December 2015

Ruthenium-Catalyzed Transformations for the Synthesis of Conjugated Dienes

Lauren Kaminsky
Syracuse University

Abstract

A general description of transition metal catalysis of alkynes and alkenes for the formation of conjugated dienes is briefly discussed. Specifically, a synopsis of ruthenium-hydride catalysis for the formation of 1,3-dienes is presented.

The development of the *trans*-silylvinylation of internal alkynes with acrylates and vinyl boronates to form conjugated dienes is discussed. This transformation was accomplished via a recently developed tandem silylative coupling using $RuHCl(CO)(PCy_3)_2$. The reaction optimization, mechanistic hypothesis and substrate scope for the coupling with acrylates and vinyl boronates is described. The vinyl boronate scope and alkyne scope is presented, in addition to the selective derivatization of the boronate moiety. The synthesis of a chiral silicon-tethered alkyne is described and its application toward a stereo- and enantioselective chiral conjugated diene utilizing the aforementioned methodology was accomplished and is discussed herein.

The development of an intramolecular *trans*-silylvinylation of internal alkynes catalyzed by $RuHCl(CO)(H_2IMes)(PPh_3)$ with methyl vinyl ketone (MVK) additive is discussed. The substrate scope of the reaction provided five-, six-, and seven-membered oxasilacycles. The ruthenium-hydride catalyzed *trans*-silylvinylation of internal alkynes under an atmosphere of ethylene gas is discussed. This methodology improved upon the reactivity of the starting alkynes and upon the selectivity of the diene products formed from the previous transformations with MVK additive. Reversal of *Z*/*E* selectivity can be obtained with increased pressures of ethylene gas. Further functionalization of the diene products to form more diverse scaffolds is described.

Lastly, the cycloisomerization of silicon-tethered 1,7-enynes to form 1,3-dienes utilizing catalytic $Cp^*Ru(COD)Cl$ is described herein. The reaction optimization, mechanistic hypothesis, substrate tolerance and synthetic utility is discussed. The question of whether a silicon atom is required in the tether of the starting enyne for the reaction to proceed is addressed.

Ruthenium-Catalyzed Transformations for the Synthesis of Conjugated Dienes

by

Lauren Kaminsky

B.S. Chemistry, York College of Pennsylvania, 2010

Dissertation

Submitted in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy in Chemistry

Syracuse University

December 2015

ACKNOWLEDGEMENTS

There are so many people who I need to thank for their support and guidance throughout my graduate career at Syracuse University. I wouldn't be here without each and every one of you, and for this I am extremely grateful.

First, I would like to thank my advisor Dr. Daniel A. Clark for his guidance over the past five years. I am incredibly fortunate for having the opportunity to work for him. His passion and knowledge of organic chemistry is astounding and has been a huge inspiration. He introduced me to the wonderful world of organocatalysis and allowed me to freely explore all research projects. The knowledge and skills I have acquired while working in his lab are something I consider myself lucky to have and will always be thankful for.

I would like to thank my committee members: Professors John Chisholm, Nancy Totah, James Hougland, Michael Sponsler and Kevin Sweder for their support and guidance. I especially would like to thank Dr. Sweder for accepting the position as chair under such short notice.

To the past and present members of the Clark group: Ijaz Ahmed, Alec Beaton, Tara Brenner, Alex "Ale" Dixon, Marty Dolan, Dr. Shasha Liu, Daniel "Little D" Nguyen, Dr. Adam Rosenberg, Chris Wilhelmsen, Theresa Williams, Rob Wilson and Dr. Jinbo Zhao, thank you for all of the valuable chemistry discussions and for sharing your enthusiasm for chemistry. I would

like to thank Shasha for teaching me the basics on how to make ruthenium hydrides. Alec and Little D, you guys were the best undergrads I could've ever had. It was a pleasure to work with both of you. I would also like to especially thank Rob for all of the lab antics, the constant laughter, for always being there to help me when I needed it and for putting up with working alongside of me the past five years.

I would like to thank Dr. Kathleen Halligan for being a wonderful mentor throughout my undergraduate and graduate career. Because of you, I fell in love with organic chemistry and I can definitely say I wouldn't be here without you.

I owe a big thank you to my friends from Lancaster and Syracuse. Kyle Howard, thank you for going on this crazy journey with me. It wouldn't have been the same without you! You made the transition a lot easier and the road trips home were always much more enjoyable when you tagged along. Lindz, Leen and Bay, thank you for always making time for me (no matter what!) when I came home to visit. Hannah and Sam, I'm so lucky to have bumped into you on that random night at Al's. Thank you for the many fun nights downtown, "girl talks" and encouragement when I was having a bad day. Valerie, I am so lucky to have you as a best friend. I would not have been able to do this without you. Thank you for your support and for being my inner voice of reason. I will cherish the memories we made here in Syracuse and I'm looking forward to many more! Justin, thank you for never giving up on me. You always brightened my day and were that something to look forward to at the end of the day. You opened up my eyes to many new and unique experiences that I will never forget. I look forward to our next adventure and whatever the future has in store for us.

Lastly, I would like to thank my family, especially my parents Deb, Dan and John. Without you this would not have been possible. Thank you for always pushing me to work hard and for the constant encouragement, guidance and love. This is for you!

TABLE OF CONTENTS

LIST OF SCHEMES

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

δ	chemical shift in parts per million
μ	micro
[α]	specific rotation
Å	angstrom(s)
Ac	acetyl
Ad	adamantyl
Anal.	combustion elemental analysis
app	apparent
Ar	aromatic
atm	atmosphere
Bn	benzyl
br	broad
c	concentration
calcd	calculated
cm	centimeters
cm^{-1}	wavenumber(s)
COD	1,5-cyclooctadiene
conv	conversion
COSY	correlated spectroscopy
cot	1,3,5-cyclooctatriene
Cp	cyclopentadiene
Cp*	pentamethylcyclopentadiene
Cy	cyclohexyl
°C	degrees Celsius
d	doublet
DCE	1,2-dichloroethane
DCM	dichloromethane
DEPT	distortionless enhancement by polarization transfer
dd	doublet of doublets
ddd	doublet of doublet of doublets
DHP	dihydropyran
DIAD	diisopropyl azodicarboxylate
DIPEA	diisopropylethylamine

DMA	dimethylacetamide
DMAP	*N*,*N*-dimethylaminopyridine
DME	1,2-dimethoxyethane
DMF	dimethylformamide
dppe	diphenylphosphinoethane
dq	doublet of quartets
dr	diastereomeric ratio
dt	doublet of triplets
ESI	electrospray ionization
Et	ethyl
equiv	equivalents
eq	equation
EWG	electron withdrawing group
FT-IR	Fourier transform infrared
g	gram(s)
Gen	generation
h	hour(s)
HMPA	hexamethylphosphoric triamide
HRMS	high-resolution mass spectrometry
HSQC	heteronuclear single quantum correlation
Hz	hertz
*i*Pr	isopropyl
J	coupling constant
KHMDS	potassium hexamethyldisilazane
L	liter
LDA	lithium diisopropylamine
m	multiplet
M	molar (moles per liter)
Me	methyl
MeCN	acetonitrile
Mes	mesityl
Men	menthyl
mg	milligram(s)
MHz	megahertz
MIDA	*N*-methyliminodiacetic acid
min	minutes
mL	milliliter(s)
mol	mole(s)
mmol	millimole(s)
mp	melting point
MVK	methyl vinyl ketone
Nap	napthyl
N/D	not determined

NHC	*N*-heterocyclic carbene
NMR	nuclear magnetic resonance
NOESY	nuclear Overhauser effect spectroscopy
nOe	nuclear Overhauser effect
Ph	phenyl
ppm	part(s) per million
PPTS	pyridinium *p*-toluenesulfonate
Pr	propyl
psi	pounds per square inch
q	quartet
RBF	round bottom flask
ref	reference
R_f	retention factor
rt	room temperature
NMP	*N*-methylpyrrolidinone
s	singlet
t	triplet
TBAF	tetrabutylammonium fluoride
TBS	*tert*-butyldimethylsilyl
*t*Bu	*tert*-butyl
td	triplet of doublets
temp	temperature
Tf	trifluoromethanesulfonyl
THF	tetrahydrofuran
TMS	trimethylsilane
Tol	tolyl (toluene)
Ts	*p*-toluenesulfonyl
Xyl	xylyl

PREFACE

This thesis has been adapted from the following published articles co-written by the author:

"Ethylene Transposition: Ruthenium Hydride Catalyzed Intramolecular *trans*-Silylvinylation of Internal Alkynes." Liu, S.; Zhao, J.; Kaminsky, L.; Wilson, R. J.; Marino, N.; Clark, D. A. *Org. Lett.* **2014**, *16,* 4456-4459.

"Ruthenium Catalyzed Cycloisomerization of Silicon-Tethered 1,7-Enynes To Give Exocyclic 1,3-Dienes." Kaminsky, L.; Clark, D. A. *Org. Lett.* **2014**, *16*, 5450-5453.

"Stereo- and Regioselective Formation of Silyl-Dienyl Boronates." Kaminsky, L.; Wilson, R. J.; Clark, D. A. *Org. Lett*. **2015**, *17*, 3126-3129.

"Ruthenium Hydride Catalyzed Silylvinylation of Internal Alkynes Using Ethylene Gas." Wilson, R. J.; Kaminsky, L.; Ahmed, I.; Clark, D. A. *J. Org. Chem*. **2015**, *80*, 8290-8299.

1.0 INTRODUCTION

Transition metal-catalyzed coupling reactions between alkynes and alkenes are useful synthetic protocols for the formation of conjugated dienes.[1] Conjugated dienes are of great importance due to their prevalence in a variety of natural products that possess a wide array of biological activity, including those shown in Figure 1.

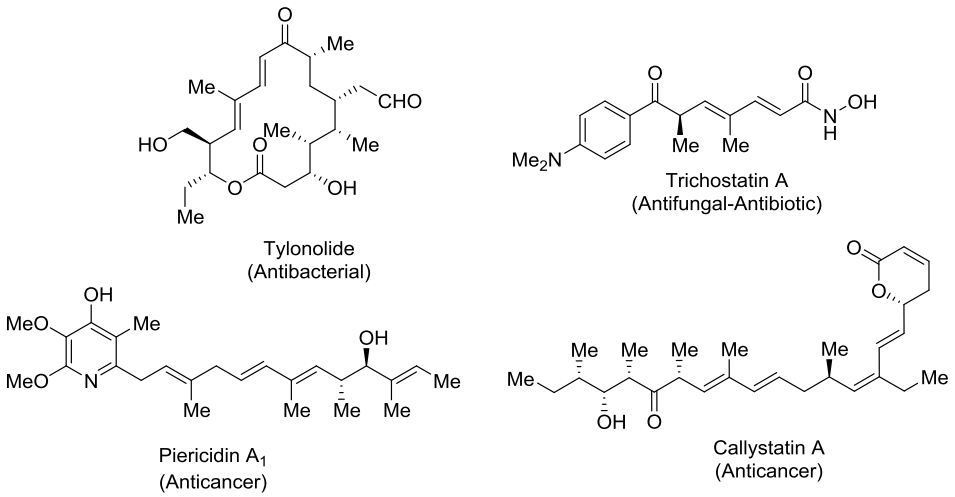
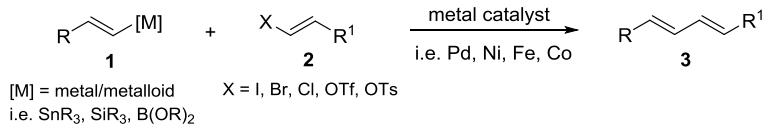


Figure 1. Select diene-containing natural products

However, one of the drawbacks of utilizing transition metals to form dienes is the need for one or both of the coupling partners to be activated before the coupling can occur (Scheme 1).



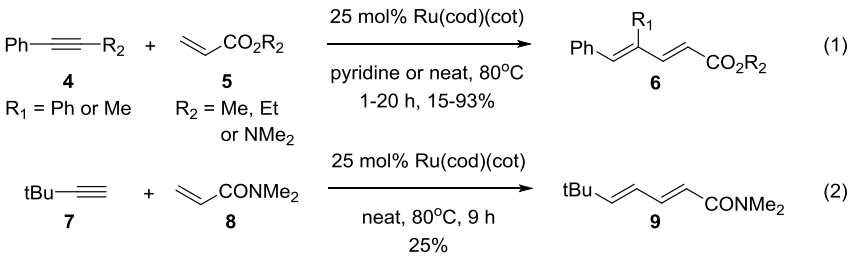
Scheme 1. Classic cross-couplings for formation of dienes

Generally, one coupling partner is functionalized with a metal or metalloid species (i.e. boron, tin, silicon; compound **1**) and the other (compound **2**) a halogen (bromine, chlorine) or pseudo-halogen (triflate, tosylate).[2] In many cases one or both of the activated olefin coupling partners are derived from alkynes. The use of a metal-hydride catalyst to facilitate the formation of conjugated dienes is of particular interest as it could potentially eliminate the need for intermediate activated cross-coupling partners shown in Scheme 1. Development of a methodology that does not require functionalization of the olefin and/or alkyne is of great importance because it increases efficiency and eliminates the need for intermediates that can generate toxic by-products.

The use of ruthenium catalysts to couple alkenes and alkynes is a reliable method for carbon-carbon bond formation. Such methods can lead to the formation of complex diene systems and furthermore, polyketide synthesis.[3] An advantage of utilizing ruthenium is that there is no need for pre-activation of the alkyne and olefin coupling partner.[4] Such ruthenium-catalyzed reactions can be classified as four major groups based on mechanistic identity: metallocycles[5, 6] (Alder-Ene/cycloisomerization), C-H activation,[7-10] vinyl carbenes[11-13] and the least explored, ruthenium hydrides.[14-16]

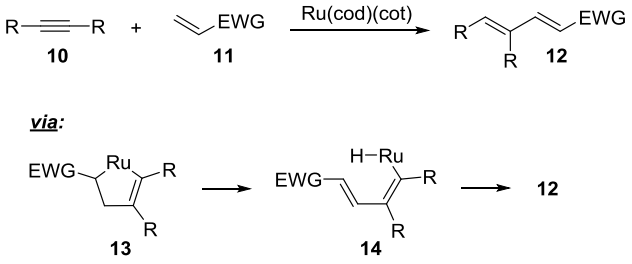
The first reported use of ruthenium to form diene systems via a ruthenium hydride intermediate was by Watanabe e*t al.*[17] These researchers coupled acetylenes (**4**) and alkenes (**5**)

to give dienes (**6**) with high levels of regioselectivity in good yields (Scheme 2, eq. 1). This methodology worked well with internal alkynes but gave poor yields when terminal alkynes (**7**) were used (Scheme 2, eq. 2). In addition, high catalyst loadings (25 mol%) were required for complete conversion of the starting alkynes.



Scheme 2. Ru(cod)(cot)-catalyzed intermolecular coupling of alkynes and olefins

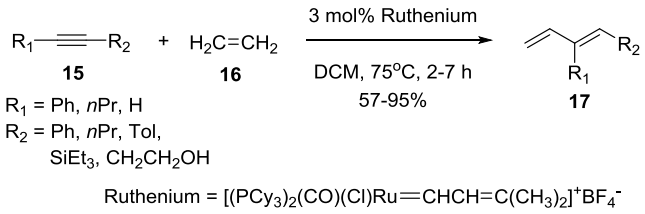
The researchers proposed that the coupling of acetylenes with electron withdrawing olefins proceeded via a ruthenacyclopentene intermediate (Scheme 3).



Scheme 3. Mechanistic rationale

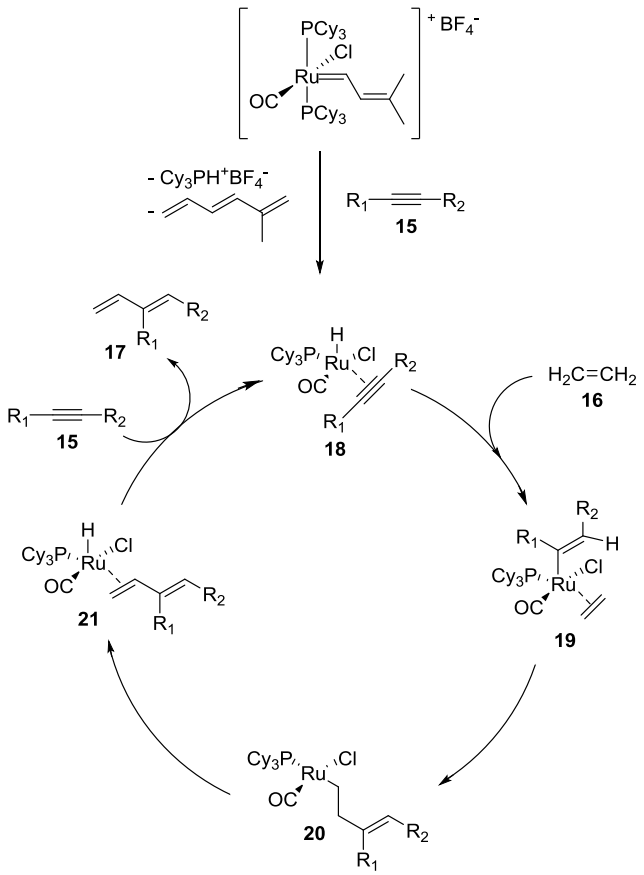
Coordination of alkyne **10** and alkene **11** with a zero-valent ruthenium complex yields ruthenacyclopentene **13**, which undergoes β-hydride elimination to give vinyl ruthenium hydride **14**. Reductive elimination of **14** yields the product diene **12**.

The hydrovinylation of alkynes (**15**) catalyzed by a cationic-alkylidene ruthenium complex is known to give diene scaffolds (**17**) in good yields (Scheme 4).[18] These conditions tolerate a variety of substituents on the alkyne terminus, including aryl, alkyl and alcohol functionality.



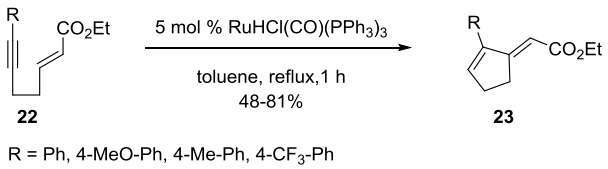
Scheme 4. Hydrovinylation of alkynes with ethylene

Yi *et al.* proposed the hydrovinylation of alkynes as follows (Scheme 5): Deprotonation of the δ-methyl group of the initial cationic ruthenium complex and elimination of $Cy_3PH^+BF_4^-$ and the triene, followed by coordination of alkyne **15** generated ruthenium intermediate **18**. Alkyne insertion and olefin coordination gave intermediate **19**. Subsequent olefin (ethylene) insertion (**20**) yielded ruthenium hydride **21**, which underwent β-hydride elimination to yield the diene product **17**.



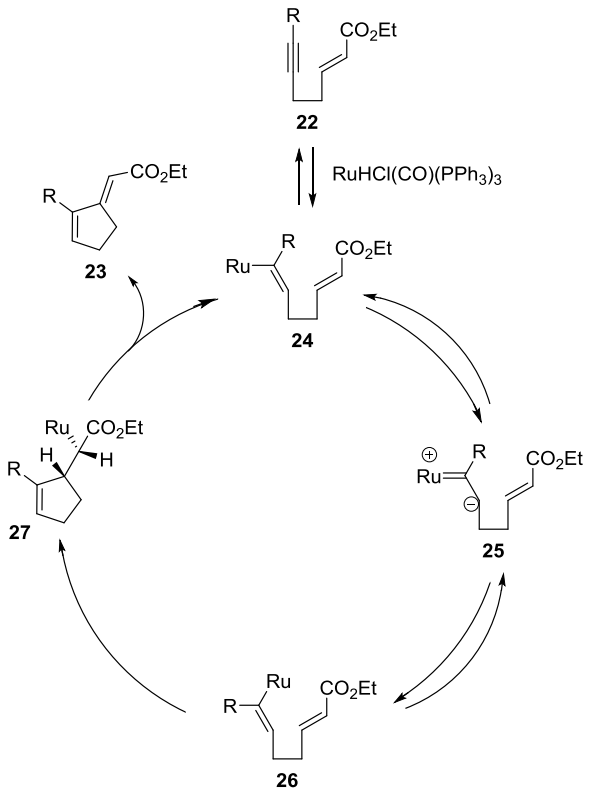
Scheme 5. Mechanistic hypothesis for the hydrovinylation of alkynes

The first intramolecular cyclization of enynes (**22**) to give 1,3-dienes (**23**) using catalytic $RuHCl(CO)(PPh_3)_3$ was accomplished by Mori's group (Scheme 6).[1] The cyclization proceeded in one hour and gave fair to good yields of the cyclopentene derivatives. However, the scope of investigation was somewhat limited because only aromatic groups on the alkyne terminus were investigated.



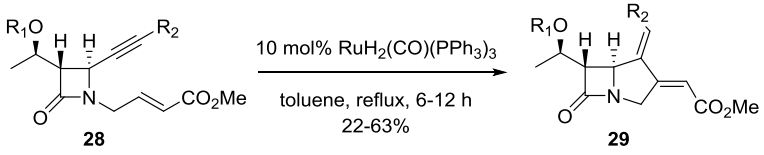
Scheme 6. Cyclization of enynes using $RuHCl(CO)(PPh_3)_3$

Mori *et al.* envisioned the reaction mechanism as follows (Scheme 7): Hydroruthenation (*cis* addition) of enyne **22** generates vinyl ruthenium **24**, which isomerizes to vinyl ruthenium complex **26** via the dipolar intermediate **25**. Subsequent intramolecular olefin insertion yields cyclopentene **27**, which subsequently undergoes *trans* β-hydride elimination to yield diene product **23**.



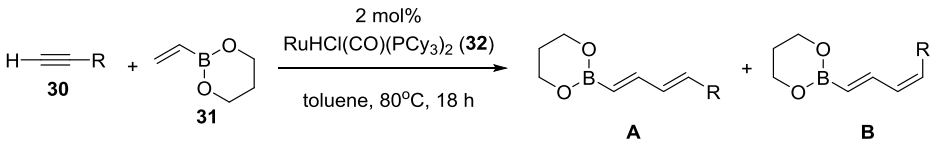
Scheme 7. Mechanistic proposal for the intramolecular cyclization of enynes

The Mori group later extended the methodology using Murai's catalyst to include the preparation of heterocycles and utilized it for the synthesis of Carbapenam skeletons (Scheme 8).[19] This process was useful in the fact that they obtained the desired products, but complete conversion of the starting enynes was not achieved resulting in poor to average yields.



Scheme 8. Intramolecular cyclization to afford Carbapenam skeletons

Alternatively, intermolecular couplings of alkynes with vinyl boronates in the presence of ruthenium hydride $RuHCl(CO)(PCy_3)_2$ (**32**) has been explored by Marciniec (Table 1).[20] Although one regioisomer was generated, stereocontrol was problematic with only isomers **A** and **B** isolated. In addition, only terminal alkynes were utilized, providing minimal functionality on the diene scaffold.



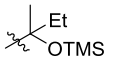
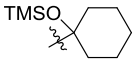
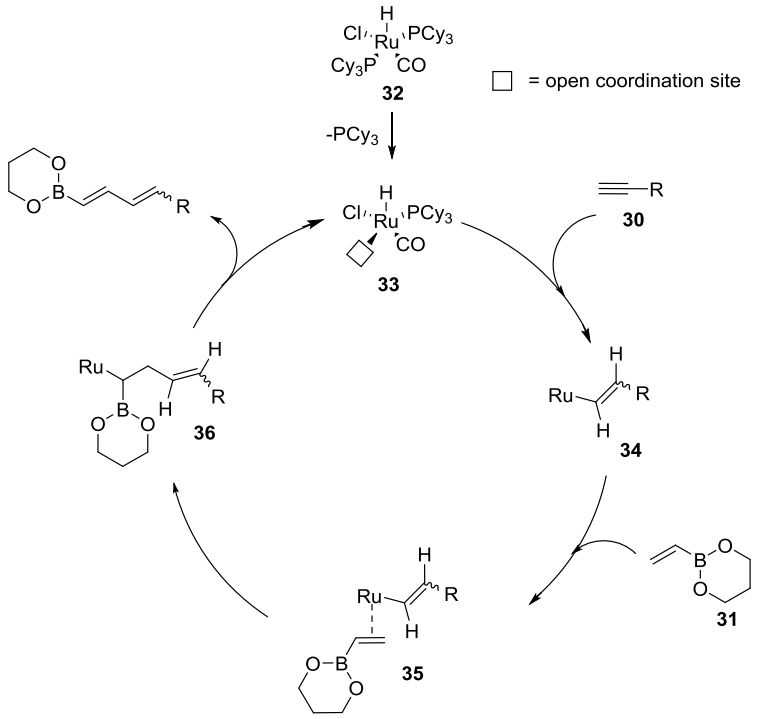
R	A:B	yield (%)
Cy	83:15	74
$SiEt_3$	80:13	78
	84:16	66
	81:19	70
Hexyl	60:40	nd

Table 1. Coupling of terminal alkynes with vinyl boronates

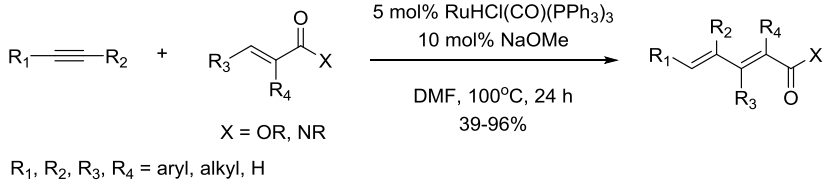
This group believed the coupling to proceed as follows (Scheme 9): Dissociation of a phosphine ligand from ruthenium hydride **32** generates a highly reactive 14-electron complex **33**.



Scheme 9. Mechanistic proposal for the coupling of alkynes with vinyl boronates

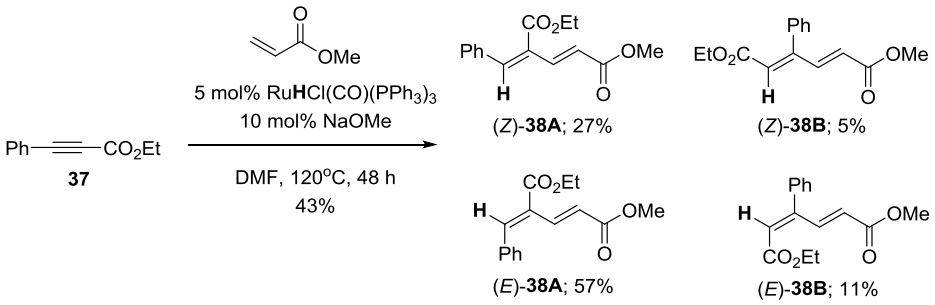
Subsequent *cis*-hydroruthenation of alkyne **30** generates vinyl ruthenium intermediate **34**. Coordination (intermediate **35**) and subsequent insertion of vinyl boronate **31** yields the boro-ruthenate species **36**. β-Hydride elimination produces the dienyl boronate product and regenerates the active catalytic species.

More recently, Plietker's group reported an intermolecular ruthenium-catalyzed hydrovinylation of alkynes to give 1,3-dienes (Scheme 10).[21] The active catalytic species, $RuH_2(CO)(PPh_3)_3$, is generated *in situ* by treatment of catalytic sodium methoxide with DMF.



Scheme 10. Hydrovinylation with internal alkynes and acrylates

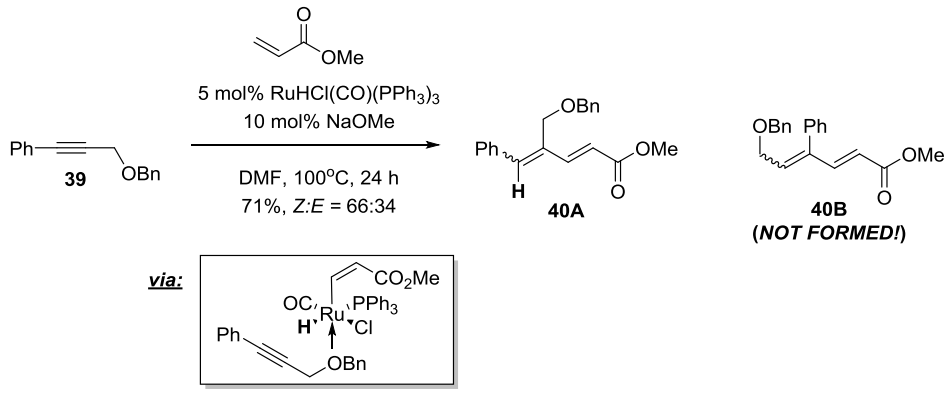
This methodology was tolerable to a wide variety of substrates, including terminal and internal alkynes with aromatic and alkyl functionality. In addition, acrylates and acrylamides proved to be superior olefin coupling partners. Despite the diverse substrate scope of the reaction, when unsymmetrical internal alkynes (such as **37**) were used a mixture of stereo- and regioisomers (**38A, 38B**) was obtained (Scheme 11).



Scheme 11. Mixture of stereo- and regioisomers with Plietker's methodology

Further, the substitution patterns of the dienes formed are somewhat limited because the products must incorporate a hydrogen atom.[22] In some cases, the regioselectivity of products could be controlled. For example, when a benzyl ether moiety was on the alkyne terminus (alkyne **39**),

solely regioisomer **40A** was observed (Scheme 12). It was proposed that the benzyl ether coordinates to the ruthenium, therefore preventing formation of regioisomer **40B.**



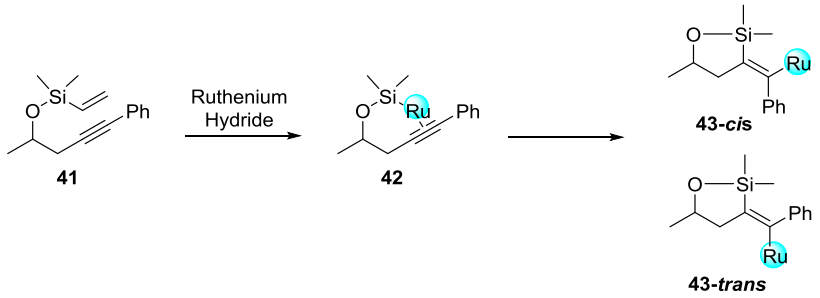
Scheme 12. Plietker's control of regioselectivity

In conclusion, several groups have utilized catalytic ruthenium to couple alkynes with alkenes for the synthesis of conjugated dienes. Despite the synthetic utility, stereo- and regiocontrol of the diene products was problematic. In addition, mandatory incorporation of a hydrogen atom on the diene scaffold was required, hence limiting the diversity on the diene backbone. In one case reported by Plietker, a benzyl ether moiety at the propargylic position of the alkyne controlled the regioselectivity of the reaction.

1.1 INTRAMOLECULAR APPROACH: USE OF A VINYL SILICON TETHER

Typically, hydrometallations to form diene scaffolds require mandatory hydrogen incorporation into the product and also give a mixture of stereo- and regioisomers. To alleviate

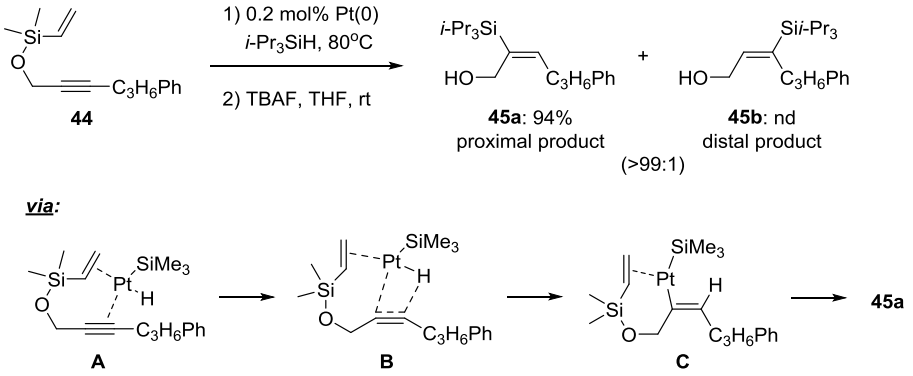
mandatory hydrogen incorporation and regioselectivity issues that arose from such methods, the Clark group envisioned utilizing an intramolecular approach that relied on the use of a vinyl silicon tether (Scheme 13).[23] Replacing a hydrogen atom with a silicon atom would provide for a more diverse diene scaffold and hence, would eliminate the need for mandatory incorporation of hydrogen.



Scheme 13. Vinyl silicon tether approach

To initiate these studies, it was envisioned that the silicon-tethered alkyne **41** could be used to direct the ruthenium species towards the pendent alkyne **42** to obtain the desired regioisomer **43**. At the time, the **43-*cis*** addition isomer was expected to be favored[24] due to the literature precedence of cis-hydroruthenations of alkynes (as discussed in Chapter 1), but we did not ignore the possibility for the formation of the **43-*trans*** isomer.

The use of a vinyl silicon tether to control regioselectivity has been reported by Tomooka, as shown in Scheme 14.[25] The researchers utilized a dimethylvinylsilicon "directing group" to obtain regiocontrol of a platinum-catalyzed hydrosilylation of unsymmetrical alkynes.



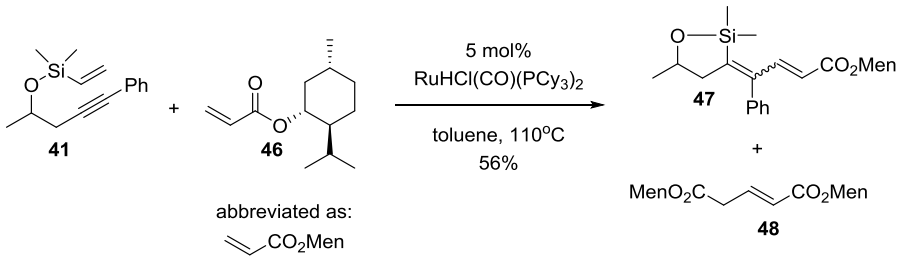
Scheme 14. Directing group controlled hydrosilylation

As depicted in Scheme 14, the platinum complex coordinates to the dimethylvinylsilicon group (**A** and **B**), which allows for the favorable formation of the proximal hydrosilylated product **45a**. The substrate scope of the directing group controlled hydrosilylation included propargyl, homopropargyl, and bis-homopropargylic silanes. This methodology is somewhat different to the Clark group's reaction design due to the fact that they utilized the directing group for sole formation of silyl-alkenes. In addition, a mandatory hydrogen atom was incorporated. The Clark group's directing group strategy allowed for the regioselective formation of a tetra-substituted double bond and an oxasilacycle is formed in the process.

1.2 *TRANS*-SILYLVINYLATION OF ALKYNES WITH ACRYLATES

1.2.1 Previous work from the Clark group[26]

Studies began with alkyne **41**[26] and L-menthyl acrylate in refluxing DCE with catalytic $RuHCl(CO)(PCy_3)_2$.[27] L-menthyl acrylate was chosen as the olefinic coupling partner because of its ease to synthesize in the laboratory in addition to its visibility by thin layer chromatography. A single diene isomer **47** was observed in 56% yield by ^1H NMR (Scheme 15). Ethylene and a small amount of the acrylate dimer **48** were the only visible by-products of the reaction observed by ^1H NMR.



Scheme 15. Initial studies of the intermolecular coupling[a]

[a] Reaction run by Shasha Liu.

Further analysis of the product by 1D and 2D NMR allowed Dr. Liu to determine the stereochemical outcome. Using NOESY NMR experiments, a strong correlation between the proton β to the acrylate moiety and the diastereotopic protons of the five-membered oxasilacycle allowed them to conclude the stereochemical outcome of the transformation (Figure 2, **47A**). Dr.

Liu did not observe an nOe correlation between the β-proton and methyl protons attached to the silicon (**47B**).

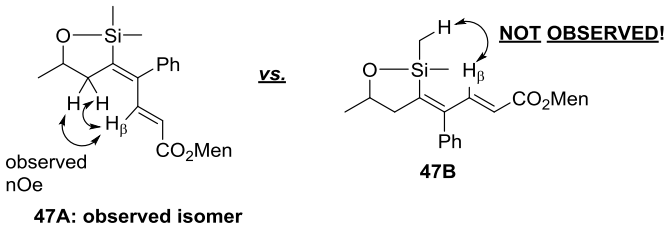
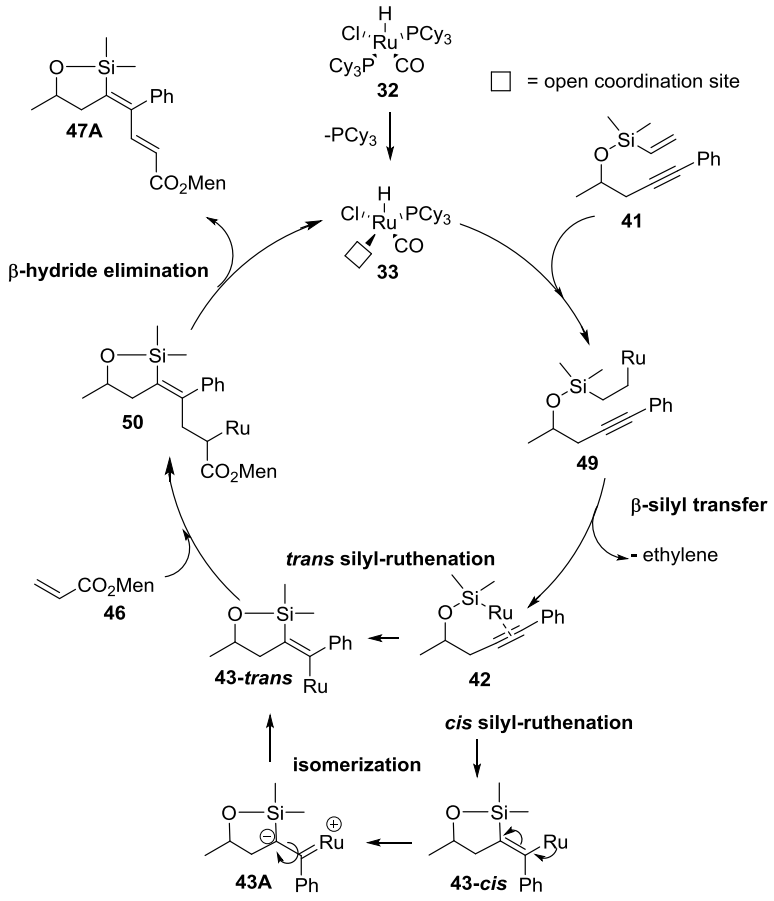


Figure 2. Stereochemical outcome

Dr. Liu did not expect to observe the *trans*-addition isomer **47A** due to the literature precedence of ruthenium-catalyzed diene formation occurring via a *cis*-metallation pathway. However, the researchers were intrigued by the unexpected product outcome. A discussion of *trans*-functionalization of alkynes will follow after the mechanistic hypothesis is explained.

1.2.2 Mechanistic hypothesis[26]

It is believed by the researchers that the transformation proceeds as follows (Scheme 16): Dissociation of a phosphine ligand from **32** gives a highly reactive 14-electron ruthenium complex **33**, which upon reaction with the silicon-tethered alkyne **41**, adds at the sterically most accessible (terminal) position of the vinyl moiety to give intermediate **49**.



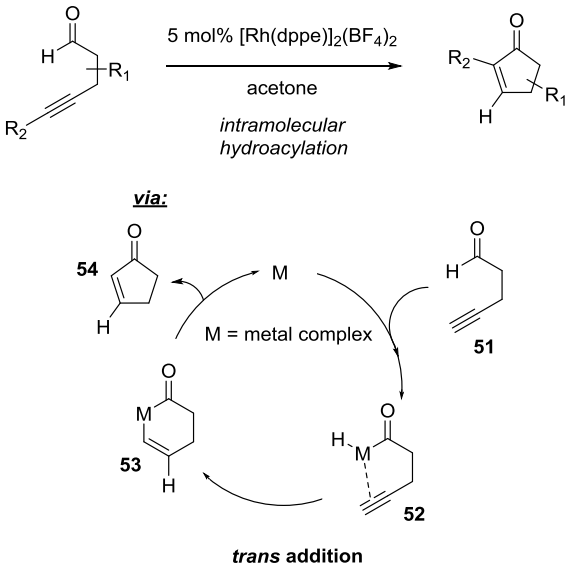
Scheme 16. Mechanistic hypothesis

β-Silyl transfer and subsequent loss of ethylene[28] results in formation of silyl-ruthenium intermediate **42**. The transformation from **42** to **43** can proceed via direct *trans* silyl-ruthenation (see section 2.2.3 for literature precedence) or by a *cis* silyl-ruthenation pathway to give intermediate **43-*cis*** followed by isomerization to generate **43-*trans***. The isomerization is proposed to proceed via a vinylidene-type intermediate **43A** (favorable due to the charge stability by the silicon atom). Intermolecular olefin insertion (acrylate **46**) at the most sterically accessible

position of the alkene yields **50**, which subsequently undergoes β-hydride elimination to give the desired diene **47A**. Upon formation of **47A**, ruthenium hydride complex **33** is regenerated.

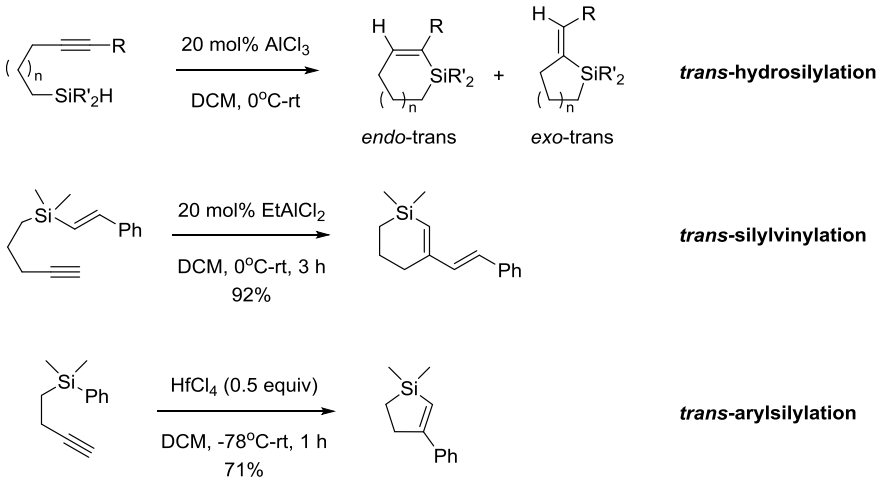
1.2.3 *Trans*-functionalization of alkynes

Metal catalyzed *trans*-functionalization of alkynes is known in the literature but is quite rare. Fu and Tanaka reported on the *trans*-hydroacylation of alkynes to give cyclopentenones using cationic rhodium (Scheme 17).[29-31] Oxidative addition of the aldehyde **51** carbon-hydrogen bond to a rhodium (I) complex yields a rhodium (III) acyl hydride **52**. Next, the rhodium hydride adds in a *trans* fashion to the coordinated alkyne to generate a rhodium metalacyclohexene **53**. Reductive elimination of **53** yields the cyclopentenone **54** and regenerates the active rhodium (I) species.



Scheme 17. Fu's hydroacylation of alkynes

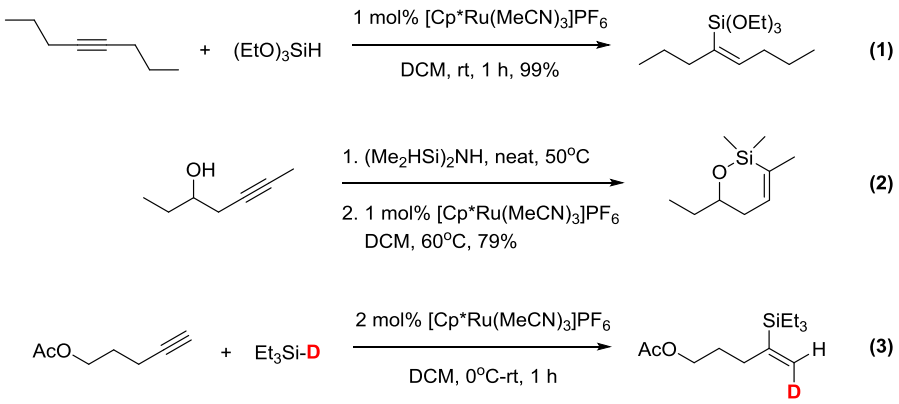
Yamamoto and co-workers reported on the Lewis acid-catalyzed intramolecular *trans*-hydrosilylation, *trans*-vinylsilylation and *trans*-arylsilylation of unactivated alkynes (Scheme 18).[32, 33] Intramolecular *trans*-silylvinylation is observed with catalytic $AlCl_3$ via coordination of the aluminum to the alkyne and intramolecular attack of a hydride from the hydrosilane on the electron-deficient sp carbon opposite of the Lewis acid (aluminum). This pathway is also observed by the Yamamoto group with the aluminum-catalyzed *trans*-silylvinylation of alkynes. The intramolecular attack by the silane moiety on the electron deficient alkyne occurs on the opposite side to the Lewis acid.



Scheme 18. Yamamoto's *trans*-functionalization of alkynes

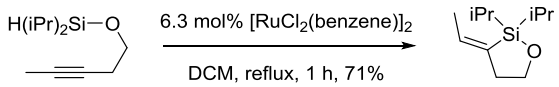
Trost and co-workers have reported on the inter- (Scheme 19, eq. 1) and intramolecular (Scheme 19, eq. 2) ruthenium catalyzed *trans*-hydrosilylation of alkynes.[34-37] They also conducted a deuterium labeling experiment to verify the *trans*-addition pathway (Scheme 19, eq. 3).[37] Reaction of the alkyne with triethylsilane-*d* and a cationic ruthenium complex gave a single

product with 100% deuterium incorporation at the *trans* vinyl position. They noted that they were able to assign this by ^{1}H NMR because the *trans* and *cis* vinyl protons relative to silicon are quite distinct in chemical shift (*trans* δ 5.65-5.75, *cis* δ 5.28-5.37).



Scheme 19. Trost's ruthenium catalyzed *trans*-hydrosilylation of alkynes

Lastly, Denmark utilized catalytic $[RuCl_2(benzene)]_2$ for an intramolecular *trans*-hydrosilylation of alkynes (Scheme 20).[38] Denmark was able to isolate exo-type products, whereas typically endo-type products are observed in *trans*-hydrosilylation protocols (as seen by Yamamoto).

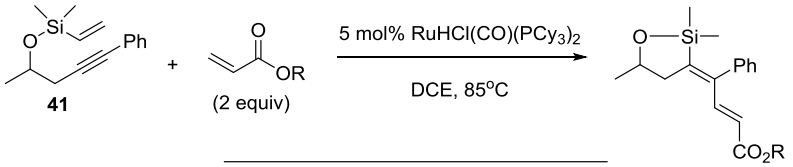


Scheme 20. Denmark's conditions for formation of oxasilacycles

After examination of the few examples in the literature of direct *trans*-addition/functionalization of alkynes, it is important to recall that the Clark group's observation of *trans*-addition products is believed to originate from a different mechanistic pathway. The formation of the unique *trans*-addition products is postulated to occur from a *cis*-addition of the ruthenium metal to the alkyne followed by isomerization.

1.2.4 Previous work from the Clark group: reaction optimization and scope[26]

With a promising result from the initial studies (Scheme 15), a solvent screen was conducted and DCE at 85°C proved to be superior reaction conditions. Additional metal hydride complexes were examined and $RuHCl(CO)(PCy_3)_2$ proved the most effective. After those conditions were established, the olefin coupling partner was examined (Table 2).



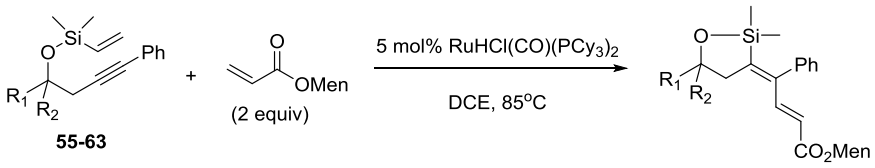
Entry	R	Yield
1	Me	55%
2	Et	54%
3	*n*Bu	51%
4	*t*Bu	58%
5	isobornyl	73%
6	CH_2biphenyl	79%
7	L-menthol	70%

Table 2. Olefin coupling partner scope[a]

[a] All reactions performed by Shasha Liu and/or Jinbo Zhao.

Alkyl-substituted acrylates (entries 1-4) gave the desired diene products in modest yields of 51%-58%. Bulkier acrylates proved to work best in the reaction (entries 5-7) and a significant improvement in product yield was obtained with 70%-79% isolated yields, respectively. The authors were pleased to discover that biphenyl acrylate (entry 6) gave the desired diene as a crystalline solid. The chemical structure of the diene product observed from this transformation was further verified with X-Ray Crystallography.

L-Menthyl acrylate was chosen as the olefin coupling partner to explore the alkyne scope. With a phenyl group at the alkyne terminus, substitution at R_1 and R_2 was examined (Table 3). Alkyl substitution (entries 1-3), including an *n*-heptyl chain and the bulky cyclohexane ring, was well tolerated, giving the desired products in good yields of 72%-77%. Aromatic substitution was also tolerated (entries 4-7) and worked best in refluxing toluene, resulting in 65%-69% yields of the products. Use of a chiral alkyne worked well to give the product as one isomer with no racemization (entry 5).



Entry[a]	Alkyne	R_1	R_2	Yield
1	**55**	H	C_7H_5	77%
2	**56**	H	$(CH_2)_2Ph$	72%
3	**57**	H	Cy	75%
4[b]	**58**	H	Ph	69%
5[b]	**59**	H	(*R*)-Ph	65%
6[b,c]	**60**	H	4-NO_2Ph	68%
7[c]	**61**	H	4-Ph-Ph	68%
8	**62**	Ph	Me	83%
9	**63**	R_2	$(CH_2)_5$	92%

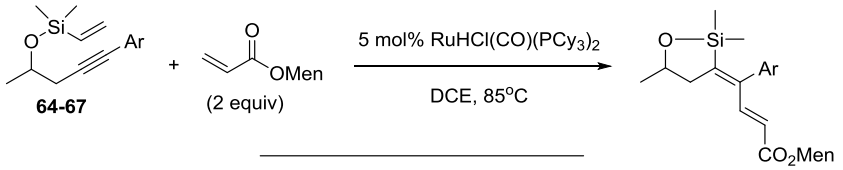
Table 3. Phenyl-substituted alkyne scope[a]

[a] All reactions performed by Shasha Liu and/or Jinbo Zhao. [b] Reaction conducted in toluene at 110°C.

[c] Biphenyl acrylate was used as the olefinic coupling partner.

Other aromatic substituents, such as 4-nitrophenyl and *p*-biphenyl (entries 6 and 7), worked best with the biphenyl acrylate coupling partner in refluxing toluene and gave the dienes in 68% yield. Increasing the Thorpe-Ingold effect[39] at the homo-propargylic position (entries 8 and 9) gave excellent product yields of 83% and 92%, respectively.

Varying the aromatic substituent at the alkyne terminus, additional alkyne substrates were examined (Table 4). The inductively withdrawing 4-fluorophenyl alkyne (entry 1) gave the resulting diene in 60% yield. The electron-donating 4-methoxyphenyl substituent (entry 2) was well tolerated in the reaction and gave the product in 73% yield. Lastly, tolyl and 3,5-xylyl substitution (entries 3 and 4) performed well and gave good yields of the products.



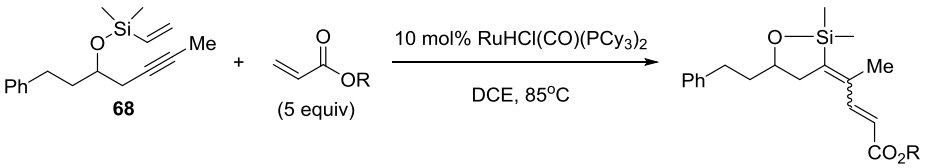
Entry[a]	Alkyne	Ar	Yield
1	**64**	4-F	60
2	**65**	4-MeO	73
3	**66**	4-Me	74
4	**67**	3,5-Xyl	74

Table 4. Aromatic-substituted alkyne scope[a]

[a] All reactions performed by Shasha Liu and/or Jinbo Zhao.

The use of alkyl-substituents at the alkyne terminus initially seemed problematic. Dr. Liu and Dr. Zhao focused on utilizing methyl-substituted alkynes due to the resulting diene products being more common in natural product scaffolds. The standard reaction conditions used for aromatic alkyne substitution (5 mol% $RuHCl(CO)(PCy_3)_2$ and 2 equivalents of menthyl acrylate) resulted in poor yields of the desired products. Increasing the catalyst loading of $RuHCl(CO)(PCy_3)_2$ to 10 mol% improved upon the product yield. However, it was also hypothesized that poor product yields could be derived from β-hydride elimination of intermediate **43**. They envisioned that increasing the amount of acrylate concentration in the reaction mixture could circumvent β-hydride elimination and favor acrylate incorporation to give the product. Using methyl-substituted alkyne **68**, an easy to handle and non-volatile starting material, subjection with 10 mol% of $RuHCl(CO)(PCy_3)_2$ and 5 equivalents of alkyl-substituted acrylates proved to be most effective (Table 5). A benefit for the use of lower-boiling acrylates is the ease of removal from the reaction mixture prior to product isolation. Subjection of alkyne **68**

to the conditions shown in Table 5 gave the desired diene in 61% yield (entry 1). However, formation of the inseparable *Z* isomer was also observed.



Entry[a]	R	Yield % (*E*:*Z*)
1	Me	61 (7.4:1)
2	Et	75 (7.5:1)
3	*t*Bu	64 (6.3:1)

Table 5. Methyl-substituted alkyne scope[a]

[a] All reactions performed by Shasha Liu and/or Jinbo Zhao

Switching from methyl acrylate to the slightly less volatile ethyl acrylate improved the product yield to 75% with the *E:Z* ratio remaining the same (entry 2). The bulkier *t*-butyl acrylate also allowed for 64% isolated yield of the diene product but with a slightly diminished *E:Z* ratio of 6.3:1 (entry 3).

In conclusion, a novel ruthenium hydride-catalyzed *trans*-silylvinylation of silicon-tethered alkynes with acrylates protocol was demonstrated by Dr. Clark and co-workers. The diene products possessed a tetra-substituted double bond and a silicon atom, which allowed for further diversity in the backbone. A variety of silicon-tethered alkynes were demonstrated, including aryl and alkyl substitution at the alkyne terminus and homopropargylic position. In addition, numerous acrylate coupling partners performed well, including the bulky L-menthol acrylate and the lower boiling methyl acrylate.

2.0 THE *TRANS*-SILYLVINYLATION OF INTERNAL ALKYNES WITH ACRYLATES AND VINYL BORONATES

2.1 *TRANS*-SILYLVINYLATION OF ALKYNES WITH ACRYLATES

2.1.1 Results: synthesis of chiral, methyl-substituted alkyne 77

It was desired to extend the aforementioned methodology by expanding the alkyne scope to further mimic such backbones present in diene-containing natural products. This extension would include introduction of chirality, functionality at the propargylic position (Figure 3, position 2) and further toleration of alkyl functionality on the alkyne terminus. At the outset of this project, the focus was synthesizing an alkyne that would include such characteristics and where product volatility would not be an issue. Inclusion of an aromatic-type moiety in the target molecule was desired in hopes of eliminating the possibility of volatility and therefore allowing for ease of handling and purification (Figure 3, target).

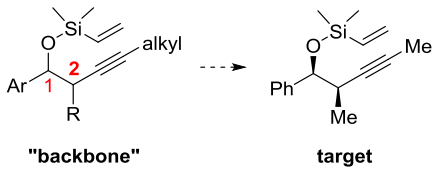
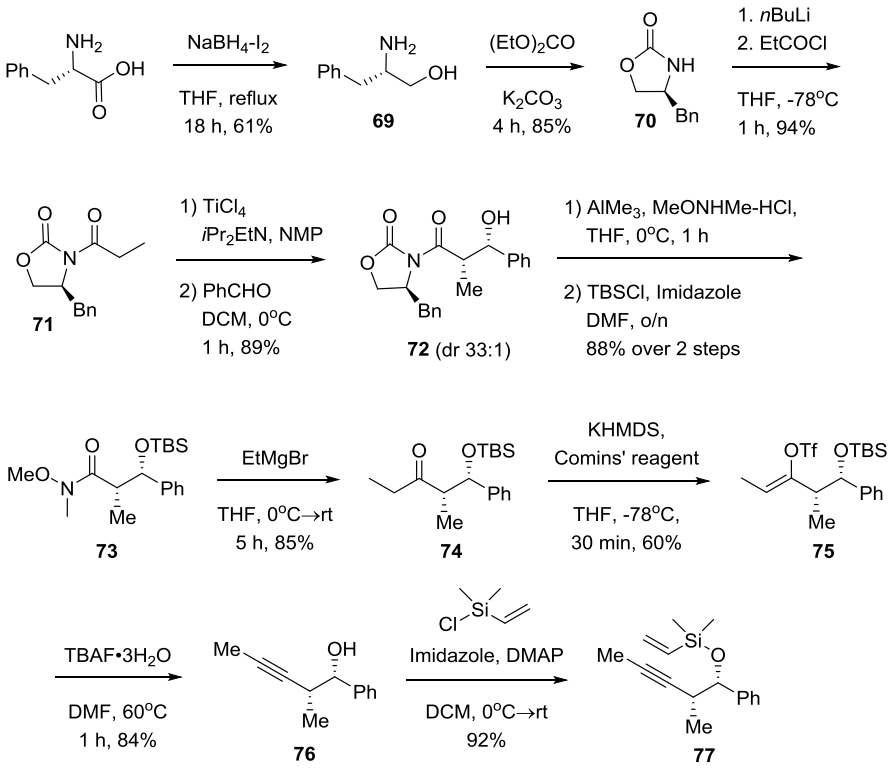


Figure 3. Desired "backbone" of a silicon-tethered alkyne substrate

To begin the synthesis (Scheme 21), commercially available L-phenylalanine was reduced via an iodine-mediated sodium borohydride reduction[40] to give L-phenylalanol **69** in 61% yield. This reaction was performed on 605 mmol (100 g) of the starting amino acid. Protection of **69** via the literature protocol[41] using diethyl carbonate and potassium carbonate afforded oxazolidinone **70** in 85% yield. Subsequent acylation with *n*BuLi and propionyl chloride via the known literature protocol[42] afforded acylated oxazolidinone **71** in an excellent yield of 94%. Originally, use of the Evans' syn aldol protocol[42] was planned as a means of obtaining our desired substrate **72**. However, after freshly preparing dibutylboron triflate[43, 44] and subjecting oxazolidinone **71** to the Evans' aldol conditions, the aldol adduct **72** was difficult to isolate due to poor conversion of the starting material. Poor yields of **72** (39%-56%) were obtained (in comparison to 93% reported in the literature). Numerous attempts were made to circumvent those issues, including: multiple distillations of benzaldehyde, multiple distillations of the freshly prepared dibutylboron triflate, use of commercial dibutylboron triflate and and use of freshly distilled reaction solvent. Those methods did not alleviate the reaction conversion and poor yields of **72** were still observed. A yield of 62% was obtained only once and occurred when the reaction was performed on a small scale (4 mmol of **71**). However, such a small scale was not practical at such an early stage of our synthetic route.



Scheme 21. Total synthesis of alkyne 77

At a later date the method developed by Crimmins[45] ($TiCl_4$, DIPEA, NMP) was employed to improve reaction conversion and yield of **72**. Full conversion of the starting material was observed and **72** was obtained in 89% yield (d.r. 33:1). Synthesis of Weinreb amide **73** was accomplished using a modified literature protocol[46] in an excellent yield of 88% (over two steps). Initially, Grignard addition into amide **73** using a solution of ethyl magnesium bromide (prepared from reagent grade magnesium turnings) was sluggish and required large amounts (3-5 equivalents) of the Grignard reagent. To resolve this issue, a fresh solution of ethyl magnesium bromide was made by mechanical activation of magnesium turnings following the procedure of Brown *et al.*[47] The protocol of mechanically activating the magnesium turnings via vigorous

stirring for 1-2 days provided finely dispersed/ground magnesium, which in turn formed a highly reactive Grignard reagent. Using this "super activated" Grignard reagent resulted in much shorter reaction times and full consumption of the starting material. Furthermore, ethyl ketone **74** was obtained in 85% yield. Formation of enol triflate **75** was attempted with LDA and McMurry's reagent[48] (Figure 4) but gave poor reaction conversion and very low yields of product (14%-18%).

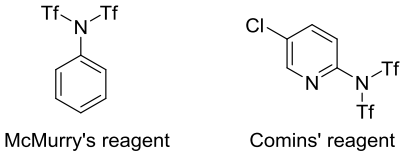


Figure 4. Triflating reagents

Use of triflic anhydride resulted in decomposition of starting material. A third triflating reagent, Comins' reagent (Figure 4), prepared by the literature procedure[49] and in combination with KHMDS gave enol triflate **75** in improved yields. It was further discovered that slow addition of the base[50] resulted in full conversion and gave the product in 60% isolated yield. NOESY data was used to confirm the isomer formed during triflation (Figure 5).

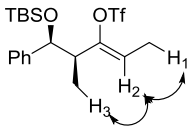
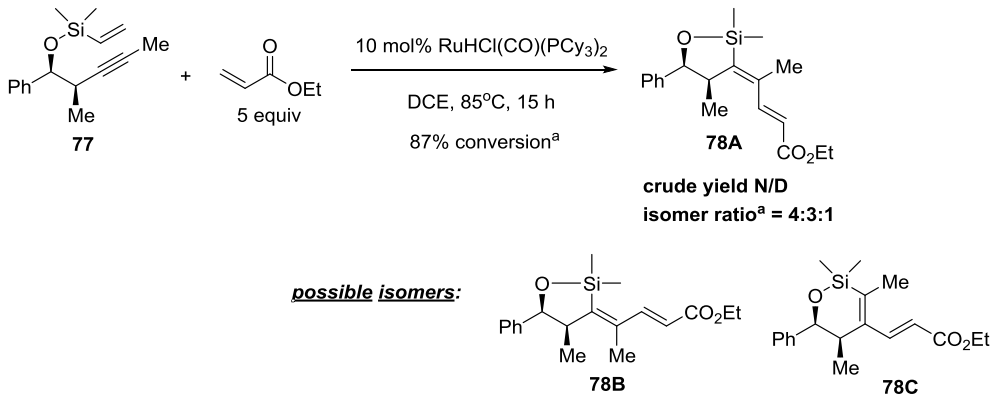


Figure 5. NOESY correlations observed for enol triflate 75

Correlation between protons H_1 (1.76 ppm), H_2 (5.39 ppm) and H_3 (0.94 ppm) (as indicated by NOESY crosspeaks) suggest the formation of isomer **75**. Elimination of the triflate and removal of the TBS group to form alkyne **76** was accomplished in one pot using solid TBAF at 60°C in DMF.[51] Lastly, silylation with dimethylvinylchlorosilane gave the desired silicon-tethered alkyne **77** in 92% yield. The synthesis of an enantiopure methyl substituted silicon-tethered alkyne possessing substitution at the propargylic position was accomplished in 10 linear steps with an overall yield of 19% from L-phenylalanine.

2.1.2 Exploration of alkyne 77 with the coupling of acrylates

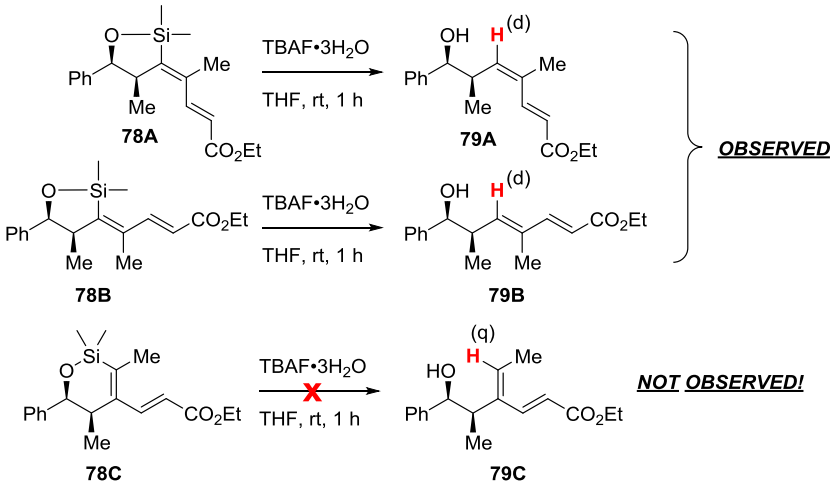
The reactivity of alkyne **77** was explored with the Clark group's previously established *trans*-silylvinylation methodology. Initially, conditions that worked well for alkyl substituted alkyne **77** were utilized (Table 5, entry 2): 10 mol% of $RuHCl(CO)(PCy_3)_2$ with 5 equivalents of ethyl acrylate in refluxing DCE (Scheme 22).



Scheme 22. Initial reactivity of alkyne 77

[a] Determined by ^1H NMR using mesitylene as an internal standard.

After 15 hours, 87% conversion of **77** was observed by ^{1}H NMR. Three product isomers was also observed in the crude ^{1}H NMR spectrum in a ratio of 4:3:1. The major isomer was believed to be the desired product **78A** but verification of its identity was needed (as well as the two minor isomers). After purification of the crude material via column chromatography, 45% was isolated as a mixture of two isomers. None of the isomer believed to be **78C** was obtained. These isomers were identical in chemical shift to the two major isomers in the crude ^{1}H NMR spectrum. In hopes of determining the identity of these compounds, the diene mixture was subjected to desilylation conditions using TBAF·3H$_2$O (Scheme 23). If **78A** and **78B** were the two major isomers isolated from the mixture, two distinct doublets (compounds **79A** and **79B**) in the ^{1}H NMR spectrum after desilylation were expected to be observed. If a quartet was observed (compound **79C**), formation of **78C** would be expected.



Scheme 23. Desilylation of diene mixture

Once the mixture was subjeced to desilylation, two distinct doublets were observed by ^{1}H NMR accounting for the formation of **79A** and **79B**. Even though **79C** was not observed after desilylation, the possibility of **78C** being the minor isomer formed in the acrylate coupling was acknowledged. At a later date, preparative thin layer chromatography was used to obtain a clean sample of **78A** for NOESY analysis (Figure 6). A clean sample of **78B** was not obtained after preparative thin layer chromatography. NOESY data confirmed **78A** as the major isomer because of strong correlation between H_1-H_2 and H_3-H_4.

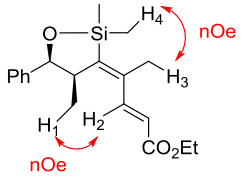
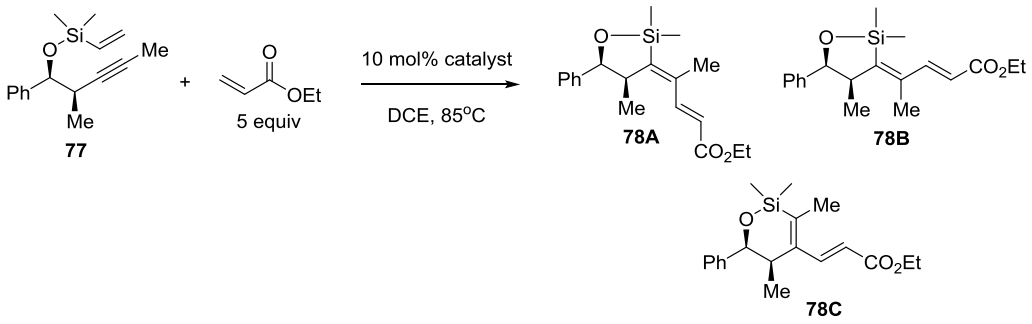


Figure 6. NOESY data obtained from major isomer 78A

Subsequently, additional ruthenium hydrides were screened in hopes of observing improved reaction conversion and product ratio (Table 6). Exchange of $RuHCl(CO)(PCy_3)_2$ for the di-*tert*-butylmethylphosphine complex $RuHCl(CO)(PtBu_2Me)_2$[52] resulted in a shorter reaction time and improved product ratio; however, the crude yield of **78A** was poor (entry 1). An increase of catalyst loading of $RuHCl(CO)(PtBu_2Me)_2$ to 20 mol% (entry 2) allowed for rapid conversion of the starting material and slightly improved crude yield (36%). Substituting complex $RuHCl(CO)(PtBu_2Me)_2$ for the triisopropylphosphine ruthenium complex $RuHCl(CO)(PiPr_3)_2$[53] proved to be less effective (entry 3) and resulted in a longer reaction time with a poor crude yield of 12%.



Entry	Catalyst	Time (h)	Conversion[a]	Ratio[a] 78A:78B:78C	Crude Yield[a] of 78A
1	$RuHCl(CO)(PtBu_2Me)_2$	3.5	91%	9:1:1	27%
2[b]	$RuHCl(CO)(PtBu_2Me)_2$	2.5	97%	7:1.6:1	36%
3	$RuHCl(CO)(PiPr_3)_2$	18	89%	6:0:1	12%
4	$RuHCl(CO)(H_2IMes)(PPh_3)$	7	84%	11:2:1	56%

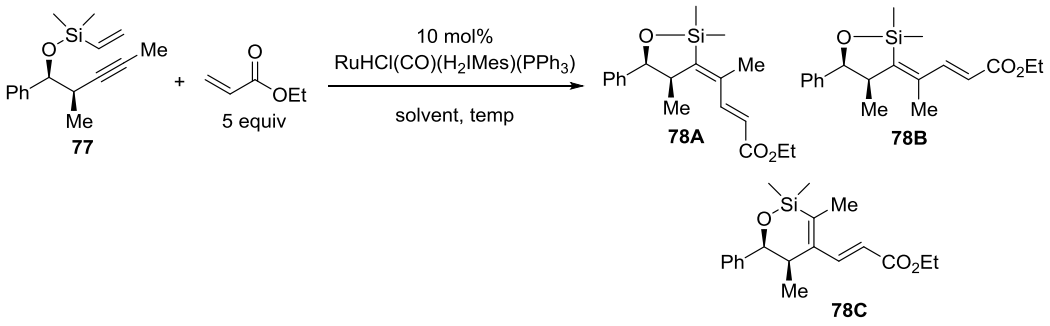
Table 6. Catalyst screen

[a] Determined by ^1H NMR using mesitylene as an internal standard. [b] Reaction performed with 20 mol% catalyst.

Lastly, ruthenium complex $RuHCl(CO)(H_2IMes)(PPh_3)$,[54] bearing a *N*-heterocyclic carbene (NHC) ligand, proved to be most successful in the transformation (entry 4). Despite only 84% conversion of the starting material after 7 hours, improvement of the isomeric ratio was observed and a 56% crude yield of **78A** was obtained.

With these results in hand, a solvent screen was pursued with $RuHCl(CO)(H_2IMes)(PPh_3)$ as the catalyst for the transformation (Table 7). Refluxing in toluene gave a shorter reaction time of two hours but a decreased crude yield of product was observed (entry 1). It was concluded that a minimum temperature of 80°C was necessary for conversion of starting material (entries 2 and 3), with an isolated yield of 55% obtained in toluene at 80°C. Decreasing the temperature to 50°C resulted in poor conversion (14%) after 22 hours (entry 3). More polar solvents, such as

α,α,α-trifluorotoluene, gave a comparable result to toluene (entry 4) albeit at slightly longer reaction times.



Entry	Solvent	Temp. (°C)	Time (h)	Conversion[a]	Ratio[a] 78A:78B:78C	Crude Yield[a,b] of 78A
1	toluene	110	30 min	92%	N/D	45%
2	toluene	80	45 min	91%	4:1:1	62% (55%)
3	toluene	50	22	14%	3:1:0	10%
4	CF_3Ph	80	2	87%	4:1:1	62% (56%)
5	hexanes	70	5.5	86%	2.5:1:0	45%

Table 7. Solvent screen

[a] Determined by ^{1}H NMR using mesitylene as an internal standard. [b] Isolated yield reported in parentheses.

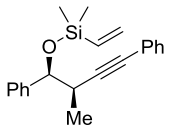
Non-polar solvents, such as hexanes, were suited to the coupling but gave a longer reaction time with decreased product yield (entry 5). Therefore, five equivalents of ethyl acrylate with 10 mol% RuHCl(CO)(H_2IMes)(PPh_3) in toluene at 80°C was established as the optimal conditions for this transformation.

In conclusion, reaction conditions were optimized for the ruthenium-hydride catalyzed *trans*-silylvinylation of alkyne **77** with ethyl acrylate. The newly formed diene was isolated in 56% yield (5.4:1 **78A**:**78B** ratio) and the resulting diene geometry was verified by NOESY NMR

analysis. With these optimized conditions in hand, broadening of the substrate scope by introduction of aryl functionality at the alkyne terminus was desired.

2.1.3 Synthesis of chiral, aryl-substituted alkyne 80

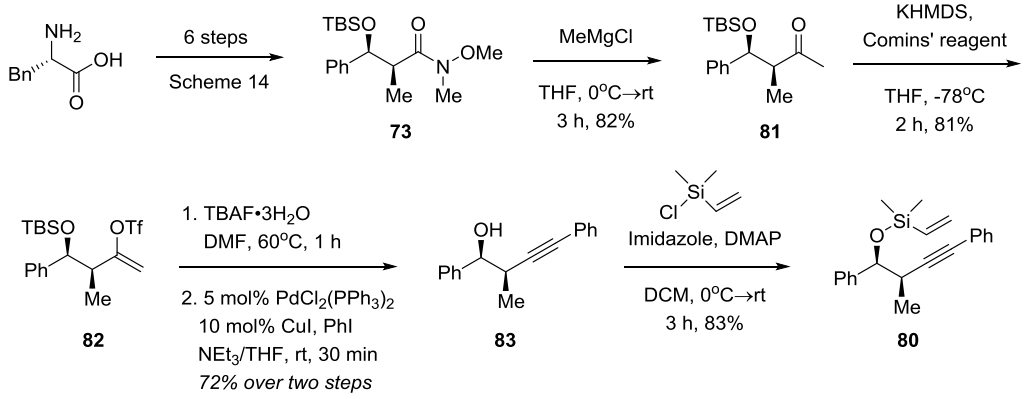
Given that multi-gram quantities of alkyne **77** was secured with relative ease, the synthesis was extended to include aromatic substitution on the alkyne terminus, such as alkyne **80** (Figure 7).



80

Figure 7. Target: phenyl-substituted alkyne 80

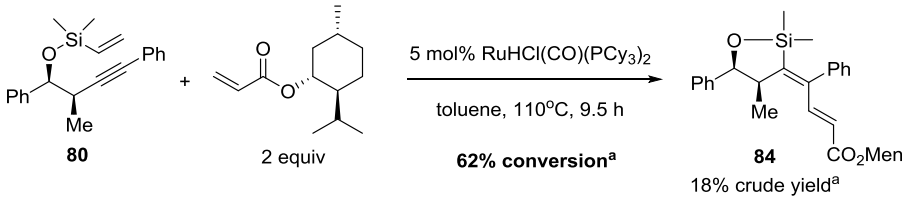
The synthetic route towards alkyne **80** began with Grignard addition into Weinreb amide **73** to give methyl ketone **81** in 82% yield (Scheme 24). Formation of enol triflate **82** proceeded uneventfully in a good yield of 81% and elimination with TBAF·$3H_2O$ gave the terminal alkyne, which was subjected crude to a Sonogashira coupling with iodobenzene to give phenyl-substituted alkyne **83** in 72% yield over two steps. Lastly, silylation with vinyldimethylchlorosilane gave silicon-tethered alkyne **80** in 83% yield. Multi-gram quantities of an enantiopure phenyl-substituted silicon-tethered alkyne possessing substitution at the propargylic position was synthesized in 11 linear steps from L-phenylalanine with an overall yield of 15%.



Scheme 24. Synthesis of alkyne 80

2.1.4 Exploration of alkyne 80 with the coupling of acrylates

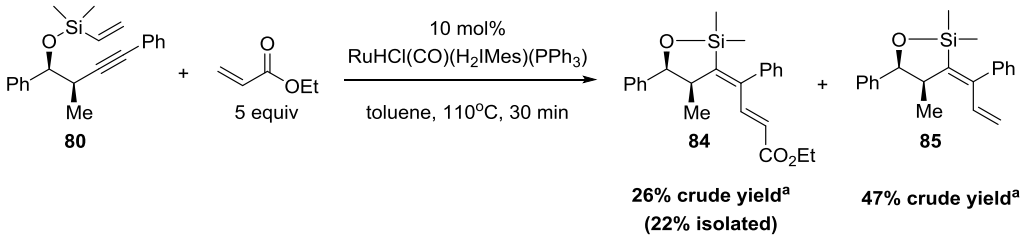
Initially, investigations began with the conditions for aryl-substituted alkynes that were previously established by the Clark group: 5 mol% $RuHCl(CO)(PCy_3)_2$, 2 equivalents of L-menthyl acrylate, toluene, reflux (Scheme 25); however, these conditions gave 62% conversion 62% of alkyne **80** with low crude yield (18%) of diene **84** after 9.5 hours.



Scheme 25. Initial studies of alkyne 80

[a] Determined by ^1H NMR using mesitylene as an internal standard.

Displeased with this result, it was questioned whether propargylic substitution was a hindrance to product formation. Since the previously developed methodology for phenyl-substituted alkynes was not successful in this case, the conditions that gave success with propargylic substituted methyl alkyne **77** were utilized (Scheme 26).



Scheme 26. Unexpected product formation

[a] Determined by ^{1}H NMR using mesitylene as an internal standard.

Alkyne **80** was subjected to 10 mol% $RuHCl(CO)(H_2IMes)(PPh_3)$ with 5 equivalents of ethyl acrylate in refluxing toluene. After 30 minutes, 100% conversion was achieved; unexpectedly diene **85** was the major product formed in the transformation. The formation of diene **85** was attributed from the loss and subsequent re-insertion of ethylene instead of acrylate incorporation. However, the acrylate incorporated diene **84** was obtained as a minor component in the reaction. Despite being able to isolate 22% of **84** as one isomer, we chose not to pursue further avenues for the coupling of alkyne **80** with acrylates.

2.1.5 Conclusion

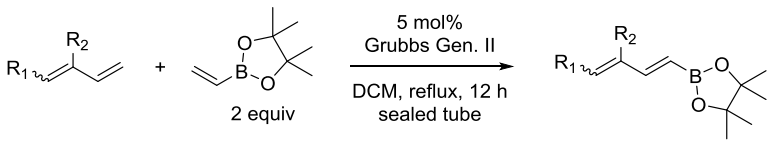
Synthetic routes were designed and optimized for chiral alkynes **77** and **80** in 10 and 11 linear steps, respectively. Such alkynes possess propargylic functionality and contain methyl and phenyl substitution at the alkyne terminus. Their synthetic applicability was demonstrated with the Clark group's previously established ruthenium hydride catalyzed *trans*-silylvinylation conditions.

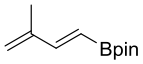
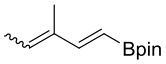
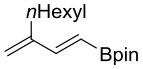
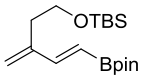
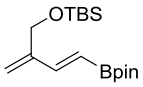
2.2 *TRANS*-SILYLVINYLATION OF ALKYNES WITH VINYL BORONATES

2.2.1 Introduction

Vinyl boronates[55-58] have played an important role as intermediates in coupling reactions that are utilized in the syntheses of highly functionalized scaffolds and complex natural products.[20, 22, 59] Specifically, silyl-dienyl boronates are of particular interest due to silicon and boron being versatile functional handles for selective functional group manipulation. Well-known methods of doing so include Suzuki-Miyaura coupling,[60, 61] Heck reaction,[62, 63] Hiyama-Denmark reaction[64] and Tamao oxidation.[65]

The use of vinyl boronates for the synthesis of dienyl boronates has been reported, one example being via cross metathesis (Table 8). Grubbs *et al.* coupled various dienes with an excess of vinyl pinacol boronate and 5 mol% Grubbs Gen. II catalyst.[66] The resulting substituted dienyl boronates were isolated in fair to good yields of 40%-80%.



Entry	Dienyl Boronate	Yield
1		48%
2		80%
3		73%
4		69%
5		~40%

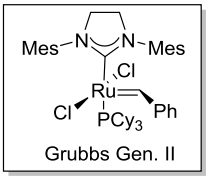
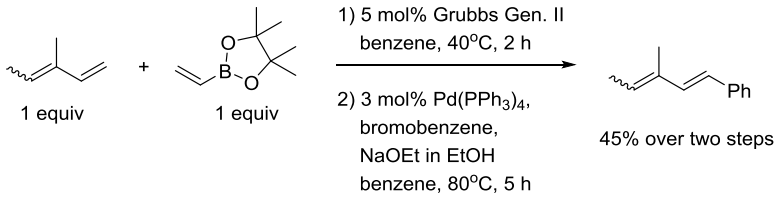


Table 8. Synthesis of dienyl boronates via cross metathesis

The utility of the dienyl boronates reported by this process was demonstrated via a one-pot cross metathesis/Suzuki coupling (Scheme 27).



Scheme 27. One-pot cross metathesis/Suzuki coupling

Despite the synthetic utility of the dienyl boronates, one drawback to the cross metathesis methodology is the requirement of synthesizing the diene precursor prior to the

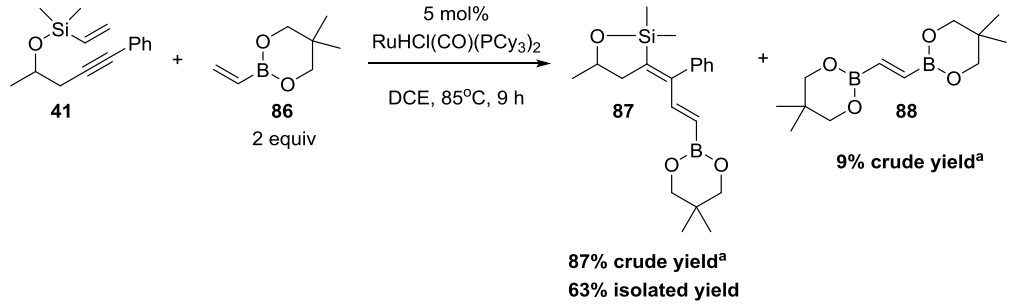
coupling/installment of the boronate moiety. In addition, some of the diene precursors are volatile, hence resulting in difficulty of handling.

As mentioned in chapter 1 (see Table 1), Marciniec reported on the synthesis of silyl-dienyl boronates via the ruthenium catalyzed coupling of silyl-acetylenes with vinyl boronates.[20] Despite the fact that bi-functional dienes were formed from this transformation, stereocontrol was problematic and alkyne dimerization was observed. In addition, the study was limited to use of terminal alkynes, limiting the substitution of the silyl-dienyl boronates.

With that being said, extension of the Clark group's previous methodology[26] to include vinyl boronate coupling partners was sought after. Such an extension of the olefin coupling partner would allow for the formation of a more diverse and synthetically useful silyl-dienyl boronate scaffold. Also, the approach produces *Z,E*-diene systems, which pose as a challenge to obtain despite their prevalence in nature.[67-69]

2.2.2 Initial investigations

We began our studies using alkyne **41**[26] and vinyl boronate **86** with the conditions previously established for our acrylate coupling (Scheme 28). Full conversion of the starting alkyne **41** was achieved after 9 hours. Upon ^{1}H NMR analysis, an 87% crude yield of desired silyl-dienyl boronate **87** was observed. The only observable by-product of the reaction was the boronate dimer **88**. A substantial loss of product yield was observed after isolation of **87** via column chromatography. This was believed to be due to hydrolysis of the product upon exposure to silica gel.



Scheme 28. Initial studies of the vinyl boronate coupling

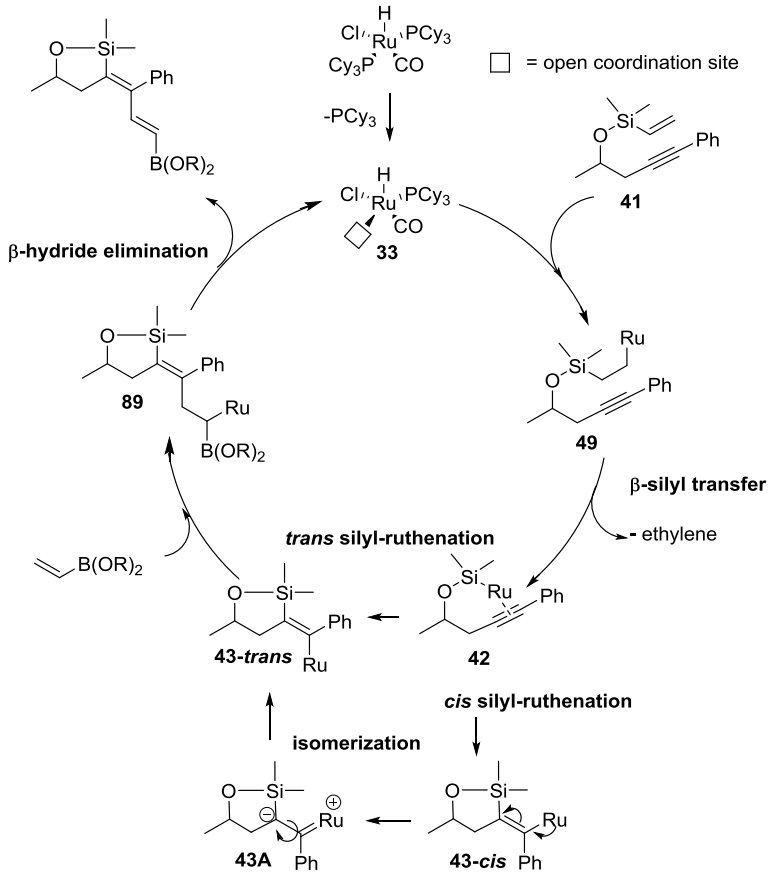
[a] Determined by ^{1}H NMR using mesitylene as an internal standard.

Deactivation of the silica gel by treatment with triethylamine, trimethylchlorosilane and boric acid[70] gave no improvement of isolated yield. Another minor setback was the difficulty of separating the boronate dimer from the product.

2.2.3 Mechanistic hypothesis[71]

The aforementioned transformation is believed to proceed as follows (Scheme 29): Dissociation of a phosphine ligand from $RuHCl(CO)(PCy_3)_2$ gives a highly reactive 14-electron ruthenium complex **33**, which upon reaction with the silicon-tethered alkyne **41**, adds at the sterically most accessible (terminal) position of the vinyl moiety to give intermediate **49**. β-Silyl transfer and subsequent loss of ethylene[28] results in formation of silyl-ruthenium intermediate **42**. The transformation from **42** to **43** can proceed via direct *trans* silyl-ruthenation (see section 1.2.3 for literature precedence) or by a *cis* silyl-ruthenation pathway to give intermediate **43-*cis*** followed by isomerization to generate **43-*trans***. The isomerization is proposed to proceed via a vinylidene-type intermediate **43A** (favorable due to the charge stability by the silicon atom).

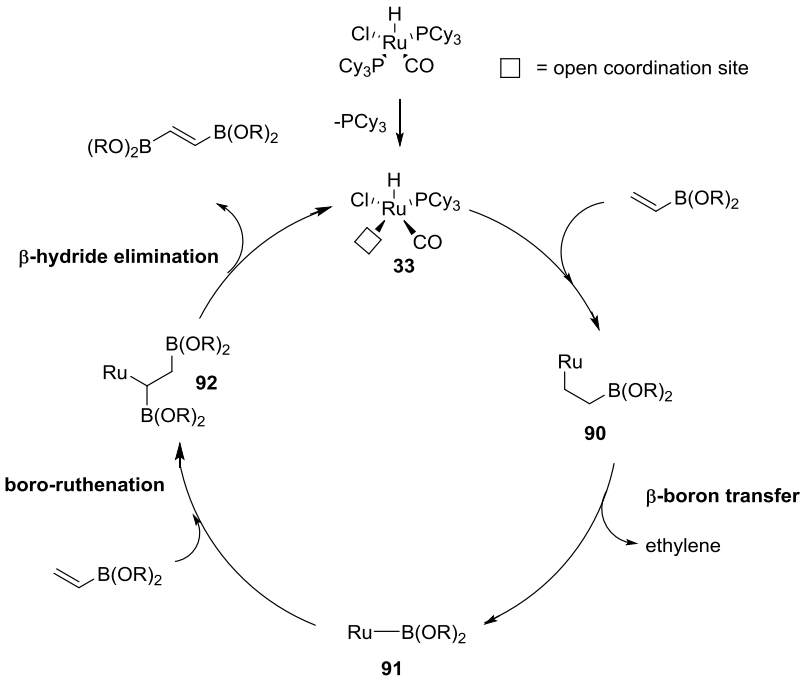
Intermolecular olefin insertion (vinyl boronate) at the most sterically accessible position of the alkene yields **89**, which subsequently undergoes β-hydride elimination to give the desired silyl-dienyl boronate. Upon formation of the product, ruthenium hydride complex **33** is regenerated.



Scheme 29. Mechanistic hypothesis

Boronate dimer formation can be attributed as follows (Scheme 30): Dissociation of a phosphine ligand from $RuHCl(CO)(PCy_3)_2$ generates a highly reactive 14-electron ruthenium complex **33**, which upon introduction with the vinyl boronate, adds at the most sterically accessible (terminal) position to give intermediate **90**. β-Boron transfer and the resulting loss of

ethylene generates boro-ruthenium intermediate **91**. Upon introduction of another molecule of vinyl boronate, boro-ruthenation of **91** occurs to generate bis-borylated species **92**. Subsequent β-hydride elimination of **92** yields the vinyl boronate dimer, upon which ruthenium intermediate **33** is regenerated.

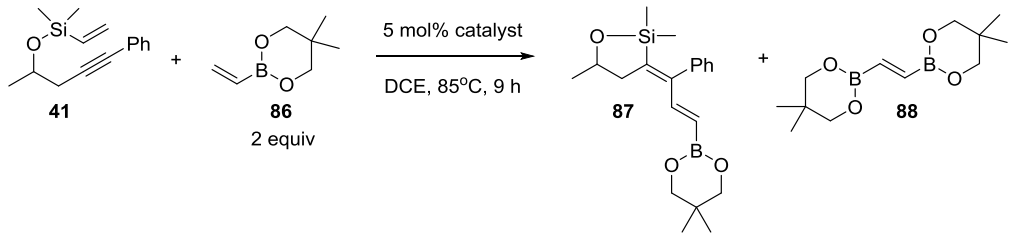


Scheme 30. Mechanistic hypothesis for vinyl boronate dimer formation

2.2.4 Reaction optimization

Further optimization of the reaction was performed to increase the crude yield of product and suppress the boronate dimer formation. A catalyst screen was conducted (Table 9), beginning with some of the previously explored ruthenium hydrides. Ruthenium complex RuHCl(CO)(P*t*Bu$_2$Me)$_2$ gave only 55% crude yield of product after 9 hours with a substantially

higher amount of dimer (entry 1). Switching to the tri-isopropylphosphine complex RuHCl(CO)(P*i*Pr$_3$)$_2$ resulted in 69% crude yield of product and only 4% crude yield of dimer (entry 2), however, the crude yield was not comparable to what was initially observed with RuHCl(CO)(PCy$_3$)$_2$.



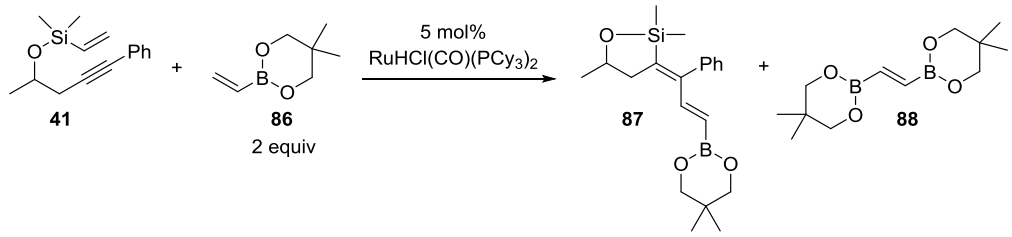
Entry	Catalyst	Crude Yield[a] of 87	Crude Yield[a] of 88
1[b]	RuHCl(CO)(P*t*Bu$_2$Me)$_2$	55%	14%
2[b]	RuHCl(CO)(P*i*Pr$_3$)$_2$	69%	4%
3[c]	RuHCl(CO)(H$_2$IMes)(PPh$_3$)	23%	12%
4	RuHCl(CO)(PAd$_2$*n*Bu)$_2$	N/D	32%
5[b,d]	RuH(OSiPh$_3$)(CO)(P*t*Bu$_2$Me)$_2$	17%	0%

Table 9. Catalyst screen with vinyl boronate 86

[a] Determined by ^{1}H NMR using mesitylene as an internal standard. [b] Starting material observed after 9 hours. [c] Reaction complete after 2 hours. [d] Reaction run by Robert Wilson.

The NHC-complex RuHCl(CO)(H$_2$IMes)(PPh$_3$) gave rapid conversion of the alkyne in 2 hours but poor product yield was observed (entry 3). The bulkier bis-adamantyl-*n*-butylphosphine complex RuHCl(CO)(PAd$_2$*n*Bu)$_2$[72] gave a large amount of boronate dimer (entry 4); poor conversion and poor product yield (17%) was observed with RuH(OSiPh$_3$)(CO)(P*t*Bu$_2$Me)$_2$[73] (entry 5).

With ruthenium hydride $RuHCl(CO)(PCy_3)_2$ being the optimal catalyst for the transformation, a solvent screen was conducted (Table 10). The use of DCE at decreased reaction temperatures was envisioned to circumvent dimer formation (entries 1 and 2); indeed, a decreased amount of dimer was observed but reaction conversion and product yield were sacrificed. Toluene at 85°C gave a shorter reaction time and less dimer was observed but the product yield was reduced (entry 3). Refluxing trifluorotoluene resulted in poor conversion and product yield after 9 hours (entry 4). Exchange for 1,4-dioxane gave similar results to toluene (entry 5) and refluxing THF resulted in no dimer formation albeit decreased product yield (64%) after 9 hours (entry 6).



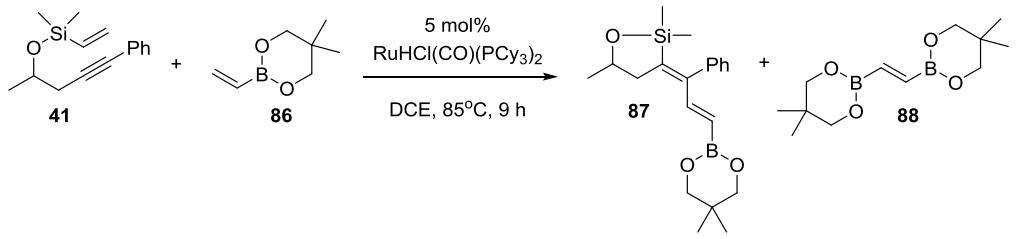
Entry	Solvent	Temp. (°C)	Time (h)	Crude Yield[a,d] of 87	Crude Yield[a] of 88
1[b,c]	DCE	70	15	65%	2%
2[b,c]	DCE	60	15	53%	1%
3	toluene	85	5.5	72% (53%)	1%
4[b,c]	CF_3Ph	105	9	45%	0
5	1,4-dioxane	85	5.5	78% (59%)	3%
6[b]	THF	70	9	64%	0
7[b,c]	DCM	45	7	27%	0
8	MeCN	70	9	NR	NR
9[c]	DMF	105	9	NR	NR

Table 10. Solvent screen with vinyl boronate 86

[a] Determined by ^1H NMR using mesitylene as an internal standard. [b] Starting material observed after designated reaction time. [c] Reaction run by Robert Wilson. [d] Isolated yield reported in parenthesis.

The lower boiling solvent DCM proved detrimental to reaction conversion and product yield (entry 7). No reactivity was observed with acetonitrile, possibly due to solvent coordination to the metal (entry 8). Additionally, no reaction occurred in DMF at 105°C (entry 9).

With these results in hand, complex $RuHCl(CO)(PCy_3)_2$ in DCE at 85°C was chosen as the optimal catalyst, solvent and temperature for the coupling with vinyl boronate **86**. Lastly, the equivalents of the vinyl boronate was varied to observe the effect on dimer formation (Table 11). Decreasing the amount of vinyl boronate from 2 equivalents (entry 3) to 1.5 equivalents (entry 2) had a significant effect on the reaction. Full conversion of the starting material was not achieved after 9 hours and the crude product yield decreased by 20%. However, as expected, the amount of dimer decreased from 9% to 3%. Further decrease of boronate to 1.2 equivalents (entry 1) gave similar results as entry 2.

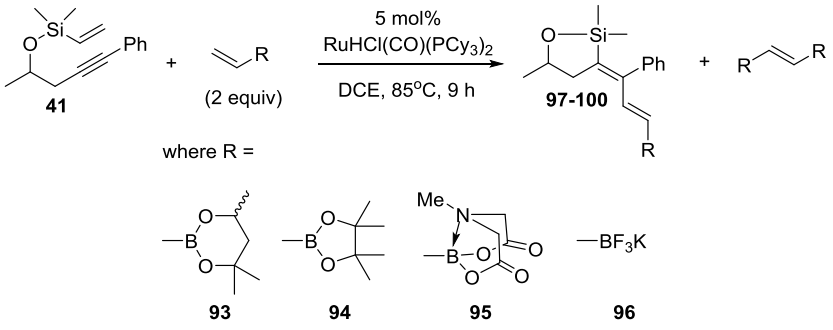


Entry	Equiv of 86	Crude Yield[a] of 87	Crude Yield[a] of 88
1[b]	1.2	63%	2%
2[b]	1.5	66%	3%
3	2	87%	9%

Table 11. Variation of equivalents of 86

[a] Determined by ^1H NMR using mesitylene as an internal standard. [b] Starting material observed after 9 hours.

After numerous attempts to improve the crude yield of **87** and decrease the amount of dimer **88**, new vinyl boronate coupling partners were explored (Table 12). Beginning with vinyl boronate **93**, which was easily prepared on multi-gram scale according to the literature protocol,[74] a 75% crude yield of product **97** and 5% boronate dimer was observed under standard reaction conditions (entry 1). We were surprised to discover that there was no observable impact on characterization (by ^{1}H NMR and ^{13}C NMR) of **97** despite a total of four stereoisomers being present. However, substantial loss of **97** was observed upon exposure to silica gel and only 55% isolated material was obtained. Despite this minor setback, the boronate dimer was easier to visualize by thin layer chromatography and therefore less of a challenge to separate compared to dimer **88**. Pinacol boronate **94**, an easy to prepare but highly volatile and readily polymerizable compound, gave a slightly lower crude yield of product **98** but with comparable isolated yield (entry 2).[74] The MIDA boronate **95**[75] and potassium trifluoroborate salt **96**,[76] both air stable solids, were unreactive in the chemistry (entries 3 and 4). Based on these results, vinyl boronate **93** was the most successful.



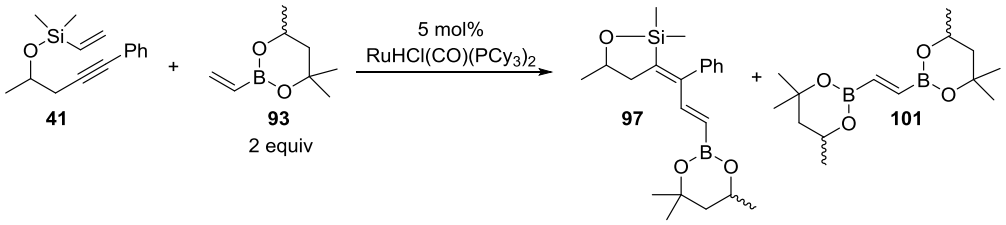
Entry	Vinyl Boronate[a]	Crude Yield[b,c] of Product	Crude Yield[b] of Dimer
1	**93**	75% (55%)	5%
2[d]	**94**	70% (55%)	ND
3[d]	**95**	NR	NR
4[d]	**96**	NR	NR

Table 12. Vinyl boronate scope

[a] All vinyl boronates made by Robert Wilson. [b] Determined by ^{1}H NMR using mesitylene as an internal standard.

[c] Isolated yield reported in parentheses. [d] Reaction run by Robert Wilson.

For the purpose of minimizing dimer formation, a solvent screen was conducted (Table 13). Reactions run in DCE, toluene and 1,4-dioxane worked well at 85°C (entries 1-3). Raising the temperature resulted in a shorter reaction time albeit increase in dimer formation (entry 3). Lowering the temperature to 70°C resulted in longer reaction times and decreased the amount of both product and dimer (entry 4). Refluxing THF compromised reaction conversion and yield of product (entry 6), and a poor crude yield of product was observed in refluxing DCM (entry 7). No reactivity was observed in acetonitrile (entry 8). Toluene at 85°C proved optimal for the reaction (entry 2) due to a shorter reaction time and minimal formation of dimer.

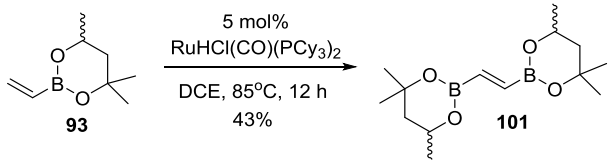


Entry	Solvent	Temp. (°C)	Time (h)	Crude Yield[a] of 97	Crude Yield[a] of 101
1	DCE	85	5	75%	5%
2	toluene	85	3.5	75%	3%
3[b]	toluene	100	3	78%	5%
4[b,c]	toluene	70	7	63%	1%
5	1,4-dioxane	85	4	67%	3%
6[c]	THF	70	7	58%	0
7[c]	DCM	45	7	27%	0
8[c]	MeCN	70	7	N/R	N/R

Table 13. Solvent screen with boronate 93

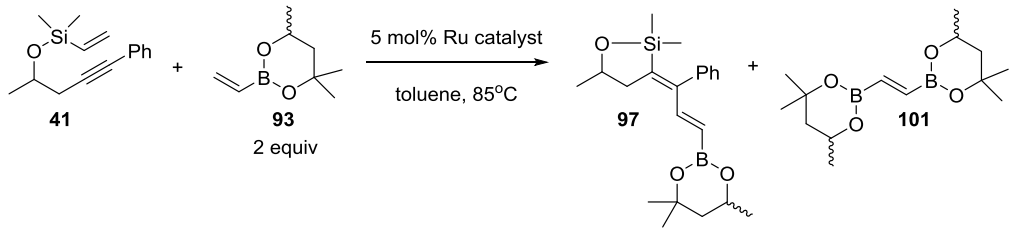
[a] Determined by ^{1}H NMR using mesitylene as an internal standard. [b] Reaction run by Robert Wilson. [c] Starting material observed after designated reaction time.

The boronate dimer **101** was independently synthesized using the optimized conditions to verify its formation (Scheme 31). One equivalent of vinyl boronate **93** with 5 mol% $RuHCl(CO)(PCy_3)_2$ in refluxing DCE gave a pale brown air stable solid **101** upon purification via column chromatography.



Scheme 31. Synthesis of boronate dimer

Additional ruthenium hydrides were also examined (Table 14). Ruthenium complex $RuHCl(CO)(PCy_3)_2$ proved to be most suitable for the coupling with vinyl boronate **93**, allowing for a short reaction time, good yield of product and minimal dimer formation (entry 1).



Entry	Catalyst	Time (h)	Crude Yield[a] of 97	Crude Yield[a] of 101
1	$RuHCl(CO)(PCy_3)_2$	3.5	75%	3%
2[b]	$RuHCl(CO)(PtBu_2Me)_2$	5	67%	10%
3[c]	$RuHCl(CO)(PiPr_3)_2$	8	72%	4%
4	$RuHCl(CO)(PtBu_2Cy)_2$	2	61%	11%
5[c]	$RuHCl(CO)(PCy_2tBu)_2$	8	60%	6%
6[b,c]	$RuHCl(CO)(PiPr_2[3,5\text{-}CF_3C_6H_3])_2$	8	15%	0

Table 14. Catalyst screen with boronate 93

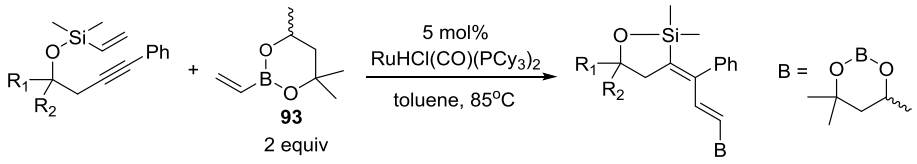
[a] Determined by ^1H NMR using mesitylene as an internal standard. [b] Reaction run by Robert Wilson. [c] Starting material observed after 8 hours.

Electron-rich ruthenium hydride complex $RuHCl(CO)(PtBu_2Me)_2$ catalyzed the transformation in a reasonable time (5 hours) but product yield was compromised and the amount of dimer increased (entry 2). Complex $RuHCl(CO)(PiPr_3)_2$ gave good product yield but required a longer reaction time of 8 hours (entry 3). Ruthenium complexes $RuHCl(CO)(PtBu_2Cy)_2$ and $RuHCl(CO)(PCy_2tBu)_2$, developed by the Clark group, catalyzed the transformation but yield was compromised and increased dimer formation was observed (entries 4 and 5). Lastly, complex $RuHCl(CO)(PiPr_2[3,5\text{-}CF_3C_6H_3])_2$,[16] bearing electron-deficient phosphine ligands,

exhibited poor reactivity and only 15% product was observed after 8 hours. After significant optimization, 5 mol% $RuHCl(CO)(PCy_3)_2$ with 2 equivalents of vinyl boronate **93** in toluene (0.5M in alkyne) at 85°C was adopted as the standard conditions for the reaction.

2.2.5 Substrate scope for vinyl boronate 93

The substrate scope was explored using the aforementioned optimized conditions for vinyl boronate **93**. We began by varying the substitution at the homopropargylic position (Table 15). Alkyl substitution at R_1 was well tolerated (entries 1-4) with isolated yields of 55%-60%. A biphenyl moiety worked well (entry 5) in the coupling with a 60% isolated yield obtained. A substrate bearing geminal substitution also worked well (entry 6), presumably due to the Thorpe-Ingold effect.[39] NOESY NMR analysis of dienyl-silyl boronates **97** and **104** verified the *Z,E* olefin geometry.



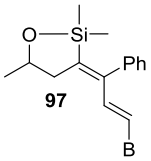
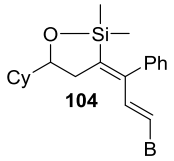
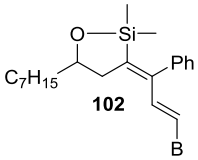
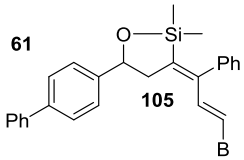
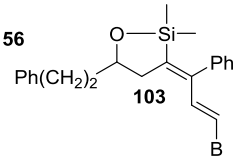
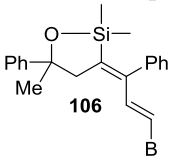
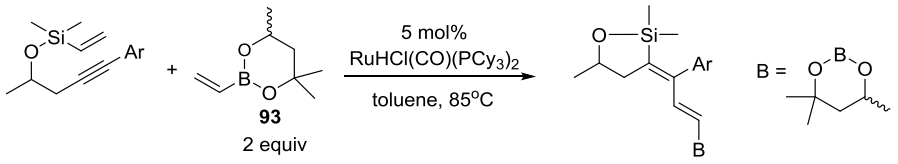
Entry	Alkyne	Product	Yield	Entry	Alkyne	Product	Yield
1	**41**	 **97**	55%	4	**57**	 **104**	60%
2	**55**	 **102**	60%	5	**61**	 **105**	57%
3	**56**	 **103**	58%	6	**62**	 **106**	55%

Table 15. Substrate scope for phenyl-substituted alkynes

Aryl groups at the alkyne terminus also worked well in the reaction (Table 16). Toluene-bearing and the 3,5-xylyl moiety gave the desired products **107** and **108** in good yields (entries 1 and 2).



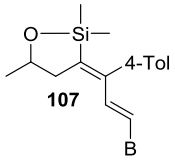
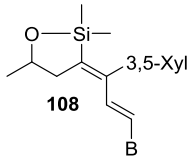
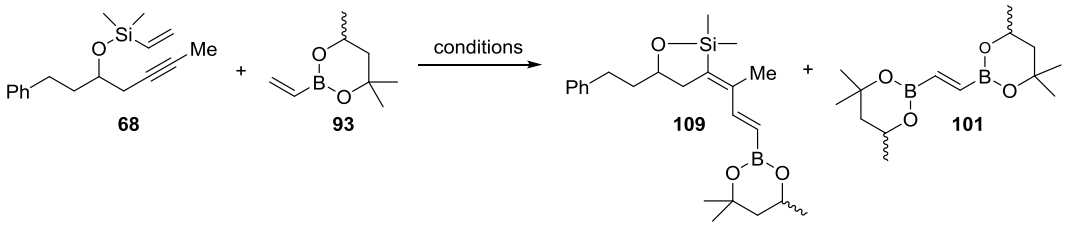
Entry	Alkyne	Product	Yield
1	**66**	 **107**	55%
2	**67**	 **108**	57%

Table 16. Substrate scope for aryl-substituted alkynes

In hopes of extending the substrate scope to include alkyl functionality on the alkyne terminus, the reactivity of alkyne **68** was explored (Table 17). Initially, the standard reaction conditions were used (entry 1), resulting in 100% conversion of starting material but only 38% crude yield (30% isolated yield) of product **109**. The catalyst loading was doubled to 20 mol% (entry 2), which in turn shortened the reaction time to 3 hours with no improvement in product yield. In hopes of increasing the crude yield of product, changes in the equivalents of vinyl boronate were explored. Three equivalents of vinyl boronate significantly improved the crude yield to 50%, however, a significant amount of boronate dimer was formed (entry 3). Further increase of the vinyl boronate to 5 equivalents did not improve product yield, but the amount of dimer doubled to 25% (entry 4). This development was problematic due to the difficulty of separating the product from the boronate dimer.



Entry	Catalyst (mol%)	Equiv of 93	Solvent	Temp (°C)	Time (h)	Crude Yield[a,b] of 109	Crude Yield[a] of 101
1	$RuHCl(CO)(PCy_3)_2$ (10)	2	toluene	85	5	38% (30%)	4%
2	$RuHCl(CO)(PCy_3)_2$ (20)	2	toluene	85	3	34%	5%
3	$RuHCl(CO)(PCy_3)_2$ (10)	3	toluene	85	5	50%	12%
4	$RuHCl(CO)(PCy_3)_2$ (10)	5	toluene	85	6	47%	25%
5	$RuHCl(CO)(PCy_3)_2$ (5)	5	toluene	85	24	40%	13%
6	$RuHCl(CO)(PCy_3)_2$ (10)	1.5	toluene	85	8	27%	2%
7	$RuHCl(CO)(PCy_3)_2$ (10)	2	THF	70	22	30%	2%
8	$RuHCl(CO)(PCy_3)_2$ (20)	2	THF	70	20	22%	3%
9[c]	$RuHCl(CO)(PtBu_2Me)_2$ (5)	2	THF	70	18	9%	0
10	$RuHCl(CO)(PtBu_2Cy)_2$ (5)	2	THF	70	3	20%	0
11	$RuHCl(CO)(PCy_3)_2$ (10)	2	1,4-Dioxane	85	7	32%	3%
12	$RuHCl(CO)(PCy_3)_2$ (20)	2	1,4-Dioxane	85	3	34%	4%

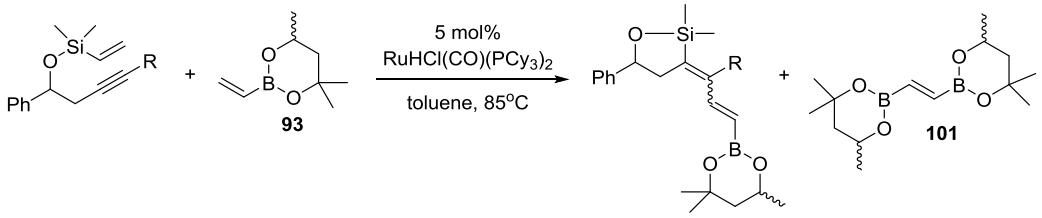
Table 17. Alkyl substrate reaction optimization

[a] Determined by ^1H NMR using mesitylene as an internal standard. [b] Isolated yield reported in parentheses. [c] Starting material observed after 18 hours.

Decreasing the catalyst loading to 5 mol% with 5 equivalents of vinyl boronate significantly reduced the amount of dimer formation (13%), but the reaction was not complete after 24 hours (entry 5). Decrease of the vinyl boronate to 1.5 equivalents resulted in only 2% dimer albeit compromised product yield was observed (entry 6). Based on the preliminary solvent screen in Table 12, THF was examined for the transformation. During the initial solvent screen, THF was sluggish for the coupling but gave the product without any formation of boronate dimer (Table 13, entry 6). In the case for alkyl-substituted alkyne **68**, THF allowed for minimal dimer formation (2%) and only 30% crude yield of **109** was observed after 22 hours (entry 7). Despite minimal dimer formation, a low crude yield was a setback due to the instability of the product on

silica gel. Increasing the catalyst loading to 20 mol% slightly improved reaction conversion after 22 hours but was detrimental to product yield (entry 8). Additional ruthenium catalysts were explored with THF but poor reactivity was observed (entries 9 and 10). Also, based on results from the preliminary solvent screen, 1,4-dioxane was briefly examined. Only a small amount of dimer (3%-4%) was observed in 1,4-dioxane at 85°C but poor crude yields of product (32%-34%) were obtained (entries 11 and 12). After considerable optimization, 10 mol% $RuHCl(CO)(PCy_3)_2$ with 3 equivalents of vinyl boronate **93** in toluene at 85°C was found to be superior for the transformation with alkyne **68** (entry 3) giving a 50% crude yield of **109** after 5 hours.

Additional alkyl-substituted alkynes were next examined in the coupling (Table 18). Poor reactivity and crude yield of product were observed with methyl- and ethyl-substituted alkynes **110** and **111** bearing a phenyl group at the homopropargylic position.



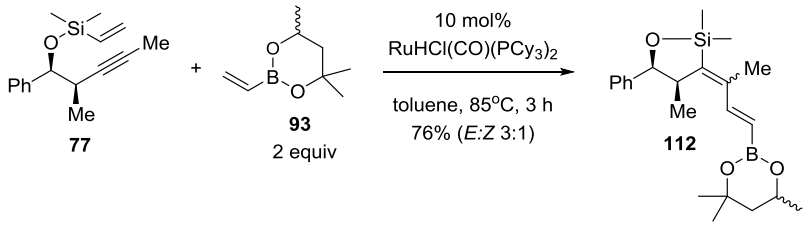
Entry	Alkyne	R	Catalyst Mol%	Equiv of 93	Time (h)	Crude Yield[a] of Product	Crude Yield[a] of 101
1	**110**	Me	10	2	8	31% (4:1)	2%
2[b]	**110**	Me	5	2.5	24	15%	4%
3	**111**	Et	10	2	5	18% (5:1)	2%
4	**111**	Et	5	2.5	7	23%	3%

Table 18. Other alkyl-substituted alkyne substrates

[a] Determined by ^1H NMR using mesitylene as an internal standard. [b] Starting material observed after 24 hours.

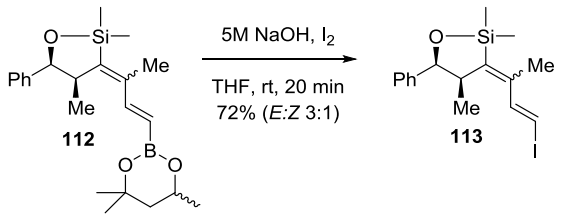
Varying the catalyst loading improved reaction time but product yield varied by substrate. Increasing the catalyst loading for the methyl-substituted alkyne significantly improved the crude product yield from 15% to 31% (entries 1 and 2), however, a *Z:E* isomeric mixture of products was observed. In regards to the ethyl-substituted alkyne (entries 3 and 4), increase of the catalyst loading was detrimental to product yield and an *Z:E* isomeric mixture was also observed. No further optimization of these substrates was performed.

The substrate scope tolerance for propargylic substitution was also investigated. Previously synthesized alkyl-substituted alkyne **77** was subjected to 10 mol% $RuHCl(CO)(PCy_3)_2$ with 2 equivalents of vinyl boronate **93** in toluene at 85°C (Scheme 32).



Scheme 32. Reactivity of alkyne 3 with vinyl boronate 93

After 3 hours 100% conversion of alkyne **77** was observed and a 76% isolated yield of **112** (3:1 *E:Z*) was obtained. It was concluded that further optimization was not necessary for alkyne **77** in the transformation. The resulting silyl-dienyl boronate **112** was subjected to iodo-deboration[77] to verify that the isomers observed from the coupling were stereoisomers and not diastereomers stemming from the vinyl boronate moiety (Scheme 33).

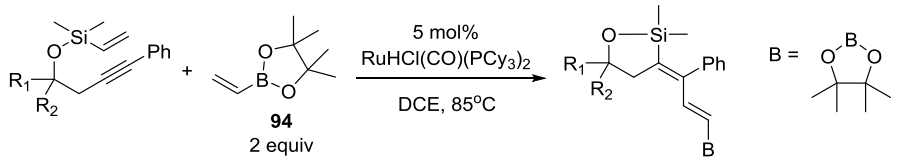


Scheme 33. Confirmation of isomeric mixture by iodo-deboration

The resulting silyl-dienyl iodide **113** was isolated in 72% yield and two isomers were observed by ^{1}H NMR in a 3:1 ratio, therefore confirming stereochemical relationship of isomers from the vinyl boronate coupling.

2.2.6 Substrate scope for vinyl boronate 94

Since isolated yields of below 70% were observed for all but one substrate with vinyl boronate **93**, a few substrates were inspected using pinacol boronate **94** (Table 19). These substrates did not give as high a crude yield as when vinyl boronate **93** was used but a majority of the dienes were more stable to isolation with little product loss. In entry 1, the isolated yield of **114** was identical to that of **97** despite a different vinyl boronate used. A significant increase in isolated yield (17%) was observed with alkyne **62** (entry 2); however, a few substrates that were scrutinized gave conflicting results. The cyclohexane-substituted diene **116** (entry 3) gave a poor crude yield of 46% (in comparison to a 60% isolated yield of **104**) so no attempts were made for isolation of **116**. In addition, the *para*-nitro phenyl-substituted diene **117** was isolated in only 49% yield (entry 4). To conclude, the vinyl pinacol boronate **94** was utilized with some of the previously screened alkyne substrates to obtain improved isolated yields of products.



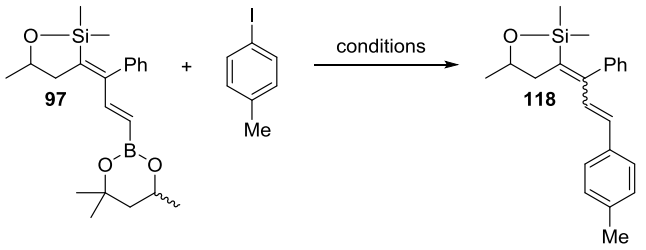
Entry	Alkyne	Product	Yield[a]	Entry	Alkyne	Product	Yield[a]
1[b]	**41**	**114**	(55%)	3	**57**	**116**	46%
2[b]	**62**	**115**	76% (72%)	4	**60**	**117**	65% (49%)

Table 19. Vinyl pinacol boronate 94 substrate scope

[a] Isolated yield reported in parentheses. Crude yield determined by ^{1}H NMR using mesitylene as an internal standard. [b] Reaction run by Robert Wilson.

2.2.7 Synthetic elaboration of silyl-dienyl boronates

Once coupling conditions were optimized and substrate scope determined for vinyl boronates **93** and **94**, demonstration of the synthetic utility of the silyl-dienyl boronates was desired. Initially, a variety of Suzuki coupling[78] conditions were explored to selectively functionalize the boronate moiety (Table 20). 4-Iodotoluene was chosen as the aryl halide due to ease of handling and storage in the glovebox. Since the aryl halide was readily available, conditions were sought after where that compound could be used in excess instead of the diene substrate. At the outset, conditions used by Whiting[79] using vinyl boronate **93** (entries 1-3) were examined. The reaction of $Pd(PPh_3)_4$ and KO*t*Bu in refluxing THF with slight excess (1.2 equivalents) of halide resulted in only 22% crude yield of product **118** (entry 1).



Entry	Equiv. of Halide	Catalyst/Ligand (mol%)	Base (Equiv.)	Solvent	Temp. (°C)	Time (h)	Crude Yield (*Z:E*)[a]
1	1.2	$Pd(PPh_3)_4$ (5)	KO*t*Bu (1.2)	THF	70	22	22% (5:1)
2[b]	1.2	$Pd(PPh_3)_4$ (5)	Ag_2O (1.2)	THF	70	22	43% (10:1)
3	1.2	$Pd(PPh_3)_4$ (5)	Ag_2O (1.2)	1,4-Dioxane	105	5	23% (1:1)
4[b]	1.2	$Pd(PPh_3)_4$ (5)	1M K_2CO_3 (1.2)	THF	50	21	26%
5[b]	1.5	$Pd(PPh_3)_4$ (5)	2M Na_2CO_3 (1.5)	THF	70	22	68% (1:1)
6[b]	1.5	$PdCl_2(PPh_3)_2$ (5)	2M Na_2CO_3 (1.5)	THF	70	22	61% (2:1)
7[b]	1.5	$Pd(PPh_3)_4$ (5)	1M K_3PO_4 (1.5)	Toluene	105	19	38% (1:1)
8[b]	1.2	$Pd(PPh_3)_4$ (5)	K_3PO_4 (1.5)	DME	85	18	64% (1:1)
9	1.2	$Pd(PPh_3)_4$ (5)	K_3PO_4 (1.5)	1,4-Dioxane	85	18	57% (1:1)
10	1.5	$Pd(OAc)_2$ (5) S-Phos (10)	55M K_3PO_4 (3)	THF	50	24	63%

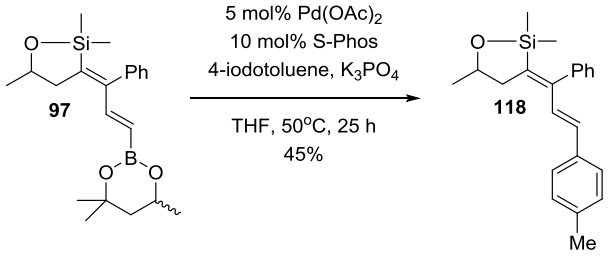
Table 20. Suzuki coupling reaction optimization

[a] Determined by crude ^{1}H NMR using mesitylene as an internal standard. [b] Starting material observed after designated reaction time.

A 5:1 ratio of *Z:E* isomers was also observed from the transformation. In hopes of improving the crude yield and minimizing additional isomer formation, the base was exchanged to silver oxide. In refluxing THF, starting material was present after 22 hours; however, the crude yield significantly increased to 43% and the isomeric ratio improved to 10:1 (entry 2). Refluxing these components in 1,4-dioxane resulted in rapid consumption of the starting material but a poor isomeric ratio of 1:1 was obtained (entry 3). After perusing several reviews,[61, 80, 81] additional conditions were screened (entries 4-9). Aqueous K_2CO_3 in THF at 50°C proved detrimental to reaction conversion but only one product isomer was observed (entry 4). A considerable crude yield of **118** (61% and 68%) was obtained with aqueous Na_2CO_3 in the presence of catalytic

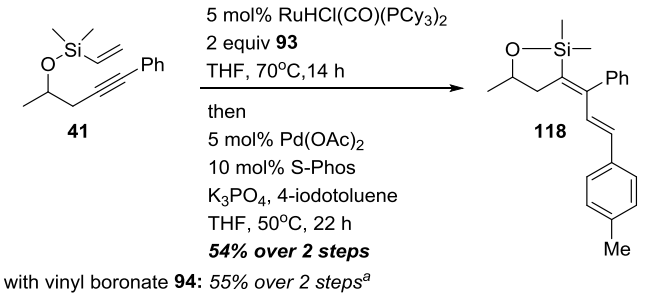
$Pd(PPh_3)_4$ (entry 5) and $PdCl_2(PPh_3)_2$ (entry 6) albeit poor isomeric ratios resulted. Aqueous K_3PO_4 in refluxing toluene gave only a 38% crude yield and a poor isomeric ratio after 19 hours (entry 7). Exchange of toluene to the more polar solvents DME and 1,4-dioxane improved product yield (64% and 57%, respectively) but the isomeric ratios remained unchanged (entries 8 and 9). When the conditions reported by Suginome *et al*[82] (5 mol% $Pd(OAc)_2$, 10 mol% *S*-Phos, 3 equivalents K_3PO_4, 3 equivalents of H_2O and 1.5 equivalents of 4-iodotoluene in THF at 50°C) were used, a 63% crude yield of **118** was obtained as a single isomer (entry 10).

Repetition of entry 10 resulted in a 45% isolated yield of diene **118** (Scheme 34).



Scheme 34. Suzuki coupling of 97 with 4-iodotoluene

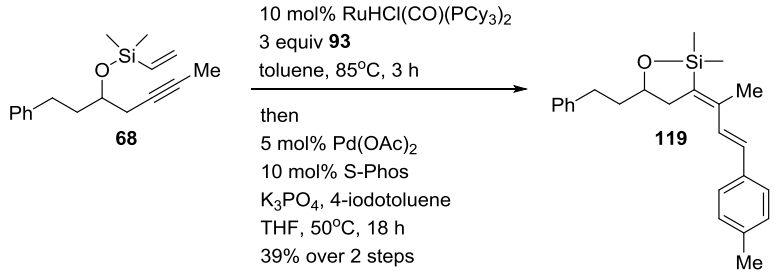
In hopes of improving overall product yield, a tandem silyl-boration of alkyne 4**1** and subsequent Suzuki coupling of **97** was performed (Scheme 35). This protocol provided diene **118** in 54% isolated yield over two steps. When these conditions were utilized with alkyne **41** and vinyl pinacol boronate **94**, diene **118** was obtained in a comparable yield of 55% over two steps (Scheme 35).



Scheme 35. Tandem silyl-boration/Suzuki coupling

[a] Reaction run by Robert Wilson.

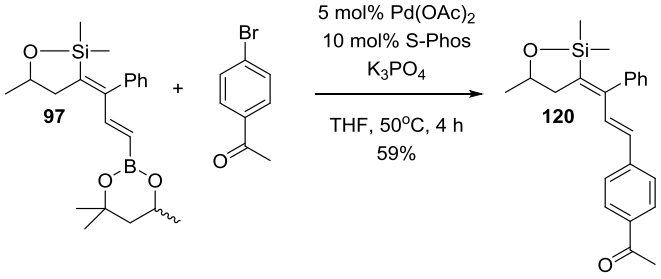
With regards to problematic alkyl-substituted alkyne **68**, the isolation difficulty of silyl-dienyl boronate **109** was circumvented by utilizing the tandem coupling/Suzuki protocol. Using the optimized vinyl boronate coupling conditions (Table 17, entry 3) and Suzuki conditions (Table 20, entry 10), diene **119** was easily separated from the boronate dimer and isolated in 39% yield over two steps (Scheme 36, *E:Z* 6:1).



Scheme 36. Tandem silyl-boration/Suzuki coupling with alkyne 68

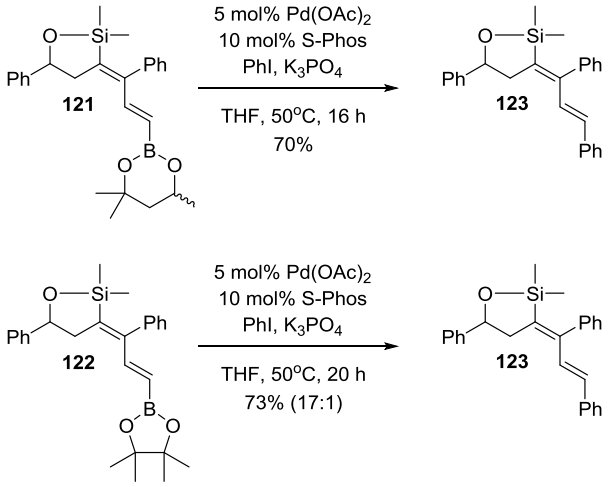
Additional aryl halide coupling partners were explored with various substrates for the Suzuki coupling. Switching to a more activated aryl halide, 4'-bromoacetophenone, was also

tolerable and gave the desired product **120** in 59% yield after 4 hours (Scheme 37).



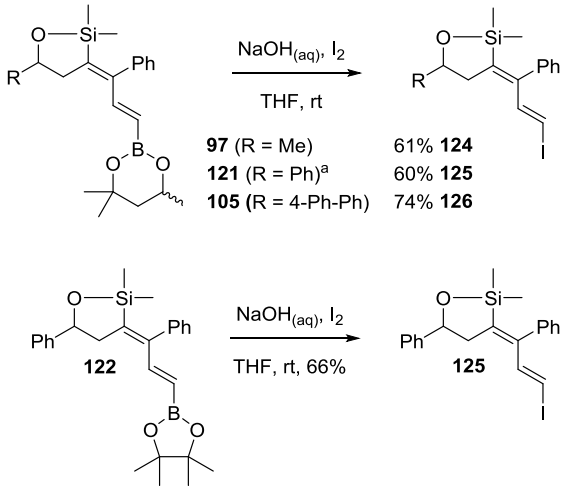
Scheme 37. Suzuki coupling with 4'-bromoacetophenone

Improved isolated yields were obtained when iodobenzene was used as the coupling partner (Scheme 38). Upon subjection of silyl-dienyl boronates **121**[71] and **122**[71] to the Suzuki conditions with iodobenzene, the resulting phenyl substituted diene **123** was isolated in 70% and 73% yields, respectively.



Scheme 38. Suzuki coupling with iodobenzene

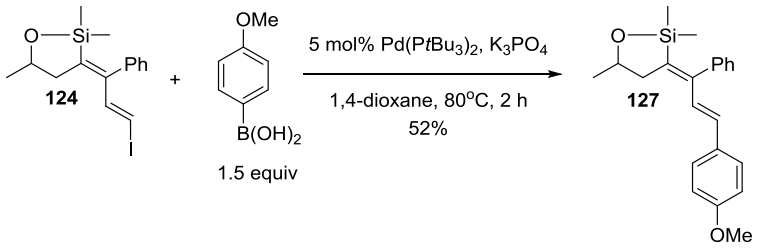
In addition to Suzuki couplings, selective functionalization of the boronate moiety was accomplished in other ways. Iodo-deboration[77] of silyl-dienyl boronates **97**, **105, 121**[71] and **122**[71] proceeded smoothly to give silyl-dienyl iodides **124-126** in good yields ranging from 60%-74% with complete retention of stereochemistry (Scheme 39).



Scheme 39. Iodo-deboration of silyl-dienyl boronates

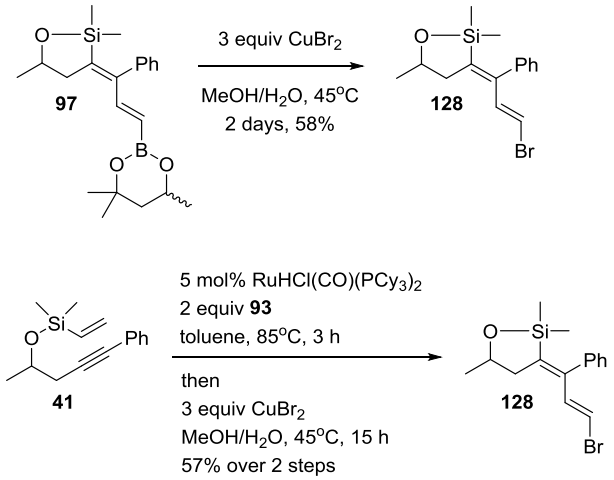
[a] Reaction run by Robert Wilson.

Formation of silyl-dienyl iodide **124** was confirmed by subjecting it in a Suzuki coupling using Fu's conditions[83] with 4-methoxyphenylboronic acid (Scheme 40). This gave the desired diene **127** in satisfactory yield as one isomer. The reaction would not proceed to yield **127** if **124** did not possess an iodide moiety.



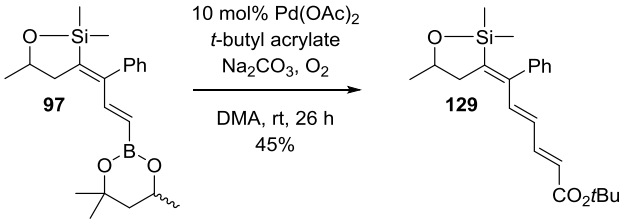
Scheme 40. Suzuki coupling with silyl-dienyl iodide 124

Bromo-deboration of silyl-dienyl boronate **97** following the conditions reported by Morken[84] and Hartwig[85] gave silyl-dienyl bromide **128** as one isomer in 58% yield (Scheme 41). In addition, suitable conditions were discovered for a tandem silyl-boration/bromo-deboration of alkyne **41** to give silyl-dienyl bromide **128** in 57% over two steps (Scheme 41). Attempts to form the *Z,Z*-dienyl bromide[77] using Br_2/NaOMe were not successful and gave unidentifiable complex mixtures.



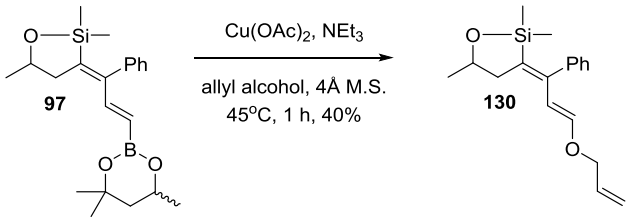
Scheme 41. Bromo-deboration and tandem silyl-boration/bromo-deboration

Another means of derivatization was conversion of silyl-dienyl boronate **97** into triene **129** via Oxidative Heck reaction (Scheme 42).[86] The resulting triene was stable to isolation via column chromatography and was obtained in 45% yield. Several attempts to improve the yield of this transformation gave no success. Surprisingly, the pinacol silyl-dienyl boronate **114** was unreactive under Oxidative Heck reaction conditions.



Scheme 42. Formation of triene 129

Lastly, boronate substrate **97** was subjected to Chan-Lam type conditions[87] using stoichiometric copper. This transformation gave allyl ether **130** in a modest 40% yield (Scheme 43). Additional attempts to improve the yield were unsuccessful.



Scheme 43. Copper-promoted etherification

2.2.8 Conclusion

In conclusion, the formation of silyl-dienyl boronates via a *trans*-silylvinylation of internal alkynes has been demonstrated. This one step regio- and stereoselective method affords bi-functional diene scaffolds in good yields. The highly substituted olefins can be transformed into more complex products by iodo- and bromo-deboration and various metal-catalyzed coupling methods. In addition, the formation of a triene was demonstrated.

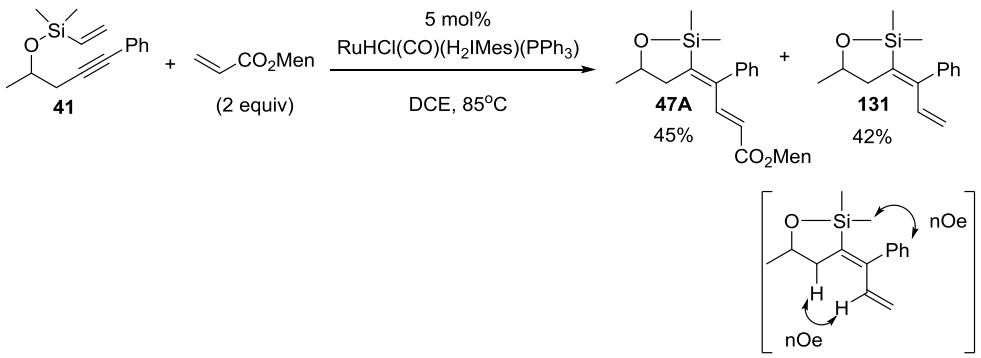
Future directions for this project would be to utilize the silyl-dienyl boronates towards the synthesis of a diene-containing natural product, an example being one from the myaxalamide family. Synthesizing a natural product would further demonstrate the synthetic applicability of the newly formed silyl-dienyl boronates.

3.0 RUTHENIUM-HYDRIDE CATALYZED *TRANS*-SILYLVINYLATION OF INTERNAL ALKYNES: EXAMINATION OF MVK ADDITIVE AND ETHYLENE ATMOSPHERE

3.1 MVK ADDITIVE[88]

3.1.1 Introduction and Reaction Discovery

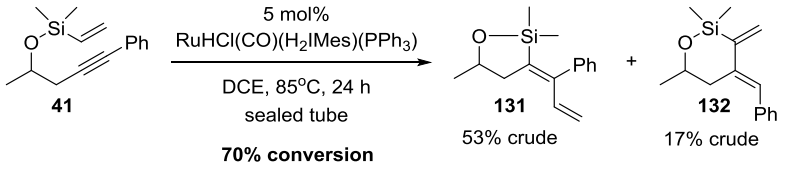
While conducting a catalyst screen for the trans-silylvinylation of internal alkynes with acrylates (see chapter 1),[26] an interesting discovery was made. In addition to the expected acrylate product **47A**, a significant amount (42%) of vinylation product **131** was observed in the presence of $RuHCl(CO)(H_2IMes)(PPh_3)$ (Scheme 44). NOE experiments later confirmed the formation and structure of **131**.



Scheme 44. Reaction discovery: unexpected formation of vinylated product[a]

[a] Reaction run by Shasha Liu and/or Jinbo Zhao.

Shortly thereafter, alkyne **41** was subjected solely to 5 mol% RuHCl(CO)(H_2IMes)(PPh_3) in refluxing DCE. After 24 hours, 70% conversion of the starting material and a 53% crude yield of diene **131** was observed. In addition, a minor by-product (17%) was also observed via ^{1}H NMR analysis of the crude reaction mixture. The minor product was assigned as cycloisomerization adduct **132** (Scheme 45).

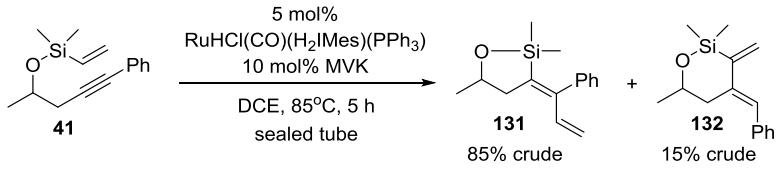


Scheme 45. Initial investigations[a]

[a] Reaction run by Shasha Liu and/or Jinbo Zhao.

3.1.2 Reaction Optimization

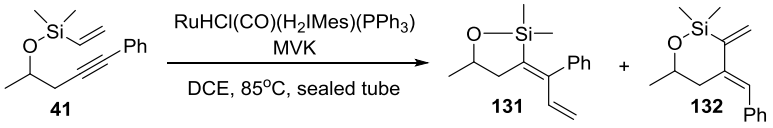
Based on these initial results, it was hypothesized that the acrylate source played an important role in the reaction. Additional electron-deficient olefinic "additives" were screened[88] and methyl vinyl ketone (MVK) proved to be superior because it provided the highest ratio of **131:132** and was easily removed from the reaction mixture (due to its volatility). Treating alkyne **41** with 5 mol% RuHCl(CO)(H_2IMes)(PPh_3) and 10 mol% MVK in refluxing DCE in a sealed tube resulted in consumption of the starting material after 5 hours. An 85% crude yield of vinylation product **131** was observed in addition to 15% of cycloisomerization product **132** (Scheme 46).



Scheme 46. *Trans*-silylvinylation of 41 with MVK additive[a]

[a] Reaction run by Shasha Liu and/or Jinbo Zhao.

The reaction was further optimized by screening the amount of RuHCl(CO)(H_2IMes)(PPh_3) in relation to MVK (Table 21). With 5 mol% RuHCl(CO)(H_2IMes)(PPh_3), decreasing the amount of MVK from 10 mol% to 5 mol% (entry 2, 1:1 ratio) gave 55% crude yield of **131** after 5 hours with 83% conversion of the starting material. Increasing the amount of MVK to 20 mol% (entry 4, 1:4 ratio) resulted in 98% conversion of the starting material after 5 hours but the yield of **131** decreased to 68% (in comparison to entry 3 with 10 mol% MVK).



Entry	Catalyst (mol%)	MVK (mol%)	Time (h)	Conv. (%)	Ratio 1V:1C[b]
1[a]	5	0	24	70	53:17
2	5	5	5	83	55:9
3[a]	5	10	5	100	85:15
4	5	20	5	98	68:11
5[a]	2.5	5	24	46	22:10
6[a]	2.5	25	24	100	88:12
7[a]	1	2	48	27	6:13
8[a]	1	25	48	91	76:8

Table 21. Optimization of RuHCl(CO)(H_2IMes)(PPh_3) and MVK additive

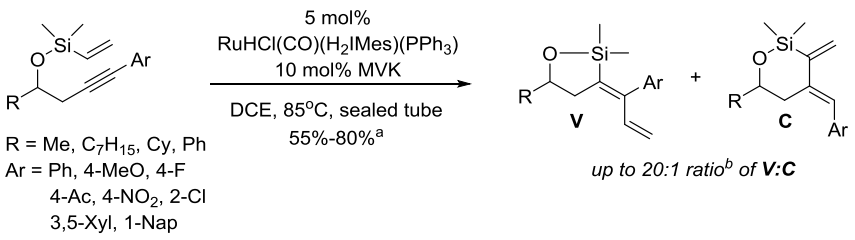
[a] Reaction run by Shasha Liu/Jinbo Zhao. [b] Crude yield determined by ^{1}H NMR using mesitylene as an internal standard.

Lowering the catalyst loading to 2.5 mol% in the presence of 5 mol% MVK resulted in only 46% conversion of starting material after 24 hours with a poor crude yield (22%) of **131** (entry 5); however, drastically increasing the amount of MVK to 25 mol% (1:10 ratio) resulted in 100% conversion after 24 hours and **131** was observed in 88% crude yield (entry 6). When the amount of RuHCl(CO)(H_2IMes)(PPh_3) was further decreased to 1 mol% with 2 mol% MVK, the cycloisomerization product **132** was favored albeit in poor yield after 48 hours (13%, entry 7). Lastly, a significant increase of MVK to 25 mol% with 1 mol% RuHCl(CO)(H_2IMes)(PPh_3) (1:25 ratio) resulted in an improved ratio of **131:132**, however, the crude yield of **131** decreased (in comparison to entry 3) and a longer reaction time was required (48 hours) to achieve 91% conversion. It was gathered from the results of Table 21 that use of 10 mol% MVK allowed for a short reaction time and superior ratio/yield of **131:132**. Additionally, it was concluded that lower loadings of RuHCl(CO)(H_2IMes)(PPh_3) were tolerated in the presence of high concentrations of

MVK but with sacrificed (longer) reaction time. Use of 5 mol% $RuHCl(CO)(H_2IMes)(PPh_3)$ and 10 mol% MVK (entry 3, results from Scheme 46), was chosen as the optimized conditions for the transformation.

3.1.3 Alkyne Substrate Tolerance

It was also discovered that a wide variety of silicon-tethered alkynes were tolerated in the *trans*-silylvinylation conditions with MVK additive (Scheme 47).[88]

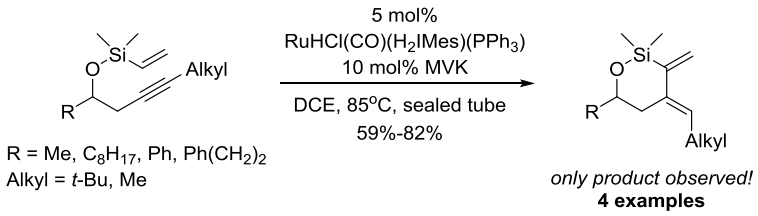


Scheme 47. Substrate scope with MVK additive[c]

[a] Isolated yields of vinylated product **V**. [b] Ratio of crude reaction mixture (determined by ^1H NMR using mesitylene as an internal standard). [c] All reactions run by Shasha Liu and Jinbo Zhao.

Alkyl and aryl substitution at the homo-propargylic position was well tolerated, in addition to various aromatic substitution at the alkyne terminus. The isolated yields of the vinylation products **V** were obtained in 55%-80% after column chromatography. In some cases, separation of the cycloisomerization product **C** from the desired product **V** was difficult; preparative thin layer chromatography was used in these cases.

The substrate scope was broadened to include alkyl substitution at the alkyne terminus. However, the expected *trans*-silylvinylation products (type **V**) were not observed; only cycloisomerization-type products were obtained from the reaction (Scheme 48).

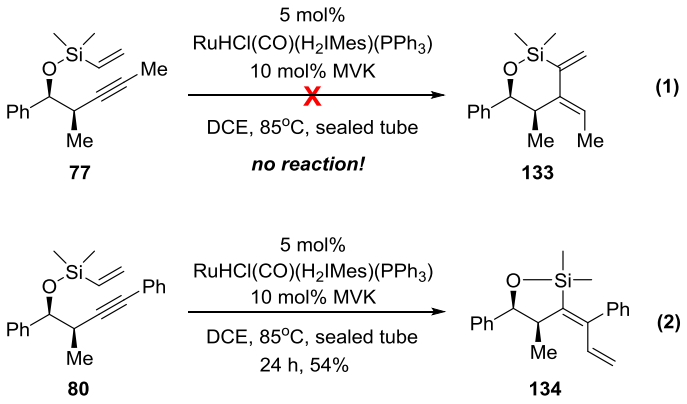


Scheme 48. Alkyl substituted alkynes with MVK additive[a]

[a] All reactions run by Shasha Liu and/or Jinbo Zhao.

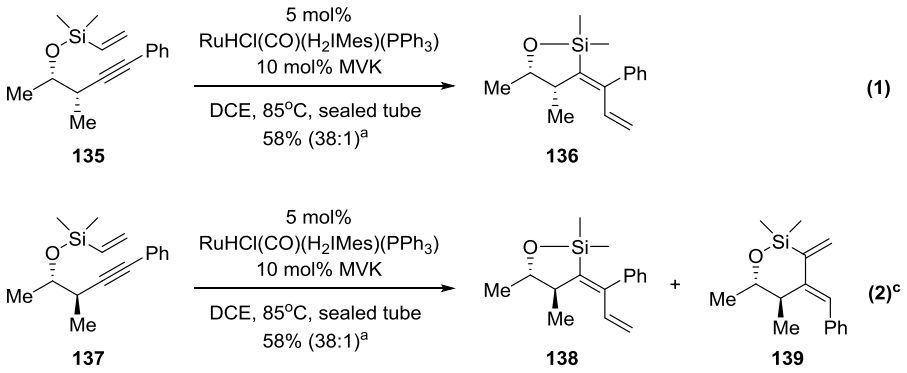
It was initially hypothesized that sterics resulting from the bulky *t*-butyl group on the alkyne played a role in this unexpected observation, but exchange for the less hindered methyl group also gave solely the cycloisomerization product. The cycloisomerization of enynes in the presence of ruthenium is known but was not initially sought after by the Clark group.

With this prior body of work, it was wanted to explore the reactivity of substrates possessing substitution at the propargylic position, i.e. alkynes **77** and **80** (Scheme 49). When the previously-synthesized methyl-substituted alkyne **77** was subjected to the optimized conditions, it was expected to observe formation of cycloisomerization product **133**.



Scheme 49. *Trans*-silylvinylation of alkynes 77 and 80 with MVK additive

However, we were perplexed to discover alkyne **77** did not react under these conditions even after 24 hours (eq. 1). It was hypothesized that propargylic substitution was the reasoning behind this discovery but confirmation was desired by examining other propargylic-substituted alkyne substrates. Subjection of phenyl-substituted alkyne **80** resulted in 100% conversion and gave solely the vinylation product **134** in 54% yield. In addition to alkynes **77** and **80**, the effect of a racemic-*syn* and racemic-*anti* relationship was also examined with propargylic-substituted alkynes **135** and **137** (Scheme 50). The racemic-*syn* alkyne **135** worked well under the optimized conditions to give vinylation product **136** in 58% isolated yield (eq. 1). A trace amount of the cycloisomerization product (~2%) was observed in the crude reaction mixture but was not obtained after purification. The reaction of racemic-*trans* alkyne **137** was comparable to *syn* alkyne **135** and the resulting product **138** was isolated in 61% yield (eq. 2). The cycloisomerization product **139** was observed in the crude reaction ratio but was separated from **138** during purification.



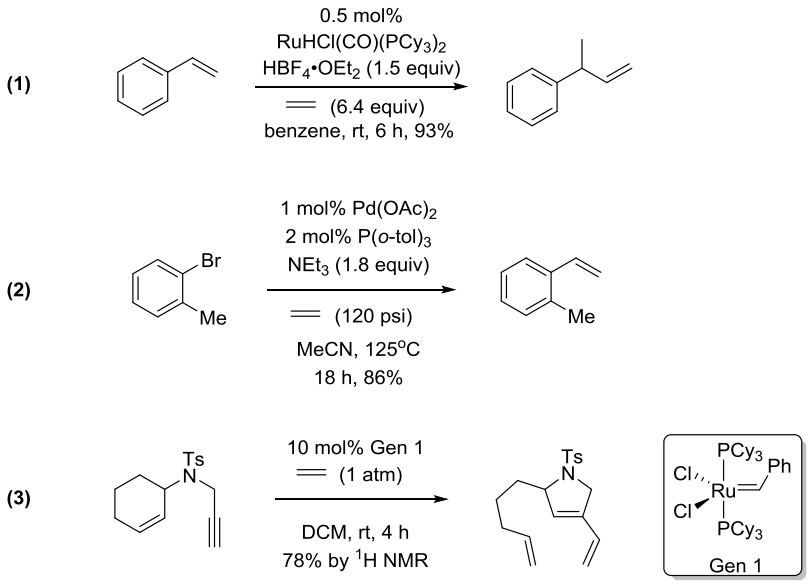
Scheme 50. *Trans*-silylvinylation of propargylic substituted alkynes with MVK additive

[a] Isolated ratio of *Z/E* isomers as determined by ^{1}H NMR. [b] Ratio of **138:139** as determined by crude ^{1}H NMR using mesitylene as an internal standard. [c] Reaction run by Robert Wilson.

3.2 ETHYLENE ATMOSPHERE

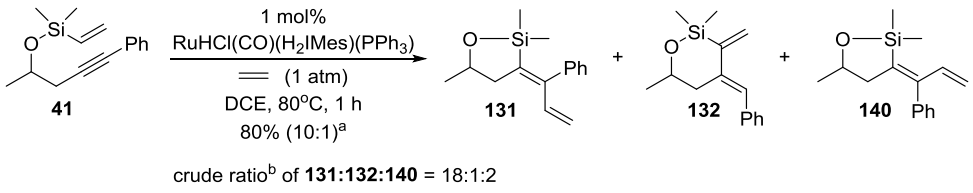
3.2.1 Introduction and Reaction Discovery

Ethylene, the simplest of all alkenes, is produced in massive quantities (approximately 150 million pounds each day).[89] It is an ideal source in vinylation chemistry because it possesses a high atom economy, having only one hydrogen lost during the vinylation process.[90] Ethylene has been utilized in numerous transformations (Scheme 51), including hydrovinylation (eq. 1),[18, 91-93] Mizoroki-Heck (eq. 2),[94, 95] and enyne metathesis (eq. 3);[96] however, its use for alkyne silylvinylation has not been thoroughly explored.



Scheme 51. Use of ethylene in various transformations

Since the presence of ethylene in silylvinylation chemistry had not been well explored, investigations and a comparison of the outcome of the silylvinylation protocol in an atmosphere of ethylene versus the previously reported MVK methodology was desired. The study began by treating alkyne **41** with RuHCl(CO)(H_2IMes)(PPh_3) in DCE at 80°C under a balloon of ethylene (Scheme 52).



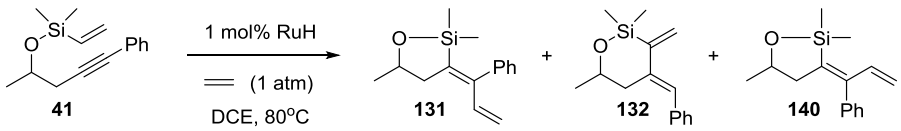
Scheme 52. Initial investigations

[a] Product was isolated as a mixture of *Z/E* isomers. Ratio (**131:140**) was determined by ^{1}H NMR. [b] Determined by crude ^{1}H NMR using mesitylene as an internal standard.

With only 1 mol% catalyst, 100% conversion of the starting alkyne was observed after 1 h. Analysis of the crude ^{1}H NMR spectrum revealed the expected major vinylation product **131** and two minor by-products, cycloisomerization adduct **132** and *E* isomer **140**. Isolation of the product **131** by column chromatography resulted in an 80% yield as a 10:1 mixture of *Z/E* isomers (**131:140**).

3.2.2 Reaction Optimization

With this promising initial result in hand a catalyst screen was conducted to determine what role, if any, the ligand environment around the metal would have in the transformation (Table 22). Exchange for $RuHCl(CO)(PCy_3)_2$, the catalyst proven optimal in the acrylate and boronate coupling methodology, resulted in only 89% conversion after a 7 hour reaction time, but an improved product ratio of 55:4:1 was observed (entry 2).



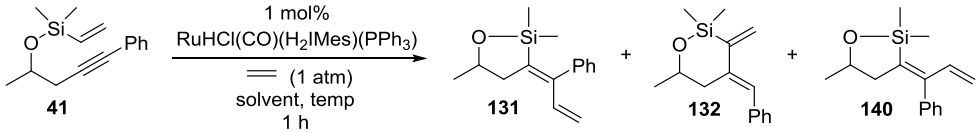
Entry	Catalyst	Time (h)	Conv.	131:132:140	Crude Yield[a] of 131
1	$RuHCl(CO)(H_2IMes)(PPh_3)$	1	100%	18:1:2	91%
2[b]	$RuHCl(CO)(PCy_3)_2$	7	89%	55:4:1	55%
3[b]	$RuHCl(CO)(PtBu_2Cy)_2$	7	43%	1:0:0	23%
4[b]	$RuHCl(CO)(PtBu_2Me)_2$	7	33%	6:1:0	18%
5[b]	$RuHCl(CO)(PiPr_2[3,5\text{-}CF_3C_6H_3])_2$	7	29%	1:0:0	11%

Table 22. Catalyst screen

[a] Determined by crude ^{1}H NMR using mesitylene as an internal standard. [b] 5 mol% catalyst used.

The bulky RuHCl(CO)(P*t*Bu$_2$Cy)$_2$ complex gave only 23% crude yield of **131** after 7 hours (entry 3). The RuHCl(CO)(P*t*Bu$_2$Me)$_2$ performed poorly, with 33% conversion of starting material and 18% crude yield of product observed after 7 hours (entry 4). Only 29% conversion and 11% crude yield of product was obtained with the electron-deficient phosphine complex RuHCl(CO)(P*i*Pr$_2$[3,5-$CF_3C_6H_3$])$_2$ (entry 5). It was concluded that the NHC-bearing complex RuHCl(CO)(H_2IMes)(PPh_3) (entry 1) proved to be the optimal ruthenium catalyst for the *trans*-silylvinylation under ethylene atmosphere.

A brief solvent screen was also conducted for the transformation (Table 23). In addition to DCE (entry 1), the reaction was complete in 1 hour in toluene and α,α,α-trifluorotoluene at 85°C.



Entry	Solvent	Temp (°C)	Ratio[a] of 131:132:140	Crude Yield[b] of 131	Isolated Yield of 131
1	DCE	80	18:1:2	91%	80% (11:0:1)
2	toluene	85	12:1:1	71%	---
3	CF_3Ph	85	26:3:1	83%	74% (18:2:1)

Table 23. Brief solvent screen

[a] Ratio of the crude reaction mixture (determined by ^{1}H NMR using mesitylene as an internal standard).

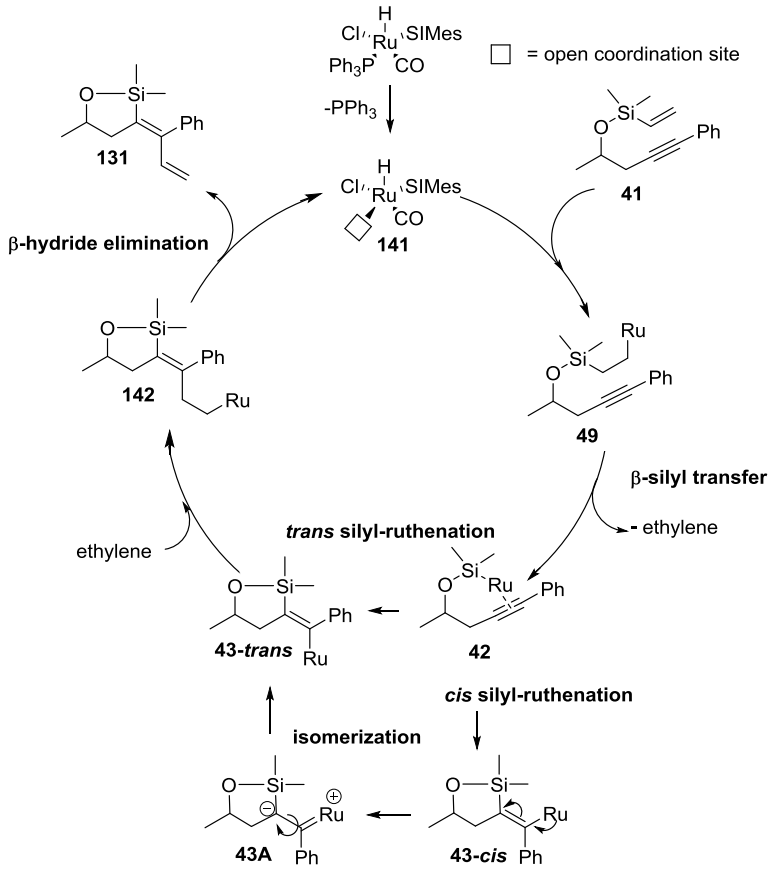
[b] Determined by crude ^{1}H NMR using mesitylene as an internal standard.

