CATALYTIC C–C SILYLATION REACTIONS

by

THIRUPATAIAH AVULLALA

Presented to the Faculty of the Graduate School of

The University of Texas at Arlington in Partial Fulfillment

of the Requirements

for the Degree of

DOCTOR OF PHILOSOPHY

THE UNIVERSITY OF TEXAS AT ARLINGTON

August 2019

Acknowledgements

I would like to convey my sincere thanks and gratitude to my research supervisor, Professor Junha Jeon, for his guidance and support over the past 5 years in achieving my dream. He warmly welcomed me to his research group even though I am away from the college for a quite a long time after my Masters. I still remember the way he taught me the basics during my initial period in his lab. I learned many reactions and purification techniques and improved my spectroscopic knowledge under his guidance. I am really grateful for his support during my struggle in the program. I am very much inspired with his planning and execution (research and writing). I am very fortunate to have him as my mentor. I pay my sincere thanks to my committee members, Professors Carl J. Lovely, Subhrangsu S. Mandal and Frank W. Foss, for their continuous feedback and suggestions on my research progress. I would like to thank Drs. Lovely, Bugarin and Foss for allowing me to borrow some chemicals from their labs which avoided delay in my research. I would like to say special thanks to our post-doctoral fellow Dr. Yuanda Hua whose knowledge and commitment is top-notch. I appreciate his helping nature and willingness to teach new graduate students. I would like to extend my gratitude to my fellow graduate students, Parham, Udaya, Appu and Hiep.

I am thankful to Jill, Debbie, Jim, Jason, Beth and Natalie for their support at various levels in my program at UTA. My sincere thanks to Drs. Brian Edwards, Roy Mc Dougald, and Chuck Savage for their trainings and help in various instruments. My heartful thanks to my friends Narsimha, Raju, Yernaidu, Biswajit, Raja, Prudhvi, Prathap, Ravi Singh, Rahul Patil, and Pawan Thapa. I am greatful to my parents, brother and sister for their unconditional love and affection.

……July 17, 2019

Abstract

Catalytic C–C Silylation Reactions

Thirupataiah Avullala, Ph.D

The University of Texas at Arlington, 2019

Supervising Professor: Junha Jeon

In my doctoral studies, the research is mainly focused on developing highly regio- and chemoselective C–C silylation of cyclopropanol derivatives with a hydrosilyl acetal directing group. This approach involves use of a relay of Ir-catalyzed hydrosilylation of inexpensive and readily prepared cyclopropanoacetates and Rh-catalyzed C–C silylation to achieve dioxasilolanes and dioxasilepines.

In Chapter 1, we have investigated a redox-neutral, catalytic C–C activation of cyclopropyl acetates to produce silicon-containing five-membered heterocycles in a highly regio- and chemoselective fashion. The umpolung α-selective silylation leading to dioxasilolanes is opposed to contemporary β-selective C–C functionalization protocols of cyclopropanols. Lewis base activation of dioxasilolanes as α-silyl carbinol equivalents undergoes the unconventional [1,2]-Brook rearrangement to form tertiary alcohols. Notably, mechanistic studies indicate that an electrophilic metal-π interaction harnessing highly fluorinated $Tp^{(CF3)2}$Rh(nbd) catalyst permitted a low temperature C–C activation.

In Chapter 2, we have developed highly efficient generation of metallo homoenolate-enol ethers (MHEE) through catalytic net oxidative C–C activation of cyclopropyl acetates in regio, stereo-, and chemoselective fashion. MHEE, the ketone α,β-dianion equivalents can be

converted to a new class of seven-membered silicon-containing heterocycles, dioxasilepines, which uniquely hold interconnected β-silyl group and Z-vinyl acetal. Scope of the hitherto unexplored reactivity of cyclopropyl acetates toward net oxidative β-C–C silylation and the versatility of the resulting dioxasilepines were demonstrated. These include late-stage, dehydrogenative C–C silylation of biologically relevant molecules, facile production of a range of α,β-difunctionalized ketones and 1,2-diols, and their application to bioconjugation chemistry. Preliminary mechanistic studies suggest that the C–C activation harnessing electron-rich Wilkinson-type catalyst is likely the turnover-determining step and a Rh-π interaction is key to the efficient metal insertion to a C–C bond.

Table of Contents

List of Illustrations

List of Tables

Note

Portions of this thesis have been taken, with permission, from the following publications:

Avullala, T.; Asgari, P.; Hua, Y.; Bokka, A. Ridlen, S. G.; Yum, K.; Dias, H. V.R.; Jeon, J. Umpolung α-Silylation of Cyclopropyl Acetates via Low-Temperature Catalytic C–C Activation. *ACS Catal*. **2019**, *138*, 402-408.

Avullala, T.; Hua, Y.; Asgari, P.; Bokka, A.; Jeon, J., Net Oxidative Inverse Polarity C–C Silylation of Cyclopropanols Involving Generation of Metallo Homoenolate-Enol Ether *(***Manuscript Under Preparation***)*.

Additional work performed while pursuing my Ph.D. that does not appear in this thesis has been published in:

Hua, Y.[§]; Asgari, P.[§]; **Avullala, T.**; Jeon, J., Catalytic Reductive ortho-C–H Silylation of Phenols with Traceless, Versatile Acetal Directing Groups and Synthetic Applications of Dioxasilines. *J. Am. Chem. Soc.* **2016,** *138*, 7982–7991.

Dakarapu, U. S.[§]; **Avullala, T.**[§]; Jeon, J. Hydrosilyl Acetal-Directed Exo-Syn Hydrosilylation of Propargyl Alcohols with $Tp^{(CF3)2}$Rh(nbd) Catalyst (**Manuscript under preparation**).

Chapter 1

Umpolung α-Silylation of Cyclopropyl Acetates via Low Temperature Catalytic C–C Activation.

Thirupataiah Avullala, Parham Asgari, Yuanda hua, Apparao Bokka, Shawn G. Ridlen, Kyungsuk Yum, H. V. Rasika Dias and Junha Jeon*

This work has been published in *ACS Catal.* 2019, 9, 402-408[a]

[a] Used with the permission of the publisher, 2019

1.1 Introduction

1.2 Importance of silicon chemistry in biology

Organosilicon compounds are attracting increasing attention from scientific researchers in both academic research and industrial applications due to their significant chemical, physical and bioactive properties[1a,1b,1c]. Particularly, there has been focused study on preparing molecules wherein one of the carbons in known bioactive and physical compounds was replaced by silicon, since possession of a silicon moiety makes such molecules acquire enhanced lipophilicity,[2,3] metabolic stability, bioavailability and binding selectivity. Typically, silicon-nitrogen containing molecules, especially silicon-nitrogen heterocycles (Figure 1.1),[4,5] have proven to be potential pharmaceuticals and drug lead compounds. Despite impressive progress in preparing silicon-nitrogen containing molecules, approaches to access silicon-nitrogen heterocycles are much less abundant and are still challenging because most of them suffer from harsh conditions with strong bases, a narrow substrate scope, multiple steps and the use of expensive silicon reagents.[9-11]

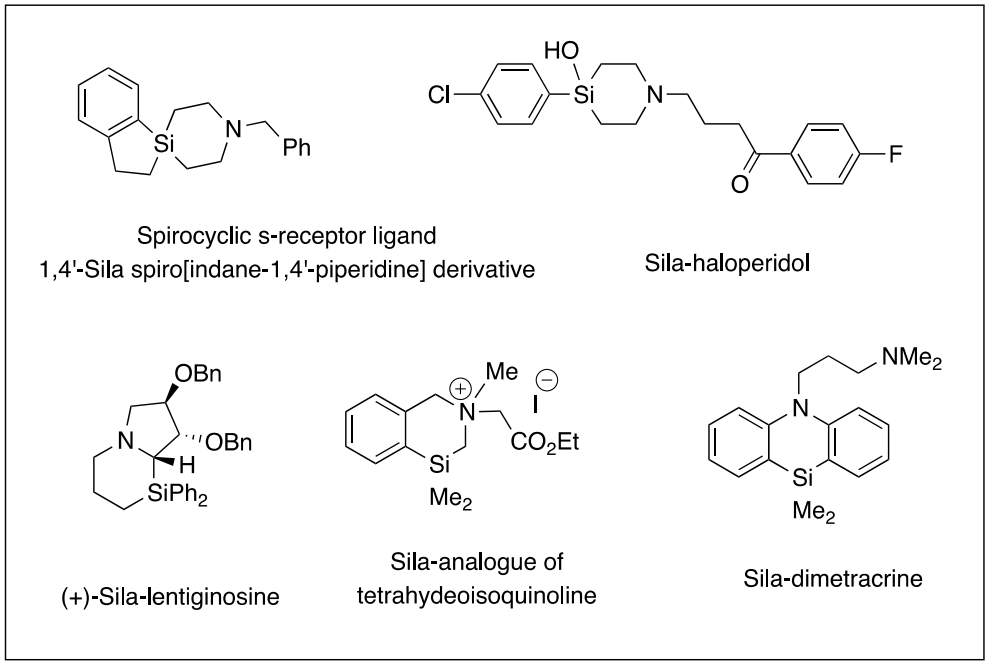


Figure 1.1 Bioactive silicon containing heterocycles

To access these useful silicon containing heterocycles, catalytic C–C bond functionalization is one of the strategies. Catalytic reactions in which oxidative addition of carbon-carbon single bonds is the elementary step are still difficult to achieve because carbon-carbon single bonds are arguably one of the least reactive functional groups especially with respect to transition metals. There are various catalytic C–C bond functionalization methods reported over the years.

1.3 Introduction to catalytic C–C bond functionalization

Carbon-carbon (C–C) functionalization approaches offer new synthetic strategies involving traditionally unimaginable bond disconnection to build important molecular architectures rapidly for chemistry, biology, and medicine.[1-14] Current strategies of C–C σ-bond metal insertion and succeeding functionalization have centered on new C–C formation. For example, carbonylation,[9,14-15] an insertion of alkene,[16] alkynes,[15,17] and C=N,[18] and others[7,19] to C–C single bond has been well demonstrated.

Bower and co-workers have reported their work recently on Rh-catalyzed carbonylative[14] C−C bond activation of aminocyclopropanes to access azepines (Figure 1.2). Bower's protecting group directed C−C bond activation of aminocyclopropanes provides rhodacyclopentanones under a CO atmosphere. These intermediates are effective for intramolecular C− H metalation of either an N-aryl or N-vinyl unit en route to azepine ring systems. These azepine ring systems are present in a wide range of bioactive compounds.

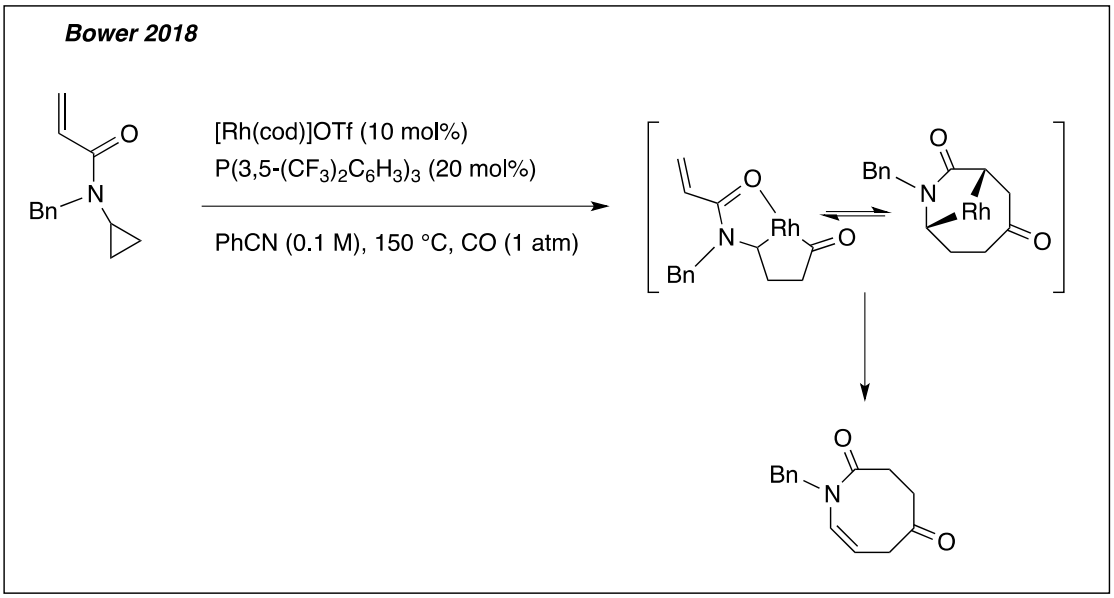


Figure 1.2 Directed Carbonylative C–C Bond Activation of Aminocyclopropanes to access Azepines

The controlled insertion of an unsaturated[16] organic functionality such as a carbon-carbon double bond into a carbon-carbon single bond would be a synthetic protocol of considerable novelty as well as utility (Figure 1.3). Murakami and co-workers[8] shown their extensive study on catalytic C–C bond functionalization of cyclobutanone insertion reactions. Rhodium catalyzed intramolecular insertion of the alkene group into a carbon-carbon single bond of the cyclobutanone was explained. The reaction success was helped by coordination of the vinyl group to rhodium facilitates its insertion.

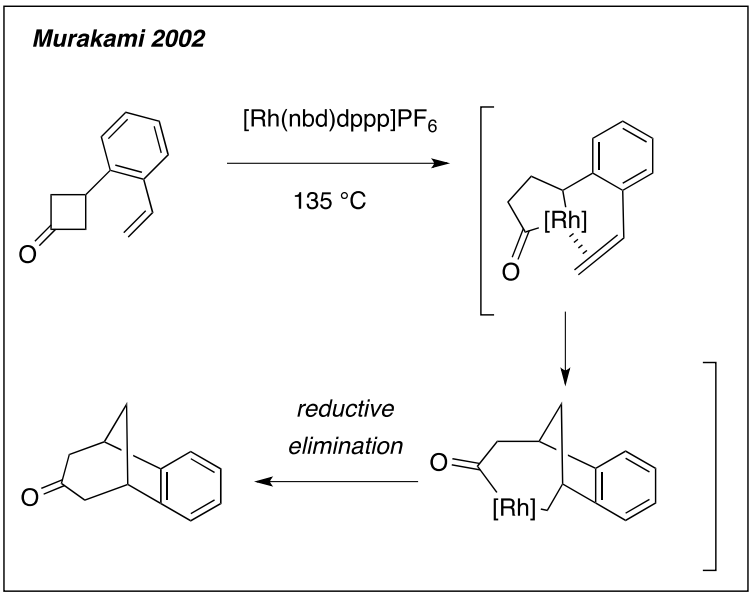


Figure 1.3 Rh-catalyzed intramolecular olefin insertion into a carbon-carbon single bond

In addition to these catalytic C–C insertion reactions, more recently Dong and co-workers published their work on Rhodium catalyzed decarbonylative coupling between isatins and alkynes[17] to synthesize 2-quinolinone derivatives. A broad range of alkynes can be coupled efficiently with high regioselectivity. This reaction is proposed to go through C–C activation of isatins, followed by decarbonylation and alkyne insertion (Figure 1.4).

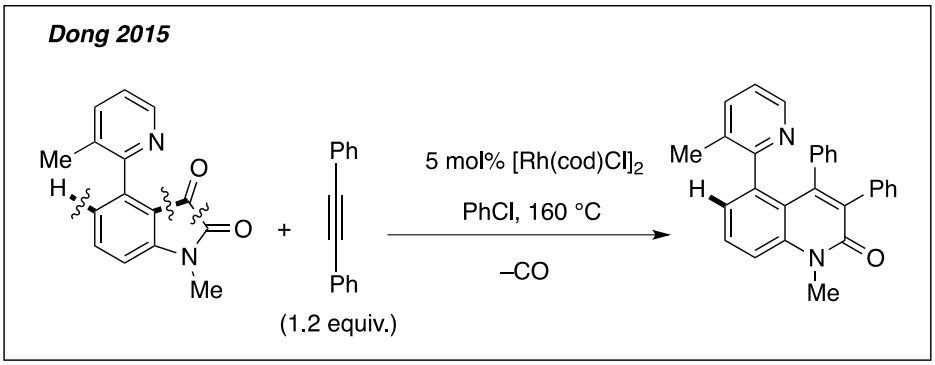


Figure 1.4 Rh-catalyzed decarbonylative coupling with alkynes via C–C activation of isatins

Emerging interests in synthetic chemistry are to develop new synthetic strategies to construct carbon–heteroatom (e.g., B, F, Si) bonds. Among them, carbon-silicon (C–Si) bond formation is attractive, due to the environmentally sustainable and ready diversification nature of organosilanes, aiming at rapid preparation of a range of bioactive molecules and new materials.[20,21]

1.4 Catalytic C–C silylations and early develeopments

Despite their established synthetic benefits, catalytic C–C silylation has been underdeveloped, primarily because of a lack of efficient catalytic protocol to effect the crucial bond scission and formation. Recently, Hayashi and co-workers (Figure 1.5) reported their remarkable palladium-catalyzed desymmetrization of alkyne-tethered silacyclobutanes[9] to give silacycles possessing a tetraorganosilicon stereocenter has been developed, and high chemo- and enantioselectivities have been achieved by the use of a newly synthesized chiral phosphoramidite Ligand. Also, Murakami and co-workers have demonstrated a novel catalytic C–C silylation reactions through unique Pd-catalyzed cross metathesis of C–C and C–Si bonds within cyclobutanones and silacyclobutanes, respectively, which builds structurally unique silacycles.[22,23]

As shown in Figure 1.6, a palladium-isocyanide complex opens the two four-membered rings of benzocyclobutenone and silacyclobutane[24] to merge them into an eight-membered ring skeleton. The present reaction provides a unique example of an intermolecular cross metathesis-type reaction between covalent σ –bonds.

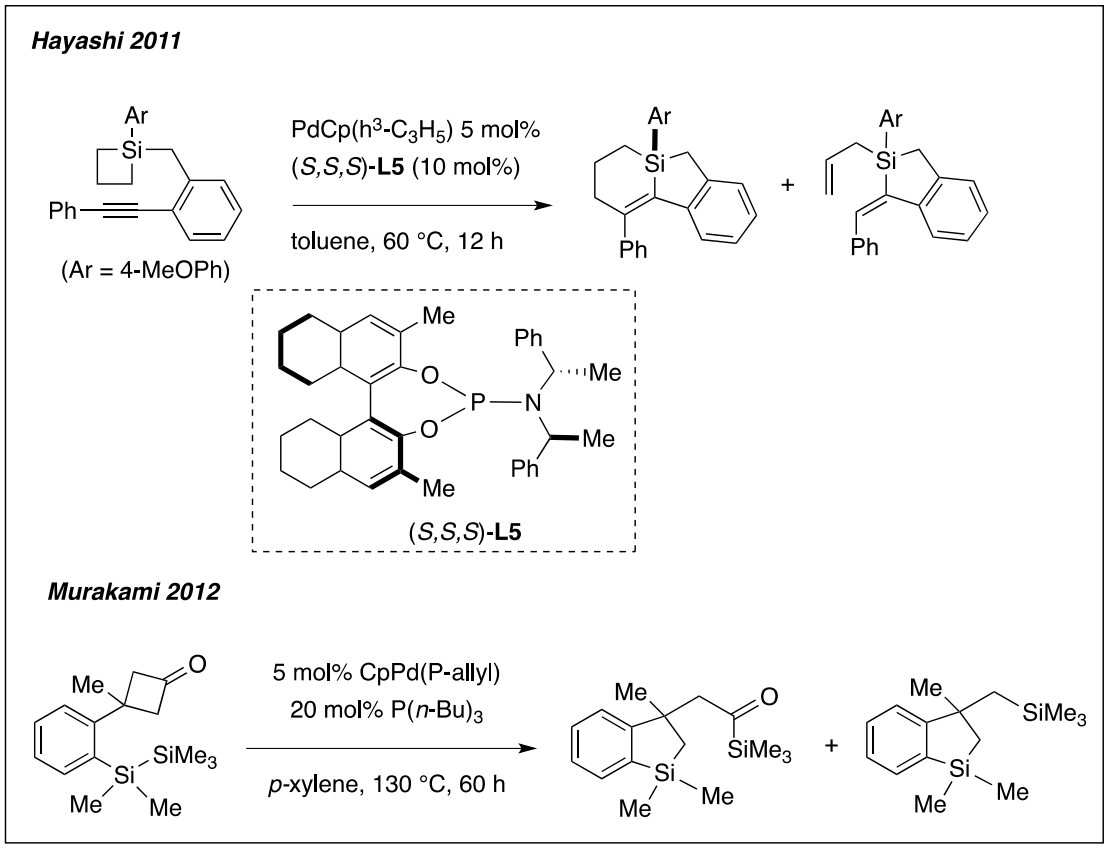


Figure 1.5 Pd-catalyzed intramolecular C–C silylation reactions

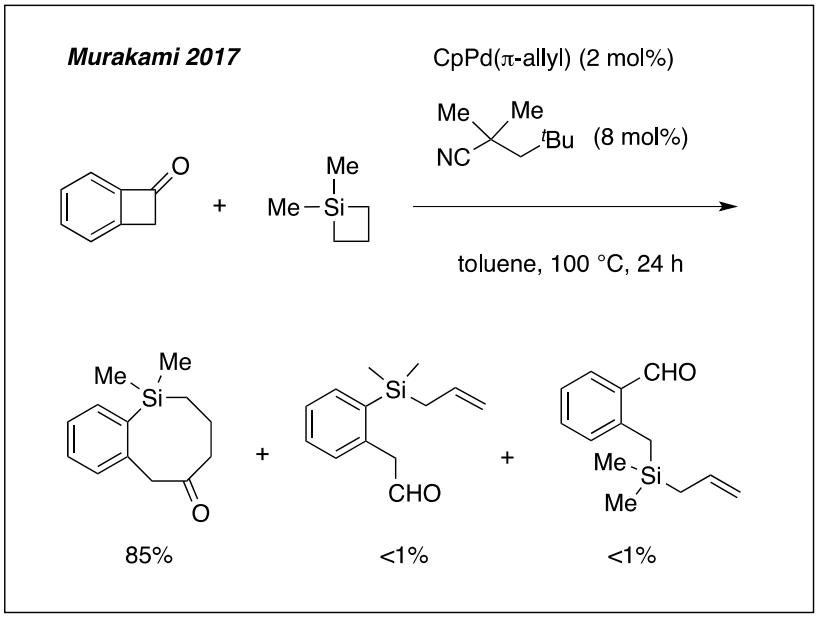


Figure 1.6 Palladium-catalyzed intermolecular C–C silylation reactions

1.5 Introduction to C–C silylations and challenges: Regioselectivity

Another important issue in C–C activation[14-17] has arisen in regioselective bond functionalization. For example, conventional C–C activation approaches of cyclopropanol derivatives[25,26-29] are limited to β–C–C functionalization to provide ketones **2** via metallohomoenolate **3** (Figure 1.7).[30]

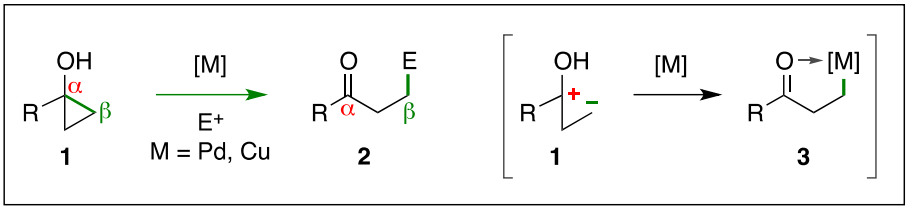


Figure 1.7 Catalytic ring-opening β–functionalization of cyclopropanols

Orellana and co-workers developed cross-coupling reactions of cyclopropanol-derived ketone homoenolates bearing β-hydrogens with aryl and heteroaryl bromides. Also, Dai and co-workers have recently reported the first Cu-catalyzed trifluoromethylation and trifluoromethylthiolation of cyclopropanols to synthesize β–substituted carbonyl compounds (Fig.1.8).

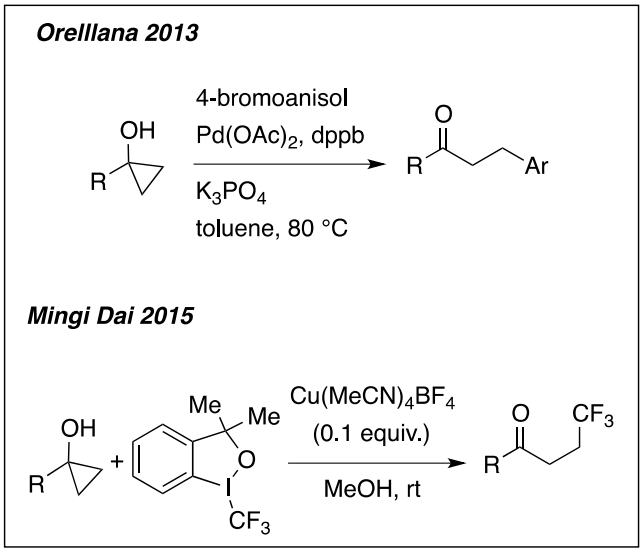


Figure 1.8 Catalytic ring-opening cross coupling reactions of cyclopropanols

1.6 Introduction to C–C silylations and challenges: Chemoselectivity

Chemoselectivity is another challenge which needs to be considered in addition to the regioselectivity in catalytic C–C bond functionalization of cyclopropanols due to the availability of reactive cyclopropane C–H bonds.[36] For example, Fagnou and co-workers have demonstrated in their work by preparing a series of tricyclic compounds via a one-pot protocol involving intramolecular palladium-catalyzed cyclopropane sp3 C–H bond functionalization and subsequent oxidation or reduction (Figure 1.9).

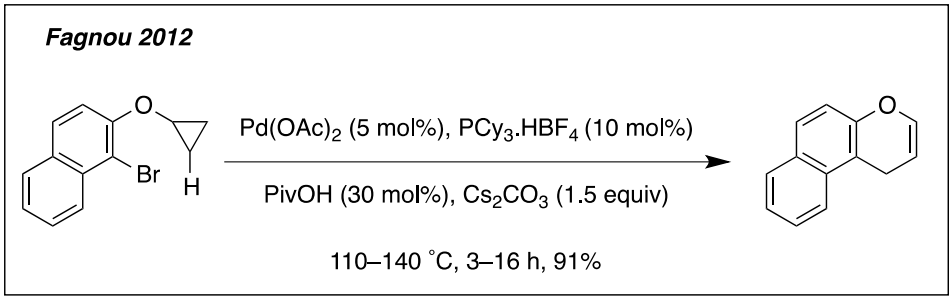


Figure 1.9 Palladium-catalyzed cyclopropane C–H bond functionalization

Another interesting work was reported by Hartwig and co-workers using Rh-catalyzed enantioselective silylation of cyclopropanes directed by a hydrosilyl group (Figure 1.10). The reaction is initiated by formation of silyl ether from cyclopropylmethanol and leads to the silylation of a cyclopropyl C–H bond[37] to form the silylcyclopropane product in high yield and with high enantioselectivity.

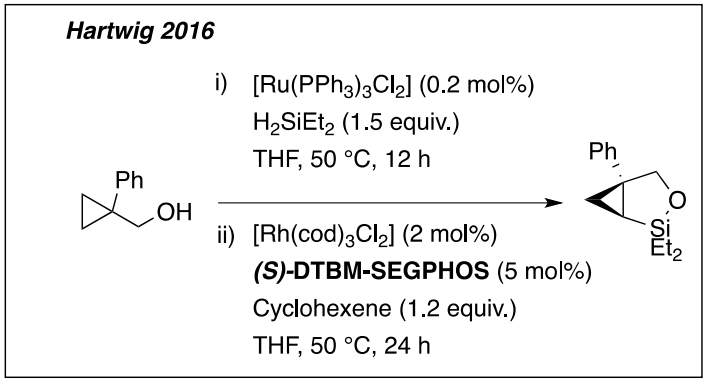


Figure 1.10 Rhodium-catalyzed cyclopropane C–H bond functionalization

1.7. Strategy for redox neutral, catalytic C–C activation of cyclopropylhydrosilyl acetals- umpolung α-silylation of cyclopropanols

There are various methods reported on catalytic β-functionalization of cyclopropanols to provide ketones **2** via metallohomoenolate **3** (as shown in Figure 1.7). However, to the best of our knowledge, catalytic α-functionalization of cyclopropanols has not been reported. Herein, we describe the umpolung α-C–C silylation of cyclopropyl acetates with highly fluorinated $Tp^{(CF3)2}$Rh(nbd) catalyst. The redox-neutral, catalytic C–C activation provides dioxasilolanes **1-3** in a highly regio- and chemoselective fashion at low temperature.

To address the synthetic challenge associated with regioselective C–C silylation of cyclopropanols, we envisioned Rh-catalyzed redox-neutral, umpolung α-selective C–C silylation of cyclopropyl acetates (Figure 1.11). Specifically, loading of metal catalyst onto cyclopropyl hydrosilyl acetals **1-2**, accessed via Ir-catalyzed ester hydrosilylation,[31] followed by cross σ-bond metathesis between C–C and Si–M bonds in **1-4** provides regioselective C(α)–Si bond formation and leads to dioxasilolanes **1-3** via **1-5** (Figure 1.12). The resulting dioxasilolanes **1-3** can serve as stable, α-silylcarbinol equivalents. Although they can be accessed by a silyl anion addition approach to ketones, the potential setbacks with this stoichiometric approach include a 1,2-silyl migration from carbon to oxygen (Brook rearrangement) of the resulting oxyanion after the nucleophilic addition,[32] enolization, and preferential 1,4-silyl nucleophile addition to α,β-unsaturated ketones to afford β-silyl ketones.

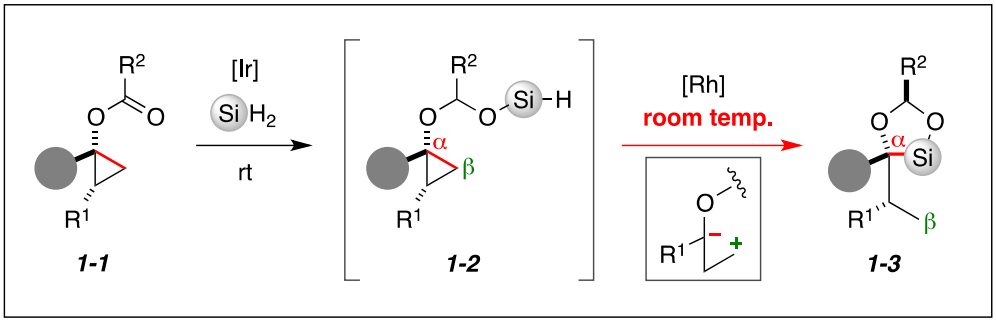


Figure 1.11. Proposed strategy for redox neutral catalytic C–C activation

Furthermore, chemoselective metal insertion into C–C bonds in the presence of largely abundant C–H bonds in close proximity, is challenging.[17] To address this issue, our strategy for chemoselective C–C silylation is predicated on the transition state-guided reaction design, harnessing analysis of each putative cyclometallated structure generated through either C–H or C–C activation.

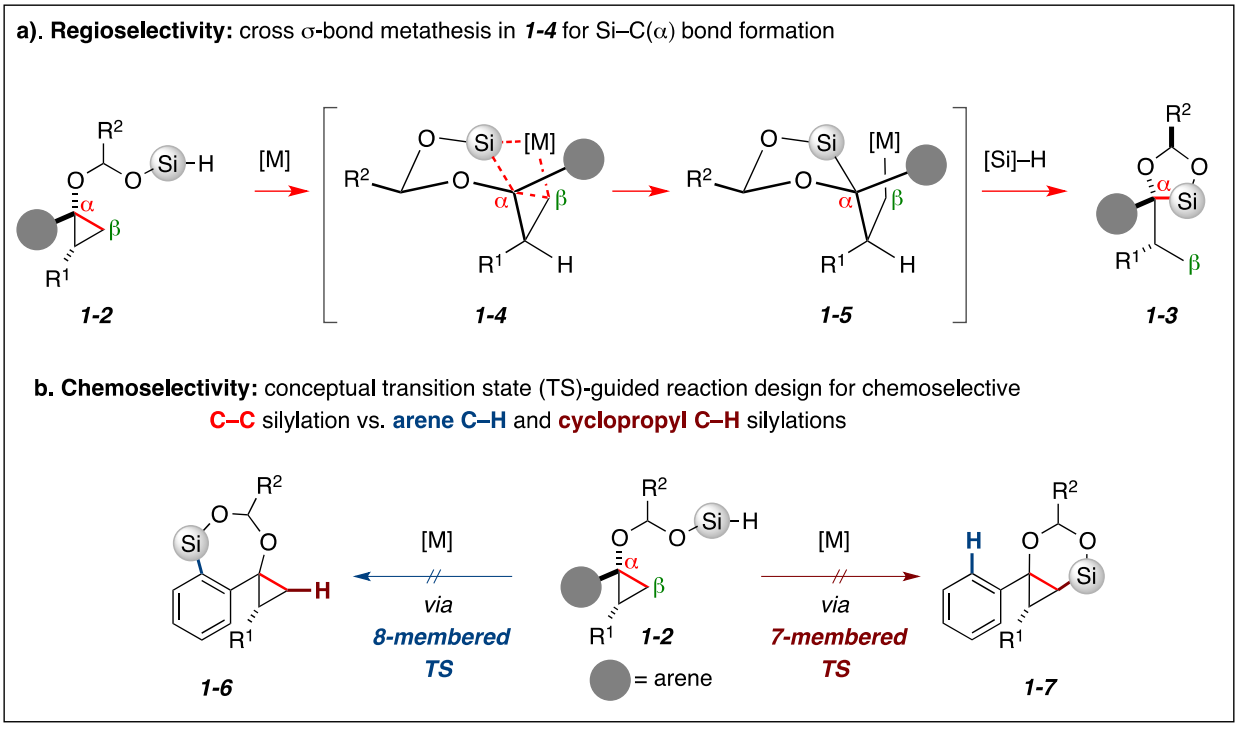


Figure 1.12 Proposed mechanism for regio- and chemoselective C–C silylation

We recognized the importance of metallated transition state (TS), to activate and functionalize specific chemical bonds successfully and selectively. Our hypothesis is that the highly chemoselective Rh-catalyzed C–C activation of **1-2** is achievable with adoption of the 5-membered TS geometry, depicted in **1-4** (Figure 1.12). In contrast, two proximal arene and cyclopropyl C–H activation[36-37] requires unfavorable 8-membered TS for **1-6** and 7-membered TS for **1-7**, respectively.

1.8. Reaction optimization for the umpolung α-silylation of cyclopropyl acetates:

1.8.1 Synthesis of cyclopropanoacetates:

Our initial investigations for the chemoselective catalytic C–C silylation were started with preparation of various cyclopropanol substrates (Figure 1.13) using following methods. These cyclopropanols were acetylated using acetic anhydride. A total of twentyfour chromatographically stable substrates were synthesized. Substrates like pyridine, pyrrole were unsuccessful in the reaction conditions. Substrate ***1-1-1*** was chosen as the master substrate and was used to optimize the reaction conditions.

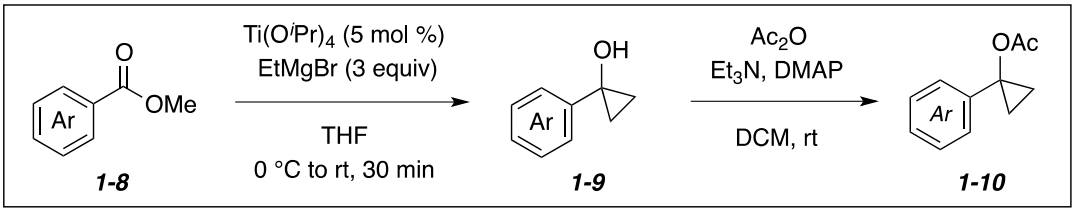


Figure 1.13 Kulinkovich reaction for the synthesis of cyclopropanols

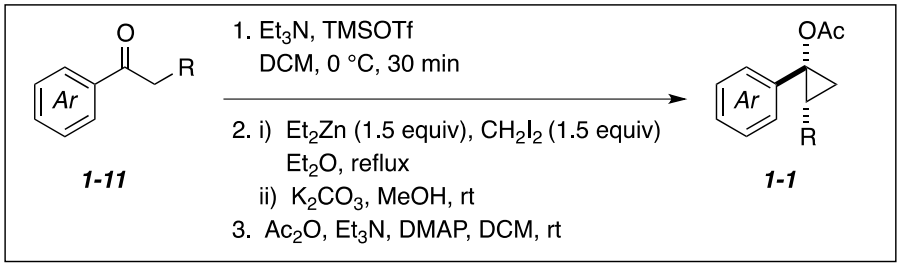


Figure 1.14 Synthesis of substituted cyclopropanoacetates

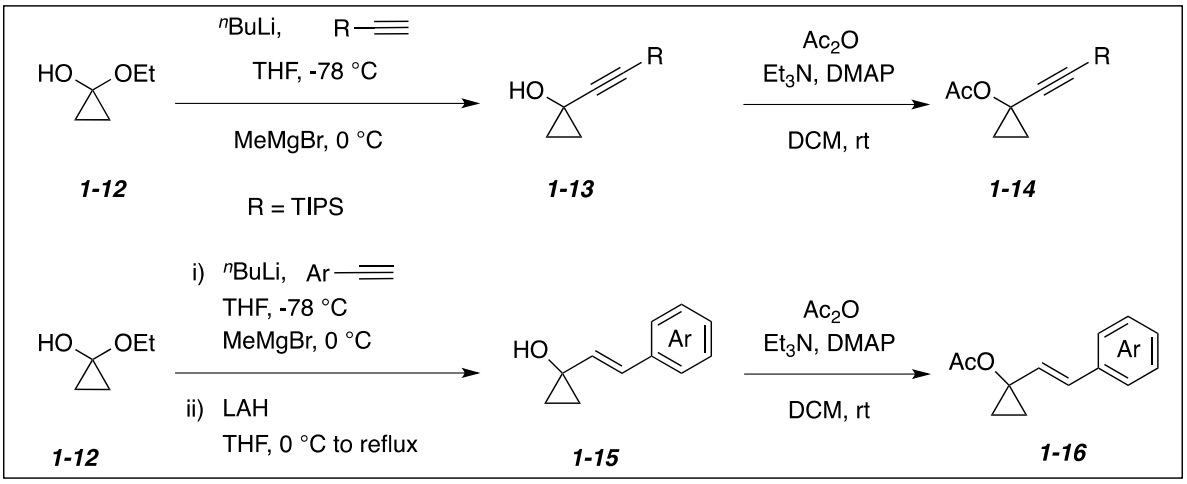


Figure 1.15 Synthesis of alkynyl and alkenyl cyclopropanoates

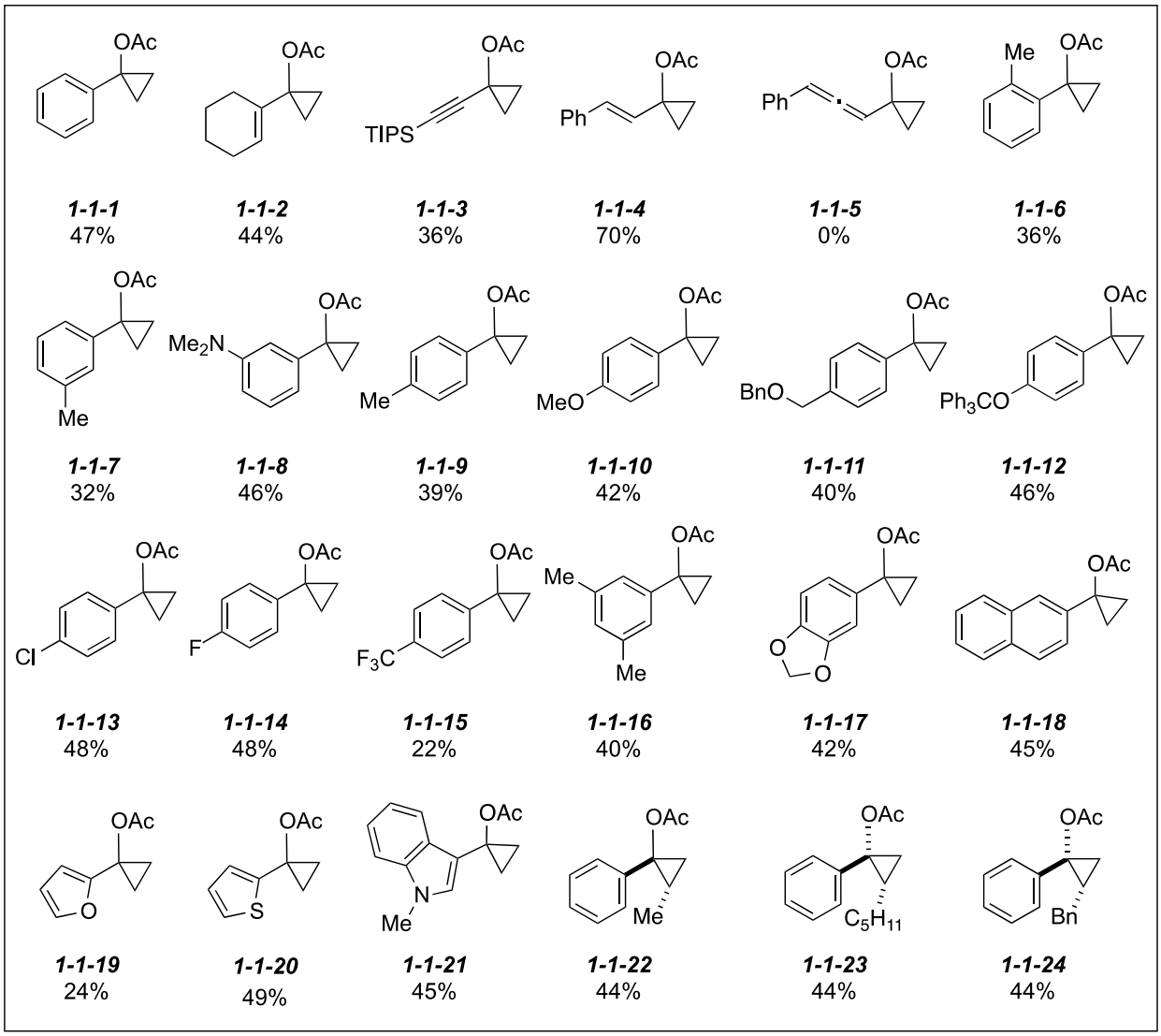
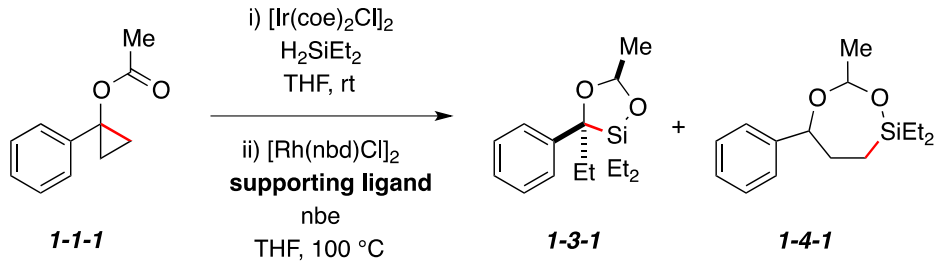


Table 1.1 Cyclopropanoacetates for C–C silylation

1.8.2 Evaluation of catalyst screening

We initially checked the feasibility of the α-selective C–C silylation, phenylcyclopropyl acetate was subjected to a sequence of Ir-catalyzed ester hydrosilylation and Rh-catalyzed C–C silylation conditions in a single pot. As a proof-of-concept of performing regio- and chemoselective catalytic C–C silylation, we prepared phenylcyclopropyl acetate **1-1-1** (Table 1.2). This substrate includes proximal arene and cyclopropyl C–H bonds and cyclopropyl C–C bond. To assess the feasibility of the α-selective C–C silylation, **1-1-1** was subjected to a sequence of Ir-catalyzed ester hydrosilylation and Rh-catalyzed C–C silylation conditions in a single pot. A series of supporting ligands including pentamethylcyclopentadienyl (Cp*) (entry 1) and tris(pyrazolyl)borate (Tp) (entries 2-4) screened exhibited that the C–C silylation was viable to afford a pair of constitutional isomers (**1-3-1** and **1-4-1**) (Table 1.2). Among them, the electron-poor Tp ligand, $[Tp^{(CF3)2}]^-$ led to highest yield of **1-3-1** (entry 4).[38-39]

Table. 1.2. Evaluation of catalyst screening



1-1-1 ***1-3-1*** ***1-4-1***

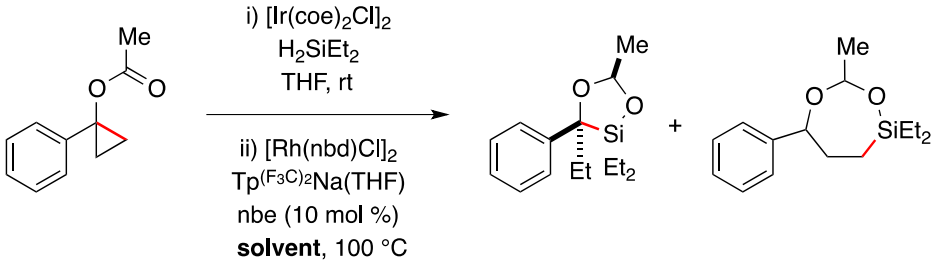
entry	supporting ligand	**1-3-1**(%)[a]	**1-4-1**(%)[a]
1	$[Cp^*]^-$	73	6
2	$^{(CH_3)2}Tp^-$	70	9
3	$^{(CF_3)Ph}Tp^-$	76	11
4	$^{(CF_3)2}Tp^-$	78	8

[a]Yields were determined by ^{1}H NMR spectroscopy utilizing an internal standard (mesitylene). The major diastereomer of **1-3-1** is shown; in all cases, the minor diastereomer of **1-3-1** was observed as determined by ^{1}H NMR and GC-MS spectrometry analyses of the crude reaction mixture. A diastereomeric ratio of **1-4-1** was not determined.

1.8.3 Evaluation of solvents for C-C silylation

We initially screened ligands with the "THF" as the solvent, we wonder if there is significant impact on yield by the choice of solvent (Table 1.3). Solvents routinely utilized in catalytic reactions such as CH_2Cl_2, PhH, $PhCH_3$, and Me-THF were employed in solvent screening. Interestingly THF (78% yield, entry 5) was superior to the rest of the solvents.

Table 1.3. Solvent screening



1-1-1 ***1-3-1*** ***1-4-1***

entry	solvent	**1-3-1**(%)[a]	**1-4-1**(%)[a]
1	CH_2Cl_2	52	9
2	PhH	18	2
3	$PhCH_3$	34	6
4	Me-THF	61	3
5	THF	78	8

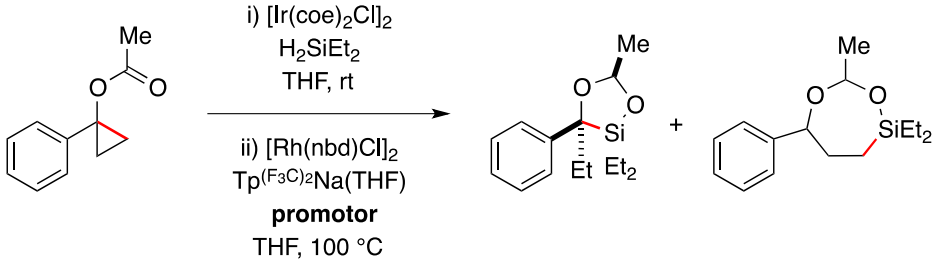
[a]Yields were determined by ^{1}H NMR spectroscopy utilizing an internal standard (mesitylene). The major diastereomer of **1-3-1** is shown; in all cases, the minor diastereomer of **1-3-1** was observed as determined by ^{1}H NMR and GC-MS spectrometry analyses of the crude reaction mixture. A diastereomeric ratio of **1-4-1** was not determined.

1.8.4 Evaluation of hydrogen acceptor

We have screened various hydrogen acceptors to test impact on yield (Table 1.4). Hydrogen acceptors such as NBE, NBD, cyclohexene, cycloheptene, cyclopentene, cyclooctene, and 1,5 COD were employed in hydrogen acceptors screening. Among a number of cyclic olefin promotors having different ring strains (entries 4-7)[40] the norbornene was found to be the most

effective and generally applicable for the C–C silylation. In any cases the competing proximal arene and cyclopropyl C–H silylations were not observed, as rationalized by the TS analysis shown in Figure 1.12.

Table.1.4. Evaluation of hydrogen acceptor



1-1-1 ***1-3-1*** ***1-4-1***

entry	promotor	relative ring strain[S1-S3]	**1-3-1**(%)[a]	**1-4-1**(%)[a]
1		2.5	13	11
2		6.7	20	9
3		6.8	26	24
4		7.4	18	9
5		13.3	20	0
6		27.2	78	8
7		34.7	37	0

[a]Yields were determined by ^{1}H NMR spectroscopy utilizing an internal standard (mesitylene). The major diastereomer of **1-3-1** is shown; in all cases, the minor diastereomer of **1-3-1** was observed as determined by ^{1}H NMR and GC-MS spectrometry analyses of the crude reaction mixture. A diastereomeric ratio of **1-4-1** was not determined.

1.9 Isolation and X-ray structure of $Tp^{(CF3)2}Rh(nbd)$ catalyst for redox-neutral, and catalytic α-C–C silylation

To test our hypothesis, we have synthesized $Tp^{(CF3)2}Rh(nbd)$ catalyst with $[Rh(nbd)Cl]_2$ with $Tp^{(CF3)2}Na(THF)$. Rh(I) with $[Tp^{(CF3)2}]^-$ coordinates in bidentate mode and the X-ray structure of $Tp^{(CF3)2}Rh(nbd)$ is shown in Figure 1.18.[41] The use of isolated $Tp^{(CF3)2}Rh(nbd)$ for the C–C silylation under the essentially identical conditions, led to **1-3-1** in 76% yield and 12:1 diastereoselectivity. A substoichiomeric amount of nbe was indeed required for the efficient reaction (cf., 39% yield without nbe), inferring that nbe is not innocent in the overall catalytic cycle.

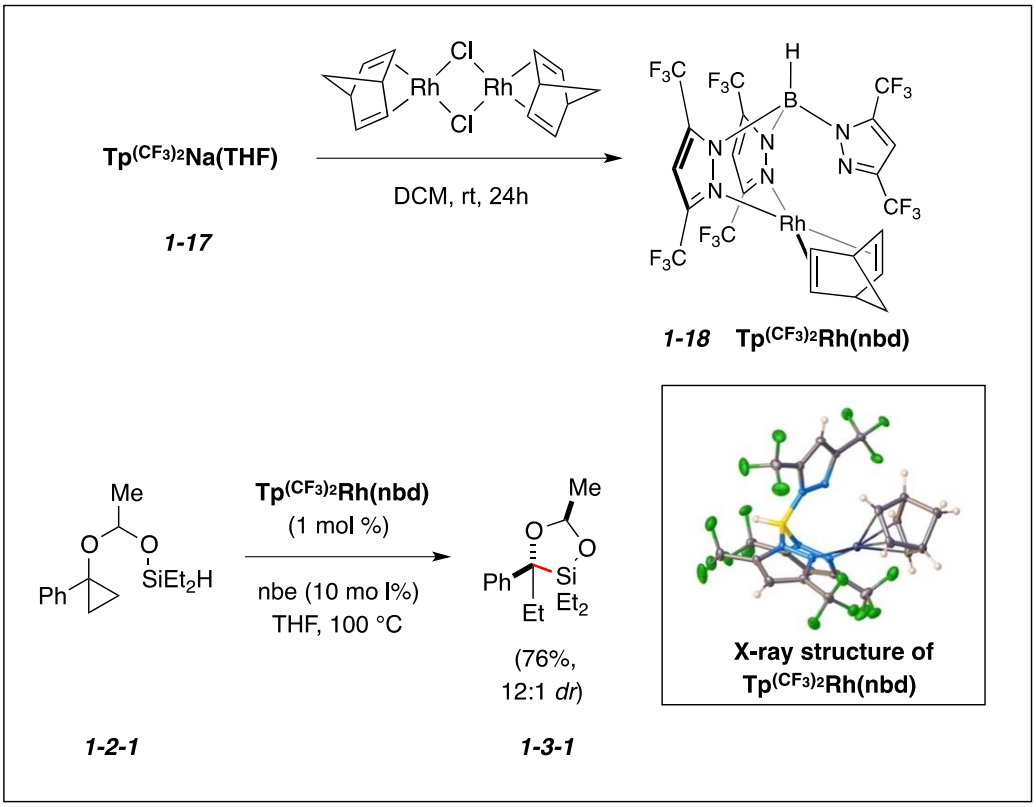


Figure 1.16 Isolation and X-ray structure of $Tp^{(CF3)2}Rh(nbd)$ catalyst

1.10 Room temperature, C–C silylation with electron-poor $Tp^{(CF3)2}Rh$ catalyst.

While we are screening temperature for the C–C silylation reactions, unexpectedly we found that the $Tp^{(CF3)2}Rh(nbd)$ catalyst permitted the *room temperature C–C silylation* of aryl, alkenyl, and alkynyl-substituted cyclopropyl hydrosilyl acetals (Figure 1.17).[42] The lower yield observed in the C–C silylation of **1-2-1** at room temperature is attributed to partial instability of **1-2-1** during the extended reaction time (24 h). In contrast to the sluggish kinetics in the formation of **1-3-1**, the reactions of the alkene and alkyne-substituted cyclopropyl hydrosilyl acetals, **1-2-2** and **1-2-3** respectively were remarkably fast to afford **1-3-2** and **1-3-3** within 40 and 30 min at room temperature, with good yields (87% and 83%, respectively) and excellent diastereoselectivity.

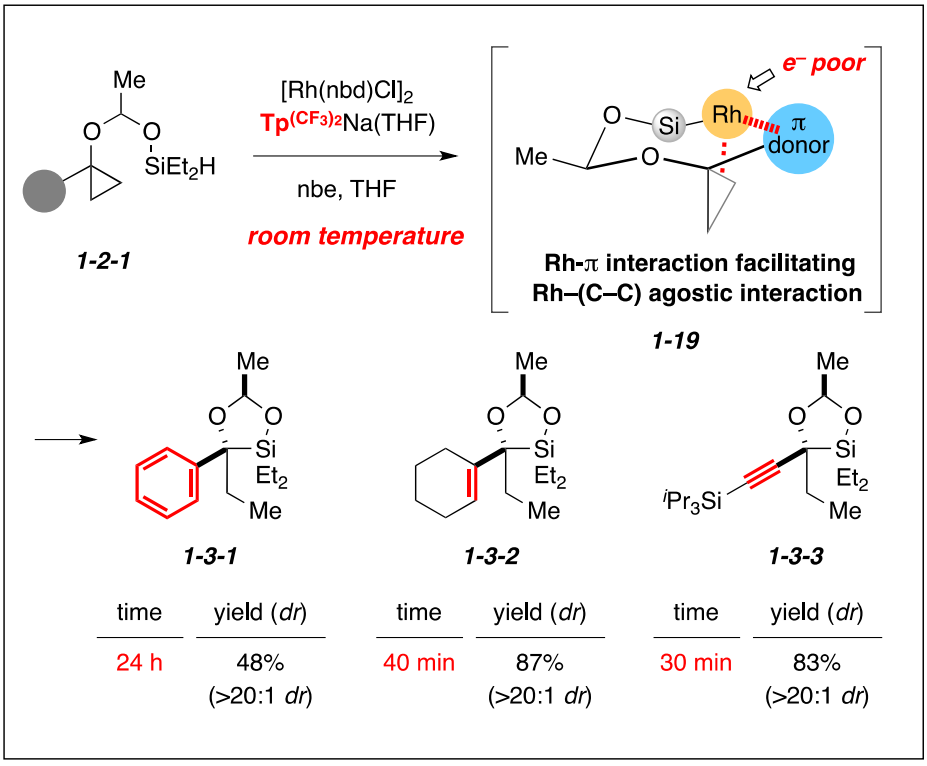
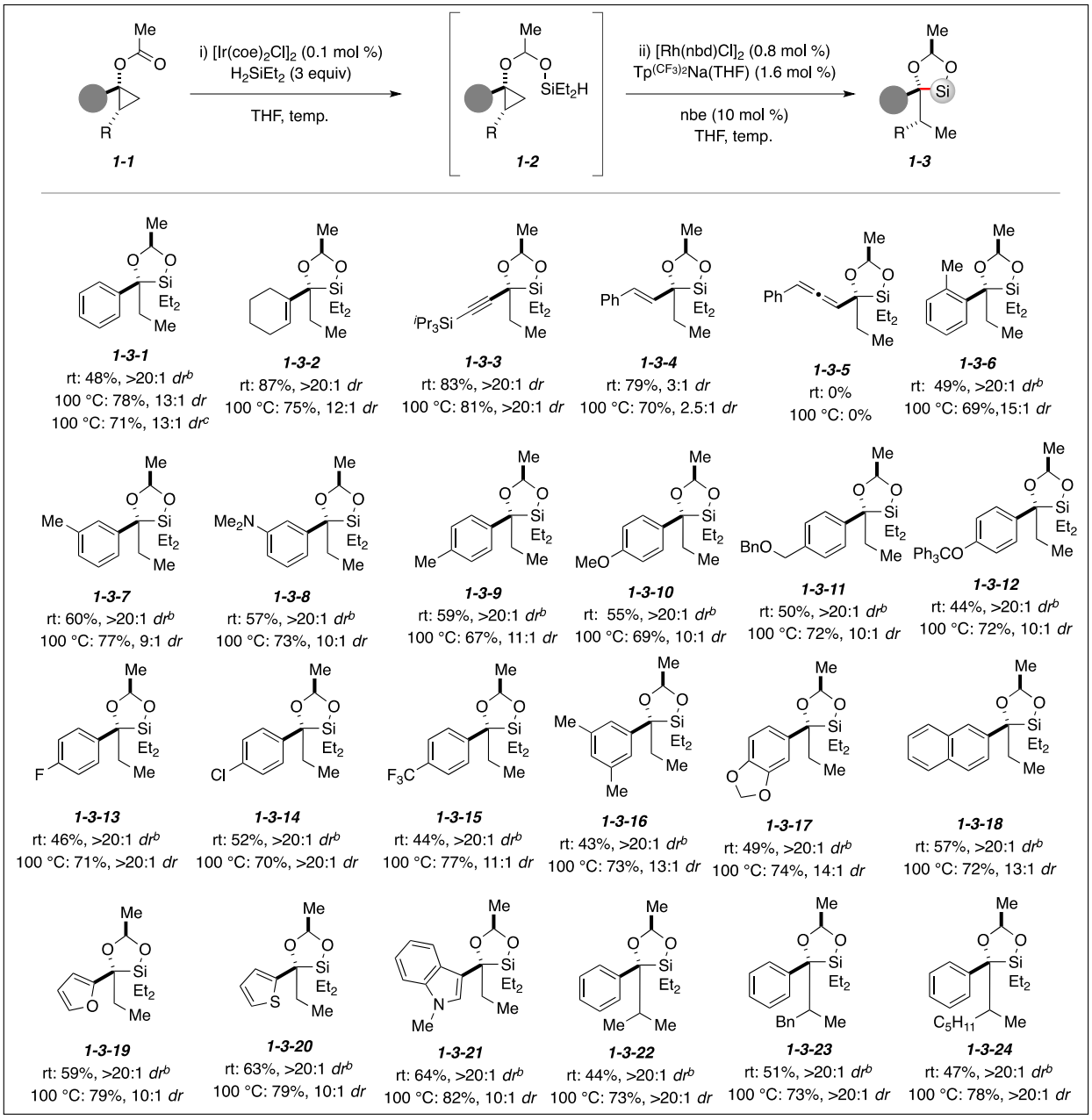


Figure 1.17 Room temperature C–C silylation with electron-poor $Tp^{(CF3)2}Rh$ catalyst

1.11 Substrate scope for C-C silylation

Under the optimized reaction conditions for a single-pot, redox-neutral C–C silylation, a range of a new class of silicon-containing heterocycles **1-3** were prepared from **1-1** with moderate to excellent yield and diastereoselectivity (Table 1.5). Dioxasilolanes **1-3** presented in Table 1.4 were chromatographically stable and a range of common functional groups including alkenes (**1-3-2**, **1-3-4**), alkyne (**1-3-3**), amine (**1-3-8**), ethers (**1-3-9** to **1-3-16**), halides (**1-3-13**, **1-3-14**), trifluoromethyl (**1-3-15**), 3,5-dimethyl (**1-3-16**), acetal (**1-3-17**), naphthalene (**1-3-18**), furan (**1-3-19**), thiophene (**1-3-20**), indole (**1-3-21**) were tolerated either at rt or 100 °C. However, a reaction with allene (**1-3-5**) gave a complex mixture. Also, the substrates with aliphatic systems were unsuccessful in reaction conditions and only starting materials were recovered even at high temperatures. The reactions with substrates holding substituted cyclopropyl ring also proceeded to furnish **1-3-22 to 1-3-24** with good yield and excellent diastereoselectivity.

Table 1.5 Scope of redox-neutral catalytic C–C silylation of cyclopropyl acetates



Yields are for isolated material over a single-pot, two-step sequence from **1-1-1** (0.2 mmol). Diastereomeric ratio (dr) was determined by 1H NMR spectroscopy and GC-MS spectrometry analyses of the crude reaction mixture. b[Rh(nbd)Cl]$_2$ (5 mol %), Tp(CF3)2Na(THF) (10 mol %), norbornene (10 mol %), THF (0.33 M), rt. c1 mmol of **1-1-1** was used.

1.12 Stereochemistry of the dioxasilolane

We have prepared various substituted cyclopropane substrates and subjected them to our catalytic conditions to make a selection of silacycles. Among them, we have chosen **1-3-22** for the nOe experiment to know about the stereochemistry. We observed the preferential activation of a more kinetically accessible C–C bond. An nOe experiment with **1-3-22** revealed that the diastereoselection was consistent with the proposed TS model **1-4** (Figure 1.20), which resulted in high diastereoselectivity.

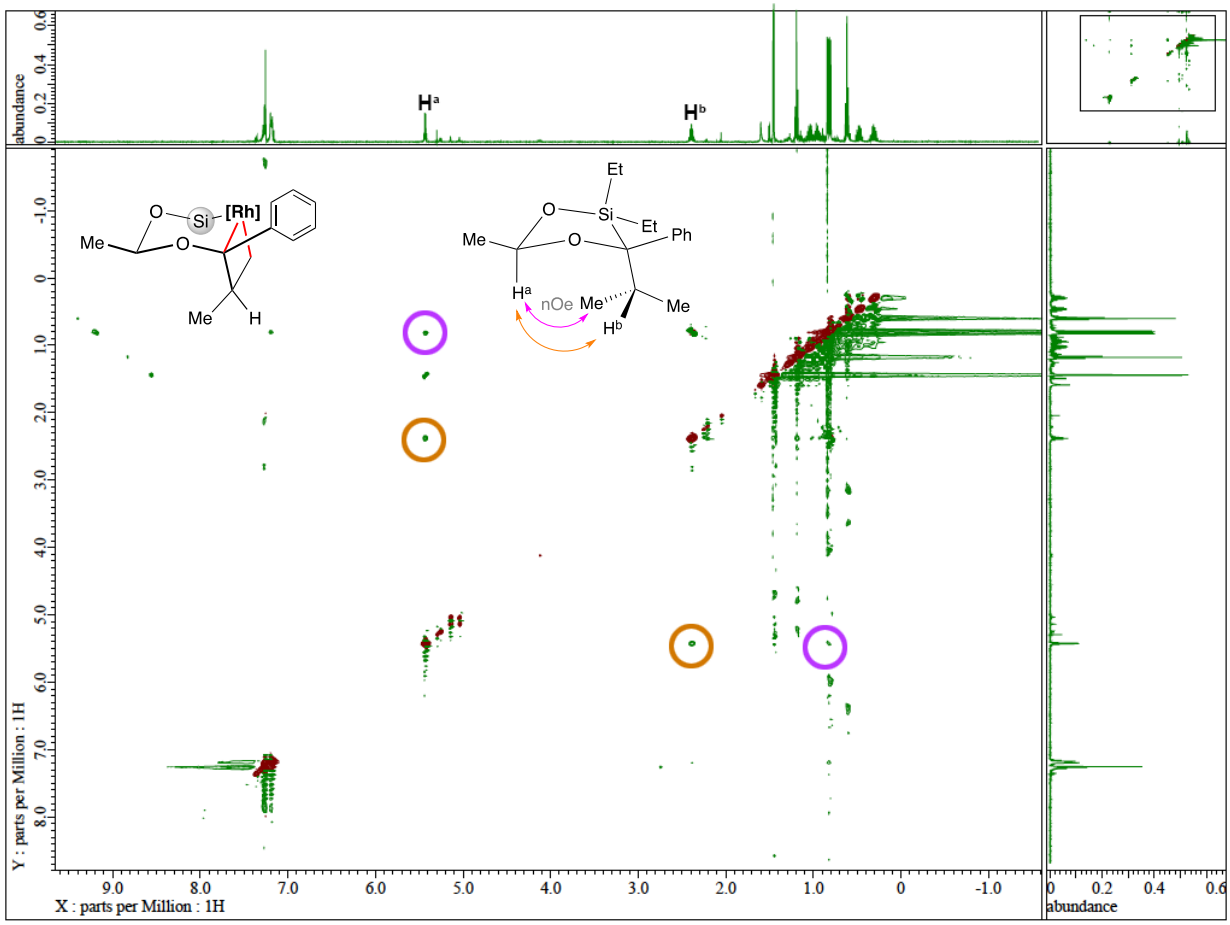


Figure 1.18 NOESY experiment of dioxasilolane **1-3-22**

1.13 Synthetic applications of dioxasilolanes

A major motivation of this work is to develop a novel strategy to umpolung α-functionalization of cyclopropanoacetates to produce dioxasilolanes. The resulting dioxasilolanes

1-3 can serve as stable, α-silylcarbinol equivalents. The cyclic silyl acetals **1-3** are chromatographically stable, yet willing acceptors of organometallic nucleophiles.[31,44-45] Upon a nucleophilic attack to **1-3-1** leading to a putative, penta-coordinated silicon species **1-23** the high thermodynamic driving force drives them rapidly and irreversibly to **1-23** in equilibrium with a strained, penta-coordinated species **1-24** (Figure 1.21). This spring-loaded nature makes **1-3** suitable for rapid diversification to tertiary alcohol derivatives. To demonstrate this aspect, we first performed the [1,2]-Brook rearrangement of **1-3-1** as α-silylcarbinol equivalents.[32] Specifically, a ring-opening of **1-3-1** with MeLi releases acetaldehyde, which can engage in additional MeLi, and a spontaneous ring-closure of **1-24** produces **1-25**. Upon addition of electrophiles and raising the temperature the reactions furnished tertiary alcohols capped with a diethylmethylsilyl group, **1-21** and **1-22**, respectively. When the reaction was quenched at –78 °C, α-silylcarbinol **1-25** was produced (88% yield).

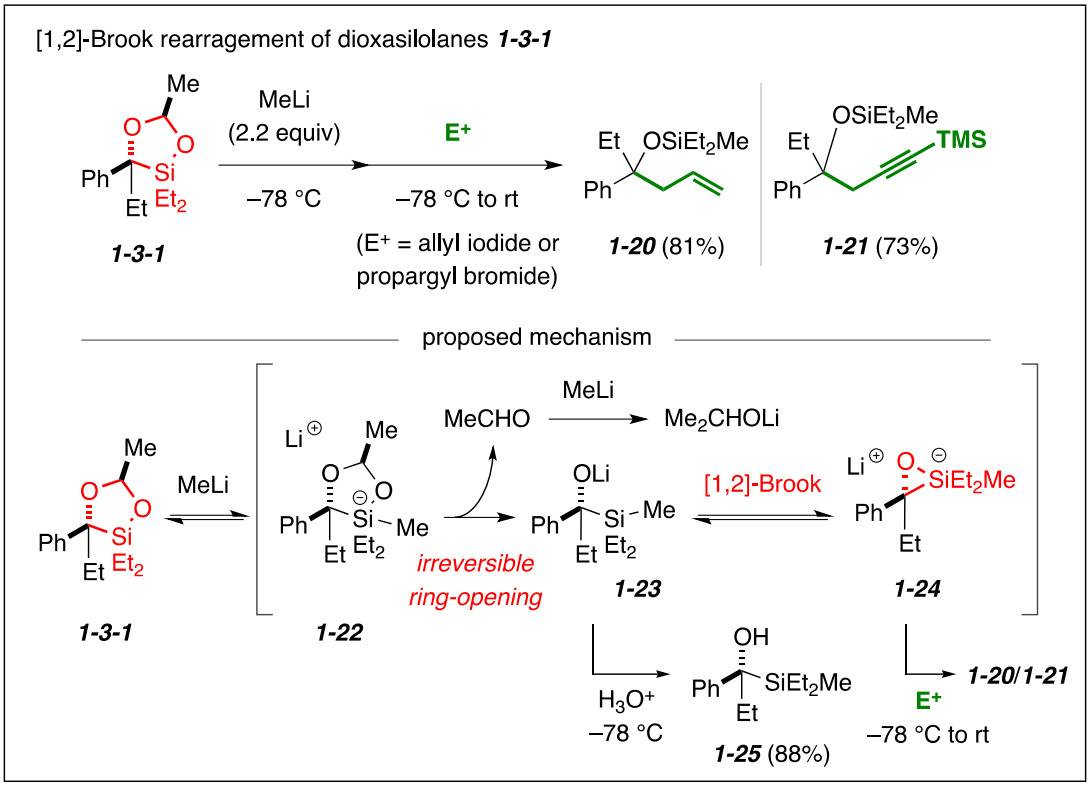


Figure 1.19 Synthetic applications of dioxasilolanes

This protocol was applied to a complex molecular setting, where estrone-derived cyclopropyl acetate **1-26** was converted into silyl ether **1-27** (85% yield, a three-step single pot from **1-26**) (Figure 1.20).

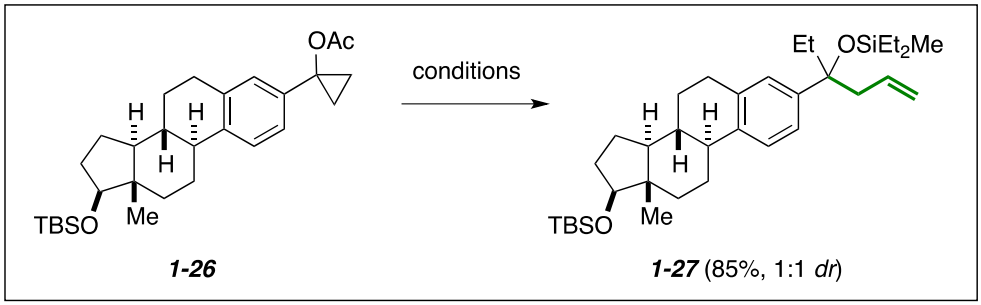
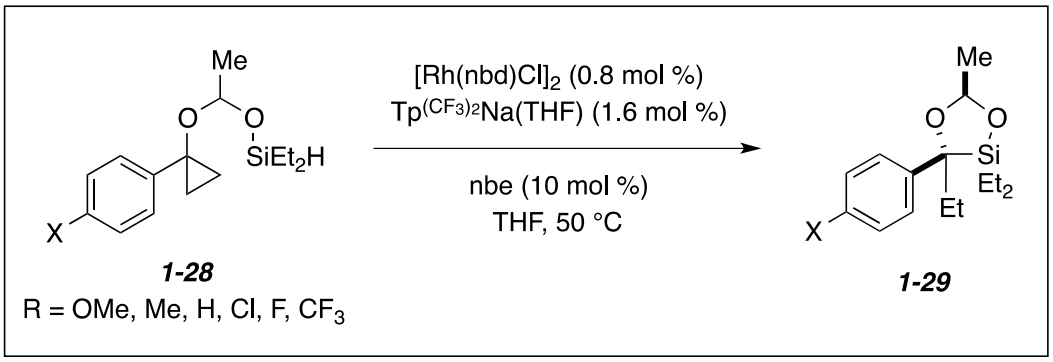


Figure 1.20 Synthetic applications of estrone-derived cyclopropyl acetate

Conditions: 1. i) $[Ir(coe)_2Cl]_2$ (0.1 mol %), H_2SiEt_2 (3 equiv), THF, rt; ii)$[Rh(nbd)Cl]_2$ (0.8 mol %), $Tp^{(CF3)2}Na(THF)$ (1.6 mol %), THF, 100 °C. 2. i) MeLi (2.2 equiv), THF, –78 °C; ii) allyl iodide, THF, –78 °C

1.14 Mechanism Studies

1.14.1 Hammett Study of dioxasilolanes



We have performed the Hammett study to understand a linear free-energy relationship of a redox-neutral C–C silylation mechanism (Figure 1.21). The rate acceleration by electron-withdrawing groups was observed in the process. Specifically, the ρ value of 0.80 indicates no appreciable accumulation of the electron density in the transition state of the C–C cleavage step. The results infer that the M-π coordination is not likely the turnover-determining step, but

increasing the electron-withdrawing nature of the aryl moiety would rather facilitate the cleavage of the neighboring cyclopropyl C–C bond.

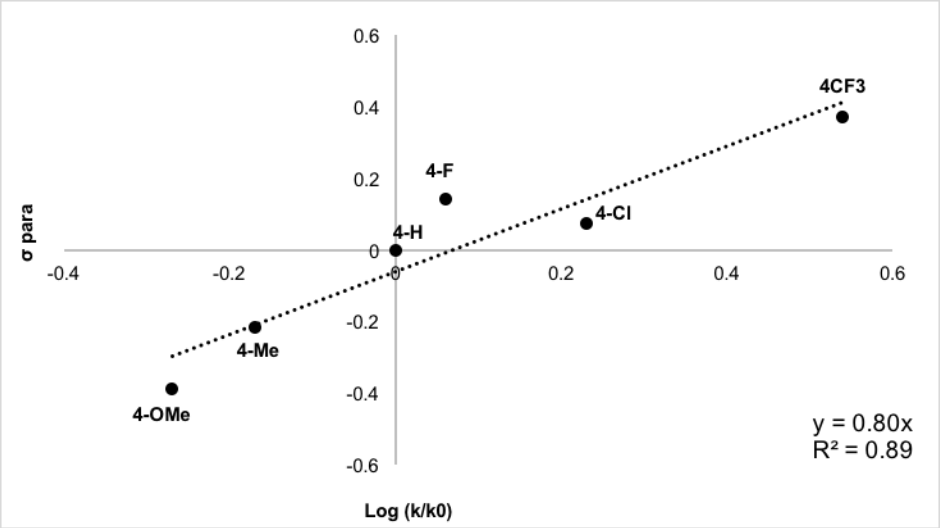


Figure 1.21. Hammett plot of dioxasilolanes.

1.14.2. Deuterium-labelling studies with tetradeuterated cyclopropane

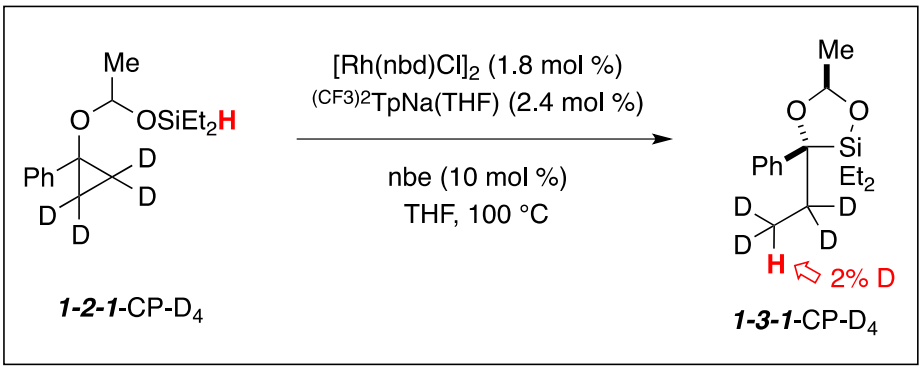


Figure 1.22 Deuterium-labelling studies with tetradeuterated cyclopropane

We have performed labelling experiments with tetradeuterated cyclopropyl hydrosilyl acetal and a fully deuterated phenyl group-substituted hydrosilyl acetal conclude to conclude there was no obvious cyclopropyl and arene C–H cleavage occurs in the course of the C–C silylation. We then conducted the kinetic isotope effect (KIE) study with **1-2-1**-CP-H_4 and **1-2-1**-CP-D_4 in a single vessel (Figure 1.22). The reaction afforded inverse secondary KIE. Subjecting tetradeuterated cyclopropyl hydrosilyl acetal **1-3-1**-CP-D_4 into the catalytic conditions led to a near quantitative transfer of hydrogen at Si to the terminal methyl in **1-3-1**-CP-D_4.

1.14.3. Deuterium-labelling studies with a pentadeuterated phenyl cyclopropanoate

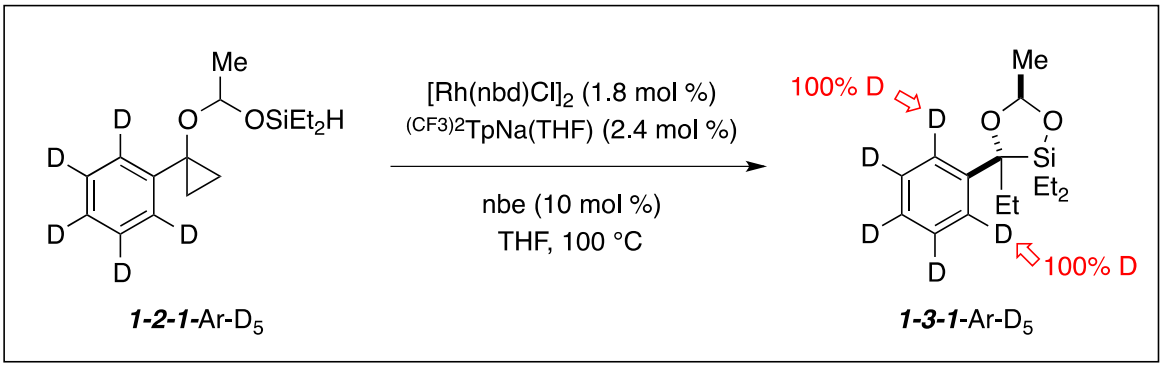


Figure 1.23 Deuterium-labelling studies with a pentadeuterated phenyl cyclopropanoate

We have performed a reaction with fully deuterated phenyl group-substituted hydrosilyl acetal to conclude that there was no obvious cyclopropyl and arene C–H cleavage occurs in the course of the C–C silylation (Figure 1.23).

1.13.4. Kinetic isotopic effect (KIE) study

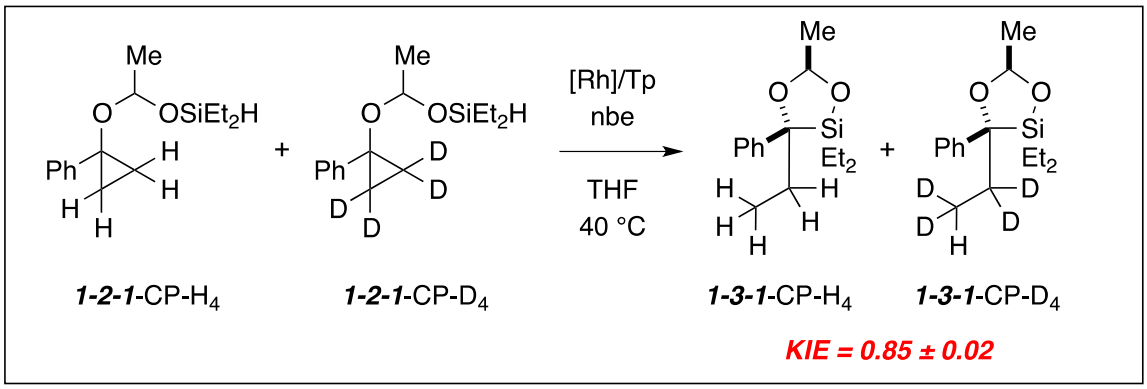


Figure 1.24 Kinetic isotopic effect of dioxasilolanes

We then conducted the kinetic isotope effect (KIE) study with **1-2-1**-CP-H_4 and **1-2-1**-CP-D_4 in a single vessel (Figure 1.24). The reaction afforded inverse secondary KIE. These results along with the Hammett studies described above suggest that the turnover-determining step is likely the C–C cleavage. We conducted the kinetic isotope effect (KIE) study with **1-2-1**-CP-H_4 and **1-2-1**-CP-D_4 in a single vessel. The reaction afforded inverse secondary KIE (0.85 ± 0.02).

1.14.5 Deuterium-labelling studies with deuteriosilyl acetal

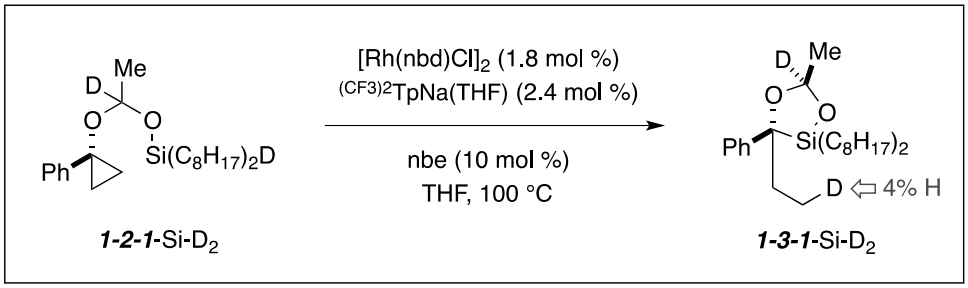


Figure 1.25 Deuterium-Labelling Studies with Deuteriated Hydrosilyl acetal.

