] Thus, focus returned to the tetraorganosilanes that can easily access a heteroatom substituted intermediate. One way this has been accomplished is developing silane with some sort of leaving group substituent, allowing for weaker source of fluoride. Denmark and co-workers have pioneered this chemistry with their

finding that silacyclobutanes can be easily activated by tetrabutylammonium fluoride (TBAF) to create silanols and disiloxanes.[120] Later, allyl-[121] and benzyl-substitued silanes emerged as similarly competent precursors for the in situ formation of silanols. Although both are easily activated by TBAF, the BDMS group has proven to be more stable and effective.[122] When subjected to TBAF, the BDMS debenzylates instantly to form a Si-F intermediate (**256)**.[123] This species, in the presence of H_2O, is likely in equilibrium with the silanol (**257**) and disiloxane (**258**) intermediates.



Scheme 4.2.3 Mechanism for fluoride acitivated BDMS groups

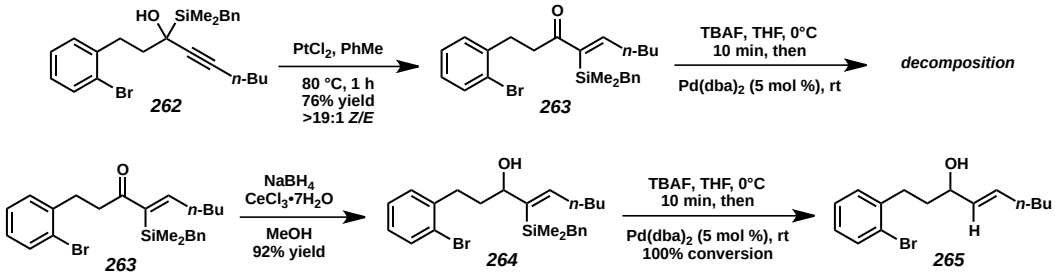
Fluoride can add into one of the Si atoms in **258** to form a pentacoordinate silicon species (**260**), which is a competent nucleophile for transmetalation onto an organopalladium catalytic intermediate.

4.3 TBAF Promoted Hiyama Coupling Reactions

4.3.1 Initial Cross Coupling Studies

To demonstrate the synthetic utility of our Pt catalyzed 1,2-silyl migration reactions described in Chapter 2, we initially wanted to directly utilize the α-BDMS enones for the synthesis of all-carbon trisubstituted alkenes. Our first attempts were routed through readily synthesized *o*-bromohydrocinnamaldehyde derived alkyne **262**. From there we subjected alkyne **262** to our

silyl migration conditions, which proceeded in good yield and excellent *Z*-selectivity (76% yield, >19:1 *Z/E*). The product enone (**263**) was then subjected to TBAF promoted cross-coupling conditions. Unfortunately, it was found that the addition of TBAF led to complete decomposition of starting material. To circumvent any unfavorable addition to the enone, it was reduced in a 1,2 fashion to produce alcohol **264** and the coupling reaction was attempted. This time, almost complete conversion of starting material to its protodesilylated counterpart (**265**) was observed.

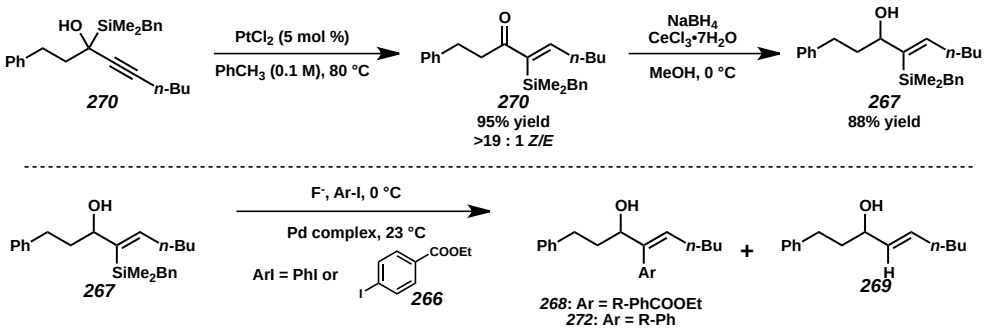


Scheme 4.3.1 First attempt at cross coupling

The protodesilylation of **264** in the presence of TBAF showed that the silicon was exclusively activated; however, the protonation pathway was clearly favored. We were concerned as to whether or not oxidative addition would be prohibitively slow for the aryl bromide under these conditions, so it was decided to explore more potent cross-coupling electrophiles. Additionally, in order for the intramolecular cross coupling to proceed, the silicon moiety must be activated and the aryl halide, on the same molecule, must also be oxidatively added across Pd. To avoid any potential unfavorable conformational issues in the intramolecular system, an intermolecular Hiyama coupling was pursued.

To that end, electron deficient 4-iodoethylbenzoate (**266**) was added as a coupling partner so that the rate of oxidative addition would be less likely to slow the catalytic cycle. Again, no cross coupling was observed. Recent examples in the literature have largely utilized $Pd_2(dba)_3$ and $Pd_2(dba)_3 \cdot CHCl_3$.[123] Gratifyingly, the coupling of vinylsilane **267** and **266** using $Pd_2(dba)_3$ worked to afford **268**, albeit in a modest yield of 30% (Table 4.3.1, entry 4). Protodesilylated product **269** was also formed in approximately equimolar amounts relative to the product. Attempting the reaction with iodobenzene, which is less prone to oxidative addition, gave similar results (Table 4.3.1, entry 5). This observation could perhaps support the notion that, for these Pd catalyzed reactions, the turnover limiting step is not oxidative addition, but instead is the transmetalation of the activated vinylsilane. Excited by these results, yet puzzled by the low yields, we began to screen conditions to try to optimize this reaction. Lowering the catalyst loading to 2.5 mol % (Table 4.3.1, entry 6) showed similar yield and the same ratio of **268** to **269**. To potentially lessen the decomposition of the air-sensitive $Pd_2(dba)_3$ complex, degassed THF was employed (Table 4.3.1, entry 8); interestingly, the yield of **268** was decreased.

Table 4.3.1 Intermolecular Hiyama coupling conditions screen



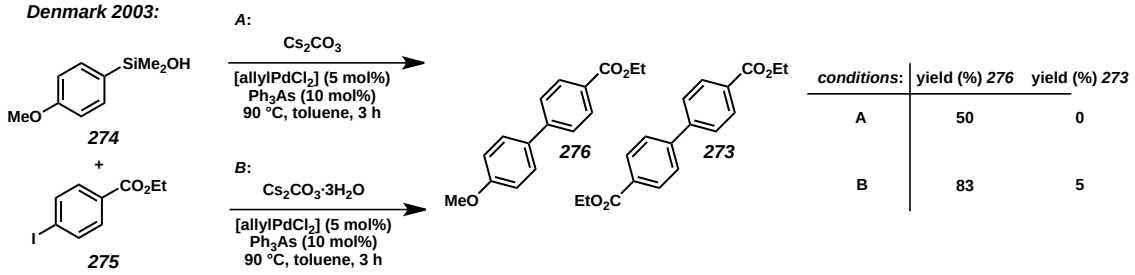
entry	solvent	ArI	F^- (equiv)	Pd complex (x mol %)	yield (%)	prod : *269*[a]
1	THF	*266*	TBAF (2)	$Pd(dba)_2$ (5 mol%)	0	–
2	THF	*266*	CsF (2)	$Pd(dba)_2$ (5 mol%)	0	–
3	THF	*266*	KF (2)	$Pd(dba)_2$ (5 mol%)	0	–
4	THF	*266*	TBAF (2.2)	$Pd_2(dba)_3$ (5 mol%)	30	1 : 1
5	THF	PhI	TBAF (2.2)	$Pd_2(dba)_3$ (5 mol%)	36	1 : 0.9
6	THF	*266*	TBAF (2.2)	$Pd_2(dba)_3$ (2.5 mol%)	45	1 : 1
7	THF	PhI	TBAF (2.2)	$Pd_2(dba)_3$ (2.5 mol%)	<5	<1 : 19
8	THF (degassed)	*266*	TBAF (2.2)	$Pd_2(dba)_3$ (2.5 mol%)	0	N/A
9[b]	THF	*266*	TBAF (2.2)	$Pd_2(dba)_3$ (2.5 mol%)	<5	<1 : 19
10	PhMe	*266*	TBAF (2.2)	$Pd_2(dba)_3$ (2.5 mol%)	25	1 : 3
11	THF	*266*	TBAF (2.2)	$Pd(dba)_2$ (10 mol%)	<5	<1 : 19
12	THF	*266*	TBAF (2.2)	$Pd_2(dba)_3$ (2.5 mol%)	15	1 : 1.1[c]

a) Measured by ^{1}H NMR b) Reaction was heated to 40 °C subsequent to the addition of the Pd complex c) 1 equiv TBAF added at 0 °C, then 1.2 equiv added slowly over the course of 30 min after the addition of the Pd complex.

The homocoupling of aryliodide **268** to biaryl **273** was also observed to be a significant competing reaction pathway. It has been shown that Pd catalyzed homocoupling of aryl halides is promoted by TBAF.[124] Milder fluoride sources (Table 4.3.1, entries 2 and 3) were attempted for activation with no observed formation of coupled product **268** or even protodesilylated product **269**. TBAF was necessary for the described coupling reactions to proceed, but care must be taken to lessen the quantity of observed homocoupling .

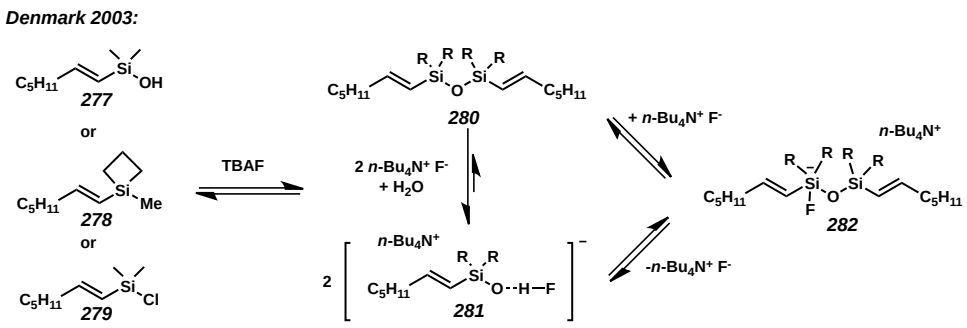
This reductive coupling was also observed by Denmark in 2003 when his group was studying the cross coupling of arylsilanols and arylhalides. In the same report they also noticed results varied even when employing supposedly identical conditions.[125] Upon further investigation of their

activator, in this case Cs_2CO_3, they noticed different levels of hydration. Furthermore, the bottle of Cs_2CO_3 with the highest amount of water (1.9 equiv per Cs_2CO_3) resulted in the highest yields of the cross coupling product (Scheme 4.3.2). After optimization, it was found that 2 to 4 equivalents of water per Cs_2CO_3 gives almost complete conversion from starting material as well as greater than 9 to 1 selectivity for the cross coupled product over the undesired homocoupled product.



Scheme 4.3.2 Denmark's first evaluation of water additive

Later that year, Denmark followed up with a kinetic analysis as well as an isolation of the purportedly necessary intermediate disiloxane using TBAF as an activator. When they subjected either vinyl silanol **277**, silacyclobutane **278**, or halosilane **279** to one equivalent of TBAF they observed a disiloxane (**289**) and an HF bound siloxane (**281**). As the stoichiometry of fluoride was changed, the ratio of **280** to **281** varied, suggesting an equilibrium between the two. Ultimately, it was found that **280** and **281** are also in equilibrium with a mono-fluoride activated disiloxane **282**,[126] which may be the active species for transmetalation.

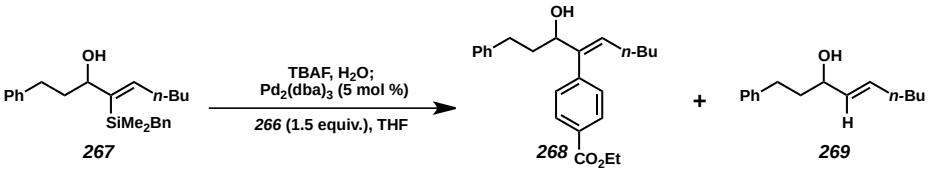


Scheme 4.3.3 Disiloxane equilibria

These studies by Denmark provide a reasonable explanation as to why our aforementioned coupling experiments of **267** resulted in low yields. In our previous TBAF promoted reactions, there was likely not enough water to favor the disiloxane intermediate. With this newfound knowledge in hand, we further pursued conditions for our cross coupling reactions.

Additional water indeed proved to be a boon for our Hiyama coupling reactions. The conditions for our system were found to be approximately 3 equivalents of water relative to **267** (Table 4.3.2, entry 2), again proving the necessity for hydrated reaction conditions. This gave a significantly improved ratio of alkenes **268** and **269** (5:1). It is important to note that the actual amount of water can vary due to the fact that commercial TBAF solutions often have varying amounts of water. Solid sources of TBAF gave subpar results; however, with optimization of water, this could likely be improved to give consistently high yields.

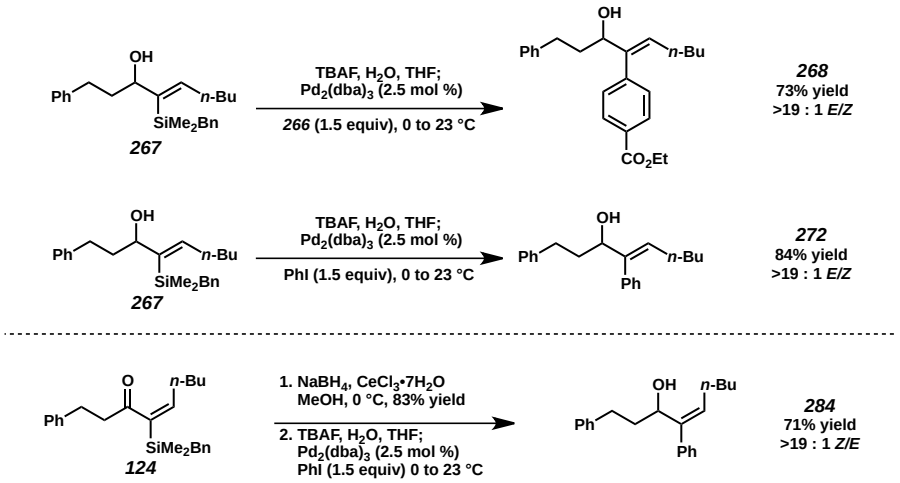
Table 4.3.2 Effects of additional H_2O



entry	TBAF (2.2 equiv)	H_2O equiv (added)	*268*/*269*[a]
1	1 M in THF	2.2	1 : 1.1
2	1 M in THF	3	5 : 1
3	1 M in THF	6	3 : 1
4	TBAF·3H_2O	0	1 : 10
5	TBAF·xH_2O	0	2.5 : 1

a) Measured by ^{1}H NMR

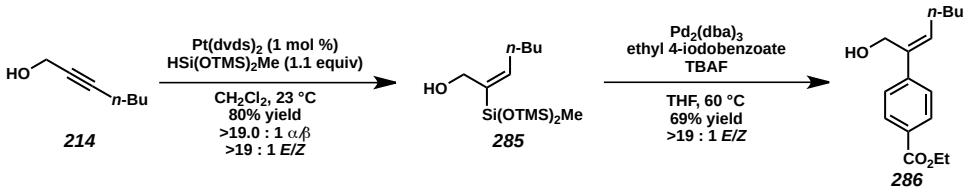
Excitingly, scale-up of the coupling reaction using 3 equivalents of water produced alkene **268** in 73% yield with only 2.5 mol% $Pd_2(dba)_3$. Applying these conditions using iodobenzene as the cross coupling electrophile works similarly well, affording 84% yield of the coupled product (**272)**. Utilizing our internal alkyne hydrosilylation methodology, we subjected ynone **121** to our prescribed conditions using BDMS-H (Chapter 3). Subsequent reduction under Luche conditions afforded alkene **283**, the geometrically complementary isomer of **271**. The cross-coupling reaction of **283** with iodobenzene proceeded smoothly, affording 71% yield. Notably, for all three reactions, there was no isomerization of the product alkenes and >19:1 selectivity for the respective coupled products was shown.



Scheme 4.3.4 TBAF promoted Hiyama coupling reactions

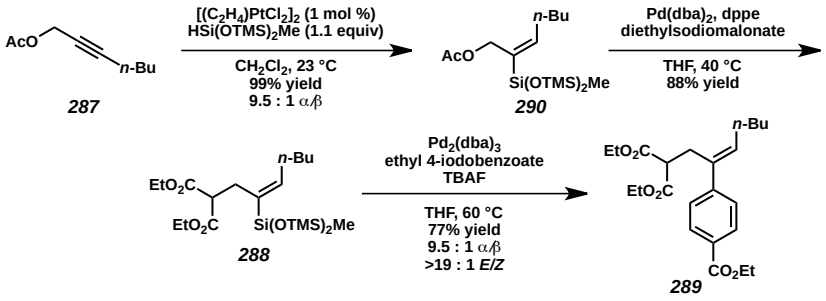
The reactions illustrated in Scheme 4.3.4 highlighted the two geometrically complementary methodologies we described in 2010.[127] Furthermore, the knowledge gleaned from these studies established the Hiyama coupling as a feasible downstream reaction for our product vinylsilanes from $PtCl_2$ catalyzed 1,2-silyl migration reactions as well as our internal alkyne hydrosilylations.

We also employed heptamethyltrisiloxane as another easily activated silicon moiety for cross coupling.[128] Hydrosilylation of propargyl alcohol **214** proceeded smoothly to afford vinylsilane **285** in high yield and excellent selectivity for the α-isomer (80% yield, >19:1 α/β). Subjecting silane **285** to the TBAF promoted coupling conditions gave a 69% yield of alkene **286**.



Scheme 4.3.5 Cross coupling of vinylsilane **285**

The robust nature of the vinylheptamethyltrisiloxane moiety allows for other transformations to be executed prior to the Hiyama coupling event. This facet is demonstrated by the hydrosilylation of propargyl acetate **287** followed by a stereoretentive Pd-catalyzed allylation with diethylmalonate to give **288**. Like with the allylic vinylsilane substrate, the cross-coupling reaction of silane **288** furnished trisubstituted alkene **289** in 77% yield.



Scheme 4.3.6 Tandem allylation and cross coupling event

Notwithstanding, many of the aforementioned studies also showed the potentially deleterious effects that TBAF can have on sensitive substrates. Consequently, we began to steer our research toward significantly more mild conditions for silicon activation.

4.4 Palladium Catalyzed Hiyama Couplings of α-Silylenoates and α-Silylenamides

4.4.1 Introduction

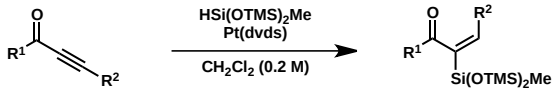
Our extensive work on the regioselective hydrosilylation of internal alkynes has resulted in the facile generation of a myriad of potentially useful vinylsilanes. Ultimately, our goal was to use these compounds as precursors for perform cross coupling reactions. These Pt-catalyzed hydrosilylation reactions are substrate controlled with the salient influence being alkyne polarization by an electron withdrawing group. The resulting vinylsilane species is electron deficient, which can present a problem if used as a cross-coupling nucleophile. Consequently,

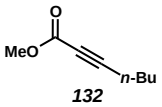
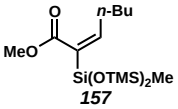
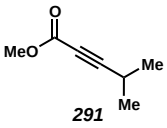
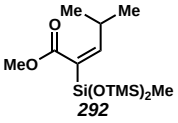
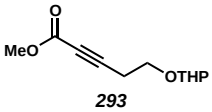
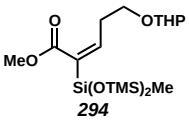
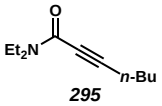
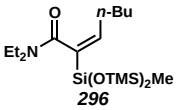
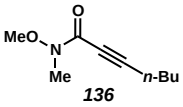
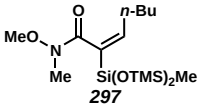
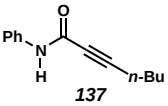
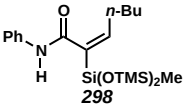
there have been very few reports of Hiyama coupling reactions that utilize electron deficient vinylsilanes.[129] With these substrates, it was crucial to develop a method that departs from the aforesaid TBAF promoted silicon activation methodology, since the addition of a hard source of fluoride could result in competitive conjugate addition or other deleterious processes with the α,β-unsaturated carbonyl substrates and thwart the desired transformation.[130]

4.4.2 Heptamethyltrisiloxane Substituted Alkenes

Because of our previous hydrosilylation and successful subsequent cross-coupling reactions, we began further studies using the vinyl heptamethyltrisiloxane[131] moiety, and in short order, we arrived at six vinylsilanes.

Table 4.4.1 Hydrosilylations of ynoates and ynamides with $HSi(OTMS)_2Me$



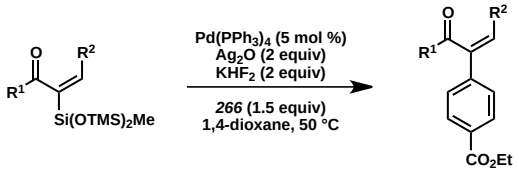
entry	substrate	product	time (h)	yield (%)	regioselectivity ($\alpha\beta$)[a]
1	 ***132***	 ***157***	4	98	16 : 1
2	 ***291***	 ***292***	7	75	>19 : 1
3	 ***293***	 ***294***	3	94	11 : 1
4	 ***295***	 ***296***	24	81	>19 : 1
5	 ***136***	 ***297***	24	98	>19 : 1
6	 ***137***	 ***298***	24	94	>19 : 1

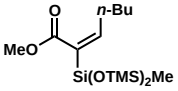
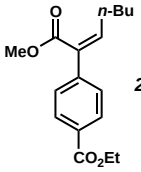
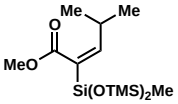
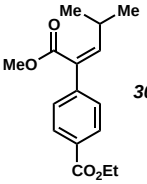
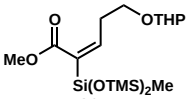
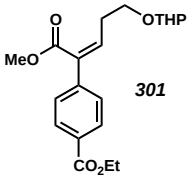
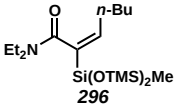
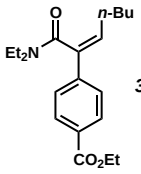
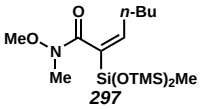
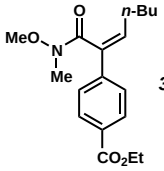
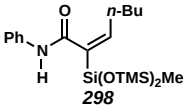
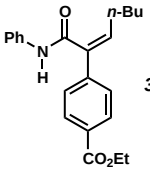
a) Measured by ^1H NMR

These six substrates were then subjected to cross coupling conditions.[132] Many non-fluoride bases were screened without sucess until we came across Ag_2O, which finally promoted the desired reaction. Upon optimization, the best conditions were found to be $Pd(PPh_3)_4$ (5 mol %) and Ag_2O (2 equiv) to couple **157** and 4-iodoanisole in a 30% yield. We hypothesized that maybe a very mild fluoride reagent would facilitate the coupling without any negative side reactions. A mild and inexpensive source of fluoride could potentially assist in silyl ether cleavage, forming an activated silyloxy species that can perform the intended transformations.

Ultimately, we settled on KHF_2 as an effective additive. With a reliable set of conditions in hand, we performed cross coupling reactions with these vinylsilanes and 4-iodoethylbenzoate (**266**). Varying alkene substitution did not affect the transformation. The distal THP group in enoate **294** was not cleaved under the reaction conditions. Varying amide substitution did not affect the yields (Table 4.4.2, Entries 4-6). All of these couplings proceeded in good to excellent yield.

Table 4.4.2 Screen of different vinyl heptamethyltrisiloxane coupling reactions

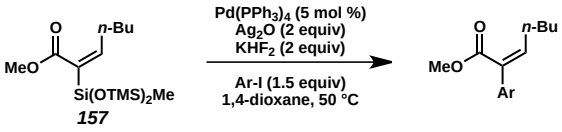


entry	substrate	product	time (h)	yield (%)
1	 *157*	 *299*	17	97
2	 *292*	 *300*	22	90
3	 *294*	 *301*	6	91
4	 *296*	 *302*	3.5	81
5	 *297*	 *303*	6	88
6	 *298*	 *304*	13	85

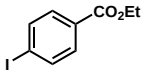
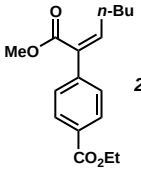
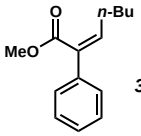
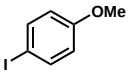
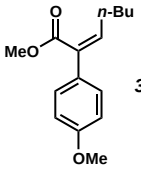
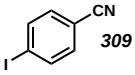
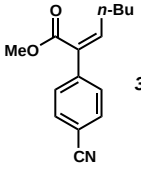
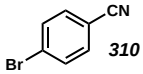
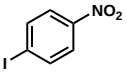
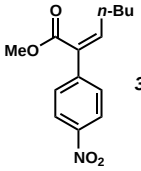
To demonstrate the generality of our prescribed cross-coupling conditions, we evaluated the coupling of several of aryl iodides and bromides to methyl enoate **157**. The reactions proceeded

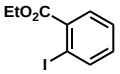
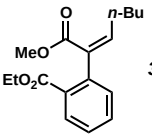
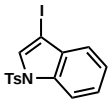
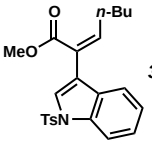
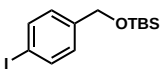
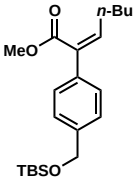
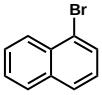
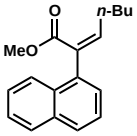
in good to excellent yields. Electron rich aryl iodides, indoles, hindered aryl iodides, and aryl bromides were all well tolerated under a uniform set of reaction conditions.

Table 4.4.3 Hiyama couplings based on enoate **157**



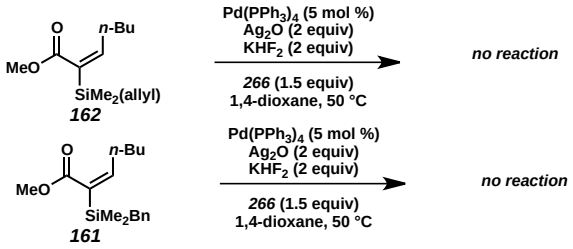
157

entry	Ar-I	product	time (h)	yield (%)
1	 266	 299	17	97
2	 205	 306	17	81
3	 307	 308	12	86
4	 309	 311	8	81
5	 310		12	93
6	 312	 313	12	88

entry	Ar-I	product	time (h)	yield (%)
7	 314	 315	22	59
8	 316	 317	7.5	62
9[a]	 318	 319	18	86
10[a]	 320	 321	60	69

a) Reaction temperature: 100 °C

Heteroatom substitution on silicon is indeed necessary for this transformation to take place. Allyl- and benzyldimethyl vinylsilanes **161**, and **162**, were completely unreactive under our KHF_2/Ag_2O promoted silicon activation conditions, suggesting that these silanes require a harder source of fluoride such as TBAF that would also initiate decomposition of the starting material.

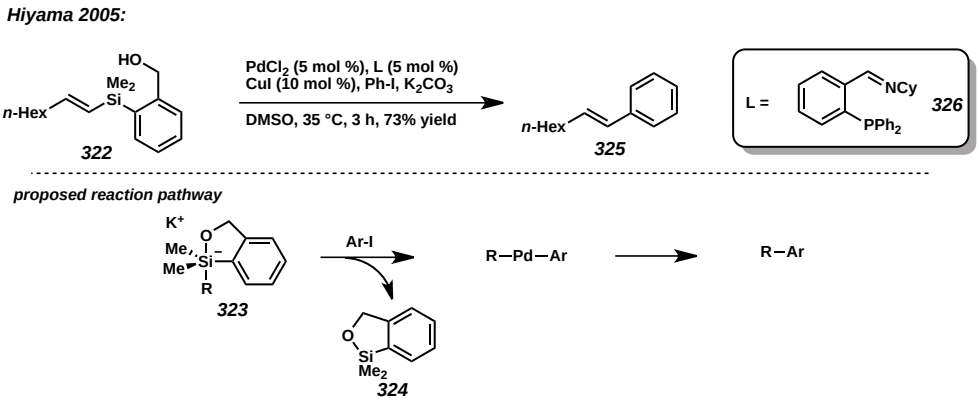


Scheme 4.4.1 Intramolecular silicon activation background

4.4.3 Intramolecular Silicon Activation

Although the KHF_2/Ag_2O promoted cross-coupling reactions worked well and were mild enough to tolerate a number of different functionalities, some reaction yields were modest and all still required a source of fluoride, albeit mild. Consequently, we felt the need to further pursue fluoride-free conditions. As previously described in this chapter, fluoride-free activation of highly stable vinylsilane moieties, such as tetraorganosilanes, is difficult. Nevertheless, there have been a couple of examples reported in the literature that can accomplish this.

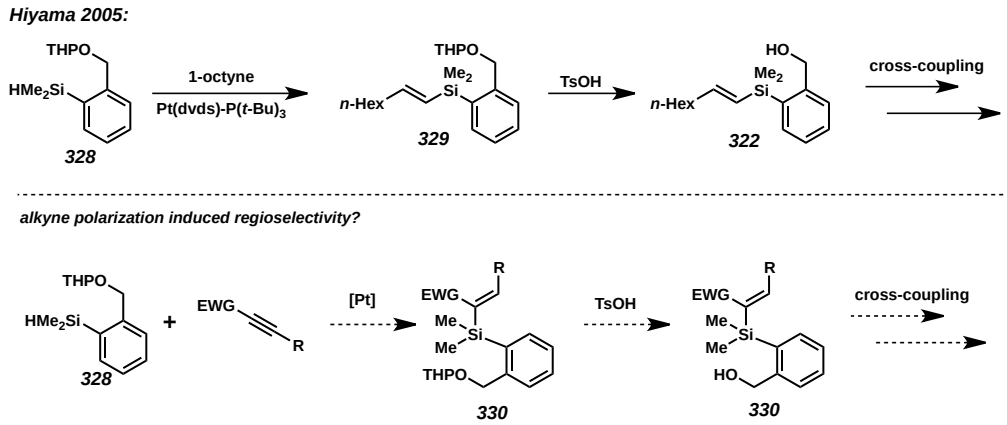
A 2005 report by Nakao, Hiyama and co-workers employed a (2-hydroxymethyl)-phenylsilane (**322**) moiety that can be simply activated under mild conditions and will undergo cross-coupling reactions.[133] In these systems, exogenous base facilitates the formation of a pendant alkoxide, which then enables an intramolecular attack of the silicon. The resulting pentacoordinate species (**323**) can likely undergo the transmetalation step in the desired cross-coupling reactions. They were able to isolate cyclic silyl ether **324** as further evidence that the reaction proceeds through pentacoordinate silicon **323**.



Scheme 4.4.2 Hiyama's (2-hydroxymethyl)phenylsilane cross coupling protocol

4.4.4 Initial Studies

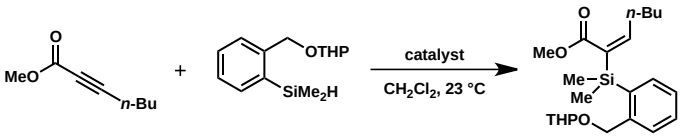
Many of the (2-hydroxymethyl)phenylvinylsilane substrates used by Hiyama were prepared via hydrosilylation of terminal or symmetrical internal alkynes. Since we had already shown highly regioselective internal alkyne hydrosilylations using phenyldimethylsilane, we surmised (2-hydroxymethyl)phenylsilane (**327**) or some derivative thereof would be amenable to our internal alkyne hydrosilylation methodology. Although Hiyama noted that hydroxysilane **327** spontaneously cyclizes to silyl ether **324**, which cannot take part in hydrosilylation reactions, they found acetate or THP- based protecting groups prevented the cyclization event.



Scheme 4.4.3 Regioselective installation of **328**

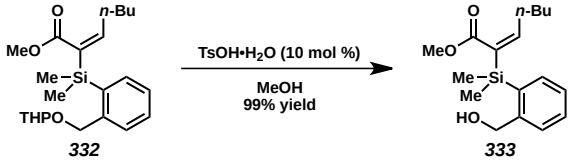
To that end, we began to investigate hydrosilylation conditions for the addition of silane **328** across methyl-2-heptynoate (**132**). Using our primary conditions described in chapter 3 (5 mol % $PtCl_2$, 1.1 equiv silane, CH_2Cl_2, 23 °C) resulted in decomposition of ynoate **132** and no observable yield of the desired product. Ziese's dimer ($[(C_2H_4)PtCl_2]_2$) did effect the hydrosilylation, albeit in only 56% yield and 7.5:1 α/β selectivity. In the case of these Pt(II) catalysts, the induction period to generate the active catalyst likely generates adventitious HCl, which can decompose the acid labile THP-protected alcohol in **328**.[134] This is shown by the formation of the same cyclic silyl ether **324** as shown in Scheme 4.4.2. Employing Pt(dvds) (1 mol %), which is zerovalent and also absent of the chloride counterion, provided a substantial improvement in the reaction yield (94% yield, 9:1 α/β). Halving catalyst loading increased the selectivity to 11:1 with only a slight decrease in yield.

Table 4.4.4 Hydrosilylation/deprotection of ynoate **132** with silane **328**



132 ***328*** ***332***

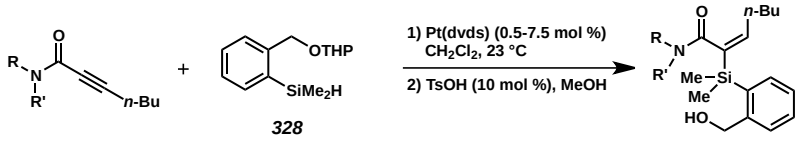
entry	catalyst (mol % Pt)	time (h)	yield (%)	regioselectivity (α : β)
1	$PtCl_2$ (5)	96	--	--
2	$[(C_2H_4)PtCl_2]_2$ (2)	23	56	7.5 : 1
3	Pt(dvds) (1)	26	94	9 : 1
4	Pt(dvds) (0.5)	30	92	11 : 1



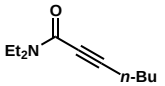
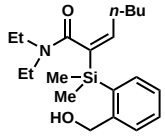
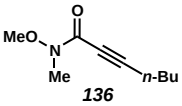
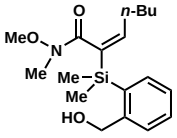
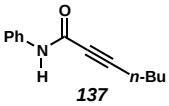
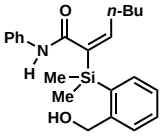
332 ***333***

With a reliable set of conditions in hand, the hydrosilylations and subsequent deprotection sequences using silane **328** and ynamides **295**, **136**, and **137** were performed.

Table 4.4.5 Ynamide hydrosilylations with silane **328**



328

entry	substrate	product		yield (%)	regioselectivity (α : β)[a]
1	 ***295***		***334***	76	>19 : 1
2	 ***136***		***335***	73	>19 : 1
3	 ***137***		***336***	89	15 : 1

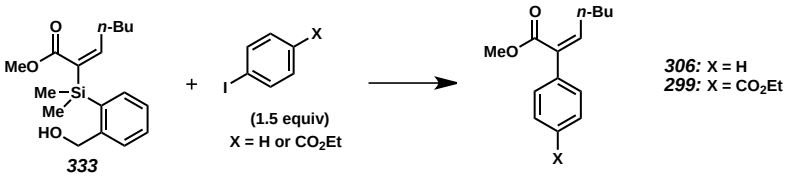
a) measured by ^1H NMR

These vinylsilanes can also be prepared in a one-pot sequence from starting material alkyne. The hydrosilylations of **132** and **137** were performed under our standard Pt(dvds) catalyzed conditions. Upon consumption of starting material a majority of CH_2Cl_2 was simply removed and replaced with MeOH and catalytic TsOH (10 mol %). This sequence afforded almost identical yields to the total yields of the respective two-pot sequences.

4.4.5 Fluoride Free Cross Coupling Reactions

With a number of (2-hydroxymethyl)phenylsilyl-alkenes in hand, we chose to evaluate intramolecular silicon activation conditions. As a logical starting point, Hiyama's reported conditions were tested and expanded upon with varying results (Table 4.4.6). Hiyama's original conditions were ineffective[133] (Entry 1). In our TBAF promoted reactions (*vide supra*) additional H_2O was beneficial, but in this case was disadvantageous. Many other bases and condition sets were screened, with limited success. This was until we again turned to Ag_2O as a base, where we found using 1.1 equivalents of Ag_2O and 5 mol % $Pd(PPh_3)_4$ showed incredibly clean conversion to the desired coupled product **299**. Upon scale-up the isolated yield was found to be 76%. Efforts to improve the yield showed that increasing the amount of Ag_2O also helped improve conversion, with a 92% yield being obtained when 2 equivalents of the silver base were used (entry 7). Again, H_2O was not beneficial, but in this case was not detrimental to reaction progress.

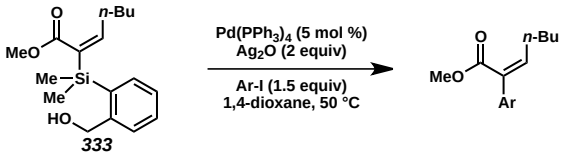
Table 4.4.6 Optimization of intramolecular silicon activation/Hiyama coupling

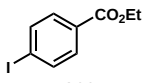
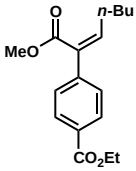
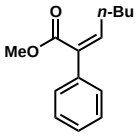
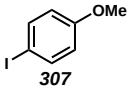
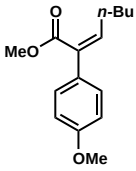
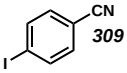
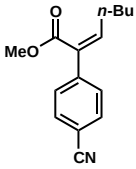
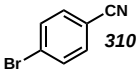
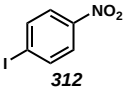
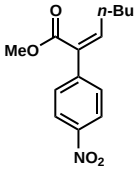
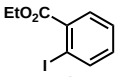
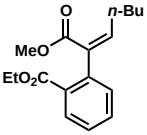
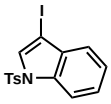
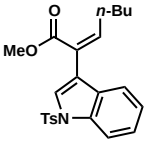
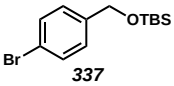
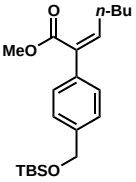
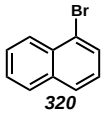
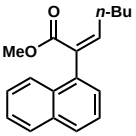
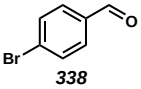
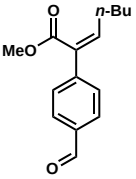


entry	Ar	catalyst (mol %)	additive(s) (equiv)	solvent, temp (°C)	time (h)	yield (%)
1	Ph	$PdCl_2$ (5) $P(2\text{-fur})_3$ (10)	K_2CO_3 (2.0)	DMSO, 50	24	0
2	Ph	Pd_2dba_3 (2.5)	CuI (0.1) K_2CO_3 (2.0) H_2O (5.0)	THF, 60	24	0
3	Ph	Pd_2dba_3 (2.5)	CuI (0.1) K_2CO_3 (2.0)	THF, 60	24	55
4	CO_2Et	$Pd(PPh_3)_4$ (5)	K_2CO_3 (2.0)	THF, 50	16	0
5	CO_2Et	$Pd(PPh_3)_4$ (5)	Ag_2O (1.1)	THF, 50	8	76
6	CO_2Et	$Pd(PPh_3)_4$ (5)	Ag_2O (1.5)	THF, 50	8	85
7	CO_2Et	$Pd(PPh_3)_4$ (5)	Ag_2O (2.0)	1,4-dioxane, 50	4	92
8	CO_2Et	$Pd(PPh_3)_4$ (5)	Ag_2O (2.0) H_2O (5.0)	1,4-dioxane, 50	8	85

Confident that we had found a reliable set of conditions, we set out to screen an array of aryl halide electrophiles. As with the vinyl siloxane (**157**), a wide variety of electrophiles were found to be highly tolerated. Notably, these reactions generally required less time and achieved higher isolated yields when compared to the reactions with siloxane **157**. The reaction using aryl bromide **227** as the cross coupling electrophile was achieved in 91% yield although the reaction required more elevated temperature (100 °C). Conversely, the same reaction with **337** and vinyl siloxane **157**, did not proceed, even at 100 °C; the transformation did occur with the corresponding aryl iodide **318** (Table 4.4.7, Entry 9). Also 4-bromobenzaldehyde (**338**) was found to be a competent cross coupling electrophile. The same aryl bromide decomposed in the similar reaction with vinylsiloxane **157**, demonstrating the mildness of the intramolecularly activated silane species.

Table 4.4.7 Hiyama couplings based on enoate **333**

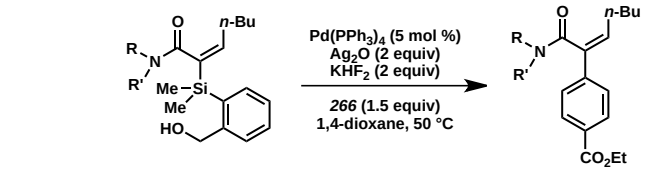


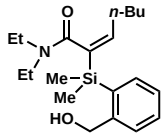
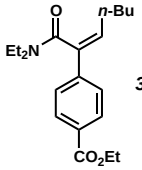
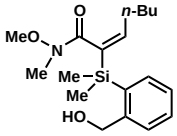
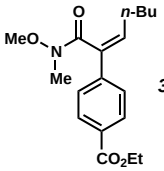
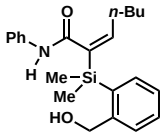
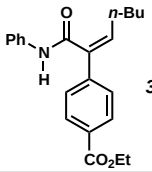
entry	Ar-I	product	time (h)	yield (%)
1	 *266*	 *299*	8	92
2	 *305*	 *306*	8	90
3	 *307*	 *308*	2	89
4	 *309*	 *311*	8	96
5	 *310*		12	78
6	 *312*	 *313*	3	79
7	 *314*	 *315*	0.75	92
8	 *316*	 *317*	2	95
9[a]	 *337*	 *319*	20	91
10	 *320*	 *321*	24	65
11	 *338*	 *339*	3	74

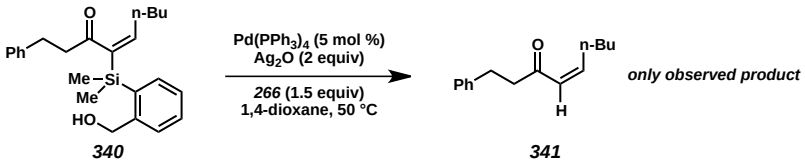
a) reaction temperature: 100 °C

Additionally, we performed the Hiyama coupling reactions with the three α,β-unsaturated amide vinylsilanes outlined in Scheme 4.4.4. For the sake of uniformity, we initially subjected these vinylsilanes to conditions identical to those used in Table 4.4.7. To our delight, all three vinylsilanes, bearing secondary, tertiary, and Weinreb amides, were excellent Hiyama coupling nucleophiles, with isolated yields over 90%. Excited by this consistently high reactivity using vinylsilanes derived from silane **328** we again attempted cross coupling with an enone substrate

(**340**). Unfortunately, all reactions using **340** as a nucleophile were unsuccessful. In this case, enone **340** is too electron deficient to efficiently transmetalate to a Pd intermediate. Consequently, protodesilylation to alkene **341** is the only viable pathway.



entry	substrate	product	time (h)	yield (%)
1	 *342*	 *343*	16	97
2	 *344*	 *345*	3	91
3	 *346*	 *347*	18	91



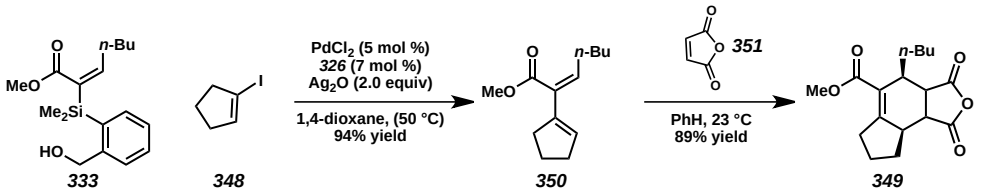
Scheme 4.4.4 Further cross coupling studies

In comparing the two methods for cross-coupling α-silylenoates and enamides we find clear advantages and disadvantages for both. The first method described utilizes an inexpensive robust silicon species, the heptamethyltrisiloxane. Yields were good, and conditions were relatively mild in these reactions. Conversely, the second method described utilized a more

complex silicon species (**328**) that is readily prepared but is not yet commercially available. Yields were generally excellent, even better than the heptamethyltrisiloxane substituted alkenes. Reaction conditions were also more mild since exogenous fluoride was unnecessary, and the transformations generally took less time.

4.4.6 Sequential Cross-Coupling/Cycloaddition Sequence

To show further synthetic utility of these Hiyama coupling reactions, we designed a simple two-step sequence that rapidly generates molecular complexity under very mild conditions. To achieve a high yield of the cross coupling with vinyl iodide **348**, a slightly different set of conditions were needed. Namely, the catalyst system was very similar to what Hiyama originally reported using the (2-hydroxymethyl)phenylsilane species ($PdCl_2$ (5 mol %), ligand **326** (7 mol %)); the activator, solvent, and temperature did not differ from our optimized conditions (Ag_2O (2 equiv), 1,4-dioxane, 50 °C). Subjecting the product diene to maleic anhydride in PhMe at room temperature afforded tricycle **349** resulting from the Diels-Alder cycloaddition. This method easily sets the stereochemistry for a highly substituted alkene which can be further translated to the diastereoselective cycloaddition.

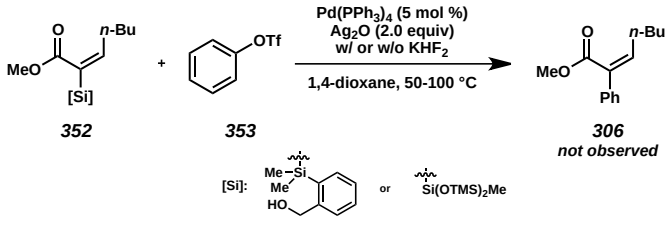


Scheme 4.4.5 Alkenyl iodide coupling/cycloaddition

4.4.7 The Role of Silver Oxide as a Hiyama Coupling Promoter

As is apparent from the above transformations, silver plays a crucial role in the success of these Hiyama cross-coupling reactions. There have been numerous accounts of Ag promoted reactions for Stille and Suzuki cross-coupling reactions.[135] In the absence of silver, yields were only modest at best (see Table 4.4.6). Although not confirmed, we consider silver to facilitate multiple processes during the transformation. The halophilic silver ion may help ionize the Pd-X bond that arises from the initial oxidative addition step. The Pd metal center would be rendered more cationic and thus more susceptible to transmetalation with the activated vinylsilicon species. Alternatively, the activated silicon species could directly transfer the pendant vinyl group to silver, and the organosilver could, in turn, transmetalate with the Pd(II) species.

Specifically, Ag_2O has been utilized several other times in the context of Hiyama couplings. Hiyama was the first to realize the benefits of Ag_2O for the cross-coupling of aryl silanols. Other Ag(I) salts such as AgOTf and $AgNO_3$ effected the coupling in significantly diminished yield. They also noted the privileged nature of the silver ion as their screen of other metal oxides resulted in zero conversion.[136] Yoshida and co-workers invoked a tridentate coordinated Ag_2O promoted activation of (2-pyridyl)allyldimethylsilanes.[137] We do not believe our reactions enter this sort of coordination manifold, however, as demonstrated in Scheme 4.4.6. The cross coupling reactions do not work with aryl triflate electrophiles, suggesting that the formation of solid AgX products may help drive the Ag_2O promoted reactions forward.



Scheme 4.4.6 Attempted Hiyama couplings with phenyl triflate

4.5 Summary of Hiyama Coupling Studies

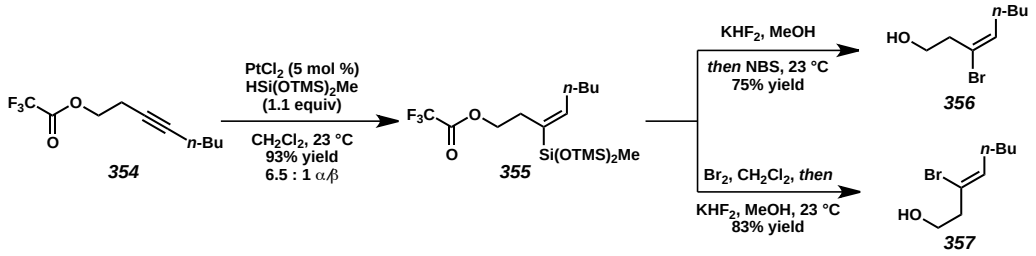
In summary, we have demonstrated a number of Hiyama cross-coupling reactions that highlight the utility of our Pt catalyzed 1,2-silicon migration reaction as well as our regioselective internal alkyne hydrosilylation protocol. In our studies we began with silicon species that required harsh activation conditions resulting from the additive TBAF. Deleterious side reactions occurred due to the highly nucleophilic F^-. This severely limited the substrate scope, and we sought to employ more mild conditions. Ultimately we found silver oxide to be an efficient mild promoter of the Hiyama coupling and subsequently were able to perform efficient cross-couplings with α-silyl-α,β-unsaturated amides and esters.

4.6 Halodesilylation Reactions

4.6.1 Halodesilylation Reactions of Electron Rich Alkenes

Chapter 3 described the powerful effect that alkyne polarization can have on the regioselectivity of their respective hydrosilylation reactions. This effect is so pronounced that homopropargyl alcohols with strong electron withdrawing effects can influence selectivity enough to produce synthetically useful product distributions. To demonstrate this, trifluoroacetate protected homopropargyl alcohol **354** was subjected to our standard hydrosilylation conditions (5 mol % $PtCl_2$, CH_2Cl_2 (0.2 M), 23 °C) in the presence of $HSi(OSiMe_3)_2Me$. This reaction afforded a 93% yield and 6.5:1 α/β selectivity of alkene **355**. These vinylsilanes can then be converted to their halogenated counterparts. Kumada has reported two similar sets of conditions to bromodesilylate trialkoxyvinylsilanes with either stereoretention or inversion.[138] Subjecting silylalkene **355** to KHF_2 in MeOH at 23 °C followed by addition of NBS gave stereoretentive bromodesilylation in 75% yield (**356**). To achieve stereoinversion, **355** was first treated with Br_2

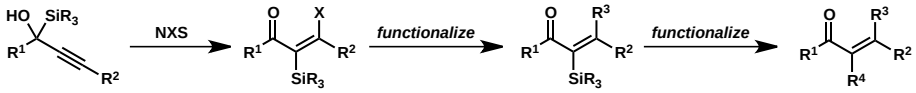
followed by KHF_2 affording an 83% yield of the bromoalkene **357**. In both cases, the trifluoroacetate is cleaved from the respective primary alcohols.



Scheme 4.6.1 Stereoretentive and stereoinverted bromodesilylations

4.6.2 Halodesilylation Reactions and Application to Synthesis

In Chapter 2, a novel 1,2-silicon migration reaction, promoted by *N*-halosuccinimides, was described. Since the net halosilylation of the alkyne is an inherently *trans*- addition, the resulting product is a stereodefined tetrasubstituted olefin. The pendant silicon and halogen moieties provide useful synthetic handles with which orthogonal functionalizations can occur to ultimately form all-carbon stereodefined tetrasubstituted alkenes.



Scheme 4.6.2 Synthetic utility of halosilylation reactions

4.6.3 Tetrasubstituted Alkenes

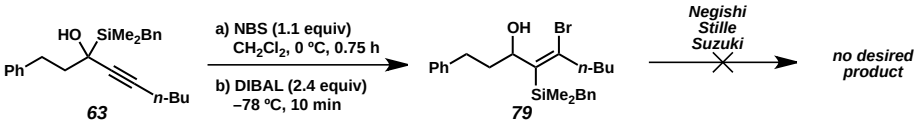
The regiocontrolled and stereoselective synthesis of all-carbon tetrasubstituted alkenes is a demonstrated challenge in organic synthesis.[139] The hindered nature of the alkene carbons can lead to deviations in traditional reactivity, rendering many functionalization techniques useless. Nevertheless, synthetic and theoretical chemists are attracted to these structural elements. Due to many of the destabilizing interactions of these congested alkenes, tetrasubstituted olefins can

often demonstrate unique structural, physical, and electronic features.[140] When the alkene is endocyclic, stereochemistry is rather straightforward to control.[141] Conversely, the generation of acyclic polysubstituted alkenes lacks the tethered control element and thus can be difficult to generate regio- and stereoselectively. Traditional methods for alkene synthesis such as Wittig-type reactions, eliminations and metathesis can become cumbersome and unselective when extended to generating hindered polysubstituted, acyclic alkene systems. Carbometalation reactions onto alkyne substrates have come to the forefront of acyclic tetrasubstituted olefin synthesis because the addition is mechanistically *cis*.[142] However, within these systems, issues such as addition regiocontrol, metal selection, and substrate tolerance can present further problems. Thus new methods of all-carbon, tetrasubstituted alkenes can prove highly useful. Our aforementioned alkyne halosilylation methodology, with its regioselective 1,2-silicon migration and stereoselective *trans* addition, is a potentially elegant solution that can complement existing methodology.

With the tremendous help of Dr. Nick Barczak, we were able to generate a number of α-silyl-β-haloenones from α-hydroxypropargylsilanes.[143] With his departure, I regained control of the project and was charged with the task of discovering a means to render the product α-silyl-β-haloenones useful. Our original idea for these systems was to perform a Suzuki-type cross coupling on the vinyl halide. Next we would attempt to activate the silicon and perform the Hiyama cross coupling, to afford an all-carbon, tetrasubstituted alkene.

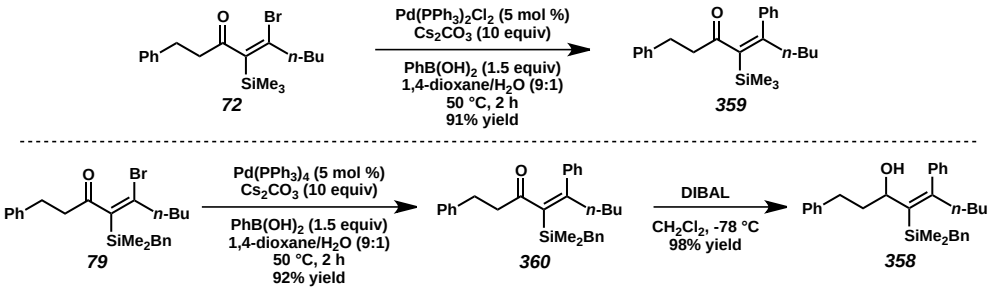
4.6.4 Initial Studies

Because of our previous work on exploring the utility of α-silyl enones, we understood that the tetraorganosilane would require a fluoride activator with the strength of TBAF and thus, the α,β-unsaturated carbonyl moiety would be incompatible. In order to save a step, we simply performed an in situ DIBAL reduction after the halosilylation step. The resulting vinyl halides were subjected to Suzuki, Stille, and Negishi coupling conditions. Unfortunately, all attempts resulted in either alkene isomerization or elimination of the silyl halide to afford a propargylic alcohol.



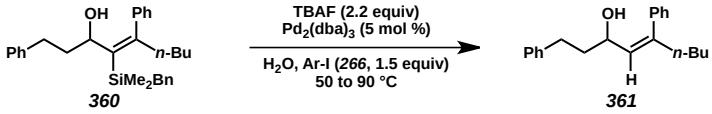
Scheme 4.6.3 Attempts at cross coupling allylic alcohol tetrasubstituted alkenes

We hypothesized that the α-silyl alcohol may present a problem for the cross-coupling reactions. Upon returning to the α-silyl-β-haloenone substrates, we again found success. Subjecting α-silyl-β-bromoenone **72** to relatively basic Suzuki conditions ($Pd(PPh_3)_4$ (5 mol %), Cs_2CO_3 (10 equiv), $ArB(OH)_2$, 1,4-dioxane/H_2O) gave efficient conversion to the cross-coupled product. At that point we still imagined carrying out a subsequent Hiyama coupling reaction, so the benzyldimethylsilyl derivative (**79**) was carried through these steps and subsequently reduced with DIBAL in high yield to afford an α-silyl allylic alcohol (**358**).



Scheme 4.6.4 First successful cross couplings of α-silyl-β-haloenone substrates

Excited by these successes, we pushed forward by attempting the subsequent TBAF promoted Hiyama coupling step. Unfortunately, all our attempts at the silicon cross-coupling reactions were met with failure; protodesilylation appeared to be the major product for every attempt.



Scheme 4.6.5 Protodesilylation arising from fluoride promoted Hiyama coupling conditions

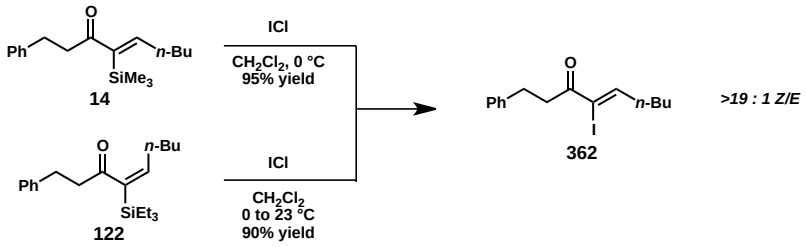
The only difference in these systems as compared to our original reports on Hiyama coupling (Scheme 4.3.4) is the additional phenyl group attached to the alkene. The additional aromatic group likely renders the activated vinylsilicon species not sufficiently nucleophilic to undergo the transmetalation step in the Hiyama coupling sequence. Consequently, we decided to take a different approach in order to render the C-Si bond synthetically useful.

4.6.5 Iododesilylation Strategy

Early on in our studies of α-silylenones, we came across a report by Negishi and Alimardanov that showed an iododesilylative ipso-substitution of similar substrates.[144] If this method were to work with our systems with high stereoretention, we felt the product α-iodoenones would be

potent electrophiles for cross-coupling reactions, and would further demonstrate the synthetic utility of our methodology to efficiently produce vinyl silanes. Furthermore, inexpensive, highly stable silicon species, such as the trimethylsilyl group, can be used for this transformation, which would allow for the departure from the more expensive benzyldimethylsilyl group.

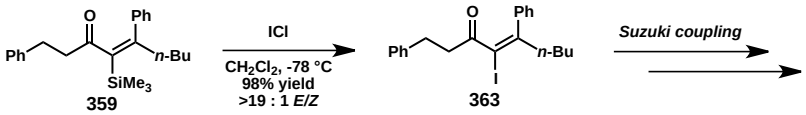
To that end, we subjected (*E*)- and (*Z*)- trisubstituted vinylsilanes **14** and **122** to Negishi's prescribed iododesilylation conditions (ICl (2 equiv), CH_2Cl_2, 0 °C). Efficient conversion was observed for both substrates, however, it was noticed that both reactions afforded the same (*Z*)-alkene **362**. This informed us that isomerization can occur under these conditions and that care must be taken to suppress any undesired isomerization.



Scheme 4.6.6 Iododesilylation of trisubstituted olefins

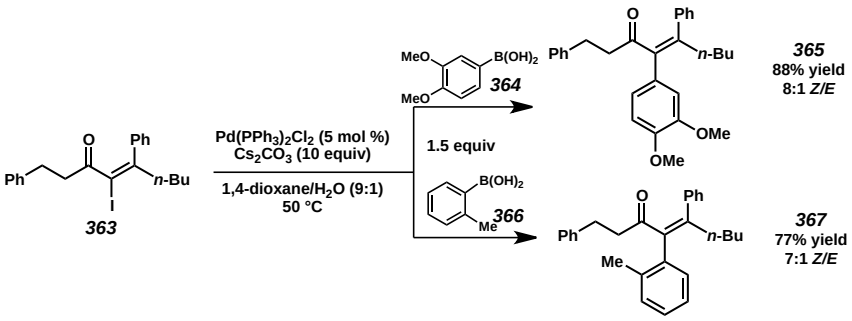
Although we were a bit discouraged by the olefin isomerization for the iododesilylation of trisubstituted olefins, we were also running out of options for vinylsilane utilization through a Hiyama protocol toward tetrasubstituted alkenes. We surmised that the tetrasubstituted systems, with their added congestion, would have a higher barrier of rotation and perhaps allow for retention of olefin stereochemistry. Tetrasubstituted alkene **359** was subjected to ICl at 0 °C. The starting material was completely consumed by the first TLC of the reaction mixture (5 min). Upon workup, it was found that the iododesilylation occurred efficiently, but isomerization occurred, affording a 1:1 mixture of (*E*)- and (*Z*)-isomers. Since the reaction was incredibly fast at 0 °C, we thought it may also occur at lower temperatures and perhaps with stereoretention.

Indeed this was the case, and when **359** was subjected to ICl in CH_2Cl_2 at -78 °C, starting material was consumed in less than 10 min. The crude product showed no observable olefin isomerization, giving analytically pure α-iodoenone **363,** which we could potentially use as an electrophile for future Suzuki cross-coupling reactions.[145]



Scheme 4.6.7 Stereoretentive iododesilylation

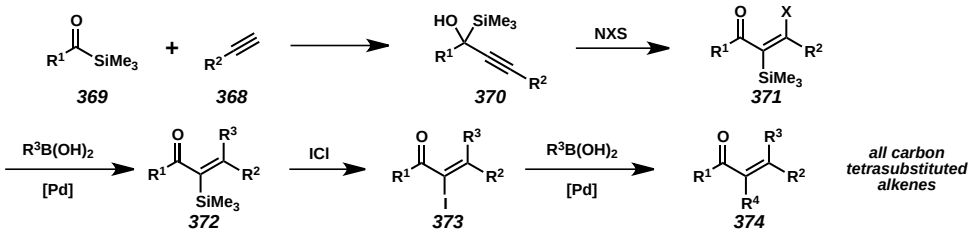
We were able to use the same basic Suzuki cross coupling conditions we used previously ($(Pd(PPh_3)_2Cl_2$ (5 mol %), Cs_2CO_3 (10 equiv), $ArB(OH)_2$, 1,4-dioxane/H_2O). Using 3,4-bismethoxy-phenylboronic acid (**364**) as a coupling partner afforded clean conversion to the all-carbon tetrasubstituted alkene (**365**, 88% yield). The less active, more hindered 2-tolyl-phenylboronic acid (**366**) also worked efficiency (**367**, 77% yield). The ability to use multiple cross-coupling nucleophiles shows potential utility for divergent syntheses of complex molecules. These unoptimized reactions both proceeded with decent stereoretention. Likely, with further optimization, conditions could be found for the cross-couplings that do not isomerize the alkene at all.



Scheme 4.6.8 Suzuki couplings of iodoenone **363**

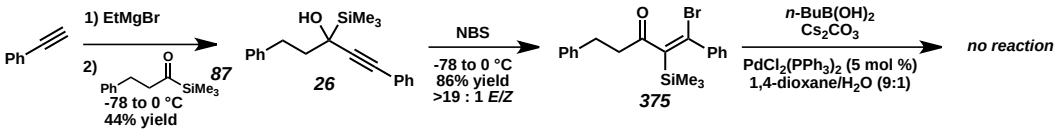
4.6.6 General Modular Approach to Tetrasubstituted Alkenes

We ultimately envisioned this methodology as a modular entry into a vast array of tetrasubstituted alkenes. Current methods lack the control to select for either the (*E*)- or (*Z*)-isomer. Our designed sequence allows for a formal 4-component coupling with judicious choice of starting materials. First R^1 and R^2 are introduced with alkyne (**368**) addition into an acylsilane (**369**) to form an α-hydroxypropargylsilane (**370**). Then compound **370** can be subjected to our halosilylation conditions, affording an α-silyl-β-haloenone (**371**). Using the silyl migration as a key step for establishing geometrical control, we envisioned having the ability to synthesize complementary (*E*)- and (*Z*)-alkene isomers. This highly functionalized alkene can then be subjected to our Suzuki coupling, iododesilylation and final Suzuki coupling to install R^3 and R^4.



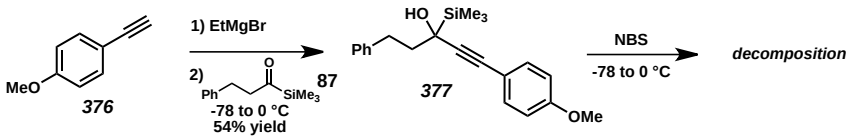
Scheme 4.6.9 Modular approach to tetrasubstituted alkene synthesis

We felt the best way to highlight the utility of this sequence was to access the *E* and *Z* isomers of a single tetrasubstituted alkene. Since we had made alkenes **365** and **367** already, we anticipated that we could synthesize their respective olefin isomers. To accomplish this, phenylacetylene was added into an acylsilane (**87**) to form α-hydroxypropargylsilane **26**. Of note, the yields for aryl acetylene Grignard additions can be somewhat lower than those with non-aryl acetylenes. This can likely be attributed to the added stability of the carbanion resulting from the Brook rearrangement. With optimization, one may likely find conditions to further avoid the undesired Brook pathway. Nonetheless, alkyne **26** was subjected to our halosilylation conditions affording good yield and selectivity for α-silyl-β-bromoenone **375** (86% yield, >19:1 *E/Z*). We then hit a roadblock with the alkyl boronic acid Suzuki coupling. Rather than finding conditions to install the alkyl group, we decided to turn to an all aryl boronic acid cross-couplings.



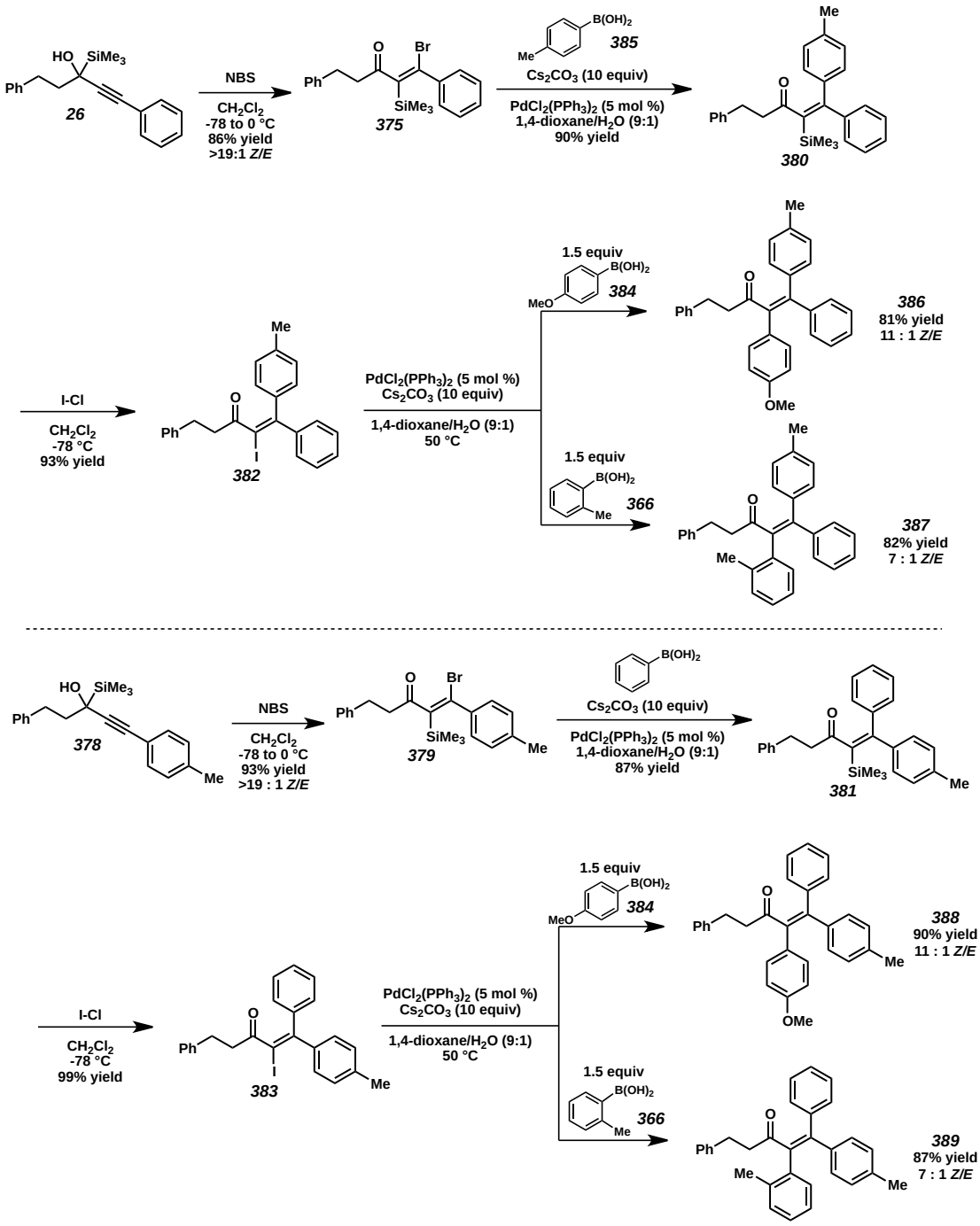
Scheme 4.6.10 Failed alkylboronic acid Suzuki coupling

Again a different course was needed. Aryl acetylene **376** was added to acylsilane **87** to afford α-hydroxypropargylsilane **377**. Unfortunately, we were met with failure when we found that the halosilylation reaction was incompatible with the electron rich aromatic ring.



Scheme 4.6.11 Incompatible NBS halosilylation

We then decided to pursue what proved to be a successful sequence. α-Hydroxypropargylsilanes **26** and **378** were successfully subjected to our designed modular sequence. For each silane, an NBS mediated halosilylation reaction occurred efficiently to form α-silyl-β-bromoenones **375** and **379**. Subsequent Suzuki couplings gave α-silylenones **380** and **381**, which are also alkene isomers of each other. These substrates were then subjected to iododesilylation conditions to give the final Suzuki coupling electrophiles (**382** and **383**). Finally, cross-coupling iodides **382** and **383** with aryl boronic acids **384** and **366** afforded two sets of complementary pairs of alkene isomers. These isomeric, acyclic tetrasubstituted alkenes would be otherwise difficult to access via standard olefination methods. The modularity of this approach also lends itself to the rapid generation of numerous, highly hindered alkenes.



Scheme 4.6.12 Selective formation of alkene isomers

4.7 Conclusion

From our methods describing silicon migrations to our regioselective internal alkyne hydrosilylation reactions, we have demonstrated facile access to a vast array of tri- and tetrasubstituted alkenes. In this chapter, we have shown a number of different cross-coupling based methods with which our product vinyl silanes can be utilized for the syntheses of highly substituted, all-carbon, single alkene isomers.

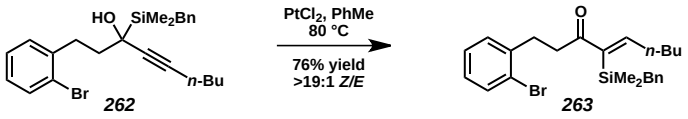
4.8 Experimental Section

4.8.1 Materials and Methods

All glassware was flame-dried prior to use. All reactions were performed under an argon atmosphere. Tetrahydrofuran (THF), ether (Et_2O), and dichloromethane (CH_2Cl_2) were degassed with argon then passed through 2 columns of anhydrous neutral A-2 alumina. Qualitative TLC analysis was performed on 250 mm thick, 60 Å, glass backed, F254 silica (Silicycle, Quebec City, Canada). Visualization was accomplished with UV light and exposure to either *p*-anisaldehyde or $KMnO_4$ stain solutions followed by heating. Flash chromatography was performed using Silicycle silica gel (230-400 mesh). ^1H NMR spectra were acquired on either a Varian Mercury 300 (at 300 MHz), a Varian Inova 400 (at 400 MHz), or a Varian 400 MR (at 400 MHz) and are reported relative to $SiMe_4$ (δ 0.00). ^{13}C NMR spectra were acquired on either a Varian Inova 400 (at 100 MHz), a Varian Mercury 300 (at 75 MHz), or a Varian 400 MR (at 100 MHz) and are reported relative to $SiMe_4$ (δ 0.0). All IR spectra were obtained on NaCl plates (film) with a Bruker Tensor 27. High resolution mass spectrometry data were acquired by the Colorado State University Central Instrument Facility on an Agilent 6210 TOF LC/MS.

4.8.2 Proceedures for 4.2 TBAF Promoted Hiyama Coupling Reactions

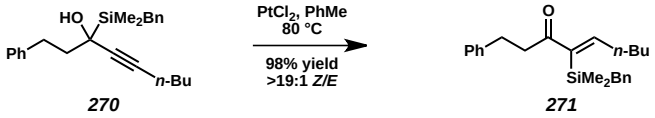
General procedure for platinum catalyzed rearrangement of α-hydroxypropargylsilanes. To an α-hydroxypropargylsilane in toluene (0.1 M) under argon was added $PtCl_2$ (5 mol %), and the reaction flask was placed in an 80 ℃ oil bath. The mixture was allowed to stir, turning brown, until the starting material was consumed as determined by TLC. The mixture was then diluted with Et_2O (~ 1.5x reaction volume) and filtered through silica gel, further rinsing with Et_2O (~ 3x reaction volume). The solvents were removed via rotary evaporation, and the resulting brown oil was purified by silica gel flash chromatography. If a mixture of enone isomers were present, the enones were generally inseparable and therefore isolated as a mixture.



Alkene 263: According to the general procedure, α-hydroxypropargylsilane **262** (209 mg, 0.561 mmol), toluene (5.6 mL), and platinum (II) chloride (7.5 mg, 0.028 mmol) were stirred under an atmosphere of argon for 1.25 h. Upon reaction completion, as judged by TLC (9:1 Hexanes/EtOAc), Et_2O was added and the mixture was filtered through a plug of silica gel. Further purification by flash chromatography (39:1 hexanes/EtOAc) afforded a colorless oil (**263**, 159 mg, .390 mmol, 76% yield, >19:1 *Z/E*).

α-Silylenone 263: ^{1}H NMR (400 MHz, $CDCl_3$,) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.26-7.21 (comp m, 2H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.09-7.04 (comp m, 2H), 6.98-6.96 (m, 2H), 6.77 (t, *J* = 7.5 Hz, 1H), 3.00 (dd, *J* = 8.5, 6.8 Hz, 2H), 2.85 (dd, *J* = 8.5, 6.8 Hz, 2H), 2.29 (s, 2H), 2.07-2.01 (m, 2H), 1.28-1.24 (comp m, 4H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 154.9, 143.4, 140.9, 140.0, 130.9, 128.2, 127.7, 124.5, 124.2, 39.8, 31.4, 31.3, 26.6, 22.6, 14.1, -0.9; IR (film) 2956, 1660, 1599, 1492, 1470, 1249, 835, 699 cm^{-1}; HRMS m/z

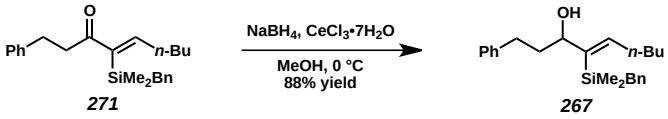
calc'd for $(M + Na)^+$ $[C_{24}H_{32}BrOSi\ Na]^+$: 427.109, found: 427.109.



270 *271*

α-Silylenone 271: According to the general procedure, α-hydroxypropargylsilane **270** (1.19 g, 3.26 mmol), toluene (15.0 mL), and platinum (II) chloride (25.1 mg, 0.0940 mmol) were stirred under an atmosphere of argon for 1.25 h. Upon reaction completion, as judged by TLC (9:1 hexanes/EtOAc), Et_2O (20 mL) was added and the mixture was filtered through a plug of silica gel then washed with more Et_2O (60 mL). Further purification by flash chromatography (39:1 to 19:1 hexanes/EtOAc) afforded **271** (1.17 mg, 98% yield, >19:1 *Z/E*) a colorless oil.

α-Silylenone 271: ^{1}H NMR (400 MHz, $CDCl_3$,) δ 7.28 (t, *J* = 7.3 Hz, 2H), 7.20-7.15 (comp m, 5H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 2.87 (app. q, 4H), 2.28 (s, 2H), 2.04 (q, *J* = 6.75 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 154.4, 143.4, 141.4, 139.8, 128.5, 128.4, 128.3, 128.1, 128.1, 126.0, 124.1, 41.4, 31.3, 30.4, 26.4, 22.4, 13.9, -1.1; IR (film) 2956, 2928, 1660, 1600, 835, 699 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{24}H_{32}OSi + Na]^+$: 387.2115, found: 387.2113.

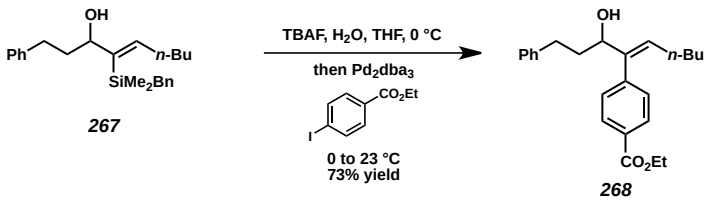


271 *267*

Vinylsilane 267: To a solution of α-silylenone **271** (1.15 g, 3.15 mmol) in methanol (15.0 mL) at 0 °C was added $CeCl_3$•$7H_2O$ (1.29 g, 3.47 mmol). Upon dissolution of the cerium salt, $NaBH_4$ (203 mg, 5.36 mmol) was added slowly. The reaction was stirred until completion (20 min) as judged by TLC (9:1 hexanes/EtOAc). Excess hydride was quenched with sat. aq. NH_4Cl (5 mL).

The mixture was extracted with Et_2O (2 x 50 mL), and the combined organic layers were washed with brine (75 mL) and dried over $MgSO_4$. The solution was concentrated in vacuo, and the residue was purified using flash chromatography (9:1 hexanes/EtOAc eluent) to afford **267** (1.10 g, 2.76 mmol, 88% yield, R_F = 0.45 in 9:1 hexanes/EtOAc) as a colorless oil.

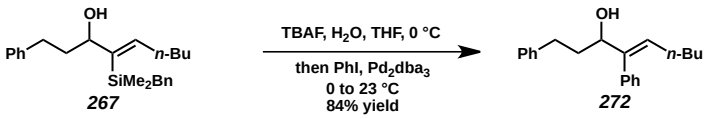
Vinylsilane 267: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (q, *J* = 7.4 Hz, 2H), 7.22-7.16 (comp m, 5H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.30 (t, *J* = 7.4 Hz, 1H), 4.06 (t, *J* = 6.4 Hz, 1H), 2.76-2.54 (comp m, 2H), 2.23 (s, 2H), 2.18 (app. q, *J* = 7.1 Hz, 2H), 1.68 (app. q, *J* = 7.2 Hz, 2H), 1.38-1.32 (comp m, 4H), 0.94 (t, *J* = 6.8 Hz, 3H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 142.3, 140.8, 140.1, 128.6, 128.4, 128.3, 125.8, 124.4, 76.1, 39.5, 32.8, 32.2, 31.8, 27.0, 22.7, 14.2, -1.1, -1.2; IR (film) 3427, 3025, 2955, 2927, 1601, 1493, 1249, 831 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{24}H_{34}OSi + Na]^+$: 389.2271, found 389.2277.



Alcohol 268: To a solution of vinylsilane **267** (102 mg, 0.278 mmol) and water (13.0 μl, 0.835 mmol) in 0.5 mL THF at 0 °C under argon was added TBAF (0.613 mL, 1.0 M in THF, 0.613 mmol) dropwise. The solution was allowed to stir for 5 min, and then ethyl 4-iodobenzoate (66.9 μl, 0.417 mmol) and Pd_2dba_3 (6.3 mg, 0.00695 mmol) were added sequentially. The reaction was allowed to slowly warm to 23 °C while monitoring with TLC (9:1 hexanes/EtOAc). Upon completion (6 h), water (1 mL) was added and the mixture was extracted with Et_2O (2 x 10 mL). The combined organic layers were washed with brine (15 mL) and dried over $MgSO_4$.

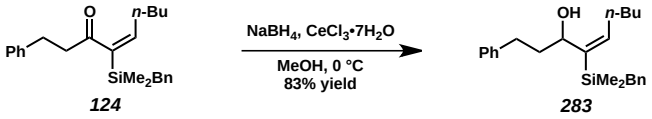
The solution was concentrated in vacuo, and the residue was purified using flash chromatography (19:1 hexanes/EtOAc eluent) to afford **268** (74.0 mg, 73% yield, R_F = 0.13 in 9:1 hexanes/EtOAc) as a colorless oil.

Alcohol 268: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (app. d, *J* = 8.3 Hz, 2H), 7.28-7.23 (comp m, 4H), 7.19-7.10 (comp m, 3H), 5.76 (t, *J* = 7.5 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.32 (t, *J* = 6.5 Hz, 2H), 2.78-2.58 (m, 2H), 1.90 (q, *J* = 7.3 Hz, 2H), 1.78-1.68 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.35-1.19 (m, 2H), 0.82 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 143.5, 142.7, 141.9, 130.3, 129.51, 129.45, 128.54, 128.51, 126.0, 76.1, 61.1, 37.4, 32.2, 32.0, 28.4, 22.4, 14.5, 14.0; IR (film) 3469, 2930, 2859, 1718, 1274, 1103, 700 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{24}H_{29}O_3]^+$: 365.2111, found 365.2118.



Alcohol 272: To a solution of vinylsilane **267** (228 mg, 0.624 mmol) and water (30.0 μl, 1.87 mmol) in 3.0 mL THF at 0 °C under argon was added TBAF (1.37 mL, 1.0 M in THF, 1.37 mmol) dropwise. The solution was allowed to stir for 5 min, and then PhI (104 μl, 0.936 mmol) and Pd_2dba_3 (14.3 mg, 0.0156 mmol) were added sequentially. The reaction was allowed to slowly warm to 23 °C while monitoring with TLC (9:1 hexanes/EtOAc). Upon completion (3 h), water (2.0 mL) was added and the mixture was extracted with Et_2O (2 x 20 mL). The combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. The solution was concentrated in vacuo, and the residue was purified using flash chromatography (19:1 hexanes/EtOAc eluent) to afford **272** (154 mg, 84% yield, R_F = 0.28 in 9:1 hexanes/EtOAc) as a colorless oil.

Alcohol 272: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (app. t, *J* = 7.2 Hz, 2H), 7.29-7.22 (comp m, 4H), 7.16-7.12 (comp m, 4H), 5.70 (t, *J* = 7.4 Hz, 1H), 4.32 (t, *J* = 6.3 Hz, 1H), 2.77-2.60 (comp m, 2H), 1.91 (q, *J* = 7.2 Hz, 2H), 1.83-1.67 (m, 2H), 1.35-1.19 (comp m, 4H), 0.81 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 142.0, 138.2, 129.3, 129.2, 128.40, 128.36, 128.3, 128.1, 126.9, 125.7, 37.2, 31.9, 28.2, 22.2, 13.9; IR (film) 3371, 3026, 2955, 2927, 1494, 1454, 700 cm^{-1}; HRMS (ESI^{+}) *m/z* calc'd for $(M - H_2O)^{+}$ $[C_{21}H_{26}O - H_2O]^{+}$: 276.1878, found 276.1878.

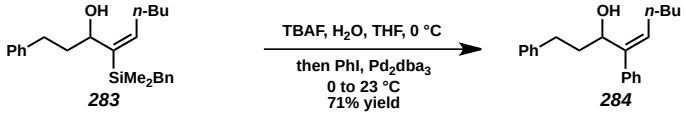


124 ***283***

Vinylsilane 283: To a solution of α-silylenone **124** (0.271 g, 0.595 mmol) in methanol (15.0 mL) at 0 °C was added $CeCl_3$•$7H_2O$ (0.244 g, 0.655 mmol). Upon dissolution of the cerium salt, $NaBH_4$ (38.2 mg, 1.01 mmol) was added slowly. The reaction was stirred until completion (1 h) as judged by TLC (9:1 hexanes/EtOAc). Excess hydride was quenched with H_2O (5 mL). The mixture was extracted with Et_2O (2 x 20 mL), and the combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. The solution was concentrated in vacuo, and the residue was purified using flash chromatography (9:1 hexanes/EtOAc eluent) to afford **283** (0.180 g, 2.76 mmol, 83% yield, R_F = 0.42 in 9:1 hexanes/EtOAc) as a colorless oil.

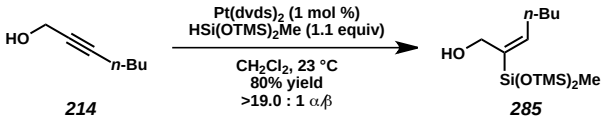
Vinylsilane 283: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.18 (comp m, 6H), 7.09-6.99 (comp m, 4H), 5.68 (t, *J* = 7.6 Hz, 1H), 4.58 (dd, *J* = 9.4, 3.8 Hz, 1H), 2.83-2.74 (m, 1H), 2.66-2.56 (m, 1H), 2.22 (app. q, *J* = 10.66 Hz, 4H), 2.02-1.86 (m 2H), 1.32-1.24 (comp m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.14 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 142.3, 142.1, 140.8, 128.6, 128.5, 128.4, 128.2, 126.0, 124.1, 72.2, 39.3, 29.0, 27.5, 22.6, 14.1, 1.5, 1.4; IR (film) 3585, 2955, 2927, 1601, 1247, 831, 699 cm^{-1}; HRMS (ESI^{+}) *m/z* calc'd for $(M + Na)^{+}$

$[C_{24}H_{34}OSi + Na]^+$: 389.2271, found 389.2275.



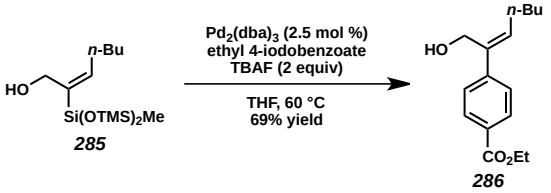
Alcohol 284: To a solution of vinylsilane **283** (123 mg, 0.336 mmol) and water (21.4 μl, 1.34 mmol) in 1.7 mL THF at 0 °C under argon was added TBAF (0.739 mL, 1.0 M in THF, 0.739 mmol) dropwise. The solution was allowed to stir for 5 min, and then PhI (56.1 μl, 0.504 mmol) and Pd_2dba_3 (7.7 mg, 0.00840 mmol) were added sequentially. The reaction was allowed to slowly warm to 23 °C while monitoring with TLC (9:1 hexanes/EtOAc). Upon completion (4 h), water (2.0 mL) was added and the mixture was extracted with Et_2O (2 x 20 mL). The combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. The solution was concentrated in vacuo, and the residue was purified using flash chromatography (19:1 hexanes/EtOAc eluent) to afford **284** as a colorless oil (69.8 mg, 71% yield, R_F = 0.30 in 9:1 hexanes/EtOAc).

Alcohol 284: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.38 (comp m, 2H), 7.33-7.22 (comp m, 5H), 7.18-7.11 (comp m, 3H), 5.60 (t, *J* = 7.5 Hz, 1H), 4.81 (dd, *J* = 7.9, 6.2 Hz, 1H), 2.74-2.55 (comp m, 2H), 2.23-2.14 (comp m, 2H), 1.98 (dddd, *J* = 13.7, 9.3, 7.8, 6.0 Hz, 1H), 1.80 (app. ddt, *J* = 13.6, 9.6, 6.3 Hz, 2H), 1.46-1.26 (comp m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 141.9, 141.2, 133.4, 128.62, 128.55, 128.5, 128.1, 127.0, 126.0, 69.8, 37.7, 32.4, 32.2, 27.6, 22.6, 14.1; IR (film) 3411, 2956, 2928, 1601, 1493, 762, 700 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M - OH)^+$ $[C_{21}H_{26}O - OH]^+$: 277.1951, found 277.1951.



Vinylsilane 283: To a solution of hept-2-yn-1-ol (**214**, 100 mg, 0.891 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (0.266 mL, 0.981 mmol) in CH_2Cl_2 (4.45 mL) at 23 °C under argon was added Pt(dvds) (57.9 mg, 0.00891 mmol, 3 wt% Pt in PDMS), and the resulting mixture was allowed to stir at 23 °C. Upon completion (6 h), as judged by TLC (4:1 hexanes/Et_2O), the mixture was diluted with hexanes and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (10 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (9:1 → 4:1 hexanes/Et_2O eluent) to afford vinylsilane **285** as a colorless oil (239 mg, 80% yield, >19.0:1 $\alpha\beta$, R_F = 0.32 in 4:1 hexanes/Et_2O).

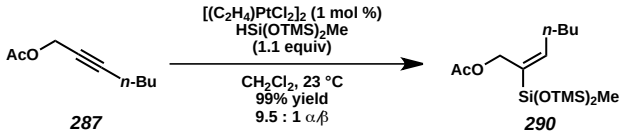
Vinylsilane 285: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (t, *J* = 7.1 Hz, 2H), 4.25 (s, 2H), 2.11 (q, *J* = 7.1 Hz, 2H), 1.67 (s, 1H), 1.36-1.26 (comp m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.13 (s, 3H), 0.09, (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 139.1, 60.6, 31.6, 28.3, 22.5, 14.1, 2.0, 0.3; IR (film) 3425, 2959, 1618, 1409, 1255, 1058 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{14}H_{34}NaO_3Si_3]^+$: 357.1713, found 357.1715.



Alkene 286: To a solution of vinylsilane **285** (101 mg, 0.302 mmol) and ethyl 4-iodobenzoate (75.9 μL, 0.453 mmol) in THF (1.51 mL) at 23 °C under argon was added $Pd_2(dba)_3$ (6.9 mg, 0.00756 mmol), and the mixture was stirred for 5 min. Then TBAF (0.604 mL, 1.0 M in THF,

0.604 mmol) was added dropwise. The flask was sealed, heated to 60 °C and stirred for 4 h, at which point water (5 mL) was added. The mixture was extracted with Et_2O (2 x 20 mL), and the combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the resulting residue was purified by flash chromatography (9:1 → 2:1 hexanes/Et_2O eluent) to afford alkene **286** (54.8 mg, 69% yield, R_F = 0.10 in 4:1 hexanes/Et_2O) as a pale yellow oil.

Alkene 286: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 6.01 (t, *J* = 7.6 Hz, 1H), 4.60 (s, 2H), 4.37 (t, *J* = 7.1 Hz, 2H), 2.32 (q, *J* = 7.4 Hz, 2H), 1.51-1.34 (comp m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 145.7, 138.1, 134.9, 129.9, 129.1, 126.2, 61.0, 59.7, 32.0, 28.4, 22.6, 14.5, 14.1; IR (film) 3412, 2958, 1716, 1607, 1275, 1107 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{16}H_{23}O_3]^+$: 263.1647, found 263.1642.

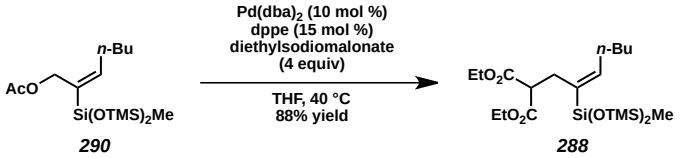


287 ***290***

Vinylsilane 290: To a solution of acetate **287** (67.8 mg, 0.435 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (130 μl, 0.479 mmol) in CH_2Cl_2 (2.17 mL) at 23 °C under argon was added $[(C_2H_4)PtCl_2]_2$ (2.6 mg, 0.00435 mmol), and the resulting mixture was allowed to stir at 23 °C. Upon completion (3 h), as judged by TLC (19:1 hexanes/Et_2O), the mixture was diluted with hexanes and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (8 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **290** (162 mg, 99% yield, 9.5:1 $\alpha\beta$, R_F = 0.38 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 290: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (t, *J* = 7.1 Hz, 1H), 4.70 (s, 2H), 2.14 (q, *J* = 7.16 Hz, 2H), 2.04 (s, 3H), 1.41-1.27 (comp m, 4H), 0.90 (t, *J* = 7.12 Hz, 3H), 0.12 (s, 3H) 0.07 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 146.6, 134.1, 62.5, 31.5, 28.7, 22.5, 21.3, 14.1, 2.0, 0.6; IR (film) 2959, 1744, 1620, 1256, 1058 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{16}H_{36}O_4Si_3Na]^+$: 399.1814, found 399.1821.

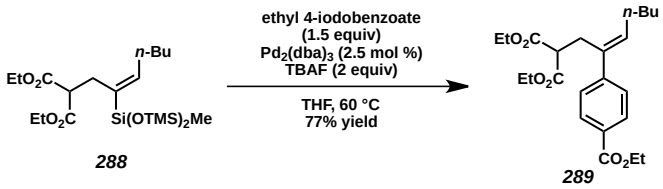
Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinyl protons (α: 6.08 ppm, β: 5.88 ppm (t)). ^{1}H and ^{13}C data for α isomer only.



Vinylsilane 288: To a solution of vinylsilane **290** (0.391 g, 1.04 mmol) in THF (0.520 mL) was added dppe (6.2 mg, 0.0156 mmol) and $Pd(dba)_2$ (6.0 mg, 0.0104 mmol) under an argon atmosphere. The mixture was stirred at 23 °C for 5 min, at which point a freshly prepared solution of diethylsodiomalonate (from diethyl malonate and NaH, 2.08 mL, 2.0 M in THF, 4.16 mmol) was added dropwise. The flask was sealed and heated to 40 °C. After stirring for 14 h, the reaction was quenched with H_2O (5 mL), and the mixture was extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford vinylsilane **288** (0.438 g, 88% yield, R_F = 0.24 in 19:1 hexanes/Et_2O) as a colorless oil. The regioisomeric ratio of product **288** remained 9.5:1 favoring the α isomer.

Vinylsilane 288: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (t, *J* = 6.9 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 4H), 3.62 (t, *J* = 7.6 Hz, 1H), 2.73 (d, *J* = 7.6 Hz, 2H), 2.11 (q, *J* = 7.0 Hz, 2H), 1.35-1.31 (comp

m, 4H), 1.23 (t, *J* = 7.1 Hz, 6H), 0.89 (t, *J* = 6.9 Hz, 3H), 0.09 (app. s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 145.1, 135.3, 61.2, 51.2, 51.6, 31.7, 28.3, 28.2, 22.6, 14.2, 14.1, 1.9, 0.3; IR (film) 2959, 1737, 1619, 1258, 1044 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{21}H_{48}NO_6Si_3]^+$: 494.2784, found 494.2787.



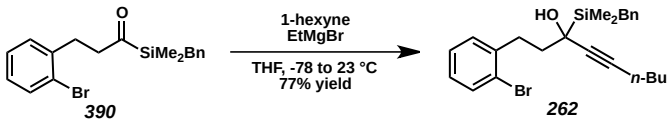
288 *289*

Alkene 289: To a solution of vinylsilane **288** (90.1 mg, 0.211 mmol) and ethyl 4-iodobenzoate (53.2 μl, 0.316 mmol) in THF (1.05 mL) at 23 °C under argon was added $Pd_2(dba)_3$ (4.8 mg, 0.00528 mmol), and the mixture was stirred for 5 min. Then TBAF (0.422 mL, 1.0 M in THF, 0.422 mmol) was added dropwise. The flask was sealed, heated to 60 °C and stirred for 4 h, at which point water (5 mL) was added. The mixture was extracted with Et_2O (2 x 20 mL), and the combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the resulting residue was purified by flash chromatography (9:1 → 4:1 hexanes/Et_2O eluent) to afford alkene **289** (65.5 mg, 77% yield, R_F = 0.29 in 4:1 hexanes/Et_2O) as a pale yellow oil. The regioisomeric ratio of product **289** remained 9.5:1 favoring the α isomer.

Alkene 289: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 5.78 (t, *J* = 7.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 4H), 3.27 (t, *J* = 7.7 Hz, 1H), 3.16 (d, *J* = 7.7 Hz, 2H), 2.24 (q, *J* = 7.2 Hz, 2H), 1.38 (app. t, *J* = 7.1 Hz, 7H), 1.19 (t, *J* = 7.1 Hz, 6H), 0.92 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 166.6, 146.6, 135.4, 134.6, 129.8, 129.1, 126.6, 61.5, 61.0, 50.7, 31.9, 28.7, 28.6, 22.6, 14.5, 14.1; IR (film) 2960,

1734, 1607, 1275, 1104 cm^{-1}; HRMS ($APCI^+$) *m/z* calc'd for $(M + H)^+$ $[C_{23}H_{33}O_6]^+$: 405.2277, found 405.2258.

4.8.3 Substrate Syntheses for TBAF Promoted Hiyama Couplings

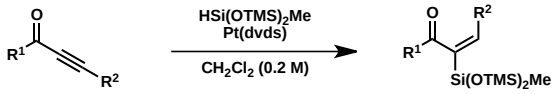


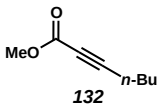
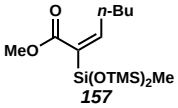
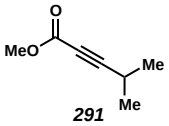
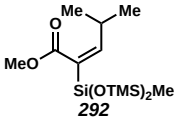
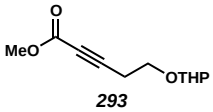
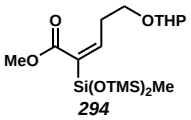
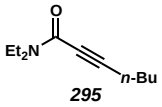
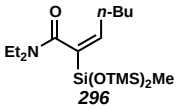
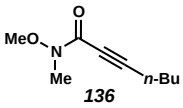
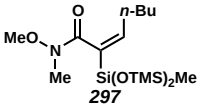
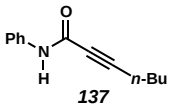
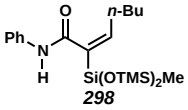
α-hydroxypropargylsilane 262: According to the general procedure, hexyne (0.173 mL, 1.52 mmol) in 6.00 mL THF was deprotonated by EtMgBr (.507 mL, 1.52 mmol). To the alkynyl Grignard was added **390** (456 mg, 1.26 mmol) in 2.00 mL THF dropwise. The reaction was stirred until completion as judged by TLC (9:1 hexanes/EtOAc). Purification by flash chromatography (19:1 hexanes/EtOAc) afforded **262** (432 mg, 0.975 mmol, 77% yield) as a colorless oil .

α-hydroxypropargylsilane 262: ^1H NMR (400 MHz, $CDCl_3$,) δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.25-7.18 (comp m, 4H), 7.07-7.01 (app. q, *J* = 8.0 Hz, 4H), 3.10-2.96 (comp m, 2H), 2.31-2.27 (m, 2H), 2.27 (s, 2H), 1.95-1.78 (comp m, 2H), 1.56-1.40 (comp m, 4H), 0.92 (t, *J* = 6.8 Hz, 3H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 139.7, 133.0, 130.7, 128.48, 128.47, 127.71, 127.66, 124.7, 124.4, 89.3, 81.9, 64.8, 38.2, 30.9, 22.7, 22.1, 18.8, 13.8, -5.9, -6.2; IR (film) 3566, 3447, 2958, 2932, 1599, 1493, 1470, 1247 cm^{-1}; HRMS *m/z* calc'd for $(M + Na)^+$ $[C_{24}H_{31}BrOSi\ Na]^+$: 465.1220, found 465.1218.

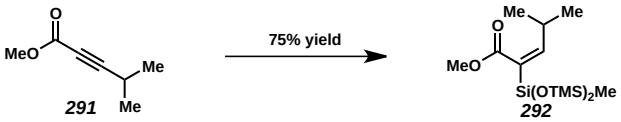
4.8.4 Hydrosilylations with Heptamethyltrisiloxane

Table 4.4.1 (*reproduced*)



entry	substrate	product	time (h)	yield (%)	regioselectivity (α/β)[a]
1	 ***132***	 ***157***	4	98	16 : 1
2	 ***291***	 ***292***	7	75	>19 : 1
3	 ***293***	 ***294***	3	94	11 : 1
4	 ***295***	 ***296***	24	81	>19 : 1
5	 ***136***	 ***297***	24	98	>19 : 1
6	 ***137***	 ***298***	24	94	>19 : 1

a) Measured by ^{1}H NMR

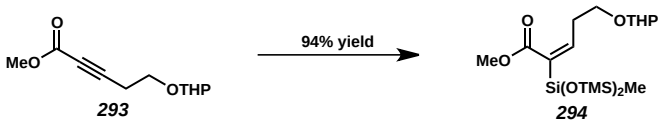


291 ***292***

Vinylsilane 292: To a solution of alkyne **291** (77.0 mg, 0.609 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (0.182 mL, 0.670 mmol) in CH_2Cl_2 (3.0 mL) was added Pt(dvds) (5.9 µl, 0.000607 mmol, 2 wt% Pt in xylenes) under ambient atmosphere. The reaction mixture was allowed to stir at room temperature for 7 h, at which point the solvent was removed by rotary

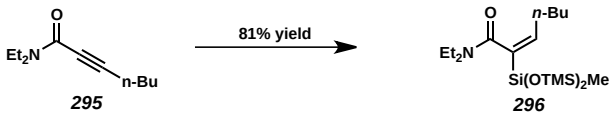
evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O) to afford vinylsilane **292** (160 mg, 75% yield, R_F = 0.61 in 9:1 hexanes/EtOAc) as a colorless oil.

Vinylsilane 292: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (d, *J* = 9.6 Hz, 1H), 3.70 (s, 3H), 3.05 (app. ddt, *J* = 13.3 9.6, 6.6 Hz, 1H), 1.00 (d, *J* = 6.6 Hz, 6H), 0.17 (s, 3H), 0.10 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 161.6, 131.1, 51.1, 51.0, 30.2, 22.5, 22.4, 1.9, 0.2; IR (film) 2960, 1721, 1610, 1356, 1258 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{14}H_{33}O_4Si_3]^+$: 349.1687, found 349.1681.



Vinylsilane 294: To a solution of alkyne **293** (100 mg, 0.471 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (0.142 mL, 0.518 mmol) in CH_2Cl_2 (2.35 mL) was added Pt(dvds) (22.9 μl, 0.00235 mmol, 2 wt% Pt in xylenes) under ambient atmosphere. The reaction mixture was allowed to stir at room temperature for 3 h, at which point the solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/EtOAc) to afford vinylsilane **294** (193 mg, 94% yield, R_F = 0.36 in 9:1 hexanes/EtOAc) as a colorless oil.

Vinylsilane 294: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (t, *J* = 6.9 Hz, 1H), 4.63 (t, *J* = 3.4 Hz, 1H), 3.91-3.82 (m, 2H), 3.73 (s, 3H), 3.51 (m, 2H), 2.77 (app. dq, *J* = 6.6, 3.4 Hz, 2H), 1.88-1.51 (comp m, 6H), 0.19 (s, 3H), 0.11 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 152.9, 135.1, 98.8, 66.4, 62.2, 51.2, 32.1, 30.9, 25.8, 19.6, 2.4, 0.4; IR (film) 2957, 1719, 1611, 1434, 1352 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{18}H_{42}NO_6Si_3]^+$: 452.2320, found 452.2314.



295 *296*

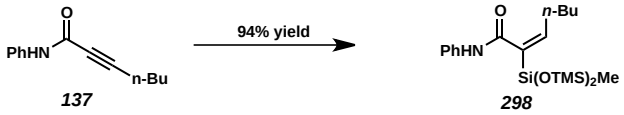
Vinylsilane 296: To a solution of alkyne **295** (50.0 mg, 0.276 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (82.5 μl, 0.303 mmol) in PhMe (1.38 mL) was added Pt(dvds) (89.7 mg, 0.138 mmol, 3 wt % Pt in PDMS) under ambient atmosphere. The reaction mixture was allowed to stir at room temperature for 24 h, at which point the solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford vinylsilane **296** (90.6 mg, 81% yield, R_F = 0.80 in 2:1 hexanes/EtOAc) as a colorless oil.

Vinylsilane 296: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (t, *J* = 7.0 Hz, 1H), 3.45-3.23 (m, 4H), 2.09-2.00 (m, 2H), 1.42-1.28 (comp m, 4H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H), 0.15 (s, 3H), 0.09 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 143.6, 139.9, 42.4, 38.2, 31.2, 31.0, 22.6, 14.3, 14.0, 13.1, 1.9, 0.4; IR (film) 2960, 1627, 1424, 1259, 1067 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{18}H_{42}NO_3Si_3]^+$: 404.2472, found 404.2467.

136 *297*

Vinylsilane 297: To a solution of alkyne **136** (0.202 g, 1.19 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (0.356 mL, 1.31 mmol) in CH_2Cl_2 (5.95 mL) was added Pt(dvds) (0.116 mL, 0.0119 mmol, 2 wt % Pt in xylenes) under ambient atmosphere. The reaction mixture was allowed to stir at room temperature for 24 h, at which point the solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford vinylsilane **297** (0.456 g, 98% yield, R_F = 0.27 in 9:1 hexanes/EtOAc)

Vinylsilane 297: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (t, *J* = 7.1 Hz, 1H), 3.76-3.54 (m, 3H), 3.20 (s, 3H), 2.12 (q, *J* = 7.2 Hz, 2H), 1.43-1.28 (comp m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.16 (s, 3H), 0.10 (s, 18H); ^{13}C NMR (75 MHz, PhMe-d_8) δ 145.3, 140.2, 137.6, 60.9, 31.9, 31.6, 22.8, 14.1, 2.1, 0.8; IR (film) 2959, 1653, 1373, 1258, 1076 cm^{-1}; LRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{16}H_{38}NO_4Si_3]^+$: 392.3, found 392.3.



137 *298*

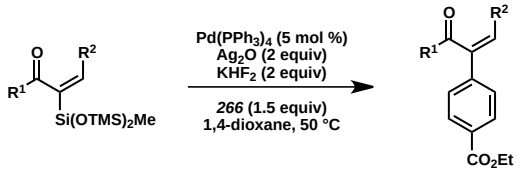
Vinylsilane 298: To a solution of alkyne **137** (150 mg, 0.745 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (0.223 mL, 0.820 mmol) in PhMe (3.72 mL) was added Pt(dvds) (72.6 μl, 0.00745 mmol, 2 wt % Pt in xylenes) under ambient atmosphere. The reaction mixture was allowed to stir at room temperature for 18 h, at which point the solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford vinylsilane **298** (0.297 g, 94% yield, R_F = 0.53 in 9:1 hexanes/EtOAc) as a white solid.

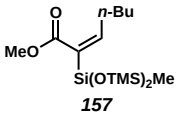
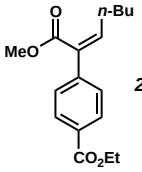
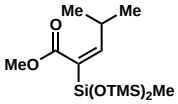
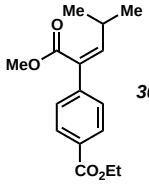
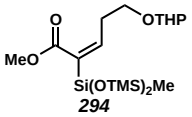
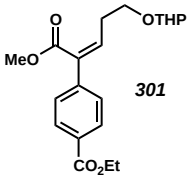
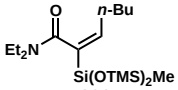
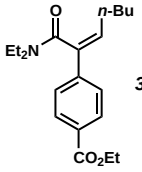
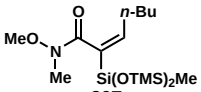
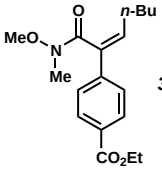
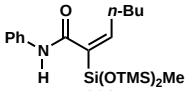
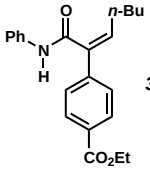
Vinylsilane 298: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (app t, *J* = 8.6 Hz, 3H), 7.19 (t, *J* = 7.9 Hz, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.08 (t, *J* = 7.2 Hz, 1H), 2.27 (q, *J* = 7.3 Hz, 2H), 1.31 (quint, *J* = 7.3 Hz, 2H), 1.21 (sextet, *J* = 7.3 Hz, 2H), 0.77 (t, *J* = 7.1 Hz, 3H), 0.11 (s, 3H), 0.01 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 150.8, 138.6, 138.6, 129.1, 129.0, 124.0, 119.7, 31.4, 31.1, 22.5, 14.0, 1.9, -0.2; IR (film) 3323, 2959, 1652, 1599, 1437, 1075 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{38}NO_3Si_3]^+$: 424.2159, found 424.2160.

4.8.5 KHF_2 and Silver Oxide Promoted Hiyama Couplings

General procedure: To a vinylsilane and aryl iodide (1.5 equiv) in dioxane (0.2 M) was added $Pd(PPh_3)_4$ (5 mol %), Ag_2O (2 equiv) and KHF_2 (2 equiv) under an atmosphere of argon. The reaction mixture was heated in an aluminum heating block. Upon consumption of starting material, as judged by TLC, the reaction was diluted with Et_2O or EtOAc and filtered through a plug of silica gel. The filtrate was concentrated in vacuo and the resulting oil was purified by silica gel flash chromatography.

Table 4.4.2 (*reproduced*)



entry	substrate	product	time (h)	yield (%)
1	 ***157***	 ***299***	17	97
2	 ***292***	 ***300***	22	90
3	 ***294***	 ***301***	6	91
4	 ***296***	 ***302***	3.5	81
5	 ***297***	 ***303***	6	88
6	 ***298***	 ***304***	13	85

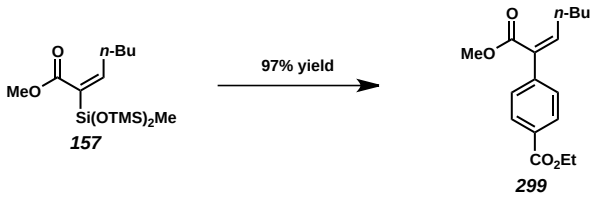


Table 4.4.2, Entry 1. According to the general procedure, to a solution of vinylsilane **157** (101 mg, 0.279 mmol) and 4-iodoethylbenzoate (95.9 mg, 0.419 mmol) in dioxane (1.39 mL) was added $Pd(PPh_3)_4$ (16.1 mg, 0.0139 mmol), Ag_2O (129 mg, 0.558 mmol) and KHF_2 (43.6 mg, 0.558 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 8 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford enoate **299** (78.4 mg, 97% yield, R_F = 0.37 in 9:1 hexanes/EtOAc).

Alkene 299: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.27 (t, *J* = 7.6 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.47 (q, *J* = 7.4 Hz, 2H), 1.50 (quint, *J* = 7.4, 2H), 1.38 (app. t, *J* = 7.1 Hz, 5H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 166.4, 143.0, 142.6, 133.8, 129.7, 129.6, 127.3, 61.1, 51.9, 31.4, 30.1, 22.5, 14.5, 14.0; IR (film) 2957, 1717, 1608, 1366, 1105 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{17}H_{23}O_4]^+$: 291.1518, found 291.1519.

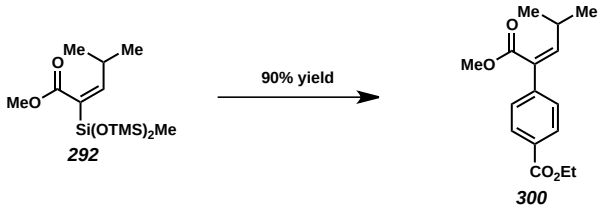


Table 4.4.2, Entry 2. According to the general procedure, to a solution of vinylsilane **292** (69.3, 0.199 mmol) and 4-iodoethylbenzoate (50.1 μl, 0.298 mmol) in dioxane (0.995 mL) was added

$Pd(PPh_3)_4$ (11.5 mg, 0.00995 mmol), Ag_2O (92.2 mg, 0.398 mmol) and KHF_2 (31.1 mg, 0.398 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 22 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm) washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford enoate **300** (49.3 mg, 90% yield, R_F = 0.36 in 9:1 hexanes/EtOAc) as a colorless oil.

Alkene 300: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 6.07 (d, *J* = 10.1 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.01 (app. ddt, *J* = 13.2, 10.1, 6.6 Hz, 1H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.12 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 166.8, 148.8, 142.7, 132.1, 130.0, 129.9, 127.6, 61.4, 52.3, 30.0, 23.0, 14.8; IR (film) 2961, 1719, 1609, 1366, 1275, 1105 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{16}H_{21}O_4]^+$: 277.1440, found 277.1434.

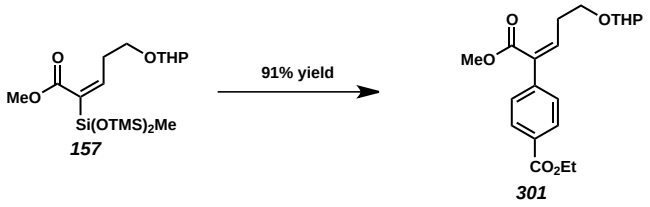


Table 4.4.2, Entry 3. According to the general procedure, to a solution of vinylsilane **157** (54.9 mg, 0.126 mmol) and 4-iodoethylbenzoate (31.9 μl, 0.189 mmol) in dioxane (0.630 mL) was added $Pd(PPh_3)_4$ (7.3 mg, 0.00630 mmol), Ag_2O (58.4 mg, 0.252 mmol) and KHF_2 (19.7 mg, 0.252 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 6 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm) washing with additional Et_2O (4 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 → 4:1 hexanes/EtOAc eluent) to

afford enoate **301** (41.5 mg, 91% yield, R_F = 0.09 in 9:1 hexanes/EtOAc) as a colorless oil.

Alkene 301: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H) 6.40 (t, *J* = 7.3 Hz, 1H), 4.64 (t, *J* = 3.5 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.94-3.83 (m, 2H), 3.82 (s, 3H), 3.62-3.50 (m, 2H), 2.82 (q, *J* = 6.9 Hz, 2H), 1.87-1.51 (comp m, 6H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 166.6, 142.7, 140.1, 140.0, 135.2, 129.84, 129.77, 127.72, 127.68, 99.1, 66.5, 62.6, 61.2, 52.2, 31.1, 30.9, 25.7, 19.7, 14.6; IR (film) 2949, 1718, 1608, 1366, 1275, 1205 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{20}H_{26}NaO_6]^+$: 385.1627, found 385.1612.

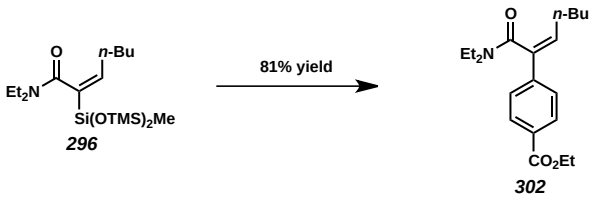


Table 4.4.2, Entry 4. According to the general procedure, to a solution of vinylsilane **296** (75.1 mg, 0.186 mmol) and 4-iodoethylbenzoate (46.9 μl, 0.279 mmol) in dioxane (0.930 mL) was added $Pd(PPh_3)_4$ (10.7 mg, 0.00930 mmol), Ag_2O (86.2 mg, 0.372 mmol) and KHF_2 (29.1 mg, 0.372 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 3.5 h, at which point EtOAc (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional EtOAc (6 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford enoate **302** (49.8 mg, 81% yield, R_F = 0.37 in 2:1 hexanes/EtOAc) as a colorless oil.

Alkene 302: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.14 (t, *J* = 7.6 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.52 (q, *J* = 7.0 Hz, 2H), 3.19 (q, *J* = 7.1 Hz, 2H), 2.21 (q, *J* = 7.2 Hz, 2H), 1.47 (quint, *J* = 7.4 Hz, 2H), 1.37 (app t, *J* = 7.1 Hz, 5H), 1.21 (t, *J*

= 7.1 Hz, 3H), 0.90 (app. q, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 166.4, 141.1, 137.2, 130.1, 129.5, 125.3, 61.1 42.6, 38.6, 31.4, 30.0, 22.7, 14.5, 14.1, 14.0, 12.9; IR (film) 2934, 1717, 1633, 1272, 1105 cm^{-1}; LRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{30}NO_3]^+$: 332.3, found 332.3.

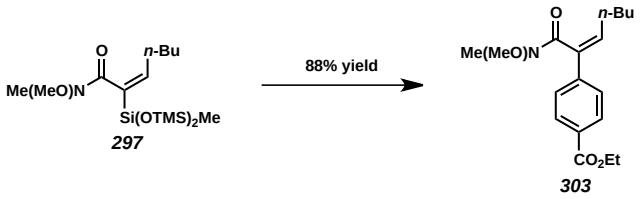


Table 4.4.2, Entry 5 According to the general procedure, to a solution of vinylsilane **297** (65.1 mg, 0.166 mmol) and 4-iodoethylbenzoate (41.9 μl, 0.269 mmol) in dioxane (0.830 mL) was added $Pd(PPh_3)_4$ (9.6 mg, 0.00830 mmol), Ag_2O (76.9 mg, 0.332 mmol) and KHF_2 (25.9 mg, 0.332 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 6 h, at which point EtOAc (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional EtOAc (6 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford enoate **303** (46.5 mg, 88% yield, R_F = 0.55 in 2:1 hexanes/EtOAc) as a colorless oil.

Alkene 303: ^{1}H NMR (300 MHz, $CDCl_3$, 50 °C) δ 7.98 (d, *J* = 8.6, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.16 (t, *J* = 7.5 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.38 (br s, 3H), 3.26 (br s, 3H), 2.27 (q, *J* = 7.4 Hz, 2H), 1.56-1.34 (comp m, 4H), 1.39 (t, *J* = 7.1 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C) δ 170.2, 166.4, 141.6, 136.3, 133.6, 130.2, 130.0, 125.5, 61.5, 61.0, 32.3, 31.5, 30.2, 22.6, 14.5, 14.0; IR (film) 2934, 1717, 1656, 1276, 1105 cm^{-1}; LRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{18}H_{26}NO_4]^+$: 320.3, found 320.3.

Note: carbon taken at room temperature and likely appears as a mixture of rotational isomers.

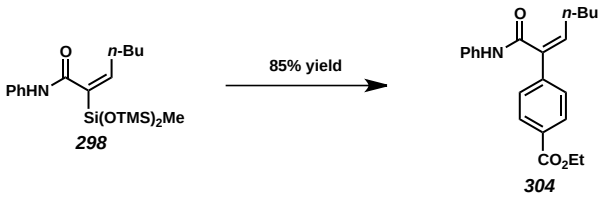
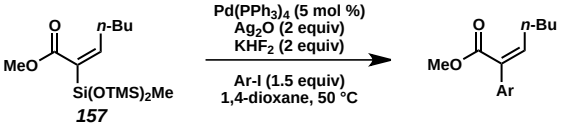
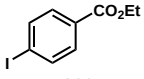
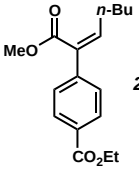
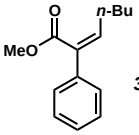
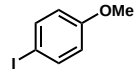
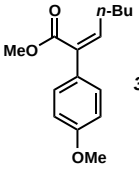
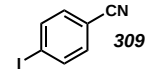
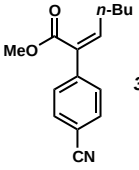
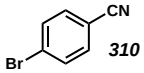
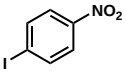
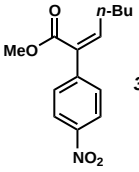
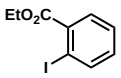
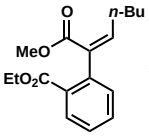
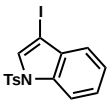
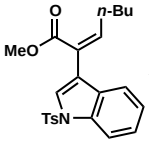
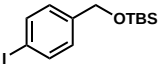
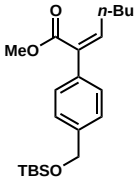
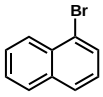
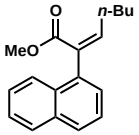


Table 4.4.2, Entry 6. According to the general procedure, to a solution of vinylsilane **298** (82.7 mg, 0.195 mmol) and 4-iodoethylbenzoate (49.2 μl, 0.293 mmol) in dioxane (0.975 mL) was added $Pd(PPh_3)_4$ (11.3 mg, 0.00975 mmol), Ag_2O (90.4 mg, 0.390 mmol) and KHF_2 (30.5 mg, 0.390 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 13 h, at which point EtOAc (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional EtOAc (6 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford enoate **304** (58.0 mg, 85% yield, R_F = 0.74 in 2:1 hexanes/EtOAc) as a white solid.

Alkene 304: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.52 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.21 (t, *J* = 7.7 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.44 (q, *J* = 7.5 Hz, 2H), 1.51 (quint, *J* = 7.4 Hz, 2H), 1.43-1.36 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 166.4, 141.4, 137.8, 137.7, 136.8, 130.1, 129.8, 129.2, 126.4, 124.8, 120.0, 61.2, 31.6, 30.0, 22.6, 14.4, 14.0; IR (film) 3294, 2959, 1717, 1600, 1277, 1107 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{22}H_{25}NNaO_3]^+$: 374.1732, found 374.1727.

Table 4.4.3 (*reproduced*)



entry	Ar-I	product	time (h)	yield (%)
1	 *266*	 *299*	17	97
2	 *205*	 *306*	17	81
3	 *307*	 *308*	12	86
4	 *309*	 *311*	8	81
5	 *310*		12	93
6	 *312*	 *313*	12	88
7	 *314*	 *315*	22	59
8	 *316*	 *317*	7.5	62
9[a]	 *318*	 *319*	18	86
10[a]	 *320*	 *321*	60	69

a) Reaction temperature: 100 °C

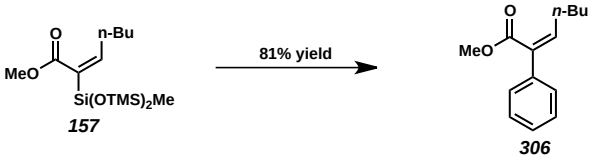


Table 4.4.3, Entry 2. According to the general procedure, to a solution of vinylsilane **157** (75.0 mg, 0.206 mmol) and iodobenzene (34.5 μl, 0.309 mmol) in dioxane (1.03 mL) was added $Pd(PPh_3)_4$ (11.9 mg, 0.0103 mmol), Ag_2O (95.5 mg, 0.412 mmol) and KHF_2 (32.2 mg, 0.412 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 17 h, at

which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford enoate **306** (36.3 mg, 81% yield, R_F = 0.50 in 9:1 hexanes/EtOAc) as a colorless oil.

Alkene 306: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (comp m, 5H), 6.19 (t, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 2.45 (q, *J* = 7.4 Hz, 2H), 1.50 (quint, *J* = 7.2 Hz, 2H), 1.40 (sextet, *J* = 7.2 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 141.0, 138.2, 128.4, 127.6, 127.4, 51.8, 31.6, 30.0, 22.5, 14.1; IR (film) 2956, 1724, 1495, 1360, 1204 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{14}H_{19}O_2]^+$: 219.1385, found 219.1380.

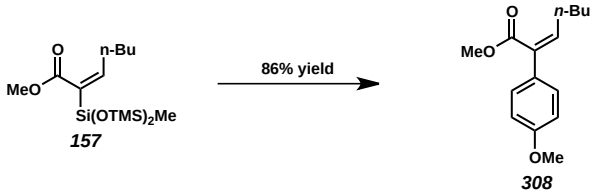


Table 4.4.3, Entry 3. According to the general procedure, to a solution of vinylsilane **157** (100 mg, 0.275 mmol) and 4-iodoanisole (96.5 mg, 0.412 mmol) in dioxane (1.37 mL) was added $Pd(PPh_3)_4$ (15.9 mg, 0.0137 mmol), Ag_2O (127 mg, 0.550 mmol) and KHF_2 (42.9 mg, 0.550 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 12 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (6 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford enoate **308** (58.8 mg, 86% yield, R_F = 0.28 in 9:1 hexanes/Et_2O) as a colorless oil.

Alkene 308: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.07 (t, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 2.39 (q, *J* = 7.4 Hz, 2H), 1.45 (quint, *J* = 7.3

Hz, 2H), 1.35 (sextet, J = 7.3 Hz, 2H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 129.2, 139.4, 133.9, 130.7, 128.8, 113.8, 55.4, 51.8, 31.7, 29.9, 22.5, 14.1; IR (film) 2956, 1723, 1608, 1512, 1250 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[ESI]^+$: 249.1491, found 249.1483.

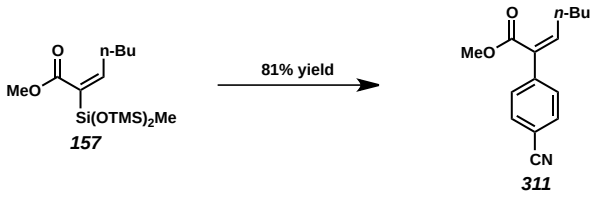


Table 4.4.3, Entry 4. According to the general procedure, to a solution of vinylsilane **157** (101 mg, 0.279 mmol) and 4-iodobenzonitrile (95.9 mg, 0.419 mmol) in dioxane (1.39 mL) was added $Pd(PPh_3)_4$ (16.1 mg, 0.0139 mmol), Ag_2O (129 mg, 0.558 mmol) and KHF_2 (43.6 mg, 0.558 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 8 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford enoate **311** (54.7 mg, 81% yield, R_F = 0.37 in 9:1 hexanes/EtOAc).

Alkene 311: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 6.27 (t, J = 7.6 Hz, 2H), 3.81 (s, 3H), 2.50 (q, J = 7.4 Hz, 2H), 1.50 (quint, J = 7.4 Hz, 2H), 1.39 (sextet, J = 7.4 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 144.8, 142.9, 133.1, 132.2, 128.3, 118.9, 111.3, 52.1, 31.4, 30.2, 22.5, 14.0; IR (film) 2957, 2861, 2228, 1724, 1209 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{18}NO_2]^+$: 244.1338, found 244.1332.

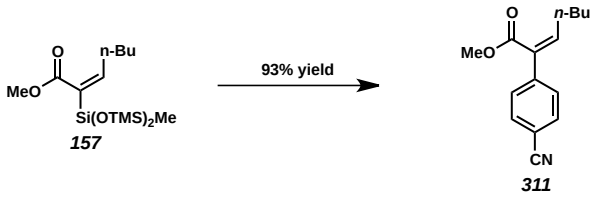


Table 4.4.3, Entry 5. According to the general procedure, to a solution of vinylsilane **157** (60.0 mg, 0.165 mmol) and 4-bromobenzonitrile (45.0 mg, 0.247 mmol) in dioxane (0.825 mL) was added $Pd(PPh_3)_4$ (9.5 mg, 0.00825 mmol), Ag_2O (76.5 mg, 0.330 mmol) and KHF_2 (26.8 mg, 0.330 mmol) under an atmosphere of argon. The reaction mixture was heated to 100 °C for 12 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford enoate **311** (37.4 mg, 93% yield, R_F = 0.37 in 9:1 hexanes/EtOAc).

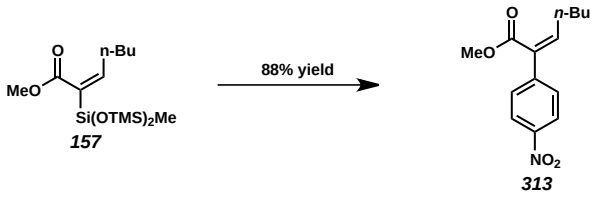


Table 4.4.3, Entry 6. According to the general procedure, to a solution of vinylsilane **157** (102 mg, 0.280 mmol) and 4-iodonitrobenzene (105 mg, 0.420 mmol) in dioxane (1.40 mL) was added $Pd(PPh_3)_4$ (16.2 mg, 0.0140 mmol), Ag_2O (130 mg, 0.560 mmol) and KHF_2 (43.7 mg, 0.560 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 12 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford enoate **313** (64.9 mg, 88% yield, R_F = 0.26 in 19:1 hexanes/Et_2O).

Alkene 313: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 8.9 Hz, 2H), 6.34 (t, *J* = 7.6 Hz, 1H), 3.82 (s, 3H), 2.52 (q, *J* = 7.4 Hz, 2H), 1.51 (quint, *J* = 7.4 Hz, 2H), 1.39 (sextet, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 147.2, 145.5, 132.8, 128.4, 123.6, 52.1, 31.3, 30.2, 22.5, 14.0; IR (film) 2957, 1722, 1519, 1346, 1208 cm^{-1}; HRMS (DART^{+}) *m/z* calc'd for $(M + NH_4)^{+}$ $[C_{14}H_{21}N_2O_4]^{+}$: 281.1501, found 281.1496

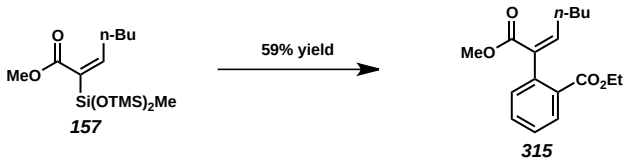


Table 4.4.3, Entry 7. According to the general procedure, to a solution of vinylsilane **157** (90.3 mg, 0.248 mmol) and 2-iodoethylbenzoate (103 mg, 0.372 mmol) in dioxane (1.24 mL) was added $Pd(PPh_3)_4$ (14.3 mg, 0.124 mmol), Ag_2O (115 mg, 0.496 mmol) and KHF_2 (38.7 mg, 0.496 mmol) under an atmosphere of argon. The reaction mixture was heated to 100 °C for 22 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford enoate **315** (42.2 mg, 59% yield, R_F = 0.39 in 9:1 hexanes/EtOAc) as a colorless oil.

Alkene 315: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 6.14 (t, *J* = 7.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 3H), 2.75 (q, *J* = 7.4 Hz, 2H), 1.51 (quint, *J* = 7.1 Hz, 2H), 1.41 (sextet, *J* = 7.3 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 166.7, 146.8, 141.3, 134.0, 132.3, 131.6, 130.2, 130.0, 127.7, 61.2, 51.4, 31.6, 29.5, 22.7, 14.3, 14.1; IR (film) 2957, 1722, 1365, 1258, 1201, 1047 cm^{-1}; HRMS (ESI^{+}) *m/z* calc'd for $(M + H)^{+}$ $[C_{17}H_{23}O_4]^{+}$: 291.1596, found 291.1586.

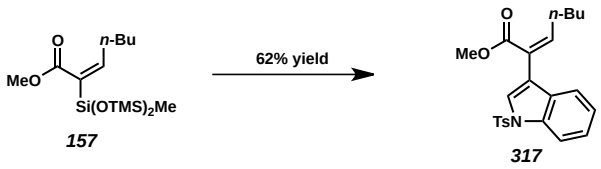


Table 4.4.3, Entry 8. According to the general procedure, to a solution of vinylsilane 157 (73.3 mg, 0.202 mmol) and 3-iodo-*N*-tosylindole **316** (120 mg, 0.302 mmol) in dioxane (1.01 mL) was added $Pd(PPh_3)_4$ (11.7 mg, 0.0101 mmol), Ag_2O (93.6 mg, 0.404 mmol) and KHF_2 (31.6 mg, 0.404 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 7.5 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (6 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford enoate **317** (51.5 mg, 62% yield, R_F = 0.42 in 9:1 hexanes/EtOAc) as a white solid.

Alkene 317: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.60 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.1 Hz, 1H), 7.25-7.20 (comp m, 3H), 6.38 (t, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 2.57 (q, *J* = 7.4 Hz, 2H), 2.34 (s, 3H), 1.51 (quint, *J* = 7.4 Hz, 2H), 1.41 (sextet, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 145.1, 144.6, 135.4, 135.0, 130.1, 129.7, 127.1, 125.2, 124.8, 124.4, 123.5, 120.5, 120.4, 113.8, 51.9, 31.6, 30.0, 22.6, 21.7, 14.1; IR (film) 2955, 1720, 1447, 1372, 1176 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{23}H_{29}N_2O_4S]^+$: 429.1848, found 429.1843.

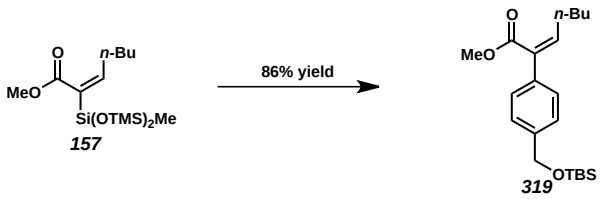


Table 4.4.3, Entry 9. According to the general procedure, to a solution of vinylsilane **157** (86.5

mg, 0.238 mmol) and aryliodide **318** (124 mg, 0.357 mmol) in dioxane (1.19 mL) was added $Pd(PPh_3)_4$ (13.8 mg, 0.0119 mmol), Ag_2O (110 mg, 0.476 mmol) and KHF_2 (37.1 mg, 0.476 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 18 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford enoate **319** (73.9 mg, 86% yield, R_F = 0.55 in 9:1 hexanes/EtOAc).

Alkene 319: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (comp m, 4H), 6.17 (t, *J* = 7.6 Hz, 1H), 4.73 (s, 2H), 3.80 (s, 3H), 2.44 (q, *J* = 7.4 Hz, 2H), 1.49 (quint, *J* = 7.3 Hz, 2H), 1.39 (sextet, *J* = 7.3 Hz, 2H), 0.94 (s, 9H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 140.9, 140.6, 136.8, 134.3, 127.2, 126.1, 64.8, 51.8, 31.6, 30.0, 26.1, 22.5, 18.6, 14.1; IR (film) 2956, 2860, 1725, 1435, 1207 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{21}H_{38}NO_3Si]^+$: 380.2621, found 380.2616.

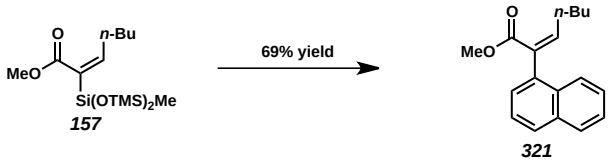


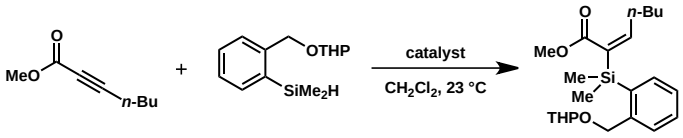
Table 4.4.3, Entry 10. According to the general procedure, to a solution of vinylsilane **157** (60.0 mg, 0.165 mmol) and 2-bromonaphthalene (34.6 μl, 0.247 mmol) in dioxane (0.825 mL) was added $Pd(PPh_3)_4$ (9.5 mg, 0.00825 mmol), Ag_2O (76.5 mg, 0.330 mmol) and KHF_2 (26.8 mg, 0.330 mmol) under an atmosphere of argon. The reaction mixture was heated to 100 °C for 60 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford

enoate **321** (30.4 mg, 69% yield, R_F = 0.46 in 9:1 hexanes/EtOAc).

Alkene 321: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (comp m, 3H), 7.48-7.43 (comp m 3H), 7.34 (d, *J* = 7.0 Hz, 1H), 6.25 (t, *J* = 7.5 Hz, 2H), 3.63 (s, 3H), 2.74 (q, *J* = 7.4 Hz, 2H), 1.55 (quint, *J* = 7.4 Hz, 2H), 1.45 (sextet, *J* = 7.3 Hz, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 148.1, 137.5, 133.6, 132.4, 132.3, 128.5, 128.2, 127.2, 126.3, 125.9, 125.5, 125.3, 51.8, 31.6, 29.8, 22.7, 14.1; IR (film) 2956, 1718, 1434, 1359, 1210 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{18}H_{21}O_2]^+$: 269.1542, found 269.1536

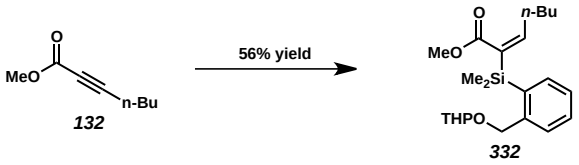
4.8.6 Catalyst Evaluation for Hydrosilylation With 328

Table 4.4.4 (*reproduced*)

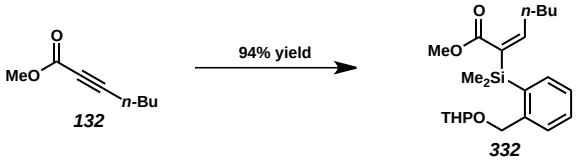


132 *328* *332*

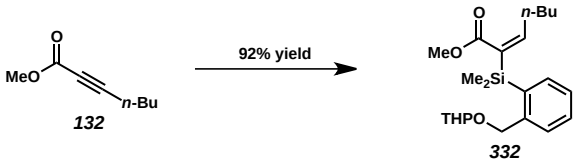
entry	catalyst (mol % Pt)	time (h)	yield (%)	regioselectivity (α : β)
1	$PtCl_2$ (5)	96	--	--
2	$[(C_2H_4)PtCl_2]_2$ (2)	23	56	7.5 : 1
3	Pt(dvds) (1)	26	94	9 : 1
4	Pt(dvds) (0.5)	30	92	11 : 1



Vinylsilane 332: To a solution of alkyne **132** (146 mg, 1.04 mmol) and silane **328** (287 mg, 1.15 mmol) in CH_2Cl_2 (5.00 mL) was added Ziese's dimer (6.1 mg, 0.0105 mmol) under ambient atmosphere. The reaction mixture was allowed to stir at room temperature for 23 h, at which point Et_2O (4 mL) was added and the mixture was filtered through a plug of silica gel washing with additional Et_2O. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 → 4:1 hexanes/EtOAc eluent) to afford vinylsilane **332** (229 mg, 56% yield, R_F = 0.27 in 9:1 hexanes/EtOAc, 7.5:1 α/β) as a colorless oil.

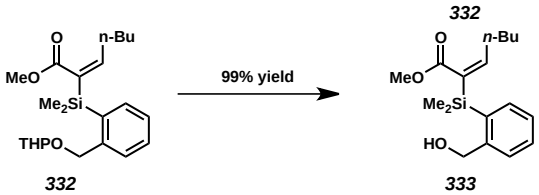


Vinylsilane 332: To a solution of alkyne **132** (0.500 g, 3.56 mmol) and silane **328** (0.983 g, 3.92 mmol) in CH_2Cl_2 (17.8 mL) was added Pt(dvds) (0.346 mL, 0.00356 mmol, 2 wt % Pt in xylenes) under ambient atmosphere. The reaction mixture was allowed to stir at room temperature for 24 h, at which point the solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 → 4:1 hexanes/EtOAc eluent) to afford vinylsilane **332** (1.31 g, 94% yield, R_F = 0.27 in 9:1 hexanes/EtOAc, 11:1 α/β) as a colorless oil.



Vinylsilane 332: To a solution of alkyne **132** (0.500 g, 3.56 mmol) and silane **328** (0.983 g, 3.92 mmol) in CH_2Cl_2 (17.8 mL) was added Pt(dvds) (0.173 mL, 0.00178 mmol, 2 wt % Pt in xylenes) under ambient atmosphere. The reaction mixture was allowed to stir at room temperature for 24 h, at which point the solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 → 4:1 hexanes/EtOAc eluent) to afford vinylsilane **332** (1.24 g, 92% yield, R_F = 0.27 in 9:1 hexanes/EtOAc, 11:1 α/β) as a colorless oil.

Vinylsilane 332: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 6.17 (t, *J* = 7.2 Hz, 1H), 4.80 (d, *J* = 12.2 Hz, 1H), 4.67 (t, *J* = 3.5 Hz, 1H), 4.55 (d, *J* = 12.2 Hz, 1H), 3.91 (ddd, *J* = 11.3, 8.2, 3.2 Hz, 1H), 3.60 (s, 3H), 3.56-3.51 (m, 1H), 2.38 (q, *J* = 7.4 Hz, 2H), 1.91-1.82 (m, 1H), 1.77-1.26 (comp m, 10H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.470 (s, 3H), 0.466 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 154.4, 144.2, 135.4, 134.6, 129.6, 128.4, 126.8, 98.0, 68.8, 62.2, 51.1, 31.7, 31.2, 25.6, 22.5, 19.5, 14.0, -0.9, -1.0; IR (film) 2953, 1716, 1433, 1200, 1031 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{22}H_{34}NaO_3Si]^+$: 413.2124, found 413.2127.

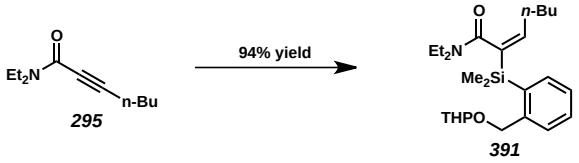


Vinylsilane 333: To a solution of vinylsilane **332** (0.974 g, 2.49 mmol) in MeOH (12.4 mL) was

added TsOH•H_2O (47.4 mg, 0.249 mmol) under ambient atmosphere. The reaction was allowed to stir at room temp for 2 h, at which point sat. aq. $NaHCO_3$ (10 mL), H_2O (20 mL) and Et_2O (150 mL) were added. The organic layer was washed with brine (75 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford vinylsilane **333** (0.757 g, 99% yield, R_F = 0.11 in 9:1 hexanes/EtOAc)

Vinylsilane 333: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.3 Hz, 1H), 6.18 (t, *J* = 7.2 Hz, 1H), 4.68 (s, 2H), 3.56 (s, 3H), 2.31 (q, *J* = 7.4 Hz, 2H), 1.44-1.26 (comp m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.45 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 152.1, 146.9, 135.6, 135.3, 134.7, 130.1, 128.8, 127.1, 65.2, 514, 31.9, 31.1, 22.5, 14.0, -1.0; IR (film) 3435, 2957, 1715, 1433, 1201, 1034 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{17}H_{26}NaO_3Si]^+$: 329.1549, found 329.1543.

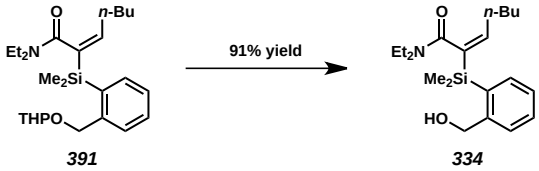
Note: The product mixture is still 11:1 mixture of regioisomers.



Vinylsilane 391: To a solution of alkyne **295** (50.0 mg, 0.276 mmol) and silane **328** (75.9 mg, 0.303 mmol) in PhMe (1.38 mL) was added Pt(dvds) (134 μl, 0.0207 mmol, 2 wt % Pt in xylenes) under ambient atmosphere. The reaction mixture was allowed to stir at 23 °C for 48 h, at which point the solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford vinylsilane **393** (100 mg, 84% yield, R_F = 0.38 in 2:1 hexanes/EtOAc) as a colorless oil.

Vinylsilane 391: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.4 Hz,

1H), 7.38 (t, *J* = 6.8 Hz, 1H), 7.28-7.25 (m, 1H), 5.75 (t, *J* = 7.0 Hz, 1H), 4.86 (d, *J* = 12.2 Hz, 1H), 4.70 (t, *J* = 3.5 Hz, 1H), 4.63 (d, *J* = 12.2 Hz, 1H), 3.91 (t, *J* = 11.0 Hz, 1H), 3.53 (dt, *J* = 11.4, 5.3 Hz, 1H), 3.46-3.21 (comp m, 4H), 3.11-3.04 (m, 1H), 2.13-1.97 (comp m, 3H), 1.88-1.83 (m, 1H), 1.77-1.70 (m, 1H), 1.68-1.51 (comp m, 4H), 1.38-1.24 (comp m 5H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.1 Hz, 3H), 0.48 (s, 3H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 144.4, 143.9, 139.1, 135.7, 129.8, 128.4, 128.3, 126.9, 98.1, 69.0, 62.3, 42.0, 37.6, 31.8, 31.0, 30.8, 25.6, 22.7, 19.6, 14.0, 12.8, -0.9, -1.0; IR (film) 2958, 1618, 1424, 1266, 1031 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{25}H_{41}NNaO_3Si]^+$: 454.2753, found 454.2748.

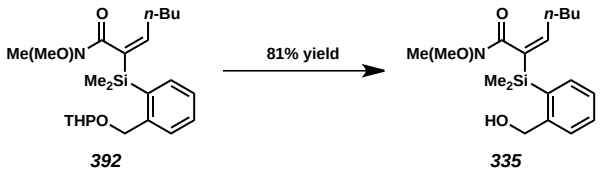


391 *334*

Vinylsilane 334: To a solution of vinylsilane **391** (0.444 g, 1.03 mmol) in MeOH (5.15 mL) was added TsOH•H_2O (19.5 mg, 0.103 mmol) under ambient atmosphere. The reaction was allowed to stir at room temp for 2 h, at which point sat. aq. $NaHCO_3$ (5 mL), H_2O (5 mL) and EtOAc (40 mL) were added. The phases were separated and the organic layer was washed with brine (30 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (2:1 hexanes/EtOAc eluent) to afford vinylsilane **334** (0.325 g, 91% yield, R_F = 0.34 in 2:1 hexanes/EtOAc) as a colorless oil.

Vinylsilane 334: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.4 Hz, 1H), 7.37-7.34 (m, 2H), 7.23 (td, *J* = 6.9, 1.9 Hz, 1H), 5.94 (t, *J* = 7.1 Hz, 1H), 4.82 (d, *J* = 12.4 Hz, 1H), 4.52 (d, *J* = 12.4 Hz, 2H), 3.50-3.20 (m, 4H), 2.19-2.10 (m, 1H), 2.06-1.97 (m, 1H), 1.45-1.25 (comp m, 4H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.1 Hz, 3H), 0.50 (s, 3H), 0.43 (s, 3H); ^{13}C NMR (100 MHz,

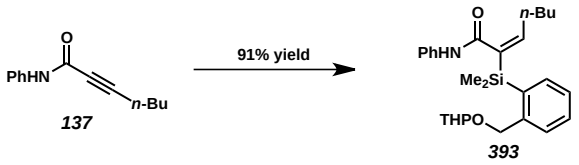
$CDCl_3$) δ 172.7, 148.3, 144.5, 139.3, 134.9, 134.7, 130.1, 129.7, 126.7, 65.0, 42.5, 38.1, 32.0, 30.9, 22.7, 14.2, 14.0, 12.6, -0.1, -0.6; IR (film) 3400, 1961, 1620, 1379, 1252 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{34}NO_2Si]^+$: 348.2359, found 348.2362.



Vinylsilane 335: To a solution of vinylsilane **392** (187 mg, 0.447 mmol) in MeOH (2.23 mL) was added $TsOH•H_2O$ (8.5 mg, 0.0447 mmol) under ambient atmosphere. The reaction was allowed to stir at room temp for 2 h, at which point sat. aq. $NaHCO_3$ (5 mL), H_2O (5 mL) and EtOAc (40 mL) were added. The phases were separated and the organic layer was washed with brine (30 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (2:1 hexanes/EtOAc eluent) to afford vinylsilane **335** (121 mg, 81% yield, R_F = 0.28 in 2:1 hexanes/EtOAc) as a colorless oil.

Vinylsilane 335: ^1H NMR (300 MHz, $CDCl_3$, 50 °C) δ 7.52 (d, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 5.96 (t, *J* = 7.3 Hz, 1H), 4.68 (s, 2H), 3.53 (s, 3H), 3.05 (s, 3H), 2.16 (q, *J* = 7.2 Hz, 2H), 1.47-1.26 (comp m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.49 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 147.8, 145.4, 139.4, 135.1, 130.0, 129.3, 126.8, 126.7, 64.9, 61.2, 32.4, 32.2, 31.3, 22.6, 14.0, -0.3; IR (film) 3411, 2958, 1620, 1379, 1249, 1080 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{18}H_{29}NNaO_3Si]^+$: 358.1814, found 358.1802.

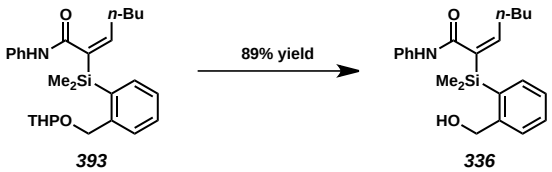
Note: rotational isomers exist in carbon NMR spectrum.



137 393

Vinylsilane 395: To a solution of alkyne **137** (0.350 g, 1.74 mmol) and silane **328** (0.479 g, 1.91 mmol) in PhMe (8.70 mL) was added Pt(dvds) (84.8 μl, 0.00870 mmol, 2 wt % Pt in xylenes) under ambient atmosphere. The reaction mixture was allowed to stir at 80 °C for 8 h, at which point the solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford vinylsilane **393** (0.712 g, 91% yield, R_F = 0.69 in 2:1 hexanes/EtOAc) as a colorless oil.

Vinylsilane 395: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 6.9 Hz, 1H), 7.30-7.17 (comp m, 5H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.07 (t, *J* = 7.1 Hz, 1H), 4.91 (d, *J* = 11.3 Hz, 1H), 4.71-4.67 (comp m, 2H), 3.96 (ddd, *J* = 11.4, 8.5, 3.1 Hz, 1H), 3.60 (dt, *J* = 10.7, 5.1 Hz, 1H), 2.39-2.20 (comp m, 2H), 1.84-1.30 (comp m, 10H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.54 (s, 3H), 0.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 145.8, 143.2, 140.8, 138.4, 135.6, 135.5, 130.2, 129.6, 128.8, 127.7, 123.7, 98.1, 68.9, 62.6, 31.5, 31.4, 30.5, 25.5, 22.6, 19.4, 14.1, -1.6, -1.7; IR (film) 3309, 1955, 1669, 1597, 1530, 1023 cm^{-1}; LRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{27}H_{37}NNaO_3Si]^+$: 474.2, found 474.2.



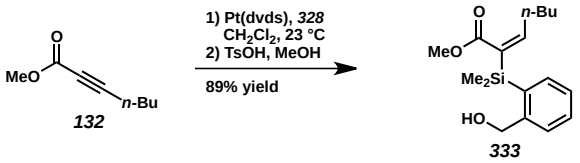
393 336

Vinylsilane 336: To a solution of vinylsilane **393** (0.448 g, 0.992 mmol) in MeOH (4.96 mL) was added TsOH•H_2O (18.9 mg, 0.0992 mmol) under ambient atmosphere. The reaction was allowed to stir at room temp for 2 h, at which point sat. aq. $NaHCO_3$ (5 mL), H_2O (5 mL) and

EtOAc (40 mL) were added. The phases were then separated and the organic layer was washed with brine (30 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford vinylsilane **336** (0.323 g, 89% yield, R_F = 0.59 in 2:1 hexanes/EtOAc) as a white solid.

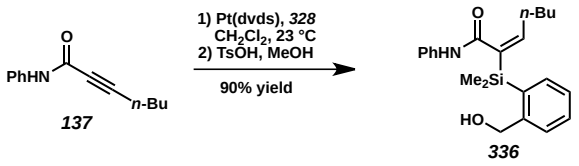
Vinylsilane 336: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.54 (d, *J* = 7.0 Hz, 1H), 7.44-7.38 (m, 2H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.12 (t, *J* = 7.2 Hz, 1H), 4.76 (s, 2H), 2.29 (q, *J* = 7.4 Hz, 2H), 1.44 (quint, *J* = 7.4 Hz, 2H), 1.32 (sextet, *J* = 7.3 Hz, 2H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 146.5, 146.3, 140.9, 138.0, 135.3, 135.2, 130.3, 129.9, 128.9, 124.2, 120.1, 65.2, 31.6, 31.3, 22.5, 14.0, 1.2; IR (film) 3270, 3058, 2957, 1644, 1255, 1104 cm^{-1}; LRMS (ESI^+) *m/z* calc'd for $(M + Na)^+$ $[C_{22}H_{29}NNaO_2Si]^+$: 390.2, found 390.2.

4.8.7 One Pot Sequences for Hydrosilylation/THP-cleavage



Vinylsilane 333: To a solution of alkyne **132** (1.00 g, 7.13 mmol) and silane **328** (1.88 g, 7.44 mmol) in CH_2Cl_2 (35.6 mL) was added Pt(dvds) (348 μl, 0.0356 mmol, 2 wt % Pt in xylenes) under ambient atmosphere. The reaction mixture was allowed to stir at 23 °C for 24 h, at which point the solvent was removed by rotary evaporation. To the resulting residue was added MeOH (15.0 mL) and TsOH•H_2O (67.8 mg, 0.356 mmol) and allowed to stir at 23 °C for 1 h, at which point $NaHCO_3$ (sat. aq., 15.0 mL), H_2O (50 mL) and Et_2O (200 mL) were added. The mixture was partitioned and the organic layer was washed with brine (50 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash

chromatography (4:1 hexanes/EtOAc eluent) to afford vinylsilane **333** (1.96 g, 89% yield, R_F = 0.11 in 9:1 hexanes/EtOAc) as a colorless oil.

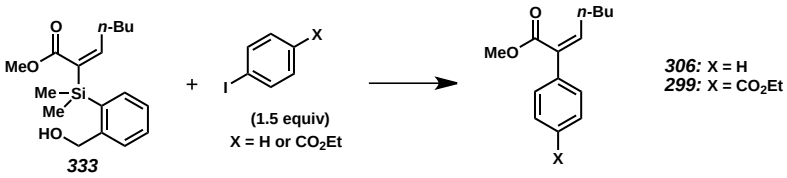


Vinylsilane 336: To a solution of alkyne **137** (60.0 mg, 0.298 mmol) and silane **328** (82.1 mg, 0.328 mmol) in PhMe (1.49 mL) was added Pt(dvds) (29.0 μl, 0.00298 mmol, 2 wt % Pt in xylenes) under ambient atmosphere. The reaction mixture was allowed to stir at 23 °C for 48 h, at which point the solvent was removed by rotary evaporation. To the resulting residue was added MeOH (1.49 mL) and TsOH•H_2O (5.7 mg, 0.0298 mmol) and allowed to stir at 23 °C for 1 h, at which point $NaHCO_3$ (sat. aq., 5.0 mL), H_2O (5 mL) and Et_2O (50 mL) were added. The mixture was partitioned and the organic layer was washed with brine (50 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford vinylsilane **336** (98.5 g, 90% yield, R_F = 0.59 in 2:1 hexanes/EtOAc) as a colorless oil.

4.8.8 Intramolecular Activation

Optimization:

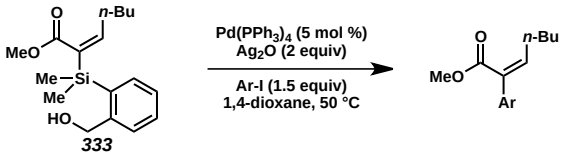
Table 4.4.6 (*reproduced***)**

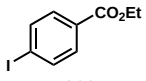
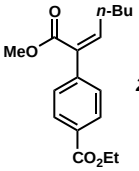
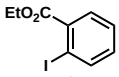
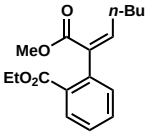
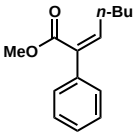
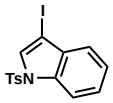
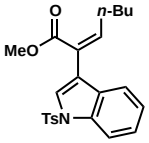
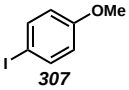
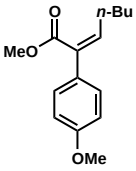
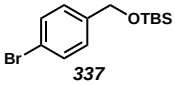
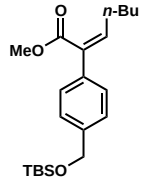
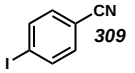
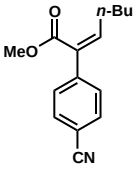
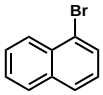
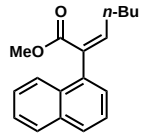
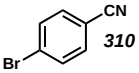
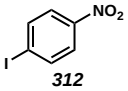
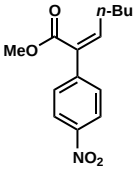
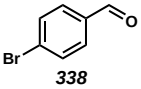
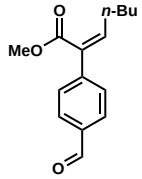


entry	Ar	catalyst (mol %)	additive(s) (equiv)	solvent, temp (°C)	time (h)	yield (%)
1	Ph	$PdCl_2$ (5) $P(2\text{-fur})_3$ (10)	K_2CO_3 (2.0)	DMSO, 50	24	0
2	Ph	Pd_2dba_3 (2.5)	CuI (0.1) K_2CO_3 (2.0) H_2O (5.0)	THF, 60	24	0
3	Ph	Pd_2dba_3 (2.5)	CuI (0.1) K_2CO_3 (2.0)	THF, 60	24	55
4	CO_2Et	$Pd(PPh_3)_4$ (5)	K_2CO_3 (2.0)	THF, 50	16	0
5	CO_2Et	$Pd(PPh_3)_4$ (5)	Ag_2O (1.1)	THF, 50	8	76
6	CO_2Et	$Pd(PPh_3)_4$ (5)	Ag_2O (1.5)	THF, 50	8	85
7	CO_2Et	$Pd(PPh_3)_4$ (5)	Ag_2O (2.0)	1,4-dioxane, 50	4	92
8	CO_2Et	$Pd(PPh_3)_4$ (5)	Ag_2O (2.0) H_2O (5.0)	1,4-dioxane, 50	8	85

General procedure: To a solution of vinylsilane **333** and aryliodide in solvent was added a catalyst and additive(s) under and atmosphere of argon. The reaction mixture was allowed to stir at elevated temperature for a given time specified in Table 1. The reactions were then diluted with Et_2O and filtered through a plug of silica gel washing with additional Et_2O. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography to afford the cross coupled product.

Table 4.4.7 (*reproduced*)



entry	Ar-I	product	time (h)	yield (%)	entry	Ar-I	product	time (h)	yield (%)
1	 *266*	 *299*	8	92	7	 *314*	 *315*	0.75	92
2	 *305*	 *306*	8	90	8	 *316*	 *317*	2	95
3	 *307*	 *308*	2	89	9[a]	 *337*	 *319*	20	91
4	 *309*	 *311*	8	96	10	 *320*	 *321*	24	65
5	 *310*		12	78					
6	 *312*	 *313*	3	79	11	 *338*	 *339*	3	74

a) reaction temperature: 100 °C

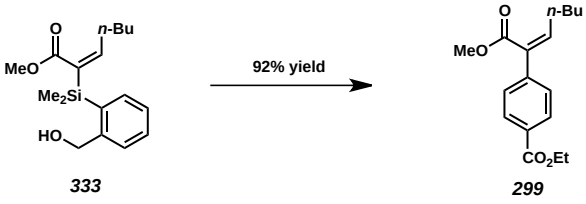
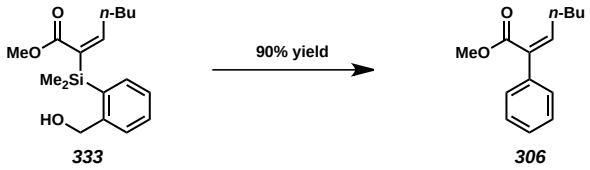


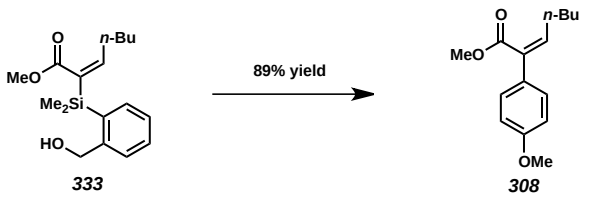
Table 4.4.7, Entry 1. According to the general procedure, to a solution of vinylsilane **333** (58.4 mg, 0.191 mmol) and 4-iodoethylbenzoate (48.2 μl, 0.282 mmol) in dioxane (0.953 mL) was added $Pd(PPh_3)_4$ (11.0 mg, 0.00955 mmol) and Ag_2O (88.3 mg, 0.382 mmol) under an

atmosphere of argon. The reaction mixture was heated to 50 °C for 8 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford enoate **299** (50.9 mg, 92% yield, R_F = 0.44 in 9:1 hexanes/EtOAc) as a colorless oil.



333 *306*

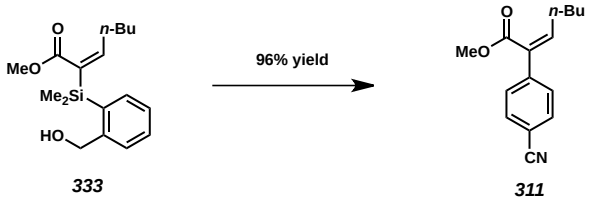
Table 4.4.7, Entry 2. According to the general procedure, to a solution of vinylsilane **333** (68.2 mg, 0.223 mmol) and iodobenzene (37.3 μl, 0.335 mmol) in dioxane (1.11 mL) was added $Pd(PPh_3)_4$ (12.9 mg, 0.0111 mmol) and Ag_2O (103 mg, 0.446 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 8 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (6 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford enoate **306** (43.8 mg, 90% yield, R_F = 0.50 in 9:1 hexanes/EtOAc).



333 *308*

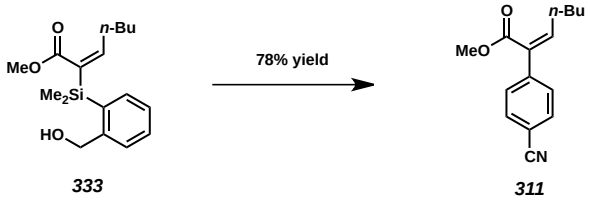
Table 4.4.7, Entry 3. According to the general procedure, to a solution of vinylsilane **333** (75.5 mg, 0.246 mmol) and 4-iodoanisole (86.5 mg, 0.370 mmol) in dioxane (1.23 mL) was added

$Pd(PPh_3)_4$ (14.2 mg, 0.0123 mmol) and Ag_2O (114 mg, 0.492 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 2 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (6 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford enoate **308** (54.4 mg, 89% yield, R_F = 0.28 in 9:1 hexanes/Et_2O) as a colorless oil.



333 *311*

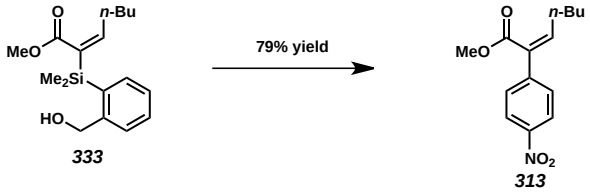
Table 4.4.7, Entry 4. According to the general procedure, to a solution of vinylsilane **333** (89.4 mg, 0.292 mmol) and 4-iodobenzonitrile (100 mg, 0.437 mmol) in dioxane (1.46 mL) was added $Pd(PPh_3)_4$ (16.9 mg, 0.0146 mmol) and Ag_2O (135 mg, 0.584 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 8 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (4:1 hexanes/Et_2O eluent) to afford enoate **311** (68.5 mg, 96% yield, R_F = 0.37 in 9:1 hexanes/EtOAc) as a colorless oil.



333 *311*

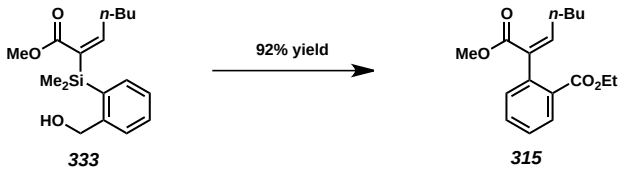
Table 4.4.7, Entry 5. According to the general procedure, to a solution of vinylsilane **333** (118

mg, 0.385 mmol) and 4-bromobenzonitrile (105 mg, 0.577 mmol) in dioxane (1.92 mL) was added $Pd(PPh_3)_4$ (22.2 mg, 0.0192 mmol) and Ag_2O (178 mg, 0.770 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 12 h at which point, Et_2O (4 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (7 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (4:1 hexanes/Et_2O eluent) to afford enoate **333** (73.3 mg, 78% yield, R_F = 0.37 in 9:1 hexanes/EtOAc) as a colorless oil.



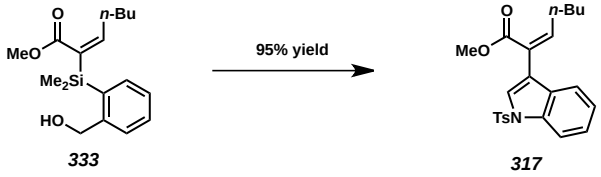
333 *313*

Table 4.4.7, Entry 6. According to the general procedure, to a solution of vinylsilane **333** (62.1 mg, 0.203 mmol) and 4-iodonitrobenzene (75.7 mg, 0.304 mmol) in dioxane (1.01 mL) was added $Pd(PPh_3)_4$ (11.7 mg, 0.0105 mmol) and Ag_2O (94.1 mg, 0.406 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 3 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford enoate **313** (42.3 mg, 79% yield, R_F = 0.26 in 19:1 hexanes/Et_2O) as a colorless oil.



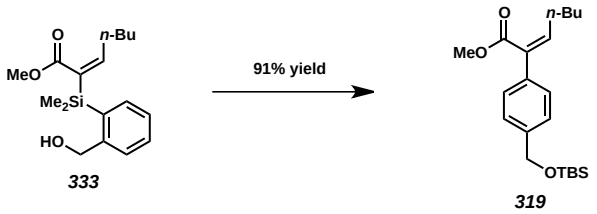
333 *315*

Table 4.4.7, Entry 7. According to the general procedure, to a solution of vinylsilane **333** (43.6 mg, 0.142 mmol) and 2-iodoethylbenzoate (58.8 mg, 0.213 mmol) in dioxane (0.710 mL) was added $Pd(PPh_3)_4$ (8.2 mg, 0.00710 mmol) and Ag_2O (65.8 mg, 0.284 mmol) under an atmosphere of argon. The reaction mixture was heated to 100 °C for 45 min, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford enoate **315** (38.1 mg, 92% yield, R_F = 0.34 in 9:1 hexanes/EtOAc).



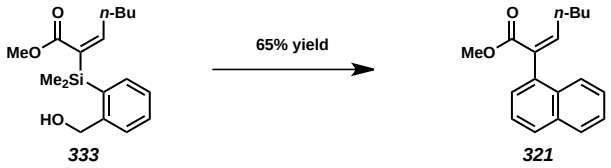
333 *317*

Table 4.4.7, Entry 8. According to the general procedure, to a solution of vinylsilane **333** (29.7 mg, 0.0969 mmol) and 3-iodo-*N*-tosylindole (**316**, 57.7 mg, 0.145 mmol) in dioxane (0.484 mL) was added $Pd(PPh_3)_4$ (5.6 mg, 0.00484 mmol) and Ag_2O (44.9 mg, 0.194 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 2 h, at which point Et_2O (2 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (4:1 → 2:1 hexanes/EtOAc eluent) to afford enoate **317** (37.8 mg, 95% yield, R_F = 0.42 in 9:1 hexanes/EtOAc).



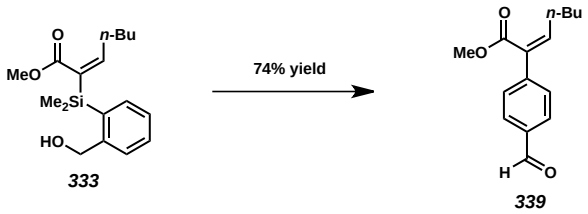
333 *319*

Table 4.4.7, Entry 9. According to the general procedure, to a solution of vinylsilane **333** (56.8 mg, 0.185 mmol) and arylbromide **337** (83.8 mg, 0.278 mmol) in dioxane (0.925 mL) was added $Pd(PPh_3)_4$ (10.7 mg, 0.00925 mmol) and Ag_2O (85.7 mg, 0.370 mmol) under an atmosphere of argon. The reaction mixture was heated to 100 °C for 20 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford enoate **319** (61.8 mg, 91% yield, R_F = 0.55 in 9:1 hexanes/EtOAc).



333 *321*

Table 4.4.7, Entry 10. According to the general procedure, to a solution of vinylsilane **333** (99.0 mg, 0.323 mmol) and 2-bromonaphthalene (67.8 μl, 0.485 mmol) in dioxane (1.61 mL) was added $Pd(PPh_3)_4$ (18.7 mg, 0.0161 mmol) and Ag_2O (150 mg, 0.646 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 24 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm) washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford enoate **321** (56.0 mg, 65% yield, R_F = 0.46 in 9:1 hexanes/EtOAc).

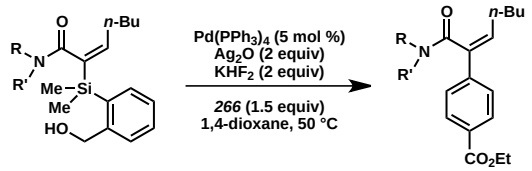


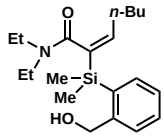
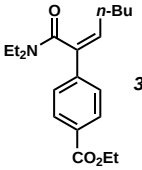
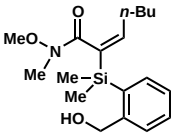
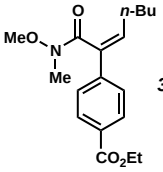
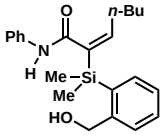
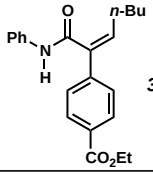
333 *339*

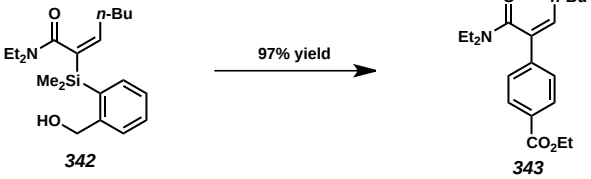
Table 4.4.7, Entry 11. According to the general procedure, to a solution of vinylsilane **333** (49.8 mg, 0.162 mmol) and 4-bromobenzaldehyde (45.1 mg, 0.244 mmol) in dioxane (0.810 mL) was added $Pd(PPh_3)_4$ (9.4 mg, 0.00810 mmol) and Ag_2O (75.1 mg, 0.324 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 3 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm) washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford enoate **339** (29.1 mg, 74% yield, R_F = 0.36 in 9:1 hexanes/EtOAc) as a colorless oil.

Alkene 339: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 6.32 (t, *J* = 7.6 Hz, 1H), 3.82 (s, 3H), 2.49 (q, *J* = 7.4 Hz, 2H), 1.51 (quint, *J* = 7.4 Hz, 2H), 1.39 (sextet, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 167.9, 144.3, 143.9, 135.5, 133.7, 129.9, 128.1, 52.0, 31.4, 30.2, 22.6, 14.0; IR (film) 2957, 2860, 1704, 1604, 1209 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{19}O_3]^+$: 247.1334, found 247.1335.

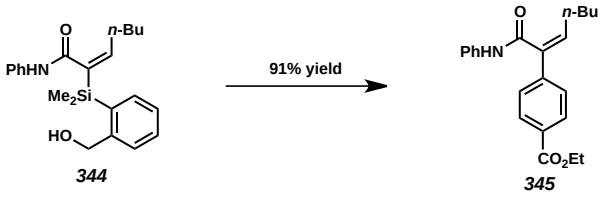
Scheme 4.4.4 (*reproduced*)



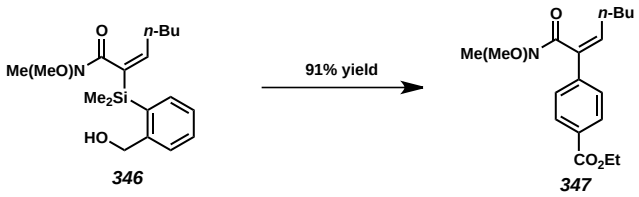
entry	substrate		product		time (h)	yield (%)
1		*342*		*343*	16	97
2		*344*		*345*	3	91
3		*346*		*347*	18	91



Scheme 4.4.4, Entry 1. According to the general procedure, to a solution of vinylsilane **342** (68.6 mg, 0.197 mmol) and 4-iodoethylbenzoate (49.8 μl, 0.296 mmol) in dioxane (0.985 mL) was added $Pd(PPh_3)_4$ (11.4 mg, 0.00985 mmol) and Ag_2O (91.3 mg, 0.394 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 16 h, at which point EtOAc (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional Et_2O (6 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford enoate **343** (63.2 mg, 97% yield, R_F = 0.37 in 2:1 hexanes/EtOAc) as a colorless oil.

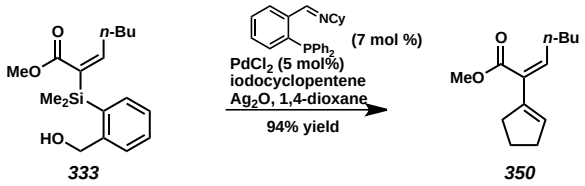


Scheme 4.4.4, Entry 2. According to the general procedure, to a solution of vinylsilane **344** (88.8 mg, 0.264 mmol) and 4-iodoethylbenzoate (66.8 μl, 0.397 mmol) in dioxane (1.32 mL) was added $Pd(PPh_3)_4$ (15.3 mg, 0.0132 mmol) and Ag_2O (122 mg, 0.528 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 3 h, at which point EtOAc (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional EtOAc (6 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 → 4:1 hexanes/EtOAc eluent) to afford enoate **345** (76.8 mg, 91% yield, R_F = 0.55 in 2:1 hexanes/EtOAc) as a colorless oil.



Scheme 4.4.4, Entry 3. According to the general procedure, to a solution of vinylsilane **346** (143 mg, 0.389 mmol) and 4-iodoethylbenzoate (98.0 μl, 0.584 mmol) in dioxane (1.94 mL) was added $Pd(PPh_3)_4$ (22.5 mg, 0.0194 mmol) and Ag_2O (180 mg, 0.778 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 18 h, at which point EtOAc (3 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm), washing with additional EtOAc (6 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (5:1 hexanes/EtOAc eluent) to afford enoate **347** (124 mg, 91% yield, R_F = 0.74 in 2:1 hexanes/EtOAc) as a white solid.

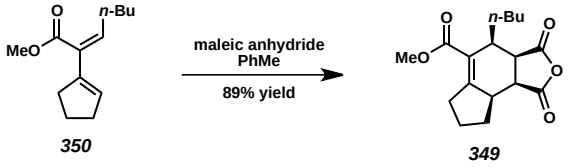
4.8.9 Synthesis of Tricycle 349



333 *350*

Diene 350: To a well stirred solution of vinylsilane **333** (134 mg, 0.437 mmol), 1-iodocyclopentene (127 mg, 0.656 mmol), $PdCl_2$ (3.9 mg, 0.0218 mmol), *N*-(2-(diphenylphosphino)benzylidene)cyclohexylamine (11.4 mg, 0.306 mmol), and dioxane (2.18 mL) was added Ag_2O (202 mg, 0.874 mmol) under an atmosphere of argon. The reaction mixture was heated to 50 °C for 7 h, at which point Et_2O (3 mL) was added and the mixture was filtered through a plug of silica washing with additional Et_2O (6 mL). The filtrate was concentrated in vacuo and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford diene **350** (85.6 mg, 94% yield, R_F = 0.58 in 9:1 hexanes/EtOAc).

Diene 350: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67-5.63 (comp m, 2H), 3.82 (s, 3H), 2.45 (app. t, *J* = 7.2 Hz, 4H), 2.16 (q, *J* = 7.4 Hz, 2H), 1.91 (quint, *J* = 7.5 Hz, 2H), 1.44-1.26 (comp m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 139.4, 133.2, 132.5, 128.9, 51.8, 33.4, 32.5, 31.7, 29.7, 22.8. 22.4, 14.0; IR (film) 2955, 1731, 1435, 1206, 1162 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{13}H_{21}O_2]^+$: 209.1542, found 209.1536.

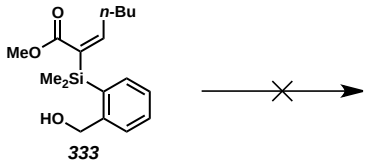


350 *349*

Tricycle 349: To a solution of diene **350** (36.0 mg, 0.173 mmol) in PhMe (0.173 mL) was added maleic anhydride (33.2 mg, 0.346 mmol). The reaction mixture was allowed to stir at room temperature for 13 h, at which point the solvent was removed by rotary evaporation and the

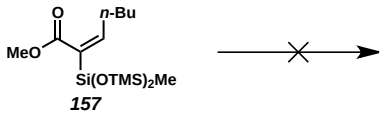
resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford tricycle **349** (47.3 mg, 89% yield, R_F = 0.52 in 2:1 hexanes/EtOAc) as a white solid.

Tricycle 349: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 3.50-3.43 (comp m, 2H), 2.67-2.56 (comp m, 2H), 2.47-2.38 (comp m, 2H), 2.31 (td, *J* = 14.0, 6.4 Hz, 1H), 2.23-2.14 (m, 1H), 2.11-1.97 (comp m, 2H), 1.84 (app. tt, *J* = 12.9, 6.5 Hz, 1H), 1.77-1.66 (m, 1H), 1.50-1.22 (comp m, 5H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 170.6, 167.0, 156.1, 125.9, 51.6, 45.2, 43.7, 41.3, 39.0, 32.1, 30.7, 27.8, 27.4, 26.3, 22.8, 14.2; IR (film) 2957, 2872, 1844, 1776, 1714, 1194 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{17}H_{23}O_5]^+$: 307.1545, found 307.1538.



333

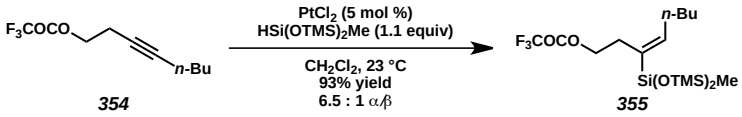
According to the general procedure, to a solution of vinylsilane **333** (92.0 mg, 0.300 mmol) and phenyl triflate (**353**, 102 mg, 0.450 mmol) in dioxane (1.5 mL), was added $Pd(PPh_3)_4$ (17.3 mg, 0.0150 mmol) and Ag_2O (139 mg, 0.600 mmol) under an atmosphere of argon. The reaction mixture was heated to 100 °C for 2 h at which point, Et_2O (2 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm) washing with additional Et_2O (5 mL). The filtrate was concentrated in vacuo and the ^{1}H NMR spectrum of the resulting residue indicated 100% consumption of starting material with no formation of the desired cross coupled product.



157

According to the general procedure, to a solution of vinylsilane **157** (44.3 mg, 0.122 mmol) and phenyl triflate (**353**, 41.3 mg, 0.183 mmol) in dioxane (0.610 mL), was added $Pd(PPh_3)_4$ (7.0 mg, 0.00610 mmol), Ag_2O (56.5 mg, 0.244 mmol) and KHF_2 (19.1 mg, 0.244 mmol) under an atmosphere of argon. The reaction mixture was heated to 100 °C for 48 h at which point, Et_2O (2 mL) was added and the mixture was filtered through a plug of silica (0.5 x 1.5 cm) washing with additional Et_2O (3 mL). The filtrate was concentrated in vacuo and the ^1H NMR spectrum of the resulting residue indicated no consumption of starting material.

4.8.10 Halodesilylation Reactions and Suzuki Cross-Couplings



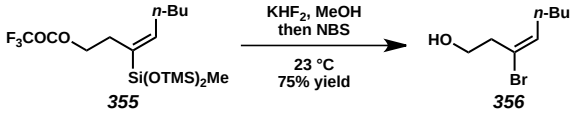
354 *355*

Vinylsilane 355: To a solution of alkyne **354** (321 mg, 1.42 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (0.424 mL, 1.56 mmol) in CH_2Cl_2 (7.10 mL) at 23 °C under argon was added $PtCl_2$ (18.9 mg, 0.0710 mmol), and the resulting mixture was allowed to stir at 23 °C overnight (12 h). The mixture was diluted with hexanes (7 mL) and filtered through a plug of silica gel (0.5 x 2 cm), and the plug was subsequently washed with Et_2O (10 mL). The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (hexanes → 19:1 hexanes/Et_2O eluent) to afford vinylsilane **355** (0.586 g, 93% yield, 6.5:1 α/β, R_F = 0.35 in 19:1 hexanes/Et_2O) as a colorless oil.

Vinylsilane 355: ^1H NMR (400 MHz, $CDCl_3$) δ 6.01 (t, *J* = 7.0 Hz, 1H), 4.28 (t, *J* = 7.8 Hz, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 2.13 (q, *J* = 7.1 Hz, 2H), 1.41-1.29 (comp m, 4H), 0.92 (t, *J* = 7.1 Hz,

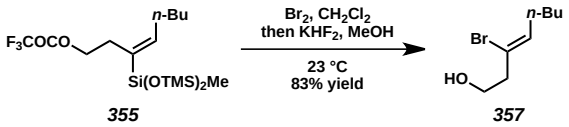
3H), 0.10 (app. s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 146.1, 133.0, 67.4, 31.6, 28.3, 27.6, 22.6, 14.1, 1.9, 0.4; IR (film) 2960, 1787, 1619, 1259, 1223, 1052 cm^{-1}; HRMS ($DART^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_{17}H_{39}F_3NO_4Si_3]^+$: 462.2139, found 462.2150.

Note: Isolated as mixture of α and β isomers. Isomeric ratio determined by integration of vinyl protons (α: 6.01 ppm, β: 5.76 ppm (t)). ^{1}H and ^{13}C data for α isomer only.



Vinyl bromide 356: To a solution of vinylsilane **355** (149 mg, 0.336 mmol) in MeOH (1.12 mL) was added KHF_2 (262 mg, 3.36 mmol) under air at 23 °C, and the mixture was stirred for 16 h. Then, NBS (65.7 mg, 0.369 mmol) was added, and the mixture was stirred for another 16 h, at which point the mixture was partitioned between Et_2O (20 mL) and sat. aq. $NaHCO_3$ (20 mL). The aqueous layer was extracted once more with Et_2O (20 mL), and the combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 → 2:1 hexanes/EtOAc eluent) to afford vinyl bromide **356** (51.6 mg, 75% yield, R_F = 0.55 in 2:1 hexanes/EtOAc eluent) as a colorless oil. The regioisomeric ratio of product **356** remained 6.5:1 favoring the α isomer.

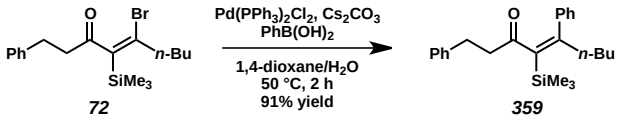
Vinyl bromide 356: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (t, *J* = 7.7 Hz, 1H), 3.81 (t, *J* = 6.1 Hz, 2H), 2.70 (t, *J* = 6.1 Hz, 2H), 2.08 (q, *J* = 7.2 Hz, 2H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 121.0, 60.7, 38.8, 31.5, 29.6, 22.4, 14.0; IR (film) 3336, 2958, 1645, 1259, 1051 cm^{-1}; HRMS ($DART^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_8H_{15}BrO]^+$: 226.0650, found 226.0649.



355 *357*

Vinyl bromide 357: To a solution of vinylsilane **355** (127 mg, 0.286 mmol) in CH_2Cl_2 (0.953 mL) was added Br_2 (6.5 μl, 0.286 mmol) dropwise under air at 23 °C. The mixture was stirred for 16 h, at which point MeOH (0.953 mL) and KHF_2 (223 mg, 2.86 mmol) were added. The mixture was stirred for another 16 h, at which point it was partitioned between Et_2O (20 mL) and sat. aq. $NaHCO_3$ (20 mL) were added. The aqueous layer was extracted once more with Et_2O (20 mL), and the combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 → 2:1 hexanes/EtOAc eluent) to afford vinyl bromide **357** (48.9 mg, 83% yield, R_F = 0.50 in 2:1 hexanes/EtOAc eluent) as a colorless oil. The regioisomeric ratio of product **357** remained 6.5:1 favoring the α isomer.

Vinyl bromide 357: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (t, *J* = 6.8 Hz, 1H), 3.79 (t, *J* = 5.9 Hz, 2H), 2.67 (t, *J* = 6.4 Hz, 2H), 2.18 (q, *J* = 7.1 Hz, 2H), 1.47-1.30 (comp m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3, 123.7, 60.4, 44.8, 31.3, 30.7, 22.4, 14.0; IR (film) 3333, 2958, 2929, 1657, 1465, 1047 cm^{-1}; HRMS (DART$^+$) *m/z* calc'd for $(M + NH_4)^+$ $[C_8H_{15}BrO]^+$: 226.0650, found 226.0653.

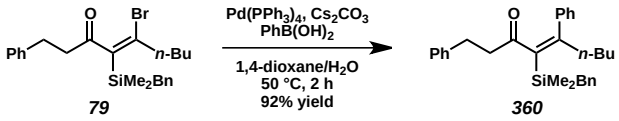


72 *359*

Silyl enone 359: A solution of bromoenone **72** (0.579 g, 1.58 mmol) in dioxane (28.2 mL) and water (5.6 mL) was degassed by the freeze-pump-thaw method (3x). To that solution was added phenylboronic acid (0.385 g, 3.15 mmol), Cs_2CO_3 (5.15 g, 15.8 mmol), and $Pd(PPh_3)_2Cl_2$ (22.1

mg, 0.0316 mmol). The reaction was heated to 50 °C and allowed to stir for 2 h at which point water was added and the mixture was extracted with Et_2O (2 x 75 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ (75 mL), H_2O (75 mL), brine (75 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford silyl enone **359** (0.521 g, 91% yield, R_F = 0.29 in 19:1 hexanes/Et_2O eluent) as a colorless oil.

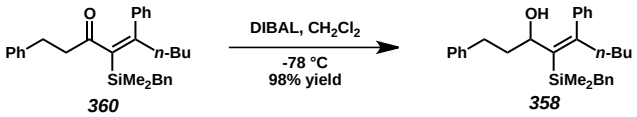
Silyl enone 359: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.15 (comp m, 8H), 6.84 (d, *J* = 8.2 Hz, 2H), 2.53 (t, *J* = 7.7 Hz, 2H), 2.43 (t, *J* = 8.0 Hz, 2H), 2.17 (t, *J* = 8.0 Hz, 2H), 1.33-1.20 (comp m, 4H), 0.84 (t, *J* = 7.0 Hz, 2H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 154.3, 145.1, 142.2, 141.5, 128.3, 128.1, 127.7, 125.8, 46.4, 37.2, 31.0, 30.0, 22.9, 14.1, 0.6; IR (film) 3027, 2957, 1680, 1586, 1496, 1251 cm^{-1}; HRMS (APCI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{24}H_{33}OSi]^+$: 365.2301, found: 365.2298.



Silyl enone 360: A solution of bromoenone **79** (0.250 g, 0.564 mmol) in dioxane (10.1 mL) and water (2.01 mL) was degassed by the freeze-pump-thaw method (3x). To that solution was added phenylboronic acid (0.138 g, 1.13 mmol), Cs_2CO_3 (1.83 g, 5.64 mmol), and $Pd(PPh_3)_4$ (32.6 mg, 0.0282 mmol). The reaction was heated to 50 °C and allowed to stir for 2 h at which point water was added and the mixture was extracted with Et_2O (2 x 75 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ (75 mL), H_2O (75 mL), brine (75 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue

was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford silyl enone **360** (0.229 g, 92% yield, R_F = 0.54 in 9:1 hexanes/Et_2O eluent) as a colorless oil.

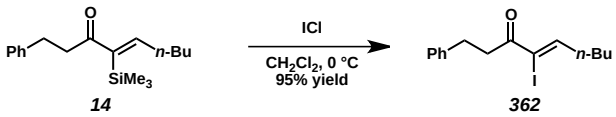
Silyl enone 360: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.03 (comp m, 10H), 6.77 (d, *J* = 7.0 Hz, 2H), 2.49-2.46 (m, 2H), 2.35-2.31 (comp m, 4H), 1.91 (app. t, *J* = 8.0 Hz, 2H), 1.30-1.10 (comp m, 4H) 0.82 (t, *J* = 7.2 Hz, 3H), 0.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 155.6, 143.3, 142.4, 141.6, 139.7, 128.8, 128.61, 128.59, 128.57, 128.5, 128.3, 128.0 125.9, 124.8, 46.0, 37.8, 31.1, 30.0 26.9, 23.2, 14.2, -1.1; IR (film) 3025, 2958, 1678, 1493, 1251, 837, 700 cm^{-1}; HRMS (APCI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{30}H_{37}OSi]^+$: 441.2614, found 441.2598.



Allylic alcohol 358: To a solution of enone **360** (180 mg, 0.425 mmol) in CH_2Cl_2 (1.70 mL) was added DIBAL (0.868 mL, 0.98 M in PhMe, 0.850 mmol) dropwise at -78 °C. The soluion was stirred for 10 min at which point sat. aq. Rochelle's salt (10 mL) and Et_2O (10 mL) were added and the mixture was allowed to stir at room temperature for 3 h. The layers were partitioned and the aqueous layer was extracted once more with Et_2O (20 mL). The combined organic layers were combined, washed with brine (20 mL) and dried over $MgSO_4$. The solution was concentrated in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford **358** (176 mg, R_F = 0.30 9:1 hexanes/Et_2O eluent).

Allylic alcohol 358: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-6.98 (comp m, 15H), 4.03 (dd, *J* = 9.4, 4.2 Hz, 1H), 2.57-2.48 (m, 1H), 2.39 (app. q, *J* = 13.3 Hz, 1H), 2.28 (ddd, *J* = 13.7, 10.5, 6.1 Hz, 2H), 1.85-1.75 (m, 1H), 1.56 (dddd, *J* = 13.7, 10.5, 6.1, 4.2 Hz, 1H), 1.31-1.16 (comp m, 4H), 0.84 (t, *J* = 7.0 Hz, 3H), 0.36 (s, 3H), 0.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 143.6,

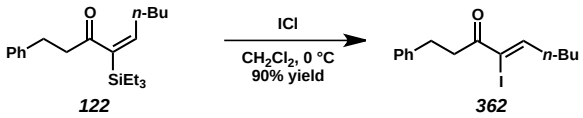
142.5, 140.9, 137.8, 128.7, 128.6, 128.5, 128.4, 126.7, 125.9, 124.6, 75.1, 39.3, 32.9, 30.9, 28.5, 23.3, 14.3, 1.5, 1.3; IR (film) XXX cm^{-1}; HRMS ($APCI^+$) *m/z* calc'd for $(M + NH_4)^+$ $[XXX]^+$: 460.3036, found 460.3039.



14 *362*

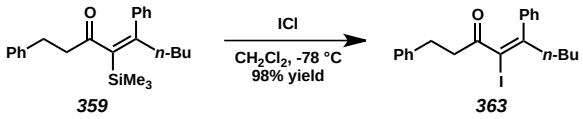
Vinyl iodide 362: To a solution of α-silylenone **14** (76.3 mg, 0.264 mmol) in dichloromethane (0.4 mL) at 0 °C under argon in the dark was added ICl (0.528 mL, 1.0 M in CH_2Cl_2, 0.528 mmol) dropwise, and the solution was allowed to stir for 2 h. The reaction was then quenched with sat. aq. $Na_2S_2O_3$ (1 mL) and allowed to stir for 5 minutes. The mixture was then extracted with Et_2O (2 x 15 mL). The combined organic layers were washed with brine (20 mL) and dried over $MgSO_4$. The solution was concentrated in vacuo, and the residue was purified using flash chromatography (39:1 hexanes/EtOAc eluent) to afford **362** (84.8 mg, 95% yield, R_F = 0.49 in 9:1 hexanes/EtOAc) as a colorless oil.

Vinyl iodide 362: ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.20 (comp m, 5H), 6.97 (t, *J* = 6.9 Hz, 1H), 3.14 (t, *J* = 7.4 Hz, 2H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.40 (app. t, *J* = 7.4 Hz, 2 H), 1.49 (quint, *J* = 7.1 Hz, 2H), 1.38 (sextet, *J* = 7.1 Hz, 2H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 152.6, 141.1, 128.8, 128.6, 126.4, 112.1, 40.0, 37.9, 37.8, 31.2, 29.9, 22.6, 14.1; IR (film) 2956, 2928, 2871, 1684, 1589, 1453 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{20}IO]^+$: 343.0553, found 343.0552.



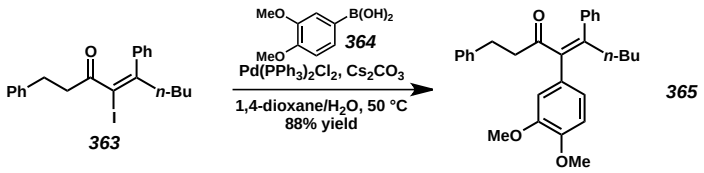
122 *362*

Vinyl iodide 362: To a solution of α-silylenone **122** (80.8 mg, 0.244 mmol) in dichloromethane (0.5 mL) at 0 °C under argon in the dark was added a 1.0 M solution of ICl (0.488 mL, 1.0 M in CH_2Cl_2, 0.488 mmol) dropwise, and the solution was allowed to warm to 23 °C and stirred overnight. The reaction was then quenched with sat. aq. $Na_2S_2O_3$ (1 mL) and allowed to stir for 5 min. The mixture was then extracted with Et_2O (2 x 15 mL). The combined organic layers were washed with brine (20 mL) and dried over $MgSO_4$. The solution was concentrated in vacuo, and the residue was purified using flash chromatography (39:1 hexanes/EtOAc eluent) to afford **362** as a colorless oil (75.3 mg, 90% yield).



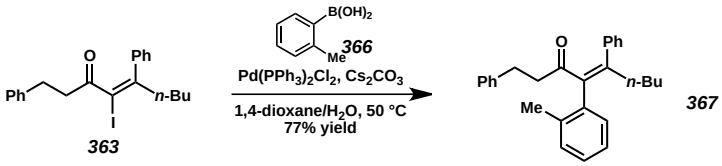
359 *363*

Vinyl iodide 363: To a solution of silyl enone **359** (161 mg, 0.443 mmol) in CH_2Cl_2 (4.43 mL) at -78 °C was added a cold solution of iodine monochloride (0.487 mL, 1M in CH_2Cl_2, 0.487 mmol). The reaction was allowed to stir for 5 min at which point excess ICl was quenched with sat. aq. $Na_2S_2O_3$ (10 mL). The mixture was extracted with Et_2O (2 x 50 mL) and the combined organic layers were washed with H_2O (50 mL), brine (50 mL), and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was filtered through silica gel (2 cm x 7 cm) washing with 9:1 hexanes/Et_2O to afford vinyl iodide **363** (182 mg, 98 % yield, R_F = 0.41 in 19:1 hexanes/Et_2O eluent) as a colorless oil which was immediately carried on to the next step.



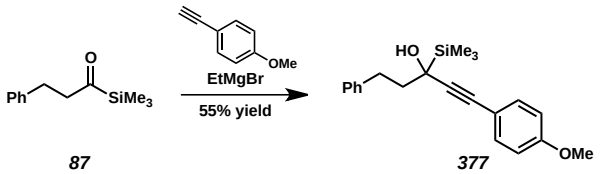
Olefin 365: A solution of iodoenone **363** (87.4 mg, 0.208 mmol) in dioxane (3.72 mL) and water (0.742 mL) was degassed by the freeze-pump-thaw method (3x). To that solution was added 3,4-dimethoxyphenylboronic acid (**365**, 76.2 mg, 0.416 mmol), Cs_2CO_3 (0.678 g, 2.08 mmol), and $Pd(PPh_3)_2Cl_2$ (7.2 mg, 0.0103 mmol). The reaction was heated to 50 °C and allowed to stir for 2 h at which point water was added and the mixture was extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ (50 mL), H_2O (50 mL), brine (50 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc eluent) to afford silyl enone **365** (78.6 mg, 88% yield, R_F = XX in 9:1 hexanes/EtOAc eluent, 8:1 *Z/E*) as a pale yellow oil.

Olefin 365: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.09 (comp m, 9H), 6.88-6.85 (comp m, 3H), 6.80-6.78 (comp m, 2H), 3.91 (s, 3H), 3.88 (s, 3H), 2.58 (t, *J* = 7.7 Hz, 2H), 2.45-2.37 (comp m, 4H), 1.26-1.14 (comp m, 4H), 0.72 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 148.9, 148.5, 144.8, 141.5, 141.2, 140.9, 130.0, 128.6, 128.41, 128.4, 127.9, 125.9, 121.6, 112.3, 111.1, 56.01, 55.98, 45.2, 34.3, 30.6, 30.2, 22.6, 13.9; IR (film) 2956, 1690, 1560, 1512, 1243, 1028 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $(M + Na)^+$ $[C_{29}H_{32}NaO_3]^+$: 451.2249, found: 451.2252.



Olefin 367: A solution of iodoenone **363** (62.2 mg, 0.149 mmol) in dioxane (2.66 mL) and water (0.532 mL) was degassed by the freeze-pump-thaw method (3x). To that solution was added 2-methylphenylboronic acid (**366**, 40.5 mg, 0.298 mmol), Cs_2CO_3 (0.485 g, 1.49 mmol), and $Pd(PPh_3)_2Cl_2$ (5.2 mg, 0.00744 mmol). The reaction was heated to 50 °C and allowed to stir for 2 h at which point water was added and the mixture was extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ (50 mL), H_2O (50 mL), brine (50 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford silyl enone **367** (42.4 mg, 75% yield, R_F = 0.23 in 19:1 hexanes/Et_2O eluent, 7:1 *Z*/*E*) as a colorless oil.

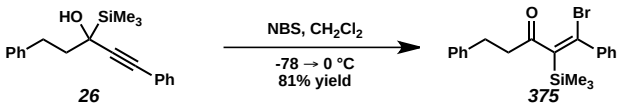
Olefin 367: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.11 (comp m, 12H), 6.84 (d, *J* = 6.5 Hz, 2H), 2.65-2.47 (m, 2H), 2.42-2.36 (m, 2H), 2.32 (s, 3H), 2.27-2.13 (m, 2H), 1.18-1.06 (comp m, 4H), 0.68 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6, 146.5, 141.3, 140.9, 140.8, 137.2, 136.5, 130.3, 129.9, 128.6, 128.4, 128.3, 127.9, 127.8, 125.93, 125.86, 45.1, 34.7, 30.3, 29.9, 22.6, 20.1, 13.8; IR (film) 3026, 2957, 1688, 1494, 1453 cm^{-1}; HRMS (APCI$^+$) *m/z* calc'd for $(M + H)^+$ $[C_{28}H_{31}O]^+$: 383.2375, found 383.2372.



α-Hydroxypropargylsilane 377: A flame-dried flask was charged with 1-ethynyl-4-methoxybenzene (1.50 g, 11.3 mmol) in 18.0 mL of dry THF. The solution was cooled to -78 ºC and EtMgBr (3.62 mL, 3.0 M in Et_2O, 10.8 mmol) was added dropwise. The solution warmed to

0 °C and stirred for 30 min. The reaction mixture was then cooled to –78 ºC. A solution of acylsilane **87** (1.86 g, 9.04 mmol) in 5.0 mL of dry THF was slowly added dropwise. The reaction mixture stirred for 30 min at –78 ºC, then warmed slowly to room temperature. Upon consumption of acylsilane, as judged by TLC, the mixture was cooled to –78 ºC and quenched with saturated aqueous ammonium chloride (10 mL). The mixture was allowed to warm to room temperature and was then extracted with Et_2O (2 x 75 mL), and the combined organic layers were washed with brine (75 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford α-hydroxypropargylsilane **377** (1.69 g, 55% yield, R_F = 0.32 in 9:1 hexanes/EtOAc) as a colorless oil.

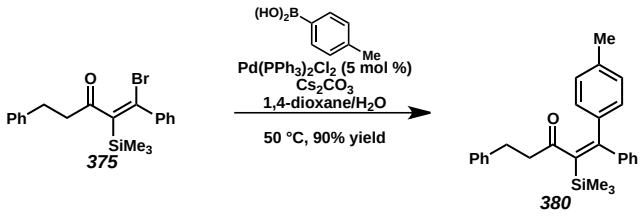
α-hydroxypropargylsilane 377: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (app. d, *J* = 8.9 Hz, 2H), 7.34-7.20 (comp m, 5H), 6.87 (app. d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H), 3.02 (ddd, *J* = 10.0, 6.6, 2.7 Hz, 2H), 2.11-1.93 (comp m, 2H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 143.1, 133.6, 129.1, 129.03, 128.99, 126.4, 116.0, 114.4, 90.5, 88.5, 65.6, 55.8, 40.1, 31.0, -3.7; IR (film) 3464, 2956, 1606, 1509, 1248, 1031, 839 cm^{-1}; LRMS (ESI$^+$) *m/z* calc'd for $(M - OH)^+$ $[C_{21}H_{25}OSi]^+$: 321.2, found 321.2.



α-Silyl-β-bromoenone 375: According to the general procedure, to α-hydroxypropargylsilane **26.** (0.758 g, 2.46 mmol) in CH_2Cl_2 (12.3 mL) was added *N*-bromosuccinimide (0.481 g, 2.70 mmol) in one portion at -78 °C under Ar. The reaction mixture was allowed to slowly warm to 0 °C. When all starting material was consumed as judged by TLC (19:1 Et_2O/hexanes), 20 mL of

pentane was added, and the reaction mixture was filtered through a small pad of celite washing with additional pentane. The solvent was removed by rotary evaporation, and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford silylenone **375** (0.774 g, 86% yield, R_F = 0.40 in 19:1 hexanes/Et_2O eluent) as a colorless oil.

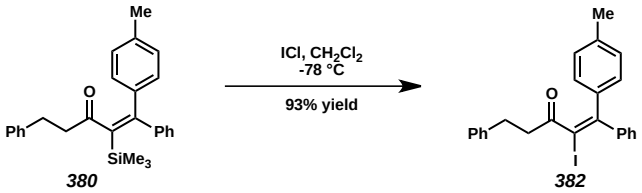
Enone 375: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.36-7.28 (comp m, 10H), 3.05 (app. s, 4H), -0.09 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 206.2, 150.3, 141.4, 141.2, 129.3, 128.71, 128.68, 128.6, 128.5, 128.4, 128.2, 126.3, 44.8, 29.6, -0.05; **IR** (film) 3028, 2956, 1695, 1587, 1116, 844 cm^{-1}; **HRMS** (ESI^+) *m/z* calc'd for $C_{20}H_{23}BrNaOSi$ $(M + Na)^+$ 411.0579, found 411.0587.



α-Silylenone 380: A solution of bromoenone **375** (0.315 g, 0.858 mmol) in 1,4-dioxane (15.3 mL) and water (3.06 mL) was degassed by the freeze-pump-thaw method (3x). To that solution was added 4-methylbenzeneboronic acid (0.233 g, 1.72 mmol), Cs_2CO_3 (2.80 g, 8.58 mmol), and $Pd(PPh_3)_2Cl_2$ (30.1 mg, 0.0429 mmol). The reaction was heated to 50 °C and allowed to stir for 1.5 h, at which point water (5 mL) was added and the mixture was extracted with Et_2O (2 x 75 mL). The combined organic layers were washed with H_2O (75 mL), brine (75 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford silylenone **380** (0.309 g, 90% yield, R_F = 0.29 in 19:1 hexanes/Et_2O eluent) as a colorless oil.

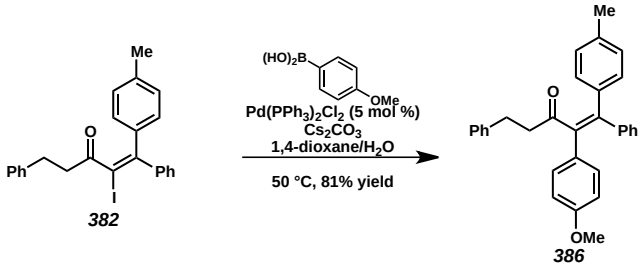
Silylenone 380: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.32-7.05 (comp m, 12H), 6.90 (d, *J* = 7.0 Hz, 2H), 2.62 (t, *J* = 7.8 Hz, 2H), 2.42 (t, *J* = 7.8 Hz, 2H), 2.31 (s, 3H), -0.11 (s, 9H); **^{13}C NMR**

($CDCl_3$, 100 MHz) δ 210.9, 154.2, 147.4, 142.7, 141.7, 139.7, 138.3, 129.4, 129.2, 129.1, 128.6, 128.5, 128.3, 127.9, 126.0, 46.4, 30.5, 21.5, 0.6; **IR** (film) 3026, 2953, 1679, 1494, 1249, 1117, 843 cm^{-1}; **HRMS** (ESI^+) *m/z* calc'd for $C_{27}H_{31}OSi$ $(M + H)^+$ 399.2144, found 399.2150.



380 *382*

α-Iodoenone 382: To a solution of silylenone **380** (205 mg, 0.516 mmol) in CH_2Cl_2 (5.16 mL) at 78 °C was added iodine monochloride (0.568 mL, 1.0 M in CH_2Cl_2, 0.568 mmol) dropwise. The reaction mixture was allowed to stir for 1 h, at which point sat. aq. $Na_2S_2O_3$ (7 mL) was added and the mixture was brought to room temperature. The mixture was extracted with Et_2O (2 x 25 mL) and the combined organic layers were washed with H_2O (25 mL) and brine (25 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation to afford iodoenone **382** (217 mg, 93% yield, R_F = 0.43 in 9:1 hexanes/Et_2O eluent) as a yellow solid, which was used for cross coupling without further purification.

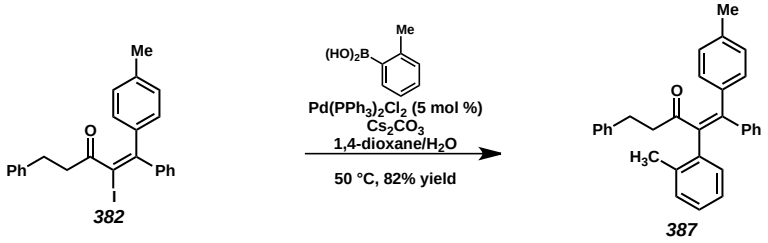


382 *386*

Alkene 386: A solution of iodoenone **382** (47.5 mg, 0.105 mmol) in 1,4-dioxane (1.87 mL) and H_2O (0.375 mL) was degassed using the freeze-pump-thaw method (3x) and placed under an atmosphere of Ar. To the degassed mixture was added (4-methoxyphenyl)boronic acid(31.9 mg,

0.210 mmol), $Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.00525 mmol) and Cs_2CO_3 (0.342 g, 1.05 mmol) and the reaction mixture was placed in a 50 °C heating block. Starting material was consumed in 1.5 h, as judged by TLC (9:1 Et_2O/hexanes) at which point H_2O (5 mL) was added and the mixture was extracted with EtOAc (2 x 15 mL). The combined organic layers were washed with H_2O (10 mL) and brine (15 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford olefin **386** (36.8 mg, 81% yield, R_F = 0.15 in 9:1 hexanes/Et_2O) as a white solid.

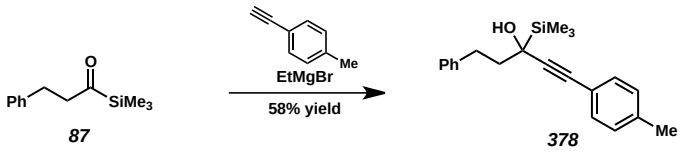
Olefin 386: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.24-7.07 (comp m, 10H), 6.99 (app. t, *J* = 6.5 Hz, 4H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 3.75 (s, 3H), 2.78 (app t, *J* = 7.6 Hz, 2H), 2.66 (app. t, *J* = 7.4 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 208.6, 158.8, 144.5, 141.7, 141.4, 141.3, 139.4, 138.6, 131.5, 131.3, 131.2, 130.2, 130.1, 129.4, 128.63, 128.60, 128.5, 128.0, 127.6, 126.1, 114.0, 113.9, 55.3, 46.0, 30.8, 21.5; **IR** (film) 3027, 2931, 1685, 1606, 1511, 1249, 1032 cm^{-1}; **HRMS** ($APCI^+$) *m/z* calc'd for $C_{31}H_{29}O_2$ $(M + H)^+$ 433.2168, found 433.2162.



Olefin 387: A solution of iodoenone **382** (47.5 mg, 0.105 mmol) in dioxane (1.87 mL) and H_2O (0.375 mL) was degassed using the freeze-pump-thaw method (3x) and placed under an atmosphere of Ar. To the degassed mixture was added o-tolylboronic acid (28.6 mg, 0.210 mmol), $Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.00525 mmol) and Cs_2CO_3 (0.342 g, 1.05 mmol) and the reaction mixture was placed in a 50 °C heating block. Starting material was consumed in 30 minutes as

judged by TLC (9:1 Et_2O/hexanes) at which point H_2O (5 mL) was added and the mixture was extracted with EtOAc (2 x 15 mL). The combined organic layers were washed with H_2O (10 mL) and brine (15 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford olefin **387** (35.9 mg, 82 % yield, R_F = 0.26 in 19:1 hexanes/Et_2O) as a white solid.

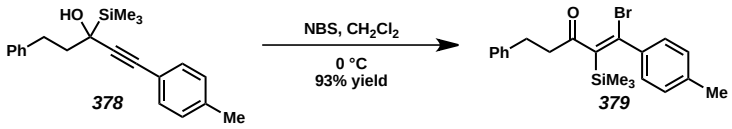
Olefin 387: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.23-6.99 (comp m, 14H), 6.93 (app. t, *J* = 8.0 Hz, 4H), 2.72, (app. t, *J* = 7.7 Hz, 2H), 2.61 (app. t, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 2.14 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 208.7, 158.8, 144.5, 141.7, 141.5, 141.4, 139.5, 138.6, 131.6, 131.4, 131.2, 130.1, 129.4, 128.7, 128.5, 128.0, 127.6, 126.1, 113.9, 55.3, 46.1, 30.9, 21.5; **IR** (thin film, cm^{-1}) 3025, 2923, 1683, 1509, 1126, 815; **HRMS** ($APCI^+$) *m/z* calc'd for $C_{31}H_{29}O$ $(M + H)^+$ 417.2218, found 417.2213.



α-Hydroxypropargylsilane 378: A flame-dried flask was charged with 4-methylphenylacetylene (1.27 g, 10.9 mmol) in 21.8 mL of dry THF. The solution was cooled to -78 ºC and EtMgBr (3.36 mL, 3.0 M in Et_2O, 10.2 mmol) was added dropwise. The solution warmed to 0 °C and stirred for 30 min. The reaction mixture was then cooled to –78 ºC. A solution of acylsilane **87** (1.50 g, 7.28 mmol) in 8.0 mL of dry THF was slowly added dropwise. The reaction mixture stirred for 30 min at –78 ºC, then warmed slowly to room temperature. Upon consumption of acylsilane, as judged by TLC, the mixture was cooled to –78 ºC and quenched with saturated aqueous ammonium chloride (10 mL). The mixture was allowed to warm to room temperature and was then extracted with Et_2O (2 x 75 mL), and the combined

organic layers were washed with brine (20 mL), and then dried over $MgSO_4$. The solution was concentrated in vacuo, and the resulting oil was purified by flash chromatography (9:1 hexanes/Et_2O eluent) to afford α-hydroxypropargylsilane **378** (1.35 g, 58% yield) as a colorless oil.

α-Hydroxypropargylsilane 378: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.35 (app. t, *J* = 7.9 Hz, 3H), 7.31-7.29 (comp m, 3H), 7.24-7.20 (m, 1H), 7.15 (d, *J* = 7.9 Hz, 2H), 3.03 (ddd, *J* = 10.1, 6.5, 3.2 Hz, 2H), 2.38 (s, 3H), 2.12-1.94 (comp m, 2H), 0.22 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 142.8, 138.4, 131.7, 129.3, 128.8, 128.7, 126.1, 120.5, 91.0, 88.4, 65.3, 39.8, 30.7, 21.7, -4.0; **IR** (thin film, cm^{-1}) 3449, 3207, 2955, 1603, 1248; **HRMS** ($APCI^+$) *m/z* calc'd for $C_{21}H_{25}Si$ $(M - OH)^+$ 305.1726, found 305.1712; **TLC** R_f = 0.15 (19:1 hexanes/Et_2O).

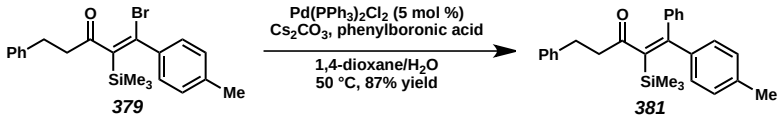


378 *379*

α-Silyl-β-bromoenone 379: According to the general procedure, to α-hydroxypropargylsilane **378** (0.326 g, 1.01 mmol) in CH_2Cl_2 (5.05 mL) was added *N*-bromosuccinimide (0.198 g, 1.11 mmol) in one portion at 0 °C under Ar. When all starting material was consumed as judged by TLC (19:1 Et_2O/hexanes), 100 mL of pentane was added, and the reaction mixture was filtered through a small pad of celite washing with additional pentane. The solvent was removed by rotary evaporation, and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford silylenone **379** (0.375 g, 93% yield, R_F = 0.29 in 19:1 hexanes/Et_2O eluent) as a colorless oil.

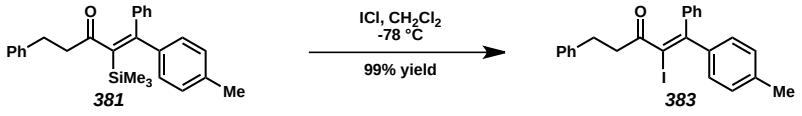
Enone 379: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.32-7.14 (comp m, 9H), 3.02 (app. s, 4H), 2.36 (s, 3H), -0.10 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 206.4, 150.0, 141.3, 139.5, 138.7, 129.1,

128.74, 128.70, 128.4, 126.3, 44.9, 29.5, 21.6; **IR** (film) 3002, 2955, 1777, 1537, 1220, 1116 cm^{-1}; **HRMS** ($APCI^+$) *m/z* calc'd for $C_{21}H_{29}BrNOSi$ $(M + NH_4)^+$ 420.1181, found 420.1178.



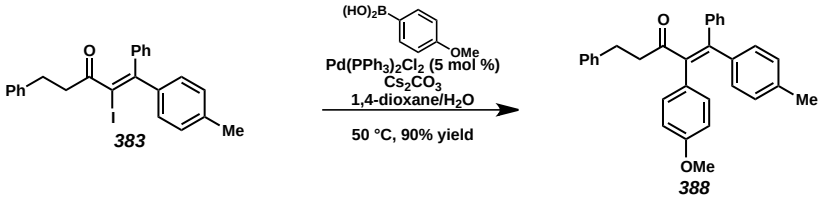
α-Silylenone 381: A solution of bromoenone **379** (0.379 g, 0.946 mmol) in 1,4-dioxane (16.9 mL) and water (3.38 mL) was degassed by the freeze-pump-thaw method (3x). To that solution was added phenylboronic acid (0.231 g, 1.89 mmol), Cs_2CO_3 (3.08 g, 9.46 mmol), and $Pd(PPh_3)_2Cl_2$ (33.2 mg, 0.0473 mmol). The reaction was heated to 50 °C and allowed to stir for 45 min, at which point water was added and the mixture was extracted with Et_2O (2 x 75 mL). The combined organic layers were washed with H_2O (75 mL), brine (75 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/Et_2O eluent) to afford silylenone **381** (0.326 g, 87% yield, R_F = 0.29 in 19:1 hexanes/Et_2O eluent) as a colorless oil.

Silylenone 379: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.27-7.10 (comp m, 12H), 6.89 (d, *J* = 6.7 Hz, 2H), 2.58 (app. t, *J* = 7.9 Hz, 2H), 2.40 (app. t, *J* = 8.1 Hz, 2H), 2.37 (s, 3H), -0.08 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 210.7, 154.2, 147.9, 142.7, 141.5, 139.7, 137.7, 129.3, 129.2, 128.5, 128.4, 128.2, 126.0, 46.5, 30.4, 21.5, 0.6; **IR** (film) 2953, 1679, 1507, 1249, 1118, 856 cm^{-1}; **HRMS** ($APCI^+$) *m/z* calc'd for $C_{27}H_{31}OSi$ $(M + H)^+$ 399.2144, found 399.2139.



α-Iodoenone 383: To a solution of silylenone **381** (49.2 mg, 0.124 mmol) in CH_2Cl_2 (1.24 mL)

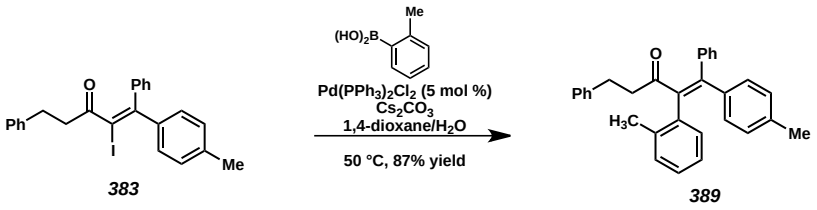
at 78 °C was added ICl (0.136 mL, 1.0 M in CH_2Cl_2, 0.136 mmol) dropwise. The reaction mixture was allowed to stir for 1 h, at which point sat. aq. $Na_2S_2O_3$ (3 mL) was added and the mixture was brought to room temperature. The mixture was extracted with Et_2O (2 x 15 mL) and the combined organic layers were washed with H_2O (15 mL) and brine (15 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation to afford iodoenone **383** (55.7 mg, 99% yield, R_F = 0.43 in 9:1 hexanes/Et_2O eluent) as a yellow solid, which was used for cross coupling without further purification.



Alkene 388: A solution of iodoenone **383** (52.8 mg, 0.117 mmol) in 1,4-dioxane (2.08 mL) and H_2O (0.417 mL) was degassed using the freeze-pump-thaw method (3x) and placed under an atmosphere of Ar. To the degassed mixture was added (4-methoxyphenyl)boronic acid(35.5 mg, 0.234 mmol), $Pd(PPh_3)_2Cl_2$ (4.1 mg, 0.00584 mmol) and Cs_2CO_3 (0.381 g, 1.17 mmol) and the reaction mixture was placed in a 50 °C heating block. Starting material was consumed in 2 h as judged by TLC (9:1 Et_2O/hexanes) at which point H_2O (5 mL) was added and the mixture was extracted with EtOAc (2 x 15 mL). The combined organic layers were washed with H_2O (10 mL) and brine (15 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to afford olefin **388** (45.2 mg, 90% yield, R_F = 0.14 in 9:1 hexanes/Et_2O) as a white solid.

Alkene 388: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.35-7.12 (comp m, 8H), 6.95 (app. dd, *J* = 10.1, 7.5 Hz, 4H), 6.87, (app. dd, *J* = 8.5, 3.3 Hz, 4H), 6.69 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H), 2.74

(app. t, J = 7.4 Hz, 2H), 2.63 (app. t, J = 8.0 Hz, 2H), 2.27 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 208.6, 158.9, 144.4, 142.6, 141.7, 141.3, 138.4, 137.6, 131.5, 131.2, 130.2, 128.8, 128.7, 128.6, 126.1, 114.0, 55.4, 46.1, 30.9, 21.5; **IR** (film) 3027, 2930, 1687, 1606, 1509, 1289, 1074 cm^{-1}; **HRMS** ($APCI^+$) *m/z* calc'd for $C_{31}H_{29}O_2$ $(M + H)^+$ 433.2168, found 433.2174.



Olefin 389: A solution of iodoenone **383** (39.2 mg, 0.0867 mmol) in dioxane (1.55 mL) and H_2O (0.310 mL) was degassed using the freeze-pump-thaw method (3x) and placed under an atmosphere of Ar. To the degassed mixture was added o-tolylboronic acid (23.6 mg, 0.173 mmol), $Pd(PPh_3)_2Cl_2$ (3.0 mg, 0.00433 mmol) and Cs_2CO_3 (0.283 g, 0.867 mmol) and the reaction mixture was placed in a 50 °C heating block. Starting material was consumed in 2 h as judged by TLC (9:1 Et_2O/hexanes) at which point H_2O (5 mL) was added and the mixture was extracted with EtOAc (2 x 15 mL). The combined organic layers were washed with H_2O (10 mL) and brine (15 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford olefin **389** (31.4 mg, 87 % yield, R_F = 0.26 in 19:1 hexanes/Et_2O) as a white solid.

Olefin 389: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.00 (comp m, 12H), 6.92 (d, J = 6.7 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 8.2 Hz, 2H), 2.73-2.67 (m, 2H), 2.58 (app t, J = 7.1 Hz, 2H), 2.22, (s, 3H), 2.13 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 206.6, 146.7, 142.2, 141.4, 138.7, 138.1, 137.8, 136.8, 130.7, 130.6, 130.5, 130.3, 128.7, 128.61, 128.58, 128.50, 128.46,

127.9, 126.1, 126.0, 45.3, 30.7, 21.4, 20.3; **IR** (thin film, cm^{-1}) 3026, 2923, 1684, 1493, 1187, 732; **HRMS** ($APCI^+$) *m/z* calc'd for $C_{31}H_{29}O$ $(M + H)^+$ 417.2218, found 417.2213.