In toluene (entry 2), a slightly decreased product ratio (12:1:1) and crude yield of **131** (71%) was obtained, so isolation was not deemed necessary. α,α,α-Trifluorotoluene gave an excellent product ratio of 26:3:1 but the crude (83%) and isolated yield of **131** were not as high as was

obtained with DCE (entry 3). It was concluded that 1 mol% $RuHCl(CO)(H_2IMes)(PPh_3)$ in DCE at 80°C proved optimal for the *trans*-silylvinylation of internal alkynes under ethylene atmosphere.

3.2.3 Mechanistic Hypothesis

A mechanism that accounts for the *trans*-silylvinylation protocol is proposed in Scheme 53: dissociation of a triphenylphosphine ligand from $RuHCl(CO)(H_2IMes)(PPh_3)$ gives **141** (possessing an open coordination site). Introduction of alkyne **41** allows for the ruthenium complex to add to the most sterically accessible position on the vinyl moiety, giving **49**. Subsequent β-silyl transfer (with loss of ethylene) gives silyl-ruthenium species **42**. *Cis* silyl-ruthenation (**43-*cis***) followed by isomerization (**43-*trans***) and subsequent ethylene insertion results in the formation of intermediate **142**. (Although direct *trans*-metallation is known in the literature[30, 37, 38, 97-99] [see section 1.2.3 in this thesis], it is believed that a *cis*-metallation followed by isomerization has occurred due to minor isomer **140** appearing in the crude reaction mixture and isolated material.) The product **131** is generated upon β-hydride elimination and the active catalytic species **141** is regenerated.

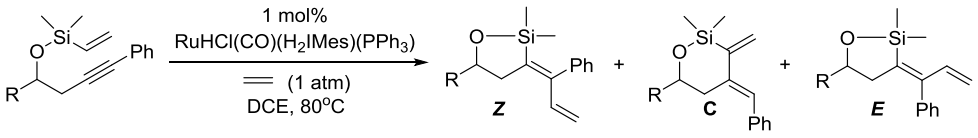


Scheme 53. Mechanistic hypothesis

3.2.4 Substrate Scope

Once the conditions were optimized, the alkyne substrate scope was evaluated. Initially alkynes bearing a phenyl group at the terminus were scrutinized (Table 24). It is important to note that the cycloisomerization by-product was observed with each alkyne substrate examined but it was separated from the desired vinylation product. However, separation of the *Z/E* stereoisomers was not successful. In some cases the ratio was improved after isolation. To begin,

the previously synthesized alkyne **80**, possessing propargylic substitution, performed well in the transformation and gave the desired product **134** in 68% yield (14:1).



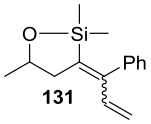
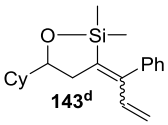
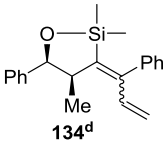
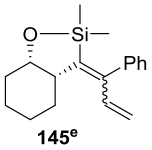
Alkyne[a]	Product	Ratio[b] Z:C:E	Isolated Yield[c]	Alkyne	Product	Ratio[b] Z:C:E	Isolated Yield[c]
41	 131	18:1:2	80% (9:1)	57	 143[d]	17:2:1	70% (17:1)
80	 134[d]	8:1:1	68% (14:1)	144	 145[e]	34:1:3	78% (11:1)

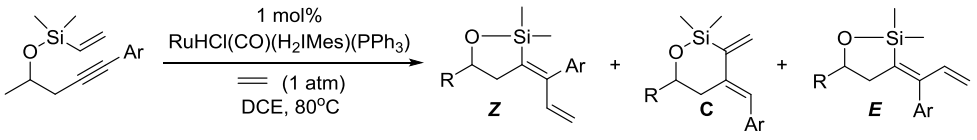
Table 24. Phenyl-substituted alkyne scope

[a] The synthesis of the alkyne substrates can be found in the experimental chapter of this thesis. [b] Ratio of the crude reaction mixture as determined by ^{1}H NMR using mesitylene as an internal standard. [c] Isolated yields are reported as a ratio of *Z/E* isomers. [d] Reaction run with 2 mol% catalyst. [e] Reaction run with 5 mol% catalyst.

The yield of **134** (68%) was substantially better under an ethylene atmosphere than in the presence of the MVK additive (54%). Additional alkyl substitution was tolerated, with the cyclohexyl-substituted **143** isolated in 70% yield (17:1). An improvement in yield compared to MVK additive was also observed (64%). Lastly, a *cis* 6,5-fused ring system was also tolerated and gave vinylation product **145** in 78% yield (11:1).

Various aryl functionality on the alkyne terminus was also examined (Table 25). *Para*-substitution was well tolerated and the 4-fluorophenyl moiety **146** was isolated in 64% yield

(20:1). The bulky napthyl group was also tolerated in the reaction and provided **148** in 73% yield (13:1). Additionally, a 3,5-xylyl group worked well and **149** was essentially isolated as one isomer (26:1) in 74% yield.



Alkyne[a]	Product	Ratio[b] Z:C:E	Isolated Yield[c]	Alkyne[a]	Product	Ratio[b] Z:C:E	Isolated Yield[c]
64	**146** 4-F	23:3:1	64% (20:1)	**67**	**149**[d] 3,5-Xyl	32:3:1	74% (26:1)
147	**148**[d] 1-Nap	24:1:2	73% (13:1)	**150**	**151**[e] 4-NO_2	4:1:2	30% (2:1)

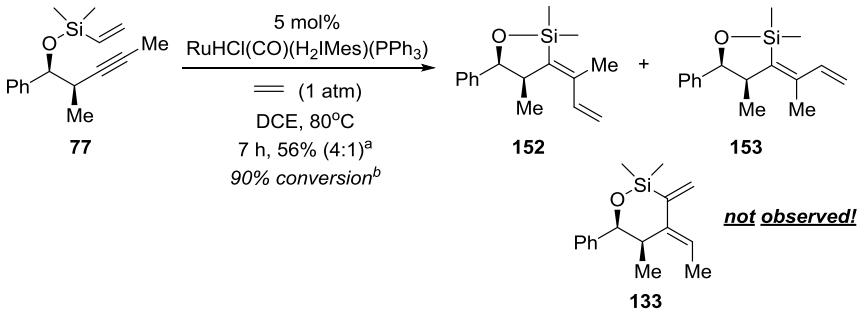
Table 25. Aryl-substituted alkyne scope

[a] The synthesis of the alkyne substrates can be found in the experimental chapter of this thesis. [b] Ratio of the crude reaction mixture as determined by ^{1}H NMR using mesitylene as an internal standard. [c] Isolated yields are reported as a ratio of ***Z:E***. [d] Reaction run with 5 mol% catalyst. [e] Reaction run with 2 mol% catalyst.

The electron-withdrawing *para*-nitro moiety was also examined, but the resulting diene **151** was isolated in only 30% yield with a poor isomeric ratio of 2:1.

It was also desired to examine the reactivity of the previously synthesized methyl-substituted alkyne **77**, which proved unreactive in the *trans*-silylvinylation protocol with MVK additive (see Scheme 49, eq. 1). It was discovered that under an atmosphere of ethylene a 90%

conversion of the alkyne **77** was observed after 7 hours in the presence of 5 mol% $RuHCl(CO)(H_2IMes)(PPh_3)$ (Scheme 54).



Scheme 54. Reactivity of alkyne 77 under ethylene atmosphere

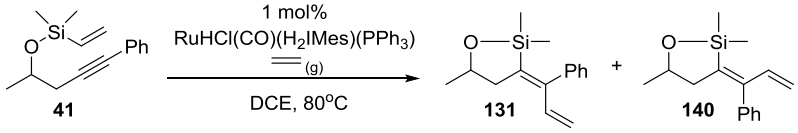
[a] Ratio of the isolated material determined by ^{1}H NMR. [b] Determined by ^{1}H NMR using mesitylene as an internal standard.

When alkyl-substituted alkynes were subjected to the silylvinylation conditions with MVK additive, the cycloisomerization-type product was the only product observed (see Scheme 48). Formation of the cycloisomerization product **133** was expected under an atmosphere of ethylene but surprising vinylation products **152** and **153** were observed. Additionally, no presence of **133** was detected in the crude reaction mixture by ^{1}H NMR. Despite not having an explanation to the aforementioned result, vinylation product **152** was isolated in 56% yield as a 4:1 isomeric mixture.

3.2.5 Increase of Ethylene Pressure

The substrates explored under an ethylene of atmosphere gave an improved ratio of vinylation to cycloisomerization (**V:C**) in comparison to MVK additive. With that in mind, the possibility of eliminating isomer **C** was desired. Based on the mechanistic hypothesis (see Scheme 53), it was envisioned that increasing the pressure of ethylene in the system would increase the production of vinylation isomer **V** and thwart production of isomer **C** due to the affinity of ethylene adding to the ruthenium. Additionally, it was predicted that an increased pressure of ethylene could trap intermediate **43-*cis*** prior to isomerization to **43-*trans***, thus decreasing or possibly eliminating the *Z* vinylation isomer altogether.

Under a balloon of ethylene a 9:1 ratio of **131:140** was observed (Table 26, entry 1). Increasing the pressure of ethylene to 20 psi increased the amount of **140** (entry 2). At 40 psi, an additional increase in formation of **140** was observed (entry 3).



Entry	Pressure	Ratio[a] 131:140
1	balloon	9:1
2[b]	20 psi	6:1
3[b]	40 psi	2.5:1
4	60 psi	1:1.4
5	80 psi	1:2
6[b,c]	80 psi $Ar_{(g)}$	1:0

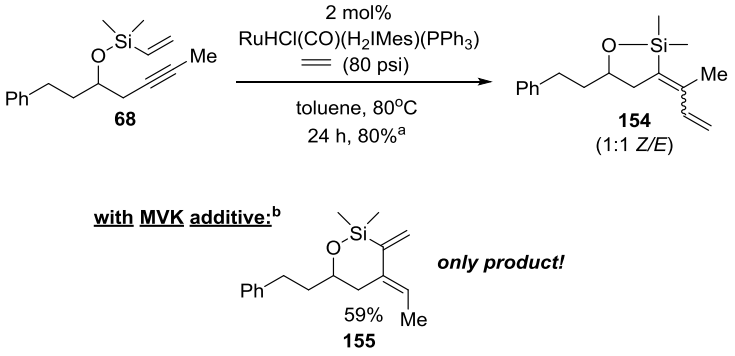
Table 26. Increase of ethylene pressure

[a] Ratio determined by crude ^{1}H NMR using mesitylene as an internal standard. [b] Reaction run by Robert Wilson.

[c] 23% conversion and 11% of **131** was observed.

At 60 psi and 80 psi a reversal in product ratio was observed, with **140** being the major isomer formed in the reaction (entries 4 and 5). In addition, no cycloisomerization product was observed under increased pressures of ethylene. Lastly, to determine if ethylene pressure or ethylene concentration influenced the selectivity outcome, an experiment with increased pressure of argon was conducted (entry 6). Under 80 psi of argon, 23% conversion of alkyne **41** was observed with an 11% crude yield of isomer **131** only. This supports the idea that increased ethylene concentration thwarts isomerization (promotes formation of **140**), thus favoring *syn*-silylvinylation.

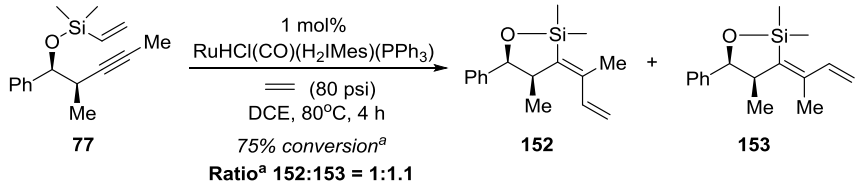
It was also desired to examine the effect of increased ethylene pressure on substrates that solely formed the cycloisomerization product, as reported in the previous methodology with MVK additive (Scheme 55). Subjection of methyl-substituted alkyne **68** to 80 psi of ethylene resulted in an 80% isolated yield of a 1:1 mixture of **154**; the cycloisomerization product **155** was not observed.



Scheme 55. Increased ethylene pressure with alkyl-substituted alkyne 68

[a] Isolated yield as a 1:1 ratio of Z/*E* isomers. [b] Reaction with MVK additive run by Shasha Liu.

The effects of increased ethylene pressure on the previously synthesized methyl substituted alkyne **77** was also examined (Scheme 56). A reversal in selectivity in comparison to balloon pressure of ethylene was observed. After 4 hours at 80 psi, the ratio of **152:153** was 1:1.1, which supports the aforementioned hypothesis. To the best of our knowledge, the use of increased pressures of ethylene to alter the stereoselectivity of a reaction has not been shown previously.

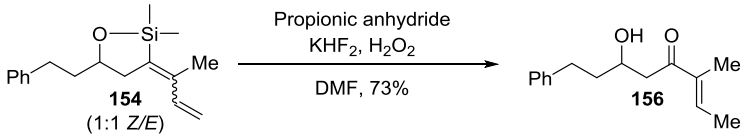


Scheme 56. Increased ethylene pressure with alkyne 77

[a] Determined by ^{1}H NMR using mesitylene as an internal standard.

3.2.6 Synthetic Elaboration

The synthetic utility of the vinylation products by various transformations was demonstrated (Scheme 57). Fleming-Tamao oxidation[100, 101] of diene **154** (1:1 mixture of *Z/E* isomers) under acidic conditions **18V** gave the desired diene **156** as one double-bond isomer in 73% yield.



Scheme 57. Synthetic elaboration

3.3 CONCLUSION

In conclusion, a ruthenium-catalyzed *trans*-silylvinylation of internal alkynes with MVK as an additive was demonstrated. This regiospecific 5-*exo*-*dig* process provided 1,3-dienes in good yields. In addition to formation of the expected vinylation products, cycloisomerization minor by-products was observed. The substrate scope of the silylvinylation included aryl-substituted alkynes and was tolerable to substitution at the propargylic substitution, however, methyl-substituted alkyne 77 was unreactive.

The ruthenium-hydride catalyzed *trans*-silylvinylation of silicon-tethered alkynes under an atmosphere of ethylene was also demonstrated. With substantially shorter reaction times, lower catalyst loadings and improved product ratio and yields, this methodology significantly improved upon the previous methodology that utilized MVK as an additive. Increased pressures of ethylene altered the *Z/E* product ratio and prevented formation of cycloisomerization isomer **C**. Use of alkyl-substituted alkynes with increased ethylene pressure allowed for isolation of only vinylation-type products. The synthetic utility of the dienes was demonstrated via a Fleming-Tamao oxidation.

Future directions for this project would be for the development of reaction conditions tolerable to terminal alkyne substrates. Conditions for tolerance of various substitution on the vinyl silicon tether (i.e. phenyl, alkyl) should also be examined to allow for greater diversity on the silicon atom. Lastly, greater pressures of ethylene (up to 1000 psi) should be examined to further evaluate the *Z/E* product ratio of the vinylation products.

4.0 RUTHENIUM CATALYZED CYCLOISOMERIZATION OF SILICON-TETHERED 1,7-ENYNES

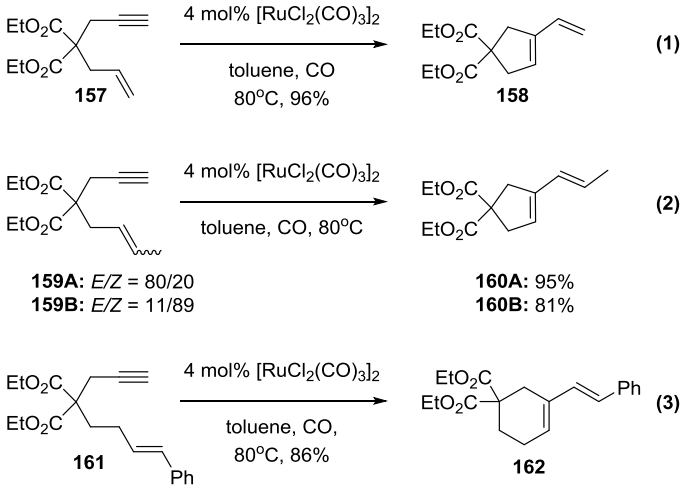
4.1 INTRODUCTION

One of the most common methods for acquiring dienes is via the cycloisomerization of enynes. This method is greatly beneficial because the reactions require the use of few reagents and generate minimal by-products.[102] Another advantage is the relative ease of synthesis of the starting enynes.[103] Additionally, transition metal-catalyzed cycloisomerization reactions are an atom-economical route to achieve molecular complexity and access diene scaffolds.[11, 104] A plethora of transition metals have been used to catalyze the cycloisomerization of enynes to form dienes: palladium (pioneered by Trost),[105-126] rhodium,[127-149] iridium,[150, 151] platinum,[152-165] gold,[162, 165-177] titanium,[178] chromium,[179] iron,[180] cobalt,[181] nickel,[182-186] silver, [187, 188] gallium,[189-191] indium[192] and lastly, ruthenium (which will be discussed in detail in this chapter).

4.1.1 Ruthenium-catalyzed cycloisomerization of enynes to form dienes

The first reported use of ruthenium to catalyze the cycloisomerization of enynes was by Chatani and Murai in 1994.[193] A catalytic amount of a ruthenium complex $[RuCl_2(CO)_3]_2$ was

utilized under an atmosphere of CO with 1,6-enynes to form 1,3-dienes selectively (Scheme 58). After exploring other ruthenium complexes, it was deemed the presence of a halide and CO ligands on ruthenium necessary for the reaction to proceed.

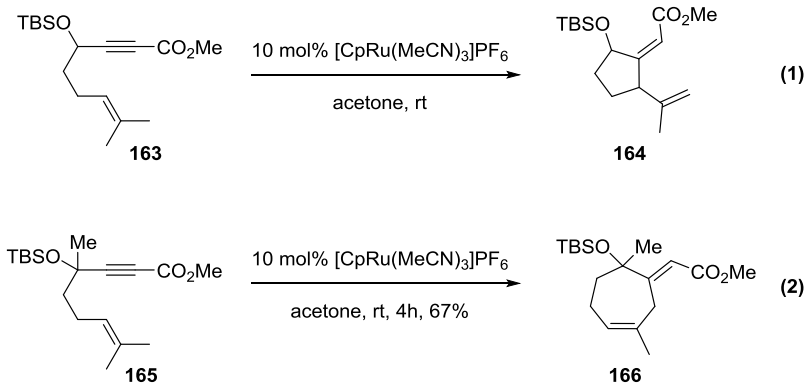


Scheme 58. Examples of the $[RuCl_2(CO)_3]_2$-catalyzed cycloisomerization of enynes

The conditions were tolerable for a substrate bearing no substitution on the alkyne terminus or on the olefinic terminus (eq. 1) and gave the product in 96% yield. Regardless of the geometry of the starting enyne, the *E* geometry was observed in the products (eq. 2). This methodology was also demonstrated with a 1,7-enyne and gave the six-membered ring product in 86% yield (eq. 3). At the time, Trost's palladium conditions in the presence of 1,7-enynes resulted solely in the formation of bicyclo[4.2.0]octene derivatives.[194]

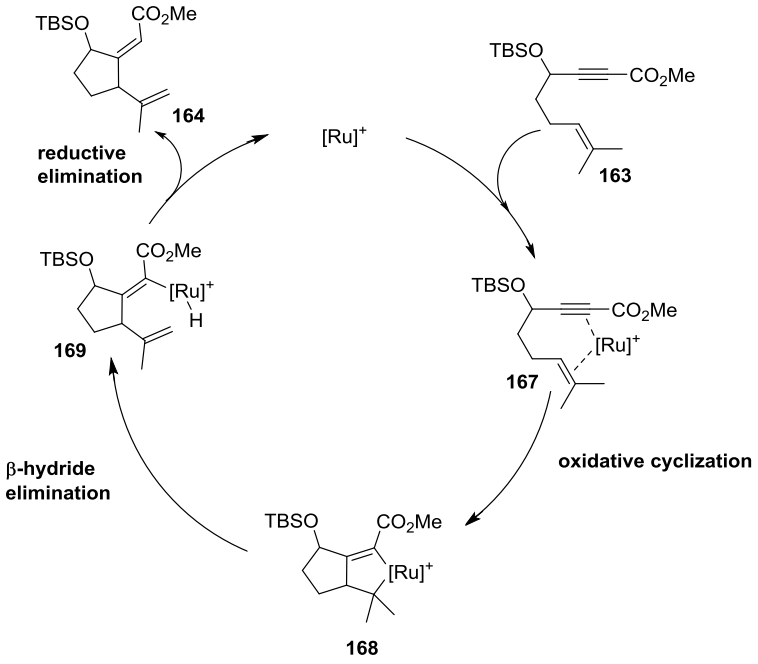
In 1995, Trost published on the intermolecular coupling of alkynes and alkenes (Alder-Ene) to give linear and branched 1,4-dienes catalyzed by CpRu(COD)Cl.[195] A few years later, Trost

and Toste were able to develop conditions for an intramolecular version utilizing 1,6-enynoates and catalyzed by the cationic ruthenium complex $[CpRu(MeCN)_3]PF_6$ (Scheme 59).[196]



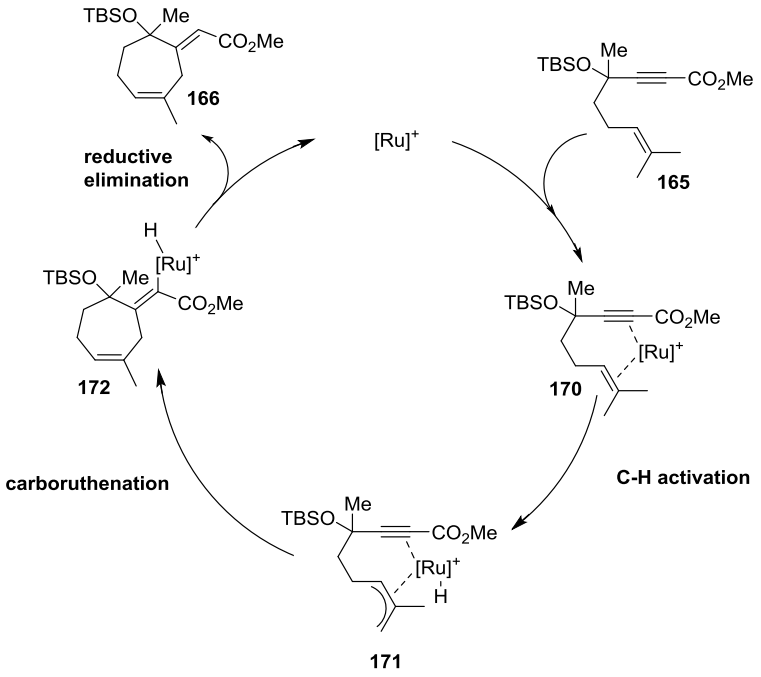
Scheme 59. Formation of cyclopentene vs. cycloheptene derivatives

Interestingly, the ring size of the product varied when the number of substituents at the propargylic position of the starting 1,6-enynoate substrate was altered. Substrate **163**, bearing a single-substituent (silyl ether) at the propargylic position, yielded a cyclopentene **164** (eq. 1); however, when a quaternary center was introduced at the propargylic position of the enynoate (**165**), cycloheptene **166** was obtained in 67% yield (eq. 2). It was determined that two different mechanistic pathways accounted for this change in selectivity. They proposed the formation of **164** as follows (Scheme 60):[196] coordination of the cationic ruthenium species to the olefin and alkyne moieties of enynoate **163** (**167**) and oxidative cyclization resulted in the formation of ruthenacyclopentene **168**. Subsequent β-hydride elimination gave vinyl ruthenium hydride **169**, which yielded diene **164** upon reductive elimination and regeneration of the active catalytic species.



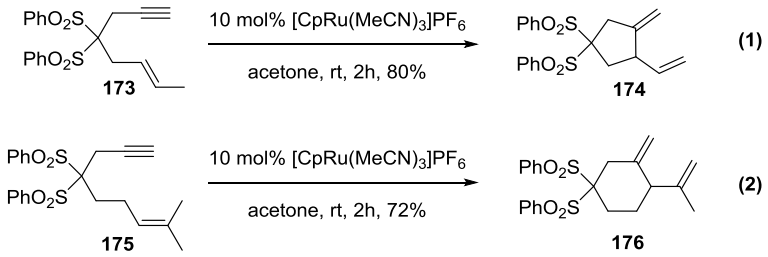
Scheme 60. Cycloisomerization via a ruthenacyclopentene intermediate

The formation of **166** is believed to proceed via an allylic C-H activation pathway (Scheme 61):[196] activation of the allylic position of enynoate **165** (**170**) generated π-allyl intermediate **171**. A 7-*exo*-*dig* carboruthenation of **171** gave vinyl ruthenium hydride **172** which subsequently underwent reductive elimination to yield cycloheptene **166**. The rationale for **165** proceeding via a C-H activation pathway is due to the avoidance of a possible steric congestion that would arise during the formation of a ruthenacyclopentene intermediate ($A_{1,3}$-type strain that would occur between the quaternary center and the methyl ester). With understanding of the reaction selectivity, Trost was able to isolate a variety of cycloheptenes by varying the substituents of the quaternary center located at the propargylic position of the 1,6-enynoates.



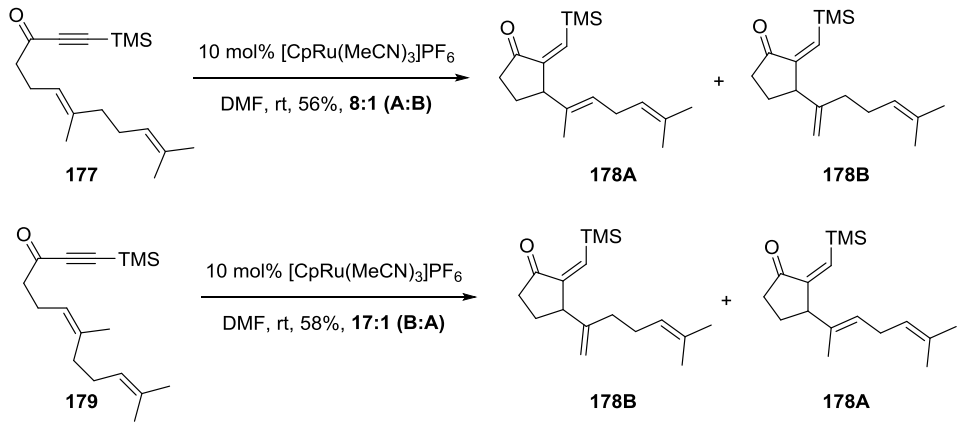
Scheme 61. Cycloisomerization via a π-allyl intermediate

Shortly thereafter, Trost and Toste extended the methodology to include enynes not containing an ester moiety on the alkyne terminus (Scheme 62).[197] With 10 mol% of cationic $[CpRu(MeCN)_3]PF_6$, the formation of 1,4-dienes was demonstrated (five- and six-membered ring products) from 1,6-enynes (eq. 1) and from 1,7-enynes (eq. 2).



Scheme 62. Examples of Trost's Ru-catalyzed cycloisomerization of 1,6- and 1,7-enynes

In addition, it was demonstrated the first example where the regioselectivity of the reaction is dependent upon the geometry of the olefin in the enyne substrate (Scheme 63).[197]



Scheme 63. Enyne geometry and regioselective outcome

The reaction of enyne **177**, possessing an *E* olefin, with 10 mol% $[CpRu(MeCN)_3]PF_6$ in DMF favored formation of the more substituted 1,4-diene **178A** (8:1). Whereas the reaction of enyne **179**, possessing a *Z* olefin, with the aforementioned conditions resulted in a complete reversal of selectivity, with 1,4-diene **178B** being favored (17:1). The regioselectivity of these transformations can be explained via examination of the ruthenacyclopentene intermediates (Figure 8). In both cases, the substituents on the ruthenacycle oriented in a pseudoequatorial manner place a hydrogen proximal to the ruthenium, which in turn allows for the overlap needed for β-hydride elimination to occur. With enyne **177**, the long alkyl chain is oriented pseudoequatorially, allowing for β-hydride elimination of H_a to give diene **178A**. With enyne **179**, the methyl group is oriented pseudoequatorially, allowing for β-hydride elimination to give the less substituted diene **178B**.

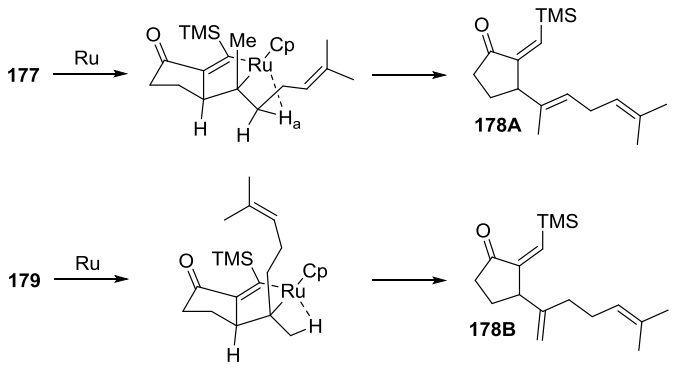
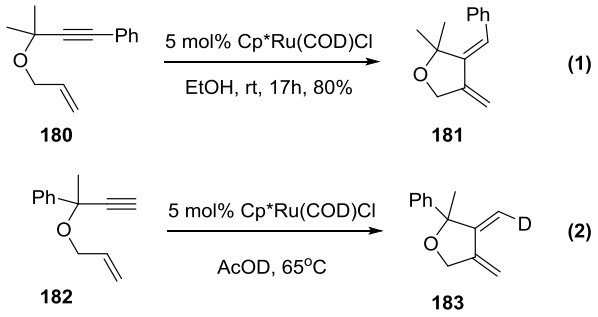


Figure 8. Explanation of regioselectivity

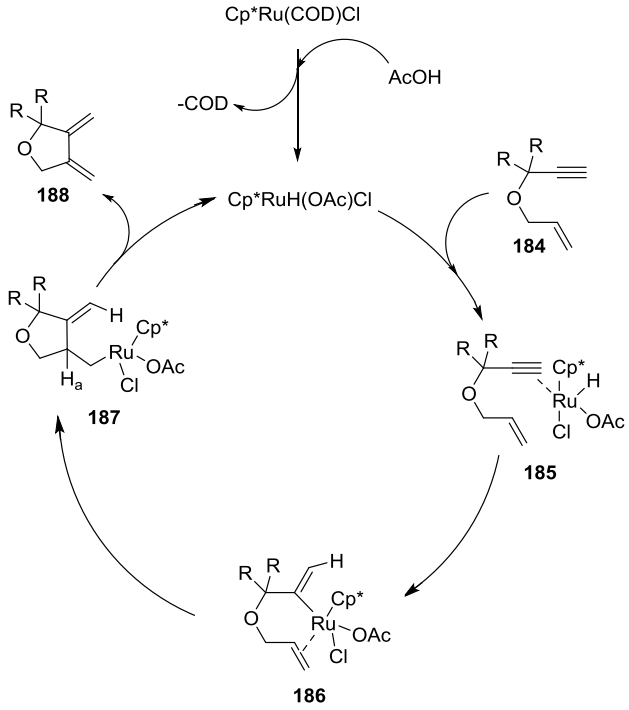
Up to this point, all cases reported by Trost *et al.* utilizing 1,6- and 1,7-enynes/enynoates result in the formation of 1,4 dienes, respectively. Shortly thereafter (in 2000), Dixneuf *et al.* synthesized 1,3-dienes using Cp*Ru(COD)Cl as a "pre-catalyst" (Scheme 64).[198]



Scheme 64. Cycloisomerization of 1,6-enynes via Cp*Ru(COD)Cl "pre-catalyst"

Various enynes were transformed into tetrahydrofurans containing a 1,3-diene moiety (one example shown in eq. 1) under catalytic amounts of Cp*Ru(COD)Cl in the presence of ethanol or acetic acid. Polymerization was observed when a terminal alkyne was reacted in ethanol; acetic acid at 65°C was used to circumvent polymerization. To account for the reaction

mechanism and active catalytic species (Scheme 65), treatment of Cp*Ru(COD)Cl in ethanol or acetic acid causes decoordination of the COD ligand and generates Cp*RuH(OAc/OEt)Cl *in situ*. Coordination of the ruthenium hydride to the alkyne moiety of enyne **184** (**185**) and cis addition to the alkyne generates vinyl ruthenium **186**, which undergoes insertion into the olefinic moiety to give the tetrahydrofuran **187**. Subsequent β-hydride elimination of H_a yields the product diene **188** and regenerates the active ruthenium hydride species.

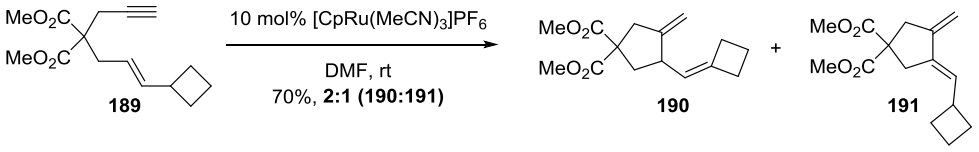


Scheme 65. Mechanistic pathway for Cp*RuH(OAc)Cl-catalyzed cycloisomerization

A deuterium label study was conducted to evaluate the mechanism (Scheme 64, eq. 2). The cycloisomerization was conducted in deuterated acetic acid and the resulting deuterated diene

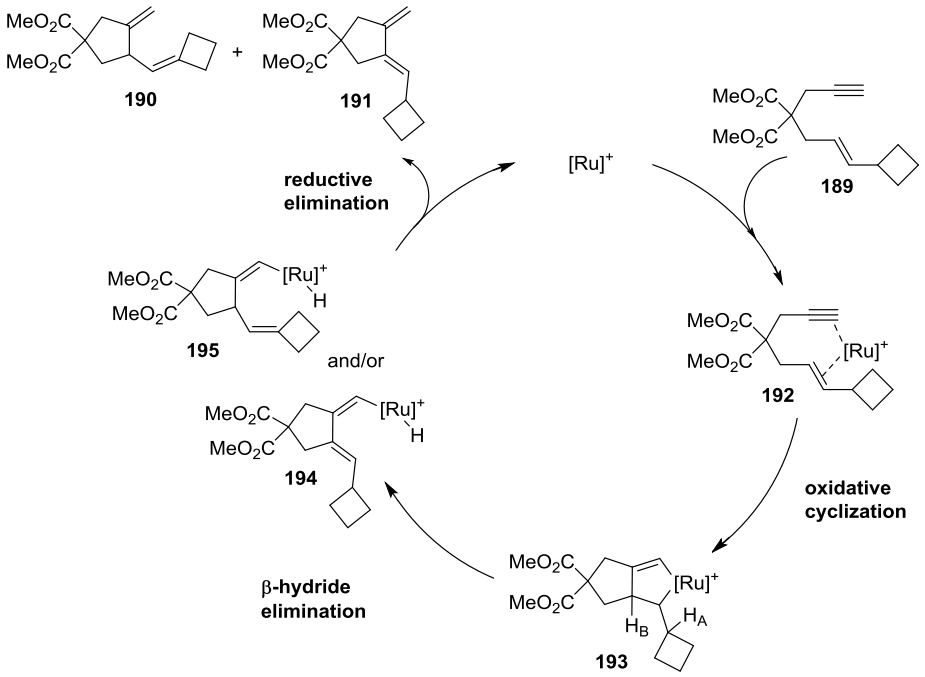
was obtained. The orientation of the deuterium atom confirmed that the addition of Ru-D occurred in a *cis* manner to the alkyne.

In 2002, Trost and Toste reported on further mechanistic investigations into their ruthenium-catalyzed cycloisomerization protocol.[103] As previously mentioned, their conditions afford 1,4-dienes, respectively. However, it was mentioned a special case in which a mixture of 1,4- and 1,3-dienes was obtained (Scheme 66).



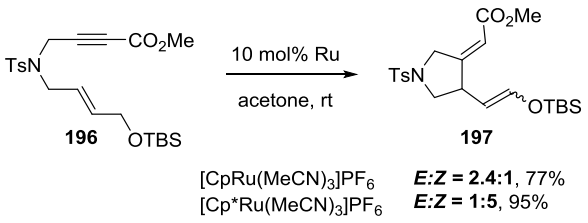
Scheme 66. Special case of Trost's conditions

The 1,6-enyne **189** bearing a cyclobutane on the olefin terminus gave a 2:1 mixture of 1,4-diene **190** and 1,3-diene **191** when subjected to their standard ruthenium conditions. The reasoning for the formation of **191** can be attributed via examination of the reaction pathway (Scheme 67). Upon oxidative cyclization of **192**, ruthenacyclopentene **193** is formed. Exocyclic β-hydride elimination of H_a to form 1,4-diene **195** is challenging (but feasible) because of the strain resulting in the formation of an alkylidenecyclobutane. The reasoning to why 1,3-diene formation occurred is due to the competition for endocyclic β-hydride elimination of H_b (**194**). After reductive elimination of the vinyl ruthenium hydride species (**194, 195**), the mixture of dienes **190** and **191** is accounted.



Scheme 67. Mechanistic explanation for 1,3-diene formation

In 2004, Trost *et al.* demonstrated the effects of an allylic silyl ether moiety on the stereoselectivity of ruthenium-catalyzed enyne cycloisomerizations (Scheme 68).[199] It was discovered that the *E/Z* product selectivity was reversed when exchanging the Cp ligand for the Cp* ligand on the ruthenium catalyst. When the starting enyne **196** was subjected to 10 mol% $[CpRu(MeCN)_3]PF_6$, the *trans* silyl enol ether **(*E*)-197** was favored 2.4:1. Exchange for $[Cp^*Ru(MeCN)_3]PF_6$ resulted in reversal of selectivity, with the *cis* silyl enol ether **(*Z*)-197** being favored 5:1.



Scheme 68. Cp vs. Cp* selectivity (*E*/*Z*) outcome

Examination of the ruthenacyclopentene intermediates formed from this transformation can account for the reversal in selectivity (Figure 9). Formation of the *E* olefin geometry resulted from β-hydride elimination of H_b. When the Cp ligand was exchanged for the Cp* ligand, the steric repulsion between the silyl ether and the Cp* ligand disfavored β-hydride elimination of H_b.

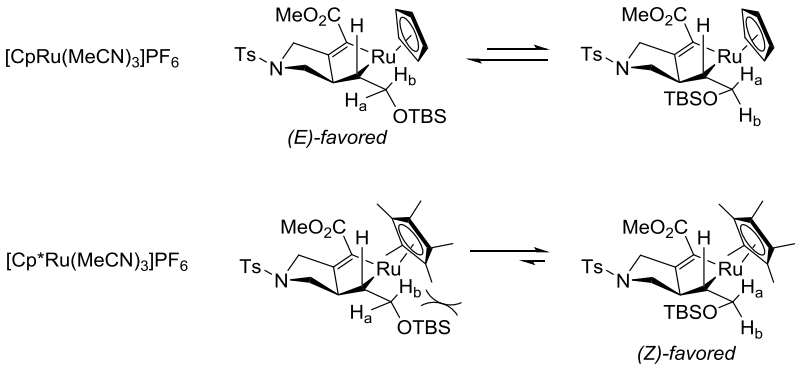
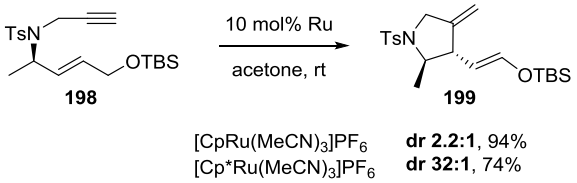


Figure 9. Comparison of intermediates: Cp vs. Cp*

When the silyl ether is orientated away from the ligand, the steric strain is relieved and H_a is placed proximally to the metal. Subsequent elimination of H_a resulted in formation of the *Z* olefin geometry.

In addition, the possible effects of the Cp and Cp* ligands on the diastereoselectivity of a cycloisomerization was examined (Scheme 69).[199]



Scheme 69. Cp vs. Cp* stereoselectivity outcome

It was observed that the diastereomeric ratio (d.r.) of the resulting diene **199** was greatly enhanced from 2.2:1 to 32:1 when the Cp ligand was exchanged for the Cp* ligand. The rationale behind the enhancement in selectively can be explained from examination of the ruthenacyclopentene intermediate formed (Figure 10).

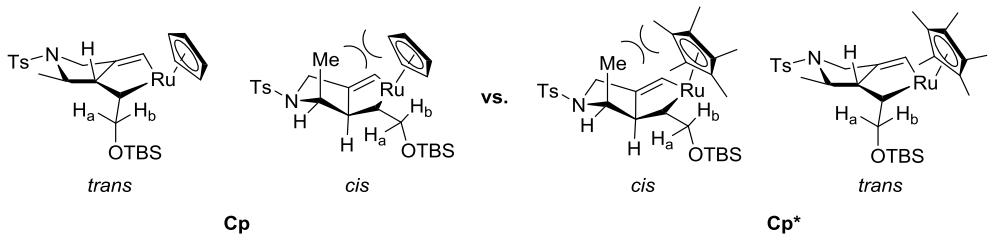
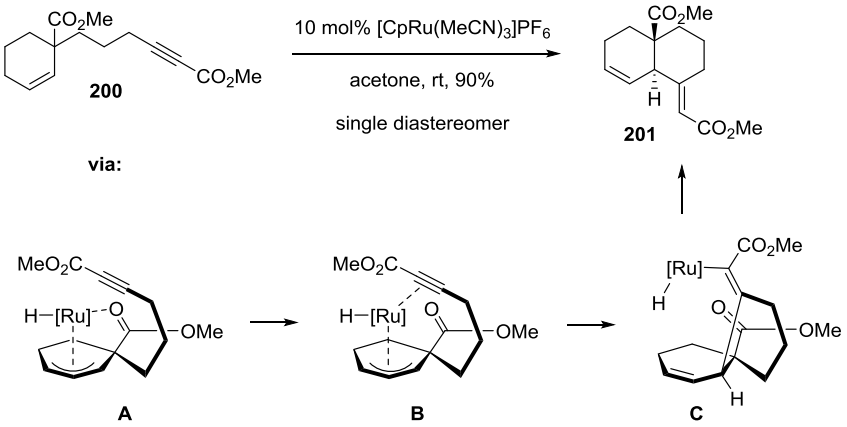


Figure 10. Comparison of intermediates to account for diastereoselectivity

In regards to the selectivity with the Cp ligand, the *trans* isomer is somewhat favored due to only a slight steric interaction being observed between the methyl group and the Cp ligand present in the *cis* intermediate. When the Cp ligand is exchanged for the Cp* ligand, the dr is dramatically

improved because the steric interaction is significantly enhanced between the ligand and methyl group.

In 2008, Trost *et al*. extended their ruthenium-catalyzed methodology to include formation of *trans*-fused decalin scaffolds (Scheme 57).[104]

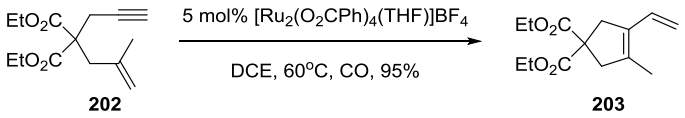


Scheme 70. Synthesis of *trans*-fused decalin system

In the presence of 10 mol% $[CpRu(MeCN)_3]PF_6$, the starting 1,7-enynoate **200** gave a 90% yield of the *trans*-decalin system **201** as a single diastereomer. A variety of 1,7-enynes were scrutinized but it was deemed necessary to have an electron withdrawing group (ester, aldehyde, amide) at the quaternary center of the enyne substrate. In addition, the enynes investigated contained an ester or amide moiety on the alkyne terminus. It was initially hypothesized by the group that a *cis*-fused decalin system would arise from the reaction conditions. It was thought that the electron withdrawing group on the alkyne would act as a directing group for allylic C-H activation. However, it was determined that since the carbon-carbon bond formation occurred syn to the ester, the C-H insertion must have occurred from the same face. Therefore, the

carbonyl moiety on the quaternary center acted as a directing group and allowed for the stereoselective formation of the allyl ruthenium species (Scheme 70). Subsequent ligand exchange, carboruthenation and reductive elimination generated the *trans*-fused decalin product as a single diastereomer.

Recently, Chatani *et al.* reported the cycloisomerization of 1,6-enynes catalyzed by a mixed valence Ru(II)-Ru(III) complex to give endocyclic 1,3-dienes in excellent yields (example shown in Scheme 71).[200] The group previously investigated the cycloisomerization of enynes catalyzed by a similar complex, $Rh_2(O_2CCF_3)_2$.[149] More recently they have investigated the catalytic activity of a $Ru_2(OAc)_4X$ complex due to its structural similarity with the rhodium species and its minimal use in organic synthesis.



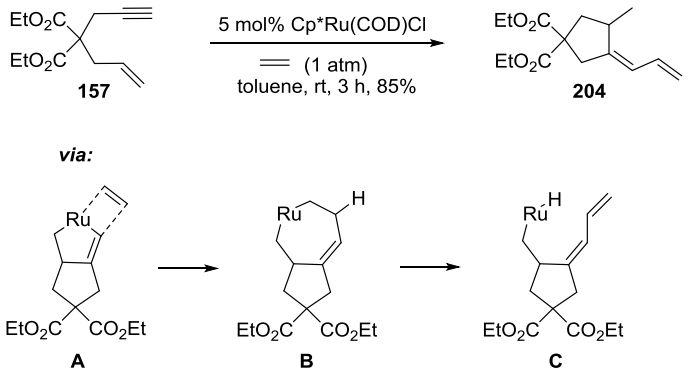
202 **203**

Scheme 71. Cycloisomerization catalyzed by a mixed valence Ru(II)-Ru(III) complex

The reaction with $[Ru_2(O_2CPh)_4(THF)]BF_4$ tolerated a variety of 1,6-enynes bearing alkyl and aromatic functionality. In addition, it was observed that the yields of the dienes were dramatically improved when the reactions were carried out under an atmosphere of CO (or O_2). It was believed that a CO atmosphere increased the electrophilicity of the catalyst by coordinating to the ruthenium, which in turn greater facilitated the interaction between the metal and the alkyne moiety due to its π-acidity.[201]

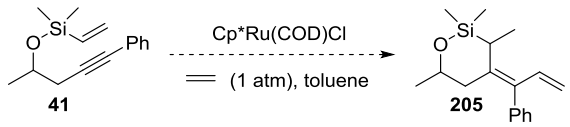
4.2 REACTION DISCOVERY

Initially, we were intrigued by methodology reported by Mori *et al.* that gave unique 1,3-diene systems (Scheme 72).[202] Subjection of 1,6-enyne **157** to 5 mol% Cp*Ru(COD)Cl under an atmosphere of ethylene produced 1,3-diene **204** in 85% yield. The methodology was intriguing because the expected reductive elimination pathway did not occur (typically observed with ruthenacyclopentene intermediates).[5]



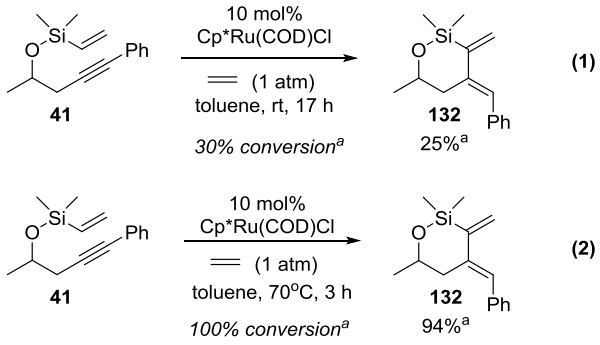
Scheme 72. Mori's novel alkenylative cyclization

Mori proposed that once oxidative cyclization of the starting enyne (ruthenacyclopentene formation) occurred, insertion of ethylene (**A** in Scheme 72) generated a ruthenacycloheptene intermediate **B**. Subsequent β-hydride elimination gave a ruthenium hydride complex **C** which underwent reductive elimination to form the 1,3-diene product **204**. We sought to apply this novel methodology to our silicon-tethered alkyne substrates (Scheme 73).



Scheme 73. Expected product with Mori's conditions

The investigation began by reacting silicon-tethered alkyne **41** with 10 mol% Cp*Ru(COD)Cl under an atmosphere of ethylene in toluene at room temperature (Scheme 74, eq. 1). After 4 hours, analysis of the reaction by TLC indicated a new spot (possibly product) but starting material remained. After 17 hours, 30% conversion of **41** was obtained and the only product observed was diene **132**, which was believed to result from a cycloisomerization pathway.



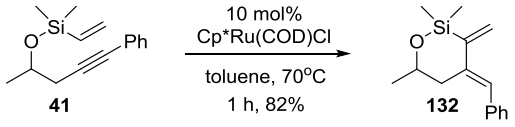
Scheme 74. Reaction discovery

[a] Conversions and crude yield were determined by H NMR using mesitylene as an internal standard.

Increasing the reaction temperature to 70°C (Scheme 74, eq. 2) resulted in 100% conversion of **41** in only 3 hours. A 94% crude yield of **132** was obtained. This type of product was seen with the silylvinylation methodology discussed in chapter 3, but only as a minor isomer. This result

was intriguing because this chemistry provided a potential route for selectively obtaining these products.

Based on the prediction of **132** resulting from a cycloisomerization pathway, it was desired to determine if an atmosphere of ethylene was necessary for the reaction to proceed (Scheme 75). The reaction of alkyne **41** with 10 mol% Cp*Ru(COD)Cl in toluene at 70°C under $Ar_{(g)}$ shortened the reaction time to 1 hour and a quantitative crude yield of **132** (82% isolated) was obtained. Based on this result, it was determined that ethylene was not needed in the reaction.



100% conversion[a]
quantitative crude yield[a]

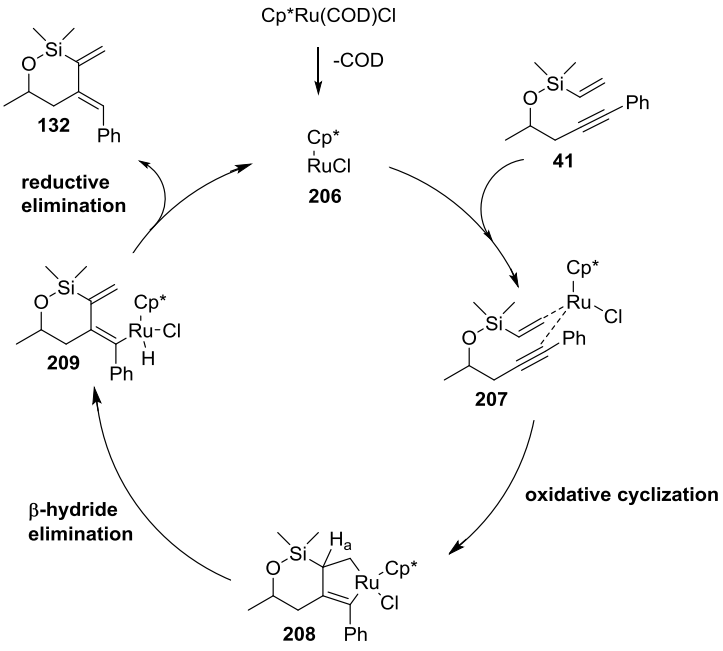
Scheme 75. Reaction discovery: argon atmosphere

[a] Determined by ^{1}H NMR using mesitylene as an internal standard.

Typically when a 1,7-enyne is subjected to ruthenium-catalyzed cycloisomerization conditions, a 1,4-diene is formed (as discussed in 4.1.1 of this thesis). It was pleasing to discover that our new methodology extended the utility of such ruthenium-catalyzed cyclization reactions to selectively give a 1,3-diene from a 1,7-enyne.

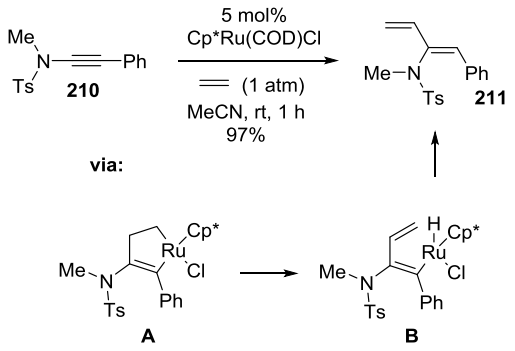
4.3 MECHANISTIC HYPOTHESIS

Mechanistically, the transformation is believed to proceed as follows (Scheme 76): dissociation of the COD ligand (**206**) and coordination to the 1,7-enyne **41** gives **207**, which undergoes oxidative cyclization to form ruthenacyclopentene **208**. To selectively obtain the exocyclic diene that was observed (**132**), it is believed that a endocyclic β-hydride elimination of H_a must occur to form the vinyl ruthenium hydride **209**. Subsequent reductive elimination produces the 1,3-diene **132** and regenerates the active catalytic species.



Scheme 76. Mechanistic hypothesis

The ruthenium complex Cp*Ru(COD)Cl has been previously shown to undergo ruthenacyclopentene formation (Scheme 77). Sato *et al.* used Cp*Ru(COD)Cl to catalyze the regio- and stereoselective formation of 2-amino-1,3-dienes.[203]



Scheme 77. Example of Cp*Ru(COD)Cl forming a ruthenacyclopentene intermediate

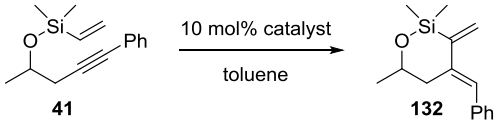
It was proposed that Cp*Ru(COD)Cl catalyzed the oxidative cyclization of ynamide **210** and ethylene to generate a ruthenacyclopentene **A**, which subsequently underwent β-hydride elimination to afford **B** and reductive elimination to give the 2-amino-1,3-diene product **211**.

4.4 REACTION OPTIMIZATION[204]

4.4.1 Catalyst Screen

It was sought to design a route to selectively obtain **132** by moving away from ruthenium hydride complexes (typically known to form dienes via hydrometallation).[1, 19] The investigation

began by treating 10 mol% of the ruthenium *p*-cymene dimer $[RuCl_2(p\text{-cymene})]_2$ with alkyne **41** in toluene at 70°C (Table 27, entry 1). After 8 hours no reaction was observed. Complexes bearing the chelating dppm ligand (entries 2 and 3) also were ineffective for the cyclization. The cationic ruthenium complex $[CpRu(MeCN)_3]PF_6$ (favored by Trost) was also unreactive (entry 4). The indenyl bis-triphenylphosphine complex in entry 5 gave only a 13% crude yield of **132** after 17 hours.



41 **132**

Entry	Catalyst	Temp (°C)	Time (h)	Yield[a]
1	$[RuCl_2(p\text{-cymene})]_2$	70	8	NR
2	RuCl(Ind)(dppm)	70	18	NR
3	CpRuCl(dppm)	70	17	NR
4	$[CpRu(MeCN)_3]PF_6$	70	6	NR
5	$RuCl(Ind)(PPh_3)_2$	70	17	13
6	$CpRuCl(PPh_3)_2$	70	18	86
7	$Cp^*RuCl(PPh_3)_2$	70	2	>98
8	Cp*Ru(COD)Cl	70	1	>98
9[b]	Cp*Ru(COD)Cl	70	20	90
10	Cp*Ru(COD)Cl	50	16	>98
11	Cp*Ru(COD)Cl	23	16	11

Table 27. Catalyst screen

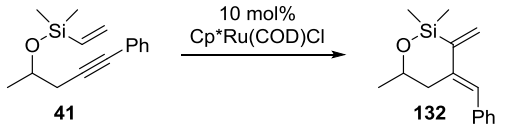
[a] Crude yield determined by ^{1}H NMR using mesitylene as an internal standard. [b] Reaction run with 5 mol% catalyst.

Full conversion of alkyne **41** was achieved after 18 hours with the Cp bis-triphenylphosphine complex in entry 6 and **132** was obtained in 86% yield. Exchange for the Cp* ligand proved more effective and gave full conversion of **41** with a quantitative yield of **132** after 2 hours (entry 7). We hypothesize that the bulky Cp* ligand increases the rate of β-hydride elimination.[205, 206] Exchange of the triphenylphosphine ligand for the COD ligand (Cp*Ru(COD)Cl, as previously

noted in Scheme 75), resulted in consumption of the starting material after 1 hour and gave quantitative crude yield of **132**. With these results in hand, it was concluded that Cp*Ru(COD)Cl proved to be optimal for the cyclization because of quantitative crude yield of **132** being obtained in a reduced reaction time of 1 hour (Table 27, entry 8). Reduction of the loading of Cp*Ru(COD)Cl to 5 mol% gave 90% crude yield of the product after 20 hours (entry 9), so \10 mol% was deemed necessary for the cyclization. Having found Cp*Ru(COD)Cl the most apt for the transformation, additional reaction temperatures were examined. Decreasing the reaction temperature to 50℃ (entry 10) resulted in quantitative yield of **132** however, a much longer reaction time was required; room temperature (entry 11) proved futile with only 11% yield of **132** observed after 16 hours. Entry 8, 10 mol% Cp*Ru(COD)Cl at 70°C, proved to be optimal for the cyclization.

4.4.2 Solvent Screen

Additional solvents were examined with 10 mol% Cp*Ru(COD)Cl (Table 28). Methanol at 70℃ consumed the starting material rapidly (30 minutes) however, the major product observed was the desilylated starting alkyne (entry 2).



Entry	Solvent	Temp (°C)	Time (h)	Conversion[a]	Yield[a]
1	Toluene	70	1	100%	>98%
2	Methanol	70	0.5	100%	15%
3	DMF	70	1.5	100%	>98%
4	DCE	70	1.5	100%	>98%
5	DCM	45	8	77%	77%
6	Acetone	60	6	100%	>98%

Table 28. Solvent screen

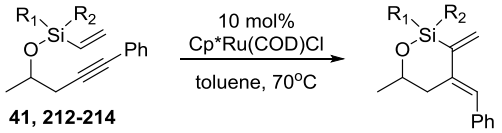
[a] Determined by crude ^{1}H NMR using mesitylene as an internal standard.

DMF, one of the solvents of choice for Trost in cycloisomerization reactions, gave 100% conversion of **41** and quantitative crude yield of **132** after 1.5 hours (entry 3); DCE gave identical results (entry 4). Only 77% conversion of the starting enyne was observed after 8 hours with DCM at reflux (entry 5). Lastly, acetone (another solvent of choice for Trost) was sluggish in the transformation but gave quantitative crude yield of **132** after 6 hours (entry 6). Based on the results from the solvent screen, it was concluded that toluene proved superior due to quantitative crude yield of product observed after 1 hour (entry 1).

4.4.3 Variation of Silicon Tether

Variations to the substituents on silicon were explored utilizing the optimized conditions (Table 29). Both methyl-phenyl (entry 2) and diphenyl (entry 3) substituted silanes (**212** and **213**) gave shorter reaction times compared to the dimethyl in entry 1, presumably due to an increased Thorpe-Ingold effect.[39, 207] Having bulky isopropyl groups on the silane hampered the

reaction and only 26% conversion of the starting alkyne **214** was observed after 45 hours. It is believed the steric bulk on the silicon hindered the formation of the ruthenacyclopentene. Although the reaction times of alkynes **212** and **213** were shorter, the dimethylvinyl silicon tether (entry 1, alkyne **41**) was chosen due the availability and low cost of the starting vinyldimethylchlorosilane (<$1 per gram from Gelest).



Entry	Alkyne[a]	R_1	R_2	Time (h)	Conversion[b]	Product	Yield[b,c]
1	**41**	Me	Me	1	100%	**132**	>98% (82%)
2	**212**	Me	Ph	0.5	100%	**215**	>98% (83%)
3	**213**	Ph	Ph	0.5	100%	**216**	>98% (85%)
4	**214**	*i*Pr	*i*Pr	45	26%	**217**	26%

Table 29. Variation of silicon tether

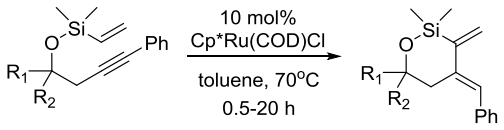
[a] The preparations for the silicon-tethered alkynes can be found in the experimental chapter of this thesis.

[b] Determined by crude ^{1}H NMR using mesitylene as an internal standard. [c] Isolated yield reported in parentheses.

4.5 SUBSTRATE SCOPE

With optimized reaction conditions in hand, the alkyne substrate tolerance for the cycloisomerization was examined. It began by exploring substrates bearing a phenyl group on the alkyne terminus (Table 30). Alkyl functionality (methyl and *n*-heptyl) at R_1 was well tolerated and gave **132** and **220** in good yields of 82% and 80% (entries 1 and 2). Hydrogen at R_1

was also tolerated (entry 3) and gave **221** in 77% yield. Cyclohexyl and phenyl groups performed well and gave dienes **222** and **223** in good yields of 88% and 75%, respectively (entries 4 and 5). A nitro group was tolerated on the phenyl ring and **224** was isolated in 71% yield (entry 6). The biphenyl moiety (entry 7) performed well and gave an excellent yield (93%) of **225**. An increase of the Thorpe-Ingold effect in the starting alkynes (entries 8 and 9) resulted in an excellent isolated yield of 94% of both **226** and **227**. Lastly, a *trans*-fused bicyclic system **228** was achieved in 73% yield (entry 10).



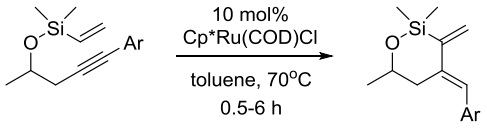
Entry	Alkyne[a]	Product	Yield[b]	Alkyne[a]	Entry	Product	Yield[b]
1	**41**	**132**	82	**117**	6	**224**	71
2	**55**	**220**	80	**61**	7	**225**	93
3	**218**	**221**	77	**62**	8	**226**	94
4	**57**	**222**	88	**63**	9	**227**	94
5	**58**	**223**	75	**219**	10	**228** (racemic)	73

Table 30. Phenyl-substituted alkyne substrate scope

[a] The preparations for the silicon-tethered alkynes can be found in the experimental chapter of this thesis. [b] Isolated yield after purification by column chromatography.

Next various aryl substitution at the alkyne terminus was examined (Table 31). The electron-donating methoxy group was well tolerated and **232** was isolated in 89% yield (entry 1). Additionally, the electron-withdrawing acetyl and nitro moieties were well tolerated and gave good yields of the desired dienes **233** and **234** (76% and 85%, entries 2 and 3). Substrates bearing tolyl and xylyl substituents (entries 4 and 5) gave the products **235** and **236** in 80% yield,

respectively. The *para*-fluoro and *ortho*-chloro moieties gave good and excellent yields of **237** and **238** (81% and 95%, entries 6 and 7). Lastly, the potentially chelating and basic pyridine moiety was tolerated in the reaction and a 52% isolated yield of **239** was obtained (entry 8).



Entry	Alkyne[a]	Product	Yield[b]	Entry	Alkyne[a]	Product	Yield[b]
1	**65**	**232** 4-MeOPh	89	5	**67**	**236** 3,5-xyl	80
2	**229**	**233** 4-AcPh	76	6	**64**	**237** 4-FPh	81
3	**150**	**234** 4-NO_2Ph	85	7	**230**	**238** 2-ClPh	95
4	**66**	**235** 4-tol	80	8[c]	**231**	**239** 3-pyr	52

Table 31. Aryl-substituted alkyne substrate scope

[a] The preparations for the silicon-tethered alkynes can be found in the experimental chapter of this thesis. [b] Isolated yield after purification by column chromatography. [c] Reaction run with 12 mol% catalyst.

The substrate scope was expanded to include alkyl functionality on the alkyne terminus (Table 32). Methyl-substituted alkyne **68** gave the desired diene **155** in 64% yield. A 5% increase in isolated yield of **155** was achieved compared to our previous methodology utilizing

MVK (chapter 3). It was pleasing to discover the reaction tolerance to cyclopropyl-substituted alkyne **240**, allowing for isolation of diene **241** in 74% yield.

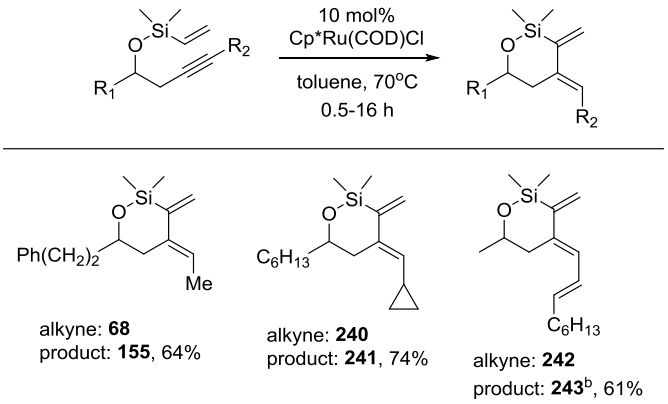
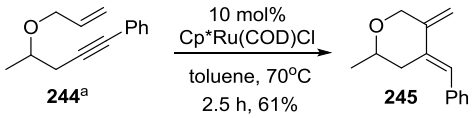


Table 32. Alkyl substrate scope[a,c]

[a] Isolated yields after purification by column chromatography. [b] Reaction run with 15 mol% catalyst. [c] The preparations for the silicon-tethered alkynes can be found in the experimental chapter of this thesis.

Lastly, olefinic substitution on the alkyne terminus was utilized and a 61% yield of triene **243** was obtained.

To finish the substrate scope, it was desired to know if silicon was needed in the tether for the cycloisomerization to proceed. This was answered by synthesizing allyl-tethered alkyne **244** and subjecting it to the standard reaction conditions (Scheme 78).



Scheme 78. Non-silicon tether variation

[a] The preparation of alkyne **244** can be found in the experimental chapter of this thesis.

The reaction proceeded smoothly and gave diene **245** in 61% isolated yield after 2.5 hours. With this result it was concluded that silicon is not needed in the tether of the substrates.

It is important to note that several alkyne substrates proved difficult with the reaction conditions (Figure 11). An alkyne bearing a bulky 1-napthyl moiety resulted in only 56% conversion and a 34% crude yield of diene **246** was observed after 7 hours. The bulkiness of the napthyl group can be attributed to the poor reactivity. A terminal alkyne possessing a biphenyl moiety at the homopropargylic position (to avoid volatility) was also examined. With 10 mol% catalyst, 40% conversion and 40% crude yield of **247** was observed. Increase of the catalyst loading to 13 mol% did not change reactivity or product yield. An attempt at forming a seven-membered ring substrate **248** was unsuccessful and only 5% conversion and 5% crude yield was observed. The addition of a methyl group alpha to the oxygen atom improved the crude yield and conversion of expected diene **249** to 20% but no further improvements were observed.

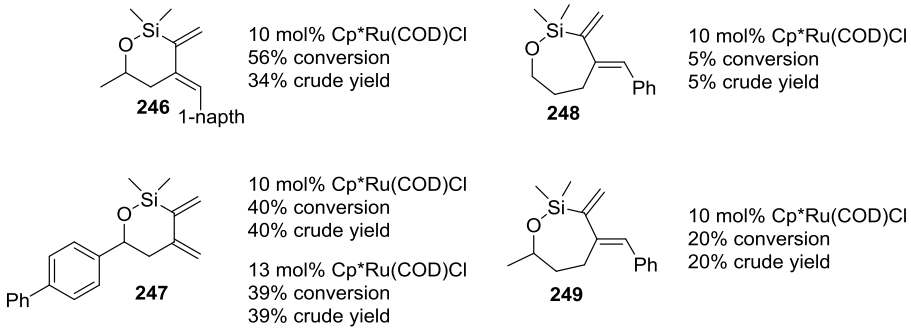


Figure 11. Difficult substrates[a]

[a] Conversions and crude yields were determined by ^{1}H NMR using mesitylene as an internal standard.

Several alkynes we examined were unreactive in the cycloisomerization (Figure 12). Alkyne **250**, bearing a bulky mesityl moiety on the alkyne terminus proved unreactive. Attempts to form a five-membered ring product from alkyne **251** and an eight-membered ring from alkyne **252** were unsuccessful. Exchange of the vinyl silicon tether for *Z* and *E* styryl tethered alkynes **253** and **254** resulted in no product formation. Lastly, acrylate-tethered alkyne **255** proved unreactive to the conditions.

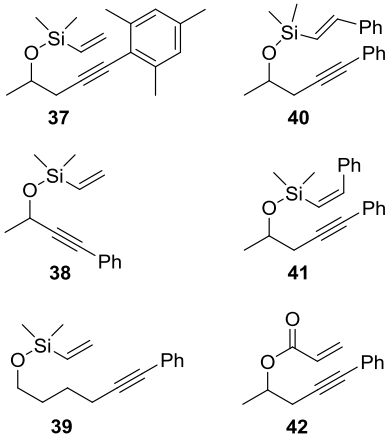


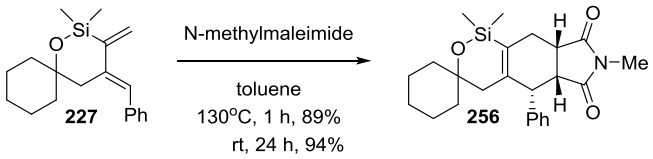
Figure 12. Unreactive alkyne substrates[a]

[a] Only starting material observed in crude ^{1}H NMR after subjection of alkyne with 10 mol% Cp*Ru(COD)Cl.

4.6 PRODUCT DERIVATIZATION

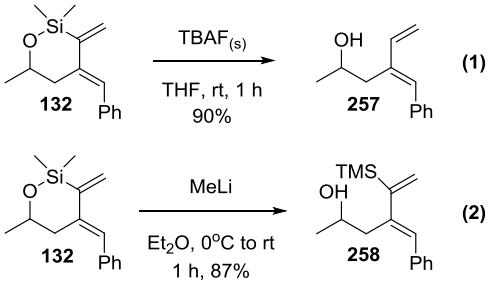
The synthetic utility of the cycloisomerization products was demonstrated utilizing various transformations. The Diels-Alder reaction of diene **227** and *N*-methylmaleimide in toluene in a sealed tube at 130°C gave the highly substituted tetracyclic system **256** as the endo

isomer (confirmed by NOESY and COSY NMR) in 89% yield (Scheme 79). It was then discovered that the reaction could be performed at room temperature with an improved isolated yield of 94%.



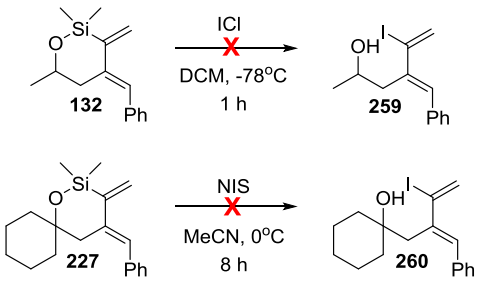
Scheme 79. Diels-Alder reaction of 227

Protiodesilylation of **132** using TFAF gave known alcohol **257**[26] in an excellent yield of 90% (Scheme 808, eq. 1). Addition of methyllithium[208] gave hydroxy silane **258** in 87% yield and required no purification (eq. 2).



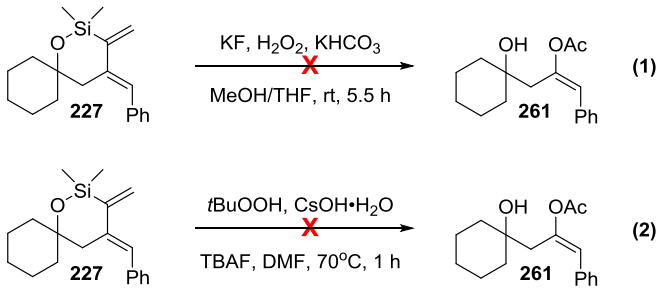
Scheme 80. Synthetic elaboration of 132

Attempts to form the vinyl iodides **259** and **260** were unsuccessful with ICl and NIS (Scheme 81). In both cases decomposition of the starting materials **132** and **227** was observed after the designated reaction time.



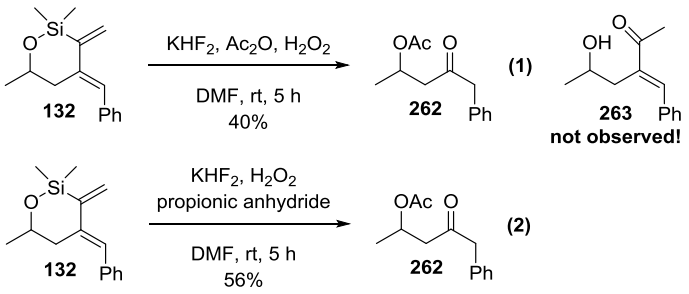
Scheme 81. Attempts at iododesilylation

Numerous attempts were made to facilitate the Fleming-Tamao oxidation of **227** (Scheme 82). Conditions reported by Marshall[209] (eq. 1) resulted in 90% recovery of starting material and conditions reported by Woerpel[210] (eq. 2) gave starting material decomposition in 1 hour.



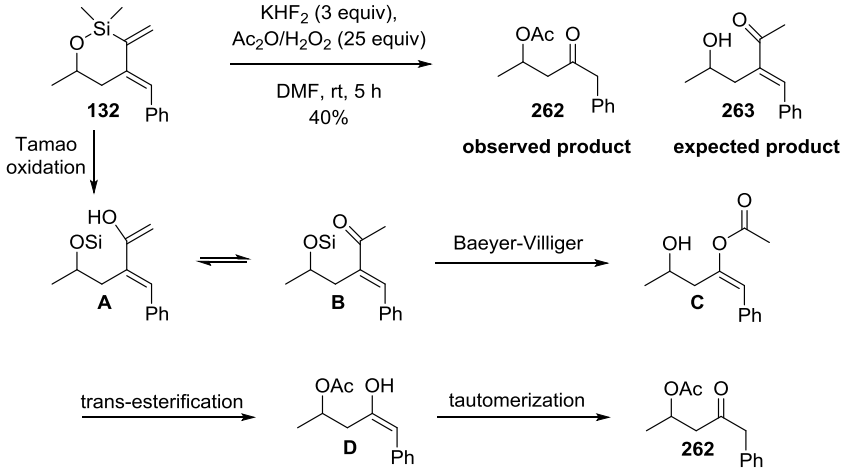
Scheme 82. Initial attempts at Fleming-Tamao oxidation of 227

Later, conditions (potassium hydrogen fluoride, acetic anhydride, peroxide, DMF) were discovered to effect the Tamao oxidation[211] however, the expected product **263** was not obtained (Scheme 83, eq. 1). Instead, keto ester **262** was isolated in 40% yield.



Scheme 83. Unexpected product from Fleming-Tamao oxidation

The formation of **262** is attributed as follows (Scheme 84): Oxidation of **132** resulted in formation of enol silane **A**, which underwent Baeyer-Villager oxidation to generate the hydroxy enol-acetate **C** (with loss of silicon). *Trans*-esterification and tautomerization formed the keto-ester **262**. To prove the mechanistic hypothesis, the oxidation was conducted with propionic anhydride (Scheme 83, eq. 2). With delight, keto ester **262** was obtained in an improved isolated yield of 56% (Scheme 83, eq. 2).



Scheme 84. Mechanistic hypothesis for Fleming-Tamao oxidation

4.7 CONCLUSION

In conclusion, the formation of 1,3-dienes by a ruthenium-catalyzed cycloisomerization of silicon-tethered 1,7-enynes was demonstrated. The transformation is believed to proceed via a ruthenacyclopentene followed by a rare endocyclic β-hydride elimination to generate the diene product. A wide variety of substitution on the starting enynes was tolerated, including both aryl and alkyl functionality in good to excellent yields. Variation of the substituents on the silicon atom was also accomplished and well tolerated. In addition, it was determined silicon is not required in the starting enyne for the reaction to proceed.

The synthetic utility of the 1,3-dienes was demonstrated via various organic transformations. A Diels-Alder reaction with *N*-methylmaleimide selectively formed the endo isomer product in excellent yield. The unexpected formation of a keto-ester was accomplished via a Fleming-Tamao oxidation. The highly functionalized cyclic and acyclic substrates obtained from the derivatization of the cycloisomerization adducts can be utilized for further elaboration into more complex molecular structures.

A future direction for this project is the development of reaction conditions that will tolerate styryl silicon tethers and various alkyl substituted olefinic silicon tethers. This would allow for further product diversity on the diene scaffold.

5.0 BIBLIOGRAPHY

1. Nishida, M.; Adachi, N.; Onozuka, K.; Matsumura, H.; Mori, M. Intramolecular Cyclizations of Enynes Using $RuClH(CO)(PPh_3)_3$. *J. Org. Chem.* **1998**, *63*, 9158-9159.

2. Trost, B. M.; Ball, Z. T. Addition of Metalloid Hydrides to Alkynes: Hydrometallation with Boron, Silicon, and Tin. *Synthesis* **2005**, *2005*, 853-887.

3. Trost, B. M.; Papillon, J. P. N.; Nussbaumer, T. Ru-Catalyzed Alkene−Alkyne Coupling. Total Synthesis of Amphidinolide P. *J. Am. Chem. Soc.* **2005**, *127*, 17921-17937.

4. Mulzer, J.; Ohler, E. *Topics Organomet. Chem.* **2004**, *13*, 269.

5. Trost, B. M.; Toste, F. D.; Pinkerton, A. B. Non-Metathesis Ruthenium-Catalyzed C−C Bond Formation. *Chem. Rev.* **2001**, *101*, 2067-2096.

6. Trost, B. M.; Frederiksen, M. U.; Rudd, M. T. Ruthenium-Catalyzed Reactions—A Treasure Trove of Atom-Economic Transformations. *Angew. Chem., Int. Ed.* **2005**, *44*, 6630-6666.

7. Kakiuchi, F.; Yamamoto, Y.; Chatani, N.; Murai, S. Catalytic Addition of Aromatic C-H Bonds to Acetylenes. *Chem. Lett.* **1995**, *24*, 681-682.

8. Kakiuchi, F.; Sato, T.; Tsujimoto, T.; Yamauchi, M.; Chatani, N.; Murai, S. New Protocol for the Siteselective Alkylation and Vinylation of Aromatic Compounds. Catalyst-Specific Reactions. *Chem. Lett.* **1998**, *27*, 1053-1054.

9. Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. Efficient catalytic addition of aromatic carbon-hydrogen bonds to olefins. *Nature* **1993**, *366*, 529-531.

10. Kakiuchi, F.; Uetsuhara, T.; Tanaka, Y.; Chatani, N.; Murai, S. Ruthenium-catalyzed addition of olefinic C–H bonds in conjugate enones to acetylenes to give conjugate dienones. *J. Mol. Catal. A: Chem.* **2002**, *182–183*, 511-514.

11. Diver, S. T.; Giessert, A. J. Enyne Metathesis (Enyne Bond Reorganization). *Chem. Rev.* **2004**, *104*, 1317-1382.

12. Hansen, E. C.; Lee, D. Search for Solutions to the Reactivity and Selectivity Problems in Enyne Metathesis. *Acc. Chem. Res.* **2006**, *39*, 509-519.

13. Diver, S. T. Ruthenium vinyl carbene intermediates in enyne metathesis. *Coord. Chem. Rev.* **2007**, *251*, 671-701.

14. Lau, C. P.; Ng, S. M.; Jia, G.; Lin, Z. Some ruthenium hydride, dihydrogen, and dihydrogen-bonded complexes in catalytic reactions. *Coord. Chem. Rev.* **2007**, *251*, 2223-2237.

15. Santos, A.; Lopez, J.; Montoya, J.; Noheda, P.; Romero, A.; Echavarren, A. M. Synthesis of New Ruthenium(II) Carbonyl Hydrido, Alkenyl, and Alkynyl Complexes with Chelating Diphosphines. *Organometallics* **1994**, *13*, 3605-3615.

16. Marchenko, A. V.; Gerard, H.; Eisenstein, O.; Caulton, K. G. A comprehensive view of M-H addition across the RCCH bond: frustration culminating in ultimate union. *New J. Chem.* **2001**, *25*, 1244-1255.

17. Mitsudo, T.-a.; Zhang, S.-W.; And, M. N.; Watanabe, Y. Ruthenium complex-catalysed highly selective codimerisation of acetylenes and alkenes. *J. Chem. Soc., Chem. Commun.* **1991**, 598-599.

18. Yi, C. S.; Lee, D. W.; Chen, Y. Hydrovinylation and [2+2] Cycloaddition Reactions of Alkynes and Alkenes Catalyzed by a Well-Defined Cationic Ruthenium−Alkylidene Complex. *Organometallics* **1999**, *18*, 2043-2045.

19. Mori, M.; Kozawa, Y.; Nishida, M.; Kanamaru, M.; Onozuka, K.; Takimoto, M. Synthesis of Carbapenam Skeletons Using a Ruthenium-Catalyzed Cyclization. *Org. Lett.* **2000**, *2*, 3245-3247.

20. Walkowiak, J.; Jankowska-Wajda, M.; Marciniec, B. A New Catalytic Route to Boryl- and Borylsilyl-Substituted Buta-1,3-dienes. *Chem.–Eur. J.* **2008**, *14*, 6679-6686.

21. Neisius, N. M.; Plietker, B. The Ruthenium-Catalyzed Hydrovinylation of Internal Alkynes by Acrylates: An Atom Economic Approach to Highly Substituted 1,3-Dienes. *Angew. Chem., Int. Ed.* **2009**, *48*, 5752-5755.

22. Marciniec, B. Catalytic Coupling of sp^2- and sp-Hybridized Carbon–Hydrogen Bonds with Vinylmetalloid Compounds. *Acc. Chem. Res.* **2007**, *40*, 943-952.

23. Bracegirdle, S.; Anderson, E. A. Recent advances in the use of temporary silicon tethers in metal-mediated reactions. *Chem. Soc. Rev.* **2010**, *39*, 4114-4129.

24. Suginome, M.; Ito, Y. Transition-Metal-Catalyzed Additions of Silicon−Silicon and Silicon−Heteroatom Bonds to Unsaturated Organic Molecules. *Chem. Rev.* **2000**, *100*, 3221-3256.

25. Kawasaki, Y.; Ishikawa, Y.; Igawa, K.; Tomooka, K. Directing Group-Controlled Hydrosilylation: Regioselective Functionalization of Alkyne. *J. Am. Chem. Soc.* **2011**, *133*, 20712-20715.

26. Zhao, J.; Liu, S.; Marino, N.; Clark, D. A. Regio- and stereoselective trans-silylvinylation of internal alkynes catalyzed by $RuHCl(CO)(PCy_3)_2$. *Chem. Sci.* **2013**, *4*, 1547-1551.

27. Beach, N. J.; Dharmasena, U. L.; Drouin, S. D.; Fogg, D. E. Improved Syntheses of Versatile Ruthenium Hydridocarbonyl Catalysts Containing Electron-Rich Ancillary Ligands. *Adv. Synth. Catal.* **2008**, *350*, 773-777.

28. Hoffmann, M.; Marciniec, B. Quantum chemical study of the mechanism of ethylene elimination in silylative coupling of olefins. *J. Mol. Model.* **2007**, *13*, 477-483.

29. Tanaka, K.; Fu, G. C. A Versatile New Method for the Synthesis of Cyclopentenones via an Unusual Rhodium-Catalyzed Intramolecular Trans Hydroacylation of an Alkyne. *J. Am. Chem. Soc.* **2001**, *123*, 11492-11493.

30. Tanaka, K.; Fu, G. C. Enantioselective Synthesis of Cyclopentenones via Rhodium-Catalyzed Kinetic Resolution and Desymmetrization of 4-Alkynals. *J. Am. Chem. Soc.* **2002**, *124*, 10296-10297.

31. Chung, L. W.; Wiest, O.; Wu, Y.-D. A Theoretical Study on the trans-Addition Intramolecular Hydroacylation of 4-Alkynals Catalyzed by Cationic Rhodium Complexes. *J. Org. Chem.* **2008**, *73*, 2649-2655.

32. Sudo, T.; Asao, N.; Yamamoto, Y. Synthesis of Various Silacycles via the Lewis Acid-Catalyzed Intramolecular Trans-Hydrosilylation of Unactivated Alkynes. *J. Org. Chem.* **2000**, *65*, 8919-8923.

33. Asao, N.; Shimada, T.; Shimada, T.; Yamamoto, Y. Lewis Acid Catalyzed Stereoselective Carbosilylation. Intramolecular trans-Vinylsilylation and trans-Arylsilylation of Unactivated Alkynes. *J. Am. Chem. Soc.* **2001**, *123*, 10899-10902.

34. Trost, B. M.; Ball, Z. T. Markovnikov Alkyne Hydrosilylation Catalyzed by Ruthenium Complexes. *J. Am. Chem. Soc.* **2001**, *123*, 12726-12727.

35. Trost, B. M.; Ball, Z. T. Intramolecular Endo-Dig Hydrosilylation Catalyzed by Ruthenium: Evidence for a New Mechanistic Pathway. *J. Am. Chem. Soc.* **2003**, *125*, 30-31.

36. Chung, L. W.; Wu, Y.-D.; Trost, B. M.; Ball, Z. T. A Theoretical Study on the Mechanism, Regiochemistry, and Stereochemistry of Hydrosilylation Catalyzed by Cationic Ruthenium Complexes. *J. Am. Chem. Soc.* **2003**, *125*, 11578-11582.

37. Trost, B. M.; Ball, Z. T. Alkyne Hydrosilylation Catalyzed by a Cationic Ruthenium Complex: Efficient and General Trans Addition. *J. Am. Chem. Soc.* **2005**, *127*, 17644-17655.

38. Denmark, S. E.; Pan, W. Intramolecular Anti-Hydrosilylation and Silicon-Assisted Cross-Coupling: Highly Regio- and Stereoselective Synthesis of Trisubstituted Homoallylic Alcohols. *Org. Lett.* **2002**, *4*, 4163-4166.

39. Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. The formation and stability of spiro-compounds. Part I. spiro-Compounds from cyclohexane. *Journal of the Chemical Society, Transactions* **1915**, *107*, 1080-1106.

40. McKennon, M. J.; Meyers, A. I.; Drauz, K.; Schwarm, M. A convenient reduction of amino acids and their derivatives. *J. Org. Chem.* **1993**, *58*, 3568-3571.

41. Gage, J. R.; Evans, D. A. *(S)*-4-(Phenylmethyl)-2-oxazolidinone. *Org. Synth.* **1990**, *68*, 77-82.

42. Gage, J. R.; Evans, D. A. Diastereoselective aldol condensation using a chiral oxazolidinone auxiliary: (2*S**, 3*S**)-3-Hydroxy-3-phenyl-2-methylpropanoic acid. *Org. Synth.* **1990**, *68*, 83-91.

43. Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. Stereoselective aldol condensations via boron enolates. *J. Am. Chem. Soc.* **1981**, *103*, 3099-3111.

44. Inoue, T.; Mukaiyama, T. Regio- and Stereoselective Cross-aldol Reactions via Dialkylboryl Triflates. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 174-178.

45. Crimmins, M. T.; She, J. An Improved Procedure for Asymmetric Aldol Additions with N-Acyl Oxazolidinones, Oxazolidinethiones and Thiazolidinethiones. *Synlett* **2004**, *2004*, 1371-1374.

46. Evans, D. A.; Kaldor, S. W.; Jones, T. K.; Clardy, J.; Stout, T. J. Total synthesis of the macrolide antibiotic cytovaricin. *J. Am. Chem. Soc.* **1990**, *112*, 7001-7031.

47. Baker, K. V.; Brown, J. M.; Hughes, N.; Skarnulis, A. J.; Sexton, A. Mechanical activation of magnesium turnings for the preparation of reactive Grignard reagents. *J. Org. Chem.* **1991**, *56*, 698-703.

48. Mc Murry, J. E.; Scott, W. J. A method for the regiospecific synthesis of enol triflates by enolate trapping. *Tetrahedron Lett.* **1983**, *24*, 979-982.

49. Comins, D. L.; Dehghani, A.; Foti, C. J.; Joseph, S. P. Pyridine-derived triflating reagents: N-(2-Pyridyl)-triflimide and N-(5-Chloro-2-pyridyl)triflimide. *Org. Synth.* **1997**, *74*, 77-83.

50. Ramharter, J.; Weinstabl, H.; Mulzer, J. Synthesis of the Lycopodium Alkaloid (+)-Lycoflexine. *J. Am. Chem. Soc.* **2010**, *132*, 14338-14339.

51. Betík, R.; Kotora, M. Enantioselective Synthesis of (–)-Methoxyestrone. *Eur. J. Org. Chem.* **2011**, *2011*, 3279-3282.

52. Gill, D. F.; Shaw, B. L. Five-coordinate complexes [$RuHCl(CO)(PBut_2R)_2$] (R = Me or Et) formed from ruthenium trichloride and the Tertiary Phosphine in 2-methoxyethanol. *Inorg. Chim. Acta* **1979**, *32*, 19-23.

53. Esteruelas, M. A.; Werner, H. Five- and six-coordinate hydrido(carbonyl)-ruthenium(II) and -osmium(II) complexes containing triisopropylphosphine as ligand. *J. Organomet. Chem.* **1986**, *303*, 221-231.

54. Dharmasena, U. L.; Foucault, H. M.; dos Santos, E. N.; Fogg, D. E.; Nolan, S. P. N-Heterocyclic Carbenes as Activating Ligands for Hydrogenation and Isomerization of Unactivated Olefins. *Organometallics* **2005**, *24*, 1056-1058.

55. Hansen, E. C.; Lee, D. Synthesis of β,β-Disubstituted Vinyl Boronates via the Ruthenium-Catalyzed Alder Ene Reaction of Borylated Alkynes and Alkenes. *J. Am. Chem. Soc.* **2005**, *127*, 3252-3253.

56. Satoh, Y.; Serizawa, H.; Miyaura, N.; Hara, S.; Suzuki, A. Organic synthesis using haloboration reactions. A formal carboboration reaction of 1-alkynes and its application to the di- and trisubstituted alkene synthesis. *Tetrahedron Lett.* **1988**, *29*, 1811-1814.

57. Lightfoot, A. P.; Twiddle, S. J. R.; Whiting, A. A stereoselective synthesis of 1,6-diphenyl-1,3,5-hexatrienes utilising 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane as a two-carbon alkenyl building block. *Org. Biomol. Chem.* **2005**, *3*, 3167-3172.

58. Suzuki, A. New application of organoboron compounds in organic synthesis. *Pure Appl. Chem.* **1986**, *58*, 629-638.

59. Thirsk, C.; Whiting, A. Polyene natural products. *J. Chem. Soc., Perkin Trans. 1* **2002**, 999-1023.

60. Johansson Seechurn, C. C. C.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. Palladium-Catalyzed Cross-Coupling: A Historical Contextual Perspective to the 2010 Nobel Prize. *Angew. Chem., Int. Ed.* **2012**, *51*, 5062-5085.

61. Suzuki, A. Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles, 1995–1998. *J. Organomet. Chem.* **1999**, *576*, 147-168.

62. Heck, R. F.; Nolley, J. P. Palladium-catalyzed vinylic hydrogen substitution reactions with aryl, benzyl, and styryl halides. *J. Org. Chem.* **1972**, *37*, 2320-2322.

63. Mizoroki, T.; Mori, K.; Ozaki, A. Arylation of Olefin with Aryl Iodide Catalyzed by Palladium. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581-581.

64. Denmark, S. E.; Sweis, R. F. Design and Implementation of New, Silicon-Based, Cross-Coupling Reactions: Importance of Silicon−Oxygen Bonds. *Acc. Chem. Res.* **2002**, *35*, 835-846.

65. Tamao, K.; Kumada, M.; Maeda, K. Silafunctional compounds in organic synthesis. Hydrogen peroxide oxidation of alkenyl(alkoxy)silanes. *Tetrahedron Lett.* **1984**, *25*, 321-324.

66. Funk, T. W.; Efskind, J.; Grubbs, R. H. Chemoselective Construction of Substituted Conjugated Dienes Using an Olefin Cross-Metathesis Protocol. *Org. Lett.* **2004**, *7*, 187-190.

67. Wang, Z.; Lu, X.; Lei, A.; Zhang, Z. Efficient Preparation of Functionalized (*E*,*Z*) Dienes Using Acetylene as the Building Block. *J. Org. Chem.* **1998**, *63*, 3806-3807.

68. Charette, A. B.; Berthelette, C.; St-Martin, D. An expedient approach to *E,Z*-dienes using the Julia olefination. *Tetrahedron Lett.* **2001**, *42*, 5149-5153.

69. Woerly, E. M.; Roy, J.; Burke, M. D. Synthesis of most polyene natural product motifs using just 12 building blocks and one coupling reaction. *Nat. Chem.* **2014**, *6*, 484-491.

70. Hitosugi, S.; Tanimoto, D.; Nakanishi, W.; Isobe, H. A Facile Chromatographic Method for Purification of Pinacol Boronic Esters. *Chem. Lett.* **2012**, *41*, 972-973.

71. Kaminsky, L.; Wilson, R. J.; Clark, D. A. Stereo- and Regioselective Formation of Silyl-Dienyl Boronates. *Org. Lett.* **2015**, *17*, 3126-3129.

72. Jiang, G.; List, B. Enantioselective hydrovinylation via asymmetric counteranion-directed ruthenium catalysis. *Chem. Comm*. **2011**, *47*, 10022-10024.

73. Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. $RuHX(CO)(PR_3)_2$: Can νCO Be a Probe for the Nature of the Ru-X Bond? *Inorg. Chem.* **1994**, *33*, 1476-1485.

74. Lightfoot, A. P.; Maw, G.; Thirsk, C.; Twiddle, S. J. R.; Whiting, A. 4,4,6-Trimethyl-2-vinyl-1,3,2-dioxaborinane: a superior 2-carbon building block for vinylboronate Heck couplings. *Tetrahedron Lett.* **2003**, *44*, 7645-7648.

75. Uno, B. E.; Gillis, E. P.; Burke, M. D. Vinyl MIDA boronate: a readily accessible and highly versatile building block for small molecule synthesis. *Tetrahedron* **2009**, *65*, 3130-3138.

76. Molander, G. A.; Rivero, M. R. Suzuki Cross-Coupling Reactions of Potassium Alkenyltrifluoroborates *Org. Lett.* **2001**, *4*, 107-109.

77. Morrill, C.; Grubbs, R. H. Synthesis of Functionalized Vinyl Boronates via Ruthenium-Catalyzed Olefin Cross-Metathesis and Subsequent Conversion to Vinyl Halides. *J. Org. Chem.* **2003**, *68*, 6031-6034.

78. Heravi, M. M.; Hashemi, E. Recent applications of the Suzuki reaction in total synthesis. *Tetrahedron* **2012**, *68*, 9145-9178.

79. Lightfoot, A. P.; Twiddle, S. J. R.; Whiting, A. 4,4,6-Trimethyl-2-vinyl-1,3,2-dioxaborinane: An Efficient and Selective 2-Carbon Building Block for Vinylboronate Suzuki-Miyaura Coupling Reactions. *Synlett* **2005**, *2005*, 529-531.

80. Chemler, S. R.; Trauner, D.; Danishefsky, S. J. The B-Alkyl Suzuki–Miyaura Cross-Coupling Reaction: Development, Mechanistic Study, and Applications in Natural Product Synthesis. *Angew. Chem., Int. Ed.* **2001**, *40*, 4544-4568.

81. Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95*, 2457-2483.

82. Ohmura, T.; Takasaki, Y.; Furukawa, H.; Suginome, M. Stereoselective Synthesis of cis-β-Methyl- and Phenyl-Substituted Alkenylboronates by Platinum-Catalyzed Dehydrogenative Borylation. *Angew. Chem., Int. Ed.* **2009**, *48*, 2372-2375.

83. Littke, A. F.; Fu, G. C. A Convenient and General Method for Pd-Catalyzed Suzuki Cross-Couplings of Aryl Chlorides and Arylboronic Acids. *Angew. Chem., Int. Ed.* **1998**, *37*, 3387-3388.

84. Le, H.; Kyne, R. E.; Brozek, L. A.; Morken, J. P. Catalytic Enantioselective Allyl–Allyl Cross-Coupling with a Borylated Allylboronate. *Org. Lett.* **2013**, *15*, 1432-1435.

85. Murphy, J. M.; Liao, X.; Hartwig, J. F. Meta Halogenation of 1,3-Disubstituted Arenes via Iridium-Catalyzed Arene Borylation. *J. Am. Chem. Soc.* **2007**, *129*, 15434-15435.

86. Yoon, C. H.; Yoo, K. S.; Yi, S. W.; Mishra, R. K.; Jung, K. W. Oxygen-Promoted Palladium(II) Catalysis: Facile $C(sp^2)–C(sp^2)$ Bond Formation via Cross-Coupling of Alkenylboronic Compounds and Olefins. *Org. Lett.* **2004**, *6*, 4037-4039.

87. Shade, R. E.; Hyde, A. M.; Olsen, J.-C.; Merlic, C. A. Copper-Promoted Coupling of Vinyl Boronates and Alcohols: A Mild Synthesis of Allyl Vinyl Ethers. *J. Am. Chem. Soc.* **2010**, *132*, 1202-1203.

88. Liu, S.; Zhao, J.; Kaminsky, L.; Wilson, R. J.; Marino, N.; Clark, D. A. Ethylene Transposition: Ruthenium Hydride Catalyzed Intramolecular trans-Silylvinylation of Internal Alkynes. *Org. Lett.* **2014**, *16*, 4456-4459.

89. Saini, V.; Stokes, B. J.; Sigman, M. S. Transition-Metal-Catalyzed Laboratory-Scale Carbon–Carbon Bond-Forming Reactions of Ethylene. *Angew. Chem., Int. Ed.* **2013**, *52*, 11206-11220.

90. Denmark, S. E.; Butler, C. R. Palladium- (and nickel-) catalyzed vinylation of aryl halides. *Chem. Comm.* **2009**, 20-33.

91. RajanBabu, T. V. In Pursuit of an Ideal Carbon-Carbon Bond-Forming Reaction: Development and Applications of the Hydrovinylation of Olefins. *Synlett* **2009**, *2009*, 853-885.

92. Mans, D. J.; Cox, G. A.; RajanBabu, T. V. Ethylene in Organic Synthesis. Repetitive Hydrovinylation of Alkenes for Highly Enantioselective Syntheses of Pseudopterosins. *J. Am. Chem. Soc.* **2011**, *133*, 5776-5779.

93. Yi, C. S.; He, Z.; Lee, D. W. Hydrovinylation of Alkenes Catalyzed by the Ruthenium−Hydride Complex Formed in Situ from $(PCy_3)_2(CO)RuHCl$ and $HBF_4{\cdot}OEt_2$. *Organometallics* **2001**, *20*, 802-804.

94. Saini, V.; Sigman, M. S. Palladium-Catalyzed 1,1-Difunctionalization of Ethylene. *J. Am. Chem. Soc.* **2012**, *134*, 11372-11375.

95. Plevyak, J. E.; Heck, R. F. Palladium-catalyzed arylation of ethylene. *J. Org. Chem.* **1978**, *43*, 2454-2456.

96. Kitamura, T.; Mori, M. Ruthenium-Catalyzed Ring-Opening and Ring-Closing Enyne Metathesis. *Org. Lett*. **2001**, *3*, 1161-1163.

97. Na, Y.; Chang, S. Highly Stereoselective and Efficient Hydrosilylation of Terminal Alkynes Catalyzed by $[RuCl_2(p\text{-cymene})]_2$. *Org. Lett.* **2000**, *2*, 1887-1889.

98. Mori, A.; Takahisa, E.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. $RhCl(PPh_3)_3$/NaI Catalyst System for Hydrosilylation of 1-Alkynes: Stereodivergent Syntheses of *E*- and *Z*-Alkenylsilanes with Heteroatom Substituents on Silicon. *Chem. Lett.* **1998**, *27*, 443-444.

99. Matsuda, T.; Kadowaki, S.; Yamaguchi, Y.; Murakami, M. Gold-catalysed intramolecular trans-allylsilylation of alkynes forming 3-allyl-1-silaindenes. *Chem. Comm.* **2008**, 2744-2746.

100. Fleming, I. Tilden Lecture. Some uses of silicon compounds in organic synthesis. *Chem. Soc. Rev*. **1981**, *10*, 83-111.

101. Tamao, K.; Sumitani, K.; Kumada, M. Selective carbon-carbon bond formation by cross-coupling of Grignard reagents with organic halides. Catalysis by nickel-phosphine complexes. *J. Am. Chem. Soc.* **1972**, *94*, 4374-4376.

102. Trost, B. The atom economy--a search for synthetic efficiency. *Science* **1991**, *254*, 1471-1477.

103. Trost, B. M.; Toste, F. D. Mechanistic Dichotomy in $CpRu(CH_3CN)_3PF_6$ Catalyzed Enyne Cycloisomerizations. *J. Am. Chem. Soc.* **2002**, *124*, 5025-5036.

104. Trost, B. M.; Ferreira, E. M.; Gutierrez, A. C. Ruthenium- and Palladium-Catalyzed Enyne Cycloisomerizations: Differentially Stereoselective Syntheses of Bicyclic Structures. *J. Am. Chem. Soc*. **2008**, *130*, 16176-16177.

105. Trost, B. M.; Tanoury, G. J. An unusual mechanism of a palladium-catalyzed intramolecular carbametalation. A novel palladium-catalyzed rearrangement. *J. Am. Chem. Soc.* **1988**, *110*, 1636-1638.

106. Trost, B. M.; Lautens, M. Cyclization via isomerization: a palladium(2+)-catalyzed carbocyclization of 1,6-enynes to 1,3- and 1,4-dienes. *J. Am. Chem. Soc.* **1985**, *107*, 1781-1783.

107. Trost, B. M.; Chung, J. Y. L. Unusual substituent effect on a palladium-mediated cyclization: a total synthesis of (+/-)-sterepolide. *J. Am. Chem. Soc.* **1985**, *107*, 4586-4588.

108. Trost, B. M.; Lautens, M. An unusual dichotomy in the regioselectivity of a metal catalyzed versus thermal ene reaction. *Tetrahedron Lett.* **1985**, *26*, 4887-4890.

109. Trost, B. M.; Lee, D. C.; Rise, F. A new palladium catalyst for intramolecular carbametalations of enynes. *Tetrahedron Lett.* **1989**, *30*, 651-654.

110. Trost, B. M.; Lautens, M.; Chan, C.; Jebaratnam, D. J.; Mueller, T. Annulation via alkylation-Alder ene cyclizations. Palladium-catalyzed cycloisomerization of 1,6-enynes. *J. Am. Chem. Soc.* **1991**, *113*, 636-644.

111. Trost, B. M.; Tanoury, G. J.; Lautens, M.; Chan, C.; MacPherson, D. T. Pd-Catalyzed Cycloisomerization to 1,2- Dialkylidenecycloalkanes. *J. Am. Chem. Soc.* **1994**, *116*, 4255-4267.

112. Trost, B. M.; Romero, D. L.; Rise, F. Pd-Catalyzed Cycloisomerization to 1,2-Dialkylidenecycloalkanes. Alternative Catalyst System. *J. Am. Chem. Soc.* **1994**, *116*, 4268-4278.

113. Trost, B. M.; Czeskis, B. A. Asymmetric induction in Pd catalyzed enyne cycloisomerizations. *Tetrahedron Lett.* **1994**, *35*, 211-214.

114. Trost, B. M.; Li, Y. A New Catalyst for a Pd Catalyzed Alder Ene Reaction. A Total Synthesis of (+)-Cassiol. *J. Am. Chem. Soc.* **1996**, *118*, 6625-6633.

115. Goeke, A.; Kuwano, R.; Ito, Y.; Sawamura, M. Enantioselective Cycloisomerization of 1,6-Enynes Catalyzed by Chiral Diphosphane–Palladium Complexes. *Angew. Chem., Int. Ed.* **1996**, *35*, 662-663.

116. Hatano, M.; Terada, M.; Mikami, K. Highly Enantioselective Palladium-Catalyzed Ene-Type Cyclization of a 1,6-Enyne. *Angew. Chem., Int. Ed.* **2001**, *40*, 249-253.

117. Hatano, M.; Mikami, K. Highly Enantioselective Quinoline Synthesis via Ene-type Cyclization of 1,7-Enynes Catalyzed by a Cationic BINAP−Palladium(II) Complex. *J. Am. Chem. Soc.* **2003**, *125*, 4704-4705.

118. Delgado, A.; Rodríguez, J. R.; Castedo, L.; Mascareñas, J. L. Palladium-Catalyzed [3+2] Intramolecular Cycloaddition of Alk-5-ynylidenecyclopropanes: A Rapid, Practical Approach to Bicyclo[3.3.0]octenes. *J. Am. Chem. Soc.* **2003**, *125*, 9282-9283.

119. Kressierer, C. J.; Müller, T. J. J. A Novel One-Pot Cycloisomerization-Wittig Sequence with Yne-Allyl Alcohols. *Synlett* **2004**, *2004*, 655-658.

120. Kressierer, C. J.; Müller, T. J. J. Novel One-Pot Cycloisomerization-Knoevenagel Condensation Sequences with Yne Allyl Alcohols. *Synlett* **2005**, *2005*, 1721-1725.

121. Durán, J.; Gulías, M.; Castedo, L.; Mascareñas, J. L. Ligand-Induced Acceleration of the Intramolecular [3 + 2] Cycloaddition between Alkynes and Alkylidenecyclopropanes. *Org. Lett.* **2005**, *7*, 5693-5696.

122. Hercouet, A.; Berrée, F.; Lin, C. H.; Toupet, L.; Carboni, B. Boronated Enynes as Versatile Sources of Stereodefined and Skeletally Diverse Molecules. *Org. Lett.* **2007**, *9*, 1717-1720.

123. Trost, B. M.; Dong, L.; Schroeder, G. M. Exploiting the Pd- and Ru-Catalyzed Cycloisomerizations: Enantioselective Total Synthesis of (+)-Allocyathin B2. *J. Am. Chem. Soc.* **2005**, *127*, 10259-10268.

124. Zilke, L.; Hall, D. G. Synthetic Studies Towards the Core Tricyclic Ring System of Pradimicin A. *Eur. J. Org. Chem.* **2012**, *2012*, 4153-4163.

125. Yanagita, Y.; Suto, T.; Matsuo, N.; Kurosu, Y.; Sato, T.; Chida, N. Synthesis of Diazatricyclic Common Structure of Madangamine Alkaloids. *Org. Lett.* **2015**, *17*, 1946-1949.

126. Trost, B. M. When Is a Proton Not a Proton? *Chem.–Eur. J.* **1998**, *4*, 2405-2412.

127. Grigg, R.; Stevenson, P.; Worakun, T. Rhodium (I) catalysed regiospecific cyclisation of 1,6-enynes to methylenecyclohex-2-enes. *Tetrahedron* **1988**, *44*, 4967-4972.

128. Wender, P. A.; Takahashi, H.; Witulski, B. Transition Metal Catalyzed [5+2] Cycloadditions of Vinylcyclopropanes and Alkynes: A Homolog of the Diels-Alder Reaction for the Synthesis of Seven-Membered Rings. *J. Am. Chem. Soc.* **1995**, *117*, 4720-4721.

129. Wender, P. A.; Sperandio, D. A New and Selective Catalyst for the [5+2] Cycloaddition of Vinylcyclopropanes and Alkynes. *J. Org. Chem.* **1998**, *63*, 4164-4165.

130. Gilbertson, S. R.; Hoge, G. S. Rhodium catalyzed intramolecular [4+2] cycloisomerization reactions. *Tetrahedron Lett.* **1998**, *39*, 2075-2078.

131. Gilbertson, S. R.; Hoge, G. S.; Genov, D. G. Rhodium-Catalyzed Asymmetric [4+2] Cycloisomerization Reactions. *J. Org. Chem.* **1998**, *63*, 10077-10080.

132. Wender, P. A.; Dyckman, A. J. Transition Metal-Catalyzed [5+2] Cycloadditions of 2-Substituted-1-vinylcyclopropanes: Catalyst Control and Reversal of Regioselectivity. *Org. Lett.* **1999**, *1*, 2089-2092.

133. Wender, P. A.; Dyckman, A. J.; Husfeld, C. O.; Kadereit, D.; Love, J. A.; Rieck, H. Transition Metal-Catalyzed [5+2] Cycloadditions with Substituted Cyclopropanes: First Studies of Regio- and Stereoselectivity. *J. Am. Chem. Soc.* **1999**, *121*, 10442-10443.

134. Cao, P.; Wang, B.; Zhang, X. Rh-Catalyzed Enyne Cycloisomerization. *J. Am. Chem. Soc.* **2000**, *122*, 6490-6491.

135. Cao, P.; Zhang, X. The First Highly Enantioselective Rh-Catalyzed Enyne Cycloisomerization. *Angew. Chem., Int. Ed.* **2000**, *39*, 4104-4106.

136. Wang, B.; Cao, P.; Zhang, X. An efficient Rh-catalyst system for the intramolecular [4+2] and [5+2] cycloaddition reactions. *Tetrahedron Lett.* **2000**, *41*, 8041-8044.

137. Oh, C. H.; Sung, H. R.; Jung, S. H.; Lim, Y. M. Rhodium catalyzed [2+2+2] cyclizations of 1,6-enynes. *Tetrahedron Lett.* **2001**, *42*, 5493-5495.

138. Lei, A.; He, M.; Wu, S.; Zhang, X. Highly Enantioselective Rh-Catalyzed Intramolecular Alder–Ene Reactions for the Syntheses of Chiral Tetrahydrofurans. *Angew. Chem., Int. Ed.* **2002**, *41*, 3457-3460.

139. Lei, A.; Waldkirch, J. P.; He, M.; Zhang, X. Highly Enantioselective Cycloisomerization of Enynes Catalyzed by Rhodium for the Preparation of Functionalized Lactams. *Angew. Chem., Int. Ed.* **2002**, *41*, 4526-4529.

140. Wender, P. A.; Williams, T. J. [(arene)Rh(cod)]$^+$ Complexes as Catalysts for [5+2] Cycloaddition Reactions. *Angew. Chem., Int. Ed.* **2002**, *41*, 4550-4553.

141. Evans, P. A.; Robinson, J. E.; Baum, E. W.; Fazal, A. N. Intermolecular Transition Metal-Catalyzed [4+2+2] Cycloaddition Reactions: A New Approach to the Construction of Eight-Membered Rings. *J. Am. Chem. Soc.* **2002**, *124*, 8782-8783.

142. Hashmi, A. S. K.; Haufe, P.; Rivas Nass, A. On the Enantioselective Rhodium-Catalyzed Enyne Cyclization. *Adv. Synth. Catal.* **2003**, *345*, 1237-1241.

143. Evans, P. A.; Baum, E. W. Diastereoselective Intramolecular Temporary Silicon-Tethered Rhodium-Catalyzed [4+2+2] Cycloisomerization Reactions: Regiospecific Incorporation of Substituted 1,3-Butadienes. *J. Am. Chem. Soc.* **2004**, *126*, 11150-11151.

144. Mikami, K.; Kataoka, S.; Aikawa, K. Tropos or Atropos Nature of Rhodium Complexes Bearing a Tetrakis(phosphanyl)terphenyl Ligand: Highly Enantioselective Catalysis of Ene-Type Cyclization. *Org. Lett.* **2005**, *7*, 5777-5780.

145. Ashfeld, B. L.; Miller, K. A.; Smith, A. J.; Tran, K.; Martin, S. F. $[Rh(CO)_2Cl]_2$-Catalyzed Domino Reactions Involving Allylic Substitution and Subsequent Carbocyclization Reactions. *Org. Lett.* **2005**, *7*, 1661-1663.

146. Miura, T.; Shimada, M.; Murakami, M. Rhodium-Catalyzed Cyclization of 1,6-Enynes Triggered by Addition of Arylboronic Acids. *J. Am. Chem. Soc.* **2005**, *127*, 1094-1095.

147. Lee, S. I.; Park, S. Y.; Park, J. H.; Jung, I. G.; Choi, S. Y.; Chung, Y. K.; Lee, B. Y. Rhodium N-Heterocyclic Carbene-Catalyzed [4+2] and [5+2] Cycloaddition Reactions. *J. Org. Chem.* **2006**, *71*, 91-96.

148. Evans, P. A.; Baum, E. W.; Fazal, A. N.; Lai, K. W.; Robinson, J. E.; Sawyer, J. R. New metal-catalyzed carbocyclization reactions for the constructin of complex natural products. *ARKIVOC* **2006**, *7*, 338-358.

149. Ota, K.; Lee, S. I.; Tang, J.-M.; Takachi, M.; Nakai, H.; Morimoto, T.; Sakurai, H.; Kataoka, K.; Chatani, N. Rh(II)-Catalyzed Skeletal Reorganization of 1,6- and 1,7-Enynes through Electrophilic Activation of Alkynes. *J. Am. Chem. Soc.* **2009**, *131*, 15203-15211.

150. Chatani, N.; Inoue, H.; Morimoto, T.; Muto, T.; Murai, S. Iridium(I)-Catalyzed Cycloisomerization of Enynes. *J. Org. Chem.* **2001**, *66*, 4433-4436.

151. Kezuka, S.; Okado, T.; Niou, E.; Takeuchi, R. Iridium Complex-Catalyzed Reaction of 1,6-Enynes: Cycloaddition and Cycloisomerization. *Org. Lett.* **2005**, *7*, 1711-1714.

152. Fürstner, A.; Szillat, H.; Gabor, B.; Mynott, R. Platinum- and Acid-Catalyzed Enyne Metathesis Reactions: Mechanistic Studies and Applications to the Syntheses of Streptorubin B and Metacycloprodigiosin. *J. Am. Chem. Soc.* **1998**, *120*, 8305-8314.

153. Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. $PtCl_2$-Catalyzed Conversion of 1,6- and 1,7-Enynes to 1-Vinylcycloalkenes. Anomalous Bond Connection in Skeletal Reorganization of Enynes. *Organometallics* **1996**, *15*, 901-903.

154. Fürstner, A.; Szillat, H.; Stelzer, F. Novel Rearrangements of Enynes Catalyzed by $PtCl_2$. *J. Am. Chem. Soc.* **2000**, *122*, 6785-6786.

155. Trost, B. M.; Doherty, G. A. An Asymmetric Synthesis of the Tricyclic Core and a Formal Total Synthesis of Roseophilin via an Enyne Metathesis. *J. Am. Chem. Soc.* **2000**, *122*, 3801-3810.

156. Fernández-Rivas, C.; Méndez, M.; Echavarren, A. M. Metal-Catalyzed Carbocyclization by Intramolecular Reaction of Allylsilanes and Allylstannanes with Alkynes. *J. Am. Chem. Soc.* **2000**, *122*, 1221-1222.

157. Méndez, M.; Muñoz, M. P.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. Cyclizations of Enynes Catalyzed by $PtCl_2$ or Other Transition Metal Chlorides: Divergent Reaction Pathways. *J. Am. Chem. Soc.* **2001**, *123*, 10511-10520.

158. Oi, S.; Tsukamoto, I.; Miyano, S.; Inoue, Y. Cationic Platinum-Complex-Catalyzed Skeletal Reorganization of Enynes. *Organometallics* **2001**, *20*, 3704-3709.

159. Fürstner, A.; Stelzer, F.; Szillat, H. Platinum-Catalyzed Cycloisomerization Reactions of Enynes. *J. Am. Chem. Soc.* **2001**, *123*, 11863-11869.

160. Fernández-Rivas, C.; Méndez, M.; Nieto-Oberhuber, C.; Echavarren, A. M. Reaction of Allylsilanes and Allylstannanes with Alkynes Catalyzed by Electrophilic Late Transition Metal Chlorides. *J. Org. Chem.* **2002**, *67*, 5197-5201.

161. Bajracharya, G. B.; Nakamura, I.; Yamamoto, Y. $PtBr_2$-Catalyzed Consecutive Enyne Metathesis−Aromatization of 1-(1-Methoxy-but-3-enyl)-2-(1-alkynyl)benzenes: Dual Role of the Pt Catalyst. *J. Org. Chem.* **2005**, *70*, 892-897.

162. Sun, J.; Conley, M. P.; Zhang, L.; Kozmin, S. A. Au- and Pt-Catalyzed Cycloisomerizations of 1,5-Enynes to Cyclohexadienes with a Broad Alkyne Scope. *J. Am. Chem. Soc.* **2006**, *128*, 9705-9710.

163. Marco-Contelles, J.; Arroyo, N.; Anjum, S.; Mainetti, E.; Marion, N.; Cariou, K.; Lemière, G.; Mouriès, V.; Fensterbank, L.; Malacria, M. $PtCl_2$- and $PtCl_4$-Catalyzed Cycloisomerization of Polyunsaturated Precursors. *Eur. J. Org. Chem.* **2006**, *2006*, 4618-4633.

164. Bhanu Prasad, B. A.; Yoshimoto, F. K.; Sarpong, R. Pt-Catalyzed Pentannulations from In Situ Generated Metallo−Carbenoids Utilizing Propargylic Esters. *J. Am. Chem. Soc.* **2005**, *127*, 12468-12469.

165. Zhang, L.; Sun, J.; Kozmin, S. A. Gold and Platinum Catalysis of Enyne Cycloisomerization. *Adv. Synth. Catal.* **2006**, *348*, 2271-2296.

166. Hashmi, A. S. Homogeneous gold catalysts and alkynes: A successful liaison. *Gold Bull* **2003**, *36*, 3-9.

167. Stephen, A.; Hashmi, K. Homogeneous catalysis by gold. *Gold Bull* **2004**, *37*, 51-65.

168. Nieto-Oberhuber, C.; Muñoz, M. P.; Buñuel, E.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. Cationic Gold(I) Complexes: Highly Alkynophilic Catalysts for the exo- and endo-Cyclization of Enynes. *Angew. Chem., Int. Ed.* **2004**, *43*, 2402-2406.

169. Zhang, L.; Kozmin, S. A. Gold-Catalyzed Cycloisomerization of Siloxy Enynes to Cyclohexadienes. *J. Am. Chem. Soc.* **2004**, *126*, 11806-11807.

170. Mézailles, N.; Ricard, L.; Gagosz, F. Phosphine Gold(I) Bis-(trifluoromethanesulfonyl)imidate Complexes as New Highly Efficient and Air-Stable Catalysts for the Cycloisomerization of Enynes. *Org. Lett.* **2005**, *7*, 4133-4136.

171. Nieto-Oberhuber, C.; López, S.; Muñoz, M. P.; Cárdenas, D. J.; Buñuel, E.; Nevado, C.; Echavarren, A. M. Divergent Mechanisms for the Skeletal Rearrangement and [2+2] Cycloaddition of Enynes Catalyzed by Gold. *Angew. Chem., Int. Ed.* **2005**, *44*, 6146-6148.

172. Gagosz, F. Unusual Gold(I)-Catalyzed Isomerization of 3-Hydroxylated 1,5-Enynes: Highly Substrate-Dependent Reaction Manifolds. *Org. Lett.* **2005**, *7*, 4129-4132.

173. Ma, S.; Yu, S.; Gu, Z. Gold-Catalyzed Cyclization of Enynes. *Angew. Chem., Int. Ed.* **2006**, *45*, 200-203.

174. Lee, S. I.; Kim, S. M.; Kim, S. Y.; Chung, Y. K. The Gold(I)-Catalyzed Cycloisomerization of 1,6-Enynes to 1,4-Dienes. *Synlett* **2006**, *2006*, 2256-2260.

175. Freytag, M.; Ito, S.; Yoshifuji, M. Coordination Behavior of Sterically Protected Phosphaalkenes on the AuCl Moiety Leading to Catalytic 1,6-Enyne Cycloisomerization. *Chemistry – An Asian Journal* **2006**, *1*, 693-700.

176. Shibata, T.; Ueno, Y.; Kanda, K. Cationic Au(I)-Catalyzed Cycloisomerization of Aromatic Enynes for the Synthesis of Substituted Naphthalenes. *Synlett* **2006**, *2006*, 0411-0414.

177. Nieto-Oberhuber, C.; Muñoz, M. P.; López, S.; Jiménez-Núñez, E.; Nevado, C.; Herrero-Gómez, E.; Raducan, M.; Echavarren, A. M. Gold(I)-Catalyzed Cyclizations of 1,6-Enynes: Alkoxycyclizations and exo/endo Skeletal Rearrangements. *Chem.–Eur. J.* **2006**, *12*, 1677-1693.

178. Sturla, S. J.; Kablaoui, N. M.; Buchwald, S. L. A Titanocene-Catalyzed Intramolecular Ene Reaction: Cycloisomerization of Enynes and Dienynes. *J. Am. Chem. Soc.* **1999**, *121*, 1976-1977.

179. Nishikawa, T.; Shinokubo, H.; Oshima, K. Cyclization of 1,6-Enynes with Allylic Chromate Species. *Org. Lett.* **2002**, *4*, 2795-2797.

180. Fürstner, A.; Martin, R.; Majima, K. Cycloisomerization of Enynes Catalyzed by Iron(0)−Ate Complexes. *J. Am. Chem. Soc.* **2005**, *127*, 12236-12237.

181. Ajamian, A.; Gleason, J. L. Cobalt-Catalyzed Cycloisomerization of 1,6-Enynes and Allyl Propargyl Ethers. *Org. Lett.* **2003**, *5*, 2409-2411.

182. Trost, B. M.; Tour, J. M. A novel nickel-chromium catalyst system for cyclization via intramolecular carbametalation. *J. Am. Chem. Soc.* **1987**, *109*, 5268-5270.

183. Wender, P. A.; Smith, T. E. Transition metal-catalyzed intramolecular [4+2] cycloadditions: Mechanistic and synthetic investigations. *Tetrahedron* **1998**, *54*, 1255-1275.

184. Ni, Y.; Montgomery, J. An Efficient [4+2+1] Entry to Seven-Membered Rings. *J. Am. Chem. Soc.* **2004**, *126*, 11162-11163.

185. Ikeda, S.-i.; Daimon, N.; Sanuki, R.; Odashima, K. Catalytic Cycloisomerization of Enynes by Using a Nickel-Zinc-Acid System. *Chem.–Eur. J.* **2006**, *12*, 1797-1806.

186. Tekavec, T. N.; Louie, J. Nickel-catalyzed cycloisomerization of enynes: catalyst generation via C–H activation of carbene ligands. *Tetrahedron* **2008**, *64*, 6870-6875.

187. Harrison, T. J.; Dake, G. R. Pt(II) or Ag(I) Salt Catalyzed Cycloisomerizations and Tandem Cycloadditions Forming Functionalized Azacyclic Arrays. *Org. Lett.* **2004**, *6*, 5023-5026.

188. Porcel, S.; Echavarren, A. M.,Intramolecular Carbostannylation of Alkynes Catalyzed by Silver(I) Species. *Angew. Chem., Int. Ed.* **2007**, *46*, 2672-2676.

189. Chatani, N.; Inoue, H.; Kotsuma, T.; Murai, S. Skeletal Reorganization of Enynes to 1-Vinylcycloalkenes Catalyzed by $GaCl_3$. *J. Am. Chem. Soc.* **2002**, *124*, 10294-10295.

190. Simmons, E. M.; Sarpong, R. Ga(III)-Catalyzed Cycloisomerization Strategy for the Synthesis of Icetexane Diterpenoids: Total Synthesis of (±)-Salviasperanol. *Org. Lett.* **2006**, *8*, 2883-2886.

191. Kim, S. M.; Lee, S. I.; Chung, Y. K. $GaCl_3$-Catalyzed Formation of Eight-Membered Rings from Enynes Bearing a Cyclic Olefin. *Org. Lett.* **2006**, *8*, 5425-5427.

192. Miyanohana, Y.; Chatani, N. Skeletal Reorganization of Enynes Catalyzed by $InCl_3$. *Org. Lett.* **2006**, *8*, 2155-2158.

193. Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. Highly Selective Skeletal Reorganization of 1,6- and 1,7-Enynes to 1-Vinylcycloalkenes Catalyzed by $[RuCl_2(CO)_3]_2$. *J. Am. Chem. Soc.* **1994**, *116*, 6049-6050.

194. Trost, B. M.; Yanai, M.; Hoogsteen, K. A palladium-catalyzed [2+2] cycloaddition. Mechanism of a Pd-catalyzed enyne metathesis. *J. Am. Chem. Soc.* **1993**, *115*, 5294-5295.

195. Trost, B. M.; Indolese, A. F.; Mueller, T. J. J.; Treptow, B. A Ru Catalyzed Addition of Alkenes to Alkynes. *J. Am. Chem. Soc.* **1995**, *117*, 615-623.

196. Trost, B. M.; Toste, F. D. Ruthenium-Catalyzed Cycloisomerization of 1,6-Enynes Initiated by C−H Activation. *J. Am. Chem. Soc.* **1999**, *121*, 9728-9729.

197. Trost, B. M.; Toste, F. D. Ruthenium-Catalyzed Cycloisomerizations of 1,6- and 1,7-Enynes. *J. Am. Chem. Soc.* **2000**, *122*, 714-715.

198. Le Paih, J.; Cuervo Rodríguez, D.; Dérien, S.; Dixneuf, P. H. A New Cycloisomerisation Catalyst of Enynes: One-Step Synthesis of 3,4-Dialkylidenetetrahydrofurans from Allyl Propargyl Ethers. *Synlett* **2000**, *2000*, 95-97.

199. Trost, B. M.; Surivet, J.-P.; Toste, F. D. Ruthenium-Catalyzed Enyne Cycloisomerizations. Effect of Allylic Silyl Ether on Regioselectivity. *J. Am. Chem. Soc.* **2004**, *126*, 15592-15602.

200. Nakae, T.; Yasunaga, T.; Kamiya, M.; Fukumoto, Y.; Chatani, N. Skeletal Reorganization of Enynes Catalyzed by a Ru(II)-Ru(III) Mixed-valence Complex under an Atmosphere of O_2 or CO. *Chem. Lett.* **2013**, *42*, 1565-1567.

201. Gimbert, Y.; Fensterbank, L.; Gandon, V.; Goddard, J.-P.; Lesage, D. Ligand Effect in Platinum-Catalyzed Cycloisomerization of 1,6-Enynes: Water or Carbon Monoxide, a Similar Role despite Distinct Electronic Properties? *Organometallics* **2013**, *32*, 374-376.

202. Mori, M.; Saito, N.; Tanaka, D.; Takimoto, M.; Sato, Y. Novel Alkenylative Cyclization Using a Ruthenium Catalyst. *J. Am. Chem. Soc.* **2003**, *125*, 5606-5607.

203. Saito, N.; Saito, K.; Shiro, M.; Sato, Y. Regio- and Stereoselective Synthesis of 2-Amino-1,3-diene Derivatives by Ruthenium-Catalyzed Coupling of Ynamides and Ethylene. *Org. Lett.* **2011**, *13*, 2718-2721.

204. Kaminsky, L.; Clark, D. A. Ruthenium Catalyzed Cycloisomerization of Silicon-Tethered 1,7-Enynes To Give Exocyclic 1,3-Dienes. *Org. Lett.* **2014**, *16*, 5450-5453.

205. Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Itoh, K. Cp*Ru(cod)Cl-Catalyzed [2+2+2] Cycloaddition of 1,6-Heptadiynes with Allylic Ethers. A Decisive Role of Coordination to the Ether Oxygen Atom. *J. Org. Chem.* **1998**, *63*, 9610-9611.

206. Trost, B. M.; Harrington, P. E.; Chisholm, J. D.; Wrobleski, S. T. Total Synthesis of (+)-Amphidinolide A. Structure Elucidation and Completion of the Synthesis. *J. Am. Chem. Soc.* **2005**, *127*, 13598-13610.

207. Luh, T.-Y.; Hu, Z. Thorpe-Ingold effect in organosilicon chemistry. *Dalton Trans.* **2010**, *39*, 9185-9192.

208. Marshall, J. A.; Yanik, M. M. Synthesis of β-Hydroxy Ketones and Vinylsilanes from Homopropargylic Alcohols by Intramolecular Hydrosilation. *Org. Lett.* **2000**, *2*, 2173-2175.

209. Marshall, J. A.; Yanik, M. M. Synthesis of a C_1−C_{21} Subunit of the Protein Phosphatase Inhibitor Tautomycin: A Formal Total Synthesis. *J. Org. Chem.* **2001**, *66*, 1373-1379.

210. Smitrovich, J. H.; Woerpel, K. A. Oxidation of Sterically Hindered Alkoxysilanes and Phenylsilanes under Basic Conditions. *J. Org. Chem.* **1996**, *61*, 6044-6046.

211. Diethelm, S.; Carreira, E. M. Total Synthesis of (±)-Gelsemoxonine. *J. Am. Chem. Soc.* **2013**, *135*, 8500-8503.

212. Bowers, K. G.; Mann, J.; Walsh, E. B.; Howarth, O. W. Thromboxane A_2 analogues from 8-oxabicyclo[3.2.1]oct-6-en-3-ones. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1657-1666.

213. Trost, B. M.; Yang, H.; Probst, G. D. A Formal Synthesis of (−)-Mycalamide A. *J. Am. Chem. Soc.* **2004**, *126*, 48-49.

214. Trost, B. M.; Rudd, M. T. Chemoselectivity of the Ruthenium-Catalyzed Hydrative Diyne Cyclization: Total Synthesis of (+)-Cylindricine C, D, and E. *Org. Lett.* **2003**, *5*, 4599-4602.

215. Martin, P.; McManus, N. T.; Rempel, G. L. A detailed study of the hydrogenation of nitrile-butadiene rubber and other substrates catalyzed by Ru(II) complexes. *J. Mol. Catal. A: Chem.* **1997**, *126*, 115-131.

6.0 EXPERIMENTALS

General Procedures: Unless otherwise indicated, all reactions were conducted in oven-(140^{o}C) or flame-dried glassware using distilled and degassed solvents under positive pressure of dry argon with standard Schlenk techniques. All air-sensitive reagents were stored in an MBraun labmaster glovebox containing dry argon gas. Dry dichloromethane (DCM), toluene, diethyl ether (Et_2O) and tetrahydrofuran (THF) was obtained by passing commercially available pre-dried, oxygen-free formulations through two activated alumina columns using an MBraun MB-SPS solvent purification system. Stainless steel syringes or cannulae that had been oven-dried (140^{o}C) and cooled under argon atmosphere or in a desiccator were used to transfer air- and moisture-sensitive liquids. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on precoated glass plates of silica gel (0.25 mm) 60 F_{254} from EMD Chemicals Inc. using the indicated solvent system. Visualization was accomplished with ultraviolet light (UV 254 nm). Alternatively, plates were treated with one of the following solutions (this was accomplished by holding the edge of the TLC plate with forceps or tweezers and immersing the plate into a wide-mouth jar containing the desired staining solution) and carefully heating with a hot-air gun (450^{o}C) for approximately 1-2 min: anisaldehyde in ethanol with 10% sulfuric acid. Flash column chromatography was performed using Silia Flash P60

silica gel (40-63 μm) from Silicycle. All work-up and purification procedures were carried out with reagent grade solvents (purchased from VWR) in air.

Instrumentation: Infrared (IR) spectra were recorded on a Thermo Nicolet IR-100 spectrometer, ν_{max} in cm^{-1}, and were obtained from samples prepared as thin films between NaCl plates for samples. ^{1}H NMR spectra were recorded on a Bruker Avance DPX-300 (300 MHz) spectrometer or a Bruker Avance DPX-400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) and are calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity, coupling constants (Hz) and integration. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, dq = doublet of quartets. ^{13}C NMR spectra were recorded on a Bruker Avance DPX-300 (75 MHz) spectrometer or a Bruker Avance DPX-400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm and are calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: δ 77.23 ppm). 2D NMR spectra were recorded on a Bruker Avance DPX-600 spectrometer. Melting points (m.p.) are uncorrected and were recorded using an Electrothermal Mel-Temp melting point apparatus. Elemental analyses were performed on a Costech Instruments ECS 4010 elemental analyzer with a 2 meter GC column maintained at 65°C and thermal conductivity detector.

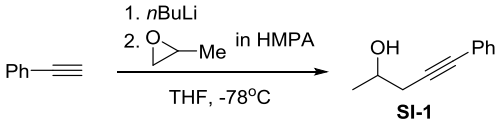
Reagents and Catalysts: Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated.

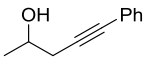
Compounds 55, **56**, **57**, **61**, **62**, **63, 66**, **SI-3**, **SI-8, SI-11** were prepared by co-workers according to the literature procedure.[26]

Compounds 218, 230, SI-16 were prepared by co-workers according to the literature protocol.[88]

Compounds 86, 93, 121, **122** were prepared by Robert Wilson according to the literature protocol.[71]

RuHCl(CO)(H_2IMes)(PPh_3) was prepared by Robert Wilson according to the literature protocol.[54]



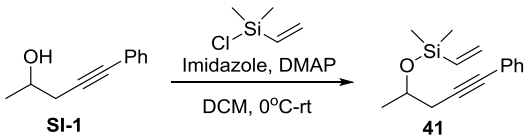


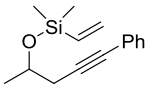
Alcohol SI-1

To a flame-dried 3-neck 500 mL RBF equipped with magnetic stir bar and pressure equalizing addition funnel under $Ar_{(g)}$ was added phenylacetylene (16.5 mL, 150 mmol, 1 equiv) and THF (160 mL). The solution was cooled to -78°C (dry ice/acetone bath) and *n*BuLi (72 mL, 180 mmol, 1.2 equiv) was added dropwise over 45 min. After stirring for 1 h at -78°C, a solution of propylene oxide (34 mL, 480 mmol, 3.2 equiv) in HMPA (40 mL) was added dropwise over 25 min. Once addition was complete, the resulting green/brown solution stirred at rt for 3 h. The reaction mixture was poured into H_2O (475 mL) and extracted with hexanes (3 x 120 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. The oil was dissolved in ether (100 mL) and washed with 10% HCl (3 x 50 mL). The organic layer was refluxed over activated carbon for 30 min, dried over $MgSO_4$, filtered through Celite and concentrated *in vacuo* to give alcohol **SI-1** as off-white crystals (22.6 g, 94%). Spectroscopic data corresponded to what was reported in the literature.[212]

R_f (50% EtOAc/hexanes) = 0.54

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43-7.40 (m, 2H), 7.31-7.28 (m, 3H), 4.10-4.00 (m, 1H), 2.59 (d ABq, 2H, J_{AB} = 16.7 Hz, J_{AX} = 5.1 Hz, J_{BX} = 6.6 Hz), 2.06 (br s, 1H), 1.33 (d, 3H, J = 6.2 Hz)



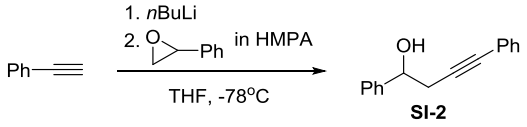


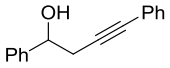
Silicon-Tethered Alkyne 41

To an oven-dried 250 mL RBF equipped with magnetic stir bar under $Ar_{(g)}$ was added alcohol **SI-1** (2.4 g, 15 mmol, 1 equiv) and DCM (100 mL). To the resulting pale yellow solution was added imidazole (2.04 g, 30 mmol, 2 equiv) and DMAP (367 mg, 3.0 mmol, 0.2 equiv). The solution was cooled to 0°C (ice/H_2O bath) and vinyldimethylchlorosilane (3.1 mL, 22.5 mmol, 1.5 equiv) was added. The suspension stirred at rt for 5 h and was quenched by sat. $NH_4Cl_{(aq)}$ (100 mL). The aqueous layer was extracted with DCM (3 x 50 mL) then the combined organic layers were washed with brine (2 x 100 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification via column chromatography (silica gel 4.5 x 12 cm; gradient elution with 2%-6% ether/hexanes) gave alkyne **41** as a clear oil (3.39 g, 92%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (20% ether/hexanes) = 0.70

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43-7.40 (m, 2H), 7.31-7.27 (m, 3H), 6.21 (dd, 1H, *J* = 26.6, 19.8 Hz), 6.04 (dd, 1H, *J* = 19.8, 5.6 Hz), 5.83 (dd, 1H, *J* = 19.9, 4.3 Hz), 4.12-4.01 (m, 1H), 2.55 (d ABq, 2H, J_{AB} = 16.5 Hz, J_{AX} = 6.0 Hz, J_{BX} = 7.0 Hz), 1.32 (d, 3H, *J* = 6.03 Hz), 0.25 (d, 6H, *J* = 1.02 Hz)



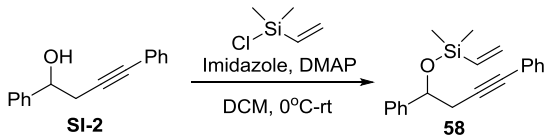


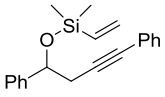
Alcohol SI-2

To a flame-dried 3-neck 500 mL RBF equipped with magnetic stir bar and pressure equalizing addition funnel under $Ar_{(g)}$ was added phenylacetylene (20 mL, 180 mmol, 1.2 equiv) and THF (160 mL). The solution was cooled to -78°C (dry ice/acetone bath) and *n*BuLi (72 mL, 180 mmol, 1.2 equiv) was added dropwise over 15 min. After stirring for 1 h at -78°C, a solution of styrene oxide (17 mL, 150 mmol, 1 equiv) in HMPA (39 mL) was added dropwise over 20 min. Once addition was complete, the resulting brown solution stirred at rt overnight. The reaction mixture was poured into H_2O (450 mL) then the layers were separated. The organic layer was washed with H_2O (200 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a dark red oil. Hexanes (190 mL) was added to the oil, the flask was capped and the solution was shaken vigorously (with periodic venting) to induce precipitation. The resulting suspension was then opened to the air and stirred vigorously at rt for 1.5 h. Filtration of the suspension yielded alcohol **SI-2** as a cream-colored power (19.7 g). A second (3.56 g) and third crop (2.45 g) were obtained from the mother liquor (25.7 g total, 75%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (20% EtOAc/hexanes) = 0.36

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46-7.44 (m, 2H), 7.40-7.37 (m, 4H), 7.34-7.28 (m, 4H), 4.99-4.95 (m, 1H), 2.92-2.82 (app m, 2H), 2.42 (d, 1H, *J* = 3.5 Hz)



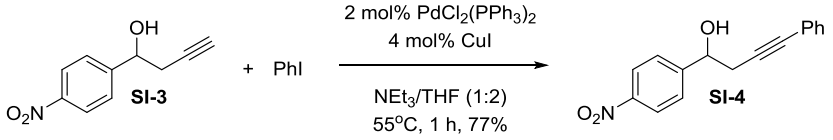


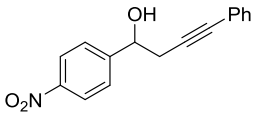
Silicon-Tethered Alkyne 58

To a 250 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added **SI-2** (4.56 g, 20 mmol, 1 equiv), DCM (130 mL), imidazole (2.72 g, 40 mmol, 2 equiv) and DMAP (488 mg, 4 mmol, 0.2 equiv). The pale yellow solution was cooled to 0°C (ice/H_2O bath) then vinyldimethylchlorosilane (3.3 mL, 24 mmol, 1.2 equiv) was added via syringe. The resulting yellow suspension stirred at rt for 6 h, was quenched with sat. $NH_4Cl_{(aq)}$ (100 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 50 mL) then the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give an orange residue. Hexanes (50 mL) was added to the residue and the resulting cloudy orange suspension stirred vigorously at rt for 15 min. The solid was filtered away and the resulting hexanes filtrate was treated with activated carbon, stirred at rt for 30 min then filtered through a pad of silica gel (eluted with ether). Concentration *in vacuo* afforded alkyne **58** as a yellow oil (5.8 g, 95%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (10% ether/hexanes) = 0.72

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41-7.25 (m, 10H), 6.10 (dd, 1H, J = 20.3, 14.7 Hz), 5.97 (dd, 1H, J = 14.7, 4.1 Hz), 5.75 (dd, 1H, J = 19.9, 4.1 Hz), 4.93-4.90 (m, 1H), 2.77 (d ABq, 2H, J_{AB} = 16.6 Hz, J_{AX} = 7.4 Hz, J_{BX} = 5.5 Hz), 0.19 (s, 3H), 0.14 (s, 3H)



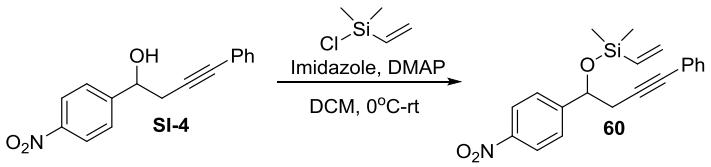


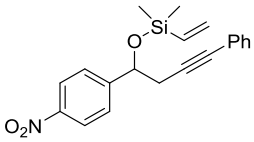
Alcohol SI-4

To an oven-dried 3-neck 100 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added $PdCl_2(PPh_3)_2$ (70 mg, 0.10 mmol, 0.02 equiv), CuI (40 mg, 0.21 mmol, 0.04 equiv), alkyne **SI-3**[26] (1 g, 5.2 mmol, 1 equiv), THF (30 mL), NEt_3 (15 mL) and iodobenzene (0.7 mL, 6.2 mmol, 1.2 equiv). The resulting dark red solution was subjected to three cycles of freeze/pump/thaw then placed under $Ar_{(g)}$. Once warmed to rt the red/orange suspension stirred at 55°C. After 1 h, the resulting orange suspension was cooled to rt then filtered through celite. The filtrate was washed with brine (2 x 75 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a dark red oil. Purification by column chromatography (silica gel 2.5 x 12 cm; gradient elution with 20%-50% EtOAc/hexanes) gave alcohol **SI-4** as a red/orange solid (1.07 g, 77%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (30% EtOAc/hexanes) = 0.29

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.24 (d, 2H, *J* = 9.8 Hz), 7.63 (d, 2H, *J* = 9.8 Hz), 7.39-7.29 (m, 5H), 5.07 (t, 1H, *J* = 5.8 Hz), 2.97-2.81 (app m, 2H), 2.59 (br s, 1H)



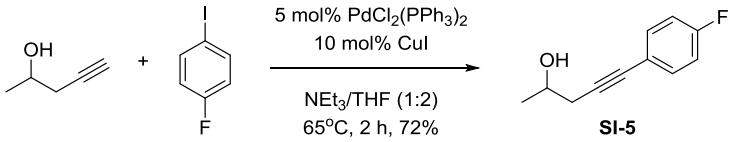


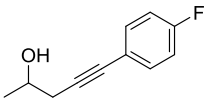
Silicon-Tethered Alkyne 60

To an oven-dried 100 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added **SI-4** (1.09 g, 4.1 mmol, 1 equiv), DCM (27 mL), imidazole (556 mg, 8.2 mmol, 2 equiv) and DMAP (100 mg, 0.82 mmol, 0.2 equiv). The orange solution was cooled to 0°C (ice/H_2O bath) then vinyldimethylchlorosilane (0.85 mL, 6.1 mmol, 1.5 equiv) was added via syringe. The resulting yellow suspension stirred at rt overnight, was quenched with sat. $NH_4Cl_{(aq)}$ (25 mL) then the layers were separated. The aqueous layer was extracted with DCM (2 x 25 mL) then the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give an orange oil. Purification by column chromatography (silica gel 2.5 x 13 cm; gradient elution with 3%-4% EtOAc/hexanes) gave alkyne **60** as a bright yellow oil (1.31 g, 92%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (10% EtOAc/hexanes) = 0.63

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.21 (d, 2H, *J* = 8.5 Hz), 7.59 (d, 2H, *J* = 8.5 Hz), 7.35-7.27 (m, 5H), 6.08 (dd, 1H, *J* = 18.4, 14.7 Hz), 5.99 (dd, 1H, *J* = 14.7, 5.5 Hz), 5.77 (dd, 1H, *J* = 18.6, 5.7 Hz), 4.99 (t, 1H, *J* = 6.6 Hz), 2.80 (d ABq, 2H, J_{AB} = 16.6 Hz, J_{AX} = 6.6 Hz, J_{BX} = 6.6 Hz), 0.23 (s, 3H), 0.17 (s, 3H)



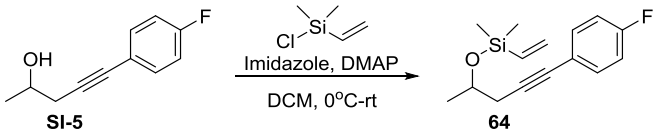


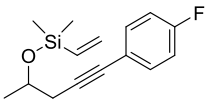
Alcohol SI-5

To an oven-dried 3-neck 100 mL RBF equipped with a magnetic stir bar and reflux condenser under $Ar_{(g)}$ was added $PdCl_2(PPh_3)_2$ (351 mg, 0.5 mmol, 0.05 equiv), CuI (190 mg, 0.10 mmol, 0.10 equiv), THF (20 mL), NEt_3 (10 mL), 4-pentyn-2-ol (0.9 mL, 10 mmol, 1 equiv) and 4-fluoroiodobenzene (1.4 mL, 12 mmol, 1.2 equiv). The resulting dark brown solution was subjected to three cycles of freeze/pump/thaw then placed under $Ar_{(g)}$. Once warmed to rt the dark brown suspension stirred at 65°C. After 2 h, the resulting red/orange suspension was cooled to rt and sat. $NH_4Cl_{(aq)}$ (30 mL) was added. The reaction was extracted with ether (3 x 30 mL) then the combined organics were washed with brine (2 x 75 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give red/orange oil. Purification by column chromatography (silica gel 4.5 x 12 cm; gradient elution with 20%-40% EtOAc/hexanes) gave **SI-5** as a red/brown solid (1.28 g, 72%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (20% EtOAc/hexanes; developed 2x) = 0.43

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.41-7.36 (m, 2H), 7.02-6.96 (m, 2H), 4.06-4.01 (m, 1H), 2.57 (d ABq, 2H, J_{AB} = 16.6 Hz, J_{AX} = 5.4 Hz, J_{BX} = 6.4 Hz), 1.94 (br s, 1H), 1.32 (d, 3H, J = 6.2 Hz)



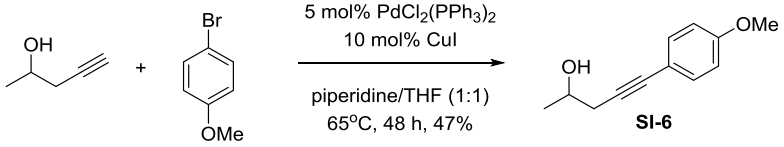


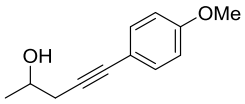
Silicon Tethered Alkyne 64

To an oven-dried 100 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ - was added **SI-5** (1.28 g, 7.2 mmol, 1 equiv), DCM (40 mL), imidazole (981 mg, 14.4 mmol, 2 equiv) and DMAP (176 mg, 1.44 mmol, 0.2 equiv) sequentially. The yellow solution was cooled to 0°C (ice/H_2O bath) and vinyldimethylchlorosilane (1.5 mL, 10.8 mmol, 1.5 equiv) was added via syringe. The yellow suspension stirred at rt overnight then was quenched by sat. $NH_4Cl_{(aq)}$ (40 mL). The aqueous layer was extracted with DCM (2 x 25 mL) then the combined organics were washed with brine (2 x 50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give an orange oil. Purification by column chromatography (silica gel 2.5 x 11.5 cm; gradient elution with 1%-2% ether/hexanes) gave **64** as a pale yellow oil (1.53 g, 81%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (10% EtOAc/hexanes) = 0.63

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39-7.34 (m, 2H), 7.00-6.94 (m, 2H), 6.18 (dd, 1H, *J* = 19.9, 14.7 Hz), 6.02 (dd, 1H, *J* = 14.7, 4.3 Hz), 5.80 (dd, 1H, *J* = 19.9, 4.3 Hz), 4.09-3.98 (m, 1H), 2.52 (d ABq, 2H, J_{AB} = 16.6 Hz, J_{AX} = 5.7 Hz, J_{BX} = 7.1 Hz), 1.29 (d, 3H, *J* = 6.2 Hz), 0.22 (s, 6H)



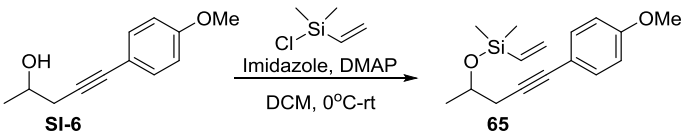


Alcohol SI-6

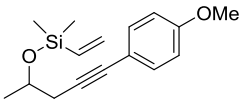
To an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar and reflux condenser under $Ar_{(g)}$ was added $PdCl_2(PPh_3)_2$ (526 mg, 0.75 mmol, 0.05 equiv), CuI (286 mg, 1.5 mmol, 0.10 equiv), piperidine (15 mL), 4-pentyn-2-ol (1.4 mL, 15 mmol, 1 equiv) and 4-bromoanisole (2.3 mL, 18 mmol, 1.2 equiv) in THF (15 mL). The resulting brown solution was subjected to three cycles of freeze/pump/thaw, placed under $Ar_{(g)}$ then stirred at 65°C for 48 h. The resulting black solution was cooled to rt then sat. $NH_4Cl_{(aq)}$ (30 mL) was added. The aqueous layer was extracted with ether (3 x 50 mL) then the combined organics were washed with brine (2 x 75 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a brown oil. Purification via column chromatography (silica gel 4.5 x 13.5 cm; gradient elution with 25%-35% EtOAc/hexanes) gave **SI-6** as an orange solid (1.33 g, 47%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (25% EtOAc/hexanes) = 0.34

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.37-7.33 (app m, 2H), 6.85-6.80 (app m, 2H), 4.08-4.00 (m, 1H), 3.81 (s, 3H), 2.57 (d ABq, 2H, J_{AB} = 16.6 Hz, J_{AX} = 5.1 Hz, J_{BX} = 6.7 Hz), 1.79 (br s, 1H), 1.32 (d, 3H, J = 6.3 Hz)



SI-6 **65**

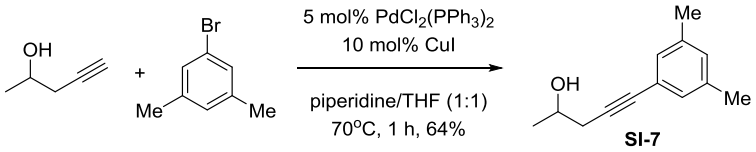


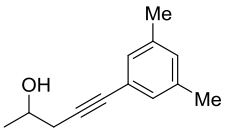
Silicon-Tethered Alkyne 65

To a 250 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added **SI-6** (1.33 g, 7 mmol, 1 equiv), DCM (47 mL), imidazole (953 mg, 14 mmol, 2 equiv) and DMAP (171 mg, 1.4 mmol, 0.2 equiv). The pale yellow solution was cooled to 0°C (ice/H_2O bath) then vinyldimethylchlorosilane (1.5 mL, 10.5 mmol, 1.5 equiv) was added dropwise via syringe. The resulting yellow suspension stirred at rt overnight, was quenched with sat. $NH_4Cl_{(aq)}$ (50 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 35 mL) then the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give an orange oil. Purification by column chromatography (silica gel 2.5 x 13 cm; gradient elution with 2%-3% ether/hexanes) gave alkyne **65** as a clear oil (1.69 g, 88%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (25% EtOAc/hexanes) = 0.58

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.32 (d, 2H, *J* = 8.5 Hz), 6.82 (d, 2H, *J* = 8.5 Hz), 6.18 (ddd, 1H, *J* = 20.0, 14.9, 0.5 Hz), 5.99 (ddd, 1H, *J* = 14.7, 4.2, 0.5 Hz), 5.80 (ddd, 1H, *J* = 20.0, 4.2, 0.4 Hz), 4.08-3.98 (m, 1H), 3.80 (s, 3H), 2.51 (d ABq, 2H, J_{AB} = 16.6 Hz, J_{AX} = 5.9 Hz, J_{BX} = 7.2 Hz), 1.29 (d, 3H, *J* = 6.2), 0.23 (s, 6H)



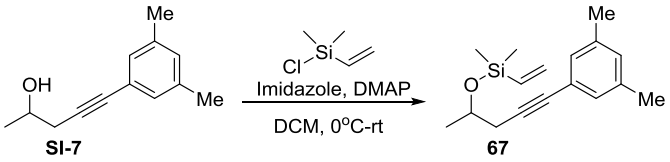


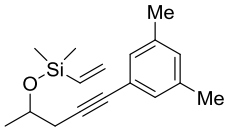
Alcohol SI-7

To an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar under $Ar_{(g)}$ was added $PdCl_2(PPh_3)_2$ (175 mg, 0.025 mmol, 0.05 equiv), CuI (95.2 mg, 0.5 mmol, 0.10 equiv), THF (5 mL), piperidine (5 mL), 4-pentyn-2-ol (0.47 mL, 5 mmol, 1 equiv) and 1-bromo-3,5-dimethylbenzene (0.82 mL, 6 mmol, 1.2 equiv). The resulting green suspension was subjected to three cycles of freeze/pump/thaw then placed under $Ar_{(g)}$. Once warmed to rt, a cold-finger was quickly attached and the orange solution stirred at 70°C. After 1 h, the resulting black solution was cooled to rt then diluted with ether (10 mL) and sat. $NH_4Cl_{(aq)}$ (10 mL). The organic layer was washed with brine (2 x 25 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a brown oil. Purification via column chromatography (silica gel 2.5 x 12 cm; eluted with 15% EtOAc/hexanes) gave **SI-7** as an orange oil (605 mg, 64%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (30% EtOAc/hexanes) = 0.41

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.05 (s, 2H), 6.93 (s, 1H), 4.08-3.98 (m, 1H), 2.57 (d ABq, 2H, J_{AB} = 16.1 Hz, J_{AX} = 5.2 Hz, J_{BX} = 6.5 Hz), 2.28 (s, 6H), 1.81 (br s, 1H), 1.32 (d, 3H, J = 6.1 Hz)



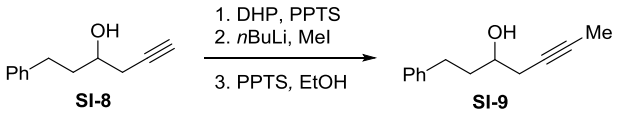


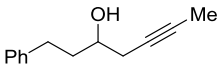
Silicon Tethered Alkyne 67

To an oven-dried 50 mL RBF equipped with magnetic stir bar under $Ar_{(g)}$ was added alcohol **SI-7** (469 mg, 2.5 mmol, 1 equiv) and DCM (15 mL). To the resulting yellow solution was added imidazole (339 mg, 5 mmol, 2 equiv) and DMAP (61 mg, 0.5 mmol, 0.2 equiv). The solution was cooled to 0°C (ice/H_2O bath) and vinyldimethylchlorosilane (0.52 mL, 3.7 mmol, 1.5 equiv) was added. The suspension stirred at rt overnight then was quenched by sat. $NH_4Cl_{(aq)}$ (20 mL). The aqueous layer was extracted with DCM (3 x 15 mL) then the combined organic layers were washed with brine (2 x 50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 12.5 cm; gradient elution with 1%-2% ether/hexanes) gave alkyne **67** as a clear oil (559 mg, 82%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (20% EtOAc/hexanes) = 0.72

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.03 (s, 2H), 6.91 (s, 1H), 6.18 (dd, 1H, *J* = 20.0, 15.2 Hz), 6.02 (dd, 1H, *J* = 14.9, 4.2 Hz), 5.81 (dd, 1H, *J* = 19.9, 4.2 Hz), 4.08-3.98 (m, 1H), 2.52 (d ABq, 2H, J_{AB} = 16.5 Hz, J_{AX} = 5.8 Hz, J_{BX} = 7.2 Hz), 2.27 (s, 6H), 1.29 (d, 3H, *J* = 6.0 Hz), 0.22 (d, *J* = 0.9 Hz)





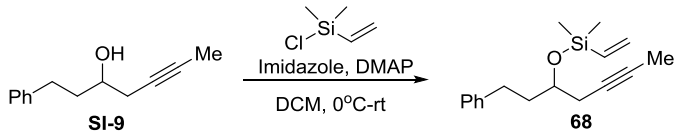
Alcohol SI-9

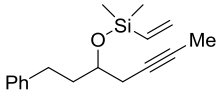
To an oven-dried 100 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added **SI-8**[26] (2.50 g, 14.4 mmol, 1 equiv), DCM (40 mL) and PPTS (362 mg, 1.44 mmol, 0.10 equiv). The pale yellow solution was cooled to 0°C (ice/H_2O bath) and DHP (2.6 mL, 28.8 mmol, 2 equiv) was added via syringe. The resulting solution stirred at rt for 5.5 h then was quenched by sat. $NaHCO_{3(aq)}$ (40 mL). The organic layer was washed with brine (2 x 50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a red/orange oil, 3.34 g. The oil was dissolved in THF (65 mL) and added to an oven-dried 3-neck 250 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$. The solution was cooled to -78°C (dry ice/acetone bath) and *n*BuLi (7.7 mL, 15.5 mmol, 1.2 equiv) was added dropwise over 10 min. The resulting brown solution stirred at -78°C for 1 h then MeI (1.2 mL, 19.4 mmol, 1.5 equiv) was added. The orange solution stirred at rt for 5 h then was quenched by sat. $NH_4Cl_{(aq)}$ (60 mL). The aqueous layer was extracted with ether (2 x 50 mL) and the combined organic layers were washed with brine (2 x 75 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a dark red oil, 2.50 g. The oil was dissolved in EtOH (25 mL) and added to an oven-dried 100 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$. PPTS (694 mg, 2.76 mmol, 0.30 equiv) was subsequently added and the light orange solution stirred at 50°C for 4 h. The solution was then cooled to rt and concentrated *in vacuo* to give an orange oil. The oil was dissolved in DCM, washed with brine (2 x 25 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a dark orange oil.