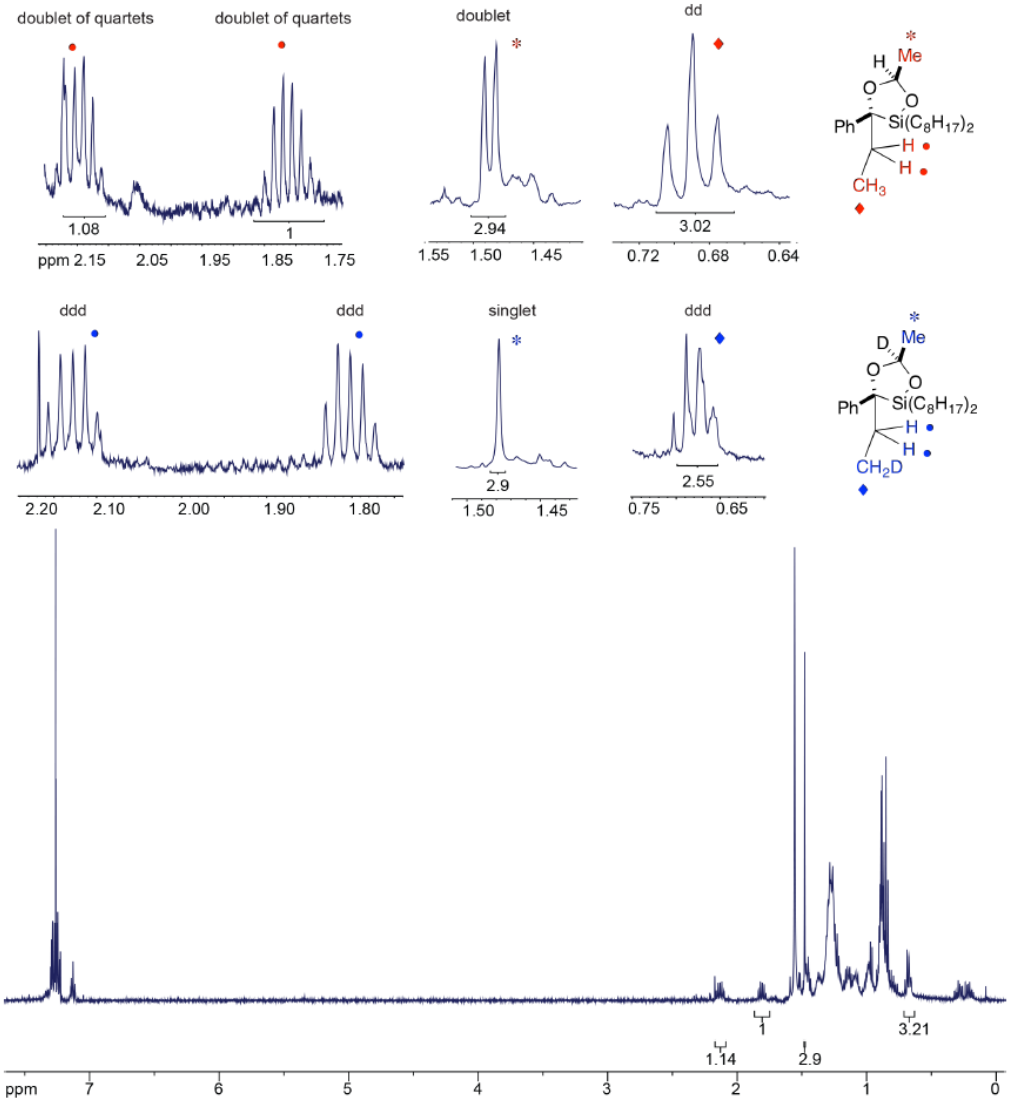


Figure 1.26. ^{1}H NMR ($CDCl_3$, 500 MHz) of **1-3-1**-Si-D_2.

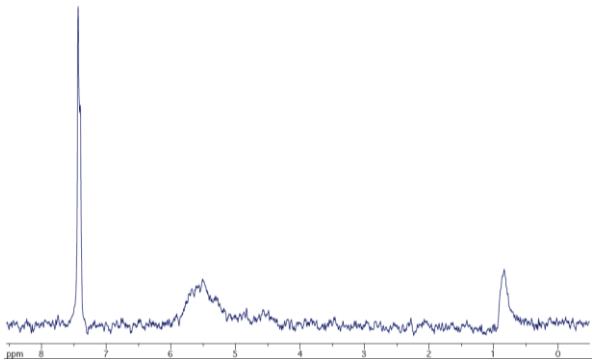


Figure 1.27 ^{2}H-NMR ($CDCl_3$, 300 MHz) of **1-3-1**-Si-D_2

1.15 Possible mechanism for the umpolung α-silylation

Based upon our preliminary mechanistic studies along with literature precedents,[46-49] the proposed mechanisms accounting for formation of **1-3** and **1-4** proceeds through a common bis-silyl rhodium intermediate **C** (Figure 1.30). Oxidative addition of cyclopropyl hydrosilyl acetal **1-2** to $Tp^{(CF3)2}$Rh(nbd) generates Rh-silyl hydride **A**, which was identified as a major species observed through ^{1}H NMR spectroscopy.[48-49] Norbornene is indispensable to produce **C** efficiently; olefin migratory insertion to form **B**, followed by oxidative addition of **5** and reductive elimination could generate norbornane (observed by ^{1}H NMR) and **C**, which is in equilibrium with **D**. Considering the bonding similarities between the Cp* and Tp ligands, structurally similar Cp*Rh($SiEt_3$)$_2$ species were proposed by Berry in the context of C–H silylation.[48] Once the rhodium-π interaction that facilitates a tightly organized geometry and thus would develop putative C–C agostic interaction with the metal center, are established within **D**, direct cross metathesis of Si–Rh and C–C within **D**, which is a turnover-determining step, can give rise to the intermediates **E** (major) and **F** (minor). We rationalize that **F** requires a significantly distorted geometry for the putative intramolecular bond exchange process. Since the steric bulk from the proximal, fully substituted carbon center is present next to the metal, σ-bond metathesis between hydrosilyl acetal **1-2** and **E** furnishes **1-3**, where the β-hydride elimination

adduct **G** was not observed. The cross-over experiment between protiosilyl acetal and deuteriosilyl acetal established that the final hydrogen transfer occurs intramolecularly. On the other hand, the reaction between the alkylrhodium species **F** holding the bidentate RhTp and **1-2** leads to a minor constitutional isomer **1-4** (**H** was not observed). We made an observation on the alkene transposition adduct **1-32** (9% yield) along with **1-3-4** (79% yield) from **1-2-4**, suggesting that formation of the fully substituted alkylrhodium species **1-30** underwent [1,3]-rhodium shift[25] to produce less hindered **1-31** and thus **F** is responsible for formation of dioxasilepanes **1-4**.

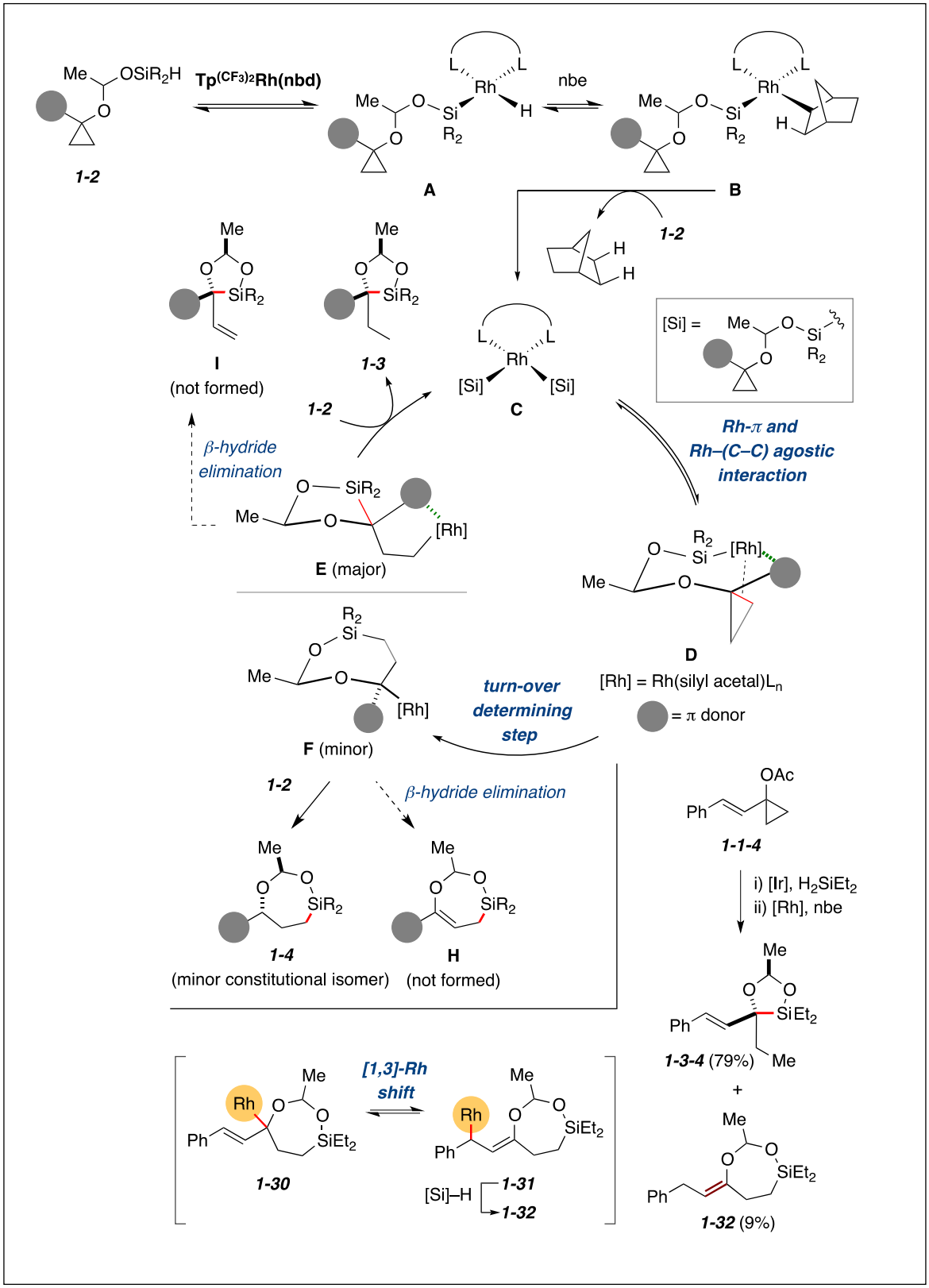


Figure 1.28 Possible mechanism for the umpolung α-silylation

1.16 Summary of Chapter 1

In summary, we have developed umpolung α-silylation of cyclopropyl acetates via redox-neutral catalytic C–C activation to produce silicon-containing five-membered heterocycles with high regio- and chemoselectivities. Synthetic applicability of the methods was demonstrated through the rapid preparation of tertiary alcohols vis Lewis base-mediated unconventional [1,2]-Brook rearrangement of the resulting chromatographically stable dioxasilolanes. Finally, preliminary mechanistic studies support that an electrophilic metal center harnessing highly fluorinated $Tp^{(CF3)2}$Rh(nbd) catalyst is a key for the facile, low temperature C–C silylation. Studies toward an enantioselective variant of this reaction are underway and will be reported in due course.

Chapter 2

Net Oxidative Inverse Polarity C–C Silylation of Cyclopropanols Involving Generation of Metallo Homoenolate-Enol Ether

Thirupataiah Avullala, Yuanda Hua, Parham Asgari, Apparao Bokka, and Junha Jeon*

2.1 Introduction

2.2 Uses and importance of metallo enolate and metallo homoenolate enolether

Carbon-carbon (C–C) bond activation and functionalization strategies of cyclopropanols **3** [50-54] have offer merits to construct a range of useful β-functionalized ketones. [55-74] As depicted in Figure 2.1, a formal charge affinity pattern of metallo homoenolate **4** differs from a location of negative charge of *C*-metallo enolate **2**. The nucleophilic metallo homoenolate **4**[75] generated through the non-insertive C–C ring-opening of cyclopropanol derivatives **3** has been served as an important inverse polarity (i.e., umpolung)[76-78] synthon of Michael acceptors. This species can engage in β-functionalization reactions including addition[74] or cross-coupling to form new C–C, C–N, and C–S bonds.[79-82] Subsequently, metallo enolate-homoenolate species **6 or 8** merging metallo enolate **2** and metallo homoenolate **4** have been introduced. This species holds two nucleophilic sites, which can engage in either inverse polarity β-functionalization (σ) or umpolung, SN2'-type reactions

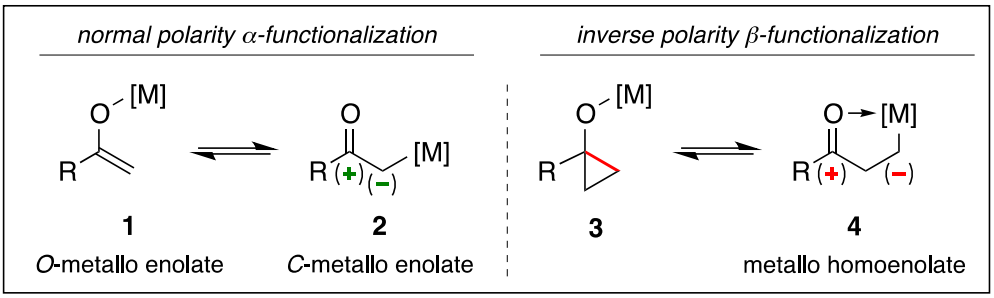


Figure 2.1 Known charge affinity patterns of metallo enolate and metallo homoenolate

Ryu and Sonoda first demonstrated that lithium enolate of β–lithio ketone **6** was produced through a stoichiometric protocol involving metal-halogen exchange of lithium enolates of β-stannyl **5** (Figure 2.2).[83-84]

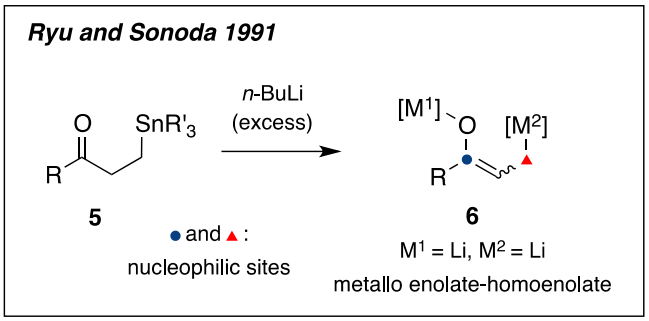


Figure 2.2 Ryu and Sonoda's β–lithio ketone: metallo enolate and metallo homoenolate

Matsubara produced zinc enolate-homoenolate **8** by stoichiometric 1,4-addition of bis(iodozincio)methane to enones.[85] Also, Ogoshi reported the first catalytic generation of ketone α,β-dianion equivalents **10** via normal polarity 1,4-disilylation of enones under nucleophilic palladation conditions (Figure 2.3).[86]

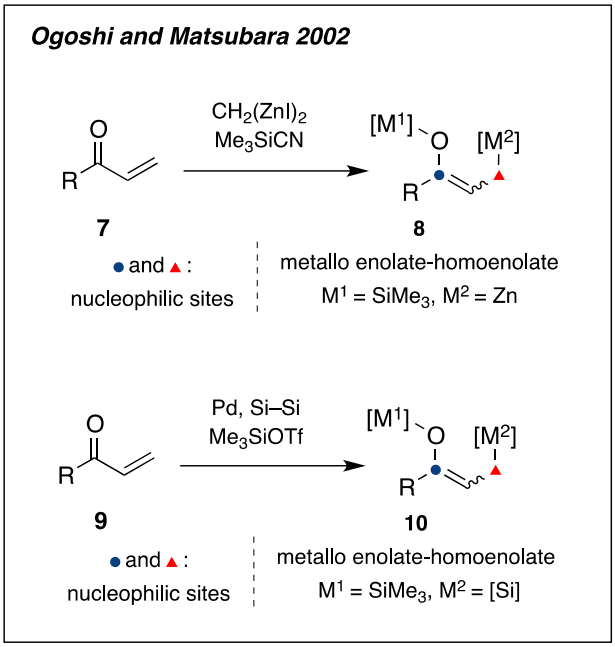


Figure 2.3 Ketone α,β-dianion equivalents

In these studies, a high level of regiochemistry selecting a nucleophilic site as well as stereochemistry providing *Z*-enolates were predominantly achieved by chelation or reagent control.

2.3 Strategy for catalytic redox-neutral and net oxidative C–C activations: Regioselective umpolung α-silylation and dehydrogenative β-silylation of cyclopropyl acetates.

In this work, we describe the hitherto unexplored reactivity of cyclopropanol derivatives **11** to formally generate a net oxidation intermediate, metallo homoenolate-enol ether [(*Z*)-MHEE,**12**] in a regio-, stereo-, and chemoselective fashion is descibed (Figure 2.4). This reaction involves catalytic, net oxidative C–C activation, leading to inverse polarity β-metallation of **11** to provide **12**. They serve as ketone α,β-dianion equivalents to prepare a range of α,β-difunctionalized ketones **13** employing diverse normal polarity α-functionalization reactions.

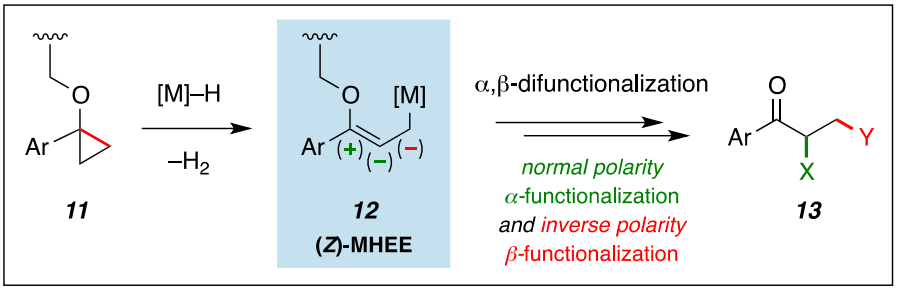


Figure 2.4 Catalytic metallo homoenolate-enol ether through net oxidative inverse polarity C–C activation of cyclopropanols

Significant advancement on carbon-silicon (C–Si) bond formation has been made for production of environmentally sustainable materials and bioactive molecules. [87-88] Despite the importance, a very few catalytic methods have been developed for generally applicable, catalytic silylation by non-polar C–C σ-bond activation.[89-91] In parallel with extensive recent efforts on the development of a unactivated bond-activation catalysis, we recently reported first, redox-neutral, catalytic α-selective C–C silylation protocol using cyclopropyl acetates **2-1** to access unprecedented, 5-membered silicon-containing heterocycles, dioxasilines **2-3**, summarized in Figure 2.5. [92] The observed umpolung α–regioselectivity through reversal of the cyclopropanol polarity is opposed to well-established β-selective functionalization of cyclopropanols (**3** to **4**, Figure 2.1).[51-54, 74] Notable features of this method are two-fold: (1) Only redox-neutral, α- and

β-silylation products [**2-3** (major) and **2-4** (minor), respectively] were produced among possible two pairs of constitutional isomers (i.e., redox-neutral products **2-3** and **2-4**; net oxidation products **2-5** and **2-6**) (Figure 2.5, middle). (2) Our preliminary mechanistic studies suggested that the reaction entirely proceeds through a Rh^{III} cycle (Figure 2a, bottom); the C–C activation is the turn-over determining step, achieved by a direct cross-metathesis between Si–Rh^{III} comprising electron-poor, bidentate $Tp^{(CF3)2}Na(THF)$ supporting ligand and the C–C bond to give the intermediate **15** via **14**. In any cases, net oxidative C–C silylation reactions to afford **12** and **13** have never been observed.

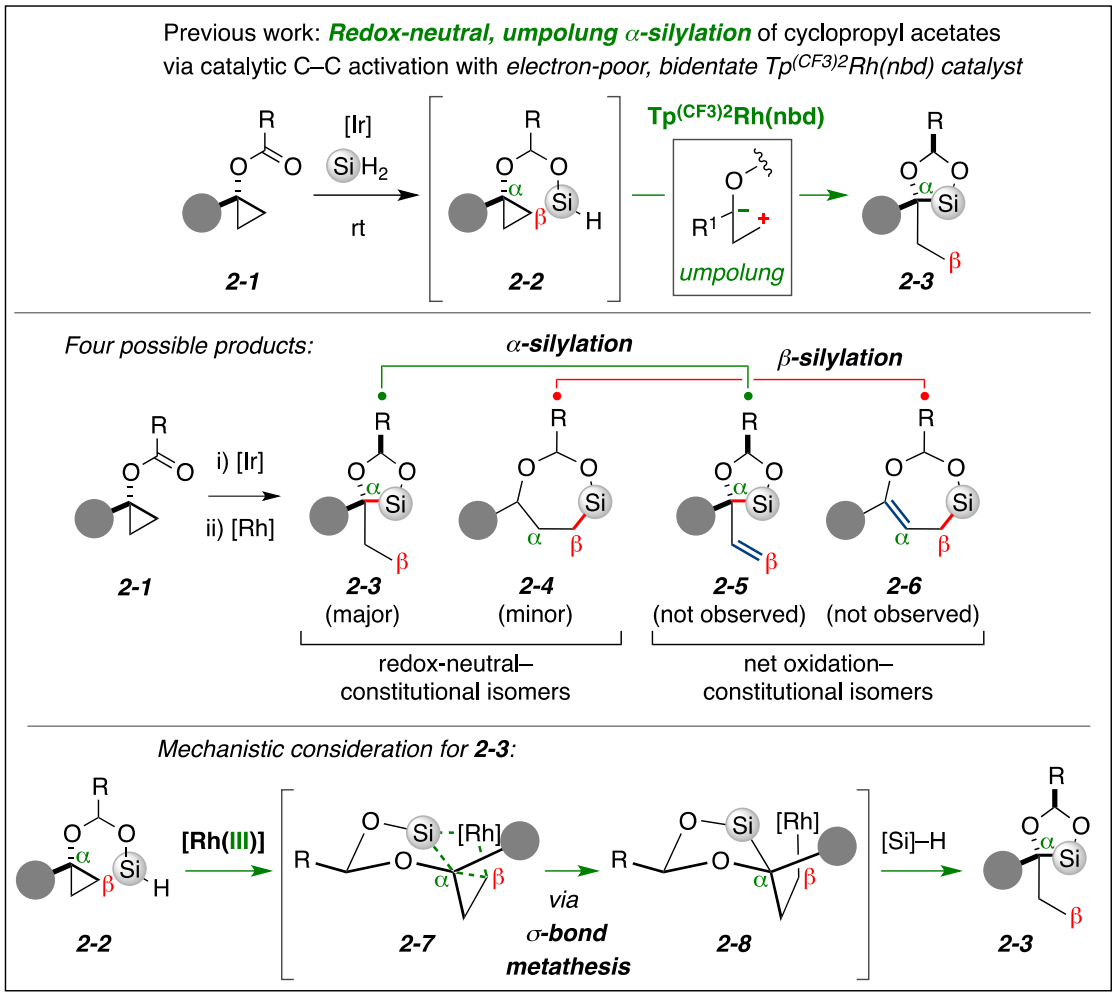


Fig. 2.5 Strategy for catalytic redox-neutral and net oxidative C–C activations

To achieve net oxidative silylation of cyclopropanol derivatives, we have developed catalytic

net oxidative β-C–C activation of **11** to formally generate the MHEE **12**. This strategy can provide chromatographically stable, 7-membered silicon-containing heterocycles, dioxasilepines **2-6**, uniquely holding both β-silyl and *Z*-vinyl acetal moieties (Figure 2.6, top). Our initial hypothesis on achieving the catalytic net oxidative C–C silylation was depicted in Figure 2b, middle. (1) The regioselectivity of the process can be altered by use of more electron-rich metal catalyst for a facile C–C metal insertion (cf., direct cross-metathesis). (2) Net oxidative C–C activation can be accessed through implementing more dissociable, monodentate supporting ligand for facile β-H elimination. To this end, the previously used electron-poor, bidentate $Tp^{(CF3)2}Na(THF)$ ligand was replaced with electron-rich, monodentate phosphine ligand. However, it was still elusive whether the previously observed intramolecular donor-acceptor interaction between an electron-poor rhodium center and an neighboring π bond, which is key to the Rh–(C–C) agostic interaction[62,93] for the C–C activation, can be established with an electron-rich rhodium center (Figure 2.6, middle). If successful, the reaction can proceed through a Rh^{I}–Rh^{III}–Rh^{I} cycle. Specifically, a Si–Rh^{I} intermediate inserts to a C–C bond to produce a putative rhodacyclobutane intermediate **2-12** (Rh^{III}), and a highly selective Si–C(β) reductive elimination to an alkyl Rh^{I} species **2-13** and succeeding β–H elimination can afford **2-6** and Rh^{I}–H (Figure 2.6, bottom). Since potential β-H elimination within **2-12** is not feasible due to lack of periplanar β-hydrogen, two alkyl rhodium species, i.e., **2-8** (Figure 2.5, bottom) and **2-13** (Figure 2.6, bottom) can be only formed by two competing reductive eliminations. For a catalyst turn-over, an electron-rich rhodium center coordinated with more dissociable, monodentate ligand facilitates a β-H agostic interaction with the metal center to accelerate the rate of β-H elimination, leading to **2-6**.

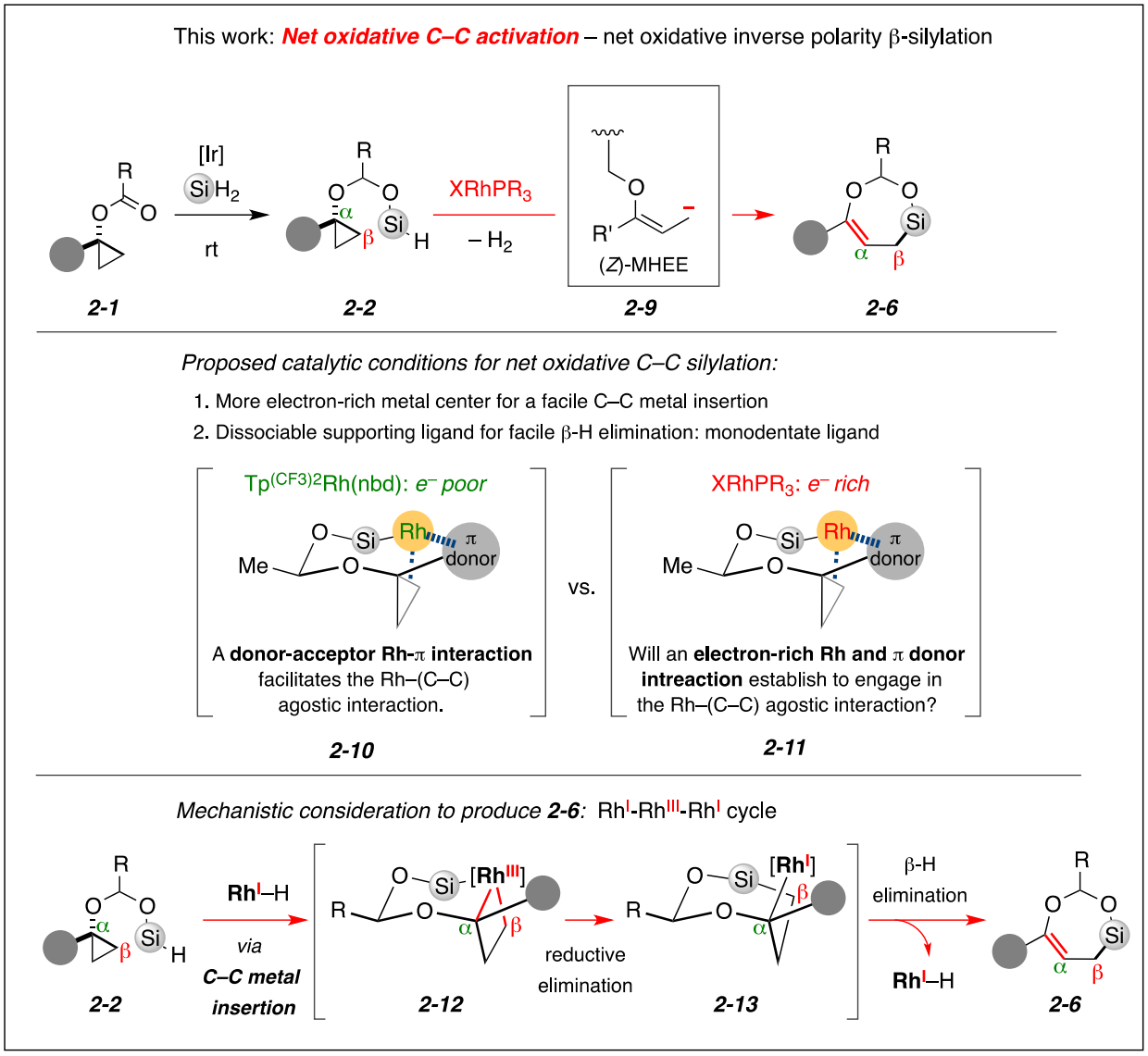


Figure 2.6 Strategy for catalytic redox-neutral and net oxidative C–C activations

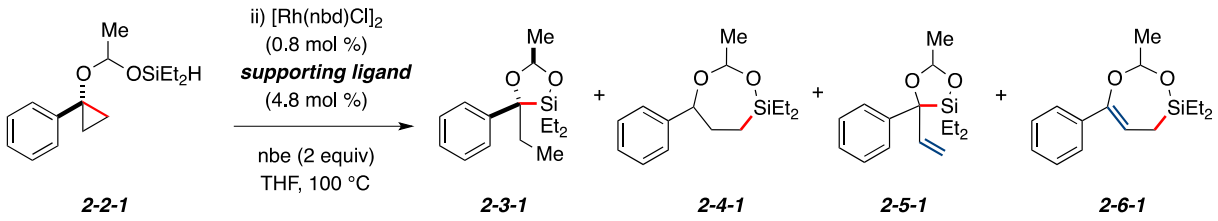
2.4 Reaction optimization study on rhodium-catalyzed, net oxidative β-C–C silylation of cyclopropyl acetates.

2.4.1 Ligand screening

We began our study to find out catalytic conditions to give **2-6**. Phenyl-substituted cyclopropyl hydrosilyl acetal **2-2-1** was first conveniently prepared through Ir-catalyzed hydrosilylation of corresponding phenylcyclopropyl acetate **2-1-1** in nearly quantitative yield (Figure 3). A range of monodentate phosphine supporting ligands were examined in the

presence of $[Rh(nbd)Cl]_2$ (nbd: norbornadiene) and norbornene (nbe). The reactions produced two pairs of constitutional isomers (**2-3-1**, **2-4-1**, **2-5-1**, **2-6-1**), as determined by ^1H NMR spectroscopic and GC-MS spectrometric analyses (Table 2.1). Generally, rhodium catalysts based upon trialkyl phosphines (PR_3) and dialkylmonoaryl phosphines ($PArR_2$) predominantly effected the redox-neural C–C silylation to provide α-silylation **2-3-1** as major (shown in Table 2.1).[94-95]

Table.2.1 Reaction optimization study on rhodium-catalyzed, net oxidative β-C–C silylation



2-2-1 *2-3-1* *2-4-1* *2-5-1* *2-6-1*

entry	supporting ligand	**2-3-1**(%)[a]	**2-4-1**(%)[a]	**2-5-1** (%)[a]	**2-6-1** (%)[a]
1	P^tBu_3	16	12	7	8
2	Ad_2PBu	52	6	21	7
3	PCy_3	55	13	8	7
4	JohnPhos	67	16	7	4
5	RuPhos	49	5	2	6
6	XPhos	57	14	5	6
7	SPhos	62	17	4	4
8	PPh_2Cy	6	3	8	81
9	PPh_2Me	5	2	8	85
10	PPh_2Et	4	2	8	86
11	PPh_2Bn	15	2	7	76
12	$P(4OMePh)_3$	0	0	0	91
13	$P(furyl)_3$	30	11	13	57
14	PPh_3	21	36	37	41

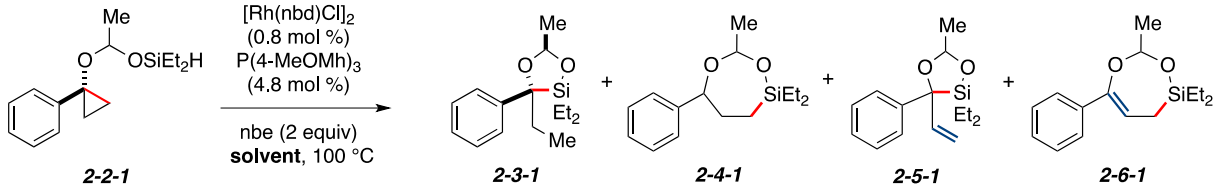
[a]Yields were determined by ^1H NMR spectroscopy utilizing an internal standard (mesitylene). A diastereomeric ratio of **2-5-1** was not determined.

Switching ligand to monoalkyldiaryl phosphines (PAr_2R) and electron-rich triaryl phosphines (PAr_3) furnished cyclic □-silyl *Z*-vinyl acetals **2-6-1** as major. Remarkably, $P(4\text{-MeOPh})_3$ ligand associated with rhodium effected the β-C–C silylation in a dehydrogenative fashion to provide **2-6-1** as a sole product. In all cases exceptional chemoselectivity was exhibited, where potential competing arene and cyclopropyl C–H silylations were not observed.

2.4.2 Solvent screening

We initially screened ligands with the "THF" as the solvent, we wonder if there is significant impact on yield by the choice of solvent (Table 2.2). Solvents routinely utilized in catalytic reactions such as CH_2Cl_2, PhH, $PhCH_3$, and Me-THF were employed in solvent screening. Interestingly THF (91% yield, entry 5) was superior to the rest of the solvents.

Table 2.2. Solvent Screening



2-2-1 *2-3-1* *2-4-1* *2-5-1* *2-6-1*

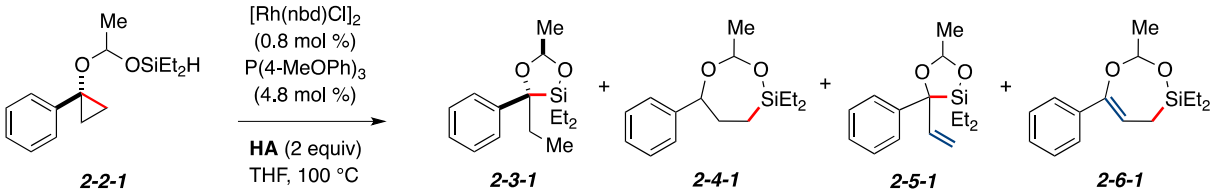
entry	solvent	**2-3-1**(%)[a]	**2-4-1**(%)[a]	**2-5-1** (%)[a]	**2-6-1** (%)[a]
1	CH_2Cl_2	2	0	0	17
2	PhH	6	8	0	9
3	$PhCH_3$	2	0	0	12
4	Me-THF	0	0	0	42
5	THF	0	0	0	91

[a]Yields were determined by ^{1}H NMR spectroscopy utilizing an internal standard (mesitylene). A diastereomeric ratio of **2-5-1** was not determined

2.4.3 Evaluation of hydrogen acceptors

We have screened various hydrogen acceptors to test impact on yield (Table 1.3). Hydrogen acceptors such as NBE, NBD, cyclohexene, cycloheptene, cyclopentene, cyclooctene, and 1,5 COD were employed in hydrogen acceptors screening. Interestingly THF (91% yield, entry 6) was superior to the rest of the hydrogen acceptors.

Table 2.3. Evaluation of Hydrogen Acceptors



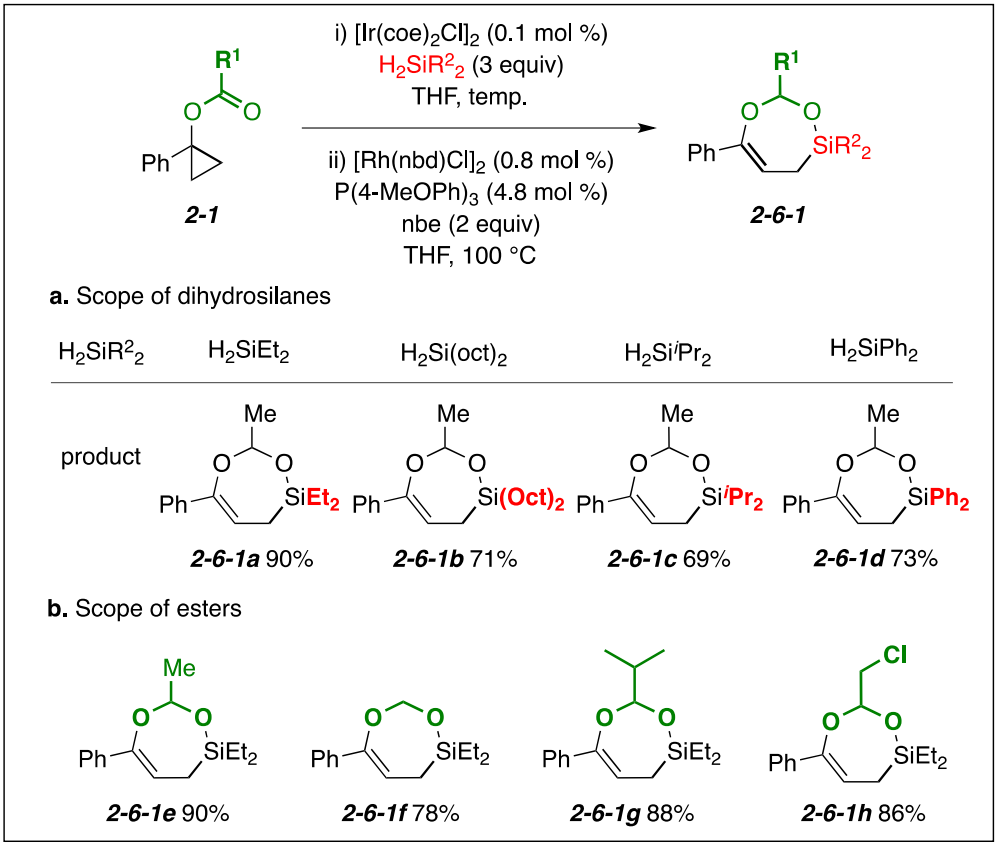
entry	HA	relative ring strain[S1]	**2-3-1**(%)[a]	**2-4-1**(%)[a]	**2-5-1** (%)[a]	**2-6-1** (%)[a]
1		2.5	2	0	0	16
2		6.7	12	2	3	18
3		6.8	5	12	1	26
4		7.4	0	1	0	21
5		13.3	0	7	0	86
6		27.2	0	0	0	91
7		34.7	0	8	0	45

[a]Yields were determined by ^{1}H NMR spectroscopy utilizing an internal standard (mesitylene). A diastereomeric ratio of **2-5-1** was not determined

2.5. Scope of dihydrosilanes and esters

We first investigated the impact of hydrosilyl acetals driven from cyclopropyl acetates **2-1** on the C–C silylation. Sterically varied dialkyl-substituted dihydrosilanes [H_2SiEt_2, $H_2Si(oct)_2$, $H_2Si^iPr_2$] gave the **2-6-1a**, **2-6-1b**, and **2-6-1c** in moderate to excellent yields (Table 1a). Specifically, the Ir-catalyzed ester hydrosilylation of **2-1** with those silanes generally deliver the corresponding hydrosilyl acetals in nearly quantitative yields. However, net oxidative C–C silylation with sterically demanding dioctyldihydrosilane and diisopropyldihydrosilane afford **2-6-1b**, and **2-6-1c** in moderate yields. Diphenyldihydrosilane also underwent sequential Ir and Rh catalysis to provide **2-6-1d** in 73% yield.

Table 2.4. Scope of dihydrosilanes and esters[a]



[a]Conditions: i) **8** (0.2 mmol), rt. Yields are for isolated material over a single-pot, two-step sequence from **8**. bi) 80 °C, 24 h. ci) 80 °C, 24 h, ii) 24 h.

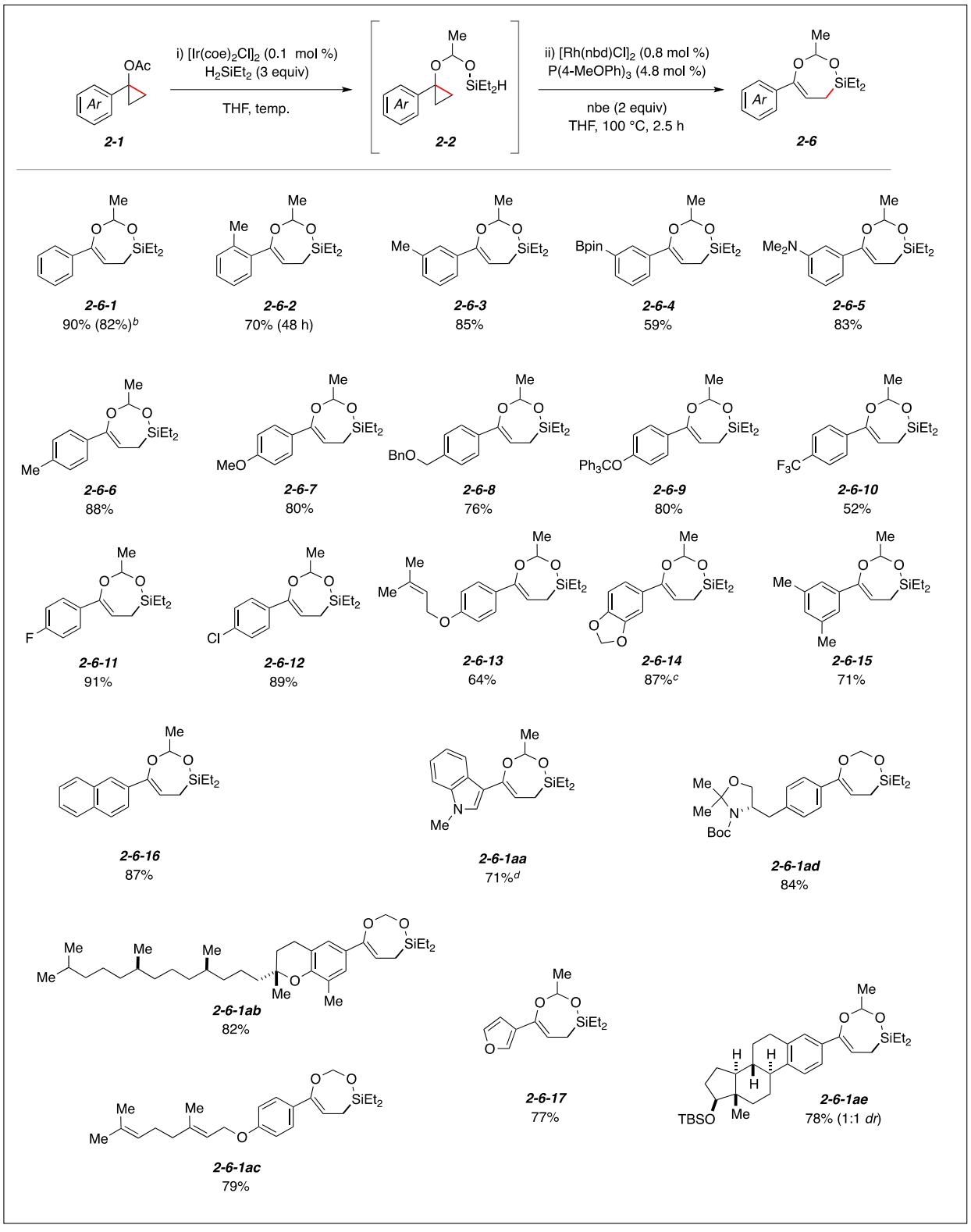
Next, we examined C–C silylation varying the ester substituents. Ir-catalyzed ester hydrosilylation of sterically and electronically differentiated cyclopropyl acetates afforded hydrosilyl acetals (Table 2.4). As demonstrated in our previous traceless acetal-directed arene C–H silylation,[100-101] sterically less encumbered esters underwent the dehydrogenative β-C–C silylation (68-84%) efficiently. Sterically demanding ester and electron-deficient ester exhibited significantly slower kinetics of hydrosilylation (12 h), but the C–C silylation of those two hydrosilyl acetals showed comparable rates with substrates.

2.6. Scope of dioxasilepines

We lastly examined the scope of aryl-substituted cyclopropyl acetates was examined (Table 2.5). A range of substrates **2-1** were converted to the corresponding dioxasilepines **13** with moderate to excellent yield (52–91%). The product selectivity of the reaction was exceptional and a high level of chemoselectivity was achieved (no arene and cyclopropyl C_{sp2}–H silylation). The sterically hindered *ortho*-substituted substrate **2-6-2** required an extended reaction time (48 h), to be fully transformed to **2-6-2**. However, aryl-substituted cyclopropyl acetates bearing the *meta or para*-substituent generally furnished **2-6-3** to **2-6-13** within 2.5 h. Although disubstituted substrates readily participated in the catalytic C–C silylation to deliver **2-6-13** and **2-6-15**, in the case of **2-6-13** we note that it was crucial to use a slight excess of Rh catalyst (1.2 mol %). Relatively good functional group tolerance was observed, including boronic ester (**2-6-4**), amine (**2-6-5**), ethers (**2-6-7** to **2-6-9**), trifluoromethyl (**2-6-10**), aryl halides (**2-6-11**, **2-6-12**), alkene (**2-6-13**), acetal (**2-6-14**), 3,5-dimethyl (**2-6-15**), naphthalene (**2-6-16**), furan (**2-6-17**), and indole (**2-6-1aa**). Substrates having a substituted cyclopropyl ring did not undergo the C–C silylation, presumably due to steric impediment between an incoming catalyst architecture and a substituent in the ring. Also, substrates with aliphatic systems were unsuccessful in reaction conditions and only starting materials were recovered even at elevated

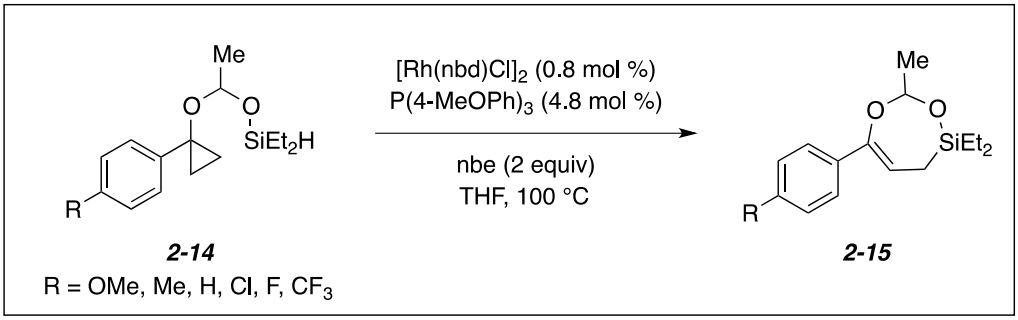
temperatures. Finally, to identify whether this catalytic net oxidative β-C–C silylation process would be applicable to the late-stage modification of bioactive molecules to prepare their biologically relevant analogues, cyclopropyl acetates derived from δ–tocopherol (vitamin E), tyrosine (amino alcohol), geraniol (terpenoid), and estradiol (steroid) were subjected to the reaction conditions. Gratifyingly, these reactions afforded the corresponding dioxasilepines (**2-6-1ab**-**2-6-1ae**) with moderate to good yields and exclusive β-regioselectivity and excellent chemo- and product-selectivity were achieved.

Table 2.5 Scope of dioxasilepines



2.7 Mechanism Studies

2.7.1 Hammett Study of Dioxasilolanes



2-14

R = OMe, Me, H, Cl, F, CF_3

2-15

We performed the Hammett study to understand a linear free-energy relationship of a net oxidative C–C silylation mechanism (Figure 2.7). The rate acceleration by electron-withdrawing groups was observed in the process. Specifically, the ρ value of 0.95 indicates no appreciable accumulation of the electron density in the transition state of the C–C cleavage step. The results infer that the M-π coordination is not likely the turnover-determining step, but increasing the electron-withdrawing nature of the aryl moiety would rather facilitate the cleavage of the neighboring cyclopropyl C–C bond.

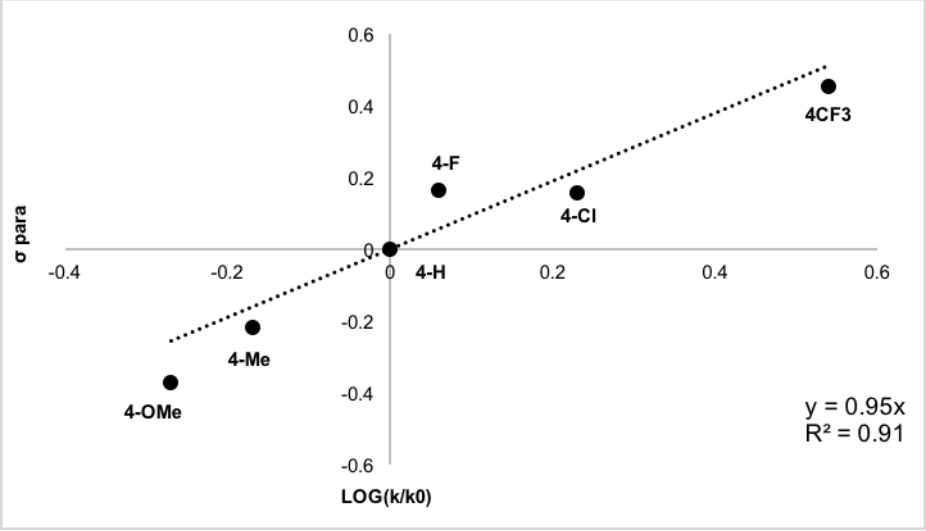


Figure 2.7 Hammett plot of dioxasilepines.

2.7.2 Deuterium-labelling studies with tetradeuterated cyclopropane

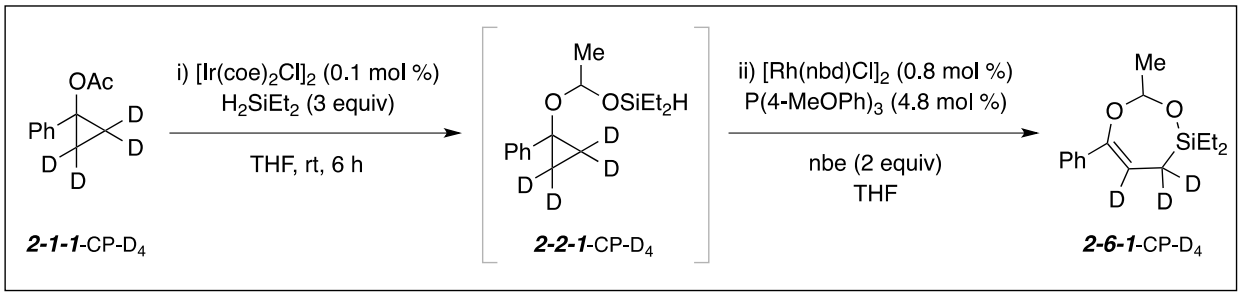


Figure 2.8 Deuterium-labelling studies with tetradeuterated cyclopropane

We have performed labelling experiments with tetradeuterated cyclopropyl hydrosilyl acetal and a fully deuterated phenyl group-substituted hydrosilyl acetal and this conclude that no obvious cyclopropyl and arene C–H cleavage occurs in the course of the C–C silylation (Figure 6b and 6c, respectively). We then conducted the kinetic isotope effect (KIE) study with **2-1-1**-CP-H_4 and **2-1-1**-CP-D_4 in a single vessel (Figure 6d). The reaction afforded inverse secondary KIE.

2.7.3. Deuterium-labelling studies with a pentadeuterated phenyl cyclopropanoate

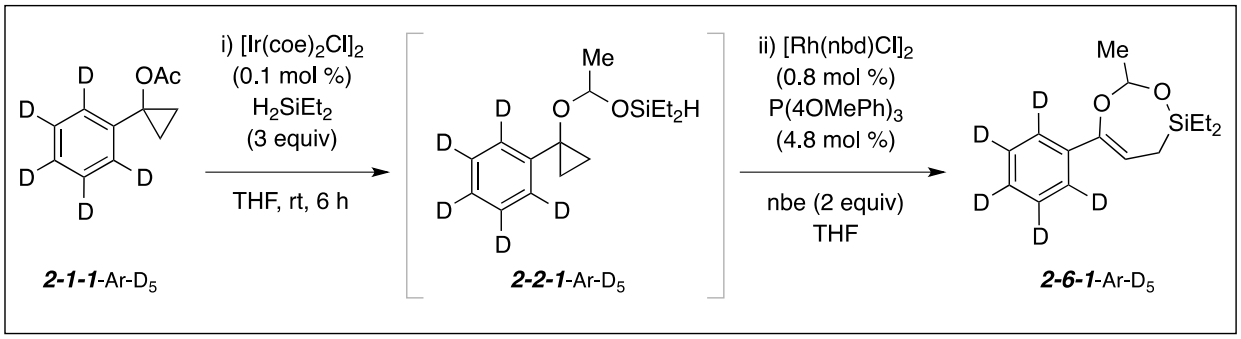


Figure 2.9. Deuterium-labelling studies with a pentadeuterated phenyl cyclopropanoate

We have performed labelling experiments fully deuterated phenyl group-substituted hydrosilyl acetal concludeand this concluses that no obvious arene C–H cleavage occurs in the course of the C–C silylation (Figure 2.9).

2.7.4. Kinetic isotopic effect (KIE) study.

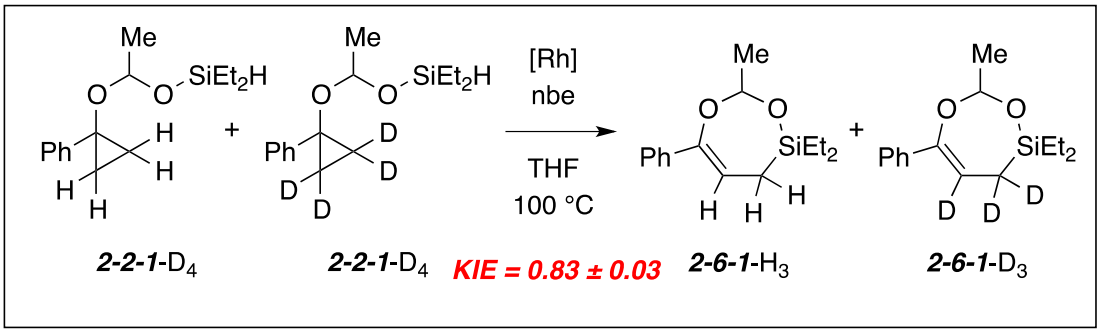


Figure 2.10. Kinetic isotopic effect of dioxasilepines

We then conducted the kinetic isotope effect (KIE) study with **2-2-1**-CP-H_4 and **2-2-1**-CP-D_4 in a single vessel (Figure 2.9). The reaction afforded inverse secondary KIE. These results along with the Hammett studies described above suggest that the turnover-determining step is likely the C–C cleavage. We conducted the kinetic isotope effect (KIE) study with **-2-1**-CP-H_4 and **2-2-1**-CP-D_4 in a single vessel. The reaction afforded inverse secondary KIE (0.83 ± 0.03).

2.8. Proposed mechanism

Based on our preliminary mechanistic studies and observations the plausible mechanism accounting for formation of two net oxidation products, dioxasilepines **2-6** and its constitutional isomer **2-4** and two redox-neutral counterparts **2-2** and **2-3**, through C–C silylation of cyclopropyl hydrosilyl acetals is depicted in Figure 5. The requisite intermediate Rh^{I}–H **B** for the oxidative addition of a C–C bond to the rhodium center is generated by two organometallic steps; oxidative addition of hydrosilyl acetals **2-2** to the Wilkinson-type precatalyst generates Rh^{III}–silyl hydride **A**, which was identified as a major species observed through ^{1}H and ^{31}P NMR spectroscopy in the presence or absence of norbornene.[96-97] A subsequence of reductive elimination of Si and Cl gives **B** and chlorosilane **C**.[98-99] Then, three step sequence involving olefin migratory insertion (to **D**), oxidative addition of **2-2 (**to **D**), and reductive elimination produce **F** and norbornane (detected in ^{1}H NMR spectroscopy). The adjacent π donor is

indispensable for the C–C metal insertion to provide a putative [6,4]-bicyclic fused rhodacyclobutane intermediate **G**; alkyl-substituted cyclopropyl hydrosilyl acetals lacking a π donor were not able to undergo the C–C silylation, recovering a starting material cleanly. As observed in our previous study on redox-neutral C–C silylation, the rhodium-π interaction is key to the successful C–C silylation, presumably by developing productive Rh–(C–C) agostic interaction in **F**. Then, the reductive elimination of Si and less hindered carbon center [e.g., C(β)] in **G** gives the alkylrhodium species **H** (α-metallation). Because **H** bearing an electron-rich rhodium coordinated with more dissociable, monodentate phosphine ligand undergoes β-H elimination to produce **2-6** and regenerate Rh^{I}–H **B**. σ-bond metathesis of **H** with **2-2** can give the redox-neutral dioxasilepane **2-4**. In the context of formation of their constitutional isomers (**2-3** and **2-5**) the intermediate **G** undergoes competing reductive elimination of Si and more hindered carbon center [e.g., C(α)] to give the alkyl rhodium species **I** (β-metallation). Then either σ-bond metathesis of I with 9 or β-H elimination of I provides **2-3** and **2-11**, respectively.

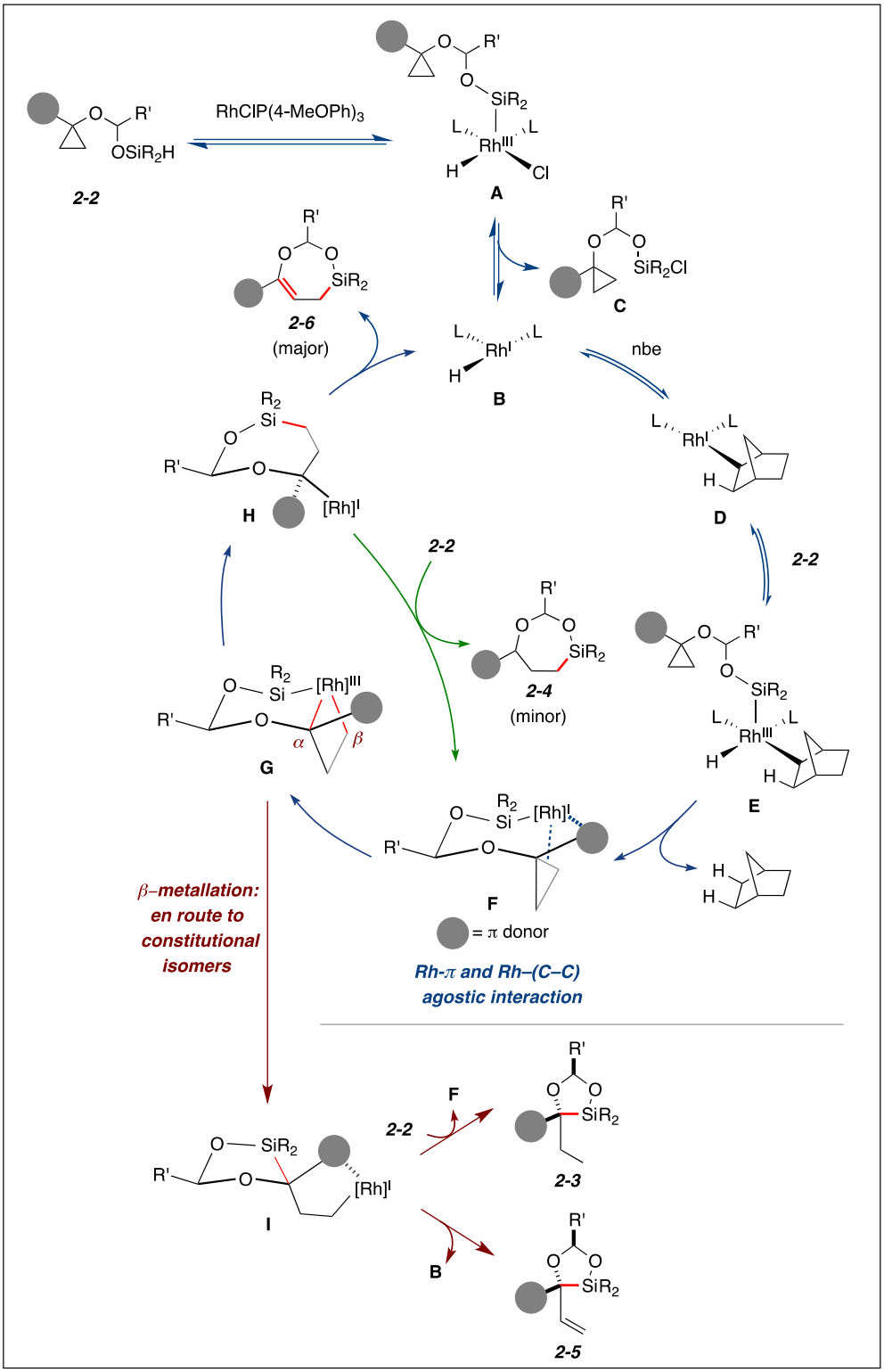


Figure 2.11. Proposed mechanism for dioxasilepines

2.9 Synthetic applications of dioxasilepines

These dioxasilepines **2-6** are constituted by two interconnected groups, a β-silyloxy moiety and *Z*-vinyl acetal. They can generally serve as stable and chromatographically isolable β-silyl enolate equivalents. In detail, a Lewis base activation of the silane moiety in **2-6** affords putative, penta-coordinated silicon species **2-16** (Figure 2.12). This triggers irreversible ring-opening of the activated cyclic vinyl acetal **2-16** to give β-silyl metallo enolate **2-17** and aldehyde **2-18**, which can further react with nucleophile to produce alkoxide **2-19**.[100, 102-103] Upon work-up the inverse polarity β-functionalization provides β-silyl ketones **2-20**. This approach is notable, because it affords not only β-silyl ketones, but also diversely functionalized β-silyl ketones can be prepared with ease through a post-introduction of an array of new substituents to the silyl moiety. This feature substantially improves the scope of silanes, as opposed to a limited silane scope found in many silylation chemistry.[92, 100] To this end, upon treatment of **2-6-1** with MeLi and lithium acetylide β-silyl ketones **2-21** and **2-22** were produced in good yields, respectively (Figure. 2.12b). Furthermore, estrone-derived dioxasilepine **2-6-1f** was able to be converted to **2-23** (71% yield).

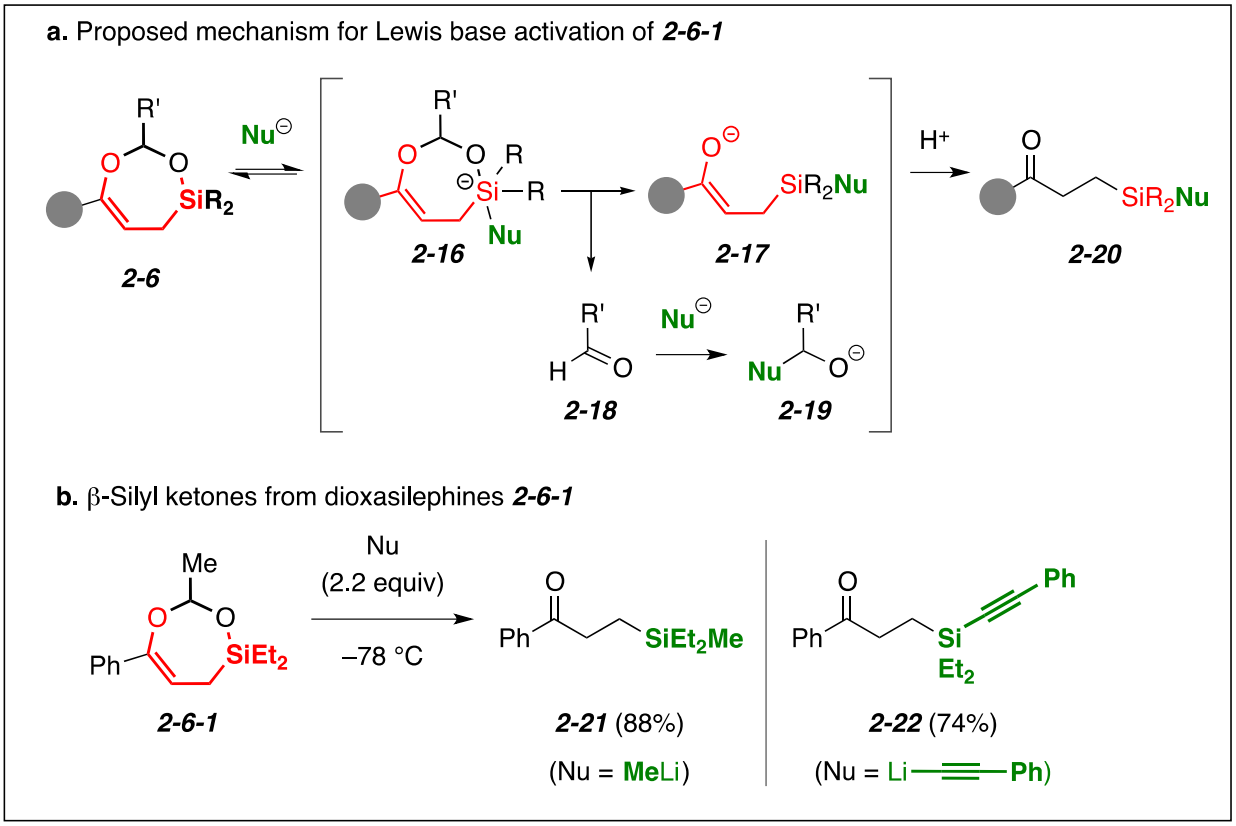


Figure 2.12. Dioxasilephines as β-Silyl ketones

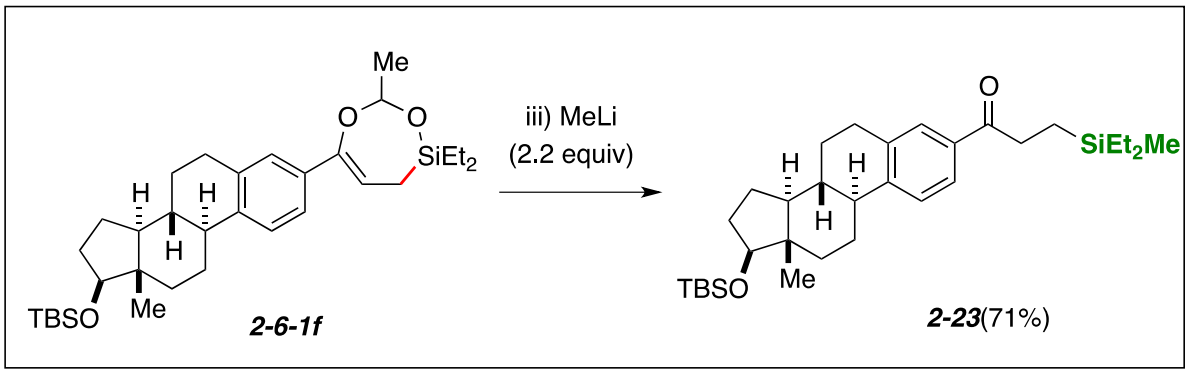


Figure 2.13. Synthetic applications on estrone-derived dioxasilepine

Furthermore, the rapid diversification nature of dioxasilepines **2-6** involving the β-silyl post-modification strategy can be applied for the copper-catalyzed azide-alkyne cycloaddition (CuAAC). The Click chemistry has been a valuable tool for efficient bioconjugation of small molecular spectroscopic probes to a wide range of biomolecular targets in chemistry, biology and

material sciences,[104-106] and stable and environmentally benign organosilanes make them suitable for their biological application. To do so, β-alkynylsilyl ketone **2-24** was prepared via net oxidative β-C–C silylation followed by addition of lithium acetylide in a single pot, and we demonstrated the CuACC between **2-24** and an azide-tagged fluorophore (i.e., **biotin-N_3**), which afforded triazole **2-25** in a good yield (86%) (Figure 2.14).

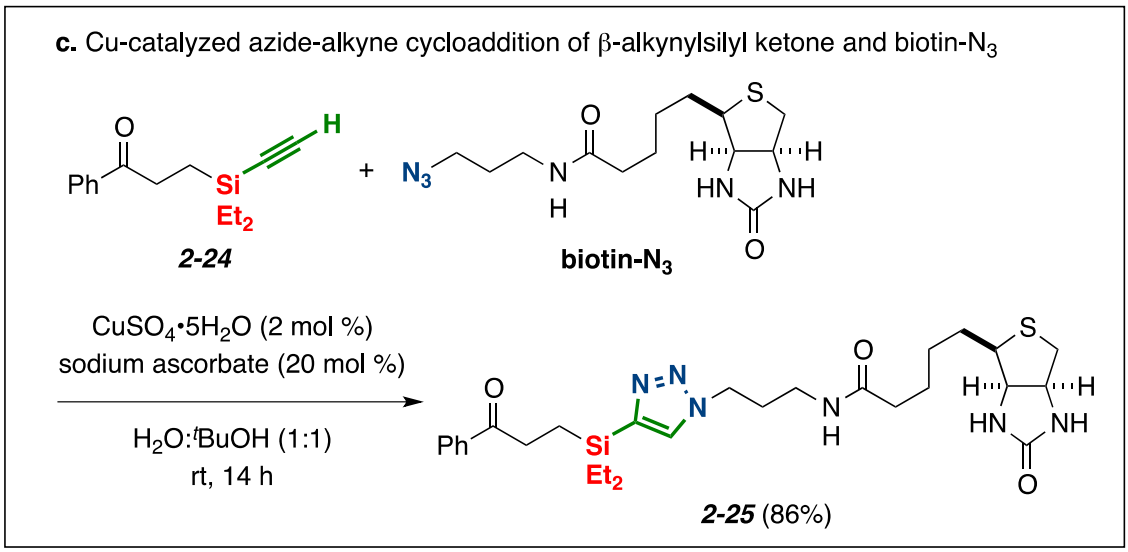


Figure 2.14. Cu-catalyzed azide-alkyne cycloaddition of β-alkynylsilyl ketone and biotin-N_3

2.9.1 α,β-Difunctionalized ketones from dioxasilephine

In contrast to traditional strategies involving C–C activation of cyclopropanols to provide mono-β-functionalized ketones, the net oxidative β-C–C silylation developed in this study leading to dioxasilepines **2-6** as MHEE equivalents are more versatile to prepare not only β-silyl ketones, but also α,β-difunctionalized ketones via the inverse polarity β-functionalization followed by the normal polarity α-functionalization in a rapid fashion. This aspect was demonstrated by several α-functionalization chemistries of **2-6-1**; a single-pot, ring-opening of **2-6-1** with MeLi, followed by Pd-catalyzed α-arylation, α-fluorination, and α-alkylation yielded α,β-difunctionalized ketones (**2-26** to **2-28**) in good yields (Figure 2.15a). Since a silyl moiety

can serve as hydroxy equivalent, desilylative oxidation of **2-6-1** gave β-hydroxy ketone **2-29** (86% yield), depicted in Figure 7b. Furthermore, the oxidative rearrangement of **2-6-1** with DMDO, followed by MeLi treatment afforded silyl *anti*-1,2-diol **2-30** (77% yield, 6:1 *dr*) (Figure 2.15b).

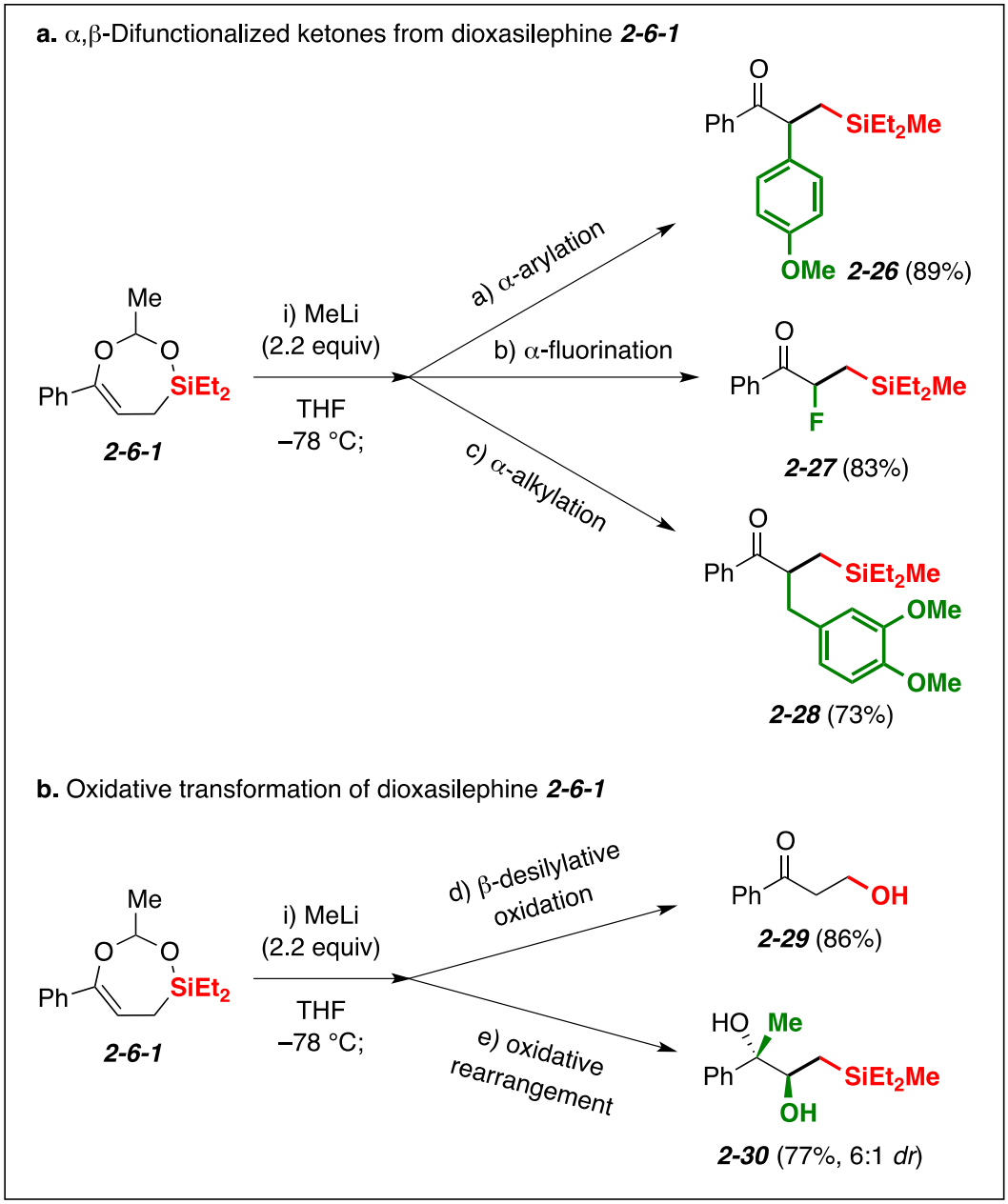


Figure 2.12. α,β-Difunctionalized ketones from dioxasilephine

2.10 Summery of Chapter 2.

We have developed a new strategy for generating metallo homoenolate enol-ether (MHEE) through catalytic net oxidative C–C activation of cyclopropyl acetates. The regio-, stereo-, and chemoselective inverse polarity, dehydrogenative β–silylation provided a new class of seven-membered silicon-containing heterocycles, dioxasilepines. This was achieved through highly efficient C–C metal insertion with electron-rich Wilkinson-type catalyst. Scope of dihydrosilanes, esters, and cyclopropyl acetates has been established. This includes several late-stage, net oxidative β–C–C silylation of biologically relevant molecules, and the versatility of dioxasilepines as ketone α,β-dianion equivalents was demonstrated to yield a range of α,β-difunctionalized ketones and diols harnessing several useful normal polarity α-functionalization reactions and oxidative transformations. In addition, an application of dioxasilepines toward bioconjugation chemistry was shown. Finally, preliminary studies to account for an associated mechanism for the net oxidative C–C activation suggest that the rhodium-π interaction entails for establishing the Rh–(C–C) agostic interaction and the succeeding C–C metal insertion is likely the turnover-determining step. This study underscores an importance of a choice of metal catalyst and an analysis of transition state geometry for the highly regio- and chemoselective C–C activation.

Appendix A: List of Abbreviations

δ: chemical shift (ppm)

μL: microliter

Ac: acetate

Ad: adamantyl

Ar: aryl group or substituent, general

Bn: benzyl

Bu: butyl

*t*Bu: tert-butyl

C: Celsius

calcd: calculated

cat.: catalyst, catalytic amount

COD: 1,5-cyclooctadiene

Cy: cyclohexyl

DCM: dichloromethane

Eq.: equation

equiv.: equivalent

Et: ethyl

g: gram

GCMS: gas chromatography mass spectrometry

h: hours

HRMS: high resolution mass spectrometry

Hz: hertz

IR: infrared spectroscopy

J: coupling constant, NMR spectroscopy

M: metal, general

M: molar

[M+]: molecular ion

Me: methyl

mg: milligram

MHz: megahertz

mL: milliliter

mmol: millimole

MW: molecular weight

min.: minutes

n/a: not applicable

NHC: *N*-heterocyclic carbene ligand

NMR: nuclear magnetic resonance spectroscopy

Appendix B: Experimental Procedures

General Experimental

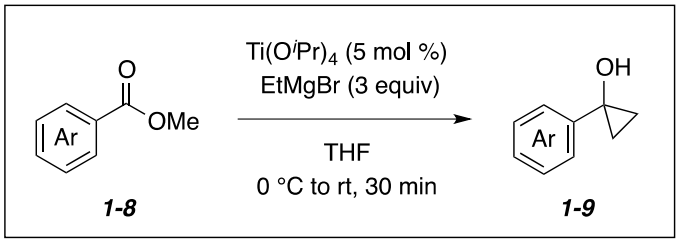
Reactions requiring anhydrous conditions were performed under an atmosphere of nitrogen or argon in a VAC glovebox or using standard Schlenk techniques with flame or oven dried glassware. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium and benzophenone. Triethylamine and pyridine were distilled from KOH. DMF and DMSO were stored over 4Å molecular sieves. All other solvents and reagents from the commercial sources were used as received. ^1H, ^2H, and ^{13}C NMR spectra were recorded on JEOL Eclipse Plus 500 (500 MHz) and JEOL ECX 300 (300 MHz) spectrometers. ^1H NMR chemical shifts are referenced to chloroform (7.26 ppm), THF-d_8 (1.72 ppm), and benzene-d_6 (7.16 ppm). ^2H NMR chemical shifts are referenced to chloroform (7.26 ppm) and benzene (7.16 ppm). ^{13}C NMR chemical shifts are referenced to $^{13}CDCl_3$ (77.23 ppm). The following abbreviations are used to describe multiplets: s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), m (multiplet), nfom (non-first-order multiplet), and br (broad). The following format was used to report peaks: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. ^1H NMR assignments are indicated by structure environment, e.g., CH_aH_b. Coupling constant analysis was guided by methods we have described elsewhere.[174] ^1H NMR and ^{13}C NMR were processed with iNMR software program. Infrared (IR) spectra were recorded on a Bruker Alpha-P FT-IR spectrometer using neat (for liquid compound) or a thin film from a concentrated DCM solution. Absorptions are reported in cm^{-1}. Only the most intense and/or diagnostic peaks are reported. MPLC refers to medium pressure liquid chromatography (25-200 psi) using hand-packed columns of Silasorb silica gel (20-45 µm, spherical, 70 Å pore size), a Waters HPLC pump, and a Waters R401 differential refractive index detector. High-resolution mass spectra (HRMS) were recorded in Electrospray ionization time-of-flight (ESI-TOF) mode using a Shimadzu LC/MS IT-TOF. Samples were introduced as solutions in mixed solution of methanol and methylene chloride (DCM). GC/MS data were

recorded on a Varian 450-GC/Varian 240-MS System. The methods used are noted parenthetically: 5025015 refers to 2 min @ 50 °C – 20 °C/min – 3 min @ 250 °C (a 50 °C initial temperature that was held for 2 minutes followed by a 20 °C/min ramp to a final temperature of 250 °C that was held for 3 minutes for a total run time of 15 minutes). 5029017 refers to: 2 min @ 50 °C – 20 °C/min – 3 min @ 290 °C. 5029019 refers to: 2 min @ 50 °C – 20 °C/min – 5 min @ 290 °C. 5032021 refers to: 2 min @ 50 °C – 20 °C/min – 5 min @ 320 °C. Analytical TLC experiments were performed on EMD Merck F254 plate, 250 μm thickness. Detection was performed by UV light or potassium phosphomolybdic acid, permanganate, *p*-anisaldehyde staining.

General Experimental Procedure: Chapter 1

B.1. General procedure for preparation of aryl cyclopropanoacetates:

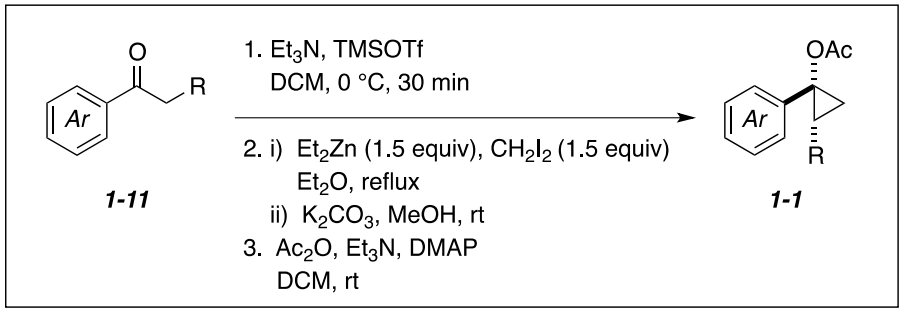
B.1.1 Preparation of cyclopropanols using the Kulinkovich reaction:



A flame-dried 100 mL round-bottom flask equipped with a stir bar was charged with esters **1-8** (5 mmol), THF (30 mL, 0.17 M) and titanium tetraisopropoxide (148 μL, 0.5 mmol). The resulting solution was cooled to 0 °C with an ice bath. Ethylmagnesium bromide (5 mL, 15 mmol, 3.0 M in Et_2O) was added dropwise over a period of 30 min, and the reaction mixture was warm to ambient temperature and stirred for 12 h. The progress of the reaction was monitored by thin-layer chromatography (TLC). The reaction was quenched with water. A precipitate was formed, and the solution was then filtered through a pad of Celite®. The solution was extracted with Et_2O, washed with water and saturated aqueous brine, dried over Na_2SO_4, and filtered

through a pad of Celite®. The resulting solution was concentrated under reduced pressure to afford crude cyclopropanols **1-9**, which were used directly to the next acetylation reaction.