CHAPTER FOUR NOTES AND REFERENCES

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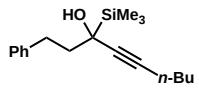
APPENDIX ONE

Spectra Relevant to Chapter Two:

$PtCl_2$ Catalyzed and *N*-Halosuccinimide Mediated 1,2-Silyl Migration Reactions



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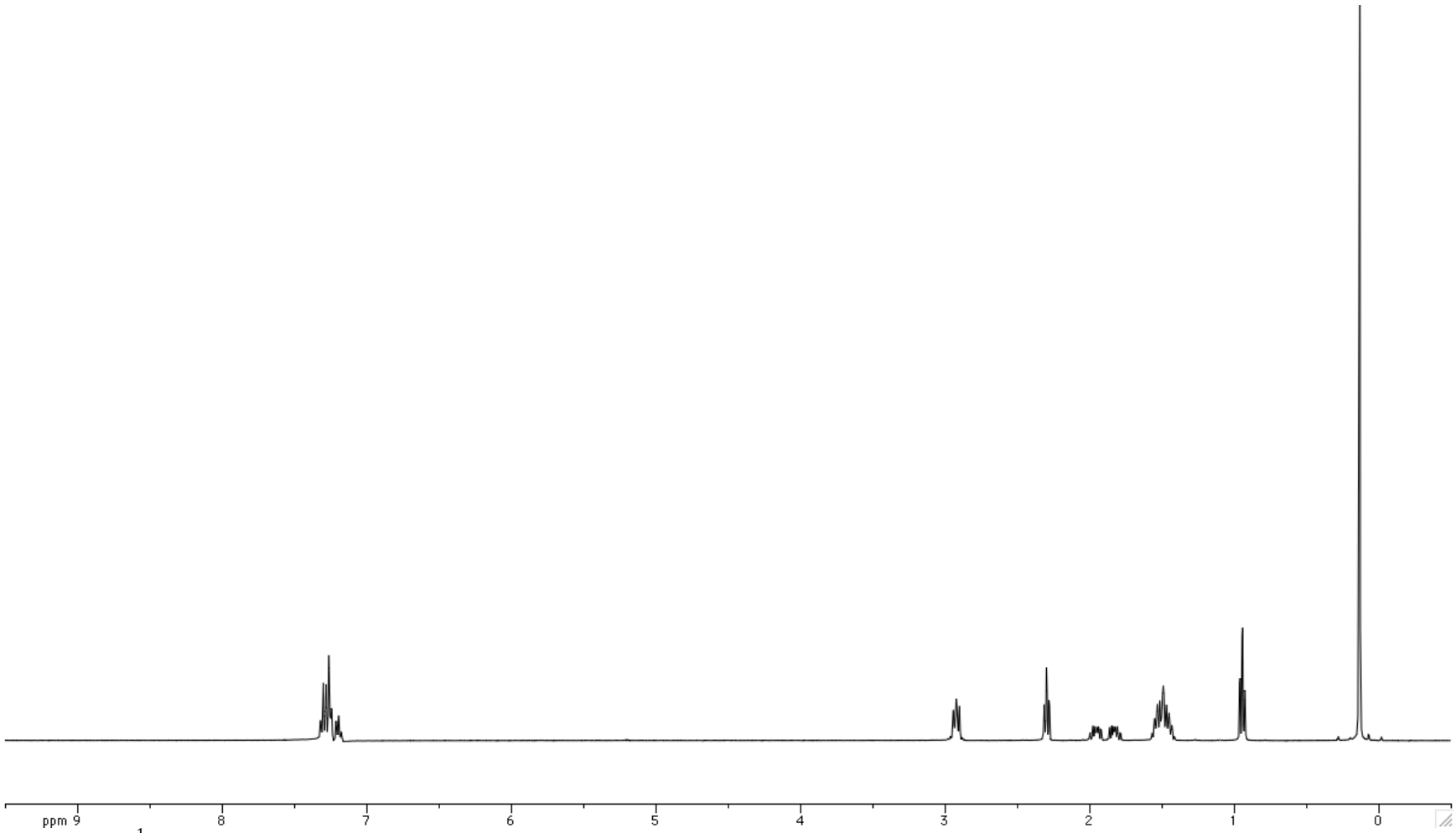


Figure A1.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **12**

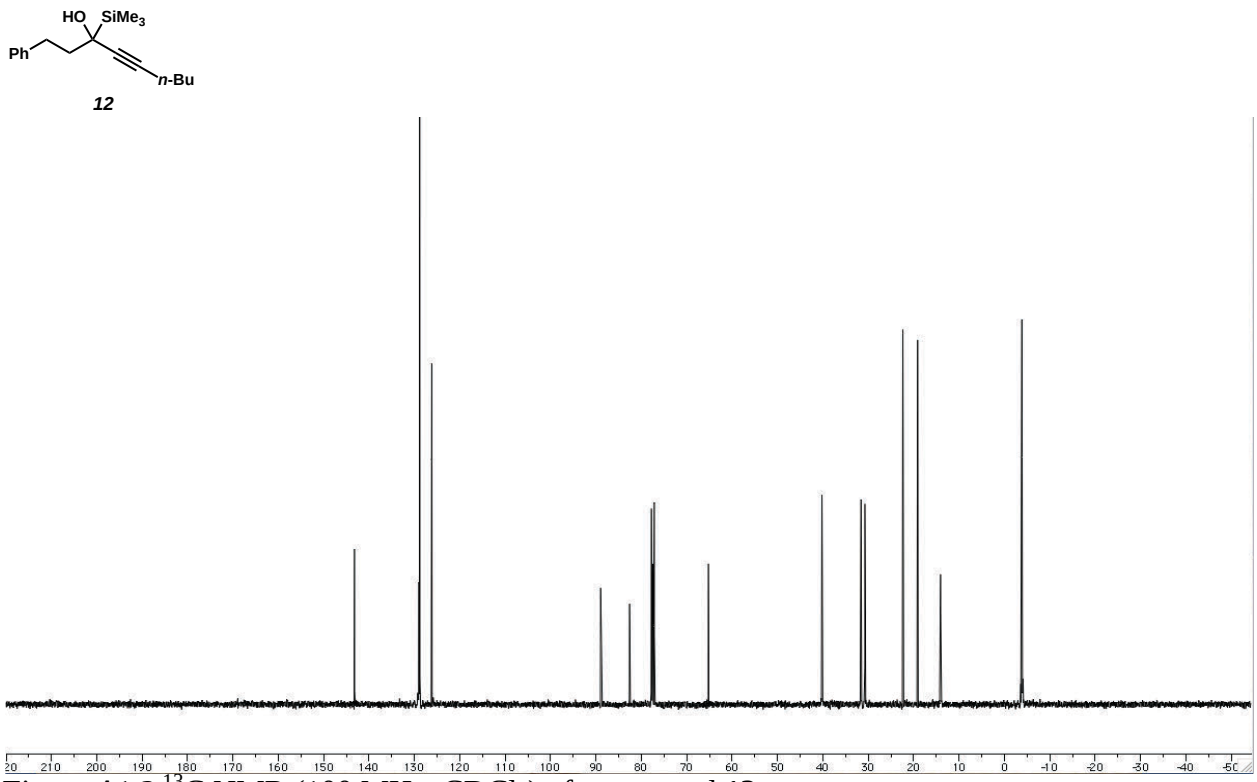


Figure A1.2 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **12**

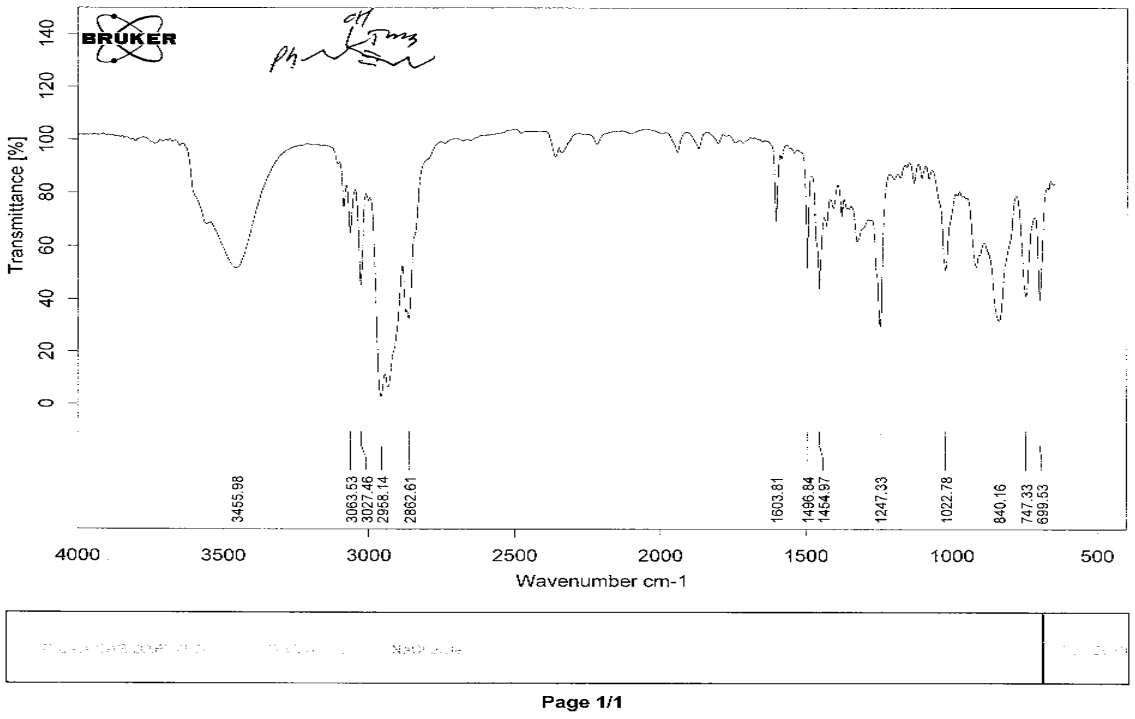
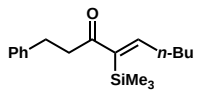


Figure A1.3 Infrared spectrum (thin film) of compound **12**



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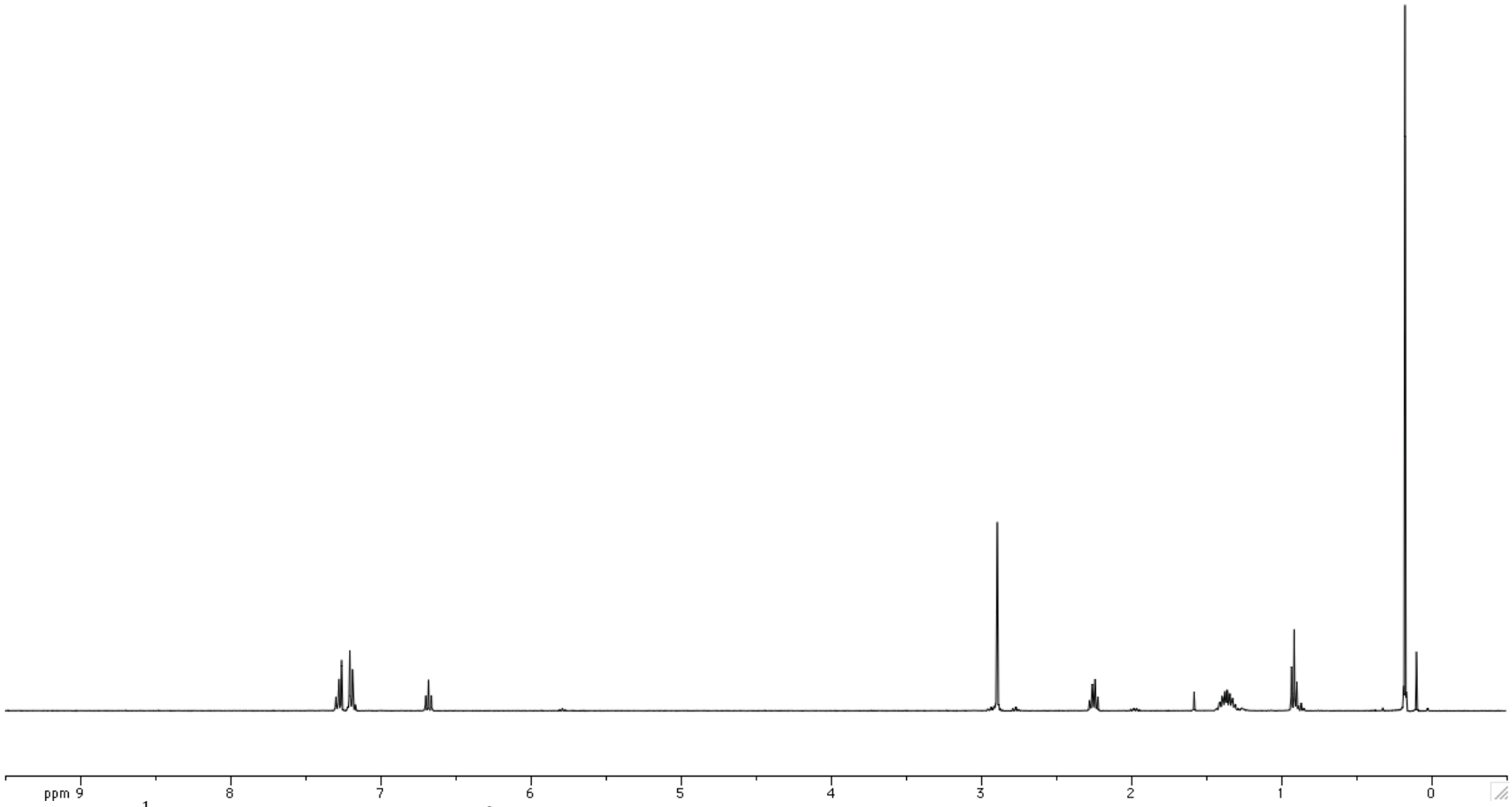
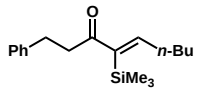


Figure A1.4 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **14**



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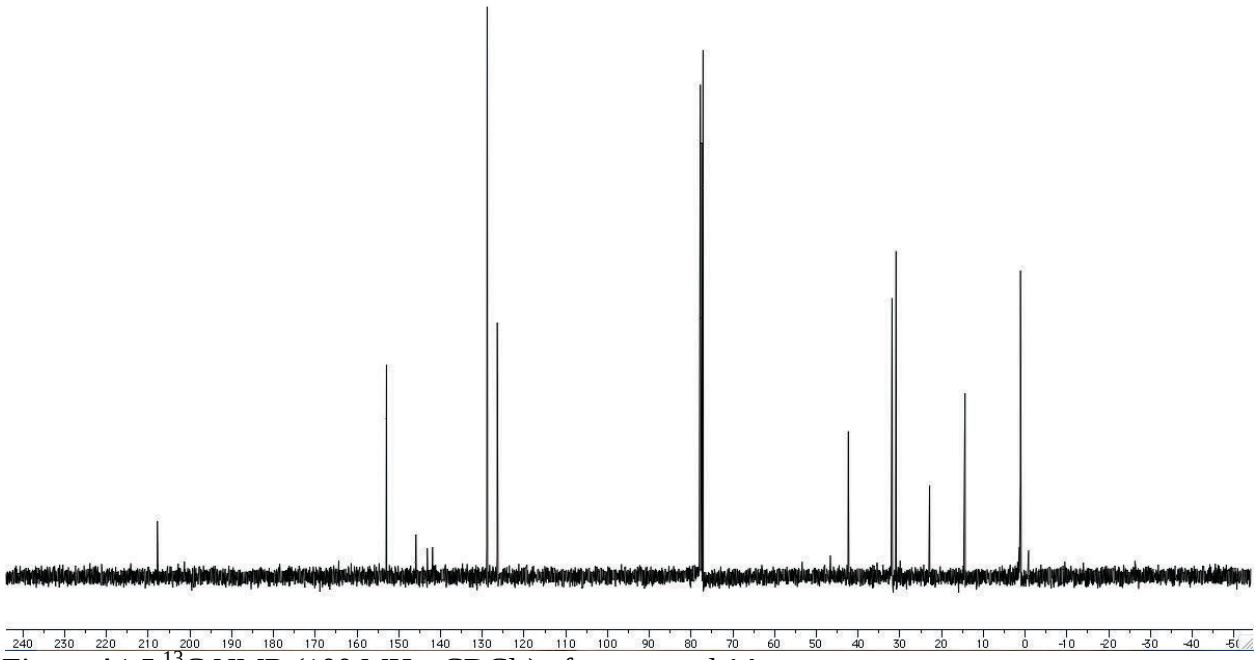

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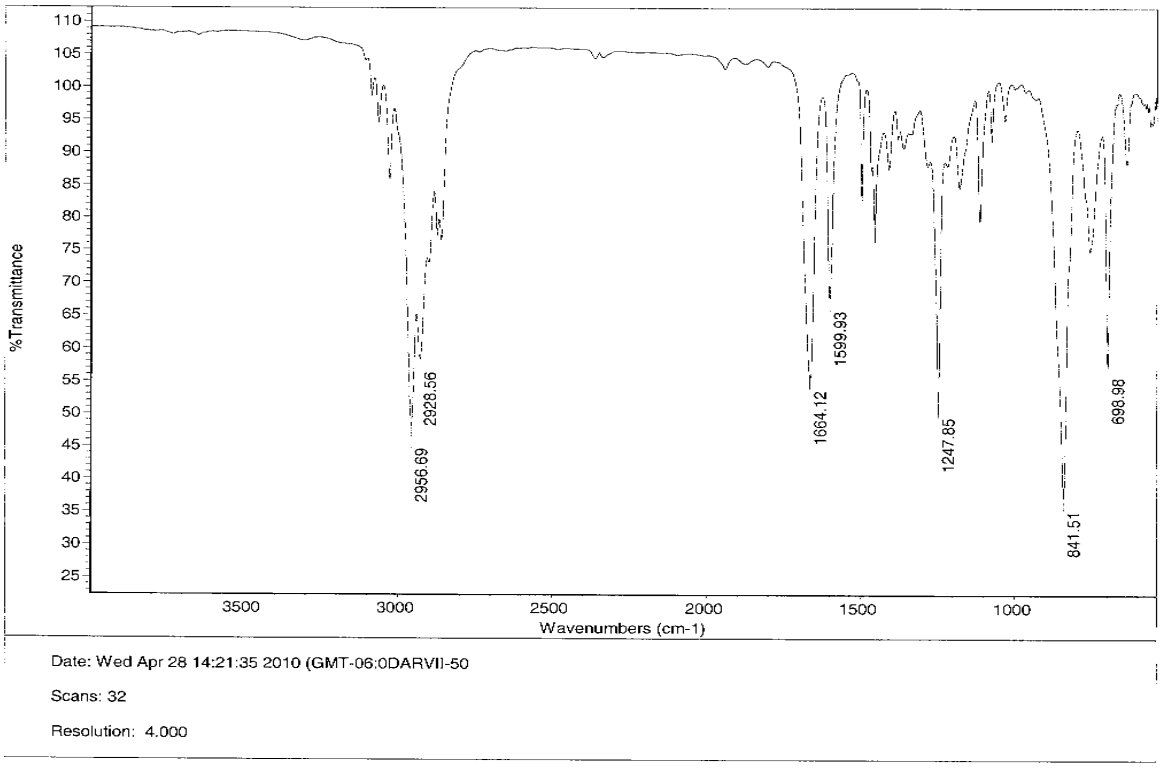
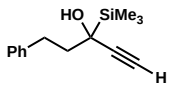


Figure A1.6 Infrared spectrum (thin film) of compound **14**



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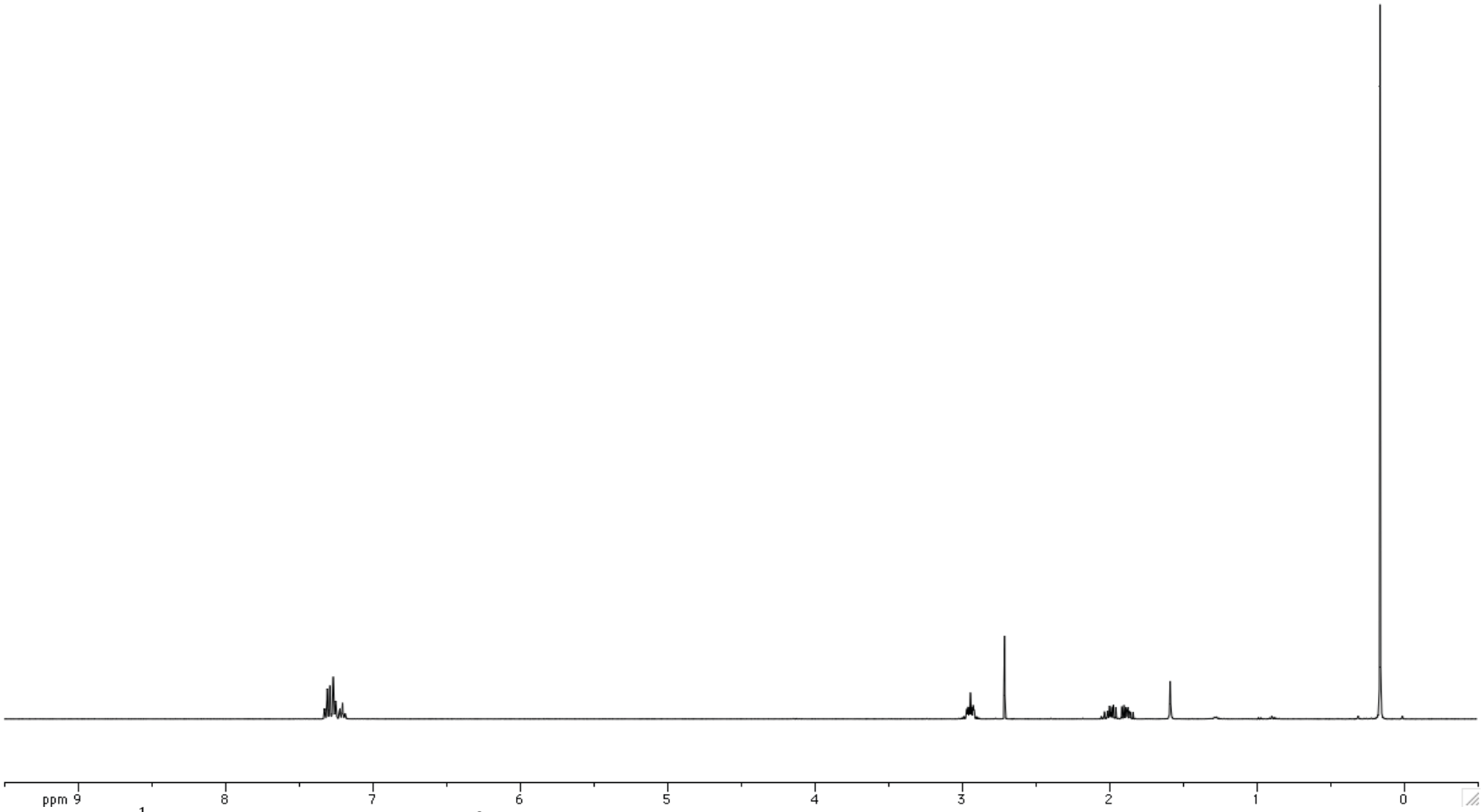


Figure A1.7 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **22**

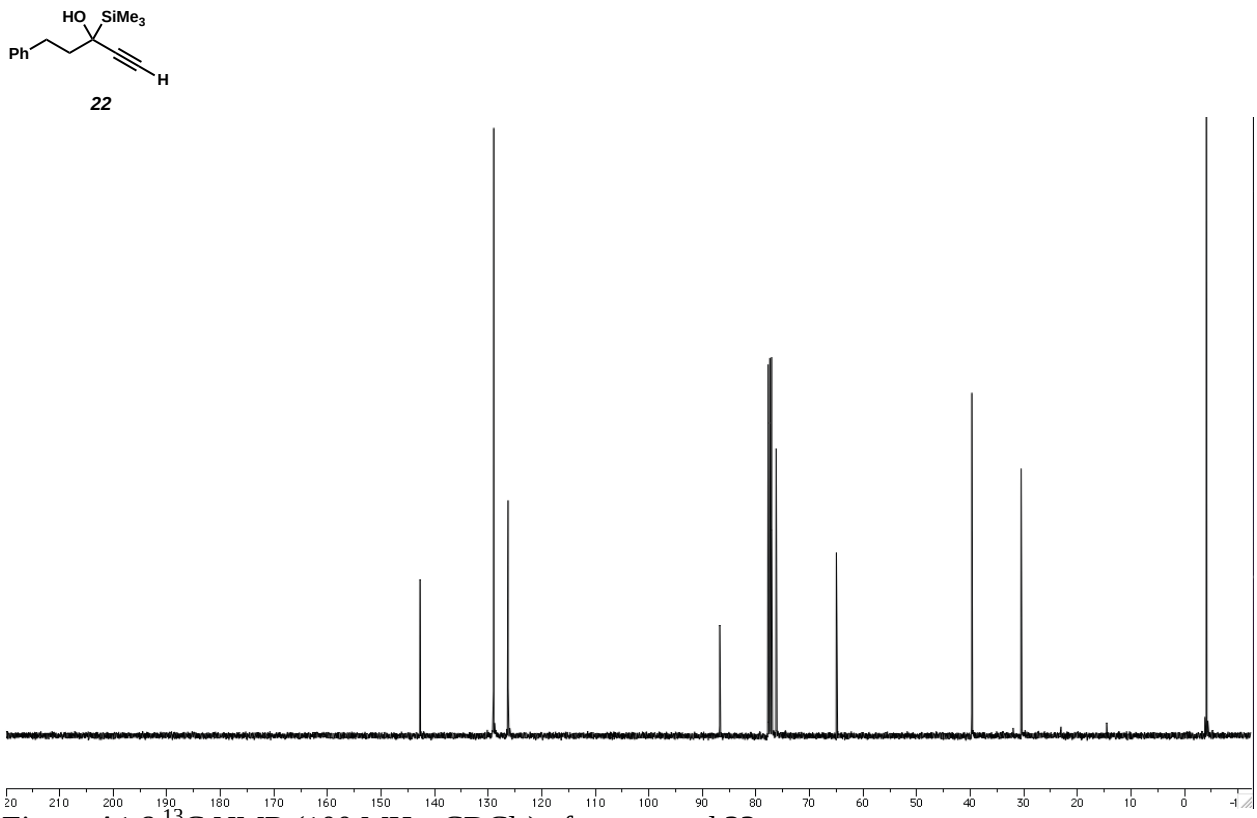
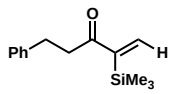


Figure A1.8 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **22**

Figure A1.9 Infrared spectrum (thin film) of compound **22**



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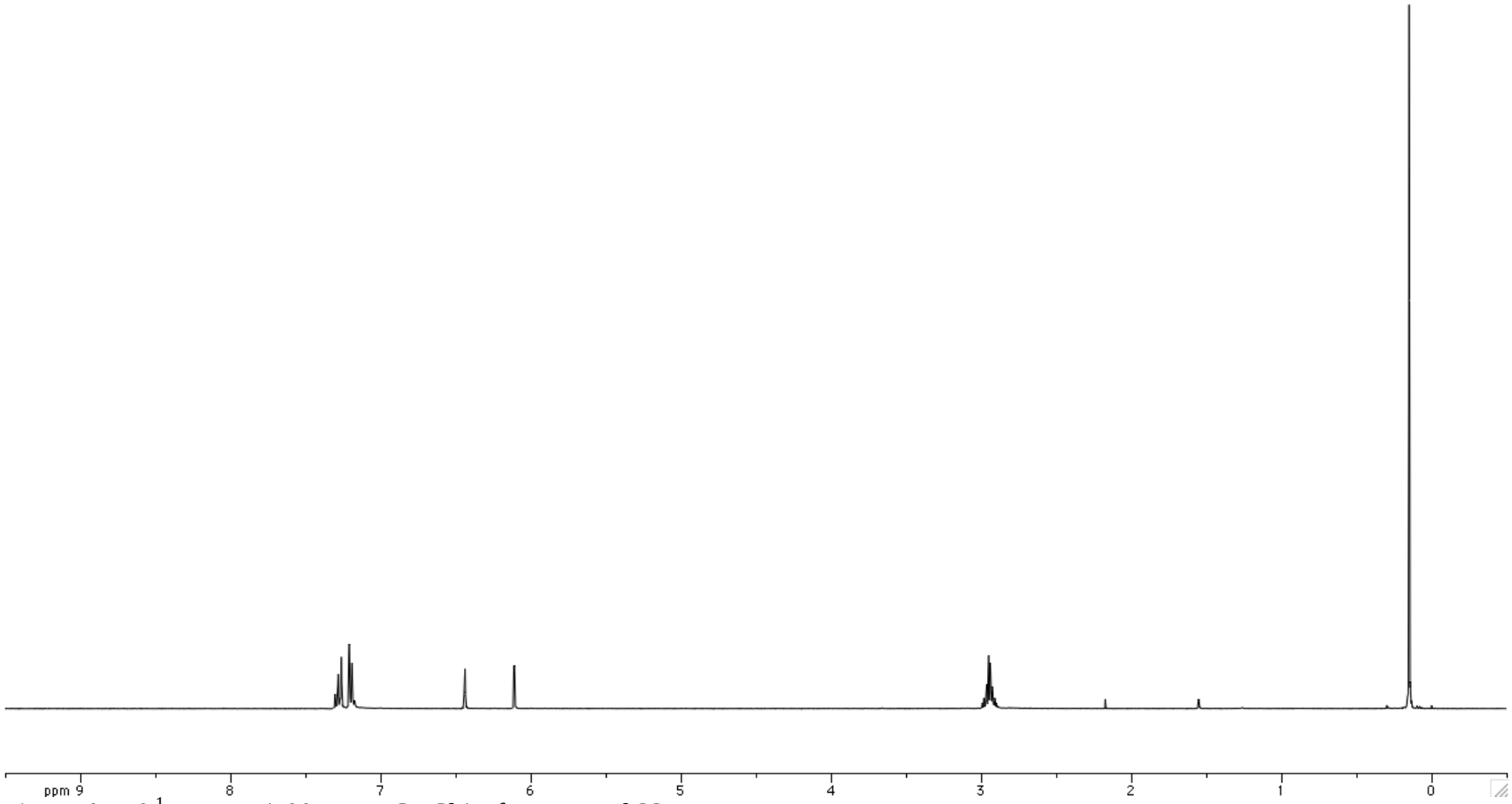


Figure A1.10 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **23**

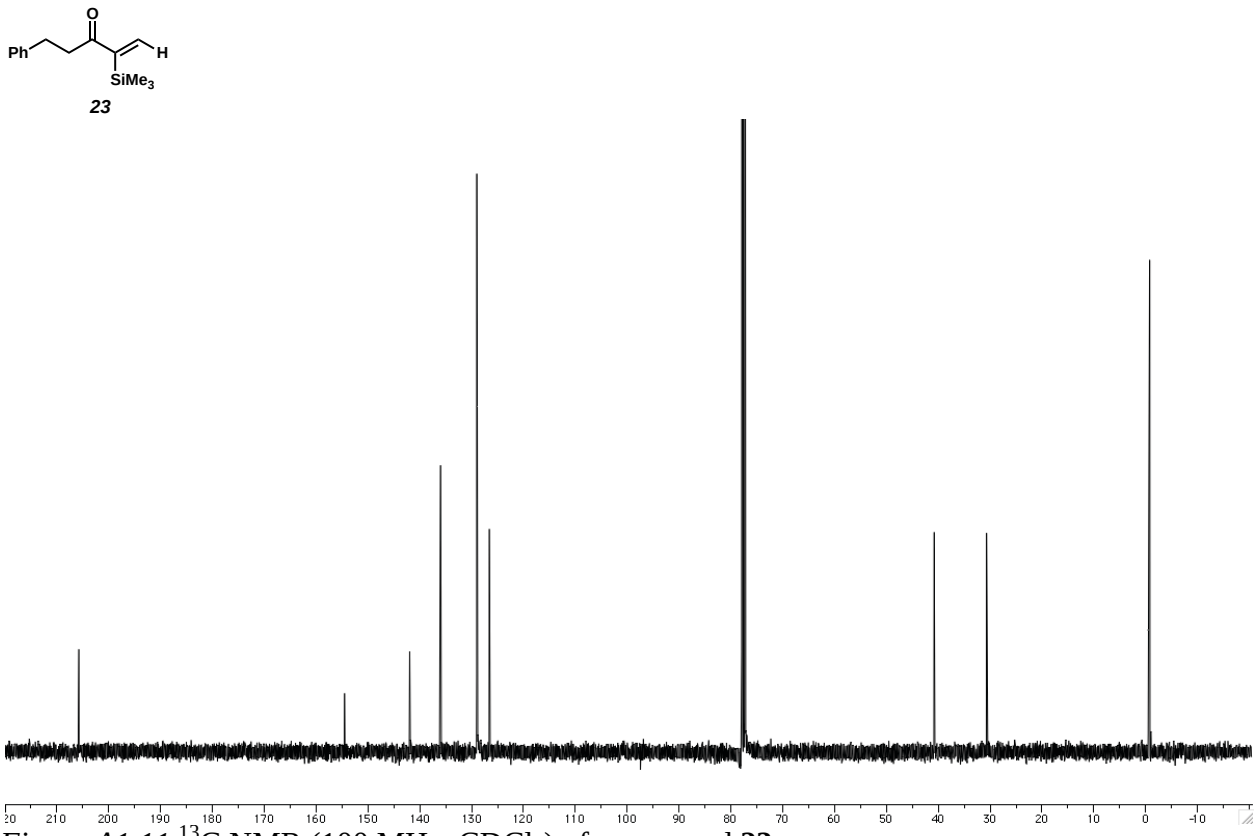
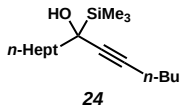


Figure A1.11 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **23**

Figure A1.12 Infrared spectrum (thin film) of compound **23**



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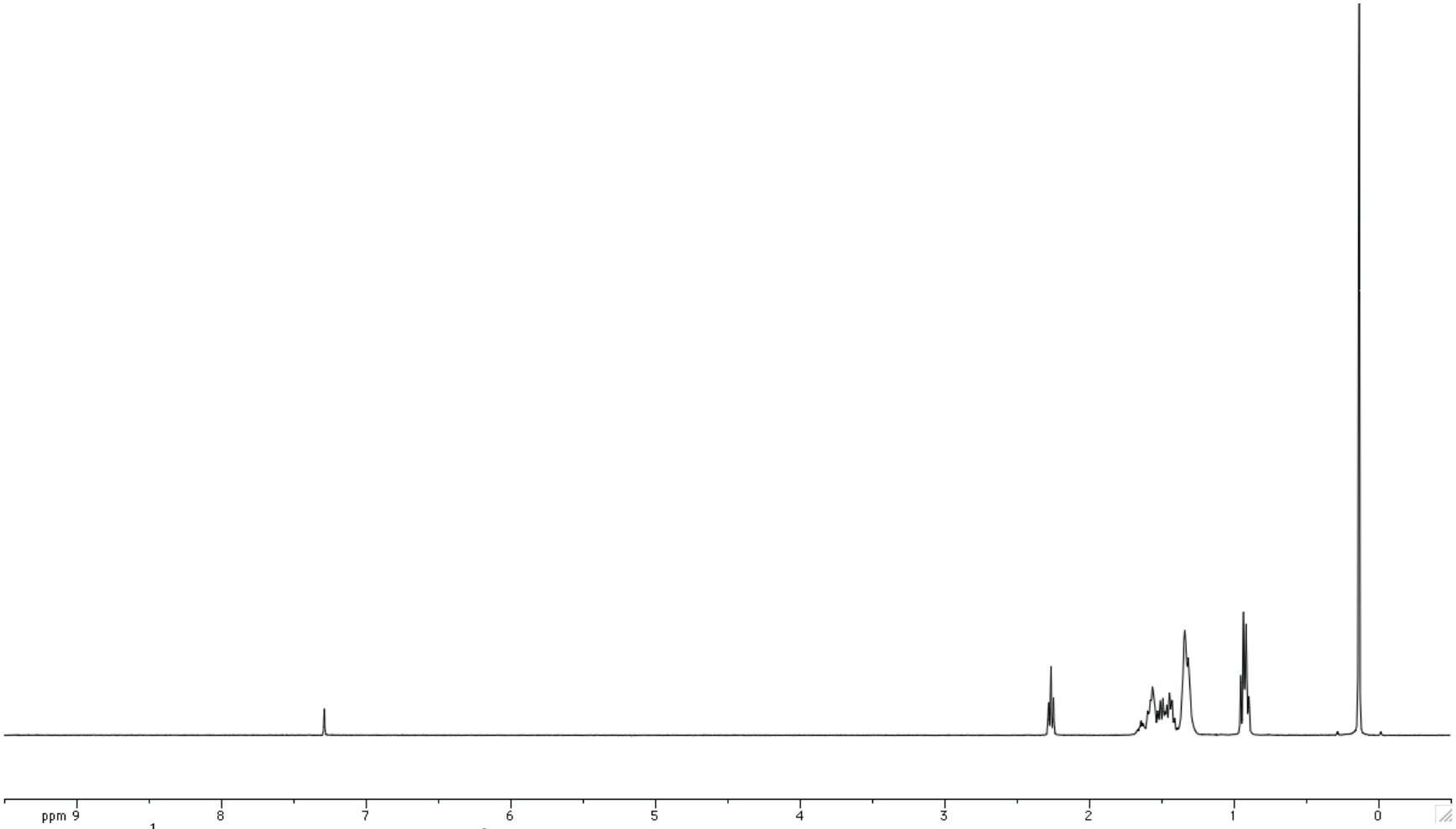
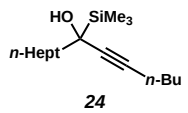


Figure A1.13 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **24**



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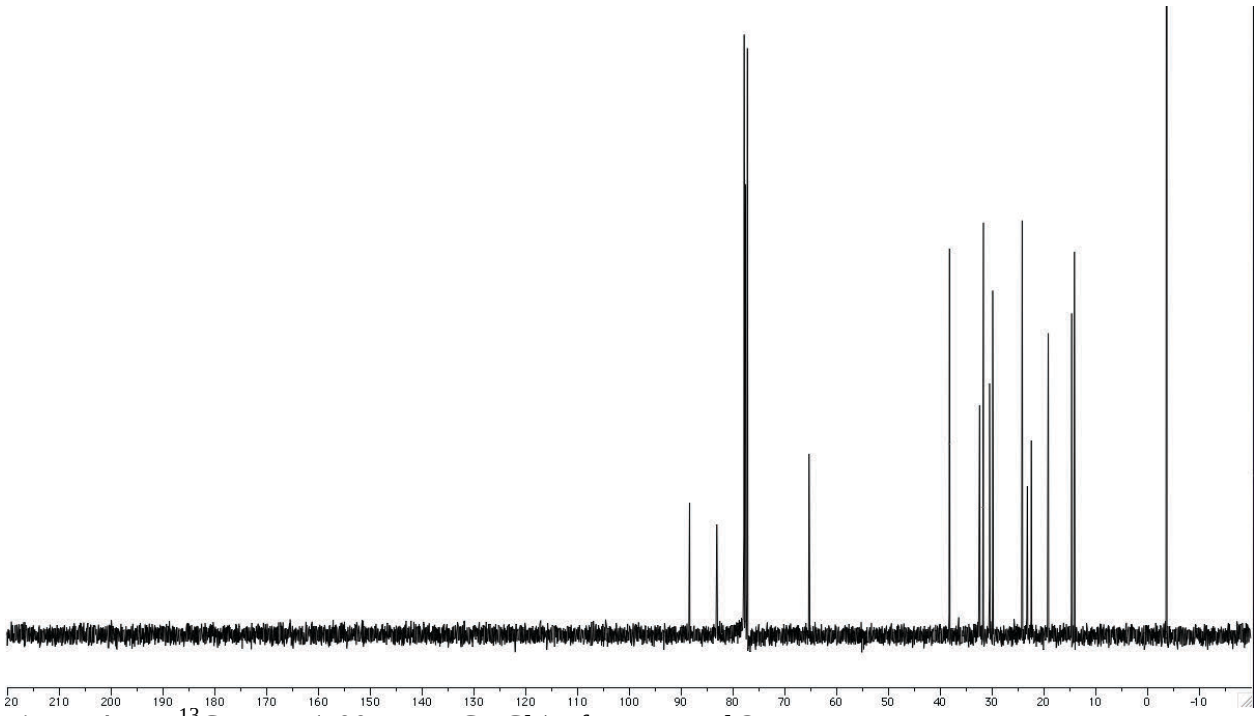


Figure A1.14 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **24**

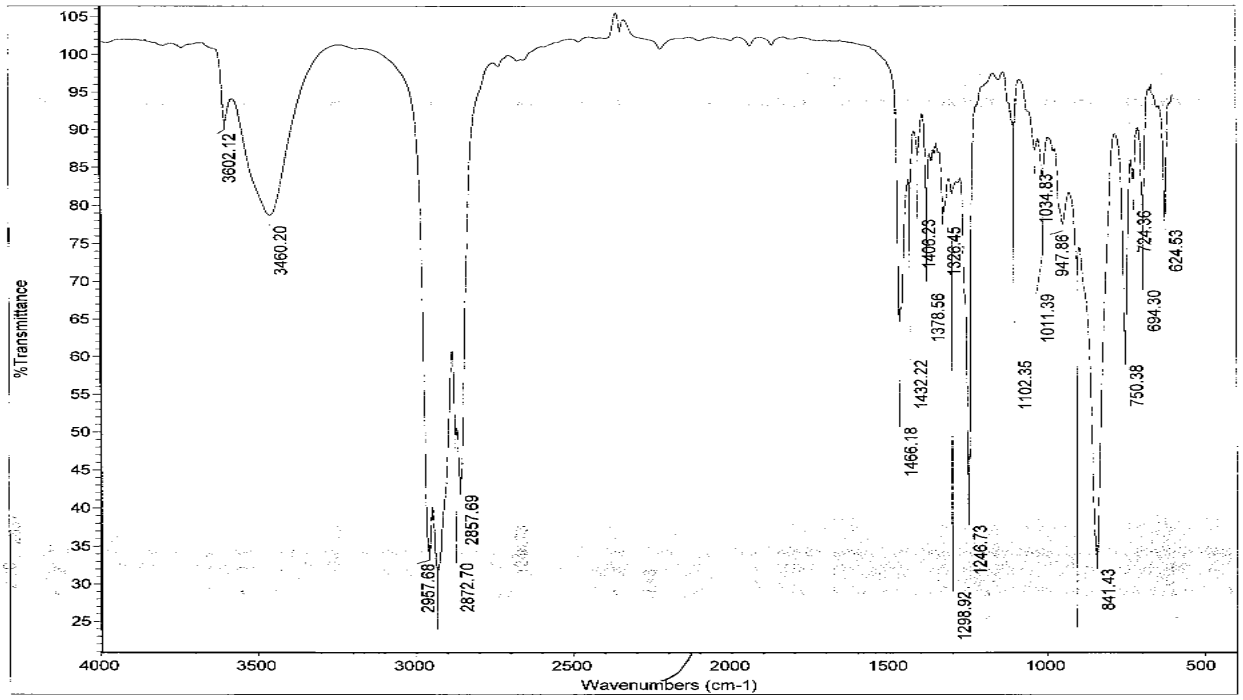
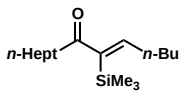


Figure A1.15 Infrared spectrum (thin film) of compound **24**



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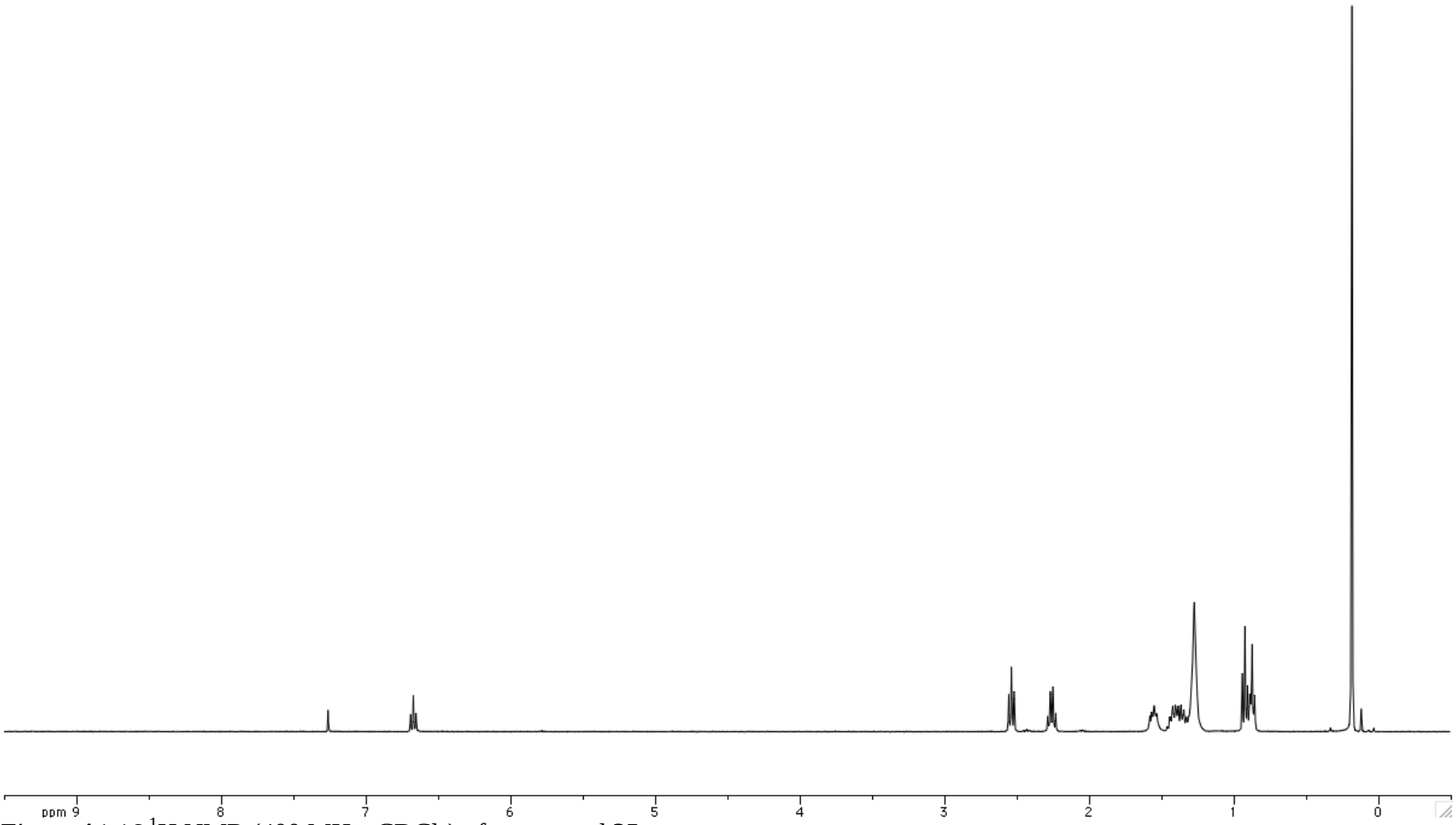

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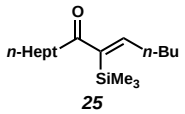

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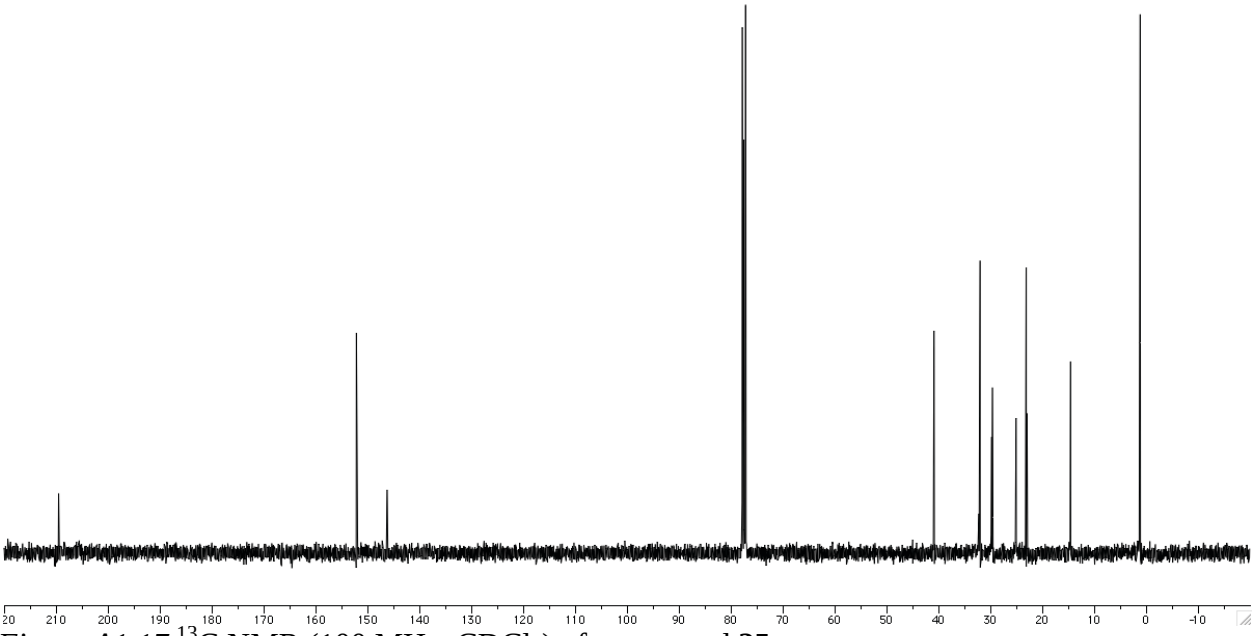

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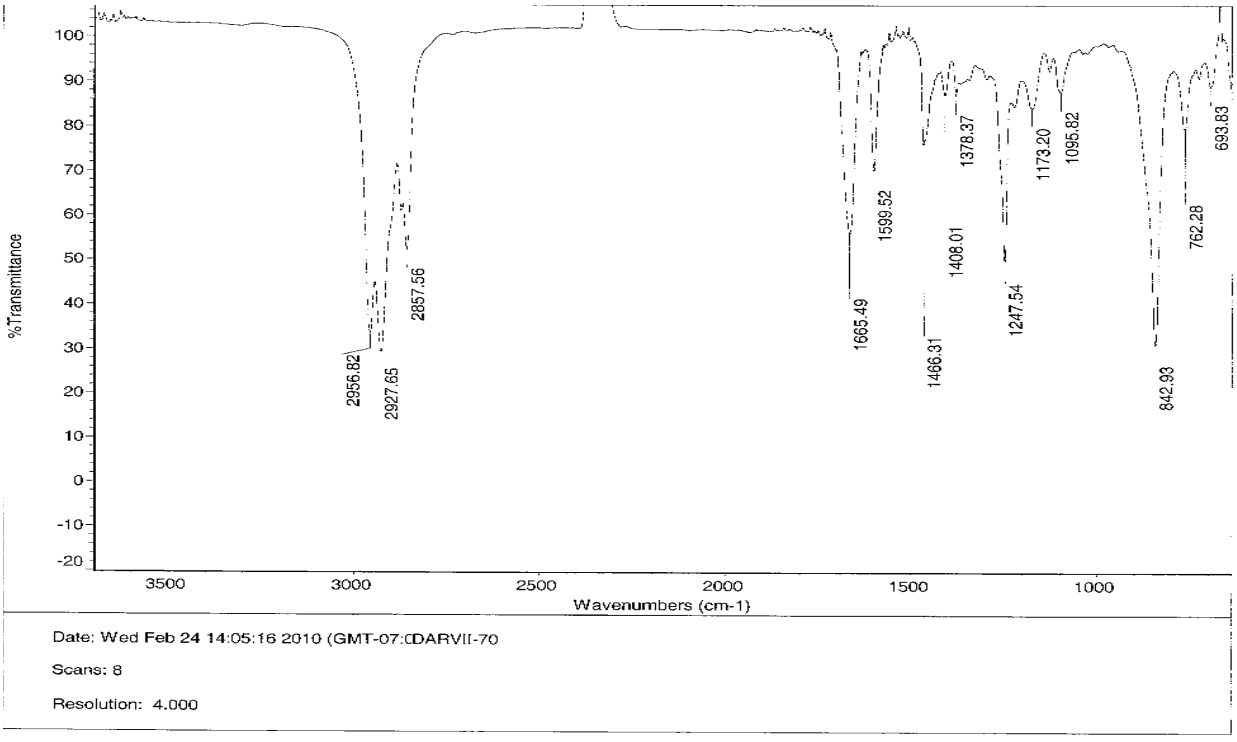
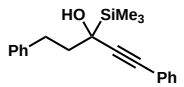


Figure A1.18 Infrared spectrum (thin film) of compound **25**



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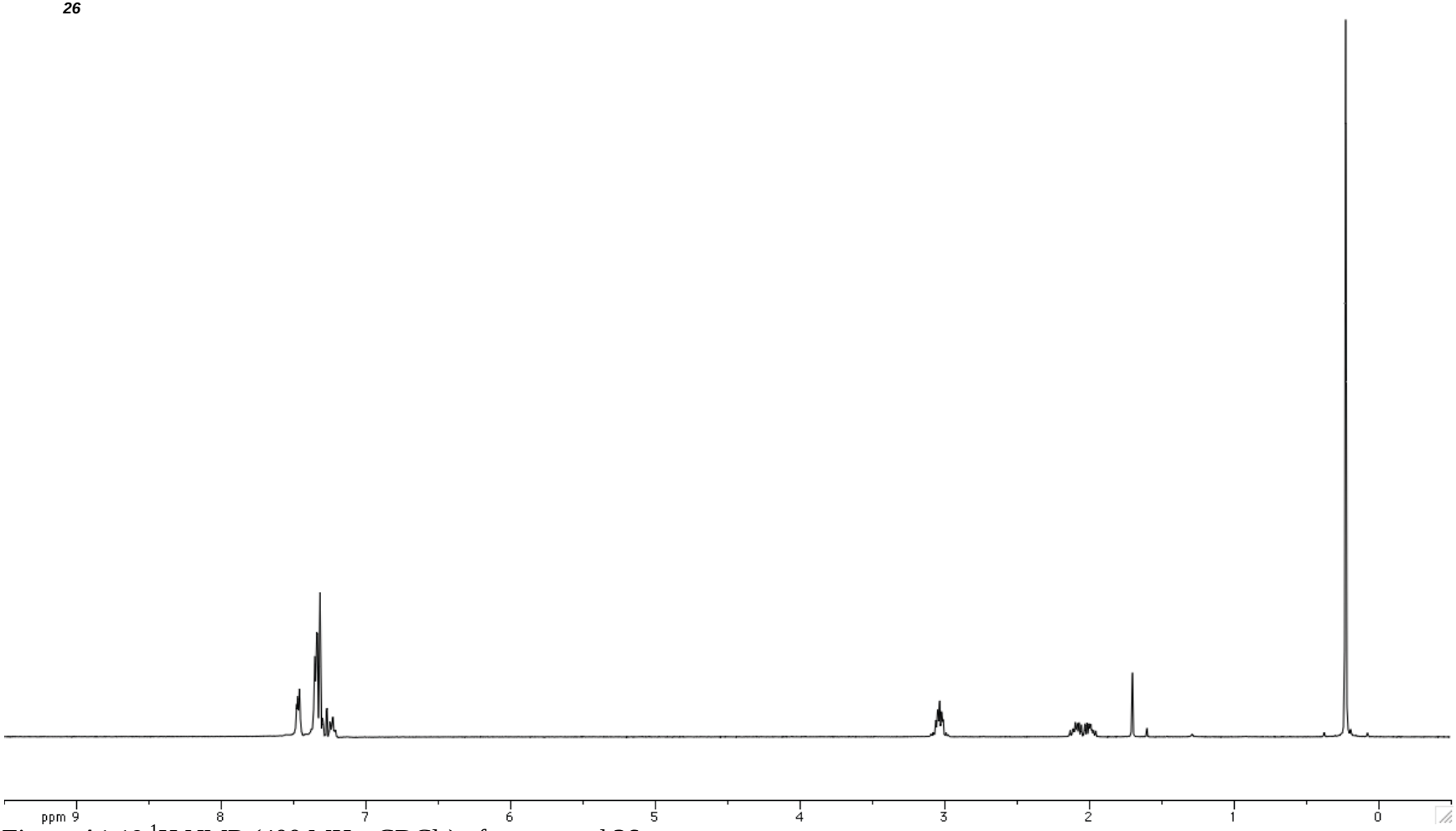


Figure A1.19 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **26**

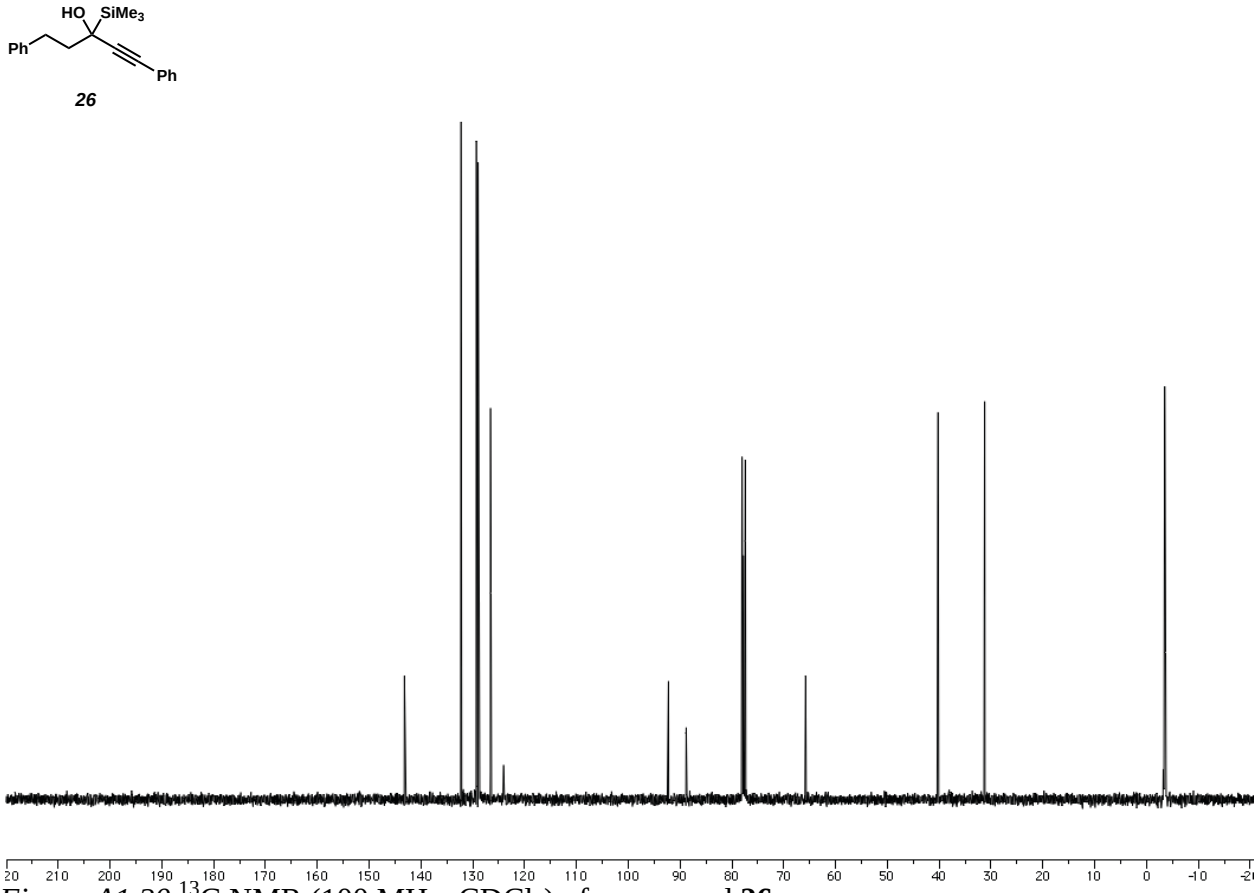


Figure A1.20 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **26**

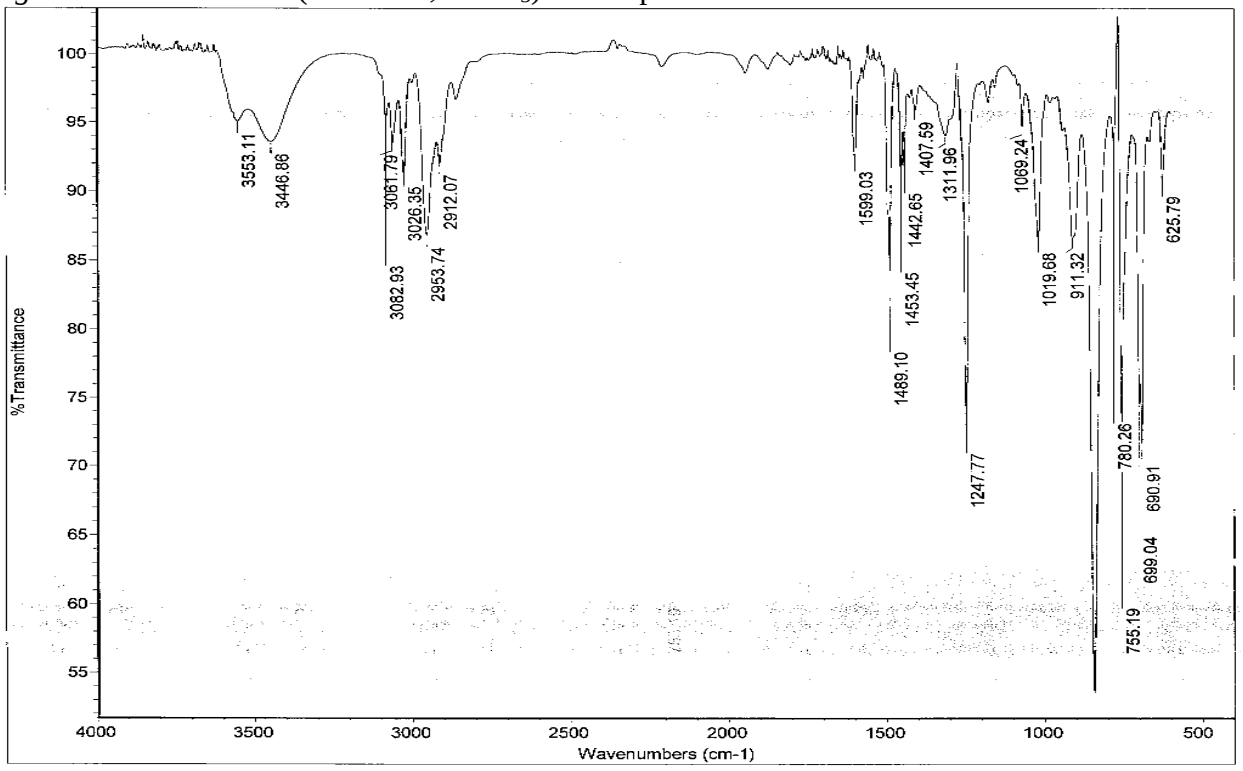
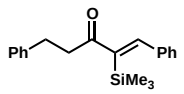


Figure A1.21 Infrared spectrum (thin film) of compound **26**



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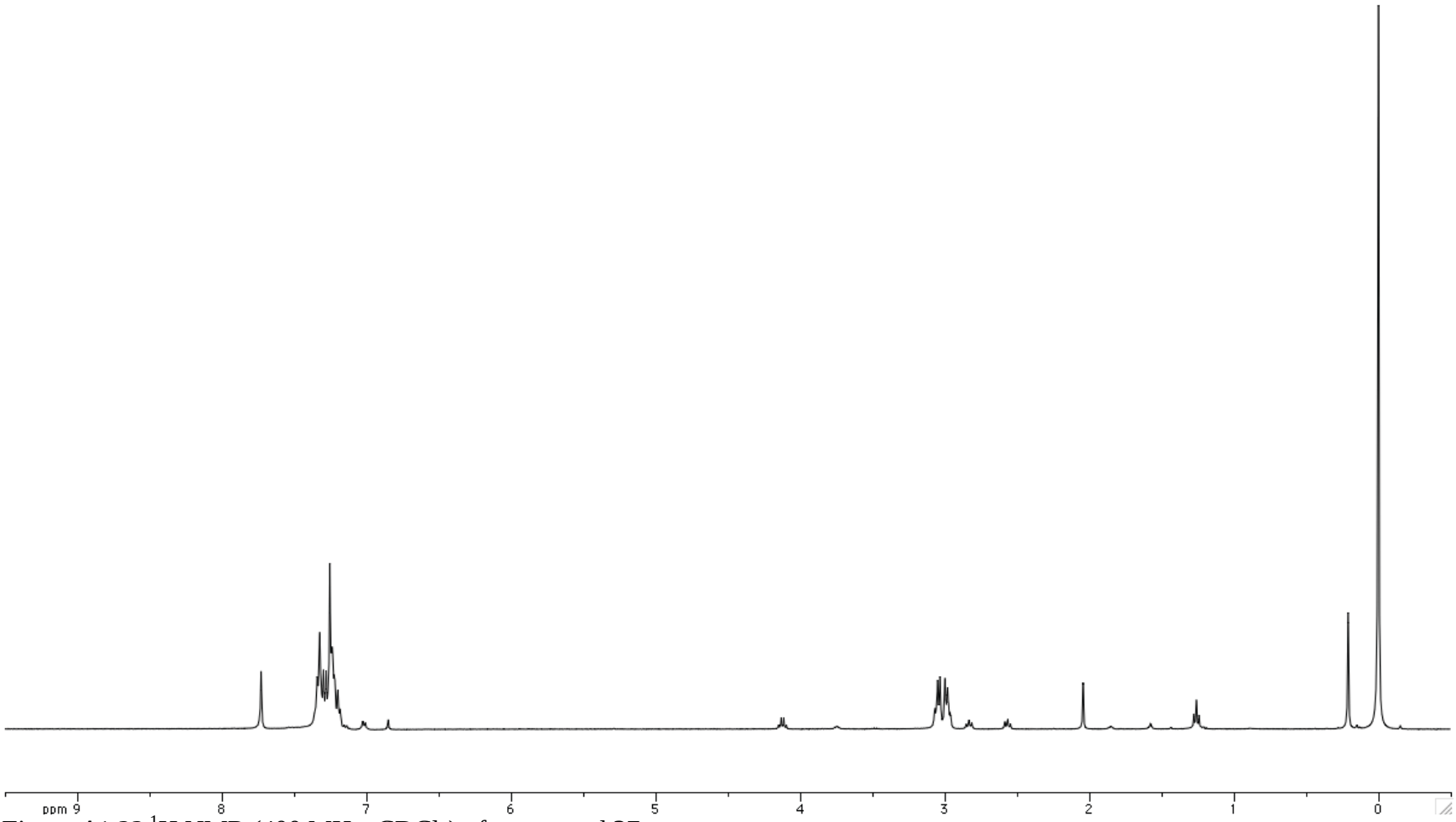
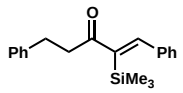


Figure A1.22 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **27**



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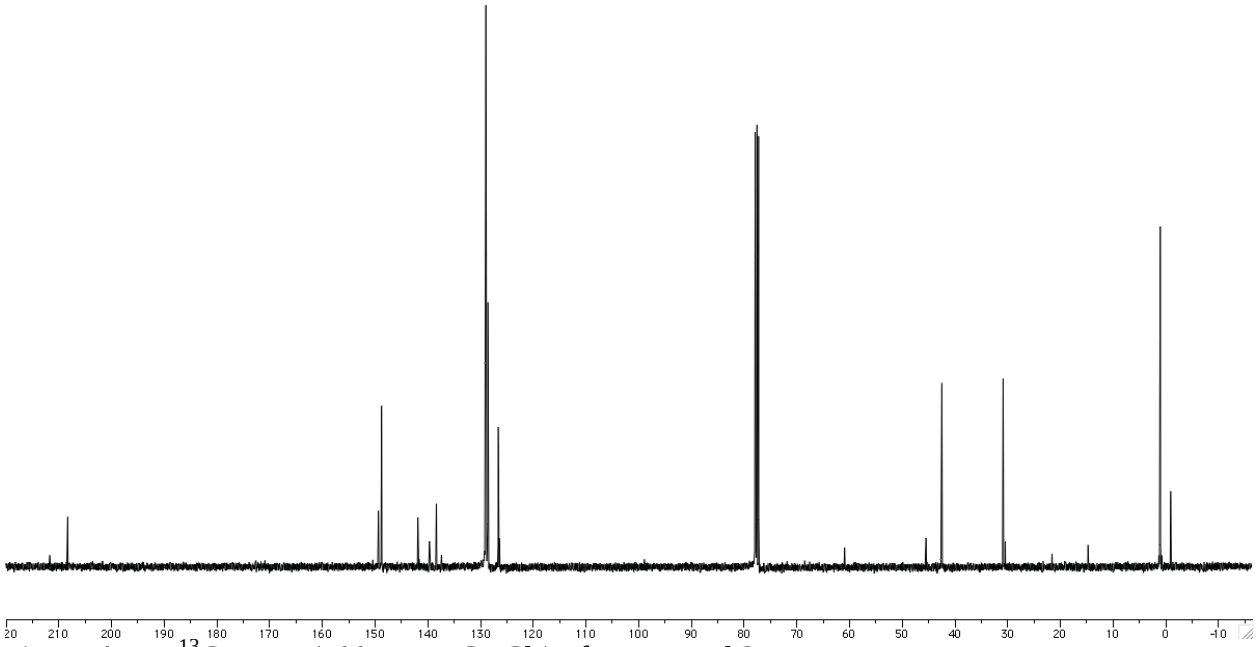


Figure A1.23 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **27**

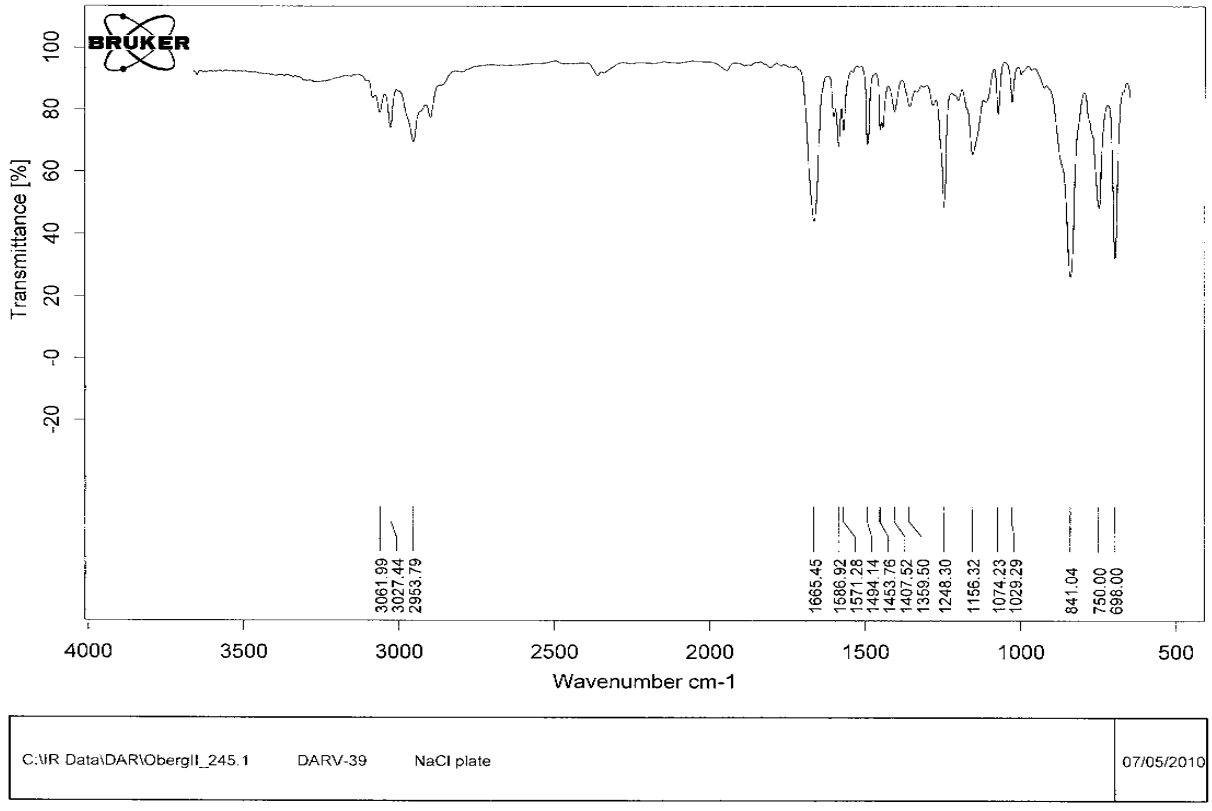


Figure A1.24 Infrared spectrum (thin film) of compound **27**

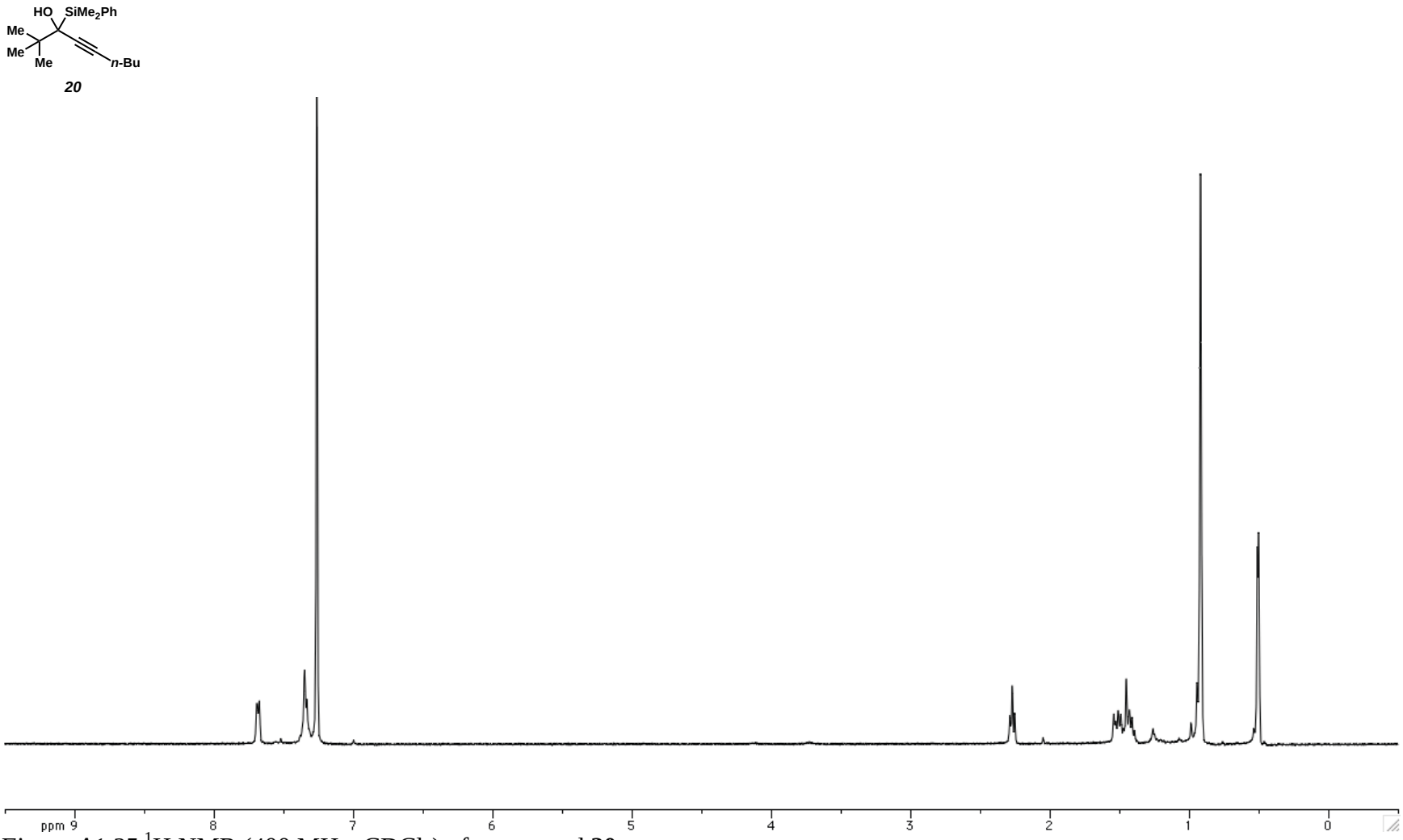
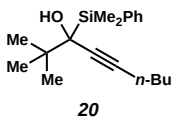


Figure A1.25 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **20**



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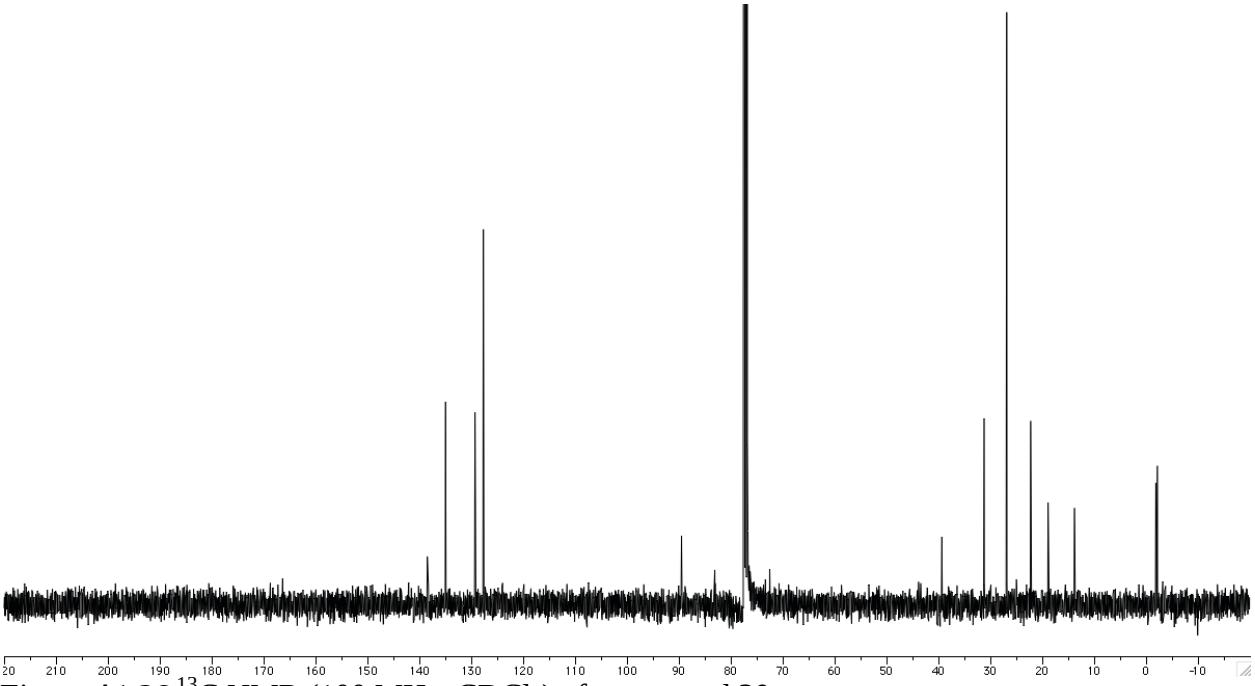


Figure A1.26 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **20**

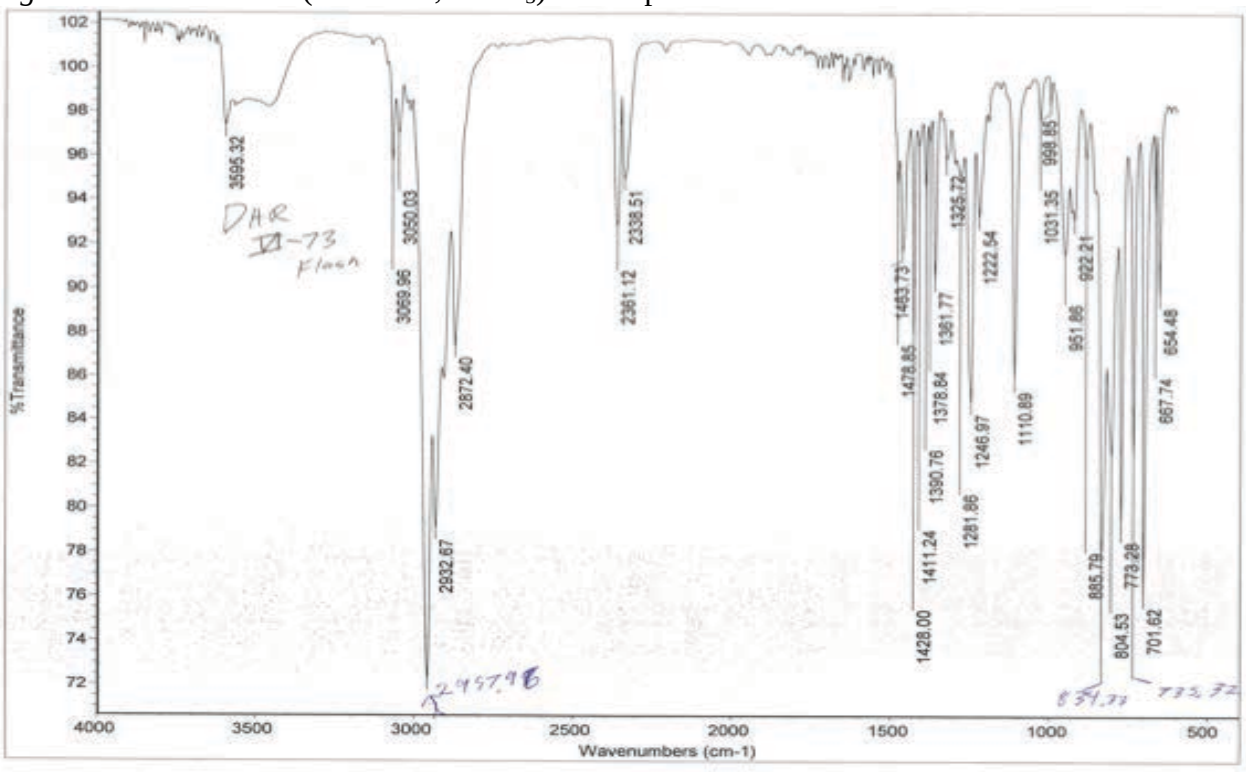
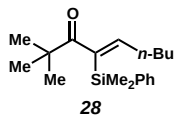


Figure A1.27 Infrared spectrum (thin film) of compound **20**



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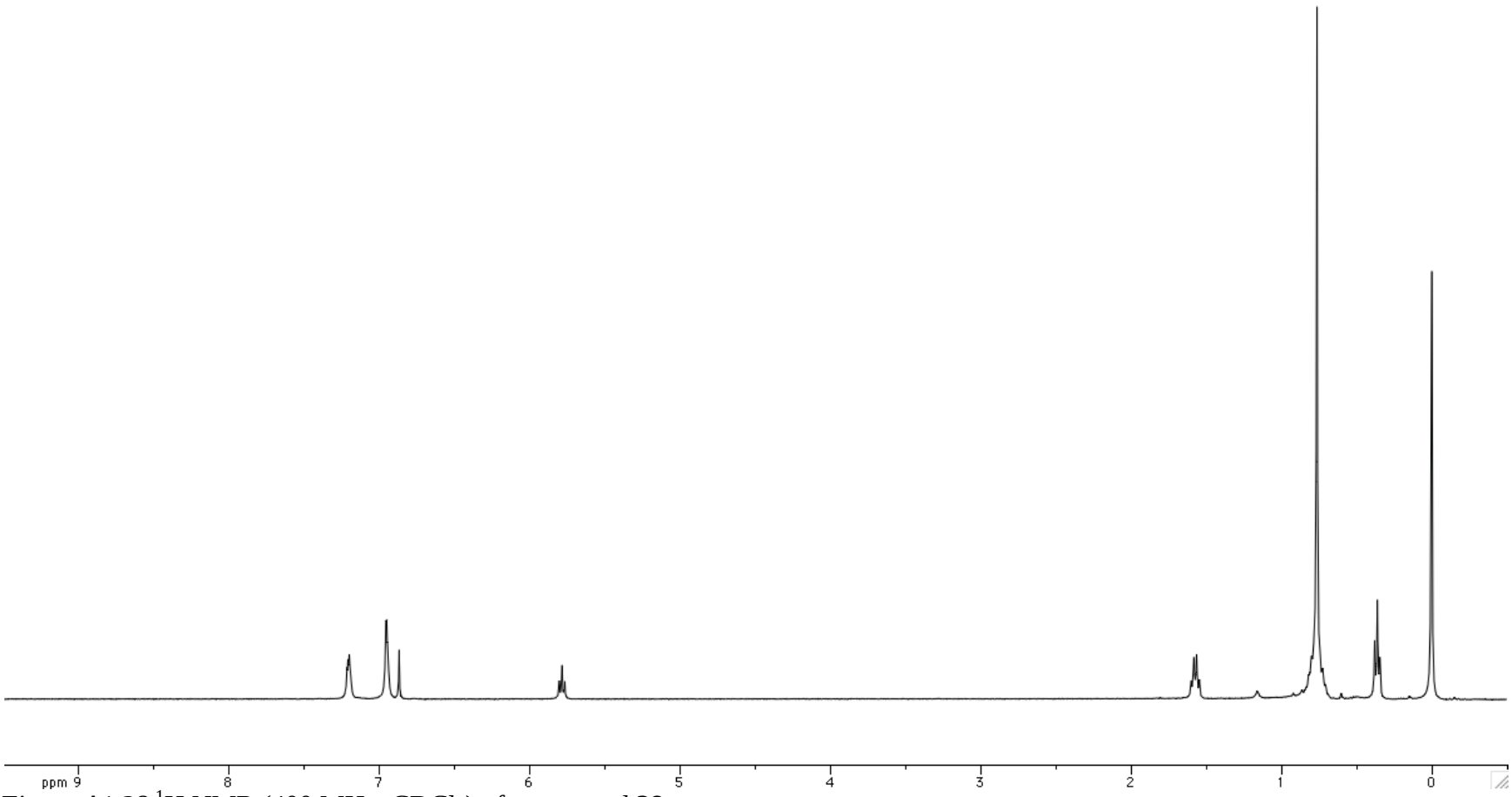
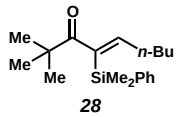


Figure A1.28 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **28**



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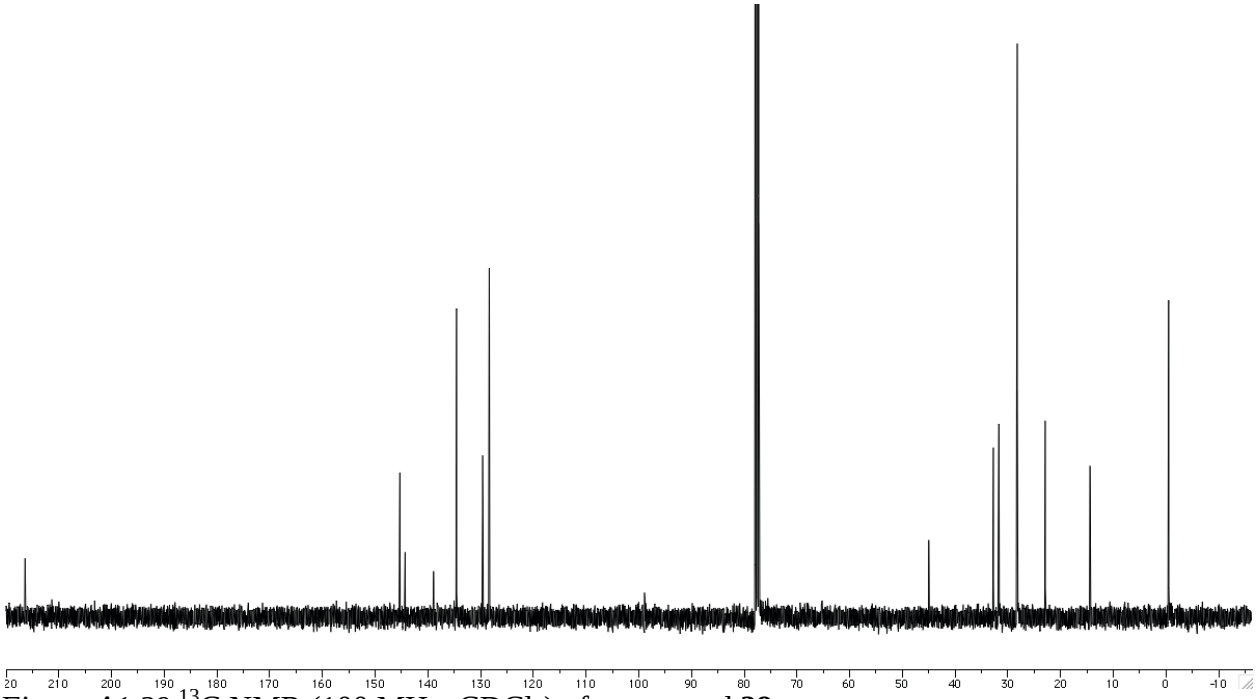


Figure A1.29 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **28**

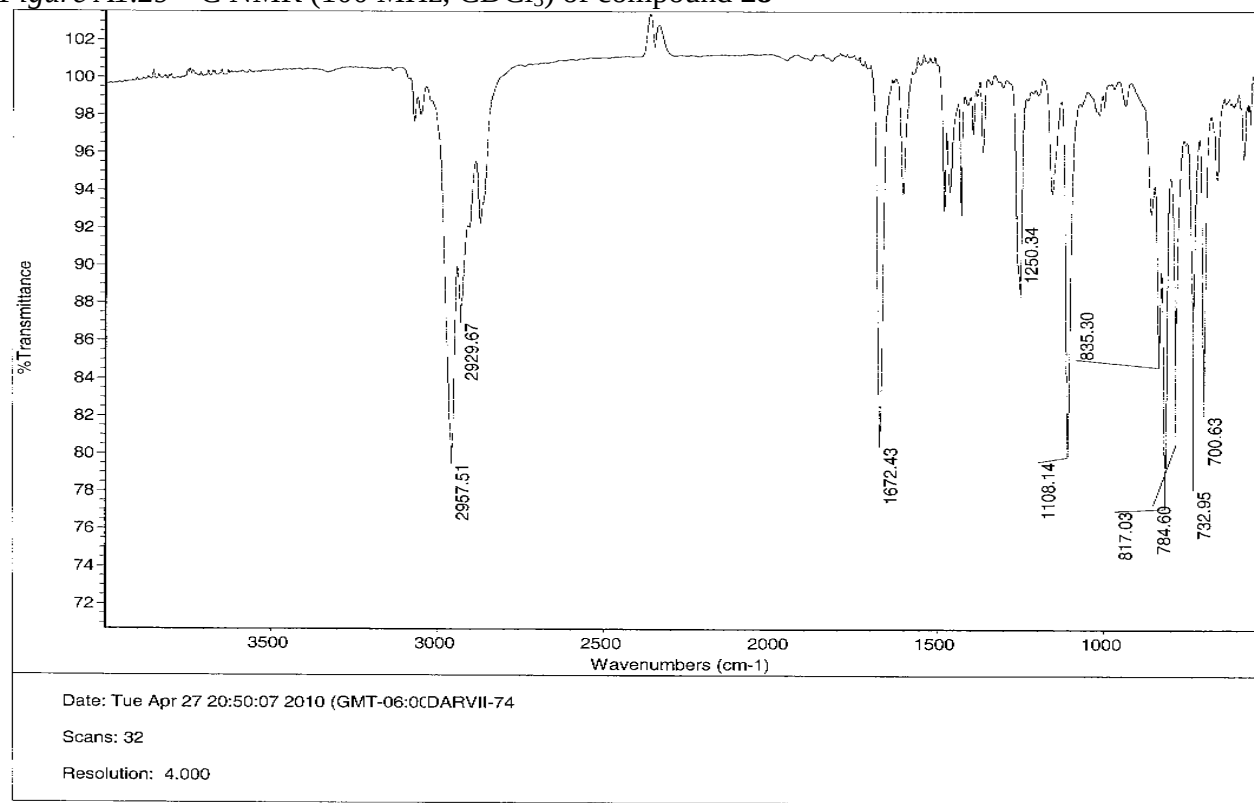
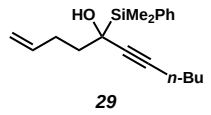


Figure A1.30 Infrared spectrum (thin film) of compound **28**



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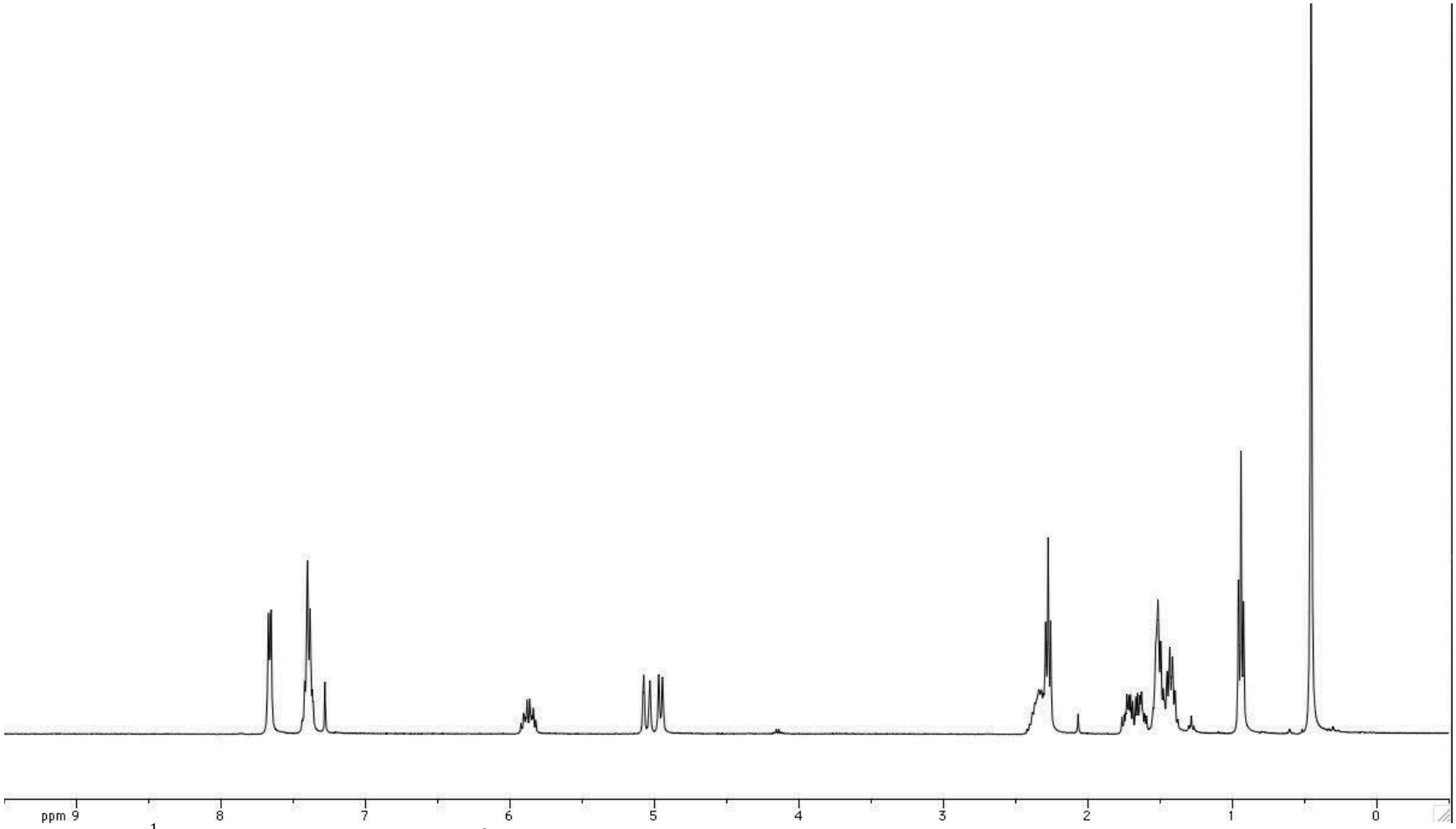


Figure A1.31 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **29**

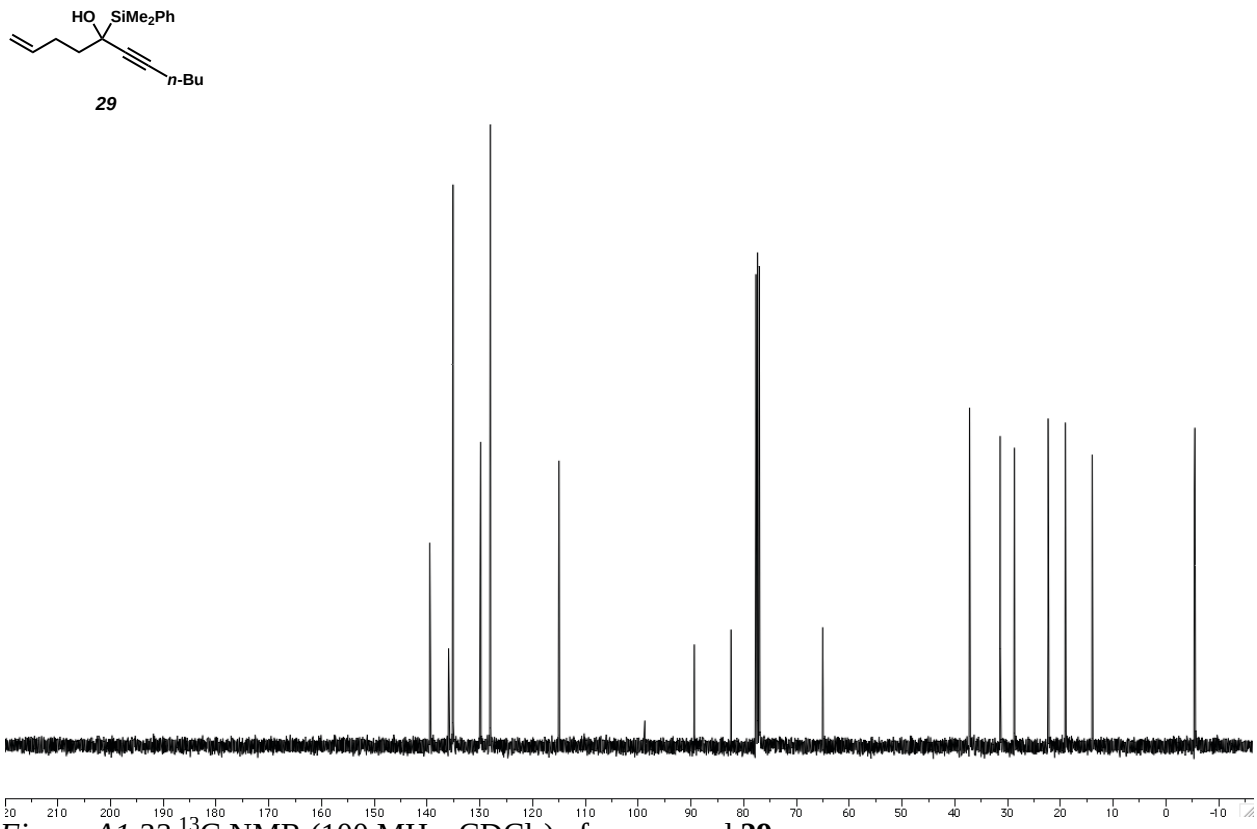


Figure A1.32 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **29**

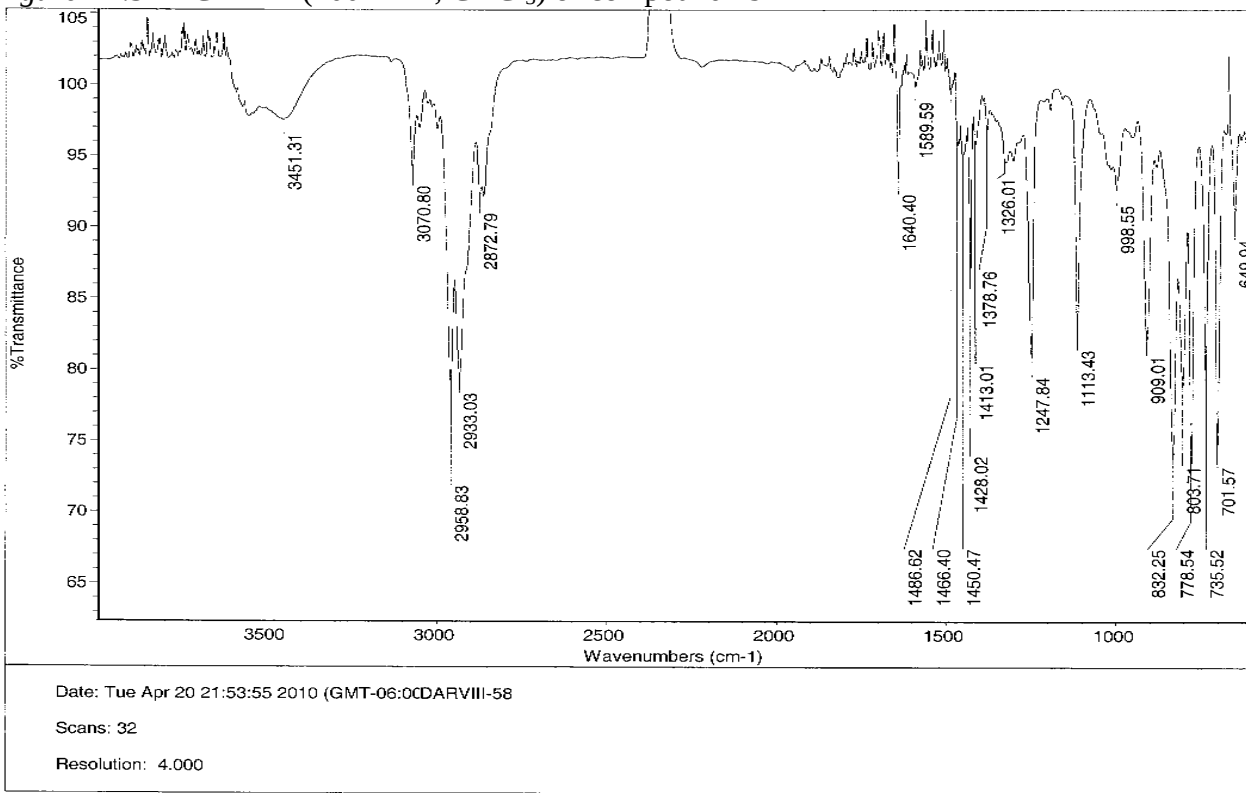
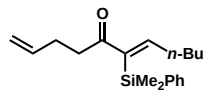


Figure A1.33 Infrared spectrum (thin film) of compound **29**



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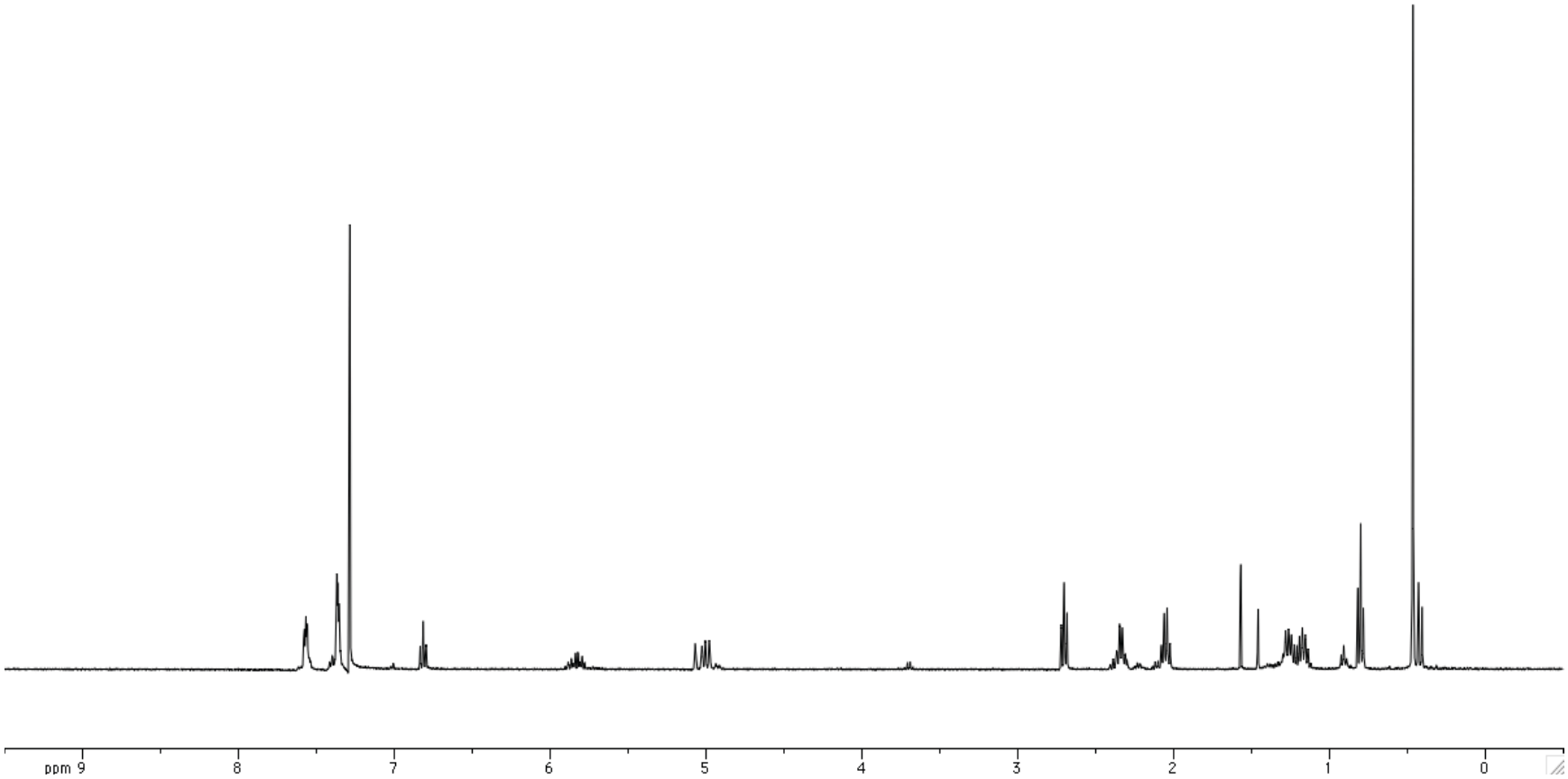


Figure A1.34 Infrared spectrum (thin film) of compound **30**

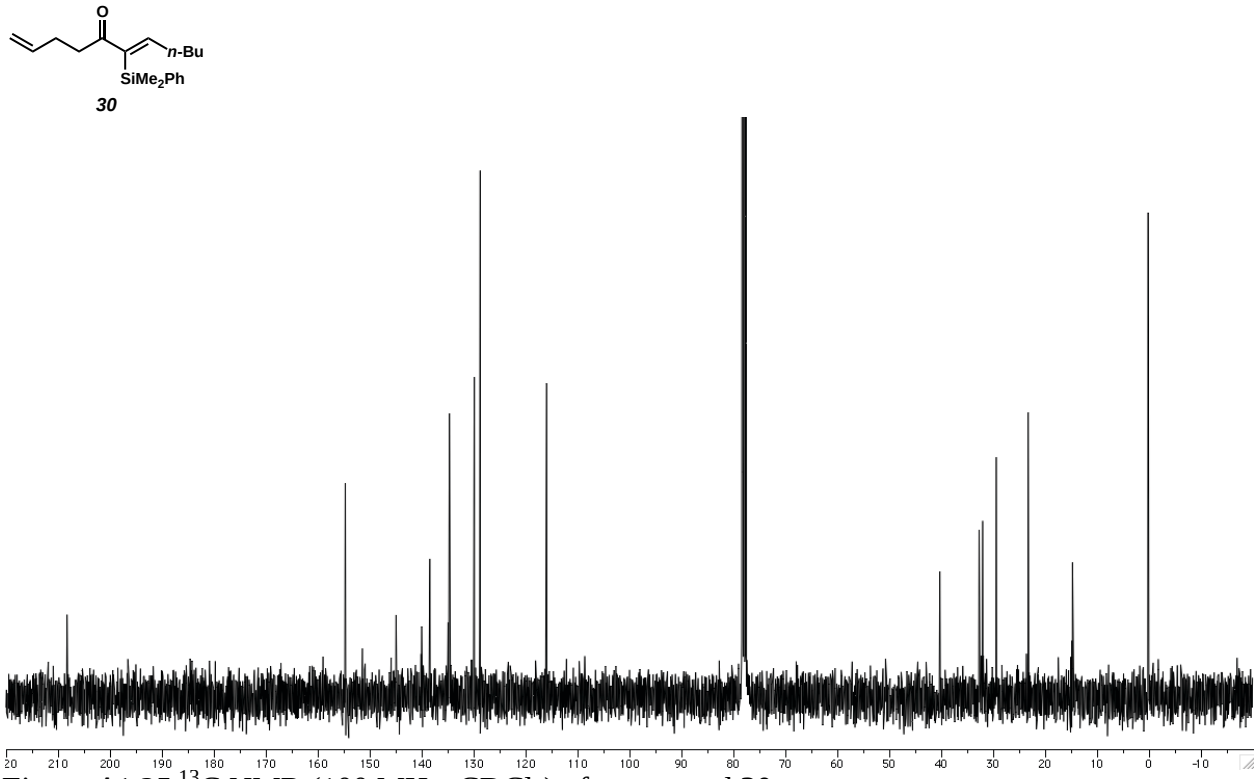


Figure A1.35 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **30**

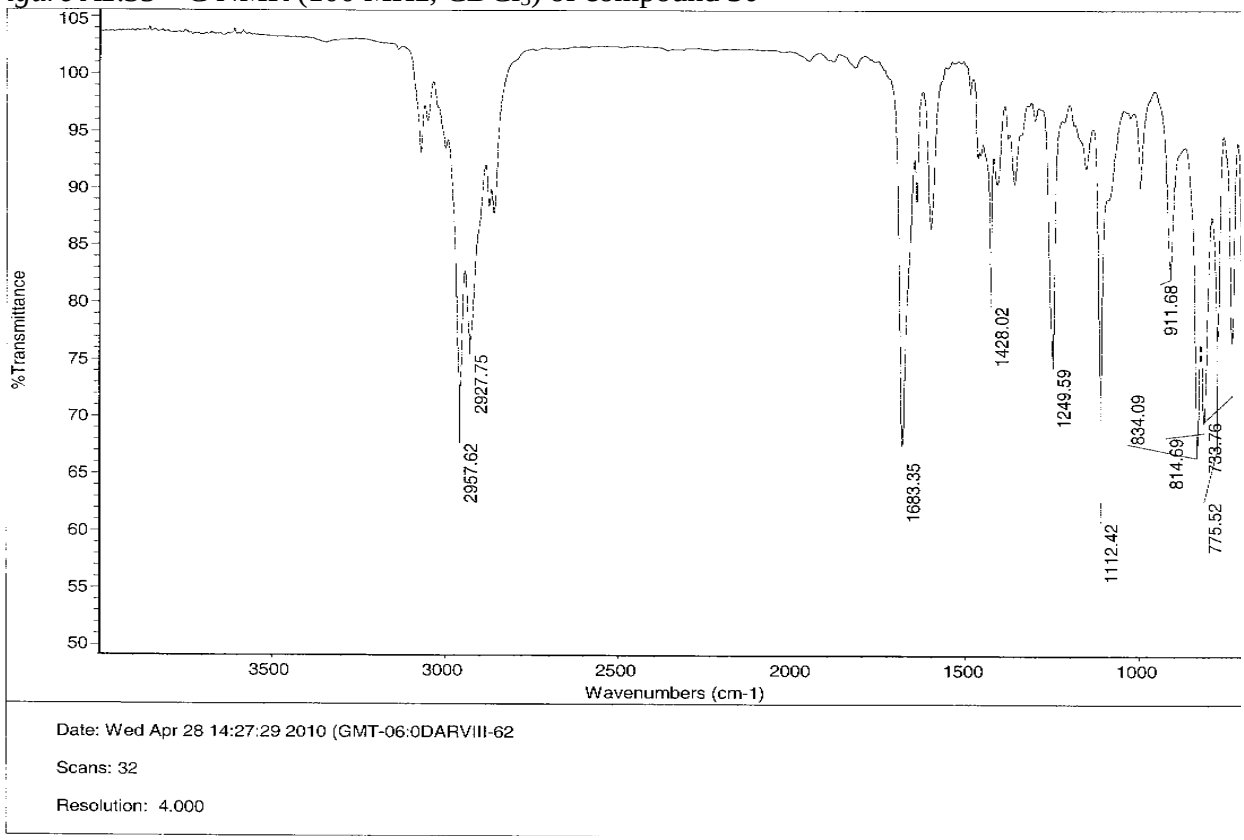
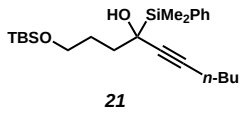


Figure A1.36 Infrared spectrum (thin film) of compound **30**



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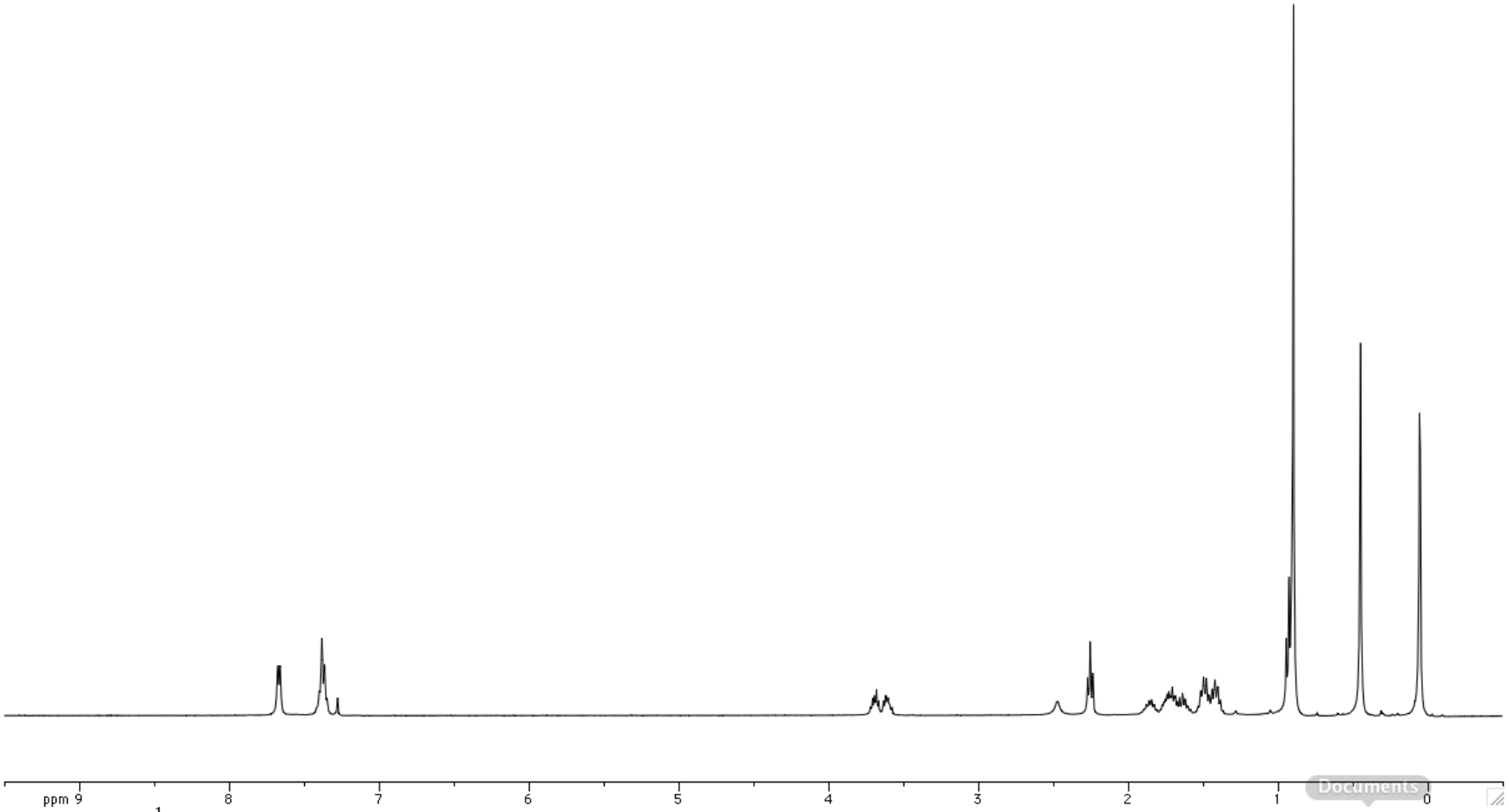
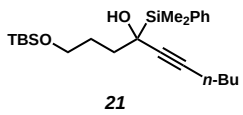


Figure A1.37 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **21**



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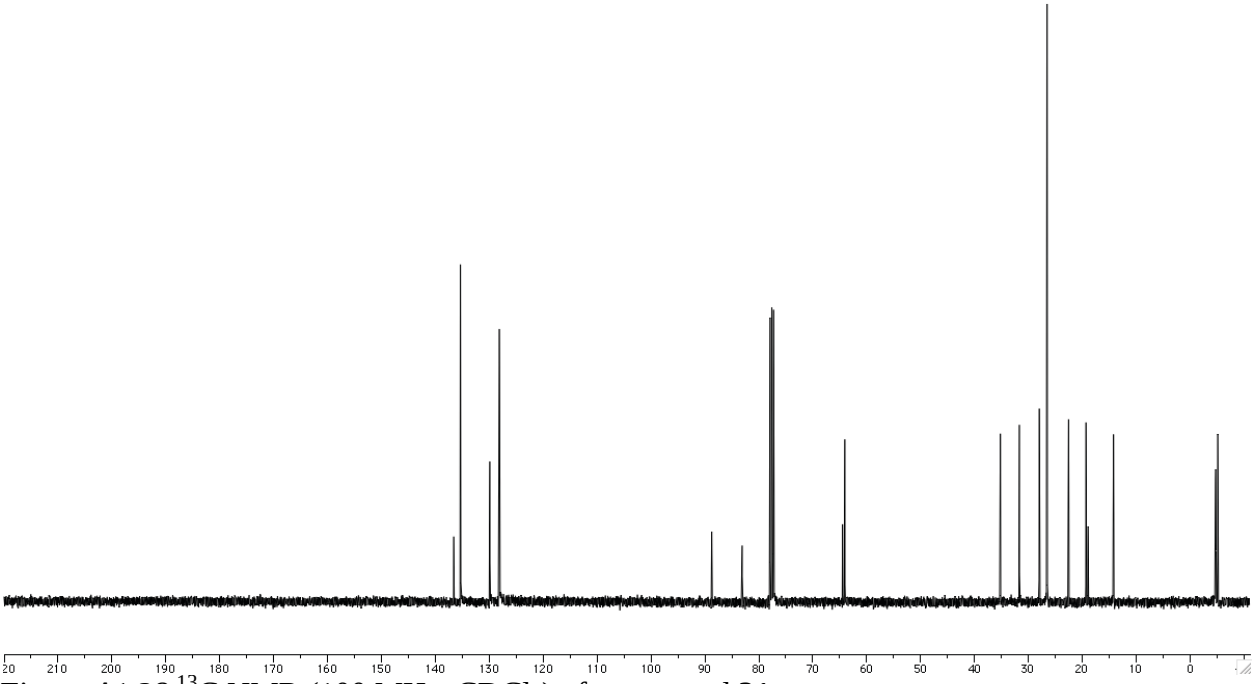


Figure A1.38 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **21**

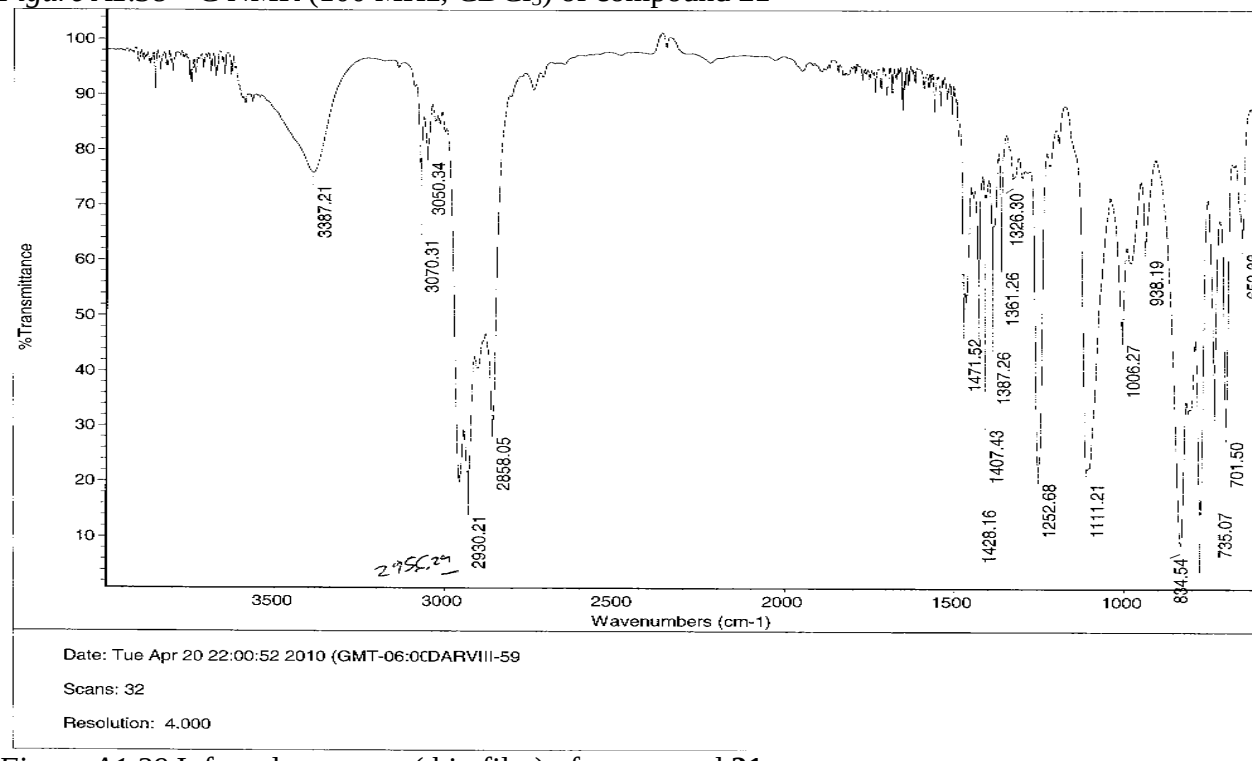
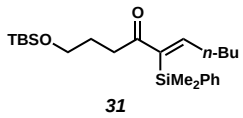


Figure A1.39 Infrared spectrum (thin film) of compound **21**



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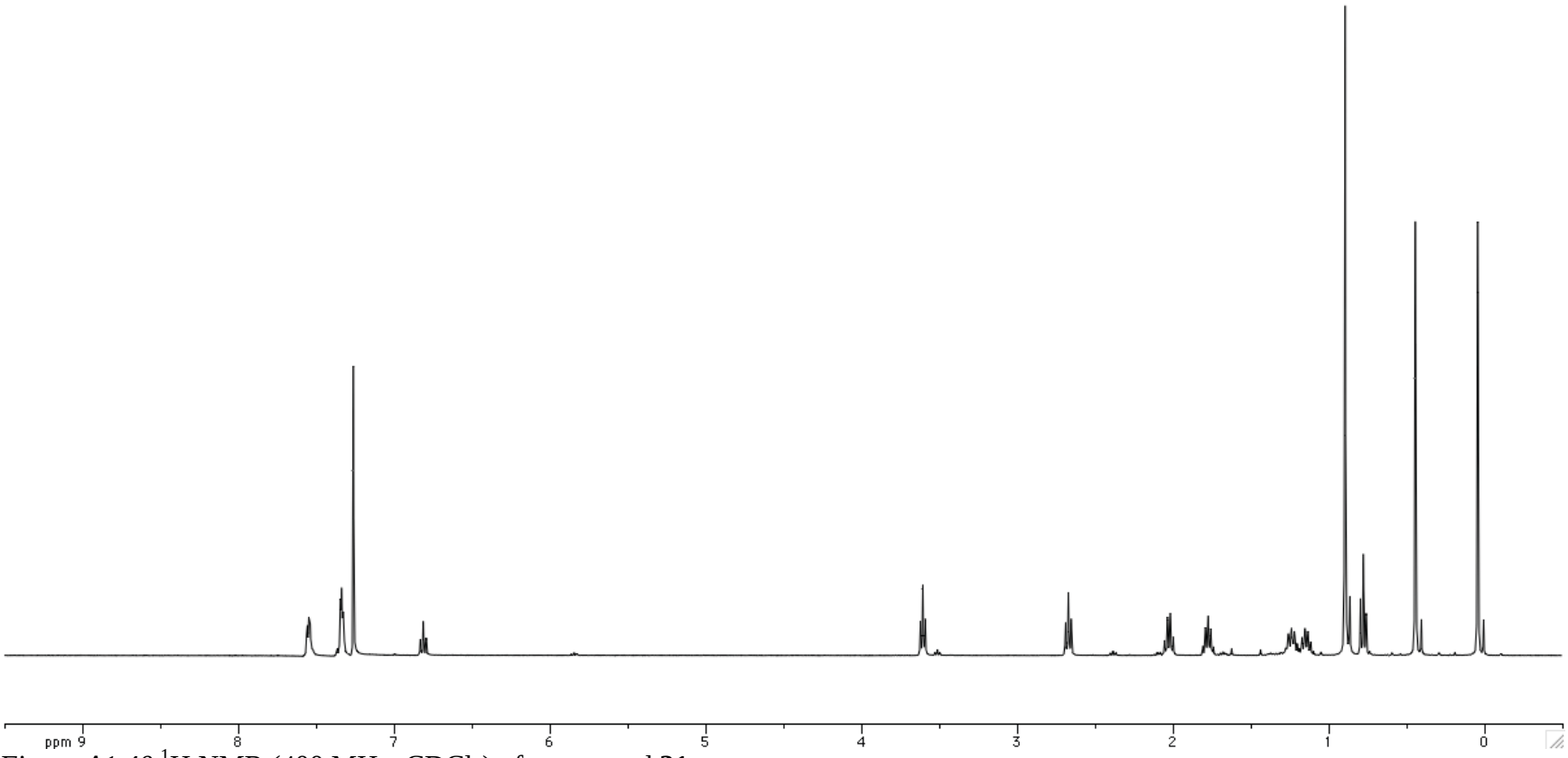
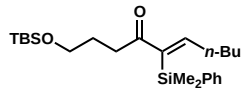


Figure A1.40 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **31**



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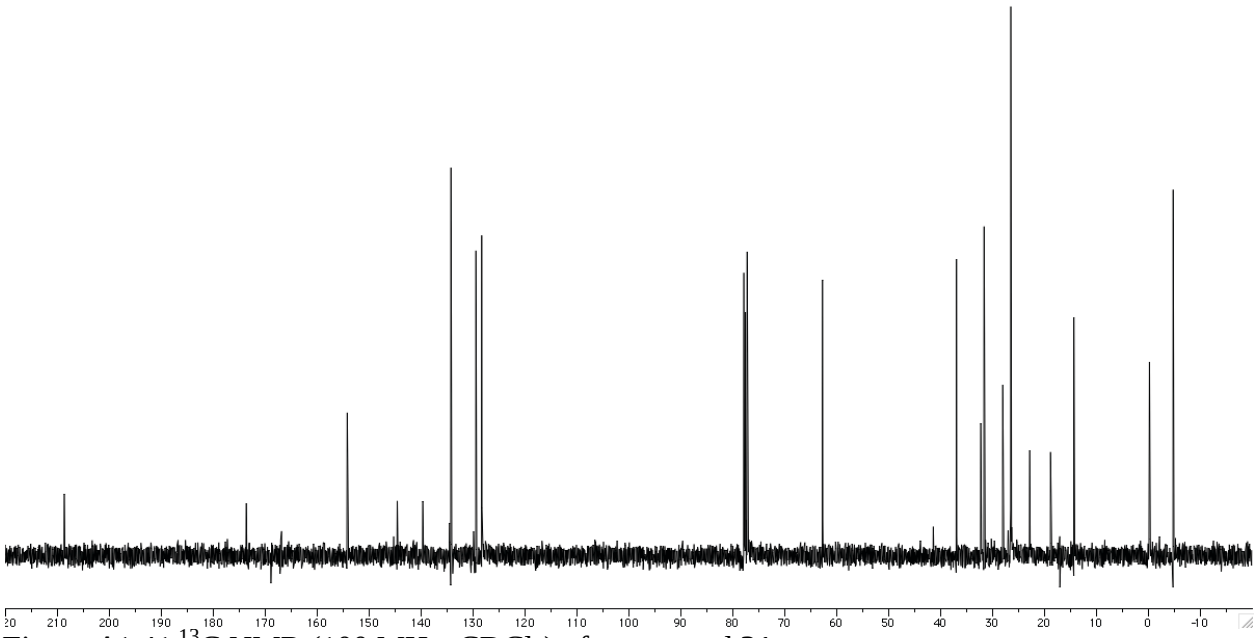


Figure A1.41 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **31**

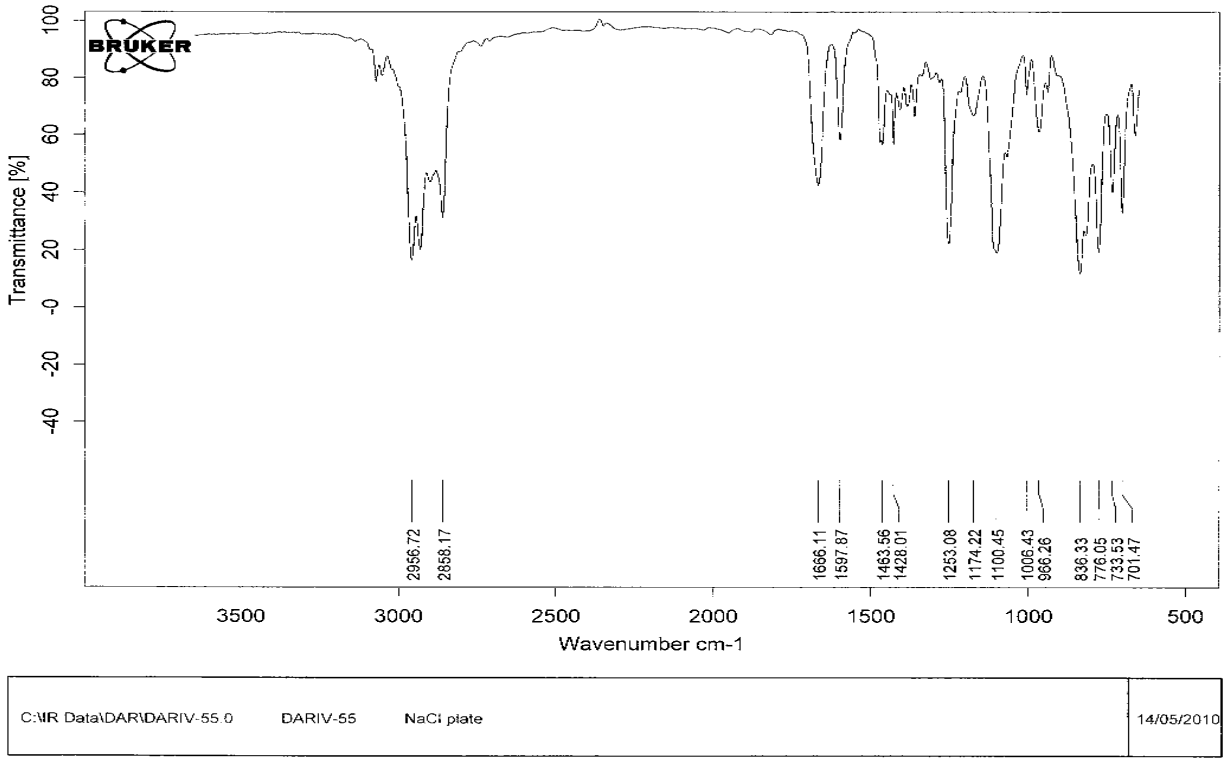
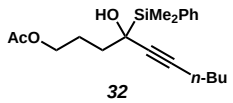


Figure A1.42 Infrared spectrum (thin film) of compound **31**



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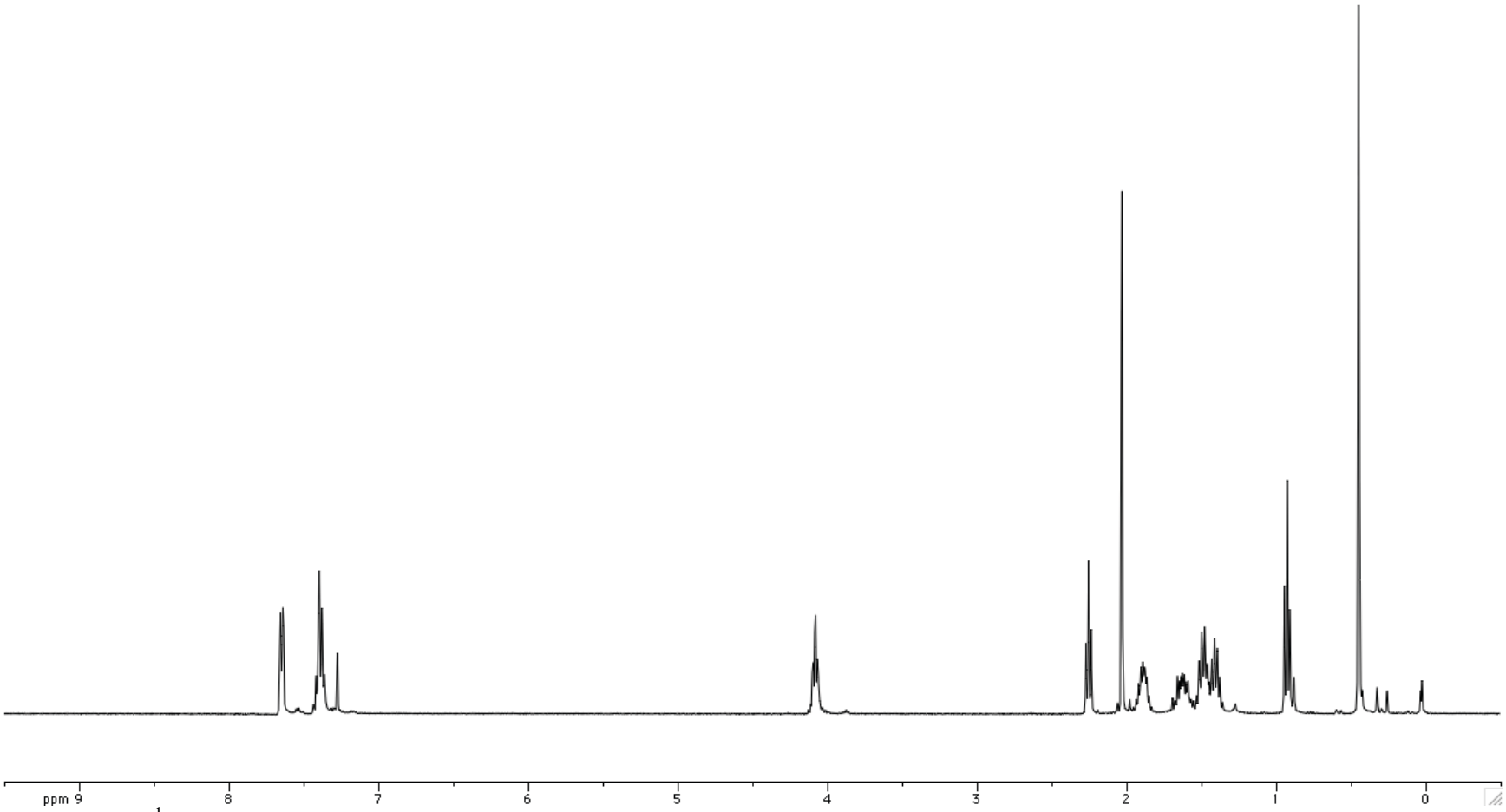


Figure A1.43 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **32**

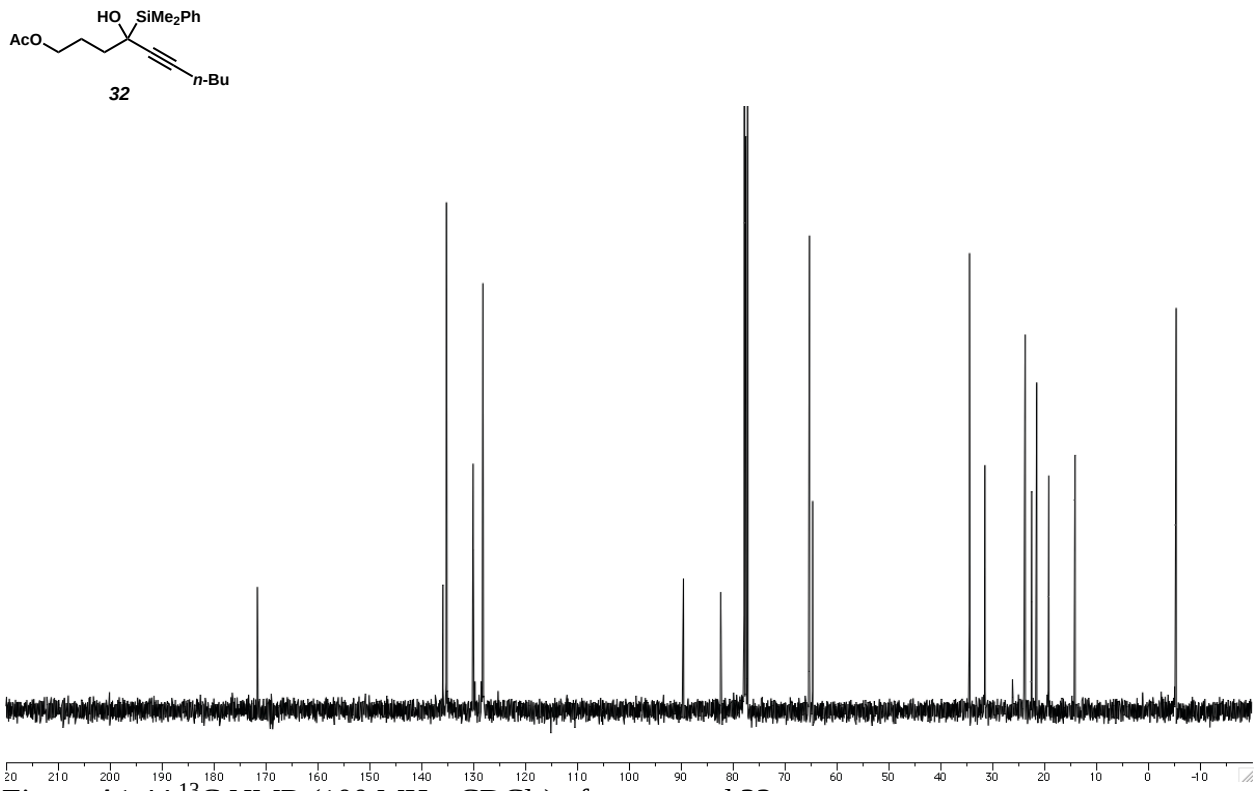


Figure A1.44 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **32**

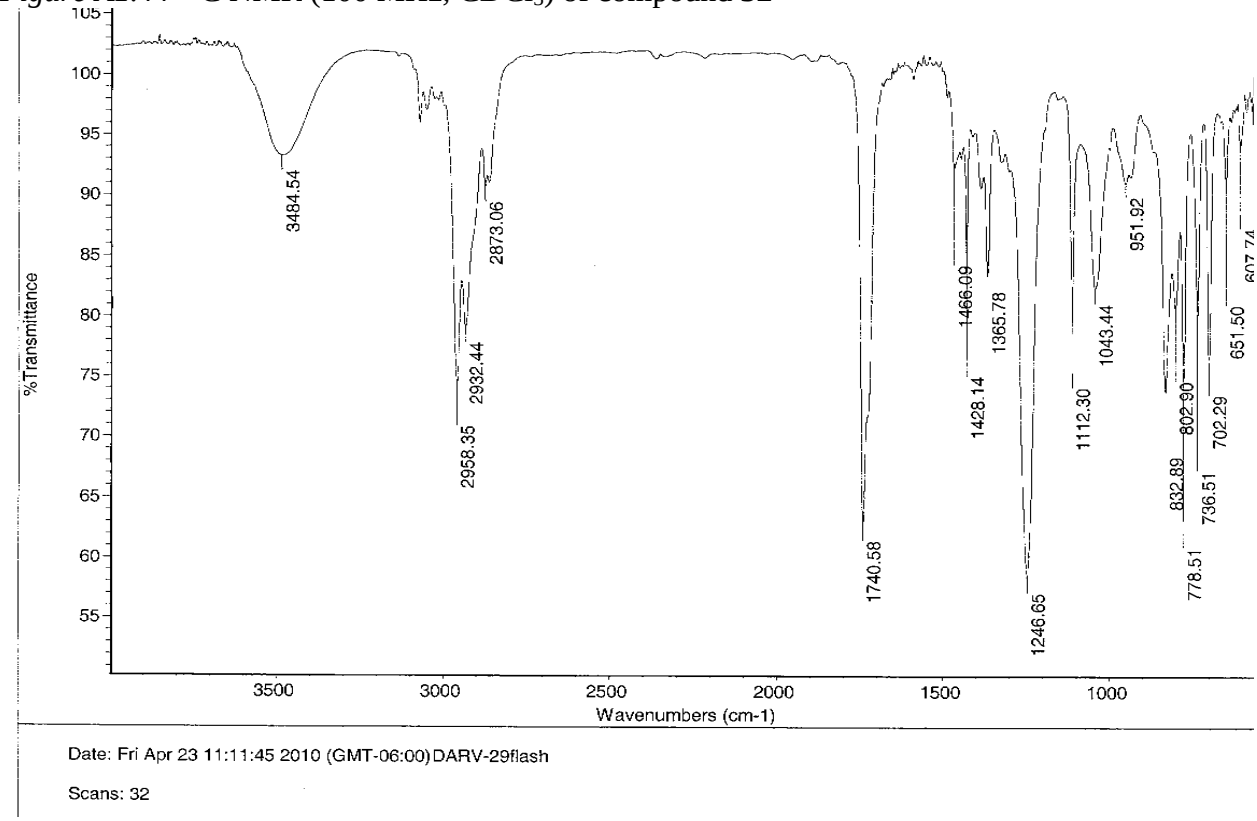
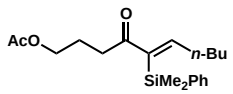


Figure A1.45 Infrared spectrum (thin film) of compound **32**



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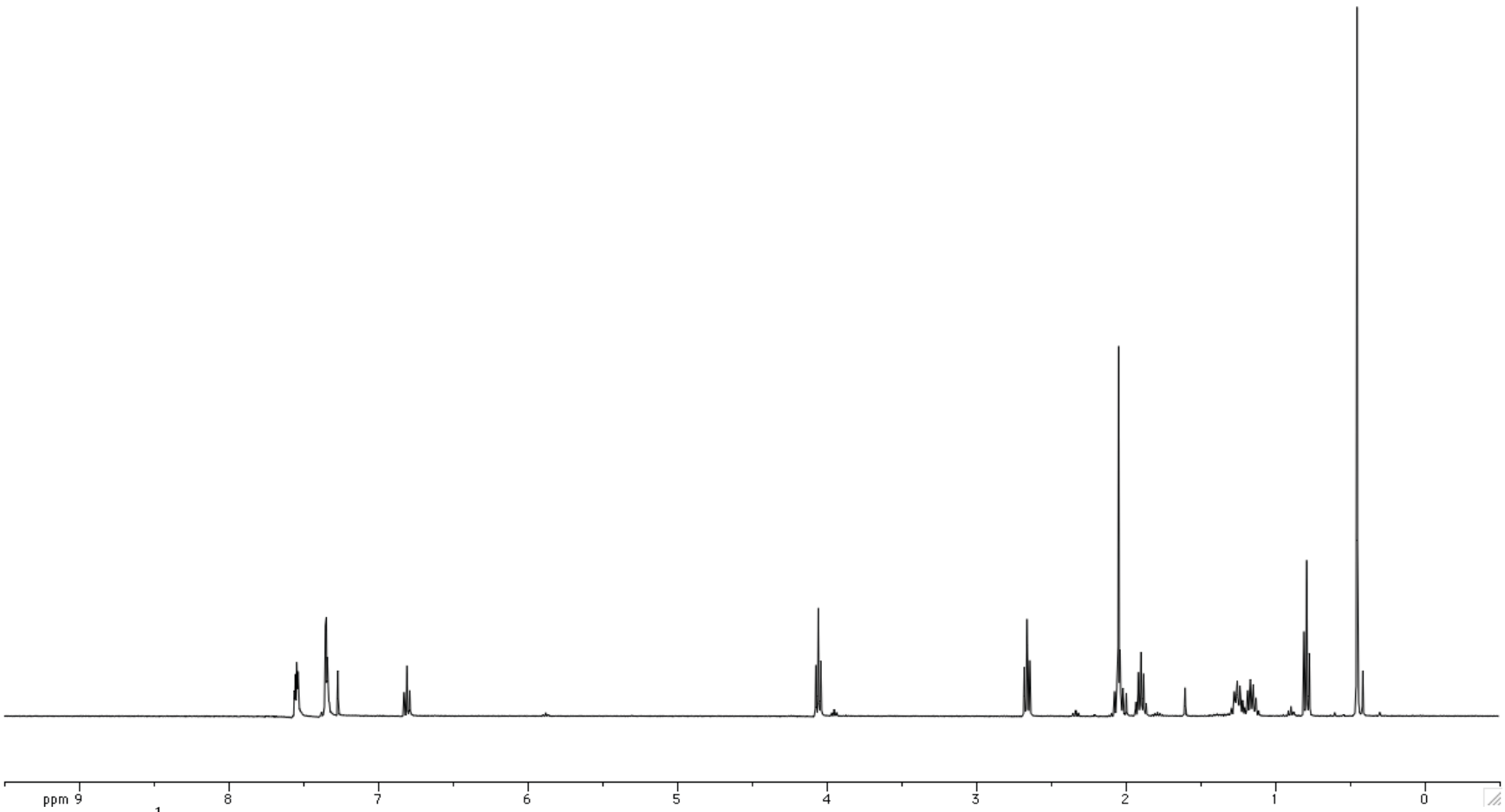


Figure A1.46 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **33**

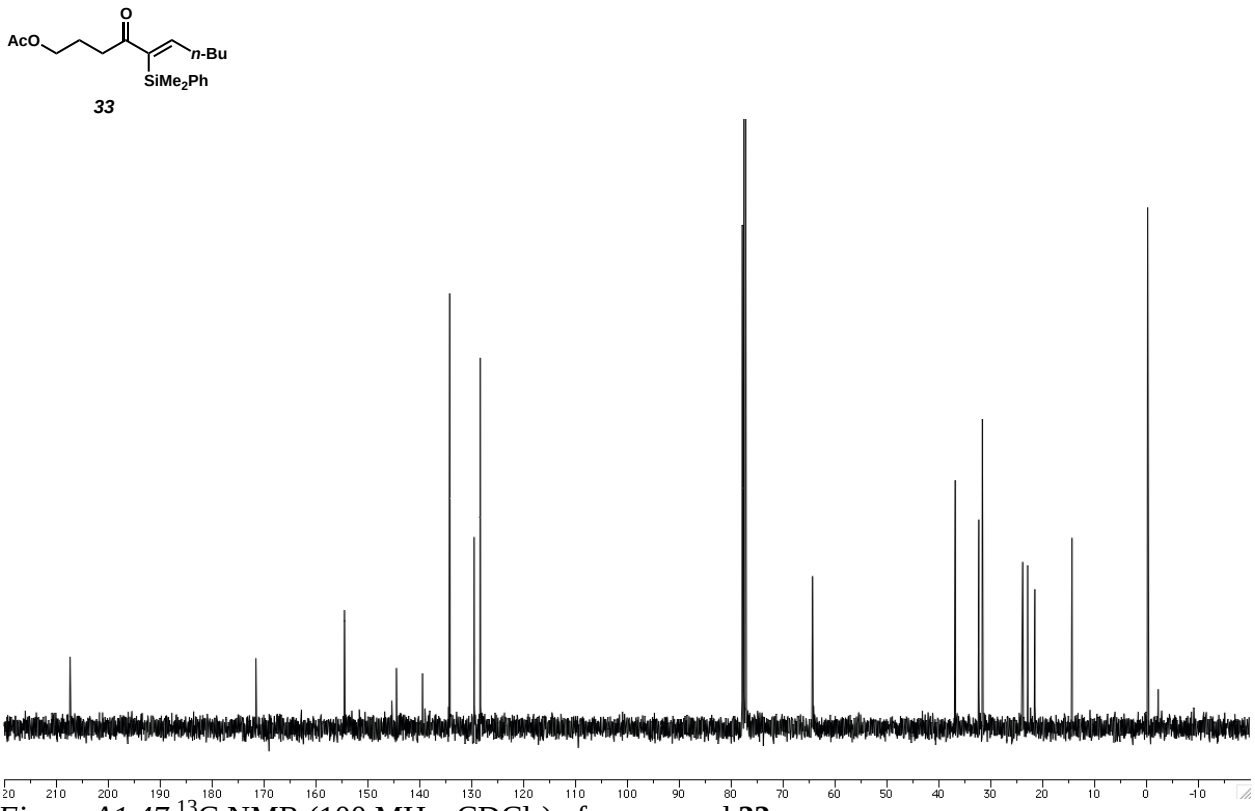


Figure A1.47 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **33**

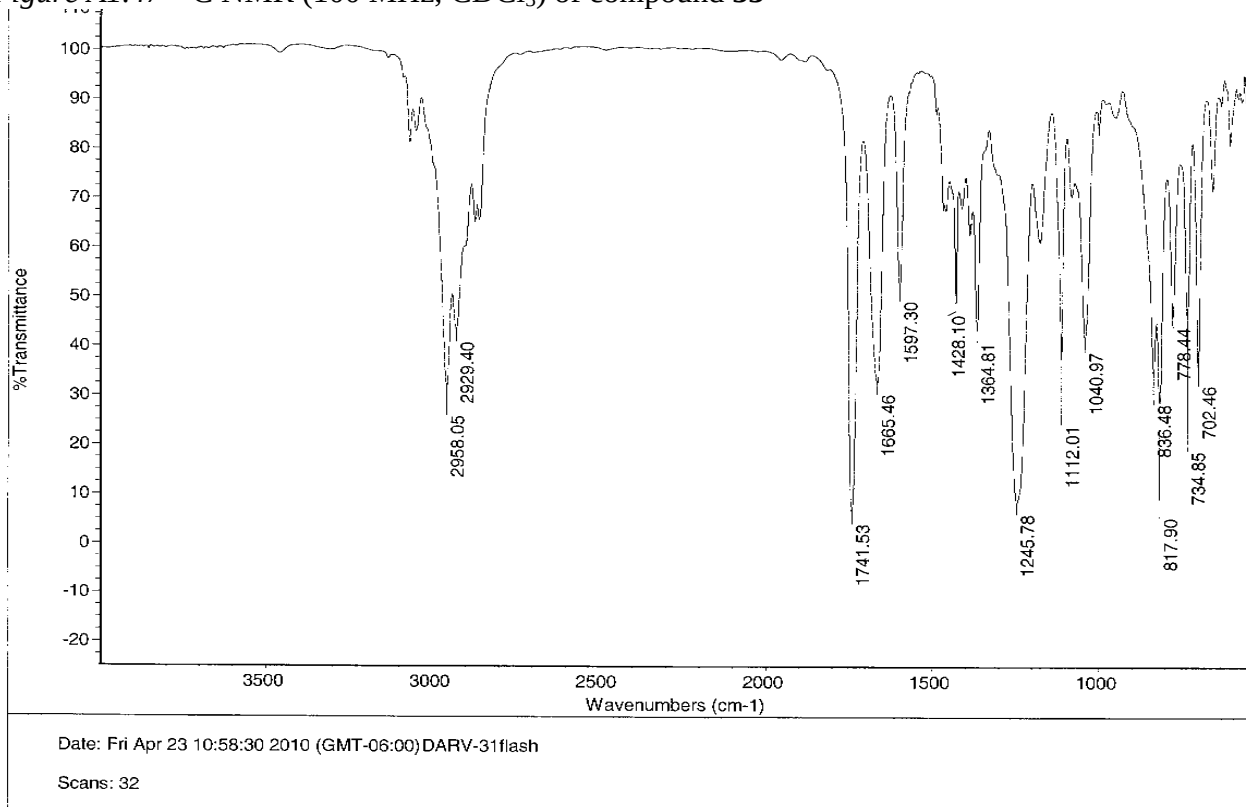
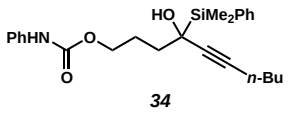


Figure A1.48 Infrared spectrum (thin film) of compound **33**



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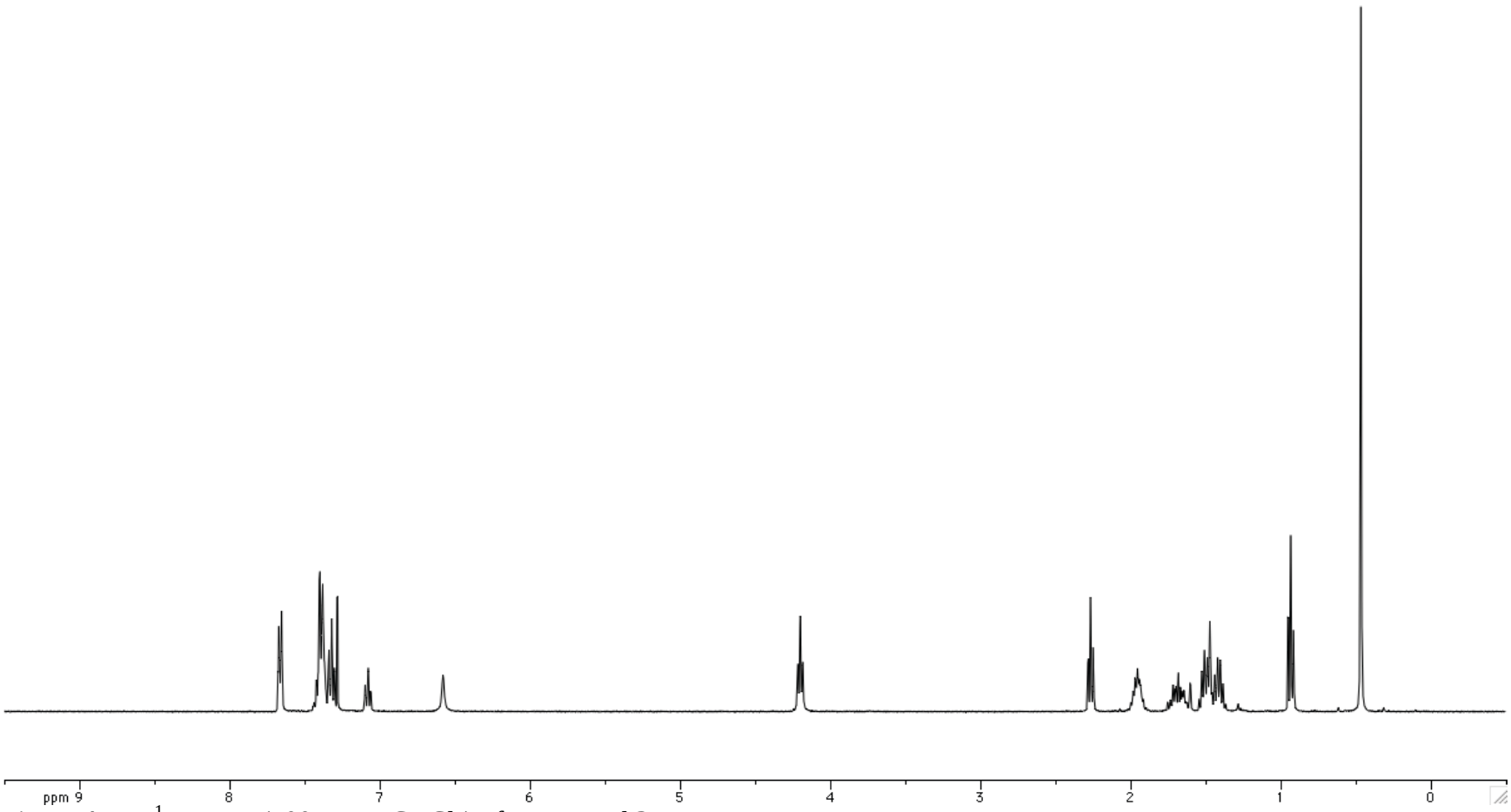


Figure A1.49 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **34**

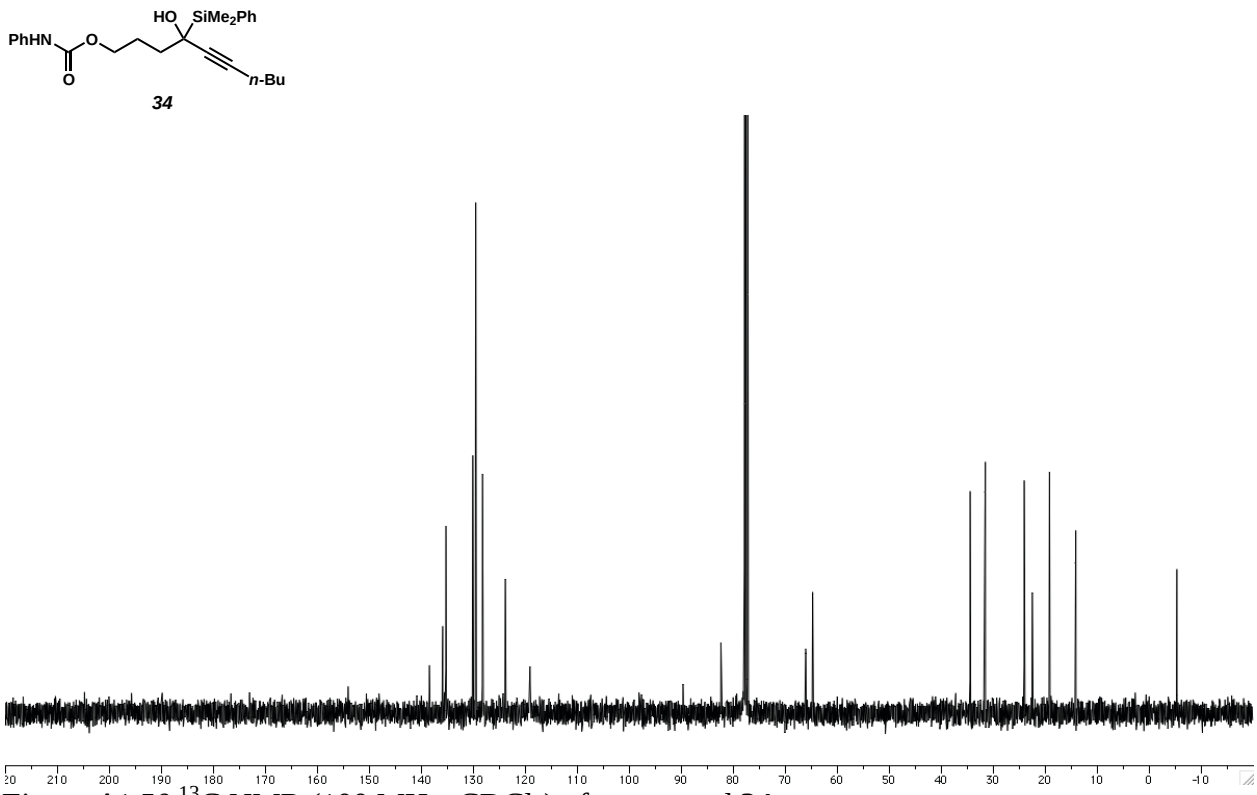


Figure A1.50 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **34**

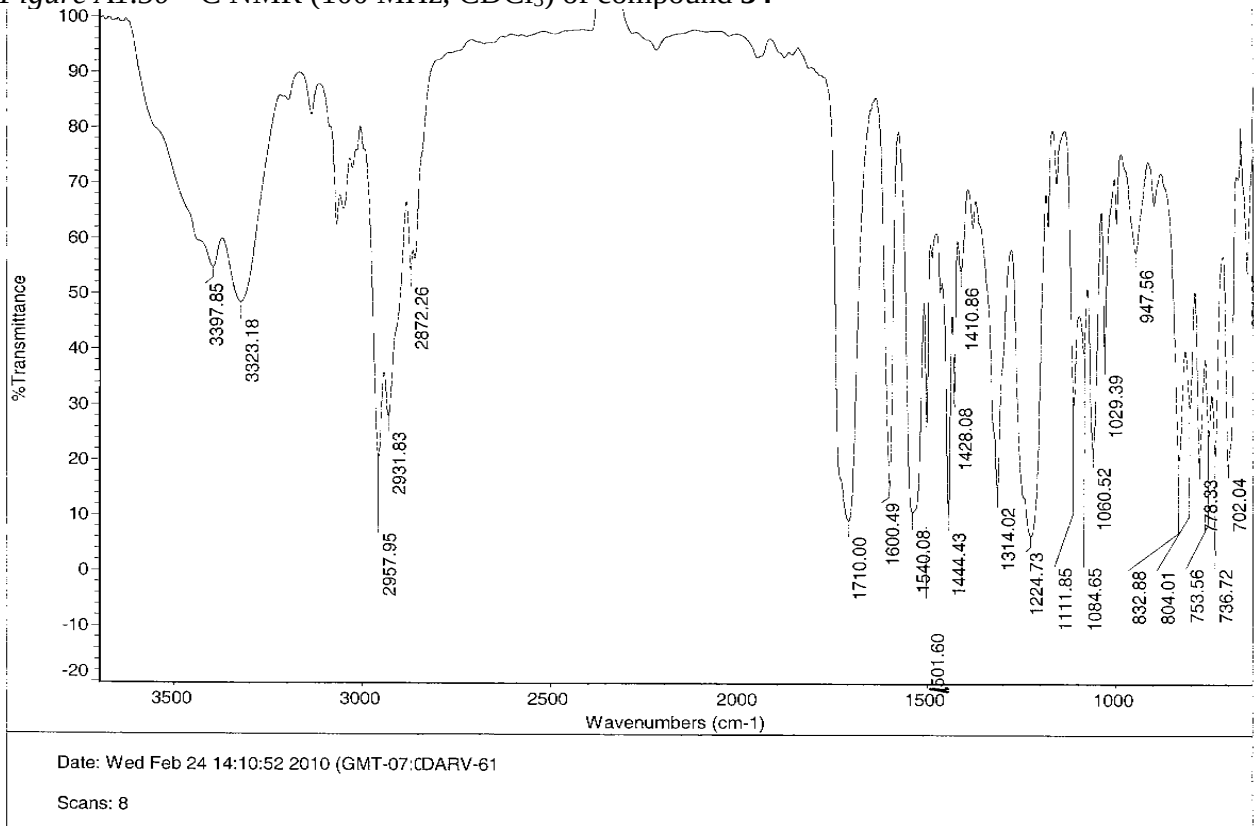
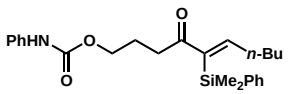


Figure A1.51 Infrared spectrum (thin film) of compound **34**



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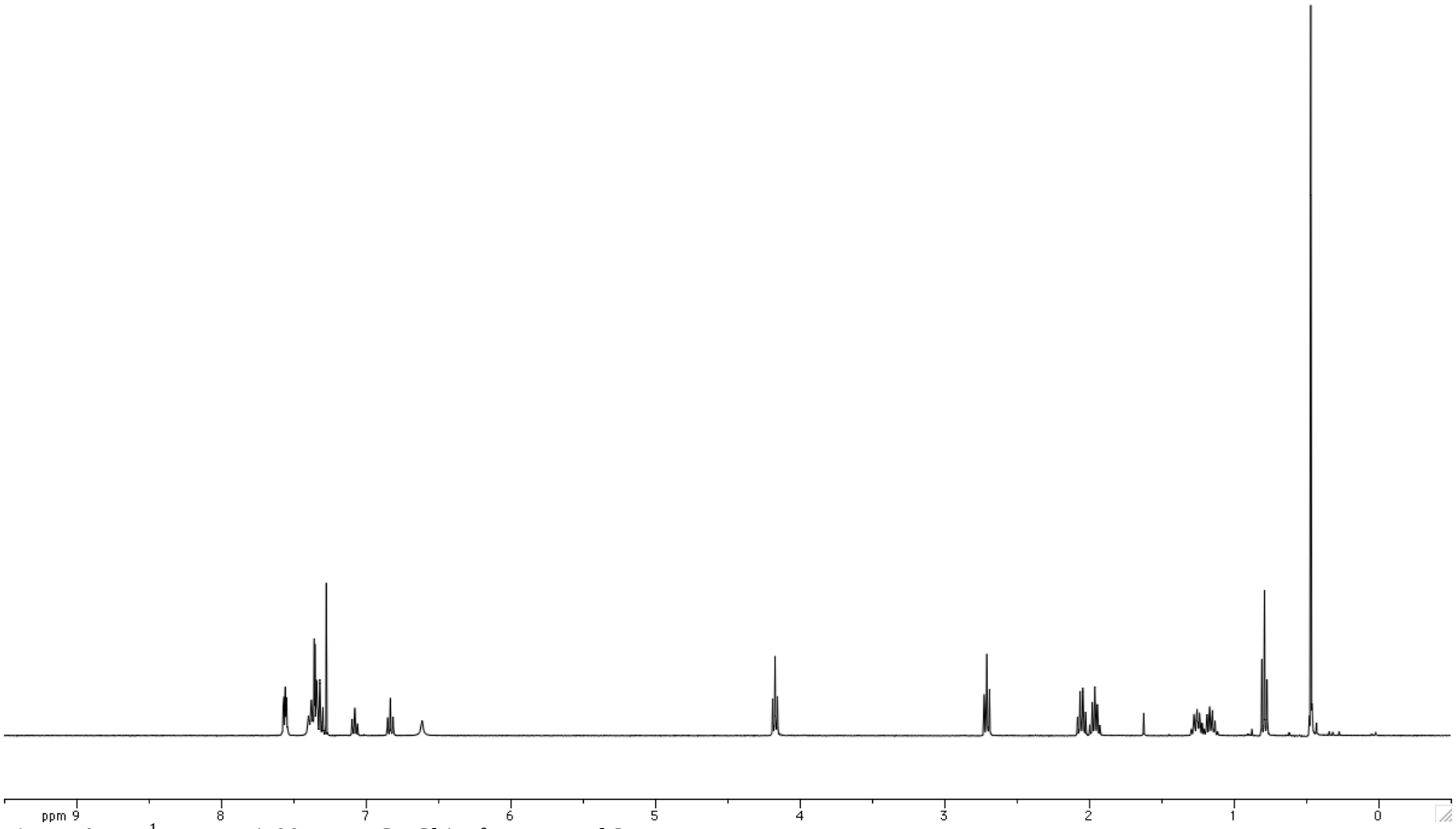
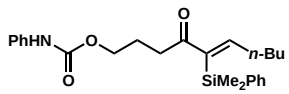


Figure A1.52 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **35**



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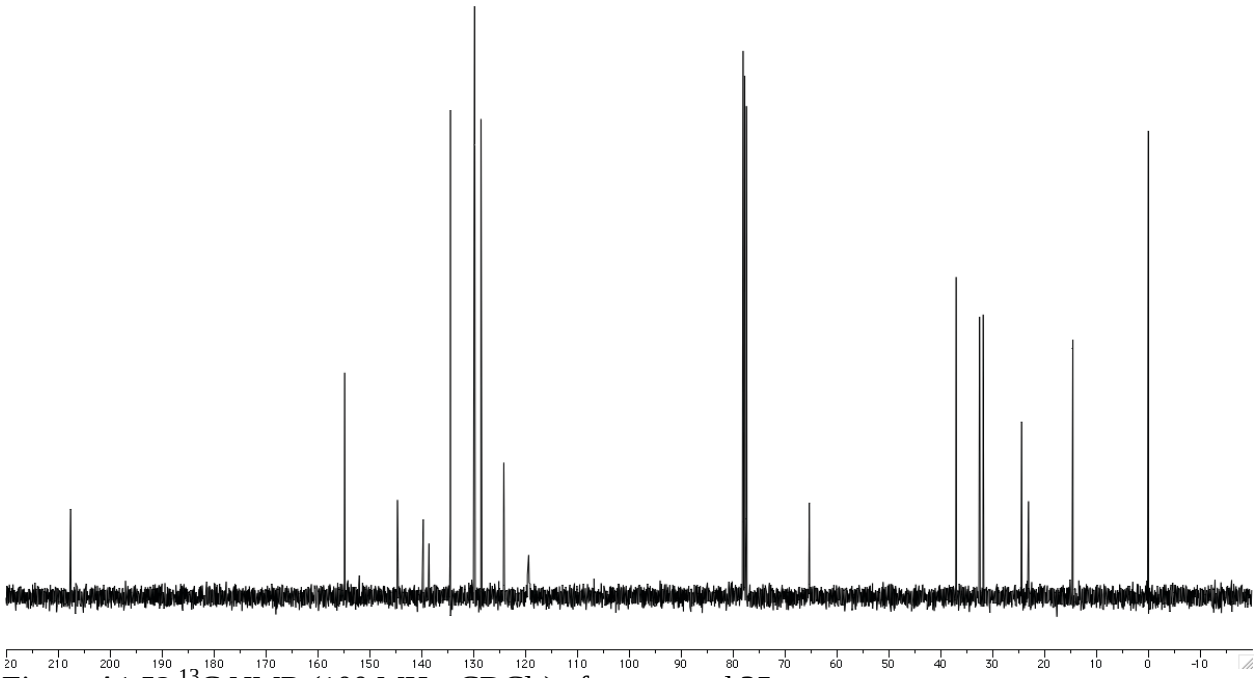


Figure A1.53 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **35**

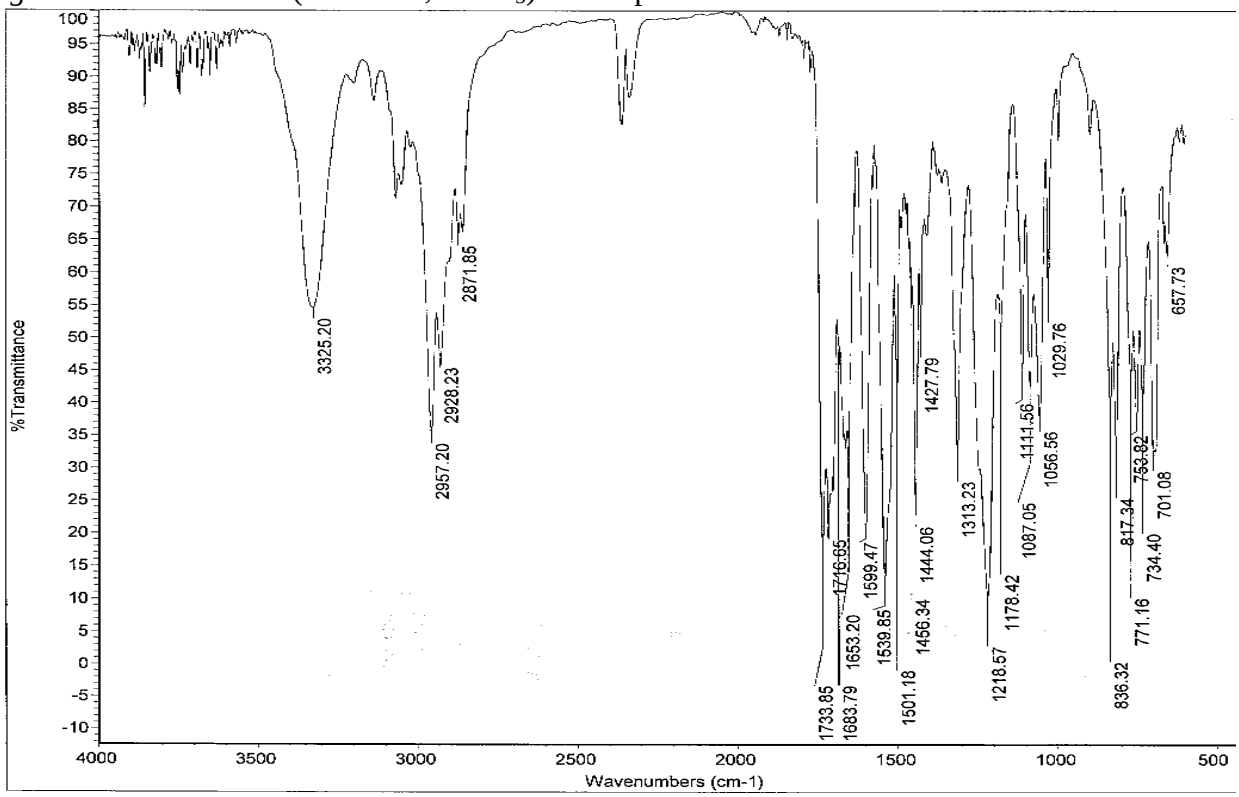
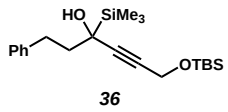


Figure A1.54 Infrared spectrum (thin film) of compound **35**



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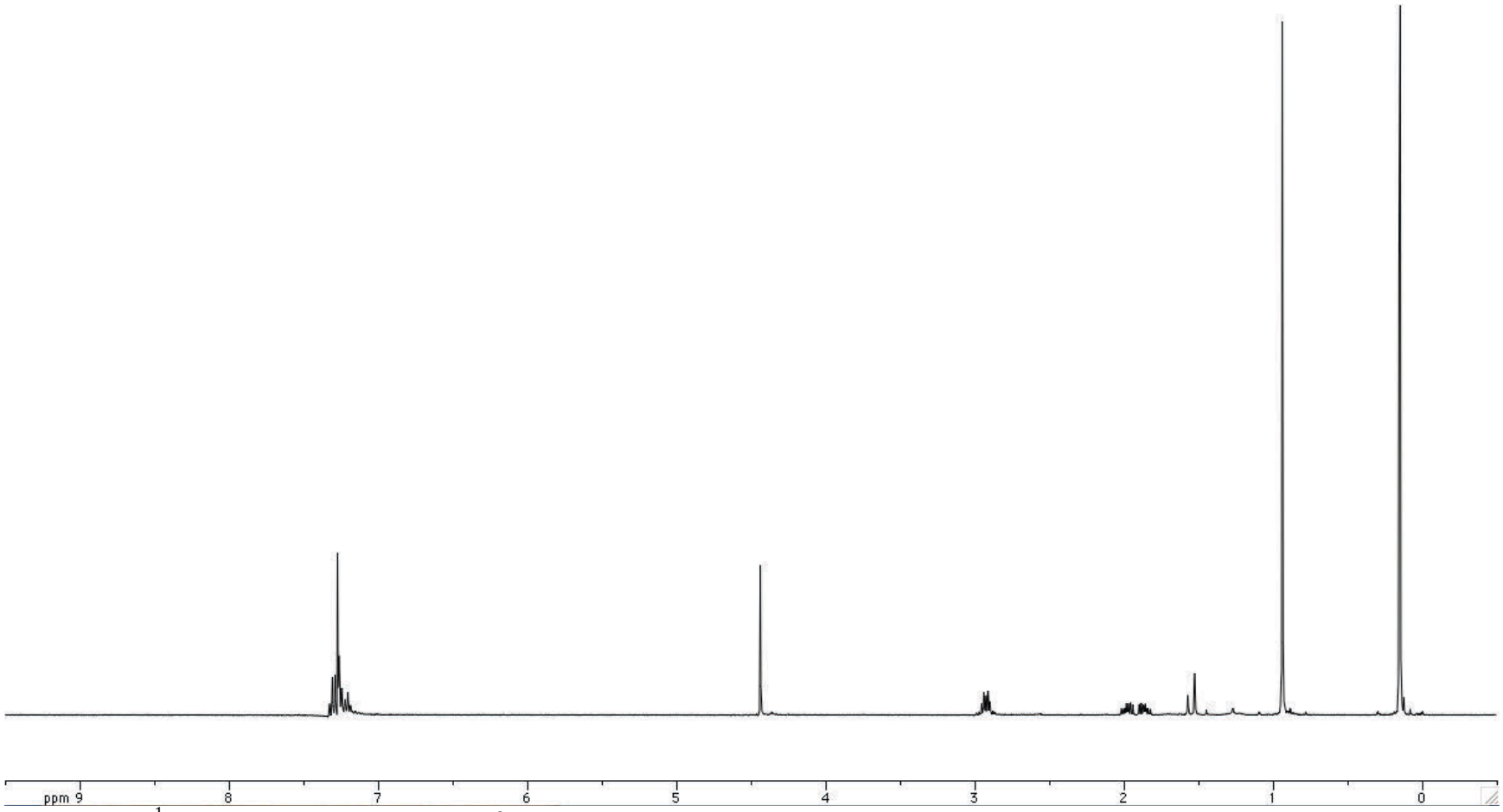
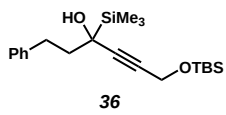


Figure A1.55 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **36**



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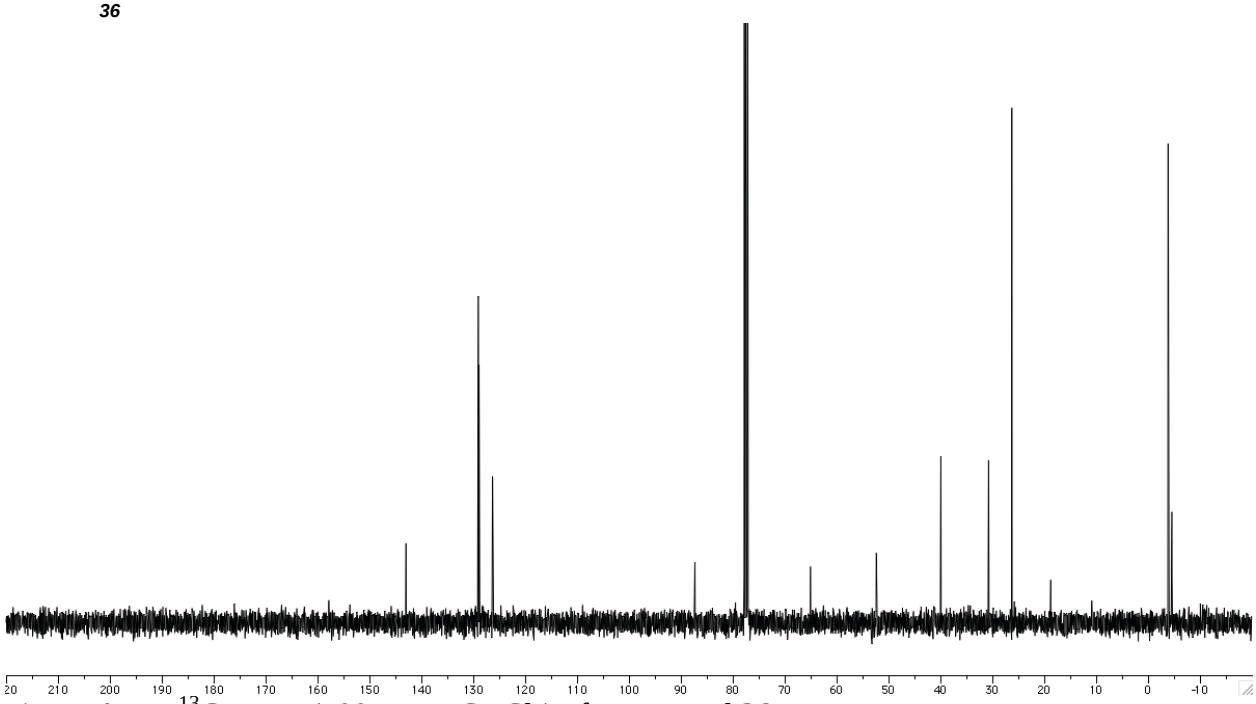


Figure A1.53 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **36**

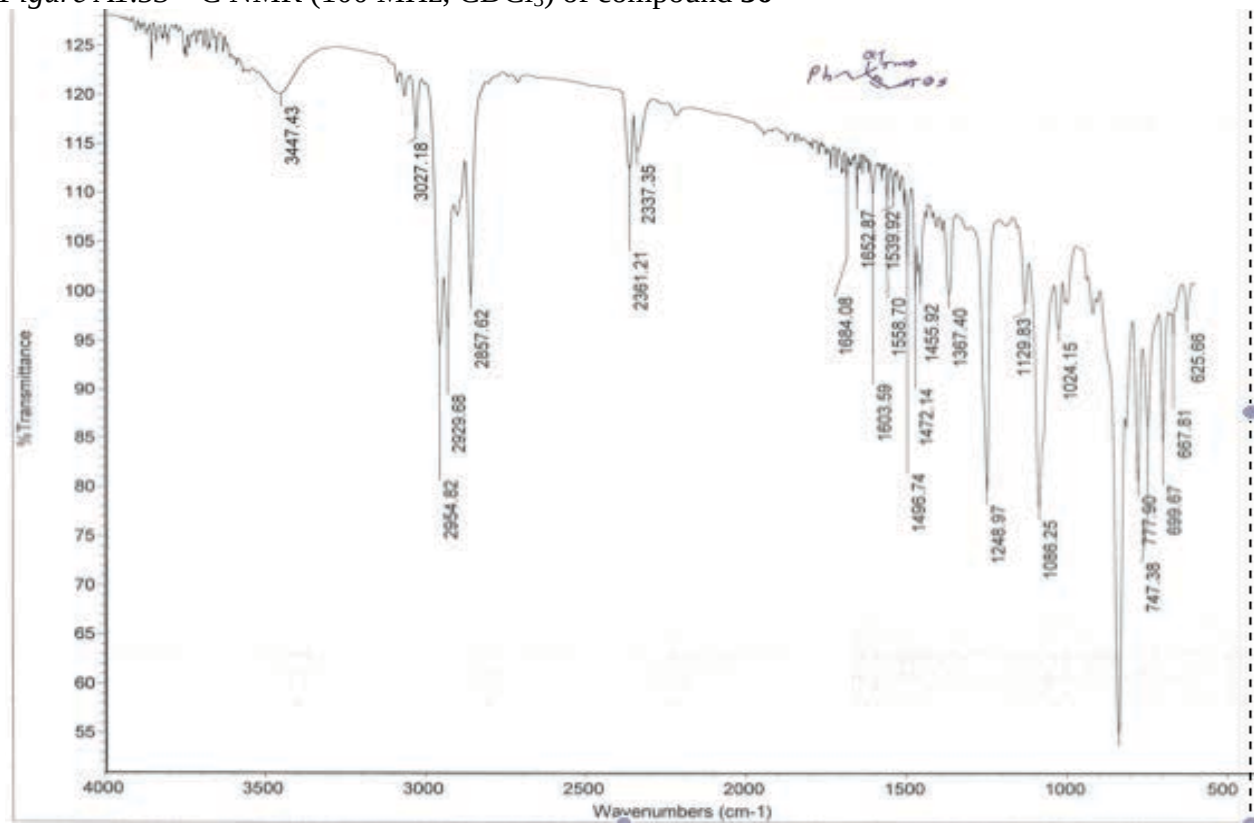
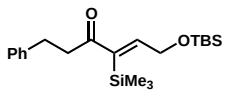


Figure A1.54 Infrared spectrum (thin film) of compound **36**



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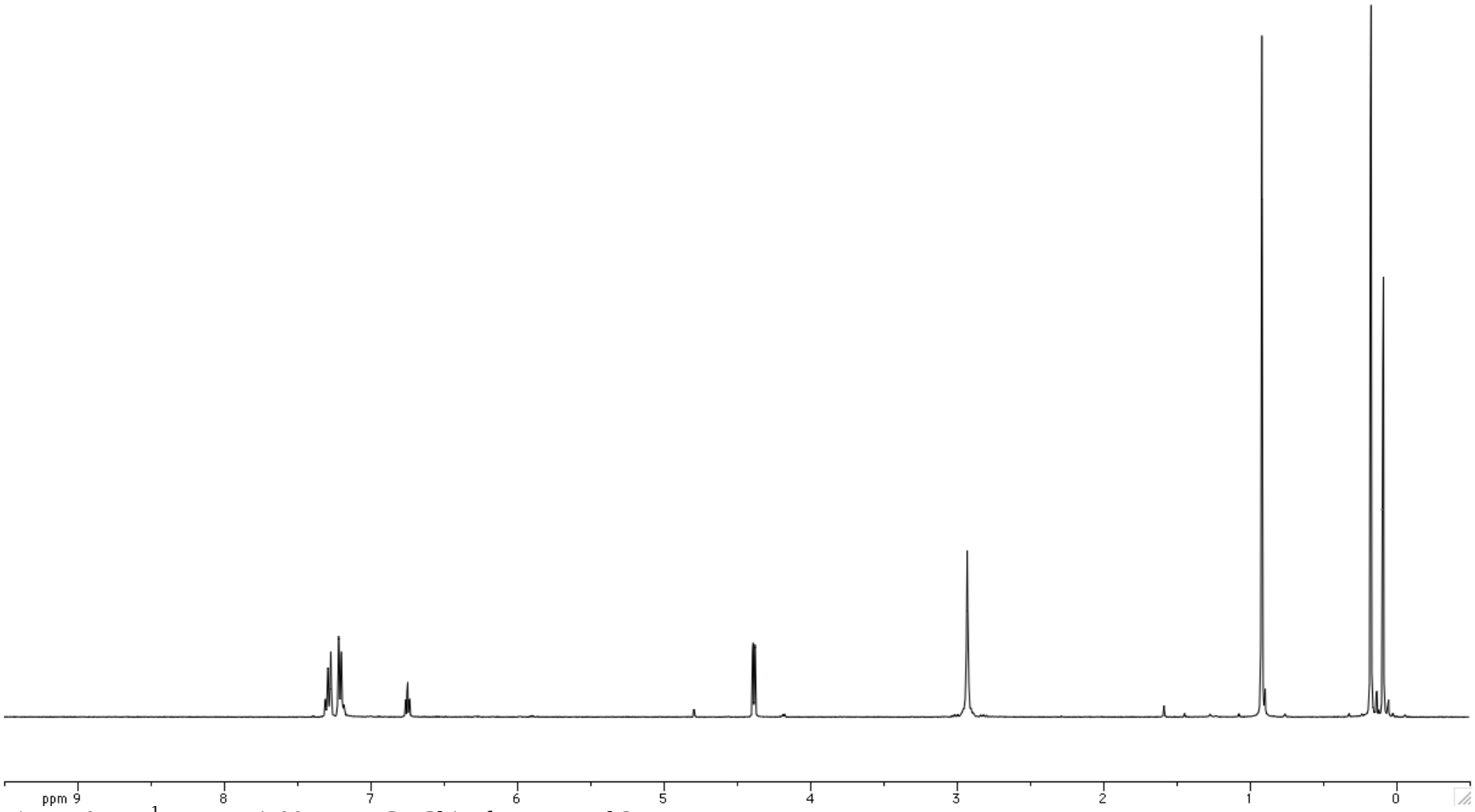


Figure A1.55 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **37**

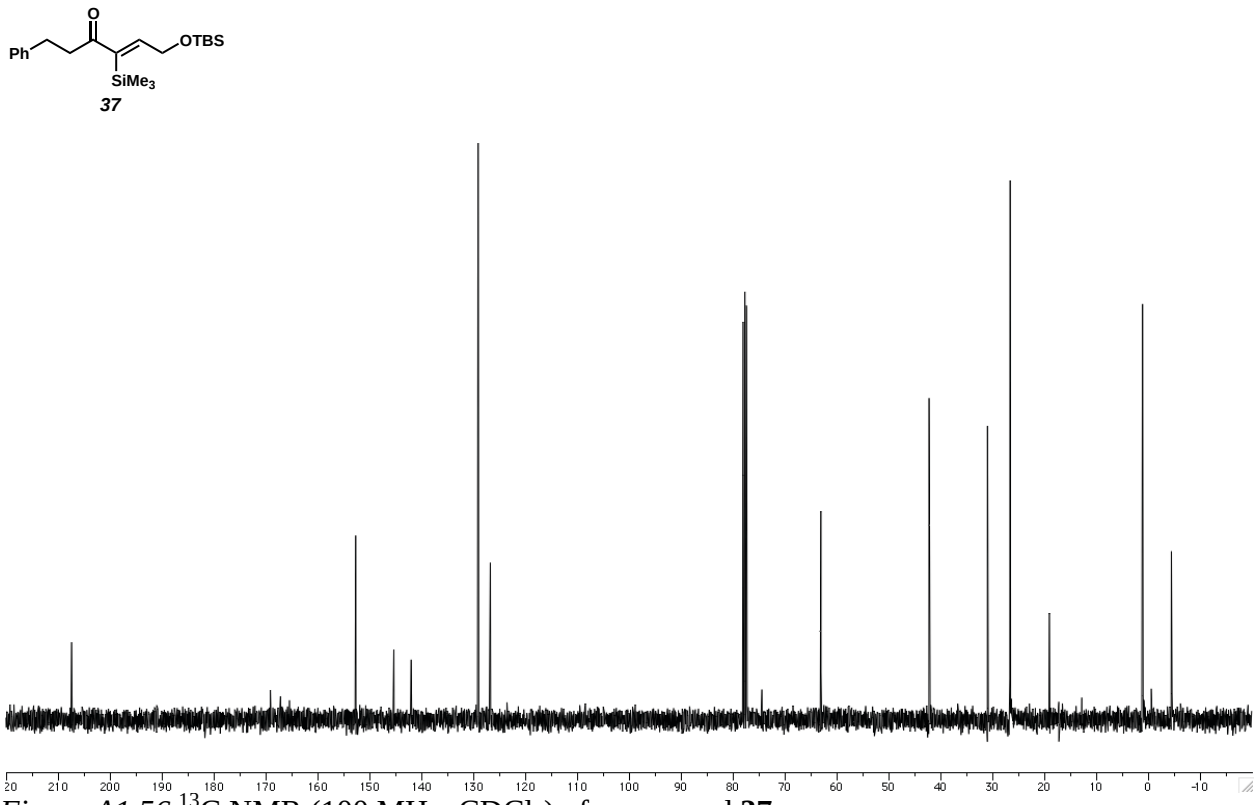


Figure A1.56 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **37**

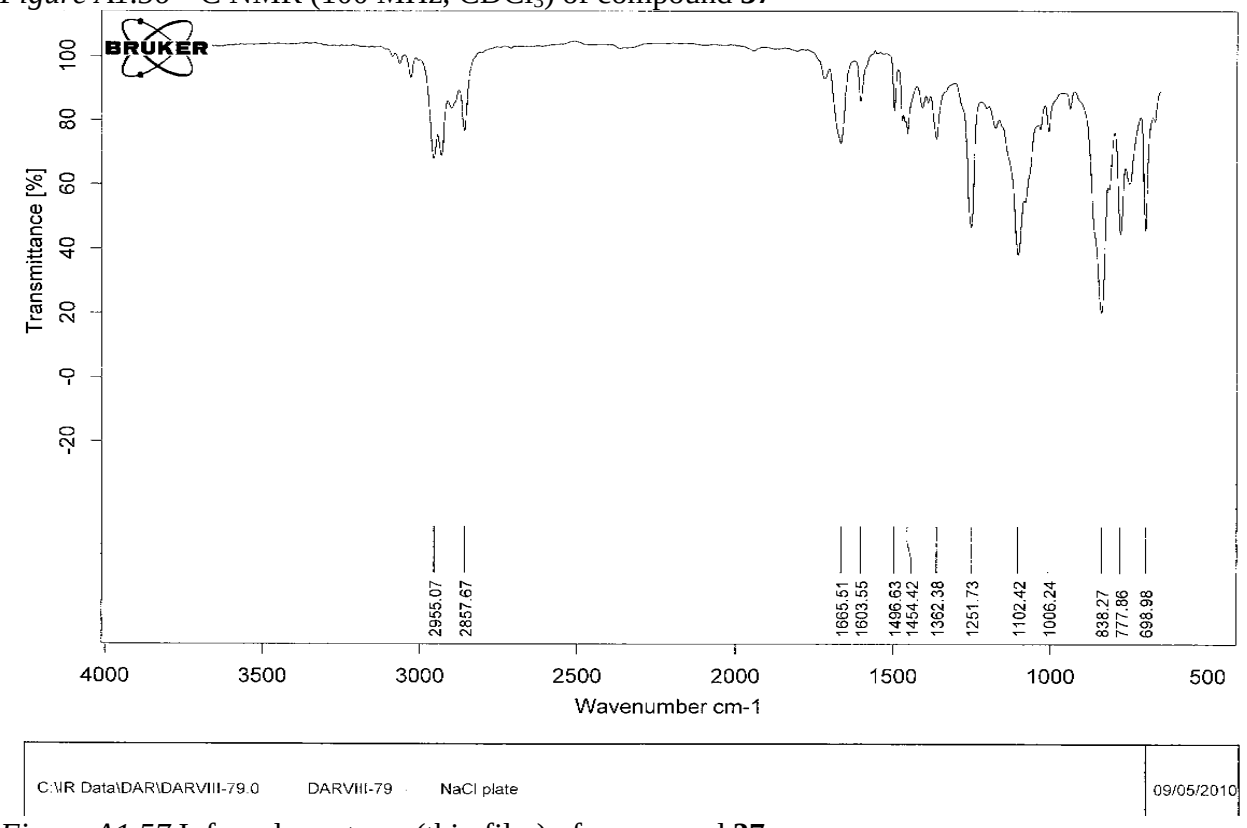
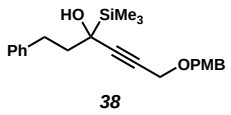


Figure A1.57 Infrared spectrum (thin film) of compound **37**



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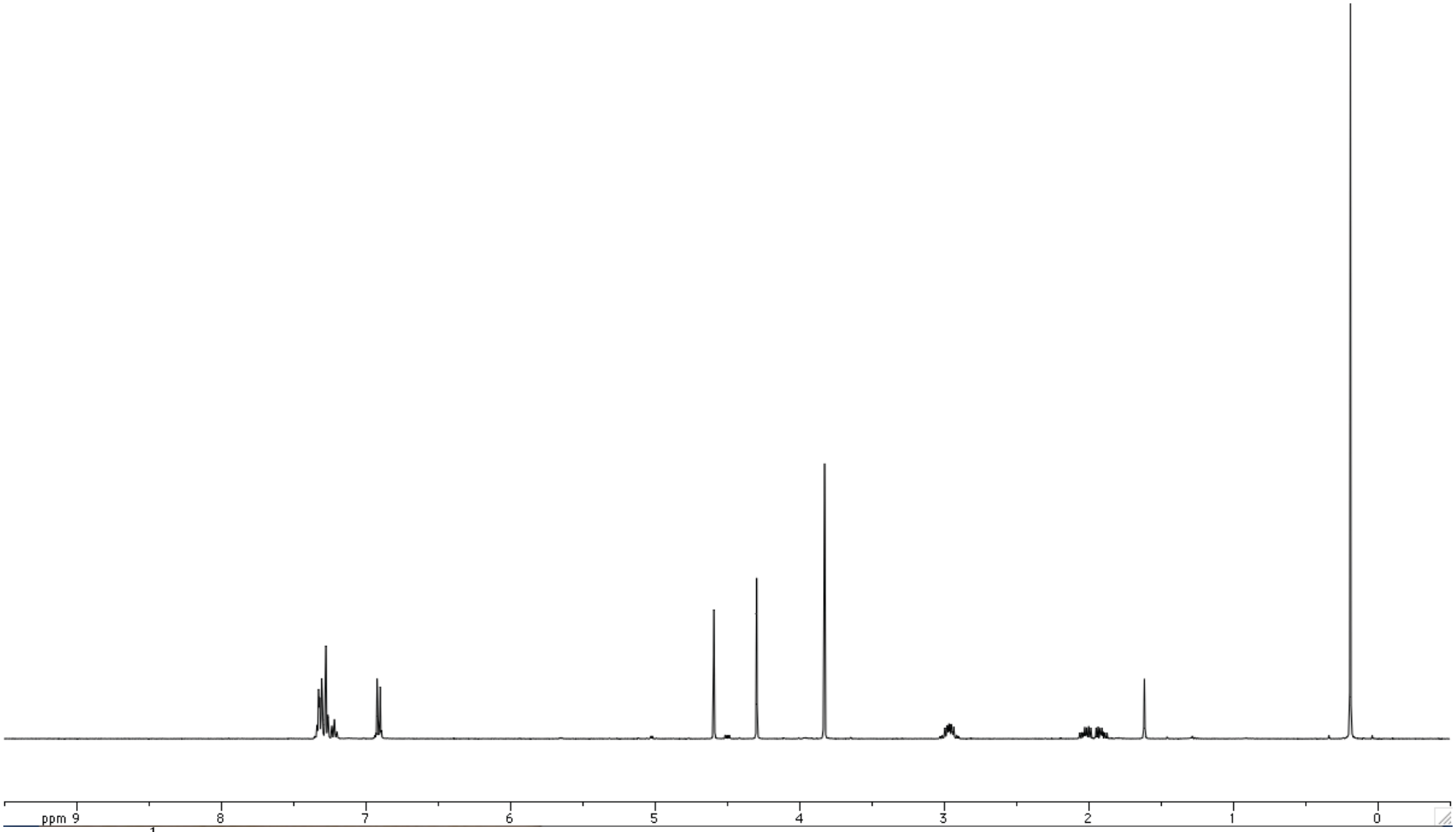


Figure A1.58 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **38**

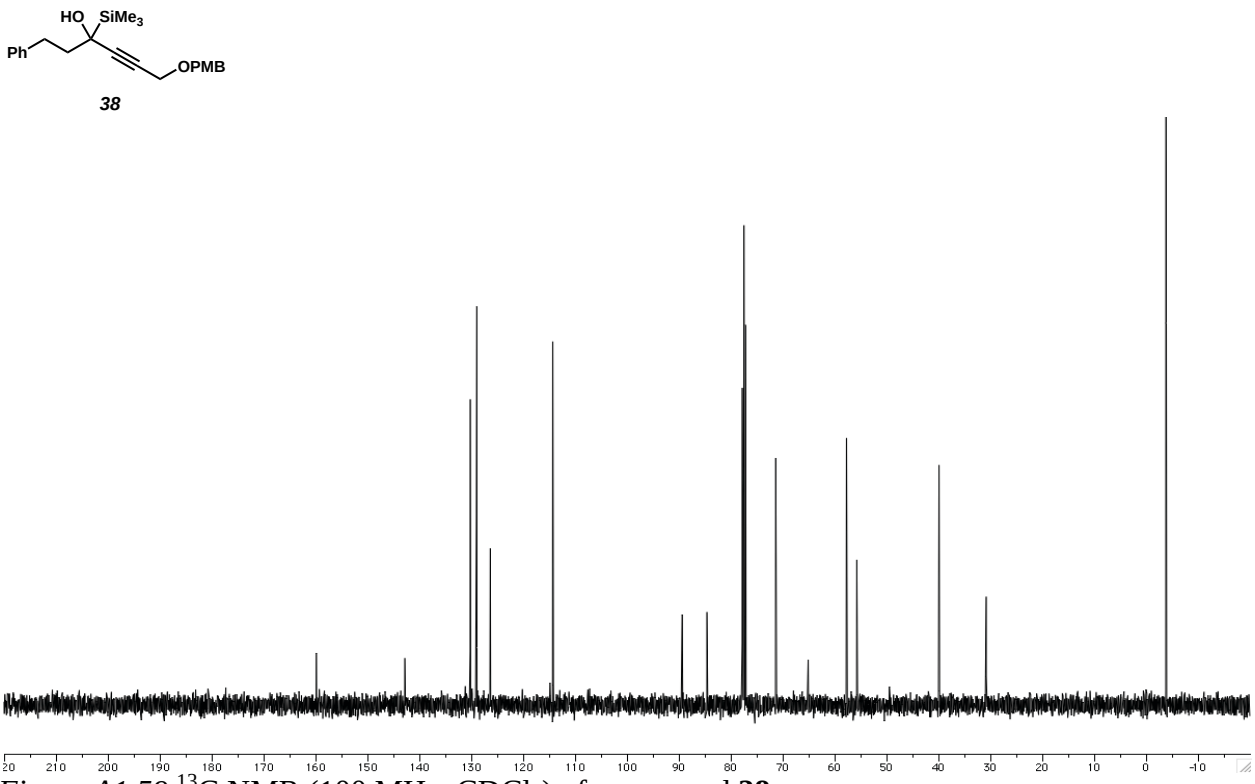


Figure A1.59 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **38**

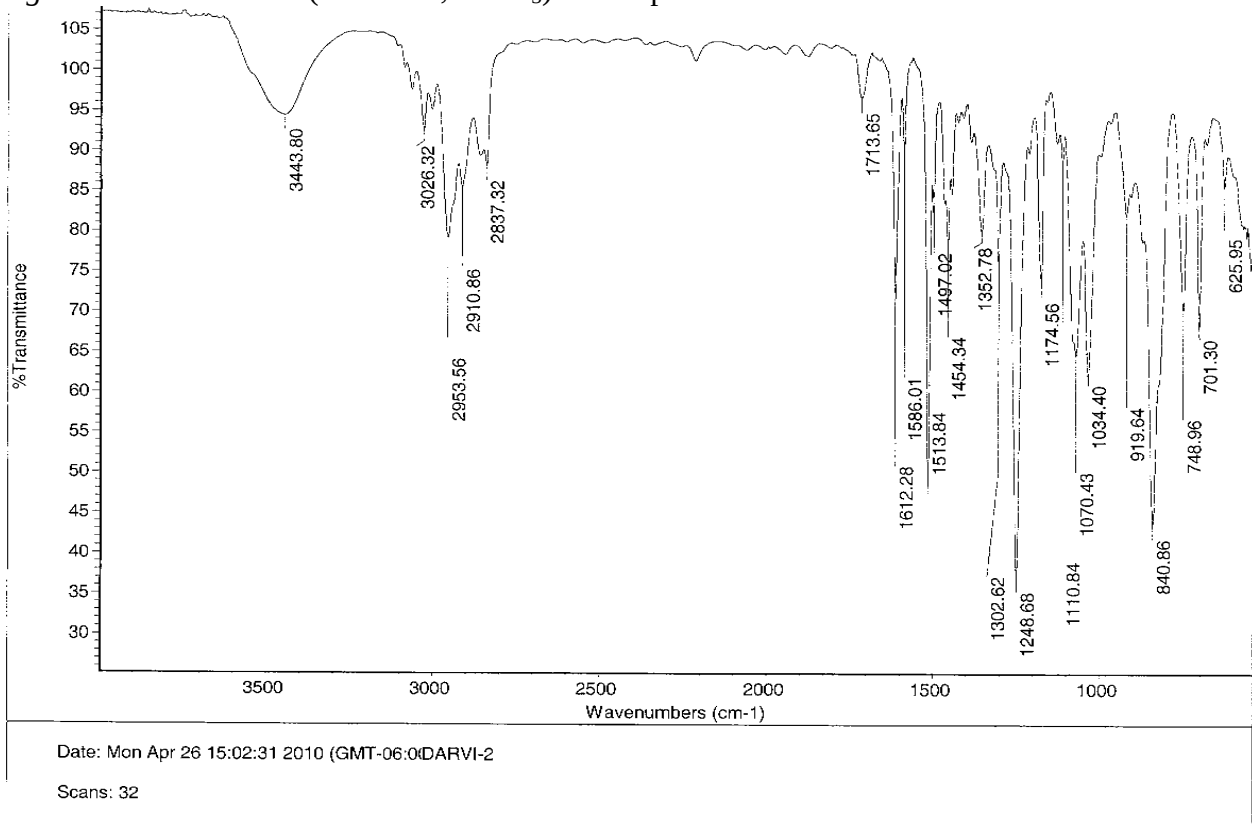
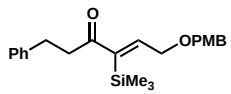


Figure A1.60 Infrared spectrum (thin film) of compound **38**



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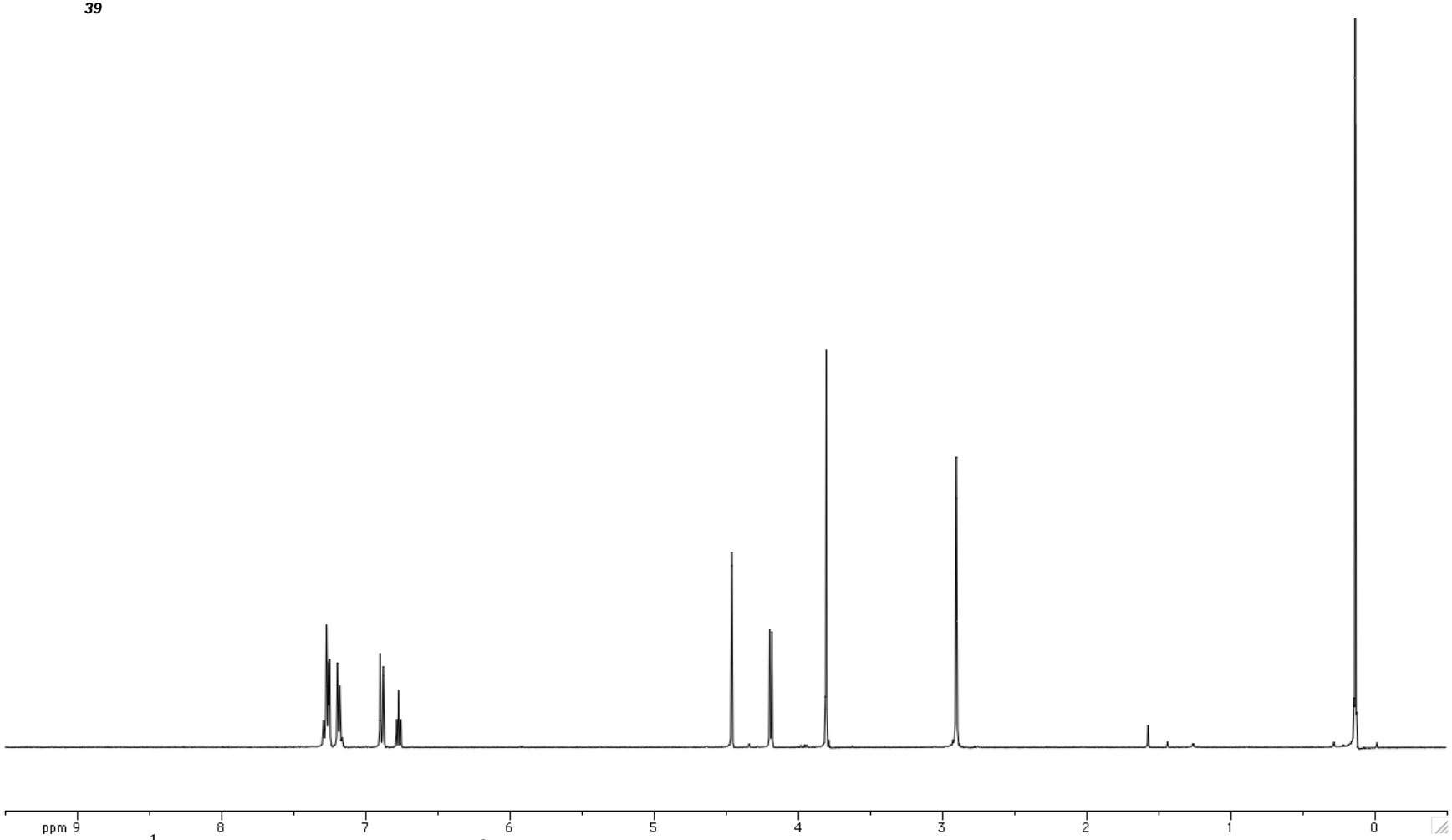
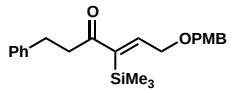


Figure A1.61 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **39**



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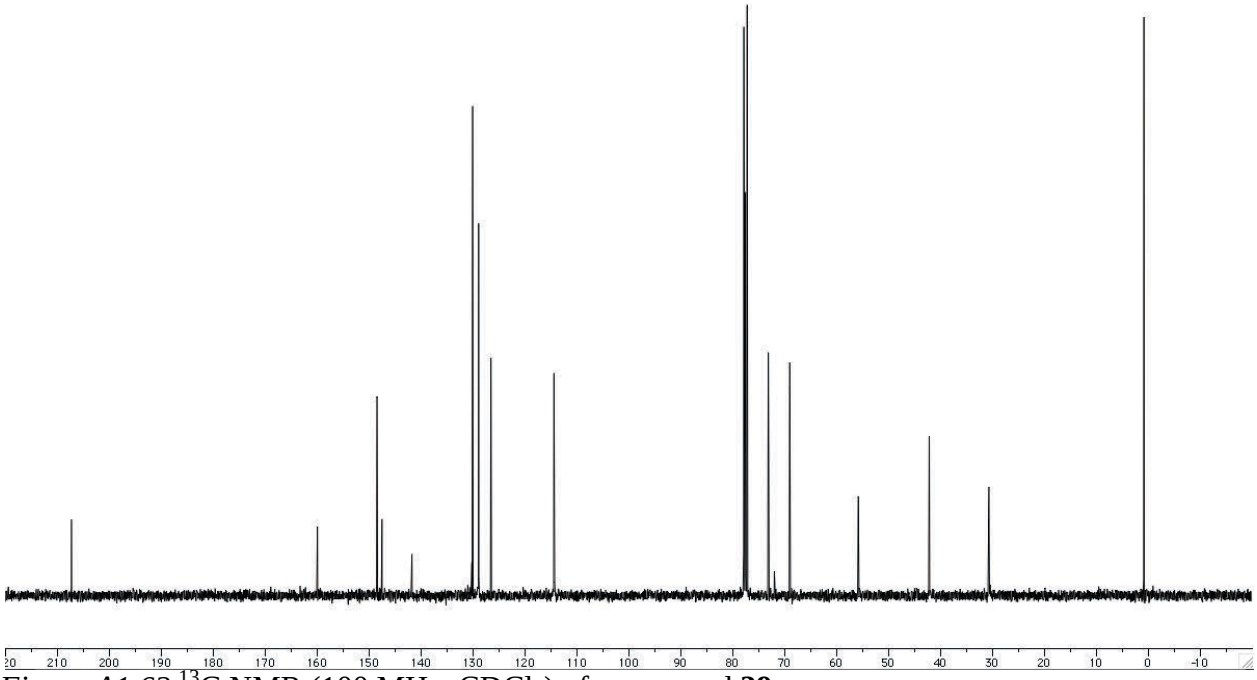


Figure A1.62 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **39**

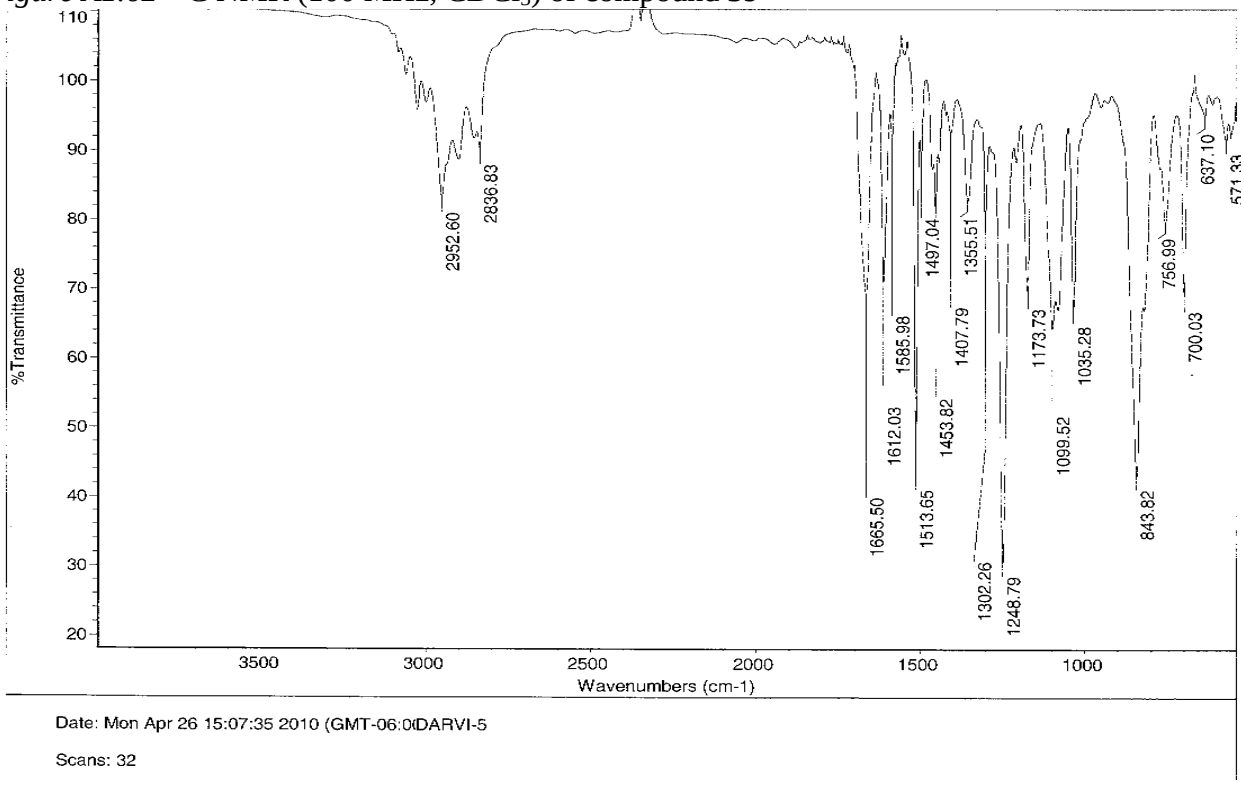
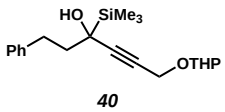


Figure A1.63 Infrared spectrum (thin film) of compound **39**



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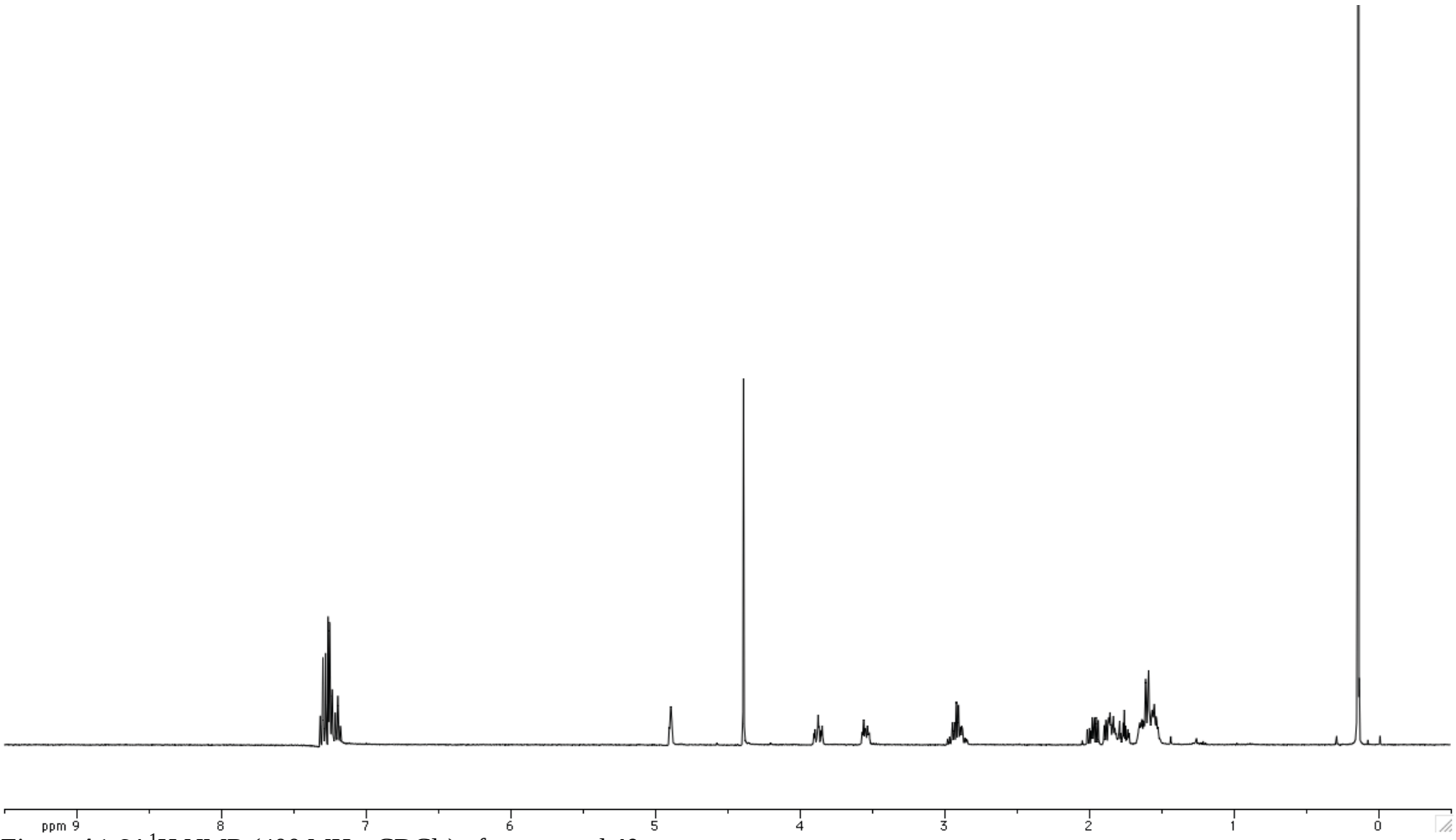


Figure A1.64 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **40**

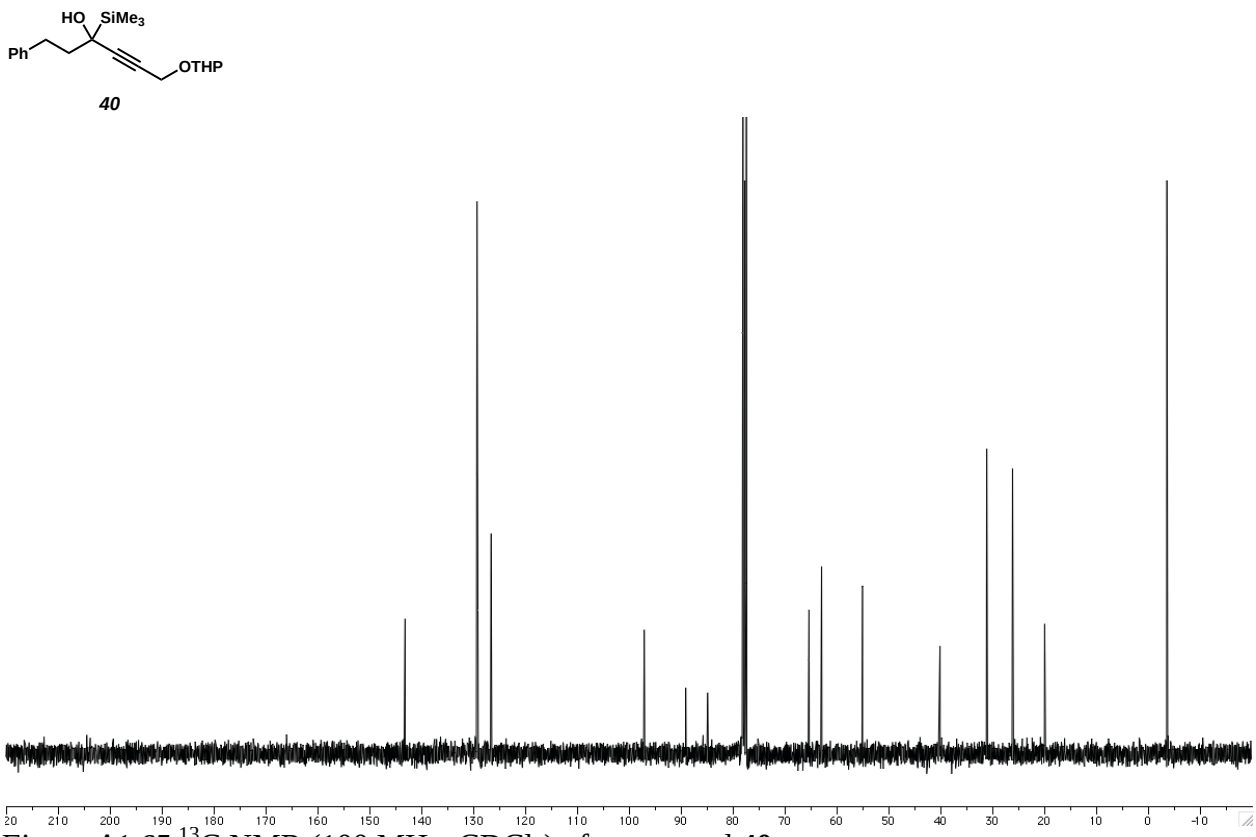


Figure A1.65 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **40**

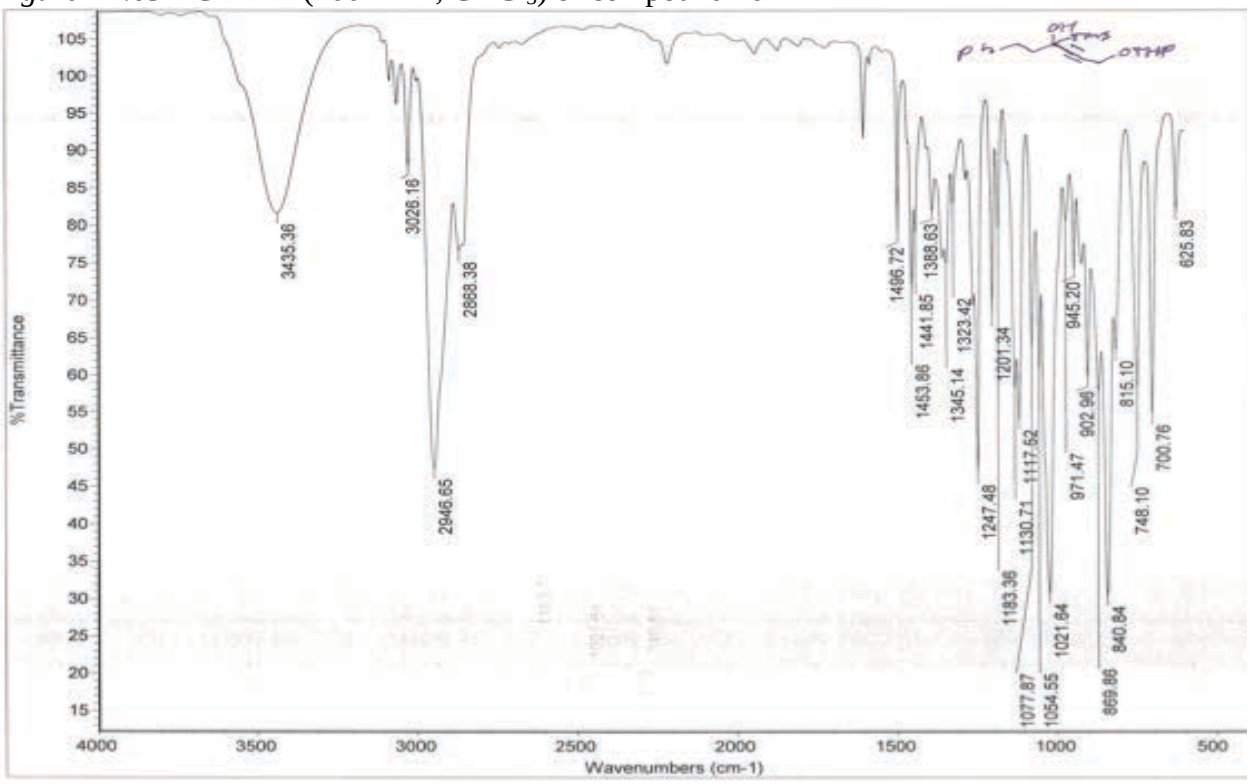
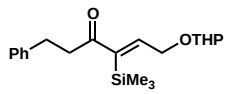


Figure A1.66 Infrared spectrum (thin film) of compound **40**



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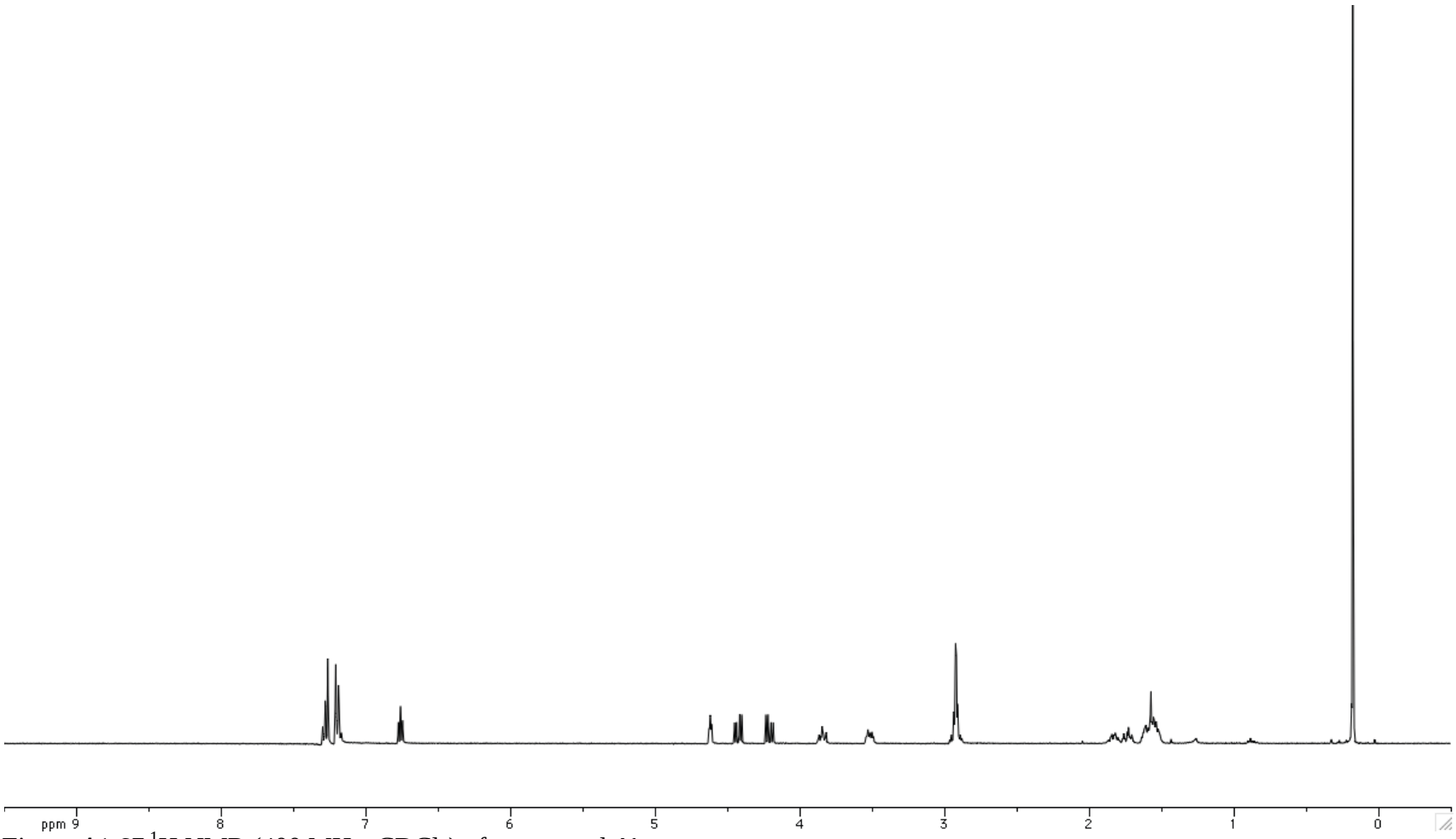


Figure A1.67 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **41**

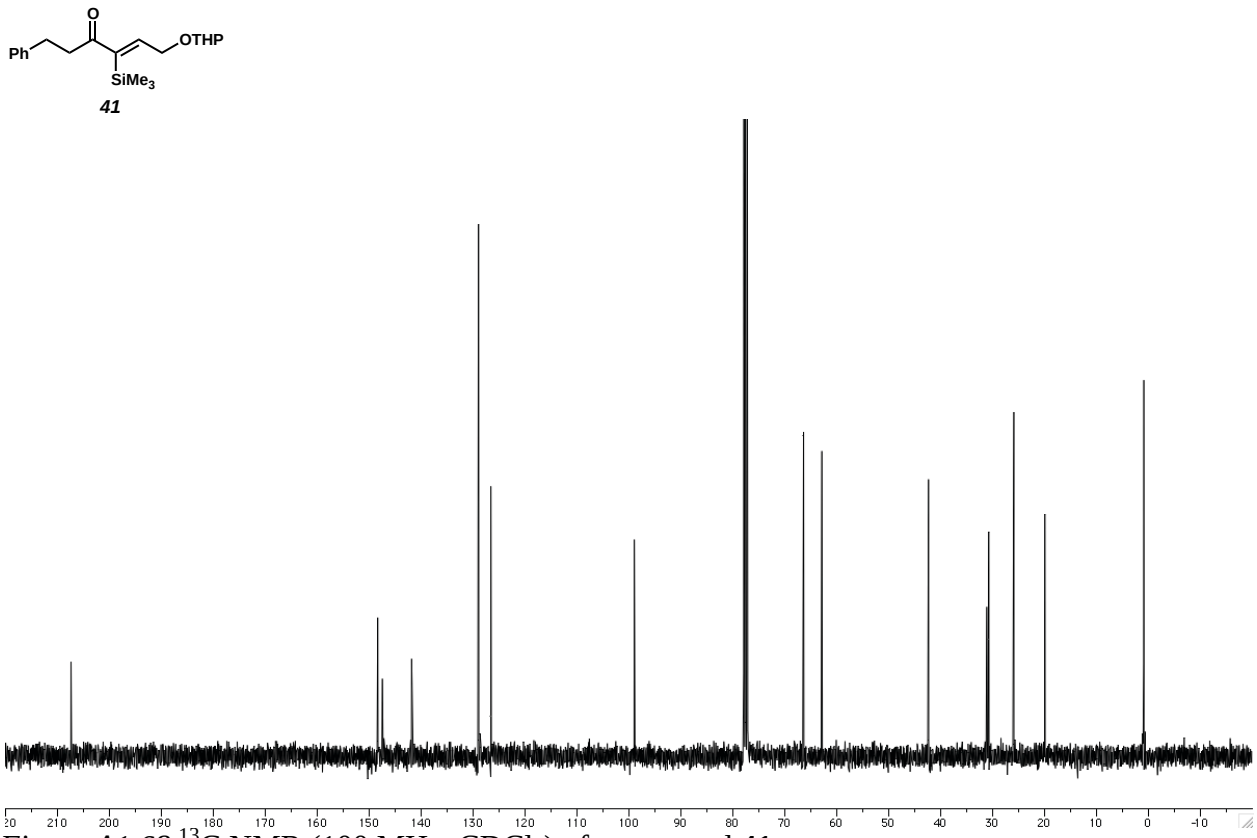


Figure A1.68 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **41**

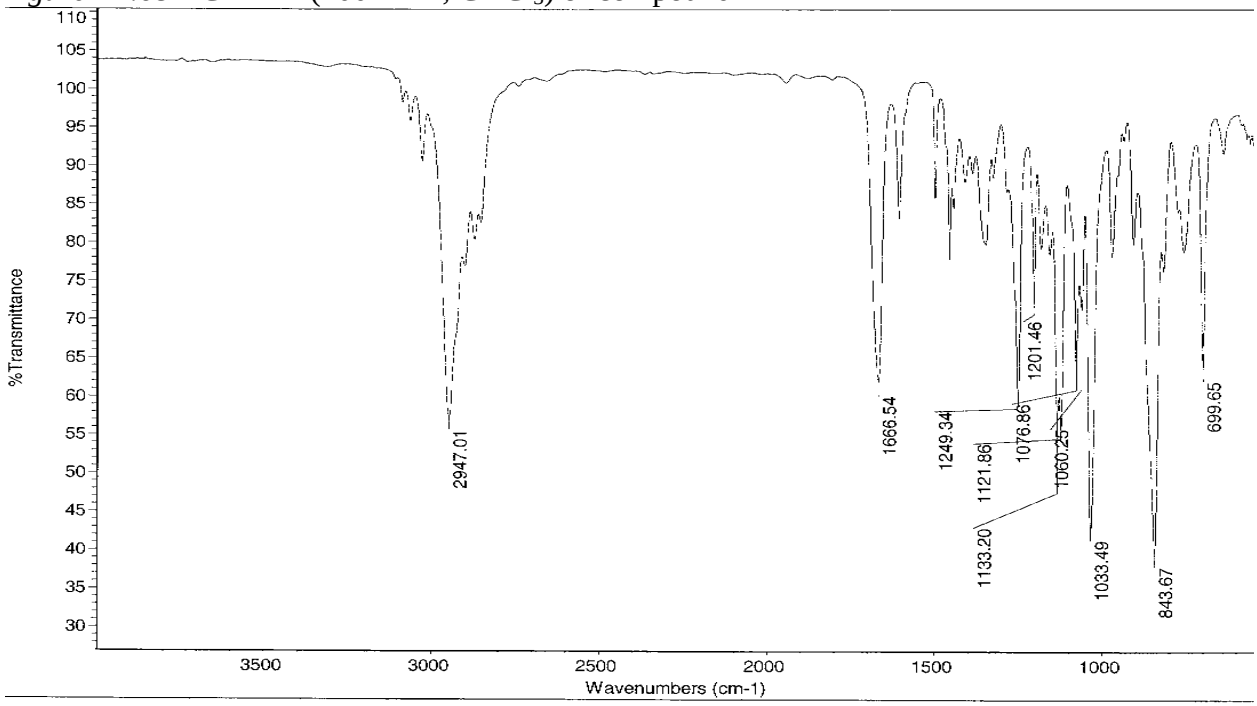
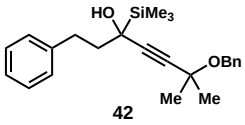


Figure A1.69 Infrared spectrum (thin film) of compound **41**



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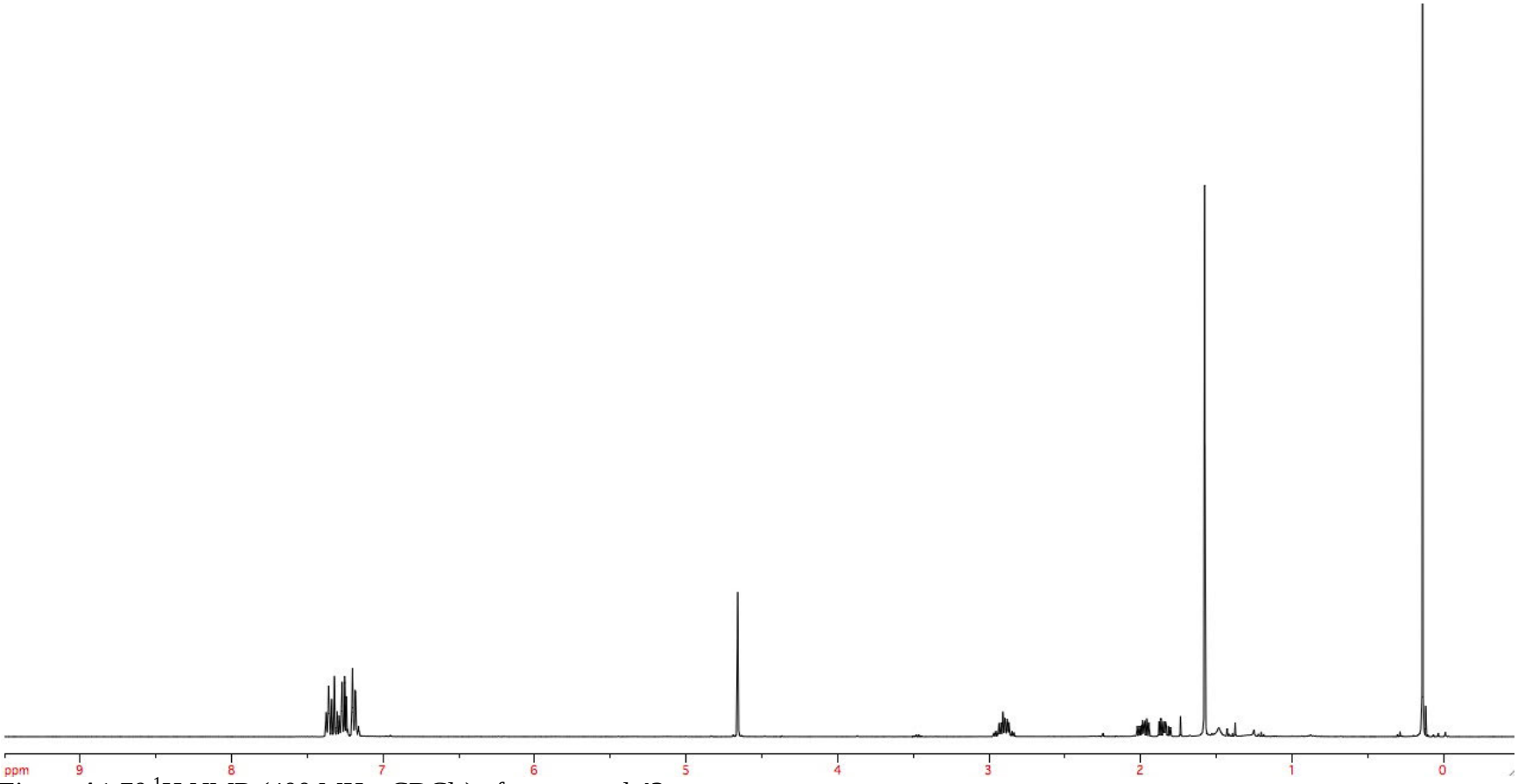
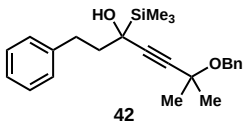


Figure A1.70 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **42**



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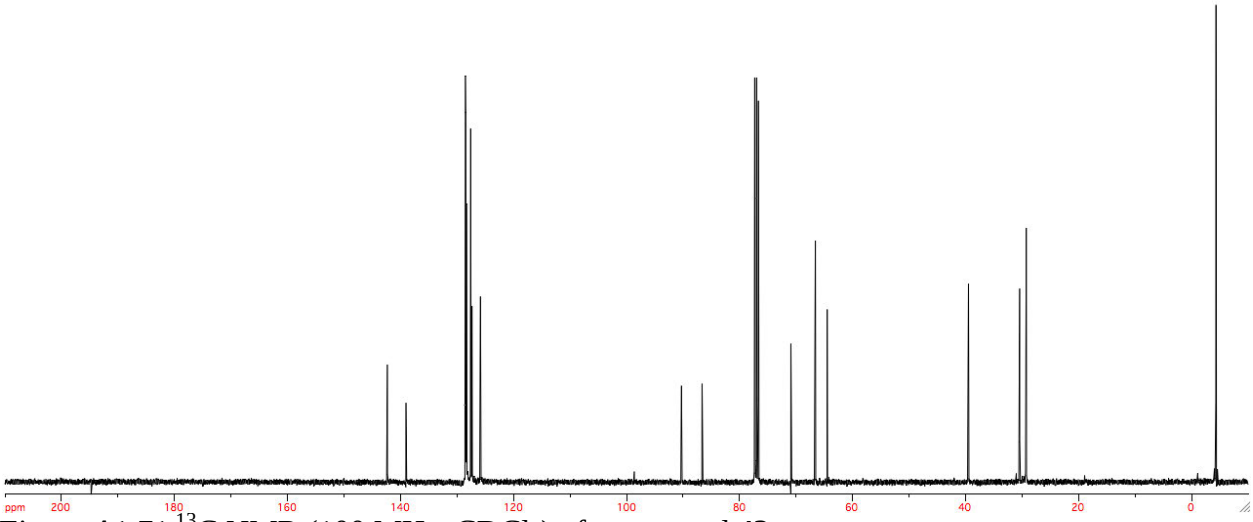


Figure A1.71 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **42**

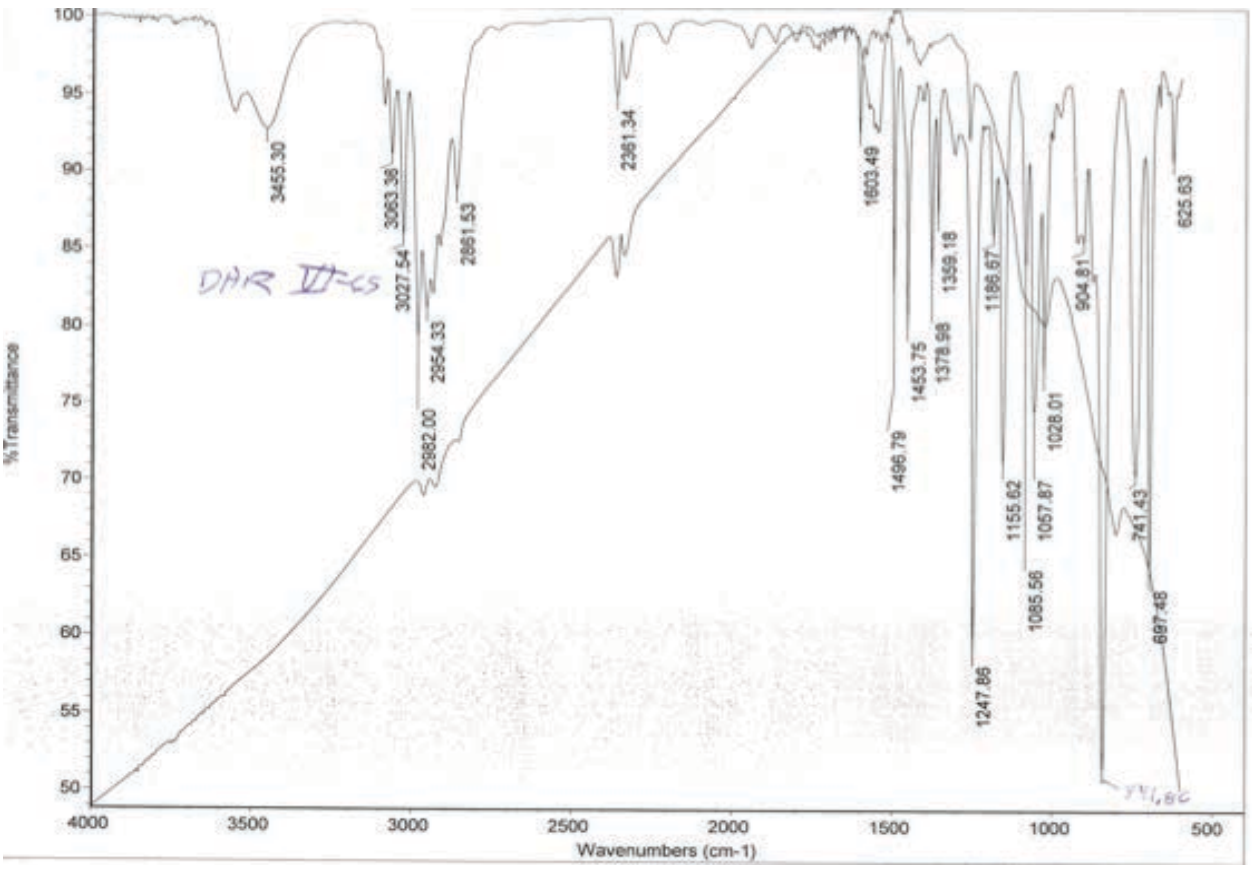
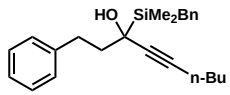


Figure A1.72 Infrared spectrum (thin film) of compound **42**



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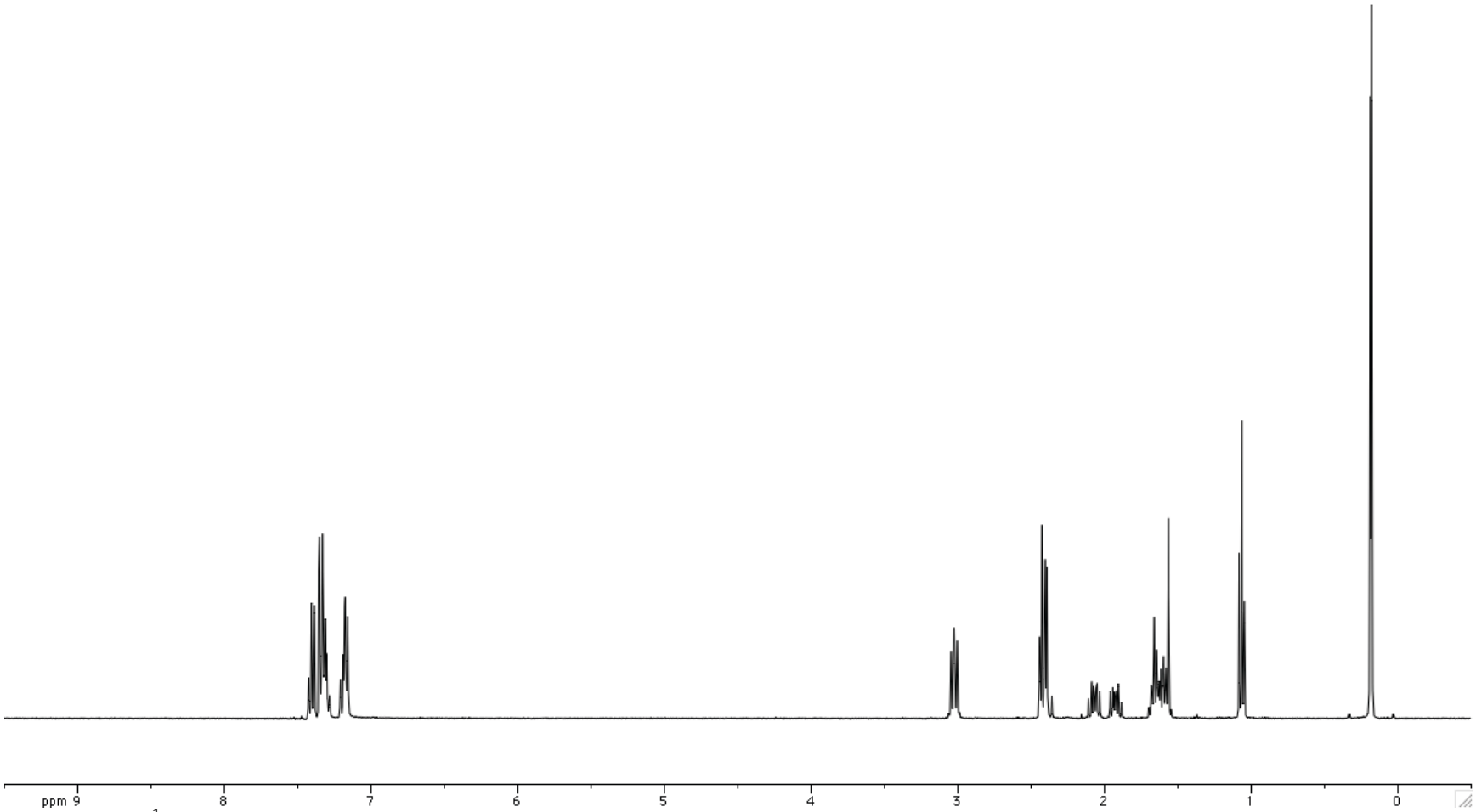


Figure A1.73 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **63**

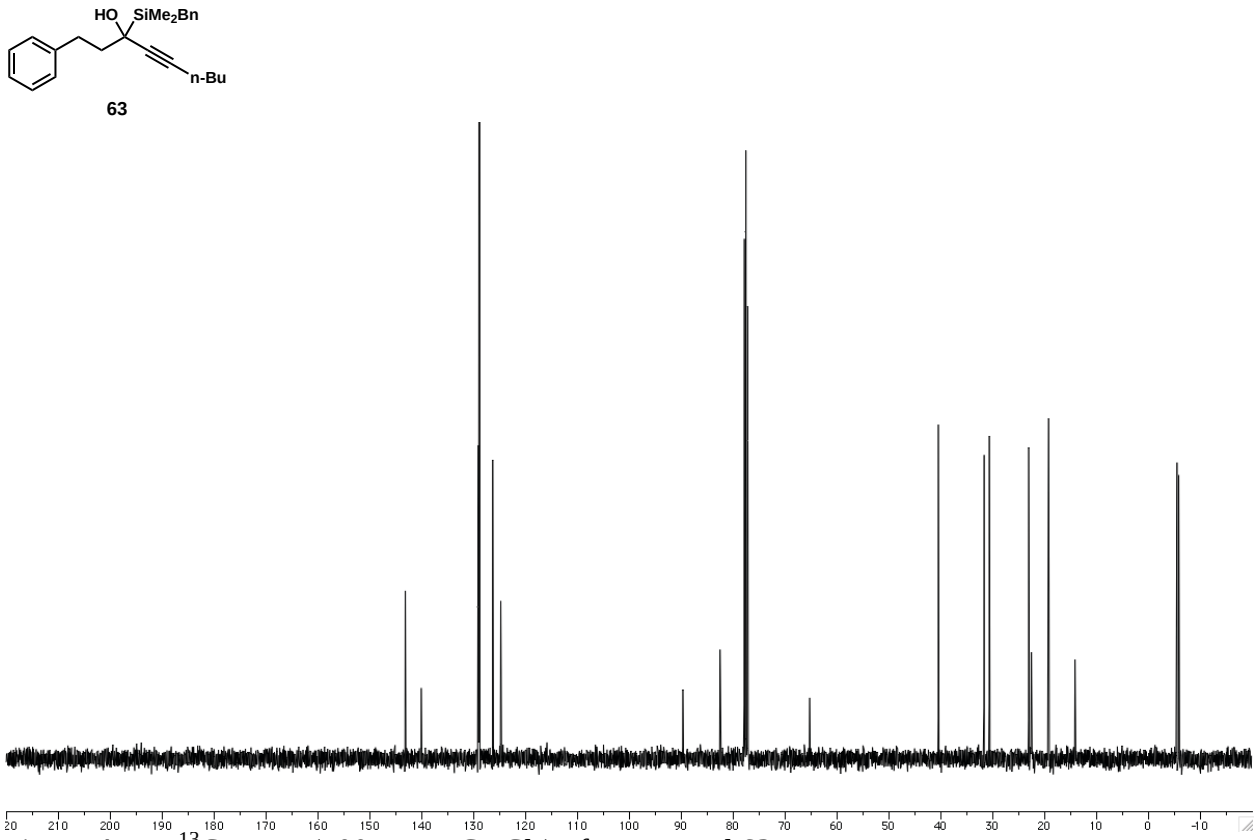


Figure A1.74 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **63**

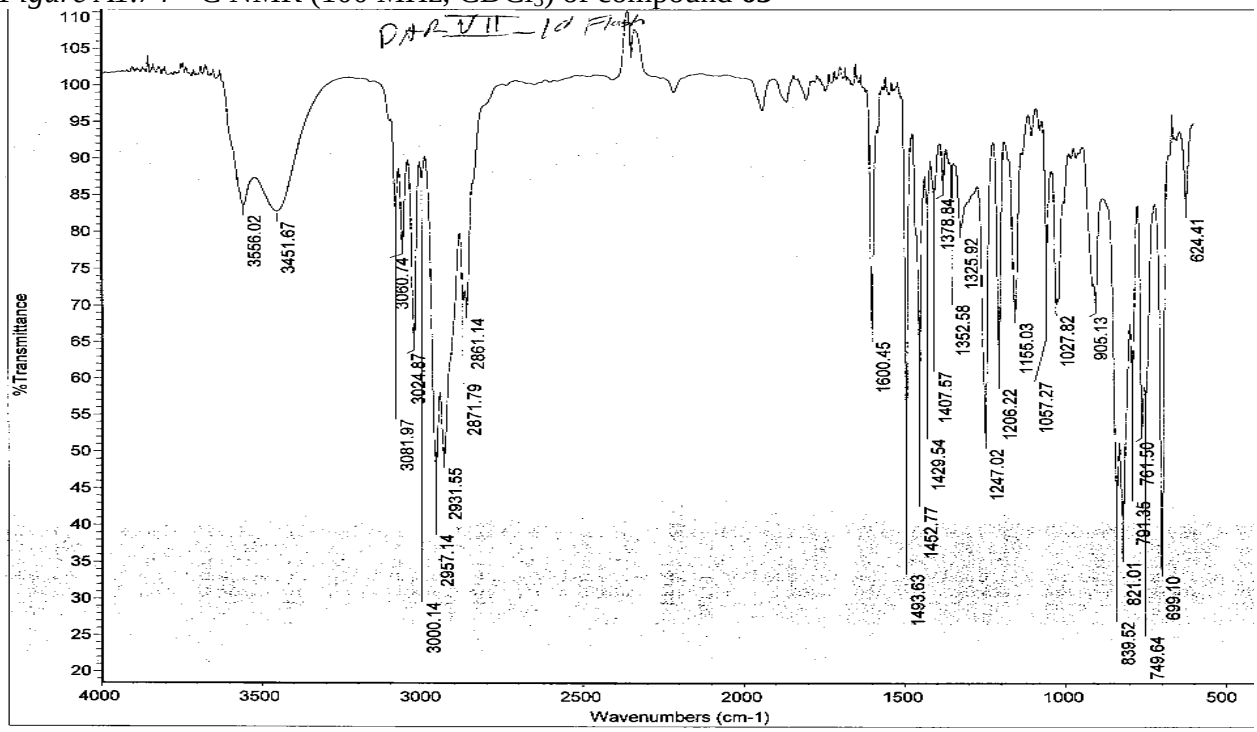
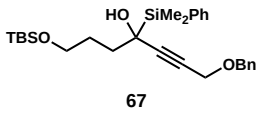


Figure A1.75 Infrared spectrum (thin film) of compound **63**



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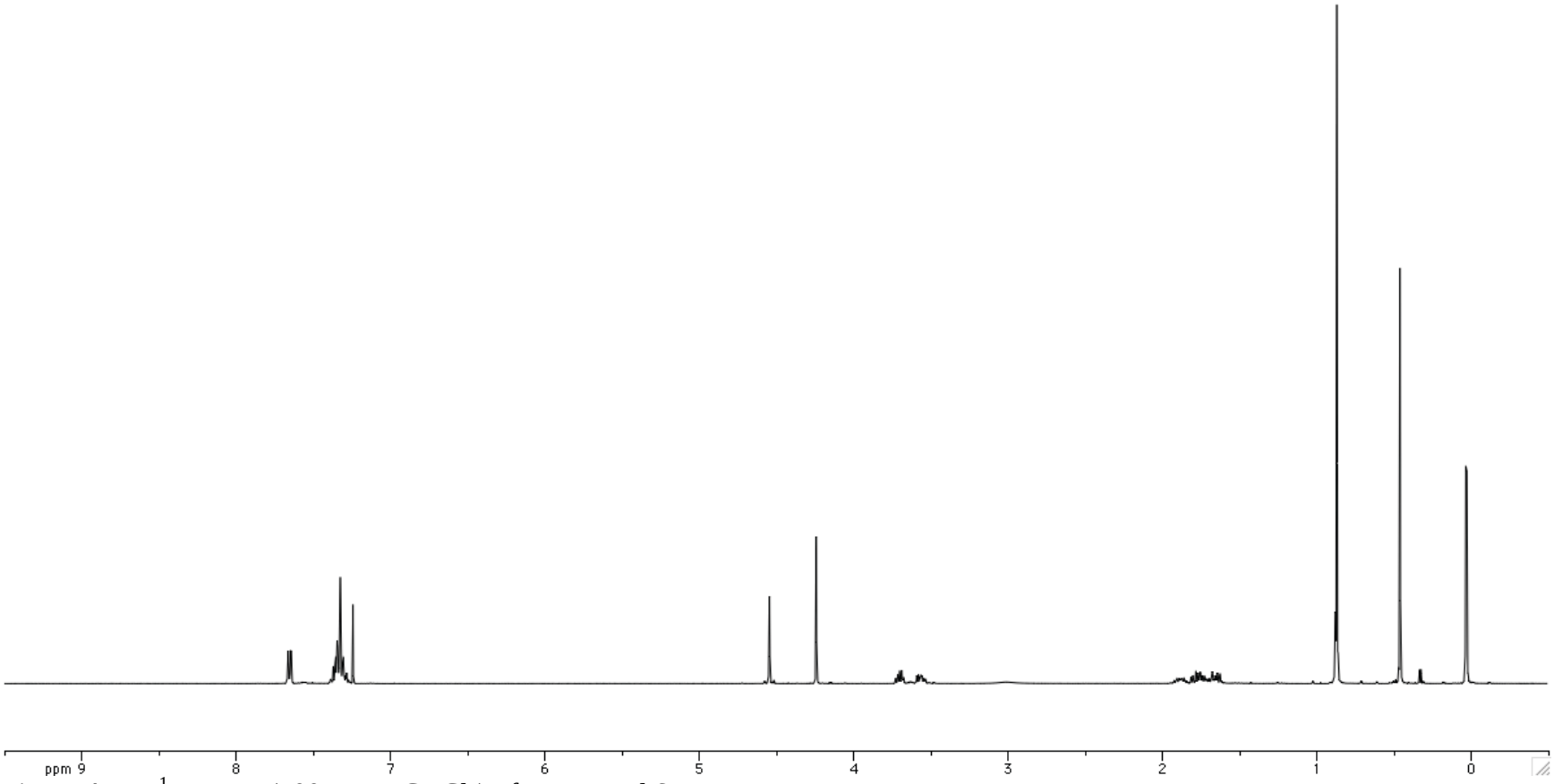
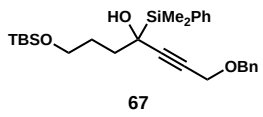