Purification via column chromatography (silica gel 2.5 x 12 cm; gradient elution with 10%-13% EtOAc/hexanes) gave alcohol **SI-9** as a yellow oil (900 mg, 33% over 3 steps). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (20% EtOAc/hexanes) = 0.45

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.33-7.16 (m, 5H), 3.75-3.67 (m, 1H), 2.86-2.64 (m, 2H), 2.45-2.31 (m, 2H), 1.88-1.80 (m, 6H)



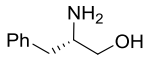


Silicon-Tethered Alkyne 68

To an oven-dried 100 mL RBF equipped with magnetic stir bar under $Ar_{(g)}$ was added **SI-9** (900 mg, 4.8 mmol, 1 equiv), DCM (30 mL), imidazole (654 mg, 9.6 mmol, 2 equiv) and DMAP (117 mg, 0.96 mmol, 0.20 equiv). The solution was cooled to 0°C (ice/H_2O bath) and vinyldimethylchlorosilane (0.9 mL, 6.2 mmol, 1.3 equiv) was added. The white suspension stirred at rt overnight then was quenched by sat. $NH_4Cl_{(aq)}$ (35 mL). The aqueous layer was extracted with DCM (3 x 25 mL) then the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 13 cm; gradient elution with 2%-3% ether/hexanes) gave alkyne **68** as a clear oil (1.05 g, 80%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (10% ether/hexanes) = 0.45

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.31-7.26 (m, 2H), 7.21-7.15 (m, 3H), 6.18 (dd, 1H, *J* = 20.0, 14.9 Hz), 6.02 (dd, 1H, *J* = 14.9, 4.2 Hz), 5.79 (dd, 1H, *J* = 19.9, 4.2 Hz), 3.85-3.77 (m, 1H), 2.76 (ddd, 1H, *J* = 16.4, 10.9, 5.6 Hz), 2.58 (ddd, 1H, *J* = 16.6, 10.9, 5.9 Hz), 2.39-2.23 (m, 2H), 2.00-1.88 (m, 1H), 1.87-1.74 (m, 1H), 1.78 (t, 3H, *J* = 2.5 Hz), 0.22 (d, 6H, *J* = 1.2 Hz)

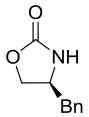


***(S)*-Phenylalanol (69)**

To an oven-dried 3-neck 3 L RBF equipped with overhead mechanical stirrer, pressure equalizing addition funnel and reflux condenser under $Ar_{(g)}$ was added L-phenylalanine (100 g, 605 mmol, 1 equiv), THF (1 L) and sodium borohydride (55 g, 1.45 mol, 2.4 equiv). The white suspension was cooled to 0°C (ice/H_2O bath) and a solution of iodine (154 g, 605 mmol, 1 equiv) in THF (400 mL) was added dropwise over 4 h. (Caution: Vigorous gas evolution!) Once the addition was complete, the cloudy reaction mixture was slowly warmed to rt then stirred at reflux overnight. The reaction mixture was cooled to rt and quenched by dropwise addition of MeOH (200 mL over 1.5 h) until the solution turned clear. (Caution: Vigorous gas evolution!) The solution stirred at rt for 30 min then concentrated *in vacuo* to give a white paste. The paste was dissolved in 20% $KOH_{(aq)}$ (650 mL) and stirred at rt for 4 h. The mixture was extracted with DCM (3 x 600 mL) [note: DCM is top layer], dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow oil. To the oil was added EtOAc (100 mL) and the solution stirred vigorously until precipitation occurred. The resulting suspension was concentrated *in vacuo* to yield a white pasty solid, which was recrystallized from EtOAc (350 mL) to give **69** as a white powder (36.7 g). A second (17.9 g) and third crop (1.22 g) were obtained for a total yield of 55.8 g (61%). Spectroscopic data corresponded to what was reported in the literature.[40]

mp = 89-92°C

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34-7.18 (m, 5H), 3.64 (dd, 1H, *J* = 10.5, 3.9 Hz), 3.38 (dd, 1H, *J* = 10.5, 7.2 Hz), 3.17-3.08 (m, 1H), 2.80 (dd, 1H, *J* = 13.5, 5.1 Hz), 2.53 (dd, 1H, *J* = 13.5, 8.7 Hz), 1.93 (s, 3H)

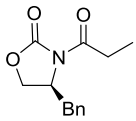


Oxazolidinone 70

To a flame-dried 3-neck 100 mL RBF equipped with a magnetic stir bar and 12 inch Vigreux column fitted with a distillation head and 25 mL collection flask under $Ar_{(g)}$ was added **69** (9.72 g, 64 mmol, 1 equiv), diethyl carbonate (16 mL, 132 mmol, 2.1 equiv) and K_2CO_3 (885 mg, 6.4 mmol, 0.10 equiv). The white suspension was heated to 135°C. The collection flask was cooled in an ice-bath and ethanol was collected over a 4 h period. Upon cessation of ethanol distillation, the reaction mixture was cooled to rt, diluted with DCM (50 mL) and washed with H_2O (50 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give an off-white solid. Recrystallization from 2:1 EtOAc/hexanes (60 mL) gave **70** as white needles (9.5 g, 85%). Spectroscopic data corresponded to what was reported in the literature.[41]

mp = 86-89°C

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.37-7.25 (m, 3H), 7.19-7.17 (m, 2H), 5.62 (br s, 1H), 4.48-4.42 (m, 1H), 4.18-4.04 (m, 2H), 2.88 (d, 2H, *J* = 6.6 Hz)



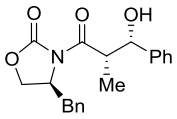
Acylated Oxazolidinone 71

To an oven-dried 2-neck 2L flask equipped with a magnetic stir bar and pressure equalizing addition funnel under $Ar_{(g)}$ was added **70** (51 g, 288 mmol, 1 equiv) and THF (870 mL). The solution was cooled to -78°C (dry ice/acetone bath) and *n*BuLi (116 mL, 291 mmol, 1.01 equiv) was added dropwise over 30 min, followed by addition of propionyl chloride (28 mL, 317 mmol, 1.1 equiv) in one portion. The reaction stirred at -78°C for 30 min then was warmed to rt over 1 h. Upon warming, the orange solution was quenched by sat. $NH_4Cl_{(aq)}$ (175 mL) and concentrated *in vacuo* to give an orange suspension. The suspension was extracted with DCM (3 x 225 mL) and the combined organic layers were washed with 1M $NaOH_{(aq)}$ (400 mL) and brine (400 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow oil. The oil was placed in the freezer overnight to yield a yellow solid, which was pulverized and triturated with cold hexanes to give **71** as a white powder (59 g). A second crop (4.3 g) was obtained to give a total yield of 63.3 g (94%). Spectroscopic data corresponded to what was reported in the literature.[42]

R_f (25% EtOAc/hexanes) = 0.59

mp = 42-44°C

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.37-7.20 (m, 5H), 4.72-4.64 (m, 1H), 4.24-4.15 (m, 2H), 3.31 (dd, 1H, *J* = 13.3, 3.3 Hz), 3.07-2.86 (m, 2H), 2.77 (dd, 1H, *J* = 13.4, 9.6 Hz), 1.21 (t, 3H, *J* = 7.3 Hz)



Aldol Adduct 72

Evans method: To an oven-dried 100 mL 3-neck RBF equipped with a magnetic stir bar and internal thermometer under $Ar_{(g)}$ was added **71** (1.0 g, 4.3 mmol, 1 equiv) and DCM (8.5 mL). The solution was cooled to 0°C and Bu_2BOTf (1.4 mL, 6.5 mL, 1.5 equiv) was added dropwise at such a rate to maintain the internal temperature below 3°C. Once the addition was complete, NEt_3 (0.8 mL, 5.7 mmol, 1.32 equiv) was added dropwise at such a rate to maintain the internal temperature below 3°C. Once the addition was complete, the resulting light yellow solution was cooled to -78°C (dry ice/acetone bath) and benzaldehyde (0.5 mL, 4.7 mmol, 1.1 equiv) was added dropwise. The solution stirred at -78°C for 2 h then stirred at rt overnight. The reaction mixture was quenched with pH 7 phosphate buffer (5 mL), cold methanol (15 mL) then dropwise addition of a 2:1 MeOH/30% H_2O_2 solution (15 mL) at such a rate to maintain the internal temperature below 10°C. After stirring in an ice bath for 1 h, the reaction mixture was concentrated *in vacuo* to give a white slurry, which was then extracted with ether (25 mL). The organics were washed with 5% $NaHCO_3$ (25 mL) and brine (25 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a pale yellow solid. Recrystallization from 1:2 EtOAc/hexanes (2 mL) gave **72** as a white solid (911 mg, 62%). Spectroscopic data corresponded to what was reported in the literature.[42]

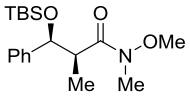
Crimmins method: To a flame-dried 50 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added **71** (233 mg, 1.0 mmol, 1 equiv) and DCM (10 mL). The solution was cooled to 0°C (ice/H_2O bath) and $TiCl_4$ (0.12 mL, 1.05 mmol, 1.05 equiv) was added dropwise. The resulting yellow suspension stirred at 0°C for 15 min then DIPEA (0.14 mL, 1.10 mmol, 1.1 equiv) was

added dropwise. The dark-colored solution stirred at 0°C for 40 min then NMP (0.10 mL, 1.0 mmol, 1 equiv) was added dropwise. After stirring at 0°C for 10 min, benzaldehyde (0.11 mL, 1.10 mmol, 1.1 equiv) was added in one portion. After stirring at 0°C for 1 h, the reaction mixture was quenched by sat. $NH_4Cl_{(aq)}$ (25 mL). The aqueous layer was extracted with DCM (3 x 20 mL) and the combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo* to give an orange oil. Purification via column chromatography (silica gel 2.5 x 11 cm; eluted with 25% EtOAc/Hexanes) gave **72** as a pale yellow solid (33:2:1, 301 mg, 89%). Spectroscopic data corresponded to what was reported in the literature.[45]

R_f (20% EtOAc/hexanes) = 0.12

mp = 92-94°C

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42-7.19 (m, 10H), 5.11-5.09 (m, 1H), 4.64-4.57 (m, 1H) 4.17-4.05 (m, 3H), 3.25 (dd, 1H, *J* = 13.2, 3.3 Hz), 3.06 (d, 1H, *J* = 2.4 Hz), 2.78 (dd, 1H, *J* = 13.5, 9.6 Hz), 1.23 (d, 3H, *J* = 6.9 Hz)



Weinreb Amide 73

To an oven-dried 3-neck 500 mL RBF equipped with magnetic stir bar and pressure equalizing addition funnel under $Ar_{(g)}$ was added Weinreb salt (10.4 g, 106 mmol, 3 equiv) and THF (55 mL). The suspension was cooled to 0°C (ice/H_2O bath) and $AlMe_3$ (54 mL, 107 mmol, 3.02 equiv) was added dropwise over 30 min. (Caution: Vigorous gas evolution!) Once the addition was complete the cooling bath was removed and the cloudy solution stirred at rt for 30 min. The solution was re-cooled to -15°C (salt/ice/H_2O bath) and a solution of aldol adduct **72** (12.0 g, 35.4 mmol, 1 equiv) in THF (55 mL) was added dropwise. (Caution: Vigorous gas evolution!) The reaction mixture stirred for 45 min then was quenched by cannula transfer into a 2 L RBF cooled at 0°C (ice/H_2O bath) containing 1:2 DCM/1N $HCl_{(aq)}$ (780 mL). (Caution: Vigorous gas evolution!) After stirring for 30 min the layers were separated and the aqueous was extracted with DCM (3 x 250 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow oil. To the oil was added DMF (55 mL), imidazole (4.8 g, 71 mmol, 2 equiv) and TBSCl (5.9 g, 39 mmol, 1.1 equiv). The yellow solution stirred at rt overnight then poured into H_2O (200 mL) and extracted with EtOAc (3 x 200 mL). The organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow oil. Purification via column chromatography (silica gel 4.5 x 10 cm; gradient elution with 10%-30% EtOAc/hexanes) gave **73** as a clear oil (10.5g, 88% over two steps).

R_f (30% EtOAc/hexanes) = 0.56

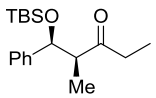
$[\alpha]_D^{24}$ = -2.1° (*c* = 1.030 in $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34-7.17 (m, 5H), 4.80 (d, 1H, *J* = 8.6 Hz), 3.26 (s, 3H), 3.16 (bs, 1H), 2.95 (s, 3H), 1.27 (d, 3H, *J* = 6.8 Hz), 0.87 (s, 9H), 0.04 (s, 3H), -0.22 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.6, 144.3, 128.0, 127.4, 127.0, 76.6, 61.3, 45.5, 31.9, 26.0, 18.4, 15.0, -4.4, -4.8

FT-IR (NaCl, thin film) ν = 3499, 3032, 2959, 1660, 1462, 1256 cm^{-1}

Anal. calcd for $C_{18}H_{31}NO_3Si$: C 64.05, H 9.26, N 4.15; found: C 63.99, H 9.33, N 4.07



Ethyl Ketone 74

To a flame-dried 50 mL 3-neck RBF equipped with a magnetic stir bar and pressure equalizing addition funnel under $Ar_{(g)}$ was added a solution of Weinreb amide **73** (2.2 g, 6.5 mmol, 1 equiv) in THF (13 mL). The reaction mixture was cooled to 0°C (ice/water bath) and ethyl magnesium bromide (13.3 mL, 19.5 mmol, 3 equiv) was added dropwise. The dark grey solution stirred at 0°C for 5 min then was warmed to rt and stirred for 5 h. The reaction mixture was poured into 1M HCl and the layers were separated. The aqueous phase was extracted with ether (3 x 40 mL) then the combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 15 cm; gradient elution with 2%-6% EtOAc/hexanes) gave **74** as a clear oil (1.70 g, 85%).

R_f (5% EtOAc/hexanes) = 0.26

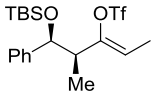
$[\alpha]_D^{24}$ = -3.9° (*c* = 2.428 in EtOAc)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.30-7.18 (m, 5H), 4.75 (d, 1H, *J* = 7.5 Hz), 2.87-2.30 (m, 1H), 2.24 (dq, 1H, *J* = 18.3, 7.2 Hz), 1.90 (dq, 1H, *J* = 18.0, 7.2 Hz), 1.17 (d, 3H, *J* = 6.9 Hz), 0.86 (s, 9H), 0.79 (t, 3H, *J* = 7.2 Hz), 0.01 (s, 3H), -0.24 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 213.3, 143.5, 128.0, 127.3, 126.5, 76.6, 55.4, 36.5, 25.8, 18.0, 13.3, 7.1, -4.6, -4.8

FT-IR (NaCl, thin film) ν = 3032, 2933, 1714, 1454, 1361, 1256 cm^{-1}

HRMS (ESI) calcd for $(C_{18}H_{30}O_2Si)Na^+$: 329.1907; found 329.1911.



Enol Triflate 75

To a flame-dried 250 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added ethyl ketone **74** (3.73 g, 12.2 mmol, 1 equiv) and THF (100 mL). Comins' reagent[49] (9.6 g, 24.4 mmol, 2 equiv) was added in one portion. The clear solution was cooled to -78°C (dry ice/acetone bath) and freshly prepared KHMDS (0.90M in THF, 15 mL, 13.4 mmol, 1.1 equiv) was added dropwise over 15 min. The orange solution stirred at -78°C for 30 min then an additional portion of KHMDS (0.90M in THF, 7.4 mL, 6.7 mmol, 0.55 equiv) was added dropwise over 10 min. The red/orange solution continued stirring at -78°C for 30 min then an additional portion of KHMDS (0.90M in THF, 3.4 mL, 3.1 mmol, 0.25 equiv) was added dropwise over 5 min. After stirring an additional 15 min, the reaction mixture was warmed slightly and then quenched by addition of sat. $NaHCO_{3(aq)}$ (100 mL). The layers were separated and the aqueous phase was extracted with DCM (3 x 50 mL). The combined organics were washed with brine (2 x 100 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a brown oil. Purification via column chromatography (silica gel 4.5 x 12 cm; gradient elution with hexanes-10% EtOAc/hexanes) gave **75** as a clear oil (3.2 g, 60%).

R_f (10% EtOAc/hexanes) = 0.62

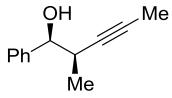
$[\alpha]_D^{24}$ = +9.1° (*c* = 0.610 in $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33-7.21 (m, 5H), 5.38 (dq, 1H, *J* = 6.9, 0.9 Hz), 4.99 (d, 1H, *J* = 2.6 Hz), 2.68-2.63 (m, 1H), 1.76 (dd, 3H, *J* = 7.0, 1.4 Hz), 0.94 (d, 3H, *J* = 6.9 Hz), 0.90 (s, 9H), -0.03 (s, 3H), -0.18 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.9, 143.0, 128.2, 127.3, 126.2, 118.7 (q, $J_{C\text{-}F}$ = 317.5 Hz), 117.0, 73.1, 46.8, 26.0, 18.4, 11.5, 10.5, -4.6, -5.5

FT-IR (NaCl, thin film) ν = 3499, 2957, 2860, 1645, 1414, 1244, 1211, 1135 cm^{-1}

HRMS (ESI) calcd for $(C_{19}H_{29}F_3O_4SSi)Na^+$: 461.1400; found 461.1411.



Alcohol 76

To a 100 mL RBF equipped with a magnetic stir bar was added a solution of enol triflate **75** (3.0 g, 6.84 mmol, 1 equiv) in DMF (18 mL). To the clear solution was added TBAF·$3H_2O$ (8.9 g, 34.2 mmol, 5 equiv) then the solution stirred at 60°C for 1 h. The reaction mixture was cooled to rt, quenched with water (60 mL) and the layers were separated. The aqueous phase was extracted with DCM (3 x 30 mL) then the combined organic extracts were washed with brine (60 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 13 cm; gradient elution with 3%-4% EtOAc/hexanes) gave **76** as a clear oil (997 mg, 84%).

R_f (10% EtOAc/hexanes) = 0.14

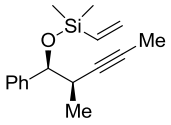
$[\alpha]_D^{24}$ = -41.1° (*c* = 0.50 in $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39-7.26 (m, 5H), 4.70 (d, 1H, *J* = 5.1 Hz), 2.87-2.77 (m, 1H), 2.31 (bs, 1H), 1.79 (d, 3H, *J* = 2.4 Hz), 1.05 (d, 3H, *J* = 7.2 Hz)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 141.7, 128.2, 127.7, 126.6, 80.7, 78.8, 76.5, 34.4, 15.8, 3.7

FT-IR (NaCl, thin film) ν = 3401, 3030, 2974, 1593, 1513, 1452, 1022 cm^{-1}

Anal. calcd for $C_{12}H_{14}O$: C 82.72, H 8.10; found: C 82.56, H 8.07.



Silicon Tethered Alkyne 77

To a flame-dried 50 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added a solution of alcohol **76** (450 mg, 2.6 mmol, 1 equiv) in DCM (17 mL). To the clear solution was added imidazole (354 mg, 5.2 mmol, 2 equiv) and DMAP (64 mg, 0.52 mmol, 0.2 equiv). The solution was cooled to 0°C (ice/water bath) and vinyldimethylchlorosilane (0.54 mL, 3.9 mmol, 1.5 equiv) was added in one portion via syringe. The white suspension stirred at 0°C for 5 min then was warmed to rt and stirred for 1 h. The reaction was quenched by addition of sat. $NH_4Cl_{(aq)}$ (20 mL) and extracted with DCM (3 x 25 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification via column chromatography (silica gel; gradient elution with hexanes-3% EtOAc/hexanes) gave **77** as a clear oil (616 mg, 92%).

R_f (10% EtOAc/hexanes) = 0.53

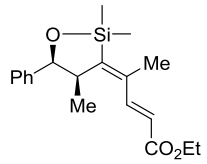
$[\alpha]_D^{24}$ = -30.5° (*c* = 0.934 in $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.35-7.21 (m, 5H), 6.07 (dd, 1H, *J* = 19.5, 14.9 Hz), 5.95 (dd, 1H, *J* = 14.8, 4.8 Hz), 5.72 (dd, 1H, *J* = 19.5, 4.8 Hz), 4.59 (d, 1H, *J* = 6.5 Hz), 2.68-2.58 (m, 1H), 1.72 (d, 3H, *J* = 2.4 Hz), 1.12 (d, 3H, *J* = 6.9 Hz), 0.13 (s, 3H), 0.09 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.4, 137.9, 133.1, 127.8, 127.3, 126.9, 81.7, 78.4, 77.6, 35.5, 16.9, 3.7, -1.3, -1.5

FT-IR (NaCl, thin film) ν = 3051, 2968, 1595, 1494, 1453, 1253, 1086 cm^{-1}

HRMS (ESI) calcd for $(C_{16}H_{22}OSi)Na^+$: 281.1332; found: 281.1338.



Diene 78A

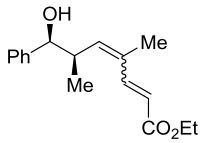
To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar in an $Ar_{(g)}$ filled glovebox was added $RuHCl(CO)(H_2IMes)(PPh_3)$ (15 mg, 0.021 mmol, 0.10 equiv) and a solution of alkyne **77** (55 mg, 0.21 mmol, 1 equiv) and ethyl acrylate (114 µL, 1.05 mmol, 5 equiv) in toluene (0.42 mL). The Schlenk tube was sealed with a rubber septum, removed from the glovebox and stirred under $Ar_{(g)}$ at 80°C. After 45 min, the brown solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a brown oil. Purification via column chromatography (silica gel 1.5 x 8.5 cm; eluted with 3% ether/hexanes) gave diene **78A** as a clear oil (38 mg, 55%, 5.4:1 **78A:78B**). Further purification via preparative thin layer chromatography (gradient elution with 3%-5% ether/hexanes) provided **78A** in a 10:1 ratio (**78A:78B**).

R_f (1:15 ether/hexanes) = 0.34

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.65 (d, 1H, *J* = 15.6 Hz), 7.36-7.22 (m, 5H), 5.96 (d, 1H, *J* = 15.6 Hz), 5.13 (d, 1H, *J* = 4.2 Hz), 4.24 (q, 2H, *J* = 11.4, 4.2 Hz), 3.33-3.29 (m, 1H), 1.96 (s, 3H), 1.32 (t, 3H, *J* = 5.1 Hz), 0.61 (d, 3H, *J* = 7.2 Hz), 0.46 (s, 3H), 0.40 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.9, 157.4, 142.2, 141.5, 137.3, 128.5, 127.3, 126.0, 119.4, 80.5, 60.8, 44.0, 20.8, 16.6, 14.7, 0.6, -0.1

FT-IR (NaCl, thin film) ν = 2965, 1713, 1620, 1597, 1451, 1367, 1293, 1253, 1177 cm^{-1}

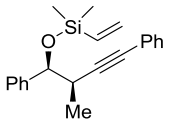


Diene Mixture 79A & 79B

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under $Ar_{(g)}$ was added diene mixture (1.5:1 **78A:78B**, 52 mg, 0.16 mmol, 1 equiv) and THF (0.8 mL). To the pale yellow solution was added TBAF (1M in THF, 0.32 mL, 0.32 mmol, 2 equiv). After stirring at rt for 1 h the reaction mixture was concentrated *in vacuo* to give an orange oil. Purification via column chromatography (silica gel; eluted with 30% ether/hexanes) gave the alcohol mixture as a clear oil (2:1 **79A:79B**, 13 mg, 30%).

R_f (40% ether/hexanes) = 0.26

^{1}H NMR (300 MHz, $CDCl_3$) δ = **isomer 79A:** 7.63 (d, 1H, *J* = 15.9 Hz), 7.32-7.24 (m, 5H), 5.81 (d, 1H, *J* = 15.5 Hz), 5.56 (d, 1H, *J* = 9.8 Hz), 4.59 (d, 1H, *J* = 6.0 Hz), 4.21 (q, 1H, *J* = 14.3, 7.2 Hz), 3.20-3.08 (m, 1H), 1.86 (br s, 1H), 1.79 (d, 3H, *J* = 1.3 Hz), 1.31 (t, 3H, *J* = 7.1 Hz), 1.05 (d, 3H, *J* = 6.8 Hz); **isomer 79B diagnostic peaks:** 5.72 (d, 1H, *J* = 15.6 Hz), 5.69 (d, 1H, *J* = 9.7 Hz), 4.55 (d, 1H, *J* = 6.8 Hz), 4.18 (q, 1H, *J* = 13.5, 7.5 Hz), 2.99-2.86 (m, 1H), 1.86 (br s, 1H), 1.59 (d, 1H, *J* = 1.2 Hz), 1.28 (t, 3H, *J* = 7.1 Hz), 1.09 (d, 3H, *J* = 6.8 Hz)



Silicon Tethered Alkyne 80

To a flame-dried 50 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added a solution of alcohol **83** (296 mg, 1.3 mmol, 1 equiv) in DCM (9 mL). To the yellow solution was added imidazole (177 mg, 2.6 mmol, 2 equiv) and DMAP (32 mg, 0.26 mmol, 0.2 equiv). The solution was cooled to 0°C (ice/water bath) and vinyldimethylchlorosilane (0.27 mL, 2.0 mmol, 1.5 equiv) was added in one portion via syringe. The yellow suspension stirred at 0°C for 5 min then was warmed to rt and stirred overnight. The reaction was quenched by addition of sat. $NH_4Cl_{(aq)}$ (10 mL) and extracted with DCM (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 10 cm; gradient elution with hexanes-3% EtOAc/hexanes) gave silicon-tethered alkyne **80** as a clear oil (348 mg, 83%).

R_f (10% EtOAc/hexanes) = 0.53

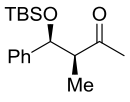
$[\alpha]_D^{24}$ = +25.4° (*c* = 0.956 in $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.47-7.30 (m, 10H), 6.18 (dd, 1H, *J* = 19.7, 4.9 Hz), 6.04 (dd, 1H, *J* = 14.9, 10.3 Hz), 5.82 (dd, 1H, *J* = 19.7, 15.2 Hz), 4.79 (d, 1H, *J* = 6.8 Hz), 3.04-2.95 (m, 1H), 1.36 (d, 3H, *J* = 6.9 Hz), 0.24 (s, 3H), 0.20 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.6, 138.0, 133.6, 131.9, 128.6, 128.2, 128.0, 127.8, 127.3, 124.3, 92.8, 82.9, 78.6, 36.6, 17.1, -1.0, -1.1

FT-IR (NaCl, thin film) ν = 3053, 2967, 2887, 1597, 1491, 1452, 1407, 1253, 1086, 1070 cm^{-1}

Anal. calcd for $C_{21}H_{24}OSi$: C 78.70, H 7.55; found: C 78.58, H 7.81.



Methyl Ketone 81

To a flame-dried 25 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added a solution of Weinreb amide **73** (1.0 g, 3.0 mmol, 1 equiv) in THF (6 mL). The reaction mixture was cooled to 0°C (ice/water bath) and methylmagnesium chloride (2 mL, 6.0 mmol, 2 equiv) was added dropwise. The reaction stirred at 0°C for 5 min then was warmed to rt and stirred for 3 h. The white suspension was poured into 1M HCl (10 mL) and the layers were separated. The aqueous phase was extracted with ether (3 x 10 mL) then the combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 15 cm; gradient elution with 1%-4% EtOAc/hexanes) gave **81** as a clear oil (718 mg, 82%).

R_f (15% EtOAc/hexanes) = 0.59

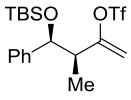
$[\alpha]_D^{24}$ = -16.9° (*c* = 0.946 in $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.33-7.21 (m, 5H), 4.83 (d, 1H, *J* = 6.8 Hz), 2.86-2.77 (m, 1H), 1.91 (s, 3H), 1.16 (d, 3H, *J* = 6.9 Hz), 0.88 (s, 9H), 0.03 (s, 3H), -0.22 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 211.2, 143.4, 128.1, 127.5, 126.3, 76.3, 56.0, 30.5, 25.9, 18.2, 12.6, -4.5, -5.1

FT-IR (NaCl, thin film) ν = 2959, 1715, 1454, 1360, 1256 cm^{-1}

Anal. calcd for $C_{17}H_{28}O_2Si$: C 69.81, H 9.65; found C 69.65, H 9.52.



Enol Triflate 82

To a oven-dried 100 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added freshly prepared KHMDS (1M in THF, 7.5 mmol, 1.1 equiv). The pale yellow solution was cooled to -78°C (dry ice/acetone bath) and methyl ketone **81** (2.0 g, 6.8 mmol, 1 equiv) in THF (6.8 mL) was added dropwise. Comins' reagent[49] (5.3 g, 13.6 mmol, 2 equiv) in THF (6.8 mL) was subsequently added in one portion. The yellow solution stirred at -78°C for 2 h. The reaction mixture was warmed slightly and quenched with H_2O (15 mL). The layers were separated and the aqueous phase was extracted with DCM (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. The residue was purified by column chromatography (silica gel; gradient elution with 1%-2% EtOAc/hexanes) to give **82** as a clear oil (2.35 g, 81%).

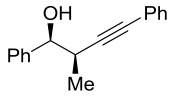
R_f (10% EtOAc/hexanes) = 0.68

$[\alpha]_D^{24}$ = +1.4° (*c* = 0.946 in $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34-7.21 (m, 5H), 5.17 (d, 1H, *J* = 3.8 Hz), 4.95-4.93 (m, 2H), 2.67-2.59 (m, 1H), 1.05 (d, 3H, *J* = 6.9 Hz), 0.91 (s, 9H), 0.02 (s, 3H), -0.18 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.6, 142.8, 128.2, 127.6, 126.4, 118.8 (q, J_{C-F} = 316.4 Hz), 105.5, 74.0, 47.7, 26.0, 18.5, 11.3, -4.5, -5.3

Anal. calcd for $C_{18}H_{27}F_3O_4SSi$: C 50.92, H 6.41; found C 50.47, H 6.38.



Alcohol 83

To an oven-dried 100 mL RBF equipped with a magnetic stir bar was added a solution of enol triflate **82** (2.56 g, 6.0 mmol, 1 equiv) in DMF (25 mL). To the clear solution was added TBAF·$3H_2O$ (7.8 g, 30 mmol, 5 equiv) then the solution stirred at 60°C for 1 h. The reaction mixture was cooled to rt, quenched with water (50 mL) and the layers were separated. The aqueous phase was extracted with DCM (3 x 30 mL) then the combined organic extracts were washed with brine (2 x 60 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil, 875 mg. The oil was dissolved in THF (22 mL) and added to an oven-dried 100 mL Schlenk tube under $Ar_{(g)}$ containing $PdCl_2(PPh_3)_2$ (197 mg, 0.28 mmol, 0.05 equiv), CuI (105 mg, 0.55 mmol, 0.10 equiv), NEt_3 (2.3 mL, 16.5 mmol, 3 equiv) and iodobenzene (0.92 mL, 8.3 mmol, 1.5 equiv). The orange solution was subjected to three cycles of freeze/pump/thaw then stirred at rt under $Ar_{(g)}$. After 30 min, the brown suspension was diluted with ether (20 mL), washed with sat. $NH_4Cl_{(aq)}$ (2 x 35 mL) and brine (2 x 35 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a red/orange oil. Purification via column chromatography (silica gel 2.5 x 15 cm; gradient elution with 10%-20% EtOAc/hexanes) gave **83** as an orange oil (1.02 g, 72% over two steps).

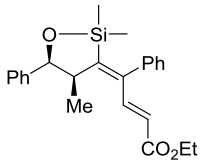
R_f (20% EtOAc/hexanes) = 0.33

$[\alpha]_D^{24}$ = -14.9° (*c* = 0.728 in $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.50-7.30 (m, 10H), 4.80 (d, 1H, *J* = 3.7 Hz), 3.17-3.08 (m, 1H), 2.67 (s, 1H), 1.30 (d, 3H, *J* = 7.0 Hz)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 141.7, 131.7, 128.3, 128.2, 128.0, 127.9, 126.8, 123.5, 91.3, 83.3, 76.8, 35.1, 16.3

Anal. calcd for $C_{17}H_{16}O$: C 86.40, H 6.82; found C 86.46, H 6.64.

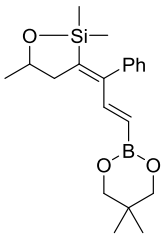


Diene 84

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar in an $Ar_{(g)}$ filled glovebox was added $RuHCl(CO)(H_2IMes)(PPh_3)$ (12 mg, 0.016 mmol, 0.10 equiv) and a solution of alkyne **80** (50 mg, 0.16 mmol, 1 equiv) and ethyl acrylate (87 µL, 0.80 mmol, 5 equiv) in toluene (0.5 mL). The vessel was sealed with a rubber septum, removed from the glovebox and placed under $Ar_{(g)}$. The septum was removed, a cold-finger was quickly attached then the solution stirred at 110°C. After 30 min the brown solution was cooled to rt, filtered through a plug of silica gel (eluted with DCM) and concentrated *in vacuo* to give a brown oil. Purification via column chromatography (silica gel 1.5 x 8.5 cm; gradient elution with 1%-4% ether/hexanes) gave diene **84** as a clear oil (14 mg, 22%).

R_f (1:15 ether/hexanes) = 0.22

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.85 (d, 1H, *J* = 15.8 Hz), 7.40-7.24 (m, 8H), 7.18-7.14 (m, 2H), 5.57 (d, 1H, *J* = 15.4 Hz), 5.18 (d, 1H, *J* = 4.1 Hz), 4.20 (q, 1H, *J* = 14.4, 7.2 Hz), 3.51-3.42 (m, 1H), 1.27 (t, 3H, *J* = 7.1 Hz), 0.75 (d, 3H, *J* = 7.2 Hz), 0.30 (s, 3H), -0.30 (s, 3H)



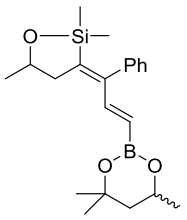
Silyl-Dienyl Boronate 87

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar in an argon filled glovebox was added $RuHCl(CO)(PCy_3)_2$ (9.4 mg, 0.013 mmol, 0.05 equiv), alkyne **41** (62.9 mg, 0.26 mmol, 1 equiv) in DCE (0.52 mL) and vinyl boronate **86** (82 µL, 0.52 mmol, 2 equiv). The vessel was sealed with a rubber septum, removed from the glovebox and placed under $Ar_{(g)}$. A cold-finger was quickly attached then the reaction stirred at 85°C for 3.5 h. The brown solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a brown oil. Purification via column chromatography (silica gel 1.5 x 11 cm; gradient elution with 5%-40% ether/hexanes) gave **87** as a light brown oil (58.6 mg, 63%).

R_f (10% ether/hexanes) = 0.10

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.45 (d, 1H, *J* = 17.8 Hz), 7.29-7.23 (m, 3H), 7.09-7.05 (m, 2H), 5.20 (d, 1H, *J* = 17.8 Hz), 4.24-4.14 (m, 1H), 3.62 (s, 4H), 3.08 (dd, 1H, *J* = 16.2, 5.3 Hz), 2.40 (dd, 1H, *J* = 16.2, 8.2 Hz), 1.31 (d, 3H, *J* = 6.1 Hz), 0.95 (s, 6H), -0.09 (s, 3H), -0.23 (s, 3H)

General Procedure A: Vinyl Boronate Coupling



Silyl-Dienyl Boronate 97

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar in an argon filled glovebox was added $RuHCl(CO)(PCy_3)_2$ (9.4 mg, 0.013 mmol, 0.05 equiv), alkyne **41** (62.9 mg, 0.26 mmol, 1 equiv) in toluene (0.52 mL) and vinyl boronate **93** (90 µL, 0.52 mmol, 2 equiv). The vessel was sealed with a rubber septum, removed from the glovebox, placed under $Ar_{(g)}$, then stirred at 85°C for 3.5 h. The orange/brown solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give an amber-colored oil. Purification via column chromatography (silica gel 2.5 x 12 cm; eluted with 10% ether/hexanes) gave **97** as a light brown oil (53.2 mg, 55%).

R_f (10% ether/hexanes) = 0.14

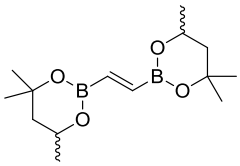
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43 (dd, 1H, *J* = 18.0, 1.5 Hz), 7.29-7.22 (m, 3H), 7.08-7.05 (m, 2H), 5.20 (d, 1H, *J* = 17.7 Hz), 4.23-4.16 (m, 1H), 3.07 (ddd, 1H, *J* = 16.5, 5.1, 3.9 Hz), 2.40 (ddd, 1H, *J* = 16.5, 8.1, 4.2 Hz), 1.77 (dd, 1H, *J* = 14.1, 3.0 Hz), 1.47 (dd, 1H, *J* = 13.8, 11.7 Hz), 1.33-1.24 (m, 12H), -0.09 (s, 1.5H), -0.11 (s, 1.5H), -0.24 (s, 1.5H), -0.26 (s, 1.5H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.4, 145.9, 144.7, 141.9, 129.9, 127.9, 127.2, 72.7, 71.0, 65.0, 46.1, 40.8, 31.4, 28.3, 24.2, 23.3, 0.7, 0.6, -0.3, -0.4

^{11}B NMR (96 MHz, $CDCl_3$) δ = 28.7

FT-IR (NaCl, thin film) ν = 2976, 1629, 1384, 1306, 1260, 1209, 1170, 1090, 807 cm^{-1}

Anal. calcd for $C_{21}H_{31}BO_3Si$: C 68.10, H 8.44; found C 67.91, H 8.73.



Boronate Dimer 101

To an oven-dried 25 mL Schlenk tube with stir bar under $Ar_{(g)}$ was added $RuHCl(CO)(PCy_3)_2$ (36 mg, 0.05 mmol, 0.05 equiv), vinyl boronate **93** (0.17 mL, 1.0 mmol, 1 equiv) and DCE (1 mL). A cold-finger was quickly attached and the orange suspension stirred at 85°C overnight. The resulting red/brown solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a brown oil. Purification via column chromatography (silica gel 2.5 x 15 cm; gradient elution with 10%-20% ether/hexanes) gave **101** as a light brown solid (60 mg, 43%).

R_f (20% ether/hexanes) = 0.12

mp = 57-59°C

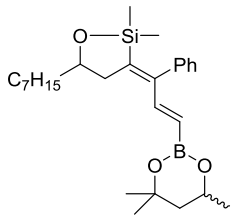
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.50 (s, 2H), 4.23-4.15 (m, 2H), 1.76 (dd, 2H, *J* = 13.6, 2.8 Hz), 1.44 (dd, 2H, *J* = 13.6, 11.6 Hz), 1.26 (s, 12H), 1.23 (d, 6H, *J* = 6.4 Hz)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 70.8, 64.8, 46.1, 31.4, 28.2, 23.3

^{11}B NMR (128 MHz, $CDCl_3$) δ = 25.4

FT-IR (NaCl, thin film) ν = 2976, 2910, 2362, 1945, 1394, 1266, 1208, 1178, 1031 cm^{-1}

Anal. calcd for $C_{14}H_{26}B_2O_4$: C 60.06, H 9.36; found C 60.14, H 9.36.



Silyl-Dienyl Boronate 102

Following general procedure A: $RuHCl(CO)(PCy_3)_2$ (9.1 mg, 0.0125 mmol, 0.05 equiv), alkyne **55**[26] (82.0 mg, 0.25 mmol, 1 equiv) in toluene (0.5 mL) and vinyl boronate **93** (87 µL, 0.50 mmol, 2 equiv) were combined and stirred at 85°C for 3 h. The residue was purified by column chromatography (silica gel 2.5 x 12 cm; eluted with 10% ether/hexanes) to give **102** as a pale brown oil (68.3 mg, 60%).

R_f (10% ether/hexanes) = 0.19

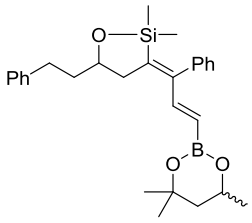
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43 (dd, 1H, *J* = 17.7, 1.5 Hz), 7.27-7.23 (m, 3H), 7.07-7.04 (m, 2H), 5.20 (d, 1H, *J* = 17.7 Hz), 4.23-4.19 (m, 1H), 4.07-4.03 (m, 1H), 3.04 (dt, 1H, *J* = 15.9, 4.8 Hz), 2.45 (ddd, 1H, *J* = 16.2, 7.5, 3.6 Hz), 1.77 (dd, 1H, *J* = 13.8, 2.7 Hz), 1.48 (t, 1H, *J* = 11.7 Hz), 1.95-0.99 (m, 24H), -0.12 (s, 1.5H), -0.14 (s, 1.5H), -0.22 (s, 1.5H), -0.24 (s, 1.5H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.4, 145.8, 144.8, 142.0, 129.9, 127.9, 127.1, 76.7, 71.0, 65.0, 46.1, 38.9, 38.6, 32.0, 31.4, 29.9, 29.5, 28.3, 25.9, 23.3, 22.9, 14.3, 0.7, 0.6, -0.2, -0.3

^{11}B NMR (96 MHz, $CDCl_3$) δ = 27.5

FT-IR (NaCl, thin film) ν = 2930, 2858, 1597, 1583, 1417, 1390, 1324, 1291, 1272, 1200 cm^{-1}

HRMS (ESI) calcd for $(C_{27}H_{43}BO_3Si)Na^+$: 477.2967; found: 477.2966.



Silyl-Dienyl Boronate 103

Following general procedure A: $RuHCl(CO)(PCy_3)_2$ (9.1 mg, 0.0125 mmol, 0.05 equiv), alkyne **56**[26] (82.7 mg, 0.25 mmol, 1 equiv) in toluene (0.5 mL) and vinyl boronate **93** (87 µL, 0.50 mmol, 2 equiv) were combined and stirred at 85°C for 6 h. The residue was purified by column chromatography (silica gel 2.5 x 12.5 cm; eluted with 10% ether/hexanes) to give **103** as a pale brown oil (67 mg, 58%).

R_f (10% ether/hexanes) = 0.16

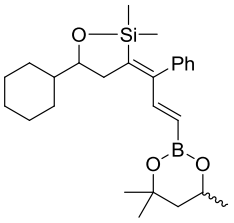
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.45 (dd, 1H, *J* = 17.7, 1.5 Hz), 7.33-7.07 (m, 10H), 5.24 (d, 1H, *J* = 17.7 Hz), 4.26-4.20 (m, 1H), 4.16-4.07 (m, 1H), 3.07 (dt, 1H, *J* = 15.9, 5.1 Hz), 2.90-2.69 (m, 2H), 2.53 (ddd, 1H, *J* = 16.2, 7.2, 4.2 Hz), 1.91 (m, 2H), 1.79 (dd, 1H, *J* = 13.8, 3.0 Hz), 1.50 (t, 1H, *J* = 11.7 Hz), 1.30-1.27 (m, 9H), -0.06 (s, 1.5H), -0.08 (s, 1.5H), -0.16 (s, 1.5H), -0.18 (s, 1.5H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.5, 145.4, 144.7, 142.5, 142.0, 129.9, 128.6, 128.5, 127.9, 127.2, 125.9, 75.9, 71.0, 65.0, 46.1, 40.2, 38.9, 32.3, 31.4, 28.3, 23.3, 0.7, 0.6, -0.2, -0.3

^{11}B NMR (96 MHz, $CDCl_3$) δ = 27.6

FT-IR (NaCl, thin film) ν = 3029, 2977, 2933, 1583, 1390, 1303, 1290, 1272, 1252, 1200 cm^{-1}

HRMS (ESI) calc. for $(C_{28}H_{37}BO_3Si)Na^+$: 483.2497; found 483.2496.



Silyl-Dienyl Boronate 104

Following general procedure A: $RuHCl(CO)(PCy_3)_2$ (9.1 mg, 0.0125 mmol, 0.05 equiv), alkyne **57**[26] (78.9 mg, 0.25 mmol, 1 equiv) in toluene (0.5 mL) and vinyl boronate **93** (87 µL, 0.50 mmol, 2 equiv) were combined and stirred at 85°C for 4.5 h. The residue was purified by column chromatography (silica gel 2.5 x 12 cm; eluted with 5% ether/hexanes) to give **104** as a pale brown oil (66.3 mg, 60%).

R_f (10% ether/hexanes) = 0.37

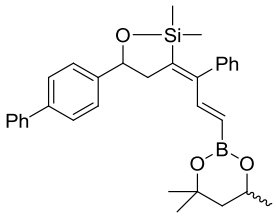
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43 (dd, 1H, *J* = 18.0, 2.1 Hz), 7.28-7.24 (m, 3H), 7.07-7.04 (m, 2H), 5.20 (d, 1H, *J* = 17.7 Hz), 4.23-4.20 (m, 1H), 3.77 (q, 1H, *J* = 6.5 Hz), 2.99 (ddd, 1H, *J* = 16.5, 5.7, 3.6 Hz), 2.51 (ddd, 1H, *J* = 16.5, 8.4, 1.5 Hz), 1.95-1.09 (m, 1H), 1.80-1.00 (m, 21H), -0.10 (s, 1.5H), -0.12 (s, 1.5H), -0.26 (s, 1.5H), -0.28 (s, 1.5H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.1, 146.0, 144.7, 142.1, 129.9, 127.9, 127.1, 80.9, 71.0, 65.0, 46.1, 44.8, 36.0, 31.4, 29.2, 28.8, 28.3, 26.8, 26.4, 26.3, 23.3, 0.5, 0.4, -0.3, -0.4

^{11}B NMR (96 MHz, $CDCl_3$) δ = 28.0

FT-IR (NaCl, thin film) ν = 2974, 2927, 2854, 1597, 1583, 1416, 1390, 1291, 1250, 1206, 1163, 1030 cm^{-1}

HRMS (ESI) calc. for $(C_{26}H_{39}BO_3Si)Na^+$: 461.2654; found: 461.2651.



Silyl-Dienyl Boronate 105

Following general procedure A: $RuHCl(CO)(PCy_3)_2$ (9.1 mg, 0.0125 mmol, 0.05 equiv), alkyne **61**[26] (94.8 mg, 0.25 mmol, 1 equiv) in toluene (0.5 mL) and vinyl boronate **93** (87 µL, 0.50 mmol, 2 equiv) were combined and stirred at 85°C for 3.5 h. The residue was purified by column chromatography (silica gel 2.5 x 13.5 cm; eluted with 5% ether/hexanes) to give **105** as a pale yellow solid (72.2 mg, 57%).

R_f (10% ether/hexanes) = 0.31

mp = 51-54°C

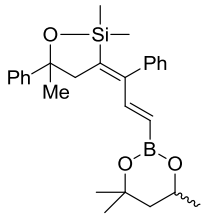
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.64-7.13 (m, 15H), 5.28 (d, 1H, *J* = 17.7 Hz), 5.11 (dd, 1H, *J* = 9.6, 5.4 Hz), 4.24-4.19 (m, 1H), 3.46 (ddd, 1H, *J* = 16.5, 5.4, 2.7 Hz), 2.72 (dd, 1H, *J* = 16.2, 9.6 Hz), 1.78 (dd, 1H, *J* = 14.1, 3.0 Hz), 1.49 (t, 1H, *J* = 11.7 Hz), 1.29-1.25 (m, 9H), 0.12 (s, 1.5H), 0.11 (s, 1.5H), -0.15 (s, 1.5H), -0.17 (s, 1.5H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.6, 145.1, 144.6, 143.9, 143.8, 141.9, 141.3, 140.5, 129.9, 128.9, 128.0, 127.4, 127.3, 126.2, 77.9, 71.1, 65.0, 46.1, 42.2, 42.1, 31.4, 28.3, 23.3, 0.6, 0.5, -0.5, -0.6

^{11}B NMR (96 MHz, $CDCl_3$) δ = 28.1

FT-IR (NaCl, thin film) ν = 3057, 2793, 1598, 1583, 1417, 1346, 1251, 1207 cm^{-1}

Anal. calcd for $C_{32}H_{37}BO_3Si$: C 75.58, H 7.33; found C 75.98, H 7.62.



Silyl-Dienyl Boronate 106

Following general procedure A: $RuHCl(CO)(PCy_3)_2$ (9.1 mg, 0.0125 mmol, 0.05 equiv), alkyne **62**[26] (79.2 mg, 0.25 mmol, 1 equiv) in toluene (0.5 mL) and vinyl boronate **93** (87 µL, 0.50 mmol, 2 equiv) were combined and stirred at 85°C for 2 h. The residue was purified by column chromatography (silica gel 2.5 x 13 cm; gradient elution with 5%-10% ether/hexanes) to give **106** as a pale brown oil (61.7 mg, 55%).

R_f (10% ether/hexanes) = 0.35

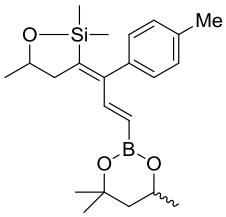
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.53-7.06 (m, 11H), 5.24 (d, 1H, *J* = 17.7 Hz), 4.29-4.18 (m, 1H), 3.25 (d, 1H, *J* = 16.2 Hz), 3.04 (d, 1H, *J* = 16.2 Hz), 1.79 (dd, 1H, *J* = 13.8, 2.7 Hz), 1.58 (s, 3H), 1.54-1.46 (m, 1H), 1.30-1.27 (m, 9H), -0.06 (s, 3H), -0.17 (d, 3H, *J* = 2.1 Hz)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.5, 148.9, 145.4, 144.5, 142.0, 129.9, 128.2, 128.0, 127.2, 126.6, 124.9, 81.7, 71.1, 65.0, 46.5, 46.1, 31.9, 31.4, 28.3, 23.4, 0.92, 0.90, 0.85, 0.83

^{11}B NMR (96 MHz, $CDCl_3$) δ = 27.6

FT-IR (NaCl, thin film) ν = 3060, 3028, 2975, 1584, 1493, 1418, 1391, 1324, 1291, 1252, 1207, 1162 cm^{-1}

HRMS (ESI) calc. for $(C_{27}H_{35}BO_3Si)Na^+$: 469.2341; found 469.2339.



Silyl-Dienyl Boronate 107

Following general procedure A: $RuHCl(CO)(PCy_3)_2$ (9.1 mg, 0.0125 mmol, 0.05 equiv), alkyne **66**[26] (64.4 mg, 0.25 mmol, 1 equiv) in toluene (0.5 mL) and vinyl boronate **93** (87 µL, 0.50 mmol, 2 equiv) were combined and stirred at 85°C for 4.5 h. The residue was purified by column chromatography (silica gel 2.5 x 12 cm; eluted with 10% ether/hexanes) to give **107** as a pale brown oil (53 mg, 55%).

R_f (10% ether/hexanes) = 0.20

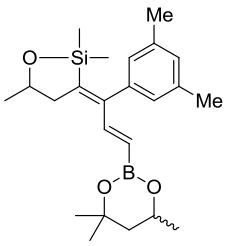
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42 (dd, 1H, *J* = 17.7, 1.5 Hz), 7.08-7.05 (m, 2H), 6.96-6.93 (m, 2H), 5.21 (d, 1H, *J* = 18.0 Hz), 4.23-4.16 (m, 2H), 3.06 (ddd, 1H, *J* = 16.2, 5.1, 3.9 Hz), 2.39 (ddd, 1H, *J* = 16.2, 8.1, 3.9 Hz), 2.32 (s, 3H), 1.77 (dd, 1H, *J* = 13.8, 3.0 Hz), 1.47 (dd, 1H, *J* = 13.8, 11.7 Hz), 1.33-1.24 (m, 12H), -0.08 (s, 1.5H), -0.10 (s, 1.5H), -0.22 (s, 1.5H), -0.24 (s, 1.5H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.4, 145.6, 144.9, 138.9, 136.7, 129.8, 128.6, 72.7, 71.0, 65.0, 46.1, 40.8, 31.4, 28.3, 24.2, 23.4, 21.4, 0.8, 0.7, -0.2, -0.3

^{11}B NMR (96 MHz, $CDCl_3$) δ = 28.6

FT-IR (NaCl, thin film) ν = 2973, 1583, 1510, 1390, 1346, 1291, 1206, 1123, 1060 cm^{-1}

HRMS (ESI) calc. for $(C_{22}H_{33}BO_3Si)Na^+$: 407.2184; found 407.2183.



Silyl-Dienyl Boronate 108

Following general procedure A: $RuHCl(CO)(PCy_3)_2$ (8.7 mg, 0.012 mmol, 0.05 equiv), alkyne **67** (65.2 mg, 0.24 mmol, 1 equiv) in toluene (0.48 mL) and vinyl boronate **93** (83 µL, 0.48 mmol, 2 equiv) were combined and stirred at 85°C for 5 h. The residue was purified by column chromatography (silica gel 2.5 x 12 cm; eluted with 10% ether/hexanes) to give **108** as a pale brown oil (54.5 mg, 57%).

R_f (10% ether/hexanes) = 0.20

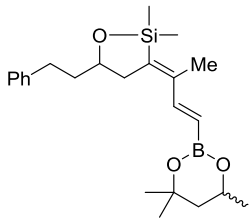
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.41 (dd, 1H, *J* = 17.7, 1.8 Hz), 6.86 (s, 1H), 6.66 (s, 2H), 5.26 (d, 1H, *J* = 17.7 Hz), 4.24-4.15 (m, 2H), 3.05 (dt, 1H, *J* = 15.9, 5.1 Hz), 2.37 (ddd, 1H, *J* = 16.2, 8.1, 5.1 Hz), 2.25 (s, 6H), 1.77 (dd, 1H, *J* = 13.8, 3.0 Hz), 1.48 (dd, 1H, *J* = 13.8, 11.7 Hz), 1.37-1.29 (m, 12H), -0.04 (s, 1.5H), -0.08 (s, 1.5H), -0.18 (s, 1.5H), -0.21 (s, 1.5H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.7, 145.4, 144.8, 141.8, 137.1, 128.6, 127.6, 72.7, 71.0, 65.0, 46.1, 40.7, 31.4, 28.3, 24.2, 23.4, 21.4, 0.7, 0.6, -0.3, -0.4

^{11}B NMR (96 MHz, $CDCl_3$) δ = 27.6

FT-IR (NaCl, thin film) ν = 2973, 2927, 1598, 1417, 1346, 1230, 1207, 1162, 1124 cm^{-1}

HRMS (ESI) calc. for $(C_{23}H_{35}BO_3Si)Na^+$: 421.2341; found 421.2340.



Silyl-Dienyl Boronate 109

Following general procedure A: $RuHCl(CO)(PCy_3)_2$ (20 mg, 0.027 mmol, 0.10 equiv), alkyne **68** (73.1 mg, 0.27 mmol, 1 equiv) in toluene (0.54 mL) and vinyl boronate **93** (94 µL, 0.54 mmol, 2 equiv) were combined and stirred at 85°C for 5 h. The residue was purified by column chromatography (silica gel 1.5 x 15 cm; gradient elution with 4%-8% ether/hexanes) to give **109** as a pale brown oil (32.4 mg, 30%, 16:3:1).

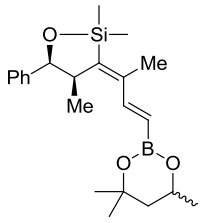
R_f (10% ether/hexanes) = 0.26

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21-7.07 (m, 6H), 5.51 (d, 1H, *J* = 18.0 Hz), 4.21-4.11 (m, 1H), 4.01-3.94 (m, 1H), 2.87-2.81 (m, 1H), 2.77-2.59 (m, 3H), 2.32-2.25 (m, 1H), 1.81 (s, 3H), 1.72 (dd, 2H, *J* = 13.9, 2.8 Hz), 1.44 (dd, 1H, *J* = 13.7, 11.8 Hz), 1.24 (d, 6H, *J* = 2.8 Hz), 1.21 (d, 3H, *J* = 6.3 Hz), 0.25 (s, 3H), 0.21 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.1, 142.6, 142.5, 140.5, 128.6, 128.5, 125.9, 76.2, 71.0, 65.0, 46.2, 40.2, 38.6, 32.3, 31.4, 28.3, 23.4, 20.4, 0.5, 0.0

FT-IR (NaCl, thin film) ν = 3062, 2973, 2933, 1590, 1418, 1391, 1298, 1201, 1163 cm^{-1}

Anal. calcd for $C_{32}H_{37}BO_3Si$: C 69.34, H 8.85; found C 69.39, H 9.05.



Silyl-Dienyl Boronate 112

Following general procedure A: $RuHCl(CO)(PCy_3)_2$ (28 mg, 0.039 mmol, 0.10 equiv), alkyne **77** (101 mg, 0.39 mmol, 1 equiv) in toluene (0.8 mL) and vinyl boronate **93** (0.14 mL, 0.78 mmol, 2 equiv) were combined and stirred at 85°C for 3 h. The residue was purified by column chromatography (silica gel 2.5 x 15 cm; gradient elution with 3%-6% ether/hexanes) to give **112** as a brown oil (114 mg, 76%, 3:1 *E:Z*).

R_f (10% ether/hexanes) = 0.32

$[\alpha]_D^{24}$ = -36.0° (*c* = 0.464 in DCM)

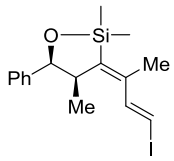
^{1}H NMR (300 MHz, $CDCl_3$) δ = **major isomer:** 7.31-7.16 (m, 6H), 5.58 (d, 1H, *J* = 17.9 Hz), 5.04 (d, 1H, *J* = 4.3 Hz), 4.24-4.13 (m, 1H), 3.28-3.23 (m, 1H), 1.87 (s, 3H), 1.74 (dd, 1H, *J* = 13.9, 2.9 Hz), 1.46 (dd, 1H, *J* = 13.6, 11.7 Hz), 1.26-1.20 (m, 12H), 0.39 (s, 3H), 0.31 (s, 3H); **minor isomer diagnostic peaks:** 6.97 (d, 1H, *J* = 17.5 Hz), 5.49 (d, 1H, *J* = 17.5 Hz), 5.07 (d, 1H, *J* = 4.3 Hz), 3.02-2.93 (m, 1H), 1.84 (s, 3H), 0.50 (d, 3H, *J* = 6.9 Hz), 0.42 (s, 3H), 0.37 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = **major isomer:** 149.2, 144.3, 141.9, 140.3, 128.1, 126.9, 126.0, 80.6, 71.0, 65.0, 46.2, 43.1, 31.4, 28.30, 23.4, 20.7, 16.1, 0.6, -0.2; **minor isomer diagnostic peaks:** 152.8, 151.0, 142.6, 125.9, 80.3, 70.9, 64.9, 46.1, 44.5, 28.34, 14.6, 1.0, 0.4

^{11}B NMR (96 MHz, $CDCl_3$) δ = 26.7

FT-IR (NaCl, thin film) ν = 2972, 2929, 2869, 1589, 1496, 1391, 1297 cm^{-1}

Anal. calcd for $C_{22}H_{33}BO_3Si$: C 68.74, H 8.65; found C 68.97, H 8.72.



Silyl-Dienyl Iodide 113

To an oven-dried 25 mL Schlenk tube with stir bar was added silyl dienyl boronate **112** (113 mg, 0.29 mmol, 1 equiv) and THF (0.6 mL). A solution of 5M NaOH (0.17 mL, 0.87 mmol, 3 equiv) was added dropwise and the tan-colored reaction mixture stirred at rt. After 15 min, I_2 (147 mg, 0.58 mmol, 2 equiv) in THF (0.6 mL) was added. The reaction stirred in the dark at rt for 20 min then was quenched by sat. $Na_2S_2O_{3(aq)}$ (3 mL). After extraction with DCM (3 x 3 mL), the combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The orange residue was purified by column chromatography (silica gel 1.5 x 7 cm; eluted with 3% ether/hexanes) to give **113** as a yellow oil (80.2 mg, 72%, 3:1 *E:Z*).

R_f (10% ether/hexanes) = 0.56

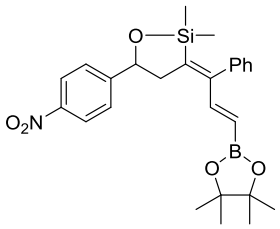
$[\alpha]_D^{24}$ = -22.0° (*c* = 1.538 in $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ = **major isomer:** 7.35 (d, 1H, *J* = 14.6 Hz), 7.24-7.13 (m, 5H), 6.21 (d, 1H, *J* = 14.6 Hz), 5.02 (d, 1H, *J* = 4.4 Hz), 3.08-3.01 (m, 1H), 1.81 (s, 3H), 0.51 (d, 3H, *J* = 7.3 Hz), 0.37 (s, 3H), 0.30 (s, 3H); **minor isomer diagnostic peaks:** 6.94 (d, 1H, *J* = 14.3 Hz), 6.29 (d, 1H, *J* = 14.4 Hz), 5.03 (d, 1H, *J* = 4.3 Hz), 2.95-2.88 (m, 1H), 1.79 (s, 3H), 0.48 (d, 3H, *J* = 7.2 Hz), 0.39 (s, 3H), 0.32 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = **major isomer:** 149.0, 148.1, 144.2, 141.43, 138.7, 128.2, 125.8, 80.2, 79.7, 43.4, 20.3, 16.0, 0.5, -0.2; **minor isomer diagnostic peaks:** 151.2, 141.41, 141.4, 127.0, 80.1, 76.5, 44.4, 15.0, 14.5, 1.1, 0.4

FT-IR (NaCl, thin film) ν = 3027, 2962, 2924, 1603, 1494, 1251, 1093, 1064, 993 cm^{-1}

Anal. calcd for $C_{16}H_{21}IOSi$: C 50.00, H 5.51; found C 49.84, H 5.43.



Silyl-Dienyl Boronate 117

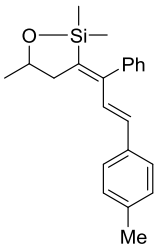
To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar in an $Ar_{(g)}$ filled glovebox was added $RuHCl(CO)(PCy_3)_2$ (11 mg, 0.015 mmol, 0.05 equiv), alkyne **60** (102.7 mg, 0.29 mmol, 1 equiv), vinyl boronate **94** (89.3 mg, 0.58 mmol, 2 equiv) and DCE (0.58 mL). The vessel was sealed with a rubber septum, removed from the glovebox then placed under $Ar_{(g)}$. The septum was removed, a cold-finger was quickly attached and the orange solution stirred at 85°C. After 2 h, the resulting brown solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated to give a brown oil. Purification via column chromatography (silica gel 2.5 x 15 cm; gradient elution with 5%-15% ether/hexanes) gave **117** as a pale brown solid (68 mg, 49%, 11:1 *Z:E*).

R_f (10% ether/hexanes) = 0.14

^{1}H NMR (400 MHz, $CDCl_3$) δ = **major isomer:** 8.18 (d, 2H, *J* = 8.8 Hz), 7.53 (d, 2H, *J* = 8.4 Hz), 7.43 (d, 1H, *J* = 18.5 Hz), 7.30-7.23 (m, 3H), 7.07-7.05 (m, 2H), 5.28 (d, 1H, *J* = 18.5 Hz), 5.12-5.08 (m, 1H), 3.45 (dd, 1H, *J* = 16.4, 5.6 Hz), 2.52 (dd, 1H, *J* = 16.4, 9.6 Hz), 1.20 (s, 12H), 0.05 (s, 3H), -0.20 (s, 3H); **minor isomer diagnostic peaks:** 5.60 (d, 1H, *J* = 14.5 Hz), 3.21 (dd, 1H, *J* = 16.2, 5.4 Hz), 0.13 (s, 3H), -0.17 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = **major isomer:** 152.3, 148.9, 147.3, 146.8, 145.2, 141.1, 129.8, 128.1, 127.6, 126.2, 123.9, 83.6, 77.0, 41.8, 24.9, 0.4, -0.6; **minor isomer diagnostic peaks:** 152.6, 149.1, 148.1, 143.7, 142.7, 137.2, 129.2, 128.3, 127.8, 126.1, 83.3, 76.7, 43.2, 25.1, 0.8, -0.6

Anal. calcd for $C_{26}H_{32}BNO_5Si$: C 65.41, H 6.76, N 2.93; found C 65.48, H 6.89, N 2.81.



Diene 118

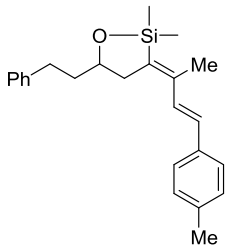
Following general procedure A: $RuHCl(CO)(PCy_3)_2$ (10.2 mg, 0.014 mmol, 0.05 equiv), alkyne **41** (67.7 mg, 0.28 mmol, 1 equiv) in THF (0.6 mL) and vinyl boronate **93** (97 µL, 0.56 mmol, 2 equiv) were combined and stirred at 70°C overnight. In a separate oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under $Ar_{(g)}$ was added $Pd(OAc)_2$ (3.1 mg, 0.014 mmol, 0.05 equiv), S-Phos (11.5 mg, 0.028 mmol, 0.10 equiv), 4-iodotoluene (91.6 mg, 0.42 mmol, 1.5 equiv), K_3PO_4 (2M, freshly prepared and degassed prior, 0.84 mmol, 0.42 mL, 3 equiv) and THF (2.2 mL, degassed). To the resulting orange solution was added the crude diene reaction mixture then the dark brown mixture stirred at 50°C overnight. The solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a brown oil. The residue was purified by column chromatography (silica gel 1.5 x 13 cm; gradient elution with 5%-10% ether/hexanes) to give **118** as an orange oil (50.4 mg, 54% over two steps).

R_f (10% ether/hexanes) = 0.18

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39-7.08 (m, 10H), 6.16 (d, 1H, *J* = 15.9 Hz), 4.30-4.20 (m, 1H), 3.07 (dd, 1H, *J* = 16.2, 5.1 Hz), 2.43 (dd, 1H, *J* = 16.2, 8.4 Hz), 2.32 (s, 3H), 1.36 (d, 3H, *J* = 6.0 Hz), -0.07 (s, 3H), -0.19 (s, 3H)

FT-IR (NaCl, thin film) ν = 3078, 3026, 2966, 2866, 2241, 1603, 1584, 1510, 1491, 1376, 1249, 1124, 1095 cm^{-1}

Anal. calcd for $C_{22}H_{26}OSi$: C 78.99, H 7.83; found C 78.77, H 7.44.



Diene 119

Following general procedure A: $RuHCl(CO)(PCy_3)_2$ (17.4 mg, 0.024 mmol, 0.10 equiv), alkyne **68** (66.2 mg, 0.24 mmol, 1 equiv) in toluene (0.48 mL) and vinyl boronate **93** (125 µL, 0.72 mmol, 3 equiv) were combined and stirred at 85°C for 3 h. In a separate oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under $Ar_{(g)}$ was added $Pd(OAc)_2$ (3 mg, 0.012 mmol, 0.05 equiv), S-Phos (10 mg, 0.024 mmol, 0.10 equiv) and 4-iodotoluene (239 mg, 1.2 mmol, 5 equiv). The crude silyl-dienyl boronate was dissolved in THF (2.4 mL) and degassed for 30 min then added to the solids, followed by K_3PO_4 (2M, freshly prepared and degassed prior, 2.4 mmol, 1.2 mL, 10 equiv). The brown reaction mixture stirred at 50°C overnight. The solution was cooled to rt, dried over $MgSO_4$ while stirring, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a brown oil. The residue was purified by column chromatography (silica gel 2.5 x 17 cm; gradient elution with 3%-5% ether/hexanes) to give **119** as an orange oil (3 isomers, 34 mg, 39% over two steps, 6:1 *E:Z*).

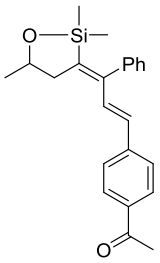
R_f (10% ether/hexanes) = 0.53

^{1}H NMR (300 MHz, $CDCl_3$) δ = **major isomer *(E)*:** 7.16-6.93 (m, 9H), 6.85 (d, 1H, *J* = 16.2 Hz), 6.40 (d, 1H, *J* = 16.1 Hz), 3.94-3.85 (m, 1H), 2.74-2.48 (m, 3H), 2.21-2.08 (m, 1H), 2.15 (s, 3H), 1.81 (s, 3H), 1.74-1.60 (m, 2H), 0.17 (s, 3H), 0.13 (s, 3H); **minor isomer diagnostic peaks *(Z)*:** 6.52 (d, 1H, *J* = 15.8 Hz), 6.34 (d, 1H, *J* = 16.1 Hz)

^{13}C NMR (75 MHz, $CDCl_3$) δ = **major isomer:** 142.5, 140.5, 139.4, 137.7, 135.1, 129.6, 128.7, 128.5, 127.3, 126.8, 126.4, 125.9, 76.2, 40.2, 38.8, 32.3, 21.4, 20.9, 0.6, 0.2

FT-IR (NaCl, thin film) ν = 3026, 2925, 2860, 1602, 1510, 1452, 1377, 1253, 1052 cm^{-1}

Anal. calcd for $C_{24}H_{30}OSi$: C 79.50, H 8.34; found C 79.49, H 8.59.



Diene 120

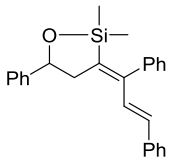
To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar under $Ar_{(g)}$ was added $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.05 equiv), S-Phos (8.2 mg, 0.02 mmol, 0.10 equiv), K_3PO_4 (127 mg, 0.60 mmol, 3 equiv) and 4'-bromoacetophenone (60 mg, 0.30 mmol, 1.5 equiv). The solids were purged with vacuum then placed under $Ar_{(g)}$. To the solids was then added silyl dienyl boronate **97** (1M in THF, 0.20 mL, 0.20 mmol, 1 equiv) and H_2O (degassed 30 min, 0.3 mL). The orange mixture stirred at 50°C for 4 h then was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a dark red oil. Purification via column chromatography (silica gel 1.5 x 10.5 cm; gradient elution with 10%-30% ether/hexanes) gave **120** as a bright yellow oil (42.6 mg, 59%).

R_f (40% EtOAc/hexanes) = 0.62

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.88 (d, 2H, *J* = 8.4 Hz), 7.45-7.36 (m, 6H), 7.20-7.17 (m, 2H), 6.20 (d, 1H, *J* = 15.9 Hz), 4.32-4.21 (m, 1H), 3.10 (dd, 1H, *J* = 16.2, 5.4 Hz), 2.58 (s, 3H), 2.46 (dd, 1H, *J* = 16.5, 8.4 Hz), 1.37 (d, 3H, *J* = 6.0 Hz), -0.06 (s, 3H), -0.18 (s, 3H)

FT-IR (NaCl, thin film) ν = 2965, 2926, 1681, 1599, 1264, 828 cm^{-1}

Anal. calcd for $C_{23}H_{26}O_2Si$: C 76.20, H 7.23; found C 75.92, H 7.24.



Diene 123

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar under $Ar_{(g)}$ was added silyl dienyl boronate **121**[71] (64.8 mg, 0.15 mmol, 1 equiv), $Pd(OAc)_2$ (1.7 mg, 0.008 mmol, 0.05 equiv), S-Phos (6.2 mg, 0.015 mmol, 0.10 equiv) and K_3PO_4 (96 mg, 0.45 mmol, 3 equiv). The vessel was evacuated then placed under $Ar_{(g)}$. To the solids was added degassed H_2O (8.1 µL, 0.45 mmol, 3 equiv), degassed THF (1.5 mL) and iodobenzene (25 µL, 0.23 mmol, 1.5 equiv). The resulting light brown suspension stirred at 50°C overnight. The brown suspension was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give an orange oil. Purification via column chromatography (silica gel 1.5 x 13 cm; gradient elution with 2%-4% ether/hexanes) gave **123** as a yellow solid (40.4 mg, 70%)

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar under $Ar_{(g)}$ was added silyl dienyl boronate **122**[71] (50.4 mg, 0.12 mmol, 1 equiv), $Pd(OAc)_2$ (1.3 mg, 0.006 mmol, 0.05 equiv), S-Phos (5.0 mg, 0.012 mmol, 0.10 equiv) and K_3PO_4 (76.4 mg, 0.36 mmol, 3 equiv). The vessel was evacuated then placed under $Ar_{(g)}$. To the solids was added degassed H_2O (6.5 µL, 0.36 mmol, 3 equiv), degassed THF (1.2 mL) and iodobenzene (20 µL, 0.18 mmol, 1.5 equiv). The resulting orange suspension stirred at 50°C overnight. The orange suspension was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give an orange oil. Purification via column chromatography (silica gel 1.5 x 15 cm; gradient elution with 2%-4% ether/hexanes) gave **123** as a yellow solid (33.3 mg, 73%).

R_f (10% ether/hexanes) = 0.35

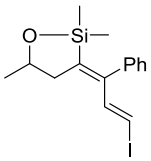
mp = 117-118°C

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37-7.09 (m, 16H), 6.13 (d, 1H, *J* = 16.0 Hz), 5.02 (m, 1H), 3.30 (dd, 1H, *J* = 16.0, 6.0 Hz), 2.61 (dd, 1H, *J* = 16.0, 9.3 Hz), 0.00 (s, 3H), -0.22 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.3, 144.9, 143.6, 142.1, 137.5, 133.5, 129.9, 128.8, 128.6, 128.2, 128.1, 128.0, 127.6, 127.5, 126.9, 125.6, 78.0, 42.4, 0.6, -0.3

FT-IR (NaCl, thin film) ν = 3059, 3030, 2927, 1599, 1492, 1447, 1249, 1031 cm^{-1}

Anal. calcd for $C_{26}H_{26}OSi$: C 81.63, H 6.85; found C 81.57, H 6.66.



Diene 124

To an oven-dried 50 mL Schlenk tube with stir bar was added silyl dienyl boronate **97** (0.805M in benzene, 163 mg, 0.44 mmol, 1 equiv) and THF (3 mL). A solution of 5M NaOH (1.32 mmol, 3.0 equiv) was added dropwise and the reaction mixture stirred at rt. After 10 min, I_2 (168 mg, 0.66 mmol, 1.5 equiv) in THF (1.8 mL) was added dropwise. The reaction stirred in the dark at rt for 2 h then was quenched by sat. $Na_2S_2O_{3(aq)}$ (5 mL). After extraction with DCM (3 x 5 mL), the combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give an orange oil. Purification via column chromatography (1.5 x 13 cm; eluted with 5% ether/hexanes) gave **124** as a yellow oil (99.9 mg, 61%).

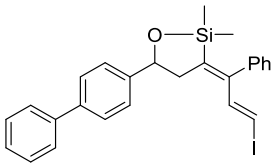
R_f (10% ether/hexanes) = 0.45

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.56 (d, 1H, *J* = 14.4 Hz), 7.34-7.30 (m, 3H), 7.13-7.10 (m, 2H), 6.03 (d, 1H, *J* = 14.1 Hz), 4.26-4.15 (m, 1H), 2.92 (dd, 1H, *J* = 16.2, 5.4 Hz), 2.28 (dd, 1H, *J* = 16.2, 8.1 Hz), 1.32 (d, 3H, *J* = 6.3 Hz), -0.08 (s, 3H), -0.21 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 146.7, 144.57, 144.55, 140.5, 129.7, 128.3, 127.8, 83.8, 72.5, 41.1, 24.1, 0.6, -0.4

FT-IR (NaCl, thin film) ν = 3058, 2965, 2924, 1591, 1491, 1249 cm^{-1}

Anal. calcd for $C_{15}H_{19}IOSi$: C 48.65, H 5.17; found C 48.92, H 5.49.



Diene 126

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under $Ar_{(g)}$ was added silyl dienyl boronate **105** (183 mg, 0.36 mmol, 1 equiv) and THF (0.85 mL). To the pale yellow solution was added NaOH (5M in H_2O, 1.08 mmol, 3 equiv). After stirring for 10 min, a solution of I_2 (183 mg, 0.72 mmol, 1.5 equiv) in THF (0.8 mL) was added dropwise. The dark red solution stirred at rt for 1 h then was quenched by addition of sat. $Na_2S_2O_{3(aq)}$ (3 mL). The aqueous layer was extracted with DCM (3 x 3 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give an orange oil. Purification via column chromatography (silica gel 1.5 x 12 cm; eluted with 5% ether/hexanes) gave **126** as a pale yellow solid (132 mg, 74%).

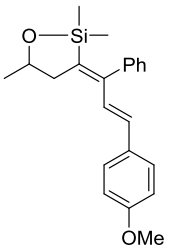
R_f (10% ether/hexanes) = 0.53

mp = 51-53°C

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60-7.15 (m, 15H), 6.09 (d, 1H, *J* = 14.8 Hz), 5.12 (dd, 1H, *J* = 9.6, 5.6 Hz), 3.27 (dd, 1H, *J* = 16.4, 5.6 Hz), 2.60 (dd, 1H, *J* = 16.4, 9.2 Hz), 0.08 (s, 3H), -0.15 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.9, 144.5, 143.8, 143.6, 141.3, 140.6, 140.5, 129.7, 129.0, 128.8, 128.5, 128.0, 127.4, 127.3, 126.0, 84.3, 42.3, 0.4, -0.5

Anal. calcd for $C_{26}H_{25}IOSi$: C 61.42, H 4.96; found C 61.10, H 5.04.



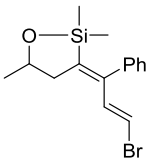
Diene 127

To an oven-dried 25 mL Schlenk tube with equipped with a magnetic stir bar in an $Ar_{(g)}$-filled glovebox was added $Pd(P\textit{t}Bu_3)_2$ (4 mg, 0.0075 mmol, 0.05 equiv), 4-methoxyphenylboronic acid (34 mg, 0.23 mmol, 1.5 equiv), K_3PO_4 (64 mg, 0.30 mmol, 2 equiv), silyl dienyl iodide **124** (1.05M in benzene, 55.5 mg, 0.15 mmol, 1 equiv) and 1,4-dioxane (0.6 mL). The vessel was sealed with a rubber septum, removed from the glovebox and placed under $Ar_{(g)}$. The dark brown reaction stirred at 80°C for 2 h then was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo*. Purification via column chromatography (silica gel 1.5 x 11.5 cm; eluted with 5% ether/hexanes) gave **127** as an orange oil (27.4 mg, 52%).

R_f (10% ether/hexanes) = 0.23

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.38-7.29 (m, 5H), 7.20-7.13 (m, 3H), 6.83 (d, 2H, *J* = 8.8 Hz), 6.14 (d, 1H, *J* = 16.0 Hz), 4.30-4.19 (m, 1H), 3.80 (s, 3H), 3.06 (dd, 1H, *J* = 16.0, 5.3 Hz), 2.42 (dd, 1H, *J* = 16.0, 8.4 Hz), 1.36 (d, 3H, *J* = 6.1 Hz), -0.07 (s, 3H), -0.20 (s, 3H)

Anal. calcd for $C_{22}H_{26}O_2Si$: C 75.38, H 7.48; found C 75.20, H 7.93.



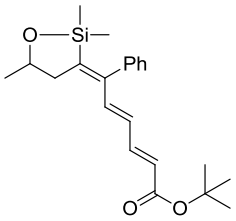
Diene 128

Following general procedure A: $RuHCl(CO)(PCy_3)_2$ (9.8 mg, 0.0135 mmol, 0.05 equiv), alkyne **41** (66.6 mg, 0.27 mmol, 1 equiv) in toluene (0.54 mL) and vinyl boronate **93** (94 µL, 0.54 mmol, 2 equiv) were combined and stirred at 85°C for 3 h. After plug filtering and concentration *in vacuo*, the crude oil was dissolved in 1:1 MeOH/H_2O (7 mL) and $CuBr_2$ (181 mg, 0.81 mmol, 3 equiv) was added in one portion. The aqua solution stirred at 45°C overnight. Upon cooling to rt, the reaction was diluted with H_2O (13 mL) and extracted with DCM (3 x 20 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a brown oil. Purification via column chromatography (silica gel 1.5 x 13 cm; gradient elution with 2%-4% ether/hexanes) gave **128** as a yellow oil (46.4 mg, 57% over two steps).

R_f (10% ether/hexanes) = 0.47

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34-7.29 (m, 3H), 7.22 (d, 1H, *J* = 13.8 Hz), 7.13-7.10 (m, 2H), 5.97 (d, 1H, *J* = 13.8 Hz), 4.26-4.15 (m, 1H), 2.90 (dd, 1H, *J* = 16.2, 5.3 Hz), 2.28 (dd, 1H, *J* = 16.3, 8.2 Hz), 1.32 (d, 3H, *J* = 6.1 Hz), -0.09 (s, 3H), -0.21 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.9, 144.8, 140.7, 140.0, 129.6, 128.4, 127.9, 112.5, 72.5, 41.1, 24.2, 0.6, -0.3



Triene 129

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar open to the air was added *tert*-butyl acrylate (66 µL, 0.45 mmol, 3 equiv) and DMA (0.75 mL). To the clear solution was added silyl dienyl boronate **97** (0.58M in benzene, 0.15 mmol, 1 equiv), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 0.10 equiv) and Na_2CO_3 (31.8 mg, 0.30 mmol, 2 equiv). The pale brown suspension was purged with $O_{2(g)}$ for 1 min then placed under a positive stream of $O_{2(g)}$ (balloon) and stirred at rt for 25 h. The reaction was diluted with EtOAc (6 mL) and washed with H_2O (3 x 3 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a brown oil. Purification by column chromatography (silica gel 1.5 x 12 cm; gradient elution with 10%-15% ether/hexanes) gave **129** as a yellow oil (25.2 mg, 45%).

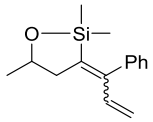
R_f (10% ether/hexanes) = 0.20

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.35-7.23 (m, 4H), 7.12-7.09 (m, 2H), 6.99 (d, 1H, *J* = 15.0 Hz), 5.91 (dd, 1H, *J* = 15.0, 11.4 Hz), 5.70 (d, 1H, *J* = 15.3 Hz), 4.27-4.17 (m, 1H), 2.99 (dd, 1H, *J* = 16.5, 5.4 Hz), 2.37 (dd, 1H, *J* = 16.5, 8.4 Hz), 1.46 (s, 9H), 1.34 (d, 3H, *J* = 6.0 Hz), -0.08 (s, 3H), -0.21 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.5, 148.9, 146.6, 143.6, 141.4, 138.4, 130.6, 129.7, 128.2, 127.7, 124.2, 80.4, 72.6, 41.2, 28.4, 24.2, 0.6, -0.3

FT-IR (NaCl, thin film) ν = 2974, 2930, 1705, 1620, 1454, 1368, 1248, 1165, 1135 cm^{-1}

Anal. calcd for $C_{22}H_{30}O_3Si$: C 71.31, H 8.16; found C 71.27, H 7.80.



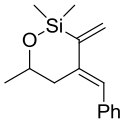
Diene 131

To an oven-dried 50 mL Schlenk tube equipped with magnetic stir bar in an Argon-filled glovebox was added $RuHCl(CO)(H_2IMes)(PPh_3)_3$ (2.2 mg, 0.003 mmol, 0.01 equiv) and a solution of alkyne **41** (74 mg, 0.30 mmol, 1 equiv) in DCE (1.2 mL). The vessel was sealed with a rubber septum, removed from the glovebox and placed under a positive stream of $Ar_{(g)}$. The yellow reaction mixture was degassed with ethylene (balloon) for ~2 minutes, then placed under an atmosphere of ethylene (balloon) and stirred at 70°C. After 1 h the yellow solution was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a light brown oil. Purification by column chromatography (silica gel 1.5 x 10 cm; gradient elution with 2%-3% ether/hexanes) gave **131** as a clear oil (59.5 mg, 80%, 11:1 *Z:E*).

R_f (10% ether/hexanes) = 0.36

^{1}H NMR (300 MHz, $CDCl_3$) **major isomer 131:** δ = 7.34-7.26 (m, 3H), 7.14-7.11 (m, 2H), 6.86 (dd, 1H, *J* = 17.1, 10.6 Hz), 5.24 (d, 1H, *J* = 10.6 Hz), 4.87 (d, 1H, *J* = 17.3 Hz), 4.26-4.15 (m, 1H), 2.96 (dd, 1H, *J* = 16.1, 5.4 Hz), 2.32 (dd, 1H, *J* = 16.1, 8.1 Hz), 1.32 (d, 3H, *J* = 6.0 Hz), -0.07 (s, 3H), -0.20 (s, 3H); **minor isomer 140 diagnostic peaks:** δ = 6.52 (dd, 1H, *J* = 16.7, 10.2 Hz), 5.09 (d, 1H, *J* = 10.5 Hz), 4.76 (d, 1H, *J* = 16.9 Hz), 4.13-4.02 (m, 1H), 2.04 (dd, 1H, *J* = 16.7, 8.4 Hz), 1.20 (d, 3H, *J* = 6.2 Hz), 0.43 (s, 3H), 0.40 (s, 3H)

General procedure for the ruthenium-catalyzed cycloisomerization:[204]



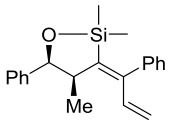
Diene 132

To a 25 mL Schlenk tube equipped with a magnetic stir bar in an argon filled glovebox was added Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne **41** (61.0 mg, 0.25 mmol, 1 equiv) in toluene (1 mL). The sealed reaction vessel was removed from the glovebox, placed under a positive stream of argon and stirred at 70°C for 1 h. TLC analysis indicated complete consumption of the starting material. The dark green suspension was cooled to rt, filtered through a plug of silica gel eluted with ether then concentrated *in vacuo* to give a dark green oil. Purification by column chromatography (silica gel 1.5 x 4 cm; eluted with 3% ether/hexanes) gave **132** as a clear oil (49.9 mg, 82%). Spectroscopic data corresponded to what was reported in the literature.[88]

R_f (5% ether/hexanes) = 0.45

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39-7.21 (m, 5H), 6.62 (s, 1H), 5.92 (d, 1H, *J* = 3.0 Hz), 5.26 (d, 1H, *J* = 3.0 Hz), 4.14-4.04 (m, 1H), 2.90 (dd, 1H, *J* = 14.7, 1.8 Hz), 2.30 (ddd, 1H, *J* = 14.4, 9.9, 1.8 Hz), 1.26 (d, 3H, *J* = 6.3 Hz), 0.34 (s, 3H), 0.27 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.4, 142.7, 137.8, 129.2, 128.2, 126.4, 123.3, 121.5, 70.0, 39.9, 24.3, -0.4, -1.0



Diene 134

MVK procedure: To an oven-dried 15 mL glass tube equipped with a magnetic stir bar was added alkyne **80** (50.0 mg, 0.16 mmol, 1 equiv). The vessel was transferred to an argon-filled glovebox then RuHCl(CO)(H_2IMes)(PPh_3) (6.0 mg, 0.008 mmol, 0.05 equiv) was added, followed by MVK (1.3 µL, 0.016 mmol, 0.10 equiv) and DCE (0.32 mL). The vessel was sealed with a teflon screw cap, removed from the glovebox then stirred at 85°C for 24 h. Upon cooling to rt, the dark orange solution was filtered through a plug of silica gel (eluted with DCM) and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 1.5 x 9 cm; eluted with 1% ether/hexanes) gave **134** as a white oil (27 mg, 54%).

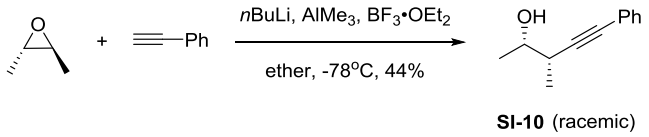
Ethylene procedure: To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H_2IMes)(PPh_3) (3.7 mg, 0.005 mmol, 0.02 equiv) and a solution of alkyne **80** (79.6 mg, 0.25 mmol, 1 equiv) in DCE (1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The dark orange solution stirred at 80°C for 2.5 h, cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a pale brown oil. Purification by preparative thin layer chromatography (eluted with 2% ether/hexanes) gave **134** as a pale yellow oil (53.8 mg, 68%, 14:1 *Z/E*).

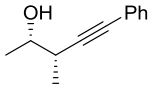
R_f (10% ether/hexanes) = 0.34

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39-7.18 (m, 10H), 6.95 (dd, 1H, *J* = 17.2, 10.6 Hz), 5.29 (dd, 1H, *J* = 10.6, 1.6 Hz), 5.18 (d, 1H, *J* = 4.4 Hz), 4.79 (dd, 1H, *J* = 17.2, 1.6 Hz), 3.38-3.29 (m, 1H), 0.73 (d, 3H, *J* = 7.2 Hz), 0.29 (s, 3H), -0.30 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.1, 147.4, 142.1, 141.8, 135.5, 130.1, 128.4, 128.3, 127.7, 127.1, 126.1, 119.2, 80.5, 43.7, 15.8, -0.9, -2.1

Anal. calcd for $C_{21}H_{24}OSi$: C 78.70, H 7.55; found C 78.53, H 7.21.



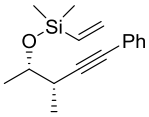


Racemic Alcohol SI-10

To a flame-dried 3-neck 250 mL RBF equipped with a magnetic stir bar and a pressure-equalizing addition funnel under $Ar_{(g)}$ was added phenylacetylene (2.6 mL, 24 mmol, 1.2 equiv) and ether (100 mL). The solution was cooled to -78°C (dry ice/acetone bath) and *n*BuLi (2.5M in hexane, 9.6 mL, 24 mmol, 1.2 equiv) was added dropwise over 20 min. After stirring at -78°C for 20 min, $AlMe_3$ (2M in hexane, 12 mL, 24 mmol, 1.2 equiv) was added dropwise over 35 min. The reaction stirred at -78°C for 30 min and -45°C for 30 min, then was cooled to -78°C, whereupon *trans*-2,3-epoxybutane (1.8 mL, 20 mmol, 1 equiv) in ether (11 mL) was added dropwise over 10 min. After stirring at -78°C for 15 min, $BF_3{\cdot}OEt_2$ (2.8 mL, 22 mmol, 1.1 equiv) in ether (11 mL) was added dropwise over 10 min. After stirring at -78°C for 1 h, methanol (36 mL) was added dropwise over 10 min, then the reaction mixture was allowed to warm to rt over 25 min. Upon warming, sat. $NH_4Cl_{(aq)}$ (36 mL) was added then the reaction stirred at rt for an additional 30 min. The mixture was then diluted with H_2O (150 mL) and extracted with ether (3 x 100 mL). The organics were dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 4.5 x 14 cm; gradient elution with 10%-50% ether/pentane) gave **SI-10** as a pale yellow oil (1.54 g, 44%). Spectroscopic data corresponded to what was reported in the literature.[213]

R_f (25% EtOAc/hexanes) = 0.21

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43-7.39 (m, 2H), 7.30-7.28 (m, 3H), 3.87-3.77 (m, 1H), 2.86-2.77 (m, 1H), 1.68 (br s, 1H), 1.32 (d, 3H, *J* = 6.3 Hz), 1.26 (d, 3H, *J* = 7.0 Hz)



Silicon Tethered Alkyne 135

To an oven dried 50 mL RBF equipped with magnetic stir bar under $Ar_{(g)}$ was added alcohol **SI-10** (508 mg, 2.9 mmol, 1 equiv), DCM (20 mL), imidazole (395 mg, 5.8 mmol, 2 equiv) and DMAP (71 mg, 0.58 mmol, 0.2 equiv). The clear solution was cooled to 0°C (ice/H_2O) bath) and vinyldimethylchlorosilane (0.6 mL, 4.35 mmol, 1.5 equiv) was added dropwise. The resulting white suspension stirred at rt for 2 h then was quenched by sat. $NH_4Cl_{(aq)}$ (20 mL). The aqueous layer was extracted with DCM (2 x 10 mL) then the combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a clear oil. Purification by column chromatography (silica gel 2.5 x 12.5 cm; gradient elution with 1%-3% ether/hexanes) gave **135** as a clear oil (672 mg, 90%).

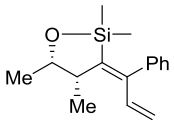
R_f (10% ether/hexanes) = 0.71

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40-7.37 (m, 2H), 7.28-7.26 (m, 3H), 6.18 (dd, 1H, *J* = 20.1, 15.0 Hz), 6.02 (dd, 1H, *J* = 14.7, 4.2 Hz), 5.80 (dd, 1H, *J* = 20.1, 4.5 Hz), 3.79-3.70 (m, 1H), 2.64-2.55 (m, 1H), 1.33 (d, 3H, *J* = 6.0 Hz), 1.25 (d, 3H, *J* = 6.9 Hz), 0.22 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.1, 133.3, 131.7, 128.3, 127.7, 124.0, 92.6, 82.2, 72.4, 35.4, 22.3, 17.8, -1.2, -1.3

FT-IR (NaCl, thin film) ν = 3054, 2973, 2879, 1597, 1491, 1372, 1252, 1099, 838 cm^{-1}

Anal. calcd for $C_{16}H_{22}OSi$: C 74.36, H 8.58; found: C 74.63, H 8.80.



Diene 136

To an oven-dried 15 mL glass tube equipped with a magnetic stir bar was added alkyne **135** (66.7 mg, 0.26 mmol, 1 equiv). The vessel was transferred to an argon-filled glovebox then RuHCl(CO)(H_2IMes)(PPh_3) (9.5 mg, 0.013 mmol, 0.05 equiv) was added, followed by MVK (2.1 µL, 0.016 mmol, 0.10 equiv) and DCE (0.52 mL). The vessel was sealed with a teflon screw cap, removed from the glovebox then stirred at 85°C for 22 h. Upon cooling to rt, the dark orange solution was filtered through a plug of silica gel (eluted with DCM) and concentrated *in vacuo* to give an orange oil. Purification by column chromatography (silica gel 1.5 x 12.5 cm; gradient elution with 2%-3% ether/hexanes) gave **136** as a clear oil (38.4 mg, 58%, 33:1 *Z:E*).

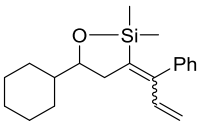
R_f (10% ether/hexanes) = 0.27

^{1}H NMR (300 MHz, $CDCl_3$) **major isomer:** δ = 7.33-7.27 (m, 3H), 7.13-7.10 (m, 2H), 6.88 (dd, 1H, *J* = 17.4, 10.8 Hz), 5.23 (dd, 1H, *J* = 10.8, 1.8 Hz), 4.86 (dd, 1H, *J* = 17.4, 1.8 Hz), 4.12-4.08 (m, 1H), 2.98-2.93 (m, 1H), 1.27 (d, 3H, *J* = 6.3 Hz), 1.17 (d, 3H, *J* = 7.2 Hz), 0.13 (s, 3H), -0.41 (s, 3H); **minor isomer diagnostic peaks:** δ = 6.48 (dd, 1H, *J* = 17.0, 10.5 Hz), 5.09 (dd, 1H, *J* = 10.4, 1.4 Hz), 4.68 (dd, 1H, *J* = 16.9, 1.2 Hz)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.5, 146.6, 141.5, 135.3, 129.8, 127.9, 127.2, 118.6, 74.5, 42.0, 19.1, 14.3, 1.7, -1.2

FT-IR (NaCl, thin film) ν = 3082, 2967, 2869, 1598, 1491, 1141, 743

Anal. calcd for $C_{16}H_{22}OSi$: C 74.36, H 8.58; found C 74.44, H 8.98.

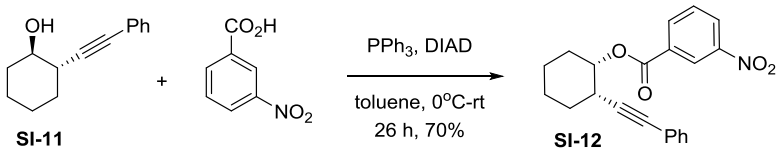


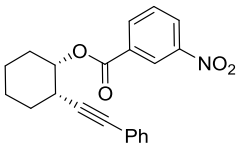
Diene 143

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added $RuHCl(CO)(H_2IMes)(PPh_3)$ (3.7 mg, 0.005 mmol, 0.02 equiv) and a solution of alkyne **57**[26] (77.7 mg, 0.25 mmol, 1 equiv) in DCE (1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 1 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a pale brown oil. Purification by preparative thin layer chromatography (eluted with 1:150 ether/hexanes) gave **143** as a pale yellow oil (54.6 mg, 70%, 17:1 *Z/E*).

R_f (10% ether/hexanes) = 0.44

^{1}H NMR (300 MHz, $CDCl_3$) **major isomer:** δ = 7.32-7.28 (m, 3H), 7.14-7.11 (m, 2H), 6.89 (dd, 1H, *J* = 17.1, 10.3 Hz), 5.23 (d, 1H, *J* = 11.1 Hz), 4.87 (dd, 1H, *J* = 17.0, 1.1 Hz), 3.82-3.75 (m, 1H), 2.87 (dd, 1H, *J* = 16.0, 5.3 Hz), 2.44 (dd, 1H, *J* = 16.2, 8.4 Hz), 1.96-1.92 (m, 1H), 1.80-1.65 (m, 4H), 1.45-0.98 (m, 6H), -0.09 (s, 3H), -0.22 (s, 3H); **minor isomer diagnostic peaks:** δ = 6.53 (dd, 1H, *J* = 17.1, 10.3 Hz), 5.23 (d, 1H, *J* = 11.1 Hz), 5.08 (d, 1H, *J* = 10.1 Hz), 4.74 (d, 1H, *J* = 17.0 Hz), 3.69-3.62 (m, 1H), 0.40 (s, 3H), 0.39 (s, 3H)



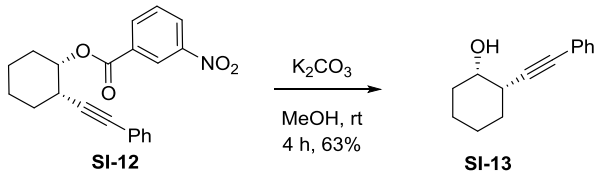


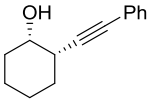
Ester SI-12

To an oven-dried 100 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added **SI-11**[26] (408 mg, 2.04 mmol, 1 equiv) and toluene (20 mL). The clear solution was cooled to 0°C (ice/H_2O bath) and the acid (682 mg, 4.08 mmol, 2 equiv) and phosphine (1.1 g, 4.08 mmol, 2 equiv) were added sequentially. DIAD (0.8 mL, 4.08 mmol, 2 equiv) in toluene (6 mL) was ten added dropwise and the resulting yellow solution warmed to rt slowly. After 26 h, the reaction mixture was quenched with sat. $NaHCO_{3(aq)}$ (20 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL) then the combined organics were washed with brine (2 x 30 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 17 cm; gradient elution with 7%-17% ether/hexanes) gave **SI-12** as a yellow oil (502 mg, 70%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (20% EtOAc/hexanes) = 0.49

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.94 (t, 1H, *J* = 1.7 Hz), 8.43-8.40 (m, 2H), 7.65 (t, 1H, *J* = 7.9 Hz), 7.42-7.39 (m, 2H), 7.30-7.27 (m, 3H), 5.23-5.19 (m, 1H), 3.29-3.27 (m, 1H), 2.11-2.01 (m, 2H), 1.88-1.75 (m, 4H), 1.59-1.46 (m, 2H)



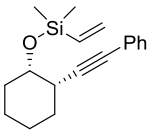


Alcohol SI-13

To a 100 mL RBF equipped with magnetic stir bar was added **SI-12** (640 mg, 1.8 mmol, 1 equiv), MeOH (35 mL) and K_2CO_3 (995 mg, 7.2 mmol, 4 equiv). The white suspension stirred at rt for 4 h then H_2O (10 mL) was added to dissolve the excess K_2CO_3. The solution was extracted with DCM (3 x 30 mL) then the combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 17 cm; eluted with 10% EtOAc/hexanes) gave **SI-13** as a clear oil (226 mg, 63%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (20% EtOAc/hexanes) = 0.34

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.45-7.41 (m, 2H), 7.31-7.28 (m, 3H), 3.78-3.73 (m, 1H), 3.07-3.03 (m, 1H), 1.98-1.90 (m, 1H), 1.78-1.34 (m, 8H)

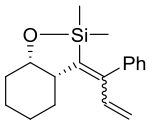


Silicon Tethered Alkyne 144

To an oven-dried 25 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added **SI-13** (278 mg, 1.39 mmol, 1 equiv), DCM (10 mL), imidazole (189 mg, 2.78 mmol, 2 equiv) and DMAP (34 mg, 0.28 mmol, 0.2 equiv) sequentially. The clear solution was cooled to 0°C (ice/H_2O bath) and vinyldimethylchlorosilane (0.23 mL, 1.67 mmol, 1.2 equiv) was added via syringe. The white suspension stirred at rt for 2 h then was quenched by sat. $NH_4Cl_{(aq)}$ (10 mL). The aqueous layer was extracted with DCM (3 x 5 mL) then the combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 10 cm; gradient elution with 2%-3% ether/hexanes) gave **144** as a clear oil (301 mg, 76%). Spectroscopic data corresponded to what was reported in the literature.[26]

R_f (10% ether/hexanes) = 0.67

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43-7.40 (m, 2H), 7.29-7.25 (m, 3H), 6.20 (dd, 1H, *J* = 20.6, 15.1 Hz), 5.99 (dd, 1H, *J* = 15.1, 4.0 Hz), 5.81 (dd, 1H, *J* = 20.2, 4.0 Hz), 3.88-3.85 (m, 1H), 2.86-2.82 (m, 1H), 1.96-1.88 (m, 1H), 1.82-1.57 (m, 5H), 1.40-1.26 (m, 2H), 0.23 (s, 3H), 0.22 (s, 3H)



Diene 145

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H_2IMes)(PPh_3) (9.0 mg, 0.0125 mmol, 0.05 equiv) and a solution of alkyne **144** (71.1 mg, 0.25 mmol, 1 equiv) in DCE (1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 1 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a pale brown oil. Purification by column chromatography (silica gel 1.5 x 11 cm; eluted with 2% ether/hexanes) gave **145** as a clear oil (55.5 mg, 78%, 11:1 *Z/E*).

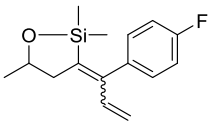
R_f = 0.34 (10% diethyl ether/hexanes)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34-7.26 (m, 3H), 7.14-7.10 (m, 2H), 6.89 (dd, *J* = 17.1, 10.5 Hz, H), 5.20 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.85 (dd, *J* = 17.1, 1.5 Hz, 1H), 4.07-4.06 (m, 1H), 2.89-2.82 (m, 1H), 2.08-2.03 (m, 1H), 1.74-1.72 (m, 1H), 1.65-1.50 (m, 4H), 1.40-1.26 (m, 2H), 0.17 (s, H), -0.39 (s, 3H); **minor isomer diagnostic peaks:** δ = 6.47 (dd, *J* = 16.8, 10.5 Hz, 1H), 5.07 (dd, *J* = 10.8, 1.2 Hz, 1H), 4.65 (dd, *J* = 16.8, 1.5 Hz, 1H), 0.48 (s, 3H), 0.39 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 146.3, 141.6, 135.5, 129.9, 128.0, 127.3, 118.3, 74.1, 44.3, 31.3, 28.4, 25.6, 19.7, 1.7, -1.1

IR (film): ν = 3054, 2931, 2851, 1582, 1491, 1441, 1249 cm^{-1}

Anal. calcd. for $C_{18}H_{24}OSi$: C 76.00, H 8.56; found: C 75.94, H 8.79

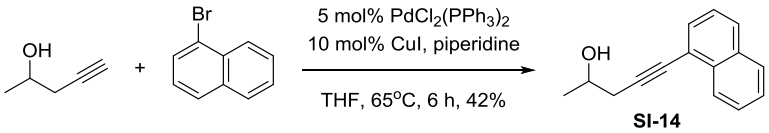


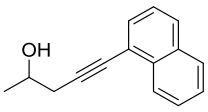
Diene 146

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H_2IMes)(PPh_3) (2.1 mg, 0.0028 mmol, 0.01 equiv) and a solution of alkyne **64** (73.9 mg, 0.28 mmol, 1 equiv) in DCE (1.1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 1 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a pale brown oil. Purification by column chromatography (silica gel 1.5 x 11 cm; gradient elution with 3%-5% ether/hexanes) gave **146** as a pale yellow oil (47.3 mg, 64%, 20:1 *Z/E*).

R_f (10% ether/hexanes) = 0.26

^{1}H NMR (300 MHz, $CDCl_3$) **major isomer:** δ = 7.11-6.98 (m, 4H), 6.84 (dd, 1H, *J* = 17.3, 10.6 Hz), 5.22 (d, 1H, *J* = 10.7 Hz), 4.80 (d, 1H, *J* = 17.0 Hz), 4.25-4.14 (m, 1H), 2.94 (dd, 1H, *J* = 16.2, 5.3 Hz), 2.30 (dd, 1H, *J* = 16.3, 8.1 Hz), 1.32 (d, 3H, *J* = 6.1 Hz), -0.07 (s, 3H), -0.19 (s, 3H); **minor isomer diagnostic peaks:** δ = 6.50 (dd, 1H, *J* = 17.3, 10.6 Hz), 5.09 (d, 1H, *J* = 10.7 Hz), 4.73 (d, 1H, *J* = 17.0 Hz), 2.02 (dd, 1H, *J* = 16.8, 8.4 Hz), 1.20 (d, 3H, *J* = 5.9 Hz), 0.41 (s, 3H), 0.38 (s, 3H)



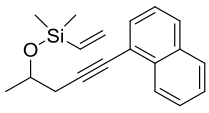


Alcohol SI-14

To an oven-dried 3-neck 250 mL RBF equipped with a magnetic stir bar and reflux condenser under $Ar_{(g)}$ was added $PdCl_2(PPh_3)_2$ (526 mg, 0.75 mmol, 0.05 equiv), CuI (286 mg, 0.15 mmol, 0.10 equiv), THF (60 mL), piperidine (3 mL, 30 mmol, 2 equiv), 4-pentyn-2-ol (1.4 mL, 15 mmol, 1 equiv) and 1-bromonapthalene (2.3 mL, 16.5 mmol, 1.1 equiv). The resulting green solution was subjected to three cycles of freeze/pump/thaw then placed under $Ar_{(g)}$. Once warmed to rt the lime green solution stirred at 65°C. After 6 h, the resulting black suspension was cooled to rt, diluted with ether (50 mL) then washed with sat. $NH_4Cl_{(aq)}$ (2 x 50 mL) and brine (2 x 50 mL). The organics were dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a dark brown oil. Purification by column chromatography (silica gel 4.5 x 12 cm; gradient elution with 25%-30% EtOAc/hexanes) gave **SI-14** as an orange oil (1.32 g, 42%). Spectroscopic data corresponded to what was reported in the literature.[88]

R_f (25% EtOAc/hexanes) = 0.33

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.33 (d, 1H, J = 8.7 Hz), 7.87-7.81 (m, 2H), 7.66 (d, 1H, J = 6.9 Hz), 7.60-7.50 (m, 2H), 7.42 (dd, 1H, J = 8.3, 7.4 Hz), 4.21-4.10 (m, 1H), 2.77 (d ABq, 2H, J_{AB} = 16.6 Hz, J_{AX} = 5.3 Hz, J_{BX} = 6.3 Hz), 2.03 (s, 1H), 1.42 (d, 3H, J = 6.4 Hz)

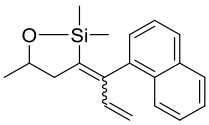


Silicon Tethered Alkyne 147

To an oven-dried 100 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added **SI-14** (1.27 g, 6 mmol, 1 equiv), DCM (40 mL), imidazole (817 mg, 12 mmol, 2 equiv) and DMAP (147 mg, 1.2 mmol, 0.2 equiv) sequentially. The yellow solution was cooled to 0°C (ice/H_2O bath) and vinyldimethylchlorosilane (1.24 mL, 9 mmol, 1.5 equiv) was added via syringe. The yellow suspension stirred at rt overnight then was quenched by sat. $NH_4Cl_{(aq)}$ (50 mL). The aqueous layer was extracted with DCM (3 x 25 mL) then the combined organics were washed with brine (2 x 50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give an orange oil. Purification by column chromatography (silica gel 2.5 x 10 cm; eluted with 5% EtOAc/hexanes) gave **147** as an orange oil (1.33 g, 75%). Spectroscopic data corresponded to what was reported in the literature.[88]

R_f (10% EtOAc/hexanes) = 0.55

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.34 (d, 1H, *J* = 8.2 Hz), 7.85-7.77 (m, 2H), 7.62 (d, 1H, *J* = 7.4 Hz), 7.58-7.47 (m, 2H), 7.40 (app t, 1H, *J* = 7.6 Hz), 6.21 (dd, 1H, *J* = 20.3, 15.0 Hz), 6.03 (ddd, 1H, *J* = 14.8, 4.2, 0.4 Hz), 5.83 (dd, 1H, *J* = 20.1, 4.2 Hz), 4.20-4.08 (m, 1H), 2.70 (d ABq, 2H, J_{AB} = 16.5 Hz, J_{AX} = 5.9 Hz, J_{BX} = 6.9 Hz), 1.38 (d, 3H, *J* = 6.0 Hz), 0.25 (s, 6H)



Diene 148

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H_2IMes)(PPh_3) (9.2 mg, 0.0125 mmol, 0.05 equiv) and a solution of alkyne **147** (74.3 mg, 0.25 mmol, 1 equiv) in DCE (1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 3 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a brown/black oil. Purification by column chromatography (silica gel 1.5 x 11.5 cm; gradient elution with 2%-3% ether/hexanes) gave **148** as a pale yellow oil (54.4 mg, 73%, 13:1 *Z/E*).

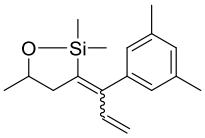
R_f = 0.44 (10% diethyl ether/hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) (mixture of rotamers): δ = 7.85-7.76 (m, 3H), 7.51-7.38 (m, 3H), 7.25 (d, *J* = 6.7 Hz, 1H), 7.01 (ddd, *J* = 17.2, 10.4, 2.4 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 4.67 (d, *J* = 17.2 Hz, 1H), 4.39-4.30 (m, 0.5H), 4.28-4.19 (m, 0.5H), 3.16 (dd, *J* = 16.1, 5.1 Hz, 0.5H), 2.42 (dd, *J* = 16.5, 5.7 Hz, 0.5H), 1.39 (d, *J* = 6.1 Hz, 1.5H), 1.36 (d, *J* = 6.1 Hz, 0.5H), 0.00 (s, 1.5H), -0.1 (s, 1.5H), -0.7 (s, 1.5H), -0.8 (1.5H); **minor isomer diagnostic peaks:** δ = 6.70 (ddd, *J* = 16.6, 10.4, 2.4 Hz, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 4.90 (d, *J* = 17.2 Hz, 1H), 1.16 (d, *J* = 6.1 Hz, 3H), 1.13 (d, *J* = 6.1 Hz, 3H), -0.1 (s, 3H), -0.2 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.8, 145.6, 145.1, 144.7, 139.2, 139.0, 135.9, 135.8, 133.6, 133.5, 132.7, 132.7, 128.2, 127.9, 127.9, 127.8, 126.8, 126.7, 125.9, 125.9, 125.3, 125.2, 118.6, 118.6, 72.8, 72.6, 40.9, 40.5, 24.3, 24.2, 1.1, 0.4, -1.1, -1.8

IR (film): ν = 3046, 2966, 2927, 1585, 1507, 1395, 1376, 1249, 1104, 1037, 944, 781 cm^{-1}

Anal. calcd. for $C_{19}H_{22}OSi$: C 77.50, H 7.53; found: C 77.48, H 7.48.

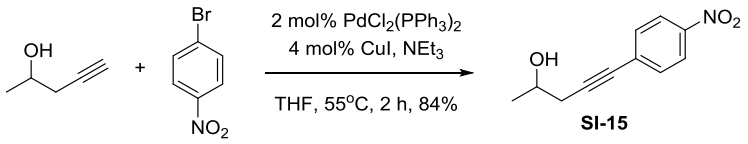


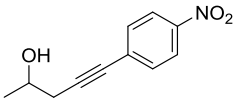
Diene 149

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H_2IMes)(PPh_3) (2 mg, 0.0027 mmol, 0.01 equiv) and a solution of alkyne **67** (73.1 mg, 0.27 mmol, 1 equiv) in DCE (1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 1 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a pale brown oil. Purification by column chromatography (silica gel 1.5 x 11 cm; gradient elution with 2%-3% ether/hexanes) gave **149** as a clear oil (54.1 mg, 74%, 26:1 *Z/E*).

R_f (10% ether/hexanes) = 0.34

^{1}H NMR (300 MHz, $CDCl_3$) **major isomer:** δ = 6.92 (s, 1H), 6.84 (dd, 1H, *J* = 17.2, 10.7 Hz), 6.75 (s, 2H), 5.22 (d, 1H, *J* = 10.6 Hz), 4.95 (dd, 1H, *J* = 17.3, 1.6 Hz), 4.25-4.14 (m, 1H), 2.93 (dd, 1H, *J* = 16.1, 5.3 Hz), 2.34-2.26 (m, 7H), 1.32 (d, 3H, *J* = 6.1 Hz), -0.07 (s, 3H), -0.20 (s, 3H); **minor isomer diagnostic peaks:** δ = 5.07 (d, 1H, *J* = 10.4 Hz), 4.78 (d, 1H, *J* = 17.0 Hz), 1.21 (d, 3H, *J* = 6.1 Hz), 0.42 (s, 3H), 0.39 (s, 3H)



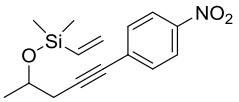


Alcohol SI-15

To an oven-dried 3-neck 250 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added $PdCl_2(PPh_3)_2$ (211 mg, 0.30 mmol, 0.02 equiv), CuI (114 mg, 0.60 mmol, 0.04 equiv), THF (60 mL), NEt_3 (3 mL), 4-pentyn-2-ol (1.4 mL, 15 mmol, 1 equiv) and 1-bromo-4-nitrobenzene (3.64 g, 18 mmol, 1.2 equiv). The resulting red/brown suspension was subjected to three cycles of freeze/pump/thaw then placed under $Ar_{(g)}$. Once warmed to rt the dark brown solution stirred at 55°C. After 2 h, the resulting black suspension was cooled to rt and sat. $NH_4Cl_{(aq)}$ (60 mL) was added. The aqueous layer was extracted with DCM (2 x 50 mL) then the combined organics were washed with brine (2 x 80 mL). The organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a dark brown oil. Purification by column chromatography (silica gel 4.5 x 12.5 cm; gradient elution with 20%-50% EtOAc/hexanes) gave **SI-15** as a dark red oil (2.60 g, 84%). Spectroscopic data corresponded to what was reported in the literature.[88]

R_f (30% EtOAc/hexanes) = 0.17

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.16 (d, 1H, *J* = 9.0 Hz), 7.54 (d, 1H, *J* = 9.0 Hz), 4.14-4.04 (m, 1H), 2.64 (d ABq, 2H, J_{AB} = 16.9 Hz, J_{AX} = 5.5 Hz, J_{BX} = 6.3 Hz), 1.84 (br s, 1H), 1.35 (d, 3H, *J* = 6.1 Hz)



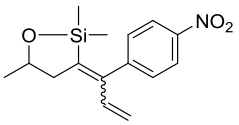
Silicon-Tethered Alkyne 150

To an oven-dried 50 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added **SI-15** (455 mg, 2.2 mmol, 1 equiv), DCM (15 mL), imidazole (300 mg, 4.4 mmol, 2 equiv) and DMAP (54 mg, 0.44 mmol, 0.2 equiv) sequentially. The yellow/orange solution was cooled to 0°C (ice/H_2O bath) and vinyldimethylchlorosilane (0.46 mL, 3.3 mmol, 1.5 equiv) was added via syringe. The yellow suspension stirred at rt for 3 h then was quenched by sat. $NH_4Cl_{(aq)}$ (15 mL). The aqueous layer was extracted with DCM (3 x 10 mL) then the combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give an orange oil. Purification by column chromatography (silica gel 2.5 x 12 cm; gradient elution with 3%-5% EtOAc/hexanes) gave **150** as a pale yellow oil (538 mg, 84%). Spectroscopic data corresponded to what was reported in the literature.[88]

R_f (20% EtOAc/hexanes) = 0.70

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.16 (d, 1H, *J* = 8.8 Hz), 7.52 (d, 1H, *J* = 8.8 Hz), 6.17 (dd, 1H, *J* = 19.8, 14.8 Hz), 6.03 (dd, 1H, *J* = 14.8, 4.3 Hz), 5.80 (dd, 1H, *J* = 19.9, 4.3 Hz), 4.12-4.02 (m, 1H), 2.57 (d ABq, 2H, J_{AB} = 16.7 Hz, J_{AX} = 5.9 Hz, J_{BX} = 6.6 Hz), 1.30 (d, 3H, *J* = 6.2 Hz), 0.23 (s, 6H)

Anal. calcd for $C_{15}H_{19}NO_3Si$: C 62.25, H 6.62, N 4.84; found C 62.64, H 6.64, N 5.13.

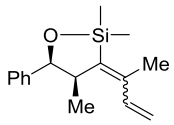


Diene 151

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added RuHCl(CO)(H_2IMes)(PPh_3) (3.8 mg, 0.0052 mmol, 0.02 equiv) and a solution of alkyne **150** (75.2 mg, 0.26 mmol, 1 equiv) in DCE (1.04 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 5 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a dark brown oil. Purification by column chromatography (silica gel 1.5 x 12 cm; gradient elution with 3%-10% ether/hexanes) then preparative thin layer chromatography (eluted with 5% ether/hexanes) gave **151** as a yellow oil (22.9 mg, 30%, 2:1 *Z/E*).

R_f (30% EtOAc/hexanes) = 0.35

^{1}H NMR (300 MHz, $CDCl_3$) **major isomer:** δ = 8.26-8.19 (m, 2H), 7.33-7.29 (m, 2H), 6.85 (dd, 1H, *J* = 17.3, 10.8 Hz), 5.28 (d, 1H, *J* = 10.8 Hz), 4.75 (d, 1H, *J* = 17.3 Hz), 4.24-4.16 (m, 1H), 2.98 (dd, 1H, *J* = 16.3, 5.2 Hz), 2.35 (dd, 1H, *J* = 16.0, 8.5 Hz), 1.33 (d, 3H, *J* = 6.3 Hz), -0.06 (s, 3H), -0.18 (s, 3H); **minor isomer diagnostic peaks:** δ = 6.51 (dd, 1H, *J* = 17.0, 10.5 Hz), 5.13 (d, 1H, *J* = 10.5 Hz), 4.67 (d, 1H, *J* = 17.0 Hz), 4.12-4.05 (m, 1H), 2.00 (ddd, 1H, *J* = 16.8, 8.3, 0.5 Hz), 1.20 (d, 3H, *J* = 6.3 Hz), 0.43 (s, 3H), 0.40 (s, 3H)



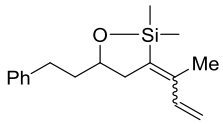
Diene 152

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar under an Argon-filled glovebox was added $RuHCl(CO)(H_2IMes)(PPh_3)$ (9.2 mg, 0.0125 mmol, 0.05 equiv) and a solution of alkyne **77** (64.7 mg, 0.25 mmol, 1 equiv) in DCE (1 mL). The vessel was sealed with a rubber septum, removed from the glovebox, degassed with ethylene (balloon) for 2 min then placed under a positive stream of ethylene (balloon). The solution stirred at 80°C for 7 h, was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a dark brown oil. Purification by preparative thin layer chromatography (eluted with 1% ether/hexanes) gave **152** as a yellow oil (36.4 mg, 56%, 4:1 *Z/E*).

R_f (10% ether/hexanes) = 0.38

^{1}H NMR (300 MHz, $CDCl_3$) **major isomer:** δ = 7.36-7.34 (m, 3H), 7.26-7.22 (m, 2H), 6.75 (dd, 1H, *J* = 17.5, 11.1 Hz), 5.33 (dd, 1H, *J* = 17.5, 1.3 Hz), 5.18 (dd, 1H, *J* = 10.9, 1.3 Hz), 5.12 (d, 1H, *J* = 4.4 Hz) 3.22-3.14 (m, 1H), 1.94 (s, 3H), 0.59 (d, 3H, *J* = 7.2 Hz), 0.46 (s, 3H), 0.39 (s, 3H); **minor isomer (153) diagnostic peaks:** δ = 6.37 (dd, 1H, *J* = 16.9, 10.6 Hz), 5.26 (d, 1H, *J* = 17.3 Hz), 3.09-3.00 (m, 1H), 1.92 (s, 3H), 0.58 (d, 3H, *J* = 7.1 Hz), 0.41(s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) **major isomer:** δ = 147.2, 142.1, 139.5, 135.7, 128.4, 127.1, 126.1, 115.2, 80.7, 43.3, 20.4, 16.0, 0.8, 0.1; **minor isomer (153) diagnostic peaks:** δ = 141.7, 140.9, 126.1, 113.4, 80.4, 44.6, 14.9, 1.2, 0.6

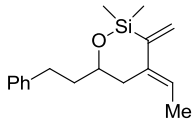


Diene 154

An oven dried Fischer Porter bottle equipped with a magnetic stir bar was brought into an argon filled glove box. To the Fischer Porter bottle was added RuHCl(CO)(H_2IMes)(PPh_3) (15 mg, 0.02 mmol, 0.02 equiv) and a solution of alkyne **68** (275 mg, 1.01 mmol, 1 equiv) in toluene. The bottle was plugged with a septum and removed from the glove box. The septum was replaced with a Swagelok regulator and the system was purged with ethylene (80 psi) and vented three times, then refilled to 80 psi and heated to 80 ^{o}C for 24 h. The reaction was cooled to rt, filtered through a plug of silica gel (eluted with ether) and concentrated *in vacuo* to give a brown oil. Purification by column chromatography (gradient elution with hexanes-4% ether/hexanes) gave **154** as a bright yellow oil (239 mg, 80%, 1:1 *Z/E*).

R_f (10% ether/hexanes) = 0.45

^{1}H NMR (300 MHz, $CDCl_3$) ***Z/E* mixture:** δ = 7.11-6.95 (m, 10H), 6.48 (dd, 1H, *J* = 17.4, 10.9 Hz), 6.13 (dd, 1H, *J* = 16.7, 10.9 Hz), 5.10-4.82 (m, 4H), 3.91-3.81 (m, 2H), 2.64-2.45 (m, 7H), 2.12-2.03 (m, 2H), 1.75-1.54 (m, 9H), 0.15 (s, 6H), 0.11 (s, 6H)



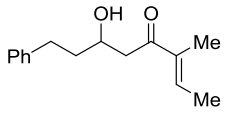
Diene 155

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.9 mg, 0.026 mmol, 0.10 equiv) and alkyne **68** (70.2 mg, 0.26 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified by column chromatography (silica gel 1.5 x 7 cm; eluted with 3% ether/hexanes) to give **155** as a clear oil (45.1 mg, 64%). Spectroscopic data correlated with what was reported in the literature.[88]

R_f (5% ether/hexanes) = 0.54

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.31-7.18 (m, 5H), 5.68 (d, 1H, *J* = 2.7 Hz), 5.61 (app q, 1H, *J* = 7.2 Hz), 5.08 (d, 1H, *J* = 3.0 Hz), 3.89-3.81 (m, 1H), 2.86-2.64 (m, 2H), 2.52 (dd, 1H, *J* = 14.7, 1.8 Hz), 2.16 (app dd, 1H, *J* = 14.7, 9.3 Hz), 1.96-1.71 (m, 2H), 1.63 (d, 3H, *J* = 6.9 Hz), 0.26 (s, 3H), 0.19 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.5, 142.3, 140.3, 128.6, 128.3, 125.7, 119.8, 117.9, 72.5, 39.5, 36.7, 31.9, 13.4, -0.2, -0.9



Hydroxy Ketone 156

To a flame dried 50 mL round bottom flask equipped with a magnetic stir bar under $Ar_{(g)}$ was added diene **154** (105 mg, 0.39 mmol, 1 equiv, 1:1 *Z/E*), DMF (15 mL), KHF_2 (91.3 mg, 1.17 mmol, 3 equiv), propionic anhydride (1.6 mL, 9.75 mmol, 25 equiv) and H_2O_2 (1.1 mL, 9.75 mmol, 25 equiv) sequentially. The reaction was stirred at rt overnight then poured into water (25 mL), extracted with ether (3 x 25 mL), washed with brine (25 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was purified by column chromatography (silica gel 2.5 x 15 cm, gradient elution with 15%-30% ether/hexanes) to afford ketone **156** as a clear oil (66 mg, 73%).

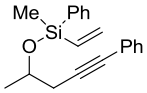
R_f (20% ether/hexanes)= 0.12

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30-7.16 (m, 5H), 6.75 (dq, *J* = 6.8, 1.6 Hz, 1H), 4.11-4.05 (m, 1H), 3.47 (br s, 1H), 2.88-2.81 (m, 2H), 2.75-2.67 (m, 2H), 1.91-1.82 (m, 4H), 1.77 (t, *J* = 1.2 Hz, 3H), 1.75-1.71 (m, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.5, 142.3, 139.0, 138.7, 128.7, 128.6, 126.0, 67.5, 43.6, 38.4, 32.1, 15.1, 11.0

IR (film): ν = 3496, 3061, 3026, 2927, 2860, 1655, 1496, 1451, 1073, 700 cm^{-1}

Anal. calcd. for $C_{15}H_{20}O_2$: C 77.55, H 8.68; found: C 77.71, H 8.54.



Silicon-Tethered Alkyne 212

To a 100 mL round bottom flask equipped with a magnetic stir bar under $Ar_{(g)}$ was added **SI-1** (801 mg, 5 mmol, 1 equiv), DCM (30 mL), imidazole (681 mg, 10 mmol, 2 equiv) and DMAP (122 mg, 1 mmol, 0.2 equiv). The pale yellow solution was cooled to 0°C (ice/H_2O bath) then vinylphenylmethylchlorosilane (1.3 mL, 7.5 mmol, 1.5 equiv) was added dropwise via syringe. The resulting white suspension stirred at rt overnight. The reaction was quenched with sat. $NH_4Cl_{(aq)}$ (35 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 30 mL) then the combined organic layers were washed with brine (2 x 50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 13 cm; eluted with 1% ether/hexanes) gave alkyne **212** as a clear oil (1:1 dr, 790 mg, 52%).

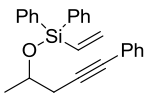
R_f (10% ether/hexanes) = 0.72

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68-7.66 (m, 2H), 7.43-7.40 (m, 5H), 7.31-7.29 (m, 3H), 6.37 (2 dd, 1H, *J* = 20.0, 14.8 Hz), 6.19 (2 dd, 1H, *J* = 14.8, 4.0 Hz), 5.94 (2 dd, 1H, *J* = 20.0, 3.6 Hz), 4.21-4.13 (2 m, 1H), 2.61 (2 d ABq, 2H, J_{AB} = 16.8 Hz, J_{AX} = 6.0 Hz, J_{BX} = 7.2 Hz), 1.35 (2 d, 3H, *J* = 6.0 Hz), 0.54 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.6, 136.1, 135.2, 134.3, 131.8, 130.0, 128.4, 128.0, 127.8, 124.0, 87.6, 82.3, 68.5, 30.4, 23.6, -2.7

FT-IR (NaCl, thin film) ν = 3052, 2972, 1595, 1490, 1429, 1378, 1254, 1118, 1007, 973 cm^{-1}

Anal. calcd for $C_{20}H_{22}OSi$: C 78.38, H 7.24; found: C 78.07, H 7.02.



Silicon-Tethered Alkyne 213

To a 100 mL round bottom flask equipped with a magnetic stir bar under $Ar_{(g)}$ was added **SI-1** (400 mg, 2.5 mmol, 1 equiv), DCM (20 mL), imidazole (341 mg, 5 mmol, 2 equiv) and DMAP (61 mg, 0.5 mmol, 0.2 equiv). The pale yellow solution was cooled to 0°C (ice/H_2O bath) then vinyldiphenylchlorosilane (0.83 mL, 3.8 mmol, 1.5 equiv) was added dropwise via syringe. The resulting white suspension stirred at rt overnight. The reaction was quenched with sat. $NH_4Cl_{(aq)}$ (10 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 10 mL) then the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 15 cm; eluted with hexanes) gave alkyne **213** as a clear oil (621 mg, 67%).

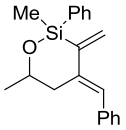
R_f (10% ether/hexanes) = 0.68

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.68-7.64 (m, 4H), 7.46-7.31 (m, 8H), 7.29-7.26 (m, 3H), 6.54 (dd, 1H, *J* = 20.4, 15.0 Hz), 6.29 (dd, 1H, *J* = 15.0, 3.9 Hz), 5.92 (dd, 1H, *J* = 20.4, 3.9 Hz), 4.28-4.18 (m, 1H), 2.63 (d ABq, 2H, J_{AB} = 16.8 Hz, J_{AX} = 5.7 Hz, J_{BX} = 6.8 Hz), 1.35 (d, 3H, *J* = 6.0 Hz)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.2, 135.1, 134.7, 134.6, 134.5, 133.9, 131.6, 129.9, 128.1, 127.8, 127.7, 127.6, 123.8, 87.3, 82.2, 68.7, 30.1, 23.3

FT-IR (NaCl, thin film) ν = 1591, 1489 cm^{-1}

HRMS (ESI) calcd. for $(C_{25}H_{24}OSi)_2Na^+$: 391.1499; found: 391.1496.



Diene 215

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne **212** (76.3 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified by column chromatography (silica gel 2.5 x 7 cm; eluted with 2% ether/hexanes) to give **215** as a clear oil (53.3 mg, 70%).

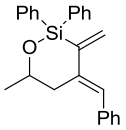
R_f (5% ether/hexanes) = 0.34

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.73-7.65 (m, 4H), 7.44-7.26 (m, 16H), 6.73 (d, 2H, *J* = 6.9 Hz,), 6.10 (dd, 2H, *J* = 5.1, 2.7 Hz), 5.43 (d, 1H, *J* = 2.7 Hz), 5.32 (d, 1H, *J* = 2.7 Hz), 4.31-4.23 (m, 1H), 4.17-4.10 (m, 1H), 2.99 (d, 1H, *J* = 14.7 Hz), 2.47 (dd, 1H, *J* = 15.0, 9.6 Hz), 2.37 (dd, 1H, *J* = 14.4, 10.2 Hz), 1.32 (d, 3H, *J* = 3.3 Hz), 1.30 (d, 3H, *J* = 3.0 Hz), 0.56 (s, 3H), 0.54 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.5, 149.4, 143.3, 142.4, 138.0, 137.9, 136.8, 136.8, 134.2, 134.0, 130.2, 130.1, 129.4, 129.3, 128.4, 128.4, 128.1, 128.1, 126.7, 70.7, 70.6, 40.1, 39.9, 24.6, 24.6, -1.6, -2.0

FT-IR (NaCl, thin film) ν = 2969, 1597, 1428, 1252, 1114 cm^{-1}

Anal. calcd for $C_{20}H_{22}OSi$: C 78.38, H 7.24; found: C 78.78, H 7.00.



Diene 216

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (8.0 mg, 0.021 mmol, 0.10 equiv) and alkyne **213** (77.7 mg, 0.21 mmol, 1 equiv) in toluene (0.84 mL) were combined and stirred at 70°C for 1 h. The residue was purified by column chromatography (silica gel 2.5 x 7 cm; eluted with 3% ether/hexanes) to give **216** a clear oil (56.2 mg, 72%).

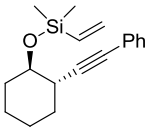
R_f (5% ether/hexanes) = 0.31

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.68-7.59 (m, 4H), 7.41-7.26 (m, 10H), 7.25-7.18 (m, 2H), 6.79 (s, 1H), 6.09 (dd, 1H, *J* = 14.7 Hz, 0.6 Hz), 4.53-4.43 (m, 1H), 2.88 (dd, 1H, *J* = 15.3 Hz, 1.5 Hz), 2.73 (dd, 1H, *J* = 15.3 Hz, 8.1 Hz), 1.29 (d, 3H, *J* = 6.6 Hz)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 153.9, 140.6, 137.2, 137.0, 136.7, 136.4, 134.7, 134.5, 134.3, 129.80, 129.75, 128.9, 128.3, 127.9, 127.1, 126.4, 72.2, 38.9, 24.2

FT-IR (NaCl, thin film): 2925, 1597, 1562, 1490 cm^{-1}

HRMS (ESI): calcd for $C_{25}H_{24}OSiNa^+$: 391.1489; found: 391.1499.



Silicon-Tethered Alkyne 219

To a 50 mL RBF equipped with a magnetic stir bar was added **SI-11**[26] (502 mg, 2.5 mmol, 1 equiv), DCM (10 mL), imidazole (341 mg, 5 mmol, 2 equiv) and DMAP (61 mg, 0.5 mmol, 0.2 equiv). The solution was cooled to 0°C (ice/H_2O bath) then vinyldimethylchlorosilane (0.52 mL, 3.8 mmol, 1.5 equiv) was added dropwise via syringe. The resulting white suspension stirred at rt overnight. The reaction was quenched with sat. $NH_4Cl_{(aq)}$ (10 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 10 mL) then the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification via column chromatography (silica gel 2.5 x 15 cm; eluted with 2% EtOAc/hexanes) gave alkyne **219** as a pale yellow oil (471 mg, 66%).

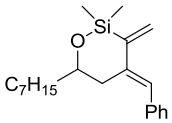
R_f (5% ether/hexanes) = 0.50

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33-7.31 (m, 2H), 7.21-7.16 (m, 3H), 6.13 (dd, 1H, *J* = 20.4, 14.8 Hz), 5.91 (dd, 1H, *J* = 14.8, 4.0 Hz), 5.72 (dd, 1H, *J* = 20.4, 4.0 Hz), 3.59-3.54 (m, 1H), 2.43 (ddd, 1H, *J* = 12.4, 8.4, 4.0 Hz), 2.01-1.96 (m, 1H), 1.86-1.81 (m, 1H), 1.66-1.57 (m, 2H), 1.45-1.35 (m, 1H), 1.32-1.11 (m, 3H), 0.16 (s, 3H), 0.15 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.4, 133.0, 131.7, 128.3, 127.6, 124.3, 93.0, 81.7, 74.0, 38.8, 34.9, 31.1, 24.6, 24.0, -1.0, -1.2

FT-IR (NaCl, thin film) ν = 2937, 2860, 1491, 1252, 1102 cm^{-1}

Anal. calcd for $C_{18}H_{24}OSi$: C 76.00, H 8.50; found: C 76.29, H 8.22.



Diene 220

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne **55**[26] (81.1 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 4.5 cm; eluted with 3% ether/hexanes) to give **220** as a pale yellow oil (64.9 mg, 80%).

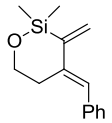
R_f (5% ether/hexanes) = 0.63

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.36-7.21 (m, 5H), 6.58 (s, 1H), 5.89 (d, 1H, *J* = 3.0 Hz), 5.22 (d, 1H, *J* = 3.0 Hz), 3.88-3.83 (m, 1H), 2.86 (app d, 1H, *J* = 15.0 Hz), 2.31 (app dd, 1H, *J* = 14.7, 9.9 Hz), 1.42-1.23 (m, 12H), 0.89-0.84 (m, 3H), 0.30 (s, 3H), 0.23 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.1, 143.1, 138.1, 129.3, 128.4, 126.6, 123.5, 121.5, 74.0, 38.3, 38.3, 32.0, 29.7, 29.5, 25.8, 22.9, 14.3, -0.1, -0.7

FT-IR (NaCl, thin film) ν = 3079, 2956, 2927, 2856, 1599, 1493, 1402, 1252, 1111, 1045 cm^{-1}

Anal. calcd for $C_{21}H_{32}OSi$: C 76.77, H 9.82; found: C 76.95, H 9.47.



Diene 221

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne **218**[88] (58.1 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via flash column chromatography (silica gel 1.5 x 5 cm; eluted with 3% ether/hexanes) to give **221** as a clear oil (45 mg, 77%).

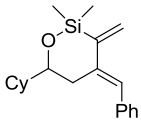
R_f (5% ether/hexanes) = 0.33

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.36-7.21 (m, 5H), 6.58 (s, 1H), 5.90 (d, 1H, *J* = 2.7 Hz), 5.24 (d, 1H, *J* = 2.7 Hz), 3.95 (t, 2H, *J* = 5.4 Hz), 2.73-2.69 (app t, 2H, *J* = 5.1 Hz), 0.28 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.0, 143.7, 138.0, 129.4, 128.4, 126.7, 123.4, 122.0, 64.3, 33.7, -0.9

FT-IR (NaCl, thin film) ν = 3079, 3048, 2958, 2858, 1599, 1401, 1253, 1083, 1045 cm^{-1}

Anal. calcd for $C_{14}H_{18}OSi$: C 72.99, H 7.88; found: C 73.11, H 8.21.



Diene 222

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne **57**[26] (78.4 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 5 cm; eluted with 3% ether/hexanes) to give **222** as a yellow oil (69.0 mg, 88%).

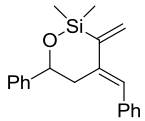
R_f (hexanes) = 0.28

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.36-7.21 (m, 5H), 6.58 (s, 1H), 5.88 (d, 1H, *J* = 2.7 Hz), 5.21 (d, 1H, *J* = 2.7 Hz), 3.63 (ddd, 1H, *J* = 9.9, 6.0, 2.1 Hz), 2.87 (app d, 1H, *J* = 13.5 Hz), 2.29 (app dd, 1H, *J* = 14.4, 10.2 Hz), 1.89-1.85 (m, 1H), 1.75-0.93 (m, 10H), 0.28 (s, 3H), 0.22 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.5, 143.5, 138.2, 129.3, 128.4, 126.5, 123.4, 121.2, 78.3, 44.4, 35.2, 28.9, 28.7, 26.7, 26.4, 26.4, -0.1, -0.7

FT-IR (NaCl, thin film) ν = 3079, 2949, 2861, 1707, 1599, 1493, 1449, 1251, 1064 cm^{-1}

Anal. calcd for $C_{20}H_{28}OSi$: C 76.86, H 9.03; found: C 76.76, H 8.71.



Diene 223

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne **58** (75.1 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 1 h. The residue was purified via column chromatography (silica gel 2.5 x 6 cm; eluted with 2% ether/hexanes) to give **223** as a clear oil (56.7 mg, 80%).

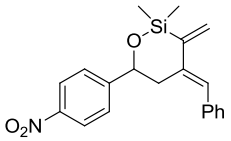
R_f (5% ether/hexanes) = 0.40

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.12 (m, 10H), 6.58 (s, 1H), 5.89 (d, 1H, *J* = 2.4 Hz), 5.24 (d, 1H, *J* = 2.8 Hz), 4.91 (dd, 1H, *J* = 10.8, 2.0 Hz), 3.05 (dd, 1H, *J* = 14.8, 2.0 Hz), 2.43 (ddd, 1H, *J* = 14.8, 10.8, 2.0 Hz), 0.34 (s, 3H), 0.25 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.6, 144.5, 142.7, 137.8, 129.3, 128.6, 128.5, 127.5, 126.7, 125.7, 124.1, 122.0, 76.1, 41.5, -0.2, -0.7

FT-IR (NaCl, thin film) ν = 3061, 3028, 2958, 2897, 1601, 1493, 1452, 1253 cm^{-1}

Anal. calcd for $C_{20}H_{22}OSi$: C 78.38, H 7.24; found: C 78.61, H 7.34.



Diene 224

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (5.7 mg, 0.015 mmol, 0.10 equiv) and alkyne **117** (54.3 mg, 0.15 mmol, 1 equiv) in toluene (0.6 mL) were combined and stirred at 70°C for 2 h. The residue was purified via column chromatography (silica gel 2.5 x 5 cm; gradient elution with 3%-4% ether/hexanes) to give **224** as a yellow oil (43.2 mg, 80%).

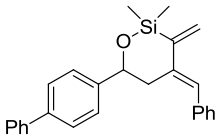
R_f (5% ether/hexanes) = 0.22

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, 2H, *J* = 8.8 Hz), 7.38 (d, 2H, *J* = 8.4 Hz), 7.24-7.22 (m, 2H), 7.16-7.12 (m, 3H), 6.60 (s, 1H), 5.89 (d, 1H, *J* = 2.4 Hz), 5.25 (d, 1H, *J* = 2.4 Hz), 4.99 (dd, 1H, *J* = 10.4, 2.0 Hz), 3.03 (dd, 1H, *J* = 14.8, 2.0 Hz), 2.38 (ddd, 1H, *J* = 14.8, 10.8, 2.0 Hz), 0.35 (s, 3H), 0.25 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.7, 150.8, 147.3, 141.5, 137.5, 129.2, 128.5, 127.0, 126.4, 124.7, 123.8, 122.6, 75.1, 41.1, -0.3, -0.6

FT-IR (NaCl, thin film) ν = 3056, 2956, 2897, 1602, 1520, 1492, 1347, 1253 cm^{-1}

Anal. calcd for $C_{20}H_{21}NO_3Si$: C 68.35, H 6.02, N 3.99; found: C 68.11, H 6.11, N 3.90.



Diene 225

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (5.3 mg, 0.014 mmol, 0.10 equiv) and alkyne **61**[26] (51.9 mg, 0.14 mmol, 1 equiv) in toluene (0.6 mL) were combined and stirred at 70 °C for 30 min. The residue was purified via column chromatography (silica gel 2.5 x 7 cm; gradient elution with 1%-4% ether/hexanes) to give **225** as a white oil (40.4 mg, 78%).

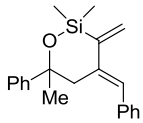
R_f (5% ether/hexanes) = 0.39

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61-7.57 (m, 4H), 7.47-7.43 (m, 4H), 7.33-7.22 (m, 6H), 6.70 (s, 1H), 6.00 (d, 1H, *J* = 2.7 Hz), 5.36 (d, 1H, *J* = 2.7 Hz), 5.06 (dd, 1H, *J* = 10.8, 2.0 Hz), 3.19 (dd, 1H, *J* = 14.8, 2.0 Hz), 2.59 (ddd, 1H, *J* = 14.7, 10.8, 1.8 Hz), 0.46 (s, 3H), 0.37 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.6, 143.5, 142.7, 141.2, 140.5, 137.8, 129.3, 128.9, 128.5, 127.4, 127.3, 126.8, 126.2, 124.2, 122.1, 75.8, 41.4, -0.2, -0.7

FT-IR (NaCl, thin film) ν = 3028, 2956, 1600, 1487, 1252, 1067 cm^{-1}

Anal. calcd for $C_{26}H_{26}OSi$: C 81.63, H 6.85; found: C 81.31, H 6.52.



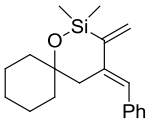
Diene 226

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne **62**[26] (81.2 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 5 cm; eluted with 3% ether/hexanes) to give **226** as a pale yellow oil (76.2 mg, 94%). Spectroscopic data corresponded to what was reported in the literature.[88]

R_f (hexanes) = 0.67

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42-7.23 (m, 10H), 6.84 (s, 1H), 6.04 (d, 1H, *J* = 2.1 Hz), 5.32 (d, 1H, *J* = 2.1 Hz), 3.11 (d, 1H, *J* = 14.4 Hz), 2.92 (d, 1H, *J* = 14.4 Hz), 1.55 (s, 3H), 0.43 (s, 3H), 0.42 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.4, 148.5, 140.0, 137.8, 129.1, 128.2, 127.8, 126.5, 126.3, 124.7, 124.5, 121.4, 78.0, 43.5, 30.4, 1.9, 1.0



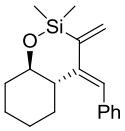
Diene 227

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (114 mg, 0.30 mmol, 0.10 equiv) and alkyne **63**[26] (896 mg, 3.0 mmol, 1 equiv) in toluene (12 mL) were combined and stirred at 70°C for 1 h. The residue was purified by column chromatography (silica gel 2.5 x 6 cm; eluted with 2% ether/hexanes) to give **227** as a pale yellow solid (840 mg, 94%). Spectroscopic data corresponded to what was reported in the literature.[88]

R_f (hexanes) = 0.38

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.38-7.22 (m, 5H), 6.78 (s, 1H), 5.97 (d, 1H, *J* = 2.7 Hz), 5.25 (d, 1H, *J* = 2.7 Hz), 2.63 (s, 2H), 1.67-1.20 (m, 10H), 0.31 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.5, 141.0, 138.1, 129.2, 128.1, 126.3, 124.0, 121.0, 75.3, 41.9, 38.5, 25.7, 22.0, 1.5



Diene 228

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne **219** (72.0 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 20 h. The residue was purified via column chromatography (silica gel 1.5 x 4 cm; eluted with 3% ether/hexanes) to give **228** as a clear oil (52.3 mg, 73%).

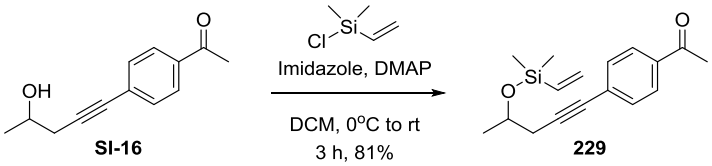
R_f (5% ether/hexanes) = 0.33

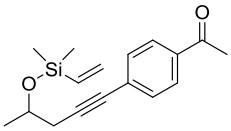
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.20 (m, 5H), 6.36 (s, 1H), 5.85 (d, 1H, *J* = 3.0 Hz), 5.28 (d, 1H, *J* = 3.3 Hz), 3.52 (td, 1H, *J* = 10.2, 3.9 Hz), 2.97 (app t, 1H, *J* = 9.9 Hz), 2.05-2.01 (m, 1H), 1.86-1.78 (m, 2H), 1.60-1.19 (m, 4H), 1.04-0.99 (m, 1H), 0.24 (s, 3H), 0.23 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 153.7, 148.4, 138.1, 128.7, 128.5, 126.5, 125.5, 122.7, 75.5, 48.1, 35.2, 29.4, 25.8, 25.4, -0.9, -2.0

FT-IR (NaCl, thin film) ν = 3048, 2932, 2858, 1598, 1493, 1446, 1251, 1057 cm^{-1}

Anal. calcd for $C_{18}H_{24}OSi$: C 76.00, H 8.50; found: C 76.09, H 8.87.



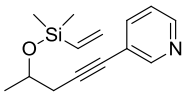


Silicon-Tethered Alkyne 229

To a flame-dried 50 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added **SI-16**[88] (555 mg, 2.74 mmol, 1 equiv), DCM (18 mL), imidazole (373 mg, 5.48 mmol, 2 equiv) and DMAP (67 mg, 0.55 mmol, 0.2 equiv). The yellow solution was cooled to 0°C (ice/H_2O bath) then vinyldimethylchlorosilane (0.57 mL, 4.11 mmol, 1.5 equiv) was added via syringe. The resulting yellow suspension stirred at rt for 3 h, was quenched with sat. $NH_4Cl_{(aq)}$ (20 mL) then the layers were separated. The organic layer was washed with brine (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 12.5 cm; gradient elution with 7%-13% ether/hexanes) gave alkyne **229** as a pale yellow oil (632 mg, 81%). Spectroscopic data corresponded to what was reported in the literature.[88]

R_f (25% EtOAc/hexanes) = 0.52

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.88 (dd, 2H, *J* = 6.5, 1.6 Hz), 7.46 (dd, 2H, *J* = 7.1, 2.2 Hz), 6.18 (dd, 1H, *J* = 20.2, 14.7 Hz), 6.02 (dd, 1H, *J* = 14.7, 4.4 Hz), 5.80 (dd, 1H, *J* = 20.2, 4.4 Hz), 4.11-4.01 (m, 1H), 2.59 (s, 3H), 2.55 (d ABq, 2H, J_{AB} = 16.9 Hz, J_{AX} = 6.0 Hz, J_{BX} = 6.5 Hz), 1.30 (d, 3H, *J* = 6.0 Hz), 0.23 (s, 6H)



Silicon-Tethered Alkyne 231

A solution of 4-pentyn-2-ol (0.57 mL, 6 mmol, 1.2 equiv), 3-bromopyridine (0.48 mL, 5 mmol, 1 equiv), CuI (95.2 mg, 0.5 mmol, 0.10 equiv), $PdCl_2(PPh_3)_2$ (176 mg, 0.25 mmol, 0.05 equiv) and Et_3N (20 mL) was degassed by freeze-pump-thaw (3 times) and refluxed under $Ar_{(g)}$ overnight. The reaction mixture was quenched with sat. $NH_4Cl_{(aq)}$ (20 mL) and extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by column chromatography on silica gel (2.5 x 15 cm; eluted with 50% EtOAc/hexanes) gave the alcohol (576 mg, 71%) as a brown oil. To a 50 mL RBF with magnetic stir bar under $Ar_{(g)}$ was added alcohol (392 mg, 2.4 mmol, 1 equiv), DCM (15 mL), imidazole (327 mg, 4.8 mmol, 2 equiv) and DMAP (59 mg, 0.48 mmol, 0.2 equiv). The orange solution was cooled to 0°C (ice/H_2O bath) then vinyldimethylchlorosilane (0.50 mL, 3.6 mmol, 1.5 equiv) was added dropwise via syringe. The resulting yellow suspension stirred at rt overnight. The reaction was quenched with sat. $NH_4Cl_{(aq)}$ (15 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 15 mL) then the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 12 cm; gradient elution with 10%-25% EtOAc/hexanes) gave alkyne **231** as a pale yellow oil (373 mg, 63%).

R_f (25% EtOAc/hexanes) = 0.45

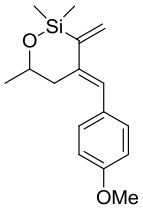
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.60 (d, 1H, *J* = 1.4 Hz), 8.46 (dd, 1H, *J* = 4.9, 1.7 Hz), 7.64 (dt, 1H, *J* = 7.9, 1.9 Hz), 7.18 (ddd, 1H, *J* = 7.9, 4.9, 0.8 Hz), 6.15 (dd, 1H, *J* = 20.4, 14.8 Hz),

5.99 (dd, 1H, J = 14.8, 4.0 Hz), 5.78 (dd, 1H, J = 20.0, 4.0 Hz), 4.07-3.99 (m, 1H), 2.52 (d ABq, 2H, J_{AB} = 16.4 Hz, J_{AX} = 6.0 Hz, J_{BX} = 6.8 Hz), 1.27 (d, 3H, J = 6.0 Hz), 0.20 (s, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.5, 148.2, 138.6, 137.8, 133.4, 123.1, 121.1, 91.3, 78.9, 67.8, 30.4, 23.6, -1.4

FT-IR (NaCl, thin film) ν = 3049, 2970, 2905, 1561, 1476, 1408, 1378, 1253, 1128, 1098, 1004, 837, 736 cm^{-1}

Anal. calcd for $C_{14}H_{19}NOSi$: C 68.52, H 7.80, N 5.71; found: C 68.88, H 8.10, N 5.88.



Diene 232

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (28.5 mg, 0.075 mmol, 0.10 equiv) and alkyne **65** (206 mg, 0.75 mmol, 1 equiv) in toluene (3 mL) were combined and stirred at 70°C for 1.5 h. The residue was purified via column chromatography (silica gel 2.5 x 5 cm; gradient elution with 3%-5% ether/hexanes) to give **232** as a clear oil (183.1 mg, 89%).

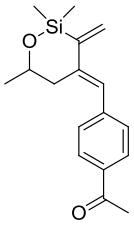
R_f (5% ether/hexanes) = 0.24

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.19 (d, 2H, *J* = 8.4 Hz), 6.88 (d, 2H, *J* = 9.0 Hz), 6.54 (s, 1H), 5.87 (d, 1H, *J* = 3.0 Hz), 5.21 (d, 1H, *J* = 2.7 Hz), 4.10-4.00 (m, 1H), 3.82 (s, 3H), 2.86 (dd, 1H, *J* = 14.7, 1.8 Hz), 2.28 (ddd, 1H, *J* = 14.4, 10.2, 1.8 Hz), 1.23 (d, 3H, *J* = 6.0 Hz), 0.30 (s, 3H), 0.23 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.4, 151.6, 141.5, 130.6, 130.6, 123.1, 121.3, 113.8, 70.1, 55.4, 40.1, 24.6, -0.1, -0.7

FT-IR (NaCl, thin film) ν = 3030, 2962, 1607, 1510 cm^{-1}

Anal. calcd for $C_{16}H_{22}O_2Si$: C 70.03, H 8.08; found: C 69.94, H 7.87.



Diene 233

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne **229** (71.1 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 6 h. The residue was purified via column chromatography (silica gel 1.5 x 4.5 cm; eluted with 20% ether/hexanes) to give **233** as a clear oil (53.9 mg, 76%).

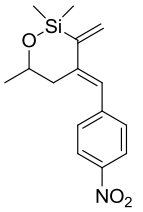
R_f (25% ether/hexanes) = 0.29

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.91 (d, 2H, *J* = 8.4 Hz), 7.32 (d, 2H, *J* = 8.4 Hz), 6.58 (s, 1H), 5.91 (d, 1H, *J* = 2.7 Hz), 5.26 (d, 1H, *J* = 2.4 Hz), 4.11-4.01 (m, 1H), 2.83 (dd, 1H, *J* = 14.4, 1.8 Hz), 2.58 (s, 3H), 2.29 (ddd, 1H, *J* = 14.4, 9.9, 1.5 Hz), 1.23 (d, 3H, *J* = 6.0 Hz), 0.30 (s, 3H), 0.24 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.7, 151.5, 145.3, 143.0, 135.2, 129.4, 128.5, 122.6, 122.4, 70.0, 40.3, 26.7, 24.5, -0.2, -0.8

FT-IR (NaCl, thin film) ν = 3046, 2969, 2897, 1683, 1601, 1505, 1406, 1268, 1122 cm^{-1}

Anal. calcd for $C_{17}H_{22}O_2Si$: C 71.28, H 7.74; found: C 70.96, H 7.39.



Diene 234

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne **150** (72.7 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 4 cm; eluted with 3% ether/hexanes) to give **234** as a pale yellow solid (62.0 mg, 85%).

R_f (5% ether/hexanes) = 0.24

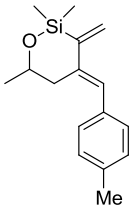
M.P. = 82-84°C

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.20 (d, 2H, *J* = 9.0 Hz), 7.39 (d, 2H, *J* = 8.7 Hz), 6.59 (s, 1H), 5.93 (d, 1H, *J* = 2.7 Hz), 5.31 (d, 1H, *J* = 2.7 Hz), 4.13-4.04 (m, 1H), 2.81 (dd, 1H, *J* = 14.4, 1.5 Hz), 2.32 (ddd, 1H, *J* = 15.6, 9.0, 1.8 Hz), 1.25 (d, 3H, *J* = 6.3 Hz), 0.32 (s, 3H), 0.26 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.3, 147.0, 146.2, 144.9, 129.9, 123.8, 123.0, 121.6, 69.8, 40.3, 24.5, -0.2, -0.8

FT-IR (NaCl, thin film) ν = 3078, 2988, 2948, 2850, 1593, 1517, 1342, 1251, 1114 cm^{-1}

Anal. calcd for $C_{15}H_{19}NO_3Si$: N 4.84, C 62.25, H 6.62; found: N 4.83, C 62.61, H 6.83.



Diene 235

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.1 mg, 0.024 mmol, 0.10 equiv) and alkyne **66**[26] (63.0 mg, 0.24 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 4 cm; eluted with 3% ether/hexanes) to give **235** as a pale yellow oil (50.6 mg, 80%).

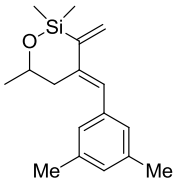
R_f (5% ether/hexanes) = 0.43

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.15 (s, 4H), 6.56 (s, 1H), 5.88 (d, 1H, *J* = 2.7 Hz), 5.22 (d, 1H, *J* = 2.7 Hz), 4.11-4.01 (m, 1H), 2.87 (dd, 1H, *J* = 14.4, 1.8 Hz), 2.35 (s, 3H), 2.27 (ddd, 1H, *J* = 14.4, 10.2, 1.8 Hz), 1.22 (d, 3H, *J* = 6.3 Hz), 0.30 (s, 3H), 0.24 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.6, 142.3, 136.3, 135.1, 129.3, 129.1, 123.5, 121.5, 70.1, 40.1, 24.6, 21.4, -0.1, -0.7

FT-IR (NaCl, thin film) ν = 3045, 2969, 1706, 1610, 1510, 1376, 1251, 1115, 1043 cm^{-1}

Anal. calcd for $C_{16}H_{22}OSi$: C 74.36, H 8.58; found: C 74.21, H 8.21.



Diene 236

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne **67** (69.2 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 4 cm; eluted with hexanes) to give **236** as a clear oil (55.7 mg, 80%).

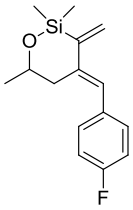
R_f (5% ether/hexanes) = 0.53

^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.87 (s, 3H), 6.53 (s, 1H), 5.86 (d, 1H, *J* = 2.7 Hz), 5.21 (d, 1H, *J* = 2.7 Hz), 4.10-4.02 (m, 1H), 2.88 (dd, 1H, *J* = 14.7, 1.8 Hz), 2.32-2.22 (m, 7H), 1.24 (d, 3H, *J* = 6.0 Hz), 0.31 (s, 3H), 0.23 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.7, 142.6, 138.0, 137.8, 128.3, 127.2, 123.7, 121.4, 70.3, 40.1, 24.6, 21.6, -0.2, -0.7

FT-IR (NaCl, thin film) ν = 3042, 2977, 2919, 2862, 1599, 1444, 1376, 1251, 1116, 1051 cm^{-1}

Anal. calcd for $C_{17}H_{24}OSi$: C 74.94, H 8.88; found: C 75.19, H 8.73.



Diene 237

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne **64** (66.8 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 4.5 cm; eluted with 3% ether/hexanes) to give **237** as a pale yellow oil (54.2 mg, 81%).