B.1.2 Preparation of cyclopropanols using the Simmons-Smith reaction:



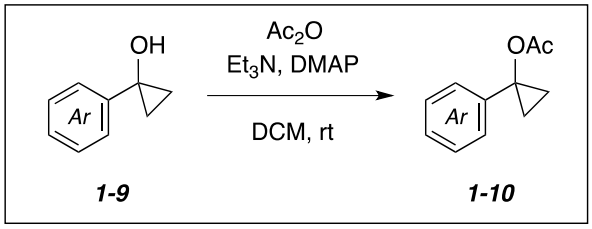
Ketones **1-11** (5 mmol), Et_3N (0.83 mL, 6 mmol), and DCM (15 mL, 1 M) were added to a flame-dried flask. The mixture was cooled to 0 °C, and TMSOTf (1.08 mL, 6 mmol) was slowly added to the mixture. The reaction was stirred for 30 min at 0 °C. The progress of the reaction was monitored by thin-layer chromatography (TLC). The reaction was quenched with saturated aqueous $NaHCO_3$. The solution was extracted with Et_2O, washed with water and saturated aqueous brine, dried over Na_2SO_4, and filtered through a pad of Celite®. The resulting solution was concentrated under reduced pressure to afford crude silyl enol ethers, which were used directly to the next cyclopropanation.

To a solution of silyl enol ethers (5 mmol) and diethyl zinc (7.5 mL, 7.5 mmol, 1 M in hexane) in Et_2O (4 mL) was added dropwise a solution of diiodomethane (0.61 mL, 7.5 mmol) in Et_2O (4 mL) over 1 h at 0 °C. The reaction was heated at reflux for 3 h to give a cloudy solution which was allowed to cool to room temprature and then quenched by the dropwise addition of pyridine (1.0 mL). The resulting suspension was filtered through a celite® pad, and the remaining solid was washed with Et_2O. After evaporation of volatiles, the crude materials were dissolved in MeOH (6 mL) followed by addition of K_2CO_3 (221 mg, 1.6 mmol). After being stirred for 30 min at room temperature, the reaction mixture was quenched by adding pH 9 buffer and

extracted with ethyl acetate. The organic layer was washed with saturated aqueous brine and dried over Na_2SO_4. The resulting solution was concentrated under reduced pressure to afford crude cyclopropanols, which were used directly to the next acetylation reaction.

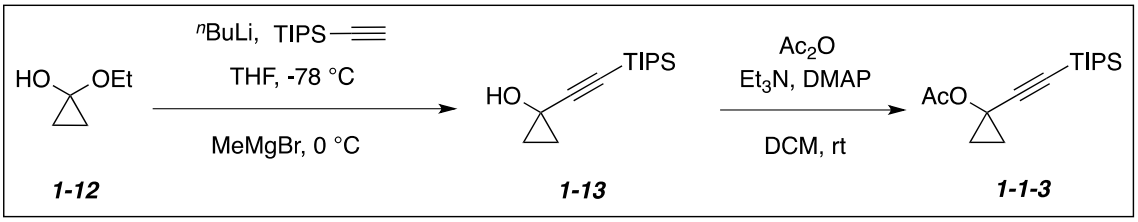
To a solution of the crude cyclopropanol (1.0 mmol), acetic anhydride (113 μL, 1.2 mmol), DMAP (6 mg, 10 mol %) in DCM (4 mL, 0.25 M), Et_3N (154 μL, 1.1 mmol) was added dropwise over 15 min. The reaction mixture was then stirred at rt for 3 h. The reaction was quenched by adding saturated aqueous $NaHCO_3$. After being stirred for 10 min, the reaction mixture was extracted with Et_2O. The organic layer was washed with water followed by saturated aqueous brine and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under reduced pressure to afford a brown oil, which was purified by column chromatography to give cyclopropanoate **1-1** as a yellow oil.

Acetylation of Cyclopropanols:



To a solution of cyclopropanol **1-9** (5 mmol), acetic anhydride (0.57 mL, 6 mmol), DMAP (61 mg, 10 mol%) in DCM (20 mL, 0.25 M), Et_3N (0.76 mL, 5.5 mmol) was added dropwise over 15 min. The reaction mixture was then stirred at rt for 3 h. The reaction was quenched by adding saturated aqueous $NaHCO_3$. After being stirred for 10 min, the reaction mixture was extracted with Et_2O. The organic layer was washed with water followed by saturated aqueous brine and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under reduced pressure to afford a brown oil, which was purified by column chromatography to give cyclopropanoates **1-10**.

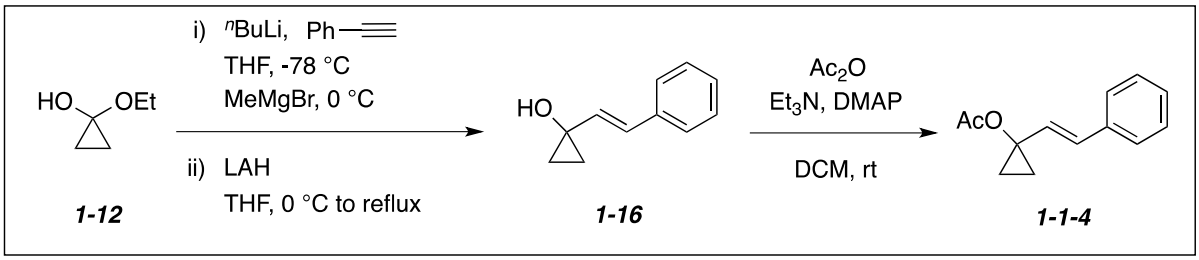
B.1.3 Preparation of alkynyl cyclopropanoate:



To a solution of 1-ethoxycyclopropanol **1-12** (102 mg, 1.0 mmol) in THF (3 ml) was added a 3 M solution of methylmagnesium bromide in Et_2O (420 μL, 1.26 mmol) at 0 °C. The suspension was stirred for 1 h at 0 °C. Meanwhile, to another solution of ethynyltriisopropylsilane (253 μL, 1.13 mmol) in Et_2O (0.5 mL, 2.2 M) was added dropwise a 2.6 M solution of *n*-butyllithium in THF (440 μL, 1.1 mmol) at –78 °C. The solution was stirred for 30 min at –78 °C and then cannulated into the suspension of magnesium salt at 0 °C. The mixture was slowly warmed to room temperature and then continued stirred at 40 °C for 16 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo* to afford alkynyl cyclopropanol **1-13** as a colorless oil, which was used directly to the next acetylation reaction.

To a solution of the crude cyclopropanol (1.0 mmol), acetic anhydride (113 μL, 1.2 mmol), DMAP (6 mg, 10 mol %) in DCM (4 mL, 0.25 M), Et_3N (154 μL, 1.1 mmol) was added dropwise over 15 min. The reaction mixture was then stirred at rt for 3 h. The reaction was quenched by adding saturated aqueous $NaHCO_3$. After being stirred for 10 min, the reaction mixture was extracted with Et_2O. The organic layer was washed with water followed by saturated aqueous brine and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under reduced pressure to afford a brown oil, which was purified by column chromatography to give cyclopropanoate **1-1-3** as a yellow oil.

B.1.4 Preparation of alkenyl cyclopropanoate:



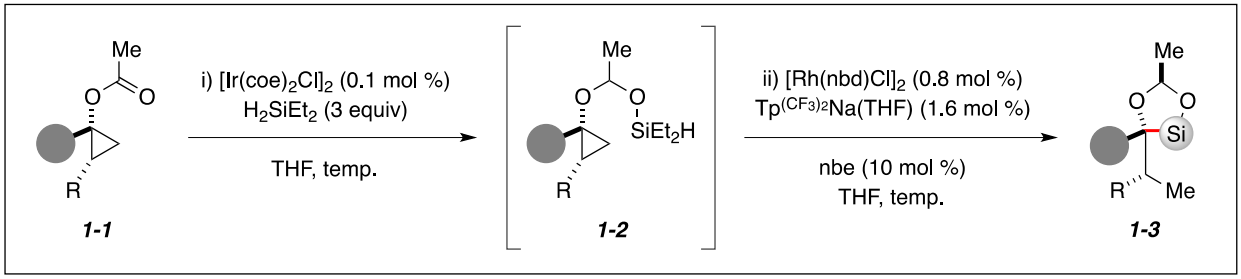
To a solution of 1-ethoxycyclopropanol **1-12** (102 mg, 1.0 mmol) in THF (3 ml) was added a 3 M solution of methylmagnesium bromide in Et_2O (420 μL, 1.26 mmol) at 0 °C. The suspension was stirred for 1 h at 0 °C. Meanwhile, to another solution of phenylacetylene (124 μL, 1.13 mmol) in Et_2O (0.5 mL, 2.2 M) was added dropwise a 2.6 M solution of *n*-butyllithium in THF (440 μL, 1.1 mmol) at –78 °C. The solution was stirred for 30 min at –78 °C and then cannulated into the suspension of magnesium salt at 0 °C. The mixture was slowly warmed to room temperature and then continued stirred at 40 °C for 16 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to afford alkynyl cyclopropanol as a colorless oil, which was used directly to the next reduction reaction.

To a suspension of LAH (38 mg, 1.0 mmol) in THF (1.0 mL, 1.0 M) was added the crude alkynyl cyclopropanol (1.0 mmol) in THF slowly at 0 °C over 15 min. After the mixture had been refluxed for 2 h, the reaction mixture was quenched with cold water. The organic layer was decanted and extracted thoroughly with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to afford alkenyl cyclopropanol **1-16**, which was used directly to the next acetylation reaction.

To a solution of the crude cyclopropanol (1.0 mmol), acetic anhydride (113 μL, 1.2

mmol), DMAP (6 mg, 10 mol %) in DCM (4 mL, 0.25 M), Et_3N (154 μL, 1.1 mmol) was added dropwise over 15 min. The reaction mixture was then stirred at rt for 3 h. The reaction was quenched by adding saturated aqueous $NaHCO_3$. After being stirred for 10 min, the reaction mixture was extracted with Et_2O. The organic layer was washed with water followed by saturated aqueous brine and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under reduced pressure to afford a brown oil, which was purified by column chromatography to give cyclopropanoate **1-1-4** as a yellow oil.

B.2. General procedure for C–C silylation to prepare dioxasilolanes 1-3:

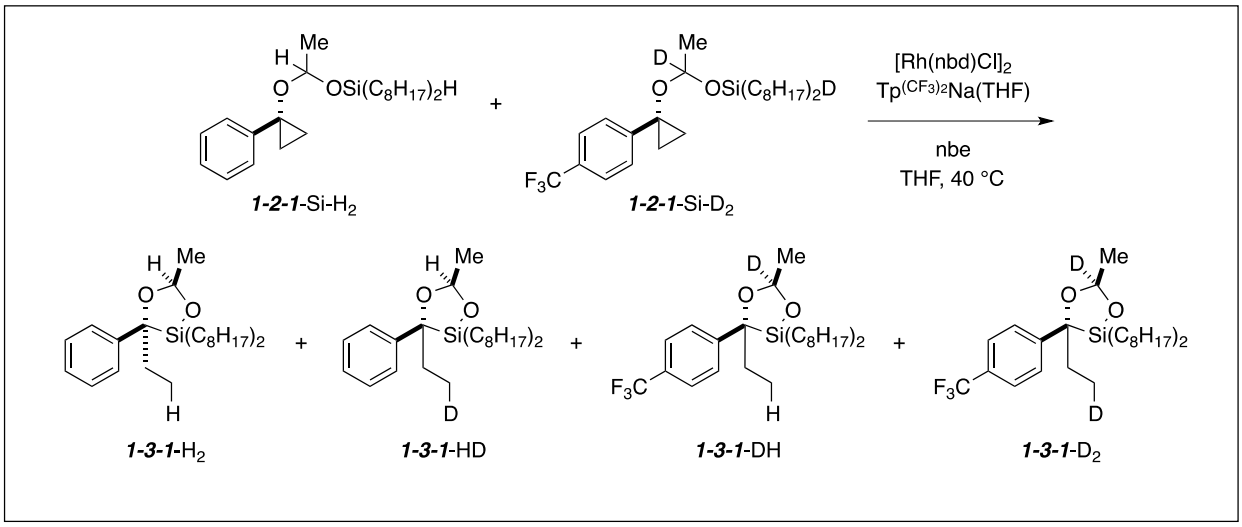


$[Ir(coe)_2Cl]_2$ (0.1 mol %) and cyclopropanoacetate **1-1** (0.2 mmol) were dissolved with THF (0.6 mL, 0.33 M). Diethylsilane (3 equiv) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was stirred for 12 h at rt or 2 h at 70 °C. The volatiles were removed *in vacuo* to afford the silyl acetal **1-2**, which were directly used for a subsequent reaction without further purification.

$[Rh(nbd)Cl]_2$ (0.7 mg, 0.8 mol%), $Tp^{(CF3)2}Na(THF)$ (2.3 mg, 1.6 mol%) and norbornene (1.9 mg, 10 mol %) were dissolved with THF (0.6 mL, 0.33 M). The crude silyl acetals **1-2** (0.2 mmol) was added to the mixture in one portion. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at rt or 100 °C unless mentioned otherwise (see Table 1 in Manuscriprt). The reaction progress was monitored by GC-MS spectrometry. The volatiles were removed *in vacuo*, and the resulting mixture was dissolved with pentane, filtered through a pad of Celite®, and concentrated *in vacuo* to afford the crude dioxasilolanes **1-3**, which

was purified by MPLC (hexanes/EtOAc =80:1, 5 mL/min).

B.3 Cross-over study:



1-2-1-Si-H_2 (0.1 mmol) and **1-2-1**-Si-D_2 (0.1 mmol) was added to a nitrogen purged Norell® pressure NMR-tube. A stock solution of $[Rh(nbd)Cl]_2$ (0.7 mg, 0.8 mol %), norbornene (1.9 mg, 10 mol %), and $^{(CF3)2}$TpNa(THF) (2.3 mg, 1.6 mol %) in THF (0.6 mL) and C_6D_6 (100 μL) were added to the NMR tube. The internal standard (mesitylene) was added to the mixture.

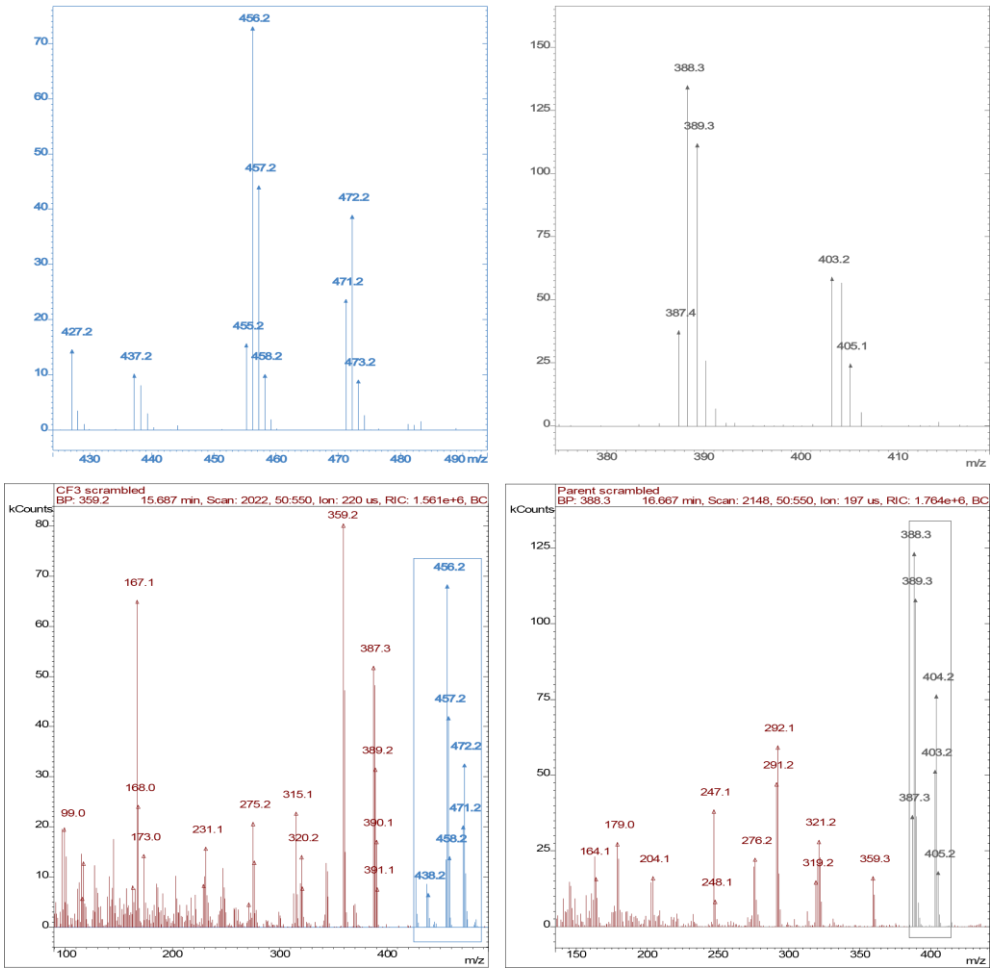
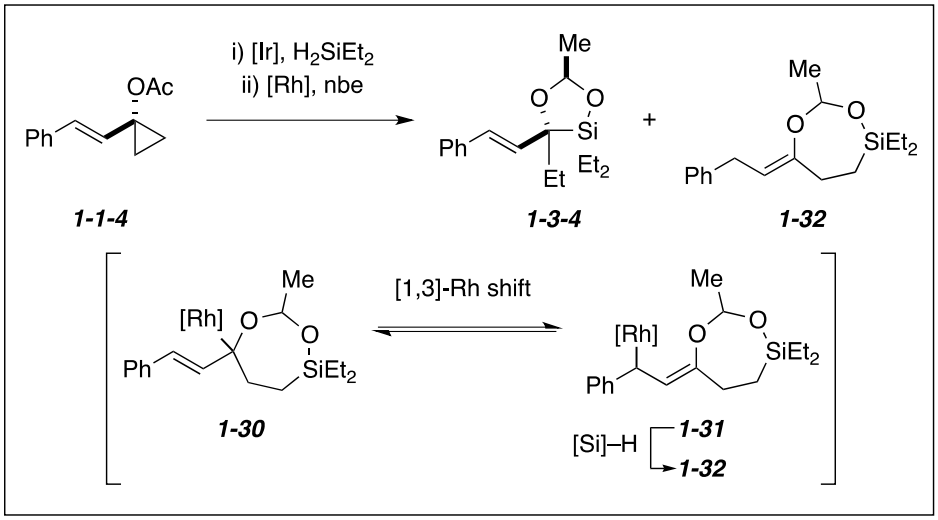


Figure 1 GC-MS analysis of the cross-over experiment between protiosilyl acetal and deuteriosilyl acetal.

To establish whether the final hydrogen transfer in the C–C silylation occurs intramolecularly or not, a cross-over experiment was performed with a 1:1 mixture of **1-2-1**-Si-H_2 and **1-2-1**-Si-D_2. The observation of all four possible dioxasilolanes (**1-3-1**-H_2, **1-3-1**-HD, **1-3-1**-D_2, and **1-3-1**-DH) by GC/MS mass spectrometry suggests that the final hydrogen delivery involves either □-bond metathesis or protonolysis with hydrosilyl acetal available in the reaction.

B.4. Alkene transposition adduct:



During the redox-neutral catalytic C–C silylation of **1-1-4** we made an observation on the alkene transposition adduct **1-32** (9% yield) along with **1-3-4** (79% yield) from **1-1-4**, suggesting that formation of the fully substituted alkylrhodium species **1-30** underwent [1,3]-rhodium shift to produce less hindered **1-31**. Thus, we can conclude that the fully substituted alkylrhodium **1-30** is responsible for formation of dioxasilepanes **1-4-1**.

B.5. NMR spectroscopic observations of the C–C silylation: Rh precatalyst preparation with $[Rh(nbd)Cl]_2$ and $Tp^{(CF_3)_2}Na(THF)$ and the resting state for the C–C silylation.

To a flame dried vial added, $[Rh(nbd)Cl]_2$ (5 mol%) and $Tp^{(CF3)2}Na(THF)$ (10 mol %) and dissolved in THF (0.5 mL). The vial was capped with a Teflon-lined screw cap, and the resulting solution was stirred at room temperature for 30 min. The volatile materials were evaporated by placing the reaction mixture directly under vacuum for 0.5 h. The precatalyst was then sequentially treated with silyl acetal (59 mg, 0.2 mmol), norbornene (38 mg, 0.4 mmol, 2 equiv) and THF-d_8 (0.70 mL). This solution was transferred to a J-Young NMR tube and the reaction was analyzed by ^{1}H spectroscopy.

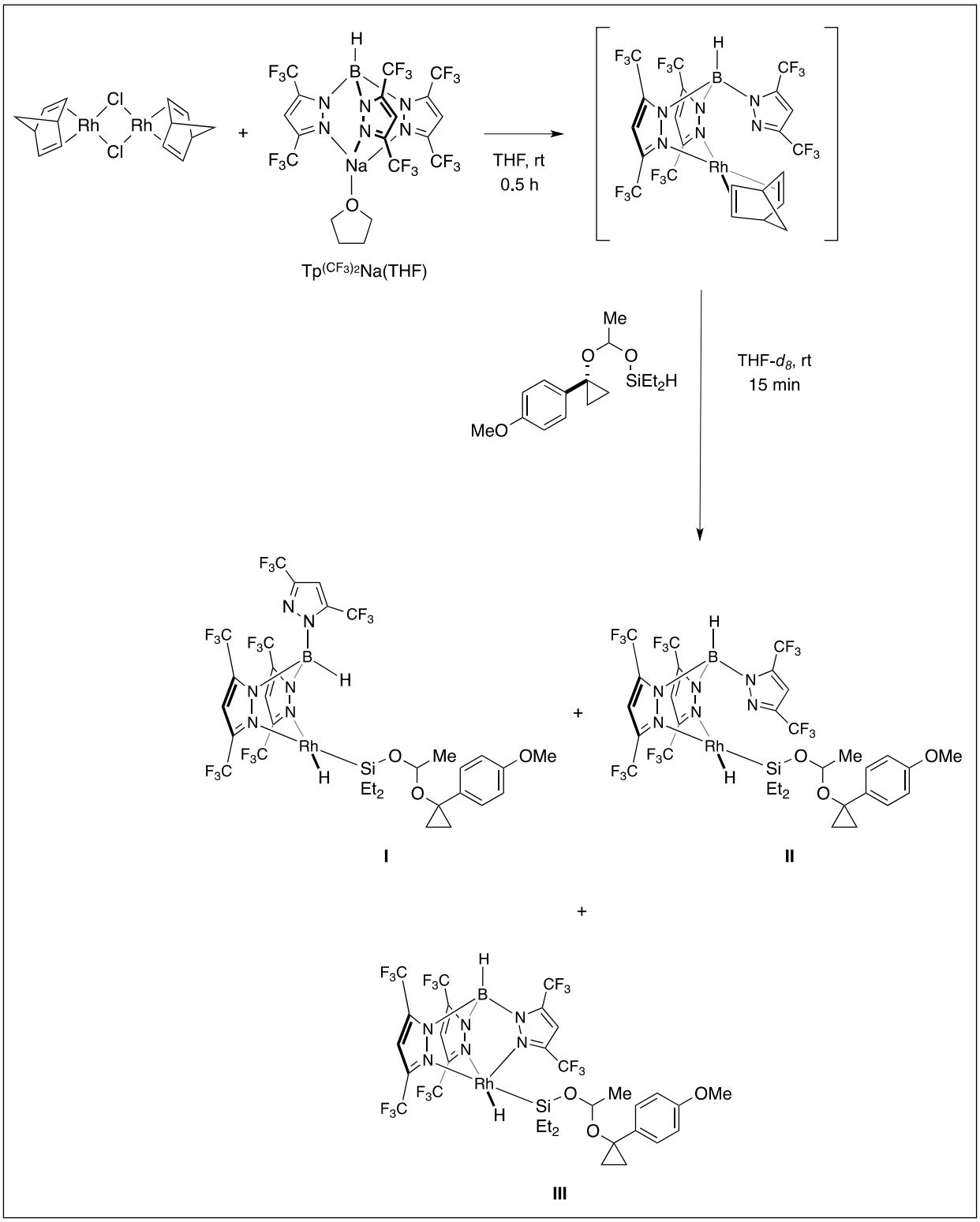


Figure B.1 Rh precatalyst preparation with $[Rh(nbd)Cl]_2$ and $Tp^{(CF_3)_2}Na(THF)$

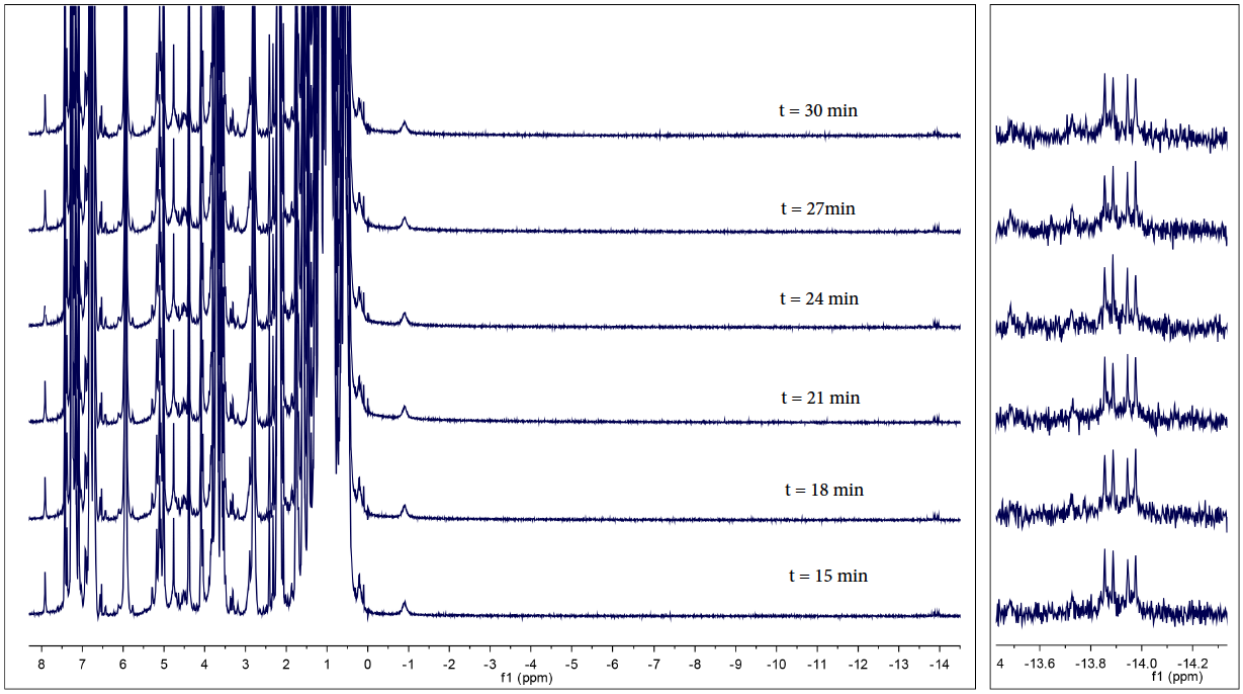
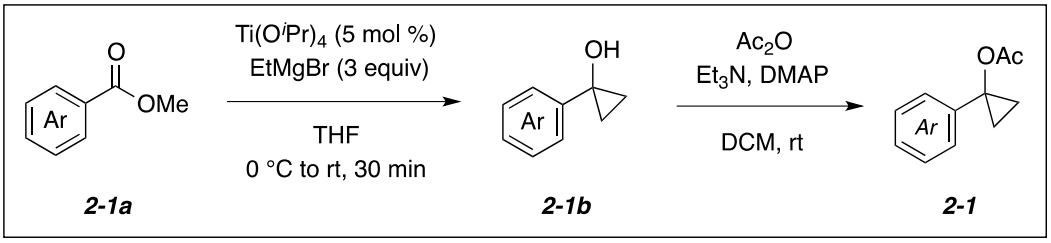


Figure B2. ^{1}H NMR spectroscopic observations of Rh precatalyst preparation with $[Rh(nbd)Cl]_2$ and $Tp^{(CF3)2}Na(THF)$ and resting state for hydrogenative C–C silyl insertion. Two Rh–H species were observed at –13.86 (d, J = 16.5 Hz) and –13.98 (d, J = 15.6 Hz), suggesting that either two κ^2-bonded tris(pyrazolyl)borate structures (**1-35** and **1-36**) or one κ^2-bonded tris(pyrazolyl)borate structure (either **1-35** or **1-36**) and κ^3-bonded tris(pyrazolyl)borate structure **1-37** are likely formed and they are resting states of the hydrogenative C–C silyl insertion.[S4]

General Experimental Procedure: Chapter 2

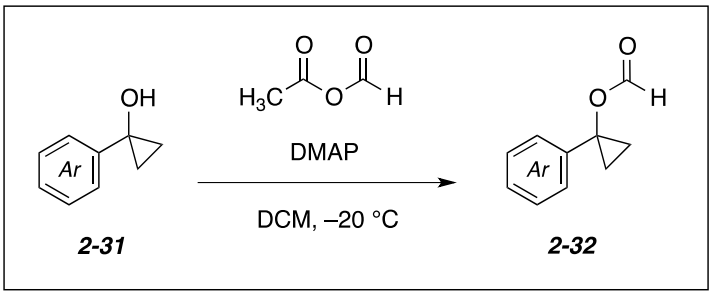
C.1. General procedure for preparation of aryl cyclopropanoacetates:



A flame-dried 100 mL round-bottom flask equipped with a stir bar was charged with esters **2-1a** (5 mmol), THF (30 mL, 0.17 M) and titanium tetraisopropoxide (148 μL, 0.5 mmol). The resulting solution was cooled to 0 °C with an ice bath. Ethylmagnesium bromide (5 mL, 15 mmol, 3.0 M in Et_2O) was added dropwise over a period of 30 min, and the reaction mixture was warm to ambient temperature and stirred for 12 h. The progress of the reaction was monitored by thin-layer chromatography (TLC). The reaction was quenched with water. A precipitate was formed, and the solution was then filtered through a pad of Celite®. The solution was extracted with Et_2O, washed with water and saturated aqueous brine, dried over Na_2SO_4, and filtered through a pad of Celite®. The resulting solution was concentrated under reduced pressure to afford crude cyclopropanols **2-1b**, which were used directly to the next acetylation reaction.

To a solution of the crude cyclopropanol (1.0 mmol), acetic anhydride (113 μL, 1.2 mmol), DMAP (6 mg, 10 mol %) in DCM (4 mL, 0.25 M), Et_3N (154 μL, 1.1 mmol) was added dropwise over 15 min. The reaction mixture was then stirred at rt for 3 h. The reaction was quenched by adding saturated aqueous $NaHCO_3$. After being stirred for 10 min, the reaction mixture was extracted with Et_2O. The organic layer was washed with water followed by saturated aqueous brine and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under reduced pressure to afford a brown oil, which was purified by column chromatography to give cyclopropanoate **2-1** as a yellow oil.

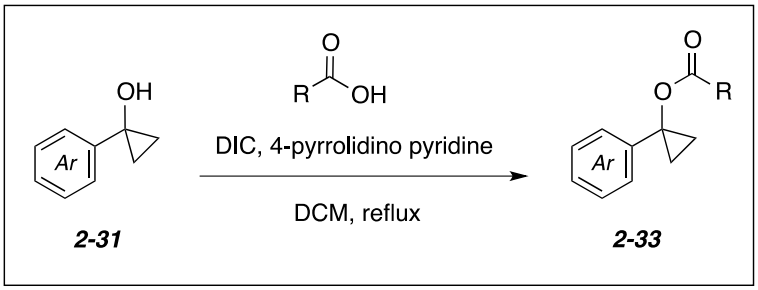
C.2 Gereral procedure for formylation of cyclopropanols:



Acetic formic anhydride was prepared by addition of acetyl chloride (0.70 mL, 10 mmol) to a solution of sodium formate (0.68 g, 10 mmol) in Et_2O (10 mL, 1M) at rt.[(ref)] The crude material was filtered through pad of silica-gel and the filterate was concentrated under reduced pressure, which was used directly to the next step.

A flame-dried 100 mL round-bottom flask equipped with a stir bar was charged with cyclopropanol **2-31** (5 mmol), DMAP (0.61 g, 5 mmol), and DCM (10 mL, 0.5 M). The resulting solution was cooled to –20 °C. Acetic formic anhydride (0.80 mL, 10 mmol) was added dropwise over 15 min. The reaction mixture was warmed to rt and stirred for 3 h. The reaction was quenched by adding saturated aqueous $NaHCO_3$. After being stirred for 10 min, the reaction mixture was extracted with Et_2O three times. The organic layer was washed with water followed by saturated aqueous brine and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under reduced pressure to afford a brown oil, which was purified by column chromatography to give **2-32** as a yellow oil.

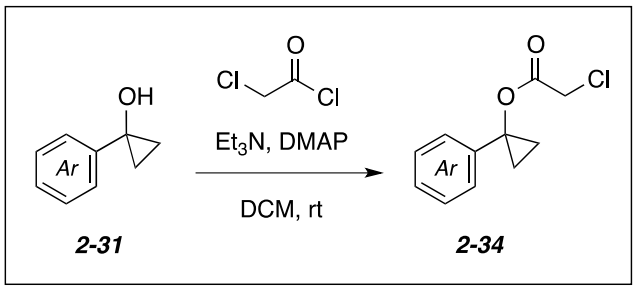
C.2. DIC coupling of cyclopropanols:



A flame-dried 100 mL round-bottom flask equipped with a stir bar was charged with

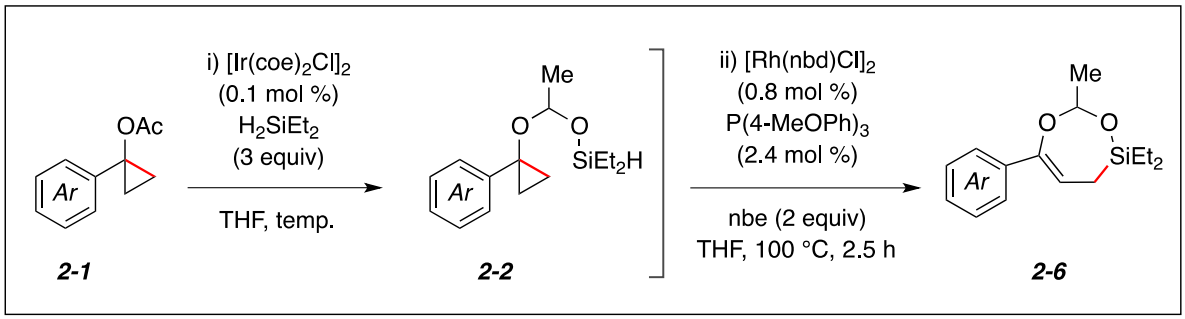
cyclopropanol **2-31** (0.5 mmol), 4-pyrrolidinopyridine (74 mg, 0.5 mmol), carboxylic acid (1.5 mmol), and DCM (10 mL, 0.05 M). The resulting solution was warmed to 50 °C. *N,N'*-Diisopropylcarbodiimide (157 μL, 10 mmol) was added dropwise over 15 min. The reaction mixture was then stirred at rt for 3 h. The reaction was quenched by adding saturated aqueous $NaHCO_3$. After being stirred for 10 min, the reaction mixture was extracted with Et_2O three times. The organic layer was washed with water followed by saturated aqueous brine and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under reduced pressure to afford a brown oil, which was purified by column chromatography to give **2-33** as a yellow oil.

C.3. Chloroacetylation of cyclopropanols:



A flame-dried 100 mL round-bottom flask equipped with a stir bar was charged with cyclopropanol **2-31** (5 mmol), chloroacetyl chloride (0.47 mL, 6 mmol) in DCM (20 mL, 0.25 M), Et_3N (0.76 mL, 5.5 mmol) was added dropwise over 15 min. The reaction mixture was then stirred at rt for 3 h. The reaction was quenched by adding saturated aqueous $NaHCO_3$. After being stirred for 10 min, the reaction mixture was extracted with Et_2O three times. The organic layer was washed with water followed by saturated aqueous brine and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under reduced pressure to afford a brown oil, which was purified by column chromatography to give cyclopropanoates **2-34** as a yellow oil.

C.4. General procedure for C-C silylation to prepare dioxasilepines 2-6:



$[Ir(coe)_2Cl]_2$ (0.2 mg, 0.1 mol %) and cyclopropanoacetate **2-1** (0.2 mmol) were dissolved with THF (0.6 mL, 0.33 M). Diethylsilane (0.6 mmol) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was stirred for 12 h at rt or 2 h at 70 °C. The volatiles were removed *in vacuo* to afford the silyl acetal **2-2**, which were directly used for subsequent reactions without further purification.

$[Rh(nbd)Cl]_2$ (0.7 mg, 0.8 mol %), *tris*(4-methoxyphenyl)phosphine (3.4 mg, 4.8 mol %,) and norbornene (38 mg, 0.4 mmol) were dissolved with THF (0.6 mL, 0.33 M). The crude silyl acetals **2-2** (0.2 mmol) was added to the mixture in one portion. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at 100 °C for 2.5 h unless mentioned otherwise (see Table 2 in Manuscriprt). The reaction progress was monitored by GC-MS spectrometry. The volatiles were removed *in vacuo*, and the resulting mixture was dissolved with pentane, filtered through a pad of Celite®, and concentrated *in vacuo* to afford the crude dioxasilolanes **2-6**, which was purified by MPLC (hexanes/EtOAc = 80:1, 5 mL/min).

C.5. NMR spectroscopic observations of dehydrogenative C–C silyl insertion

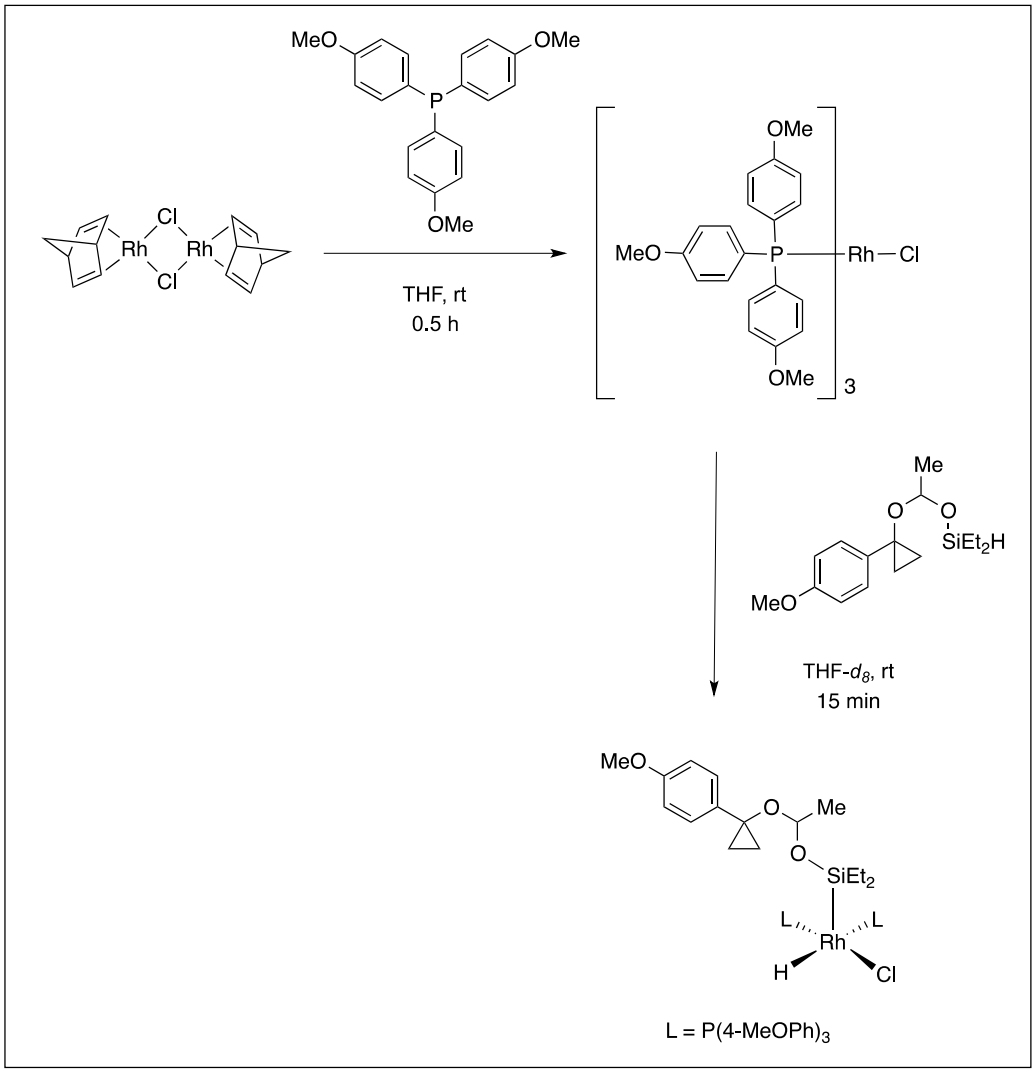


Figure C1. Rh precatalyst preparation with $[Rh(nbd)Cl]_2$ and P(4-MeOPh)$_3$ and resting state for dehydrogenative C–C silyl insertion

To a flame dried vial were added $[Rh(nbd)Cl]_2$ (5 mol %) and P(4-MeOPh)$_3$ (30 mol %) and dissolved in THF (0.5 mL). The vial was capped with a Teflon-lined screw cap, and the resulting solution was stirred at room temperature for 30 min. The volatile materials were evaporated by placing the reaction mixture directly under high vacuum for 0.5 h. The precatalyst was then sequentially treated with silyl acetal (59 mg, 0.2 mmol) norbornene (38 mg, 0.4 mmol, 2 equiv) and THF-d_8 (0.70 mL). This solution was transferred to a J-Young NMR tube and the reaction was analyzed by ^{1}H and ^{31}P NMR spectroscopy.

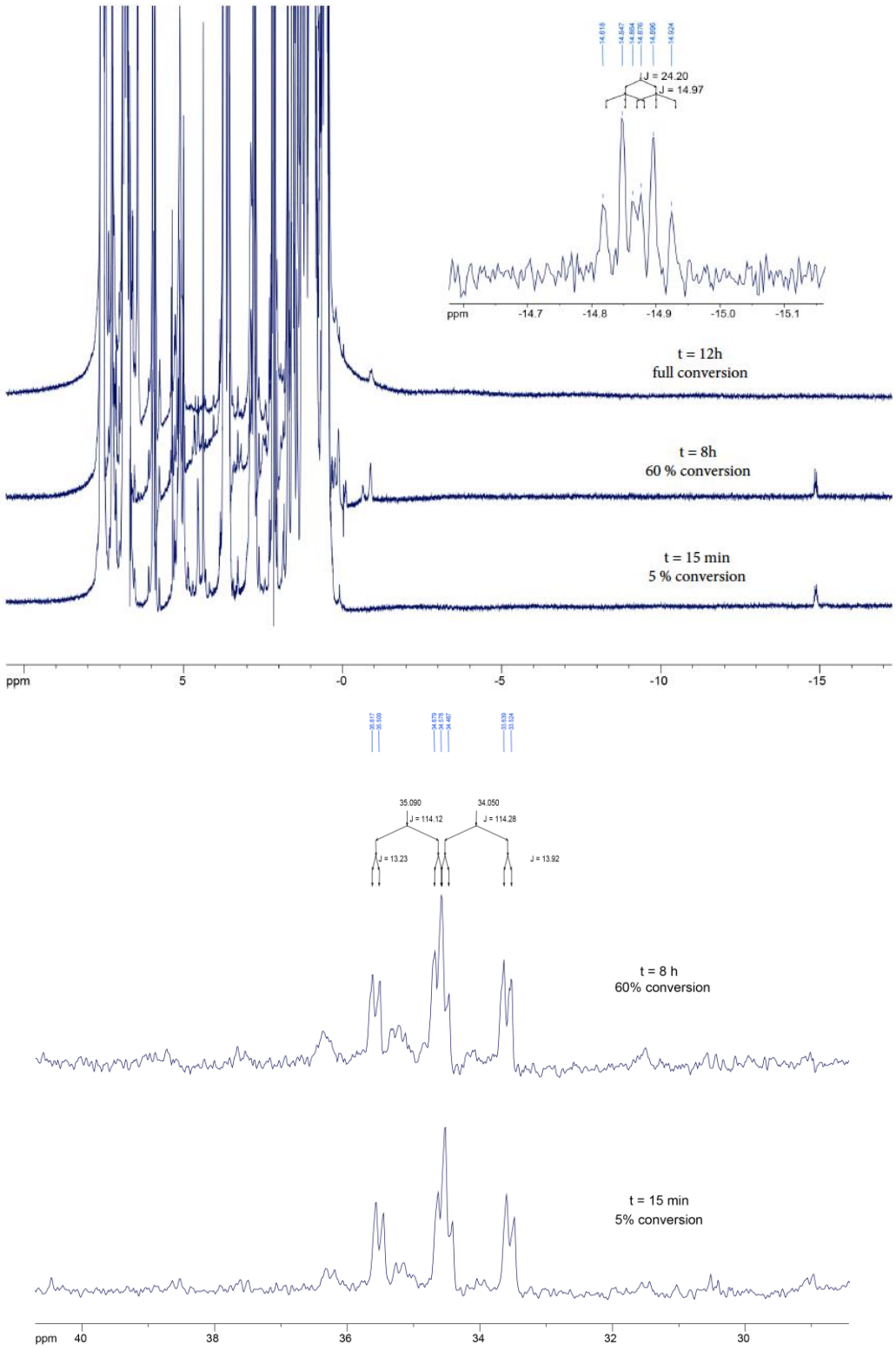
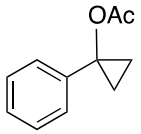


Fig. C.2 ^{1}H and ^{31}P NMR spectroscopic observations of Rh precatalyst preparation with $[Rh(nbd)Cl]_2$ and $P(4OMePh)_3$ and resting state for dehydrogenative C–C silyl insertion.

Appendix C

Spectral data of the compounds

1-Phenylcyclopropyl acetate (1-1-1)



Yield: 1 mmol scale, 70 mg, 40%. (colorless clear oil)

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.32-7.30 (nfom, 4H, Ar-*H*), 7.26-7.21 (nfom, 1H, Ar-*H*), 2.05 (s, 3H, O=CC*H*$_3$), 1.31-1.27 (m, 2H, cyp-*H*), and 1.24-1.21 (m, 2H, cyp-*H*).

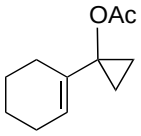
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 140.2, 128.5, 127.3, 126.3, 60.2, 21.5, and 15.1.

IR (neat): 3090 (w), 2954 (w), 1753 (s), 1603 (w), 1344 (s), 1243 (s), 1201 (s), 753 (s), and 695 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{11}H_{12}NaO_2)^+$: 199.0730. Found: 199.0709.

1-(Cyclohex-1-en-1-yl)cyclopropyl acetate (1-1-2)



Yield: 1 mmol scale, 79 mg, 44%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.66 (dddd, *J* = 5.8, 1.7, 1.7, 1.7 Hz, 1H, C=C*H*), 2.04-2.00 (m, 2H, alkyl-*H*), 1.99 (s, 3H, O=CC*H*$_3$), 1.93-1.89 (m, 2H, alkyl-*H*), 1.64-1.58 (m, 2H, alkyl-*H*), 1.56-1.50 (m, 2H, alkyl-*H*), 0.95-0.94 (m, 2H, cyp-*H*), and 0.93-0.91 (m, 2H, cyp-*H*).

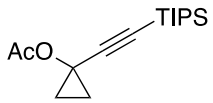
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.7, 134.6, 122.9, 61.9, 25.3, 25.1, 22.8, 22.3, 21.5, and 12.2.

IR (neat): 3092 (w), 3056 (w), 2930 (s), 2857 (m), 1749 (s), 1708 (m), 1367 (s), 1244 (s) 1199 (s) 1023 (m), and 854 (w) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+K)^+$ $(C_{11}H_{16}KO_2)^+$: 219.0782. Found: 219.0945.

1-[(Triisopropylsilyl)ethynyl]cyclopropyl acetate (1-1-3)



Yield: 1 mmol scale, 232 mg, 83%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.02 (s, 3H, O=CC*H*$_3$), 1.23-1.20 (nfom, 2H, cyp-*H*), 1.15-1.12 (nfom, 2H, cyp-*H*), and 1.05-1.02 {m, 21H, Si[C*H*(C*H*$_3$)$_2$]$_3$}.

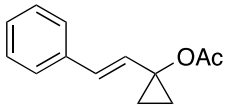
^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.9, 106.0, 84.2, 48.7, 21.2, 18.8, 16.5, and 11.3.

IR (neat): 3066 (w), 2953 (s), 2844 (m), 1745 (s), 1602 (m), 1267 (s), 1143 (s) 1063 (m), and 764 (w) cm^{-1}.

TLC: R_f = 0.6 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ ($C_{16}H_{28}NaO_2Si)^+$: 303.1751. Found: 303.1766.

(*E*)-1-Styrylcyclopropyl acetate (1-1-4)



Yield: 1 mmol scale, 173 mg, 86%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.34-7.31 (m, 2H, Ar-*H*), 7.30-7.26 (m, 1H, Ar-*H*), 7.22-7.18 (m, 2H, Ar-*H*), 6.36 (d, 1H, *J* = 16.0 Hz), 6.17 (d, 1H, *J* = 16.0 Hz), 2.09 (s, 3H, O=CC*H*$_3$), 1.21-1.18 (m, 2H, cyp-*H*), and 1.11-1.08 (m, 2H, cyp-*H*).

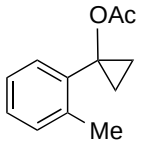
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.6, 136.6, 129.0, 128.6, 128.1, 127.5, 126.4, 59.0, 21.4, and 14.9.

IR (neat): 3092 (w), 2921 (s), 2857 (m), 1742 (s), 1367 (s), 1278 (s) 1121 (s) 1042 (m), and 766 (w) cm^{-1}.

TLC: R_f = 0.6 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ ($C_{13}H_{14}NaO_2)^+$: 225.0886. Found: 225.0815.

1-(*o*-Tolyl)cyclopropyl acetate (1-1-6)



Yield: 1 mmol scale, 68 mg, 36%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.44 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 7.21-7.13 (m, 3H, Ar-*H*), 2.50 (s, 3H, Ar-C*H*$_3$), 1.91 (s, 3H, O=CC*H*$_3$), 1.26-1.22 (m, 2H, cyp-*H*), and 1.14-1.10 (m, 2H, cyp-*H*).

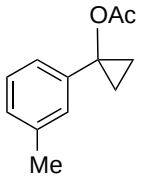
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.7, 139.3, 136.6, 131.2, 130.3, 128.5, 125.4, 59.8, 21.5, 19.4, and 12.7.

IR (neat): 3089 (w), 2954 (w), 2870 (w), 1746 (s), 1623 (m), 1519 (m), 1214 (s), 1098 (s), 756 (s), and 622 (s) cm^{-1}.

TLC: R_f = 0.4 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{12}H_{14}NaO)^+$: 213.0886. Found: 213.0855.

1-(*m*-Tolyl)cyclopropyl acetate (1-1-7)



Yield: 1 mmol scale, 89 mg, 47%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): 7.21 (dd, *J* = 7.5, 7.5 Hz, 1H, Ar-*H*), 7.12 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.10 (s, 1H, Ar-*H*), 7.05 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 2.34 (s, 3H, $ArCH_3$), 2.05 (s, 3H, O=CC*H*$_3$), 1.29-1.25 (m, 2H, cyp-*H*), 1.23-1.19 (m, 2H, cyp-*H*).

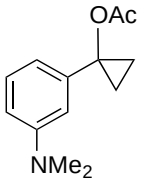
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 150.7, 141.0, 129.2, 115.0, 111.9, 110.9, 60.6, 40.9, 21.6, and 14.9.

IR (neat): 3016 (w), 2922 (w), 1752 (s), 1588 (w), 1367 (s), 1215 (s), 1024 (m), 984 (m), and 697 (s) cm^{-1}.

TLC: R_f = 0.6 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{12}H_{14}NaO_2)^+$: 213.0886. Found: 213.0812

1-[3-(Dimethylamino)phenyl]cyclopropyl acetate (1-1-8)



Yield: 1 mmol scale, 100 mg, 46%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.18 (t, *J* = 7.9 Hz, 1H, Ar-*H*), 6.73-6.69 (m, 2H, Ar-*H*), 6.63 (dd, *J* = 8.3, 2.3 Hz, 1H, Ar-*H*), 2.94 [s, 6H, N(CH_3)$_2$], 2.04 (s, 3H, O=CCH_3), 1.26-1.24 (m, 2H, cyp-*H*), and 1.23-1.21 (m, 2H, cyp-*H*).

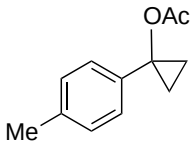
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 150.7, 141.0, 129.2, 115.0, 111.9, 110.9, 60.6, 40.9, 21.6, and 14.9.

IR (neat): 3019 (w), 2953 (w), 2922 (w), 1744 (s), 1602 (s), 1500 (s), 1362 (s), 1200 (s), 992 (s) 771 (s), and 692 (s) cm^{-1}.

TLC: 0.4 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ ($C_{13}H_{17}NNaO_2$)$^+$: 242.1151. Found: 242.1134.

1-(*p*-Tolyl)cyclopropyl acetate (1-1-9)



Yield: 1 mmol scale, 74 mg, 39%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.24 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.12 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 2.32 (s, 3H, Ar-CH_3), 2.02 (s, 3H, O=CCH_3), 1.27-1.23 (m, 2H, cyp-*H*), and 1.19-1.16 (m, 2H, cyp-*H*).

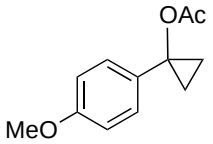
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 137.2, 136.0, 129.2, 126.7, 60.2, 21.6, 21.3, and 14.7.

IR (neat): 3094 (w), 2970 (w), 1751 (s), 1518 (m), 1366 (m), 1200 (s), 1020 (s), 843 (s), and 539 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ ($C_{12}H_{14}NaO_2$)$^+$: 213.0886. Found: 213.0870.

1-(4-Methoxyphenyl)cyclopropyl acetate (1-1-10)



Yield: 1 mmol scale, 86 mg, 42%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.84 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 3.78 [s, 3H, Ar(OC*H*$_3$)], 1.99 (s, 3H, O=CC*H*$_3$), 1.25-1.21 (m, 2H, cyp-*H*), and 1.15-1.11 (m, 2H, cyp-*H*).

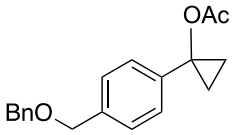
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 159.1, 132.1, 129.1, 113.8, 60.2, 55.5, 21.6, and 14.0.

IR (neat): 3078 (w), 2958 (w), 2910 (w), 1746 (s), 1611 (s), 1516 (s), 1242 (s), 1201 (s), 828 (s), and 548 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{12}H_{14}NaO_3)^+$: 229.0835. Found: 229.0896.

1-{4-[(Benzyloxy)methyl]phenyl}cyclopropyl acetate (1-1-11)



Yield: 1 mmol scale, 130 mg, 44%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.38-7.33 (m, 5H, Ar-*H*), 7.32-7.28 (m, 4H, Ar-*H*), 4.54 (s, 2H, ArC*H*$_2$), 4.53 (s, 2H, ArC*H*$_2$), 2.04 (s, 3H, O=CC*H*$_3$), 1.30-1.27 (m, 2H, cyp-*H*), and 1.22-1.19 (m, 2H, cyp-*H*).

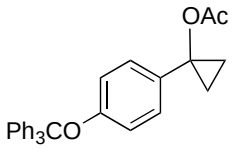
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 139.7, 138.5, 137.4, 128.6, 128.3 127.97, 127.84, 126.5, 72.3, 72.0, 60.1, 21.5, and 15.1.

IR (neat): 3064 (w), 2954 (m), 2875 (m), 1746 (s), 1612 (s), 1577 (s), 1502 (s), 1443 (s), 1233 (s), 1150 (s), 974 (s), and 685 (m) cm^{-1}.

TLC: R_f = 0.6 in 20:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{19}H_{20}NaO_3^+)^+$: 319.1305. Found: 319.1345

1-[4-(Trityloxy)phenyl]cyclopropyl acetate (1-1-12)



Yield: 1 mmol scale, 178 mg, 41%. (colorless viscous oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47-7.44 (m, 6H, Ar-*H*), 7.29-7.25 (m, 6H, Ar-*H*), 7.24-7.20 (m, 3H, Ar-*H*), 6.97 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.63 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 2.02 (s, 3H, O=CC*H*$_3$), 1.26-1.24 (m, 2H, cyp-*H*), and 1.19-1.17 (m, 2H, cyp-*H*).

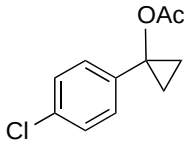
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.7, 155.7, 144.2, 132.6, 129.1, 127.9, 127.3, 127.1, 120.5, 90.4, 59.9, 21.5, and 14.6.

IR (neat): 3058 (w), 2952 (m), 2874 (m), 1742 (s), 1605 (m), 1397 (s), 1283 (s), 1070 (s), 758 (s), and 742 (s) (m) cm^{-1}.

TLC: R_f = 0.7 in 20:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{30}H_{26}NaO_3)^+$: 457.1774. Found: 457.1722.

1-(4-Chlorophenyl)cyclopropyl acetate (1-1-13)



Yield: 1 mmol scale, 100 mg, 48%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): 7.28-7.24 (m, 4H, Ar-*H*), 2.02 (s, 3H, O=CC*H*$_3$), 1.25-1.22 (m, 2H, cyp-*H*), and 1.15-1.12 (m, 2H, cyp-*H*).

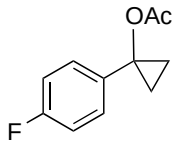
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 138.8, 133.2, 128.7, 128.1, 59.7, 21.5, and 15.0

IR (neat): 3082 (w), 2971 (w), 1748 (s), 1496 (s), 1417 (s), 1201 (s), 1098 (s), 820 (s), and 538 (s) cm^{-1}.

TLC: R_f = 0.4 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{11}H_{11}ClNaO_2)^+$: 233.0340. Found: 233.0301.

1-(4-Fluorophenyl)cyclopropyl acetate (1-1-14)



Yield: 1 mmol scale, 93 mg, 48%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36 [dd, J = 8.7, 5.3 ($^4J_{F-H}$) Hz, 2H, Ar-*H*], 6.99 [dd, *J* = 8.7, 8.7 ($^3J_{F-H}$) Hz, 2H, Ar-*H*], 2.00 (s, 3H, O=CC*H*$_3$), 1.29-1.26 (m, 2H, cyp-*H*), and 1.19-1.16 (m, 2H, 2H, cyp-*H*).

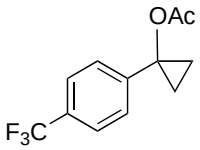
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 162.21 (d, $^1J_{F-C}$ = 246.1 Hz), 135.84 (d, $^4J_{F-C}$ = 3.5 Hz), 129.19 (d, $^3J_{F-C}$ = 8.0 Hz), 115.30 (d, $^2J_{F-C}$ = 21.6 Hz), 59.9, 21.5, and 14.4.

IR (neat): 3013 (w), 2939 (w), 1749 (s), 1513 (s), 1367 (m), 1200 (s), 1025 (m), 830 (s), and 542 (s) cm^{-1}.

TLC: R_f = 0.4 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{11}H_{11}FNaO_2)^+$: 217.0635. Found: 217.0611.

1-[4-(Trifluoromethyl)phenyl]cyclopropyl acetate (1-1-15)



Yield: 1 mmol scale, 54 mg, 22%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): 7.56 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.35 (d, *J* = 8.1 Hz, 2H, Ar-*H*)], 2.07 (s, 3H, O=CC*H*$_3$), 1.37-1.34 (m, cyp-*H*, 2H), and 1.27-1.24 (m, cyp-*H*, 2H).

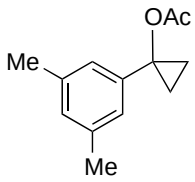
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.6, 144.4, 129.2 (q, $^2J_{F-C}$ = 32.3), 125.9, 125.4 (q, $^3J_{F-C}$ = 3.5), 124.2 (q, $^1J_{F-C}$ = 272.3 Hz), 65.4, 21.2, and 15.7.

IR (neat): 3068 (w), 2975 (w), 2877 (m), 1741 (s), 1372 (m), 1325 (s), 1121 (s), and 764 (m) cm^{-1}.

TLC: R_f = 0.6 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{12}H_{11}F_3NaO_2)^+$: 267.0603. Found: 267.0601.

1-(3,5-Dimethylphenyl)cyclopropyl acetate (1-1-16)



Yield: 1 mmol scale, 81 mg, 40%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.91 (s, 2H, Ar-*H*), 6.87 (s, 1H, Ar-*H*), 2.29 [s, 6H, Ar(CH_3)$_2$], 2.05 (s, 3H, O=CCH_3), 1.25-1.23 (m, 2H, cyp-*H*), and 1.20-1.17 (m, 2H, cyp-*H*).

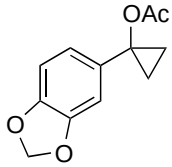
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 140.1, 138.0, 129.1, 124.0, 60.2, 21.60, 21.58, and 15.0.

IR (neat): 3064 (w), 2969 (w), 1750 (s), 1721 (s), 1199 (s), 1042 (s), 754(s), 738 (s), and 698 (m) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{13}H_{16}NaO_2)^+$: 227.1043. Found: 227.1082.

1-(Benzo[*d*][1,3]dioxol-5-yl)cyclopropyl acetate (1-1-17)



Yield: 1 mmol scale, 46 mg, 21%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): 6.92 (d, *J* = 1.7 Hz, 1H, Ar-*H*), 6.89 (dd, *J* = 8.0, 1.7 Hz, 1H, Ar-*H*), 6.74 (d, *J* = 8.0 Hz, 1H, Ar*H*), 5.93 (s, 2H, OCH_2O), 1.99 (s, 3H, O=CCH_3), 1.23-1.20 (m, 2H, cyp-*H*), and 1.14-1.11 (m, 2H, cyp-*H*).

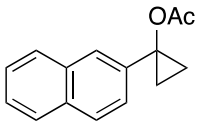
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 147.7, 147.1, 133.9, 121.2, 108.5, 108.1, 101.3, 60.4, 21.6, and 14.3.

IR (neat): 3083 (w), 2972 (w), 1749 (s), 1504 (m), 1492 (w), 1451 (m), 1229 (s), 1197 (s), 1034 (s), 922 (s), 806 (s), and 704 (m) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{12}H_{12}NaO_4)^+$: 243.0628. Found: 243.0623.

1-(Naphthalen-2-yl)cyclopropyl acetate (1-1-18)



Total Yield: 1 mmol scale, 102 mg, 45%. (white solid)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81-7.78 (m, 4H, Ar-*H*), 7.47-7.43 (m, 3H, Ar-*H*), 2.06 (s, 3H, O=CC*H*$_3$), 1.37-1.35 (m, 2H, cyp-*H*), and 1.34-1.32 (m, 2H, cyp-*H*).

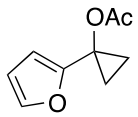
^{13}C NMR (CDCl3, 125 MHz): δ 170.8, 137.5, 133.3, 132.8, 128.29, 128.18, 127.7, 126.4, 126.1, 125.4, 124.7, 60.4, 21.6, and 15.0.

IR (neat): 3055 (w), 2958 (m), 2877 (m), 1746 (s), 1429 (s), 1395 (s), 1202 (s), 1091 (s), 1024 (m), 934 (s), and 745 (s) cm^{-1}.

TLC: R_f = 0.6 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{14}NaO_2)^+$: 249.0886. Found: 249.0869.

1-(Furan-2-yl)cyclopropyl acetate (1-1-19)



Yield: 1 mmol scale, 40 mg, 24%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 [dd, *J* = 1.8, 0.9 Hz, 1H, C(O)*H*CH], 6.31 [dd, *J* = 3.2, 1.8 Hz, 1H, C(O)HC*H*CHC], 6.28 [dd, *J* = 3.2, 0.9 Hz, 1H, C(O)HCHC*H*C], 2.03 (s, 3H, O=CC*H*$_3$), 1.26-1.25 (m, 2H, cyp-*H*), and 1.24-1.23 (m, 2H, cyp-*H*).

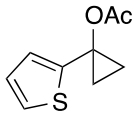
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.6, 153.2, 141.9, 110.6, 107.9, 54.1, 21.4, and 13.7

IR (neat): 3140 (w), 2982 (m), 1747 (s), 1294 (s), 1100 (s), 1013 (m), 958 (s), and 764 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_9H_{10}NaO_3)^+$: 189.0522. Found: 189.0575.

1-(Thiophen-2-yl)cyclopropyl acetate (1-1-20)



Yield: 1 mmol scale, 75 mg, 41%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): 7.21 (dd, *J* = 5.1, 1.2 Hz, 1H, thiophene-*H*), 7.06 (dd, *J* = 3.5, 1.2, Hz, 1H, thiophene-*H*), 6.91 (dd, *J* = 5.1, 3.5 Hz, 1H, thiophene-*H*), 2.00 (s, 3H, O=CC*H*$_3$), 1.32-1.30 (m, 2H, cyp-*H*), and 1.26-1.24 (m, 2H, cyp-*H*).

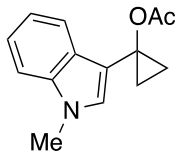
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.7, 144.0, 126.5, 126.5, 125.6, 55.8, 21.5, and 15.6.

IR (neat): 3588 (br, w), 3098 (w), 2953 (m), 1745 (s), 1606 (m), 1443 (s), 1367 (s), 1256 (s), 1168 (s), and 741 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_9H_{10}NaO_2S)^+$: 205.0294. Found: 205.0211.

1-(1-Methyl-1*H*-indol-3-yl)cyclopropyl acetate (1-1-21)



Yield: 1 mmol scale, 94 mg, 41%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): 7.93 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.33 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.29 (s, 1H, Ar-*H*), 7.27 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.21 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 3.77 (s, 3H, N-C*H*$_3$), 1.97 (s, 3H, O=CC*H*$_3$), 1.35-1.30 (m, 2H, cyp-*H*), and 1.21-1.16 (m, 2H, cyp-*H*).

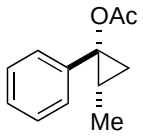
^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.0, 136.7, 130.4, 127.7, 121.9, 119.79, 119.65, 113.5, 109.5, 53.9, 32.9, 21.6, and 12.7.

IR (neat): 3050 (w), 3012 (w), 2934 (m), 1737 (s), 1426 (s), 1239 (s), 1197 (s), 1022 (m), and 740 (s) cm^{-1}.

TLC: R_f = 0.4 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF** Calcd for $(M+Na)^+$ $(C_{14}H_{15}NNaO_2)^+$: 252.0995. Found: 252.0912.

2-Methyl-1-phenylcyclopropyl acetate (1-1-22)



Yield: 1 mmol scale, 154 mg, 81%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 7.25 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 7.21 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 2.09 (s, 3H, O=CC*H*$_3$), 1.46–1.36 (m, 1H, cyp-*H*), 1.42-1.37 (m, 1H, cyp-H), 1.25 (d, *J* = 5.5 Hz, 3H, cyp-C*H*$_3$), and 0.88 (dd, *J* = 5.5, 5.5 Hz, cyp-*H*).

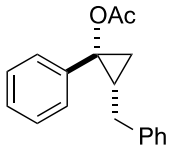
^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.0, 141.3, 128.5, 127.0, 125.8, 63.4, 21.6, 21.3, 20.9, and 13.5.

IR (neat): 3037 (w), 2972 (w), 1779 (s), 1489 (m), 1240 (s), 1169 (s), 1074 (s), 916 (w), and 771 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{12}H_{14}NaO_2)^+$: 213.0886. Found: 213.0812.

2-Benzyl-1-phenylcyclopropyl acetate (1-1-23)



Yield: 0.5 mmol scale, 99 mg, 76%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35-7.32 (m, 4H, Ar-*H*), 7.31-7.28 (m, 2H, Ar-*H*), 7.27-7.25 (m, 2H, Ar-*H*), 7.24-7.19 (m, 2H, Ar-*H*), 3.07 (dd, *J* = 14.8, 6.7 Hz, 1H, PhC*H*$_a$H$_b$), 2.73 (dd, *J* = 14.8, 7.4 Hz, 1H, PhCH$_a$*H*$_b$), 2.14 (s, 3H, O=CC*H*$_3$), 1.66 (dd, *J* = 9.5, 6.8 Hz, 1H, cyp-*H*), 1.58-1.50 (dddd, *J* = 9.5, 7.4, 7.4, 6.7 Hz, 1H, cyp-*H*), 1.12 (dd, *J* = 7.4, 6.8 Hz, 1H, cyp-*H*).

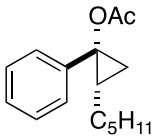
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.9, 141.3, 140.9, 128.66, 128.63, 128.5, 127.2, 126.3, 125.9, 63.3, 34.7, 27.9, 21.5, and 20.6.

IR (neat): 3061 (w), 2955 (w), 1752 (s), 1685 (m), 1367 (s), 1210 (s), 1119 (s), 845 (s), 753 (s) and 696 (s) cm^{-1}.

TLC: R_f = 0.6 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{18}H_{18}NaO_2)^+$: 289.1199. Found: 289.1201.

2-Pentyl-1-phenylcyclopropyl acetate (1-1-24)



Yield: 1 mmol scale, 202 mg, 82%. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.29 (dd, *J* = 7.8, 7.2 Hz, 2H, Ar-*H*), 7.26-7.24 (m, 2H, Ar-*H*), 7.20 (dd, *J* = 7.2, 7.2 Hz, 1H, Ar-*H*), 2.07 (s, 3H, O=CC*H*$_3$), 1.66 (dddd, *J* = 13.1, 8.4, 6.4, 6.4 Hz, 1H), 1.54-1.47 (m, 1H), 1.50 (dd, *J* = 9.6, 6.4 Hz, 1H), 1.43-1.30 (m, 5H), 1.24 (dddd, *J* = 9.6, 7.3, 7.3, 7.3 Hz, 1H), 0.94-0.86 (dd, *J* = 7.5, 6.4 Hz, 1H), and 0.90 (t, *J* = 7.0 Hz, 3H, CH_2CH_3).

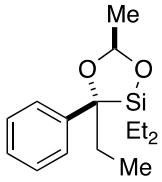
^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.0, 141.4, 128.4, 127.0, 125.9, 63.3, 31.9, 29.3, 28.6, 27.0, 22.8, 21.4, 20.4, and 14.3.

IR (neat): 3053 (w), 2929 (w), 1749 (s), 1685 (m), 1366 (s), 1210 (s), 1116 (s), 894 (s), 781 (m) and 697 (s) cm^{-1}.

TLC: R_f = 0.6 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{16}H_{22}NaO_2)^+$: 269.1512. Found: 269.1583.

2,2,3-Triethyl-5-methyl-3-phenyl-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 41 mg, 78%, 13:1 *dr*; 2) at rt: 48% (NMR yield, mesitylene as an internal standard), >20:1 *dr*; 3) 1.0 mmol scale: at 100 °C: 187 mg, 71%, 13:1 *dr*. (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.34 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.21 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 7.04 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 5.32 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 2.04 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$], 1.65 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)CH$_a$$H_bCH_3$], 1.52 (d, *J* = 4.8 Hz, 3H, OCHCH_3), 1.02 (dd, *J* = 7.8, 7.8 Hz, 3H, SiCH$_2$CH_3), 0.79 [dd, *J* = 7.2, 7.2 Hz, 3H, OC(Ar)CH$_2$CH_3], 0.76 (dq, *J* = 15.7, 7.8 Hz, 1H, SiCH_aH$_b$CH$_3$), 0.66 (dd, *J* = 7.8, 7.8 Hz, 3H, SiCH$_2$CH_3), 0.63 (dq, *J* = 15.7, 7.8 Hz, 1H, SiCH$_a$$H_bCH_3$), 0.33 (dq, *J* = 15.7, 7.8 Hz, 1H, SiCH_aH$_b$CH$_3$), and 0.29 (dq, *J* = 15.7, 7.8 Hz, 1H, SiCH$_a$$H_bCH_3$).

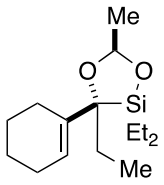
^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.4, 128.3, 125.7, 124.8, 96.9, 78.4, 26.0, 23.3, 7.3, 6.4, 6.1, 4.6, and 3.3.

IR (neat): 3083 (w), 2960 (m), 2877 (m), 1599 (w), 1444 (m), 1237 (m), 1112 (m), and 726 (s) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{24}NaO_2Si)^+$: 287.1438. Found: 287.1418.

3-(Cyclohex-1-en-1-yl)-2,2,3-triethyl-5-methyl-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 46 mg, 87%, 12:1 *dr*; 2) at rt: 87% (NMR yield, mesitylene as an internal standard), >20:1 *dr*. (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): 6.04-5.69 (m, 1H, CH_2C=C*H*), 5.26 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 2.14-1.97 (m, 3H, c-Hex), 1.87-1.79 (m, 1H, c-Hex), 1.76 (dq, *J* = 14.4, 7.2 Hz, 1H, C$H_a$$H_b$$CH_3$,), 1.64–1.48 (m, 4H, c-Hex, $CH_a$$H_b$$CH_3$), 1.40 (d, *J* = 4.8 Hz, 3H, OCHCH_3), 1.05 (dd, *J* = 7.9, 7.9 Hz, 3H, $SiCH_2C$$H_3$), 1.01 (dd, *J* = 7.9, 7.9 Hz, 3H, $SiCH_2C$$H_3$), 0.92 [dd, *J* = 7.2, 7.2 Hz, 3H, $OC(Ar)CH_2C$$H_3$], 0.79-0.67 (m, 2H, $SiC$$H_2CH_3$), and 0.63-0.54 (m, 2H, $SiC$$H_2CH_3$).

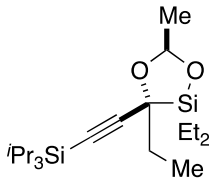
^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.4, 119.1, 96.4, 79.9, 27.4, 25.2, 23.29, 23.20, 23.0, 22.2, 7.3, 6.8, 6.3, 4.3, and 3.9.

IR (neat): 3110 (w), 2954 (m), 2876 (m), 1671 (w), 1458 (m), 1240 (m), 1068 (s), 729 (s), and 698 (m) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{28}NaO_2Si)^+$: 291.1751. Found: 291.1709.

2,2,3-Triethyl-5-methyl-3-[(triisopropylsilyl)ethynyl]-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 61 mg, 83%, >20:1 *dr*; 2) at rt: 83% (NMR yield, mesitylene as an internal standard), >20:1 *dr*. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): 5.33 (q, *J* = 4.9 Hz, 1H, OC*H*Me), 1.91 (dq, *J* = 14.8, 7.4 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$), 1.77 [dq, *J* = 14.8, 7.4 Hz, 1H, OC(Ar)CH$_a$$H_bCH_3$], 1.40 (d, *J* = 4.9 Hz, 3H, OCHCH_3), 1.11 [dd, *J* = 7.2, 7.2 Hz, 3H, OCCH$_2$CH_3], 1.10-1.01 (m, 6H, SiCH$_2$CH_3), 1.07-1.05 {m, 21H, Si[C*H*(CH_3)$_2$]$_3$}, 0.99-0.85 (m, 2H, SiCH_2CH$_3$), and 0.76-0.66 (m, 2H, SiCH_2CH$_3$).

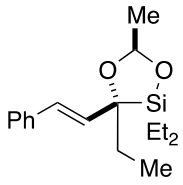
^{13}C NMR ($CDCl_3$, 125 MHz): δ 106.9, 97.8, 89.6, 72.5, 28.9, 22.6, 18.8, 11.5, 10.5, 6.78, 6.74, 3.70, and 3.58.

IR (neat):3086 (w), 2965 (w), 2951 (w), 2210 (s), 1442 (w), 1235 (s), 744 (s), and 641 (w) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{20}H_{40}NaO_2Si_2)^+$: 391.2459. Found: 391.2385.

2,2,3-Triethyl-5-methyl-3-[(*E*)-styryl]-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 42 mg, 72%, 2.5:1 *dr*; 2) at rt: 79% (NMR yield, mesitylene as a internal standard), 3:1 *dr*. (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.29 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.14 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 7.04 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 6.84 (d, *J* = 15.9 Hz, 1H, PhC*H*CH), 6.16 (d, *J* = 15.9 Hz, 1H, PhCHC*H*), 5.25 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 3.81 (ethyl acetate in benzene, CH$_3$CH_2OAc), 1.89 (dq, *J* = 14.3, 7.1 Hz, 1H, OCCH_aH$_b$CH$_3$), 1.51 (d, *J* = 4.8 Hz, 3H, OCHCH_3), 1.39 (dq, *J* = 14.3, 7.1 Hz, 1H, OCCH$_a$$H_bCH_3$), 0.99 (dd, *J* = 7.2, 7.2 Hz, 3H, OCCH$_2$CH_3), 0.98 (dd, *J* = 7.1, 7.1 Hz, 3H, SiCH$_2$CH_3), 0.94 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.72 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), 0.68 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH$_a$$H_bCH_3$), and 0.65-0.52 (m, 3H, SiCH_2CH$_3$).

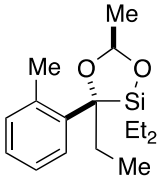
^{13}C NMR (C_6D_6, 125 MHz): δ 138.4, 131.9, 128.9, 127.0, 126.43, 126.34, 97.0, 77.8, 25.4, 23.5, 7.4, 7.1, 6.4, 4.8, and 3.2.

IR (neat): 3098 (w), 2983 (w), 2875 (m), 1664 (s), 1458 (w), 1275 (s), 948 (s), 764 (s), and 625 (w) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{17}H_{26}NaO_2Si)^+$: 313.1594. Found: 313.1532.

2,2,3-Triethyl-5-methyl-3-(o-tolyl)-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 43 mg, 77%, 15:1 *dr*; 2) at rt: 48% (NMR yield, mesitylene as an internal standard), >20:1 *dr.* (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): 6.97-6.81 (m, 3H, Ar-*H*), 6.79-6.71 (m, 1H, Ar-*H*), 5.35 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 2.30 (s, 3H, Ar-CH_3), 2.14 [dq, *J* = 14.4, 7.1 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$], 1.79 [dq, *J* = 14.4, 7.1 Hz, 1H, OC(Ar)CH$_a$$H_bCH_3$], 1.49 (d, *J* = 4.8 Hz, 3H, OCHCH_3), 1.12 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.91 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), 0.83 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH_2CH$_3$), 0.69 [dd, *J* = 7.1, 7.1 Hz, 3H, OC(Ar)CH$_2$CH_3], 0.61 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.32 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), and 0.24 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH$_a$$H_bCH_3$).

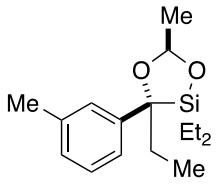
^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.49, 137.47, 126.92, 126.90, 122.55, 122.53, 96.8, 78.4, 26.0, 23.3, 21.77, 7.3, 6.5, 6.2, 4.6, and 3.3.

IR (neat): 3094 (w), 2957 (s), 2876 (s), 1602 (s), 1458 (s), 1395 (s), 1005 (s), 887 (s), and 704 (s) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{24}NaO_2Si)^+$: 301.1594. Found: 301.1571.

2,2,3-Triethyl-5-methyl-3-(m-tolyl)-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 43 mg, 77%, 9:1 *dr*; 2) at rt: 60% (NMR yield, mesitylene as an internal standard), >20:1 *dr*. (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): 7.33 (m, 1H, Ar-*H*), 7.18-7.11 (m, 1H, Ar-*H*), 7.09-7.07 (m, 1H, Ar-*H*), 7.01 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 6.89 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 5.33 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 2.19 (s, 3H, Ar-CH_3), 2.07 [dq, *J* = 14.3, 7.1 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$], 1.69 [dq, *J* = 14.3, 7.3 Hz, 1H, OC(Ar)CH$_a$$H_bCH_3$], 1.54 (d, *J* = 4.8 Hz, 3H, OCHCH_3), 1.05 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.83 [dd, *J* = 7.1, 7.1 Hz, 3H, OC(Ar)CH$_2$CH_3], 0.78 (dq, *J* = 15.9, 7.9 Hz, 1H, SiCH_2CH$_3$), 0.70 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.67 (dq, *J* = 15.9, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), 0.40 (water in benzene-d_6, H_2O), and 0.43-0.30 (m, 2H, SiCH_2CH$_3$).

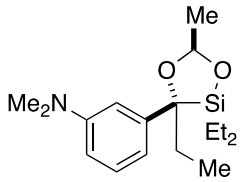
^{13}C NMR (C_6D_6, 125 MHz): δ 143.3, 137.7, 128.1, 126.0, 125.5, 121.9, 96.8, 78.4, 26.0, 23.2, 11.5, 7.3, 6.5, 6.1, 4.6, and 3.3.