Figure A1.76 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **67**



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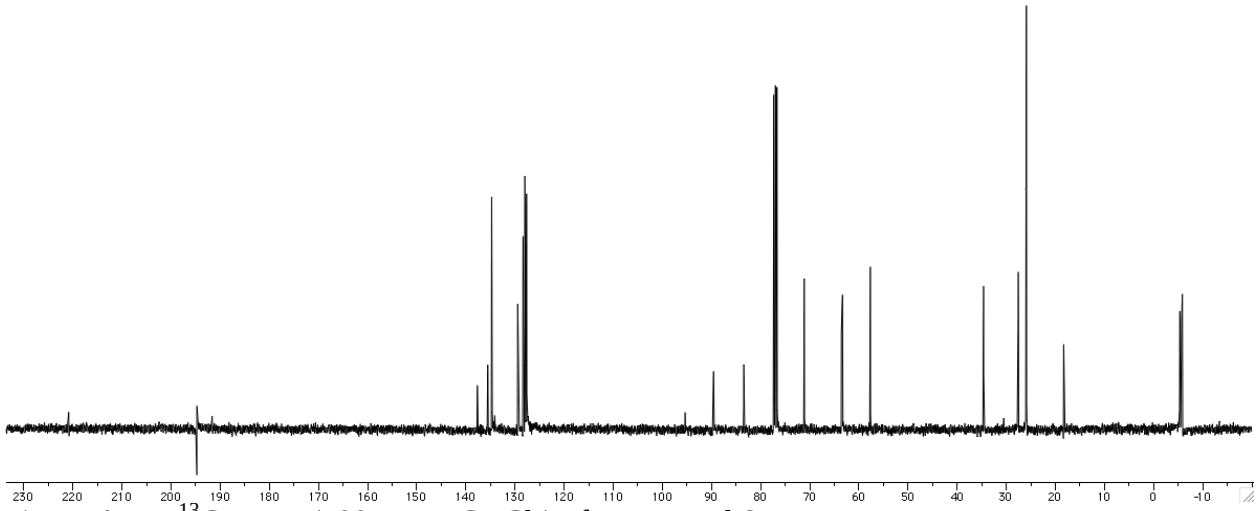
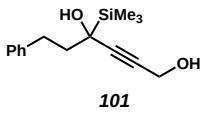


Figure A1.77 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **67**

Figure A1.78 Infrared spectrum (thin film) of compound **67**



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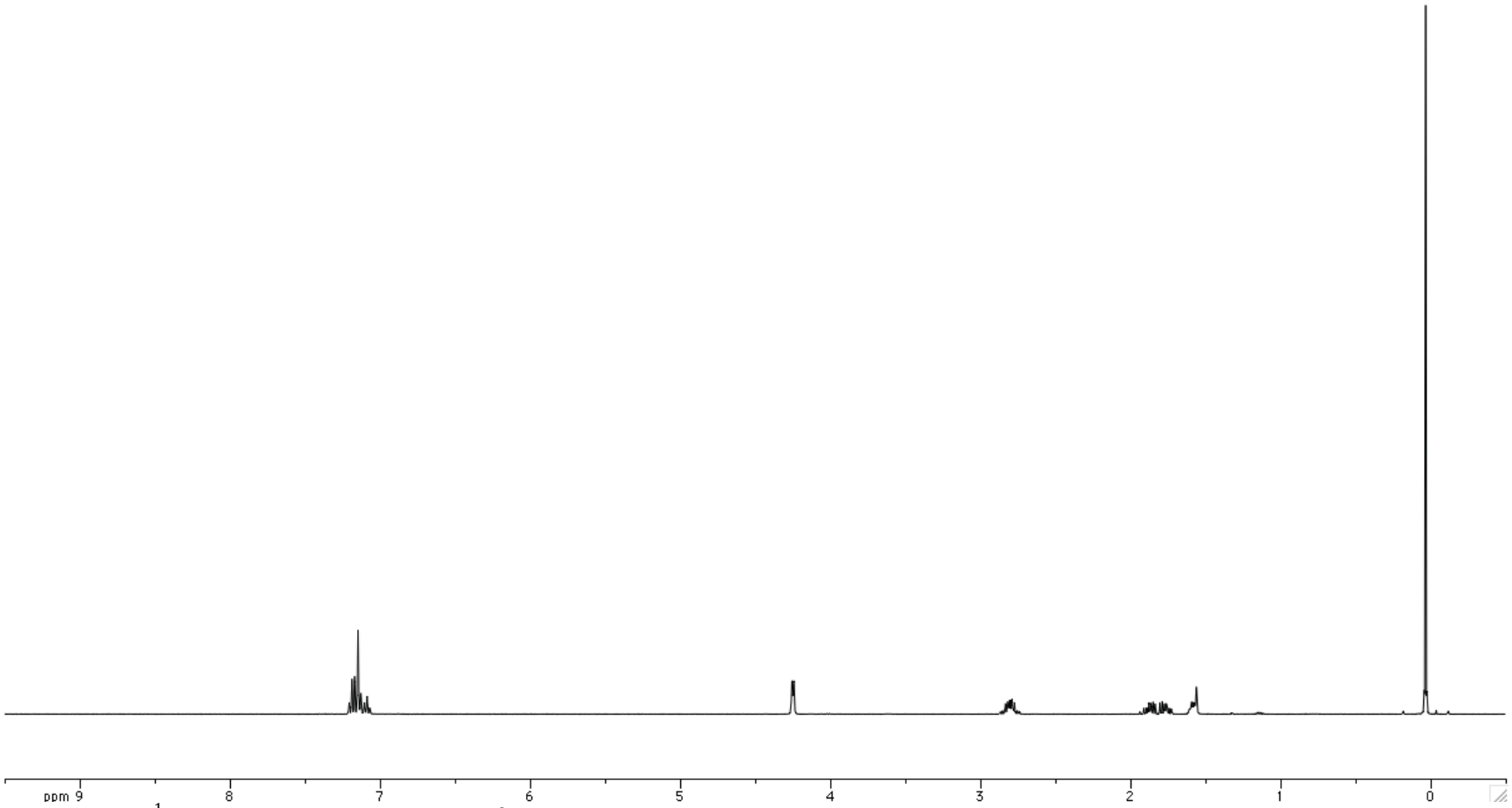
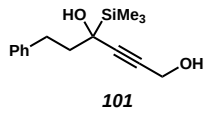


Figure A1.79 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **101**



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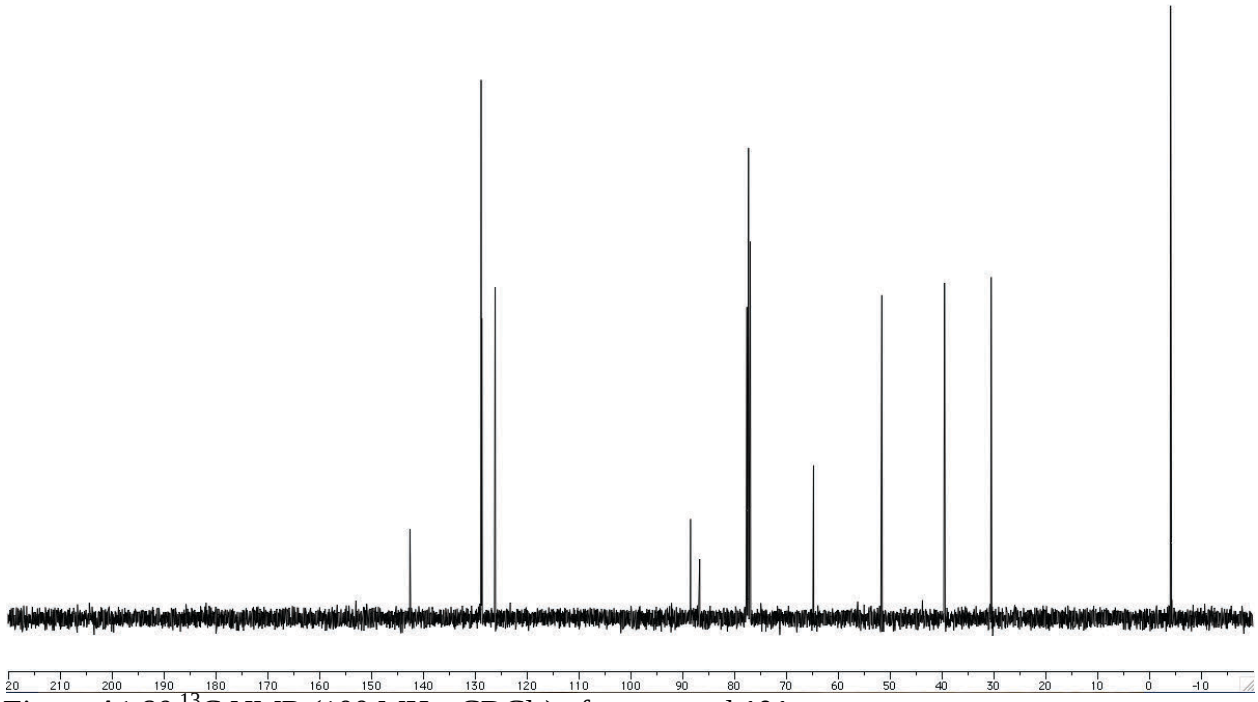


Figure A1.80 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **101**

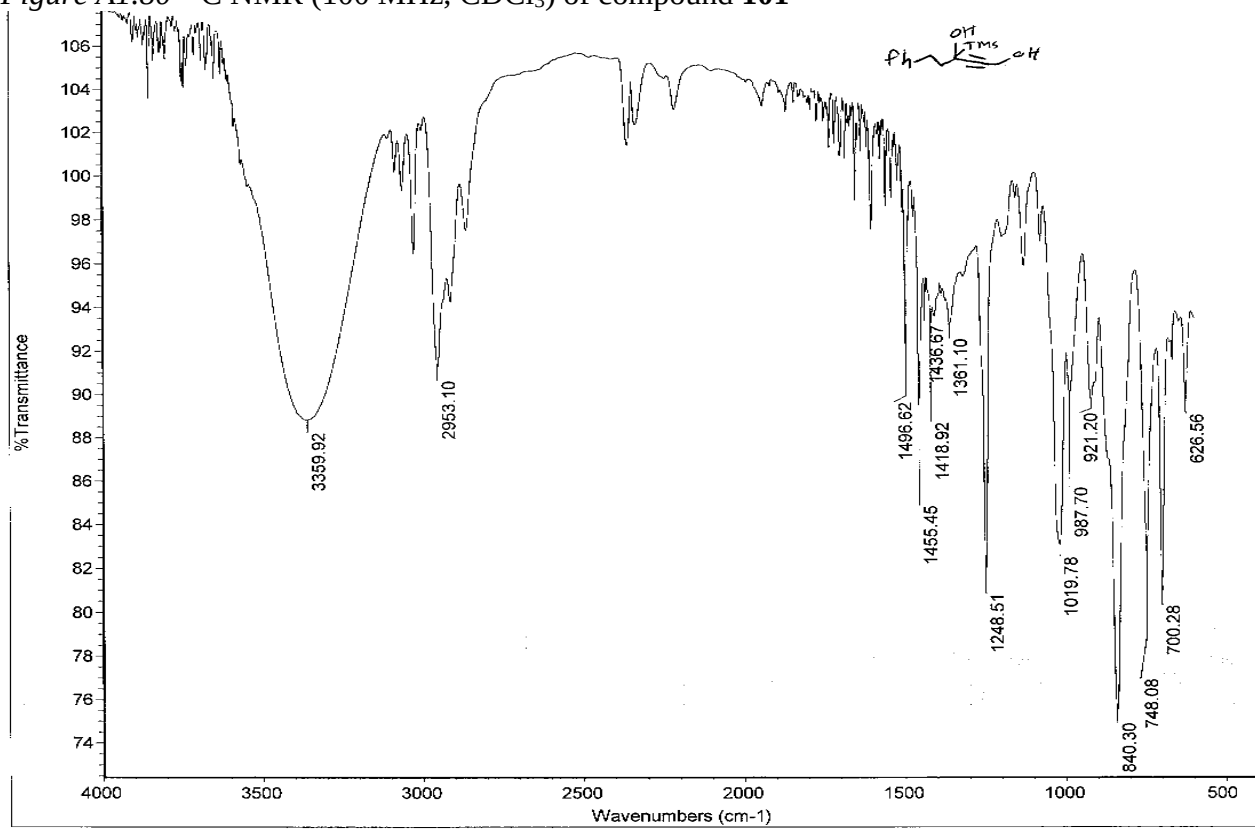
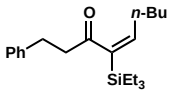


Figure A1.81 Infrared spectrum (thin film) of compound **101**

APPENDIX TWO

Spectra Relevant to Chapter Three:

The Regioselective Hydrosilylations of Internal Alkynes



123

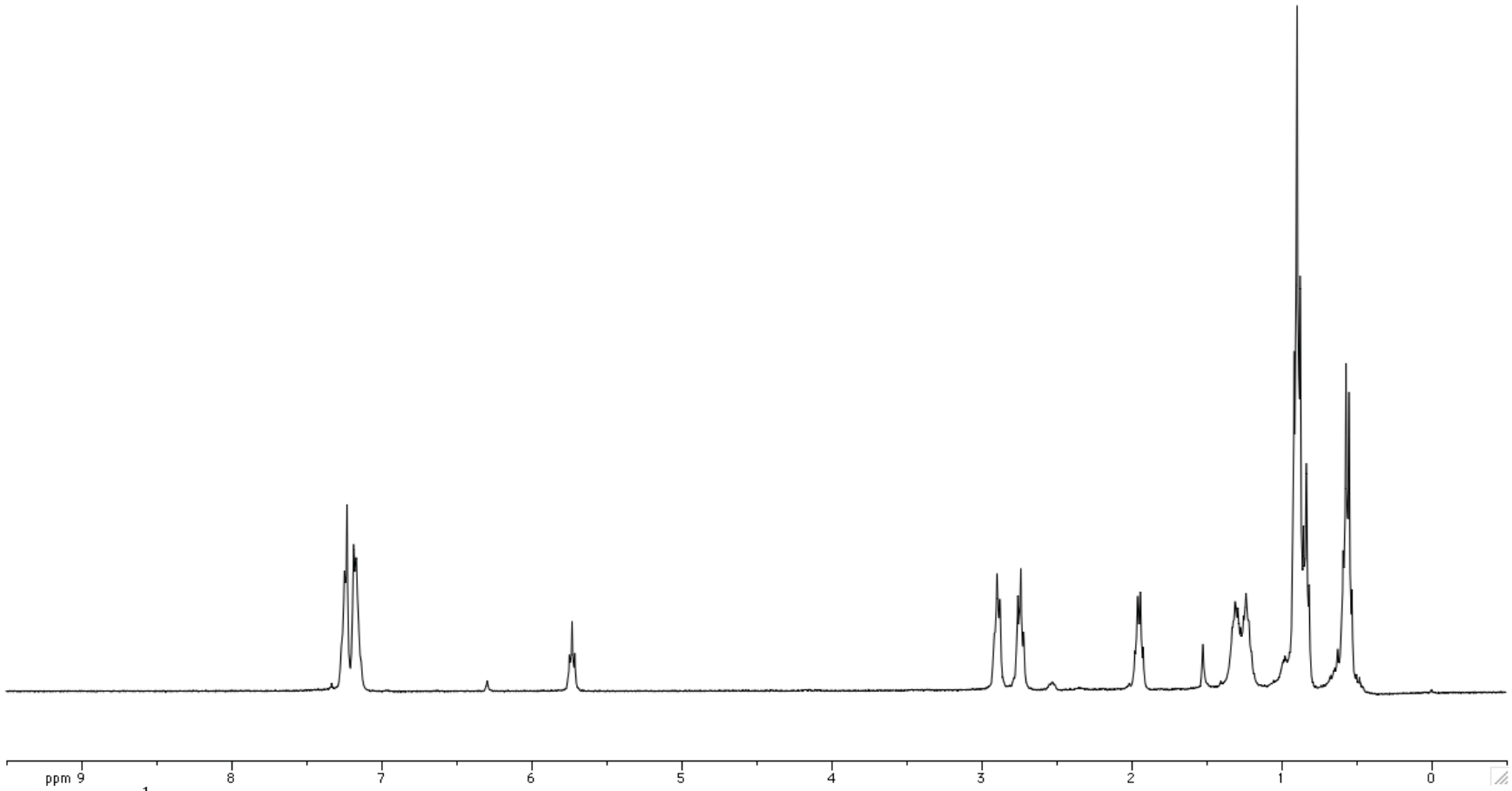


Figure A2.1 ^{1}H NMR (300 MHz, $CDCl_3$) of compound **123**

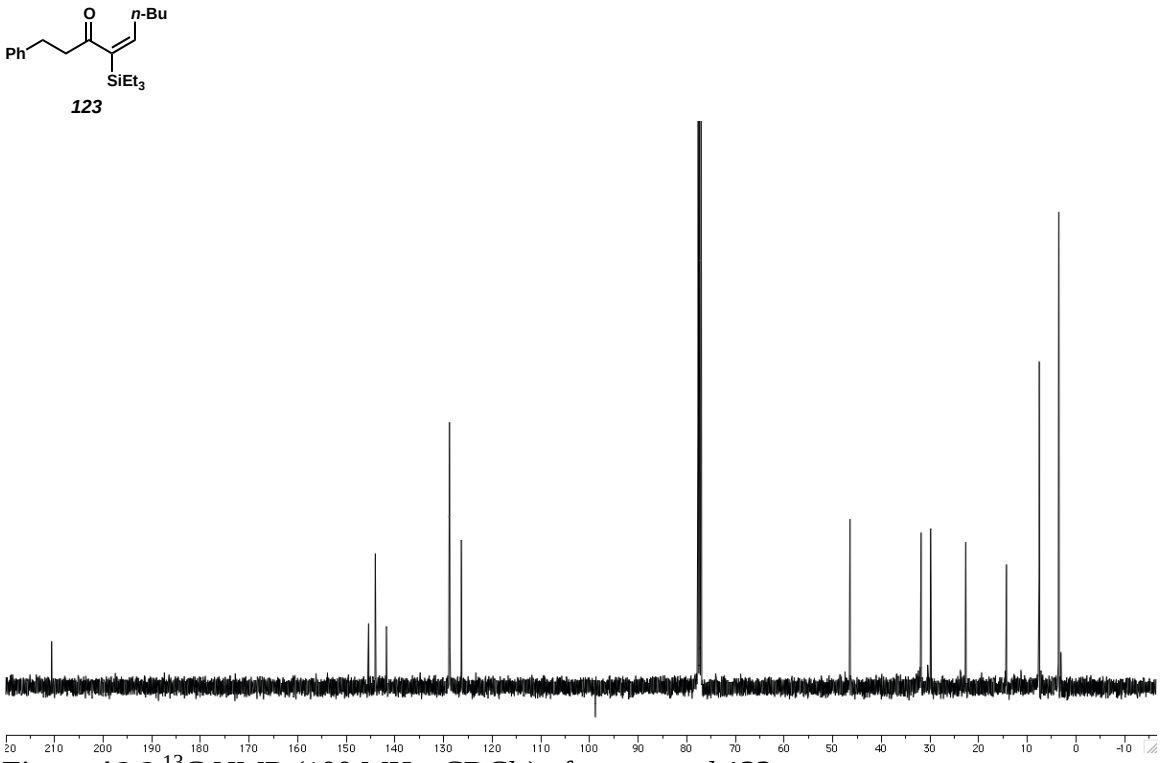


Figure A2.2 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **123**

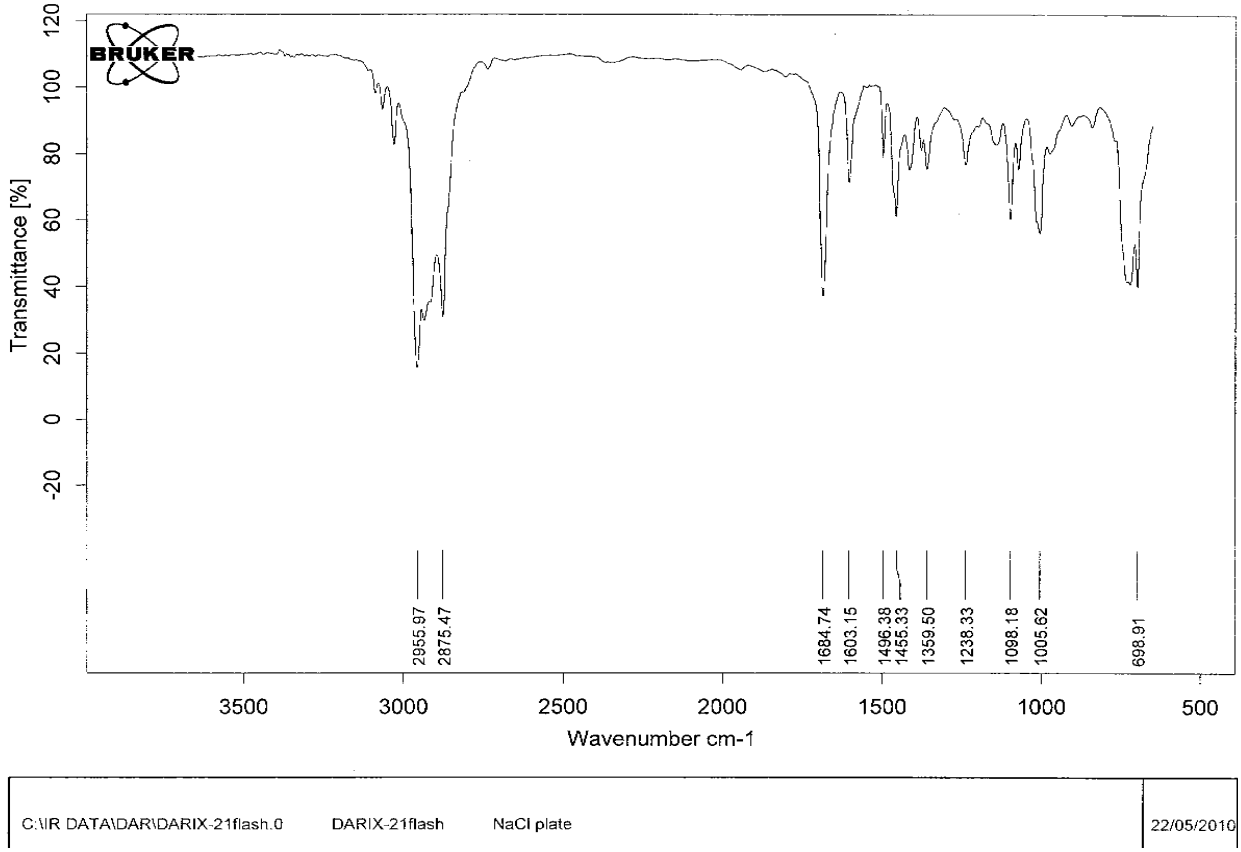
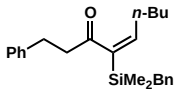


Figure A2.3 Infrared spectrum (thin film) of compound **123**



124

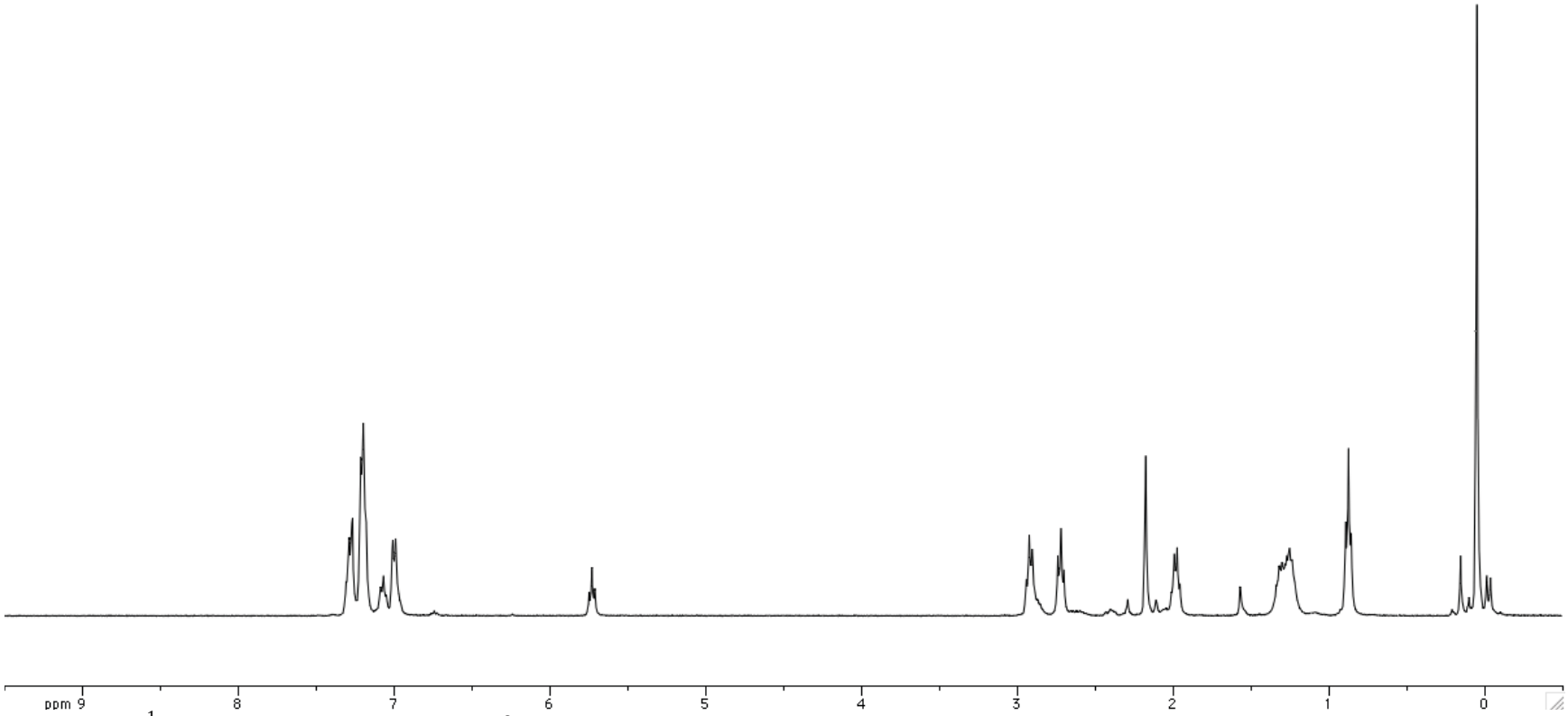


Figure A2.4 ^{1}H NMR (300 MHz, $CDCl_3$) of compound **124**

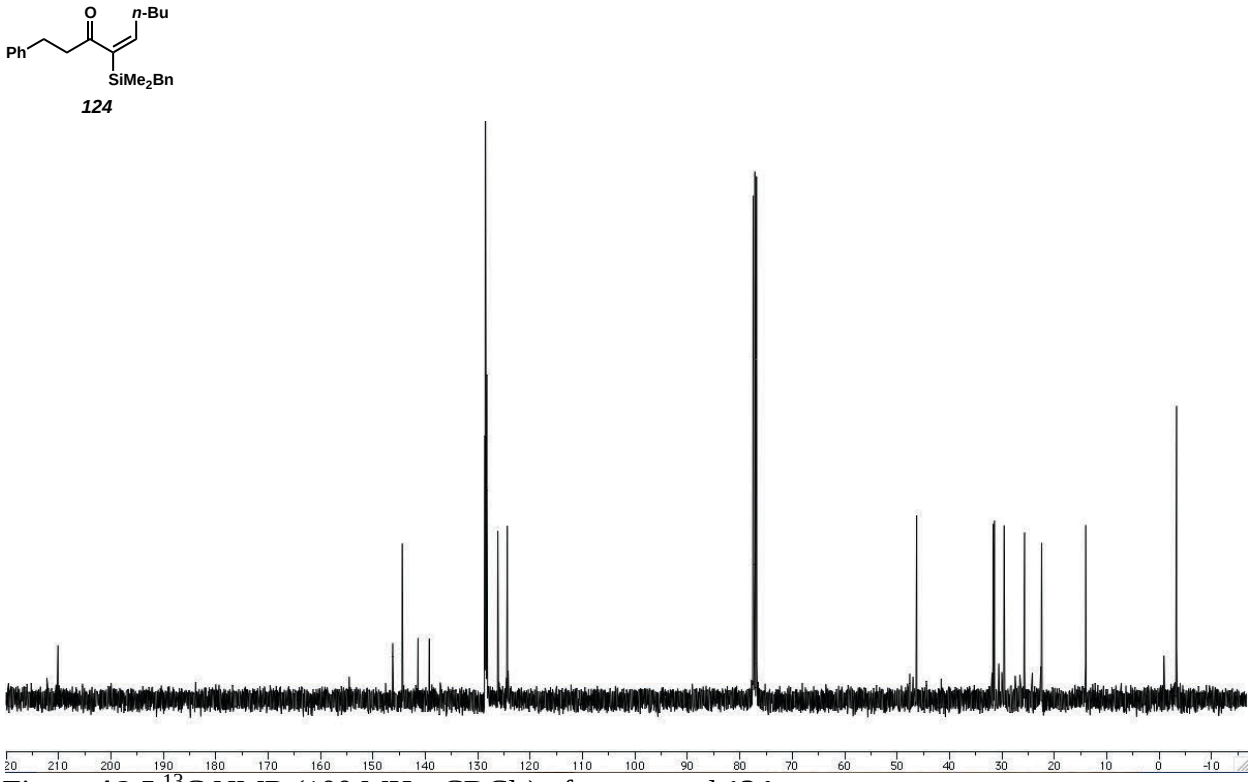


Figure A2.5 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **124**

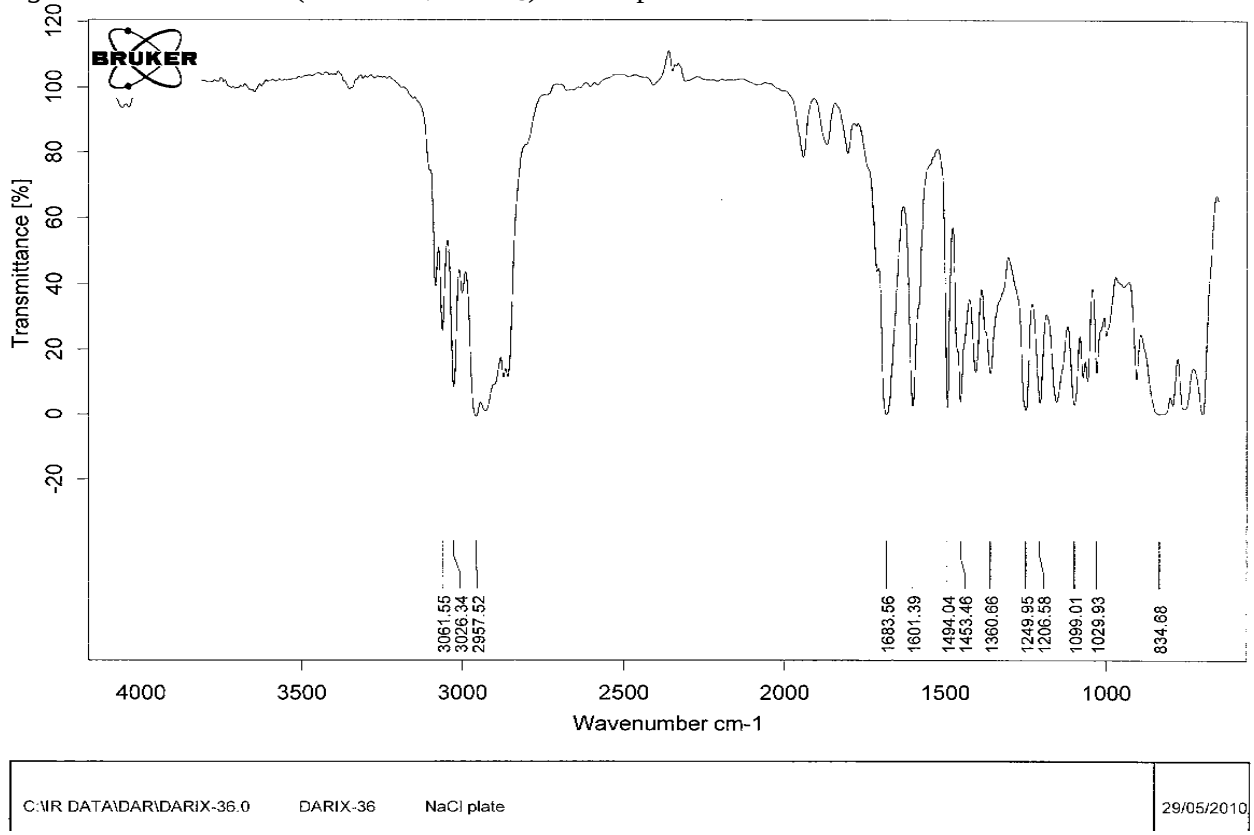
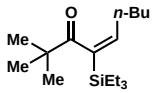


Figure A2.6 Infrared spectrum (thin film) of compound **124**



125

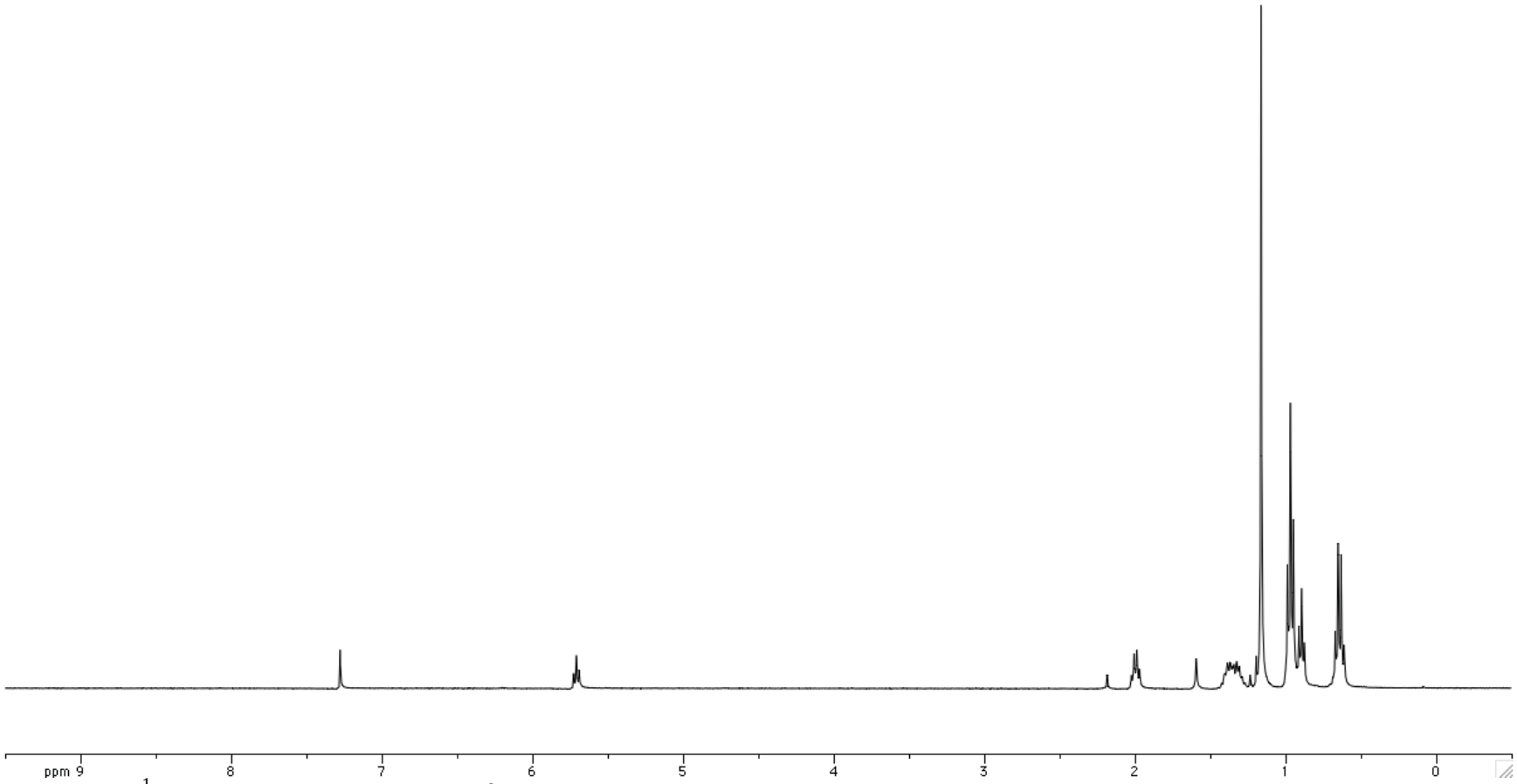
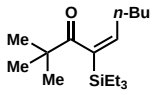


Figure A2.7 ^{1}H NMR (300 MHz, $CDCl_3$) of compound **125**



125

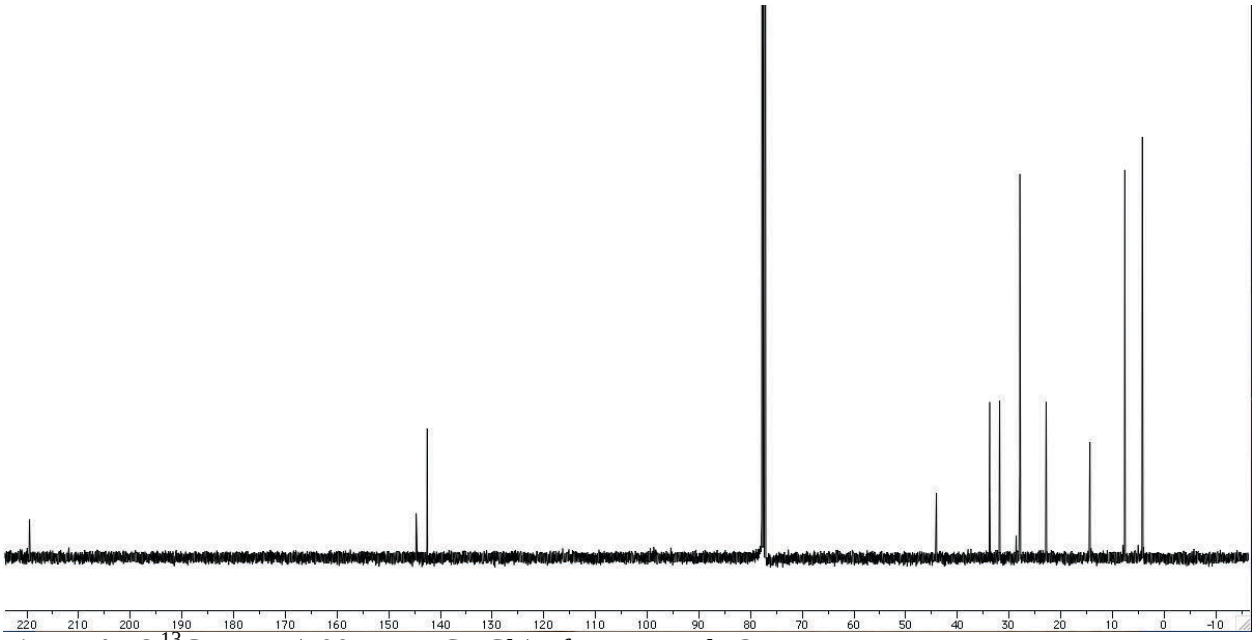


Figure A2.8 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **125**

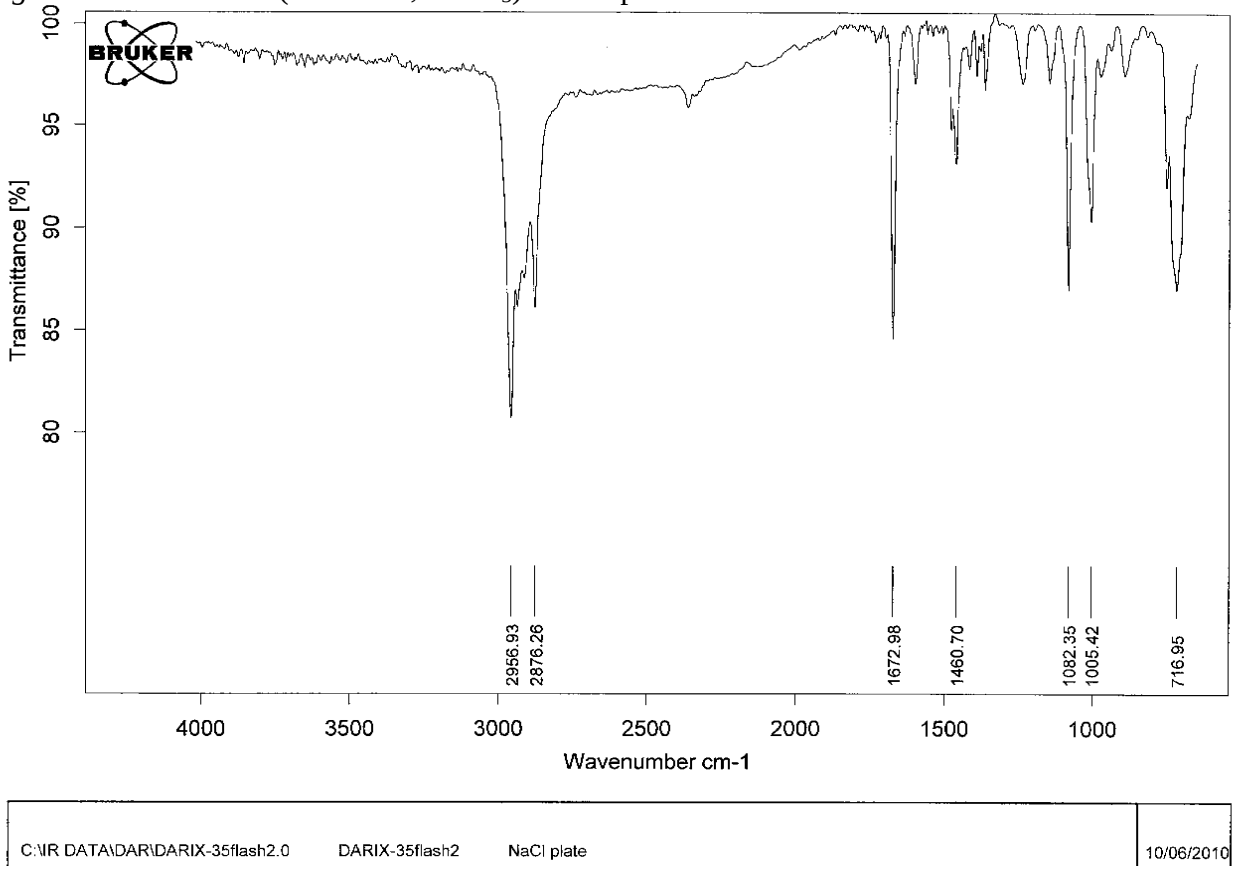
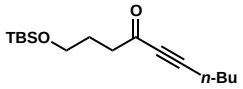


Figure A2.9 Infrared spectrum (thin film) of compound **125**



126

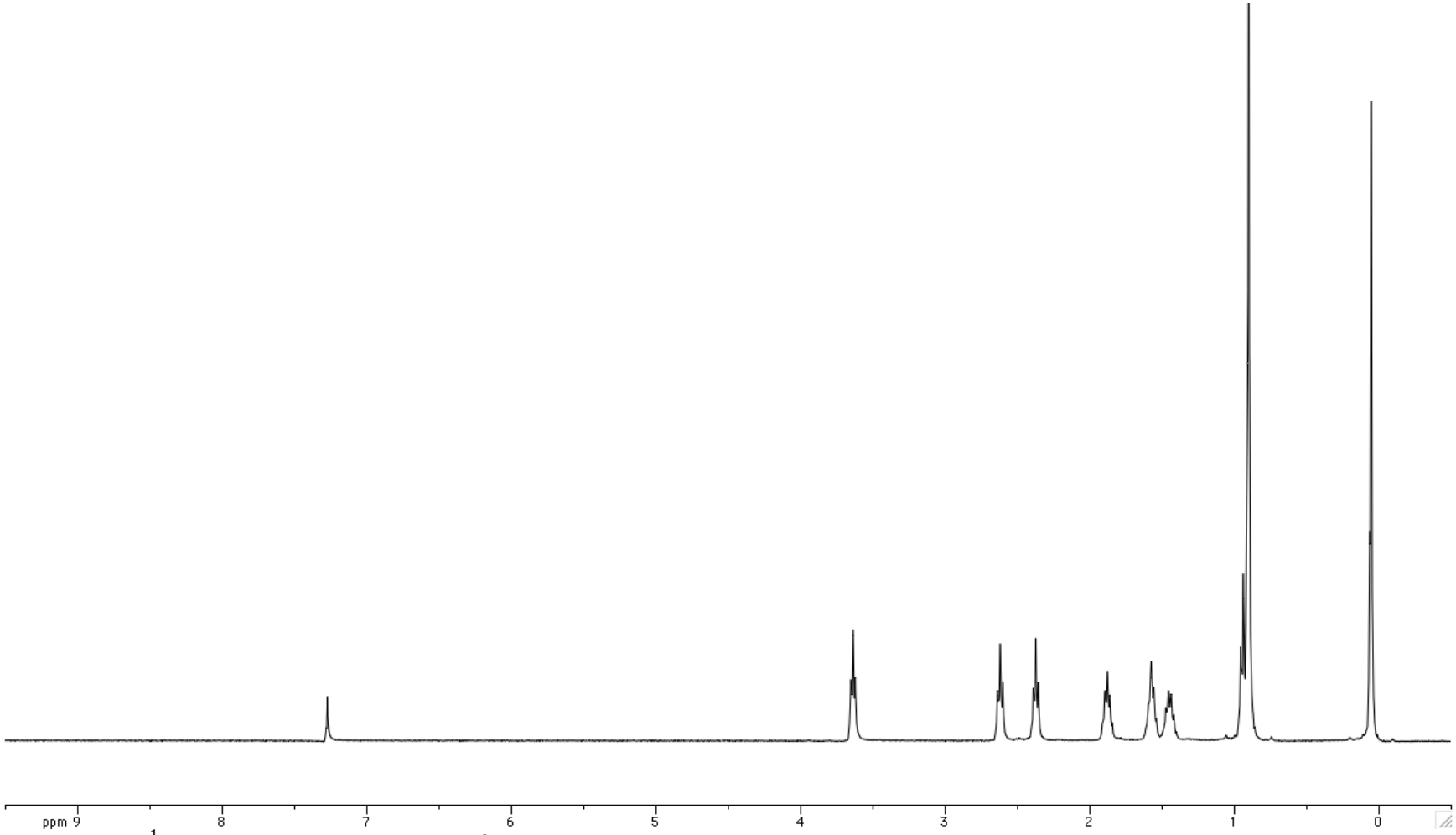


Figure A2.10 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **126**

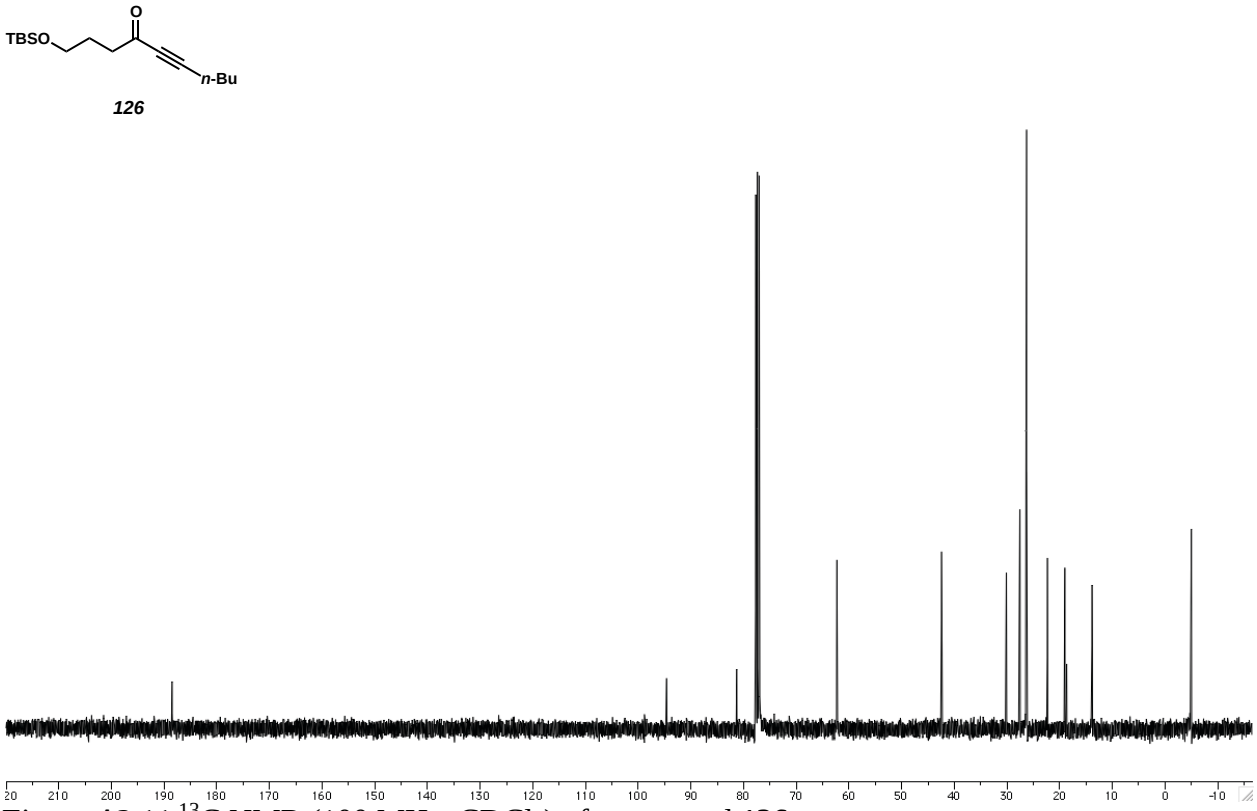


Figure A2.11 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **126**

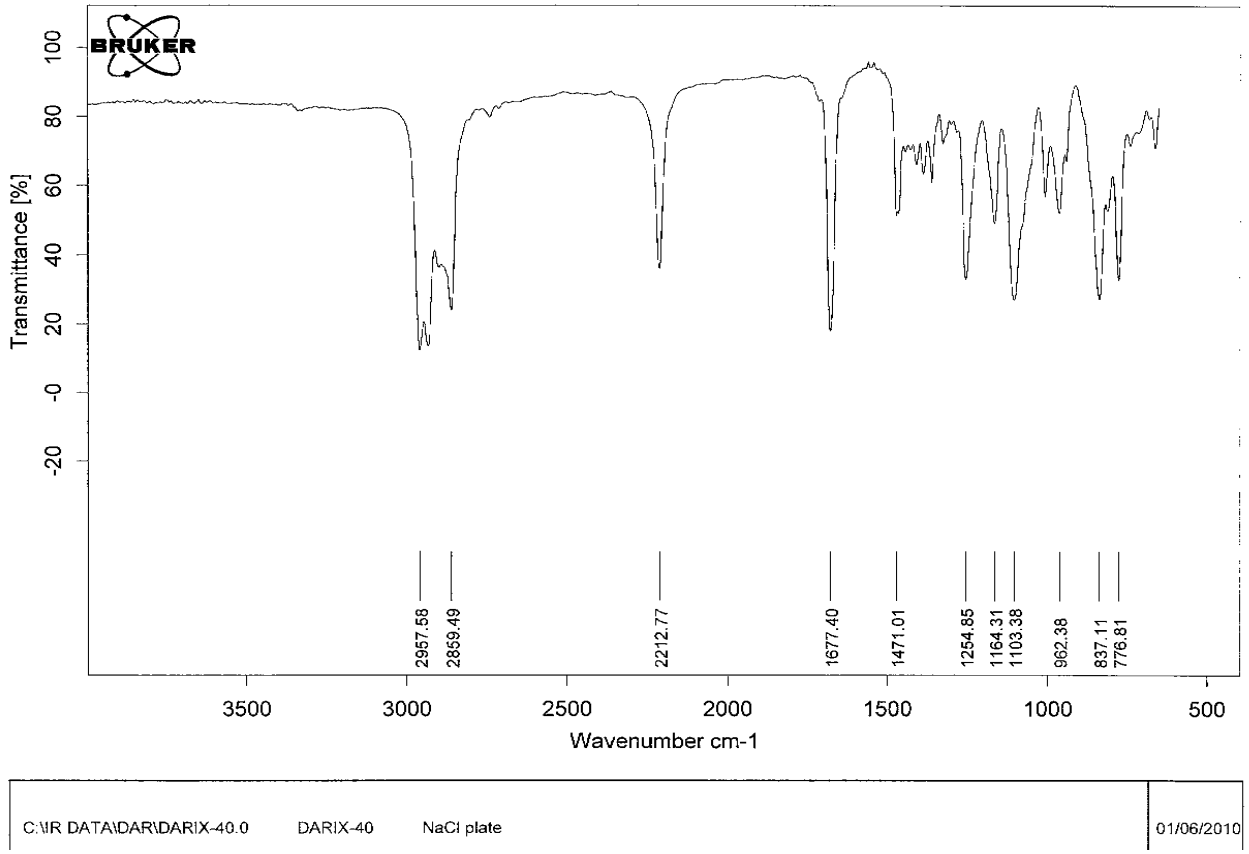
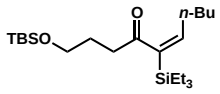


Figure A2.12 Infrared spectrum (thin film) of compound **126**



127

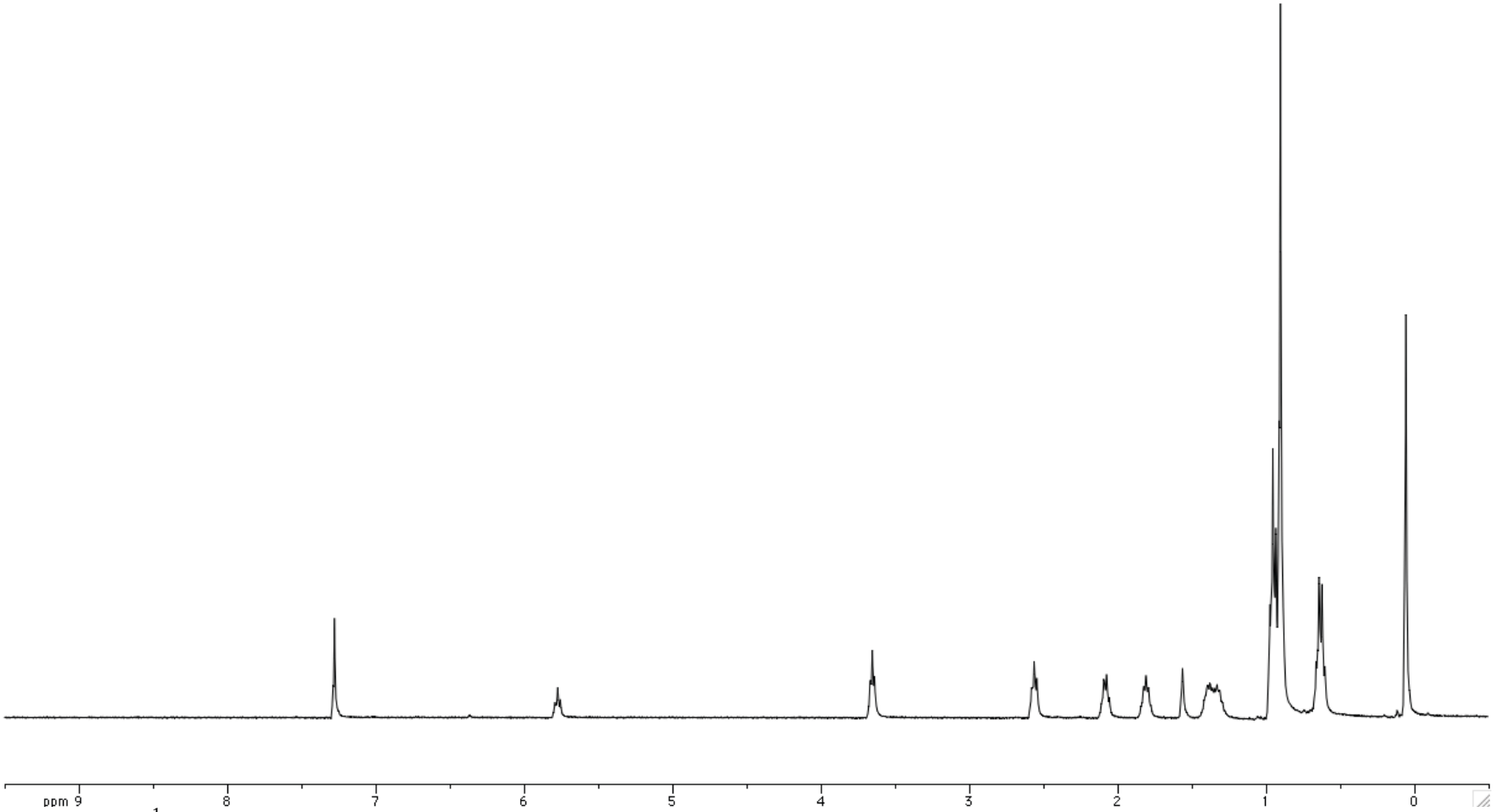


Figure A2.13 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **127**

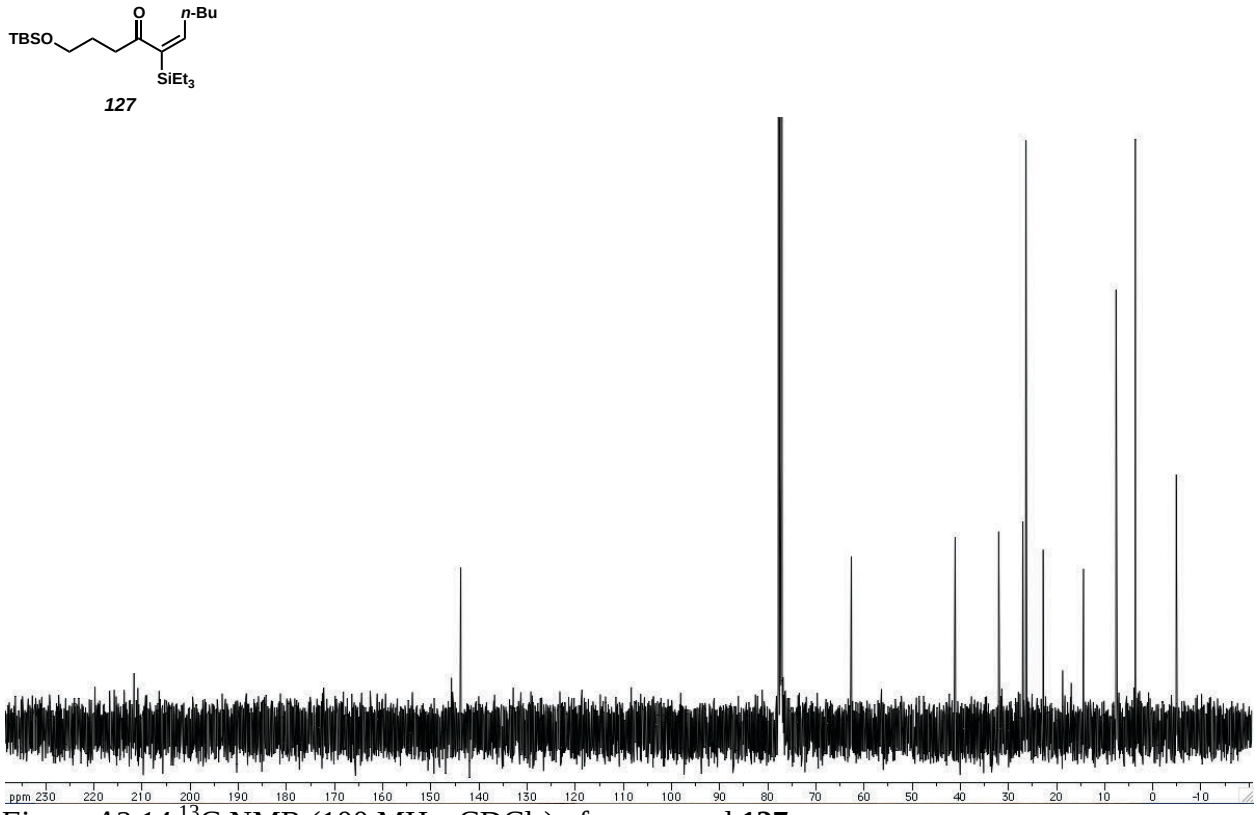


Figure A2.14 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **127**

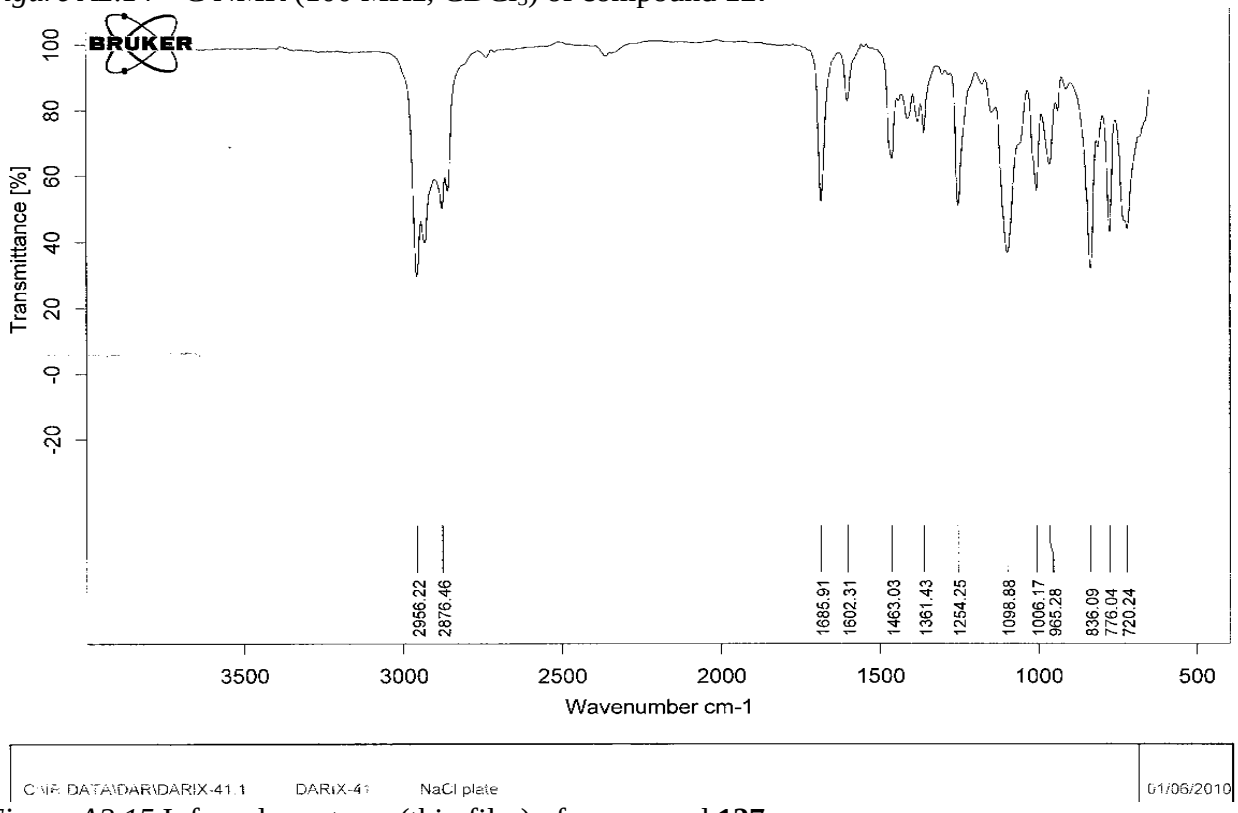
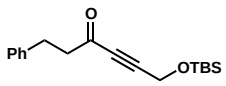


Figure A2.15 Infrared spectrum (thin film) of compound **127**



128

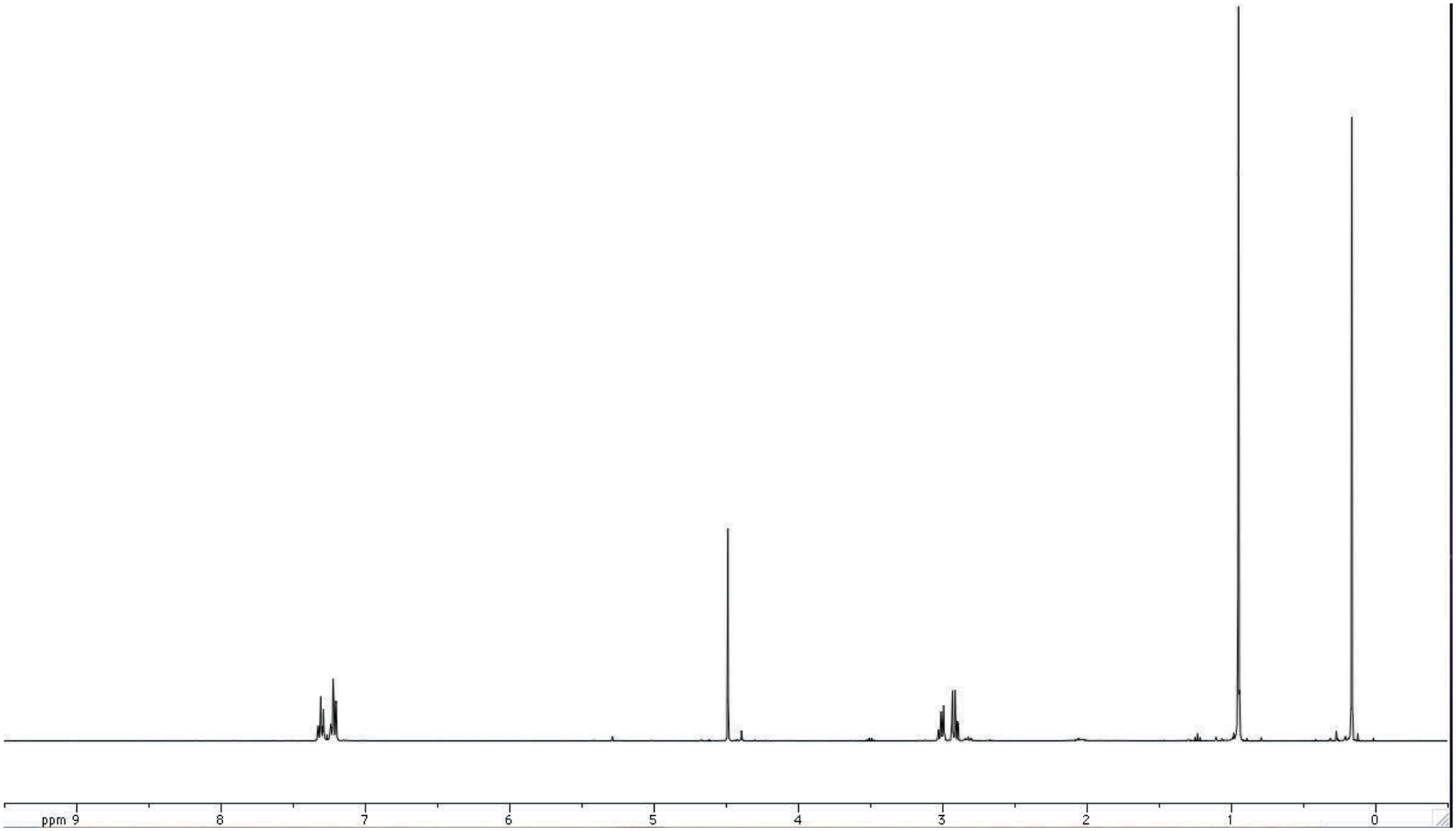
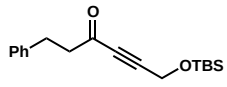


Figure A2.16 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **128**



128

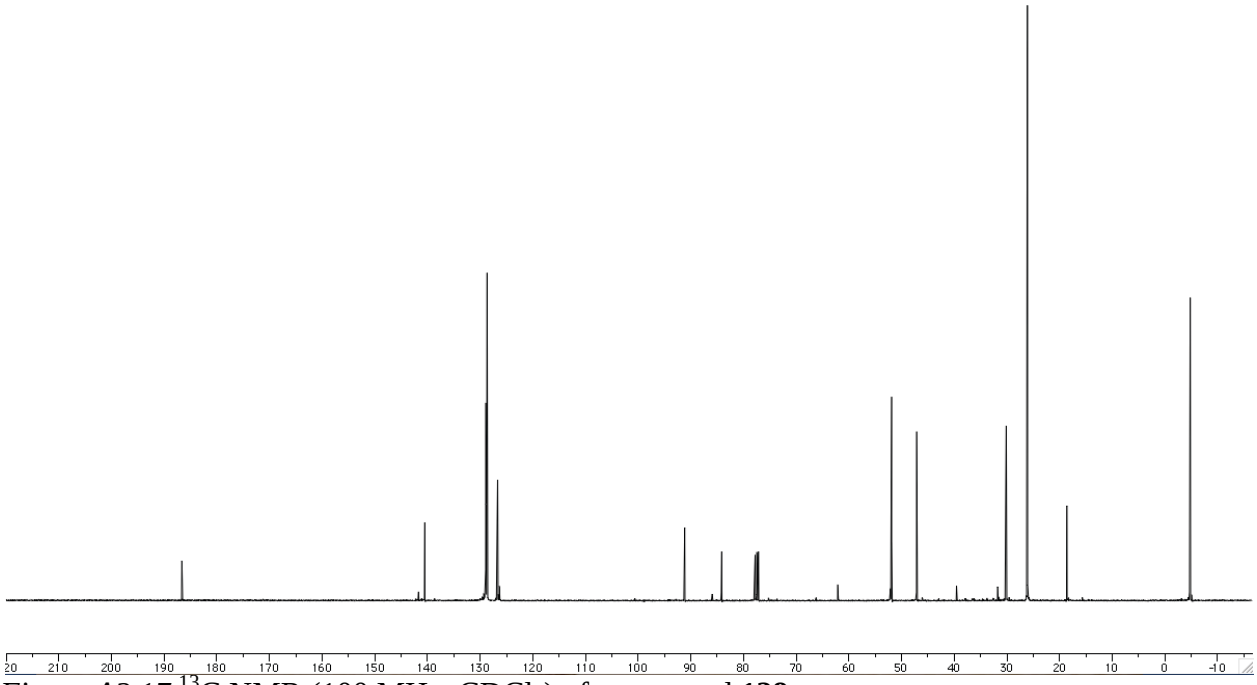


Figure A2.17 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **128**

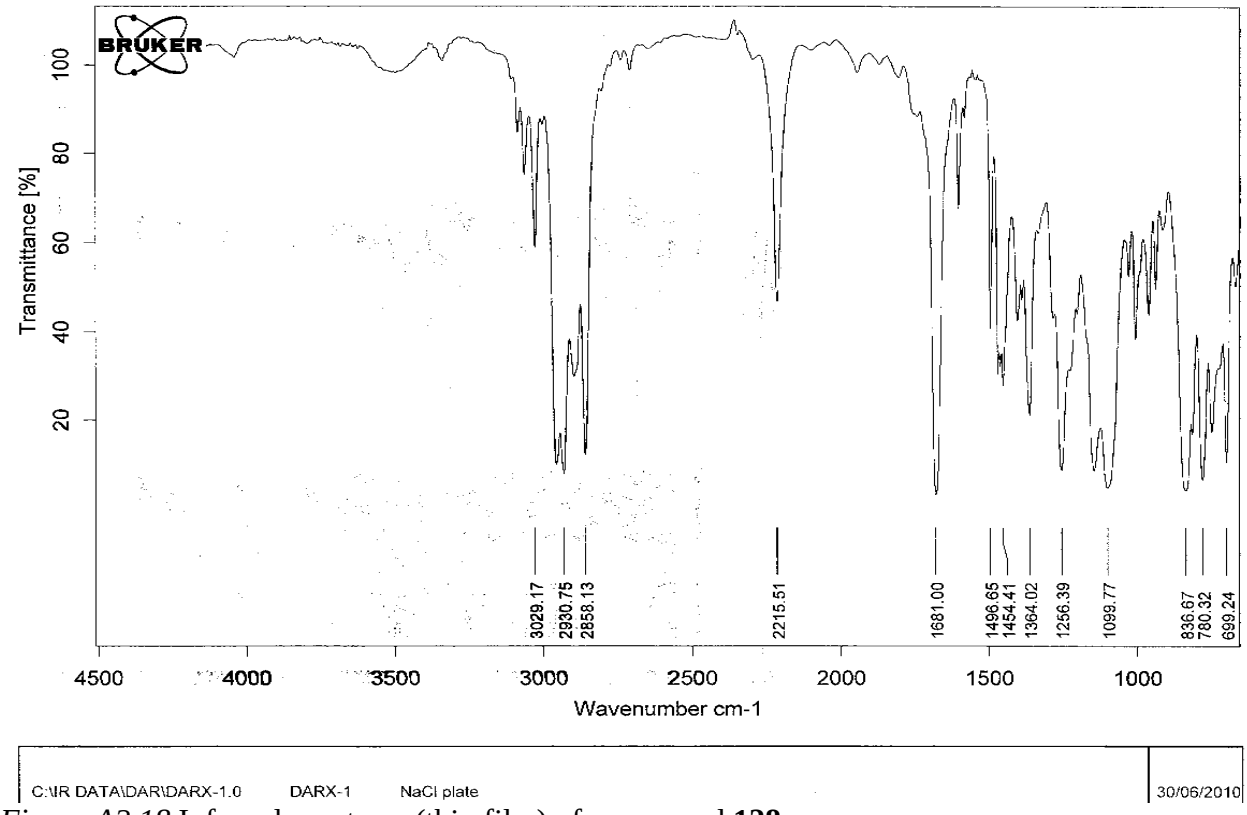
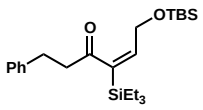


Figure A2.18 Infrared spectrum (thin film) of compound **128**



129

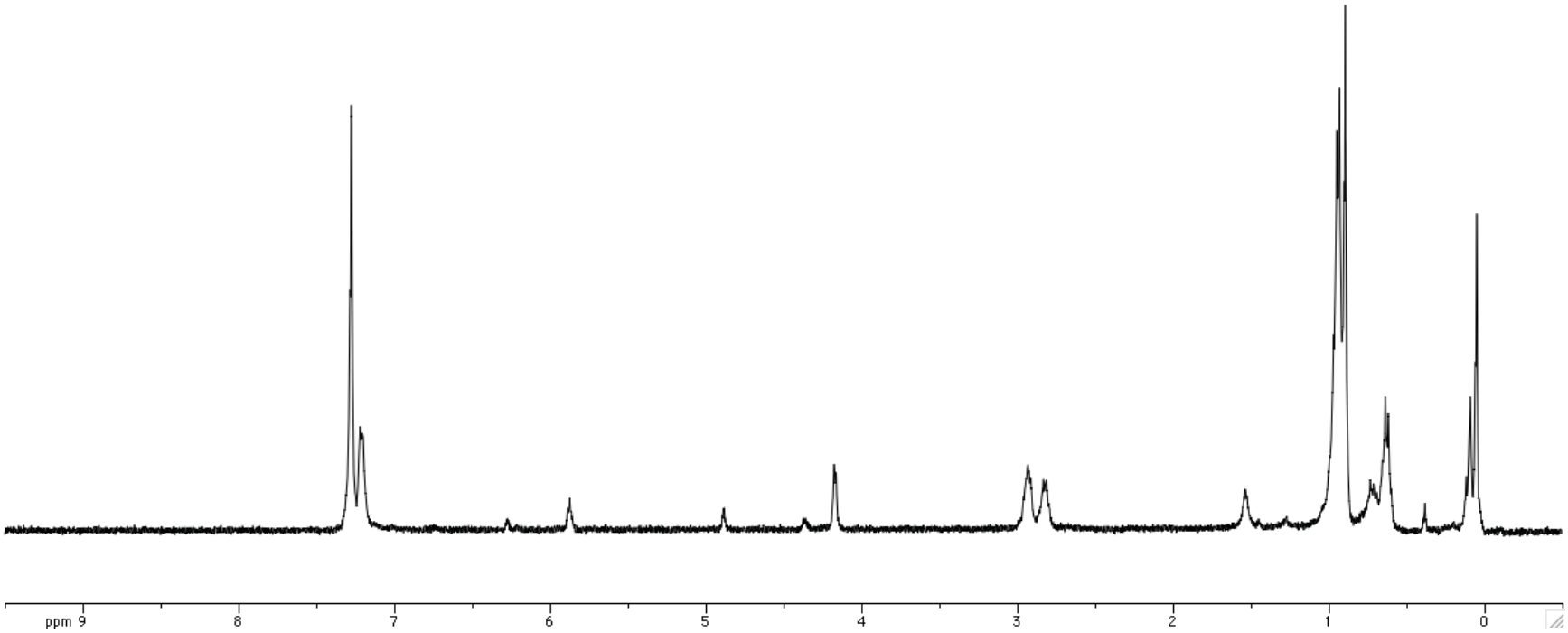


Figure A2.19 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **129**

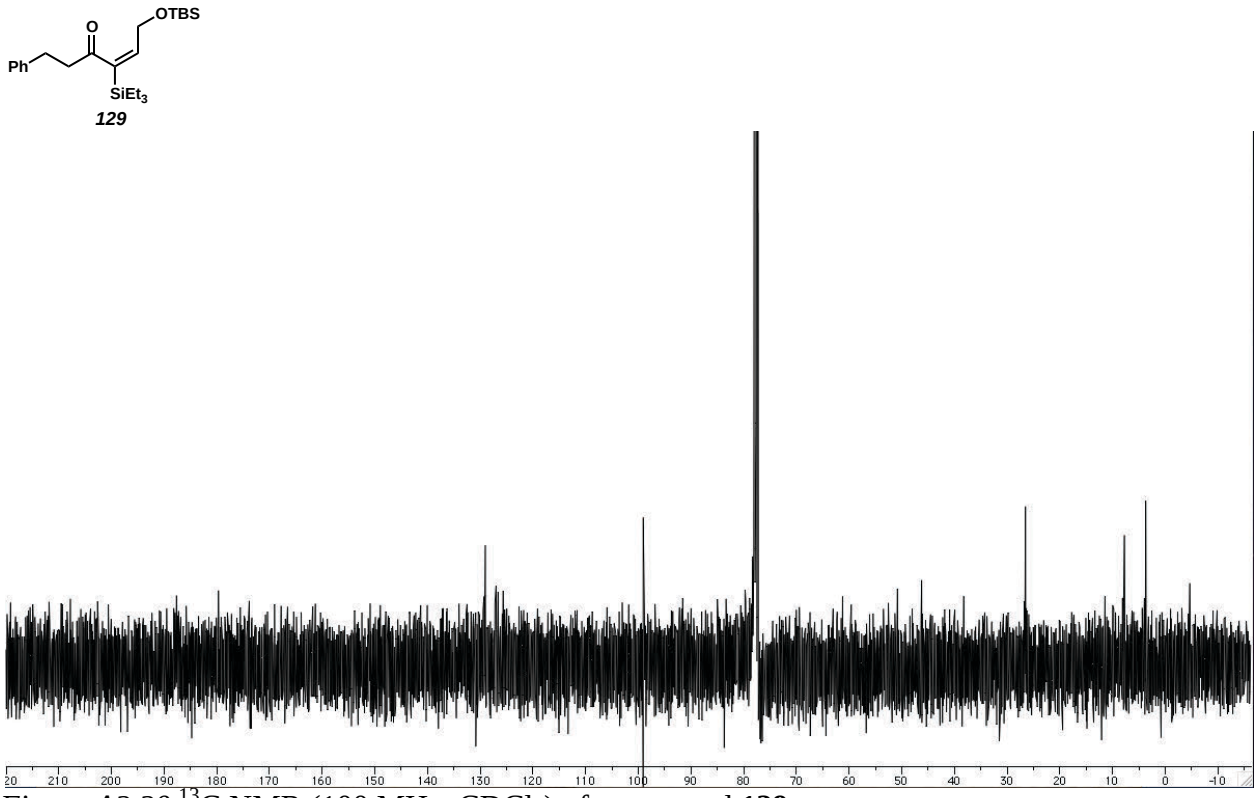


Figure A2.20 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **129**

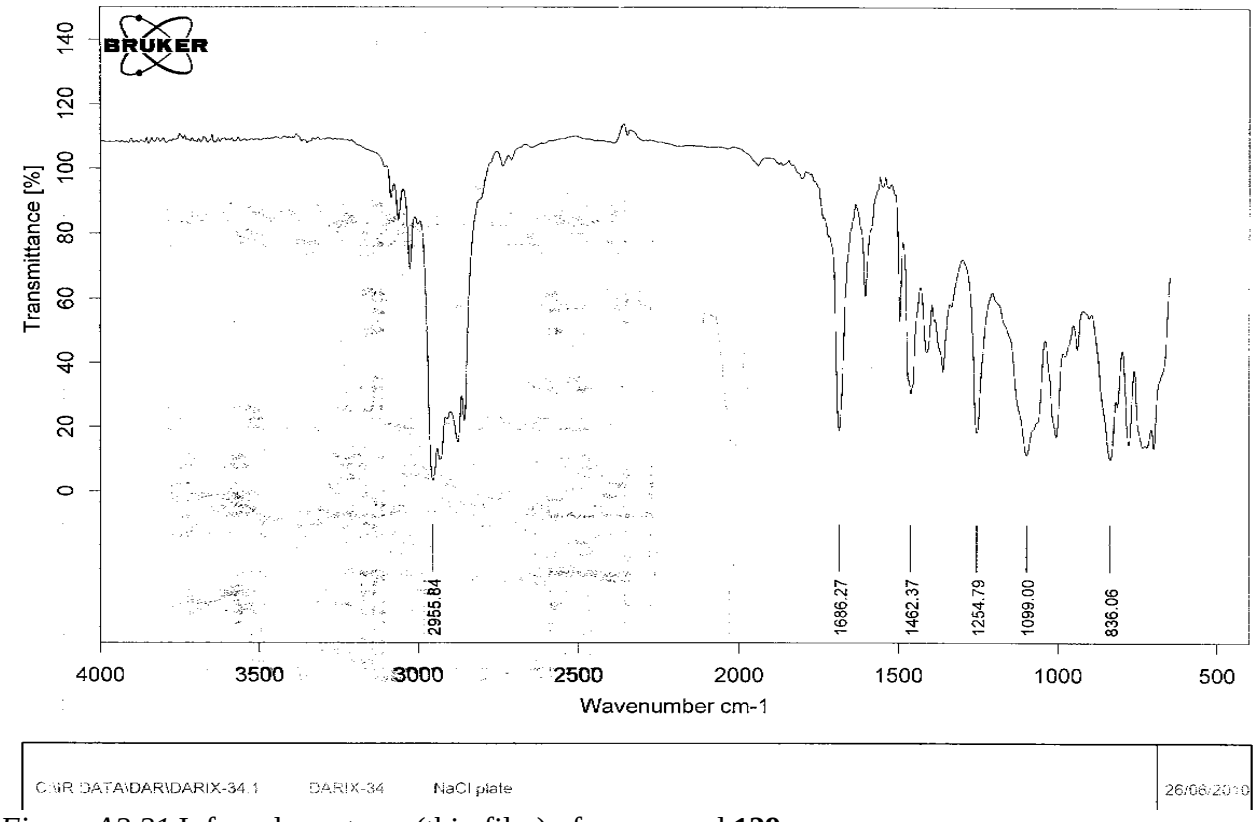
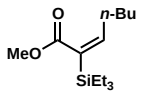


Figure A2.21 Infrared spectrum (thin film) of compound **129**



139

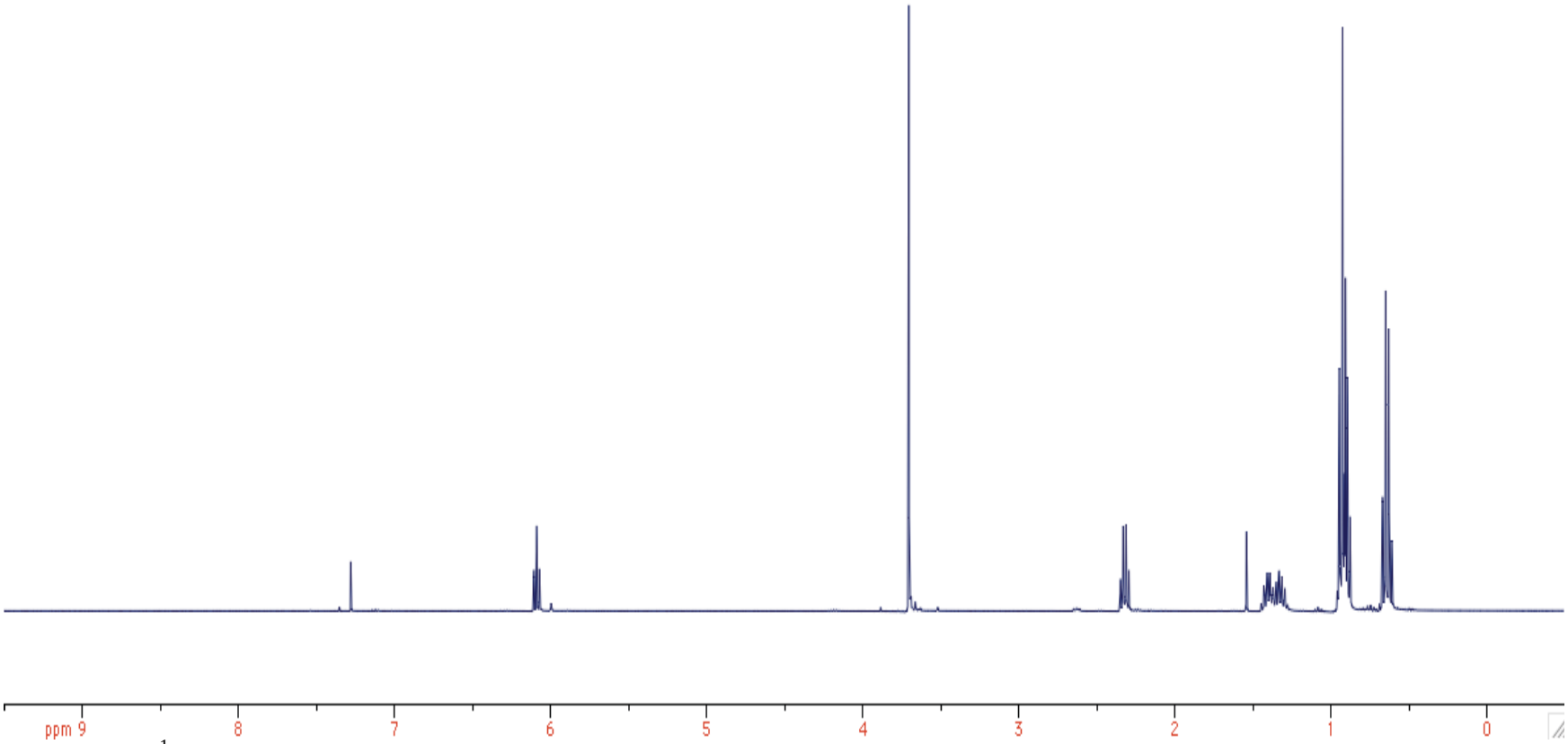


Figure A2.22 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **139**

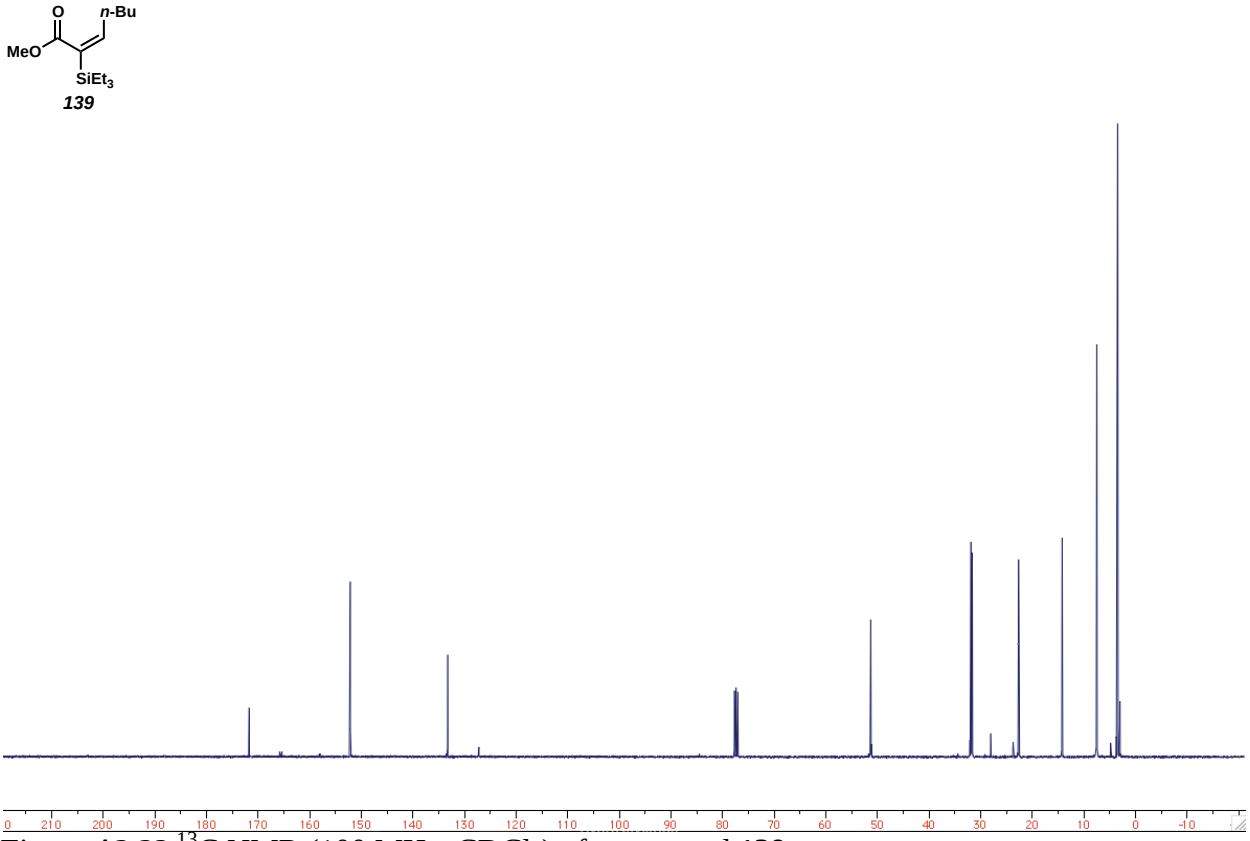


Figure A2.23 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **139**

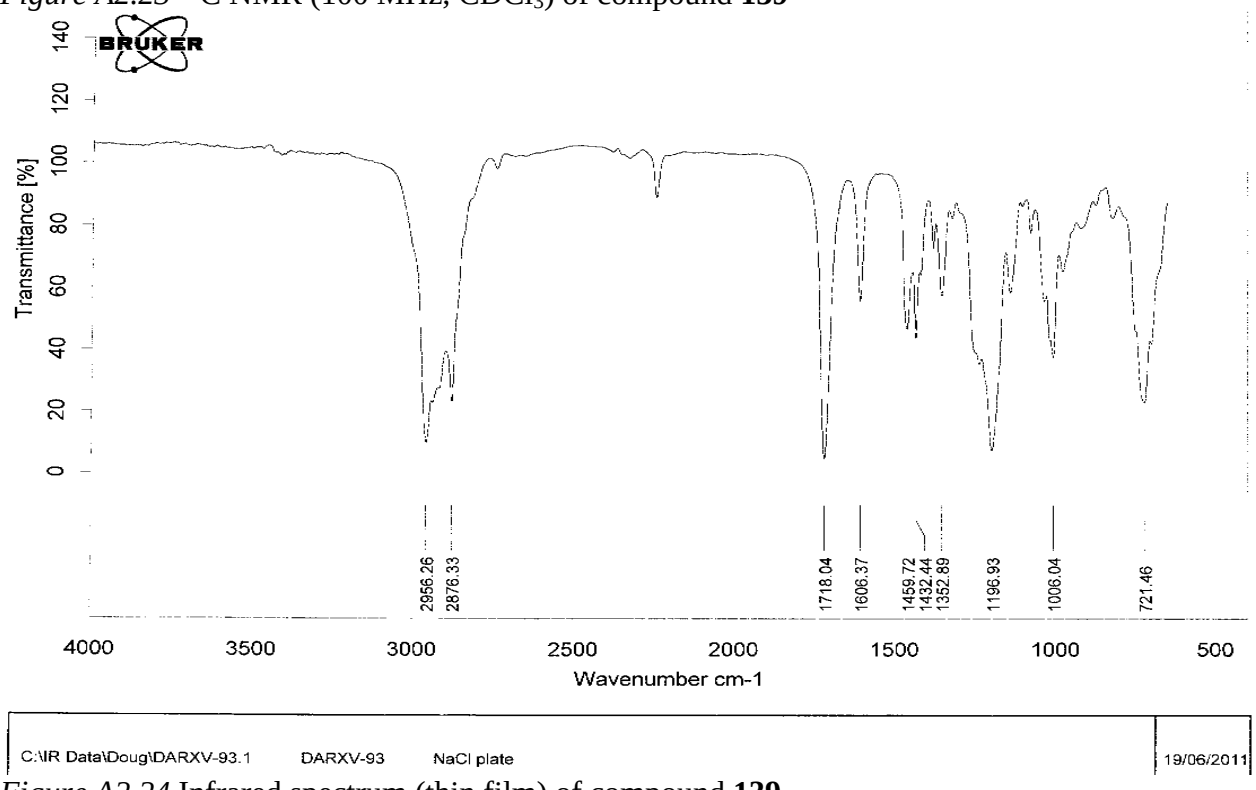
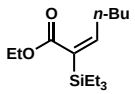


Figure A2.24 Infrared spectrum (thin film) of compound **139**



140

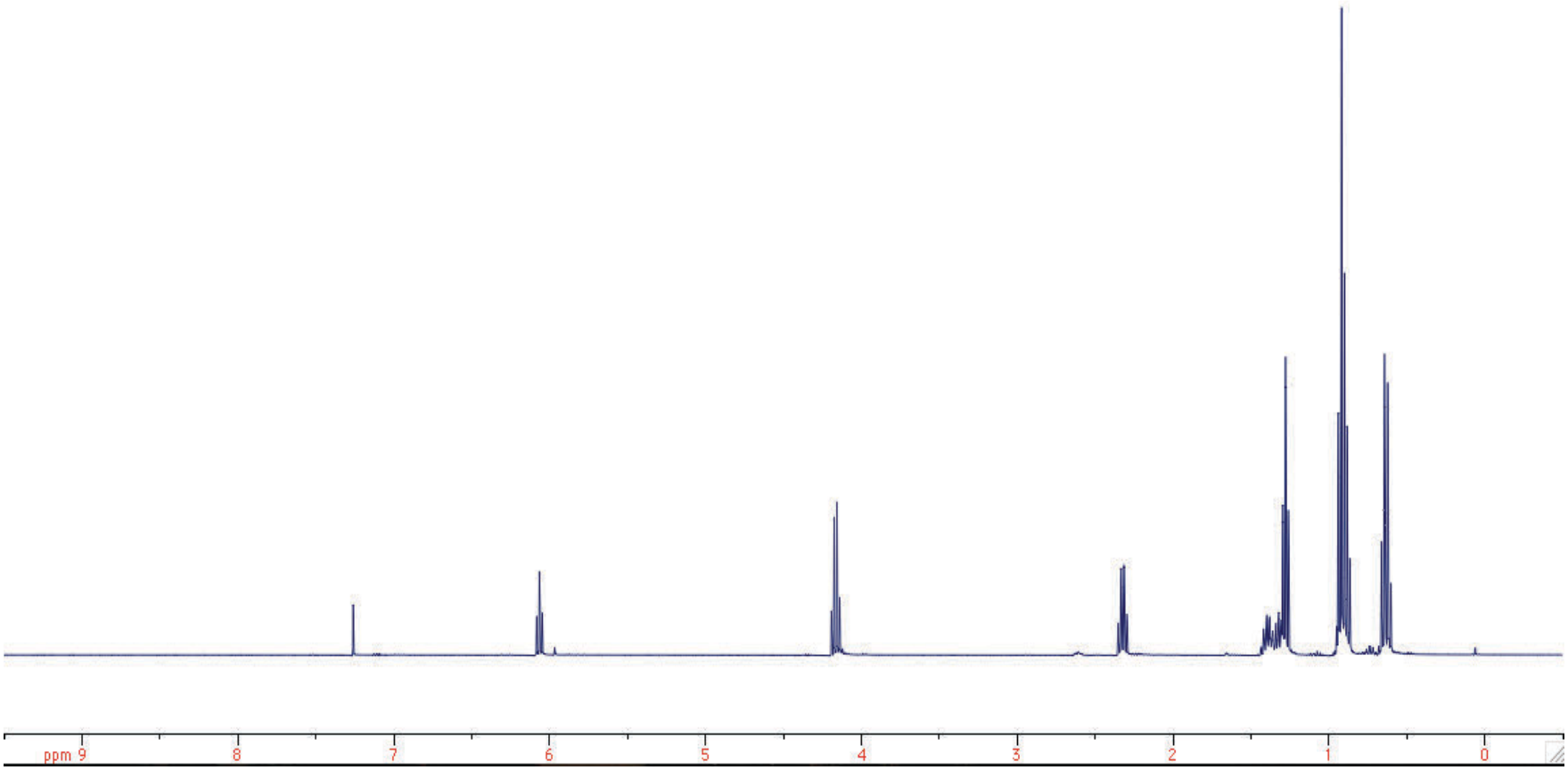
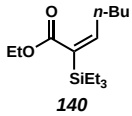


Figure A2.25 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **140**



140

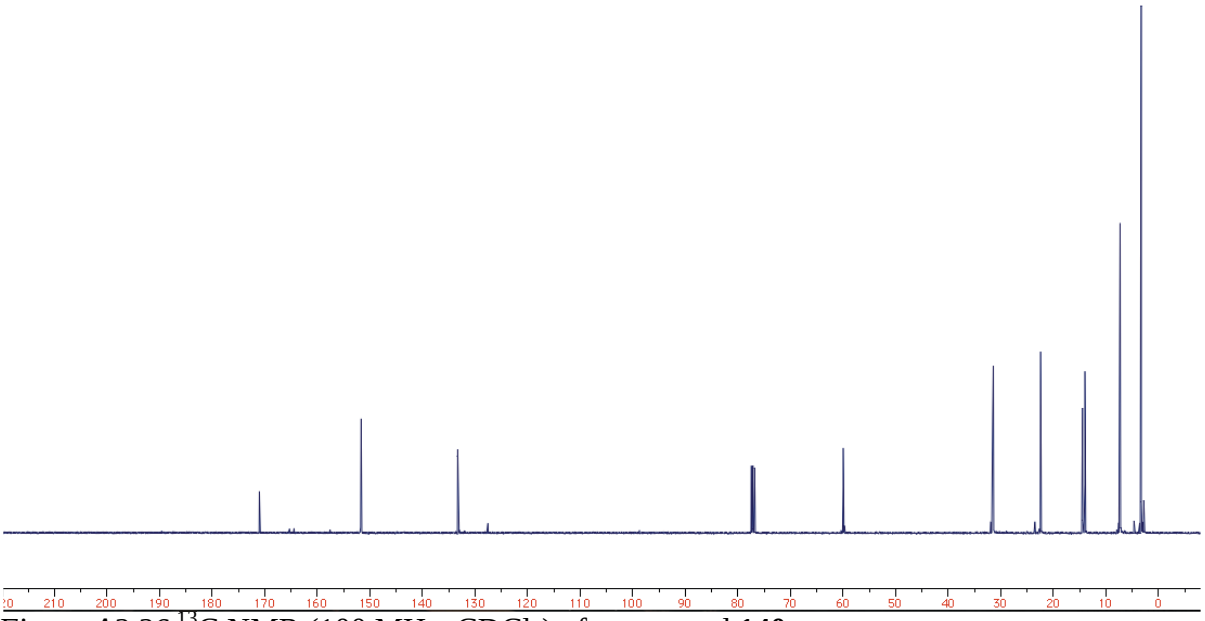


Figure A2.26 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **140**

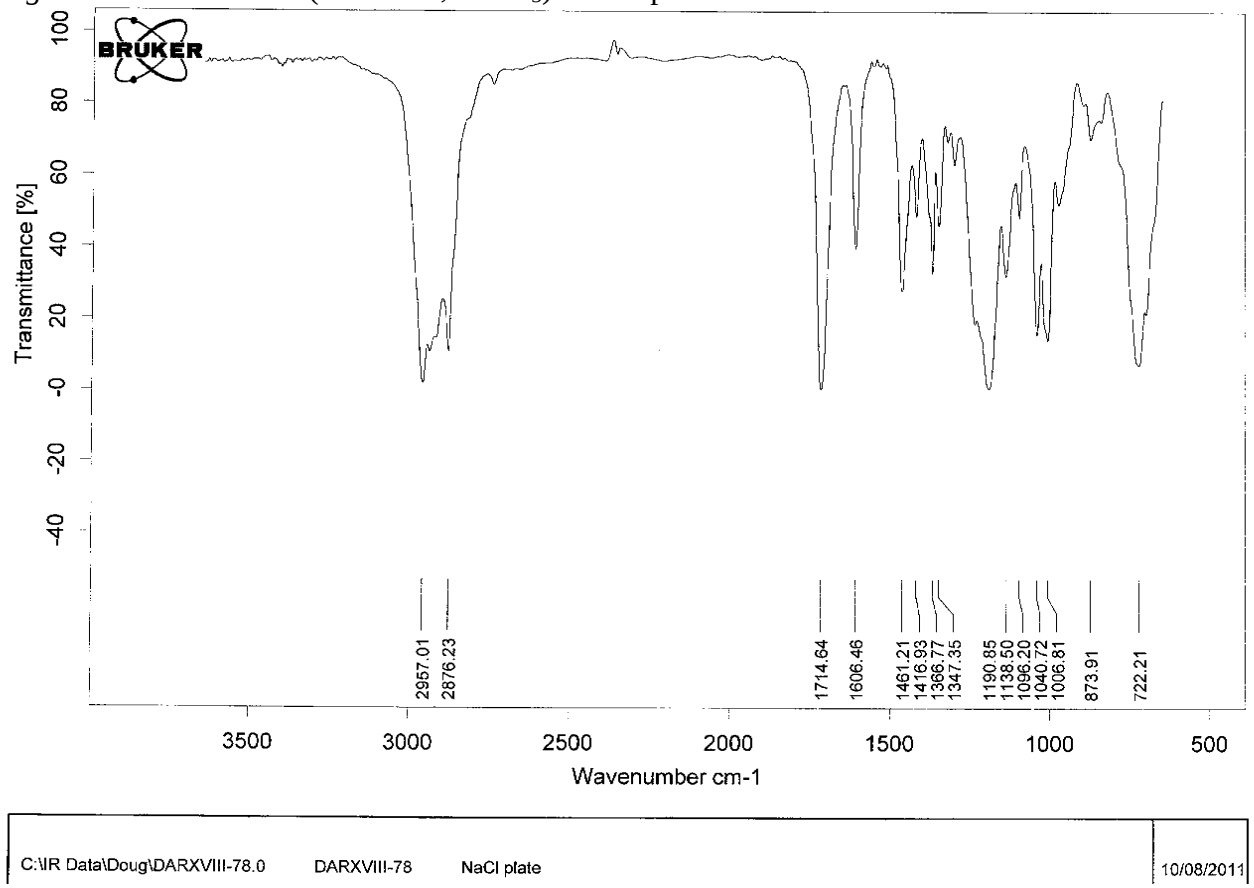
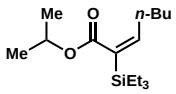


Figure A2.27 Infrared spectrum (thin film) of compound **140**



141

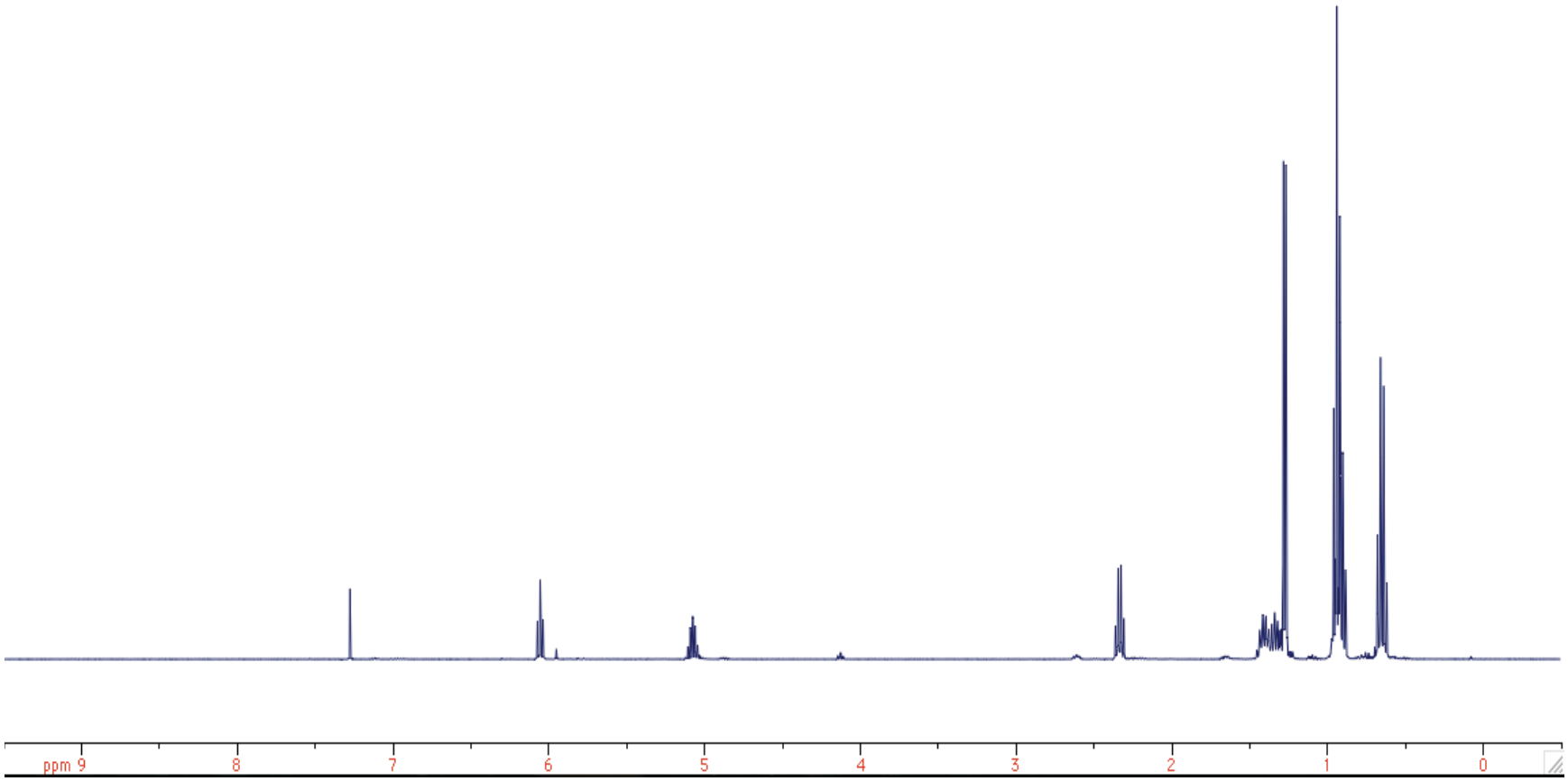


Figure A2.28 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **141**

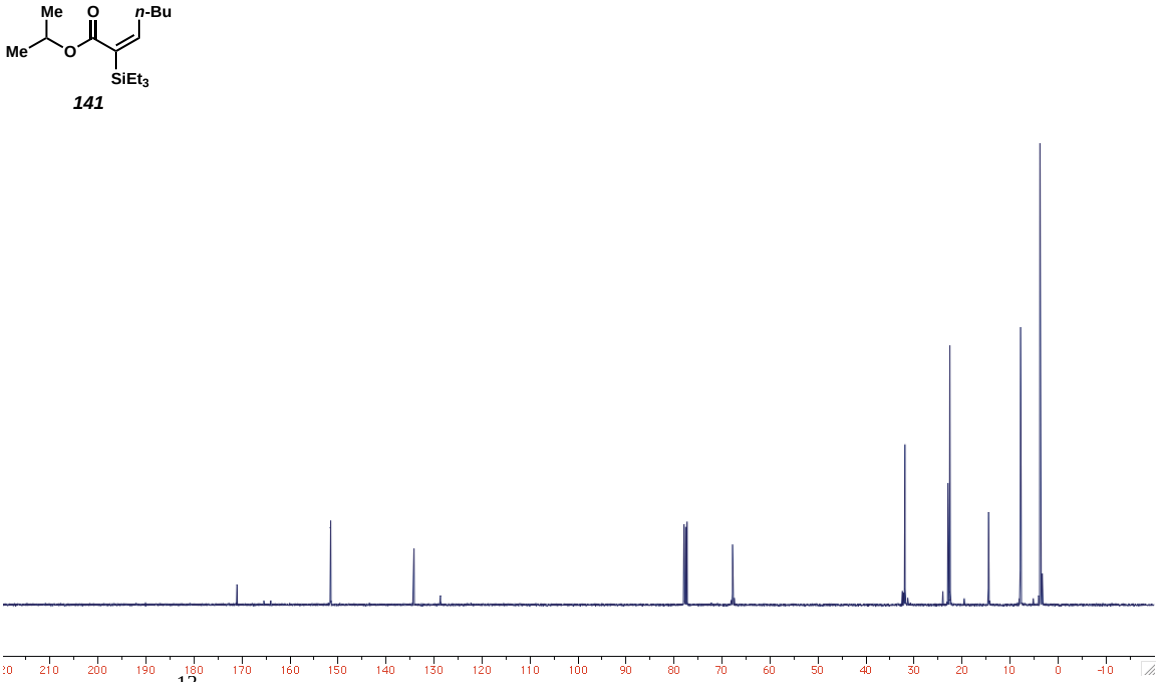


Figure A2.29 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **141**

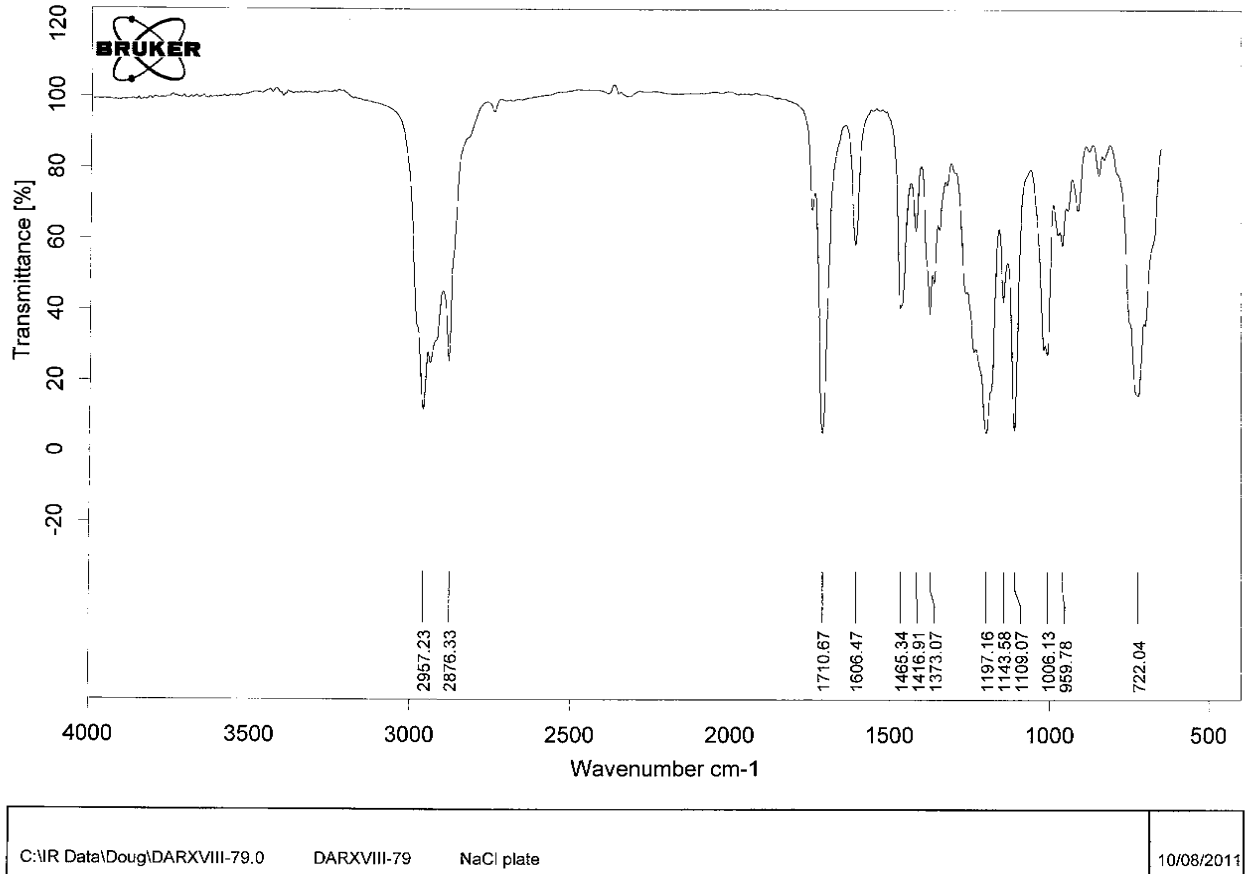
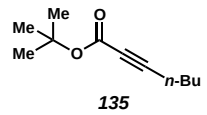


Figure A2.30 Infrared spectrum (thin film) of compound **141**



135

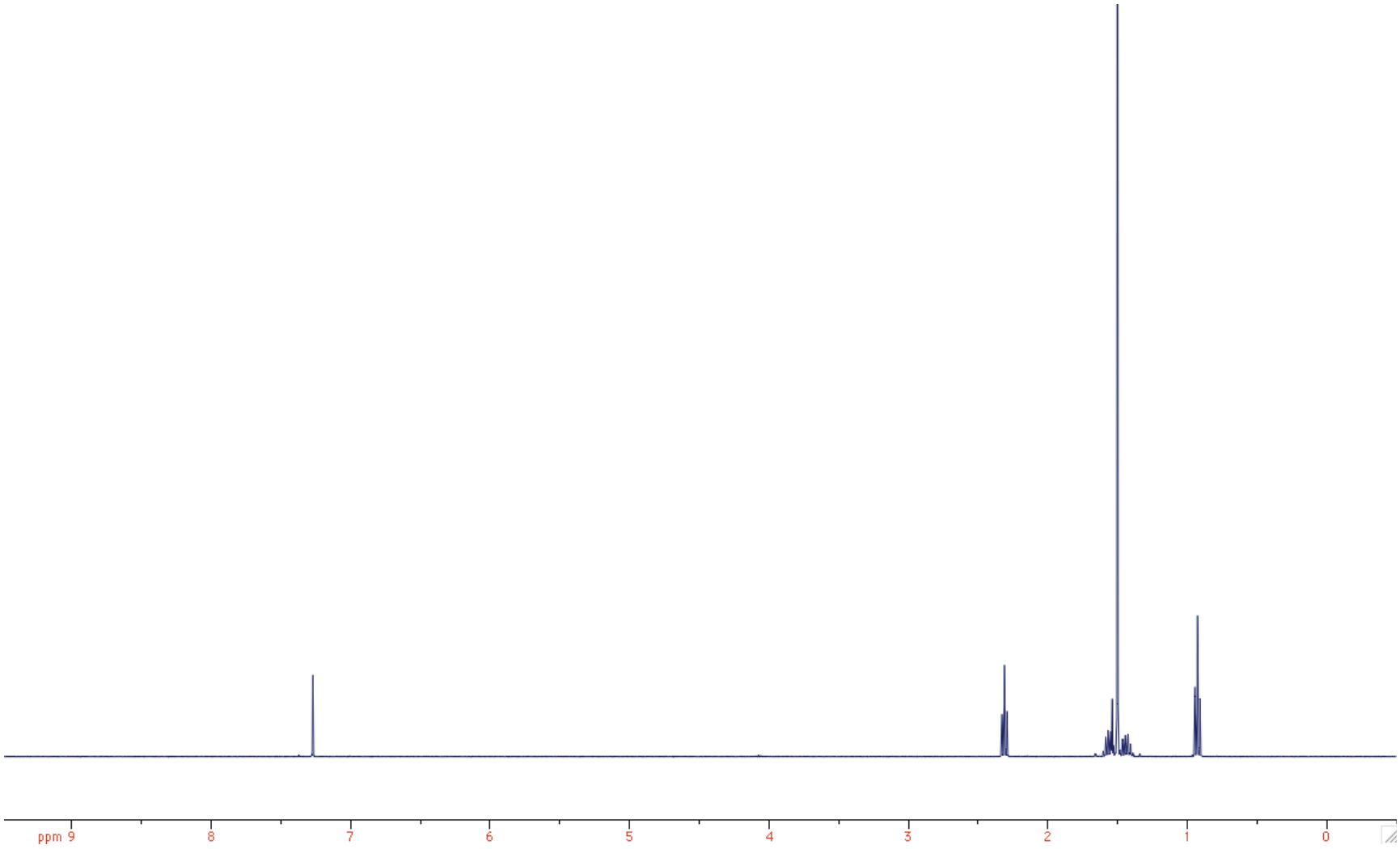


Figure A2.31 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **135**

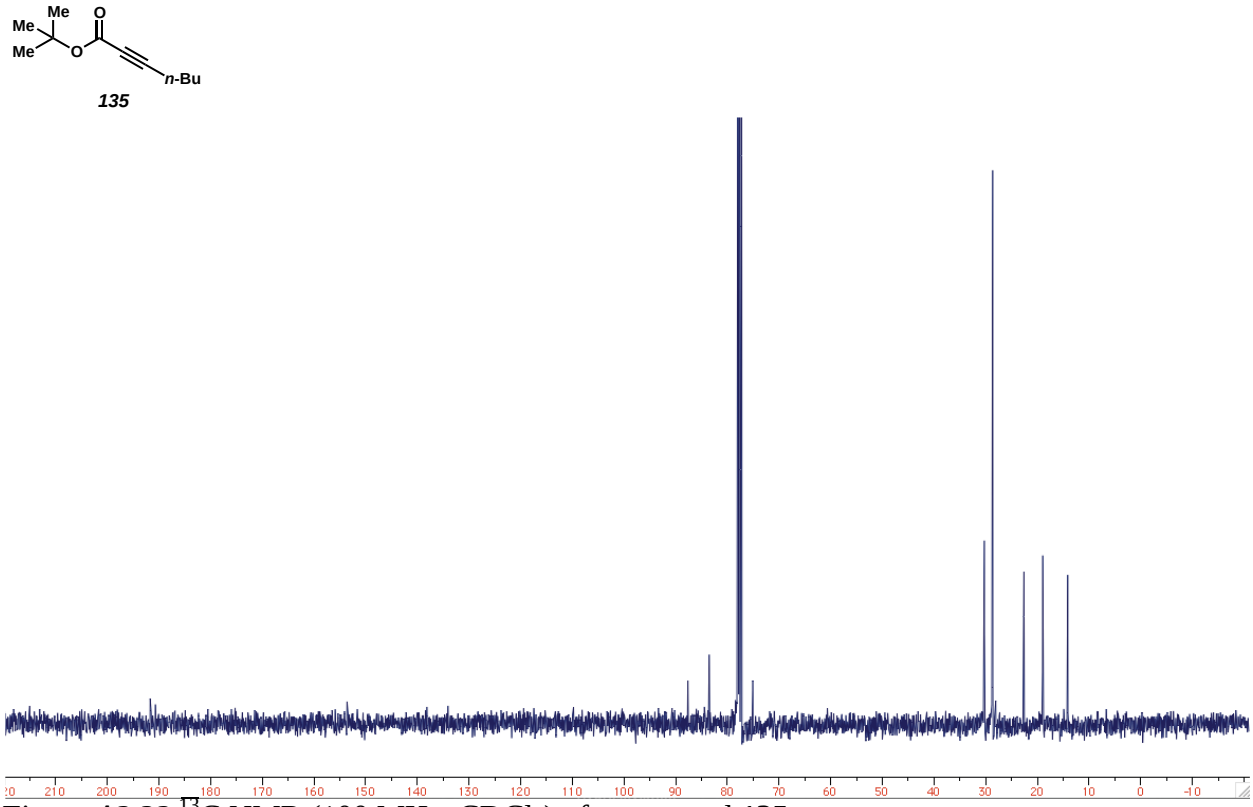


Figure A2.32 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **135**

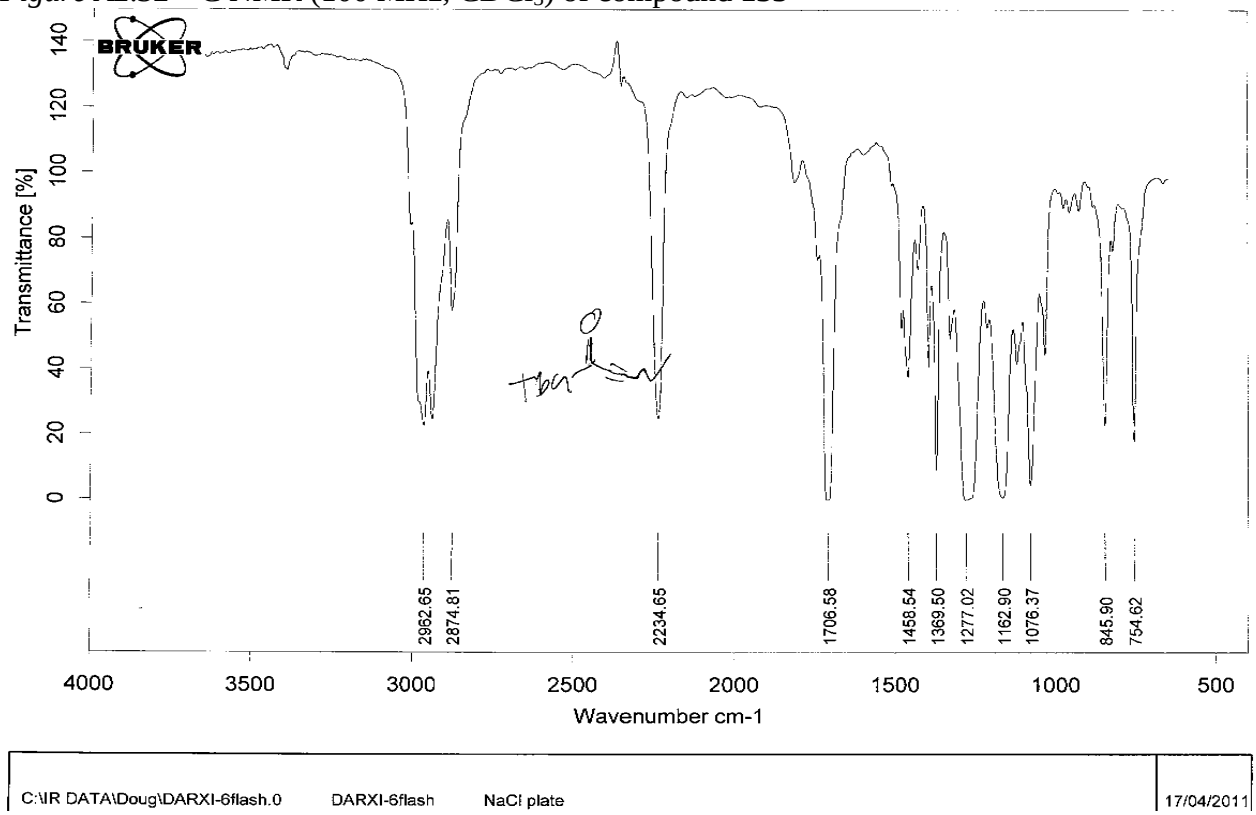
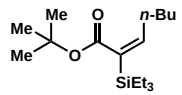


Figure A2.33 Infrared spectrum (thin film) of compound **135**



142

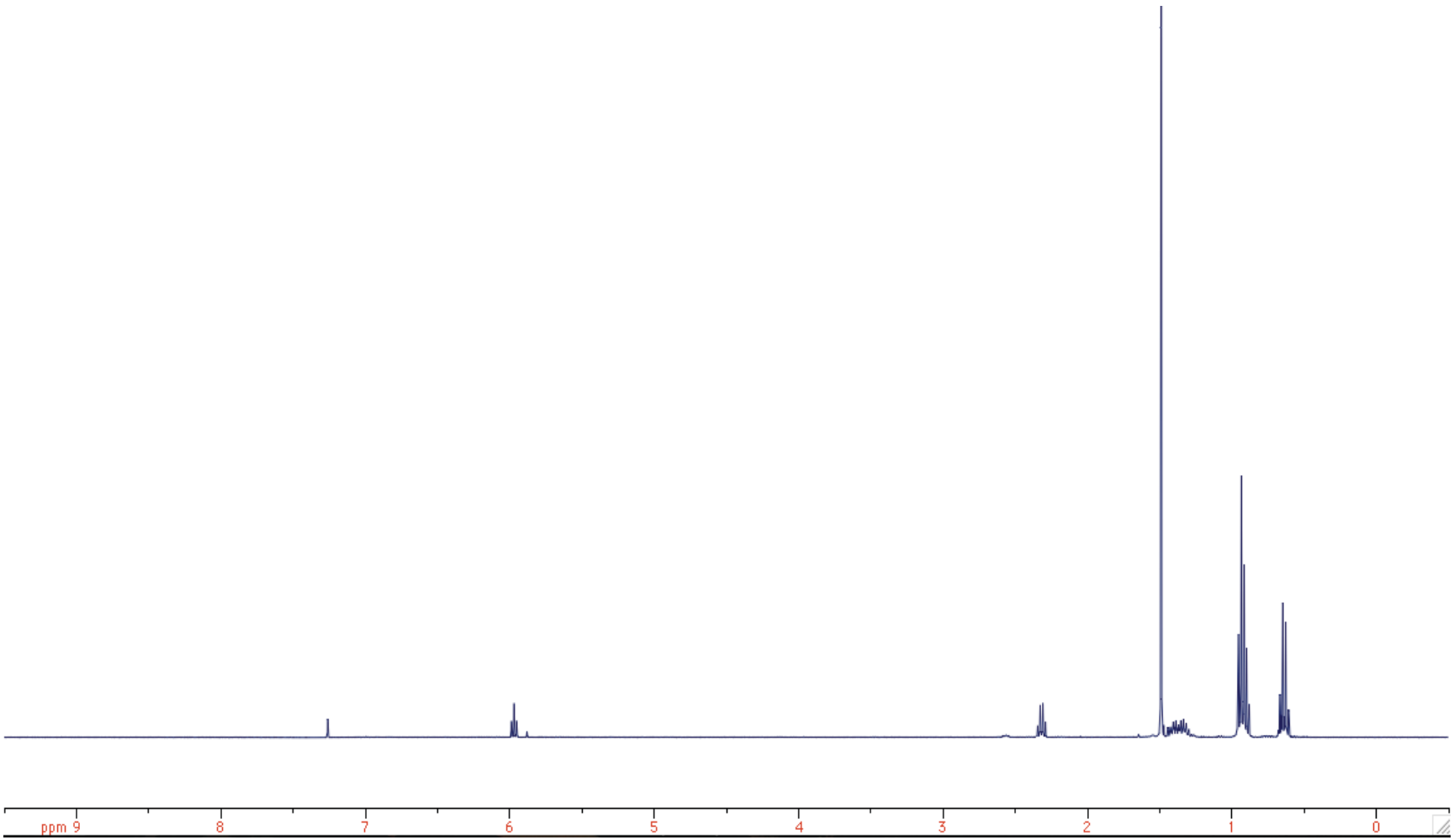
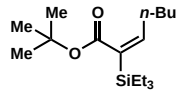


Figure A2.34 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **142**



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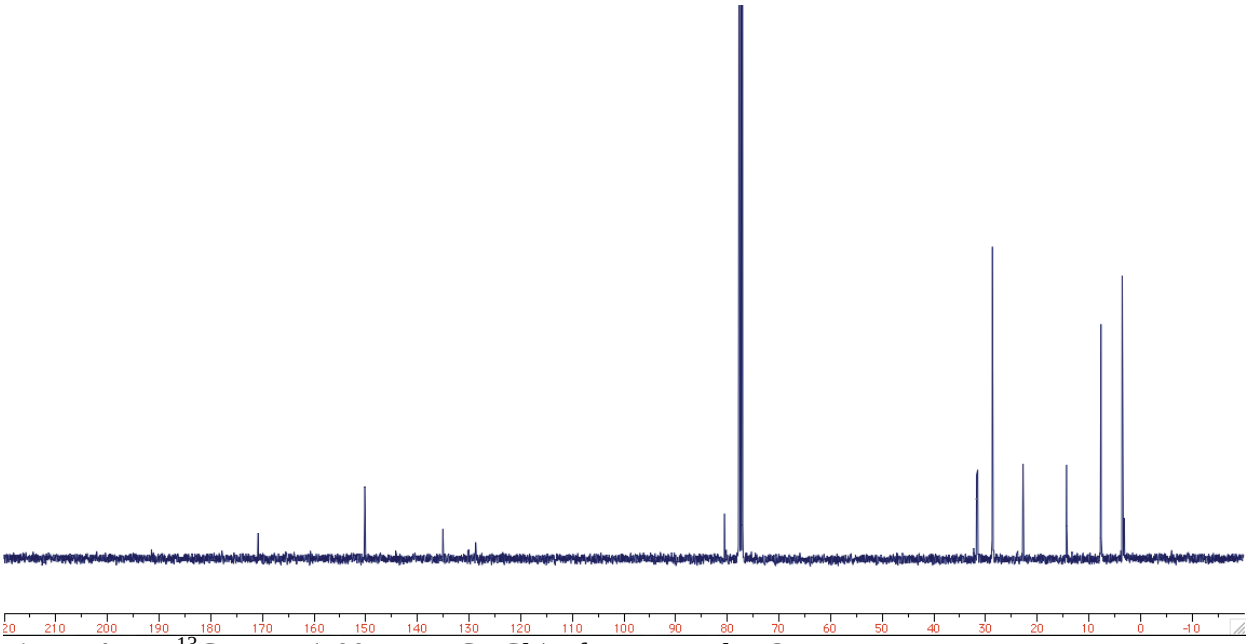


Figure A2.35 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **142**

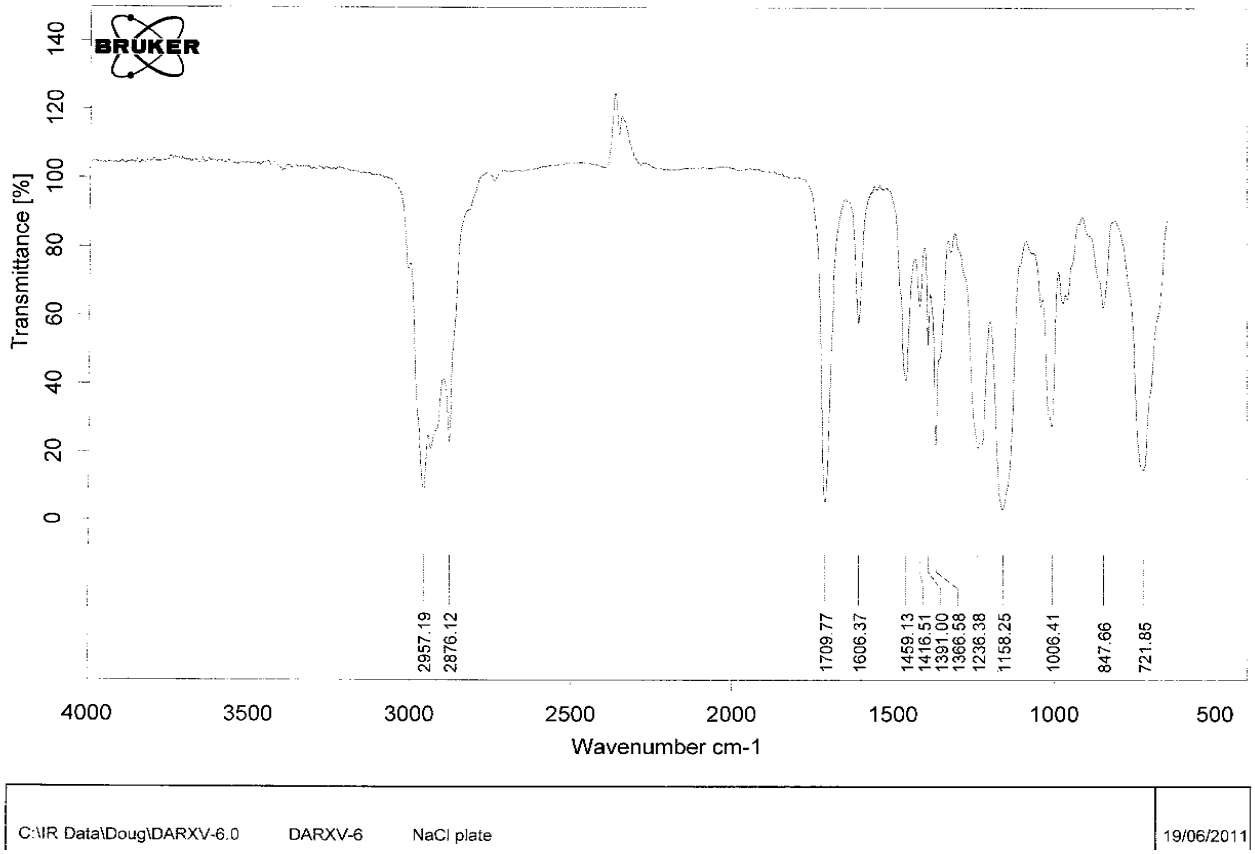
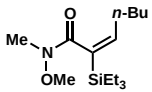


Figure A2.36 Infrared spectrum (thin film) of compound **142**



136

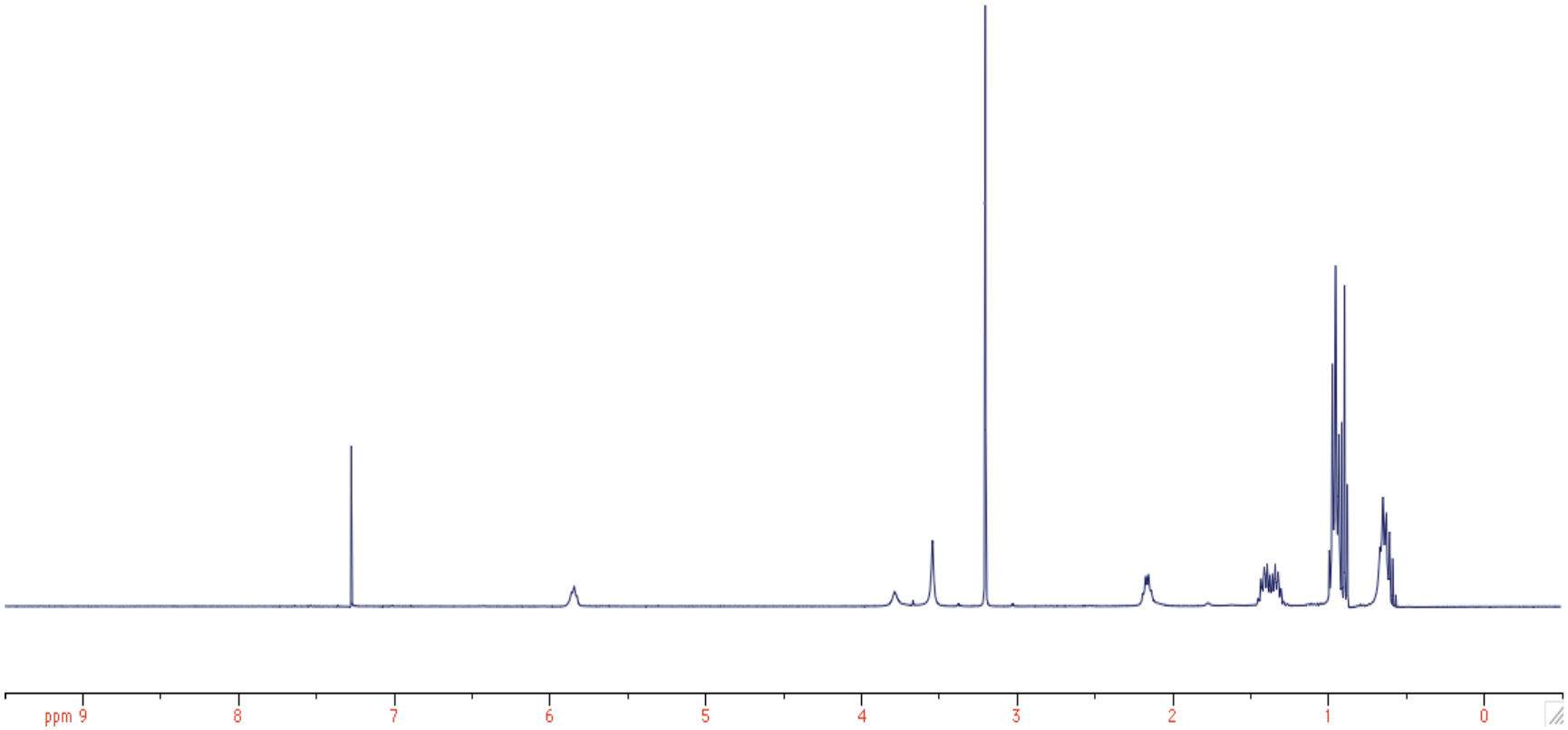
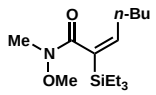


Figure A2.37 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **136**



136

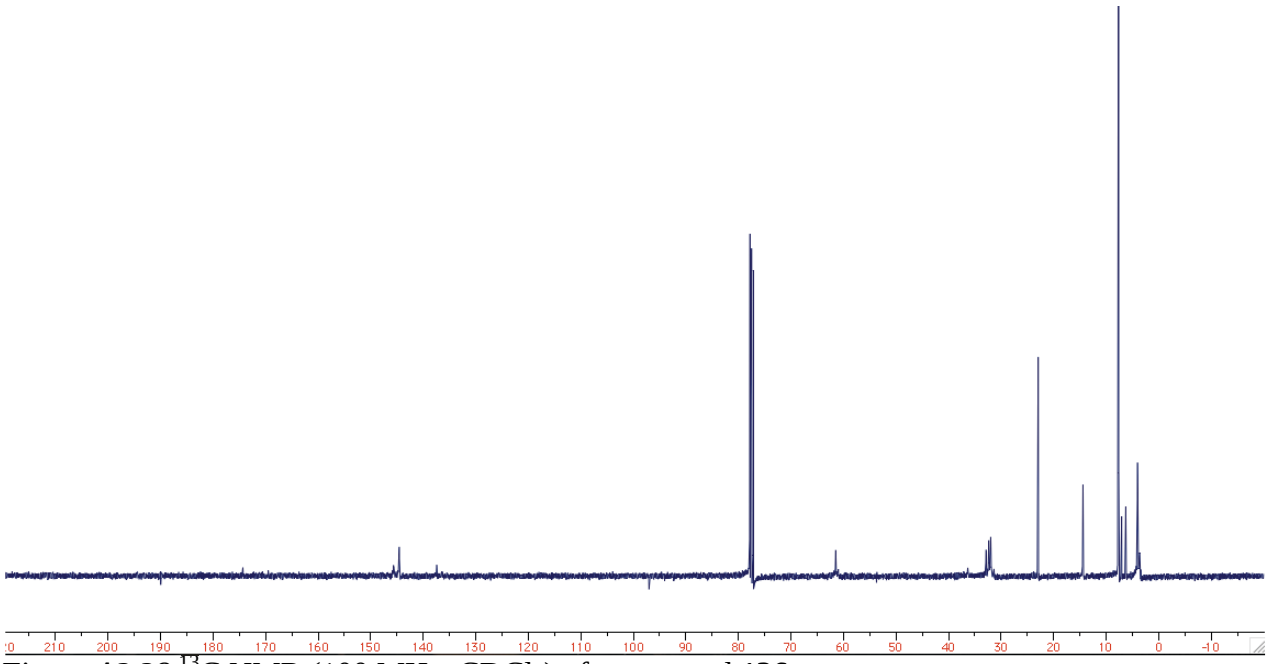


Figure A2.38 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **136**

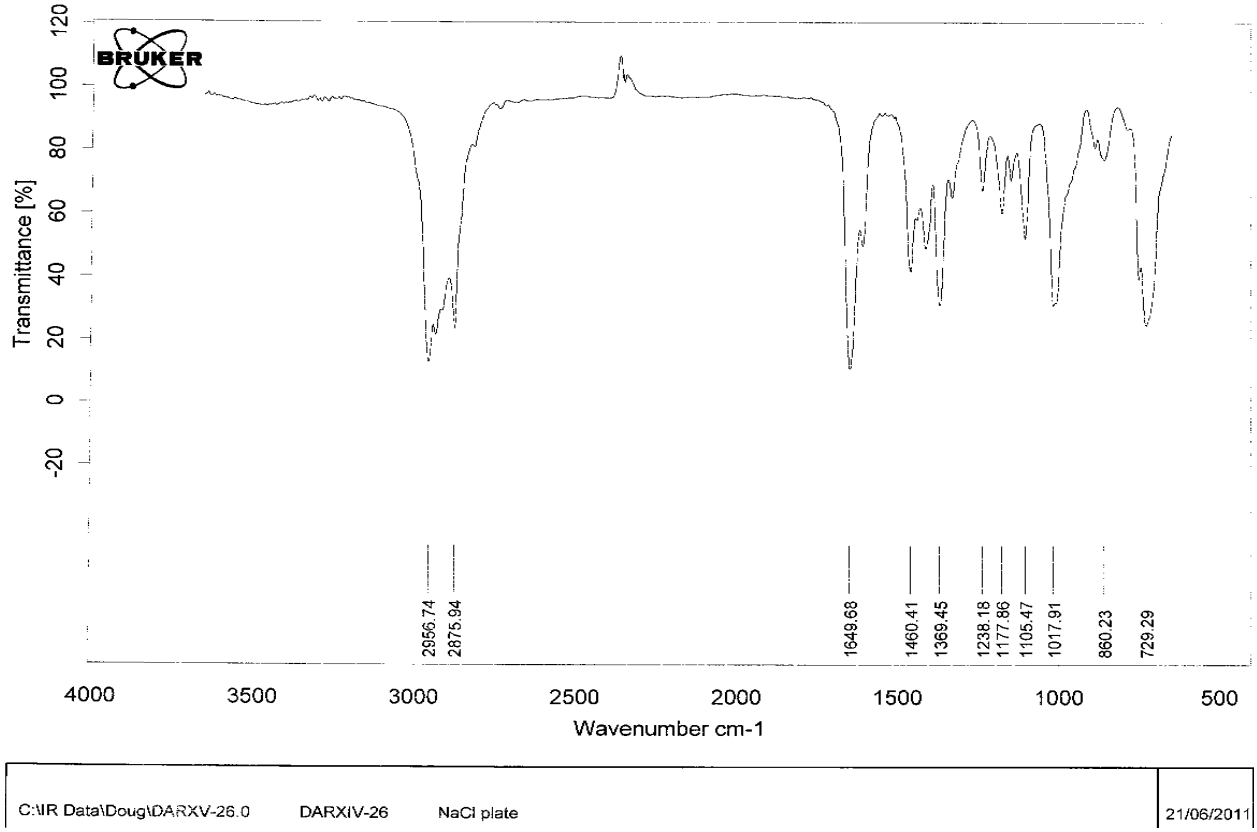
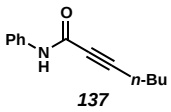


Figure A2.39 Infrared spectrum (thin film) of compound **136**



137

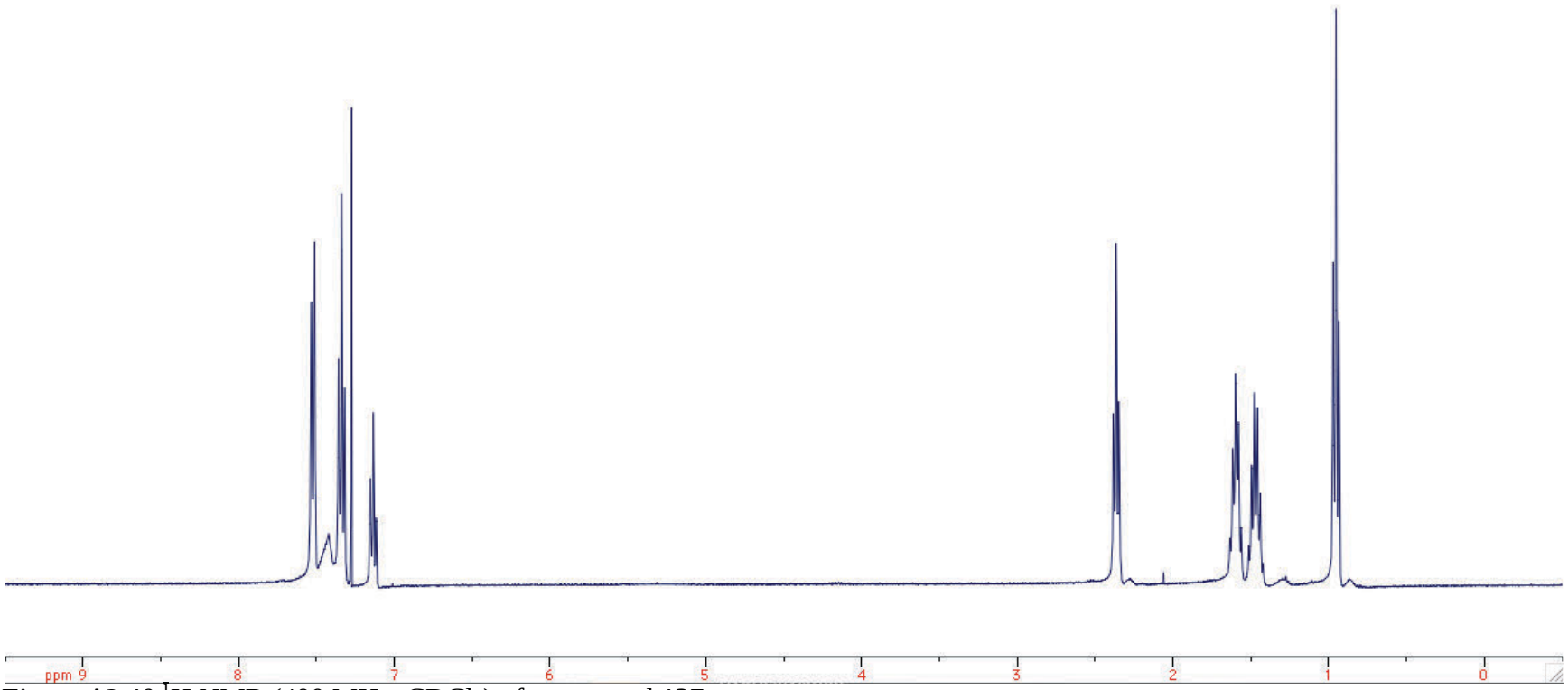
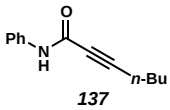


Figure A2.40 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **137**



137

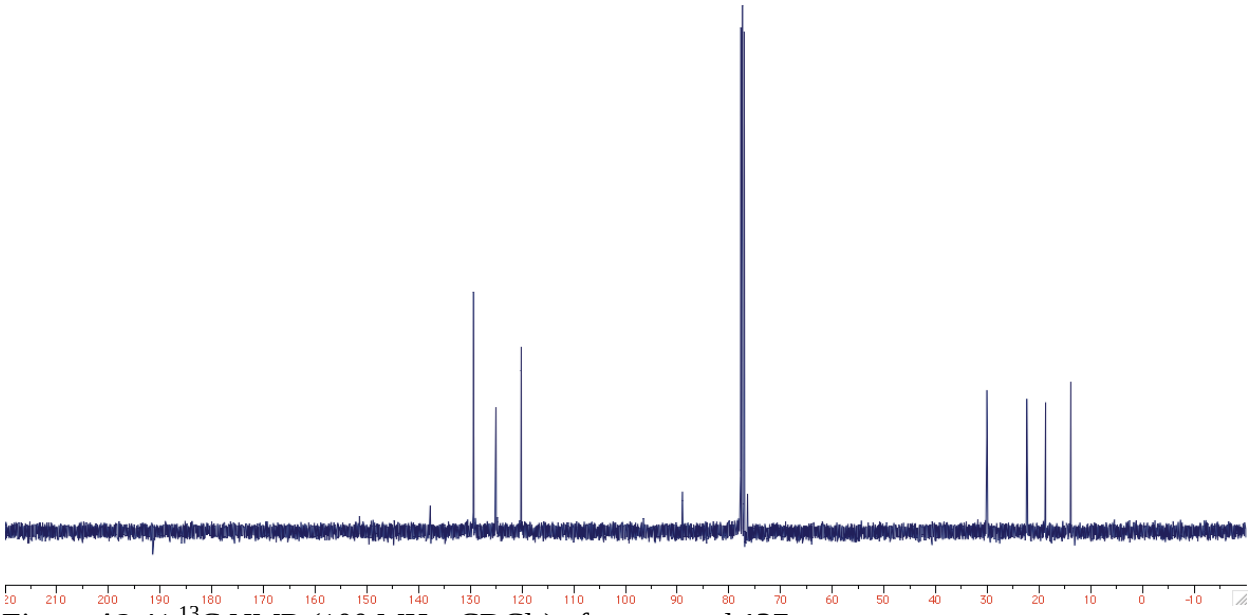


Figure A2.41 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **137**

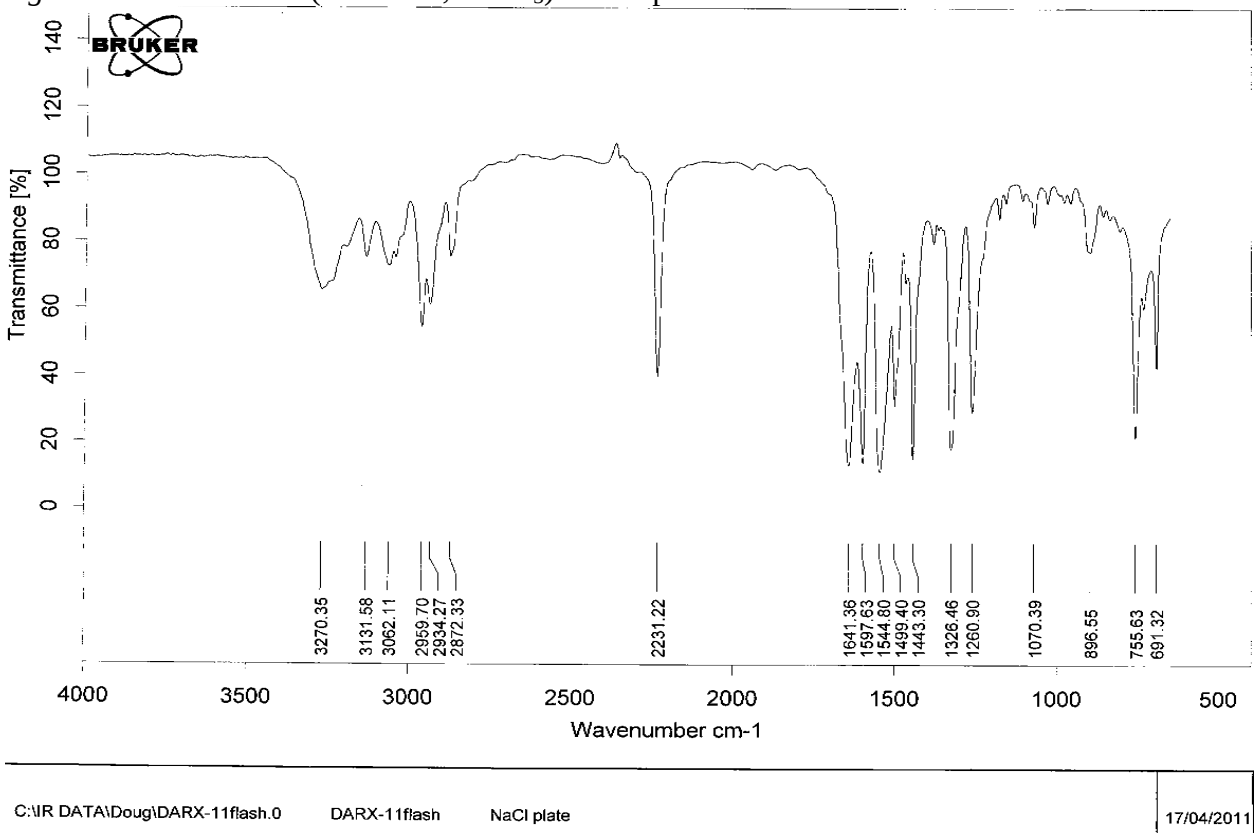


Figure A2.42 Infrared spectrum (thin film) of compound **137**

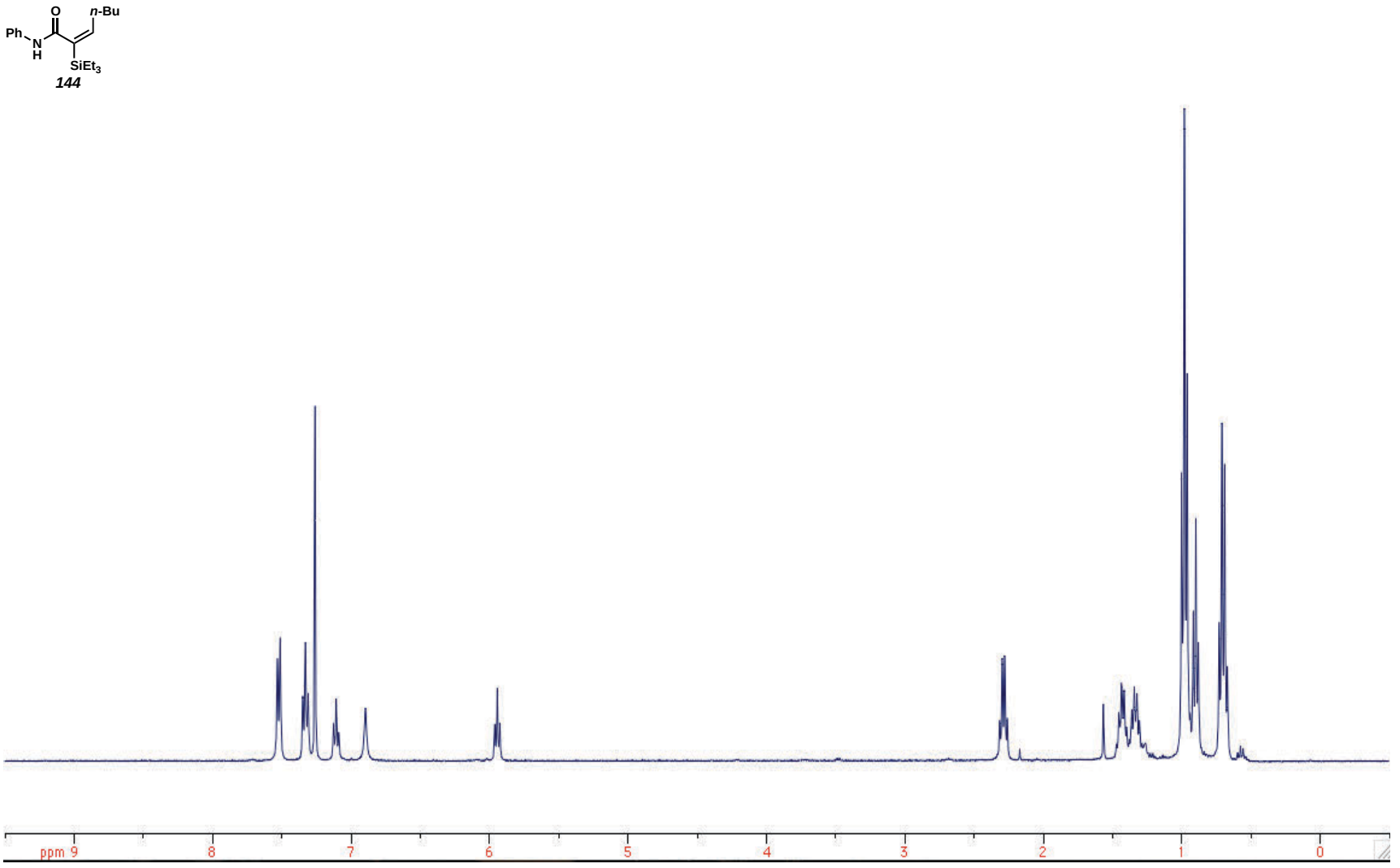


Figure A2.43 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **144**

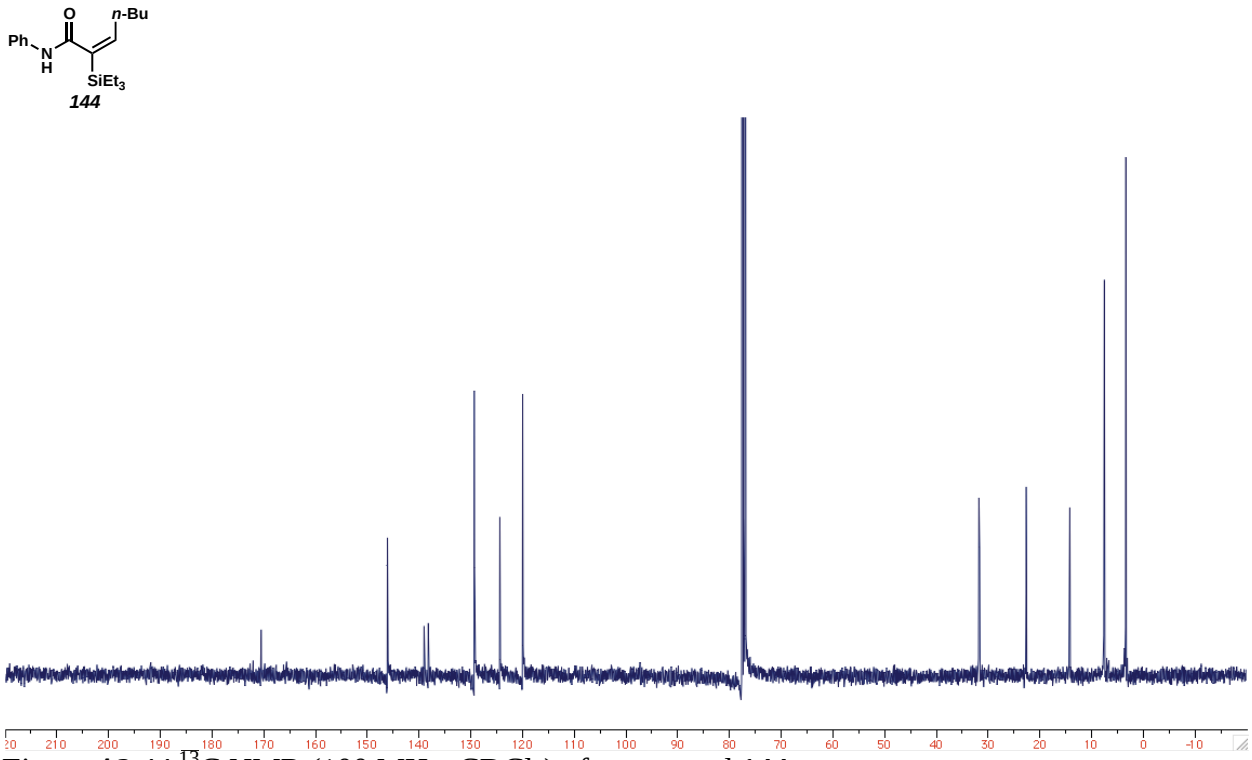


Figure A2.44 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **144**

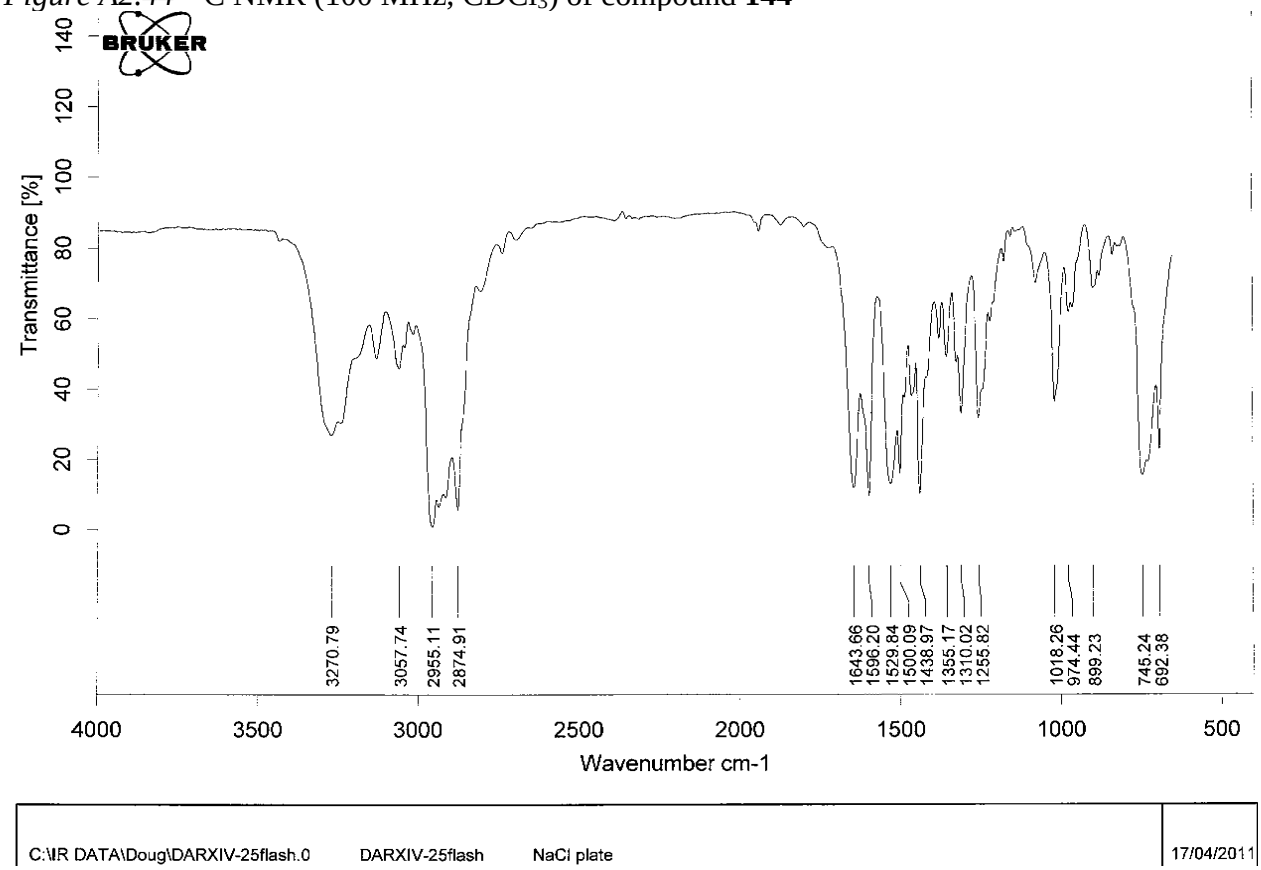
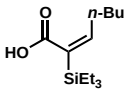


Figure A2.45 Infrared spectrum (thin film) of compound **144**



145

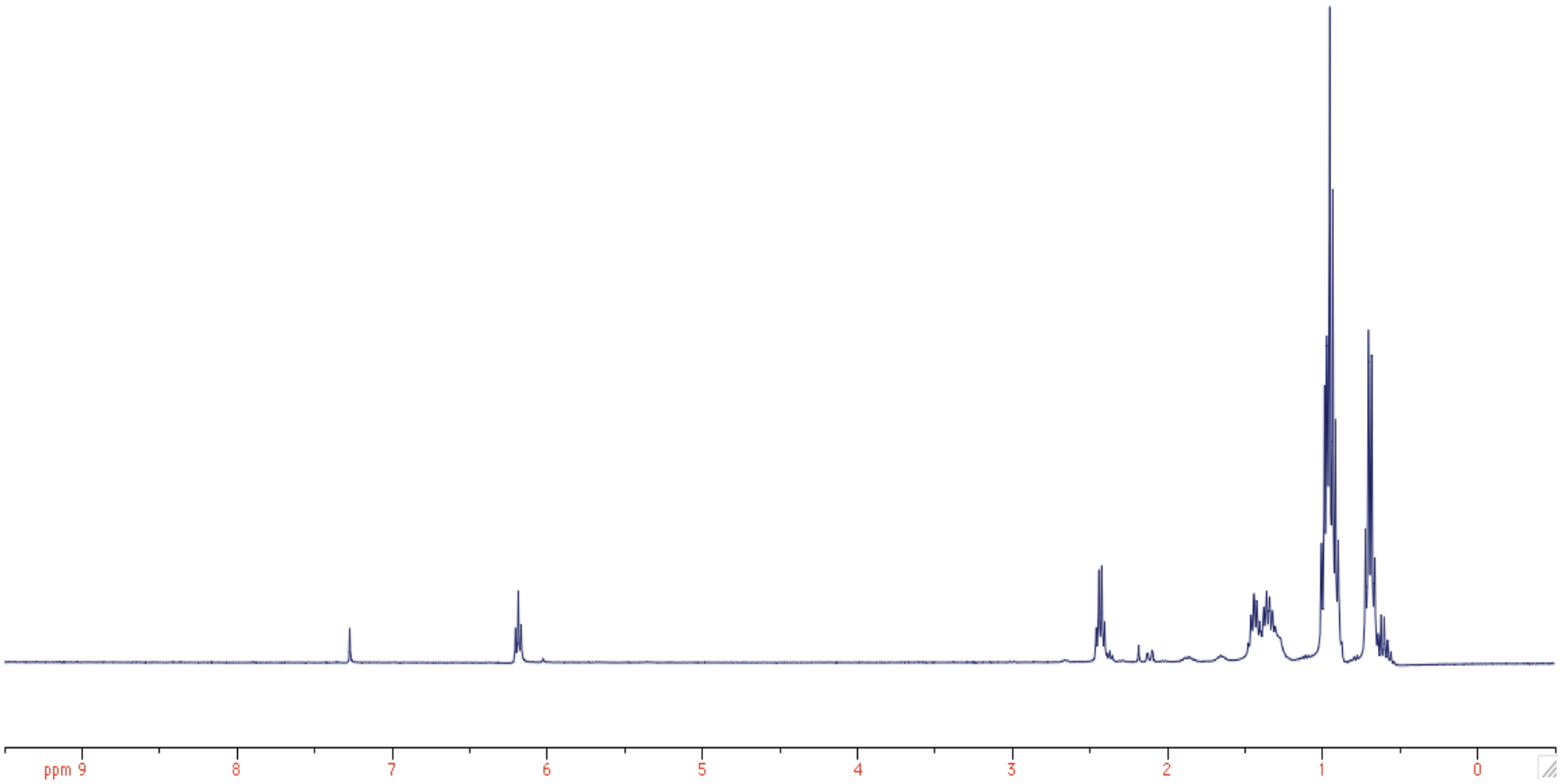


Figure A2.46 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **145**

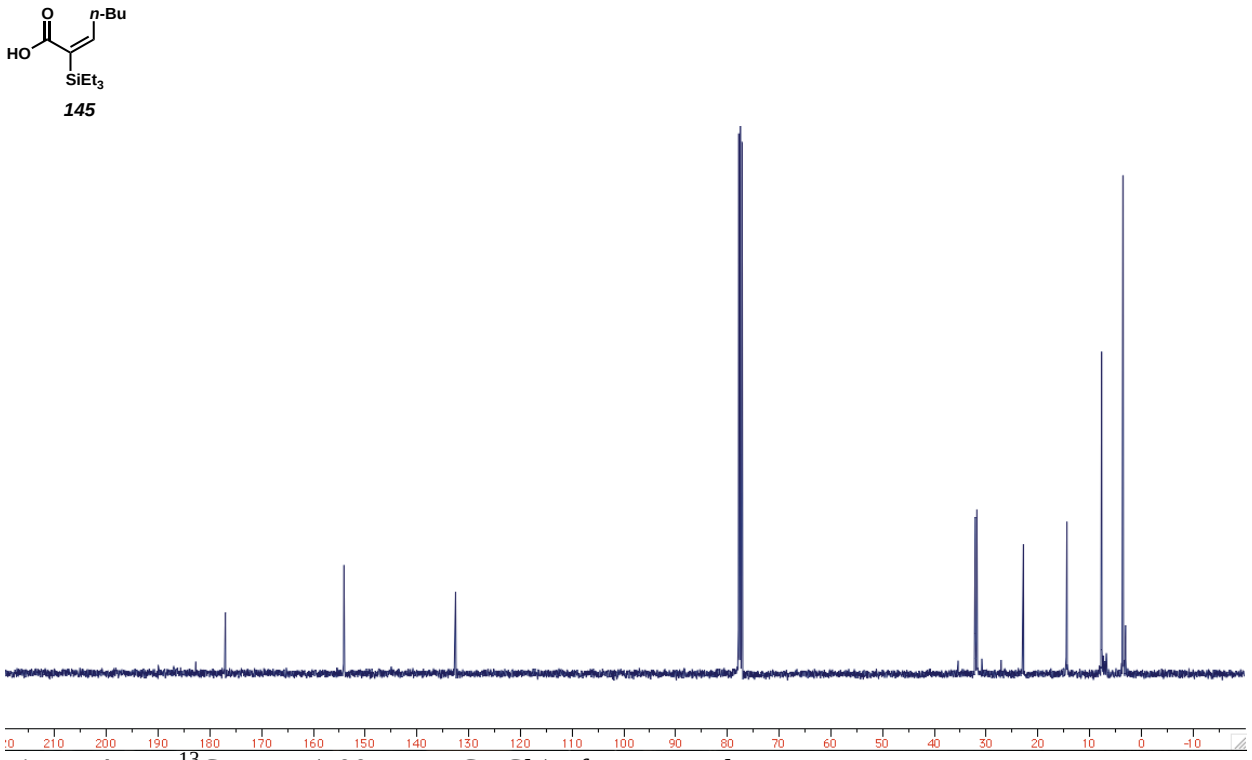


Figure A2.47 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **145**

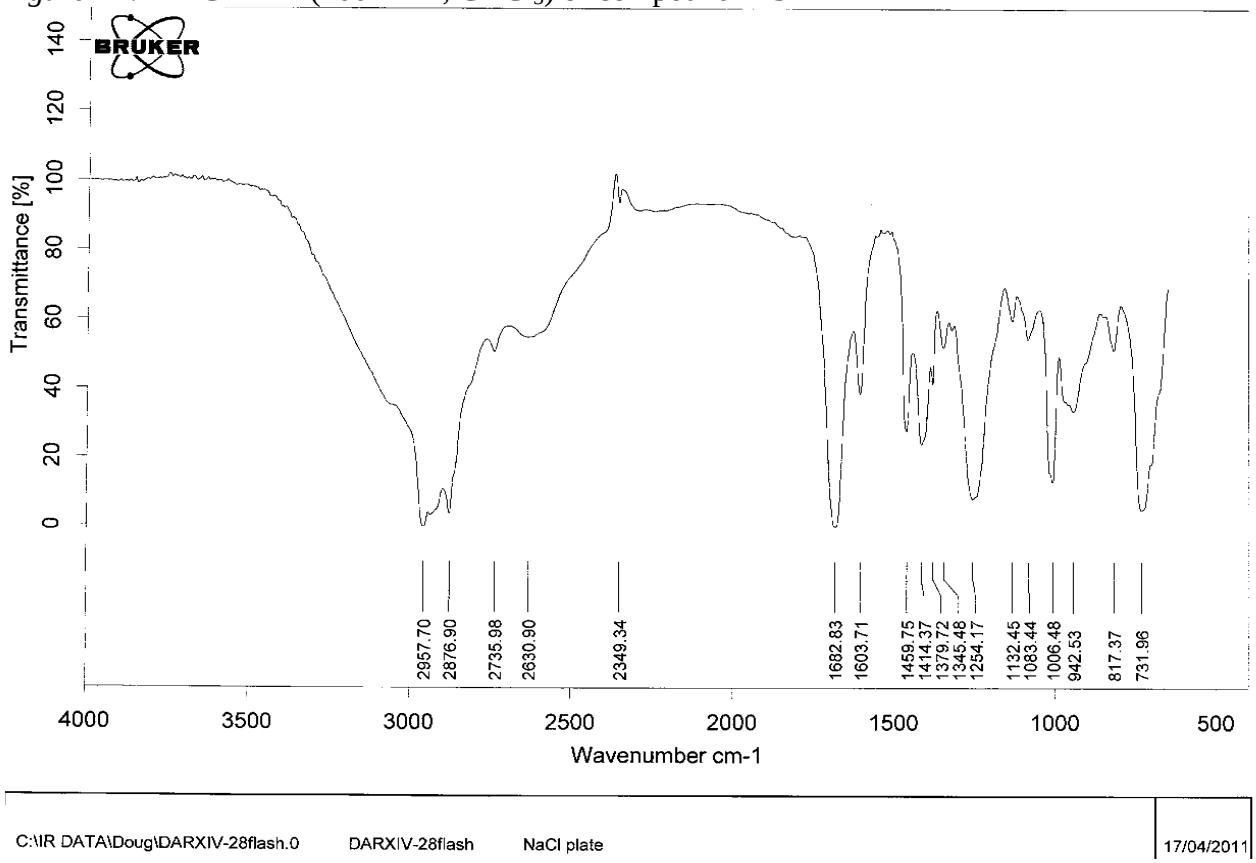
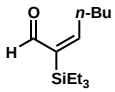


Figure A2.48 Infrared spectrum (thin film) of compound **145**



146

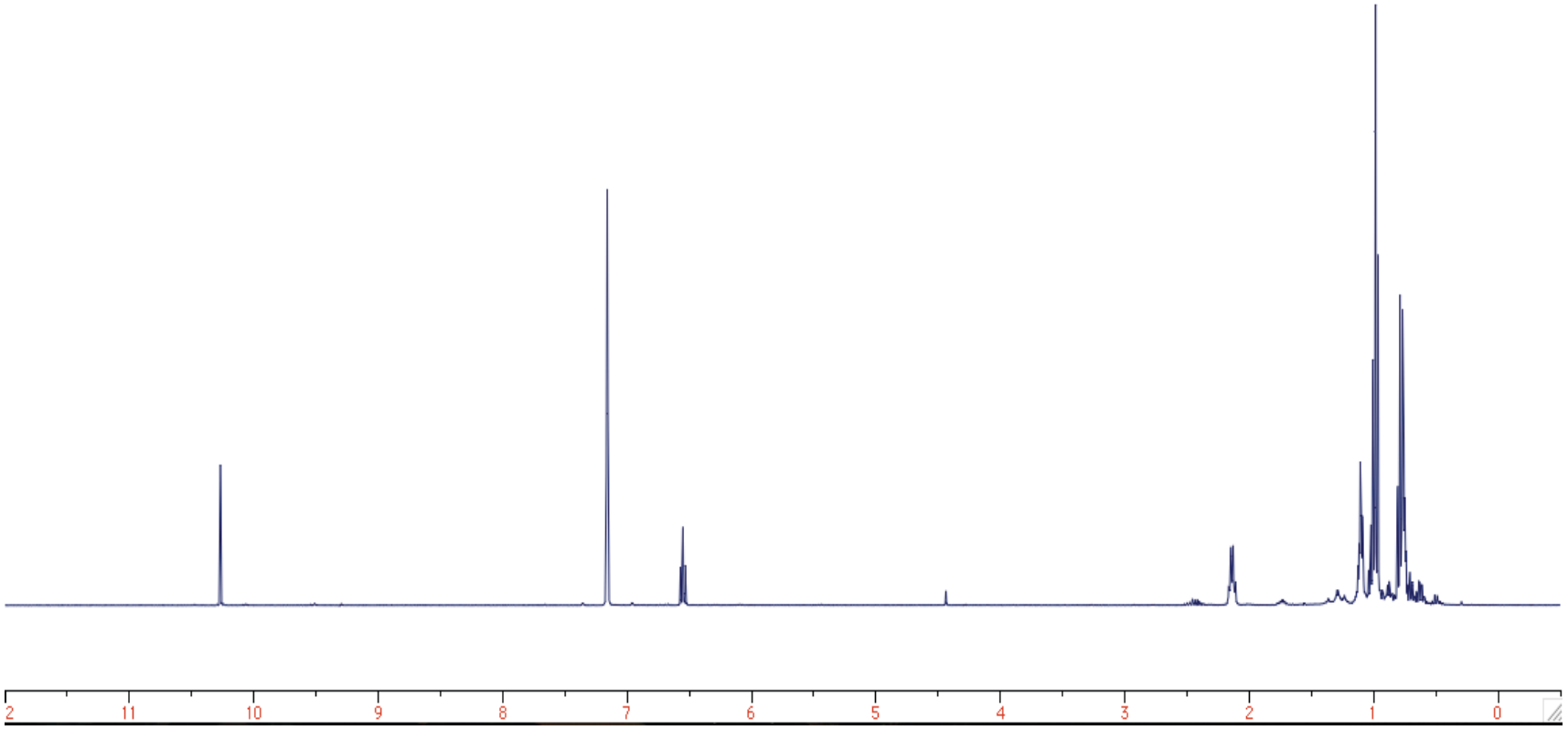


Figure A2.49 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **146**

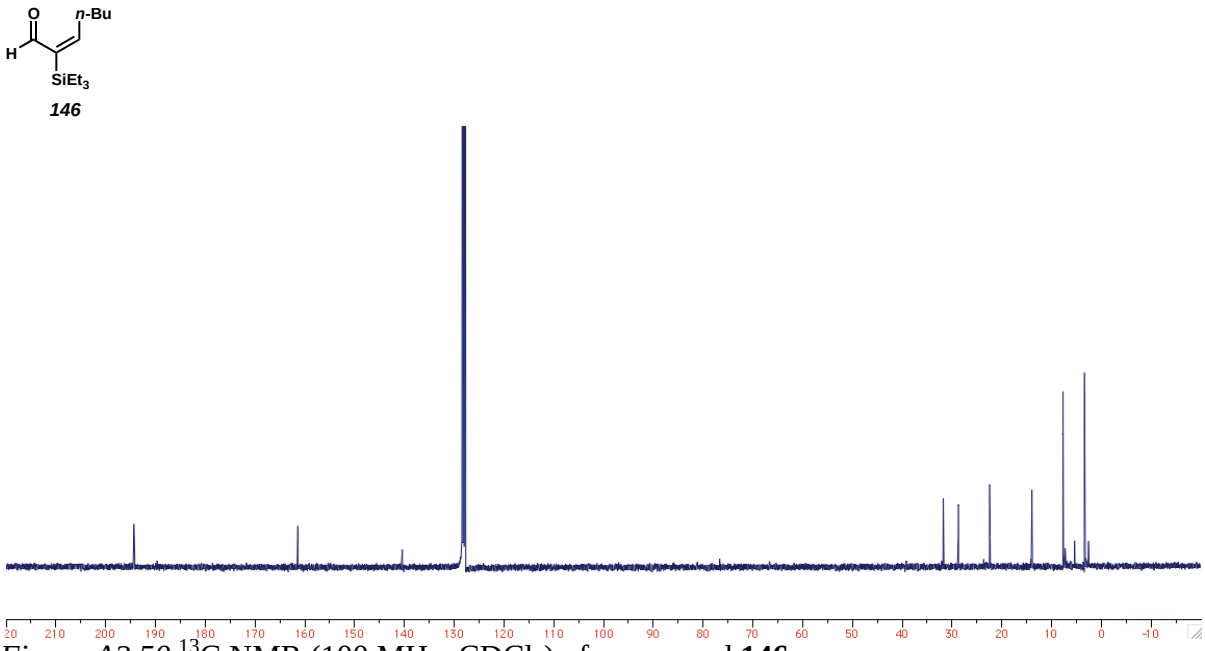


Figure A2.50 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **146**

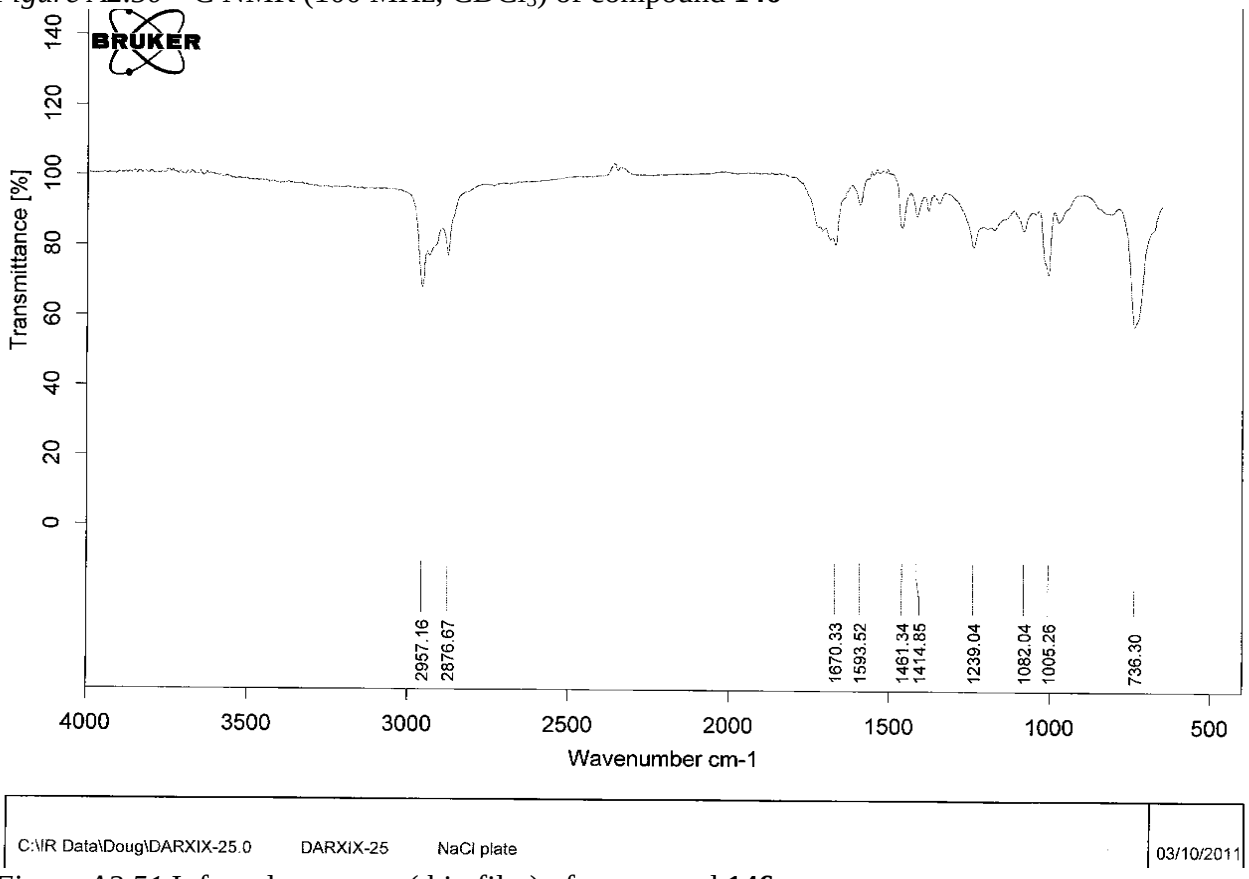
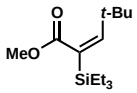


Figure A2.51 Infrared spectrum (thin film) of compound **146**



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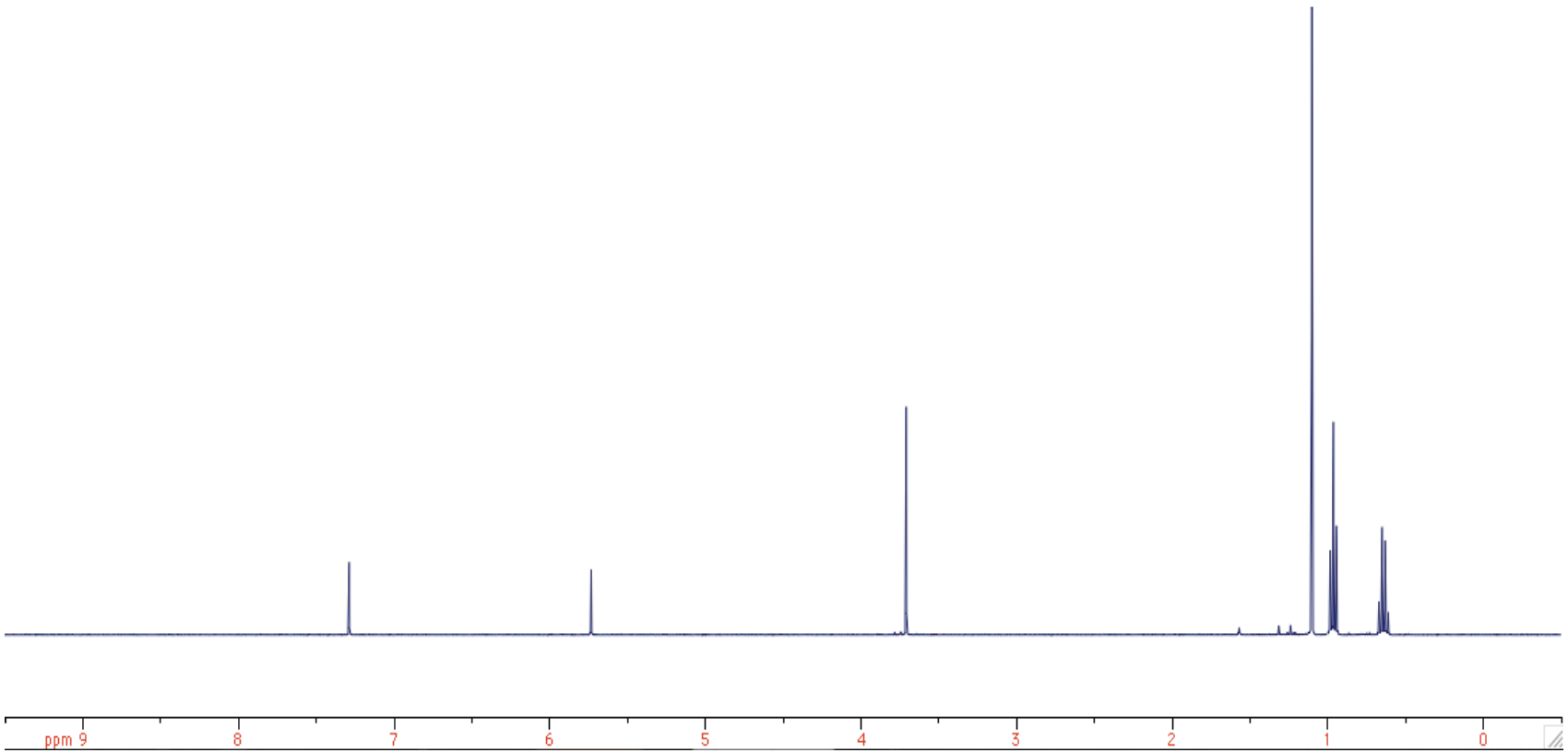


Figure A2.52 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **151**

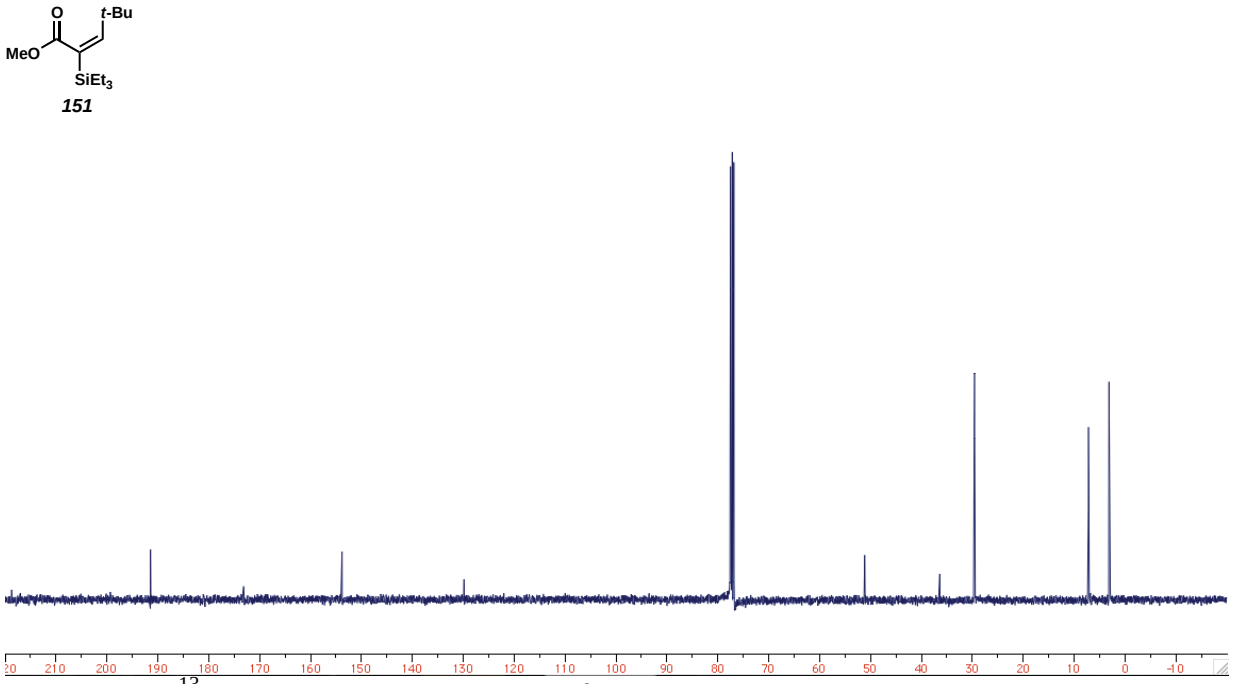


Figure A2.53 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **151**

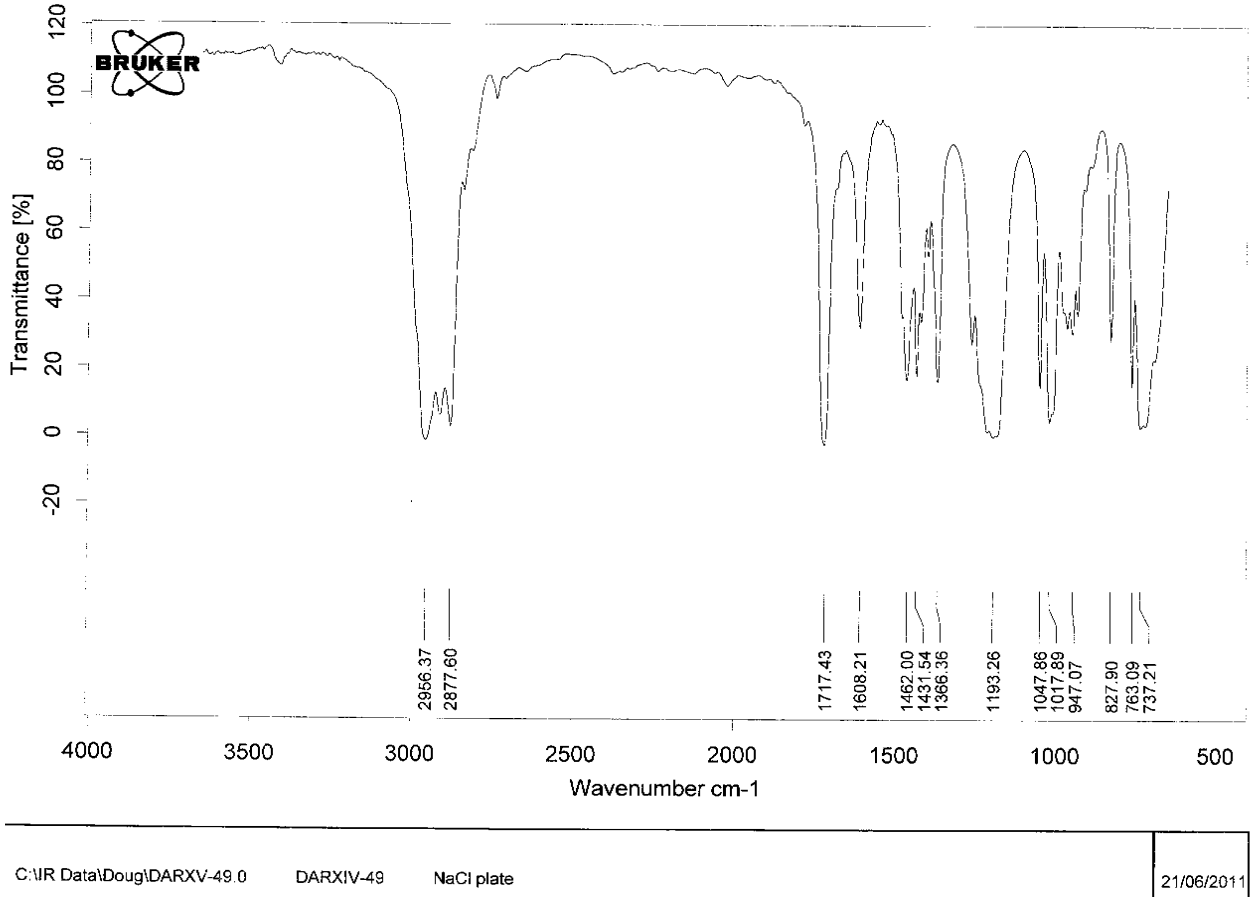
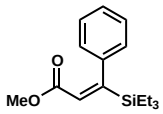


Figure A2.54 Infrared spectrum (thin film) of compound **151**



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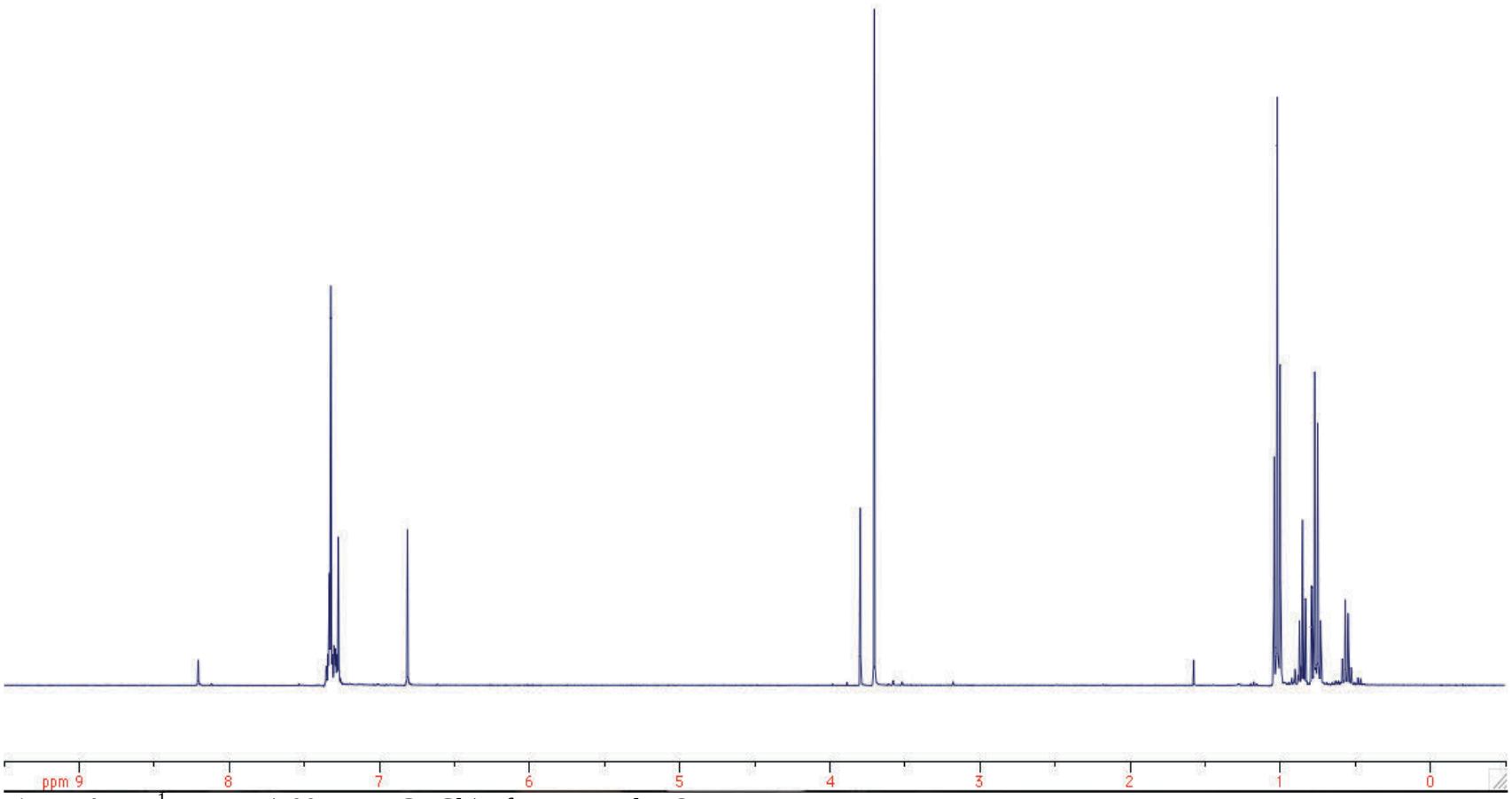
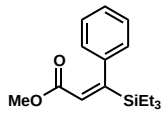


Figure A2.55 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **152**



152

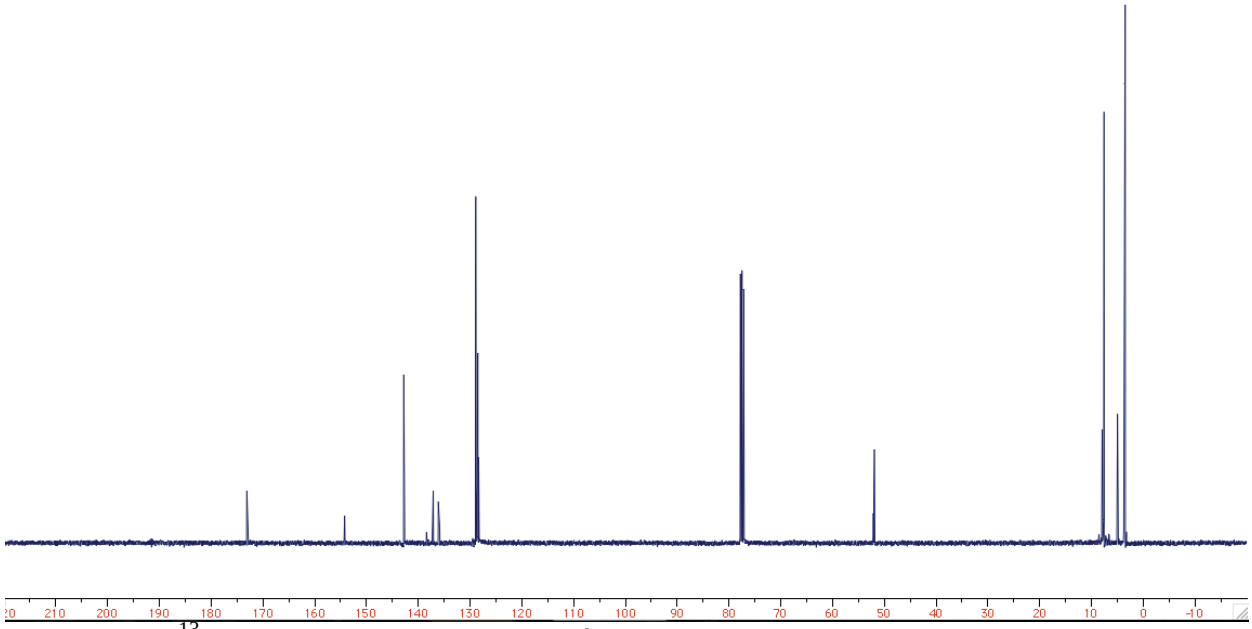


Figure A2.56 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **152**

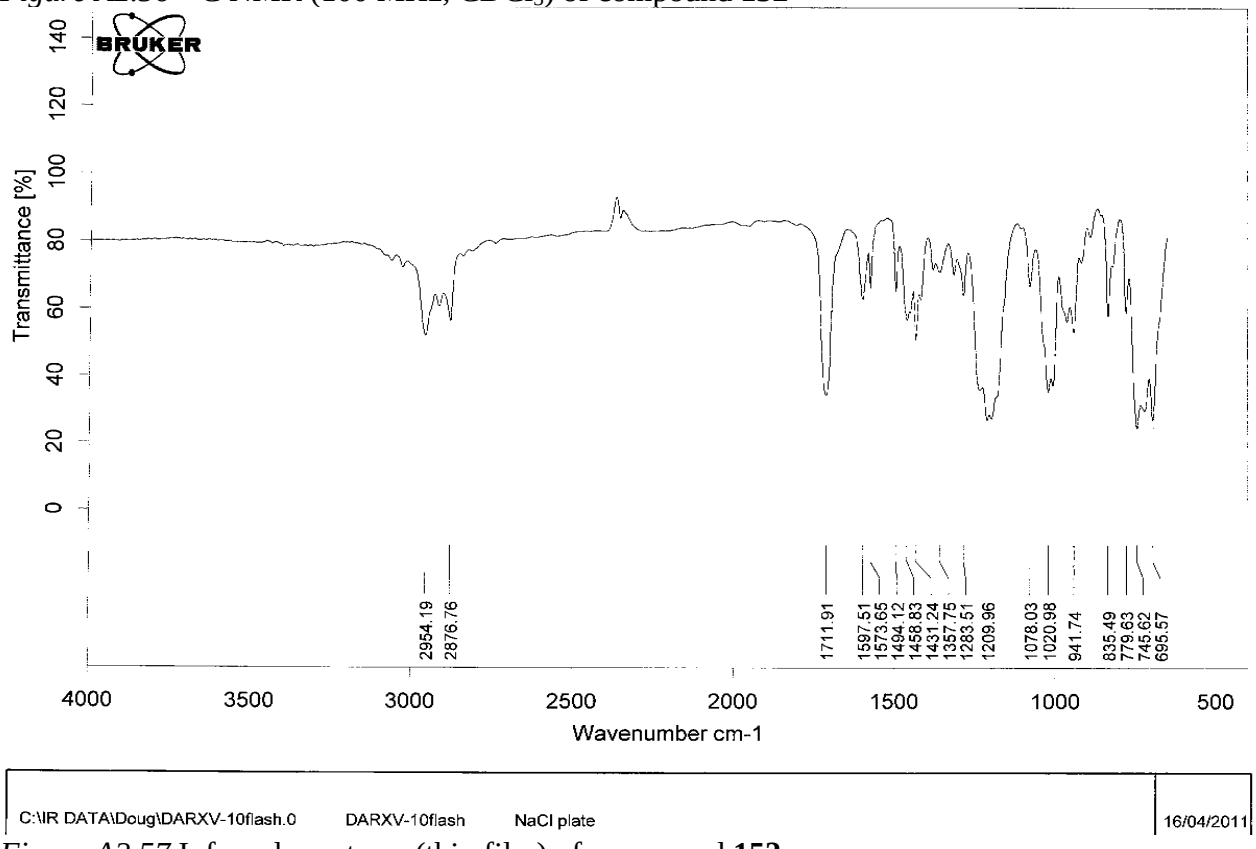
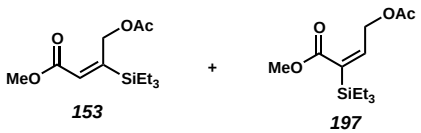


Figure A2.57 Infrared spectrum (thin film) of compound **152**



153

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197

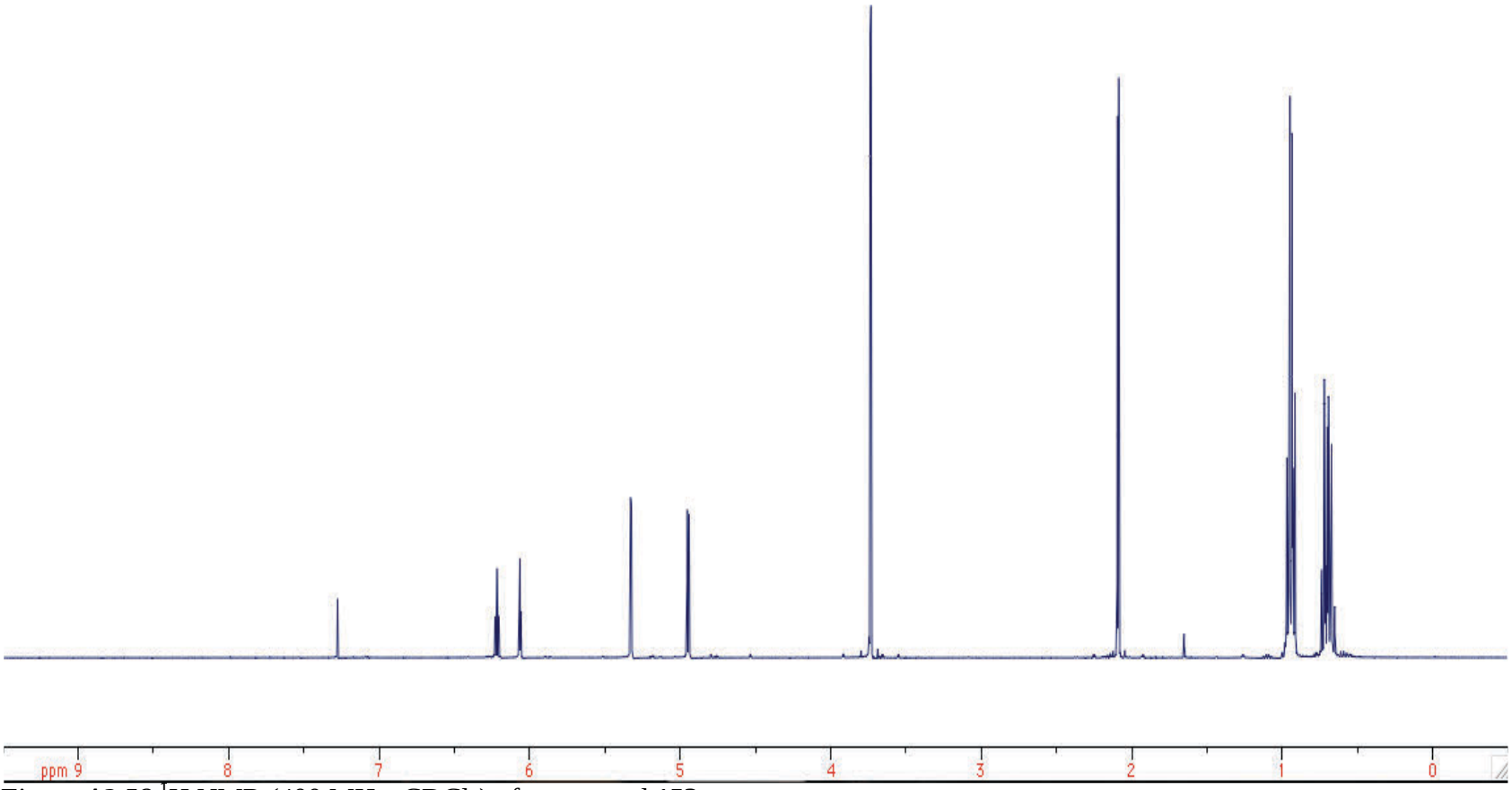
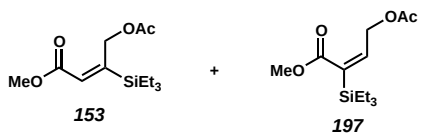


Figure A2.58 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **153**



153

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197

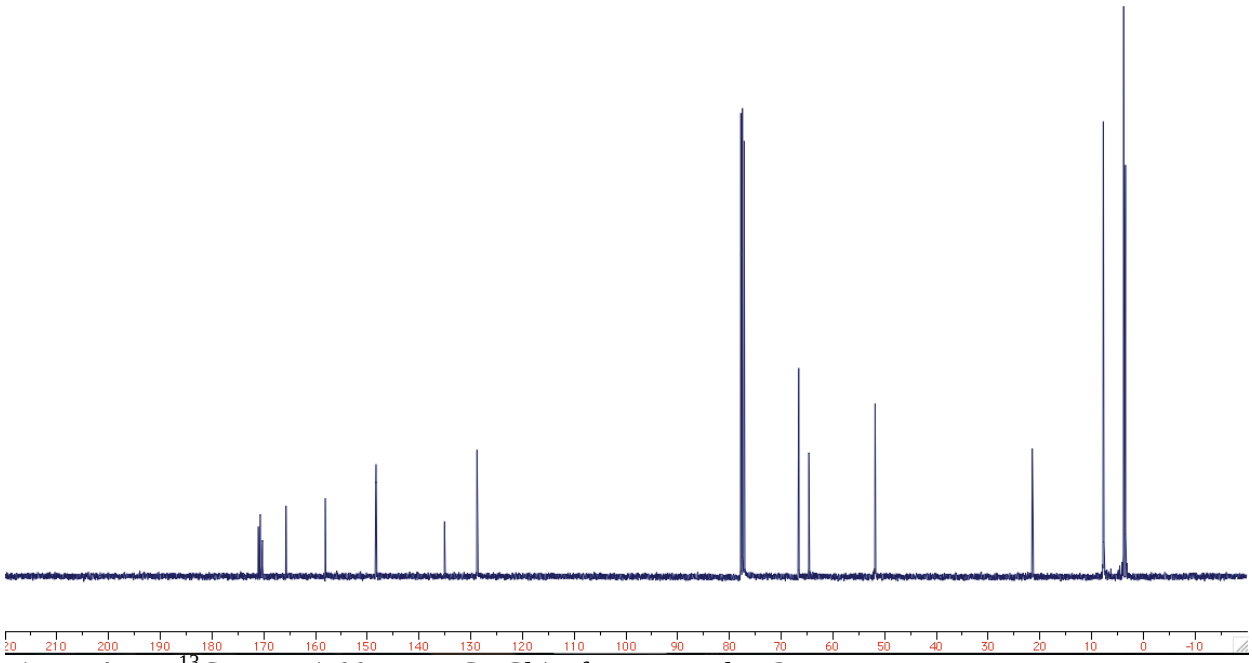


Figure A2.59 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **153**

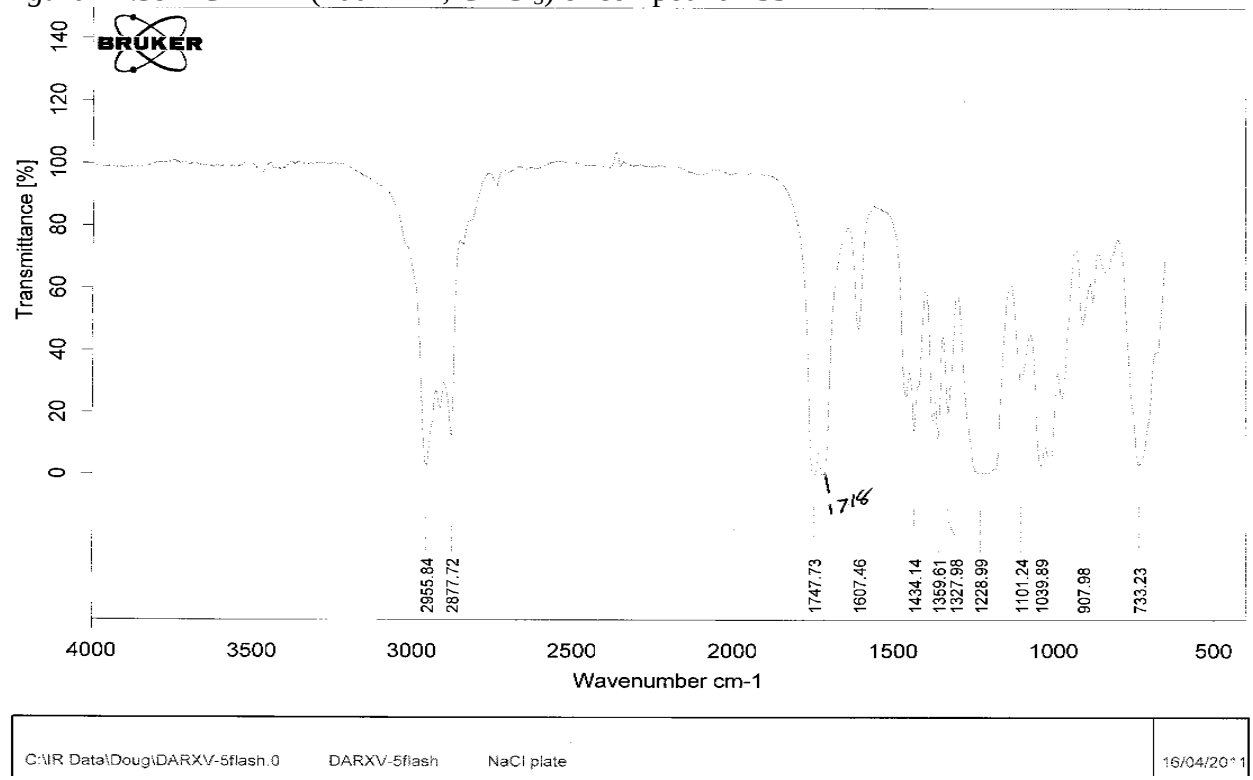
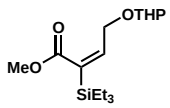


Figure A2.60 Infrared spectrum (thin film) of compound **153**



155

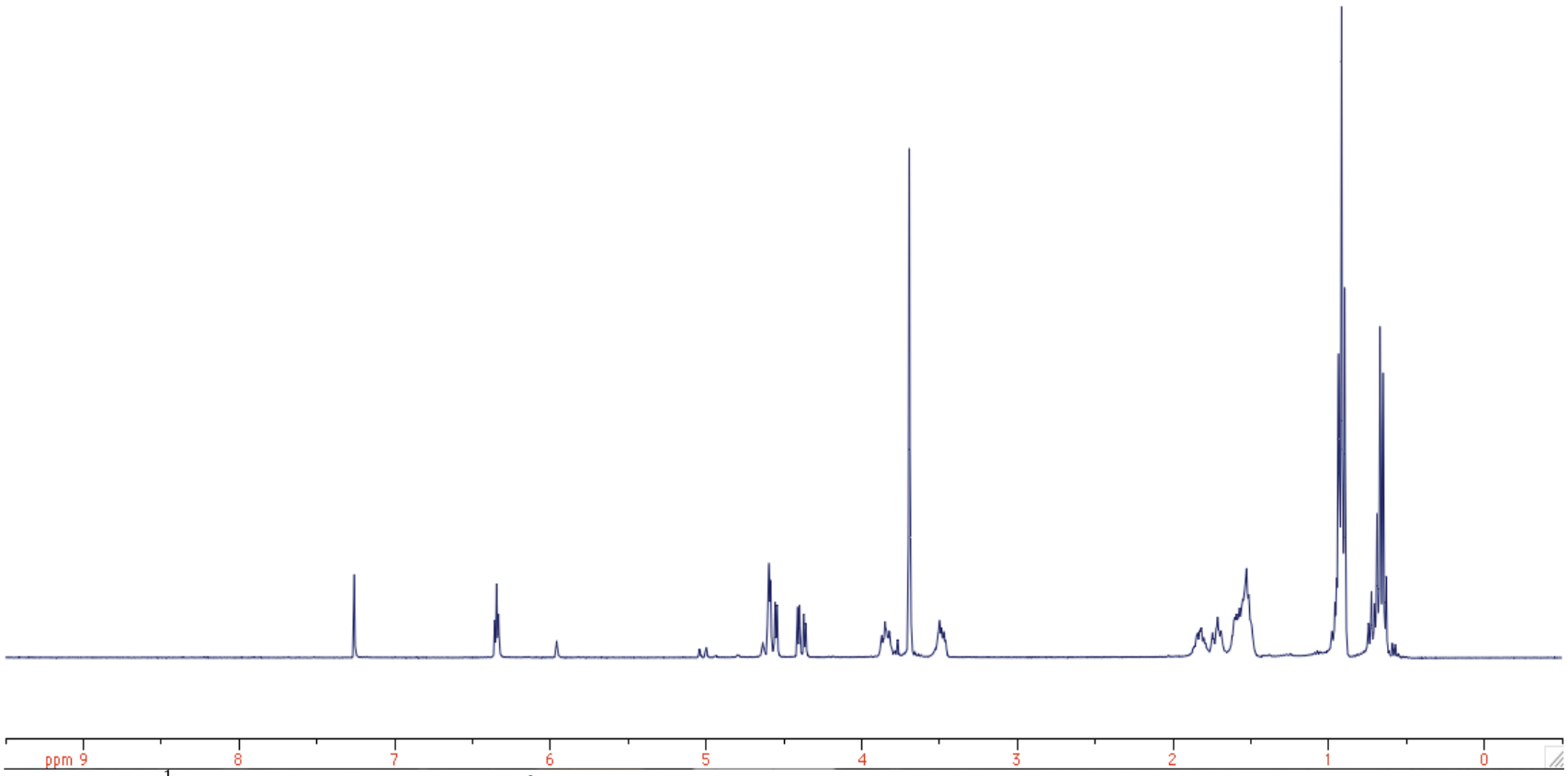


Figure A2.61 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **155**

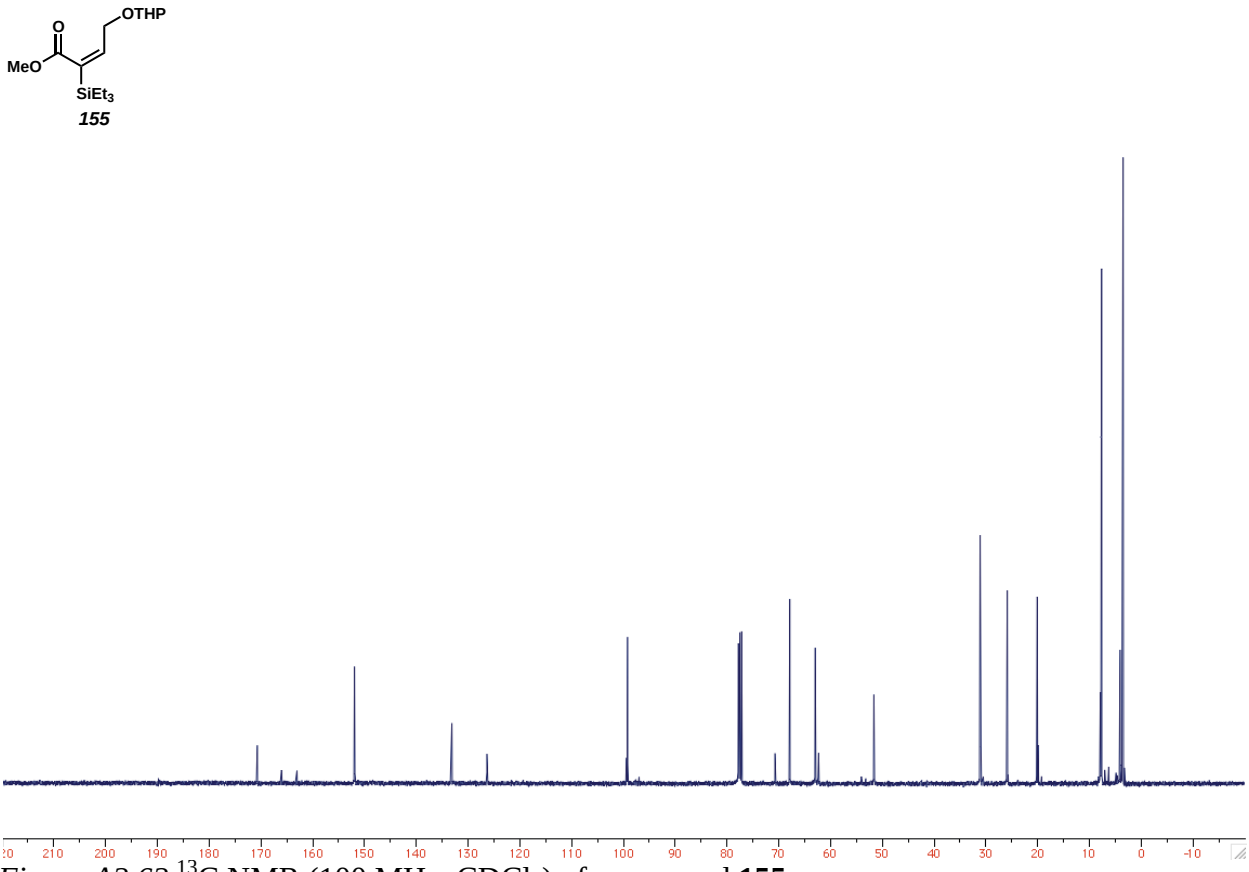


Figure A2.62 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **155**

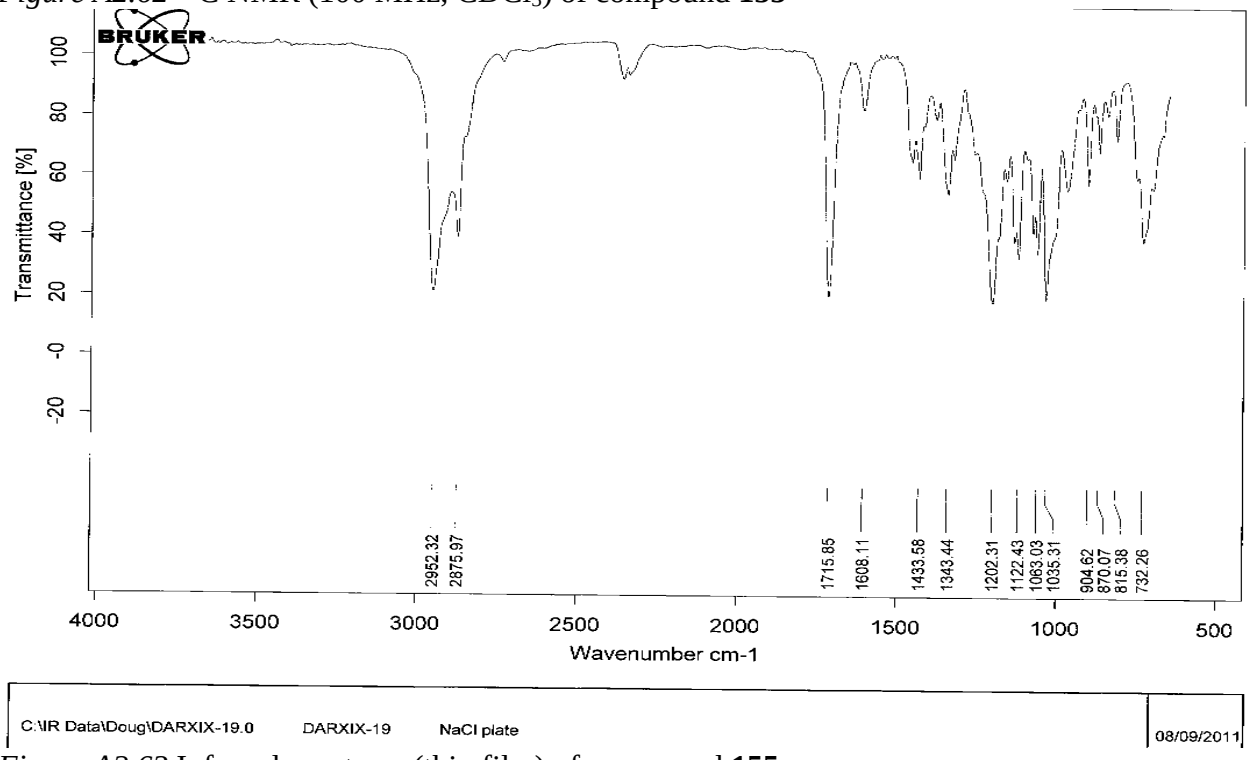
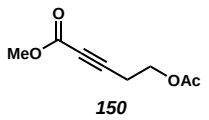


Figure A2.63 Infrared spectrum (thin film) of compound **155**



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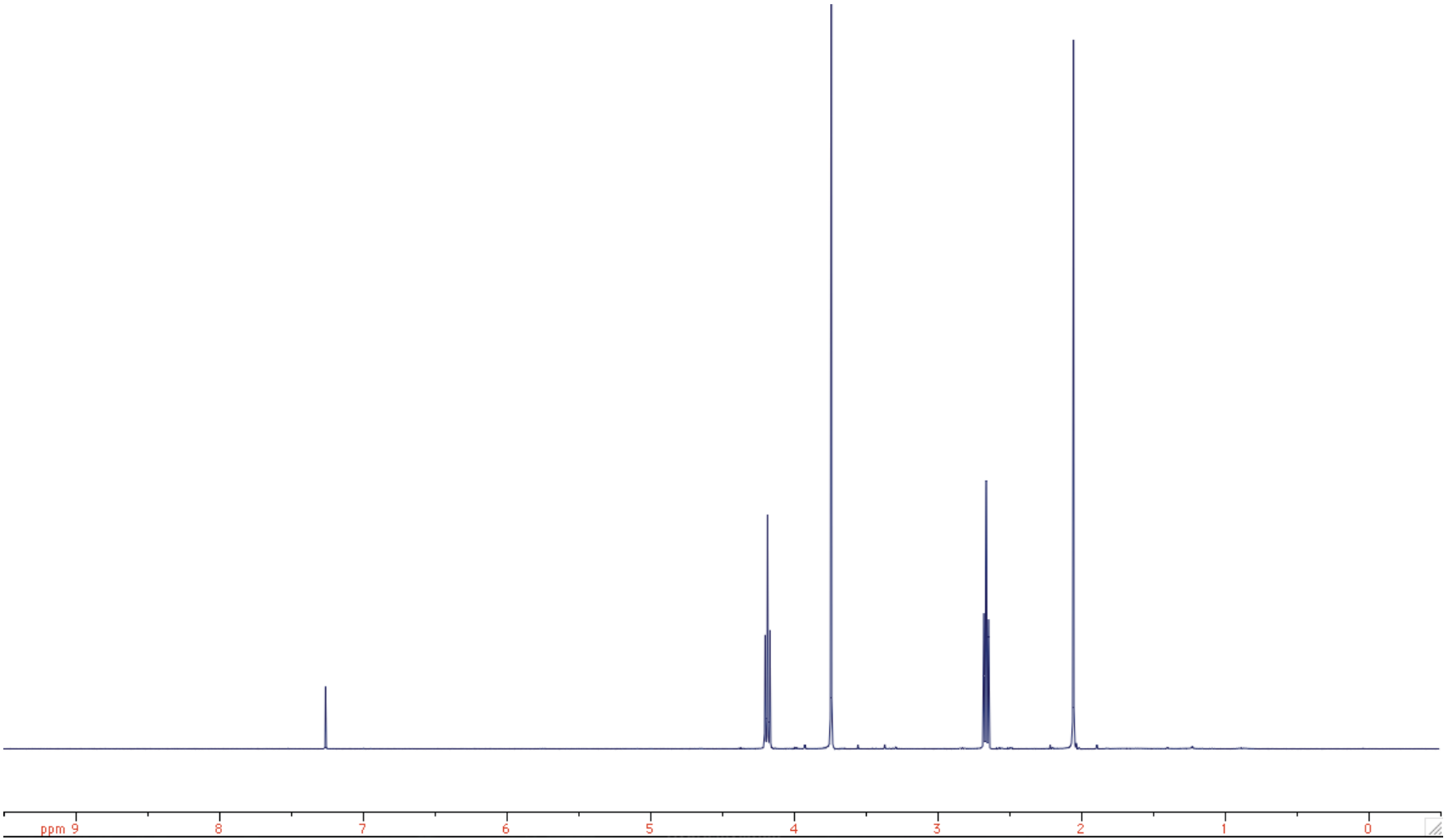


Figure A2.64 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **150**

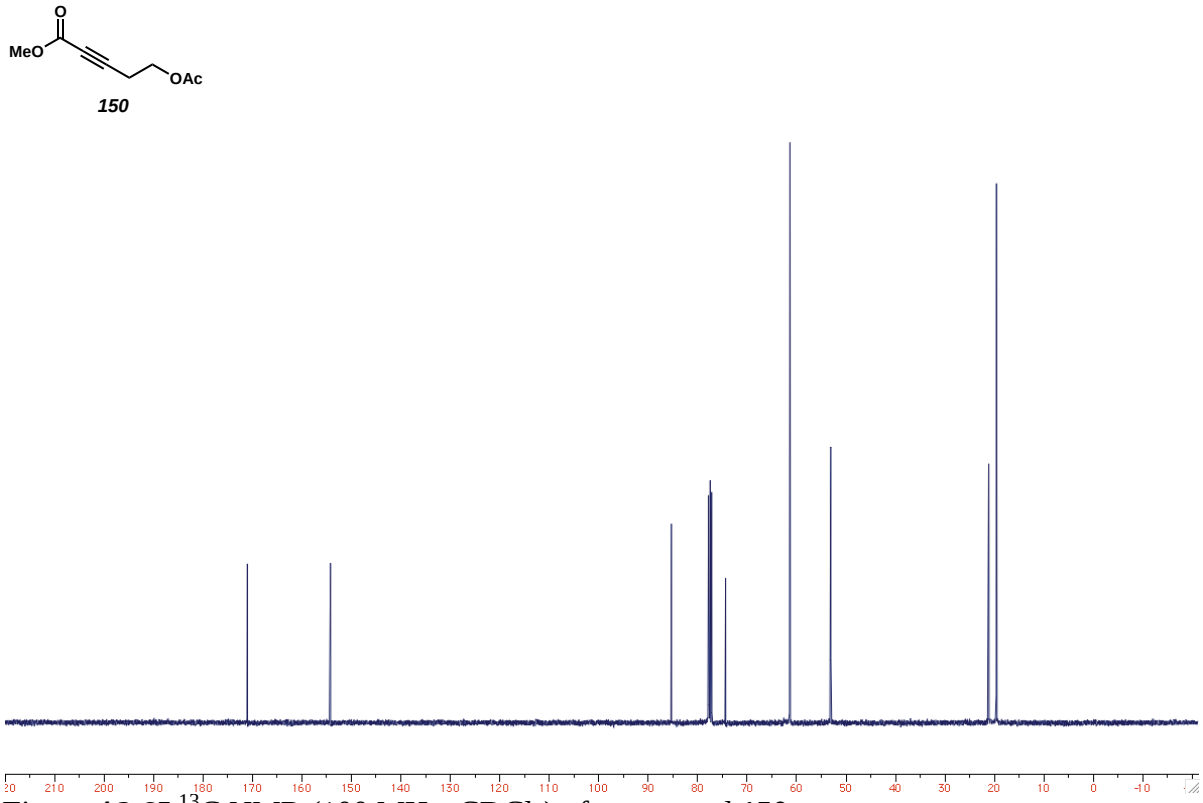


Figure A2.65 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **150**

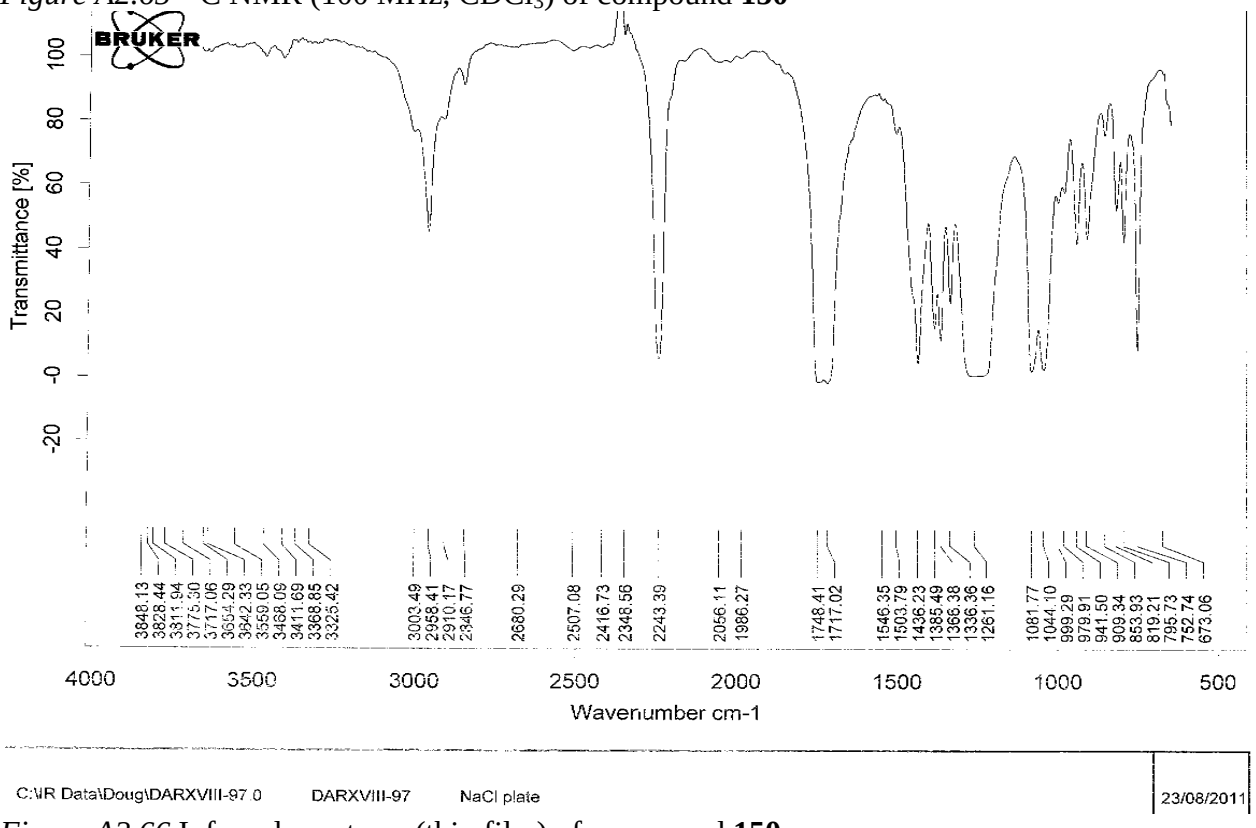
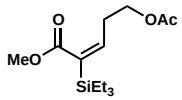


Figure A2.66 Infrared spectrum (thin film) of compound **150**



156

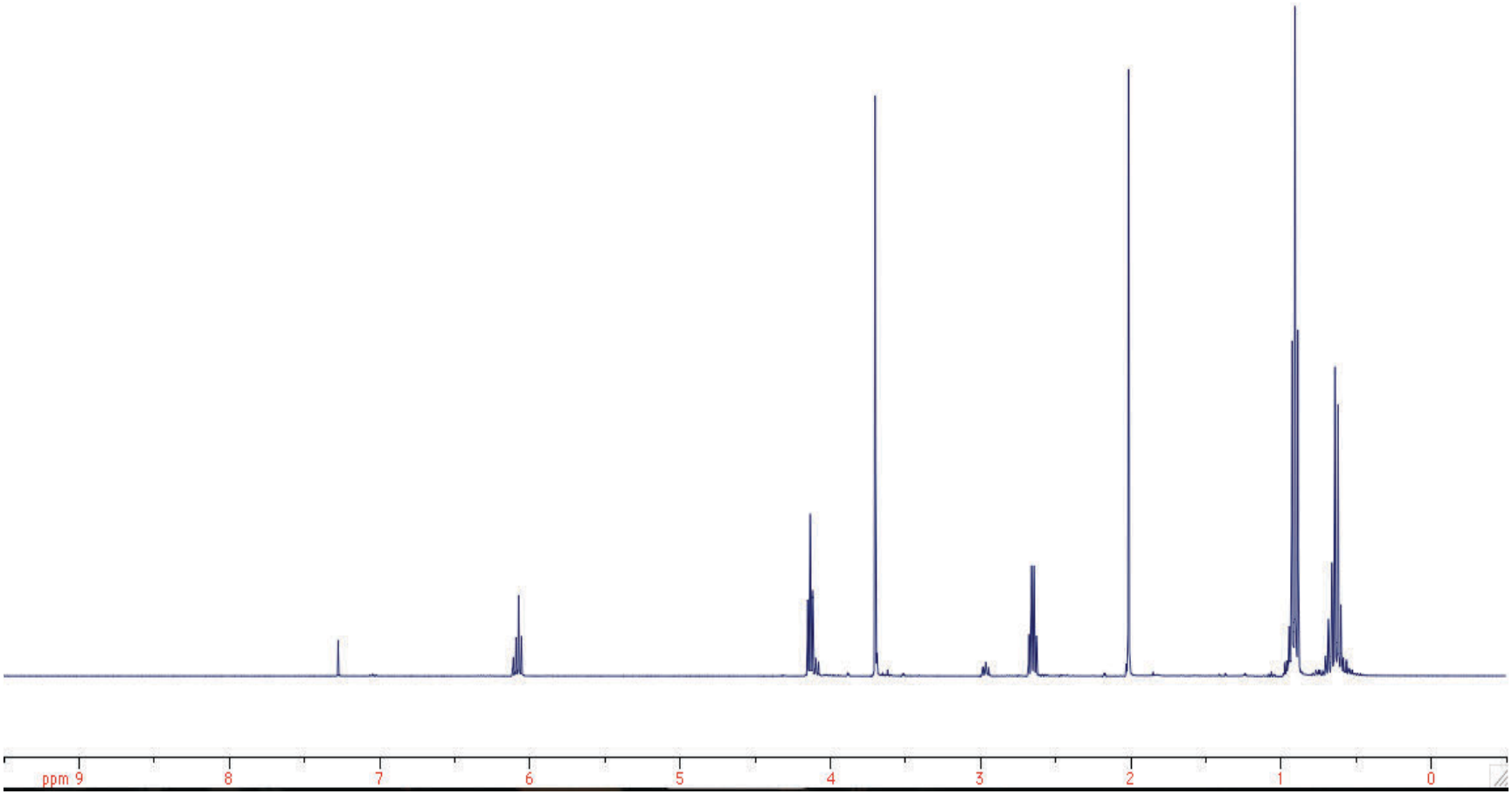
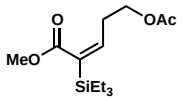