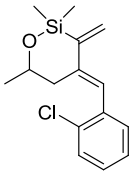
R_f (5% ether/hexanes) = 0.39

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.23-7.18 (m, 2H), 7.05-6.99 (m, 2H), 6.53 (s, 1H), 5.88 (d, 1H, *J* = 2.7 Hz), 5.23 (d, 1H, *J* = 2.7 Hz), 4.10-4.00 (m, 1H), 2.80 (dd, 1H, *J* = 14.7, 2.1 Hz), 2.25 (ddd, 1H, *J* = 15.0, 9.9, 1.5 Hz), 1.23 (d, 3H, *J* = 6.3 Hz), 0.31 (s, 3H), 0.24 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.2, 160.0, 151.4, 143.0, 134.0, 131.0, 130.9, 122.4, 121.8, 115.4, 115.2, 70.0, 40.0, 24.5, -0.2, -0.8

FT-IR (NaCl, thin film) ν = 3046, 2970, 2896, 1601, 1507, 1377, 1251, 1225, 1115, 1043 cm^{-1}

Anal. calcd for $C_{15}H_{19}FOSi$: C 68.66, H 7.30; found: C 68.68, H 7.02.



Diene 238

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.5 mg, 0.025 mmol, 0.10 equiv) and alkyne **230**[88] (69.6 mg, 0.25 mmol, 1 equiv) in toluene (1 mL) were combined and stirred at 70°C for 30 min. The residue was purified via column chromatography (silica gel 1.5 x 4 cm; eluted with 3% ether/hexanes) to give **238** as a clear oil (66.4 mg, 95%).

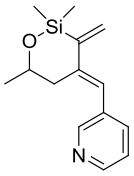
R_f (5% ether/hexanes) = 0.35

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.41-7.17 (m, 4H), 6.58 (s, 1H), 5.94 (d, 1H, *J* = 2.7 Hz), 5.28 (d, 1H, *J* = 2.7 Hz), 4.11-4.04 (m, 1H), 2.64 (dd, 1H, *J* = 14.1, 2.1 Hz), 2.18 (ddd, 1H, *J* = 14.1, 9.9, 1.8 Hz), 1.21 (d, 3H, *J* = 6.3 Hz), 0.34 (s, 3H), 0.26 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.3, 144.3, 136.4, 134.4, 131.0, 129.6, 128.2, 126.5, 122.1, 120.9, 70.3, 40.2, 24.5, -0.3, -0.8

FT-IR (NaCl, thin film) ν = 3048, 2969, 2929, 1468, 1253, 1115, 977 cm^{-1}

Anal. calcd for $C_{15}H_{19}ClOSi$: C 64.61, H 6.87; found: C 64.68, H 6.92.



Diene 239

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (9.1 mg, 0.024 mmol, 0.12 equiv) and alkyne **231** (49.9 mg, 0.20 mmol, 1 equiv) in toluene (0.8 mL) were combined and stirred at 70°C for 5 h. The residue was purified via column chromatography (silica gel 1.5 x 12 cm; eluted with 25% ether/hexanes) to give **239** as an orange oil (25.8 mg, 52%).

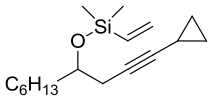
R_f (30% ether/hexanes) = 0.13

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.50 (d, 1H, *J* = 2.1 Hz), 8.43 (dd, 1H, *J* = 4.8, 1.5 Hz), 7.55-7.51 (m, 1H), 7.25 (app dd, 1H, *J* = 7.8, 4.8 Hz), 6.49 (s, 1H), 5.90 (d, 1H, *J* = 2.7 Hz), 5.26 (d, 1H, *J* = 2.7 Hz), 4.11-4.00 (m, 1H), 2.77 (dd, 1H, *J* = 14.4, 1.8 Hz), 2.27 (ddd, 1H, *J* = 14.4, 9.9, 1.8 Hz), 1.22 (d, 3H, *J* = 6.3 Hz), 0.30 (s, 3H), 0.23 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.3, 150.4, 147.6, 145.5, 136.3, 133.7, 123.3, 122.4, 119.7, 70.0, 40.1, 24.5, -0.2, -0.8

FT-IR (NaCl, thin film) ν = 2968, 2927, 1421, 1376, 1252, 1128 cm^{-1}

Anal. calcd for $C_{14}H_{19}NOSi$: C 68.52, H 7.80, N 5.71; found: C 68.53, H 8.11, N 5.75.



Silicon-Tethered Alkyne 240

*n*BuLi (2.4 M in hexanes, 12.5 mL, 30 mmol, 1.5 equiv) was added dropwise to a stirred solution of cyclopropylacetylene (2.5 mL, 30 mmol, 1.5 equiv) in dry THF (30 mL) at -78°C under $Ar_{(g)}$. After complete addition the solution was stirred at -78°C for 1 h. Next a solution of 1,2-epoxyoctane (3.1 mL, 30 mmol, 1 equiv) in dry HMPA (7 mL, 40 mmol, 2 equiv) was added and the reaction mixture was allowed to warm to rt. After being stirred at rt overnight, the reaction mixture was poured into water (100 mL) and extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the alcohol as a pale yellow oil. To a 100 mL RBF equipped with magnetic stir bar under $Ar_{(g)}$ was added alcohol (1.9 g, 9.8 mmol, 1 equiv), DCM (65 mL), imidazole (1.0 g, 14.7 mmol, 1.5 equiv) and DMAP (180 mg, 1.47 mmol, 0.15 equiv). The solution was cooled to 0°C (ice/H_2O bath) then vinyldimethylchlorosilane (1.6 mL, 11.8 mmol, 1.2 equiv) was added dropwise via syringe. The resulting white suspension stirred at rt overnight. The reaction was quenched with sat. $NH_4Cl_{(aq)}$ (50 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 50 mL) then the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 2.5 x 15 cm; eluted with 1% ether/hexanes) gave alkyne **240** as a clear oil (1.78 g, 66%).

R_f (5% ether/hexanes) = 0.59

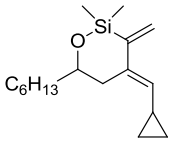
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.15 (dd, 1H, *J* = 20.4, 14.8 Hz), 5.99 (dd, 1H, *J* = 15.2, 4.0 Hz), 5.76 (dd, 1H, *J* = 20.0, 4.0 Hz), 3.72-3.69 (m, 1H), 2.23 (d ABq, 2H, J_{AB} = 16.4 Hz, J_{AX} =

6.0 Hz, J_{BX} = 6.0 Hz), 1.60-1.53 (m, 1H), 1.45-1.15 (m, 10H), 0.88 (t, 3H, J = 6.7 Hz), 0.71-0.65 (m, 1H), 0.64-0.58 (m, 1H), 0.19 (s, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.2, 133.1, 84.9, 73.0, 72.1, 36.9, 32.0, 29.5, 28.1, 25.6, 22.8, 14.3, 8.0, -0.2, -1.2

FT-IR (NaCl, thin film) ν = 2957, 2931, 2858, 1466, 1252, 1097, 1060 cm^{-1}

Anal. calcd for $C_{17}H_{30}OSi$: C 73.31, H 10.86; found: C 73.39, H 10.57.



Diene 241

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (7.2mg, 0.019 mmol, 0.10 equiv) and alkyne **240** (53.7 mg, 0.19 mmol, 1 equiv) in toluene (0.8 mL) were combined and stirred at 70°C for 1 h. The residue was purified via column chromatography (silica gel 1.5 x 6 cm; gradient elution with hexanes-3% ether/hexanes) to give **241** as a clear oil (39.7 mg, 74%).

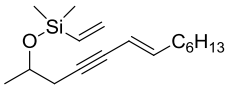
R_f (hexanes) = 0.69

^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.63 (d, 1H, *J* = 3.0 Hz), 5.03 (d, 1H, *J* = 2.7 Hz), 4.92 (d, 1H, *J* = 9.6 Hz), 4.11-4.00 (m, 1H), 2.67 (dd, 1H, *J* = 14.7, 1.8 Hz), 2.24 (ddd, 1H, *J* = 14.7, 9.0, 1.5 Hz), 1.59-1.28 (m, 8H), 0.90-0.86 (m, 6H), 0.79-0.73 (m, 2H), 0.41-0.36 (m, 2H), 0.22 (s, 3H), 0.18 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.4, 138.7, 128.3, 119.4, 73.9, 38.2, 37.4, 32.1, 29.5, 25.9, 22.9, 14.3, 10.5, 7.6, 7.5, 0.1, -0.6

FT-IR (NaCl, thin film) ν = 3002, 2957, 2929, 2857, 1250, 1046 cm^{-1}

Anal. calcd for $C_{17}H_{30}OSi$: C 73.31, H 10.86; found C 73.53, H 10.66.



Silicon-Tethered Alkyne 242

A solution of 4-pentyn-2-ol (0.94 mL, 10 mmol, 1 equiv), (*E*)-1-iodooct-1-ene[214] (2.9 g, 12 mmol, 1.2 equiv), CuI (190 mg, 1.0 mmol, 0.10 equiv), $PdCl_2(PPh_3)_2$ (351 mg, 0.5 mmol, 0.05 equiv), Et_3N (20 mL) and THF (20 mL) was degassed by freeze-pump-thaw (3 times) and refluxed under $Ar_{(g)}$ for 1 h. The reaction mixture was quenched with sat. $NH_4Cl_{(aq)}$ (35 mL) and extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (4.5 x 15 cm; gradient elution with 10%-25% EtOAc/hexanes) to give the alcohol (1.21 g, 62%) as an orange oil. To a 100 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added the alcohol (1.09 g, 5.6 mmol, 1 equiv), DCM (37 mL), imidazole (763 mg, 11.2 mmol, 2 equiv) and DMAP (137 mg, 1.12 mmol, 0.2 equiv). The yellow solution was cooled to 0°C (ice/H_2O bath) then vinyldimethylchlorosilane (0.93 mL, 6.7 mmol, 1.2 equiv) was added via syringe. The resulting yellow suspension stirred at rt overnight. The reaction was quenched with sat. $NH_4Cl_{(aq)}$ (30 mL) then the layers were separated. The aqueous layer was extracted with DCM (3 x 15 mL) then the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give an orange oil. Purification by column chromatography (silica gel 2.5 x 12 cm; eluted with 1% ether/hexanes) gave alkyne **242** as a yellow oil (750 mg, 48%).

R_f (5% ether/hexanes) = 0.52

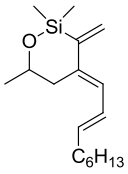
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.16 (dd, 1H, *J* = 20.0, 14.8 Hz), 6.09-5.99 (m, 2H), 5.79 (dd, 1H, *J* = 20.0, 4.0 Hz), 5.44 (doublet of quintets, 1H, *J* = 15.6, 2.0 Hz), 3.97-3.93 (m, 1H), 2.41 (d

ABq, 2H, J_{AB} = 16.8 Hz, J_{AX} = 6.0 Hz, J_{BX} = 6.0 Hz), 2.07 (q, 2H, J = 7.6 Hz), 1.40-1.23 (m, 11H), 0.88 (t, 3H, J = 6.4 Hz), 0.20 (s, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.0, 138.0, 133.3, 109.9, 85.8, 81.0, 68.1, 33.2, 31.9, 30.4, 29.0, 28.97, 23.5, 22.8, 14.3, -1.4

FT-IR (NaCl, thin film) ν = 3019, 2960, 2929, 1457, 1252, 1128, 1097 cm^{-1}

Anal. calcd for $C_{17}H_{30}OSi$: C 73.31, H 10.86; found: C 73.51, H 11.11.



Diene 243

Following the general procedure as described for compound **132**, Cp*Ru(COD)Cl (8.5 mg, 0.023 mmol, 0.15 equiv) and alkyne **242** (41.8 mg, 0.15 mmol, 1 equiv) in toluene (0.6 mL) were combined and stirred at 70°C for 16 h. The residue was purified via column chromatography (silica gel 2.5 x 5.5 cm; gradient elution with 2%-3% ether/hexanes) to give **243** as a yellow oil (25.5 mg, 61%).

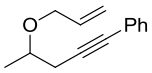
R_f (5% ether/hexanes) = 0.41

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.27-6.12 (m, 2H), 5.81-5.73 (m, 2H), 5.13 (d, 1H, *J* = 2.7 Hz), 4.11-4.03 (m, 1H), 2.68 (dd, 1H, *J* = 14.8, 1.9 Hz), 2.19 (dd, 1H, *J* = 14.6, 9.6 Hz), 2.12 (q, 2H, *J* = 7.2 Hz), 1.43-1.24 (m, 10H), 0.89 (t, 4H, *J* = 6.4 Hz), 0.25 (s, 3H), 0.19 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.2, 139.3, 136.0, 126.2, 123.4, 120.5, 70.0, 39.2, 33.4, 32.0, 29.7, 29.2, 24.5, 22.8, 14.3, 0.1, -0.6

FT-IR (NaCl, thin film) ν = 2928, 976 cm^{-1}

Anal. calcd for $C_{17}H_{30}OSi$: C 73.31, H 10.86; found: C 73.31, H 10.88.



Alkyne 244

To a 100 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added 5-phenylpent-4-yn-2-ol[212] (801 mg, 5 mmol, 1 equiv) and THF (20 mL). The solution was cooled to 0°C (ice/H_2O bath) and sodium hydride (220 mg, 5.5 mmol, 1.1 equiv) was added in one portion. After stirring at 0°C for 15 min, allyl bromide (0.47 mL, 5.5 mmol, 1.1 equiv) was added dropwise. The pale brown suspension stirred at rt for 2 h then was quenched with sat. $NH_4Cl_{(aq)}$ (20 mL). The aqueous layer was extracted with ether (3 x 50 mL) then the combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give an orange oil. Purification via column chromatography (silica 2.5 x 14 cm; gradient elution with 2%-4% ether/hexanes) gave alkyne **244** as a clear oil (300 mg, 30%).

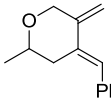
R_f (5% ether/hexanes) = 0.34

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43-7.40 (m, 2H), 7.30-7.27 (m, 3H), 6.00-5.90 (m, 1H), 5.32 (dq, 1H, *J* = 17.6, 1.6 Hz), 5.19 (dq, 1H, *J* = 10.4, 1.2 Hz), 4.08 (dt, 2H, *J* = 5.6, 1.6 Hz), 3.76-3.69 (m, 1H), 2.72 (dd, 1H, *J* = 16.4, 4.8 Hz), 2.52 (dd, 1H, *J* = 16.8, 7.2 Hz), 1.34 (d, 3H, *J* = 6.0 Hz)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 135.3, 131.7, 128.4, 127.9, 124.0, 117.0, 87.1, 82.3, 73.9, 70.0, 27.2, 20.0

FT-IR (NaCl, thin film) ν = 2976, 2930, 1599, 1491, 1128 cm^{-1}

Anal. calcd for $C_{14}H_{16}O$: C 83.96, H 8.05; found: C 83.95, H 7.93.



Diene 245

Following the general procedure as described for compound **132**, Cp*Ru(COD)C; (10.3 mg, 0.027 mmol, 0.10 equiv) and alkyne **244** (53.5 mg, 0.27 mmol, 1 equiv) in toluene (1.1 mL) were combined and stirred at 70°C for 2.5 h. The residue was purified via column chromatography (silica gel 1.5 x 4 cm; 3% ether/hexanes) to give **245** as a clear oil (32.6 mg, 61%).

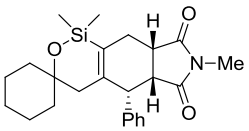
R_f (5% ether/hexanes) = 0.20

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39-7.23 (m, 5H), 6.71 (d, 1H, *J* = 2.6 Hz), 5.22 (d, 1H, *J* = 2.7 Hz), 4.86 (s, 1H), 4.38 (d, 1H, *J* = 12.7 Hz), 4.19 (dt, 1H, *J* = 12.6, 1.7 Hz) 3.59-3.50 (m, 1H), 2.86 (dd, 1H, *J* = 14.5, 2.5 Hz), 2.32-2.22 (m, 1H), 1.24 (d, 3H, *J* = 6.3 Hz)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 145.4, 137.4, 137.2, 129.5, 128.4, 127.0, 124.7, 109.5, 73.2, 72.2, 38.0, 21.9

FT-IR (NaCl, thin film) ν = 2973, 2931, 1271, 1493, 1450, 1386, 1127 cm^{-1}

Anal. calcd for $C_{14}H_{16}O$: C 83.96, H 8.05; found: C 84.15, H 8.48.



Diels-Alder Adduct 256

To a 15 mL glass tube equipped with a magnetic stir bar was added diene **227** (56.4 mg, 0.19 mmol, 1 equiv), N-methylmaleimide (22 mg, 0.20 mmol, 1.05 equiv) and toluene (0.4 mL). The vessel was sealed with a teflon screw cap and the clear solution stirred at rt for 24 h. TLC analysis indicated complete consumption of the starting material. The reaction mixture was placed directly on silica gel for purification (silica gel 2.5 x 12 cm; gradient elution with 25%-60% EtOAc/hexanes) to give **256** as a white solid (73.1 mg, 94%).

R_f (20% EtOAc/hexanes) = 0.08

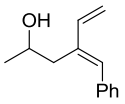
M.P.: 160-161°C

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.23-7.16 (m, 3H), 7.03-7.00 (m, 2H), 3.60 (d, 1H, *J* = 7.2 Hz), 3.28 (dd, 1H, *J* = 9.0, 7.5 Hz), 3.05 (m, 1H), 2.79 (app dd, 1H, *J* = 18.3, 4.2 Hz), 2.63 (dd, 1H, *J* = 18.3, 10.8 Hz), 2.36 (s, 3H), 2.22 (app d, 1H, *J* = 16.8 Hz), 1.98 (dd, 1H, *J* = 16.8, 1.8 Hz), 1.61-1.49 (m, 3H), 1.41-1.26 (m, 4H), 1.13-1.00 (m, 3H), 0.23 (s, 3H), 0.20 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 180.2, 178.3, 145.6, 136.8, 129.3, 128.5, 128.3, 127.7, 73.8, 47.4, 45.0, 39.5, 37.0, 36.7, 26.0, 24.0, 22.3, 22.2, 22.1, 0.2, -0.6

FT-IR (NaCl, thin film) ν = 2934, 1706, 1434, 1382, 1251, 1023 cm^{-1}

Anal. calcd for $C_{24}H_{31}NO_3Si$: C 70.38, H 7.63, N 3.42; found: C 70.23, H 7.29, N 3.81.



Alcohol 257

To a 25 mL RBF equipped with a magnetic stir bar under $Ar_{(g)}$ was added diene **132** (60.8 mg, 0.25 mmol, 1 equiv) and THF (5 mL). To the clear solution was added TBAF·$3H_2O$ (158 mg, 0.50 mmol, 2 equiv) in one portion. The pale yellow solution stirred at rt for 1 h. TLC analysis indicated complete consumption of the starting material. The reaction mixture was concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (silica gel 1.5 x 10 cm; gradient elution with 11%-14% ether/hexanes) gave **257** as a white oil (42.4 mg, 90%).

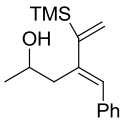
R_f (10% ether/hexanes) = 0.10

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.45-7.23 (m, 5H), 6.70 (s, 1H), 6.50 (dd, 1H, *J* = 17.7, 11.1 Hz), 5.36 (d, 1H, *J* = 17.7 Hz), 5.18 (d, 1H, *J* = 10.8 Hz), 4.15-4.06 (m, 1H), 2.78 (dd, 1H, *J* = 13.5, 8.7 Hz), 2.60 (dd, 1H, *J* = 13.8, 4.8 Hz), 1.73 (br s, 1H), 1.23 (d, 3H, *J* = 6.3 Hz)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 140.8, 137.1, 136.8, 134.3, 129.0, 128.3, 127.1, 113.7, 67.0, 36.1, 23.2

FT-IR (NaCl, thin film) ν = 3356, 2969, 1606, 1492 cm^{-1}

Anal. calcd for $C_{13}H_{16}O$: C 82.94, H 8.57; found: C 82.63, H 8.28.



Hydroxy Silane 258

To a 25 mL Schlenk tube equipped with a magnetic stir bar under $Ar_{(g)}$ was added diene **132** (58.1 mg, 0.24 mmol, 1 equiv) and ether (1 mL). The clear solution was cooled to 0°C (ice/water bath) and MeLi (0.34 mL, 0.58 mmol, 2.2 equiv) was added dropwise via syringe. The pale yellow solution stirred at 0°C for 10 min then at rt for 1 h. TLC analysis indicated complete consumption of the starting material. The reaction mixture was quenched with sat. $NH_4Cl_{(aq)}$ (2 mL). The aqueous later was extracted with ether (2 x 3 mL) and the combined organics were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give **258** as a clear oil (54.3 mg, 87%).

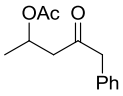
R_f (10% EtOAc/hexanes) = 0.24

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39-7.31 (m, 4H), 7.28-7.21 (m, 1H), 6.50 (s, 1H), 5.84 (d, 1H, *J* = 3.0 Hz), 5.52 (d, 1H, *J* = 2.7 Hz), 4.00-3.89 (m, 1H), 2.72 (dd, 1H, *J* = 13.8, 8.7 Hz), 2.47 (ddd, 1H, *J* = 14.1, 4.8, 0.9 Hz), 1.73 (br s, 1H), 1.18 (d, 3H, *J* = 6.3 Hz), 0.22 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ = 155.5, 143.7, 137.9, 129.2, 128.4, 126.7, 126.2, 66.7, 39.7, 23.0, -0.3

FT-IR (NaCl, thin film) ν = 3368, 2964, 1493, 1249, 1120, 1075 cm^{-1}

Anal. calcd for $C_{16}H_{24}OSi$: C 73.79, H 9.29; found C 73.39, H 9.09.



Keto Ester 262

With Acetic Anhydride: To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar was added a solution of diene **132** (63 mg, 0.26 mmol, 1 equiv) in DMF (13 mL), potassium hydrogen fluoride (61 mg, 0.78 mmol, 3 equiv), acetic anhydride (0.61 mL, 6.5 mmol, 25 equiv) and 30% hydrogen peroxide (0.7 mL, 6.5 mmol, 25 equiv). The clear solution stirred at rt for 5 h. TLC analysis indicated consumption of the starting material. The reaction mixture was poured into H_2O (20 mL) then extracted with ether (3 x 20 mL). The combined organics were washed with H_2O and brine (20 mL each), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give a clear oil. Purification by column chromatography (silica gel 1.5 x 13 cm; 10% EtOAc/hexanes) gave **262** as a clear oil (23.1 mg, 40%).

R_f (20% EtOAc/hexanes) = 0.52

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.36-7.24 (m, 3H), 7.21-7.17 (m, 2H), 5.32-5.22 (m, 1H), 3.69 (s, 2H), 2.80 (dd, 1H, *J* = 16.5, 7.2 Hz), 2.56 (dd, 1H, *J* = 16.5, 5.7 Hz), 1.97 (s, 3H), 1.21 (d, 3H, *J* = 6.3 Hz)

^{13}C NMR (151 MHz, $CDCl_3$) δ = 205.2, 170.4, 133.8, 129.6, 129.0, 127.4, 67.2, 50.7, 47.8, 21.4, 20.1

FT-IR (NaCl, thin film) ν = 3031, 2983, 2935, 1737, 1498, 1374, 1246, 1135, 1043 cm^{-1}

Anal. calcd for $C_{13}H_{16}O_3$: C 70.89, H 7.32; found: C 70.56, H 7.07.

With Propionic Anhydride: To an oven-dried 50 mL RBF equipped with a magnetic stir bar was added diene **132** (62.8 mg, 0.26 mmol, 1 equiv), DMF (10 mL), potassium hydrogen fluoride (61

mg, 0.78 mmol, 3 equiv), propionic anhydride (0.83 mL, 6.5 mmol, 25 equiv) and 30% hydrogen peroxide (0.7 mL, 6.5 mmol, 25 equiv). The clear solution stirred at rt for 3.5 h. TLC analysis indicated consumption of the starting material. The reaction mixture was poured into H_2O (20 mL) then extracted with ether (3 x 20 mL). The combined organics were washed with H_2O and brine (20 mL each), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give a clear oil. Purification by column chromatography (silica gel 1.5 x 13 cm; gradient elution with 10%-20% ether/hexanes) gave **262** as a clear oil (32.2 mg, 56%).

R_f (20% EtOAc/hexanes) = 0.50

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36-7.19 (m, 5H), 5.31-5.23 (m, 1H), 3.70 (s, 2H), 2.80 (dd, 1H, *J* = 16.4, 7.2 Hz), 2.57 (dd, 1H, *J* = 16.8, 6.0 Hz), 1.97 (s, 3H), 1.22 (d, 3H, *J* = 6.4 Hz)

$RuHCl(CO)(PCy_3)_2$

To a flame-dried 3-neck 250 mL RBF equipped with a reflux condenser and magnetic stir bar under $Ar_{(g)}$ was added $RuCl_3 \cdot 3H_2O$ (2.62 g, 10 mmol, 1 equiv) and 2-methoxyethanol (50 mL, degassed for 30 min). After stirring at rt for 10 min, PCy_3 (8.24 g, 29.4 mmol, 2.94 equiv) was quickly added in 2 equal portions. The reaction vessel was subjected to 2 cycles of vacuum/$Ar_{(g)}$ then was placed under $Ar_{(g)}$. The brown reaction mixture was heated to reflux for 20 min then NEt_3 (6 mL, 43 mmol, 4.3 equiv) was added. The dark brown reaction mixture continued to stir at reflux for 6 h. (Note: Over time, the reaction became an orange suspension.) After 6 h the reaction was cooled to rt and needle-filtered. The resulting orange powder was washed with toluene (2 x 15 mL, degassed 30 min) and ether (15 mL, degassed 30 min), needle-filtered after each wash then dried *in vacuo* to give $RuHCl(CO)(PCy_3)_2$ (6.9 g, 95%). Spectroscopic data corresponded to what was reported in the literature.[215]

^{1}H NMR (400 MHz, C_6D_6) δ = -24.2 (t, 1H, $J_{P\text{-}H}$ = 17.7 Hz)

^{31}P NMR (162 MHz, C_6D_6) δ = 46.4

$RuHCl(CO)(PtBu_2Me)_2$

To an oven-dried 3-neck 50 mL RBF equipped with a reflux condenser and magnetic stir bar under $Ar_{(g)}$ was added $RuCl_3 \cdot 3H_2O$ (1 g, 3.8 mmol, 1 equiv). The vessel was subjected to 2 cycles of vacuum/$Ar_{(g)}$, placed under $Ar_{(g)}$, then 2-methoxyethanol (25 mL, degassed 30 min) and $PtBu_2Me$ (3.7 mL, 19.1 mmol, 5 equiv) were added. The resulting dark brown reaction mixture stirred at reflux for 72 h then was cooled to rt. (Note: Upon cooling, orange crystals began to form.) Once cooled to rt, the suspension was further cooled to -10°C (salt/ice/H_2O bath) to further induce precipitation. After 2 h, the suspension was needle-filtered and the resulting orange crystalline powder was washed with ether (5 mL, degassed 30 min), needle-filtered and dried *in vacuo* to give $RuHCl(CO)(PtBu_2Me)_2$ (1.29 g, 70%). Spectroscopic data corresponded to what was reported in the literature.[52]

^{1}H NMR (400 MHz, C_6D_6) δ = -24.9 (t, 1H, $J_{P\text{-}H}$ = 15.7 Hz)

^{31}P NMR (162 MHz, C_6D_6) δ = 49.3

$RuHCl(CO)(PtBu_2Cy)_2$

To an oven-dried 25 mL three-neck round bottom flask equipped with a magnetic stir bar and reflux condenser was added $RuCl_3 \cdot 3H_2O$ (173 mg, 0.66 mmol, 1 equiv). The system was subjected to three cycles of vacuum/$Ar_{(g)}$ then placed under a positive stream of $Ar_{(g)}$. To the ruthenium was added degassed 2-methoxyethanol (10 mL) then P*t*Bu_2Cy (0.85 mL, 3.3 mmol, 5 equiv). The dark brown solution stirred in the dark at 125°C for 72 h. At this time, the orange/brown suspension was cooled to rt then further cooled to -15°C (salt/ice/H_2O bath). After 30 min the suspension was needle-filtered and the resulting crystals were washed with degassed ether (2 x 3 mL) and dried *in vacuo* to give $RuHCl(CO)(PtBu_2Cy)_2$ as orange crystals (280 mg, 68%).

^{1}H NMR (400 MHz, C_6D_6) δ = 2.46 (d, 2H, *J* = 10.4 Hz), 2.29-2.26 (m, 2H), 1.69-1.37 (m, 54H), -24.48 (t, 1H, $J_{P\text{-}H}$ = 17.4 Hz)

^{31}P NMR (162 MHz, C_6D_6) δ = 73.1

FT-IR (KBr pellet) ν = 2915, 2144 (Ru-H), 1897 (CO) cm^{-1}

Anal. calcd for $C_{29}H_{59}ClOP_2Ru$: C 55.98, H 9.56; found C 56.07, H 9.66.

$RuHCl(CO)(PCy_2tBu)_2$

To an oven-dried 25 mL three-neck round bottom flask equipped with a magnetic stir bar and reflux condenser was added $RuCl_3 \cdot 3H_2O$ (200 mg, 0.76 mmol, 1 equiv). The system was subjected to three cycles of vacuum/$Ar_{(g)}$ then placed under a positive stream of $Ar_{(g)}$. To the ruthenium was added degassed 2-methoxyethanol (10 mL) then PCy_2tBu (1.0 mL, 3.8 mmol, 5 equiv). The dark brown solution stirred in the dark at 125°C for 72 h. At this time, the reaction mixture was cooled to rt then further cooled to -15°C (salt/ice/H_2O bath) to induce precipitation. After 1 h, the resulting suspension was needle-filtered and the resulting powder was washed with degassed ether (2 x 3 mL) and dried *in vacuo* to give $RuHCl(CO)(PCy_2tBu)_2$ as a dark orange powder (320 mg, 63%).

^{1}H NMR (400 MHz, C_6D_6) δ = 2.72-2.58 (m, 4H), 2.24-2.06 (m, 8H), 1.84-1.14 (m, 50H), -22.0 (t, 1H, $J_{P\text{-}H}$ = 17.6 Hz)

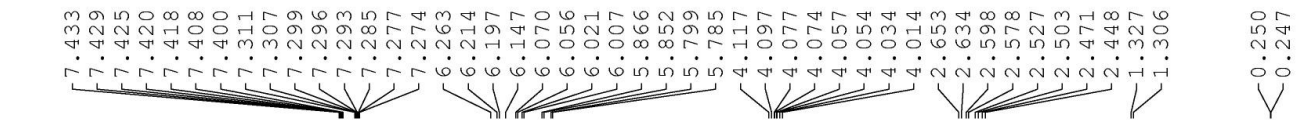
^{31}P NMR (162 MHz, C_6D_6) δ = 58.9

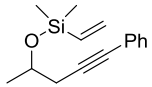
FT-IR (KBr pellet) ν = 2849, 2083 (Ru-H), 1900 (CO) cm^{-1}

Anal. calcd for $C_{33}H_{63}ClOP_2Ru$: C 58.78, H 9.42; found: C 58.95, H 9.31.

7.0 SPECTRA

LAK-3-224-1

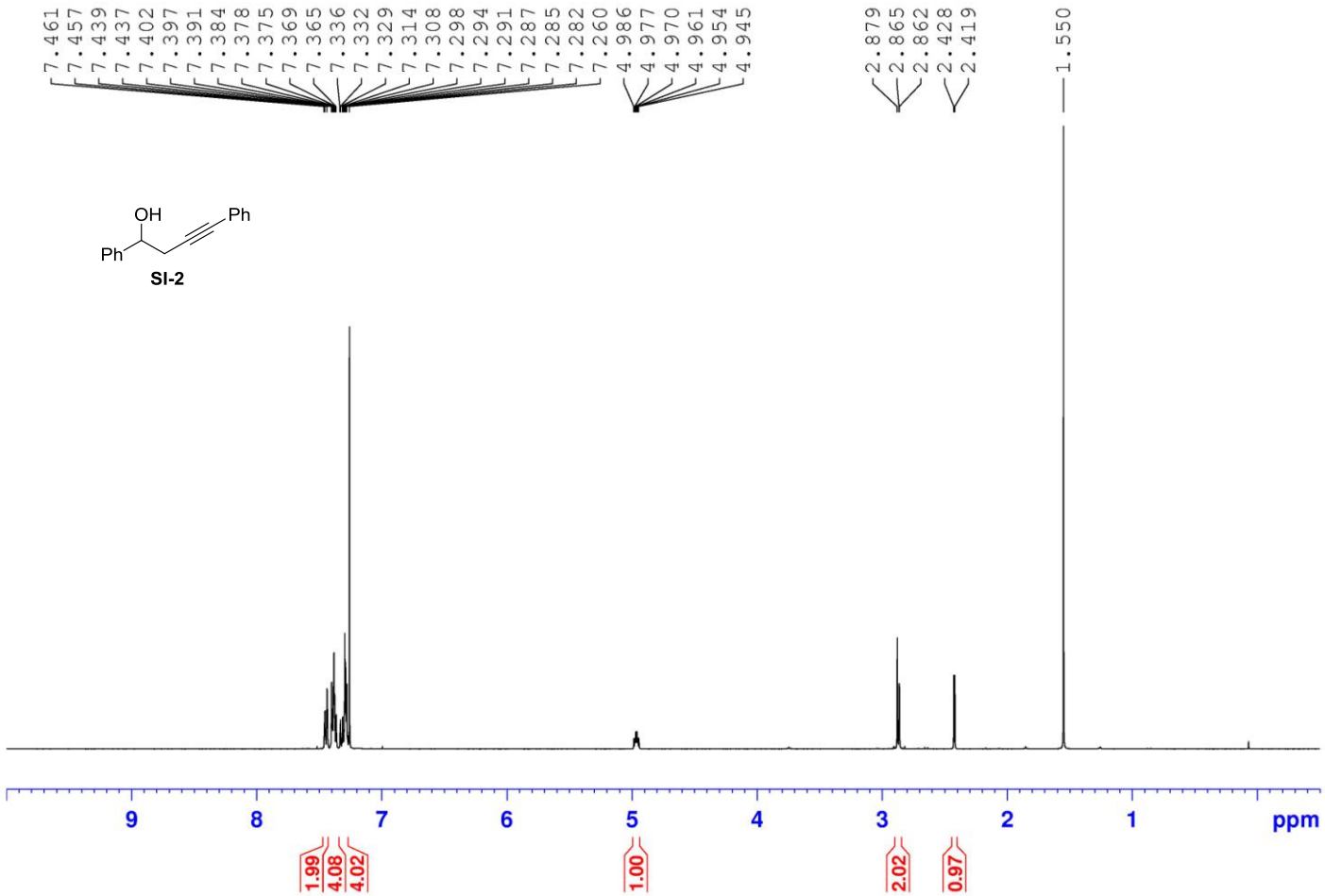

7.433
7.429
7.425
7.420
7.418
7.408
7.400
7.311
7.307
7.299
7.296
7.293
7.285
7.277
7.274
6.263
6.214
6.197
6.147
6.070
6.056
6.021
6.007
5.866
5.852
5.799
5.785
4.117
4.097
4.077
4.074
4.057
4.054
4.034
4.014
2.653
2.634
2.598
2.578
2.527
2.503
2.471
2.448
1.327
1.306
0.250
0.247


Si
O
Ph

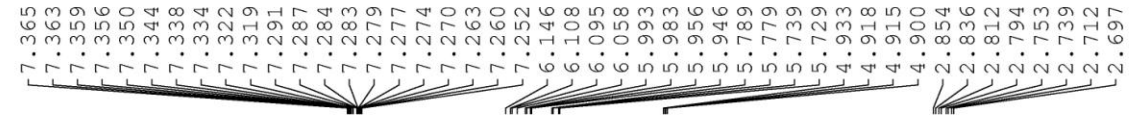
41

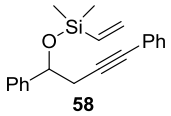
9
8
7
6
5
4
3
2
1
ppm
1.81
2.80
0.73
0.85
0.83
0.89
2.00
3.23
5.80

LAK-5-156
crop B

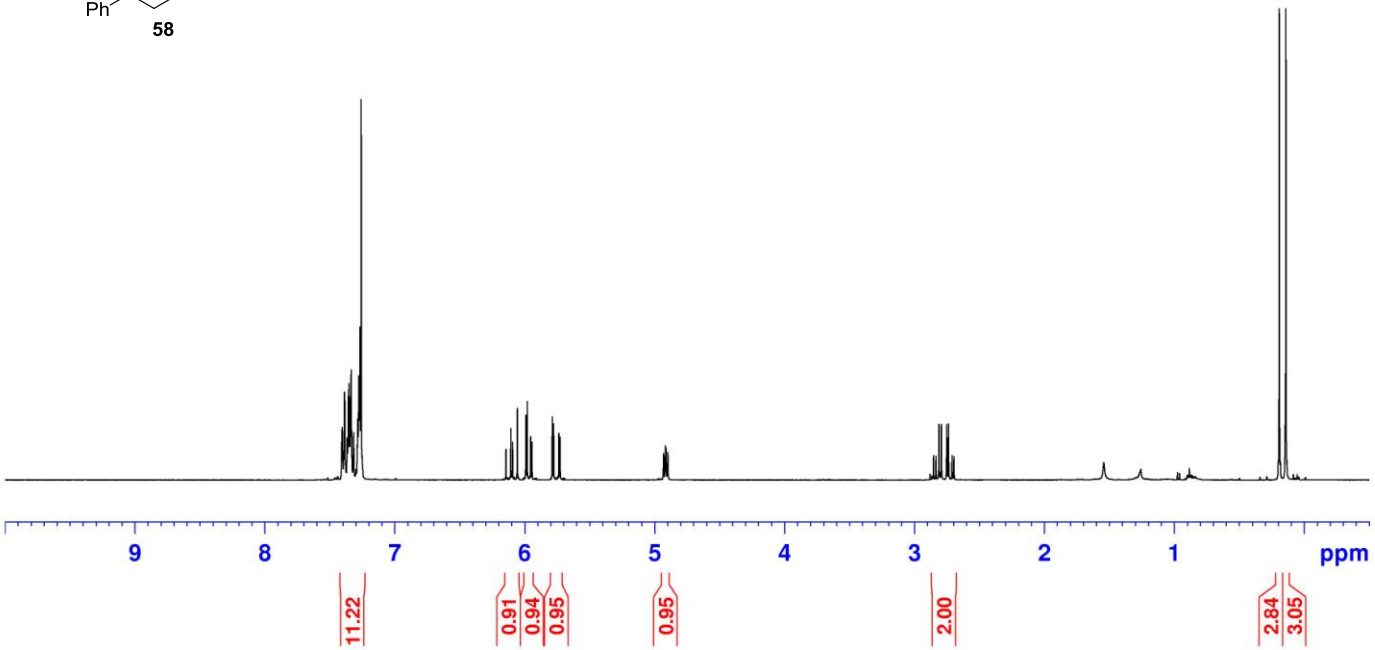


LAK-5-225
yellow oil





58

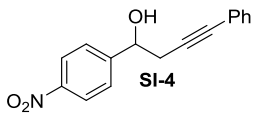


LAK-3-297

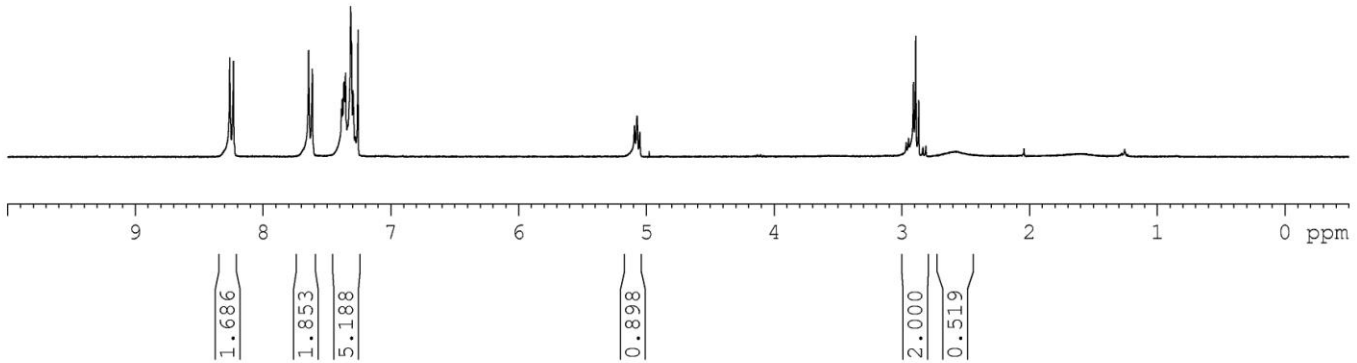
8.259
8.230
7.645
7.616
7.388
7.381
7.369
7.356
7.316
7.309
7.298
7.292
7.258

5.094
5.075
5.053

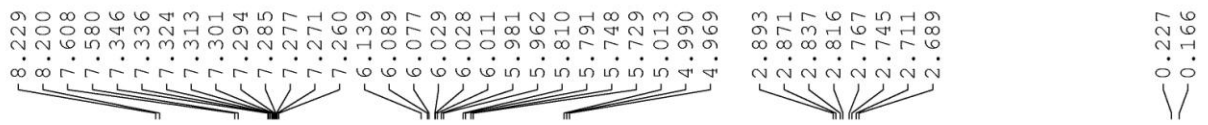
2.966
2.948
2.910
2.892
2.869
2.836
2.813
2.626
2.585
2.576
2.568
2.558

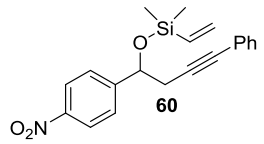


SI-4

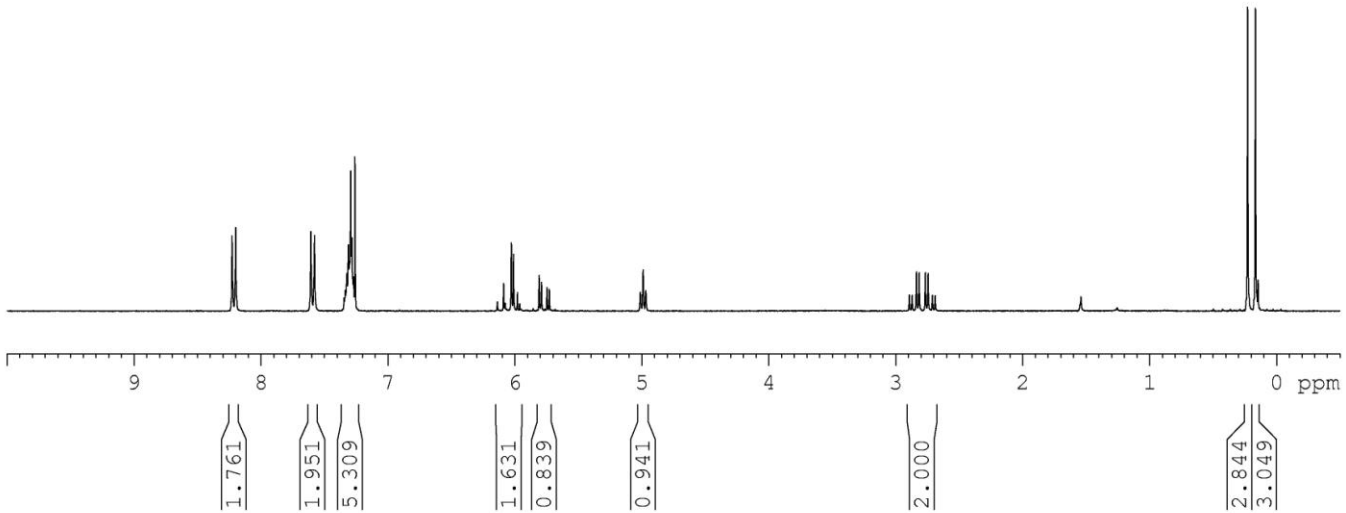


LAK-3-303

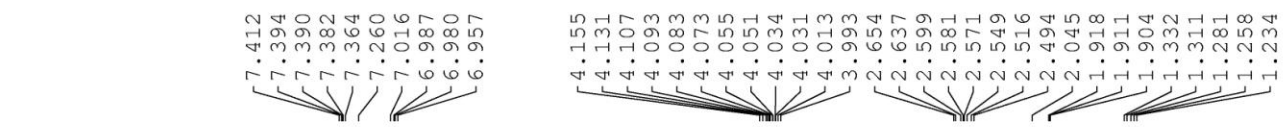

8.229
8.200
7.608
7.580
7.346
7.336
7.324
7.313
7.301
7.294
7.285
7.277
7.271
7.260
6.139
6.089
6.077
6.029
6.028
6.011
5.981
5.962
5.810
5.791
5.748
5.729
5.013
4.990
4.969
2.893
2.871
2.837
2.816
2.767
2.745
2.711
2.689
0.227
0.166

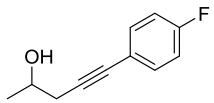

Si
O
Ph
O2N

60

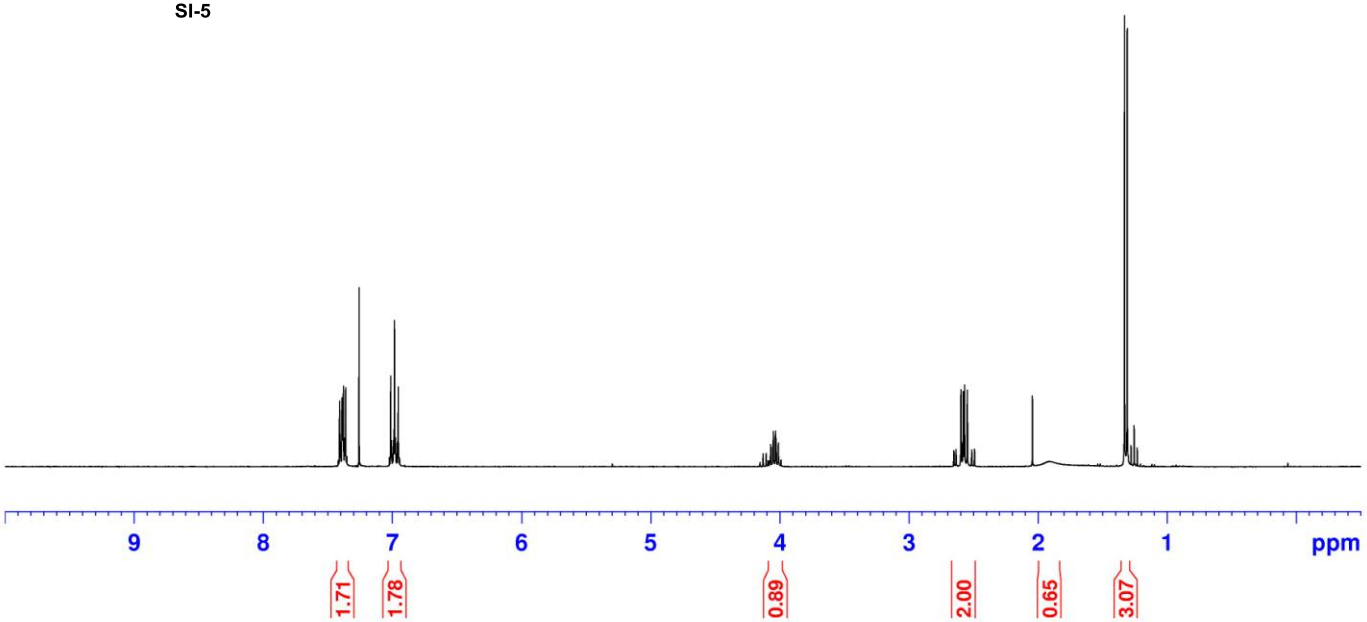

9
8
7
6
5
4
3
2
1
0 ppm
1.761
1.951
5.309
1.631
0.839
0.941
2.000
2.844
3.049

LAK-2-233 (1)

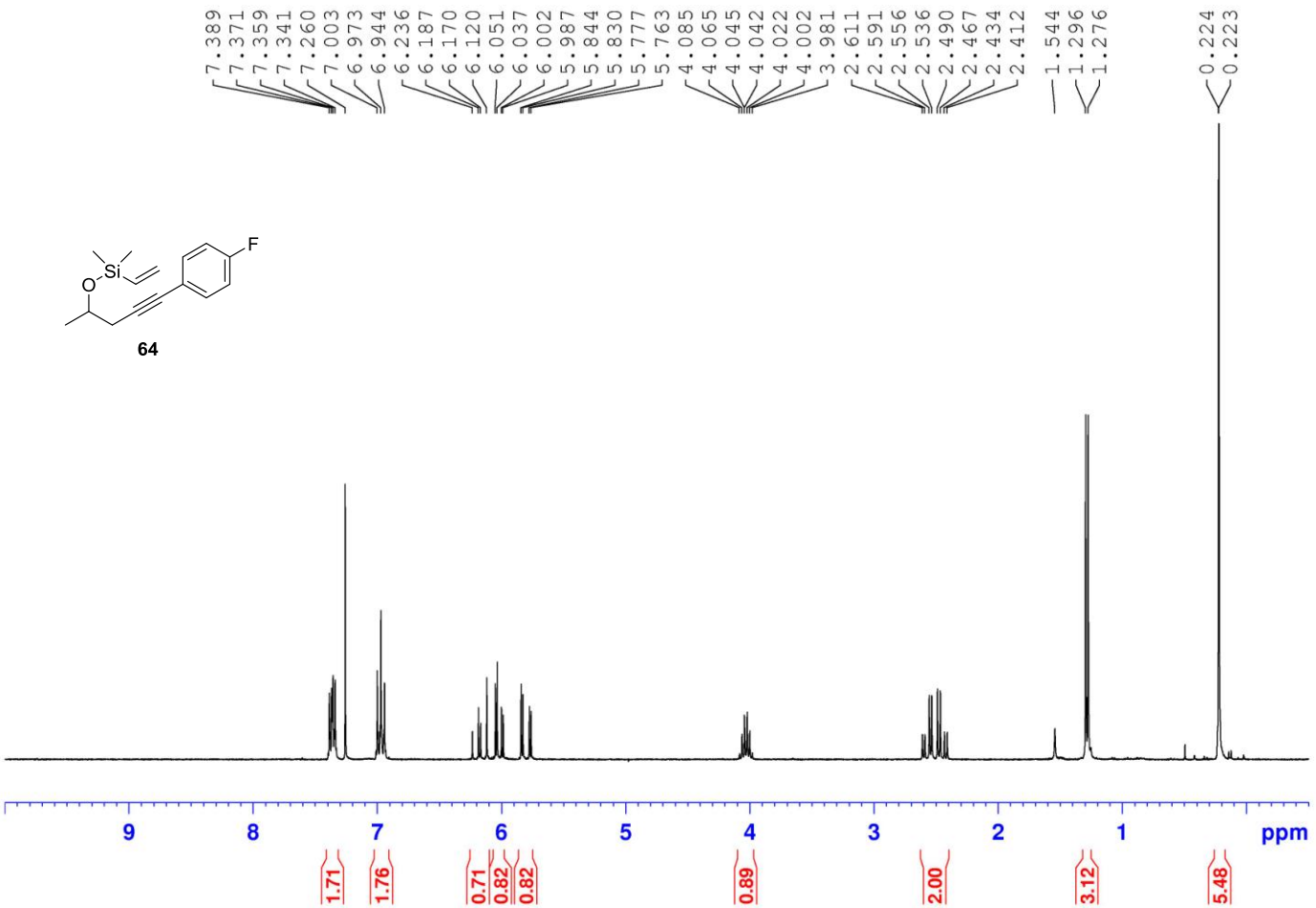




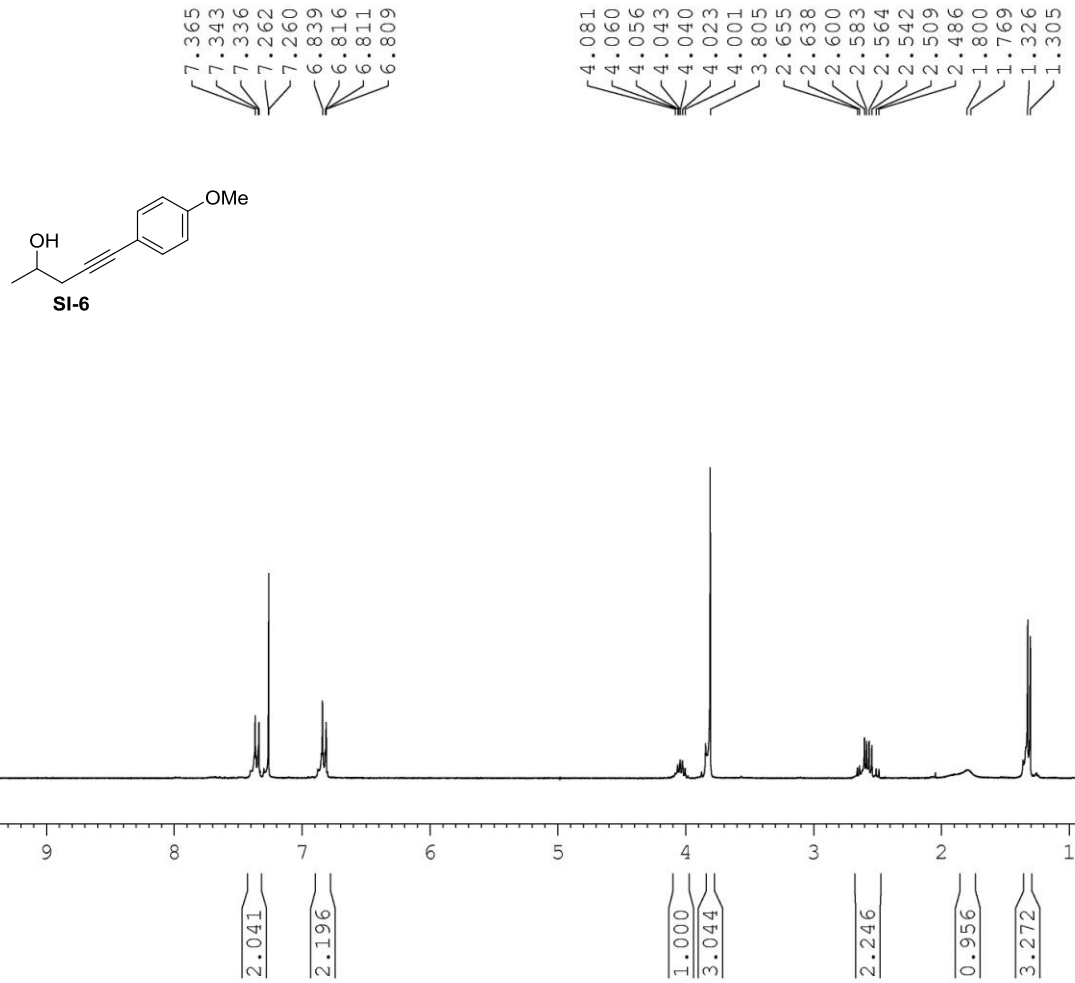
SI-5



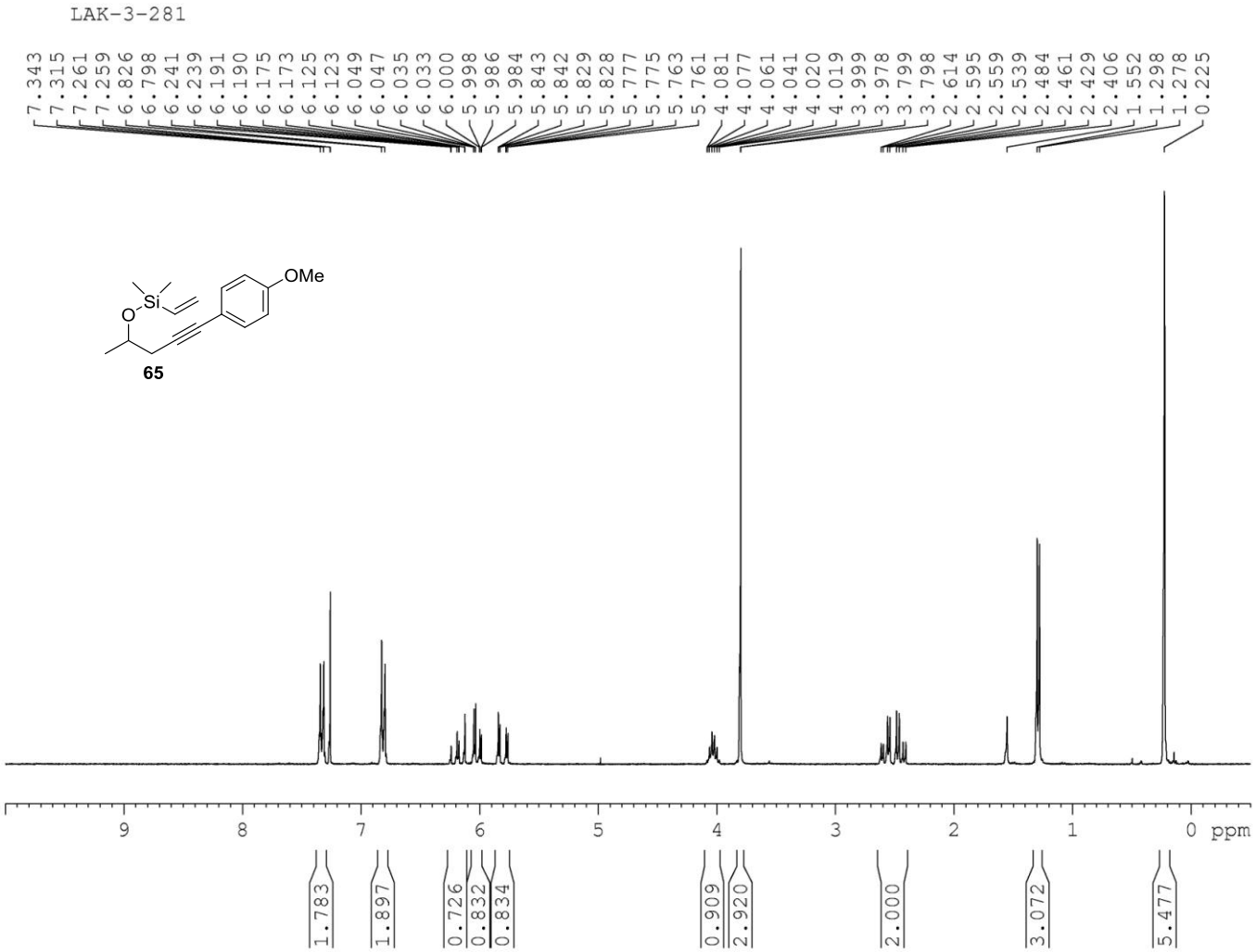
LAK-2-237


7.389
7.371
7.359
7.341
7.260
7.003
6.973
6.944
6.236
6.187
6.170
6.120
6.051
6.037
6.002
5.987
5.844
5.830
5.777
5.763
4.085
4.065
4.045
4.042
4.022
4.002
3.981
2.611
2.591
2.556
2.536
2.490
2.467
2.434
2.412
1.544
1.296
1.276
0.224
0.223
F
O
Si
64
9
8
7
6
5
4
3
2
1
ppm
1.71
1.76
0.71
0.82
0.82
0.89
2.00
3.12
5.48

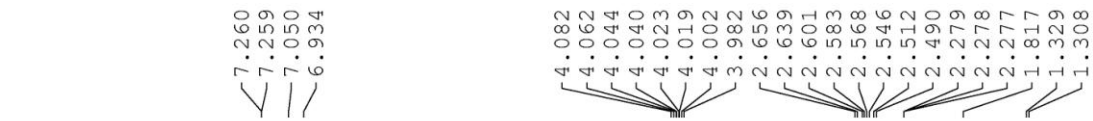
LAK-3-280

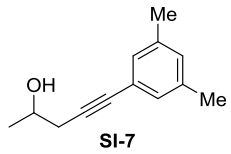

7.365
7.343
7.336
7.262
7.260
6.839
6.816
6.811
6.809
4.081
4.060
4.056
4.043
4.040
4.023
4.001
3.805
2.655
2.638
2.600
2.583
2.564
2.542
2.509
2.486
1.800
1.769
1.326
1.305
OMe
OH
9
8
7
6
5
4
3
2
1
0 ppm
2.041
2.196
1.000
3.044
2.246
0.956
3.272

SI-6

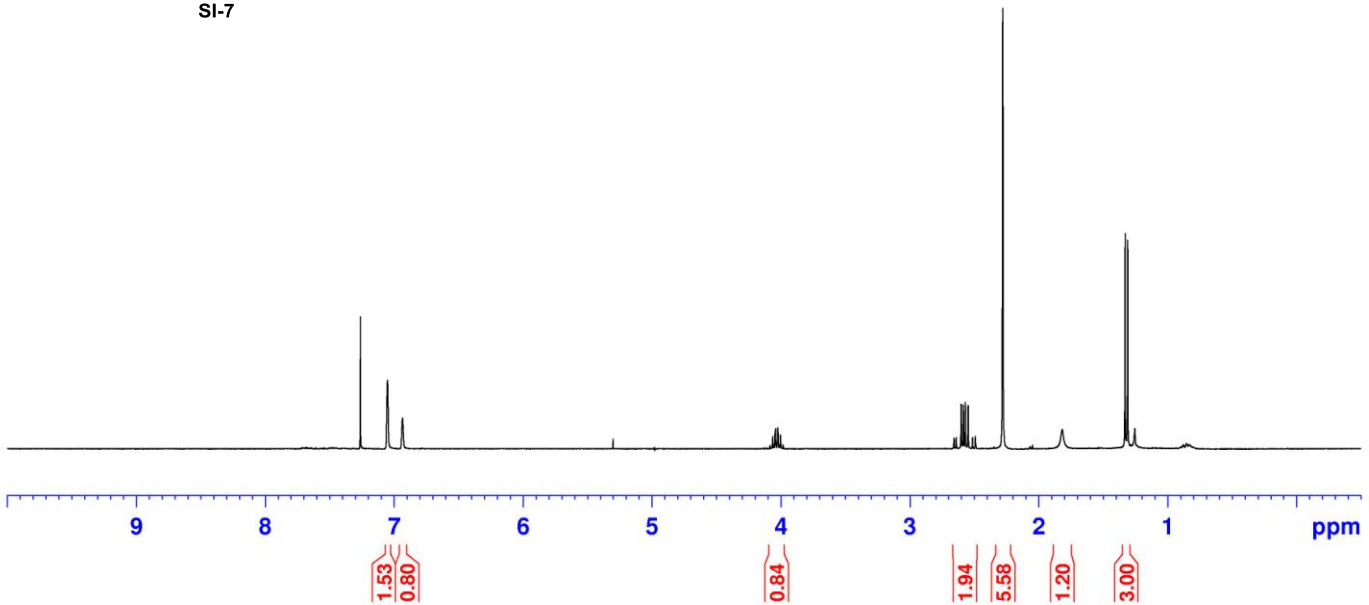

LAK-3-281
7.343
7.315
7.261
7.259
6.826
6.798
6.241
6.239
6.191
6.190
6.175
6.173
6.125
6.123
6.049
6.047
6.035
6.033
6.000
5.998
5.986
5.984
5.843
5.842
5.829
5.828
5.777
5.775
5.763
5.761
4.081
4.077
4.061
4.041
4.020
4.019
3.999
3.978
3.799
3.798
2.614
2.595
2.559
2.539
2.484
2.461
2.429
2.406
1.552
1.298
1.278
0.225
OMe
Si
O
65
9
8
7
6
5
4
3
2
1
0 ppm
1.783
1.897
0.726
0.832
0.834
0.909
2.920
2.000
3.072
5.477

LAK-3-156-1

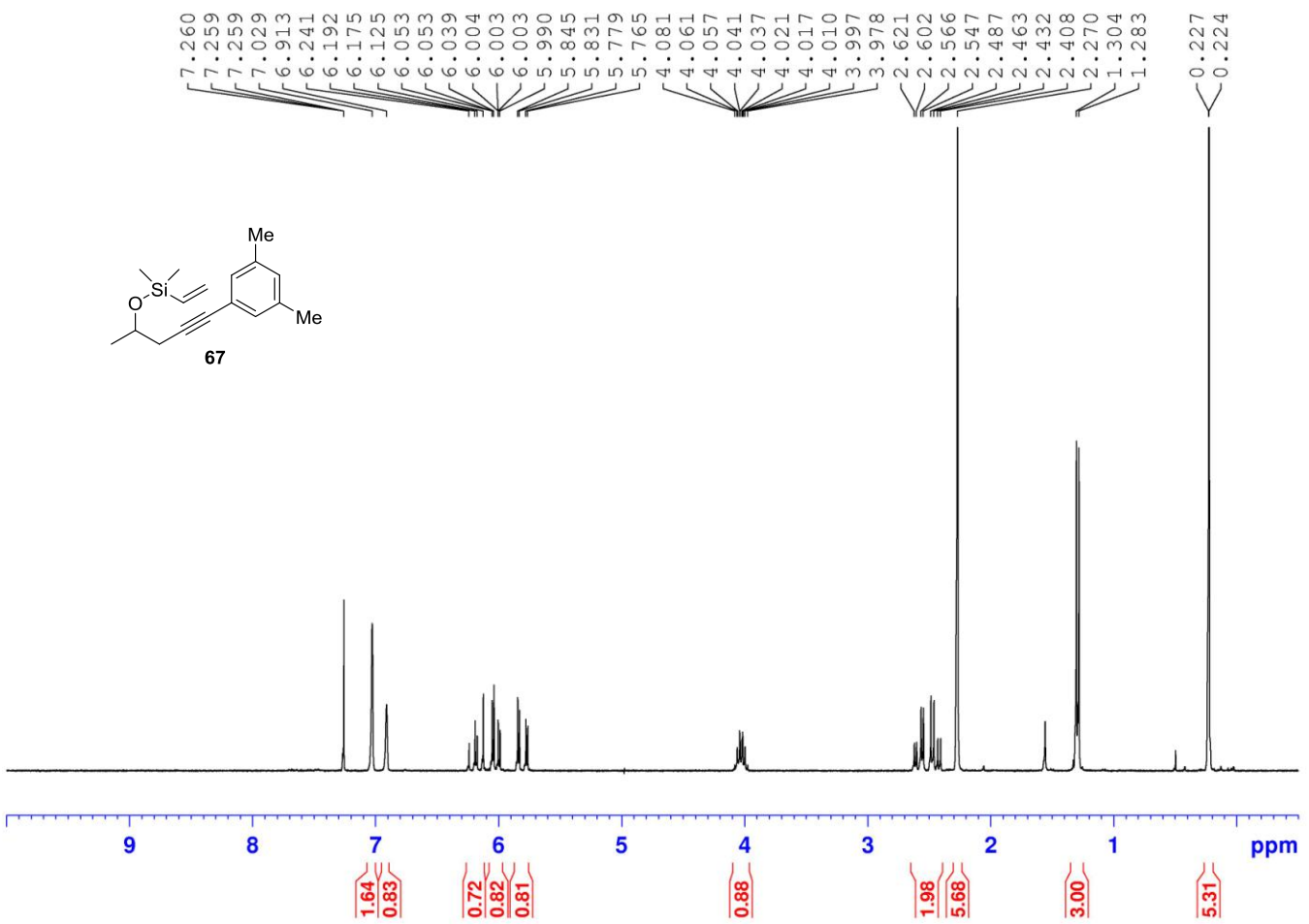




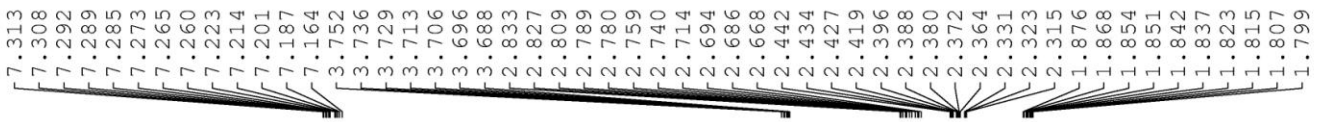
SI-7

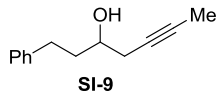


LAK-3-160

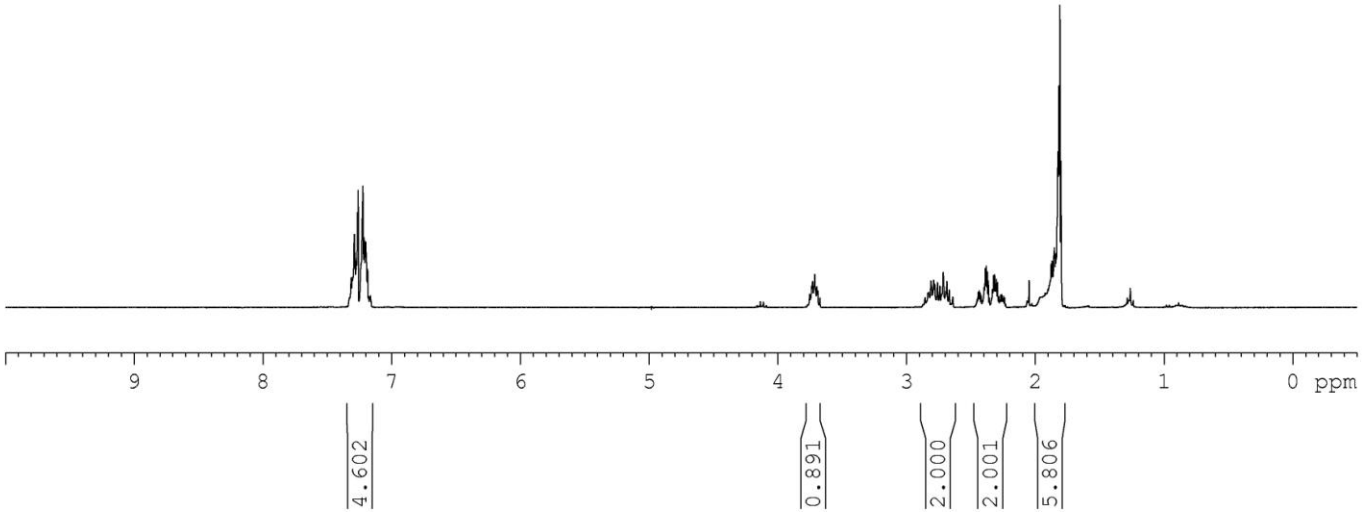

7.260
7.259
7.259
7.029
6.913
6.241
6.192
6.175
6.125
6.053
6.053
6.039
6.004
6.003
6.003
5.990
5.845
5.831
5.779
5.765
4.081
4.061
4.057
4.041
4.037
4.021
4.017
4.010
3.997
3.978
2.621
2.602
2.566
2.547
2.487
2.463
2.432
2.408
2.270
1.304
1.283
0.227
0.224
Me
Si
O
Me
67
9
8
7
6
5
4
3
2
1
ppm
1.64
0.83
0.72
0.82
0.81
0.88
1.98
5.68
3.00
5.31

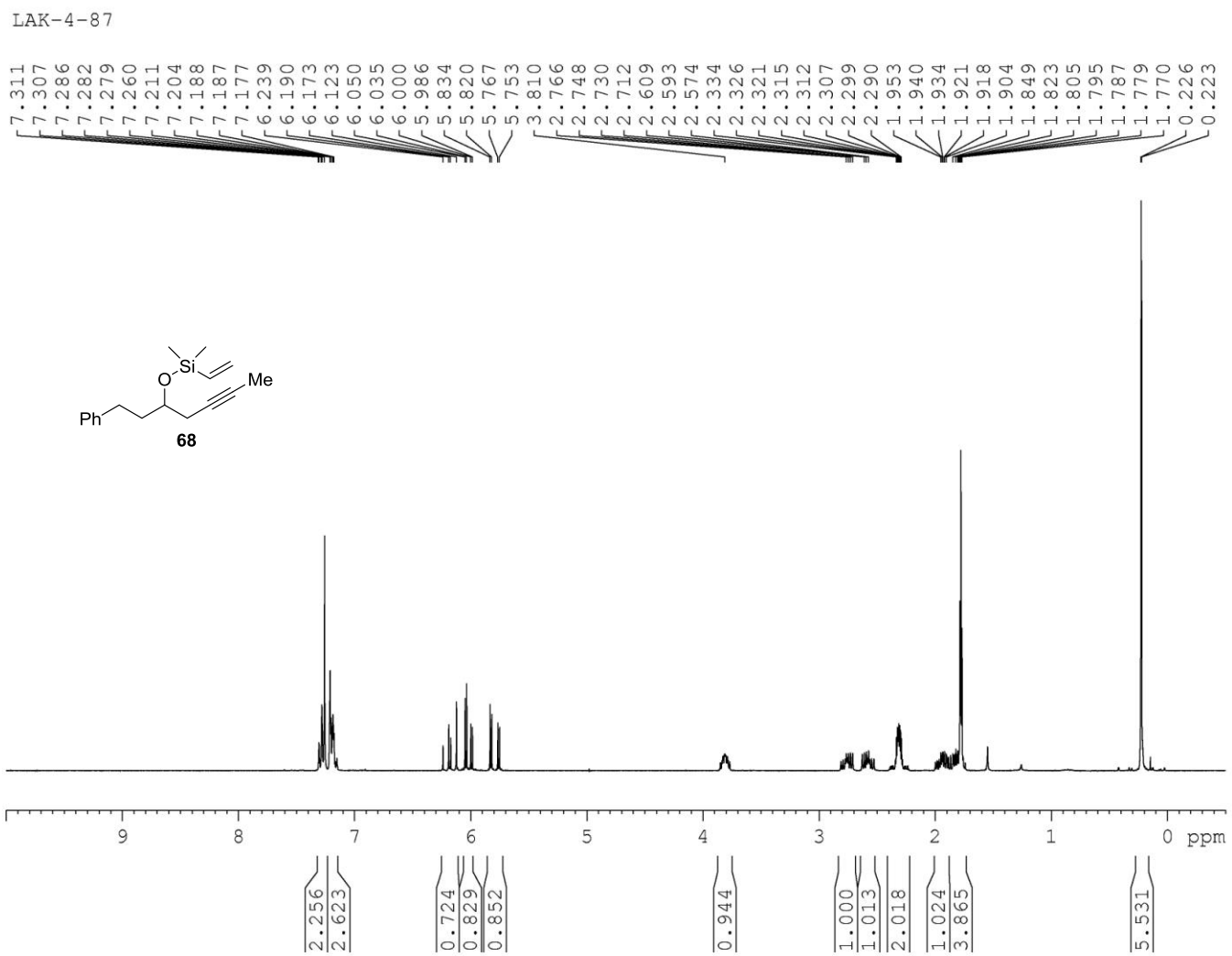
LAK-4-84


7.313
7.308
7.292
7.289
7.285
7.273
7.265
7.260
7.223
7.214
7.201
7.187
7.164
7.752
3.736
3.729
3.713
3.706
3.696
3.688
2.833
2.827
2.809
2.789
2.780
2.759
2.740
2.714
2.694
2.686
2.668
2.442
2.434
2.427
2.419
2.396
2.388
2.380
2.372
2.364
2.331
2.323
2.315
1.876
1.868
1.854
1.851
1.842
1.837
1.823
1.815
1.807
1.799


OH
Me
Ph

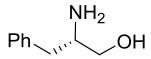
SI-9


9
8
7
6
5
4
3
2
1
0 ppm
4.602
0.891
2.000
2.001
5.806

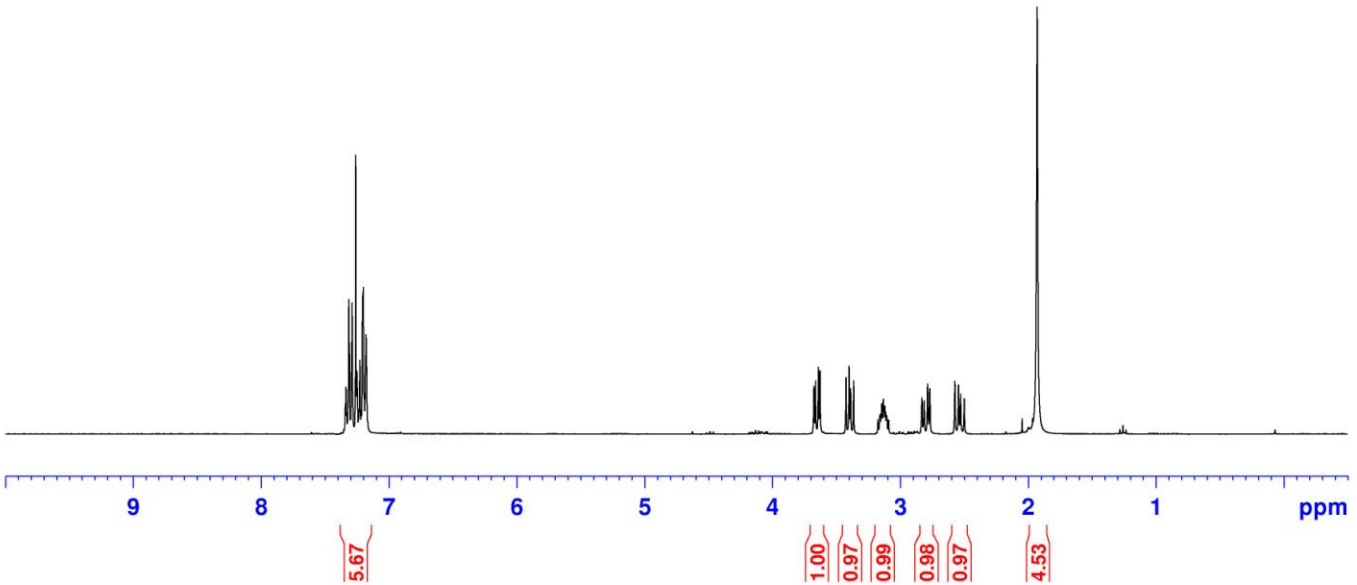

LAK-4-87
7.311
7.307
7.286
7.282
7.279
7.260
7.211
7.204
7.188
7.187
7.177
6.239
6.190
6.173
6.123
6.050
6.035
6.000
5.986
5.834
5.820
5.767
5.753
3.810
2.766
2.748
2.730
2.712
2.609
2.593
2.574
2.334
2.326
2.321
2.315
2.312
2.307
2.299
2.290
1.953
1.940
1.934
1.921
1.918
1.904
1.849
1.823
1.805
1.795
1.787
1.779
1.770
0.226
0.223
Si
O
Me
Ph
68
9
8
7
6
5
4
3
2
1
0 ppm
2.256
2.623
0.724
0.829
0.852
0.944
1.000
1.013
2.018
1.024
3.865
5.531

LAK-1-218
Crop A

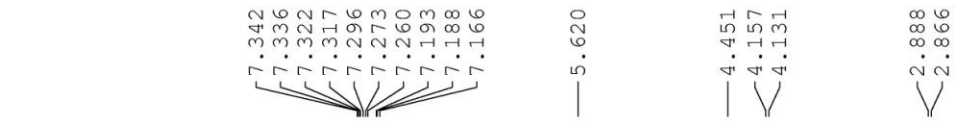
7.341
7.336
7.331
7.314
7.309
7.293
7.289
7.260
7.252
7.247
7.235
7.228
7.218
7.207
7.201
7.179
3.675
3.663
3.640
3.627
3.424
3.400
3.388
3.364
3.174
3.160
3.156
3.149
3.144
3.132
3.128
3.120
3.115
3.108
3.104
3.091
2.830
2.813
2.785
2.768
2.572
2.543
2.527
2.499
1.929

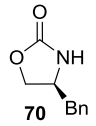


69

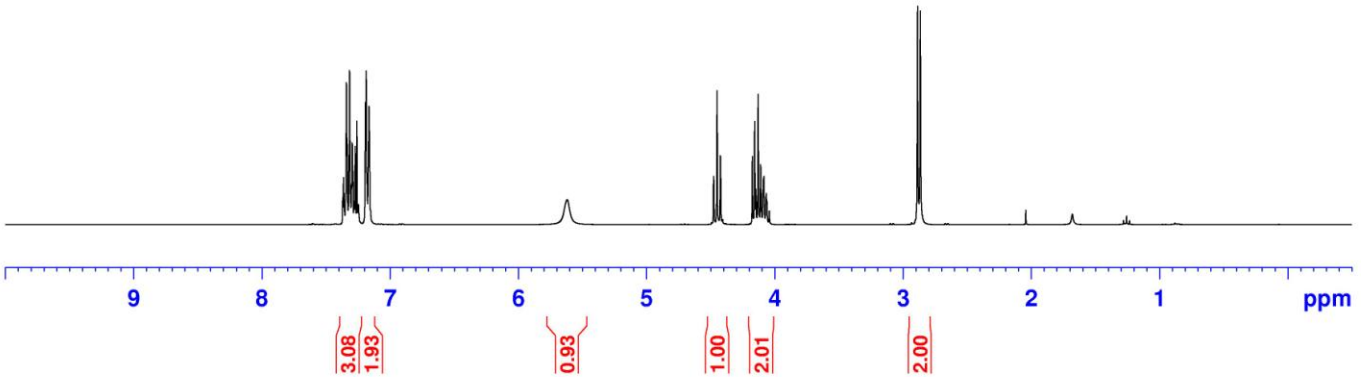


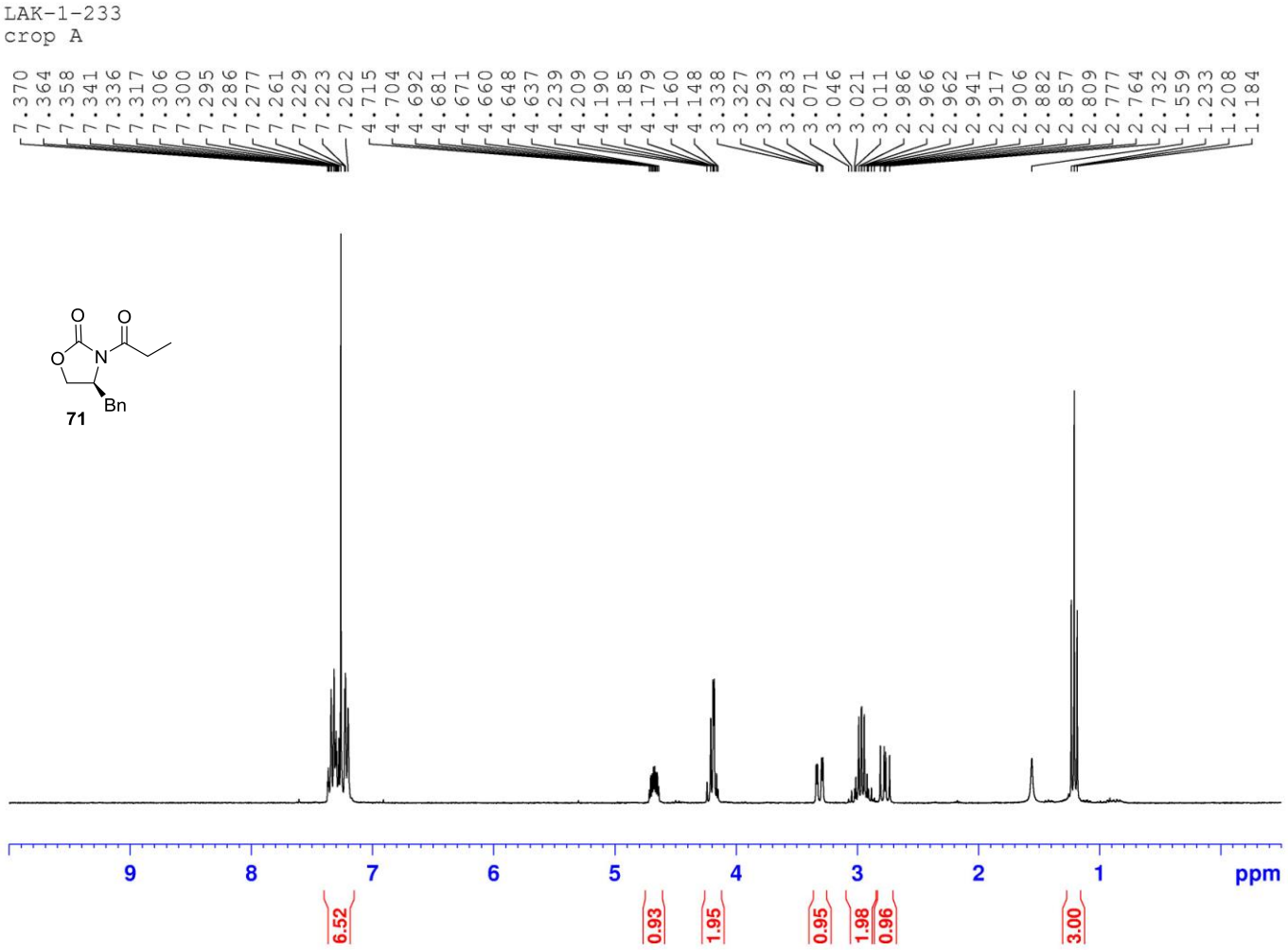
LAK-1-132
Crop A



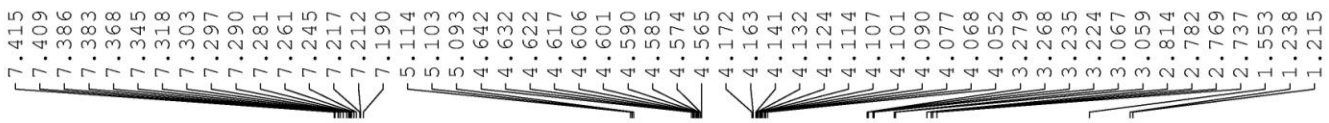


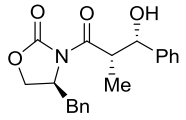
70



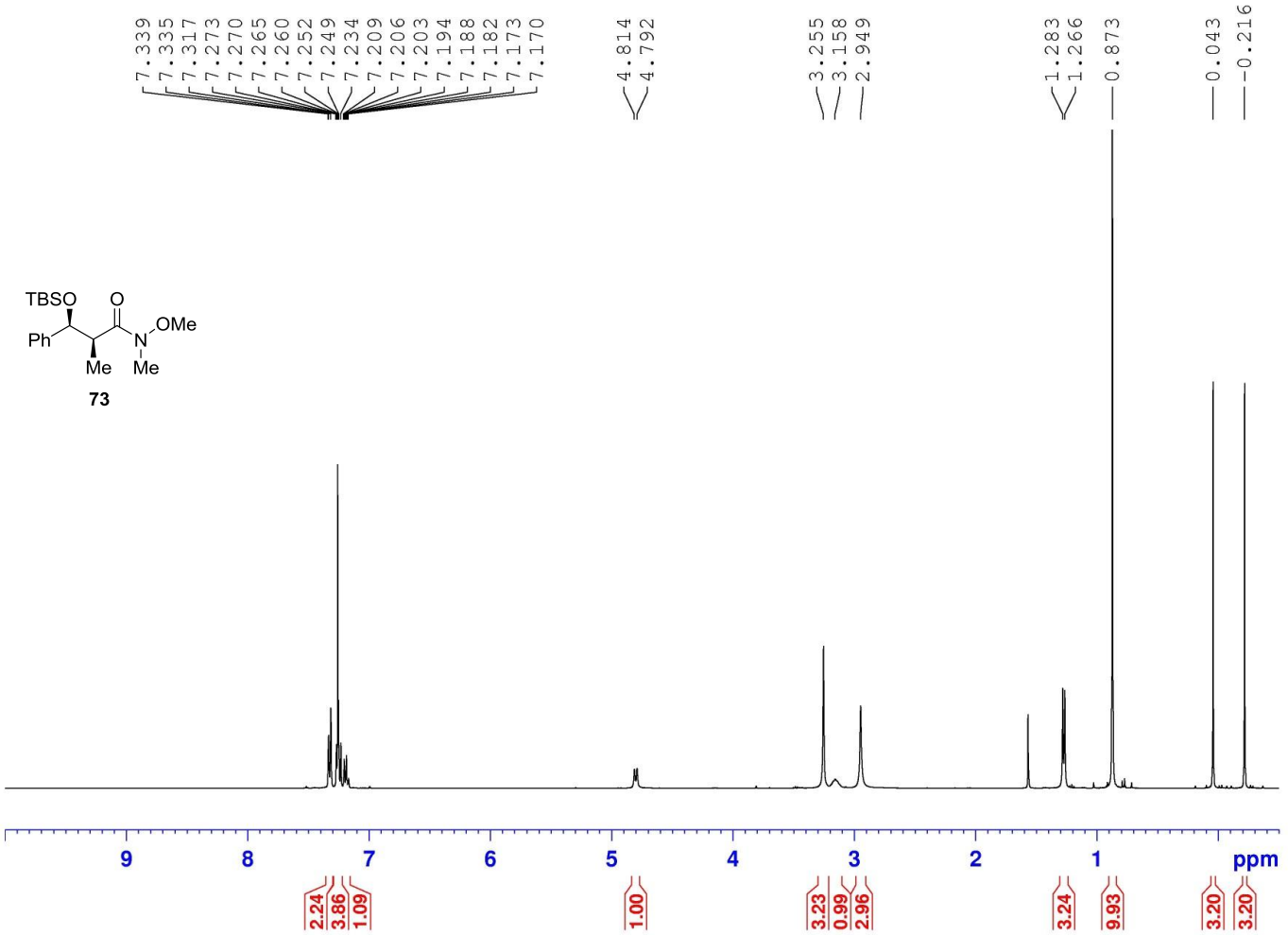

LAK-1-233
crop A
7.370
7.364
7.358
7.341
7.336
7.317
7.306
7.300
7.295
7.286
7.277
7.261
7.229
7.223
7.202
4.715
4.704
4.692
4.681
4.671
4.660
4.648
4.637
4.239
4.209
4.190
4.185
4.179
4.160
4.148
3.338
3.327
3.293
3.283
3.071
3.046
3.021
3.011
2.986
2.966
2.962
2.941
2.917
2.906
2.882
2.857
2.809
2.777
2.764
2.732
1.559
1.233
1.208
1.184
O
O
O
N
Bn
71
9
8
7
6
5
4
3
2
1
ppm
6.52
0.93
1.95
0.95
1.98
0.96
3.00

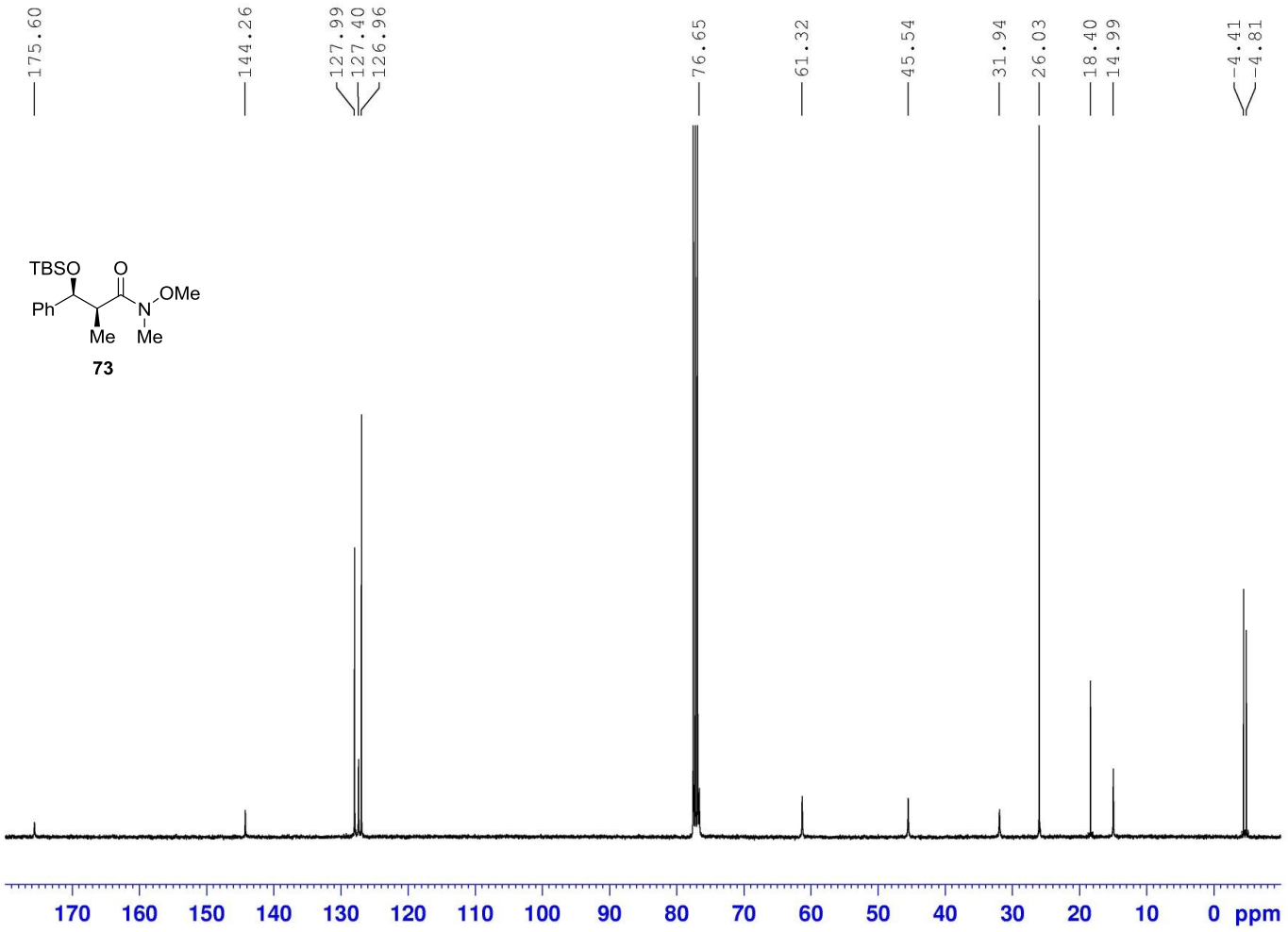
LAK-1-152 crop A

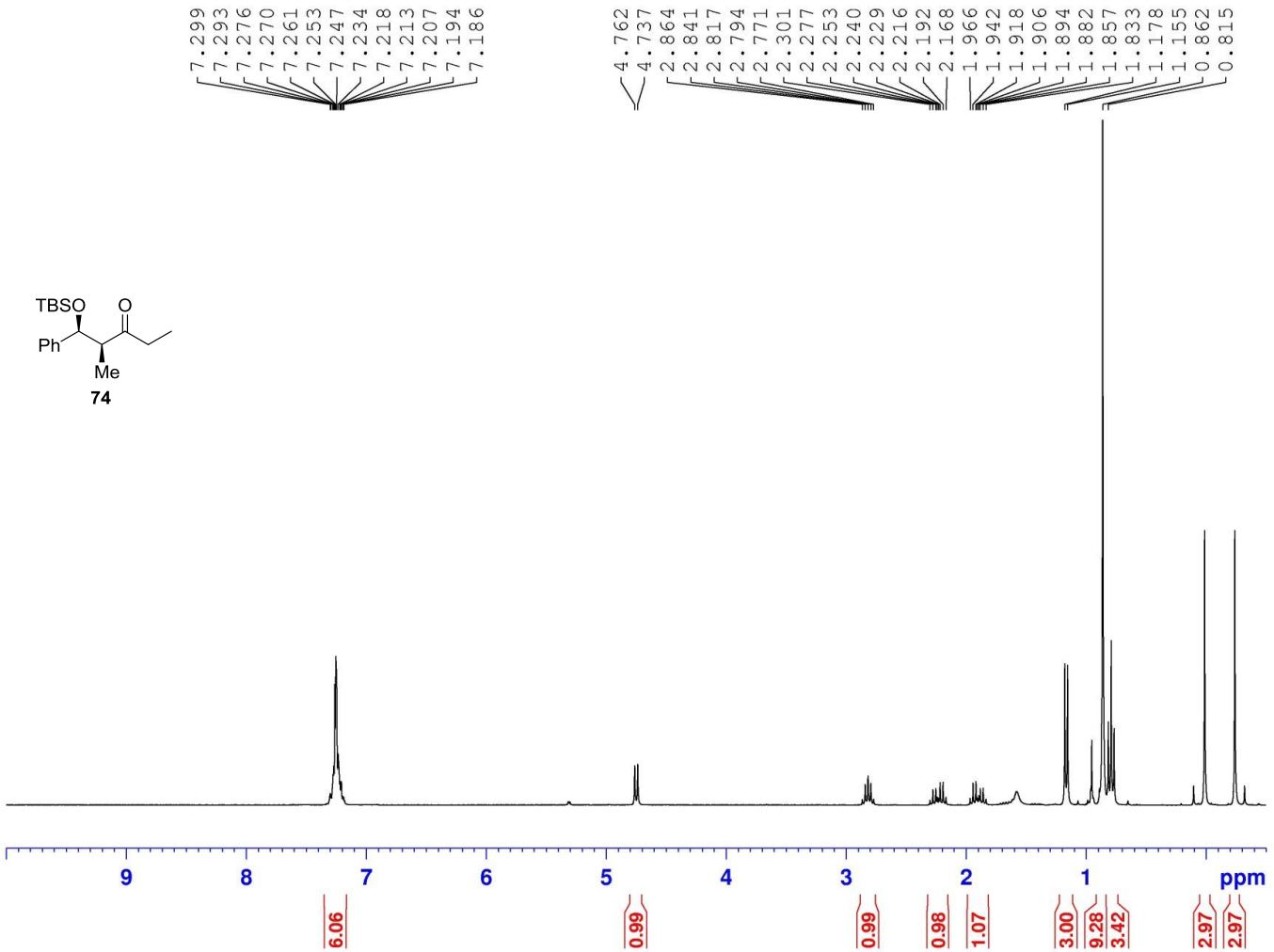


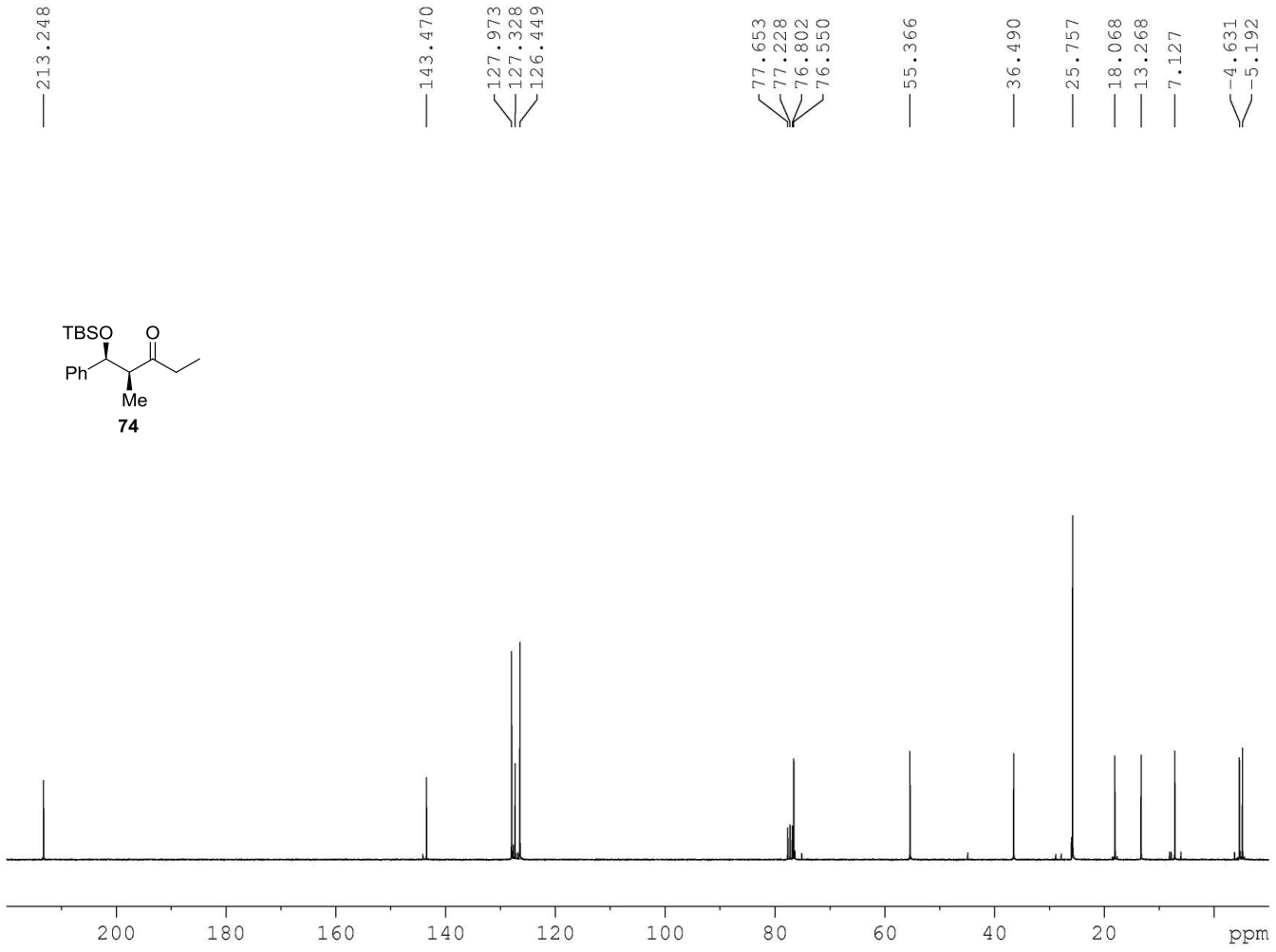


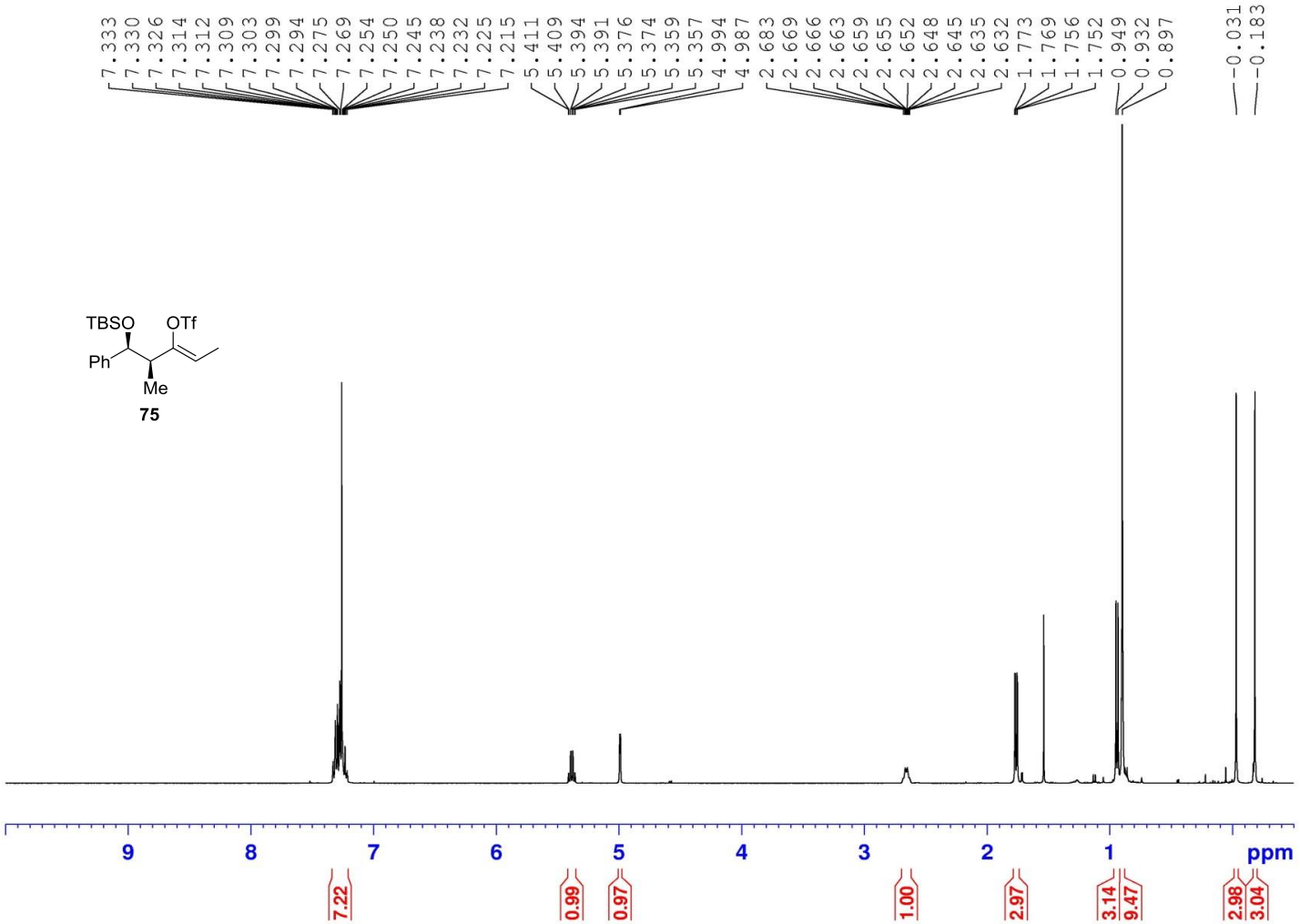
72

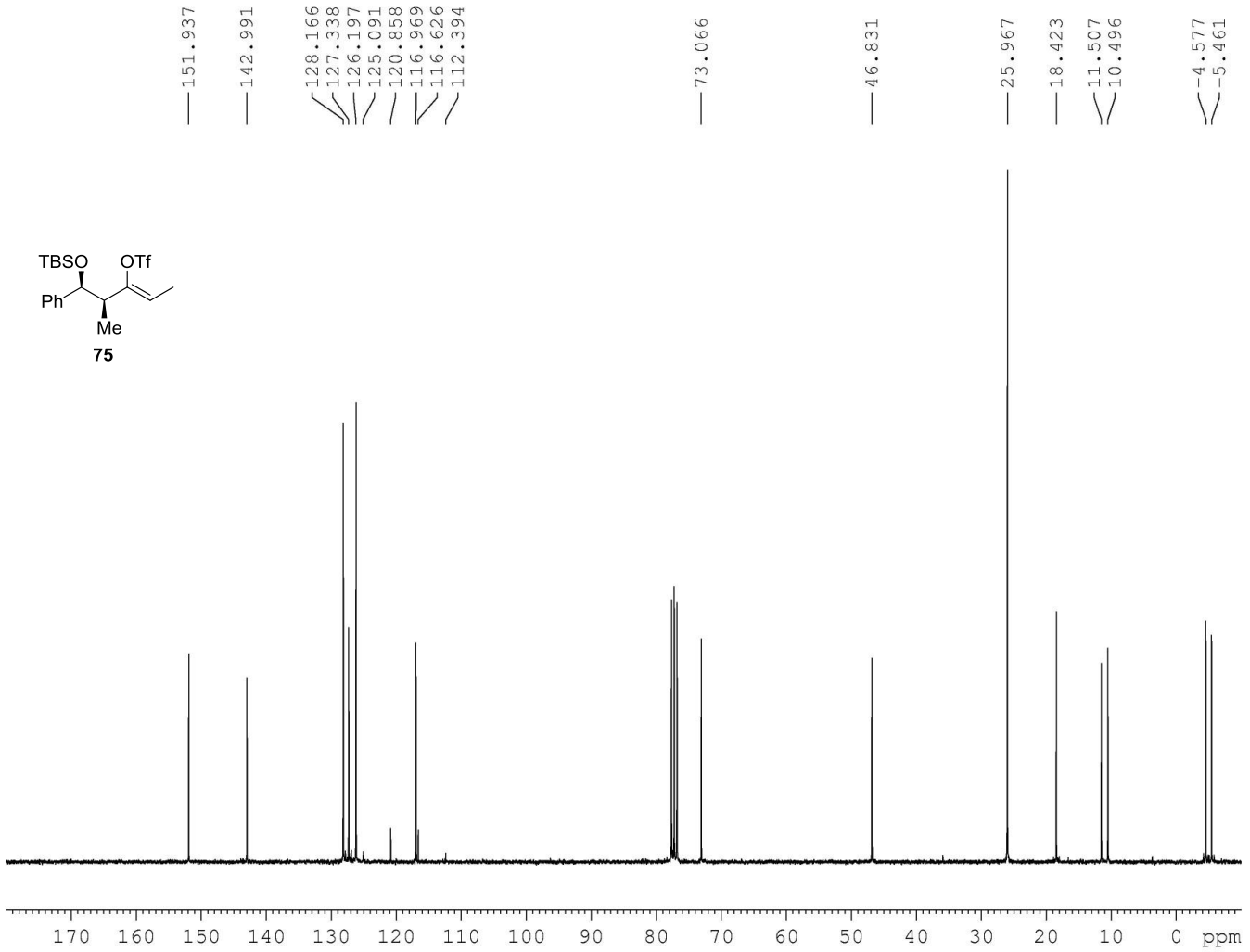

7.339
7.335
7.317
7.273
7.270
7.265
7.260
7.252
7.249
7.234
7.209
7.206
7.203
7.194
7.188
7.182
7.173
7.170
4.814
4.792
3.255
3.158
2.949
1.283
1.266
0.873
0.043
-0.216
TBSO
O
OMe
Ph
N
Me
Me
73
9
8
7
6
5
4
3
2
1
ppm
2.24
3.86
1.09
1.00
3.23
0.99
2.96
3.24
9.93
3.20
3.20

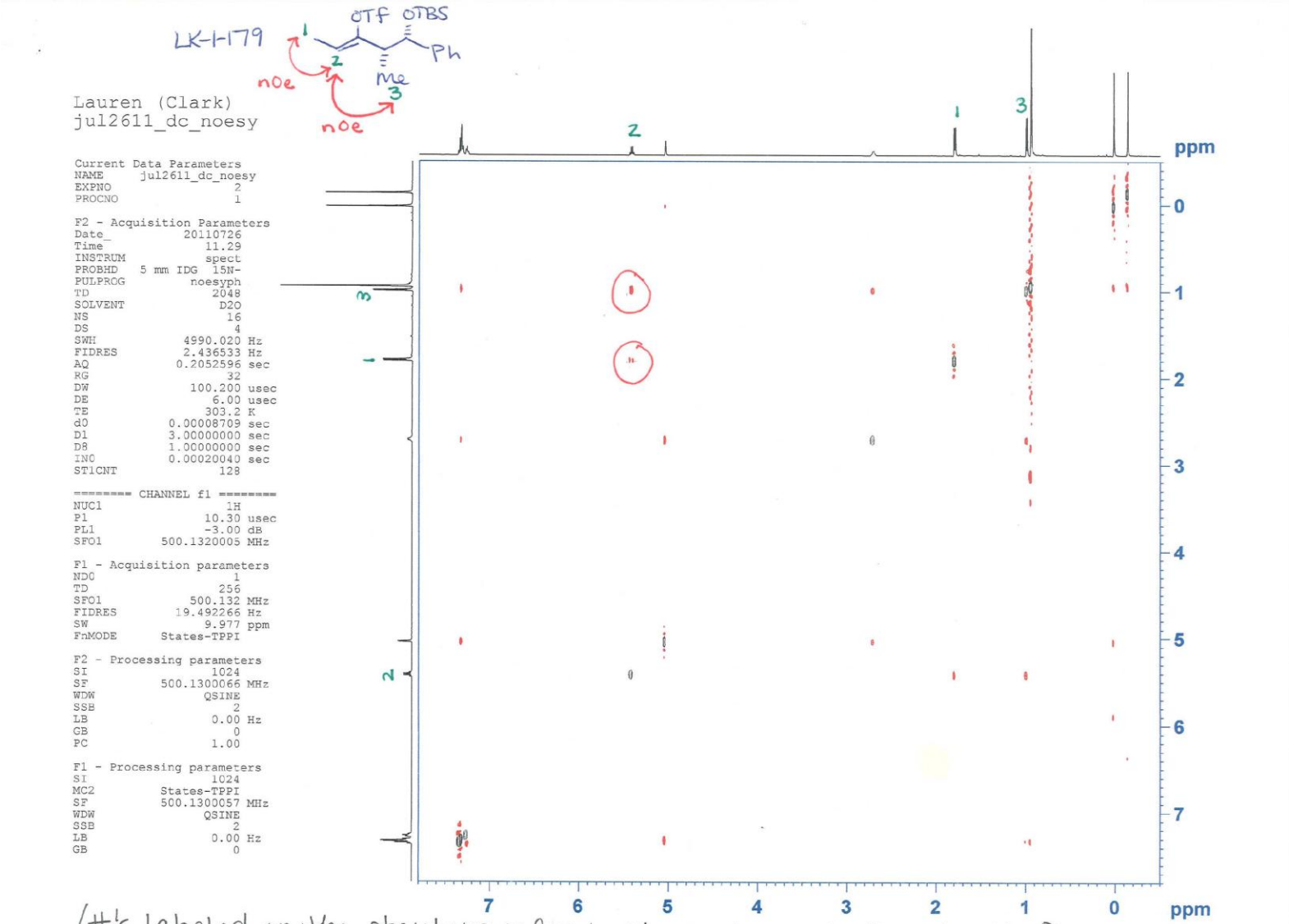

175.60
144.26
127.99
127.40
126.96
76.65
61.32
45.54
31.94
26.03
18.40
14.99
-4.41
-4.81
TBSO
O
OMe
Ph
N
Me
Me
73
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.299
7.293
7.276
7.270
7.261
7.253
7.247
7.234
7.218
7.213
7.207
7.194
7.186
4.762
4.737
2.864
2.841
2.817
2.794
2.771
2.301
2.277
2.253
2.240
2.229
2.216
2.192
2.168
1.966
1.942
1.918
1.906
1.894
1.882
1.857
1.833
1.178
1.155
0.862
0.815
TBSO
O
Ph
Me
74
9
8
7
6
5
4
3
2
1
ppm
6.06
0.99
0.99
0.98
1.07
3.00
9.28
3.42
2.97
2.97

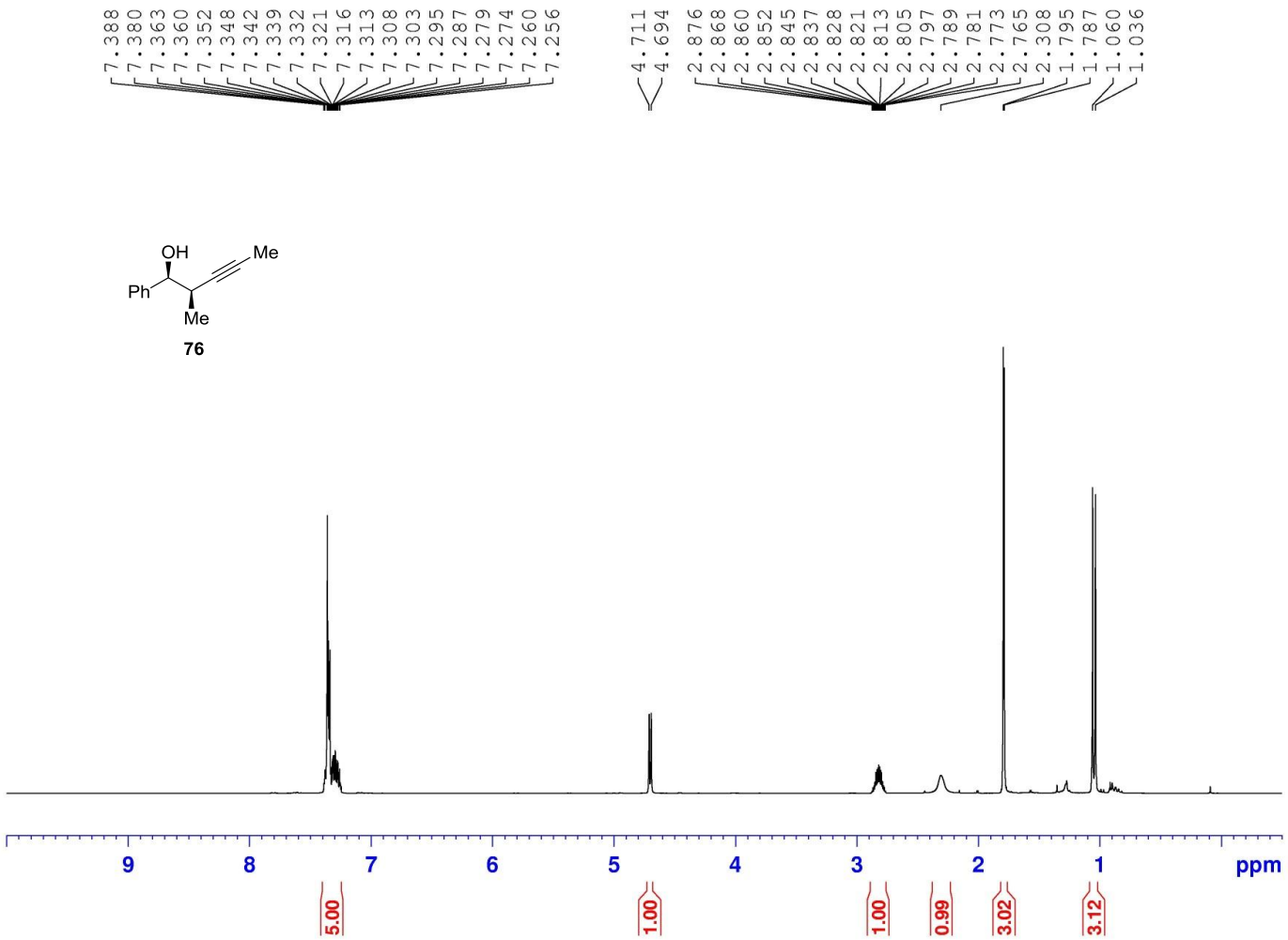

213.248
143.470
127.973
127.328
126.449
77.653
77.228
76.802
76.550
55.366
36.490
25.757
18.068
13.268
7.127
-4.631
-5.192
TBSO
O
Ph
Me
74
200
180
160
140
120
100
80
60
40
20
ppm


7.333
7.330
7.326
7.314
7.312
7.309
7.303
7.299
7.294
7.275
7.269
7.254
7.250
7.245
7.238
7.232
7.225
7.215
5.411
5.409
5.394
5.391
5.376
5.374
5.359
5.357
4.994
4.987
2.683
2.669
2.666
2.663
2.659
2.655
2.652
2.648
2.645
2.635
2.632
1.773
1.769
1.756
1.752
0.949
0.932
0.897
-0.031
-0.183
TBSO
OTf
Ph
Me
75
9
8
7
6
5
4
3
2
1
ppm
7.22
0.99
0.97
1.00
2.97
3.14
9.47
2.98
3.04

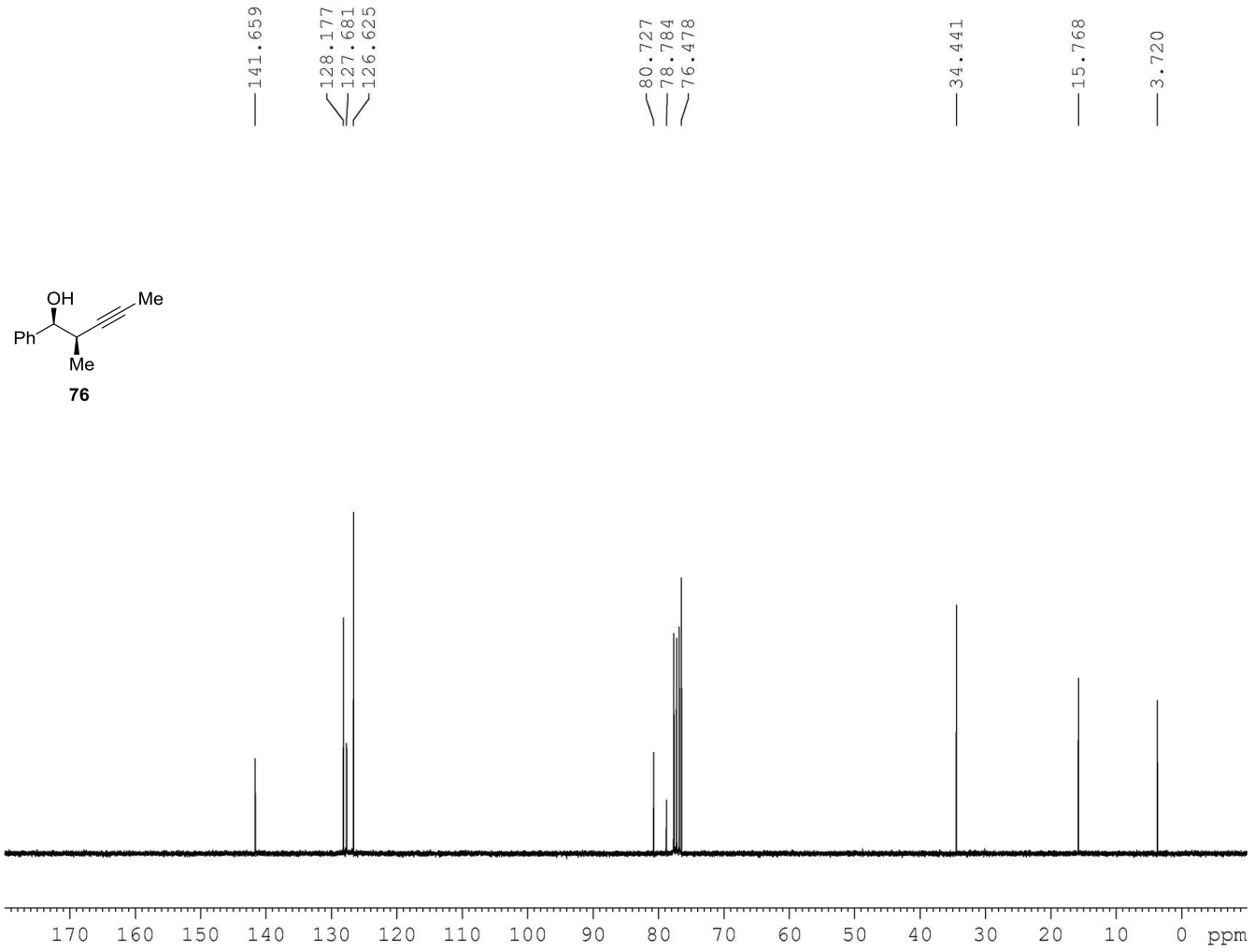

151.937
142.991
128.166
127.338
126.197
125.091
120.858
116.969
116.626
112.394
73.066
46.831
25.967
18.423
11.507
10.496
-4.577
-5.461
TBSO
OTf
Ph
Me
75
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

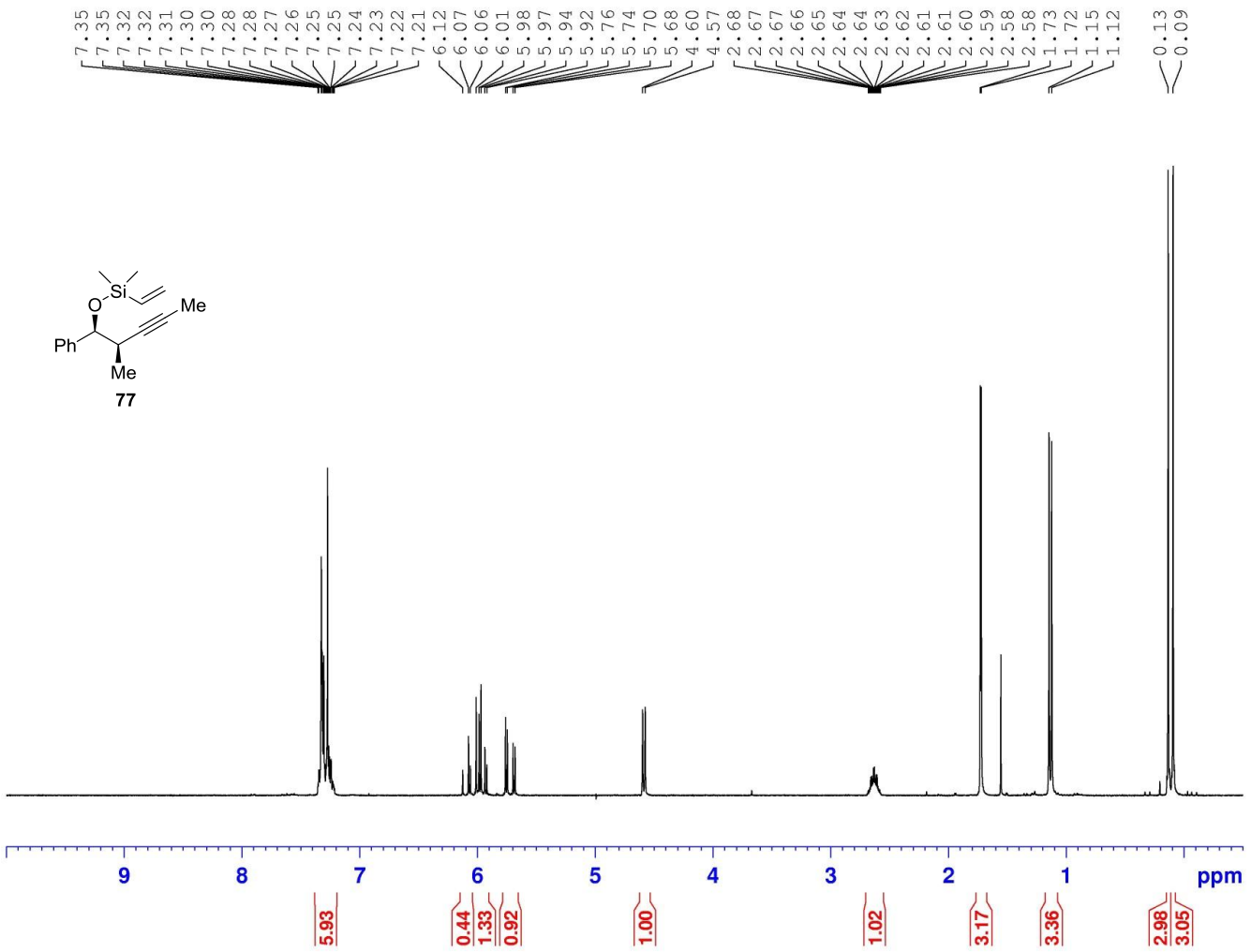


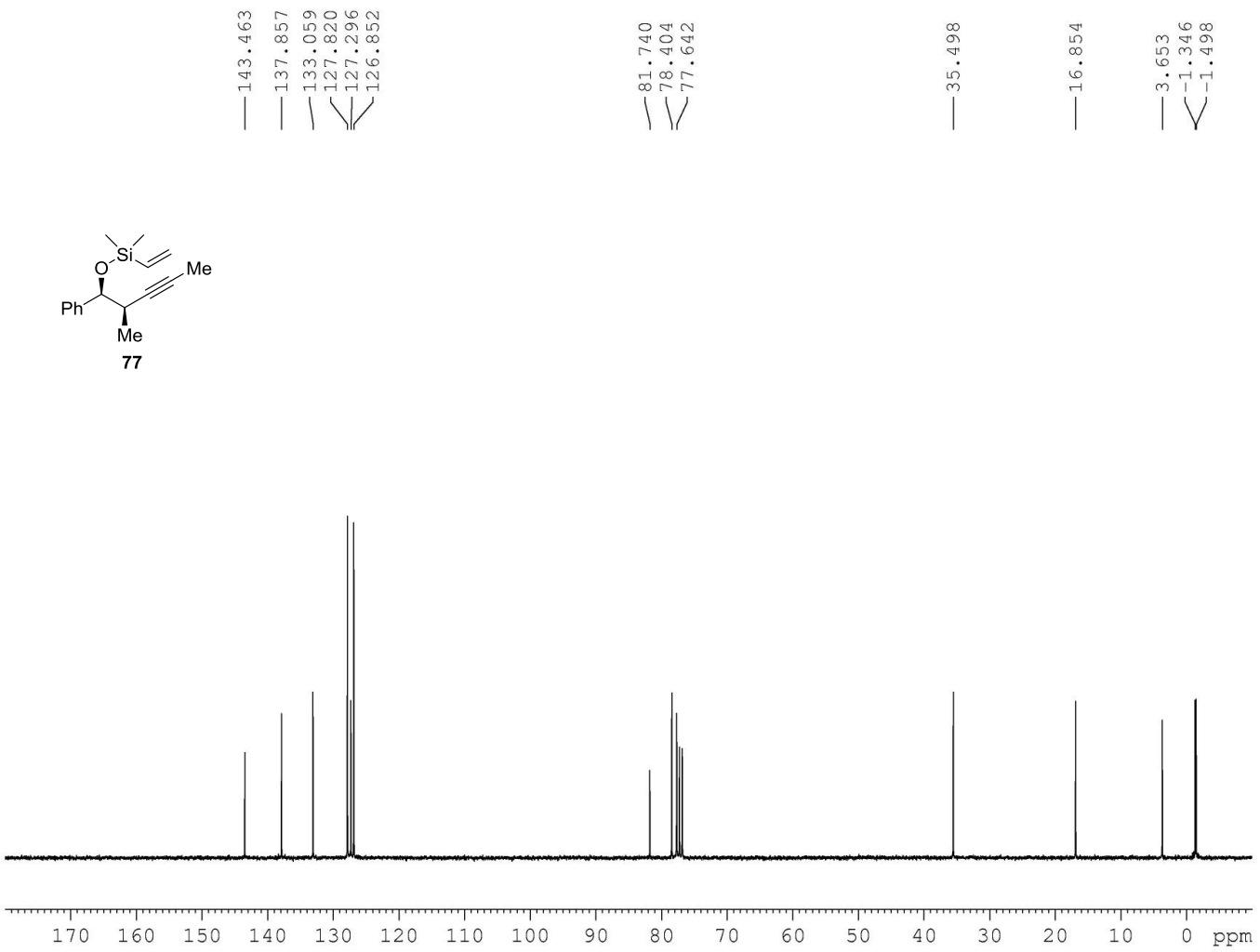
(#'s labeled on the structure refer to the protons at that location)

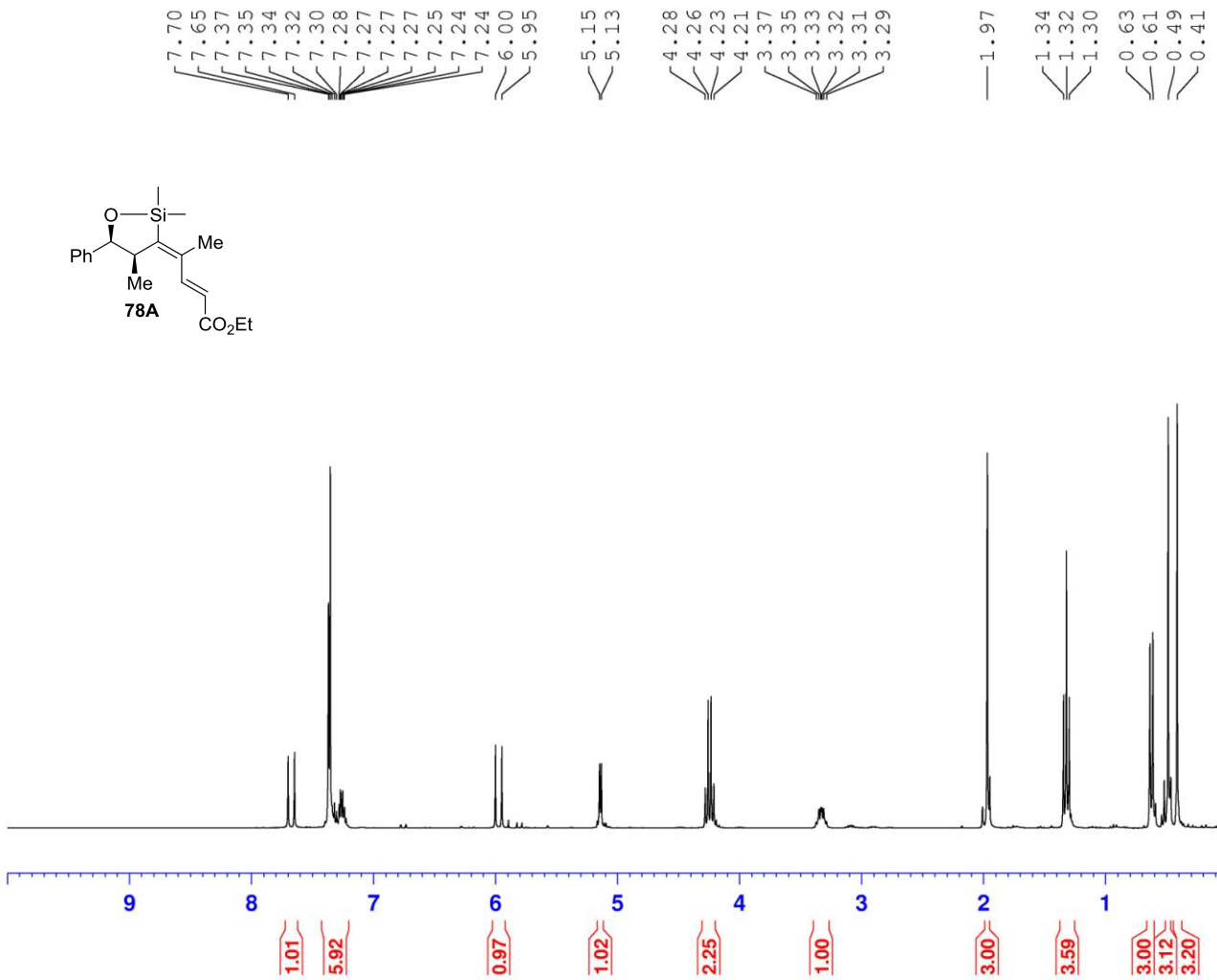

7.388
7.380
7.363
7.360
7.352
7.348
7.342
7.339
7.332
7.321
7.316
7.313
7.308
7.303
7.295
7.287
7.279
7.274
7.260
7.256
4.711
4.694
2.876
2.868
2.860
2.852
2.845
2.837
2.828
2.821
2.813
2.805
2.797
2.789
2.781
2.773
2.765
2.308
1.795
1.787
1.060
1.036
OH
Me
Ph
Me
9
8
7
6
5
4
3
2
1
ppm
5.00
1.00
1.00
0.99
3.02
3.12

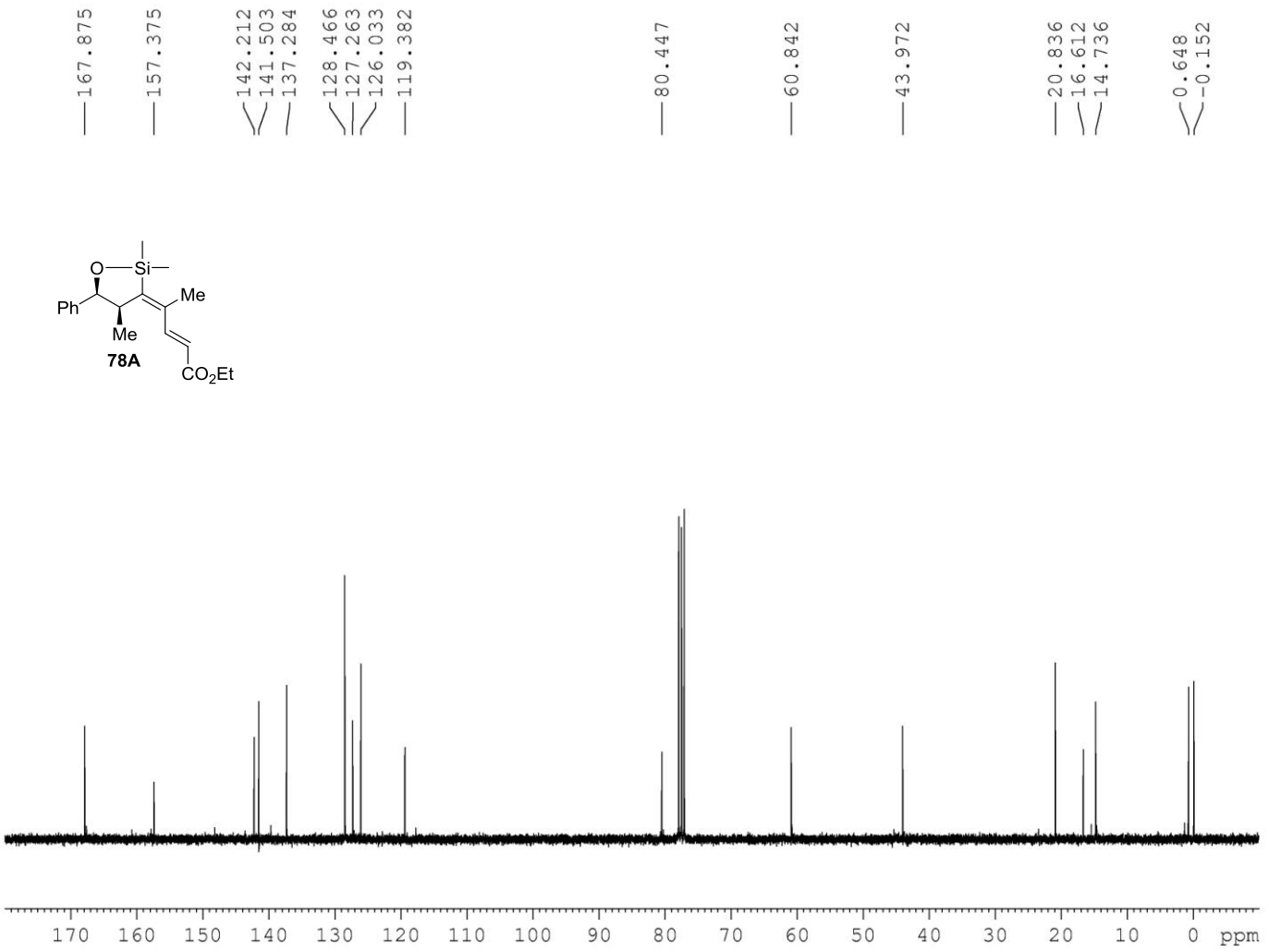
76

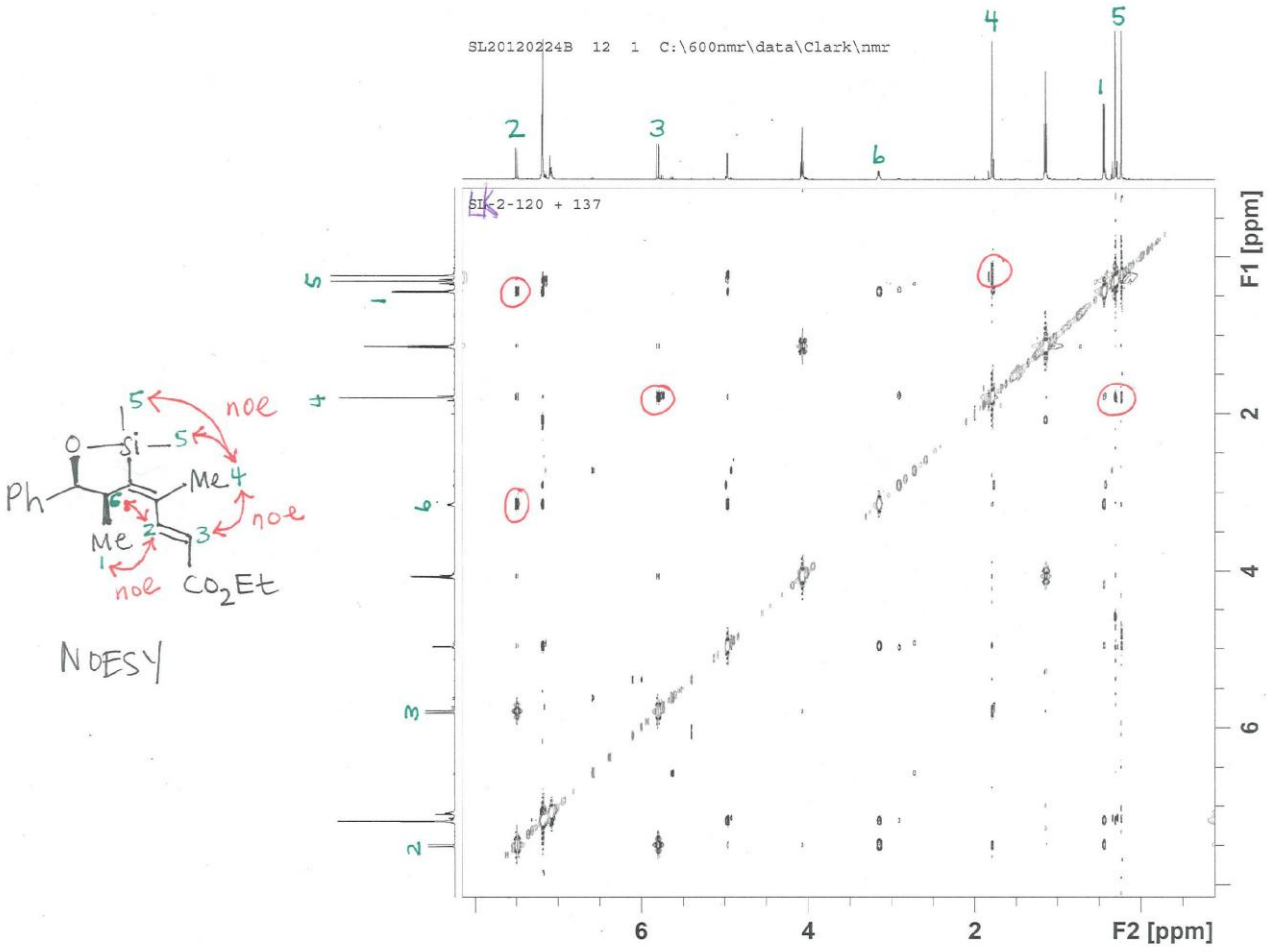

141.659
128.177
127.681
126.625
80.727
78.784
76.478
34.441
15.768
3.720
OH
Me
Ph
Me
76
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.35
7.35
7.32
7.32
7.31
7.30
7.30
7.28
7.28
7.27
7.26
7.25
7.25
7.24
7.23
7.22
7.21
6.12
6.07
6.06
6.01
5.98
5.97
5.94
5.92
5.76
5.74
5.70
5.68
4.60
4.57
2.68
2.67
2.67
2.66
2.65
2.64
2.64
2.63
2.62
2.61
2.61
2.60
2.59
2.58
1.73
1.72
1.15
1.12
0.13
0.09
Si
O
Me
Ph
Me
77
9
8
7
6
5
4
3
2
1
ppm
5.93
0.44
1.33
0.92
1.00
1.02
3.17
3.36
2.98
3.05

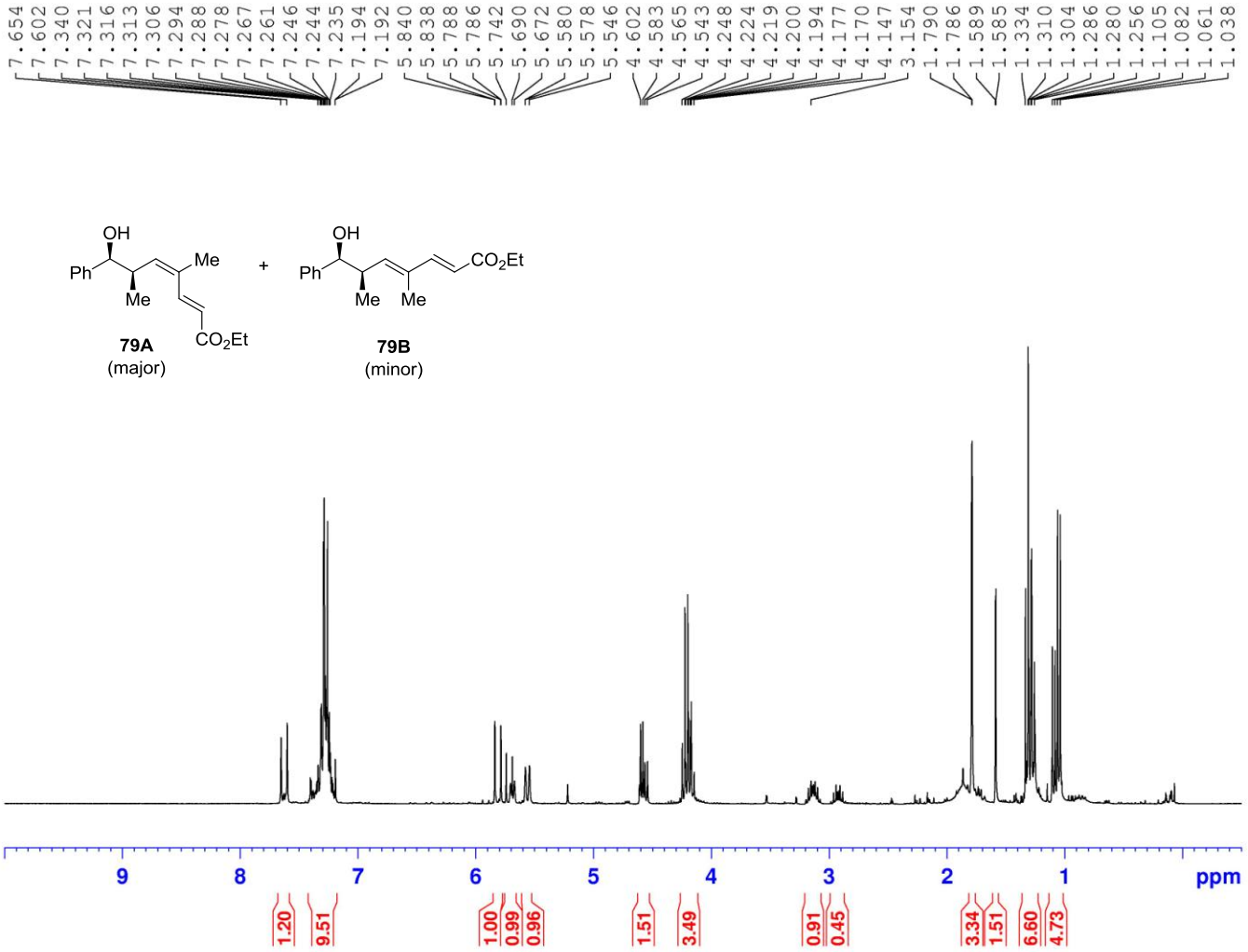

143.463
137.857
133.059
127.820
127.296
126.852
81.740
78.404
77.642
35.498
16.854
3.653
-1.346
-1.498
Si
O
Me
Ph
Me
77
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

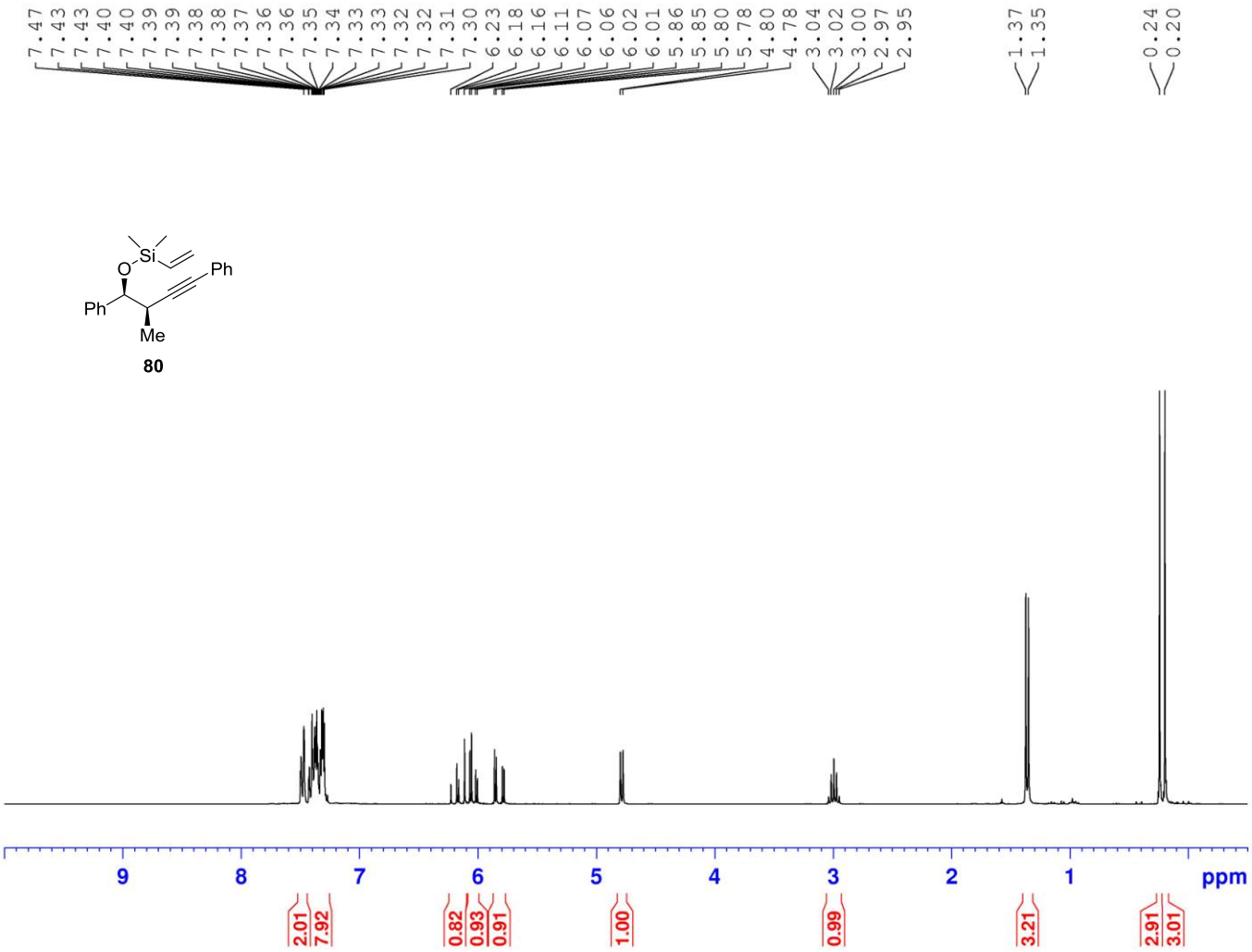

7.70
7.65
7.37
7.35
7.34
7.32
7.30
7.28
7.27
7.27
7.27
7.25
7.24
7.24
6.00
5.95
5.15
5.13
4.28
4.26
4.23
4.21
3.37
3.35
3.33
3.32
3.31
3.29
1.97
1.34
1.32
1.30
0.63
0.61
0.49
0.41
O
Si
Ph
Me
Me
78A
CO2Et
9
8
7
6
5
4
3
2
1
ppm
1.01
5.92
0.97
1.02
2.25
1.00
3.00
3.59
3.00
3.12
3.20


167.875
157.375
142.212
141.503
137.284
128.466
127.263
126.033
119.382
80.447
60.842
43.972
20.836
16.612
14.736
0.648
-0.152
O
Si
Ph
Me
Me
CO2Et
78A
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

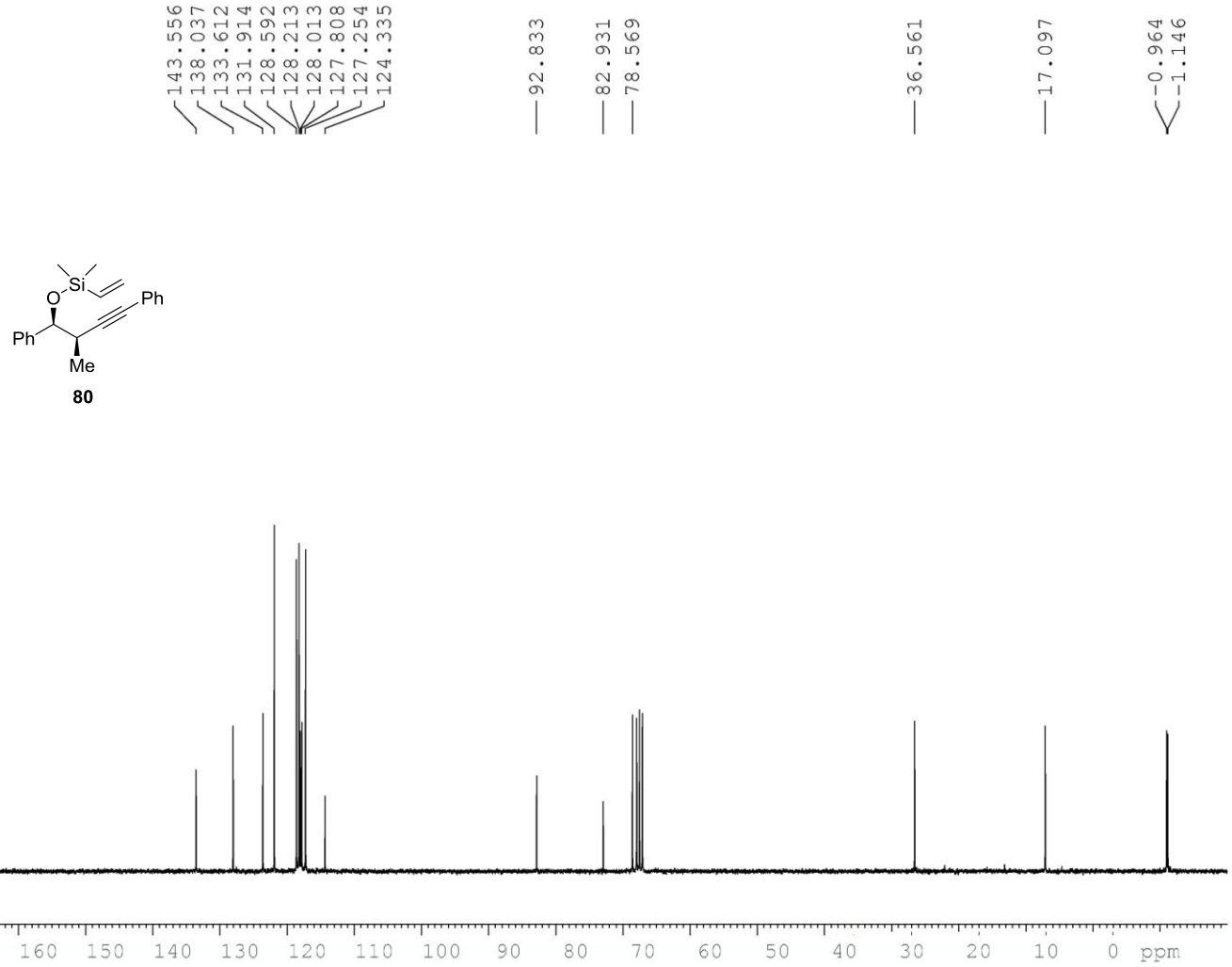


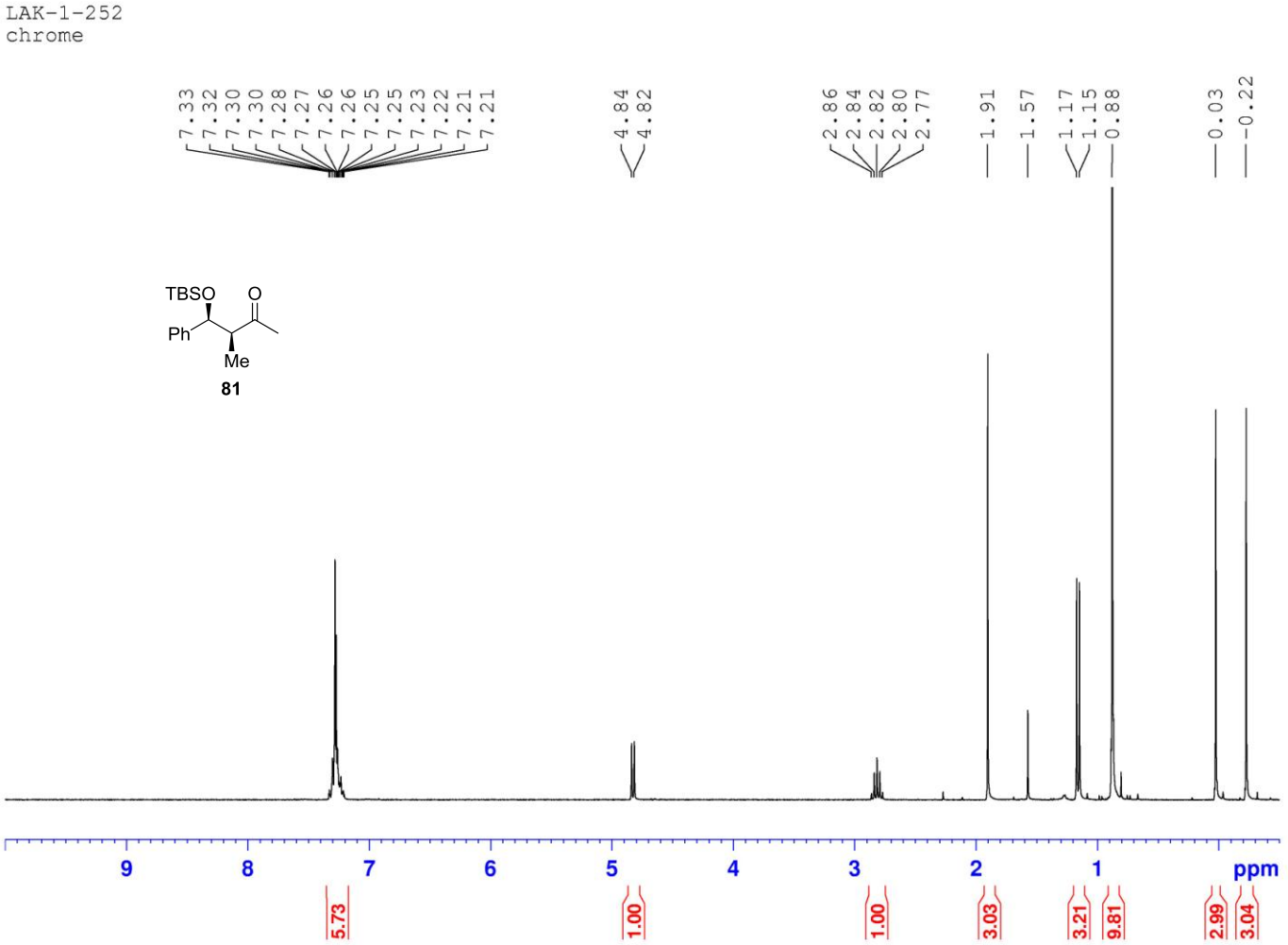
(#s labeled on the structure refer to the protons at that location)