IR (neat): 3089 (w), 2958 (s), 2876 (s), 1689 (m), 1377 (m), 1240 (s), 1005 (s), 778 (m), 703 (s), and 622 (m) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{16}H_{26}NaO_2Si)^+$: 301.1594. Found: 301.1561.

***N*,*N*-Dimethyl-3-(2,2,3-triethyl-5-methyl-1,4,2-dioxasilolan-3-yl)aniline (1-3-1)**



Yield: 0.2 mmol scale, 1) at 100 °C: 45 mg, 73%, 10:1 *dr*; 2) at rt: 57% (NMR yield, mesitylene as an internal standard), >20:1 *dr*. (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.15 [dd, *J* = 7.9, 7.9 Hz, 1H, (NMe$_2$)CCHC*H*CH], 6.72 [dd, *J* = 2.5, 1.7 Hz, 1H, (NMe$_2$)CC*H*CCO], 6.57 (ddd, *J* = 7.9, 1.5, 1.5 Hz, 1H, Ar-*H*), 6.54 (ddd, *J* = 7.9, 2.5, 1.5 Hz, 1H, Ar-*H*), 5.36 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 2.94 [s, 6H, N(CH_3)$_2$], 2.14 [dq, *J* = 14.2, 7.1 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$], 1.81 (dq, *J* = 14.2, 7.1 Hz, 1H, OC(Ar)CH$_a$$H_bCH_3$),

1.49 (d, *J* = 4.8 Hz, 3H, OCHC*H*$_3$), 1.12 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$C*H*$_3$), 0.91 (dq, *J* = 15.9, 7.9 Hz, 1H, SiC*H*$_a$H$_b$CH$_3$), 0.83 (dq, *J* = 15.9, 7.9 Hz, 1H, SiCH$_a$*H*$_b$CH$_3$), 0.72 [dd, *J* = 7.1, 7.1 Hz, 3H, OC(Ar)CH$_2$C*H*$_3$], 0.63 (t, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$C*H*$_3$), 0.36 (dq, *J* = 15.9, 7.9 Hz, 1H, SiC*H*$_a$H$_b$CH$_3$), and 0.27 (dq, *J* = 15.9, 7.9 Hz, 1H, SiCH$_a$*H*$_b$CH$_3$).

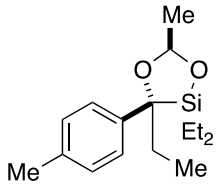
^{13}C NMR ($CDCl_3$, 125 MHz): δ 150.8, 144.2, 128.7, 113.7, 109.78, 109.66, 96.8, 78.7, 41.0, 26.1, 23.3, 7.3, 6.5, 6.3, 4.6, and 3.3.

IR (neat): 3065 (w), 2955 (s), 2876 (s), 1680 (s), 1600 (s), 1492 (m), 1239 (s), 1005 (w), 869 (s), and 746 (s) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{17}H_{29}NNaO_2Si)^+$: 330.1860. Found: 330.1559.

(2,2,3-Triethyl-5-methyl-3-(*p*-tolyl)-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 37 mg, 67%, 11:1 *dr*; 2) at rt: 59% (NMR yield, mesitylene as an internal standard), >20:1 *dr.* (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.29 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.07 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 5.35 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 2.15 (s, 3H, Ar-C*H*$_3$), 2.06 [dq, *J* = 14.6, 7.2 Hz, 1H, OC(Ar)C*H*$_a$H$_b$CH$_3$], 1.67 [dq, *J* = 14.6, 7.2 Hz, 1H, OC(Ar)CH$_a$*H*$_b$CH$_3$], 1.54 (d, *J* = 4.8 Hz, 3H, OCHC*H*$_3$), 1.04 (dd, *J* = 7.6, 7.6 Hz, 3H, SiCH$_2$C*H*$_3$), 0.83 [dd, *J* = 7.2, 7.2 Hz, 3H, OC(Ar)CH$_2$C*H*$_3$], 0.77 (dq, *J* = 15.4, 7.6 Hz, 1H, SiC*H*$_a$H$_b$CH$_3$), 0.71 (dd, *J* = 7.6, 7.6 Hz, 3H, SiCH$_2$C*H*$_3$), 0.67 (dq, *J* = 15.4, 7.6 Hz, 1H, SiCH$_a$*H*$_b$CH$_3$), 0.40 (water in benzene-d_6, H_2O), and 0.41-0.29 (m, 2H, SiC*H*$_2$CH$_3$).

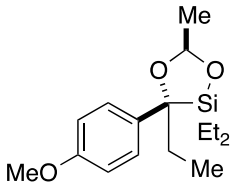
^{13}C NMR (C_6D_6, 125 MHz): δ 140.2, 134.6, 128.9, 124.7, 96.8, 78.3, 26.1, 23.3, 21.2, 7.3, 6.4, 6.1, 4.6, and 3.3.

IR (neat): 3079 (w), 2955 (w), 1756 (w), 1598 (m), 1447 (m), 1221 (s), 954 (m), and 735 (s) cm^{-1}.

TLC: R_f = 0.7 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{24}NaO_2Si)^+$: 301.1594. Found: 301.1588.

(2,2,3-Triethyl-3-(4-methoxyphenyl)-5-methyl-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 40 mg, 69%, 10:1 *dr*; 2) at rt: 55% (NMR yield, mesitylene as an internal standard), >20:1 *dr.* (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.26 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.85 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 5.33 (q, *J* = 4.8 Hz, 1H), 3.33 [s, 3H, Ar(OMe)], 2.07 [dq, *J* = 14.6, 7.1 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$], 1.63 [dq, *J* = 14.6, 7.3 Hz, 1H, OC(Ar)CH$_a$$H_bCH_3$], 1.54 (d, *J* = 4.8 Hz, 3H, OCHCH_3), 1.05 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$CH_3), 0.83 [dd, *J* = 7.3, 7.3 Hz, 3H, OC(Ar)CH$_2$CH_3], 0.79 (dq, *J* = 15.9, 8.0 Hz, 1H, SiCH_aH$_b$CH$_3$), 0.72 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$CH_3), 0.67 (dq, *J* = 15.9, 8.0 Hz, 1H, SiCH$_a$$H_bCH_3$), and 0.40 (dq, *J* = 15.3, 8.0 Hz, 1H, SiCH_aH$_b$CH$_3$), 0.40 (water in benzene-d_6, H_2O), 0.42-0.28 (m, 15.9, 8.0 Hz, 2H, SiCH_2CH$_3$).

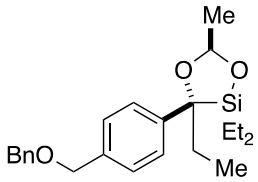
^{13}C NMR (C_6D_6, 125 MHz): δ 158.0, 135.6, 126.1, 114.0, 97.0, 78.0, 54.7, 26.4, 23.5, 7.4, 6.50, 6.38, 5.0, and 3.6.

IR (neat): 3042 (w), 2958 (m), 2876 (m), 1571 (w), 1454 (m), 1395 (m), 1142 (s), 1097 (s), 902 (s), 796 (s), and 731 (s) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ ($C_{16}H_{26}NaO_3Si)^+$: 317.1543. Found: 317.1509.

3-{4-[(Benzyloxy)methyl]phenyl}-2,2,3-triethyl-5-methyl-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 55 mg, 72%, 10:1 *dr*; 2) at rt: 50% (NMR yield, mesitylene as an internal standard), >20:1 *dr.* (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.37-7.33 (m, 4H, Ar-*H*), 2H), 7.31 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.18 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.09 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 5.32 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 4.39 (s, 2H, ArCH_2OCH$_2$Ar), 4.38 (s, 2H, ArCH$_2$OCH_2Ar), 2.06 (dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$), 1.66 (dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$), 1.53 (d, *J* = 4.8 Hz, 3H,

OCHCH_3), 1.03 (dd, J = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.81 (dd, J = 7.2, 7.2 Hz, 3H, OC(Ar)CH$_2$CH_3), 0.77 (dq, J = 15.4, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), 0.67 (dd, J = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.65 (dq, J = 15.4, 7.9 Hz, 1H, SiCH$_a$$H_bCH_3$), 0.40 (water in benzene-d_6, H_2O), 0.36 (dq, J = 15.4, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), and 0.30 (dq, J = 15.4, 7.9 Hz, 1H, SiCH$_a$$H_bCH_3$).

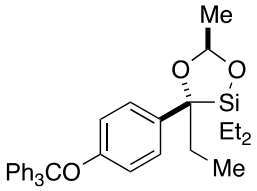
^{13}C NMR (C_6D_6, 125 MHz): δ 143.2, 139.2, 136.0, 128.6, 128.4, 127.77, 127.68, 125.1, 97.0, 78.4, 72.25, 72.14, 26.4, 23.4, 7.3, 6.6, 6.3, 5.0, and 3.5.

IR (neat): 3049 (w), 2954 (m), 2874 (m), 1593 (m), 1436 (m), 1276 (w), 1071 (m), 1020 (s), and 714 (s) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{23}H_{32}NaO_3Si)^+$: 407.2013. Found: 407.2005.

2,2,3-Triethyl-5-methyl-3-[4-(trityloxy)phenyl]-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 75 mg, 72%, 10:1 *dr*; 2) at rt: 44% (NMR yield, mesitylene as an internal standard), >20:1 *dr*. (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.59 (d, J = 7.5 Hz, 6H, Ar-*H*), 7.05 (t, J = 7.5 Hz, 6H, Ar-*H*), 6.98 (t, J = 7.5 Hz, 3H, Ar-*H*), 6.93 (d, J = 8.2 Hz, 2H, Ar-*H*), 6.81 (d, J = 8.2 Hz, 2H, Ar-*H*), 5.25 (q, J = 4.8 Hz, 1H, OC*H*Me), 1.95 (dq, J = 14.4, 7.2 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$), 1.49 (dq, J = 14.4, 7.2 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$), 1.46 (d, J = 4.8 Hz, 3H, OCHCH_3), 0.99 (dd, J = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.72 (dd, J = 7.2, 7.2 Hz, 3H, OC(Ar)CH$_2$CH_3), 0.71 (dq, J = 15.4, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), 0.60 (dd, J = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.58 (dq, J = 15.4, 7.9 Hz, 1H, SiCH$_a$$H_bCH_3$), 0.40 (water in benzene-d_6, H_2O), 0.26 (dq, J = 15.4, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), and 0.14 (dq, 1H, J = 15.4, 7.9 Hz, 1H, SiCH$_a$$H_bCH_3$).

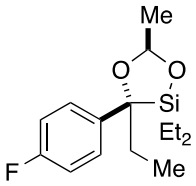
^{13}C NMR (C_6D_6, 125 MHz): δ 154.5, 145.0, 137.3, 129.6, 128.3, 127.4, 125.0, 122.4, 96.9, 91.5, 77.9, 26.1, 23.3, 7.3, 6.44, 6.46, 4.8, and 3.6.

IR (neat): 3087 (w), 3032 (w), 2955 (m), 2874 (m), 1598 (m), 1503 (s), 1447 (s), 1221 (s), 1096 (m), 1033 (m), and 735 (s) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{34}H_{38}NaO_3Si)^+$: 545.2482. Found: 545.2438.

2,2,3-Triethyl-3-(4-fluorophenyl)-5-methyl-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 40 mg, 71%, >20:1 *dr*; 2) at rt: 46% (NMR yield, mesitylene as an internal standard), >20:1 *dr*. (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.11 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.86 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 5.25 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 1.98 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$], 1.48 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)CH$_a$$H_bCH_3$], 1.49 (d, *J* = 4.8 Hz, 3H, OCHCH_3), 0.99 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.73 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), 0.72 [dd, *J* = 7.2, 7.2 Hz, 3H, OC(Ar)CH$_2$CH_3], 0.63 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.60 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH$_a$$H_bCH_3$), 0.40 (water in benzene-d_6, H_2O), 0.28 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), and 0.21 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH$_a$$H_bCH_3$).

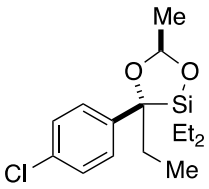
^{13}C NMR (C_6D_6, 125 MHz): δ 161.31 (d, $^1J_{F\text{-}C}$ = 243.4 Hz), 139.48 (d, $^4J_{F\text{-}C}$ = 3.1 Hz), 126.48 (d, $^3J_{F\text{-}C}$ = 7.2 Hz), 115.16 (d, $^2J_{F\text{-}C}$ = 21.6 Hz), 97.0, 77.9, 26.3, 23.3, 7.3, 6.3, 6.2, 4.8, and 3.5.

IR (neat): 3084 (w), 2955 (m), 2874 (m), 1609 (w), 1479 (m), 1250 (m), 1043 (s), 756 (s), and 702 (s) cm^{-1}.

TLC: R_f = 0.8 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{23}FNaO_2Si)^+$: 305.1344. Found: 305.1373.

3-(4-Chlorophenyl)-2,2,3-triethyl-5-methyl-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 42 mg, 70%, >20:1 *dr*; 2) at rt: 52% (NMR yield, mesitylene as an internal standard), >20:1 *dr*. (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.19 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 7.08 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 5.23 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 1.96 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$], 1.49 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)CH$_a$$H_bCH_3$], 1.47 (d, *J* = 4.8 Hz, 3H, OCHCH_3), 0.98 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.71 [dd, *J* = 7.2, 7.2 Hz, 3H, OC(Ar)CH$_2$CH_3)], 0.70 (dq, *J* = 15.4, 7.9

Hz, 1H, SiCH_aH$_b$CH$_3$), 0.62 (dd, J = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.57 (dq, J = 15.4, 7.9 Hz, 1H), SiCH_2CH$_3$), 0.40 (water in benzene-d_6, H_2O), 0.25 (dq, J = 15.4, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), and 0.18 (dq, J = 15.4, 7.9 Hz, 1H, SiCH$_a$$H_bCH_3$).

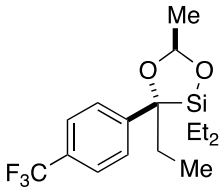
^{13}C NMR (C$_6$D$_6$, 125 MHz): δ 141.5, 130.2, 127.6, 125.5, 96.0, 77.0, 25.1, 22.3, 6.2, 5.4, 5.2, 3.8, and 2.4.

IR (neat): 3072 (w), 2953 (s), 2875 (s), 1437 (m), 1235 (m), 1092 (m), 818 (s), and 742 (s) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for (M+Na)$^+$ (C$_{15}$H$_{23}$ClNaO$_2$Si)$^+$: 321.1048. Found: 321.1099.

2,2,3-Triethyl-5-methyl-3-(4-(trifluoromethyl)phenyl)-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 51 mg, 77%, 11:1 *dr*; 2) at rt: 44% (NMR yield, mesitylene as an internal standard), >20:1 *dr*. (colorless clear oil)

^{1}H NMR (C$_6$D$_6$, 500 MHz): 7.43 (d, J = 8.1 Hz, 2H, Ar-*H*), 7.20 (d, J = 8.1 Hz, 2H, Ar-*H*), 5.22 (q, J = 4.8 Hz, 1H, OC*H*Me), 1.95 [dq, J = 14.3, 7.1 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$], 1.51 [dq, J = 14.6, 7.1 Hz, 1H, OC(Ar)CH$_a$$H_bCH_3$], 1.47 (d, J = 4.8 Hz, 3H, OCHCH_3), 0.97 (dd, J = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.70 (dq, J = 16.2, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), 0.67 [dd, J = 7.1, 7.1 Hz, 3H, OC(Ar)CH$_2$CH_3], 0.57 (dq, J = 16.2, 7.9 Hz, 1H, SiCH_2CH$_3$), 0.55 (dd, J = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.40 (water in benzene-d_6, H_2O), 0.18 (dq, J = 15.7, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), and 0.11 (dq, J = 15.7, 7.9 Hz, 1H, SiCH$_a$$H_bCH_3$).

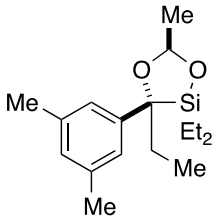
^{13}C NMR (CDCl$_3$, 125 MHz): δ 147.9, 127.4 (q, $^2J_{F\text{-}C}$ = 32.3), 125.9, 125.1 (q, $^3J_{F\text{-}C}$ = 3.5), 124.2 (q, $^1J_{F\text{-}C}$ = 271 Hz), 96.9, 78.3, 25.9, 23.1, 7.1, 5.9, 4.4, 3.2, and 1.1.

IR (neat): 3054 (w), 2954 (m), 2883 (m), 1594 (m), 1435 (m), 1296 (w), 1072 (m), 752 (s), and 700 (s) cm^{-1}.

TLC: R_f = 0.3 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for (M+Na)$^+$ (C$_{16}$H$_{23}$F$_3$NaO$_2$Si)$^+$: 355.1312. Found: 355.1301.

3-(3,5-Dimethylphenyl)-2,2,3-triethyl-5-methyl-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 43 mg, 73%, 13:1 *dr*; 2) at rt: 43% (NMR yield, mesitylene as an internal standard), >20:1 *dr.* (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.97-6.84 (m, 2H, Ar*H*), 6.81-7.72 (m, 1H, Ar*H*), 5.35 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 2.32 [s, 6H, Ar($C\mathit{H}_3$)$_2$], 2.14 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$], 1.80 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)CH$_a$$\mathit{H}_bCH_3$], 1.50 (d, *J* = 4.8 Hz, 3H, OCHCH_3), 1.12 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH_aH$_b$CH$_3$), 0.92 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), 0.83 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH$_a$$\mathit{H}_bCH_3$), 0.70 [dd, *J* = 7.2, 7.2 Hz, 3H, OC(Ar)CH$_2$CH_3], 0.61 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$CH_3), 0.33 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH_aH$_b$CH$_3$), and 0.24 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH$_a$$\mathit{H}_bCH_3$).

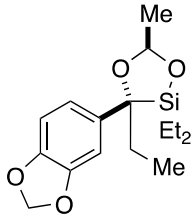
^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.0, 137.3, 126.8, 122.4, 96.7, 77.4, 25.8, 23.1, 21.6, 7.2, 6.4, 6.0, 3.21, and 3.20.

IR (neat): 3067 (w), 2953 (w), 2954 (w), 2875 (m), 1458 (w), 1275 (s), 764 (s), and 625 (w) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ ($C_{17}H_{28}NaO_2Si$)$^+$: 315.1751. Found: 315.1723.

3-(Benzo[*d*][1,3]dioxol-5-yl)-2,2,3-triethyl-5-methyl-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 45 mg, 74%, 14:1 *dr*; 2) at rt: 49% (NMR yield, mesitylene as an internal standard), >20:1 *dr.* (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.07 (d, *J* = 1.7 Hz, 1H, Ar-*H*), 6.73 (d, *J* = 8.1 Hz, 1H, Ar-*H*), 6.69 (dd, *J* = 8.1, 1.7 Hz, 1H, Ar-*H*), 5.33 [s, 2H, C(O)CH_2C(O)], 5.27 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 1.99 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$], 1.55 [dq, *J* = 14.4, 7.2 Hz, 1H,

OC(Ar)$CH_aH_bCH_3$], 1.47 (d, *J* = 4.8 Hz, 3H, OCHCH_3), 1.00 (dd, *J* = 8.0, 8.0 Hz, 3H, $SiCH_2CH_3$), 0.80 [dd, *J* = 7.2, 7.2 Hz, 3H, OC(Ar)CH_2CH_3], 0.73 (dd, *J* = 8.0, 8.0 Hz, 3H, $SiCH_aH_bCH_3$), 0.70 (dq, *J* = 15.8, 8.0 Hz, 1H, $SiCH_aH_bCH_3$), 0.60 (dq, *J* = 15.8, 8.0 Hz, 1H, $SiCH_aH_bCH_3$), 0.40 (water in benzene-d_6, H_2O), and 0.39-0.29 (m, 2H, $SiCH_2CH_3$).

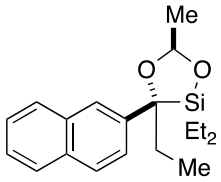
^{13}C NMR ($CDCl_3$, 125 MHz): δ 147.7, 145.1, 137.6, 117.6, 108.1, 105.9, 100.9, 96.8, 78.2, 26.2, 23.2, 7.3, 6.33, 6.22, 4.6, and 3.3.

IR (neat): 3094 (w), 2957 (s), 2774 (s), 1503 (m), 1437 (s), 1234 (m), 1038 (s), 957 (s), and 723 (s) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{16}H_{24}NaO_4Si)^+$: 331.1336. Found: 331.1311.

2,2,3-Triethyl-5-methyl-3-(naphthalen-2-yl)-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 45 mg, 72%, 13:1 *dr*; 2) at rt: 57% (NMR yield, mesitylene as an internal standard), >20:1 *dr.* (colorless clear oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81(t, *J* = 8.5 Hz, 3H, Ar-*H*), 7.78 (d, *J* = 8.5 Hz, 1H, Ar-*H*), 7.46 (t, *J* = 8.5 Hz, 1H, Ar-*H*), 7.42 (t, *J* = 8.5 Hz, 1H, Ar-*H*), 7.29 (d, *J* = 8.5 Hz, 1H, Ar-*H*), 5.44 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 2.24 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)C$H_aH_bCH_3$], 1.94 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)$CH_aH_bCH_3$], 1.57 (d, *J* = 4.8 Hz, 3H, OCHCH_3), 1.16 (dd, *J* = 7.9, 7.9 Hz, 3H, $SiCH_2CH_3$), 0.99 (dq, *J* = 15.7, 7.9 Hz, 1H, $SiCH_aH_bCH_3$), 0.90 (dq, *J* = 15.7, 7.9 Hz, 1H, $SiCH_aH_bCH_3$), 0.70 [dd, *J* = 7.2, 7.2 Hz, 3H, OC(Ar)CH_2CH_3], 0.56 (dd, *J* = 7.9, 7.9 Hz, 3H, $SiCH_2CH_3$), 0.32 (dq, *J* = 15.4, 7.9 Hz, 1H, $SiCH_aH_bCH_3$), and 0.21 (dq, *J* = 15.4, 7.9 Hz, 1H, $SiCH_aH_bCH_3$).

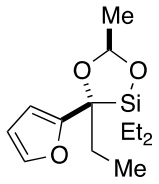
^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.9, 133.7, 131.8, 128.01, 127.83, 127.75, 126.1, 125.2, 123.66, 123.1, 97.0, 78.8, 25.9, 23.3, 7.3, 6.5, 6.2, 4.6, and 3.5.

IR (neat): 3056 (w), 2959 (w), 2876 (s), 1682 (s), 1459 (s), 1083 (s), 1005 (s), 743 (s), and 621 (w) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{19}H_{26}NaO_2Si)^+$: 337.1594. Found: 337.1660.

2,2,3-Triethyl-3-(furan-2-yl)-5-methyl-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 40 mg, 79%, 10:1 *dr*; 2) at rt: 59% (NMR yield, mesitylene as an internal standard), >20:1 *dr*. (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.09 [dd, *J* = 1.8, 0.8 Hz, 1H, Ar-*H*], 6.15-6.12 (m, 2H, Ar-*H*), 5.53 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 2.03 [app q, *J* = 7.2 Hz, 1H, OC(Ar)C*H*$_2$CH$_3$], 1.47 (d, *J* = 4.8 Hz, 3H, OCHC*H*$_3$), 1.04 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$C*H*$_3$), 0.97 [dd, *J* = 7.2, 7.2 Hz, 3H, OC(Ar)CH$_2$C*H*$_3$], 0.84 (dd, *J* = 7.9, 7.9 Hz, 3H SiCH$_2$C*H*$_3$), 0.76-0.61 (m, 2H, SiC*H*$_2$CH$_3$) and 0.40 (water in benzene-d_6, *H*$_2$O).

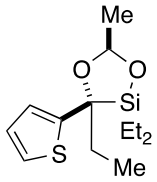
^{13}C NMR ($CDCl_3$, 125 MHz): δ 156.6, 141.3, 110.4, 105.5, 98.7, 75.5, 29.0, 23.4, 9.2, 6.8, 6.3, 4.36, and 4.32.

IR (neat): 3064 (w), 2957 (m), 2877 (m), 1459 (m), 1411 (m), 1240 (m), 1001 (m), and 737 (s) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{13}H_{22}NaO_3Si)^+$: 277.1230. Found: 277.1222.

2,2,3-Triethyl-5-methyl-3-(thiophen-2-yl)-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 43 mg, 79%, 10:1 *dr*; 2) at rt: 63% (NMR yield, mesitylene as an internal standard), >20:1 *dr*. (colorless clear oil)

^{1}H NMR (C_6D_6, 300 MHz): 6.88 (dd, *J* = 5.1, 1.2 Hz, 1H, thiophene-*H*), 6.81 (dd, *J* = 5.1, 3.5 Hz, 1H, thiophene-*H*), 6.59 (dd, *J* = 3.5, 1.2 Hz, 1H, thiophene-*H*), 5.62 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 2.03 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)C*H*$_a$H$_b$CH$_3$], 1.88 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)CH$_a$*H*$_b$CH$_3$], 1.47 (d, *J* = 4.8 Hz, 3H, OCHC*H*$_3$), 1.02 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$C*H*$_3$), 0.93 [dd, *J* = 7.2, 7.2 Hz, 3H, OC(Ar)CH$_2$C*H*$_3$], 0.63 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$C*H*$_3$), 0.77-0.59 (m, 4H, SiC*H*$_2$CH$_3$), and 0.40 (water in benzene-d_6, *H*$_2$O).

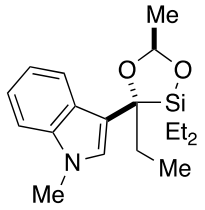
^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.9, 126.93, 126.86, 123.0, 98.6, 77.4, 32.9, 23.4, 6.6, 6.31, 6.32, 4.1, and 4.3.

IR (neat): 3069 (w), 2954 (s), 2936 (m), 2875 (m), 1605 (w), 1436 (w), 1233 (m), 1004 (s), 825 (s), and 686 (s) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{13}H_{22}NaO_2SSi)^+$: 293.1002. Found: 293.1051.

1,3-Dimethyl-2-(2,2,3-triethyl-5-methyl-1,4,2-dioxasilolan-3-yl)-1H-indole (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 52 mg, 82%, 10:1 *dr*; 2) at rt: 64% (NMR yield, mesitylene as an internal standard), >20:1 *dr.* (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.58 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.24 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 7.18 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 7.04 (d, *J* = 8.1 Hz 1H, Ar-*H*), 7.02 (s, 1H, Ar-*H*), 5.41 (q, *J* = 4.8 Hz, 1H), 2.93 (s, 3H, N-C*H*$_3$), 2.16 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)C*H*$_a$H$_b$CH$_3$], 2.02 [dq, *J* = 14.4, 7.2 Hz, 1H, OC(Ar)C*H*$_a$H$_b$CH$_3$], 1.60 (d, *J* = 4.8 Hz, 3H, OCHC*H*$_3$), 1.17 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$C*H*$_3$), 0.96 (dq, *J* = 15.4, 7.9 Hz, 1H, SiC*H*$_a$H$_b$CH$_3$), 0.92 [dd, *J* = 7.2, 7.2 Hz, 3H, OC(Ar)CH$_2$C*H*$_3$], 0.85 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH$_a$*H*$_b$CH$_3$), 0.68 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH$_2$C*H*$_3$), 0.39 (dq, *J* = 15.4, 7.9 Hz, 1H, SiC*H*$_a$H$_b$CH$_3$), and 0.35 (dq, *J* = 15.4, 7.9 Hz, 1H, SiCH$_a$*H*$_b$CH$_3$).

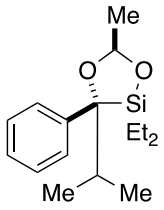
^{13}C NMR (C_6D_6, 125 MHz): δ 138.0, 125.96, 125.87, 121.6, 119.5, 119.0, 117.1, 109.9, 96.7, 75.8, 32.0, 25.5, 23.6, 7.6, 6.91, 6.79, 5.1, and 4.4.

IR (neat): 2954 (m), 2879 (m), 1588 (m), 1486 (s), 1277 (m), 1056 (m), 843 (m), and 713 (s) cm^{-1}.

TLC: R_f = 0.4 in 40:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{18}H_{27}NNaO_2Si)^+$: 340.1703. F ound: 340.1768.

2,2-Diethyl-3-isopropyl-5-methyl-3-phenyl-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 40 mg, 73%, >20:1 *dr*; 2) at rt: 44% (NMR yield, mesitylene as an internal standard), >20:1 *dr*. (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.27 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 7.22-7.15 (m, 3H, Ar-*H*), 5.42 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 2.38 [septet, *J* = 13.5, 6.7 Hz, 1H, C*H*$(CH_3)_2$], 1.44 (d, *J* = 4.8 Hz, 3H, OCHC*H*$_3$), 1.18 (dd, *J* = 7.8, 7.8 Hz, 3H, $SiCH_2CH_3$), 1.02 (dq, *J* = 15.7, 7.8 Hz, 1H, $SiCH_aH_bCH_3$), 0.94 (dq, *J* = 15.7, 7.8 Hz, 1H, $SiCH_aH_bCH_3$), 0.82 [d, *J* = 6.7, Hz, 3H, CH*(*CH_3*)*$_2$], 0.79 [dd, *J* = 6.7 Hz, 3H, CH*(*CH_3*)*$_2$], 0.46 (dq, *J* = 15.1, 7.8 Hz, 1H, $SiCH_aH_bCH_3$), 0.40 (water in benzene-d_6, H_2O), and 0.29 (dq, *J* = 15.1, 7.8 Hz, 1H, $SiCH_aH_bCH_3$).

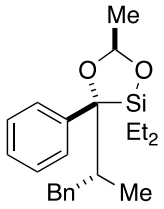
^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.7, 127.38, 127.28, 125.9, 97.4, 72.6, 30.6, 23.8, 19.3, 15.8, 7.5, 6.3, 5.7, and 5.2.

IR (neat): 3081 (w), 2969 (w), 1771 (s), 1489 (m), 1451 (m), 1214 (m), 1164 (s), 1114 (s), 938 (m), and 771 (m) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{16}H_{26}NaO_2Si)^+$: 301.1594. Found: 301.1510.

2,2-Diethyl-5-methyl-3-phenyl-3-((*S*)-1-phenylpropan-2-yl)-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 51 mg, 73%, >20:1 *dr*; 2) at rt: 51% (NMR yield, mesitylene as an internal standard), >20:1 *dr*. (colorless clear oil)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.41-7.33 (m, 2H, Ar-*H*), 7.23 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.15-7.09 (m, 3H, Ar-*H*), 7.06 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.01 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 5.42 (q, *J* = 4.8 Hz, 1H, OC*H*Me), 2.88 (dd, *J* = 13.3, 2.4 Hz, 1H, $CH_3CHCH_aH_bPh$), 2.53 (dqd, *J* = 11.8, 6.7, 2.4 Hz, 1H, CH_3CHCH_2Ph), 2.04 (dd, *J* = 13.3, 11.8 Hz, 1H, $CH_3CHCH_aH_bPh$), 1.48 (d, *J* = 4.8

Hz, 3H, OCHCH_3), 1.14 (dd, J = 7.8, 7.8 Hz, 3H, SiCH$_2$CH_3], 1.08 (dq, J = 15.0, 7.8 Hz, 1H, SiCH_aH$_b$CH$_3$), 0.90 (d, J = 6.5 Hz, 1H, CH_3CHCH$_2$Ph), 0.90-0.83 (dq, J = 15.0, 7.8 Hz, 1H, SiCH$_a$$H_bCH_3$), 0.73 (dd, J = 7.8, 7.8 Hz, 3H, SiCH$_2$CH_3], 0.49 (dq, J = 15.0, 7.8 Hz, 1H, SiCH_2CH$_3$), 0.40 (water in benzene-d_6, H_2O), and 0.37 (dq, J = 15.7, 7.8 Hz, 1H, SiCH_aH$_b$CH$_3$).

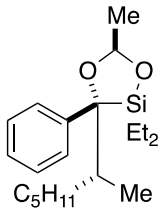
^{13}C NMR (C$_6$D$_6$, 125 MHz): δ 141.7, 141.5, 129.4, 128.6, 128.3, 127.4, 126.4, 126.2, 97.9, 82.5, 40.0, 39.1, 23.9, 12.5, 7.6, 6.5, 6.0, and 5.7.

IR (neat): 3083 (w), 2958 (w), 1600 (s), 1493 (m), 1445 (m), 1292 (m), 1097 (s), 1005 (s), 971 (m), and 796 (s) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for (M+Na)$^+$ (C$_{22}$H$_{30}$NaO$_2$Si)$^+$: 377.1907. Found: 377.1946.

2,2-Diethyl-3-((*S*)-heptan-2-yl)-5-methyl-3-phenyl-1,4,2-dioxasilolane (1-3-1)



Yield: 0.2 mmol scale, 1) at 100 °C: 52 mg, 78%, >20:1 *dr.*; 2) at rt: 47% (NMR yield, mesitylene as an internal standard), >20:1 *dr.* (colorless clear oil)

^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.38 (d, J = 7.6 Hz, 2H, Ar-*H*), 7.19 (t, J = 7.6 Hz, 2H, Ar-*H*), 7.08 (t, J = 7.6 Hz, 1H, Ar-*H*), 5.44 (q, J = 4.8 Hz, 1H, OC*H*Me), 2.20-2.13 (m, 1H, CH$_3$C*H*CH$_2$), 1.50 (d, J = 4.8 Hz, 3H, , OCHCH_3), 1.48-1.42 (m, 1H, alkyl-*H*), 1.41-1.30 (m, 2H, alkyl-*H*), 1.29-1.19 (m, 4H, alkyl-*H*), 1.15 (dd, J = 7.8, 7.8 Hz, 3H, SiCH$_2$CH_3), 1.14-1.10 (m, 3H, alkyl-*H*), 0.97 (dq, J = 15.7, 7.8 Hz, 1H, SiCH_2CH$_3$), 0.96 (d, J = 6.5 Hz, 3H, CH_3CHCH$_2$), 0.82 (dq, J = 15.7, 7.8 Hz, 1H, SiCH_2CH$_3$), 0.87 (dd, J = 7.2 Hz, 3H, CH$_2$CH$_2$CH_3), 0.86-0.84 (m, 1H, alkyl-*H*), 0.74 [dd, J = 7.8, 7.8 Hz, 3H, SiCH$_2$CH_3], 0.51 (dq, J = 15.7, 7.8 Hz, 1H, SiCH_aH$_b$CH$_3$), 0.40 (water in benzene-d_6, H_2O), and 0.39 (dq, J = 15.7, 7.8 Hz, 1H, SiCH$_a$$H_bCH_3$).

^{13}C NMR (C$_6$D$_6$, 125 MHz): δ 141.5, 127.62, 127.60, 126.2, 97.2, 82.9, 36.5, 33.9, 32.7, 28.4, 23.9, 23.1, 14.3, 12.5, 7.6, 6.5, 6.0, and 5.5.

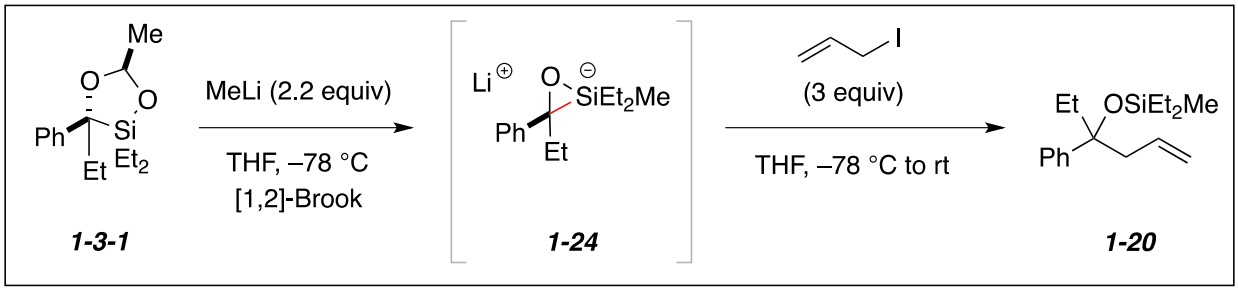
IR (neat): 3071 (w), 2955 (w), 1717 (s), 1489 (m), 1493 (m), 1211 (m), 1142 (s), 1113 (s), 953 (m), and 728 (m) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{20}H_{34}NaO_2Si)^+$: 357.2220. Found: 357.2212.

D.1. Brook rearrangement

Scheme D1. Allylation via the Brook Rearrangement



To a flame-dried vial was added a solution of dioxasilolane **1-3-1** (26 μL, 0.1 mmol) in THF (0.5 mL, 0.2 M) and cooled the mixture to –78 °C. MeLi (137μL, 1.6 M in Et_2O, 2.2 equiv) was added slowly to the reaction mixture. After being stirred for 30 min at –78 °C, a solution of allyl iodide (137μL, 0.3 mmol) in THF (0.1 mL) was added slowly. The reaction mixture was slowly allowed to room temperature by removing a dry-ice bath and stirred for 30 min at rt. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The volatiles were removed *in vacuo* to afford crude material, which was purified by MPLC (hexanes/EtOAc =80:1, 5 mL/min, retention time 15 min) to afford **1-20** (22 mg, 81% yield) as a colorless oil.

Diethyl(methyl)[(3-phenylhex-5-en-3-yl)oxy]silane (1-20)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 500 MHz): 7.35 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.29 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 7.19 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 5.59 [dddd, *J* = 17.1, 10.3, 6.8, 6.8 Hz, 1H, CH_2=C*H*CH_2], 4.94 [dddd, *J* = 17.1, 1.5, 1.5, 1.5 Hz, 1H, C$H_a$$H_b$=CH$CH_2$], 4.93 [dddd, *J* = 10.3, 1.5, 1.5, 1.5 Hz, 1H, C$H_a$$H_b$=CH$CH_2$], 2.67 [dddd, *J* = 14.4, 6.8, 1.5, 1.5 Hz, H_2C=CHC$H_a$$H_b$], 2.60 [dddd, *J* = 14.4, 6.8, 1.5, 1.5 Hz, H_2C=CHC$H_a$$H_b$], 1.92 (dq, *J* = 14.6, 7.3 Hz, 1H, OC(Ar)C$H_a$$H_b$$CH_3$), 1.82 (dq, *J* = 14.6, 7.3 Hz, 1H, OC(Ar)C$H_a$$H_b$$CH_3$), 0.97 [dd, *J* = 7.9, 7.9 Hz, 6H, $SiCH_2$(CH_3)$_2$], 0.69 (dd, *J* = 7.3, 7.3 Hz, 3H, OC(Ar)CH_2CH_3), 0.65-0.57 [m, 4H, Si(CH_2)$_2$$CH_3$], 0.09 (s, 3H, $OSiEt_2$CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.2, 134.8, 127.8, 126.33, 126.28, 117.2, 80.4, 47.3, 35.0,

31.8, 14.3, 8.74, 8.4, 7.4, and –1.7.

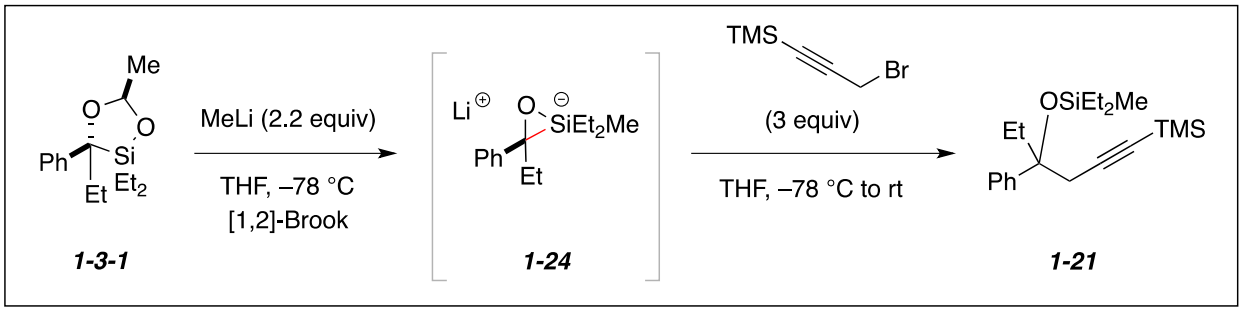
IR (neat): 3088 (w), 3019 (w), 2954 (s), 2856 (m), 1618 (m), 1467 (s), 1278 (s) 1129 (s) 1049 (m), and 762 (w) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{17}H_{28}NaOSi)^+$: 299.1802. Found: 299.1813.

D.2. Propargylation via the Brook rearrangement

Scheme D2. Propargylation via the Brook Rearrangement



To a flame-dried vial was added a solution of dioxasilolane **1-3-1** (26 μL, 0.1 mmol) in THF (0.5 mL, 0.2 M) and cooled the mixture to –78 °C. MeLi (137μL, 1.6 M in Et_2O, 2.2 equiv) was added slowly to the reaction mixture. After being stirred for 30 min at –78 °C, a solution of TMS-protected propargyl bromide (57μL, 0.3 mmol) in THF (0.1 mL) was added slowly. The reaction mixture was slowly allowed to room temperature by removing a dry-ice bath and stirred for 30 min at rt. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The volatiles were removed *in vacuo* to afford crude material, which was purified by MPLC (hexanes/EtOAc =80:1, 5 mL/min, retention time 15 min) to afford **1-21** (25 mg, 73% yield) as a colorless oil.

(4-{[Diethyl(methyl)silyl]oxy}-4-phenylhex-1-yn-1-yl)trimethylsilane (1-21)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 7.30 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 7.21 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 2.75 [d, *J* = 16.7 Hz, CH_aH$_b$CC[Si(CH$_3$)$_2$], 2.71 [d, *J* = 16.7 Hz, CH$_a$$H_b$CC[Si(CH$_3$)$_2$], 2.03 [dq, *J* = 14.6, 7.3 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$], 1.96 [dq, *J* = 14.6, 7.3 Hz, 1H, OC(Ar)CH_aH$_b$CH$_3$], 0.97 [dd, *J* = 7.9, 7.9 Hz, 6H, SiCH$_2$(CH_3)$_2$], 0.73 [dd, *J* = 7.3, 7.3

Hz, 3H, OC(Ar)CH_2CH_3], 0.69-0.60 [m, 4H, Si(CH_2)$_2CH_3$], 0.12 (s, 3H, OSiEt_2CH_3), and 0.091 (s, 9H, SiMe_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.1, 127.8, 126.6, 126.1, 104.4, 87.9, 79.7, 35.3, 34.3, 14.3, 8.66, 8.56, 8.47, 7.4, 0.1, and –1.9.

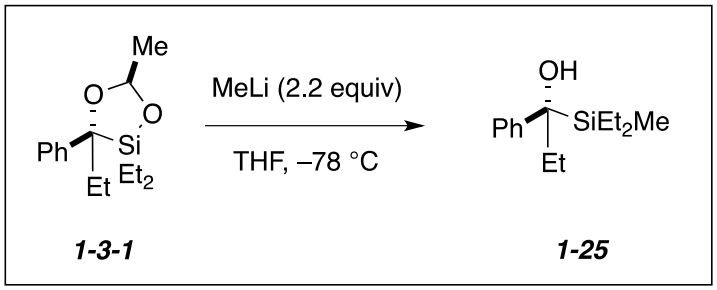
IR (neat): 3059 (w), 2956 (w), 2177 (m), 1602 (w), 1391 (m), 1249 (m), 1076 (s), 1041 (m), 840 (s), 756 (s), and 667 (s) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{20}H_{34}NaOSi_2)^+$: 369.2040. Found: 369.2062.

D.3. Procedure for nucleophilic ring opening of dioxasilolane

Scheme D.3. Nucleophilic Ring opening of dioxasilolane **1-3-1**



To a flame-dried vial was added a solution of dioxasilolane **1-3-1** (26 μL, 0.1 mmol) in THF (0.5 mL, 0.2 M) and cooled the mixture to –78 °C. MeLi (137 μL, 1.6 M in Et_2O, 2.2 equiv) was added slowly to the reaction mixture. After being stirred for 30 min at –78 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The volatiles were removed *in vacuo* to afford crude material, which was purified by MPLC (hexanes/EtOAc =80:1, 5 mL/min, retention time 15 min) to afford **1-25** (21 mg, 88% yield) as a colorless oil.

(*S*)-1-(Diethyl(methyl)silyl)-1-phenylpropan-1-ol (1-25)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.24-7.18 (nfom, 4H, Ar-*H*), 7.06-7.02 (nfom, 1H, Ar-*H*), 1.92 [dq, *J* = 14.7, 7.4 Hz, 1H, OC(Ar)C$H_aH_bCH_3$], 1.78 [dq, *J* = 14.7, 7.4 Hz, 1H, OC(Ar)C$H_aH_bCH_3$], 1.14 (br s, 1H, O*H*), 0.90 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH_2CH_3), 0.88 (dd, *J* = 7.9, 7.9 Hz, 3H, SiCH_2CH_3), 0.59 [dd, *J* = 7.3, 7.3 Hz, 3H, OC(Ar)CH_2CH_3], 0.57-0.48 [m, 4H,

Si(CH_2)$_2$$CH_3$], 0.40 (water in benzene-d_6, H_2O), and –0.03 (s, 3H, OSiEt$_2$$CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.8, 128.2, 125.18, 125.05, 73.7, 29.7, 7.85, 7.81, 6.0, 3.1, 2.95, and –8.3.

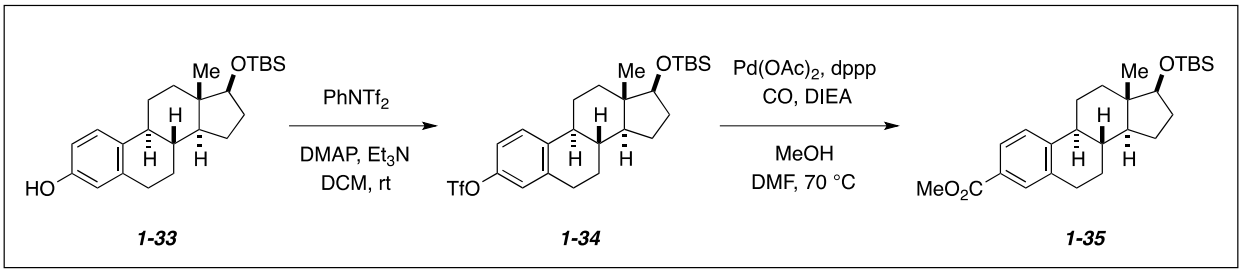
IR (neat): 3442 (br, m), 3066 (w), 2952 (w), 2169 (m), 1388 (m), 1249 (m), 1011 (s), 1084 (s), 843 (m), 755 (s), and 712 (s) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{14}H_{24}NaOSi)^+$: 259.1489. Found: 259.1466.

D.4. Procedure for preparation of Estradiol Ester 1-35

Scheme D.4. Preparation of Estradiol Ester **1-35**



Phenol **1-33** (1.4 g, 3.6 mmol, 1.0 equiv), $PhNTf_2$ (2.0 g, 5.4 mmol, 1.5 equiv), DMAP (45 mg, 0.37 mmol, 0.1 equiv) were added to a flame-dried round bottmed flask. The flask was purged with nitrogen. DCM (8 mL, 0.5 M) and Et_3N (1.5 mL, 10.6 mmol, 3 equiv) were added to the mixture and the reaction mixture was stirred at room temperature for 3 h. Volatiles were removed under reduced pressure and concentrated *in vacuo* to afford the crude material, which was purified by MPLC (hexanes/EtOAc =20:1, 5 mL/min, retention time 15 min) to afford **1-34** (1.5 g, 84% yield) as a colorless liquid.

1-34 (208 mg, 0.4 mmol, 1 equiv), dppp (9 mg, 0.02 mmol, 0.05 equiv), $Pd(OAc)_2$ (5 mg, 0.02 mmol, 0.05 equiv), diisopropylethyl amine (140 μl, 0.8 mmol, 2 equiv), MeOH (1 mL, 0.4 M), and DMF (1 mL, 0.4 M) were placed to a flame-dried pyrex tube. The reaction tube was purged twice with the CO gas using balloon. The reaction mixture was stirred at 70 °C for 24 h in CO atmosphere. Thene the mixture was diluted with water and extracted with EtOAc. The

organic layer was washed with water, followed by brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to afford a crude**1-35**, which was purified by column chromatography (Hexane: EtOAc, 20:1) to give **1-35** (132 mg, 77%) as a colorless liquid.

(8*R*,9*S*,13*S*,14*S*,17*S*)-Methyl 17-[(*tert*-butyldimethylsilyl)oxy]-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3-carboxylate (1-35)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.79 [dd, *J* = 8.1, 1.7 Hz, 1H, C(2)*H*], 7.75 [d, *J* = 1.7 Hz, 1H, C(4)*H*], 7.34 [d, *J* = 8.1 Hz, 1H, C(1)*H*], 3.89 (s, 3H, Ar-OCH_3), 3.65 [dd, *J* = 8.2, 8.2 Hz, 1H, C(17)*H*], 2.94-2.86 (m, 2H, alkyl-*H*), 2.32 (dddd, *J* = 13.5, 4.2, 4.2, 2.8 Hz, 1H, alkyl-*H*), 2.23 (ddd, *J* = 11.4, 11.4, 4.4 Hz, 1H, alkyl-*H*), 1.99-1.87 (m, 3H, alkyl-*H*), 1.67 (dddd, *J* = 12.3, 9.5, 7.2, 3.4 Hz, 1H, alkyl-*H*), 1.58-1.28 (m, 5H, alkyl-*H*), 1.22 (ddd, *J* = 12.9, 12.9, 4.1 Hz, 1H, alkyl-*H*), 1.14 (ddd, *J* = 12.2, 11.0, 7.3 Hz, 1H, alkyl-*H*), 0.91 (s, 9H, Si(CH_3)$_3$], 0.76 [s, 3H, C(18)H_3], 0.05 (s, 3H, Si^{t}BuCH_3), and 0.04 (s, 3H, Si^{t}BuCH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.5, 146.2, 137.1, 130.3, 127.4, 126.9, 125.6, 81.8, 52.0, 50.0, 45.0, 43.7, 38.5, 37.3, 31.1, 29.6, 27.2, 26.24, 26.04, 23.5, 18.3, 11.5, –4.3, and –4.6.

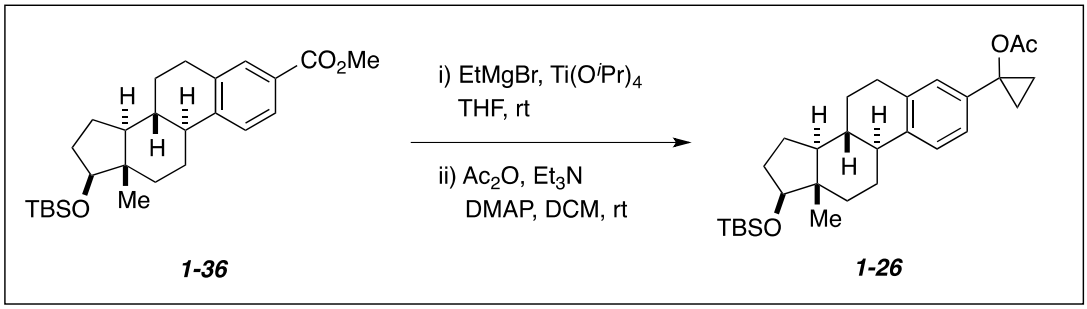
IR (neat): 3058 (w), 2930 (m), 2864 (m), 1745 (s), 1723 (m), 1435 (m), 1290 (m), 1102 (s), 834 (m), and 777 (m) cm^{-1}.

TLC: R_f = 0.5 in 20:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{26}H_{40}NaO_3Si)^+$: 451.2639. Found: 451.2624.

D.5. Preparation of Estradiol Cyclopropanoate 1-26

Scheme D.5. Preparation of Estradiol Cyclopropanoate **1-26**



1-{(8*R*,9*S*,13*S*,14*S*,17*S*)-17-[(*Tert*-butyldimethylsilyl)oxy]-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl}cyclopropyl acetate (1-26)

Yield: 1 mmol scale, 196 mg, 42%. (colorless viscous oil)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.79 [dd, *J* = 8.1, 1.7 Hz, 1H, C(2)*H*], 7.75 [d, *J* = 1.7 Hz, 1H, C(4)*H*], 7.34 [d, *J* = 8.1 Hz, 1H, C(1)*H*], 3.63 [dd, *J* = 8.2, 8.2 Hz, 1H, C(17)*H*], 2.94-2.86 (m, 2H, alkyl-*H*), 2.32-2.25 (m, 1H, alkyl-*H*), 2.24-2.16 (m, 1H, alkyl-*H*), 2.03 (s, 3H, OCH_3), 1.97-1.85 (m, 3H, alkyl-*H*), 1.70-1.61 (m, 1H, alkyl-*H*), 1.54-1.10 (m, 11H, alkyl-*H*, cyp-*H*), 0.91 (s, 9H, Si(CH_3)$_3$], 0.76 [s, 3H, C(18)H_3], 0.05 (s, 3H, Si^{t}BuCH_3), and 0.04 (s, 3H, Si^{t}BuCH_3).

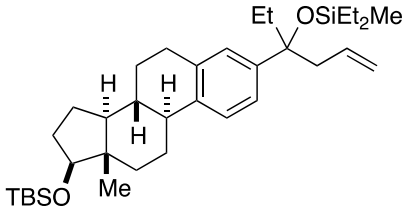
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 139.8, 137.3, 136.9, 127.0, 125.6, 123.9, 81.9, 60.1, 50.0, 44.7, 43.8, 38.8, 37.4, 31.2, 29.9, 27.4, 26.3, 26.1, 23.5, 21.6, 18.3, 14.81, 14.78, 11.5, –4.3, and –4.6.

IR (neat): 3069 (w), 2938 (m), 2864 (m), 1741 (s), 1714 (m), 1493 (m), 1313 (m), 1185 (s), 1055 (m), and 924 (m) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ ($C_{29}H_{44}NaO_3Si)^+$: 491.2952. Found: 491.2926.

(3*S*)-3-{[(8*R*,9*S*,13*S*,14*S*,17*S*)-17-(*Tert*-butyldimethylsilyl)oxy]-13-methyl 7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl}-2,2,3-triethyl-5-methyl-1,4,2-dioxasilolane (1-27):



Yield: 0.2 mmol scale, 96 mg, 85%, 1:1 *dr*. (colorless viscous oil)

^{1}H NMR (C_6D_6, 500 MHz, a 1:1 mixture of two diastereomers): δ 7.31-7.22 (m, 6H, Ar*H*), 5.796 [dddd, *J* = 17.1, 10.3, 6.8, 6.8 Hz, 1H, CH_2=C*H*CH_2 (from one diastereomer)], 5.785 [dddd, *J* = 17.1, 10.3, 6.8, 6.8 Hz, 1H, CH_2=C*H*CH_2 (from the other diastereomer)], 4.94 [m, 4H, CH_2=CHCH_2], 3.43 [app t, *J* = 8.4 Hz, 2H, C(17)*H*], 2.85-2.80 (m, 4H), 2.72-2.65 (m, 2H), 2.63-2.57 (m, 2H), 2.21-2.15 (m, 2H), 2.11-2.04 (m, 2H), 1.92-1.67 (m, 12H), 1.50-1.04 (m, 14H), 1.01 [app t, *J* = 7.9 Hz, 12H, $SiCH_2$(CH_3)$_2$], 0.96 (s, 9H, Si(CH_3)$_3$], 0.84 (app t, *J* = 7.1 Hz, 6H,

OC(Ar)$CH_2C\mathit{H_3}$), 0.81-0.77 (m, 4H, Si($C\mathit{H_2}CH_3)_2$], 0.70 [s, 6H, C(18)$\mathit{H_3}$], 0.68-0.61 (m, 4H, Si($C\mathit{H_2}CH_3)_2$], 0.11 (s, 6H, $OSiEt_2C\mathit{H_3}$), 0.047 (s, 6H, Si^{t}Bu$C\mathit{H_3}$), and 0.033 (s, 6H, Si^{t}Bu$C\mathit{H_3}$).

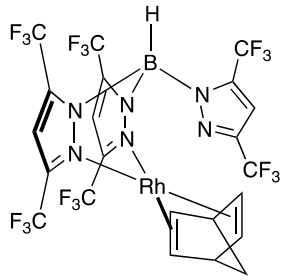
^{13}C NMR (C_6D_6, 125 MHz): δ 143.6, 138.7, 136.1, 135.2, 127.1, 125.2, 124.0, 117.2, 100.3, 82.1, 80.5, 49.8, 47.4, 47.3, 44.8, 43.8, 39.05, 39.04, 37.6, 35.27, 35.22, 32.0, 31.4, 30.4, 27.8, 26.6, 26.2, 23.5, 23.1, 18.4, 14.4, 11.6, 9.0, 8.7, 7.6, –1.6, –4.2, and –4.5.

IR (neat): 3088 (w), 2952 (s), 2874 (s), 1685 (m), 1360 (w), 1247 (s), 1139 (m), 1092 (s), 834 (m), 773 (s), and 7667 (w) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{35}H_{60}NaO_2Si_2)^+$: 591.4024. Found: 591.4088.

D.6. Procedure for synthesis of [HB(3,5-$(CF_3)_2$Pz)$_3$]Rh(nbd), $Tp^{(CF_3)_2}$Rh(nbd)



This was reported earlier and prepared using a procedure slightly different from that described in Inorganica Chimica Acta, **1995**, *240*, 631-639.[S5] $[Rh(nbd)Cl]_2$ (0.032 g, 0.0694 mmol), and $Tp^{(CF_3)_2}$Na(THF) (0.100 g, 0.140 mmol) were placed in a flask and dissolved in dichloromethane (10 mL). The resulting orange solution was allowed to stir for 48 h at room temperature and the precipitated NaCl was removed by filtration through a bed of Celite. The solvent was removed under reduced pressure to obtain the product $Tp^{(CF_3)_2}$Rh(nbd) as an orange solid. Yield: 0.084 g, 74%. Spectroscopic data agree well with the reported values. X-ray quality crystals were grown from toluene at –20 °C.

mp. 137–139 °C. (Yellow crystalline solid)

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K) δ (ppm): 7.05 (s, 3H, Pz-C*H*), 4.05 (q, 4H, *J* = 2.3 Hz, C*H*=C*H*), 3.51 (br, 2H, C*H*), 1.16 (t, 2H, *J* = 1.4 Hz, C*H*).

^{13}C NMR ($CDCl_3$, 125 MHz, 298 K) δ (ppm): 144.4 [q, $^2J(C,F)$ = 40 Hz *C*CF_3], 140.4 [q, $^2J(C,F)$ = 40 Hz, *C*CF_3], 120.2 [q, $^1J(C,F)$ = 269 Hz, *C*F_3], 119.1 [q, $^1J(C,F)$ = 272 Hz, *C*F_3], 108.6 (s, Pz-*C*H), 63.2 [d, $^3J(Rh,C)$ = 7.2 Hz], 59.1 [d, CH=CH, $^1J(Rh,C)$ = 9.6 Hz], 50.2.

^{19}F NMR ($CDCl_3$, 470.62 MHz, 298 K) δ (ppm): –59.5 [d, 9F, $J(H,F)$ = 4.3 Hz, C*F*$_3$], –60.0 (s, 9F, C*F*$_3$).

ATR-FTIR (Selected peak, cm^{-1}): 2540 (B-H).

Anal. Calc. for $C_{17}H_{17}AgBF_9N_6$: C, 34.32; H, 2.88; N, 14.12. Found: C, 34.38; H, 2.77; N, 13.74.

D.7. X-ray crystallographic data:

A suitable crystal of $Tp^{(CF_3)_2}Rh(nbd)$ covered with a layer of hydrocarbon/Paratone-N oil was selected and mounted on a Cryo-loop, and immediately placed in the low temperature nitrogen stream. The X-ray intensity data were measured at 100(2) K on a Bruker D8 Quest with a Photon 100 CMOS detector equipped with an Oxford Cryosystems 700 series cooler, a Triumph monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å). Intensity data were processed using the Bruker Apex3 program suite. Absorption corrections were applied by using SADABS. Initial atomic positions were located by direct methods using XT, and the structures of the compounds were refined by the least-squares method using SHELXL[S6] within Olex2[S6] GUI. $Tp^{(CF_3)_2}Rh(nbd)$ crystallizes with a molecule of toluene in the asymmetric unit. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms on alkene moiety and on the boron were located from the difference map and included in the refinement. Rest of the hydrogen atoms were included at calculated positions and refined riding on corresponding carbons. X-ray structural figures were generated using Olex2. Further details are given in the CIF. Further details are given in the CIF. CCDC 1838203 contains the supplementary crystallographic data.

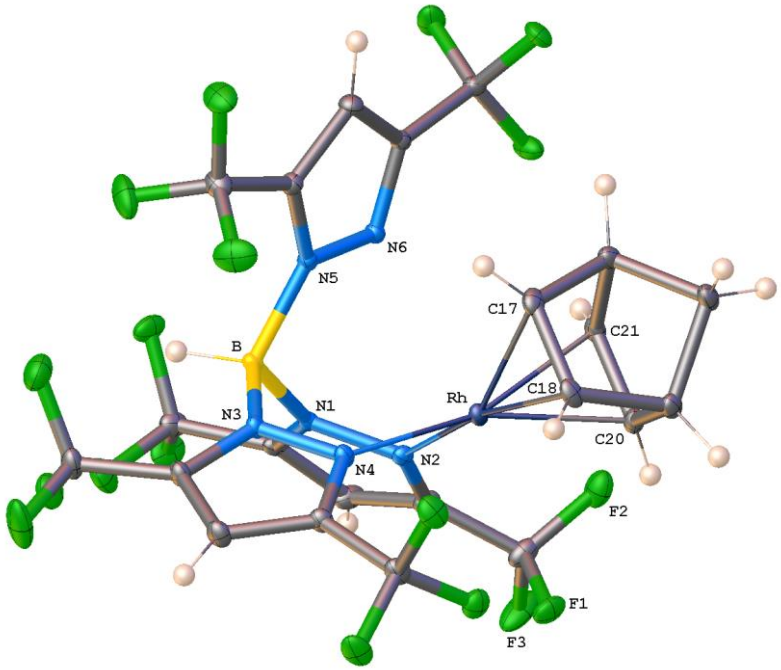


Figure D.7. Molecular structure of $Tp^{(CF_3)_2}Rh(nbd)$. Thermal ellipsoids are given at 50% probability level

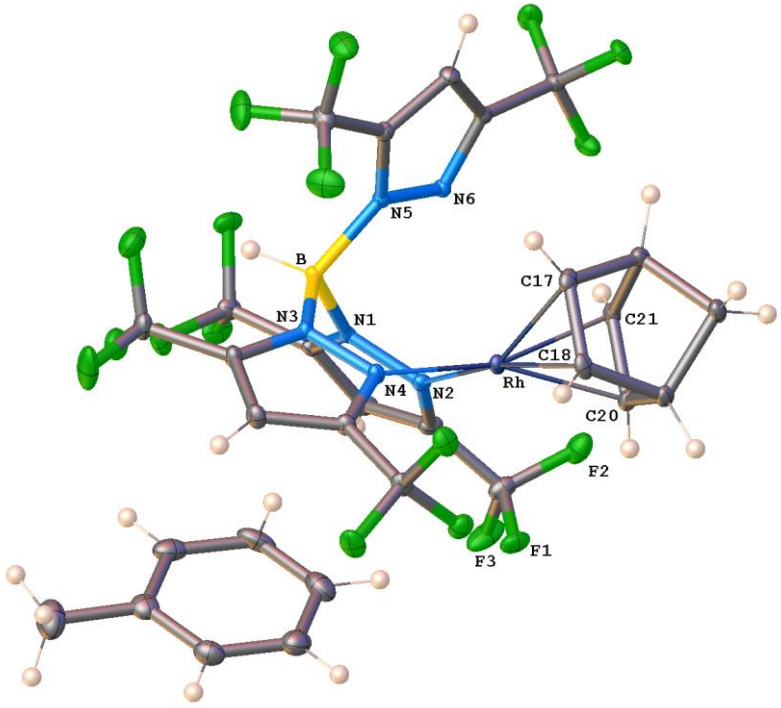


Figure D.8. A view of the asymmetric unit showing toluene of crystallization

Table D.1. Crystal data and structure refinement for $Tp^{(CF_3)_2}Rh(nbd)$•toluene

Identification code	rad411_0m_a
Empirical formula	$C_{29}H_{20}BF_{18}N_6Rh$
Formula weight	908.23
Temperature/K	101.05
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.0106(8)
b/Å	9.0679(4)
c/Å	19.7109(9)
α/°	90
β/°	96.859(2)
γ/°	90
Volume/Å^3	3196.1(2)
Z	4
ρ_{calc}g/cm^3	1.887
μ/mm^{-1}	0.674
F(000)	1792.0
Crystal size/mm^3	0.41 × 0.41 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.554 to 61.138
Index ranges	$-25 \leq h \leq 25$, $-12 \leq k \leq 12$, $-28 \leq l \leq 28$
Reflections collected	42504
Independent reflections	9783 [R_{int} = 0.0200, R_{sigma} = 0.0161]
Data/restraints/parameters	9783/0/517
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0237, wR_2 = 0.0564
Final R indexes [all data]	R_1 = 0.0272, wR_2 = 0.0579
Largest diff. peak/hole / e Å^{-3}	0.59/-0.60

Table D.2. Bond Lengths for $Tp^{(CF3)2}Rh(nbd)$•toluene

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Rh	N2	2.1523(10)	N5	N6	1.3584(14)
Rh	N4	2.1248(11)	N5	C13	1.3658(16)
Rh	C17	2.1145(13)	N5	B	1.5653(16)
Rh	C18	2.1238(12)	N6	C11	1.3308(15)
Rh	C20	2.1404(13)	C1	C2	1.3916(18)
Rh	C21	2.1309(12)	C1	C4	1.4918(19)
F1	C4	1.3367(16)	C2	C3	1.3738(19)
F2	C4	1.3389(19)	C3	C5	1.4944(18)
F3	C4	1.3350(17)	C6	C7	1.3912(18)
F4	C5	1.3372(16)	C6	C9	1.4942(18)
F5	C5	1.3288(16)	C7	C8	1.3721(18)
F6	C5	1.3418(17)	C8	C10	1.4989(18)
F7	C9	1.3414(16)	C11	C12	1.3985(17)
F8	C9	1.3361(17)	C11	C14	1.4905(17)
F9	C9	1.3394(15)	C12	C13	1.3728(17)
F10	C10	1.3178(19)	C13	C15	1.4866(18)
F11	C10	1.3316(18)	C16	C17	1.5342(19)
F12	C10	1.3447(16)	C16	C21	1.5384(19)
F13	C14	1.3393(15)	C16	C22	1.5492(18)
F14	C14	1.3369(15)	C17	C18	1.3955(19)
F15	C14	1.3388(15)	C18	C19	1.5362(19)
F16	C15	1.3384(16)	C19	C20	1.5324(19)
F17	C15	1.3394(17)	C19	C22	1.5420(19)
F18	C15	1.3352(18)	C20	C21	1.3923(18)
N1	N2	1.3612(14)	C23	C24	1.388(2)
N1	C3	1.3546(15)	C23	C28	1.397(2)
N1	B	1.5526(17)	C23	C29	1.504(3)

N2	C1	1.3408(16)	C24	C25	1.384(2)
N3	N4	1.3645(14)	C25	C26	1.383(3)
N3	C8	1.3595(16)	C26	C27	1.387(3)
N3	B	1.5509(17)	C27	C28	1.380(3)
N4	C6	1.3404(16)			

Table D.3. Bond Angles for $Tp^{(CF3)2}$Rh(nbd)•toluene

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N4	Rh	N2	84.98(4)	F8	C9	F9	107.55(11)
N4	Rh	C20	156.81(5)	F8	C9	C6	113.13(11)
N4	Rh	C21	162.80(5)	F9	C9	F7	106.84(11)
C17	Rh	N2	148.97(5)	F9	C9	C6	109.71(11)
C17	Rh	N4	102.20(5)	F10	C10	F11	107.91(12)
C17	Rh	C18	38.45(5)	F10	C10	F12	107.24(13)
C17	Rh	C20	79.59(5)	F10	C10	C8	113.39(12)
C17	Rh	C21	66.98(5)	F11	C10	F12	106.04(12)
C18	Rh	N2	170.08(5)	F11	C10	C8	113.33(12)
C18	Rh	N4	100.10(5)	F12	C10	C8	108.51(12)
C18	Rh	C20	66.72(5)	N6	C11	C12	112.57(11)
C18	Rh	C21	79.85(5)	N6	C11	C14	120.22(11)
C20	Rh	N2	105.53(5)	C12	C11	C14	127.21(11)
C21	Rh	N2	97.83(5)	C13	C12	C11	103.21(11)
C21	Rh	C20	38.05(5)	N5	C13	C12	109.12(11)
N2	N1	B	122.06(10)	N5	C13	C15	124.63(11)
C3	N1	N2	109.27(10)	C12	C13	C15	126.18(12)
C3	N1	B	128.67(10)	F13	C14	C11	112.18(10)
N1	N2	Rh	117.34(8)	F14	C14	F13	106.89(10)
C1	N2	Rh	136.33(9)	F14	C14	F15	106.52(10)

C1	N2	N1	106.02(10)	F14	C14	C11	111.43(11)
N4	N3	B	120.89(10)	F15	C14	F13	106.94(11)
C8	N3	N4	109.00(10)	F15	C14	C11	112.51(10)
C8	N3	B	129.48(10)	F16	C15	F17	106.70(12)
N3	N4	Rh	118.93(8)	F16	C15	C13	110.44(11)
C6	N4	Rh	134.02(9)	F17	C15	C13	112.40(12)
C6	N4	N3	106.15(10)	F18	C15	F16	106.73(12)
N6	N5	C13	109.56(10)	F18	C15	F17	106.74(12)
N6	N5	B	118.26(10)	F18	C15	C13	113.43(12)
C13	N5	B	131.60(10)	C17	C16	C21	99.36(10)
C11	N6	N5	105.53(10)	C17	C16	C22	100.90(11)
N2	C1	C2	111.46(12)	C21	C16	C22	100.86(11)
N2	C1	C4	123.11(11)	C16	C17	Rh	97.18(8)
C2	C1	C4	125.41(12)	C18	C17	Rh	71.14(8)
C3	C2	C1	103.93(11)	C18	C17	C16	106.60(11)
N1	C3	C2	109.32(11)	C17	C18	Rh	70.42(7)
N1	C3	C5	124.12(12)	C17	C18	C19	106.11(11)
C2	C3	C5	126.49(12)	C19	C18	Rh	97.05(8)
F1	C4	F2	106.94(12)	C18	C19	C22	101.17(11)
F1	C4	C1	112.26(12)	C20	C19	C18	99.67(10)
F2	C4	C1	112.55(12)	C20	C19	C22	100.94(11)
F3	C4	F1	107.51(12)	C19	C20	Rh	96.49(8)
F3	C4	F2	106.98(13)	C21	C20	Rh	70.61(7)
F3	C4	C1	110.31(12)	C21	C20	C19	106.64(12)
F4	C5	F6	106.77(11)	C16	C21	Rh	96.38(8)
F4	C5	C3	109.14(12)	C20	C21	Rh	71.35(7)
F5	C5	F4	107.82(11)	C20	C21	C16	106.19(11)
F5	C5	F6	107.31(12)	C19	C22	C16	93.96(10)
F5	C5	C3	113.35(11)	N1	B	N5	107.42(10)

F6	C5	C3	112.15(11)	N3	B	N1	107.52(10)
N4	C6	C7	111.40(11)	N3	B	N5	112.59(10)
N4	C6	C9	123.42(12)	C24	C23	C28	117.83(16)
C7	C6	C9	125.17(12)	C24	C23	C29	120.42(17)
C8	C7	C6	104.17(11)	C28	C23	C29	121.74(17)
N3	C8	C7	109.27(11)	C25	C24	C23	121.36(16)
N3	C8	C10	125.26(11)	C26	C25	C24	120.23(17)
C7	C8	C10	125.45(12)	C25	C26	C27	119.09(17)
F7	C9	C6	112.05(12)	C28	C27	C26	120.59(16)
F8	C9	F7	107.27(11)	C27	C28	C23	120.89(16)

Table D.4. Selected bond distances (Å) of several structurally characterized Rh(nbd) complexes supported by tris- and bis-(pyrazolyl)borate ligands

Parameter	κ^2-$Tp^{(CF_3)2}$Rh(nbd)	κ^2-$Bp^{(CH_3)2}$Rh(nbd)	κ^2-$Tp^{(4\text{-}MeOPh)}$Rh(nbd)	κ^3-$Tp^{(CH_3)2}$Rh(nbd)	κ^3-$Tp^{(CH_3)}$Rh(nbd)
Rh-N	2.1248(11)	2.109(2)	2.111(8)	2.139(2)	2.247(9)
	2.1523(10)	2.109(2)	2.087(9)	2.235(2)	2.147(7)
				2.233(3)	2.25(1)
av. Rh-N	*2.138*	*2.109*	*2.099*	*2.202*	*2.215*
Rh-C	2.1145(13)	2.116(2)	2.109(12)	2.079(2)	2.07(1)
	2.1238(12)	2.115(2)	2.126(12)	2.078(3)	2.09(1)
	2.1309(12)	2.116(2)	2.134(12)	2.149(2)	2.154(8)
	2.1404(14)	2.115(2)	2.095(11)	2.148(2)	2.16(1)
av. Rh-C	*2.127*	*2.116*	*2.116*	*2.113*	*2.01*
C=C	1.3955(19)	1.391(3)	1.39(2)	1.383(5)	1.45(3)

	1.3923(18)	1.391(3)	1.40(2)	1.438(5)	1.37(3)
av. C=C	*1.394*	*1.391*	*1.40*	*1.410*	*1.41*
Ref	This work	*Dalton Trans.*, **2008**, 2680	*J.Organomet.Chem.*, **2000**, 605, 117	*Dalton Trans.*, **2008**, 2680	*Inorg. Chem.* **1995**, 34, 66-74.

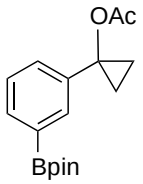
The X-ray crystal structure of $Tp^{(CF3)2}$Rh(nbd) is illustrated in Figure D.7 shows that the tris(pyrazolyl)borate ligand is κ^2-bonded and the Rh atom adopts a distorted square planar geometry. Interestingly, the solution ^{103}Rh NMR spectroscopic data of the compound $Tp^{(CF3)2}$Rh(nbd) (and $Tp^{CF3,CH3}$Rh(nbd)) have been reported and indicate the existence of a four-coordinate rhodium species in solution as well. The non-fluorinated analog $Tp^{(CH3)2}$Rh(nbd) in contrast, exists predominantly as a five-coordinate species in solution.[S5] Although there are no X-ray structural data on rhodium-nbd complexes supported by fluorinated tris(pyrazolyl)borates, there are a few reports of related compounds featuring more electron rich, non-fluorinated tris- and bis(pyrazolyl)borate supporting ligands. Selected bond distances of most closely related analogs are summarized in Table D.1 for metrical data comparison. The data show that the rhodium-nbd complexes supported by more electron-rich tris(pyrazolyl)borates containing smaller methyl substituents at the pyrazolyl ring 3-positions, e.g., $Tp^{(CH3)2}$Rh(nbd) and $Tp^{(CH3)}$Rh(nbd), feature five coordinate, pseudo trigonal bipyramidal rhodium atoms and κ^3-bonded tris(pyrazolyl)borates while those containing bulkier substituents at the pyrazolyl ring 3-positions (e.g., κ^2-$Tp^{(4\text{-MeOPh})}$Rh(nbd)) adopt square planar structures with κ^2-bonded tris(pyrazolyl)borates. The Rh-N bond distances of $Tp^{(CF3)2}$Rh(nbd) are slightly longer than the corresponding distances of $Tp^{(4\text{-MeOPh})}$Rh(nbd) and the bis(pyrazolyl)borate $Bp^{(CH3)2}$Rh(nbd). This is probably a result of weakly donating nature of fluorinated pyrazolyl groups. A comparison of Rh-N distances of 4- and 5-coordinate systems based on κ^2- and κ^3-bonded tris(pyrazolyl)borates indicates that the former group with a fewer coordination number has

shorter Rh-N distances, as expected. Interestingly, the Rh-C and C=C distances of these complexes do not respond drastically to the changes of tris(pyrazolyl)borate ligand steric and electronic effects.

Chapter 2

Net Oxidative Inverse Polarity C–C Silylation of Cyclopropanols Involving Generation of Metallo Homoenolate-Enol Ether

1-[3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]cyclopropyl acetate (2-1-4)



Yield: 1 mmol scale, 96 mg, 32%.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.90 (nfom, 1H, Ar-*H*), 7.71 (ddd, *J* = 7.3, 1.2, 1.2 Hz, 1H, Ar-*H*), 7.47 (ddd, *J* = 7.8, 2.0, 1.2 Hz, 1H, Ar-*H*), 7.32 (dd, *J* = 7.8, 7.3 Hz, 1H, Ar-*H*), 2.03 (s, 3H, O=CC*H*$_3$), 1.33 (s, 12H), 1.27-1.25 (m, 2H, cyp-*H*), and 1.25-1.23 (m, 2H, cyp-*H*).

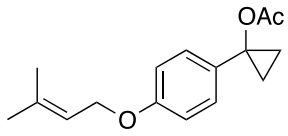
^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 139.4, 134.9, 133.9, 132.5, 129.7, 127.8, 84.0, 60.3, 25.1, 21.5, and 14.8.

IR (neat): 3071 (w), 2977 (w), 1742 (m), 1646 (s), 1557 (s), 1370 (s), 1212 (m), and 763(s)cm^{-1}.

TLC: R_f = 0.6 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{17}H_{23}BNaO_4)^+$: 325.1582. Found: 325.1506.

1-{4-[(3-Methylbut-2-en-1-yl)oxy]phenyl}cyclopropyl acetate (2-1-13)



Yield: 1 mmol scale, 99 mg, 48%.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.34 (d, *J* = 8.9 Hz, 2H, Ar-*H*), 6.85 (d, *J* = 8.9 Hz, 2H, Ar-*H*), 5.48 (tq, *J* = 6.8, 1.3 Hz, 1H, C*H*=CCH_3CH_3), 4.48 (d, *J* = 6.8 Hz, 2H, ArOC*H*$_2$), 1.99 (s, 3H, O=CC*H*$_3$), 1.79 (s, 3H, CH=CCH_3C*H*$_3$), 1.73 (s, 3H, C*H*=CCH_3C*H*$_3$), 1.25-1.19 (m, 2H, cyp-*H*), and 1.17-1.11 (m, 2H, cyp-*H*).

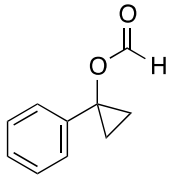
^{13}C NMR (CDCl3, 125 MHz): δ 170.8, 158.4, 138.4, 131.9, 129.0, 119.8, 114.4, 64.9, 60.2, 26.0, 21.5, 18.3, 14.0

IR (neat): 3063 (w), 3006 (w), 2941 (m), 1742 (s), 1416 (s), 1256 (s), 1227 (s), 1066 (m), and 742 (s) cm^{-1}.

TLC: R_f = 0.4 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF** Calcd for $(M+Na)^+$ $(C_{16}H_{20}NaO_3)^+$: 283.1005. Found: 283.1041.

1-Phenylcyclopropyl formate (2-32)



Yield: 5 mmol scale, 0.39 g, 49% (over two steps from ester).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.07 (s, 1H, O=C*H*), 7.30-7.25 (nfom, 4H, Ar-*H*), 7.26-7.21 (nfom, 1H, Ar-*H*), 1.40-1.33 (m, 2H, cyp-*H*), and 1.30-1.24 (m, 2H, cyp-*H*).

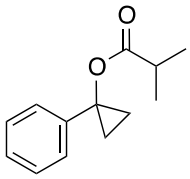
^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.5, 139.4, 128.7, 127.8, 126.6, 60.9, and 14.8.

IR (neat): 3086 (w), 2952 (w), 1751 (s), 1543 (m), 1294 (m), 1243 (s), 1211 (s), 752 (s), and 712 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{10}H_{10}NaO_2)^+$: 185.0573. Found: 185.0519.

1-Phenylcyclopropyl isobutyrate (2-33)



Yield: 0.5 mmol scale, 41 mg, 40% (over two steps from ester).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.34-7.27 (nfom, 4H, Ar-*H*), 7.25-7.19 (nfom, 1H, Ar-*H*), 2.53 [sept, *J* = 7.0 Hz, 1H, $(CH_3)_2C$*H*], 1.26-1.23 (m, 2H, cyp-*H*), 1.22-1.20 (m, 2H, cyp-*H*), and 1.14 [d, *J* = 7.0 Hz, 6H, $(CH_3)_2CH$].

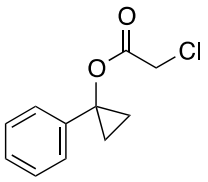
^{13}C NMR ($CDCl_3$, 125 MHz): δ 176.8, 141.0, 128.5, 126.6, 126.1, 59.9, 29.7, 19.0, 18.9, and 15.1.

IR (neat): 3095 (w), 2954 (w), 1753 (s), 1603 (w), 1344 (s), 1243 (s), 1201 (s), 753 (s), and 695 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{13}H_{16}NaO_2^+)^+$: 227.1043. Found: 227.1031.

1-Phenylcyclopropyl 2-chloroacetate (2-34)



Yield: 5 mmol scale, 0.52 g, 48% (over two steps from ester).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.38 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.33 (t, *J* = 7.3 Hz, 2H, Ar-*H*), 7.27 (t, *J* = 7.3 Hz, 1H, Ar-*H*), 4.00 (s, 2H, O=CCH_2), 1.38-1.30 (m, 2H, cyp-*H*), and 1.29-1.23 (m, 2H, cyp-*H*).

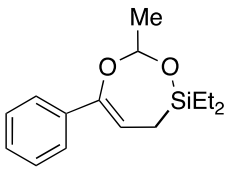
^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.0, 139.0, 133.1, 128.6, 127.1, 62.1, 41.1, and 14.5.