Figure A2.67 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **156**



156

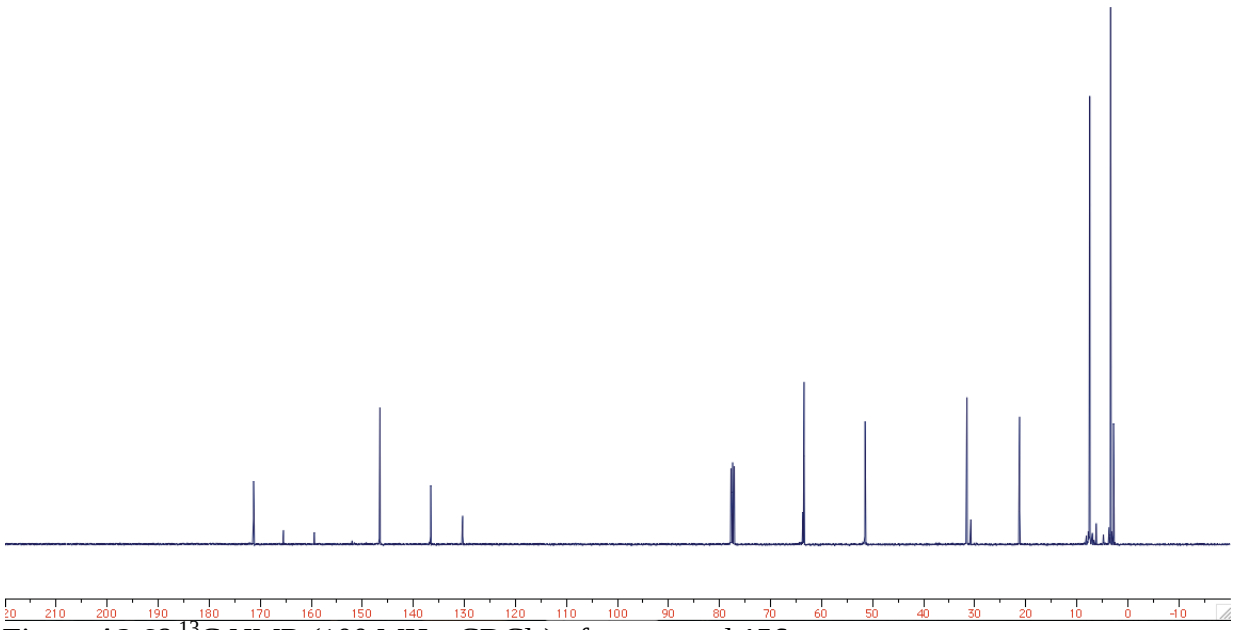


Figure A2.68 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **156**

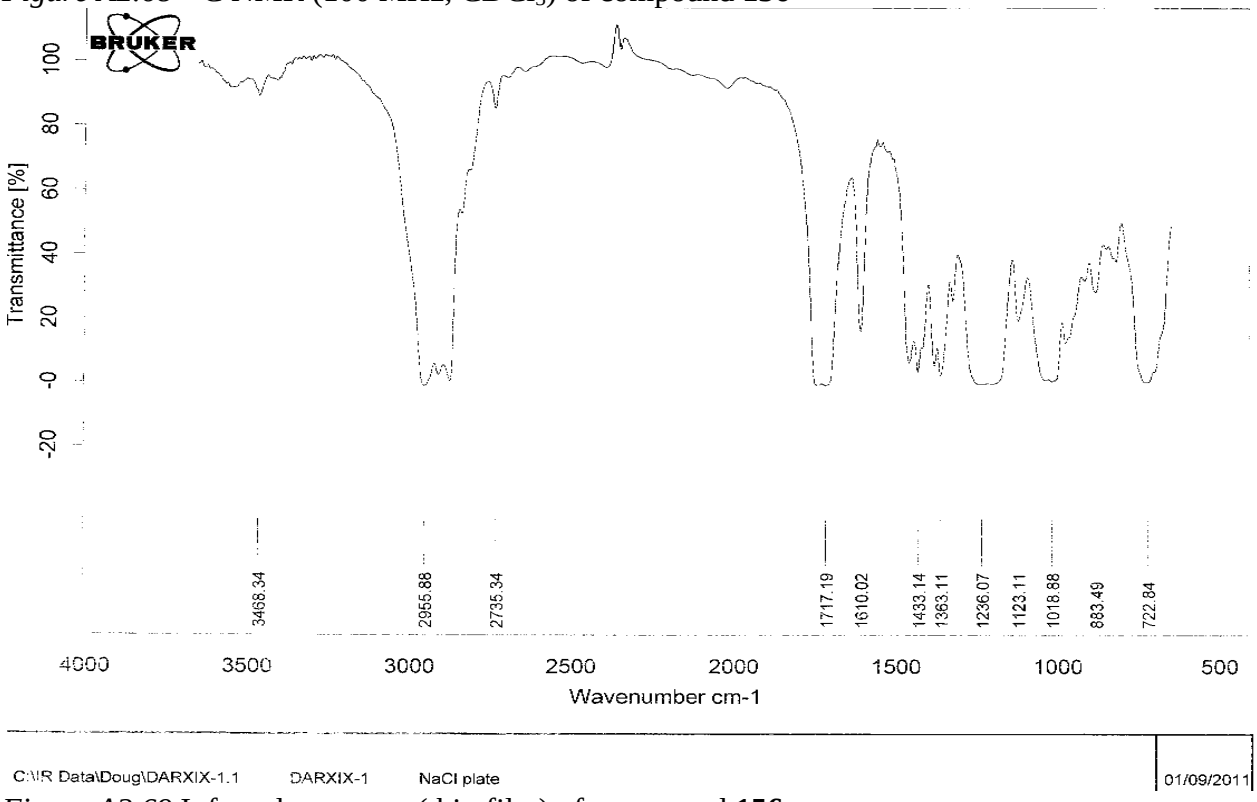
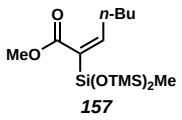


Figure A2.69 Infrared spectrum (thin film) of compound **156**



157

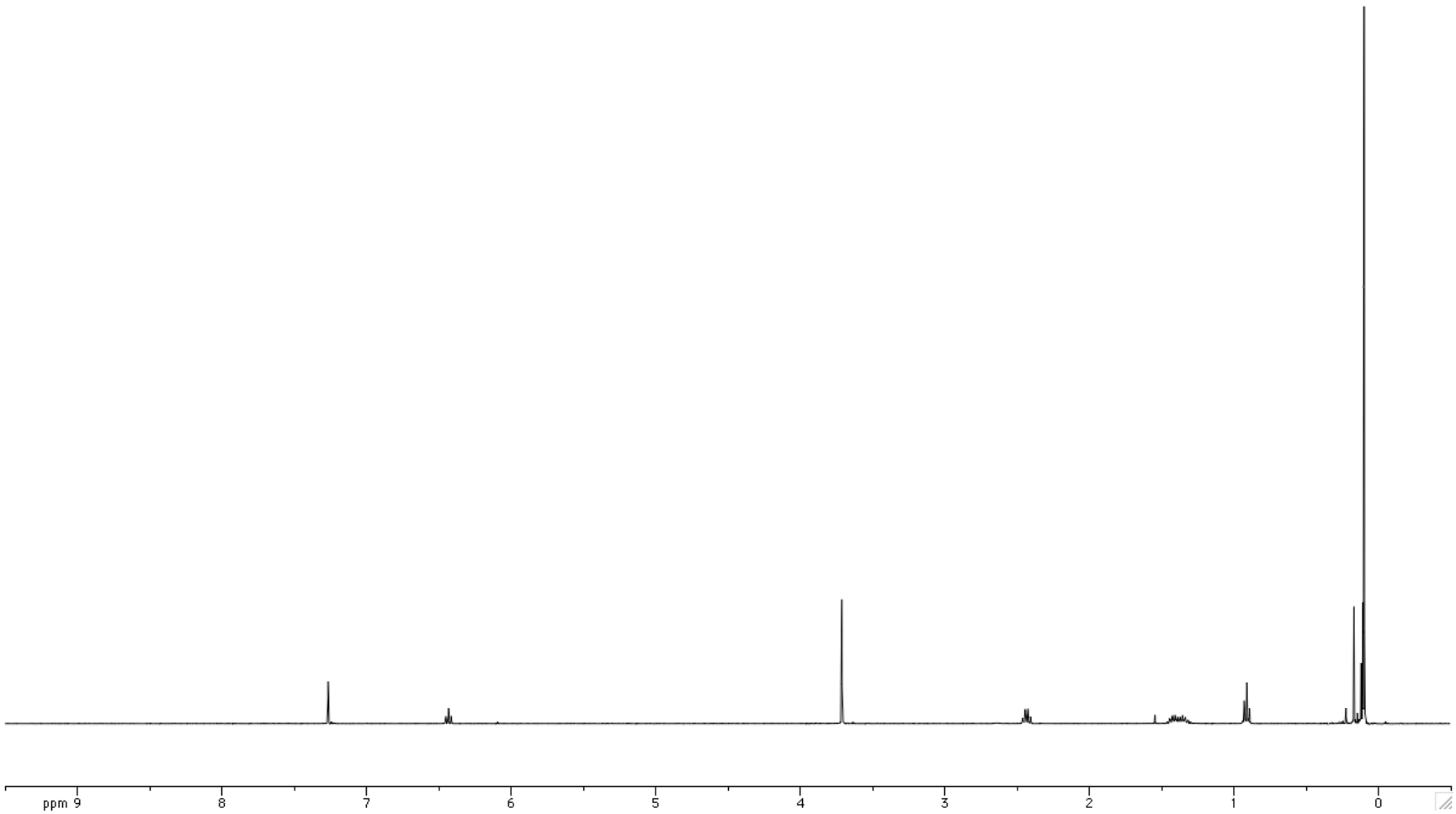


Figure A2.70 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **157**

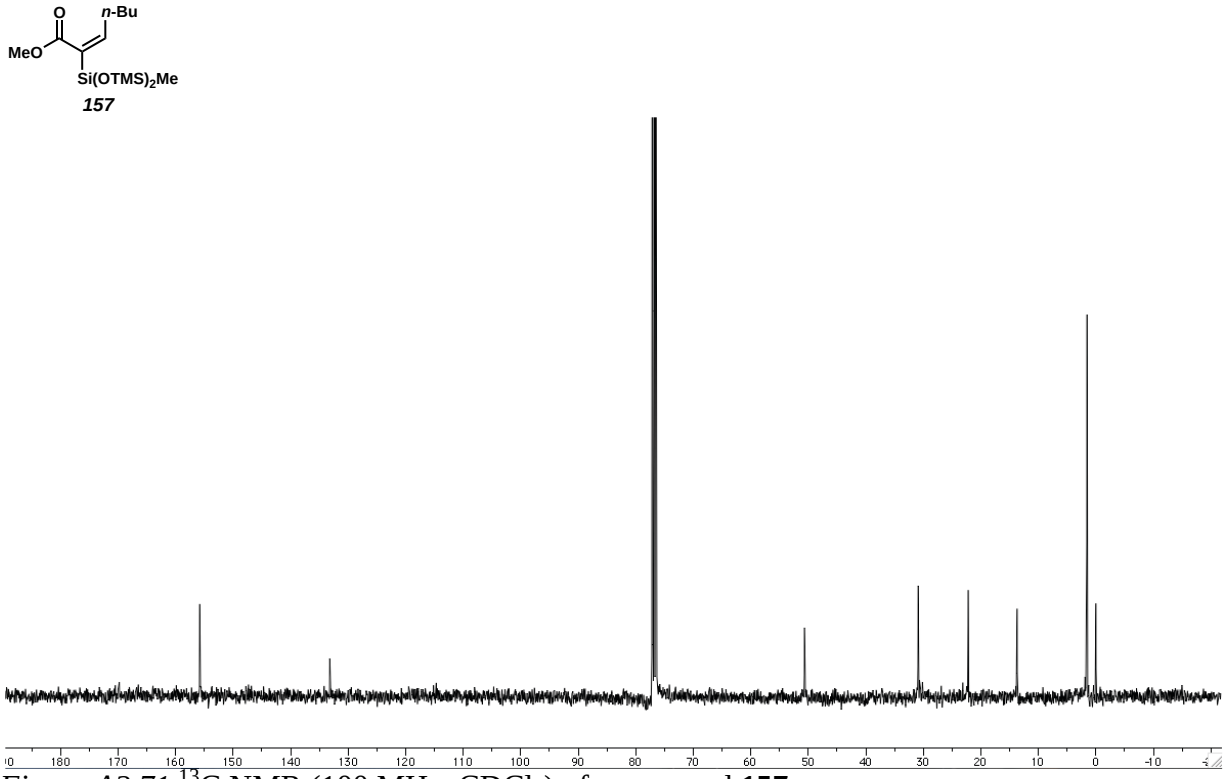


Figure A2.71 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **157**

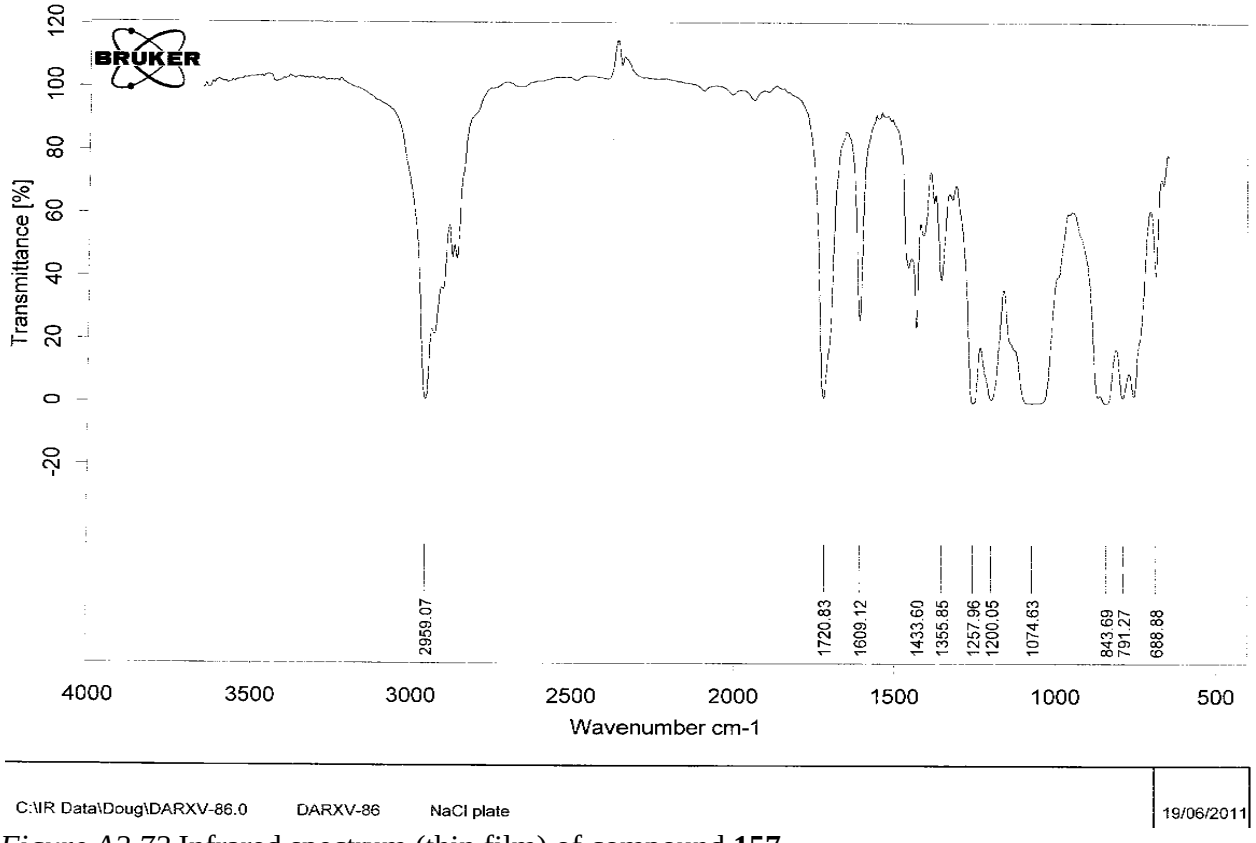
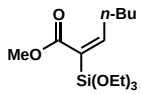


Figure A2.72 Infrared spectrum (thin film) of compound **157**



158

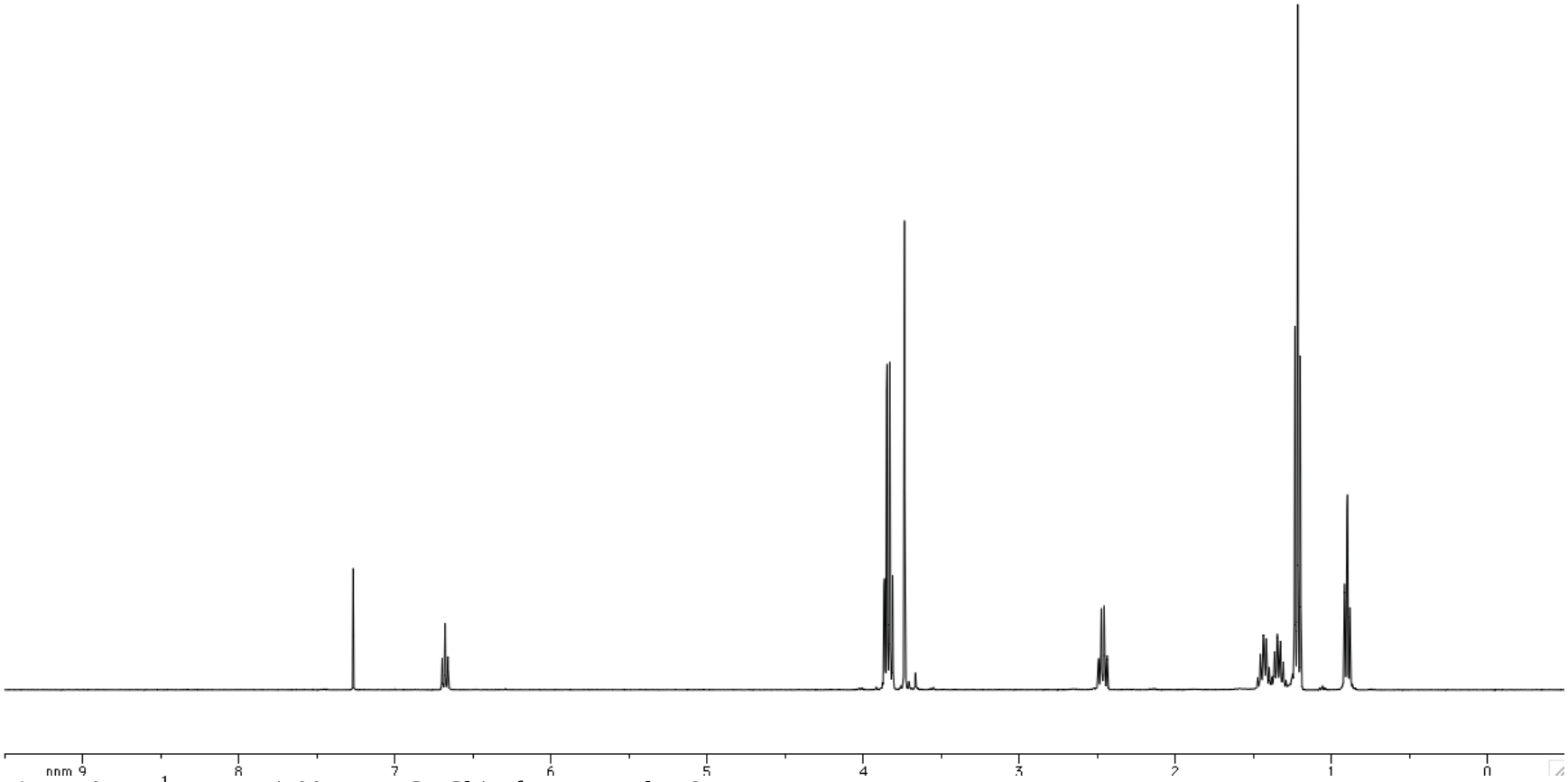
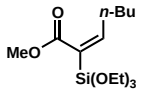


Figure A2.73 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **158**



158

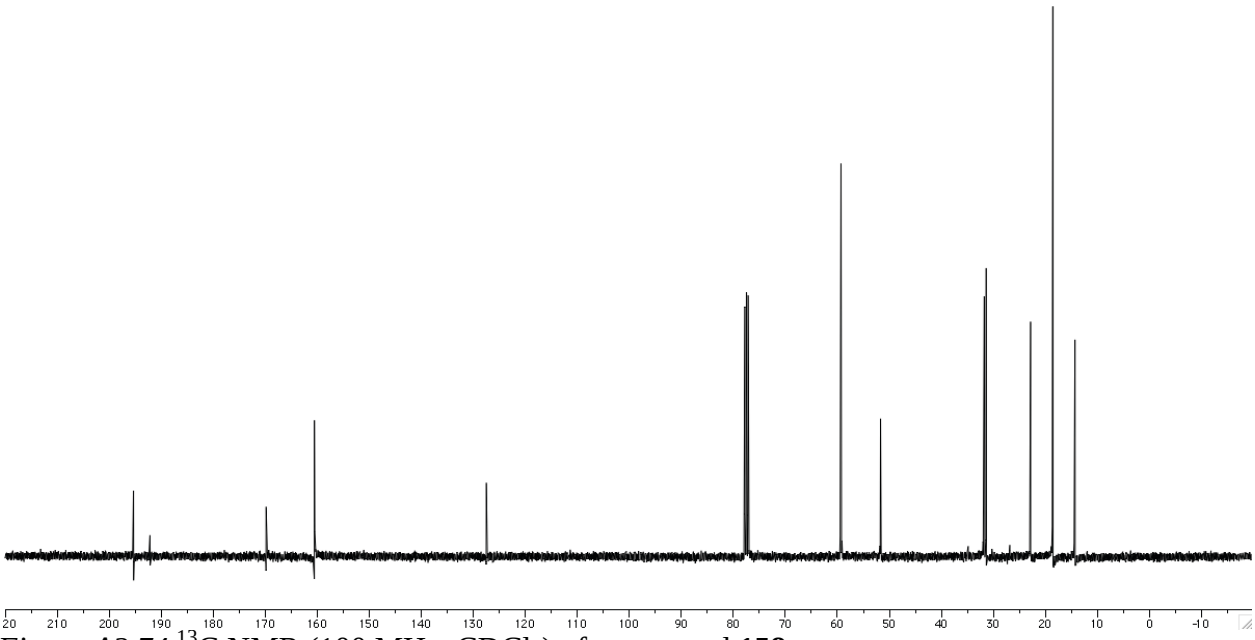


Figure A2.74 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **158**

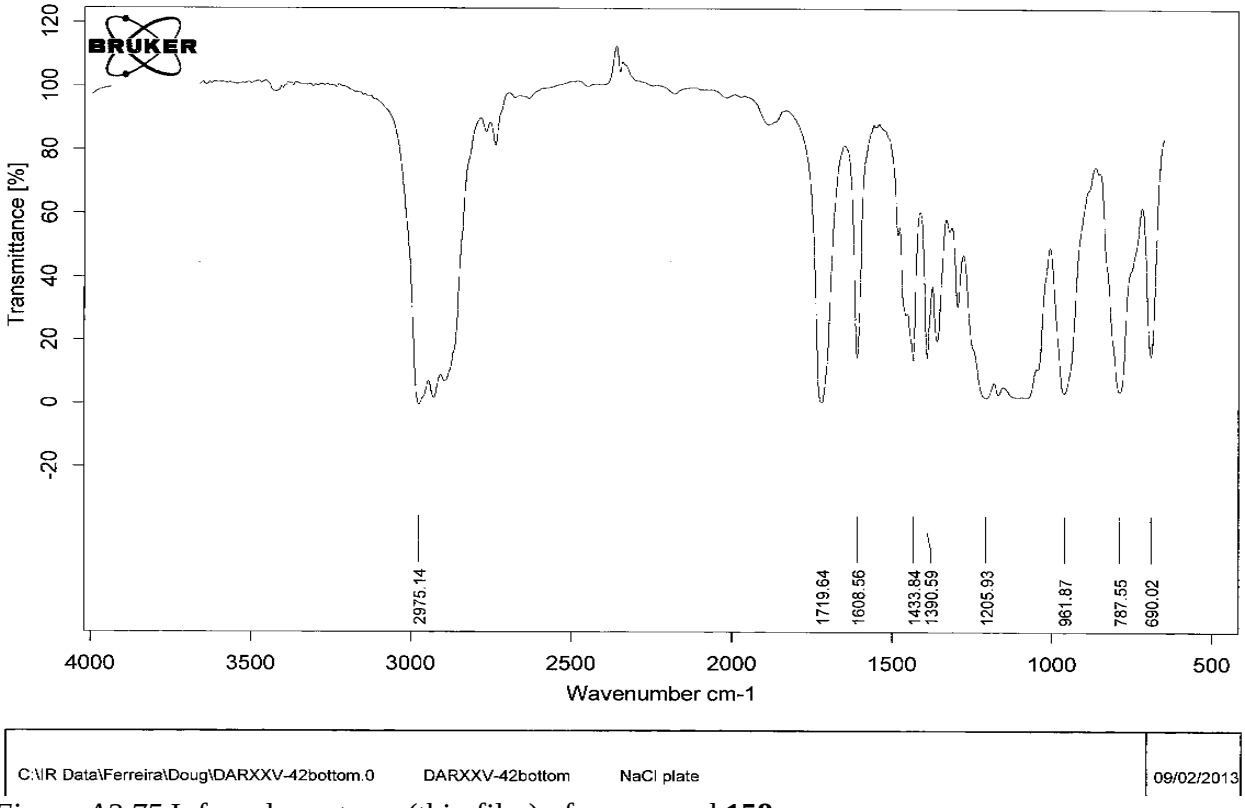
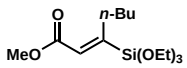


Figure A2.75 Infrared spectrum (thin film) of compound **158**



158b

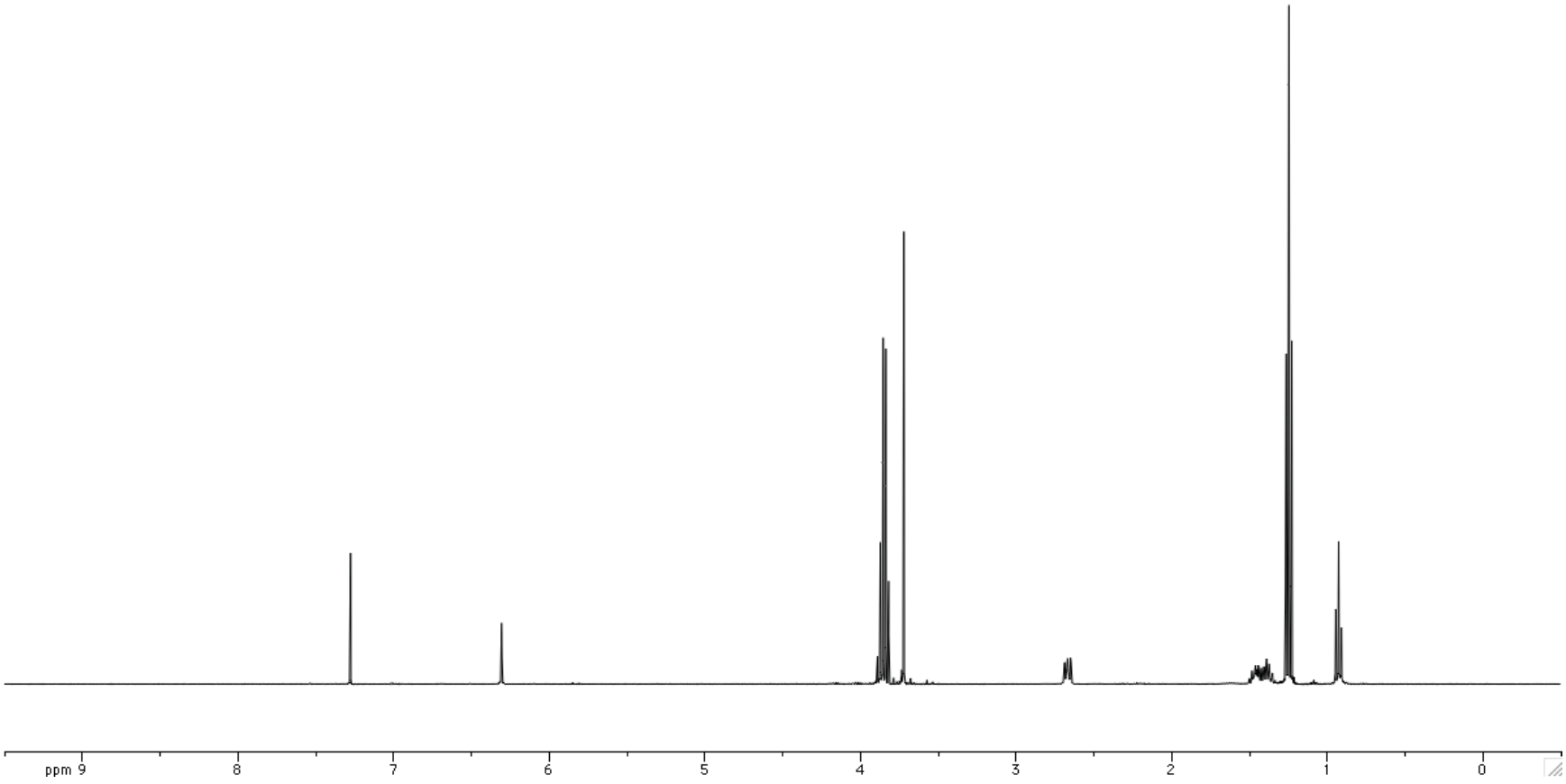
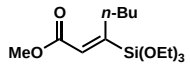


Figure A2.76 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **158b**



158b

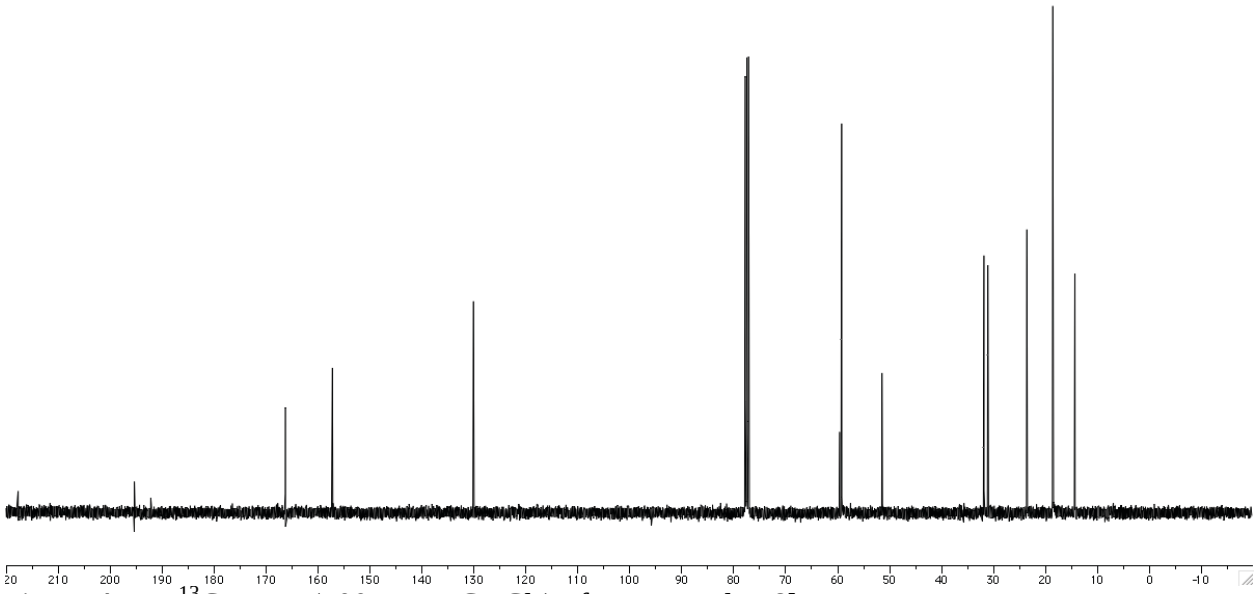


Figure A2.77 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **158b**

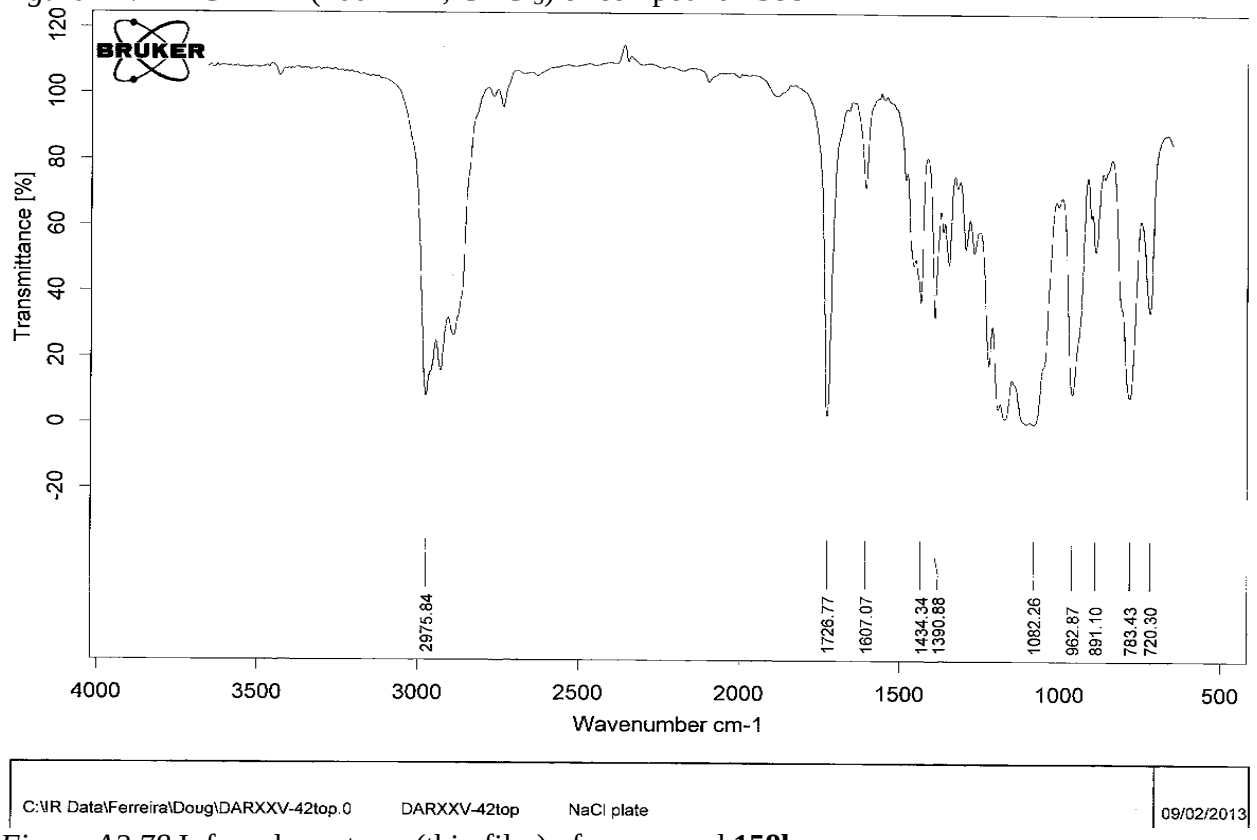
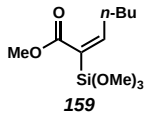


Figure A2.78 Infrared spectrum (thin film) of compound **158b**



159

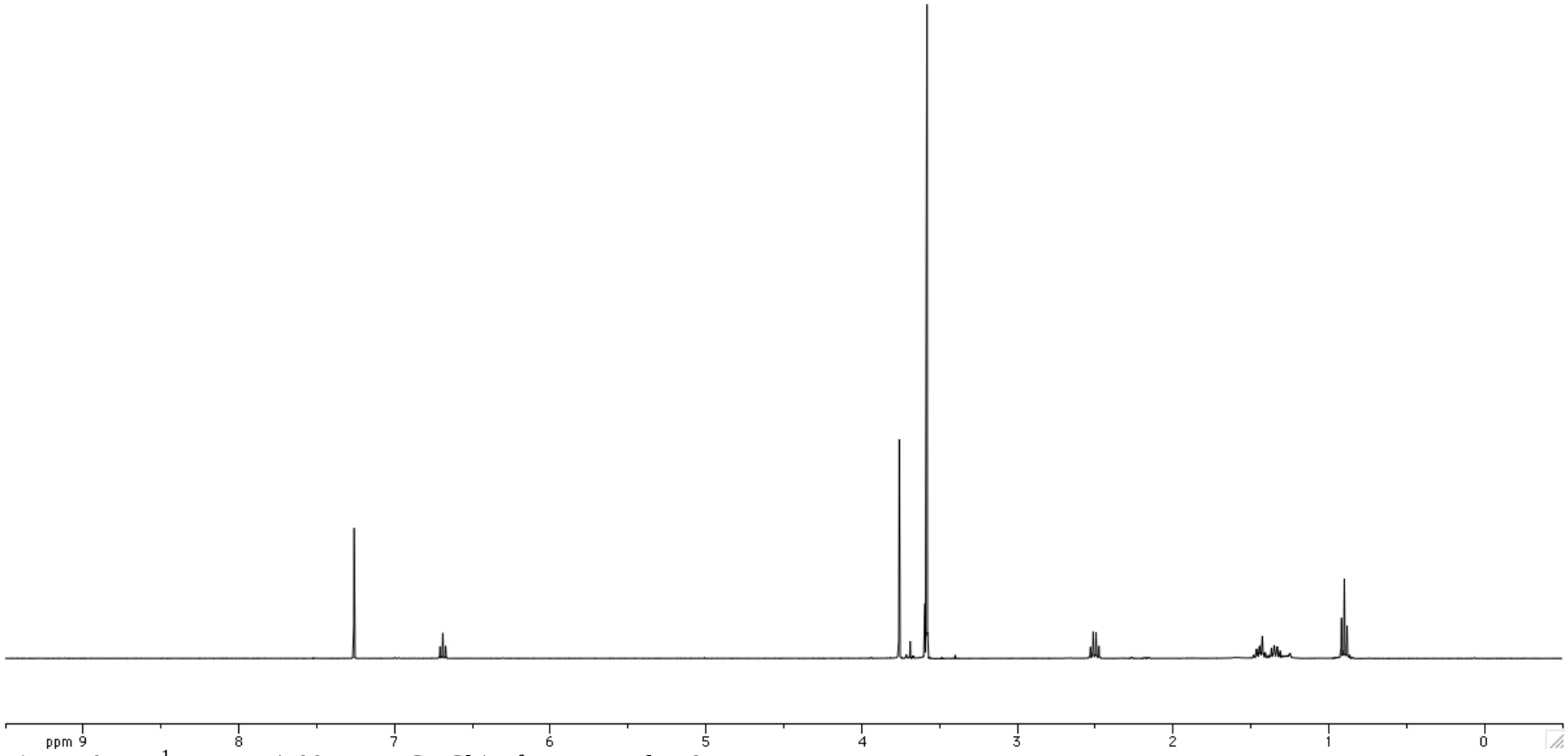


Figure A2.79 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **159**

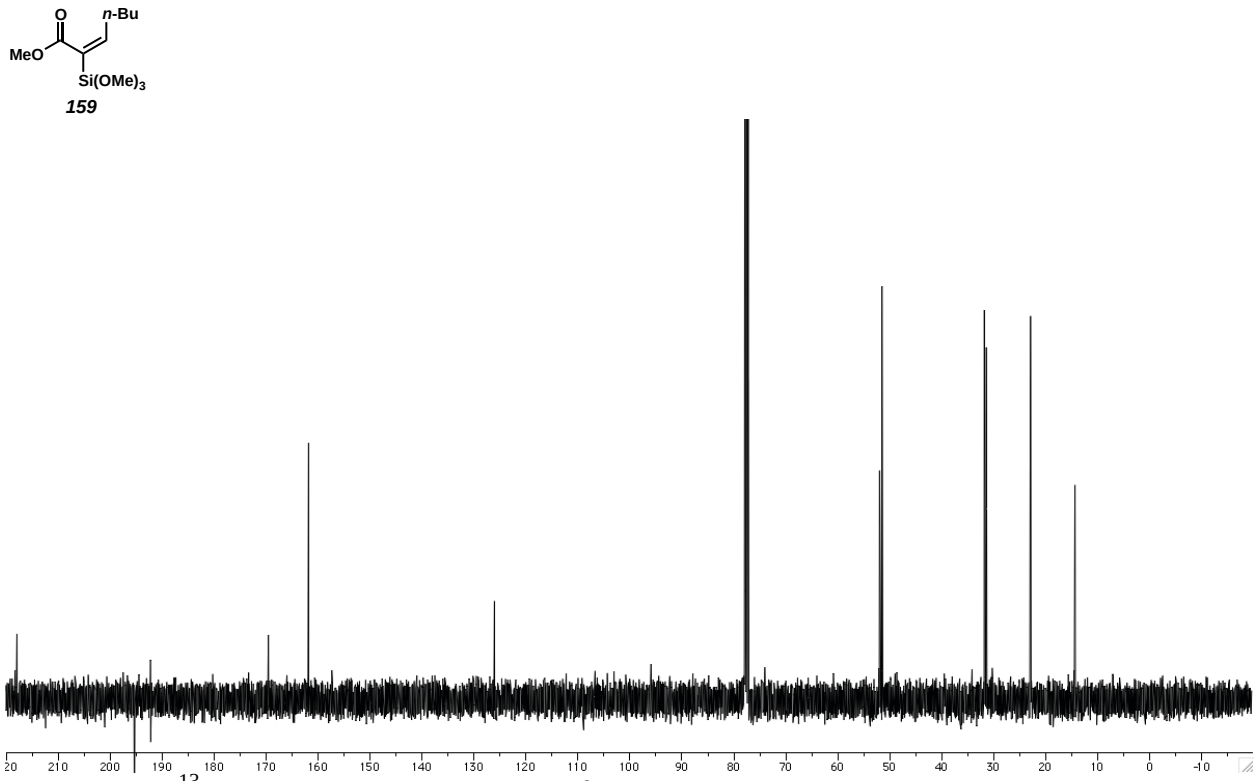


Figure A2.80 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **159**

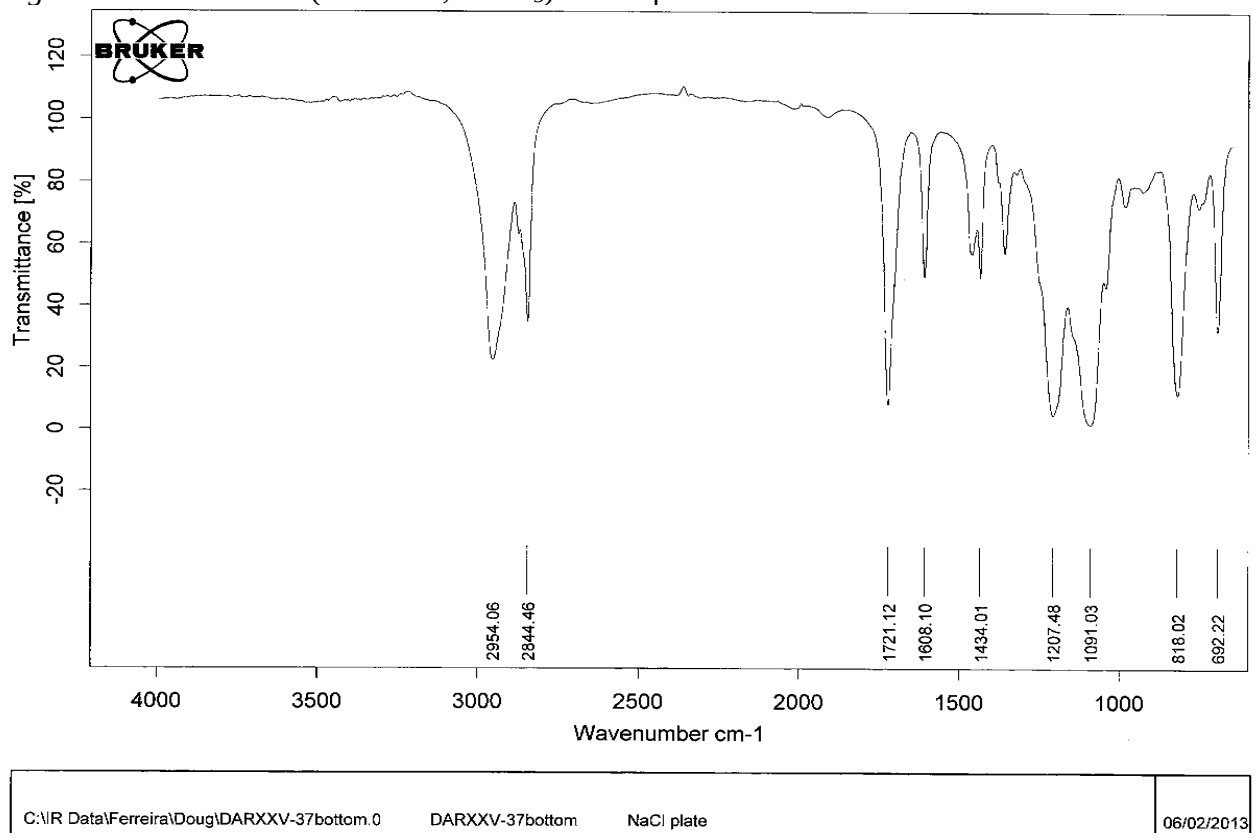
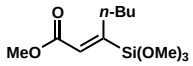


Figure A2.81 Infrared spectrum (thin film) of compound **159**



159b

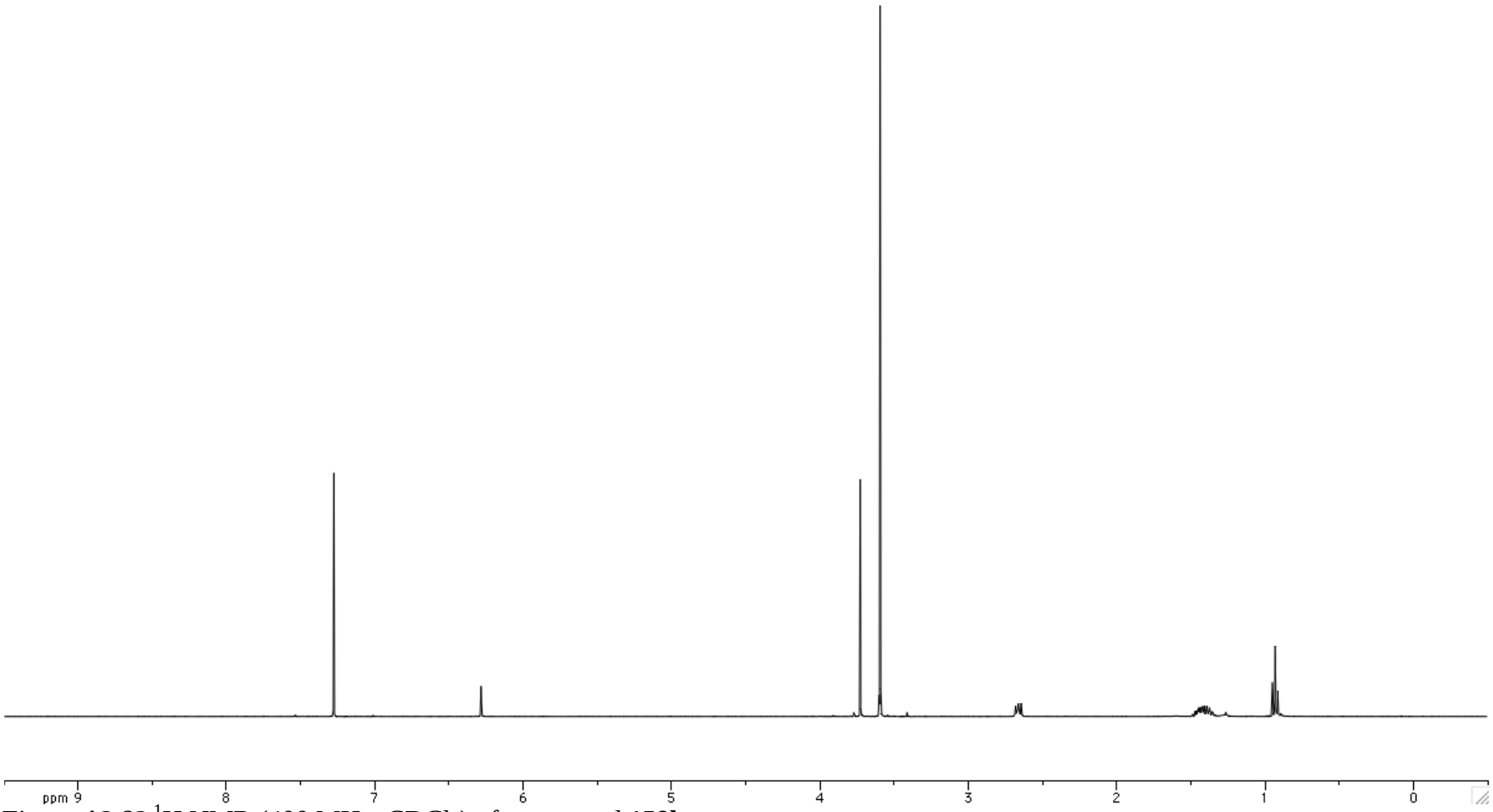
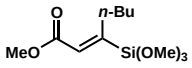


Figure A2.82 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **159b**



159b

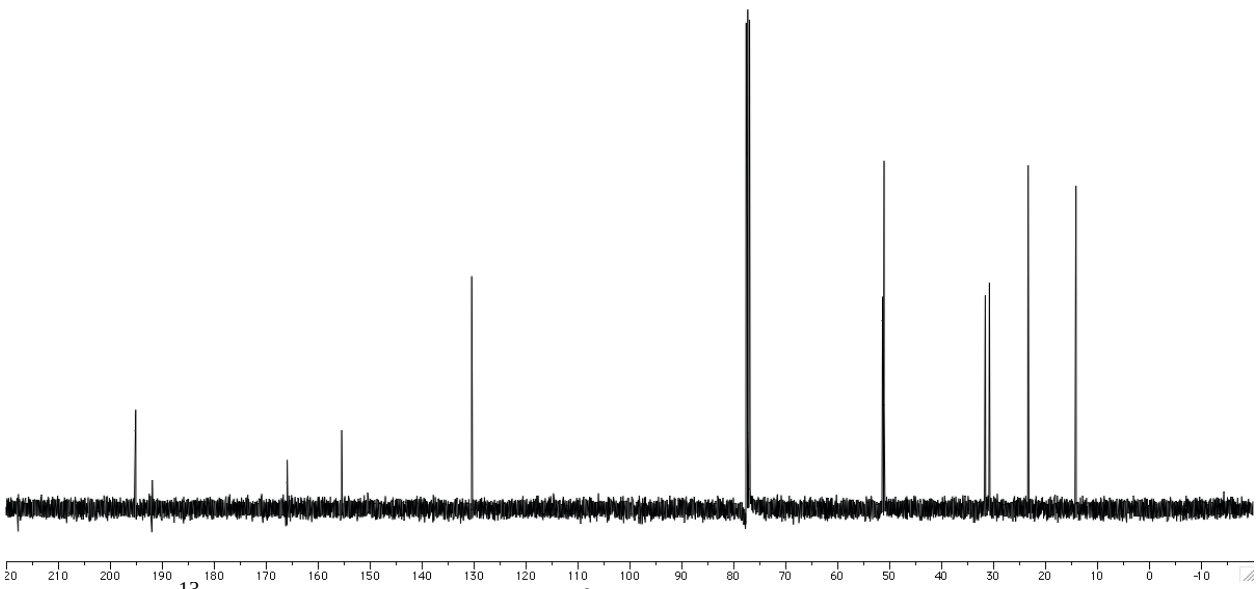


Figure A2.83 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **159b**

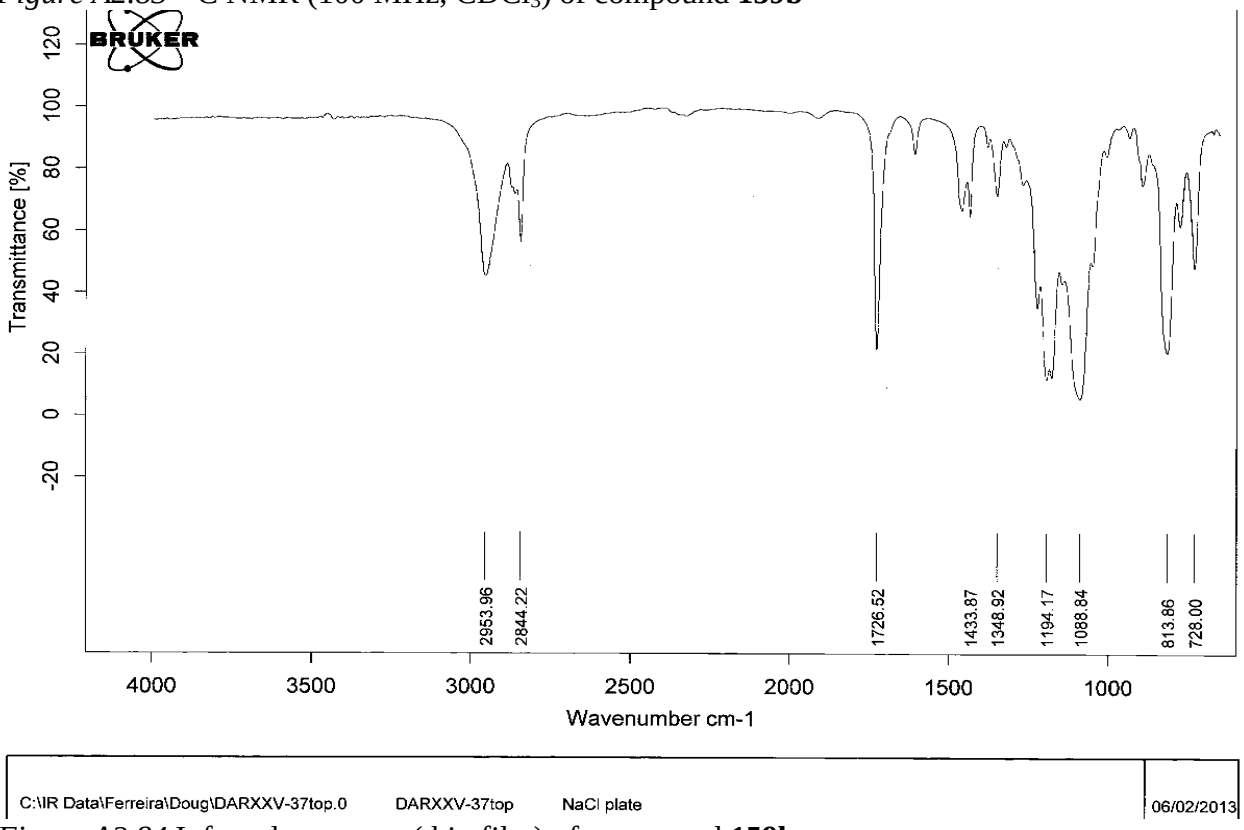
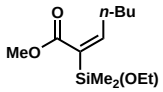


Figure A2.84 Infrared spectrum (thin film) of compound **159b**



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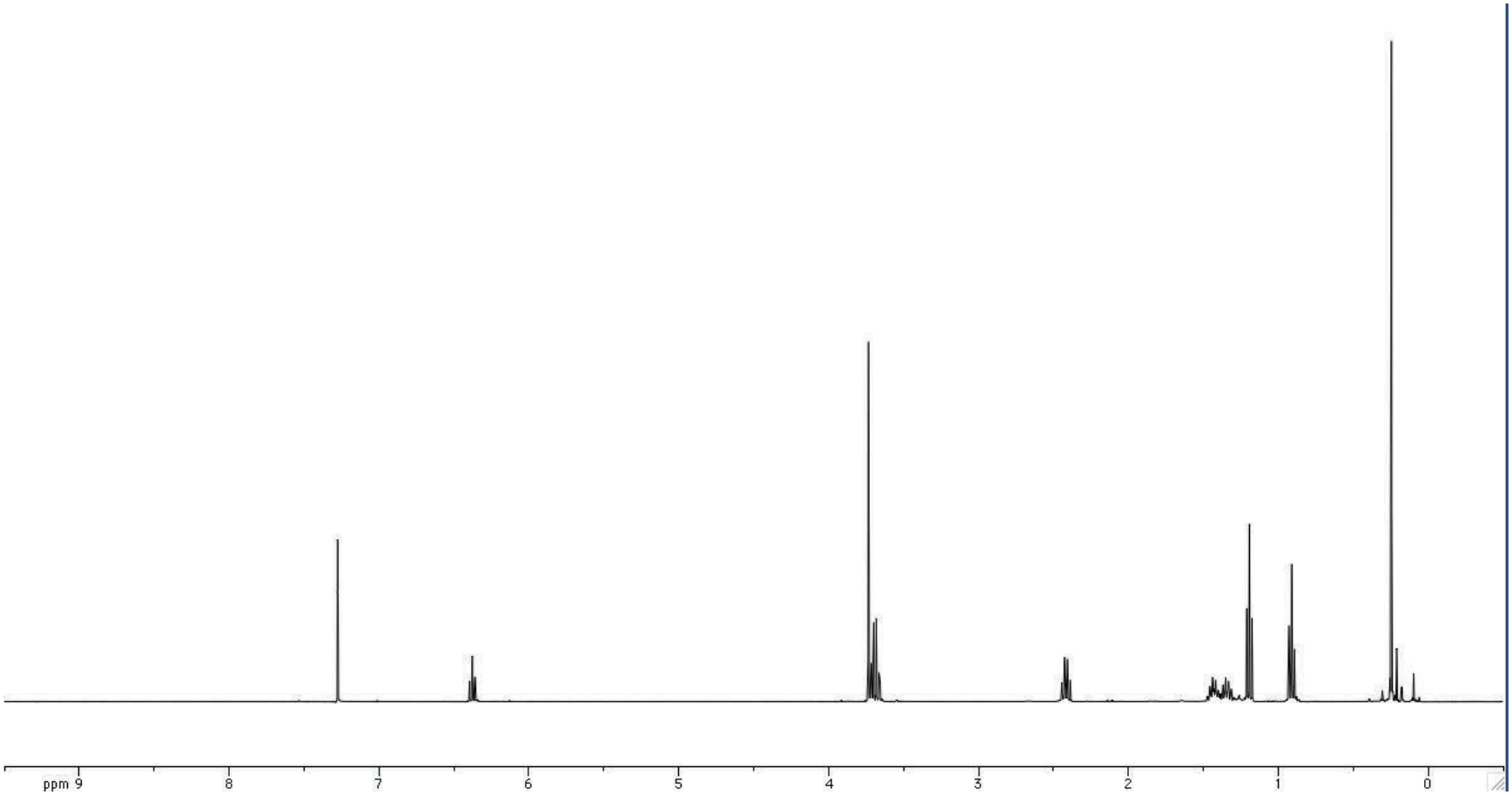
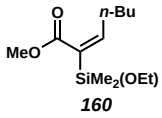


Figure A2.85 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **160**



160

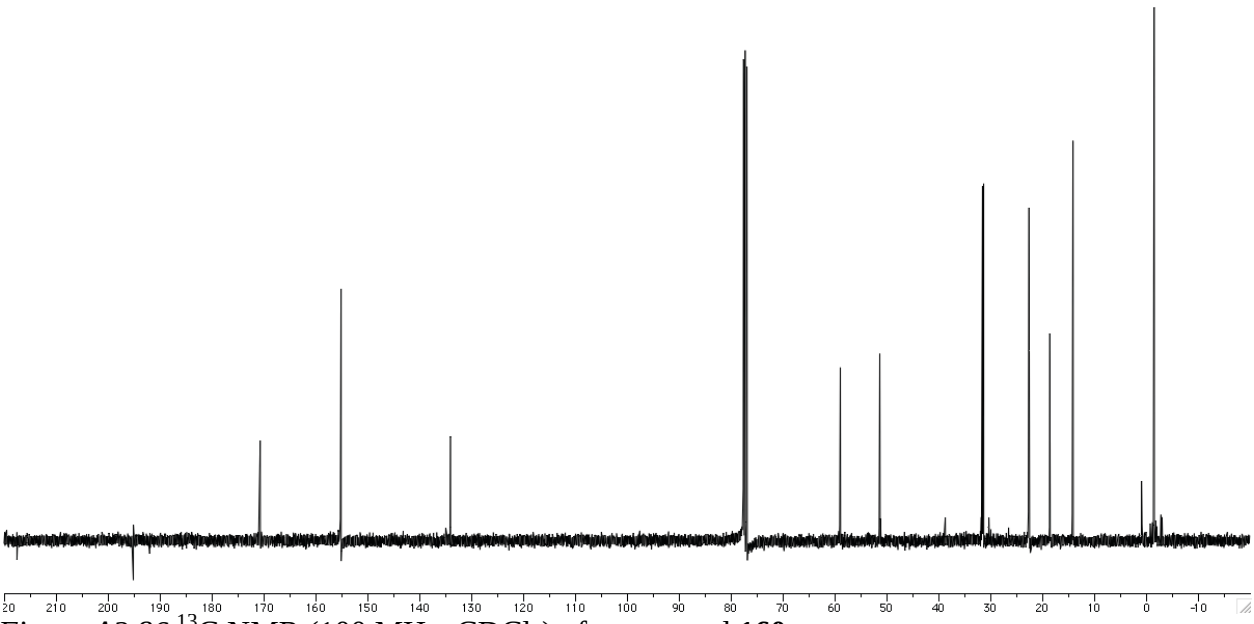


Figure A2.86 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **160**

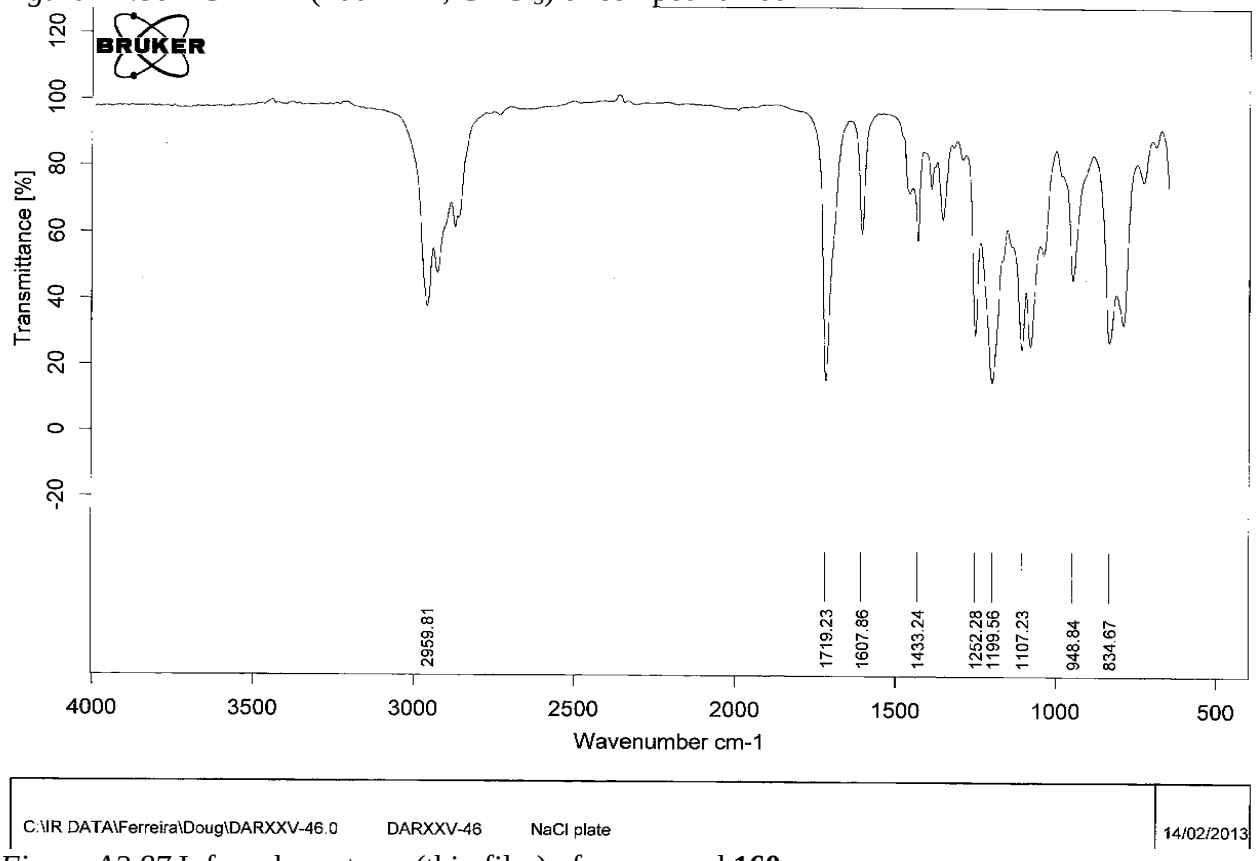
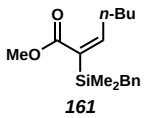


Figure A2.87 Infrared spectrum (thin film) of compound **160**



161

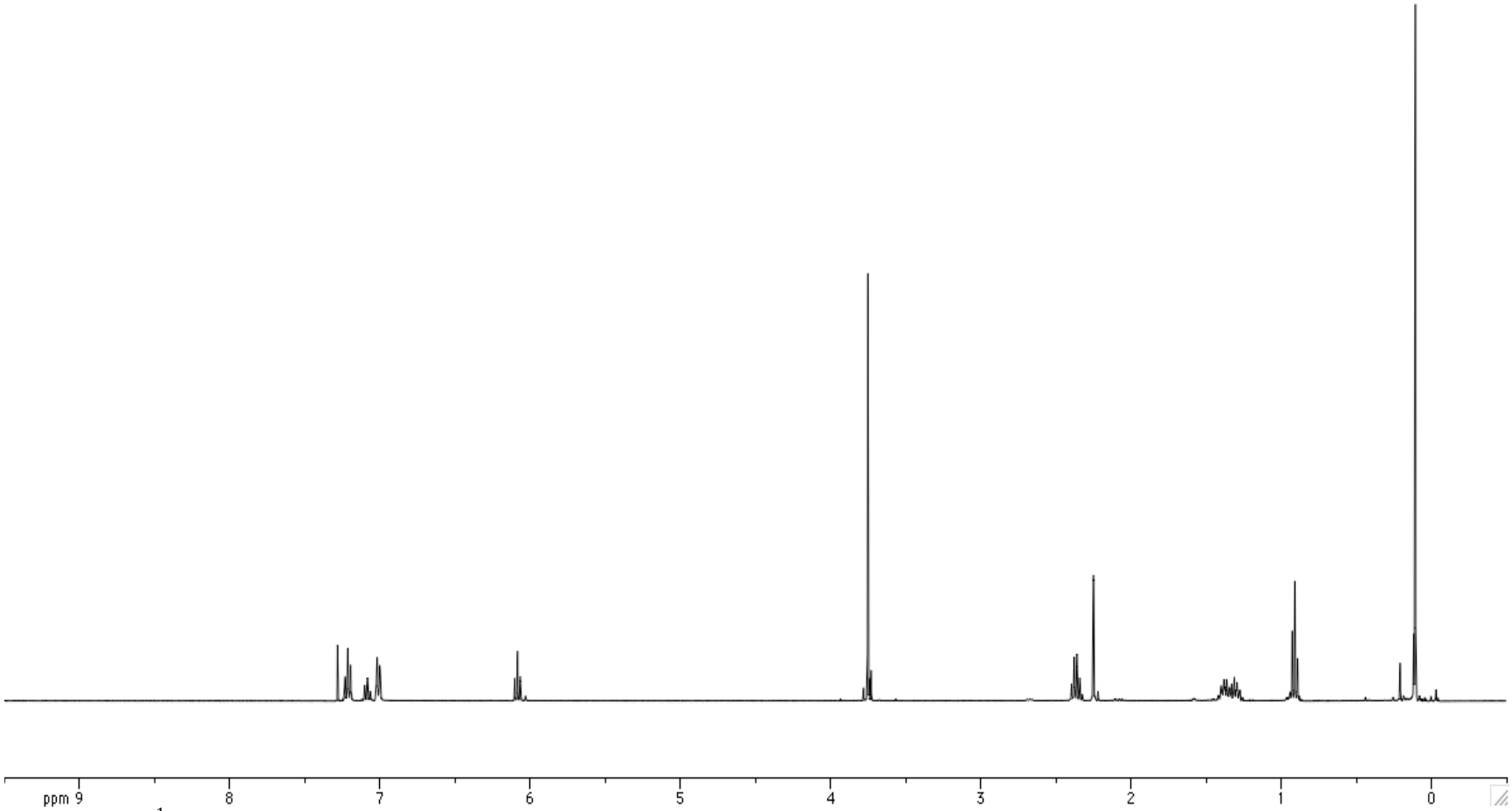


Figure A2.88 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **161**

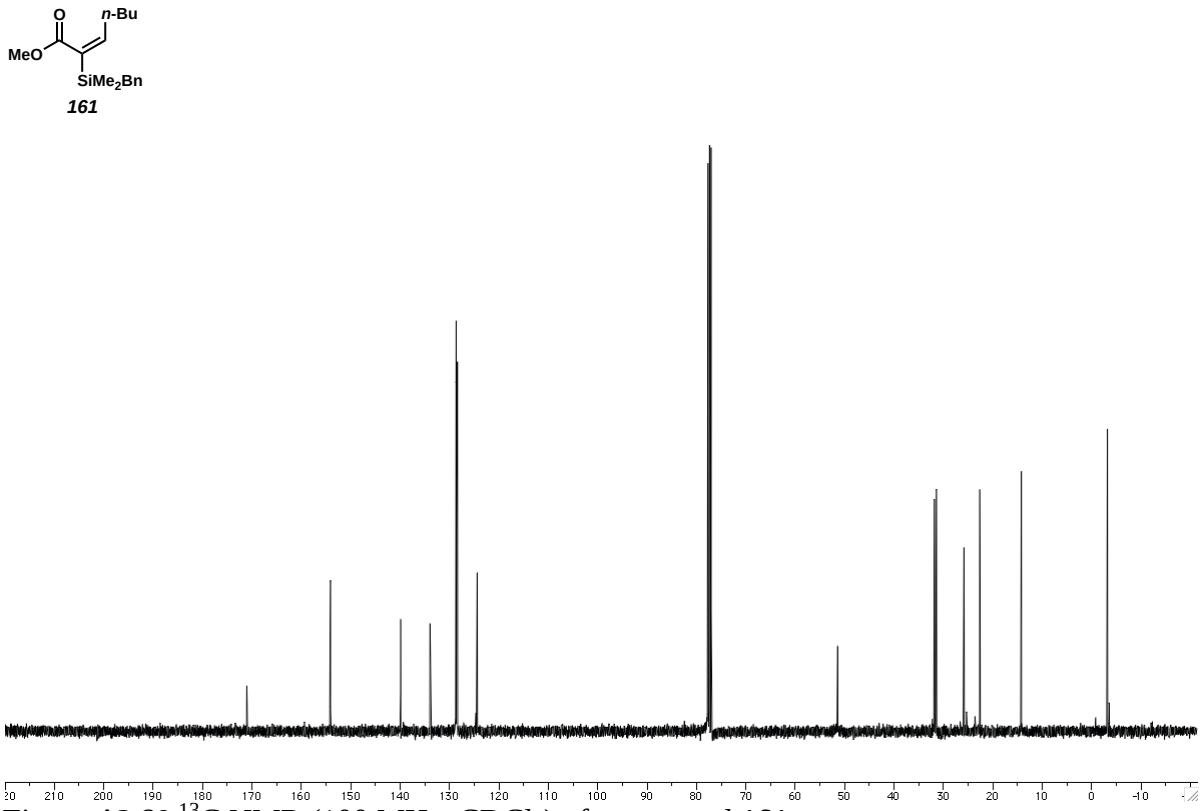


Figure A2.89 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **161**

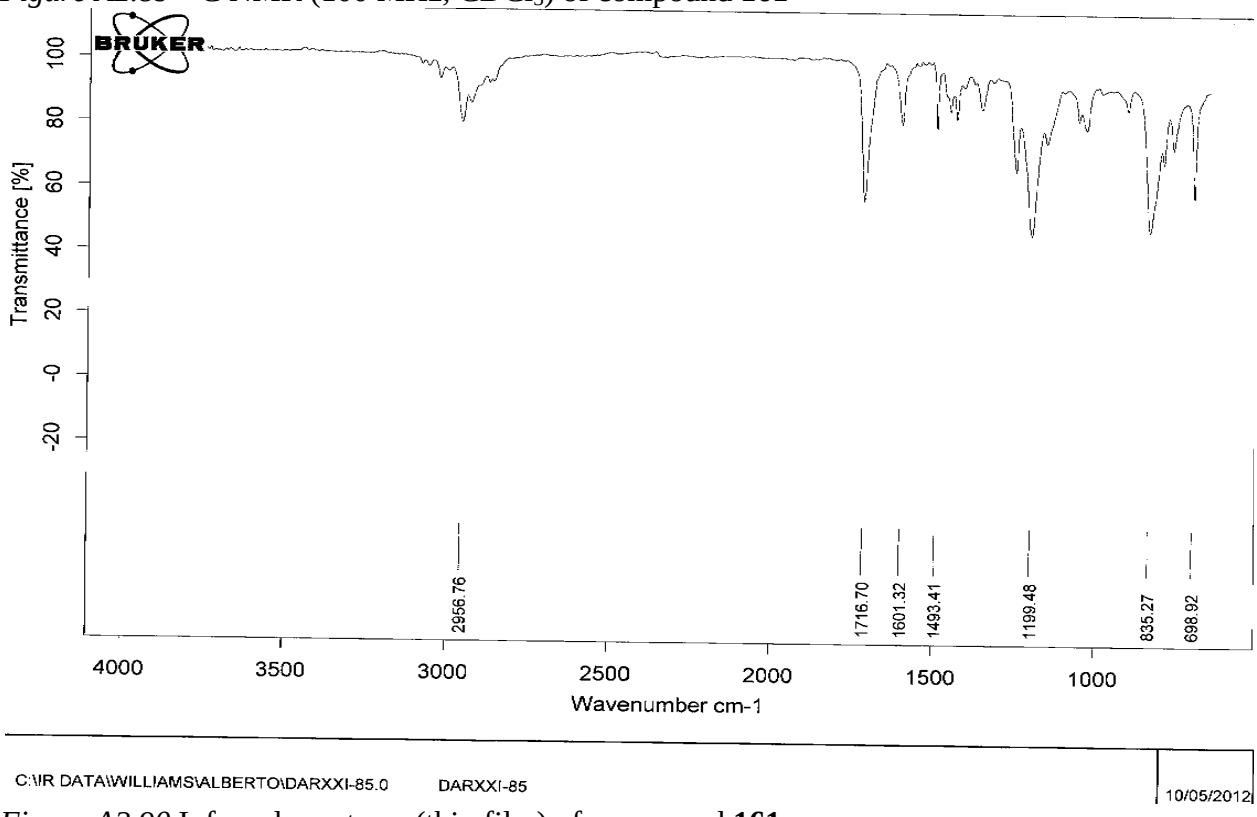
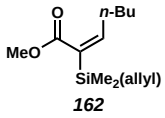


Figure A2.90 Infrared spectrum (thin film) of compound **161**



162

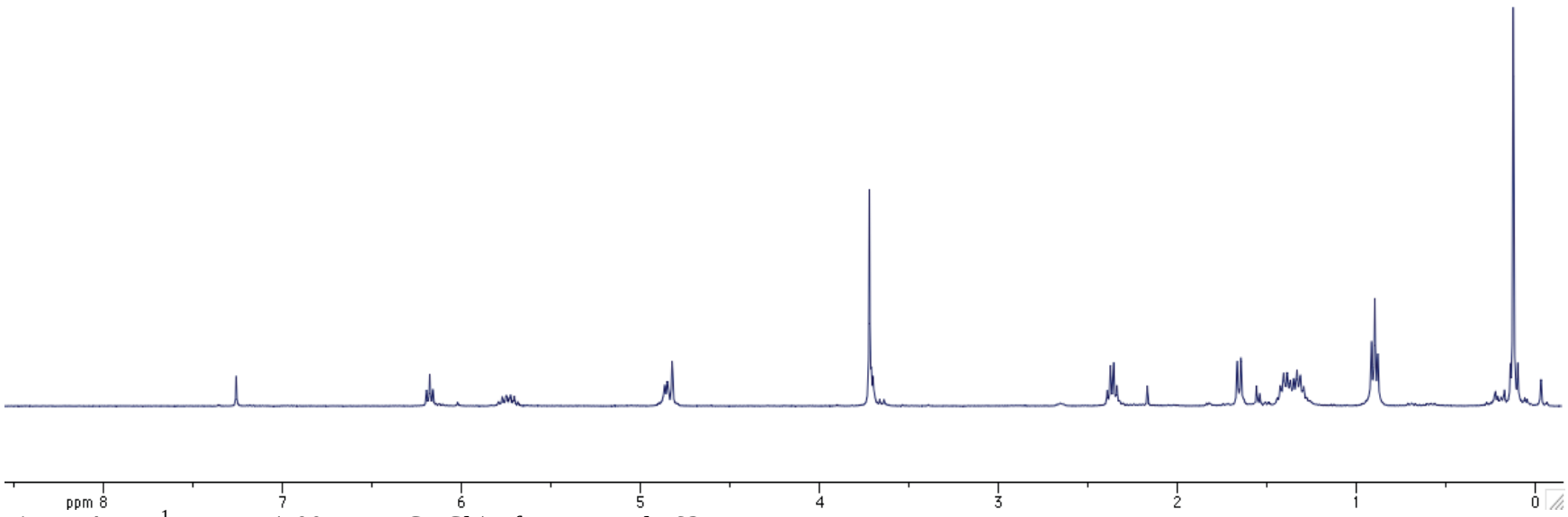


Figure A2.91 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **162**

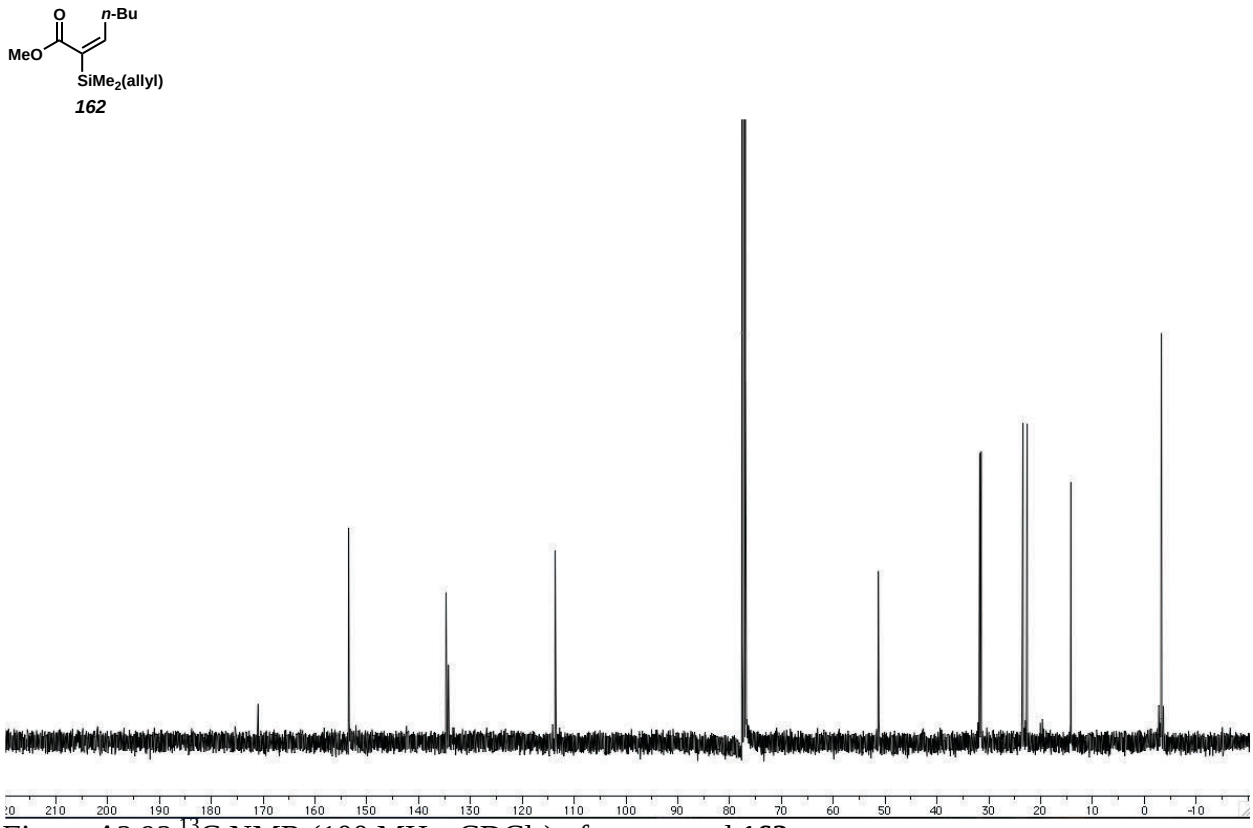


Figure A2.92 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **162**

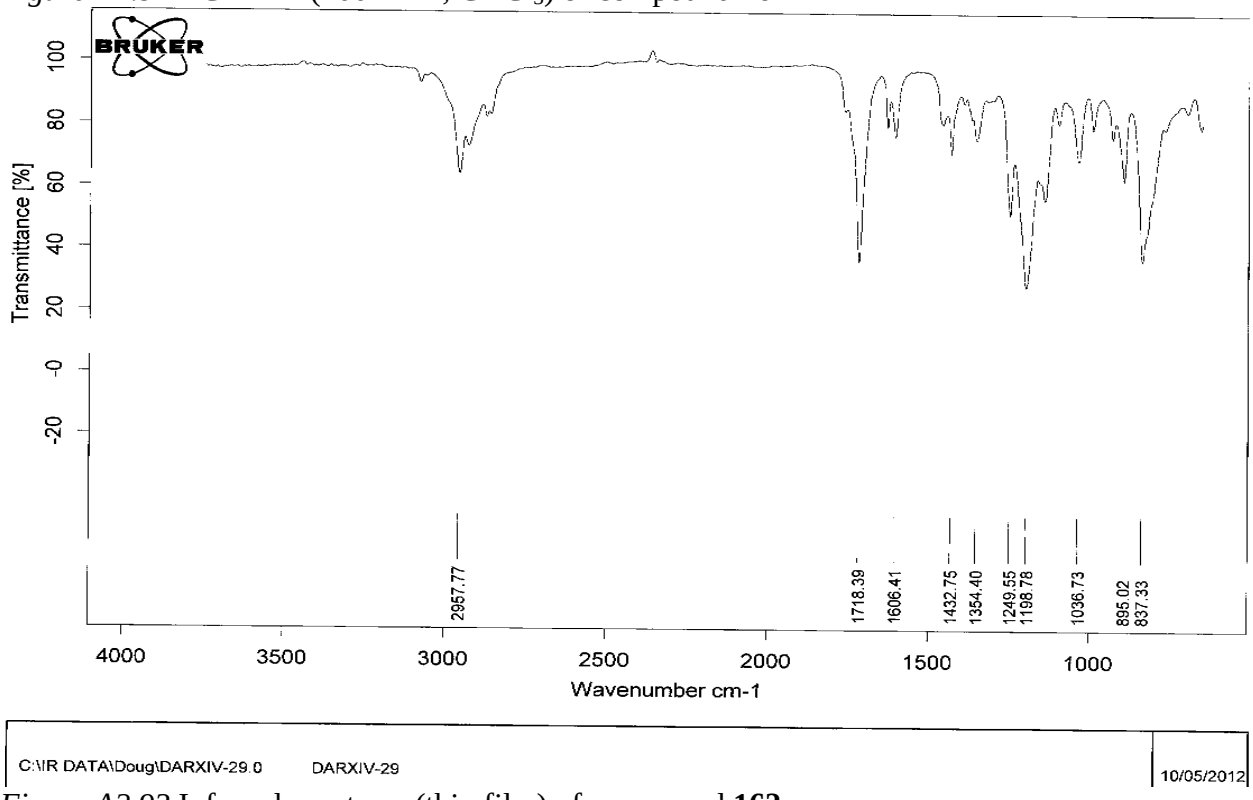
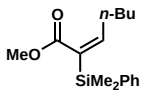


Figure A2.93 Infrared spectrum (thin film) of compound **162**



163

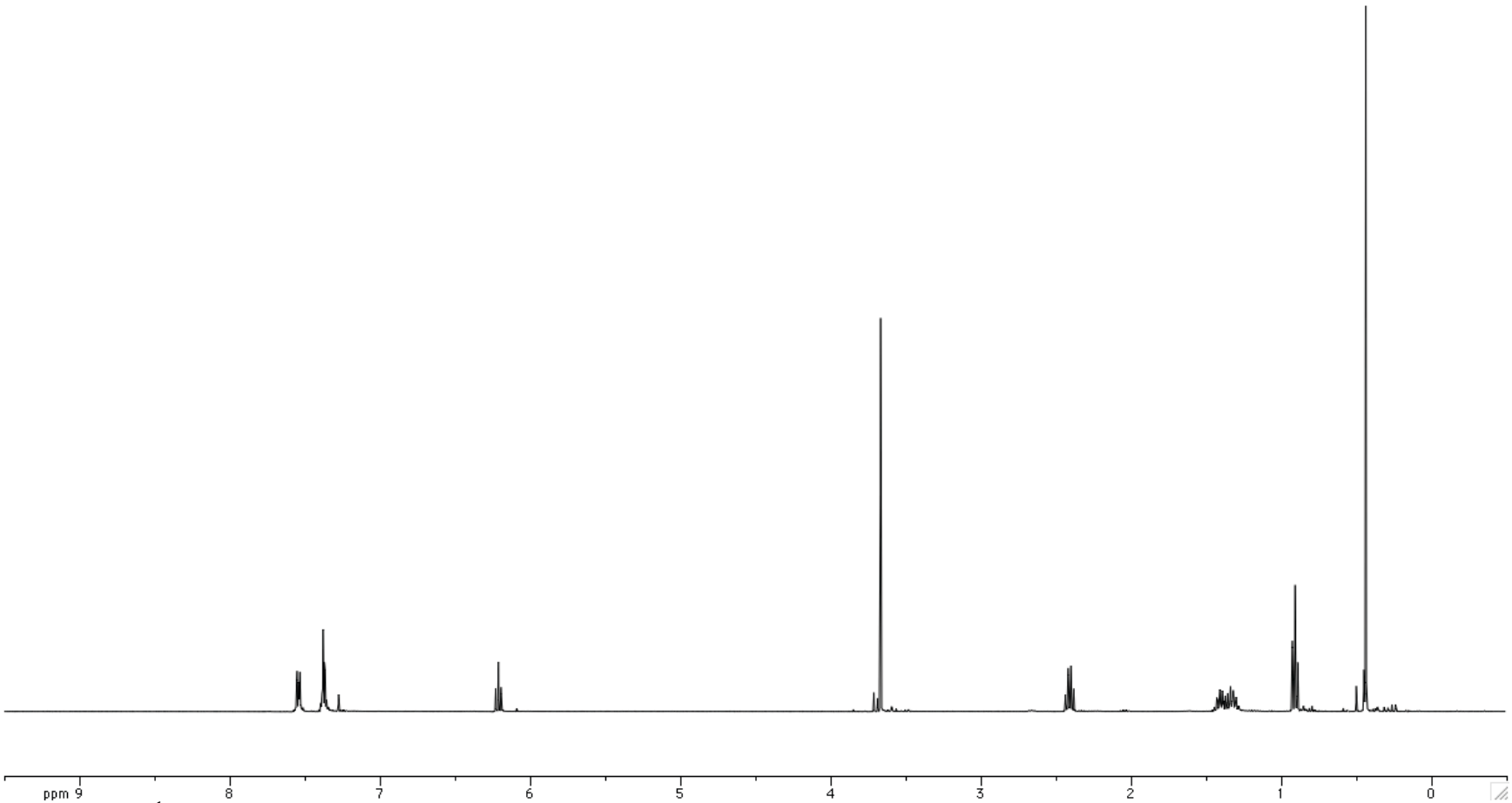
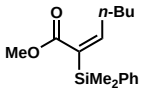


Figure A2.94 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **163**



163

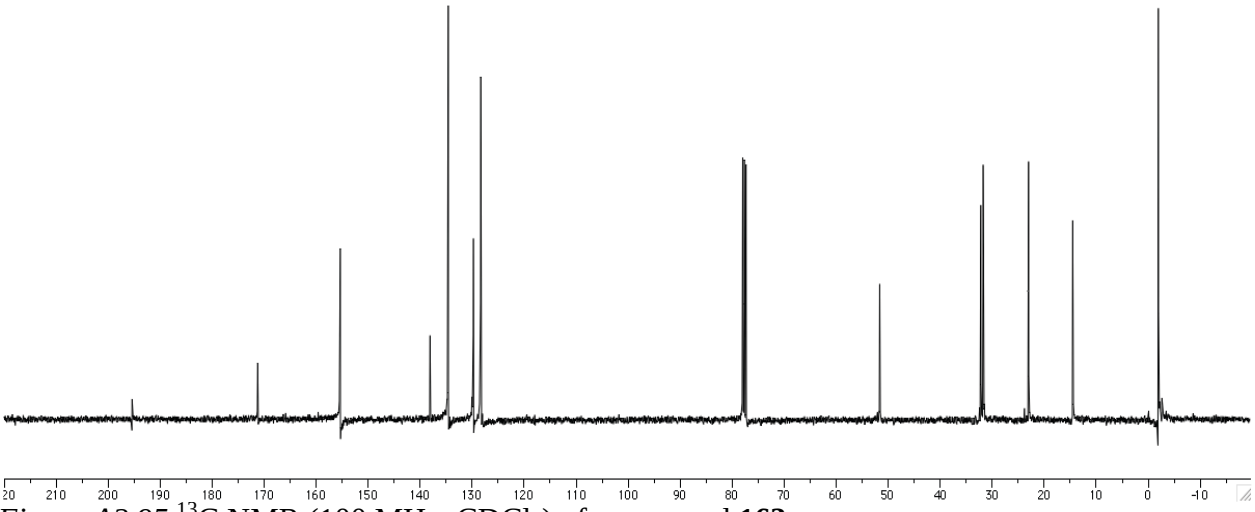


Figure A2.95 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **163**

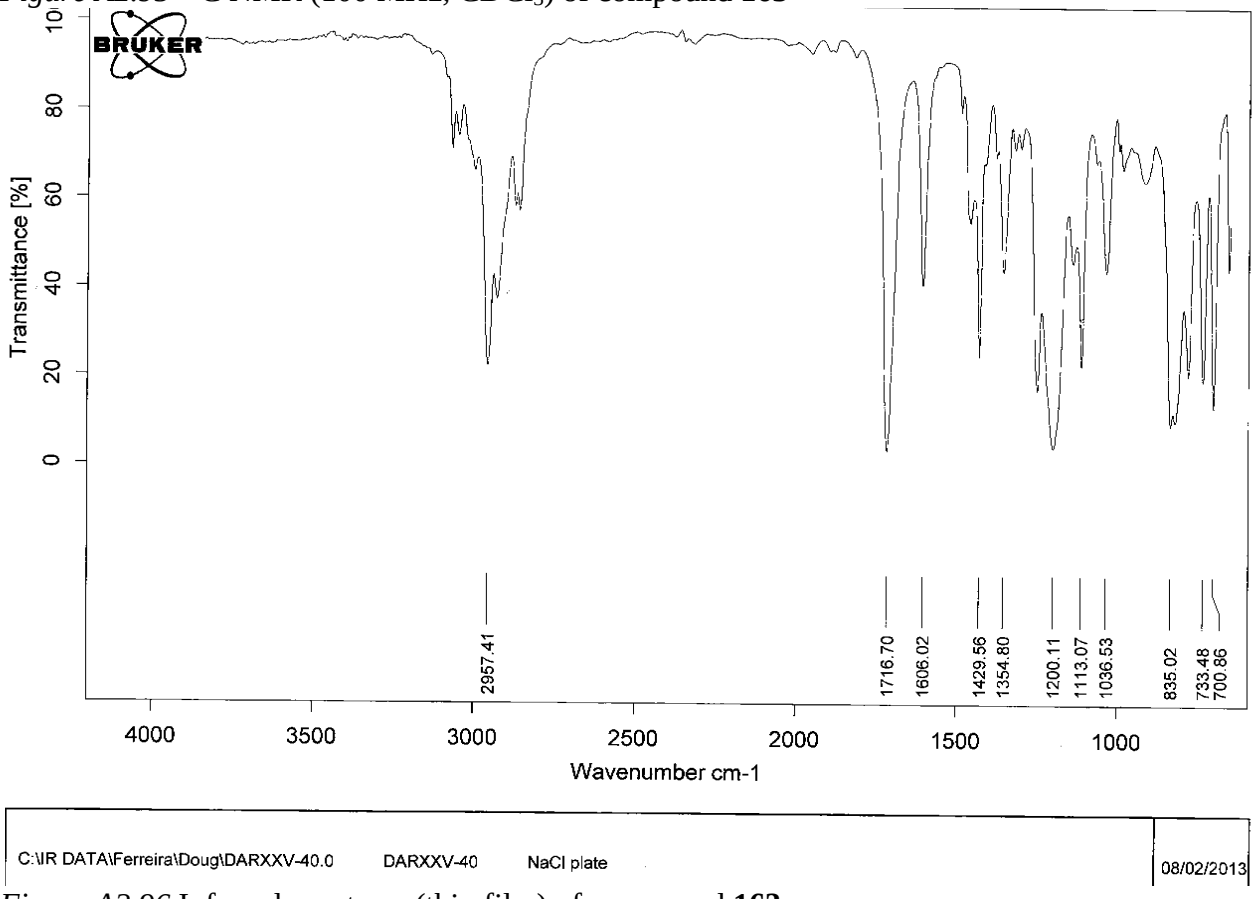
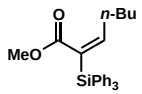


Figure A2.96 Infrared spectrum (thin film) of compound **163**



164

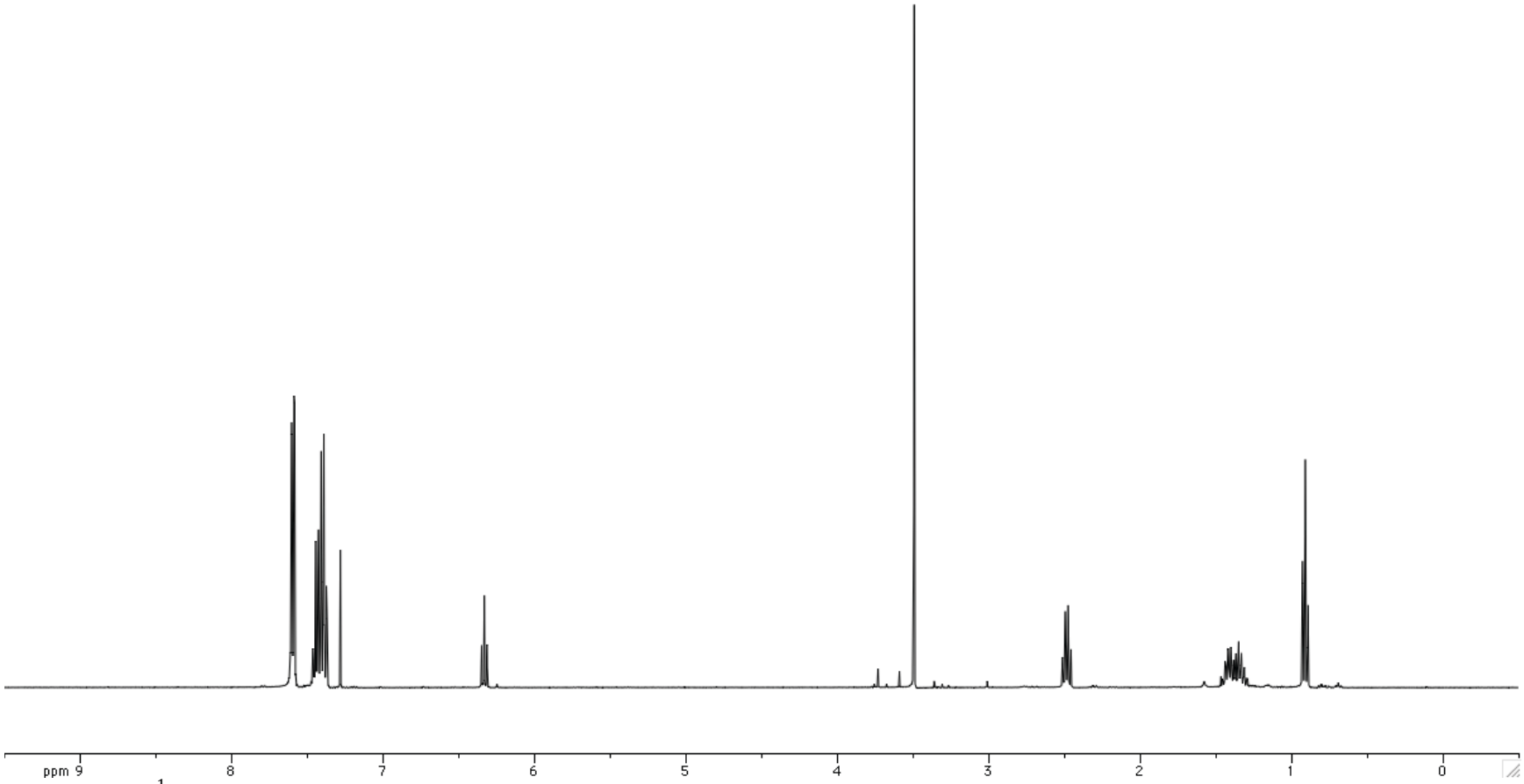


Figure A2.97 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **164**

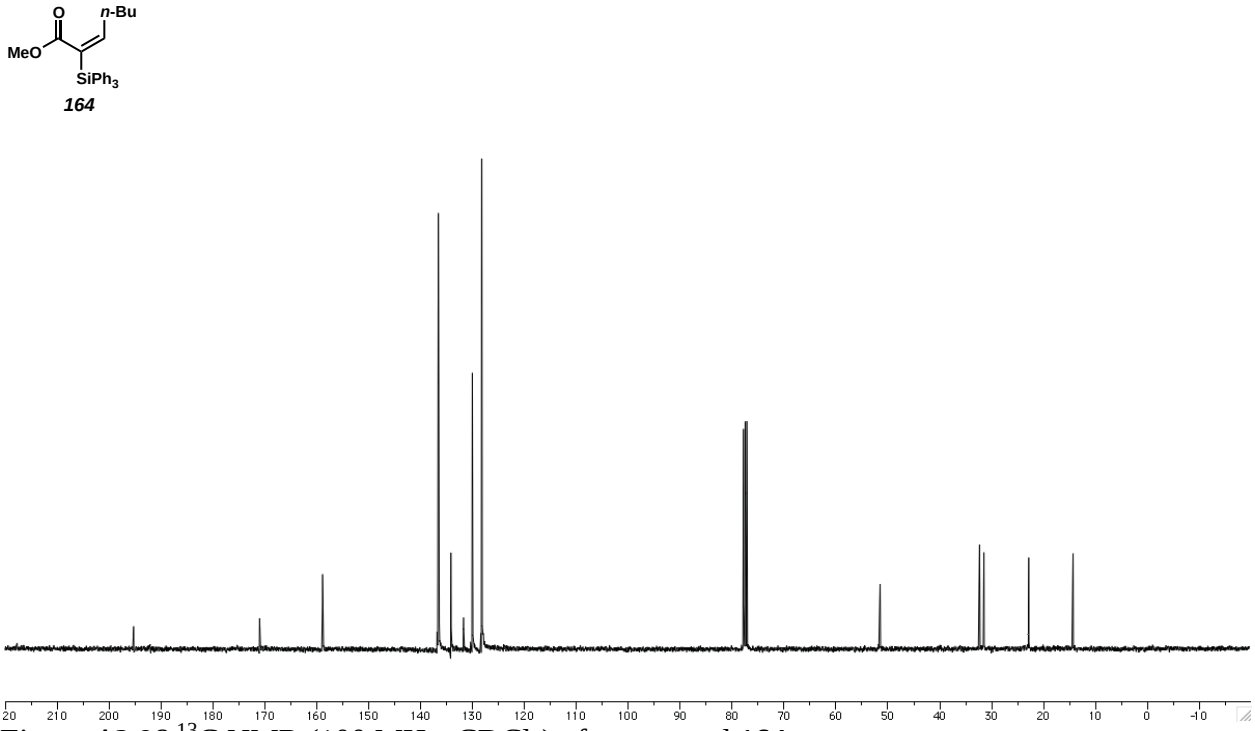


Figure A2.98 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **164**

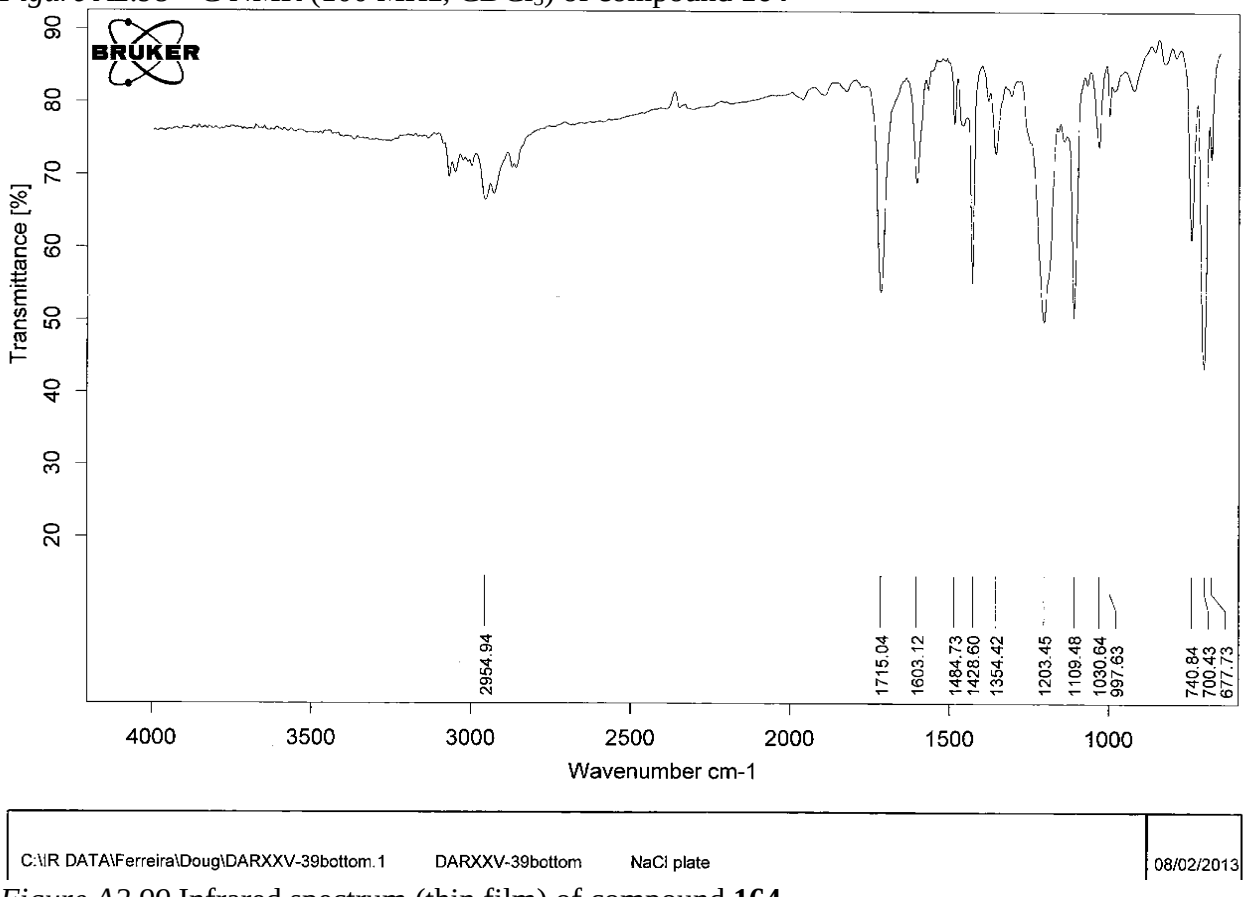
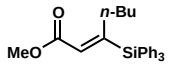


Figure A2.99 Infrared spectrum (thin film) of compound **164**



164b

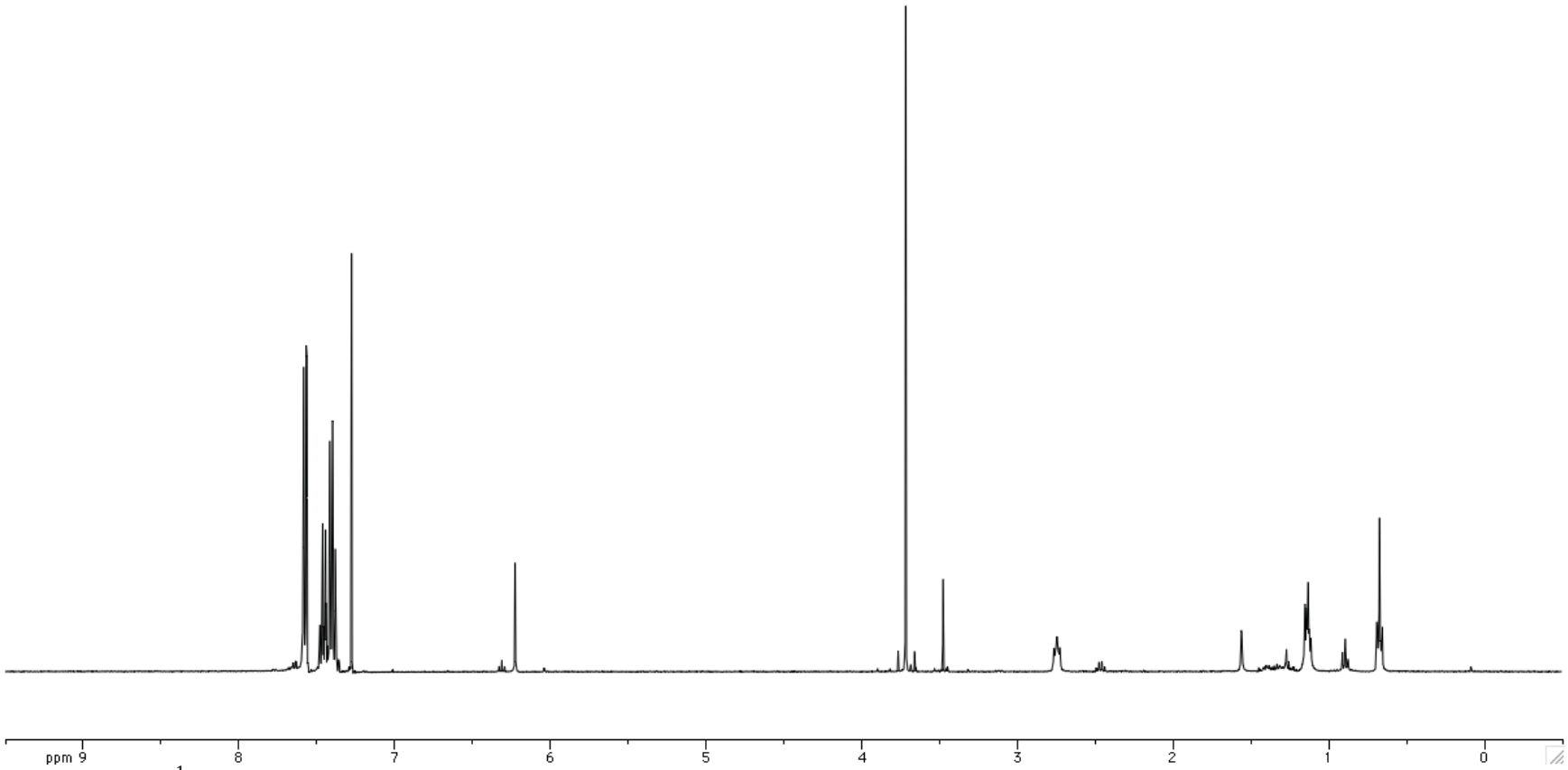
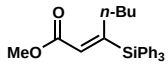


Figure A2.100 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **164b**



164b

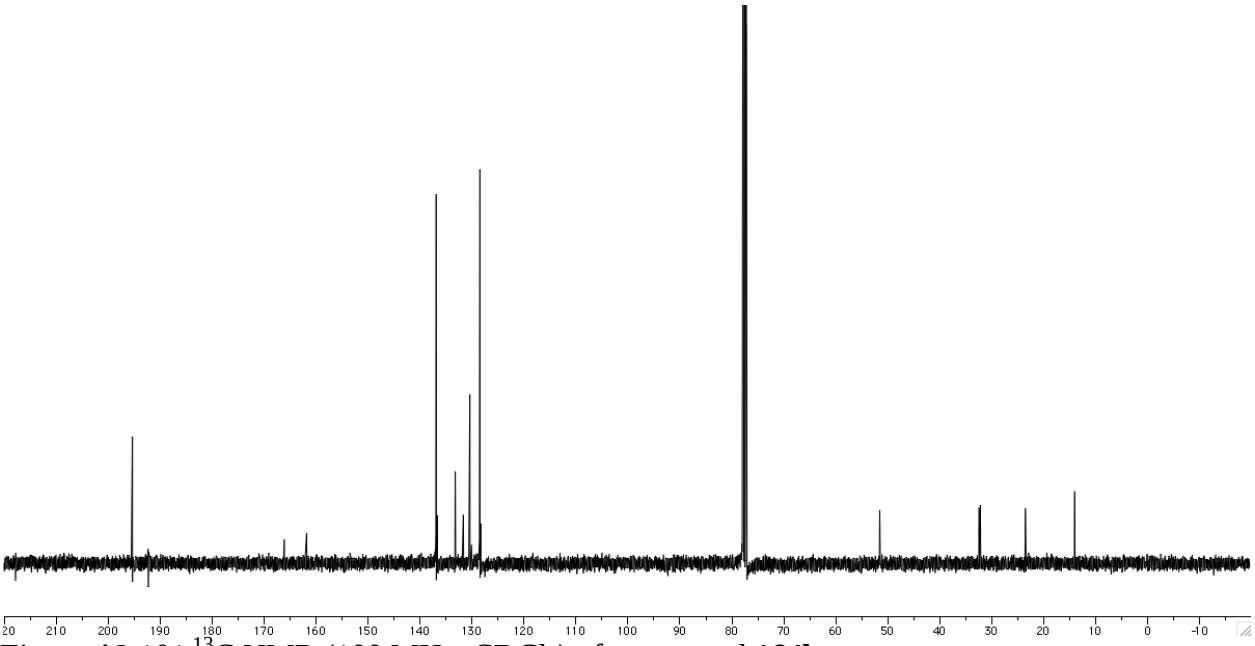


Figure A2.101 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **164b**

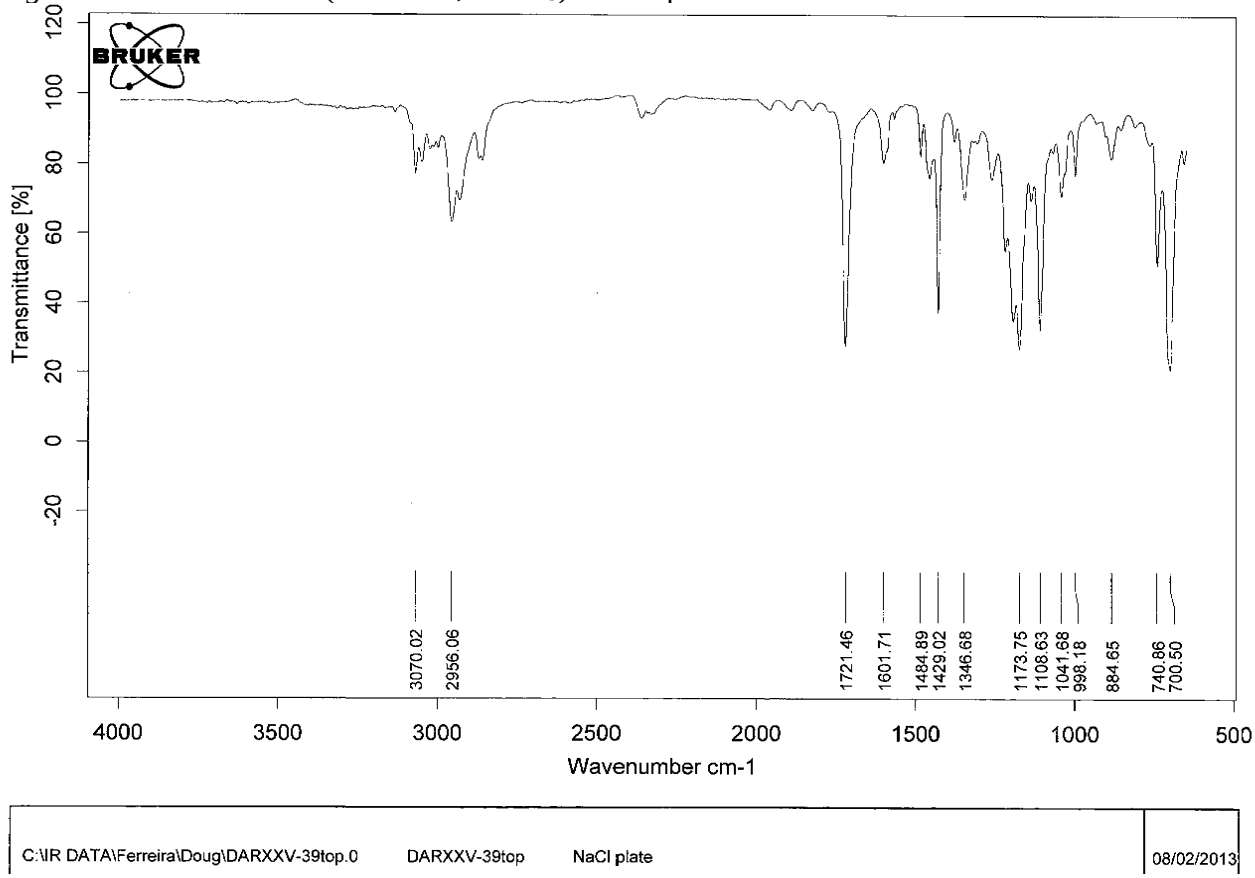
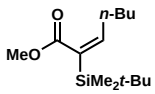


Figure A2.102 Infrared spectrum (thin film) of compound **164b**



165

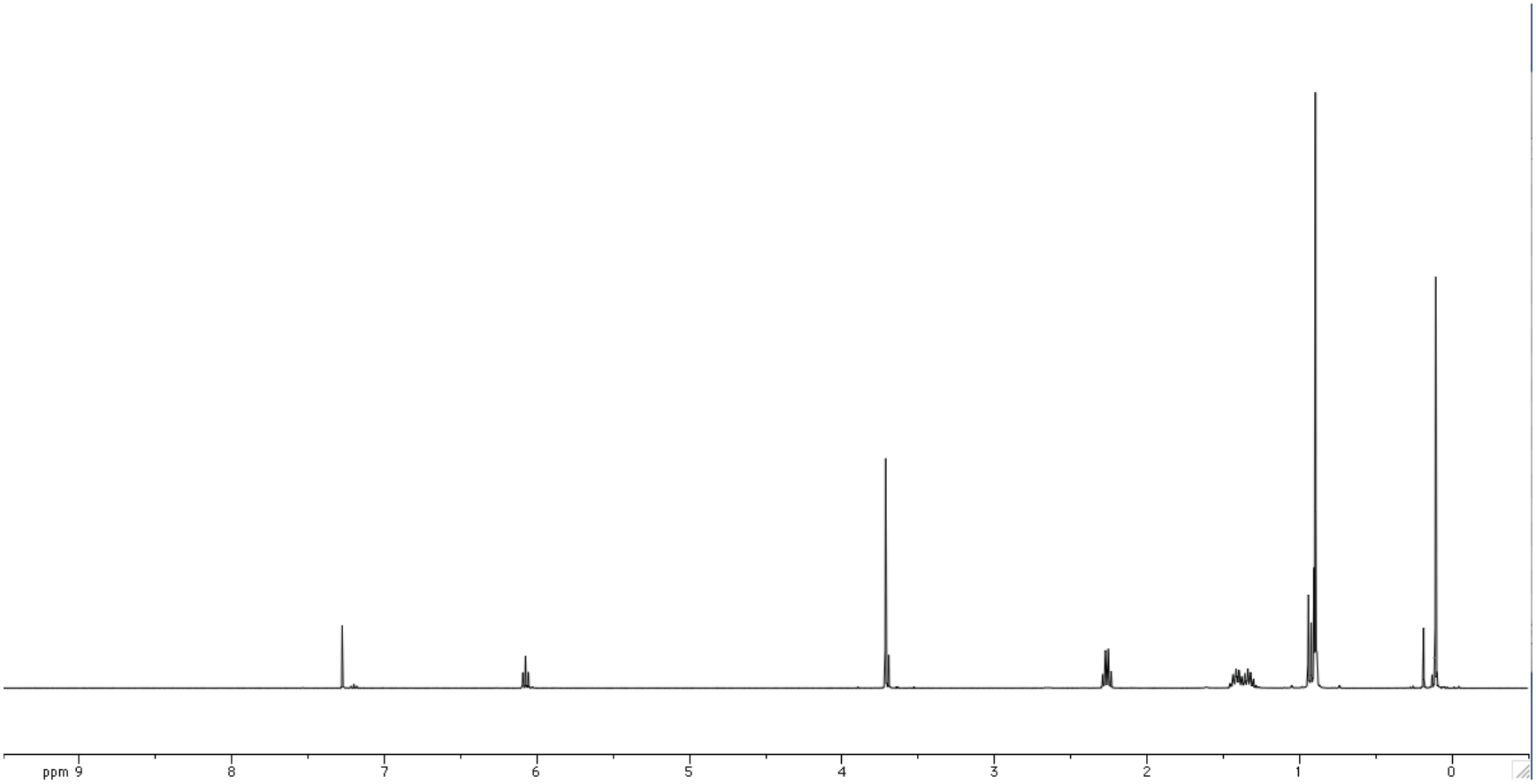
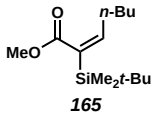


Figure A2.103 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **165**



165

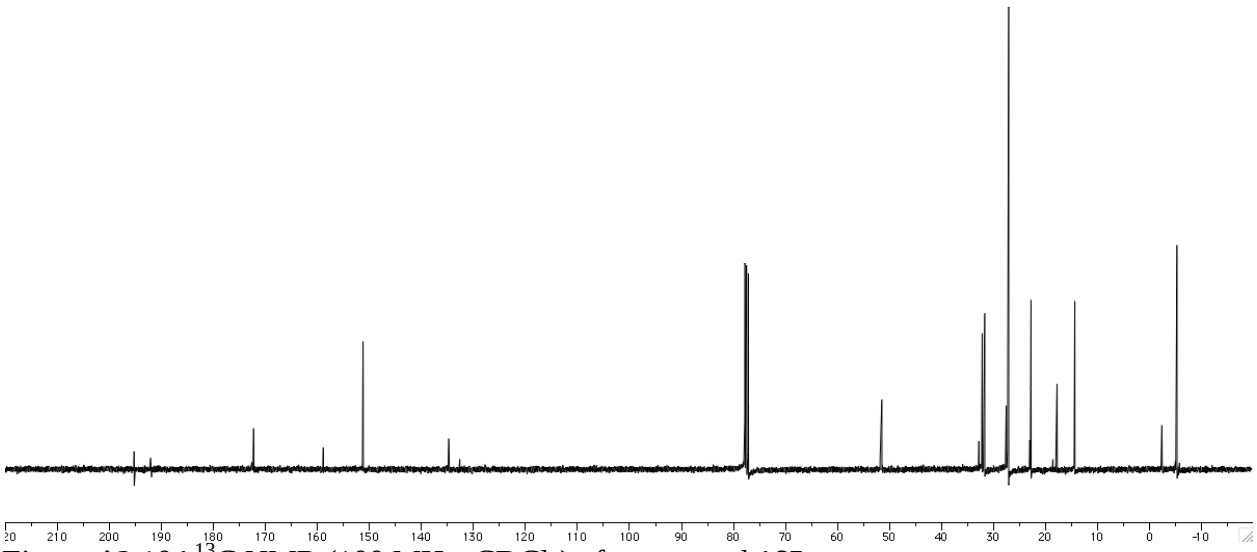


Figure A2.104 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **165**

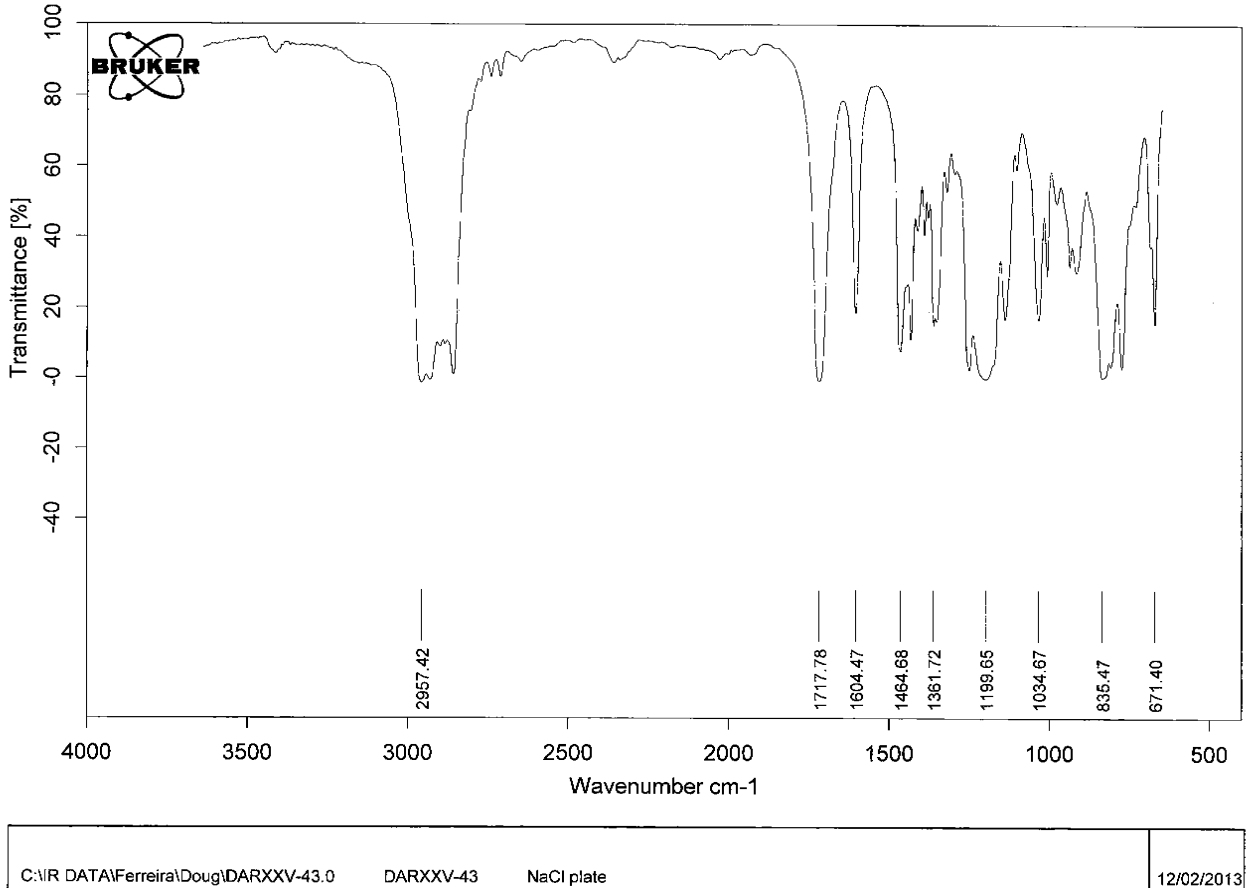
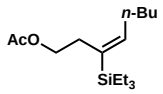


Figure A2.105 Infrared spectrum (thin film) of compound **165**



167

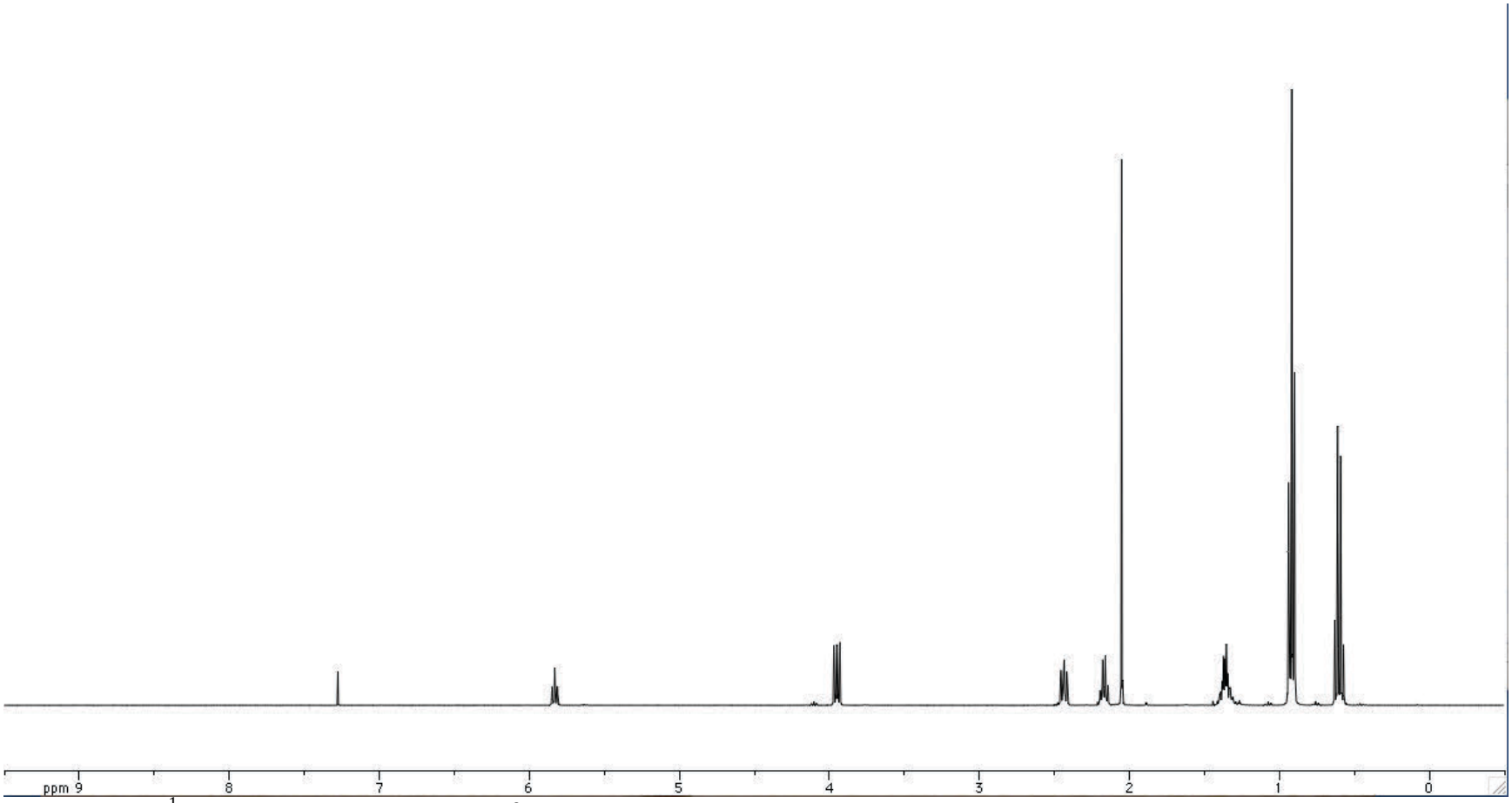
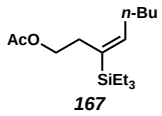


Figure A2.106 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **167**



167

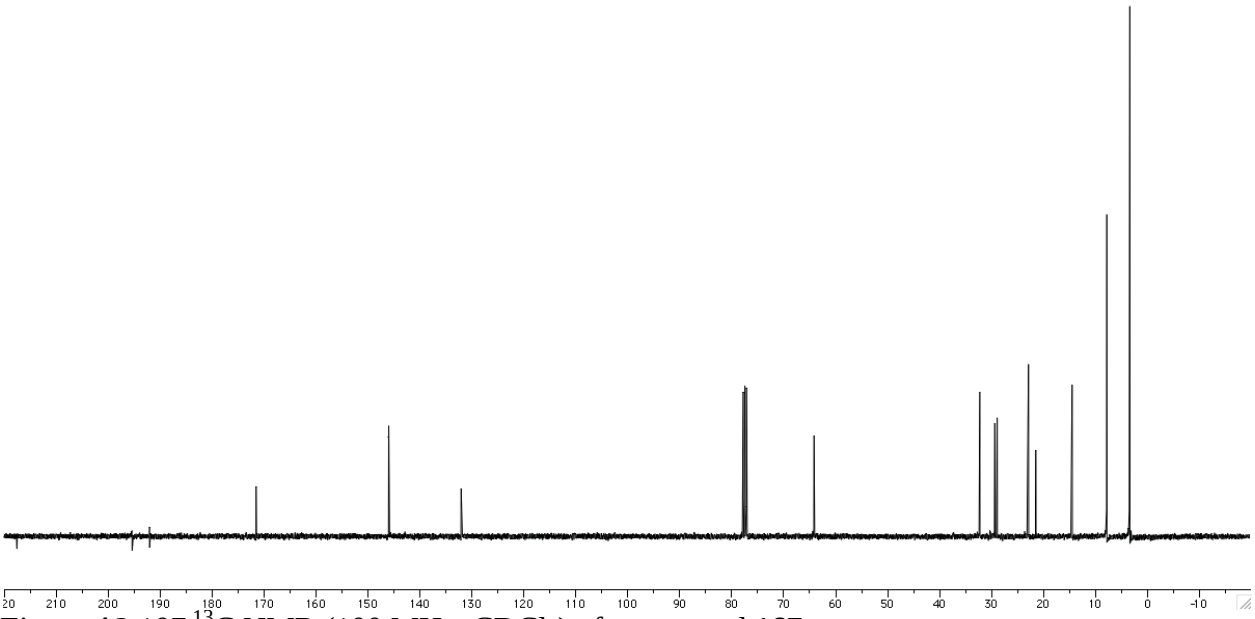


Figure A2.107 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **167**

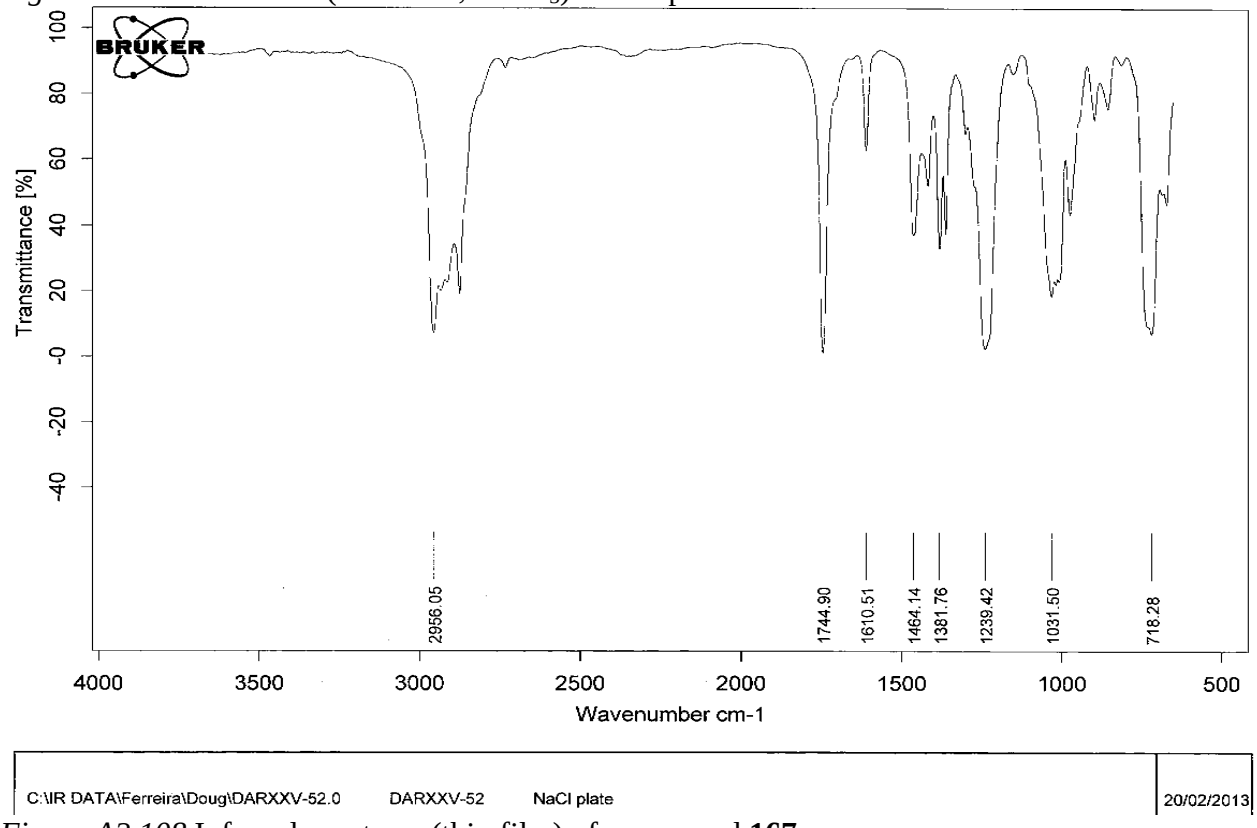
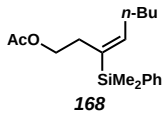


Figure A2.108 Infrared spectrum (thin film) of compound **167**



168

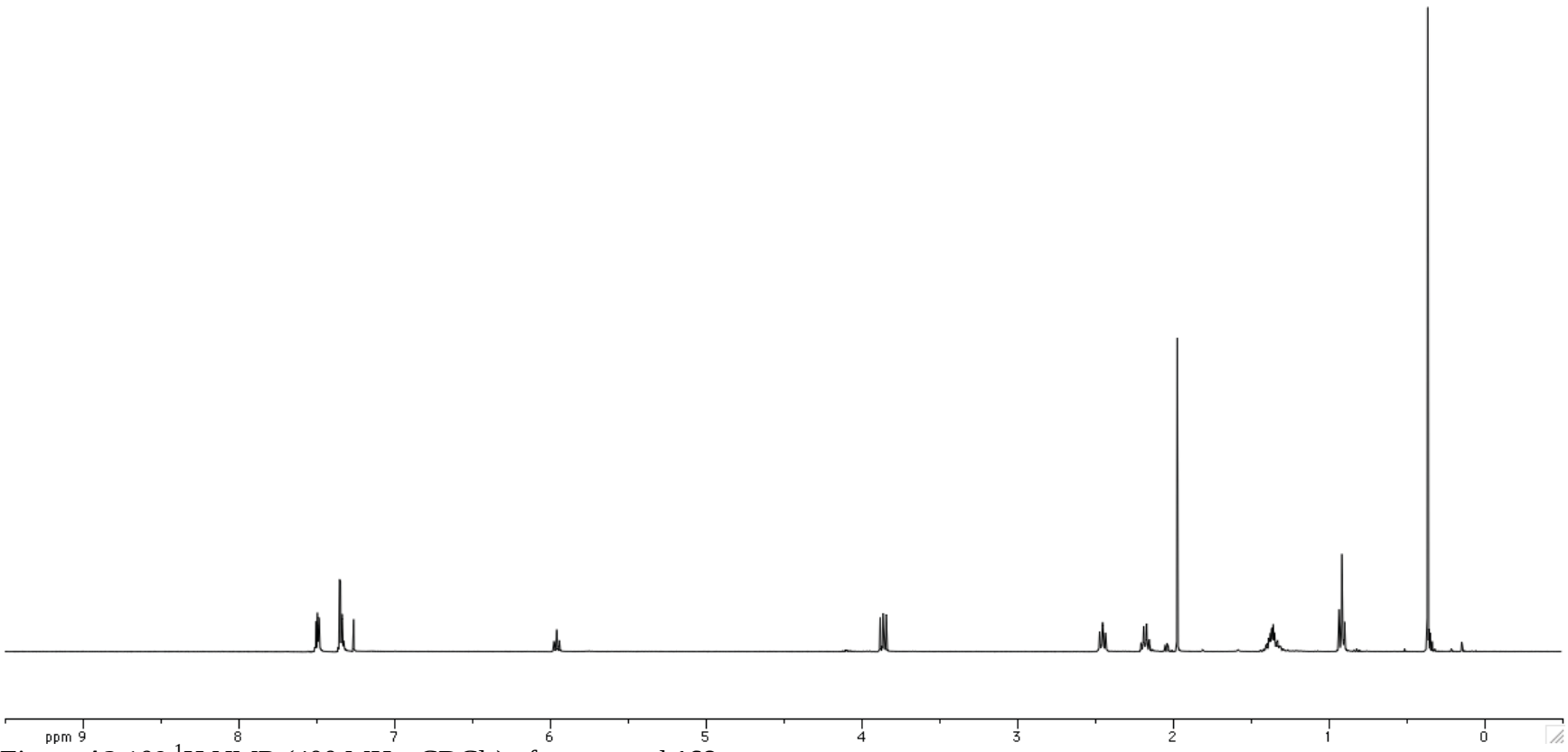
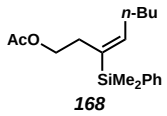


Figure A2.109 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **168**



168

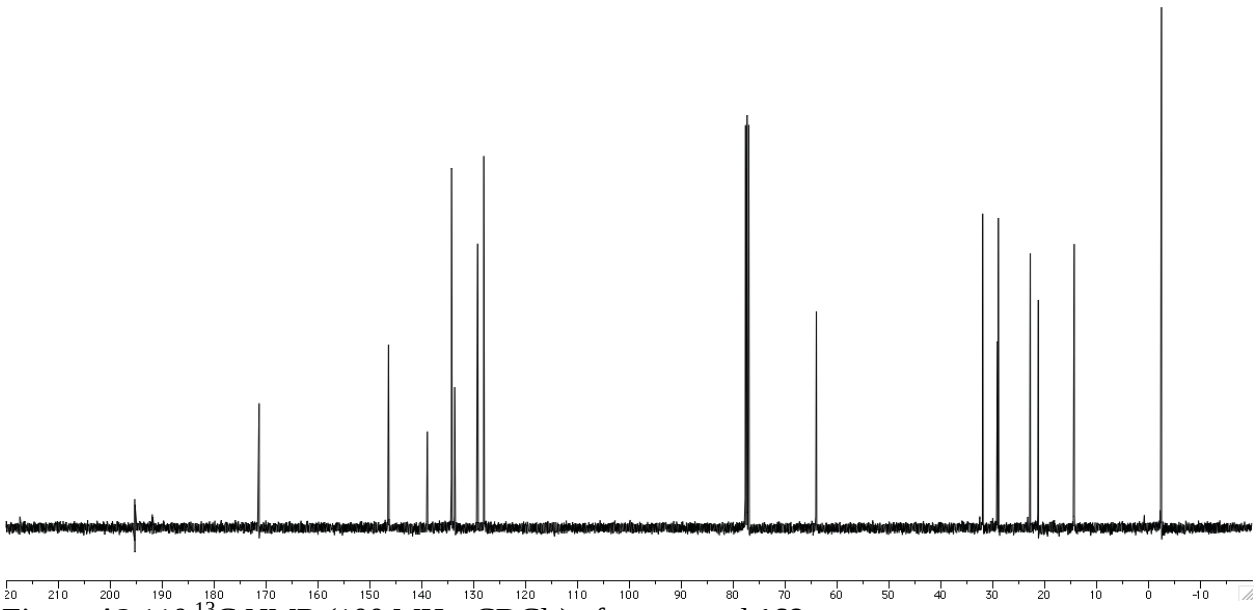


Figure A2.110 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **168**

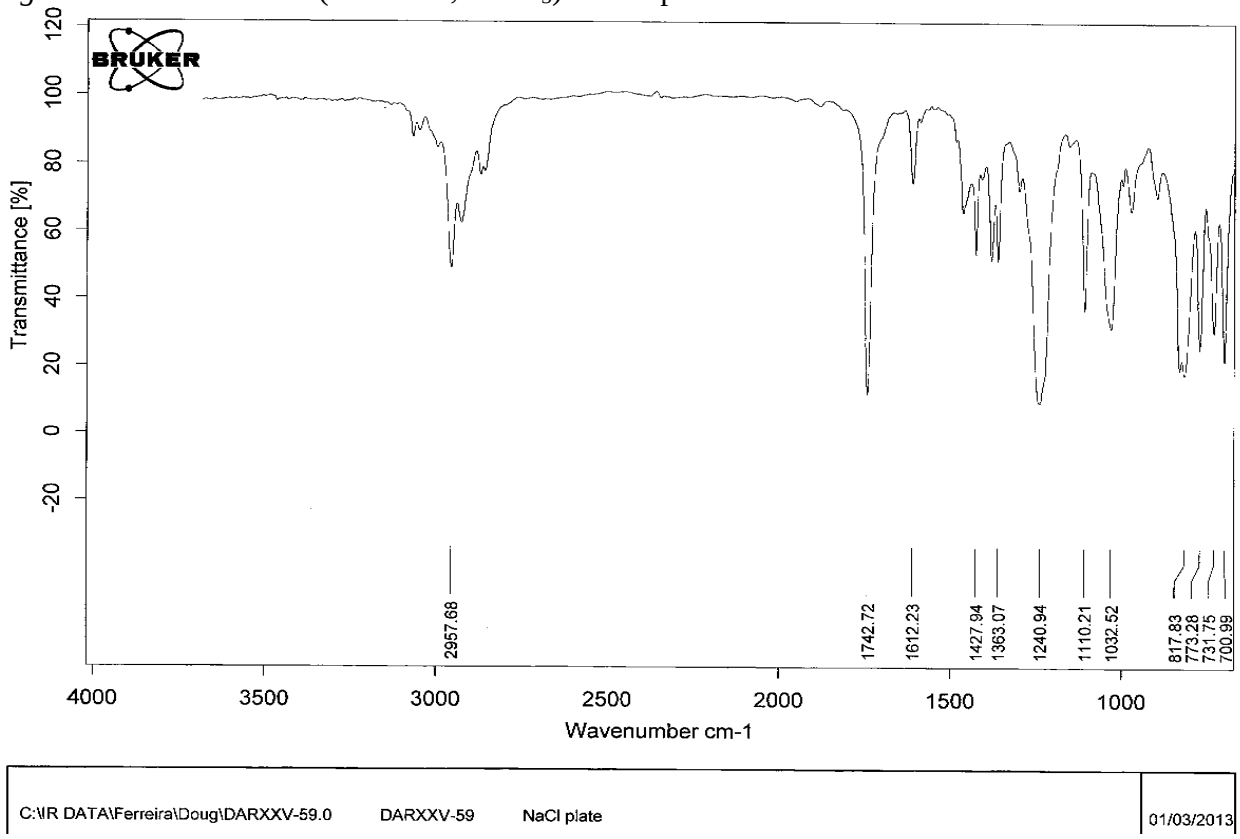
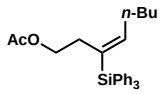


Figure A2.111 Infrared spectrum (thin film) of compound **168**



169

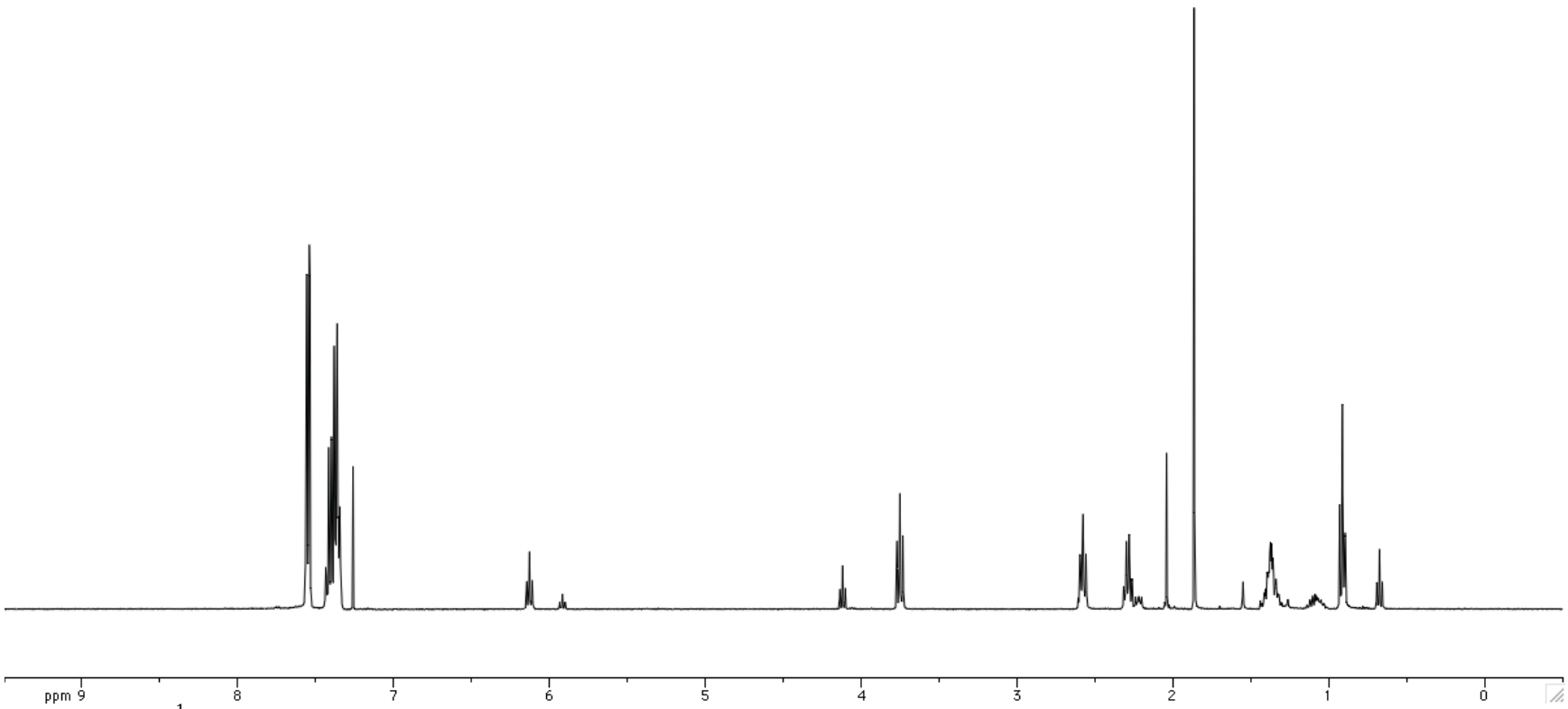
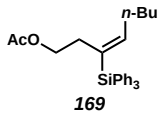


Figure A2.112 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **169**



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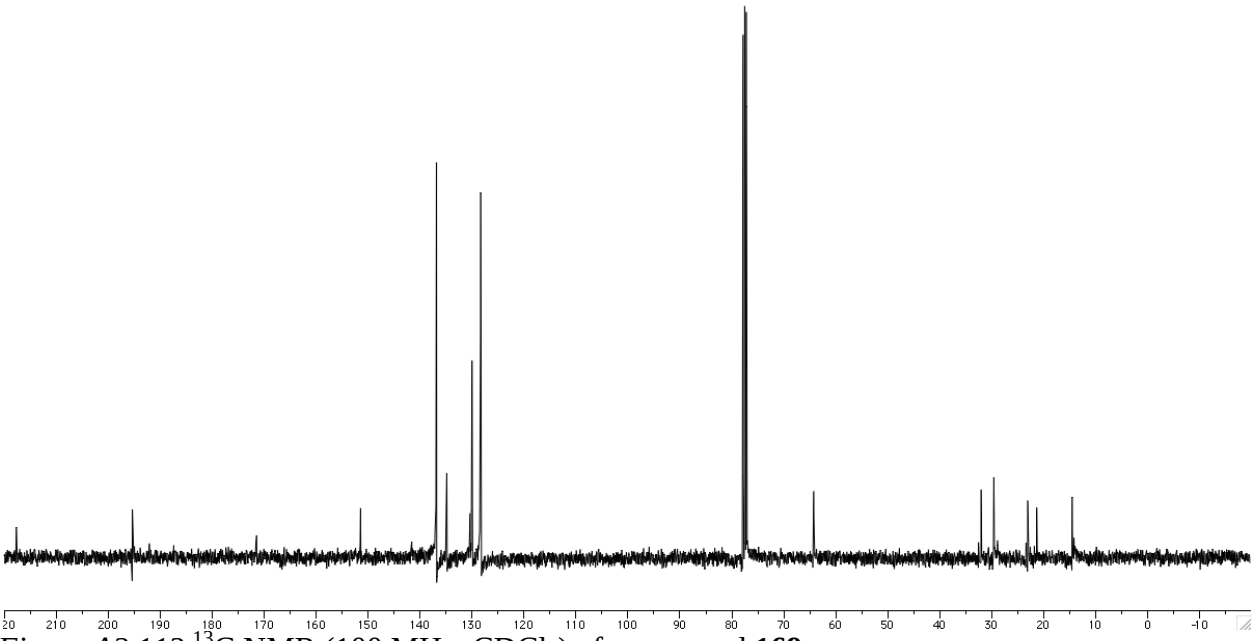


Figure A2.113 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **169**

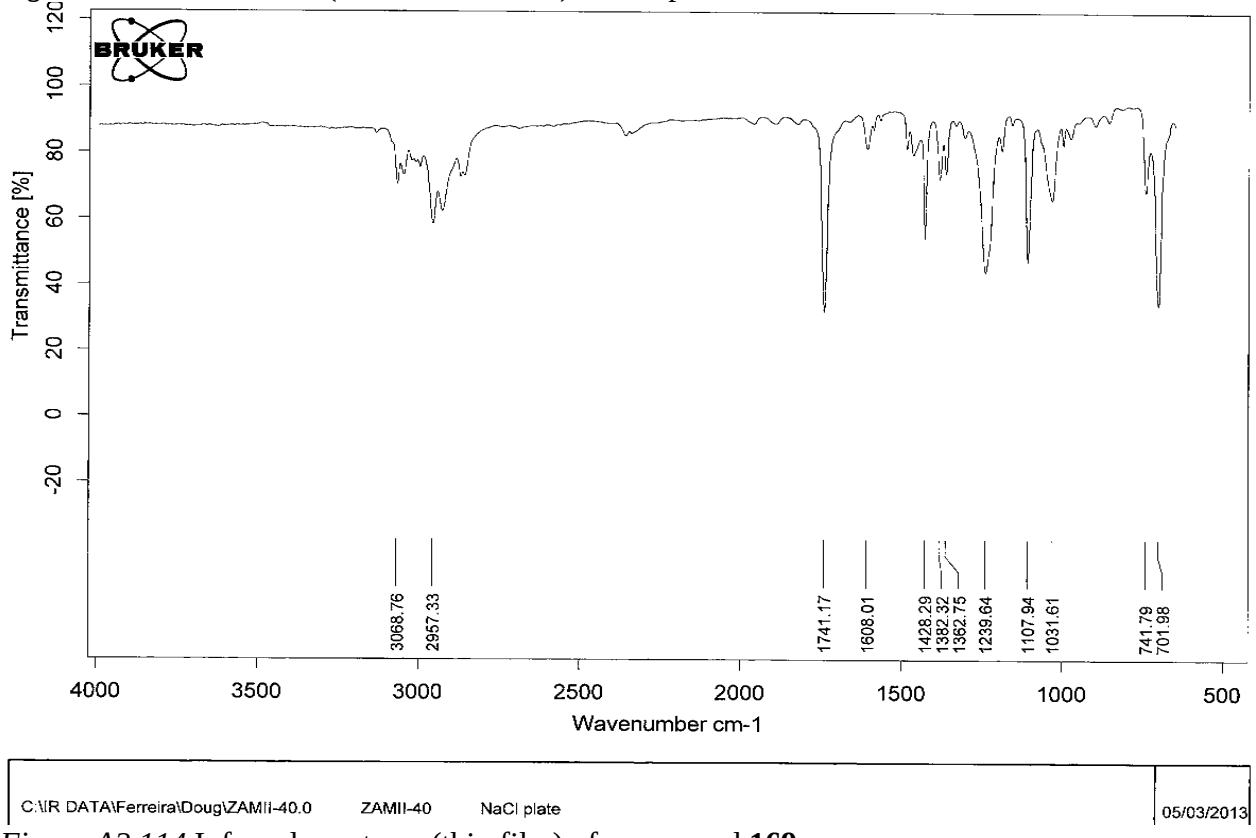
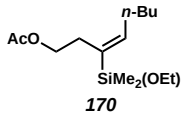


Figure A2.114 Infrared spectrum (thin film) of compound **169**



170

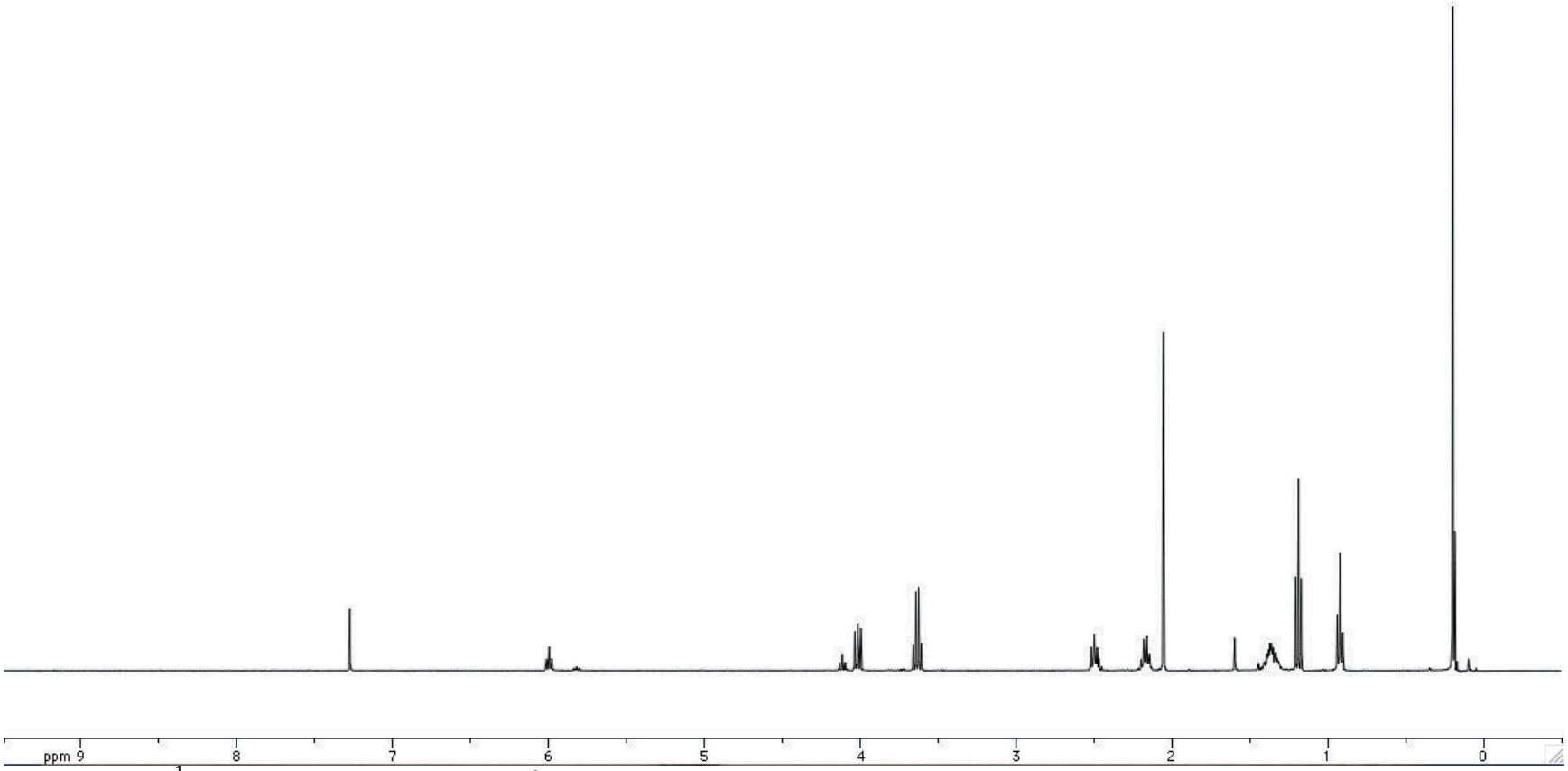


Figure A2.115 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **170**

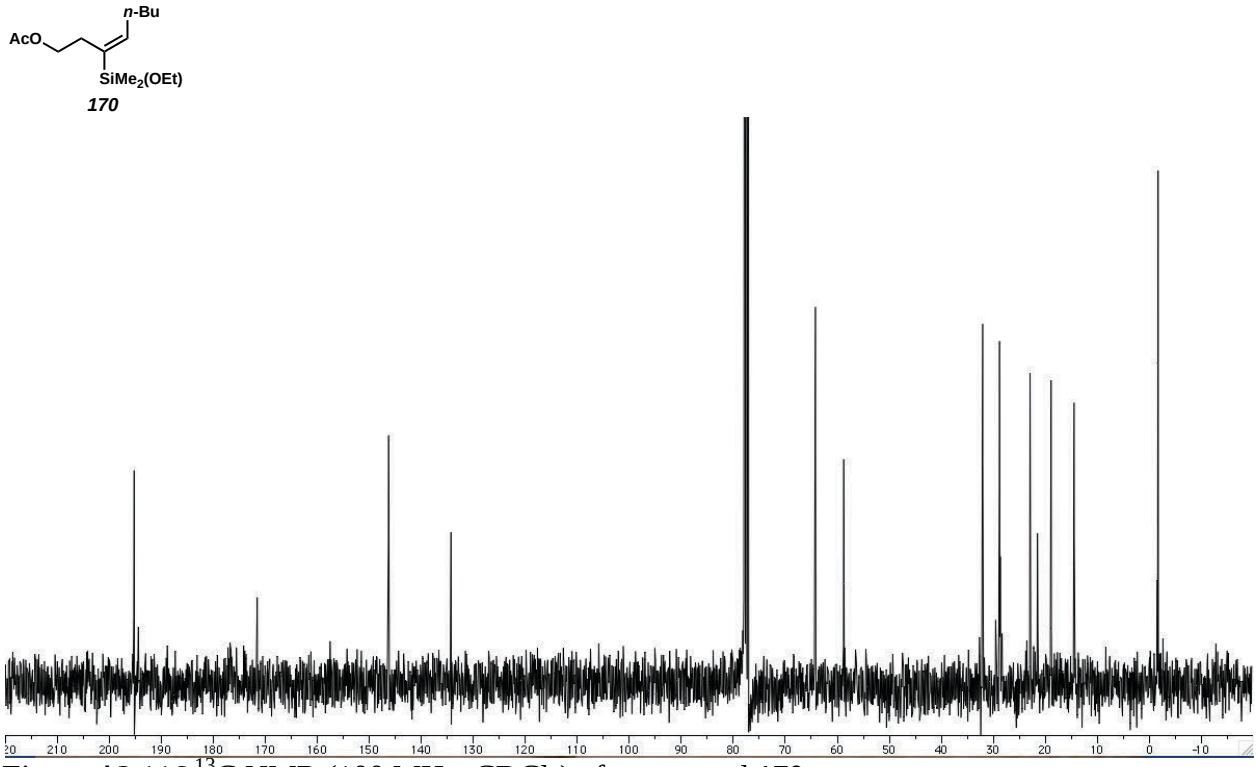


Figure A2.116 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **170**

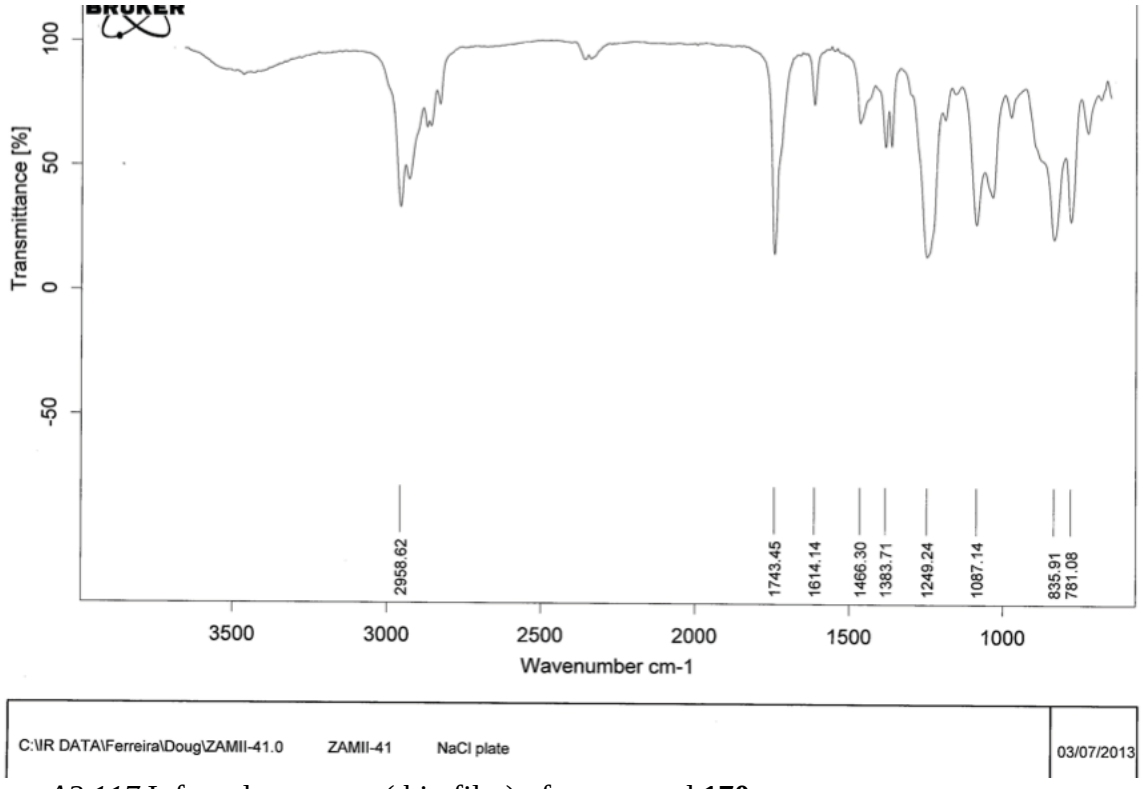


Figure A2.117 Infrared spectrum (thin film) of compound **170**

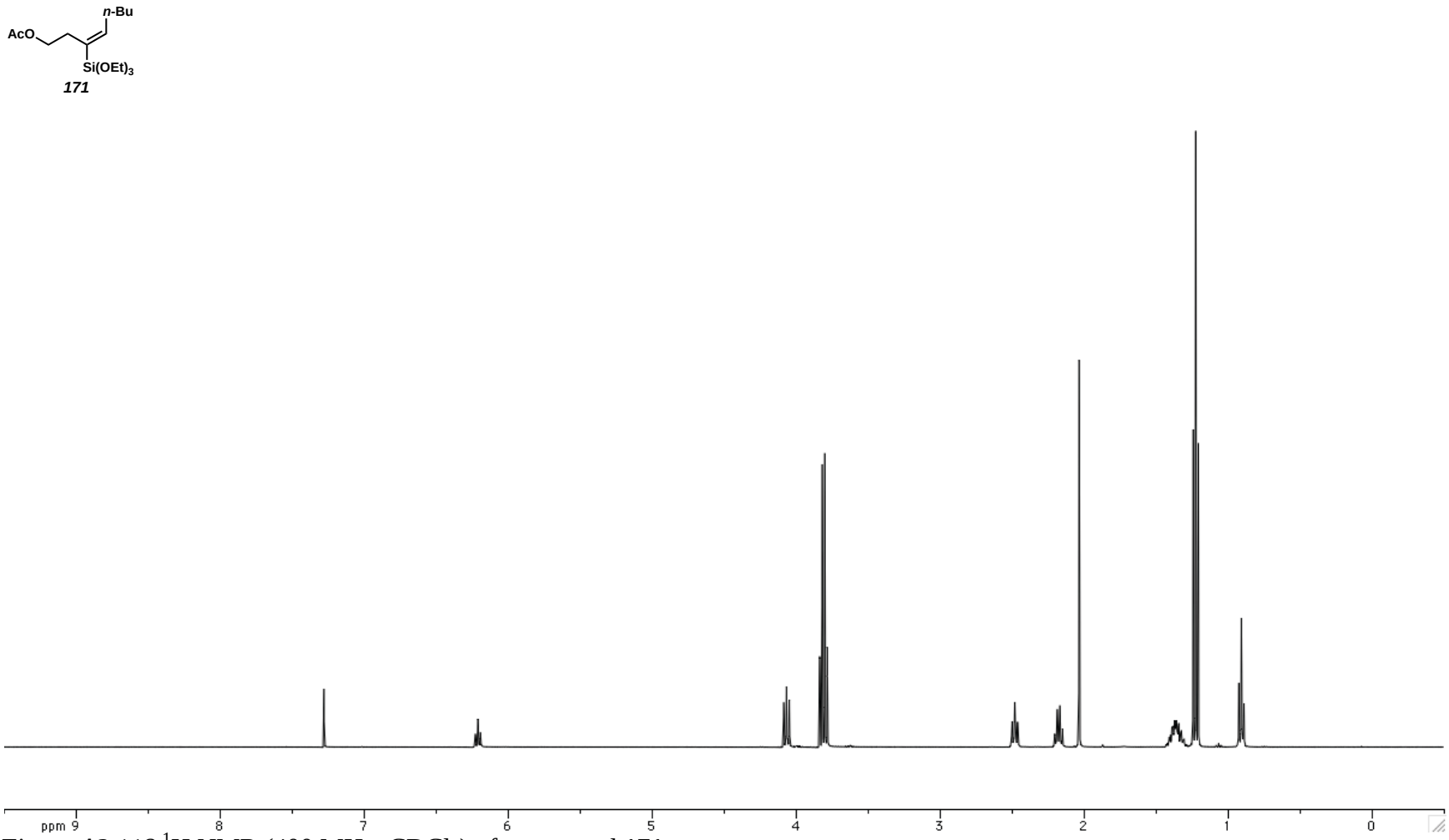


Figure A2.118 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **171**

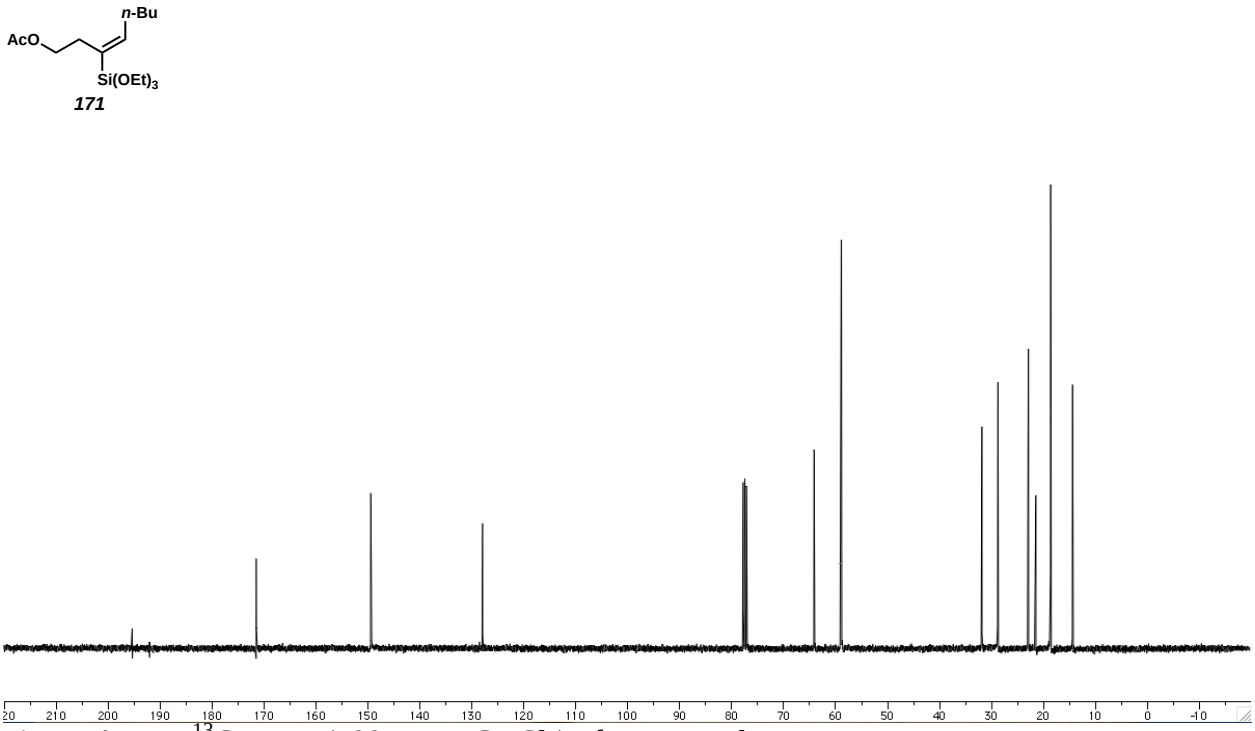


Figure A2.119 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **171**

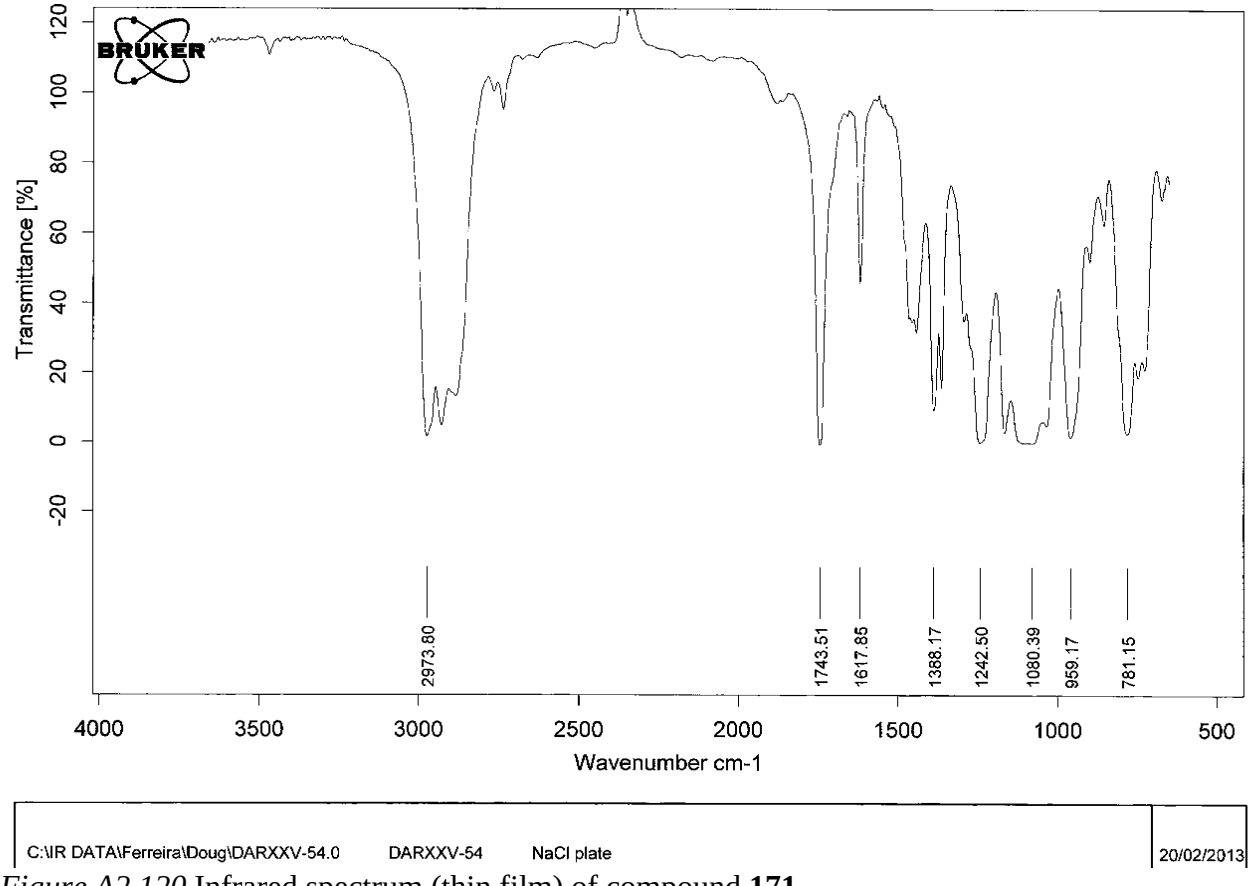


Figure A2.120 Infrared spectrum (thin film) of compound **171**

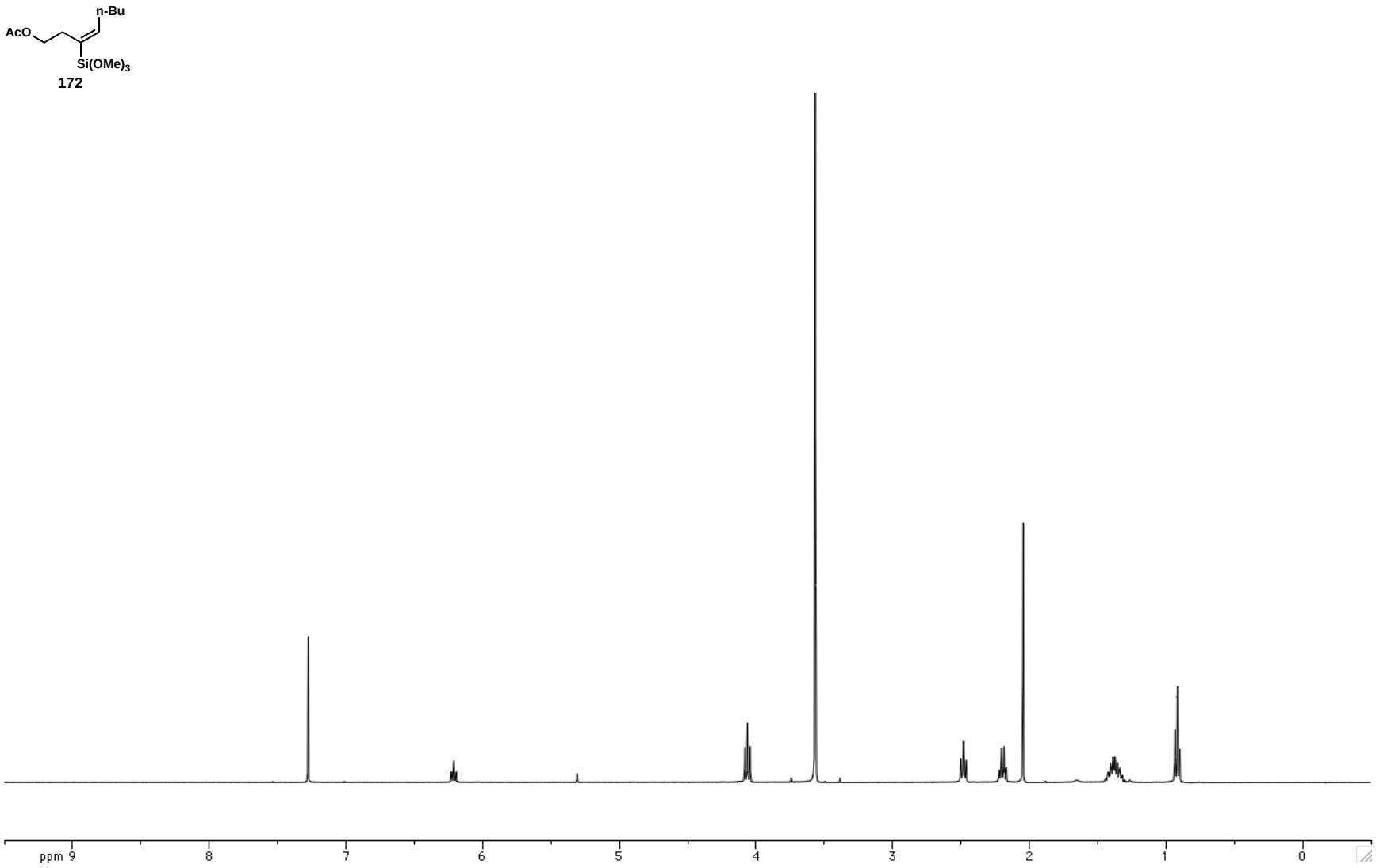


Figure A2.121 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **172**

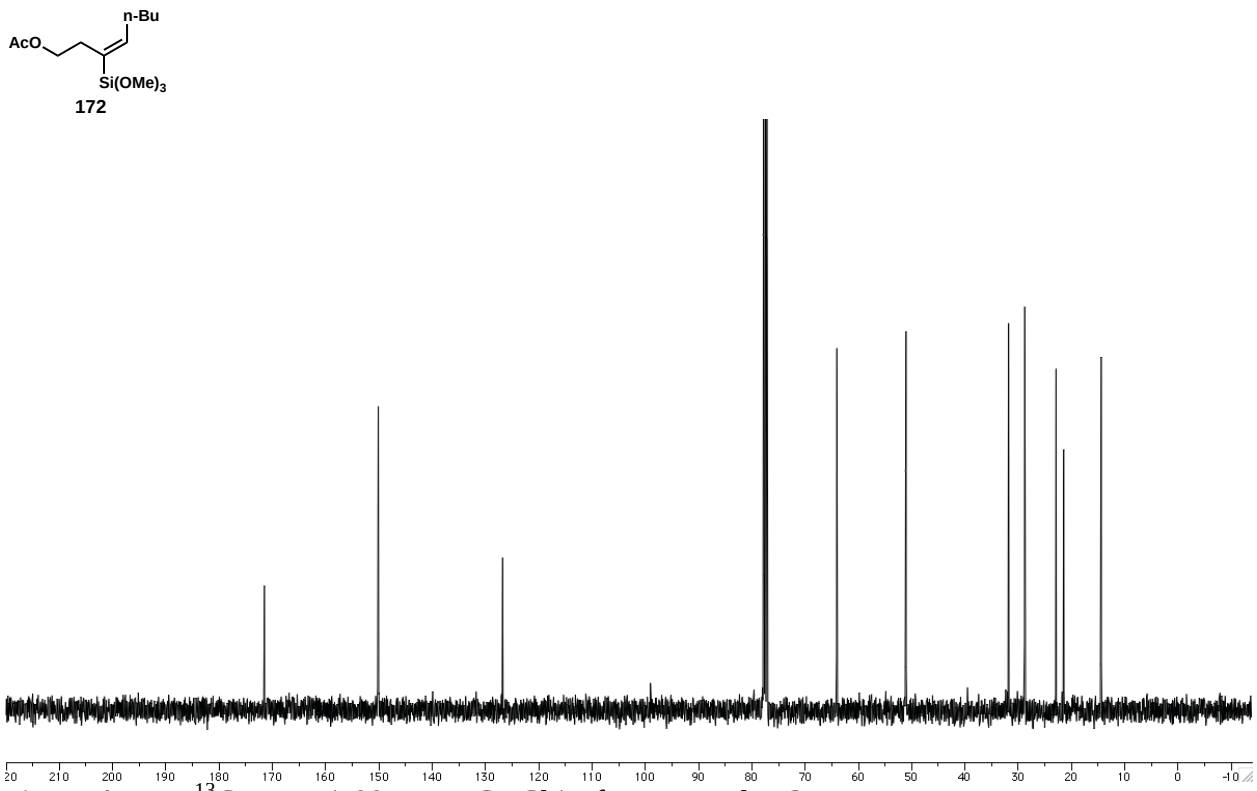


Figure A2.122 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **172**

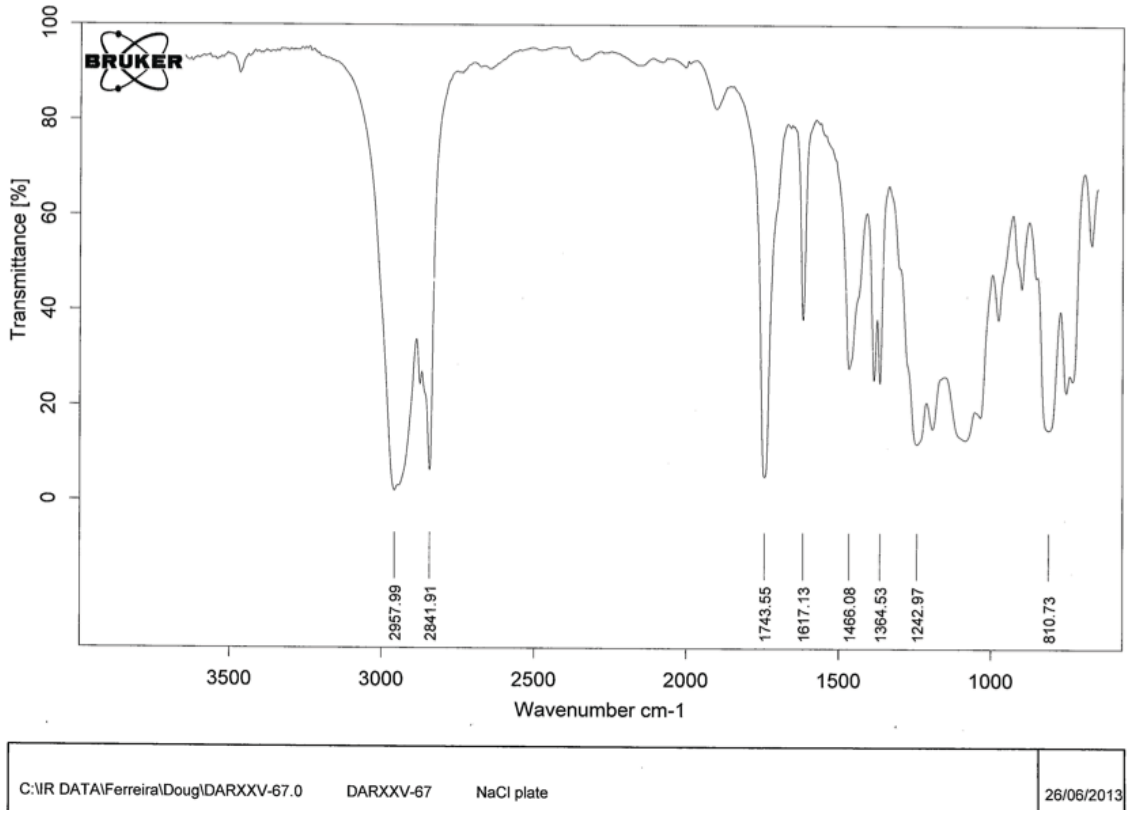
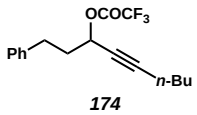


Figure A2.123 Infrared spectrum (thin film) of compound **172**



174

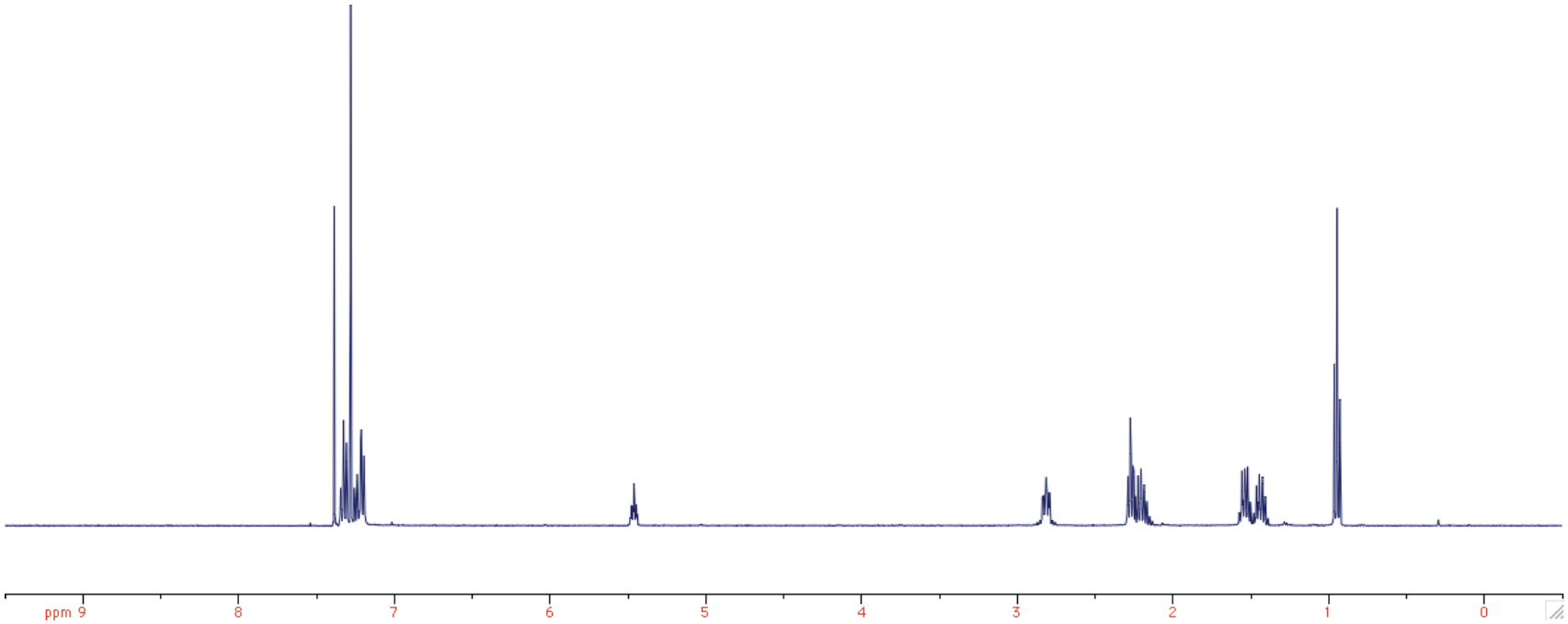


Figure A2.124 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **174**

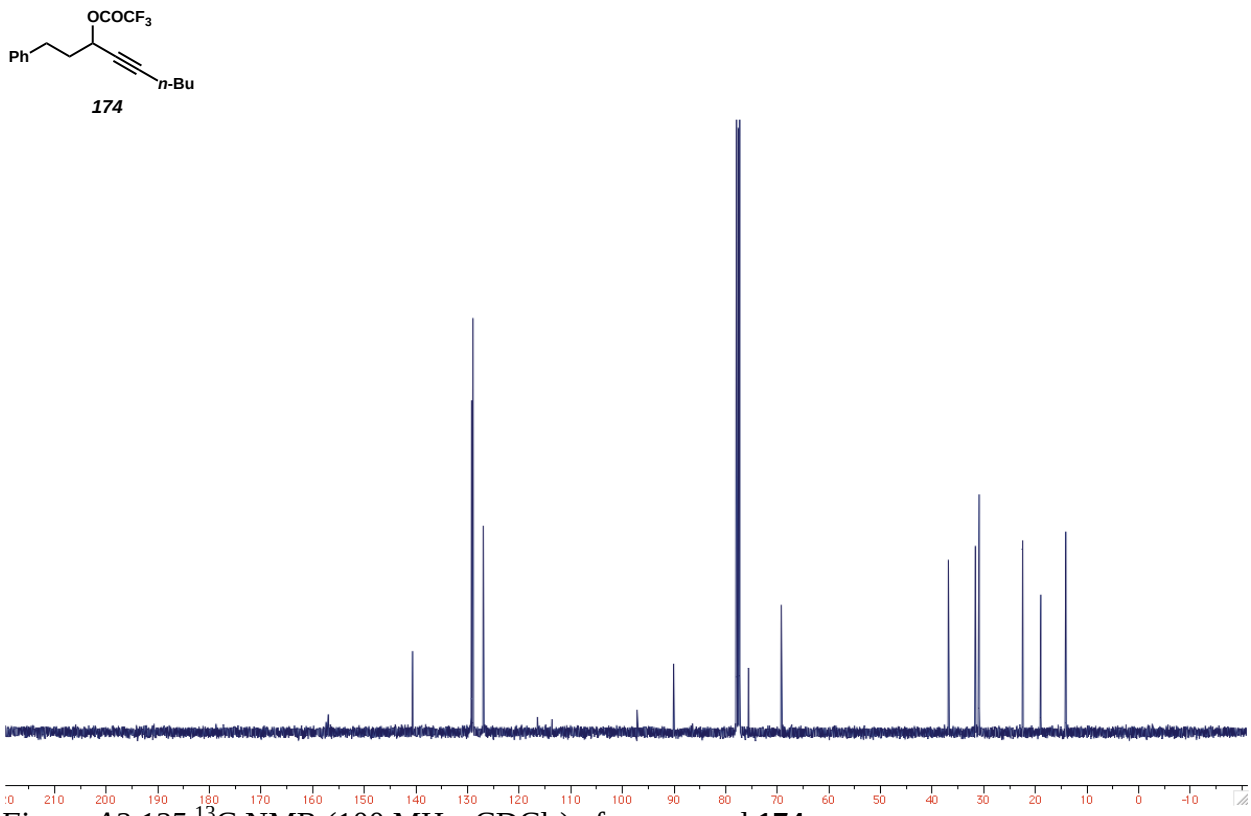


Figure A2.125 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **174**

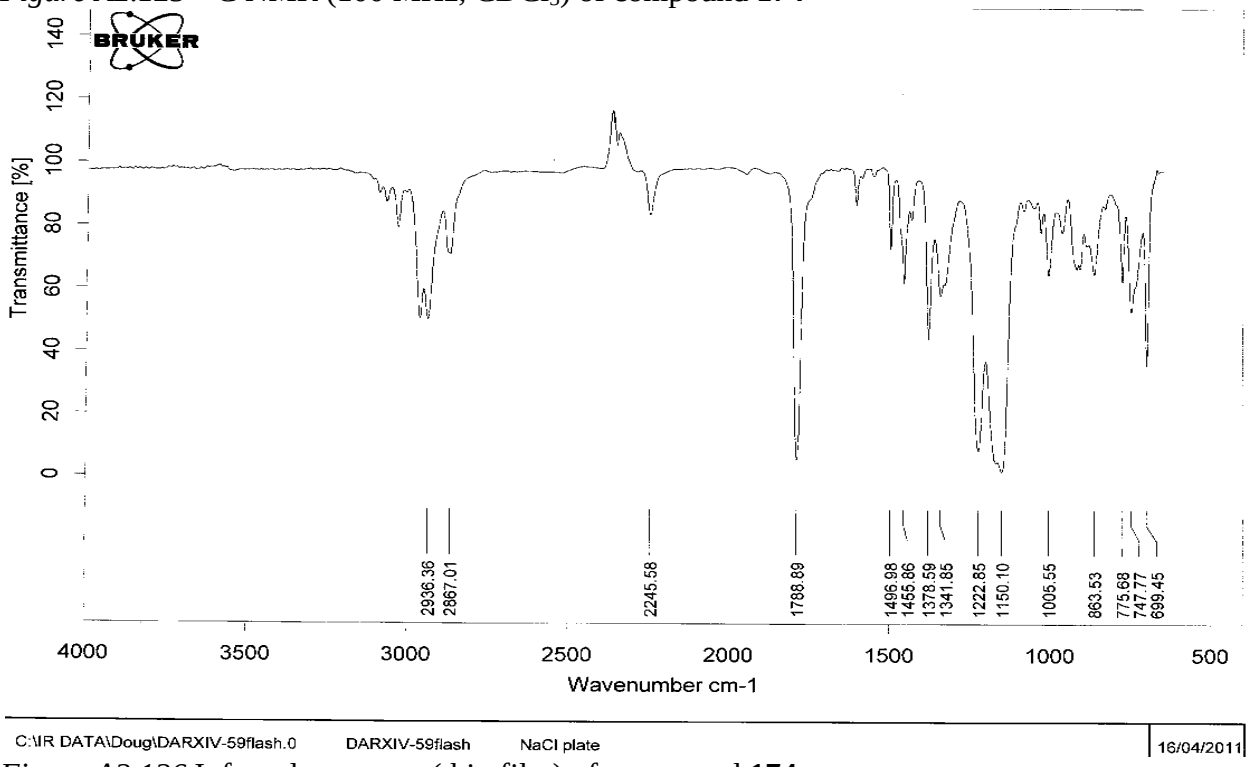
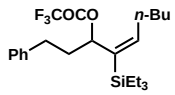


Figure A2.126 Infrared spectrum (thin film) of compound **174**



177

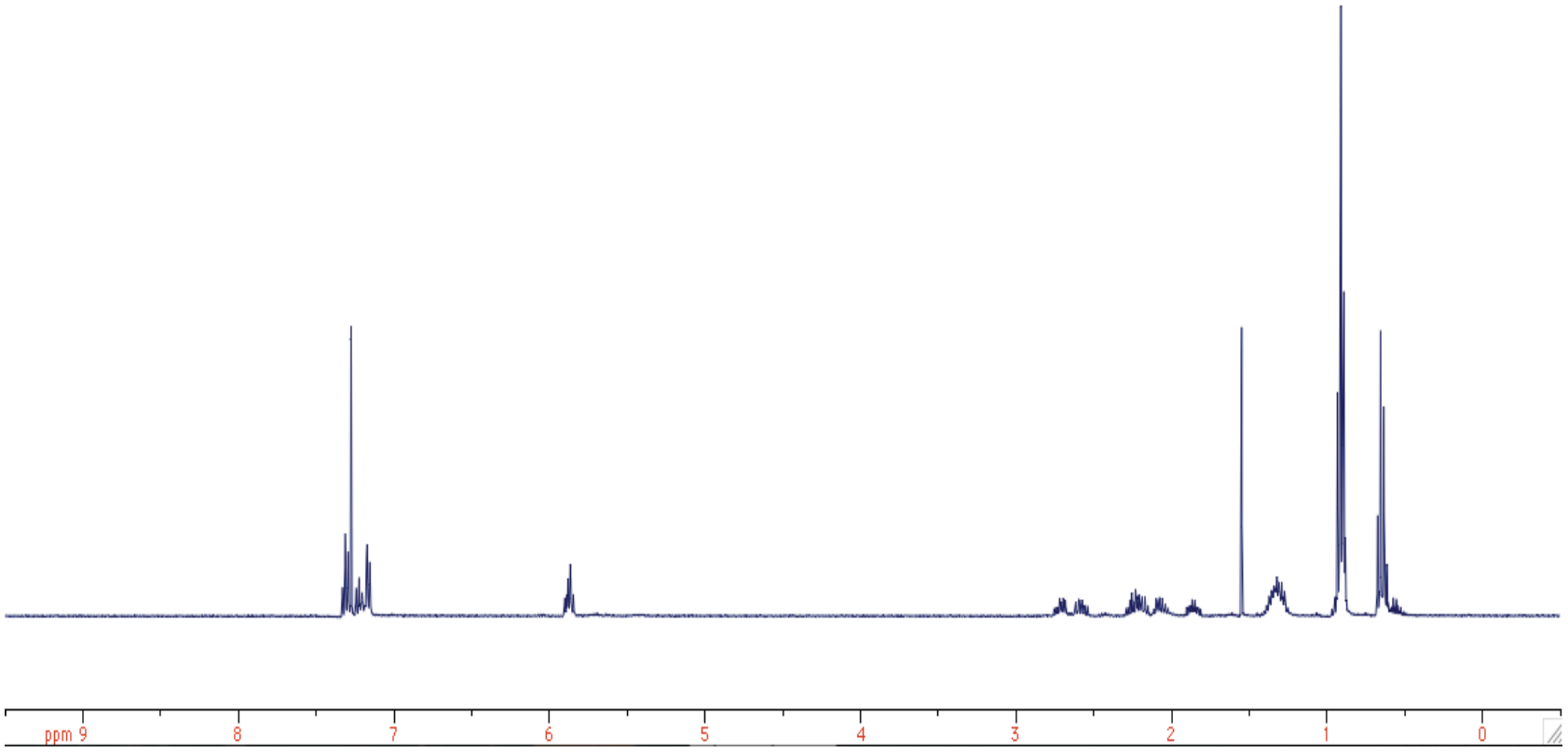


Figure A2.127 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **177**

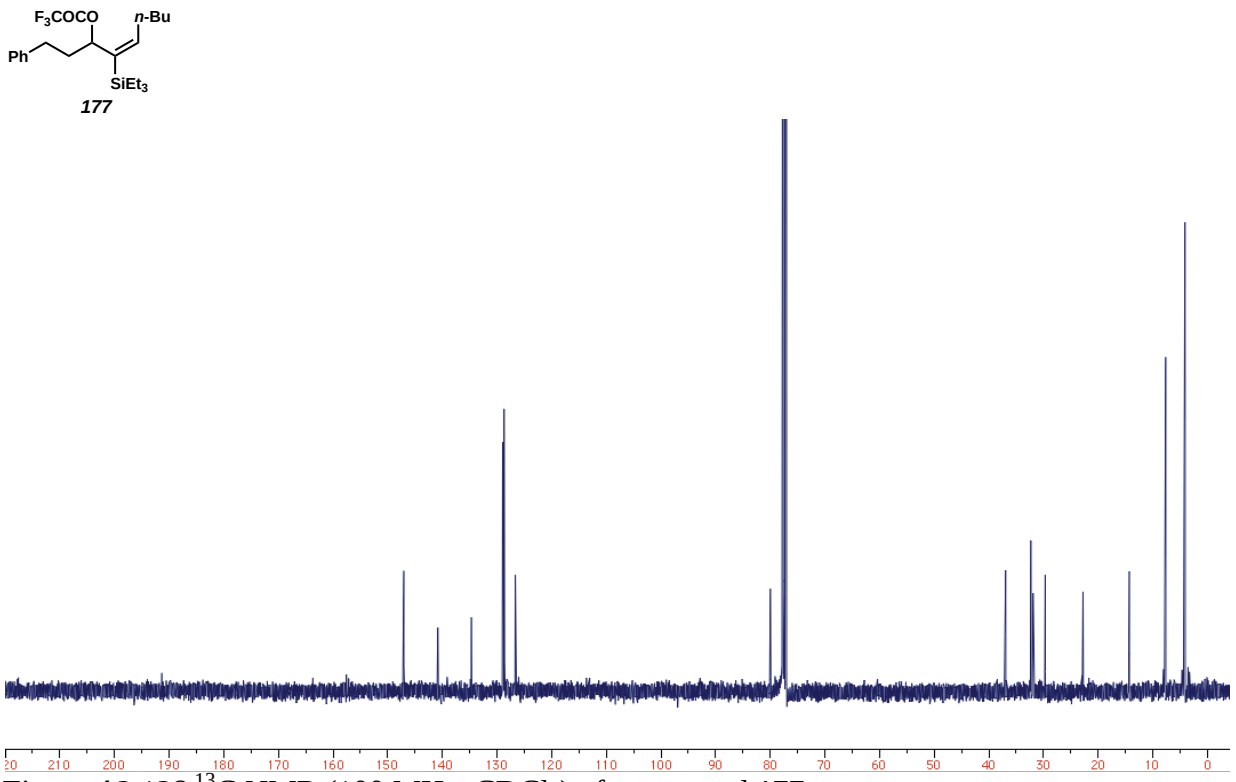


Figure A2.128 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **177**

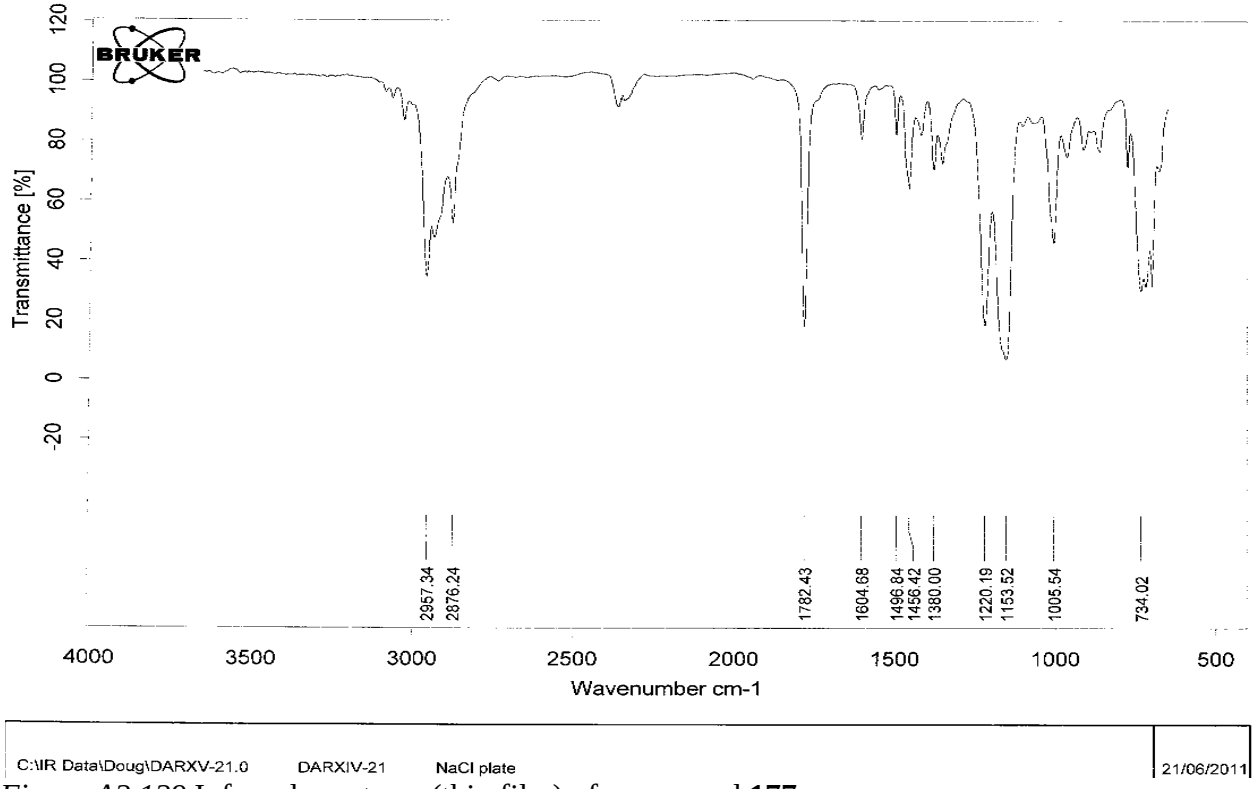
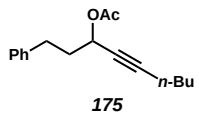


Figure A2.129 Infrared spectrum (thin film) of compound **177**



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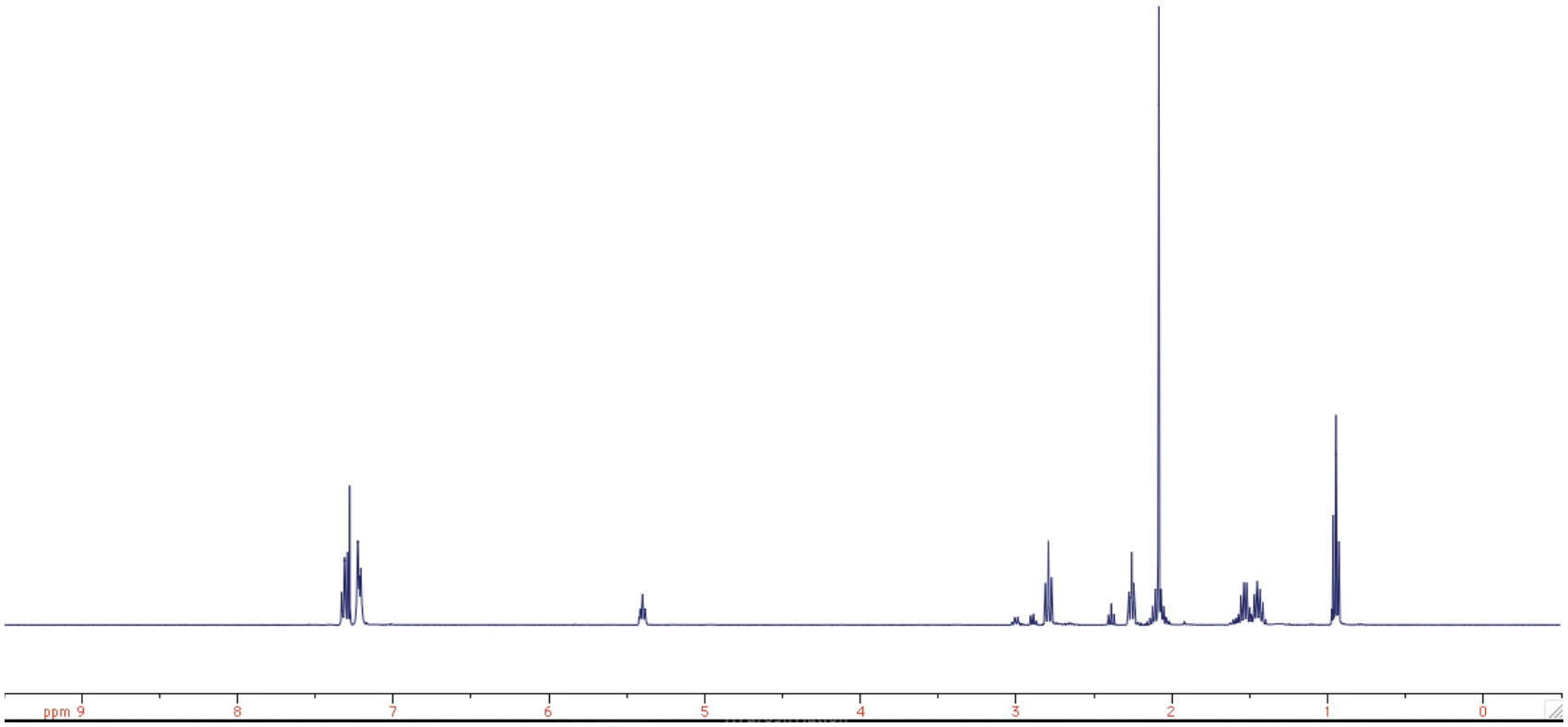


Figure A2.130 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **175**

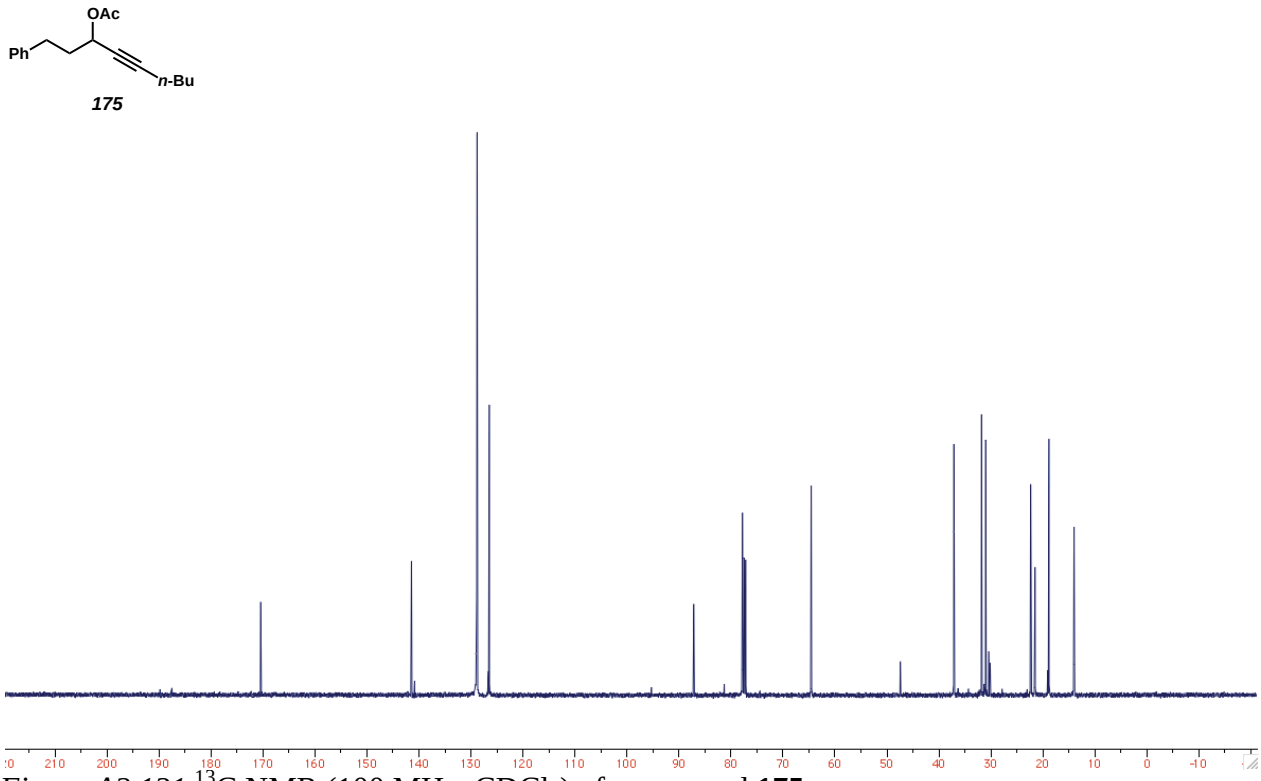


Figure A2.131 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **175**

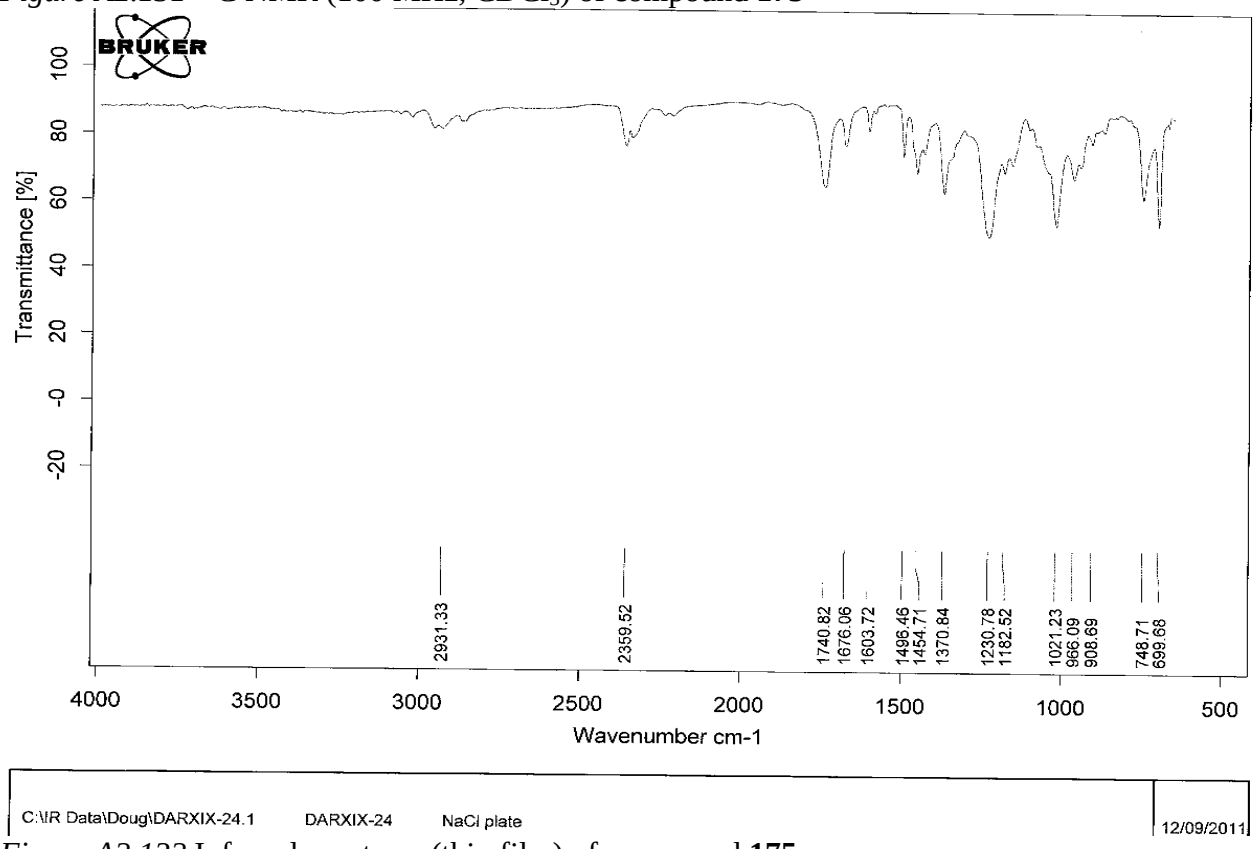


Figure A2.132 Infrared spectrum (thin film) of compound **175**

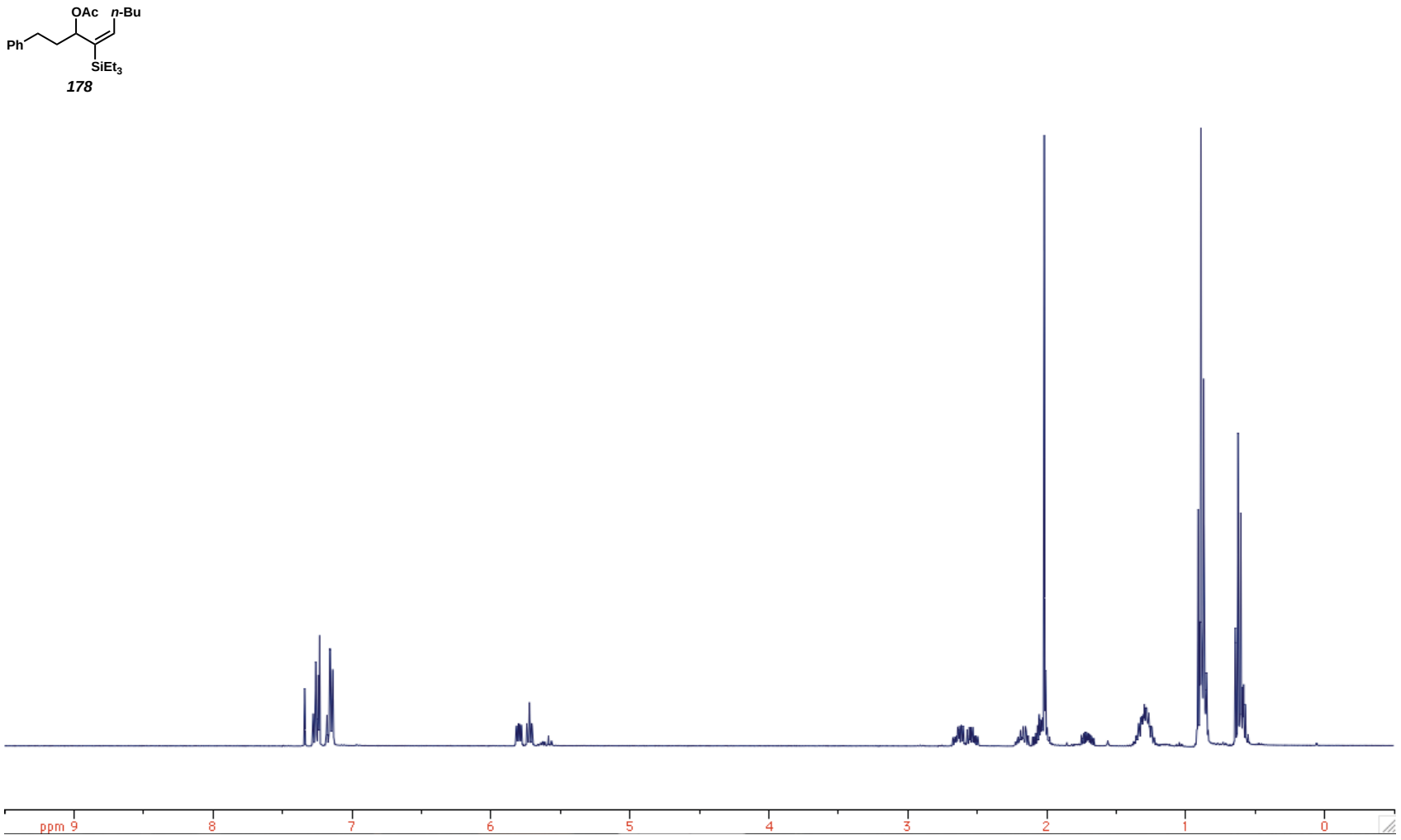
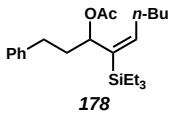


Figure A2.133 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **178**



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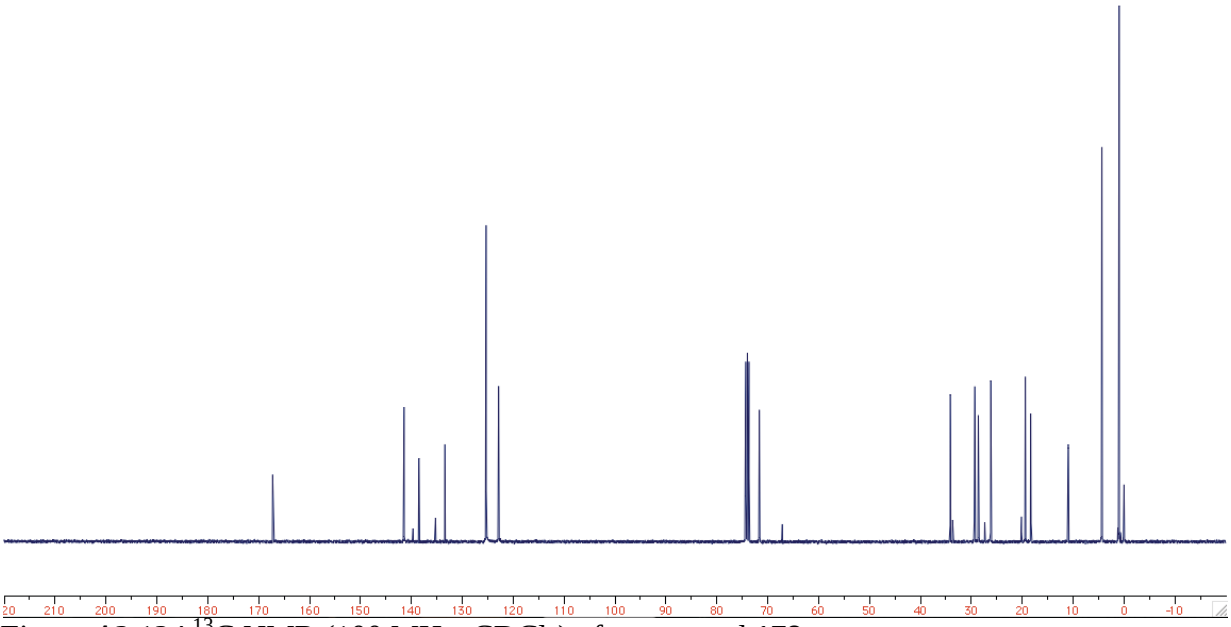


Figure A2.134 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **178**

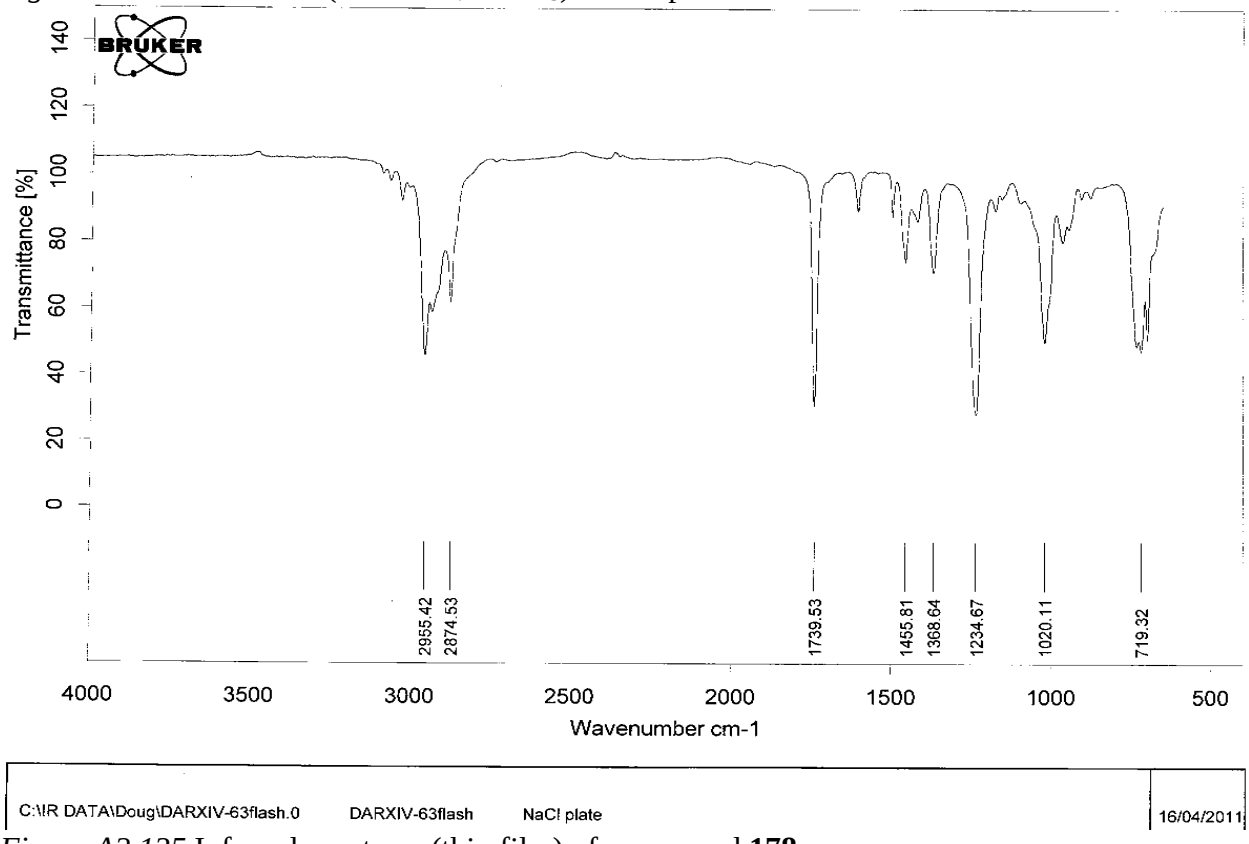
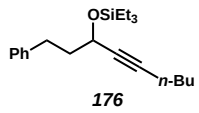


Figure A2.135 Infrared spectrum (thin film) of compound **178**



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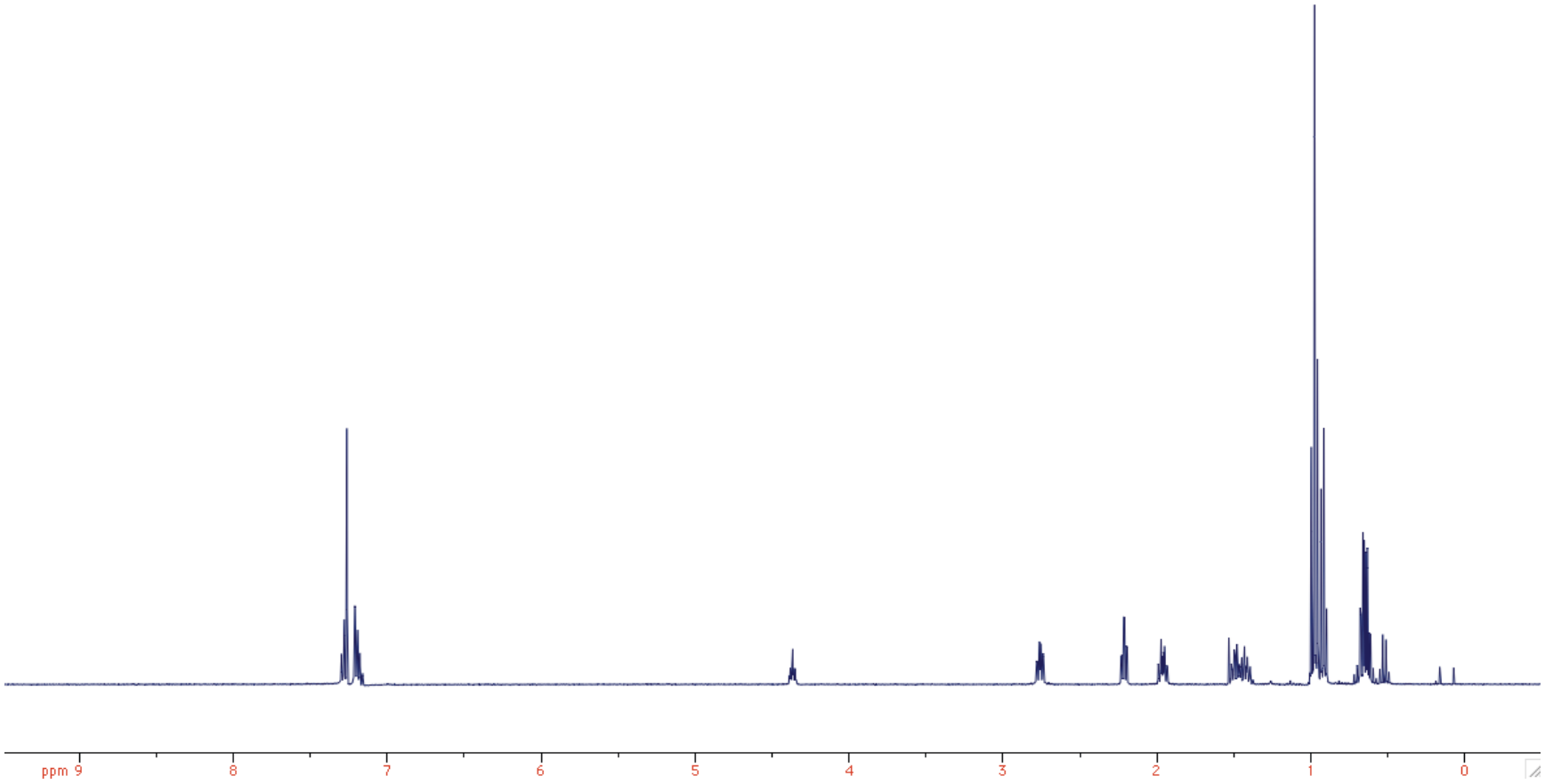


Figure A2.136 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **176**

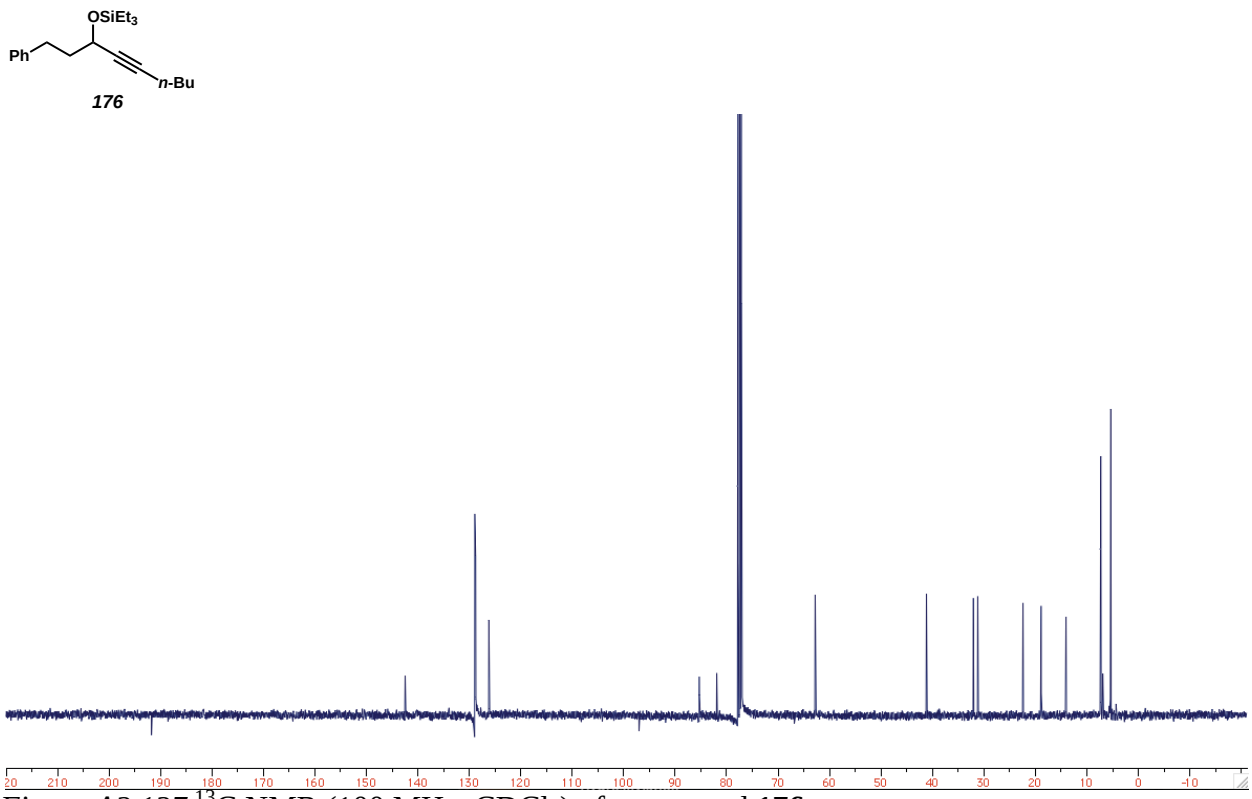


Figure A2.137 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **176**

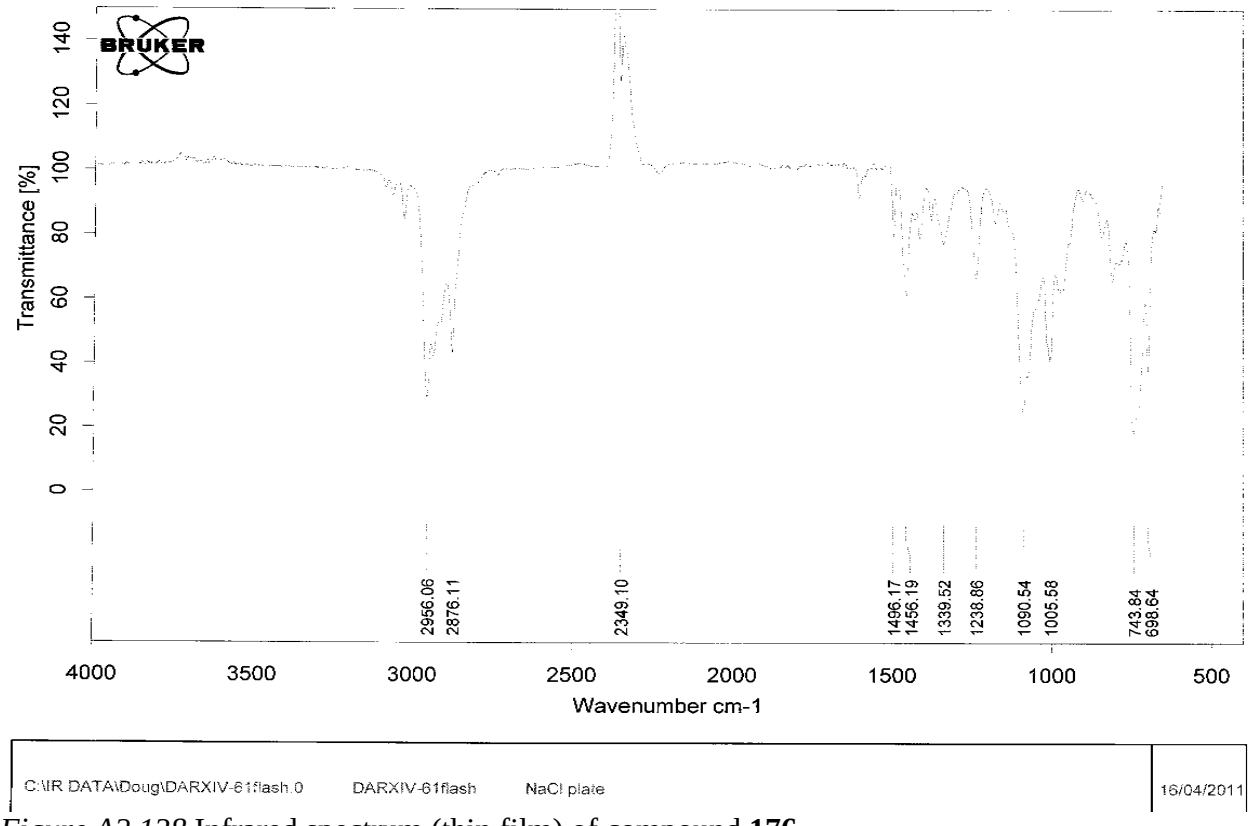
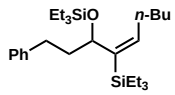


Figure A2.138 Infrared spectrum (thin film) of compound **176**



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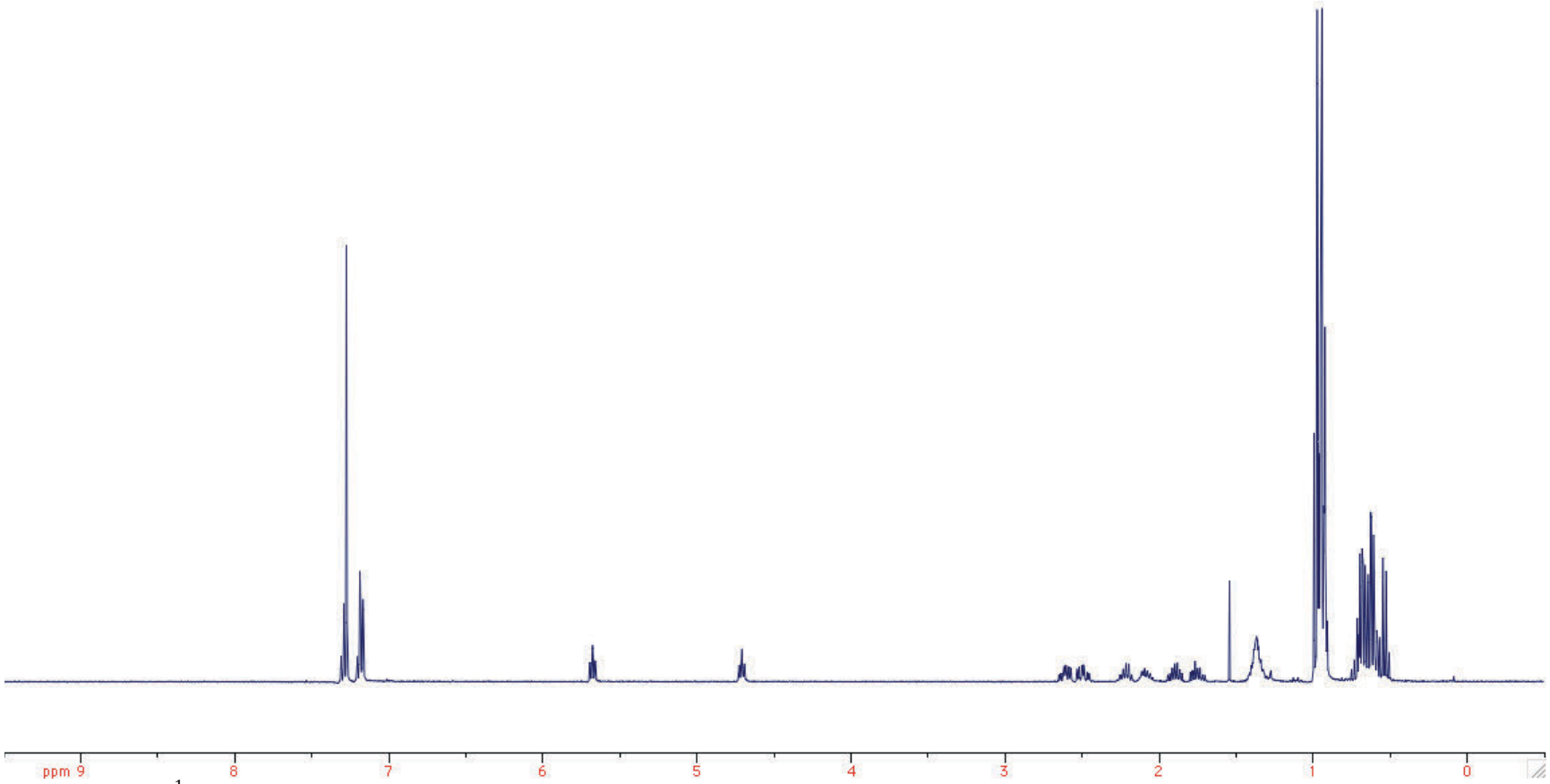


Figure A2.139 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **179**

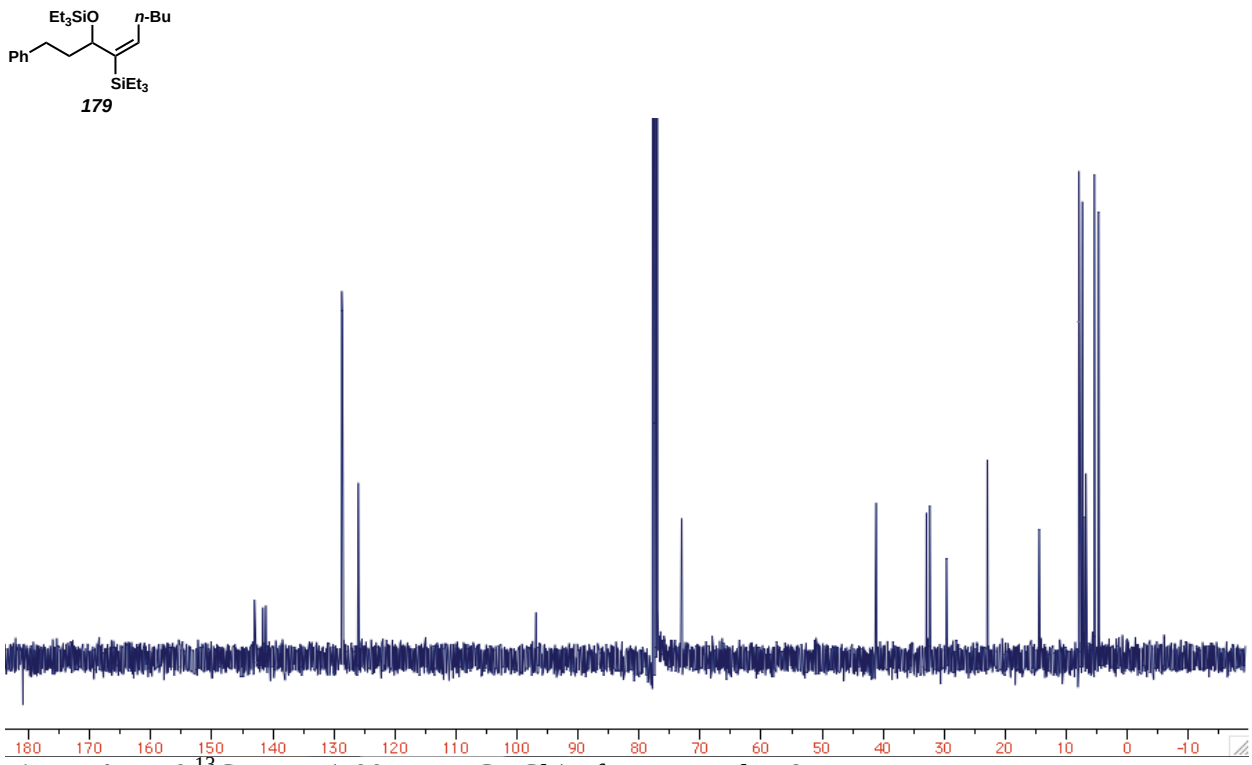


Figure A2.140 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **179**

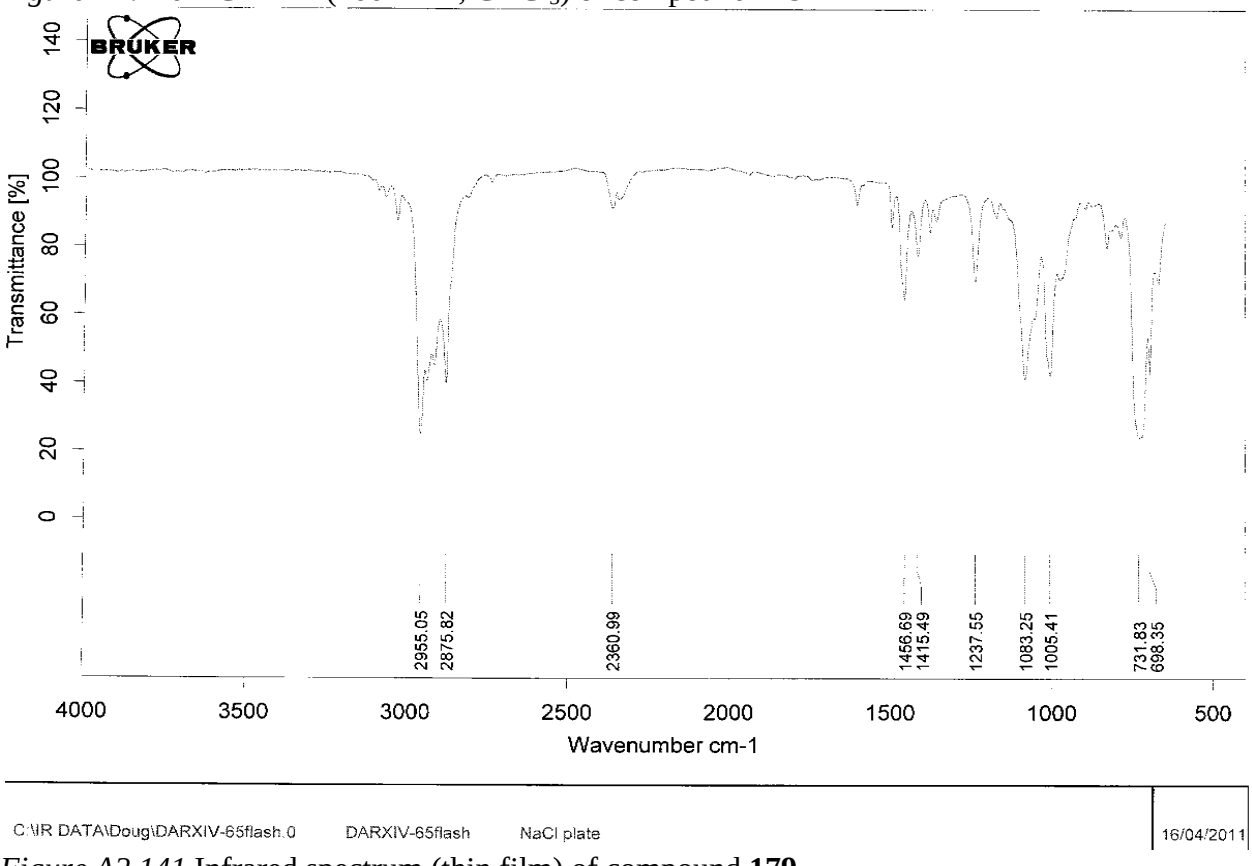
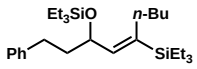