7.654
7.602
7.340
7.321
7.316
7.313
7.306
7.294
7.288
7.278
7.267
7.261
7.246
7.244
7.235
7.194
7.192
5.840
5.838
5.788
5.786
5.742
5.690
5.672
5.580
5.578
5.546
4.602
4.583
4.565
4.543
4.248
4.224
4.219
4.200
4.194
4.177
4.170
4.147
3.154
1.790
1.786
1.589
1.585
1.334
1.310
1.304
1.286
1.280
1.256
1.105
1.082
1.061
1.038
OH
Ph
Me
Me
CO2Et
79A
(major)
+
OH
Ph
Me
Me
CO2Et
79B
(minor)
9
8
7
6
5
4
3
2
1
ppm
1.20
9.51
1.00
0.99
0.96
1.51
3.49
0.91
0.45
3.34
1.51
6.60
4.73


7.47
7.43
7.43
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.30
6.23
6.18
6.16
6.11
6.07
6.06
6.02
6.01
5.86
5.85
5.80
5.78
4.80
4.78
3.04
3.02
3.00
2.97
2.95
1.37
1.35
0.24
0.20
Si
O
Ph
Ph
Me
9
8
7
6
5
4
3
2
1
ppm
2.01
7.92
0.82
0.93
0.91
1.00
0.99
3.21
2.91
3.01

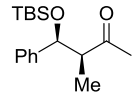
80


143.556
138.037
133.612
131.914
128.592
128.213
128.013
127.808
127.254
124.335
92.833
82.931
78.569
36.561
17.097
-0.964
-1.146
Si
O
Ph
Ph
Me
80
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

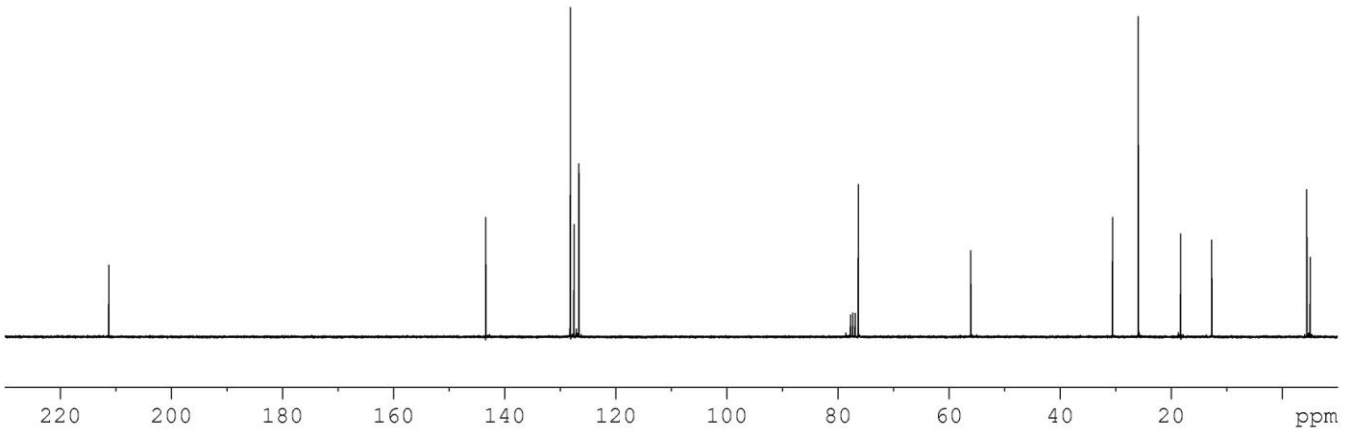

LAK-1-252
chrome
7.33
7.32
7.30
7.30
7.28
7.27
7.26
7.26
7.25
7.25
7.23
7.22
7.21
7.21
4.84
4.82
2.86
2.84
2.82
2.80
2.77
1.91
1.57
1.17
1.15
0.88
0.03
-0.22
TBSO
O
Ph
Me
81
9
8
7
6
5
4
3
2
1
ppm
5.73
1.00
1.00
3.03
3.21
9.81
2.99
3.04

LAK-1-252

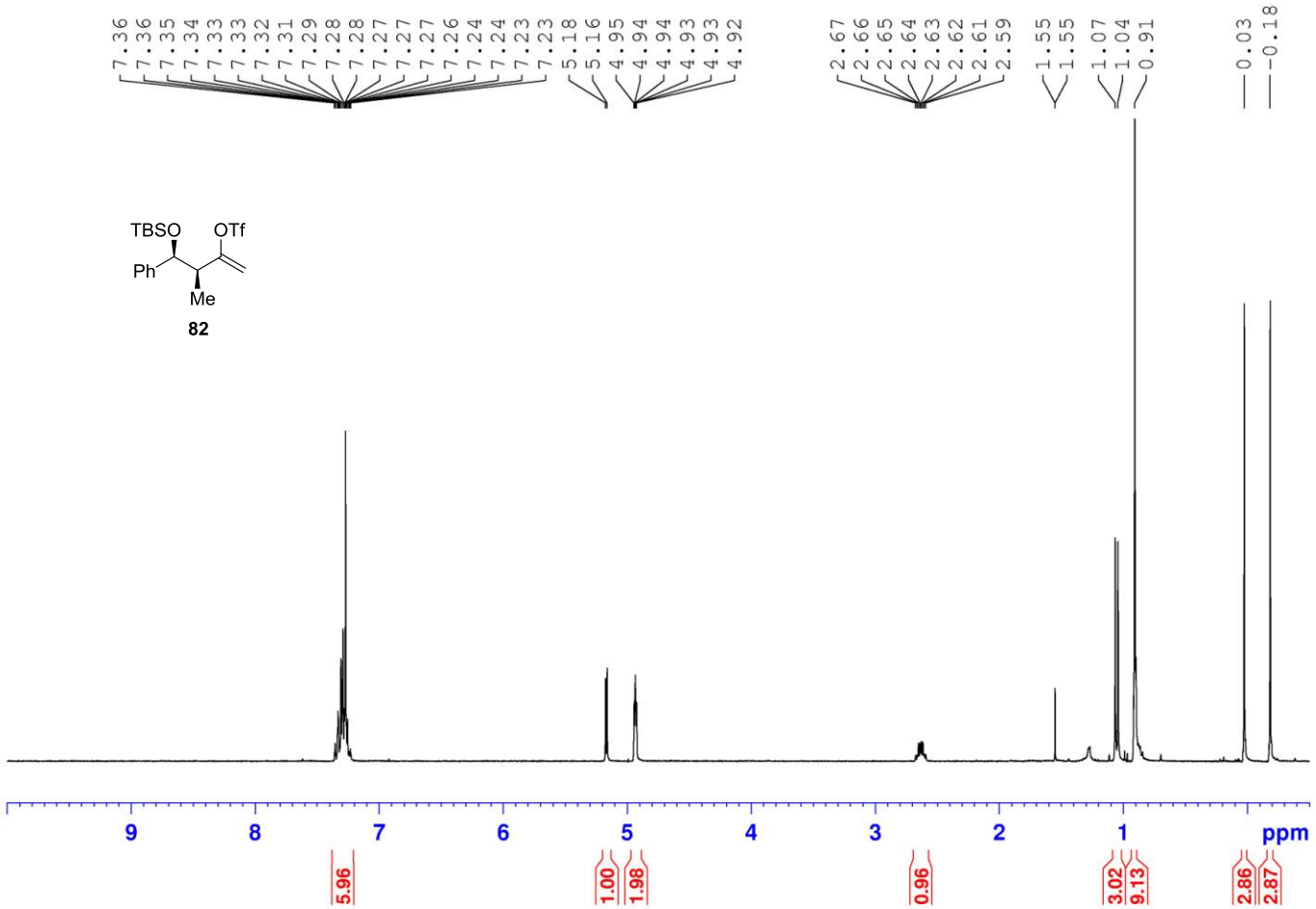
211.185
143.385
128.131
127.475
126.590
76.293
56.031
30.502
25.889
18.210
12.638
-4.499
-5.081

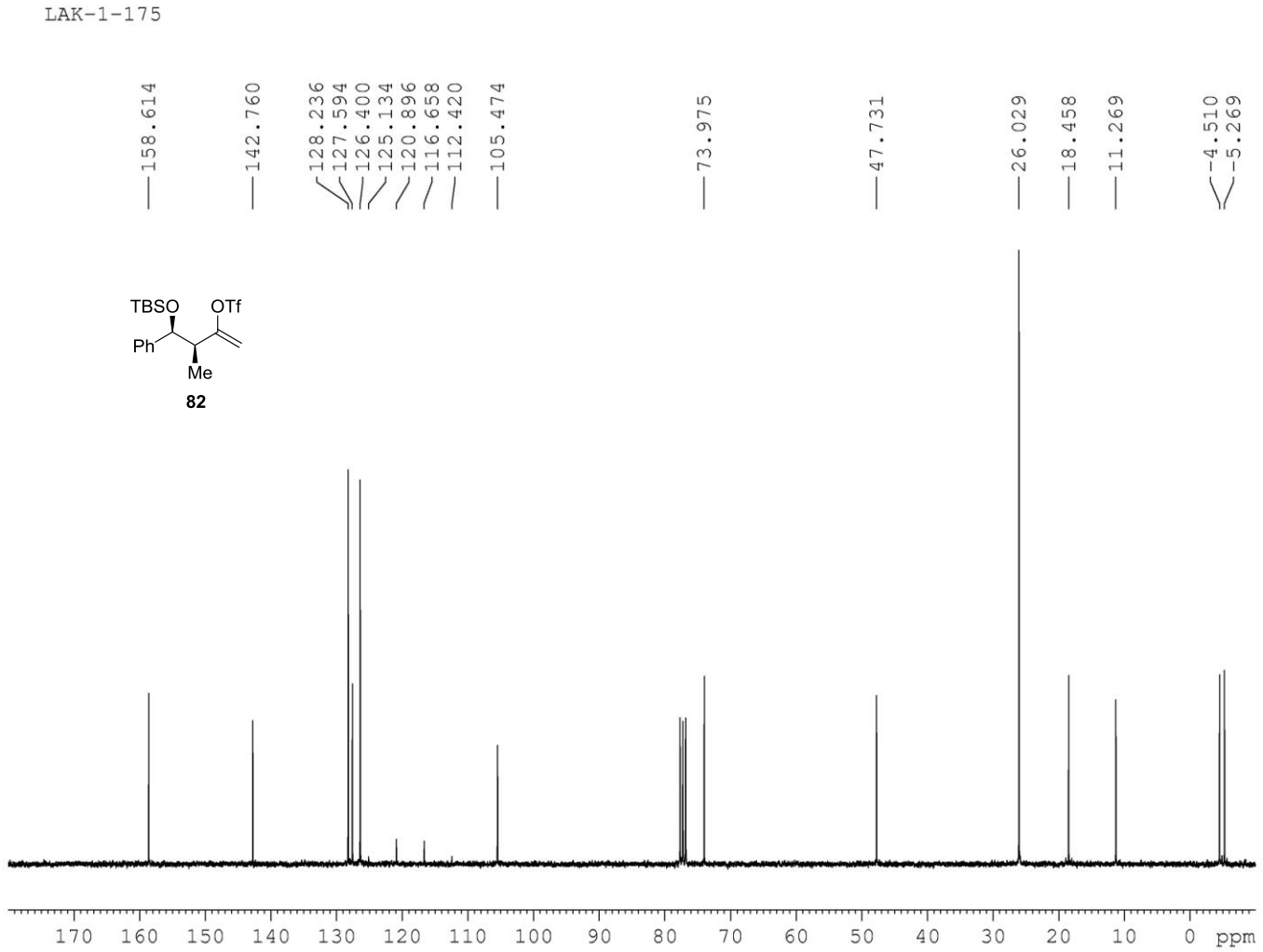


81

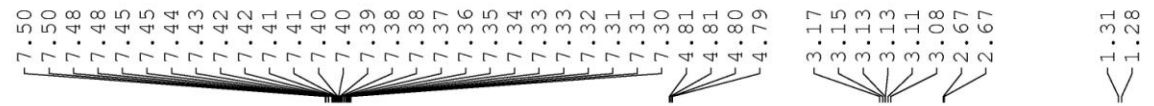


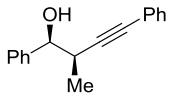
LAK-2-166


7.36
7.36
7.35
7.34
7.33
7.33
7.32
7.31
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.24
7.24
7.23
7.23
5.18
5.16
4.95
4.94
4.94
4.93
4.93
4.92
2.67
2.66
2.65
2.64
2.63
2.62
2.61
2.59
1.55
1.55
1.07
1.04
0.91
0.03
-0.18
TBSO
OTf
Ph
Me
82
9
8
7
6
5
4
3
2
1
ppm
5.96
1.00
1.98
0.96
3.02
9.13
2.86
2.87

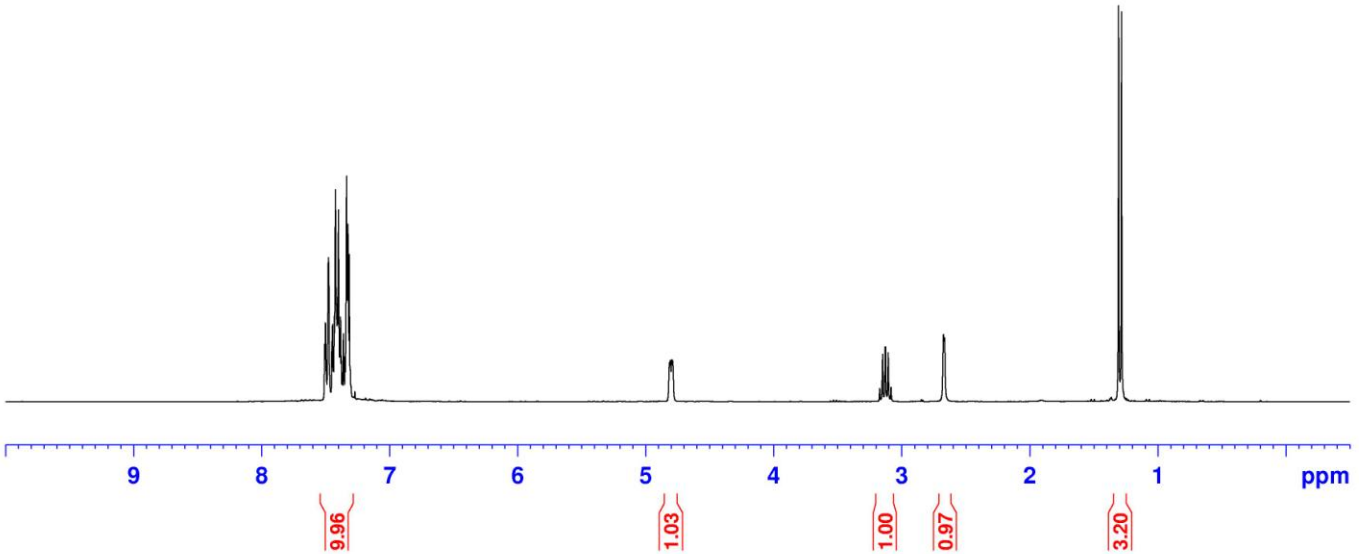

LAK-1-175
158.614
142.760
128.236
127.594
126.400
125.134
120.896
116.658
112.420
105.474
73.975
47.731
26.029
18.458
11.269
-4.510
-5.269
TBSO
OTf
Ph
Me
82
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

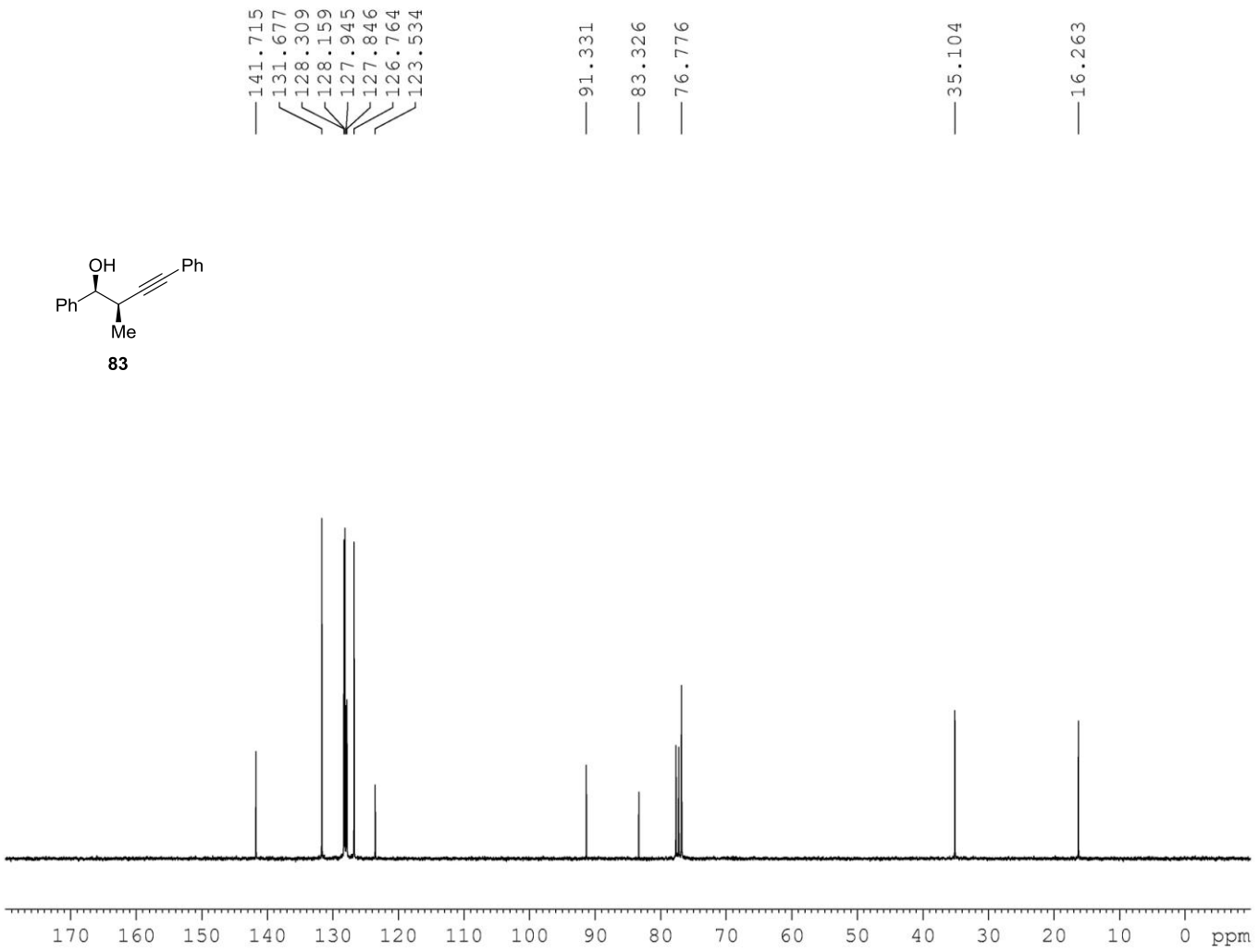
LAK-1-291


7.50
7.50
7.48
7.48
7.45
7.45
7.44
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.30
4.81
4.81
4.80
4.79
3.17
3.15
3.13
3.13
3.11
3.08
2.67
2.67
1.31
1.28

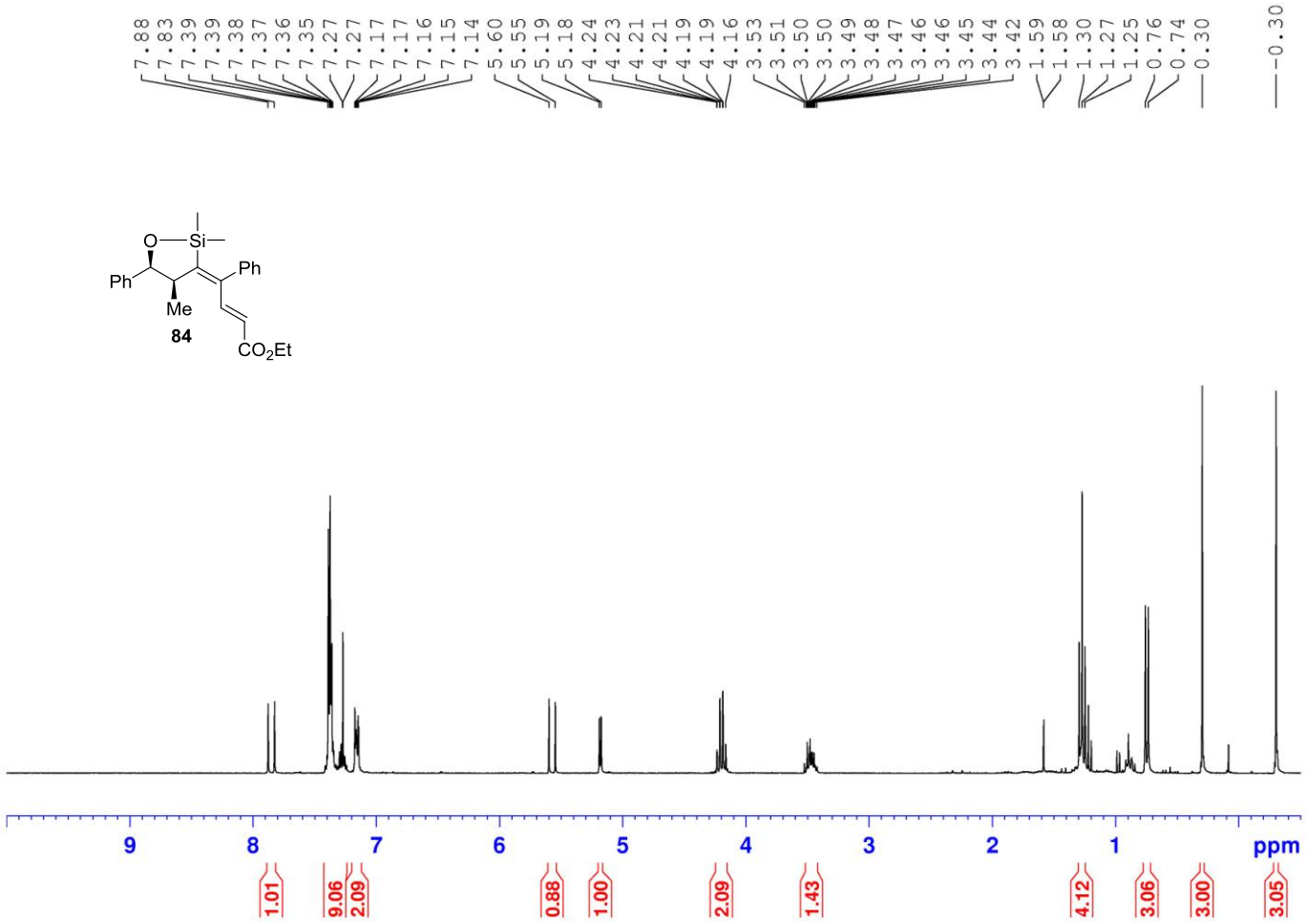

OH
Ph
Ph
Me

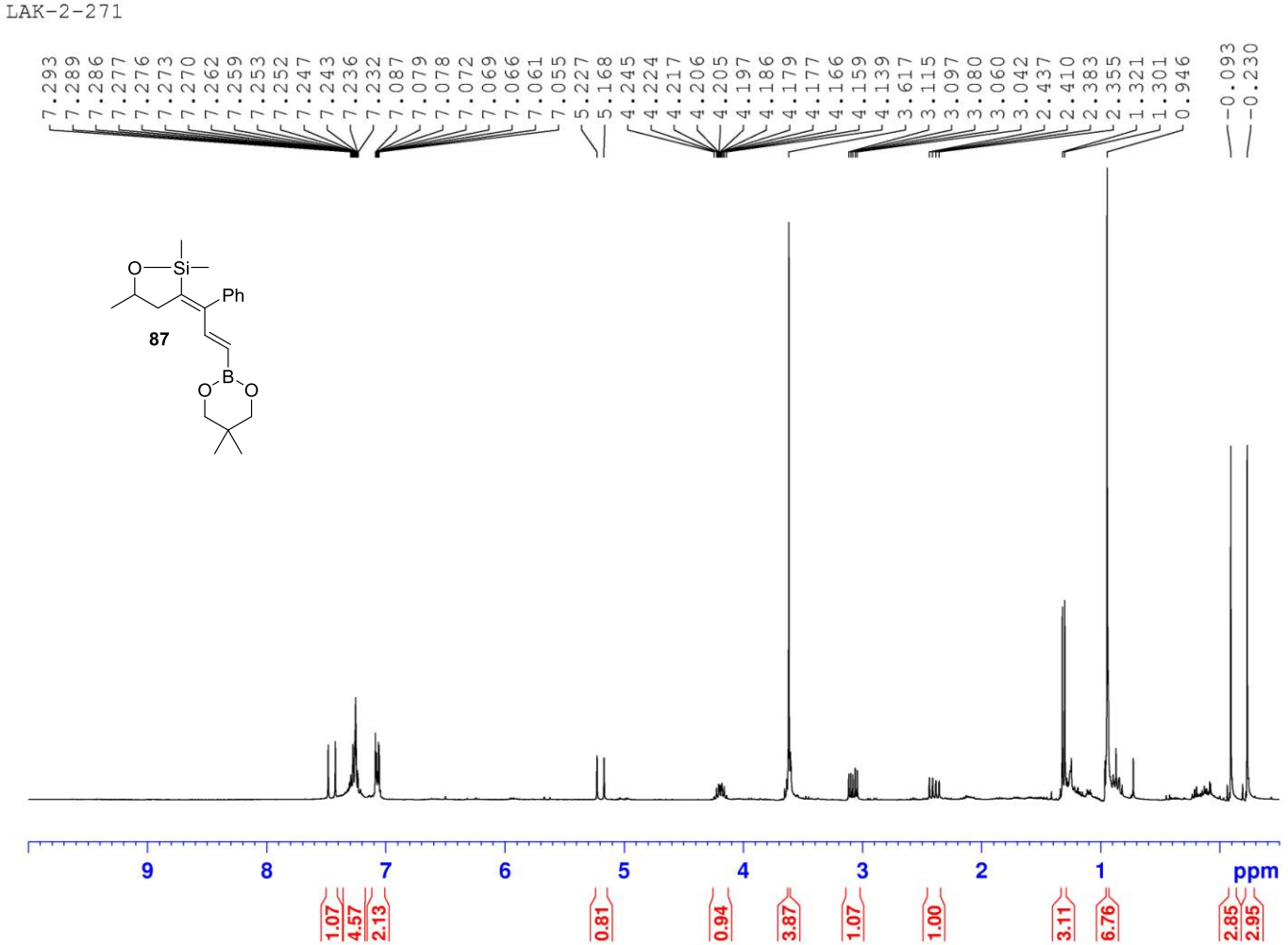
83


9
8
7
6
5
4
3
2
1
ppm
9.96
1.03
1.00
0.97
3.20

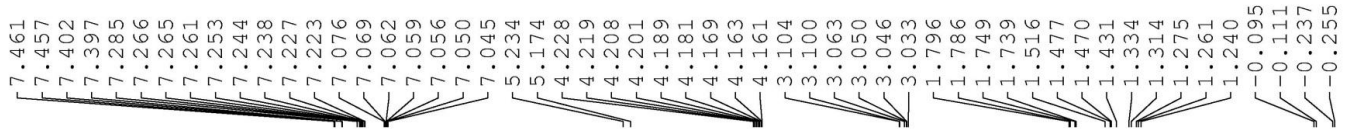

141.715
131.677
128.309
128.159
127.945
127.846
126.764
123.534
91.331
83.326
76.776
35.104
16.263
OH
Ph
Ph
Me
83
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

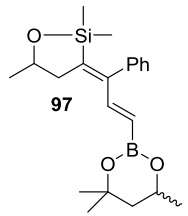
LAK-2-87 (2)


7.88
7.83
7.39
7.39
7.38
7.37
7.36
7.35
7.27
7.27
7.17
7.17
7.16
7.15
7.14
5.60
5.55
5.19
5.18
4.24
4.23
4.21
4.21
4.19
4.19
4.16
3.53
3.51
3.50
3.50
3.49
3.48
3.47
3.46
3.46
3.45
3.44
3.42
1.59
1.58
1.30
1.27
1.25
0.76
0.74
0.30
-0.30
O
Si
Ph
Ph
Me
84
CO2Et
9
8
7
6
5
4
3
2
1
ppm
1.01
9.06
2.09
0.88
1.00
2.09
1.43
4.12
3.06
3.00
3.05


LAK-2-271
7.293
7.289
7.286
7.277
7.276
7.273
7.270
7.262
7.259
7.253
7.252
7.247
7.243
7.236
7.232
7.087
7.079
7.078
7.072
7.069
7.066
7.061
7.055
5.227
5.168
4.245
4.224
4.217
4.206
4.205
4.197
4.186
4.179
4.177
4.166
4.159
4.139
3.617
3.115
3.097
3.080
3.060
3.042
2.437
2.410
2.383
2.355
1.321
1.301
0.946
-0.093
-0.230
O
Si
Ph
87
B
O
O
9
8
7
6
5
4
3
2
1
ppm
1.07
4.57
2.13
0.81
0.94
3.87
1.07
1.00
3.11
6.76
2.85
2.95

LAK-3-157


7.461
7.457
7.402
7.397
7.285
7.266
7.265
7.261
7.253
7.244
7.238
7.227
7.223
7.076
7.069
7.062
7.059
7.056
7.050
7.045
5.234
5.174
4.228
4.219
4.208
4.201
4.189
4.181
4.169
4.163
4.161
3.104
3.100
3.063
3.050
3.046
3.033
1.796
1.786
1.749
1.739
1.516
1.477
1.470
1.431
1.334
1.314
1.275
1.261
1.240
-0.095
-0.111
-0.237
-0.255

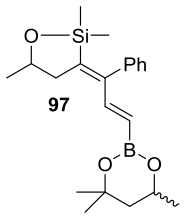

O
Si
Ph
B
O
O

97

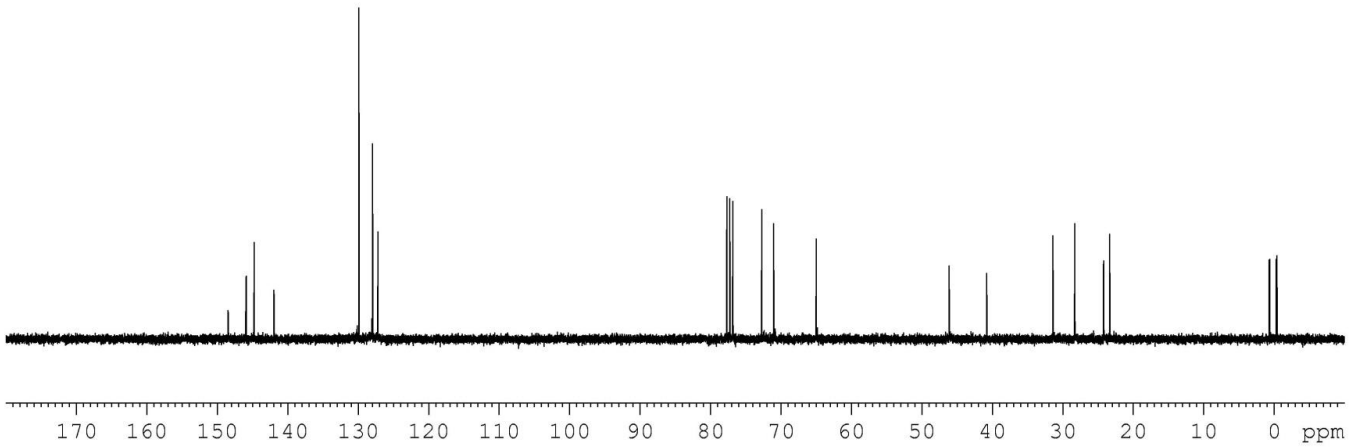
9
8
7
6
5
4
3
2
1
ppm
1.19
3.74
2.12
0.90
2.28
1.00
1.05
1.34
1.30
15.68
3.12
3.10

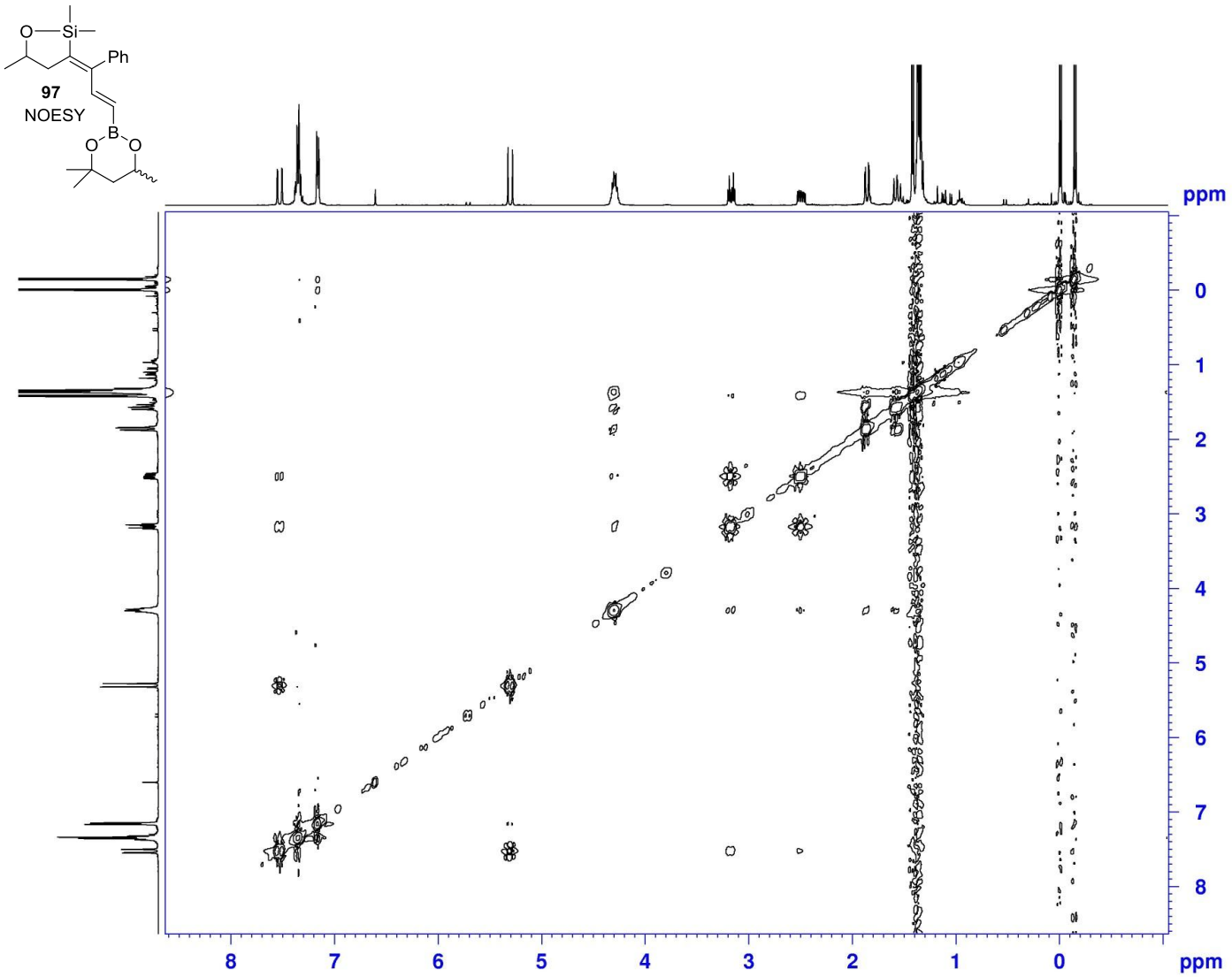
LAK-3-157 carbon

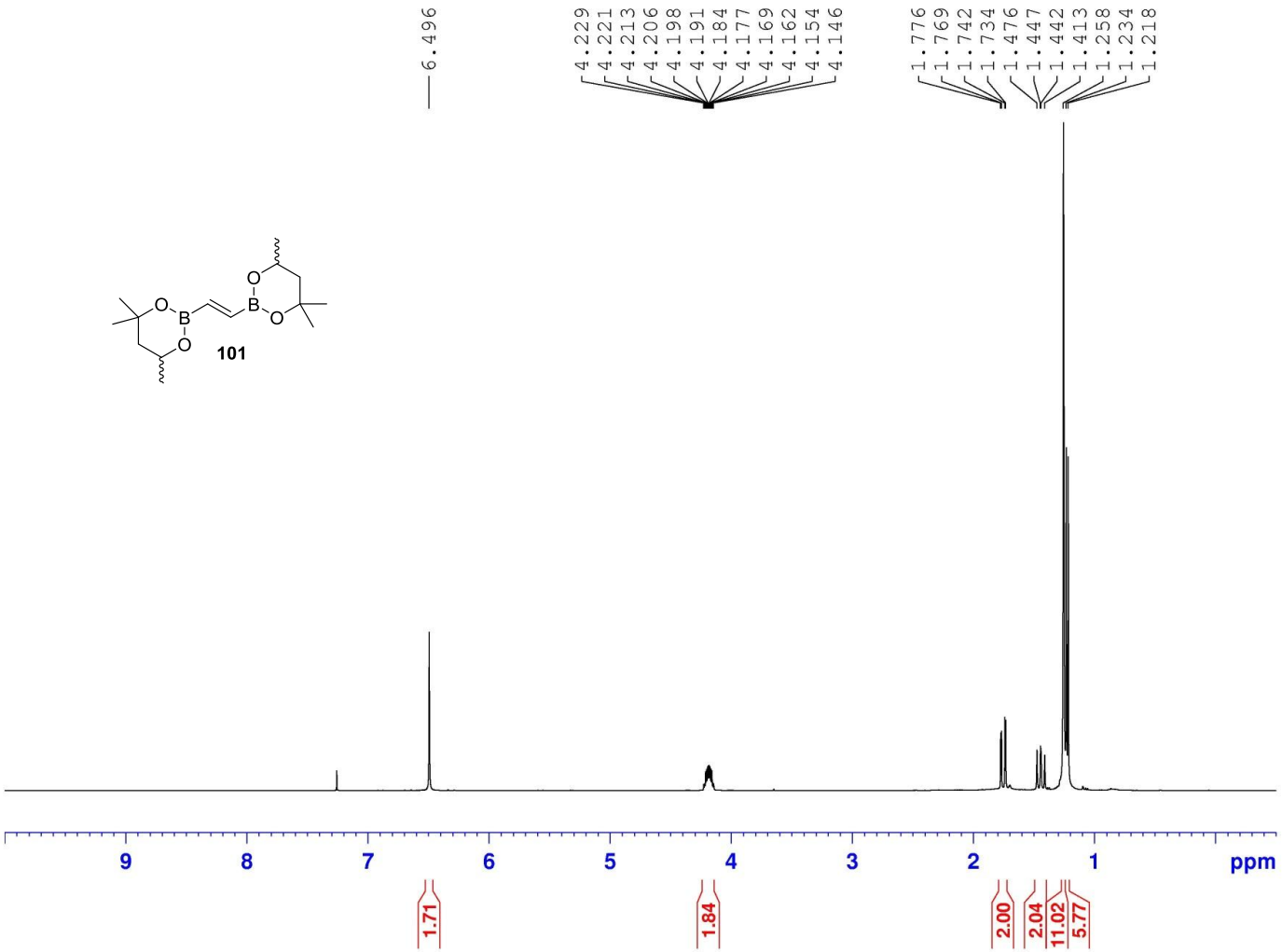
148.433
145.891
145.861
144.742
141.929
129.868
127.922
127.167
77.656
77.232
76.810
72.713
71.031
64.970
46.112
40.772
31.375
28.272
24.188
24.174
23.331
0.702
0.611
-0.310
-0.409

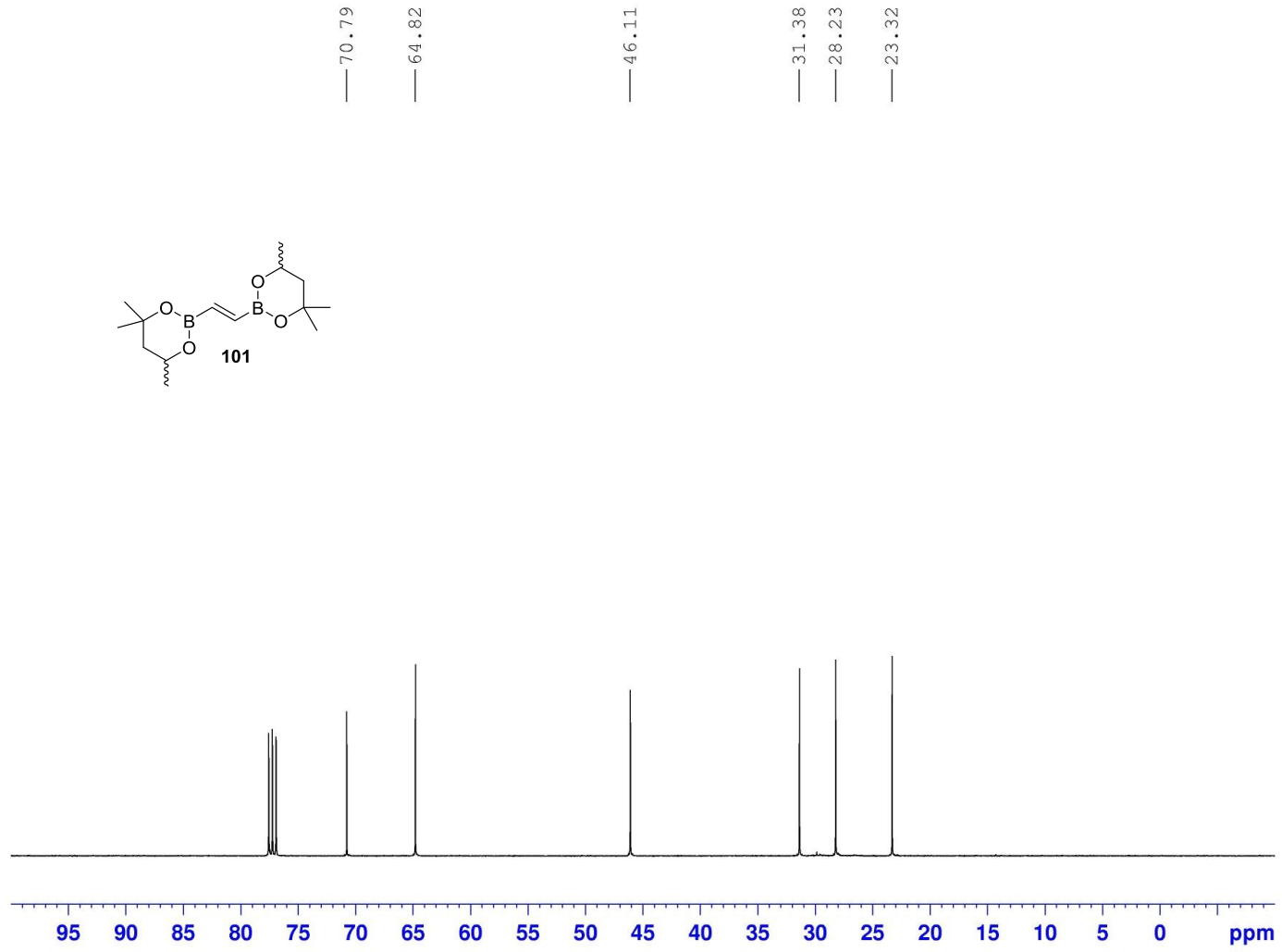


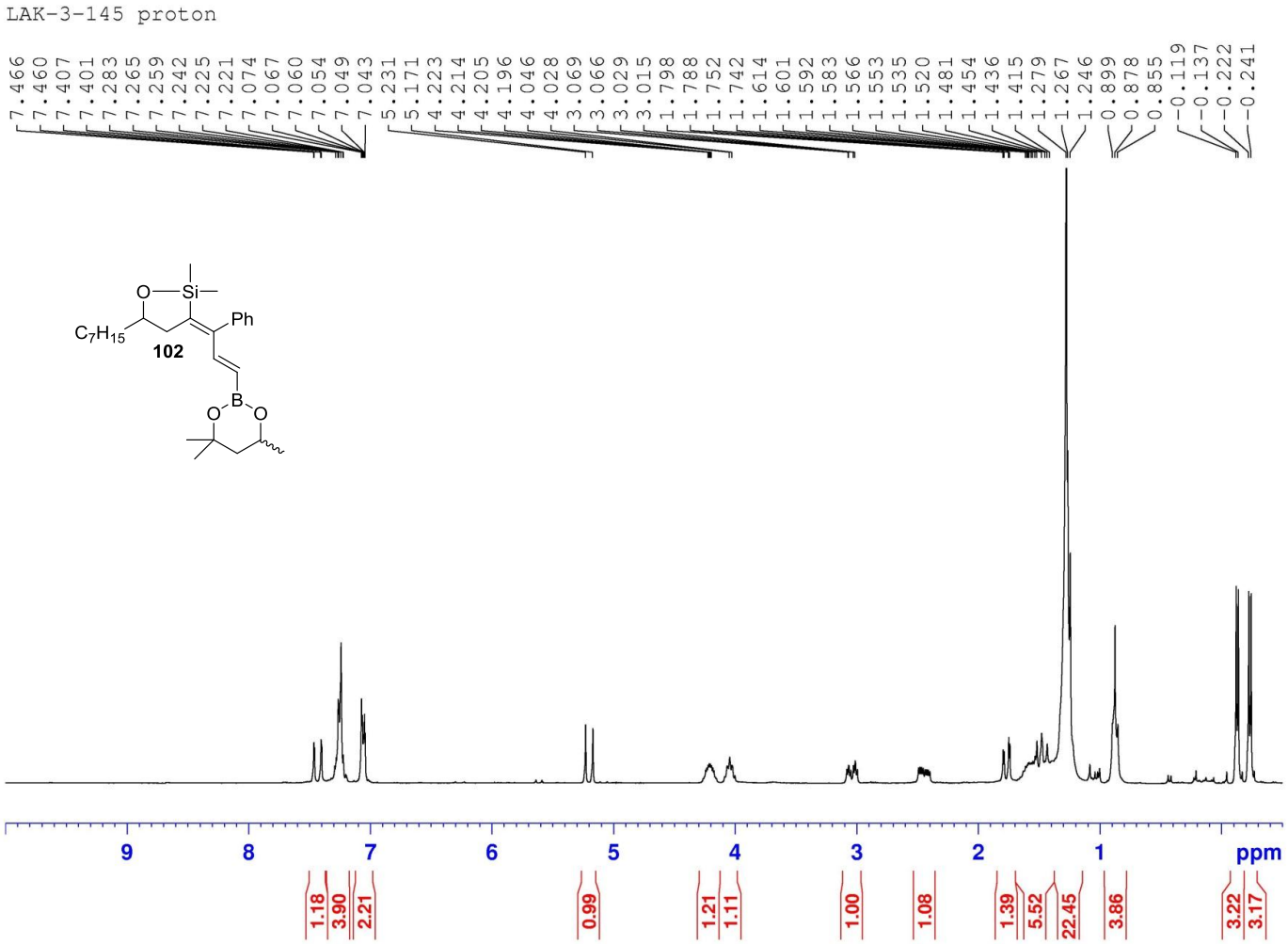
97



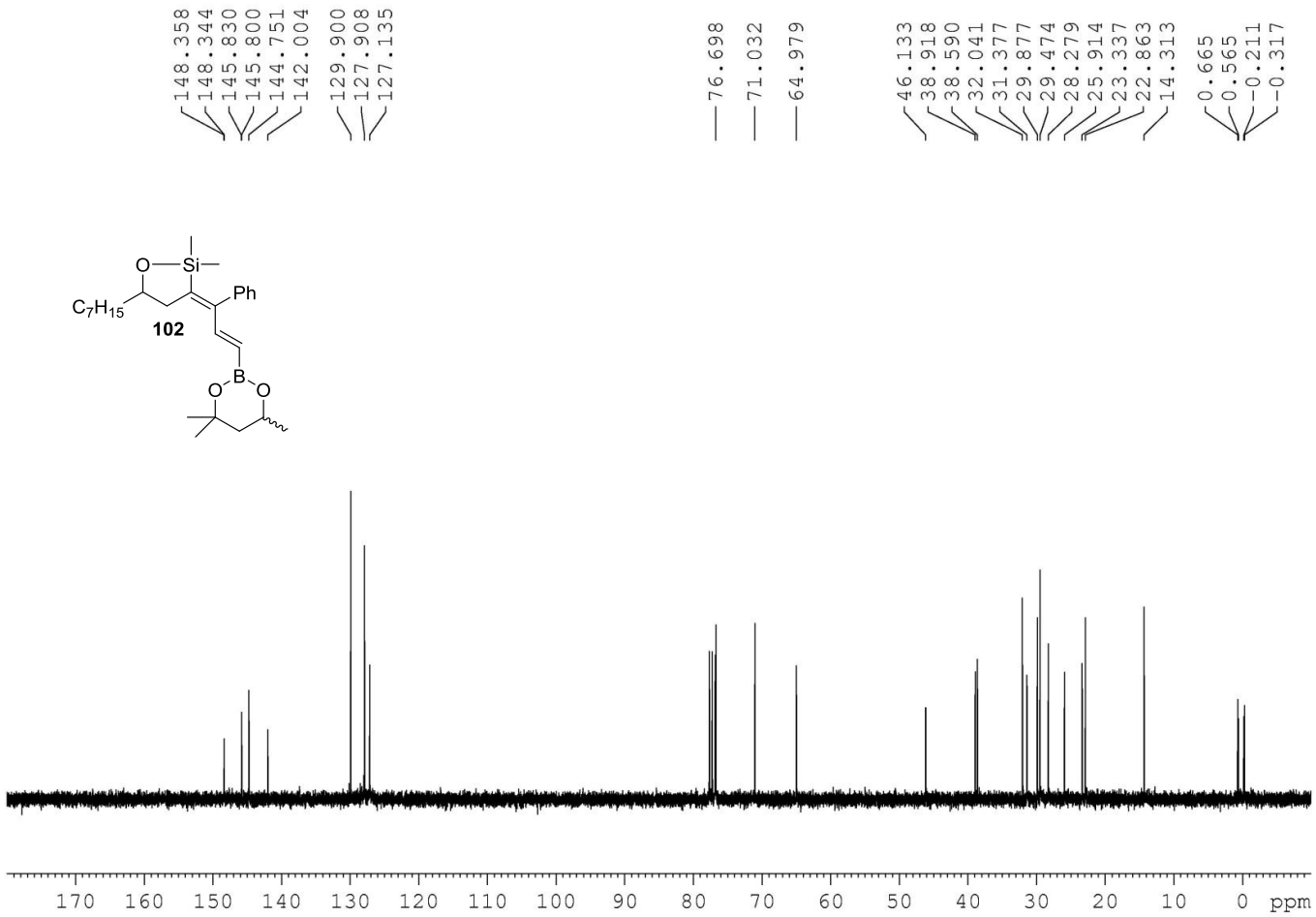

O
Si
Ph
97
NOESY
B
O
O
ppm
0
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
0
ppm

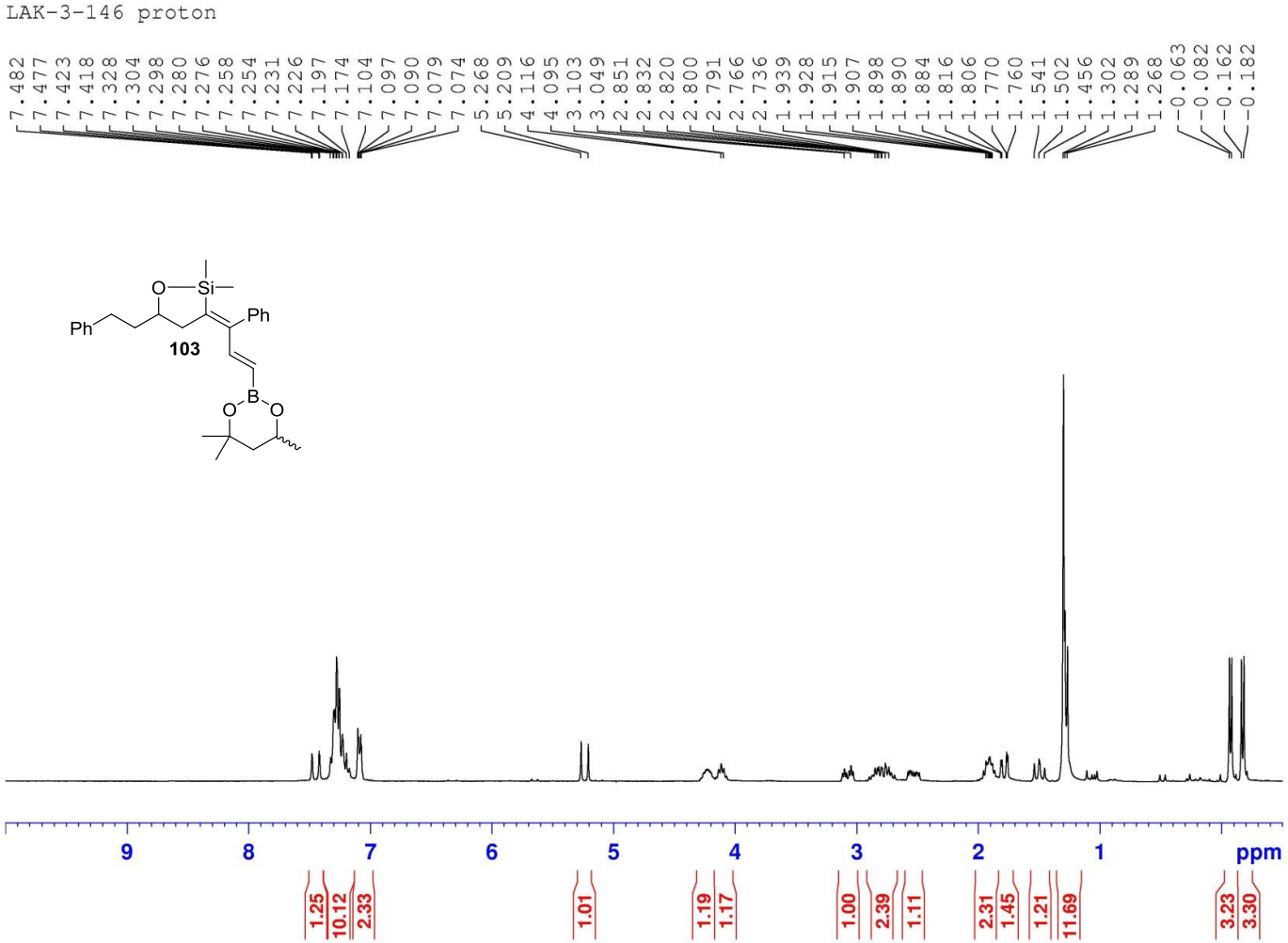

6.496
4.229
4.221
4.213
4.206
4.198
4.191
4.184
4.177
4.169
4.162
4.154
4.146
1.776
1.769
1.742
1.734
1.476
1.447
1.442
1.413
1.258
1.234
1.218
O
B
O
B
O
O
101
9
8
7
6
5
4
3
2
1
ppm
1.71
1.84
2.00
2.04
11.02
5.77


70.79
64.82
46.11
31.38
28.23
23.32
101
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm


LAK-3-145 proton
7.466
7.460
7.407
7.401
7.283
7.265
7.259
7.242
7.225
7.221
7.074
7.067
7.060
7.054
7.049
7.043
5.231
5.171
4.223
4.214
4.205
4.196
4.046
4.028
3.069
3.066
3.029
3.015
1.798
1.788
1.752
1.742
1.614
1.601
1.592
1.583
1.566
1.553
1.535
1.520
1.481
1.454
1.436
1.415
1.279
1.267
1.246
0.899
0.878
0.855
-0.119
-0.137
-0.222
-0.241
O
Si
Ph
C7H15
102
B
O
O
9
8
7
6
5
4
3
2
1
ppm
1.18
3.90
2.21
0.99
1.21
1.11
1.00
1.08
1.39
5.52
22.45
3.86
3.22
3.17

LAK-3-145 carbon




LAK-3-146 proton
7.482
7.477
7.423
7.418
7.328
7.304
7.298
7.280
7.276
7.258
7.254
7.231
7.226
7.197
7.174
7.104
7.097
7.090
7.079
7.074
5.268
5.209
4.116
4.095
3.103
3.049
2.851
2.832
2.820
2.800
2.791
2.766
2.736
1.939
1.928
1.915
1.907
1.898
1.890
1.884
1.816
1.806
1.770
1.760
1.541
1.502
1.456
1.302
1.289
1.268
-0.063
-0.082
-0.162
-0.182
O
Si
Ph
Ph
103
B
O
O
9
8
7
6
5
4
3
2
1
ppm
1.25
10.12
2.33
1.01
1.19
1.17
1.00
2.39
1.11
2.31
1.45
1.21
11.69
3.23
3.30

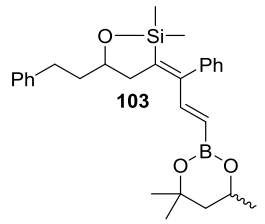
LAK-3-146 carbon

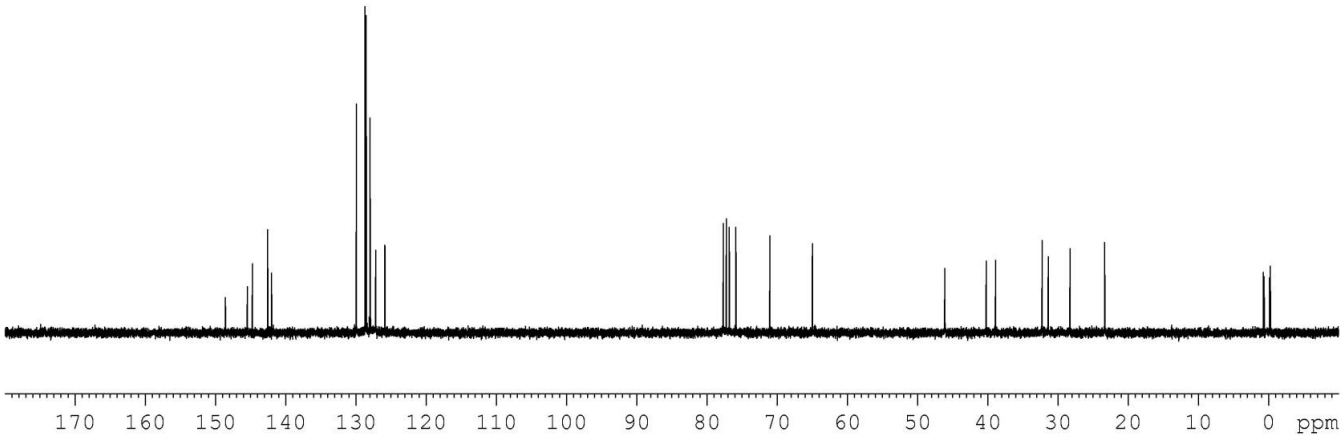
148.541
148.518
145.411
145.373
144.685
142.494
141.946
129.875
128.642
128.482
127.926
127.174
125.858

75.859
71.030
64.970

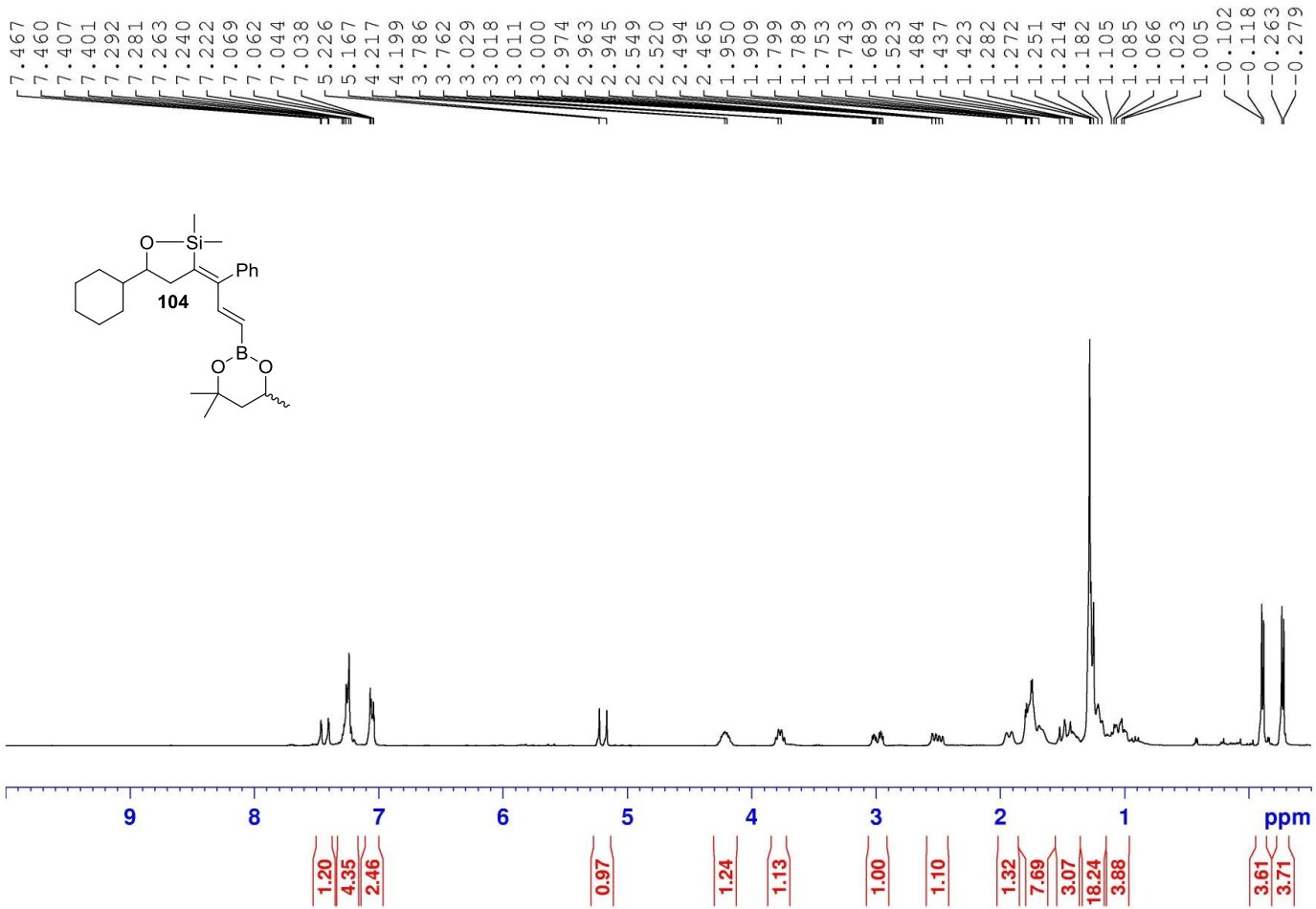
46.106
40.212
38.880
32.246
31.374
28.273
23.334

0.718
0.619
-0.157
-0.264

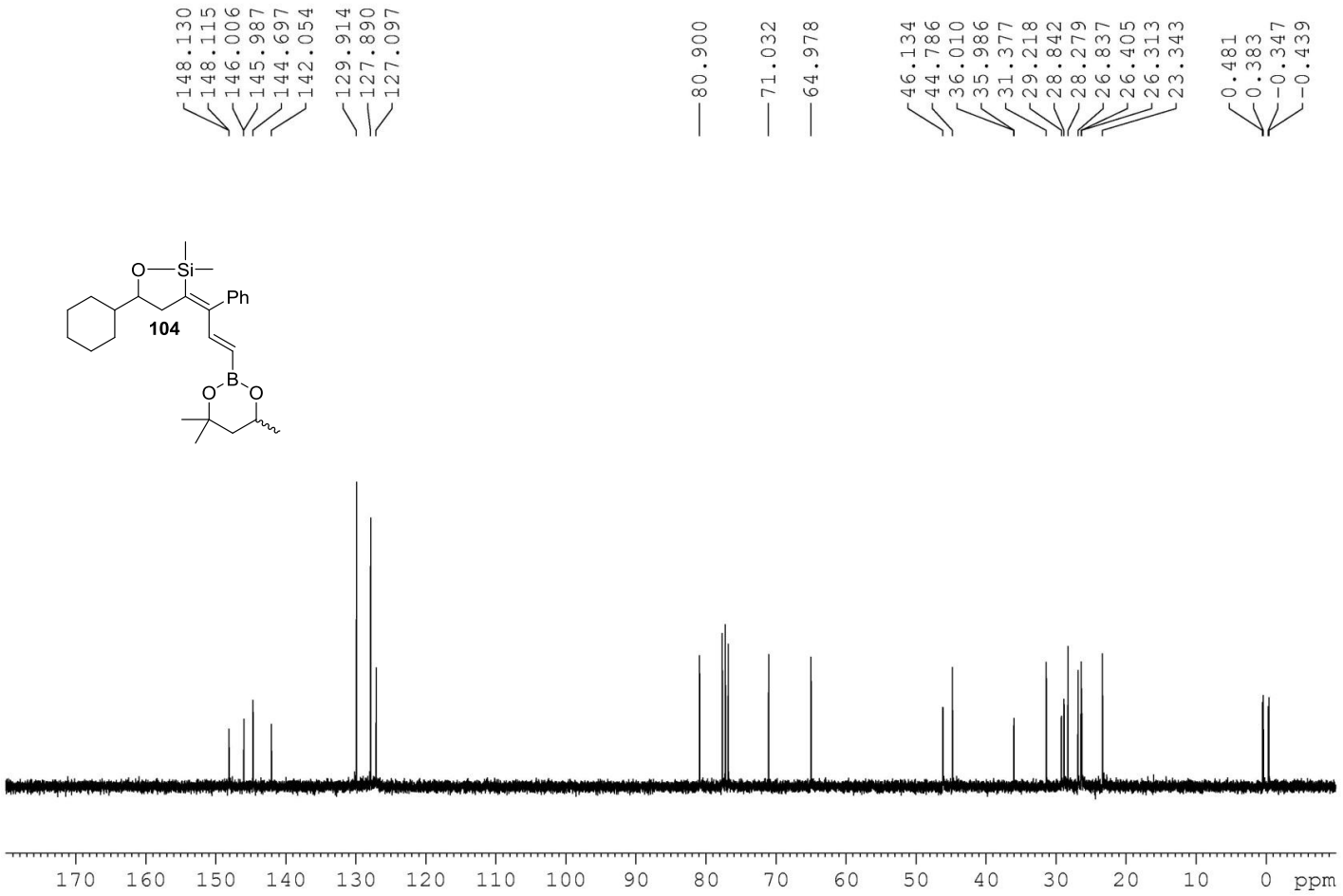


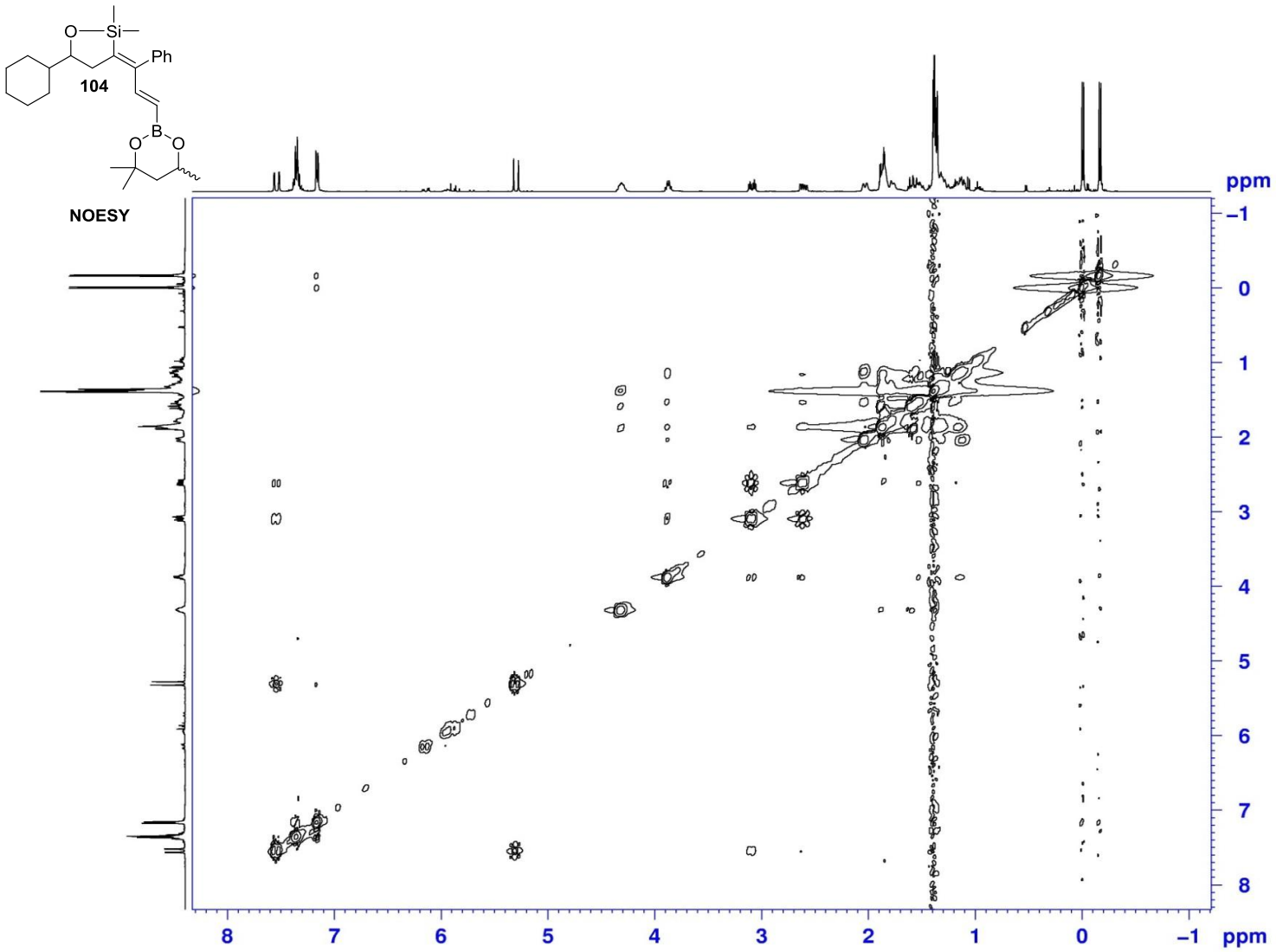


LAK-3-148 proton

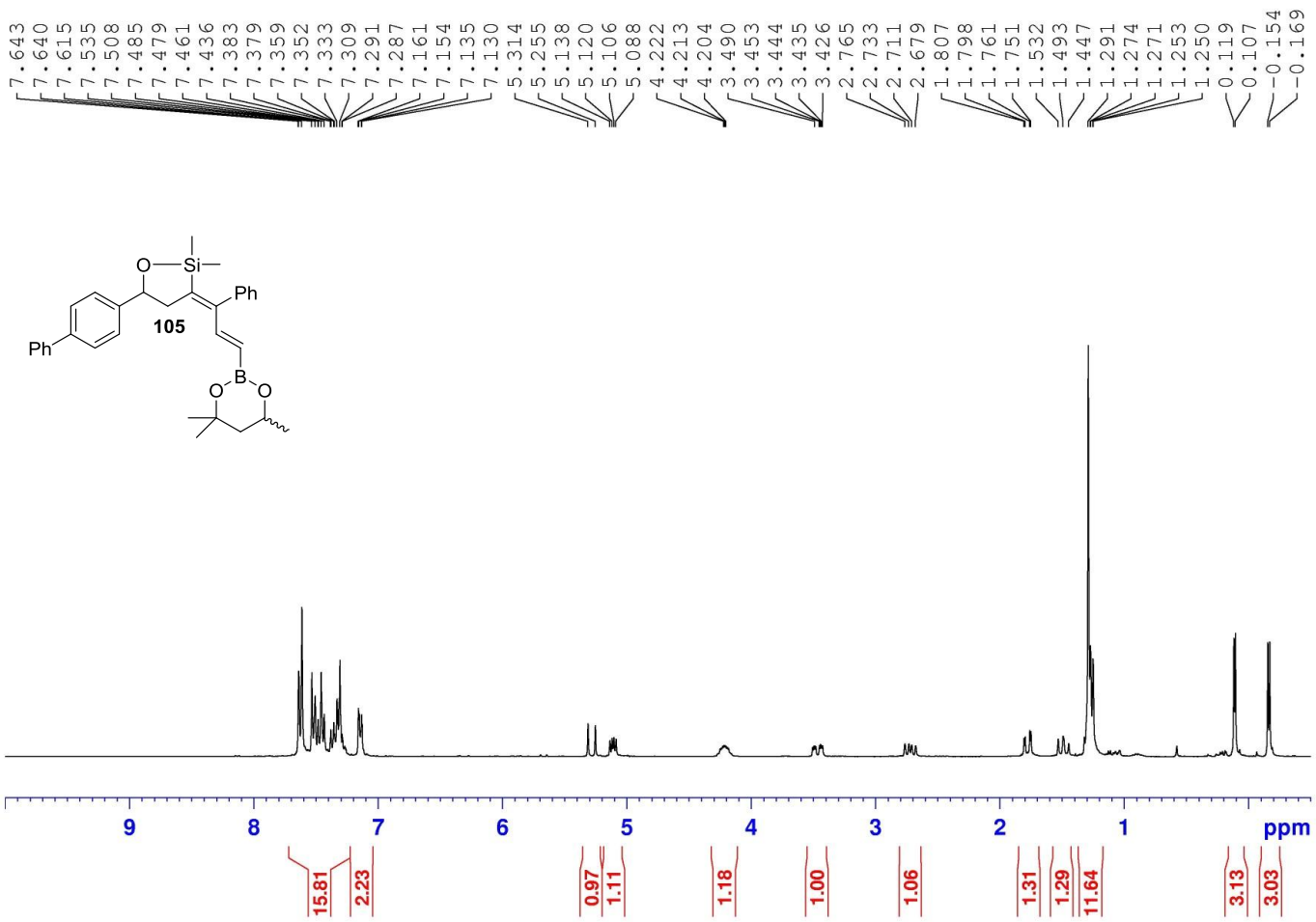


LAK-3-148 carbon

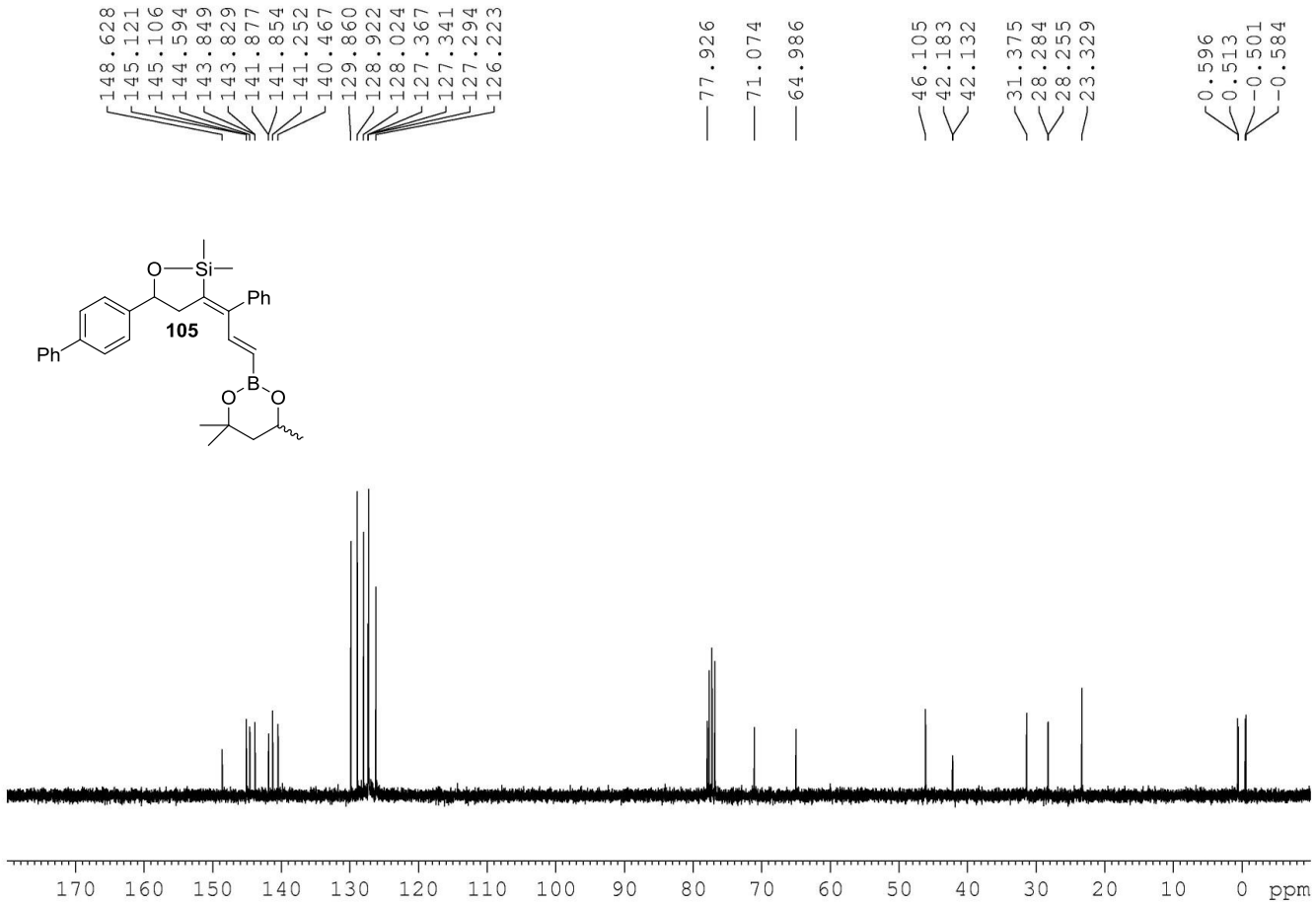



O
Si
Ph
104
B
O
O
NOESY
ppm
–1
0
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
0
–1
ppm

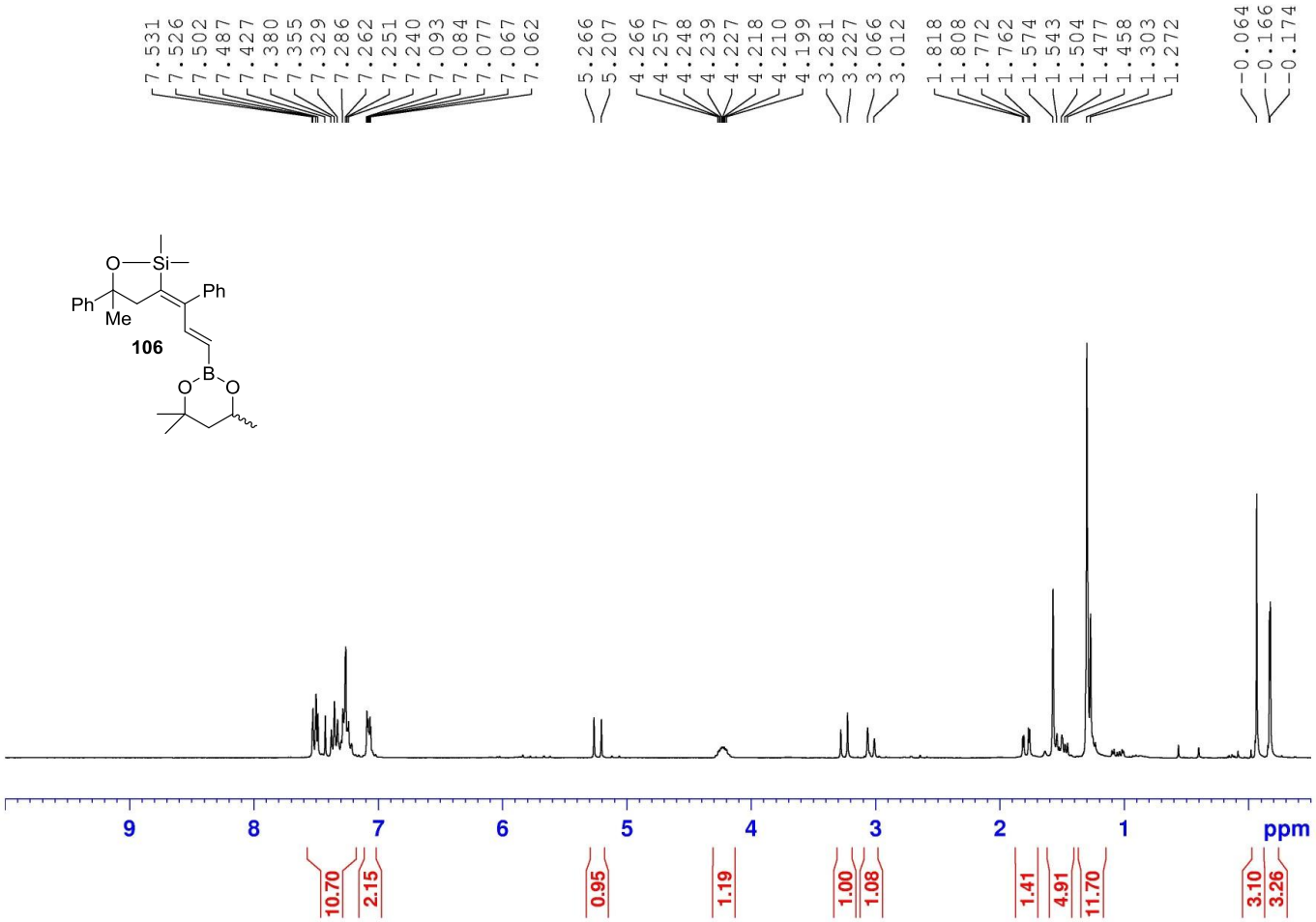
LAK-3-165


7.643
7.640
7.615
7.535
7.508
7.485
7.479
7.461
7.436
7.383
7.379
7.359
7.352
7.333
7.309
7.291
7.287
7.161
7.154
7.135
7.130
5.314
5.255
5.138
5.120
5.106
5.088
4.222
4.213
4.204
3.490
3.453
3.444
3.435
3.426
2.765
2.733
2.711
2.679
1.807
1.798
1.761
1.751
1.532
1.493
1.447
1.291
1.274
1.271
1.253
1.250
0.119
0.107
-0.154
-0.169
O
Si
Ph
105
Ph
O
B
O
9
8
7
6
5
4
3
2
1
ppm
15.81
2.23
0.97
1.11
1.18
1.00
1.06
1.31
1.29
11.64
3.13
3.03

LAK-3-165 carbon

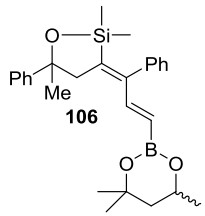


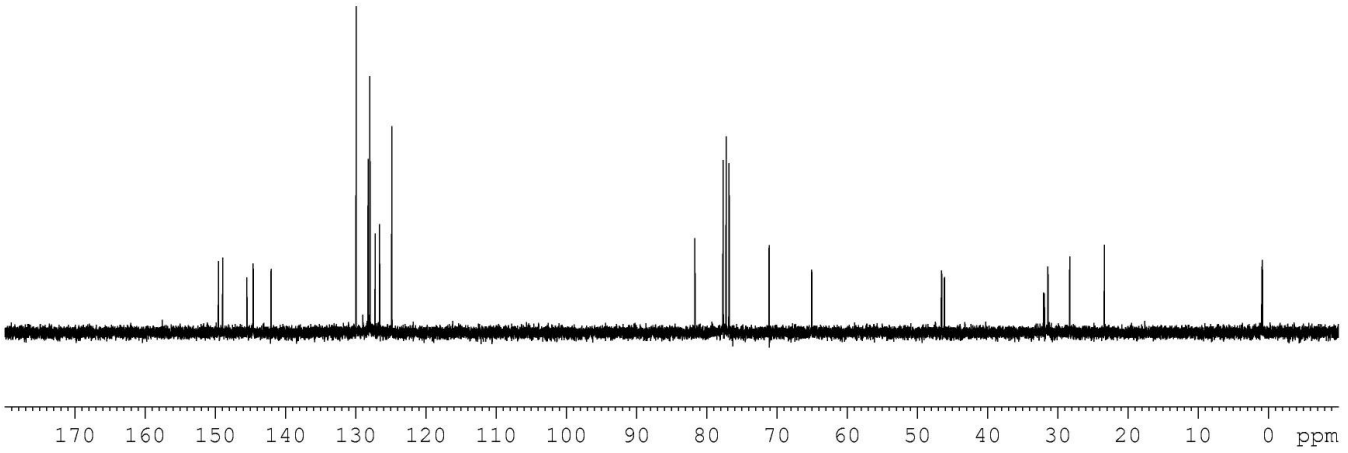
LAK-3-151-1

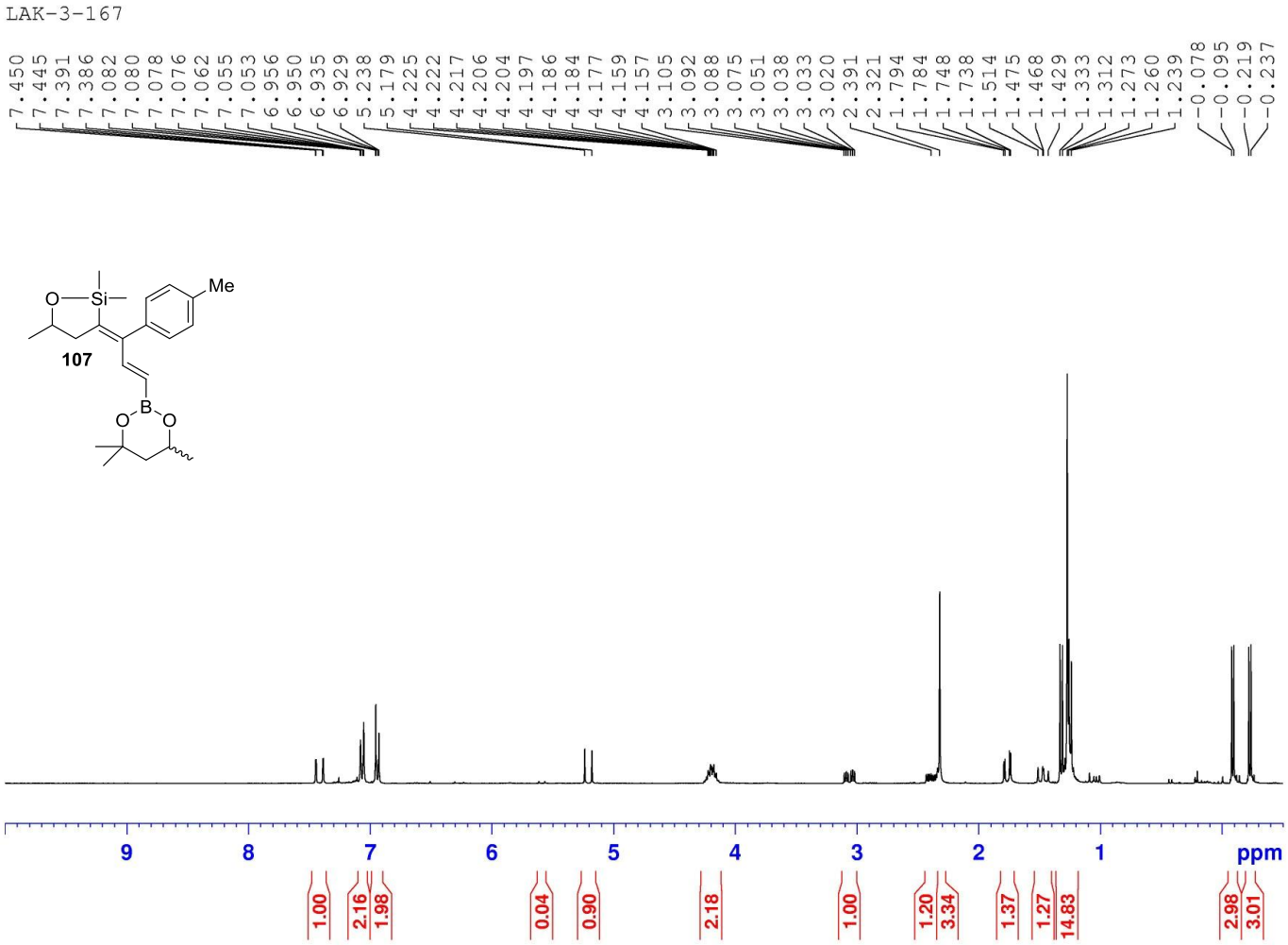

7.531
7.526
7.502
7.487
7.427
7.380
7.355
7.329
7.286
7.262
7.251
7.240
7.093
7.084
7.077
7.067
7.062
5.266
5.207
4.266
4.257
4.248
4.239
4.227
4.218
4.210
4.199
3.281
3.227
3.066
3.012
1.818
1.808
1.772
1.762
1.574
1.543
1.504
1.477
1.458
1.303
1.272
-0.064
-0.166
-0.174
O
Si
Ph
Ph
Me
106
B
O
O
9
8
7
6
5
4
3
2
1
ppm
10.70
2.15
0.95
1.19
1.00
1.08
1.41
4.91
11.70
3.10
3.26

LAK-3-151 carbon

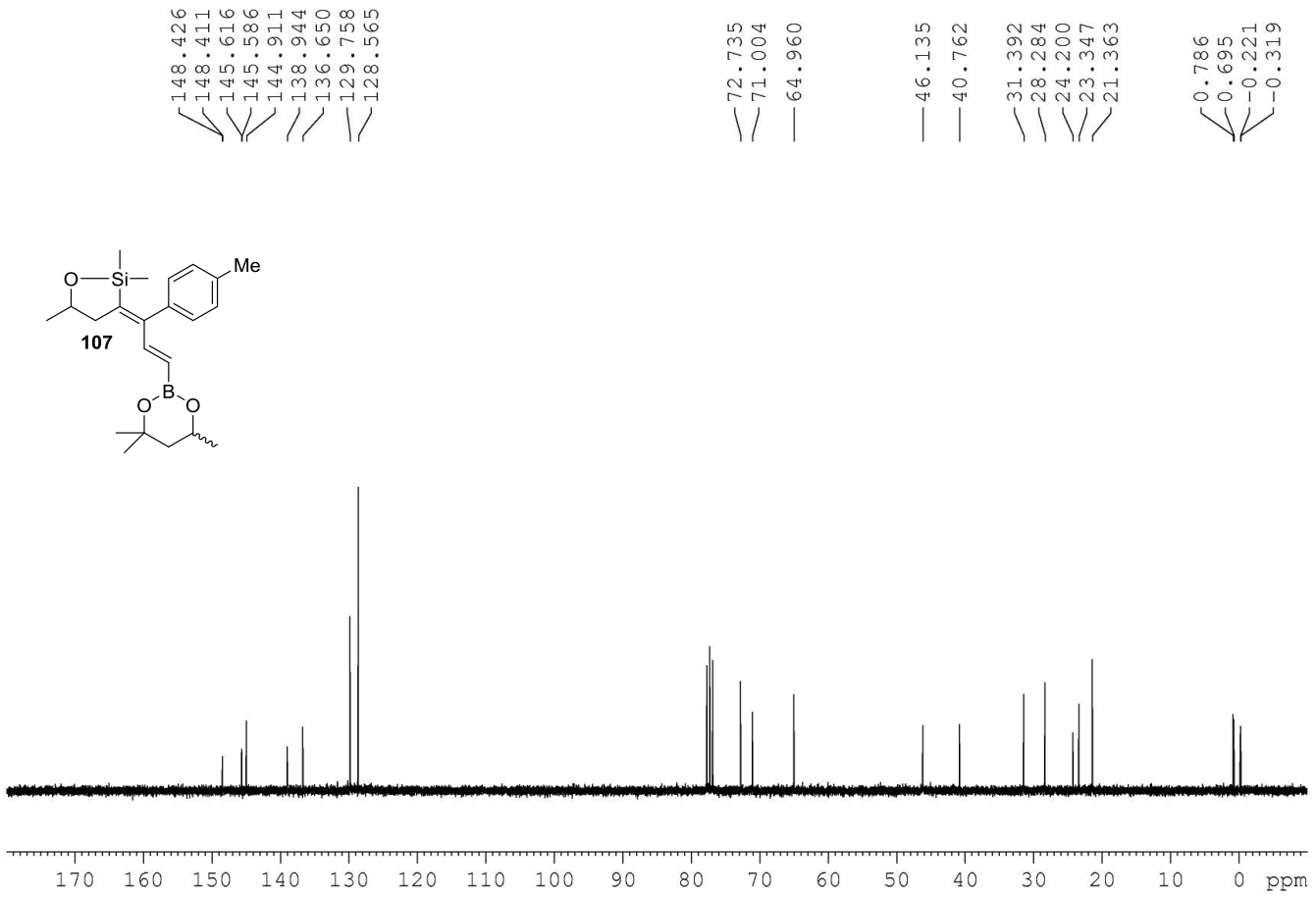
149.492
149.477
148.890
145.433
145.418
144.534
142.006
141.991
129.860
128.224
127.964
127.219
126.593
124.856
124.842
81.678
71.107
71.092
65.045
65.008
46.570
46.509
46.131
31.997
31.891
31.398
28.321
28.278
23.355
0.916
0.899
0.846
0.827



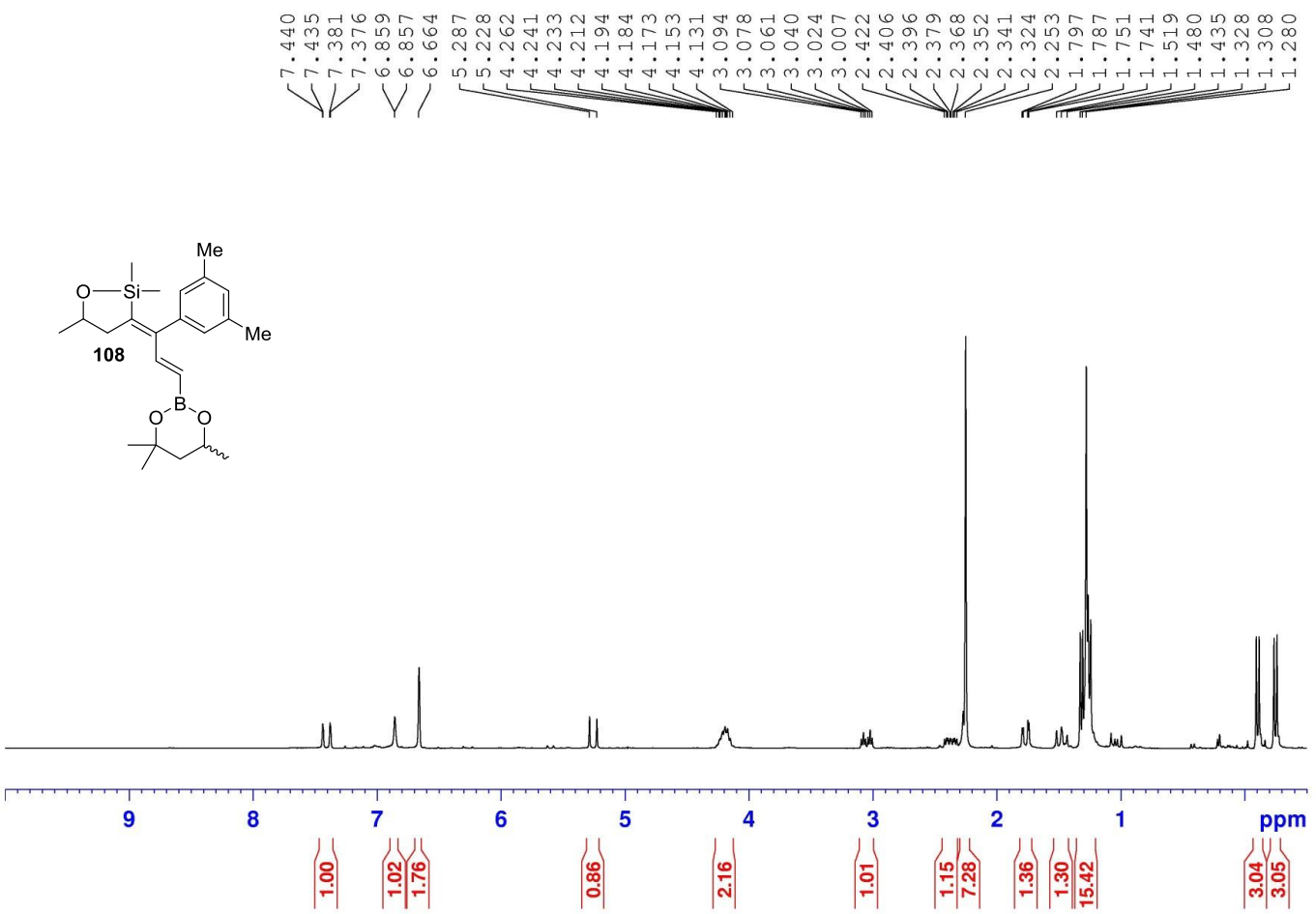



LAK-3-167
7.450
7.445
7.391
7.386
7.082
7.080
7.078
7.076
7.062
7.055
7.053
6.956
6.950
6.935
6.929
5.238
5.179
4.225
4.222
4.217
4.206
4.204
4.197
4.186
4.184
4.177
4.159
4.157
3.105
3.092
3.088
3.075
3.051
3.038
3.033
3.020
2.391
2.321
1.794
1.784
1.748
1.738
1.514
1.475
1.468
1.429
1.333
1.312
1.273
1.260
1.239
-0.078
-0.095
-0.219
-0.237
O
Si
Me
107
B
O
O
9
8
7
6
5
4
3
2
1
ppm
1.00
2.16
1.98
0.04
0.90
2.18
1.00
1.20
3.34
1.37
1.27
14.83
2.98
3.01

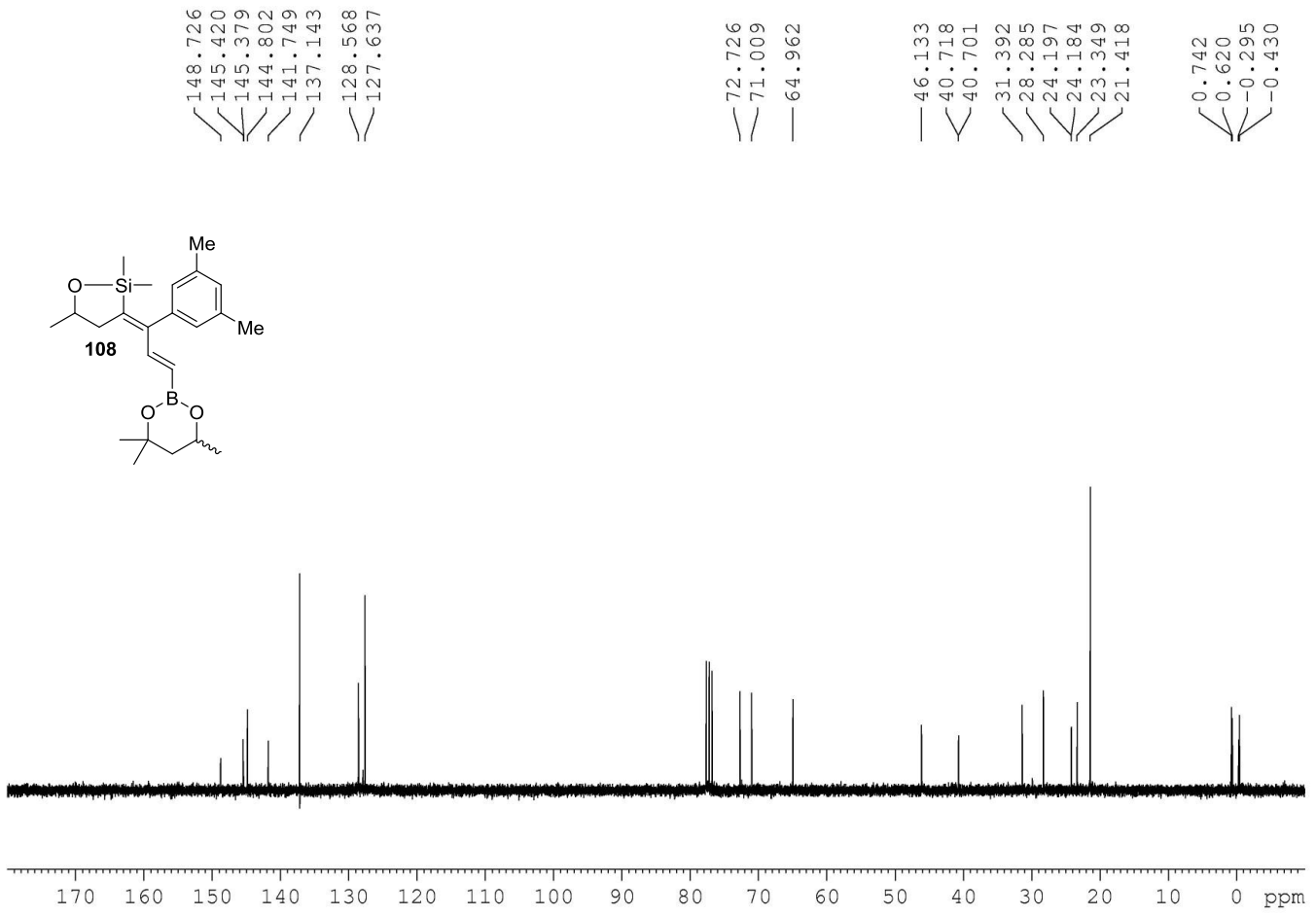
LAK-3-167 carbon



LAK-3-173

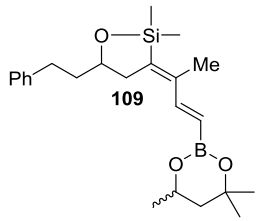

7.440
7.435
7.381
7.376
6.859
6.857
6.664
5.287
5.228
4.262
4.241
4.233
4.212
4.194
4.184
4.173
4.153
4.131
3.094
3.078
3.061
3.040
3.024
3.007
2.422
2.406
2.396
2.379
2.368
2.352
2.341
2.324
2.253
1.797
1.787
1.751
1.741
1.519
1.480
1.435
1.328
1.308
1.280
Me
O
Si
Me
108
B
O
O
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
1.76
0.86
2.16
1.01
1.15
7.28
1.36
1.30
15.42
3.04
3.05

LAK-3-154 carbon

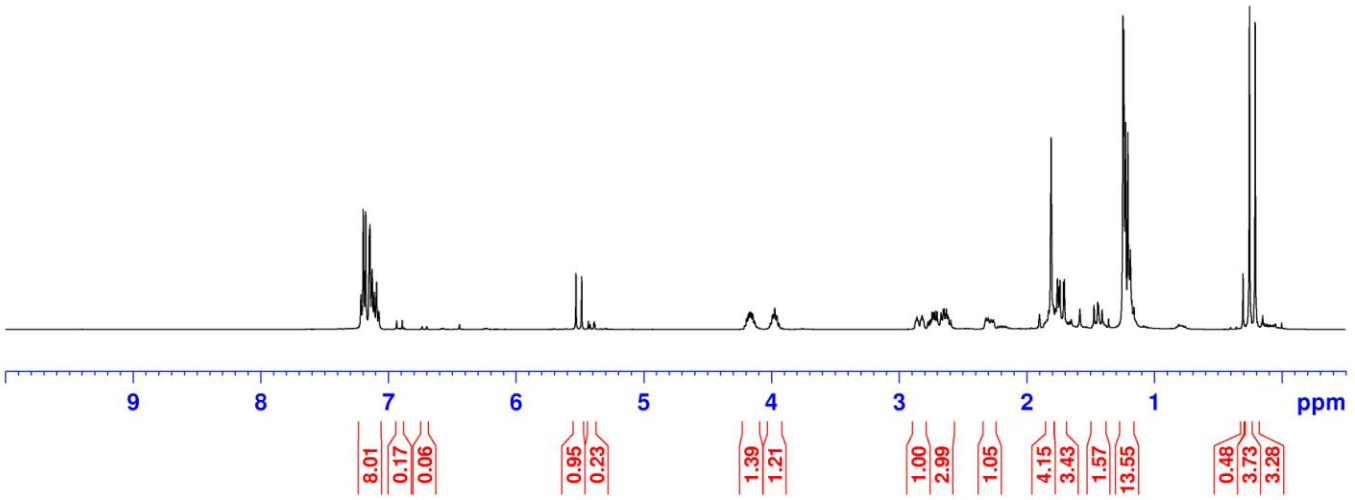


LAK-6-105

7.215
7.211
7.196
7.183
7.177
7.148
7.144
7.127
7.113
7.110
7.092
7.074
5.530
5.485
4.179
4.172
4.165
4.157
4.150
4.143
3.987
3.972
2.817
2.739
2.725
2.715
2.700
2.669
2.652
2.645
2.634
2.628
2.618
1.807
1.757
1.744
1.737
1.709
1.702
1.471
1.441
1.437
1.407
1.244
1.237
1.226
1.221
1.206
1.201
1.192
1.185
0.303
0.253
0.208

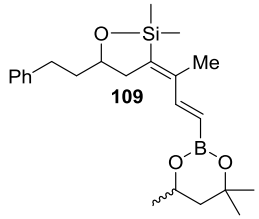


109

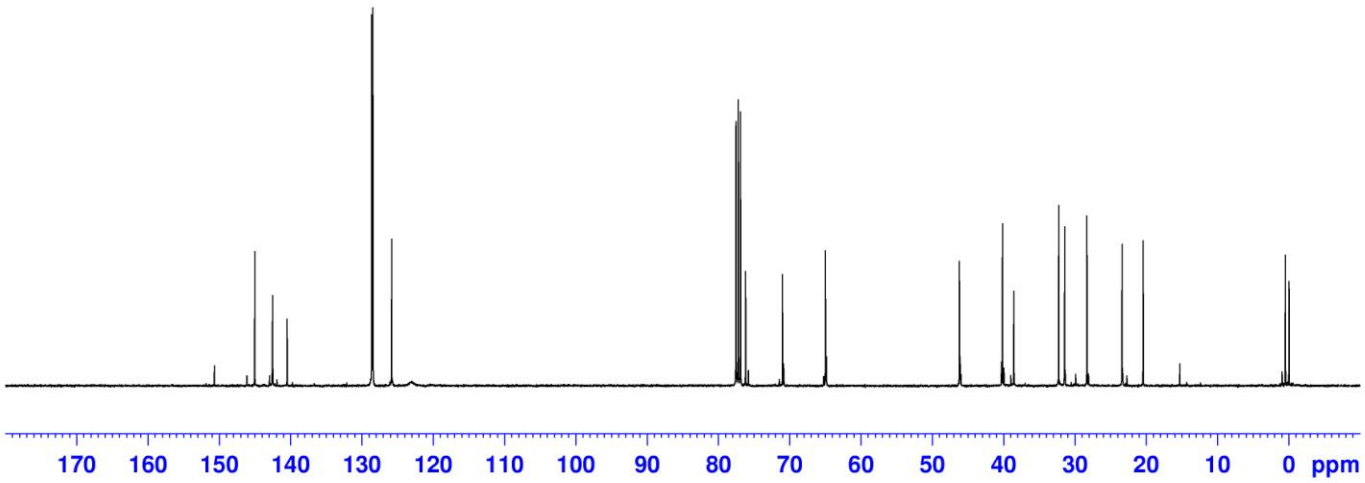


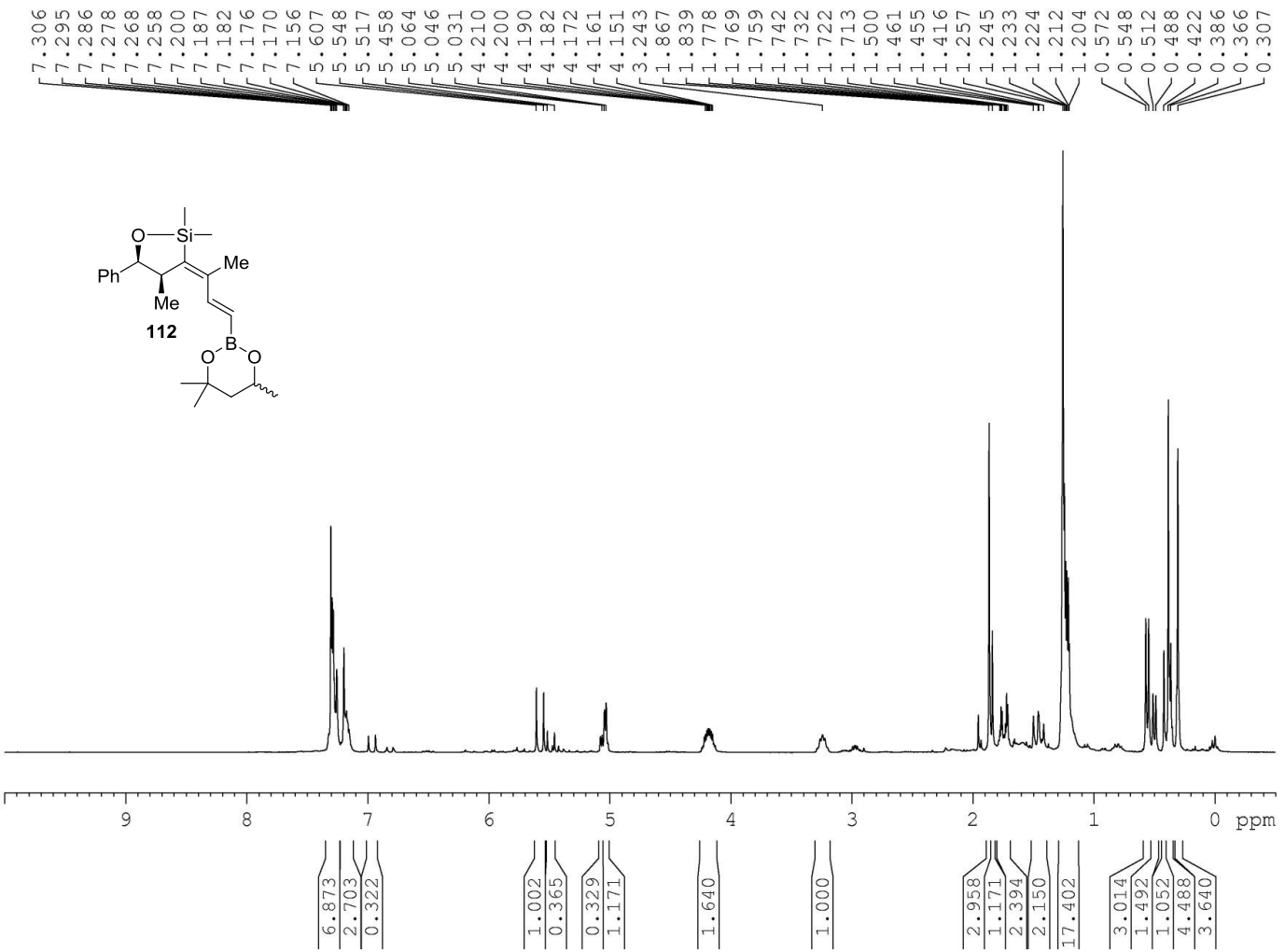
LAK-6-105

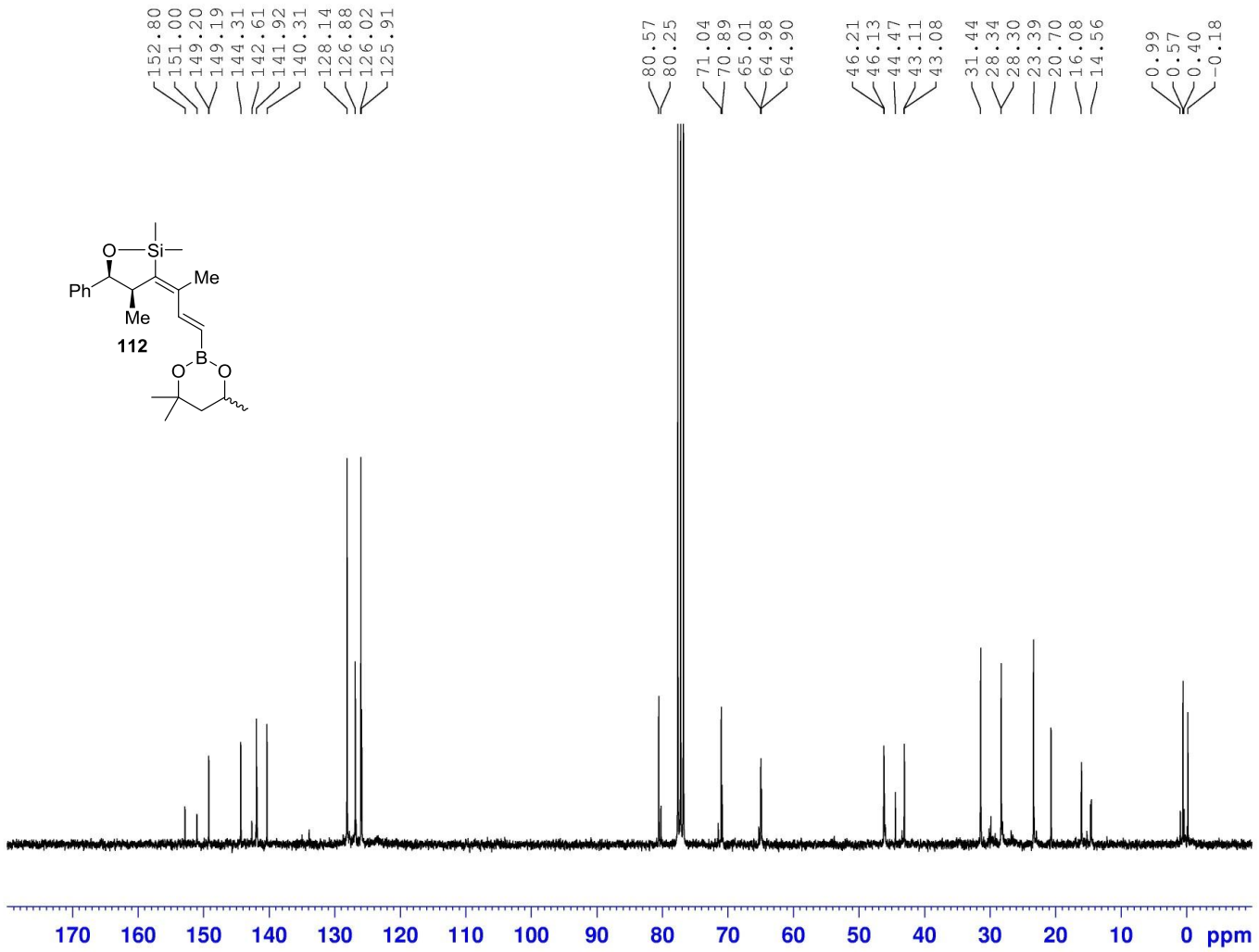
145.05
142.57
142.54
140.51
128.65
128.48
125.85
76.20
71.03
65.00
46.21
40.16
38.57
32.27
31.45
28.31
23.40
20.44
0.48
-0.04

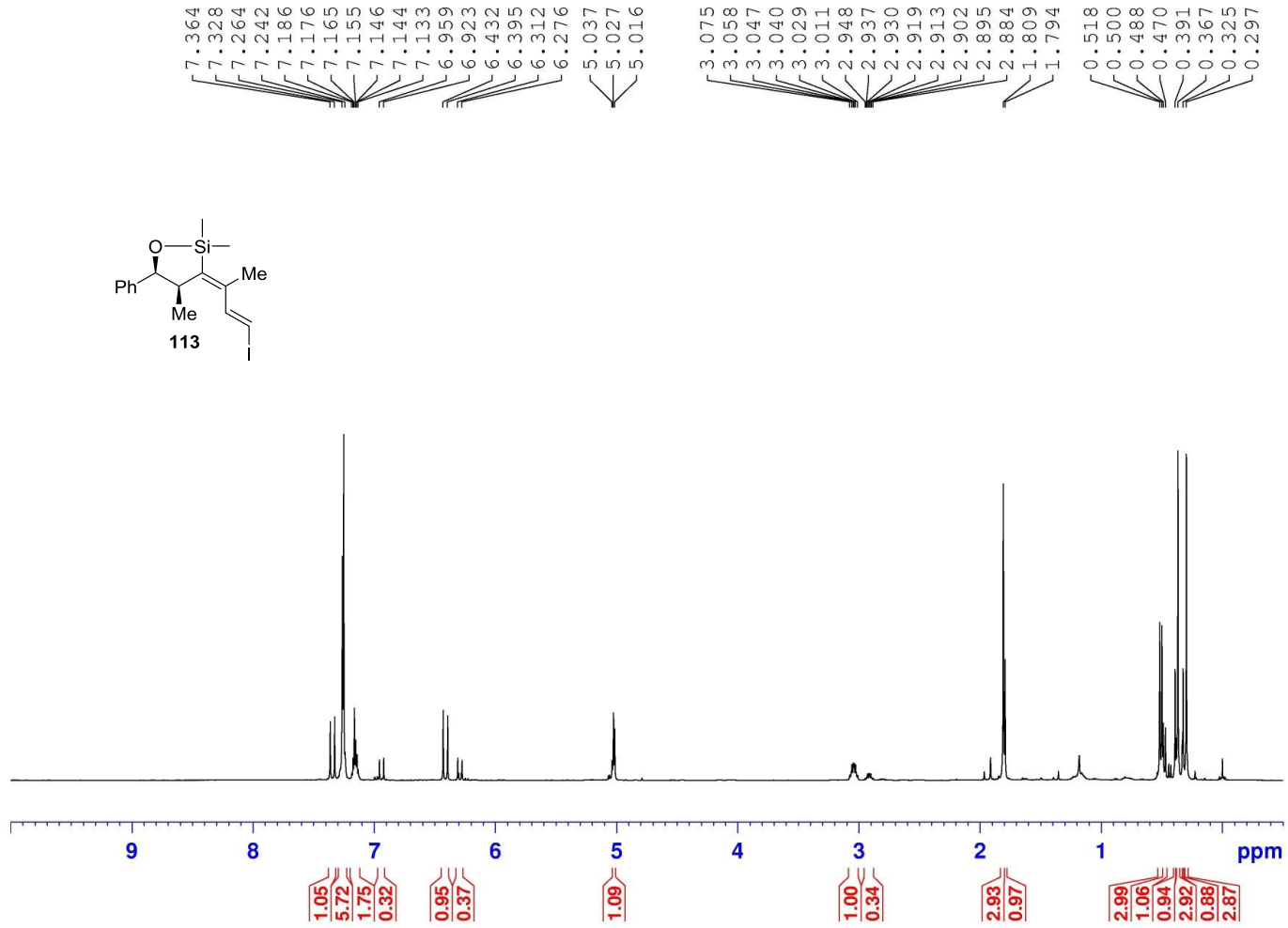


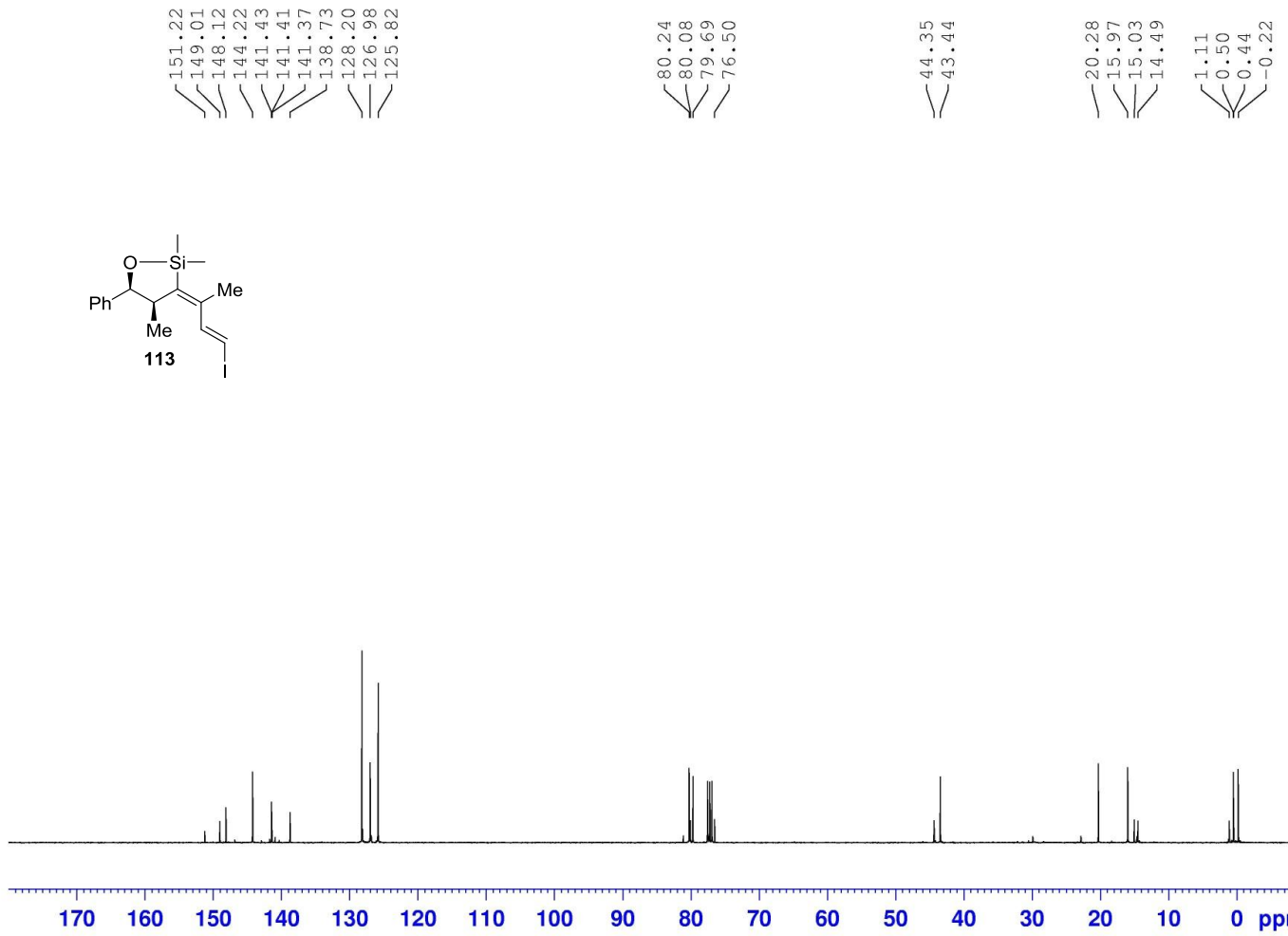
109

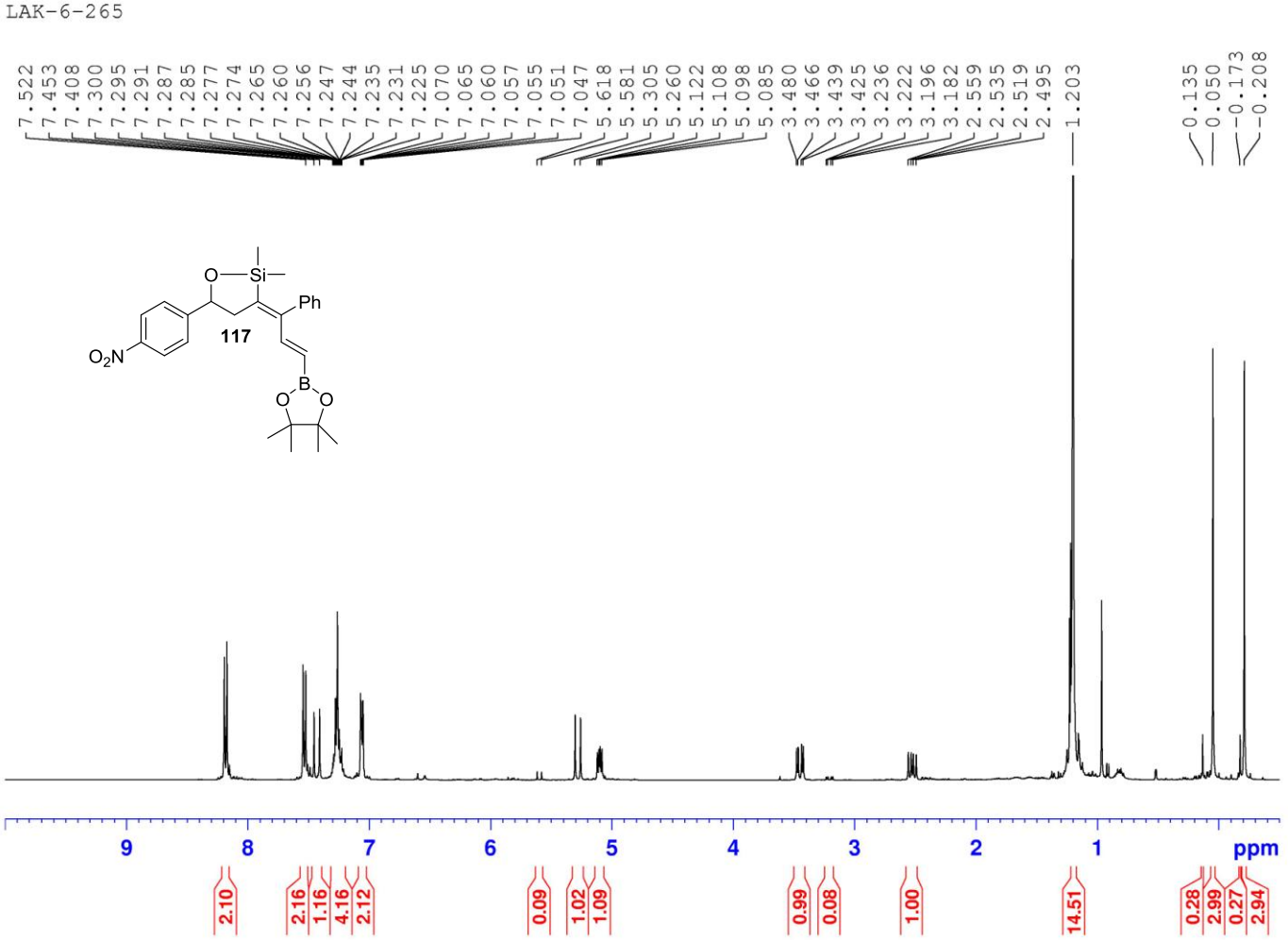



7.306
7.295
7.286
7.278
7.268
7.258
7.200
7.187
7.182
7.176
7.170
7.156
5.607
5.548
5.517
5.458
5.064
5.046
5.031
4.210
4.200
4.190
4.182
4.172
4.161
4.151
3.243
1.867
1.839
1.778
1.769
1.759
1.742
1.732
1.722
1.713
1.500
1.461
1.455
1.416
1.257
1.245
1.233
1.224
1.212
1.204
0.572
0.548
0.512
0.488
0.422
0.386
0.366
0.307
O
Si
Me
Ph
Me
112
B
O
O
9
8
7
6
5
4
3
2
1
0 ppm
6.873
2.703
0.322
1.002
0.365
0.329
1.171
1.640
1.000
2.958
1.171
2.394
2.150
17.402
3.014
1.492
1.052
4.488
3.640

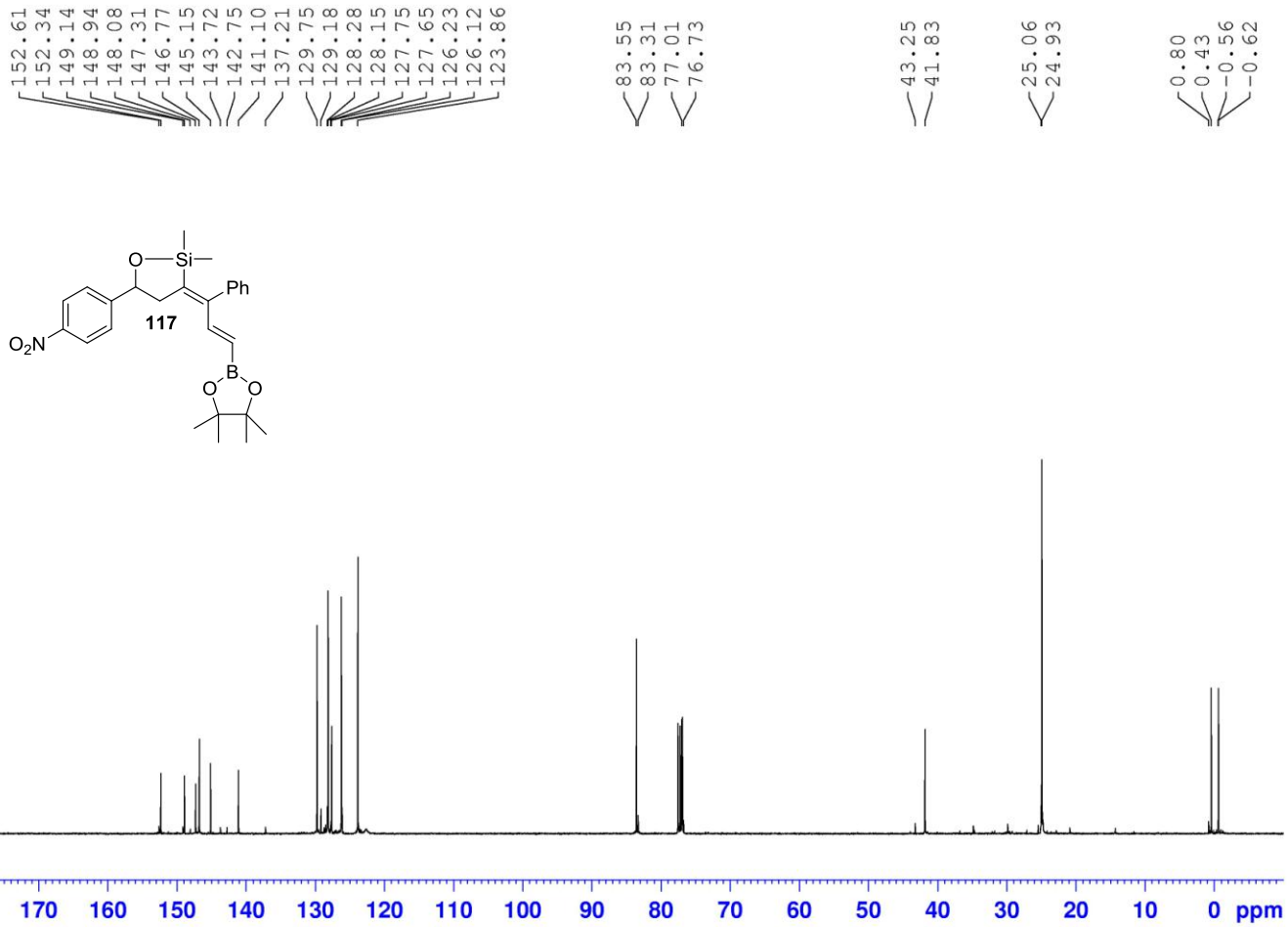

152.80
151.00
149.20
149.19
144.31
142.61
141.92
140.31
128.14
126.88
126.02
125.91
80.57
80.25
71.04
70.89
65.01
64.98
64.90
46.21
46.13
44.47
43.11
43.08
31.44
28.34
28.30
23.39
20.70
16.08
14.56
0.99
0.57
0.40
-0.18
O
Si
Ph
Me
Me
112
B
O
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

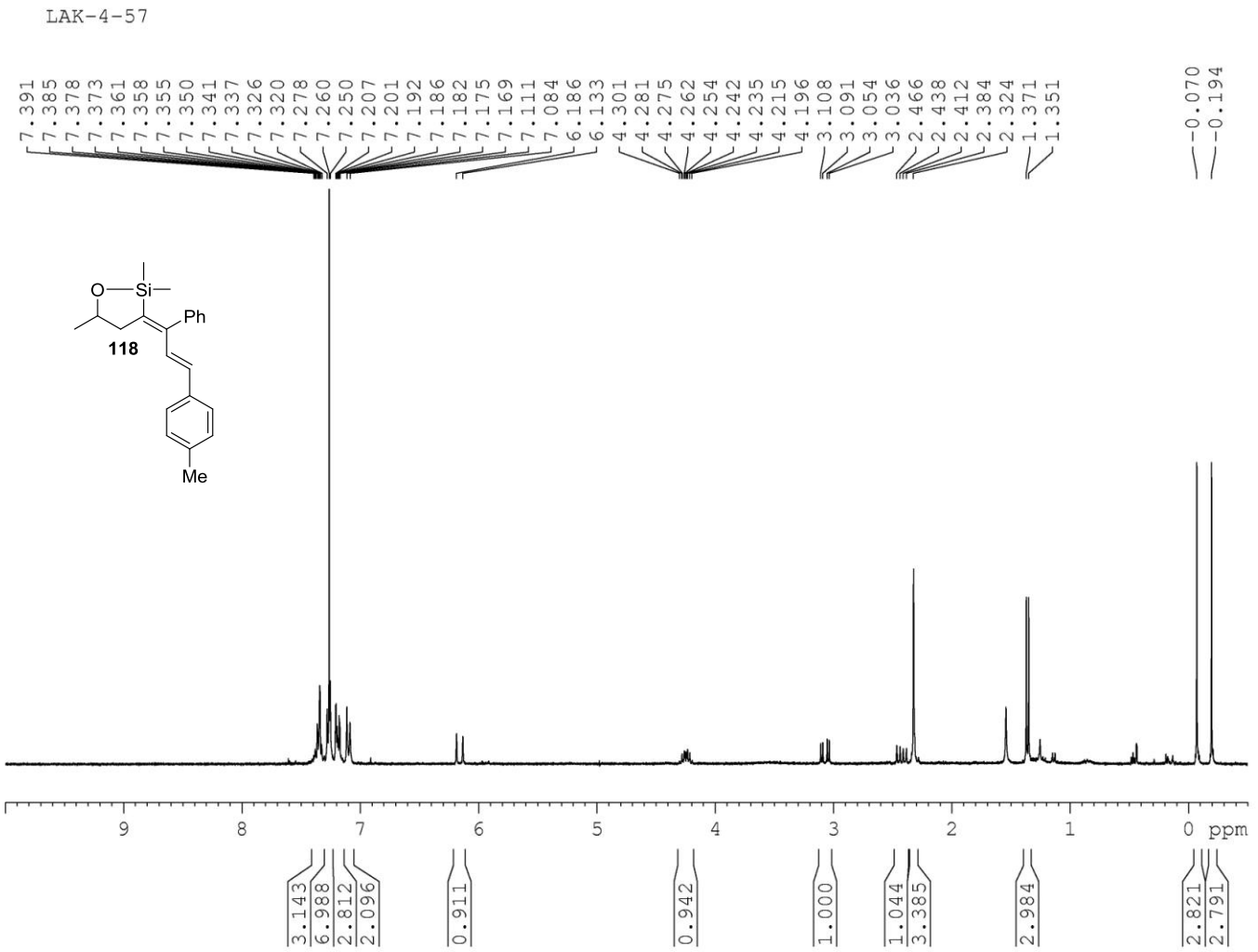

7.364
7.328
7.264
7.242
7.186
7.176
7.165
7.155
7.146
7.144
7.133
6.959
6.923
6.432
6.395
6.312
6.276
5.037
5.027
5.016
3.075
3.058
3.047
3.040
3.029
3.011
2.948
2.937
2.930
2.919
2.913
2.902
2.895
2.884
1.809
1.794
0.518
0.500
0.488
0.470
0.391
0.367
0.325
0.297
O
Si
Ph
Me
Me
I
113
9
8
7
6
5
4
3
2
1
ppm
1.05
5.72
1.75
0.32
0.95
0.37
1.09
1.00
0.34
2.93
0.97
2.99
1.06
0.94
2.92
0.88
2.87

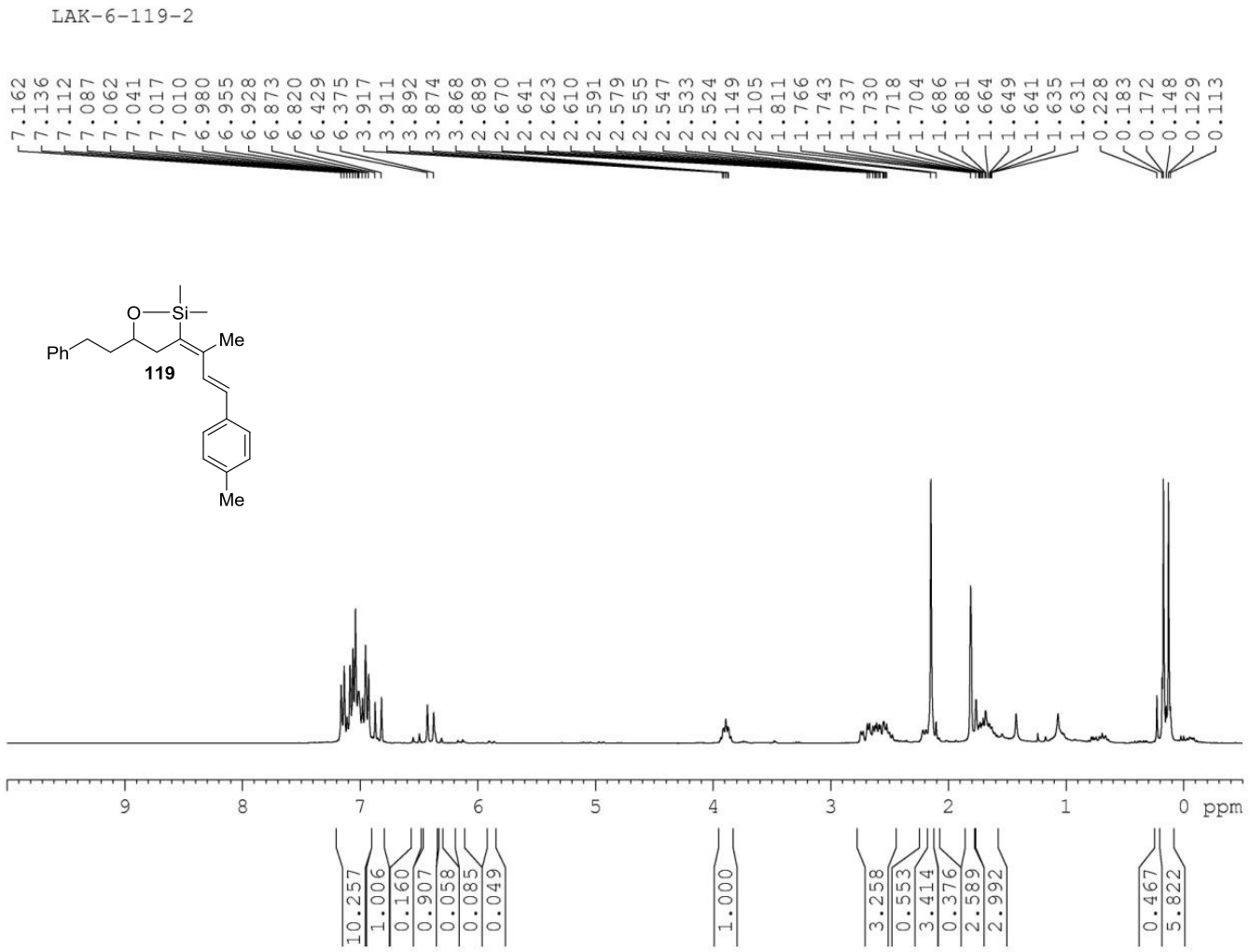

151.22
149.01
148.12
144.22
141.43
141.41
141.37
138.73
128.20
126.98
125.82
80.24
80.08
79.69
76.50
44.35
43.44
20.28
15.97
15.03
14.49
1.11
0.50
0.44
-0.22
O
Si
Ph
Me
Me
I
113
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


LAK-6-265
7.522
7.453
7.408
7.300
7.295
7.291
7.287
7.285
7.277
7.274
7.265
7.260
7.256
7.247
7.244
7.235
7.231
7.225
7.070
7.065
7.060
7.057
7.055
7.051
7.047
5.618
5.581
5.305
5.260
5.122
5.108
5.098
5.085
3.480
3.466
3.439
3.425
3.236
3.222
3.196
3.182
2.559
2.535
2.519
2.495
1.203
0.135
0.050
-0.173
-0.208
O
Si
Ph
117
O2N
B
O
O
9
8
7
6
5
4
3
2
1
ppm
2.10
2.16
1.16
4.16
2.12
0.09
1.02
1.09
0.99
0.08
1.00
14.51
0.28
2.99
0.27
2.94

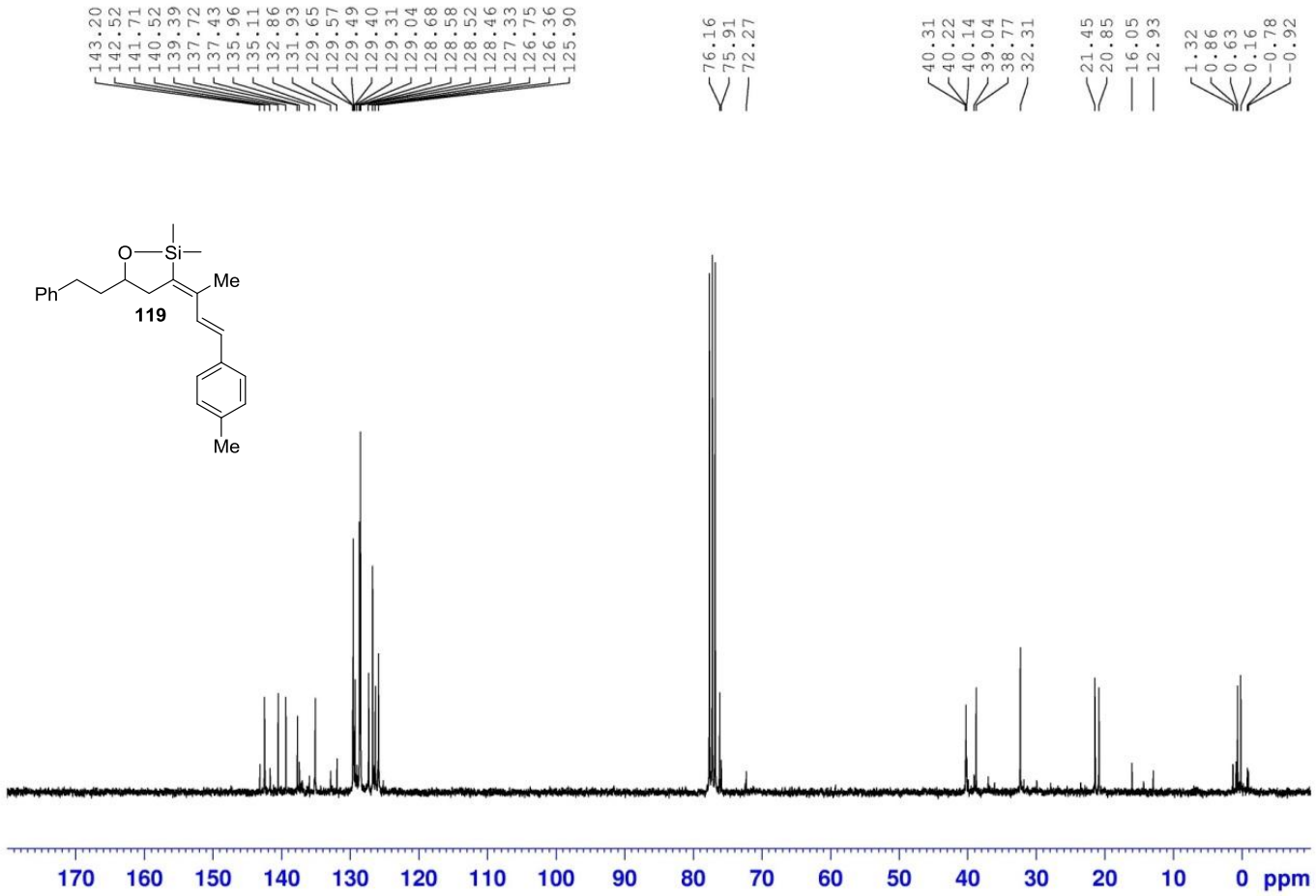
LAK-6-265

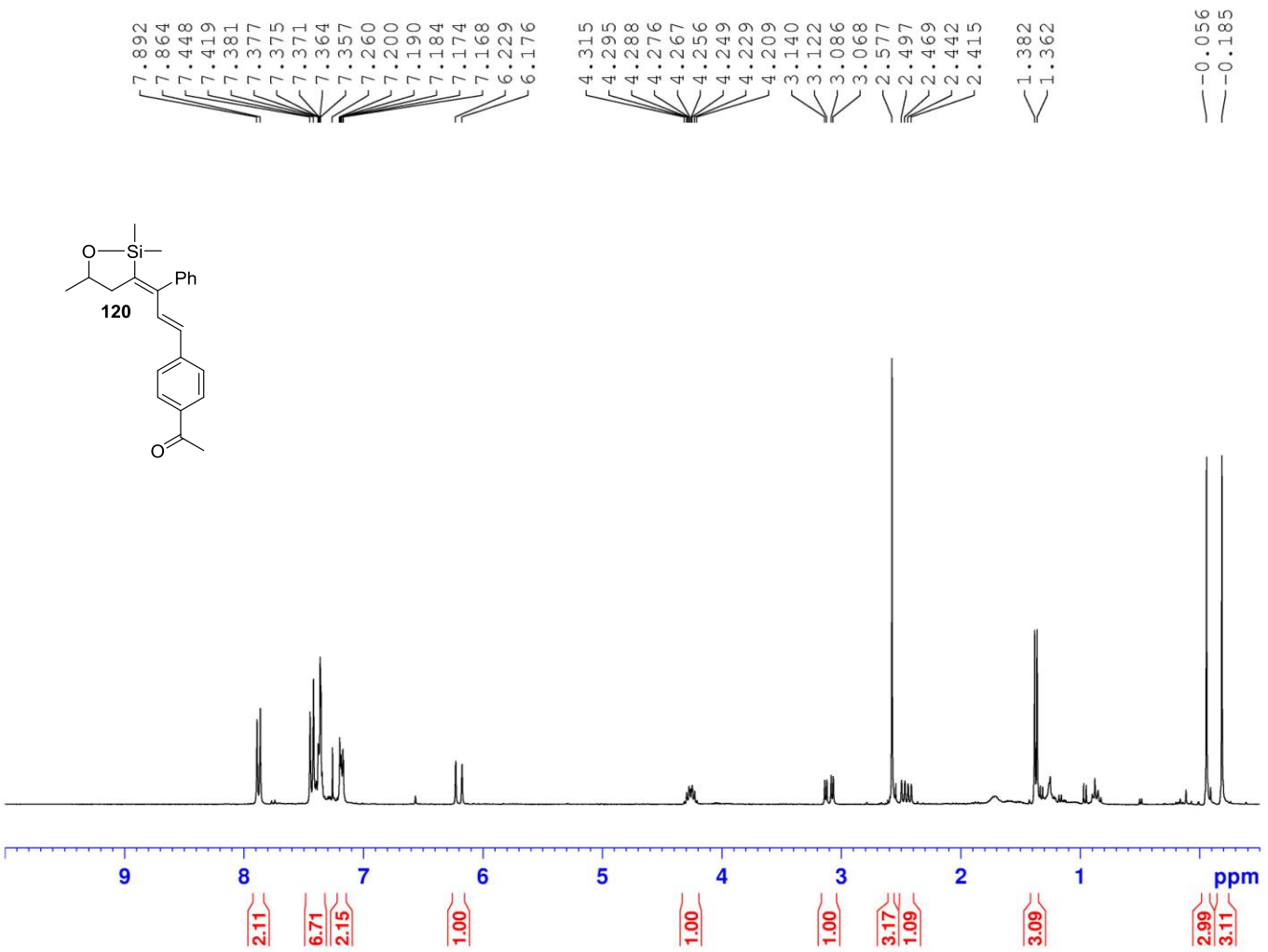

152.61
152.34
149.14
148.94
148.08
147.31
146.77
145.15
143.72
142.75
141.10
137.21
129.75
129.18
128.28
128.15
127.75
127.65
126.23
126.12
123.86
83.55
83.31
77.01
76.73
43.25
41.83
25.06
24.93
0.80
0.43
-0.56
-0.62
O
Si
Ph
117
O2N
B
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

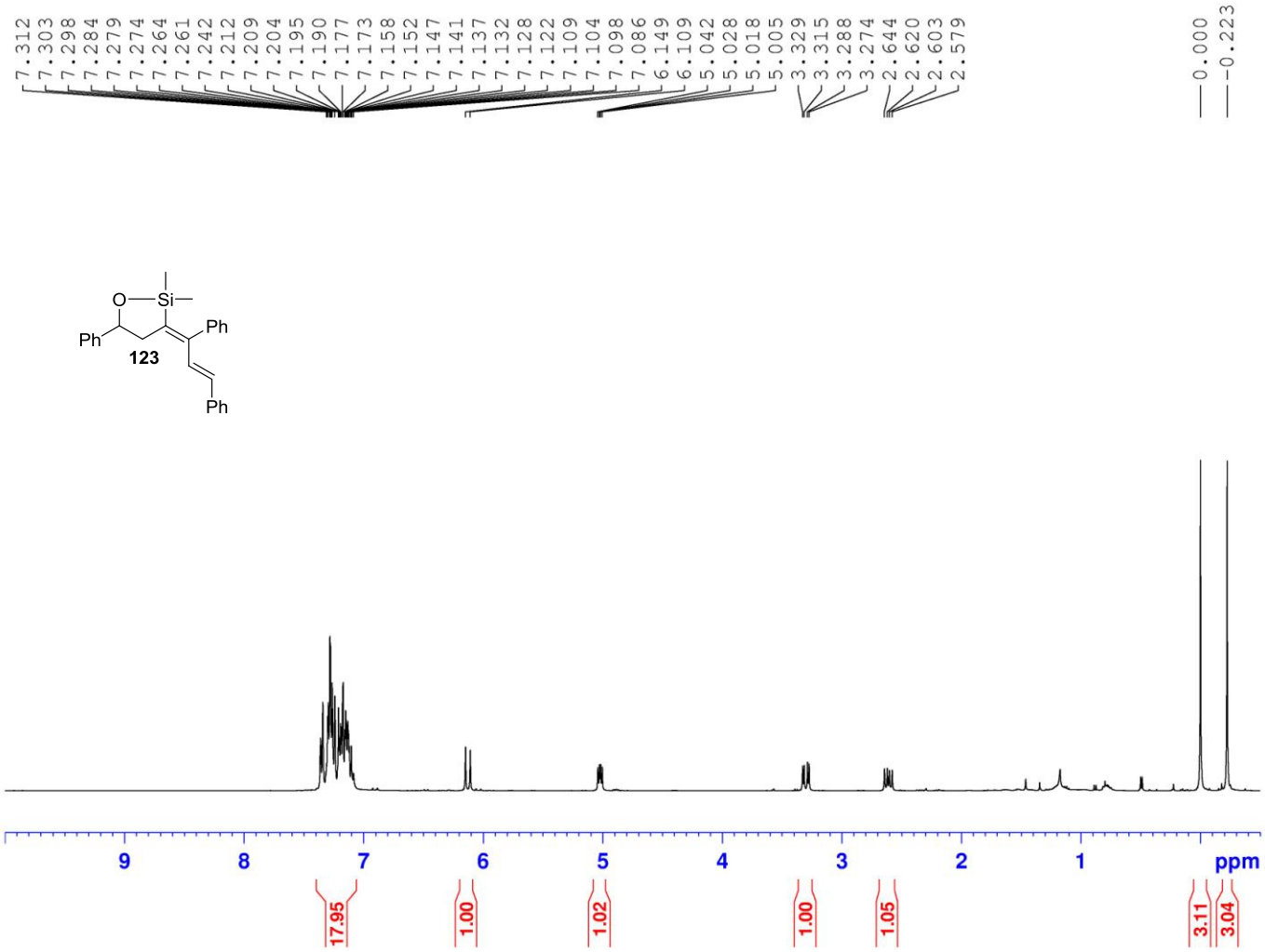

LAK-4-57
7.391
7.385
7.378
7.373
7.361
7.358
7.355
7.350
7.341
7.337
7.326
7.320
7.278
7.260
7.250
7.207
7.201
7.192
7.186
7.182
7.175
7.169
7.111
7.084
6.186
6.133
4.301
4.281
4.275
4.262
4.254
4.242
4.235
4.215
4.196
3.108
3.091
3.054
3.036
2.466
2.438
2.412
2.384
2.324
1.371
1.351
-0.070
-0.194
O
Si
Ph
Me
118
9
8
7
6
5
4
3
2
1
0
ppm
3.143
6.988
2.812
2.096
0.911
0.942
1.000
1.044
3.385
2.984
2.821
2.791


LAK-6-119-2
7.162
7.136
7.112
7.087
7.062
7.041
7.017
7.010
6.980
6.955
6.928
6.873
6.820
6.429
6.375
3.917
3.911
3.892
3.874
3.868
3.689
2.670
2.641
2.623
2.610
2.591
2.579
2.555
2.547
2.533
2.524
2.149
2.105
1.811
1.766
1.743
1.737
1.730
1.718
1.704
1.686
1.681
1.664
1.649
1.641
1.635
1.631
0.228
0.183
0.172
0.148
0.129
0.113
O
Si
Me
Ph
119
Me
9
8
7
6
5
4
3
2
1
0 ppm
10.257
1.006
0.160
0.907
0.058
0.085
0.049
1.000
3.258
0.553
3.414
0.376
2.589
2.992
0.467
5.822

LAK-6-119-2
carbon

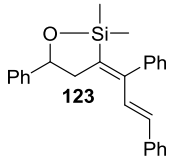



7.892
7.864
7.448
7.419
7.381
7.377
7.375
7.371
7.364
7.357
7.260
7.200
7.190
7.184
7.174
7.168
6.229
6.176
4.315
4.295
4.288
4.276
4.267
4.256
4.249
4.229
4.209
3.140
3.122
3.086
3.068
2.577
2.497
2.469
2.442
2.415
1.382
1.362
-0.056
-0.185
O
Si
Ph
120
O
9
8
7
6
5
4
3
2
1
ppm
2.11
6.71
2.15
1.00
1.00
1.00
3.17
1.09
3.09
2.99
3.11

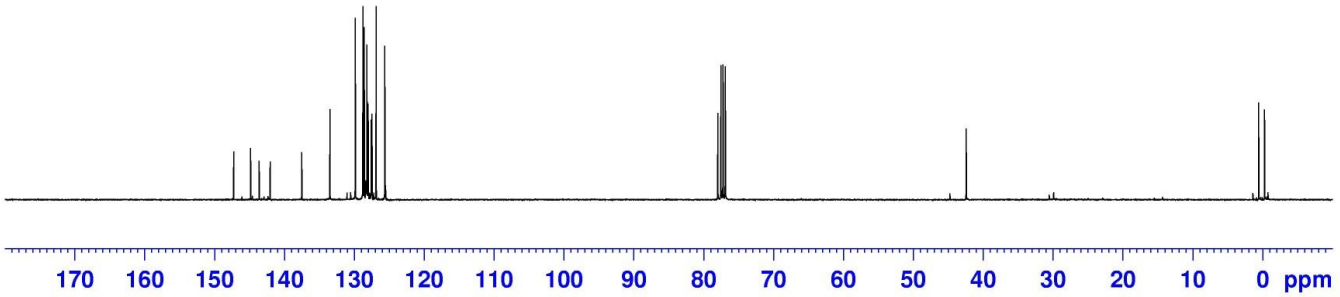

7.312
7.303
7.298
7.284
7.279
7.274
7.264
7.261
7.242
7.212
7.209
7.204
7.195
7.190
7.177
7.173
7.158
7.152
7.147
7.141
7.137
7.132
7.128
7.122
7.109
7.104
7.098
7.086
6.149
6.109
5.042
5.028
5.018
5.005
3.329
3.315
3.288
3.274
2.644
2.620
2.603
2.579
0.000
-0.223
O
Si
Ph
Ph
Ph
123
9
8
7
6
5
4
3
2
1
ppm
17.95
1.00
1.02
1.00
1.05
3.11
3.04