IR (neat): 3088 (w), 2951 (s), 1749 (s), 1609 (w), 1249 (s), 1151 (s), 751 (s), and 699 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{11}H_{11}ClNaO_2)^+$: 233.0340. Found: 233.0374.

2,2-Diethyl-7-methyl-5-phenyl-2,3-dihydro-1,6,2-dioxasilepine (2-6-1e)



Yield: a) 0.2 mmol scale, 47 mg, 90%, b) 1 mmol scale, 213 mg, 82%

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.48 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.32 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.25 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 5.93 (dd, *J* = 7.3, 5.9 Hz, 1H, ArC=C*H*), 5.34 (q, *J* = 5.1 Hz, 1H, OC*H*Me), 1.86 (dd, *J* = 16.0, 5.9 Hz, 1H, C=CCH_aH$_b$), 1.56 (d, *J* = 5.1 Hz, 3H, OCHCH_3), 1.48 (dd, *J* = 16.0, 7.3 Hz, 1H, C=CCH$_a$$H_b$), 1.04 (t, *J* = 8.0 Hz, 3H, SiCH$_2$CH_3), 0.98 (t, *J* = 8.0 Hz, 3H, SiCH$_2$CH_3), 0.75 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$), and 0.67 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$).

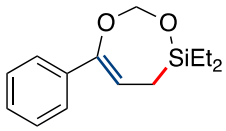
^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.3, 136.9, 128.5, 127.6, 124.6, 109.3, 97.5, 24.7, 12.2, 7.1, 6.93, 6.81, and 5.4.

IR (neat): 3092 (w), 2955 (m), 2876 (m), 1692 (s), 1582 (m), 1412 (s), 1176 (s), 1002 (s), 851 (s), and 736 (s) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{22}NaO_2Si)^+$: 285.1281. Found: 285.1295.

2,2-Diethyl-5-phenyl-2,3-dihydro-1,6,2-dioxasilepine (2-6-1f)



Yield: 0.2 mmol scale, 43 mg, 78%

^{1}H NMR (C_6D_6, 500 MHz): δ 7.49 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.16 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.08 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 5.75 (d, *J* = 6.6 Hz, 1H, ArC=C*H*), 5.13 (s, 2H, OCH_2), 1.48 (d, *J* = 6.6 Hz, 2H, C=CCH_2), 0.99 (t, *J* = 8.0 Hz, 6H, SiCH$_2$CH_3), 0.67 (q, *J* = 8.0 Hz, 4H, SiCH_2CH$_3$), and 0.40 (H_2O in benzene-d_6).

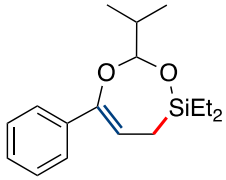
^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.2, 136.8, 128.6, 126.5, 124.9, 109.0, 91.0, 12.3, 6.9, and 6.1.

IR (neat): 3055 (w), 2953 (m), 2846 (s), 1691 (s), 1676 (m), 1410 (s), 1171 (s), 1042 (s), 751 (s), and 742 (s) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ ($C_{15}H_{22}NaO_2Si)^+$: 285.1281. Found: 285.1295.

2,2-Diethyl-7-isopropyl-5-phenyl-2,3-dihydro-1,6,2-dioxasilepine (2-6-1g)



Yield: 0.2 mmol scale, 47 mg, 88%

^{1}H NMR (C_6D_6, 500 MHz): δ 7.59 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.17 (t, *J* = 7.3 Hz, 2H, Ar-*H*), 7.08 (t, *J* = 7.3 Hz, 1H, Ar-*H*), 5.66 (dd, *J* = 7.3, 5.9 Hz, 1H, ArC=C*H*), 5.00 (d, *J* = 4.4 Hz, 1H, OC*H*CHMe$_2$), 2.05 (doublet of septet, *J* = 6.7, 4.4 Hz, 1H, OCHC*H*Me$_2$), 1.67 (dd, *J* = 16.0, 7.3 Hz, 1H, C=CCH_aH$_b$), 1.37 (dd, *J* = 16.0, 5.9 Hz, 1H, C=CCH$_a$$H_b$), 1.04 [d, *J* = 6.7 Hz, 6H, OCHCH(CH_3)$_2$], 1.03 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$CH_3), 0.97 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$CH_3), 0.71 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$), 0.59 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$) and 0.40 (H_2O in benzene-d_6).

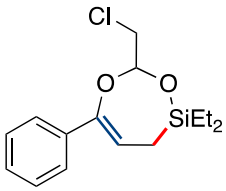
^{13}C NMR (C_6D_6, 125 MHz): δ 154.1, 137.9, 128.5, 127.7, 125.3, 107.4, 103.4, 35.8, 17.9, 16.8, 11.9, 7.2, 7.0, 6.9, and 5.8.

IR (neat): 3092 (w), 2955 (m), 2876 (m), 1692 (s), 1582 (m), 1412 (s), 1176 (s), 1002 (s), 851 (s), and 736 (s) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{17}H_{26}NaO_2Si)^+$: 313.1594. Found: 313.1531.

7-(Chloromethyl)-2,2-diethyl-5-phenyl-2,3-dihydro-1,6,2-dioxasilepine (2-6-1h)



Yield: 0.2 mmol scale, 50 mg, 84%

^{1}H NMR (C_6D_6, 500 MHz): δ 7.64 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.17 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.08 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 5.66 (dd, *J* = 6.6, 6.6 Hz, 1H, ArC=C*H*), 5.21 (dd, *J* = 6.0, 3.7 Hz, 1H, OC*H*CH_2), 3.53 (dd, *J* = 11.3, 6.0 Hz, OCHC*H*$_a$H$_b$Cl), 3.39 (dd, *J* = 11.3, 3.7 Hz, OCHCH$_a$*H*$_b$Cl), 1.61 (dd, *J* = 16.0, 6.6 Hz, 1H, C=CC*H*$_a$H$_b$), 1.24 (dd, *J* = 16.0, 6.6 Hz, 1H, C=CCH$_a$*H*$_b$), 0.95 (t, *J* = 7.9 Hz, 3H, SiCH$_2$C*H*$_3$), 0.91 (t, *J* = 7.9 Hz, 3H, SiCH$_2$C*H*$_3$), 0.62 (app q, *J* = 7.9 Hz, 2H, SiC*H*$_2$CH$_3$), 0.52 (app q, *J* = 7.9 Hz, 2H, SiC*H*$_2$CH$_3$), and 0.40 (H_2O in benzene-d_6).

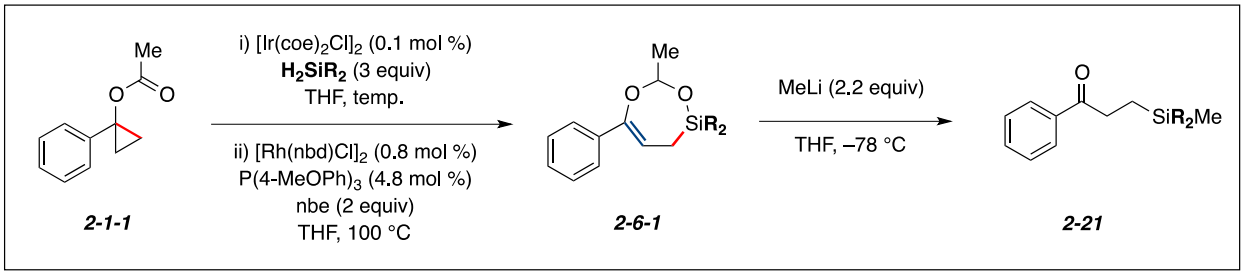
^{13}C NMR (C_6D_6, 125 MHz): δ 153.4, 136.7, 128.6, 127.9, 125.3, 108.6, 98.4, 47.1, 11.7, 7.1, 6.8, 6.7, and 5.6.

IR (neat): 3083 (w), 2951 (m), 2884 (m), 1591 (s), 1533 (m), 1402 (s), 1002 (s), 891 (s), and 705 (s) cm^{-1}.

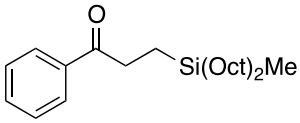
TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{21}ClNaO_2Si)^+$: 319.0892. Found: 319.0823.

Scheme E.1. Silanes scope of dioxasilepines



3-(Methyldioctylsilyl)-1-phenylpropan-1-one (2-6-1b)



Yield: 0.2 mmol scale, 66 mg, 82%

^{1}H NMR (C_6D_6, 500 MHz): δ 7.94 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.05-7.12 (m, 3H, Ar-*H*), 2.82-2.75 (nfom, 2H, CH_2CH_2C=O), 1.40-1.25 (m, 28H, alkyl-*H*), 1.08-1.01 (nfom, 2H, CH_2CH_2C=O), 0.94-0.89 (m, 6H, alkyl-*H*), 0.62-0.55 (m, 4H, alkyl-*H*), 0.40 (H_2O in benzene-d_6), and 0.036 (s, 3H, Si(Oct)$_2$CH_3).

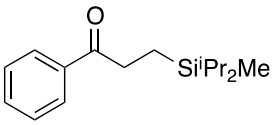
^{13}C NMR ($CDCl_3$, 125 MHz): δ 199.6, 137.6, 132.6, 128.7, 128.4, 34.3, 33.2, 32.4, 29.7, 24.4, 23.1, 14.4, 14.16, 14.12, 8.3, and -5.0.

IR (neat): 3092 (w), 2955 (m), 2876 (m), 1692 (s), 1582 (m), 1412 (s), 1176 (s), 1002 (s), 851 (s), and 736 (s) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{22}NaO_2Si)^+$: 285.1281. Found: 285.1295.

7-Methyl-2,2,5-triphenyl-2,3-dihydro-1,6,2-dioxasilepine: (2-6-1c)



Yield: 0.2 mmol scale, 47 mg, 90%

^{1}H NMR (C_6D_6, 500 MHz): δ 7.94 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.14 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.08 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 2.79-2.73 (nfom, 2H, CH_2CH_2C=O), 1.03-0.99 (nfom, 2H, CH_2CH_2C=O), 0.96 {d, 6H, Si[CH(CH_3)$_2$]}, 1.04-0.96 {m, 1H, Si[C*H*(CH_3)$_2$]}, 0.82-0.78 {m, 1H, Si[C*H*(CH_3)$_2$]}, 0.40 (H_2O in benzene-d_6), and –0.13 (s, 3H, Si^{i}Pr$_2$CH_3).

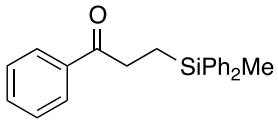
^{13}C NMR ($CDCl_3$, 125 MHz): δ 199.5, 137.6, 132.6, 128.7, 128.4, 33.4, 18.3, 12.1, 5.0, and –9.1

IR (neat): 3092 (w), 2955 (m), 2876 (m), 1692 (s), 1582 (m), 1412 (s), 1176 (s), 1002 (s), 851 (s), and 736 (s) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{22}NaO_2Si)^+$: 285.1281. Found: 285.1295.

2,2-Diisopropyl-7-methyl-5-phenyl-2,3-dihydro-1,6,2-dioxasilepine: (2-6-1d)



Yield: 0.2 mmol scale, 52 mg, 79%

^{1}H NMR (C_6D_6, 500 MHz): δ 7.48 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.50-7.45 (m, 4H, Ar-*H*), 7.19-7.17 (m, 6H, Ar-*H*), 7.08 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 6.99 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 2.79-2.74 (nfom, 2H, CH_2CH_2C=O), 1.59-1.49 (nfom, 2H, CH_2CH_2C=O), 0.46 (s, 3H, $SiPh_2CH_3$), and 0.40 (H_2O in benzene-d_6,).

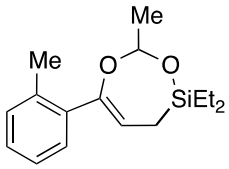
^{13}C NMR ($CDCl_3$, 125 MHz): δ 199.2, 137.4, 137.0, 134.9, 132.5, 129.6, 128.6, 128.3, 128.1, 33.0, 8.3, and –4.2.

IR (neat): 3092 (w), 2955 (m), 2876 (m), 1692 (s), 1582 (m), 1412 (s), 1176 (s), 1002 (s), 851 (s), and 736 (s) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{22}NaO_2Si)^+$: 285.1281. Found: 285.1295.

2,2-Diethyl-7-methyl-5-(*o*-tolyl)-2,3-dihydro-1,6,2-dioxasilepine (2-6-2)



Yield: 0.2 mmol scale, 38 mg, 70%.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.39-7.35 (m, 1H, Ar-*H*), 7.09-7.03 (m, 3H, Ar-*H*), 5.43 (q, *J* = 5.0 Hz, 1H, OC*H*Me), 5.17 (dd, *J* = 7.3, 5.9 Hz, 1H, ArC=C*H*), 2.40 (s, 3H, Ar-CH_3), 1.54-1.42 (m, 2H, C=CCH_aH_b, C=CCH_aH_b), 1.36 (d, *J* = 5.0 Hz, 3H, OCHCH_3), 1.06 (dd, *J* = 8.0 Hz, 3H,

$SiCH_2CH_3$), 0.99 (dd, J = 8.0 Hz, 3H, $SiCH_2CH_3$), 0.77 (app q, J = 8.0 Hz, 2H, $SiCH_2CH_3$), and 0.69-0.53 (m, 2H, $SiCH_2CH_3$), and 0.40 (water in benzene-d_6, H_2O).

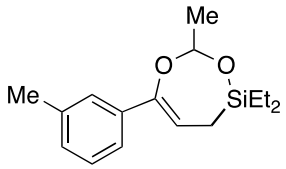
^{13}C NMR (C_6D_6, 125 MHz): δ 155.0, 138.8, 130.7, 129.6, 128.4, 127.5, 125.8, 109.1, 96.3, 24.5, 23.4, 20.9, 11.4, 6.97, 6.96, and 6.3.

IR (neat): 3069 (w), 2953 (m), 2875 (m), 1682 (s), 1573 (s), 1411 (m), 1230 (s), 1123 (s), 964 (s), and 726 (s) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{16}H_{24}NaO_2Si)^+$: 299.1438. Found: 299.1455.

2,2-Diethyl-7-methyl-5-(*m*-tolyl)-2,3-dihydro-1,6,2-dioxasilepine (2-6-3)



Yield: 0.2 mmol scale, 47 mg, 85%.

^{1}H NMR (C_6D_6, 500 MHz): 7.30 (s, 1H, Ar-*H*), 7.29 (d, J = 7.5 Hz, 1H, Ar-*H*), 7.21 (t, J = 7.5 Hz, 1H, Ar-*H*), 7.07 (d, J = 7.5 Hz, 1H, Ar-*H*), 5.91 (dd, J = 7.3, 5.9 Hz, 1H, ArC=C*H*), 5.34 (q, J = 5.1 Hz, 1H, OC *H*Me), 2.36 (s, 3H, Ar-CH_3), 1.85 (dd, J = 16.0, 5.9 Hz, 1H, C=CCH_aH_b), 1.56 (d, J = 5.1 Hz, 3H, OCHCH_3), 1.51 (dd, J = 16.0, 7.3 Hz, 1H, C=CCH_aH_b), 1.04 (t, J = 8.0 Hz, 3H, $SiCH_2CH_3$), 0.98 (t, J = 8.0 Hz, 3H, $SiCH_2CH_3$), 0.73 (app q, J = 8.0 Hz, 2H, $SiCH_2CH_3$), and 0.67 (app q, J = 8.0 Hz, 2H, $SiCH_2CH_3$).

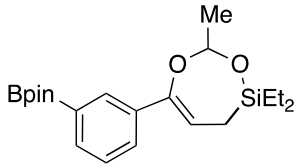
^{13}C NMR (C_6D_6, 125 MHz): δ 154.2, 126.2, 121.5, 7.8, 5.5, and –5.5.

IR (neat): 3061 (w), 2954 (m), 2878 (m), 1688 (s), 1575 (s), 1331 (m), 1230 (s), 1128 (s), 969 (s), and 722 (s) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{16}H_{24}NaO_2Si^+)^+$: 299.1438. Found: 299.1455.

2,2-Diethyl-7-methyl-5-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-2,3-dihydro-1,6,2-dioxasilepine (2-6-4)



Yield: 0.2 mmol scale, 46 mg, 59%.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.92 (s, 1H, Ar-*H*), 7.70 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.55 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.32 (dd, *J* = 7.5, 7.5 Hz, 1H, Ar-*H*) 5.86 (dd, *J* = 7.1, 6.0 Hz, 1H, ArC=C*H*), 5.33 (q, *J* = 5.1 Hz, 1H, OC*H*Me), 2.33 (s, 3H, Ar-CH_3), 1.82 (dd, *J* = 16.0, 6.0 Hz, 1H, C=CCH_aH$_b$), 1.55 (d, *J* = 5.1 Hz, 3H, OCHCH_3), 1.51 (dd, *J* = 16.0, 7.1 Hz, 1H, C=CCH$_a$$H_b$), 1.35 (s, 12H, Bpin), 1.02 (t, *J* = 7.9 Hz, 3H, SiCH$_2$CH_3), 0.96 (t, *J* = 8.0 Hz, 3H, SiCH$_2$CH_3), 0.73 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$), and 0.65 (app q, *J* = 7.9 Hz, 2H, SiCH_2CH$_3$).

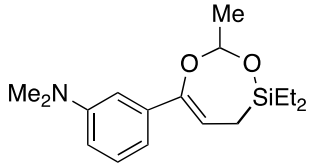
^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.3, 136.3, 134.0, 132.4, 131.1, 128.0, 127.4, 109.4, 97.6, 84.0, 25.08, 25.05, 24.7, 17.6, 12.1, 7.0, and 5.4.

IR (neat): 3065 (w), 2955 (m), 2876 (w), 1686 (m), 1445 (m), 1357 (s), 1004 (s), 737 (s), and 577 (m) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{21}H_{33}BNaO_4Si)^+$: 411.2133. Found: 411.2073.

3-(2,2-Diethyl-7-methyl-2,3-dihydro-1,6,2-dioxasilepin-5-yl)-*N*,*N*-dimethylaniline (2-6-5)



Yield: 0.2 mmol scale, 51 mg, 83%.

^{1}H NMR (CDCl3, 500 MHz): δ δ 7.19 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 6.92-6.85 (m, 2H, Ar-*H*), 6.67 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 5.93 (dd, *J* = 7.5, 5.9 Hz, 1H, ArC=C*H*), 5.31 (q, *J* = 5.0 Hz, 1H, OC*H*Me), 2.96 [s, 6H, N(*CH*$_3$)$_2$], 1.88 [dd, *J* = 16.0, 5.9 Hz, 1H, C=CCH_aH$_b$), 1.55 (d, *J* = 5.0 Hz, 3H, OCHCH_3), 1.47 (dd, *J* = 16.0, 7.5 Hz, 1H, C=CCH$_a$$H_b$), 1.03 (t, *J* = 8.0 Hz, 3H, SiCH$_2$CH_3), 0.97 (t, *J* = 8.0 Hz, 3H, SiCH$_2$CH_3), 0.75 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$), and 0.67 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$).

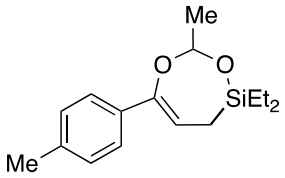
^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.8, 150.9, 137.6, 129.1, 113.4, 112.1, 109.4, 108.9, 97.4, 40.8, 24.6, 12.1, 7.1, 6.8, 6.7 and 5.2.

IR (neat): 3021 (w), 2953 (m), 2874 (w), 1598 (s), 1496 (m), 1058 (m), 1222 (s), 1058 (s), 851 (m), and 728 (s) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{17}H_{27}NNaO_2Si)^+$: 328.1703. Found: 328.1733.

2,2-Diethyl-7-methyl-5-(*p*-tolyl)-2,3-dihydro-1,6,2-dioxasilepin (2-6-6)



Yield: 0.2 mmol scale, 48 mg, 88%.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.12 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 5.86 (dd, *J* = 7.3, 5.9 Hz, 1H, ArC=C*H*), 5.31 (q, *J* = 5.1 Hz, 1H, OC*H*Me), 2.33 (s, 3H, Ar-CH_3), 1.84 (dd, *J* = 16.0, 5.9 Hz, 1H, C=CC$H_a$$H_b$), 1.54 (d, *J* = 5.1 Hz, 3H, OCHCH_3), 1.48 [dd, *J* = 16.0, 7.3 Hz, 1H, C=CC$H_a$$H_b$), 1.02 (dd, *J* = 8.0, 8.0 Hz, 3H, $SiCH_2CH_3$), 0.96 (dd, *J* = 8.0, 8.0 Hz, 3H, $SiCH_2CH_3$), 0.74 (app q, *J* = 8.0 Hz, 2H, $SiCH_2CH_3$), and 0.66 (app q, *J* = 8.0 Hz, 2H, $SiCH_2CH_3$).

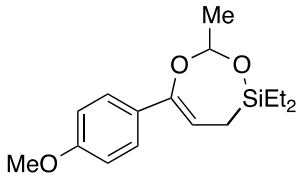
^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.3, 137.4, 134.1, 129.2, 124.6, 108.4, 97.4, 24.7, 21.3, 12.1, 7.2, 6.94, 6.82, and 5.4.

IR (neat): 3094 (w), 2952 (m), 2873 (m), 1598 (m), 1388 (m), 1243 (m), 1071 (m), 738 (s), and 679 (m) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{16}H_{24}NaO_2Si)^+$: 299.1438. Found: 299.1406.

2,2-Diethyl-5-(4-methoxyphenyl)-7-methyl-2,3-dihydro-1,6,2-dioxasilepine (2-6-7)



Yield: 0.2 mmol scale, 47 mg, 80%.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.47 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.78 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 5.67 (dd, *J* = 6.9, 5.9 Hz, 1H, ArC=C*H*), 5.34 (q, *J* = 5.0 Hz, 1H, OC*H*Me), 3.30 (s, 3H, Ar-OC*H*$_3$), 1.77 (dd, *J* = 16.0, 5.9 Hz, 1H, C=CC*H*$_a$H$_b$), 1.54 (d, *J* = 5.0 Hz, 3H, OCHC*H*$_3$), 1.47 (dd, *J* = 16.0, 6.9 Hz, 1H, C=CCH$_a$*H*$_b$), 1.05 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$C*H*$_3$), 0.99 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$C*H*$_3$), 0.76 (app q, *J* = 8.0 Hz, 2H, SiC*H*$_2$CH$_3$), and 0.66-0.60 (app q, 2H, *J* = 8.0 Hz, SiC*H*$_2$CH$_3$).

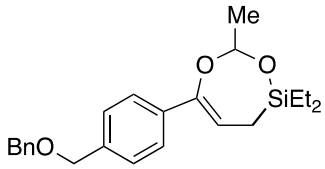
^{13}C NMR (C_6D_6, 125 MHz): δ 159.9, 153.8, 130.1, 126.3, 114.1, 106.8, 97.7, 54.8, 24.8, 12.1, 7.5, 7.07, 6.95, and 5.7.

IR (neat): 3084 (w), 2998 (m), 2875 (m), 2875 (m), 1674 (m), 1600 (s), 1237 (m), 1170 (s), 792 (s), and 661 (w) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{22}NaO_3Si)^+$: 315.1387. Found: 315.1387.

5-{4-[(Benzyloxy)methyl]phenyl}-2,2-diethyl-7-methyl-2,3-dihydro-1,6,2-dioxasilepine (2-6-8)



Yield: 0.2 mmol scale, 58 mg, 76%.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.54 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.31 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.29 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.18 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.11 (t, *J* = 8.3 Hz, 1H, Ar-*H*), 5.78 (dd, *J* = 7.1, 6.1 Hz, 1H, ArC=C*H*), 5.31 (q, *J* = 5.1 Hz, 1H, OC*H*Me), 4.38 (s, 2H, C*H*$_2$OCH$_2$), 4.38 (s, 2H, CH$_2$OC*H*$_2$), 1.78 (dd, *J* = 16.0, 5.9 Hz, 1H, C=CC*H*$_a$H$_b$), 1.52 (d, *J* = 5.1 Hz, 3H, OCHC*H*$_3$), 1.30 (dd, *J* = 16.0, 7.1 Hz, 1H, C=CCH$_a$*H*$_b$), 1.04 (dd, *J* = 8.0 Hz, 3H, SiCH$_2$C*H*$_3$), 0.97 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$C*H*$_3$), 0.74 (app q, *J* = 8.0 Hz, 2H, SiC*H*$_2$CH$_3$), and 0.62 (app q, *J* = 8.0 Hz, 2H, SiC*H*$_2$CH$_3$).

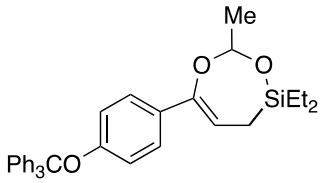
^{13}C NMR (C_6D_6, 125 MHz): δ 153.7, 139.1, 138.4, 136.7, 128.6, 128.35, 127.98, 127.7, 125.0, 109.0, 97.7, 72.1, 71.9, 24.8, 12.2, 7.4, 7.05, 6.92, and 5.7.

IR (neat): 3491 (br, w), 2953 (m), 2874 (m), 1628 (m), 1497 (s), 1243 (s), 1048 (s), 788 (s), and 737 (s) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{23}H_{30}NaO_3Si)^+$: 405.1856. Found: 405.1832.

2,2-Diethyl-7-methyl-5-[4-(trityloxy)phenyl]-2,3-dihydro-1,6,2-dioxasilepine (2-6-9)



Yield: 0.2 mmol scale, 83 mg, 80%.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.57 (d, *J* = 7.5 Hz, 6H, Ar-*H*), 7.20 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.05 (d, *J* = 7.5 Hz, 6H, Ar-*H*), 6.96 (d, *J* = 7.5 Hz, 3H, Ar-*H*), 6.84 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 5.48 (dd, *J* = 7.0, 6.0 Hz, 1H, ArC=C*H*), 5.14 (q, *J* = 5.1 Hz, 1H, OC*H*Me), 1.66 (dd, *J* = 16.0, 6.0 Hz, 1H, C=CCH_aH$_b$), 1.39 (d, *J* = 5.1 Hz, 3H, OCHCH_3), 1.22 (dd, *J* = 16.0, 7.0 Hz, 1H, C=CCH$_a$$H_b$), 0.99 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$CH_3), 0.93 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$CH_3), 0.69 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$), and 0.56 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$).

^{13}C NMR (C_6D_6, 125 MHz): δ 156.6, 153.7, 144.7, 130.6, 128.4, 128.1, 127.5, 125.3, 120.9, 107.1, 97.7, 91.0, 24.7, 12.0, 7.3, 7.02, 6.9, and 5.5.

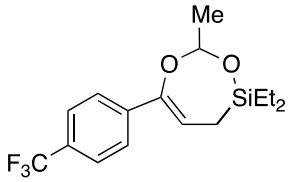
IR (neat): 3570 (br, w), 2952 (m), 2873 (m), 1465 (m), 1234 (m), 1172 (s), 850 (s), and 738 (s) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

GCMS (5029017): t_R = 9.75 min, m/z 223 $[(M+H)^+$, 5], 207 $[(M-Me)^+$, 6], 193 $[(M-Et)^+$, 11], and 165 (100).

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{34}H_{36}NaO_3Si)^+$: 543.2326. Found: 543.2311.

2,2-Diethyl-7-methyl-5-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1,6,2-dioxasilepine (2-6-10)



Yield: 0.2 mmol scale, 34 mg, 52%.

^{1}H NMR (C_6D_6, 500 MHz): 7.34 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.29 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 5.67 (dd, *J* = 7.1, 6.3 Hz, 1H, ArC=C*H*), 5.17 (q, *J* = 5.1 Hz, 1H, OC*H*Me), 1.71 (dd, *J* = 15.9, 6.3 Hz, 1H, C=CCH_aH$_b$), 1.45 (d, *J* = 5.1 Hz, 3H, OCHCH_3), 1.27 (dd, *J* = 15.9, 7.1 Hz, 1H, C=CCH$_a$$H_b$), 1.02 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$CH_3), 0.96 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$CH_3), 0.70 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$), and 0.59 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$).

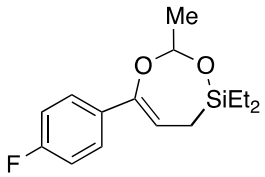
^{13}C NMR (C_6D_6, 125 MHz): δ 152.3, 140.7, 129.38 (q, $^{2}J_{F\text{-}C}$ = 32.3), 125.57 (q, $^{3}J_{F\text{-}C}$ = 3.5), 125.10 (q, $^{1}J_{F\text{-}C}$ = 272.1 Hz), 124.9, 111.7, 97.6, 24.6, 12.4, 7.3, 6.97, 6.82, and 5.6.

IR (neat): 3406 (br, w), 2955 (m), 2875 (m), 1654 (m), 1460 (m), 1091 (m), 1014 (m), 881 (s), and 750 (s) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ ($C_{16}H_{21}F_3NaO_2Si)^+$: 353.1155. Found: 353.1129.

2,2-Diethyl-5-(4-fluorophenyl)-7-methyl-2,3-dihydro-1,6,2-dioxasilepin (2-6-11)



Yield: 0.2 mmol scale, 51 mg, 91%.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 [dd, *J* = 8.8, 5.4 ($^{4}J_{F\text{-}H}$) Hz, 2H, Ar-*H*], 6.99 [dd, *J* = 8.6, 8.6 ($^{3}J_{F\text{-}H}$) Hz, 2H, Ar-*H*], 5.80 (dd, *J* = 7.0, 6.1 Hz, 1H, ArC=C*H*), 5.33 (q, *J* = 5.1 Hz, 1H, OC*H*Me), 1.79 (dd, *J* = 16.1, 6.1 Hz, 1H, C=CCH_aH$_b$), 1.53 (d, *J* = 5.1 Hz, 3H, OCHCH_3), 1.51 (dd, *J* = 16.1, 7.0 Hz, 1H, C=CCH$_a$$H_b$), 1.01 (dd, *J* = 8.1, 8.1 Hz, 3H, SiCH$_2$CH_3), 0.96 (dd, *J* = 8.1, 8.1 Hz, 3H, SiCH$_2$CH_3), 0.73 (app q, *J* = 7.7 Hz, 2H, SiCH_2CH$_3$), and 0.65 (app q, *J* = 7.7 Hz, 2H, SiCH_2CH$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.6 (d, $^{1}J_{F\text{-}C}$ = 246.9 Hz), 152.5, 133.2 (d, $^{4}J_{F\text{-}C}$ = 3.6 Hz),

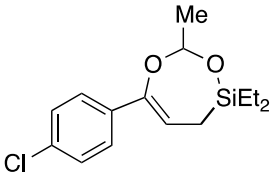
126.4 (d, $^{3}J_{F\text{-}C}$ = 7.9 Hz), 115.3 (d, $^{2}J_{F\text{-}C}$ = 21.6 Hz), 108.5 (d, $^{5}J_{F\text{-}C}$ = 1.8 Hz), 97.3, 24.6, 12.0, 7.1, 6.9, 6.8, and 5.3.

IR (neat): 3044 (w), 2954 (m), 2874 (m), 1595 (w), 1484 (m), 1387 (m), 1287 (s), 1071 (m), 788 (s), and 739 (m) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{21}FNaO_2Si)^+$: 303.1187. Found: 303.1162.

5-(4-Chlorophenyl)-2,2-diethyl-7-methyl-2,3-dihydro-1,6,2-dioxasilepine (2-6-12)



Yield: 0.2 mmol scale, 53 mg, 89%.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.39 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 7.27 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 5.88 (dd, *J* = 7.1, 6.1 Hz, 1H, ArC=C*H*), 5.32 (q, *J* = 5.1 Hz, 1H, OC*H*Me), 1.82 (dd, *J* = 16.0, 6.1 Hz, 1H, C=CC$H_a$$H_b$), 1.53 (d, *J* = 5.1 Hz, 3H, OCHCH_3), 1.52 (dd, *J* = 16.0, 7.1 Hz, 1H, C=CC$H_a$$H_b$), 1.01 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH_2CH_3), 0.98 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH_2CH_3), 0.73 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH_3), and 0.65 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH_3).

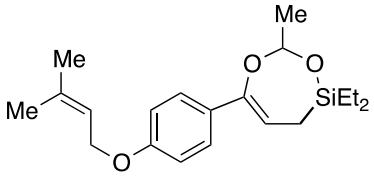
^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.3, 135.5, 133.3, 128.6, 125.9, 109.7, 97.5, 24.7, 12.2, 7.09, 6.91, 6.78, and 5.4.

IR (neat): 3091 (w), 2953 (m), 2874 (m), 1585 (w), 1461 (m), 1400 (m), 1322 (m), 1165 (m), 1006 (m), 790 (s), and 720 (m) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{21}ClNaO_2Si)^+$: 319.0892. Found: 319.1082.

2,2-Diethyl-7-methyl-5-(4-((3-methylbut-2-en-1-yl)oxy)phenyl)-2,3-dihydro-1,6,2-dioxasilepine (2-6-13)



Yield: 0.2 mmol scale, 53 mg, 87%.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.50 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.89 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 5.68 (dd, *J* = 7.1, 5.9 Hz, 1H, ArC=C*H*), 5.49 (m, 1H, C*H*=CCH$_3$CH$_3$), 5.35 (q, *J* = 5.0 Hz, 1H, OC*H*Me), 4.34 (app d, *J* = 6.3 Hz, 1H, ArOC*H*$_2$), 1.78 (dd, *J* = 16.1, 5.9 Hz, 1H, C=CC*H*$_a$H$_b$), 1.55 (s, 3H, CH=CCH$_3$C*H*$_3$), 1.54 (d, *J* = 5.0 Hz, 3H, OCHC*H*$_3$), 1.43 (s, 3H, C*H*=CCH$_3$C*H*$_3$), 1.32 (dd, *J* = 16.1, 7.1 Hz, 1H, C=CCH$_a$*H*$_b$), 1.06 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$C*H*$_3$), 0.99 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$C*H*$_3$), 0.76 (app q, *J* = 8.0 Hz, 2H, SiC*H*$_2$CH$_3$), 0.64 (app q, *J* = 8.0 Hz, 2H, SiC*H*$_2$CH$_3$) and 0.40 (water in benzene-*d*$_6$, *H*$_2$O).

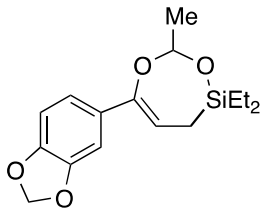
^{13}C NMR (C_6D_6, 125 MHz): δ 159.3, 153.9, 137.0, 130.0, 126.3, 120.8, 114.9, 106.8, 97.7, 64.9, 25.6, 24.8, 18.0, 12.1, 7.5, 7.08, 6.95, and 5.7.

IR (neat): 3078 (w), 3045 (w), 2956 (m), 2875 (m), 1681 (m), 1588 (m), 1412 (m), 1230 (s), 1062 (s), 1004 (s), and 729 (s) cm^{-1}.

TLC: R_f = 0.4 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{20}H_{30}NaO_3Si)^+$: 369.1856. Found: 369.1888.

5-(Benzo[*d*][1,3]dioxol-5-yl)-2,2-diethyl-7-methyl-2,3-dihydro-1,6,2-dioxasilepine (2-6-14)



Yield: 0.2 mmol scale, 53 mg, 87%.

^{1}H NMR (C_6D_6, 500 MHz): 7.11 (d, *J* = 1.7 Hz, 1H, Ar*H*), 7.01 (dd, *J* = 8.1, 1.7 Hz, 1H, Ar*H*), 6.65 (d, *J* = 8.1 Hz, 1H, Ar*H*), 5.51 (dd, *J* = 7.1, 5.9 Hz, 1H, ArC=C*H*), 5.21 (d, *J* = 2.2 Hz, 2H, OC*H*$_2$O), 5.21 (q, *J* = 5.1 Hz, 1H, OC*H*Me), 1.67 (dd, *J* = 16.0, 5.9 Hz, 1H, C=CC*H*$_a$H$_b$), 1.40 (d, *J* = 5.1 Hz, 3H, OCHC*H*$_3$), 1.19 (dd, *J* = 16.0, 7.1 Hz, 1H, C=CCH$_a$*H*$_b$), 0.97 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$C*H*$_3$), 0.91 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$C*H*$_3$), 0.66 (app q, *J* = 8.0 Hz, 2H,

Si$CH_2$$CH_3$), 0.55 (app q, J = 8.0 Hz, 2H, Si$CH_2$$CH_3$), and 0.40 (water in benzene-d_6, H_2O).

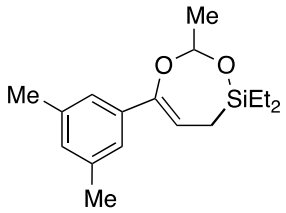
^{13}C NMR (C_6D_6, 125 MHz): δ 153.2, 148.1, 147.4, 131.6, 118.4, 108.0, 107.4, 105.4, 100.8, 97.4, 24.4, 11.8, 7.1, 6.73, 6.59, and 5.3.

IR (neat): 3058 (w), 2957 (m), 2875 (m), 1727 (m), 1398 (m), 1266 (m), 1131 (s), 738 (s), and 596 (m) cm^{-1}.

TLC: R_f = 0.3 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{16}H_{22}NaO_4Si^+)^+$: 329.1180. Found: 329.1098.

5-(3,5-Dimethylphenyl)-2,2-diethyl-7-methyl-2,3-dihydro-1,6,2-dioxasilepine (2-6-15)



Yield: 0.2 mmol scale, 41 mg, 71%.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.09-7.08 (m, 2H, Ar-*H*) 6.89-6.88 (m, 1H, Ar-*H*), 5.87 (dd, J = 7.3, 5.9 Hz, 1H, ArC=C*H*), 5.31 (q, J = 5.1 Hz, 1H, OC*H*Me), 2.30 [s, 6H, Ar(CH_3)$_2$], 1.83 [dd, J = 16.0, 5.9 Hz, 1H, C=CC$H_a$$H_b$], 1.55 (d, J = 5.1 Hz, 3H, OCHCH_3), 1.48 (dd, J = 16.0, 7.3 Hz, 1H, C=CC$H_a$$H_b$), 1.02 (dd, J = 8.0, 8.0 Hz, 3H, SiCH_2CH_3), 0.97 (dd, J = 8.0, 8.0 Hz, 3H, SiCH_2CH_3), 0.73 (app q, J = 8.0 Hz, 2H, Si$CH_2$$CH_3$), and 0.66 (app q, J = 8.0 Hz, 2H, Si$CH_2$$CH_3$).

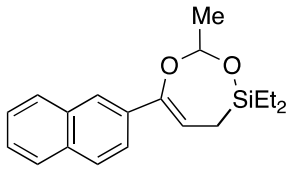
^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.5, 138.0, 136.8, 129.4, 122.5, 109.1, 97.5, 24.7, 21.65, 12.2, 7.2, 6.9, 6.8, and 5.4.

IR (neat): 3066 (br, w), 2955 (m), 2876 (m), 1610 (s), 1405 (w), 1318 (s), 1115 (s), 1075 (s), 788 (m), and 746 (m) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{17}H_{26}NaO_2Si)^+$: 331.1594. Found: 331.1566.

2,2-Diethyl-7-methyl-5-(naphthalen-2-yl)-2,3-dihydro-1,6,2-dioxasilepine (2-6-16)



Yield: 0.2 mmol scale, 54 mg, 87%.

^{1}H NMR (C_6D_6, 500 MHz): δ 8.05 (s, 1H, Ar-*H*), 7.66 (d, *J* = 8.7 Hz, 1H, Ar-*H*), 7.62 (d, *J* = 8.7 Hz, 1H, Ar-*H*), 7.61-7.58 (m, 2H, Ar-*H*), 7.28-7.21 (m, 2H, Ar-*H*), 5.90 (dd, *J* = 7.3, 6.1 Hz, 1H, ArC=C*H*), 5.34 (q, *J* = 5.1 Hz, 1H, OC*H*Me), 1.85 (dd, *J* = 16.0, 6.1 Hz, 1H, C=CCH_aH$_b$), 1.58 (d, *J* = 5.1 Hz, 3H, OCHCH_3), 1.35 (dd, *J* = 16.0, 7.3 Hz, 1H, C=CCH$_a$$H_b$), 1.06 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$CH_3), 0.99 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$CH_3), 0.77 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$), 0.65 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$) and 0.40 (water in benzene-d_6, H_2O).

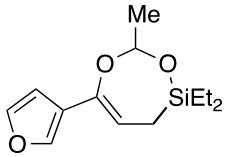
^{13}C NMR (C_6D_6, 125 MHz): δ 153.5, 135.6, 134.3, 133.8, 133.1, 128.4, 128.0, 126.2, 125.8, 123.3, 123.0, 109.9, 97.5, 24.5, 12.2, 7.1, 6.8, 6.6, and 5.4.

IR (neat): 3056 (w), 2954 (m), 2874 (m), 1677 (w), 1576 (w), 1411 (w), 1045 (m), 1002 (m), 743 (s), and 473 (s) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{19}H_{24}NaO_2Si)^+$: 335.1438. Found: 335.1806.

2,2-Diethyl-5-(furan-2-yl)-7-methyl-2,3-dihydro-1,6,2-dioxasilepine (2-6-17)



Yield: 0.2 mmol scale, 39 mg, 77%.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.02 [dd, *J* = 1.8, 0.9 Hz, 1H, C(O)*H*CH], 6.26 [dd, *J* = 3.2, 1.8 Hz, 1H, C(O)HC*H*CHC], 6.09 [dd, *J* = 3.2, 0.9 Hz, 1H, C(O)HCHC*H*C], 5.96 (dd, *J* = 7.5, 5.9 Hz, 1H, ArC=C*H*), 5.29 (q, *J* = 5.1 Hz, 1H, OC*H*Me), 1.71 (dd, *J* = 16.0, 5.9 Hz, 1H, C=CCH_aH$_b$), 1.47 (d, *J* = 5.1 Hz, 3H, OCHCH_3), 1.25 (dd, *J* = 16.0, 7.5 Hz, 1H, C=CCH$_a$$H_b$), 0.98 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$CH_3), 0.91 (dd, *J* = 8.0, 8.0 Hz, 3H, SiCH$_2$CH_3), 0.67 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$), 0.65 (app q, *J* = 8.0 Hz, 2H, SiCH_2CH$_3$) and 0.40 (water in benzene-d_6, H_2O).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 151.6, 146.2, 142.2, 111.2, 108.0, 105.2, 98.20, 70.6, 24.7,

11.6, 6.80, 6.69, and 5.0.

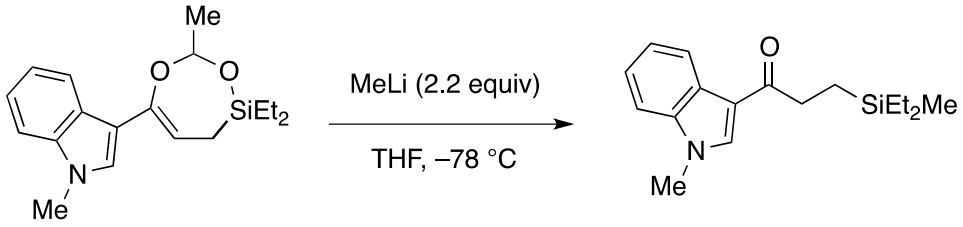
IR (neat): 3262 (br, w), 2955 (m), 2876 (m), 1718 (m), 1285 (m), 1187 (m), 1041 (s), and 730 (s) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{13}H_{20}NaO_3Si)^+$: 275.1074. Found: 275.1022.

Scheme. E.2. Nucleophilic ring opening of indole substrate:

3-(Diethyl(methyl)silyl)-1-(1-methyl-1*H*-indol-3-yl)propan-1-one (2-6-1aa)



Due to the instability of dioxasilepine upon purification, the crude compound was reacted with MeLi to give ring opened ketone compound.

Yield: 0.2 mmol scale, 41 mg, 71%.

^{1}H NMR (C_6D_6, 500 MHz): δ 8.96 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 7.29 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 7.19 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 7.01 (s, 1H, Ar-*H*), 6.89 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 2.82-2.77 (nfom, 2H, CH_2CH_2C=O), 2.73 (s, 3H, N-CH_3), 1.22-1.16 (nfom, 2H, CH_2CH_2C=O), 0.99 [t, *J* = 7.9 Hz, 6H, $Si(CH_2CH_3)_2$], 0.57 [q, *J* = 7.9 Hz, 2H, $Si(CH_2CH_3)_2$], 0.40 (water in benzene-d_6, H_2O) and 0.038 (s, 3H, $SiEt_2CH_3$).

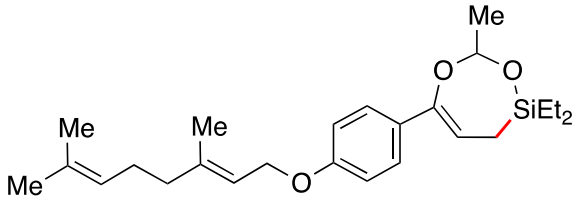
^{13}C NMR (C_6D_6, 125 MHz): δ 194.9, 161.3, 134.2, 123.5, 123.3, 122.8, 117.4, 116.8, 109.6, 34.5, 32.3, 8.0, 7.7, 5.5, and –5.9.

IR (neat): 3045 (w), 2951 (s), 2873 (s), 1682 (s), 1647 (s), 1530 (s), 1465 (m), 1391 (m), 1218 (s), 1085 (s), 1012 (s), 744 (s) cm^{-1}.

TLC: R_f = 0.5 in 20:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{17}H_{25}NNaOSi)^+$: 310.1598. Found: 310.1514.

(*E*)-5-{4-[(3,7-Dimethylocta-2,6-dien-1-yl)oxy]phenyl}-2,2-diethyl-7-methyl-2,3-dihydro-1,6,2-dioxasilepine (2-6-1ae)



Yield: 0.2 mmol scale, 86 mg, 78%

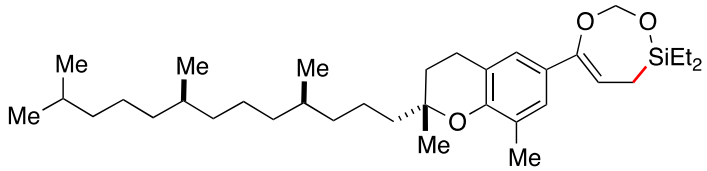
^{1}H NMR (C_6D_6, 500 MHz): δ 7.50 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.90 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 5.68 (dd, *J* = 7.0, 5.9 Hz, 1H, ArC=C*H*), 5.56 (doublet of doublet of app sextet, *J* = 6.3, 6.3, 1.2 Hz, 1H, OCH_2CH=C), 5.35 (q, *J* = 5.0 Hz, 1H, OC*H*Me), 5.14 (ddqq, *J* = 6.9, 6.9, 1.2, 1.2 Hz, 1H, CH_2CH_2CH=C), 4.50 (app d, *J* = 6.3 Hz, 2H OCH_2CH=C), 2.13-2.07 (m, 2H, CH_2CH_2CH), 2.02-1.96 (m, 2H, CH_2CH_2CH), 1.78 (dd, *J* = 16.0, 5.9 Hz, 1H, C=CCH_aH_b), 1.65 [s, 3H,C=C(CH_3)], 1.54 (d, *J* = 5.0 Hz, 3H, OCHCH_3), 1.52 [s, 3H C=C(CH_3)], 1.49 [s, 3H, C=C(CH_3)], 1.33 (dd, *J* = 16.0, 7.0 Hz, 1H, C=CCH_aH_b), 1.06 (app t, *J* = 7.9 Hz, 3H, $SiCH_2CH_3$), 0.99 (app t, *J* = 7.9 Hz, 3H, $SiCH_2CH_3$), 0.76 (app q, *J* = 8.0 Hz, 2H, $SiCH_2CH_3$), 0.64 (app q, *J* = 8.0 Hz, 2H, $SiCH_2CH_3$) and 0.40 (H_2O in benzene-d_6).

IR (neat): 3113 (w), 2961 (s), 2874 (m), 1735 (w), 1460 (m), 1247 (s), 1139 (m), 1006 (s), 834 (s), and 734 (s) cm^{-1}.

TLC: R_f = 0.6 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+H)^+$ $(C_{33}H_{54}NaO_3Si_2)^+$: 577.3504. Found: 577.3512.

5-[(*R*)-2,8-Dimethyl-2-{(4*R*,8*R*)-4,8,12-trimethyltridecyl}chroman-6-yl]-2,2-diethyl-2,3-dihydro-1,6,2-dioxasilepine (2-6-1ac)



^{1}H NMR ($CDCl_3$,500 MHz): δ 7.34 (s, 1H, Ar-*H*), 7.28 (s, 1H, Ar-*H*), 5.72 (dd, *J* = 6.5, 6.5 Hz, 1H, ArC=C*H*), 5.26 (s, 2H, OCH_2O), 2.55 (dd, *J* = 6.7, 6.7 Hz, 2H, Ar-CH_2CH_2), 2.34 (s, 3H, Ar-CH_3), 1.59 (d, *J* = 6.5 Hz, 1H, C=CCH_2), 1.55-1.22 (m, 22H, alkyl-*H* and Ar-CH_2CH_2), 1.16 [s, 3H, C(CH_3)], 1.03 (dd, *J* = 8.0, 8.0 Hz, 6H, $SiCH_2CH_3$), 0.96-0.88 (m, 13H, alkyl-*H*), 0.71 (app q, *J* = 8.0 Hz, 2H, $SiCH_2CH_3$), 0.88-0.84 (m, 17H, alkyl-*H*), and 0.40 (H_2O in benzene-d_6).

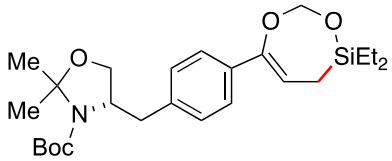
^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.8, 152.5, 128.3, 126.3, 125.7, 124.0, 120.3, 106.1, 91.1, 76.3, 40.5, 39.8, 37.95, 37.76, 35.0, 33.27, 33.11, 32.0, 31.5, 28.4, 25.6, 25.3, 25.0, 24.3, 23.06, 22.94, 22.85, 22.73, 21.4, 20.03, 19.90, 16.6, 14.4, 12.2, 7.0, and 6.2.

IR (neat): 3066 (w), 2948 (m), 2872 (w), 1541 (m), 1431 (m), 1245 (s), 1002 (s), 735 (s), and 697 (m) cm^{-1}.

TLC: R_f = 0.5 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{35}H_{60}NaO_3Si)^+$: 579.4204. Found: 579.4233.

(*S*)-*Tert*-butyl 4-{4-(2,2-diethyl-2,3-dihydro-1,6,2-dioxasilepin-5-yl)benzyl}-2,2-dimethyloxazolidine-3-carboxylate (2-6-1ad)



Yield: 0.2 mmol scale, 81 mg, 72%.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.48 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.43 (d, *J* = 7.8 Hz, 0.6H, Ar-*H*), 7.19 (d, *J* = 7.8 Hz, 0.6H, Ar-*H*), 7.07 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 5.77 (dd, *J* = 6.5, 6.5 Hz, 1H, ArC=C*H*), 5.70 (dd, *J* = 6.5, 6.5 Hz, 1H, ArC=C*H*), 5.16 (s, 2H, OCH_2O), 5.11 (s, 1.2H, OCH_2O), 4.21-4.14 [m, 0.6H, C*H*N(Boc)], 3.90-3.83 [m, 1H, C*H*N(Boc)], 3.68 (dd, *J* = 10.4, 9.3 Hz, 1.6H, C$H_a$$H_b$CHN), 3.50 (ddd, *J* = 8.9, 5.6, 1.1 Hz, 1.6H, CHC$H_a$$H_b$O), 3.43 (app d, *J* = 12.8 Hz, 0.6H, NCHC$H_a$$H_b$), 3.13 (app d, *J* = 12.8 Hz, 1H, NCHC$H_a$$H_b$), 2.73 (dd, *J* = 12.3, 10.6 Hz, 0.6H, NCHC$H_a$$H_b$), 2.66 (dd, *J* = 12.3, 10.6 Hz, 1H, NCHC$H_a$$H_b$), 1.85 [s, 3H, (C$H_3$)$_2$C], 1.61 [s, 1.5 H, (C$H_3$)$_2$C], 1.59 [s, 3H, (C$H_3$)$_2$C], 1.54 (d, *J* = 6.5 Hz, 2H ArC=CHCH_2), 1.51 (dd, *J* = 6.5 Hz, 1H, ArC=CHCH_2), 1.48 [s, 9H, OC(CH_3)$_3$], 1.45 [s, 5H, OC(CH_3)$_3$], 1.41 [s, 1.5H, (CH_3)$_2$C], 1.04-0.95 [m, 10H, Si(CH$_2$CH_3)$_2$], 0.70-0.61 [m, 7H, Si(CH_2CH$_3$)$_2$], and 0.40 (H_2O in benzene-d_6).

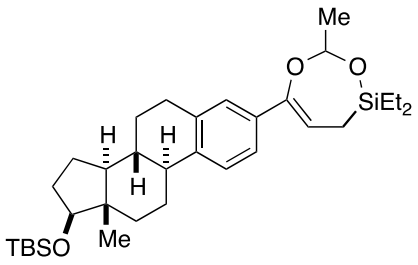
^{13}C NMR (C_6D_6, 125 MHz): δ 154.16, 154.14, 140.2, 136.8, 134.77, 134.75, 125.86, 125.84, 125.63, 125.60, 122.62, 122.59, 108.20, 108.13, 97.7, 82.1, 49.8, 44.89, 44.85, 43.8, 39.0, 37.6, 31.4, 30.5, 30.17, 30.13, 27.70, 27.69, 26.6, 26.2, 24.9, 23.5, 18.4, 12.2, 11.68, 11.65, 7.53, 7.51, 7.12, 6.98, 5.8, –4.2, and –4.5.

IR (neat): 3114 (w), 2952 (s), 2874 (m), 1724 (w), 1460 (m), 1247 (s), 1139 (m), 1006 (s), 834 (s), and 734 (s) cm^{-1}.

TLC: R_f = 0.7 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{33}H_{54}NaO_3Si_2)^+$: 577.3504. Found: 577.3512.

5-[{(8*R*,9*S*,13*S*,14*S*,17*S*)-17-(*Tert*-butyldimethylsilyl)oxy}-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl]-2,2-diethyl-7-methyl-2,3-dihydro-1,6,2-dioxasilepine (2-6-1af)



Yield: 0.2 mmol scale, 86 mg, 78%, 1:1 *dr*.

^{1}H NMR (C_6D_6, 500 MHz, a 1:1 mixture of two diastereomers): δ 7.48 [d, *J* = 8.1 Hz, 2H, C(1)*H*], 7.42 [s, 2H, C(2)*H*], 7.29 [d, *J* = 8.1 Hz, 2H, C(4)*H*], 5.87 [dd, *J* = 7.1, 5.8 Hz, 1H, ArC=C*H* (from one diastereomer)], 5.86 [dd, *J* = 7.1, 6.0 Hz, 1H, ArC=C*H* (from the other diastereomer)], 5.43 [q, *J* = 5.1 Hz, 1H, OC*H*Me, (from one diastereomer)], 5.41 [q, *J* = 5.1 Hz, 1H, OC*H*Me, (from the other diastereomer)], 3.43 [app t, *J* = 8.3 Hz, 2H, C(17)*H*], 2.82-2.76 (m, 4H, alkyl-*H*), 2.22-2.16 (m, 2H, alkyl-*H*), 2.14-2.06 (m, 2H, alkyl-*H*), 1.91-1.78 (m, 6H, alkyl-*H*), 1.76-1.70 (m, 2H, alkyl-*H*), 1.60 [d, *J* = 5.1 Hz, 3H, OCHCH_3, (from the other diastereomer)], 1.59 [d, *J* = 5.1 Hz, 3H, OCHCH_3, (from the other diastereomer), 1.55-1.41 (m, 8H, alkyl-*H*), 1.38-1.30 (m, 4H, alkyl-*H*), 1.25-1.14 (m, 6H, alkyl-*H*), 1.07 (app t, *J* = 7.9 Hz, 6H, Si(CH_2CH_3)$_2$], 1.04 (s, 18H, Si(CH_3)$_3$], 1.00 (app t, *J* = 7.9 Hz, 6H, Si(CH_2CH_3)$_2$], 0.80 [s, 6H, C(18)H_3], 0.80-0.75 (m, 4H, Si(CH_2CH_3)$_2$], 0.69-0.63 (m, 4H, Si(CH_2CH_3)$_2$], 0.12 (s, 6H, Si^{t}BuCH_3), and 0.10 (s, 6H, Si^{t}BuCH_3).

^{13}C NMR (C_6D_6, 125 MHz): δ 154.16, 154.14, 140.2, 136.8, 134.77, 134.75, 125.86, 125.84, 125.63, 125.60, 122.62, 122.59, 108.20, 108.13, 97.7, 82.1, 49.8, 44.89, 44.85, 43.8, 39.0, 37.6, 31.4, 30.5, 30.17, 30.13, 27.70, 27.69, 26.6, 26.2, 24.9, 23.5, 18.4, 12.2, 11.68, 11.65, 7.53, 7.51, 7.12, 6.98, 5.8, –4.2, and –4.5.

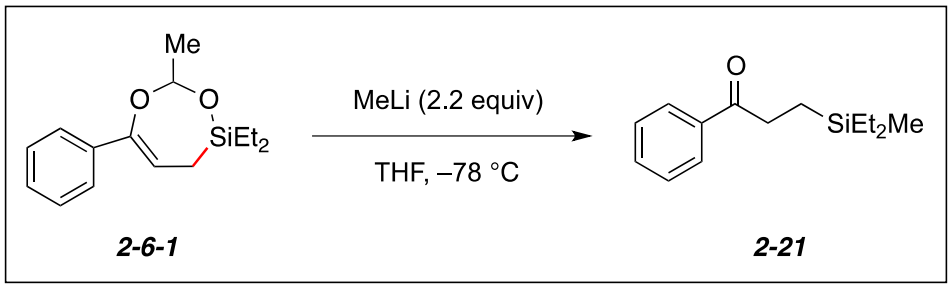
IR (neat): 3114 (w), 2952 (s), 2874 (m), 1724 (w), 1460 (m), 1247 (s), 1139 (m), 1006 (s), 834 (s), and 734 (s) cm^{-1}.

TLC: R_f = 0.7 in 80:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+H)^+$ $(C_{33}H_{54}NaO_3Si_2)^+$: 577.3504. Found: 577.3512.

F. Applications of Dioxasilepines (2-6):

F.1.Nucleophilic ring-opening of dioxasilepines (2-6):



To a flame dried vial was added a solution of dioxasilepine **2-6-1** (26 mg, 0.1 mmol) in THF (0.5 mL, 0.2 M) which was cooled the mixture to –78 °C. MeLi (137 μL, 1.6 M in Et_2O, 2.2 equiv) was added dropwise to the mixture. After being stirred for 30 min at –78 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The volatiles were removed *in vacuo* to afford crude material, which was purified by MPLC (hexanes/EtOAc =20:1, 5 mL/min, retention time 15 min) to provide **2-21** (20 mg, 88% yield) as a colorless oil.

3-[Diethyl(methyl)silyl]-1-phenylpropan-1-one (2-21)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.55 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.46 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 2.98-2.89 (nfom, 2H, CH_2CH_2C=O), 0.95 [t, *J* = 8.1 Hz, 6H, $Si(CH_2CH_3)_2$], 0.94-0.88 (nfom, 2H, CH_2CH_2C=O), 0.55 [q, *J* = 8.1 Hz, 2H, $Si(CH_2CH_3)_2$], and –0.01 (s, 3H, $SiEt_2CH_3$).

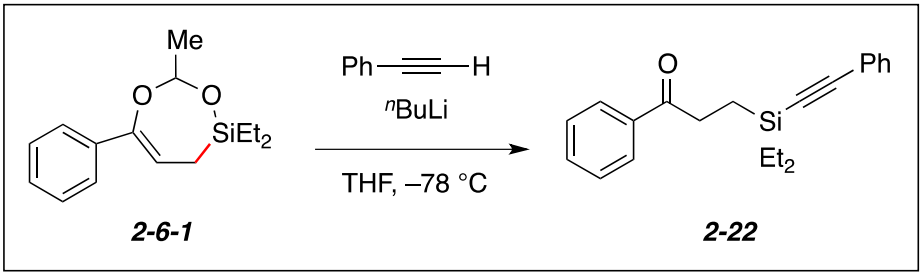
^{13}C NMR ($CDCl_3$, 125 MHz): δ 201.6, 137.0, 133.0, 128.8, 128.3, 70.6, 33.3, 7.6, 5.1, and –6.0.

IR (neat): 3047 (w), 2951 (m), 2873 (m), 1685 (s), 1598 (m), 1448 (m), 1377 (m), 1225 (s), 1075 (s), 962 (s), 788 (s), and 740 (s) cm^{-1}.

TLC: R_f = 0.5 in 20:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{14}H_{22}NaOSi)^+$: 257.1332. Found: 257.1356.

F.2. Nucleophilic Ring-Opening of Dioxasilepine 2-6-1 with Lithium Acetylide



To a flame dried vial was added a solution of phenyl acetylene (66 μL, 1.2 equiv, 0.6 mmol) in THF (0.5 mL) which was cooled the mixture to –78 °C. ^{n}BuLi (192 μL, 2.6 M in hexane, 1.0 equiv, 0.5 mmol) was added dropwise to the reaction mixture. After the mixture was stirred for 10 min at –78 °C, a solution of dioxasilepine **2-6-1** (131 mg, 1 equiv, 0.5 mmol) in THF (0.1 mL) was added. After being stirred for 30 min at –78 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The volatiles were removed *in vacuo* to afford crude material, which was purified by MPLC (hexanes/EtOAc =20:1, 5 mL/min, retention time 15 min) to afford **2-22** (74%, 118 mg) as a colorless oil.

3-[Diethyl(phenylethynyl)silyl]-1-phenylpropan-1-one (2-22)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.55 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.45 (t, *J* = 7.5 Hz, 4H, Ar-*H*), 7.30 (t, *J* = 7.5 Hz, 3H, Ar-*H*), 3.15-3.10 (nfom, 2H, $COCH_2CH_2$), 1.11-1.08 (nfom, 2H, $COCH_2CH_2$), 1.07 [t, 6H, *J* = 8.1 Hz, $Si(CH_2CH_3)_2$], and 0.55 [q, 4H, *J* = 8.1 Hz, $Si(CH_2CH_3)_2$].

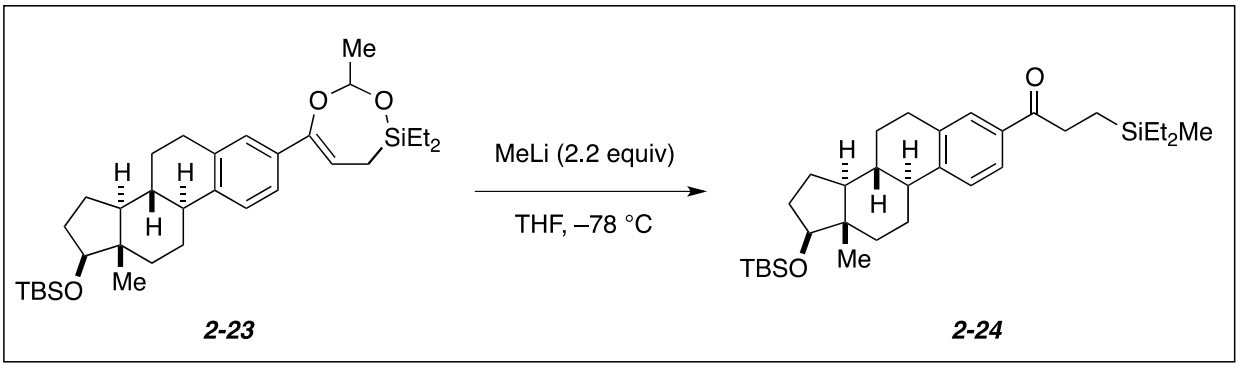
^{13}C NMR ($CDCl_3$, 125 MHz): δ 201.2, 137.0, 133.1, 132.3, 128.8, 128.44, 128.34, 123.2, 107.4, 100.1, 90.9, 33.5, 7.7, 6.9, and 5.1.

IR (neat): 3042 (w), 2953 (s), 2152 (m), 1685 (s), 1448 (w), 1391 (m), 1012 (s), 963 (s), 931 (s), and 721 (s) cm^{-1}.

TLC: R_f = 0.6 in 20:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+H)^+$ $(C_{21}H_{24}NaOSi)^+$: 343.1489. Found: 343.1489.

F.3. Nucleophilic Ring-Opening of Dioxasilepine 2-6-1f with MeLi



2-23 ***2-24***

1-{(8*R*,9*S*,13*S*,14*S*,17*S*)-17-[(*Tert*-butyldimethylsilyl)oxy]-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl}-3-[diethyl(methyl)silyl]propan-1-one (2-24)

Yield: 0.2 mmol scale, 92 mg, 88% yield.

^{1}H-NMR (C_6D_6, 500 MHz): δ 7.87 [d, *J* = 1.6 Hz, 1H, C(4)*H*], 7.82 [dd, *J* = 8.1, 1.6 Hz, 1H, C(2)*H*], 7.23-7.21 [d, *J* = 8.1 Hz, 1H, C(1)*H*], 3.43 [dd, *J* = 8.3, 8.3 Hz, 1H, C(17)*H*], 2.83-2.80 (nfom, 2H, CH_2CH_2CO), 2.67-2.62 (m, 2H, alkyl-*H*), 2.06 (m, *J* = 13.4, 7.1, 4.1 Hz, 1H, alkyl-*H*), 1.96 (ddd, *J* = 11.2, 11.2, 4.1 Hz, 1H, alkyl-*H*), 1.82 (ddd, *J* = 12.8, 3.5, 3.5 Hz, 1H, alkyl-*H*), 1.76 (dddd, *J* = 12.8, 9.2, 7.5, 3.3 Hz, 1H, al kyl-*H*), 1.60 (dddd, *J* = 12.5, 5.5, 2.8, 2.8 Hz, 1H, alkyl-*H*), 1.49-0.83 (m, 8H), 0.98 (s, 9H, $Si(CH_3)_3$], 0.89 (dd, *J* = 7.9, 7.9 Hz, 6H, $Si(CH_2CH_3)_2$], 0.71 [s, 3H, C(18)H_3], 0.45 (q, *J* = 7.9 Hz, 4H, $Si(CH_2CH_3)_2$], 0.07 (s, 3H, Si^{t}BuCH_3), 0.05 (s, 3H, Si^{t}BuCH_3), and –0.09 (s, 3H, $SiEt_2CH_3$).

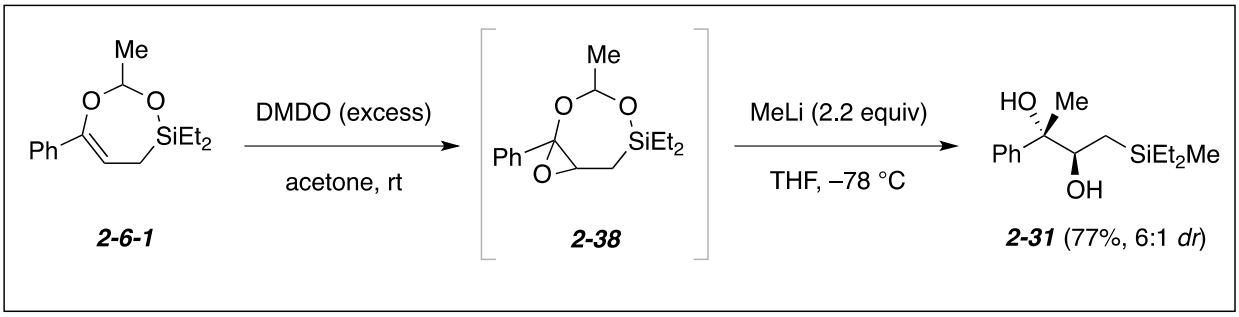
^{13}C NMR (C_6D_6, 125 MHz): δ 199.7, 145.8, 137.3, 135.2, 129.2, 125.96, 125.92, 82.1, 49.8, 45.1, 43.7, 38.6, 37.5, 33.2, 31.3, 29.8, 27.4, 26.4, 26.2, 23.4, 18.4, 11.6, 7.68 (2), 7.66 (2), 5.4, –4.2, –4.5, and –6.0.

IR (neat): 3114 (w), 2952 (s), 2874 (m), 1724 (w), 1460 (m), 1247 (s), 1139 (m), 1006 (s), 834 (s), and 734 (s) cm^{-1}.

TLC: R_f = 0.5 in 40:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{32}H_{54}NaO_2Si_2^+)^+$: 549.3555. Found: 549.3531.

F.5. Oxidative rearrangement



To a flame dried vial with dioxasilepine **2-6-1** (131 mg, 0.5 mmol) was added DMDO (50 μL, 0.05 M in acetone, 2.5 mmol, 5 equiv) at –78 °C. The mixture was brought to room temperature by removing a dry-ice bath. The mixture was stirred for 1 h at rt. GC-MS and ^{1}H NMR analyses confirmed that **2-6-1** was fully consumed and the epoxide intermediate **2-38** was formed. The reaction mixture was cooled to –78 °C, and MeLi (687 μL, 1.6 M in Et_2O, 2.2 equiv) was added dropwise to the mixture. After being stirred for 30 min at –78 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The volatiles were removed *in vacuo* to afford crude material, which was purified by MPLC (hexanes/EtOAc = 5:1, 5 mL/min, retention time 15 min) to provide **2-31** [102 mg, 77% yield (6:1 *dr*)] as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz, include ca. 5% of diastereomer): δ 7.95 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.55 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 7.46 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 3.87 [dd, *J* = 10.3, 3.4 Hz, 1H, C*H*(OH)], 1.93 (br s, 1H, O*H*), 1.59 [s, 3H, ArC(OH)CH_3CH], 1.25 (s, 1H, O*H*), 0.88-0.80 [m, 7H, Si(CH_2CH_3)$_2$, CH_aH$_b$SiEt$_2$Me], 0.56-0.49 [m, 4H, Si(CH_2CH$_3$)$_2$, CH$_a$$H_b$SiEt$_2$Me], and –0.06 (s, 3H, SiEt$_2$CH_3).

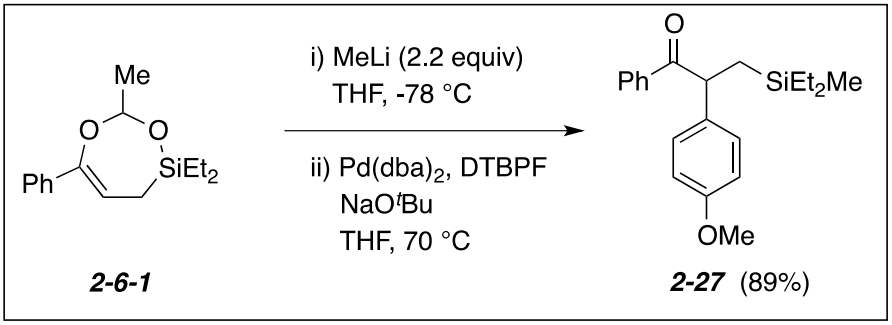
^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.1, 128.3, 127.1, 125.6, 77.8, 76.4, 29.9, 26.5, 15.8, 7.5, 5.72, 5.65, and –5.3.

IR (neat): 3452 (br, w), 3041 (w), 2951 (m), 2884 (m), 1615 (w), 1577 (w), 1446 (m), 1232 (m), 1038 (s), 1012 (s), 931 (s), 760 (s), and 698 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{26}NaO_2Si)^+$: 289.1594. Found: 289.1531

F.6. Arylation



To a flame dried vial was added a solution of dioxasilepine **2-6-1** (26 mg, 0.1 mmol) in THF (0.5 mL. 0.2 M) which was cooled the mixture to –78 °C. Then MeLi (137μL, 1.6 M in Et_2O, 2.2 equiv, 0.22 mmol) was added dropwise to the mixture. After the reaction mixture was stirred for 30 min at –78 °C, $Pd(dba)_2$ (4 mol %), DTBPF (10 mol %), NaO^tBu (1.5 equiv), and 4-bromo anisole (1.2 equiv) were added successively. The mixture was warmed to 70 °C and stirred for overnight. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The volatiles were removed *in vacuo* to afford crude material, which was purified by MPLC (hexanes/EtOAc =20:1, 5 mL/min, retention time 15 min) to afford **2-27** (30 mg, 89% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 7.47 (dd, *J* = 7.4, 7.4 Hz, 1H, Ar-*H*), 7.40 (dd, *J* = 7.7, 7.4 Hz, 2H, Ar-*H*), 7.23 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 6.81 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 4.64 [dd, 1H, *J* = 7.8, 7.3 Hz, CH_2(Ar)C*H*C=O], 3.74 (s, 3H, Ar-OCH_3), 1.49 [dd, *J* = 14.8, 7.3 Hz, 1H, CH_aH$_b$SiEt$_2$Me], 1.17 [dd, *J* = 14.8, 7.8 Hz, 1H, CH$_a$$H_b$SiEt$_2$Me], 0.87 [dd, *J* = 8.1, 8.1 Hz, 3H, Si(CH$_2$CH_3)$_2$], 0.86 [dd, *J* = 8.1, 8.1 Hz, 3H, Si(CH$_2$CH_3)$_2$], 0.48-0.31 [m, 4H, Si(CH_2CH$_3$)$_2$], and –0.18 (s, 3H, SiEt$_2$CH_3).

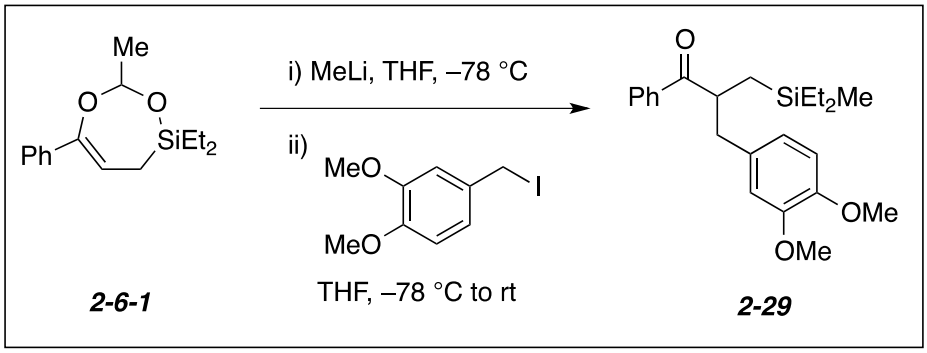
^{13}C NMR ($CDCl_3$, 125 MHz): δ 200.8, 158.7, 136.9, 133.8, 132.8, 129.4, 128.80, 128.70, 114.4, 55.4, 48.4, 18.7, 7.5 (2), 5.55, 5.49, and –5.5.

IR (neat): 3042 (w), 2953 (s), 2875 (s), 1686 (s), 1514 (m), 1411 (m), 1391 (m), 1235 (s), 1091 (s), 1011 (s), 881 (s), 721 (s), and 630 (s) cm^{-1}.

TLC: R_f = 0.6 in 20:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+H)^+$ $(C_{21}H_{29}O_2Si)^+$: 341.1931. Found: 341.1935.

F.7. Alkylation



To a flame dried vial was added a solution of dioxasilepine **2-6-1** (26 mg, 0.1 mmol) in THF (0.5 mL, 0.2 M) which was cooled the mixture to –78 °C. MeLi (137 μL, 1.6 M in Et_2O, 2.2 equiv, 0.22 mmol) was added dropwise to the mixture. After the reaction mixture was stirred for 30 min at –78 °C, a solution of alkyl iodide (3 equiv) in 0.1 mL THF at –78 °C was added to the mixture. After being stirred for 1 h at –78 °C, the reaction mixture was warmed to rt. The mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The volatiles were removed *in vacuo* to afford crude material, which was purified by MPLC (hexanes/EtOAc =20:1, 5 mL/min, retention time 15 min) to afford **2-29** (28 mg, 73% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.83 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.50 (dd, *J* = 7.4, 7.4 Hz, 1H, Ar-*H*), 7.40 (dd, *J* = 7.6, 7.4 Hz, 2H, Ar-*H*), 6.72 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 6.69 (dd, *J* = 8.2, 1.8 Hz, 1H, Ar-*H*), 6.63 (d, *J* = 1.8 Hz, 1H, Ar-*H*), 3.80 (s, 3H, Ar-OCH_3), 3.80-3.71 [m, 1H, O=CC*H*], 3.78 (s, 3H, Ar-OCH_3), 3.09 (dd, *J* = 13.6, 8.2 Hz, Ar-CH_aH$_b$), 2.66 (dd, *J* = 13.6, 5.8 Hz, ArCH$_a$$H_b$), 1.11 (dd, *J* = 14.8, 7.7 Hz, 1H, CH_aH$_b$SiEt$_2$Me), 0.88 [dd, *J* = 7.9, 7.9 Hz, 3H, Si(CH$_2$CH_3)$_2$], 0.87 [dd, *J* = 7.9, 7.9 Hz, 3H, Si(CH$_2$CH_3)$_2$], 0.78 (dd, *J* = 14.8, 6.3 Hz, 1H, CH$_a$$H_b$SiEt$_2$Me), 0.50-0.42 [m, 4H, Si(CH_2CH$_3$)$_2$], and –0.08 (s, 3H, SiEt$_2$CH_3).

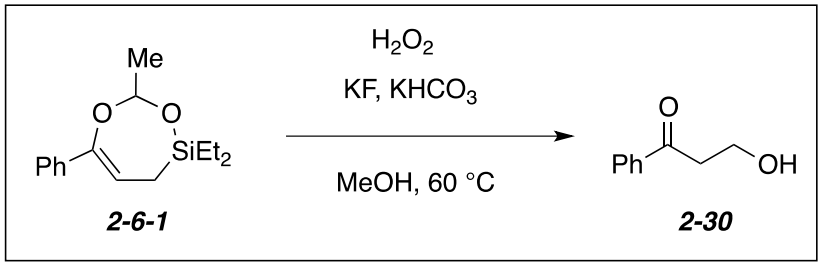
^{13}C NMR ($CDCl_3$, 125 MHz): δ 204.3, 148.8, 147.6, 137.2, 133.0, 132.8, 128.8, 128.4, 121.1, 112.6, 111.3, 56.04, 55.99, 44.3, 41.2, 16.5, 7.5 (2), 5.81, 5.78, and –5.1.

IR (neat): 3038 (w), 2950 (s), 1680 (s), 1593 (m), 1514 (s), 1447 (s), 1236 (s), 1156 (s), 1029 (s), 931 (s), and 799 (s) cm^{-1}.

TLC: R_f = 0.4 in 20:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ ($C_{23}H_{32}NaO_3Si$)$^+$: 407.2013. Found: 407.2088.

F.8. Oxidation:



To a flame dried vial was added a solution of dioxasilepine **2-6-1** (26 mg, 1.0 equiv, 0.1 mmol), $KHCO_3$ (40 mg, 4.0 equiv, 0.4 mmol), KF (23 mg, 4.0 equiv, 0.4 mmol), MeOH (1 mL, 0.1 M), and H_2O_2 (93 μL, 30% solution in H_2O, 12 equiv, 1.2 mmol). The reaction mixture was then warmed to 60 °C for 2 h (Caution! Explosive. Do not use a reaction vessel.). The reaction mixture was then diluted with EtOAc, washed with aqueous NaOH (3.0 M) and brine, and dried over Na_2SO_4. The volatiles were removed *in vacuo* to afford crude material, which was purified by MPLC (hexanes/EtOAc =5:1, 5 mL/min, retention time 15 min) to afford **2-30** (26 mg, 86% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ δ 7.95 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.55 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.46 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 4.04 (t, *J* = 5.3 Hz, 2H, C=OC*H*$_2$CH$_2$), 3.24 (t, *J* = 5.3 Hz, 2H, C=OCH$_2$C*H*$_2$), and 2.42 (br s, 1H, CH$_2$O*H*).

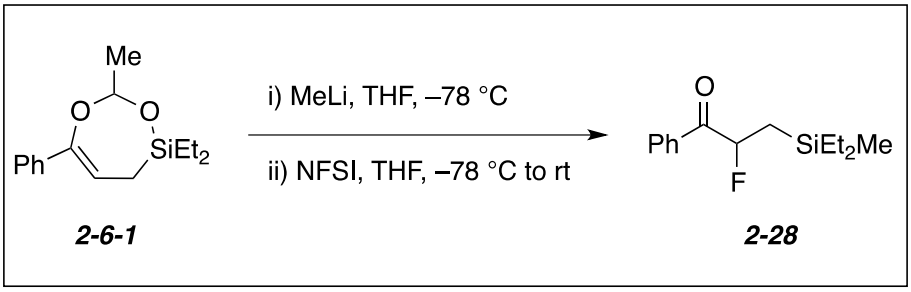
^{13}C NMR ($CDCl_3$, 125 MHz): δ 200.8, 136.8, 133.8, 128.9, 128.3, 58.3, and 40.6.

IR (neat): 3442 (br, w), 3025(w), 2954 (m), 1681 (s), 1586 (w), 1486 (s), 1354 (m), 1239 (m), 1082 (s), 738 (s), and 721 (s) cm^{-1}.

TLC: R_f = 0.5 in 10:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_9H_{10}NaO_2)^+$: 173.0573. Found: 173.0542.