Figure A2.141 Infrared spectrum (thin film) of compound **179**



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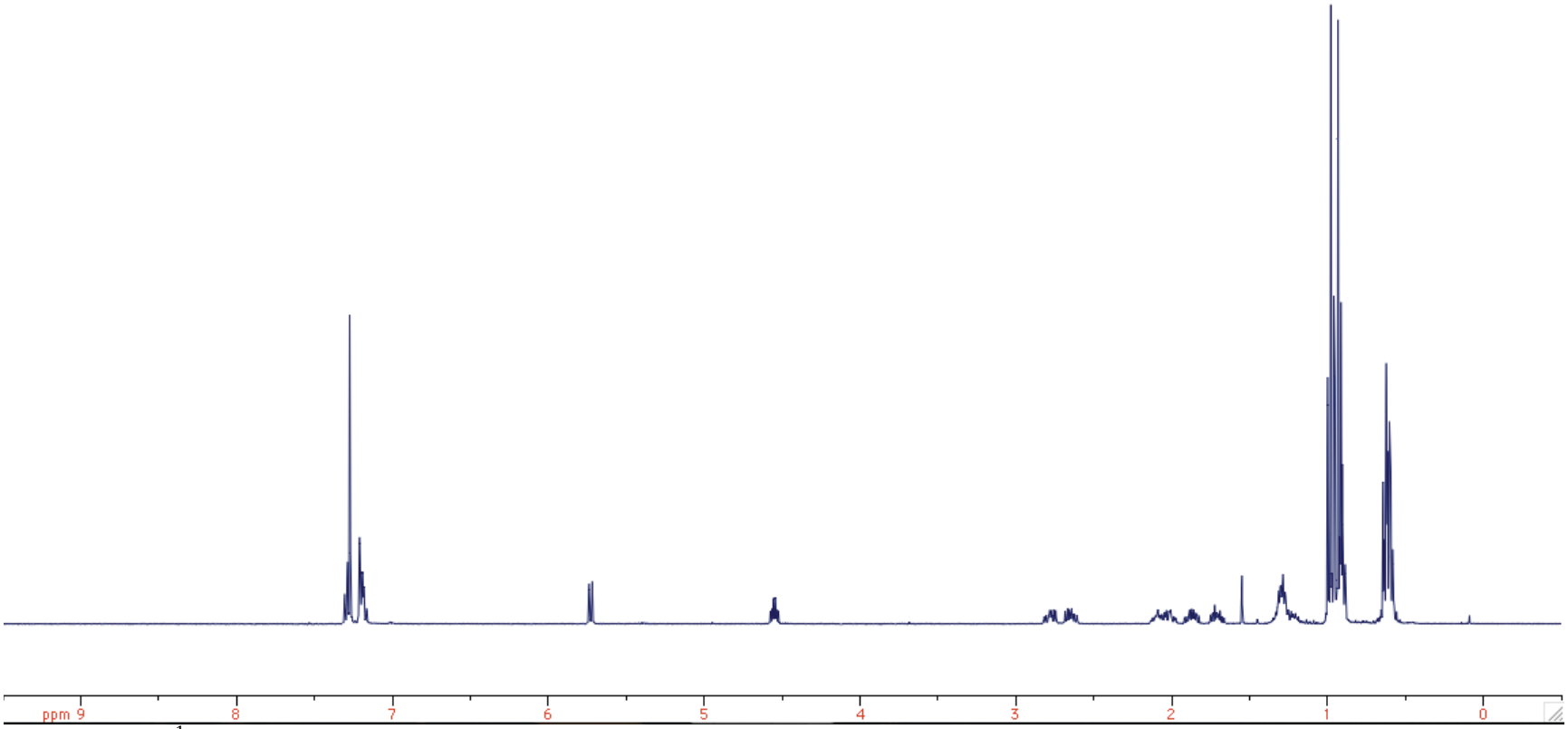


Figure A2.142 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **180**

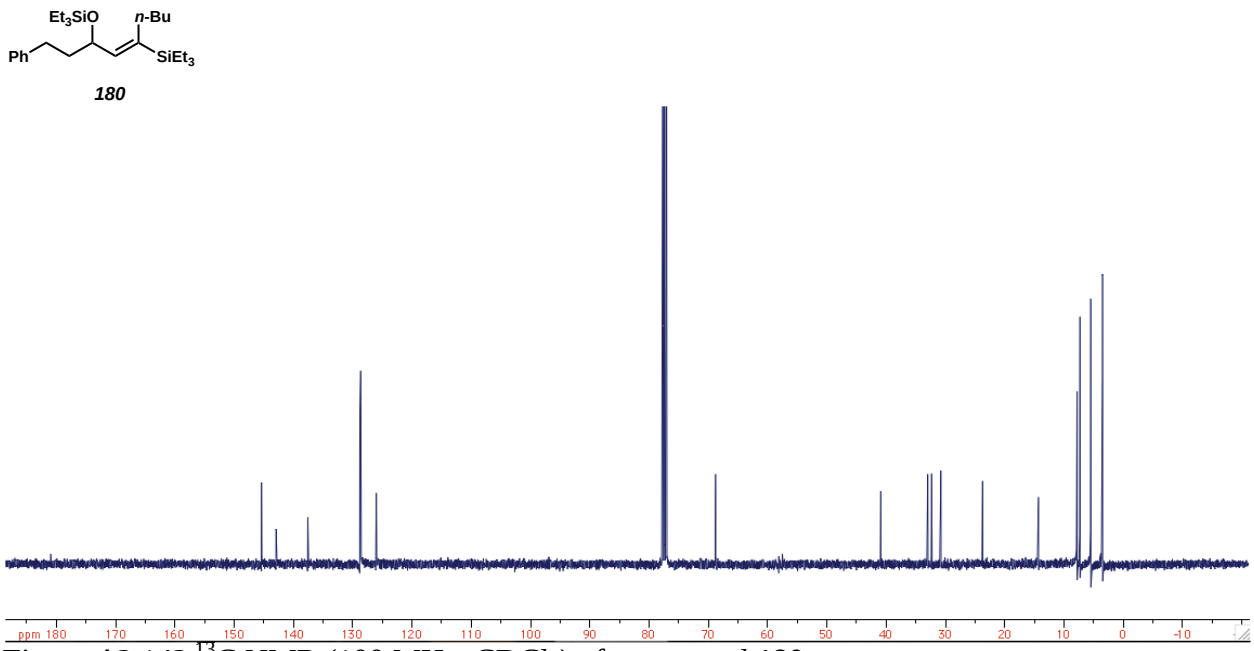


Figure A2.143 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **180**

Figure A2.144 Infrared spectrum (thin film) of compound **180**

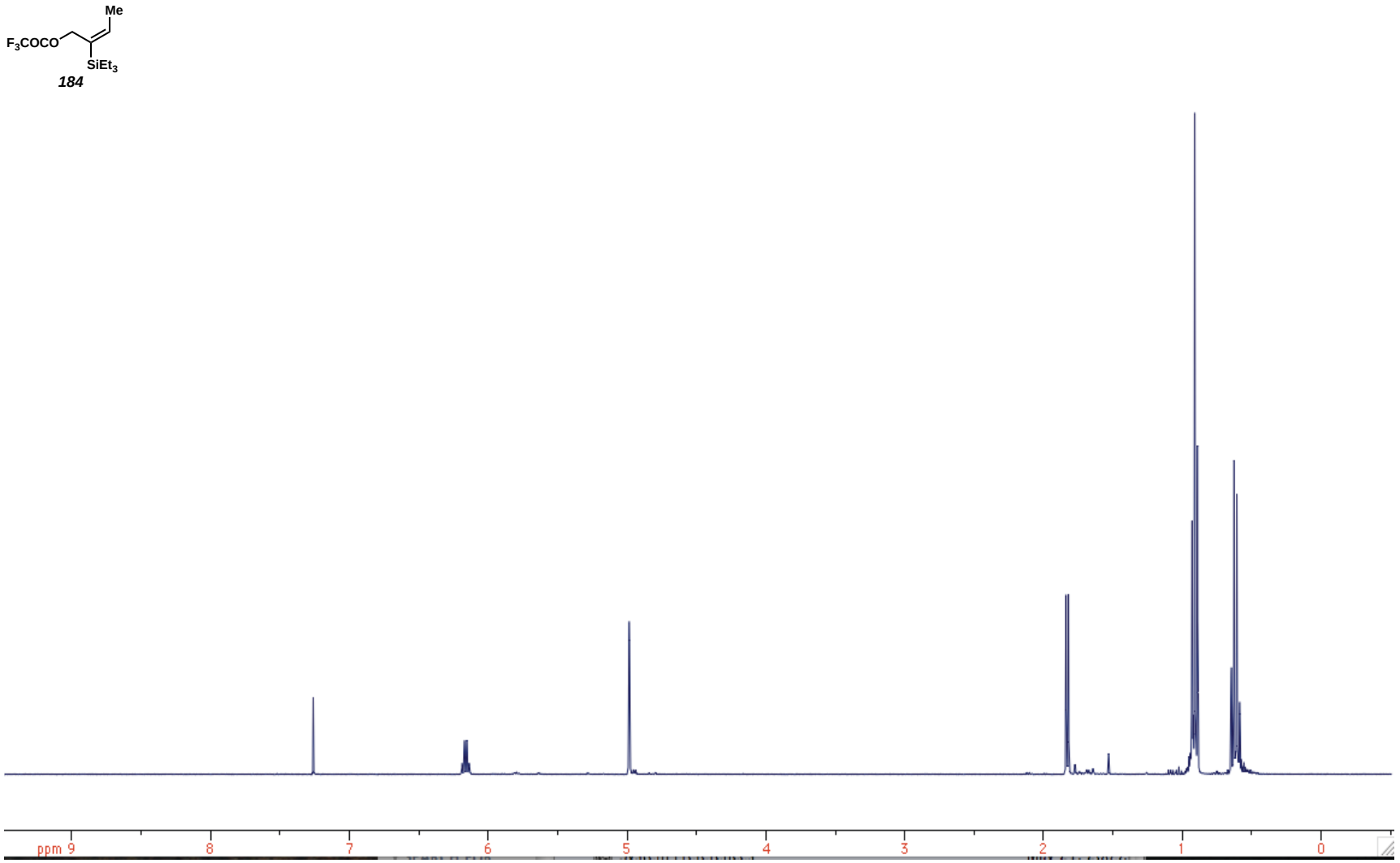


Figure A2.145 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **184**

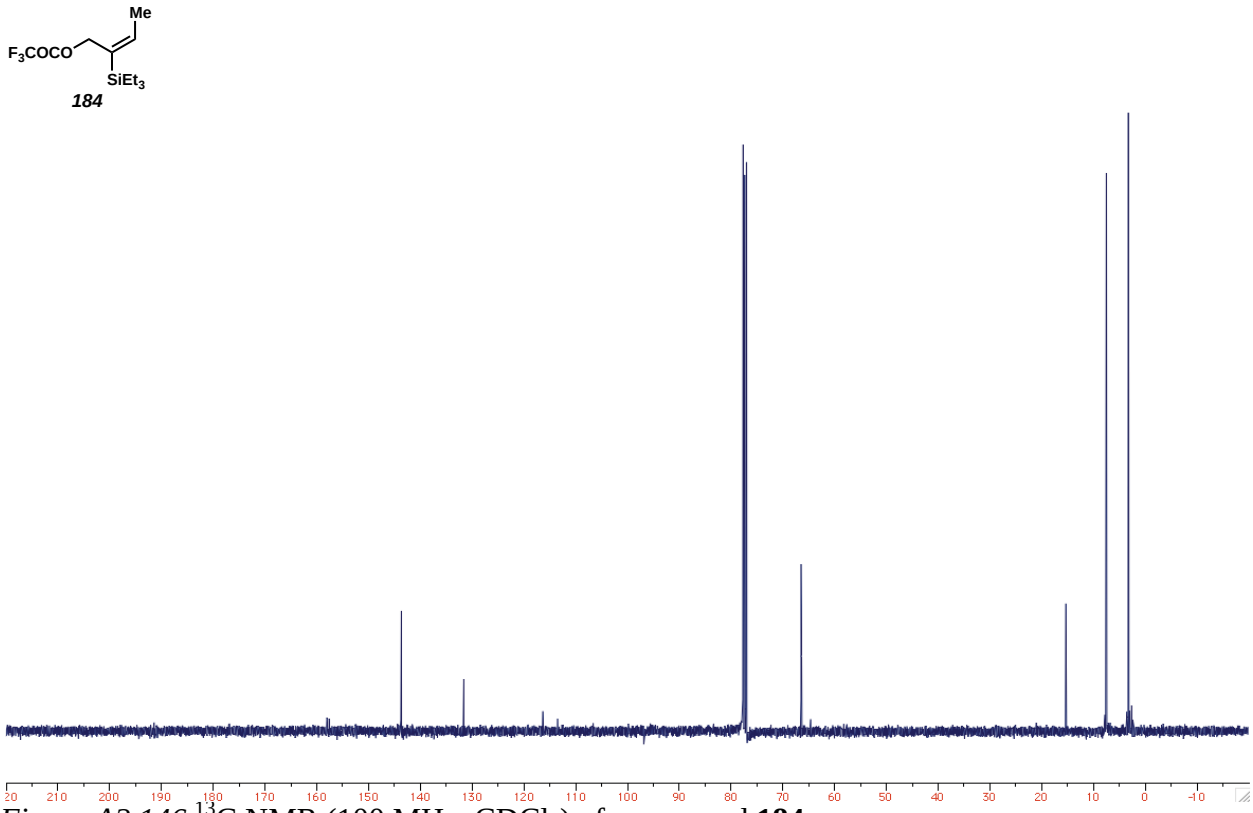


Figure A2.146 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **184**

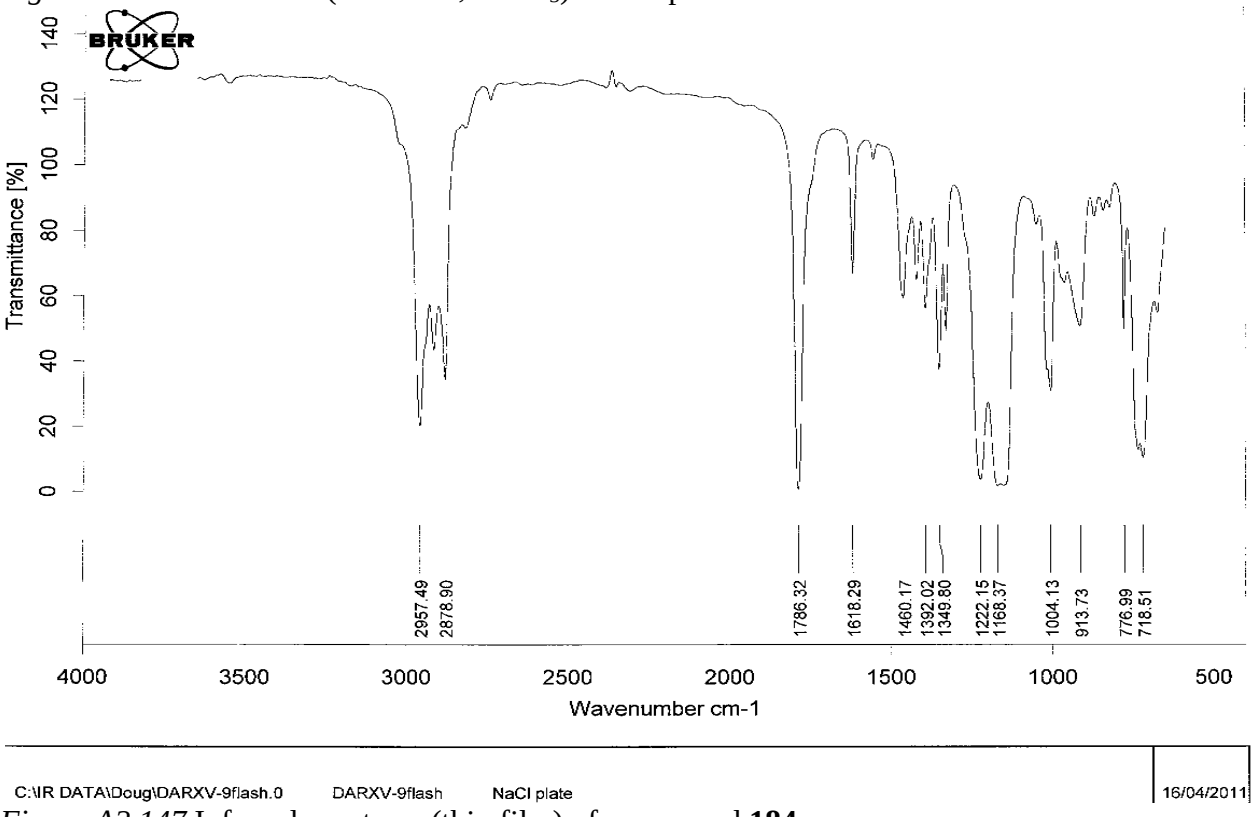
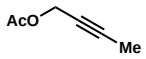


Figure A2.147 Infrared spectrum (thin film) of compound **184**



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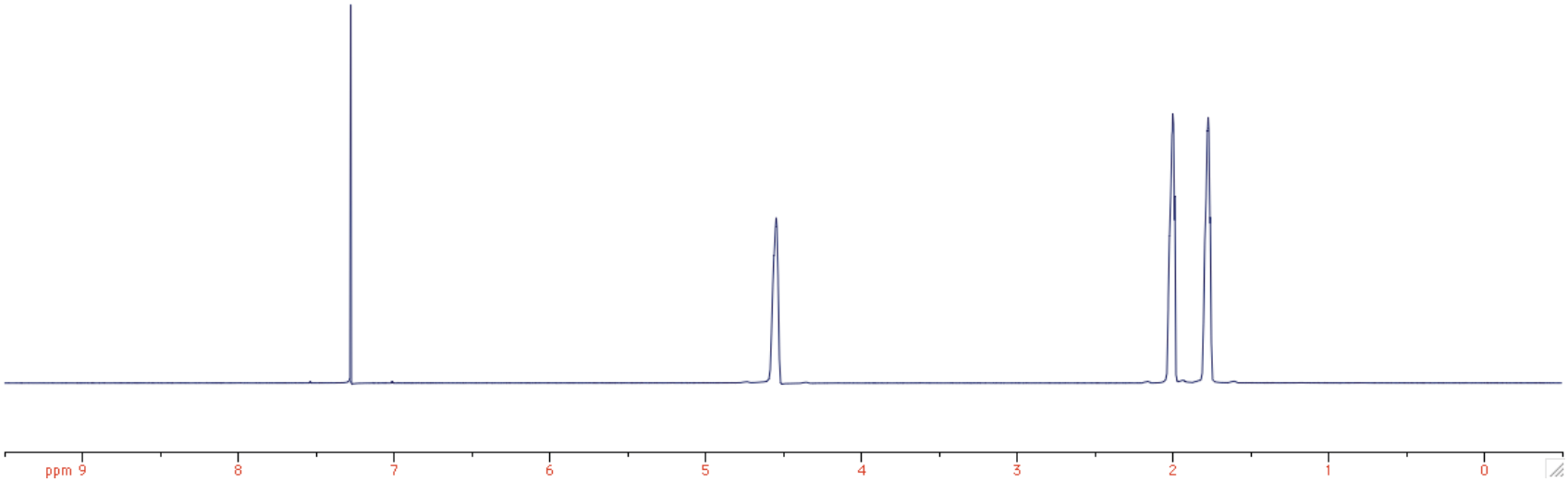
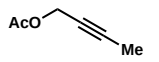


Figure A2.148 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **185**



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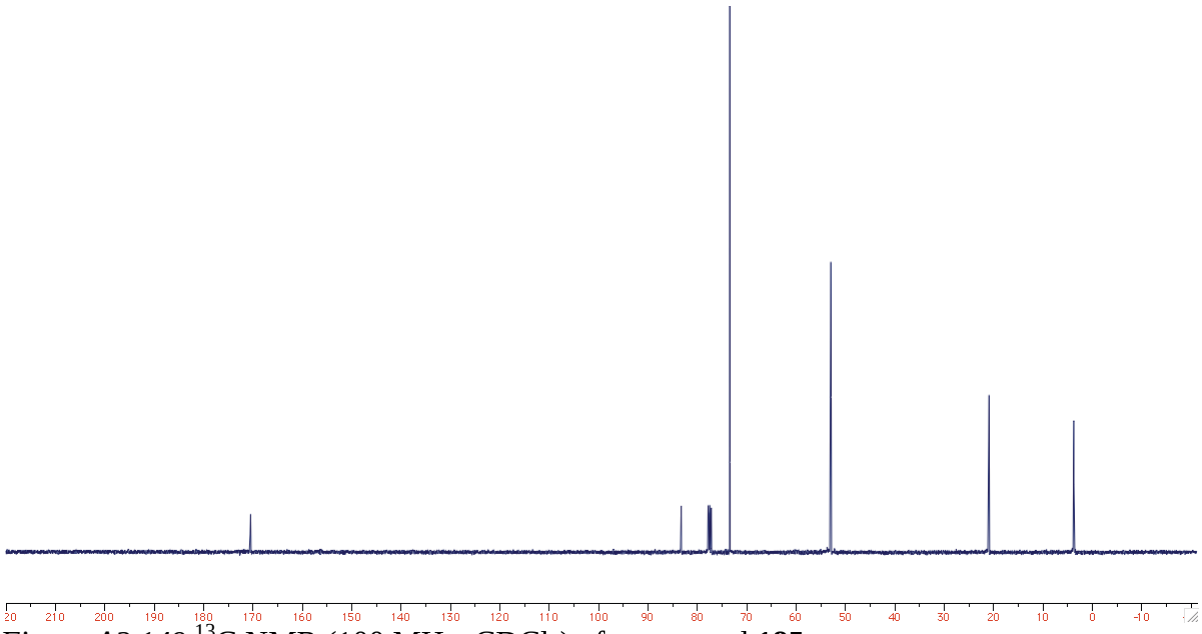


Figure A2.149 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **185**

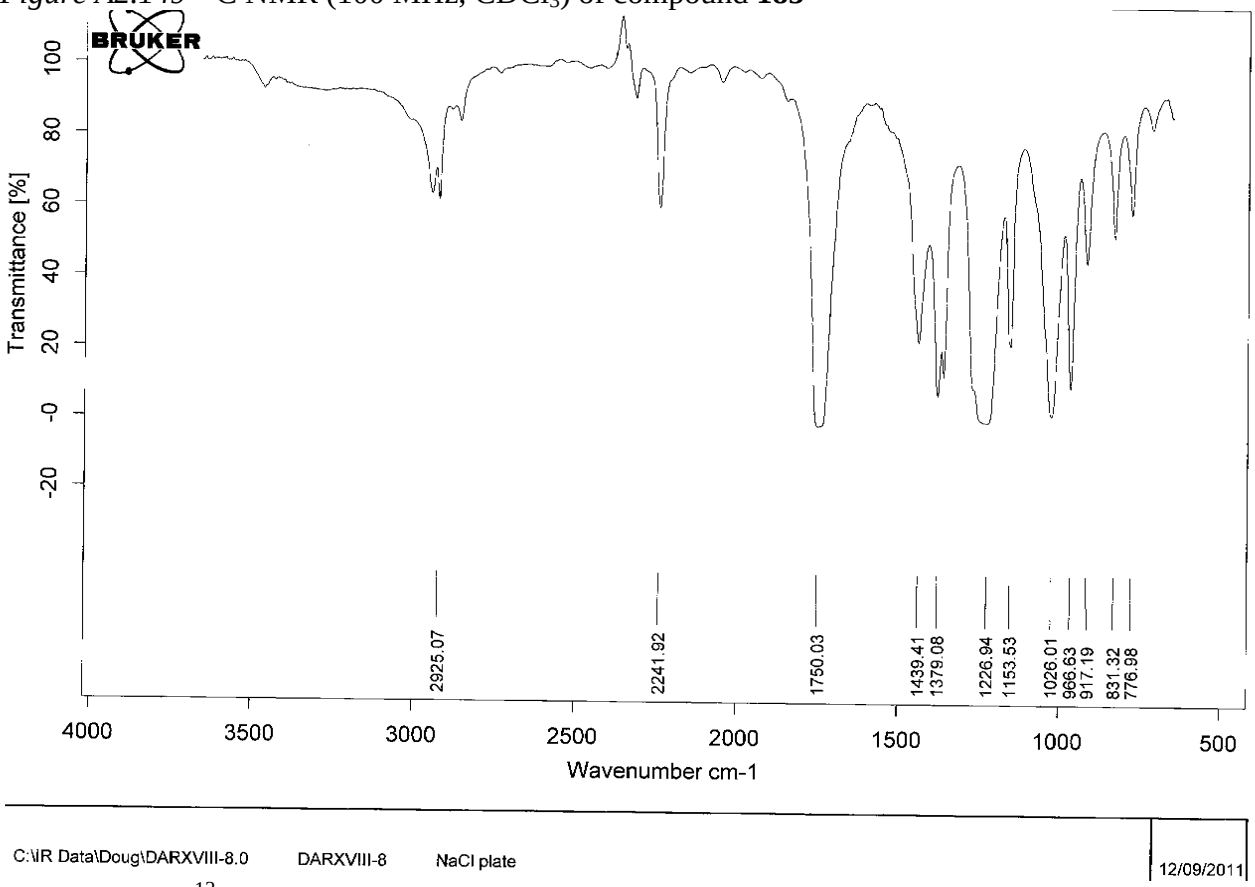
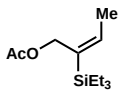


Figure A2.150 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **185**



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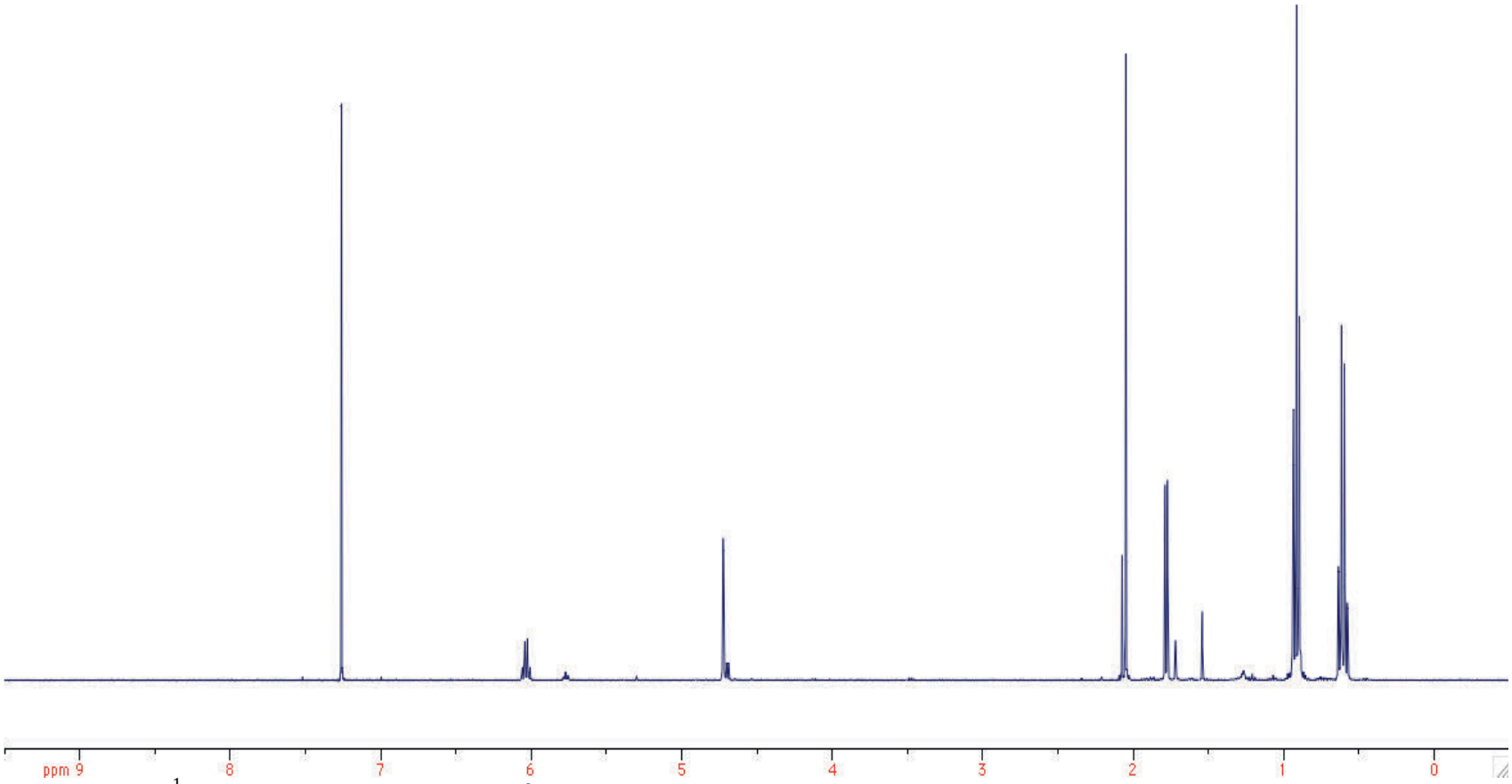


Figure A2.148 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **186**

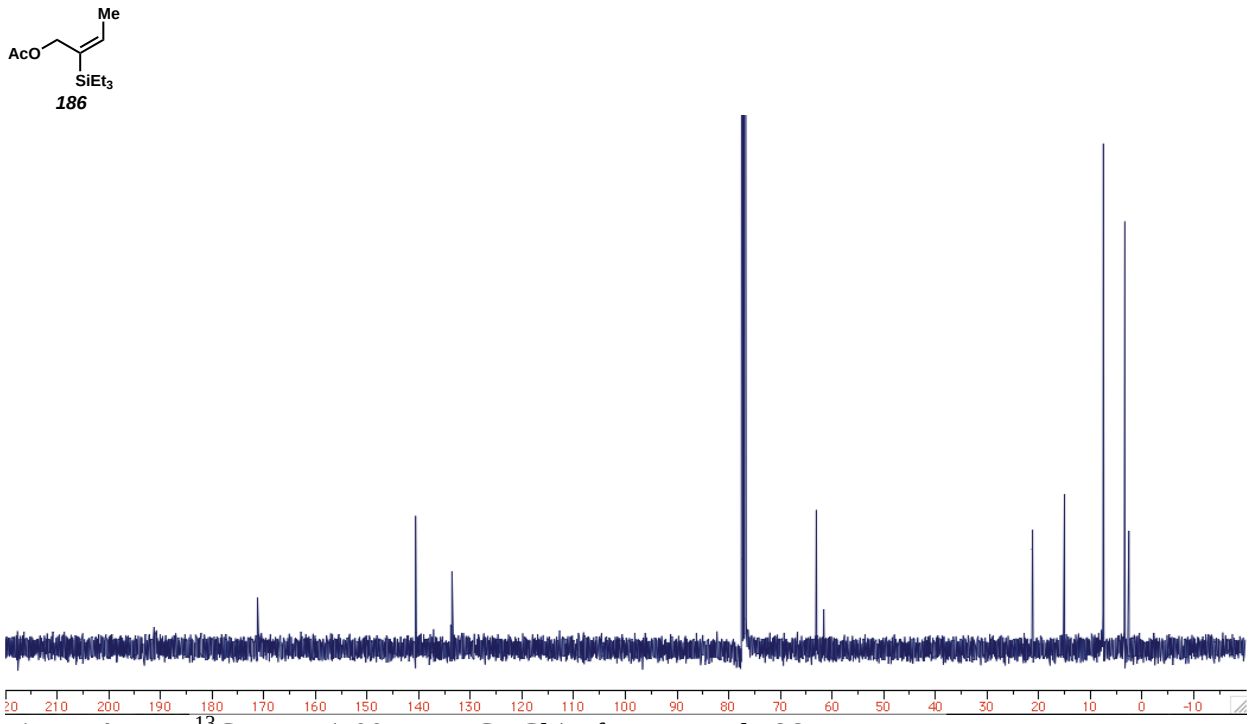


Figure A2.149 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **186**

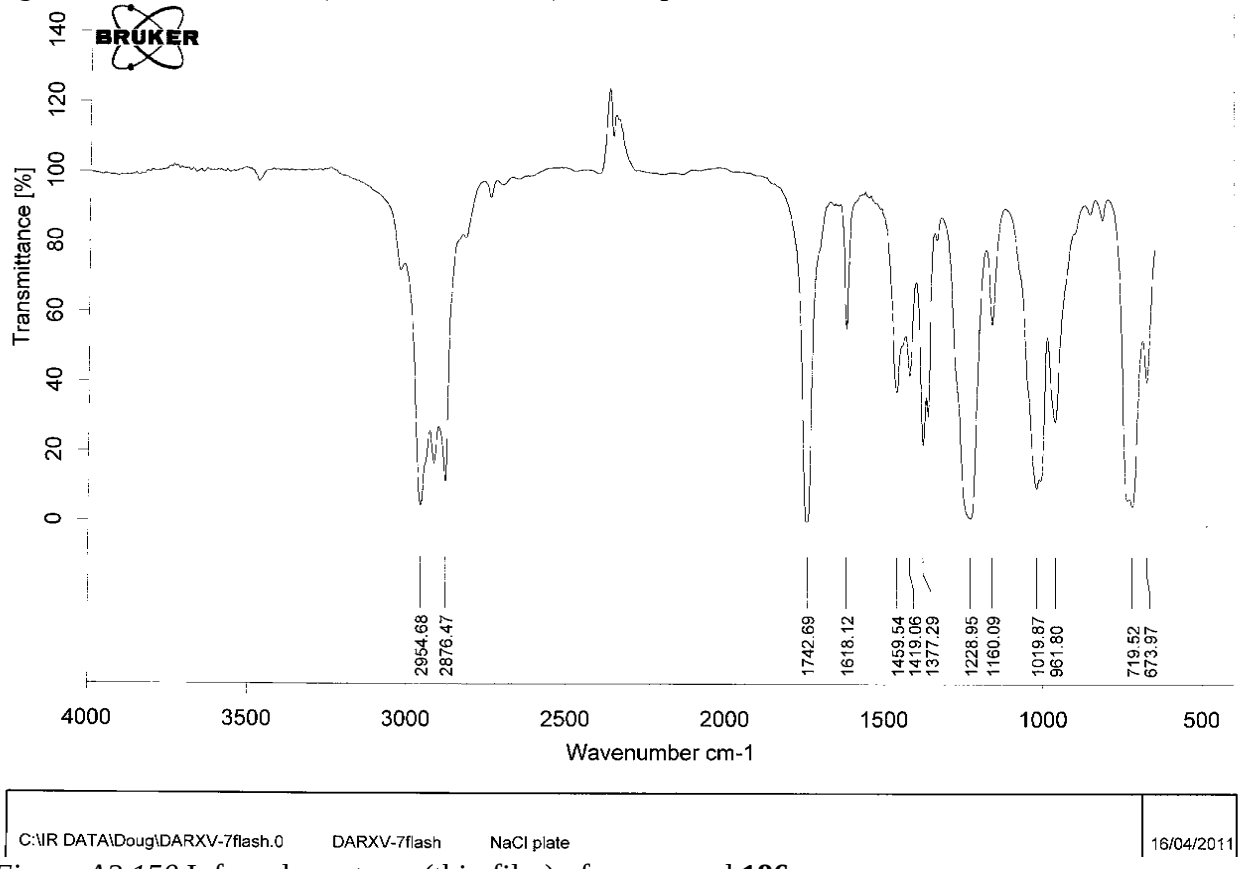
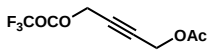


Figure A2.150 Infrared spectrum (thin film) of compound **186**



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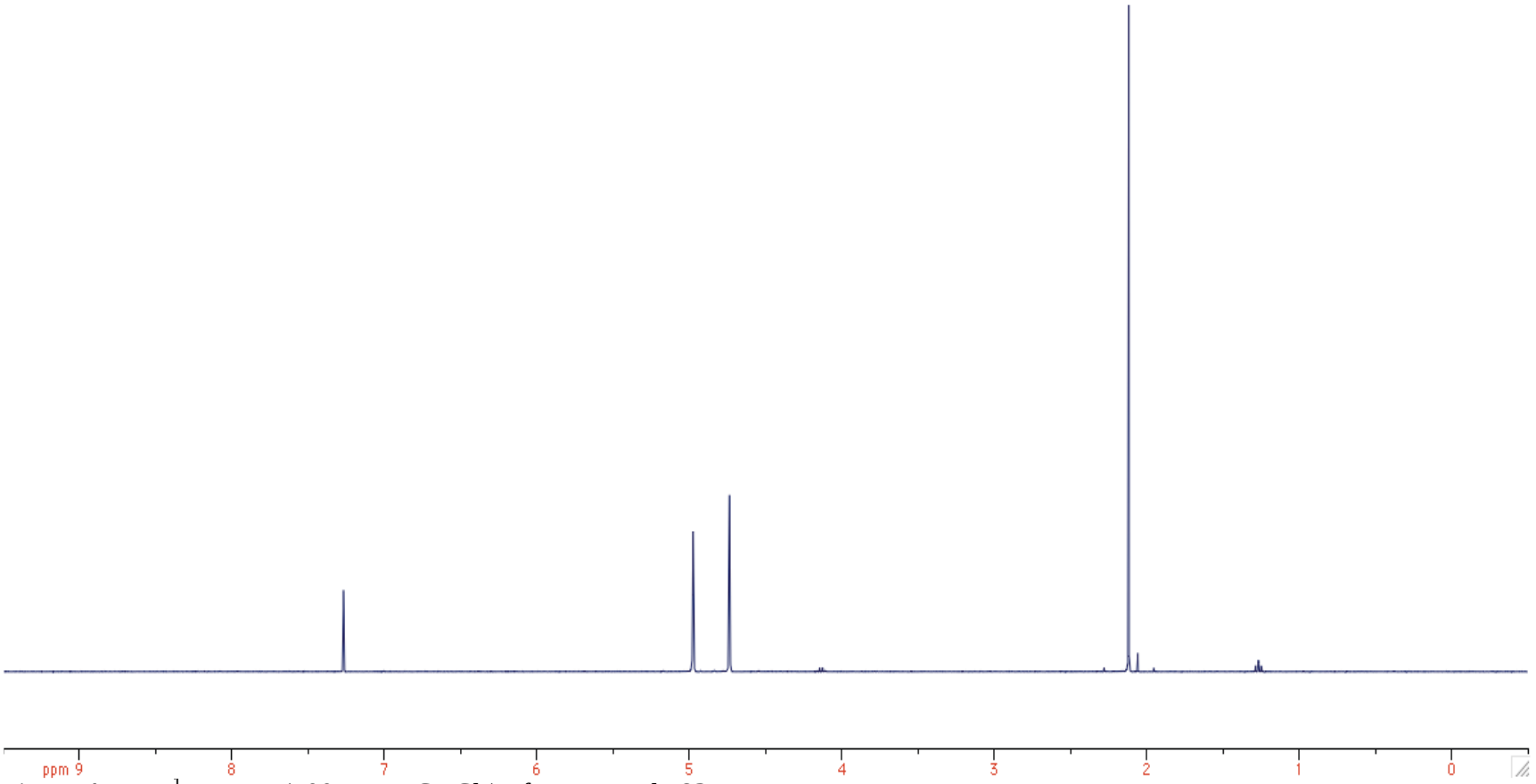


Figure A2.151 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **183**

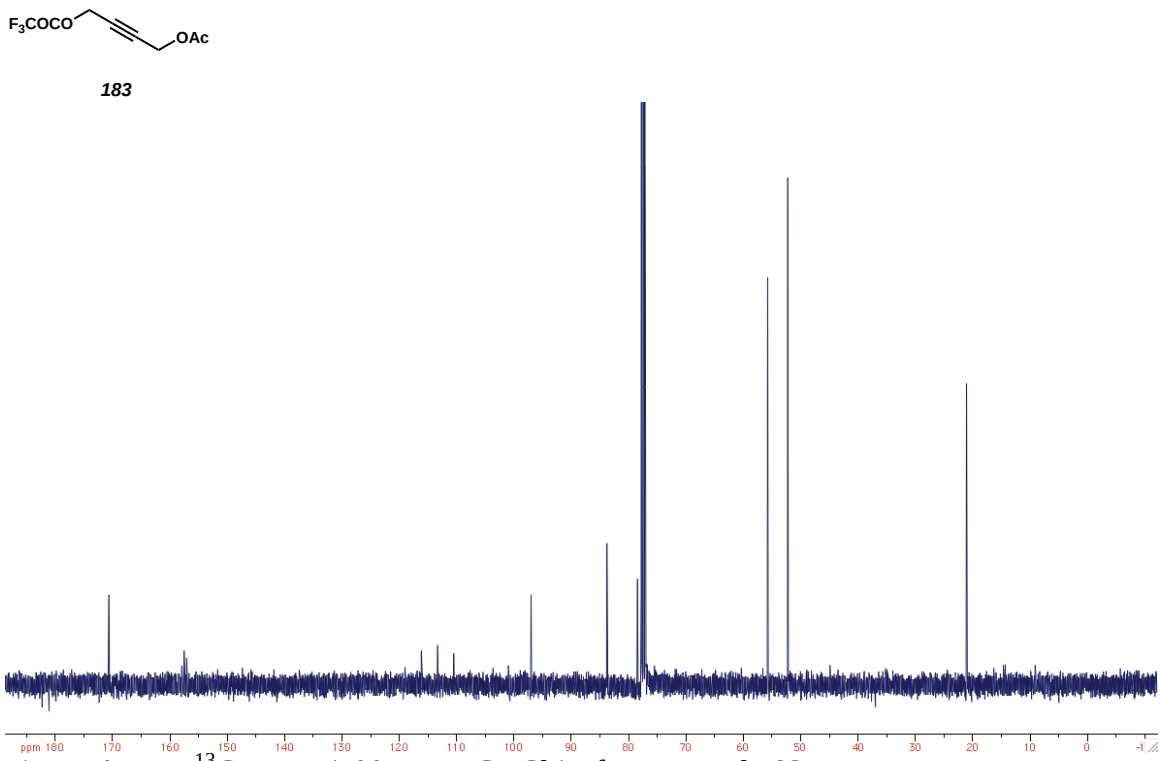


Figure A2.152 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **183**

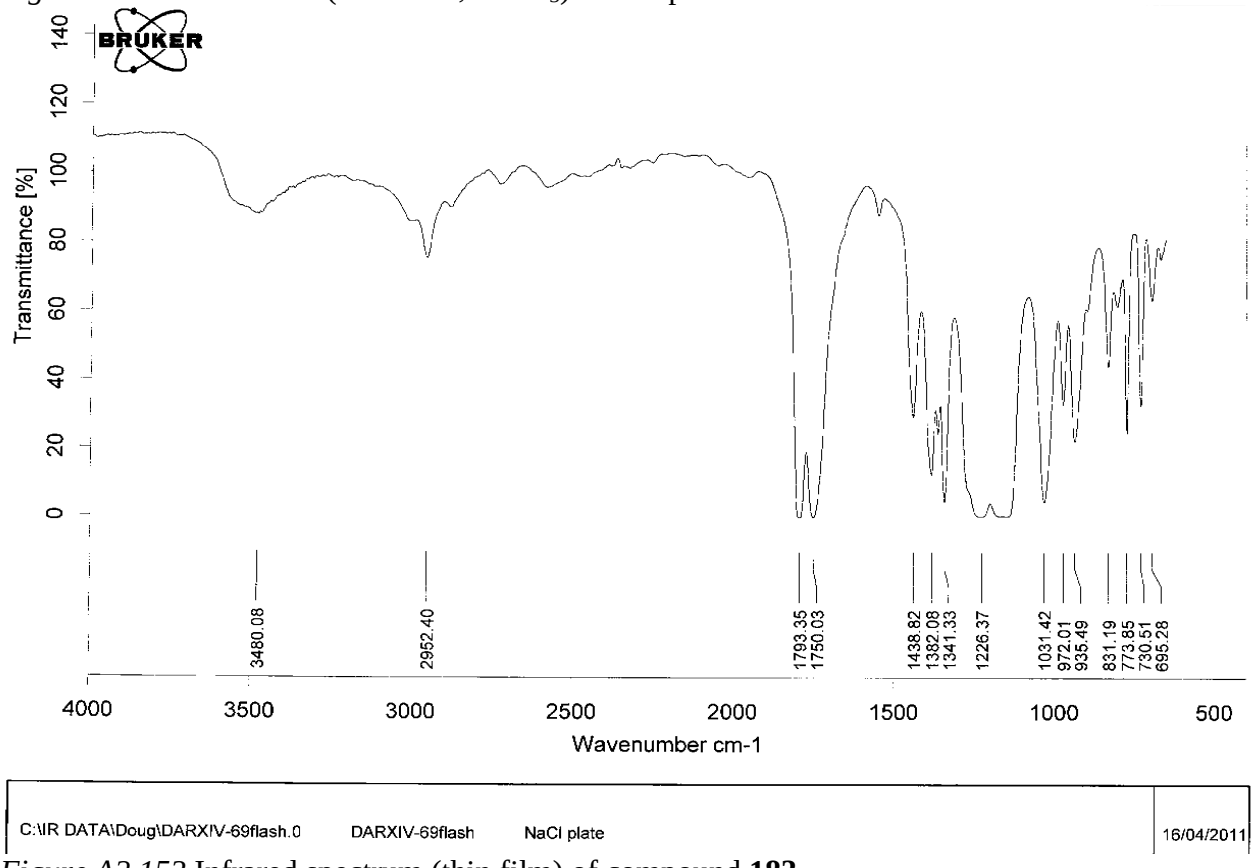
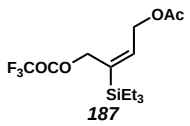


Figure A2.153 Infrared spectrum (thin film) of compound **183**



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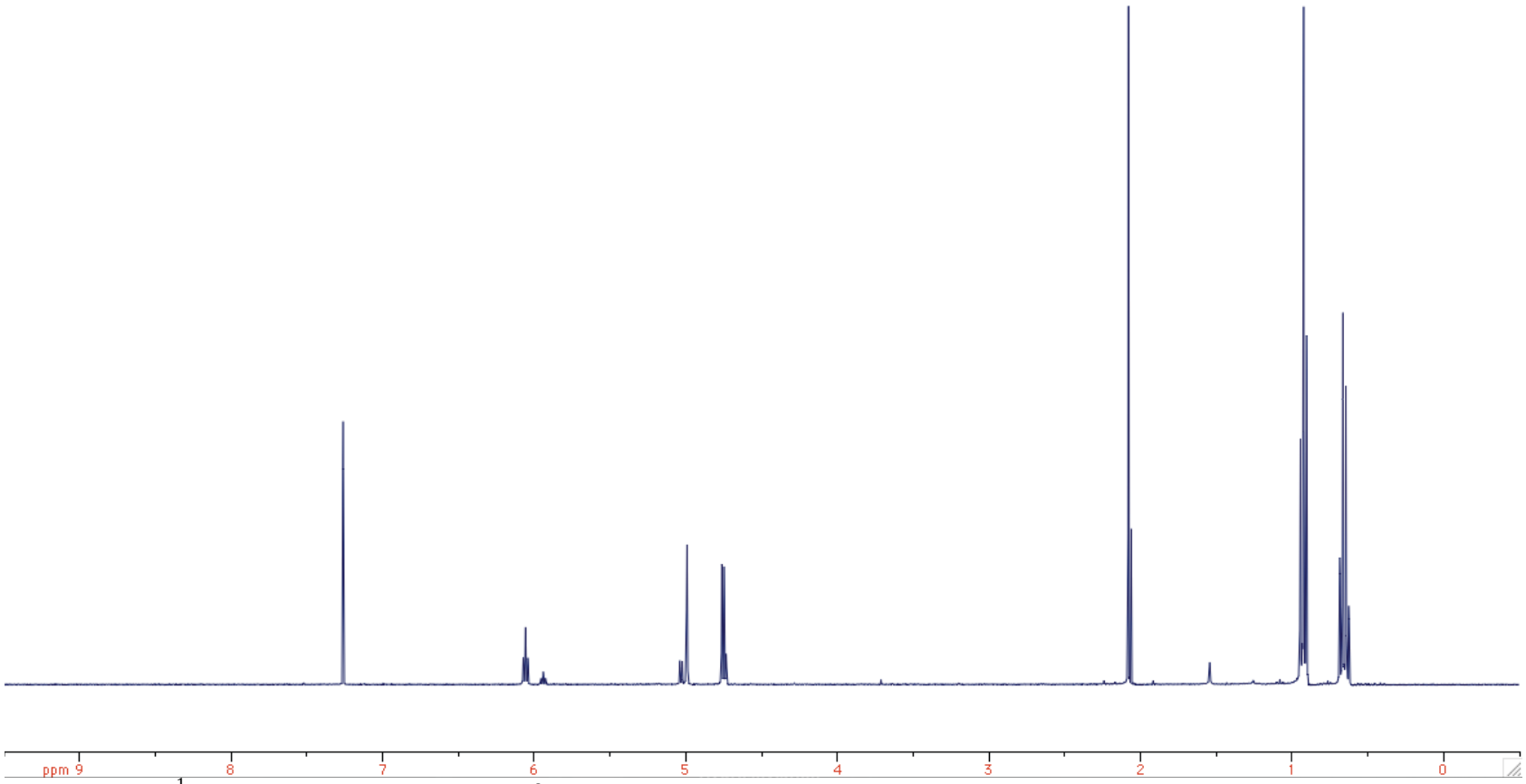


Figure A2.154 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **187**

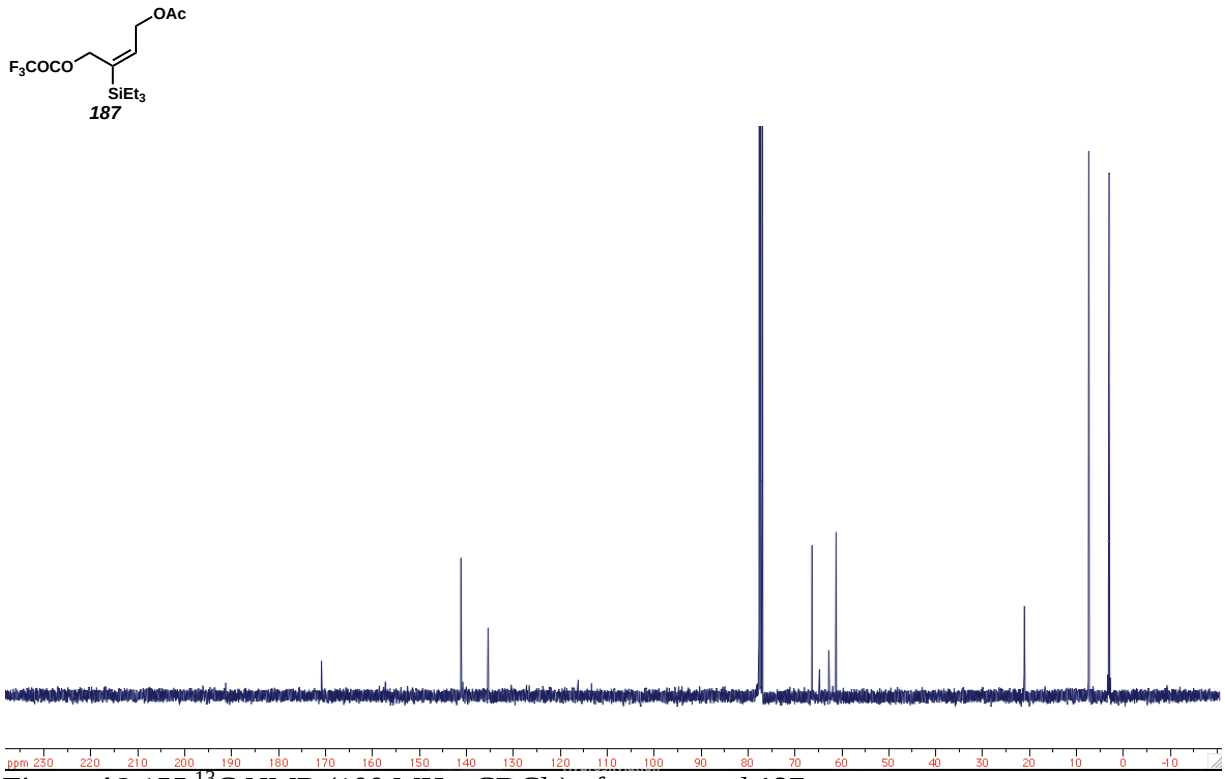


Figure A2.155 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **187**

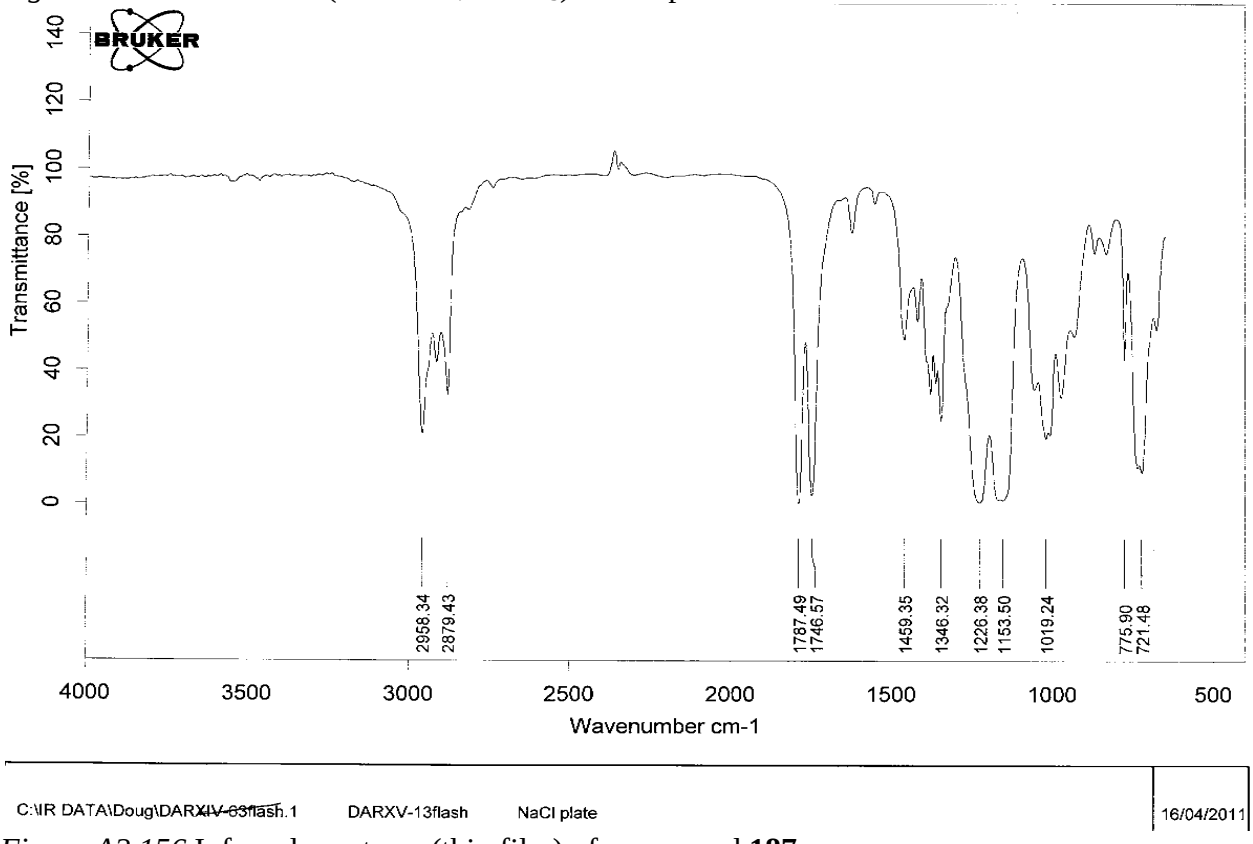
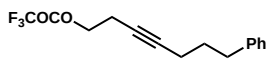


Figure A2.156 Infrared spectrum (thin film) of compound **187**



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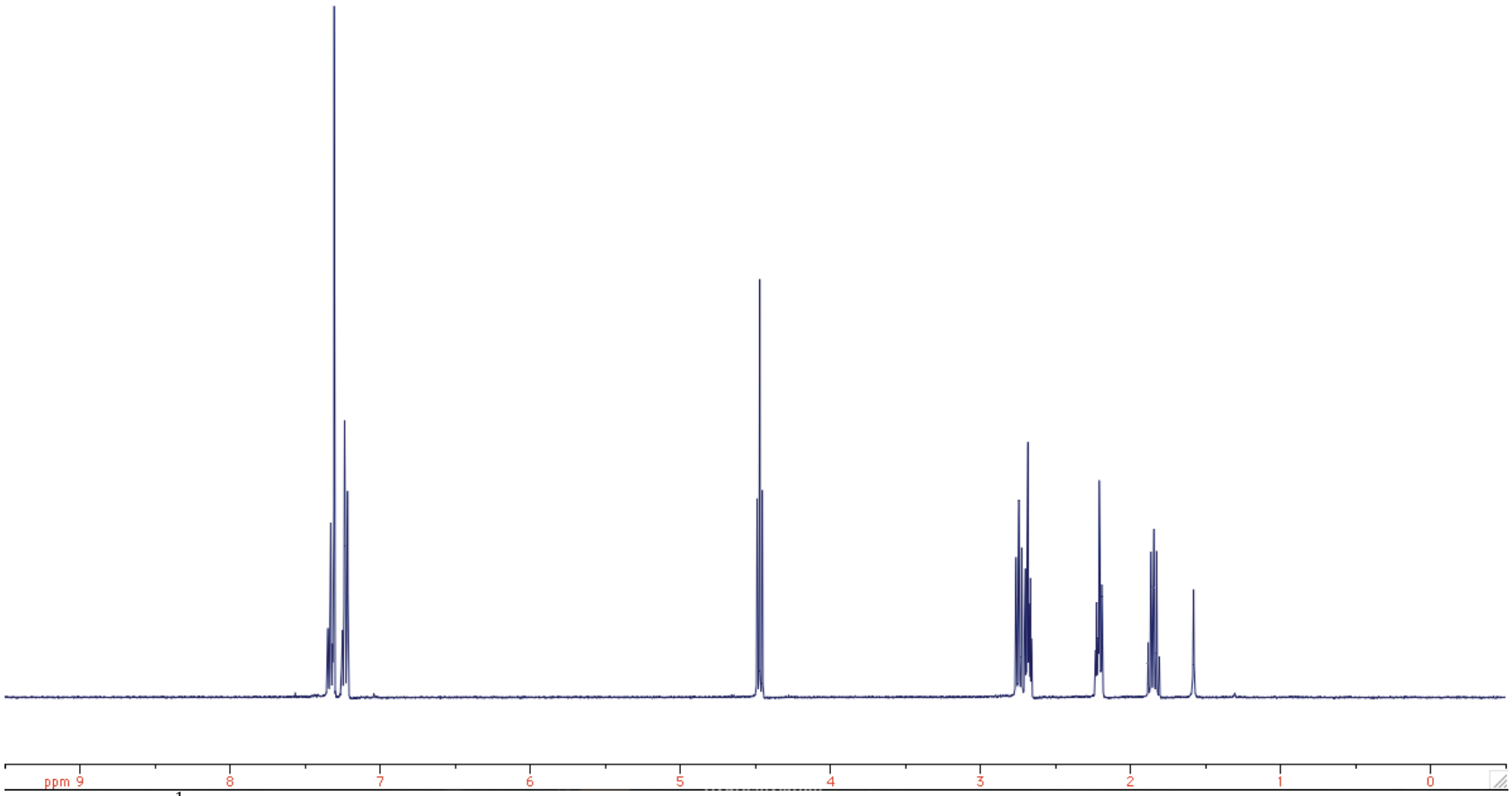
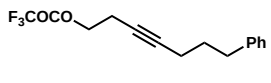


Figure A2.157 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **188**



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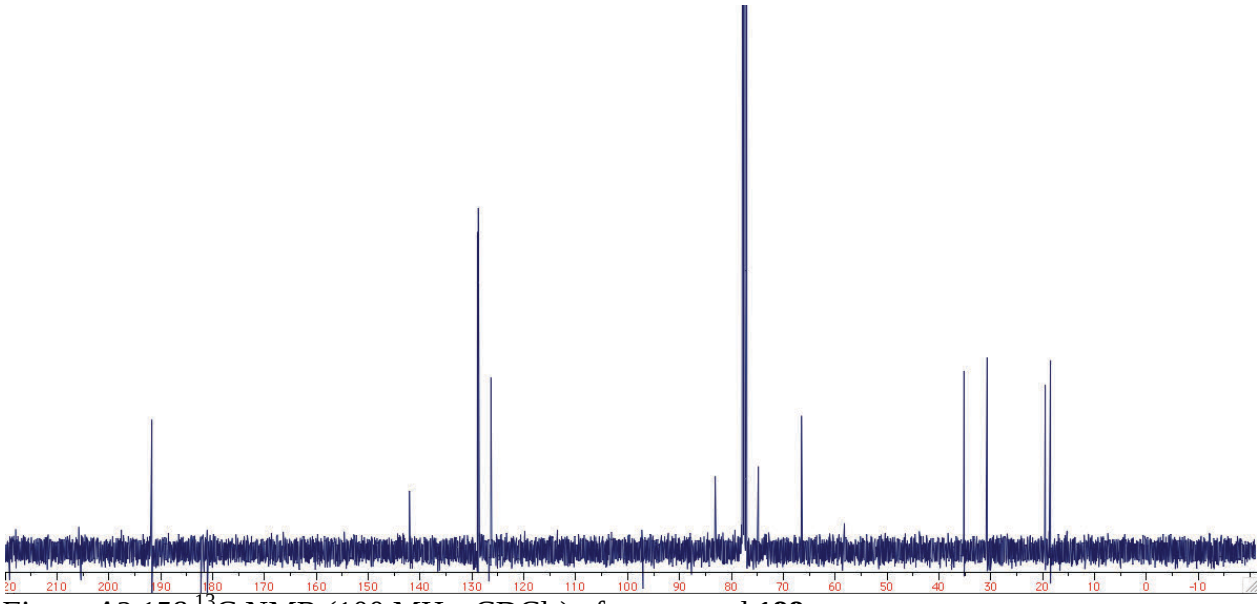


Figure A2.158 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **188**

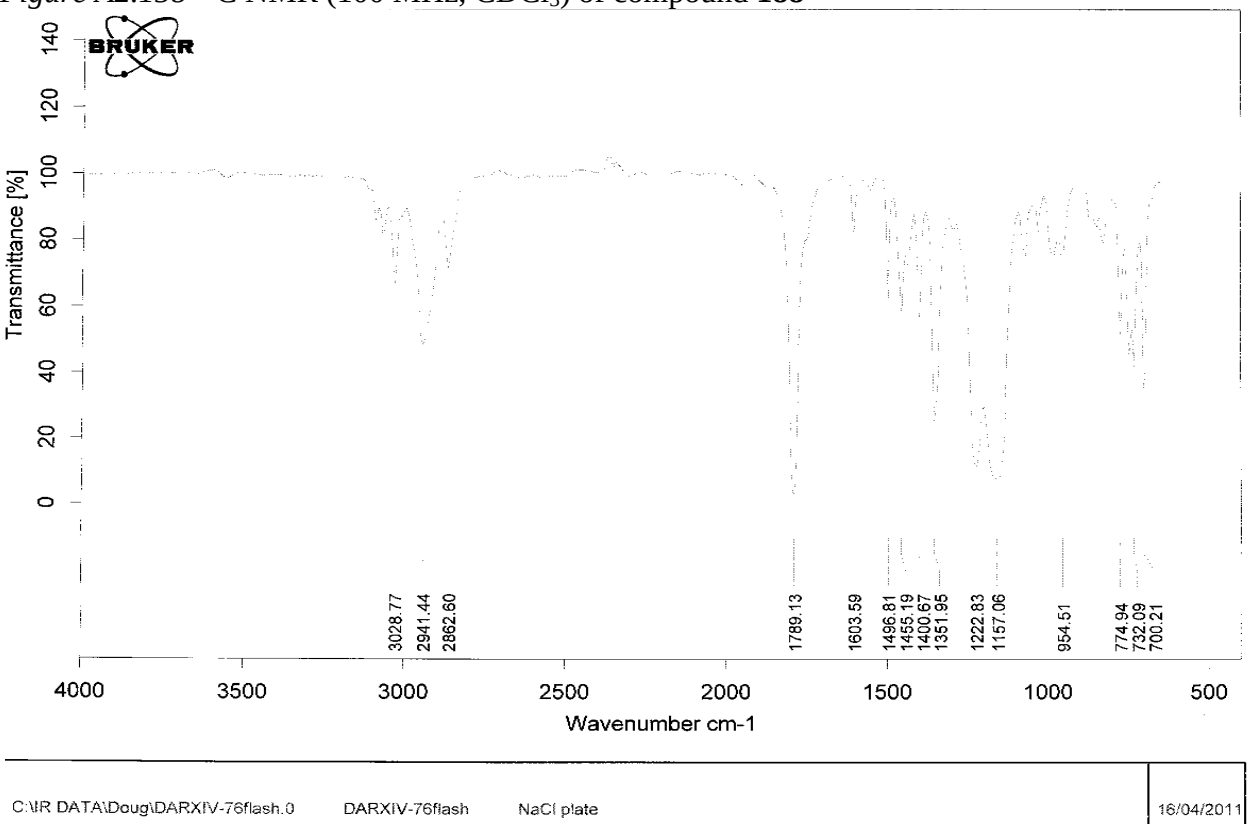


Figure A2.159 Infrared spectrum (thin film) of compound **188**

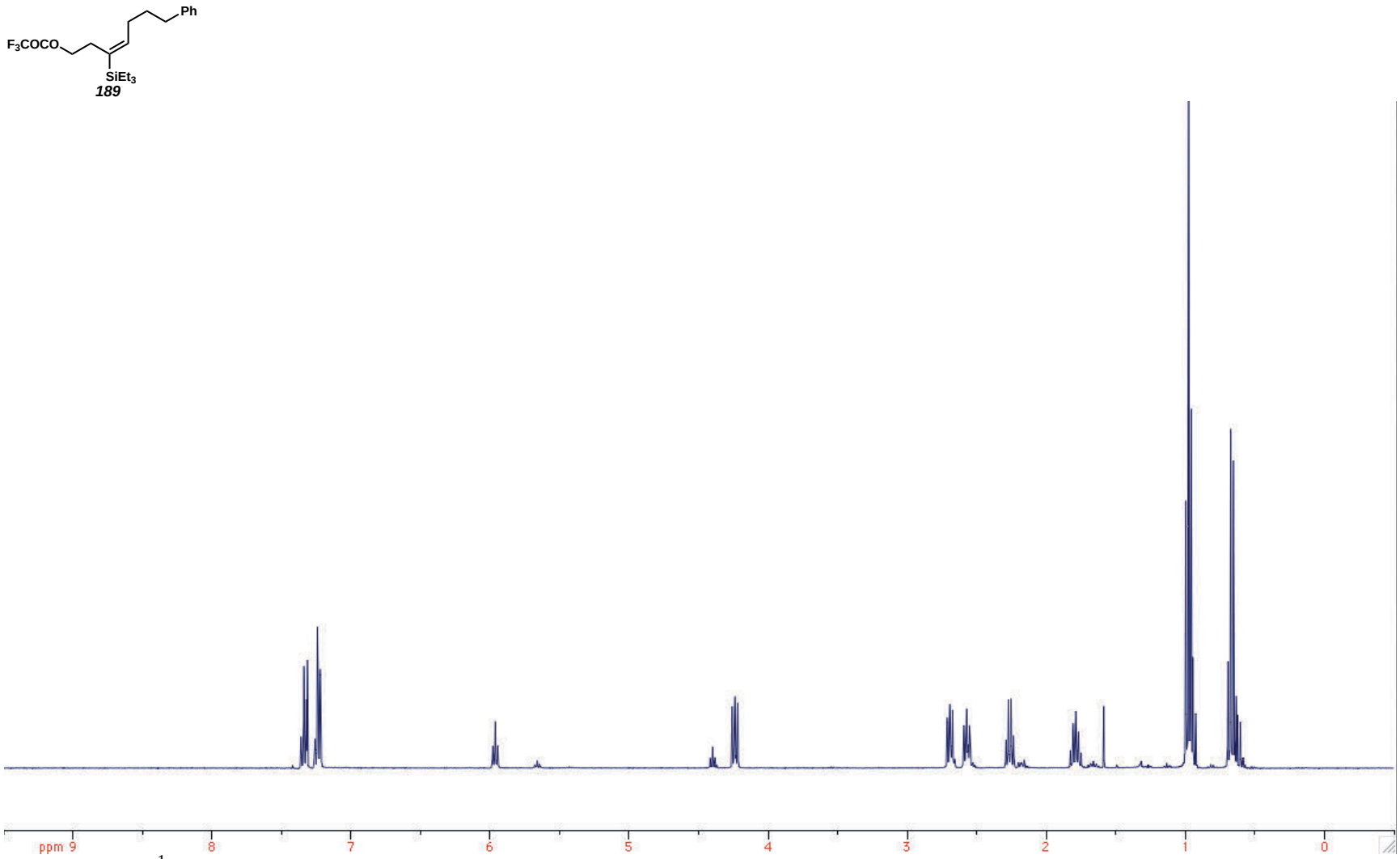
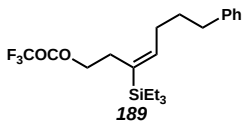


Figure A2.160 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **189**



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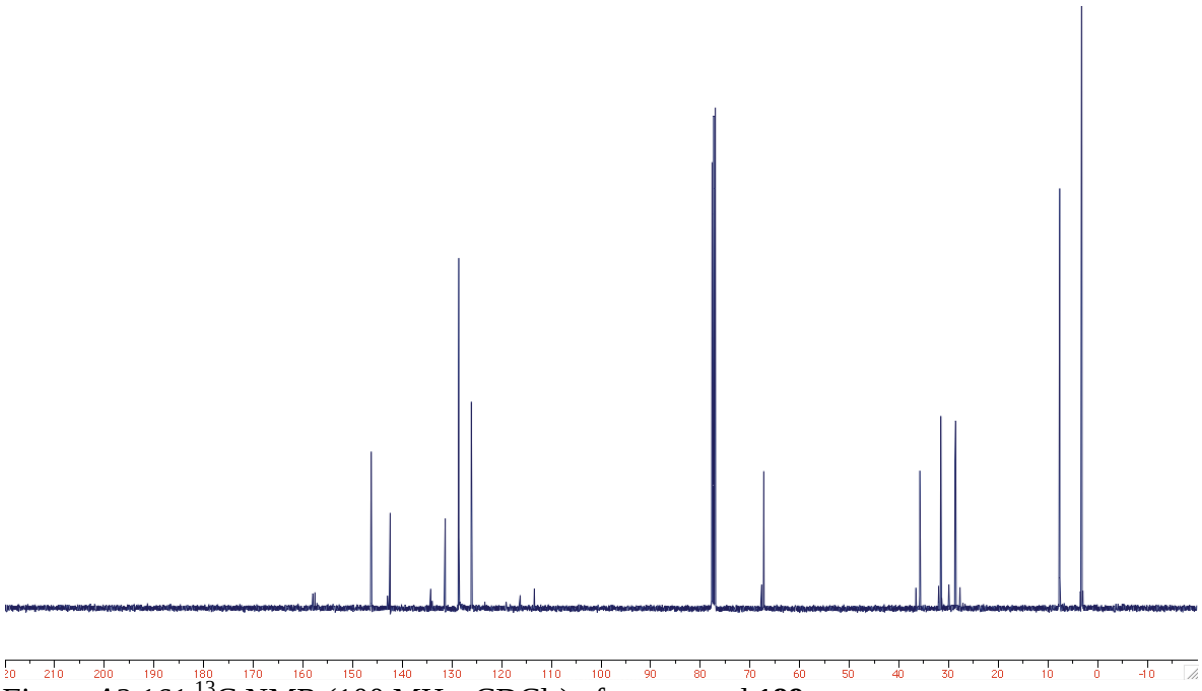


Figure A2.161 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **189**

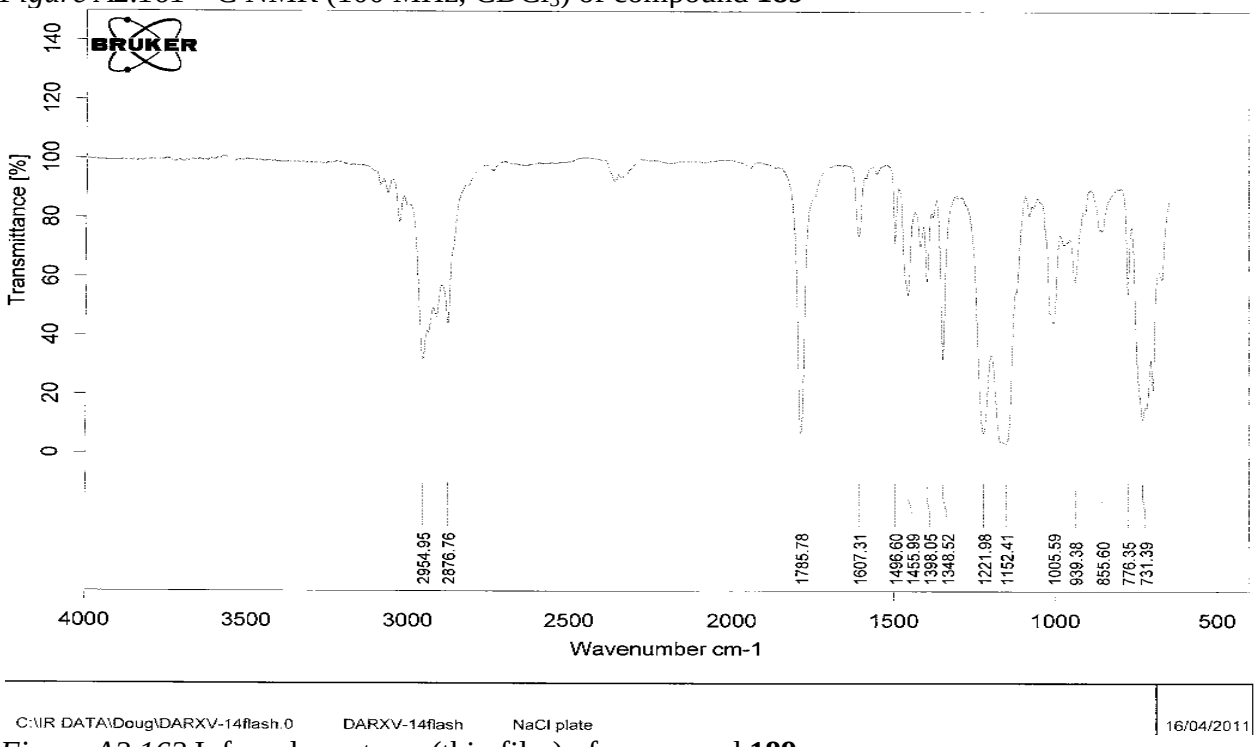
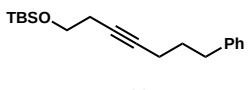


Figure A2.162 Infrared spectrum (thin film) of compound **189**



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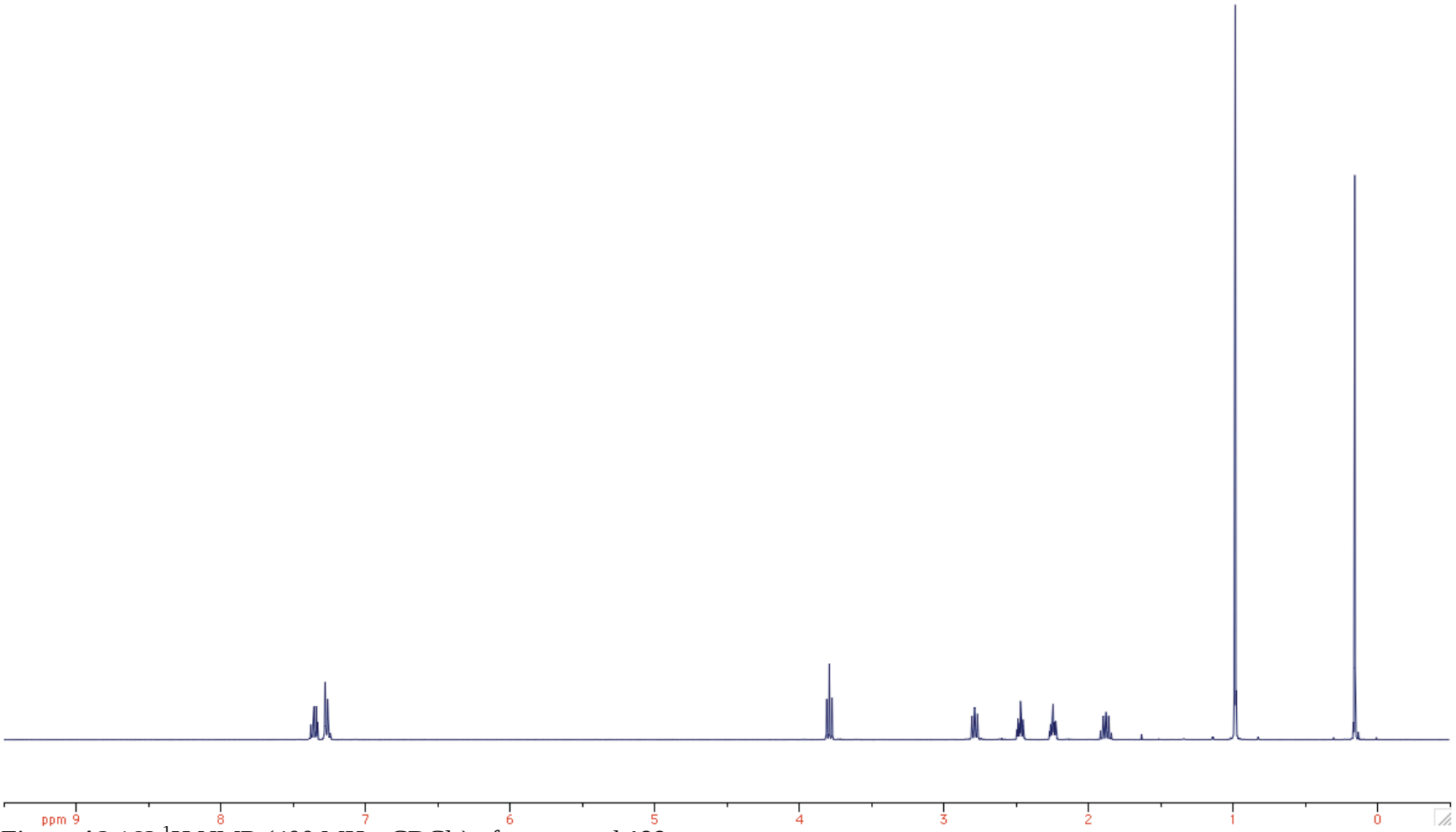
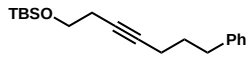


Figure A2.163 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **199**



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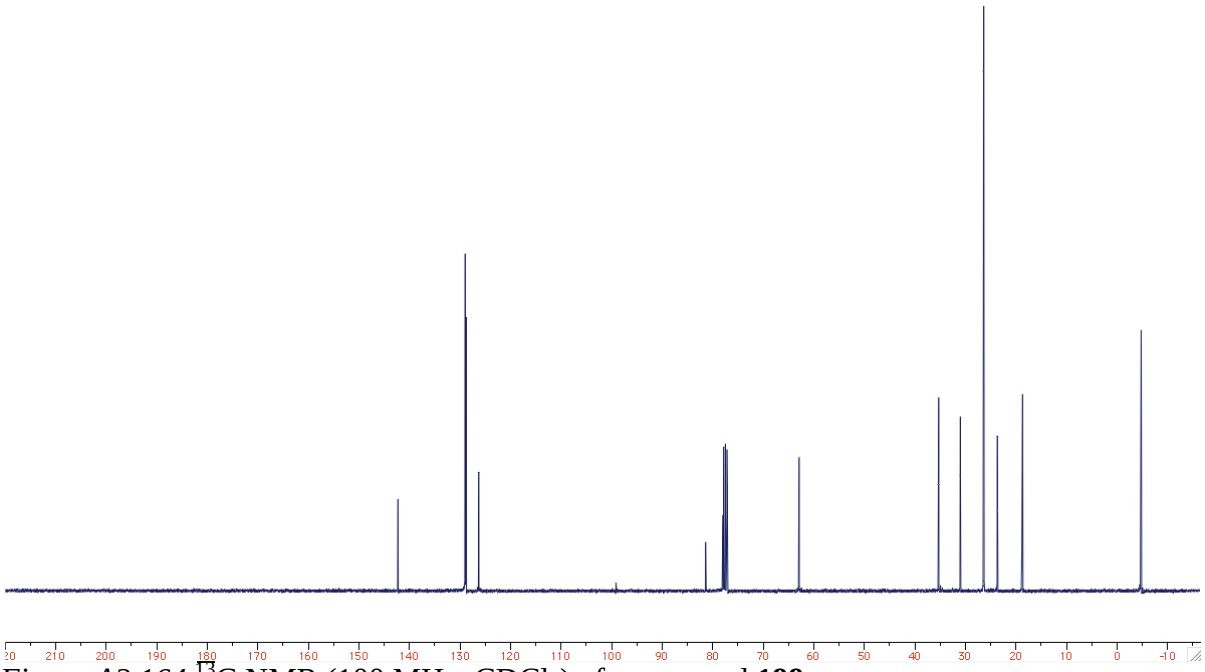


Figure A2.164 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **199**

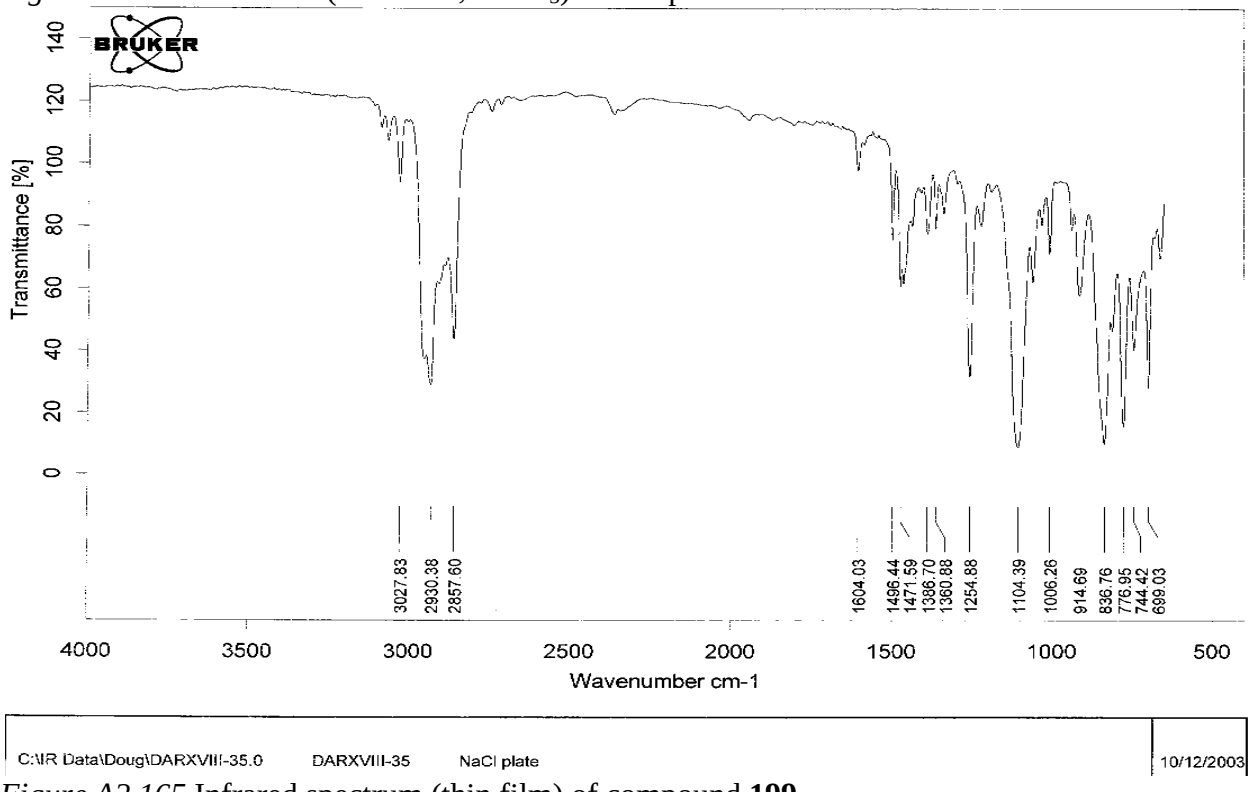
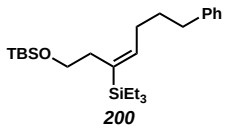


Figure A2.165 Infrared spectrum (thin film) of compound **199**



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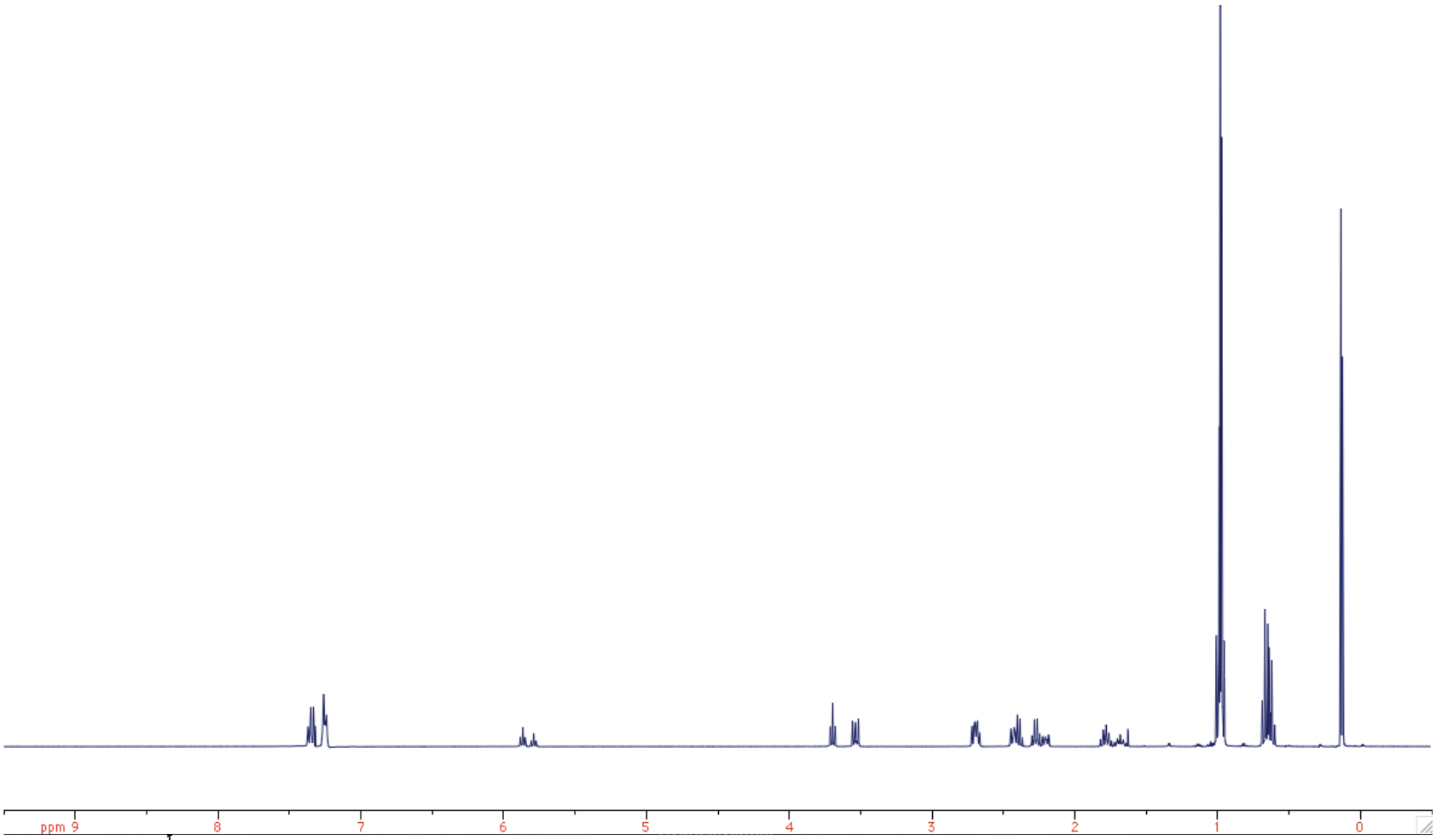
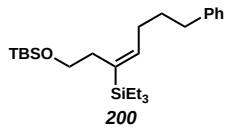


Figure A2.166 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **200**



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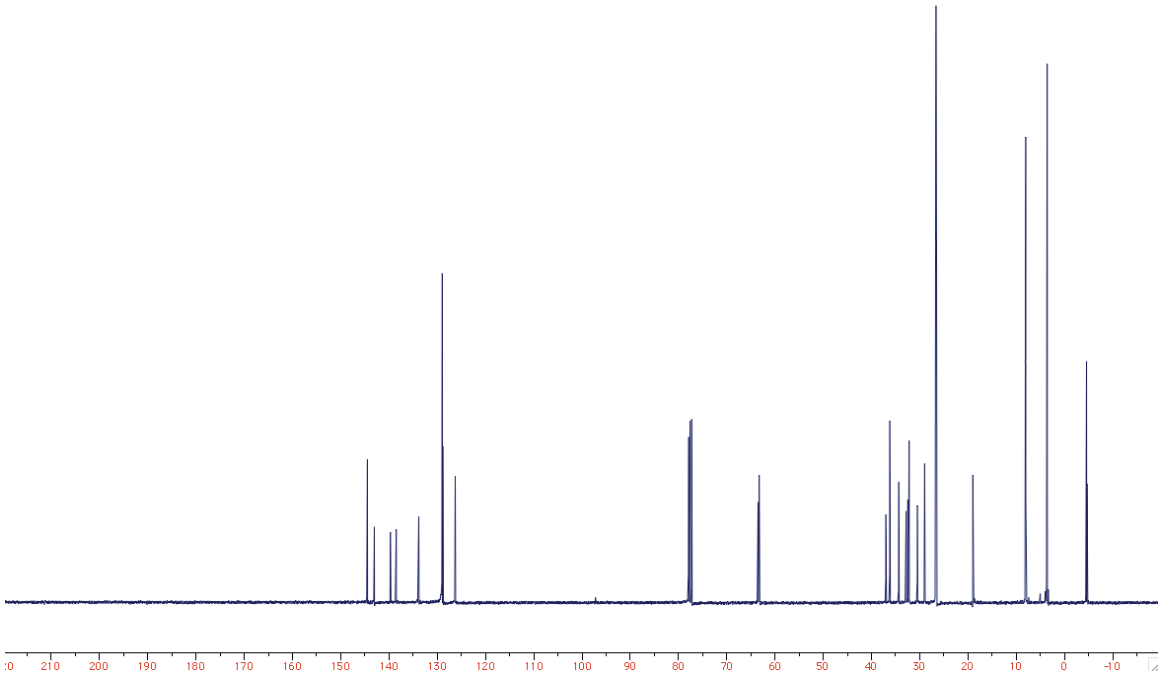


Figure A2.167 Infrared spectrum (thin film) of compound **200**

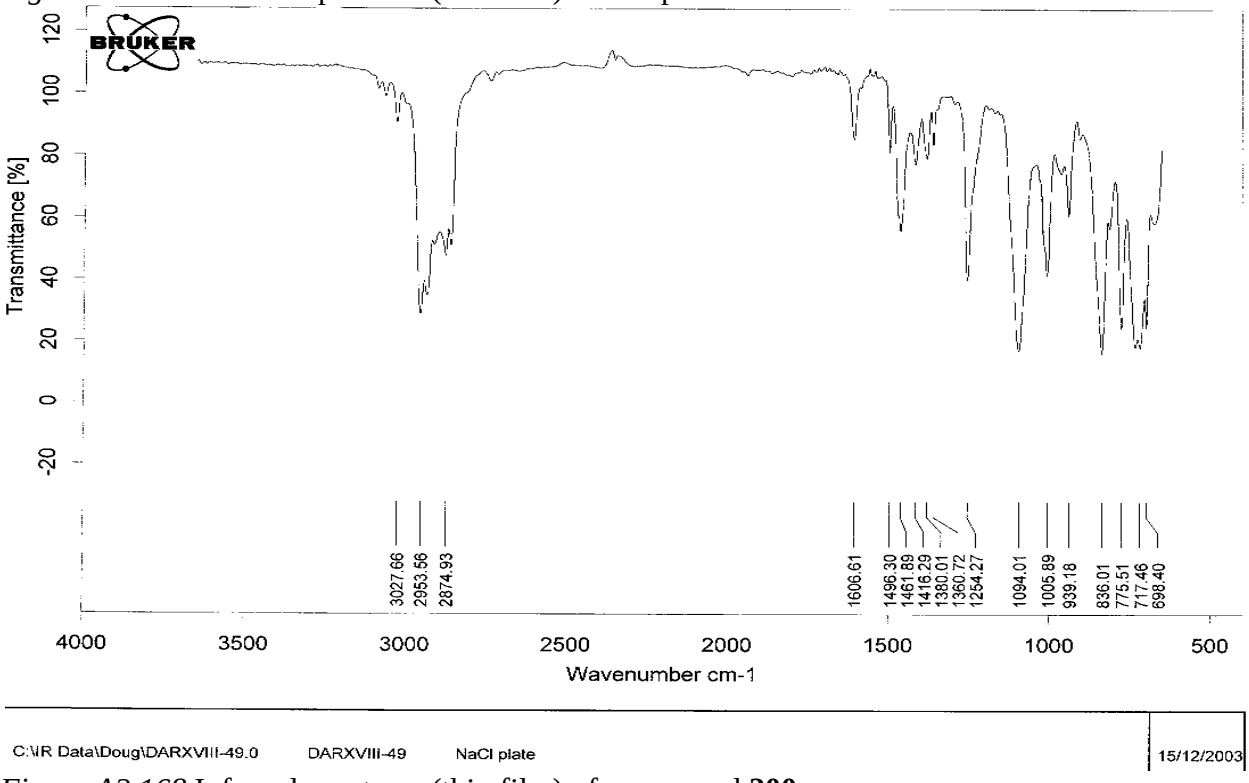
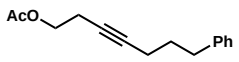


Figure A2.168 Infrared spectrum (thin film) of compound **200**



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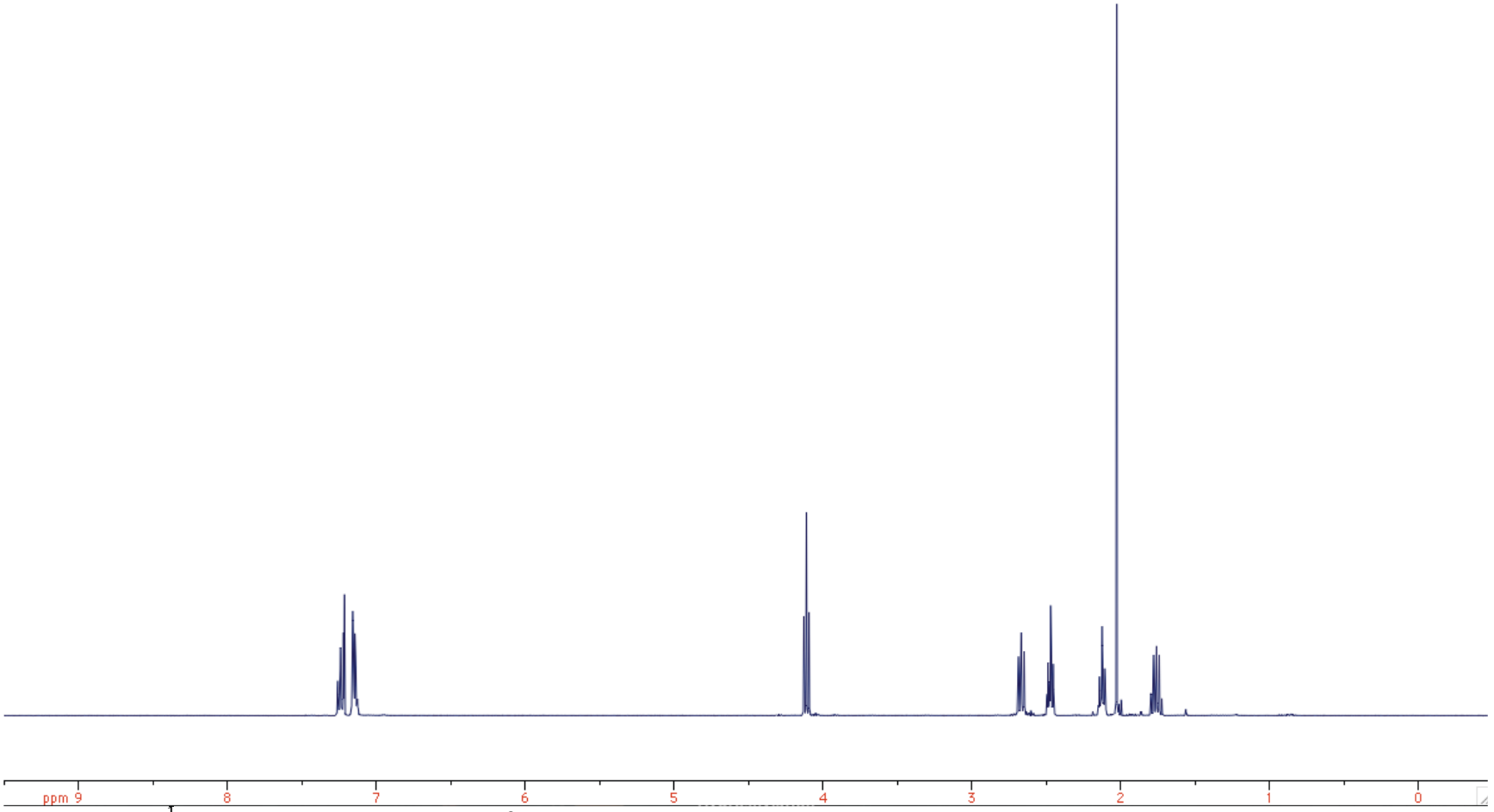
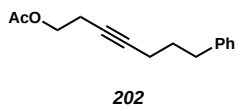


Figure A2.169 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **202**



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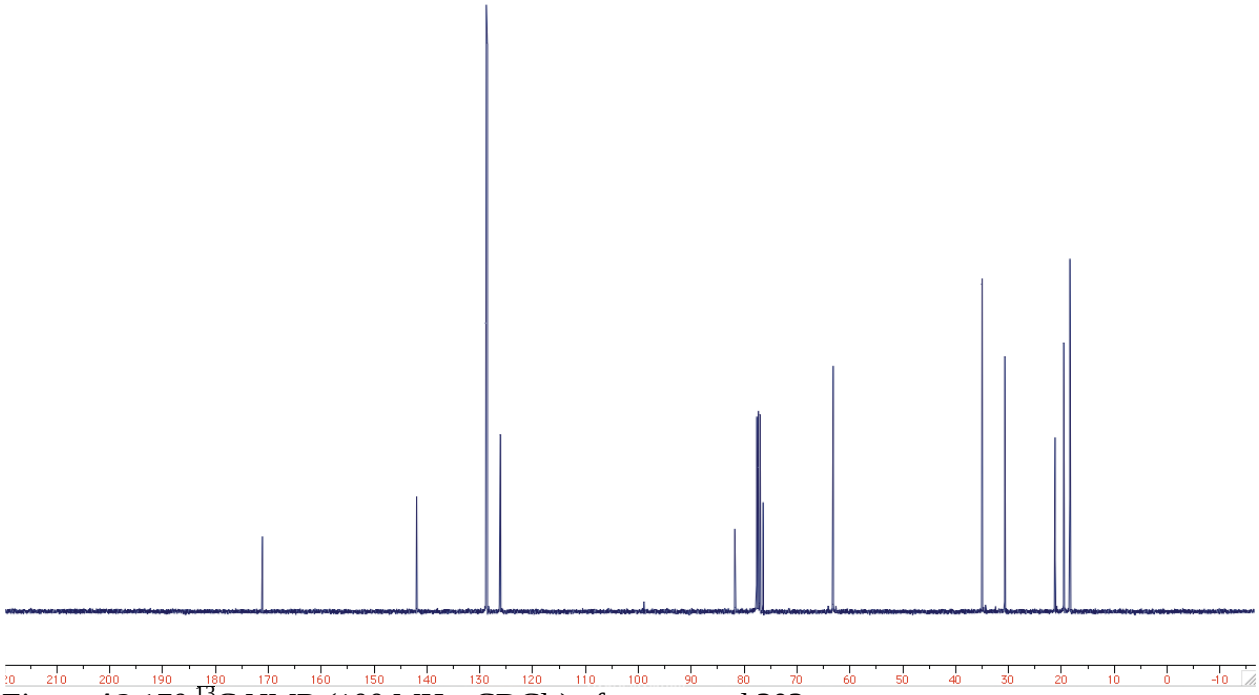


Figure A2.170 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **202**

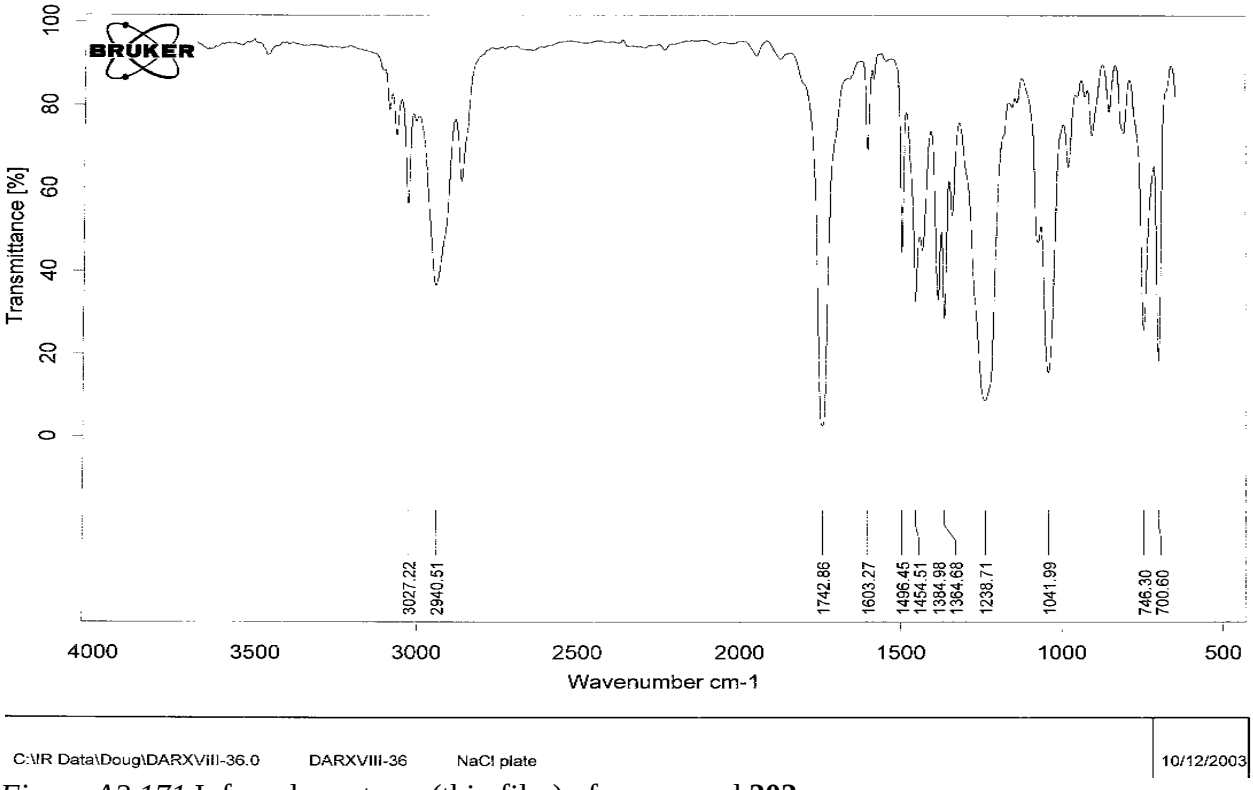
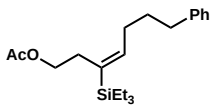


Figure A2.171 Infrared spectrum (thin film) of compound **202**



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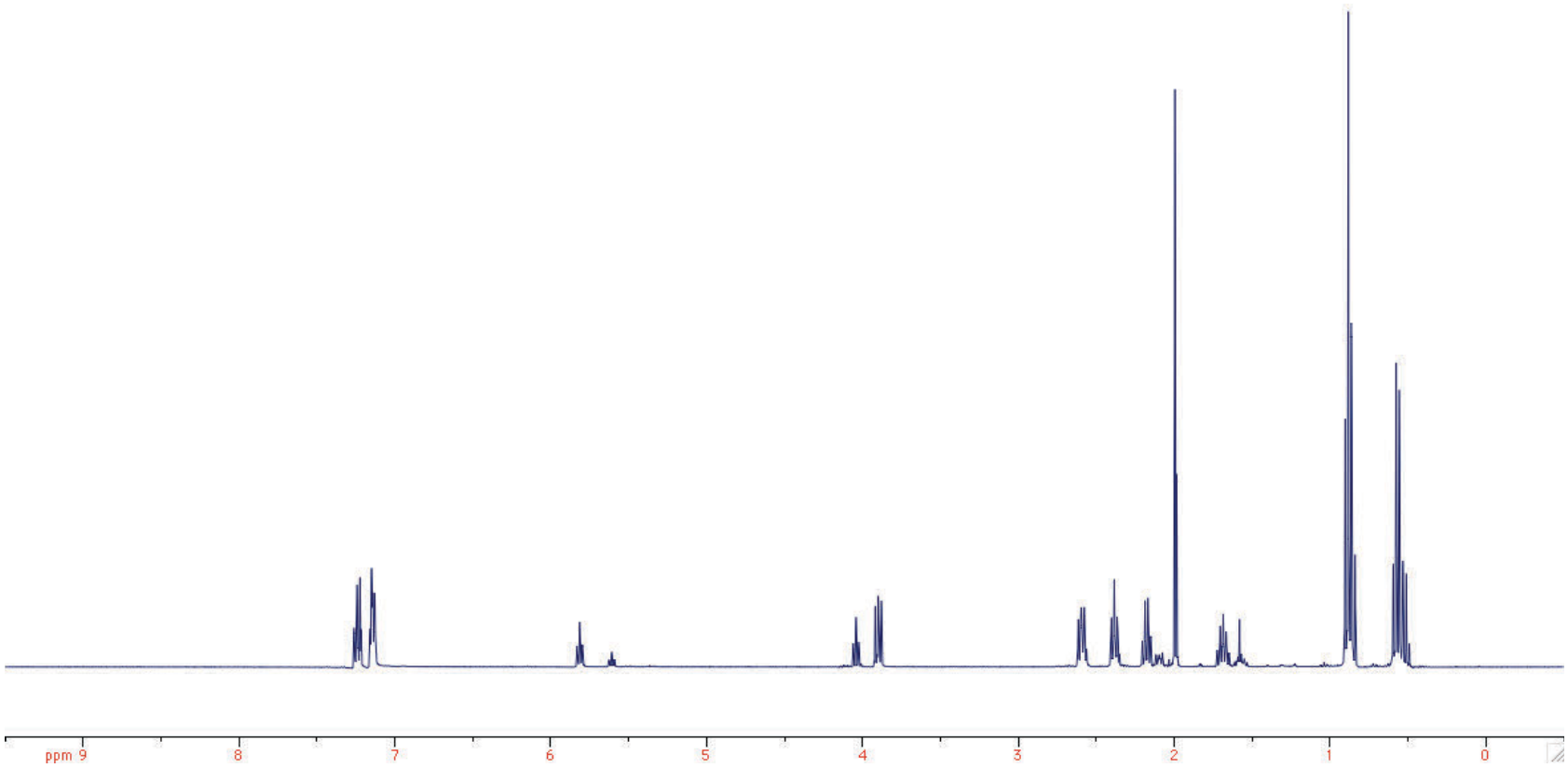


Figure A2.172 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **203**

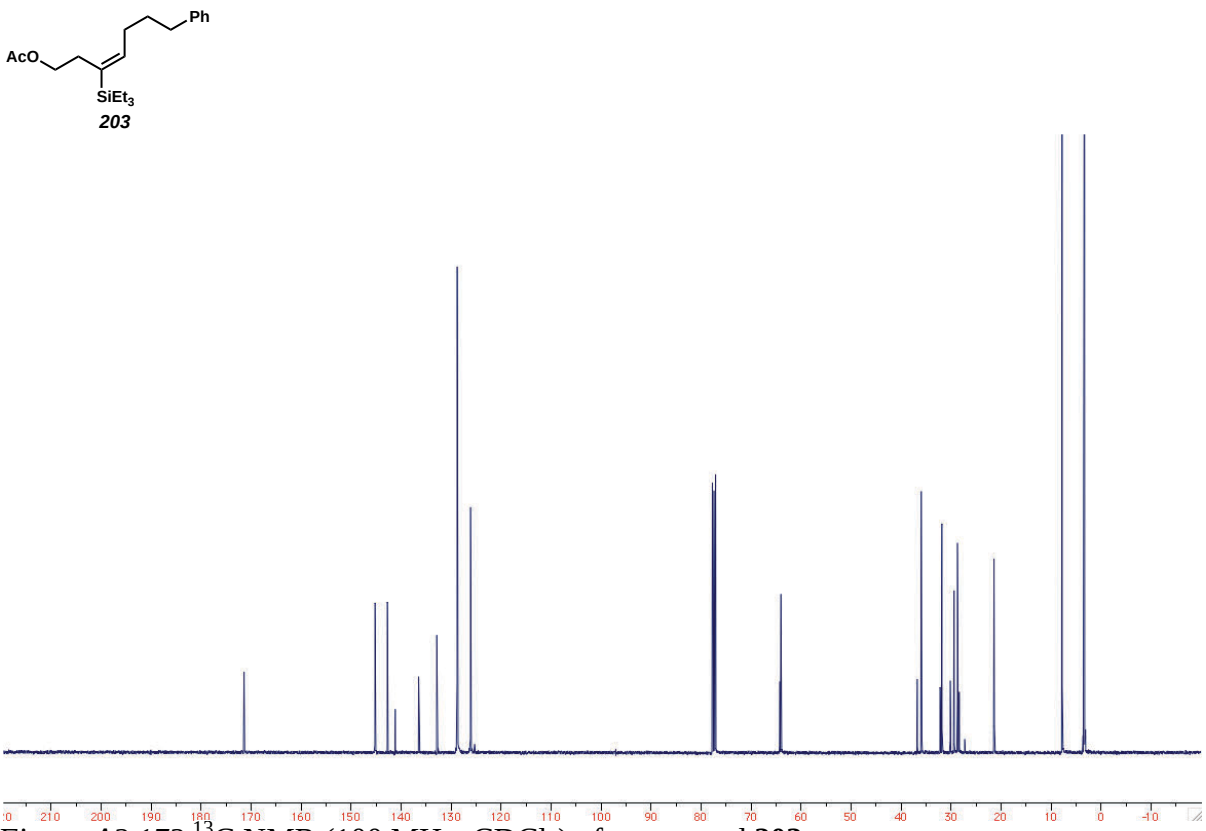


Figure A2.173 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **203**

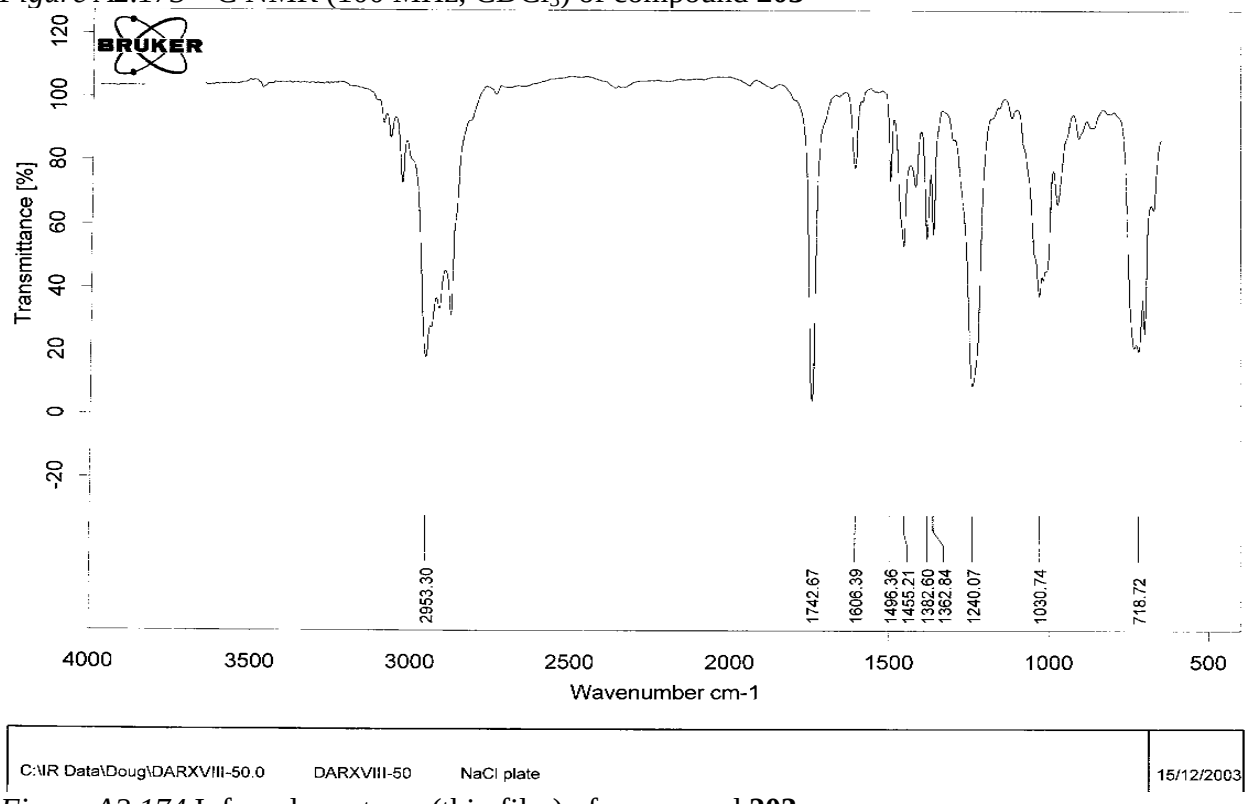
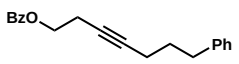


Figure A2.174 Infrared spectrum (thin film) of compound **203**



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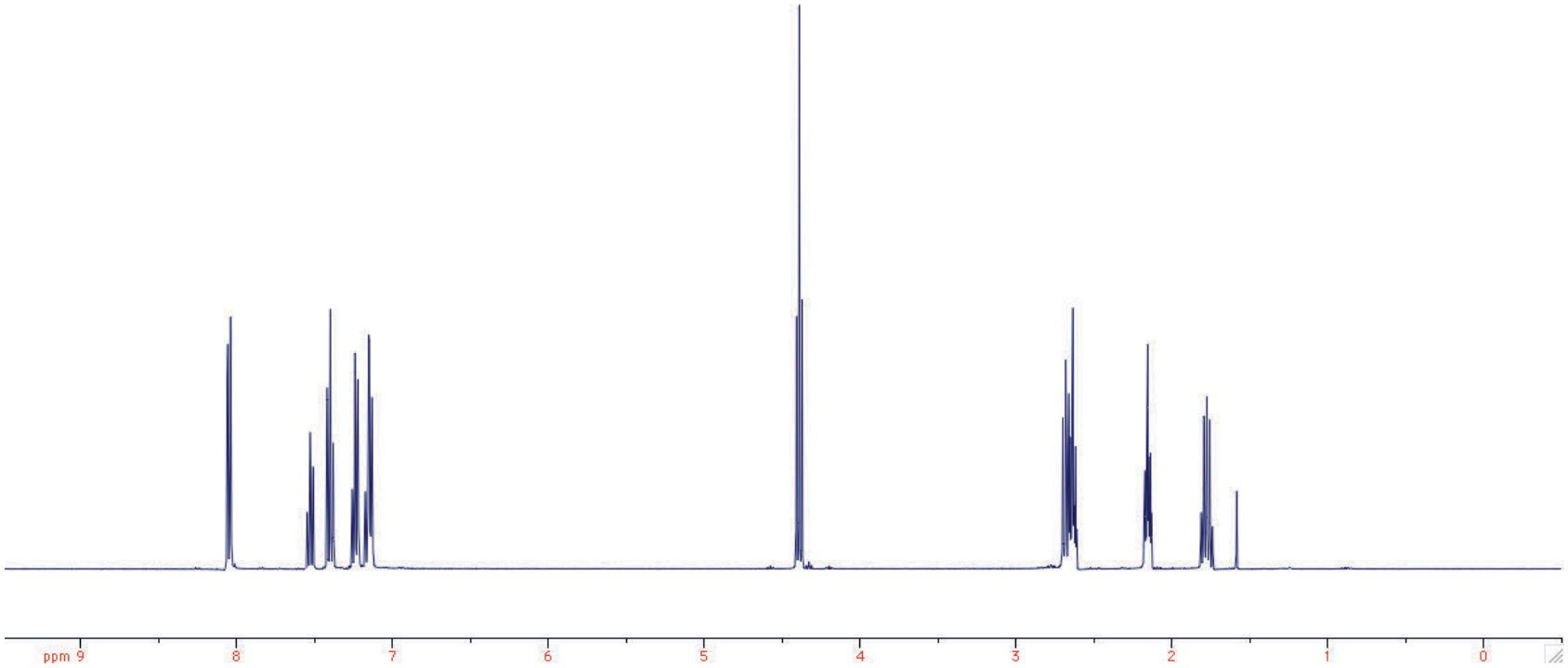
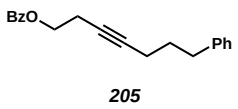


Figure A2.175 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **205**



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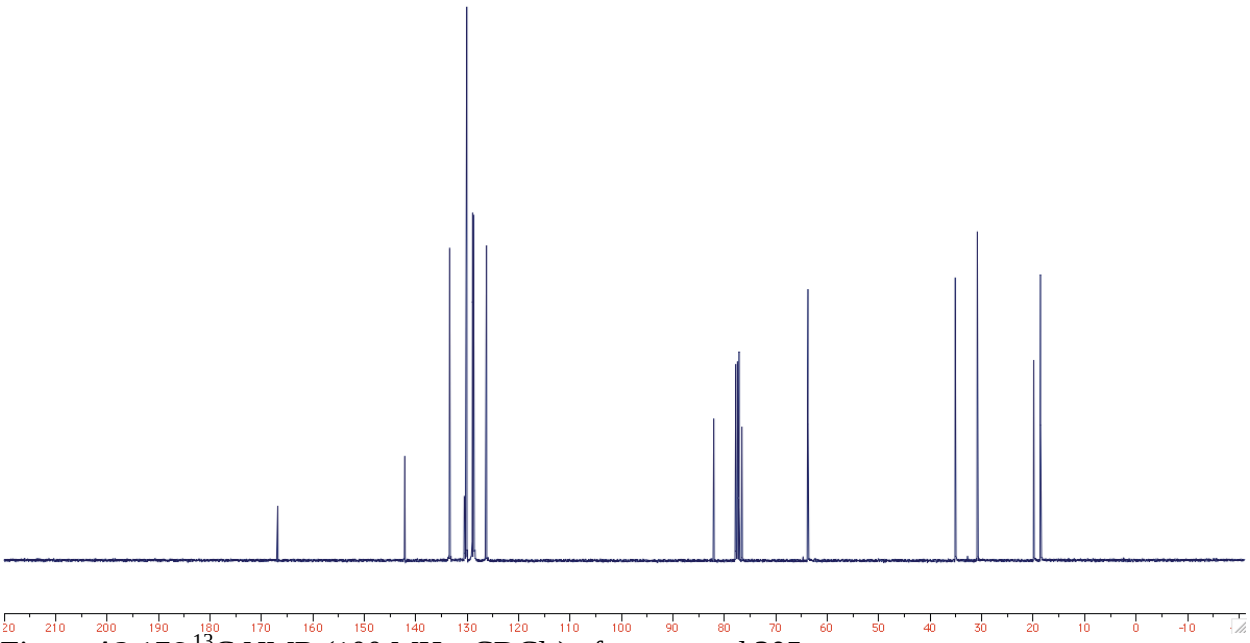


Figure A2.176 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **205**

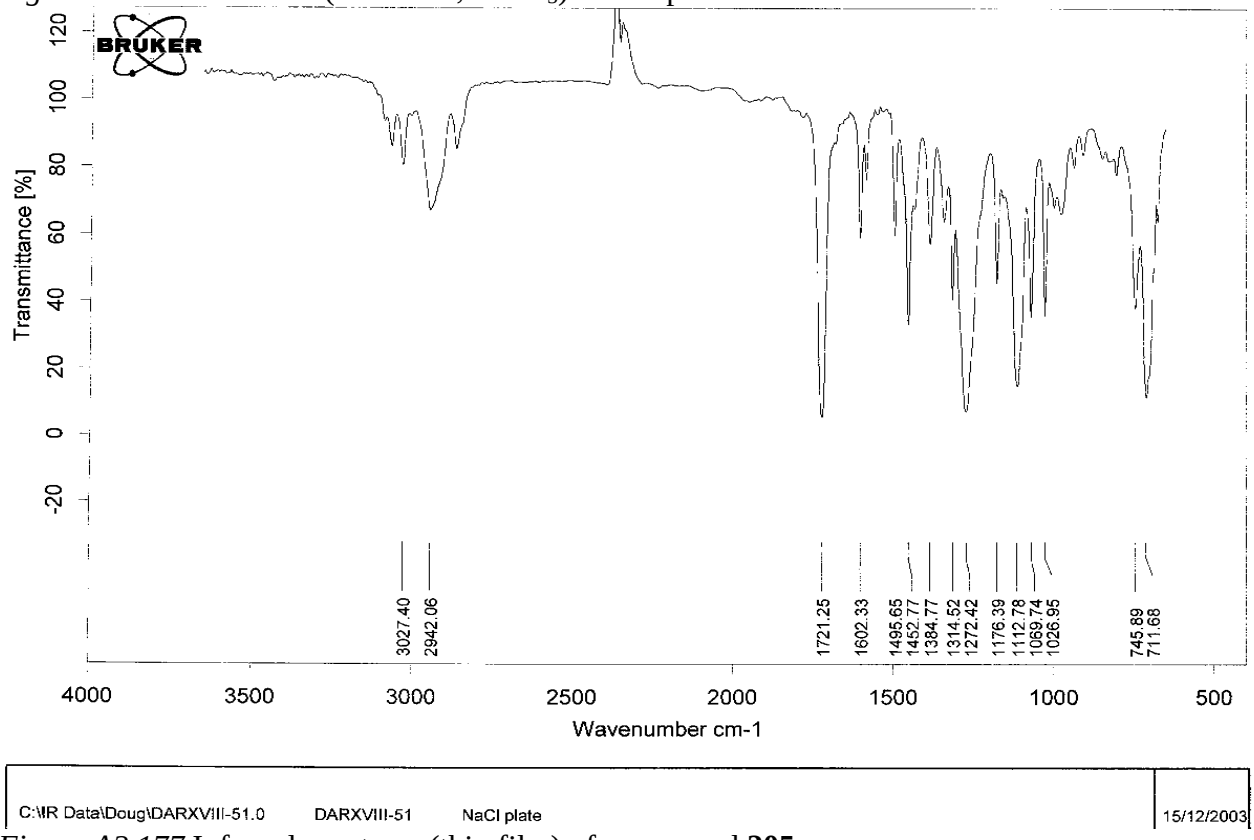
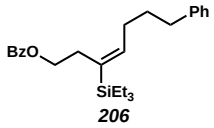


Figure A2.177 Infrared spectrum (thin film) of compound **205**



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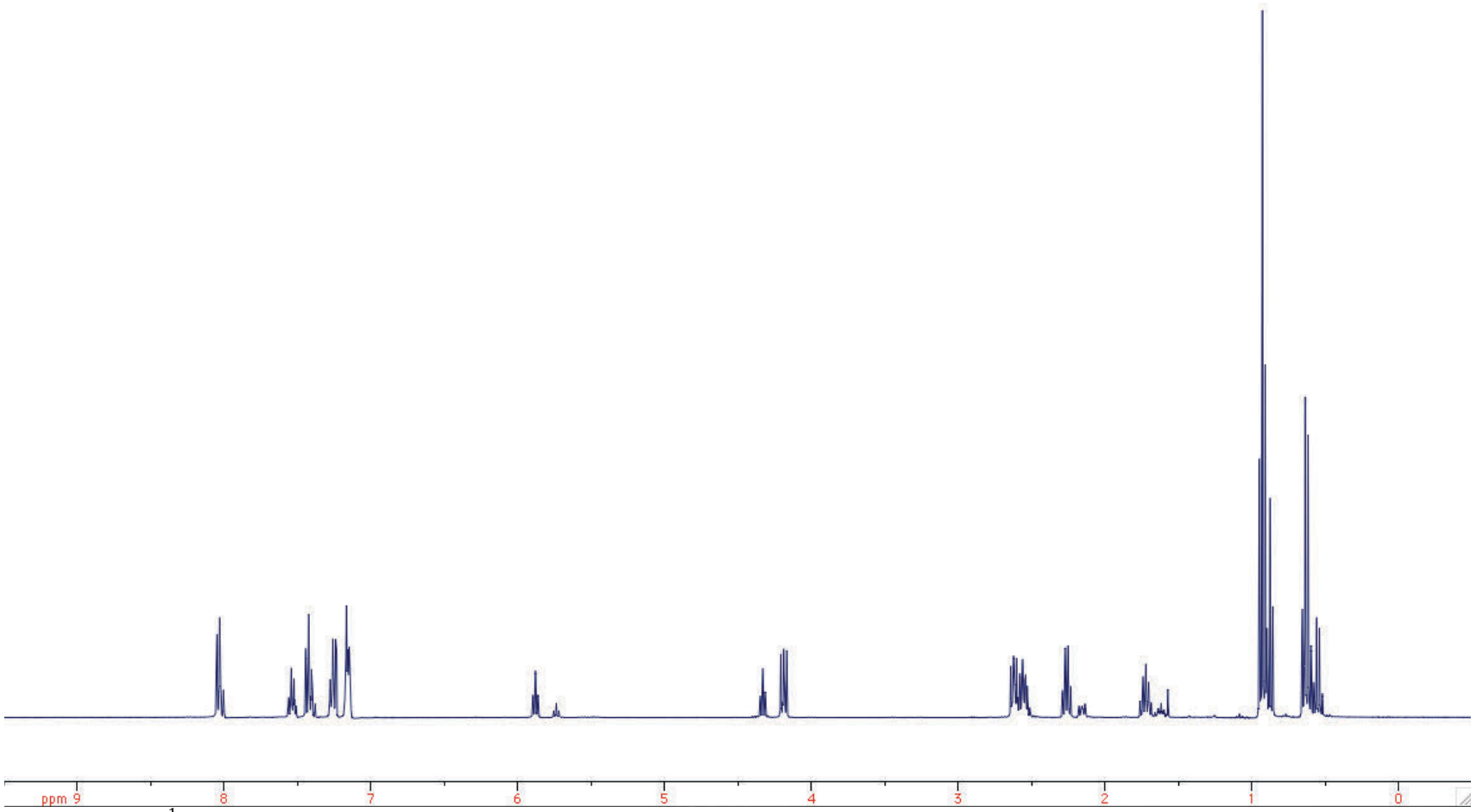


Figure A2.178 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **206**

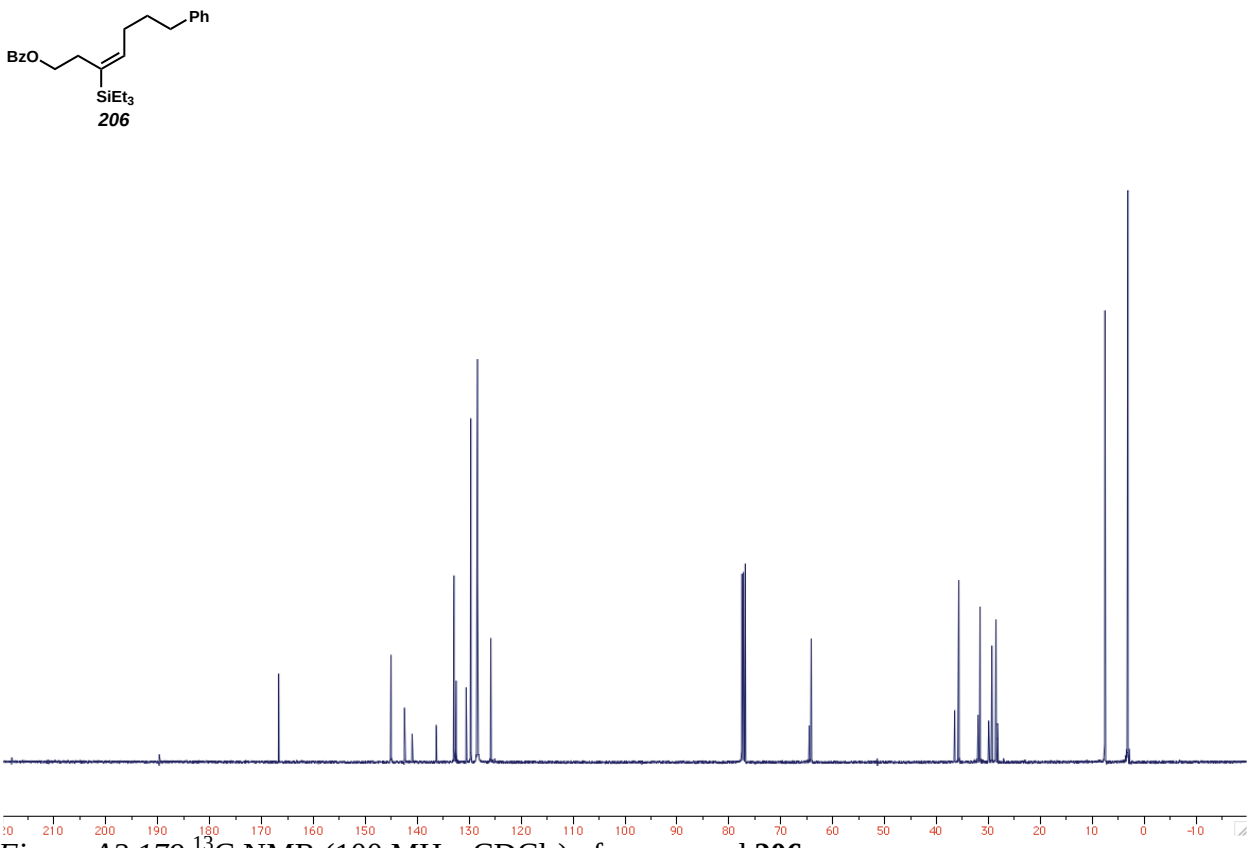


Figure A2.179 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **206**

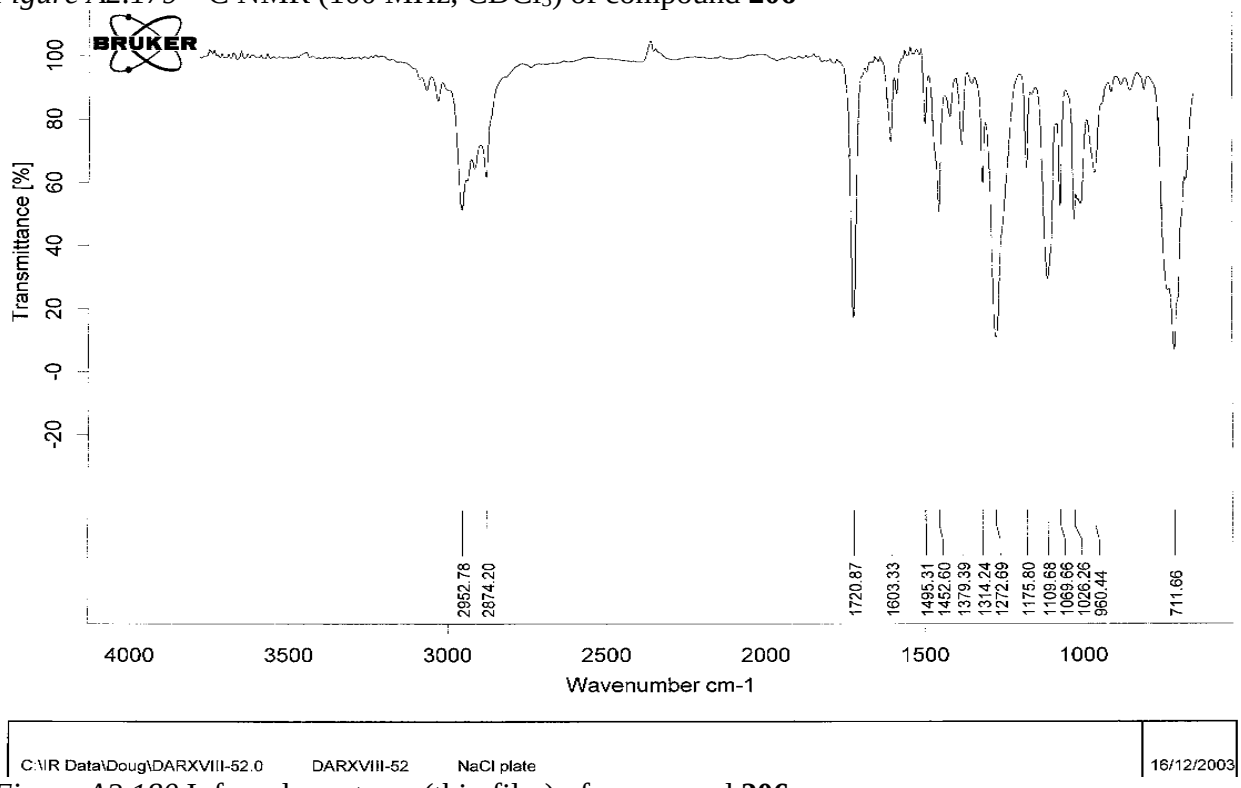


Figure A2.180 Infrared spectrum (thin film) of compound **206**

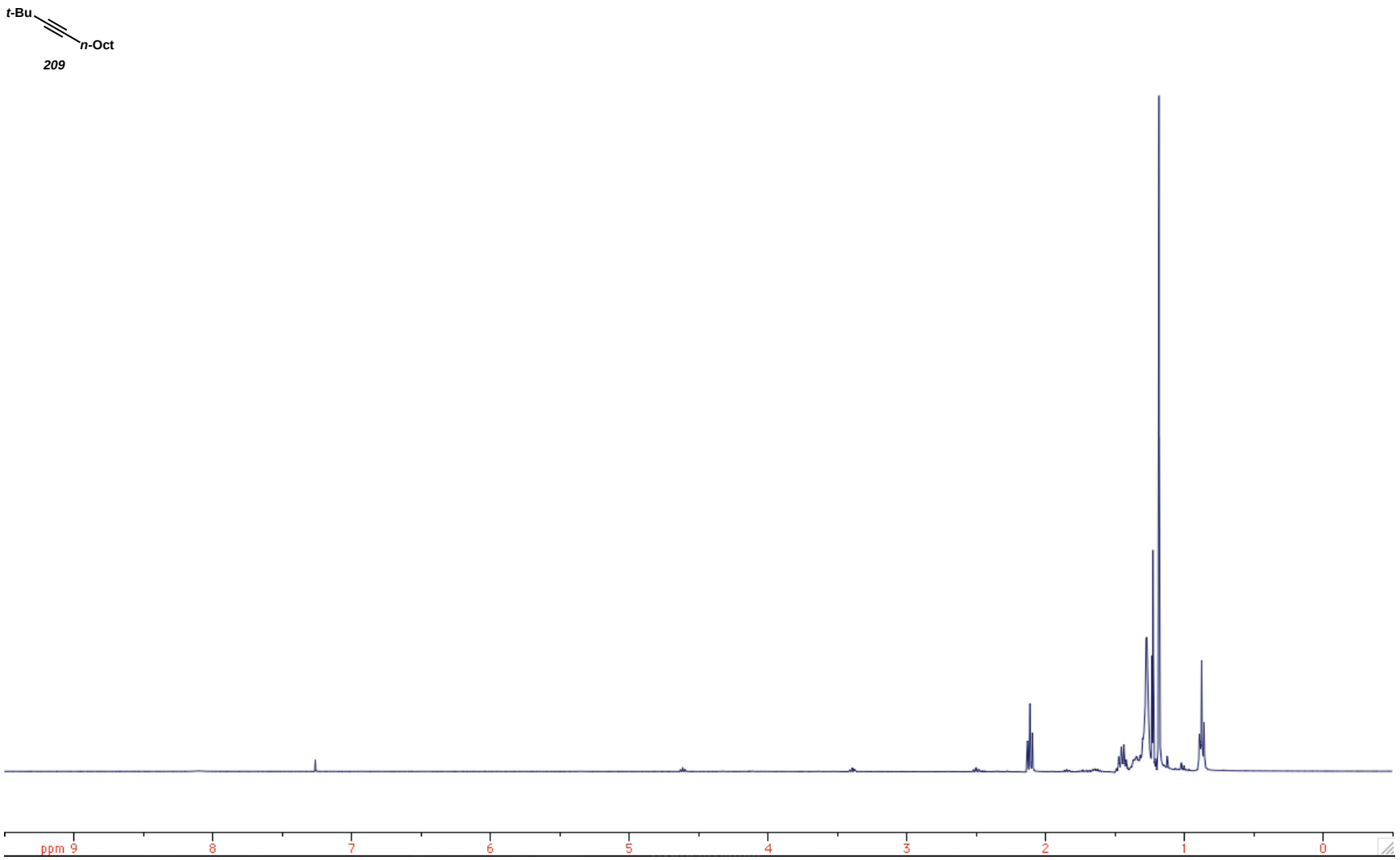


Figure A2.181 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **209**

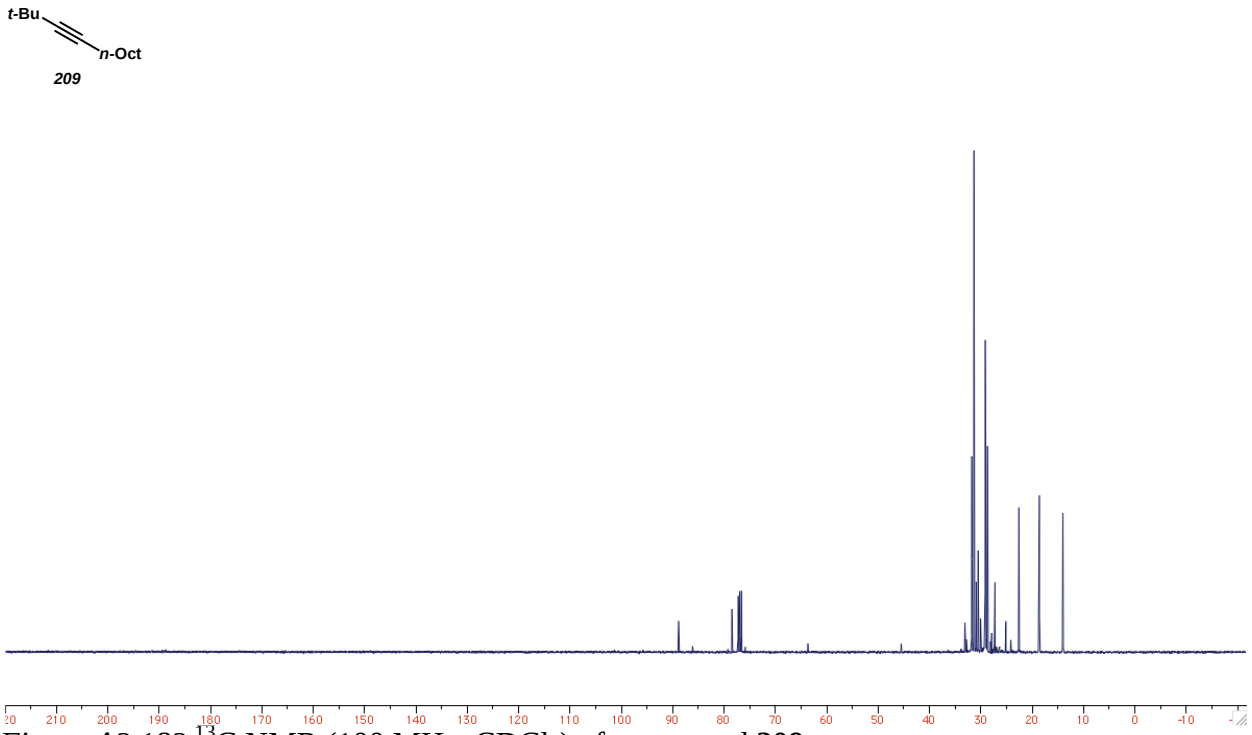


Figure A2.182 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **209**

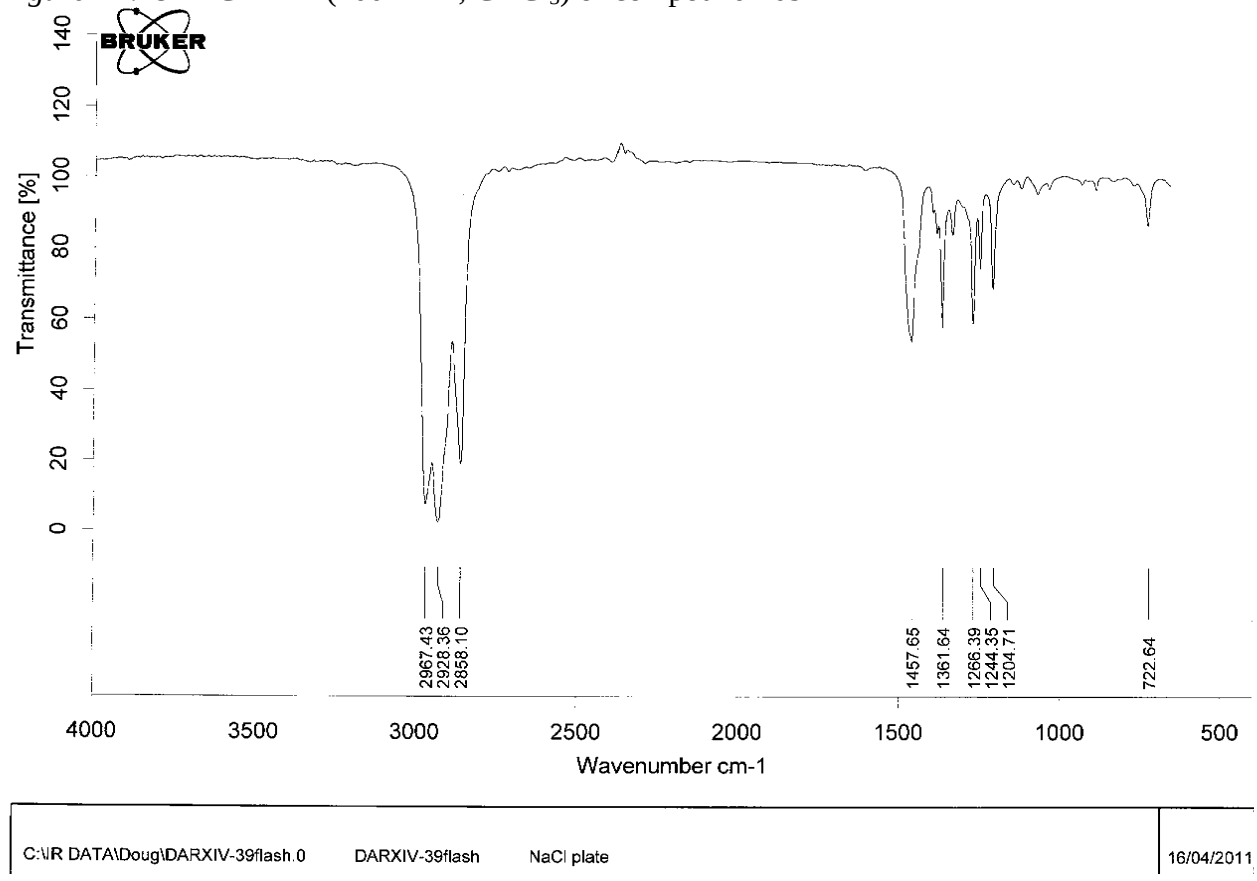
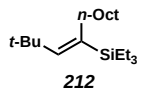


Figure A2.183 Infrared spectrum (thin film) of compound **209**



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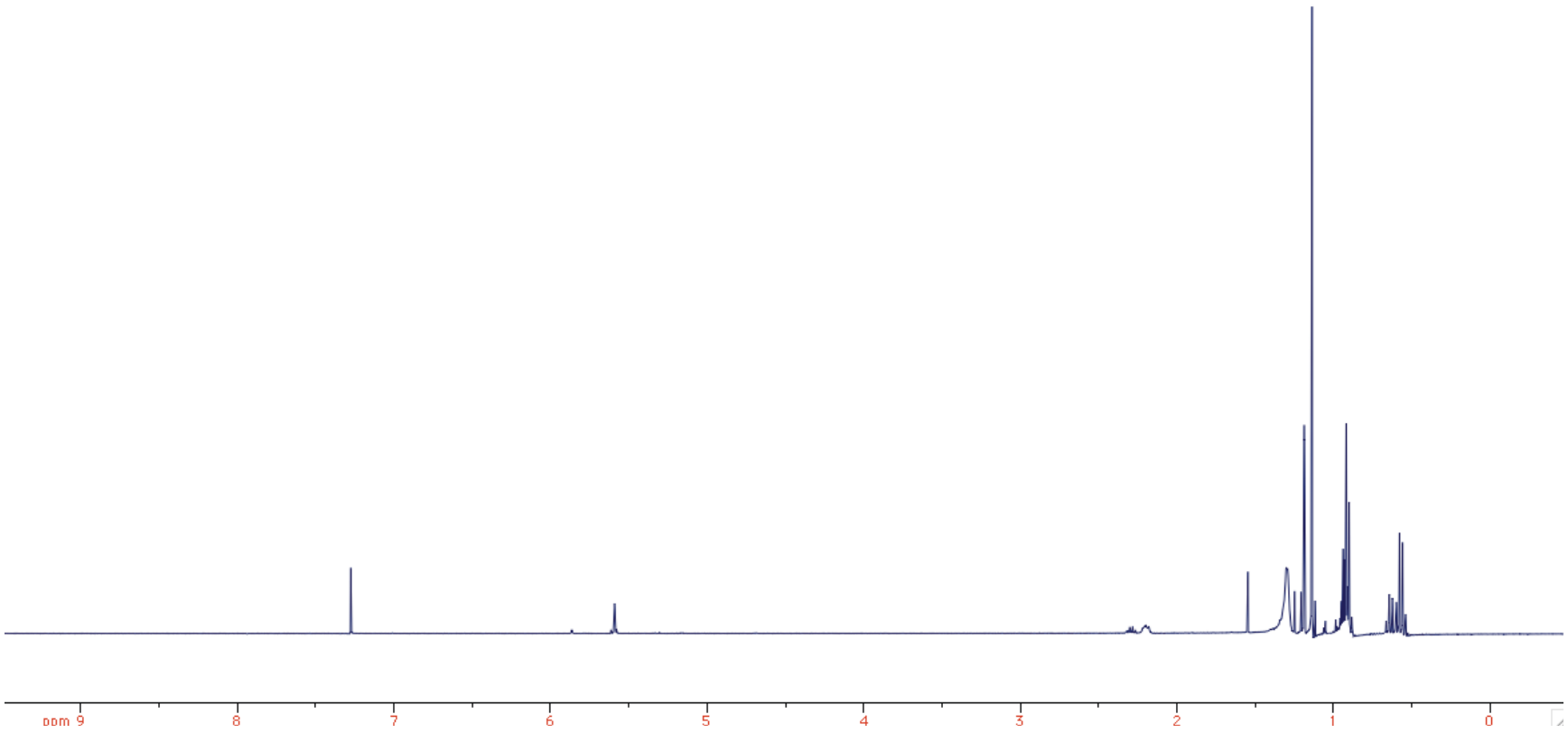


Figure A2.184 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **212**

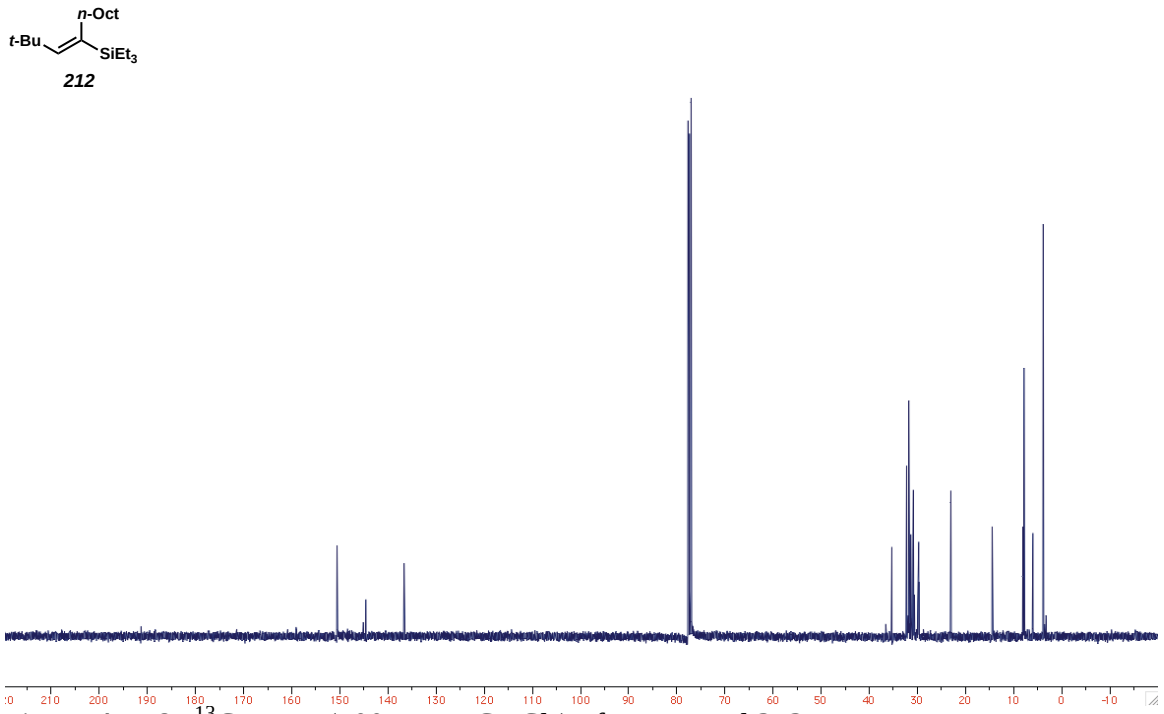


Figure A2.185 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **212**

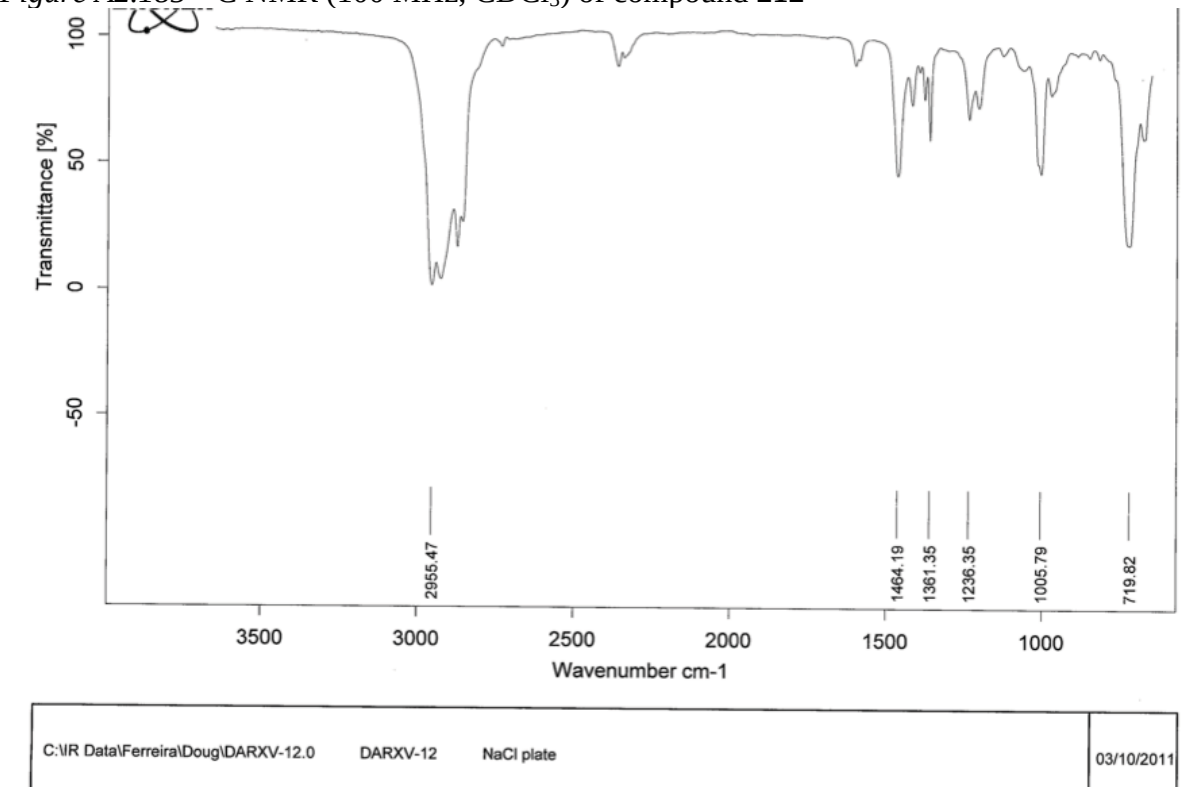
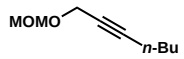


Figure A2.186 Infrared spectrum (thin film) of compound **212**



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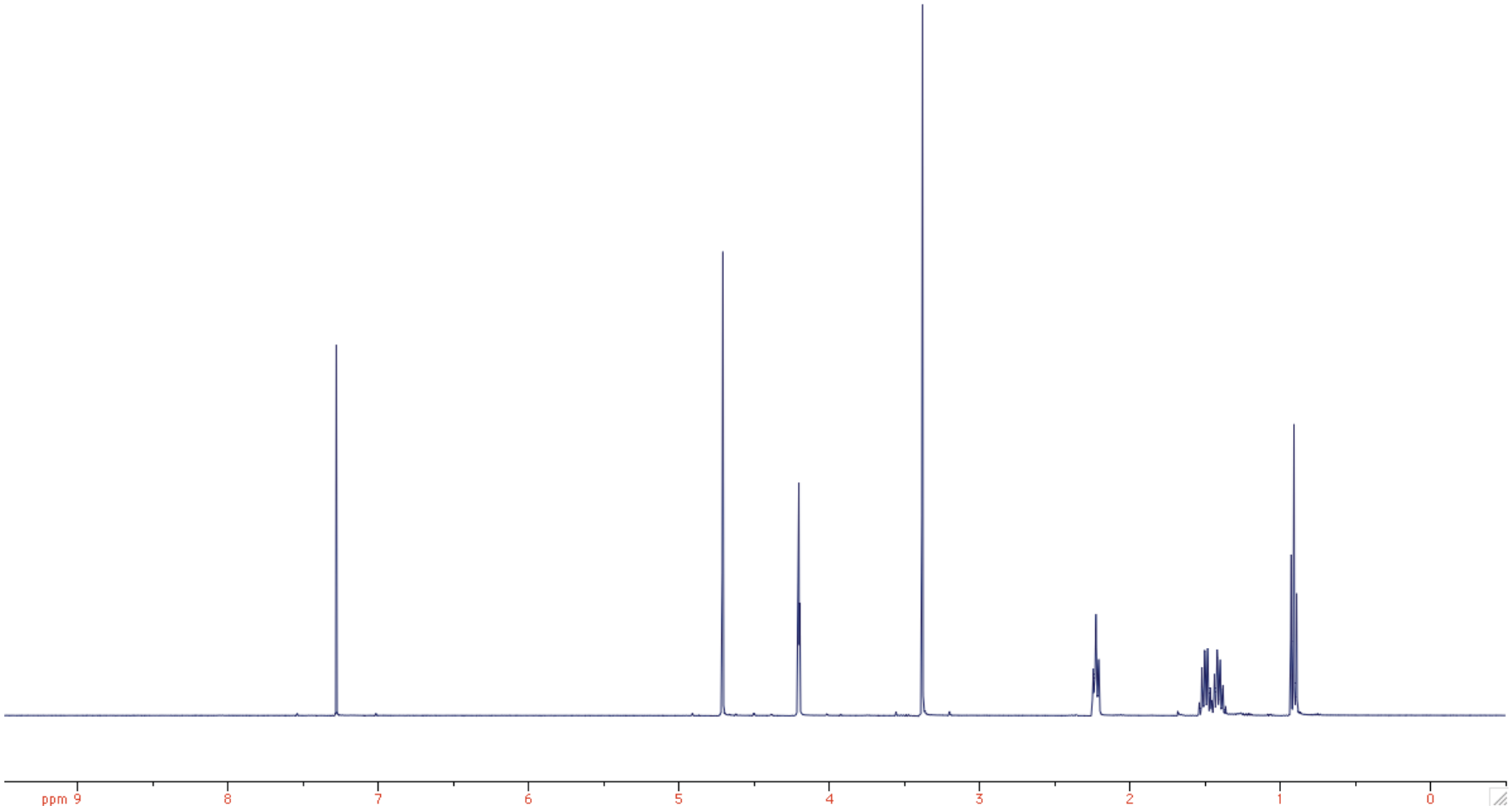


Figure A2.187 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **215**

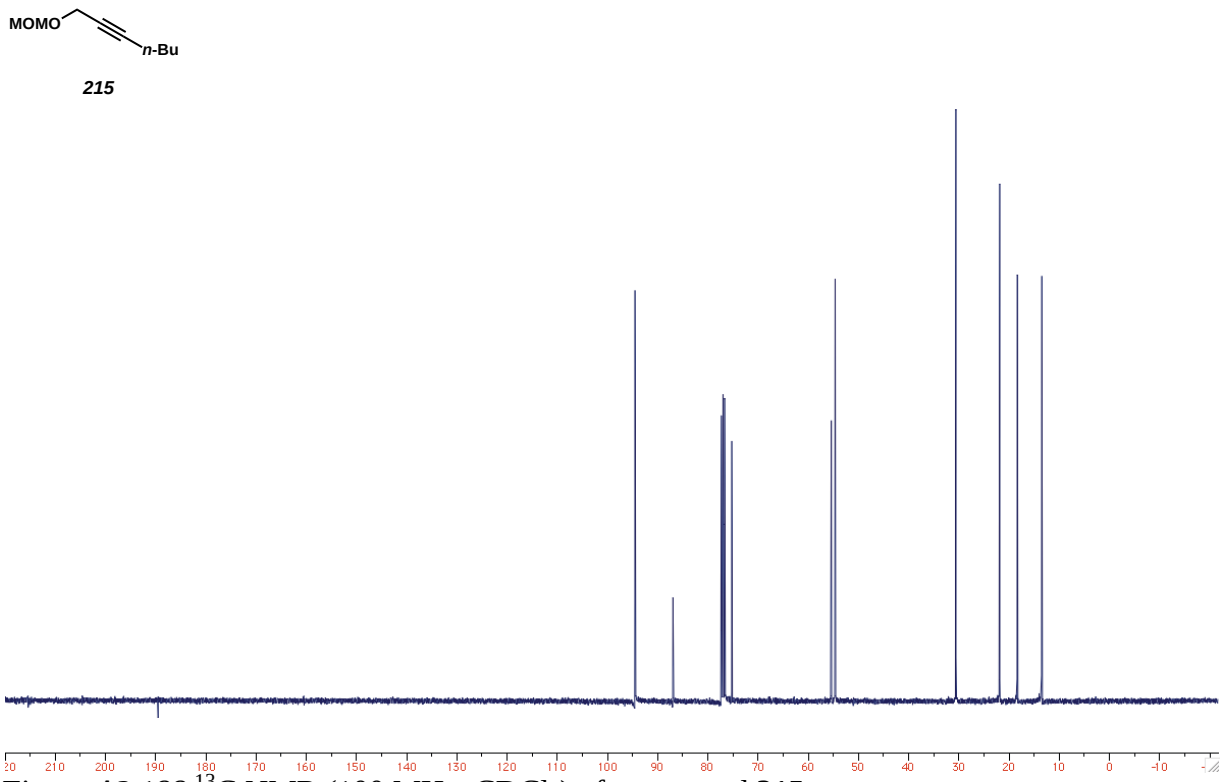


Figure A2.188 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **215**

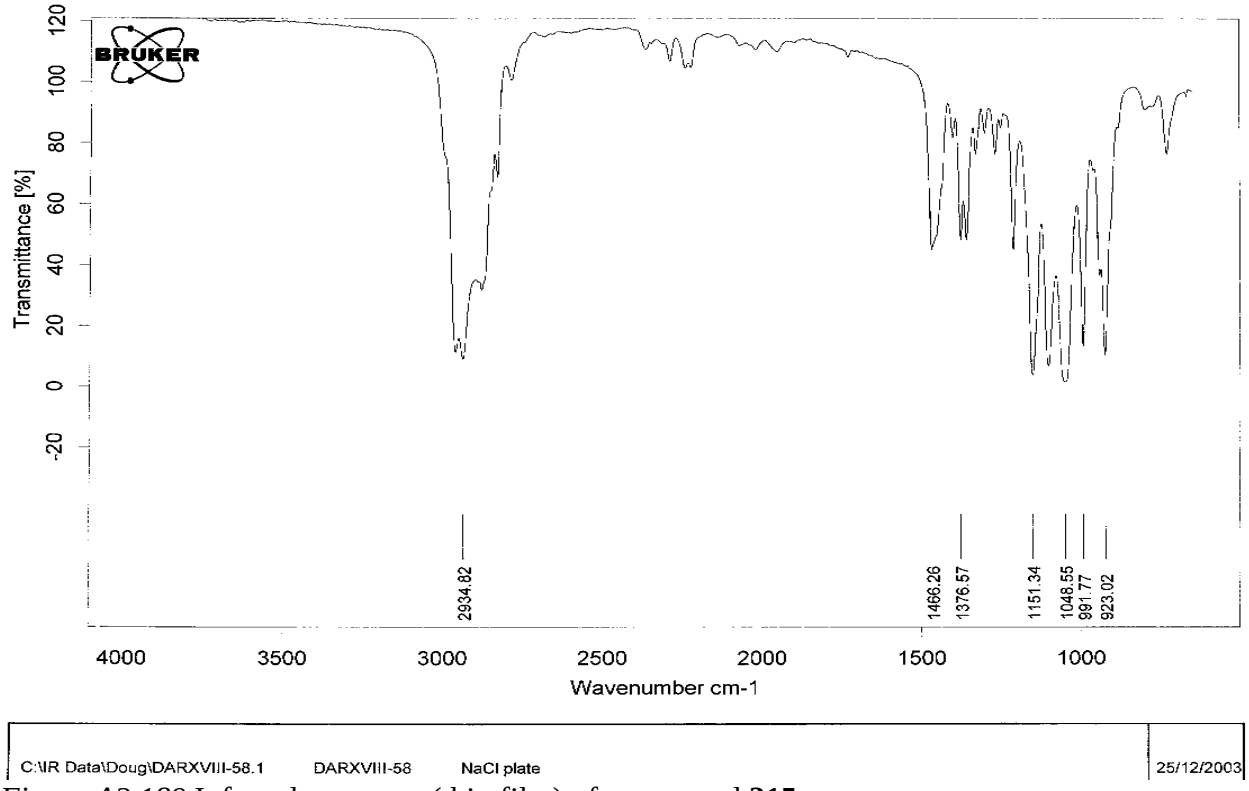


Figure A2.189 Infrared spectrum (thin film) of compound **215**

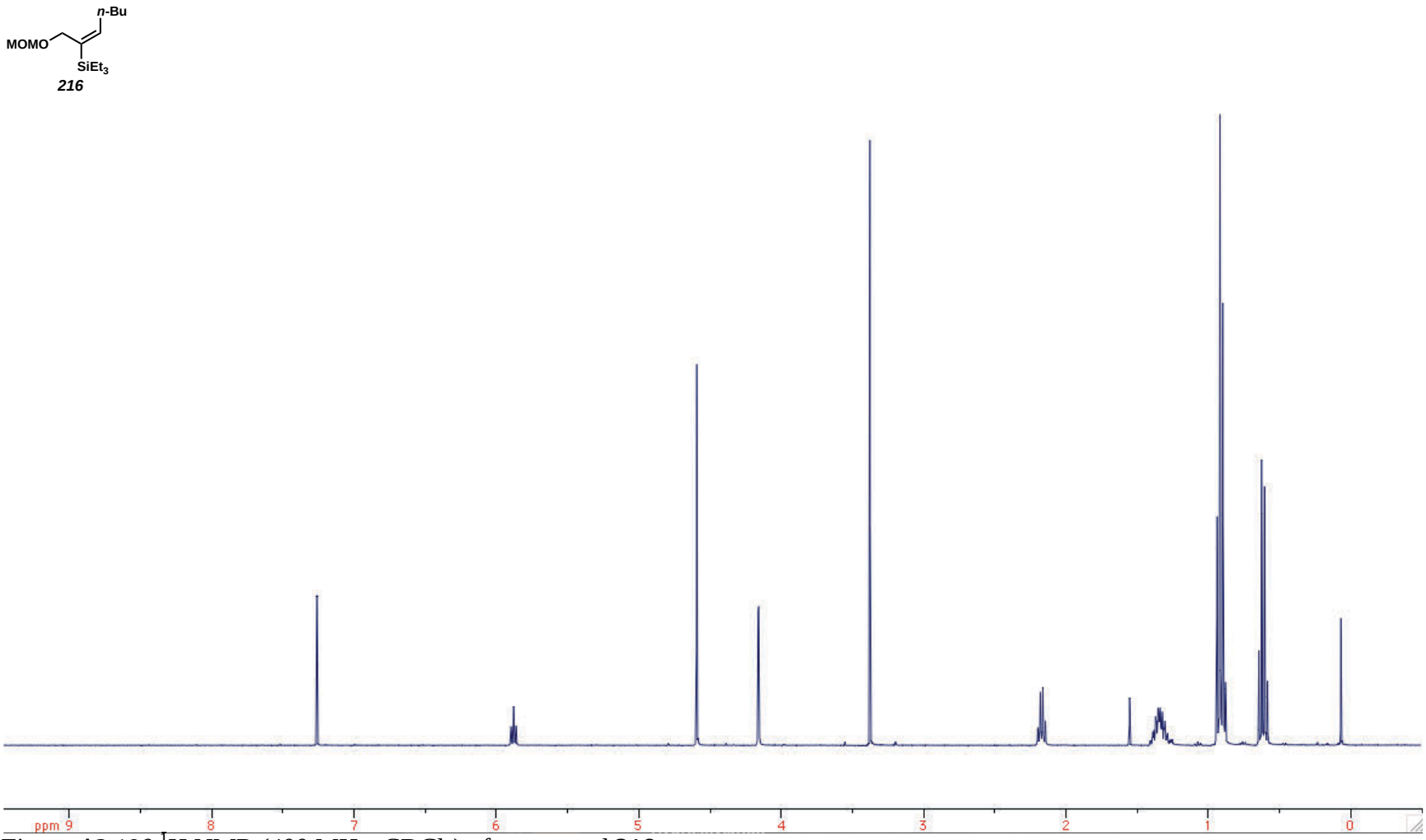


Figure A2.190 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **216**

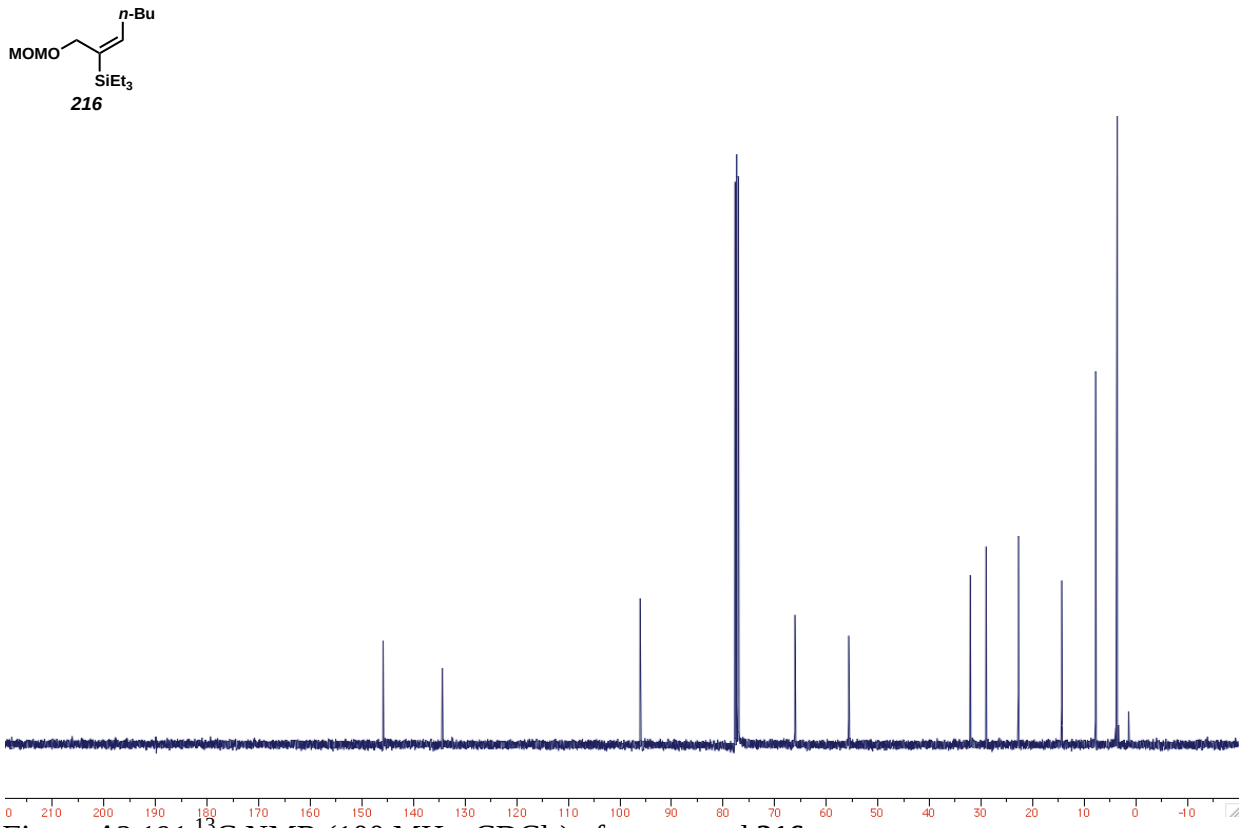


Figure A2.191 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **216**

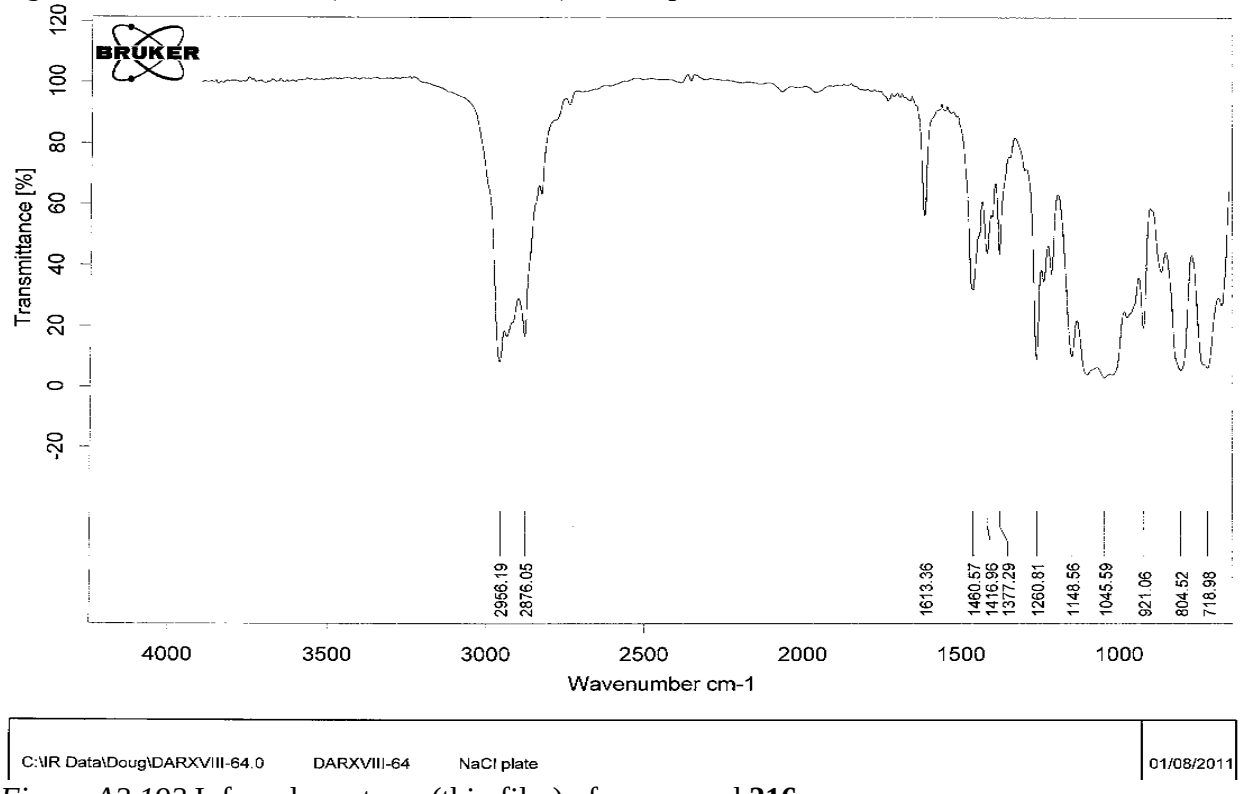


Figure A2.192 Infrared spectrum (thin film) of compound **216**

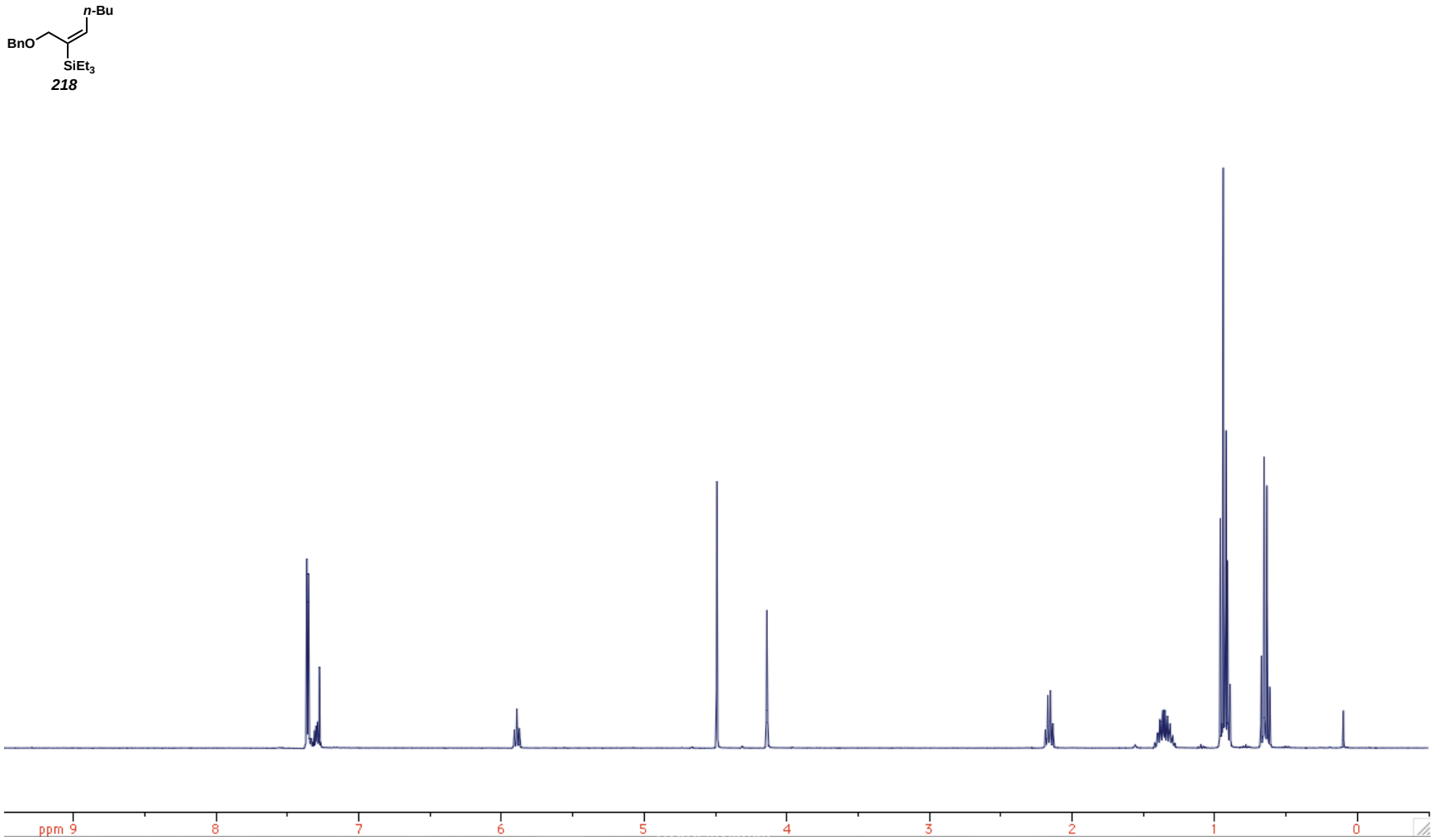


Figure A2.193 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **218**

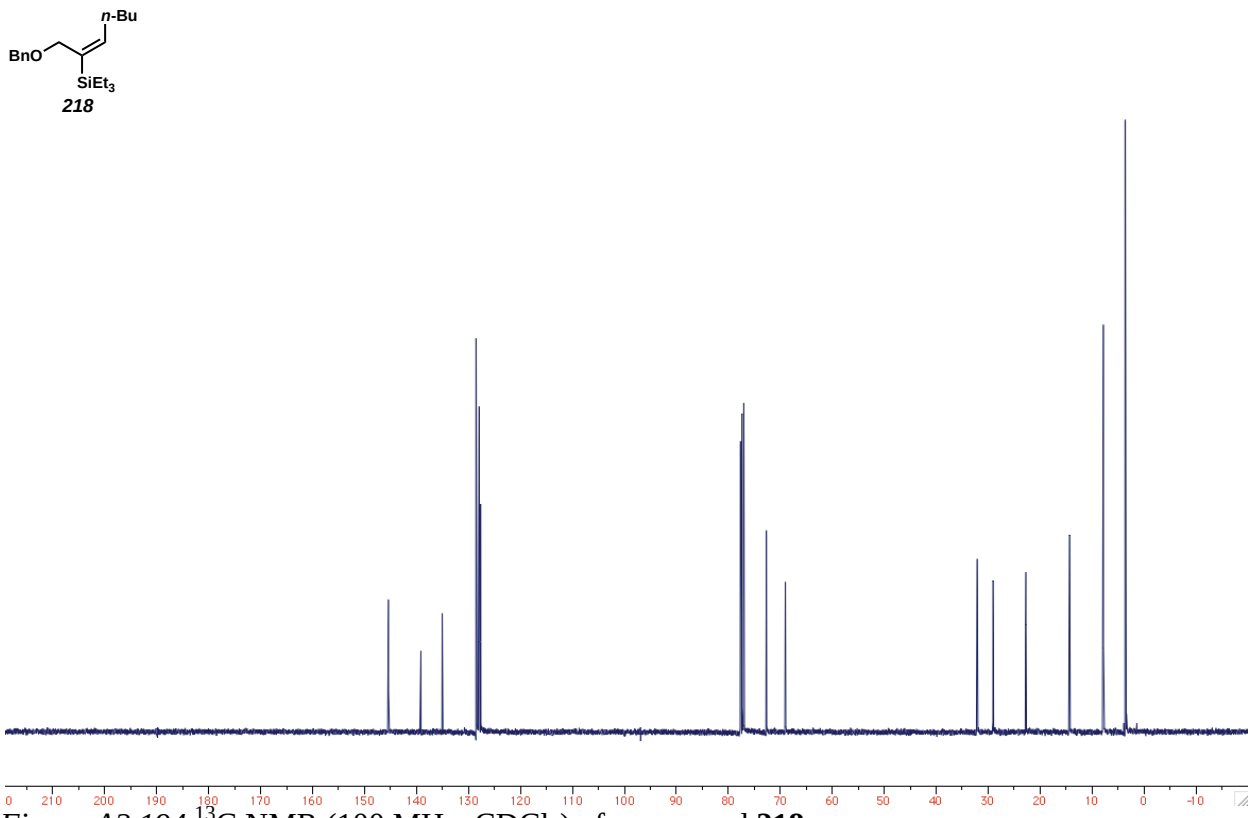


Figure A2.194 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **218**

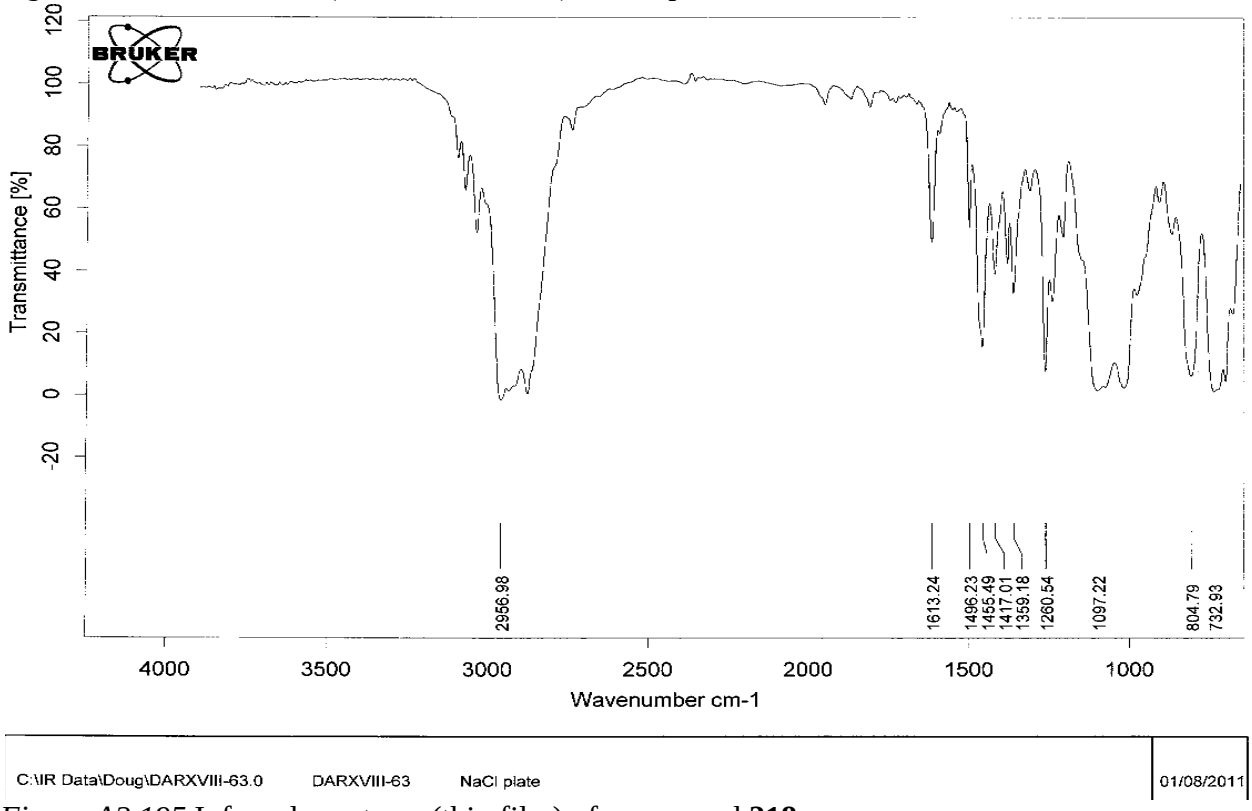
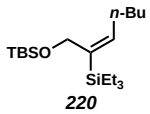


Figure A2.195 Infrared spectrum (thin film) of compound **218**



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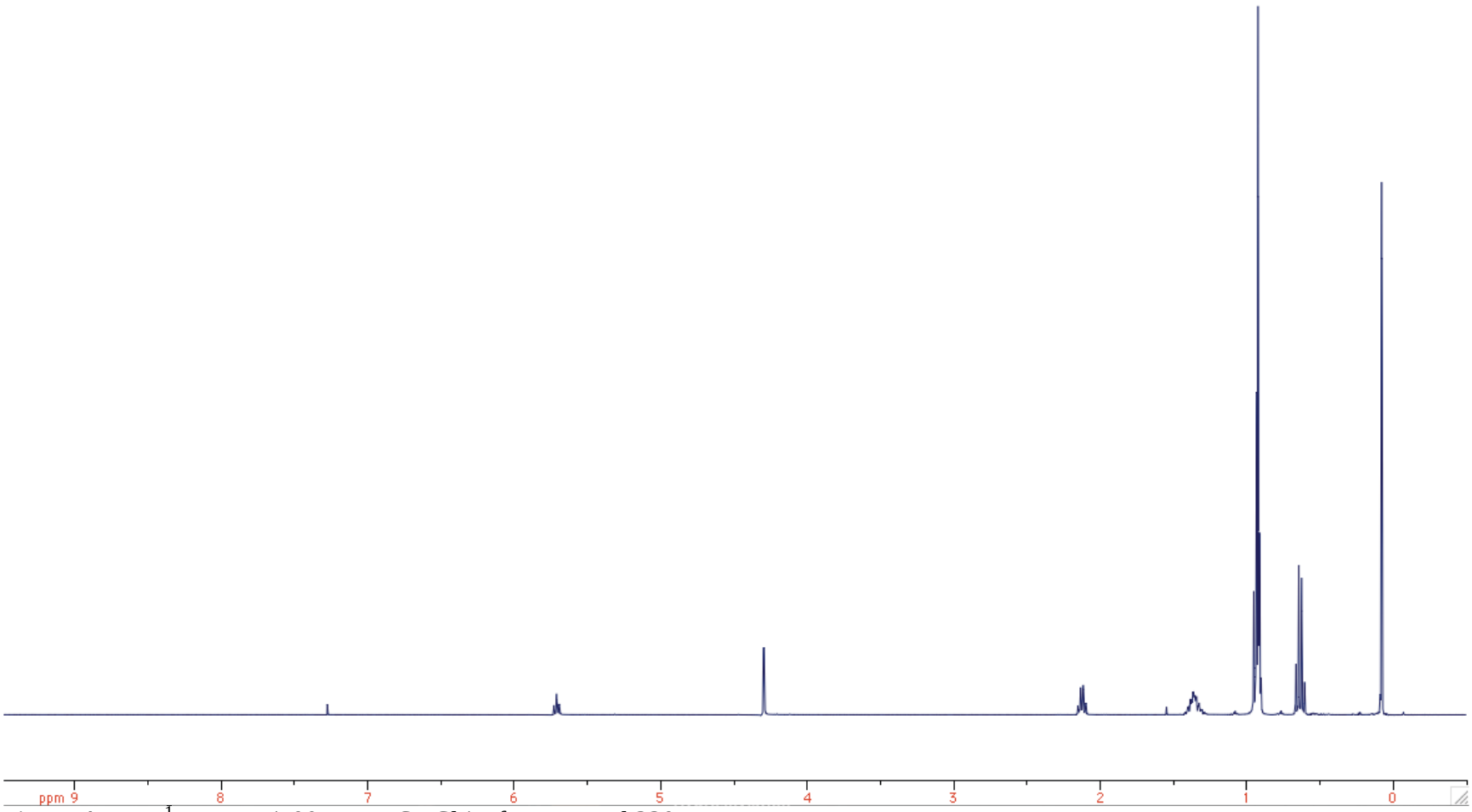
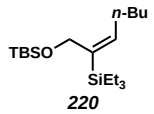


Figure A2.196 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **220**



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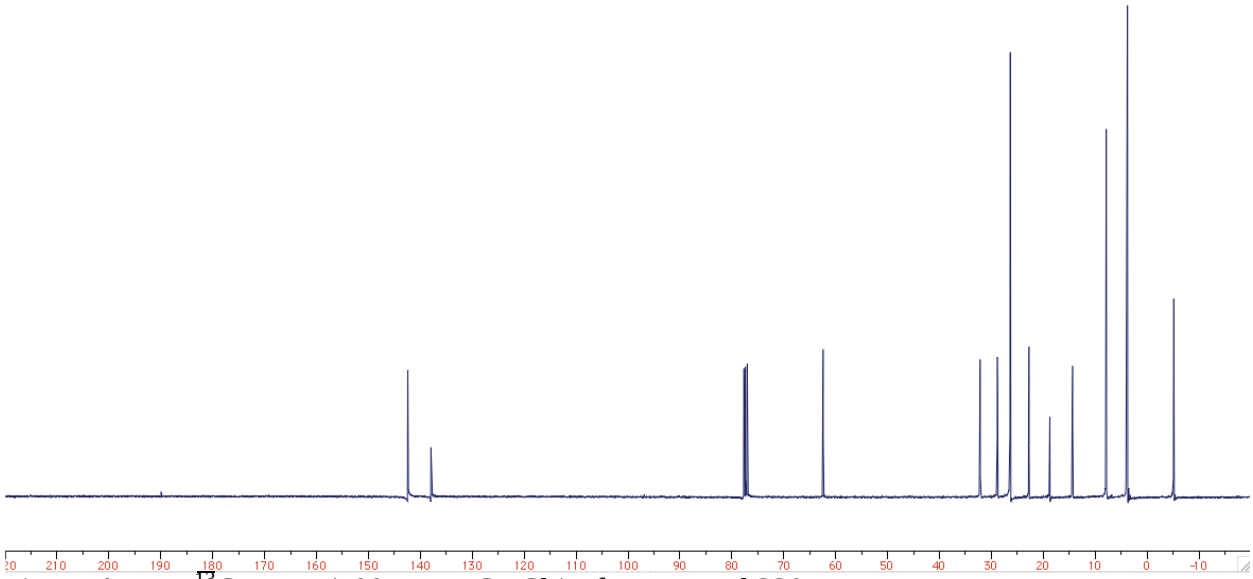


Figure A2.197 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **220**

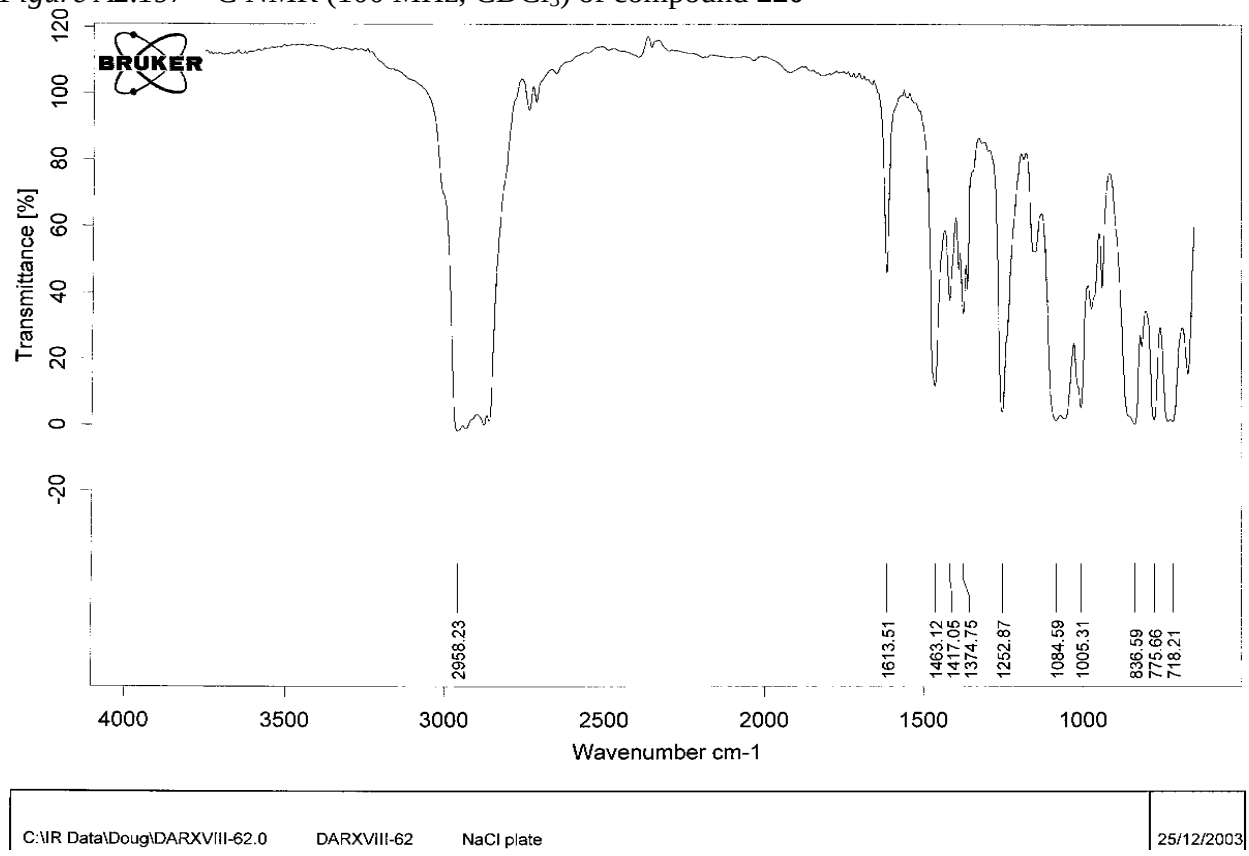
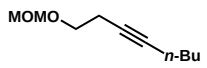


Figure A2.198 Infrared spectrum (thin film) of compound **220**



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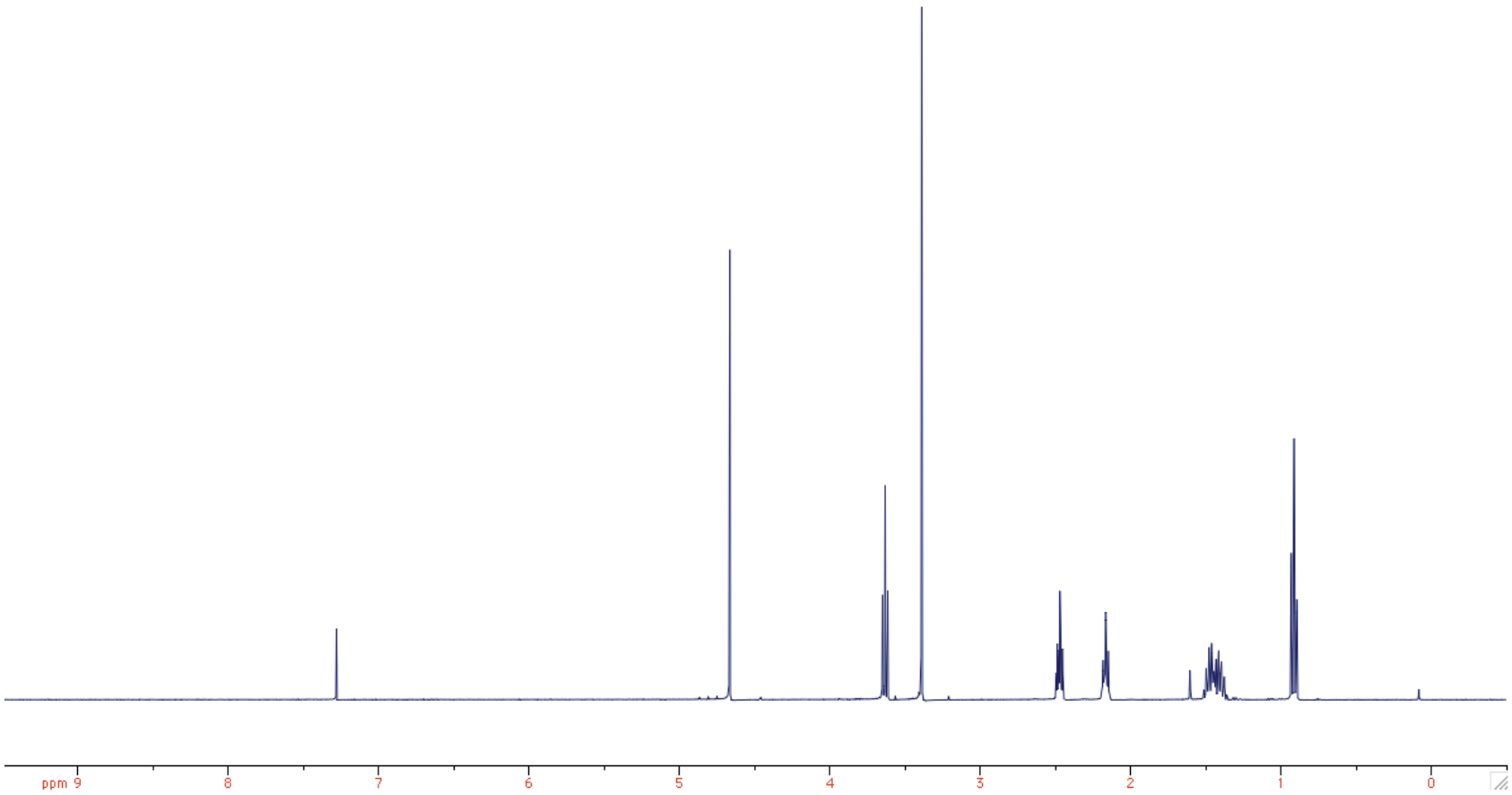
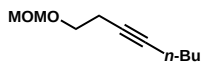


Figure A2.199 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **222**



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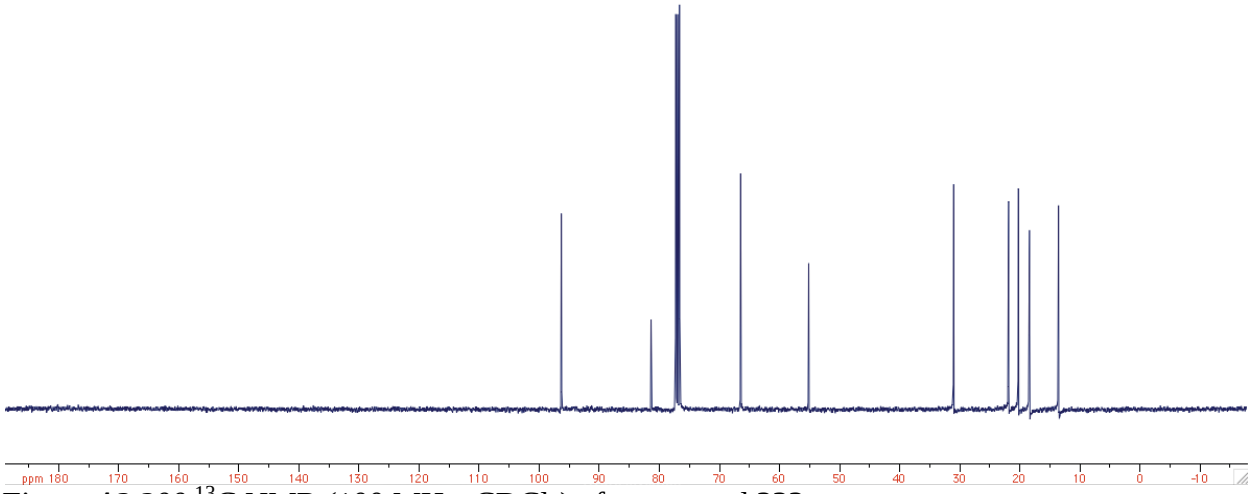


Figure A2.200 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **222**

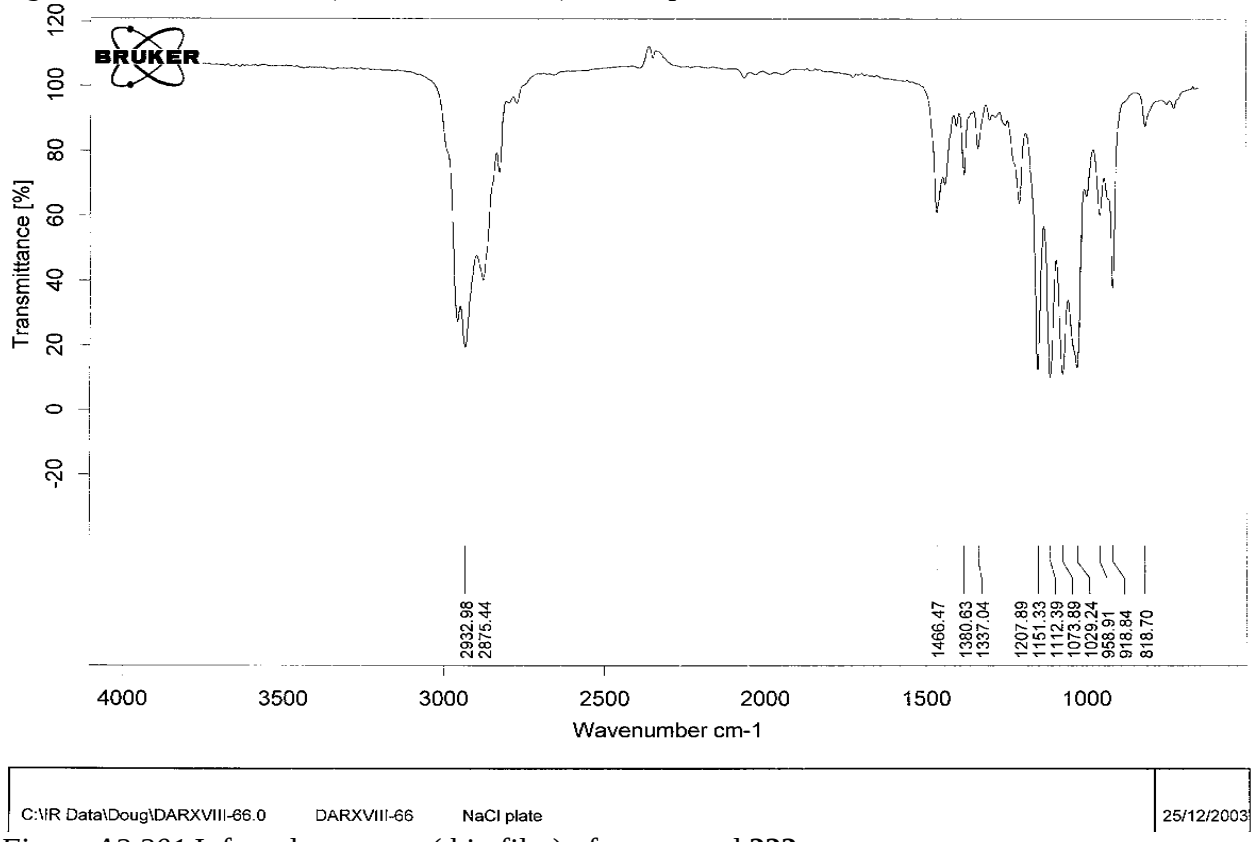
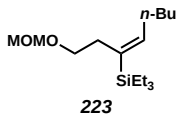


Figure A2.201 Infrared spectrum (thin film) of compound **222**



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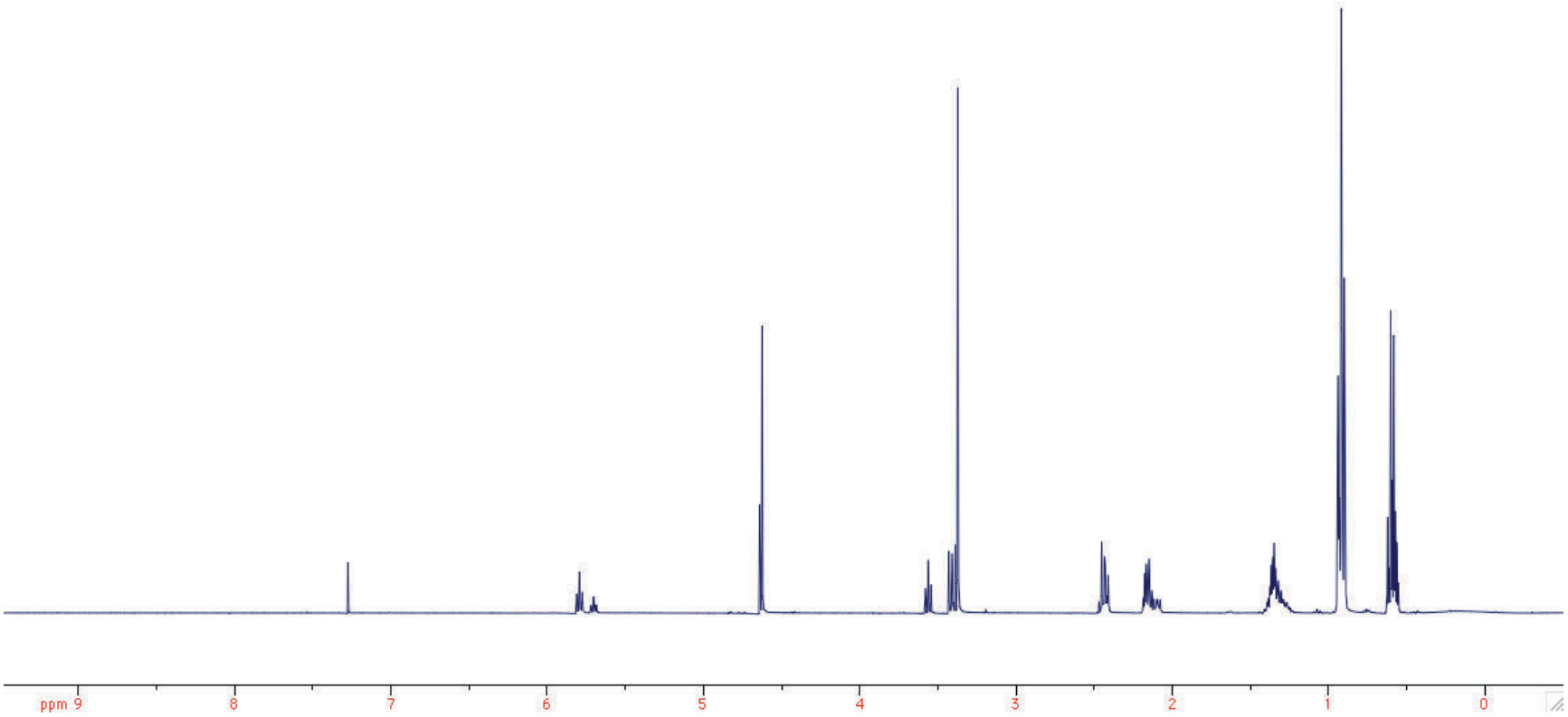


Figure A2.202 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **223**

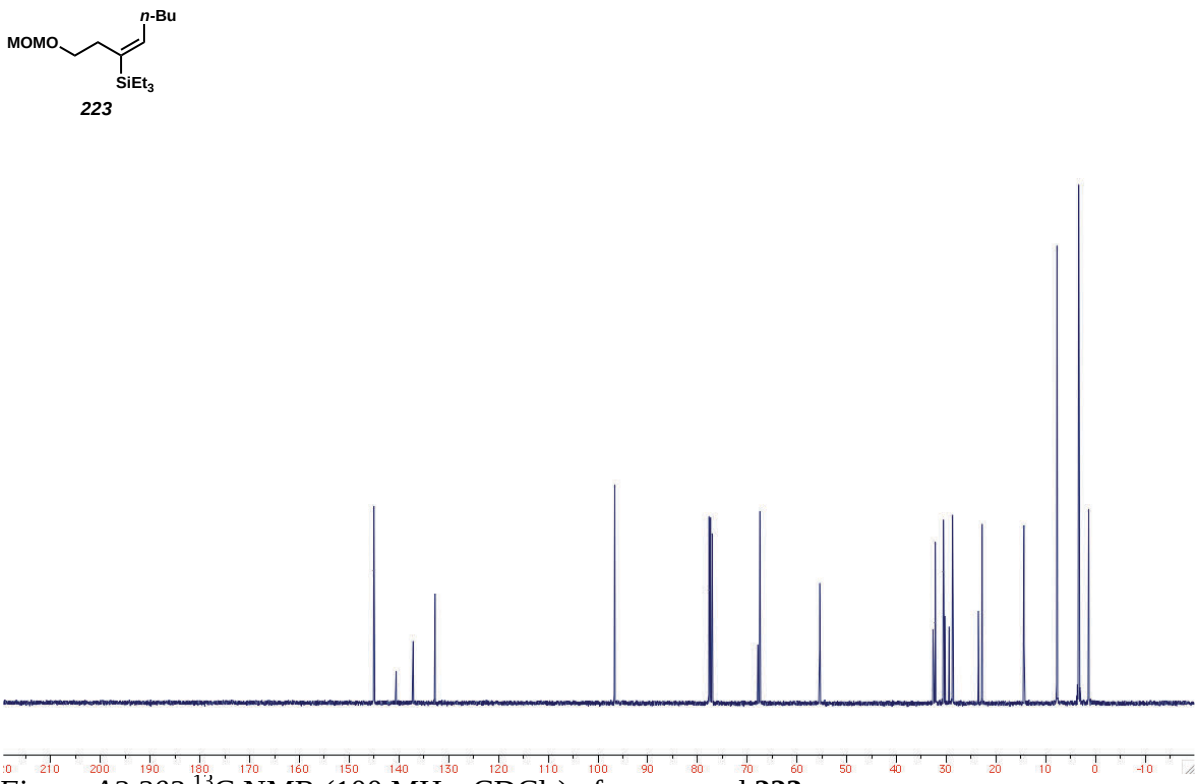


Figure A2.203 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **223**

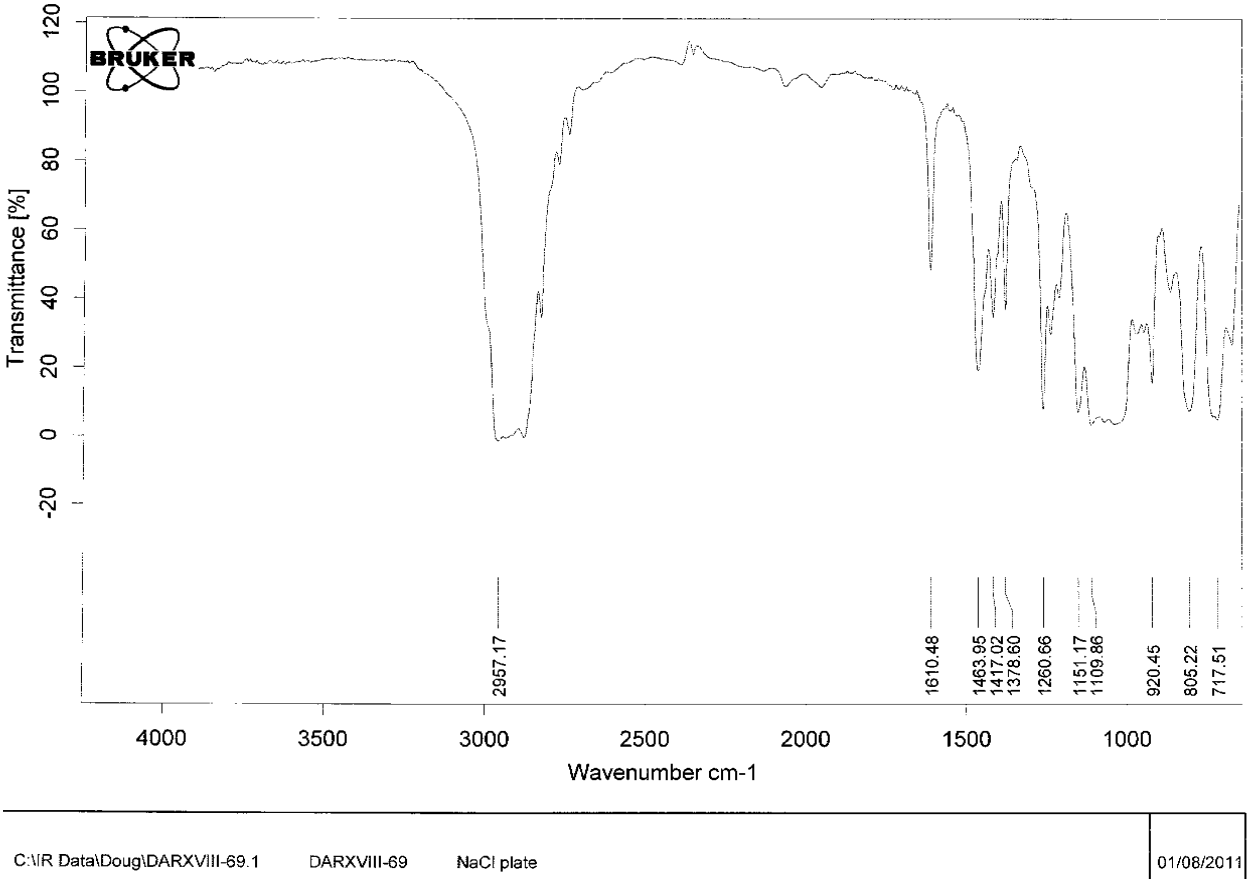
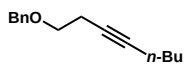


Figure A2.204 Infrared spectrum (thin film) of compound **223**



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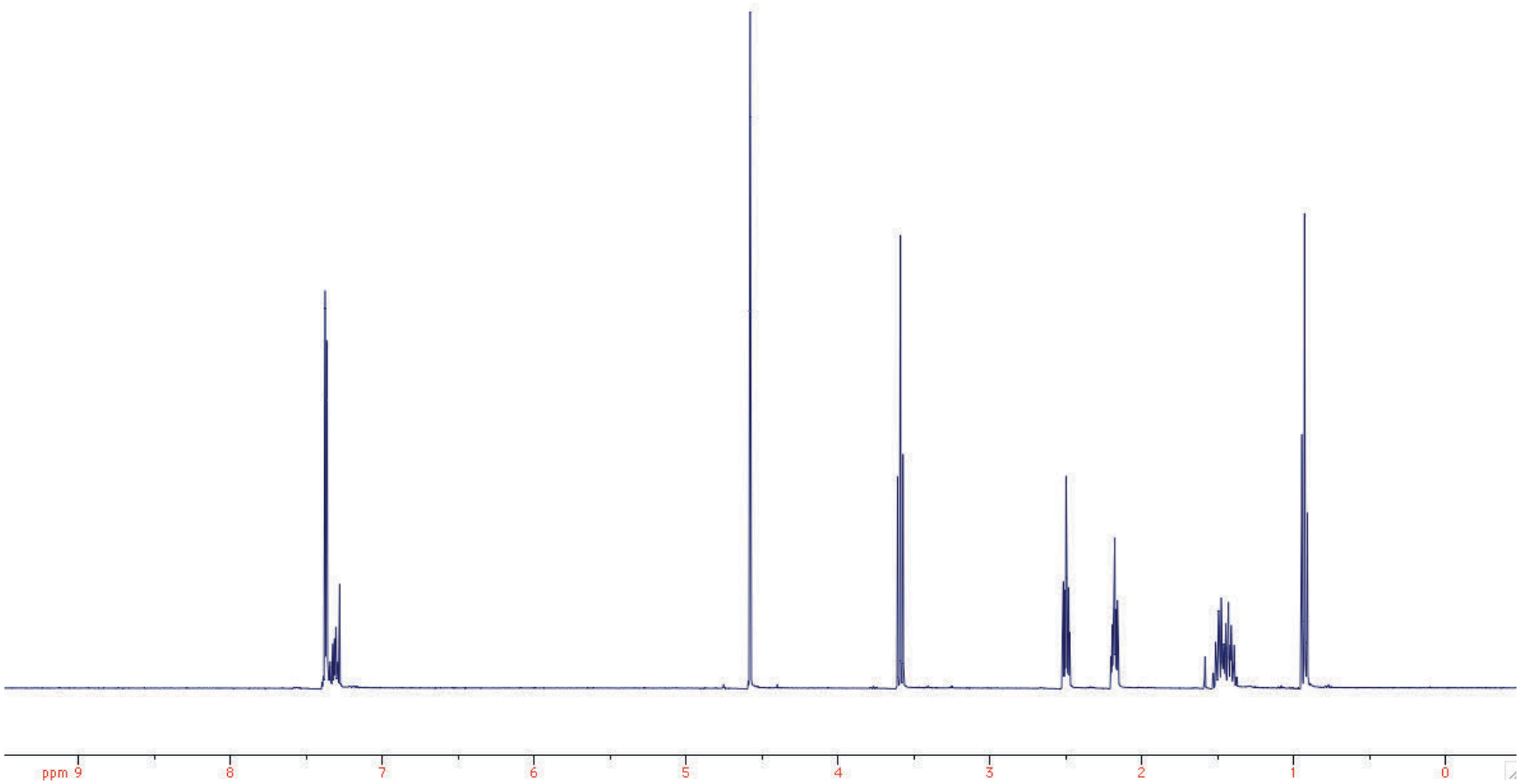
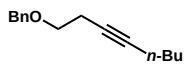


Figure A2.205 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **224**



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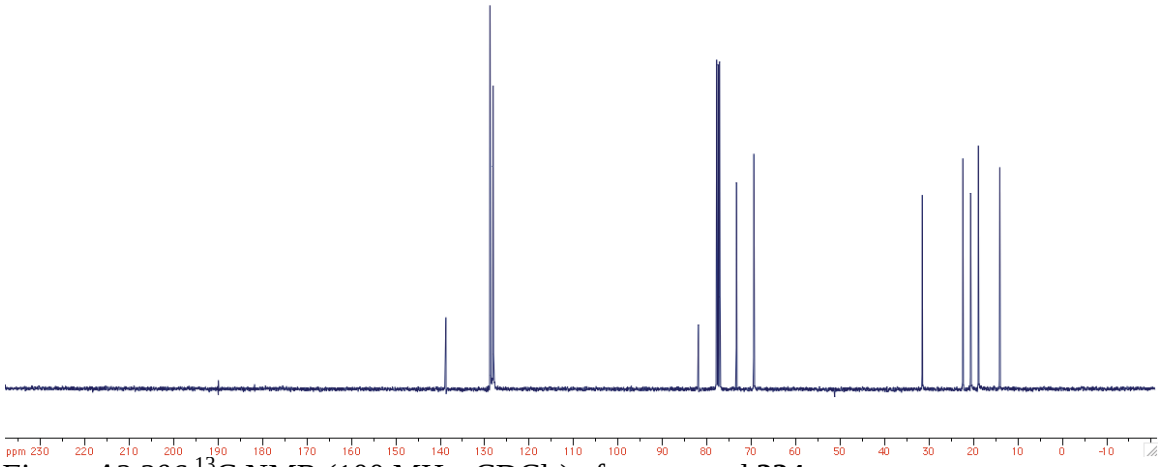


Figure A2.206 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **224**

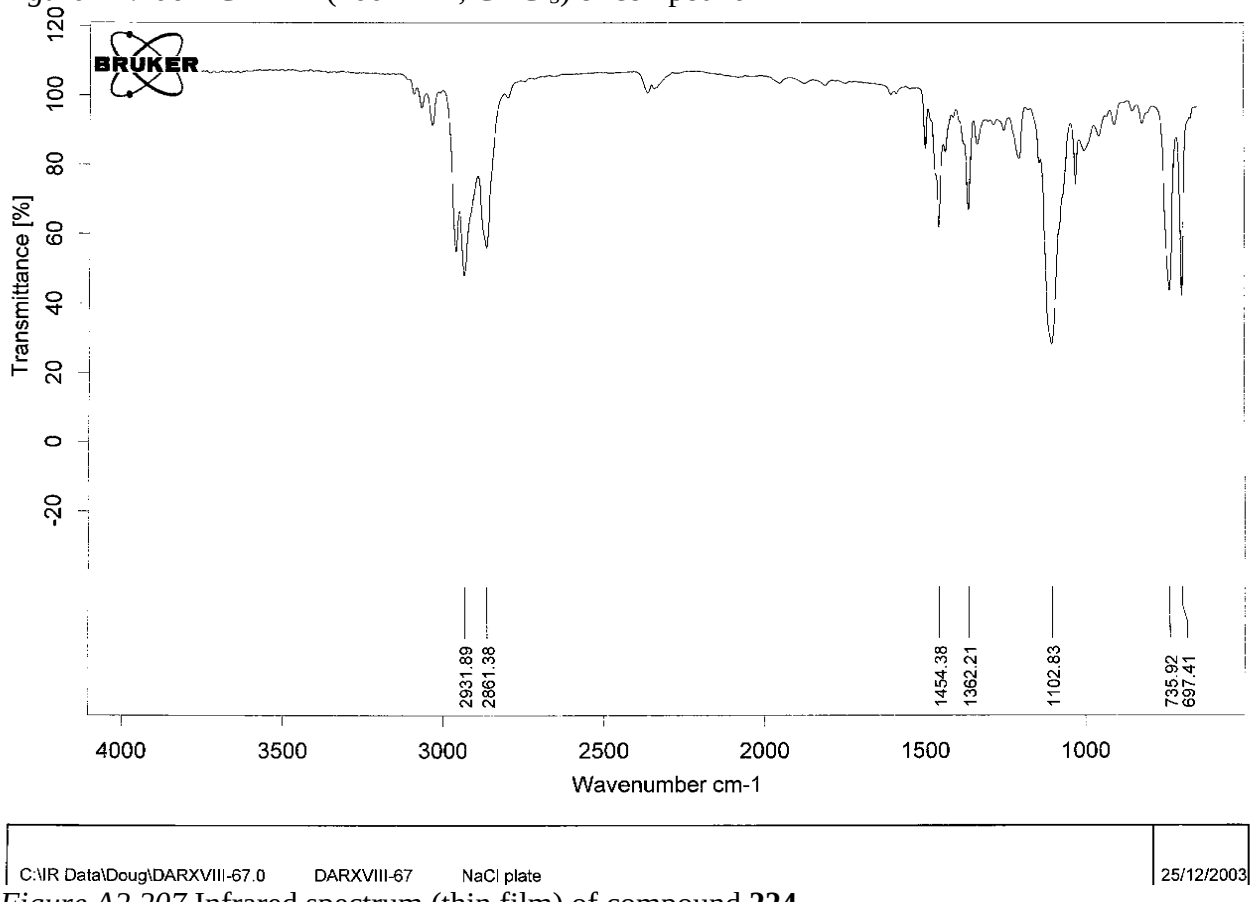
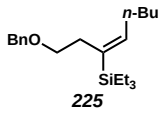


Figure A2.207 Infrared spectrum (thin film) of compound **224**



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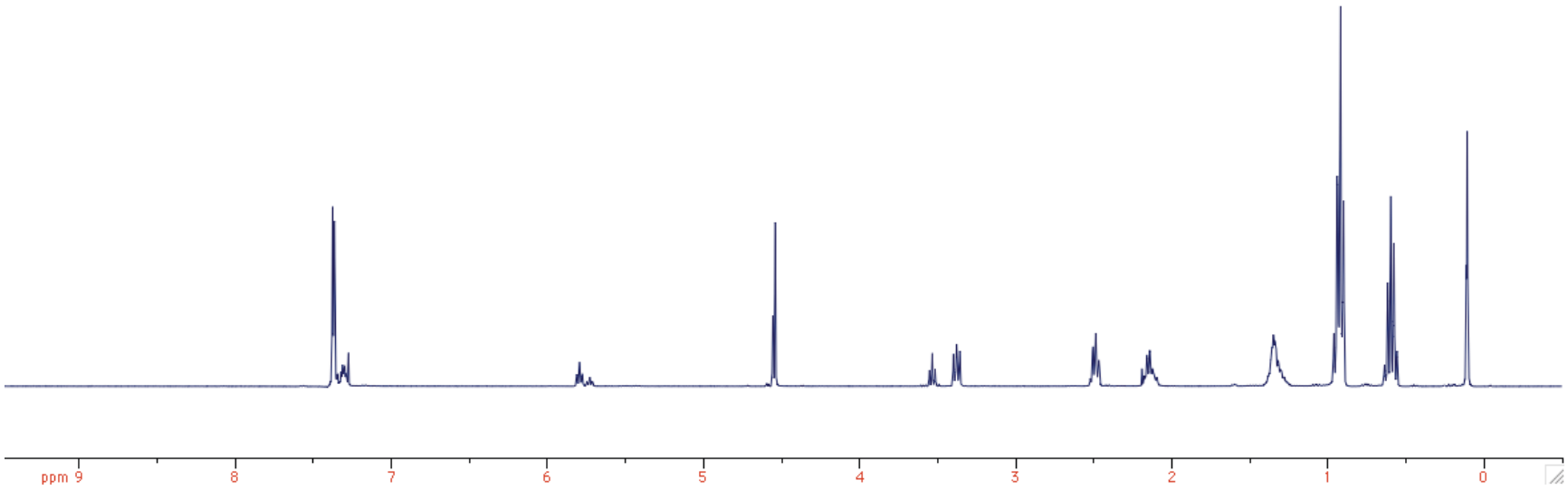
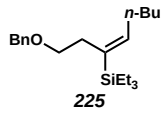


Figure A2.208 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **225**



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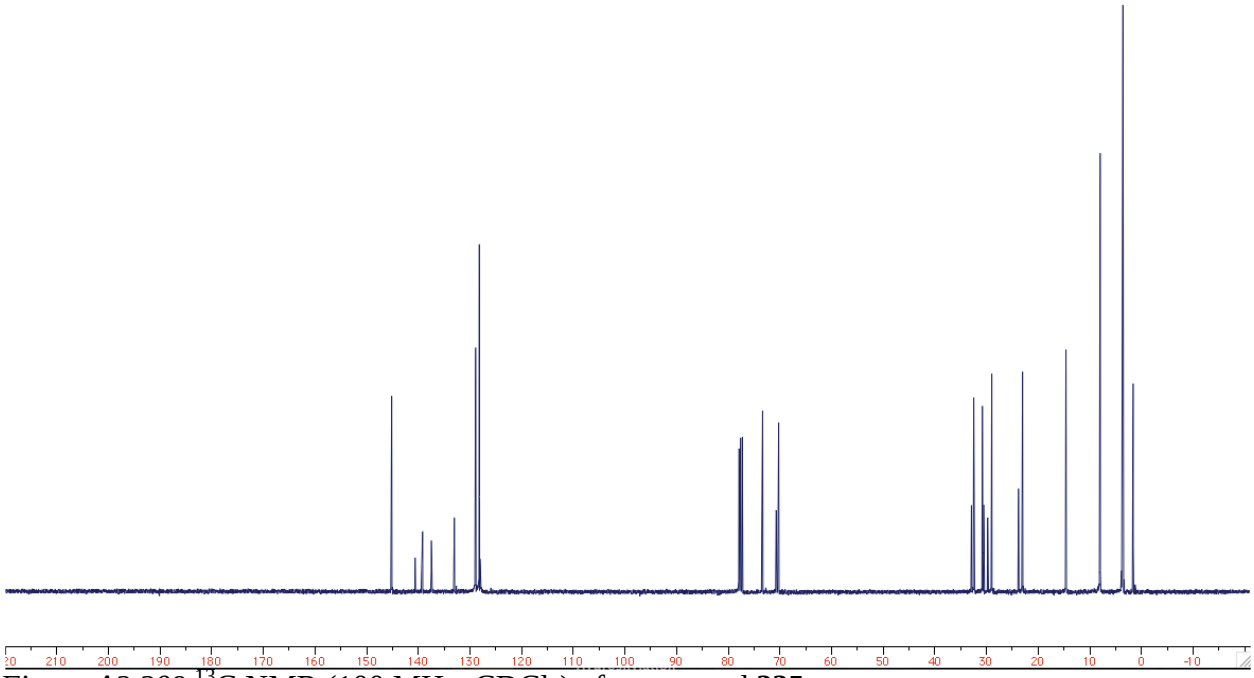


Figure A2.209 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **225**

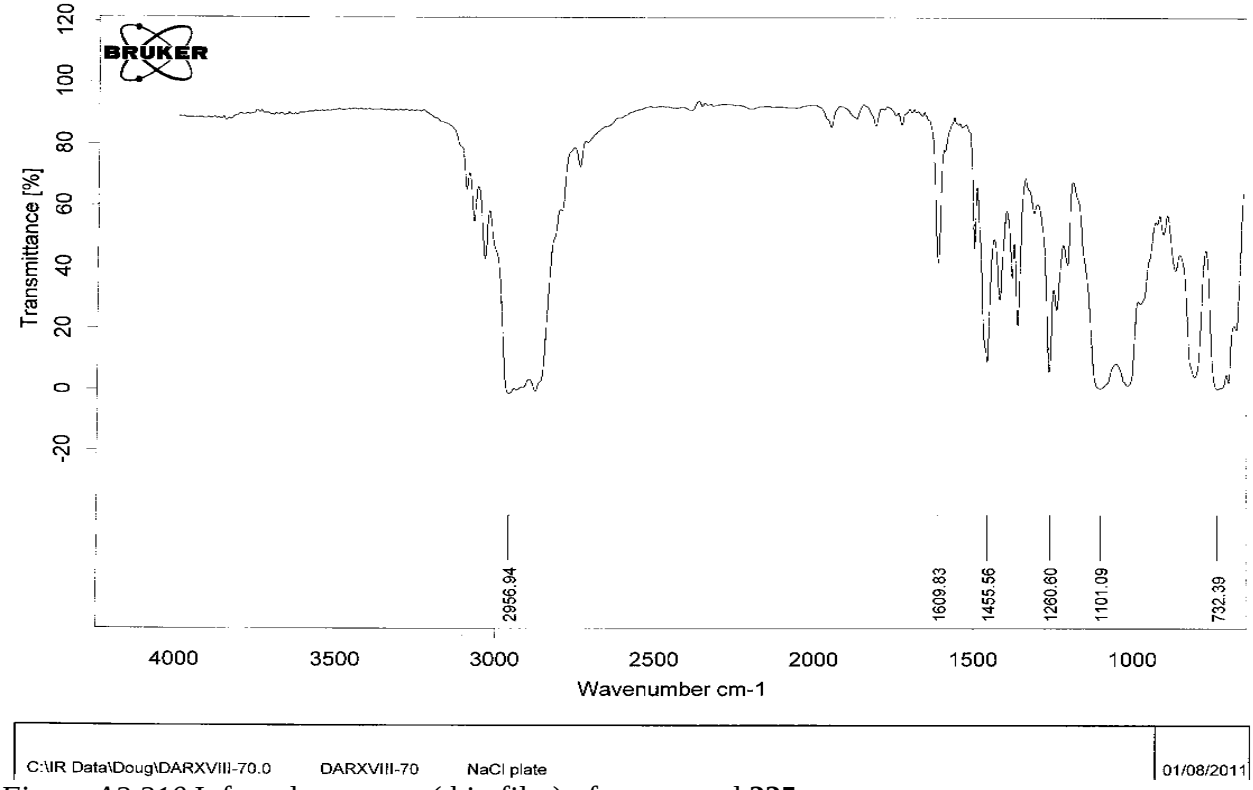
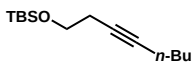


Figure A2.210 Infrared spectrum (thin film) of compound **225**



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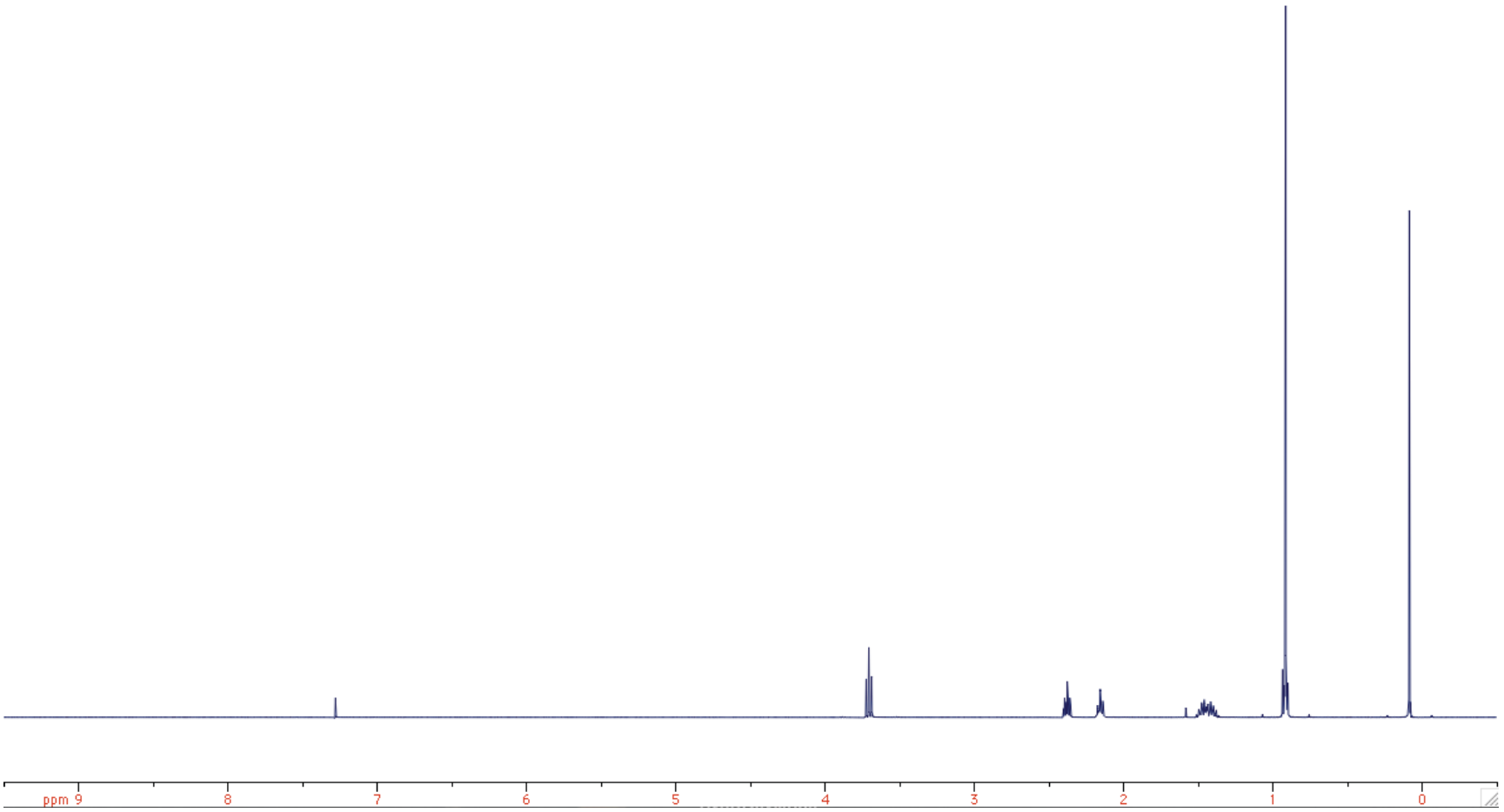
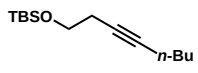


Figure A2.211 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **226**



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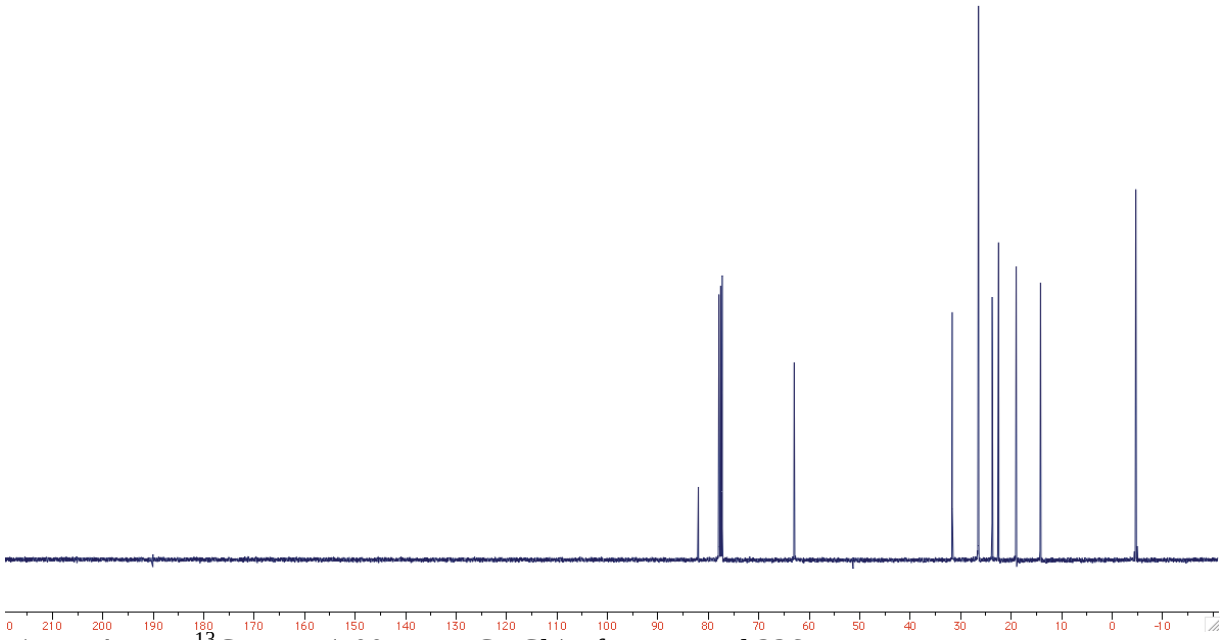