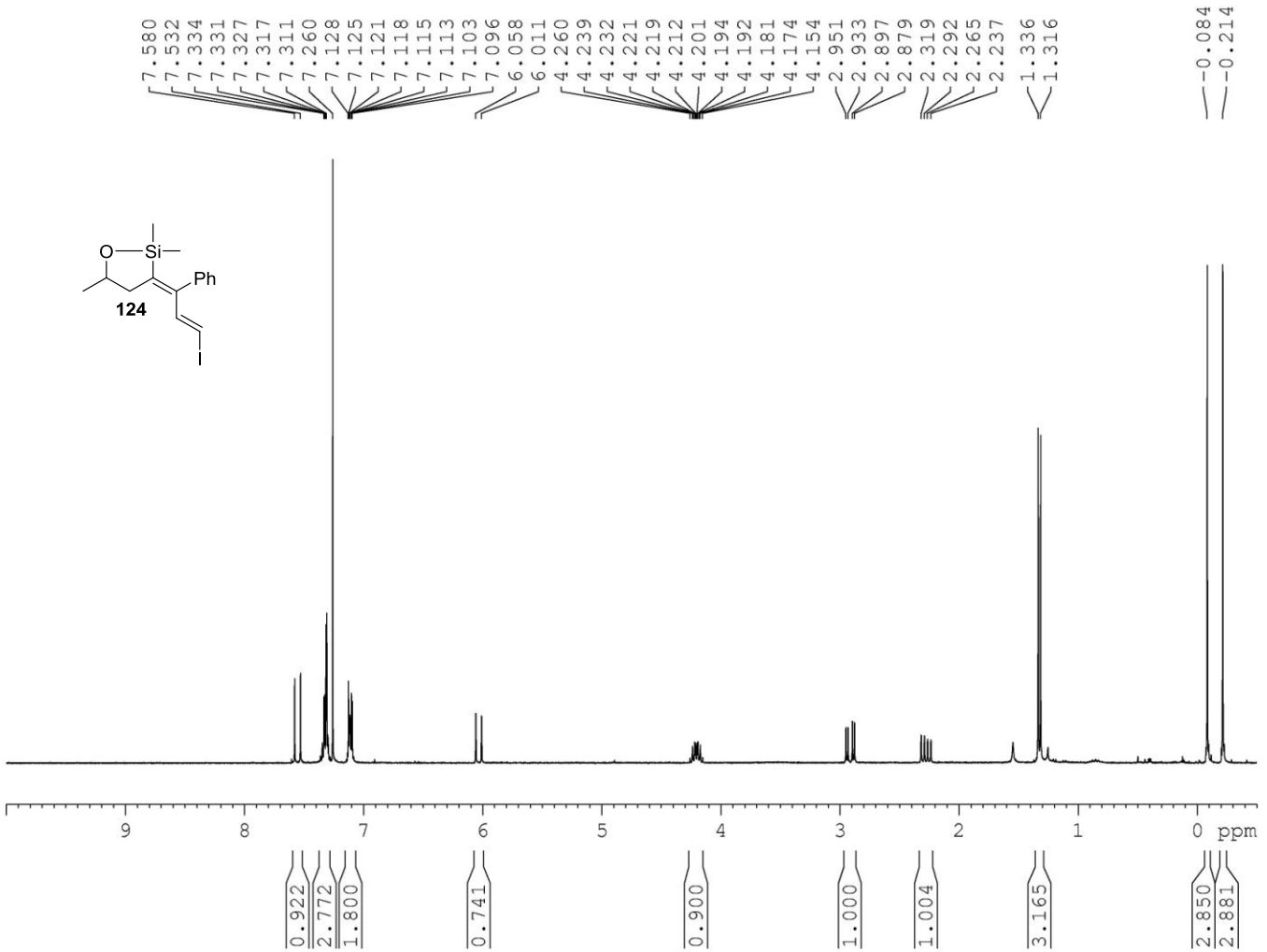
LAK-6-220

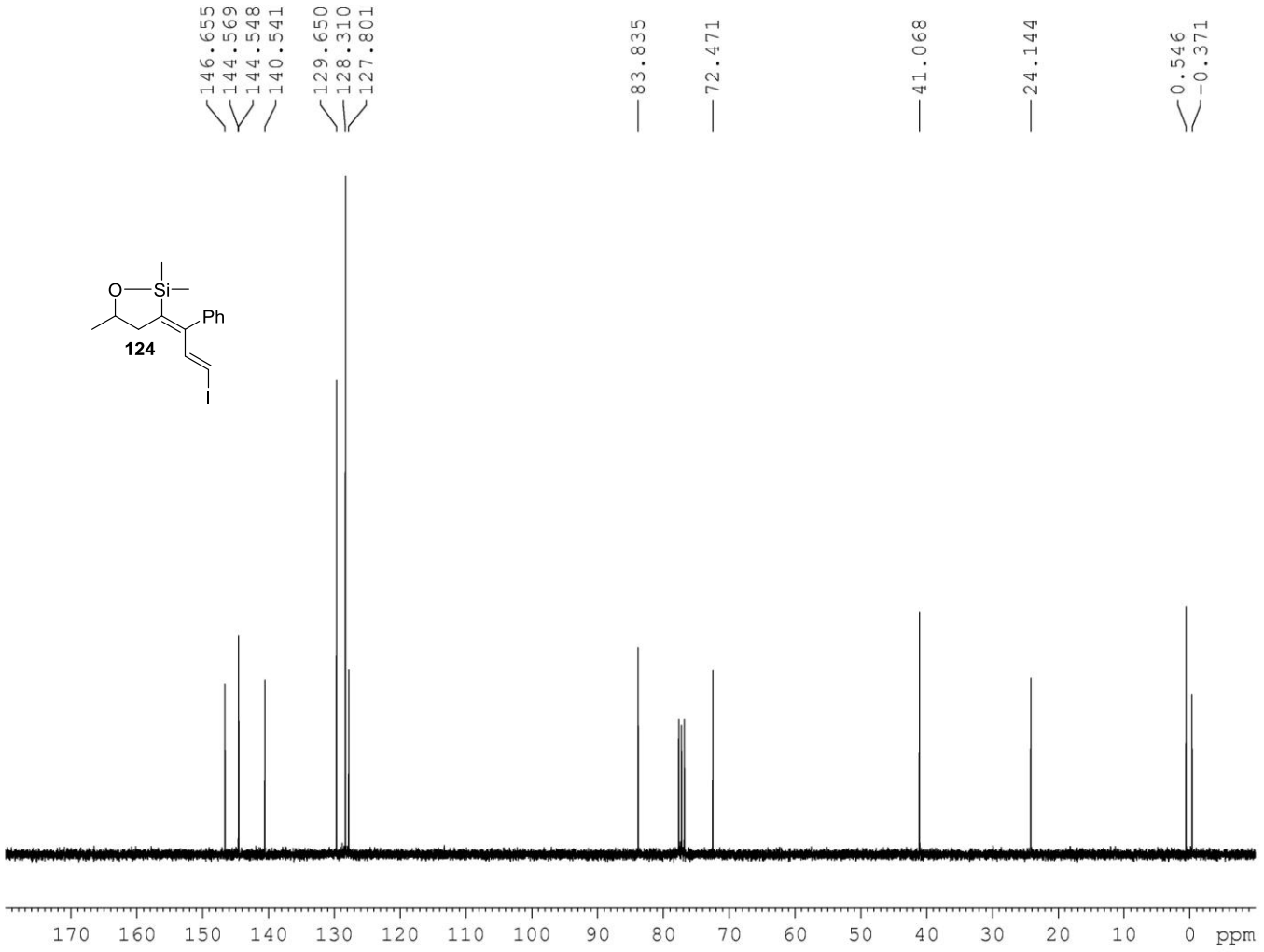

147.30
144.86
143.64
142.08
137.54
133.51
129.88
128.79
128.61
128.22
128.07
128.01
127.61
127.50
126.90
125.65
77.99
42.43
0.56
-0.28


O
Si
Ph
Ph
Ph

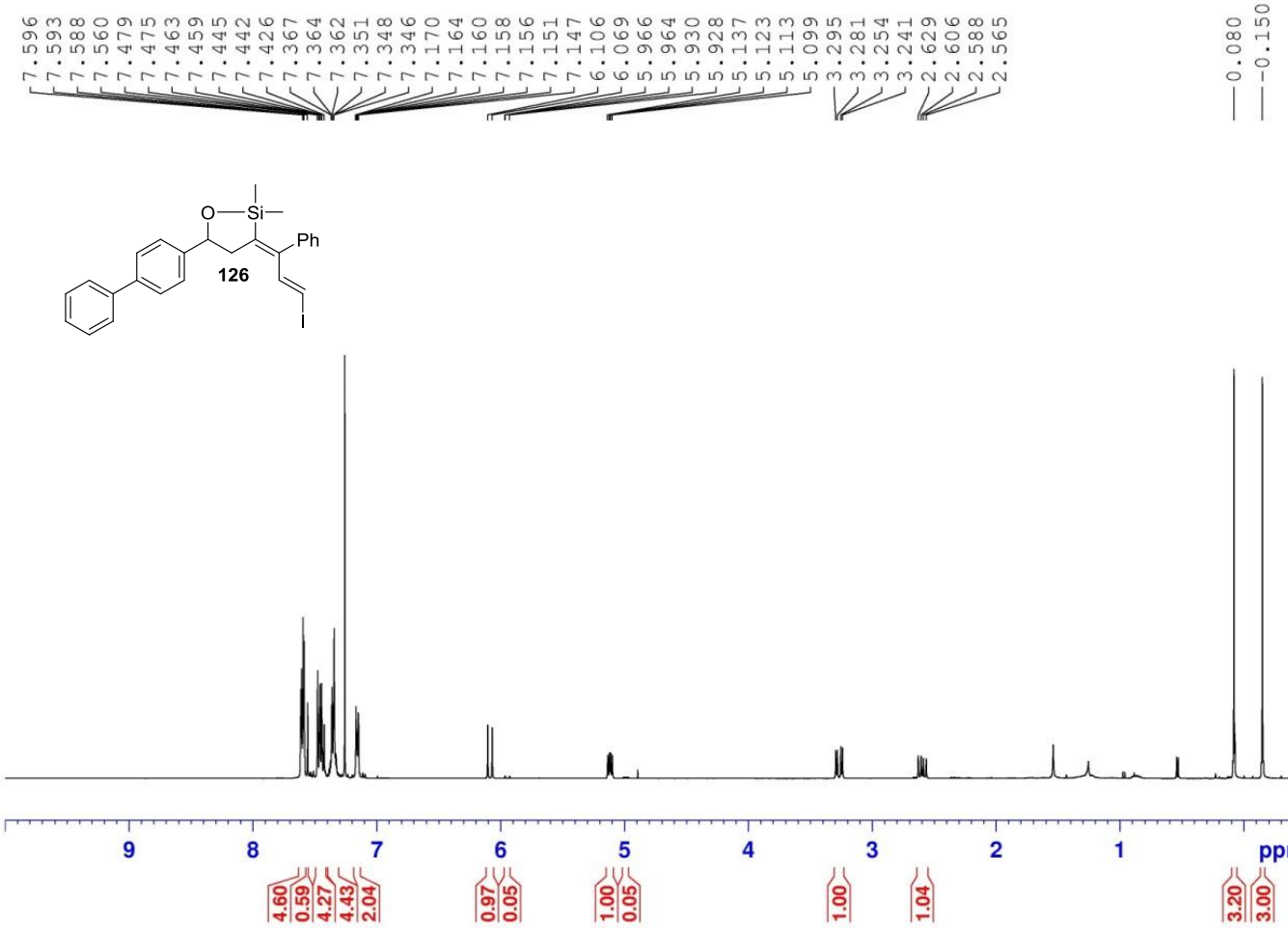
123

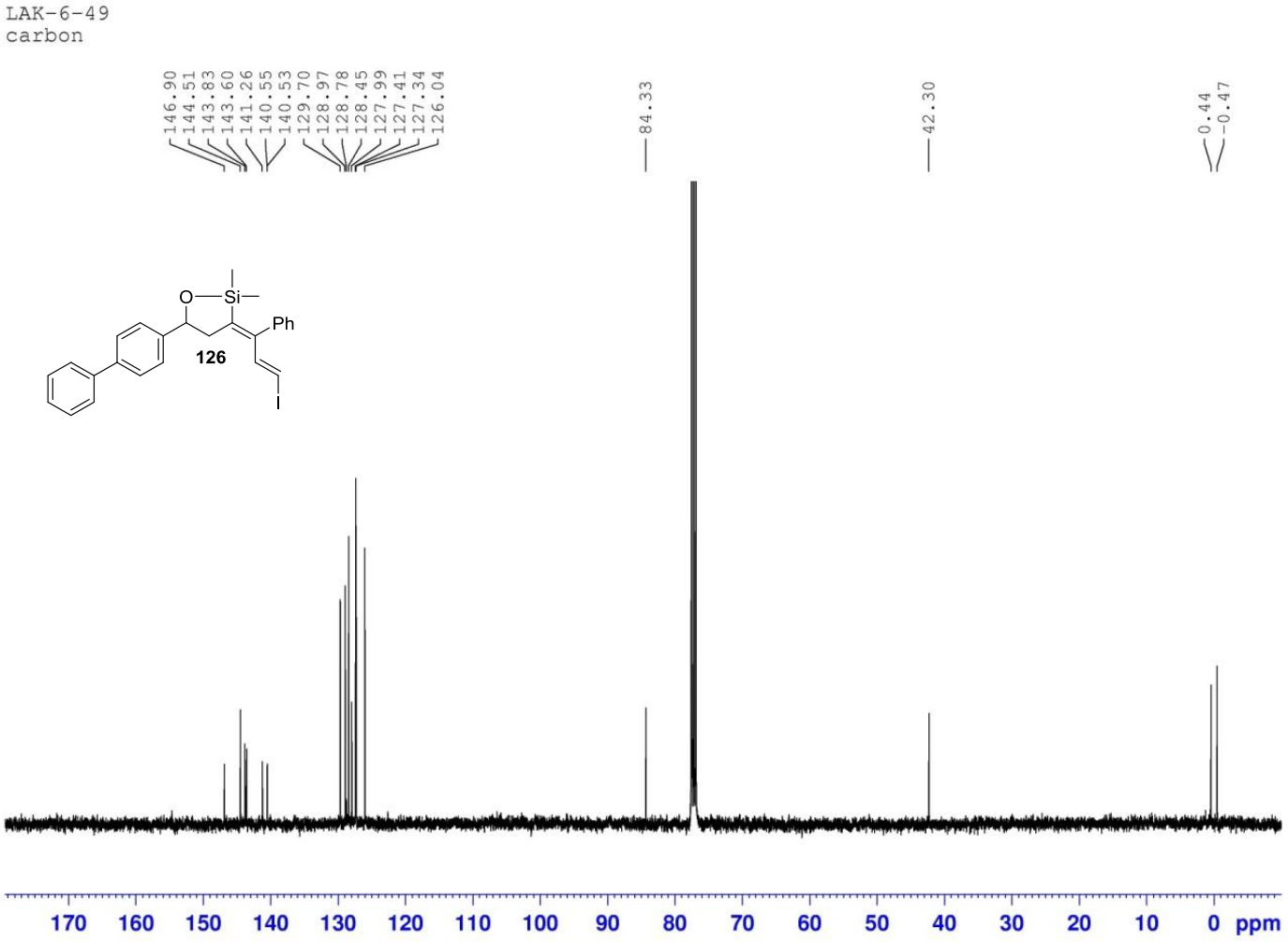

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

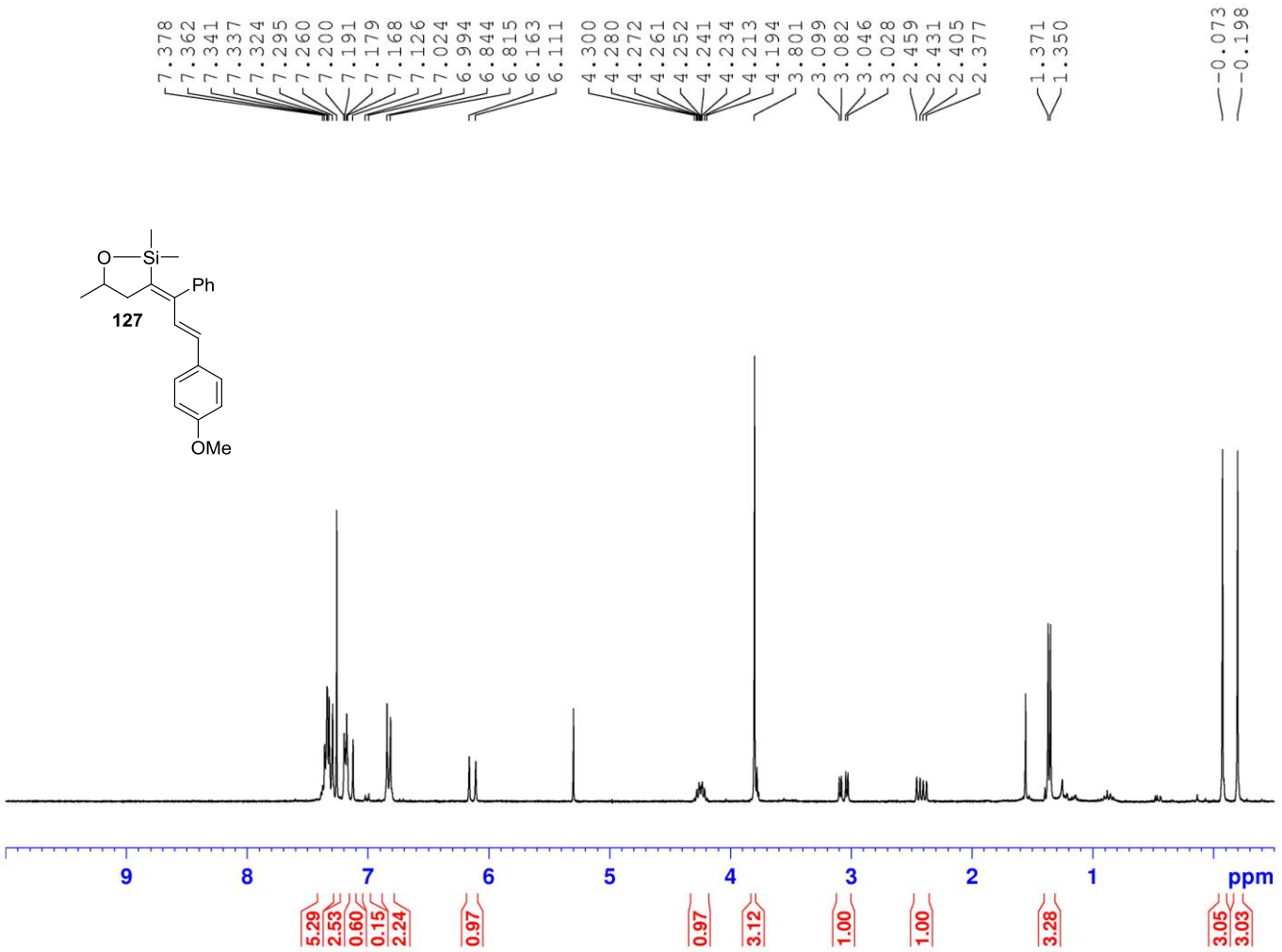

7.580
7.532
7.334
7.331
7.327
7.317
7.311
7.260
7.128
7.125
7.121
7.118
7.115
7.113
7.103
7.096
6.058
6.011
4.260
4.239
4.232
4.221
4.219
4.212
4.201
4.194
4.192
4.181
4.174
4.154
2.951
2.933
2.897
2.879
2.319
2.292
2.265
2.237
1.336
1.316
-0.084
-0.214
O
Si
Ph
I
124
9
8
7
6
5
4
3
2
1
0 ppm
0.922
2.772
1.800
0.741
0.900
1.000
1.004
3.165
2.850
2.881


146.655
144.569
144.548
140.541
129.650
128.310
127.801
83.835
72.471
41.068
24.144
0.546
-0.371
O
Si
Ph
I
124
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

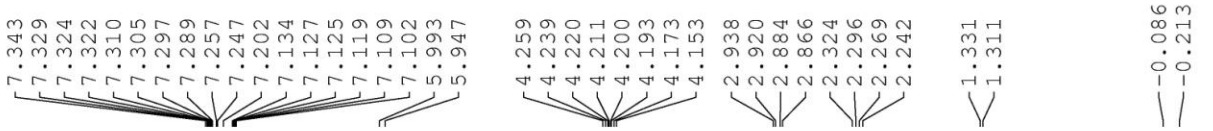
LAK-6-49

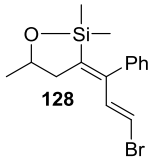

7.596
7.593
7.588
7.560
7.479
7.475
7.463
7.459
7.445
7.442
7.426
7.367
7.364
7.362
7.351
7.348
7.346
7.170
7.164
7.160
7.158
7.156
7.151
7.147
6.106
6.069
5.966
5.964
5.930
5.928
5.137
5.123
5.113
5.099
3.295
3.281
3.254
3.241
2.629
2.606
2.588
2.565
0.080
0.150
O
Si
Ph
126
I
9
8
7
6
5
4
3
2
1
ppm
4.60
0.59
4.27
4.43
2.04
0.97
0.05
1.00
0.05
1.00
1.04
3.20
3.00


LAK-6-49
carbon
146.90
144.51
143.83
143.60
141.26
140.55
140.53
129.70
128.97
128.78
128.45
127.99
127.41
127.34
126.04
84.33
42.30
0.44
-0.47
O
Si
Ph
126
I
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

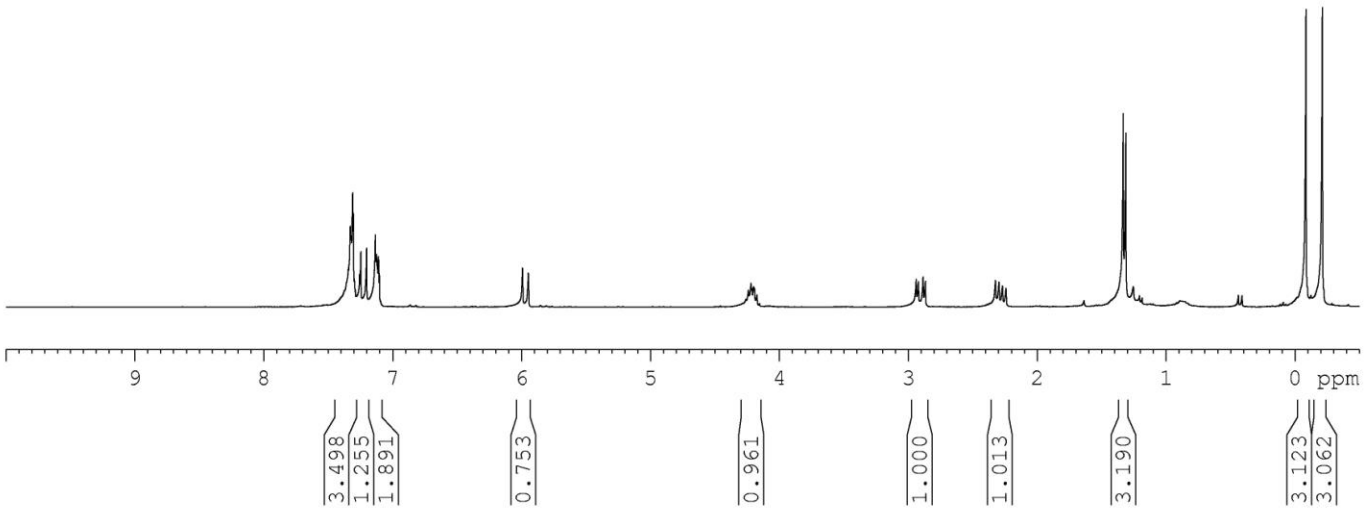

7.378
7.362
7.341
7.337
7.324
7.295
7.260
7.200
7.191
7.179
7.168
7.126
7.024
6.994
6.844
6.815
6.163
6.111
4.300
4.280
4.272
4.261
4.252
4.241
4.234
4.213
4.194
3.801
3.099
3.082
3.046
3.028
2.459
2.431
2.405
2.377
1.371
1.350
-0.073
-0.198
O
Si
Ph
OMe
127
9
8
7
6
5
4
3
2
1
ppm
5.29
2.53
0.60
0.15
2.24
0.97
0.97
3.12
1.00
1.00
3.28
3.05
3.03

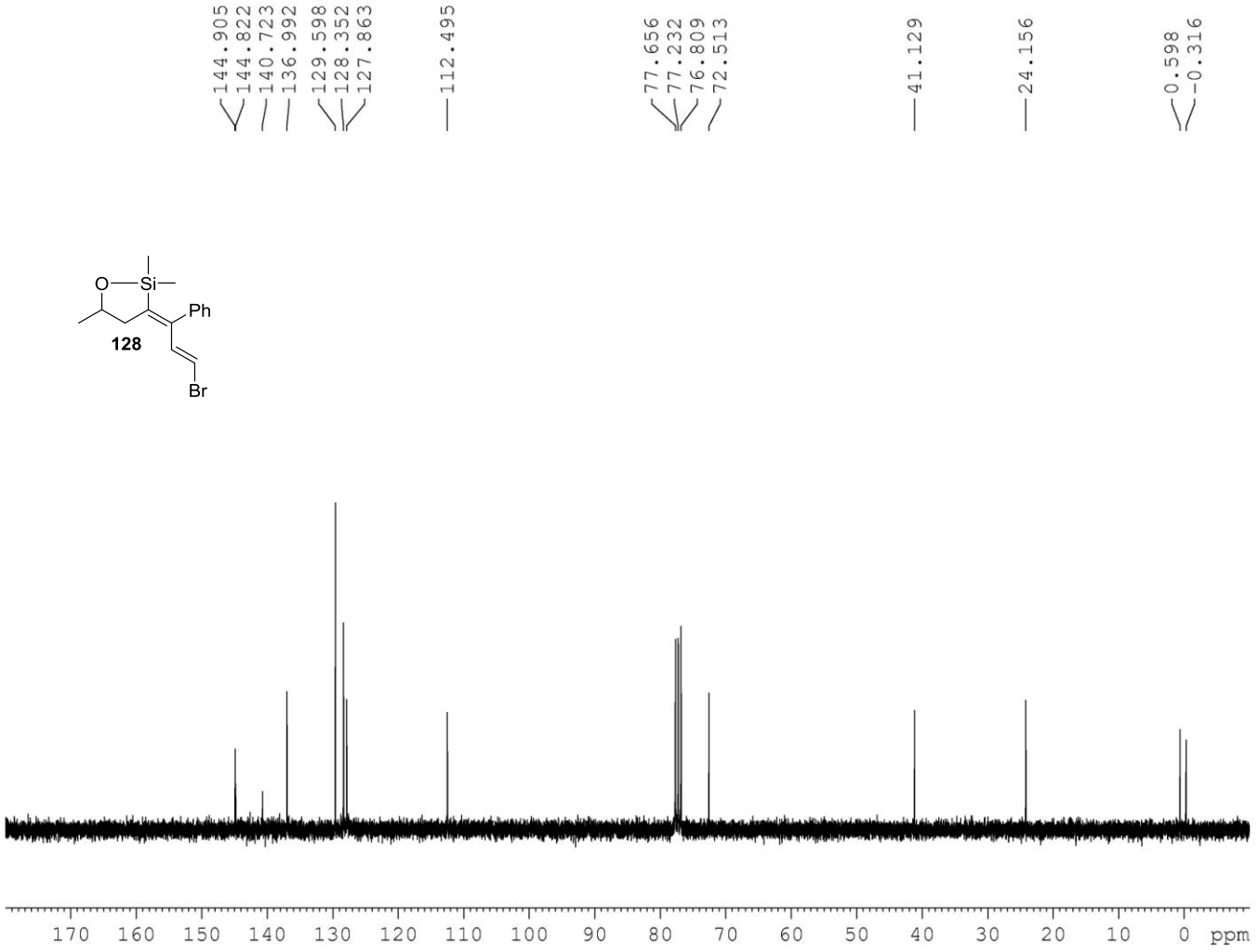
LAK-4-207

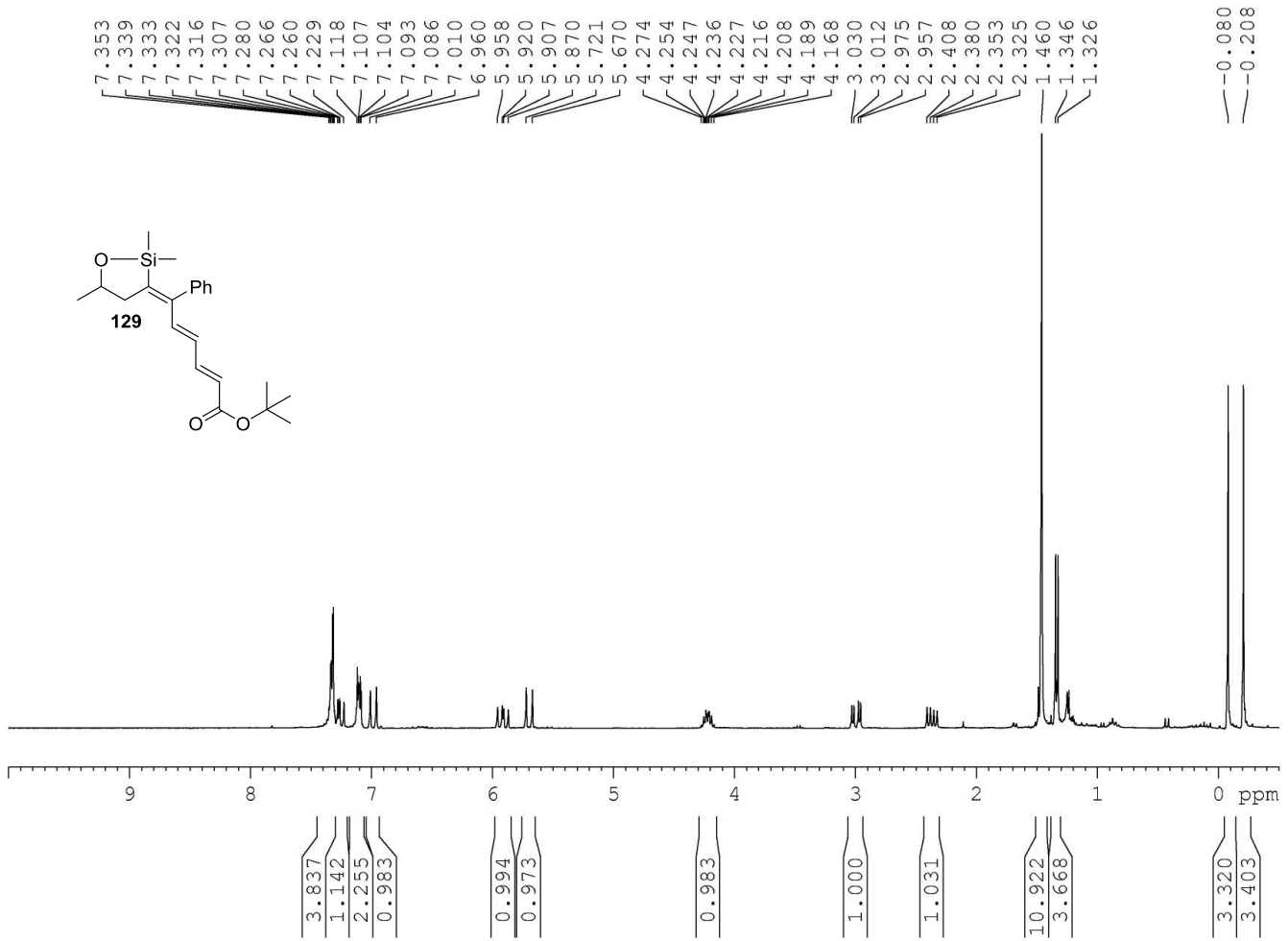

7.343
7.329
7.324
7.322
7.310
7.305
7.297
7.289
7.257
7.247
7.202
7.134
7.127
7.125
7.119
7.109
7.102
5.993
5.947
4.259
4.239
4.220
4.211
4.200
4.193
4.173
4.153
2.938
2.920
2.884
2.866
2.324
2.296
2.269
2.242
1.331
1.311
-0.086
-0.213

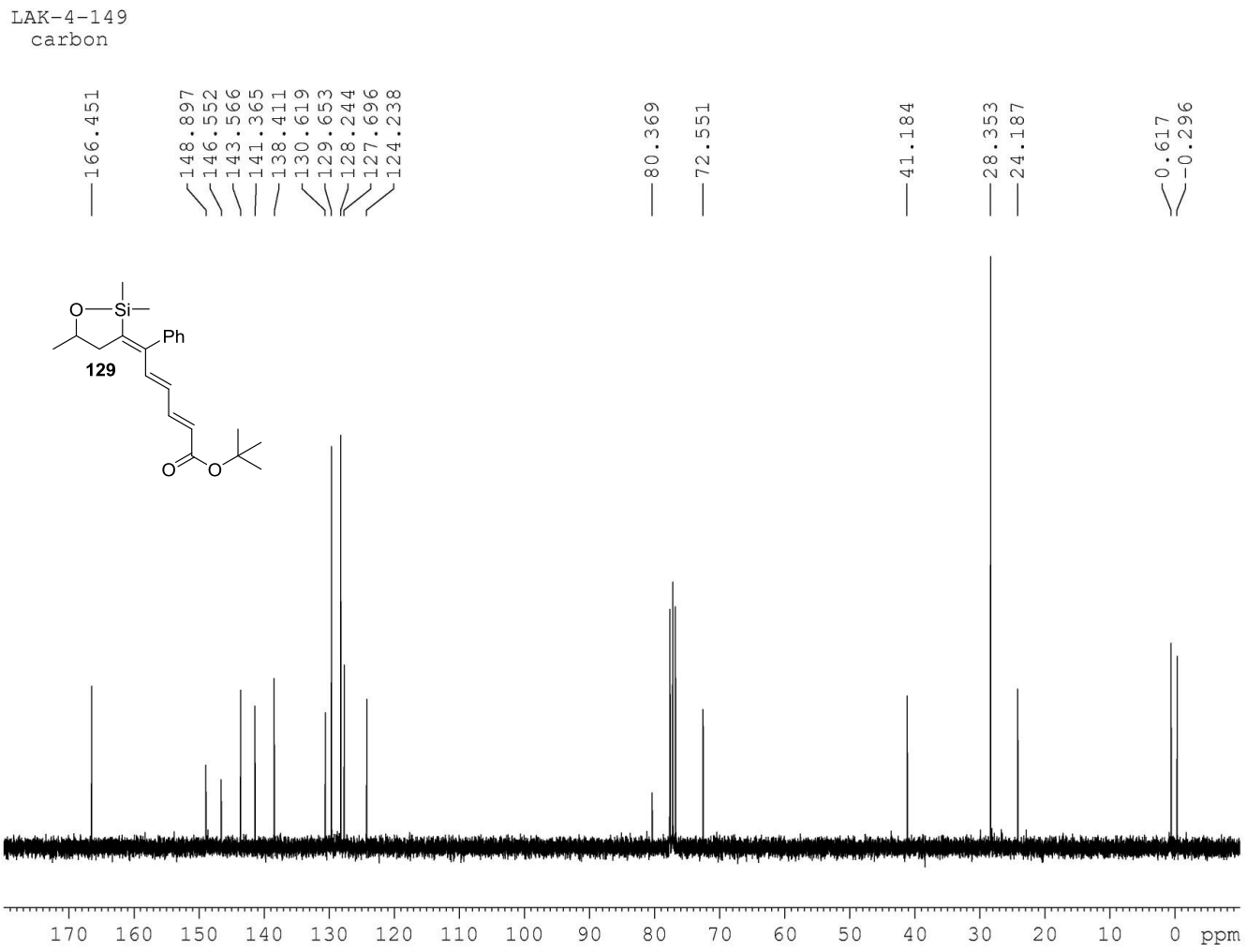

O
Si
Ph
Br

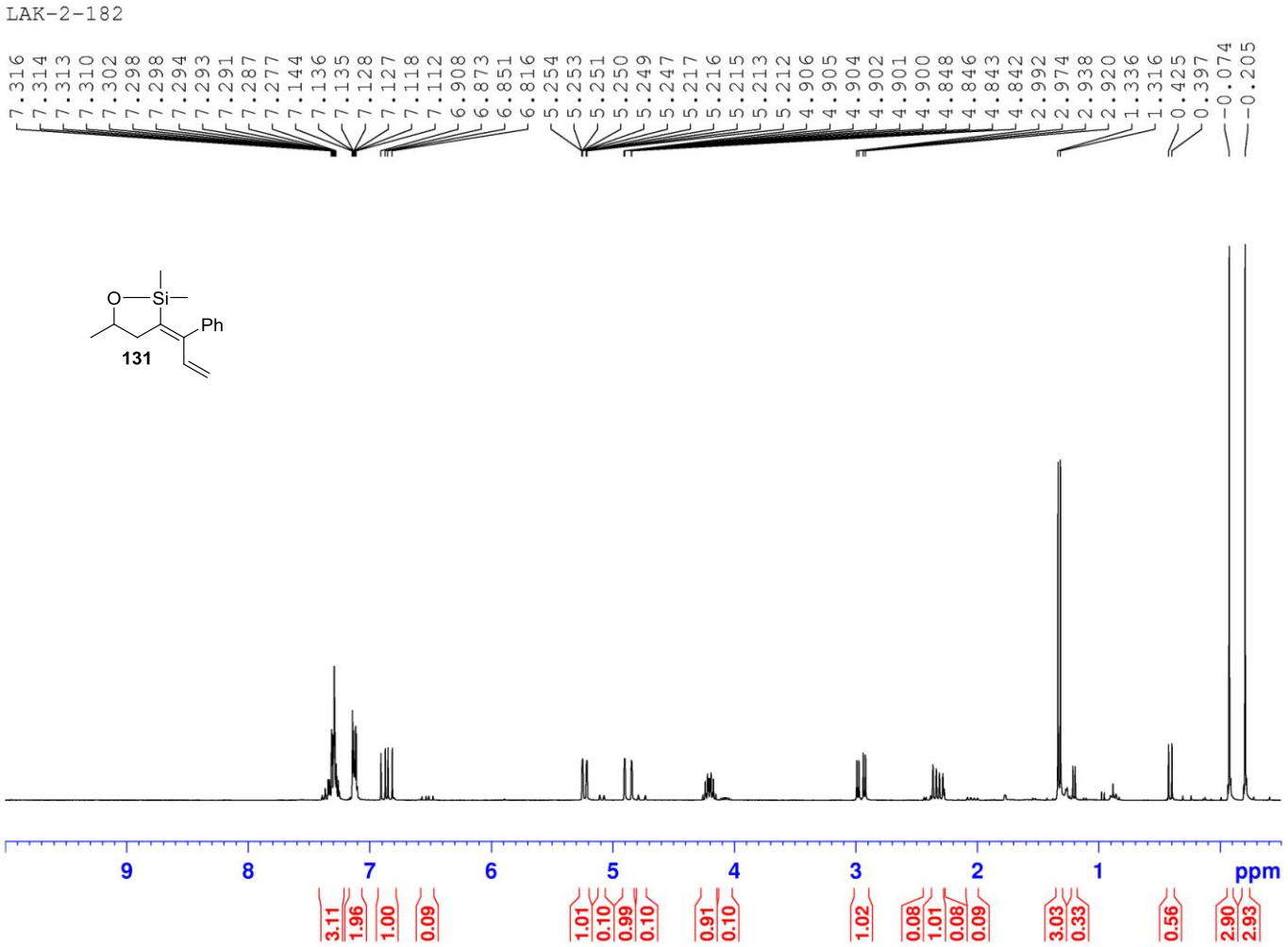
128


9
8
7
6
5
4
3
2
1
0
ppm
3.498
1.255
1.891
0.753
0.961
1.000
1.013
3.190
3.123
3.062

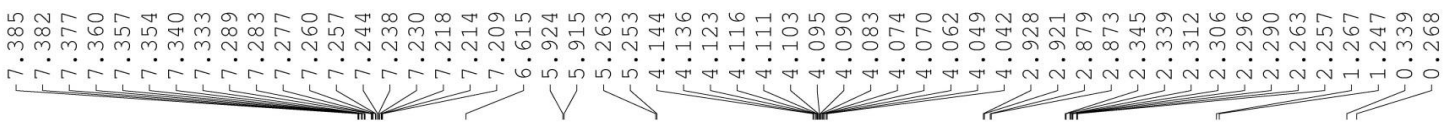

144.905
144.822
140.723
136.992
129.598
128.352
127.863
112.495
77.656
77.232
76.809
72.513
41.129
24.156
0.598
-0.316
O
Si
Ph
Br
128
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

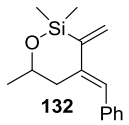

7.353
7.339
7.333
7.322
7.316
7.307
7.280
7.266
7.260
7.229
7.118
7.107
7.104
7.093
7.086
7.010
6.960
5.958
5.920
5.907
5.870
5.721
5.670
4.274
4.254
4.247
4.236
4.227
4.216
4.208
4.189
4.168
3.030
3.012
2.975
2.957
2.408
2.380
2.353
2.325
1.460
1.346
1.326
-0.080
-0.208
O
Si
Ph
129
O
O
9
8
7
6
5
4
3
2
1
0 ppm
3.837
1.142
2.255
0.983
0.994
0.973
0.983
1.000
1.031
10.922
3.668
3.320
3.403


LAK-4-149
carbon
166.451
148.897
146.552
143.566
141.365
138.411
130.619
129.653
128.244
127.696
124.238
80.369
72.551
41.184
28.353
24.187
0.617
-0.296
O
Si
Ph
129
O
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

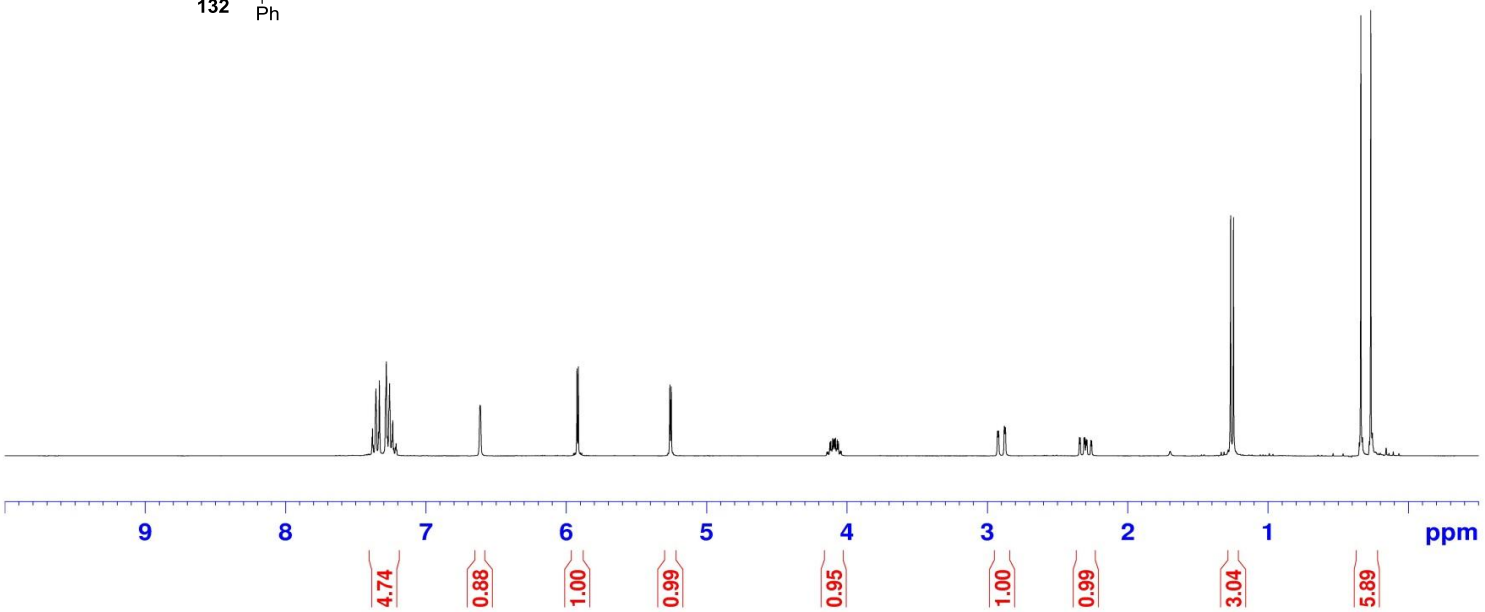

LAK-2-182
7.316
7.314
7.313
7.310
7.302
7.298
7.298
7.294
7.293
7.291
7.287
7.277
7.144
7.136
7.135
7.128
7.127
7.118
7.112
6.908
6.873
6.851
6.816
5.254
5.253
5.251
5.250
5.249
5.247
5.217
5.216
5.215
5.213
5.212
4.906
4.905
4.904
4.902
4.901
4.900
4.848
4.846
4.843
4.842
2.992
2.974
2.938
2.920
1.336
1.316
0.425
0.397
-0.074
-0.205
O
Si
Ph
131
9
8
7
6
5
4
3
2
1
ppm
3.11
1.96
1.00
0.09
1.01
0.10
0.99
0.10
0.91
0.10
1.02
0.08
1.01
0.08
0.09
3.03
0.33
0.56
2.90
2.93

LAK-3-122

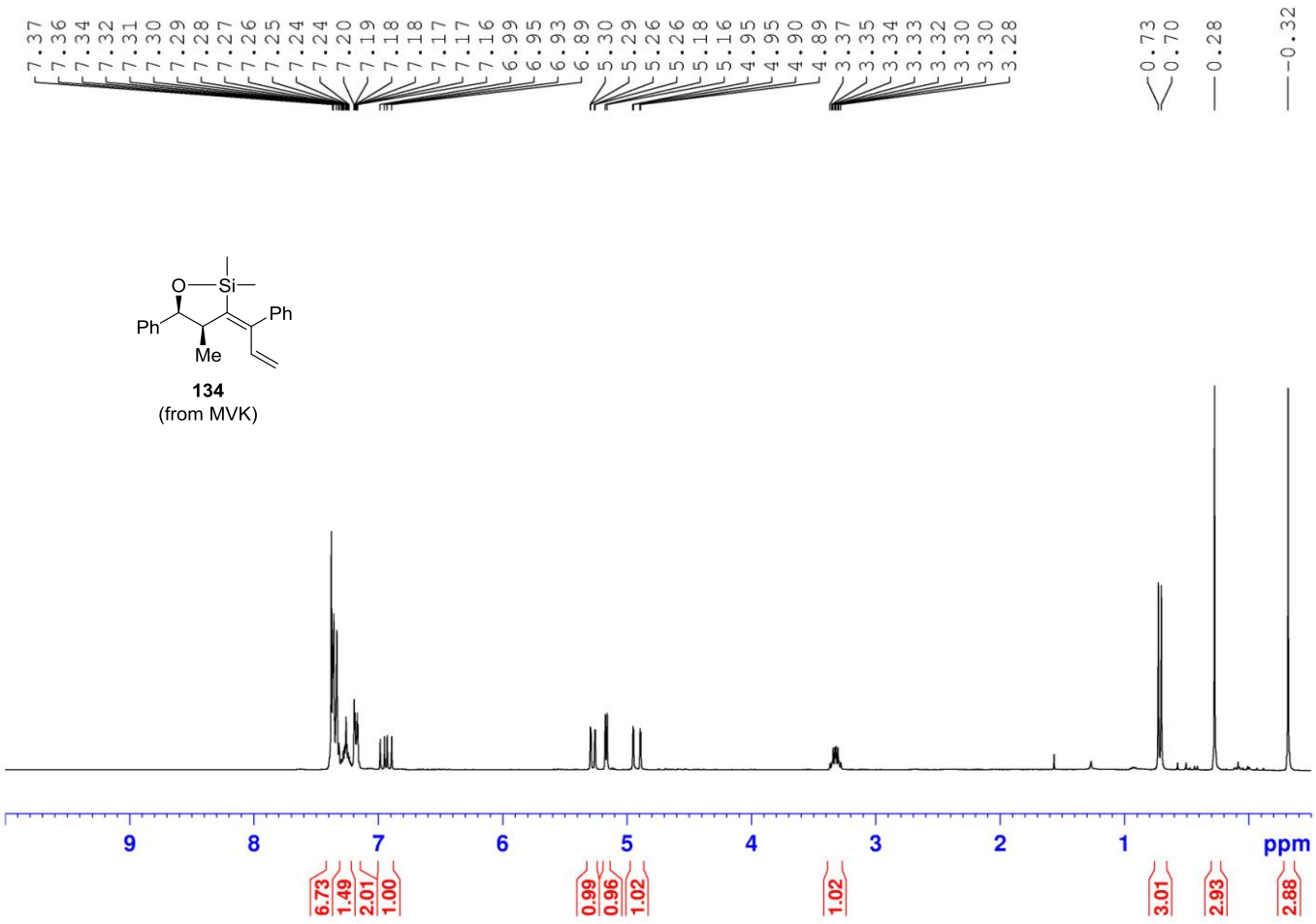

7.385
7.382
7.377
7.360
7.357
7.354
7.340
7.333
7.289
7.283
7.277
7.260
7.257
7.244
7.238
7.230
7.218
7.214
7.209
6.615
5.924
5.915
5.263
5.253
4.144
4.136
4.123
4.116
4.111
4.103
4.095
4.090
4.083
4.074
4.070
4.062
4.049
4.042
2.928
2.921
2.879
2.873
2.345
2.339
2.312
2.306
2.296
2.290
2.263
2.257
1.267
1.247
0.339
0.268


Si
O
Ph

132

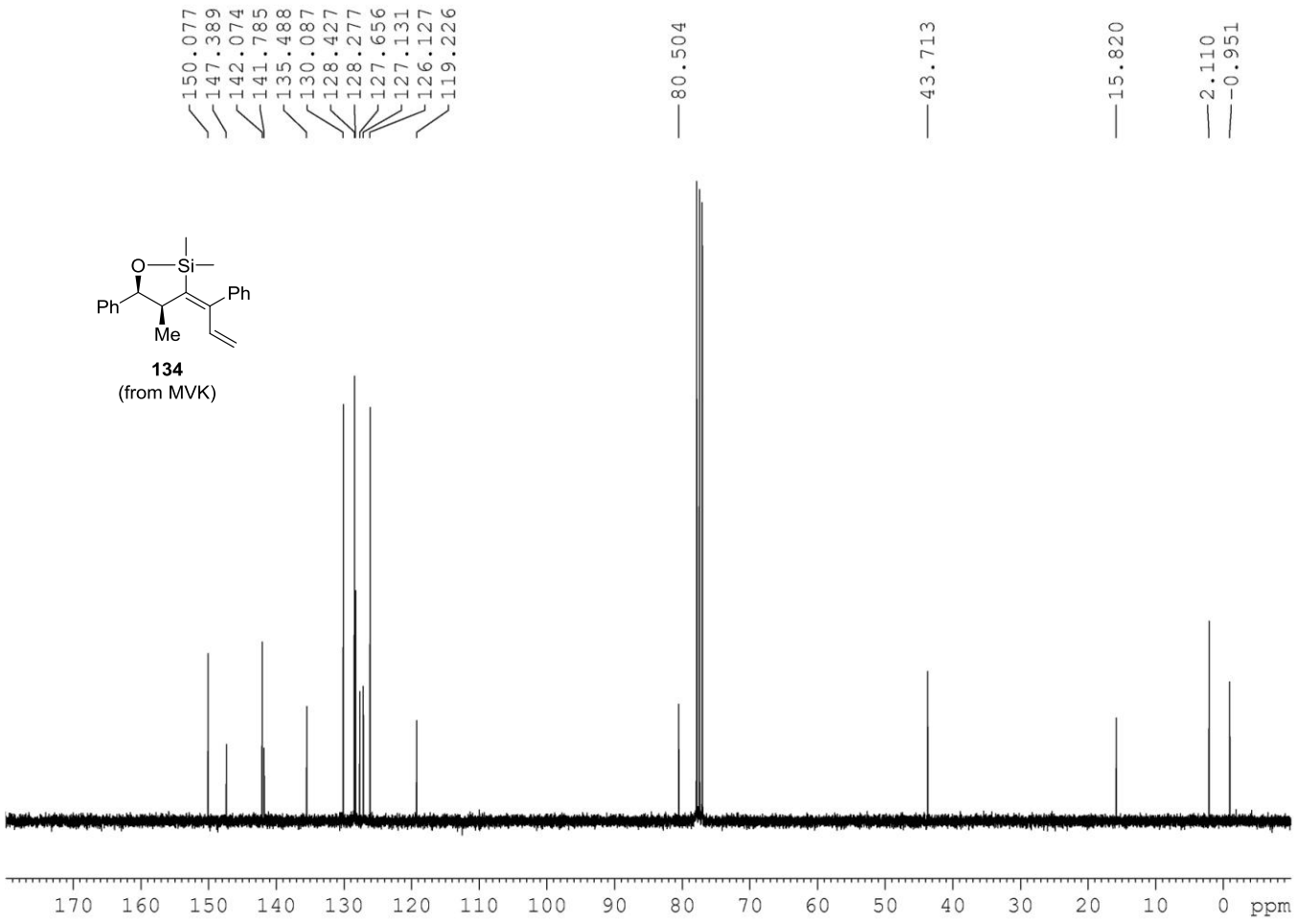

9
8
7
6
5
4
3
2
1
ppm
4.74
0.88
1.00
0.99
0.95
1.00
0.99
3.04
5.89

LAK-2-97



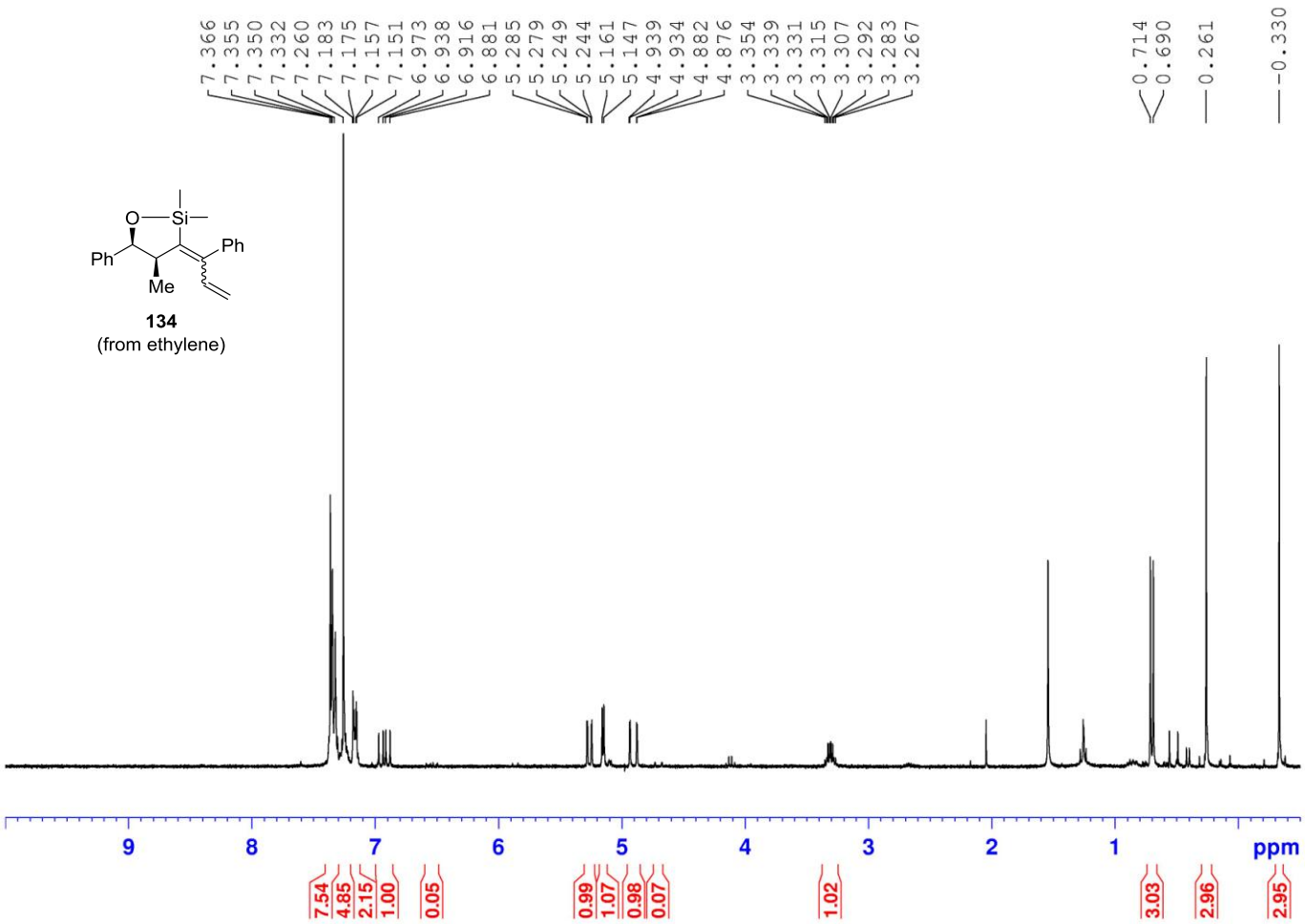
134
(from MVK)

LAK-2-97



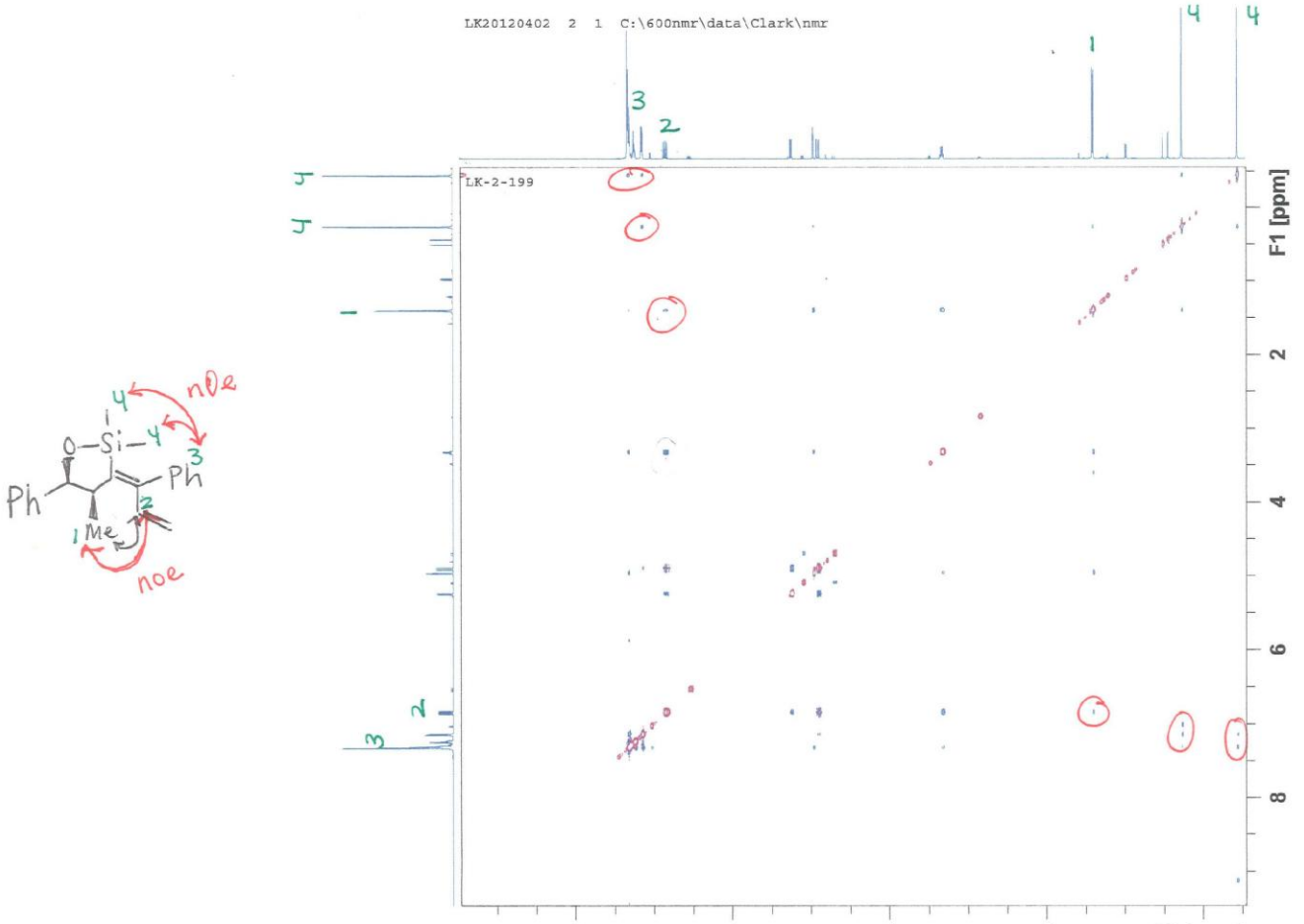
134
(from MVK)

LAK-2-199



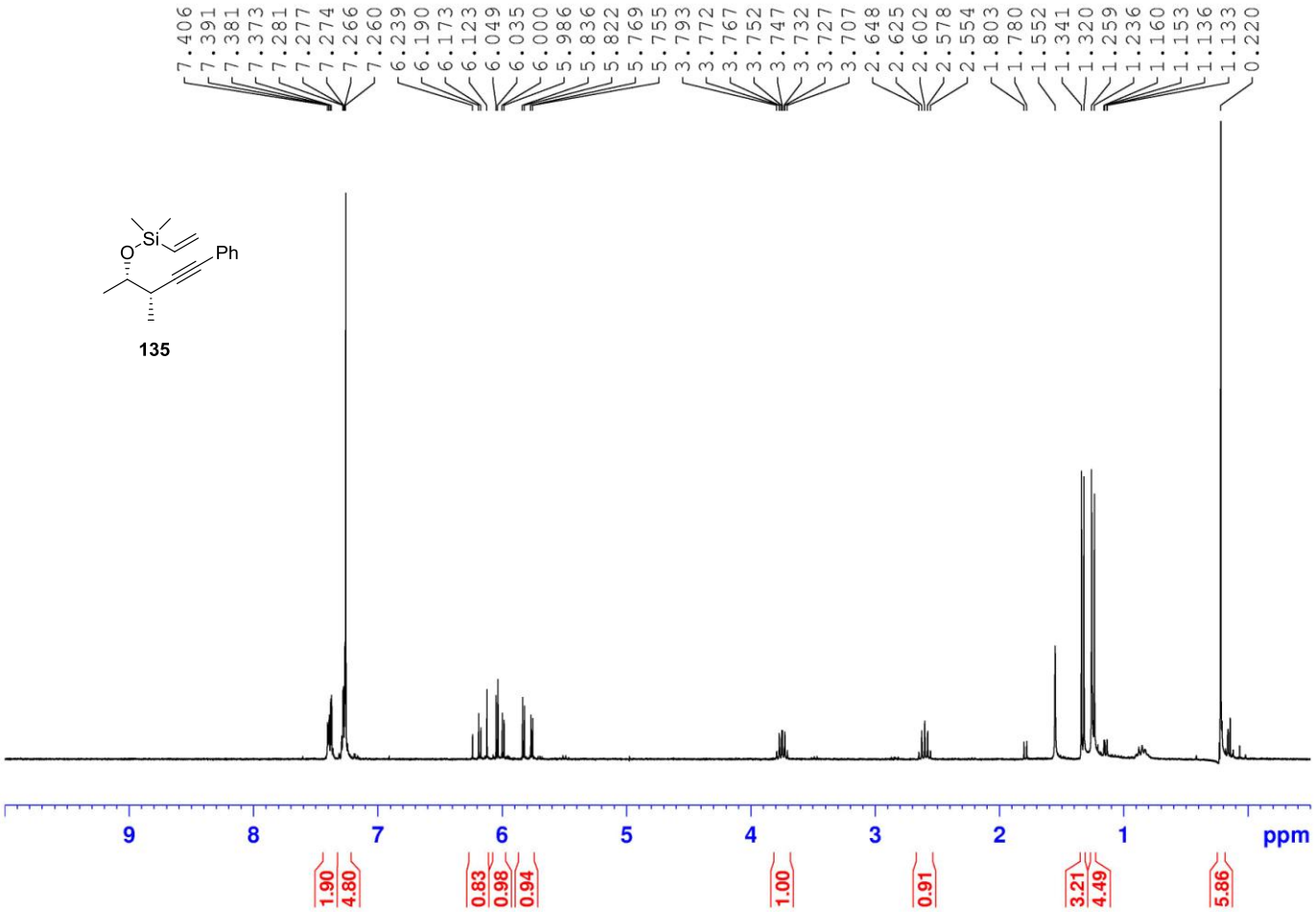
134
(from ethylene)

LK-2-199



(#'s labeled on the structure refer to the protons at that location)

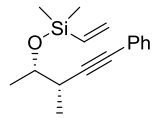
LAK-2-232


7.406
7.391
7.381
7.373
7.281
7.277
7.274
7.266
7.260
6.239
6.190
6.173
6.123
6.049
6.035
6.000
5.986
5.836
5.822
5.769
5.755
3.793
3.772
3.767
3.752
3.747
3.732
3.727
3.707
2.648
2.625
2.602
2.578
2.554
1.803
1.780
1.552
1.341
1.320
1.259
1.236
1.160
1.153
1.136
1.133
0.220
Si
O
Ph
9
8
7
6
5
4
3
2
1
ppm
1.90
4.80
0.83
0.98
0.94
1.00
0.91
3.21
4.49
5.86

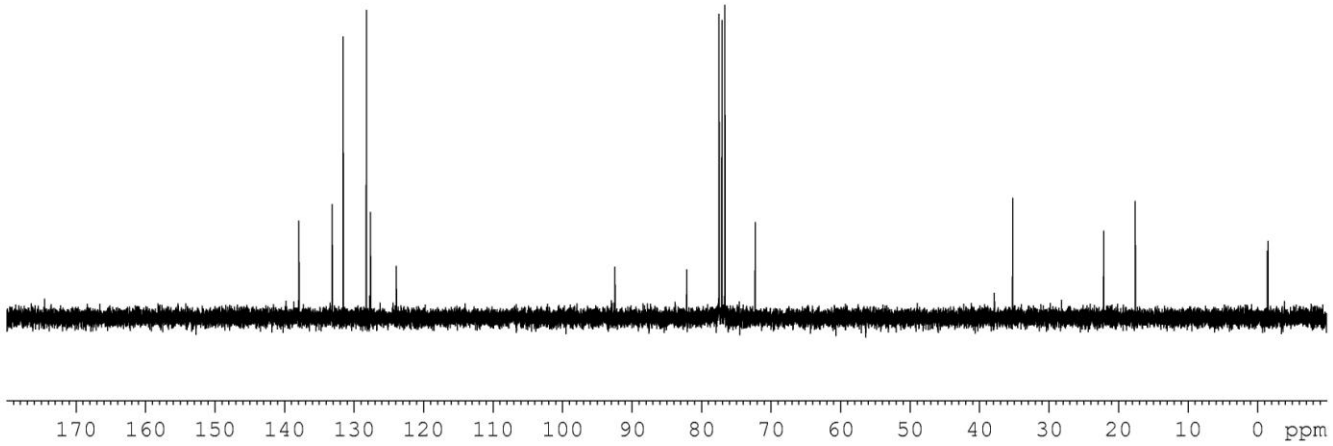
135

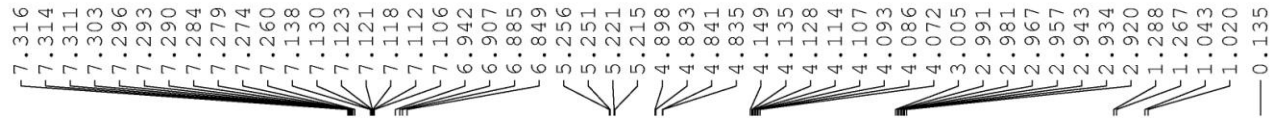
LAK-2-232
carbon

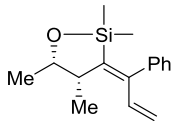
137.879
133.066
131.512
128.138
127.560
123.836
92.392
82.042
72.210
35.230
22.122
17.585
-1.448
-1.528



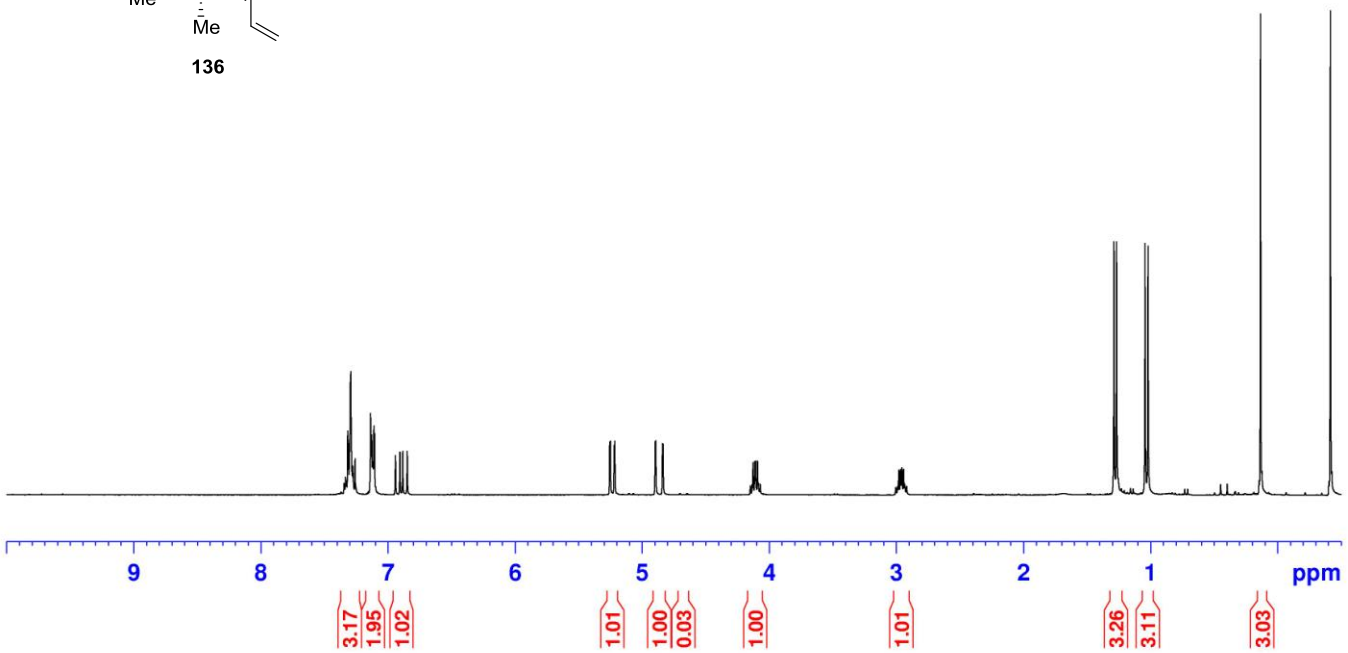
135

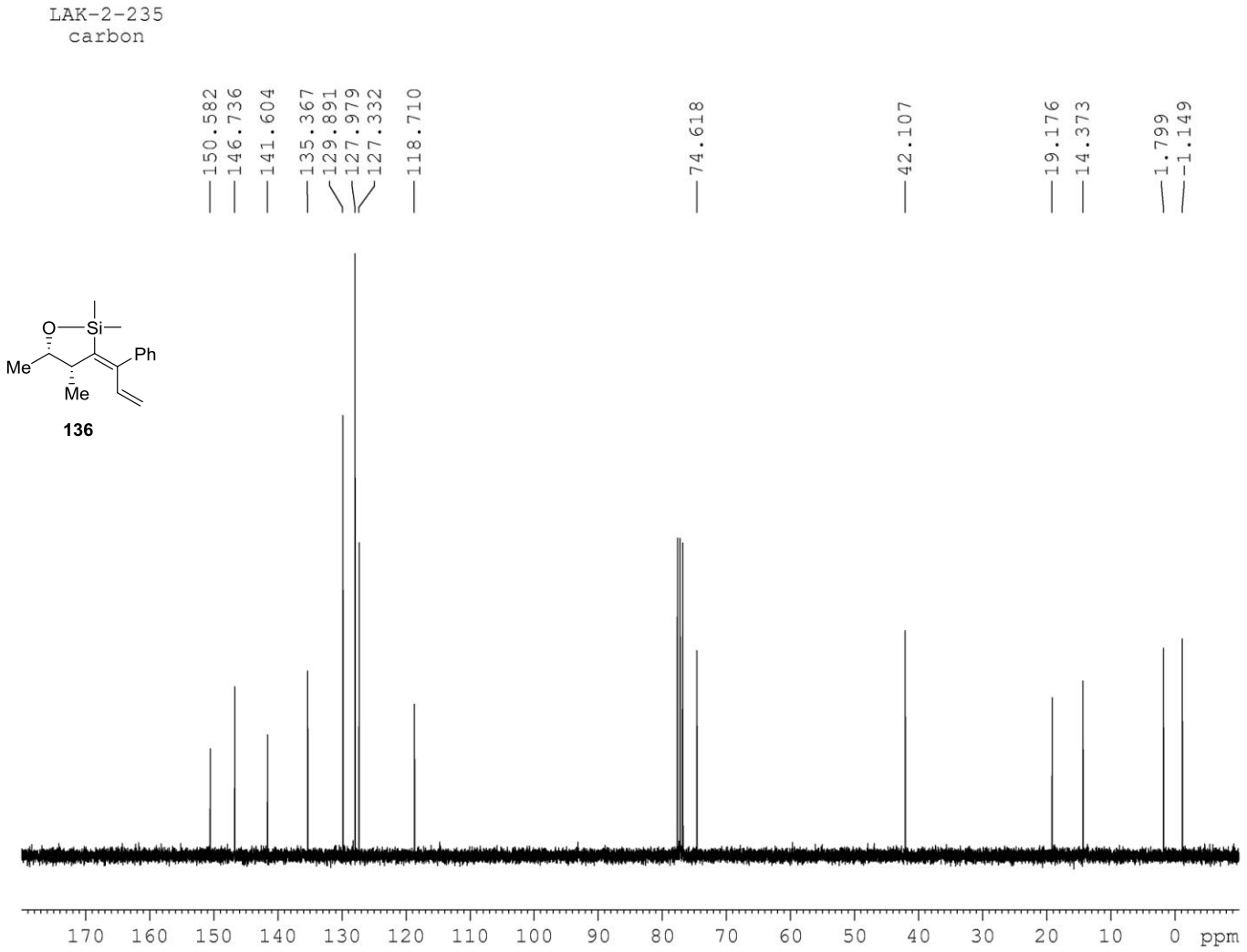



7.316
7.314
7.311
7.303
7.296
7.293
7.290
7.284
7.279
7.274
7.260
7.138
7.130
7.123
7.121
7.118
7.112
7.106
6.942
6.907
6.885
6.849
5.256
5.251
5.221
5.215
4.898
4.893
4.841
4.835
4.149
4.135
4.128
4.114
4.107
4.093
4.086
4.072
3.005
2.991
2.981
2.967
2.957
2.943
2.934
2.920
1.288
1.267
1.043
1.020
0.135


O
Si
Me
Me
Ph

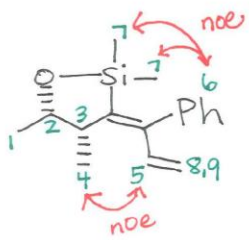
136


9
8
7
6
5
4
3
2
1
ppm
3.17
1.95
1.02
1.01
1.00
0.03
1.00
1.01
3.26
3.11
3.03


LAK-2-235
carbon
150.582
146.736
141.604
135.367
129.891
127.979
127.332
118.710
74.618
42.107
19.176
14.373
1.799
-1.149
O
Si
Me
Me
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

136

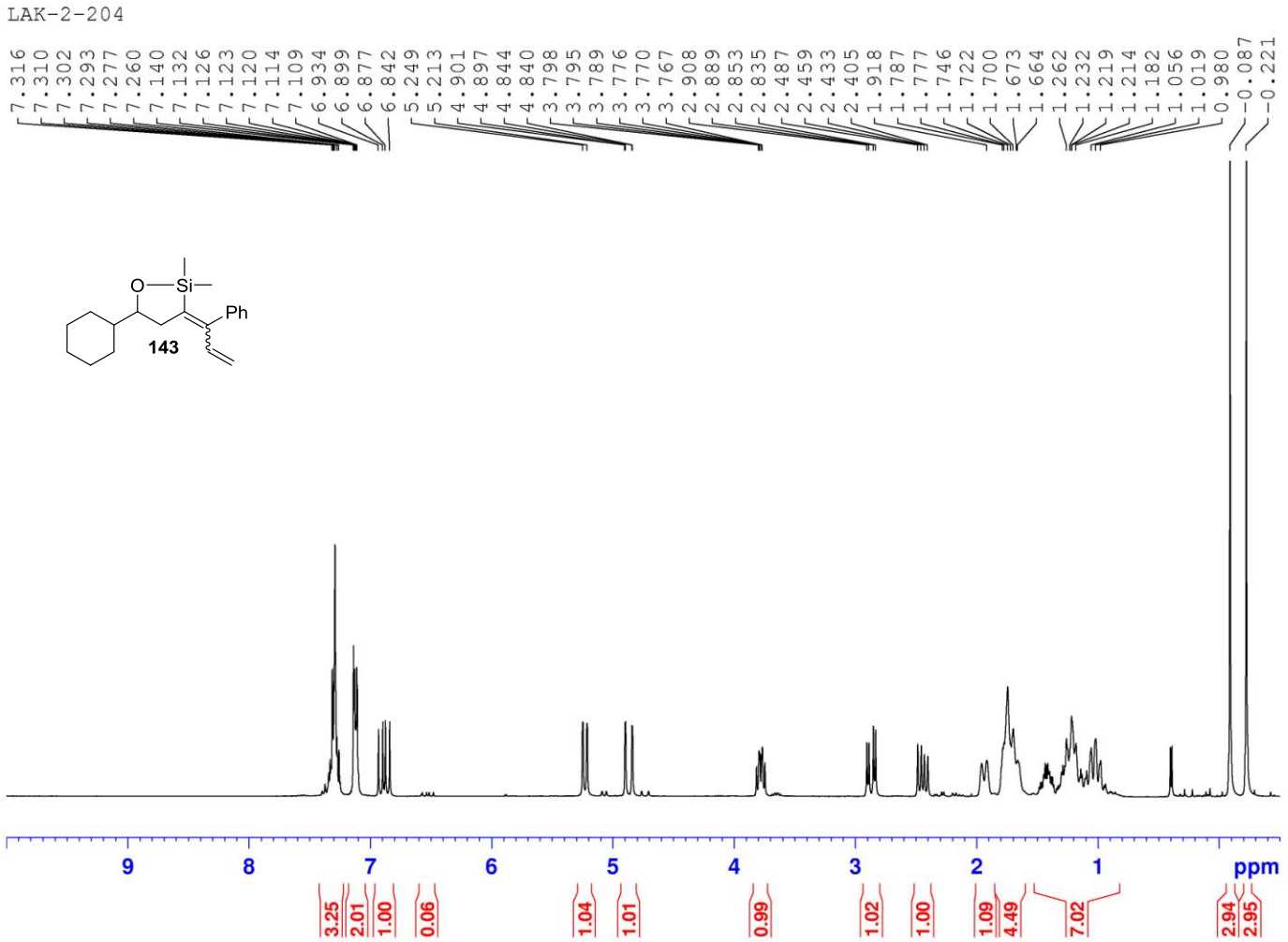
(#'s labeled on the structure refer to the protons at that location)

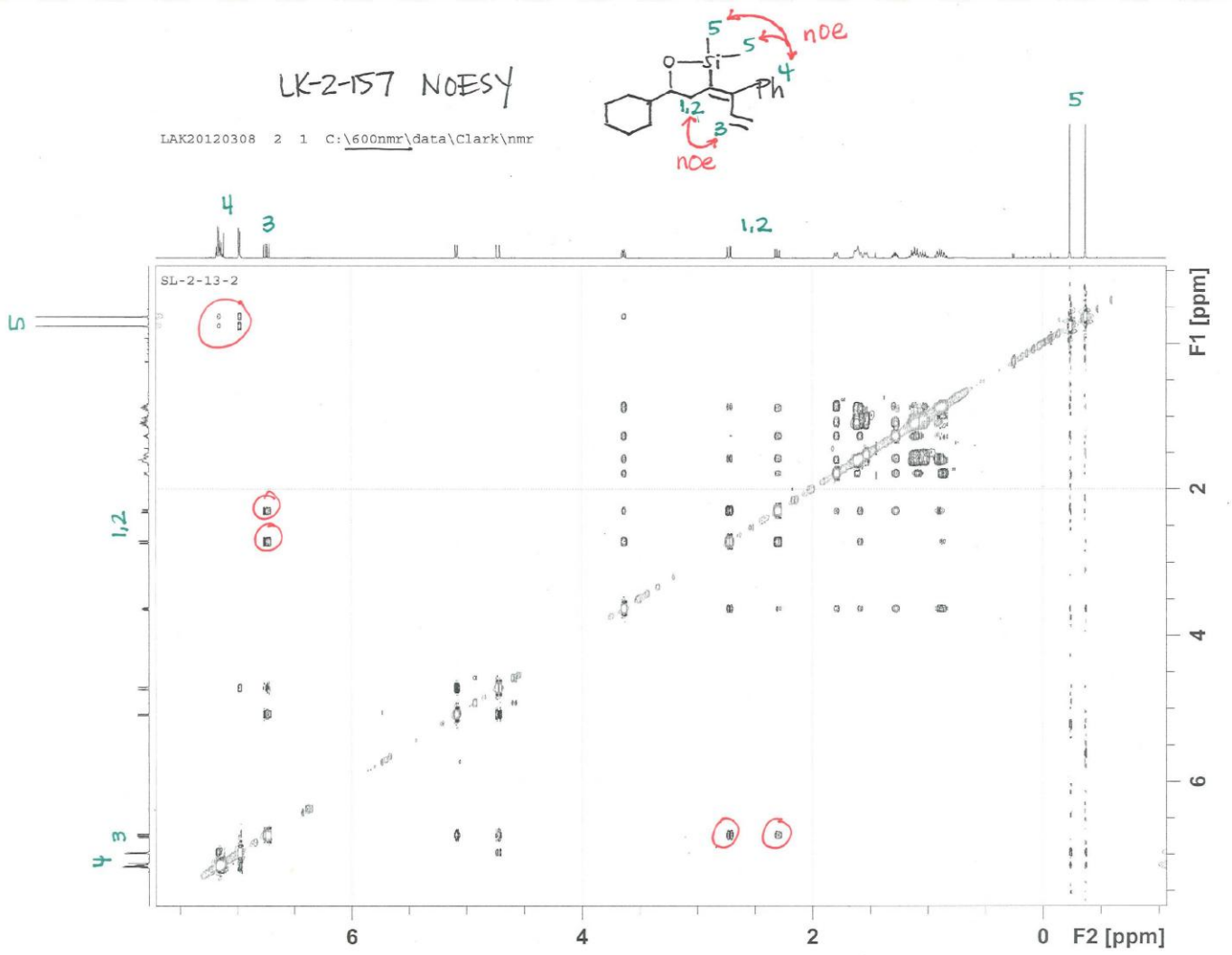


NOESY

BRUKER

```
Current Data Parameters
NAME            LK20120514
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_              20120514
Time                 19.47
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG           noesyph
TD                   2048
SOLVENT              CDCl3
NS                      8
DS                      4
SWH              2997.602 Hz
FIDRES           1.463673 Hz
AQ               0.3416564 sec
RG                     64
DW                166.800 usec
DE                  6.00 usec
TE                 303.2 K
d0             0.00015645 sec
D1             2.70000005 sec
D8             1.00000000 sec
IN0            0.00033360 sec
ST1CNT                128

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.13 usec
PL1                1.00 dB
SFO1         300.1312005 MHz

F1 - Acquisition parameters
ND0                    1
TD                   256
SFO1          300.1312 MHz
FIDRES       11.709382 Hz
SW                9.988 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                  1024
SF          300.1300000 MHz
WDW                 QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
PC                  1.00

F1 - Processing parameters
SI                  1024
MC2          States-TPPI
SF          300.1300000 MHz
WDW                 QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
```

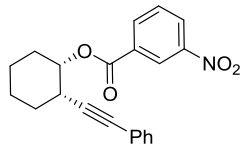

LAK-2-204
7.316
7.310
7.302
7.293
7.277
7.260
7.140
7.132
7.126
7.123
7.120
7.114
7.109
6.934
6.899
6.877
6.842
5.249
5.213
4.901
4.897
4.844
4.840
3.798
3.795
3.789
3.776
3.770
3.767
2.908
2.889
2.853
2.835
2.487
2.459
2.433
2.405
1.918
1.787
1.777
1.746
1.722
1.700
1.673
1.664
1.262
1.232
1.219
1.214
1.182
1.056
1.019
0.980
-0.087
-0.221
O
Si
Ph
143
9
8
7
6
5
4
3
2
1
ppm
3.25
2.01
1.00
0.06
1.04
1.01
0.99
1.02
1.00
1.09
4.49
7.02
2.94
2.95



(#'s labeled on the structure refer to the protons at that location)

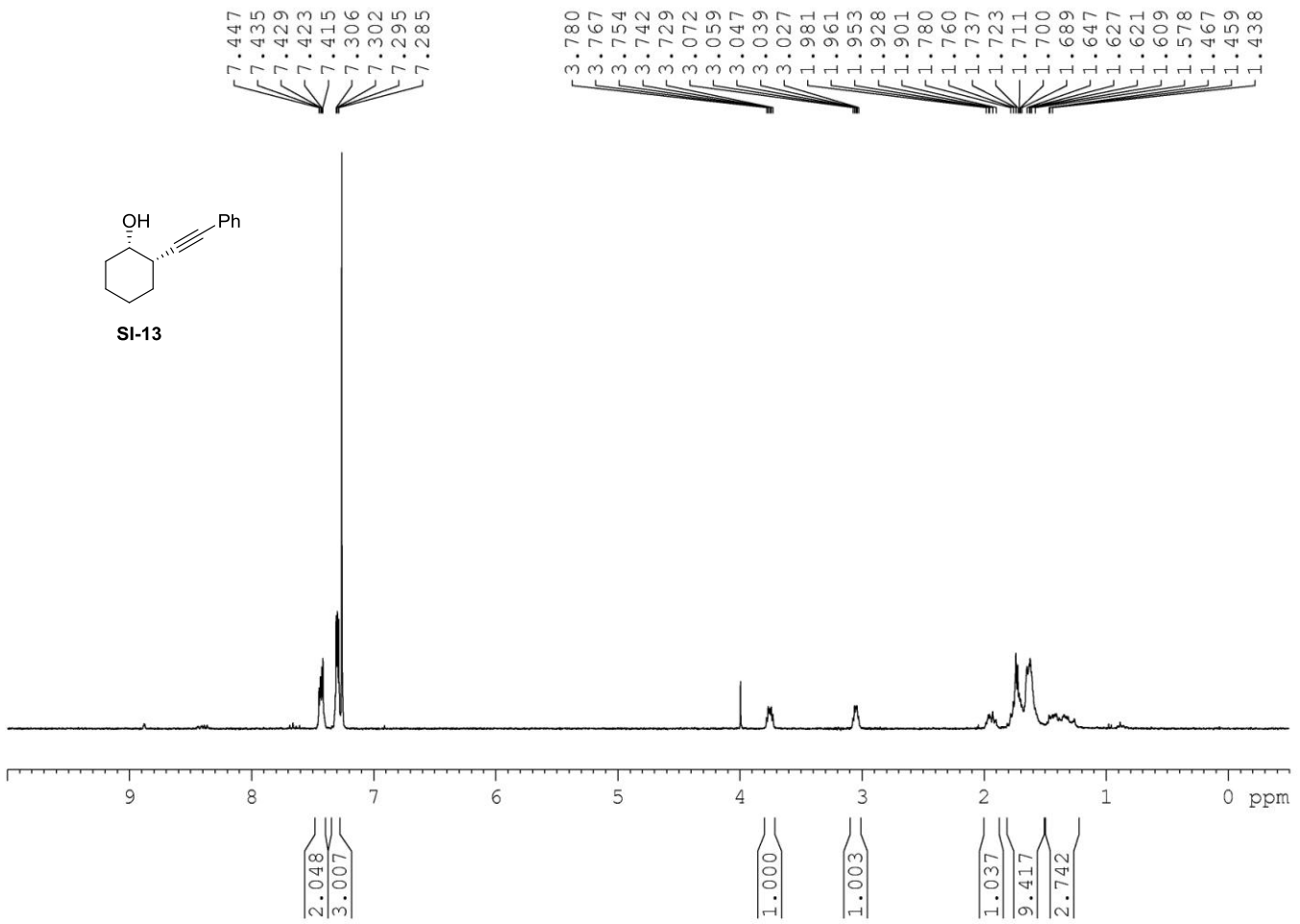
LAK-6-80

8.947 8.942 8.938 8.427 8.424 8.422 8.419 8.411 8.408 8.407 8.404 8.401 8.398 7.667 7.647 7.627 7.627 7.418 7.415 7.412 7.408 7.399 7.393 7.299 7.297 7.294 7.289 7.286 7.283 7.278 7.272 7.267 7.260 5.219 5.210 5.205 5.196 3.281 3.272 2.098 2.073 2.055 2.049 2.044 2.033 1.867 1.859 1.844 1.837 1.820 1.797 1.775 1.523 1.504 1.494

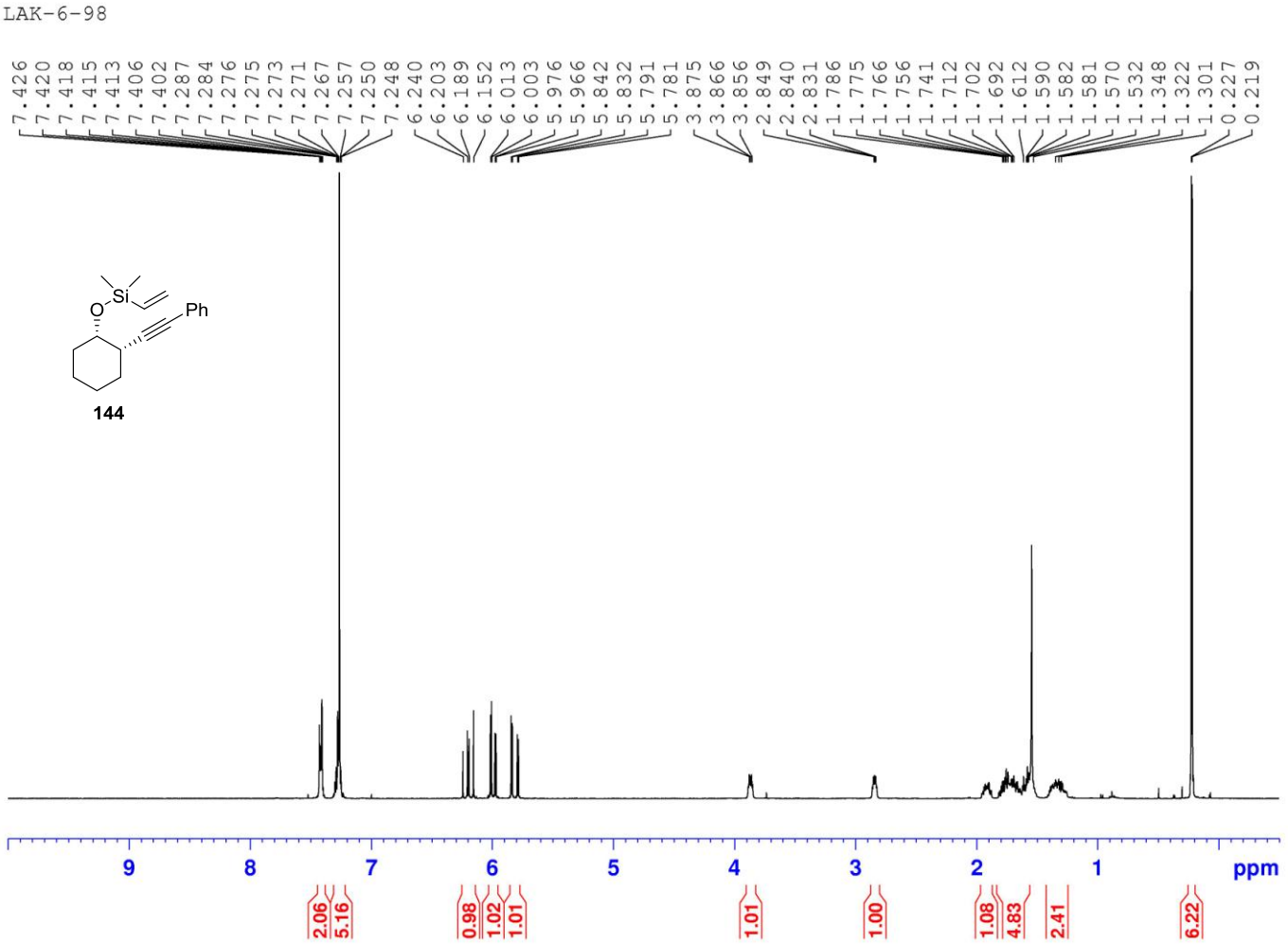


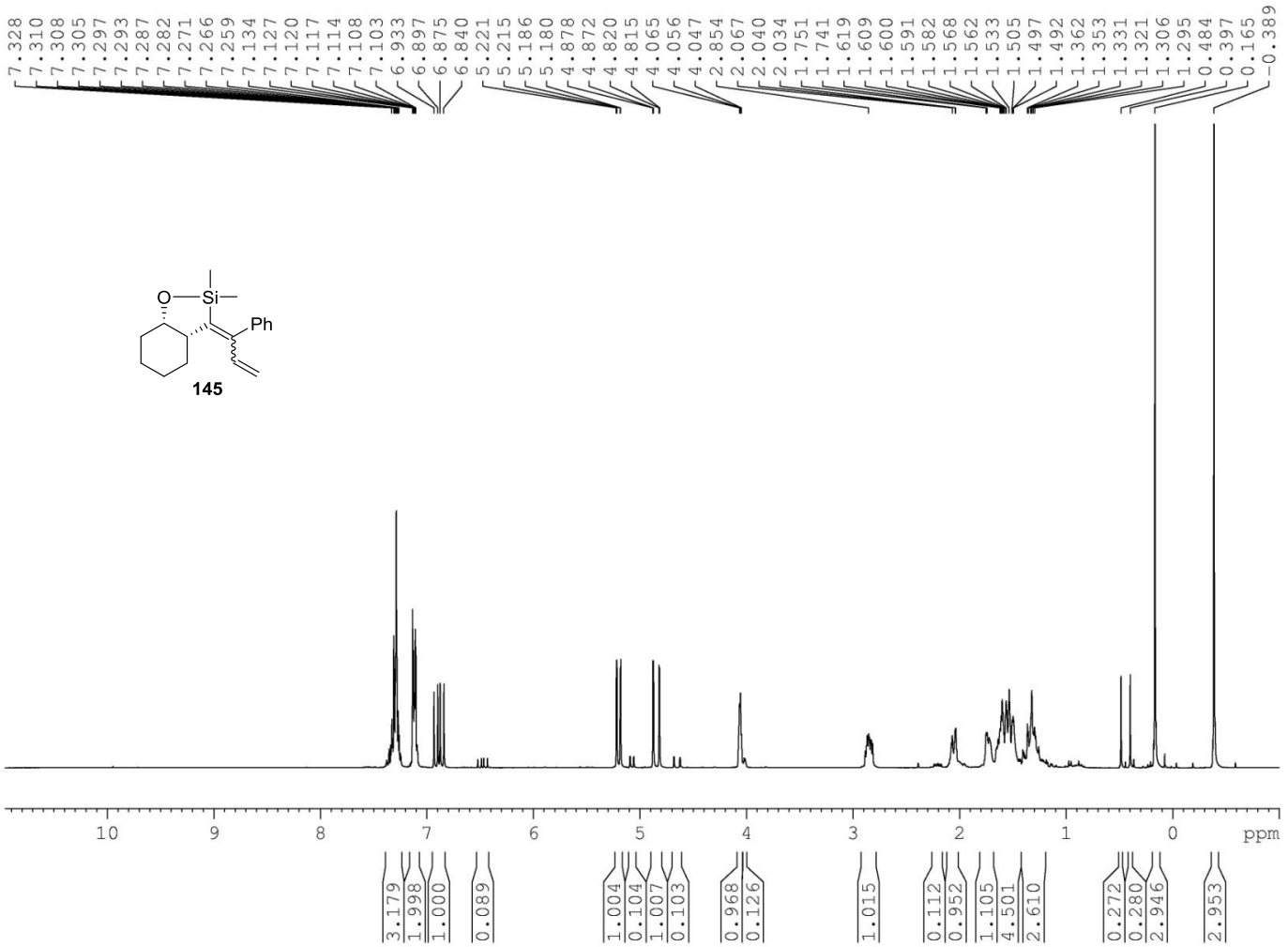
SI-12

LAK-6-91

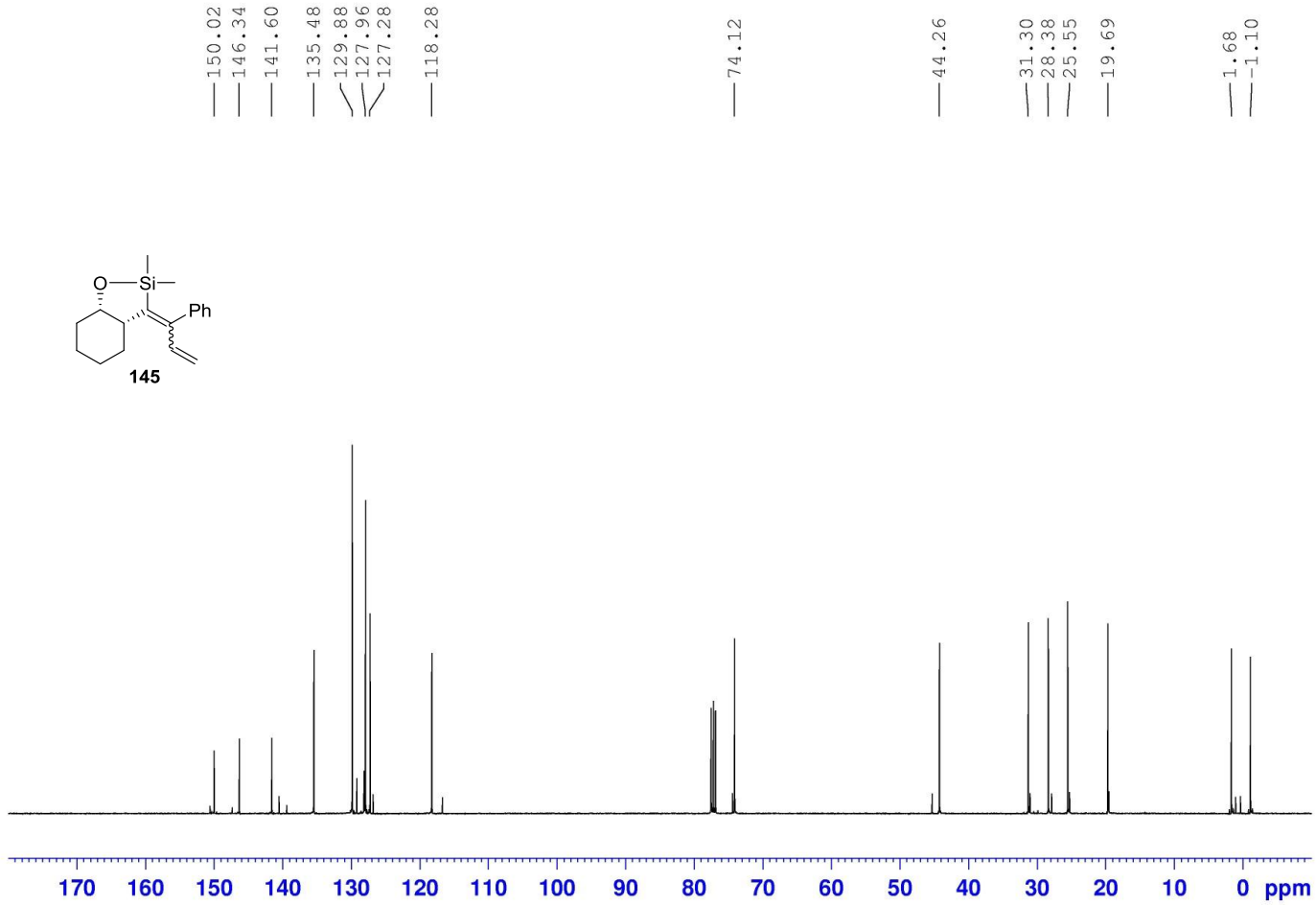

7.447
7.435
7.429
7.423
7.415
7.306
7.302
7.295
7.285
3.780
3.767
3.754
3.742
3.729
3.072
3.059
3.047
3.039
3.027
1.981
1.961
1.953
1.928
1.901
1.780
1.760
1.737
1.723
1.711
1.700
1.689
1.647
1.627
1.621
1.609
1.578
1.467
1.459
1.438
OH
Ph
9
8
7
6
5
4
3
2
1
0 ppm
2.048
3.007
1.000
1.003
1.037
9.417
2.742

SI-13

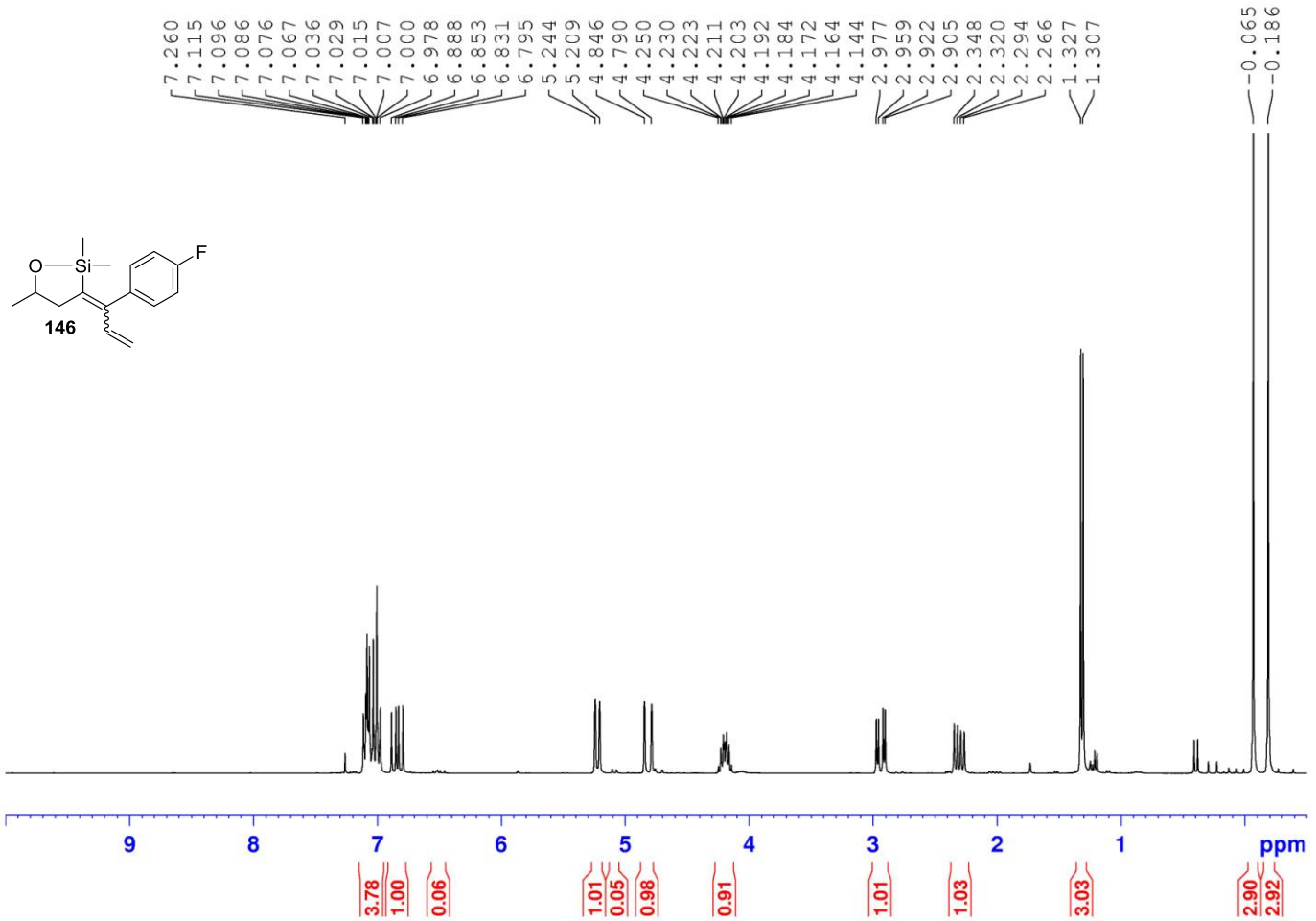

LAK-6-98
7.426
7.420
7.418
7.415
7.413
7.406
7.402
7.287
7.284
7.276
7.275
7.273
7.271
7.267
7.257
7.250
7.248
6.240
6.203
6.189
6.152
6.013
6.003
5.976
5.966
5.842
5.832
5.791
5.781
3.875
3.866
3.856
2.849
2.840
2.831
1.786
1.775
1.766
1.756
1.741
1.712
1.702
1.692
1.612
1.590
1.582
1.581
1.570
1.532
1.348
1.322
1.301
0.227
0.219
Si
O
Ph
144
9
8
7
6
5
4
3
2
1
ppm
2.06
5.16
0.98
1.02
1.01
1.01
1.00
1.08
4.83
2.41
6.22


7.328
7.310
7.308
7.305
7.297
7.293
7.287
7.282
7.271
7.266
7.259
7.134
7.127
7.120
7.117
7.114
7.108
7.103
6.933
6.897
6.875
6.840
5.221
5.215
5.186
5.180
4.878
4.872
4.820
4.815
4.065
4.056
4.047
2.854
2.067
2.040
2.034
1.751
1.741
1.619
1.609
1.600
1.591
1.582
1.568
1.562
1.533
1.505
1.497
1.492
1.362
1.353
1.331
1.321
1.306
1.295
0.484
0.397
0.165
-0.389
O
Si
Ph
145
10
9
8
7
6
5
4
3
2
1
0
ppm
3.179
1.998
1.000
0.089
1.004
0.104
1.007
0.103
0.968
0.126
1.015
0.112
0.952
1.105
4.501
2.610
0.272
0.280
2.946
2.953

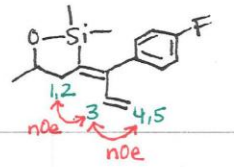
LAK-6-278

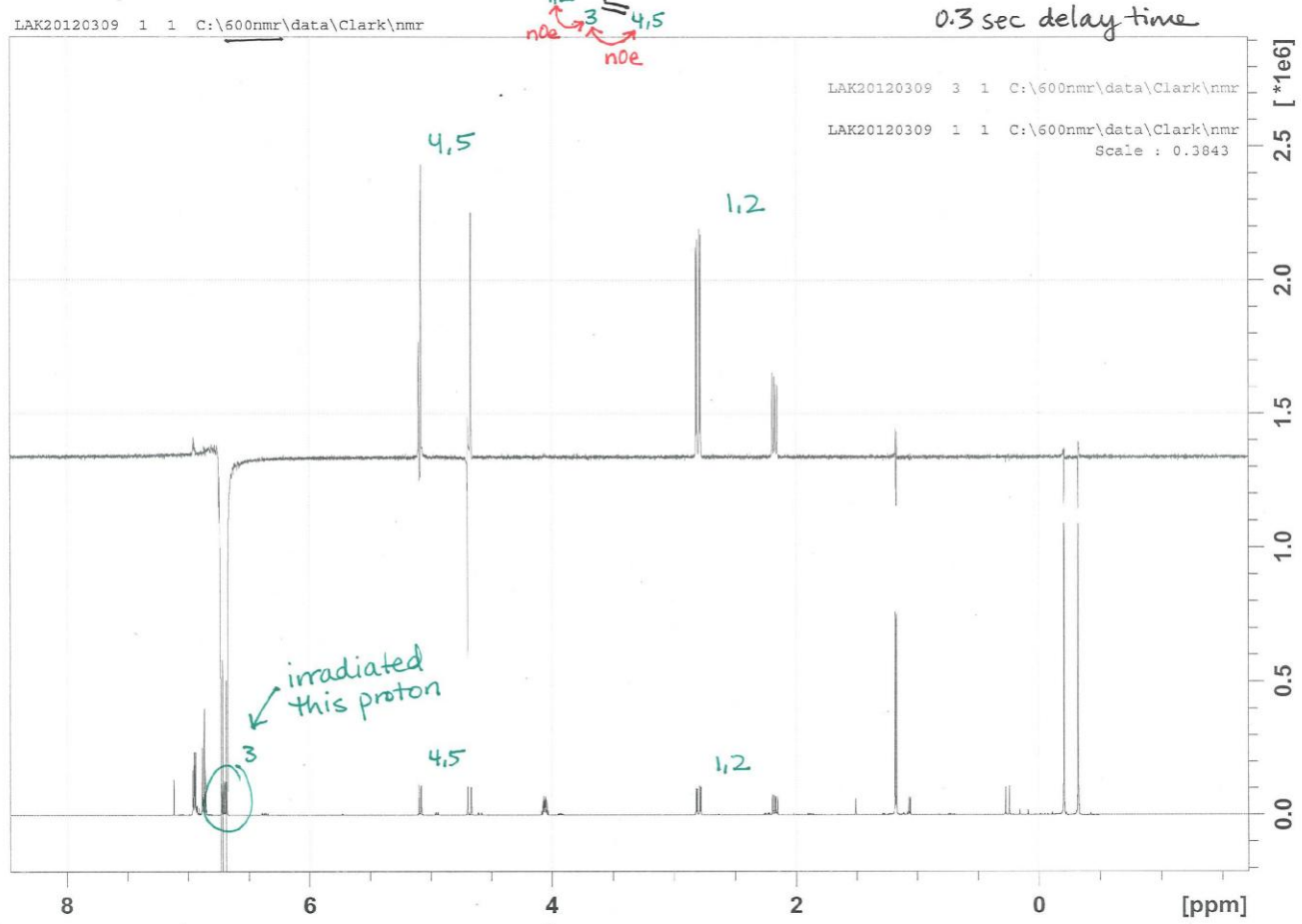

150.02
146.34
141.60
135.48
129.88
127.96
127.28
118.28
74.12
44.26
31.30
28.38
25.55
19.69
1.68
1.10
O
Si
Ph
145
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LAK-2-208


7.260
7.115
7.096
7.086
7.076
7.067
7.036
7.029
7.015
7.007
7.000
6.978
6.888
6.853
6.831
6.795
5.244
5.209
4.846
4.790
4.250
4.230
4.223
4.211
4.203
4.192
4.184
4.172
4.164
4.144
2.977
2.959
2.922
2.905
2.348
2.320
2.294
2.266
1.327
1.307
-0.065
-0.186
O
Si
F
146
9
8
7
6
5
4
3
2
1
ppm
3.78
1.00
0.06
1.01
0.05
0.98
0.91
1.01
1.03
3.03
2.90
2.92

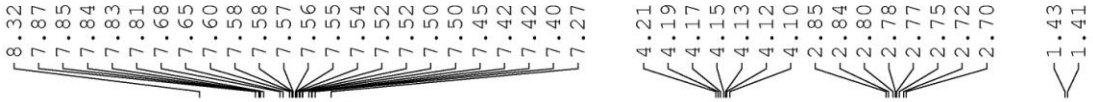
LK-2-165 noe

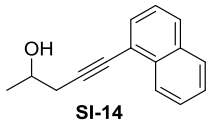




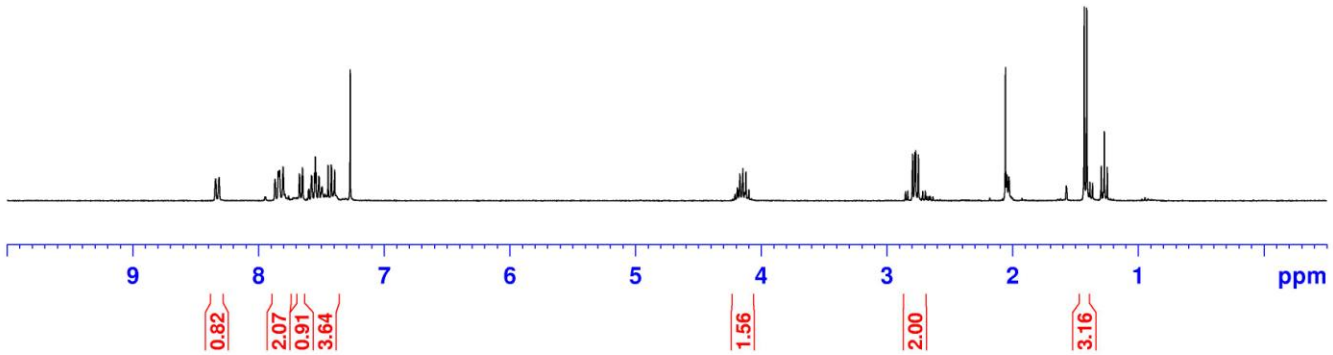
(#'s labeled on the structure refer to the protons at that location)

LAK-2-162
chrome

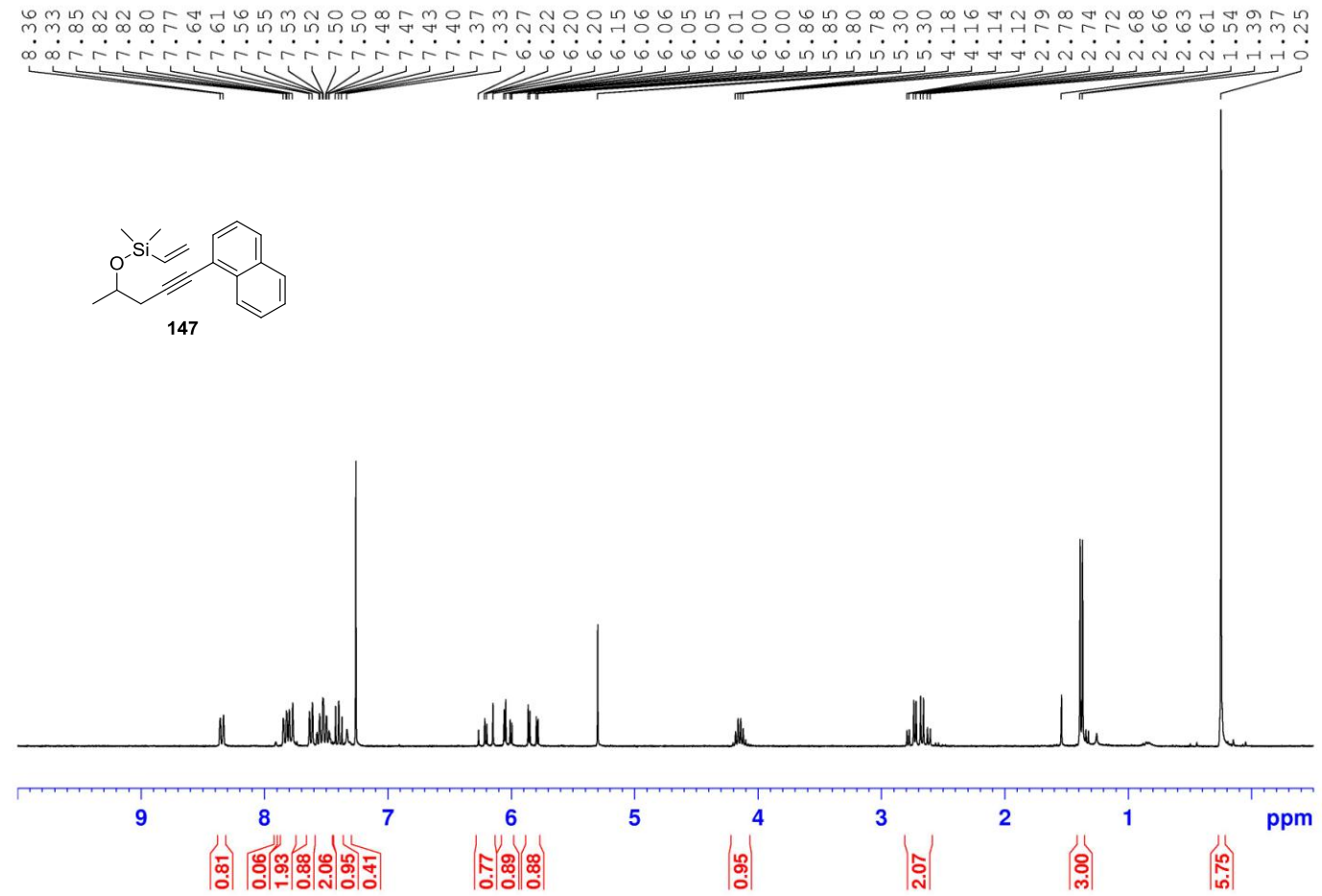




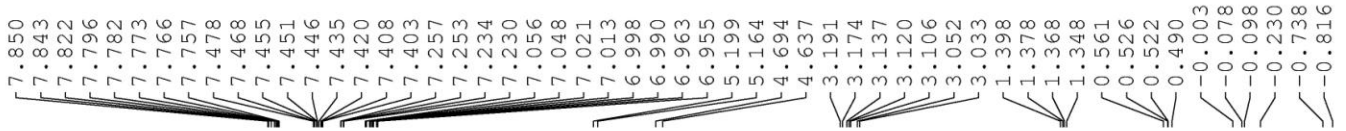
SI-14

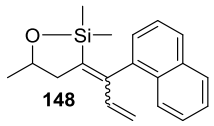


LAK-2-164

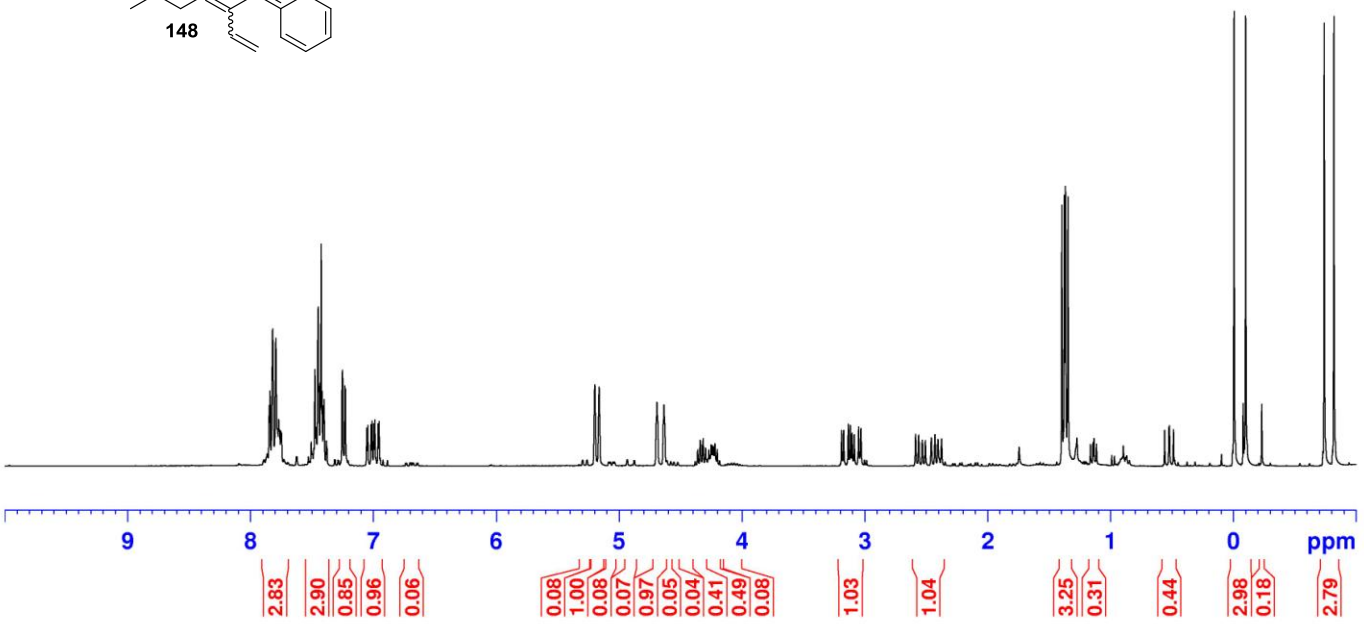

8.36
8.33
7.85
7.82
7.82
7.80
7.77
7.64
7.61
7.56
7.55
7.53
7.52
7.50
7.50
7.48
7.47
7.43
7.40
7.37
7.33
6.27
6.22
6.20
6.20
6.15
6.06
6.06
6.05
6.05
6.01
6.00
6.00
5.86
5.85
5.80
5.78
5.30
5.30
4.18
4.16
4.14
4.12
2.79
2.78
2.74
2.72
2.68
2.66
2.63
2.61
1.54
1.39
1.37
0.25
O
Si
147
9
8
7
6
5
4
3
2
1
ppm
0.81
0.06
1.93
0.88
2.06
0.95
0.41
0.77
0.89
0.88
0.95
2.07
3.00
5.75

LAK-2-207

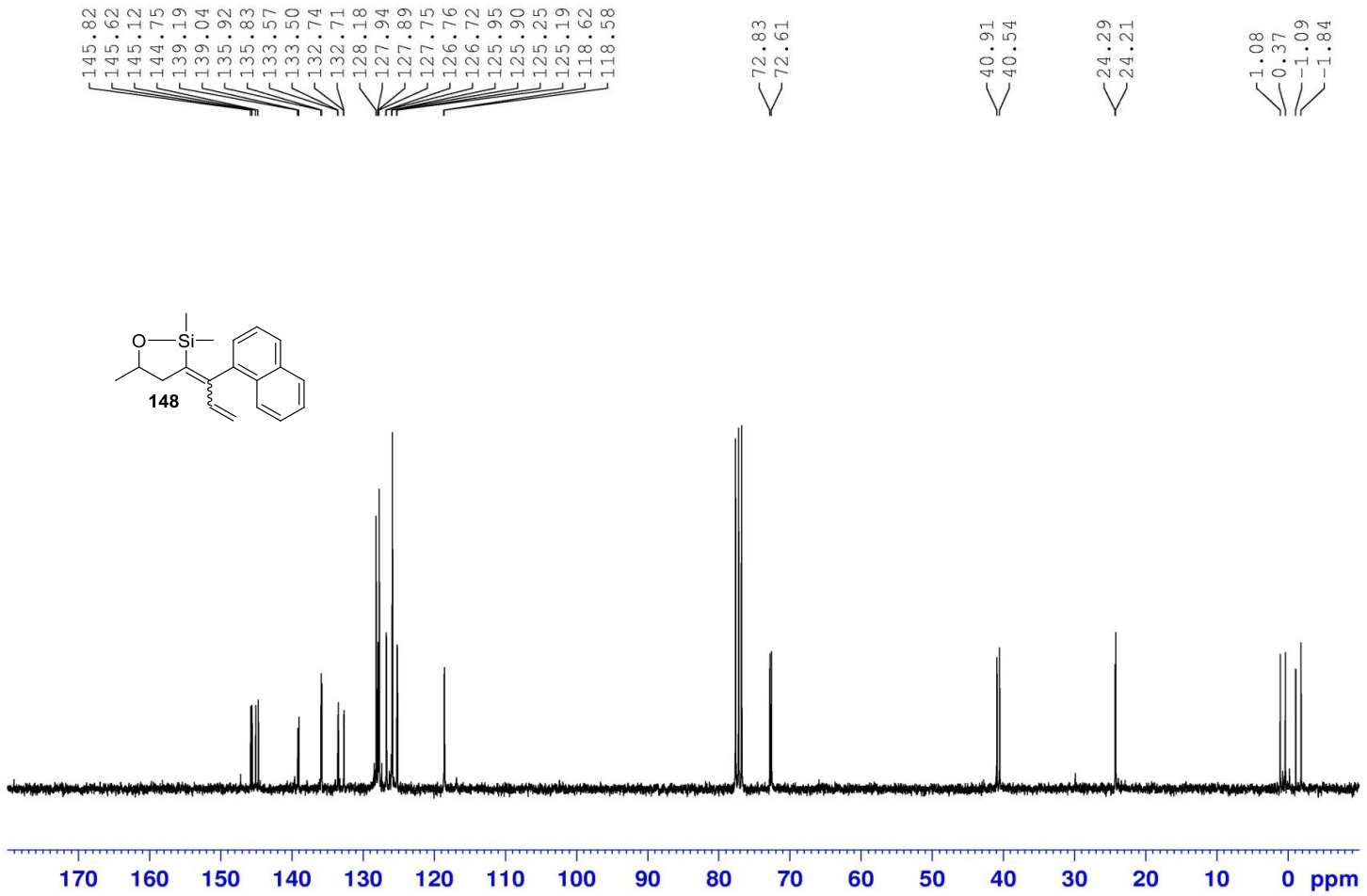

7.850
7.843
7.822
7.796
7.782
7.773
7.766
7.757
7.478
7.468
7.455
7.451
7.446
7.435
7.420
7.408
7.403
7.257
7.253
7.234
7.230
7.056
7.048
7.021
7.013
6.998
6.990
6.963
6.955
5.199
5.164
4.694
4.637
3.191
3.174
3.137
3.120
3.106
3.052
3.033
1.398
1.378
1.368
1.348
0.561
0.526
0.522
0.490
-0.003
-0.078
-0.098
-0.230
-0.738
-0.816

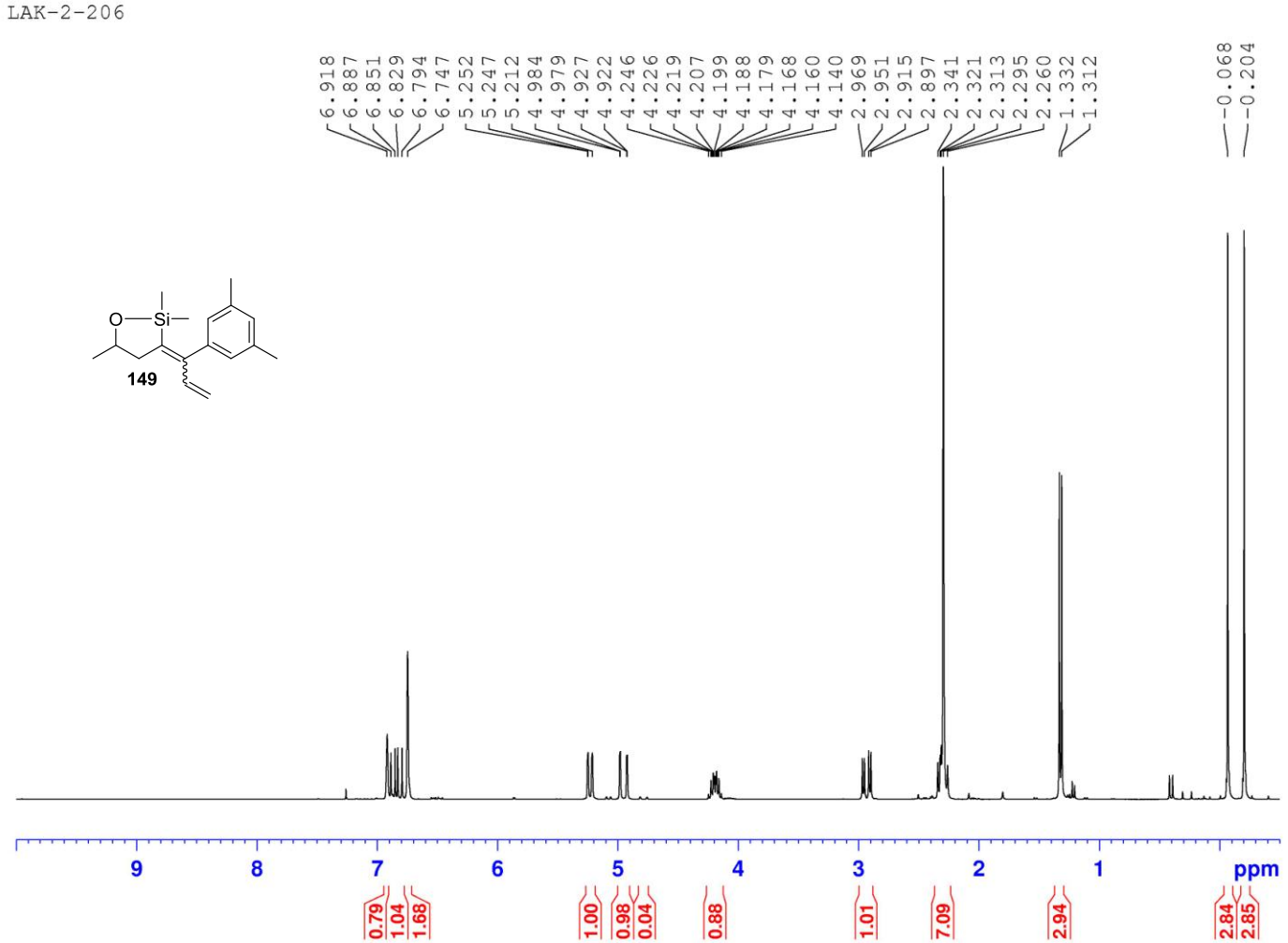

O
Si

148

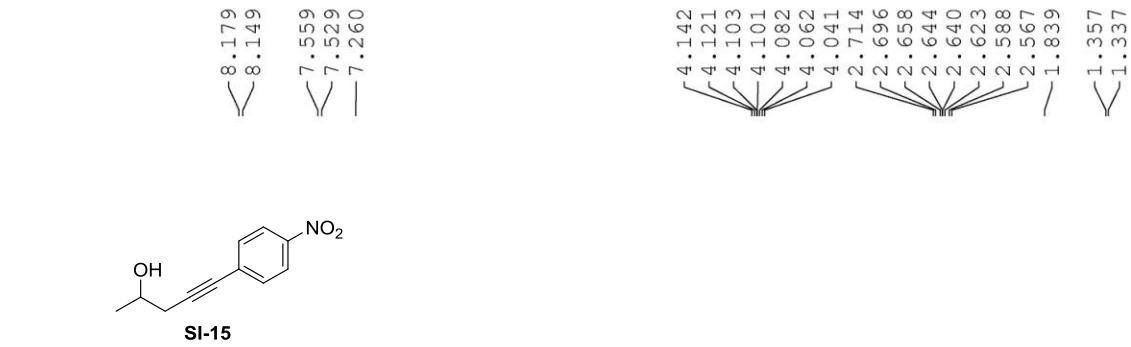

9
8
7
6
5
4
3
2
1
0
ppm
2.83
2.90
0.85
0.96
0.06
0.08
1.00
0.08
0.07
0.97
0.05
0.04
0.41
0.49
0.08
1.03
1.04
3.25
0.31
0.44
2.98
0.18
2.79

LAK-6-279

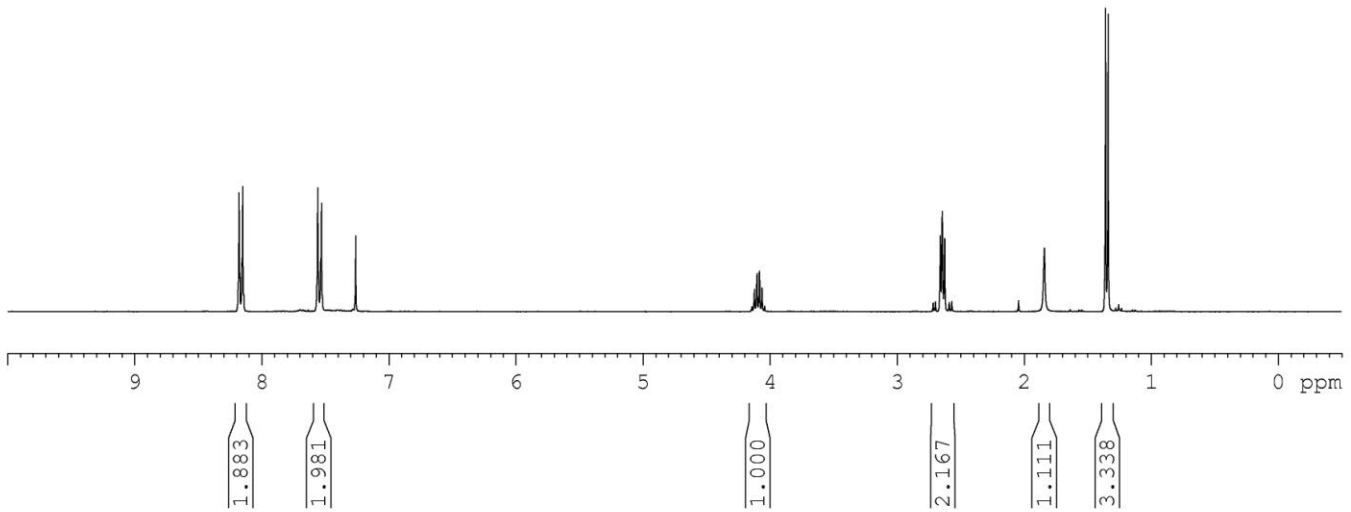

145.82
145.62
145.12
144.75
139.19
139.04
135.92
135.83
133.57
133.50
132.74
132.71
128.18
127.94
127.89
127.75
126.76
126.72
125.95
125.90
125.25
125.19
118.62
118.58
72.83
72.61
40.91
40.54
24.29
24.21
1.08
0.37
-1.09
-1.84
O
Si
148
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


LAK-2-206
6.918
6.887
6.851
6.829
6.794
6.747
5.252
5.247
5.212
4.984
4.979
4.927
4.922
4.246
4.226
4.219
4.207
4.199
4.188
4.179
4.168
4.160
4.140
2.969
2.951
2.915
2.897
2.341
2.321
2.313
2.295
2.260
1.332
1.312
-0.068
-0.204
O
Si
149
9
8
7
6
5
4
3
2
1
ppm
0.79
1.04
1.68
1.00
0.98
0.04
0.88
1.01
7.09
2.94
2.84
2.85

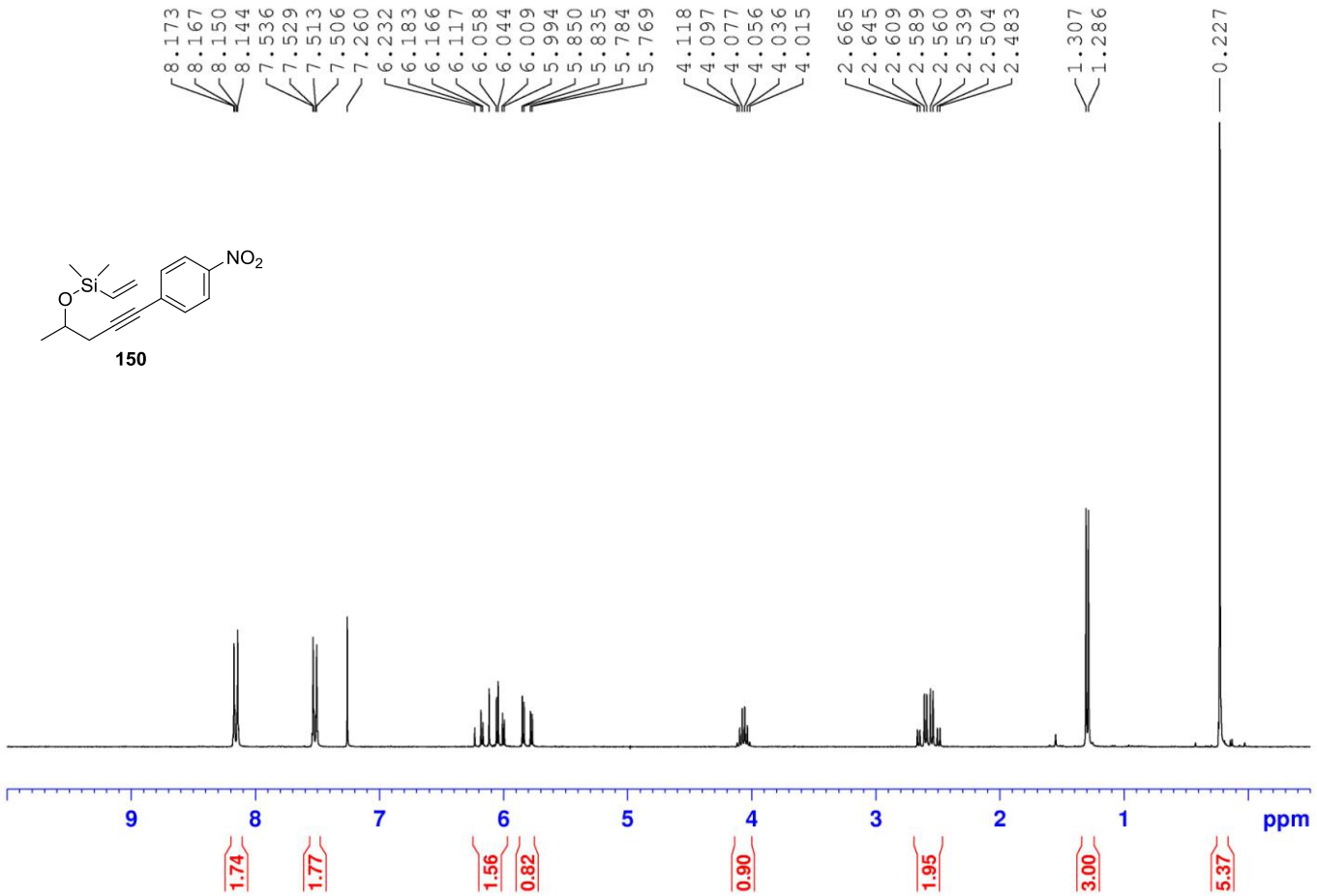
LAK-3-284



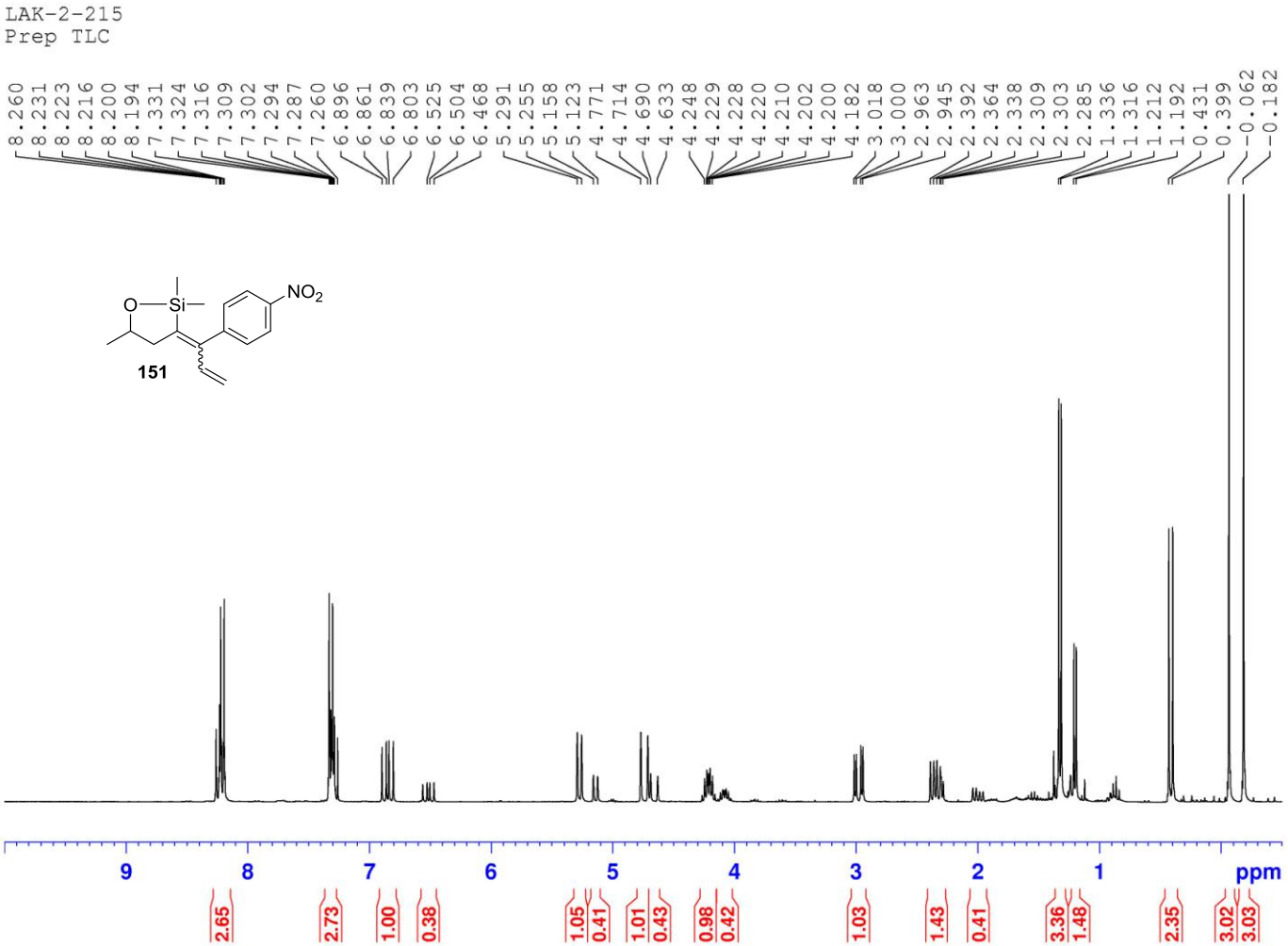
SI-15



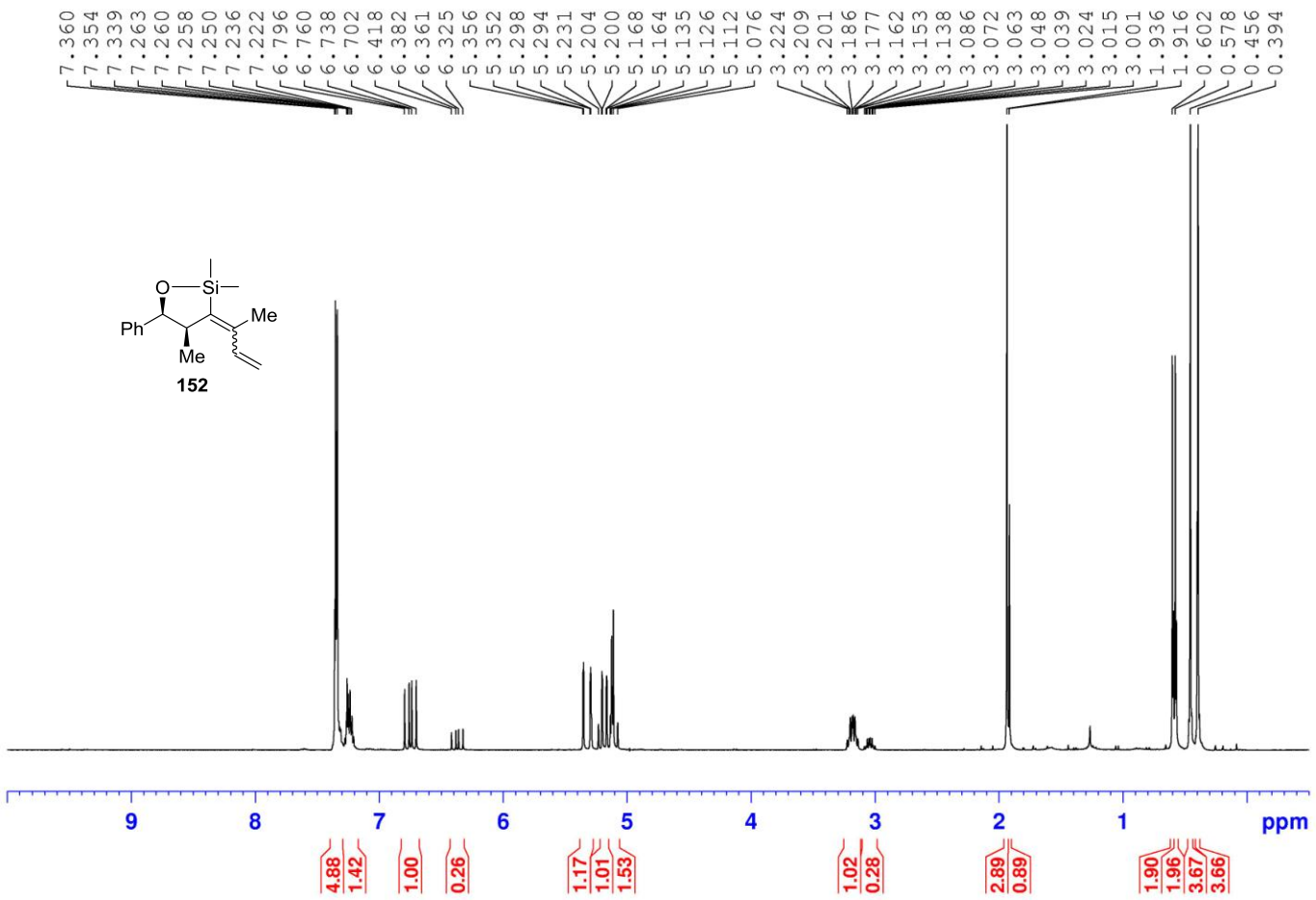
LAK-2-210


8.173
8.167
8.150
8.144
7.536
7.529
7.513
7.506
7.260
6.232
6.183
6.166
6.117
6.058
6.044
6.009
5.994
5.850
5.835
5.784
5.769
4.118
4.097
4.077
4.056
4.036
4.015
2.665
2.645
2.609
2.589
2.560
2.539
2.504
2.483
1.307
1.286
0.227
NO2
Si
O
9
8
7
6
5
4
3
2
1
ppm
1.74
1.77
1.56
0.82
0.90
1.95
3.00
5.37

150

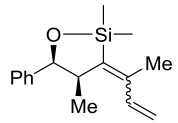

LAK-2-215
Prep TLC
8.260
8.231
8.223
8.216
8.200
8.194
7.331
7.324
7.316
7.309
7.302
7.294
7.287
7.260
6.896
6.861
6.839
6.803
6.525
6.504
6.468
5.291
5.255
5.158
5.123
4.771
4.714
4.690
4.633
4.248
4.229
4.228
4.220
4.210
4.202
4.200
4.182
3.018
3.000
2.963
2.945
2.392
2.364
2.338
2.309
2.303
2.285
1.336
1.316
1.212
1.192
0.431
0.399
-0.062
-0.182
O
Si
NO2
151
9
8
7
6
5
4
3
2
1
ppm
2.65
2.73
1.00
0.38
1.05
0.41
1.01
0.43
0.98
0.42
1.03
1.43
0.41
3.36
1.48
2.35
3.02
3.03

LAK-2-205
major

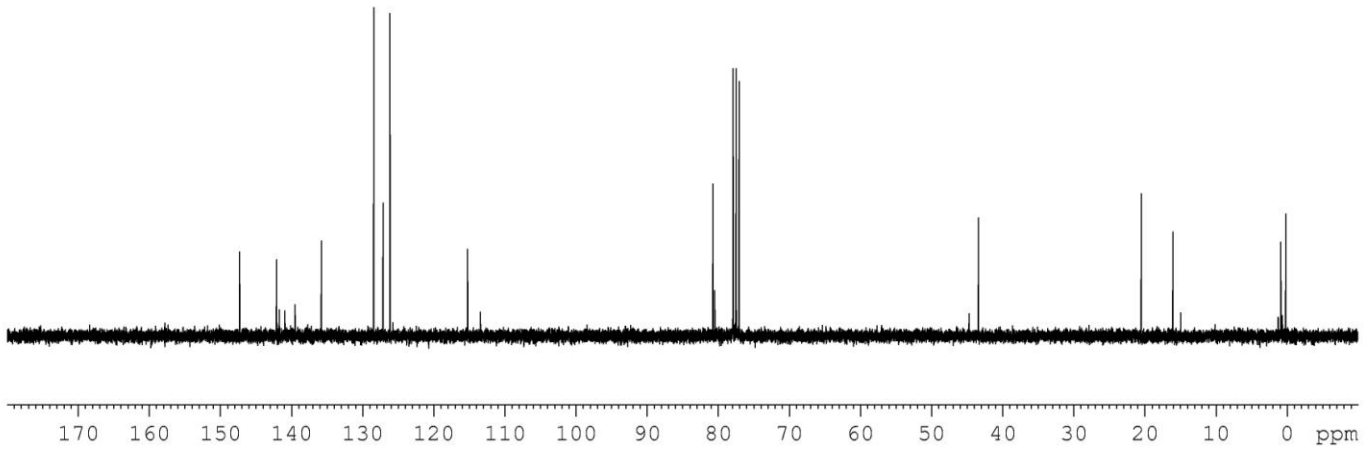


AK-2-205

147.229
142.051
141.677
140.880
139.470
135.738
128.382
127.079
126.111
126.096
115.176
113.372
80.686
80.450
44.637
43.339
20.448
15.992
14.887
1.200
0.837
0.606
0.129

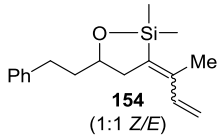


152

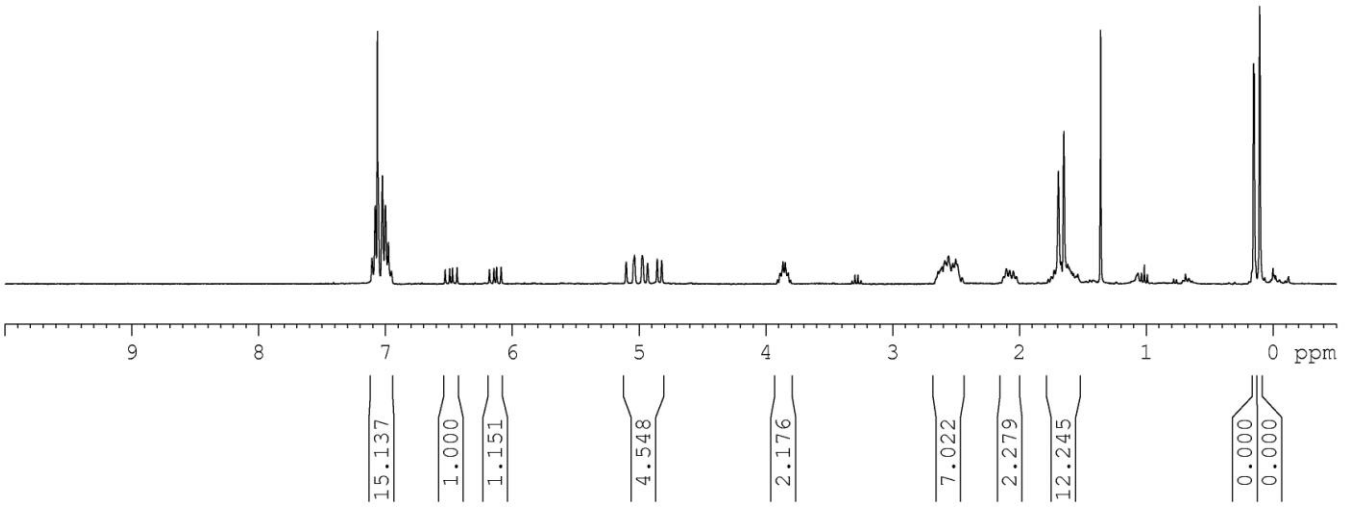


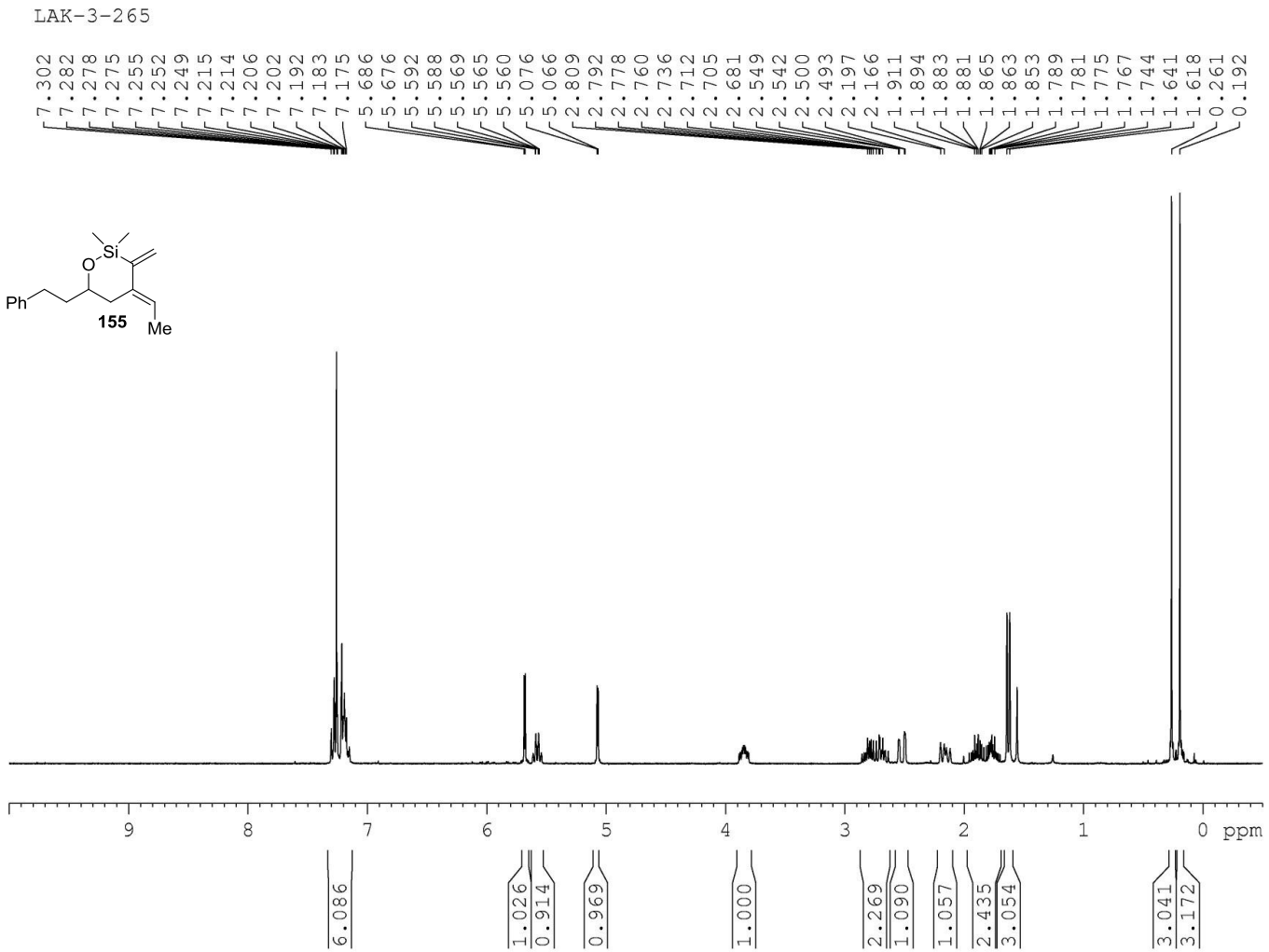
LAK-6-280

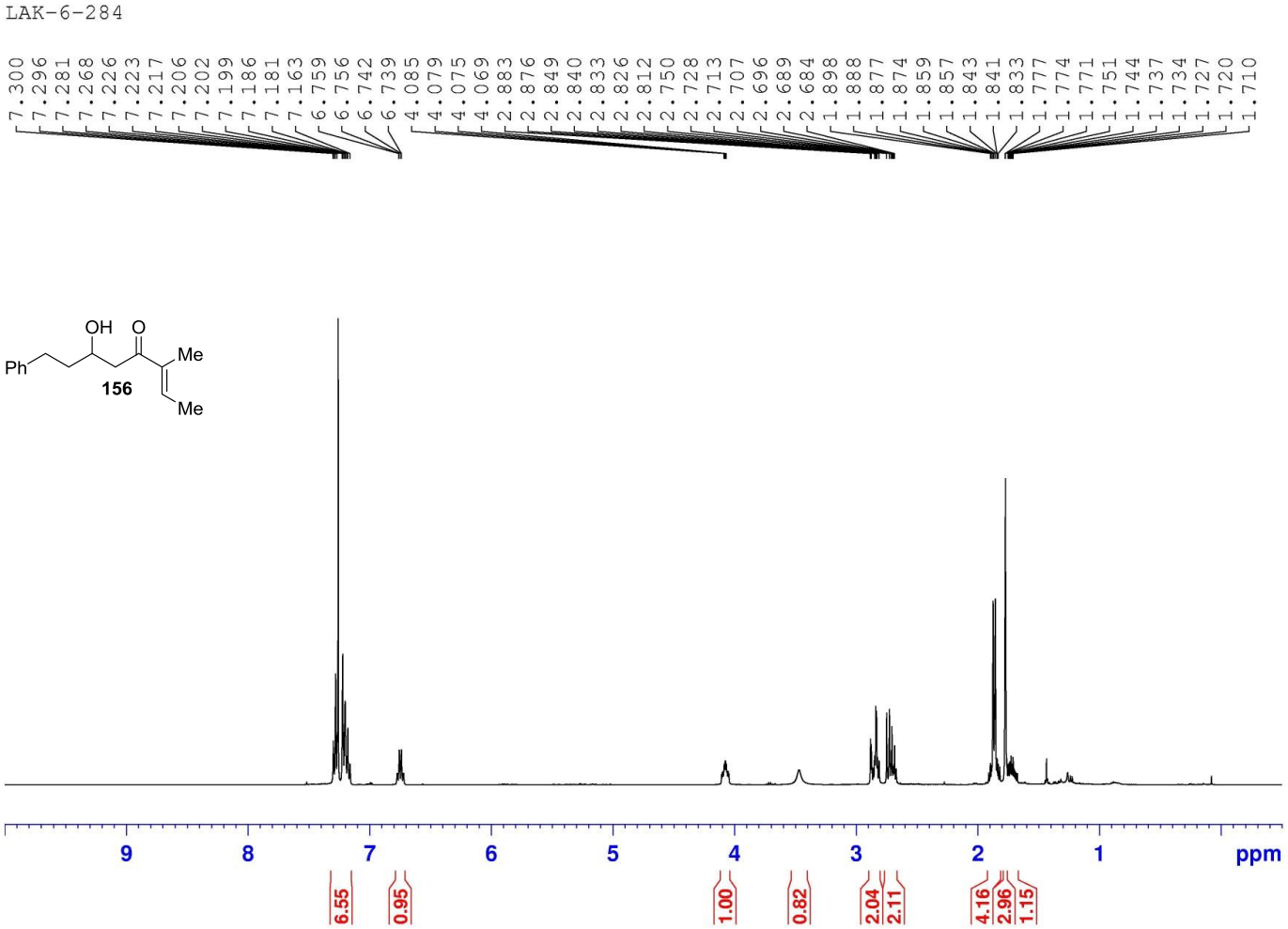
7.107 7.082 7.064 7.025 7.001 6.977 6.955 6.530 6.494 6.471 6.436 6.181 6.145 6.124 6.088 5.102 5.036 4.975 4.933 4.857 4.822 3.890 3.883 3.866 3.848 3.831 3.824 2.642 2.611 2.588 2.575 2.563 2.557 2.525 2.502 2.488 2.122 2.103 2.076 2.049 1.724 1.693 1.672 1.649 1.618 1.607 1.596 1.585 1.573 1.552 1.540 0.153 0.147 0.106