F.9. Fluorination



2-6-1 ***2-28***

To a flame dried vial was added a solution of dioxasilepine **2-6-1** (26 mg, 1.0 equiv, 0.1 mmol) in THF (0.5 mL) which was cooled the mixture to –78 °C. MeLi (137 μL, 1.6 M in Et_2O, 2.2 equiv, 0.22 mmol) was added dropwise to the solution of dioxasilepine and the mixture was stirred at –78 °C for 15 min. To the mixture was added a solution of NFSI (94 mg, 3.0 equiv, 0.3 mmol) in THF (0.1 mL, 3 M) at –78 °C, and the mixture was brought to room temperature and stirred for 30 min at rt. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The volatiles were removed *in vacuo* to afford crude material, which was purified by MPLC (hexanes/EtOAc =20:1, 5 mL/min, retention time 15 min) to afford **2-28** (21 mg, 83% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.59 (dd, *J* = 7.4, 7.4 Hz, 1H, Ar-*H*), 7.48 (dd, *J* = 7.8, 7.4 Hz, 2H, Ar-*H*), 5.65 [dq, *J* = 49 ($^2J_{F-H}$), 10, 5.3 Hz, 1H, C=OC*H*F], 1.41-1.19 (m, 2H, CH_2SiEt$_2$Me), 0.95 [app t, *J* = 7.9 Hz, 6H, Si(CH$_2$CH_3)$_2$], 0.61 [app q, *J* = 7.9 Hz, 4H, Si(CH_2CH$_3$)$_2$], and 0.68 (s, 3H, SiEt$_2$CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 197.6 (d, $^2J_{F-C}$ = 21.6 Hz), 134.2, 133.8, 129.3 (d, $^4J_{F-C}$ = 3.5 Hz), 128.9, 93.1 (d, $^1J_{F-C}$ = 180.7 Hz), 18.6 (d, $^2J_{F-C}$ = 26.4 Hz), 7.4 (2), 5.66, 5.58, and –5.4.

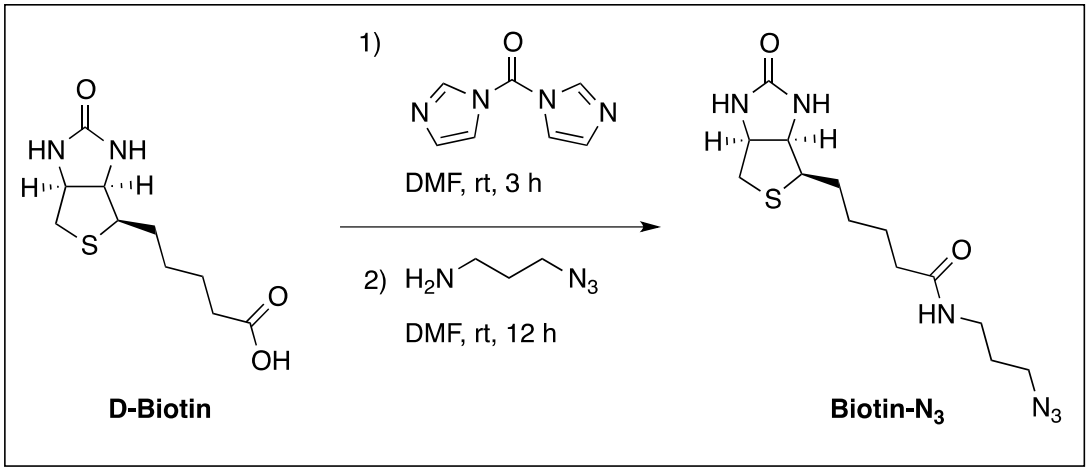
IR (neat): 3049 (w), 2954 (s), 1685 (s), 1555 (m), 1518 (s), 1348 (s), 1202 (s), 1122 (s), 1025 (s), 942 (s), and 726 (s) cm^{-1}.

TLC: R_f = 0.4 in 20:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for (M+Na)$^+$ ($C_{14}H_{21}FNaOSi^+$)$^+$: 275.1238. Found: 275.1292.

F.10. Click Reaction

F.10.1.Preparation of Biotin-N_3:

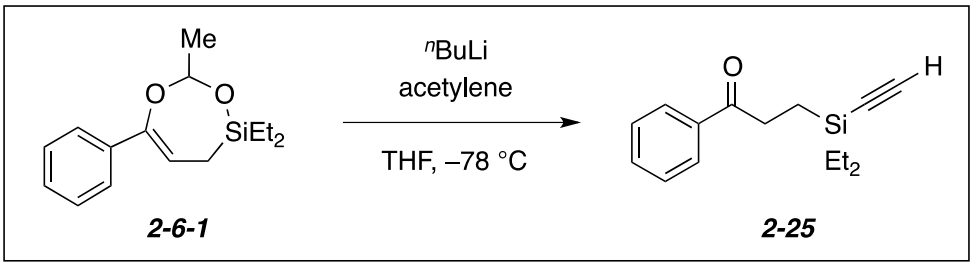


Biotin (0.61 g, 2.5 mmol) in a flame dried flask was dissolved in DMF (15 mL, 0.16 M) at 55 °C. After the mixture was cooled to room temperature, CDI (0.73 g, 4.5 mmol) in DMF (3 mL) was slowly added to the mixture, which was stirred for 3 h at room temperature. Subsequently, 1-azido-3-aminopropane (0.75 g, 7.5 mmol) in DMF (6 mL) was added dropwise to the reaction mixture over about 0.5 h, and the reaction mixture was stirred for 12 h. The solvent was then removed *in vacuo* and the residues were purified by recrystallization in a mixture of 1-butanol/acetic acid/water (70:7:10, v/v/v). The white solid obtained was washed with diethyl ether three times and dried *in vacuo* to afford **Biotin-N_3** (668 mg, 82% yield) as a white solid.

^{1}H NMR (CD_3OD, 500 MHz): δ 4.50 (m, 1H, SCH_2CH), 4.33 (m, 1H, $SCHCH$), 3.38 (m, 4H, $CH_2CH_2CH_2N_3$), 3.22 (m, 1H, $SCHCH$), 2.93 (dd, J = 7.8, 7.4 Hz, 1H, SCH_aH_bCH), 2.72 (dd, J = 7.8, 7.4 Hz, 1H, SCH_aH_bCH), 2.19 (t, J = 7.8 Hz, 2H, $CH_2CONHCH_2$), 1.54–1.83 (m, 6H, $CH_2CH_2CH_2CH_2CO$), and 1.44 (m, 2H, $CH_2CH_2CH_2N_3$).

^{13}C NMR (CD_3OD, 125 MHz): δ 176.2, 166.1, 63.4, 61.6, 57.0, 50.1, 41.0, 37.7, 36.8, 29.8, 29.5, 26.8, and 21.1.

F.10.2. Preparation of 3-[Diethyl(ethynyl)silyl]-1-phenylpropan-1-one (2-25):



To a flame-dried vial THF (2 mL) was added. After the vial was cooled to –78 °C, ^{n}BuLi (192 μL, 2.6 M in hexane, 1.25 equiv, 0.5 mmol) was added, and dry acetylene was blown over the clear solution held below –70 °C for 45 min. Neat dioxasilepine **2-6-1** (105 mg, 0.4 mmol) was added to a solution of lithium acetylide. The reaction mixture was stirred for additional 30 min at the same temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The volatiles were removed *in vacuo* to afford crude material, which was purified by MPLC (hexanes/EtOAc = 20:1, 5 mL/min, retention time 15 min) to afford β-silyl ketone **2-25** (67 mg, 69% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.55 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.46 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 3.10-3.06 (nfom, 2H, CH_2CH_2CO), 2.41 (s, 1H, Et_2SiCCH), 1.06-1.01 (nfom, 2H, CH_2CH_2CO), 1.04 [t, *J* = 8.1 Hz, 6H, $Si(CH_2CH_3)_2$], and 0.69 [q, *J* = 7.9 Hz, 4H, $Si(CH_2CH_3)_2$].

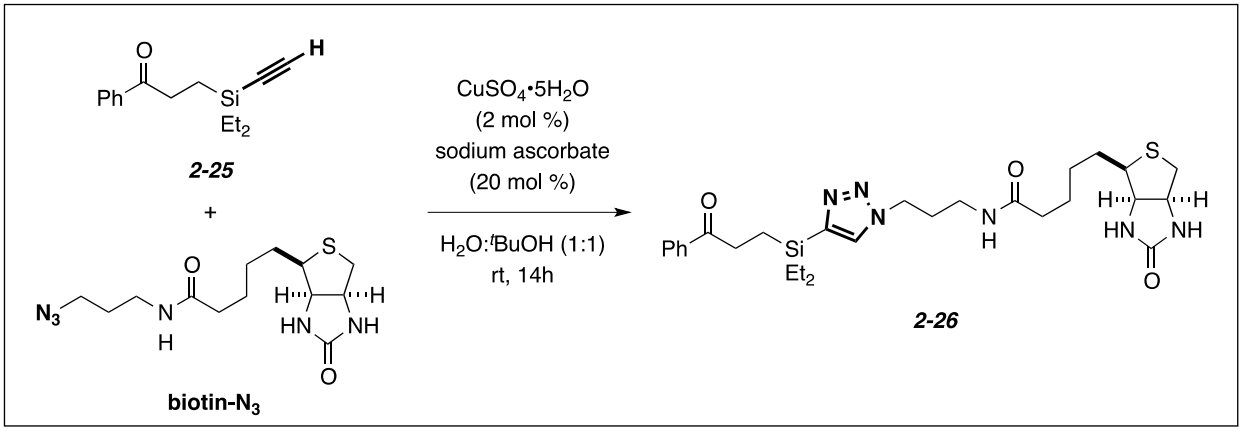
^{13}C NMR ($CDCl_3$, 125 MHz): δ 200.9, 137.0, 133.1, 128.8, 128.3, 95.2, 87.0, 33.3, 7.5, 6.4, and 4.8.

IR (neat): 3346 (m), 2954 (m), 2166 (m), 1612 (w), 1581 (w), 1336 (m), 1242 (m), 1092 (s), 1041 (m), 933 (s), 732 (s), and 682 (s) cm^{-1}.

TLC: R_f = 0.5 in 20:1 hexanes: EtOAc.

HRMS (**APCI/TOF**): Calcd for $(M+Na)^+$ $(C_{15}H_{20}NaOSi)^+$: 267.1176. Found: 267.1181.

F.10.3. Cu-catalyzed azide-alkyne cycloaddition:



β-Silyl ketone **2-25** (49 mg, 1.0 equiv, 0.2 mmol), **Biotin-N_3** (65 mg, 1.0 equiv, 0.2 mmol), and a 1:1 mixture of water and *tert*-butyl alcohol (1.0 mL) were added to a flame dried flask. Sodium ascorbate (30μL of freshly prepared 1 M solution in water, 0.02 mmol) and $CuSO_4$•$5H_2O$ (50μL of water, 0.002 mmol) were added to the suspension. The heterogeneous mixture was stirred vigorously overnight, at which point it cleared, and TLC analysis indicated complete consumption of the reactants. The reaction mixture was diluted with water (2 mL), cooled in ice, and the white precipitate was collected by filtration. The precipitate was washed with cold water, and dried under vacuum to afford triazole **2-26** (98 mg, 86% yield) as an orange solid.

^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.21 (s, 1H, Et_2SiC=C*H*), 7.93 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.62 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.51 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 4.50 (m, 1H, SCH_2CH), 4.33 (m, 1H, SCHC*H*), 3.38 (m, 4H, $CH_2CH_2CH_2N_3$), 3.22 (m, 1H, SC*H*CH), 3.04-2.99 (nfom, 2H, CH_2CH_2CO), 2.93 (dd, *J* = 7.8, 7.4 Hz, 1H, SCH_aH_bCH), 2.72 (dd, *J* = 7.8, 7.4 Hz, 1H, SCH_aH_bCH), 2.19 (t, *J* = 7.8 Hz, 2H, $CH_2CONHCH_2$), 1.54–1.83 (m, 6H, $CH_2CH_2CH_2CH_2CO$), 1.44 (m, 2H, $CH_2CH_2CH_2N_3$). 1.10-1.04 (nfom, 2H, CH_2CH_2CO), 1.04 [t, *J* = 8.1 Hz, 6H, $Si(CH_2CH_3)_2$], and 0.69 [q, *J* = 7.9 Hz, 4H, $Si(CH_2CH_3)_2$].

^{13}C NMR (DMSO-d_6, 125 MHz): δ 200.4, 172.2, 162.7, 136.5, 136.4, 133.0, 131.3, 128.7, 127.9, 61.0, 59.2, 55.4, 35.7, 35.2, 32.4, 32.0, 30.0, 28.23, 28.03, 25.3, 8.2, 7.3, 6.7, 6.0, 5.5, and 3.5.

References:

(1). a) Hernandez, D.; Nielsen, L.; Lindsay, K. B.; Garcia, M. L. A.; Bjerglund, K.; Skrydstrup, T. Stereocontrolled Synthesis of 2-Substituted-1,3-Azasilaheterocycles. *Org. Lett.* **2010**, *12*, 3528-3531. b) Wu, L. J.; Yang, Y.; Song, R. J.; Yu, J. X.; Li, J. H.; He, D. L. An access to 1,3-azasiline-fused quinolinones via oxidative heteroannulation involving silyl C(sp3)–H functionalization. *Chem. Commun.* **2018**, *54*, 1367-1370. c) Tacke, R.; Heinrich, T.; Bertermann, R. D.; Burschka, C.; Hamacher, A.; Kassack, M. U. Sila-haloperidol: A Silicon Analogue of the Dopamine (D2) Receptor Antagonist Haloperidol. *Organometallics* **2004**, *23*, 4468-4477.

(2) Crabtree, R. H. Organometallic Chemistry of Alkanes. *Chem. Rev.* **1985,** *85*, 245-269.

(3) Jones, W. D. The Fall of the C–C Bond. *Nature* **1993,** *364*, 676-677.

(4) Rybtchinski, B.; Milstein, D. Metal Insertion into C−C bonds in Solution. *Angew. Chem. Int. Ed.* **1999,** *38*, 870-883.

(5) Murakami, M.; Ito, Y. Cleavage of Carbon–Carbon Single Bonds by Transition Metals. *Top. Organomet. Chem.* **1999,** *3*, 97-129.

(6) Jun, C.-H.; Lee, H. Catalytic Carbon−Carbon Bond Activation of Unstrained Ketone by Soluble Transition-Metal Complex. *J. Am. Chem. Soc.* **1999,** *121*, 880-881.

(7) Xia, Y.; Lu, G.; Liu, P.; Dong, G. Catalytic Activation of Carbon–Carbon Bonds in Cyclopentanones. *Nature* **2016,** *539*, 546-550.

(8) Murakami, M.; Itahashi, T.; Ito, Y. *J. Am. Chem. Soc*. **2002**, *124*, 13976.

(9) Shintani, R.; Moriya, K.; Hayashi, T. *J. Am. Chem. Soc*. **2011**, *133*, 16440–16443.

(10) Seiser, T.; Saget, T.; Tran, D. N.; Cramer, N. Cyclobutanes in Catalysis. *Angew. Chem. Int. Ed.* **2011,** *50*, 7740-7752.

(11) Souillart, L.; Cramer, N. Catalytic C–C Bond Activations via Oxidative Addition to Transition Metals. *Chem. Rev.* **2015,** *115*, 9410-9464.

(12) Fumagalli, G.; Stanton, S.; Bower, J. F. Recent Methodologies That Exploit C–C Single-Bond Cleavage of Strained Ring Systems by Transition Metal Complexes. *Chem. Rev.* **2017,** *117*, 9404-9432.

(13) Gao, X.-F.; Fu, Z.-X. In *C–C Bond Activation*; Dong, D. Ed.; Springer: Berlin, 2014, Vol. *346*, pp 195-232.

(14) Wang, G.-W.; Bower, J. F. Modular Access to Azepines by Directed Carbonylative C–C Bond Activation of Aminocyclopropanes. *J. Am. Chem. Soc.* **2018,** *140*, 2743-2747

(15) Shaw, M. H.; Melikhova, E. Y.; Kloer, D. P.; Whittingham, W. G.; Bower, J. F. Directing Group Enhanced Carbonylative Ring Expansions of Amino-Substituted Cyclopropanes: Rhodium-Catalyzed Multicomponent Synthesis of N-Heterobicyclic Enones. J. Am. Chem. Soc. 2013, 135, 4992-4995.

(16) Li, H.; Li, Y.; Zhang, X.; Chen, K.; Wang, X.; Shi, Z. Pyridinyl Directed Alkenylation with Olefins via Rh(III)-Catalyzed C–C Bond Cleavage of Secondary Arylmethanols. *J. Am. Chem. Soc.* **2011,** *133*, 15244-15247.

(17) Zeng, R.; Dong, G. Rh-Catalyzed Decarbonylative Coupling with Alkynes via C–C Activation of Isatins. *J. Am. Chem. Soc.* **2015,** *137*, 1408-1411.

(18) Li, B.; Wang, Y.; Jin, Z.; Zheng, P.; Ganguly, R.; Chi, Y. Carbon-carbon Bond Activation of Cyclobutenones Enabled by the Addition of Chiral Organocatalyst to Ketone. *Nat. Commun.* **2015,** *6*, 6207.

(19) Xia, Y.; Wang, J.; Dong, G. Distal-Bond-Selective C−C Activation of Ring-Fused Cyclopentanones: An Efficient Access to Spiroindanones. *Angew. Chem. Int. Ed.* **2017,**

56, 2376-2380.

(20) Nakao, Y.; Hiyama, T. Silicon-Based Cross-Coupling Reaction: An Environmentally Benign Version. *Chem. Soc. Rev.* **2011,** *40*, 4893-4901.

(21) Ramesh, R.; Reddy, D. S. Quest for Novel Chemical Entities through Incorporation of Silicon in Drug Scaffolds. *J. Med. Chem.* **2018**, *61*, 3779-3798.

(22) Ishida, N.; Ikemoto, W.; Murakami, M. Intramolecular σ-Bond Metathesis Between Carbon–Carbon and Silicon–Silicon Bonds. *Org. Lett.* **2012,** *14*, 3230-3232.

(23) Ishida, N.; Ikemoto, W.; Murakami, M. Cleavage of C–C and C–Si σ-Bonds and Their Intramolecular Exchange. *J. Am. Chem. Soc.* **2014,** *136*, 5912-5915.

(24) Okumura, S.; Sun, F.; Ishida, N.; Murakami, M. Palladium-Catalyzed Intermolecular Exchange Between C–C and C–Si σ-Bonds. *J. Am. Chem. Soc.* **2017,** *139*, 12414-12417.

(25) Chen, D. Y.-K.; Pouwer, R. H.; Richard, J.-A. Recent Advances in the Total Synthesis of Cyclopropane-Containing Natural Products. *Chem. Soc. Rev.* **2012,** *41*, 4631-4642.

(26) Kulinkovich, O. G. The Chemistry of Cyclopropanols. *Chem. Rev.* **2003,** *103*, 2597-2632.

(27) Lee, J.; Kim, H.; Cha, J. K. A New Variant of the Kulinkovich Hydroxycyclopropanation. Reductive Coupling of Carboxylic Esters with Terminal Olefins. *J. Am. Chem. Soc.* **1996,** *118*, 4198-4199.

(28) Rubin, M.; Rubina, M.; Gevorgyan, V. Transition Metal Chemistry of Cyclopropenes and Cyclopropanes. *Chem. Rev.* **2007,** *107*, 3117-3179.

(29) Carson, C. A.; Kerr, M. A. Heterocycles from Cyclopropanes: Applications in Natural Product Synthesis. *Chem. Soc. Rev.* **2009,** *38*, 3051-3060.

(30) Epstein, O. L.; Lee, S.; Cha, J. K. Formation of Seven-Membered Carbocycles by the Use of Cyclopropyl Silyl Ethers as Homoenols. *Angew. Chem.* **2006,** *118*, 5110-5113.

(31) Hua, Y.; Asgari, P.; Avullala, T.; Jeon, J. Catalytic Reductive ortho-C–H Silylation of Phenols with Traceless, Versatile Acetal Directing Groups and Synthetic Applications of Dioxasilines. *J. Am. Chem. Soc.* **2016,** *138*, 7982–7991.

(32) Brook, A. G. Molecular Rearrangements of Organosilicon Compounds. *Acc. Chem. Res.* **1974,** *7*, 77-84.

(33) Gilman, H.; Lichtenwalter, G. D. The Syntheses and Some Reactions of α-Silylcarbinols. *J. Am. Chem. Soc.* **1958,** *80*, 2680-2682.

(34) Chénedé, A.; Rahman, N. A.; Fleming, I. Dehydration of α-Silylalcohols in the Reductive Conversion of Esters and Ketones into Alkenes. *Tetrahedron Lett.* **1997,** *38*, 2381-2382.

(35) Still, W. C. Conjugate Addition of Trimethysilyllithium. A Preparation of 3-Silyl Ketones. *J. Org. Chem.* **1976,** *41*, 3063-3064.

(36) Rousseaux, S.; Liégault, B.; Fagnou, K. Palladium (0)-Catalyzed Cyclopropane C–H Bond Functionalization: Synthesis of Quinoline and Tetrahydroquinoline Derivatives. *Chem. Sci.* **2012,** *3*, 244-248.

(37) Lee, T.; Hartwig, J. F. Rhodium-Catalyzed Enantioselective Silylation of Cyclopropyl C−H Bonds. *Angew. Chem. Int. Ed.* **2016,** *55*, 8723-8727.

(38) *e-EROS Encyclopedia of Reagents for Organic Synthesis*: Silver, [tris[3,5-bis(trifluoromethyl)-1*H*-pyrazolato-κ*N*1]hydroborato(1-)-κ*N*2, κ*N*2′, κ*N*2″]¯, DOI:10.1002/047084289X.rn00663.

(39) Dias, H. R.; Kim, H.-J.; Lu, H.-L.; Rajeshwar, K.; de Tacconi, N. R.; Derecskei-Kovacs, A.; Marynick, D. S. Investigation of the Electronic and Geometric Effects of Trifluoromethyl Substituents on Tris(pyrazolyl)borate Ligands Using Manganese(I) and Copper(I) Complexes. *Organometallics* **1996,** *15*, 2994-3003.

(40) Allinger, N. L.; Sprague, J. T. Conformational analysis. LXXXIV. Study of the Structures and Energies of Some Alkenes and Cycloalkenes by the Force Field Method. *J. Am. Chem. Soc.* **1972,** *94*, 5734-5747.

(41) Del Ministro, E.; Renn, O.; Rüegger, H.; Venanzi, L. M.; Burckhardt, U.; Gramlich, V. Rhodium (I) Complexes of the Type [$Tp^{3R,5R}$Rh(LL)] (LL= 2CO, NBD, COD) with Trifluoromethyl Substituted Tris(pyrazolyl)borate Ligands and Their Dynamic Behaviour in Solution. The X-Ray Crystal Structure of $Tp^{CF3,Me}Rh(CO)_2$. *Inorg. Chim. Acta* **1995,** *240*, 631-639.

(42) Tamaki, T.; Ohashi, M.; Ogoshi, S. [3+ 2] Cycloaddition Reaction of Cyclopropyl Ketones with Alkynes Catalyzed by Nickel/Dimethylaluminum Chloride. *Angew. Chem. Int. Ed.* **2011,** *50*, 12067-12070.

(43) Halpern, J. Determination and Significance of Transition Metal-Alkyl Bond Dissociation Energies. *Acc. Chem. Res.* **1982,** *15*, 238-244.

(44) Frauenrath, H. Vinyl Acetals and Related Compounds in Organic Synthesis. *Synthesis* **1989**, 721-734.

(45) Nasveschuk, C. G.; Jui, N. T.; Rovis, T. A Modular Approach to the Synthesis of 2,3,4-Trisubstituted Tetrahydrofurans. *Chem. Commun.* **2006**, 3119-3121.

(46) Karmel, C.; Li, B.-J.; Hartwig, J. F. Rhodium-Catalyzed Regioselective Silylation of C–H Bonds for the Synthesis of 1, 4-Diols. *J. Am. Chem. Soc.* **2018,** *140*, 1460-1470.

(47) Cheng, C.; Hartwig, J. F. Mechanism of the Rhodium-Catalyzed Silylation of Arene C–H Bonds. *J. Am. Chem. Soc.* **2014,** *136*, 12064-12072.

(48) Ezbiansky, K.; Djurovich, P. I.; LaForest, M.; Sinning, D. J.; Zayes, R.; Berry, D. H. Catalytic C−H Bond Functionalization: Synthesis of Arylsilanes by Dehydrogenative

Transfer Coupling of Arenes and Triethylsilane. *Organometallics* **1998,** *17*, 1455-1457.

(49) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B.; Kotz, K.; Yeston, J.; Wilkens, M.; Frei, H.; Bergman, R. G. The Mechanism of a CH Bond Activation Reaction in Room-Temperature Alkane Solution. *Science* **1997,** *278*, 260-263.

(50) Chen, D. Y.-K.; Pouwer, R. H.; Richard, J.-A. Recent advances in the total synthesis of cyclopropane-containing natural products. *Chem. Soc. Rev.* **2012,** *41*, 4631-4642.

(51) Kulinkovich, O. G. The Chemistry of Cyclopropanols. *Chem. Rev.* **2003,** *103*, 2597-2632.

(52) Lee, J.; Kim, H.; Cha, J. K. A New Variant of the Kulinkovich Hydroxycyclopropanation. Reductive Coupling of Carboxylic Esters with Terminal Olefins. *J. Am. Chem. Soc.* **1996,** *118*, 4198-4199.

(53) Rubin, M.; Rubina, M.; Gevorgyan, V. Transition Metal Chemistry of Cyclopropenes and Cyclopropanes. *Chem. Rev.* **2007,** *107*, 3117-3179.

(54) Carson, C. A.; Kerr, M. A. Heterocycles from cyclopropanes: applications in natural product synthesis. *Chem. Soc. Rev.* **2009,** *38*, 3051-3060.

(55) Crabtree, R. H. The organometallic chemistry of alkanes. *Chem. Rev.* **1985,** *85*, 245-269.

(56) Jones, W. D. The fall of the C-C bond. *Nature* **1993,** *364*, 676-677.

(57) Murakami, M.; Amii, H.; Ito, Y. Selective activation of carbon–carbon bonds next to a carbonyl group. *Nature* **1994,** *370*, 540-541.

(58) Rybtchinski, B.; Milstein, D. Metal Insertion into C−C Bonds in Solution. *Angew. Chem. Int. Ed.* **1999,** *38*, **870–883**.

(59) Murakami, M.; Ito, Y. Cleavage of Carbon—Carbon Single Bonds by Transition Metals. *Top. Organomet. Chem.* **1999,** *3*, 97-129.

(60) Jun, C.-H.; Lee, H. Catalytic carbon− carbon bond activation of unstrained ketone by soluble transition-metal complex. *J. Am. Chem. Soc.* **1999,** *121*, 880-881.

(61) Xia, Y.; Lu, G.; Liu, P.; Dong, G. Catalytic activation of carbon–carbon bonds in cyclopentanones. *Nature* **2016,** *539*, 546-550.

(62) Jun, C. Transition metal-catalyzed carbon-carbon bond activation. *Chem. Soc. Rev.* **2004,** *33*, 610-8.

(63) Murakami, M.; Matsuda, T. Metal-catalysed cleavage of carbon-carbon bonds. *Chem. Commun.* **2011,** *47*, 1100-1105.

(64) Seiser, T.; Saget, T.; Tran, D. N.; Cramer, N. Cyclobutanes in Catalysis. *Angew. Chem. Int. Ed.* **2011,** *50*, 7740-7752.

(65) Souillart, L.; Cramer, N. Catalytic C–C Bond Activations via Oxidative Addition to Transition Metals. *Chem. Rev.* **2015,** *115*, 9410-9464.

(66) Fumagalli, G.; Stanton, S.; Bower, J. F. Recent methodologies that exploit C–C single-bond cleavage of strained ring systems by transition metal complexes. *Chem. Rev.* **2017,** *117*, 9404-9432.

(67) *C-C Bond Activation*. Springer: 2016; Vol. 346.

(68) Wang, G.-W.; Bower, J. F. Modular Access to Azepines by Directed Carbonylative C–C Bond Activation of Aminocyclopropanes. *J. Am. Chem. Soc.* **2018,** *140*, 2743-2747.

(69) Shaw, M. H.; Melikhova, E. Y.; Kloer, D. P.; Whittingham, W. G.; Bower, J. F. Directing Group Enhanced Carbonylative Ring Expansions of Amino-Substituted Cyclopropanes: Rhodium-Catalyzed Multicomponent Synthesis of N-Heterobicyclic Enones. *Journal of the American Chemical Society* **2013,** *135*, 4992-4995.

(70) Li, H.; Li, Y.; Zhang, X.; Chen, K.; Wang, X.; Shi, Z. Pyridinyl directed alkenylation with olefins via Rh(III)-catalyzed C-C bond cleavage of secondary arylmethanols. *J. Am. Chem. Soc.* **2011,** *133*, 15244-7.

(71) Zeng, R.; Dong, G. Rh-Catalyzed decarbonylative coupling with alkynes via C-C activation of isatins. *J. Am. Chem. Soc.* **2015,** *137*, 1408-11.

(72) Li, B.; Wang, Y.; Jin, Z.; Zheng, P.; Ganguly, R.; Chi, Y. Carbon-carbon bond activation of cyclobutenones enabled by the addition of chiral organocatalyst to ketone. *Nat Commun.* **2015,** *6*, 6207.

(73) Xia, Y.; Wang, J.; Dong, G. Distal-Bond-Selective C−C Activation of Ring-Fused Cyclopentanones: An Efficient Access to Spiroindanones. *Angew. Chem. Int. Ed.* **2017,** *56*, 2376-2380.

(74) Epstein, O. L.; Lee, S.; Cha, J. K. Formation of Seven-Membered Carbocycles by the Use of Cyclopropyl Silyl Ethers as Homoenols. *Angew. Chem.* **2006,** *118*, 5110-5113.

(75) Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino, H.; Kuwajima, I. Carbon-carbon bond-forming reactions of zinc homoenolate of esters. A novel three-carbon nucleophile with general synthetic utility. *J. Am. Chem. Soc.* **1987,** *109*, 8056-8066.

(76) Seebach, D. Methods of Reactivity Umpolung. *Angewandte Chemie International Edition in English* **1979,** *18*, 239-258.

(77) Evans, D. A.; Andrews, G. C. Allylic sulfoxides. Useful intermediates in organic synthesis. *Acc. Chem. Res.* **1974,** *7*, 147-155.

(78) Werstiuk, N. H. Homoenolate anions and homoenolate anion equivalents: Mechanistic aspects and synthetic applications. *Tetrahedron* **1983,** *39*, 205-268.

(79) Kuwajima, I.; Nakamura, E. In *Metal homoenolates from siloxycyclopropanes*, Berlin, Heidelberg, Springer Berlin Heidelberg: Berlin, Heidelberg, 1990; pp 1-39.

(80) Nithiy, N.; Orellana, A. Palladium-Catalyzed Cross-Coupling of Benzyl Chlorides with Cyclopropanol-Derived Ketone Homoenolates. *Org. Lett.* **2014,** *16*, 5854-5857.

(81) Li, Y.; Ye, Z.; Bellman, T. M.; Chi, T.; Dai, M. Efficient Synthesis of β-CF3/SCF3-Substituted Carbonyls via Copper-Catalyzed Electrophilic Ring-Opening Cross-Coupling of Cyclopropanols. *Org. Lett.* **2015,** *17*, 2186-2189.

(82) Ye, Z.; Dai, M. An Umpolung Strategy for the Synthesis of β-Aminoketones via Copper-Catalyzed Electrophilic Amination of Cyclopropanols. *Org. Lett.* **2015,** *17*, 2190-2193.

(83) Ryu, I.; Nakahira, H.; Ikebe, M.; Sonoda, N.; Yamato, S.-y.; Komatsu, M. Chelation-Aided Generation of Ketone α,β-Dianions and Their Use as Copper Ate Complexes. Unprecedented Enolate Intervention in the Conjugate Addition to Enones. *J. Am. Chem. Soc.* **2000,** *122*, 1219-1220.

(84) Nakahira, H.; Ryu, I.; Ikrbe, M.; Kambe, N.; Sonoda, N. β-Lithio Ketone Enolates: Generation and Reactions with Electrophiles. *Angewandte Chemie International Edition in English* **1991,** *30*, 177-179.

(85) Hoppe, D. The Homoaldol Reaction, or How to Overcome Problems of Regio- and Stereo-selectivity. *Angewandte Chemie International Edition in English* **1984,** *23*, 932-948.

(86) Ogoshi, S.; Tomiyasu, S.; Morita, M.; Kurosawa, H. Palladium/Me3SiOTf-Catalyzed Bis-silylation of α,β-Unsaturated Carbonyl Compounds without Involving Oxidative Addition of Disilane. *J. Am. Chem. Soc.* **2002,** *124*, 11598-11599.

(87) Nakao, Y.; Hiyama, T. Silicon-based cross-coupling reaction: an environmentally benign version. *Chemical Society Reviews* **2011,** *40*, 4893-4901.

(88) Ramesh, R.; Reddy, D. S. Quest for Novel Chemical Entities through Incorporation of Silicon in Drug Scaffolds. *J. Med. Chem.* **2017**.

(89) Ishida, N.; Ikemoto, W.; Murakami, M. Intramolecular σ-Bond Metathesis Between Carbon–Carbon and Silicon–Silicon Bonds. *Org. Lett.* **2012,** *14*, 3230-3232.

(90) Ishida, N.; Ikemoto, W.; Murakami, M. Cleavage of C-C and C-Si σ-bonds and their intramolecular exchange. *J. Am. Chem. Soc.* **2014,** *136*, 5912-5.

(91) Okumura, S.; Sun, F.; Ishida, N.; Murakami, M. Palladium-Catalyzed Intermolecular Exchange between C–C and C–Si σ-Bonds. *J. Am. Chem. Soc.* **2017,** *139*, 12414-12417.

(92) Avullala, T.; Asgari, P.; Hua, Y.; Bokka, A.; Ridlen, S. G.; Yum, K.; Dias, H. V. R.; Jeon, J. Umpolung α-Silylation of Cyclopropyl Acetates via Low-Temperature Catalytic C–C Activation. *ACS Catal.* **2019,** *9*, 402-408.

(93) Halpern, J. Determination and significance of transition metal-alkyl bond dissociation energies. *Acc. Chem. Res.* **1982,** *15*, 238-244.

(94) Dias, H. V. R. Silver,[tris [3, 5-bis (trifluoromethyl)-1H-pyrazolato-κN1] hydroborate (1-)-κN2, κN2′, κN2 ″]−. *e-EROS Encycl. Reagents Org. Synth* **2006**, 1-3.

(95) Dias, H. R.; Kim, H.-J.; Lu, H.-L.; Rajeshwar, K.; de Tacconi, N. R.; Derecskei-Kovacs, A.; Marynick, D. S. Investigation of the electronic and geometric effects of trifluoromethyl substituents on tris (pyrazolyl) borate ligands using manganese (I) and copper (I) complexes. *Organometallics* **1996,** *15*, 2994-3003.

(96) Ezbiansky, K.; Djurovich, P. I.; LaForest, M.; Sinning, D. J.; Zayes, R.; Berry, D. H. Catalytic C− H bond functionalization: Synthesis of arylsilanes by dehydrogenative transfer coupling of arenes and triethylsilane. *Organometallics* **1998,** *17*, 1455-1457.

(97) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B.; Kotz, K.; Yeston, J.; Wilkens, M.; Frei, H.; Bergman, R. G. The mechanism of a CH bond activation reaction in room-temperature alkane solution. *Science* **1997,** *278*, 260-263.

(98) Karmel, C.; Li, B.-J.; Hartwig, J. F. Rhodium-Catalyzed Regioselective Silylation of Alkyl C–H Bonds for the Synthesis of 1, 4-Diols. *J. Am. Chem. Soc.* **2018,** *140*, 1460-1470.

(99) Bokka, A.; Hua, Y.; Berlin, A. S.; Jeon, J. Mechanistic Insights into Grubbs-Type Ruthenium-Complex-Catalyzed Intramolecular Alkene Hydrosilylation: Direct –Bond Metathesis in the Initial Stage of Hydrosilylation. *ACS Catal.* **2015,** *5*, 3189-3195.

(100) Hua, Y.; Asgari, P.; Avullala, T.; Jeon, J. Catalytic Reductive ortho-C–H Silylation of Phenols with Traceless, Versatile Acetal Directing Groups and Synthetic Applications of Dioxasilines. *J. Am. Chem. Soc.* **2016,** *138*, 7982–7991.

(101) Hua, Y.; Asgari, P.; Dakarapu, U. S.; Jeon, J. Reductive arene ortho-silanolization of aromatic esters with hydridosilyl acetals. *Chem. Commun.* **2015,** *51*, 3778-3781.

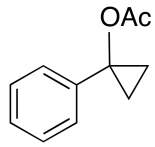
(102) Frauenrath, H. Vinyl acetals and related compounds in organic synthesis. *Synthesis* **1989**, 721-734.

(103) Nasveschuk, C. G.; Jui, N. T.; Rovis, T. A modular approach to the synthesis of 2, 3, 4-trisubstituted tetrahydrofurans. *Chem. Commun.* **2006**, 3119-3121.

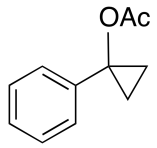
(104) Tornoe, C.; Christennsen, C.; Meldal, M.; Rostovtsev, V.; Green, L.; Fokin, V.; Sharpless, K. A stepwise Huisgen cycloaddition process: Copper (I)-catalyzed regioselective "ligation" of azides and terminal alkynes. *J. Org. Chem.* **2002,** *67*, 3057-3064.

(105) Tornøe, C. W.; Christensen, C.; Meldal, M. Peptidotriazoles on solid phase:[1, 2, 3]-triazoles by regiospecific copper (I)-catalyzed 1, 3-dipolar cycloadditions of terminal alkynes to azides. *The Journal of organic chemistry* **2002,** *67*, 3057-3064.

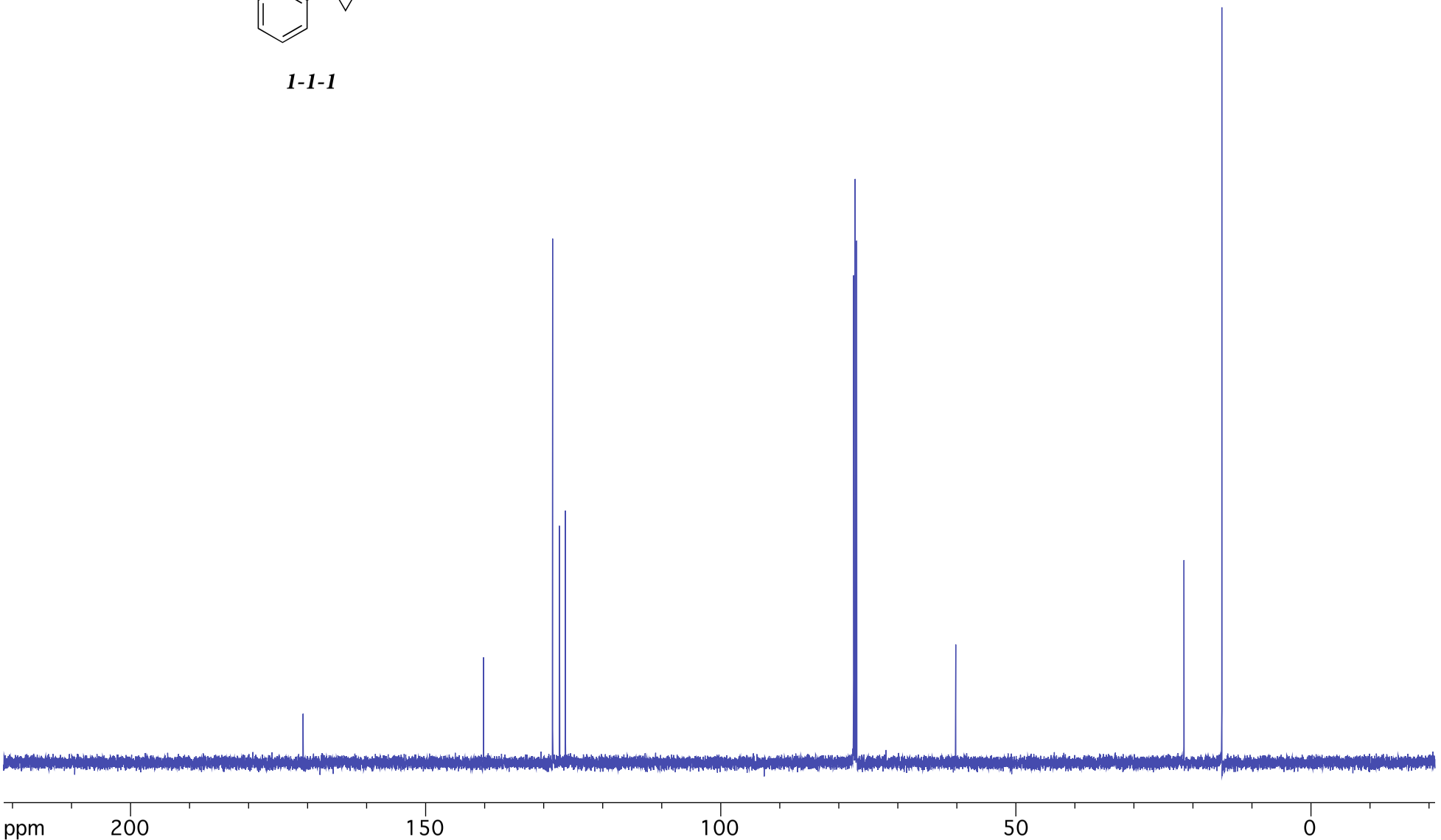
(106) Presolski, S. I.; Hong, V. P.; Finn, M. Copper-Catalyzed Azide–Alkyne Click for Bioconjugation. *Curr. Protoc. Chem. Biol.* **2011**, 153-162.