Figure A2.212 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **226**

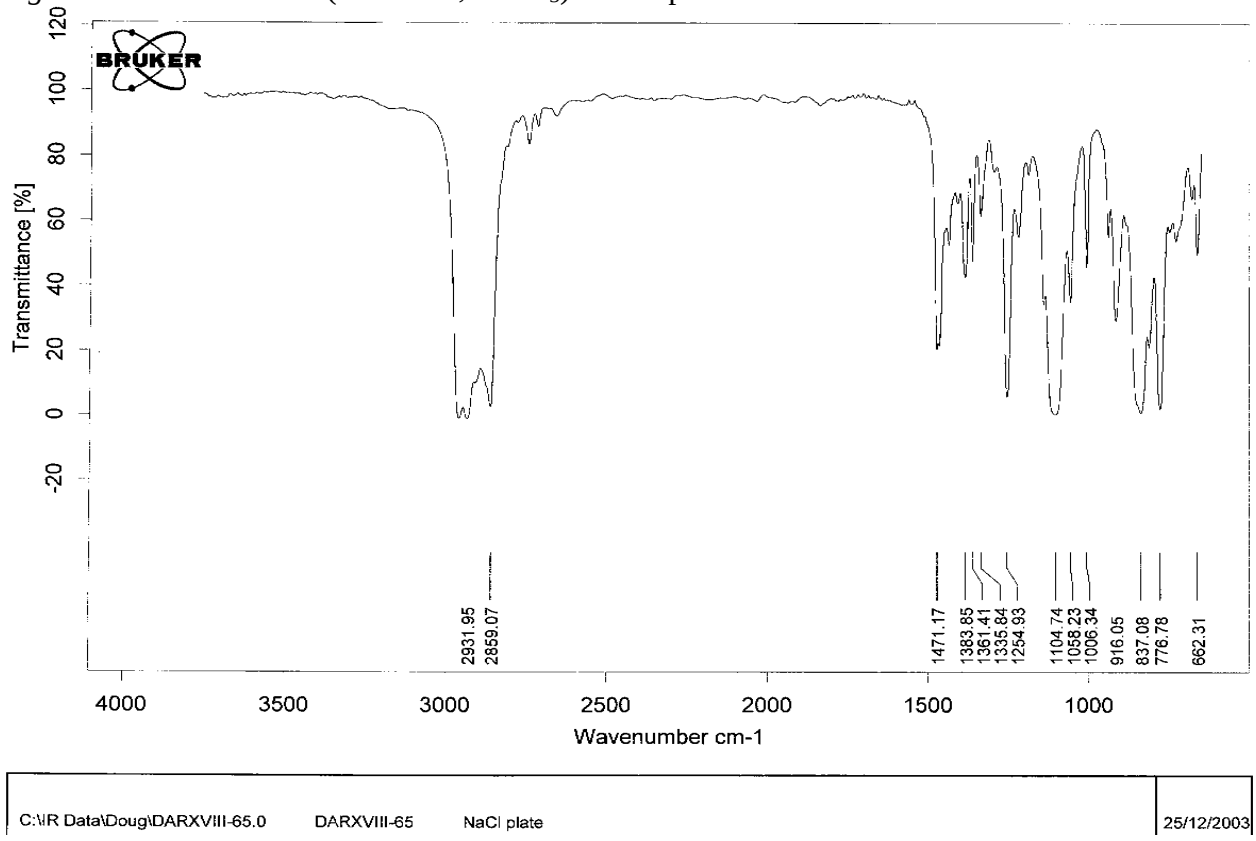


Figure A2.213 Infrared spectrum (thin film) of compound **226**

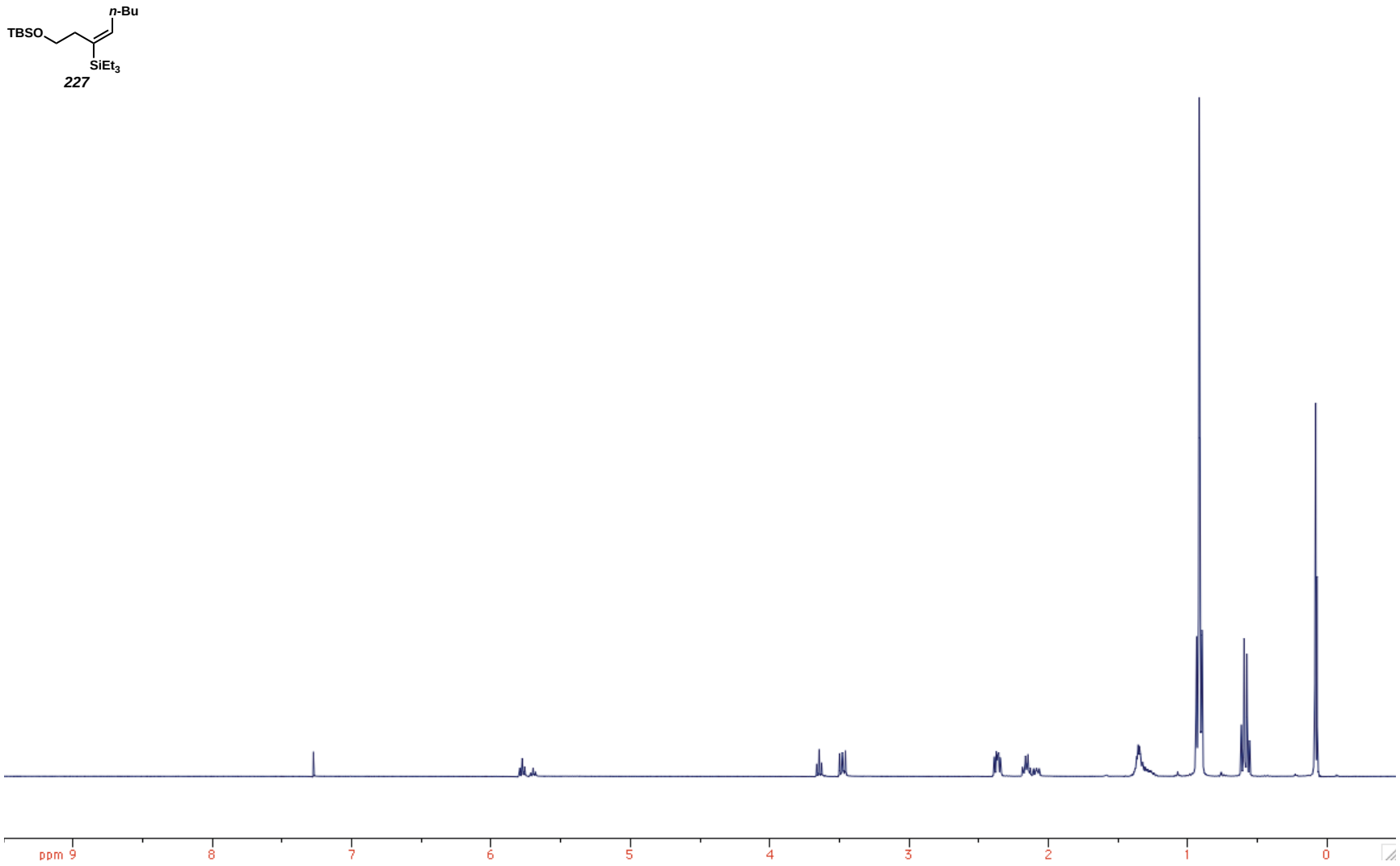
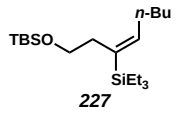


Figure A2.214 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **227**



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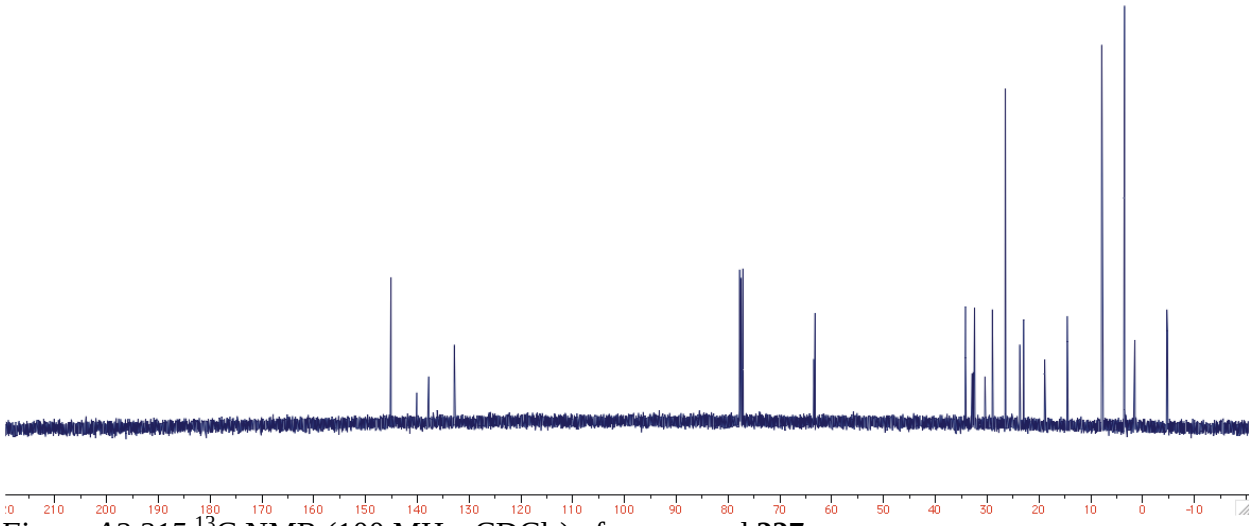


Figure A2.215 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **227**

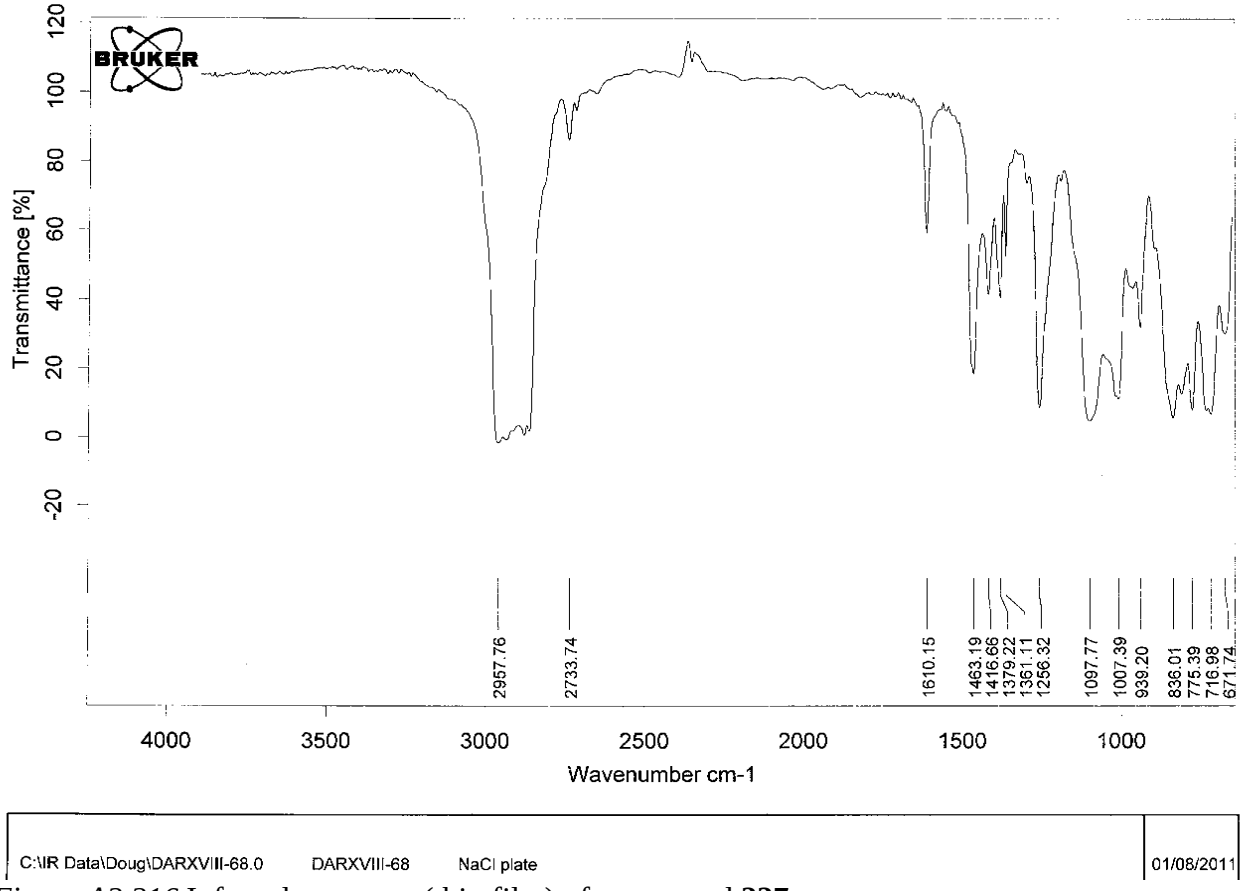


Figure A2.216 Infrared spectrum (thin film) of compound **227**

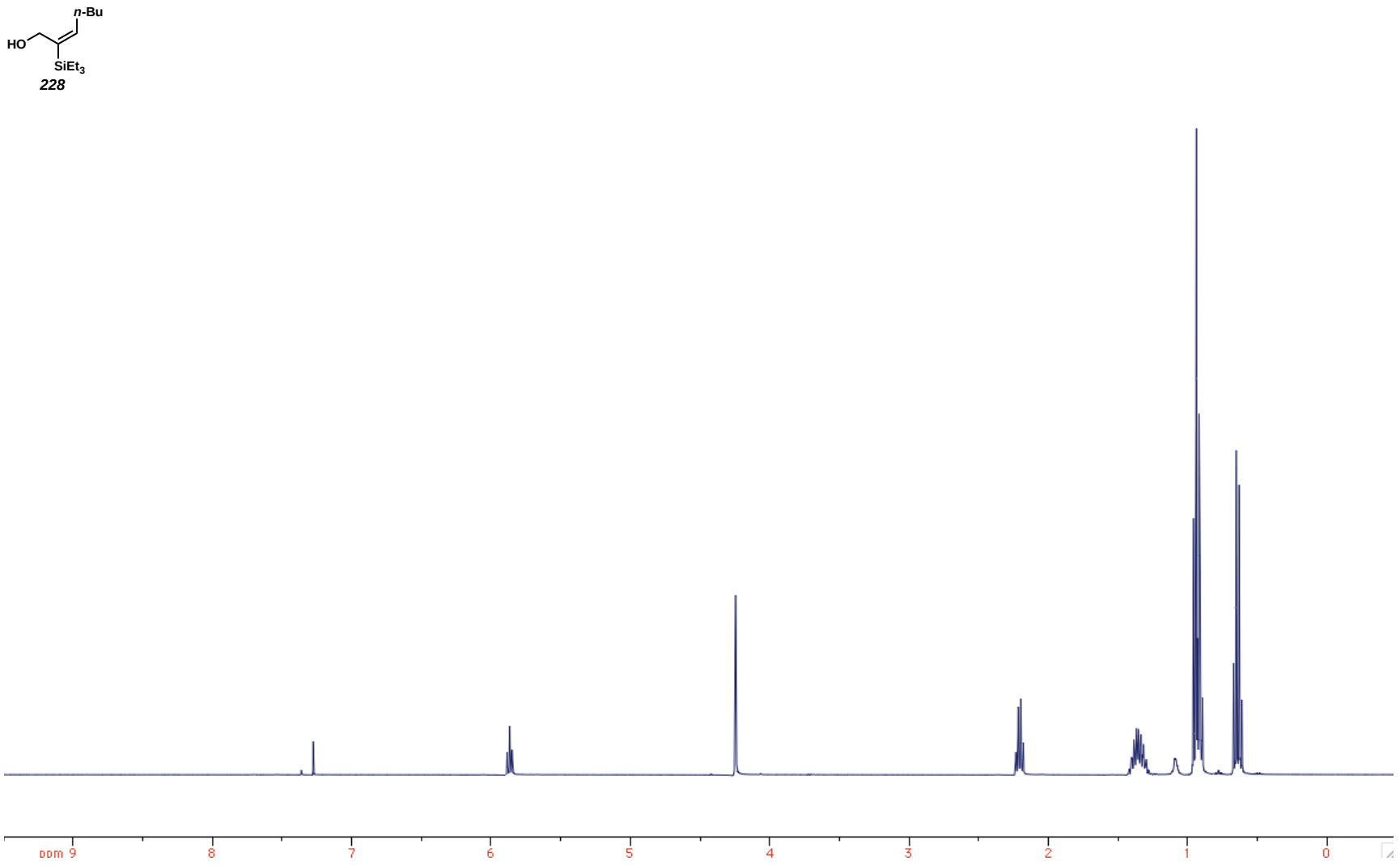


Figure A2.217 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **228**

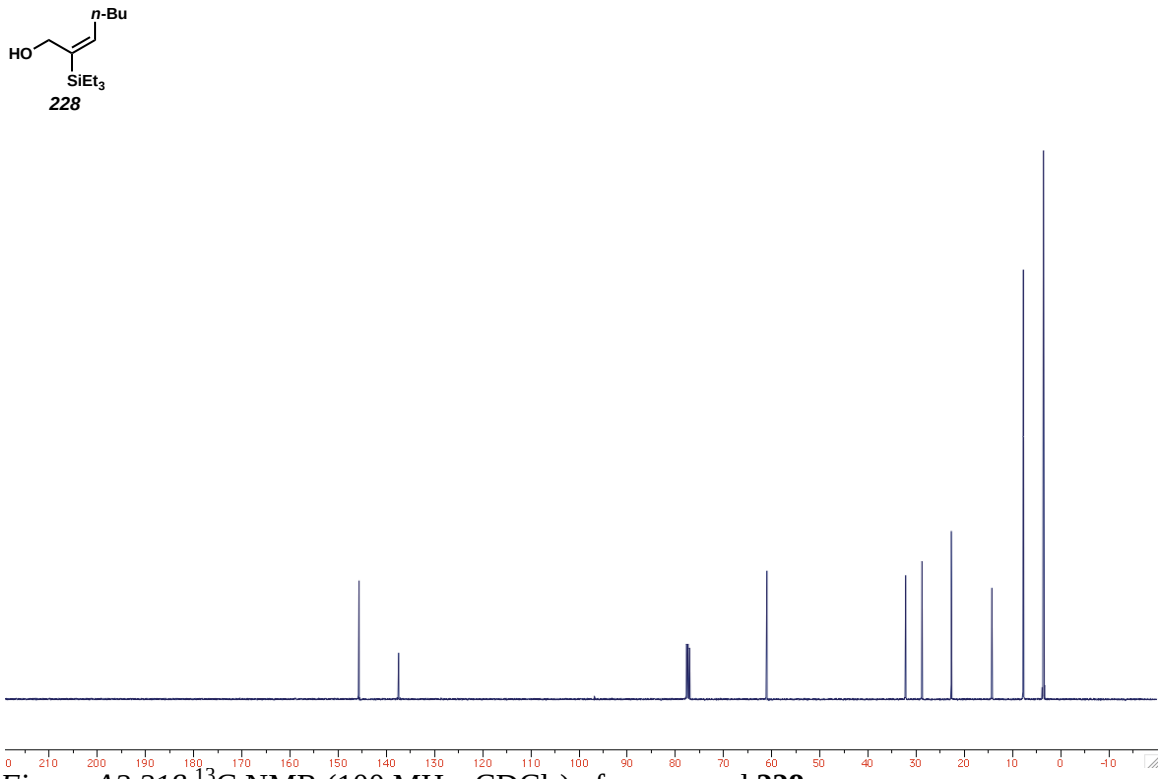


Figure A2.218 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **228**

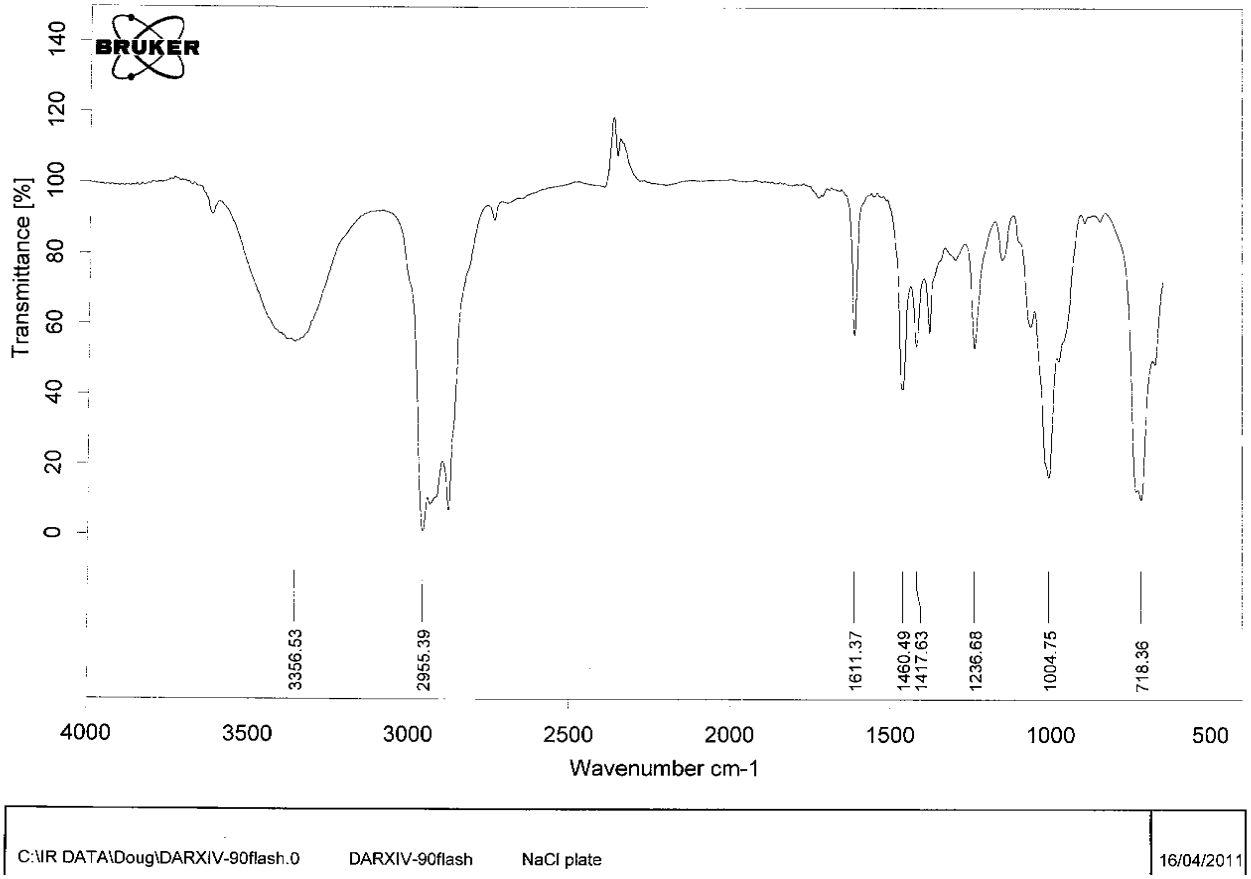


Figure A2.219 Infrared spectrum (thin film) of compound **228**

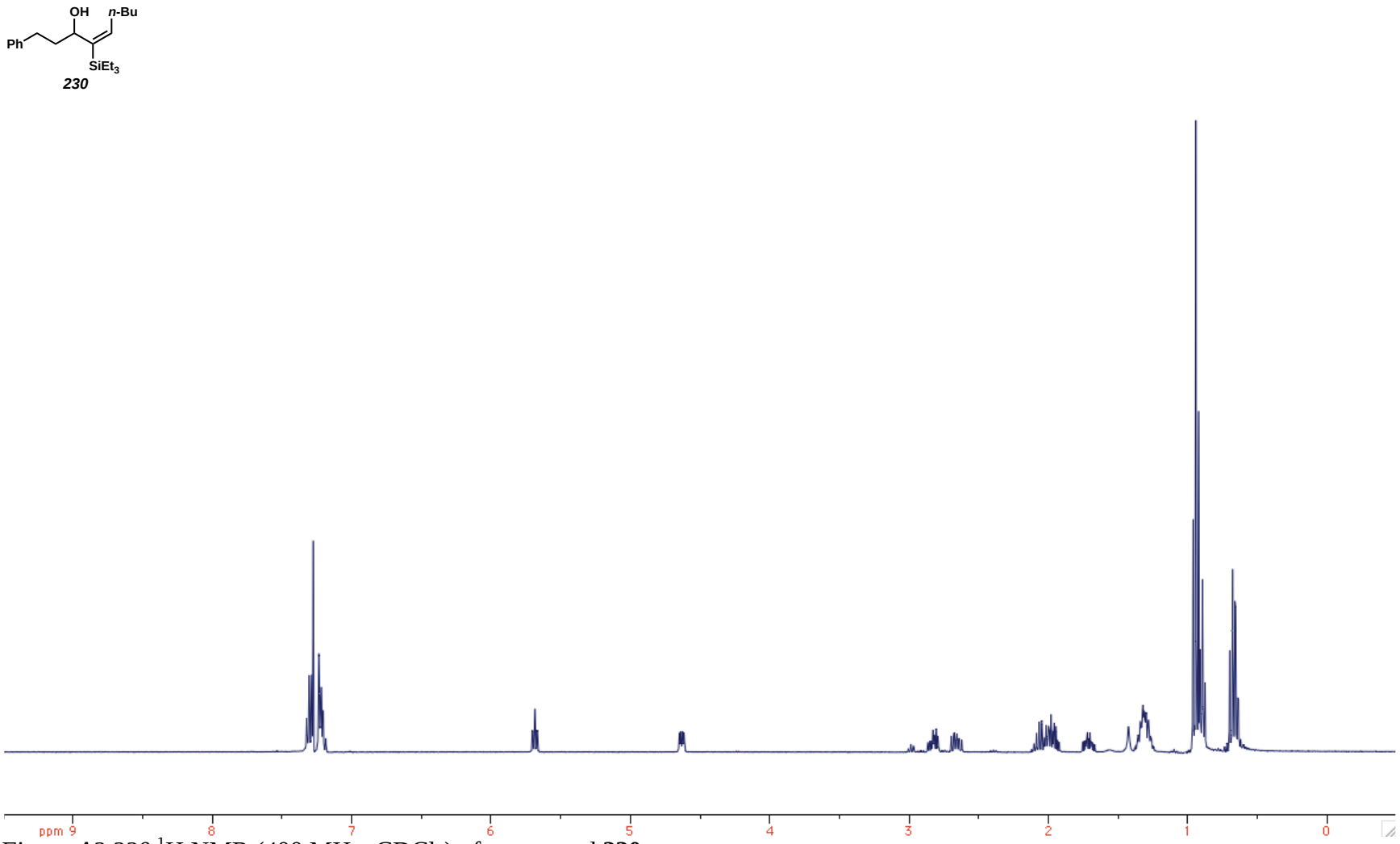


Figure A2.220 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **230**

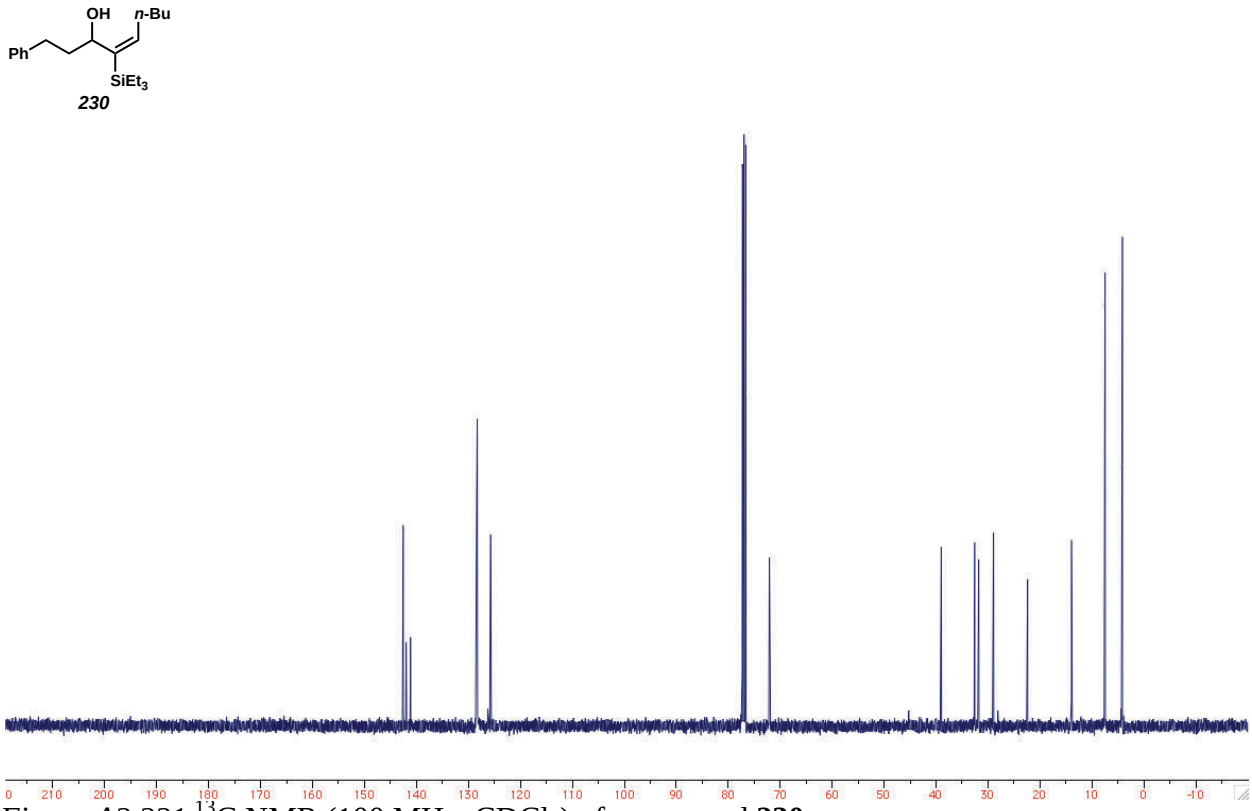


Figure A2.221 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **230**

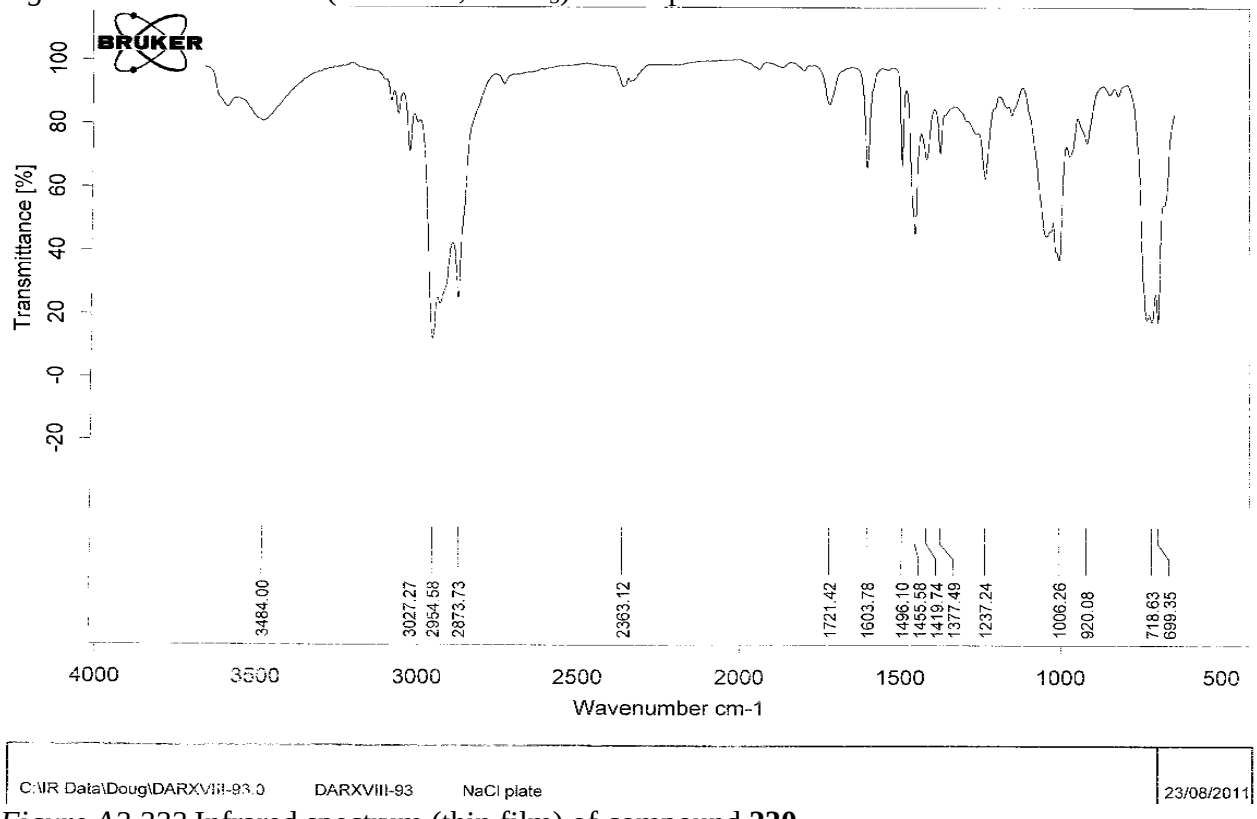
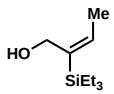


Figure A2.222 Infrared spectrum (thin film) of compound **230**



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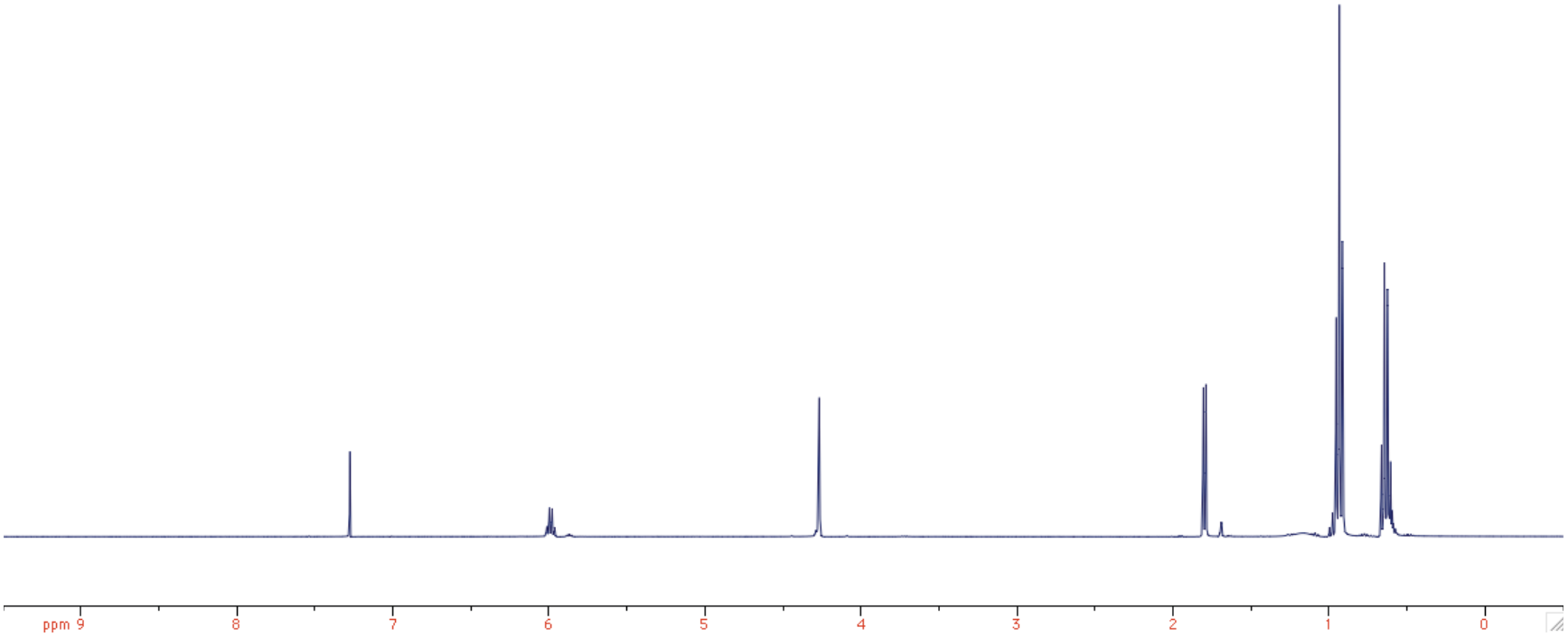
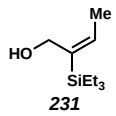


Figure A2.223 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **231**



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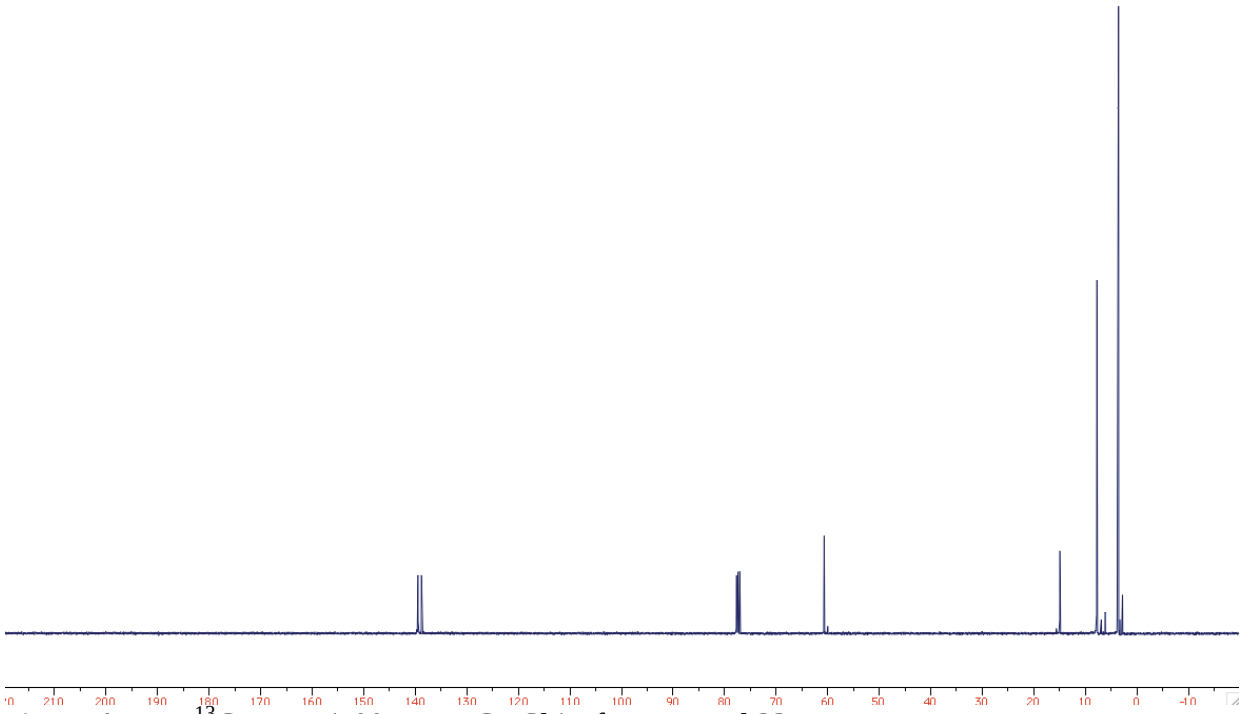


Figure A2.224 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **231**

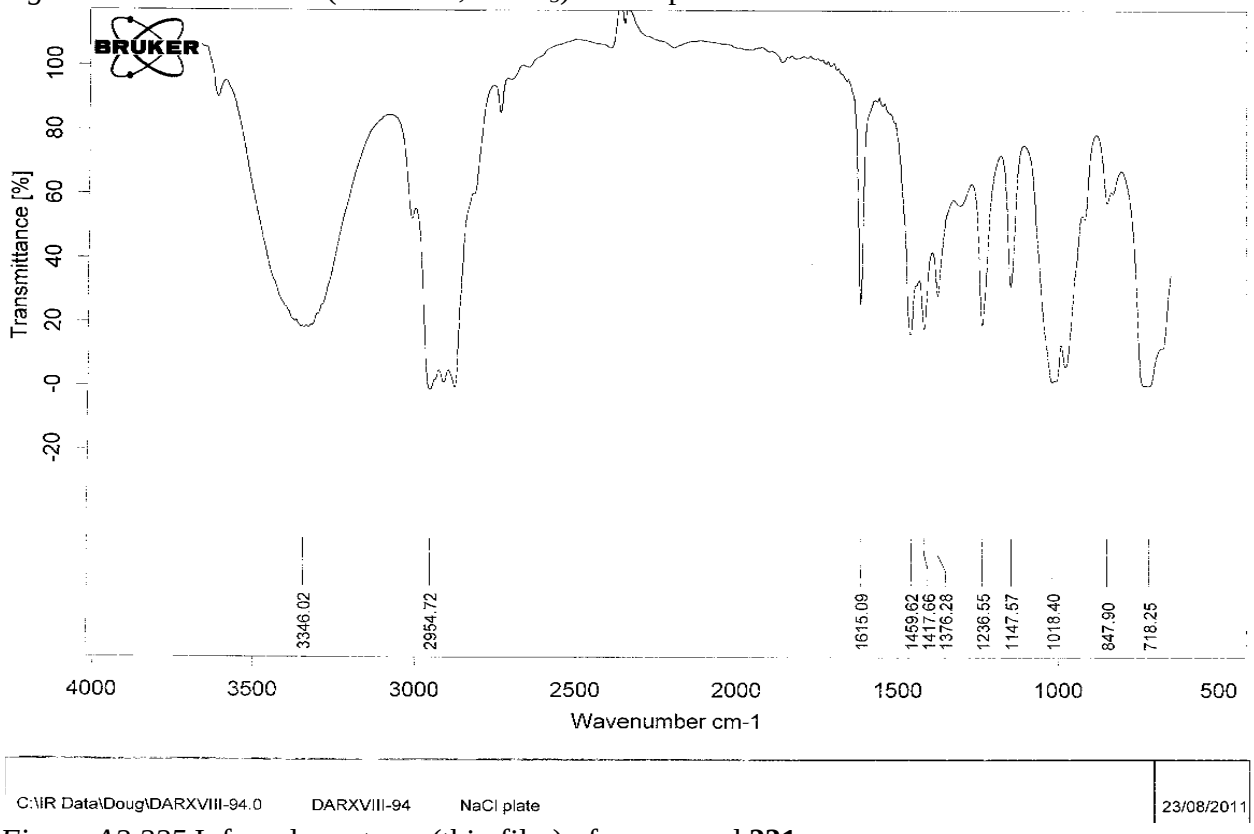
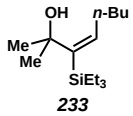


Figure A2.225 Infrared spectrum (thin film) of compound **231**



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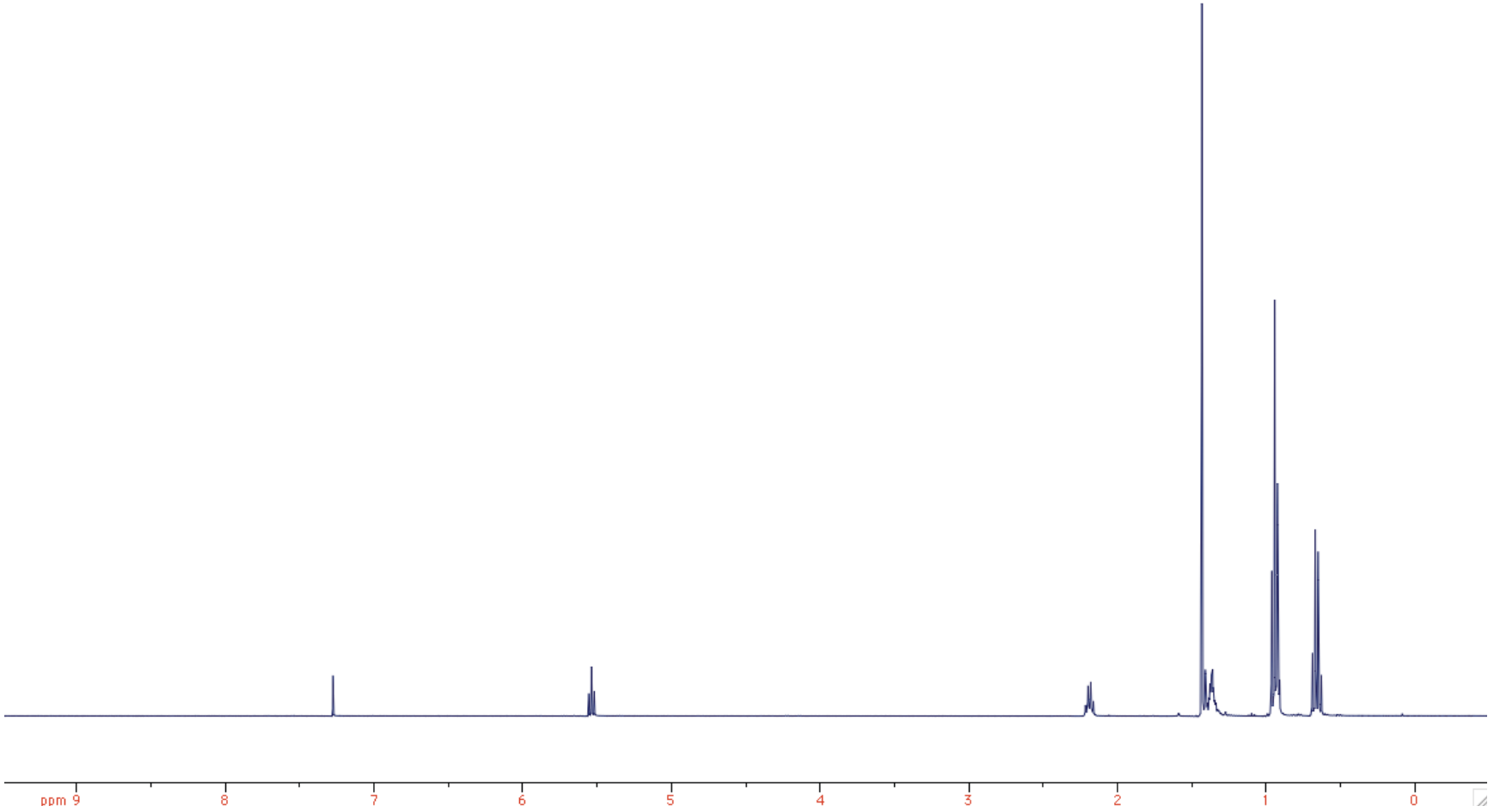


Figure A2.226 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **233**

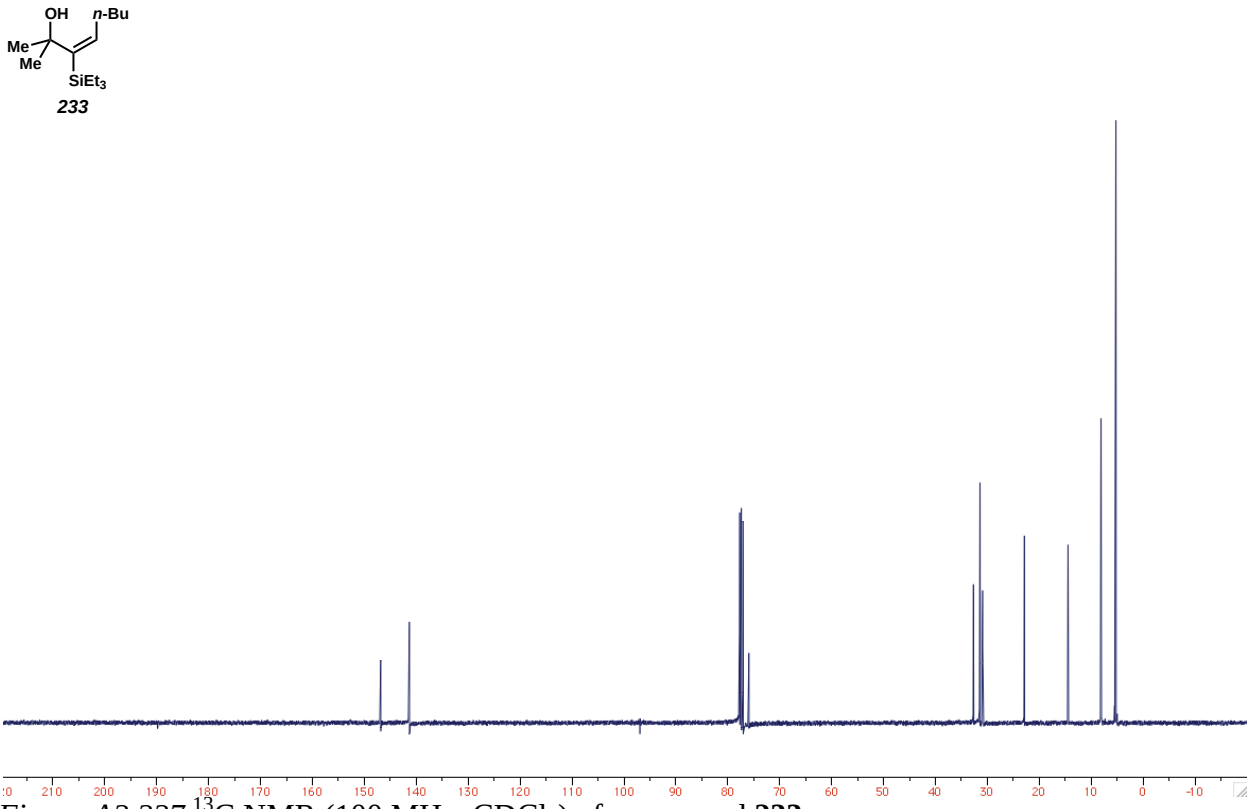


Figure A2.227 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **233**

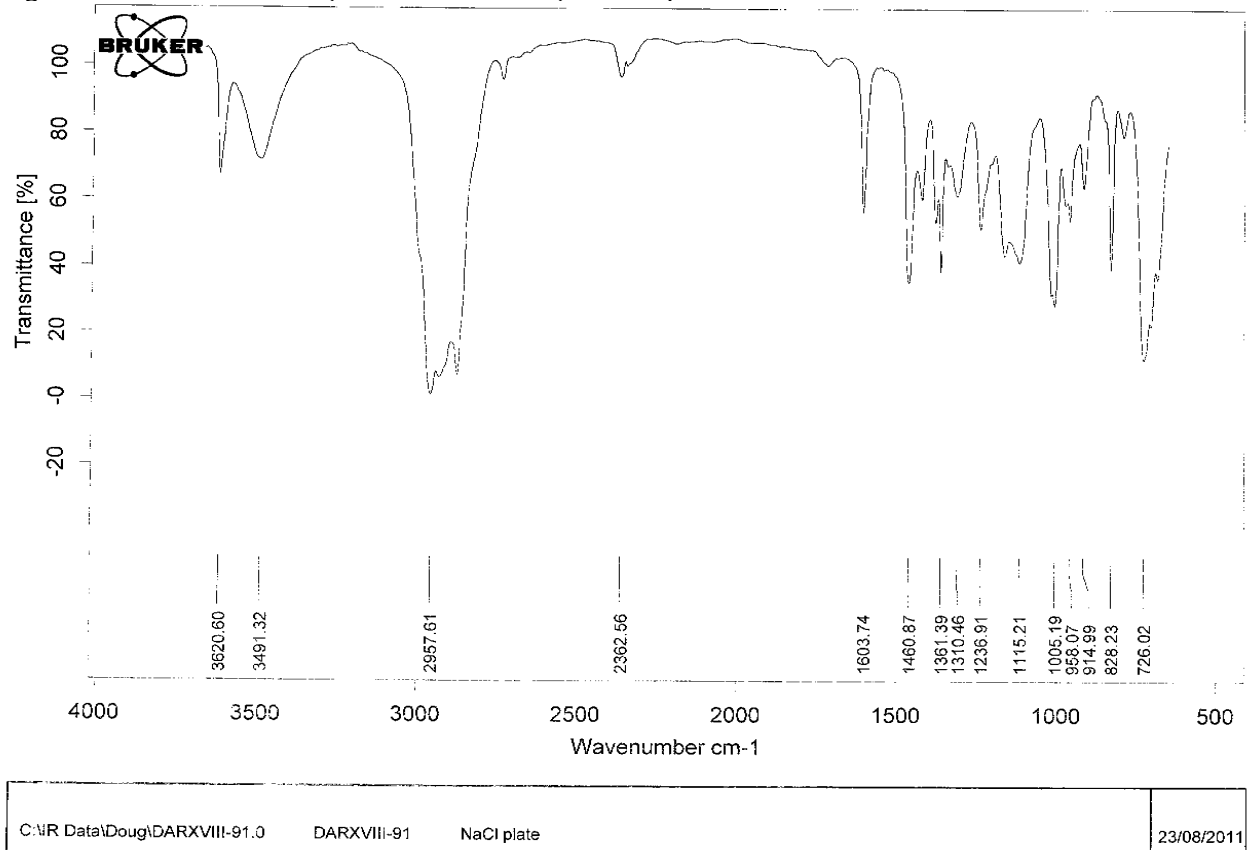
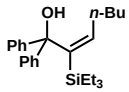


Figure A2.228 Infrared spectrum (thin film) of compound **233**



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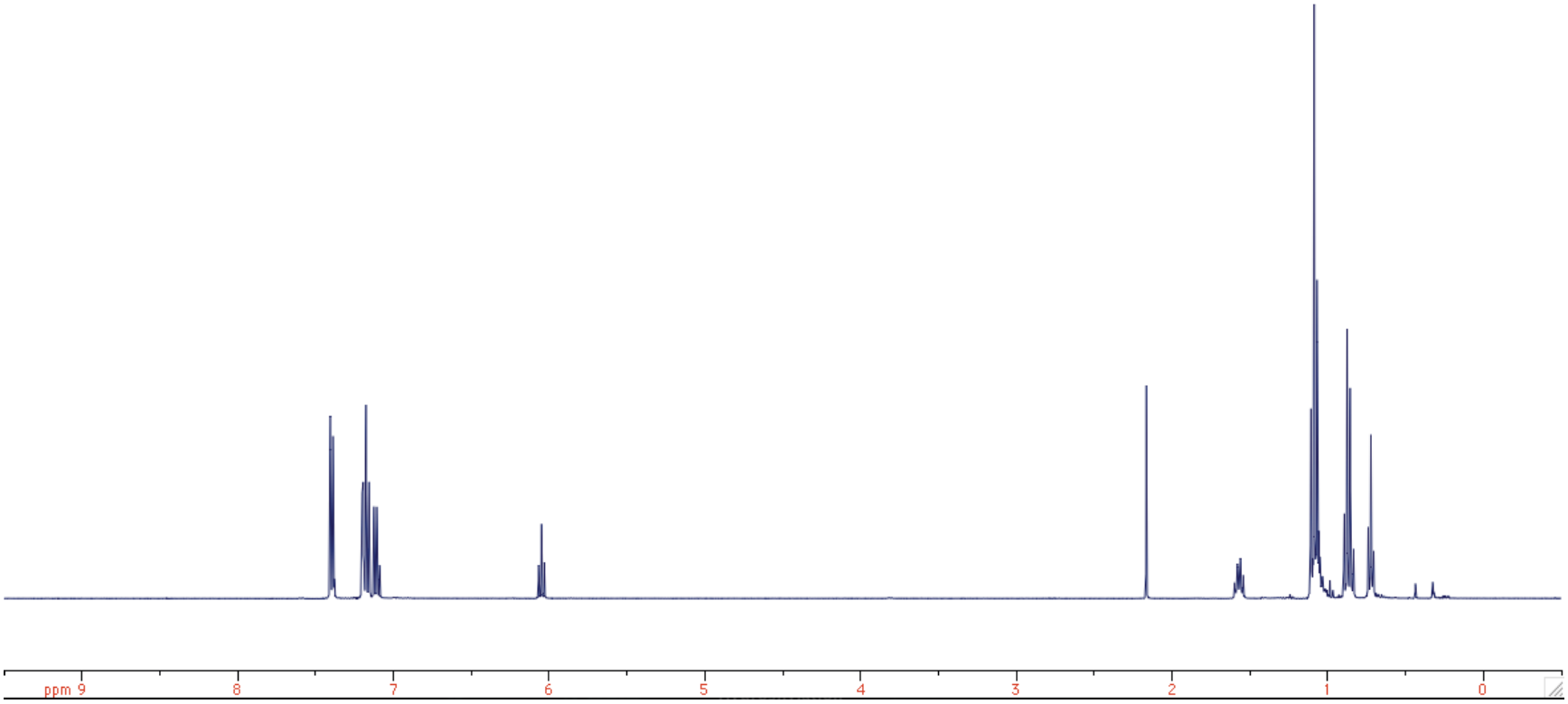


Figure A2.229 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **235**

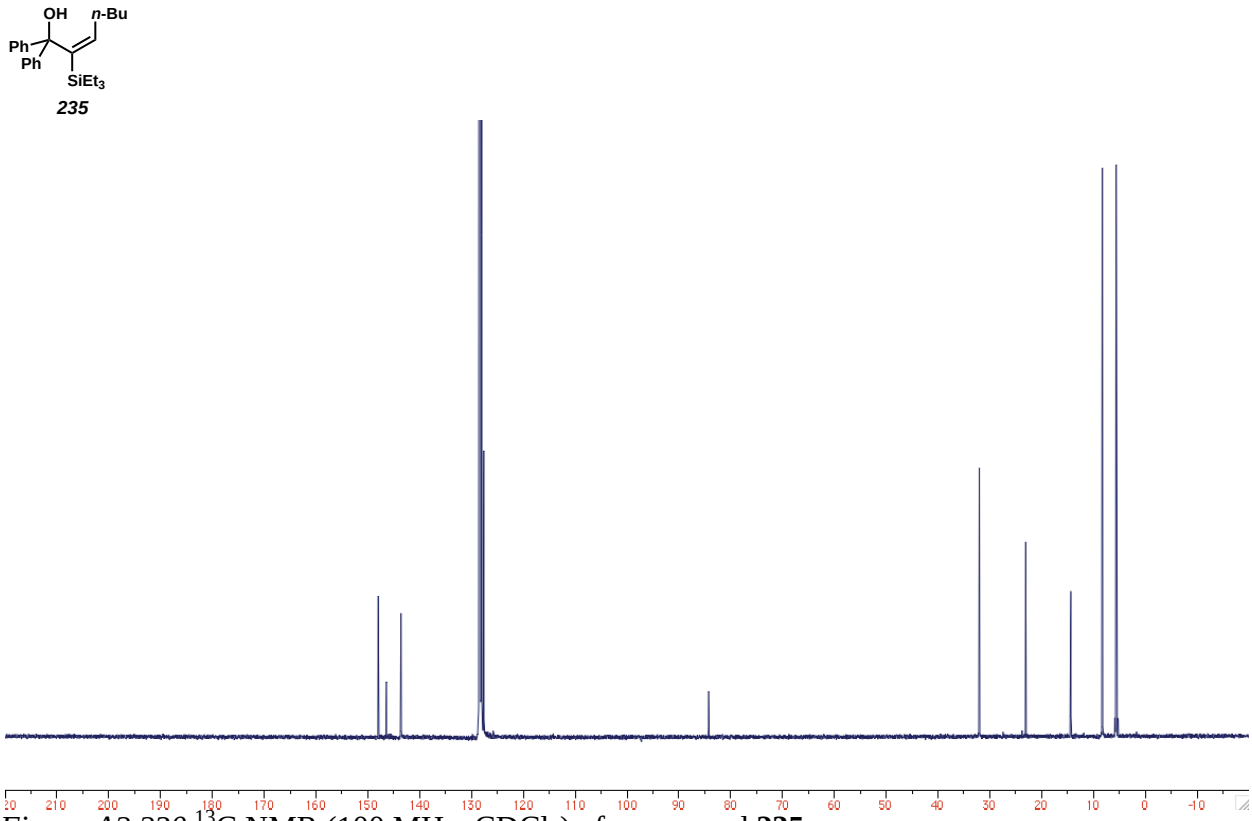


Figure A2.230 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **235**

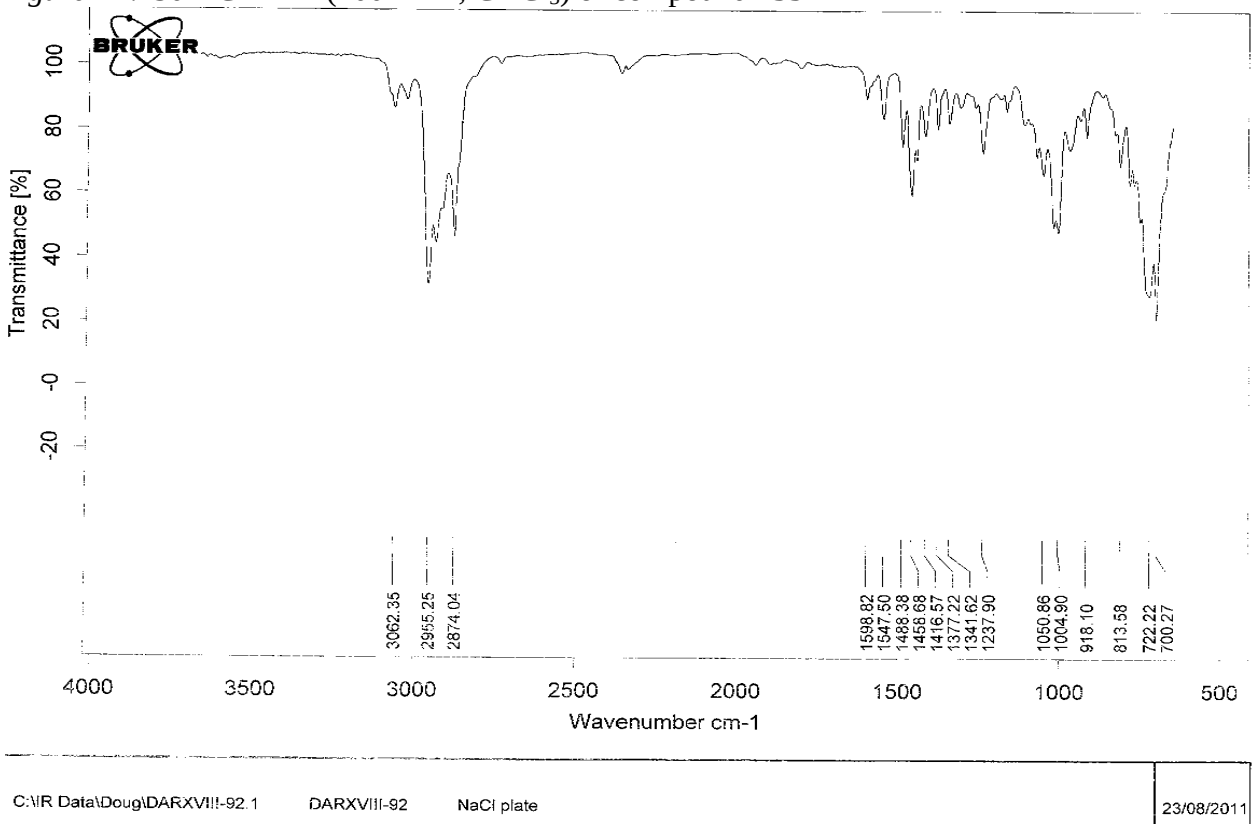


Figure A2.231 Infrared spectrum (thin film) of compound **235**

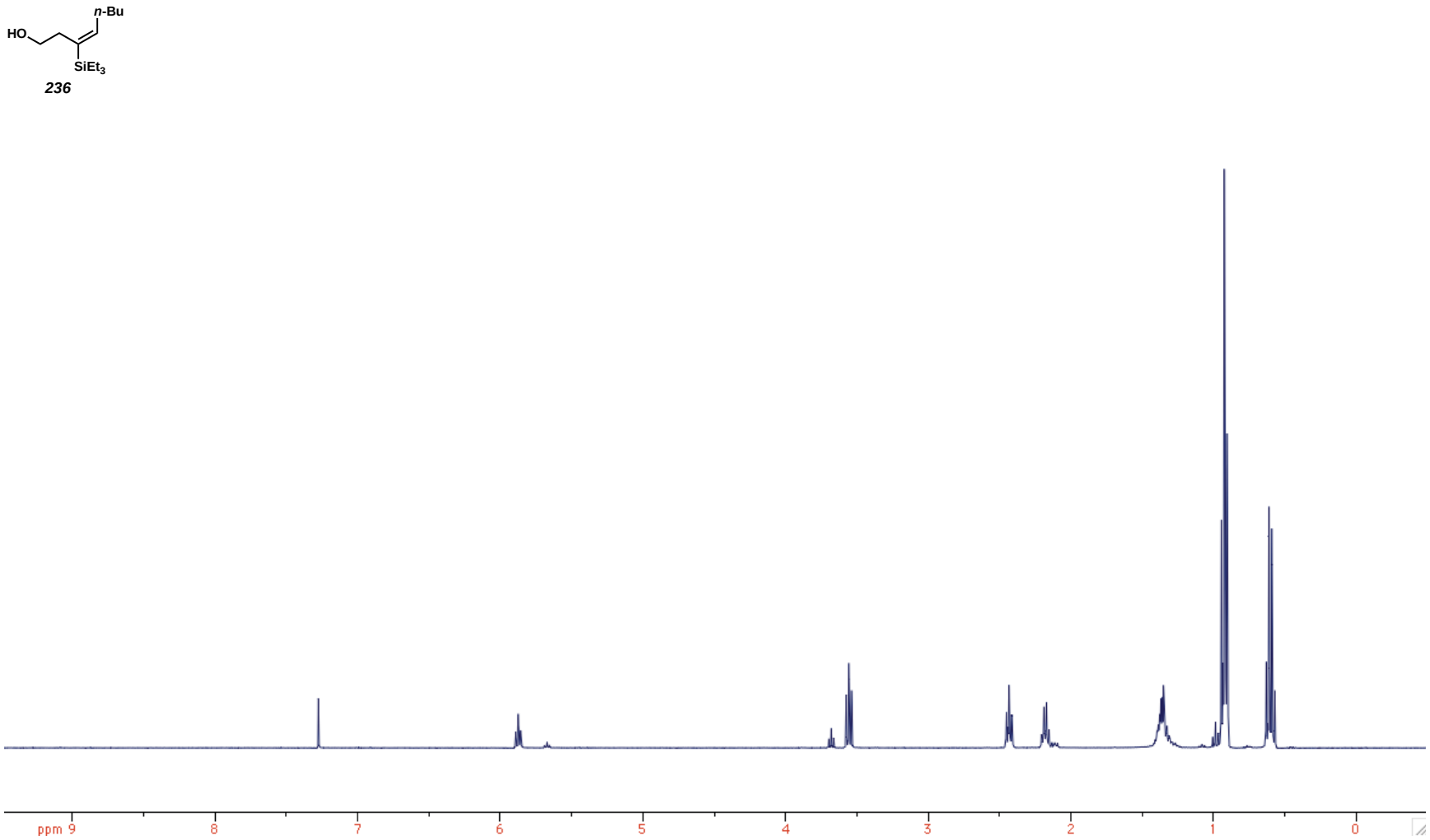
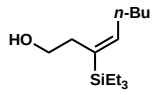


Figure A2.232 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **236**



236

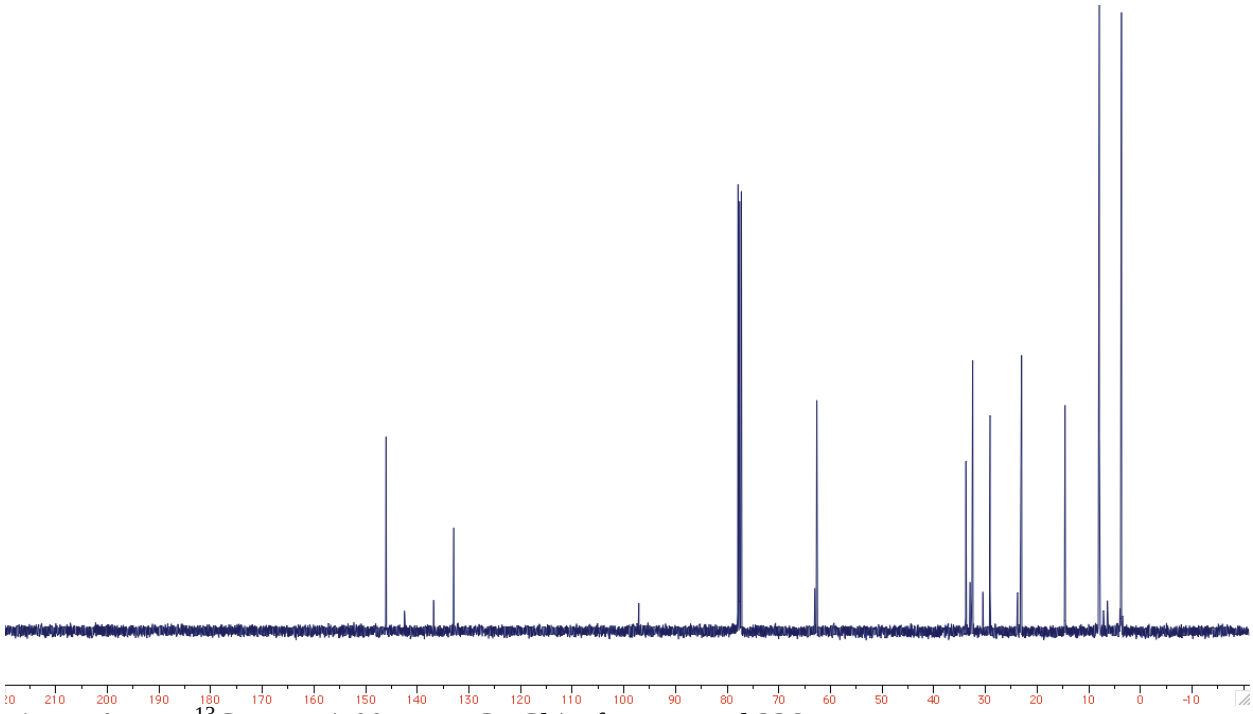


Figure A2.233 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **236**

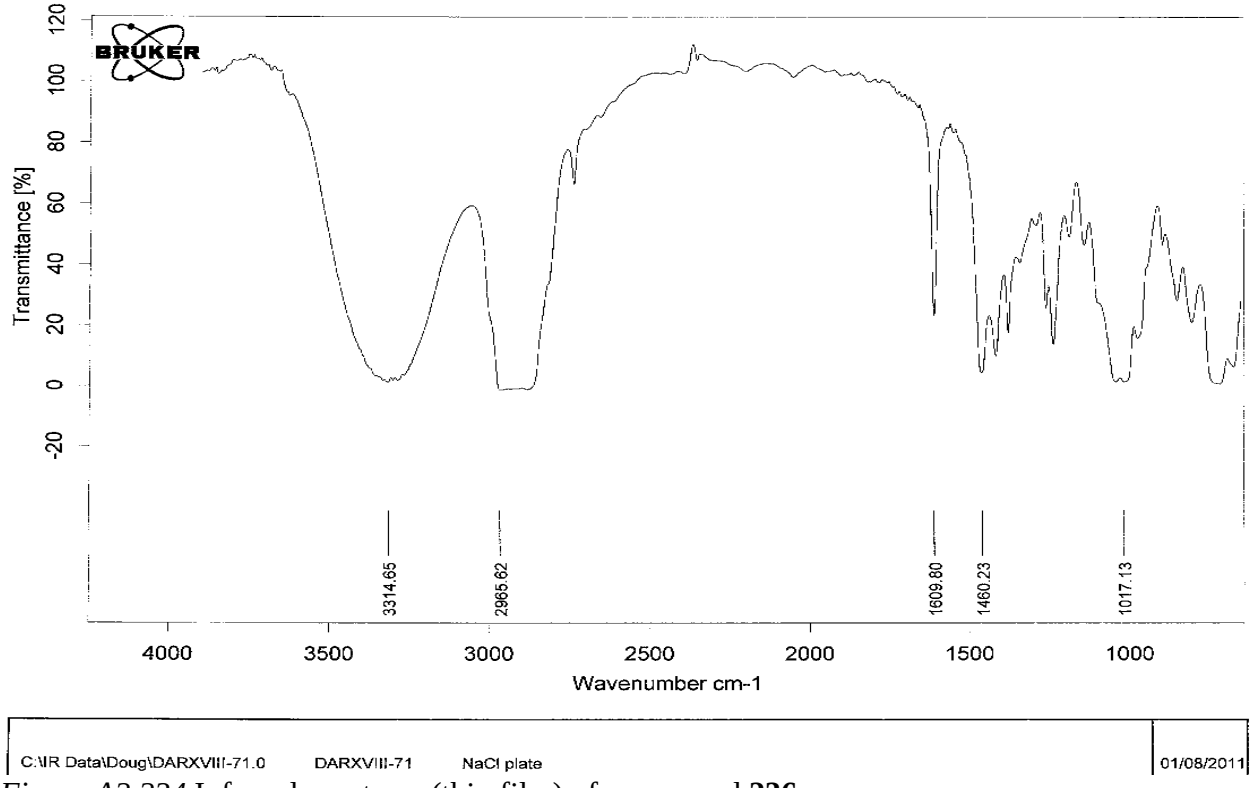
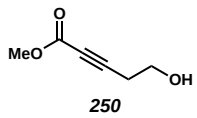


Figure A2.234 Infrared spectrum (thin film) of compound **236**



250

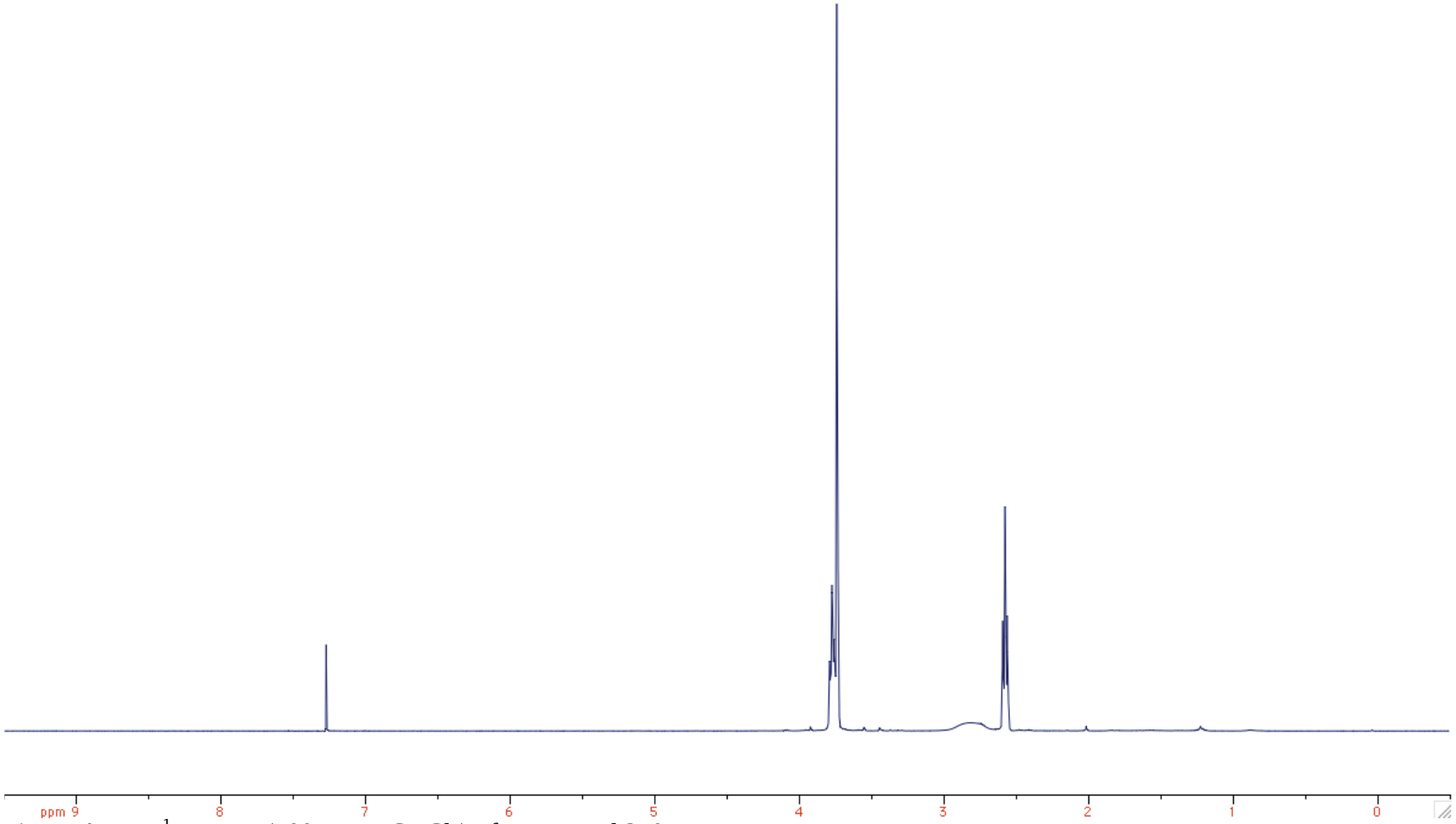


Figure A2.235 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **250**

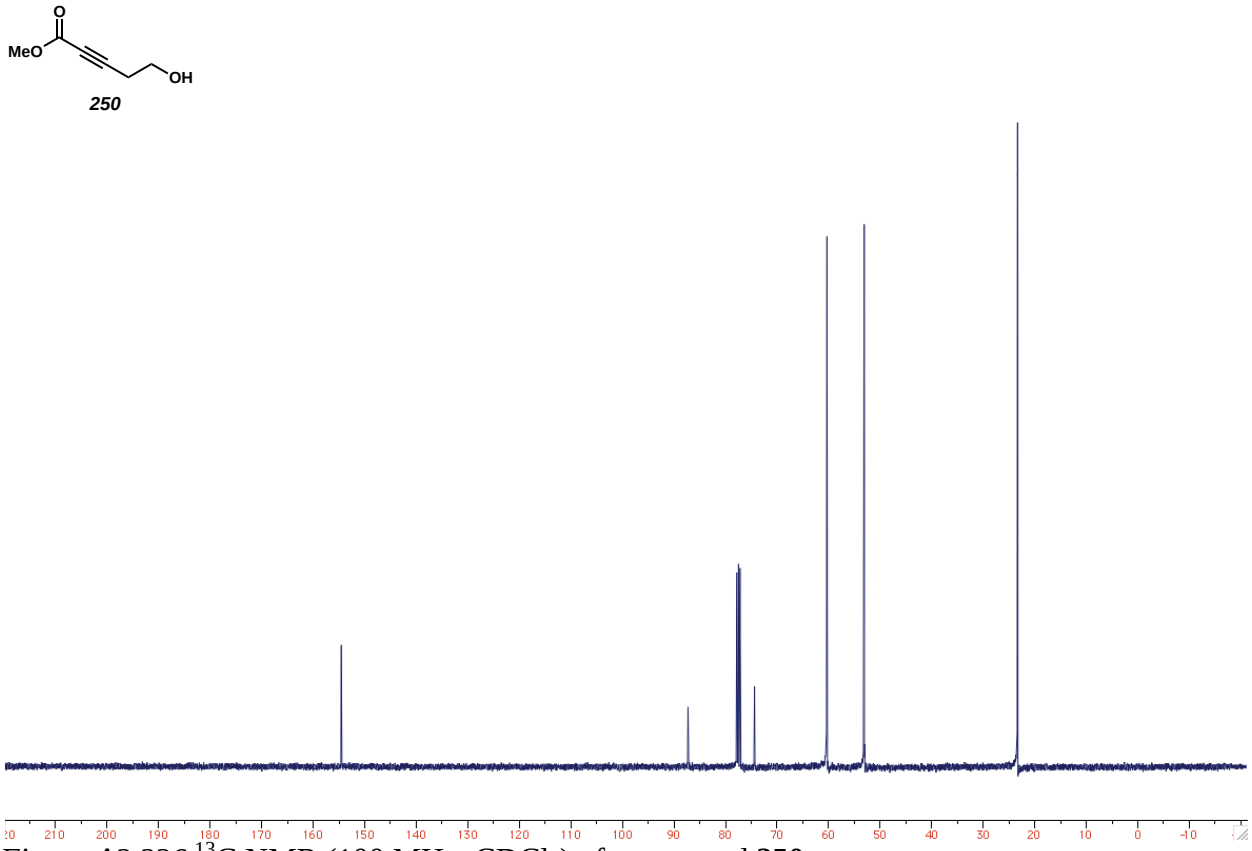


Figure A2.236 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **250**

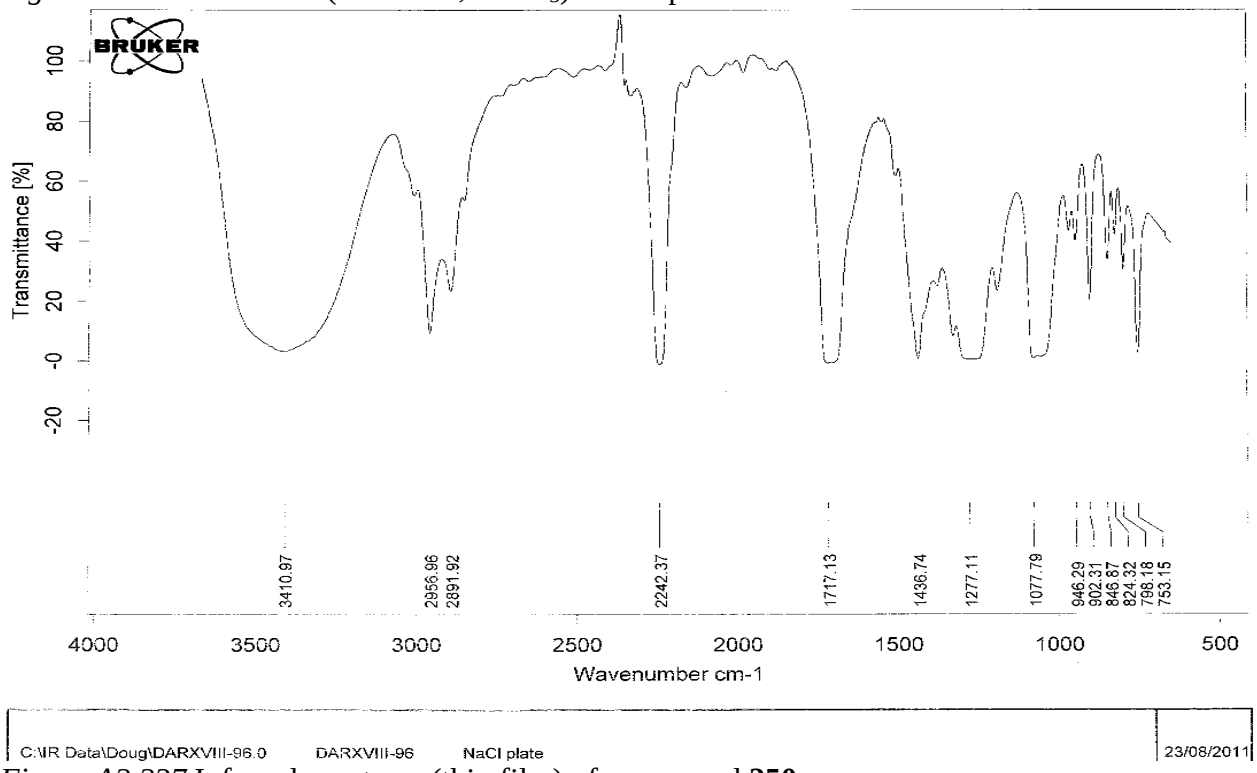
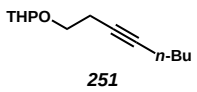


Figure A2.237 Infrared spectrum (thin film) of compound **250**



251

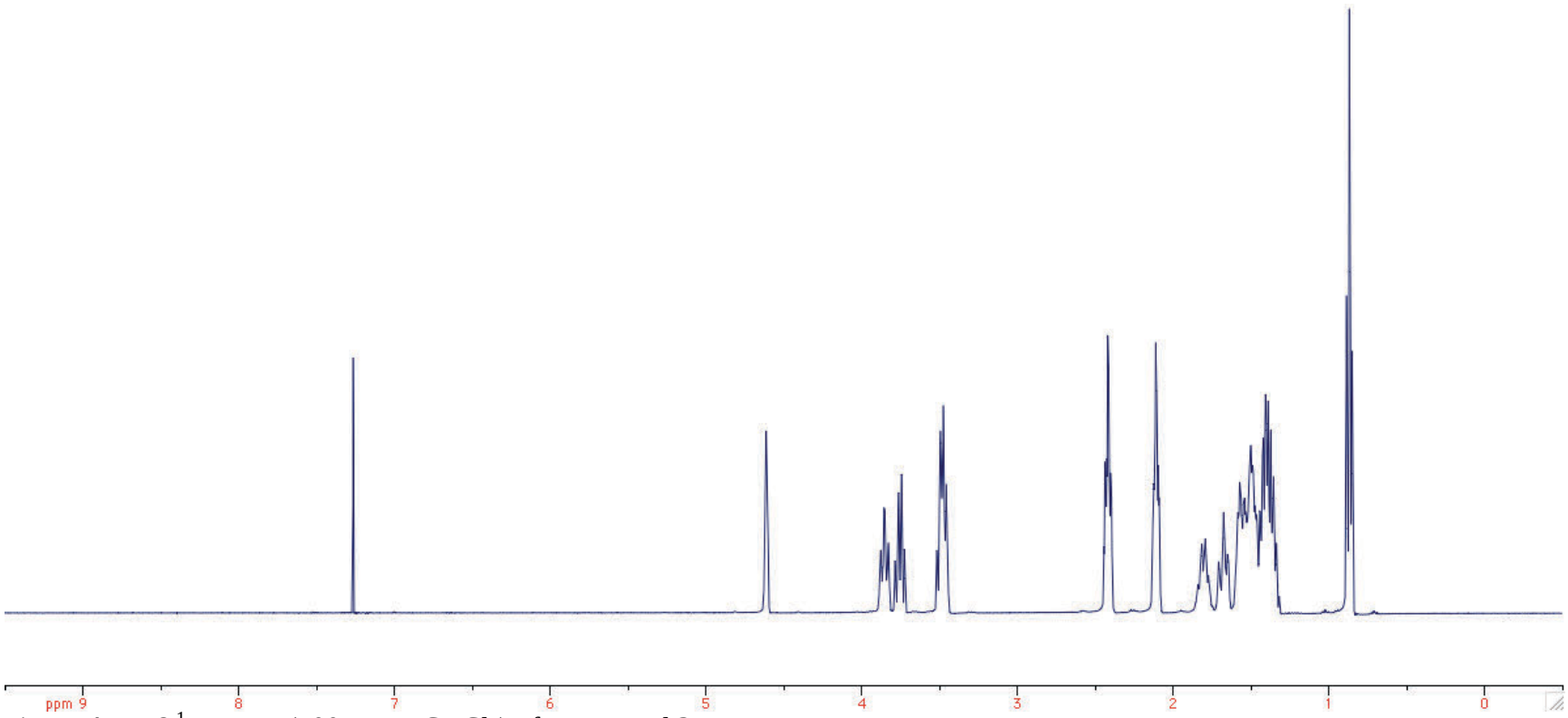
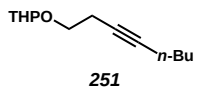


Figure A2.238 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **251**



251

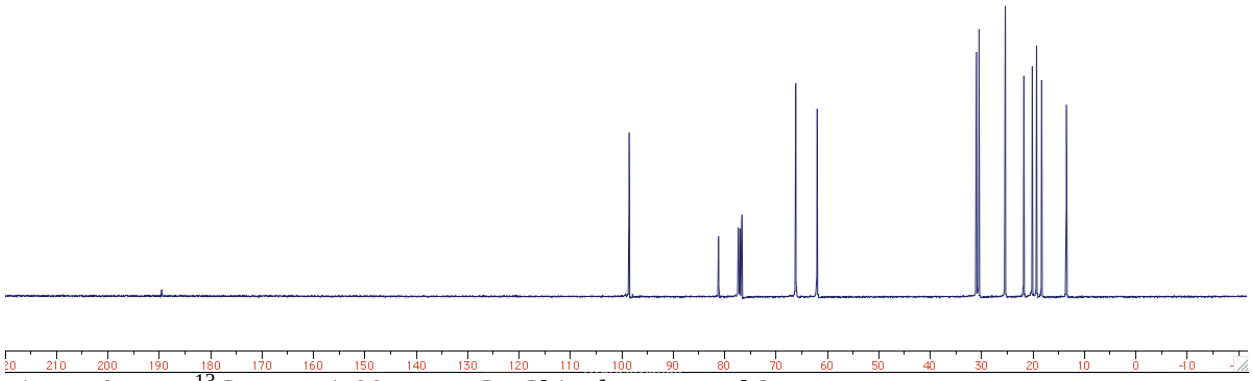


Figure A2.239 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **251**

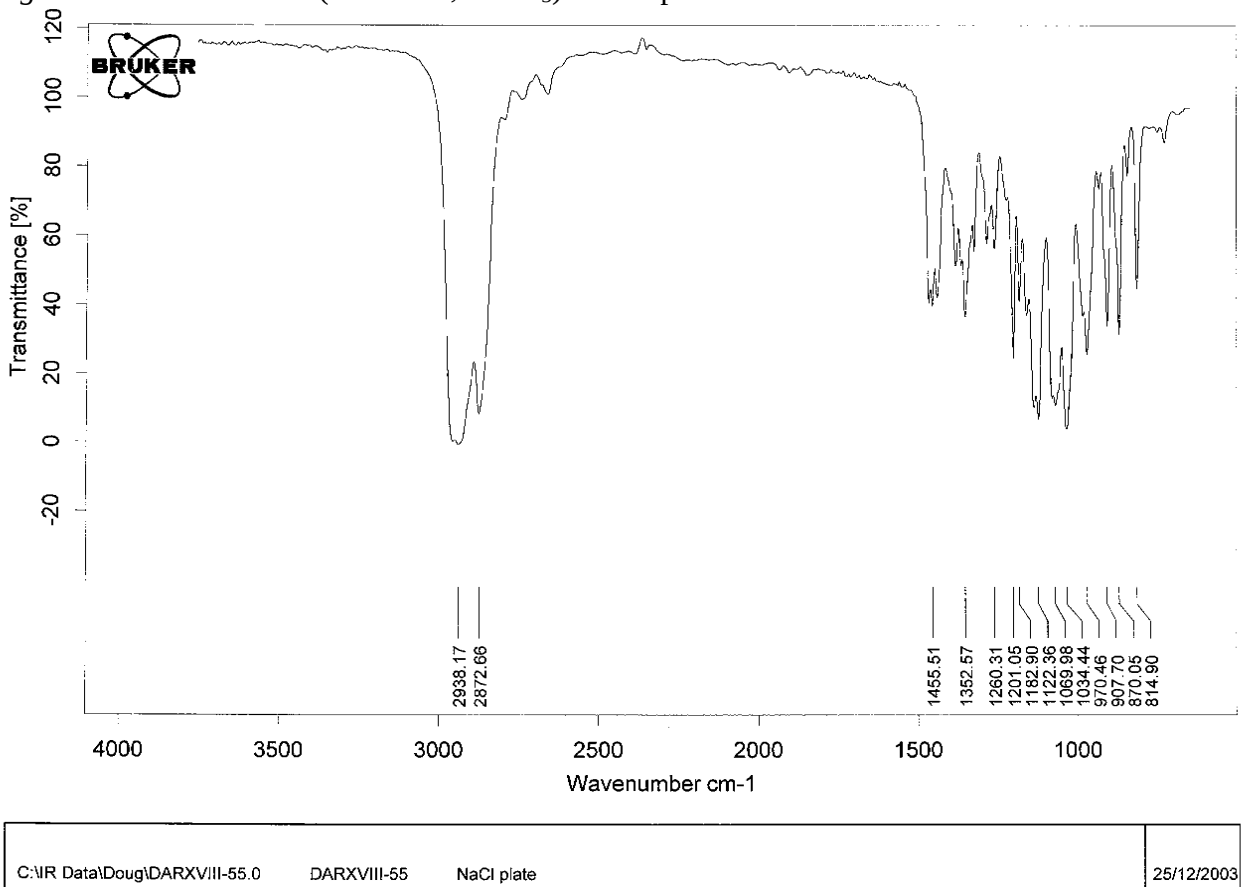


Figure A2.240 Infrared spectrum (thin film) of compound **251**

APPENDIX THREE

Spectra Relevant to Chapter Four:

The Utilization of Tri- and Tetrasubstituted Vinylsilanes for the Formation of Stereodefined All-Carbon Alkenes

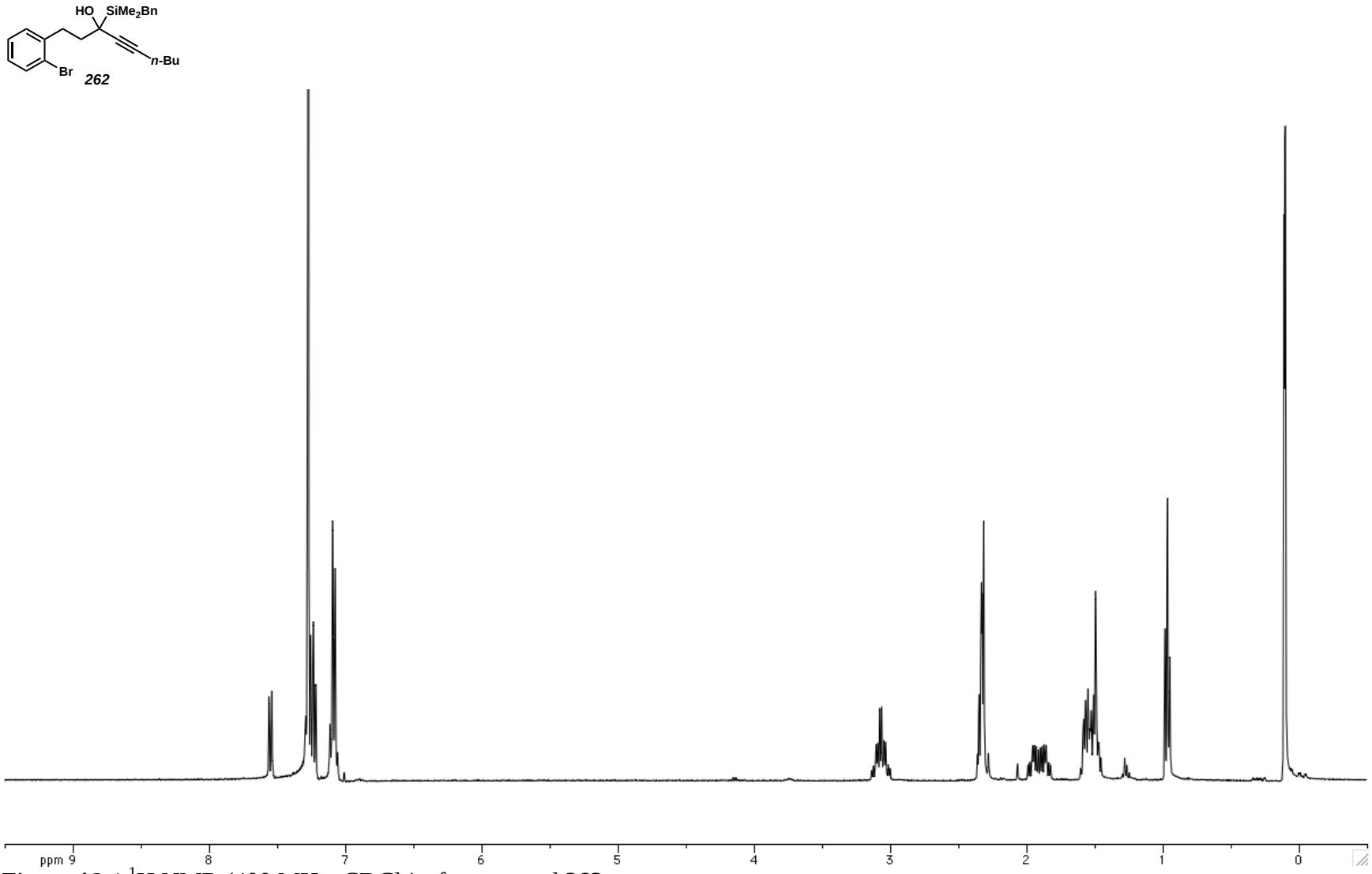
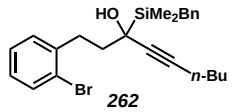


Figure A3.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **262**



262

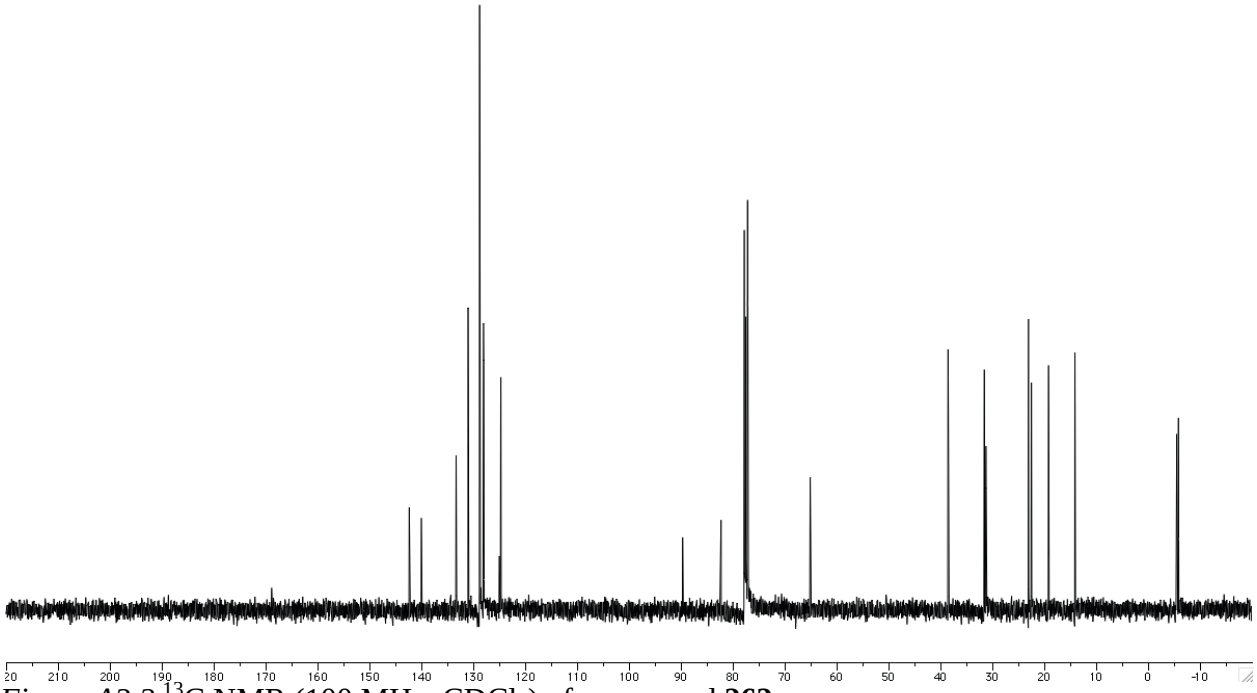


Figure A3.2 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **262**

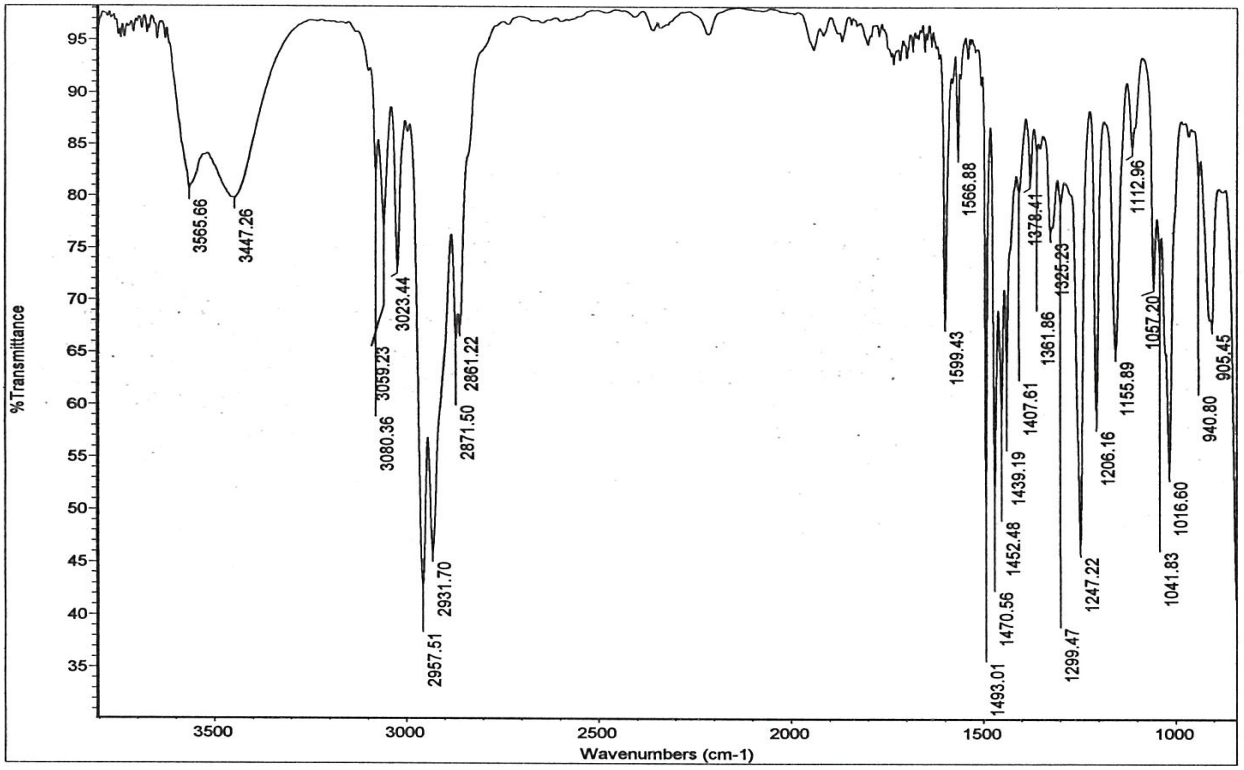
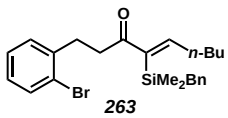


Figure A3.3 Infrared spectrum (thin film) of compound **262**



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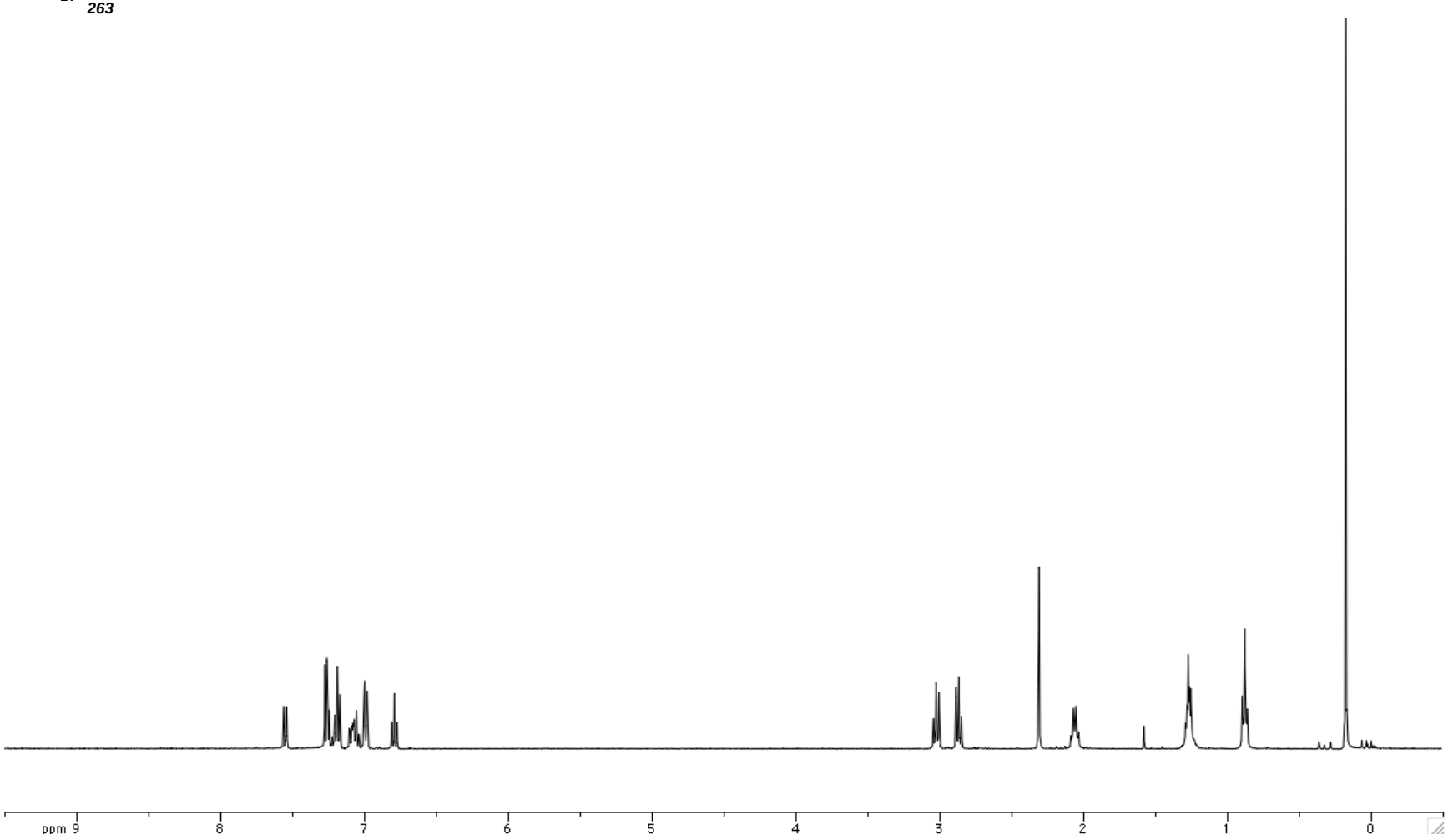
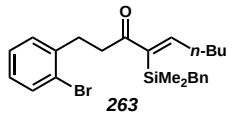


Figure A3.4 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **263**



263

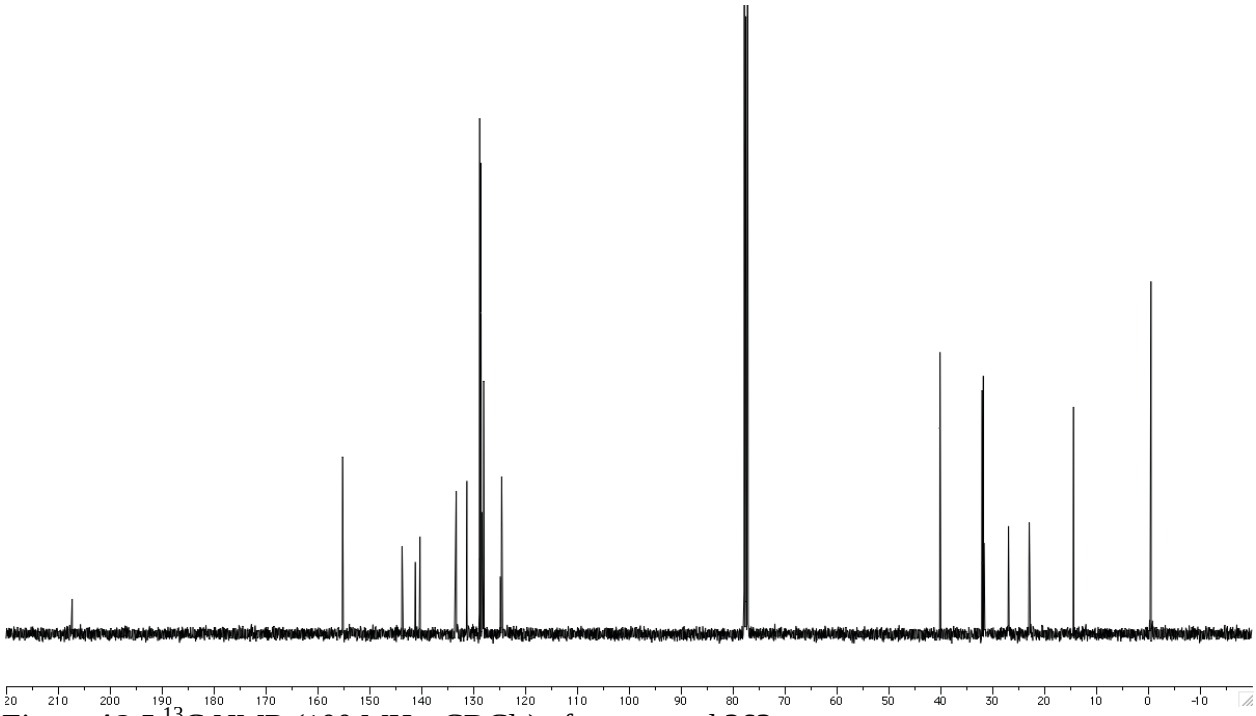


Figure A3.5 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **263**

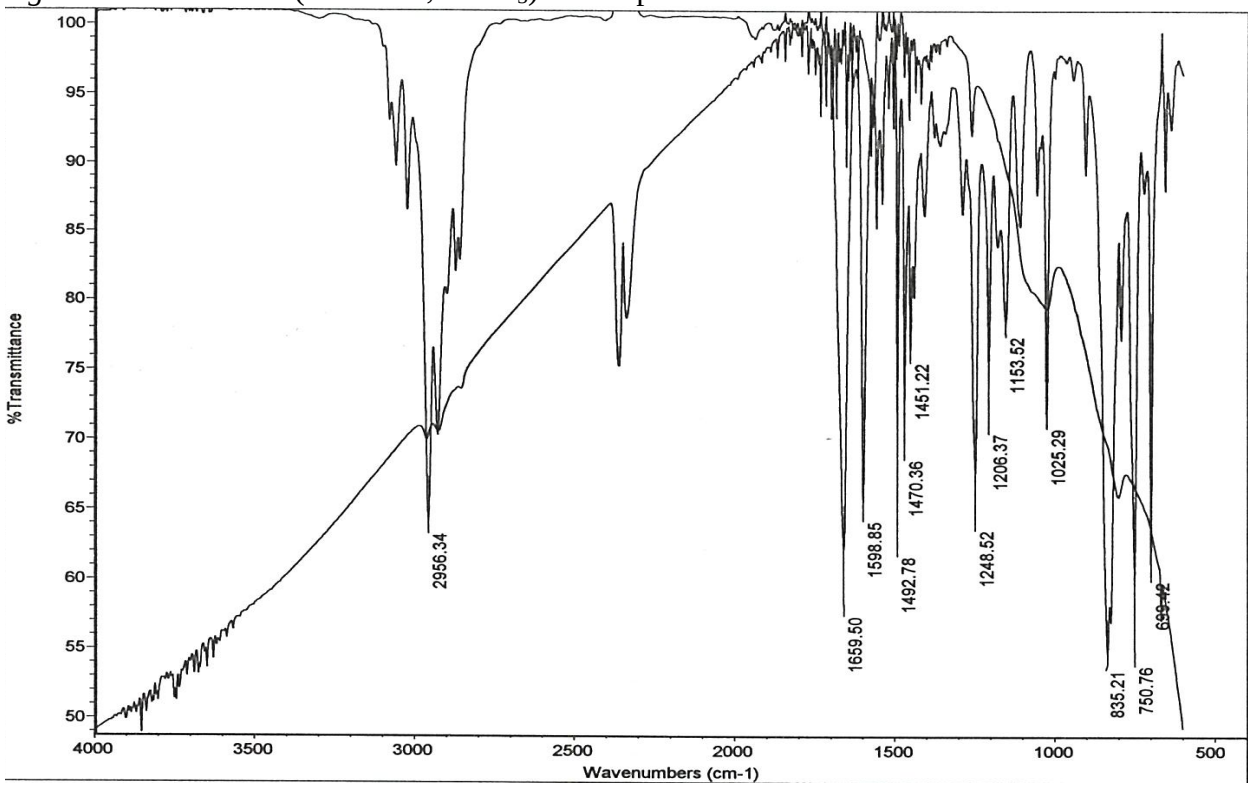
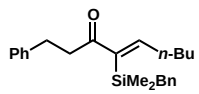


Figure A3.6 Infrared spectrum (thin film) of compound **263**



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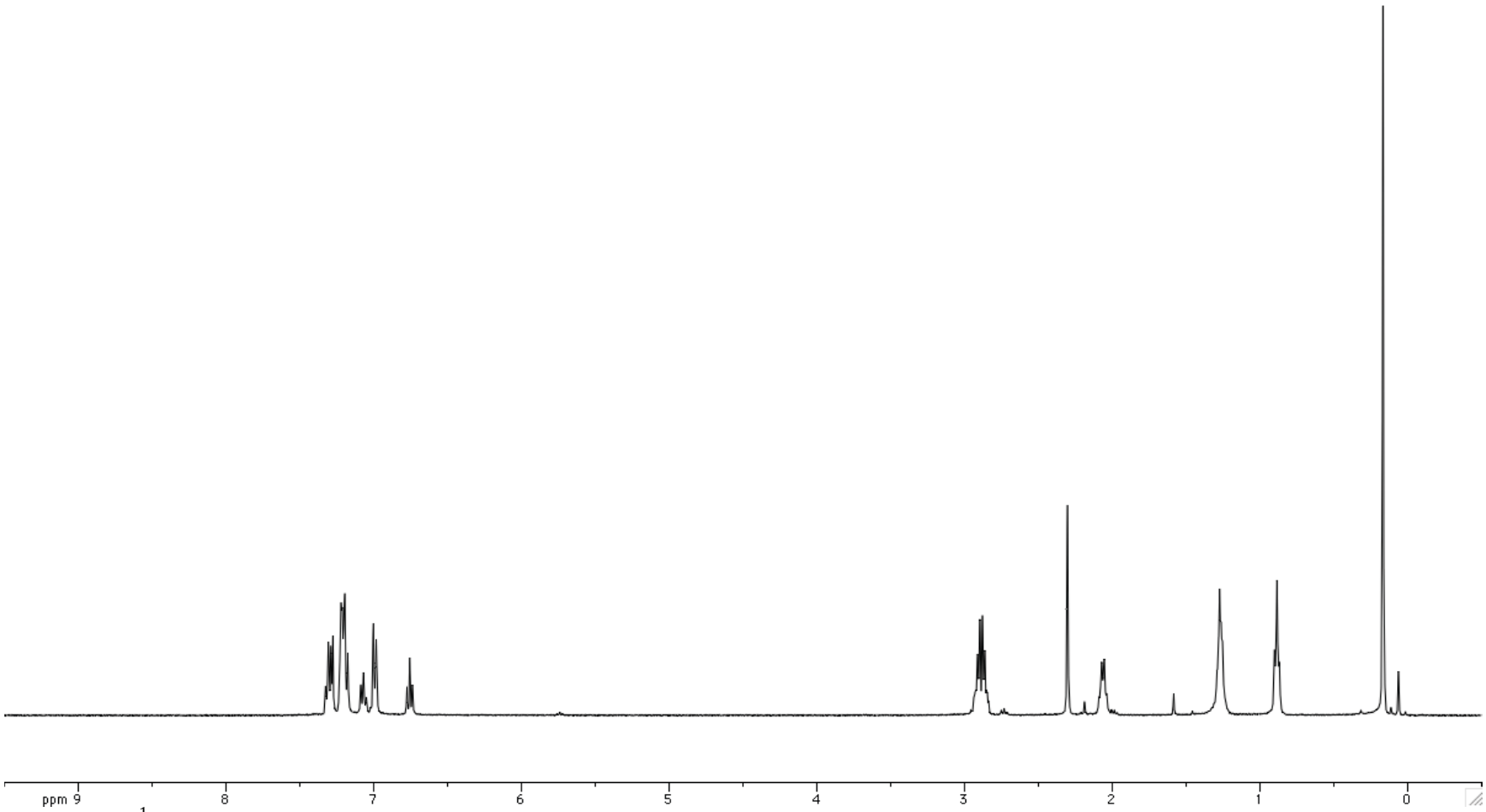


Figure A3.7 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **271**

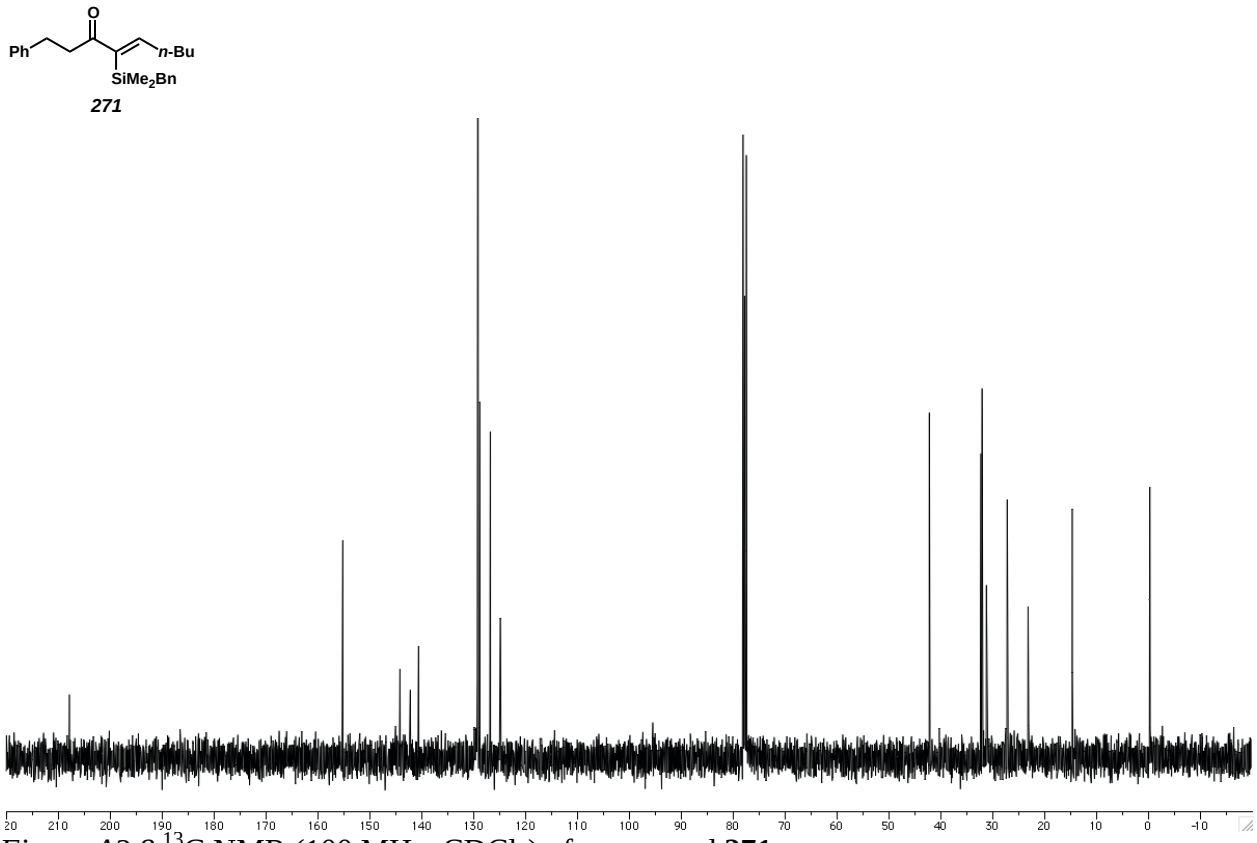


Figure A3.8 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **271**

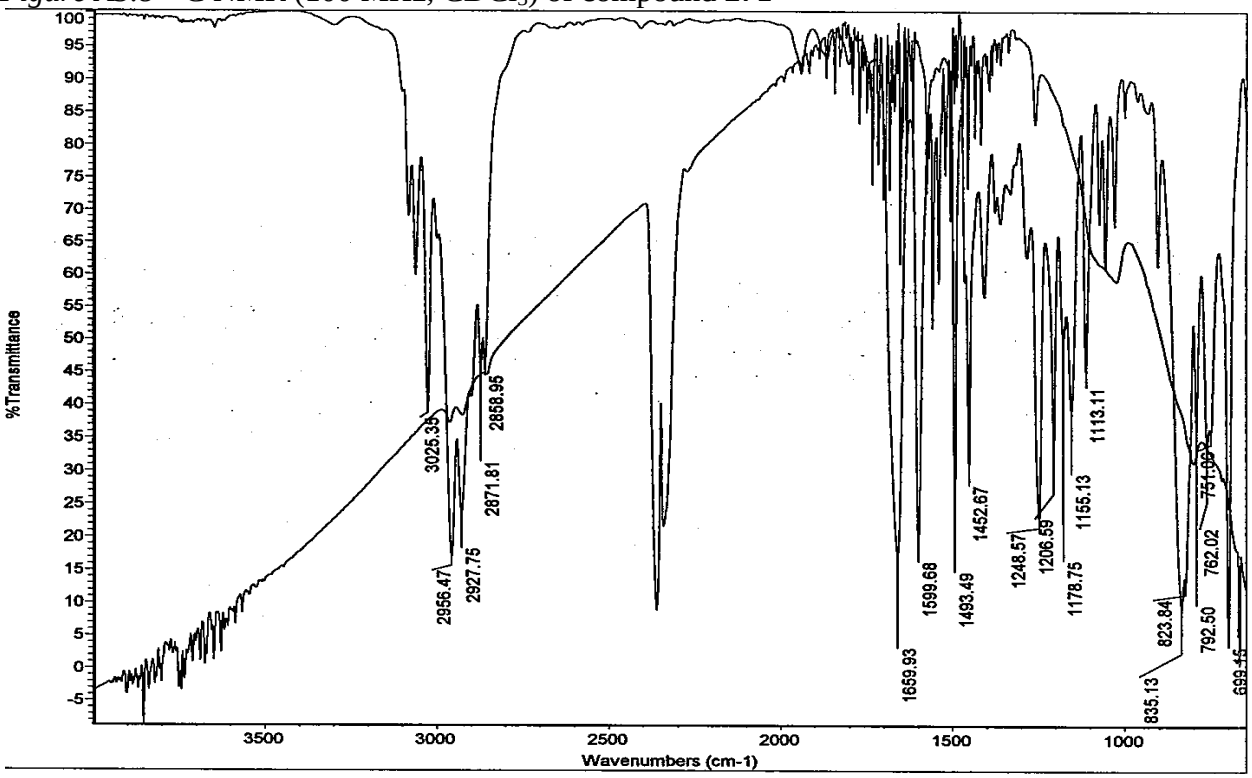
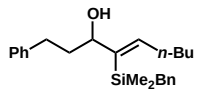


Figure A3.9 Infrared spectrum (thin film) of compound **271**



267

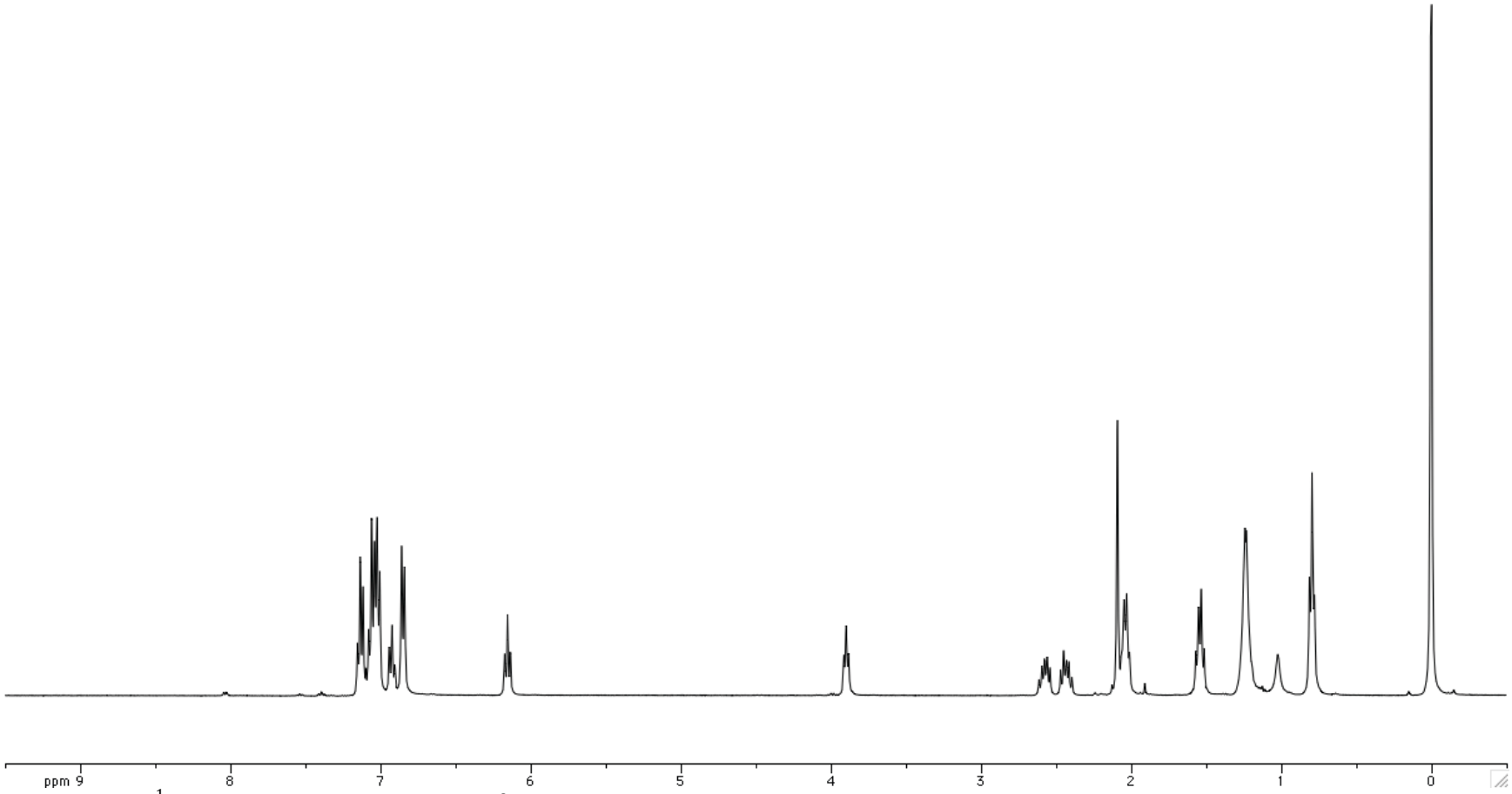


Figure A3.10 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **267**

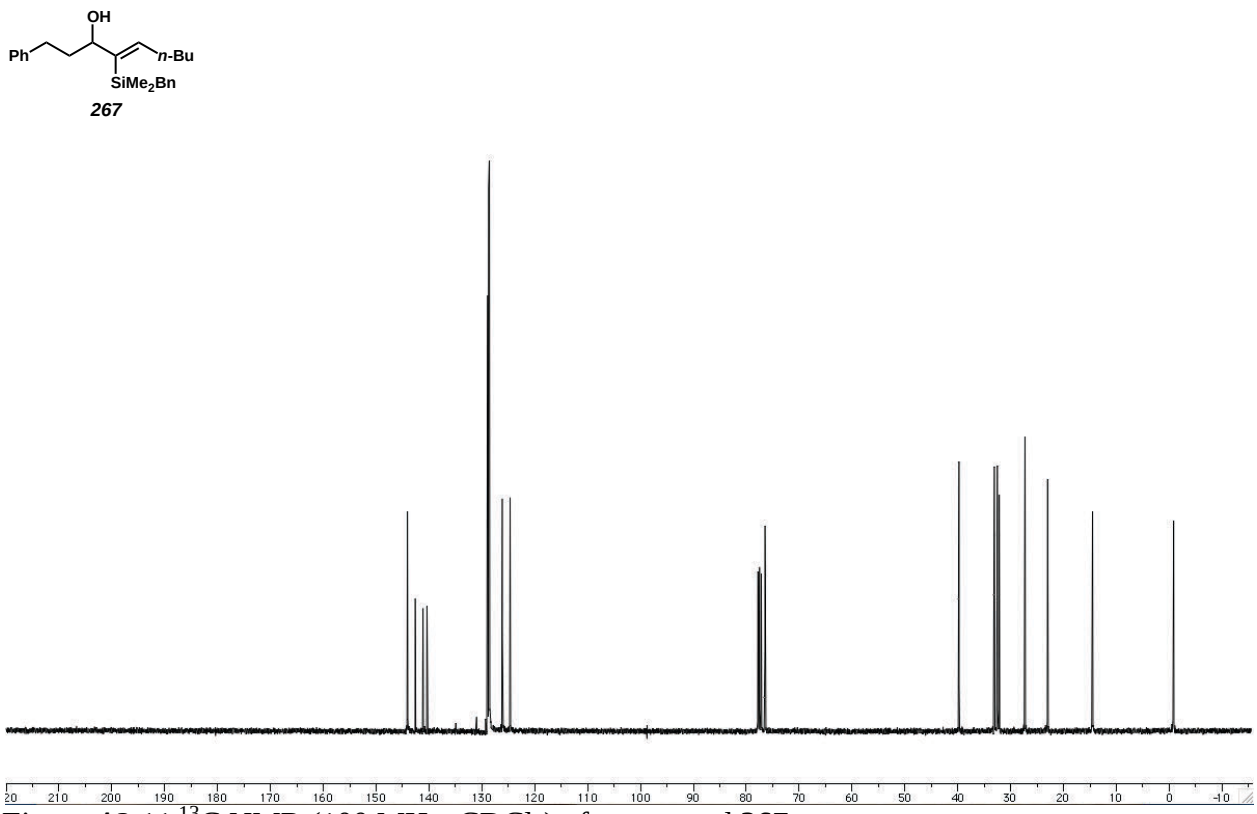


Figure A3.11 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **267**

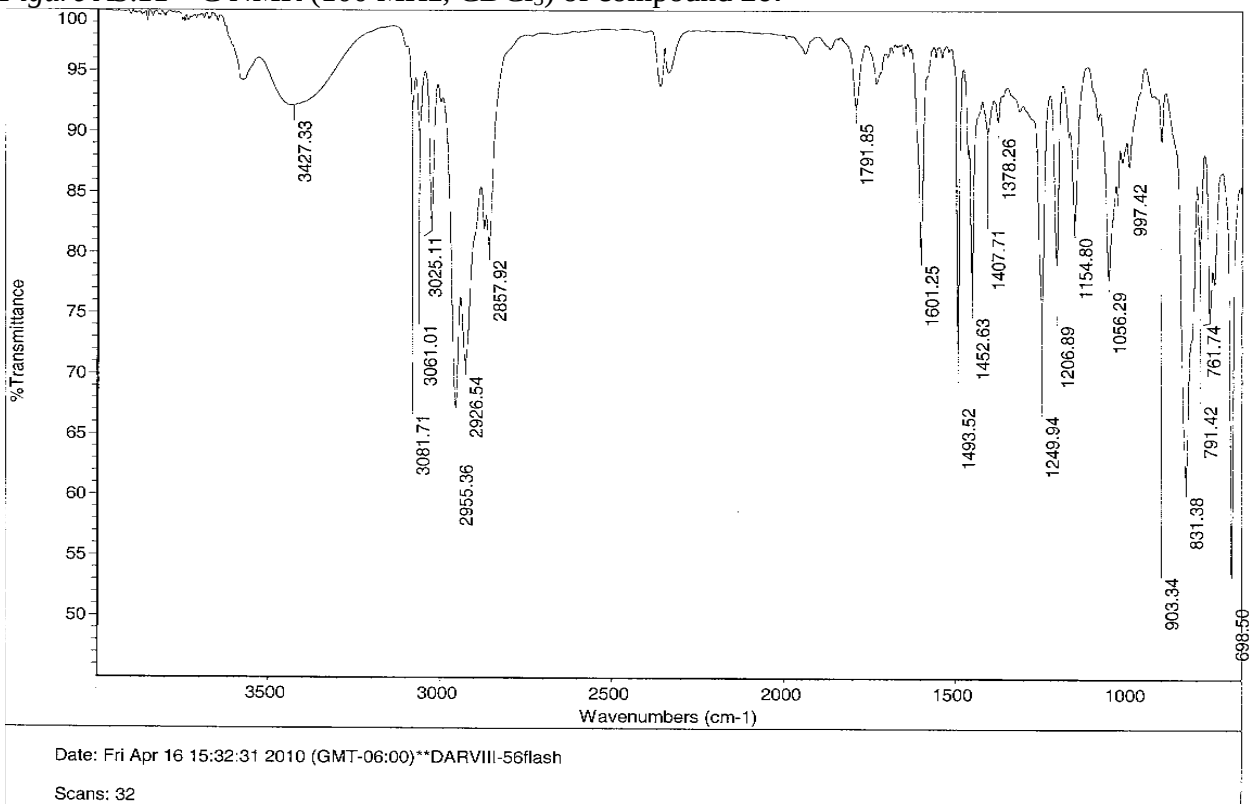
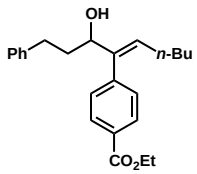


Figure A3.12 Infrared spectrum (thin film) of compound **267**



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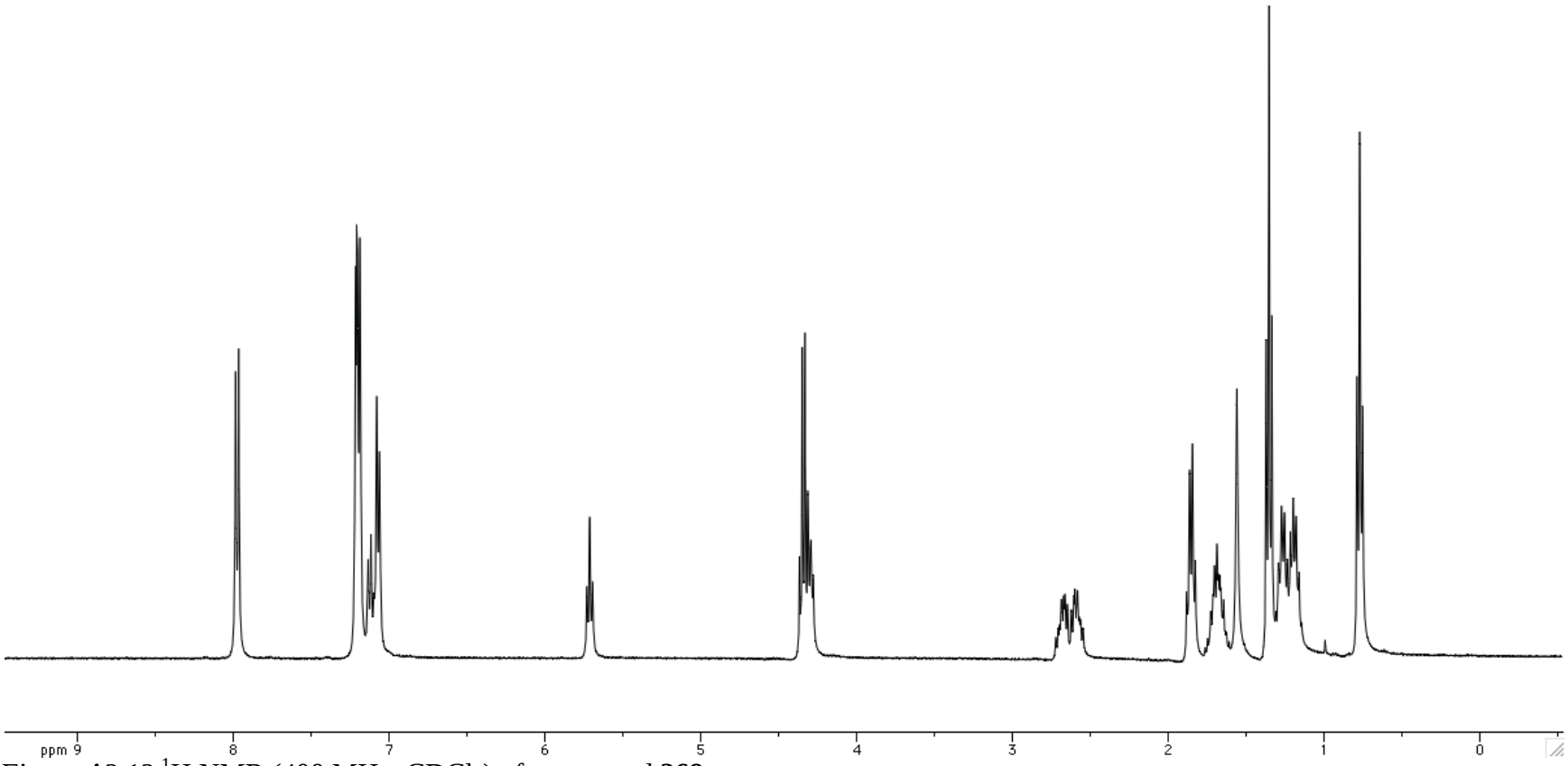


Figure A3.13 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **268**

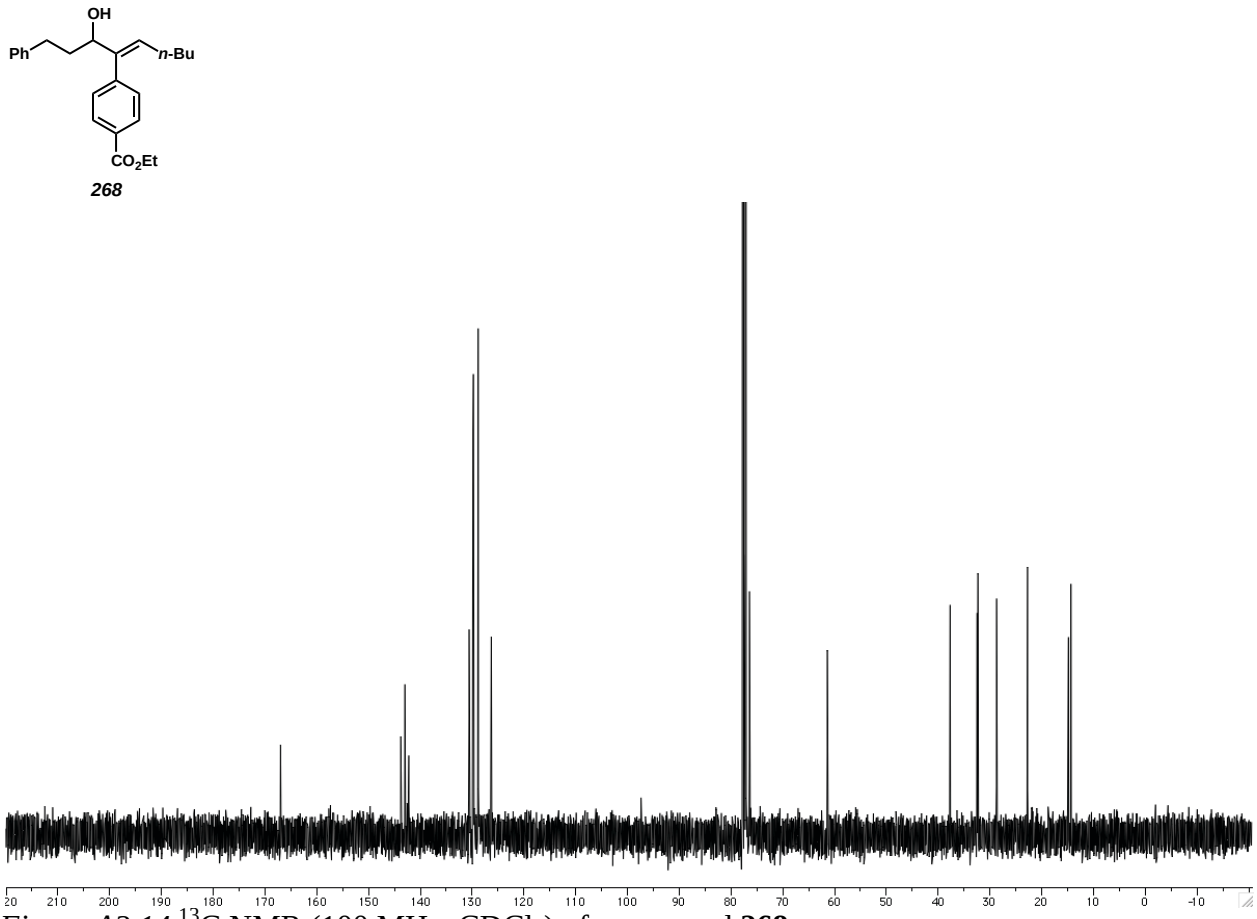


Figure A3.14 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **268**

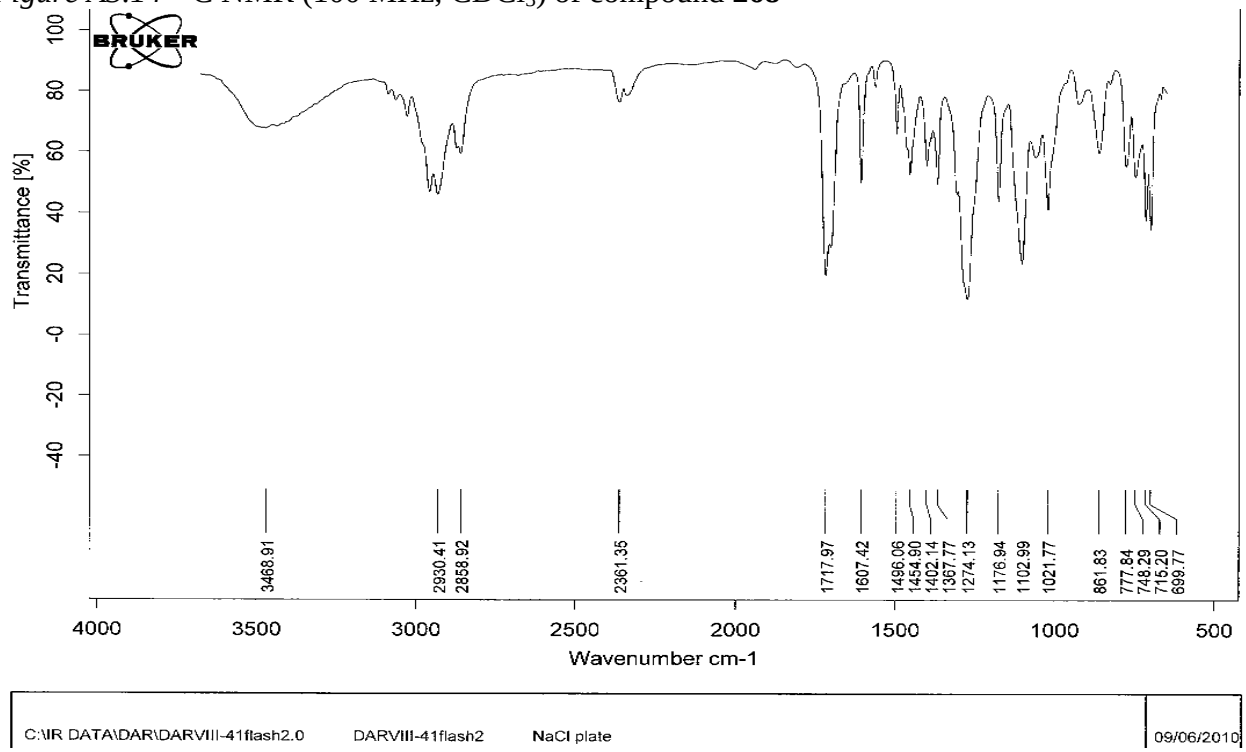
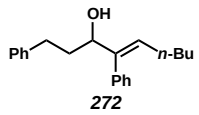


Figure A3.15 Infrared spectrum (thin film) of compound **268**



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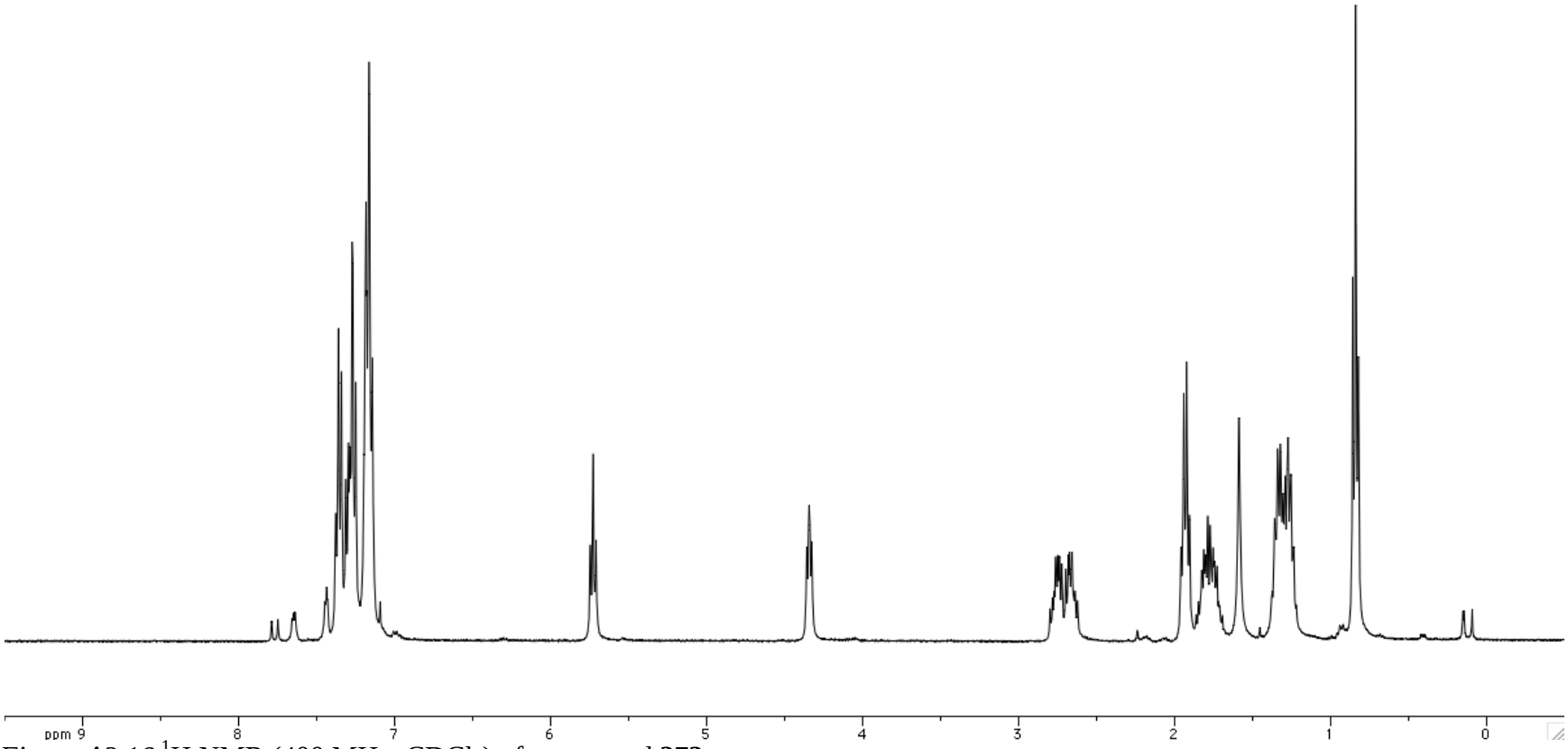


Figure A3.16 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **272**

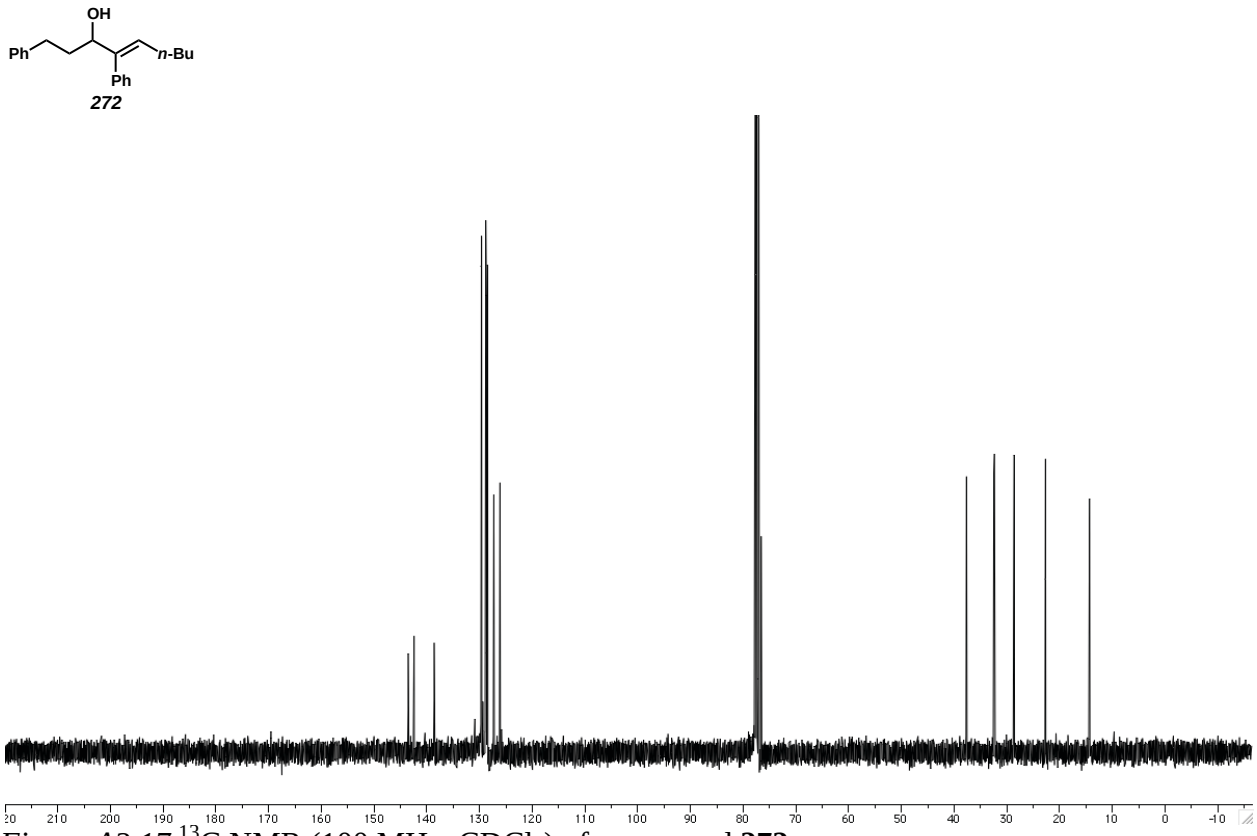


Figure A3.17 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **272**

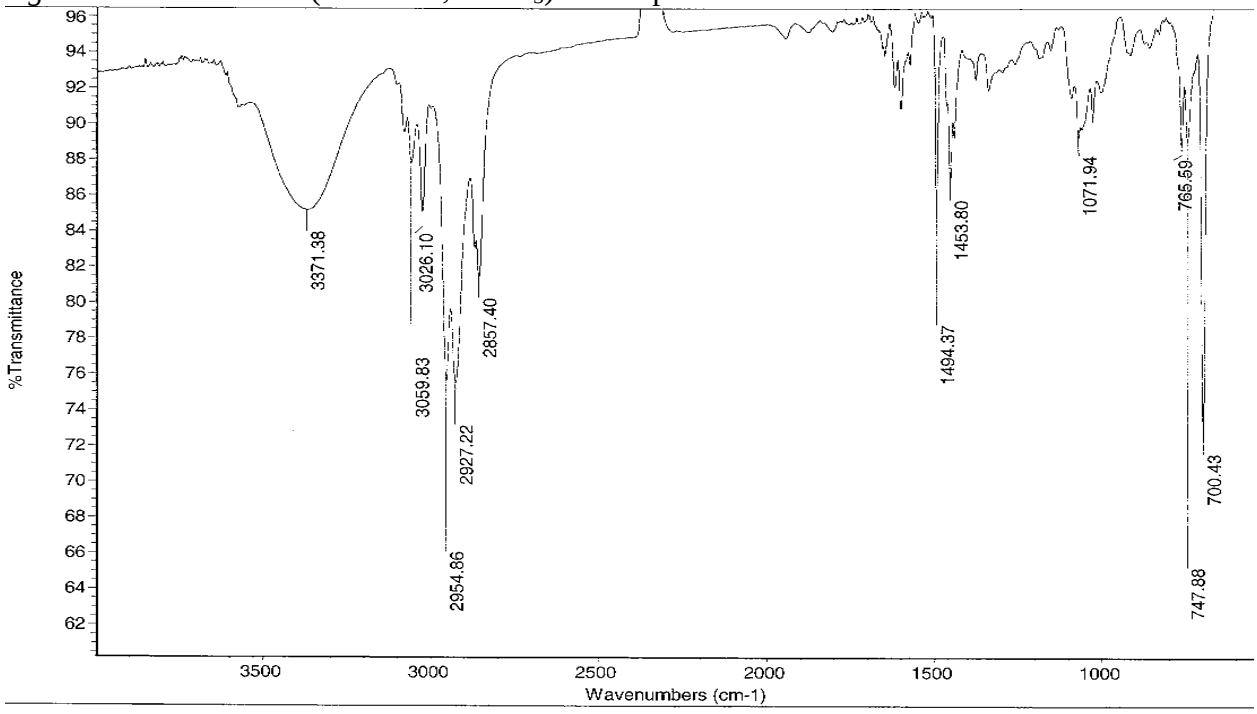
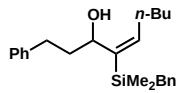


Figure A3.18 Infrared spectrum (thin film) of compound **272**



283

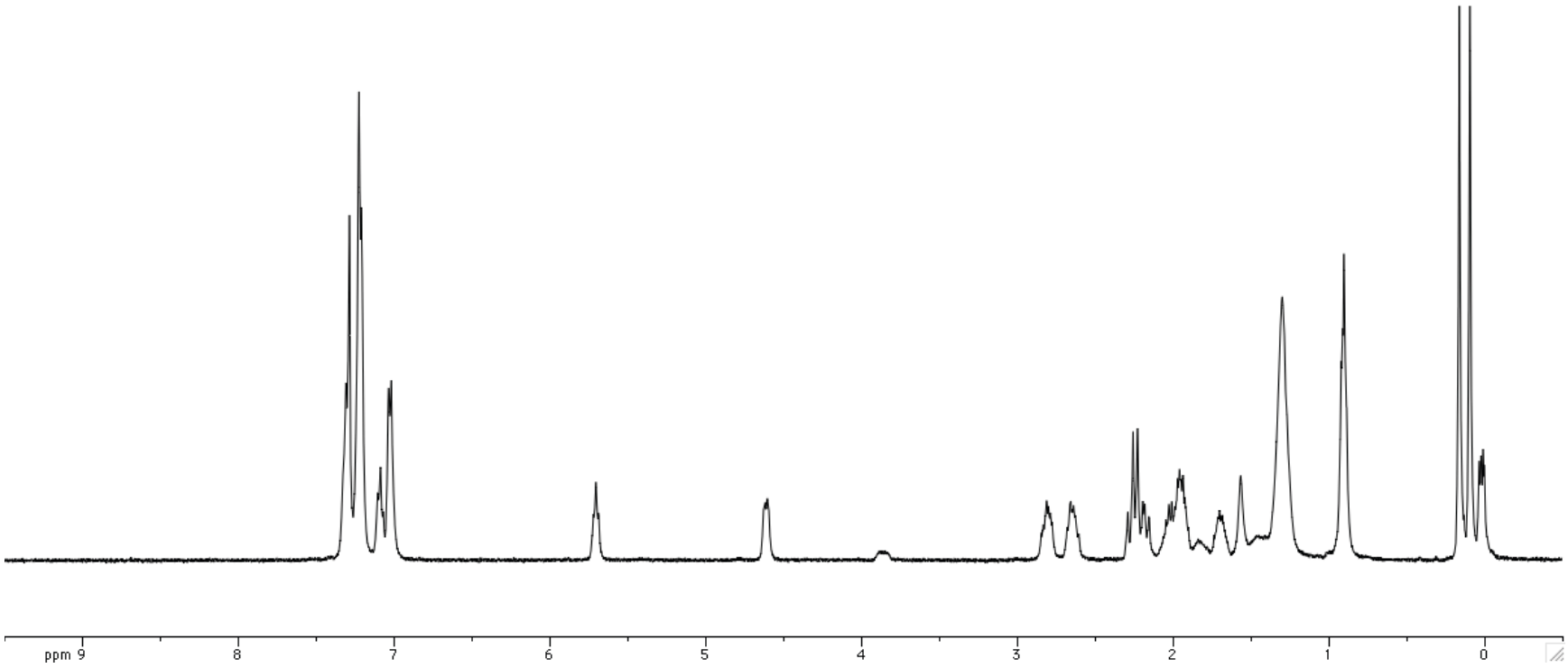
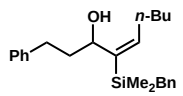


Figure A3.19 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **283**



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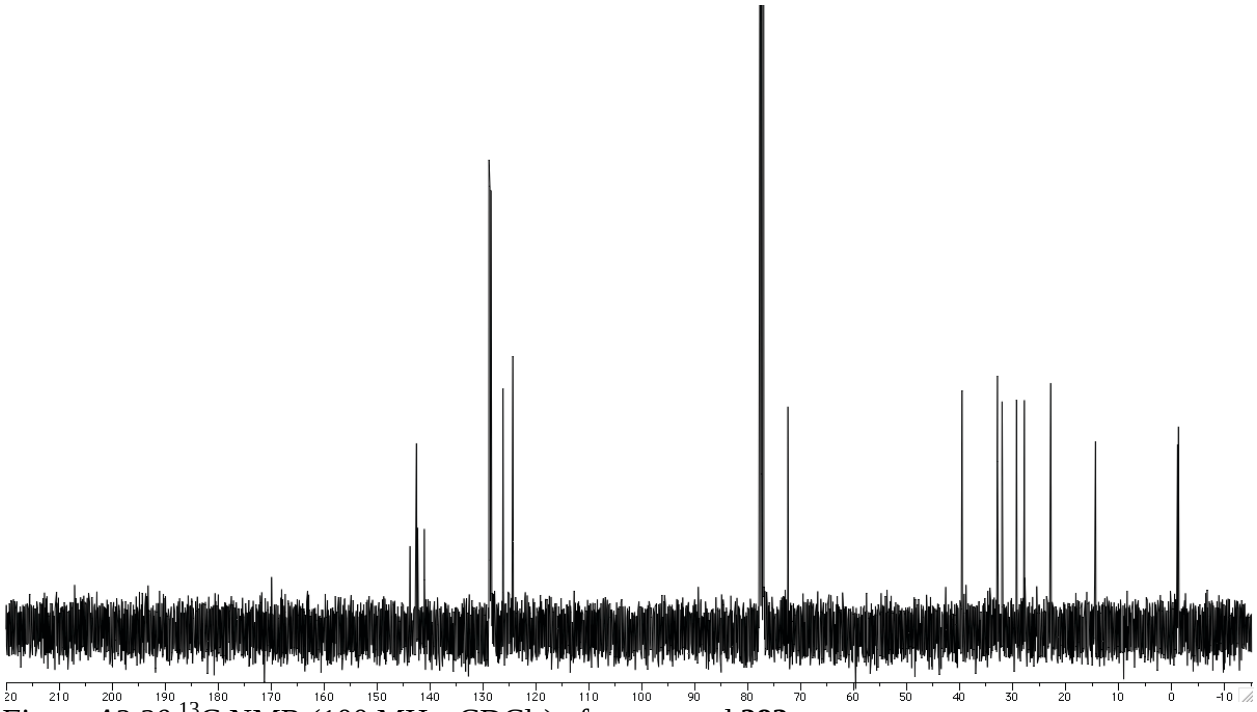


Figure A3.20 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **283**

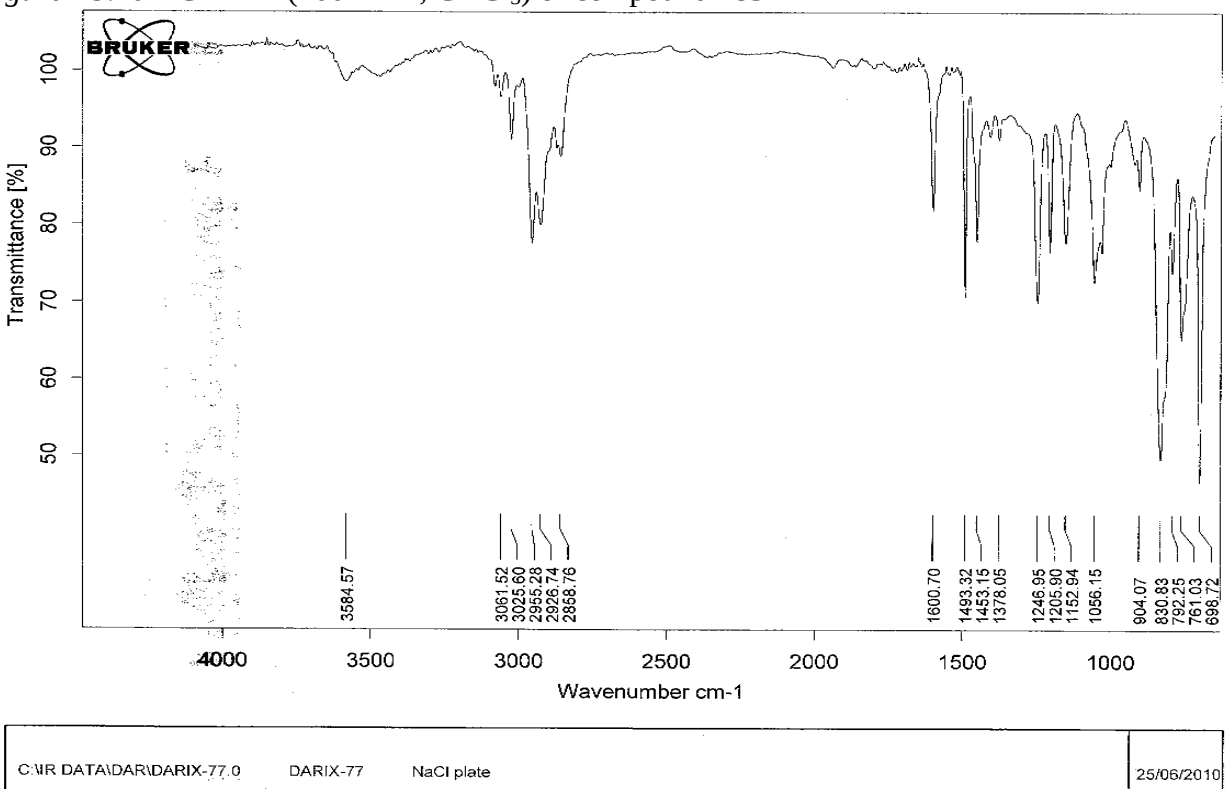
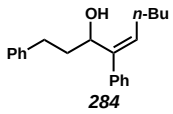


Figure A3.21 Infrared spectrum (thin film) of compound **283**



284

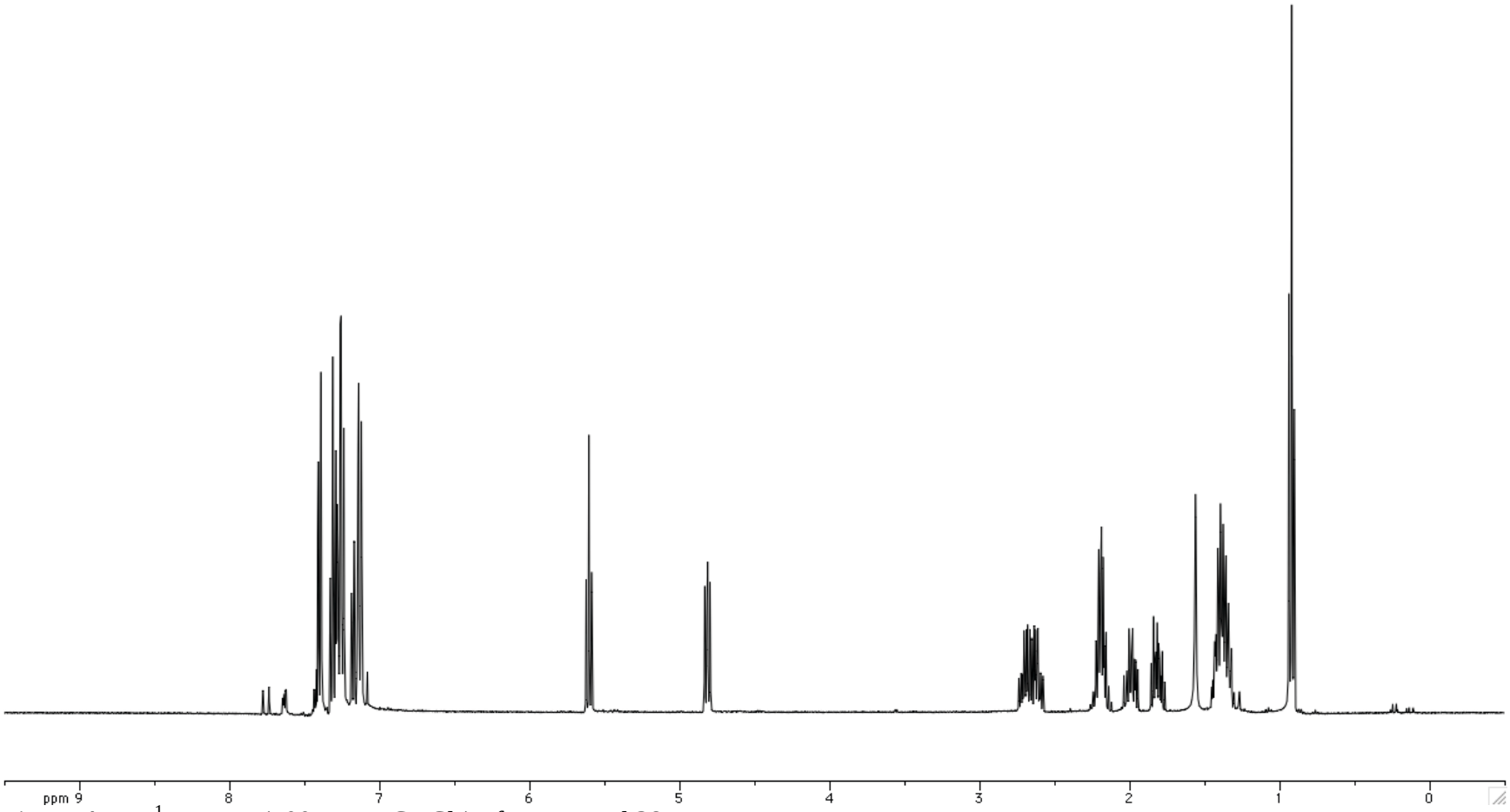


Figure A3.22 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **284**

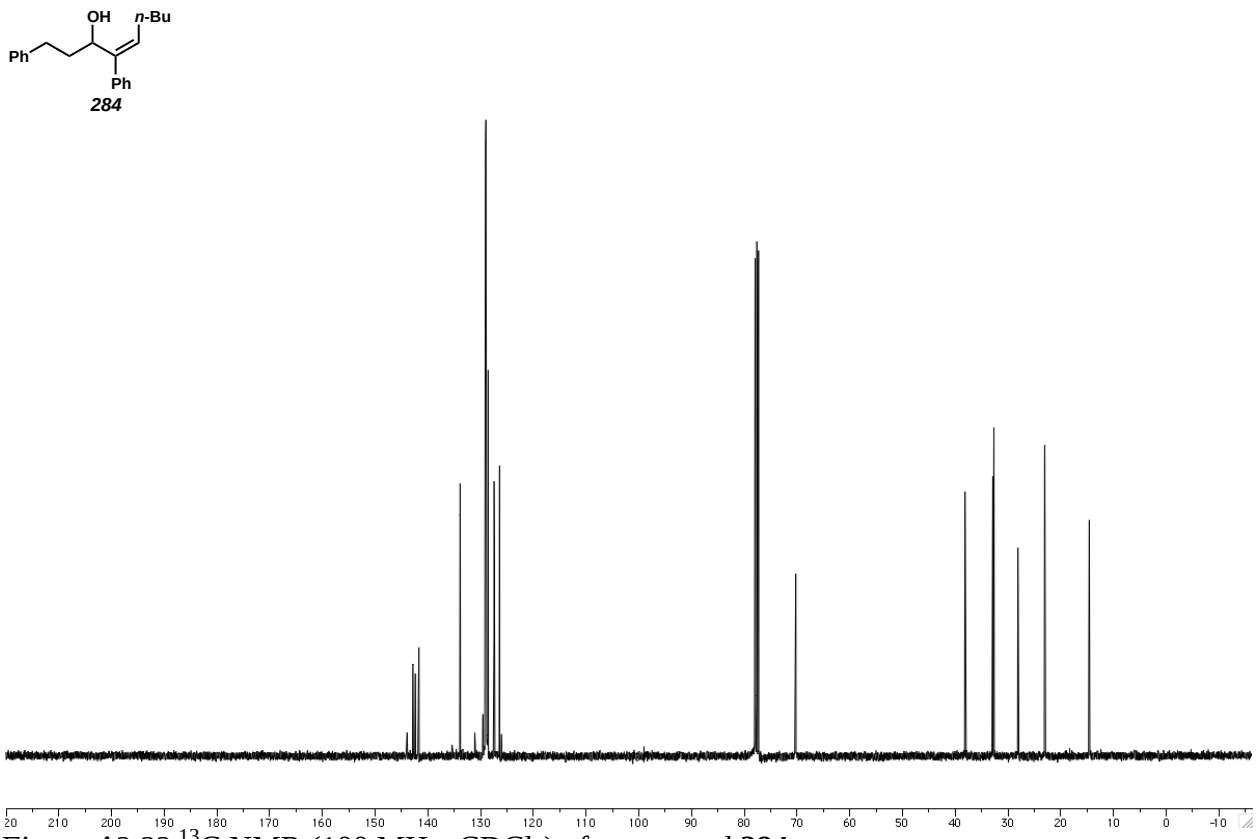


Figure A3.23 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **284**

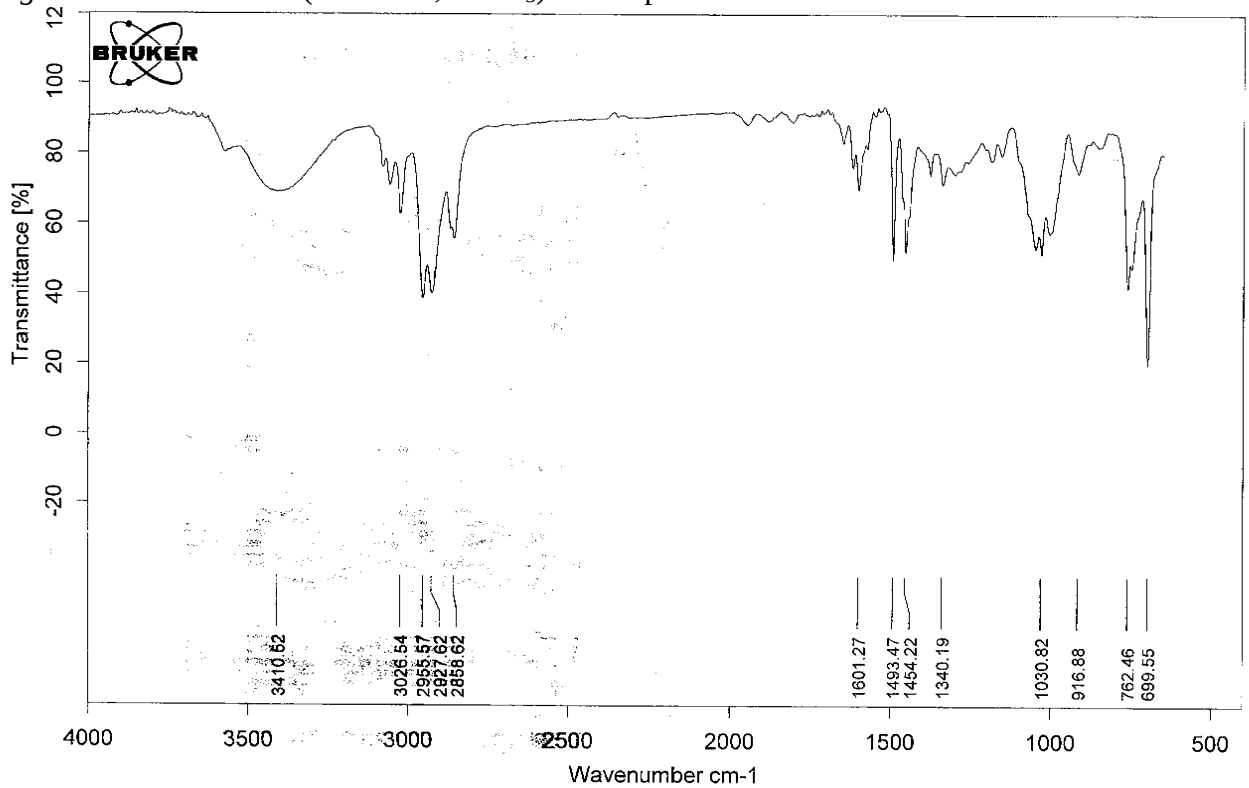
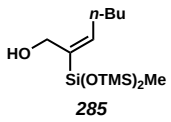


Figure A3.24 Infrared spectrum (thin film) of compound **284**



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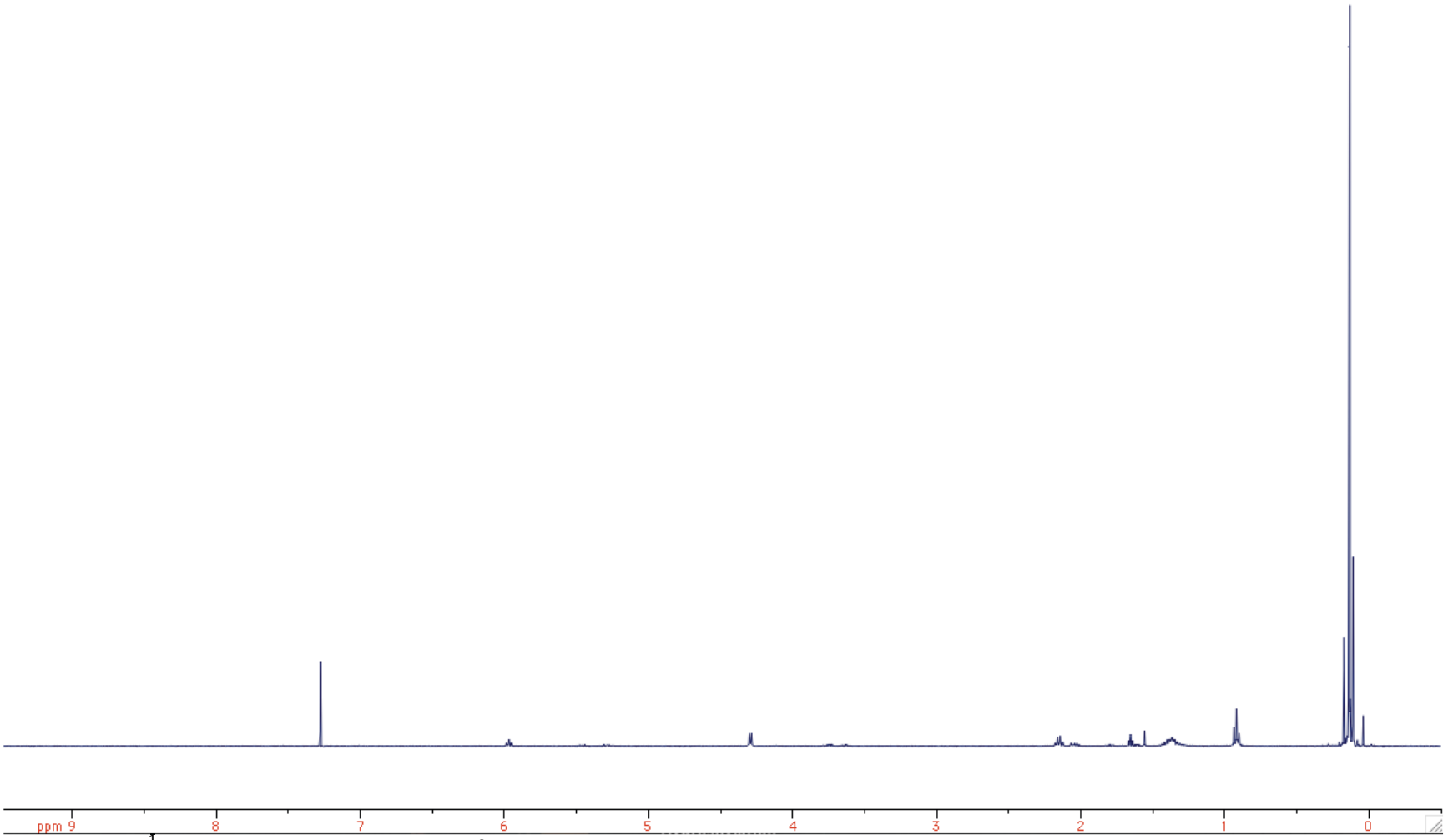


Figure A3.25 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **285**

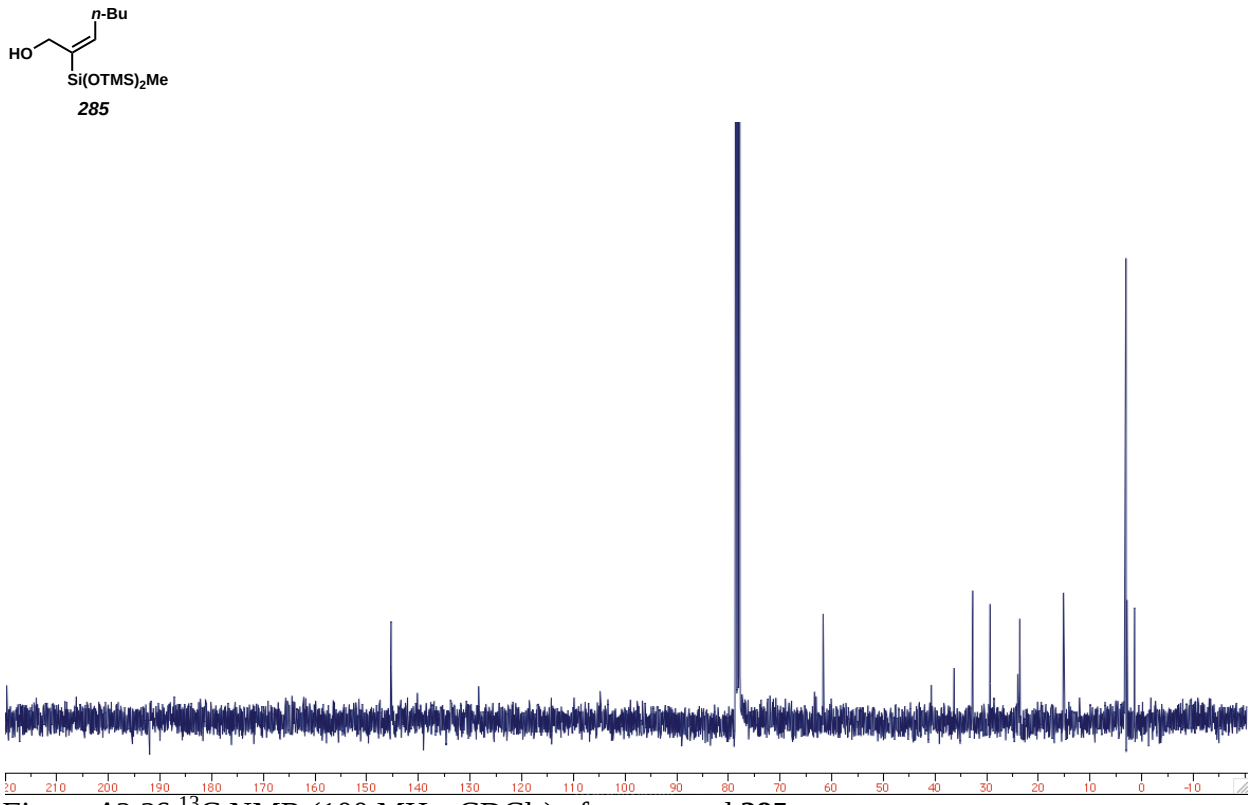


Figure A3.26 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **285**

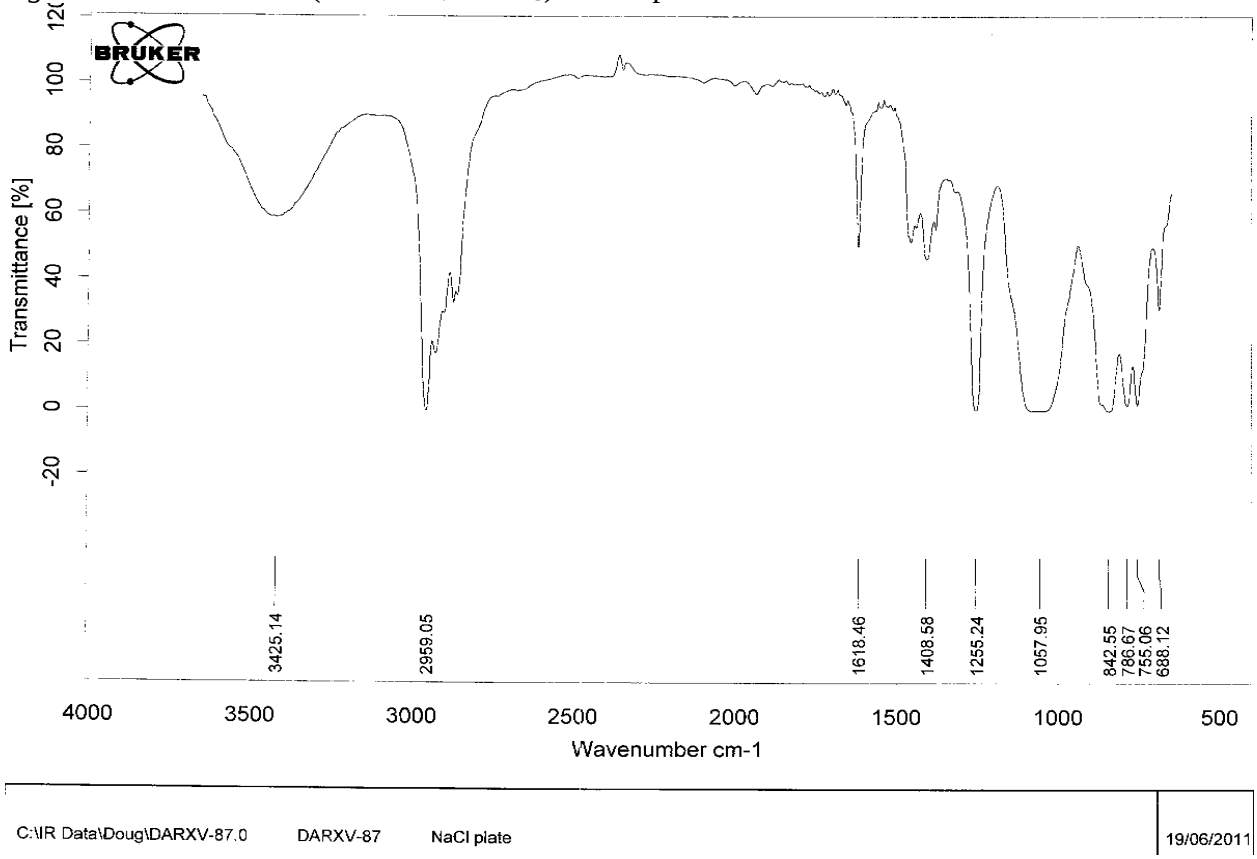
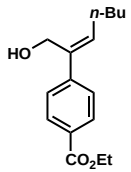


Figure A3.27 Infrared spectrum (thin film) of compound **283**



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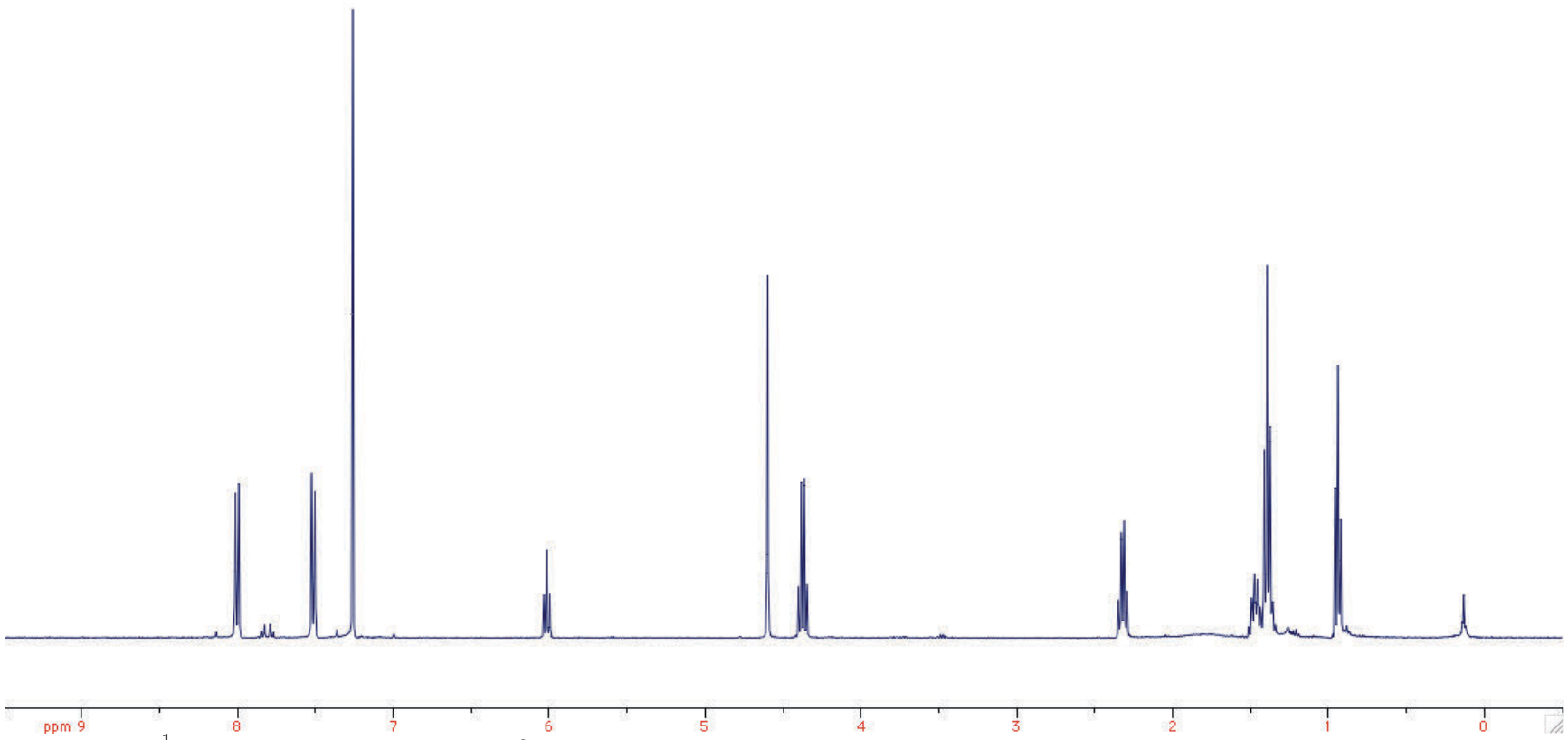
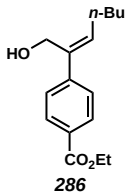


Figure A3.28 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **286**



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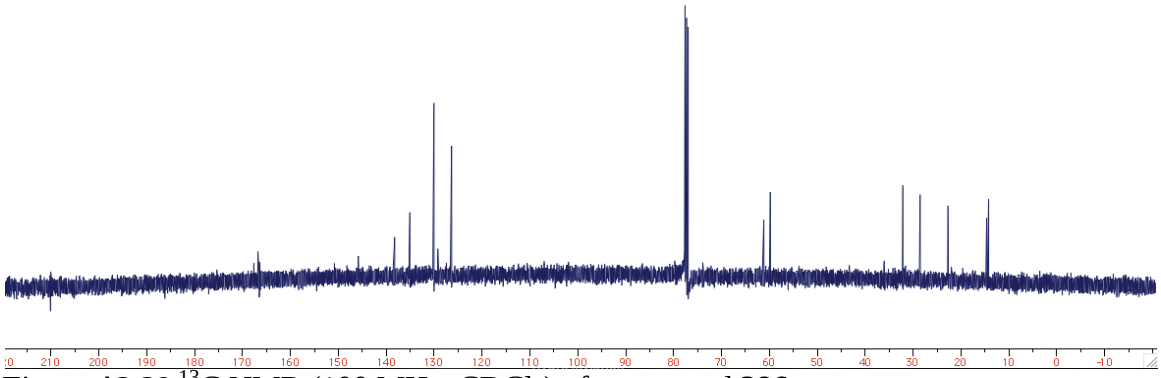


Figure A3.29 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **286**

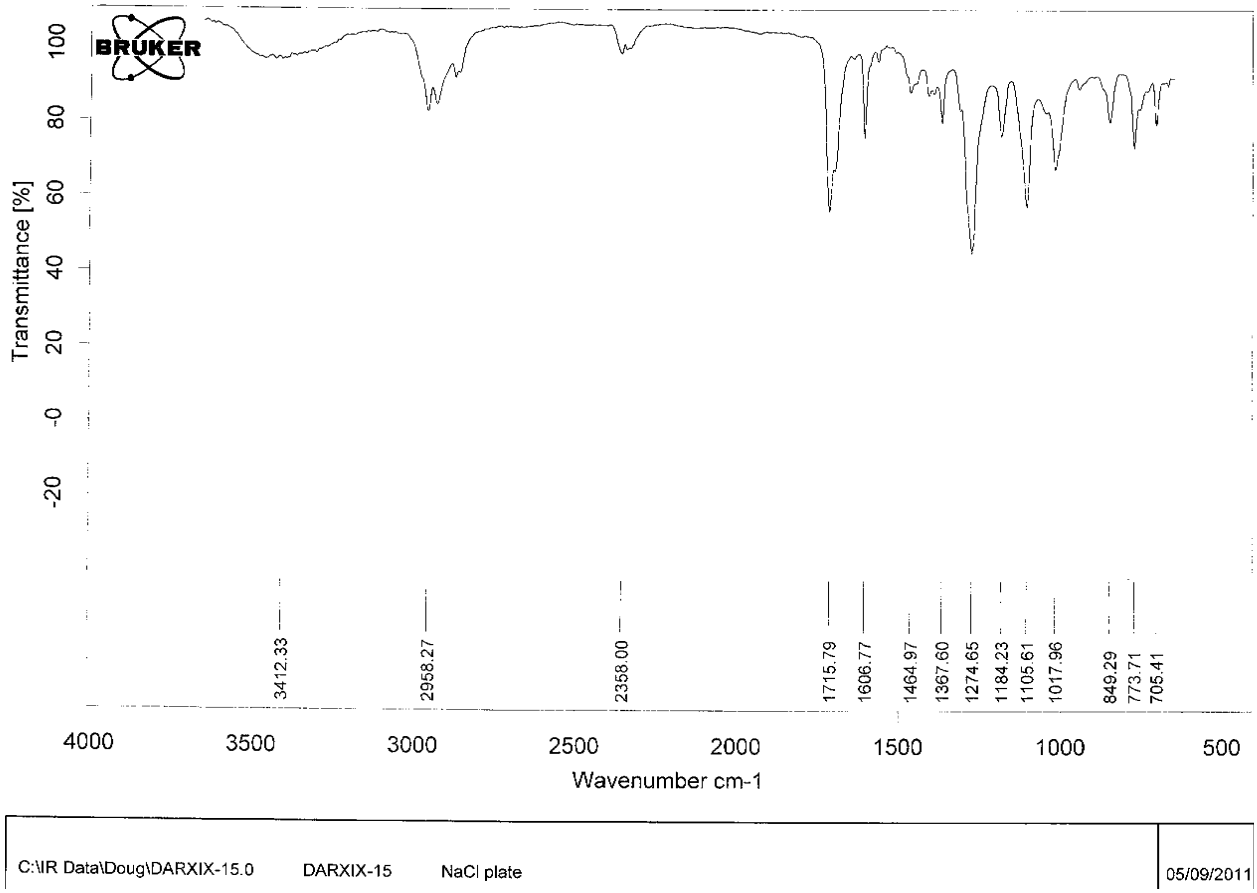
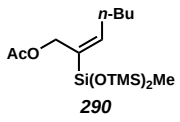


Figure A3.30 Infrared spectrum (thin film) of compound **286**



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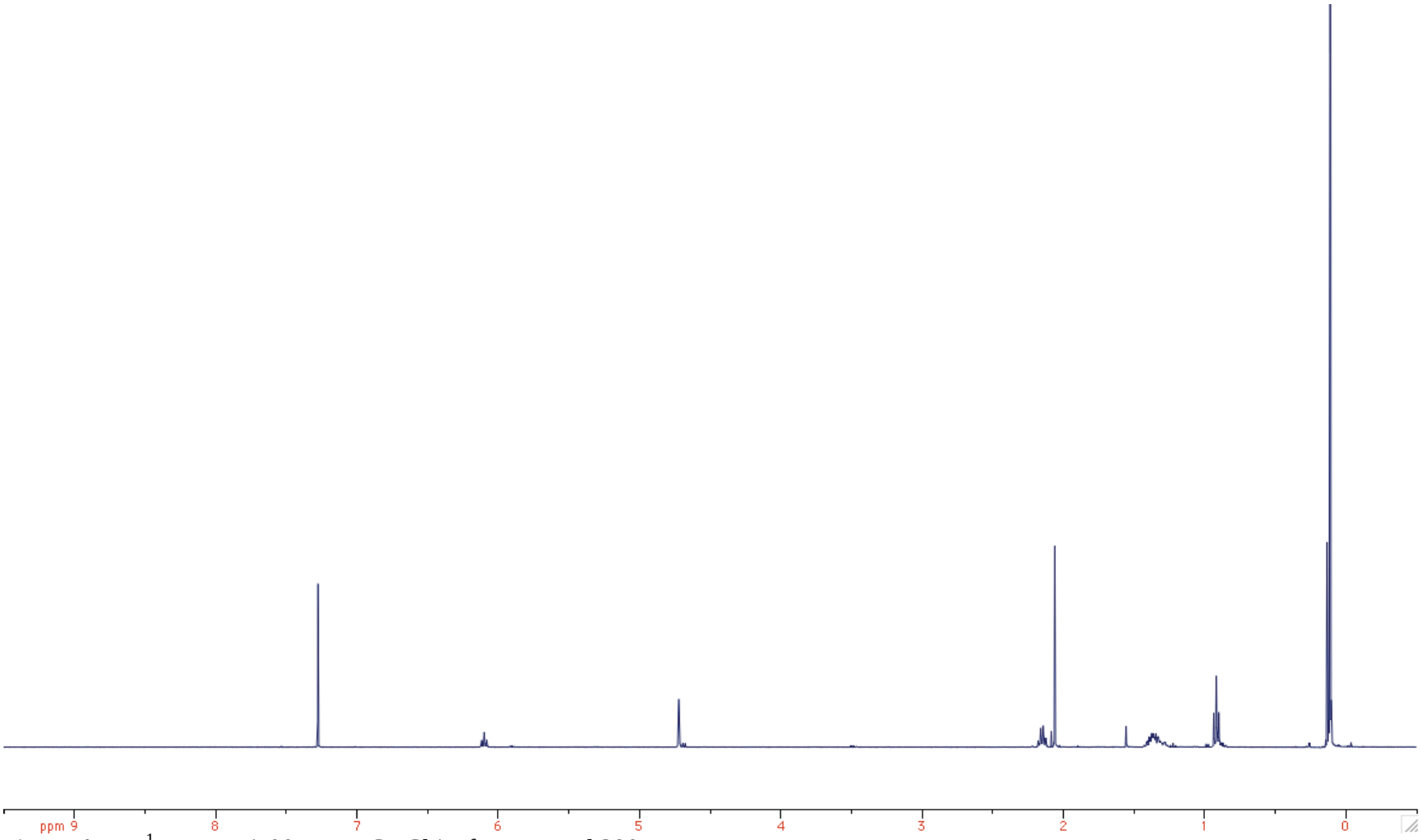
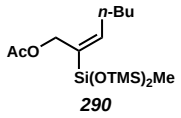


Figure A3.31 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **290**



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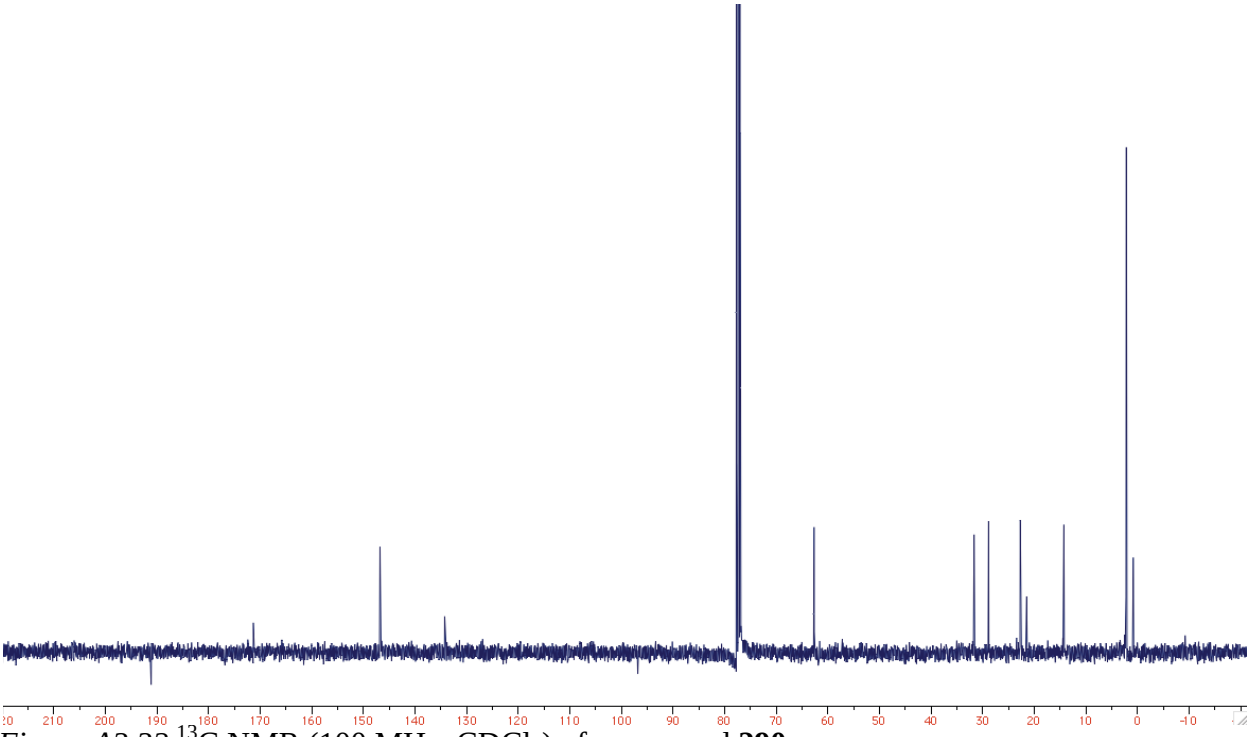


Figure A3.32 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **290**

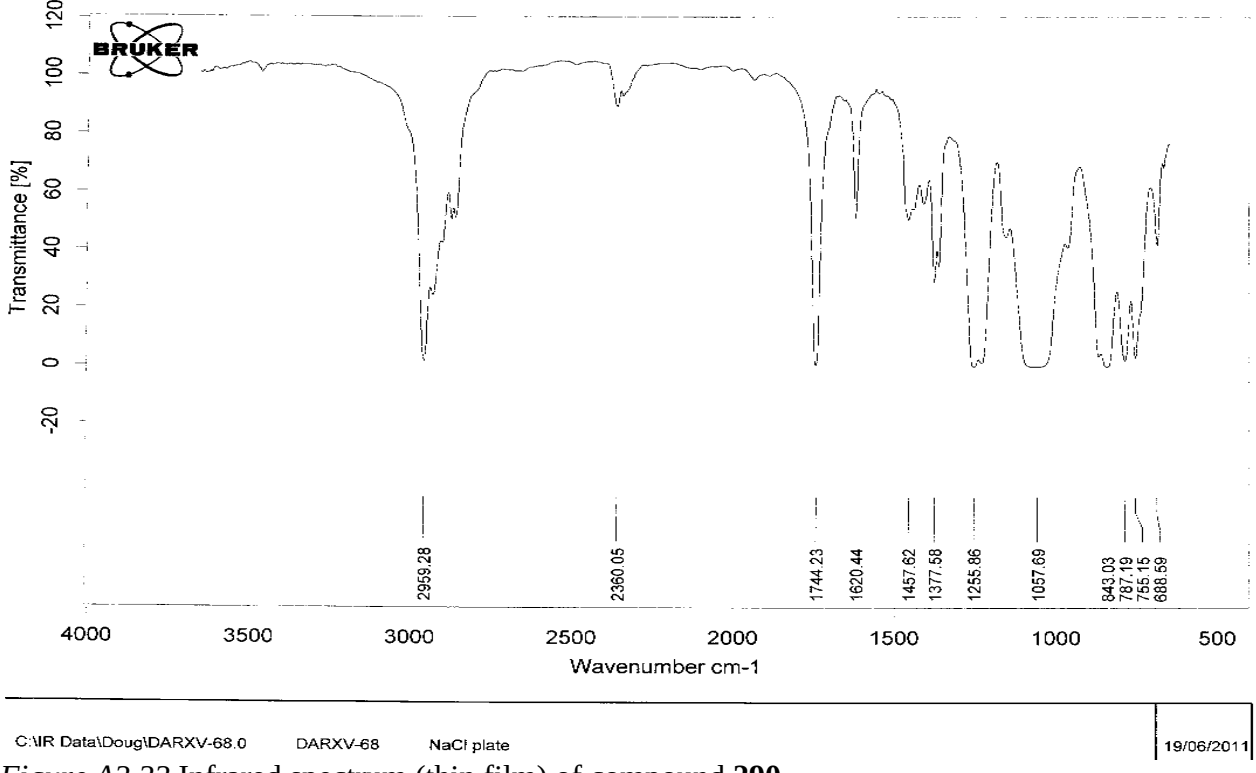
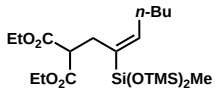


Figure A3.33 Infrared spectrum (thin film) of compound **290**



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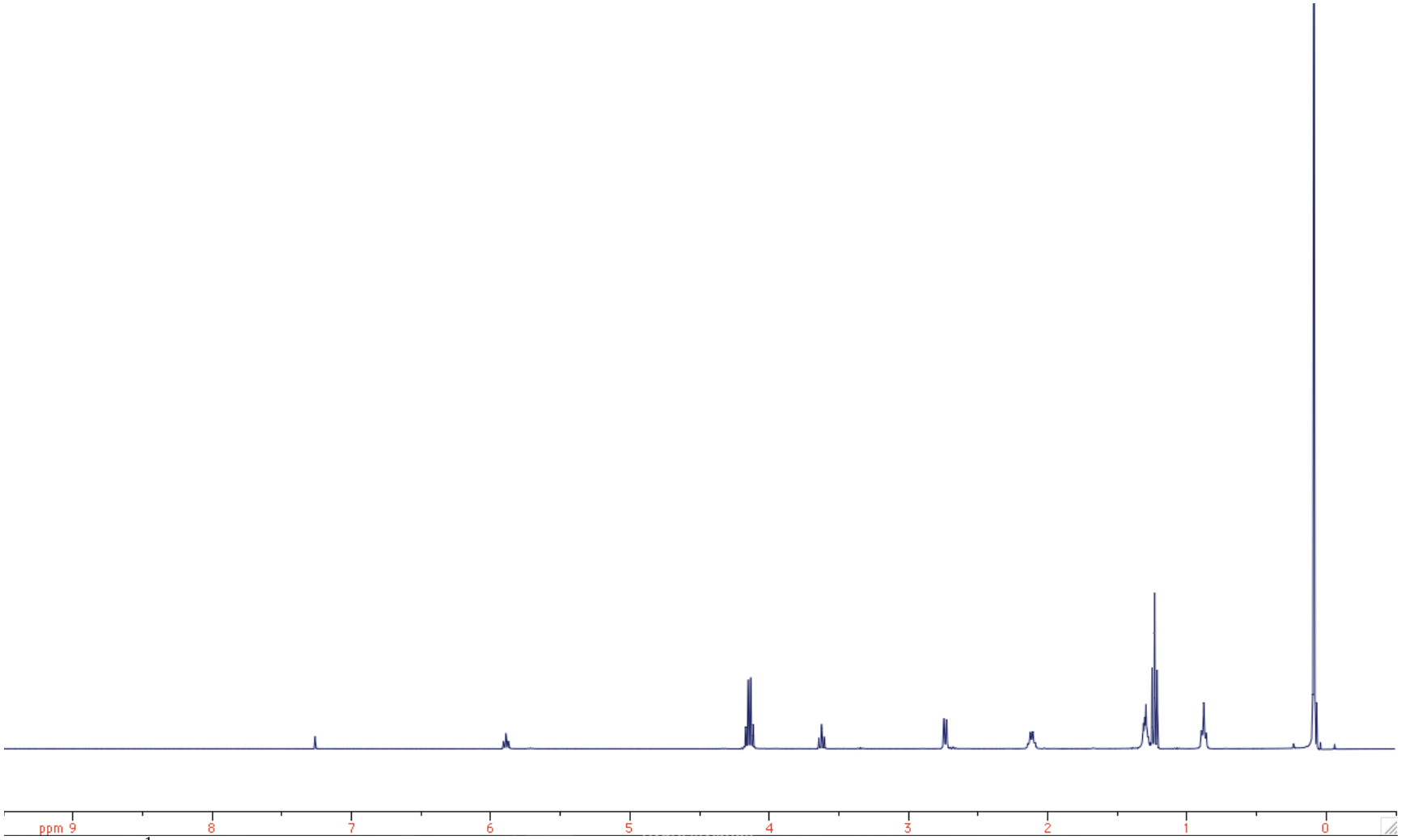
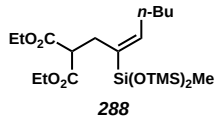


Figure A3.34 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **288**



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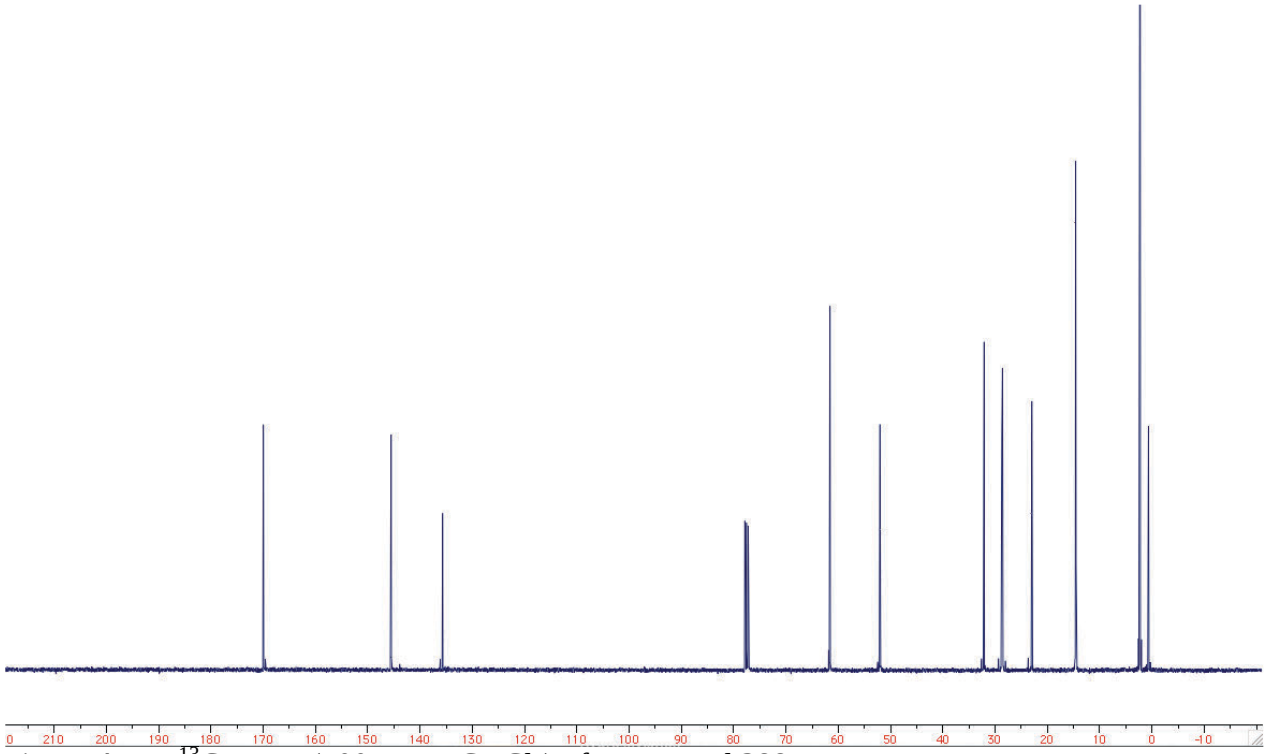


Figure A3.35 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **288**

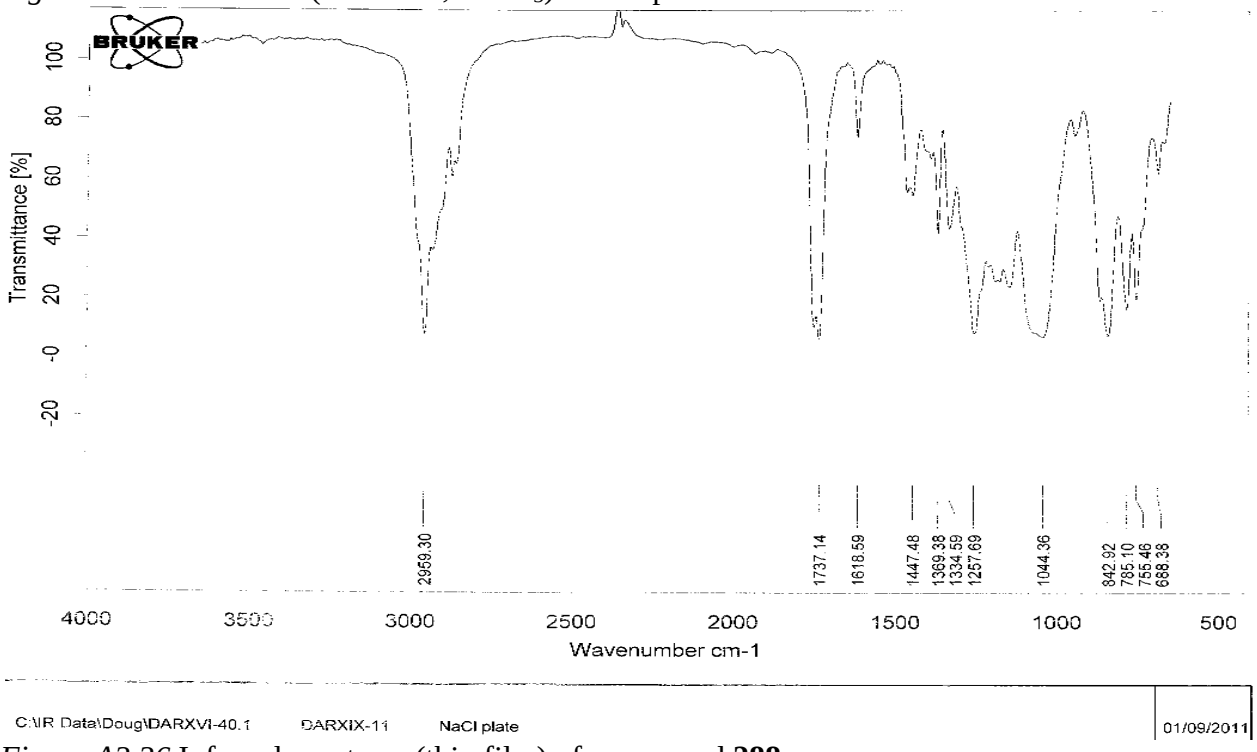
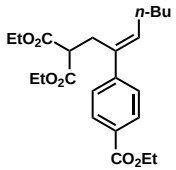


Figure A3.36 Infrared spectrum (thin film) of compound **288**



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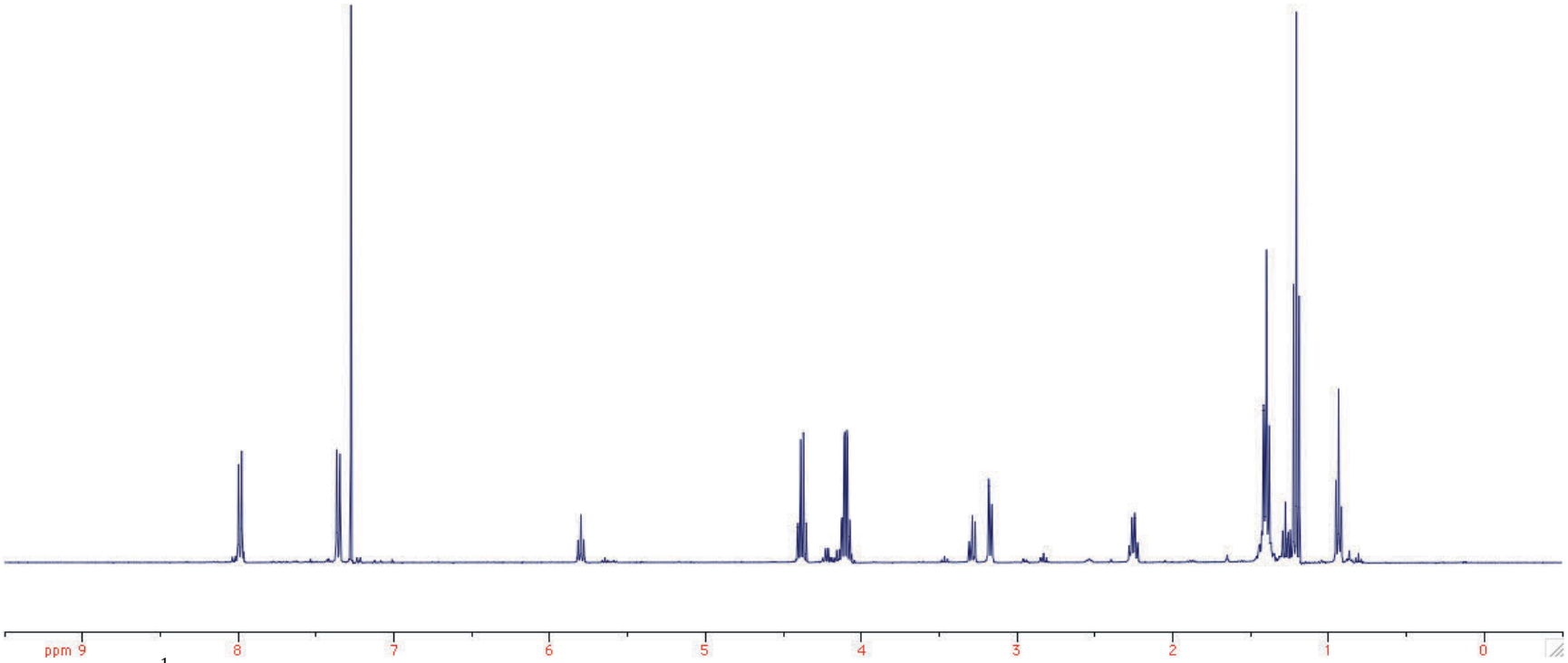
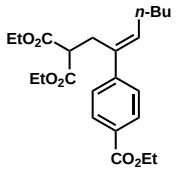


Figure A3.37 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **289**



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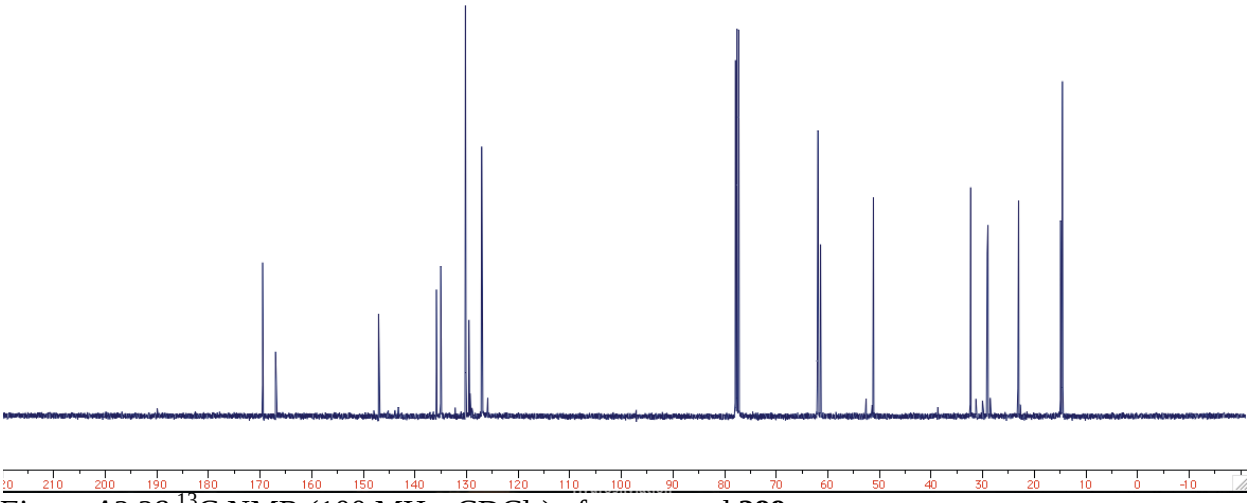


Figure A3.38 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **289**

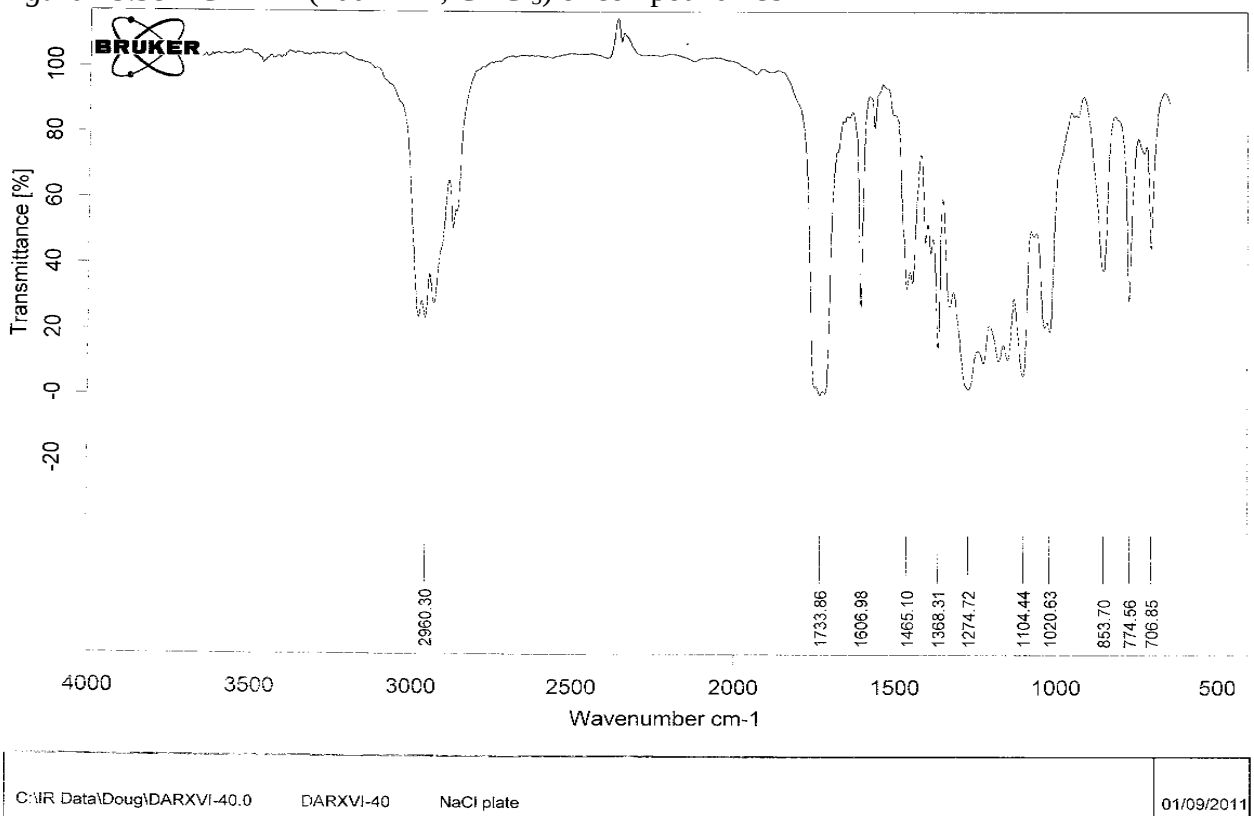
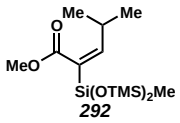


Figure A3.39 Infrared spectrum (thin film) of compound **289**



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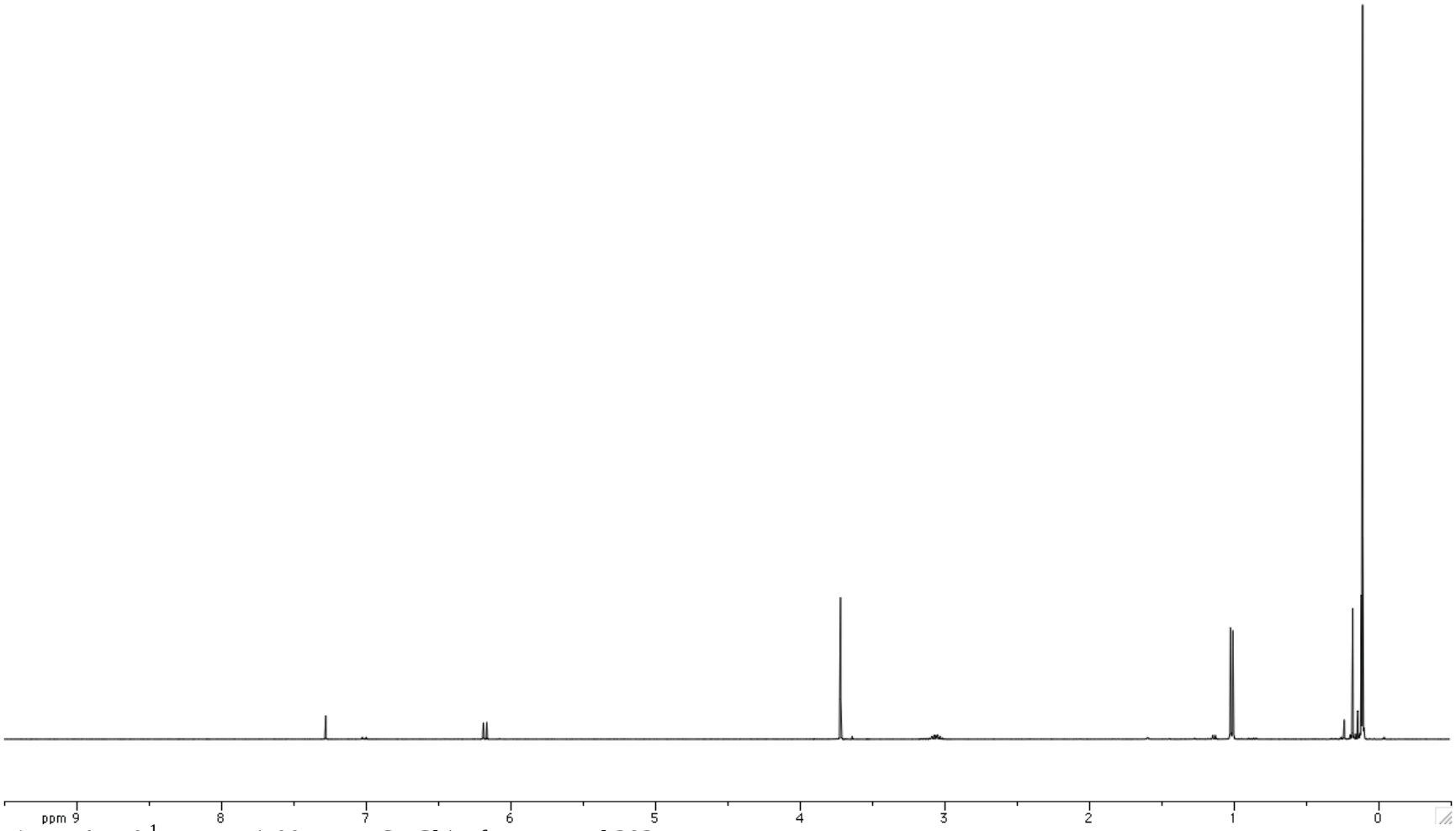
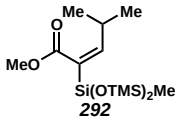


Figure A3.40 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **292**



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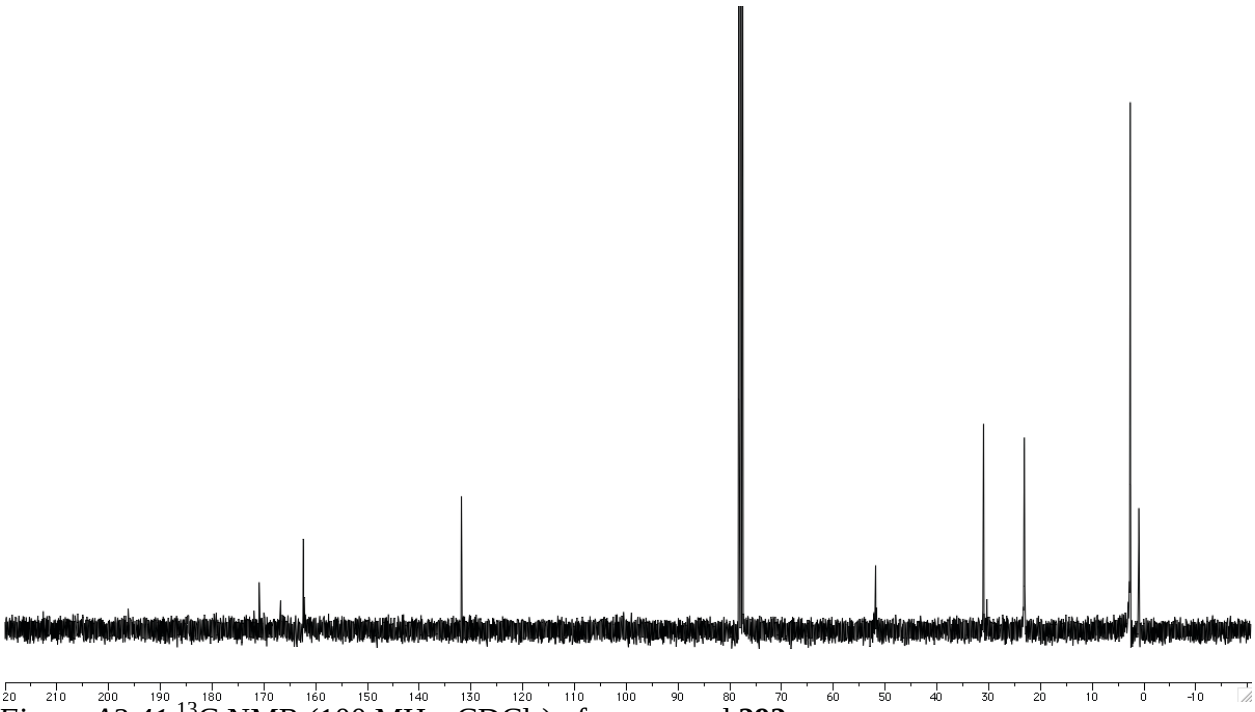


Figure A3.41 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **292**

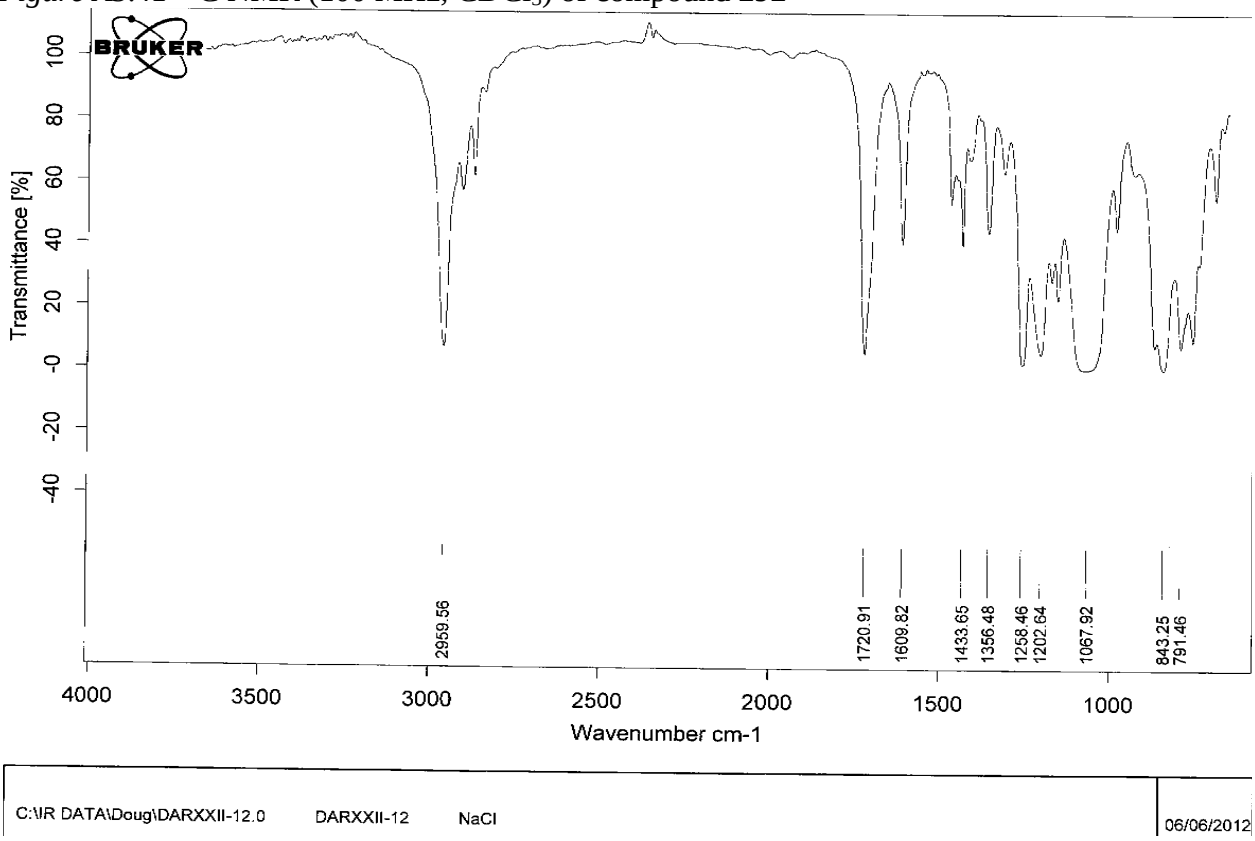
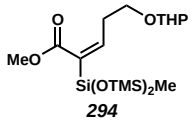


Figure A3.42 Infrared spectrum (thin film) of compound **292**



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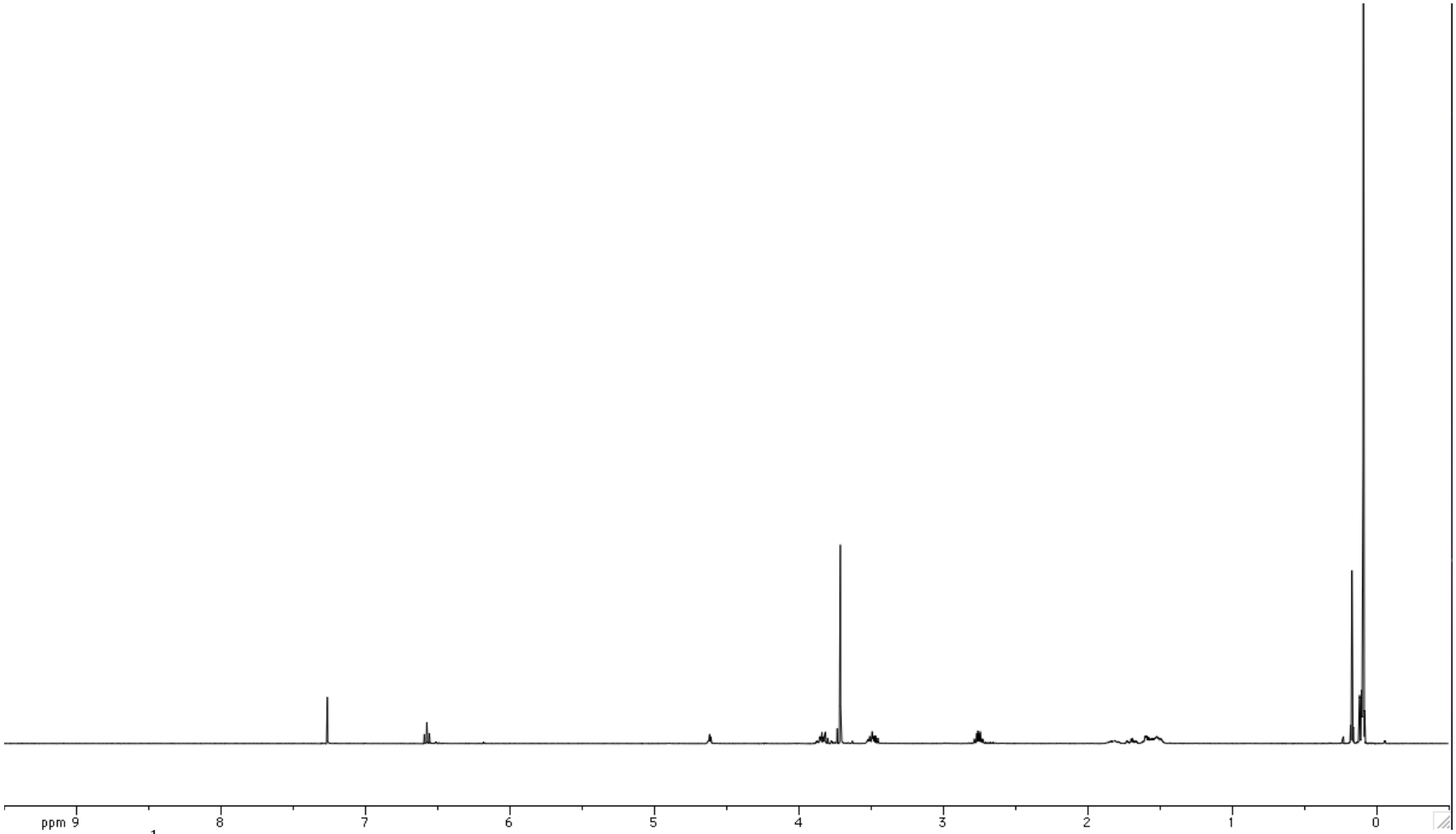
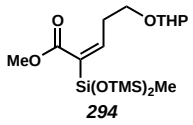


Figure A3.43 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **294**



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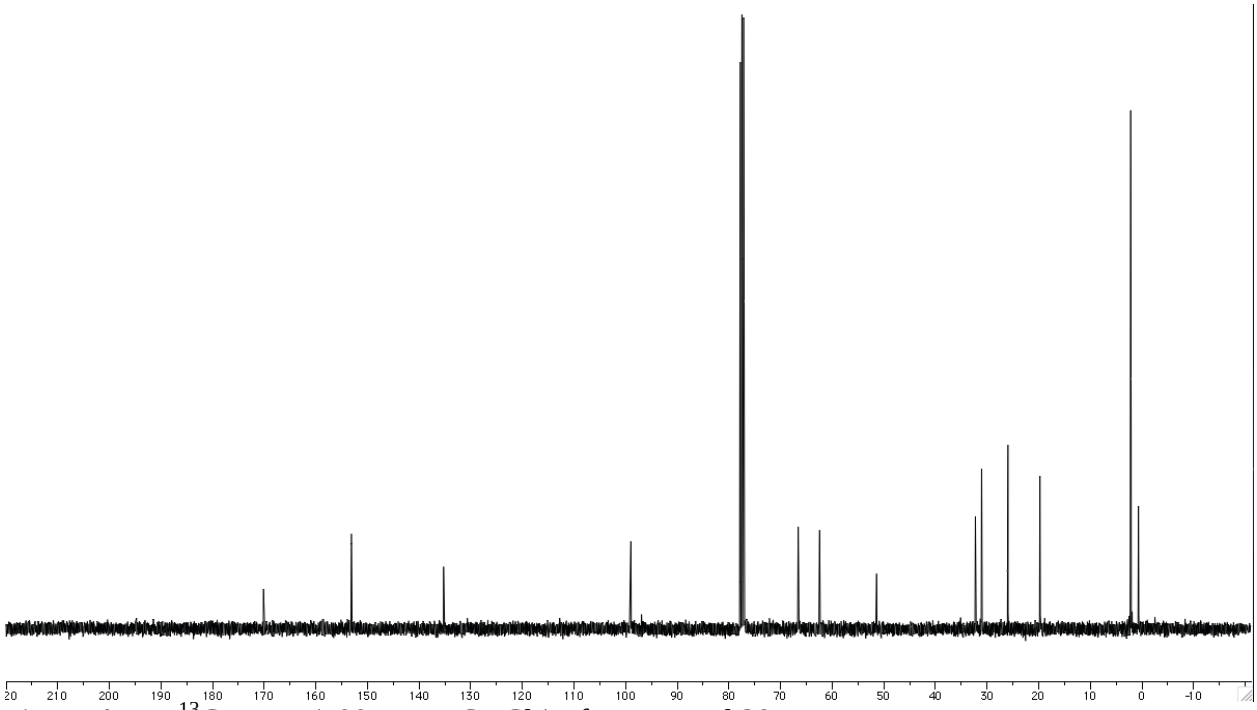