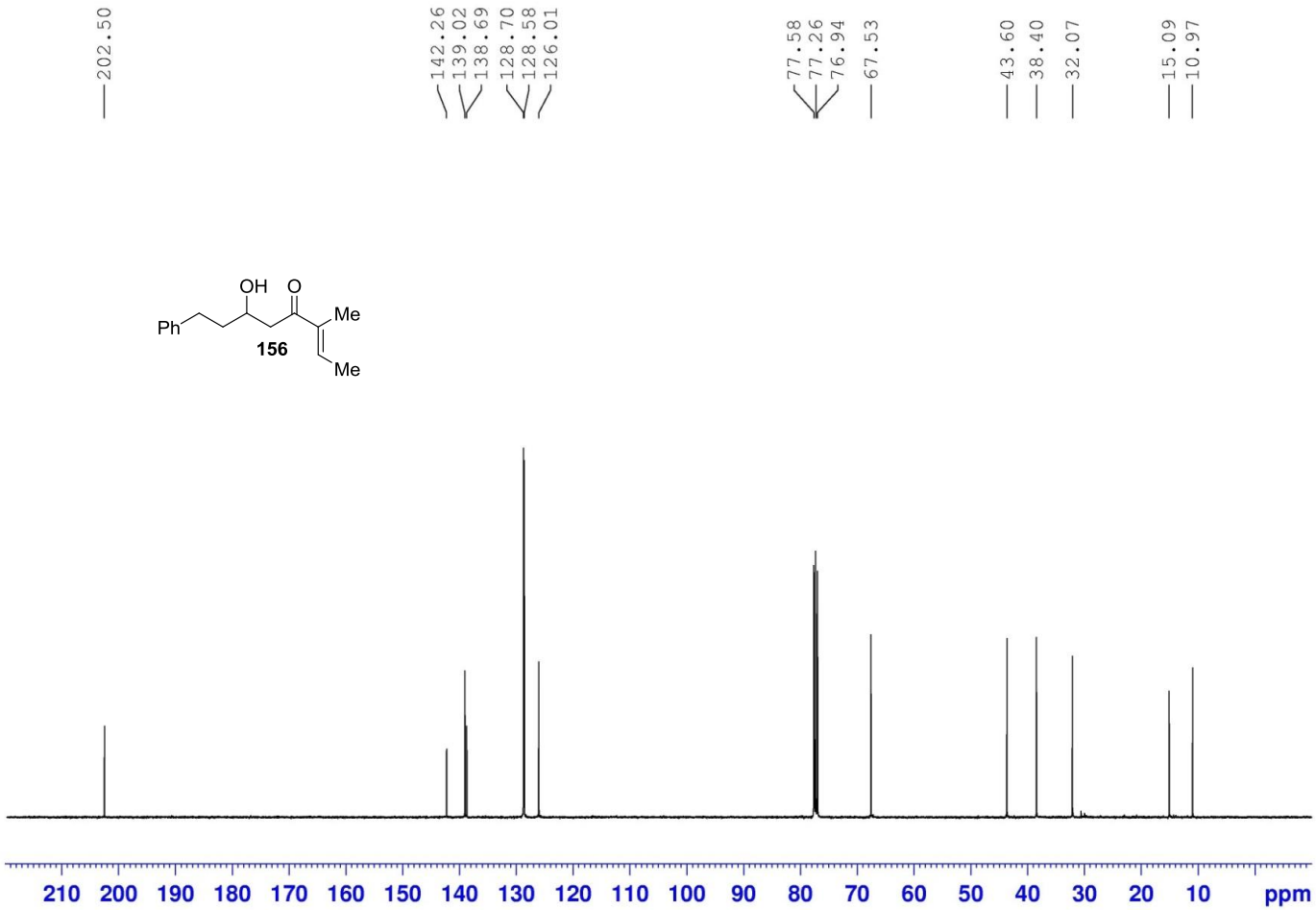
154
(1:1 *Z*/*E*)



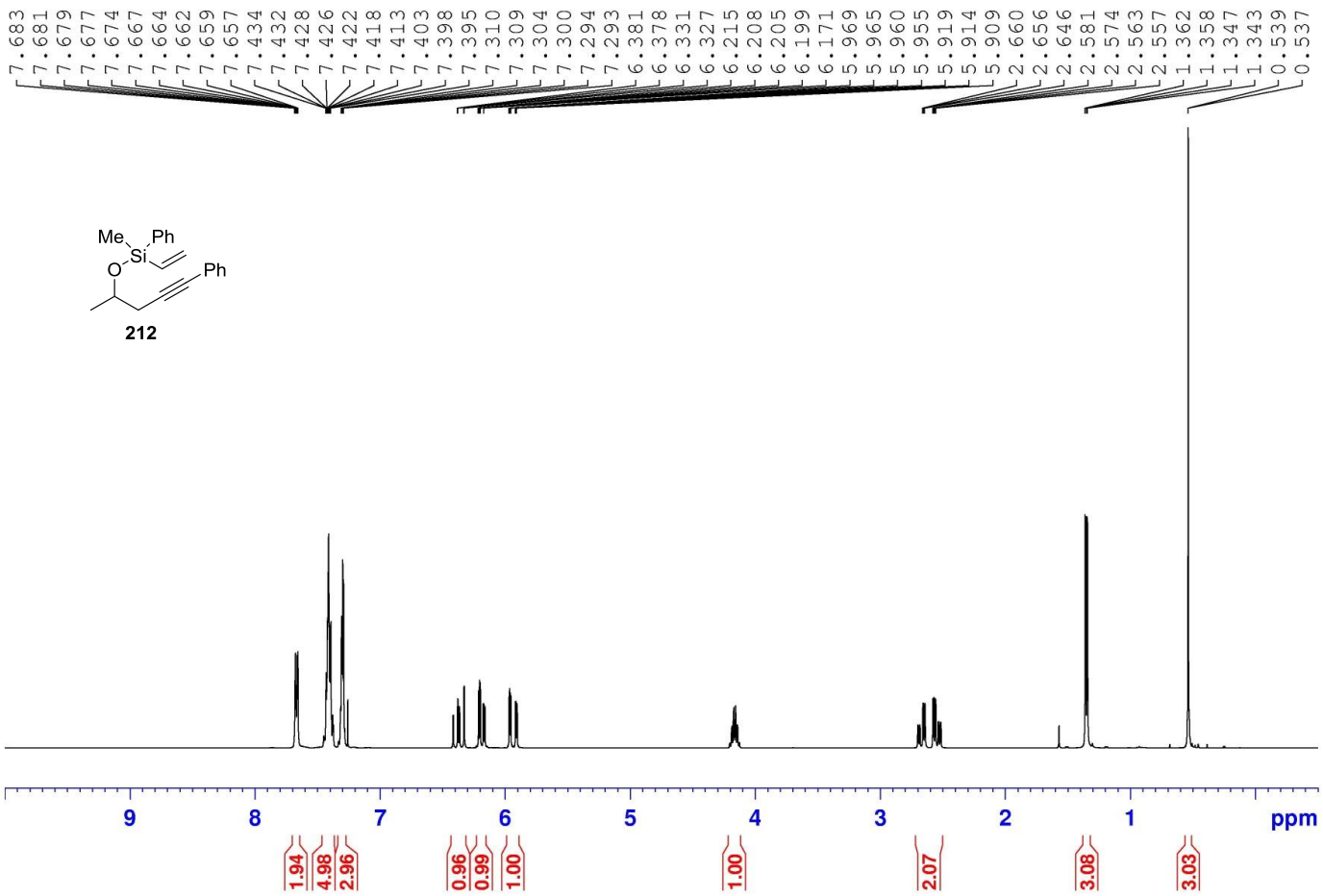

LAK-3-265
7.302
7.282
7.278
7.275
7.255
7.252
7.249
7.215
7.214
7.206
7.202
7.192
7.183
7.175
5.686
5.676
5.592
5.588
5.569
5.565
5.560
5.076
5.066
2.809
2.792
2.778
2.760
2.736
2.712
2.705
2.681
2.549
2.542
2.500
2.493
2.197
2.166
1.911
1.894
1.883
1.881
1.865
1.863
1.853
1.789
1.781
1.775
1.767
1.744
1.641
1.618
0.261
0.192
Si
O
Ph
155
Me
9
8
7
6
5
4
3
2
1
0 ppm
6.086
1.026
0.914
0.969
1.000
2.269
1.090
1.057
2.435
3.054
3.041
3.172


LAK-6-284
7.300
7.296
7.281
7.268
7.226
7.223
7.217
7.206
7.202
7.199
7.186
7.181
7.163
6.759
6.756
6.742
6.739
4.085
4.079
4.075
4.069
2.883
2.876
2.849
2.840
2.833
2.826
2.812
2.750
2.728
2.713
2.707
2.696
2.689
2.684
1.898
1.888
1.877
1.874
1.859
1.857
1.843
1.841
1.833
1.777
1.774
1.771
1.751
1.744
1.737
1.734
1.727
1.720
1.710
OH
O
Ph
Me
Me
156
9
8
7
6
5
4
3
2
1
ppm
6.55
0.95
1.00
0.82
2.04
2.11
4.16
2.96
1.15

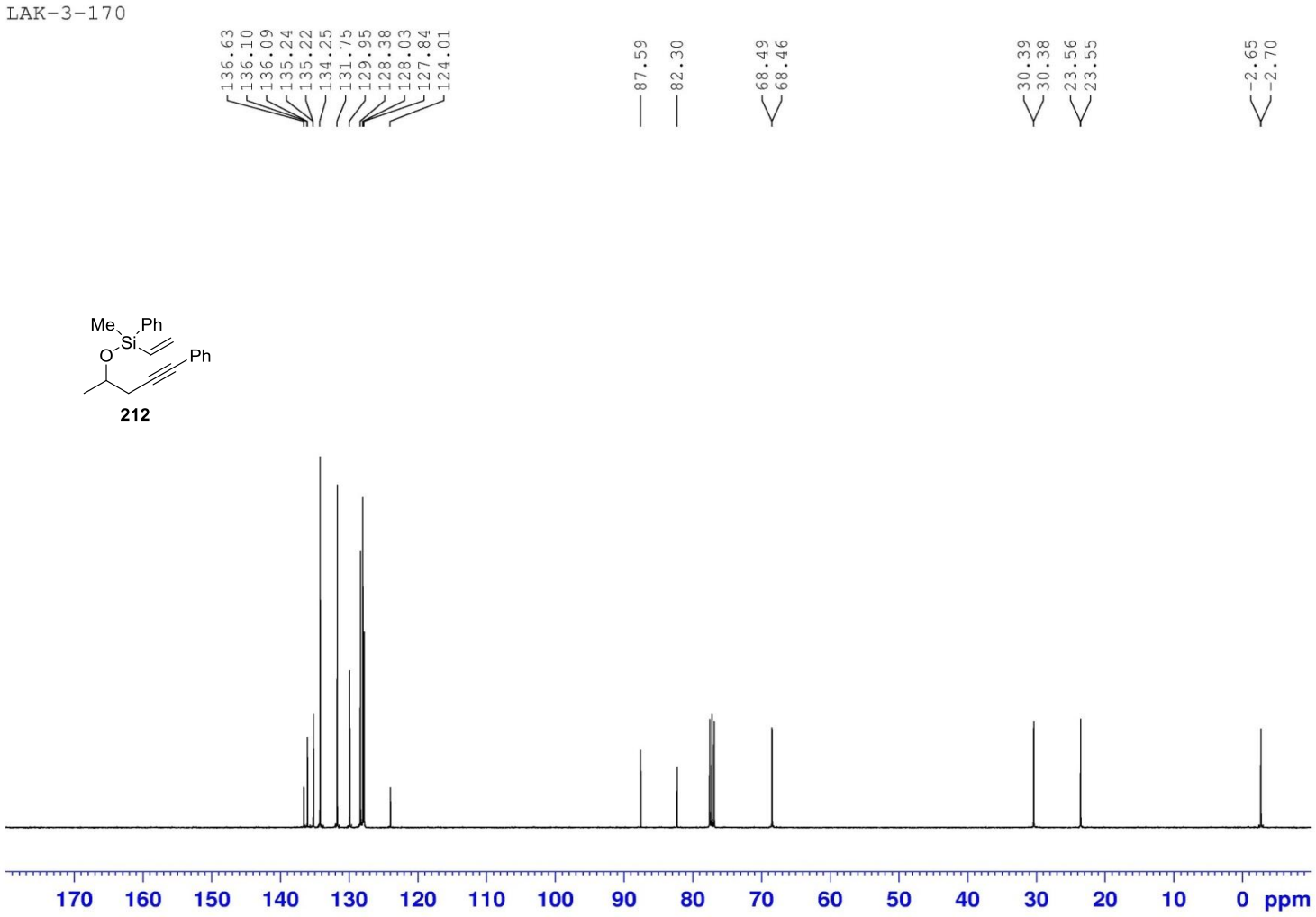
LAK-6-284

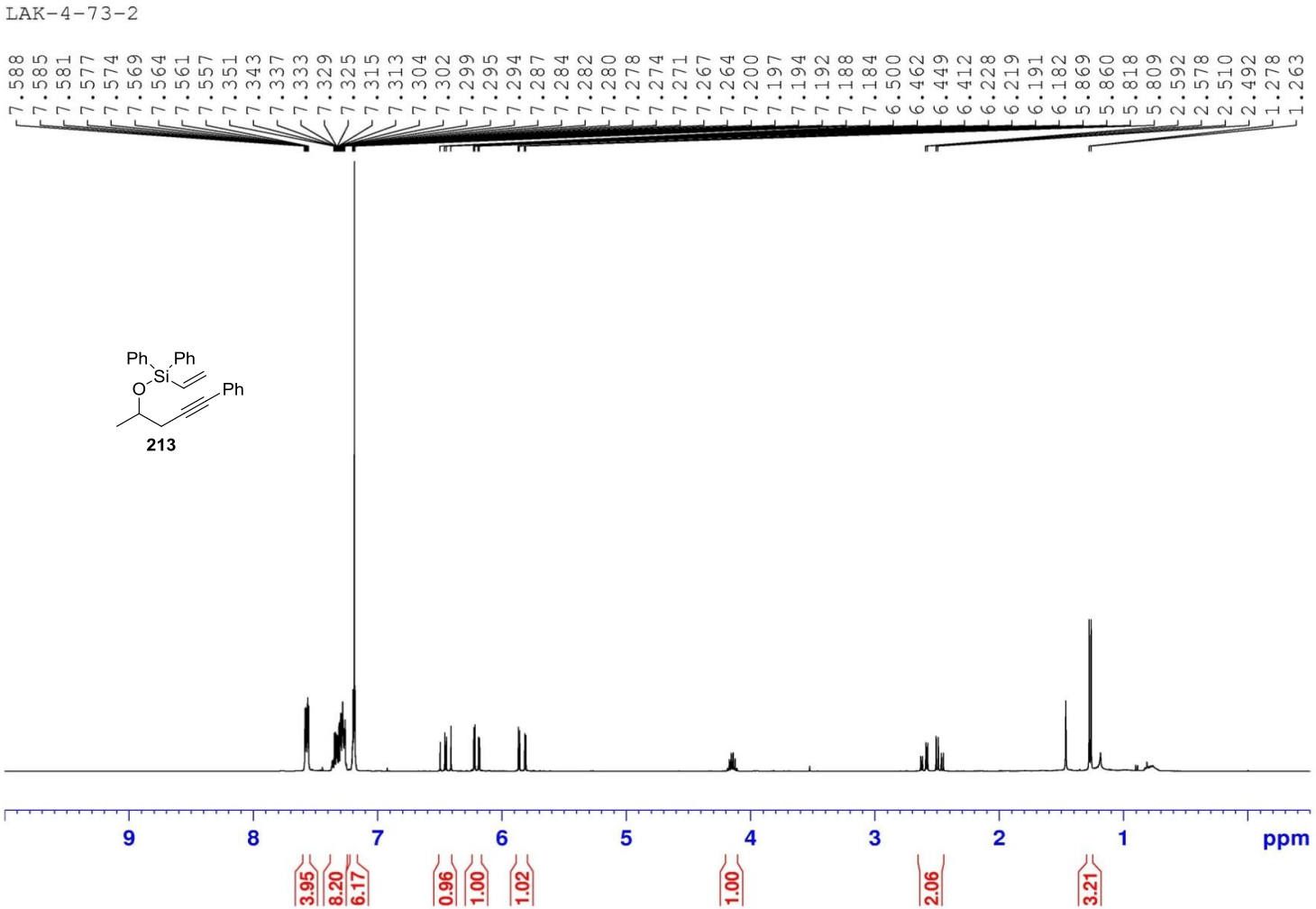

202.50
142.26
139.02
138.69
128.70
128.58
126.01
77.58
77.26
76.94
67.53
43.60
38.40
32.07
15.09
10.97
OH
O
Ph
Me
Me
156
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

LAK-3-170

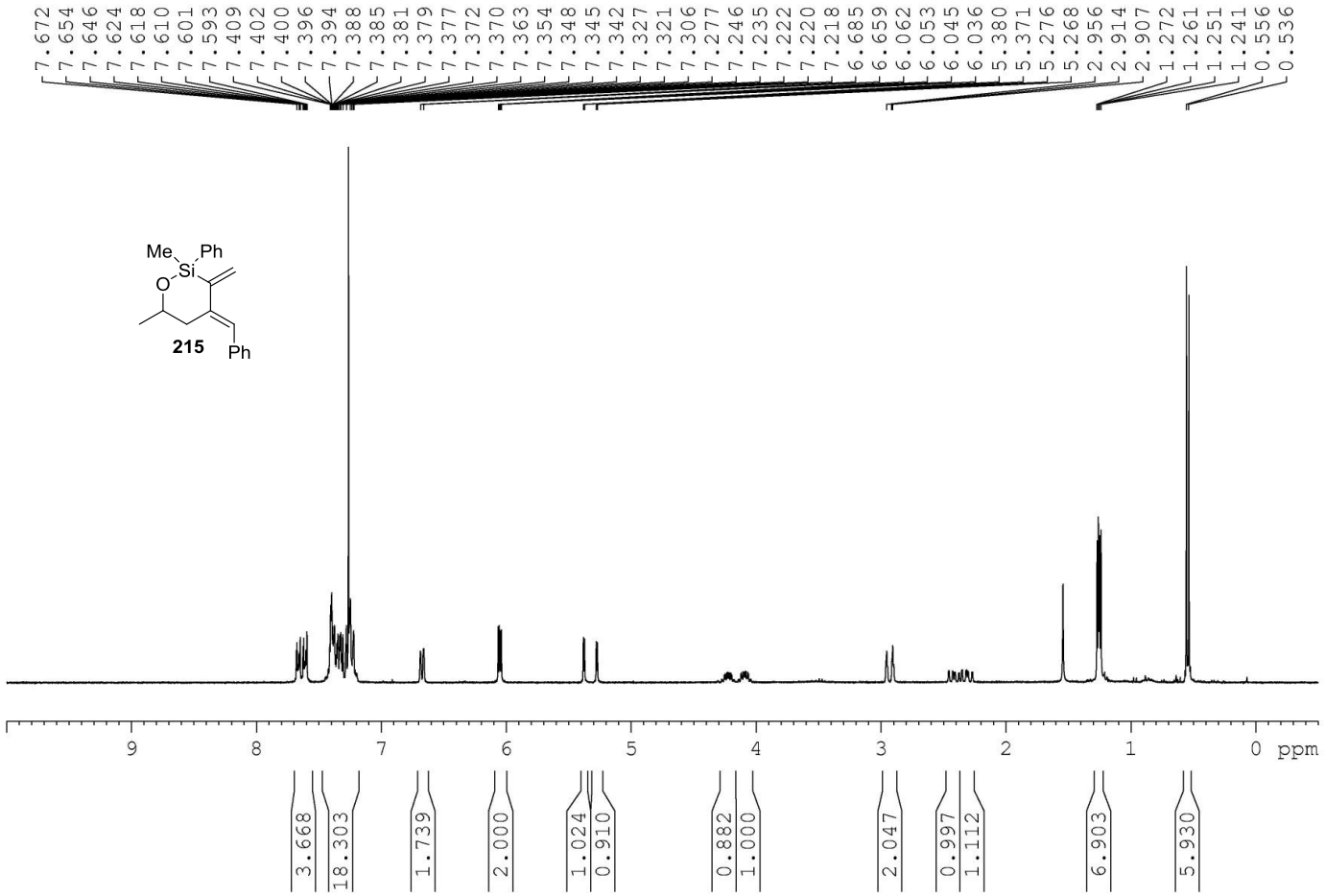

7.683
7.681
7.679
7.677
7.674
7.667
7.664
7.662
7.659
7.657
7.434
7.432
7.428
7.426
7.422
7.418
7.413
7.403
7.398
7.395
7.310
7.309
7.304
7.300
7.294
7.293
6.381
6.378
6.331
6.327
6.215
6.208
6.205
6.199
6.171
5.969
5.965
5.960
5.955
5.919
5.914
5.909
2.660
2.656
2.646
2.581
2.574
2.563
2.557
1.362
1.358
1.347
1.343
0.539
0.537
Me
Ph
Si
O
Ph
9
8
7
6
5
4
3
2
1
ppm
1.94
4.98
2.96
0.96
0.99
1.00
1.00
2.07
3.08
3.03

212


LAK-3-170
136.63
136.10
136.09
135.24
135.22
134.25
131.75
129.95
128.38
128.03
127.84
124.01
87.59
82.30
68.49
68.46
30.39
30.38
23.56
23.55
-2.65
-2.70
Me
Ph
Si
O
Ph
212
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


LAK-4-73-2
7.588
7.585
7.581
7.577
7.574
7.569
7.564
7.561
7.557
7.351
7.343
7.337
7.333
7.329
7.325
7.315
7.313
7.304
7.302
7.299
7.295
7.294
7.287
7.284
7.282
7.280
7.278
7.274
7.271
7.267
7.264
7.200
7.197
7.194
7.192
7.188
7.184
6.500
6.462
6.449
6.412
6.228
6.219
6.191
6.182
5.869
5.860
5.818
5.809
2.592
2.578
2.510
2.492
1.278
1.263
Ph
Ph
Si
O
Ph
213
9
8
7
6
5
4
3
2
1
ppm
3.95
8.20
6.17
0.96
1.00
1.02
1.00
2.06
3.21

LAK-4-119


7.672
7.654
7.646
7.624
7.618
7.610
7.601
7.593
7.409
7.402
7.400
7.396
7.394
7.388
7.385
7.381
7.379
7.377
7.372
7.370
7.363
7.354
7.348
7.345
7.342
7.327
7.321
7.306
7.277
7.246
7.235
7.222
7.220
7.218
6.685
6.659
6.062
6.053
6.045
6.036
5.380
5.371
5.276
5.268
2.956
2.914
2.907
1.272
1.261
1.251
1.241
0.556
0.536
Me
Ph
Si
O
215
Ph
9
8
7
6
5
4
3
2
1
0 ppm
3.668
18.303
1.739
2.000
1.024
0.910
0.882
1.000
2.047
0.997
1.112
6.903
5.930

LAK-4-119
carbon

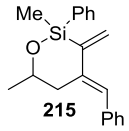
149.520
149.399
143.315
142.348
137.976
137.930
136.811
136.757
134.146
134.039
130.178
130.049
129.414
129.324
128.434
128.404
128.101
128.069
126.703
124.025
123.879
123.713
123.591

70.720
70.573

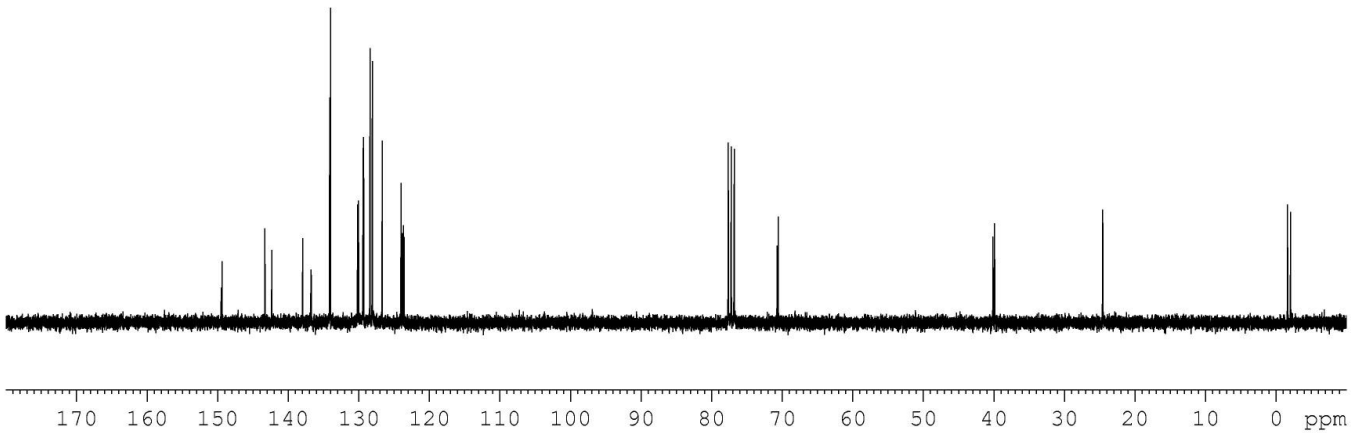
40.143
39.912

24.604
24.562

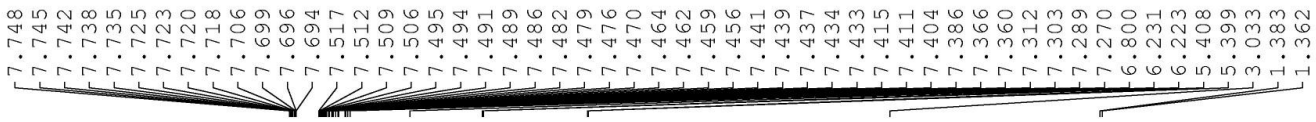
-1.600
-2.049

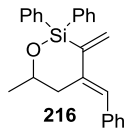


215

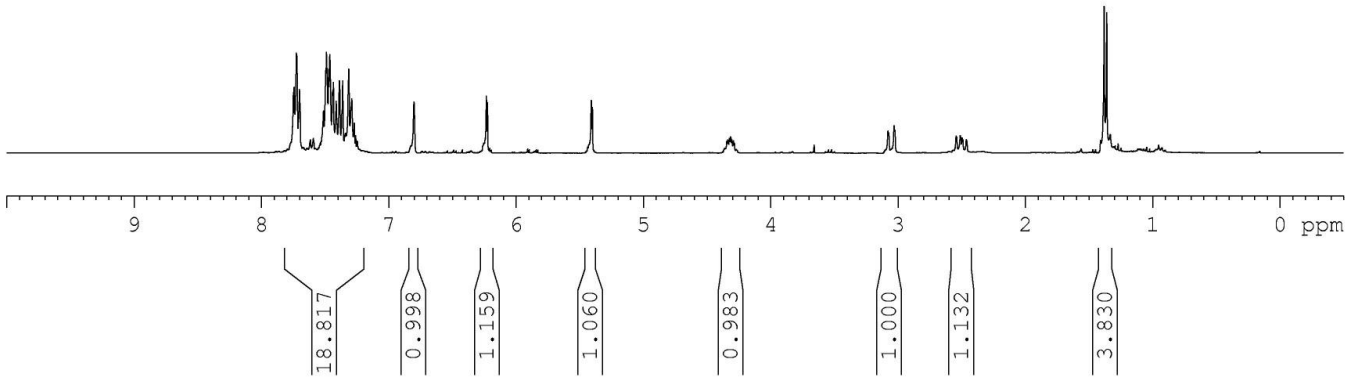


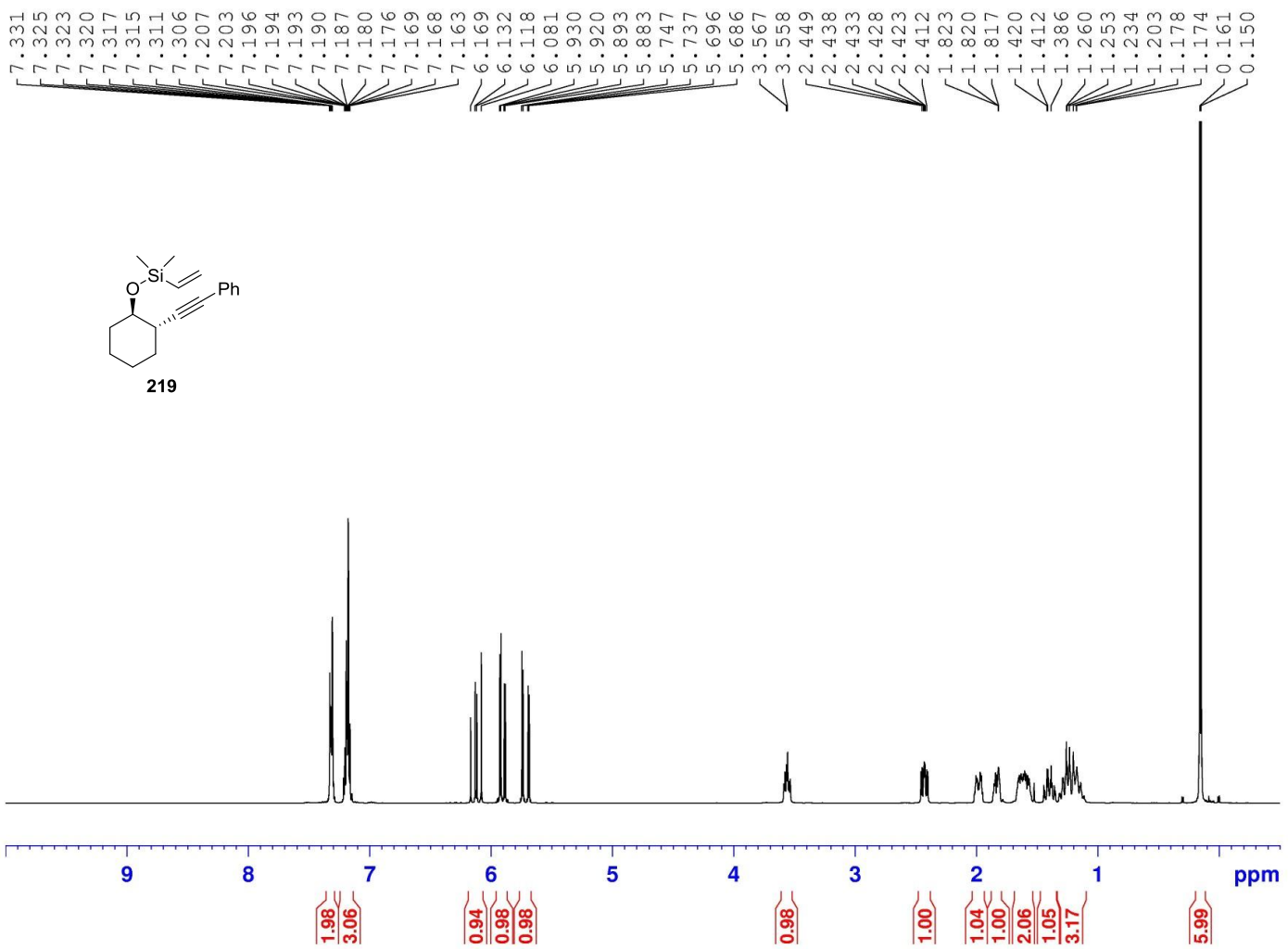
LAK-4-120

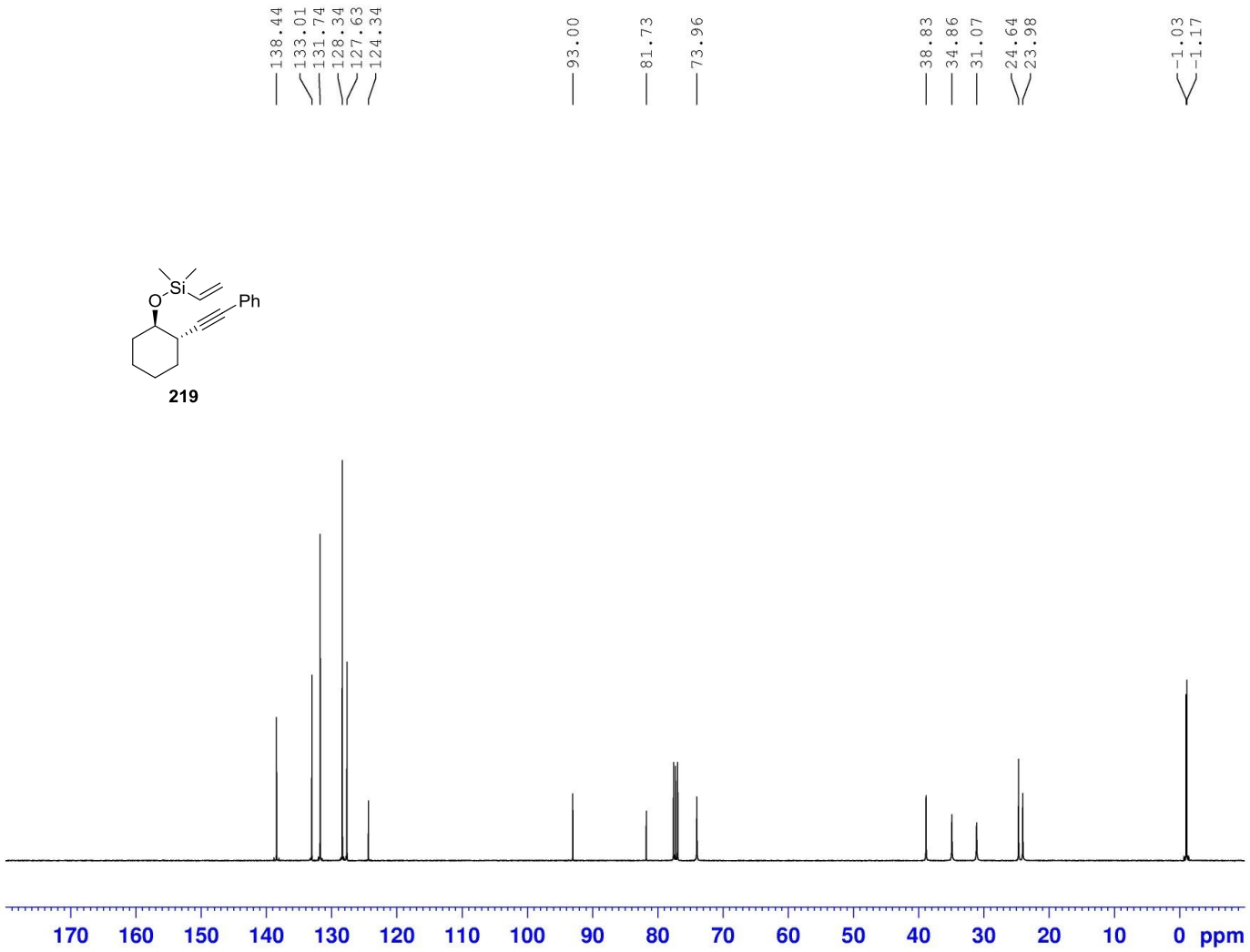

7.748
7.745
7.742
7.738
7.735
7.725
7.723
7.720
7.718
7.706
7.699
7.696
7.694
7.517
7.512
7.509
7.506
7.495
7.494
7.491
7.489
7.486
7.482
7.479
7.476
7.470
7.464
7.462
7.459
7.456
7.441
7.439
7.437
7.434
7.433
7.415
7.411
7.404
7.386
7.366
7.360
7.312
7.303
7.289
7.270
6.800
6.231
6.223
5.408
5.399
3.033
1.383
1.362


Ph
Ph
Si
O
Ph

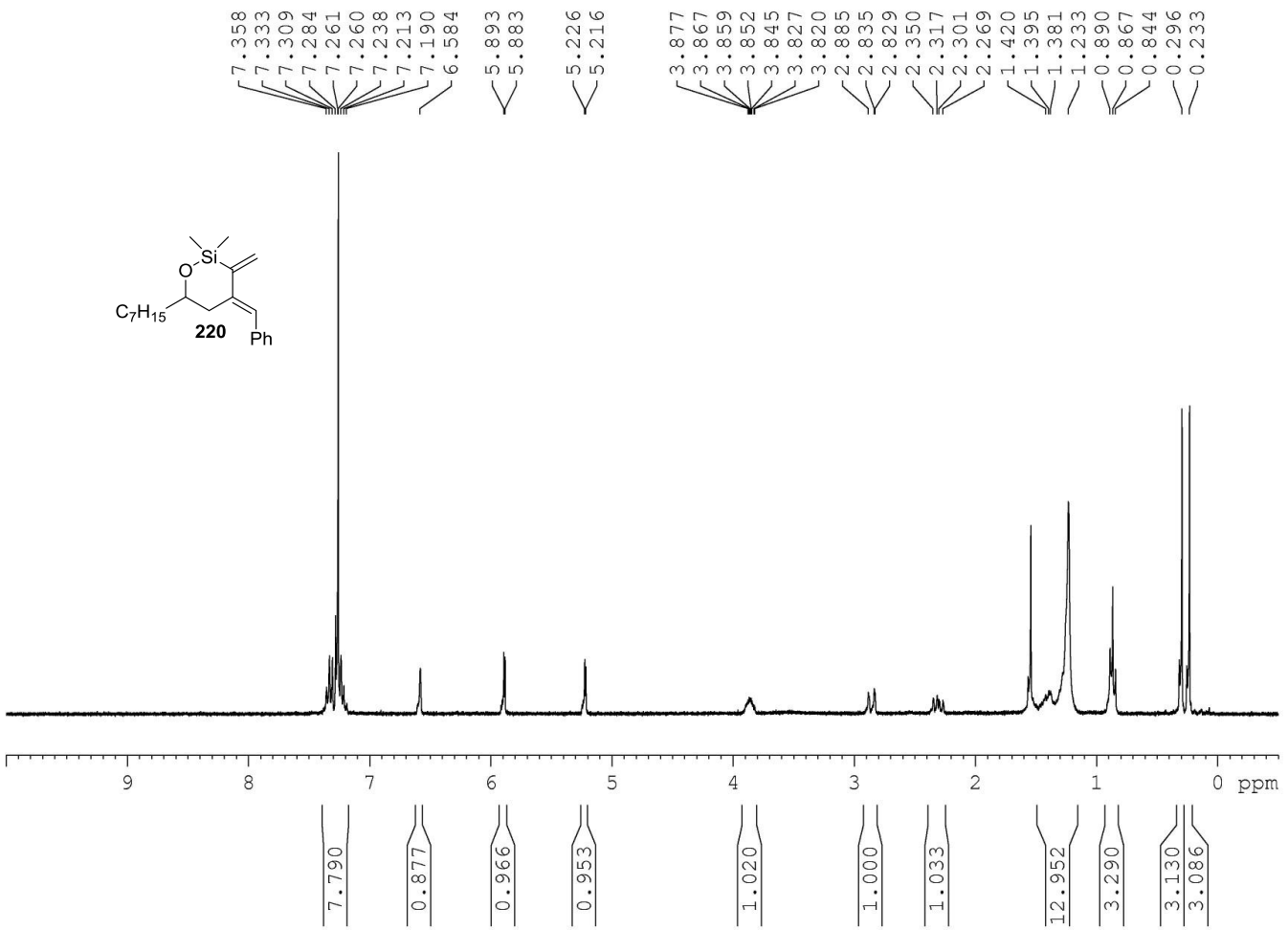
216

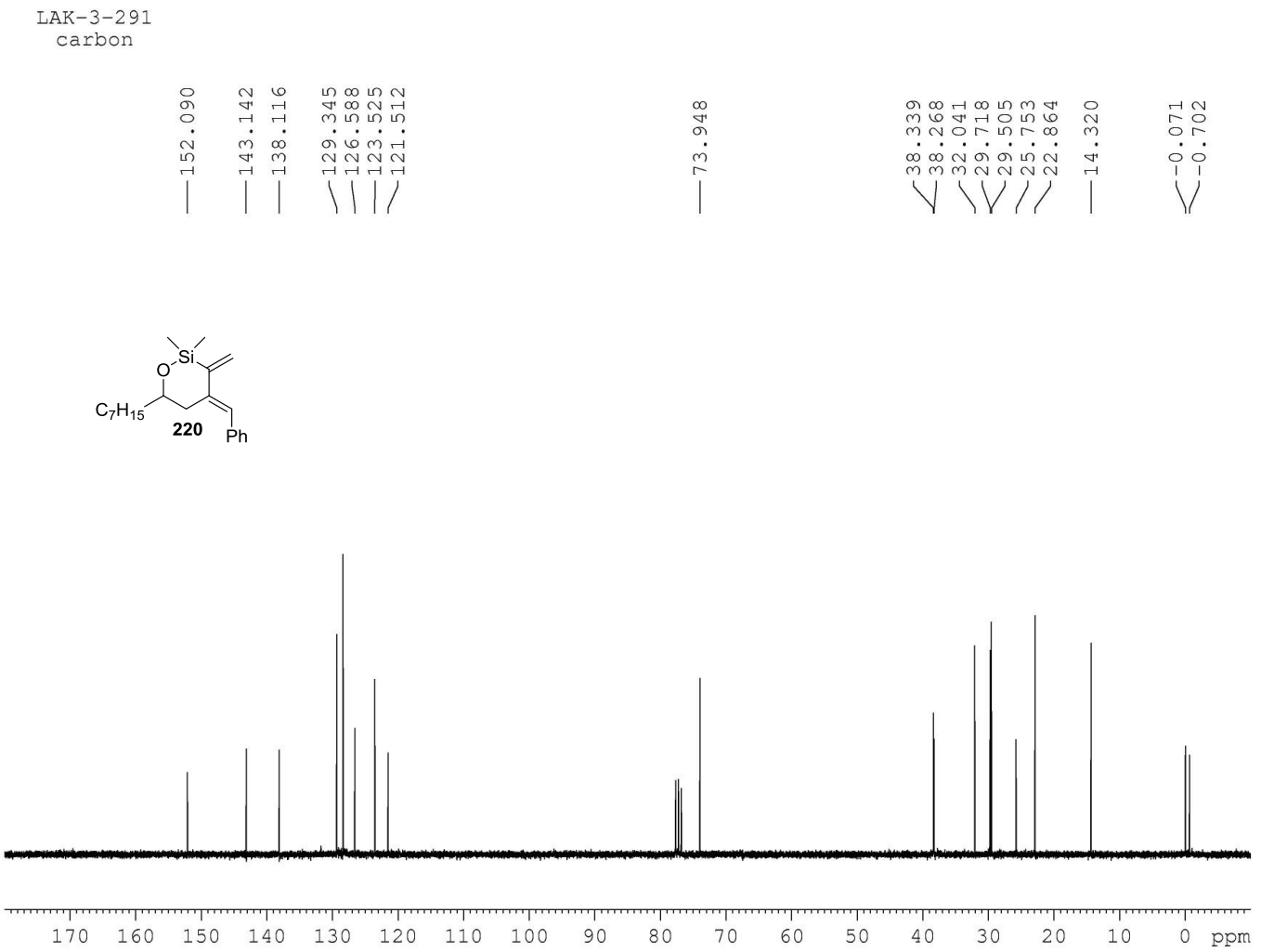

9
8
7
6
5
4
3
2
1
0 ppm
18.817
0.998
1.159
1.060
0.983
1.000
1.132
3.830


7.331
7.325
7.323
7.320
7.317
7.315
7.311
7.306
7.207
7.203
7.196
7.194
7.193
7.190
7.187
7.180
7.176
7.169
7.168
7.163
6.169
6.132
6.118
6.081
5.930
5.920
5.893
5.883
5.747
5.737
5.696
5.686
3.567
3.558
2.449
2.438
2.433
2.428
2.423
2.412
1.823
1.820
1.817
1.420
1.412
1.386
1.260
1.253
1.234
1.203
1.178
1.174
0.161
0.150
Si
O
Ph
219
9
8
7
6
5
4
3
2
1
ppm
1.98
3.06
0.94
0.98
0.98
0.98
1.00
1.04
1.00
2.06
1.05
3.17
5.99

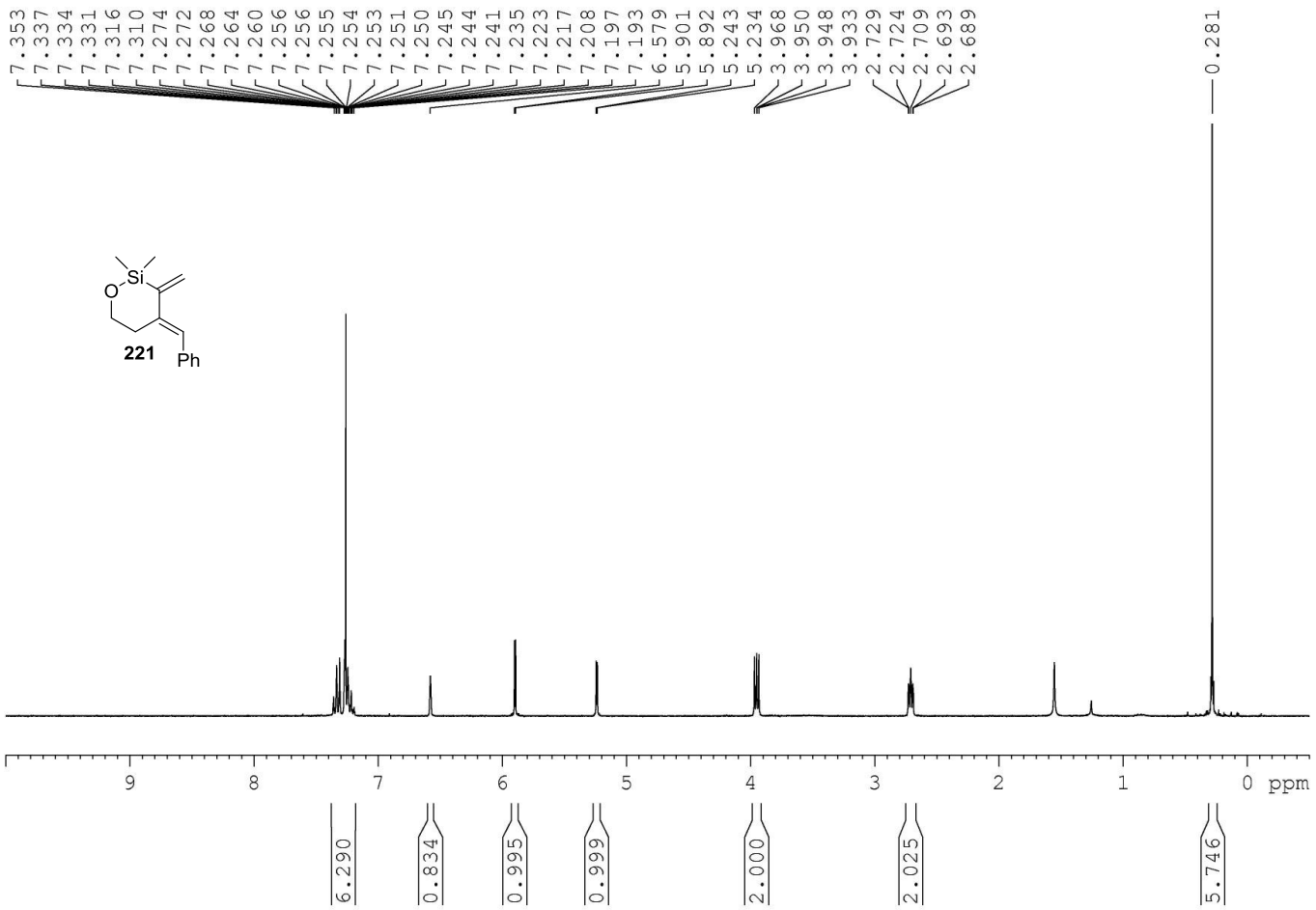

138.44
133.01
131.74
128.34
127.63
124.34
93.00
81.73
73.96
38.83
34.86
31.07
24.64
23.98
1.03
1.17
Si
O
Ph
219
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

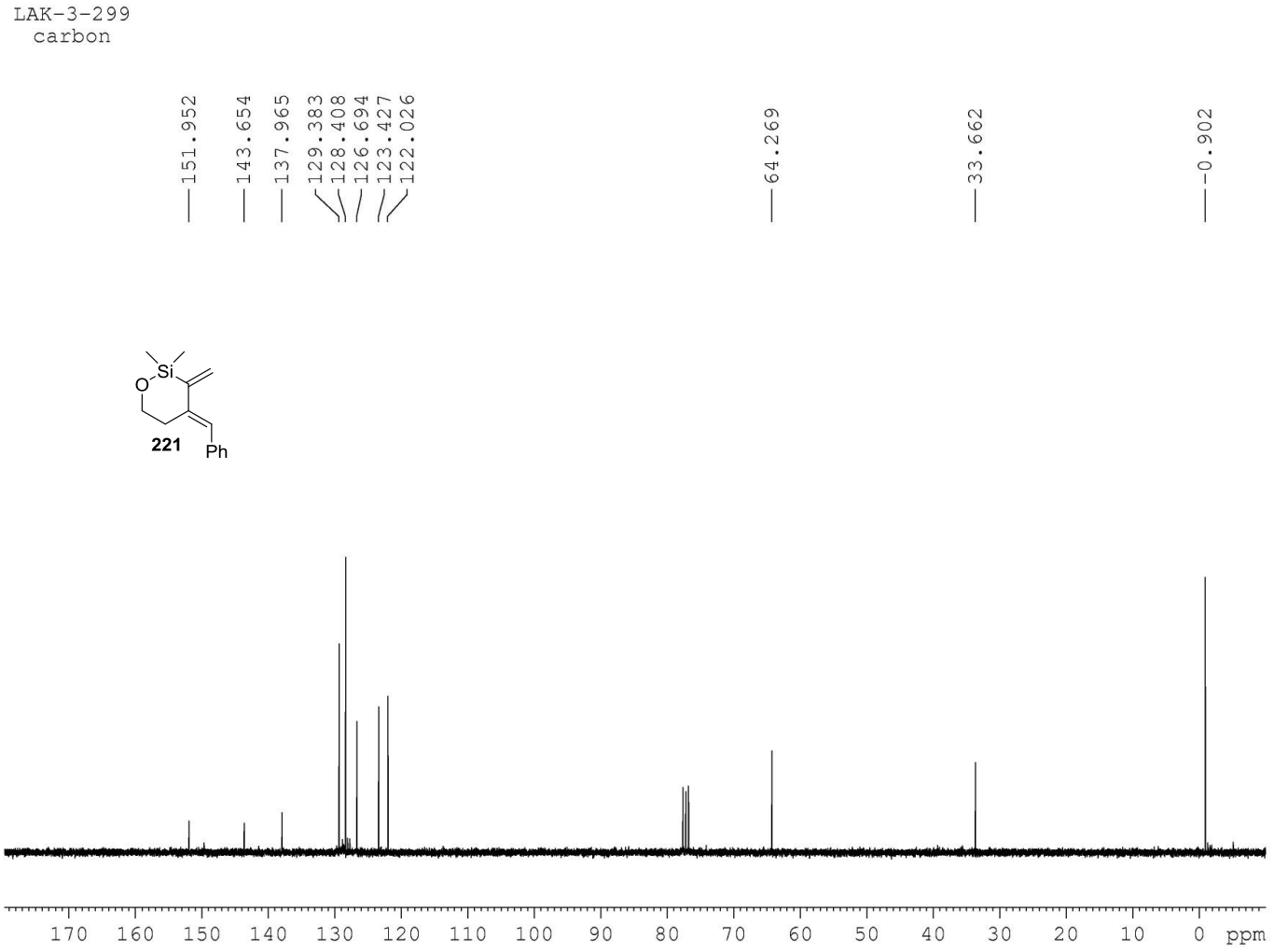
LAK-3-291

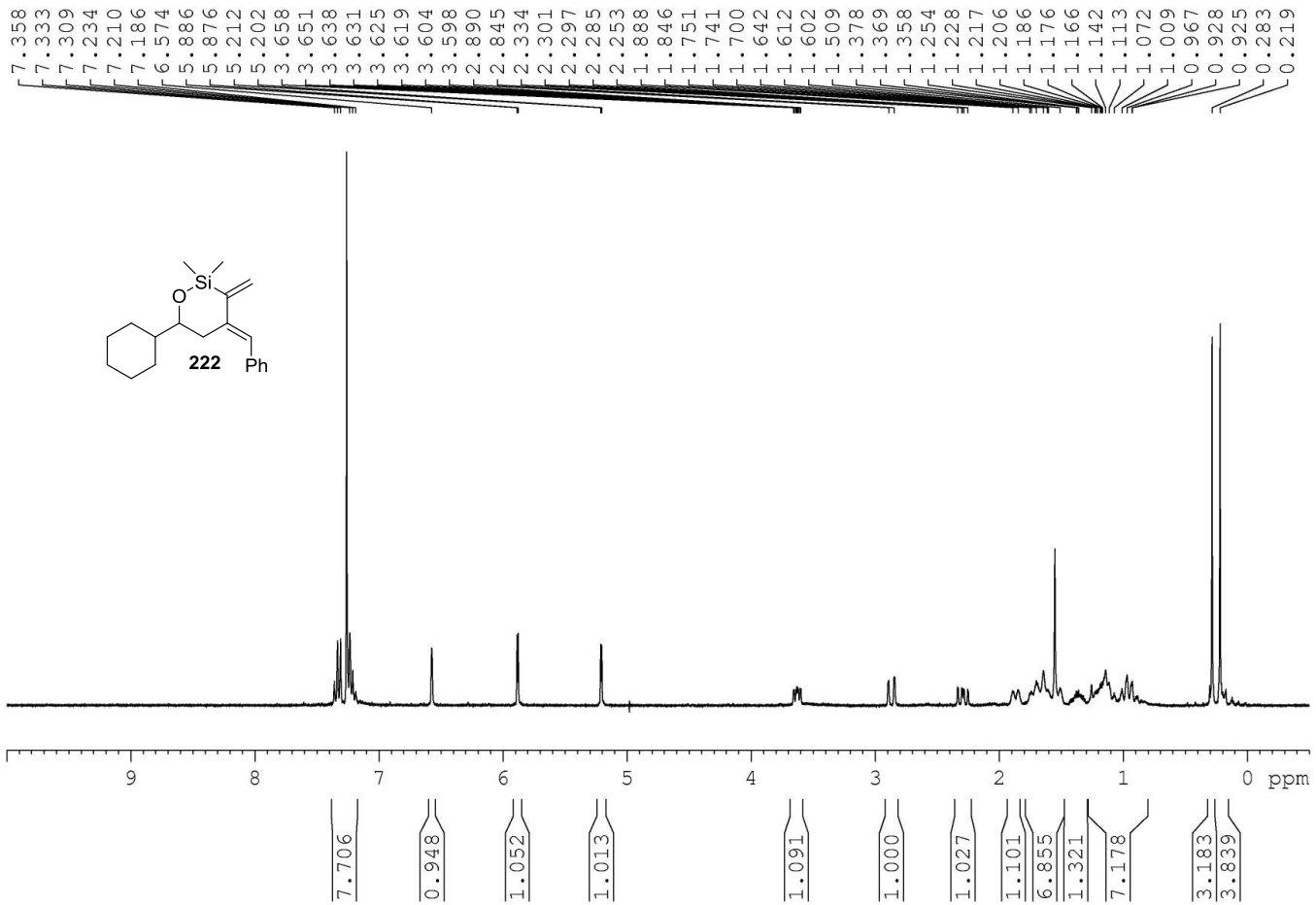

7.358
7.333
7.309
7.284
7.261
7.260
7.238
7.213
7.190
6.584
5.893
5.883
5.226
5.216
3.877
3.867
3.859
3.852
3.845
3.827
3.820
2.885
2.835
2.829
2.350
2.317
2.301
2.269
1.420
1.395
1.381
1.233
0.890
0.867
0.844
0.296
0.233
Si
O
C7H15
220
Ph
9
8
7
6
5
4
3
2
1
0 ppm
7.790
0.877
0.966
0.953
1.020
1.000
1.033
12.952
3.290
3.130
3.086

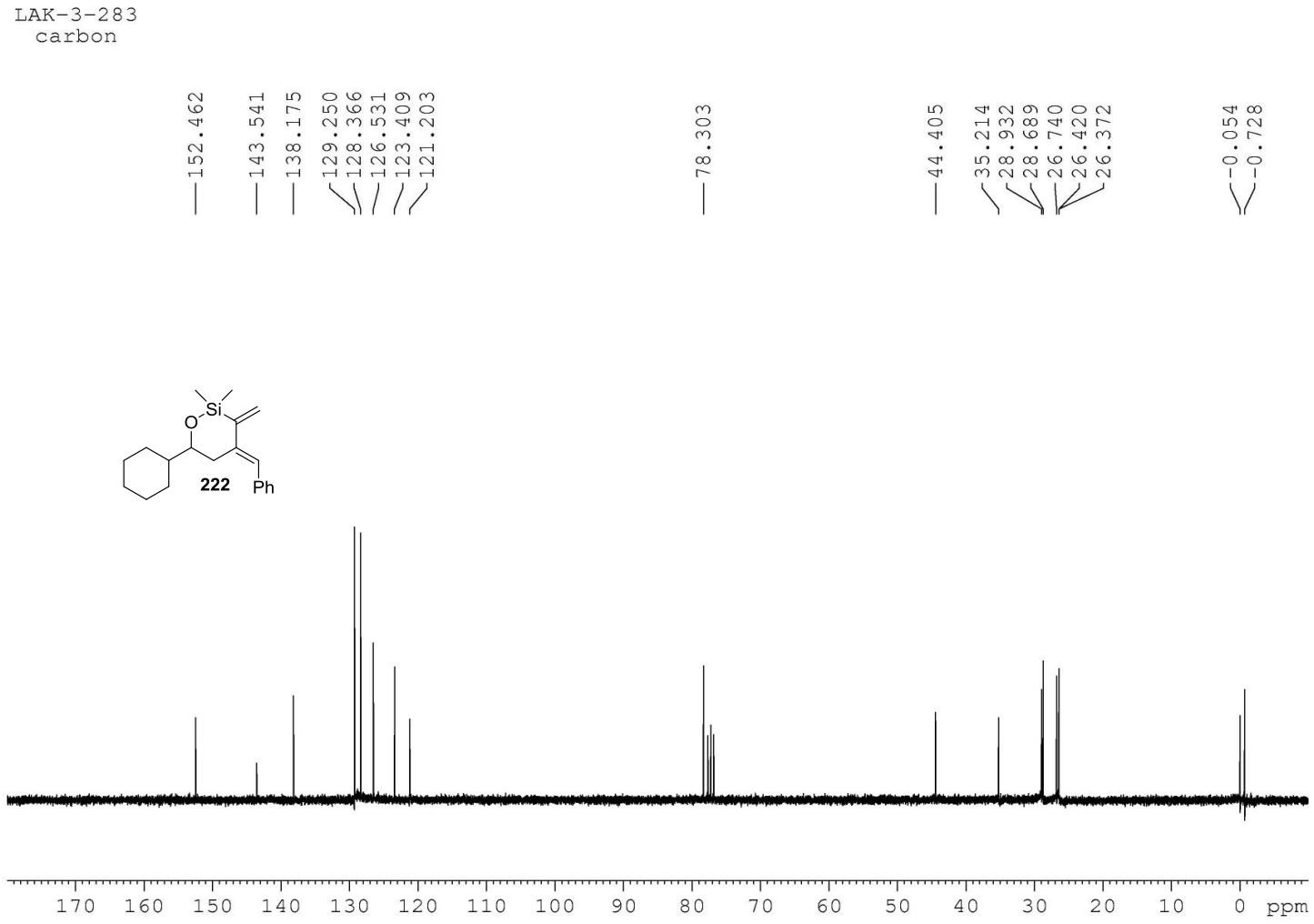

LAK-3-291
carbon
152.090
143.142
138.116
129.345
126.588
123.525
121.512
73.948
38.339
38.268
32.041
29.718
29.505
25.753
22.864
14.320
-0.071
-0.702
Si
O
C7H15
220
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LAK-3-299

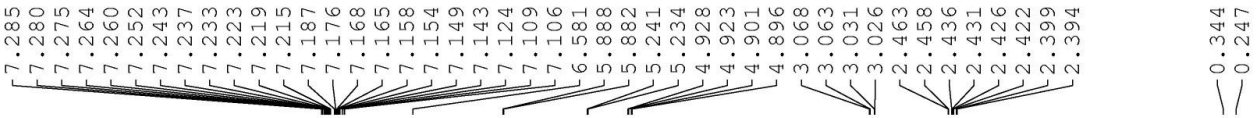

7.353
7.337
7.334
7.331
7.316
7.310
7.274
7.272
7.268
7.264
7.260
7.256
7.256
7.255
7.254
7.253
7.251
7.250
7.245
7.244
7.241
7.235
7.223
7.217
7.208
7.197
7.193
6.579
5.901
5.892
5.243
5.234
3.968
3.950
3.948
3.933
2.729
2.724
2.709
2.693
2.689
0.281
Si
O
221
Ph
9
8
7
6
5
4
3
2
1
0 ppm
6.290
0.834
0.995
0.999
2.000
2.025
5.746

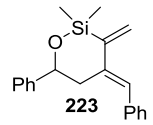

LAK-3-299
carbon
151.952
143.654
137.965
129.383
128.408
126.694
123.427
122.026
64.269
33.662
0.902
Si
O
221
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.358
7.333
7.309
7.234
7.210
7.186
6.574
5.886
5.876
5.212
5.202
3.658
3.651
3.638
3.631
3.625
3.619
3.604
3.598
2.890
2.845
2.334
2.301
2.297
2.285
2.253
1.888
1.846
1.751
1.741
1.700
1.642
1.612
1.602
1.509
1.378
1.369
1.358
1.254
1.228
1.217
1.206
1.186
1.176
1.166
1.142
1.113
1.072
1.009
0.967
0.928
0.925
0.283
0.219
Si
O
222
Ph
9
8
7
6
5
4
3
2
1
0 ppm
7.706
0.948
1.052
1.013
1.091
1.000
1.027
1.101
6.855
1.321
7.178
3.183
3.839

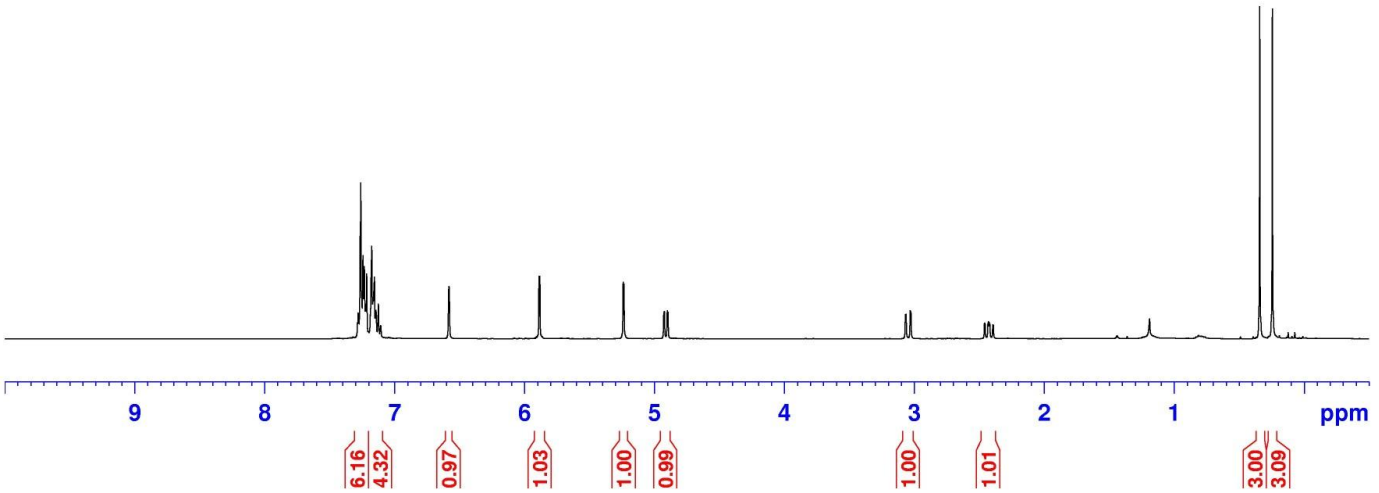

LAK-3-283
carbon
152.462
143.541
138.175
129.250
128.366
126.531
123.409
121.203
78.303
44.405
35.214
28.932
28.689
26.740
26.420
26.372
-0.054
-0.728
Si
O
222
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LAK-5-200


7.285
7.280
7.275
7.264
7.260
7.252
7.243
7.237
7.233
7.223
7.219
7.215
7.187
7.176
7.168
7.165
7.158
7.154
7.149
7.143
7.124
7.109
7.106
6.581
5.888
5.882
5.241
5.234
4.928
4.923
4.901
4.896
3.068
3.063
3.031
3.026
2.463
2.458
2.436
2.431
2.426
2.422
2.399
2.394
0.344
0.247

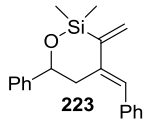

Si
O
Ph
Ph

223

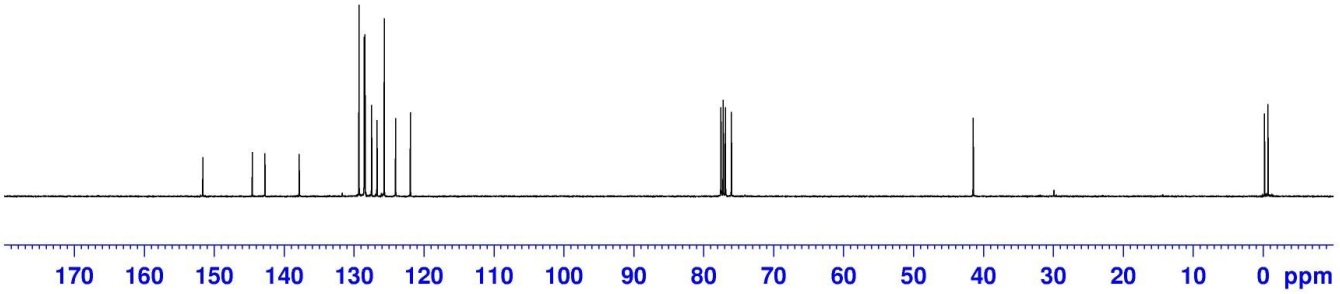

9
8
7
6
5
4
3
2
1
ppm
6.16
4.32
0.97
1.03
1.00
0.99
1.00
1.01
3.00
3.09

LAK-5-200
carbon

151.58
144.51
142.70
137.82
129.31
128.56
128.46
127.51
126.73
125.70
124.07
121.96
76.05
41.48
-0.19
-0.68

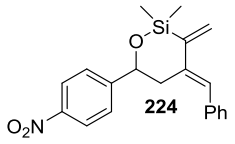


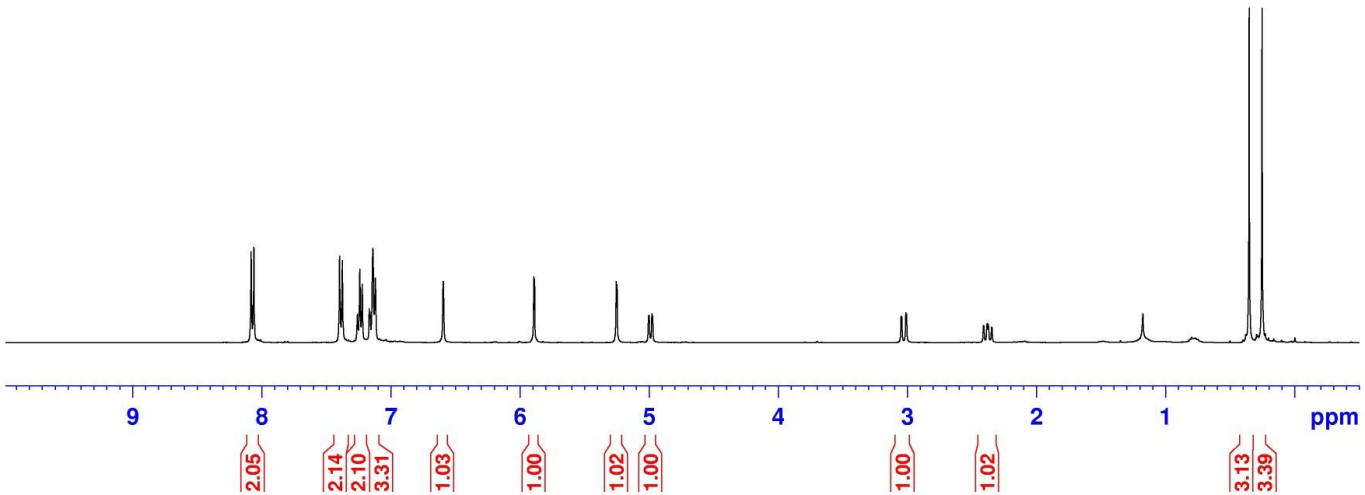
223



LAK-5-210

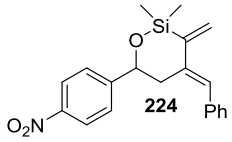

8.082
8.060
7.396
7.375
7.258
7.240
7.221
7.167
7.162
7.139
7.119
6.596
5.896
5.889
5.257
5.250
5.006
5.001
4.980
4.975
3.050
3.045
3.013
3.008
2.413
2.409
2.386
2.382
2.376
2.372
2.350
2.346
0.355
0.255


Si
O
224
Ph
O2N

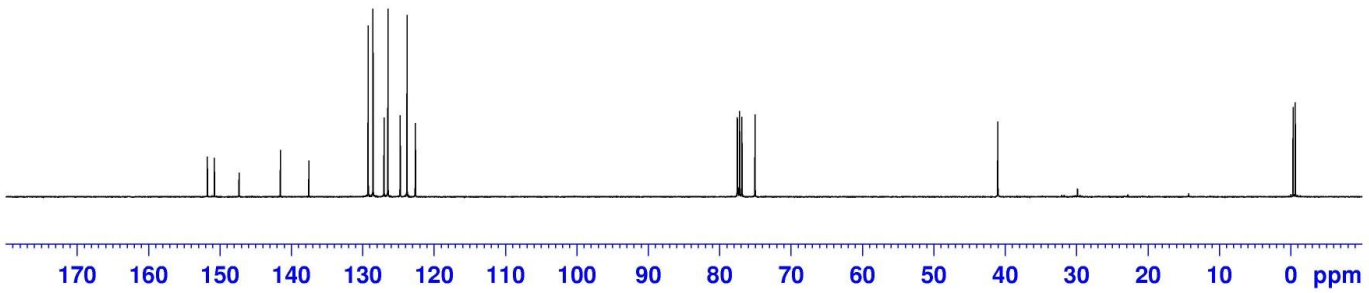

9
8
7
6
5
4
3
2
1
ppm
2.05
2.14
2.10
3.31
1.03
1.00
1.02
1.00
1.00
1.02
3.13
3.39

LAK-5-210
carbon

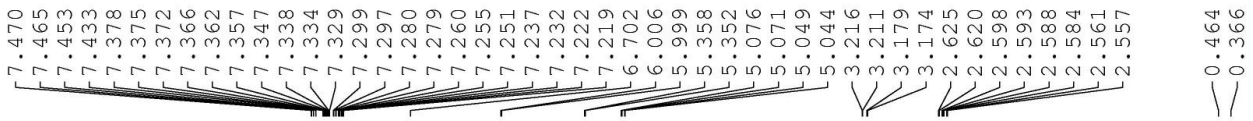
151.74
150.76
147.31
141.51
137.52
129.21
128.53
126.99
126.44
124.73
123.77
122.61
75.07
41.06
-0.29
-0.61

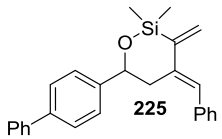


224

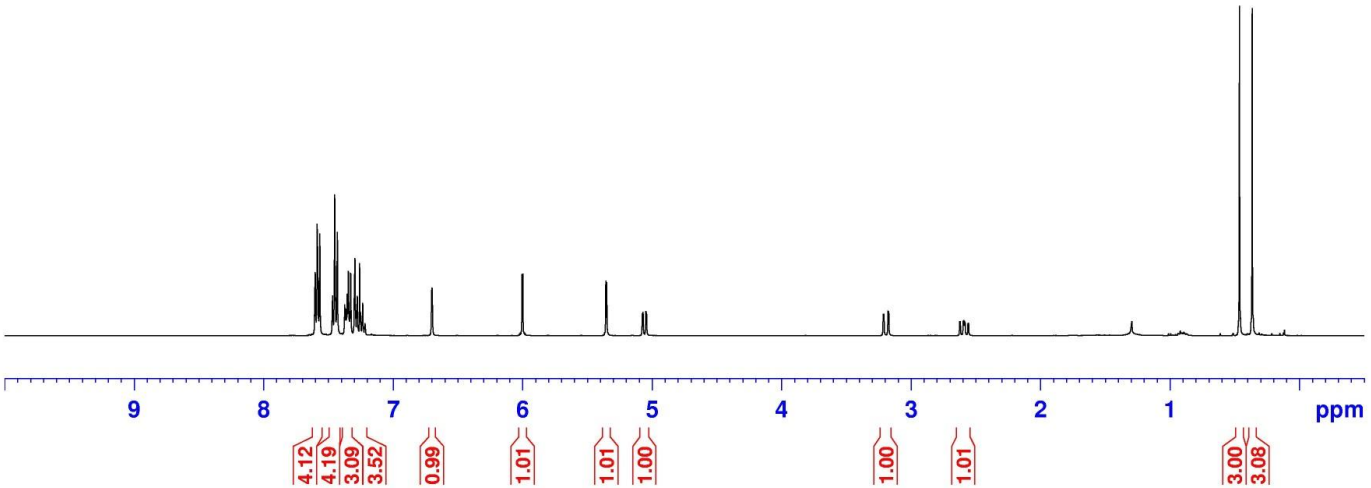


LAK-5-209-2

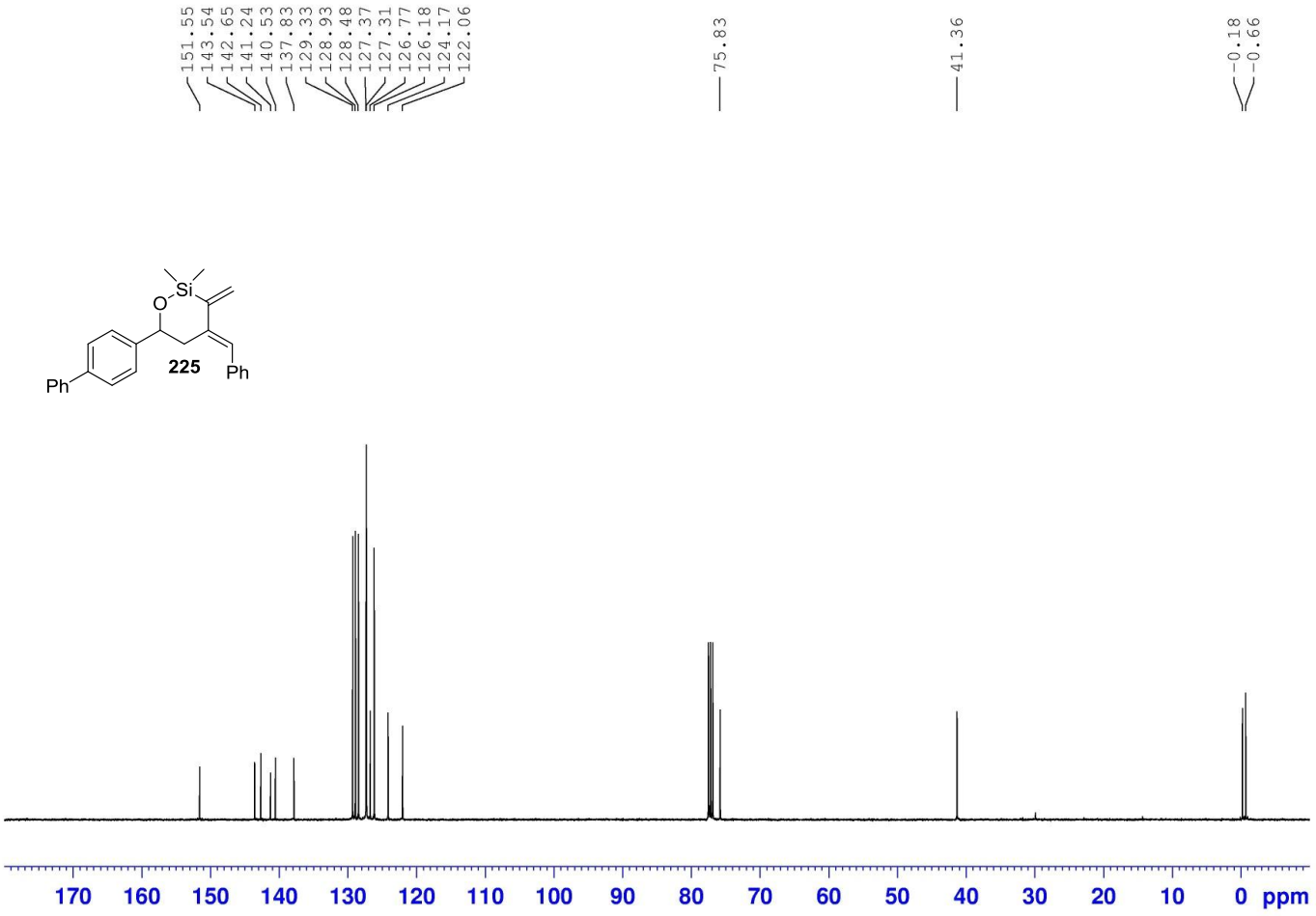




225



LAK-5-209-2
carbon



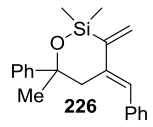
LAK-3-286

7.417
7.414
7.390
7.365
7.347
7.340
7.332
7.318
7.313
7.307
7.293
7.288
7.285
7.279
7.259
7.254
7.252
7.245
7.232
6.842
6.043
6.035
5.326
5.319

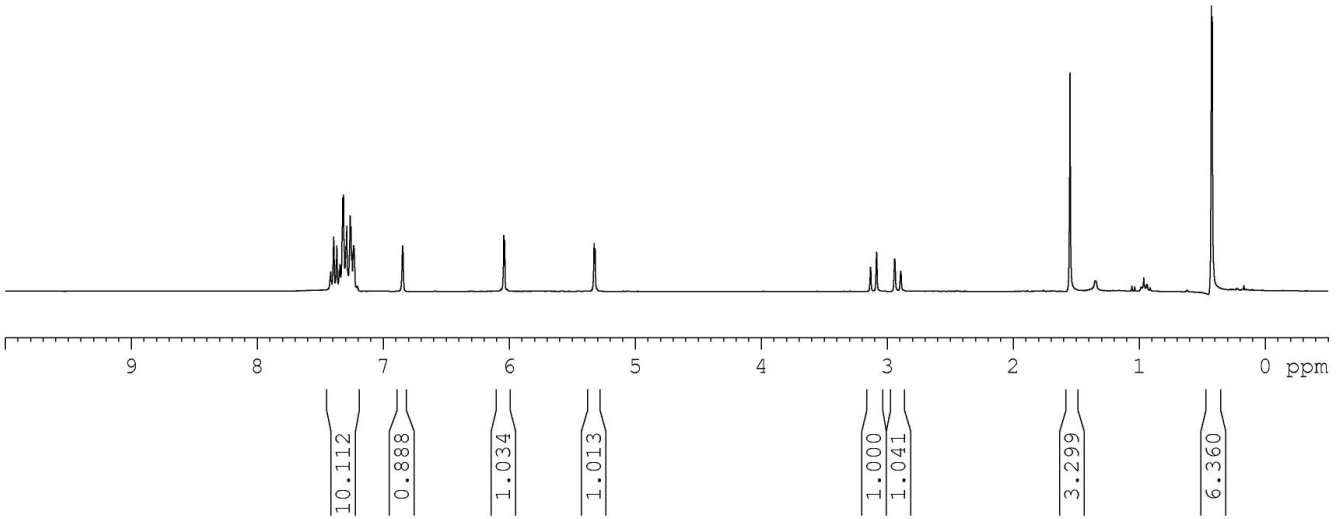
3.133
3.085
2.941
2.893

1.549

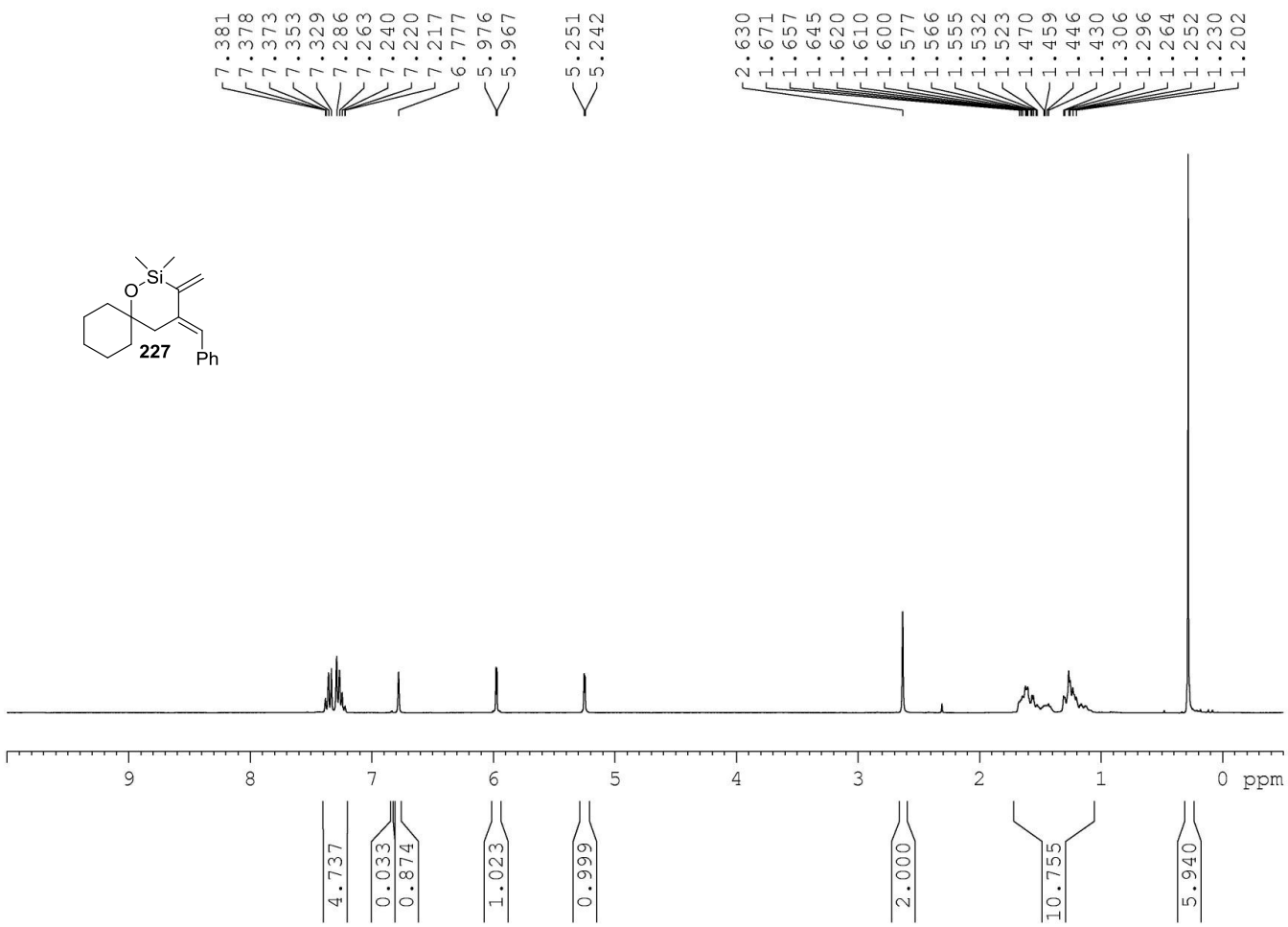
0.427
0.420

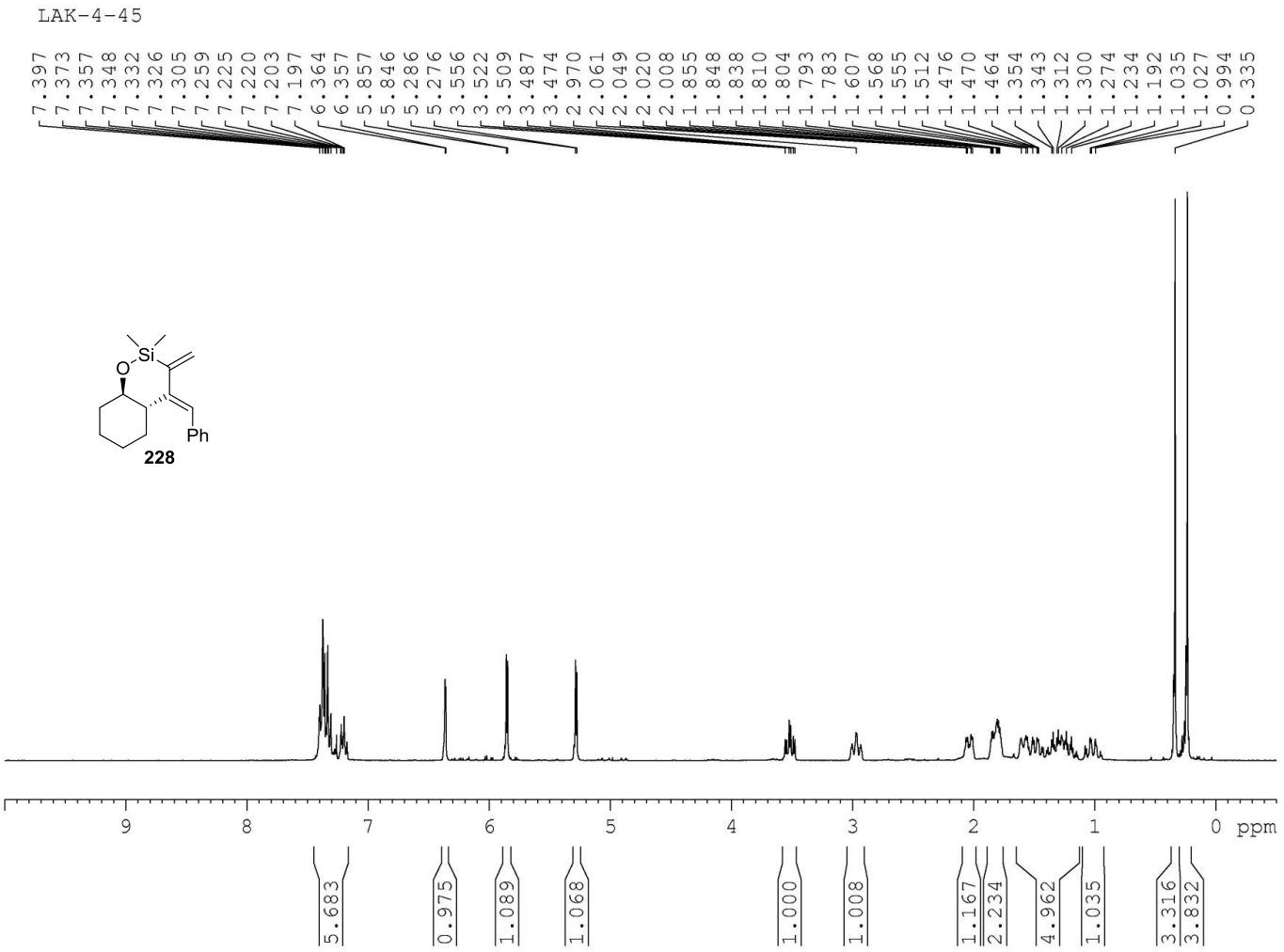


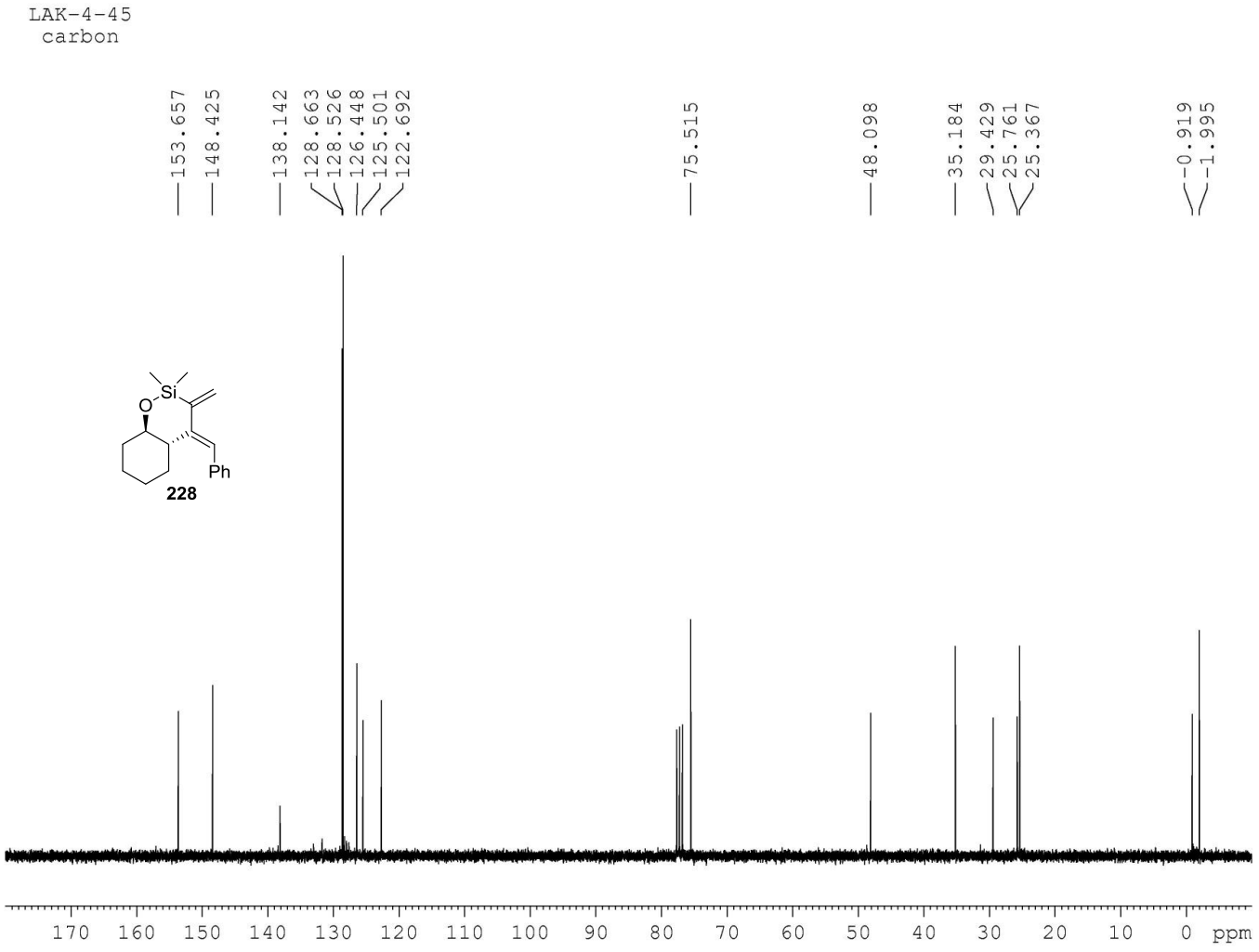
226



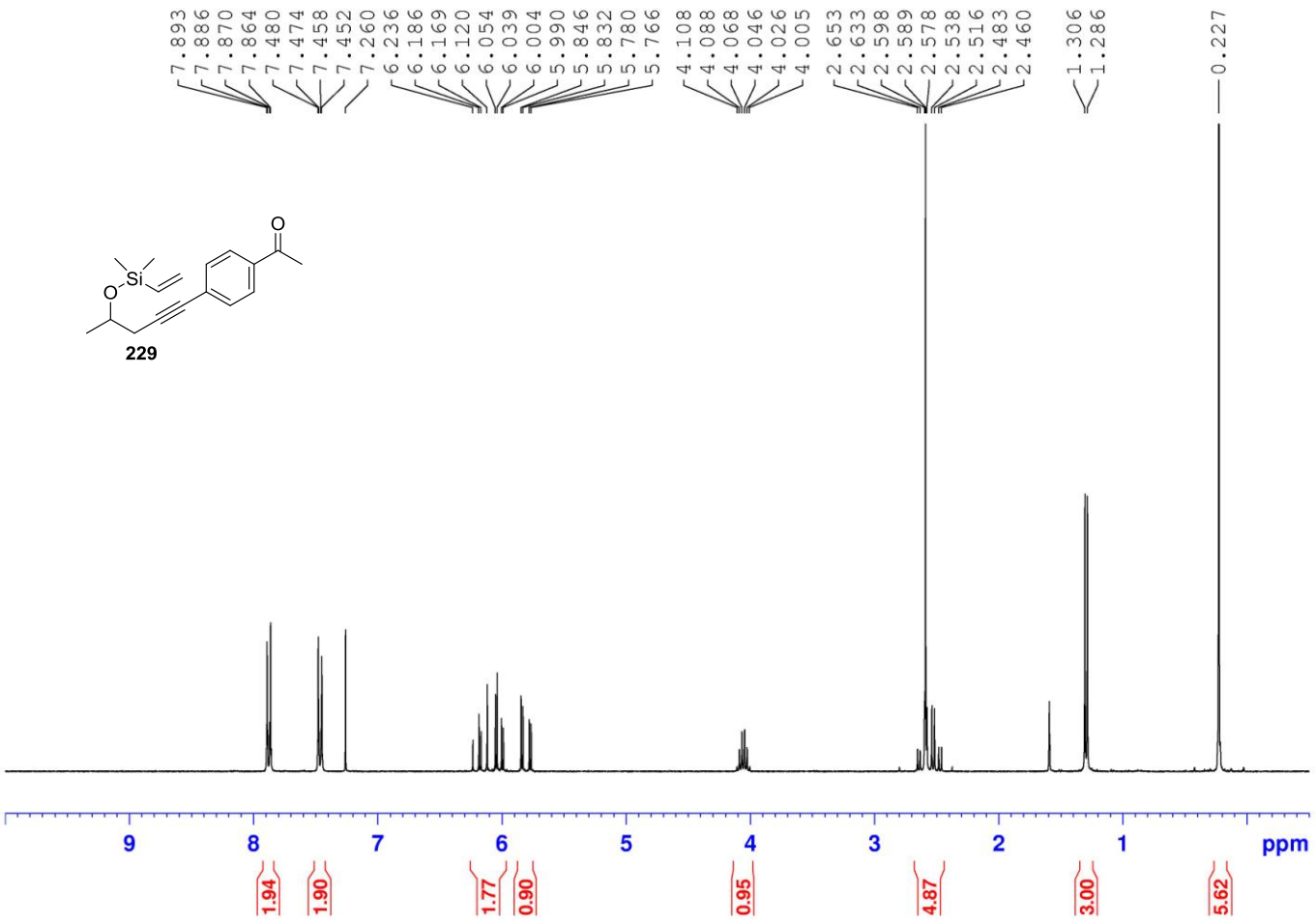
LAK-3-282


7.381
7.378
7.373
7.353
7.329
7.286
7.263
7.240
7.220
7.217
6.777
5.976
5.967
5.251
5.242
2.630
1.671
1.657
1.645
1.620
1.610
1.600
1.577
1.566
1.555
1.532
1.523
1.470
1.459
1.446
1.430
1.306
1.296
1.264
1.252
1.230
1.202
Si
O
227
Ph
9
8
7
6
5
4
3
2
1
0 ppm
4.737
0.033
0.874
1.023
0.999
2.000
10.755
5.940


LAK-4-45
7.397
7.373
7.357
7.348
7.332
7.326
7.305
7.259
7.225
7.220
7.203
7.197
6.364
6.357
5.857
5.846
5.286
5.276
3.556
3.522
3.509
3.487
3.474
2.970
2.061
2.049
2.020
2.008
1.855
1.848
1.838
1.810
1.804
1.793
1.783
1.607
1.568
1.555
1.512
1.476
1.470
1.464
1.354
1.343
1.312
1.300
1.274
1.234
1.192
1.035
1.027
0.994
0.335
Si
O
Ph
228
9
8
7
6
5
4
3
2
1
0 ppm
5.683
0.975
1.089
1.068
1.000
1.008
1.167
2.234
4.962
1.035
3.316
3.832

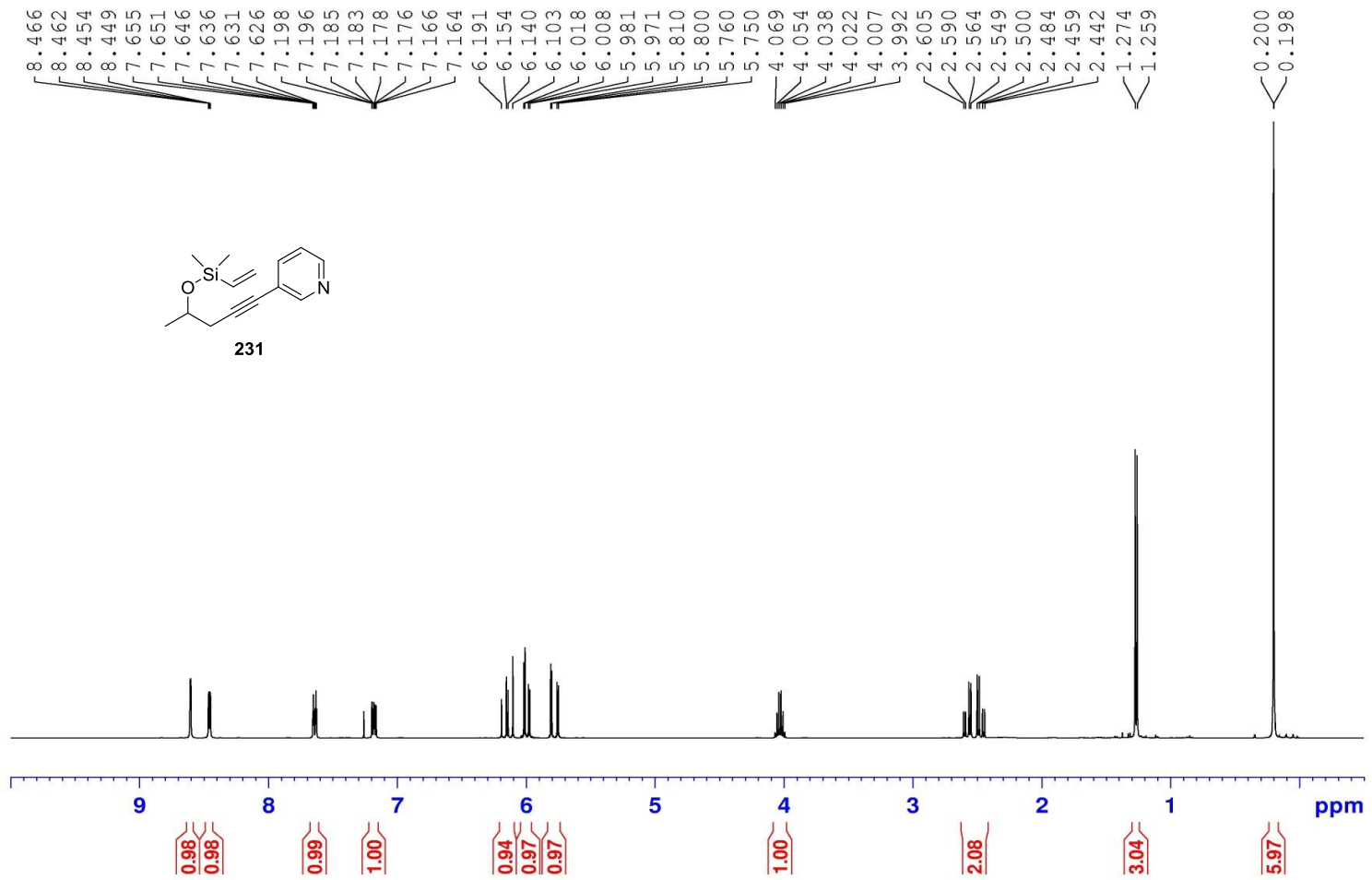

LAK-4-45
carbon
153.657
148.425
138.142
128.663
128.526
126.448
125.501
122.692
75.515
48.098
35.184
29.429
25.761
25.367
-0.919
-1.995
Si
O
Ph
228
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LAK-3-144


7.893
7.886
7.870
7.864
7.480
7.474
7.458
7.452
7.260
6.236
6.186
6.169
6.120
6.054
6.039
6.004
5.990
5.846
5.832
5.780
5.766
4.108
4.088
4.068
4.046
4.026
4.005
2.653
2.633
2.598
2.589
2.578
2.538
2.516
2.483
2.460
1.306
1.286
0.227
O
Si
O
9
8
7
6
5
4
3
2
1
ppm
1.94
1.90
1.77
0.90
0.95
4.87
3.00
5.62

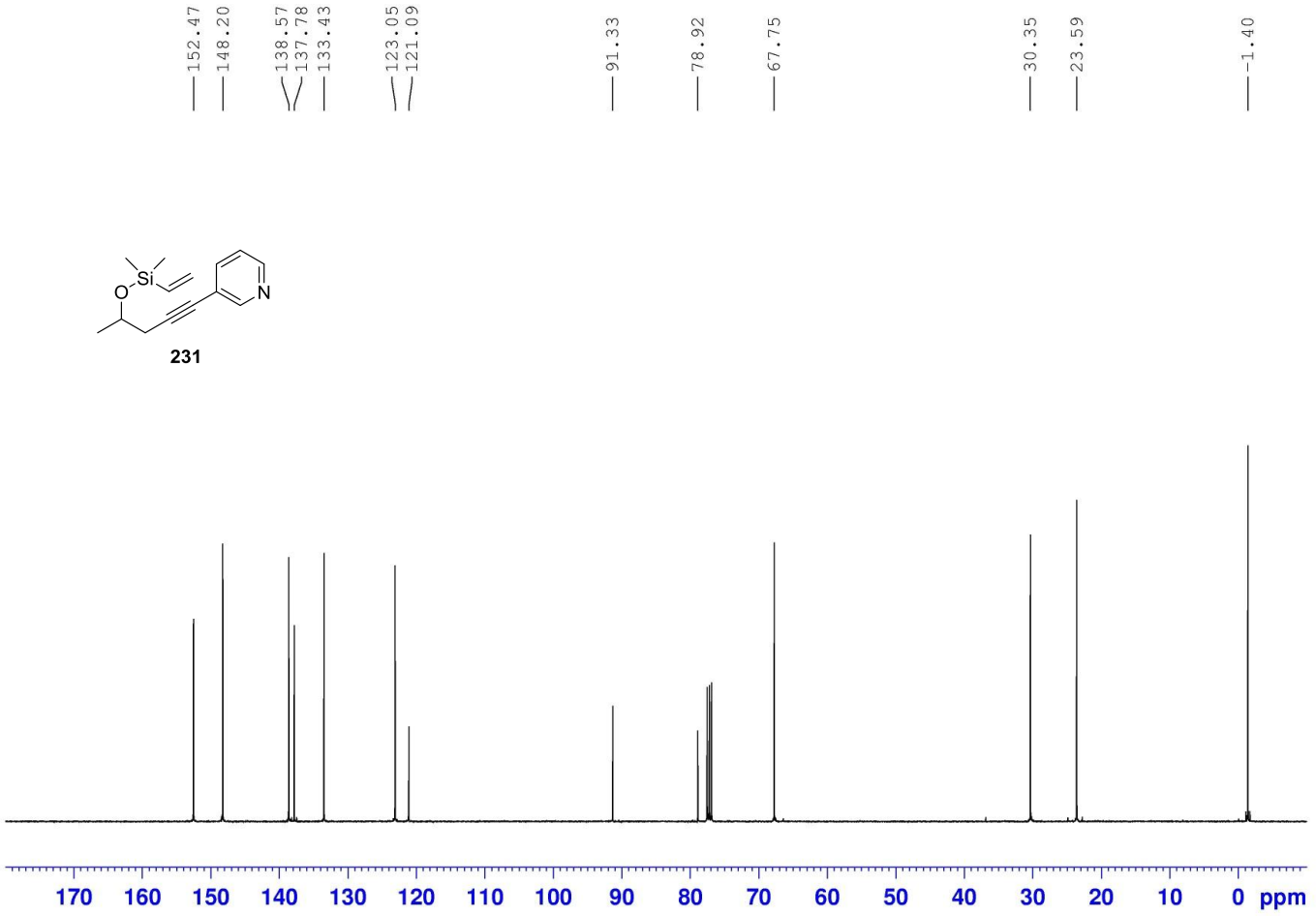
229

LAK-3-294

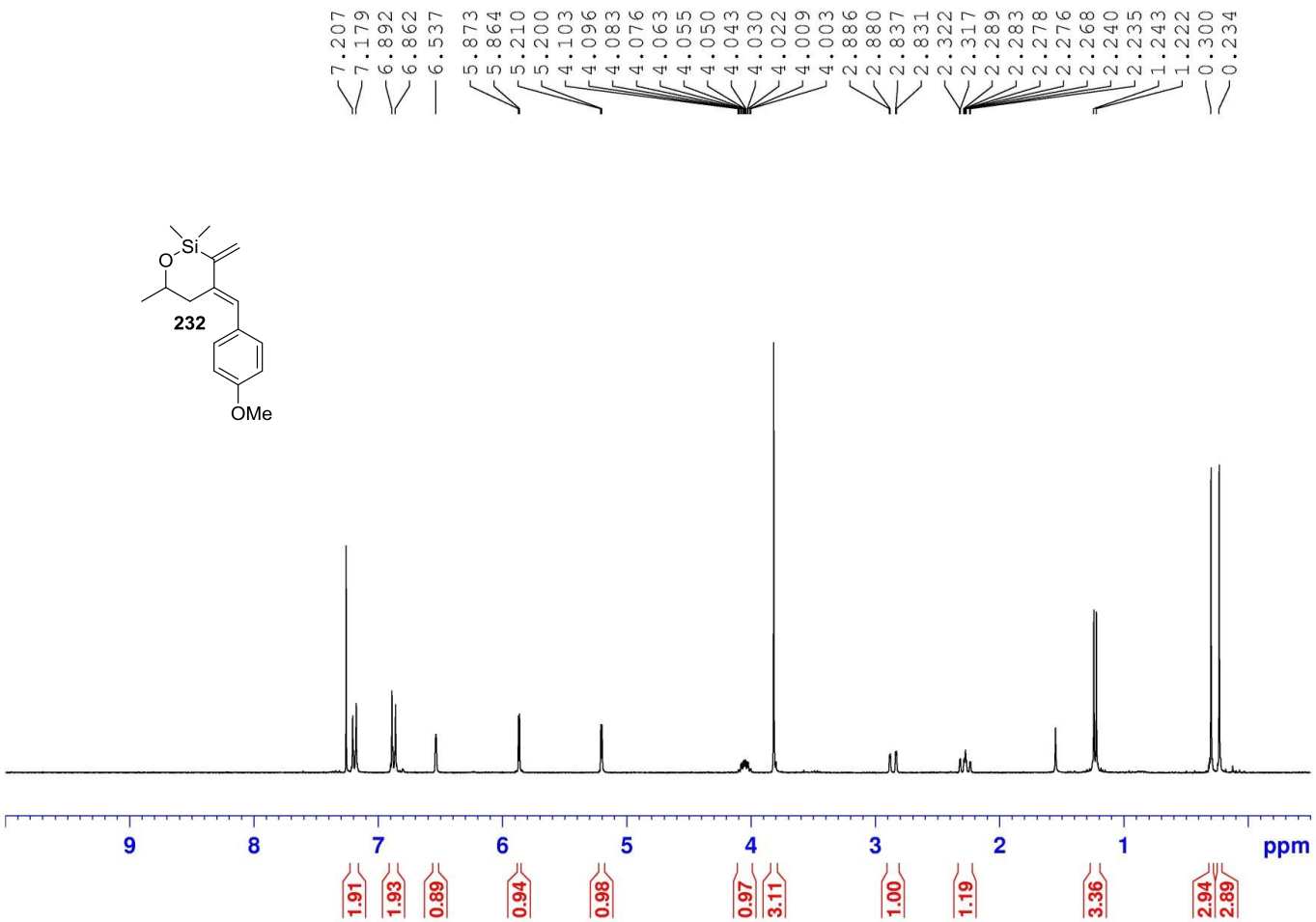

8.466
8.462
8.454
8.449
7.655
7.651
7.646
7.636
7.631
7.626
7.198
7.196
7.185
7.183
7.178
7.176
7.166
7.164
6.191
6.154
6.140
6.103
6.018
6.008
5.981
5.971
5.810
5.800
5.760
5.750
4.069
4.054
4.038
4.022
4.007
3.992
2.605
2.590
2.564
2.549
2.500
2.484
2.459
2.442
1.274
1.259
0.200
0.198
Si
O
N
9
8
7
6
5
4
3
2
1
ppm
0.98
0.98
0.99
1.00
0.94
0.97
0.97
1.00
2.08
3.04
5.97

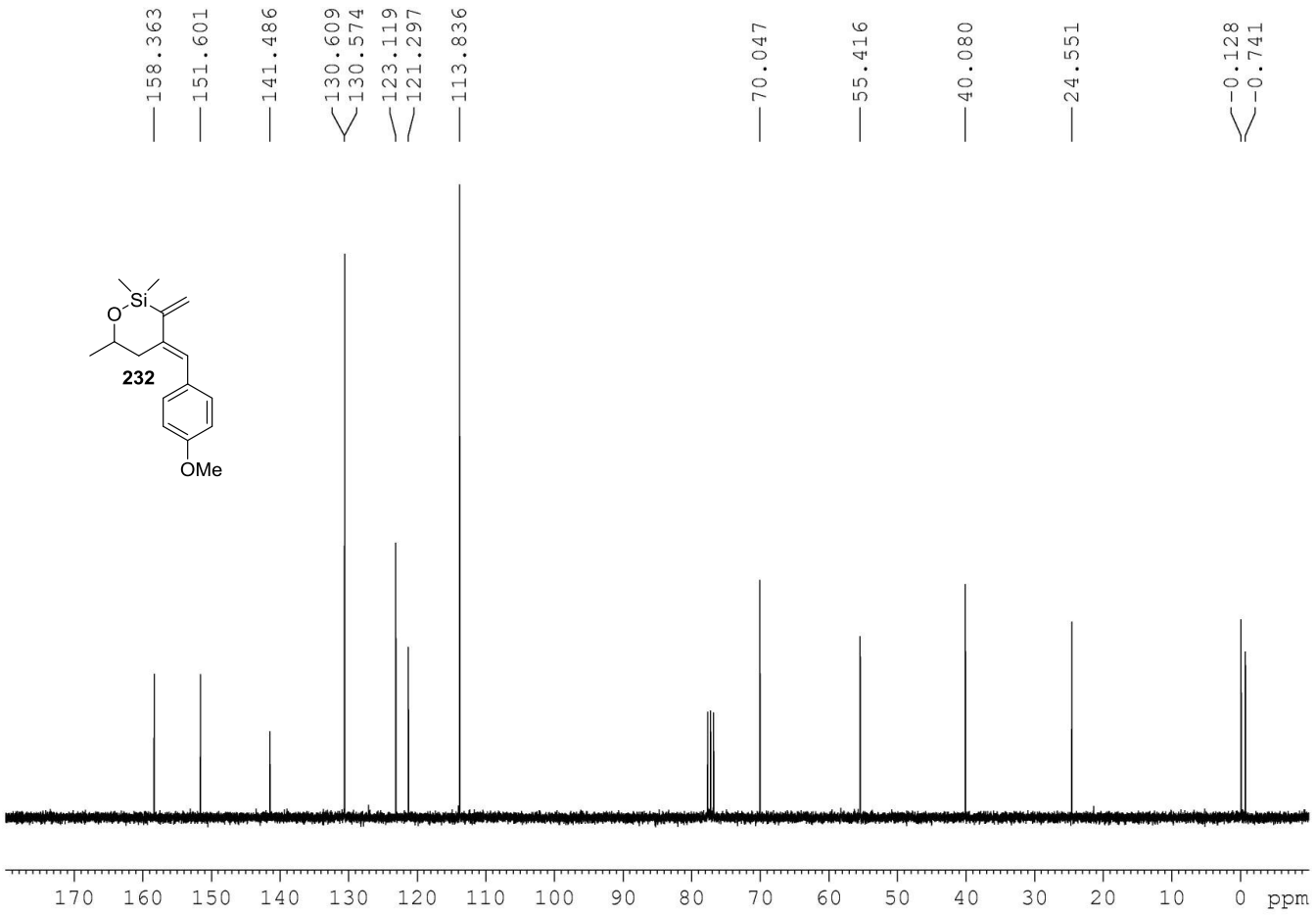
231

LAK-3-294

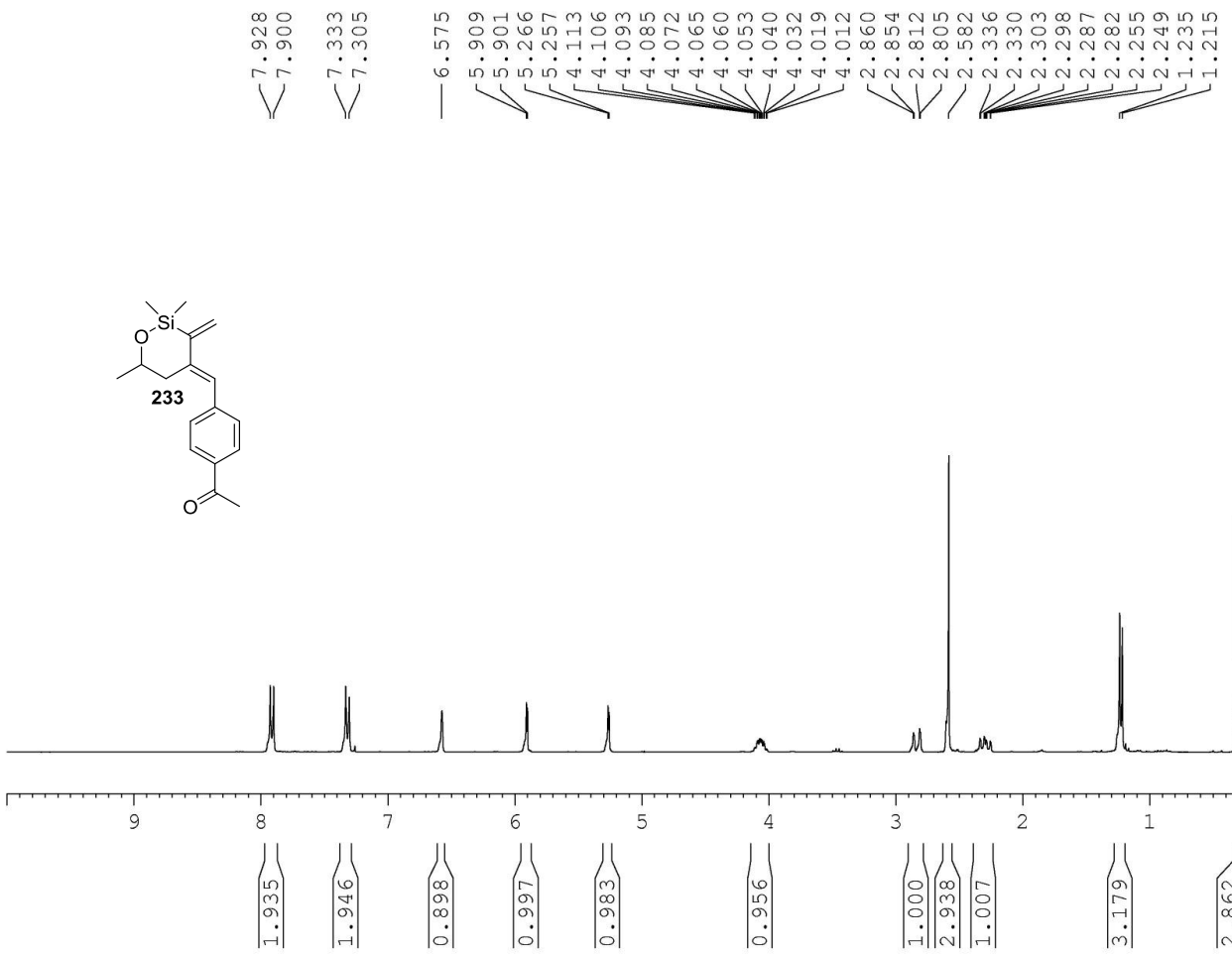

152.47
148.20
138.57
137.78
133.43
123.05
121.09
91.33
78.92
67.75
30.35
23.59
-1.40
Si
O
N
231
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

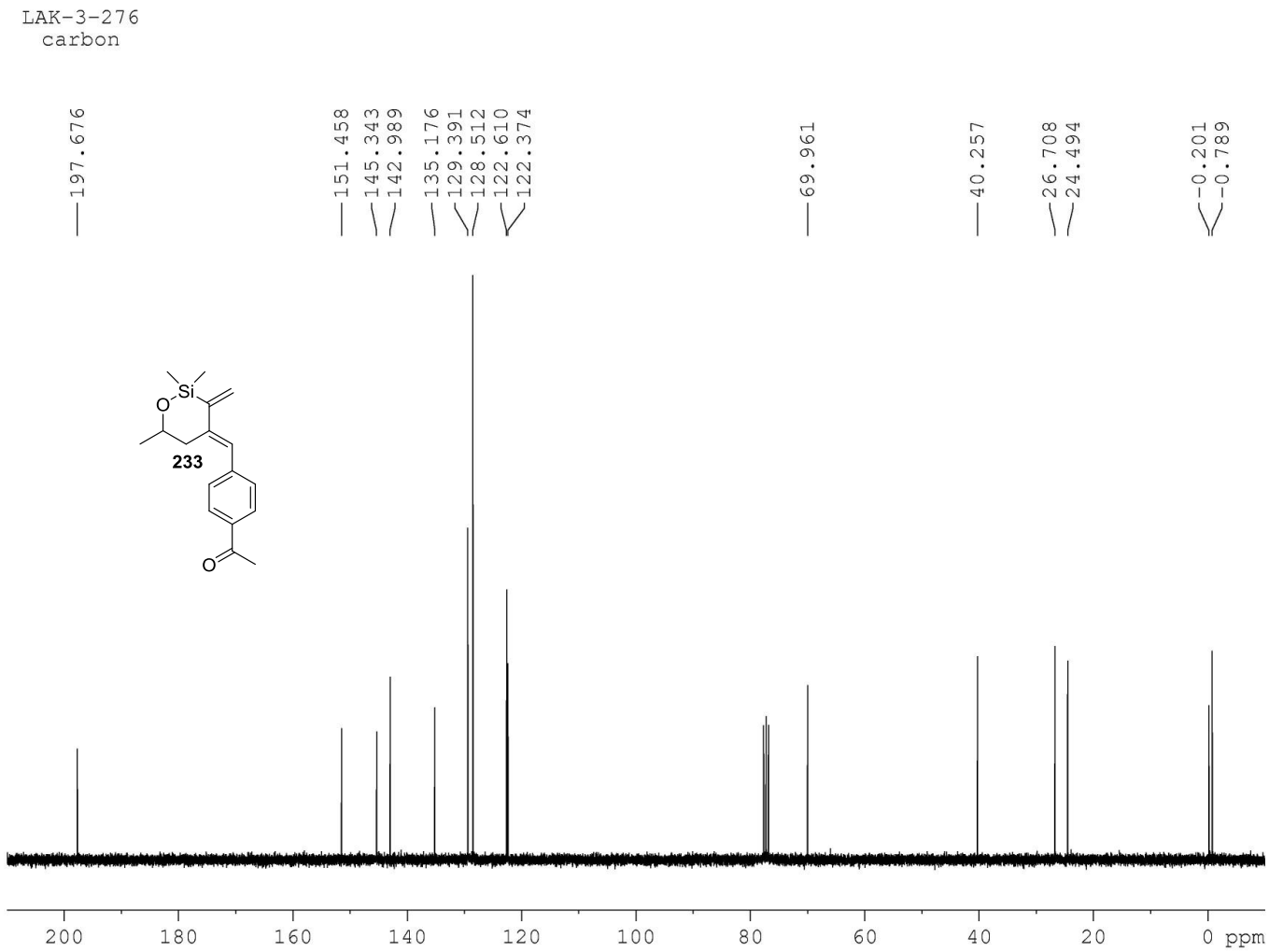
LAK-3-273

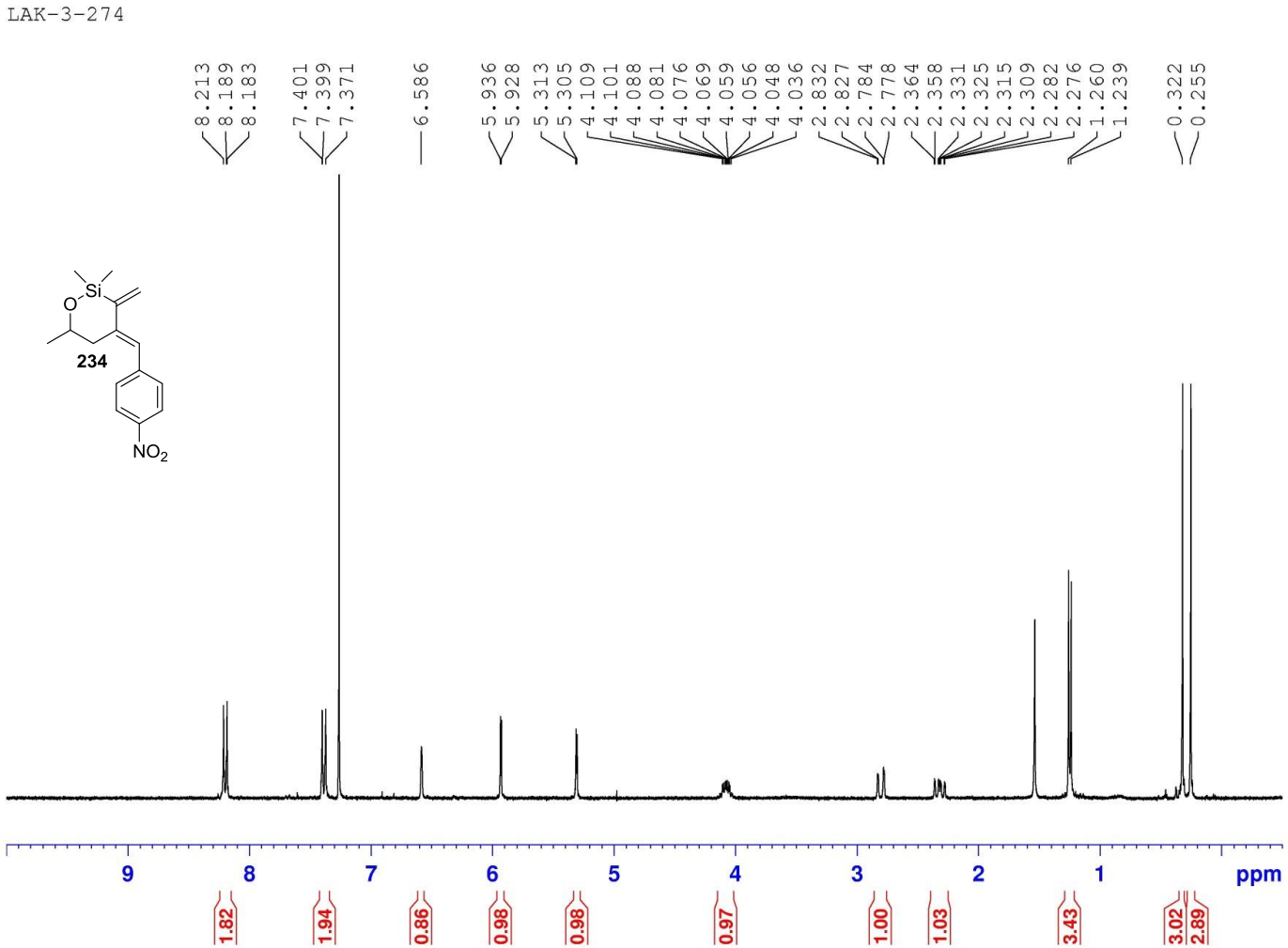

7.207
7.179
6.892
6.862
6.537
5.873
5.864
5.210
5.200
4.103
4.096
4.083
4.076
4.063
4.055
4.050
4.043
4.030
4.022
4.009
4.003
2.886
2.880
2.837
2.831
2.322
2.317
2.289
2.283
2.278
2.276
2.268
2.240
2.235
1.243
1.222
0.300
0.234
Si
O
232
OMe
9
8
7
6
5
4
3
2
1
ppm
1.91
1.93
0.89
0.94
0.98
0.97
3.11
1.00
1.19
3.36
2.94
2.89

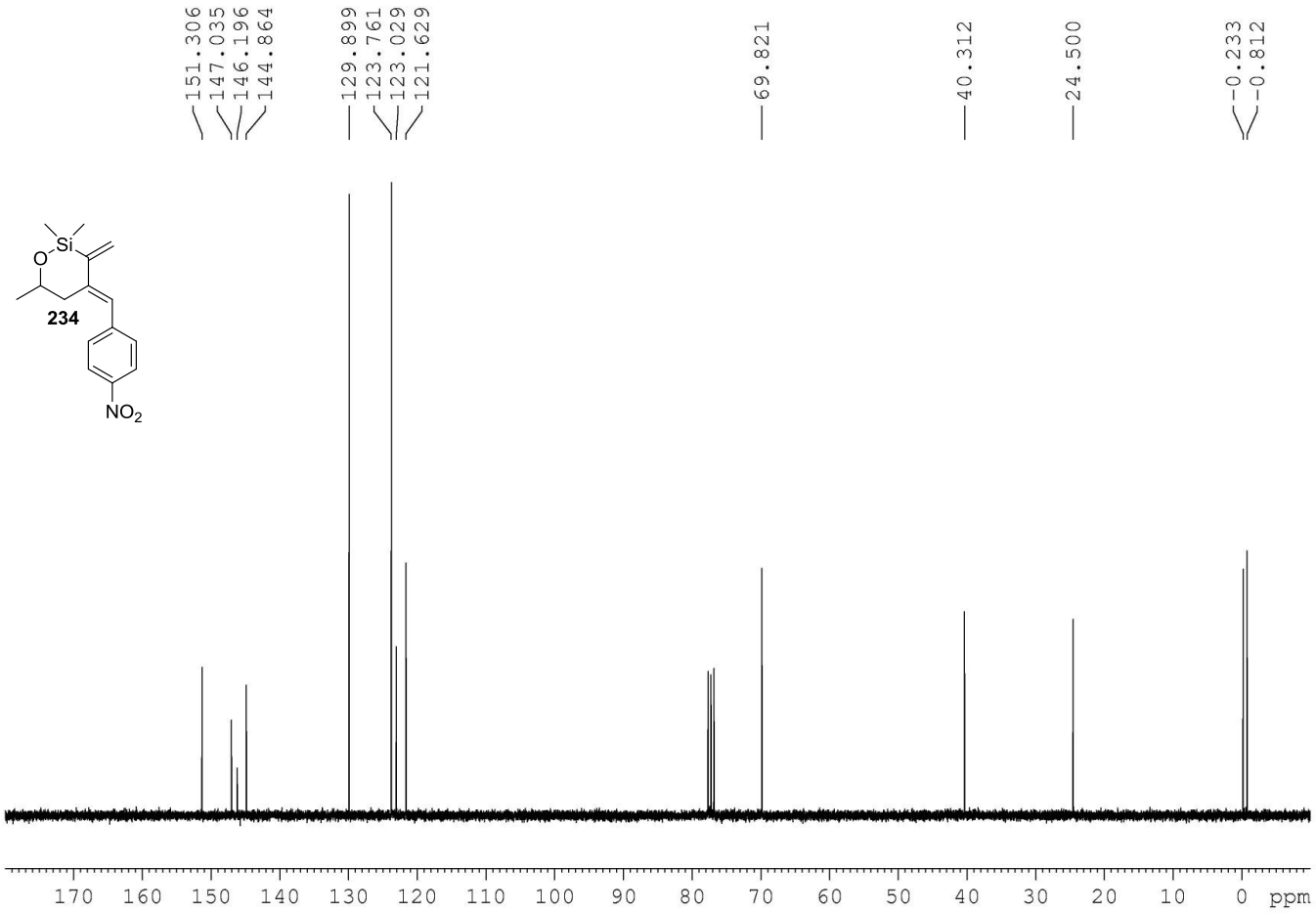

158.363
151.601
141.486
130.609
130.574
123.119
121.297
113.836
70.047
55.416
40.080
24.551
-0.128
-0.741
O
Si
232
OMe
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LAK-3-276

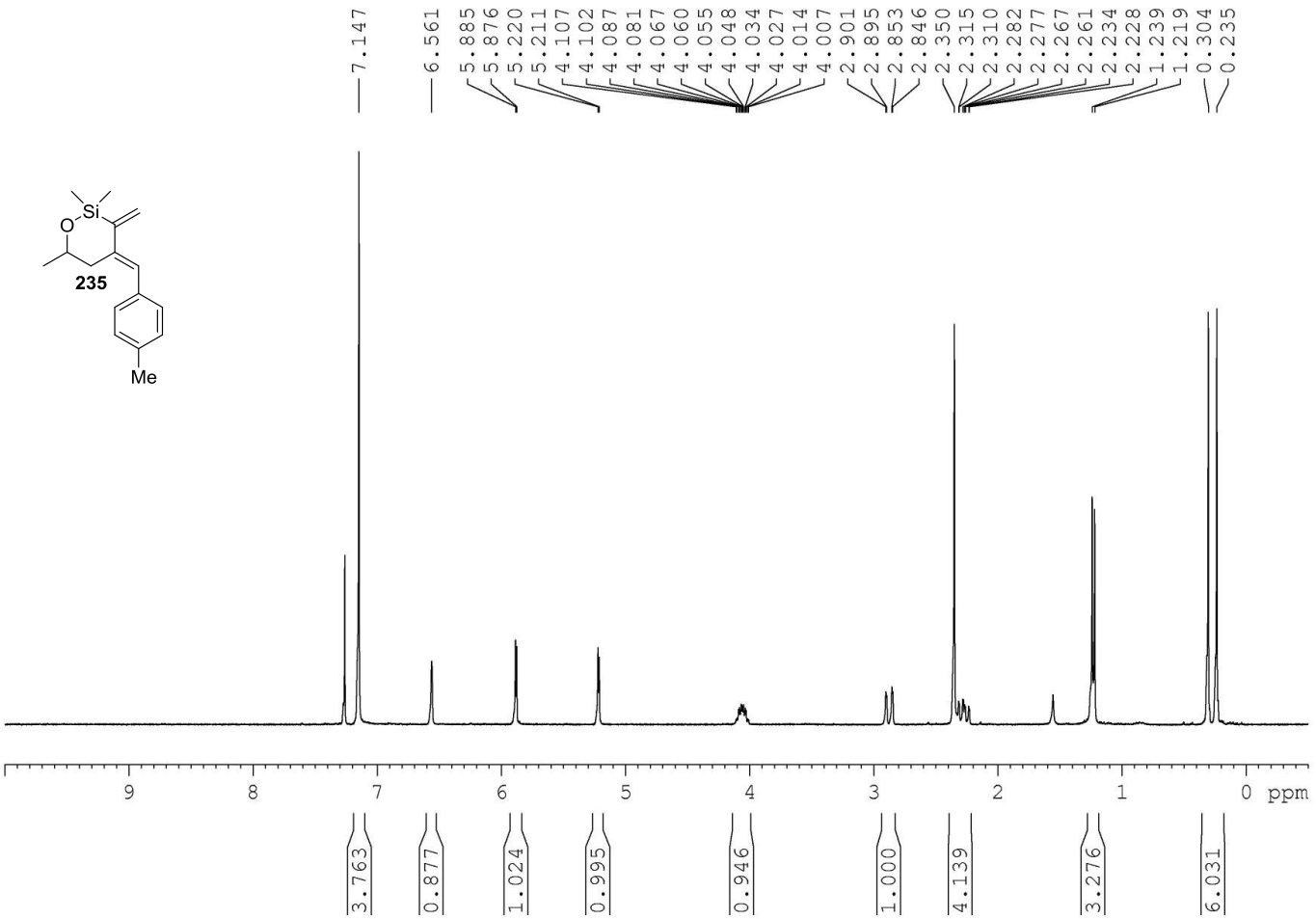

7.928
7.900
7.333
7.305
6.575
5.909
5.901
5.266
5.257
4.113
4.106
4.093
4.085
4.072
4.065
4.060
4.053
4.040
4.032
4.019
4.012
2.860
2.854
2.812
2.805
2.582
2.336
2.330
2.303
2.298
2.287
2.282
2.255
2.249
1.235
1.215
Si
O
O
233
9
8
7
6
5
4
3
2
1
0 ppm
1.935
1.946
0.898
0.997
0.983
0.956
1.000
2.938
1.007
3.179
2.862
3.074

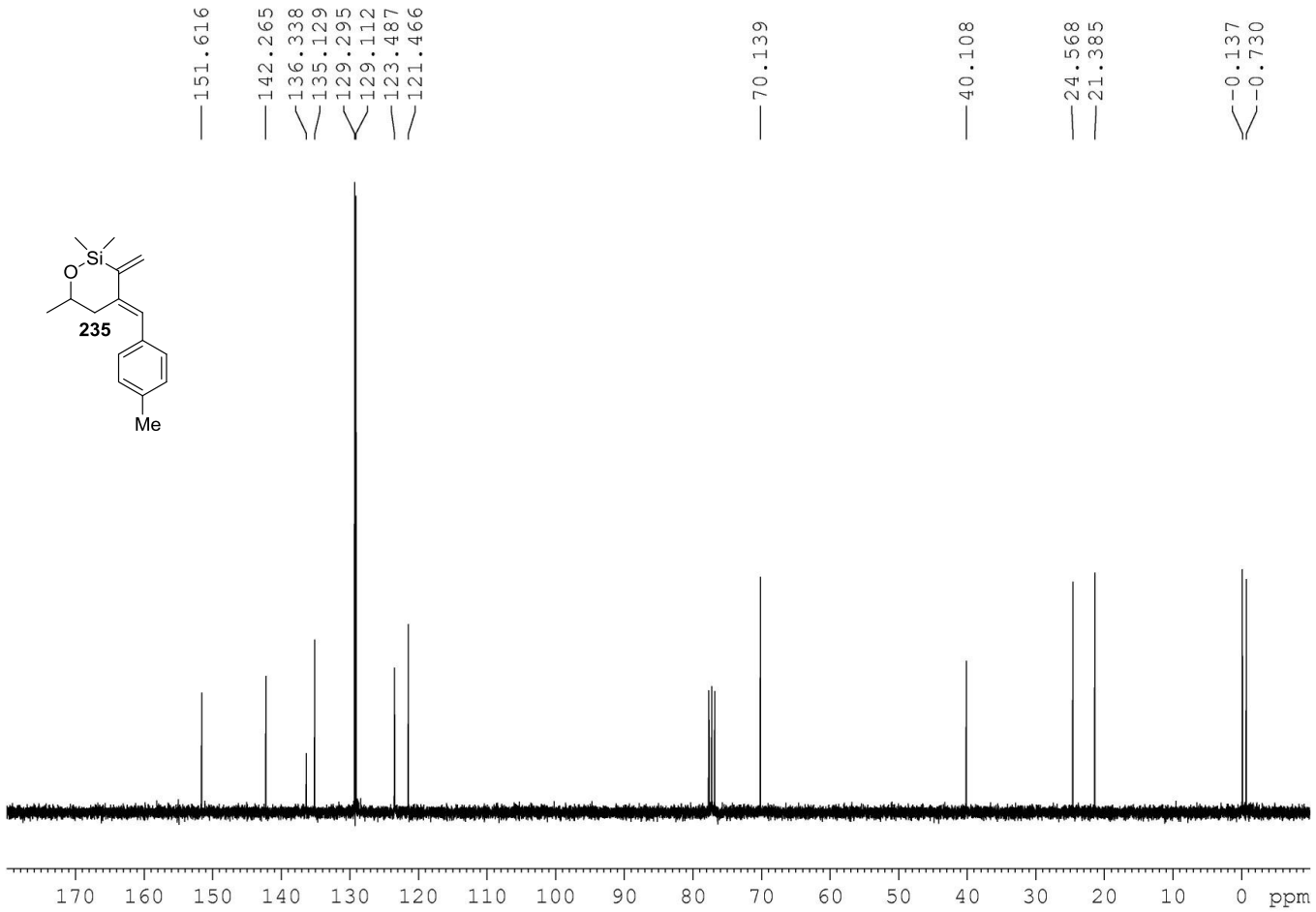

LAK-3-276
carbon
197.676
151.458
145.343
142.989
135.176
129.391
128.512
122.610
122.374
69.961
40.257
26.708
24.494
-0.201
-0.789
Si
O
O
233
200
180
160
140
120
100
80
60
40
20
0 ppm


LAK-3-274
8.213
8.189
8.183
7.401
7.399
7.371
6.586
5.936
5.928
5.313
5.305
4.109
4.101
4.088
4.081
4.076
4.069
4.059
4.056
4.048
4.036
2.832
2.827
2.784
2.778
2.364
2.358
2.331
2.325
2.315
2.309
2.282
2.276
1.260
1.239
0.322
0.255
Si
O
234
NO2
9
8
7
6
5
4
3
2
1
ppm
1.82
1.94
0.86
0.98
0.98
0.97
1.00
1.03
3.43
3.02
2.89

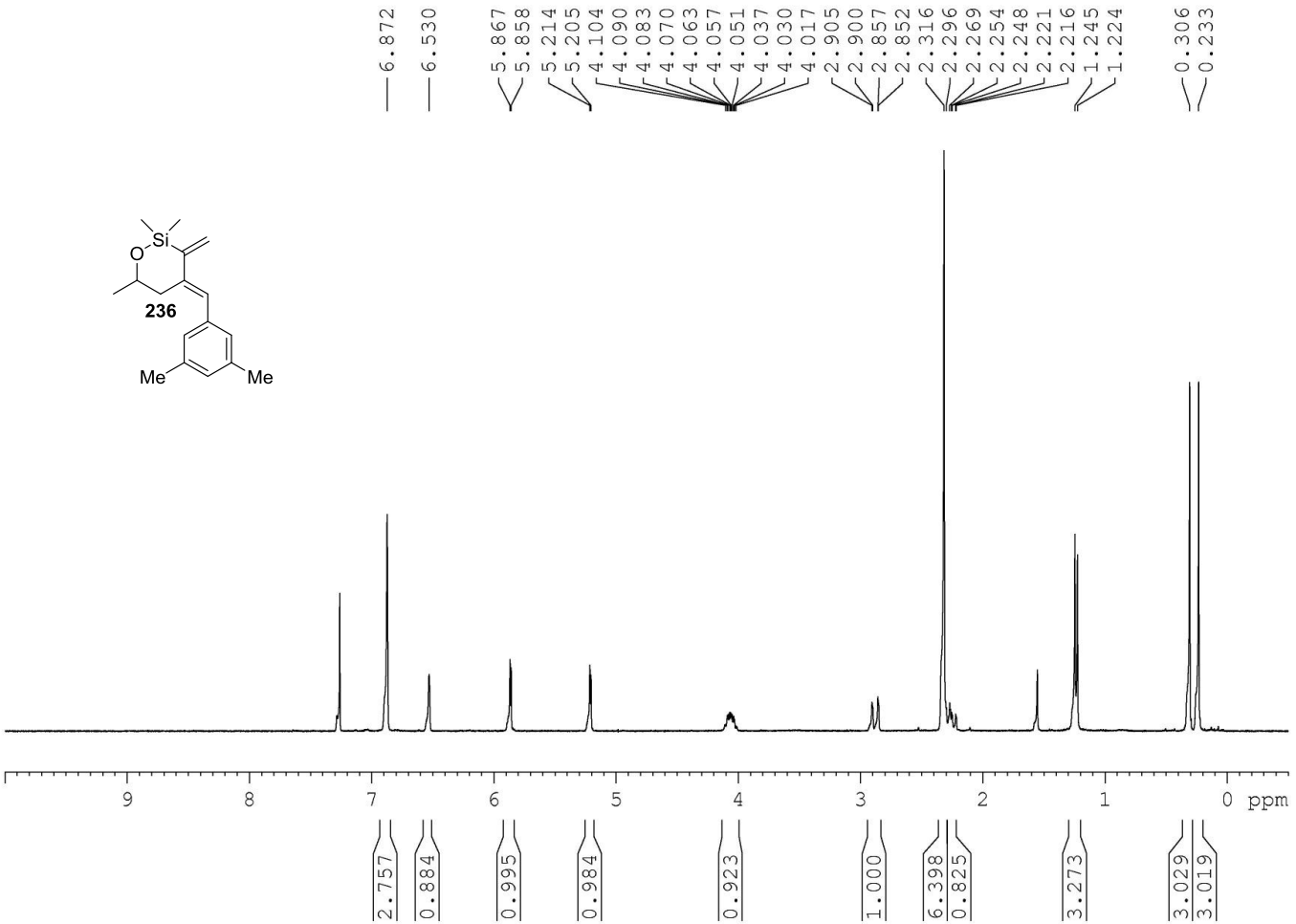

151.306
147.035
146.196
144.864
129.899
123.761
123.029
121.629
69.821
40.312
24.500
-0.233
-0.812
Si
O
234
NO2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

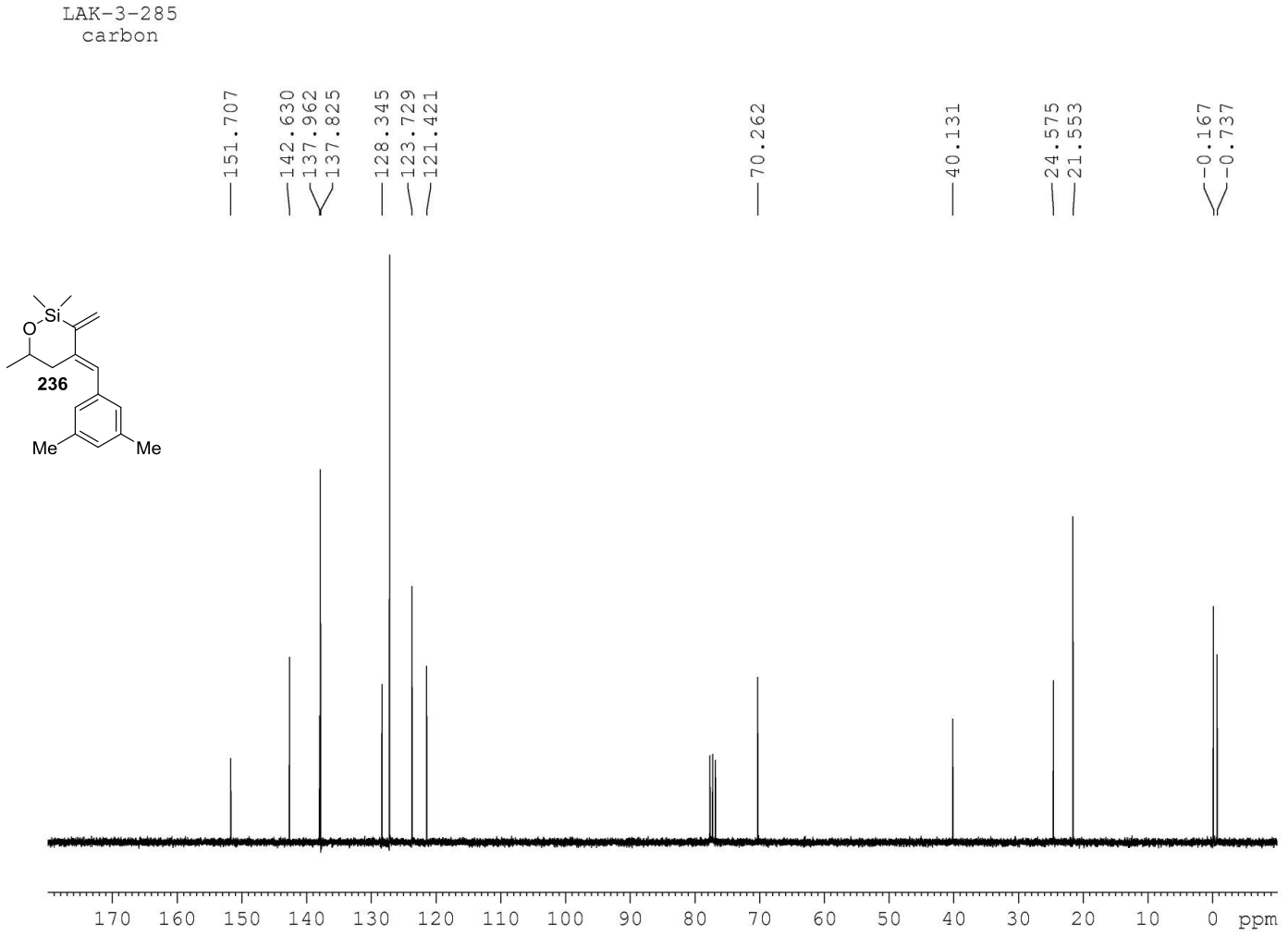
LAK-3-275


7.147
6.561
5.885
5.876
5.220
5.211
4.107
4.102
4.087
4.081
4.067
4.060
4.055
4.048
4.034
4.027
4.014
4.007
2.901
2.895
2.853
2.846
2.350
2.315
2.310
2.282
2.277
2.267
2.261
2.234
2.228
1.239
1.219
0.304
0.235
Si
O
235
Me
9
8
7
6
5
4
3
2
1
0 ppm
3.763
0.877
1.024
0.995
0.946
1.000
4.139
3.276
6.031

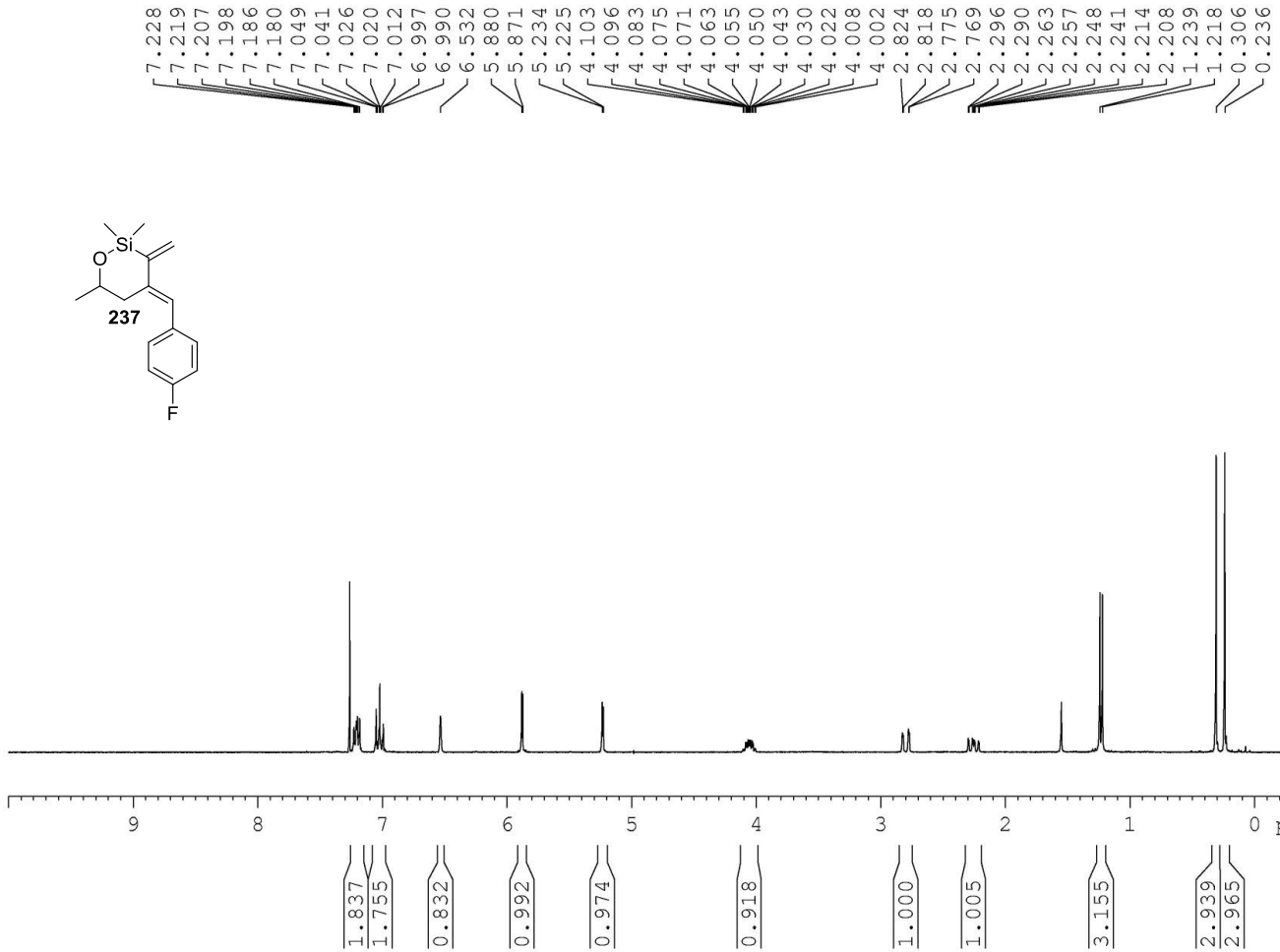

151.616
142.265
136.338
135.129
129.295
129.112
123.487
121.466
70.139
40.108
24.568
21.385
-0.137
-0.730
Si
O
235
Me
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

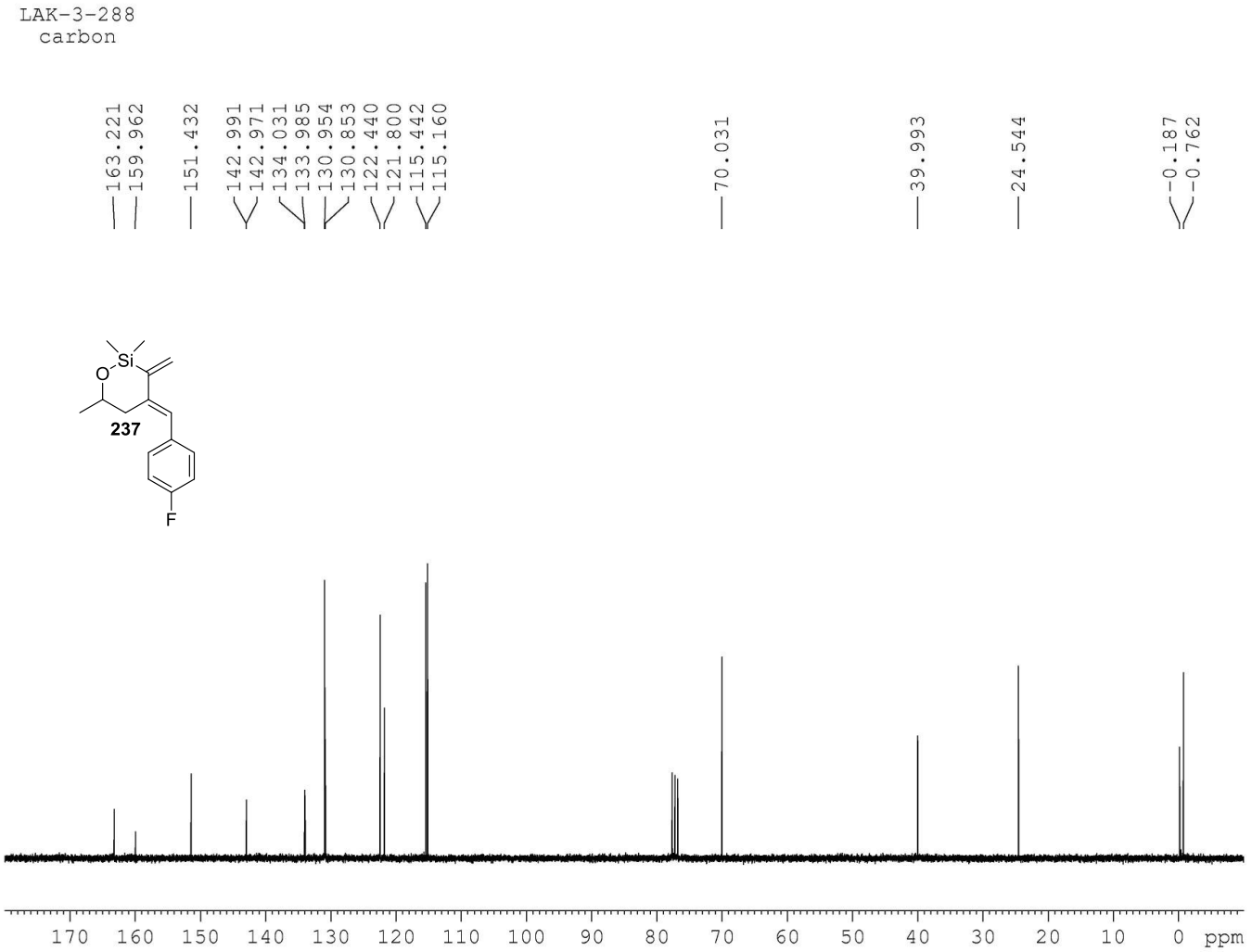
LAK-3-285


6.872
6.530
5.867
5.858
5.214
5.205
4.104
4.090
4.083
4.070
4.063
4.057
4.051
4.037
4.030
4.017
2.905
2.900
2.857
2.852
2.316
2.296
2.269
2.254
2.248
2.221
2.216
1.245
1.224
0.306
0.233
Si
O
236
Me
Me
9
8
7
6
5
4
3
2
1
0 ppm
2.757
0.884
0.995
0.984
0.923
1.000
6.398
0.825
3.273
3.029
3.019

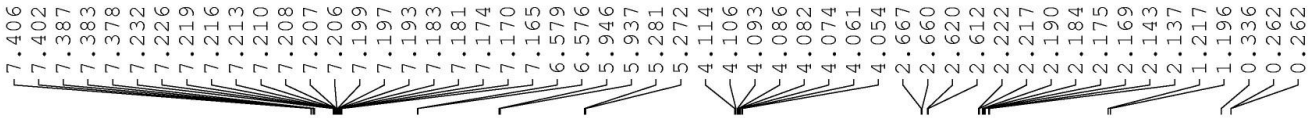

LAK-3-285
carbon
151.707
142.630
137.962
137.825
128.345
123.729
121.421
70.262
40.131
24.575
21.553
-0.167
-0.737
Si
O
Me
Me
236
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

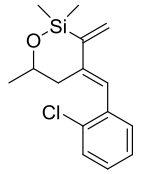
LAK-3-288


7.228
7.219
7.207
7.198
7.186
7.180
7.049
7.041
7.026
7.020
7.012
6.997
6.990
6.532
5.880
5.871
5.234
5.225
4.103
4.096
4.083
4.075
4.071
4.063
4.055
4.050
4.043
4.030
4.022
4.008
4.002
2.824
2.818
2.775
2.769
2.296
2.290
2.263
2.257
2.248
2.241
2.214
2.208
1.239
1.218
0.306
0.236
O
Si
237
F
9
8
7
6
5
4
3
2
1
0 ppm
1.837
1.755
0.832
0.992
0.974
0.918
1.000
1.005
3.155
2.939
2.965