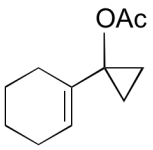


1-1-1

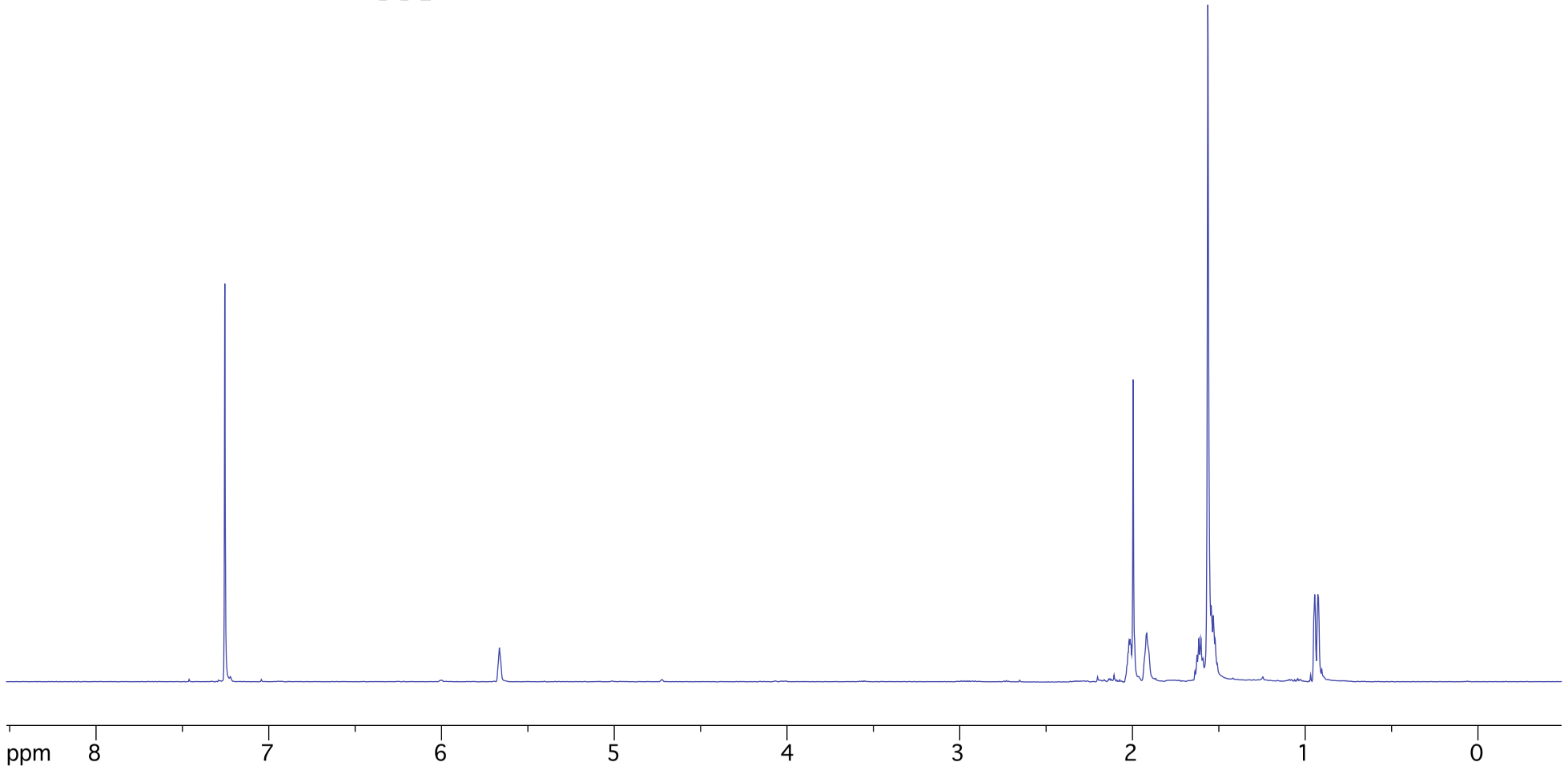


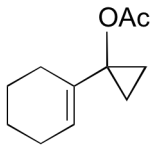
1-1-1



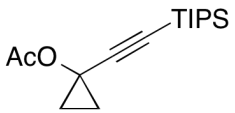


1-1-2

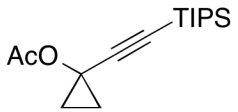




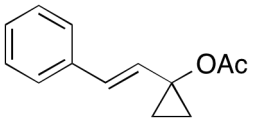
1-1-2



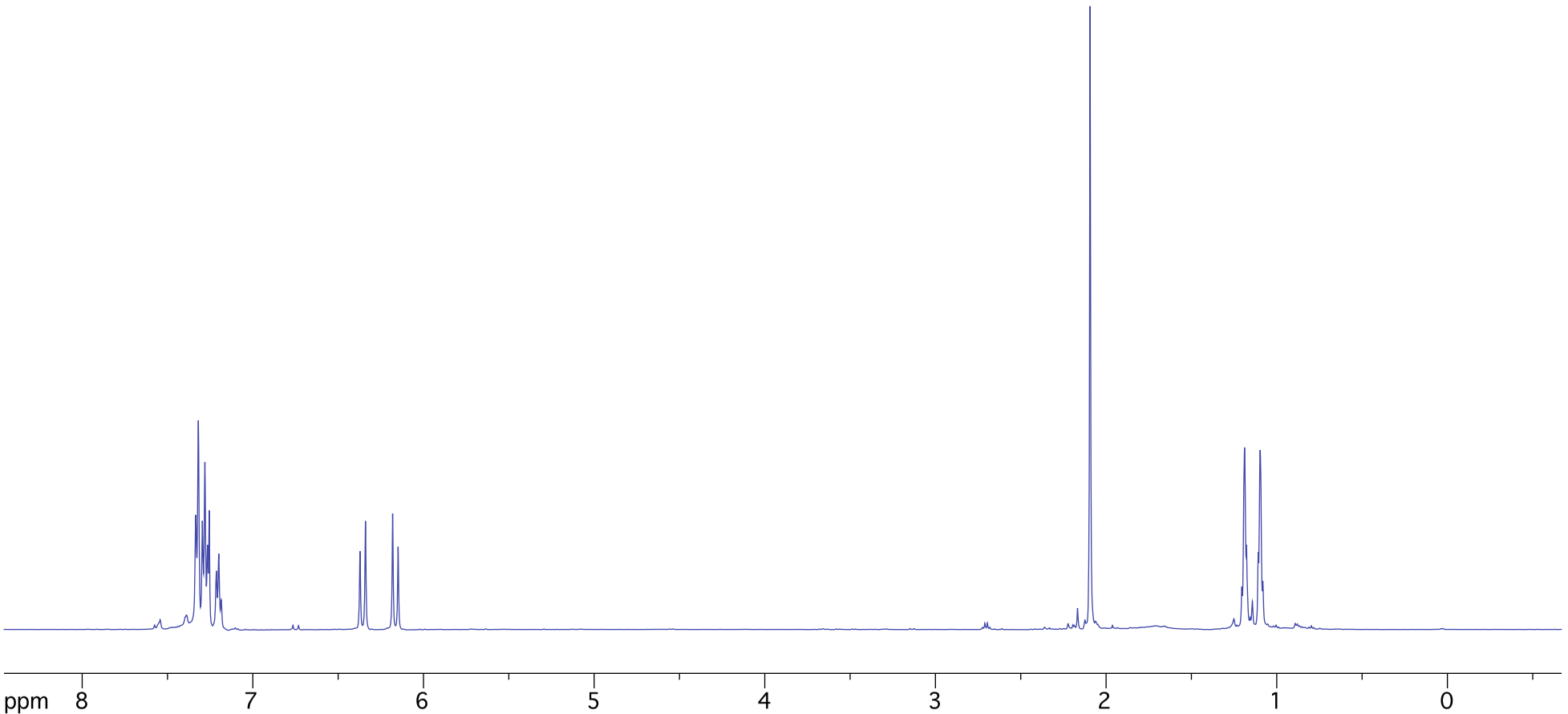
1-1-3

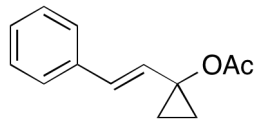


1-1-3

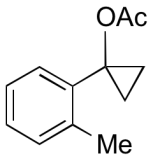


1-1-4

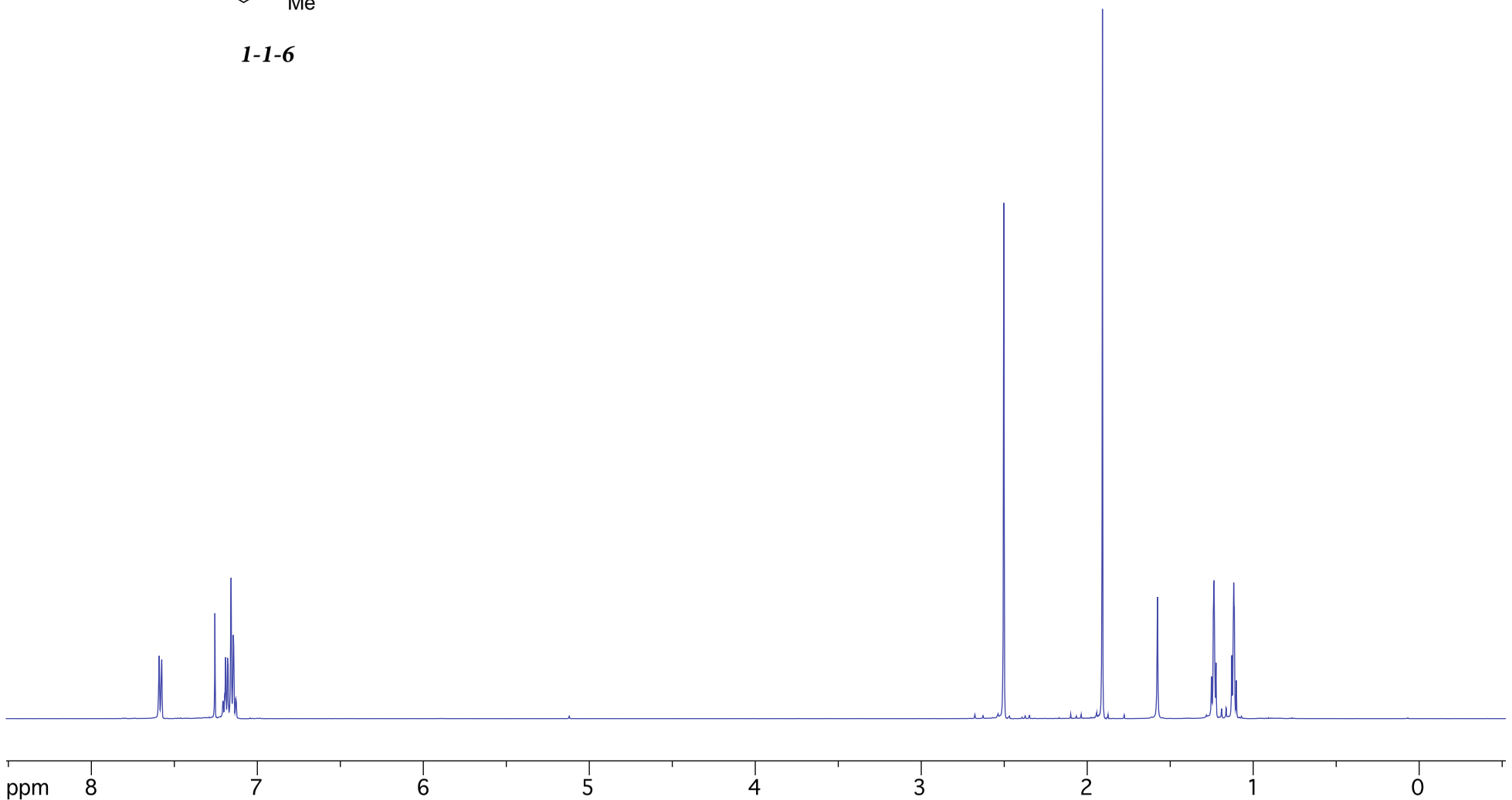


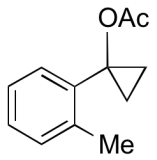


1-1-4

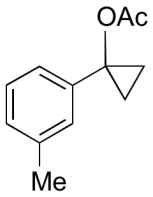


1-1-6

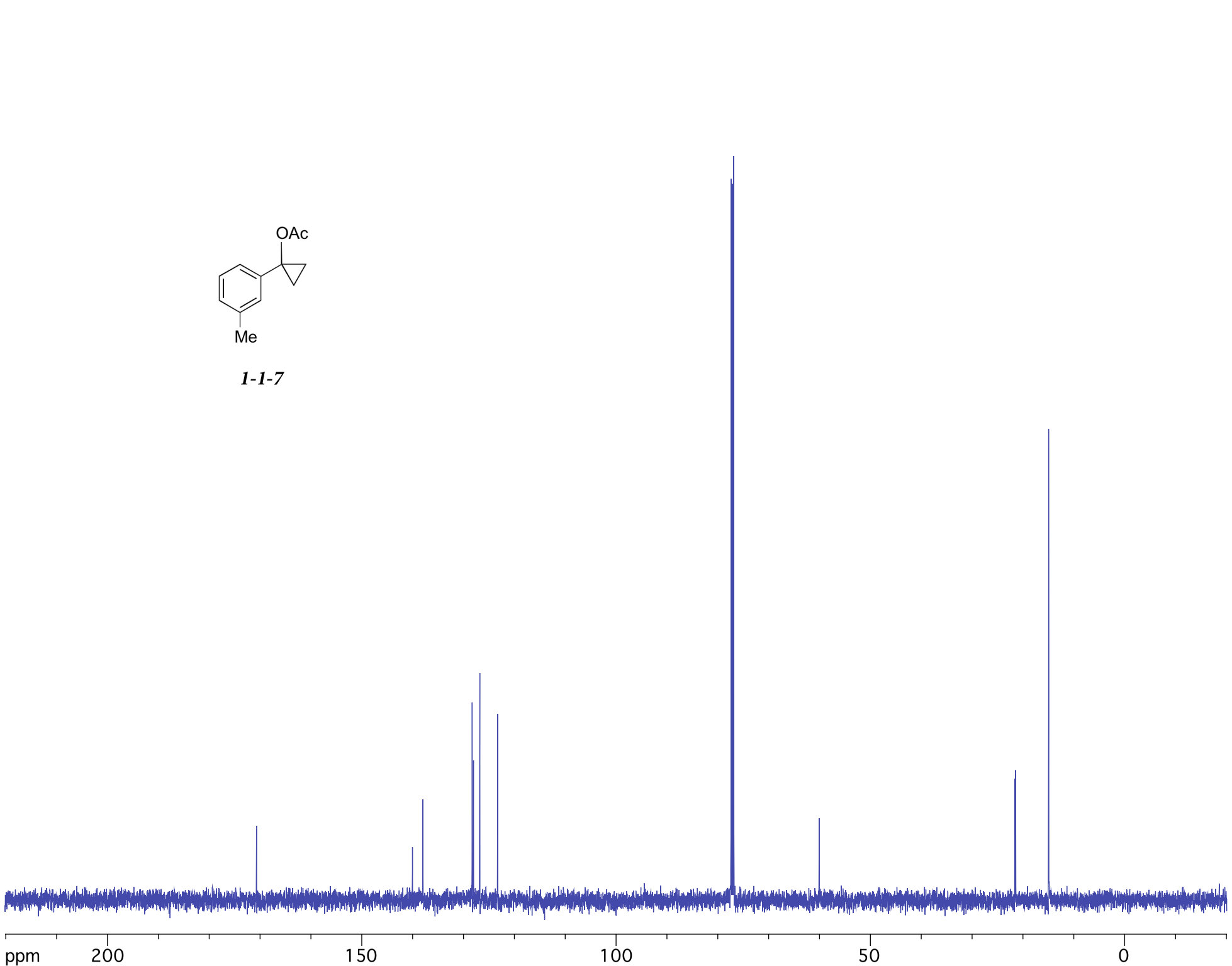




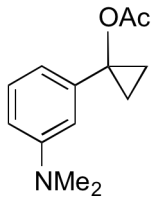
1-1-6



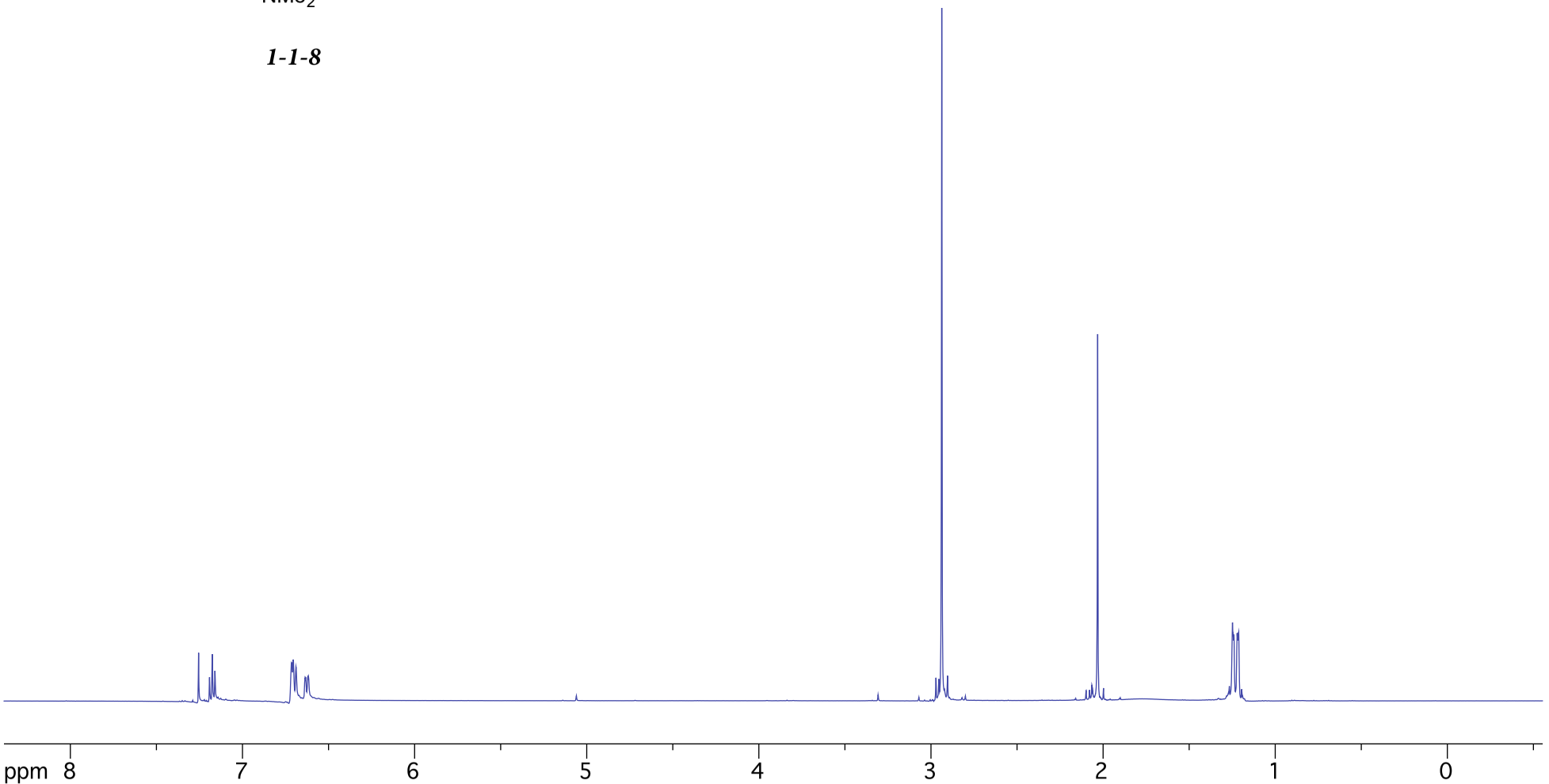
1-1-7

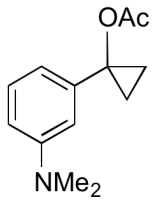


1-1-7

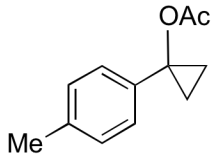


1-1-8

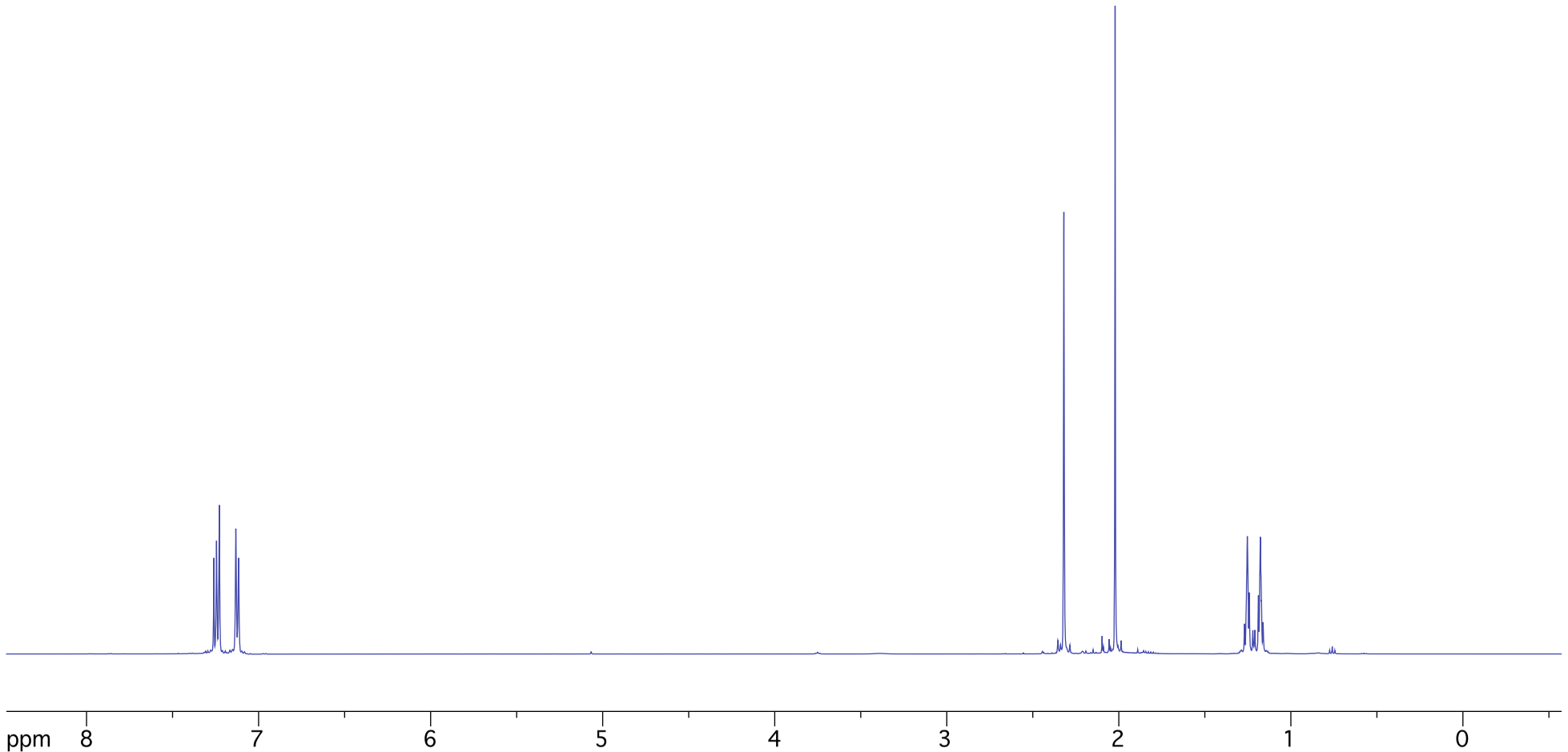


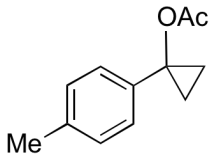


1-1-8

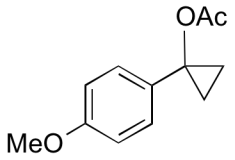


1-1-9

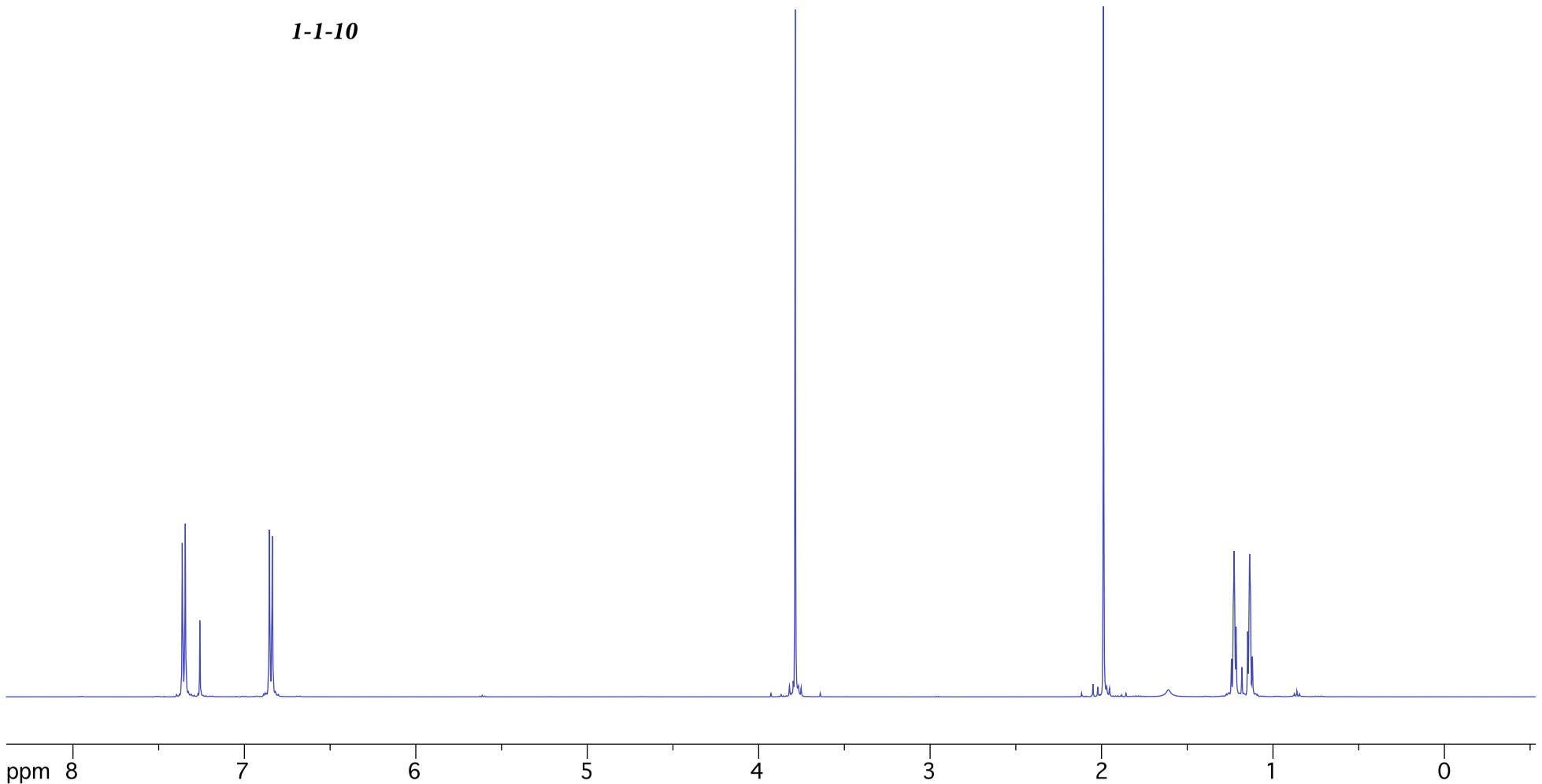


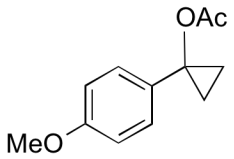


1-1-9

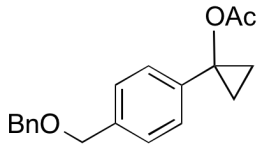


1-1-10

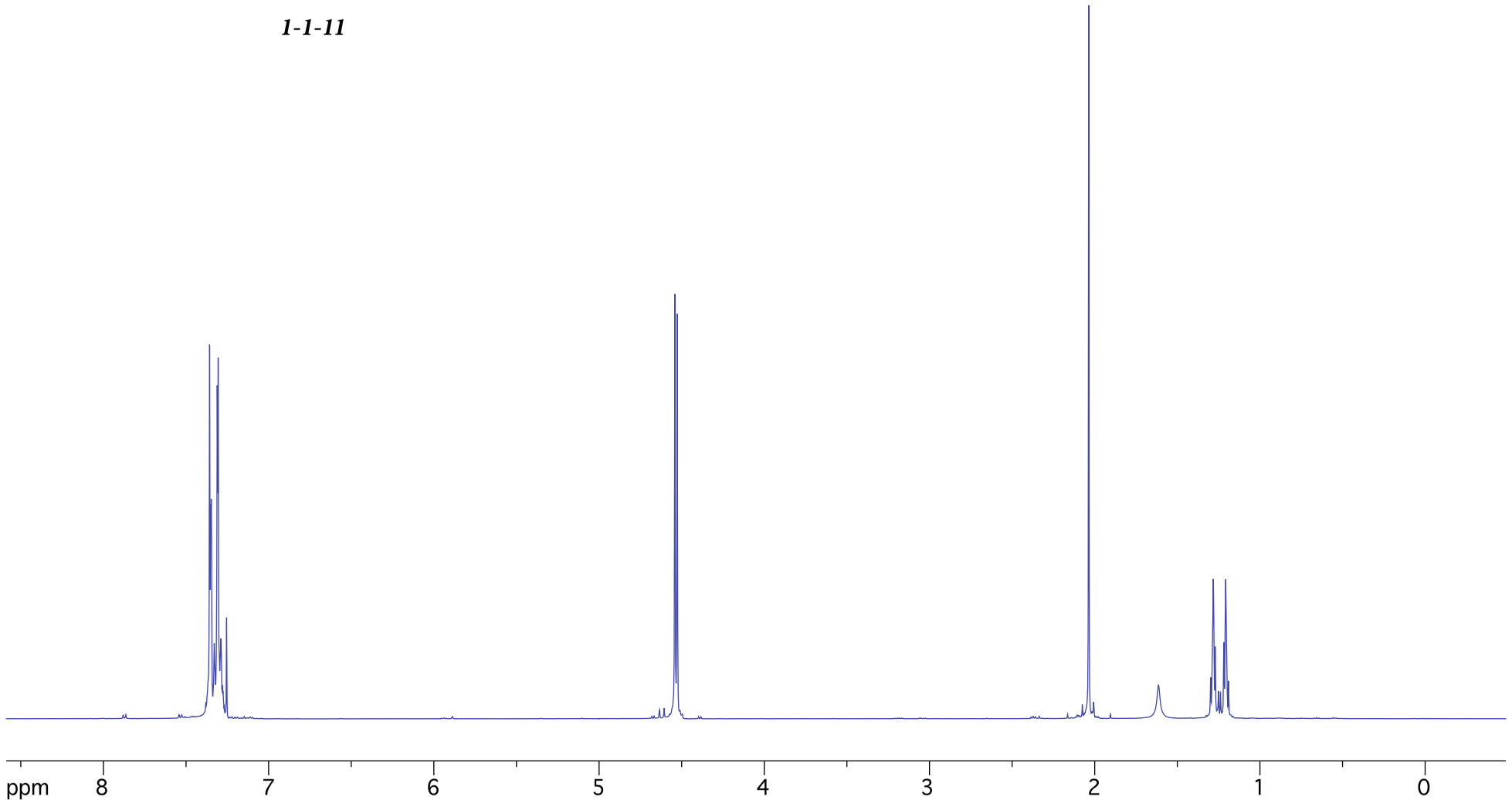


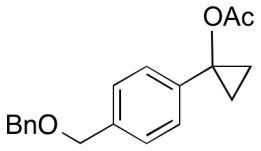


1-1-10

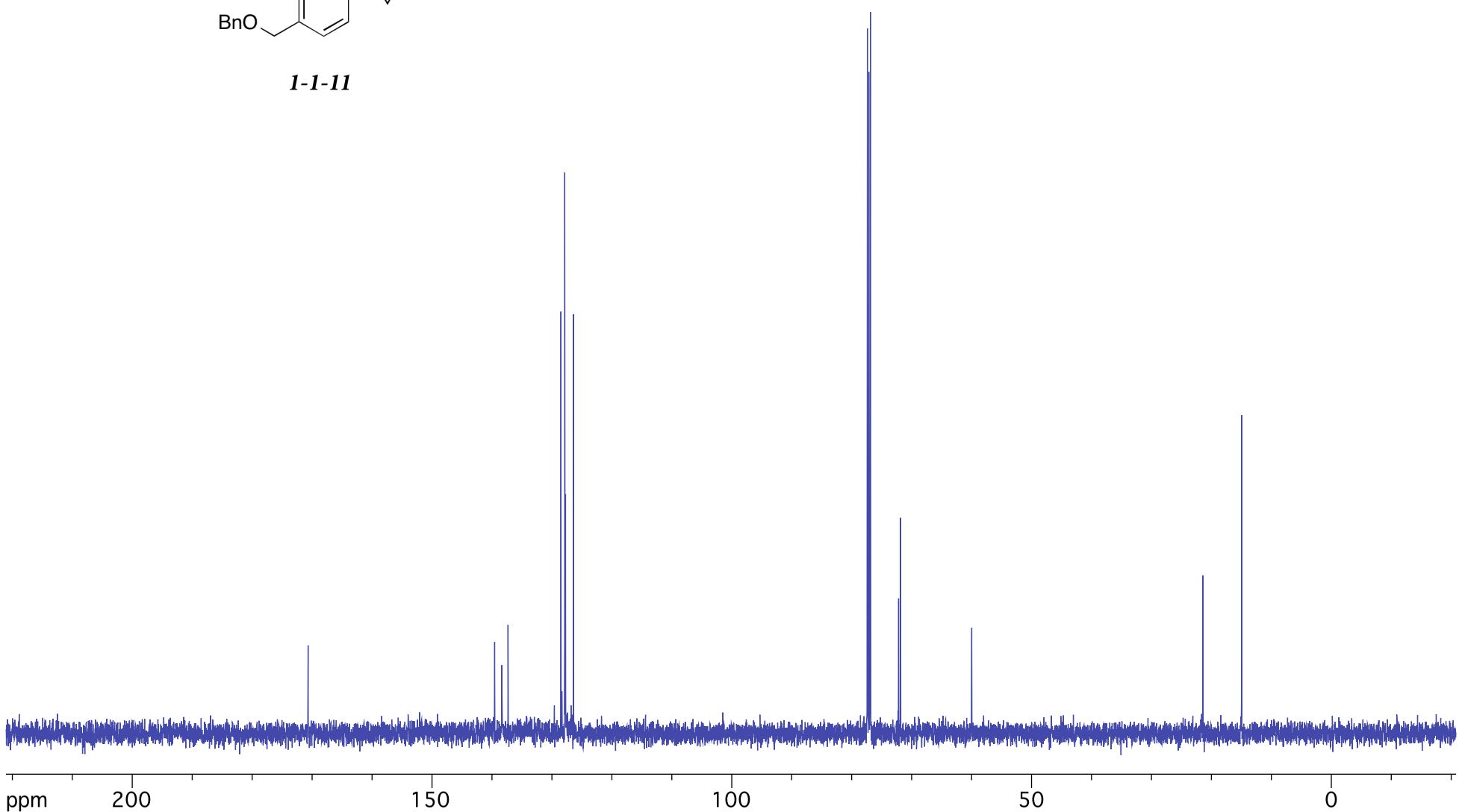


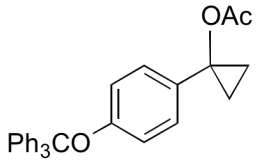
1-1-11



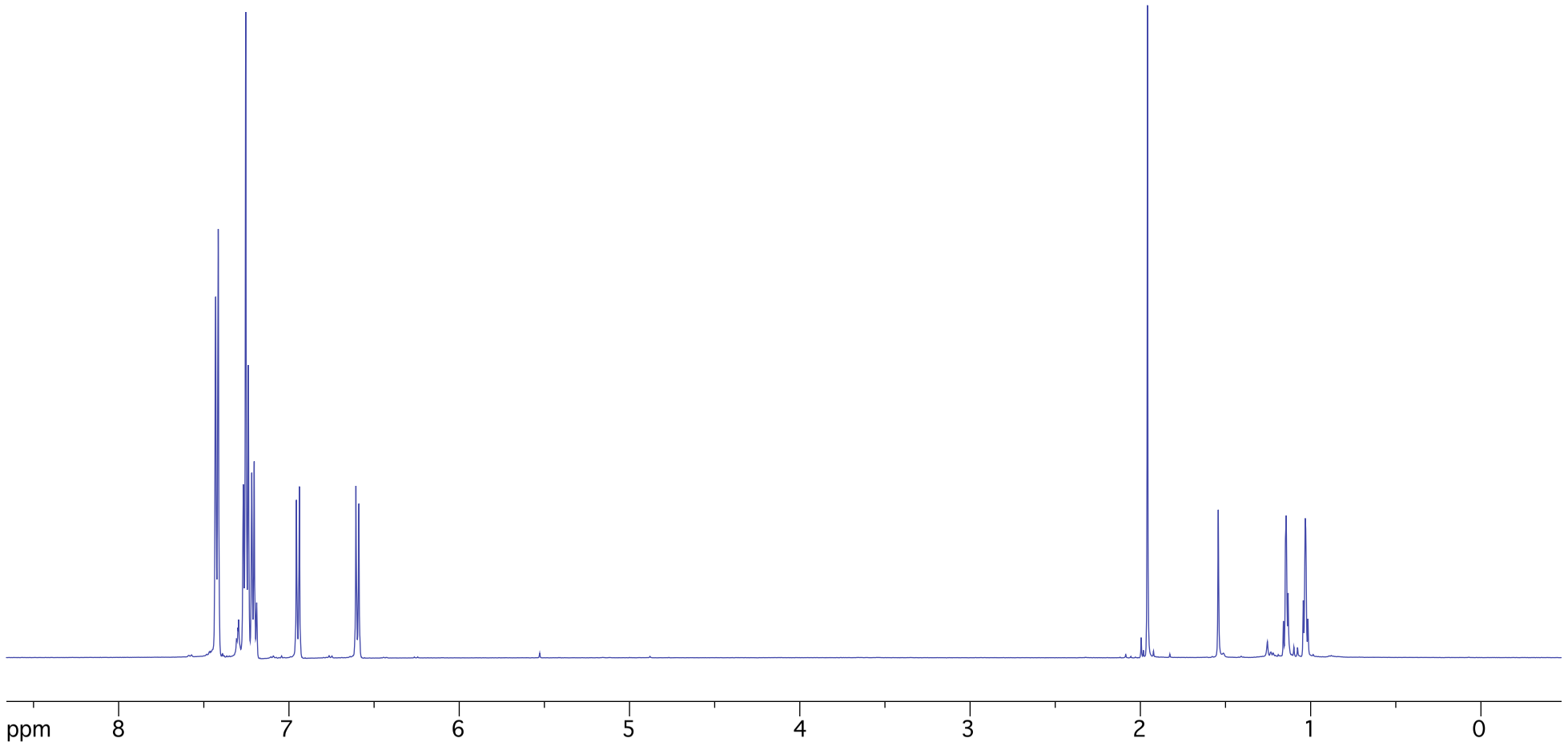


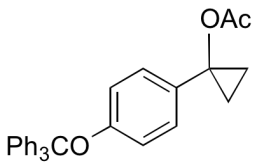
1-1-11



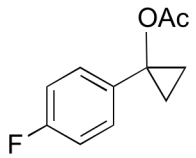


1-1-12

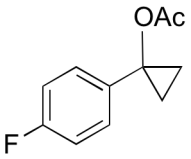




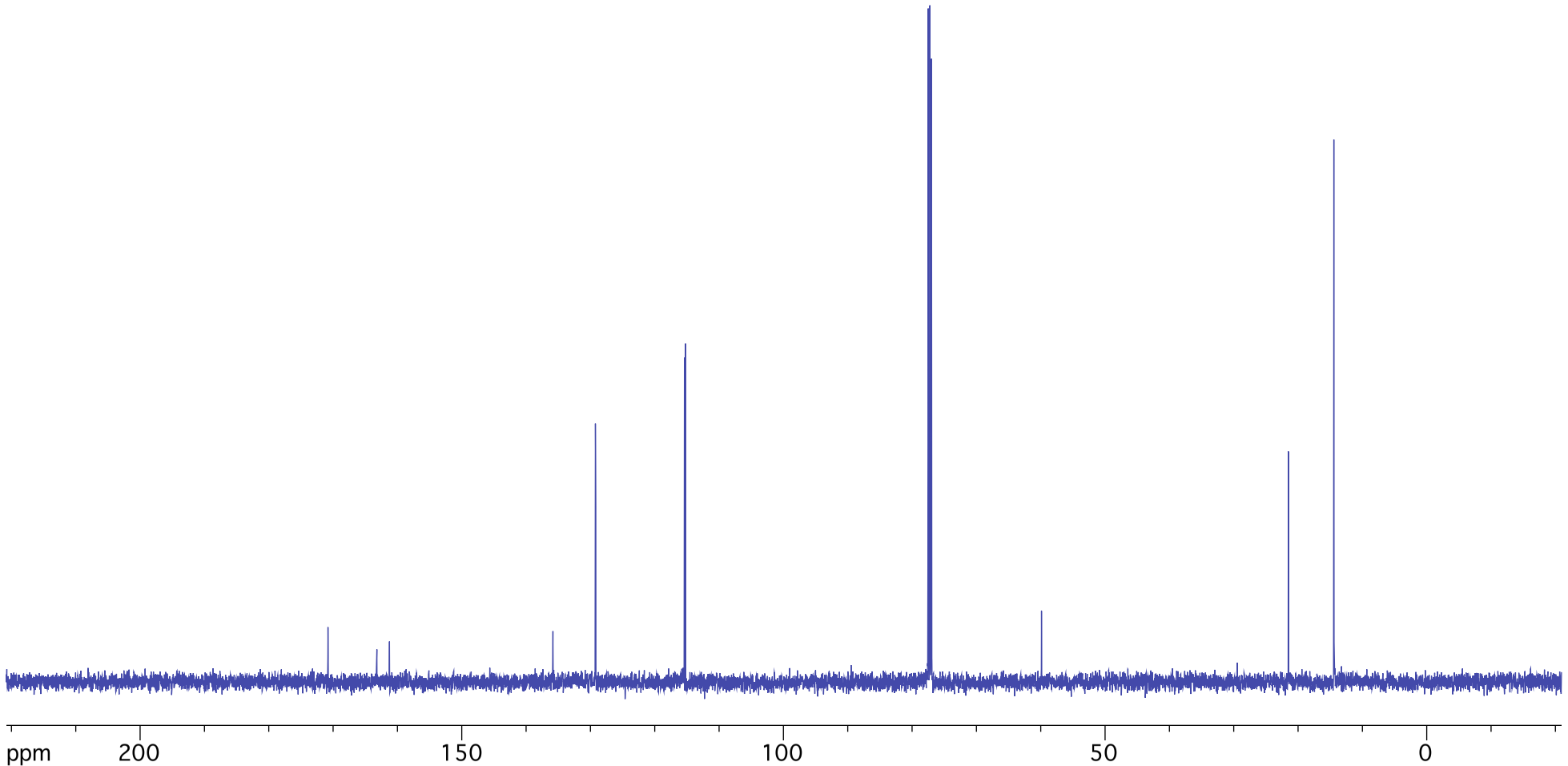
1-1-12

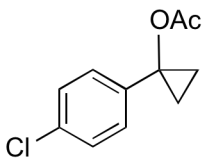


1-1-14

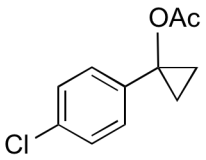


1-1-14

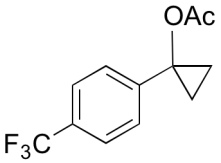




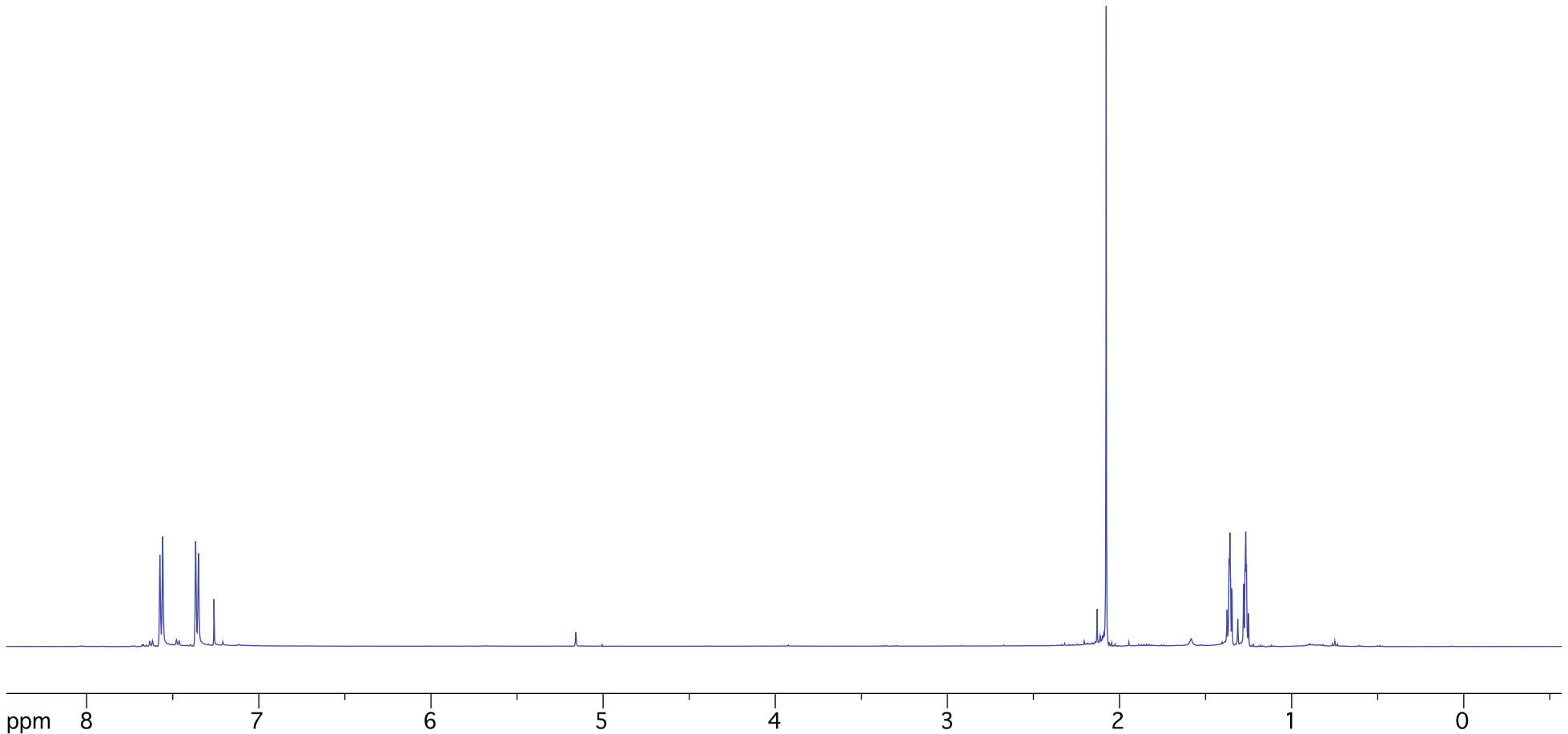
1-1-13

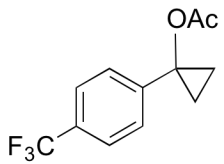


1-1-13

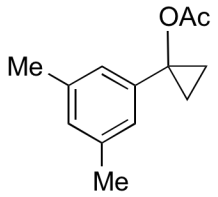


1-1-15

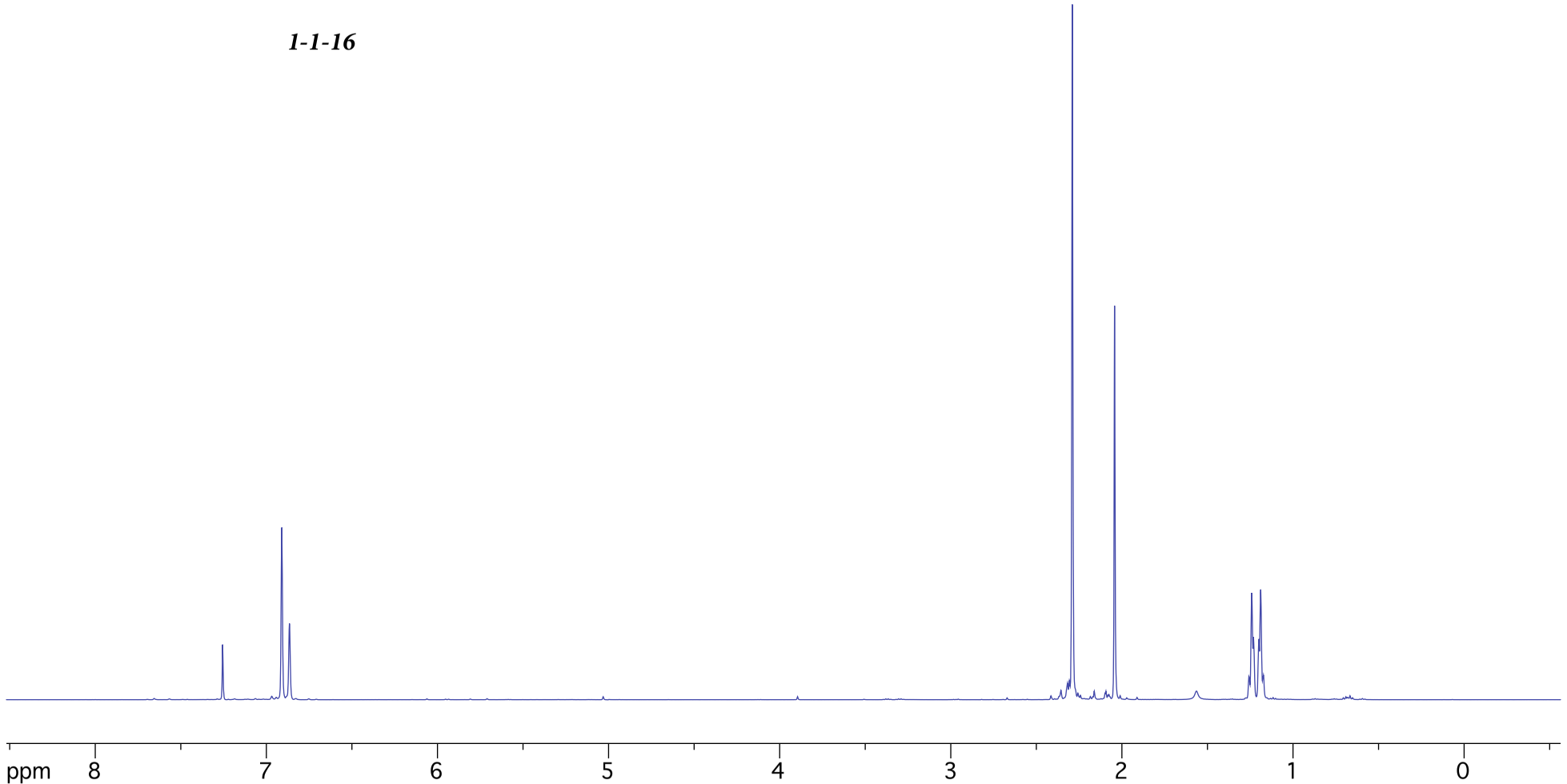


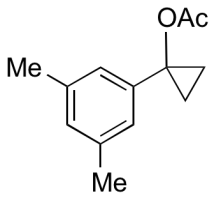


1-1-15

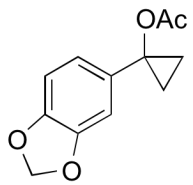


1-1-16

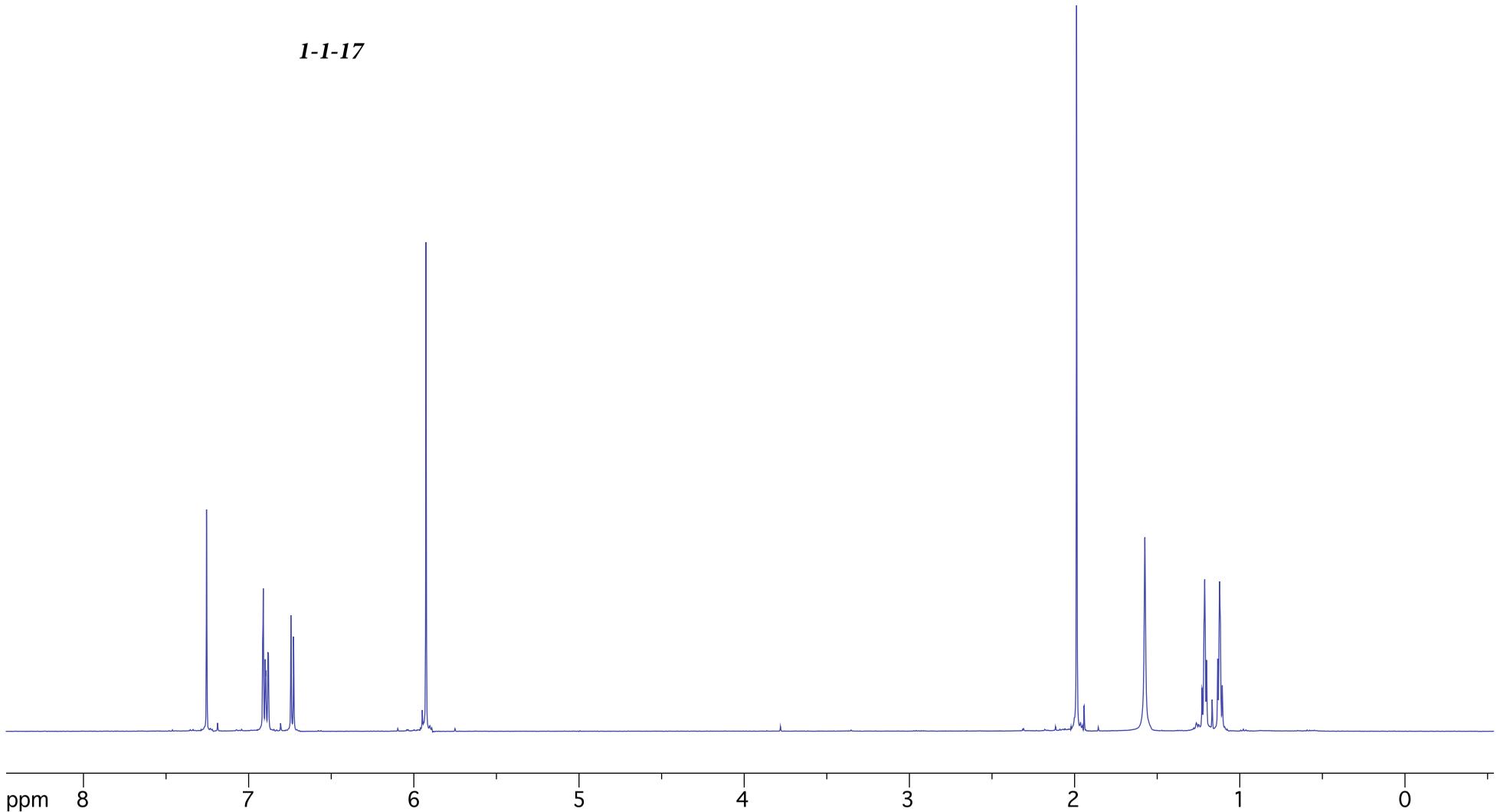


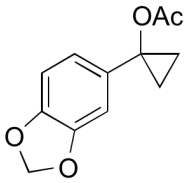


1-1-16

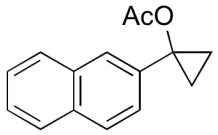


1-1-17

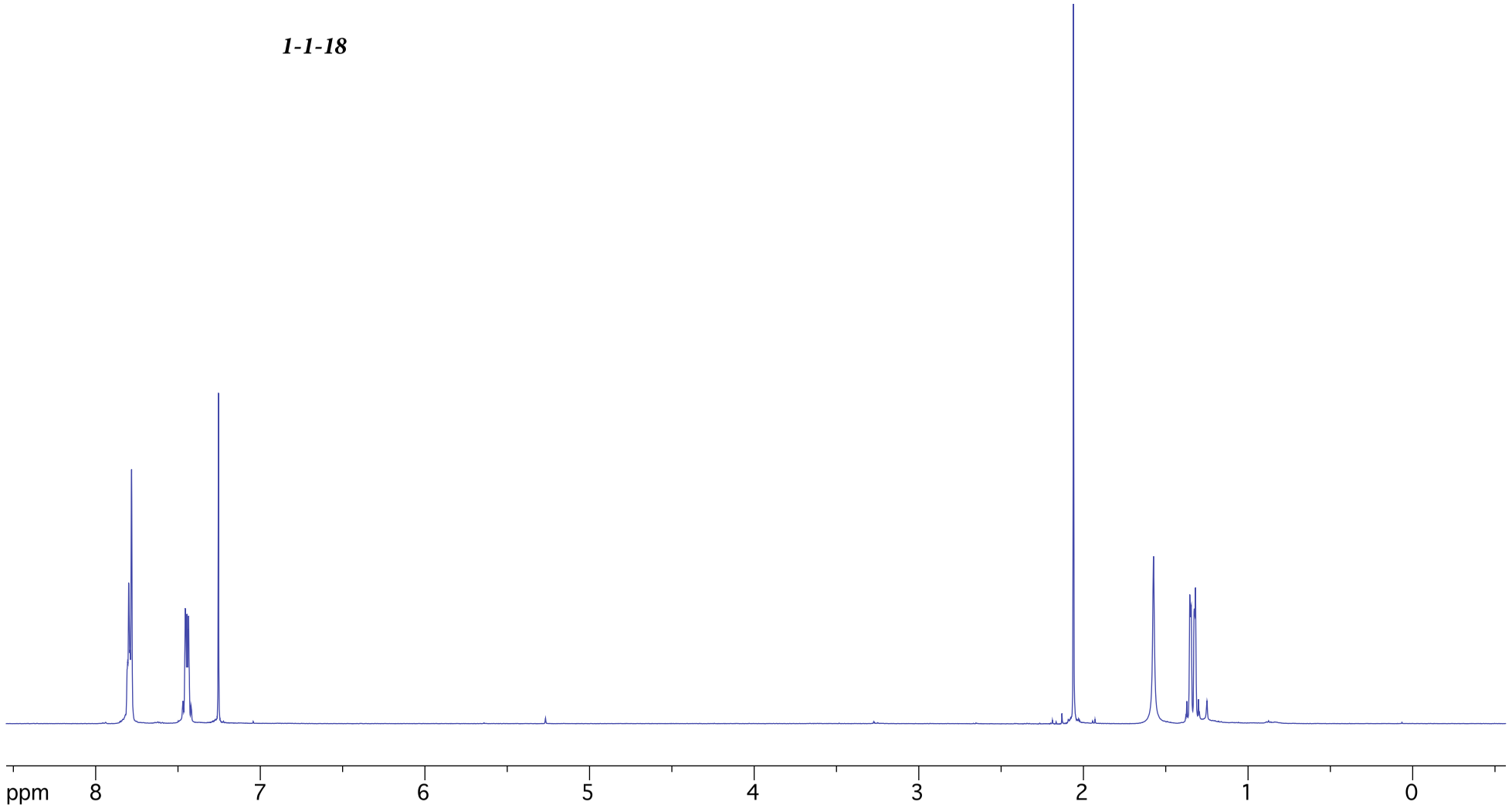


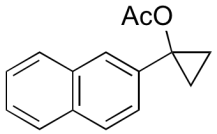


1-1-17

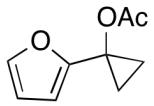


1-1-18

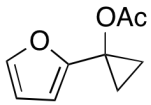




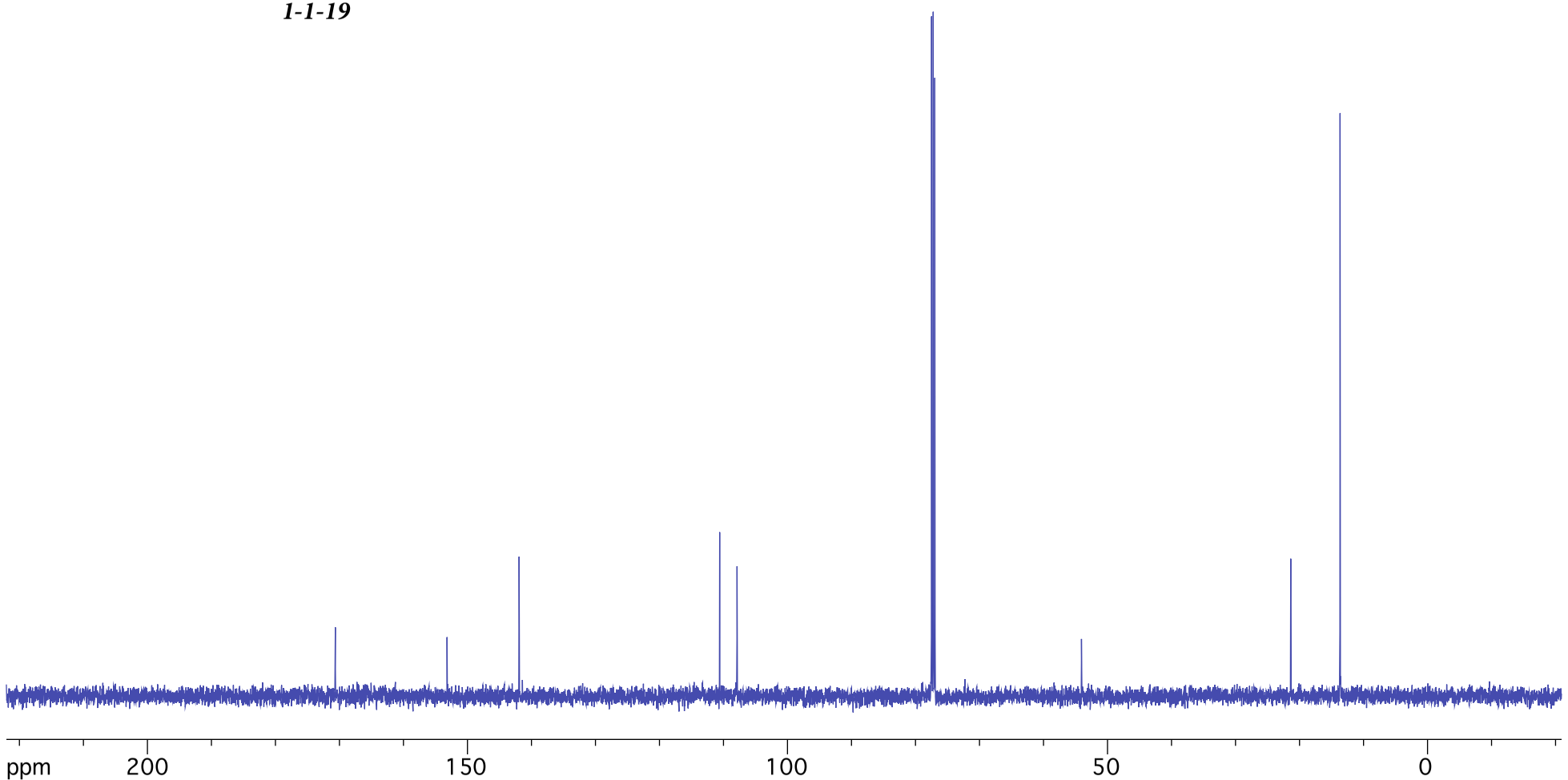
1-1-18

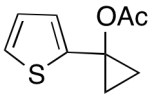


1-1-19

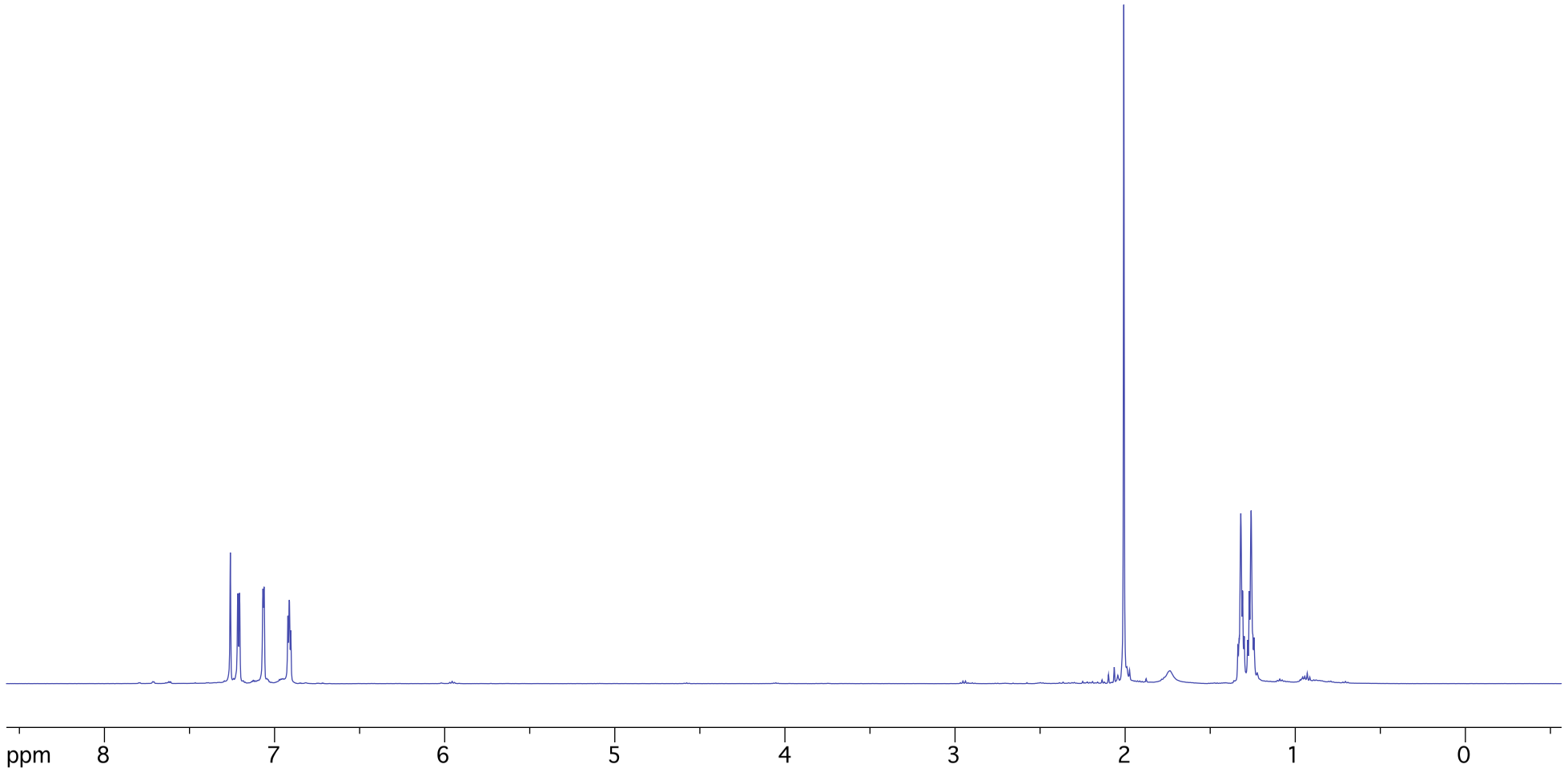


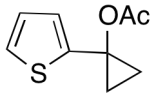
1-1-19



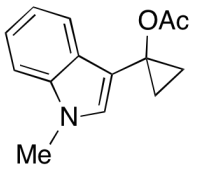


1-1-20

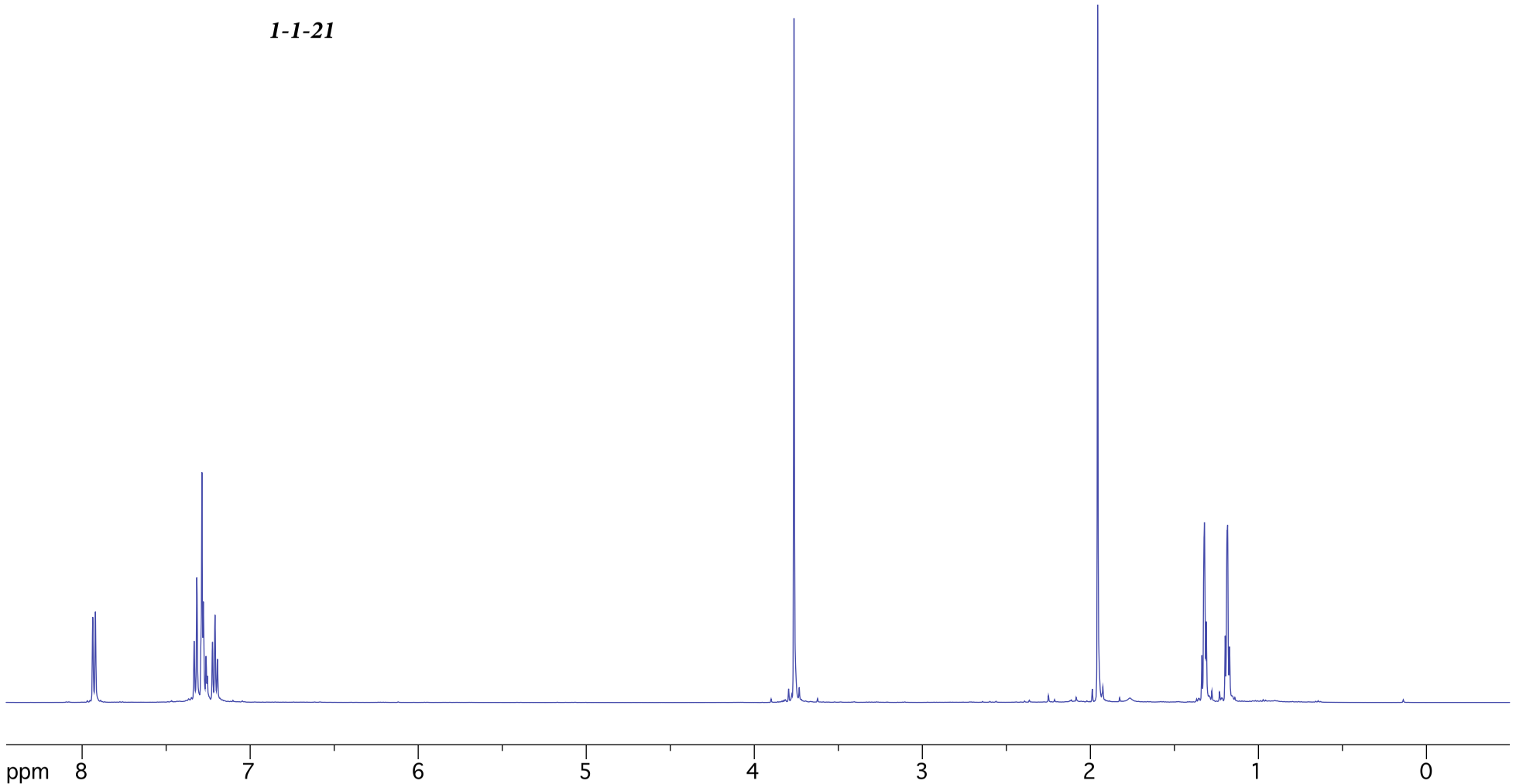


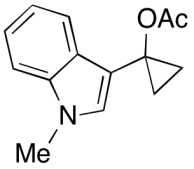


1-1-20

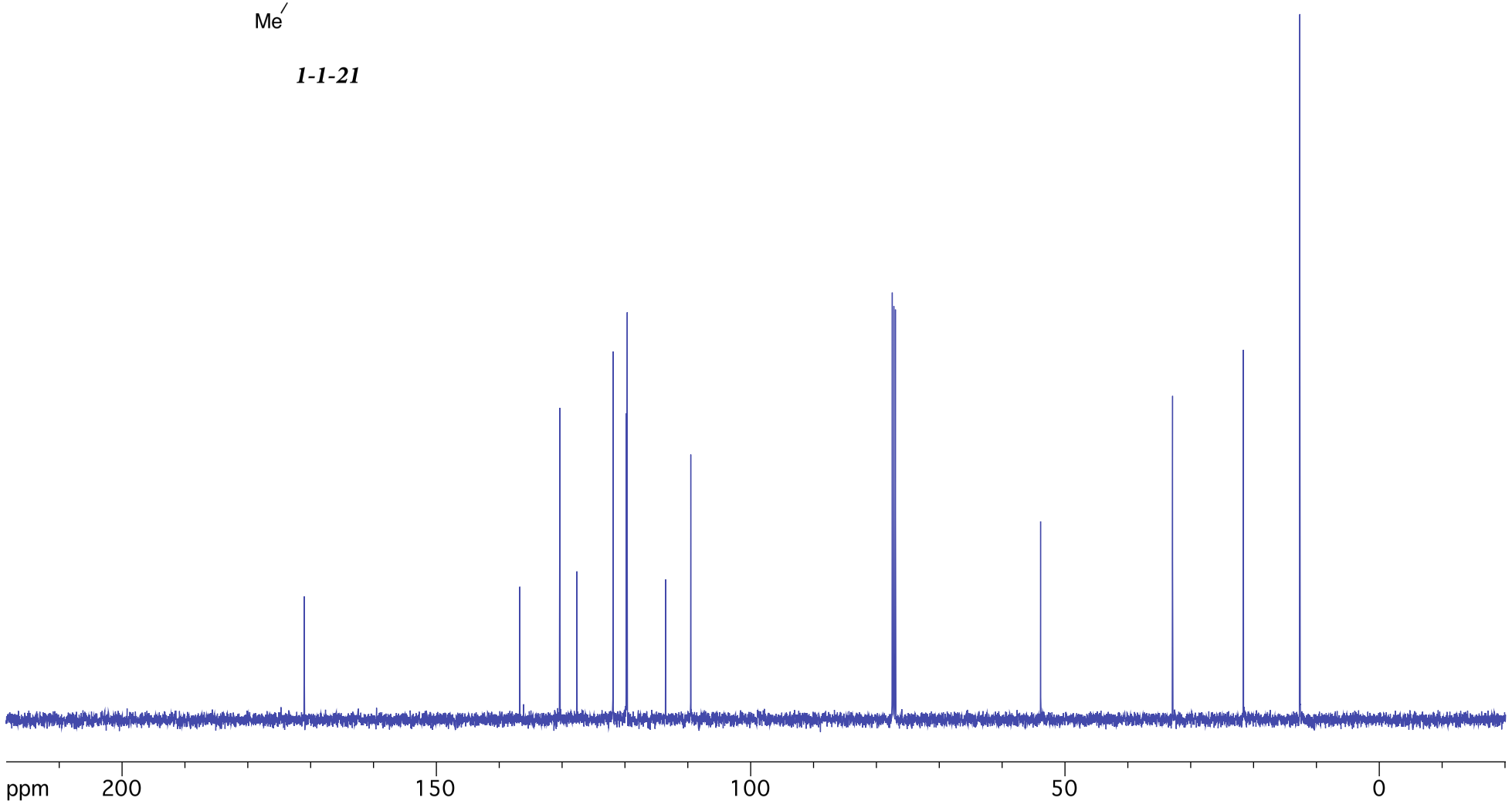


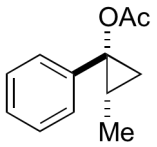
1-1-21



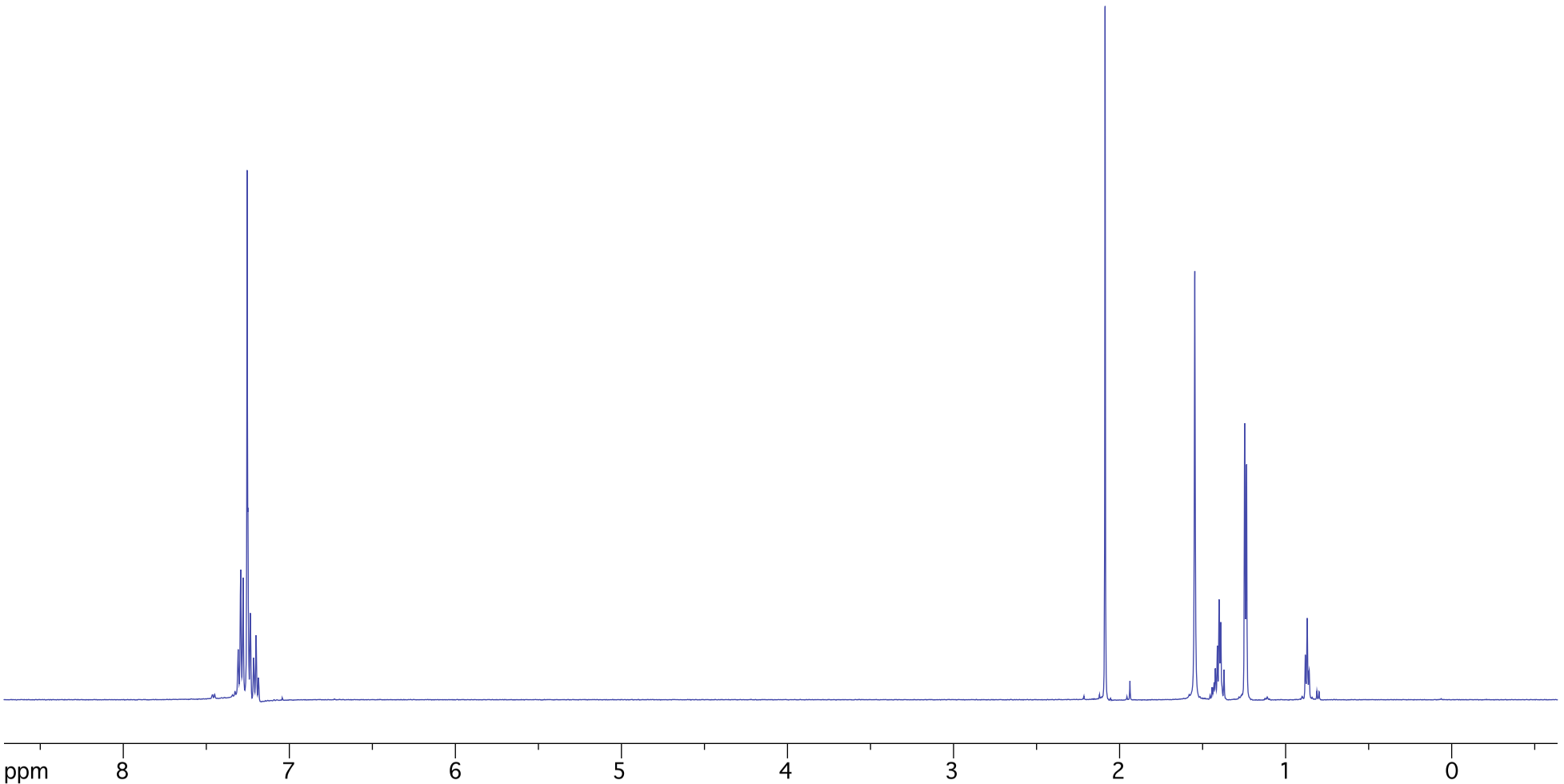


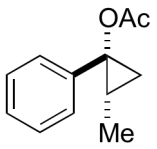
1-1-21



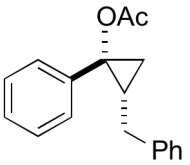


1-1-22

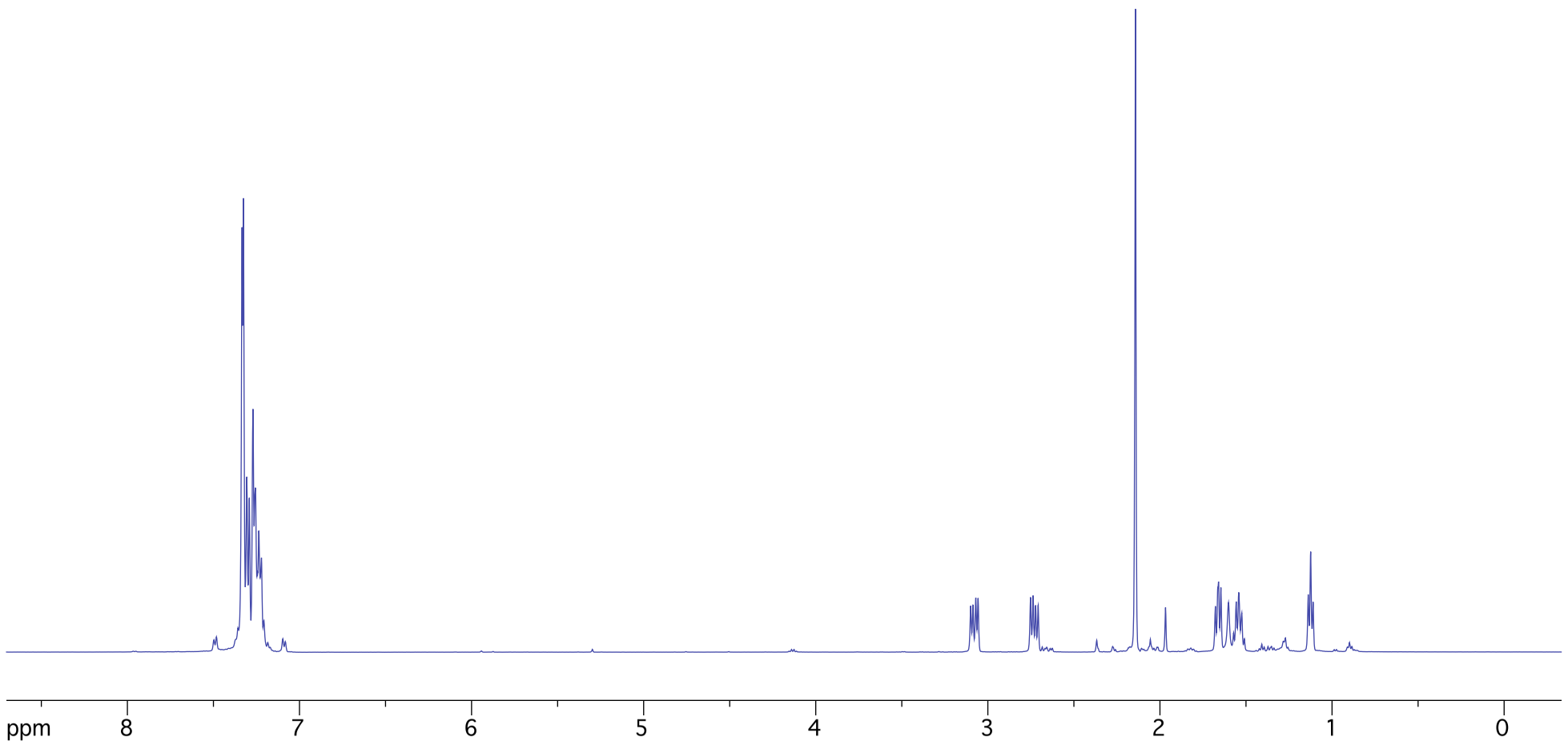


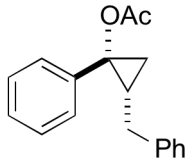


1-1-22

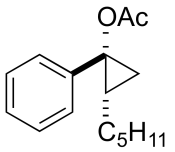


1-1-24

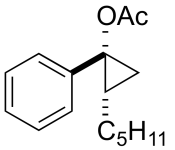




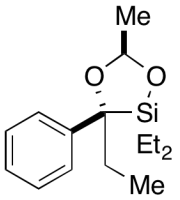
1-1-24



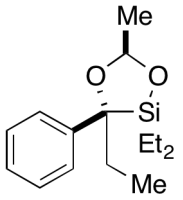
1-1-23



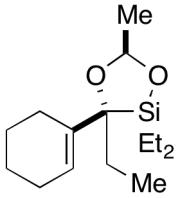
1-1-23



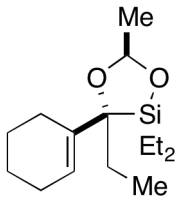
1-3-1



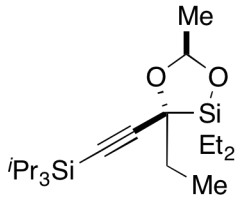
1-3-1



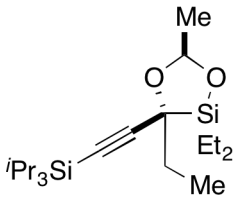
1-3-2



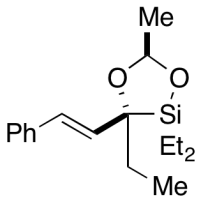
1-3-2



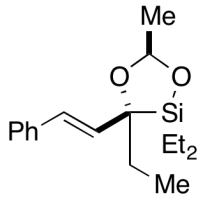
1-3-3



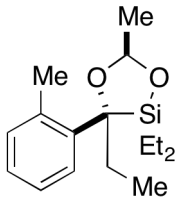
1-3-3



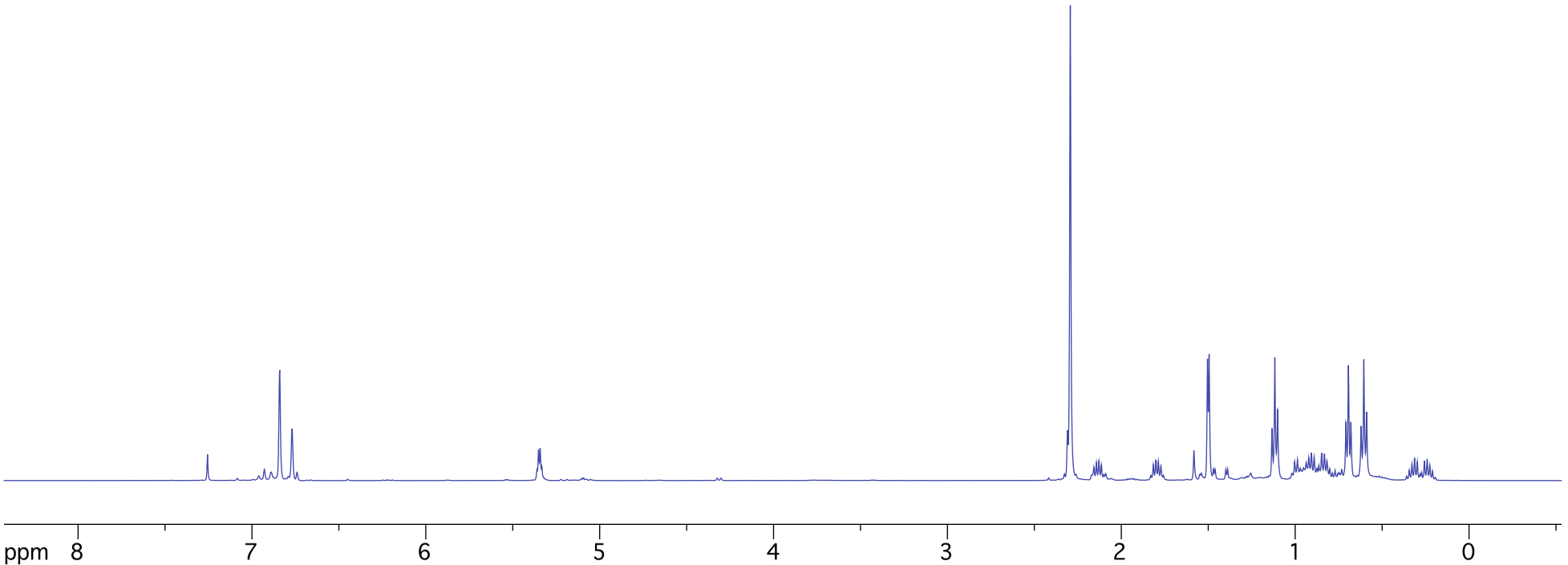
1-3-4

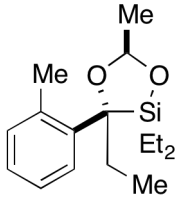


1-3-4

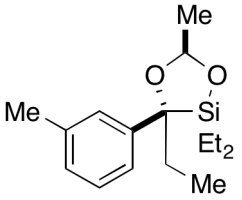


1-3-6

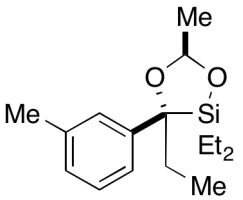




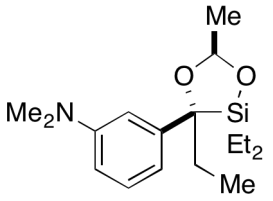
1-3-6



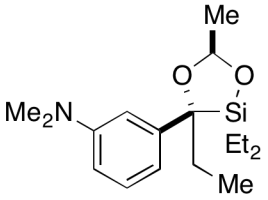
1-3-7



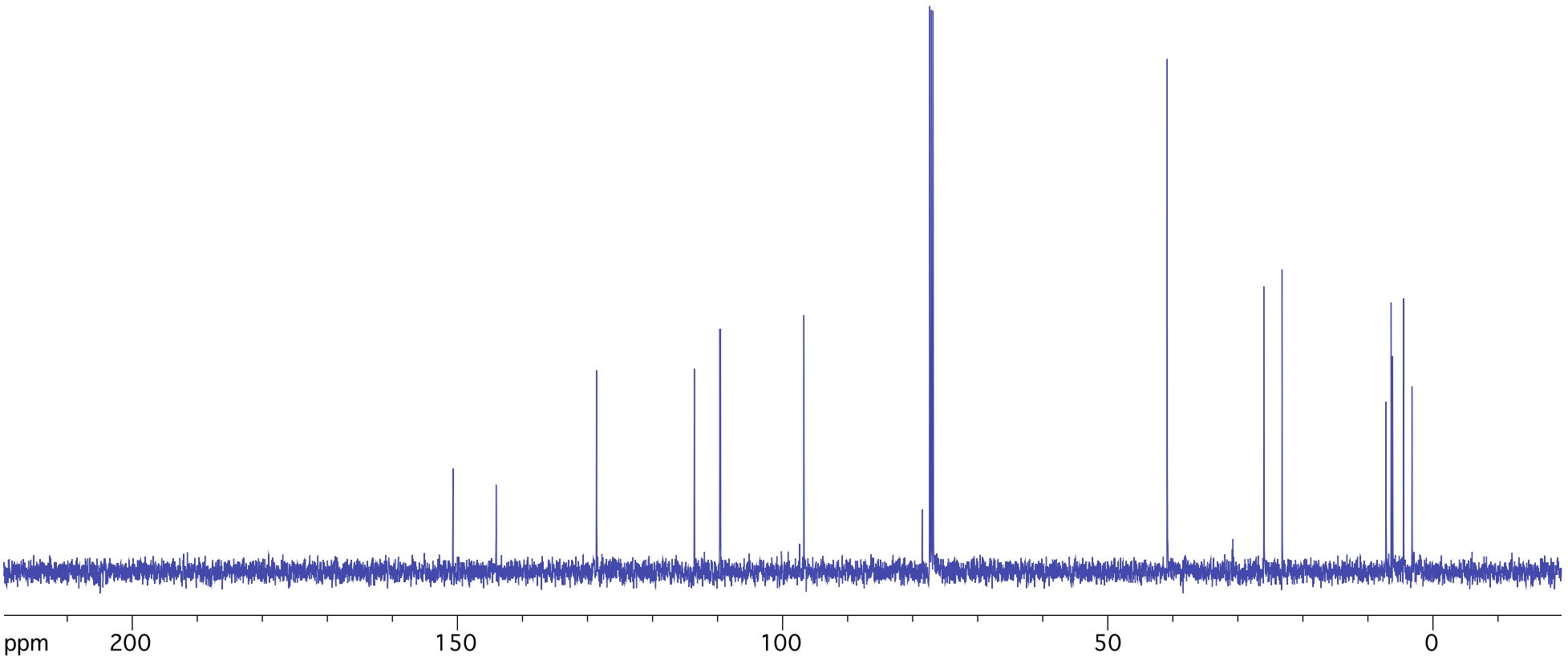
1-3-7

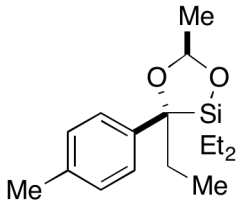


1-3-8

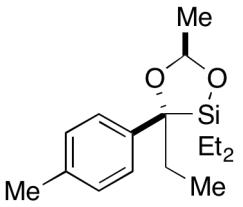


1-3-8

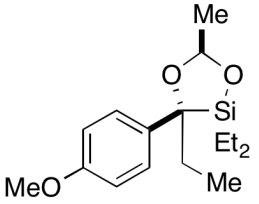




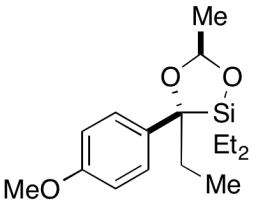
1-3-9



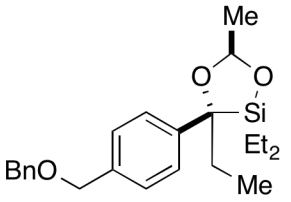
1-3-9



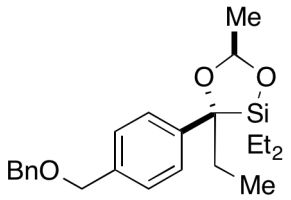
1-3-10



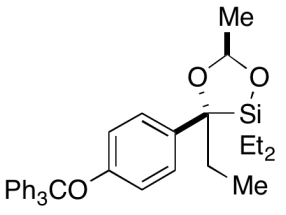
1-3-10



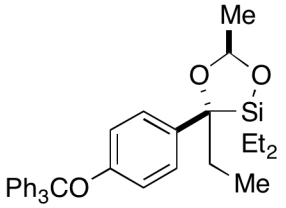
1-3-11



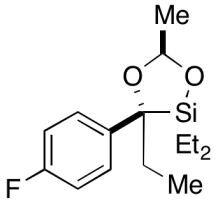
1-3-11



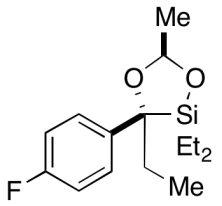
1-3-12



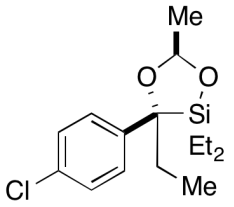
1-3-12



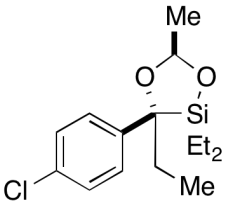
1-3-13



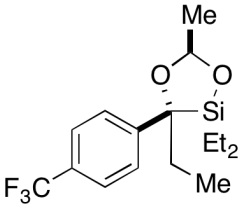
1-3-13



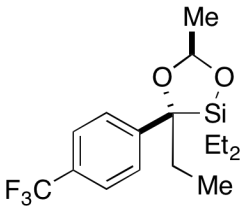
1-3-14



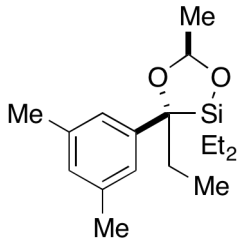
1-3-14



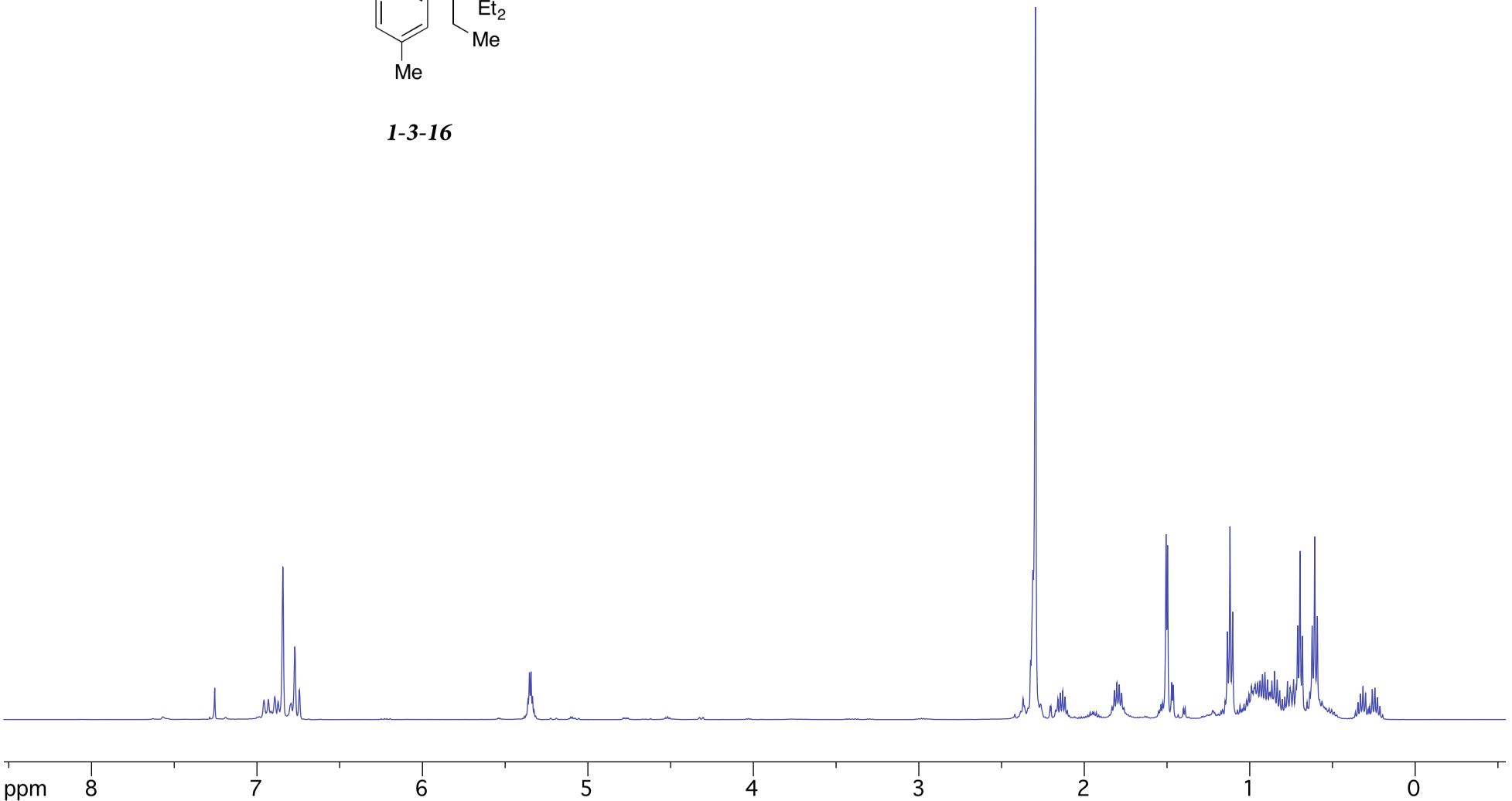
1-3-15

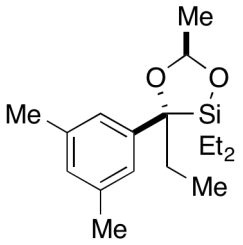


1-3-15

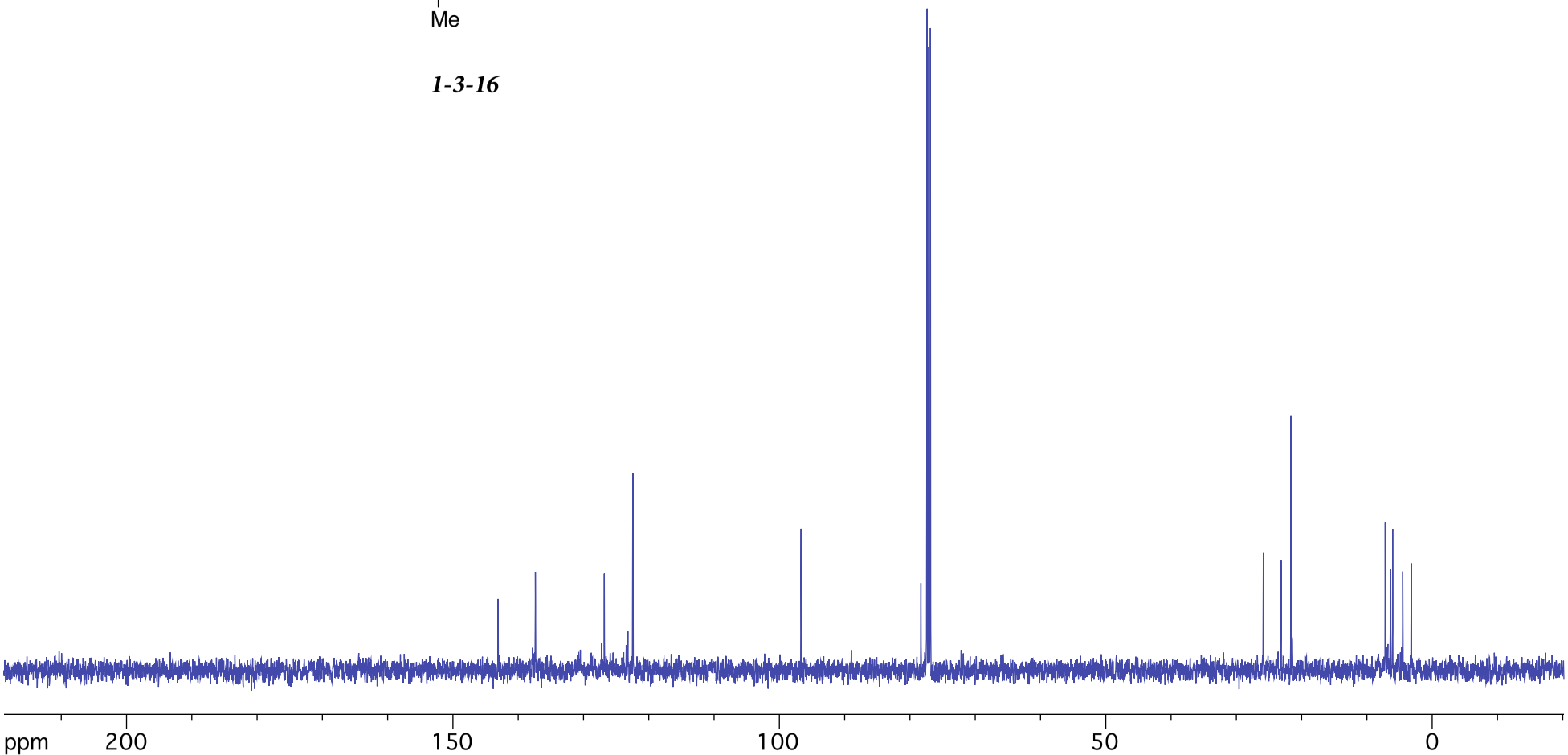


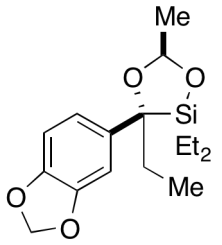
1-3-16