Figure A3.44 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **294**

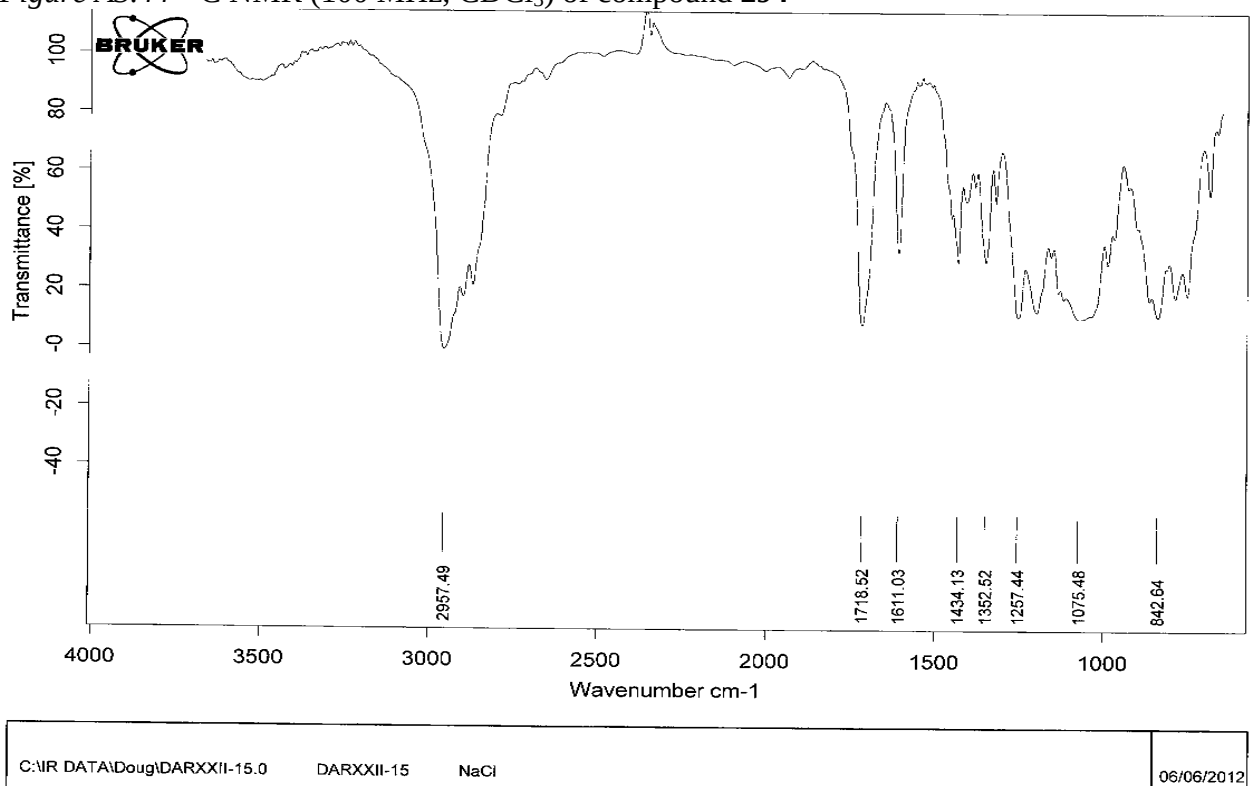
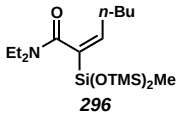


Figure A3.45 Infrared spectrum (thin film) of compound **294**



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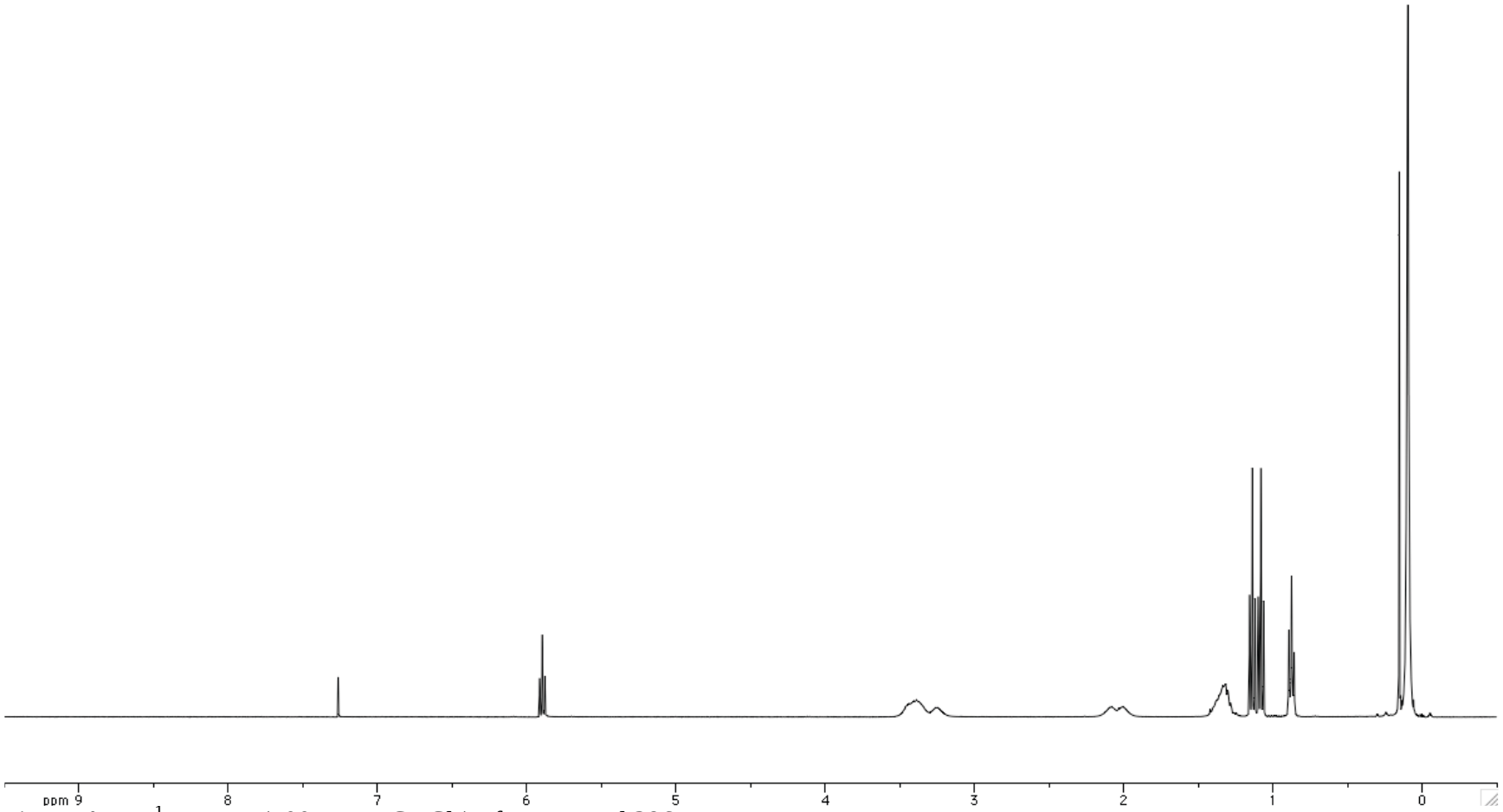
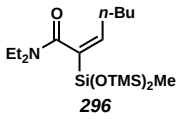


Figure A3.46 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **296**



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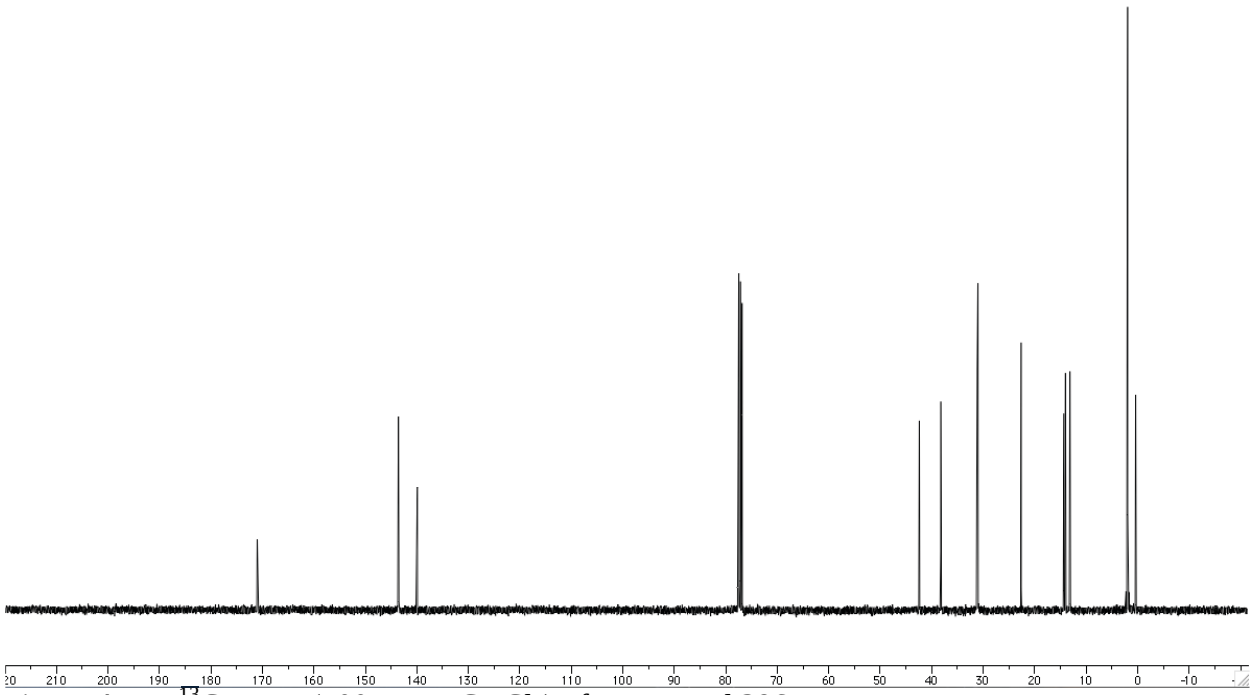


Figure A3.47 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **296**

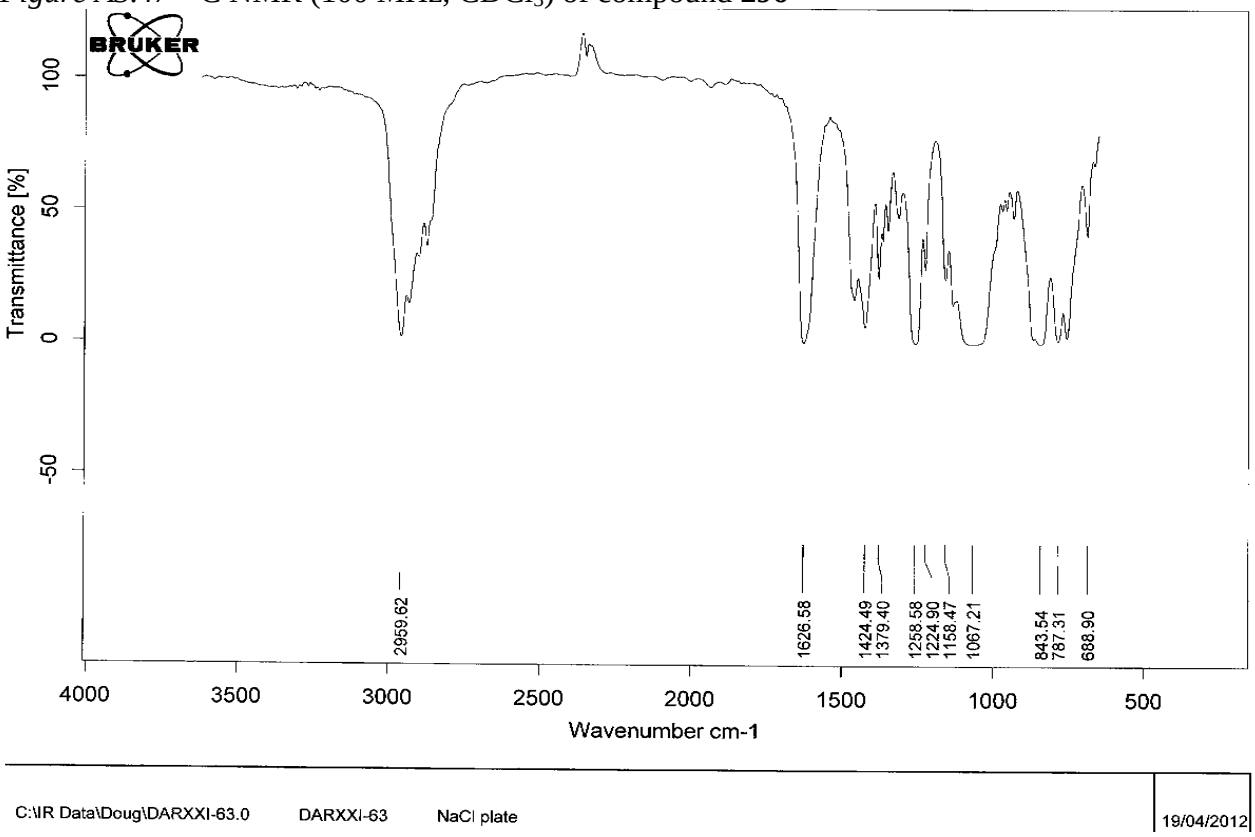
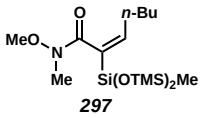


Figure A3.48 Infrared spectrum (thin film) of compound **296**



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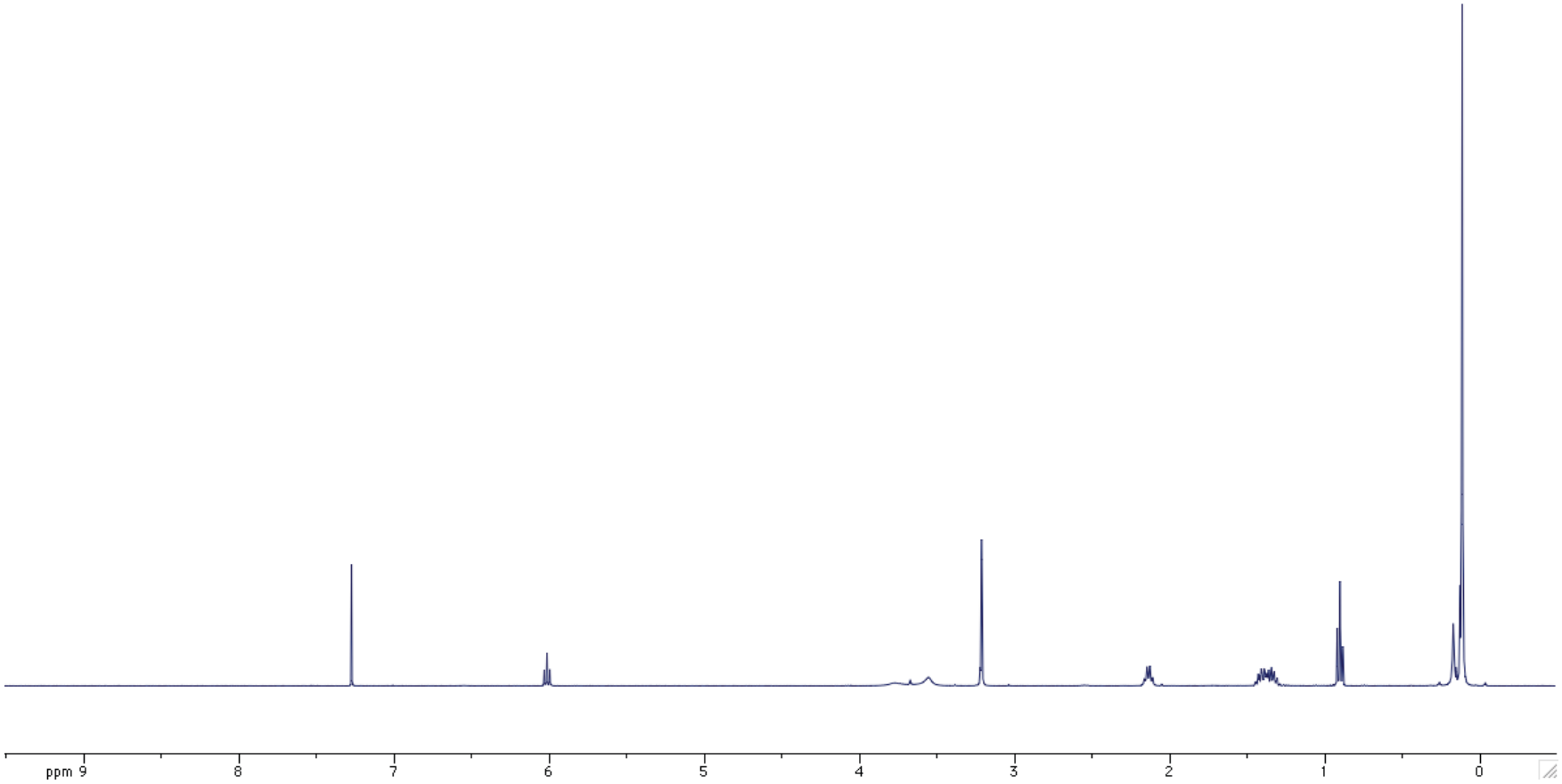


Figure A3.49 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **297**

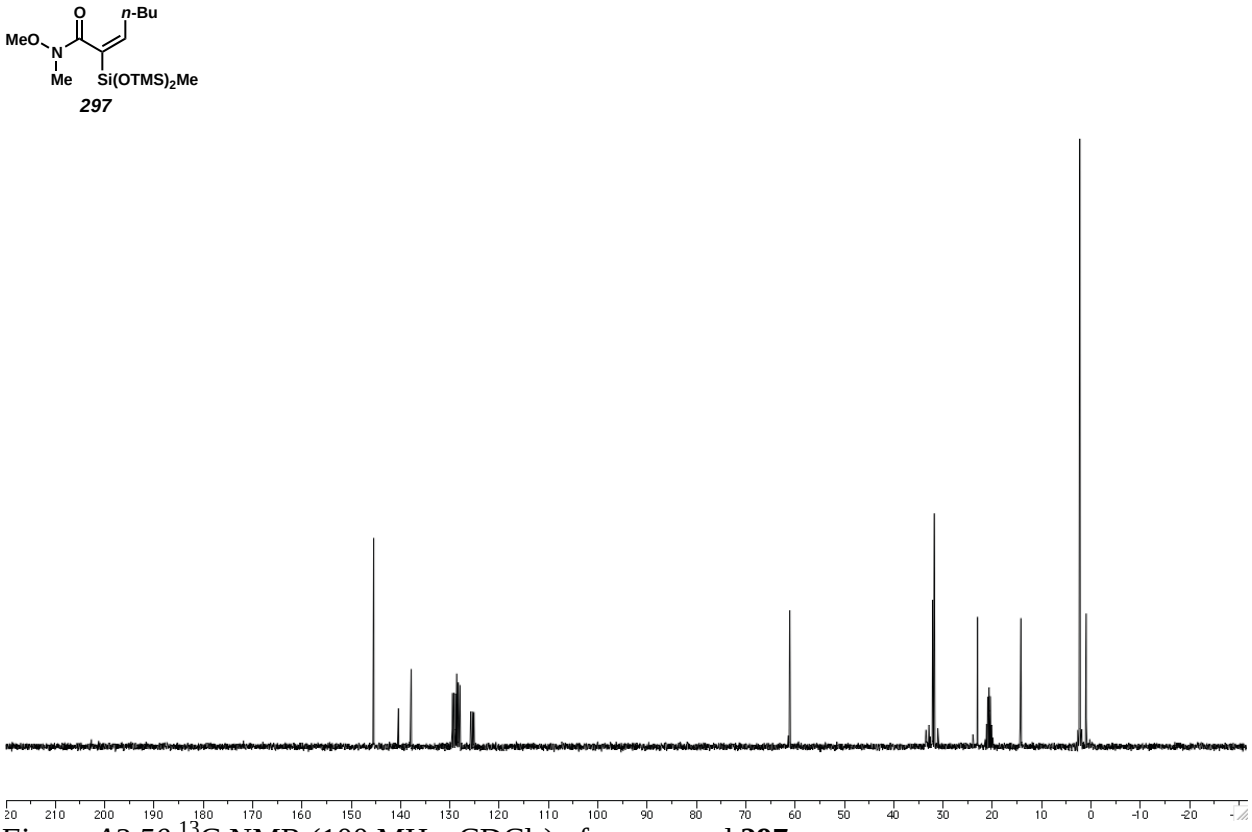


Figure A3.50 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **297**

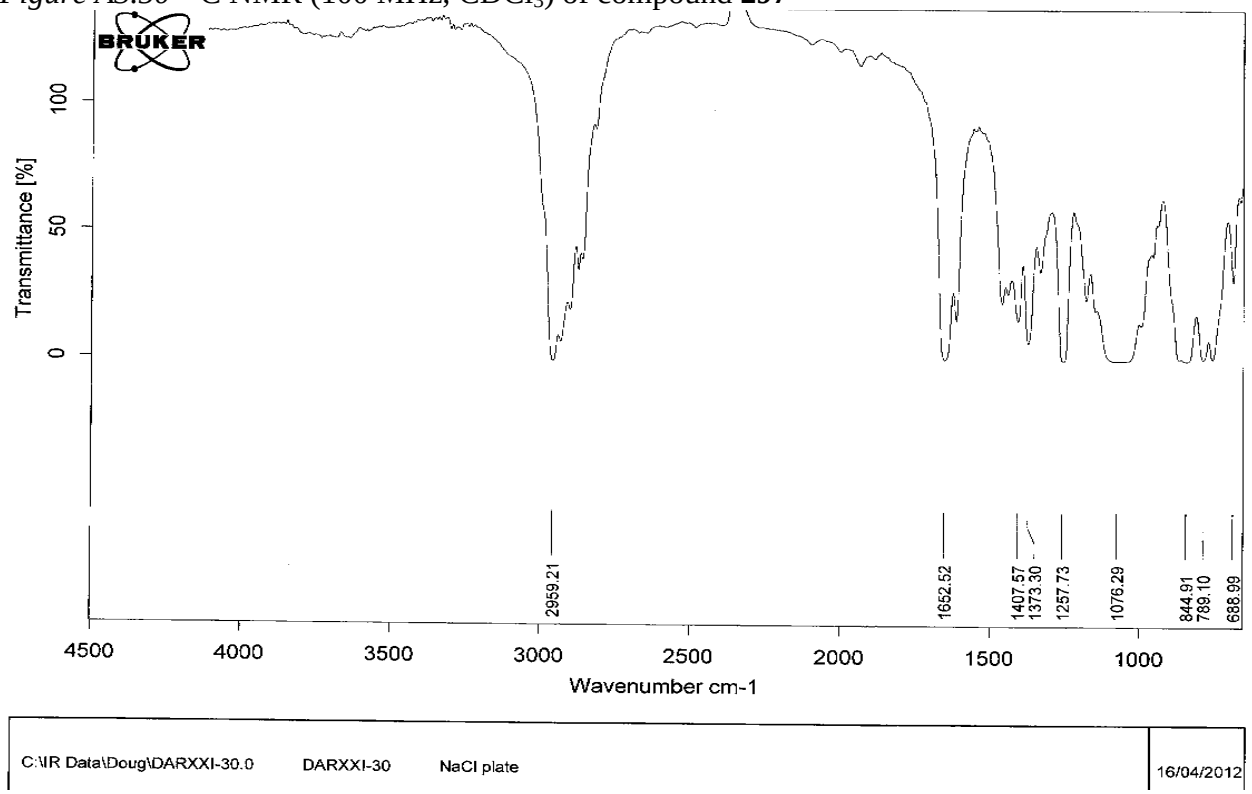
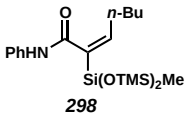


Figure A3.51 Infrared spectrum (thin film) of compound **297**



298

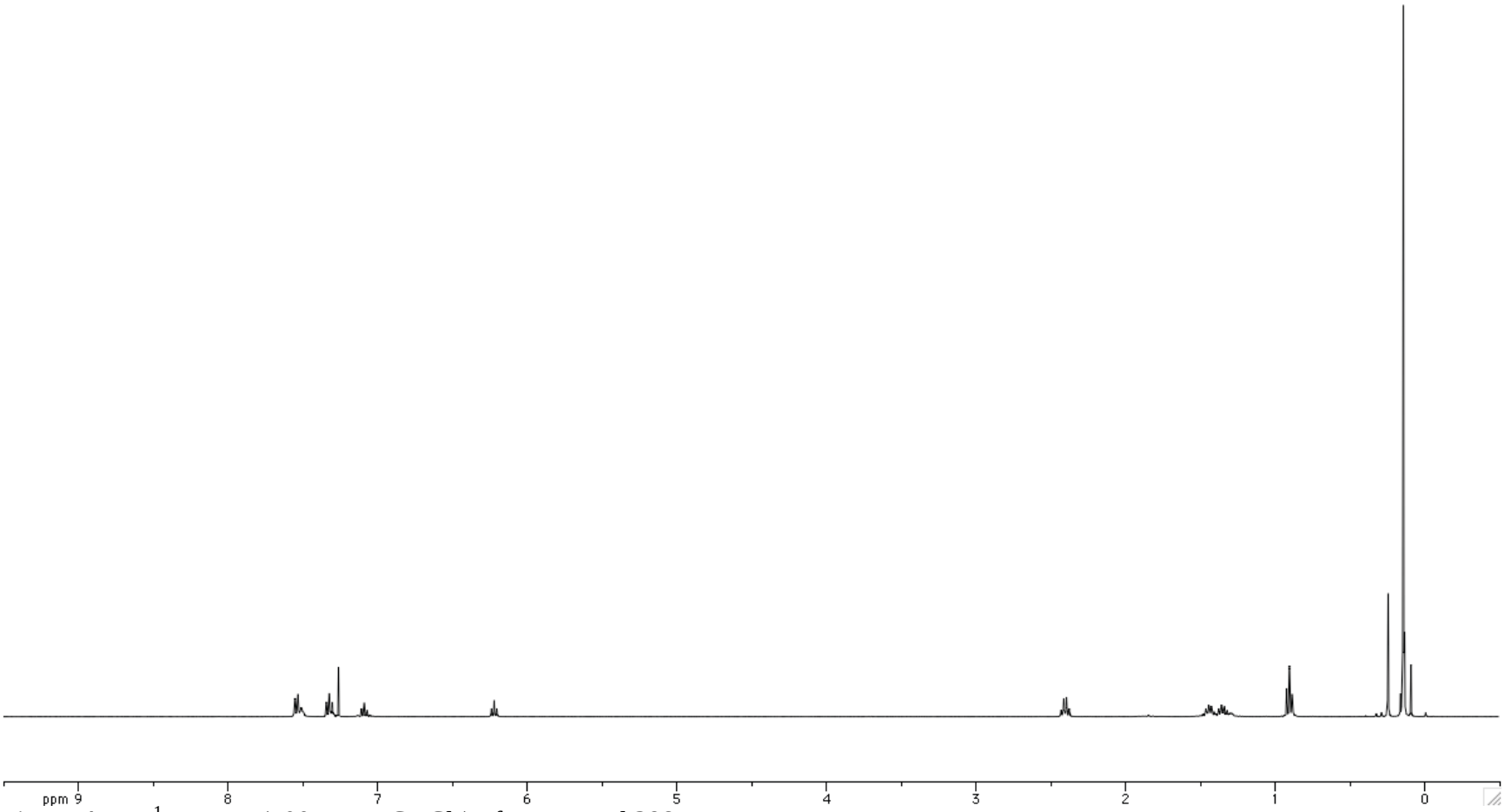


Figure A3.52 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **298**

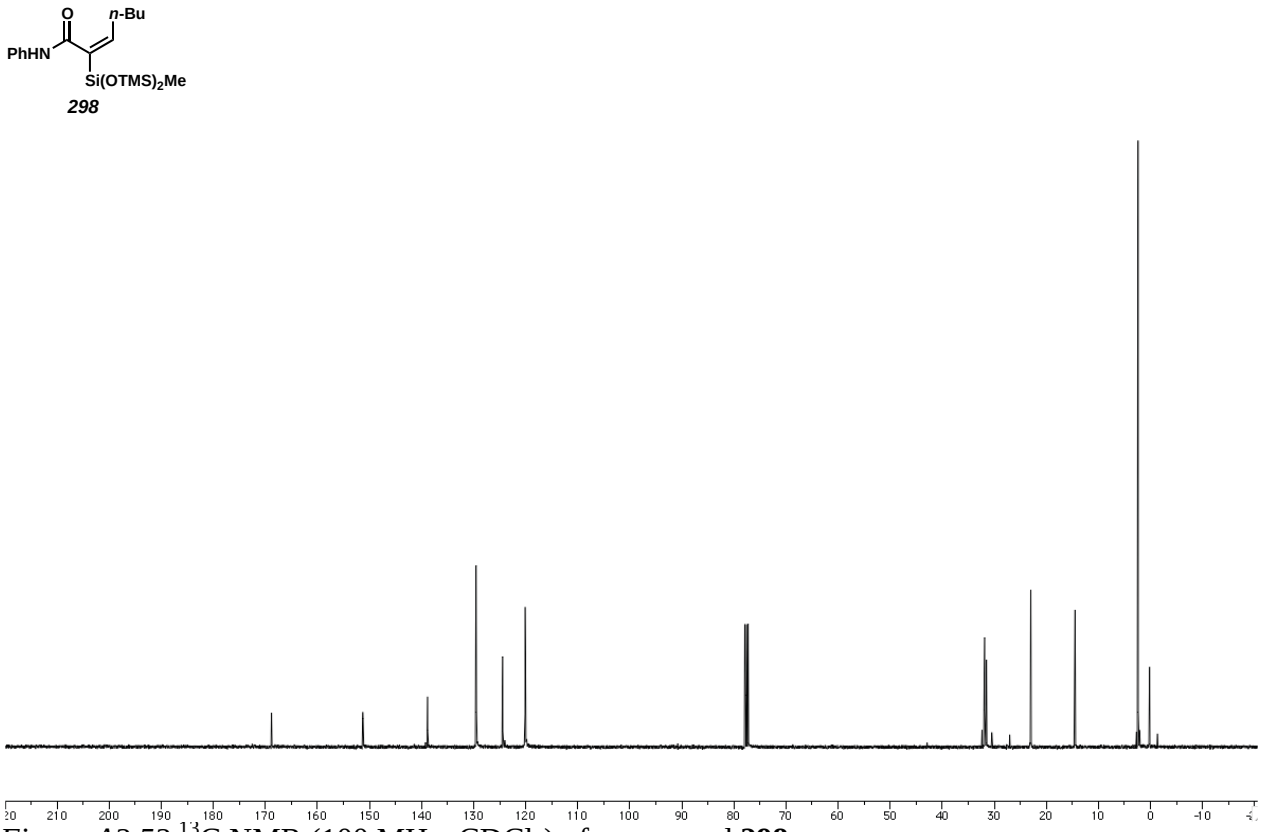


Figure A3.53 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **298**

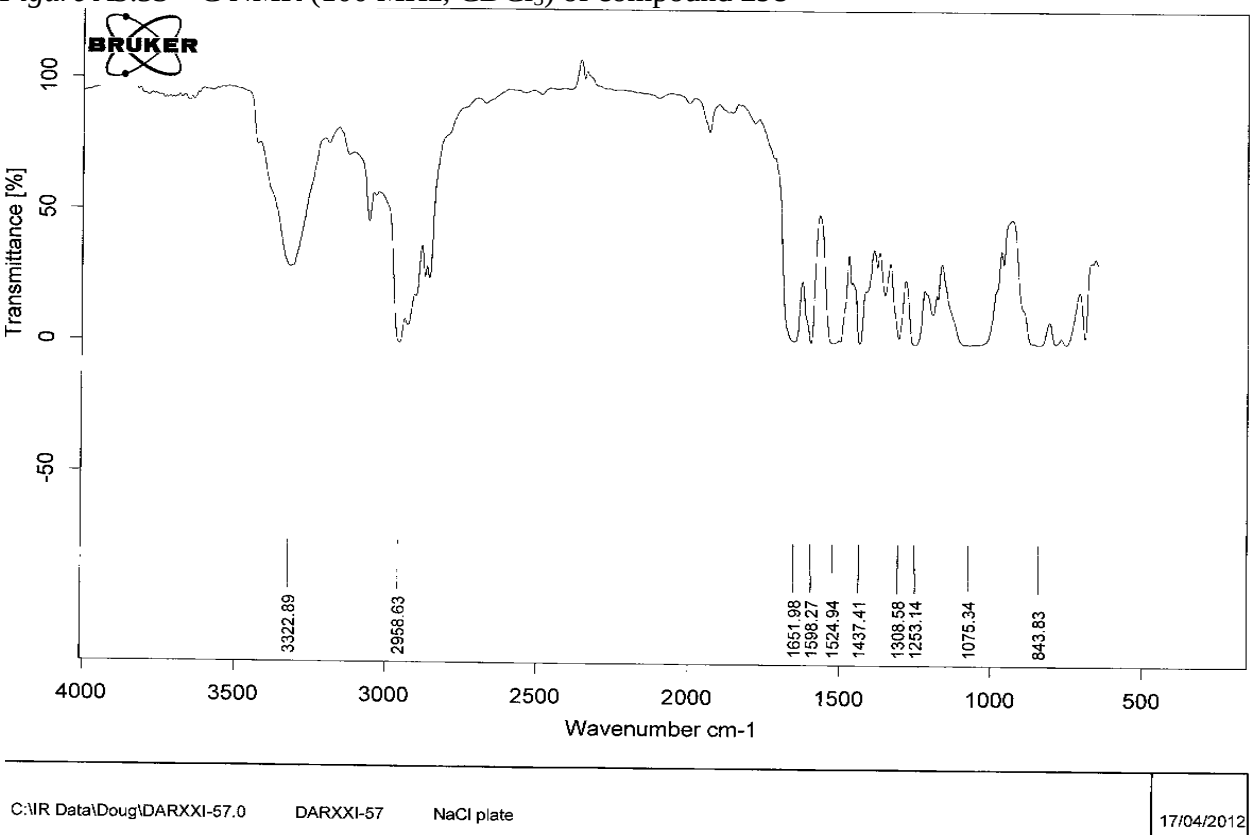
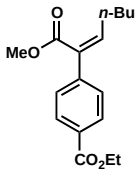


Figure A3.54 Infrared spectrum (thin film) of compound **298**



299

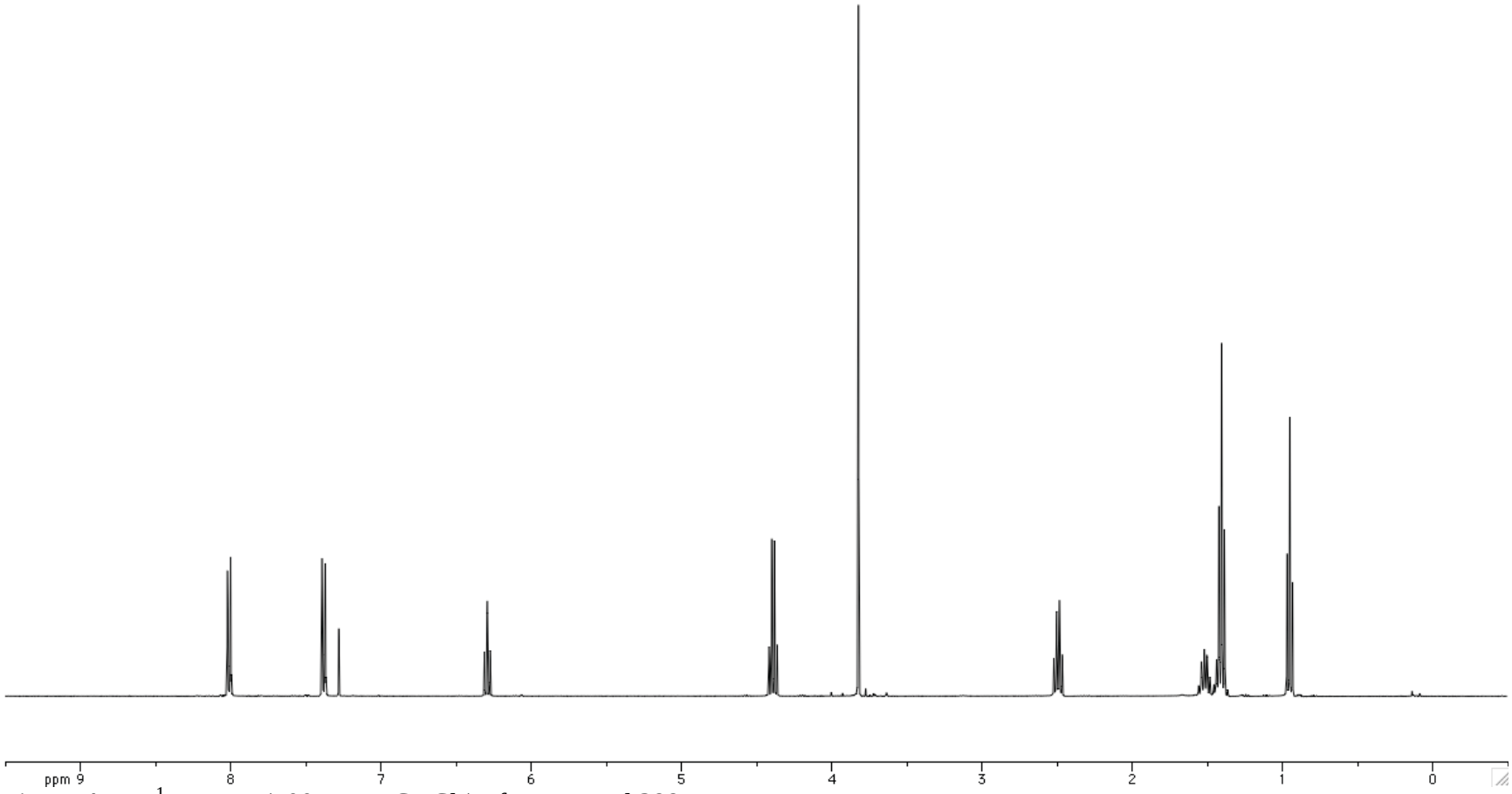
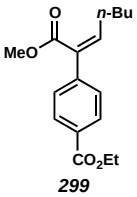


Figure A3.55 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **299**



299

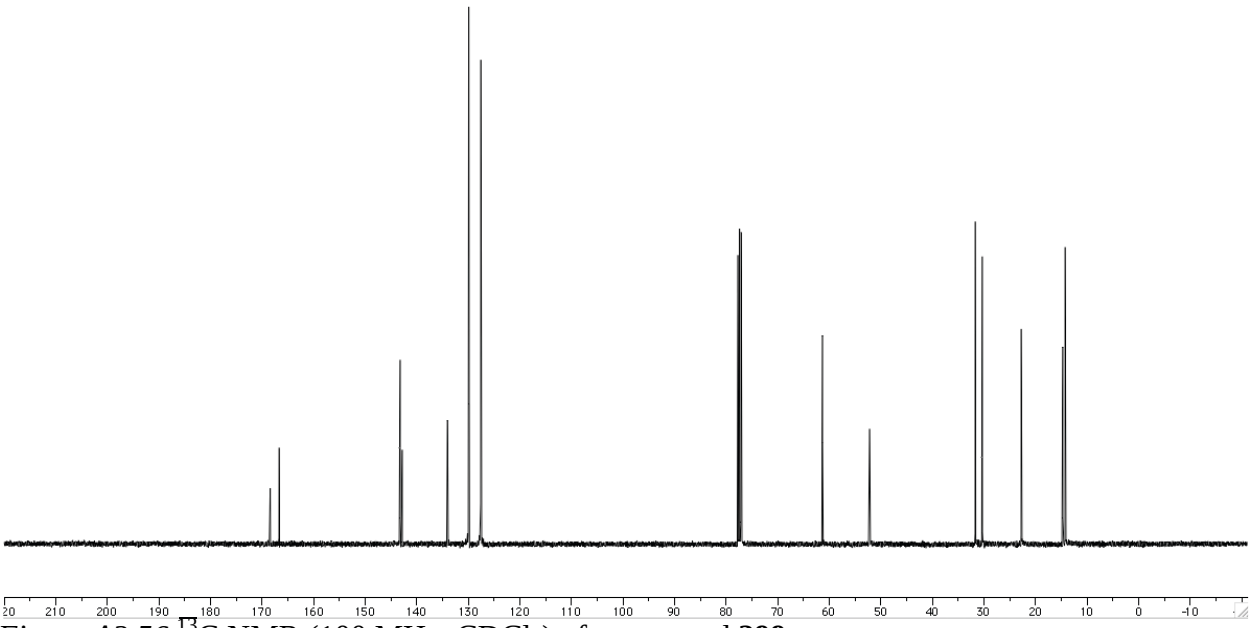


Figure A3.56 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **299**

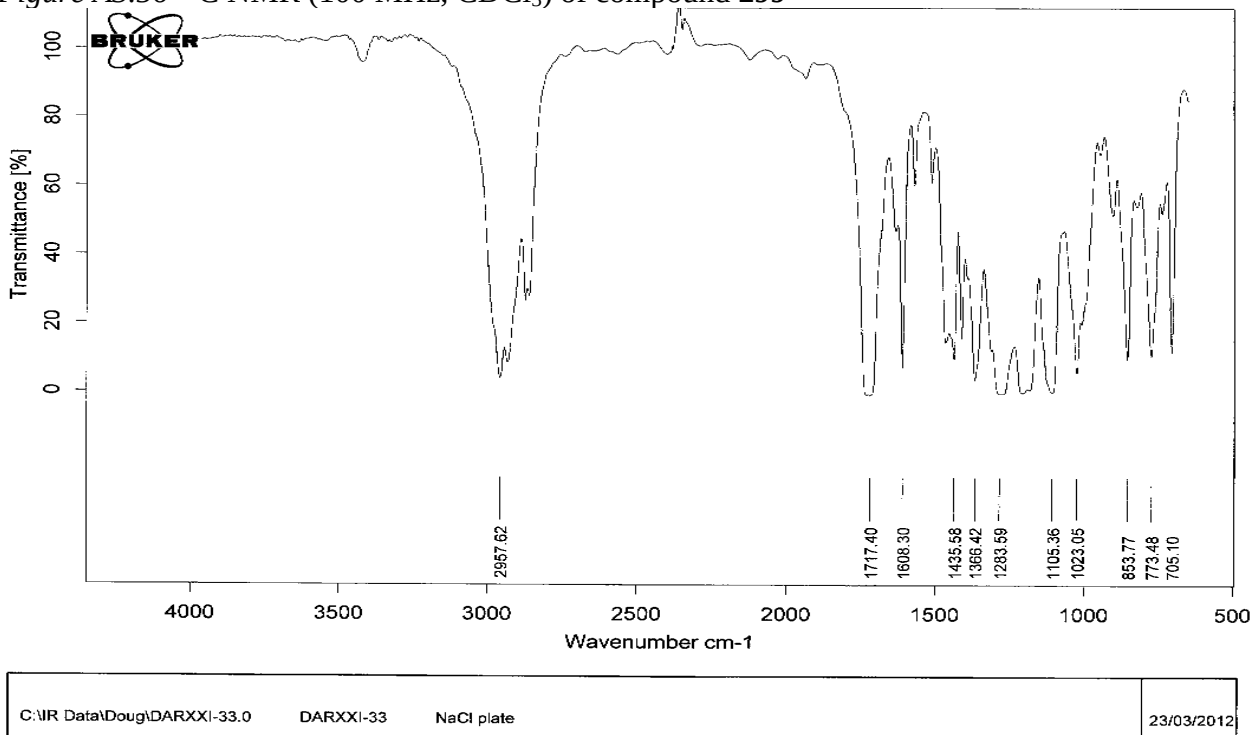
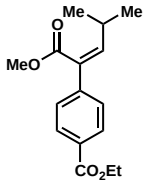


Figure A3.57 Infrared spectrum (thin film) of compound **299**



300

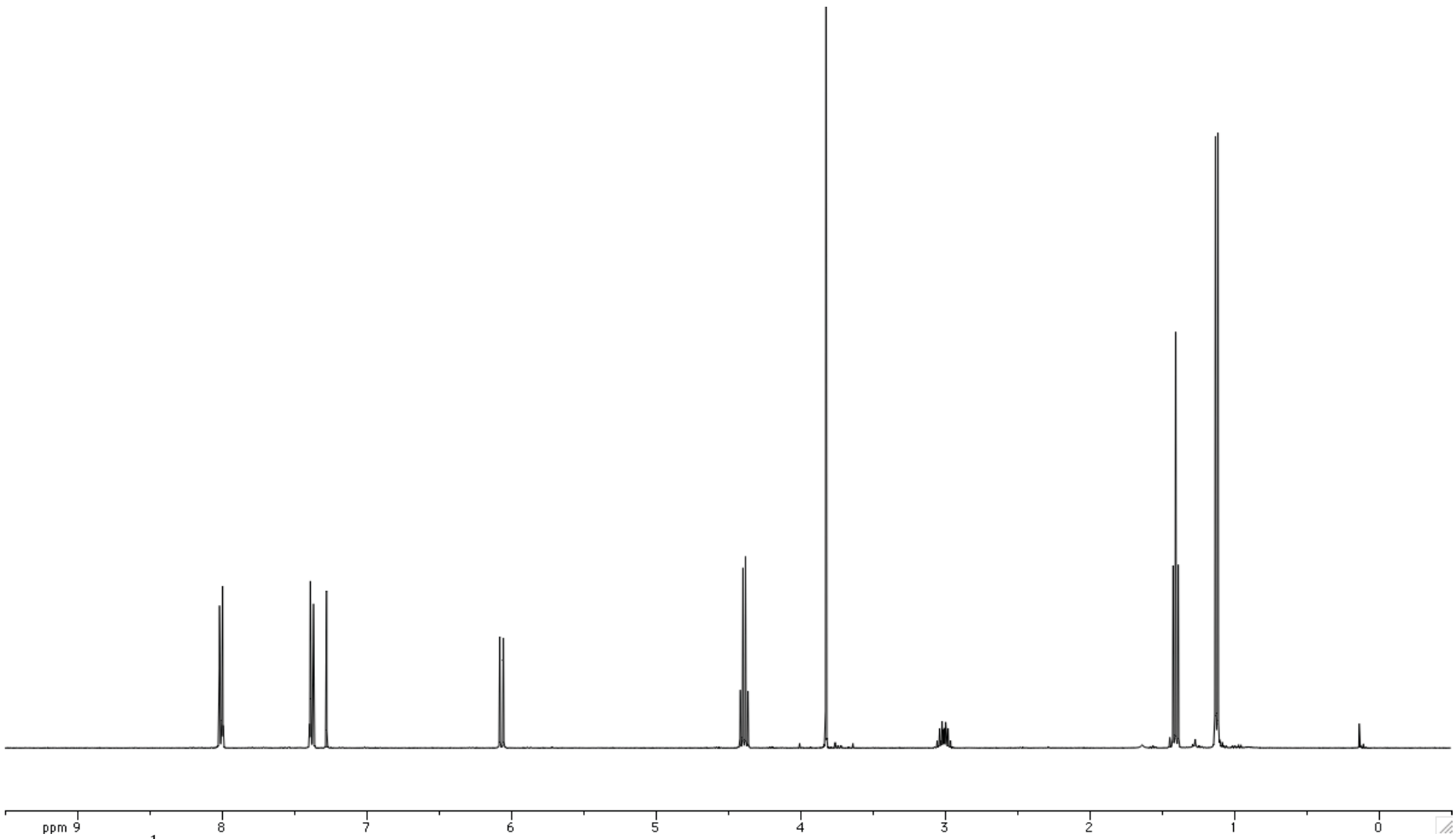


Figure A3.58 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **300**

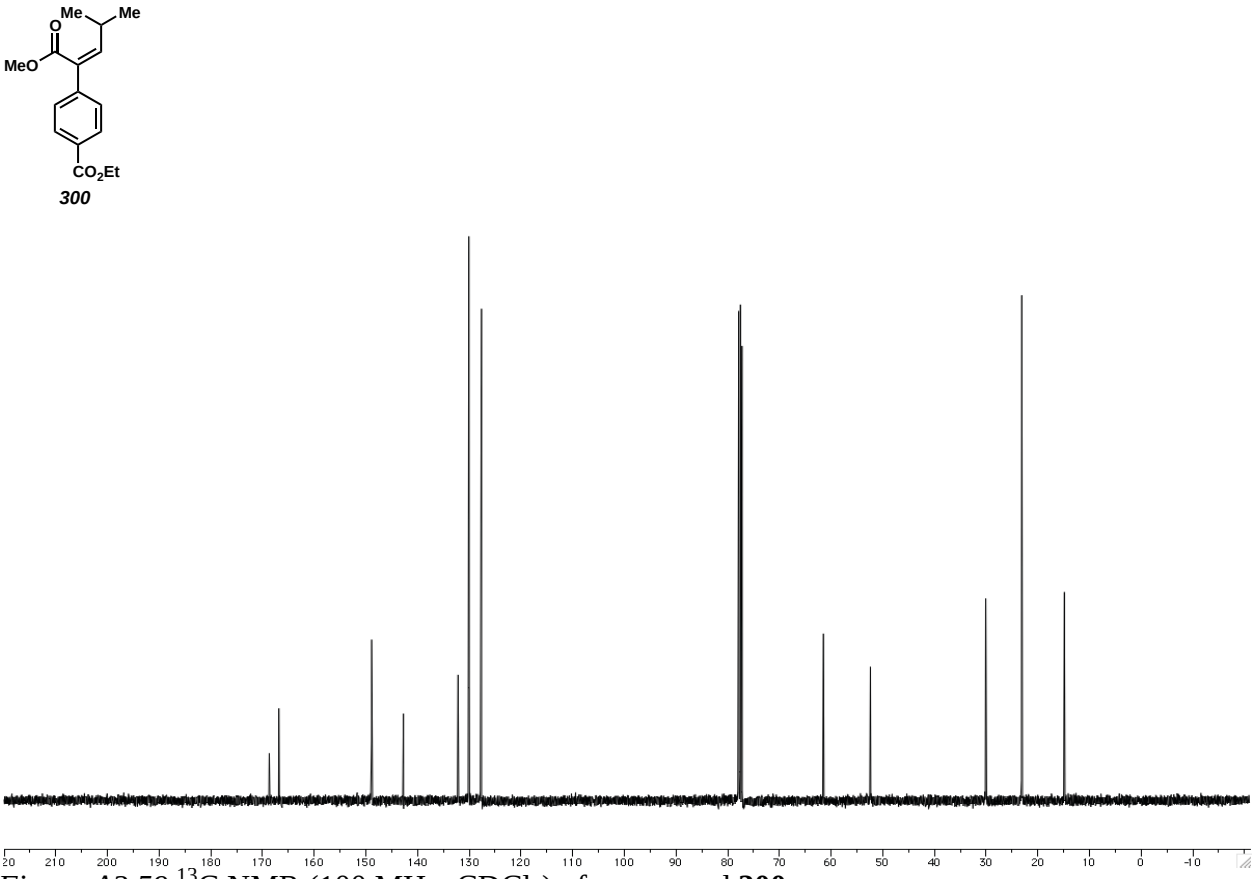


Figure A3.59 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **300**

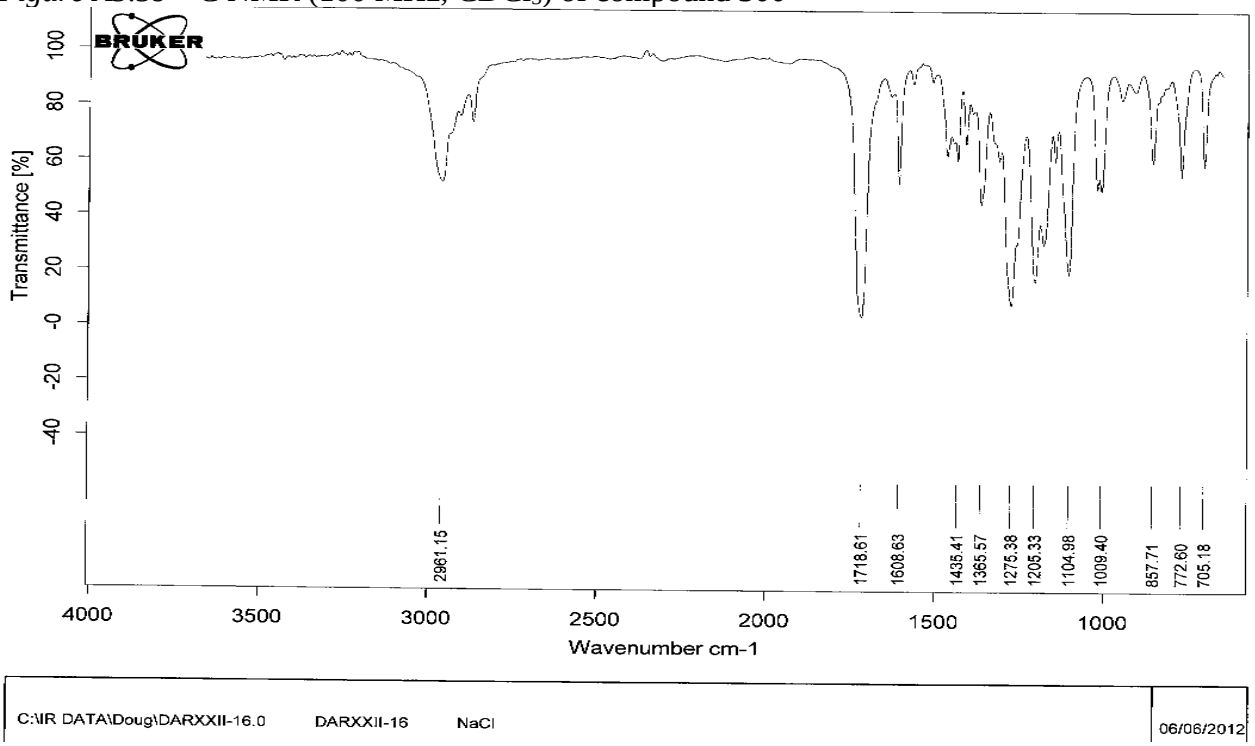
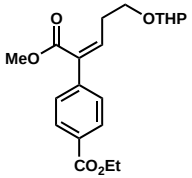


Figure A3.60 Infrared spectrum (thin film) of compound **300**



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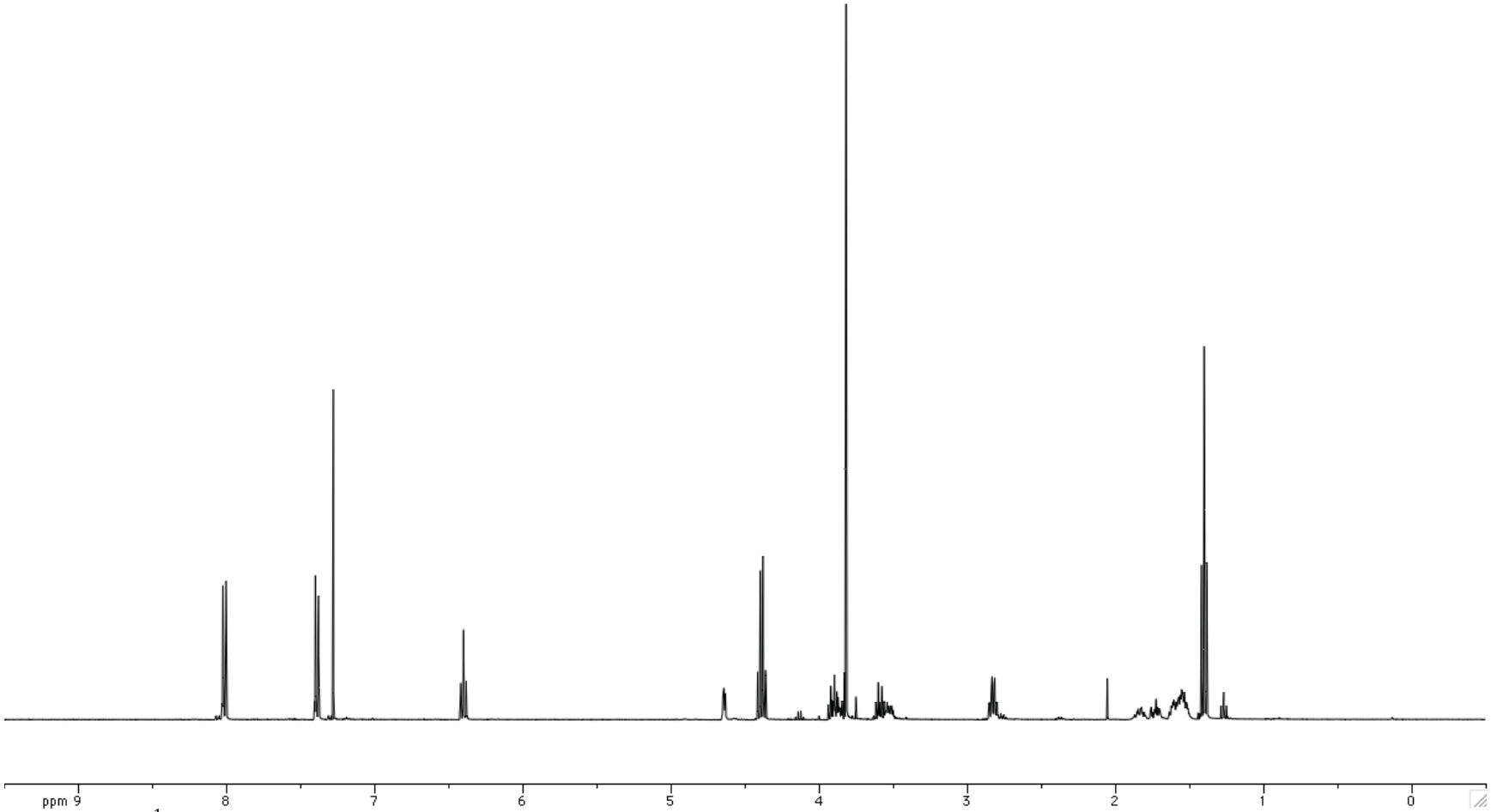
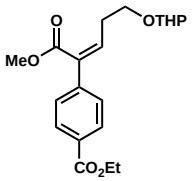


Figure A3.61 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **301**



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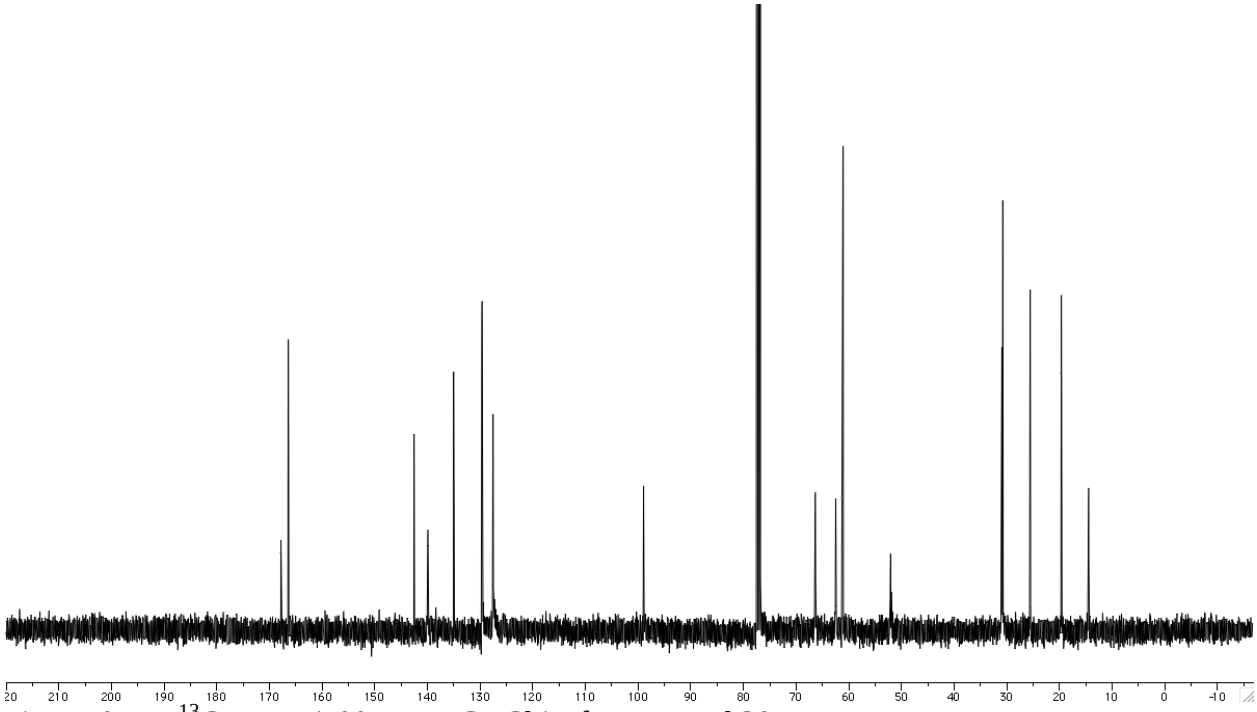


Figure A3.62 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **301**

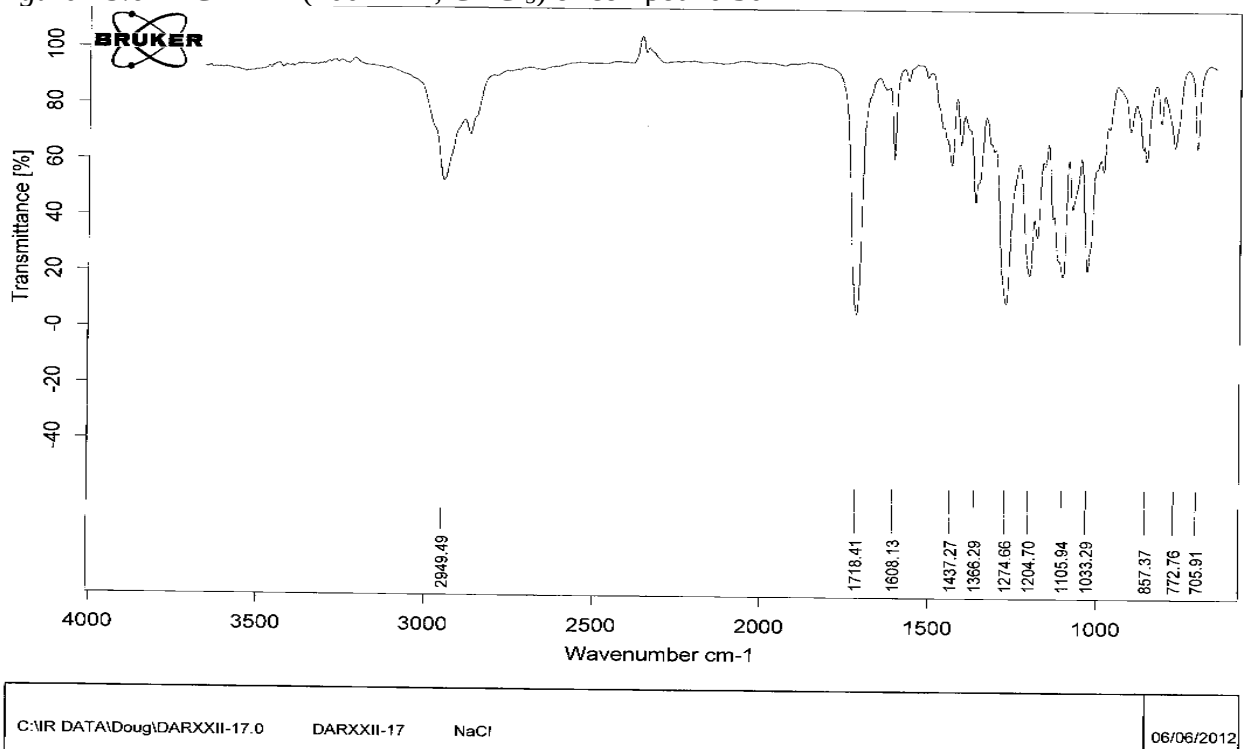
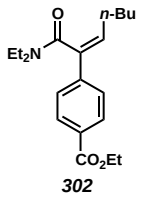


Figure A3.63 Infrared spectrum (thin film) of compound **301**



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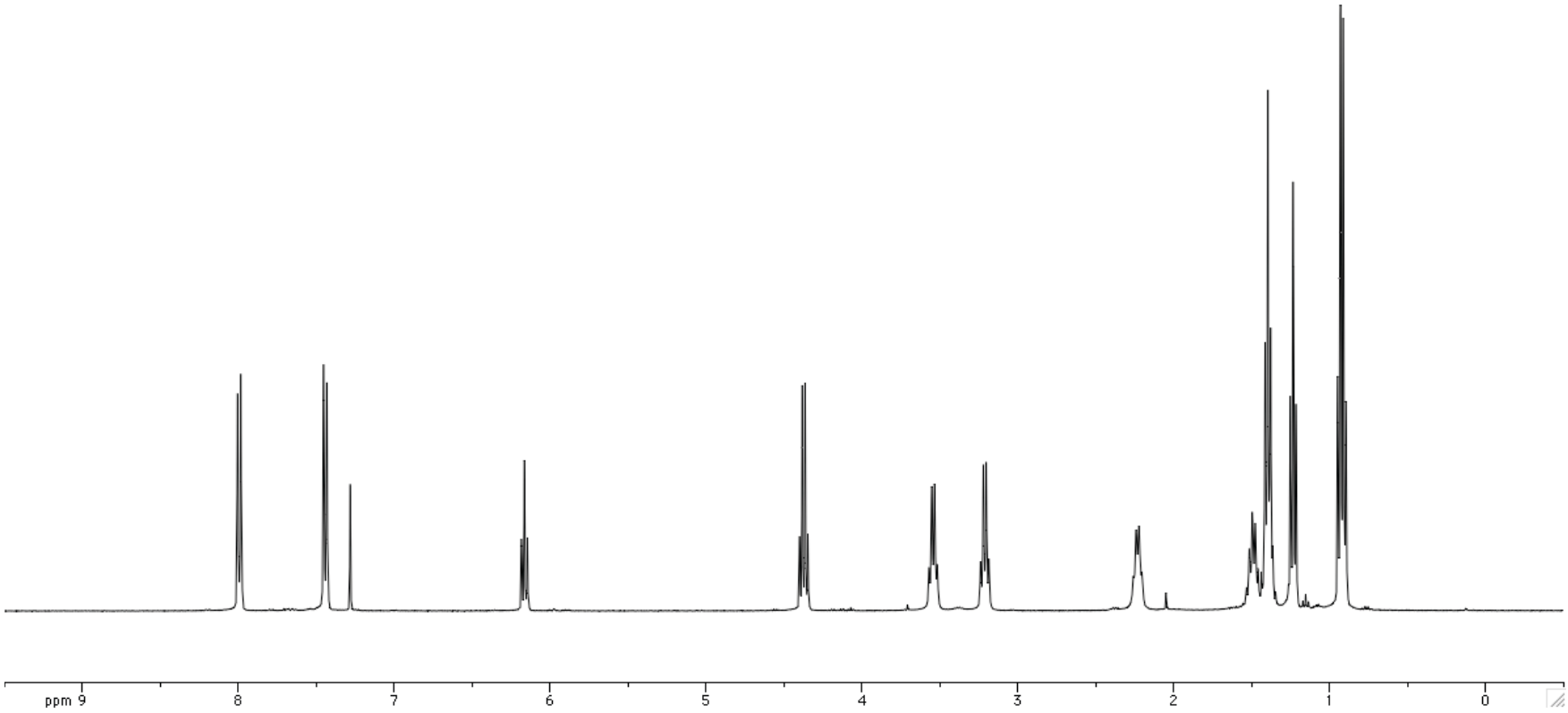
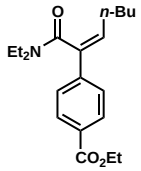


Figure A3.64 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **302**



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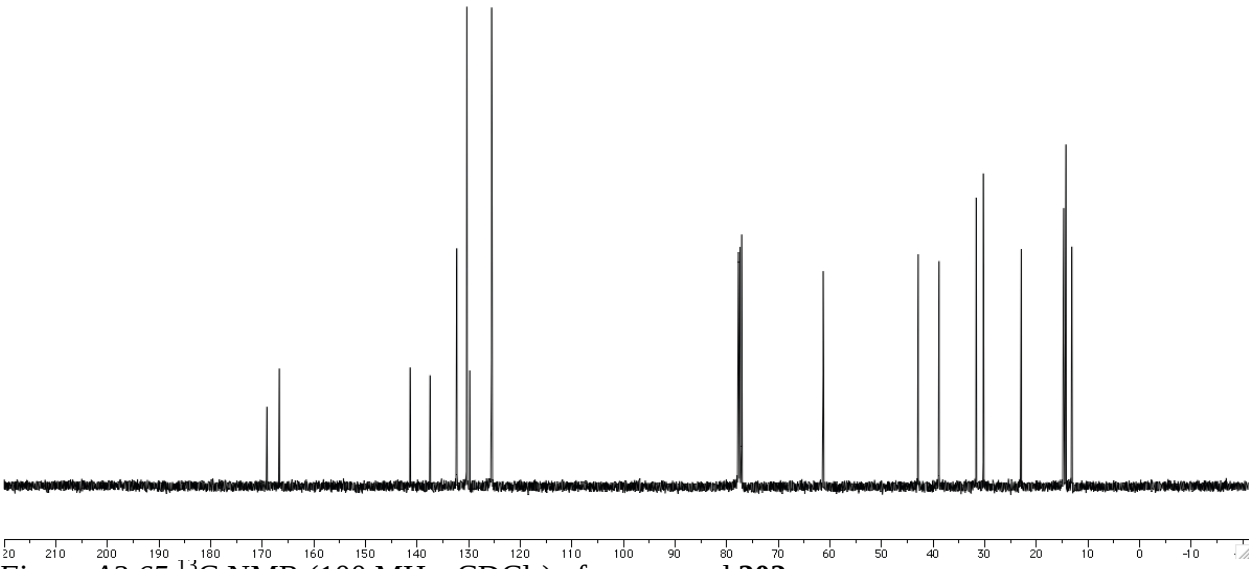


Figure A3.65 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **302**

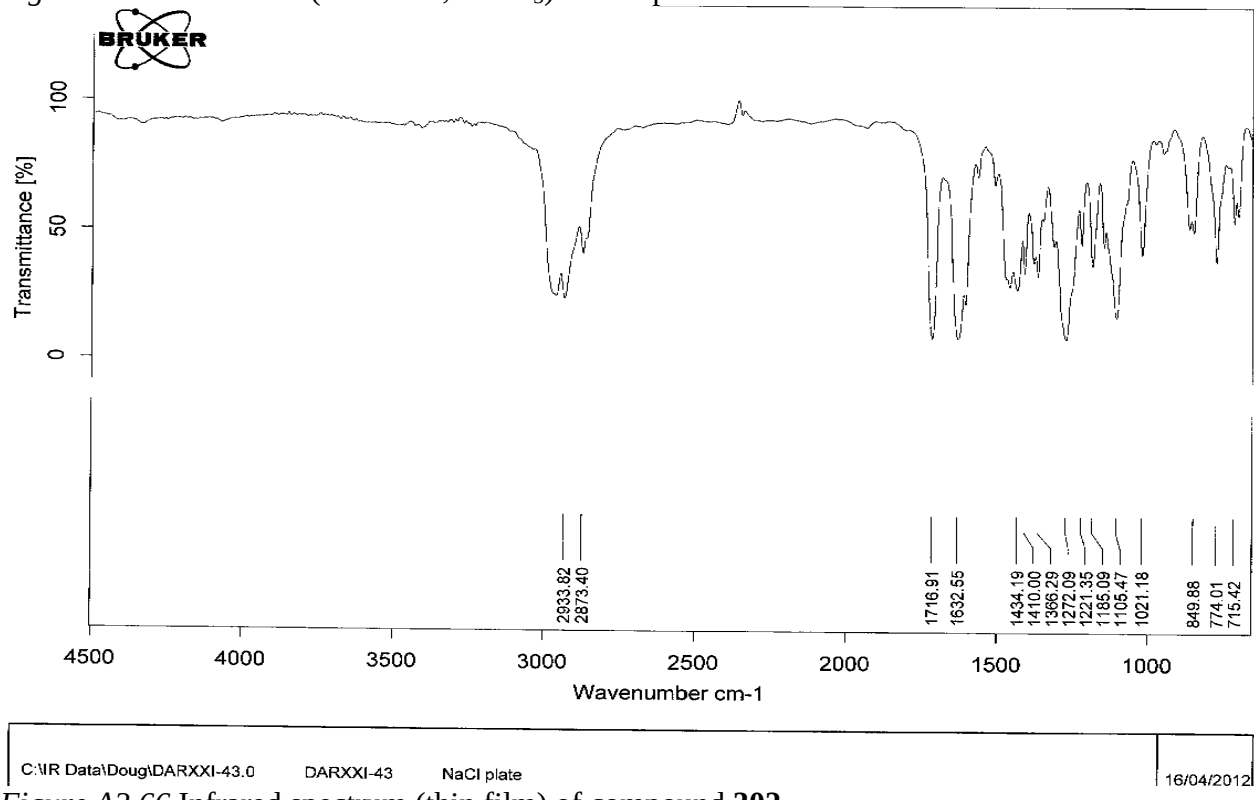
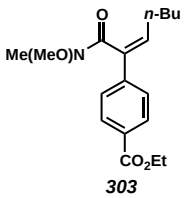


Figure A3.66 Infrared spectrum (thin film) of compound **302**



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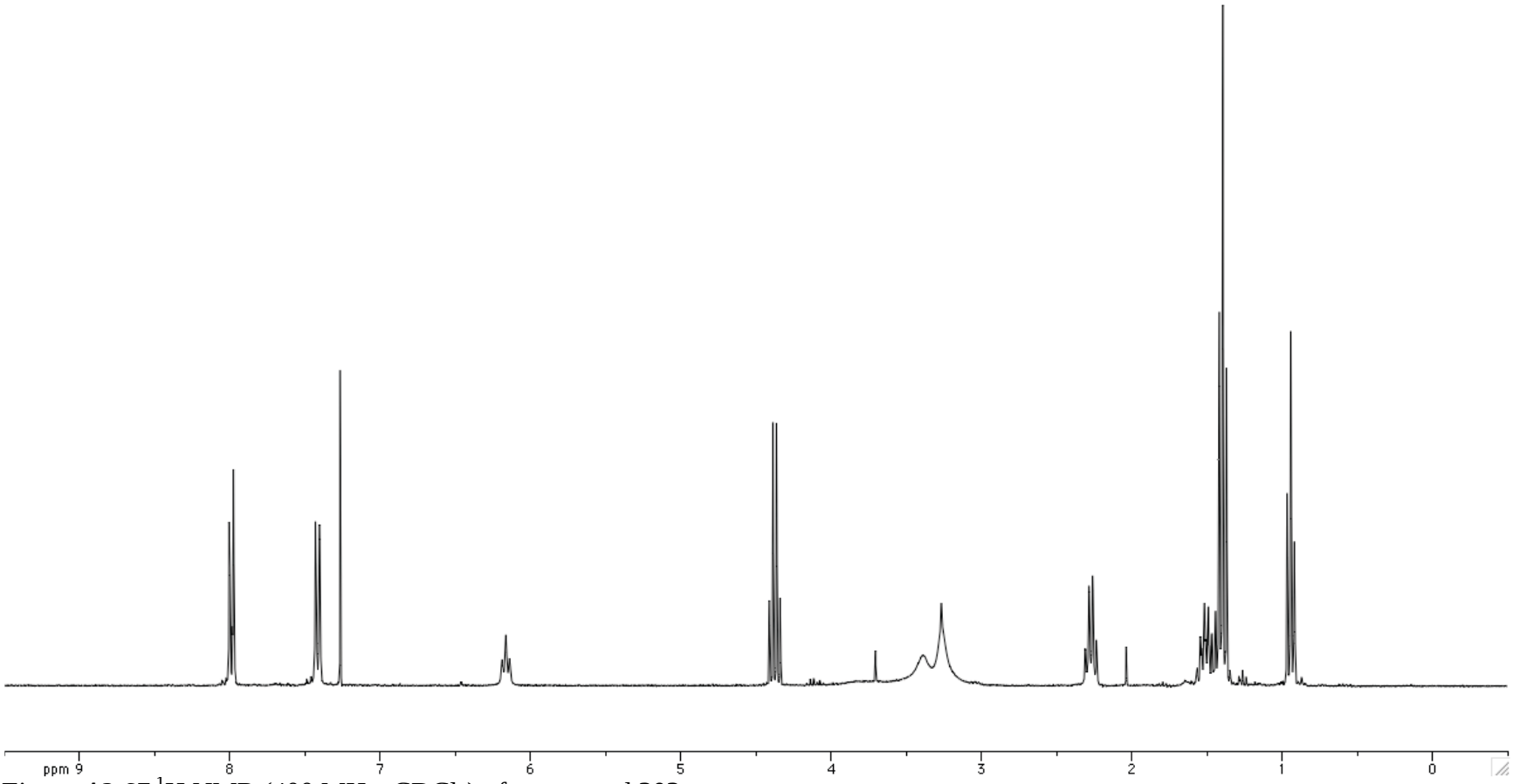


Figure A3.67 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **303**

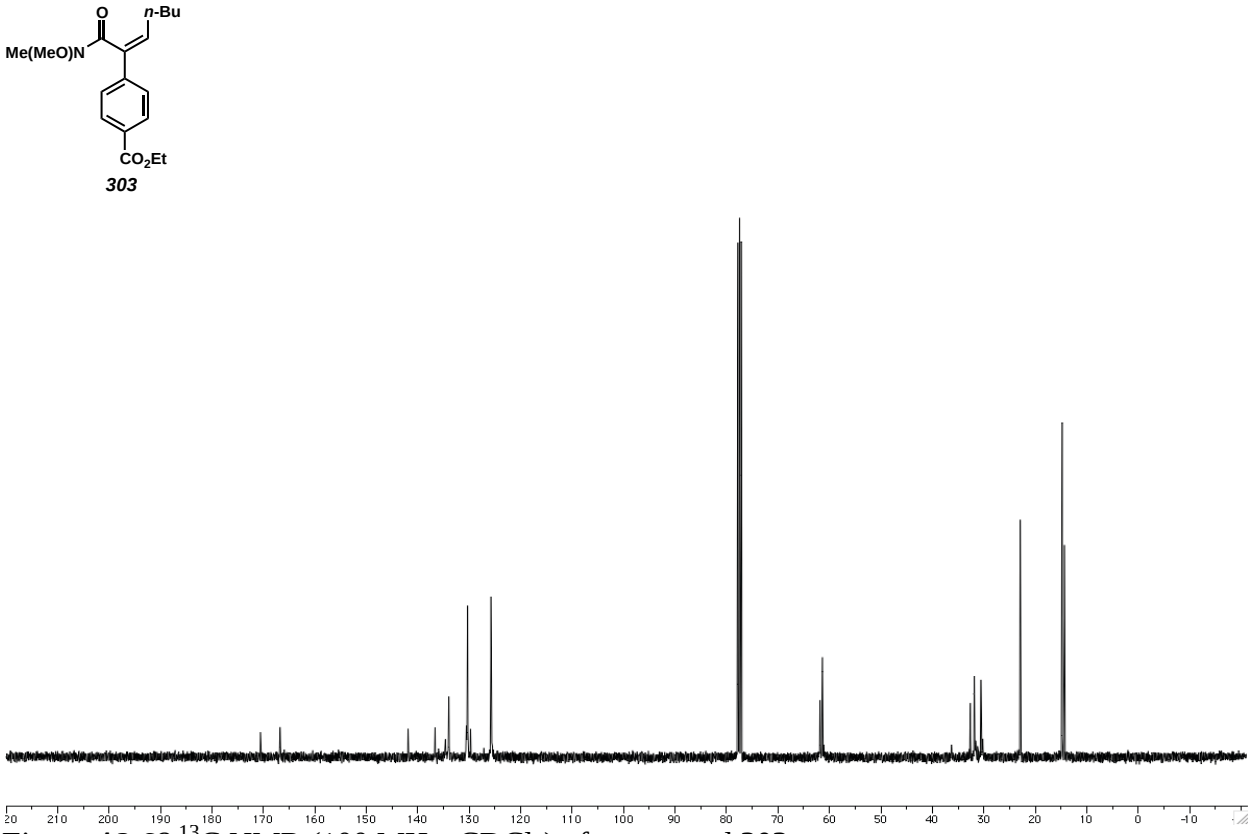


Figure A3.68 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **303**

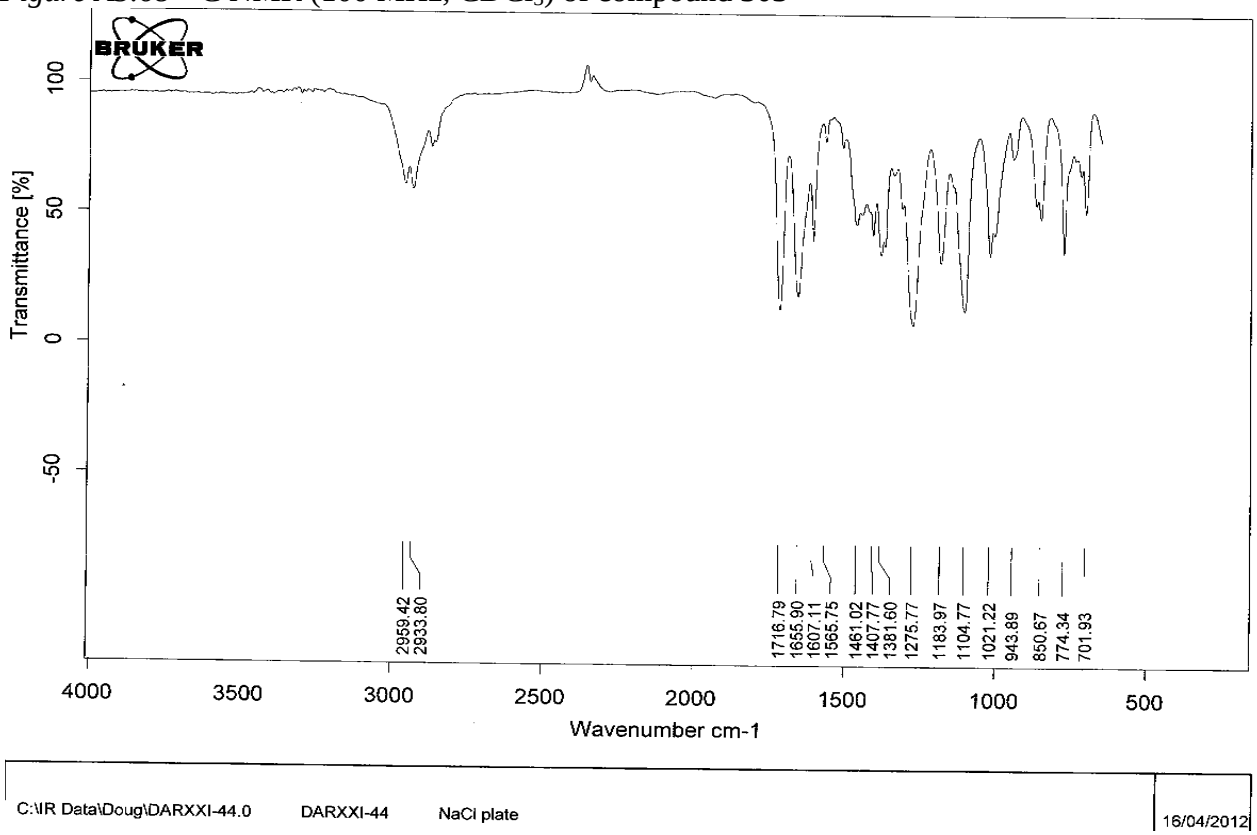
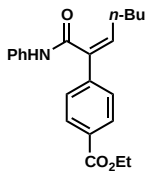


Figure A3.69 Infrared spectrum (thin film) of compound **303**



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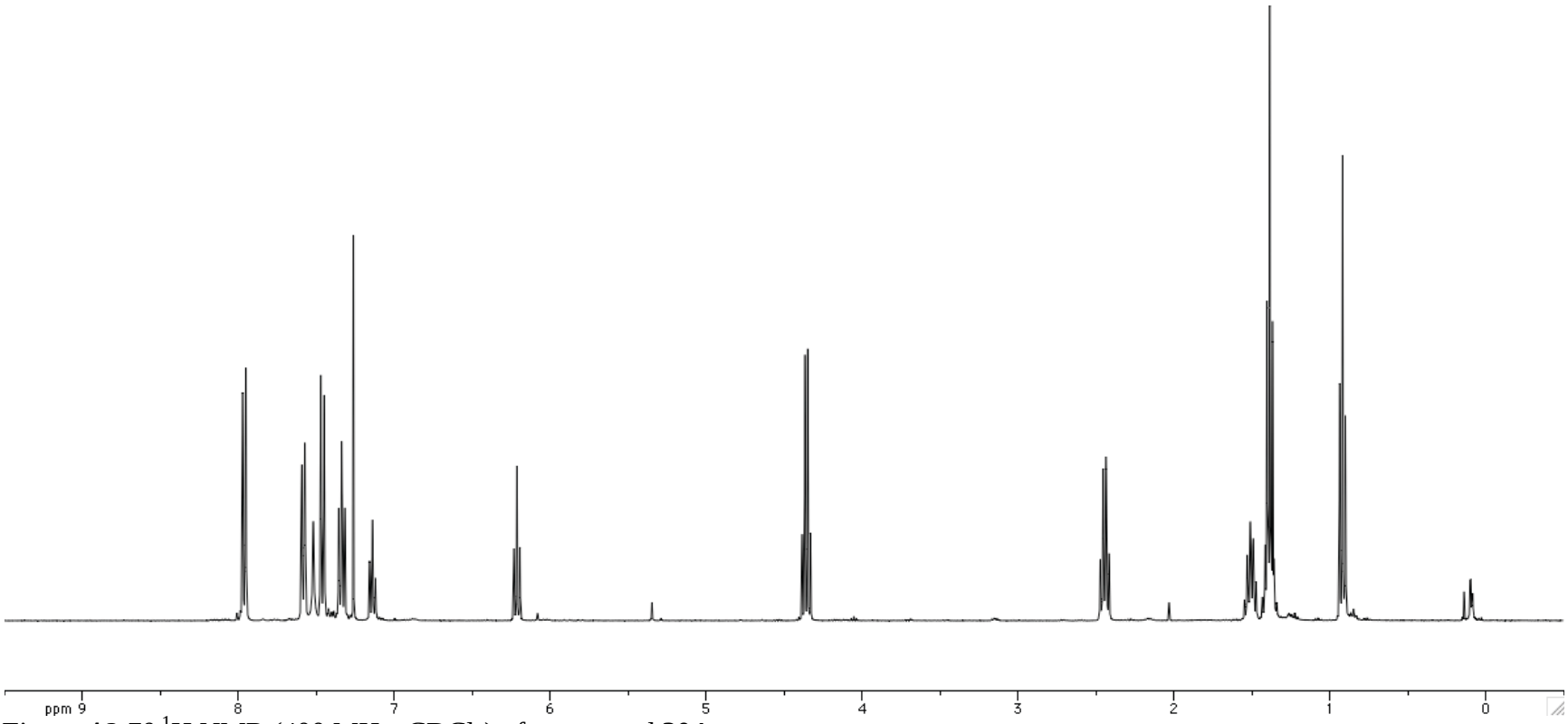
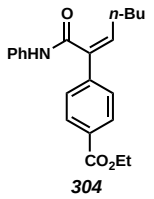


Figure A3.70 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **304**



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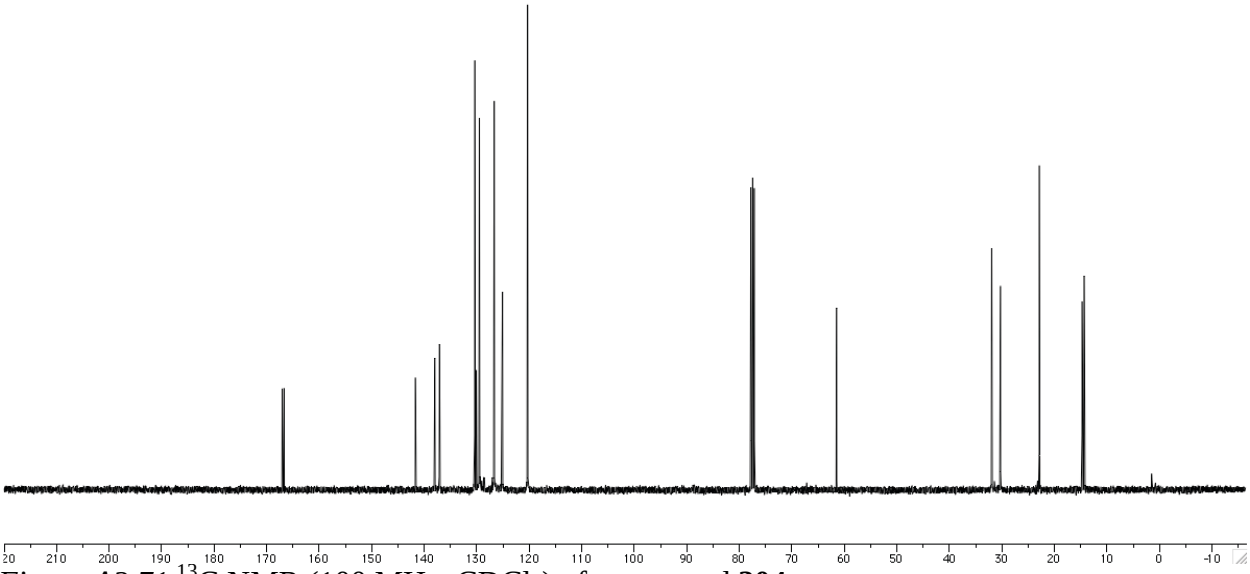


Figure A3.71 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **304**

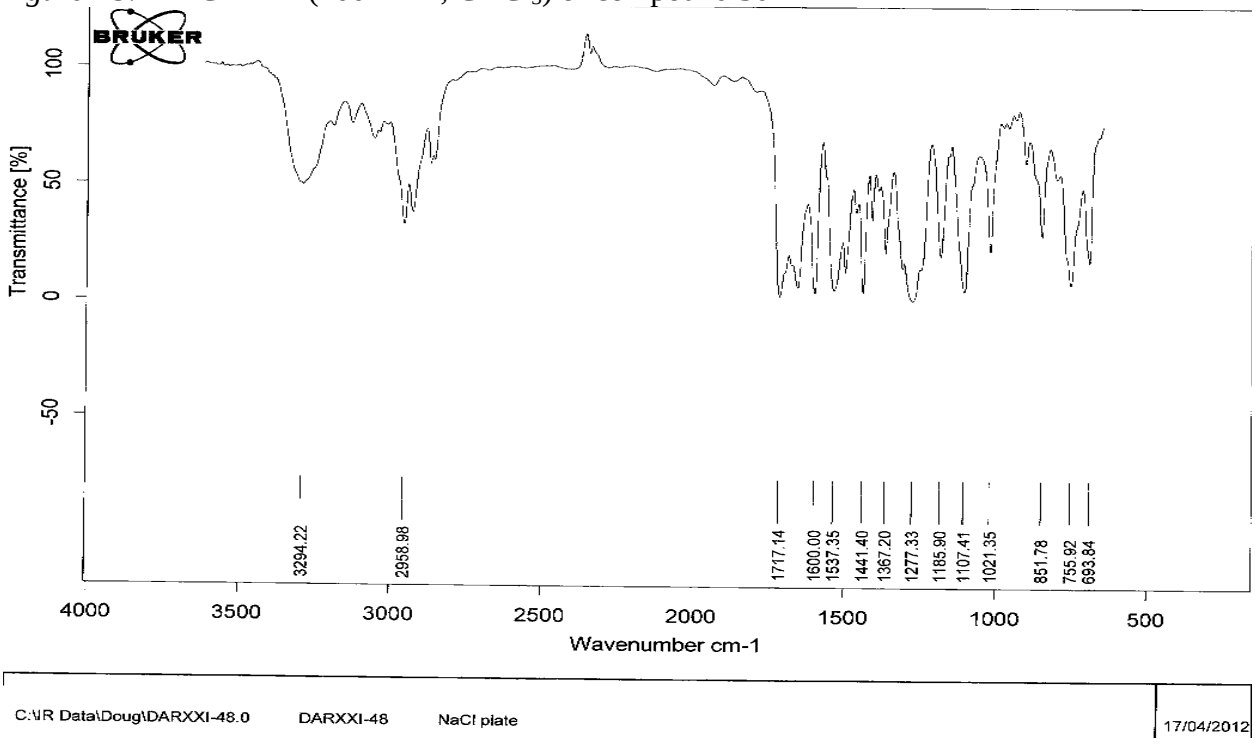
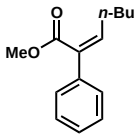


Figure A3.72 Infrared spectrum (thin film) of compound **304**



306

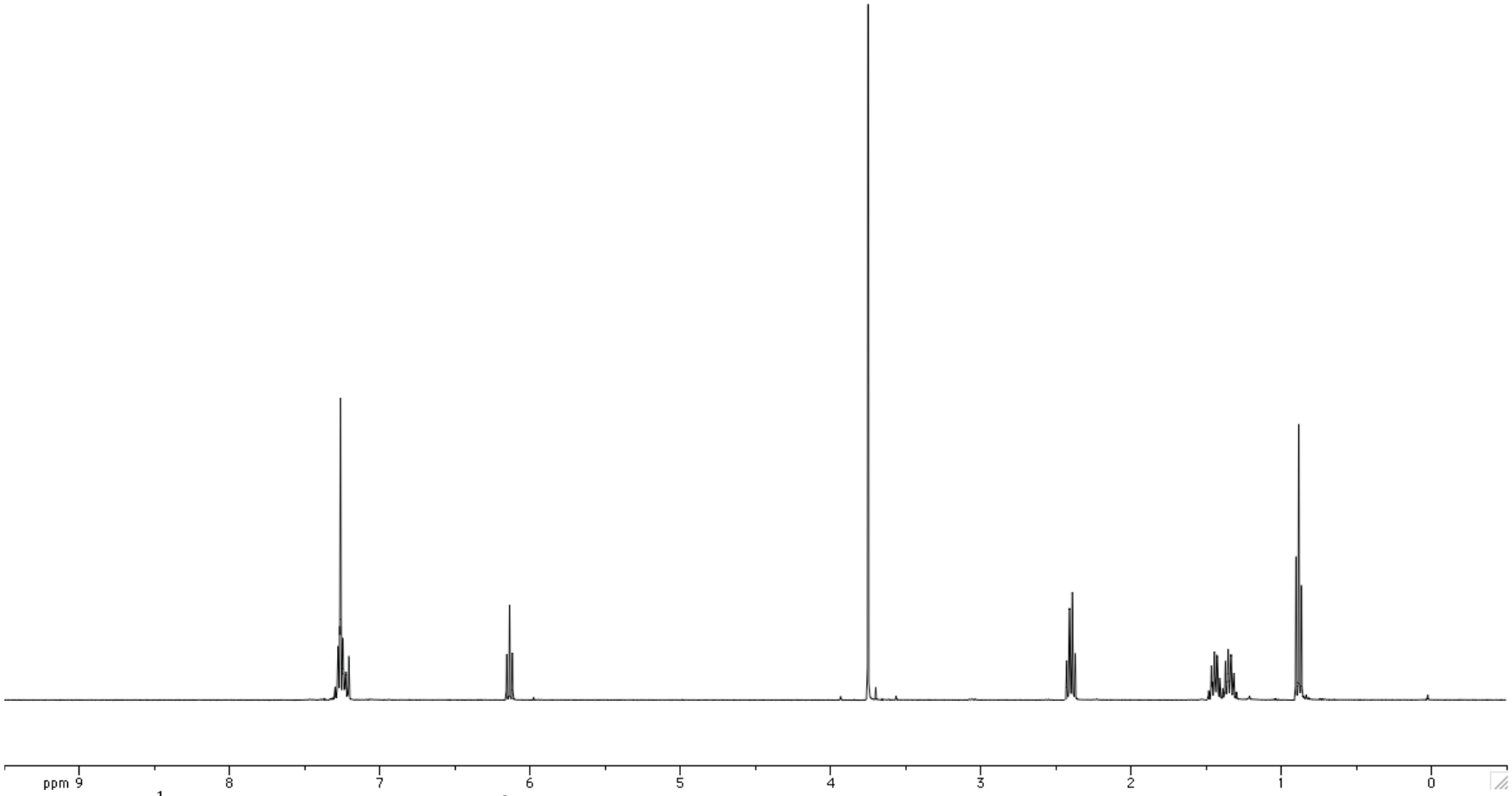


Figure A3.73 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **306**

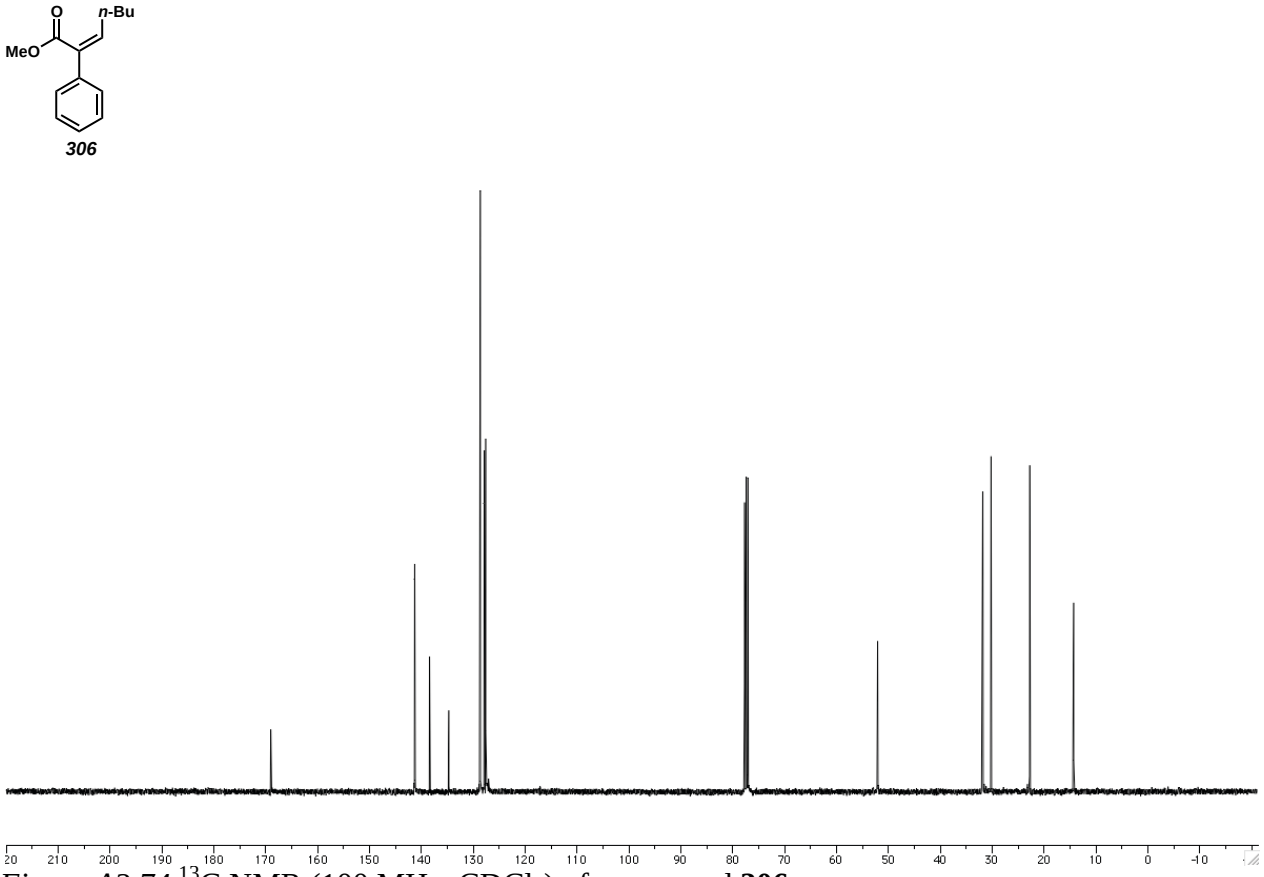


Figure A3.74 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **306**

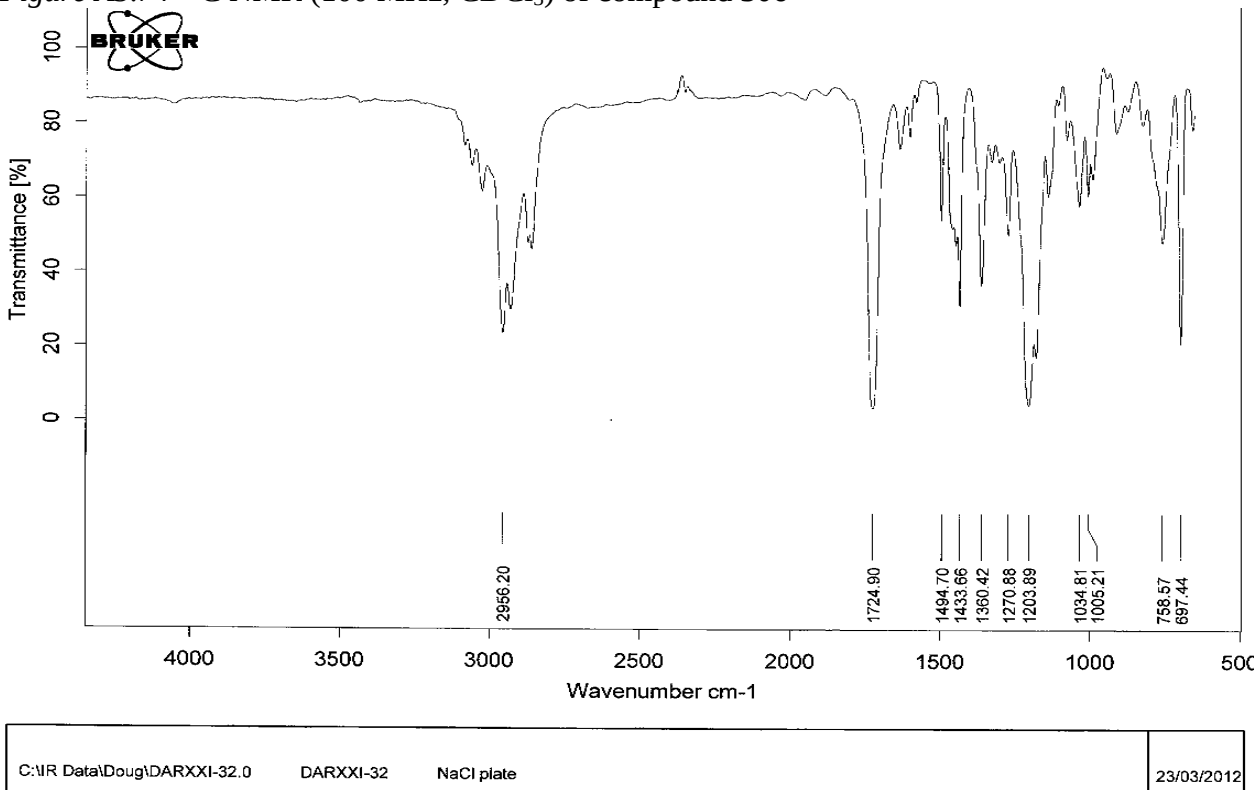
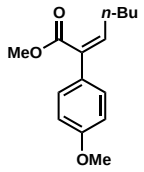


Figure A3.75 Infrared spectrum (thin film) of compound **306**



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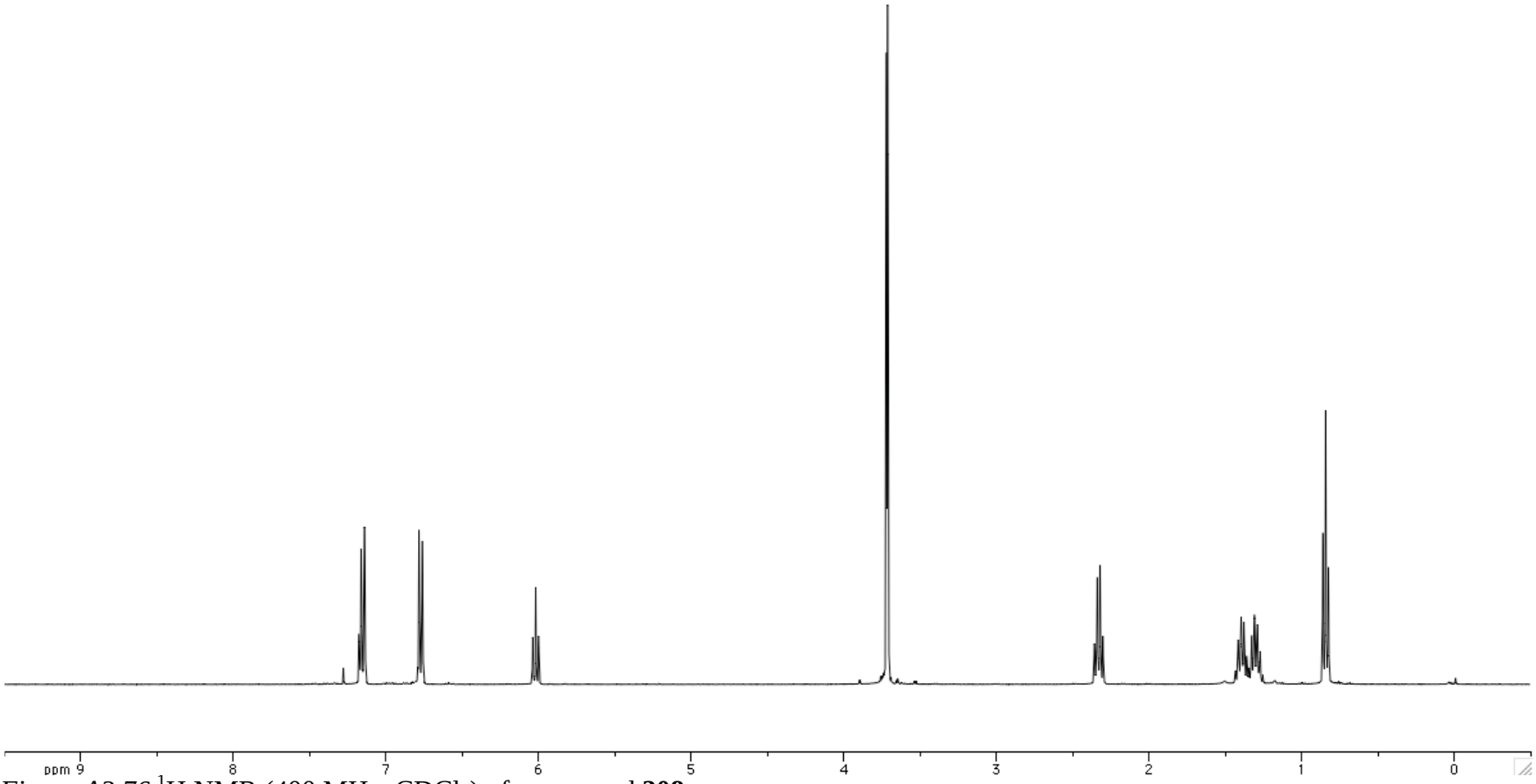
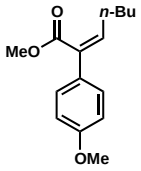


Figure A3.76 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **308**



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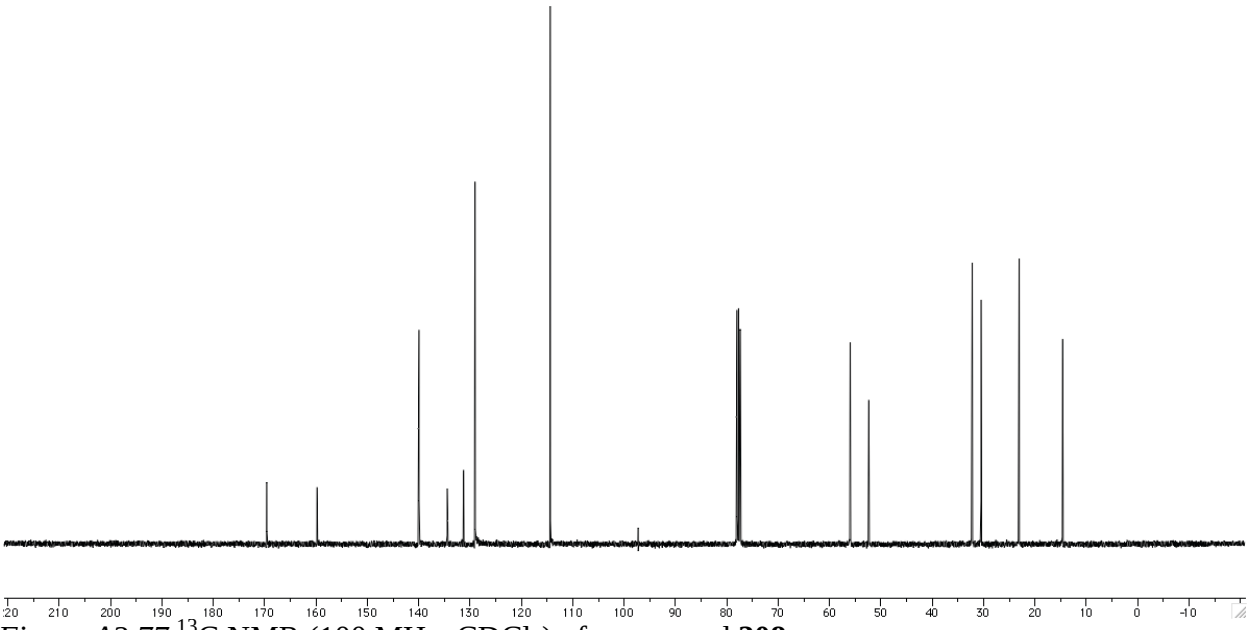


Figure A3.77 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **308**

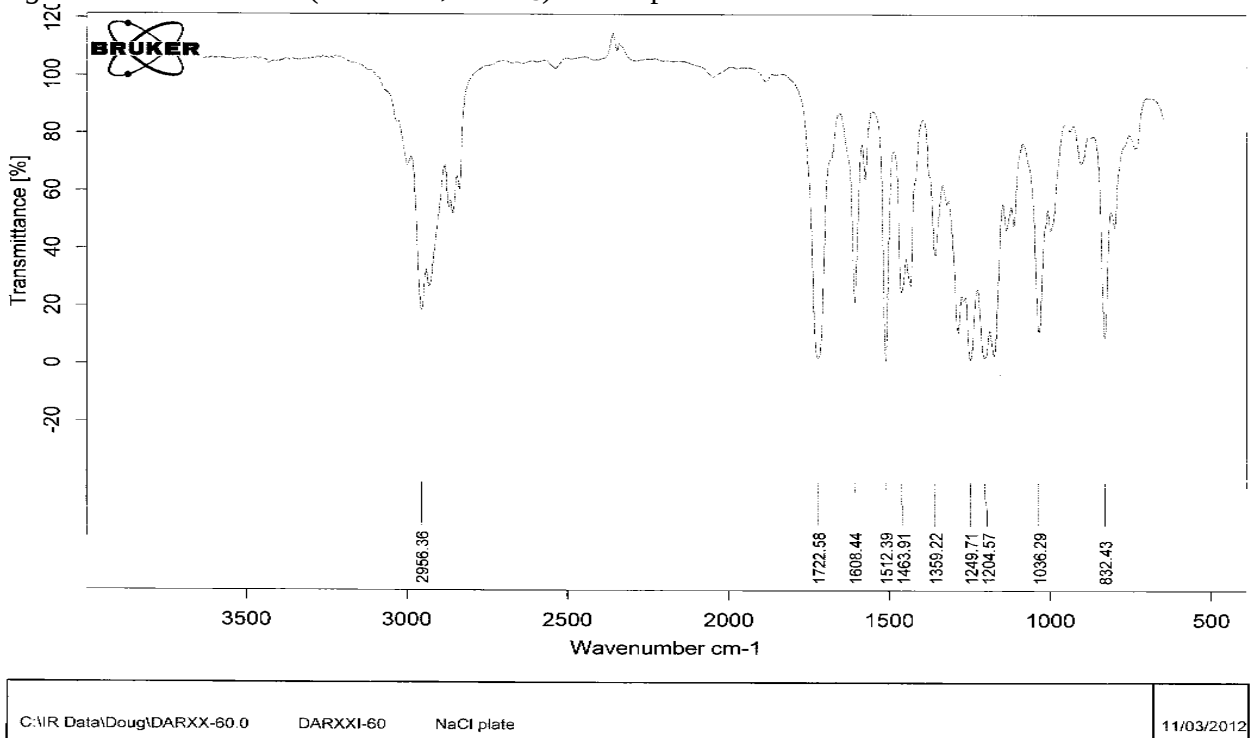
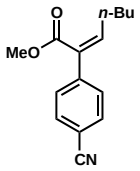


Figure A3.78 Infrared spectrum (thin film) of compound **308**



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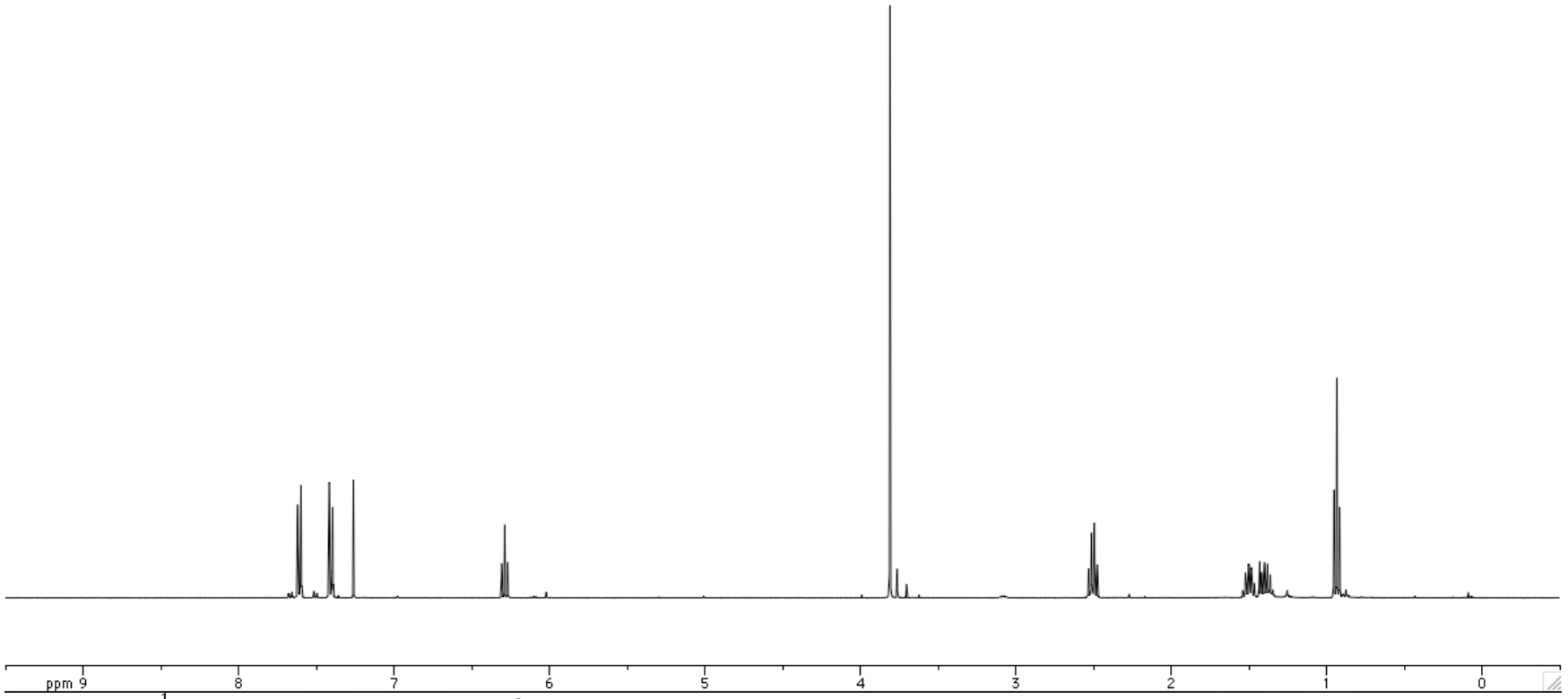


Figure A3.79 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **311**

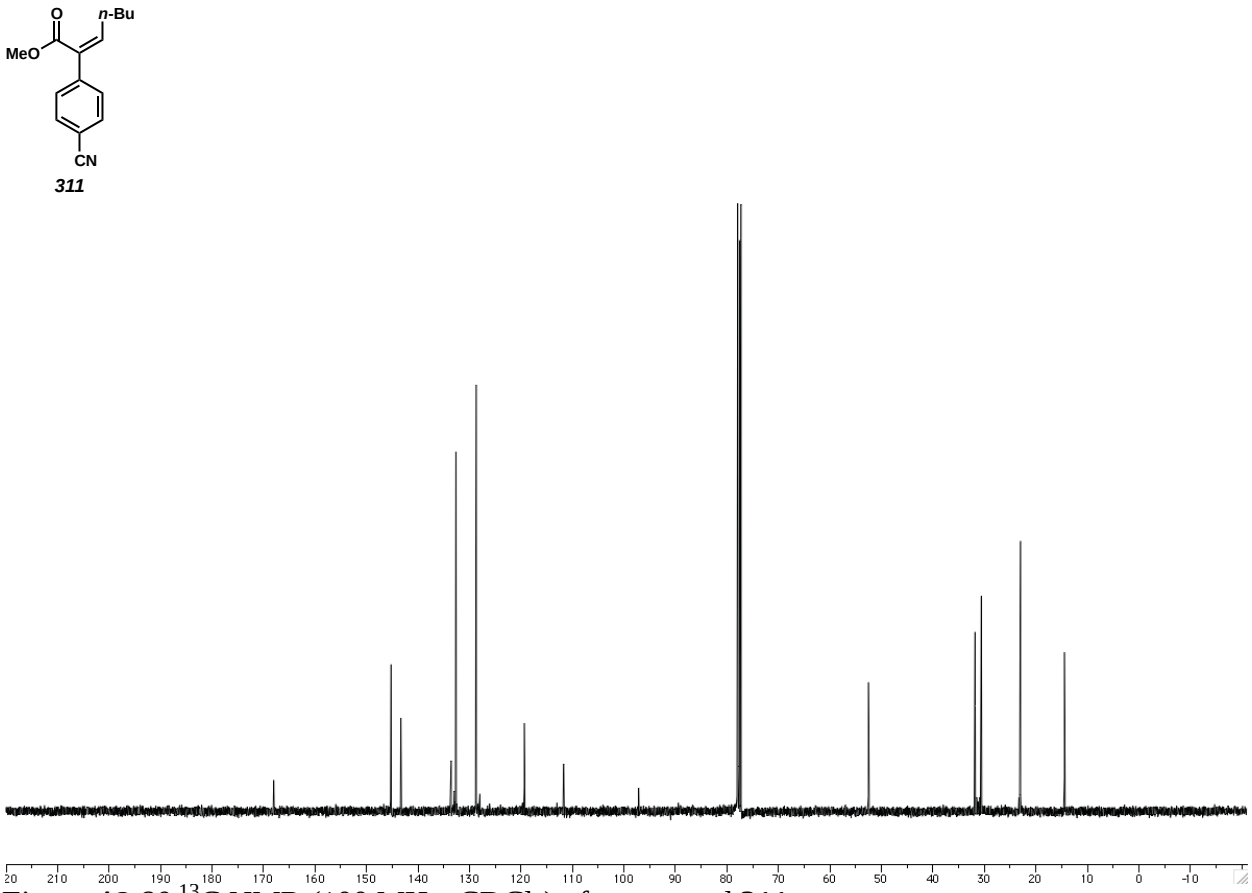


Figure A3.80 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **311**

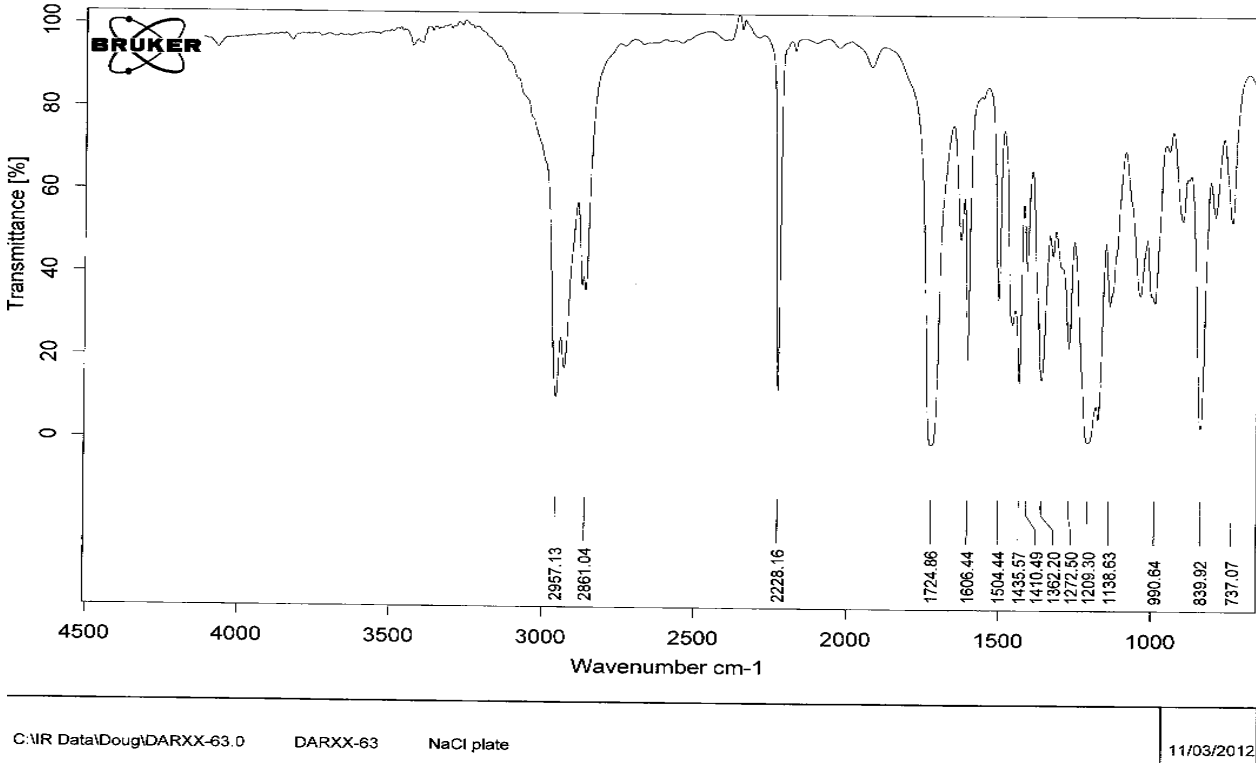
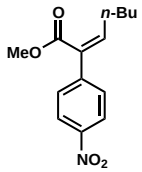


Figure A3.81 Infrared spectrum (thin film) of compound **311**



313

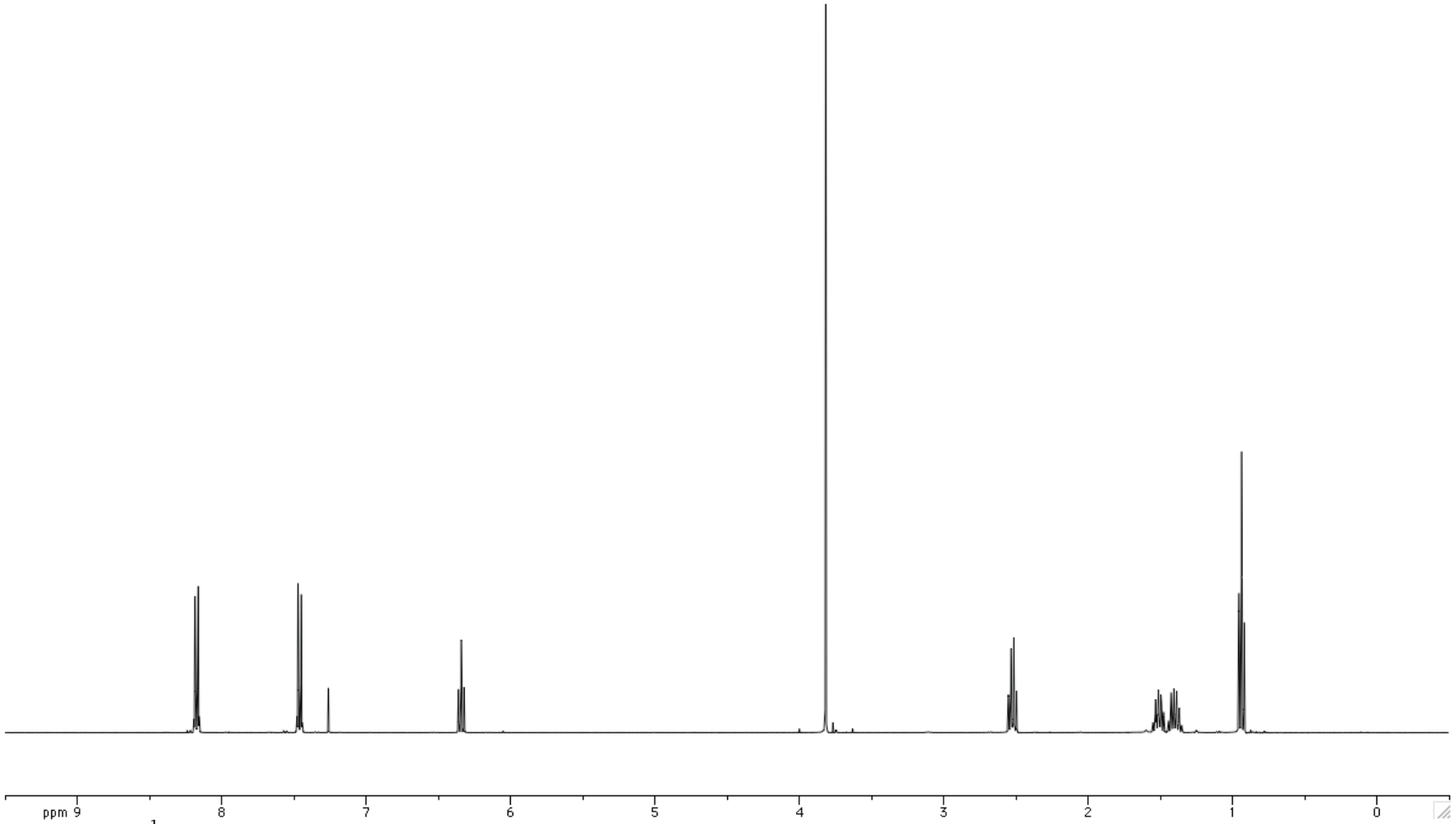


Figure A3.82 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **313**

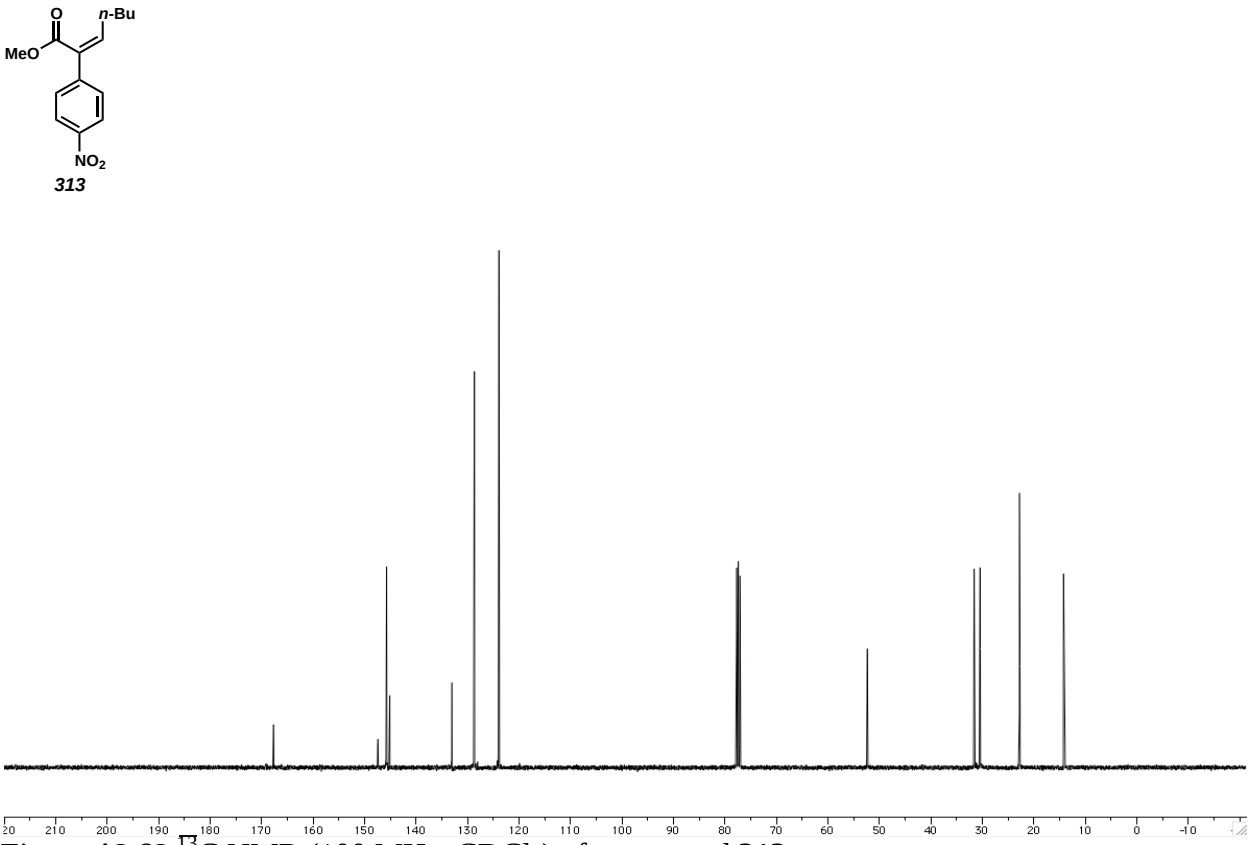


Figure A3.83 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **313**

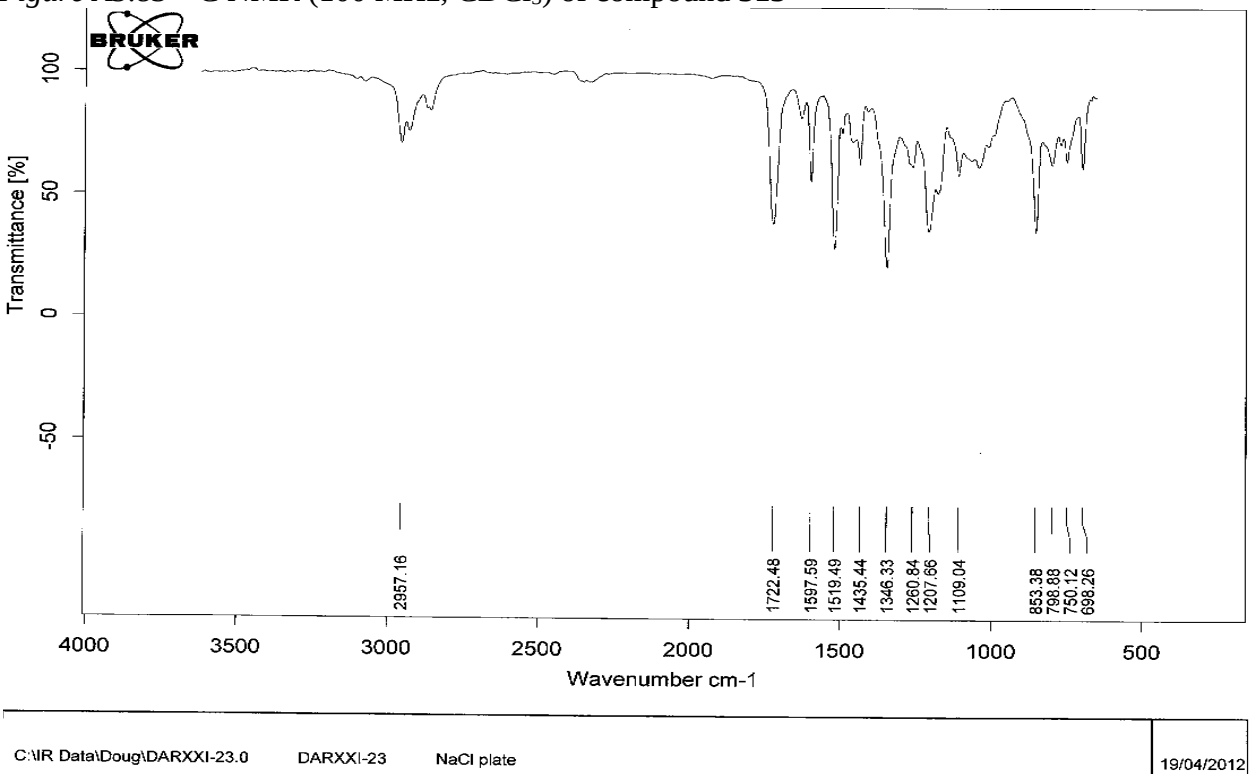
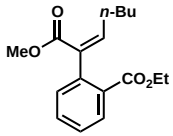


Figure A3.84 Infrared spectrum (thin film) of compound **313**



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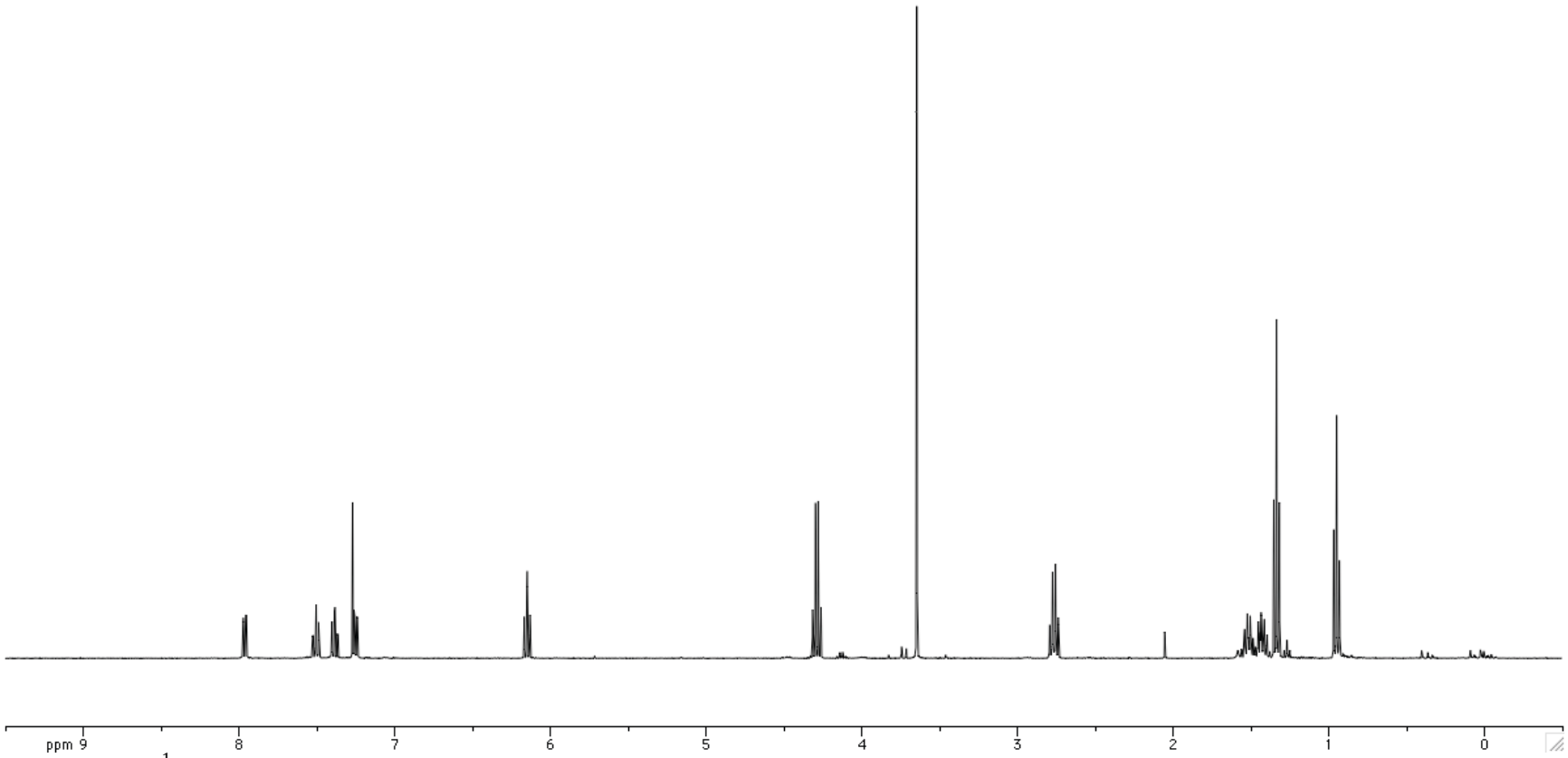
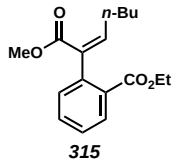


Figure A3.85 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **315**



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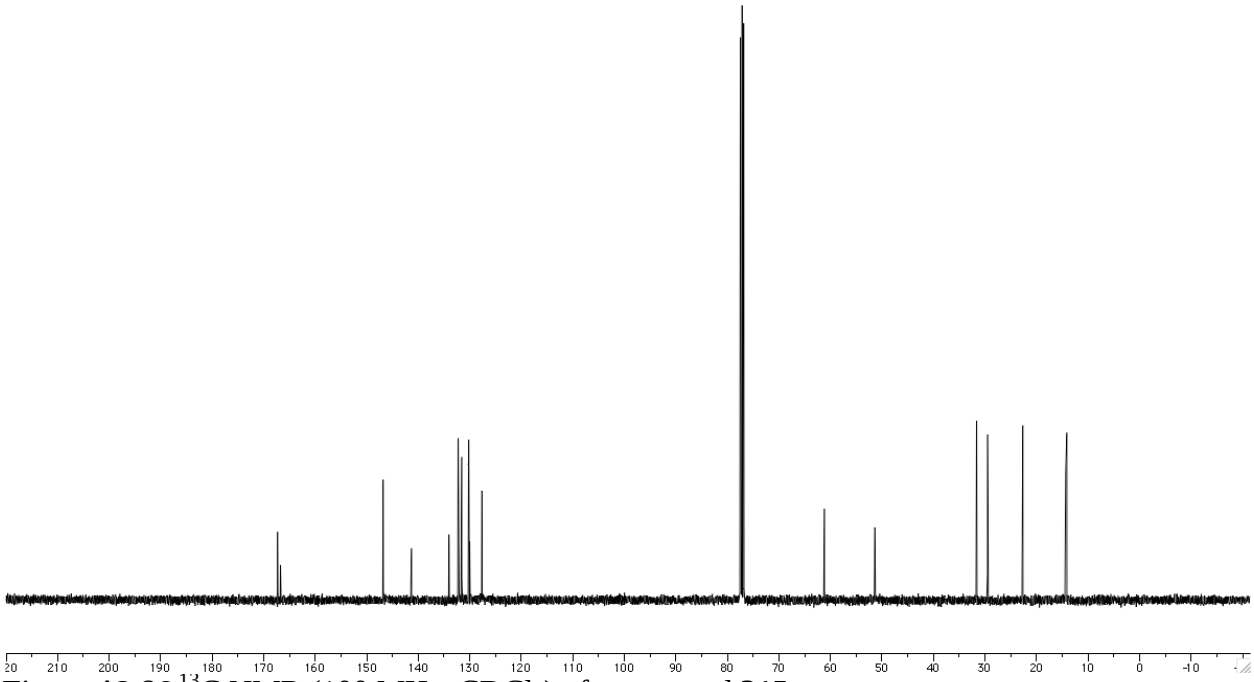


Figure A3.86 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **315**

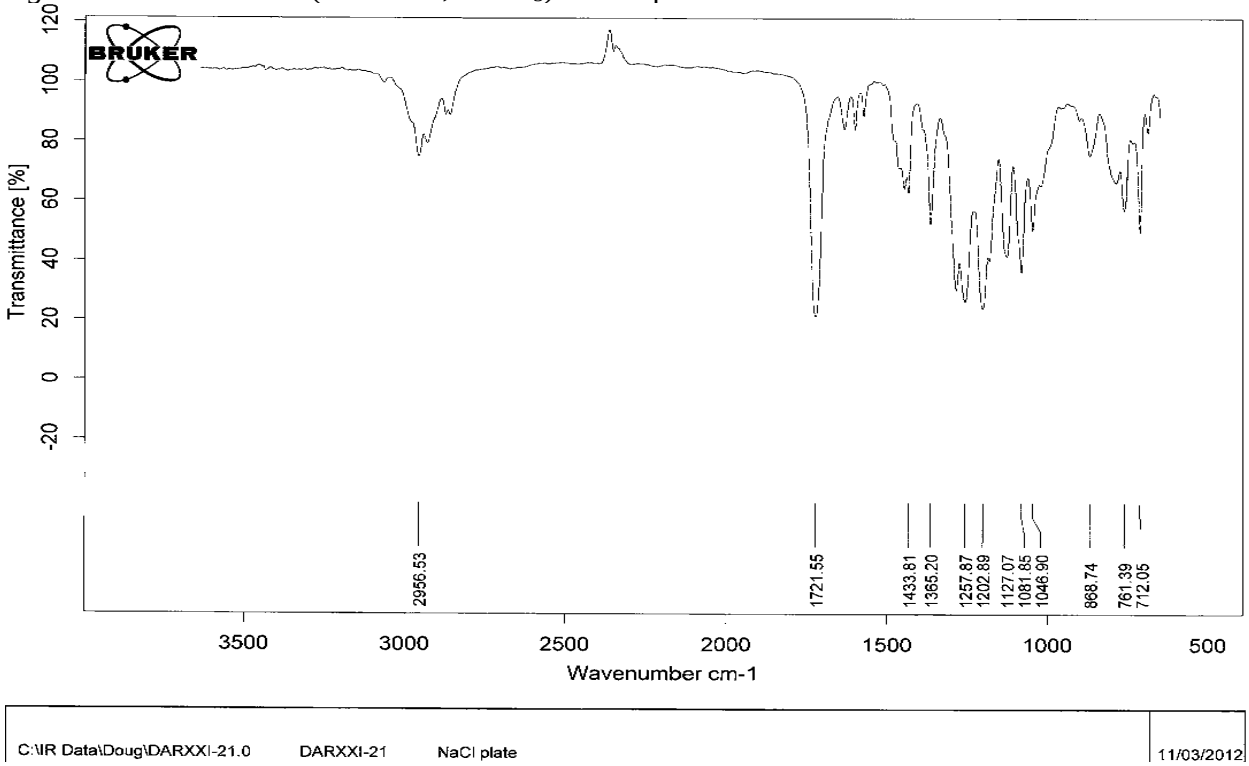
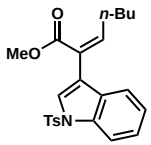


Figure A3.87 Infrared spectrum (thin film) of compound **315**



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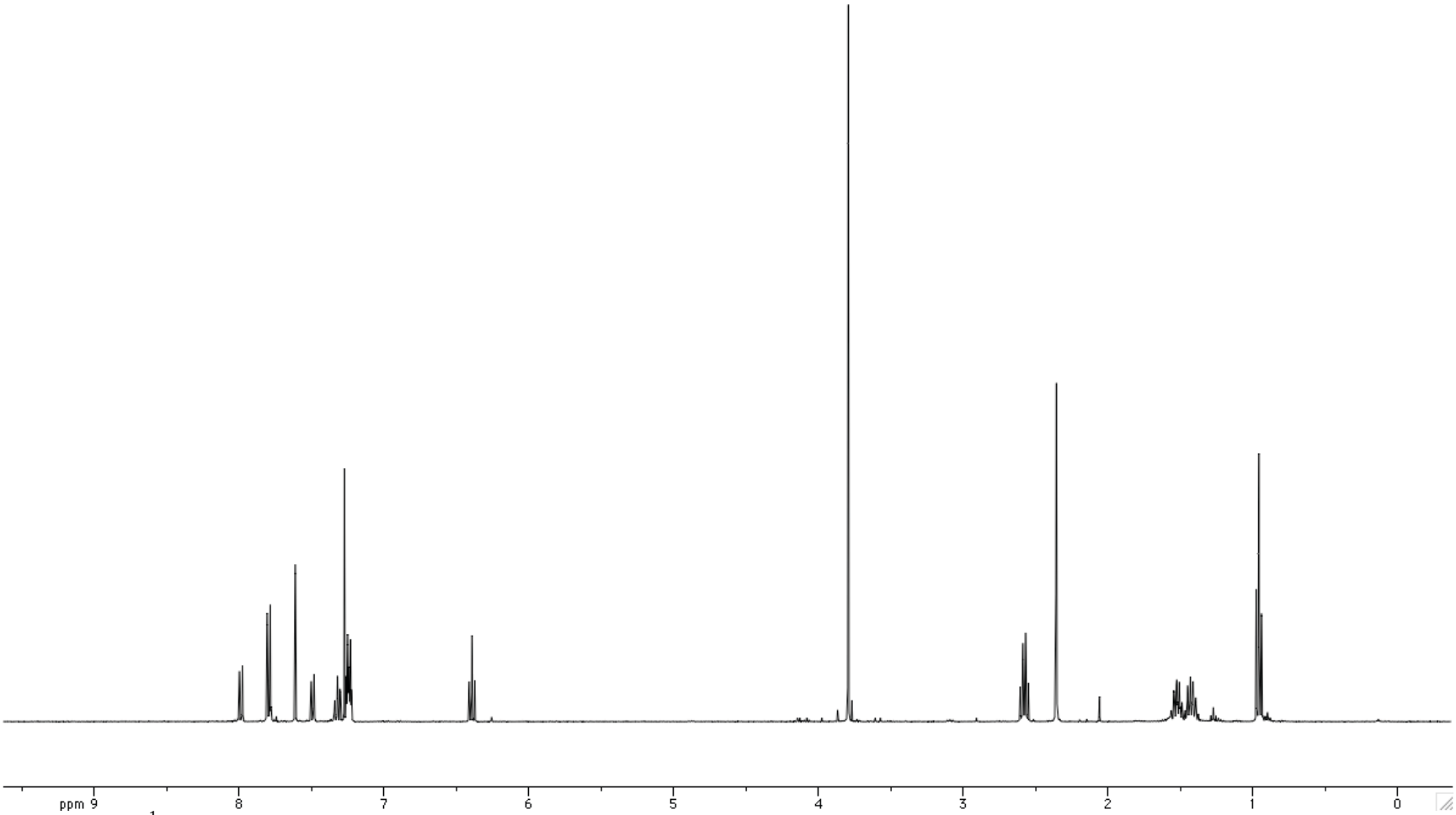
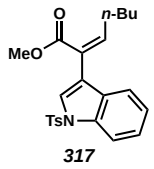


Figure A3.88 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **317**



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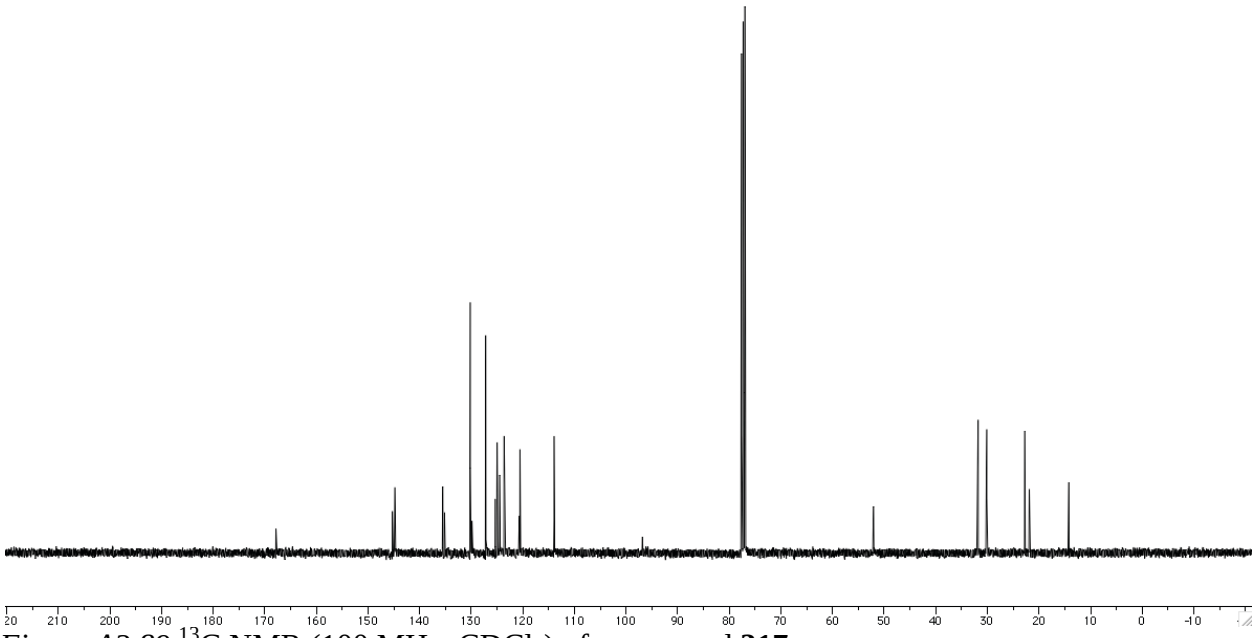


Figure A3.89 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **317**

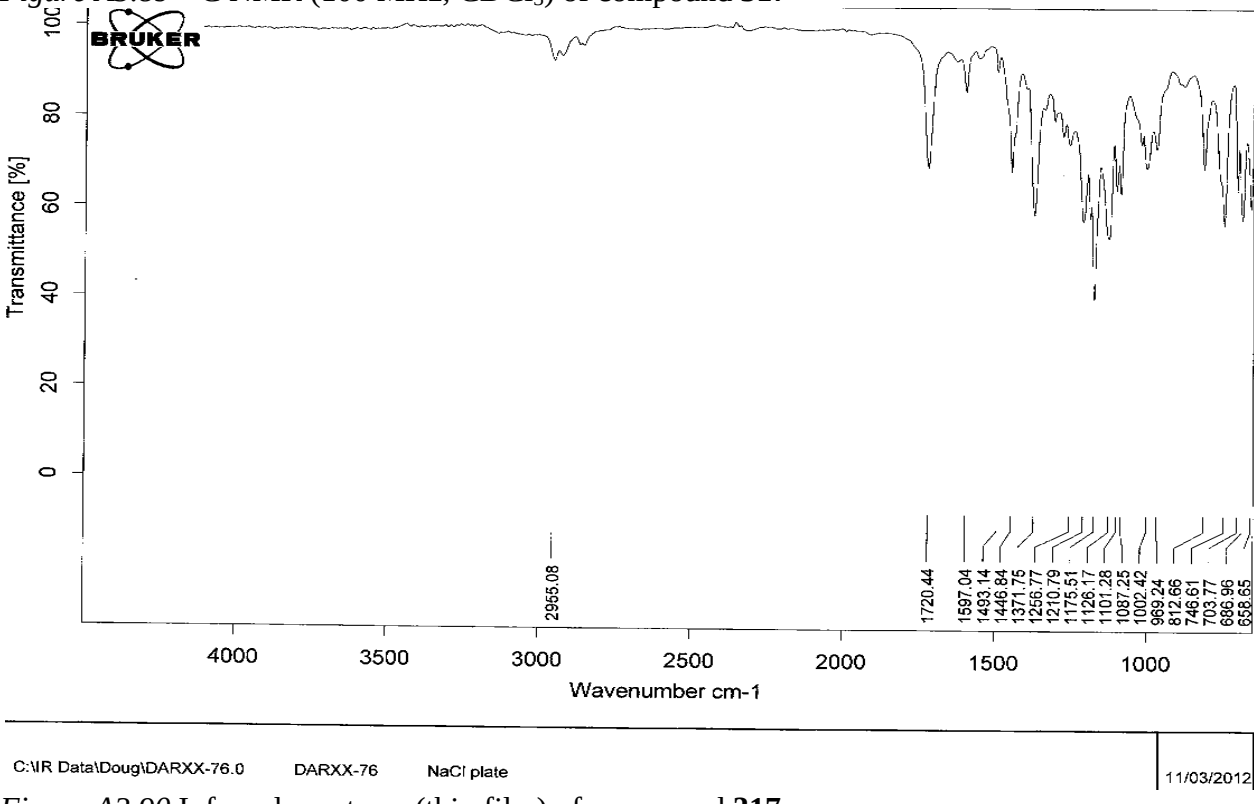
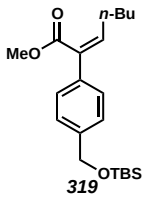


Figure A3.90 Infrared spectrum (thin film) of compound **317**



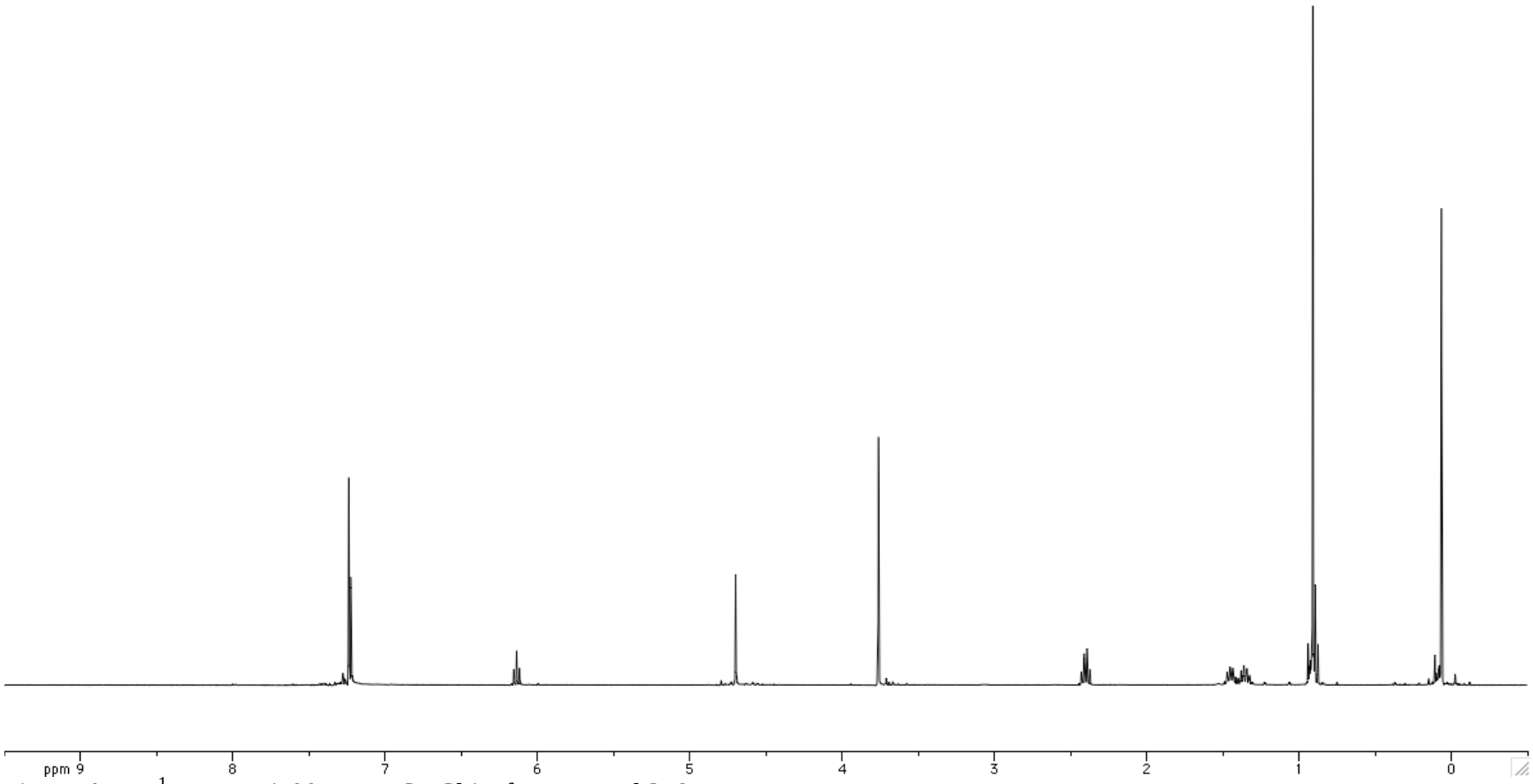
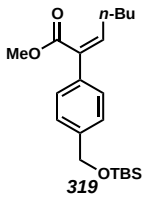


Figure A3.91 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **319**



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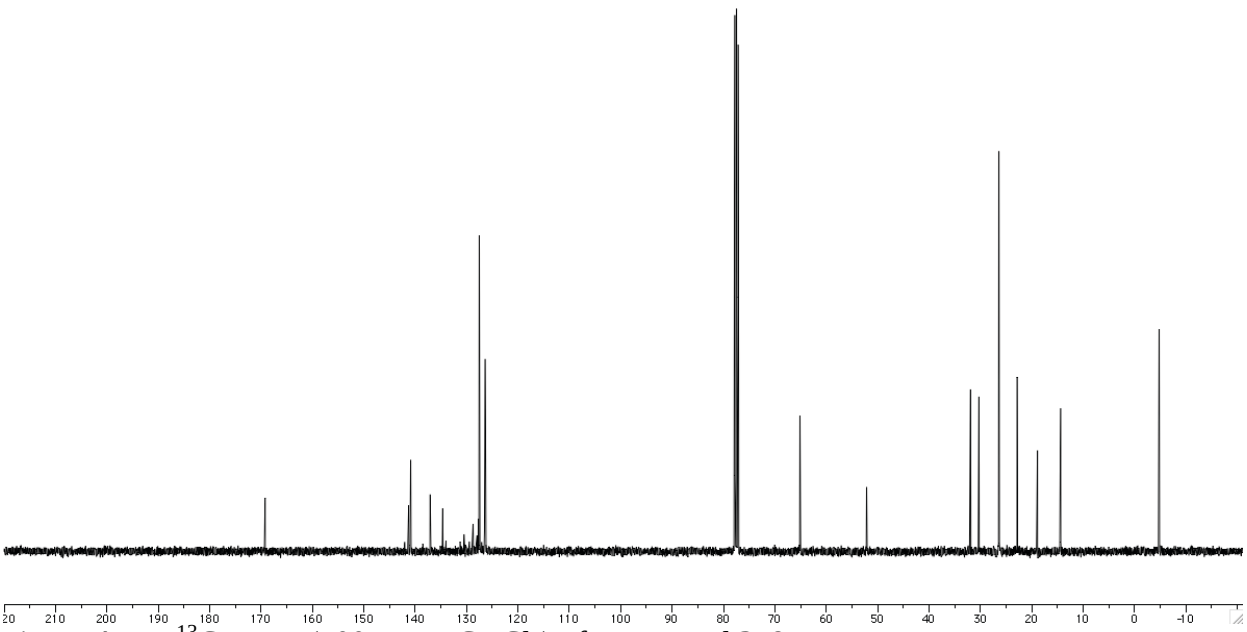


Figure A3.92 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **319**

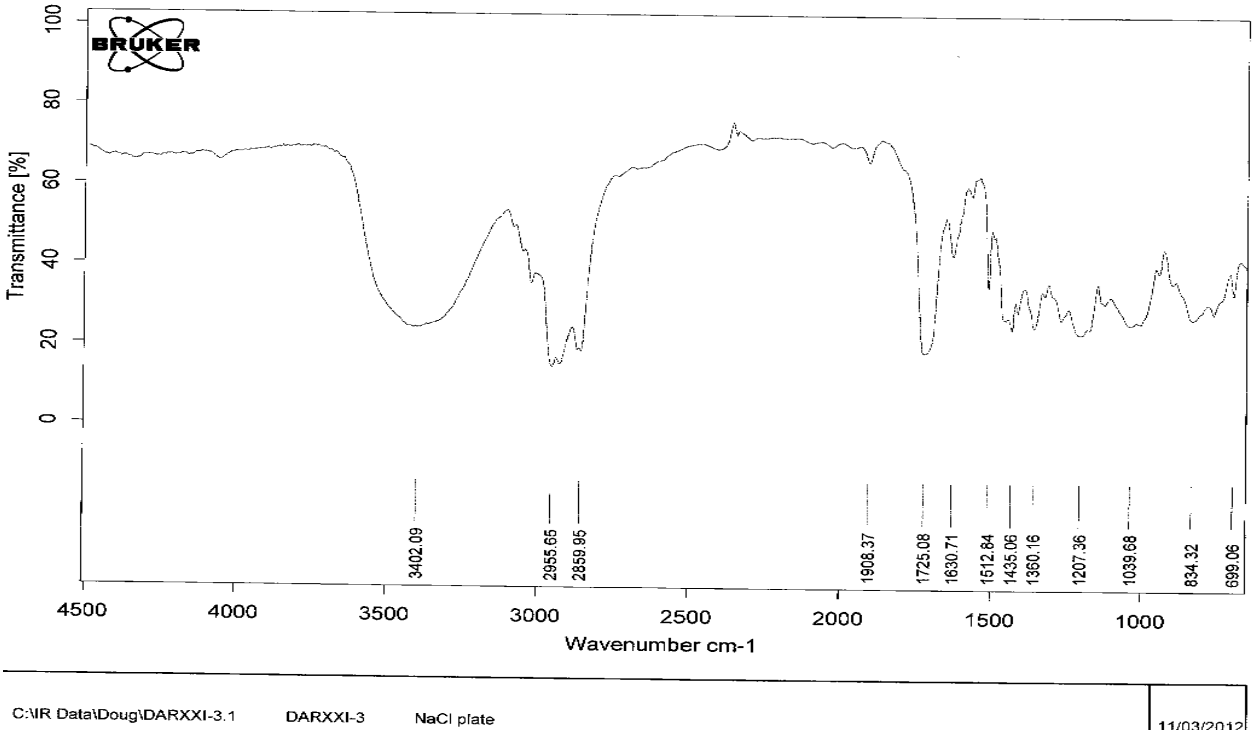
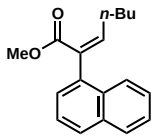


Figure A3.93 Infrared spectrum (thin film) of compound **319**



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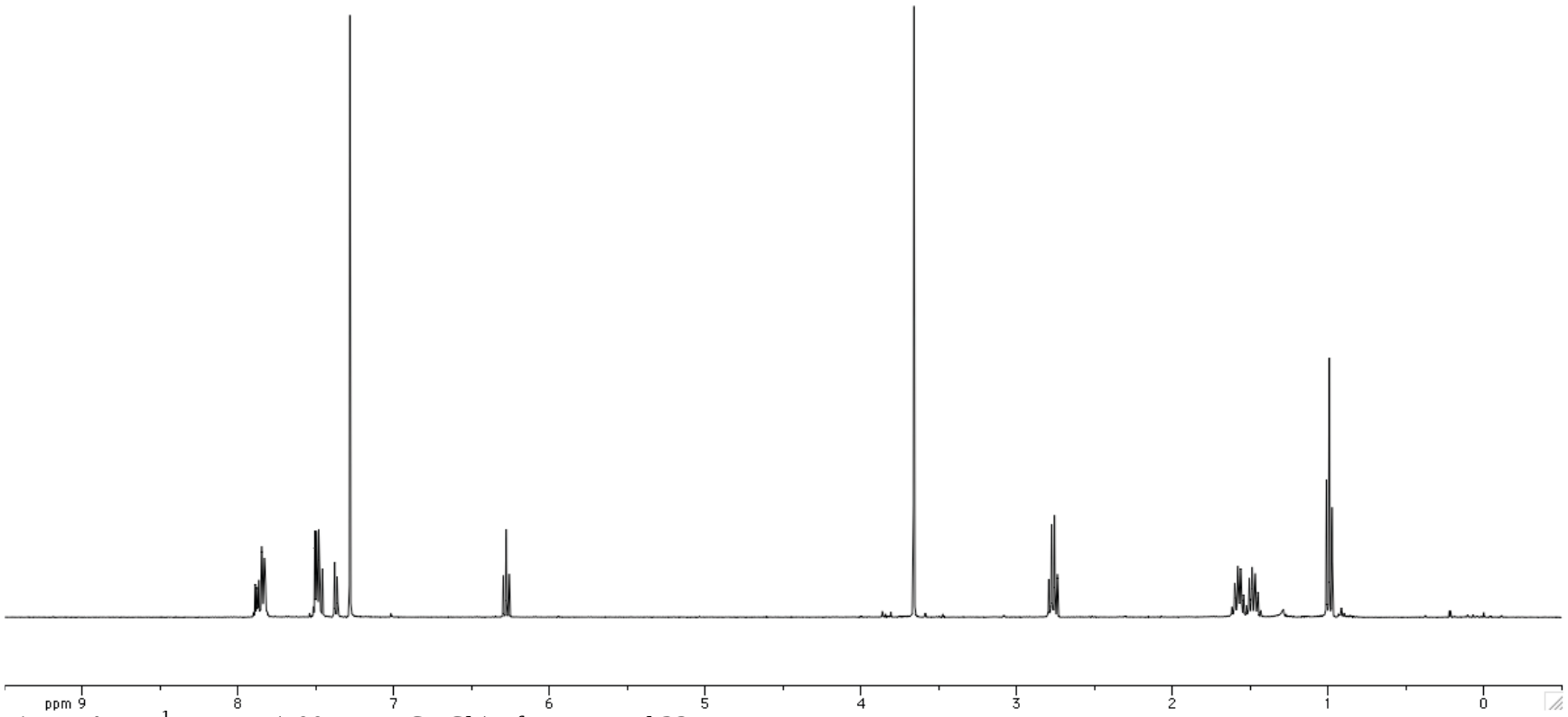
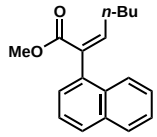


Figure A3.94 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **321**



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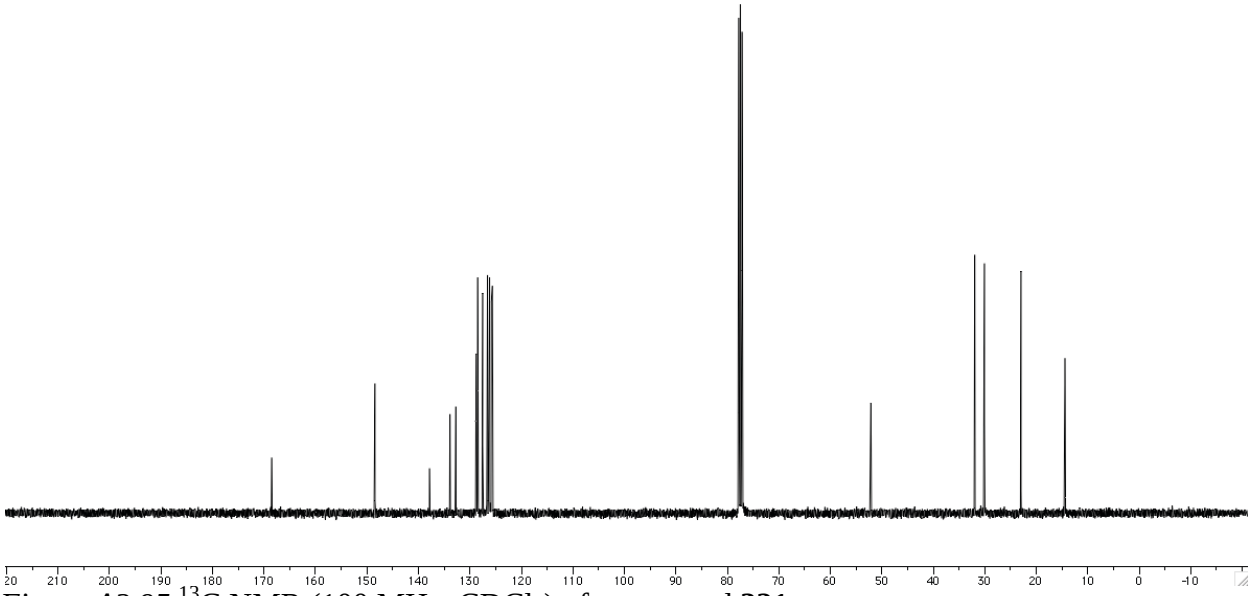


Figure A3.95 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **321**

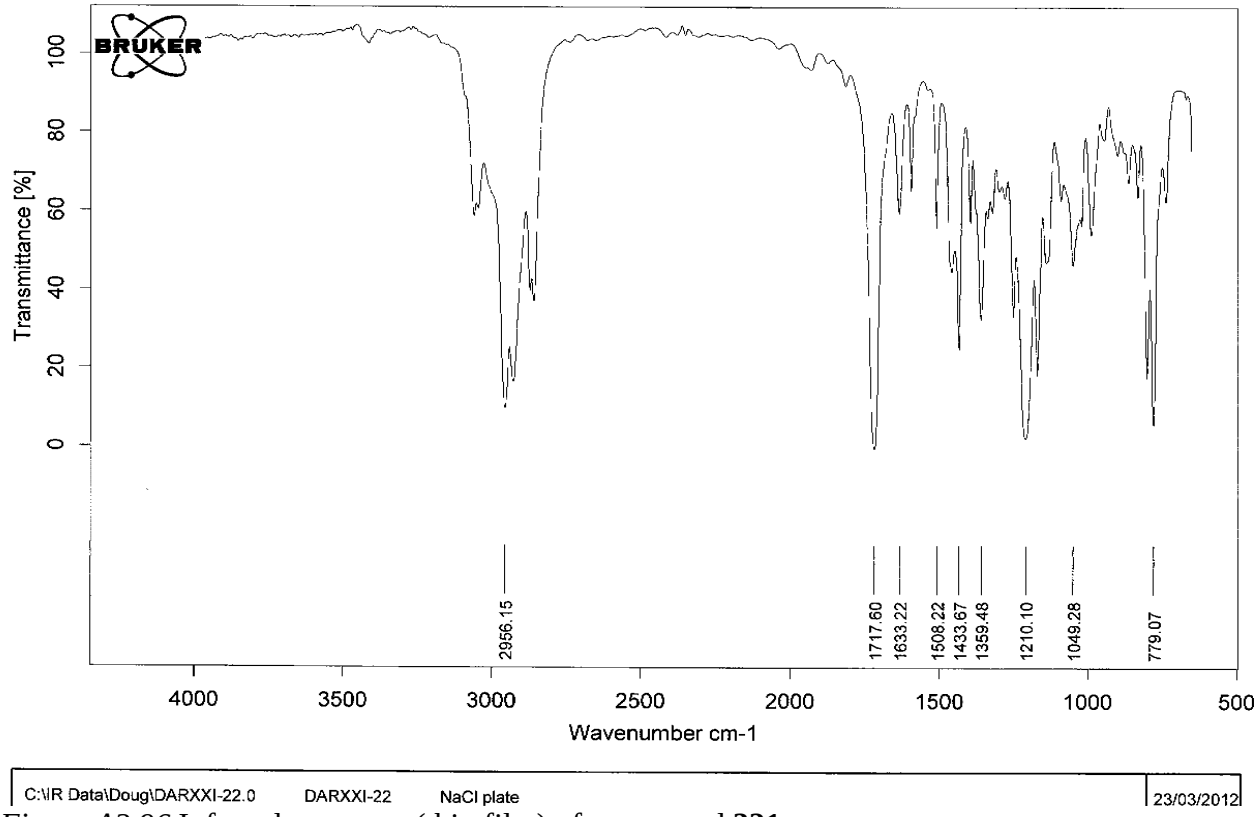
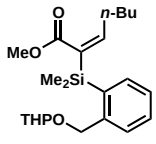


Figure A3.96 Infrared spectrum (thin film) of compound **321**



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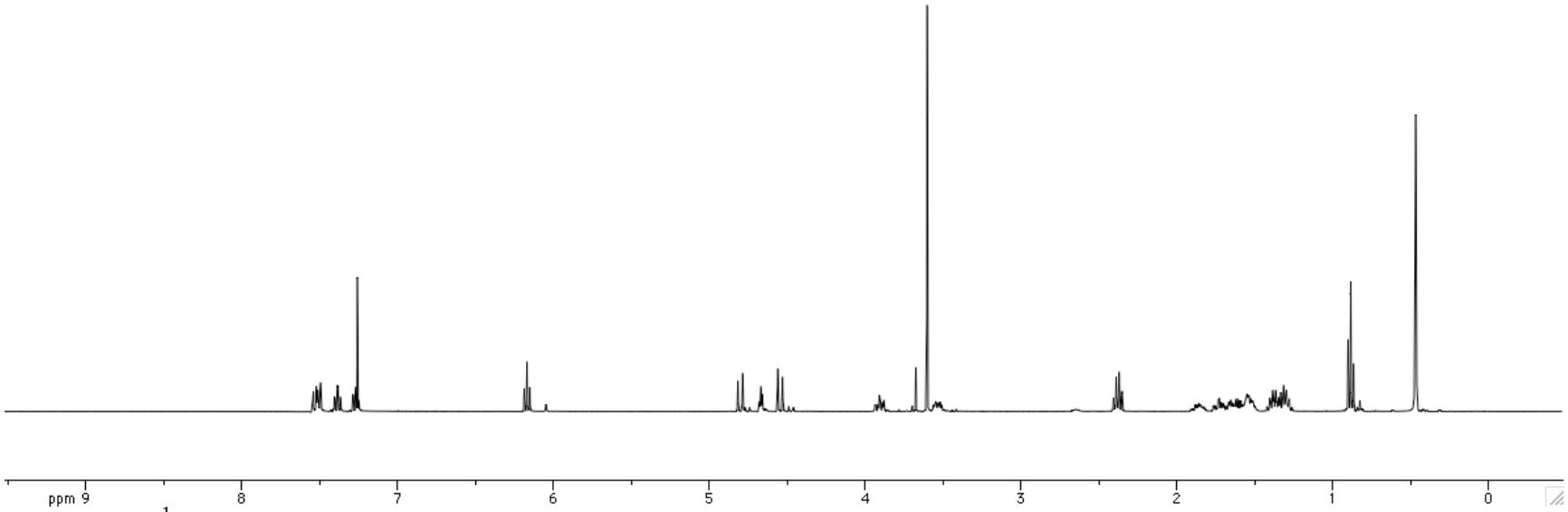
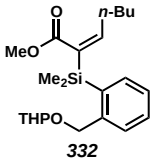


Figure A3.97 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **332**



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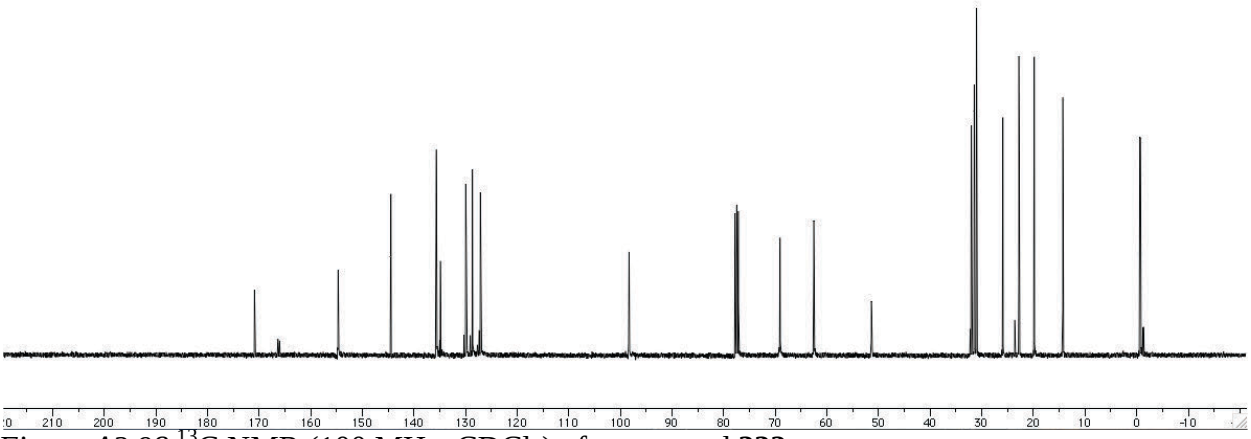


Figure A3.98 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **332**

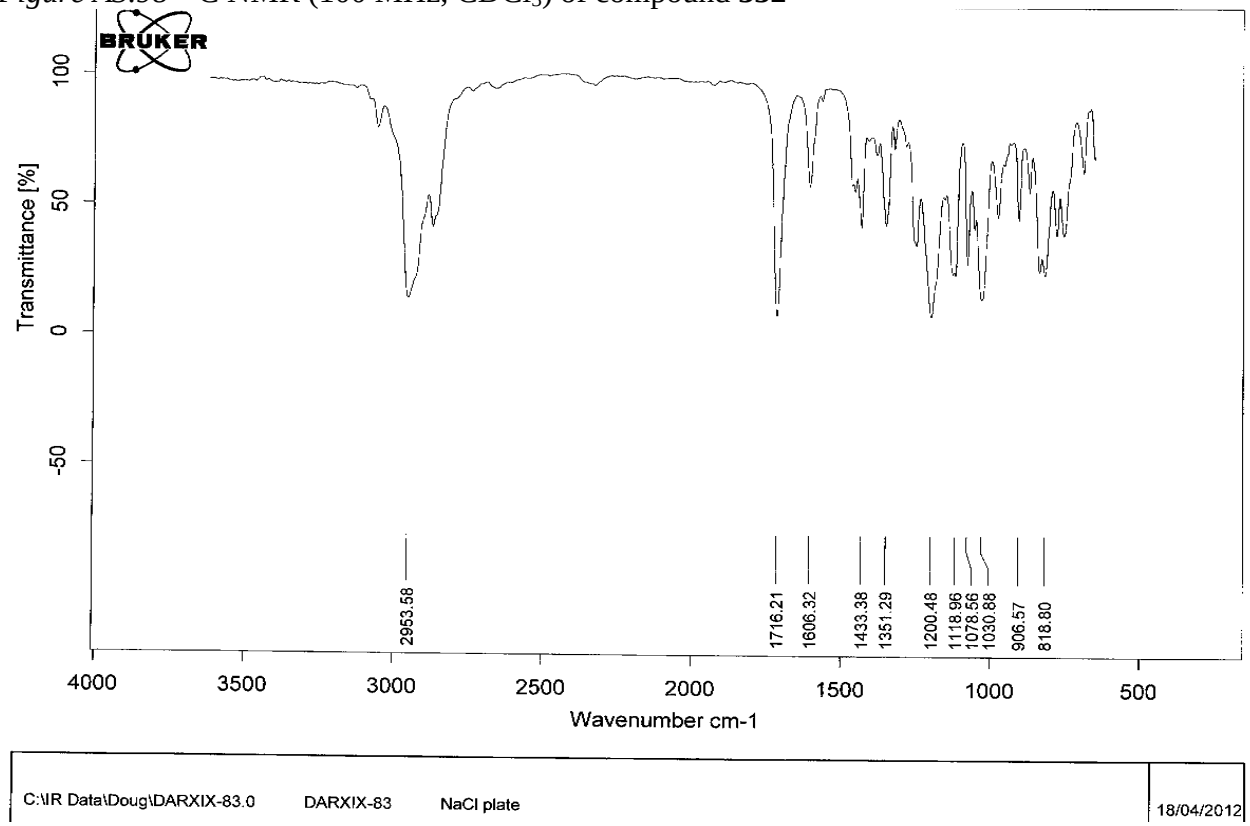
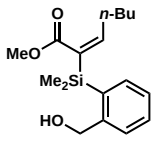


Figure A3.99 Infrared spectrum (thin film) of compound **332**



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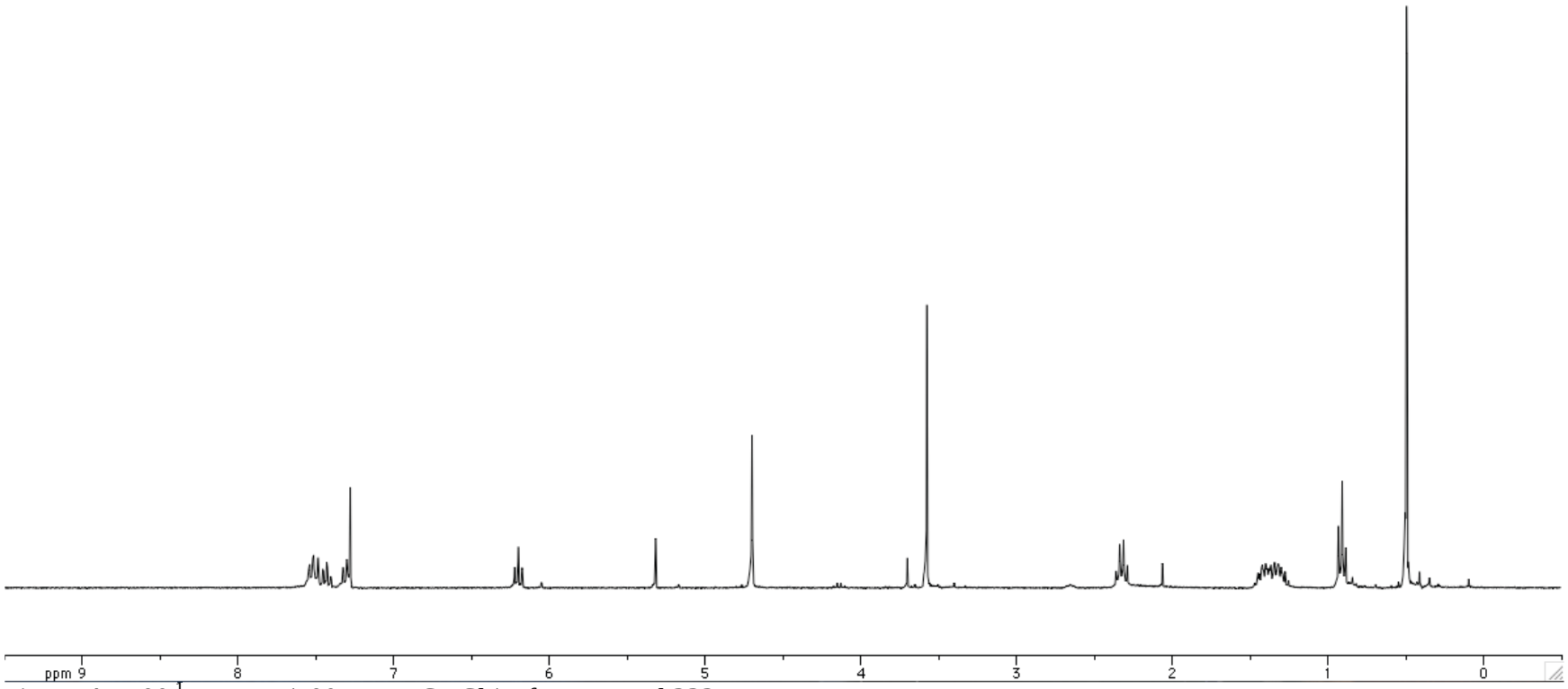
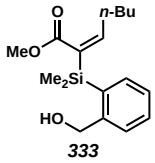


Figure A3.100 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **333**



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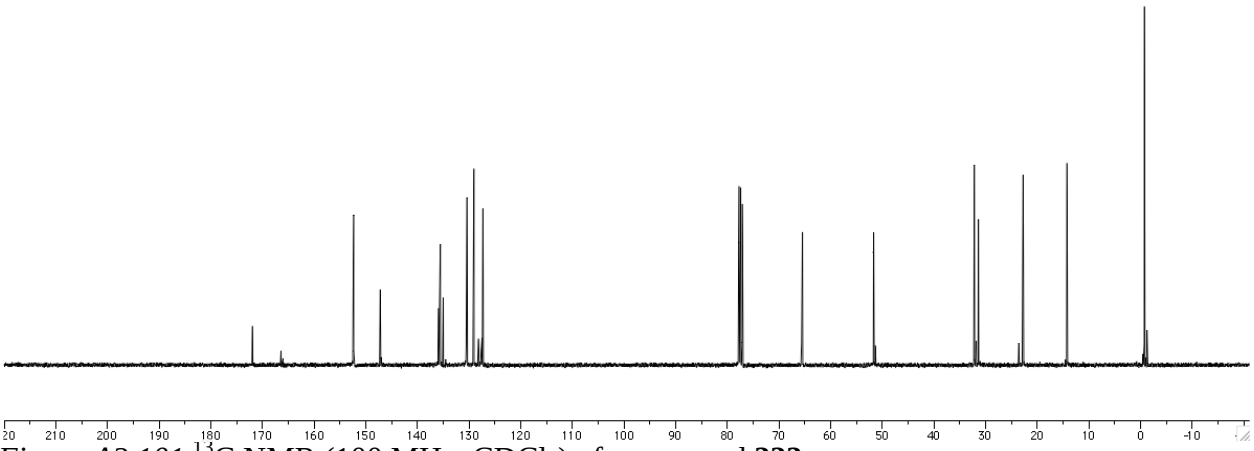


Figure A3.101 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **333**

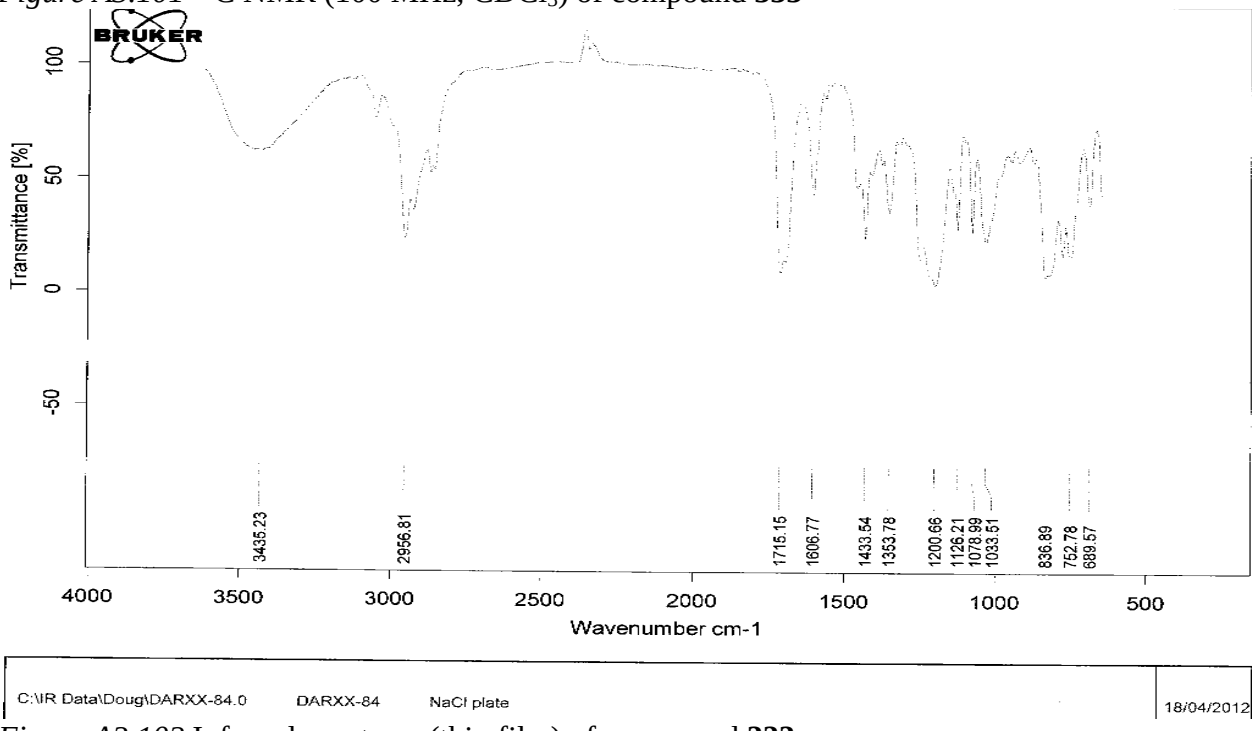
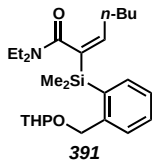


Figure A3.102 Infrared spectrum (thin film) of compound **333**



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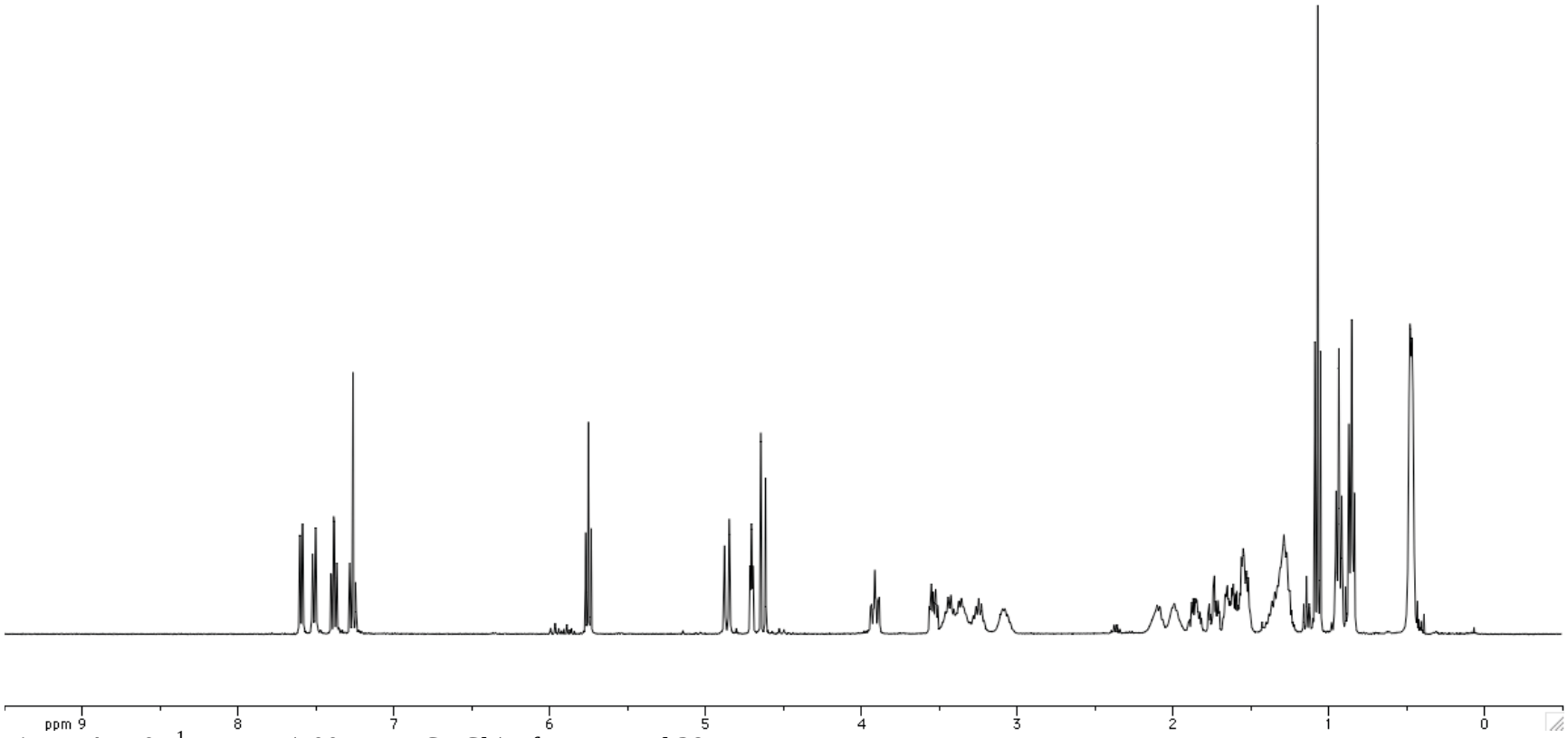
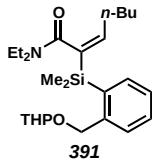


Figure A3.103 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **391**



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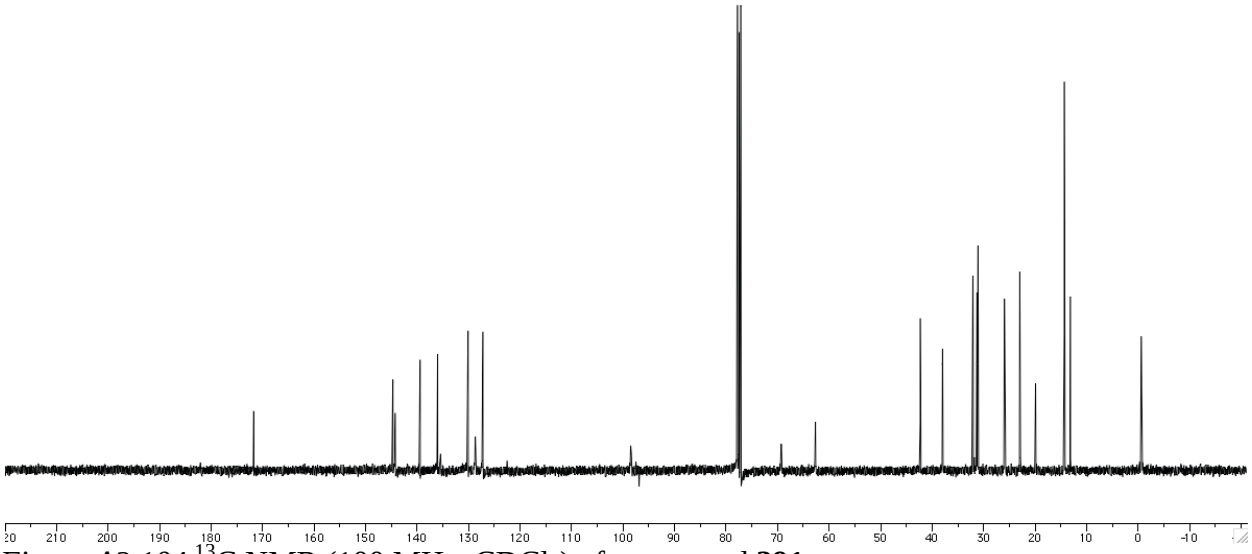


Figure A3.104 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **391**

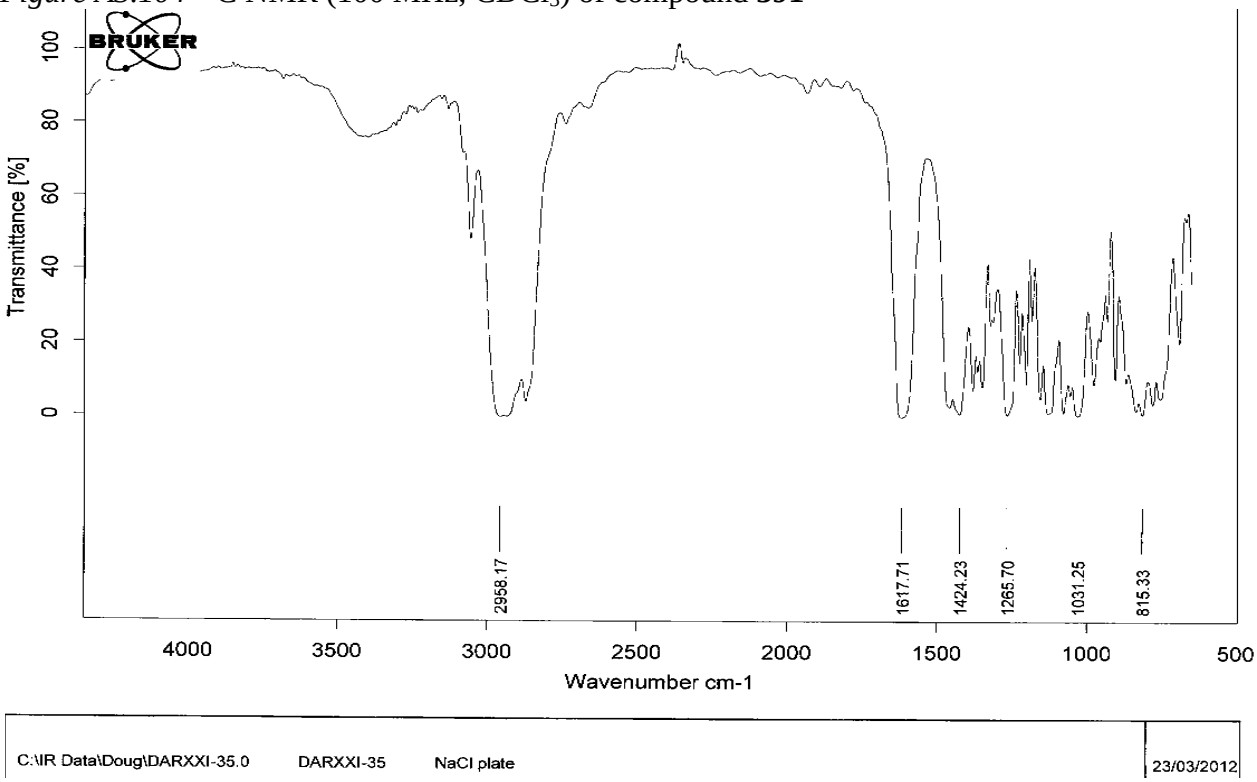
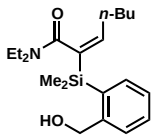


Figure A3.105 Infrared spectrum (thin film) of compound **391**



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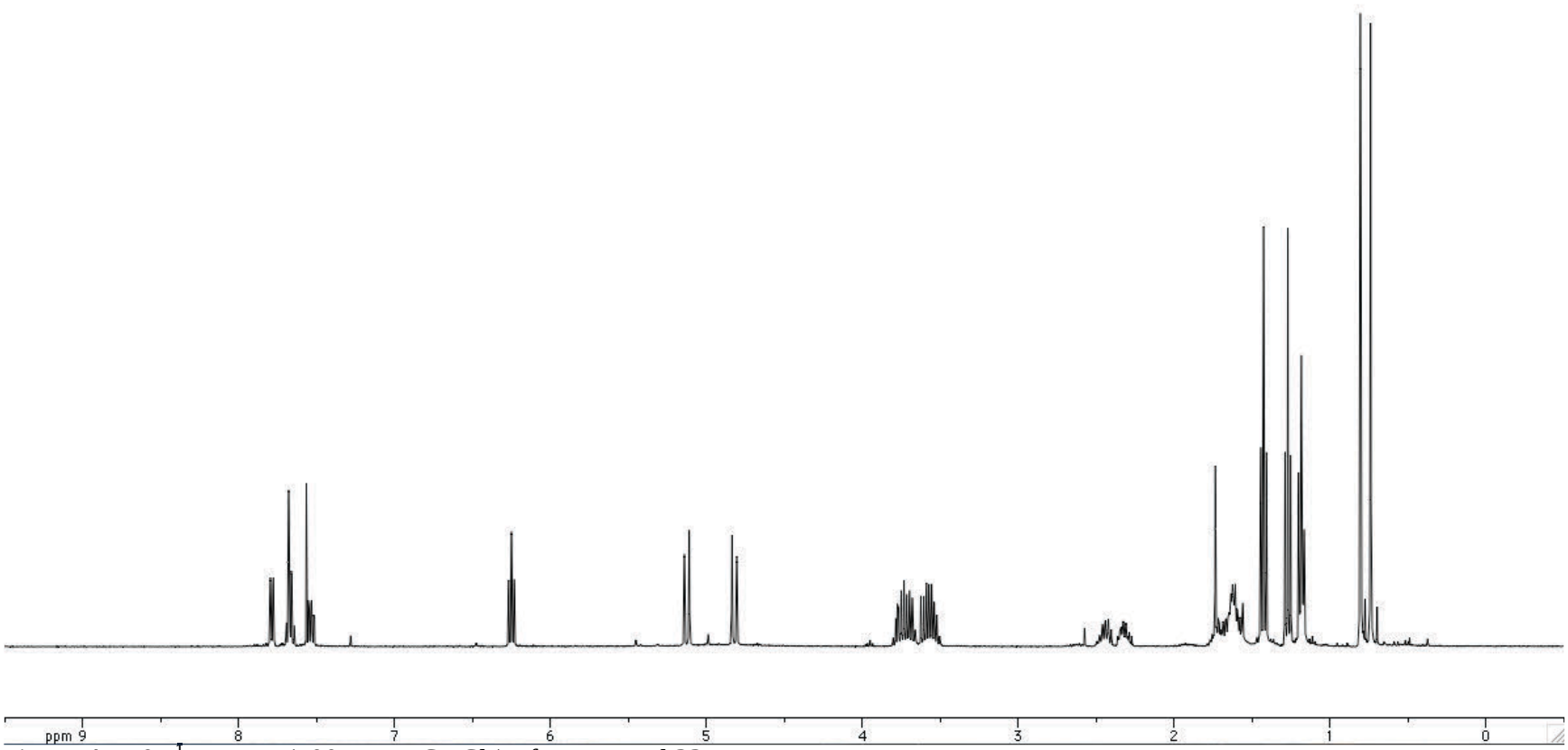
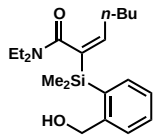


Figure A3.106 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **334**



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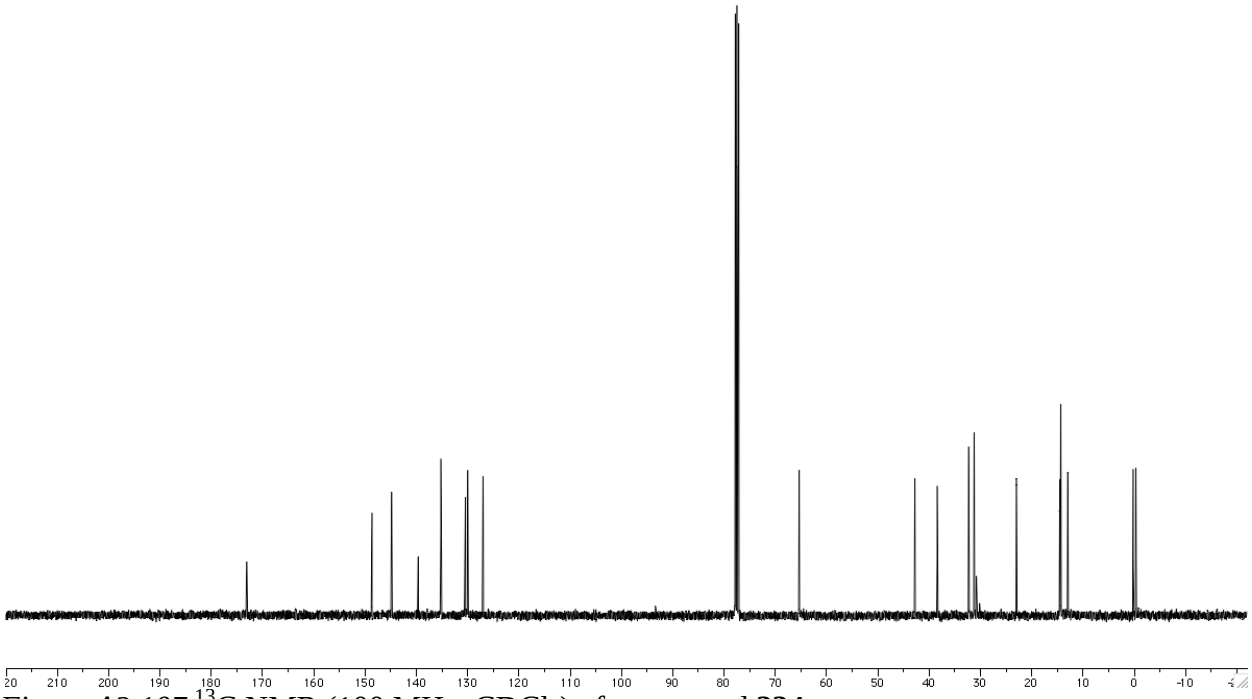


Figure A3.107 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **334**

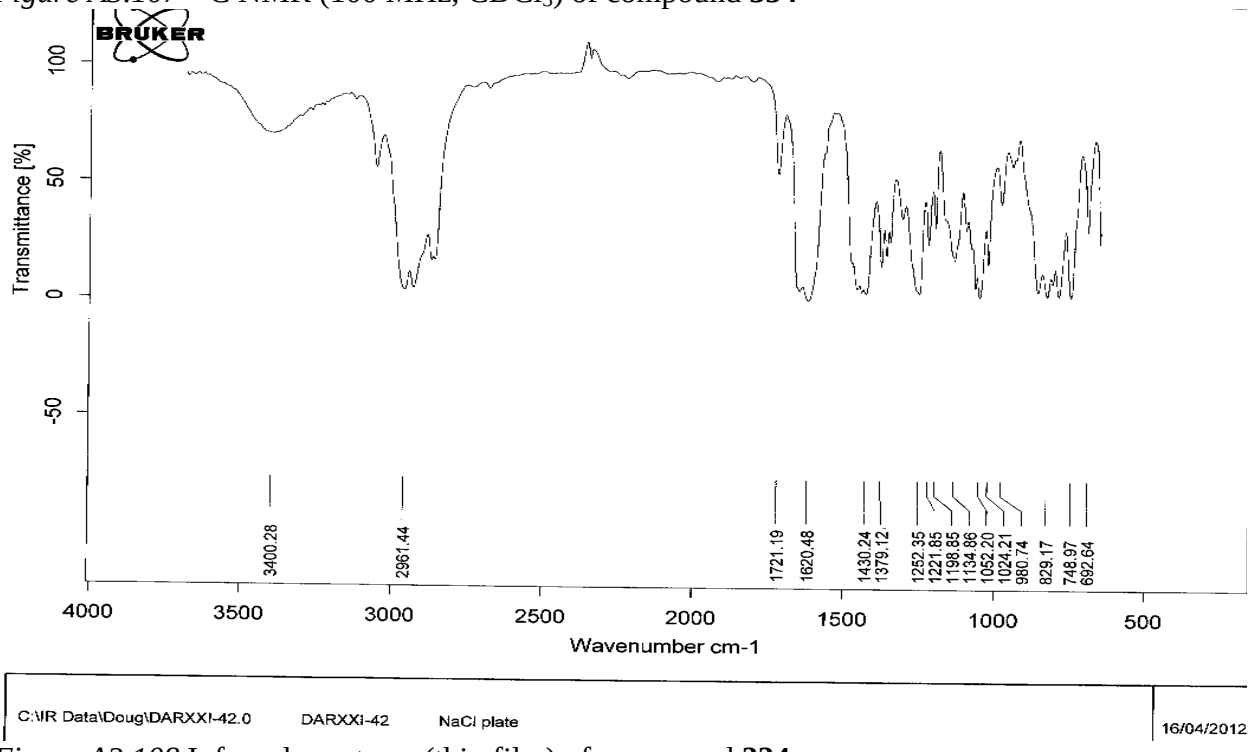
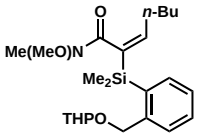


Figure A3.108 Infrared spectrum (thin film) of compound **334**



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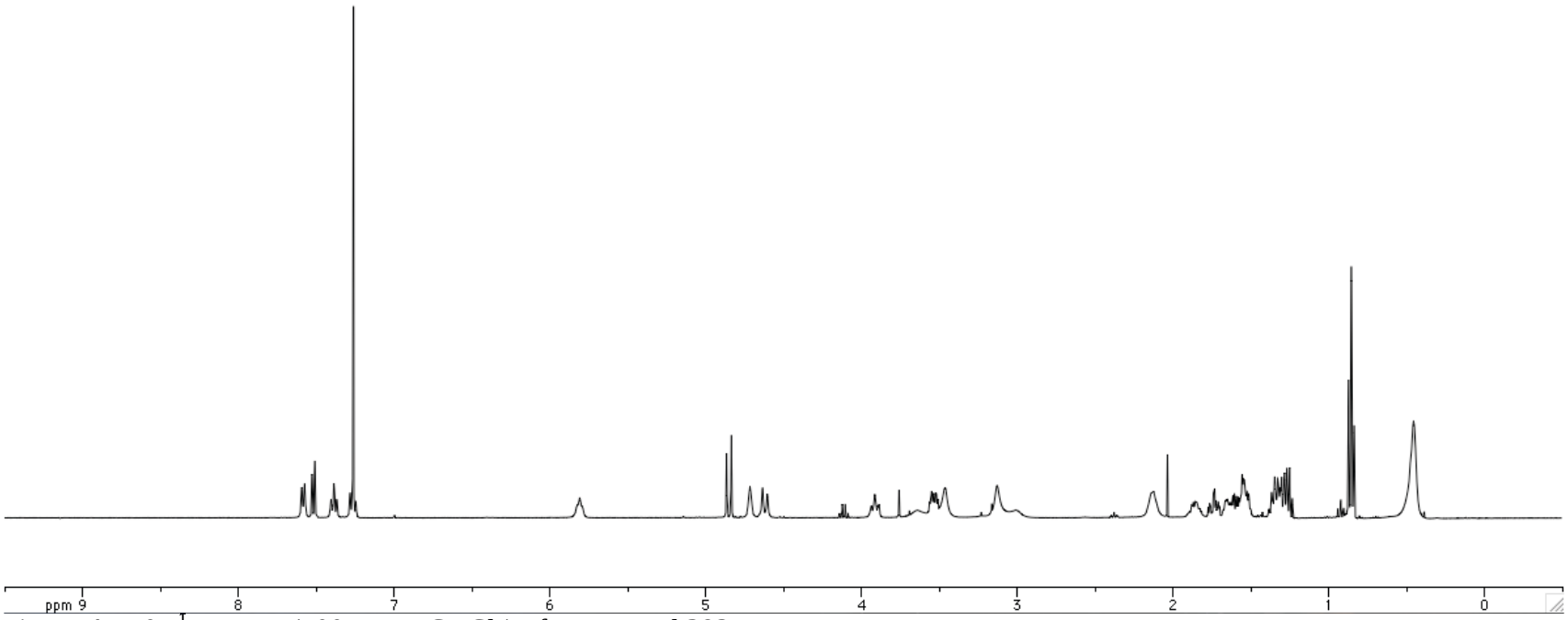
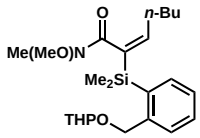


Figure A3.109 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **392**



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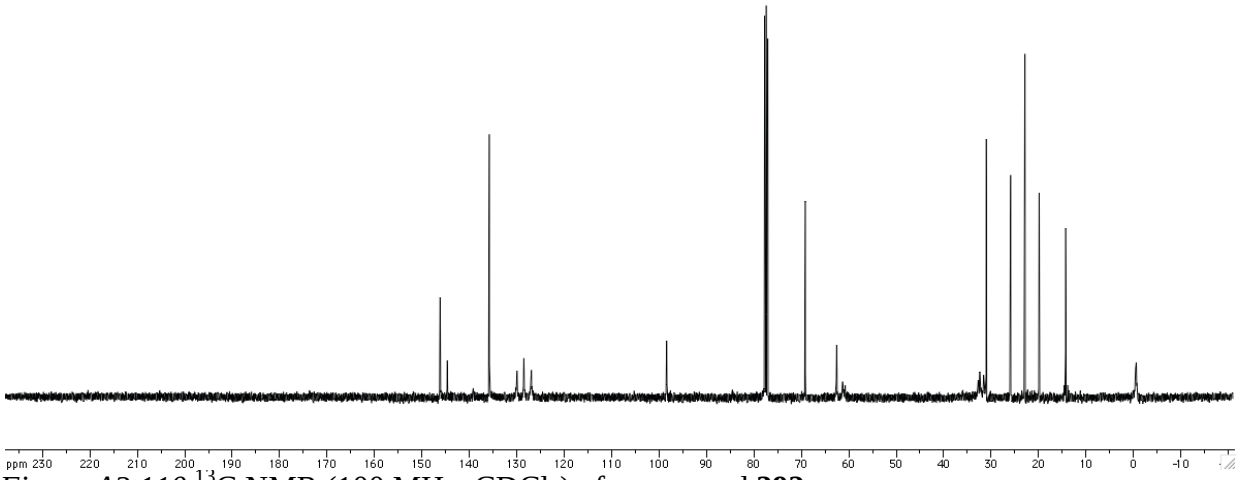


Figure A3.110 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **392**

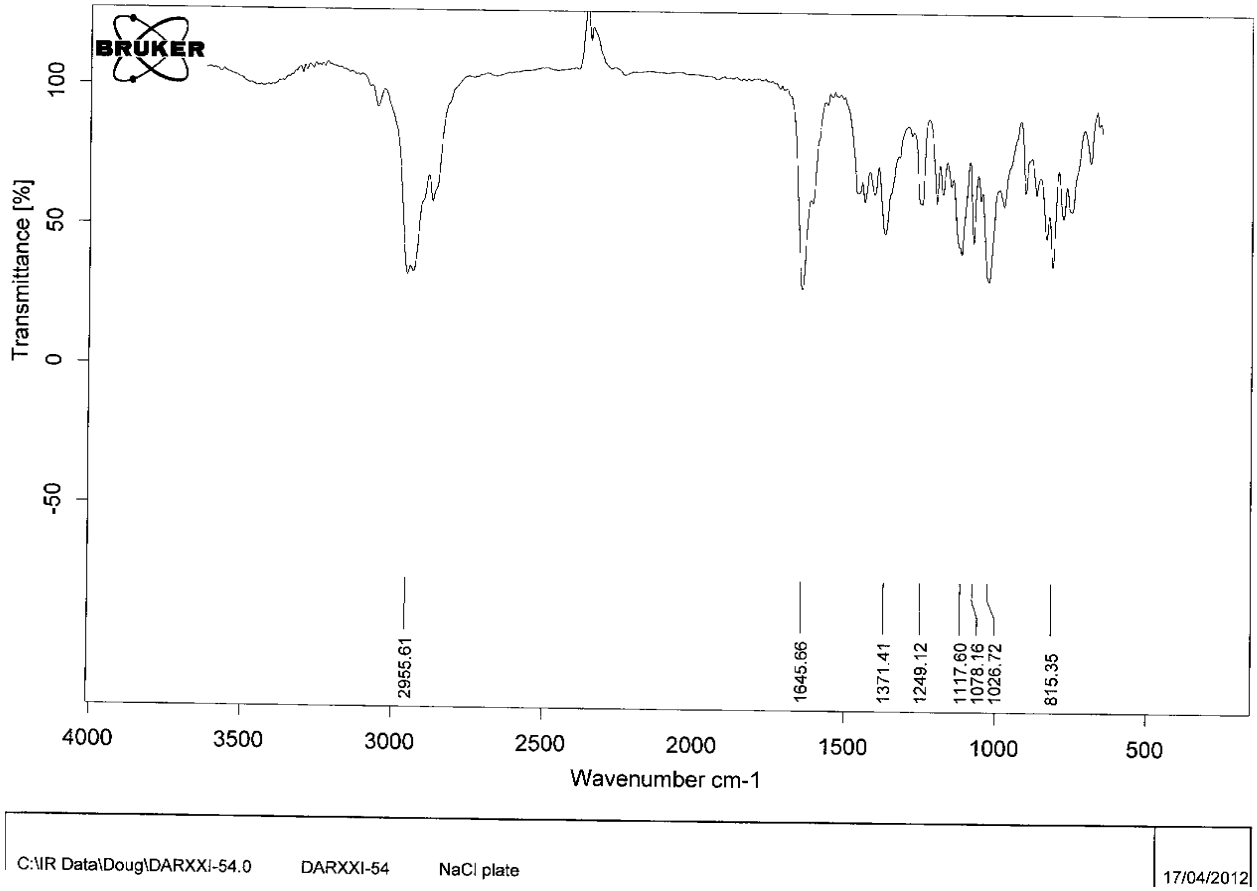
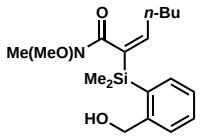


Figure A3.111 Infrared spectrum (thin film) of compound **392**



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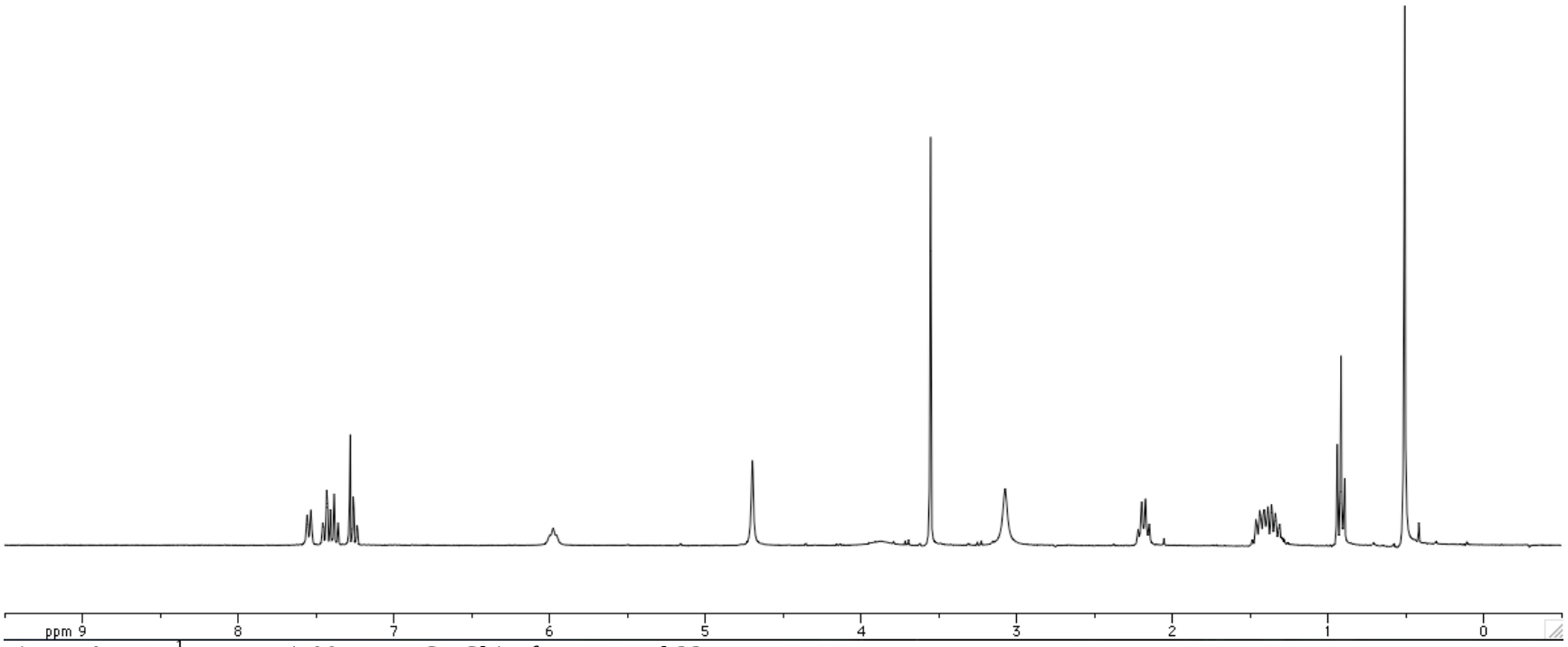
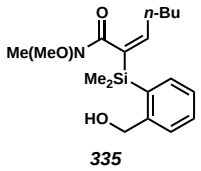


Figure A3.112 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **335**



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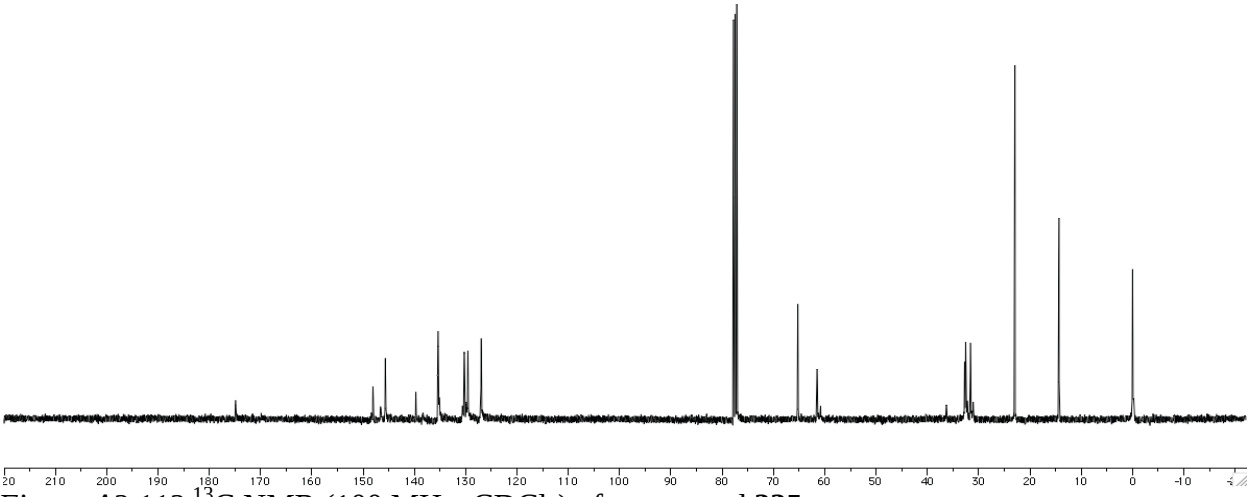


Figure A3.113 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **335**

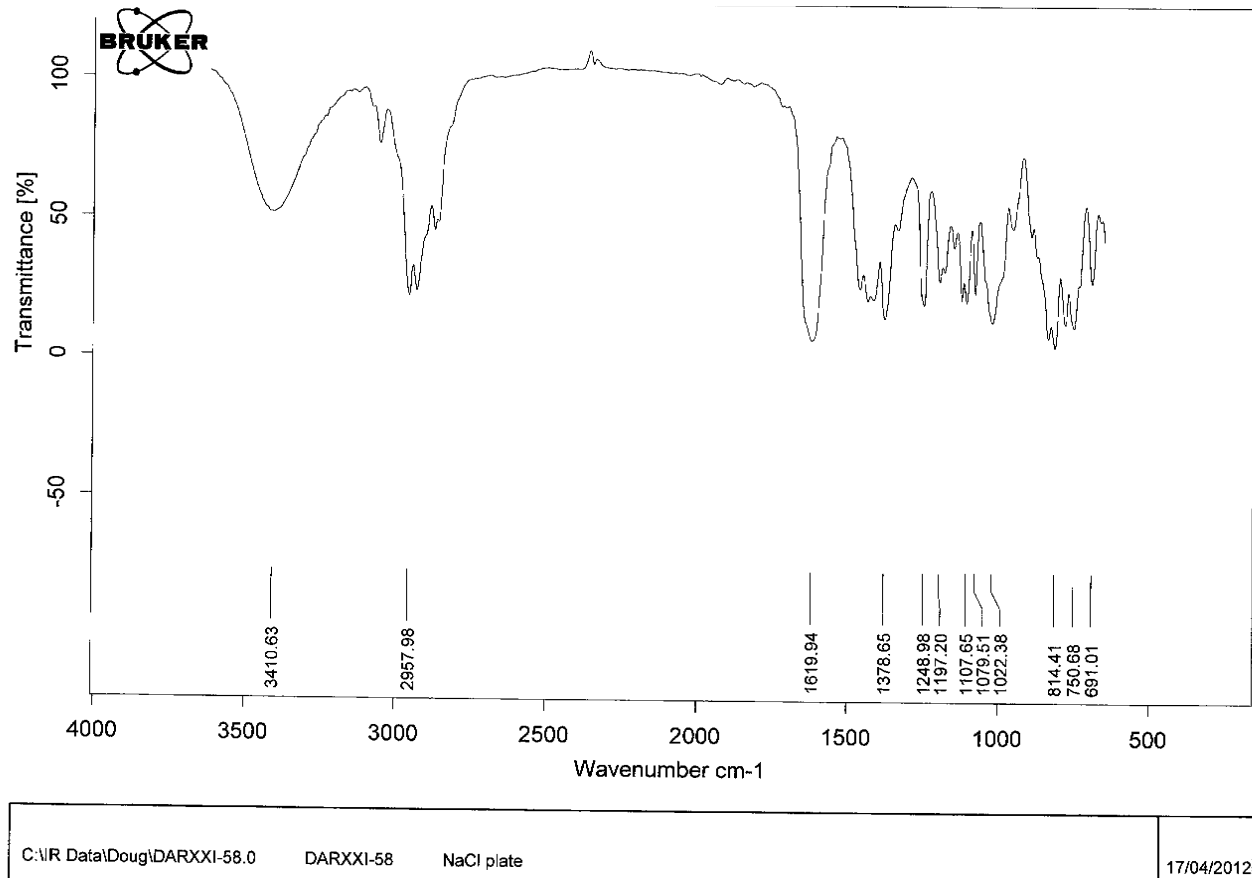
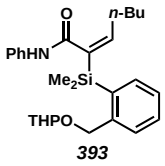


Figure A3.114 Infrared spectrum (thin film) of compound **335**



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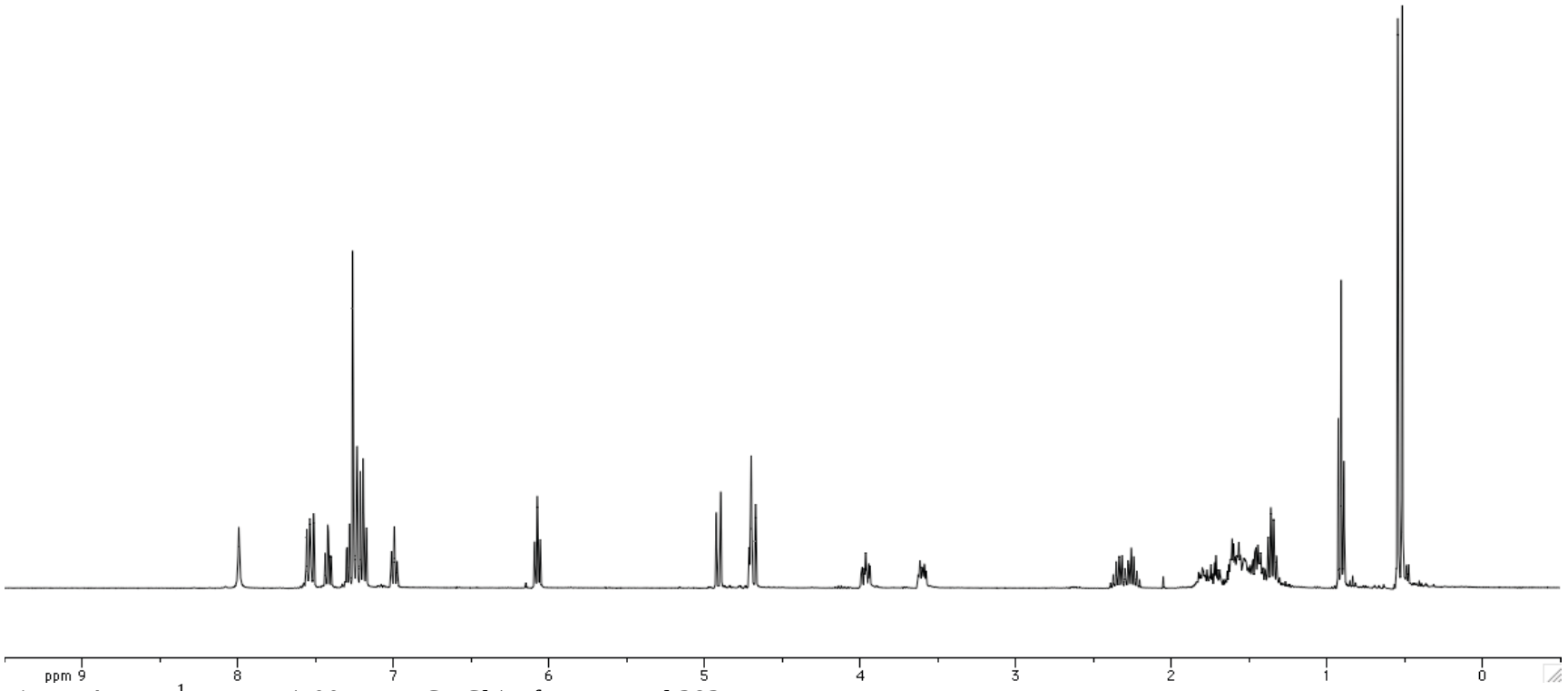


Figure A3.115 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **393**

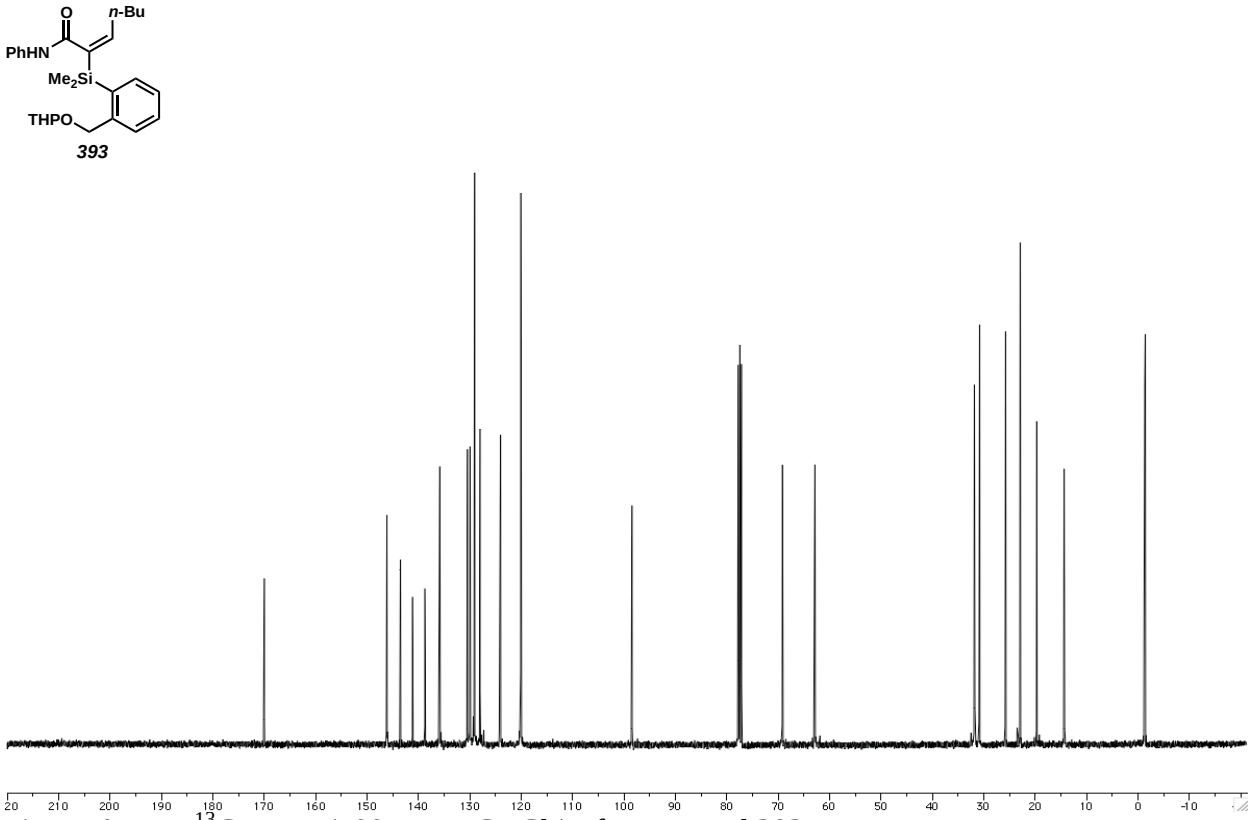


Figure A3.116 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **393**

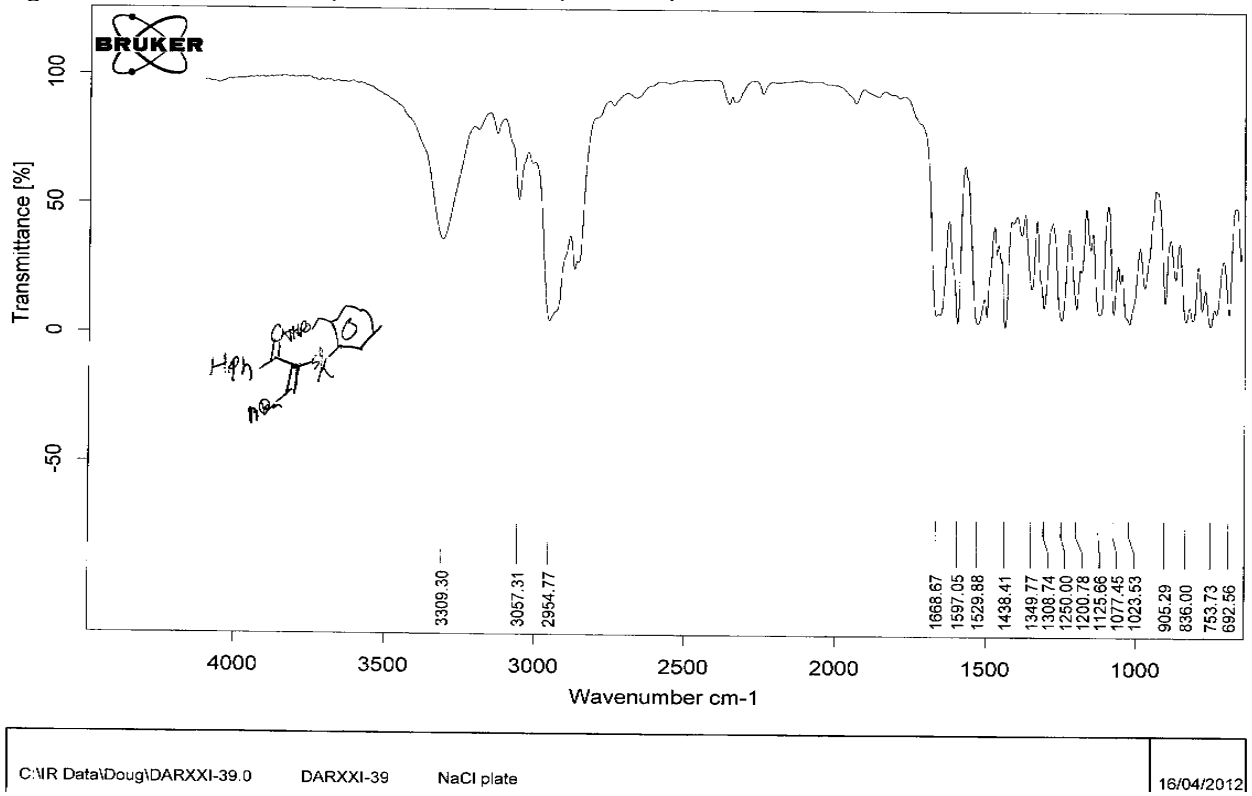
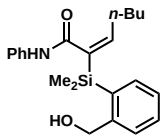


Figure A3.117 Infrared spectrum (thin film) of compound **393**



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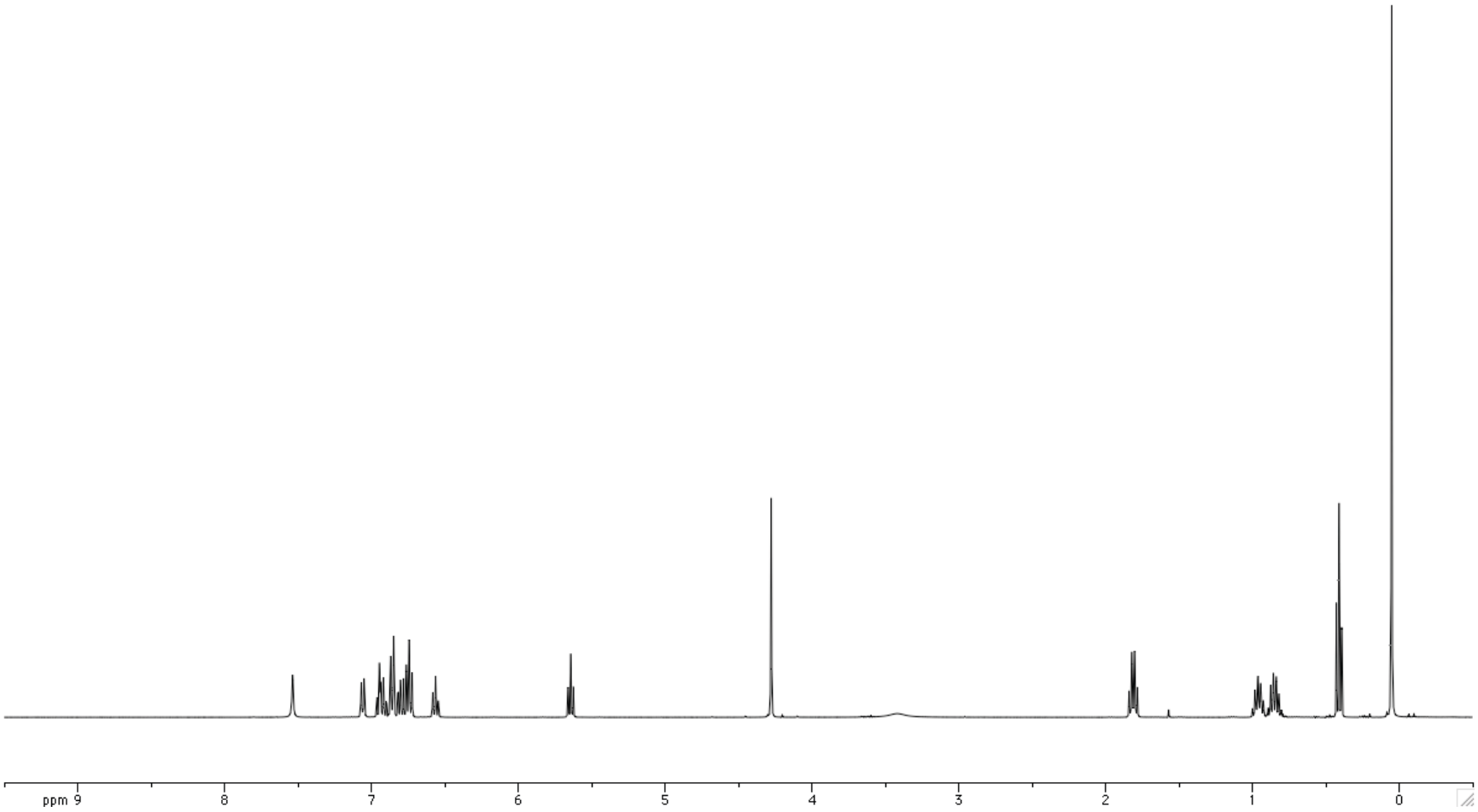
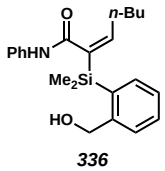