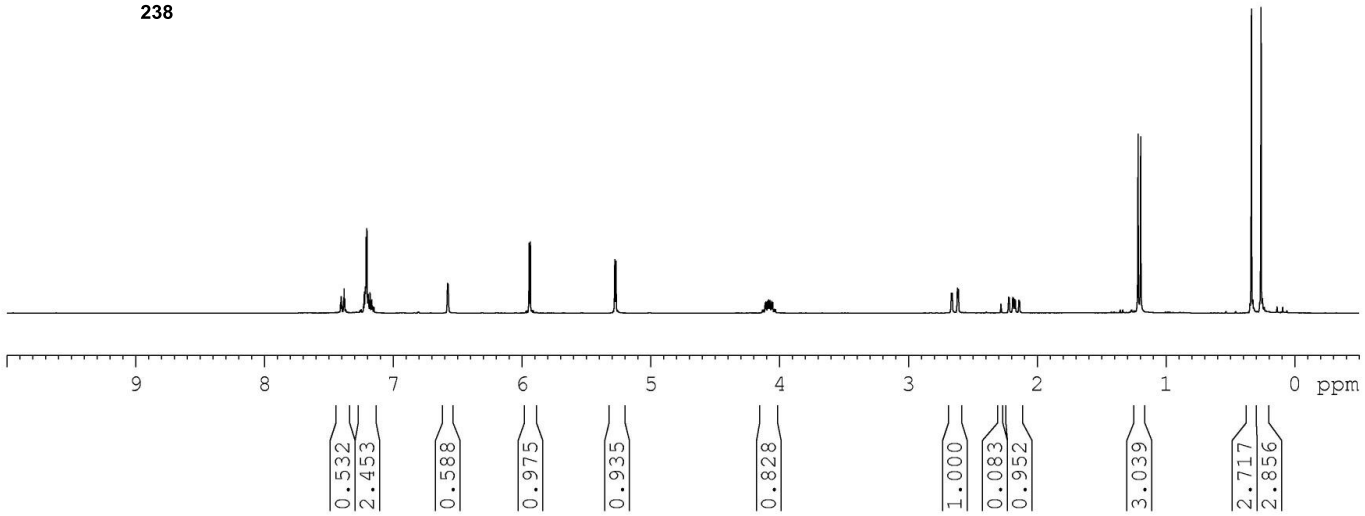

LAK-3-288
carbon
163.221
159.962
151.432
142.991
142.971
134.031
133.985
130.954
130.853
122.440
121.800
115.442
115.160
70.031
39.993
24.544
-0.187
-0.762
Si
O
F
237
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LAK-3-292


7.406
7.402
7.387
7.383
7.378
7.232
7.226
7.219
7.216
7.213
7.210
7.208
7.207
7.206
7.199
7.197
7.193
7.183
7.181
7.174
7.170
7.165
6.579
6.576
5.946
5.937
5.281
5.272
4.114
4.106
4.093
4.086
4.082
4.074
4.061
4.054
2.667
2.660
2.620
2.612
2.222
2.217
2.190
2.184
2.175
2.169
2.143
2.137
1.217
1.196
0.336
0.262
0.262

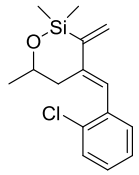

Si
O
Cl

238

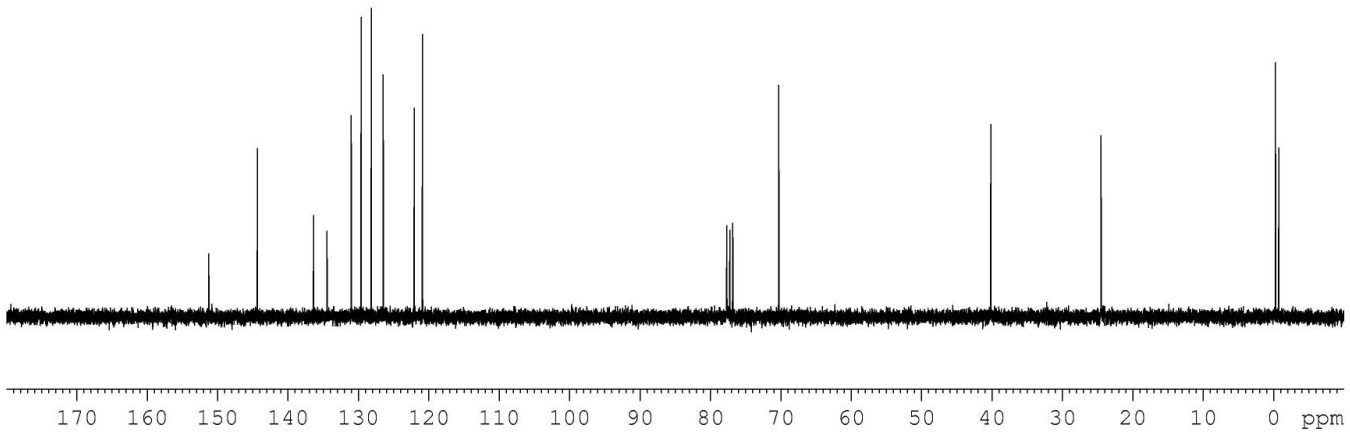

9
8
7
6
5
4
3
2
1
0 ppm
0.532
2.453
0.588
0.975
0.935
0.828
1.000
0.083
0.952
3.039
2.717
2.856

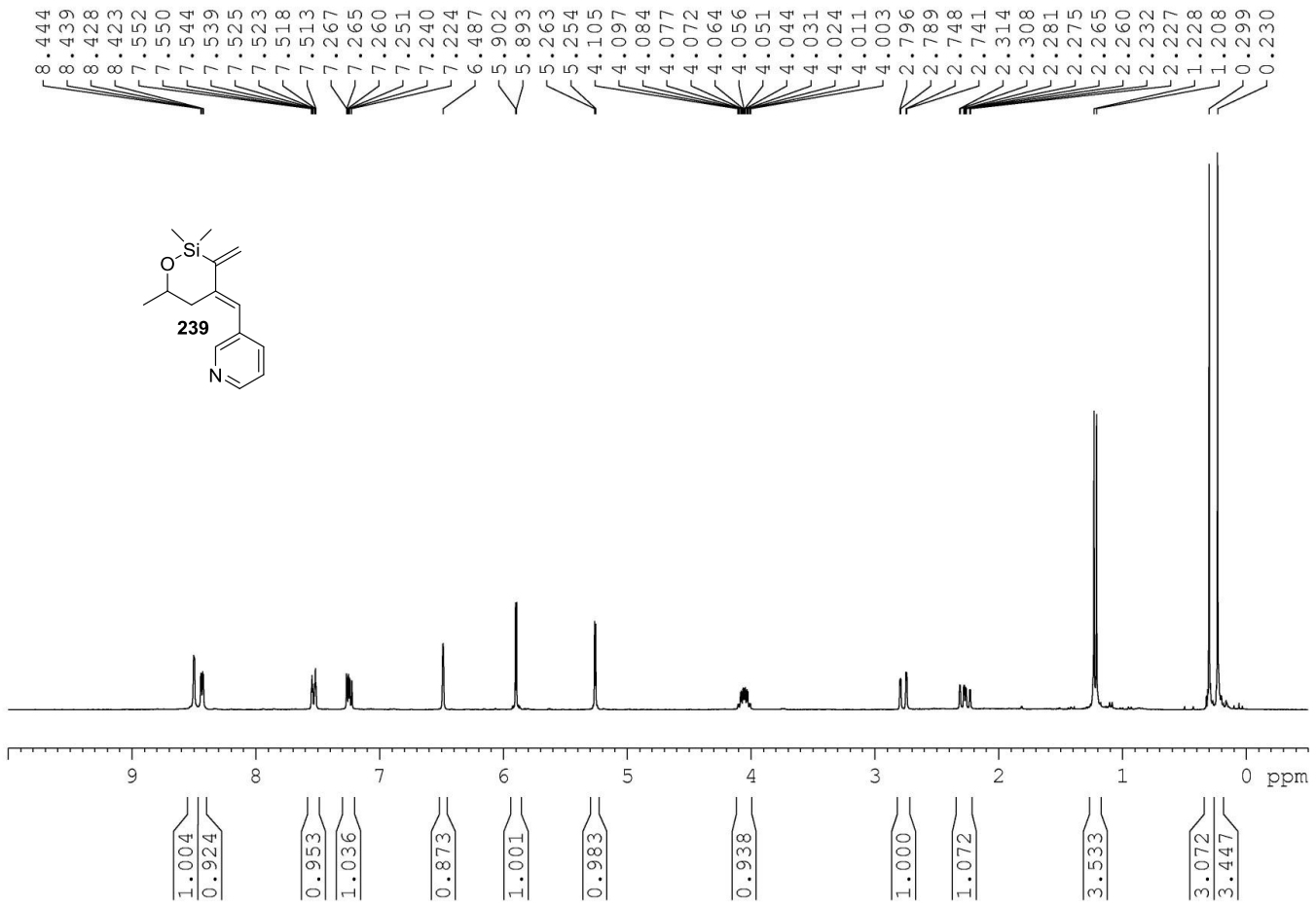
LAK-3-292
carbon

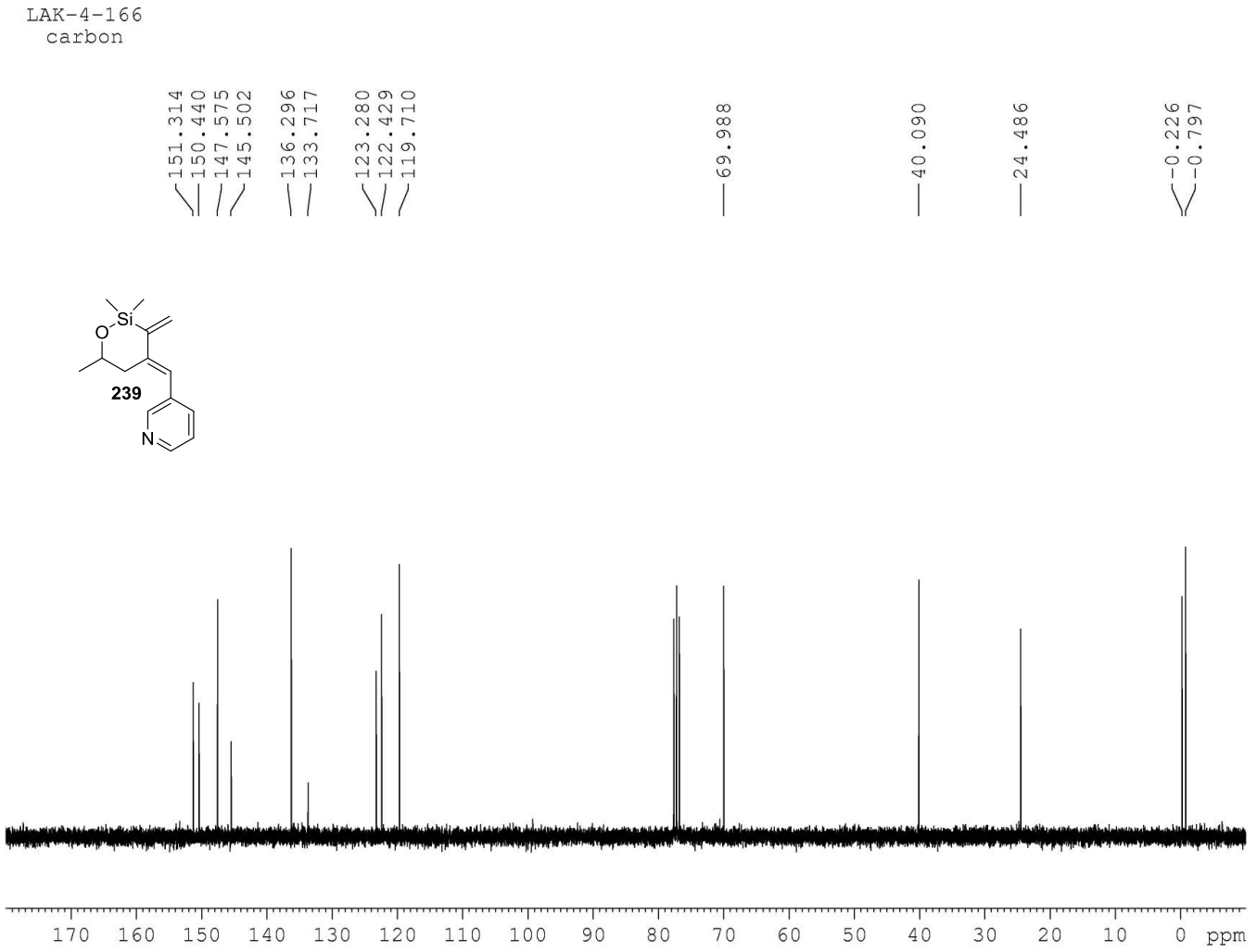
151.254
144.322
136.348
134.444
131.008
129.616
128.162
126.463
122.061
120.882
70.270
40.152
24.481
-0.295
-0.769

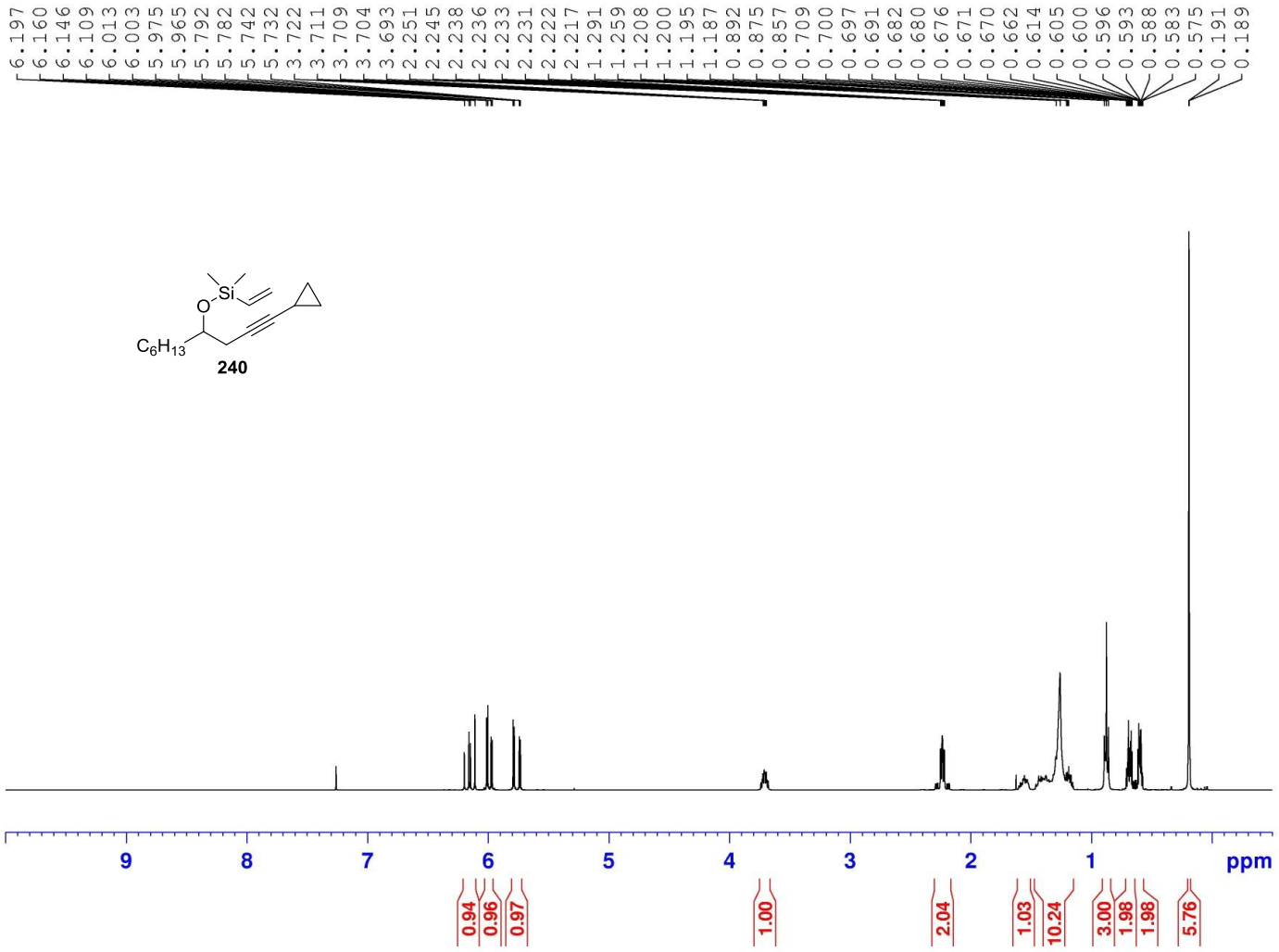


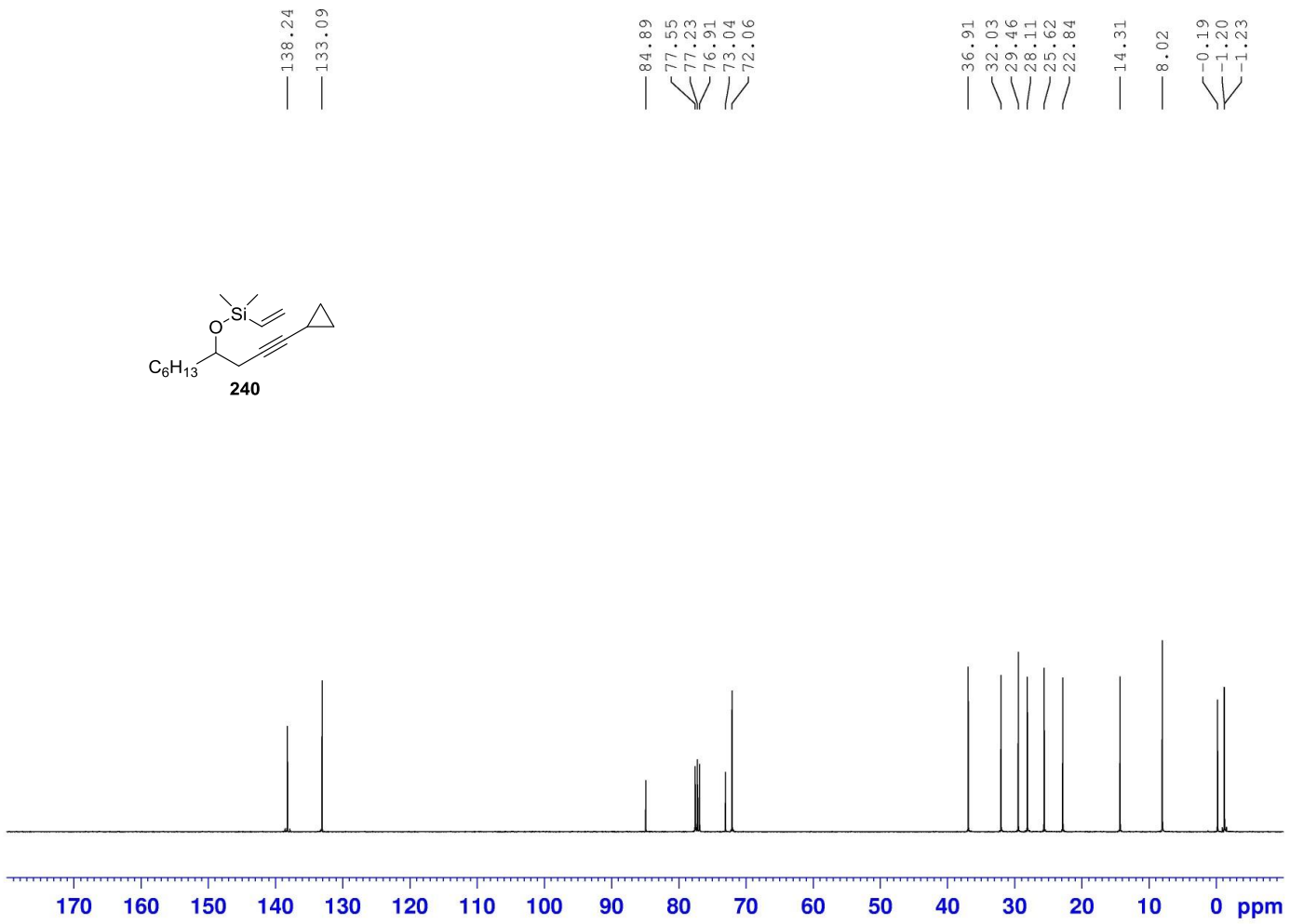
238




8.444
8.439
8.428
8.423
7.552
7.550
7.544
7.539
7.525
7.523
7.518
7.513
7.267
7.265
7.260
7.251
7.240
7.224
6.487
5.902
5.893
5.263
5.254
4.105
4.097
4.084
4.077
4.072
4.064
4.056
4.051
4.044
4.031
4.024
4.011
4.003
2.796
2.789
2.748
2.741
2.314
2.308
2.281
2.275
2.265
2.260
2.232
2.227
1.228
1.208
0.299
0.230
Si
O
N
239
9
8
7
6
5
4
3
2
1
0 ppm
1.004
0.924
0.953
1.036
0.873
1.001
0.983
0.938
1.000
1.072
3.533
3.072
3.447

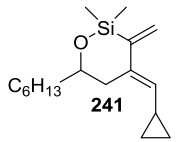

LAK-4-166
carbon
151.314
150.440
147.575
145.502
136.296
133.717
123.280
122.429
119.710
69.988
40.090
24.486
-0.226
-0.797
Si
O
N
239
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


6.197
6.160
6.146
6.109
6.013
6.003
5.975
5.965
5.792
5.782
5.742
5.732
3.722
3.711
3.709
3.704
3.693
2.251
2.245
2.238
2.236
2.233
2.231
2.222
2.217
1.291
1.259
1.208
1.200
1.195
1.187
0.892
0.875
0.857
0.709
0.700
0.697
0.691
0.682
0.680
0.676
0.671
0.670
0.662
0.614
0.605
0.600
0.596
0.593
0.588
0.583
0.575
0.191
0.189
Si
O
C6H13
240
9
8
7
6
5
4
3
2
1
ppm
0.94
0.96
0.97
1.00
2.04
1.03
10.24
3.00
1.98
1.96
5.76

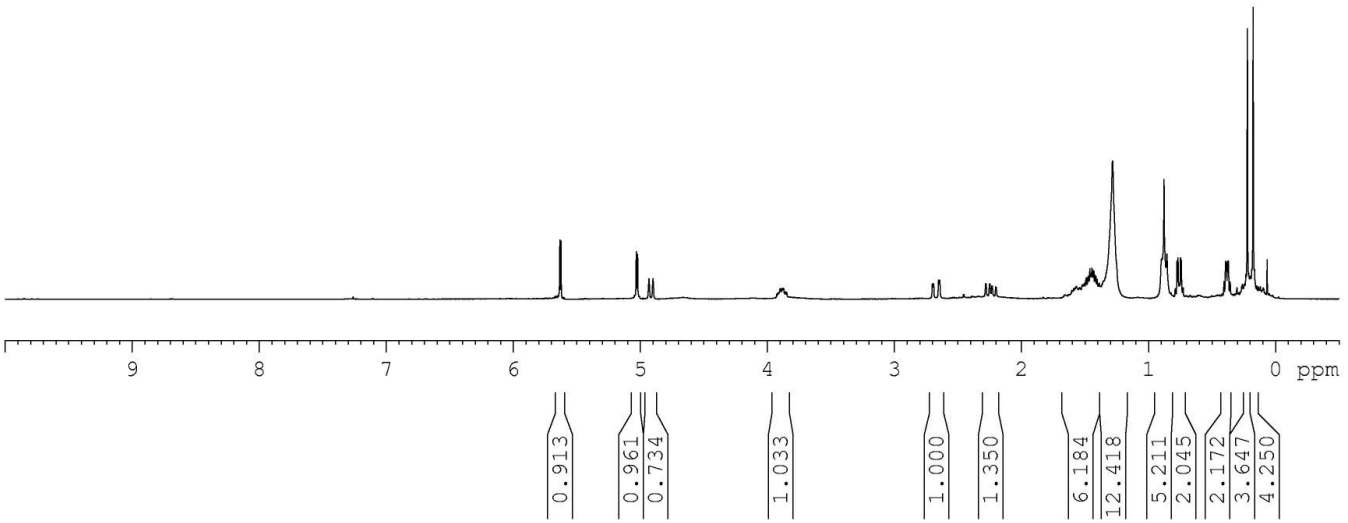

138.24
133.09
84.89
77.55
77.23
76.91
73.04
72.06
36.91
32.03
29.46
28.11
25.62
22.84
14.31
8.02
-0.19
-1.20
-1.23
Si
O
C6H13
240
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

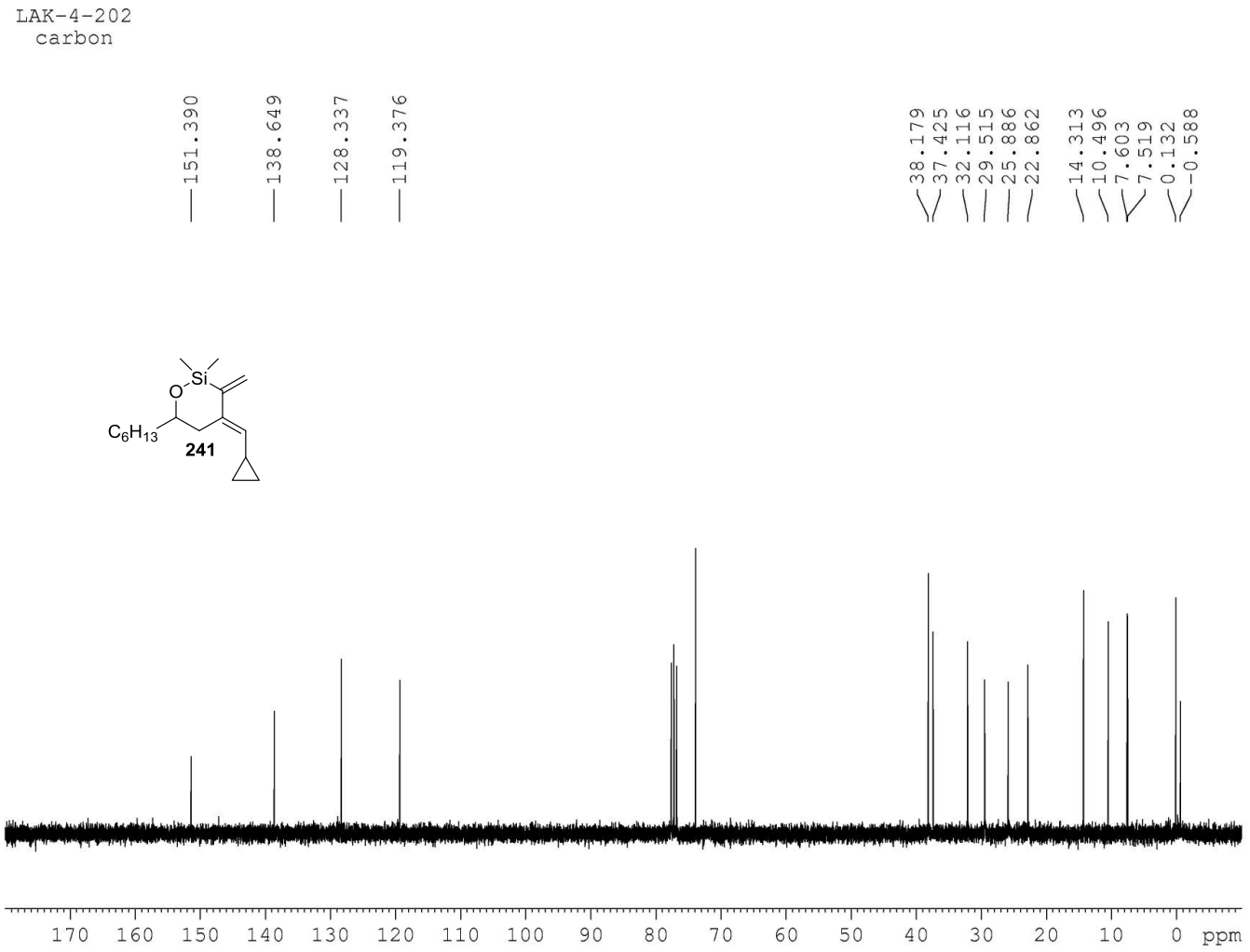
LAK-4-202

5.635 5.625 5.032 5.023 4.932 4.901 2.700 2.694 2.651 2.645 2.283 2.278 2.252 2.248 2.234 2.229 2.204 2.199 1.588 1.567 1.541 1.522 1.505 1.489 1.477 1.473 1.462 1.457 1.446 1.435 1.430 1.419 1.415 1.284 0.899 0.894 0.878 0.855 0.776 0.768 0.757 0.754 0.748 0.742 0.730 0.727 0.406 0.393 0.386 0.378 0.372 0.357 0.222 0.177

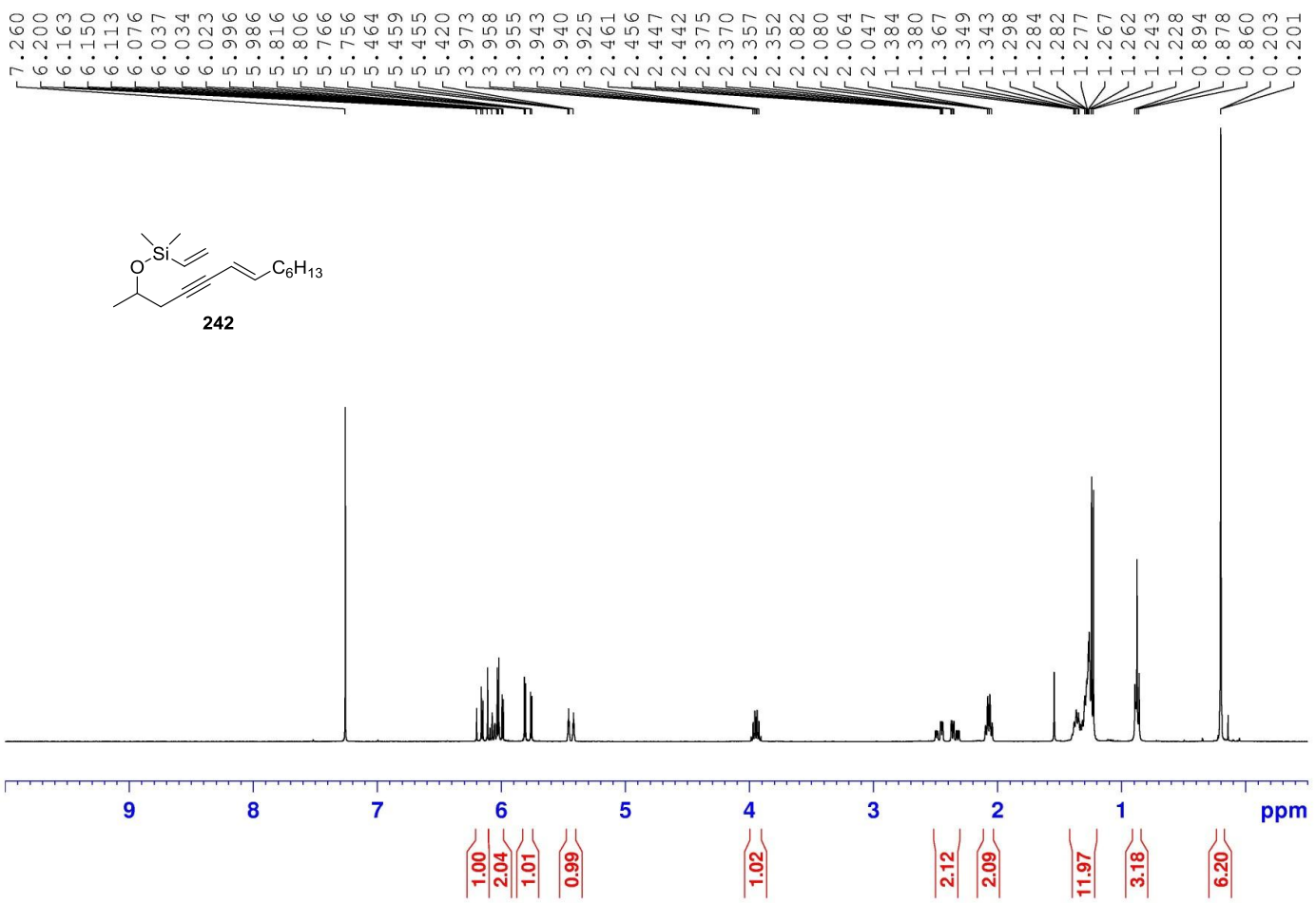


241




LAK-4-202
carbon
151.390
138.649
128.337
119.376
38.179
37.425
32.116
29.515
25.886
22.862
14.313
10.496
7.603
7.519
0.132
-0.588
Si
O
C6H13
241
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

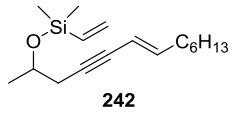
LAK-6-147


7.260
6.200
6.163
6.150
6.113
6.076
6.037
6.034
6.023
5.996
5.986
5.816
5.806
5.766
5.756
5.464
5.459
5.455
5.420
3.973
3.958
3.955
3.943
3.940
3.925
2.461
2.456
2.447
2.442
2.375
2.370
2.357
2.352
2.082
2.080
2.064
2.047
1.384
1.380
1.367
1.349
1.343
1.298
1.284
1.282
1.277
1.267
1.262
1.243
1.228
0.894
0.878
0.860
0.203
0.201
Si
O
C6H13
9
8
7
6
5
4
3
2
1
ppm
1.00
2.04
1.01
0.99
1.02
2.12
2.09
11.97
3.18
6.20

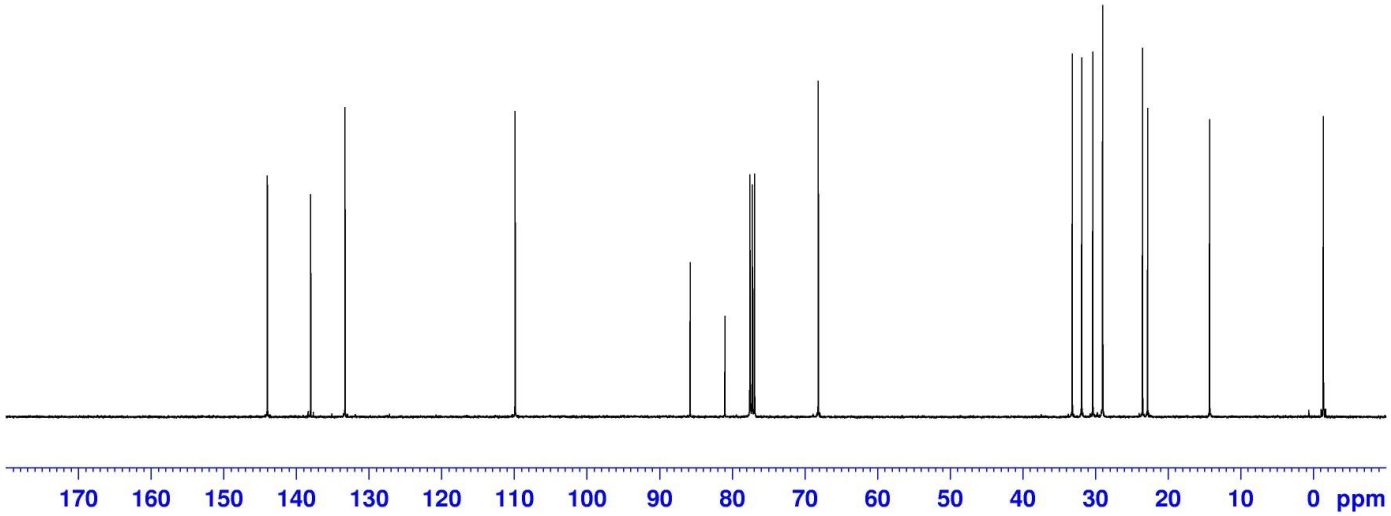
242

LAK-6-147
carbon

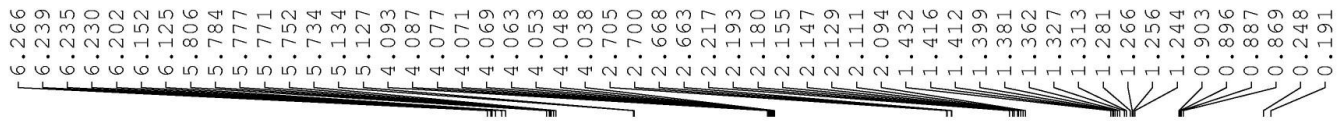
143.98
138.01
133.28
109.88
85.79
80.99
68.14
33.18
31.87
30.36
29.00
28.97
23.50
22.80
14.28
-1.37
-1.40

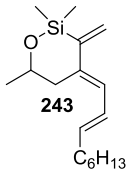


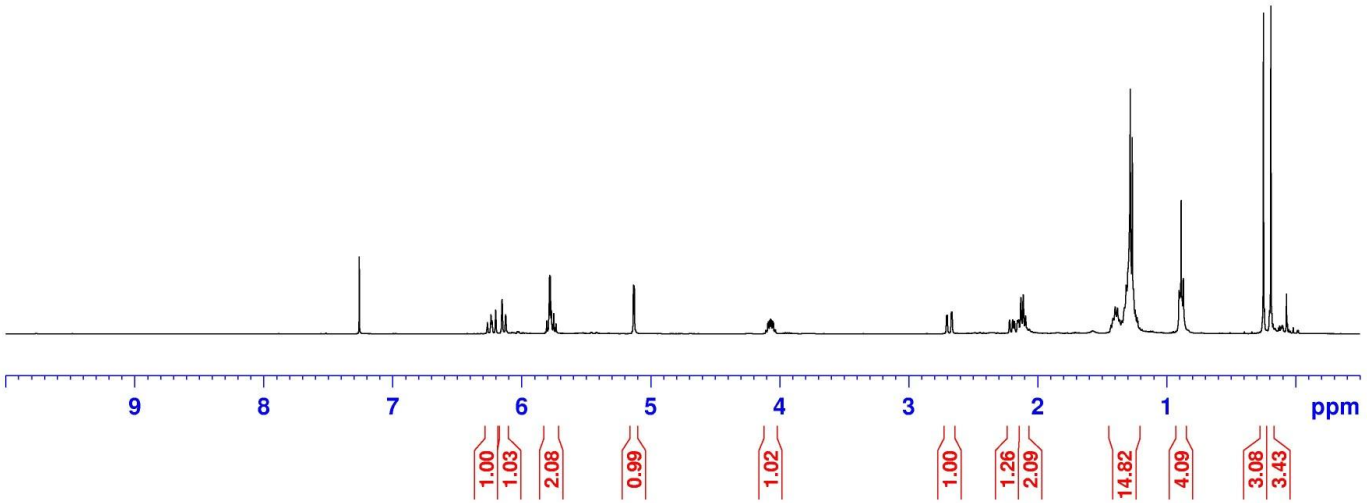
242



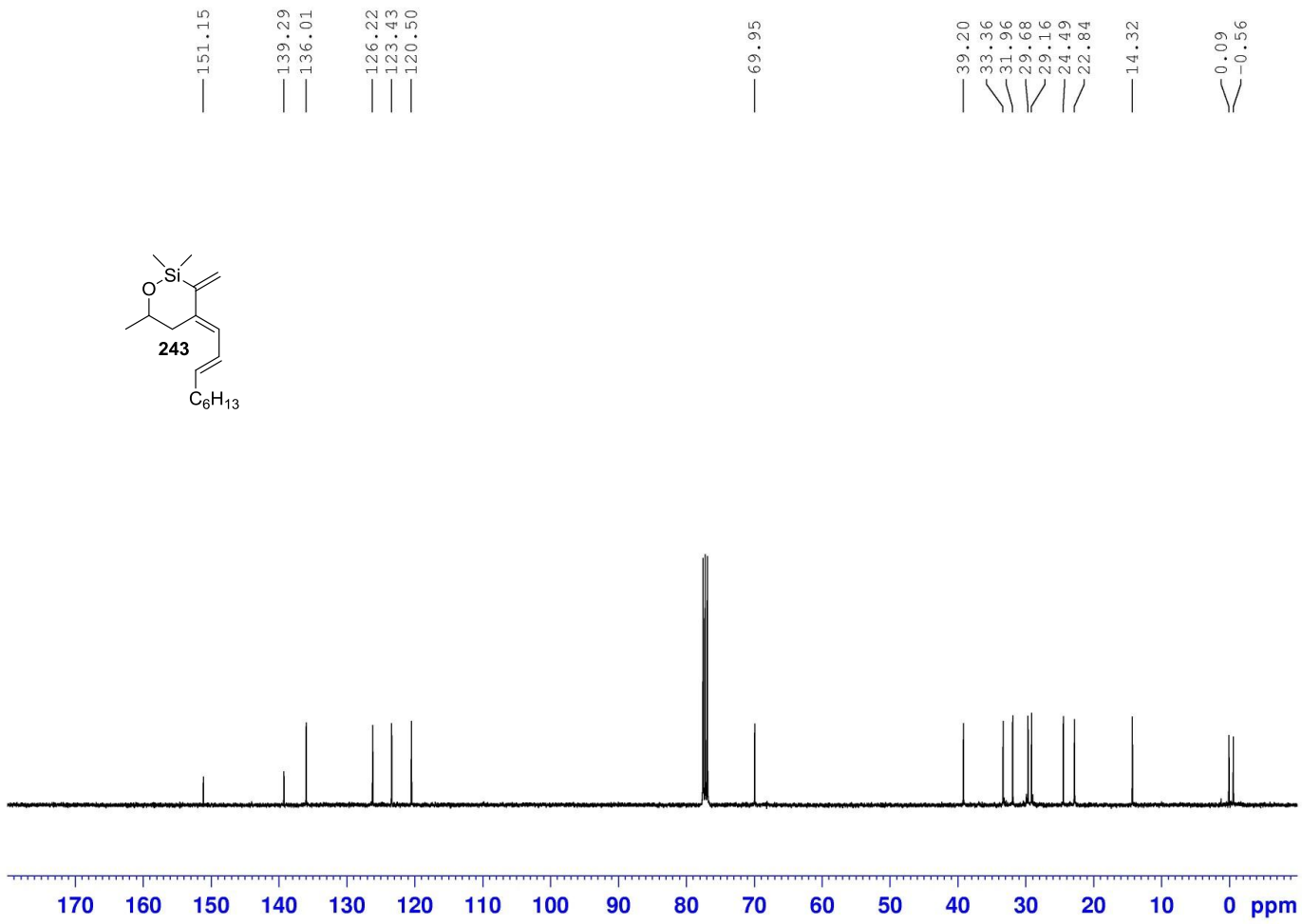
LAK-5-211


6.266
6.239
6.235
6.230
6.202
6.152
6.125
5.806
5.784
5.777
5.771
5.752
5.734
5.134
5.127
4.093
4.087
4.077
4.071
4.069
4.063
4.053
4.048
4.038
2.705
2.700
2.668
2.663
2.217
2.193
2.180
2.155
2.147
2.129
2.111
2.094
1.432
1.416
1.412
1.399
1.381
1.362
1.327
1.313
1.281
1.266
1.256
1.244
0.903
0.896
0.887
0.869
0.248
0.191

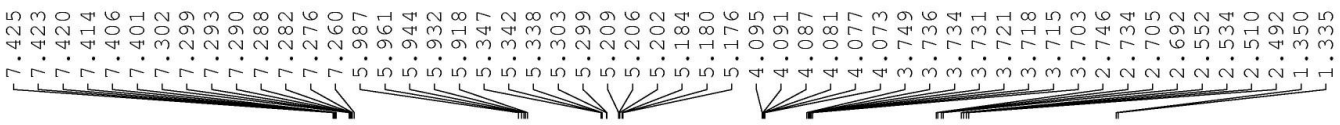

Si
O
243
C6H13

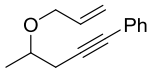

9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
2.08
0.99
1.02
1.00
1.26
2.09
14.82
4.09
3.08
3.43

LAK-5-211

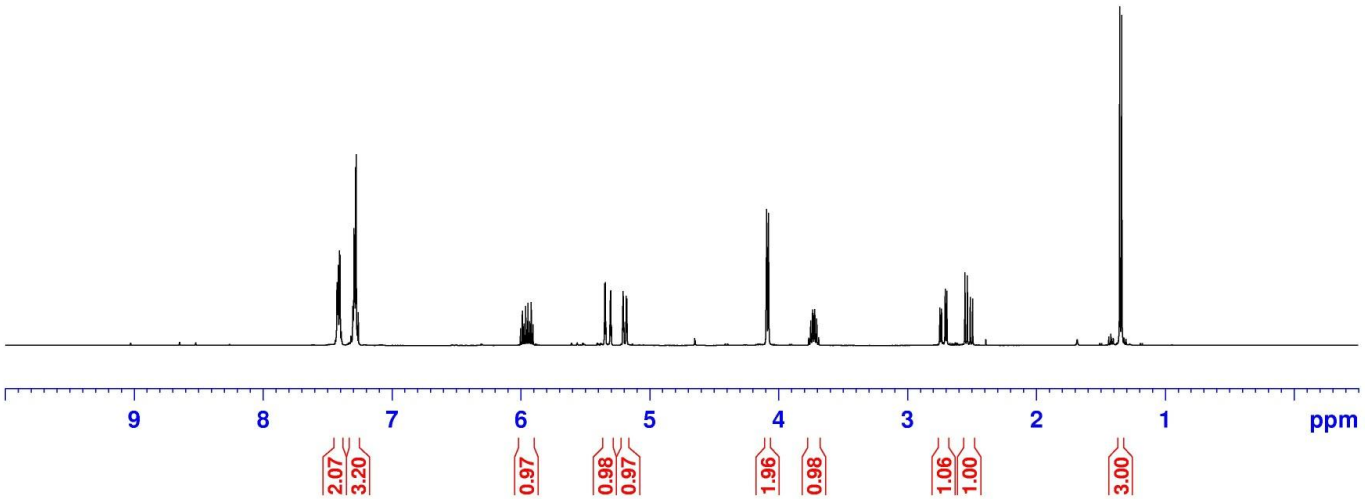

151.15
139.29
136.01
126.22
123.43
120.50
69.95
39.20
33.36
31.96
29.68
29.16
24.49
22.84
14.32
0.09
-0.56
Si
O
243
C6H13
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LAK-4-89

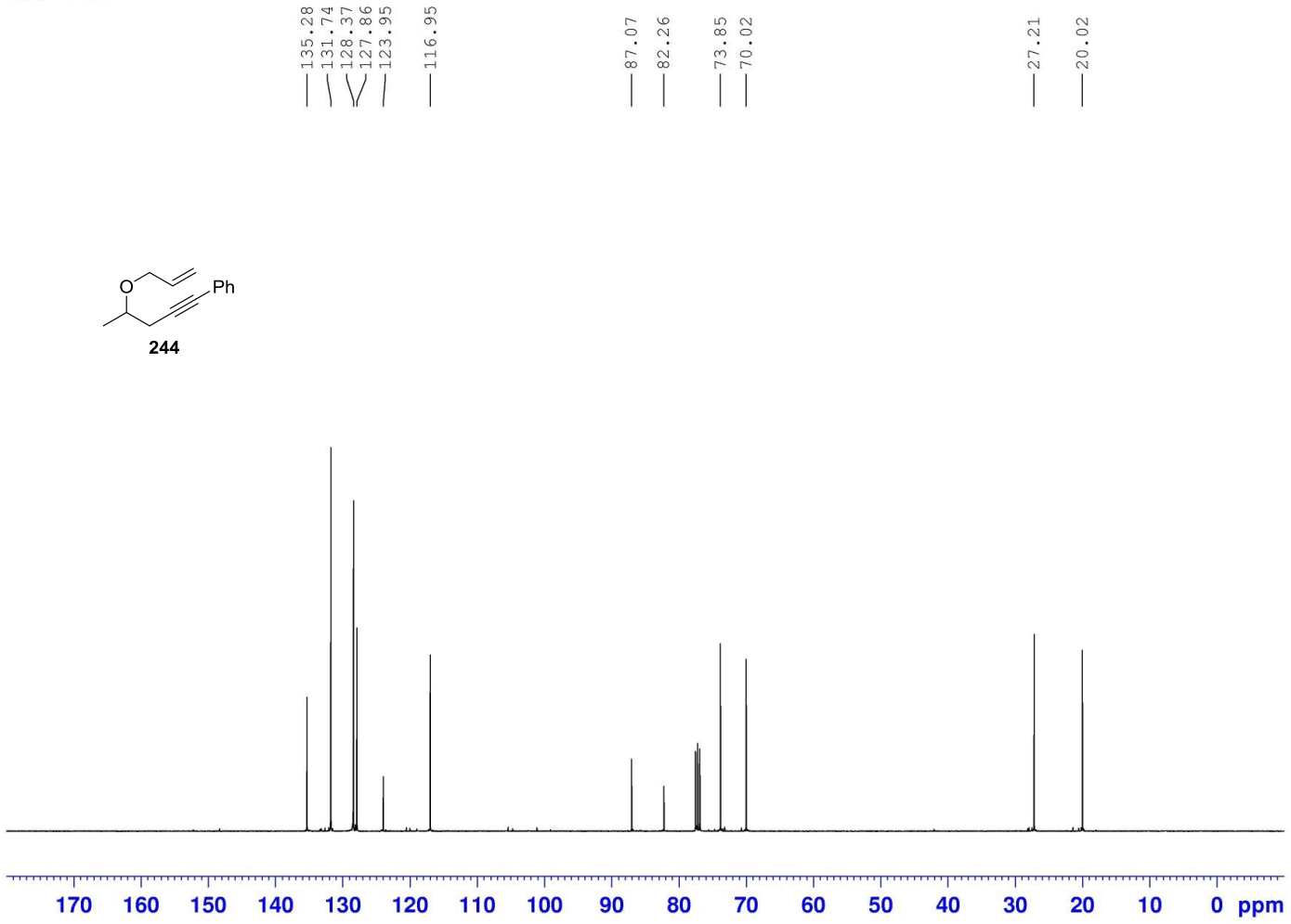

7.425
7.423
7.420
7.414
7.406
7.401
7.302
7.299
7.293
7.290
7.288
7.282
7.276
7.260
5.987
5.961
5.944
5.932
5.918
5.347
5.342
5.338
5.303
5.299
5.209
5.206
5.202
5.184
5.180
5.176
4.095
4.091
4.087
4.081
4.077
4.073
3.749
3.736
3.734
3.731
3.721
3.718
3.715
3.703
2.746
2.734
2.705
2.692
2.552
2.534
2.510
2.492
1.350
1.335

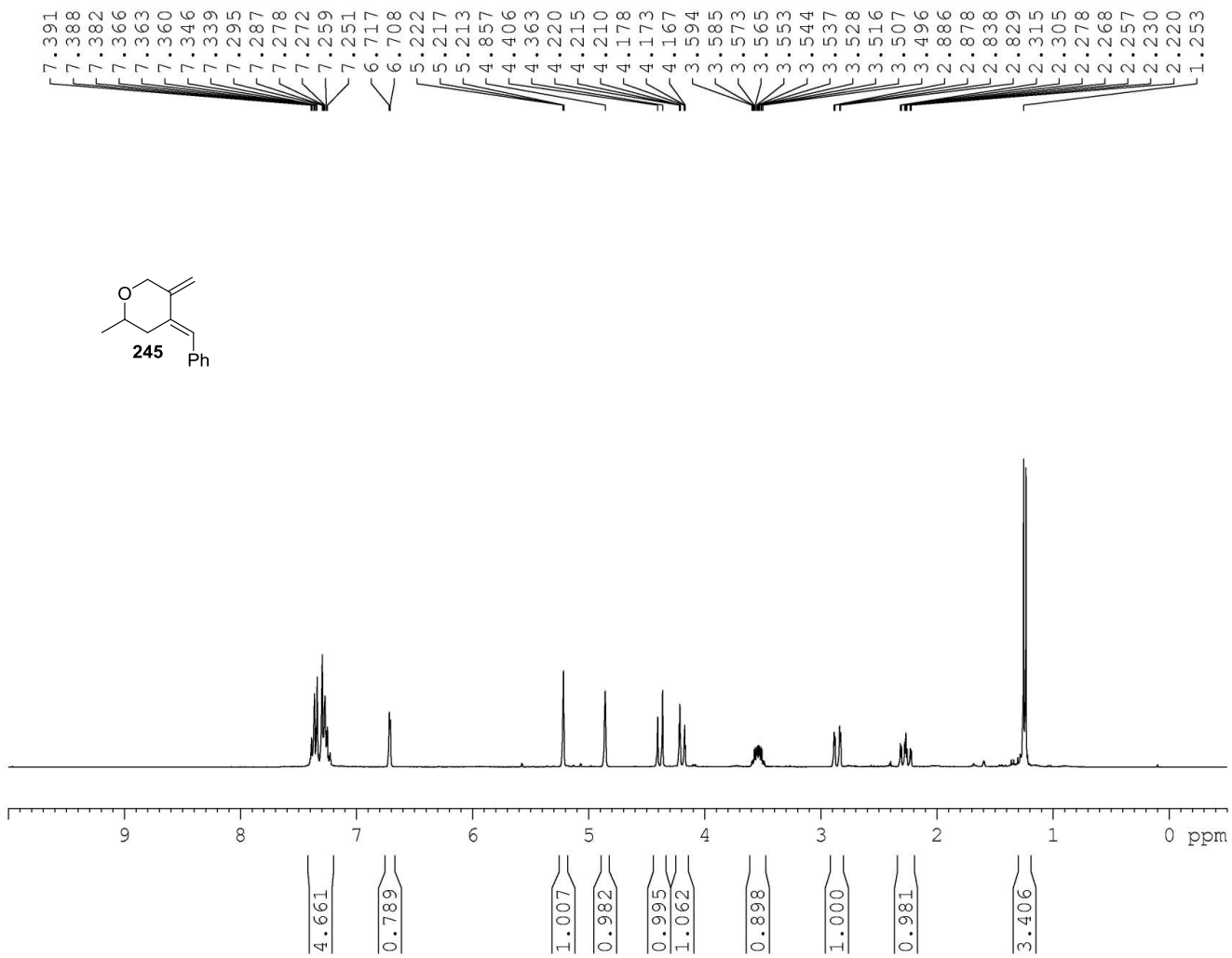

O
Ph

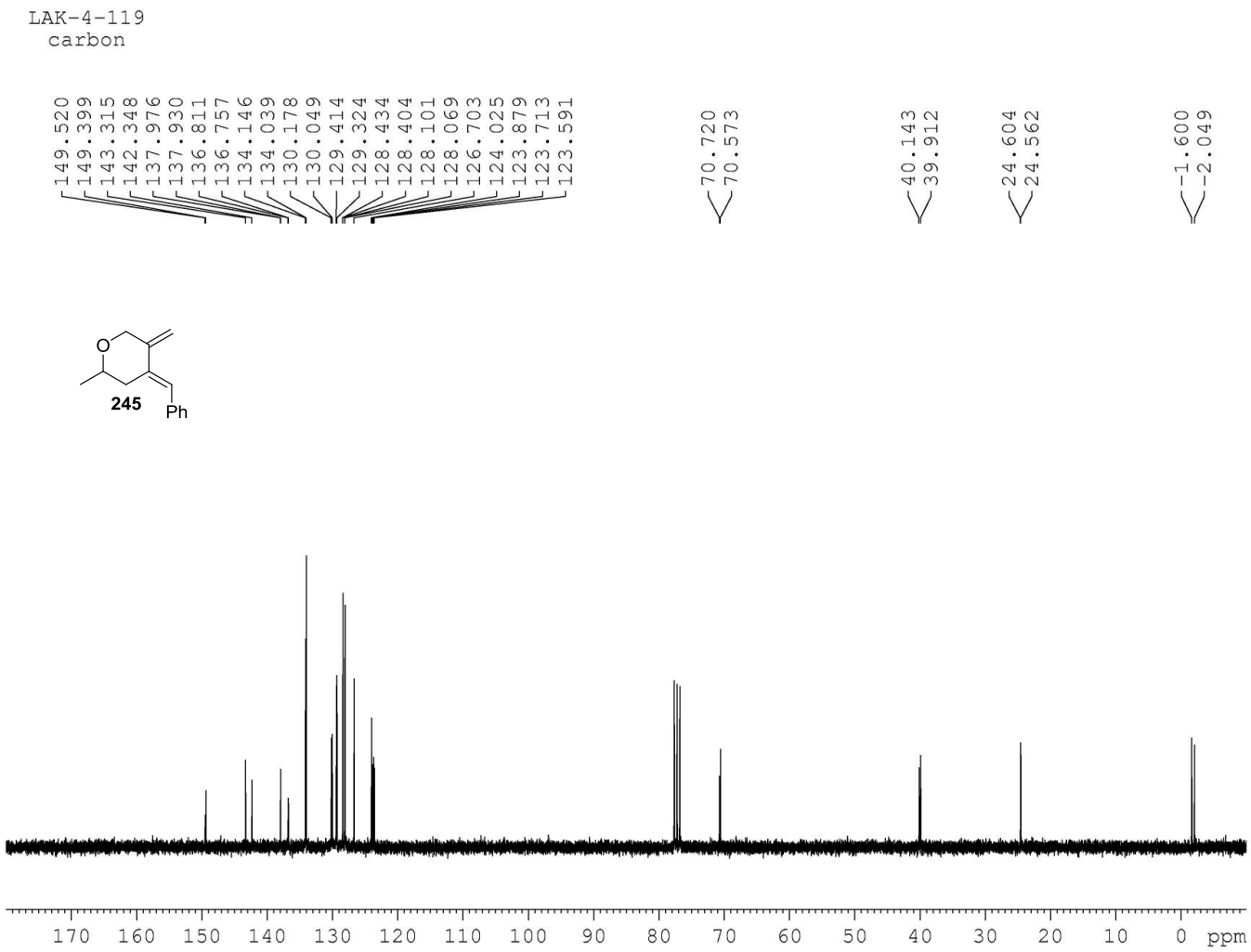
244

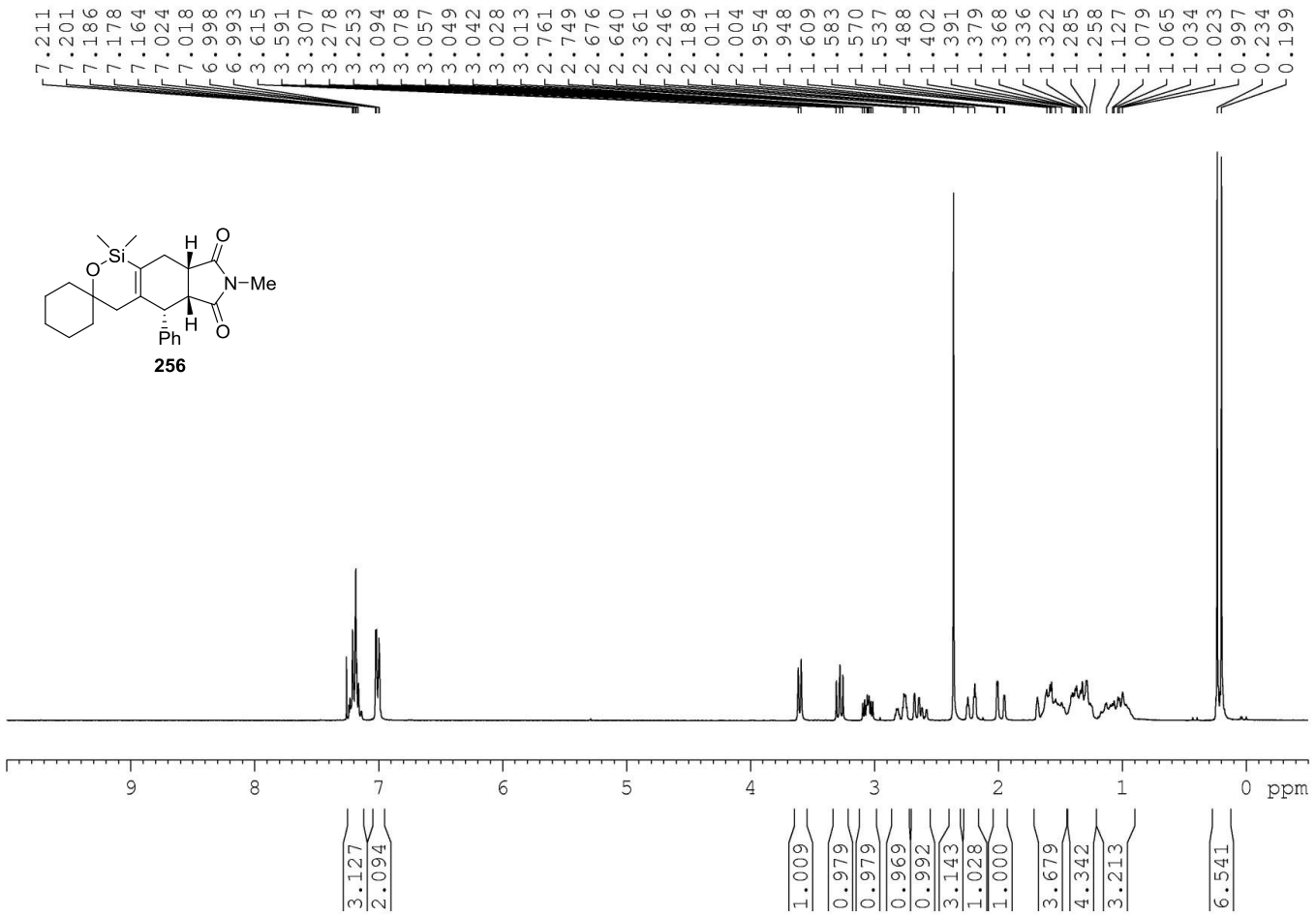

9
8
7
6
5
4
3
2
1
ppm
2.07
3.20
0.97
0.98
0.97
1.96
0.98
1.06
1.00
3.00

LAK-4-89

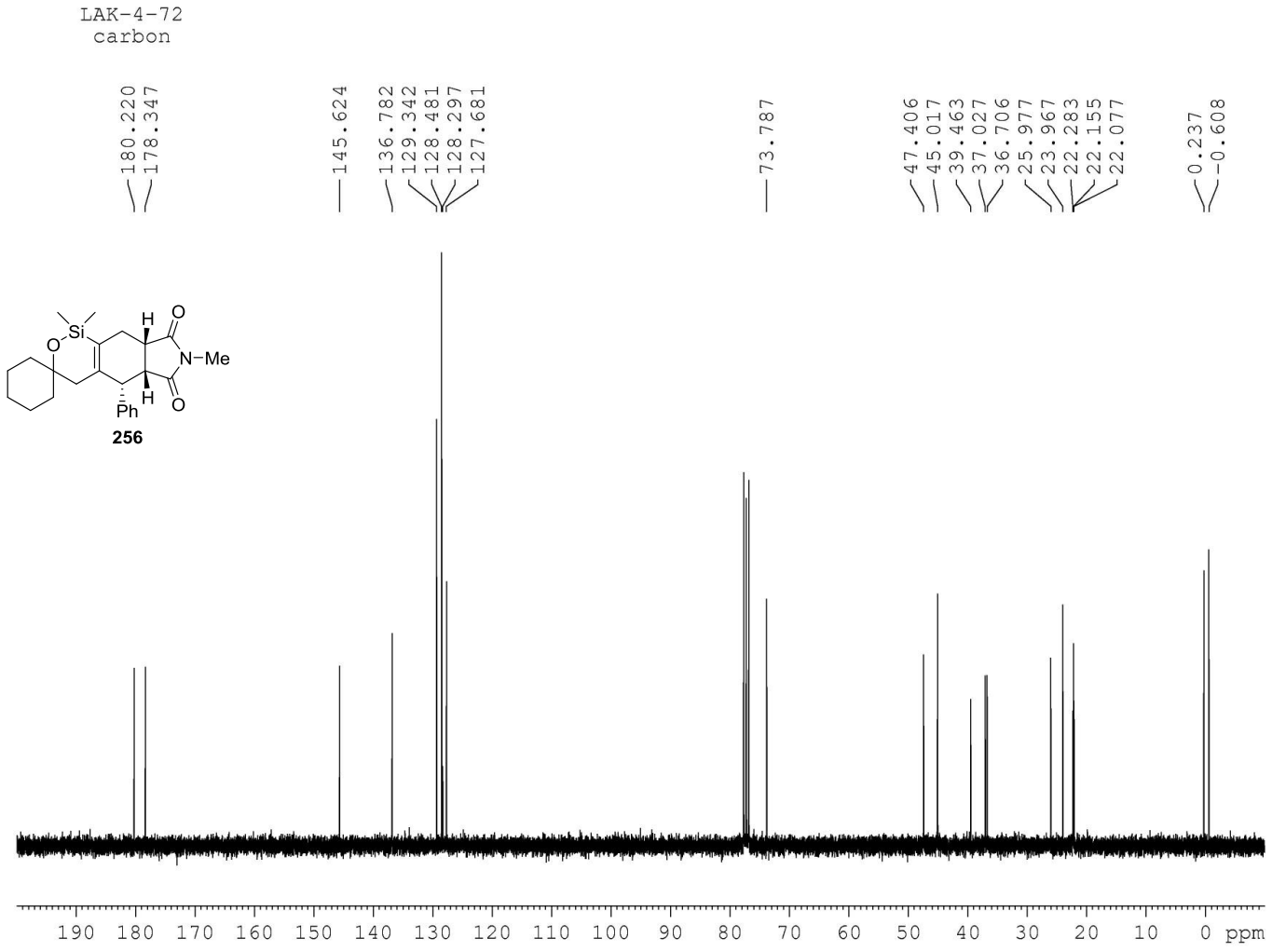

135.28
131.74
128.37
127.86
123.95
116.95
87.07
82.26
73.85
70.02
27.21
20.02
O
Ph
244
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.391
7.388
7.382
7.366
7.363
7.360
7.346
7.339
7.295
7.287
7.278
7.272
7.259
7.251
6.717
6.708
5.222
5.217
5.213
4.857
4.406
4.363
4.220
4.215
4.210
4.178
4.173
4.167
3.594
3.585
3.573
3.565
3.553
3.544
3.537
3.528
3.516
3.507
3.496
2.886
2.878
2.838
2.829
2.315
2.305
2.278
2.268
2.257
2.230
2.220
1.253
O
245
Ph
9
8
7
6
5
4
3
2
1
0 ppm
4.661
0.789
1.007
0.982
0.995
1.062
0.898
1.000
0.981
3.406


LAK-4-119
carbon
149.520
149.399
143.315
142.348
137.976
137.930
136.811
136.757
134.146
134.039
130.178
130.049
129.414
129.324
128.434
128.404
128.101
128.069
126.703
124.025
123.879
123.713
123.591
70.720
70.573
40.143
39.912
24.604
24.562
-1.600
-2.049
O
245
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

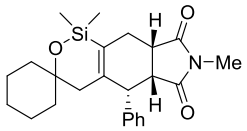

7.211
7.201
7.186
7.178
7.164
7.024
7.018
6.998
6.993
3.615
3.591
3.307
3.278
3.253
3.094
3.078
3.057
3.049
3.042
3.028
3.013
2.761
2.749
2.676
2.640
2.361
2.246
2.189
2.011
2.004
1.954
1.948
1.609
1.583
1.570
1.537
1.488
1.402
1.391
1.379
1.368
1.336
1.322
1.285
1.258
1.127
1.079
1.065
1.034
1.023
0.997
0.234
0.199
Si
O
H
O
N−Me
H
O
Ph
9
8
7
6
5
4
3
2
1
0 ppm
3.127
2.094
1.009
0.979
0.979
0.969
0.992
3.143
1.028
1.000
3.679
4.342
3.213
6.541

256

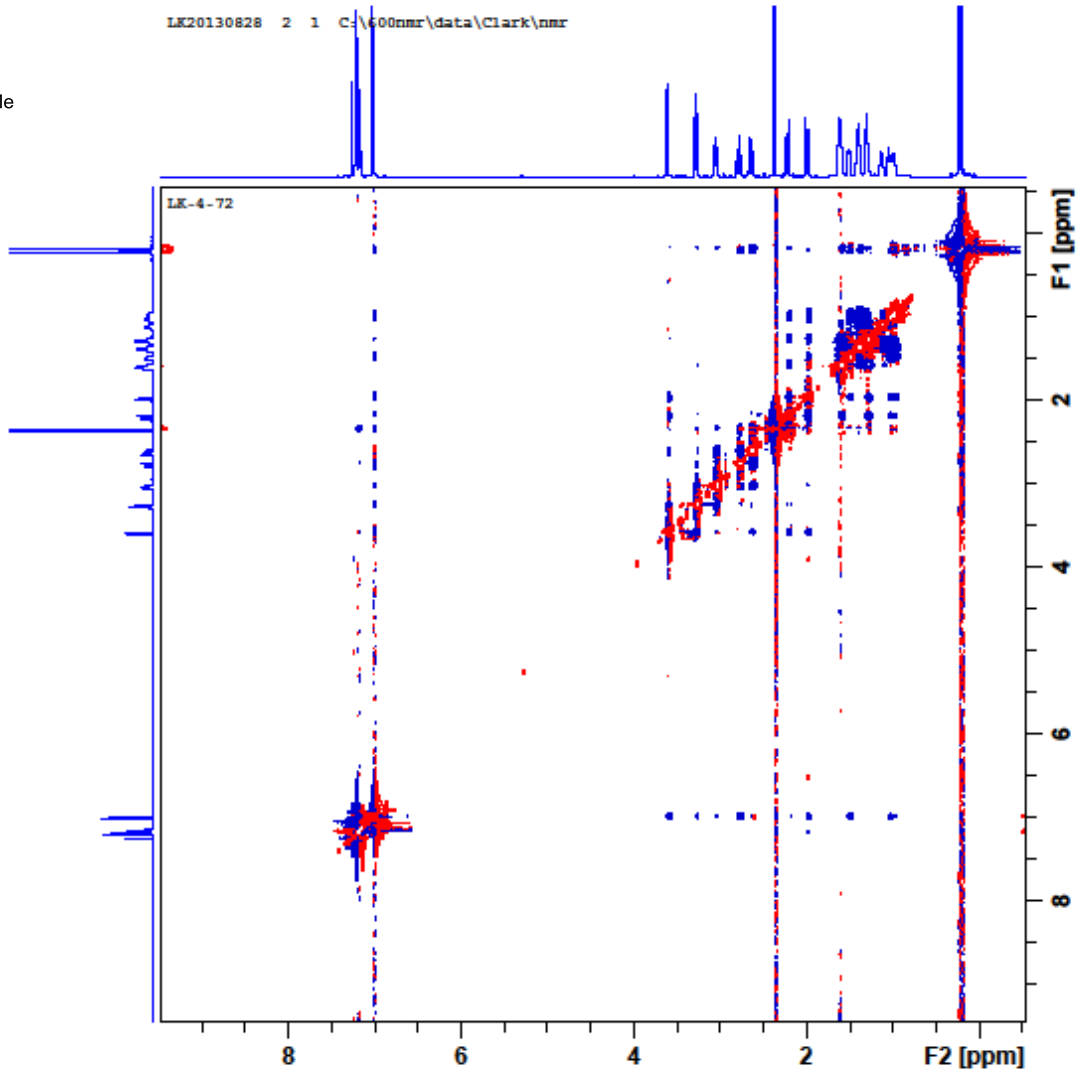

LAK-4-72
carbon
180.220
178.347
145.624
136.782
129.342
128.481
128.297
127.681
73.787
47.406
45.017
39.463
37.027
36.706
25.977
23.967
22.283
22.155
22.077
0.237
-0.608
O
Si
H
O
N–Me
Ph
H
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

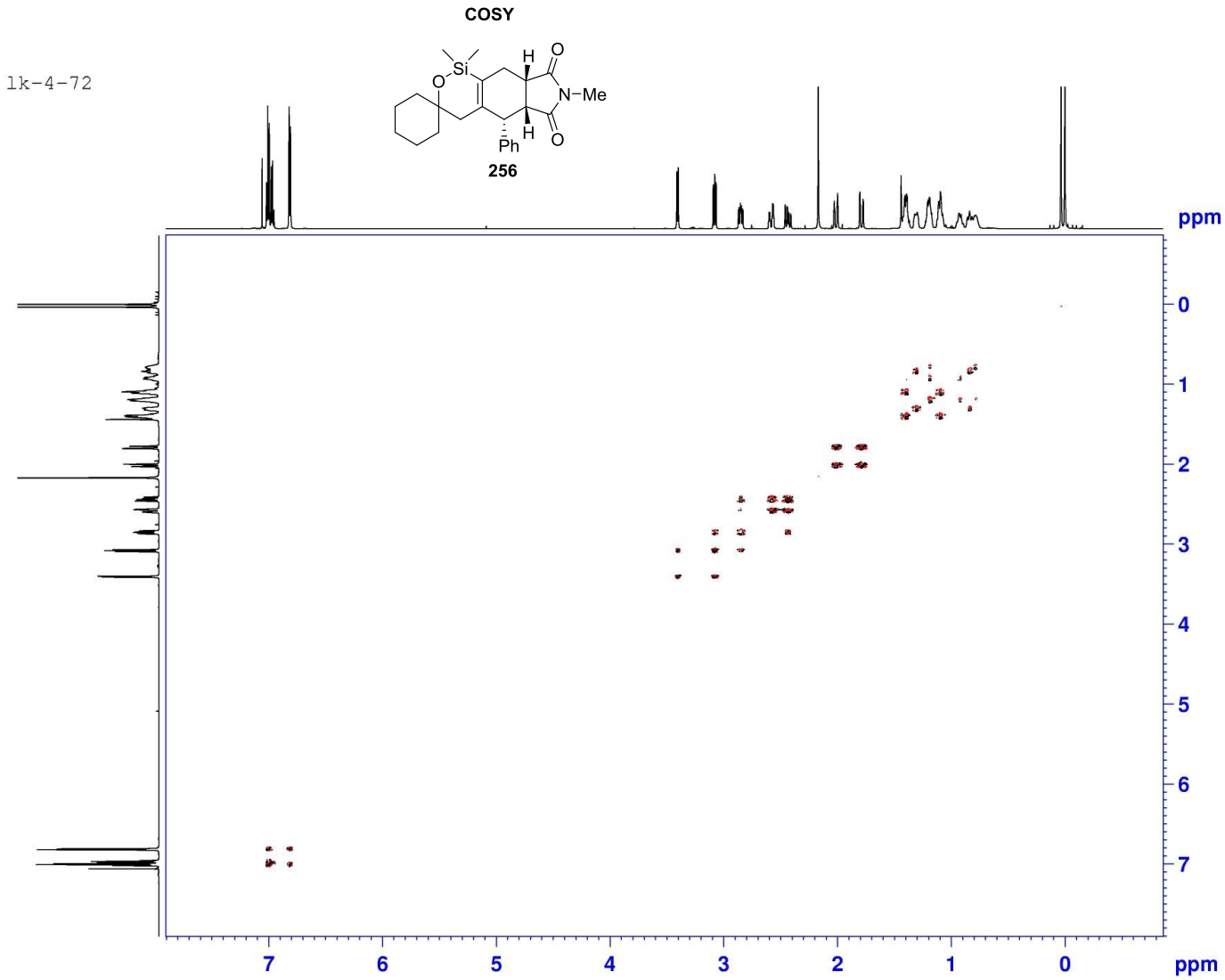
256

NOESY


Si
O
H
O
N–Me
H
Ph
O

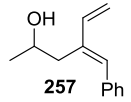
256


LK20130828 2 1 C:\600nmr\data\Clark\nmr
LK-4-72
F1 [ppm]
F2 [ppm]
2
4
6
8

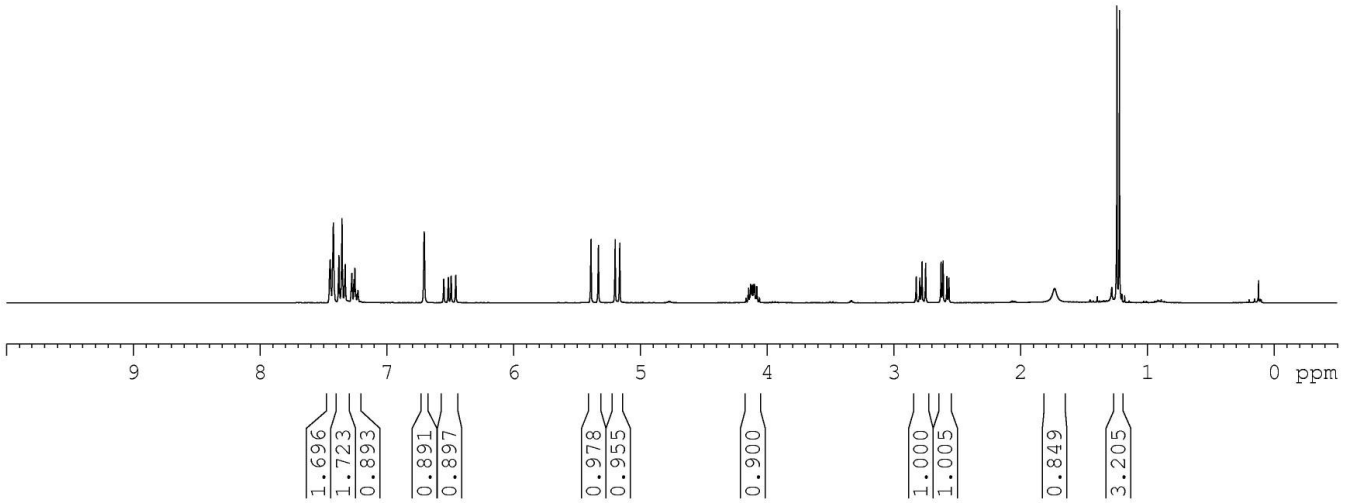

COSY
lk-4-72
256
ppm
0
1
2
3
4
5
6
7
ppm
7
6
5
4
3
2
1
0

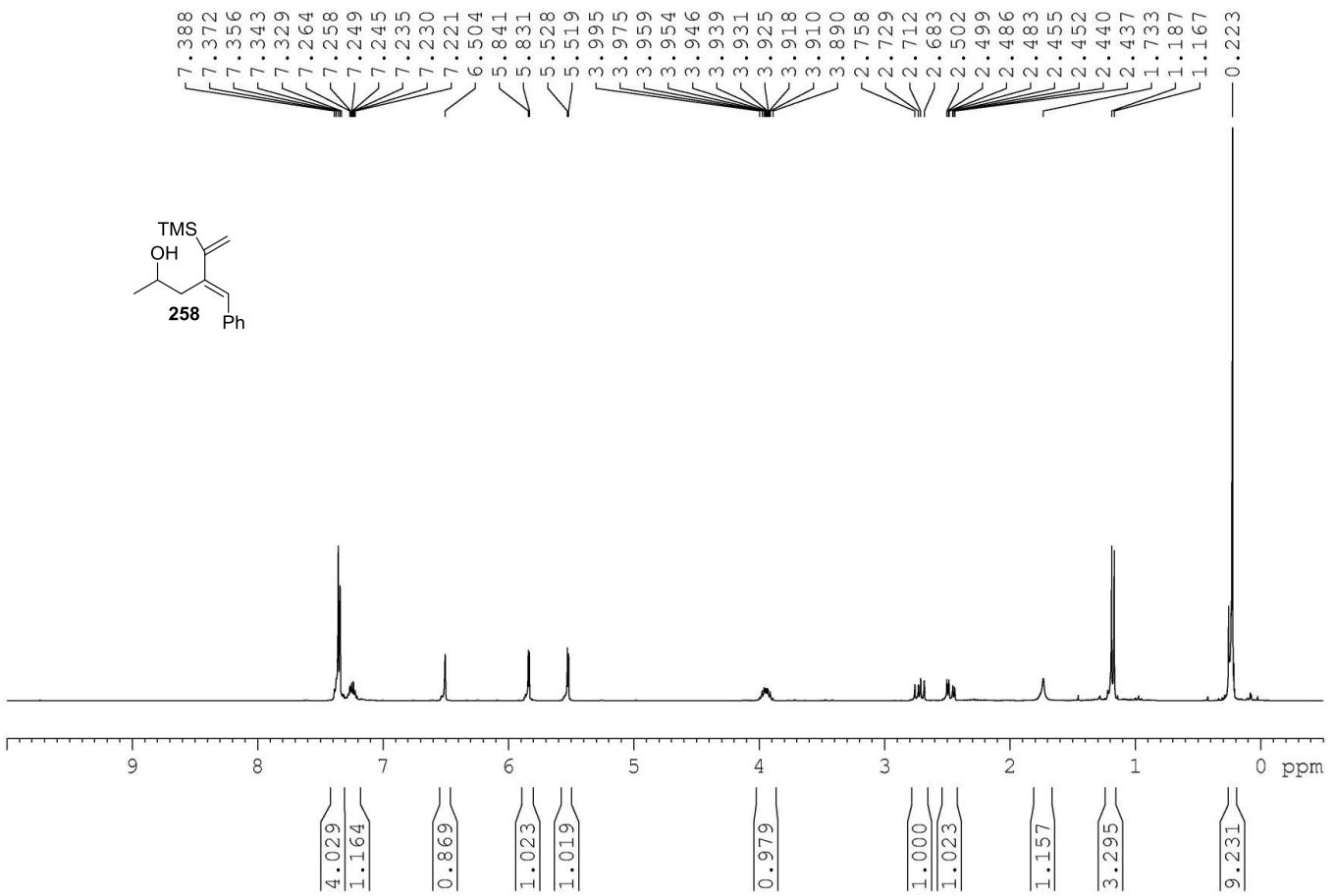
LAK-4-65

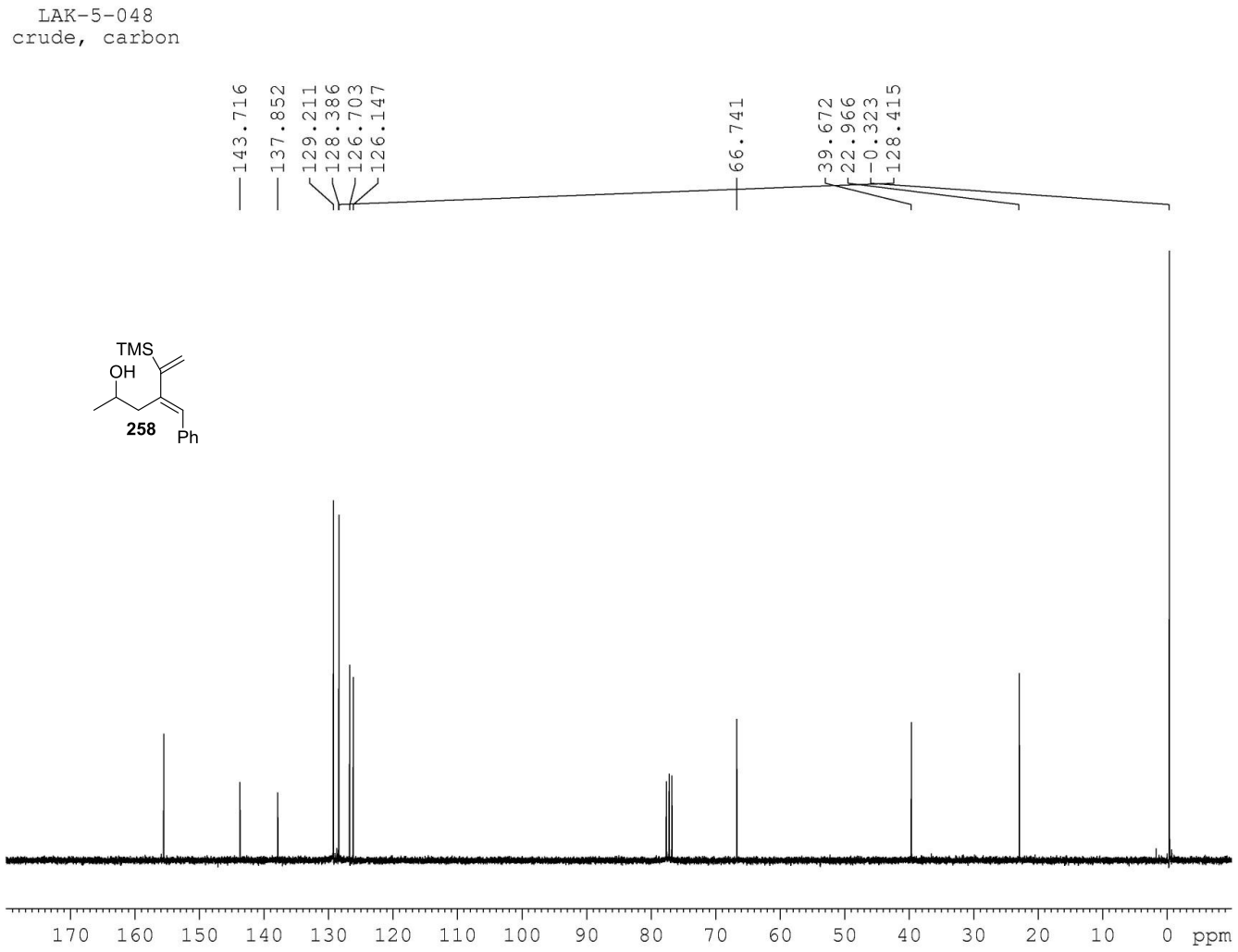
7.444
7.423
7.421
7.379
7.376
7.370
7.352
7.347
7.332
7.327
7.279
7.275
7.270
7.259
7.251
7.227
6.704
6.550
6.513
6.491
6.455
5.388
5.329
5.199
5.197
5.163
5.161
4.164
4.149
4.144
4.135
4.128
4.123
4.115
4.107
4.099
4.094
4.087
4.079
4.074
4.058
2.821
2.792
2.775
2.747
2.625
2.610
2.580
2.564
1.730
1.217

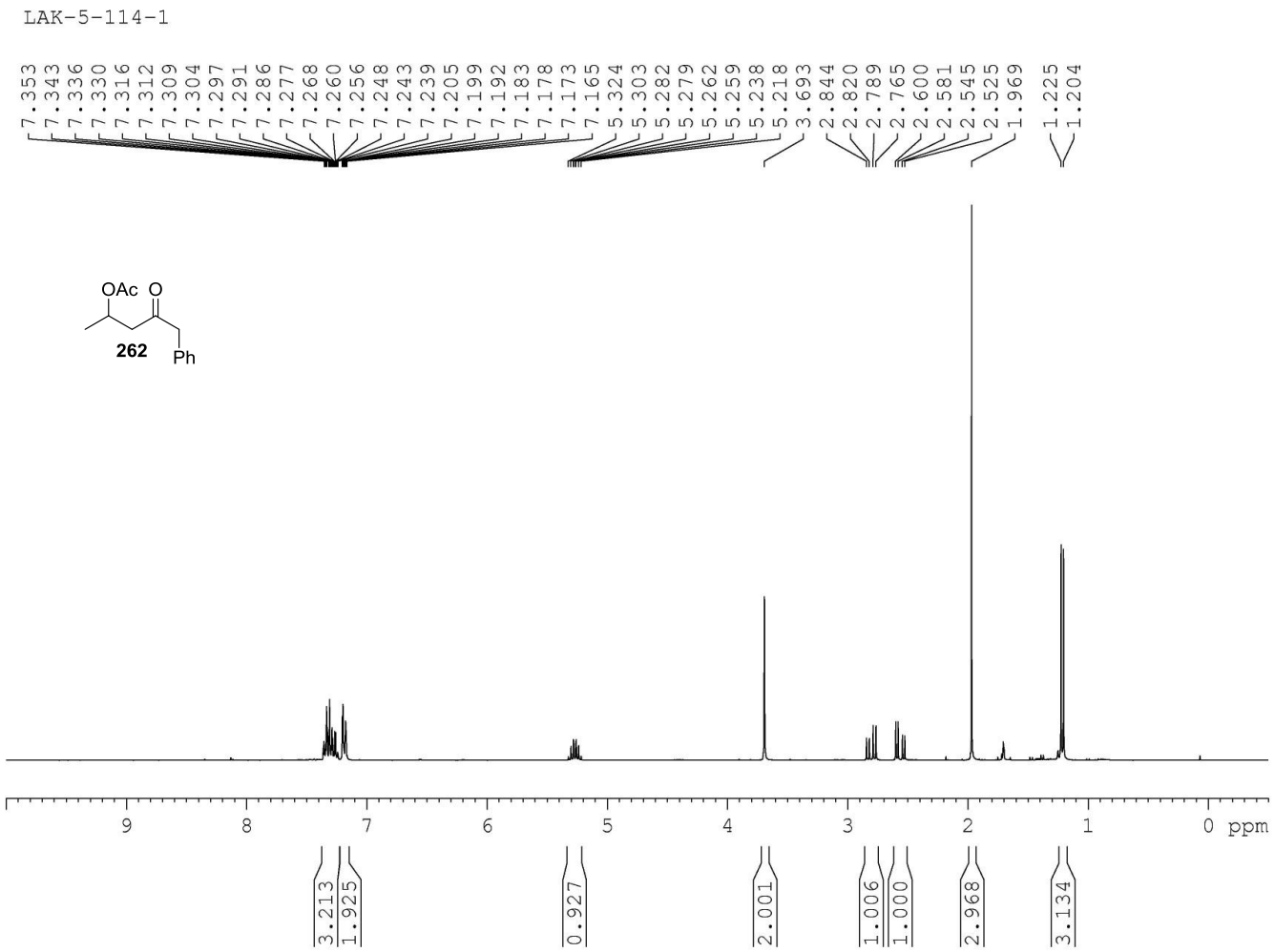


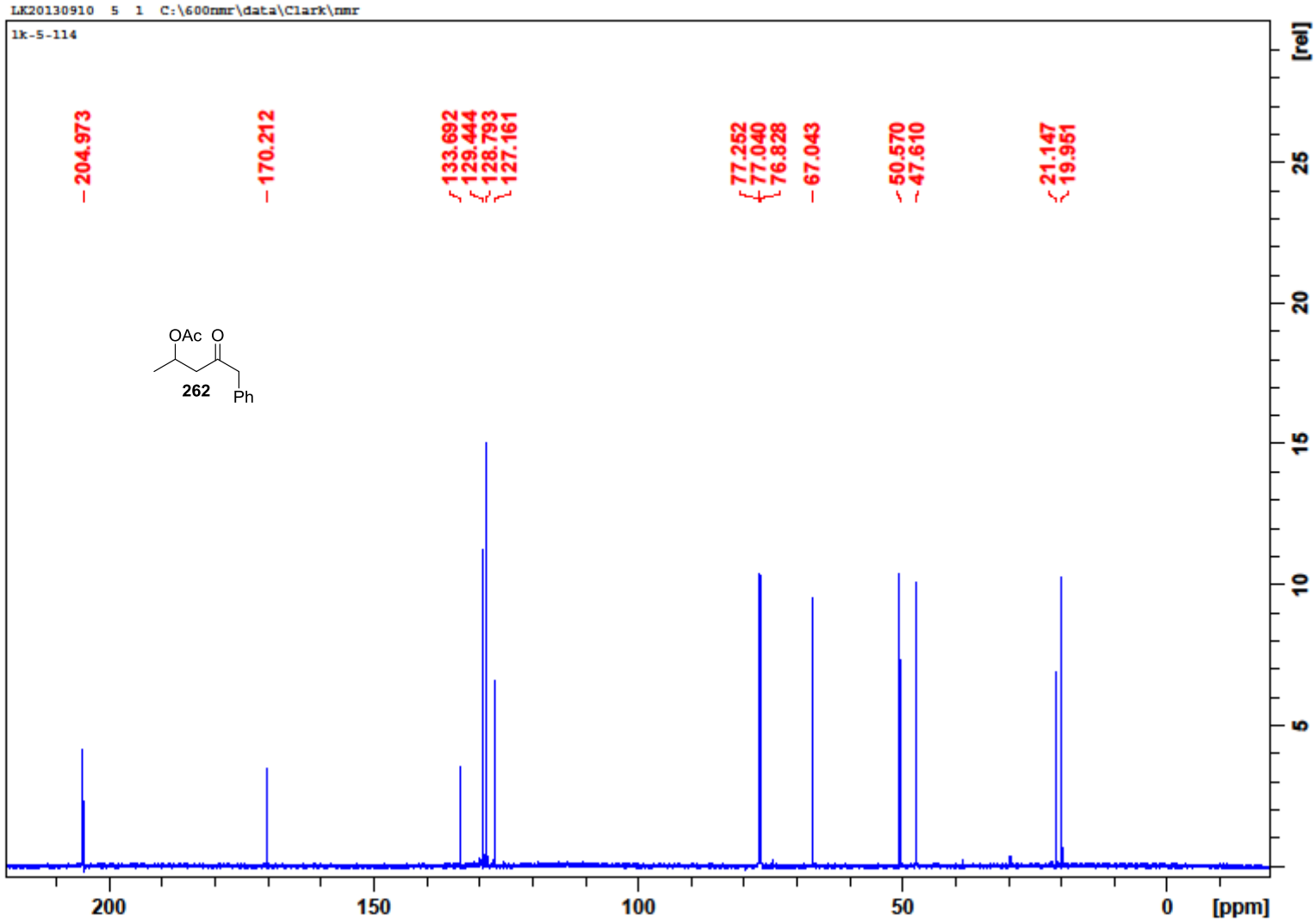
257

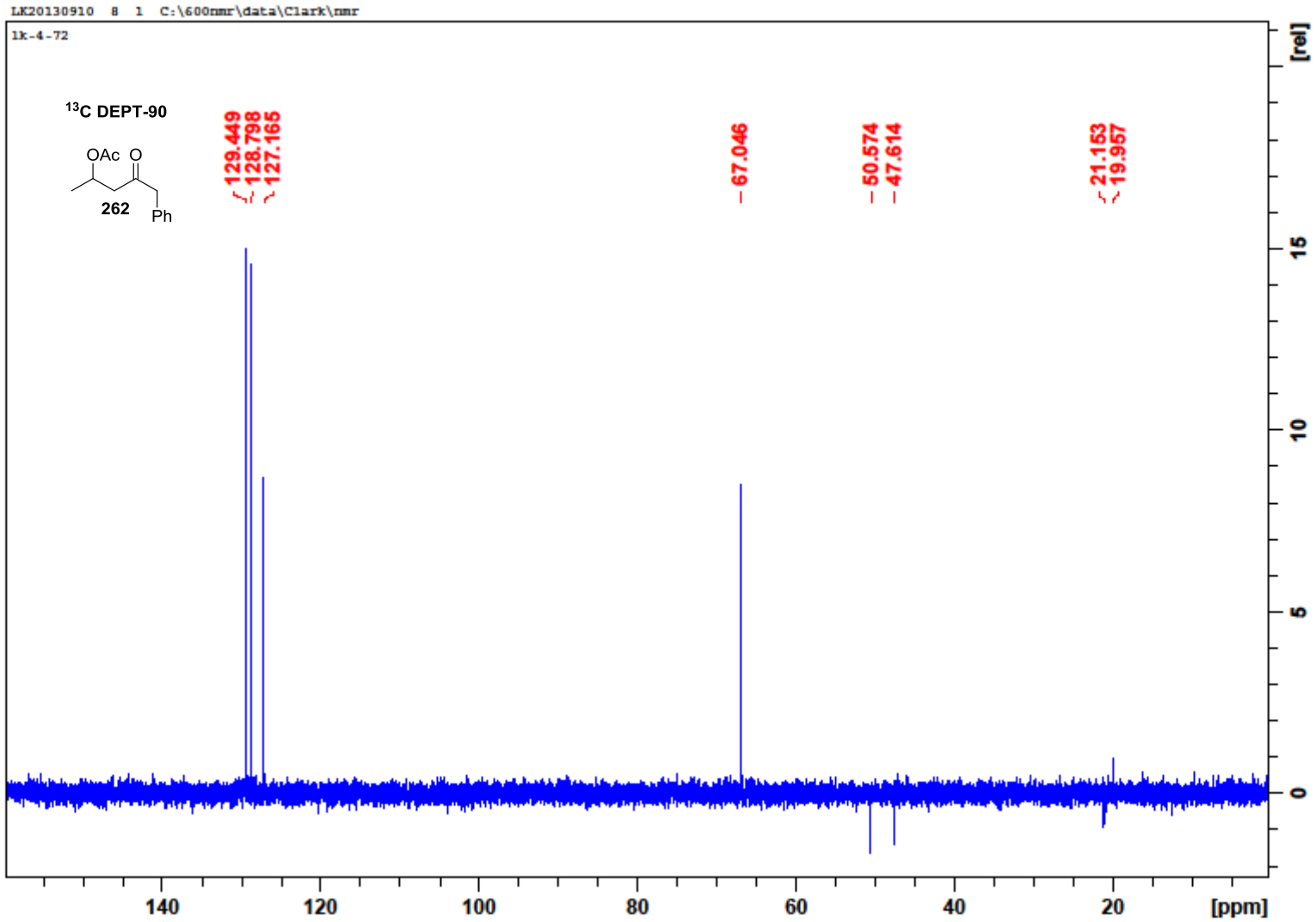


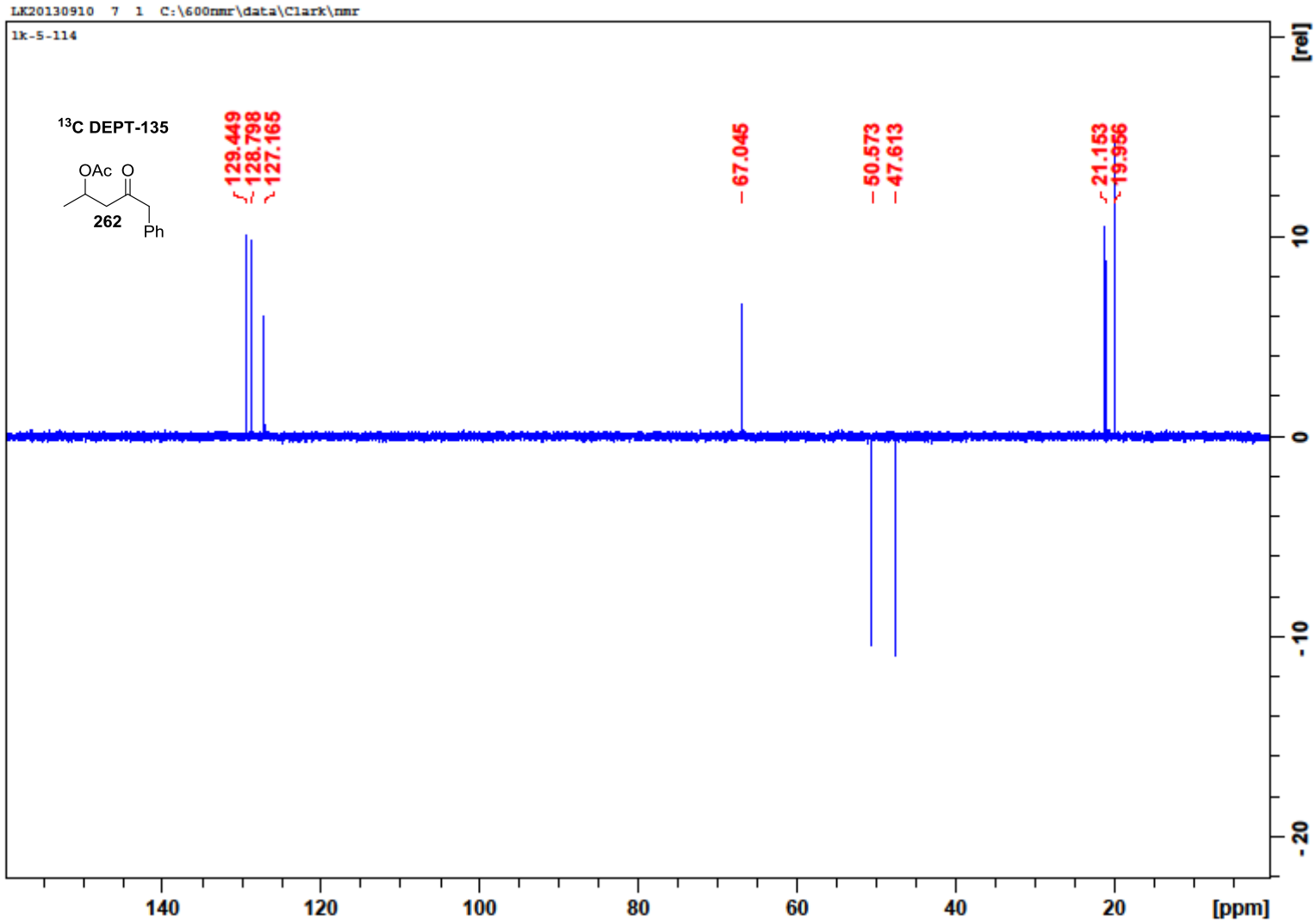

7.388
7.372
7.356
7.343
7.329
7.264
7.258
7.249
7.245
7.235
7.230
7.221
6.504
5.841
5.831
5.528
5.519
3.995
3.975
3.959
3.954
3.946
3.939
3.931
3.925
3.918
3.910
3.890
2.758
2.729
2.712
2.683
2.502
2.499
2.486
2.483
2.455
2.452
2.440
2.437
1.733
1.187
1.167
0.223
TMS
OH
258
Ph
9
8
7
6
5
4
3
2
1
0 ppm
4.029
1.164
0.869
1.023
1.019
0.979
1.000
1.023
1.157
3.295
9.231

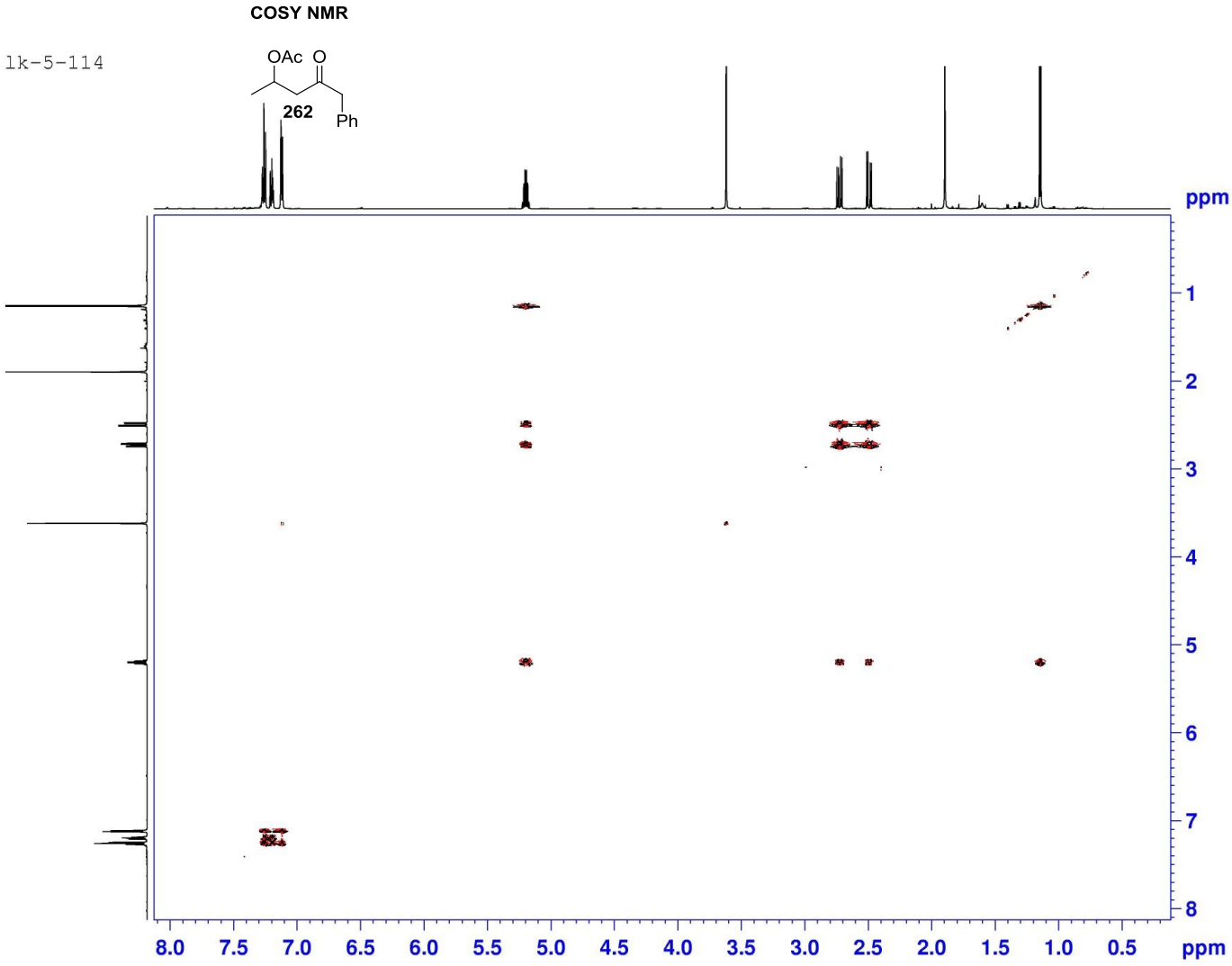

LAK-5-048
crude, carbon
143.716
137.852
129.211
128.386
126.703
126.147
66.741
39.672
22.966
-0.323
128.415
TMS
OH
258
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

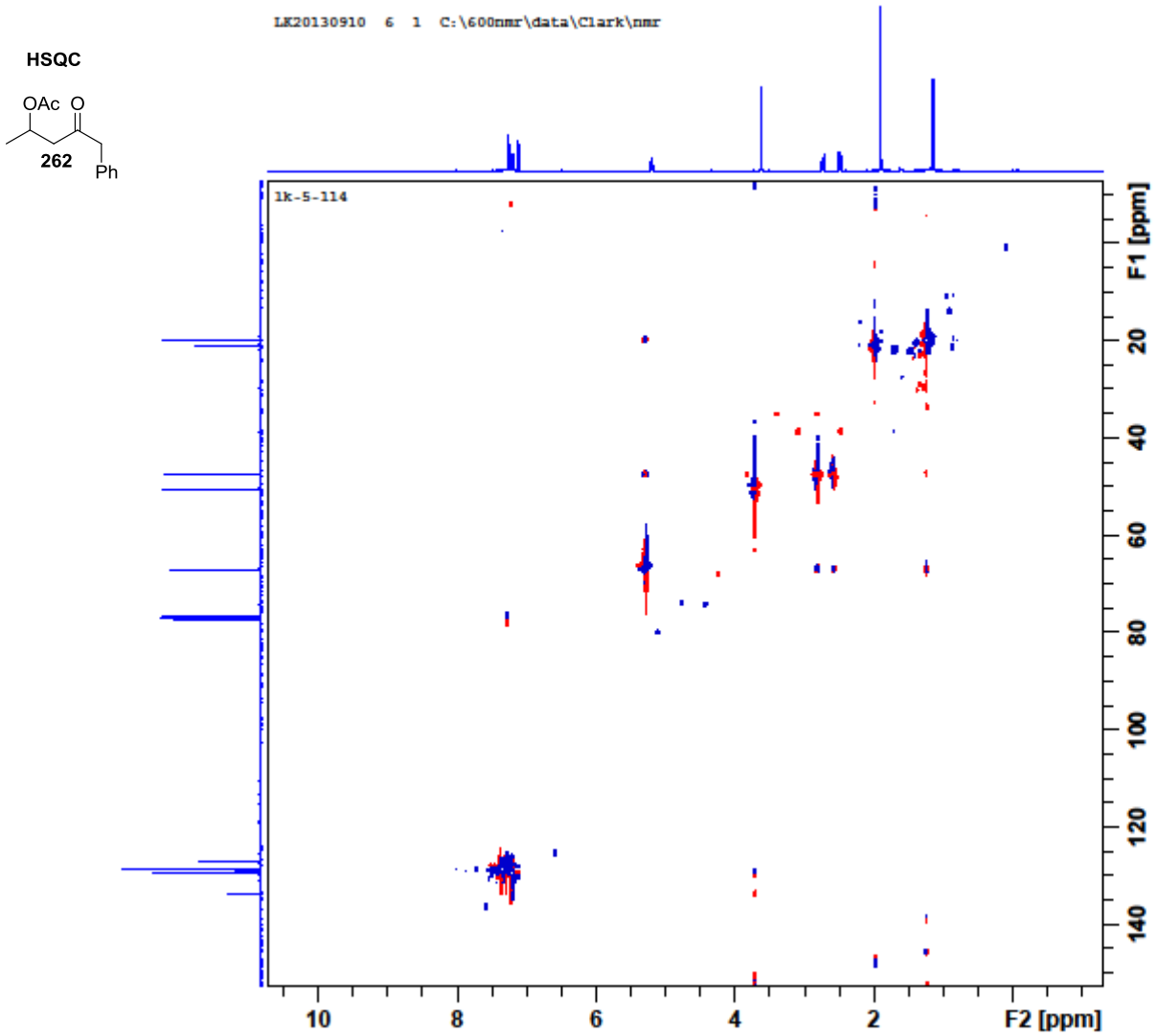

LAK-5-114-1
7.353
7.343
7.336
7.330
7.316
7.312
7.309
7.304
7.297
7.291
7.286
7.277
7.268
7.260
7.256
7.248
7.243
7.239
7.205
7.199
7.192
7.183
7.178
7.173
7.165
5.324
5.303
5.282
5.279
5.262
5.259
5.238
5.218
3.693
2.844
2.820
2.789
2.765
2.600
2.581
2.545
2.525
1.969
1.225
1.204
OAc O
262
Ph
9
8
7
6
5
4
3
2
1
0 ppm
3.213
1.925
0.927
2.001
1.006
1.000
2.968
3.134


LK20130910 5 1 C:\600nmr\data\Clark\nmr
lk-5-114
204.973
170.212
133.692
129.444
128.793
127.161
77.252
77.040
76.828
67.043
50.570
47.610
21.147
19.951
OAc
O
262
Ph
[rel]
25
20
15
10
5
200
150
100
50
0
[ppm]

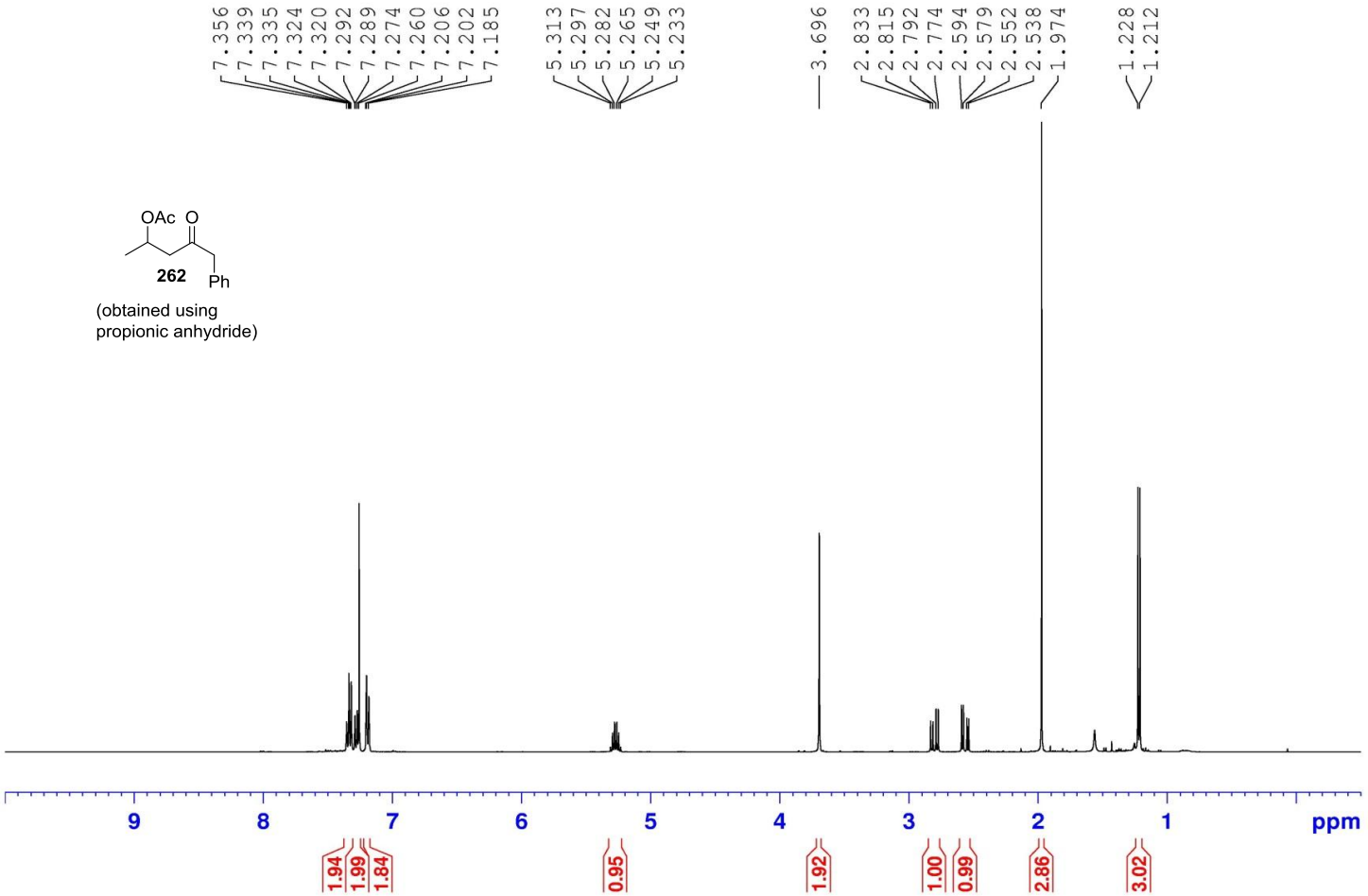

LK20130910 8 1 C:\600nmr\data\Clark\nmr
lk-4-72
^{13}C DEPT-90
OAc O
262
Ph
129.449
128.798
127.165
67.046
50.574
47.614
21.153
19.957
[rel]
15
10
5
0
140
120
100
80
60
40
20
[ppm]


LK20130910 7 1 C:\600nmr\data\Clark\nmr
lk-5-114
^{13}C DEPT-135
OAc O
262
Ph
129.449
128.798
127.165
67.045
50.573
47.613
21.153
19.956
[rel]
10
0
-10
-20
140
120
100
80
60
40
20
[ppm]

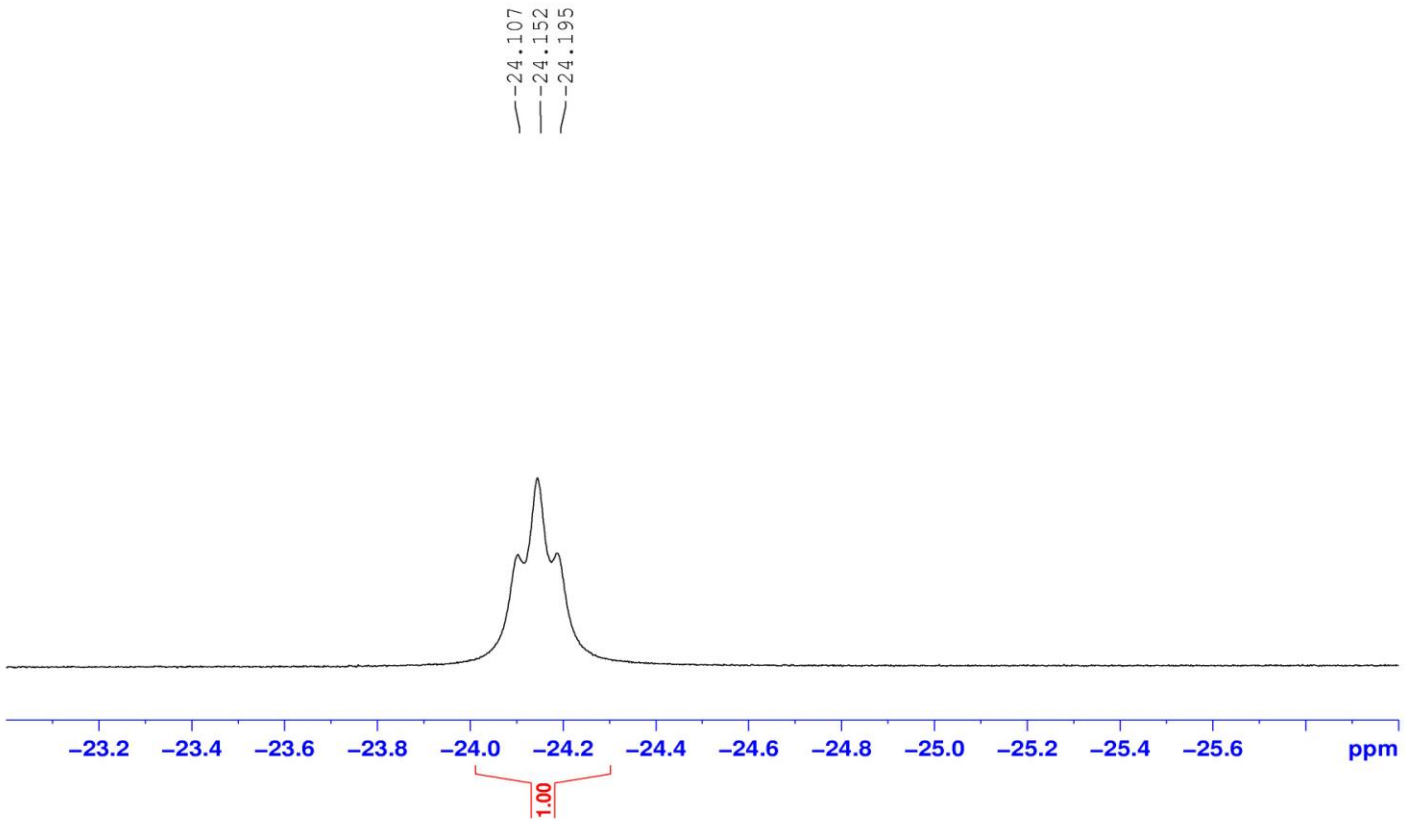

COSY NMR
lk-5-114
OAc O
262
Ph
ppm
1
2
3
4
5
6
7
8
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm


HSQC
OAc O
262
Ph
LK20130910 6 1 C:\600nmr\data\Clark\nmr
lk-5-114
F1 [ppm]
20
40
60
80
100
120
140
10
8
6
4
2
F2 [ppm]

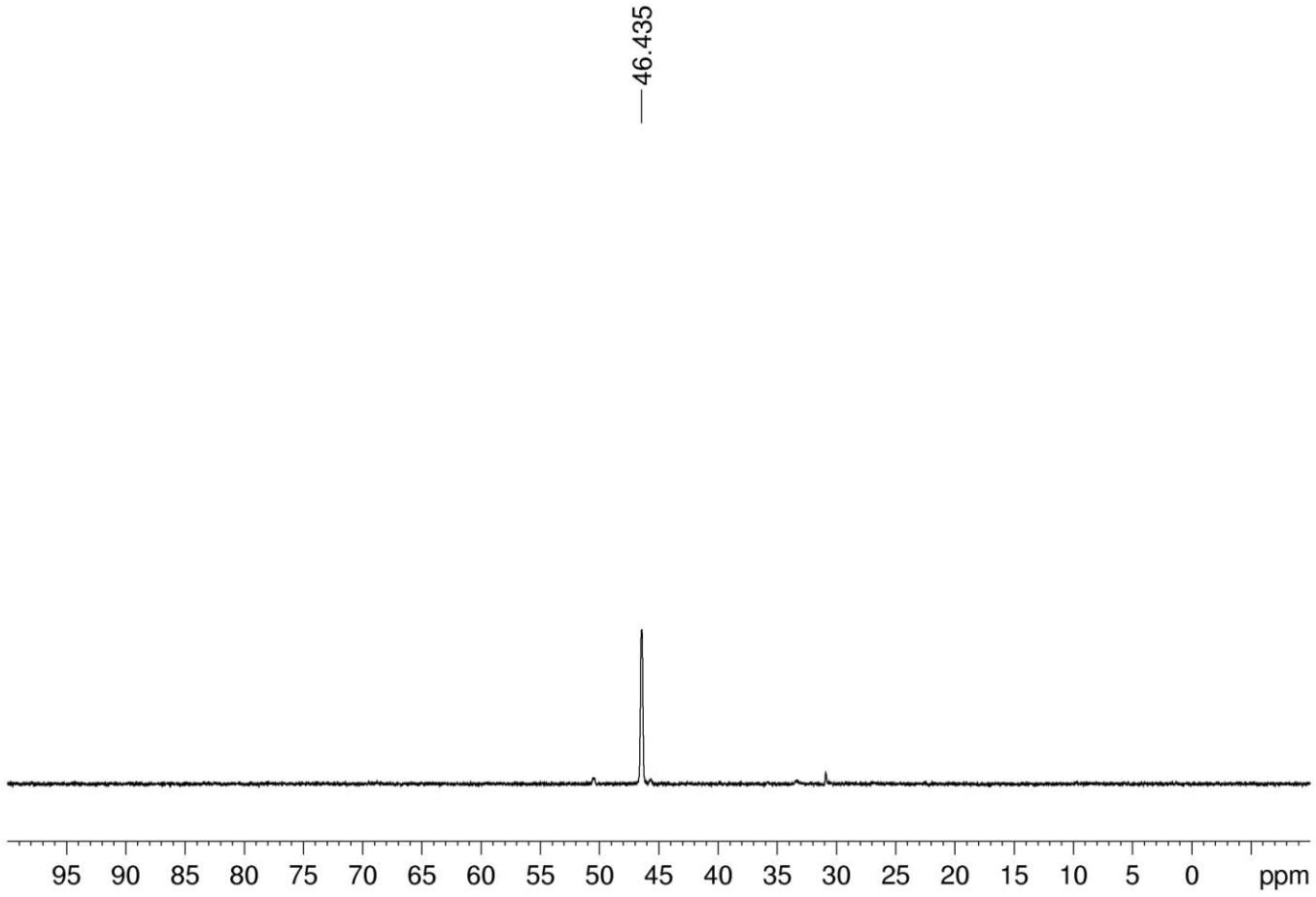
LAK-6-251-2


7.356
7.339
7.335
7.324
7.320
7.292
7.289
7.274
7.260
7.206
7.202
7.185
5.313
5.297
5.282
5.265
5.249
5.233
3.696
2.833
2.815
2.792
2.774
2.594
2.579
2.552
2.538
1.974
1.228
1.212
OAc O
262
Ph
(obtained using
propionic anhydride)
9
8
7
6
5
4
3
2
1
ppm
1.94
1.99
1.84
0.95
1.92
1.00
0.99
2.86
3.02

$RuHCl(CO)(PCy_3)_2$
^{1}H NMR

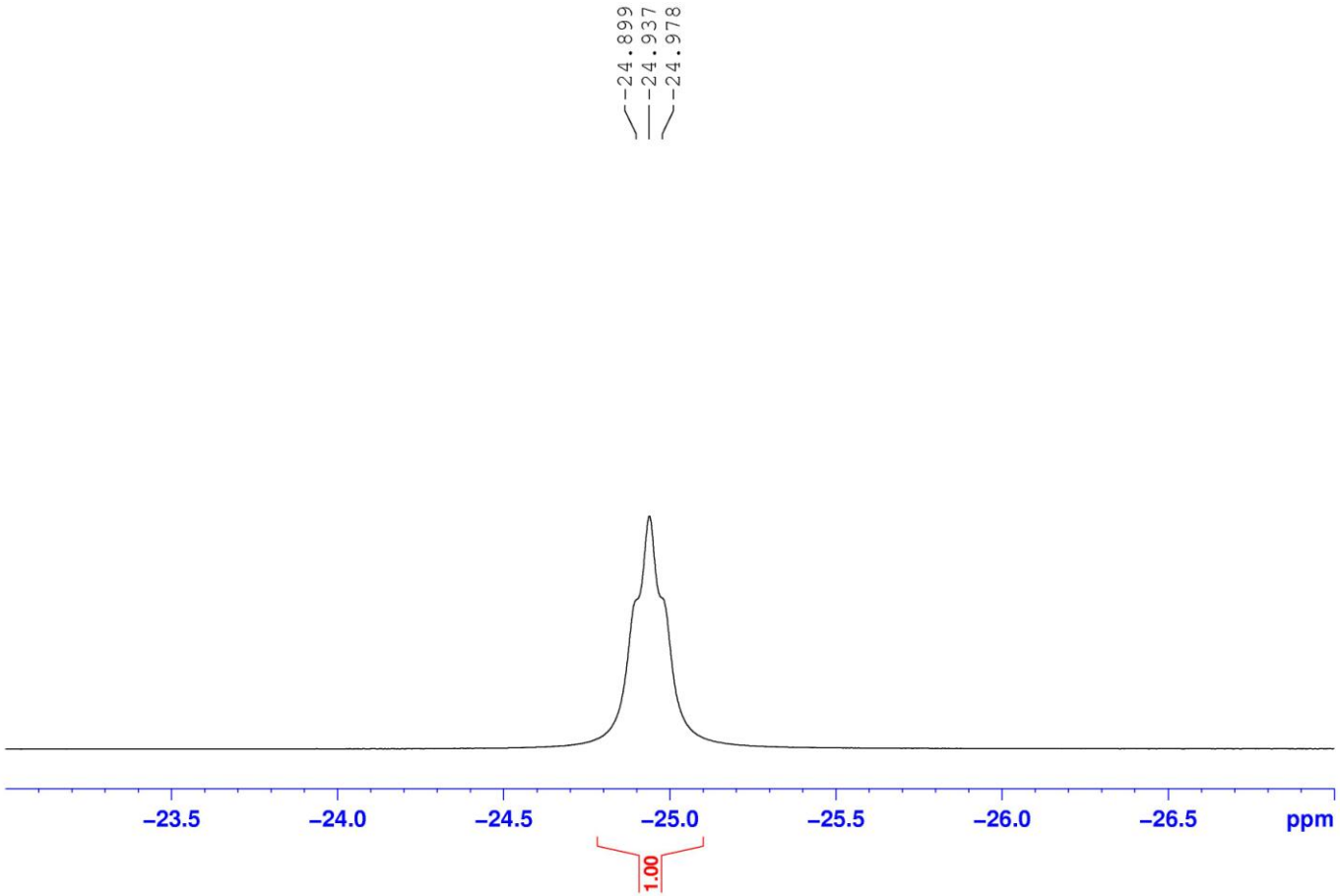


$RuHCl(CO)(PCy_3)_2$
^{31}P NMR

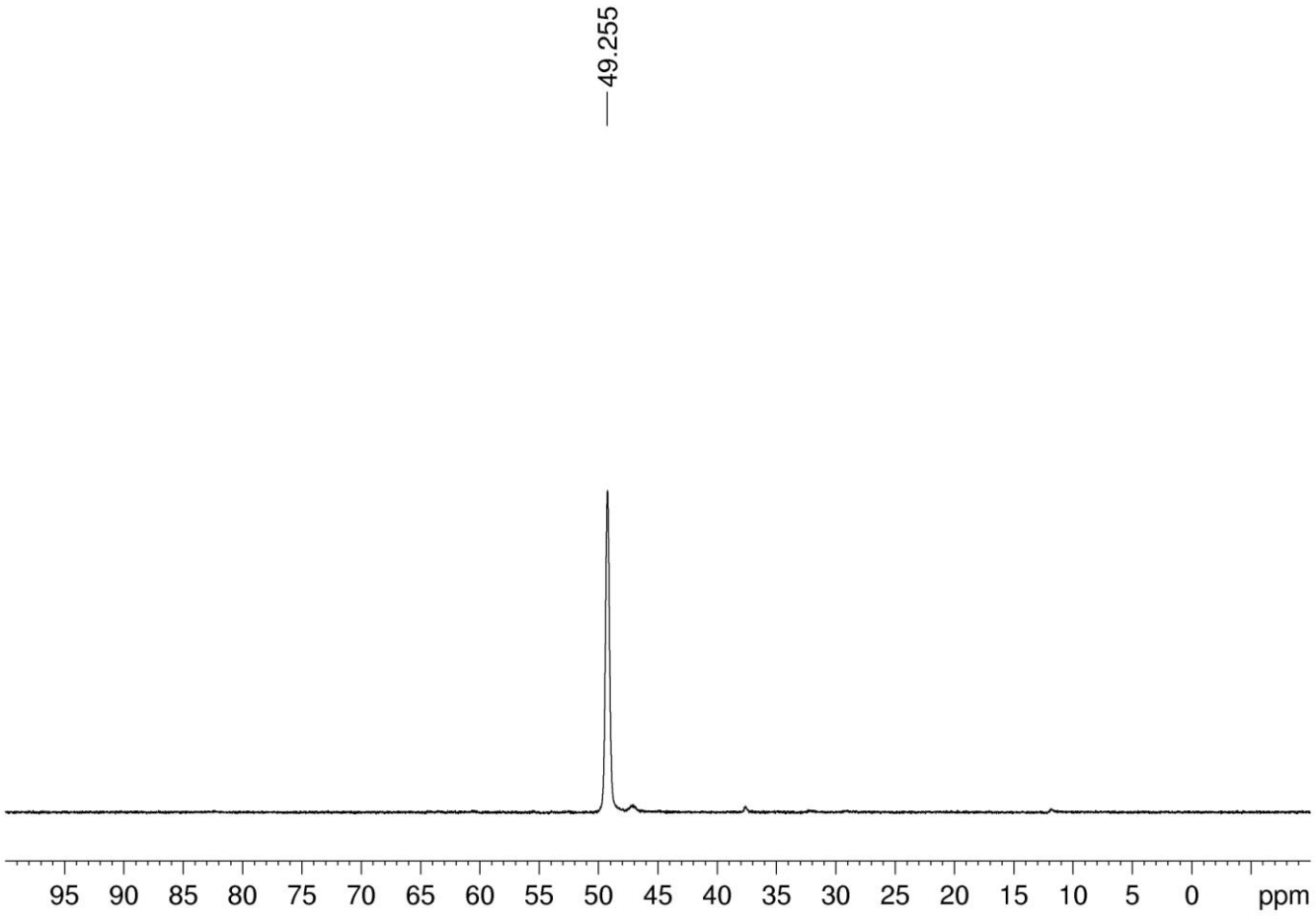


RuHCl(CO)(P*t*Bu$_2$Me)$_2$

^{1}H NMR

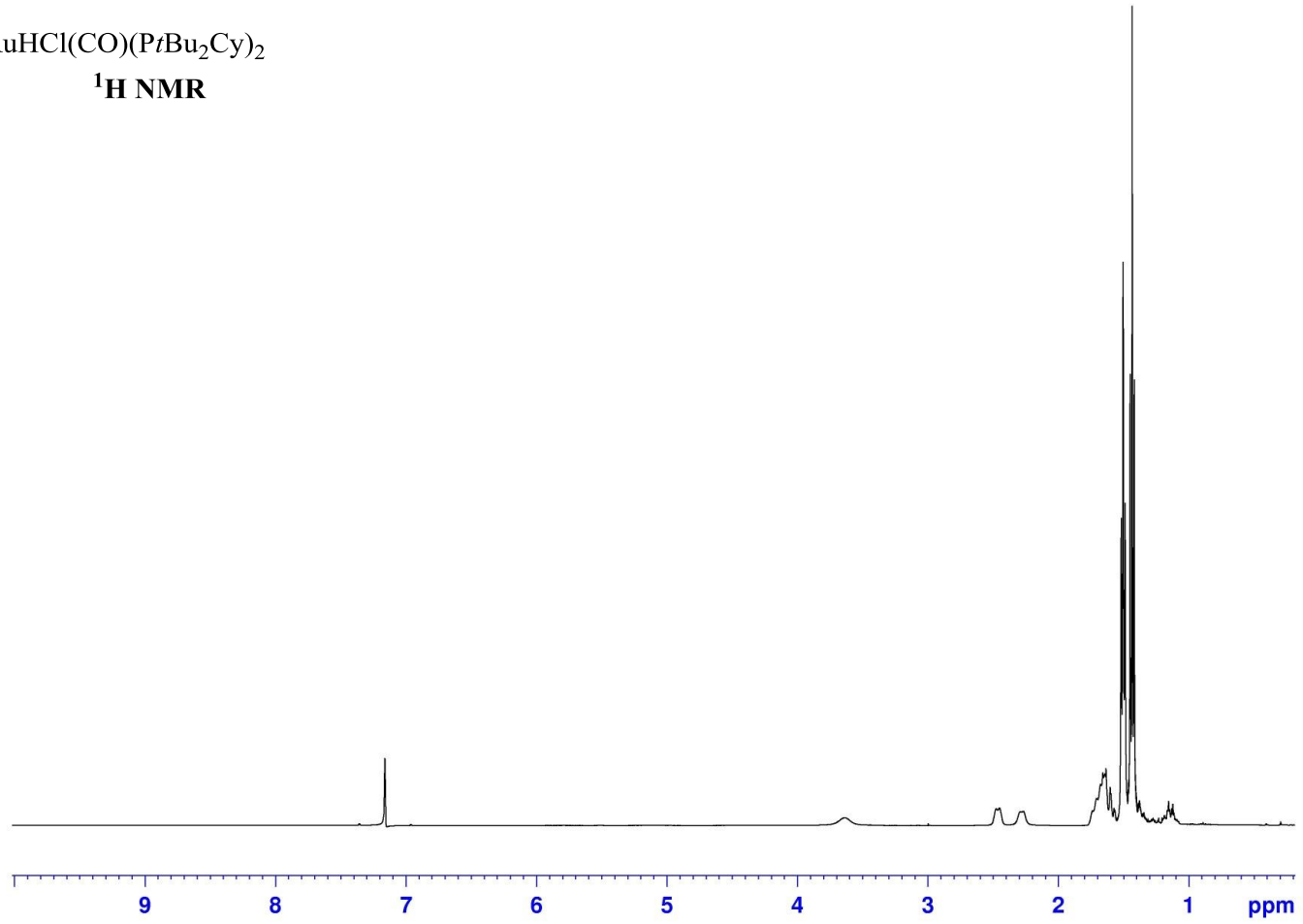


RuHCl(CO)(P*t*Bu$_2$Me)$_2$
^{31}P NMR



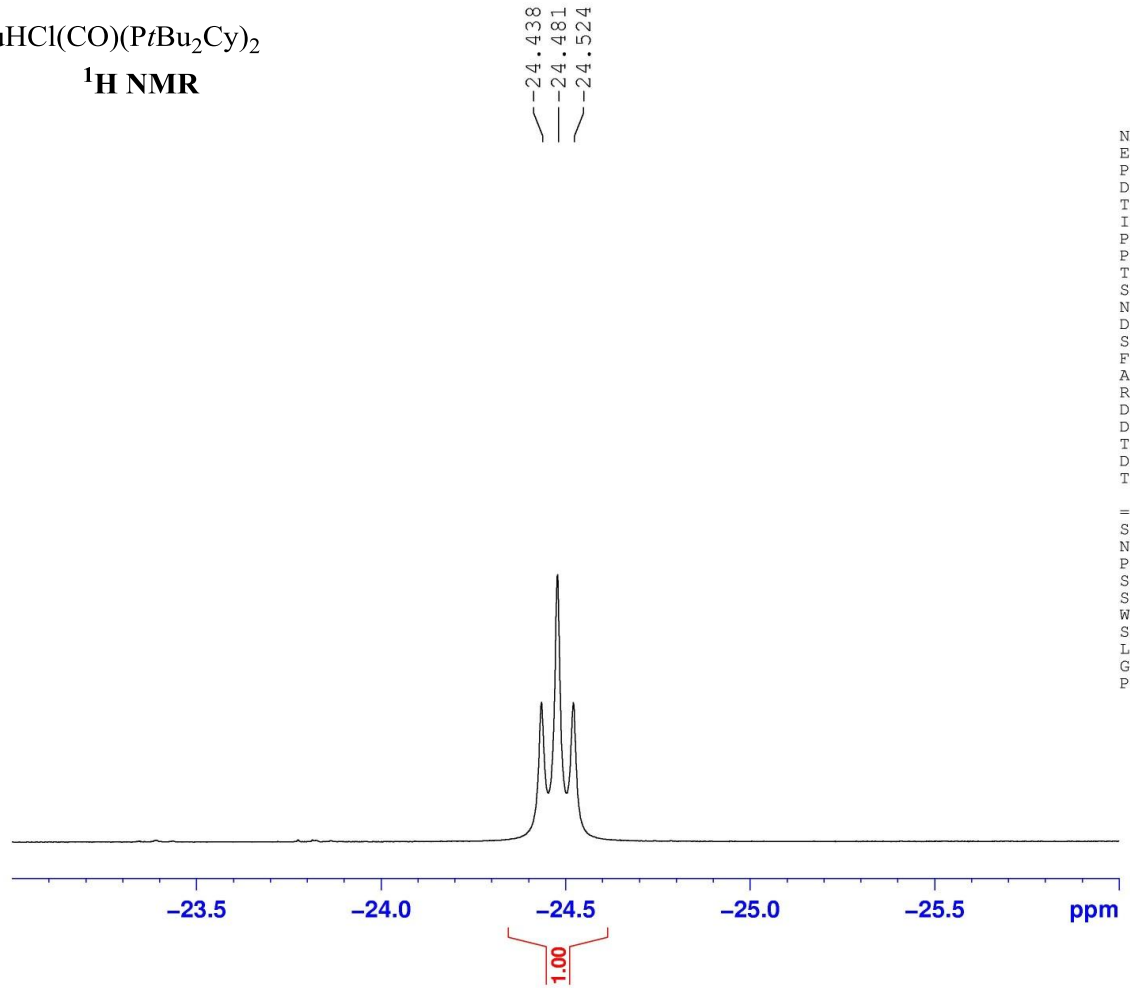
RuHCl(CO)(P*t*Bu$_2$Cy)$_2$

^{1}H NMR



$RuHCl(CO)(PtBu_2Cy)_2$

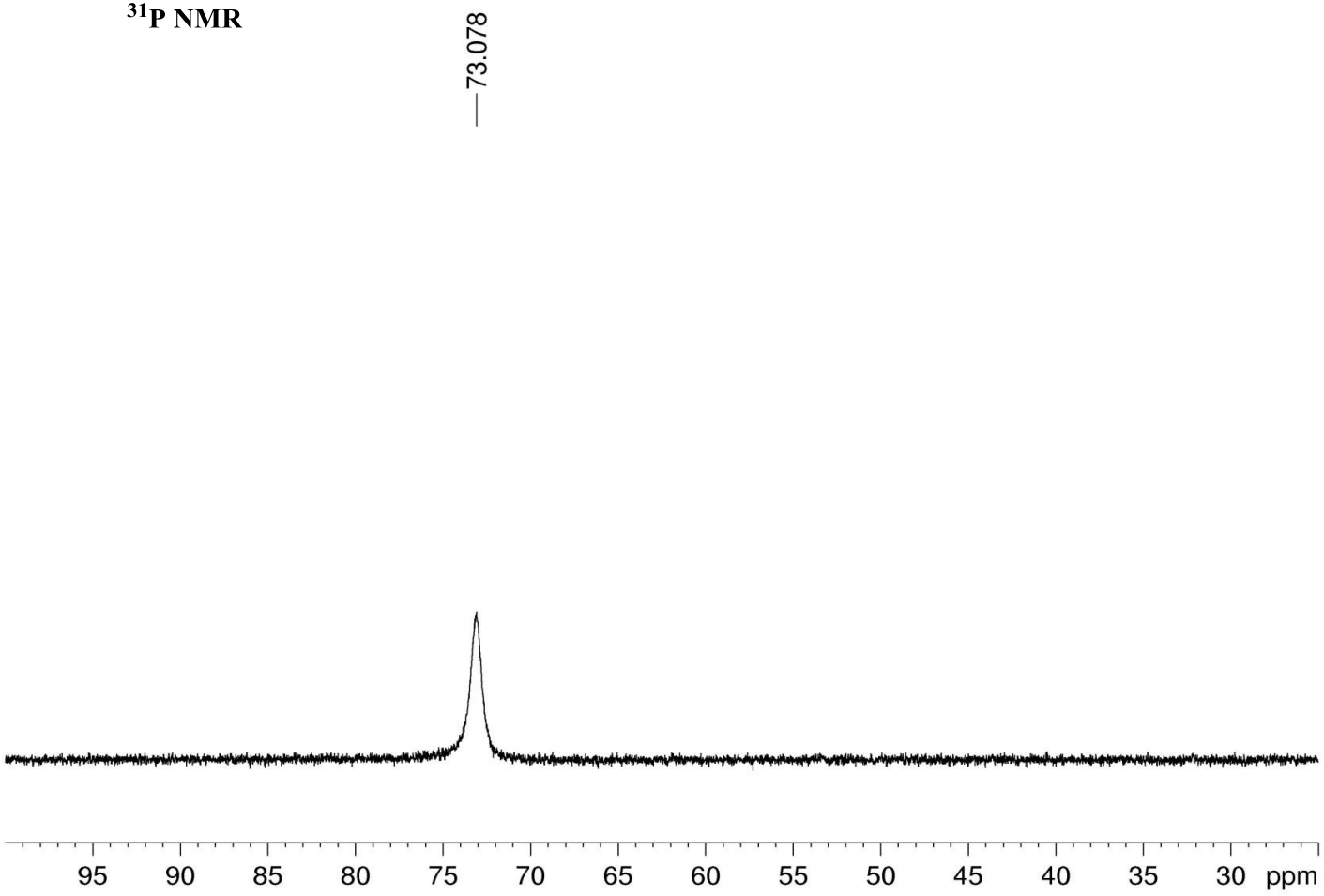
^{1}H NMR




```
NAME            LAK-3-73
EXPNO                  1
PROCNO                 1
Date_           20141027
Time                9.13
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG             zg30
TD                 65536
SOLVENT             C6D6
NS                   128
DS                     2
SWH            39682.539 Hz
FIDRES          0.605507 Hz
AQ              0.8258036 sec
RG                134.49
DW                12.600 usec
DE                10.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1300000 MHz
NUC1                   1H
P1                 12.00 usec
SI                 65536
SF           400.1299966 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

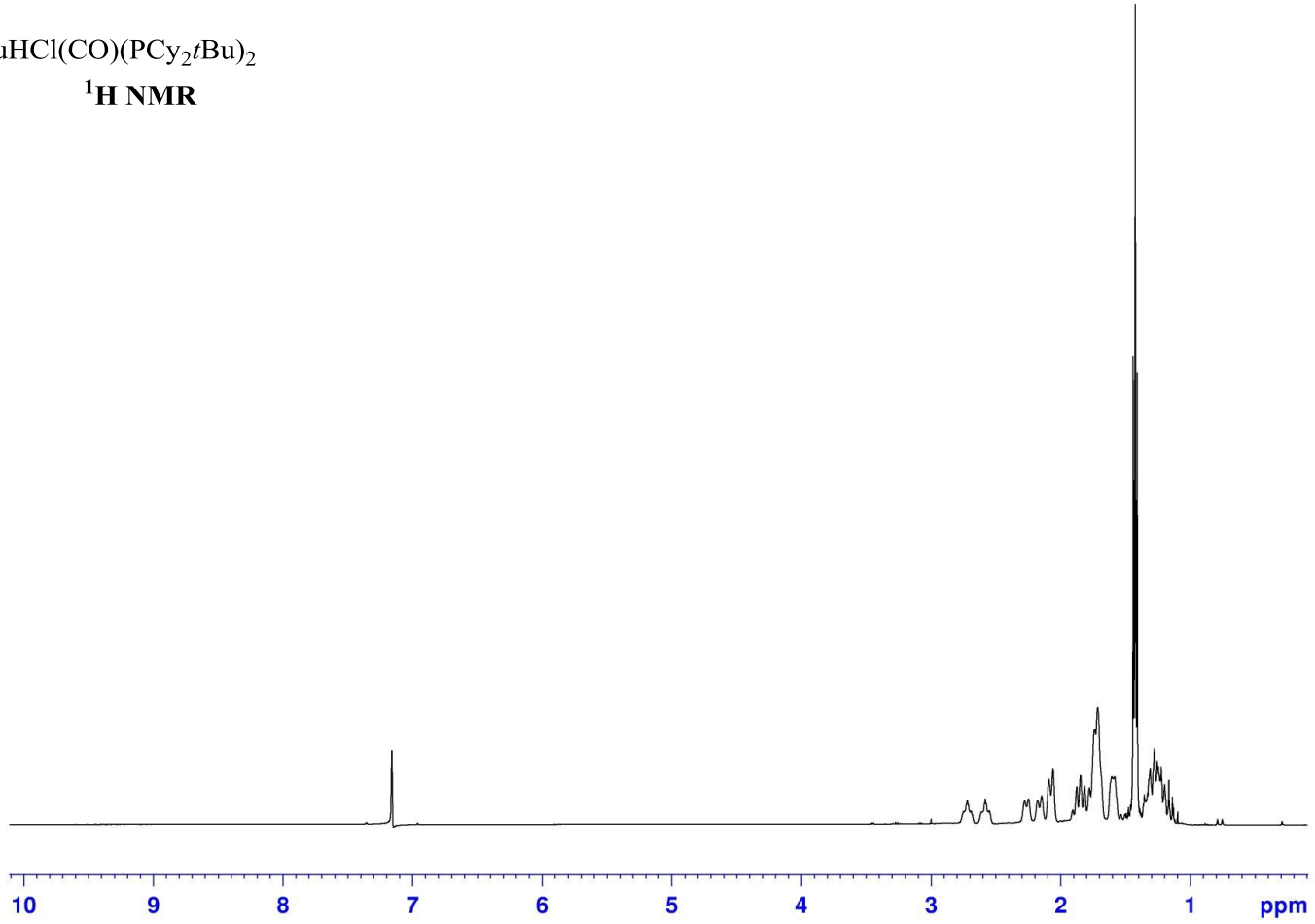
RuHCl(CO)(P*t*Bu$_2$Cy)$_2$

^{31}P NMR



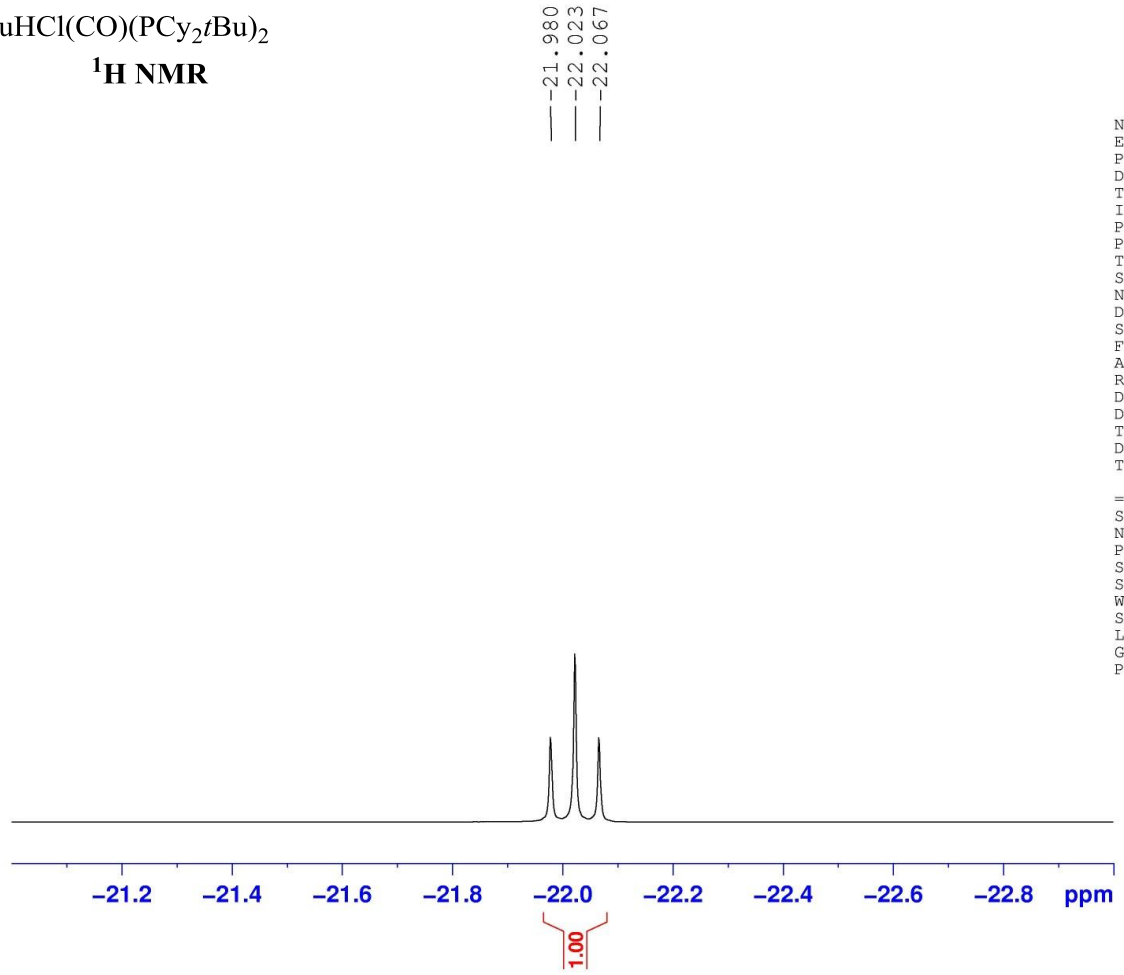
$RuHCl(CO)(PCy_2tBu)_2$

^{1}H NMR



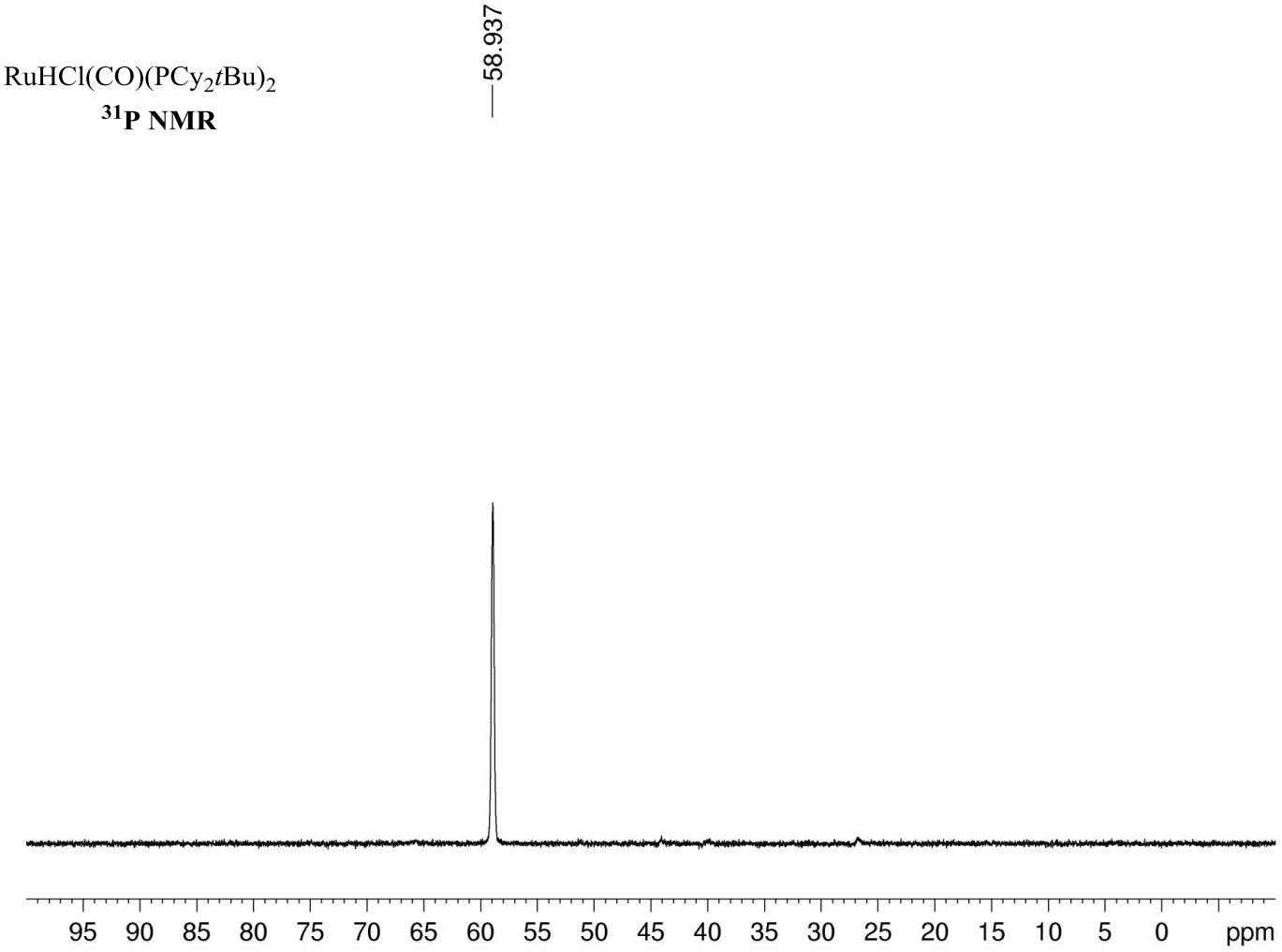
$RuHCl(CO)(PCy_2tBu)_2$

^{1}H NMR



RuHCl(CO)(PCy_2tBu)$_2$

^{31}P NMR



8.0 VITAE

Lauren Kaminsky

307 Parklawn Court
Lancaster, PA 17601
Cell: (717) 368-6644
E-mail: lkaminsky4@gmail.com

Education

Ph.D. in Organic Chemistry, August 25, 2015
Syracuse University, Syracuse, NY
Thesis: Ruthenium-Catalyzed Transformations for the Synthesis of Conjugated Dienes
Advisor: Dr. Daniel A. Clark

B.S. in Chemistry, *cum laude,* June 2010
Minor in Mathematics
York College of Pennsylvania, York, PA
Advisor: Dr. Kathleen Halligan

Research Experience

Research Assistant, Department of Chemistry
Syracuse University, August 2010 − May 2015
Advisor: Dr. Daniel A. Clark
Research Focus:
- Scalable, multi-step syntheses for various chiral and non-chiral silicon-tethered enyne substrates
- Development of a ruthenium-hydride catalyzed intermolecular coupling of silicon-tethered alkynes with vinyl boronates to give highly stereo- and regioselective tetra-substituted 1,3-dienes
- Development of a ruthenium-catalyzed cycloisomerization of silicon-tethered 1,7-enynes to selectively give exocyclic 1,3-dienes
- Synthesis of novel ruthenium and osmium hydrides for the use in organocatalytic methodology development

Independent Study Research, Department of Chemistry
York College of Pennsylvania, 2008 − 2010
Advisor: Dr. Kathleen Halligan
Research Focus:

- Worked in collaboration with the USDA-ARS Plant Mycotoxin Research group in California towards the synthesis of a tricyclic natural product as a means to combat the navel orangeworm

Skills and Techniques

- Multi-step syntheses of organic compounds
  - Experience in small and large scale synthesis
- Handling of a large variety of air-sensitive organic and inorganic reagents
- Schlenk-line techniques
- Preparation of organometallic compounds
- Glovebox use for reagent storage, reagent handling and reactions
- Chromatography
  - Flash column, Thin Layer, Preparative Thin Layer

  Spectroscopy
- 1D and 2D NMR (Proton, Carbon, Boron, Phosphorus), IR
- Excellent record-keeping with laboratory notebooks and chemical inventory
- Detail-oriented
  - Wrote standard operating procedures for new instruments
- Knowledge of chemistry software programs
  - ChemDraw, Bruker Topspin

Teaching Experience

Teaching Assistant, Syracuse University, 2011 – 2013
- Laboratory and recitation instructor for undergraduate organic chemistry courses (classes of 20-30 students)

Student Tutor, York College of Pennsylvania, 2008 – 2010

Student Laboratory Assistant, York College of Pennsylvania, 2007 – 2010

Awards

Graduate Assistance in Areas of National Need Fellowship, 2010 – 2012

Departmental Recognition, Department of Physical Sciences, York College of Pennsylvania, 2010

Outstanding College Chemistry Major, Southeastern Pennsylvania Section of the American Chemical Society, 2010

Publications

Wilson, R. J.; **Kaminsky, L.**; Ahmed, I.; Clark, D. A. "Ruthenium Hydride Catalyzed Silylvinylation of Internal Alkynes Using Ethylene Gas." *J. Org. Chem.* **2015,** *80*, 8290-8299.

Kaminsky, L.; Wilson, R. J.; Clark, D. A. "Stereo- and Regioselective Formation of Silyl-Dienyl Boronates." *Org. Lett.* **2015,** *17*, 3126-3129.

Kaminsky, L.; Clark, D. A. "Ruthenium Catalyzed Cycloisomerization of Silicon-Tethered 1,7-Enynes To Give Exocyclic 1,3-Dienes." *Org. Lett.* **2014,** *16*, 5450-5453. *Highlighted in Chem Inform:* *ChemInform* **2015,** *46*.

Rosenberg, A. J.; Ahmed, I.; Wilson, R. J.; Williams, T. M.; **Kaminsky, L.**; Clark, D. A. "An Improved Synthesis of Imidazo[4,5-*b*]pyridines and Imidazo[4,5-*b*]pyrazines by Palladium Catalyzed Amidation using Xantphos in a 1,4-Dioxane:*tert*-Amyl Alcohol Solvent System." *Adv. Synth. Catal.* **2014,** *356*, 3465-3470.

Liu, S.; Zhao, J.; **Kaminsky, L.**; Wilson, R. J.; Marino, N.; Clark, D. A. "Ethylene Transposition: Ruthenium Hydride Catalyzed Intramolecular *trans*-Silylvinylation of Internal Alkynes." *Org. Lett.* **2014,** *16*, 4456-4459. *Highlighted in Synfacts:* Lautens, M.; Kress, S. *Synfacts* **2014,** *10*, 1176.

Wilson, R. J.; Rosenberg, A. J.; **Kaminsky, L.**; Clark, D. A. "Copper- and Palladium-Catalyzed Amidation Reactions for the Synthesis of Substituted Imidazo[4,5-*c*]pyridines." *J. Org. Chem.* **2014,** *79*, 2203-2212. *Highlighted in SynFacts:* Snieckus, V.; Rantanen, T. *SynFacts* **2014,** *10*, 568.

Presentations

32nd Annual Graduate Student Symposium, The State University of New York, Buffalo, NY, May 2014

38th Northeast Regional Meeting of the American Chemical Society, Rochester, NY, October 2012

239th American Chemical Society National Meeting, Chemical Education Division, San Francisco, CA, March 2010 (Poster Presentation)

References

Daniel A. Clark
Assistant Professor
Syracuse University
Phone: (315) 443-2127
E-mail: daclar01@syr.edu

Nancy I. Totah
Associate Professor
Syracuse University
Phone: (315) 443-2657
E-mail: ntotah@syr.edu

Kathleen M. Halligan
Assistant Professor & Pre-Med Chair
York College of Pennsylvania
Phone: (717) 815-6872
E-mail: khalliga@ycp.edu