Figure A3.118 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **336**



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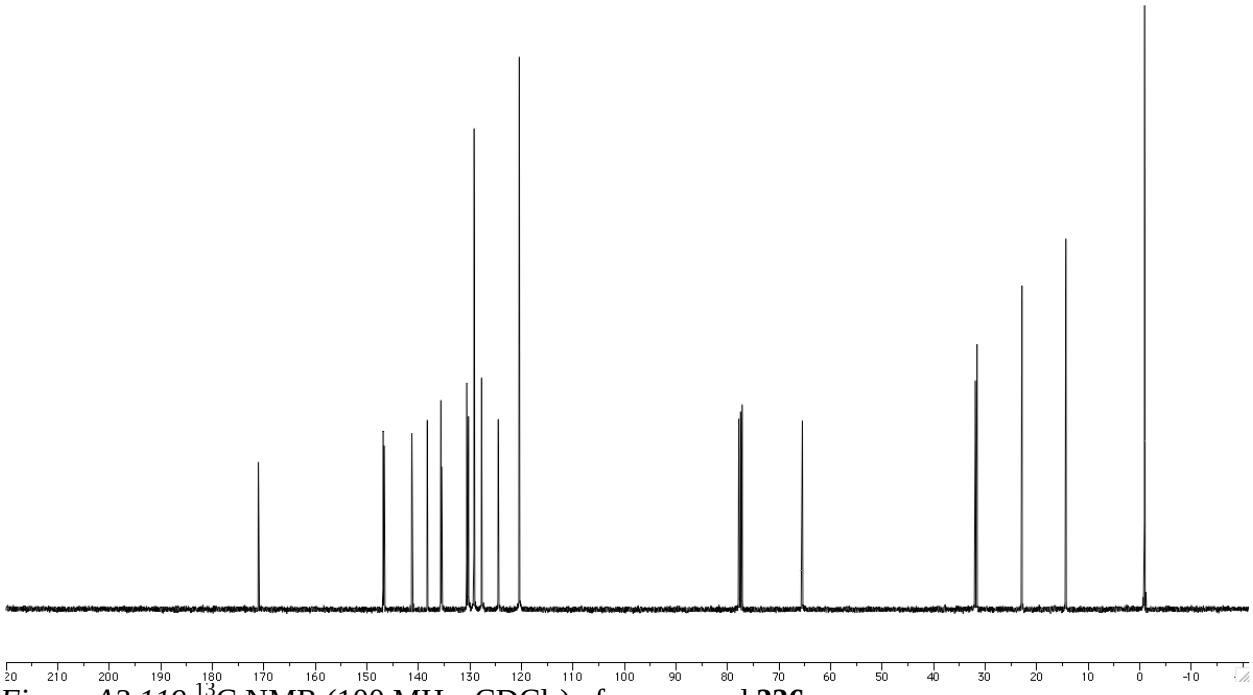


Figure A3.119 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **336**

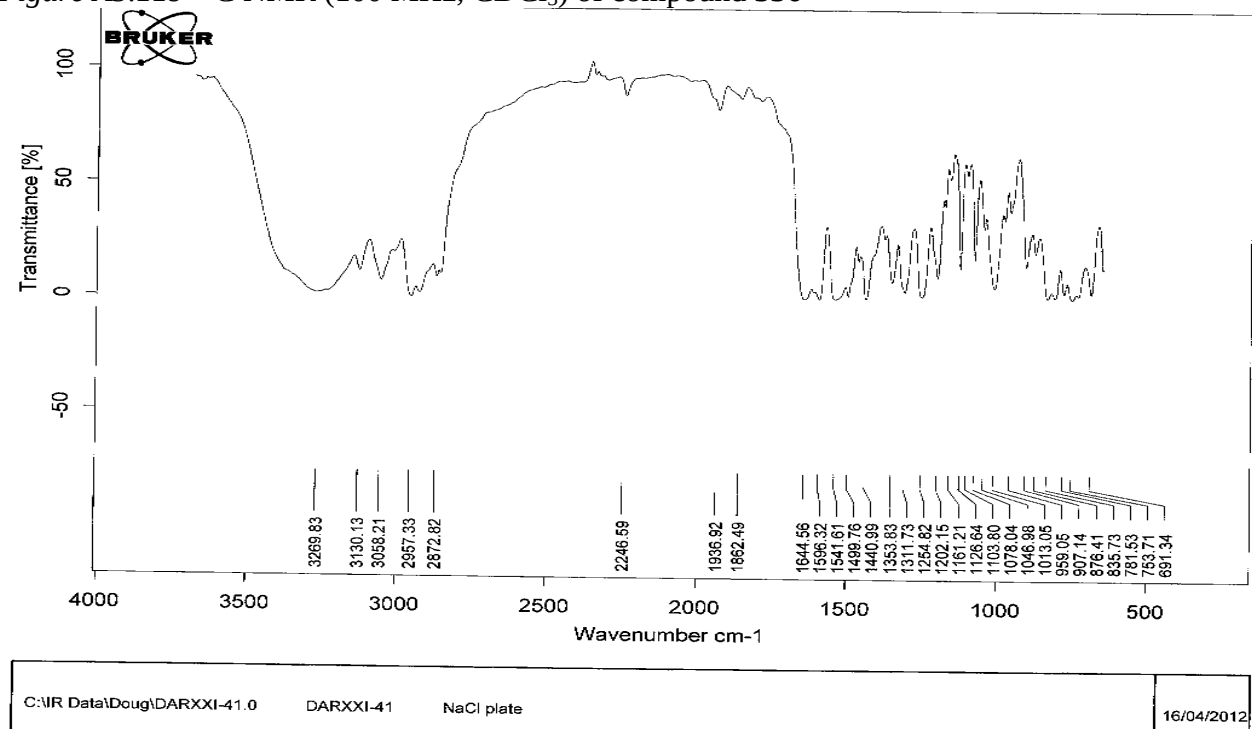
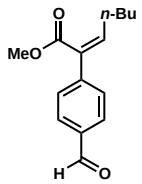


Figure A3.120 Infrared spectrum (thin film) of compound **336**



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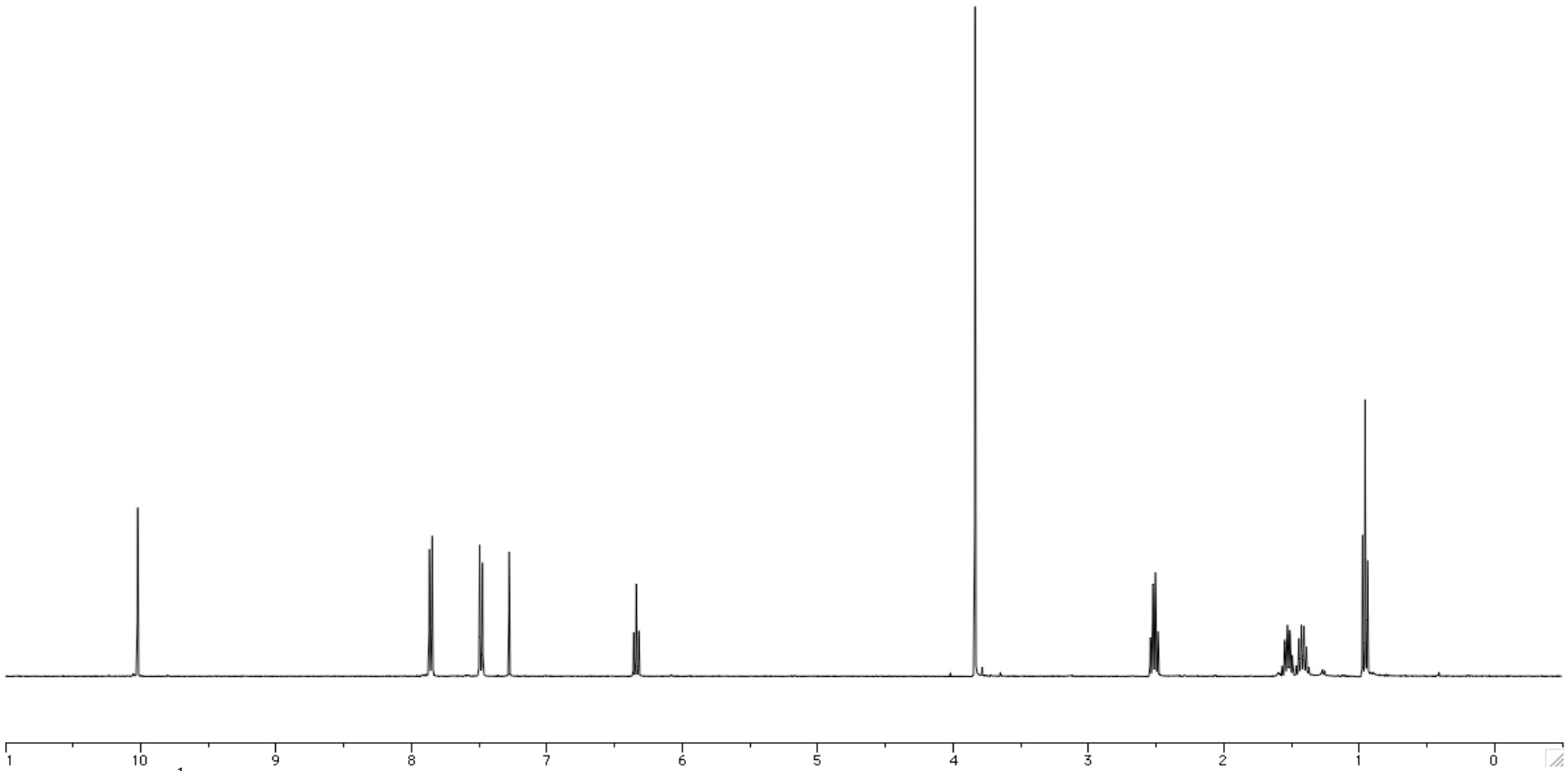
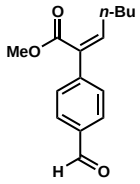


Figure A3.121 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **339**



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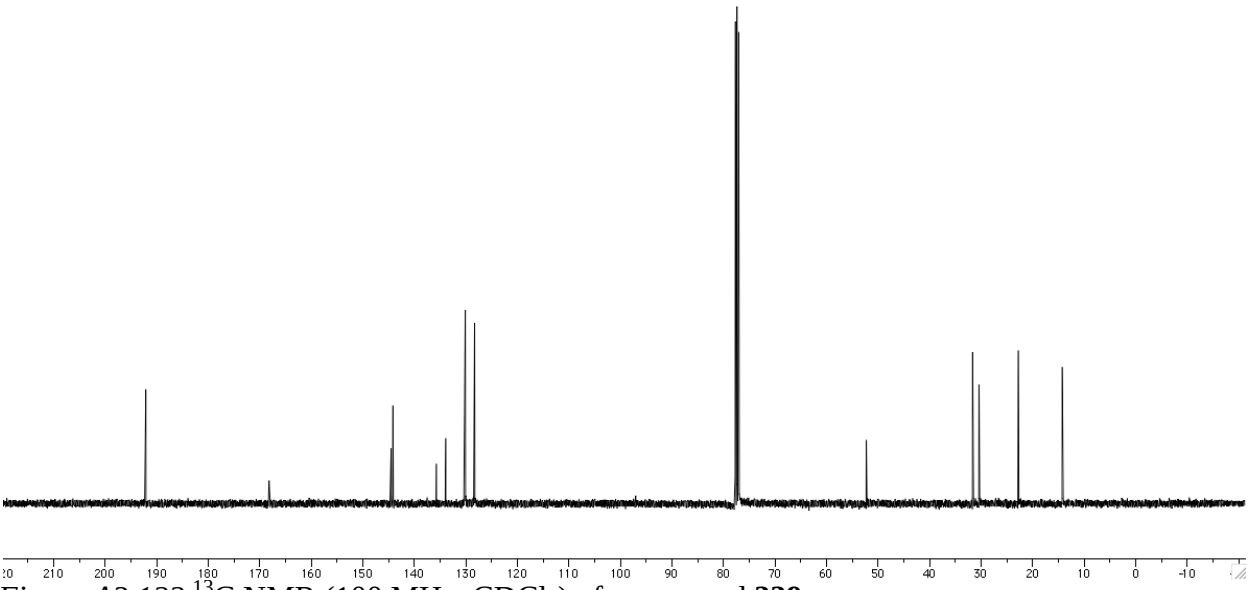


Figure A3.122 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **339**

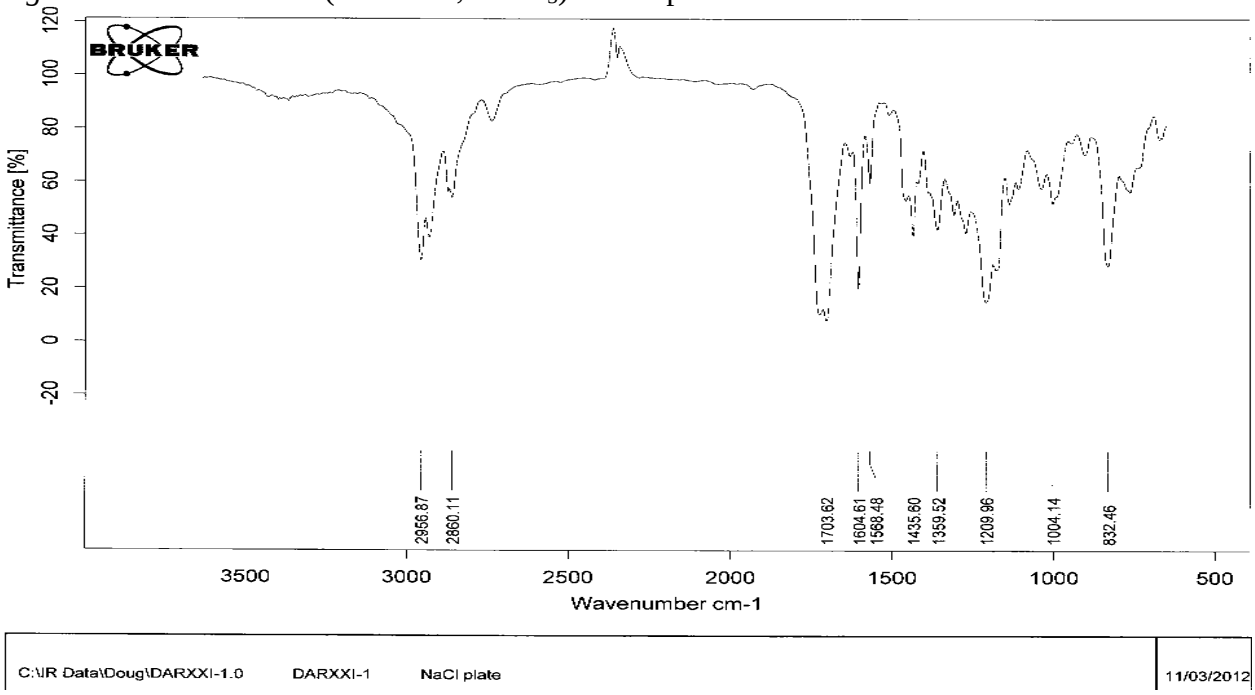
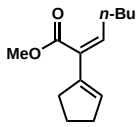


Figure A3.123 Infrared spectrum (thin film) of compound **339**



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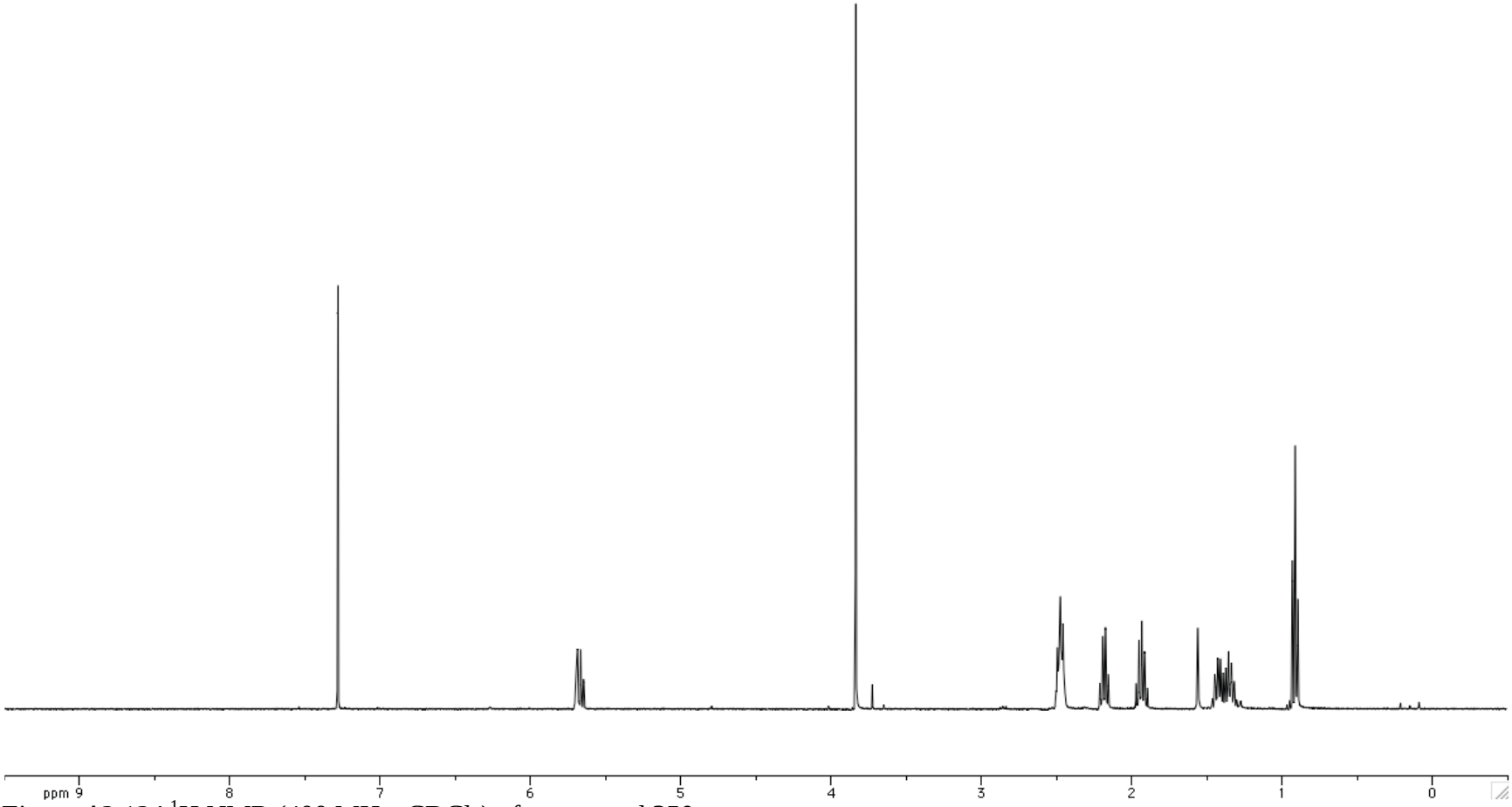
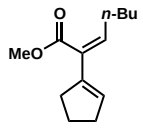


Figure A3.124 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **350**



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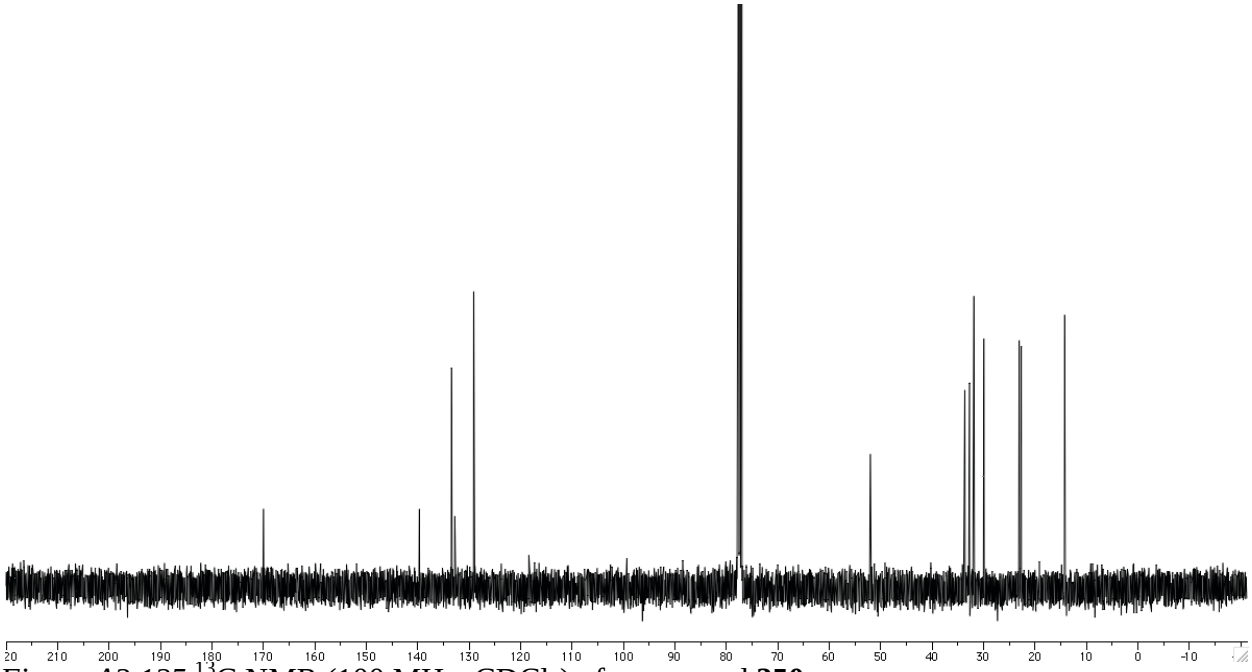


Figure A3.125 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **350**

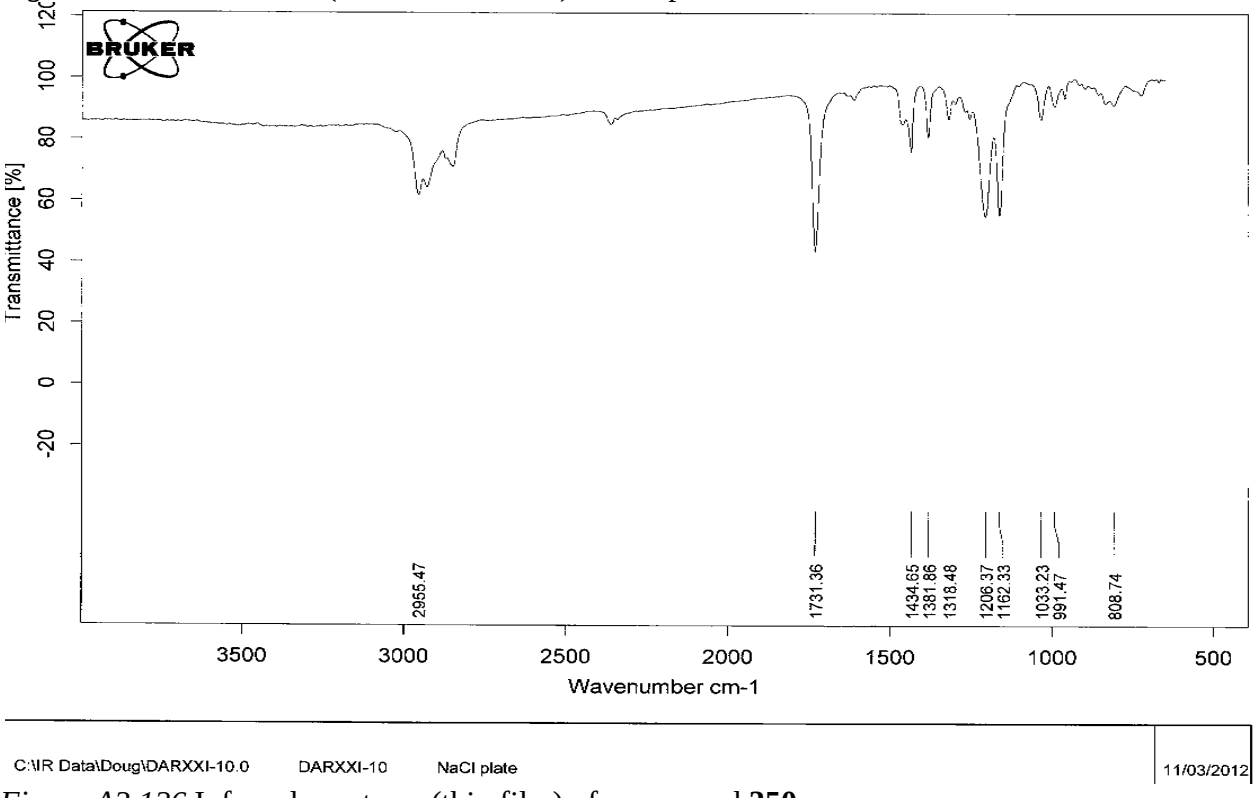
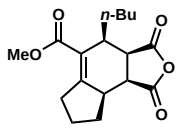


Figure A3.126 Infrared spectrum (thin film) of compound **350**



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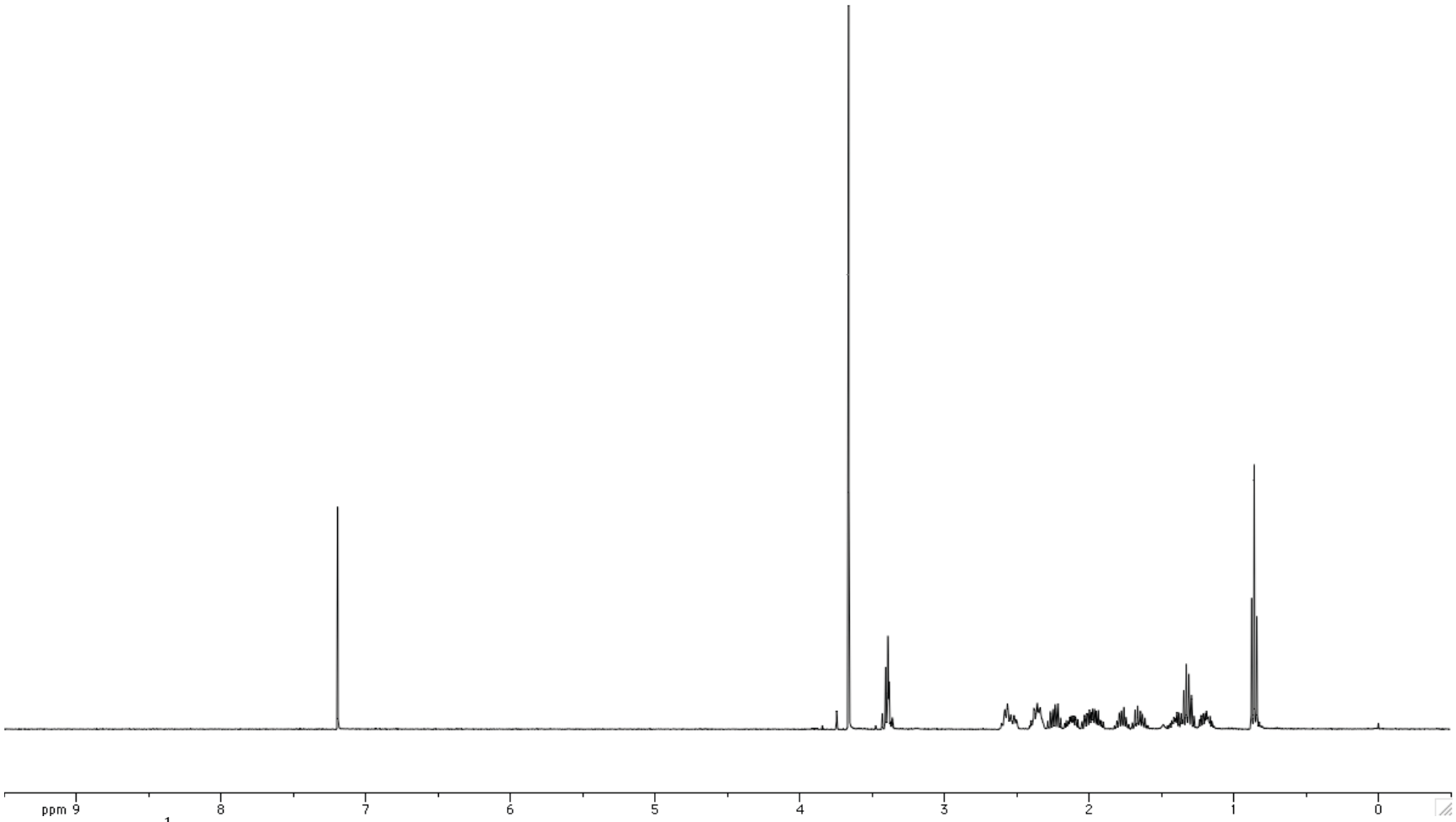
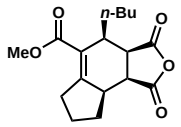


Figure A3.127 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **349**



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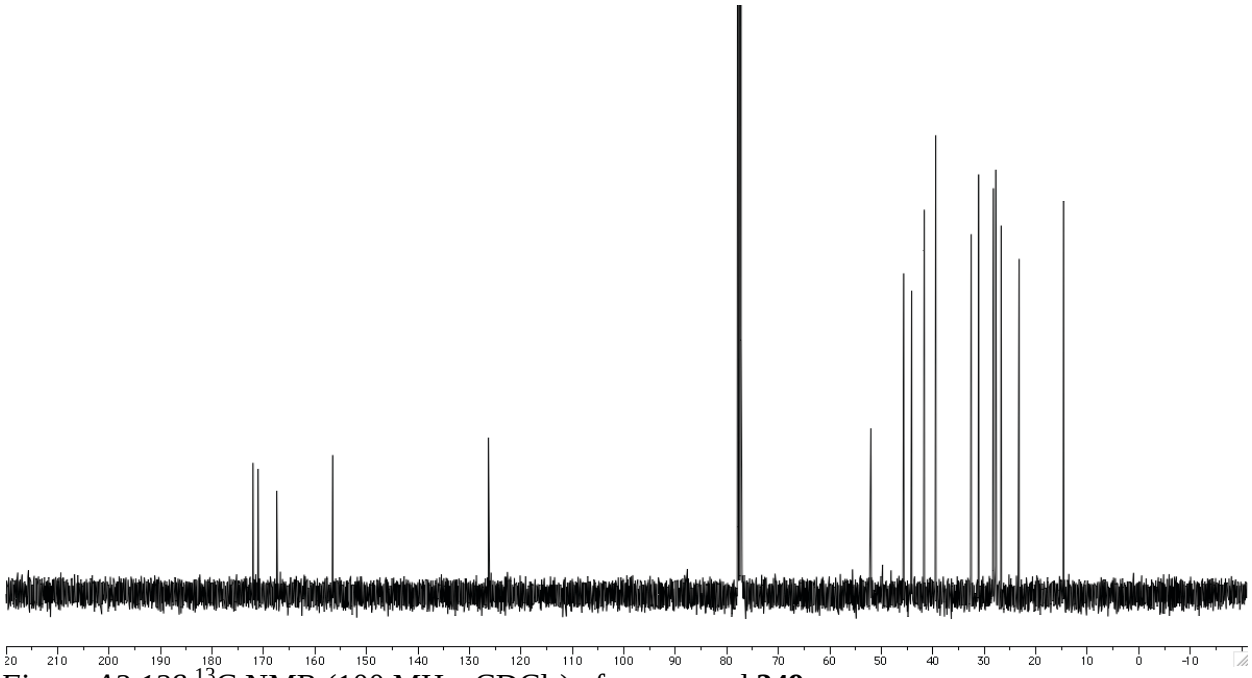


Figure A3.128 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **349**

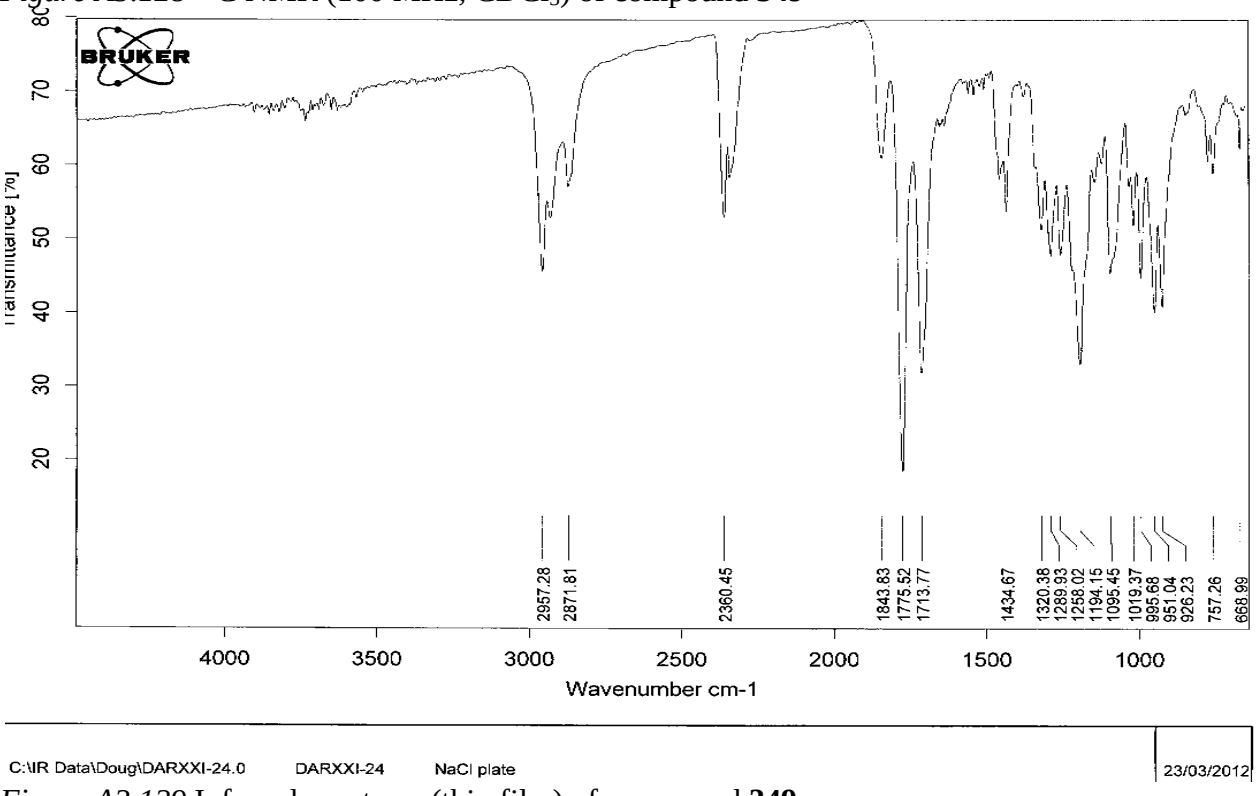
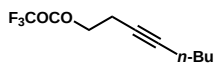


Figure A3.129 Infrared spectrum (thin film) of compound **349**



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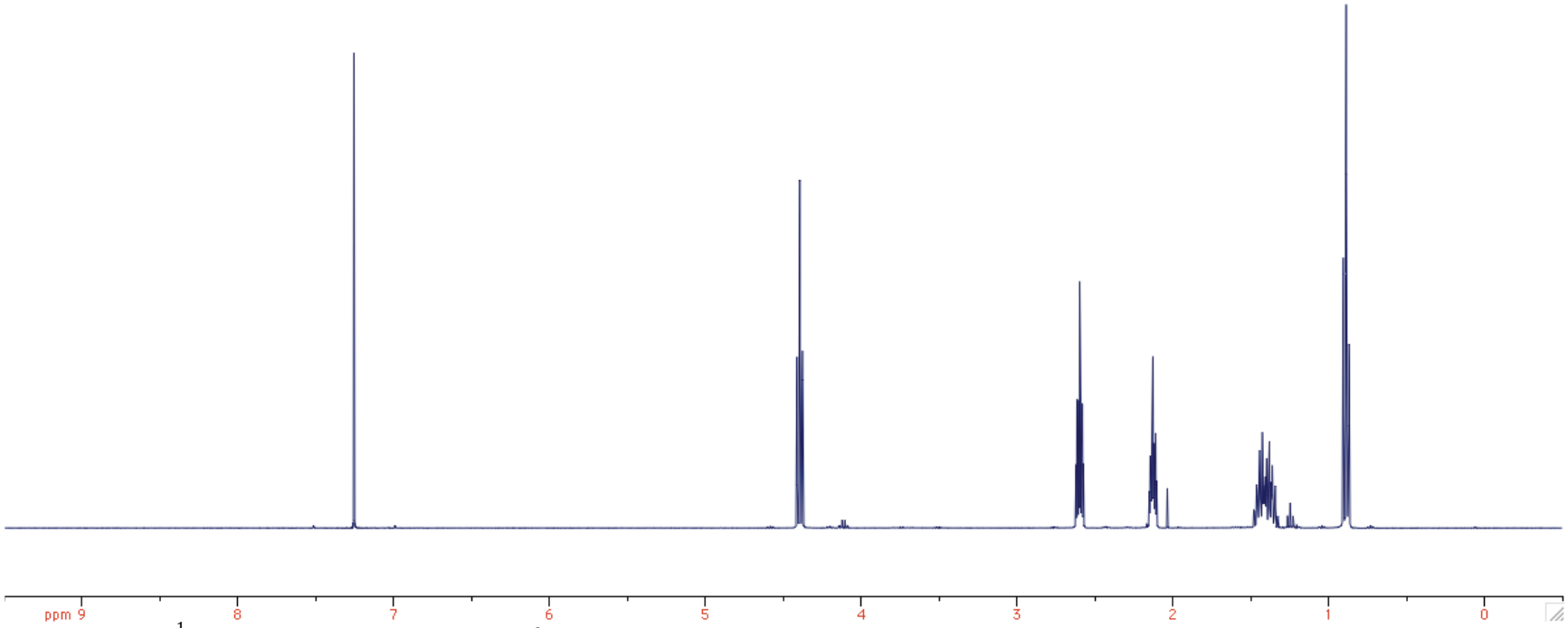
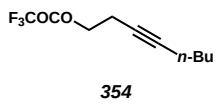


Figure A3.130 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **354**



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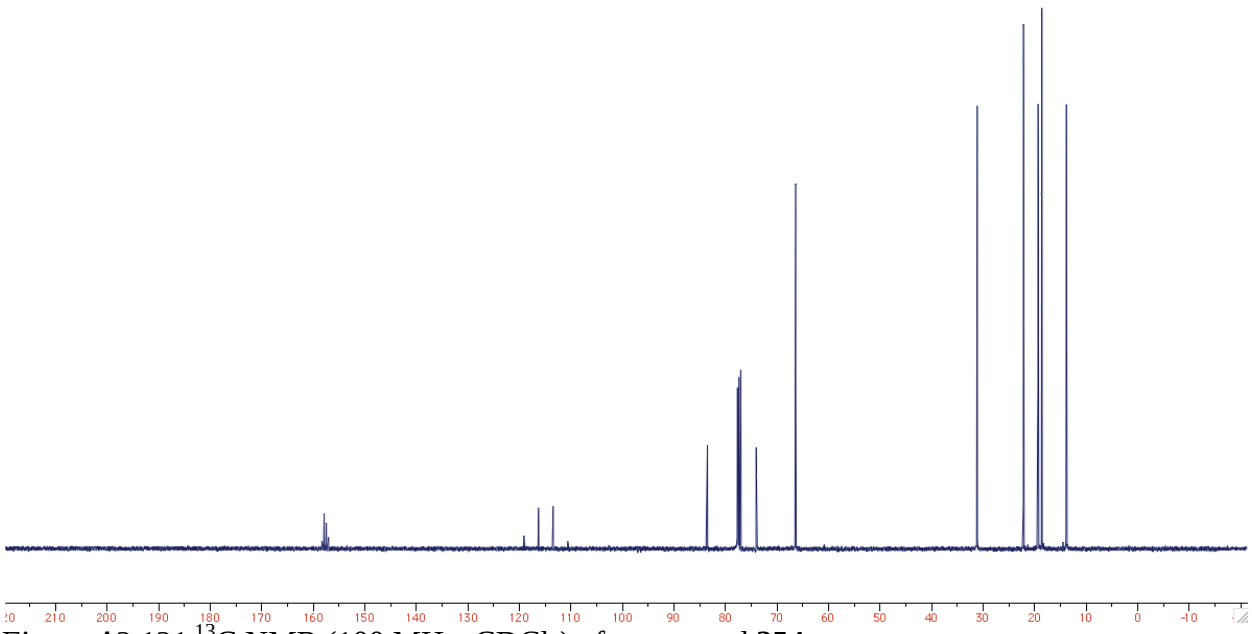


Figure A3.131 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **354**

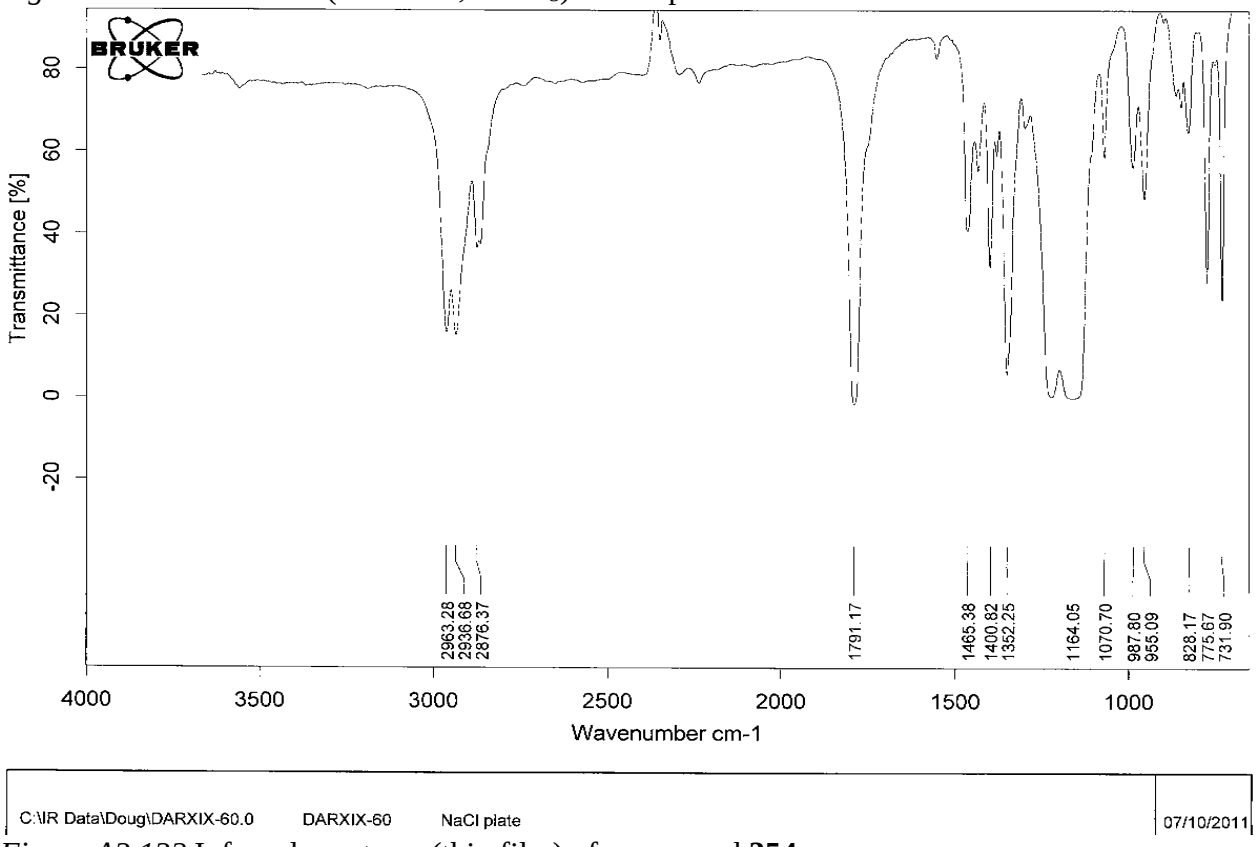
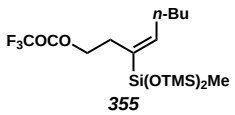


Figure A3.132 Infrared spectrum (thin film) of compound **354**



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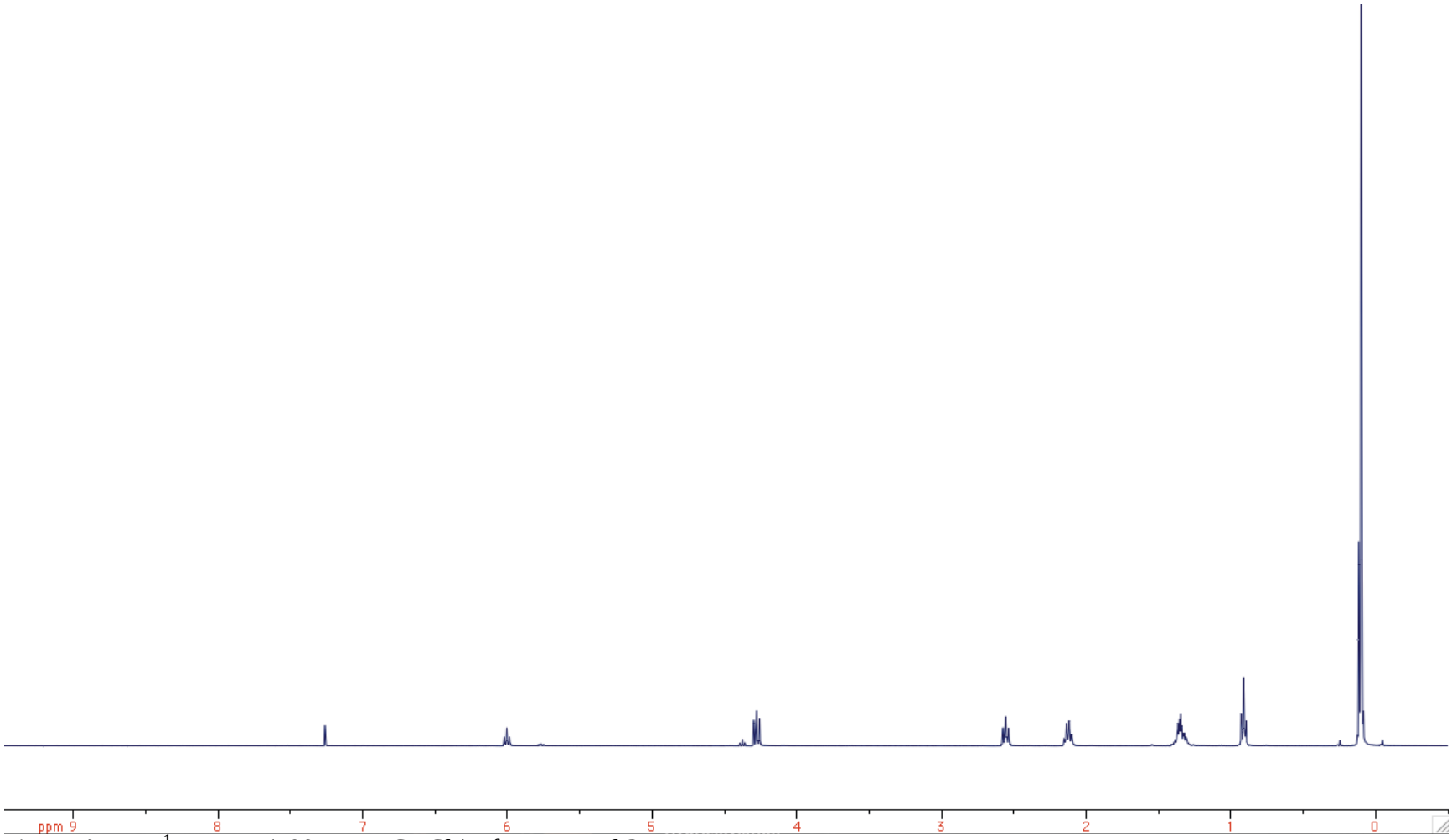
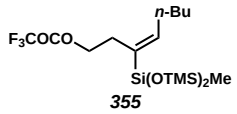


Figure A3.133 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **355**



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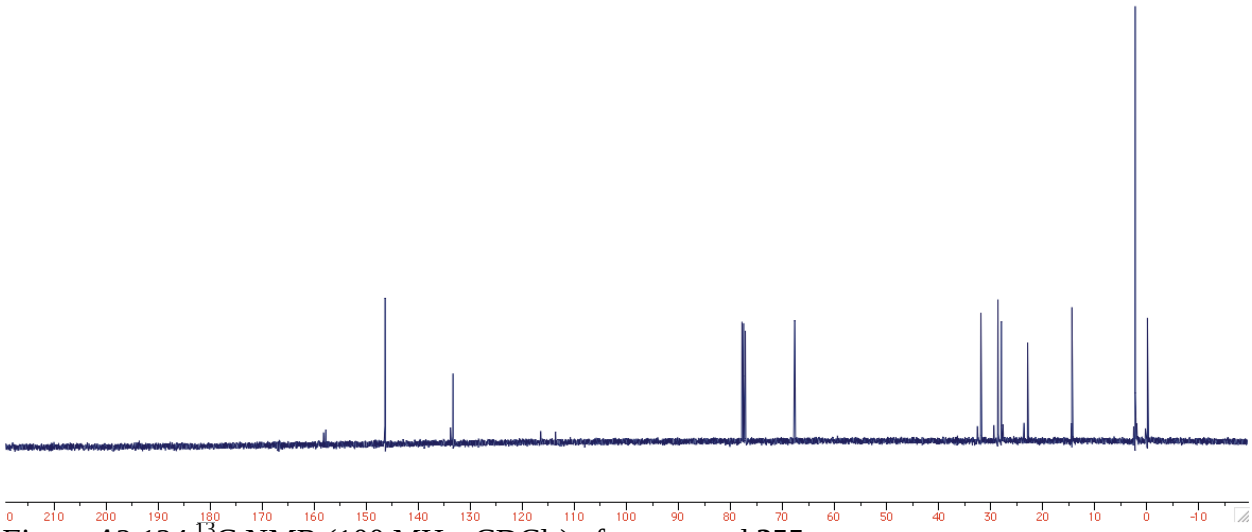


Figure A3.134 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **355**

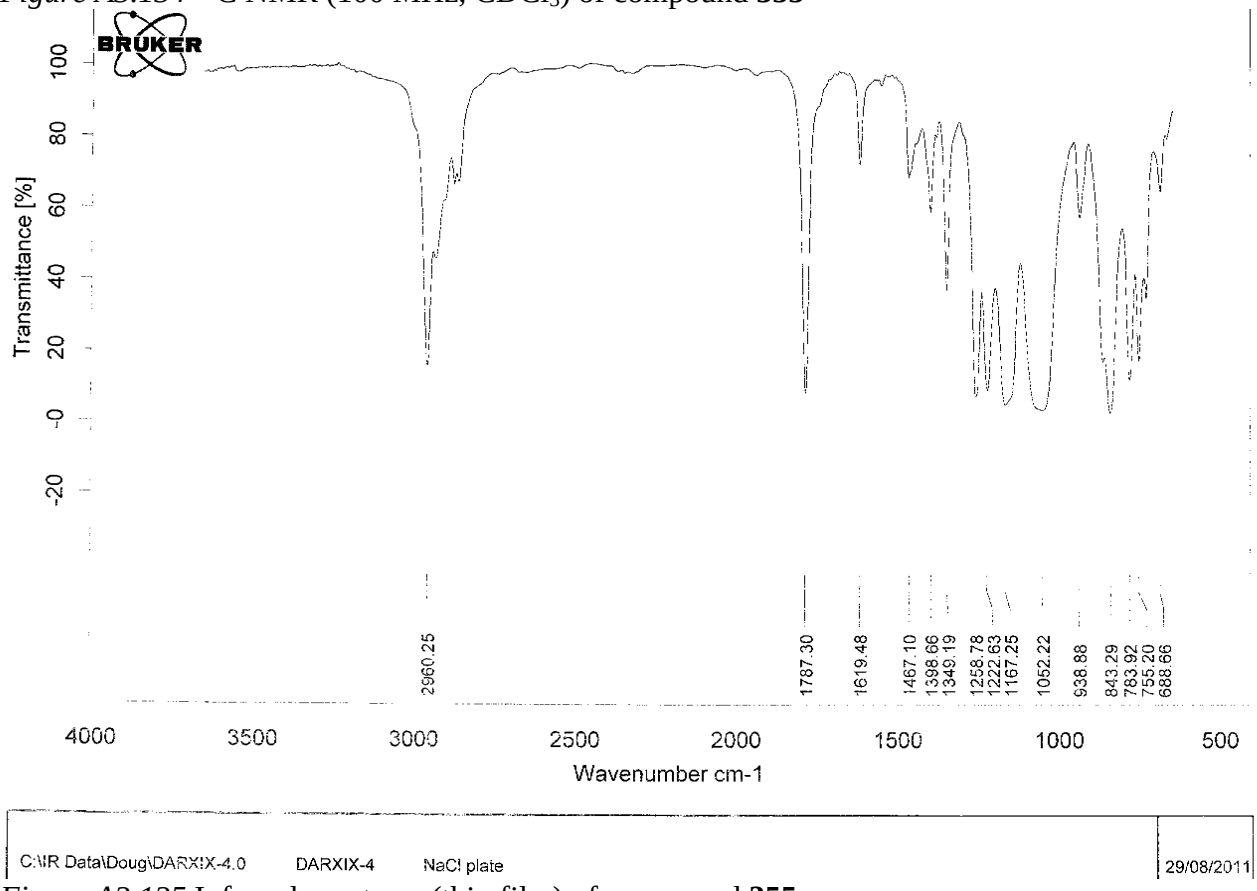
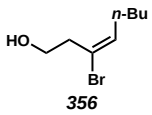


Figure A3.135 Infrared spectrum (thin film) of compound **355**



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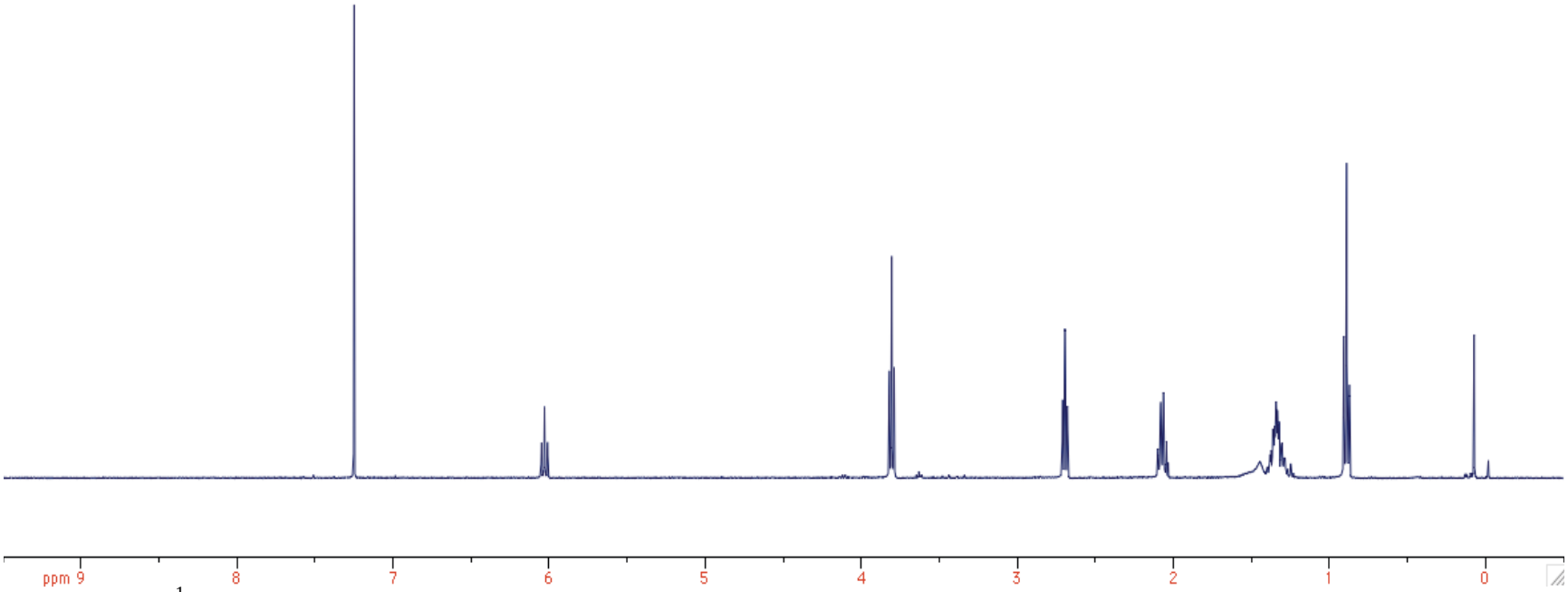


Figure A3.136 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **356**

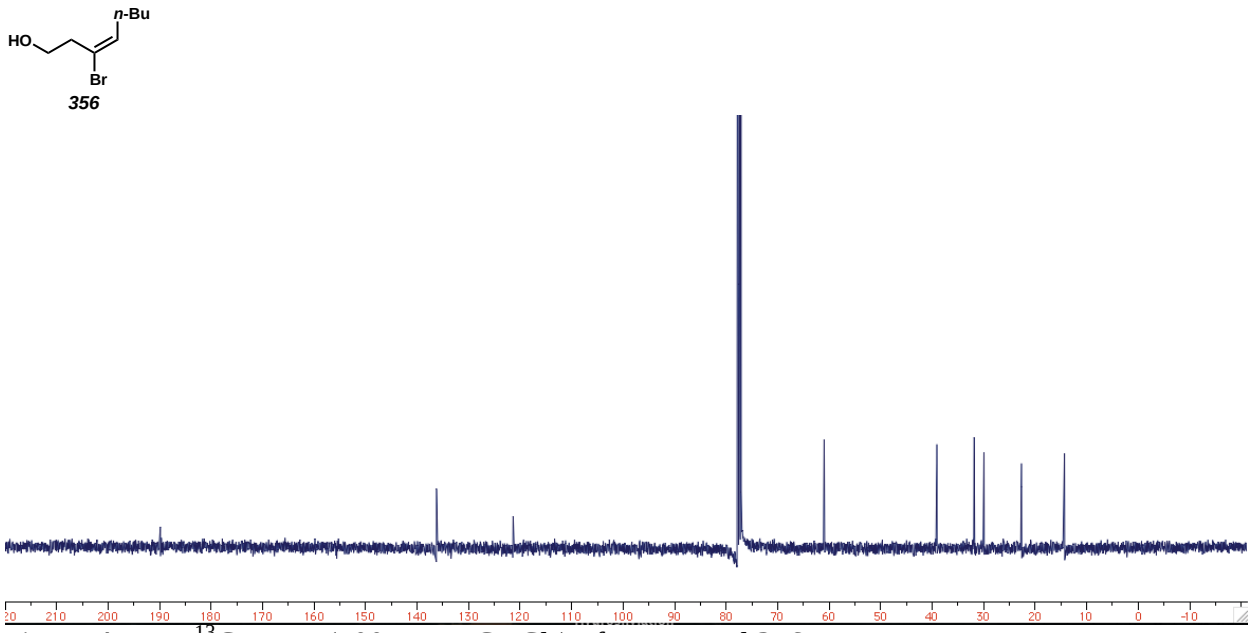


Figure A3.137 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **356**

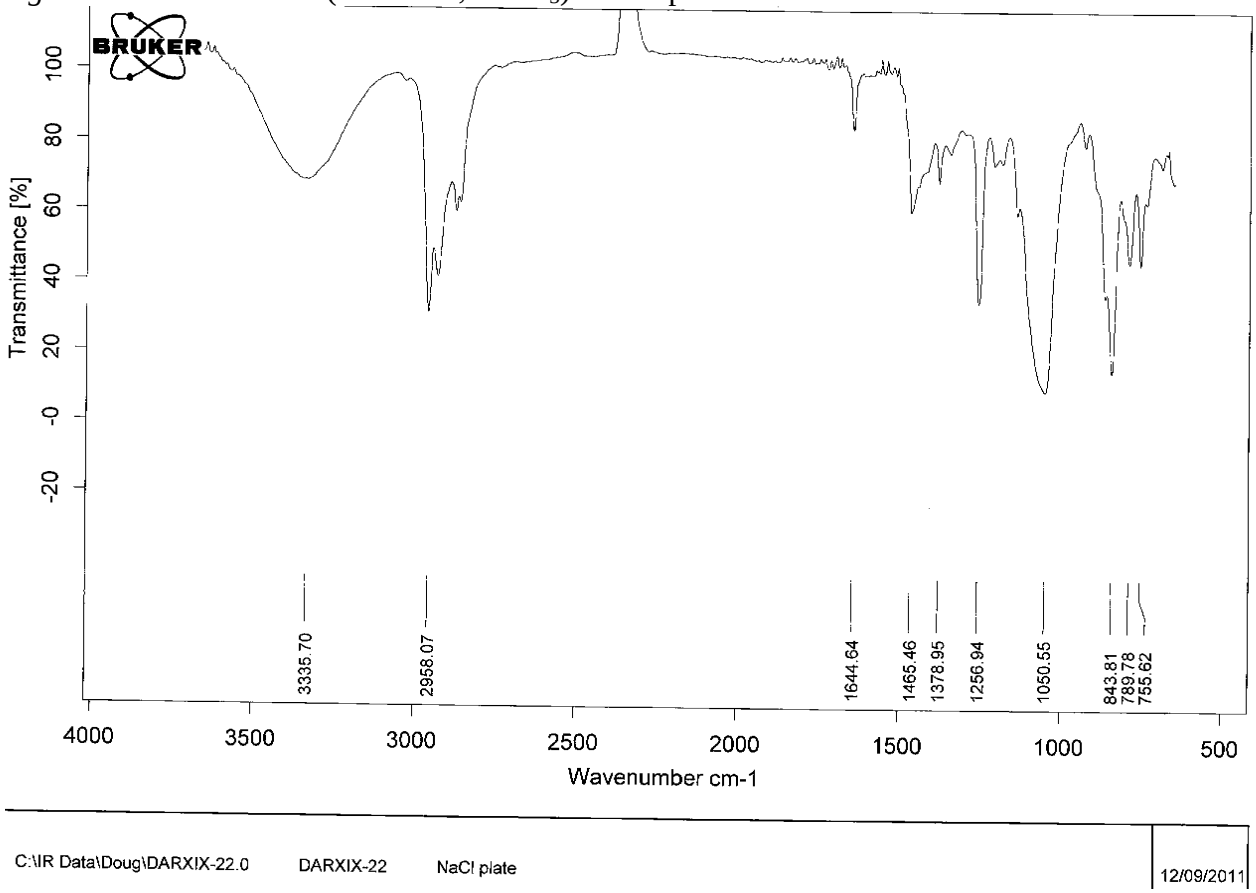
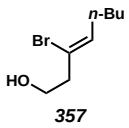


Figure A3.138 Infrared spectrum (thin film) of compound **356**



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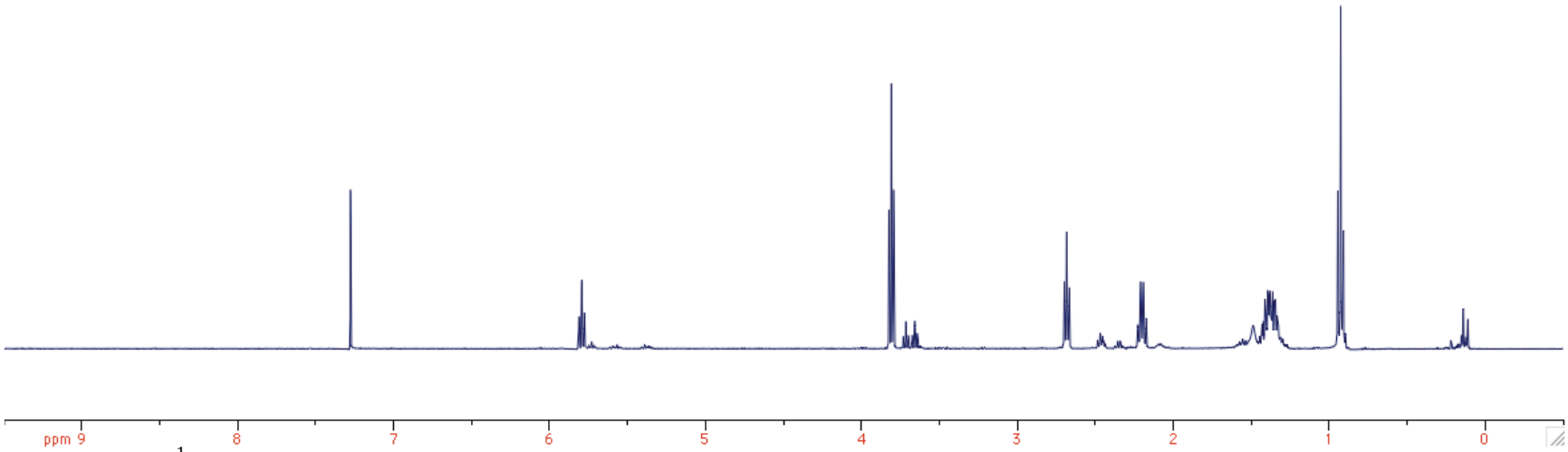
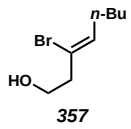


Figure A3.139 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **357**



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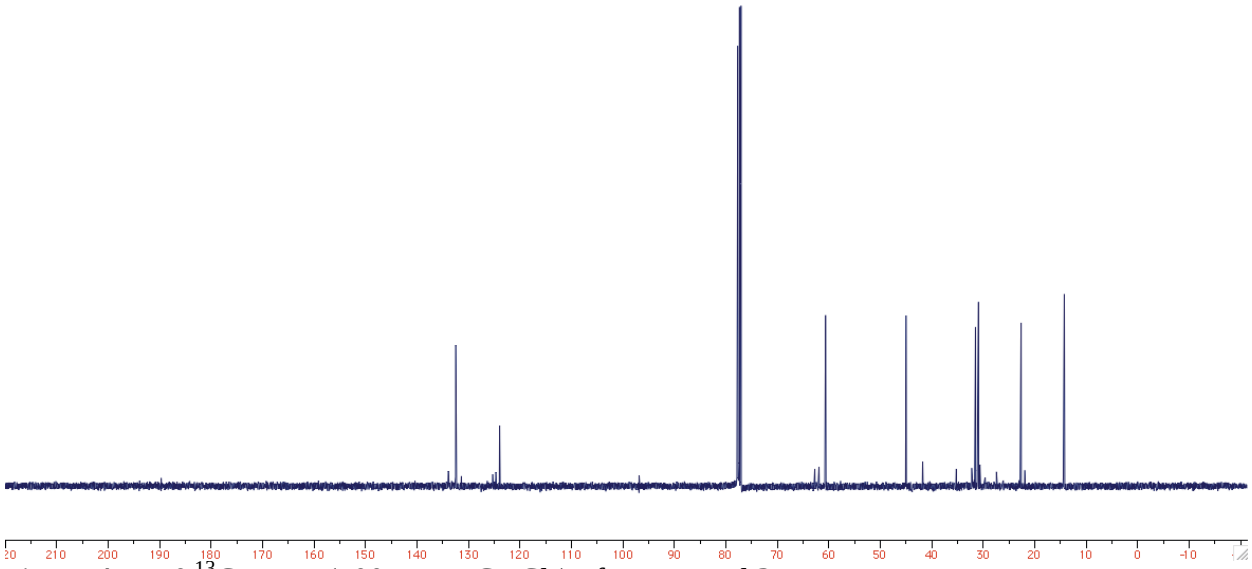


Figure A3.140 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **357**

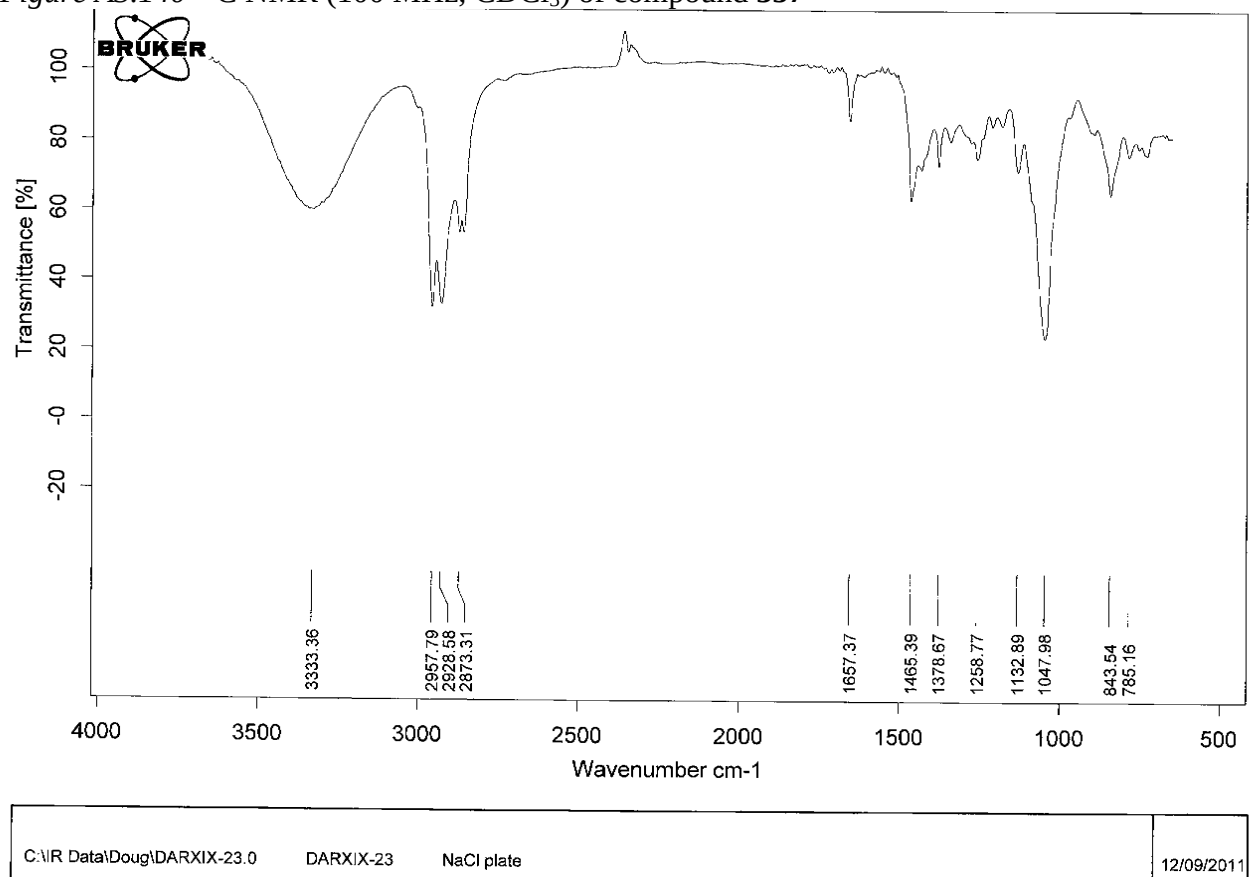
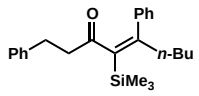


Figure A3.141 Infrared spectrum (thin film) of compound **357**



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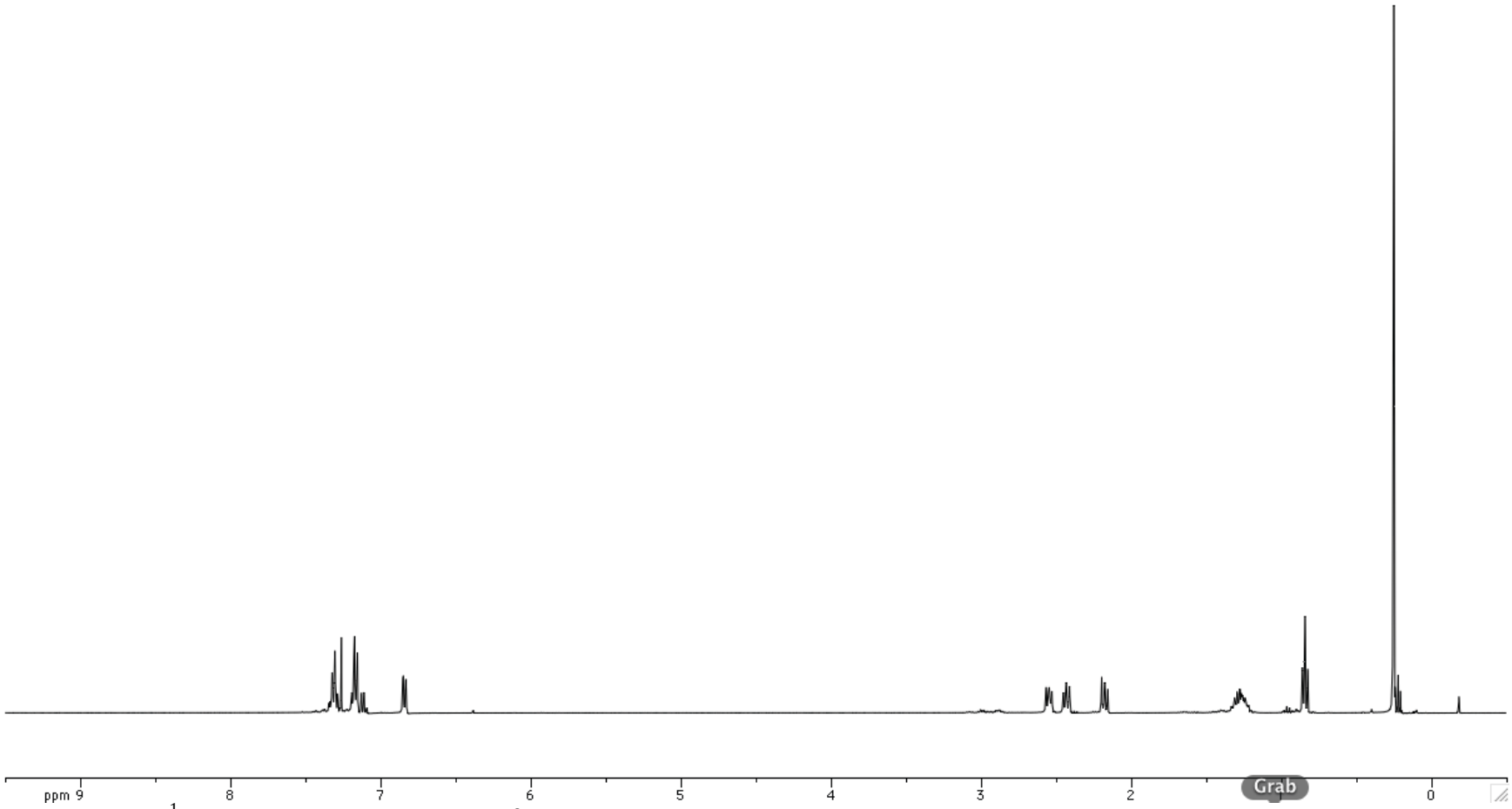


Figure A3.142 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **359**

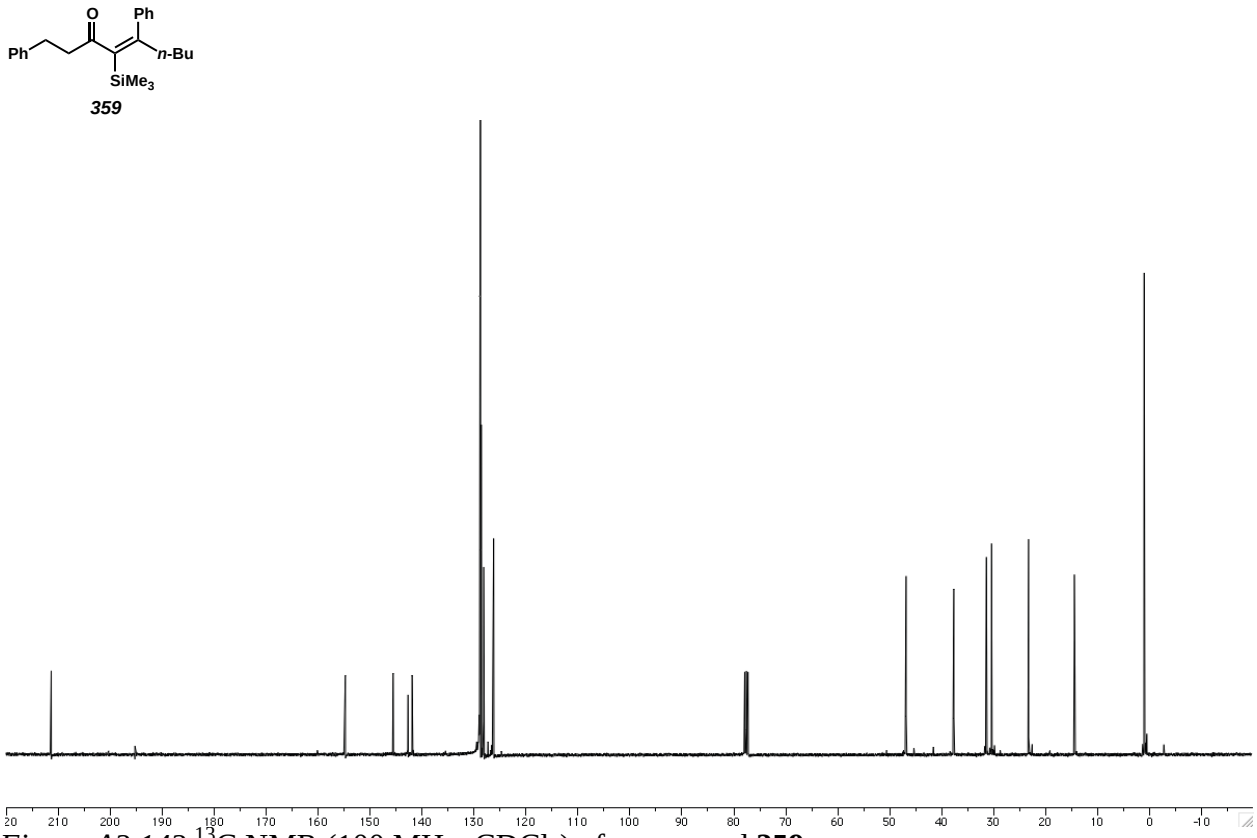


Figure A3.143 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **359**

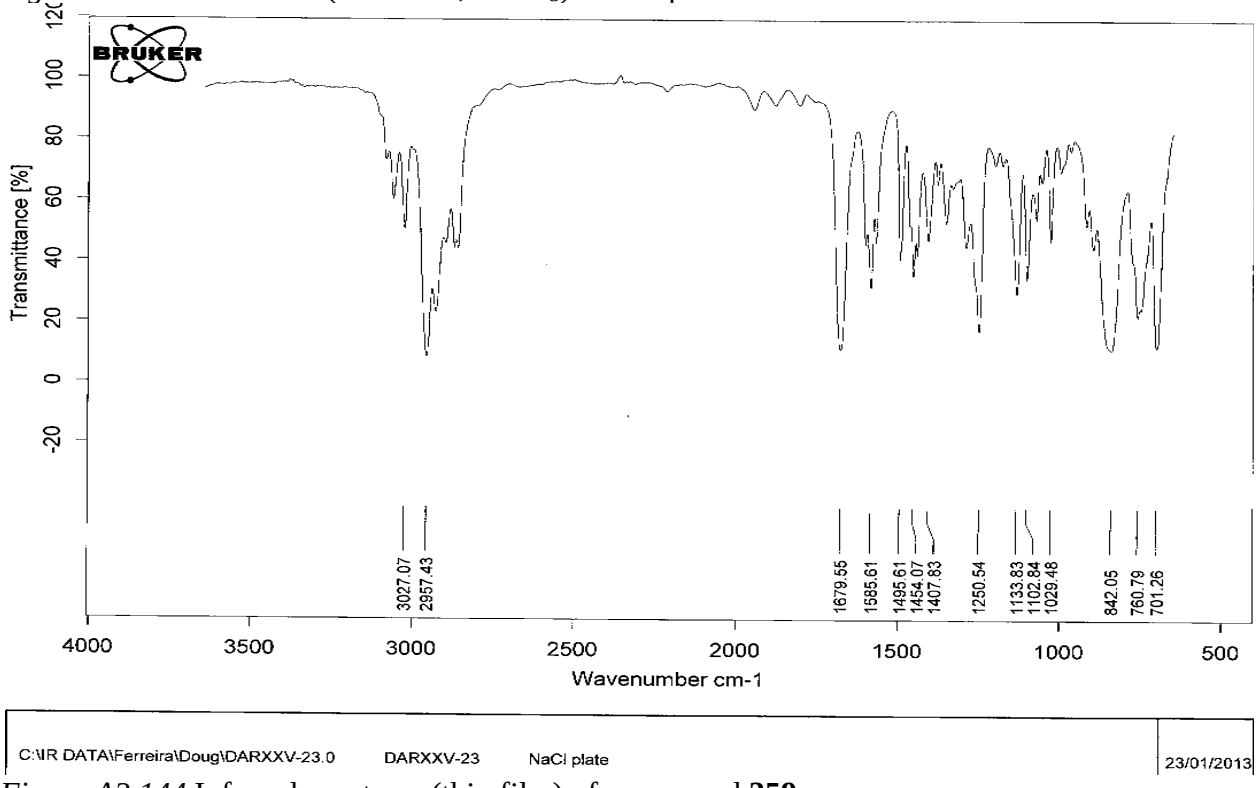
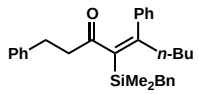


Figure A3.144 Infrared spectrum (thin film) of compound **359**



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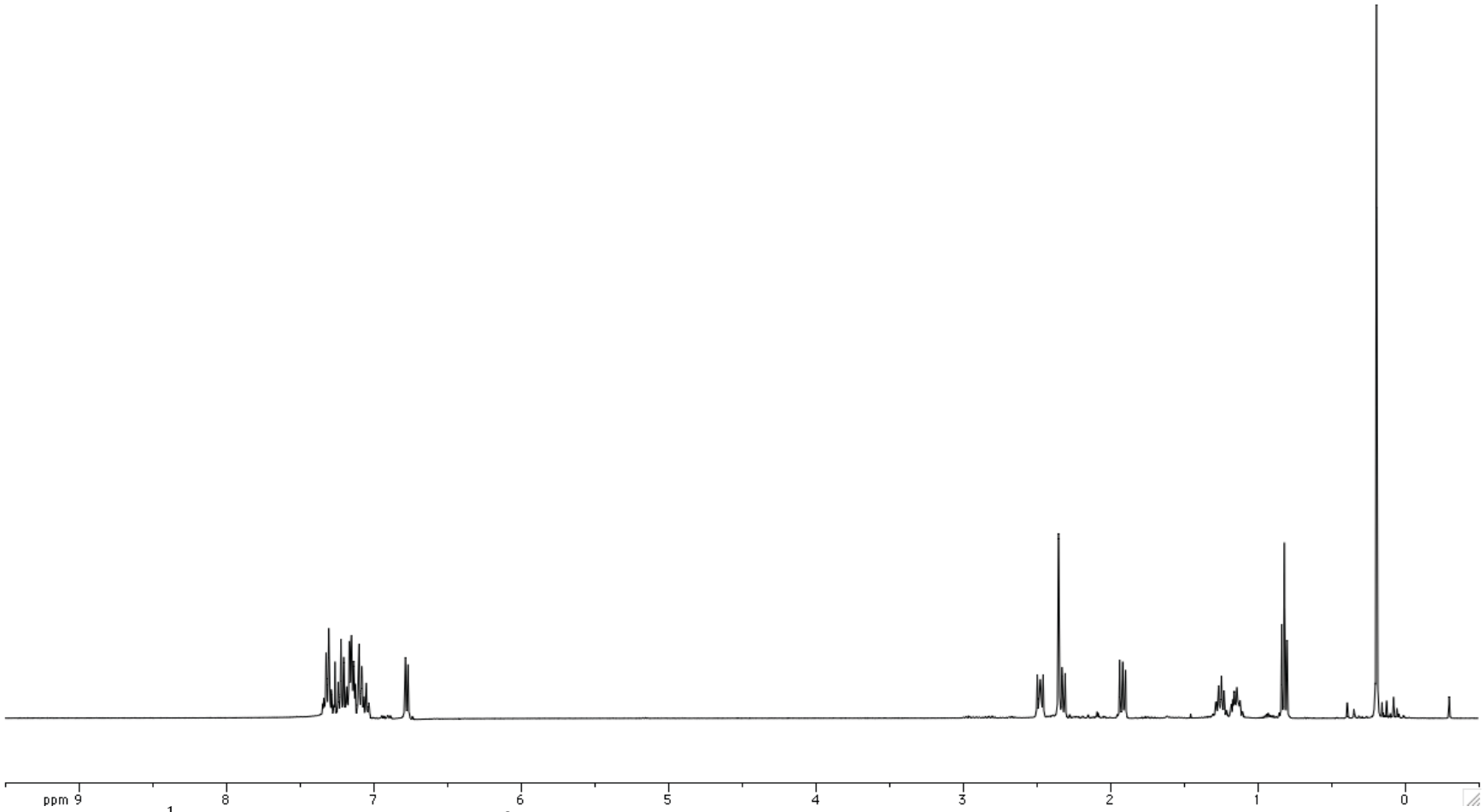


Figure A3.145 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **360**

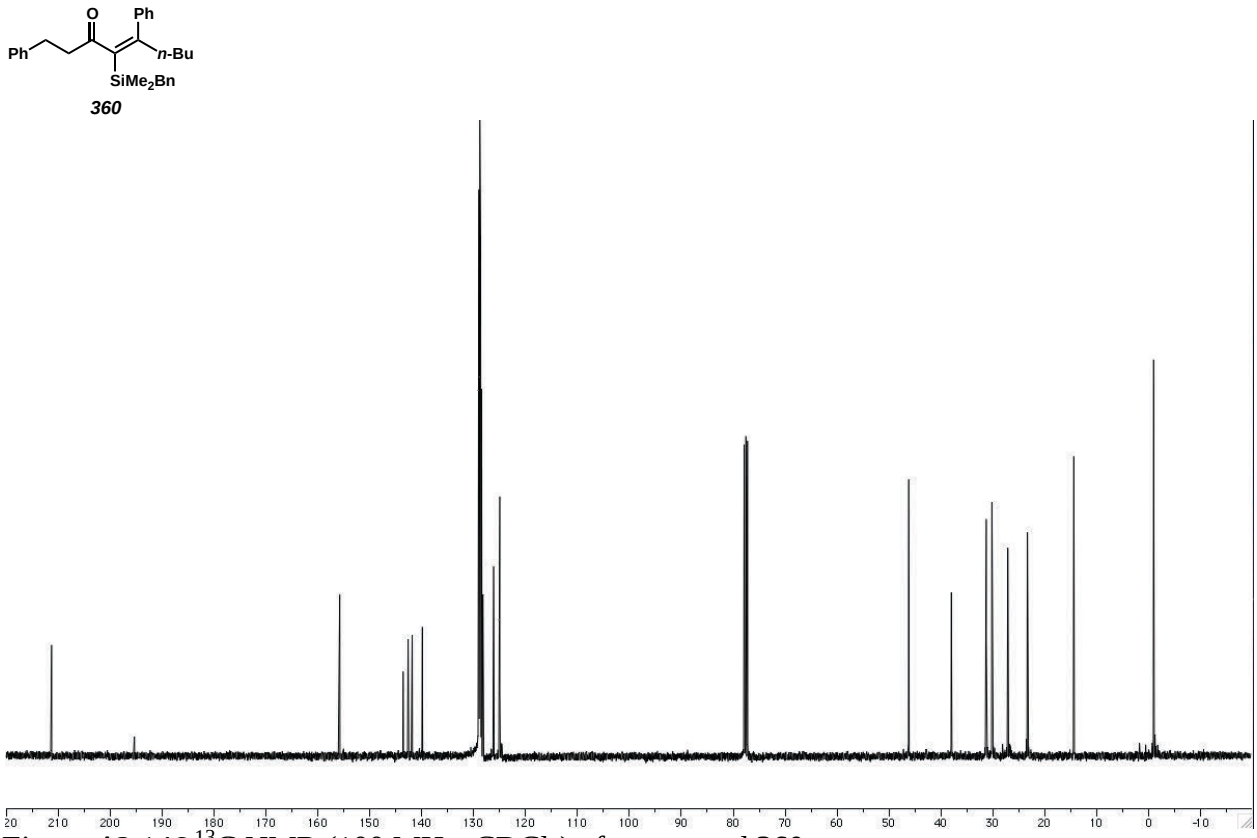


Figure A3.146 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **360**

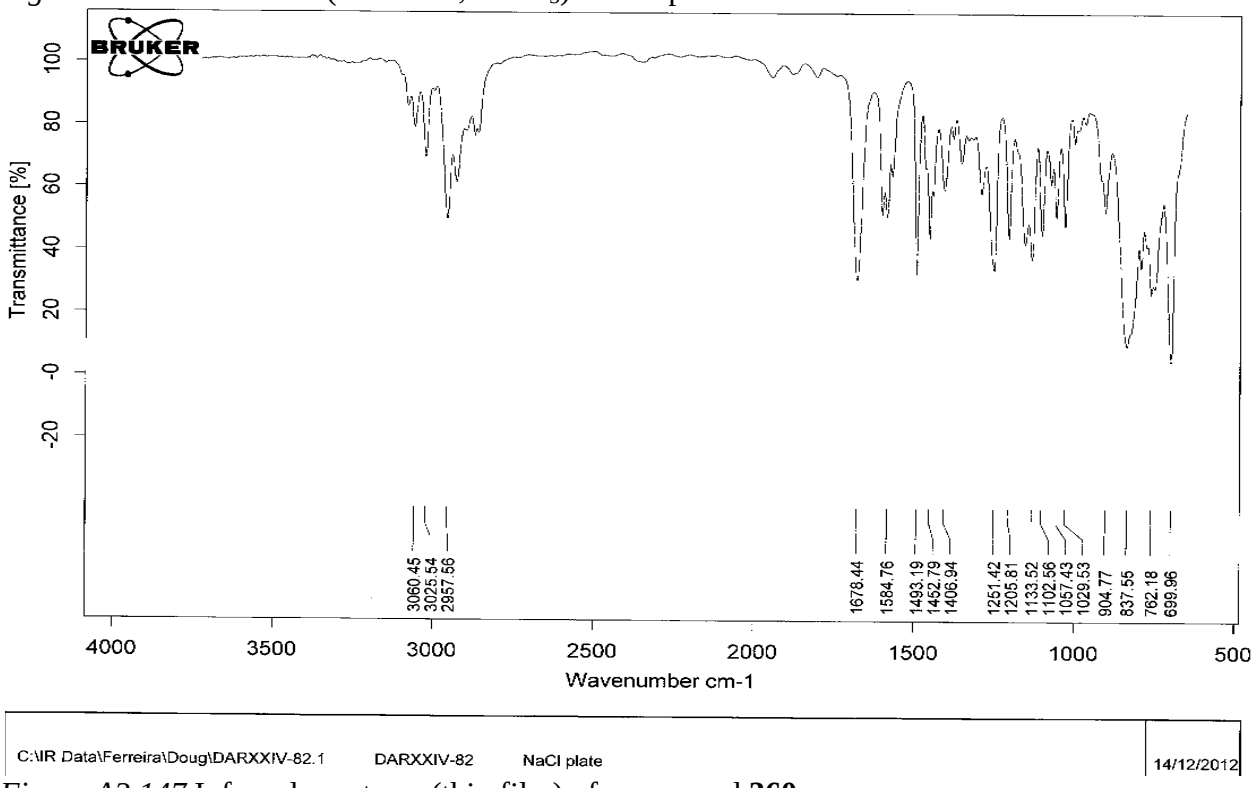
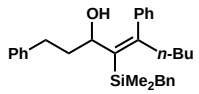


Figure A3.147 Infrared spectrum (thin film) of compound **360**



358

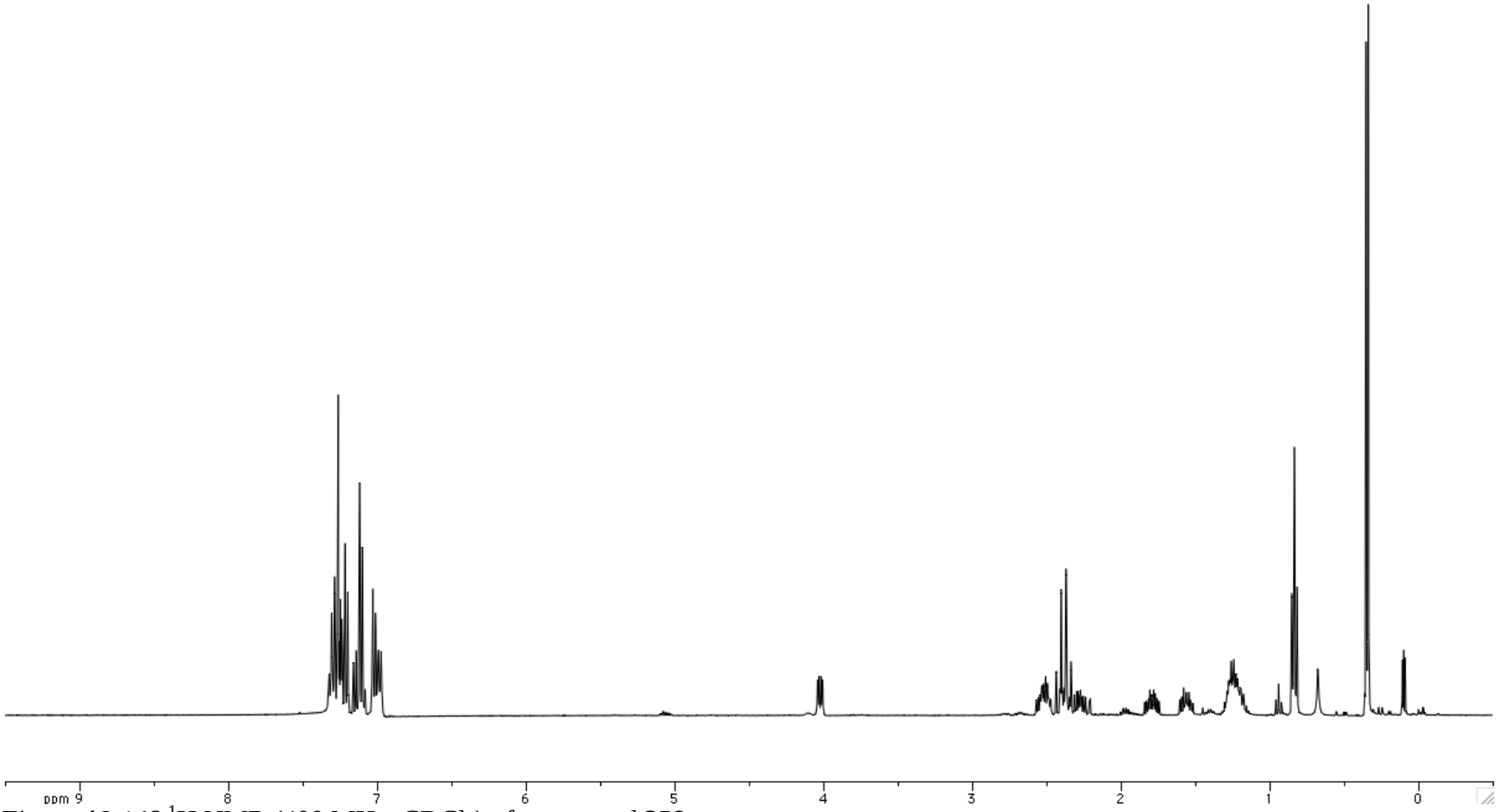


Figure A3.148 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **358**

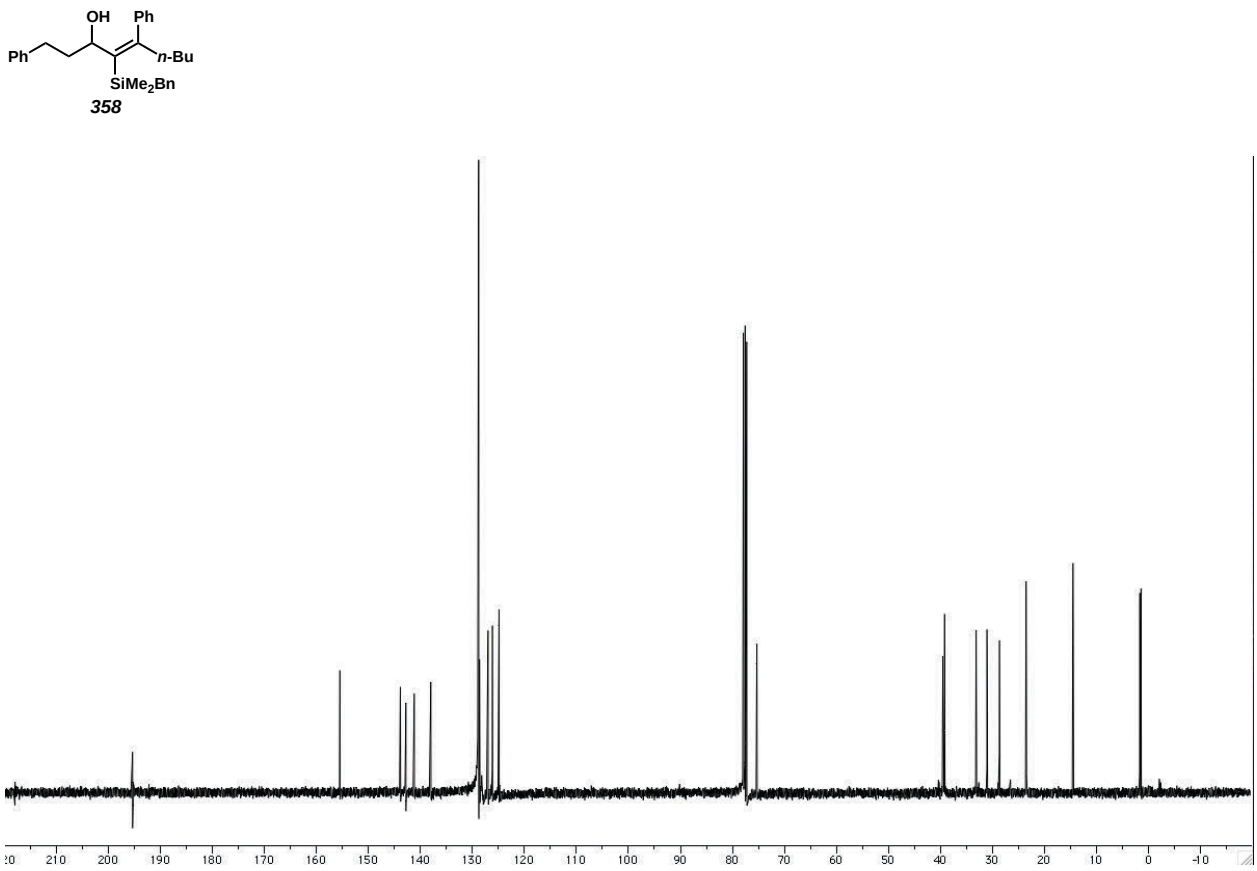
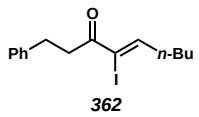


Figure A3.149 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **358**

Figure A3.150 Infrared spectrum (thin film) of compound **358**



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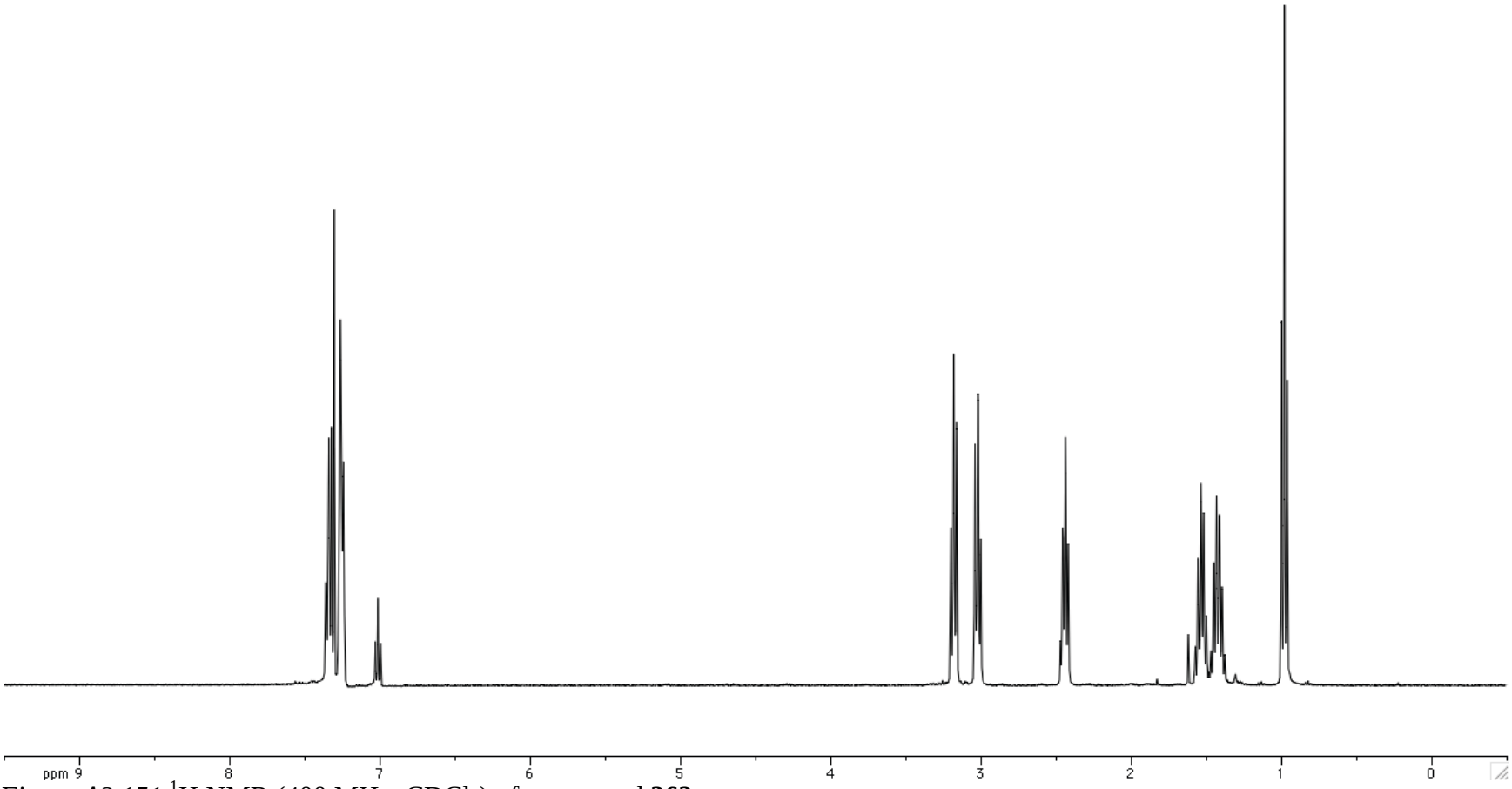


Figure A3.151 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **362**

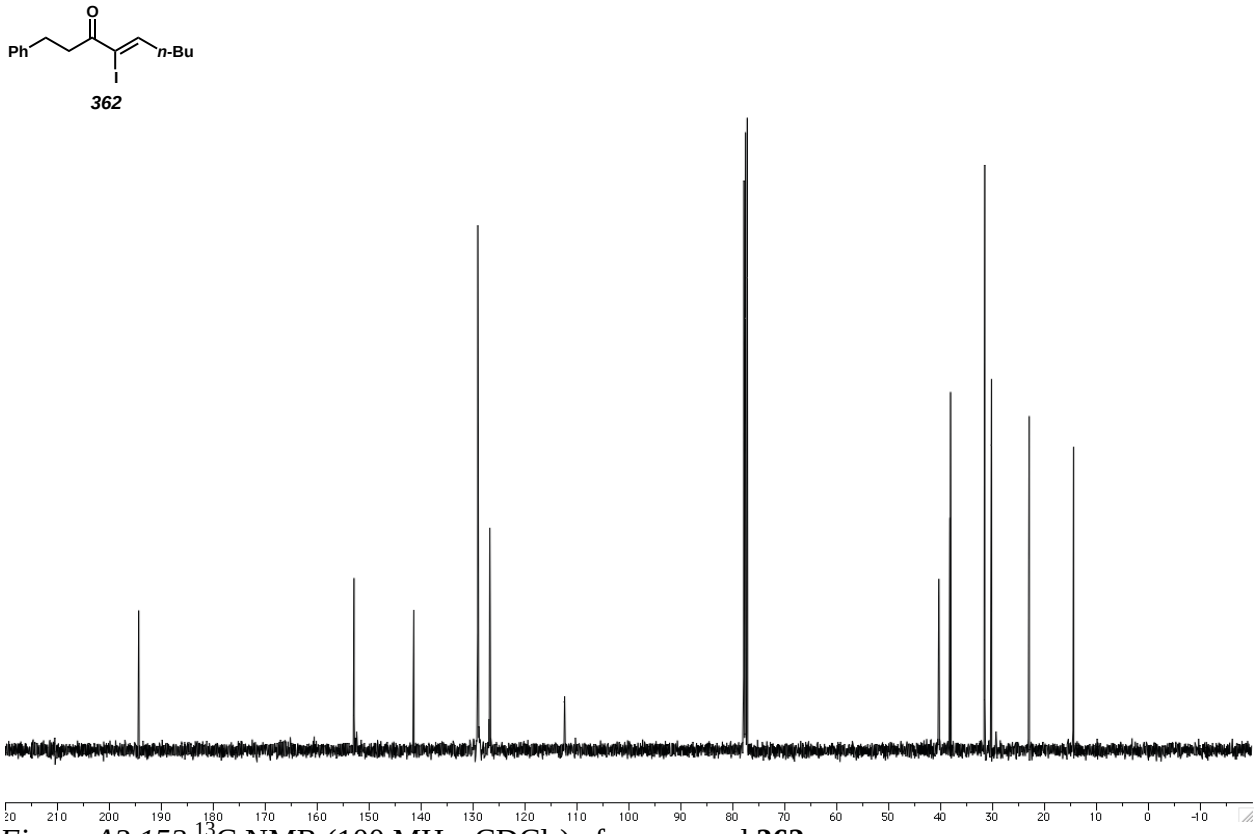


Figure A3.152 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **362**

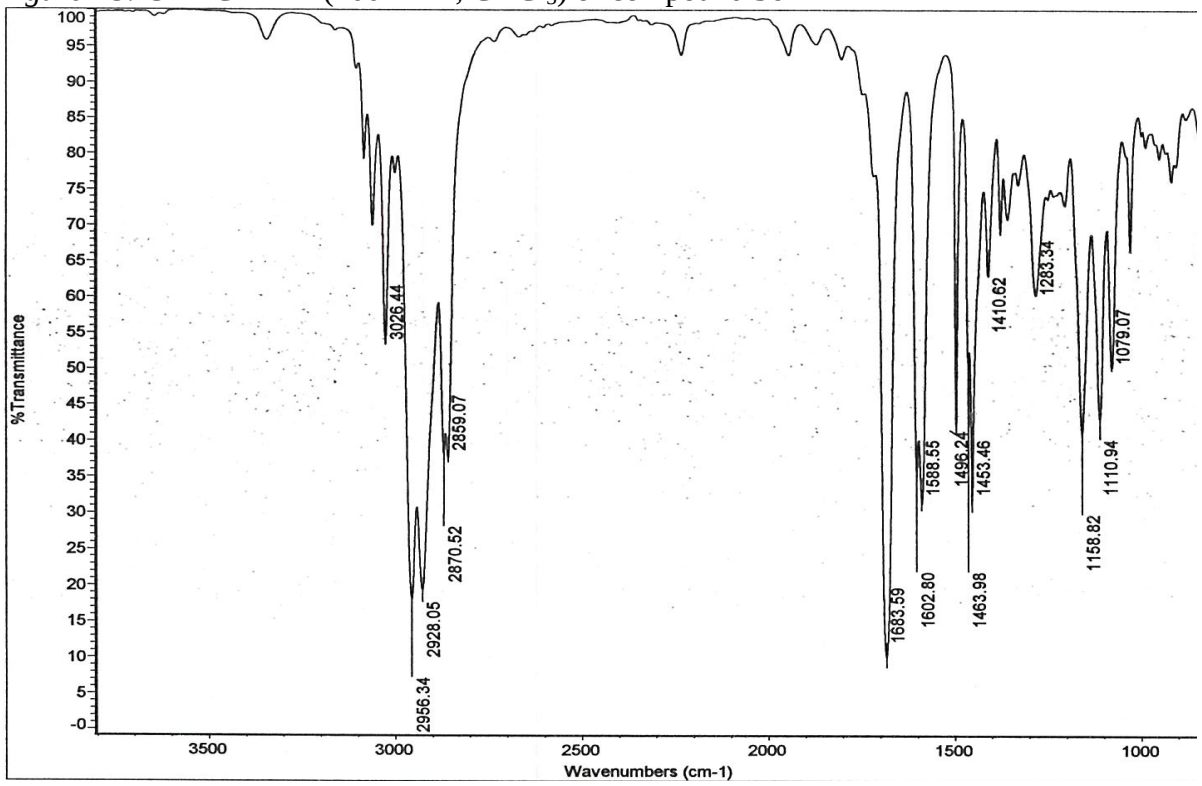
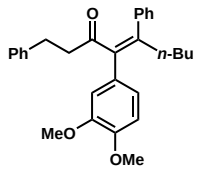


Figure A3.153 Infrared spectrum (thin film) of compound **362**



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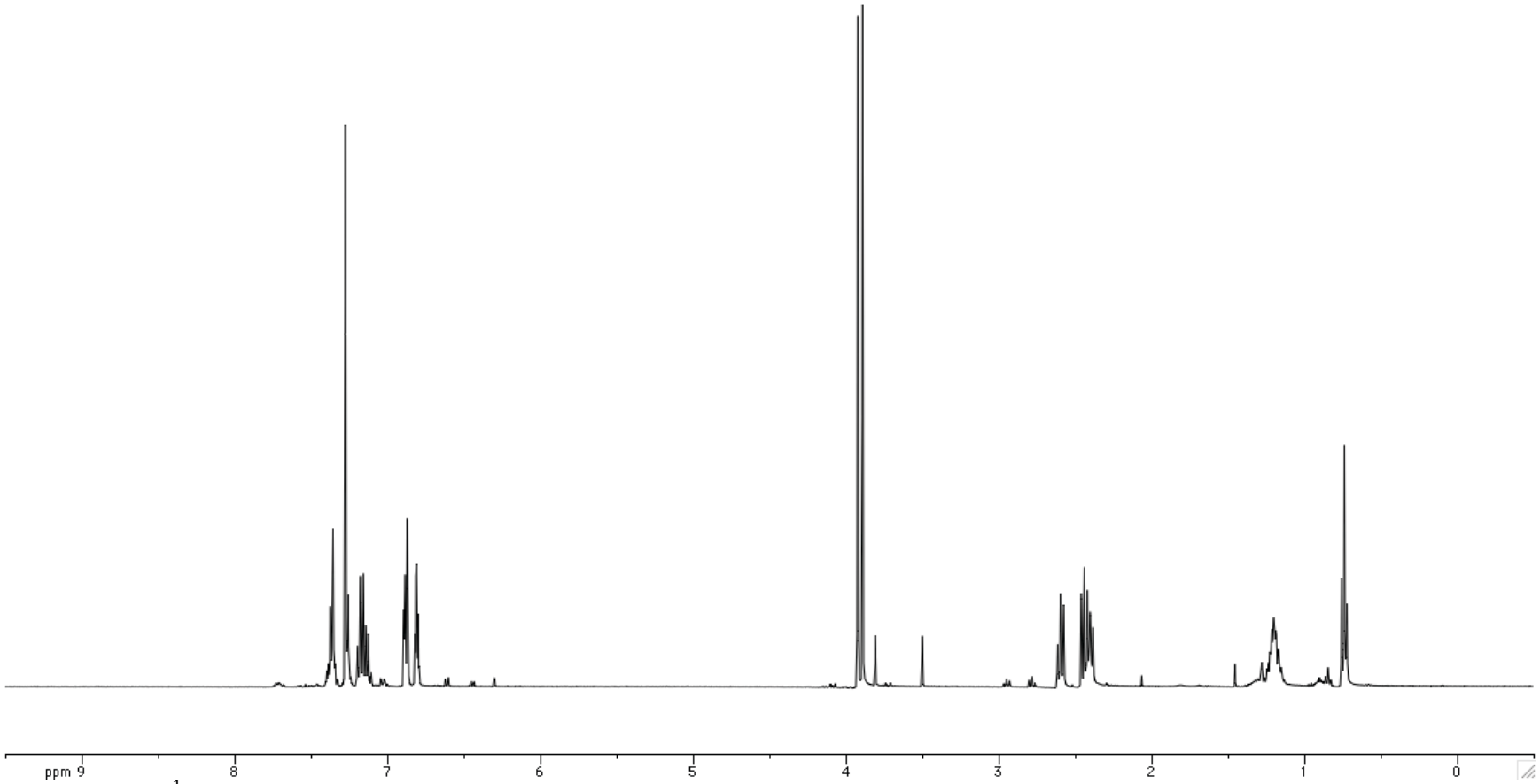
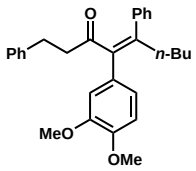


Figure A3.154 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **365**



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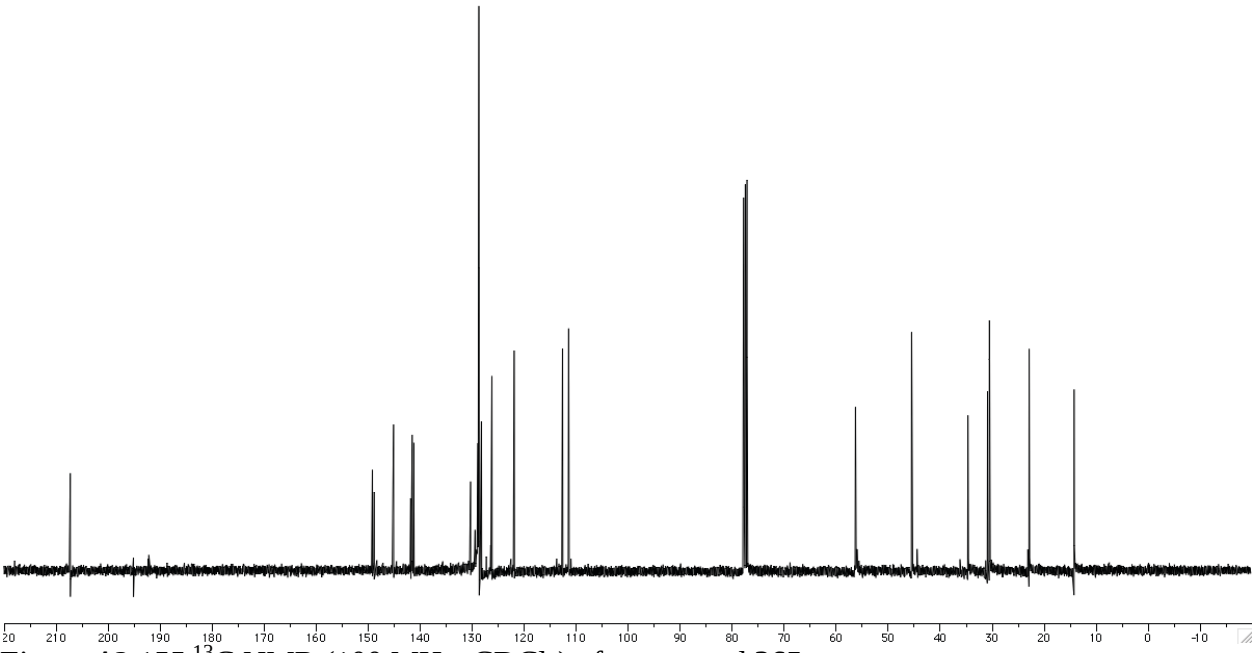


Figure A3.155 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **365**

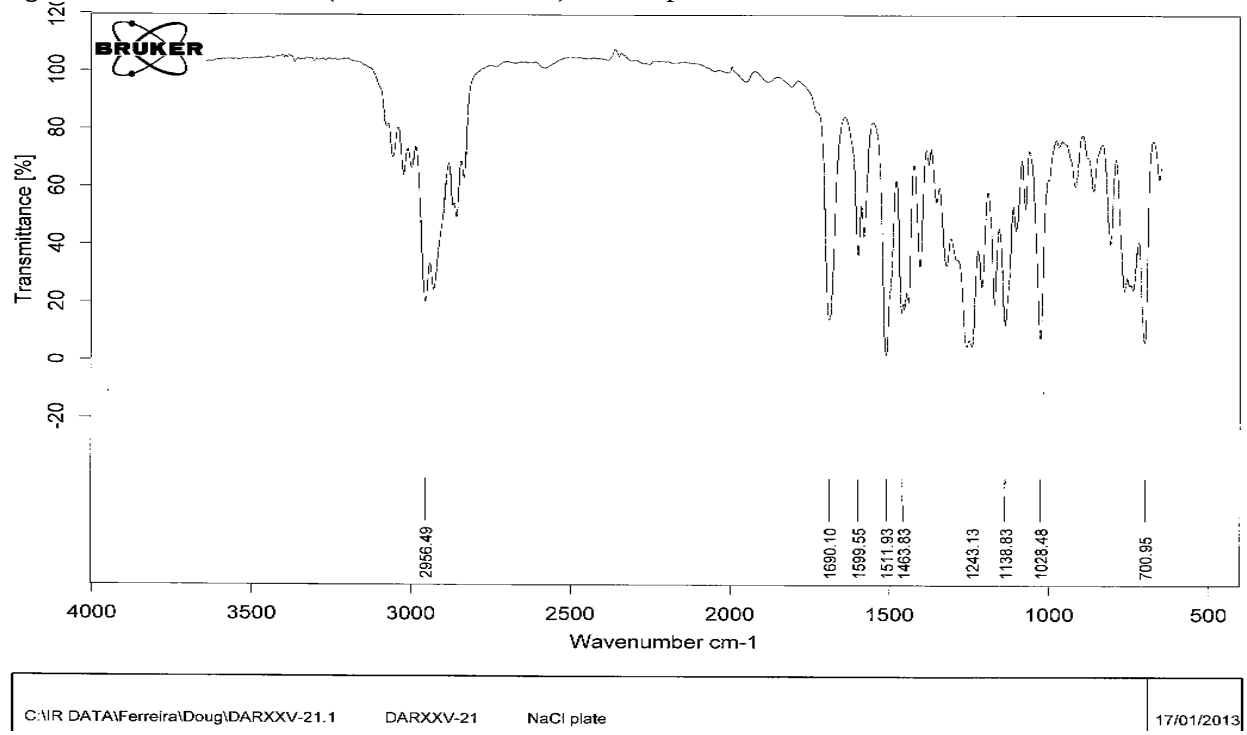
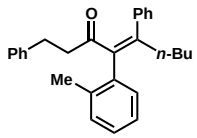


Figure A3.156 Infrared spectrum (thin film) of compound **365**



367

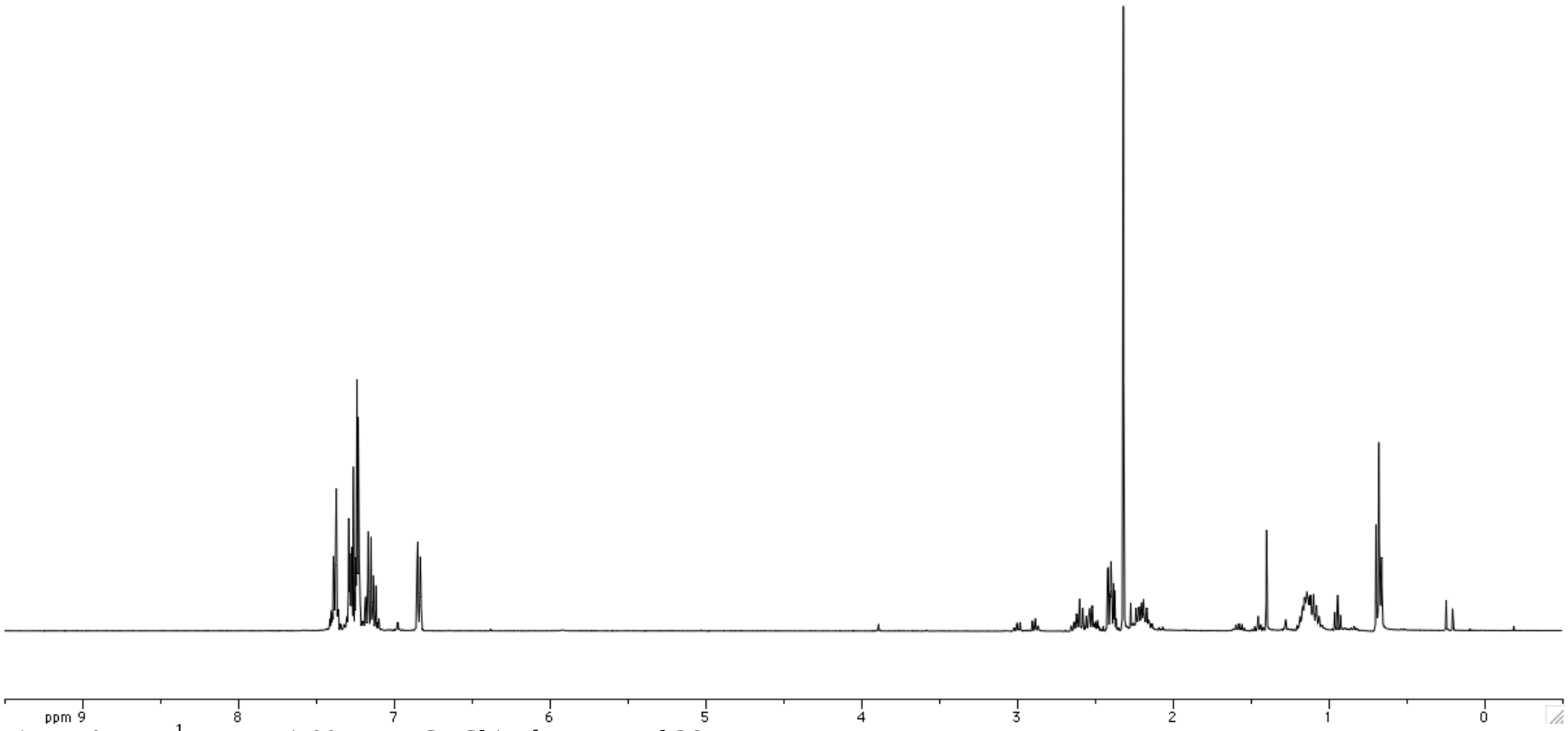


Figure A3.157 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **367**

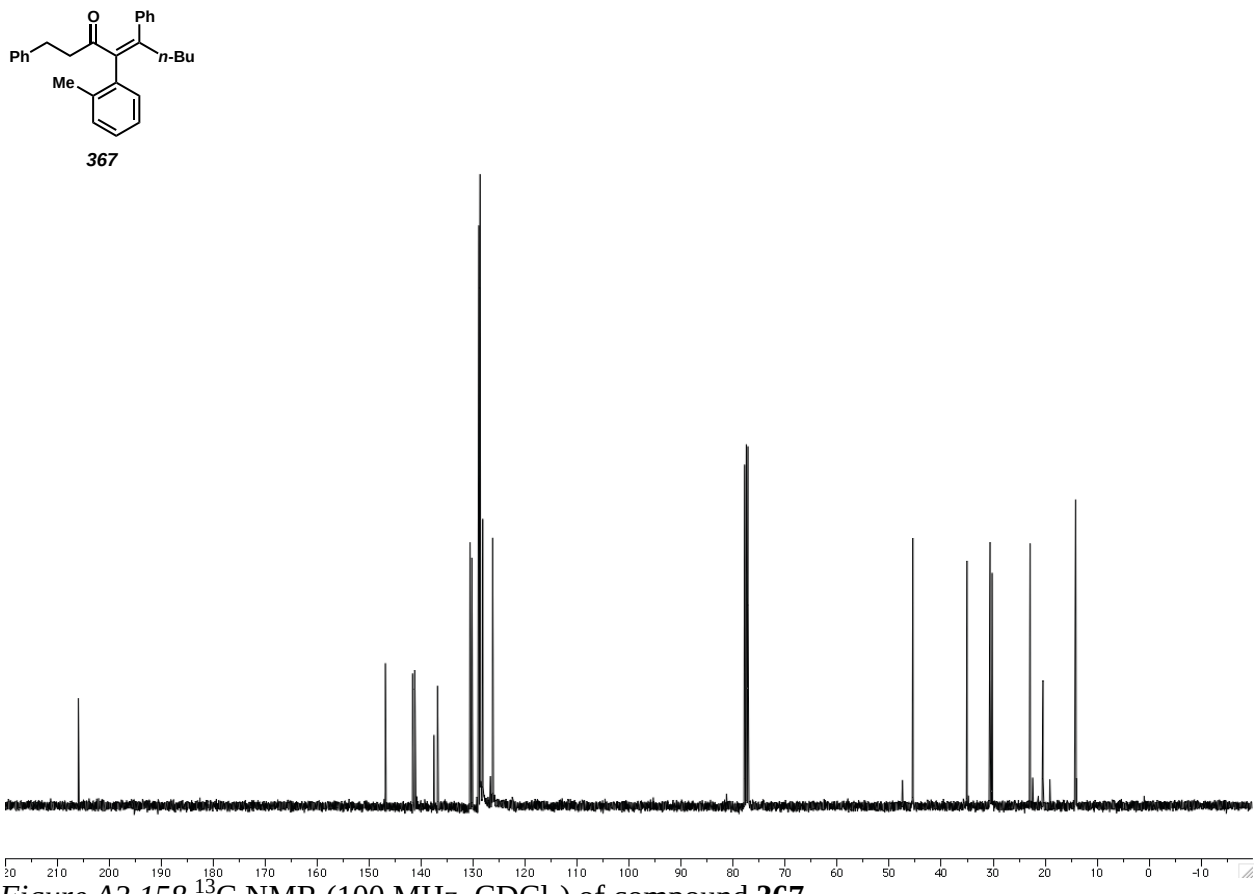


Figure A3.158 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **367**

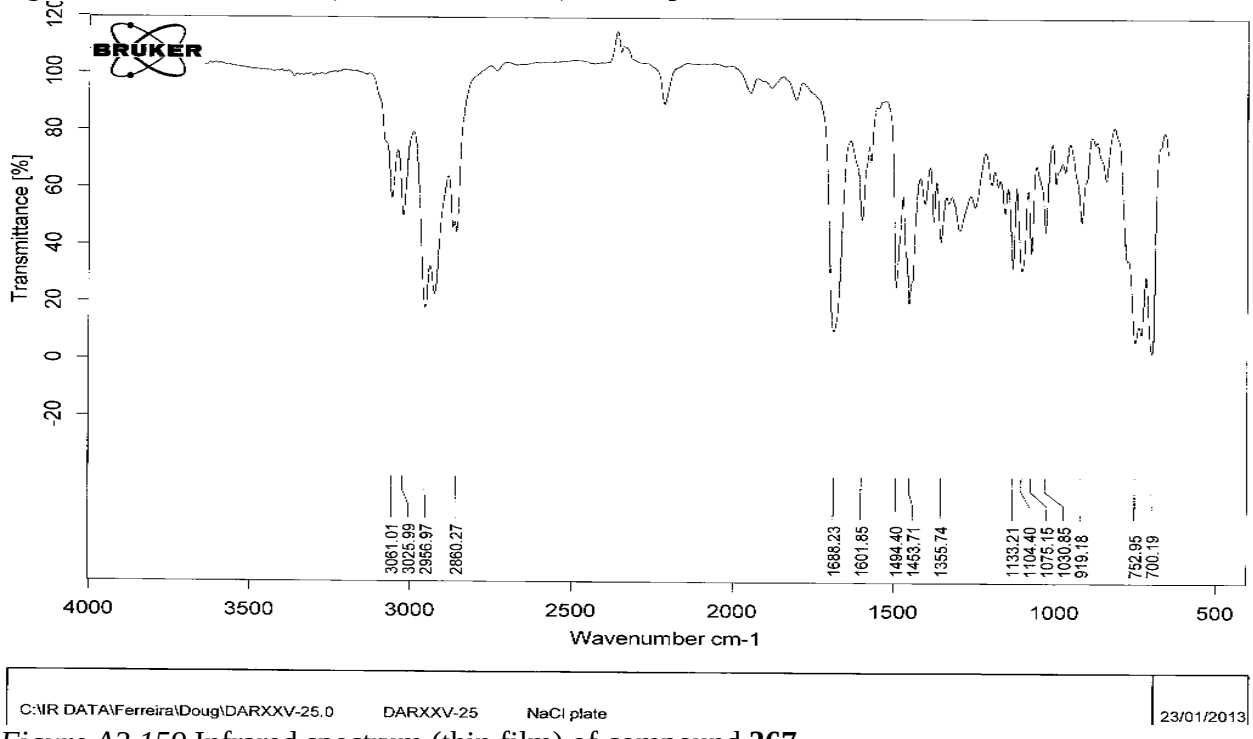
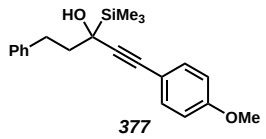


Figure A3.159 Infrared spectrum (thin film) of compound **367**



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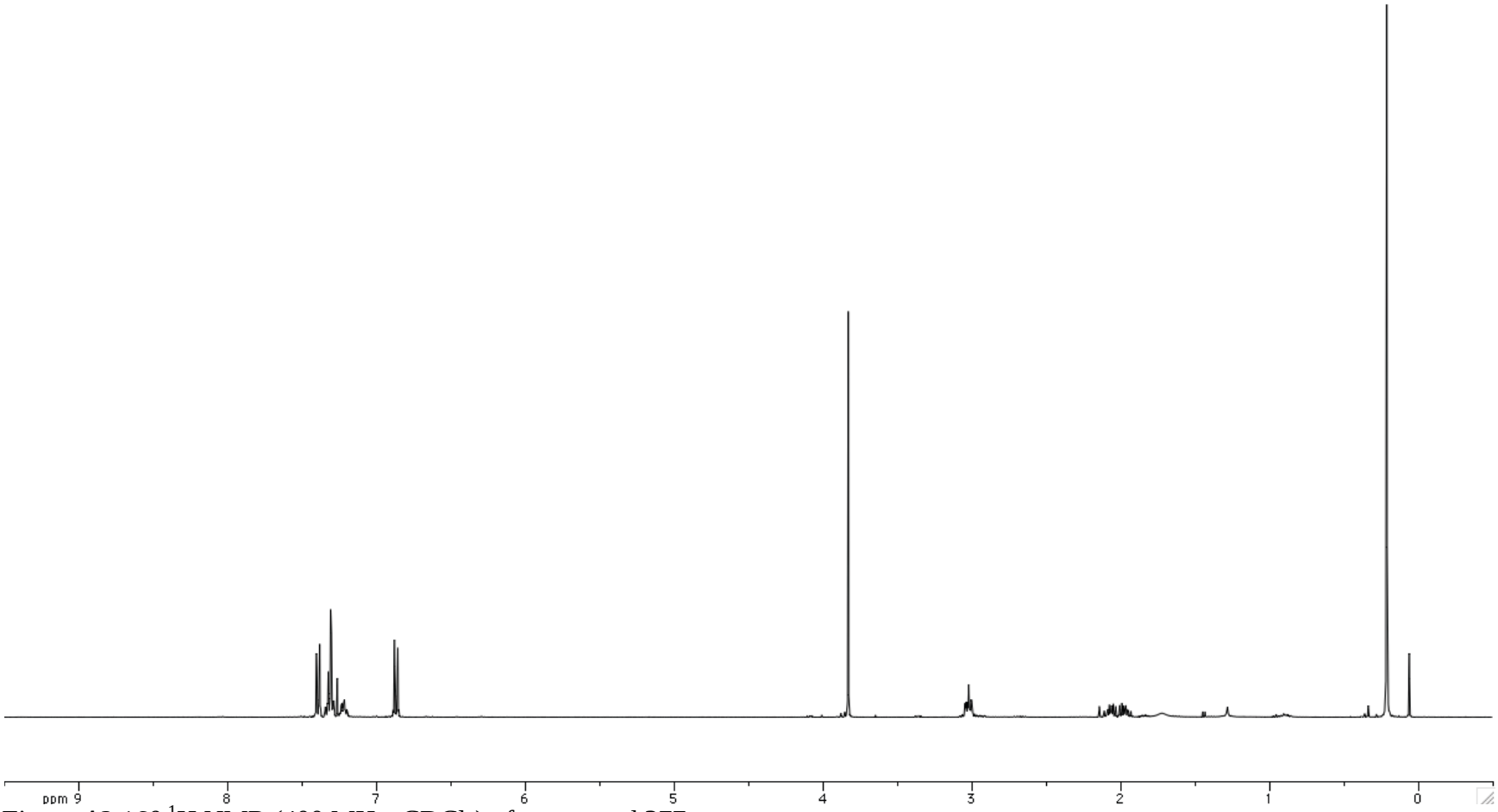


Figure A3.160 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **377**

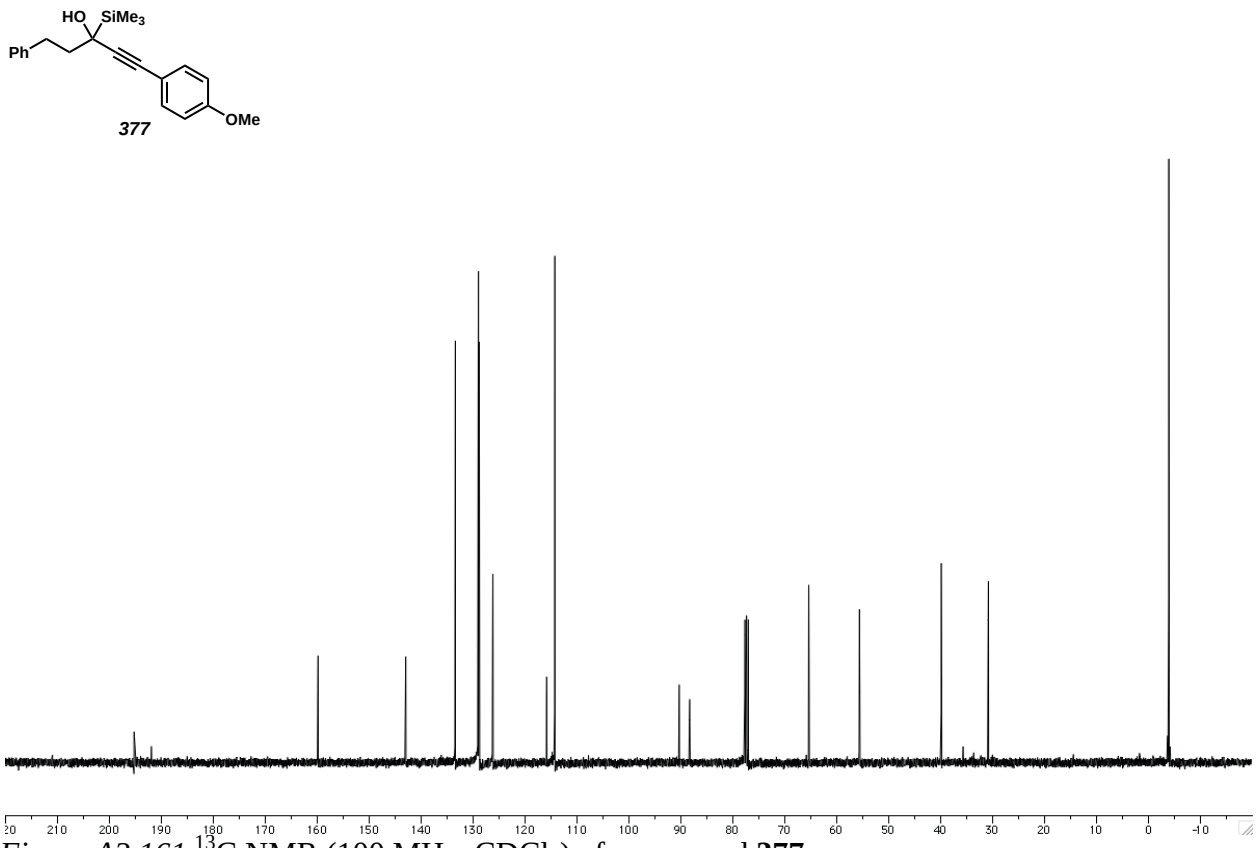


Figure A3.161 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **377**

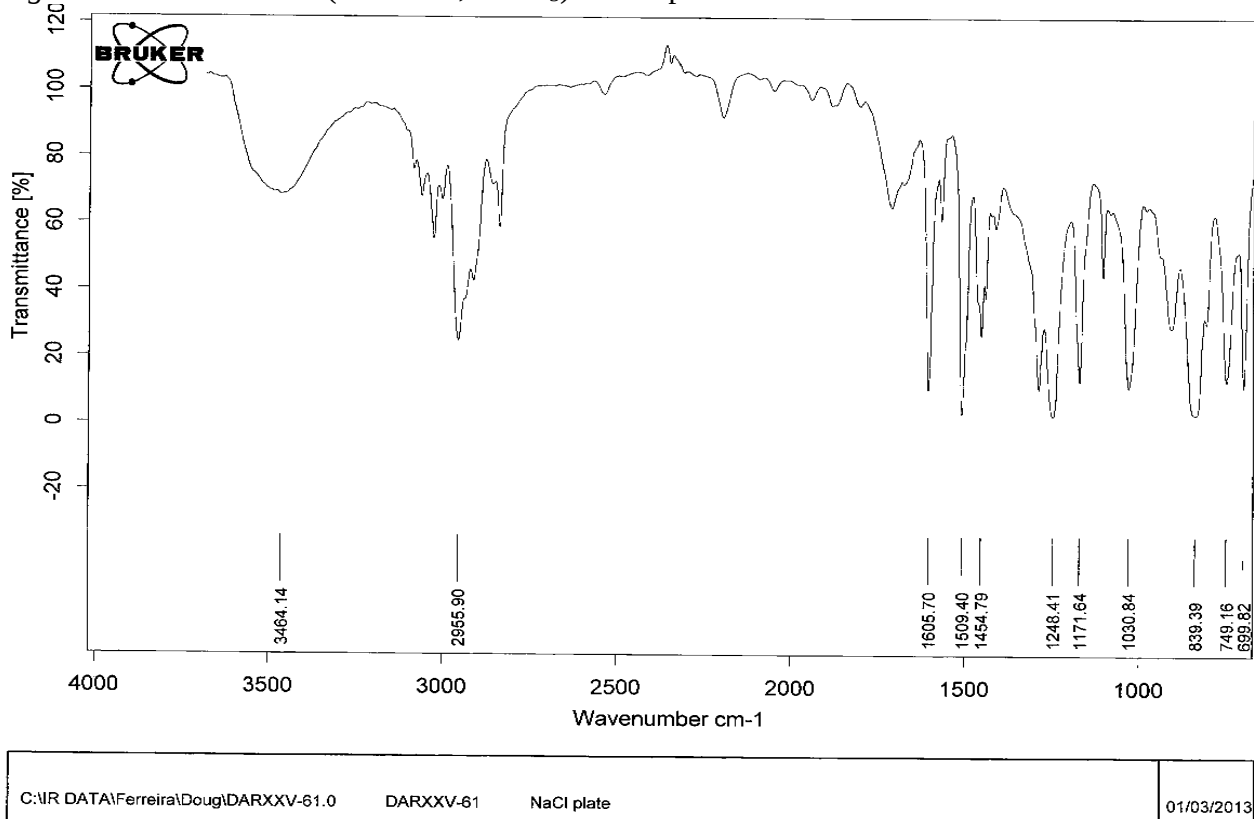
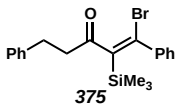


Figure A3.162 Infrared spectrum (thin film) of compound **377**



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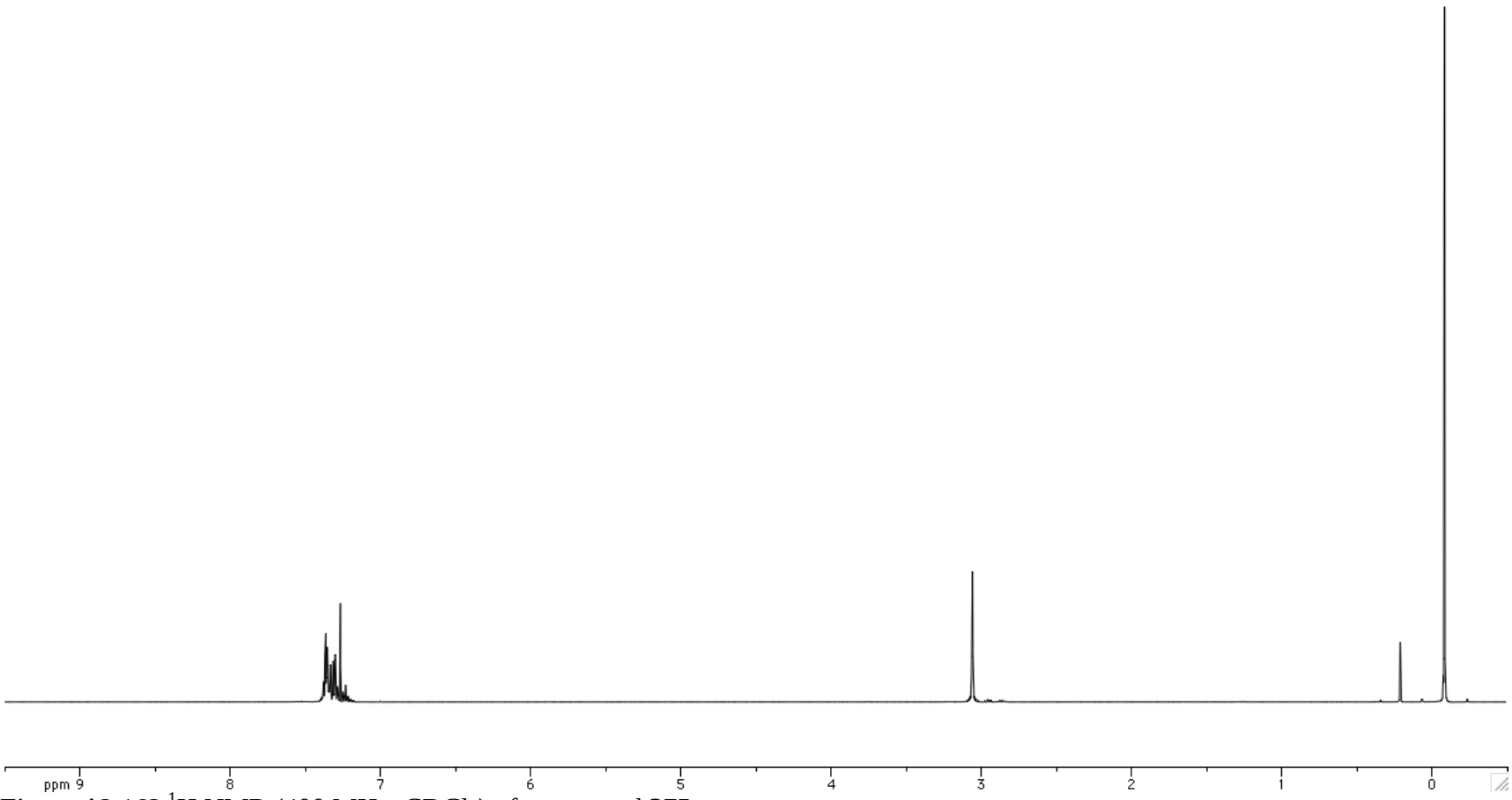


Figure A3.163 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **375**

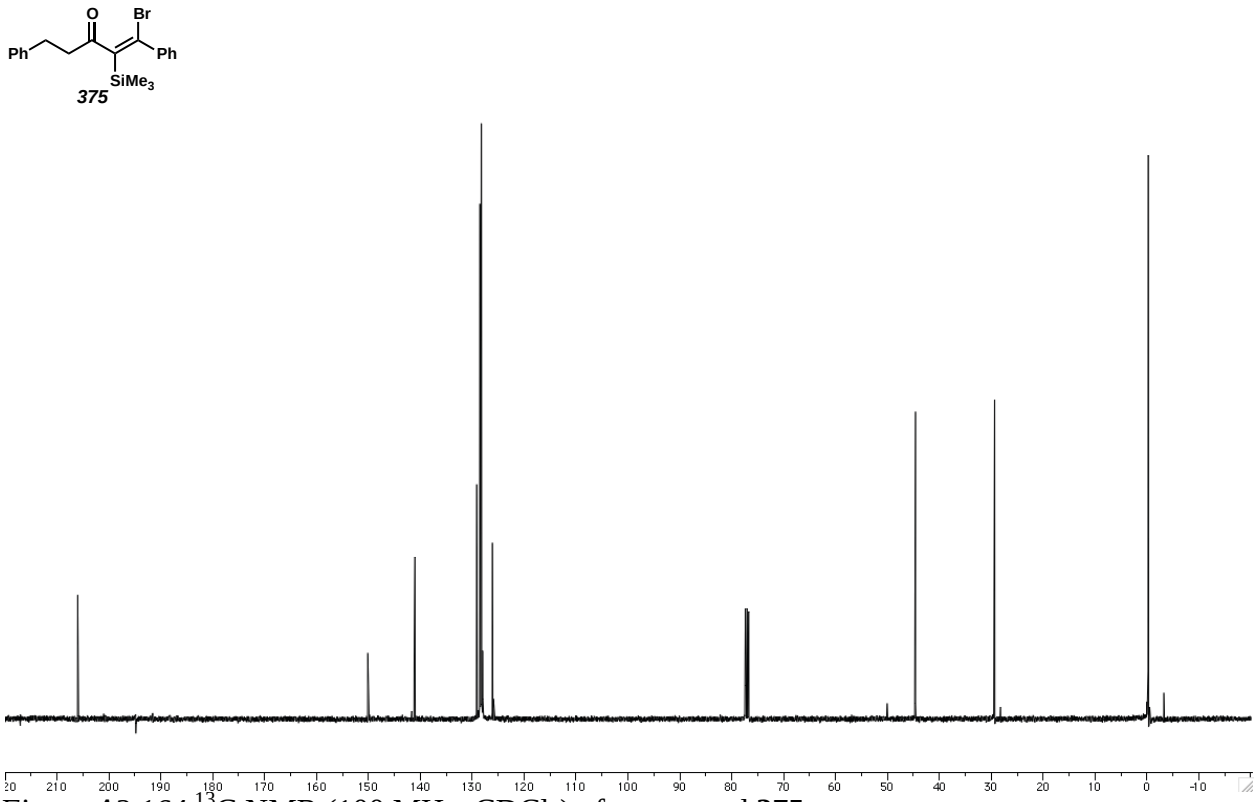


Figure A3.164 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **375**

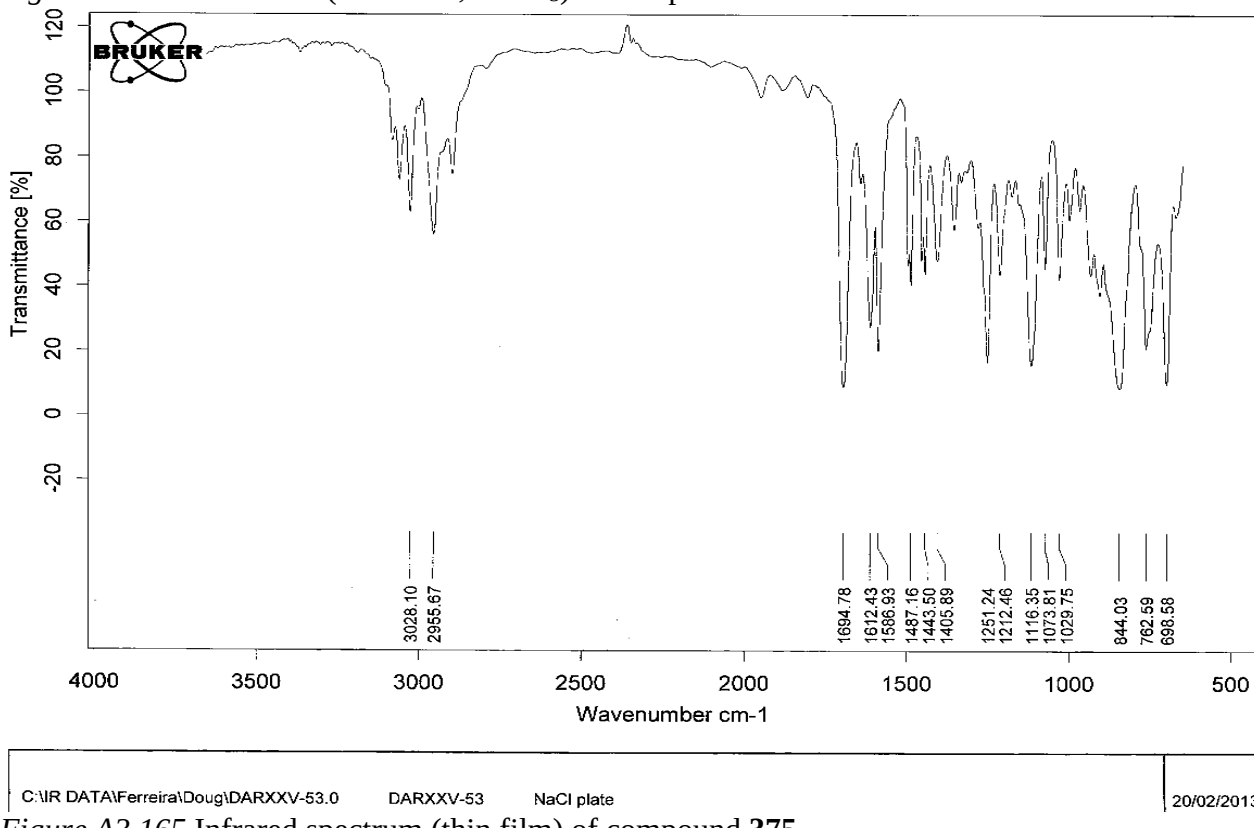
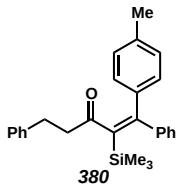


Figure A3.165 Infrared spectrum (thin film) of compound **375**



380

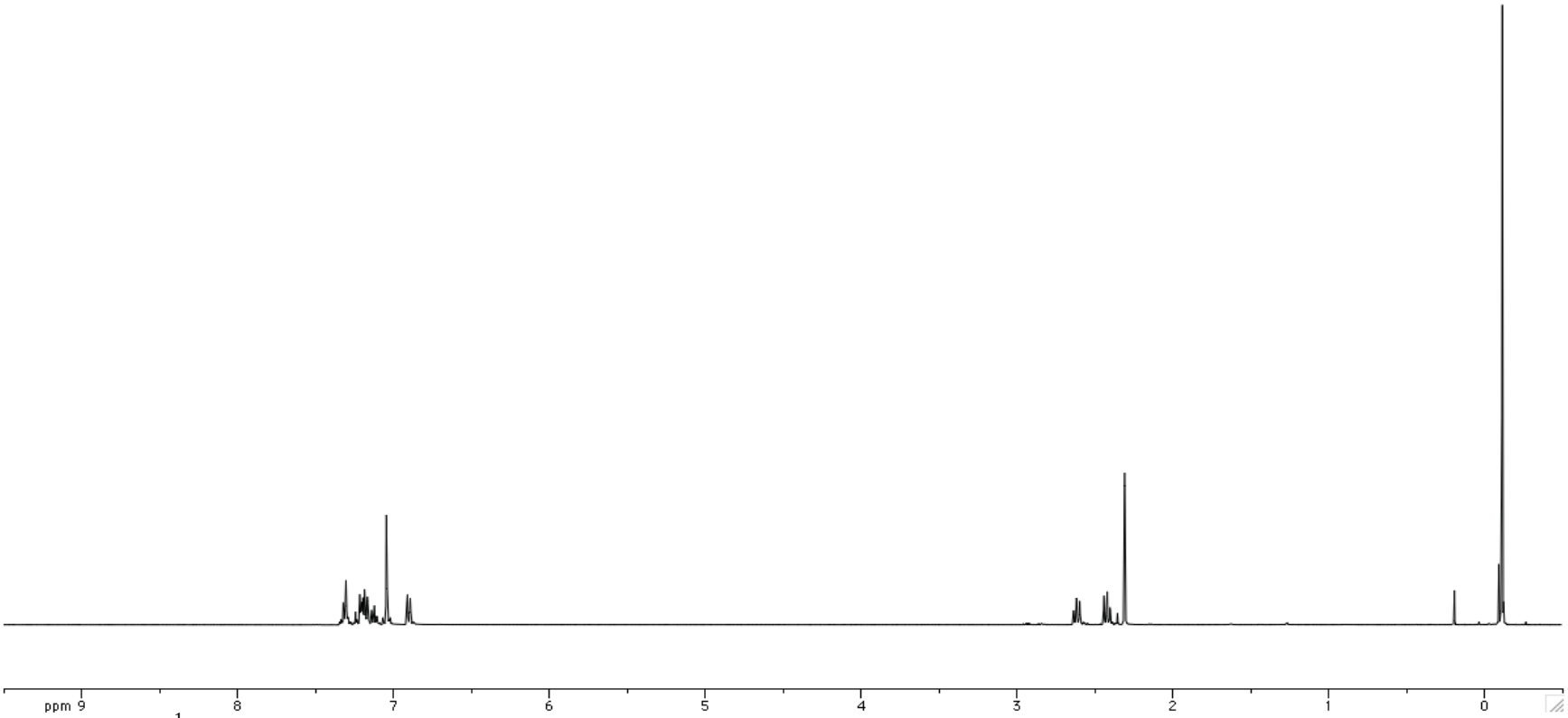


Figure A3.166 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **380**

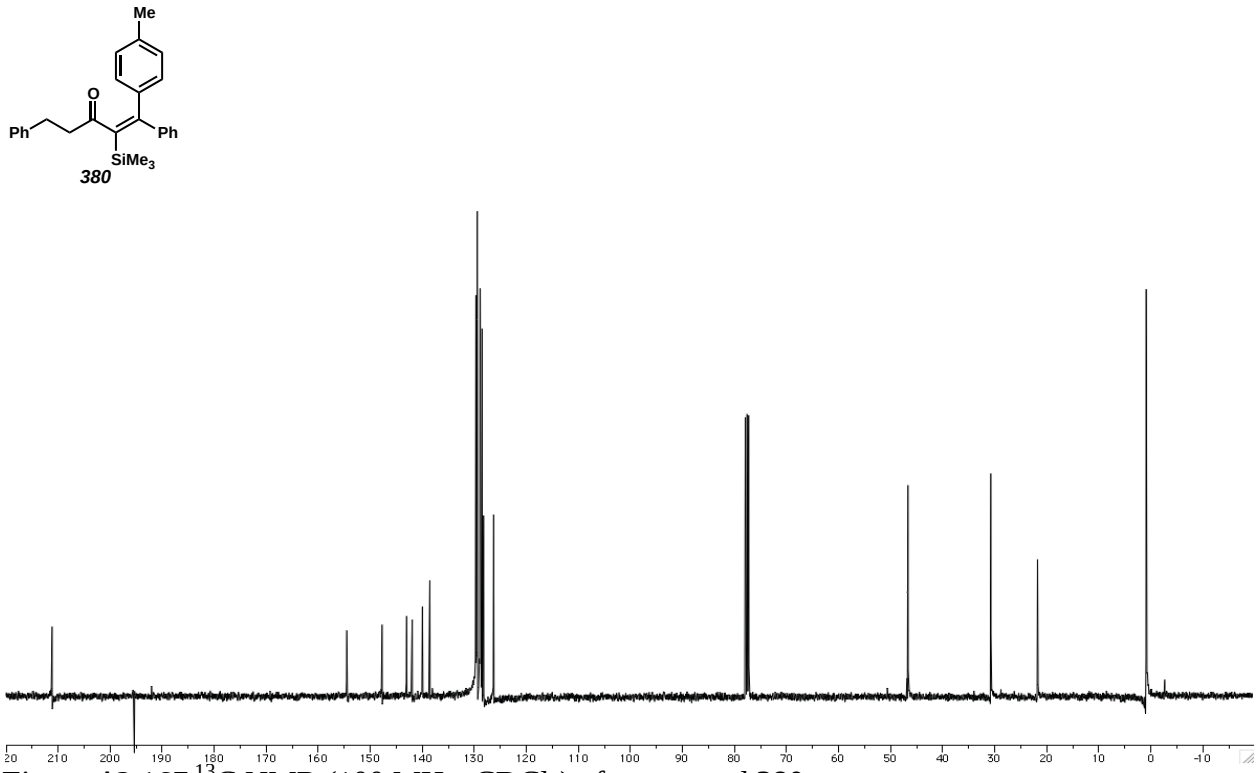


Figure A3.167 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **380**

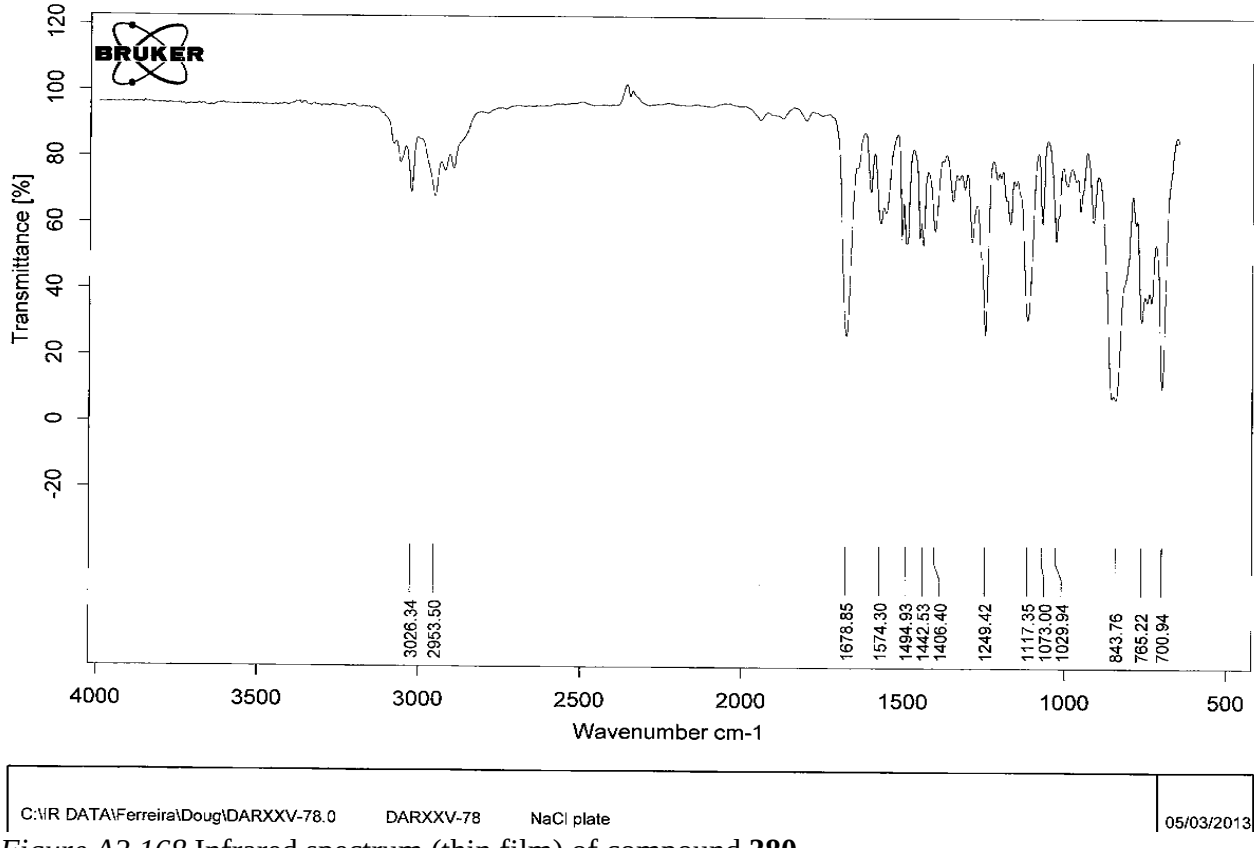
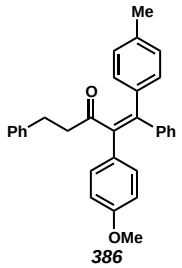


Figure A3.168 Infrared spectrum (thin film) of compound **380**



386

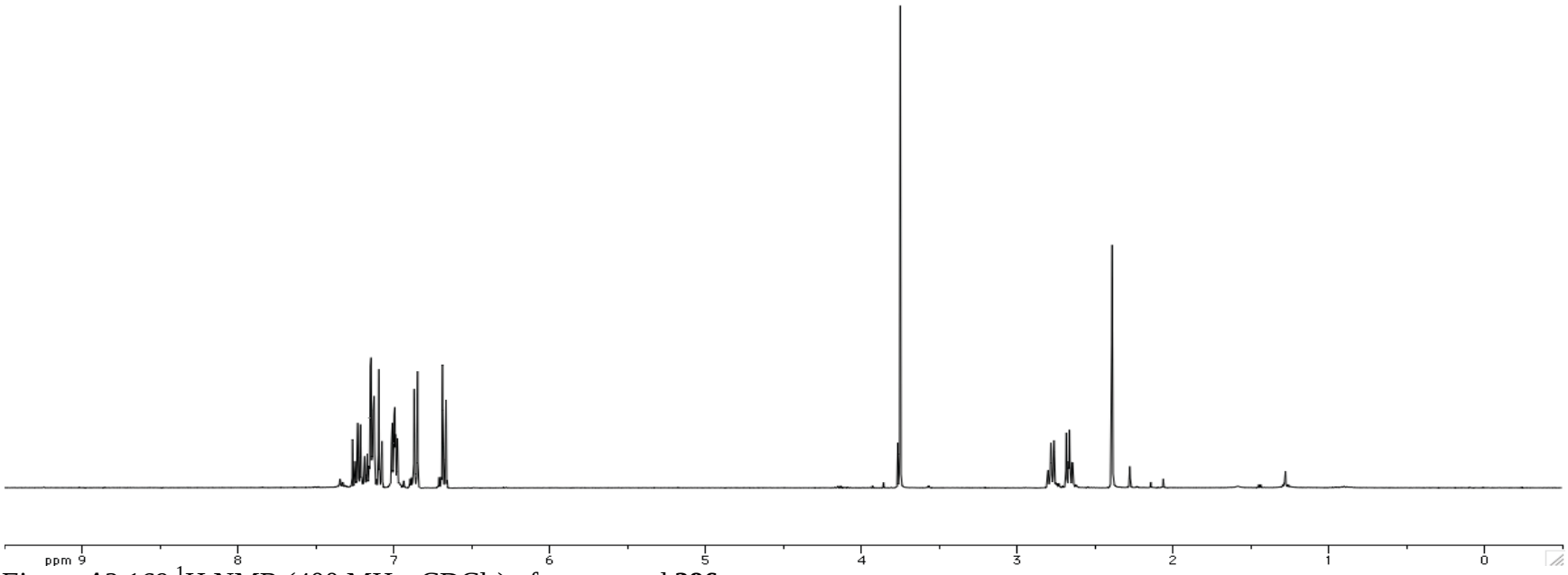
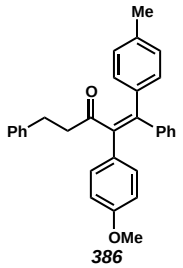


Figure A3.169 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **386**



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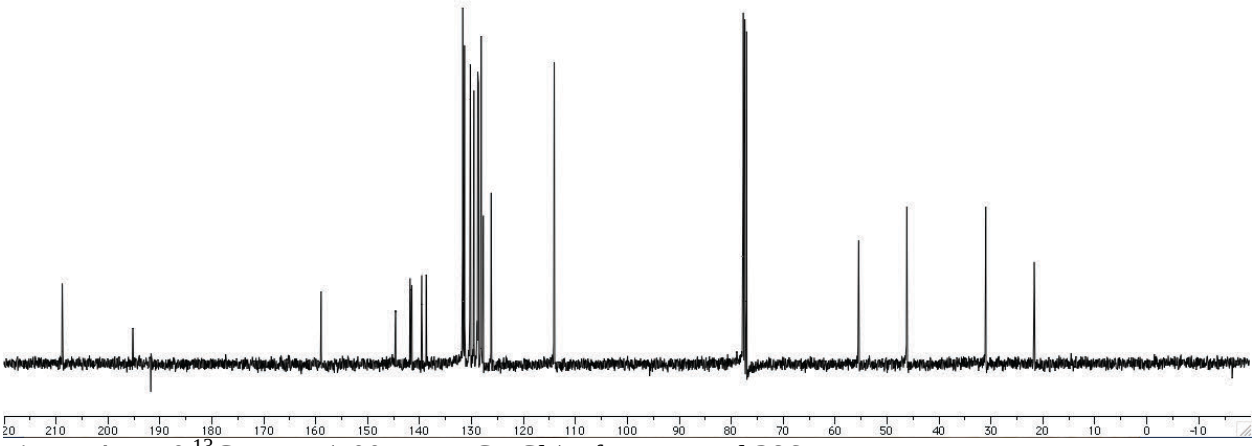


Figure A3.170 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **386**

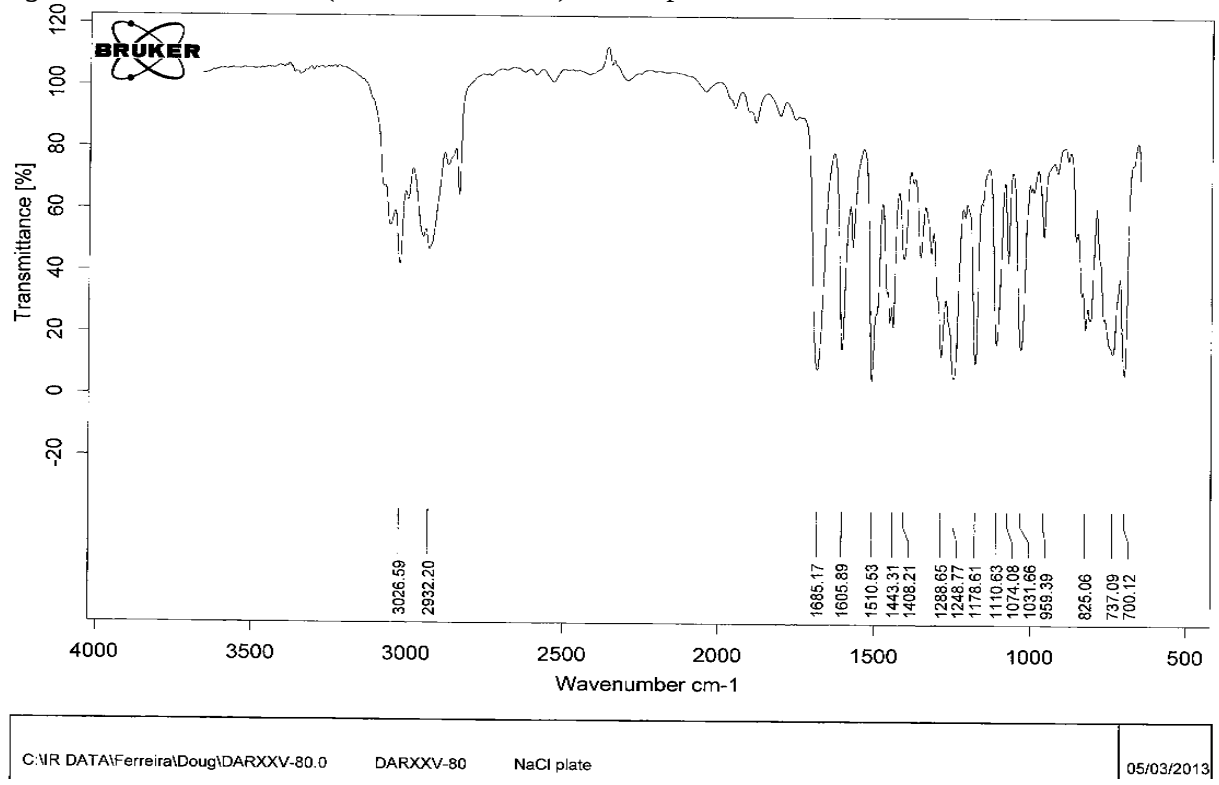
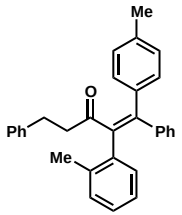


Figure A3.171 Infrared spectrum (thin film) of compound **386**



387

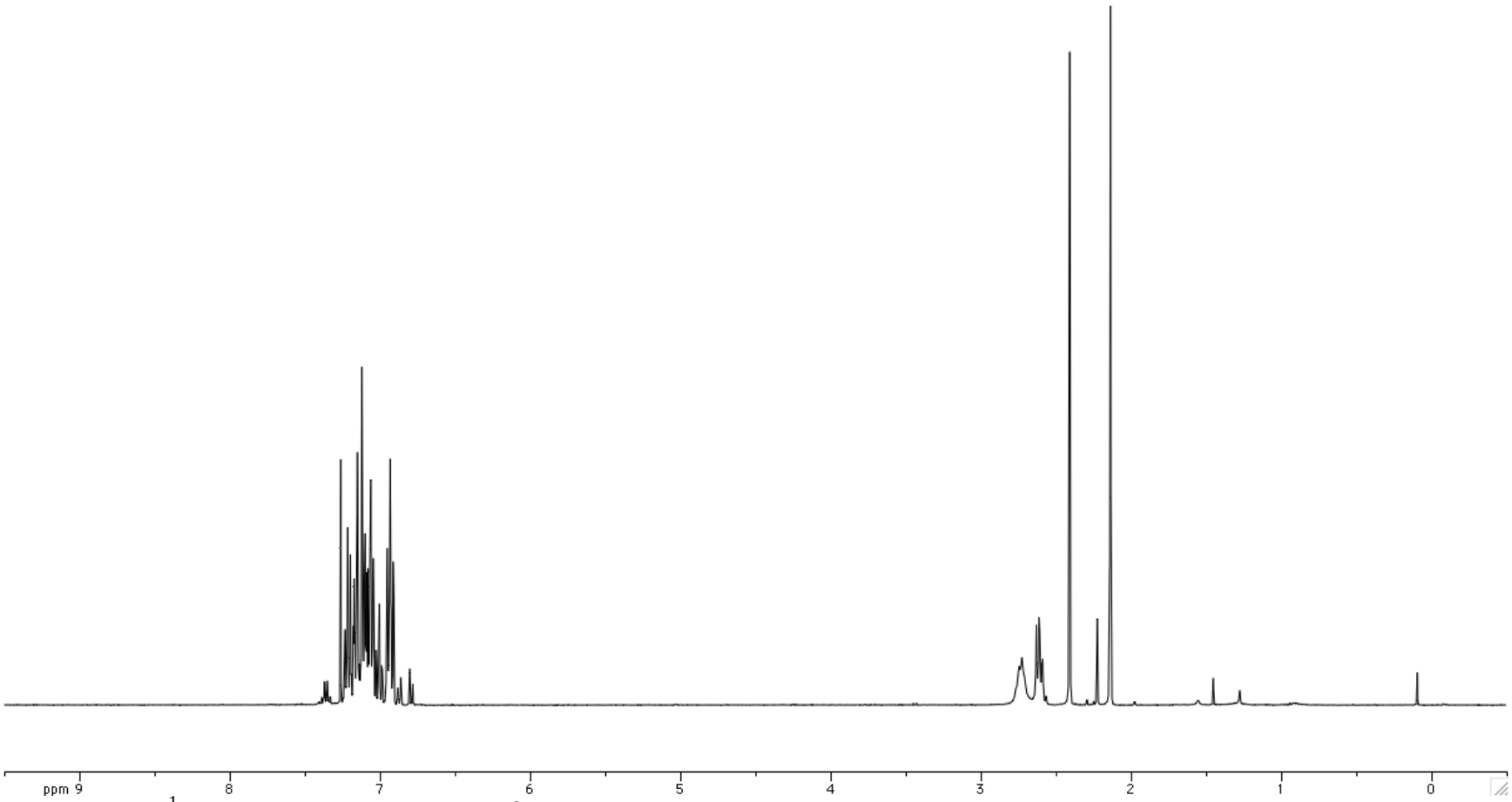
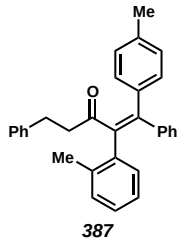


Figure A3.172 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **387**



387

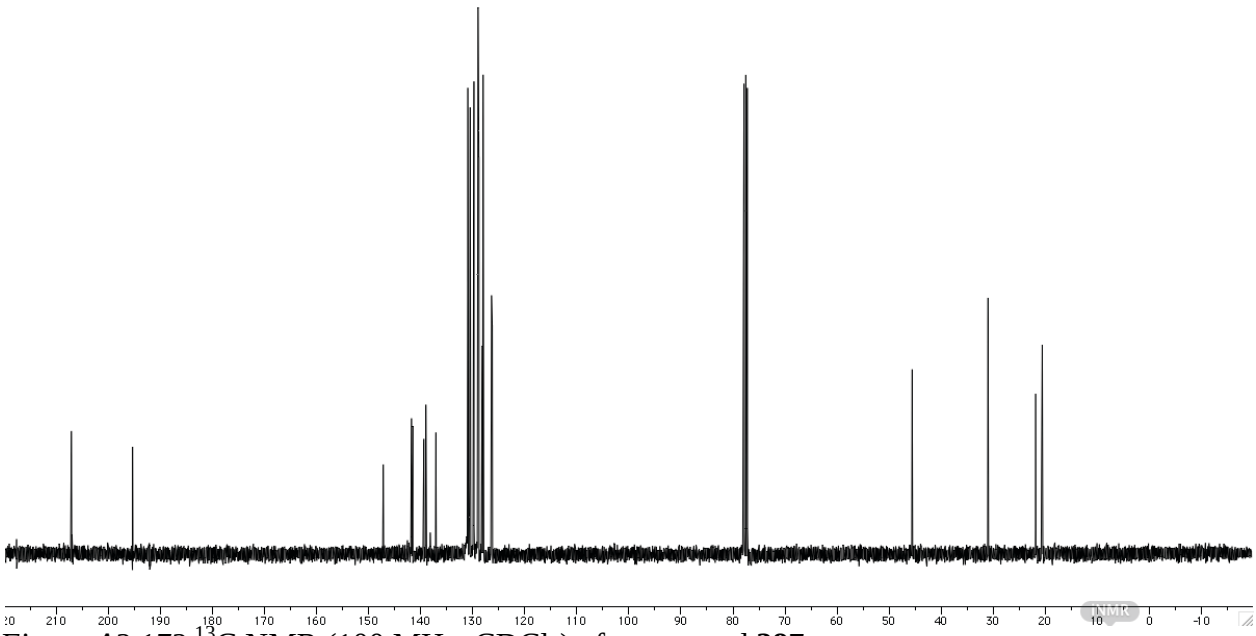


Figure A3.173 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **387**

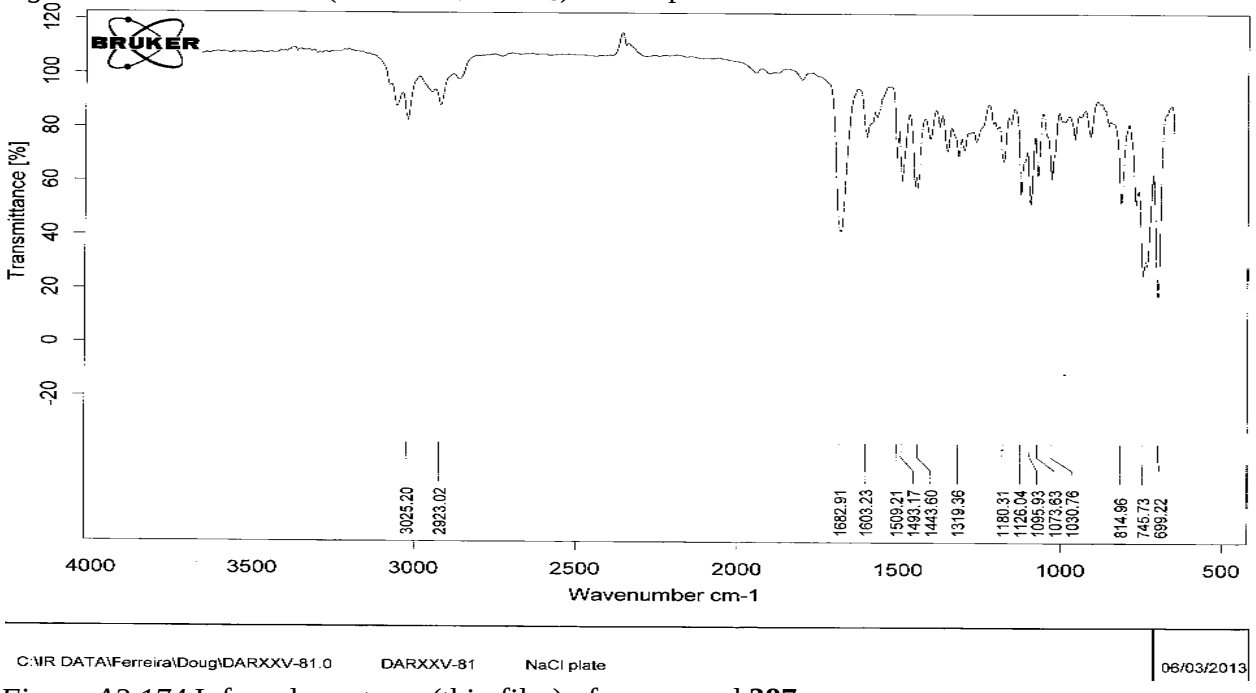
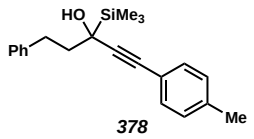


Figure A3.174 Infrared spectrum (thin film) of compound **387**



378

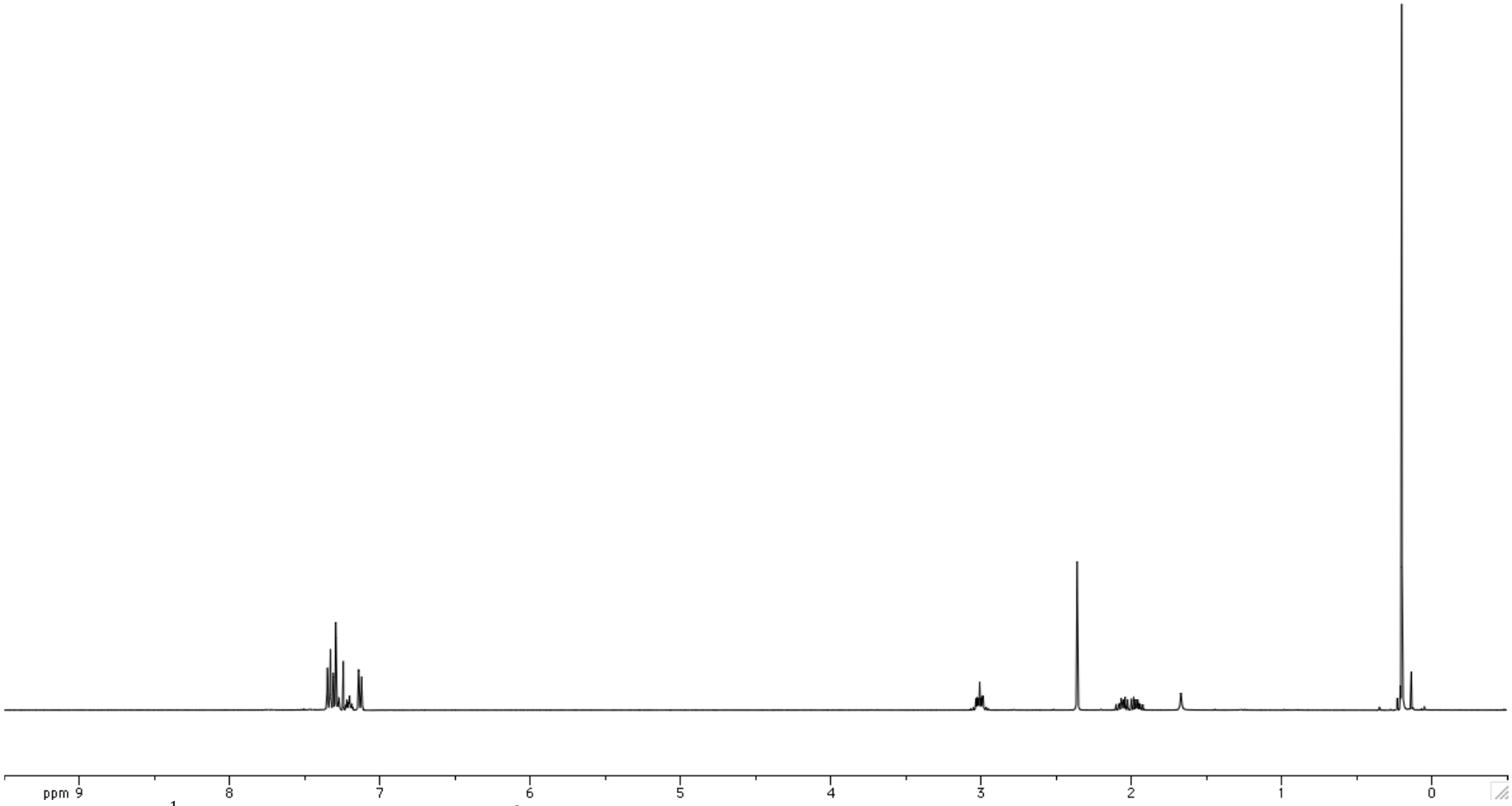
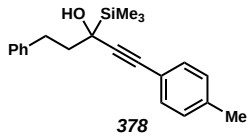


Figure A3.175 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **378**



378

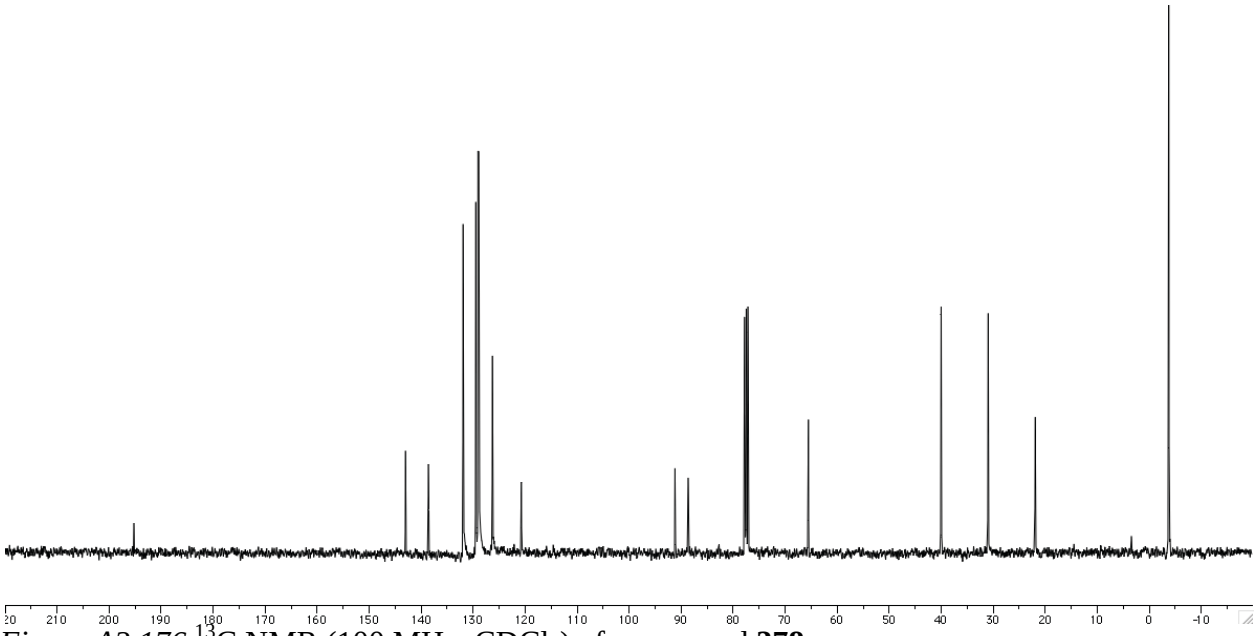


Figure A3.176 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **378**

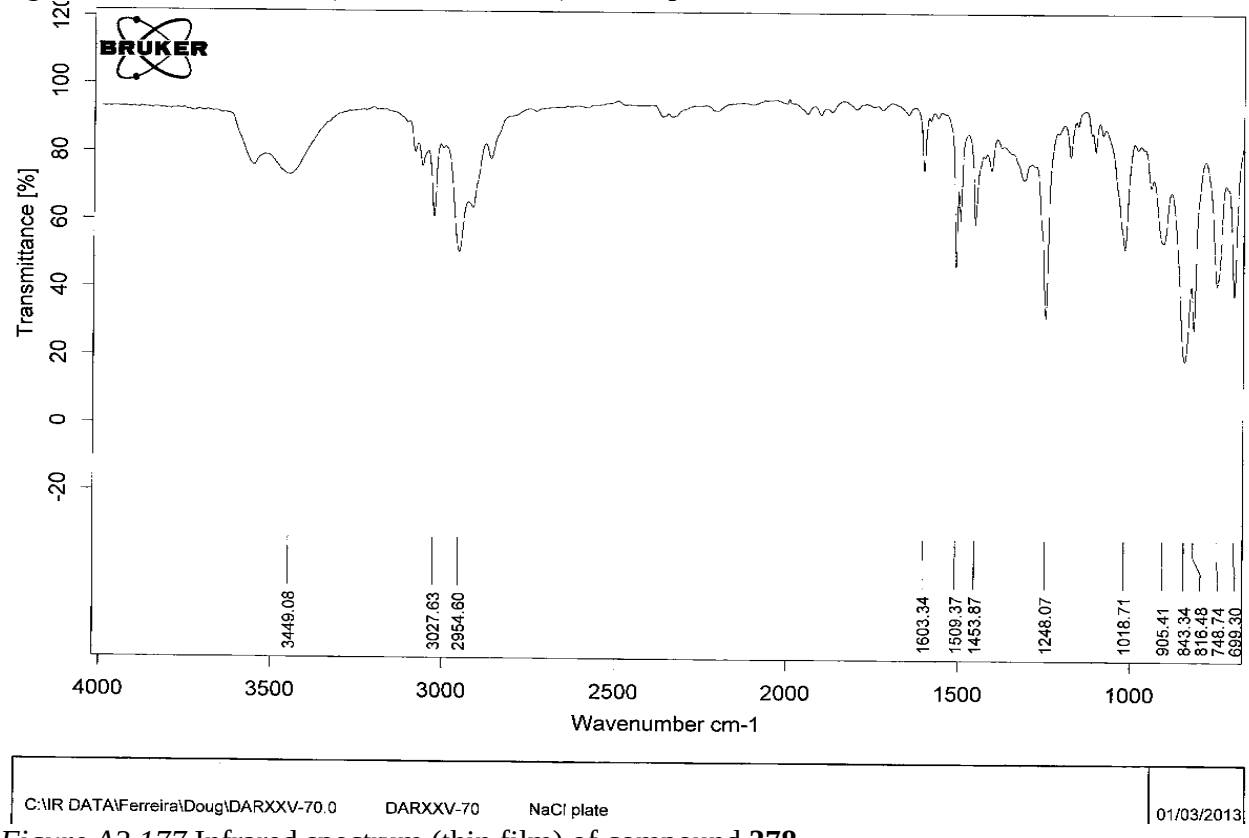
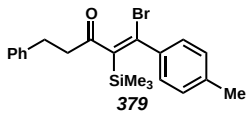


Figure A3.177 Infrared spectrum (thin film) of compound **378**



379

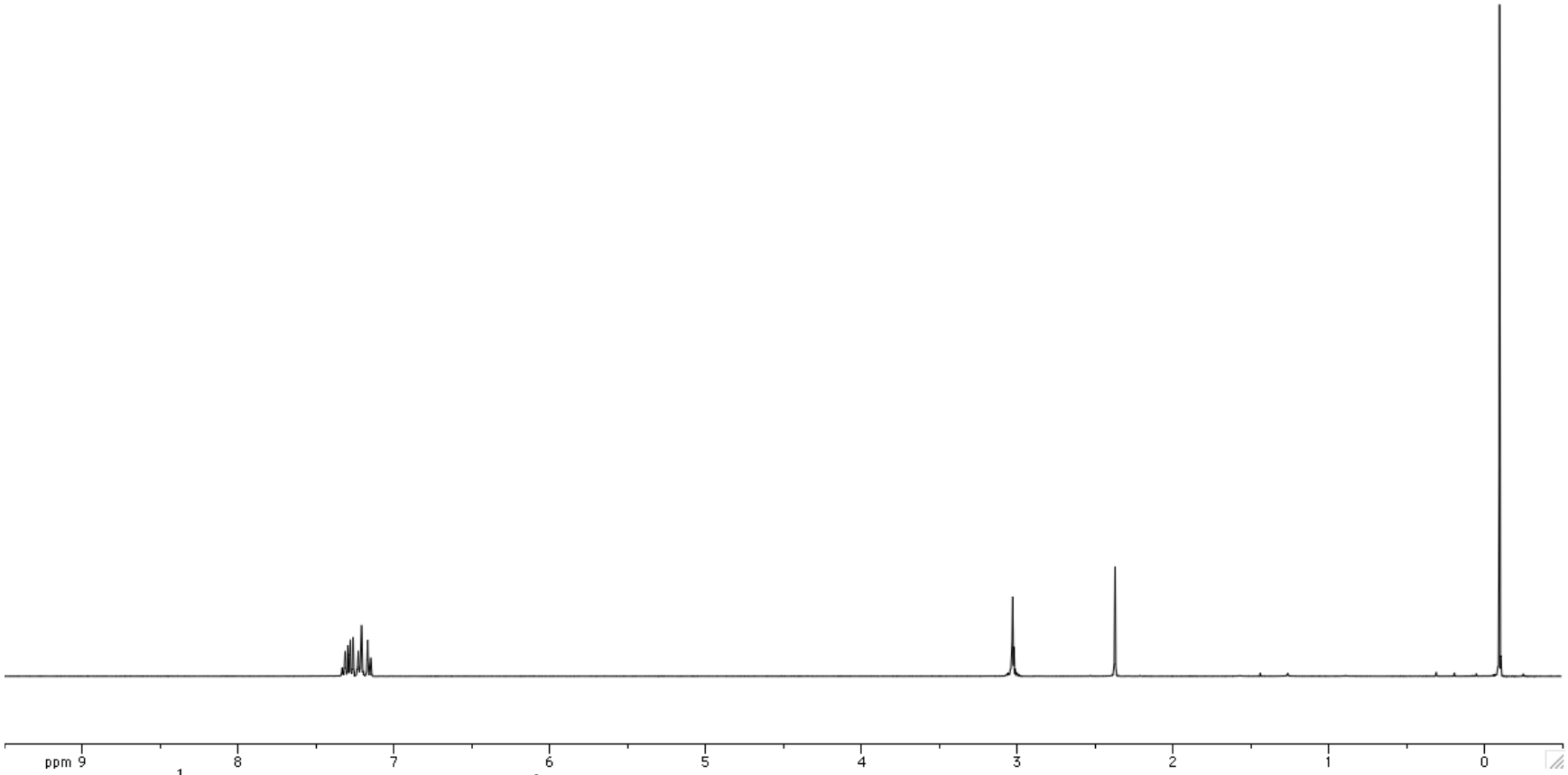


Figure A3.178 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **379**

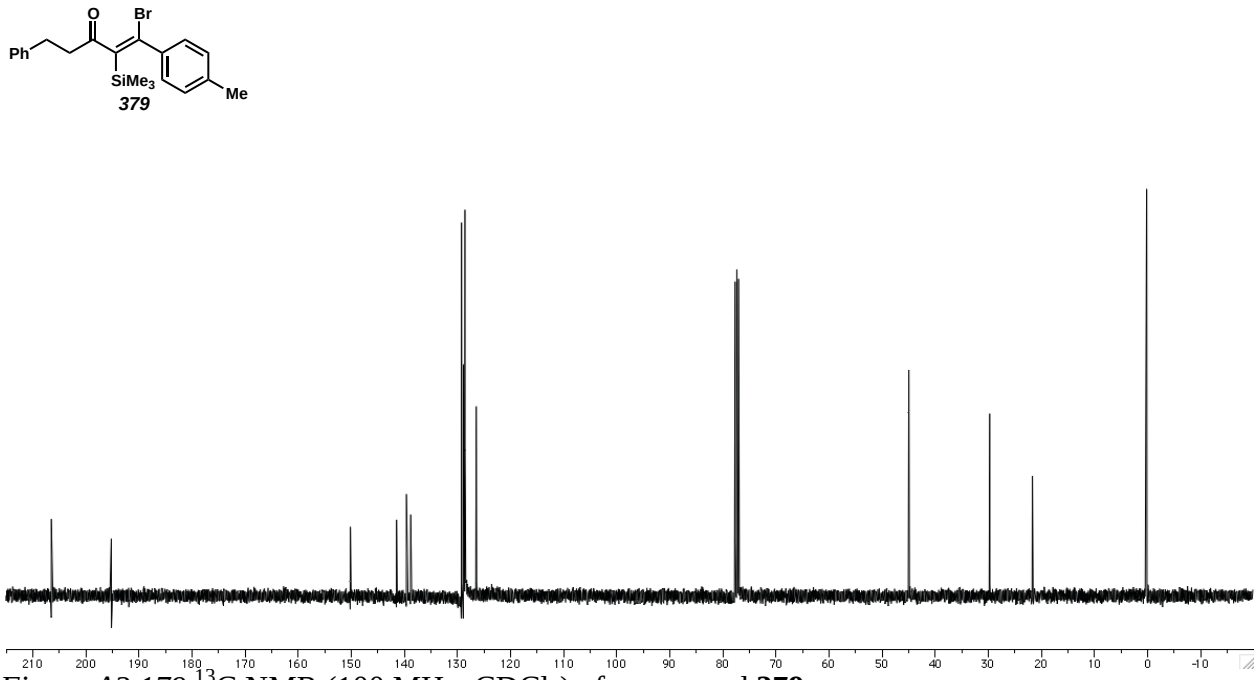


Figure A3.179 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **379**

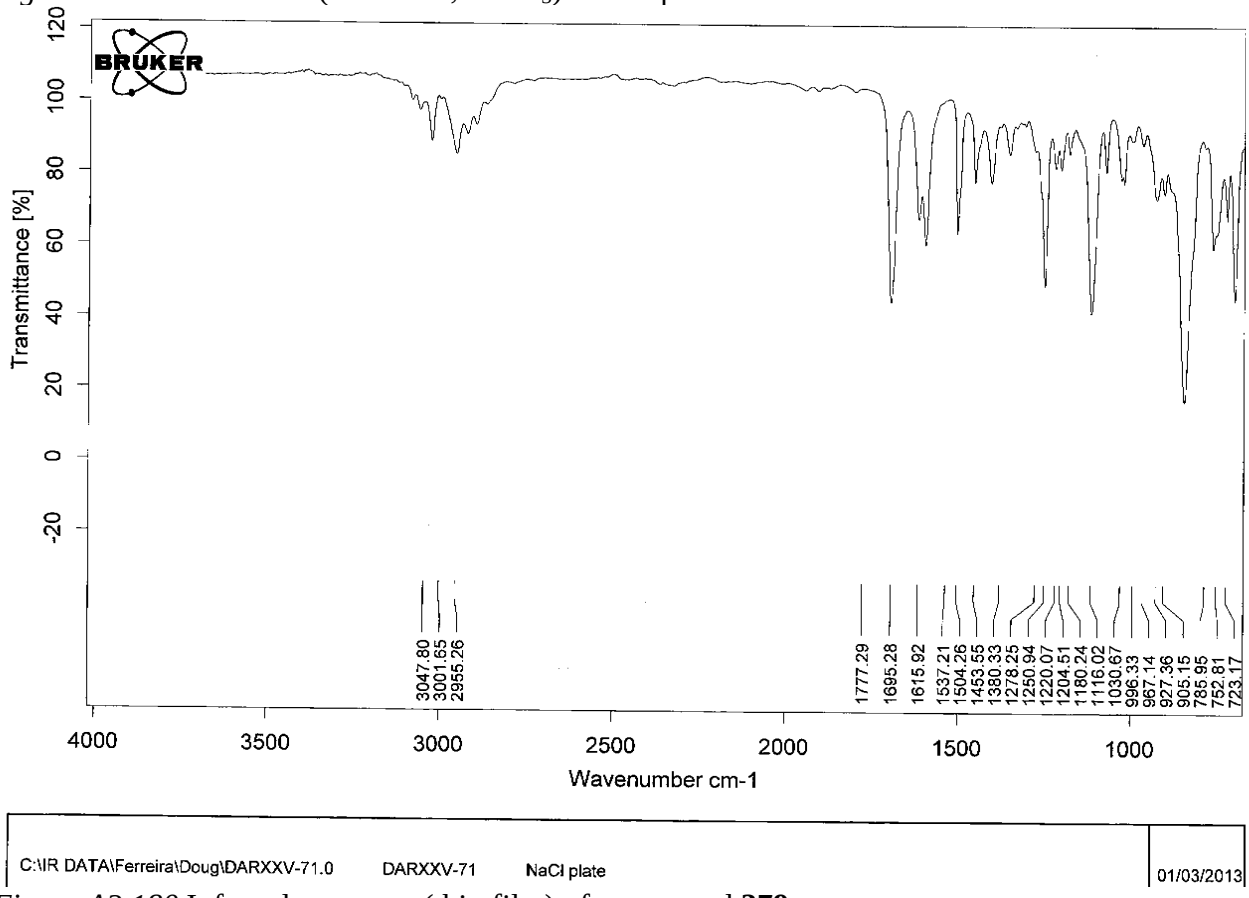
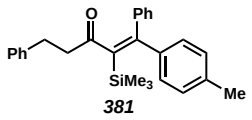


Figure A3.180 Infrared spectrum (thin film) of compound **379**



381

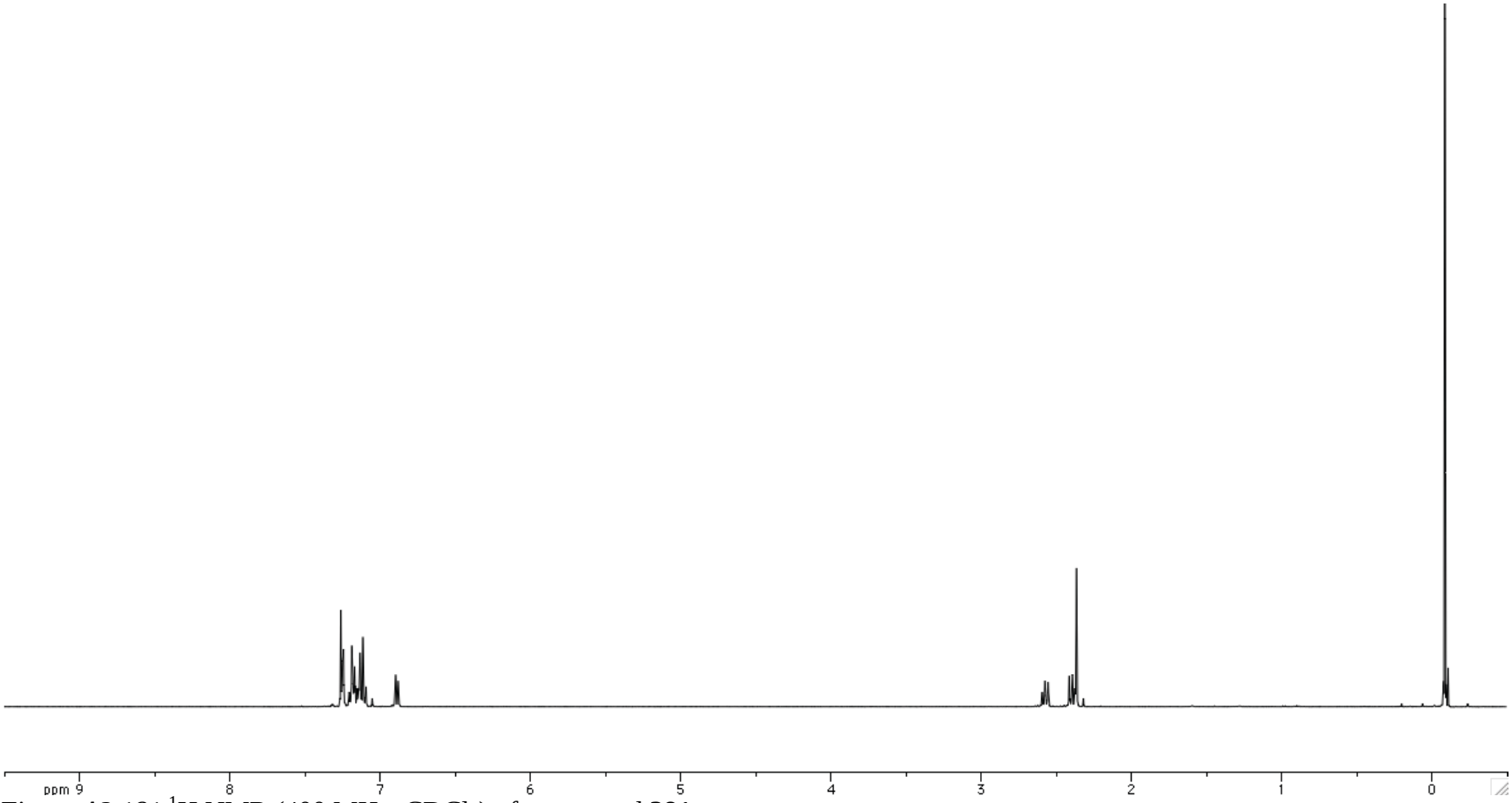


Figure A3.181 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **381**

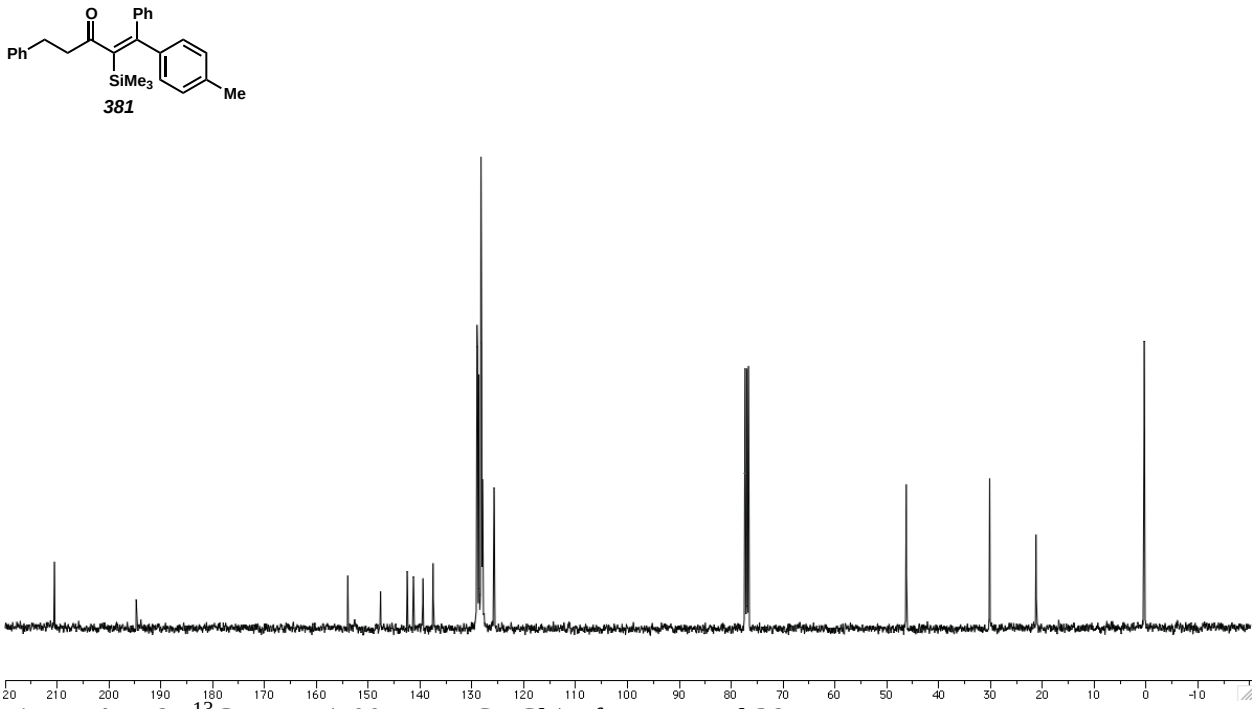


Figure A3.182 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **381**

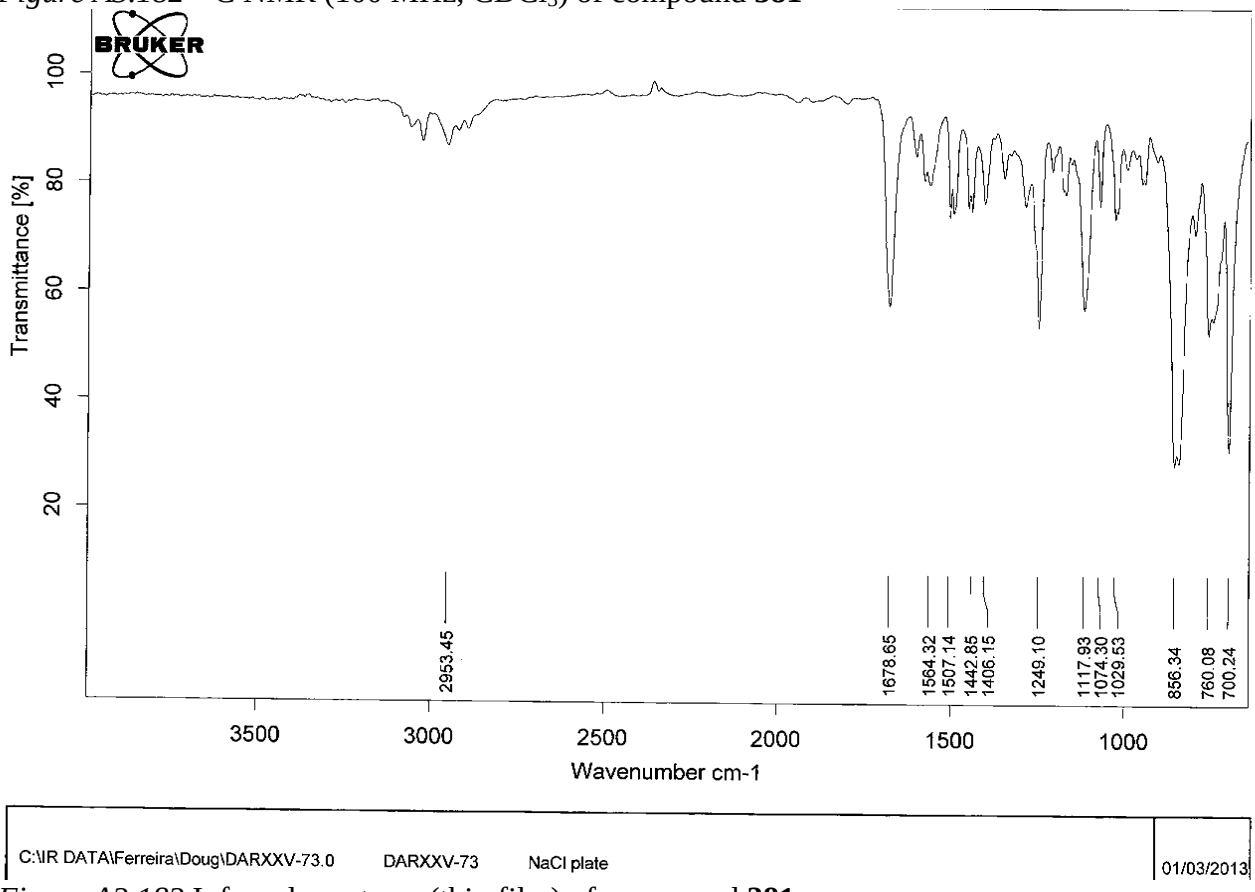
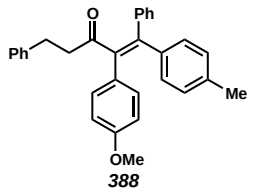


Figure A3.183 Infrared spectrum (thin film) of compound **381**



388

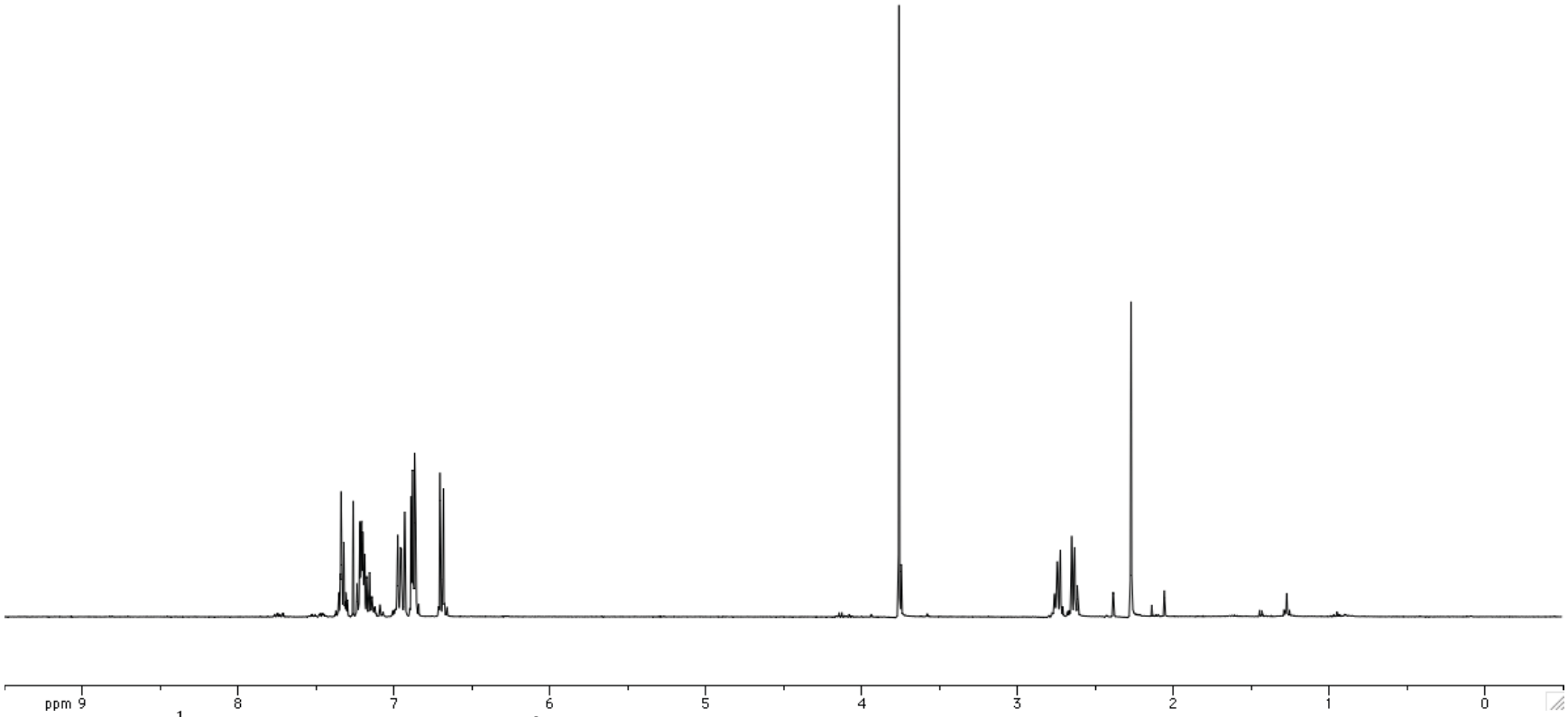


Figure A3.184 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **388**

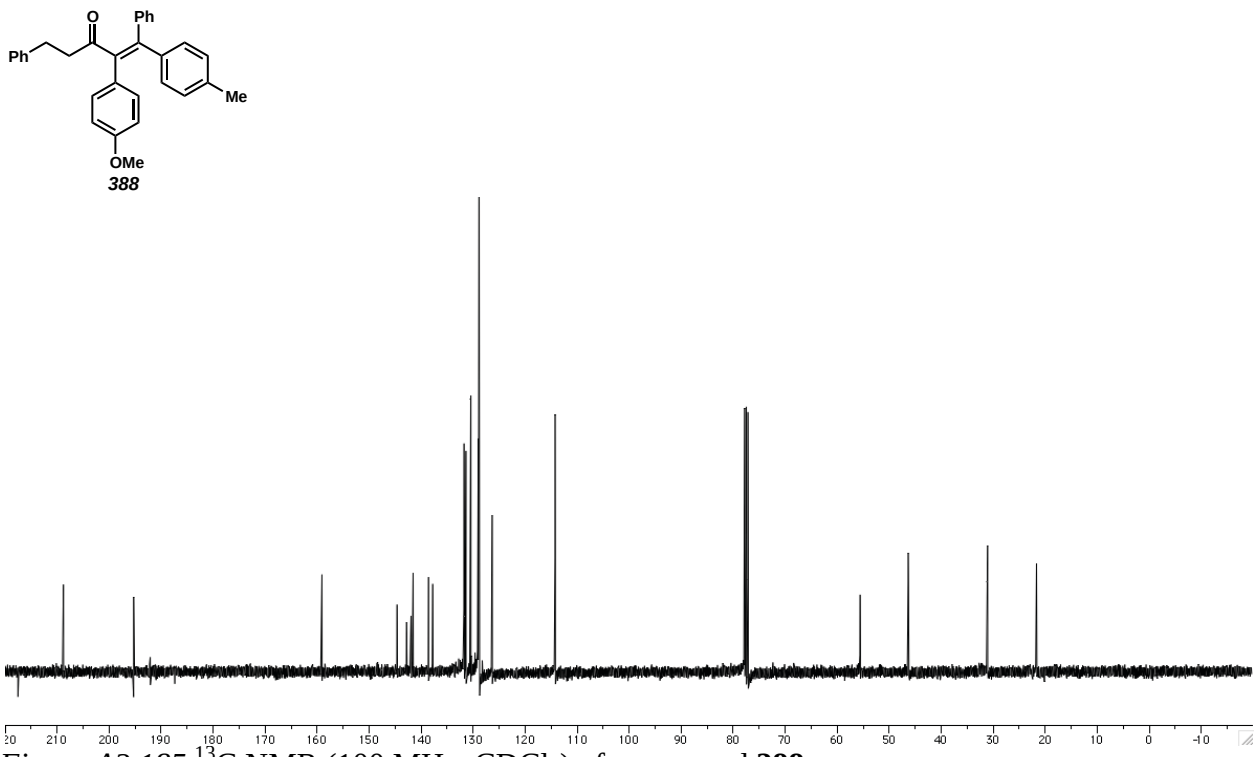


Figure A3.185 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **388**

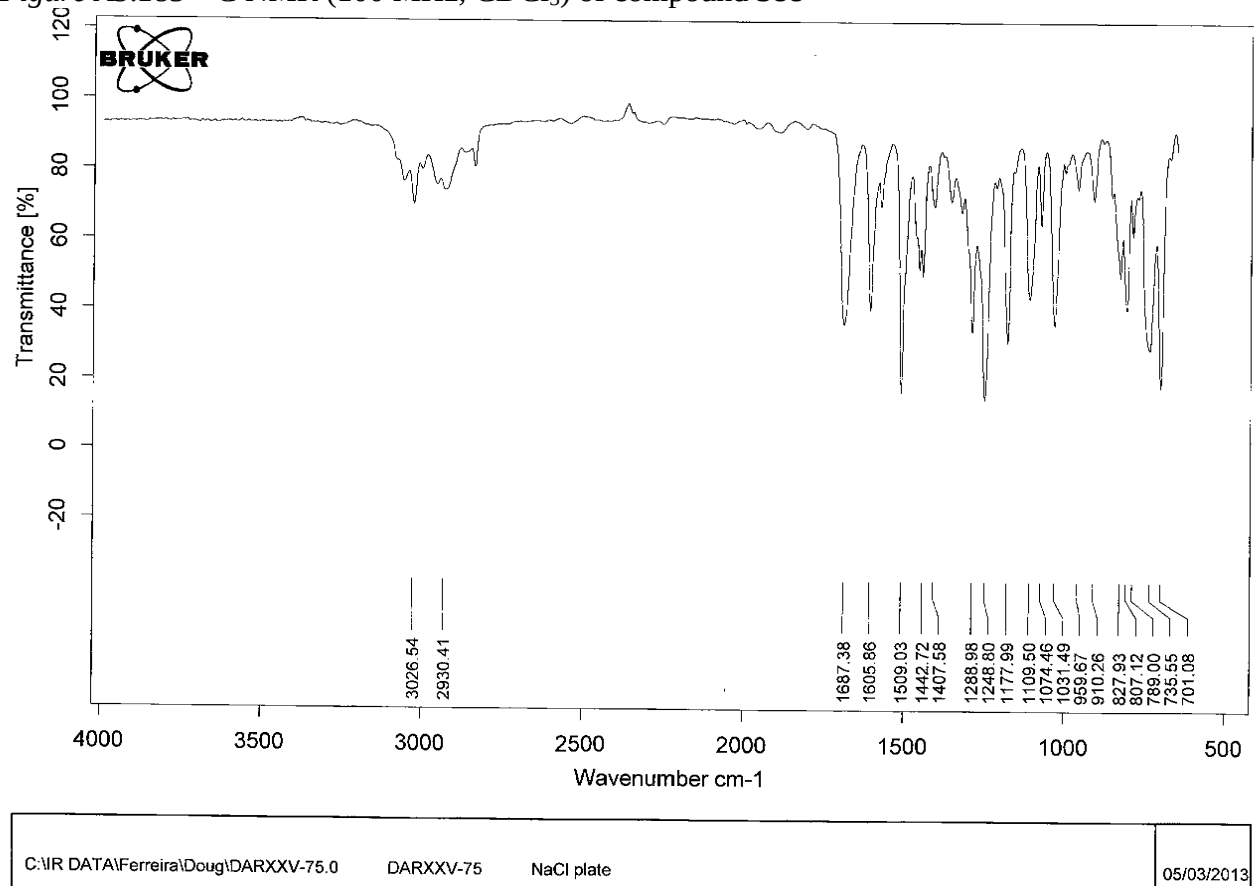
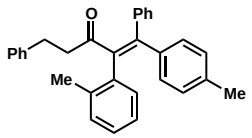


Figure A3.186 Infrared spectrum (thin film) of compound **388**



389

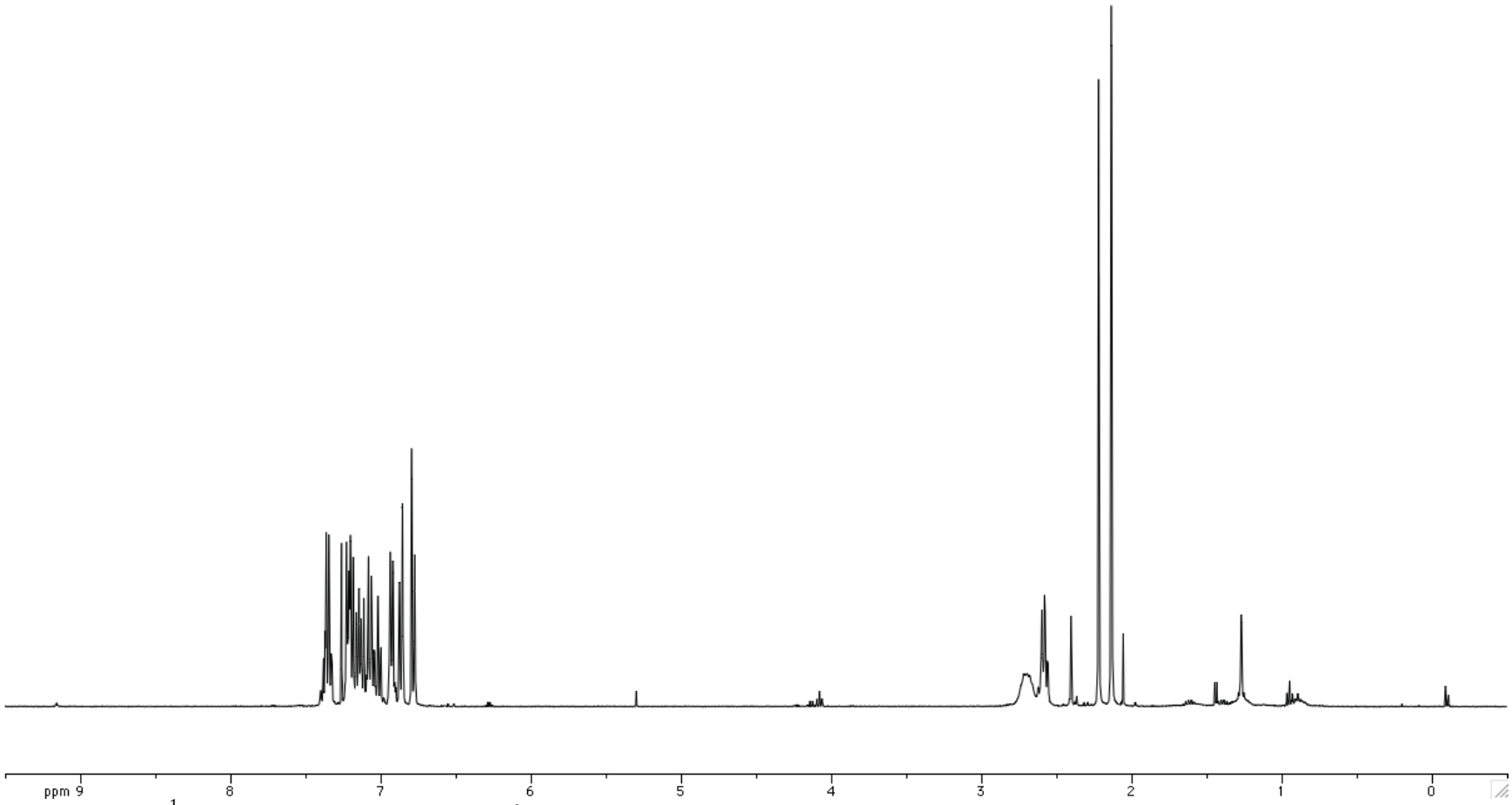
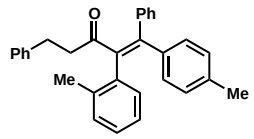


Figure A3.187 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **389**



389

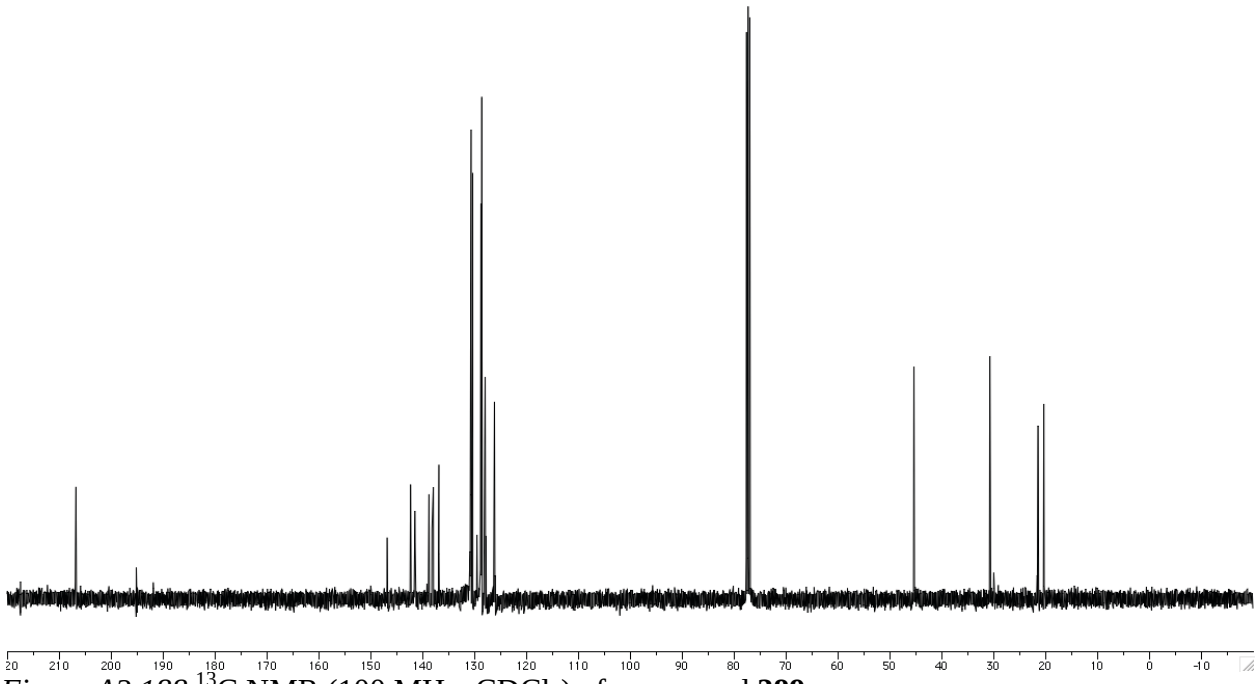


Figure A3.188 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **389**

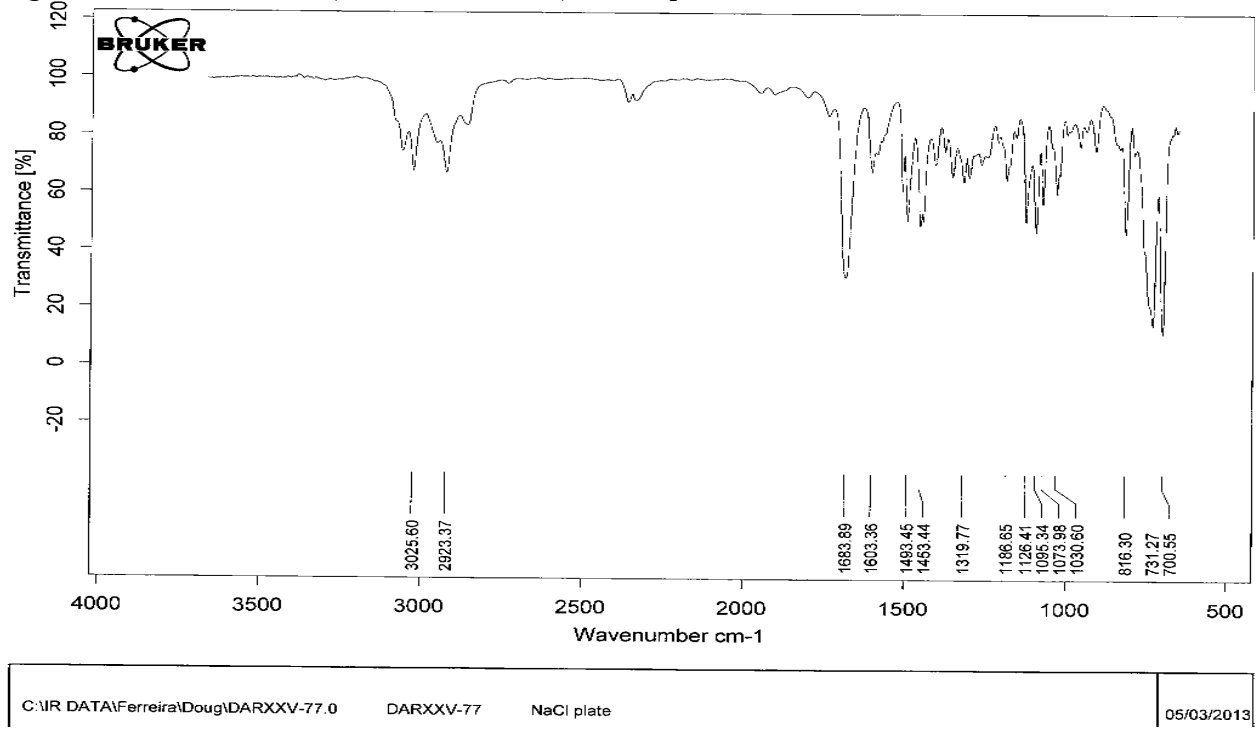


Figure A3.189 Infrared spectrum (thin film) of compound **389**

APPENDIX FOUR

Notebook Cross-Reference

The following notebook cross-reference has been included to facilitate access to the original spectroscopic data obtained for the compounds presented in this thesis. For each compound, an electronic copy of the original ^{1}H and ^{13}C NMR FID files are stored on the Ferreira Group computer as well as the group's external back-up hard drive. All of the files are organized by lab notebook and can be identified by my initials followed by the notebook and finally the page number (eg. DARXX-54). Hard copies of the IR and Mass spectra can be found in folders that have been arranged by the order in which they appear in this thesis.

Table A4.1 Compounds in Chapter 2 Listed As They Appear:

$PtCl_2$ Catalyzed and *N*-Halosuccinimide Mediated 1,2-Silyl Migration Reactions

Compound	^{1}H NMR	^{13}C NMR	IR
12	DARV-15	DARV-15	DARV-15
14	DARV-26	DARV-26	DARVII-50
22	DARX-50	DARX-50	N/A
23	DARX-53	DARX-53	N/A
24	DARII-85	DARII-85	DARII-85
25	DARVII-70	DARVII-70	DARVII-70
26	DARIII-17	DARIII-17	DARIII-17
27	DARV-39	DARV-39	DARV-39
20	DARVI-73	DARVI-73	DARVII-1
28	DARVI-74	DARVI-74	DARVI-74
29	DARVIII-58	DARVIII-58	DARVIII-58
30	DARVIII-62	DARVIII-62	DARVIII-62
21	DARVIII-59	DARVIII-59	DARVIII-59
31	DARIV-55	DARIV-55	DARIV-55

32	DARV-29	DARV-29	DARV-29
33	DARV-31	DARV-31	DARV-31
34	DARV-61	DARV-61	DARV-61
35	DARV-68	DARV-68	DARV-68
36	DARV-69	DARV-69	DARV-69
37	DARV-55	DARV-55	DARV-55
38	DARVI-2	DARVI-2	DARVI-2
39	DARVI-5	DARVI-5	DARVI-5
40	DARV-73	DARV-73	DARV-73
41	DARVI-4	DARVI-4	DARVI-4
42	DARVI-65	DARVI-65	DARVI-65
63	DARVII-10	DARVII-10	DARVII-10

Table A4.2 Compounds in Chapter 3 Listed As They Appear

The Regioselective Hydrosilylations of Internal Alkynes

Compound	^{1}H NMR	^{13}C NMR	IR
123	DARIX-21	DARIX-21	DARIX-21
124	DARIX-36	DARIX-36	DARIX-36
125	DARIX-35	DARIX-35	DARIX-35
126	DARIX-40	DARIX-40	DARIX-40
127	DARIX-41	DARIX-41	DARIX-41
128	DARX-1	DARX-1	DARX-1
129	DARIX-34	DARIX-34	DARIX-34
139	DARXV-3	DARXV-3	DARXV-93
140	DARXVIII-78	DARXVIII-78	DARXVIII-78
141	DARXVIII-79	DARXVIII-79	DARXVIII-79
135	DARXI-6	DARXI-6	DARXI-6
142	DARXV-6	DARXV-6	DARXV-6
136	DARXVIII-80	DARXVIII-80	DARXVIII-80
137	DARX-11	DARX-11	DARX-11
144	DARXIV-25	DARXIV-25	DARXIV-25
145	DARXIV-28	DARXIV-28	DARXIV-28
146	DARXIV-25	DARXIV-25	DARXIV-25
151	DARXIV-49	DARXIV-49	DARXIV-49
152	DARXV-10	DARXV-10	DARXV-10
153 and 197	DARXV-5	DARXV-5	DARXV-5
155	DARXIX-19	DARXIX-19	DARXIX-19
150	DARXVIII-97	DARXVIII-97	DARXVIII-97
156	DARXIX-1	DARXIX-1	DARXIX-1
157	DARXV-86	DARXV-86	DARXV-86
158	DARXXV-42bottom	DARXXV-42bottom	DARXXV-42bottom
158b	DARXXV-42top	DARXXV-42top	DARXXV-42top
159	DARXXV-37bottom	DARXXV-37bottom	DARXXV-37bottom
159b	DARXXV-37top	DARXXV-37top	DARXXV-37top

160	DARXXV-46	DARXXV-46	DARXXV-46
161	DARXXI-85	DARXXI-85	DARXXI-85
162	DARXIV-29	DARXIV-29	DARXIV-29
163	DARXXV-40	DARXXV-40	DARXXV-40
164	DARXXV-39bottom	DARXXV-39bottom	DARXXV-39bottom
164b	DARXXV-39top	DARXXV-39top	DARXXV-39top
165	DARXXV-43	DARXXV-43	DARXXV-43
167	DARXXV-52	DARXXV-52	DARXXV-52
168	DARXXV-59	DARXXV-59	DARXXV-59
169	ZAMII-40	ZAMII-40	ZAMII-40
170	ZAMII-41	ZAMII-41	ZAMII-41
171	DARXXV-54	DARXXV-54	DARXXV-54
172	DARXXV-67	DARXXV-67	DARXXV-67
174	DARXIV-59	DARXXV-59	DARXIV-59
177	DARXV-21	DARXV-21	DARXV-21
175	DARXIX-24	DARXIX-24	DARXIX-24
178	DARXIV-63	DARXIV-63	DARXIV-63
176	DARXIV-61	DARXIV-61	DARXIV-61
179	DARXIV-65topspot	DARXIV-65topspot	DARXIV-65topspot
180	DARXIV-65bottomspot	DARXIV-65bottomspot	N/A
184	DARXV-9	DARXV-9	DARXV-9
185	DARXVIII-8	DARXVIII-8	DARXVIII-8
186	DARXV-7	DARXV-7	DARXV-7
183	DARXIV-69	DARXIV-69	DARXIV-69
187	DARXV-13	DARXV-13	DARXV-13
188	DARXIV-76	DARXIV-76	DARXIV-76
189	DARXV-14	DARXV-14	DARXV-14
199	DARXVIII-35	DARXVIII-35	DARXVIII-35
200	DARXVIII-49	DARXVIII-49	DARXVIII-49
202	DARXVIII-36	DARXVIII-36	DARXVIII-36
203	DARXVIII-50	DARXVIII-50	DARXVIII-50
205	DARXVIII-51	DARXVIII-51	DARXVIII-51
206	DARXVIII-52	DARXVIII-52	DARXVIII-52
209	DARXIV-39	DARXIV-39	DARXIV-39

212	DARXV-12	DARXV-12	DARXV-12
215	DARXVIII-58	DARXVIII-58	DARXVII-58
216	DARXVIII-64	DARXVIII-64	DARXVIII-64
218	DARXVIII-63	DARXVIII-63	DARXVII-63
220	DARXVIII-62	DARXVIII-62	DARXVIII-62
222	DARXVIII-66	DARXVIII-66	DARXVIII-66
223	DARXVIII-69	DARXVIII-69	DARXVIII-66
224	DARXVIII-67	DARXVIII-67	DARXVIII-67
225	DARXVIII-70	DARXVIIII-70	DARXVIII-70
226	DARXVIII-65	DARXVIII-65	DARXVIII-65
227	DARXVIII-68	DARXVIII-68	DARXVIII-68
228	DARXV-28	DARXV-28	DARXIV-90
230	DARXIV-66	DARXIV-66	DARXVIII-93
231	DARXVIII-94	DARXVIII-94	DARXVIII-94
233	DARXVIII-91	DARXVIII-91	DARXVIII-91
235	DARXIX-28	DARXIX-28	DARXVIII-92
236	DARXVIII-85	DARXVIII-85	DARXVIII-71
250	DARXVIII-96	DARXVIII-96	DARXVIII-96
251	DARXVIII-55	DARXVIII-55	DARXVIII-55

Table A4.3 Compounds in Chapter 4 Listed As They Appear

The Utilization of Tri- and Tetrasubstituted Vinylsilanes for the Formation of Stereodefined All-Carbon Alkenes

Compound	^{1}H NMR	^{13}C NMR	IR
262	DARVI-77	DARXI-77	DARVI-77
263	DARVI-83	DARVI-83	DARVI-83
271	DARVII-13	DARVII-13	DARVII-13
267	DARVIII-56	DARVIII-56	DARVIII-56
268	DARVIII-41	DARVIII-41	DARVIII-41
272	DARVIII-60	DARVIII-60	DARVIII-60
283	DARIX-77	DARIX-77	DARIX-77
284	DARIX-78	DARIX-78	DARIX-78
285	DARXV-87	DARXV-87	DARXV-87
286	DARXIX-15	DARXIX-15	DARXIX-15
290	DARXV-88	DARXV-88	DARXV-68
288	DARXIX-11	DARXIX-11	DARXVI-11
289	DARXVI-40	DARXVI-40	DARXVI-40
292	DARXXII-12	DARXXII-12	DARXXII-12
294	DARXXII-15	DARXXII-15	DARXXII-15
296	DARXXI-63	DARXXI-63	DARXXI-62
297	DARXXI-30	DARXXI-30	DARXXI-30
298	DARXXI-57	DARXXI-57	DARXXI-57
299	DARXXI-33	DARXXI-33	DARXXI-33
300	DARXXII-16	DARXXII-16	DARXXII-16
301	DARXXII-17	DARXXII-17	DARXXII-17
302	DARXXI-43	DARXXI-43	DARXXI-43
303	DARXXI-44	DARXXI-44	DARXXI-44
304	DARXXI-48	DARXXI-48	DARXXI-48
306	DARXXI-32	DARXXI-32	DARXXI-32
308	DARXX-60	DARXX-60	DARXX-60
311	DARXX-63	DARXX-63	DARXX-63
313	DARXX-69	DARXX-69	DARXX-69
315	DARXXI-21	DARXXI-21	DARXXI-21
317	DARXX-76	DARXX-76	DARXX-76

319	DARXXI-3	DARXXI-3	DARXXI-3
321	DARXX-68	DARXX-68	DARXXI-22
332	DARXIX-83	DARXIX-83	DARXIX-83
333	DARXX-84	DARXX-84	DARXX-84
391	DARXXI-35	DARXXI-35	DARXXI-35
334	DARXXI-84	DARXXI-84	DARXXI-42
392	DARXXI-54	DARXXI-54	DARXXI-54
335	DARXXI-58	DARXXI-58	DARXXI-58
393	DARXXI-39	DARXXI-39	DARXXI-39
336	DARXXI-41	DARXXI-41	DARXXI-41
339	DARXXI-1	DARXXI-1	DARXXI-1
350	DARXXI-10	DARXXI-10	DARXXI-10
349	DARXXI-24	DARXXI-24	DARXXI-24
354	DARXIX-60	DARXIX-60	DARXIX-60
355	DARXIX-4	DARXIX-4	DARXXI-4
356	DARXIX-22	DARXIX-22	DARXIX-22
357	DARXIX-23	DARXIX-23	DARXIX-23
359	DARXXV-23	DARXXV-23	DARXXV-23
360	DARXXIV-82	DARXXIV-82	DARXXIV-82
358	DARXXIV-88	DARXXIV-88	N/A
362	DARVII-57	DARVII-57	DARVII-57
365	DARXXV-21	DARXXV-21	DARXXV-21
367	DARXXV-25	DARXXV-25	DARXXV-25
377	DARXXV-61	DARXXV-61	DARXXV-61
375	DARXXV-53	DARXXV-53	DARXXV-53
380	DARXXV-78	DARXXV-78	DARXXV-78
386	DARXXV-80	DARXXV-80	DARXXV-80
387	DARXXV-81	DARXXV-81	DARXXV-81
378	DARXXV-70	DARXXV-70	DARXXV-70
379	DARXXV-71	DARXXV-71	DARXXV-71
381	DARXXV-73	DARXXV-73	DARXXV-73
388	DARXXV-75	DARXXV-75	DARXXV-75
389	DARXXV-77	DARXXV-77	DARXXV-77