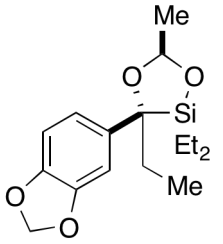


1-3-16

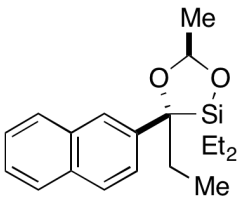




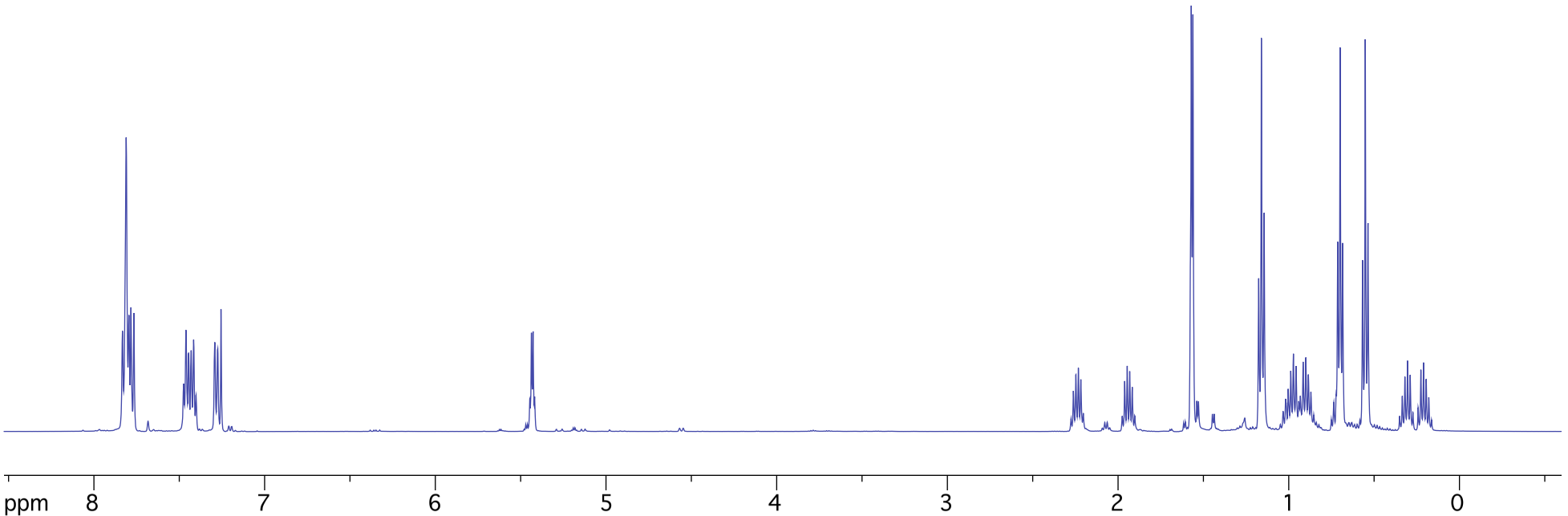
1-3-17

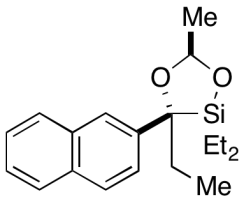


1-3-17

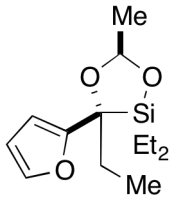


2-1-18

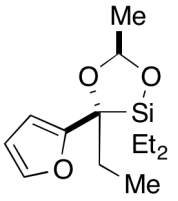




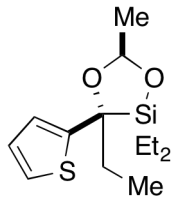
1-3-18



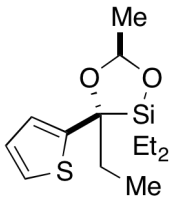
1-3-19



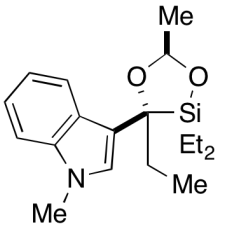
1-3-19



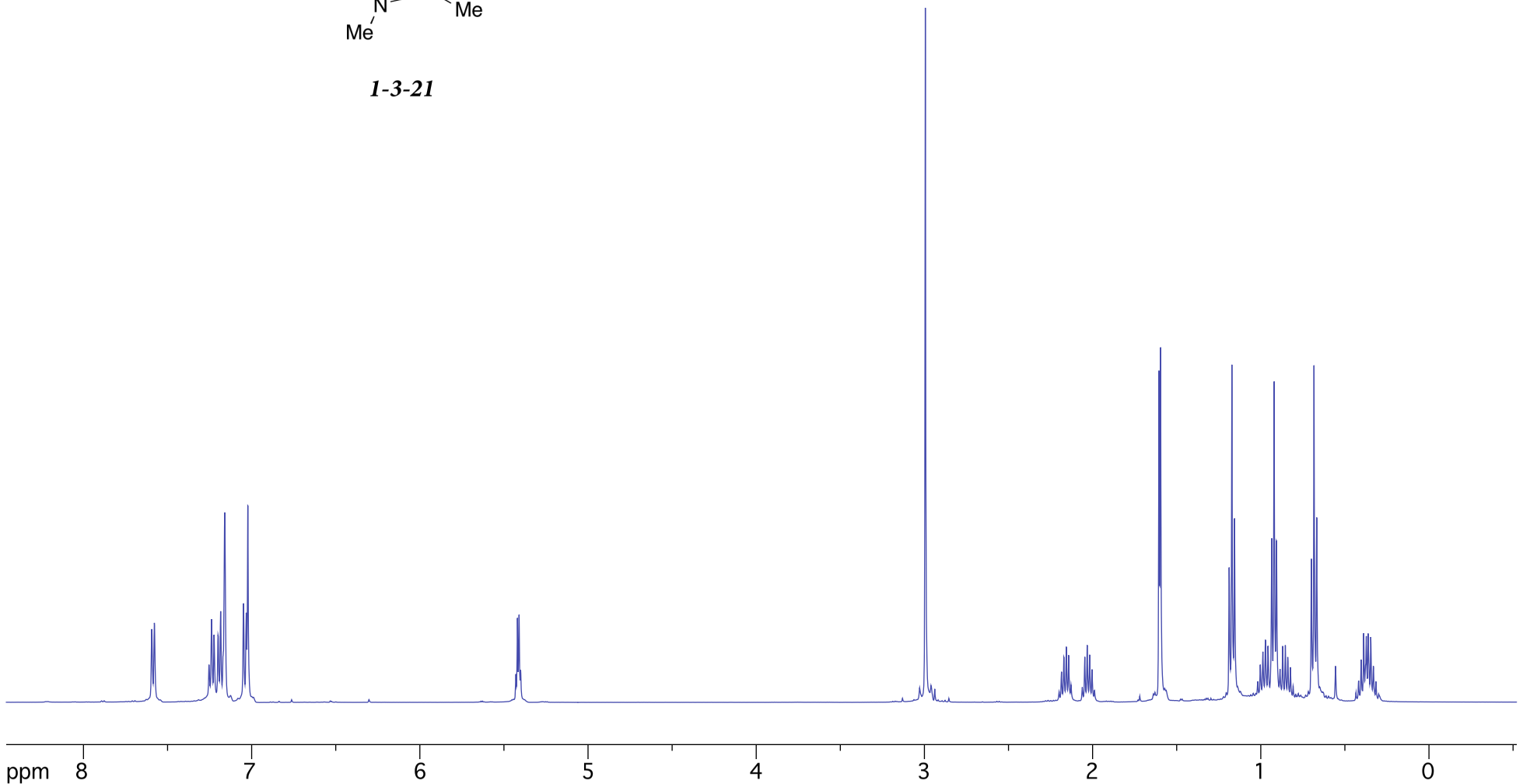
1-3-20

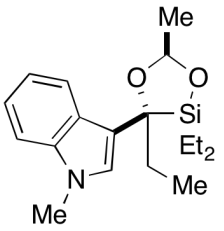


1-3-20

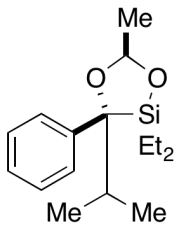


1-3-21

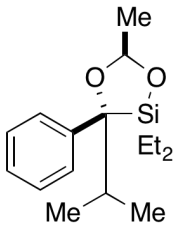




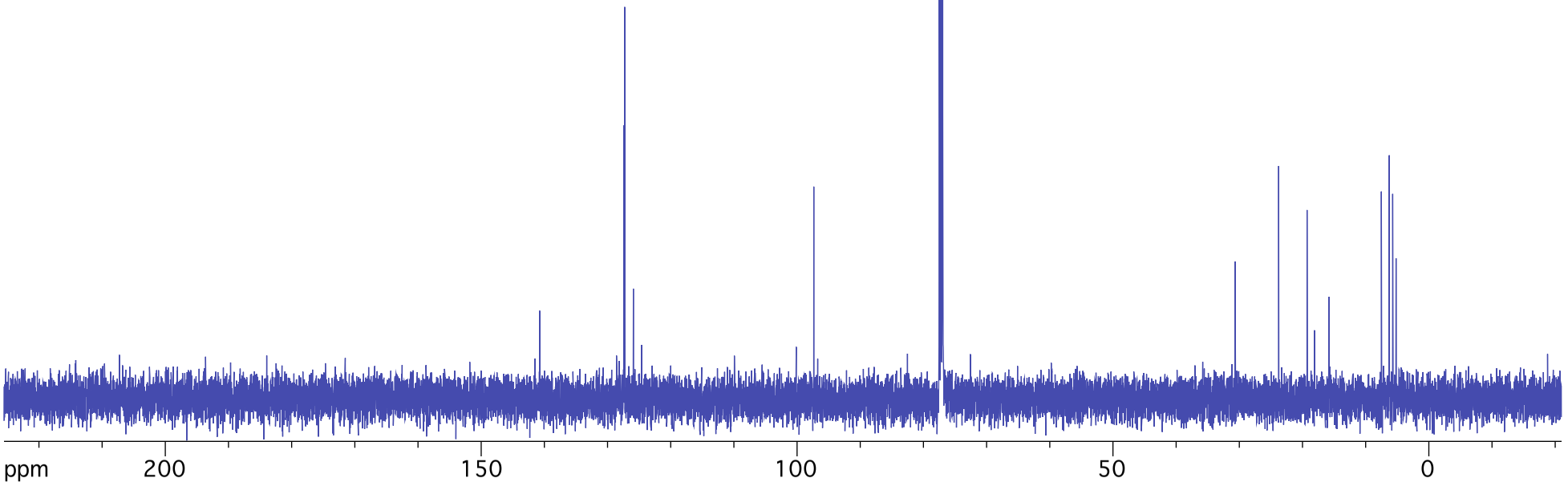
1-3-21

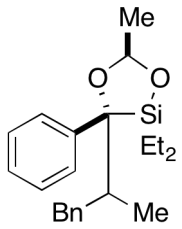


1-3-22

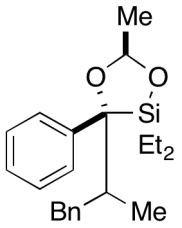


1-3-22

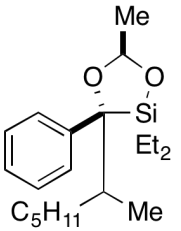




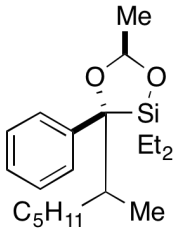
1-3-23



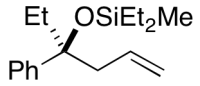
1-3-23



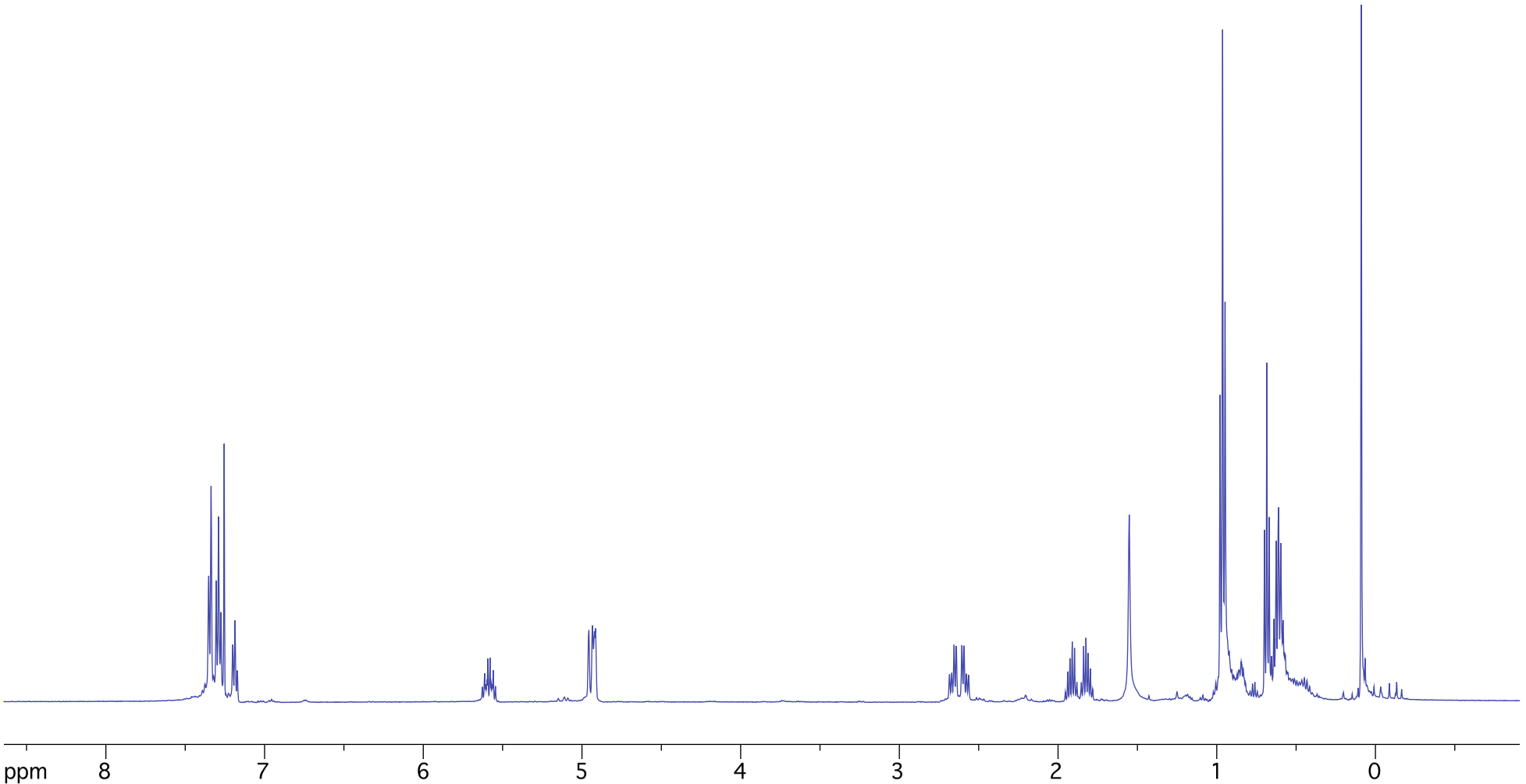
1-3-24

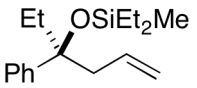


1-3-24

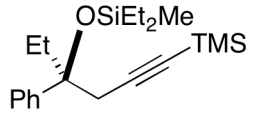


1-20

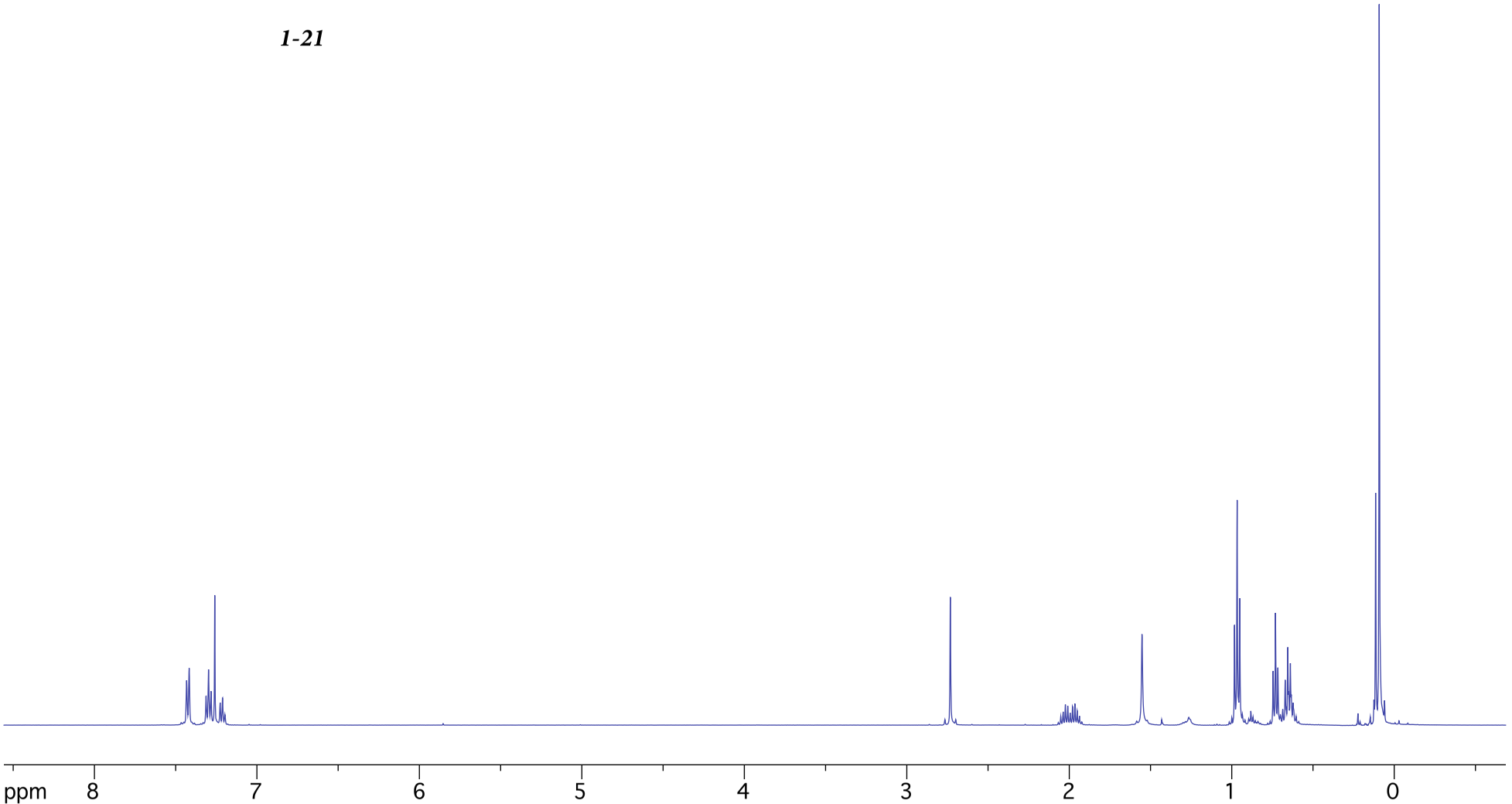


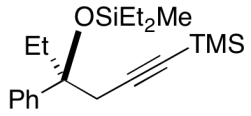


1-20

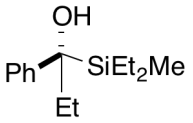


1-21

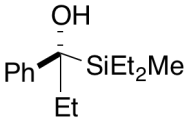




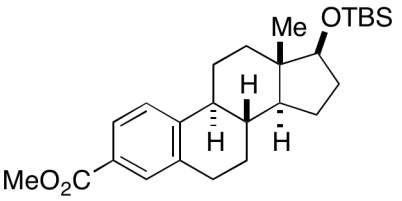
1-21



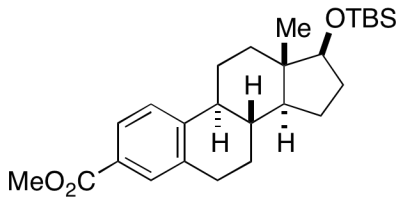
1-25



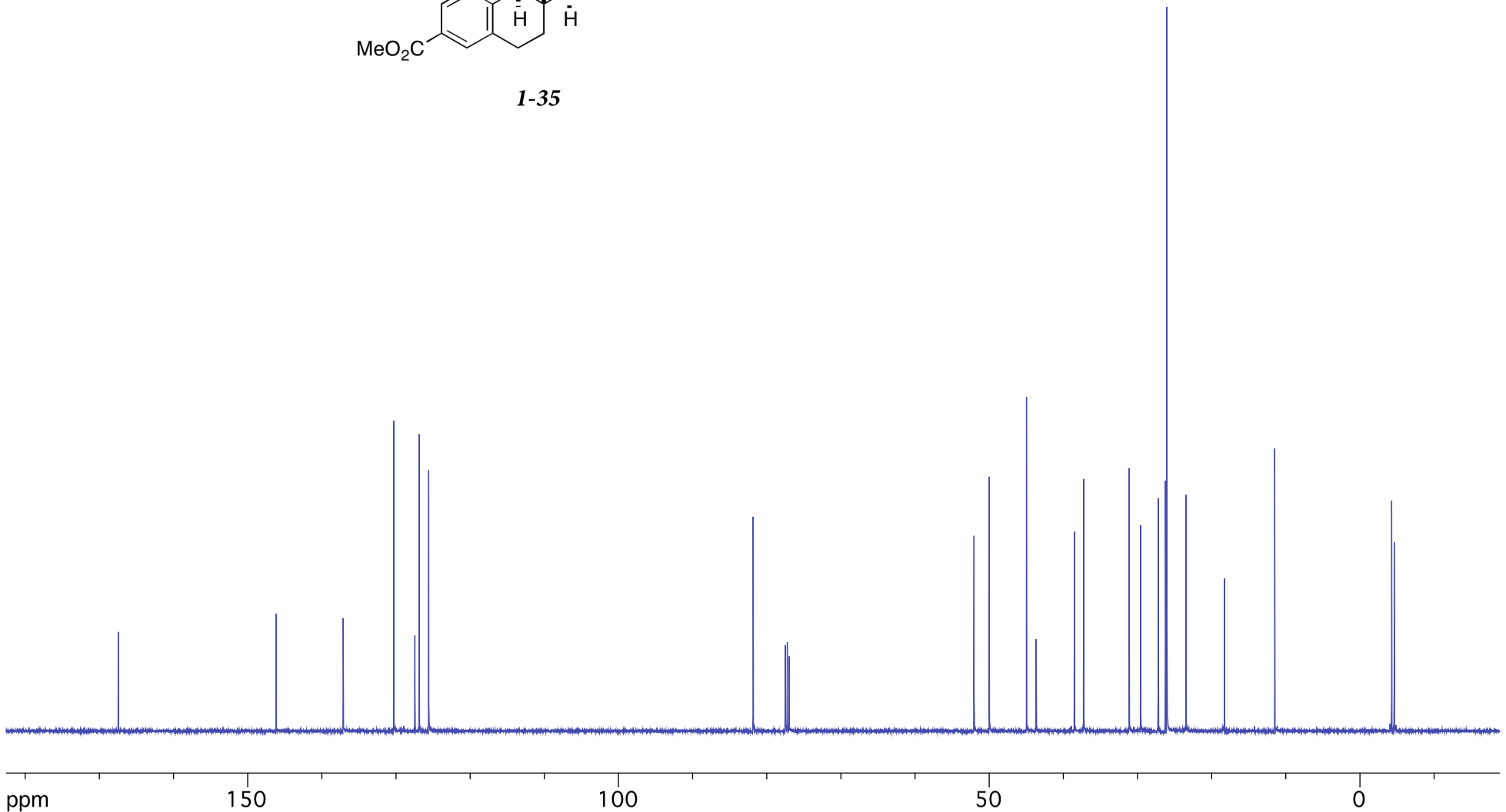
1-25

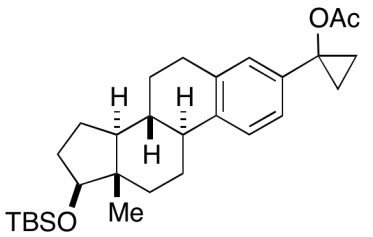


1-35

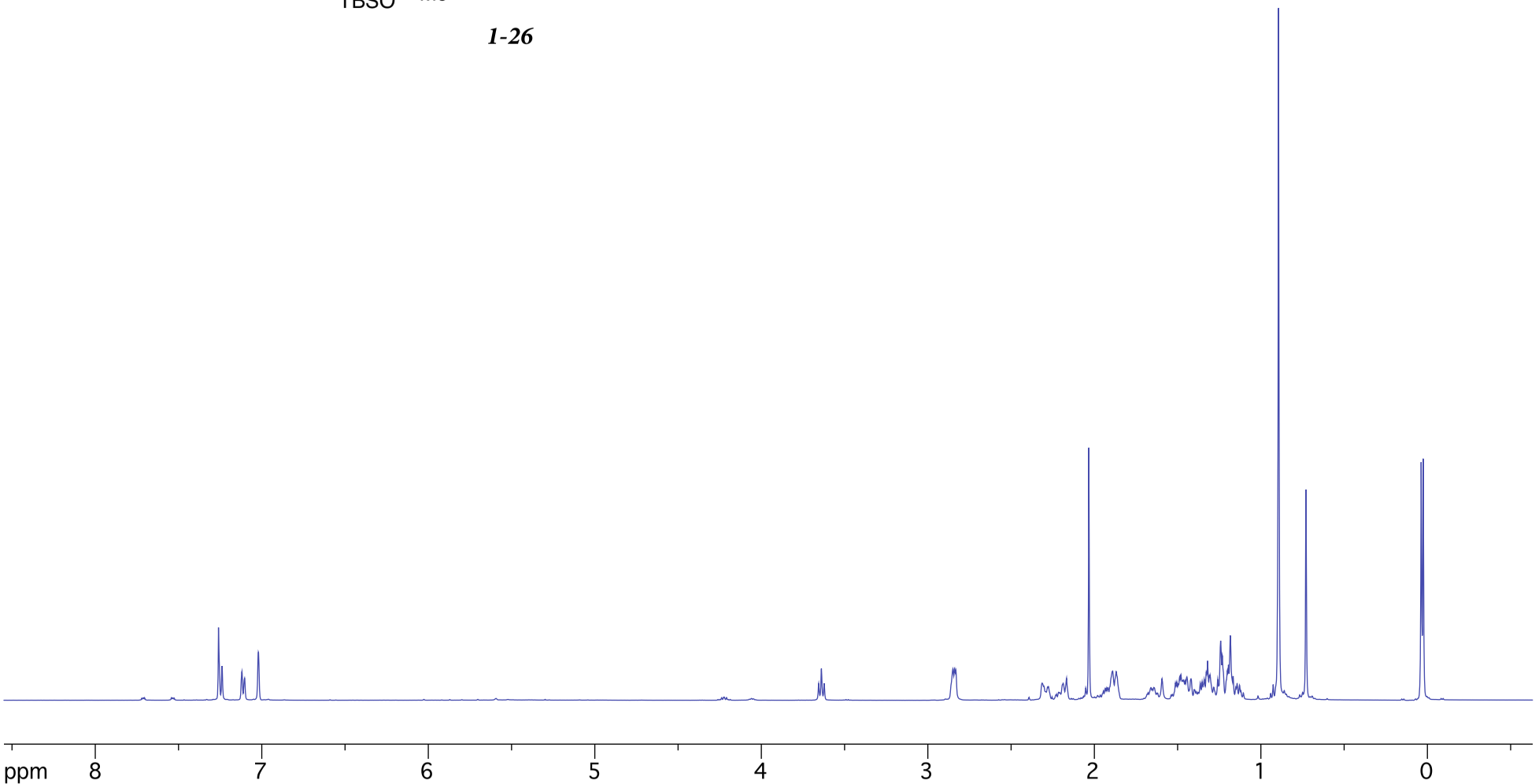


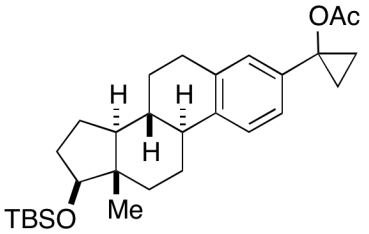
1-35



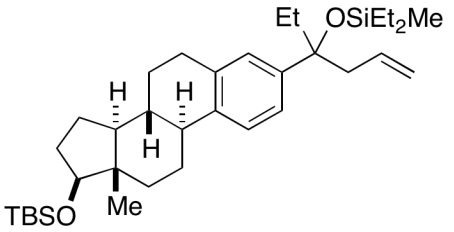


1-26

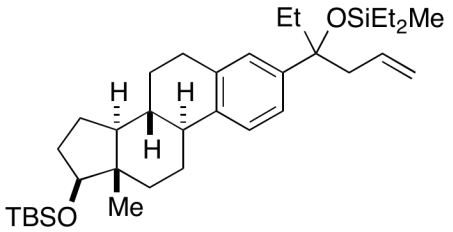




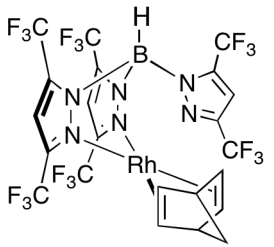
1-26



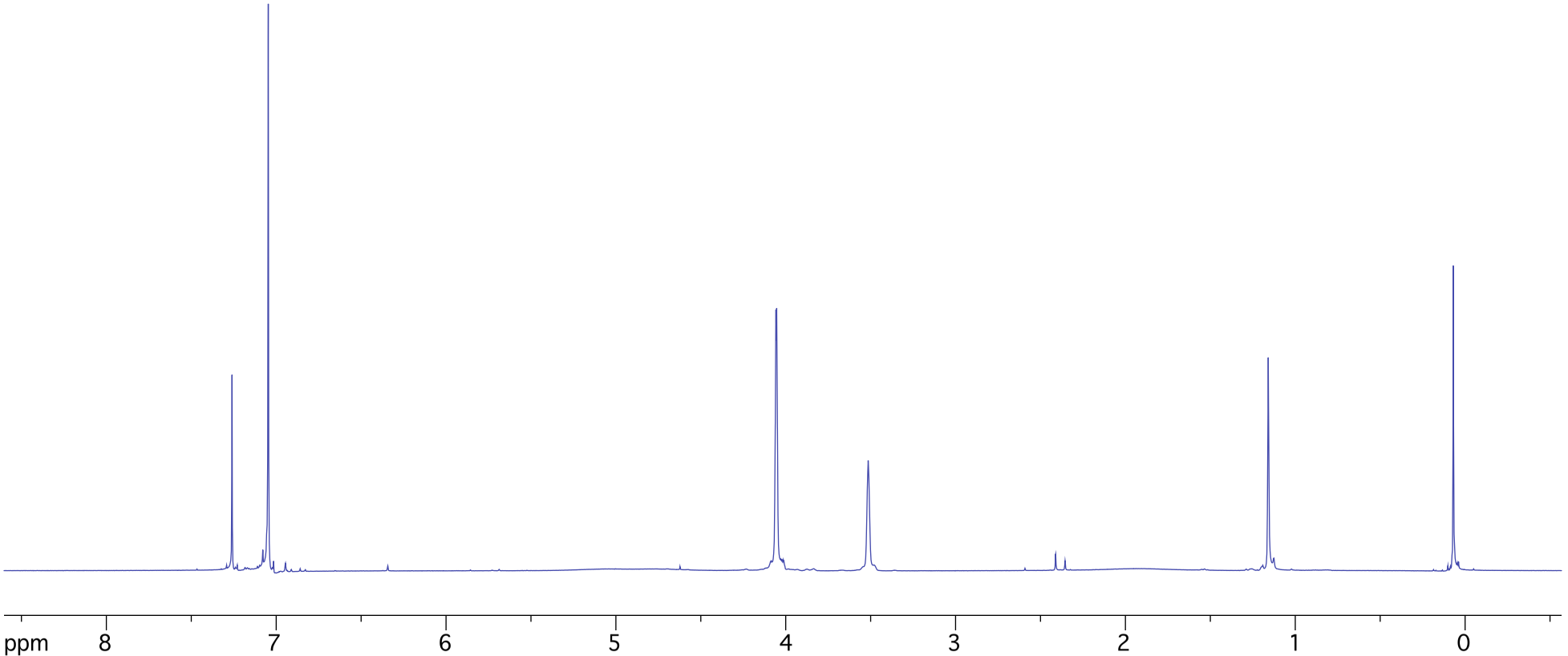
1-27

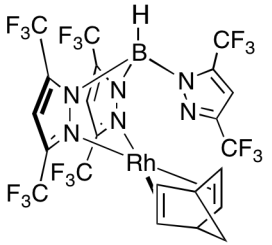


1-27



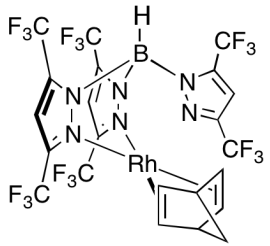
$Tp^{(CF3)2}Rh(nbd)$



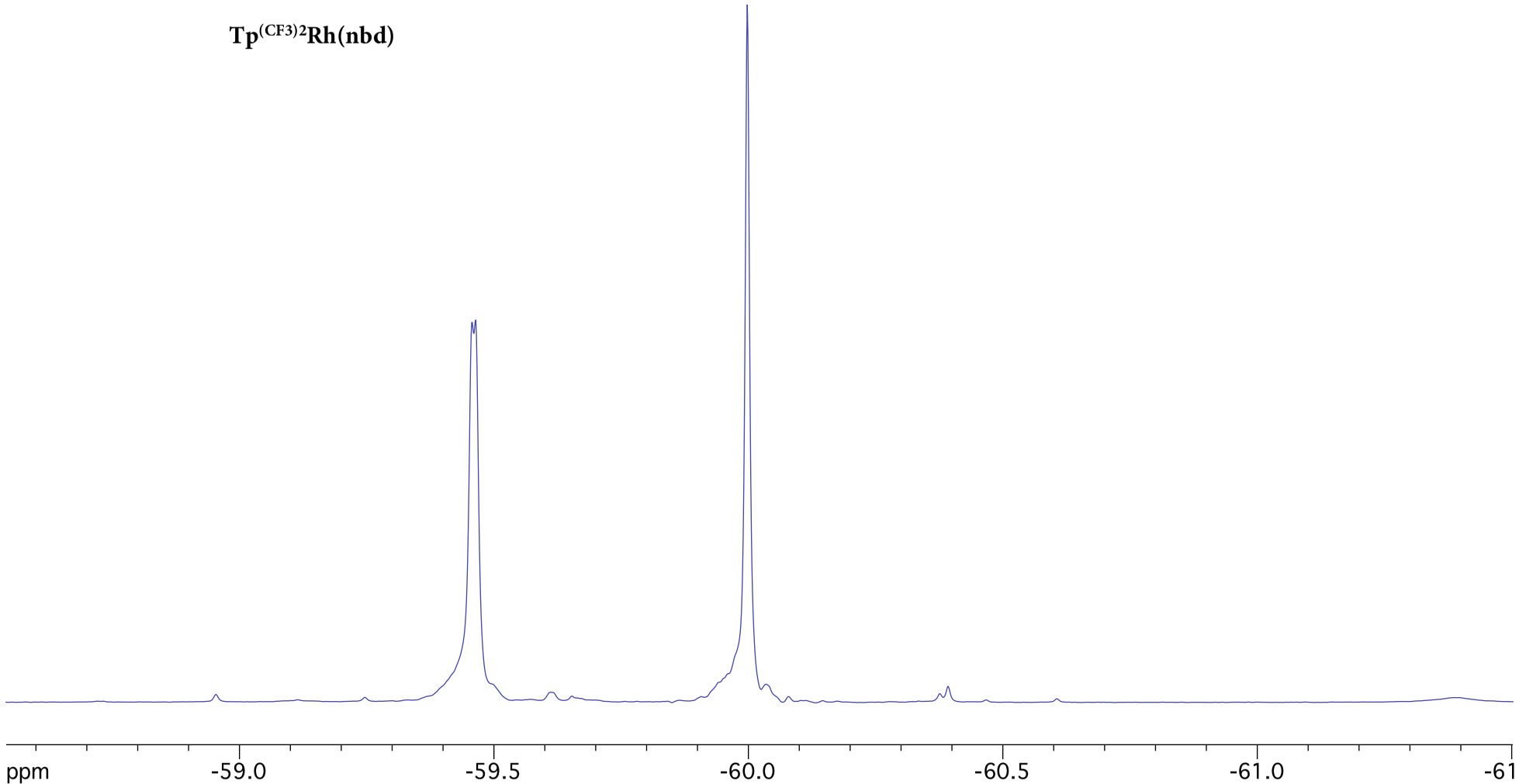


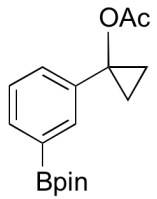
$Tp^{(CF3)2}Rh(nbd)$

ppm 200 150 100 50 0

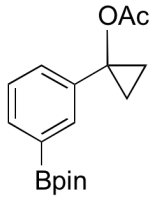


Tp$^{(CF3)2}$Rh(nbd)

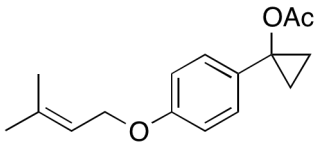




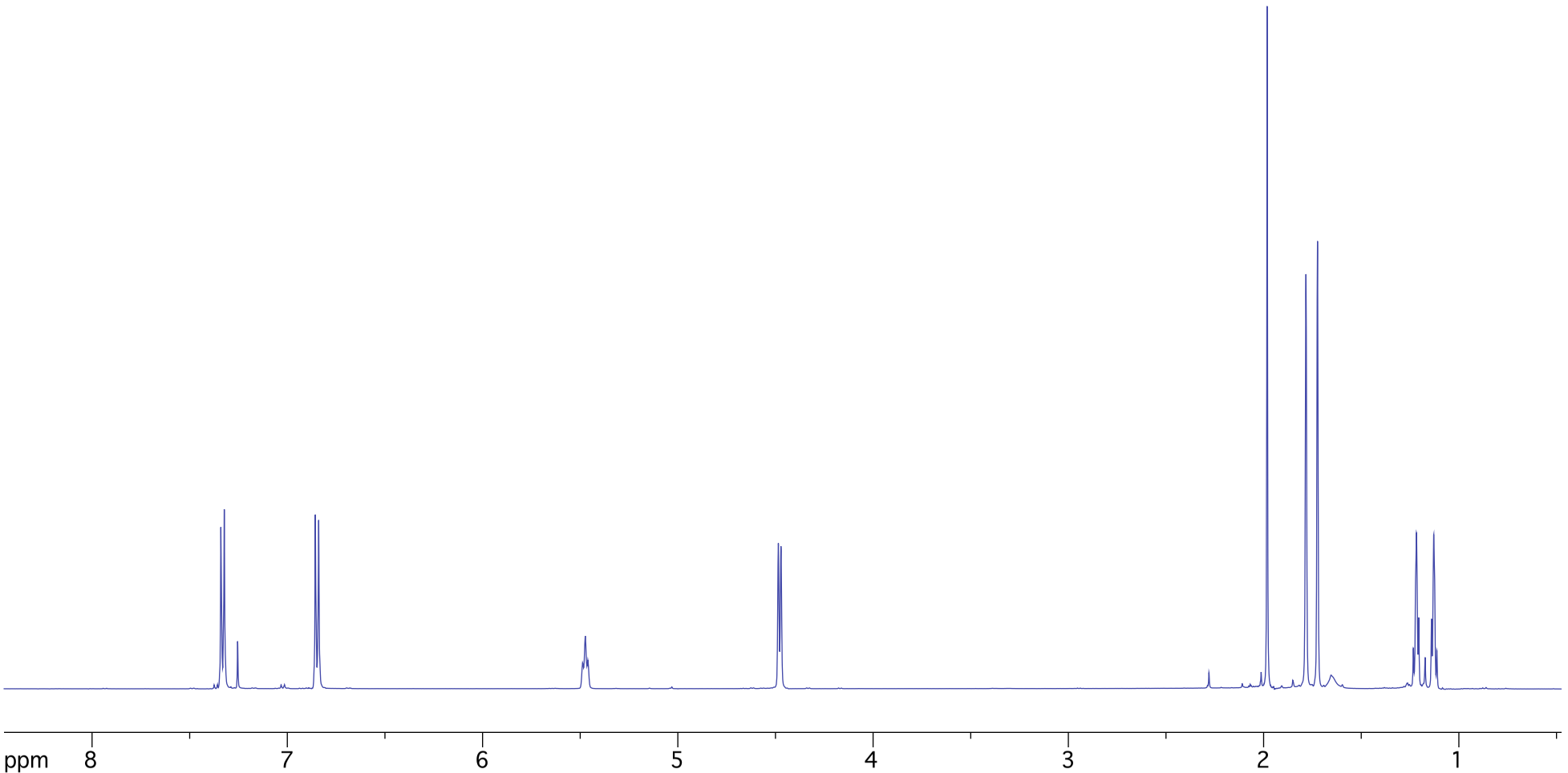
2-1-4

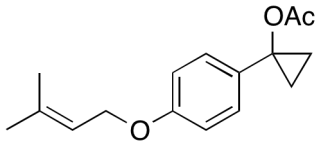


2-1-4

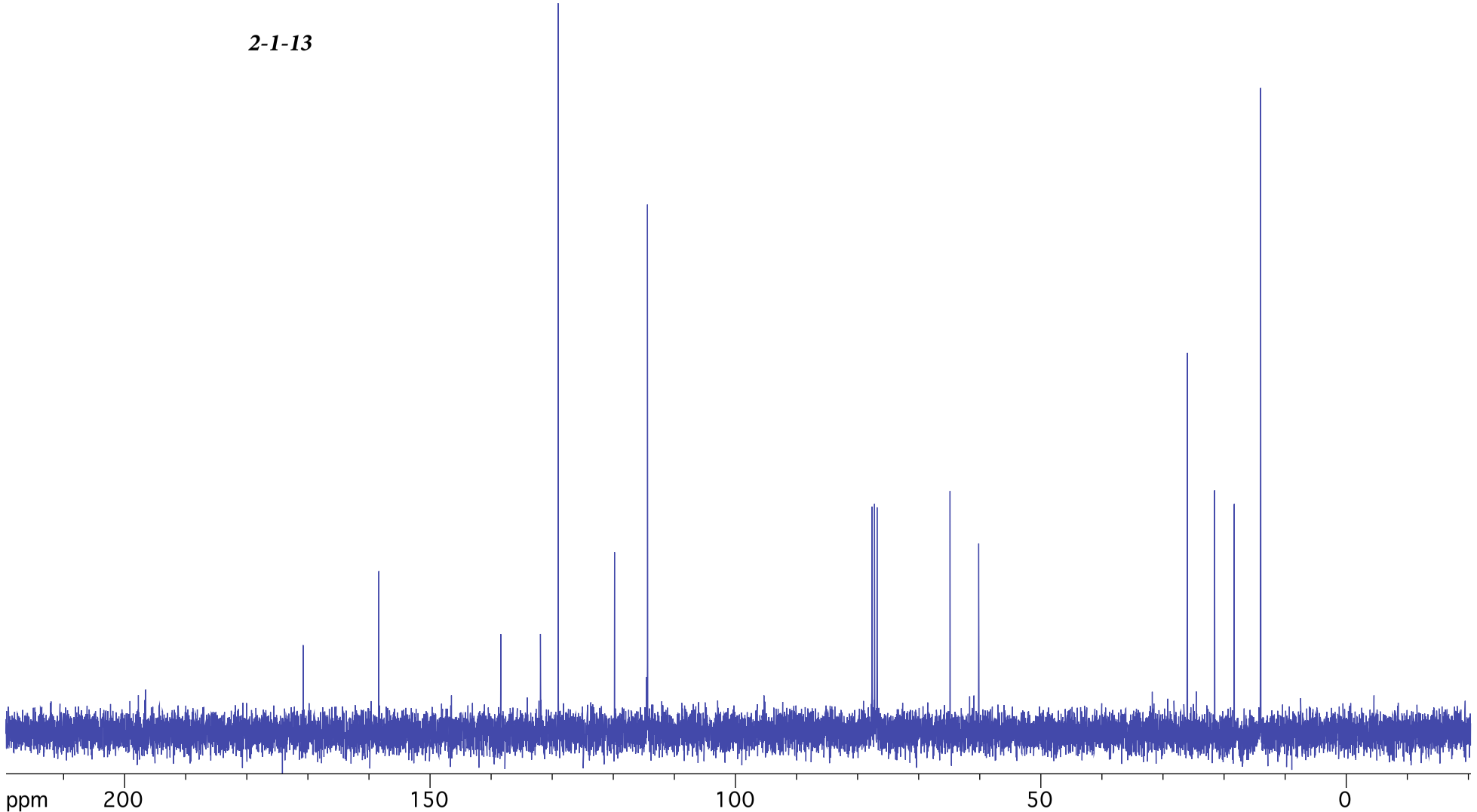


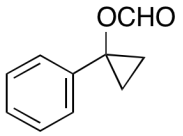
2-1-13



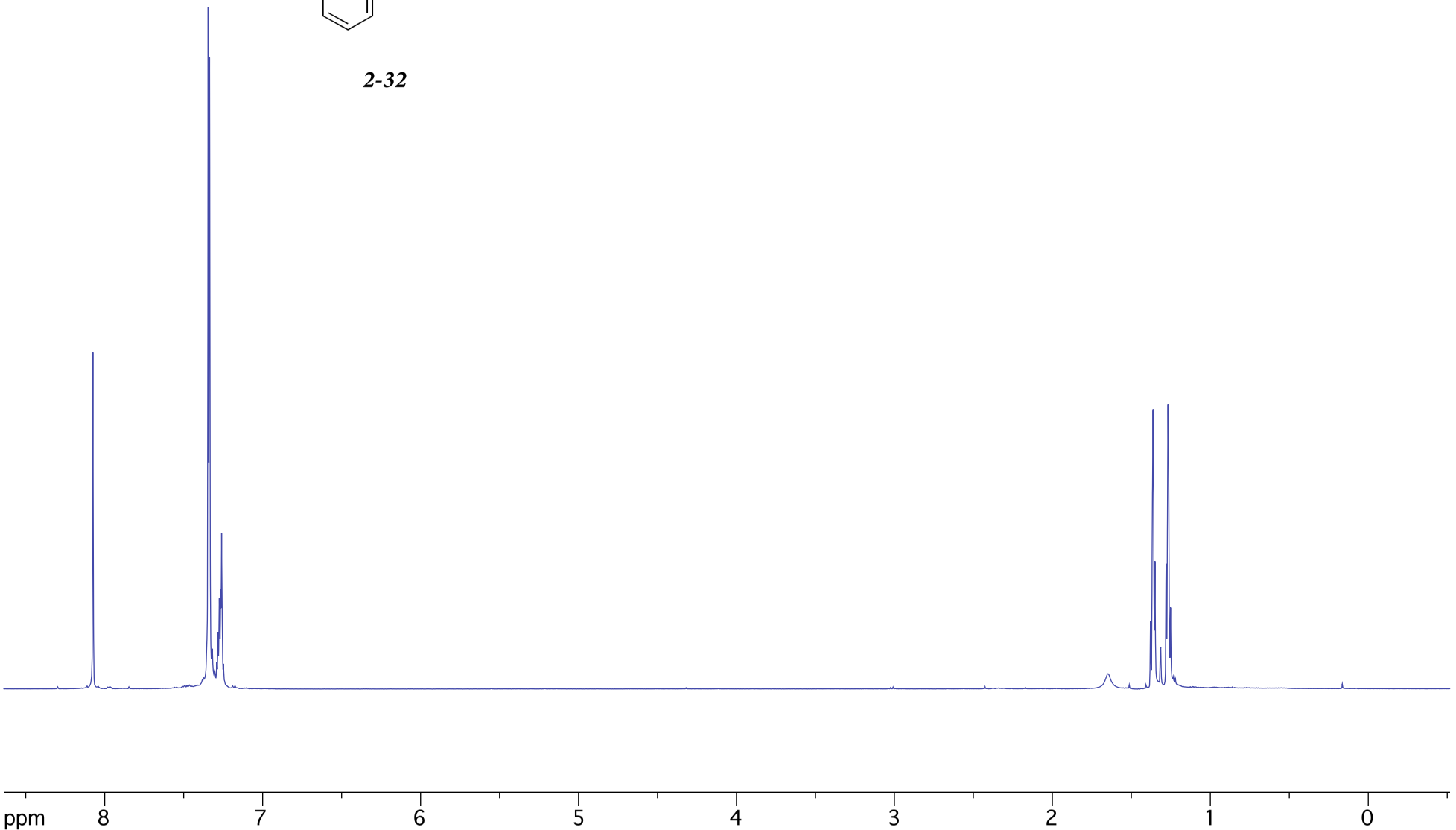


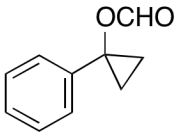
2-1-13



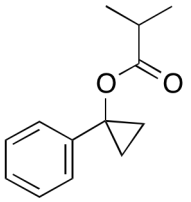


2-32

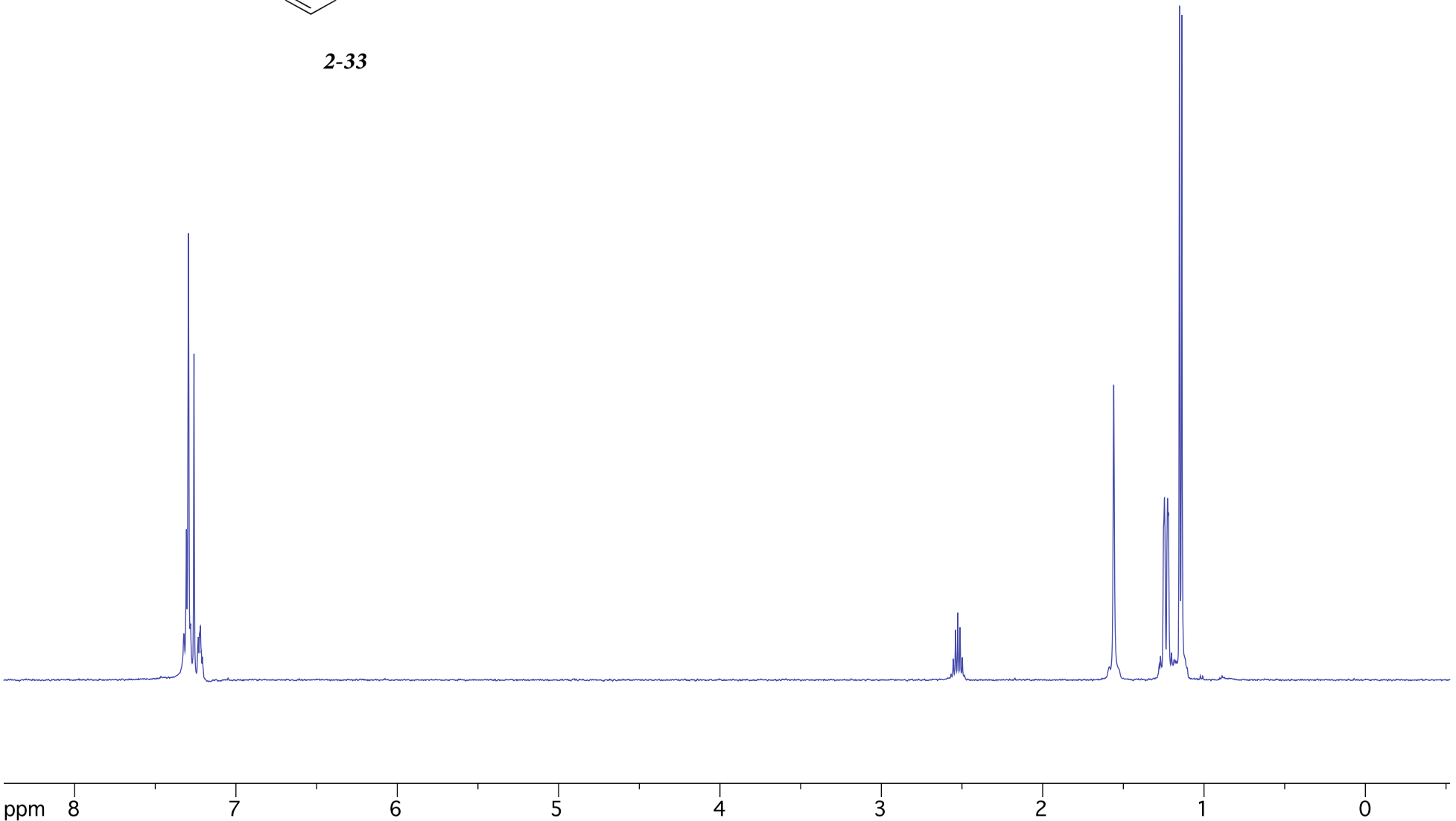


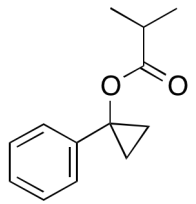


2-32

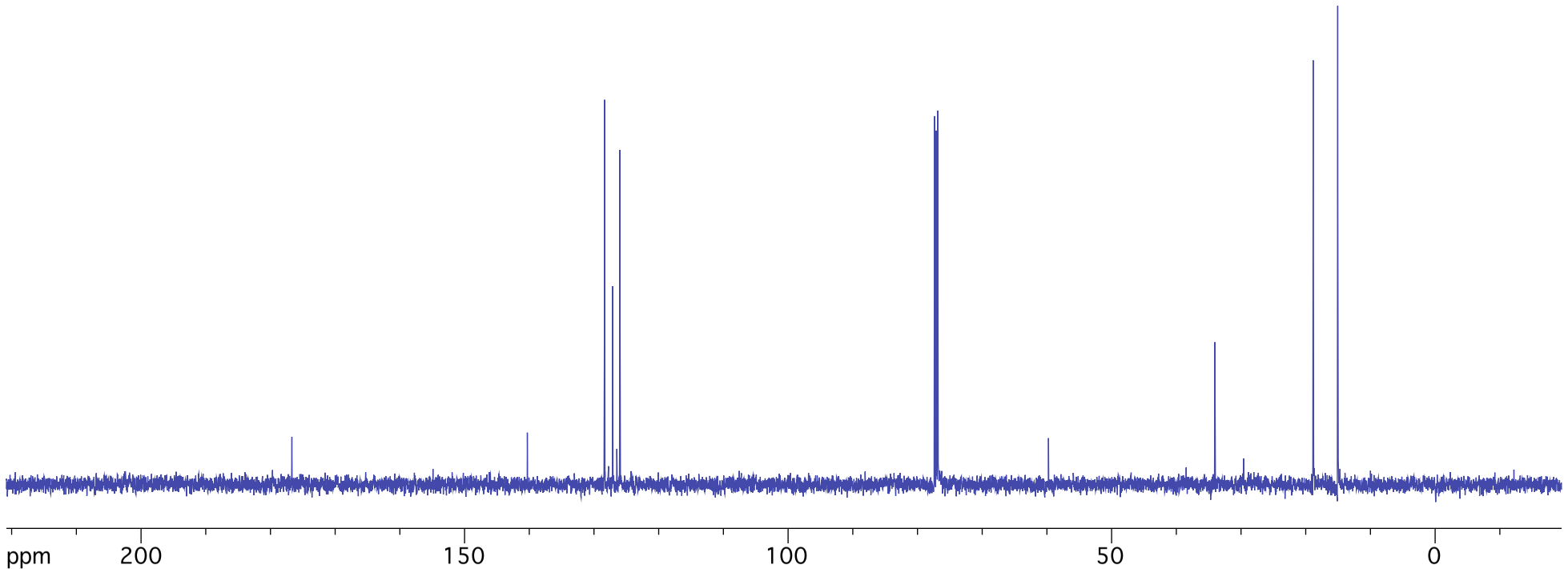


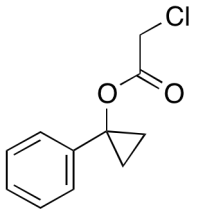
2-33



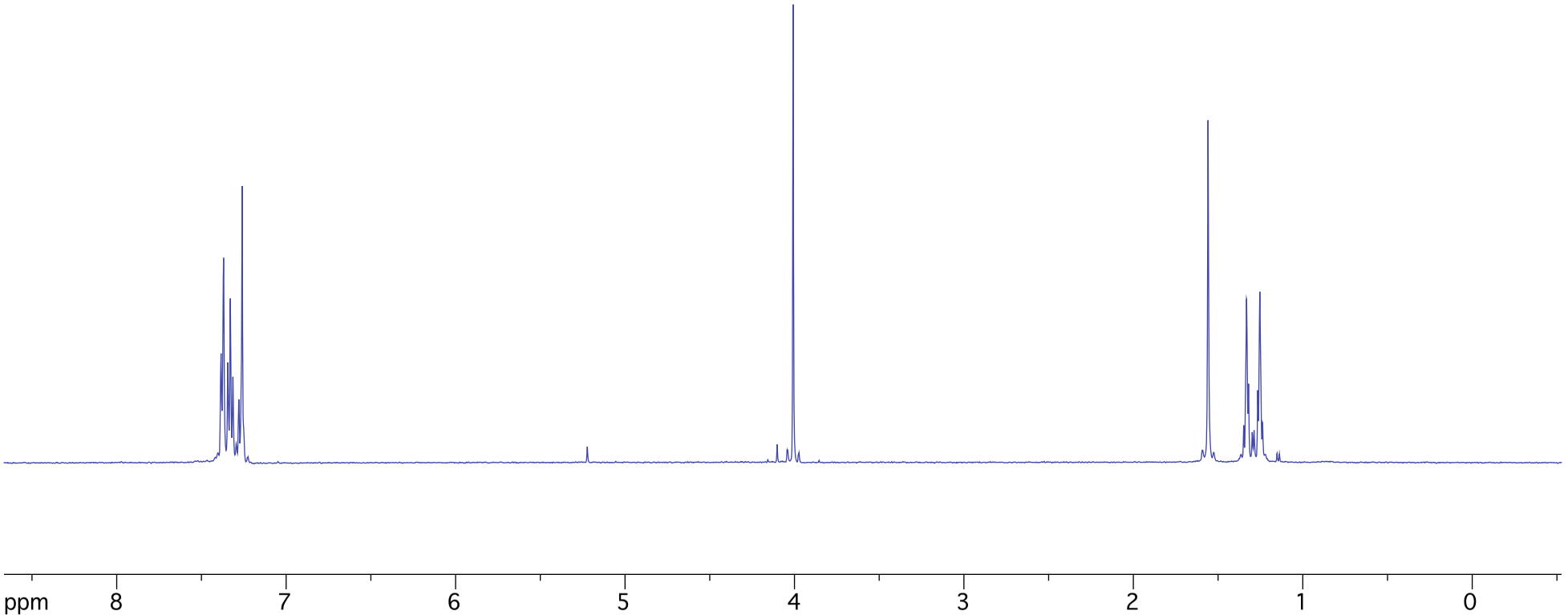


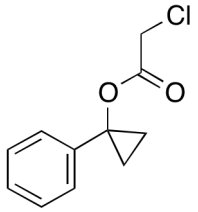
2-33



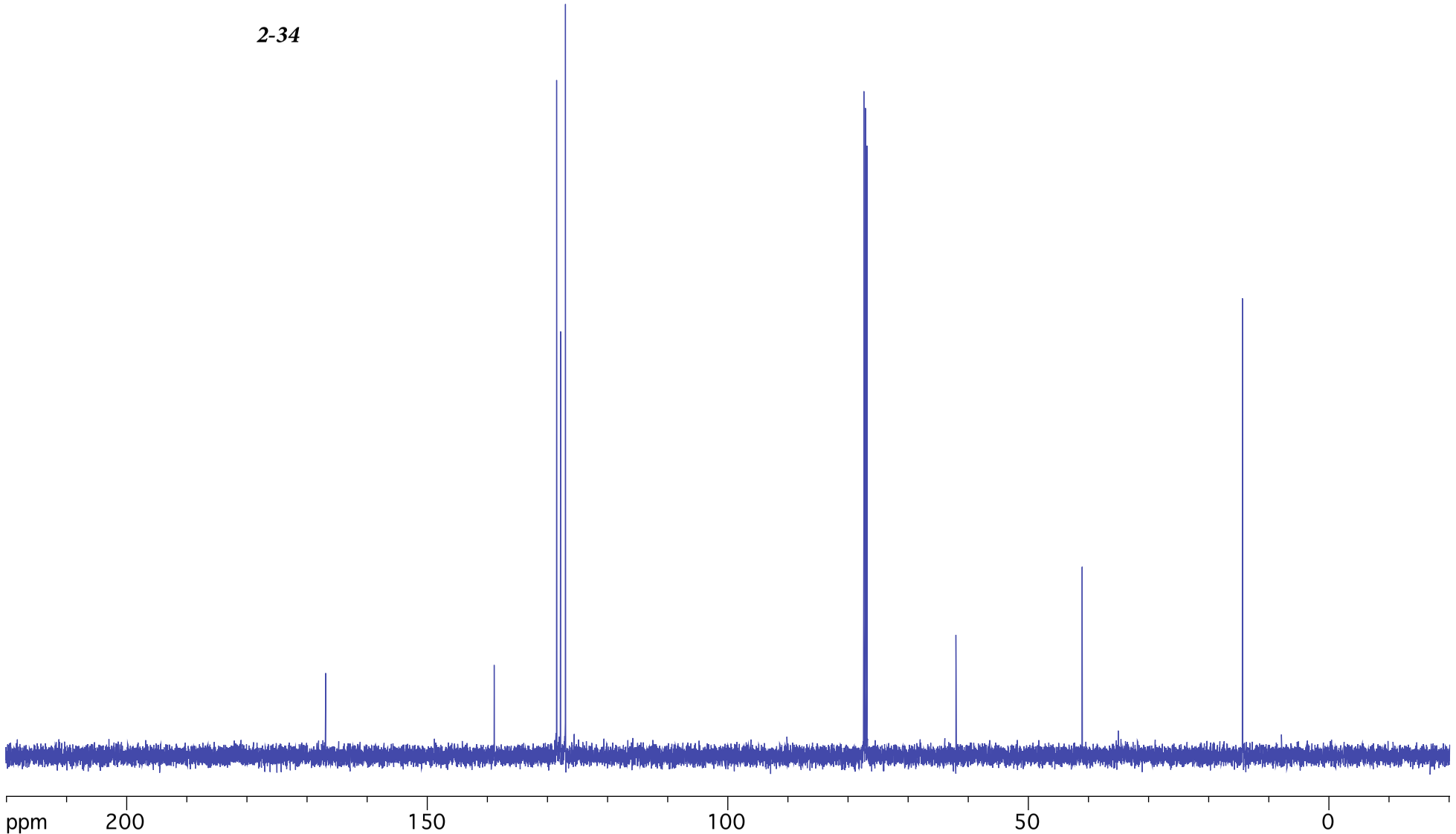


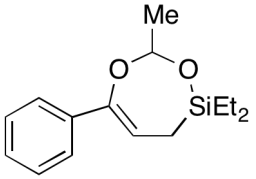
2-34



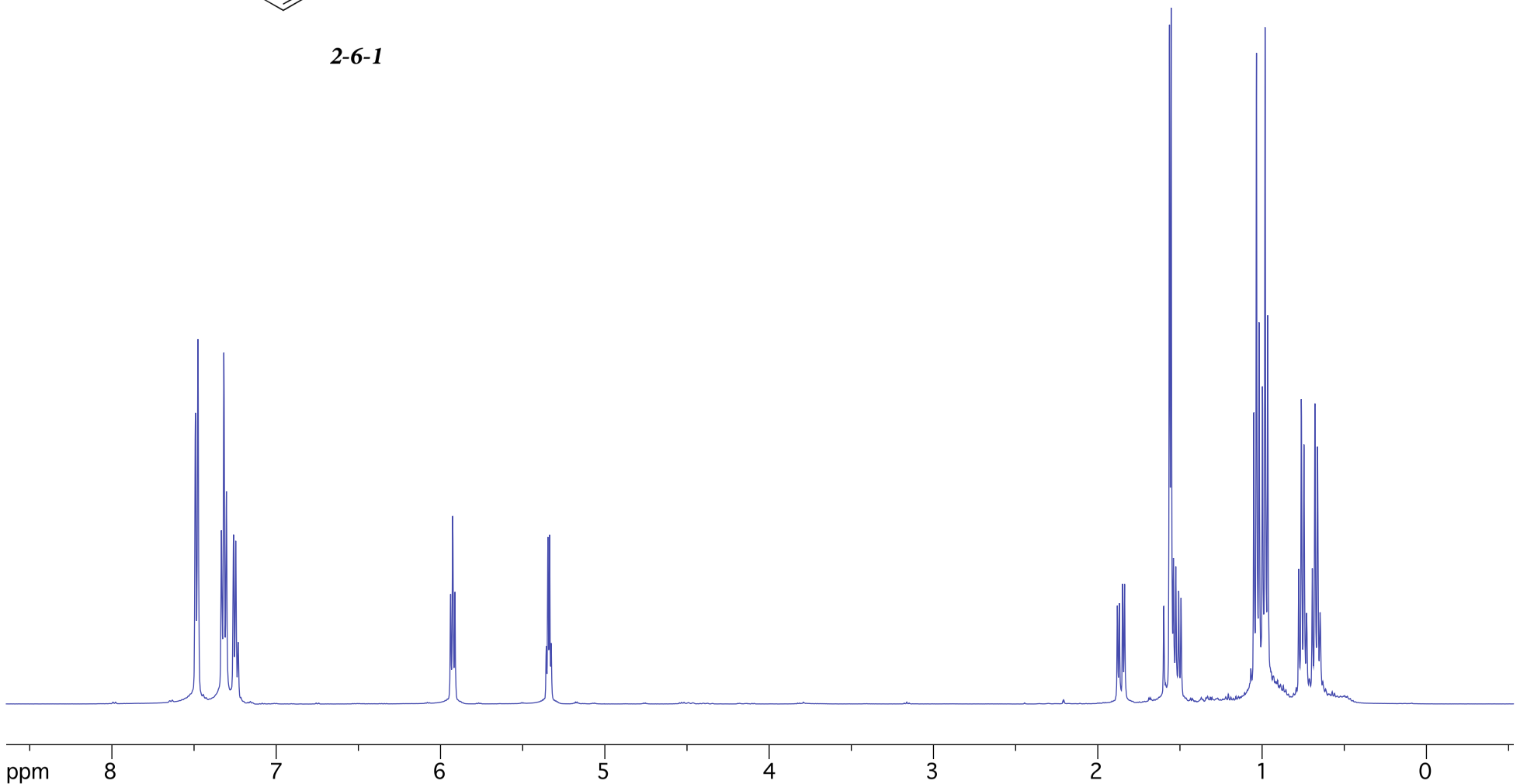


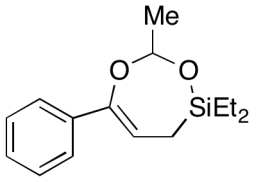
2-34



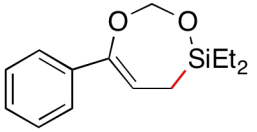


2-6-1

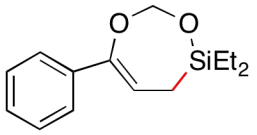




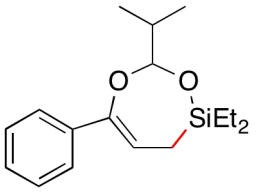
2-6-1



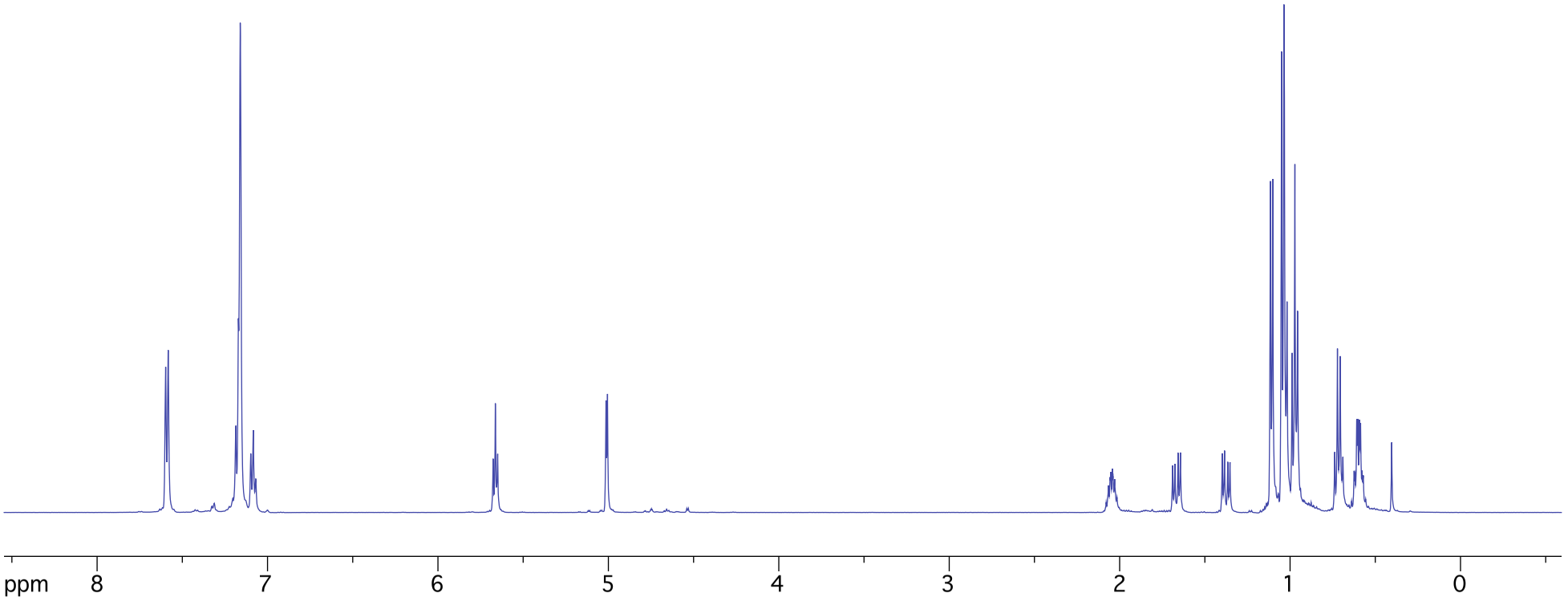
2-6-1f

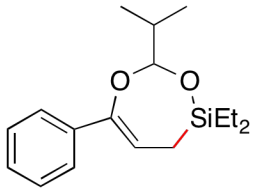


2-6-1f

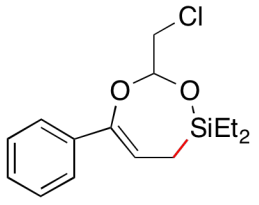


2-6-1g

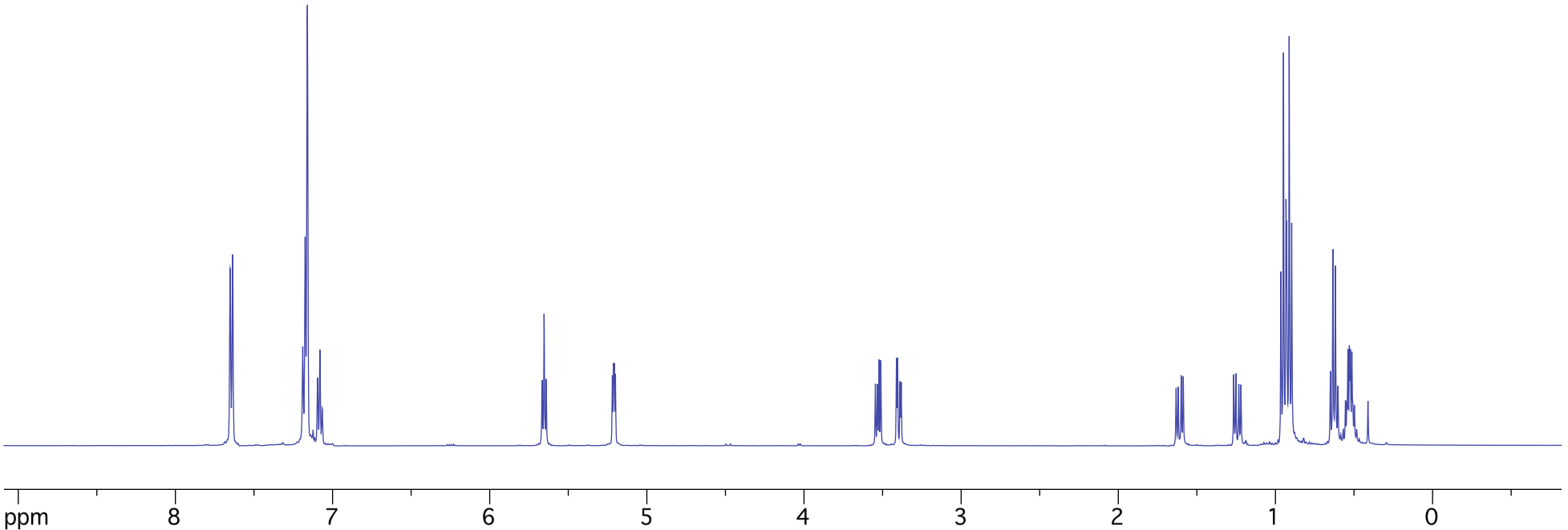


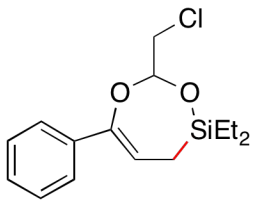


2-6-1g

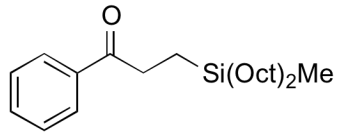


2-6-1h

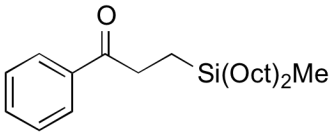




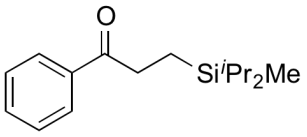
2-6-1h



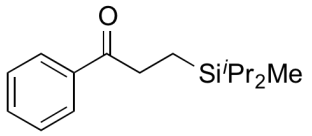
2-6-1b



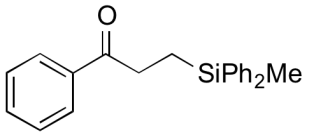
2-6-1b



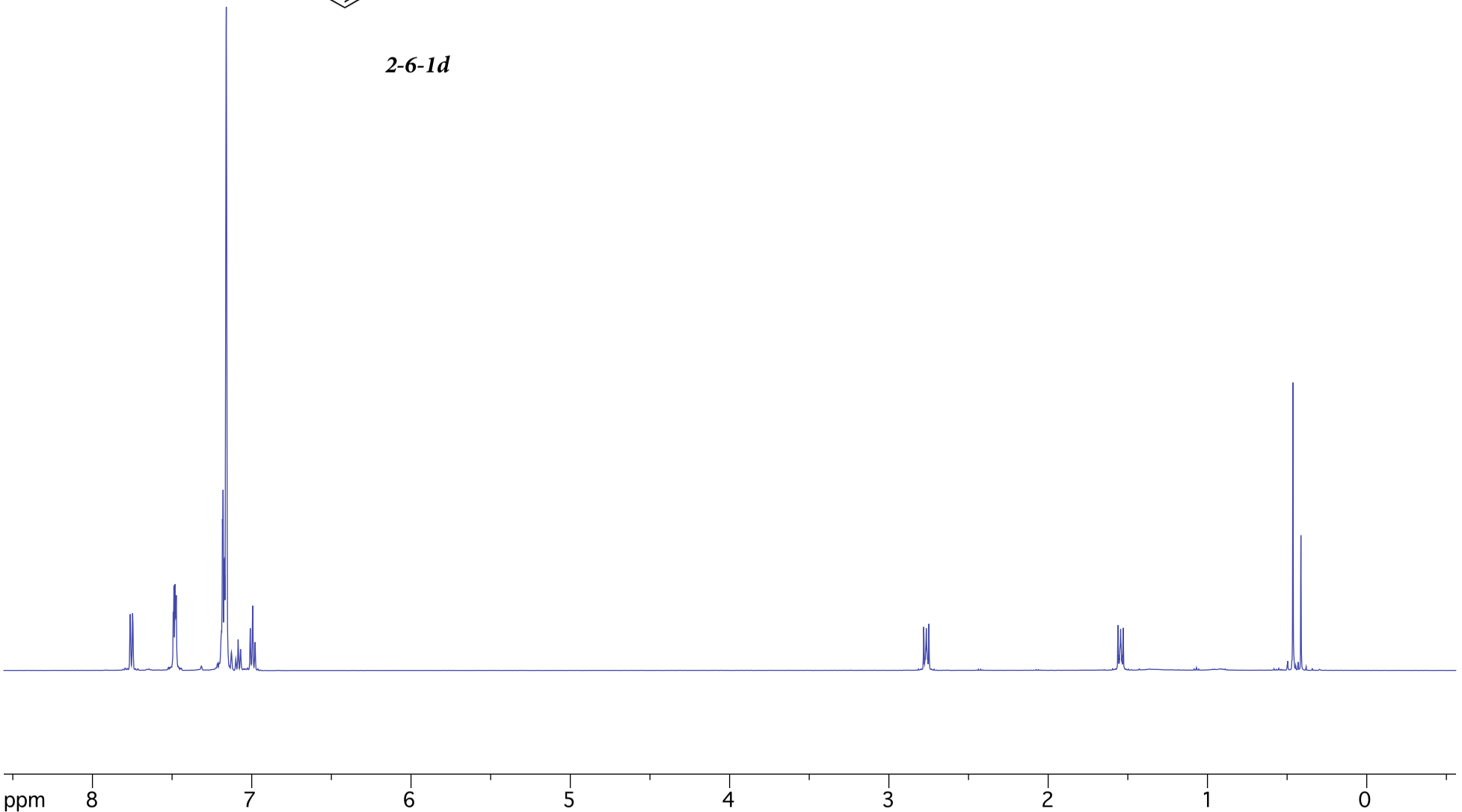
2-6-1c

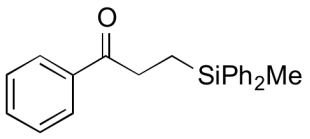


2-6-1c

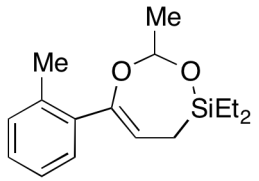


2-6-1d

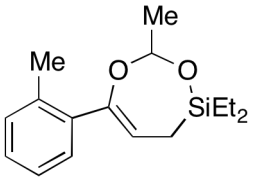




2-6-1d

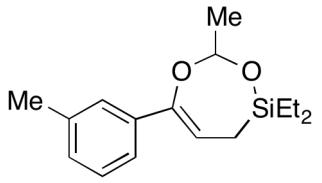


2-6-2

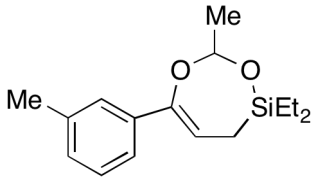


2-6-2

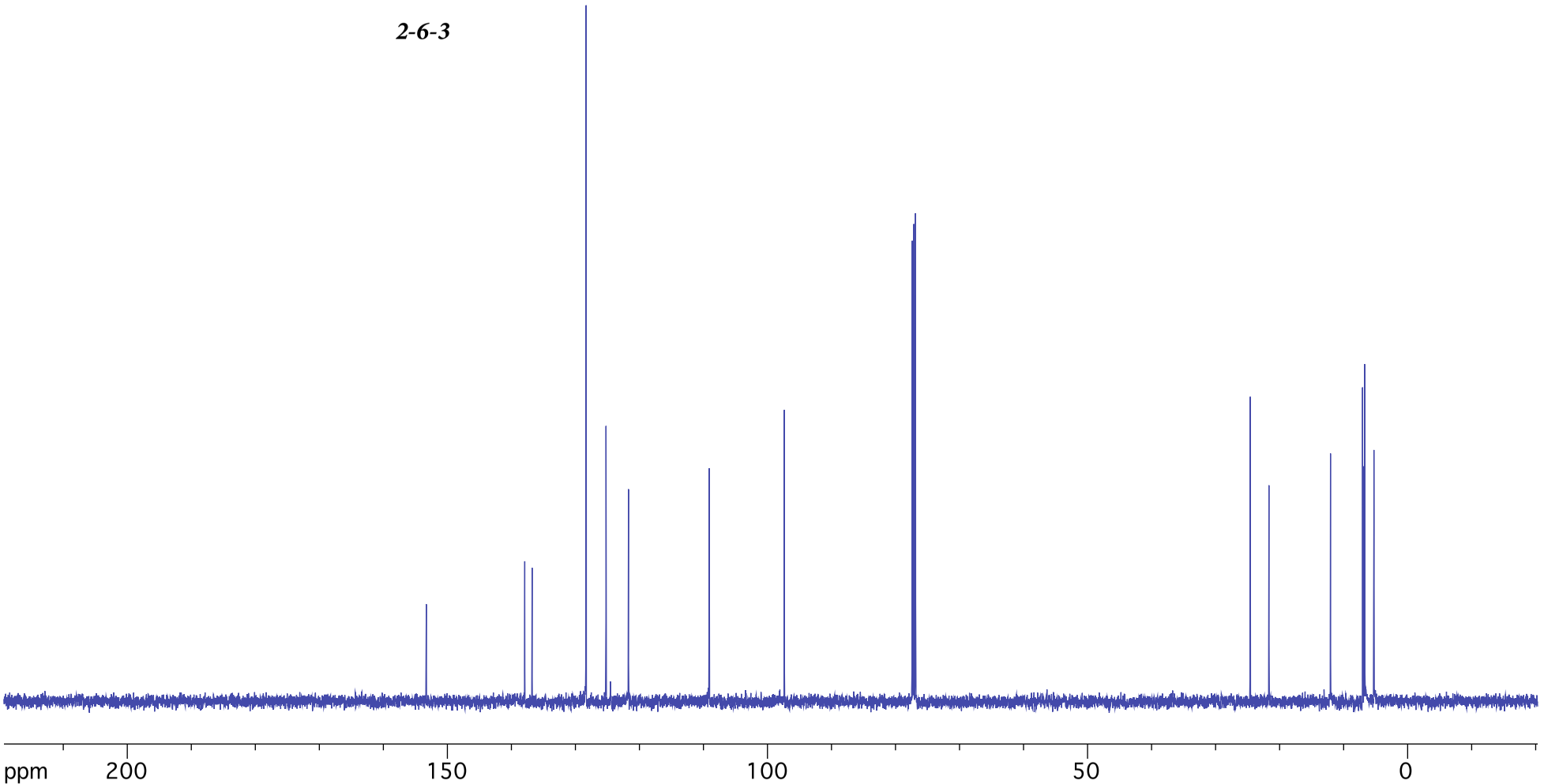
ppm 200 150 100 50 0

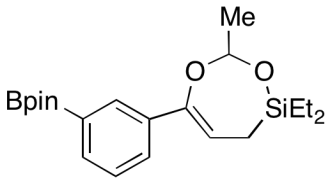


2-6-3

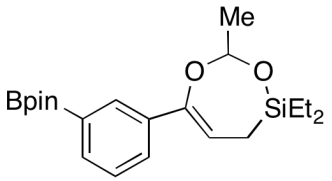


2-6-3

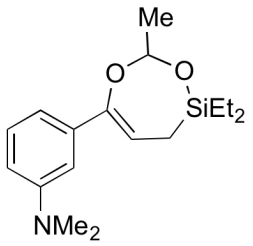




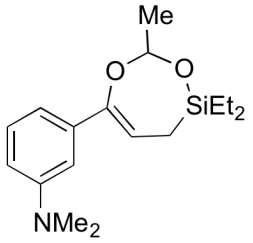
2-6-4



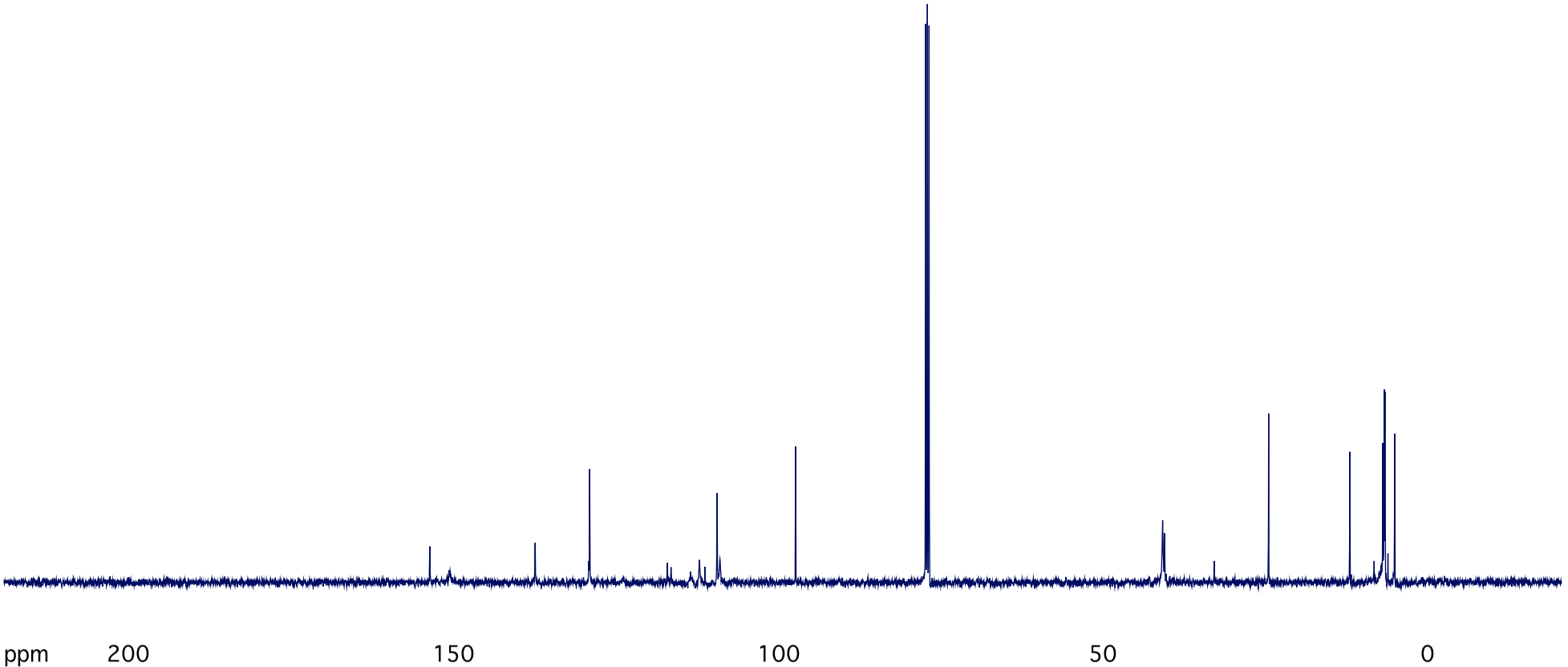
2-6-4

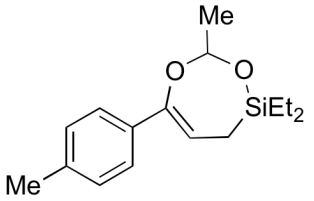


2-6-5

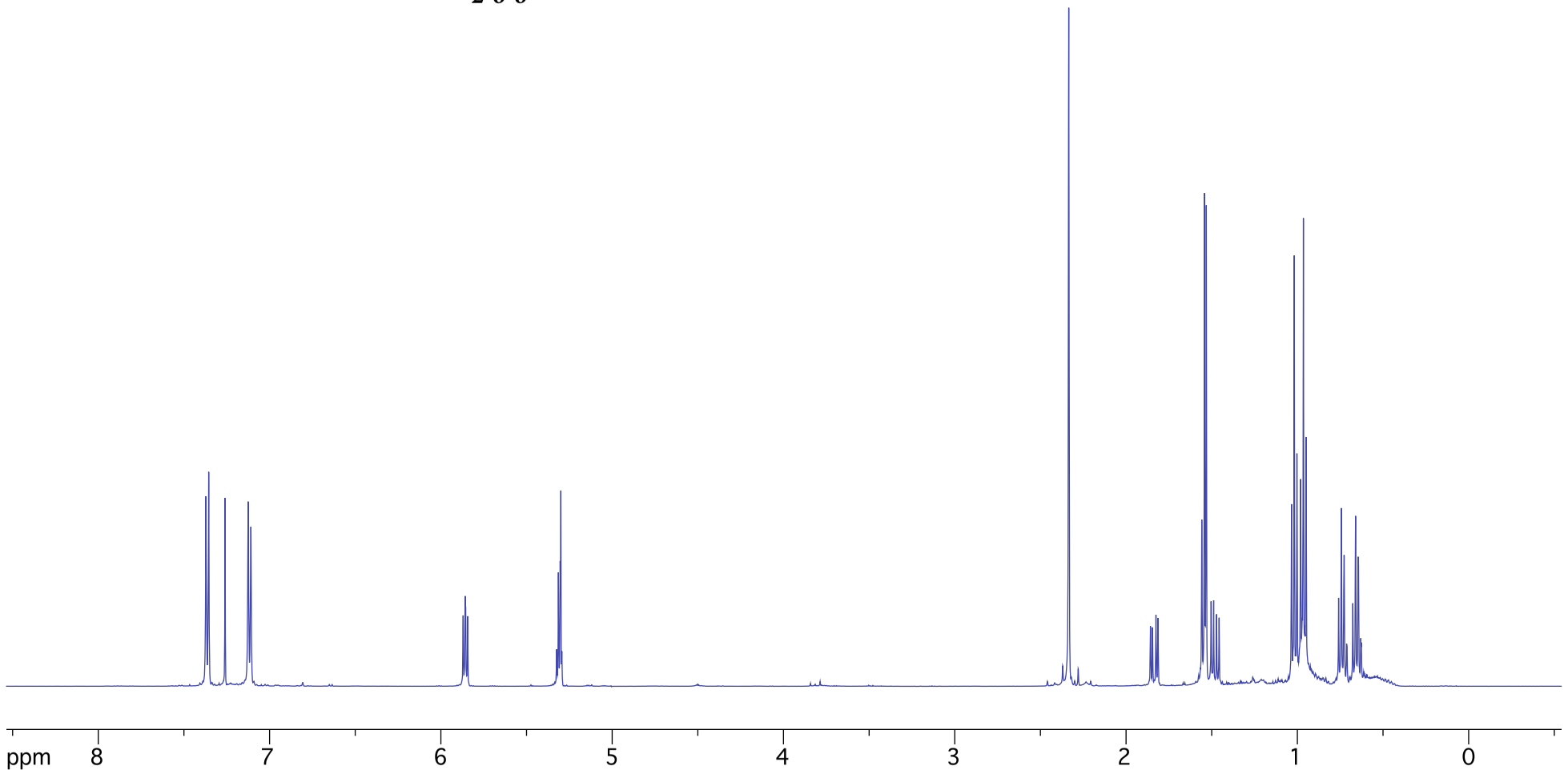


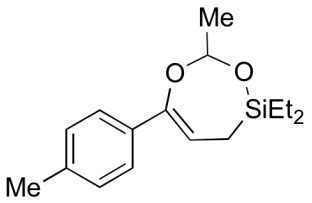
2-6-5



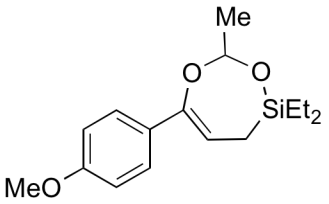


2-6-6

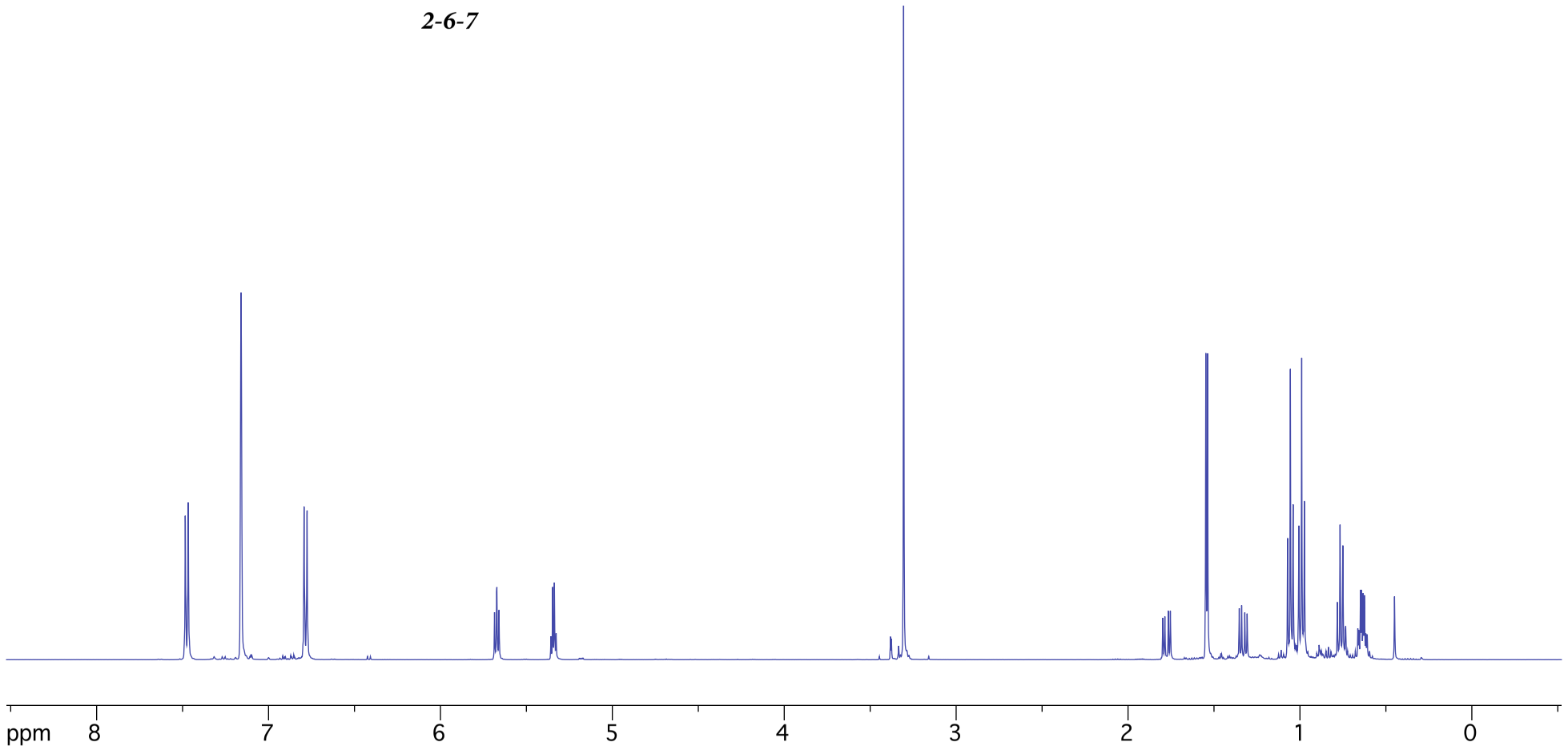


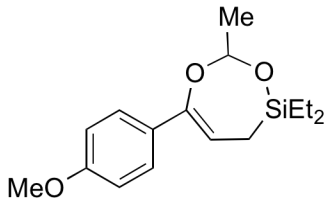


2-6-6

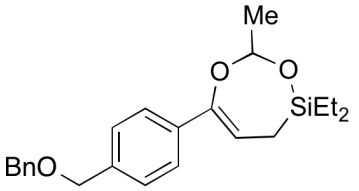


2-6-7

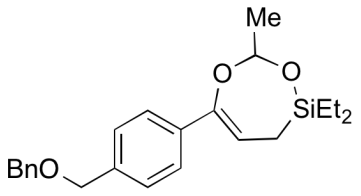




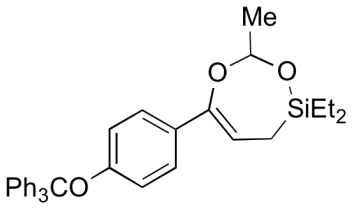
2-6-7



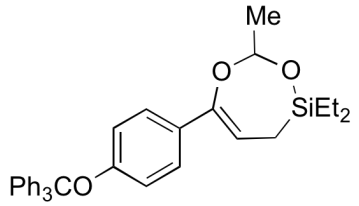
2-6-8



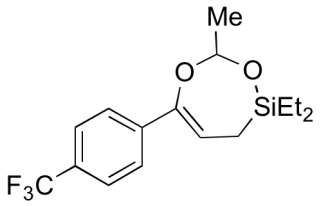
2-6-8



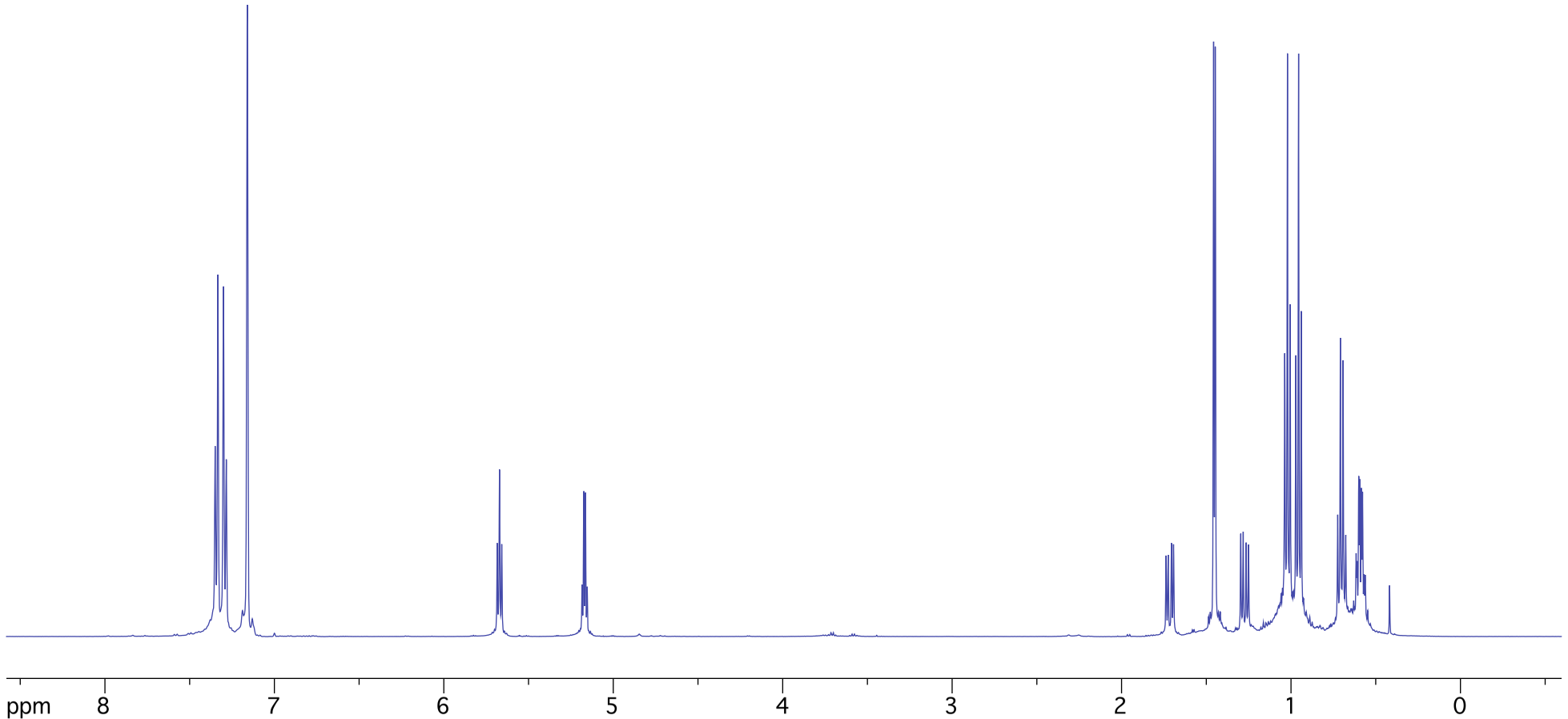
2-6-9

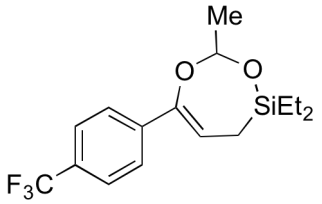


2-6-9

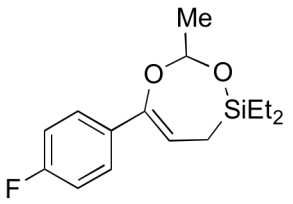


2-6-10

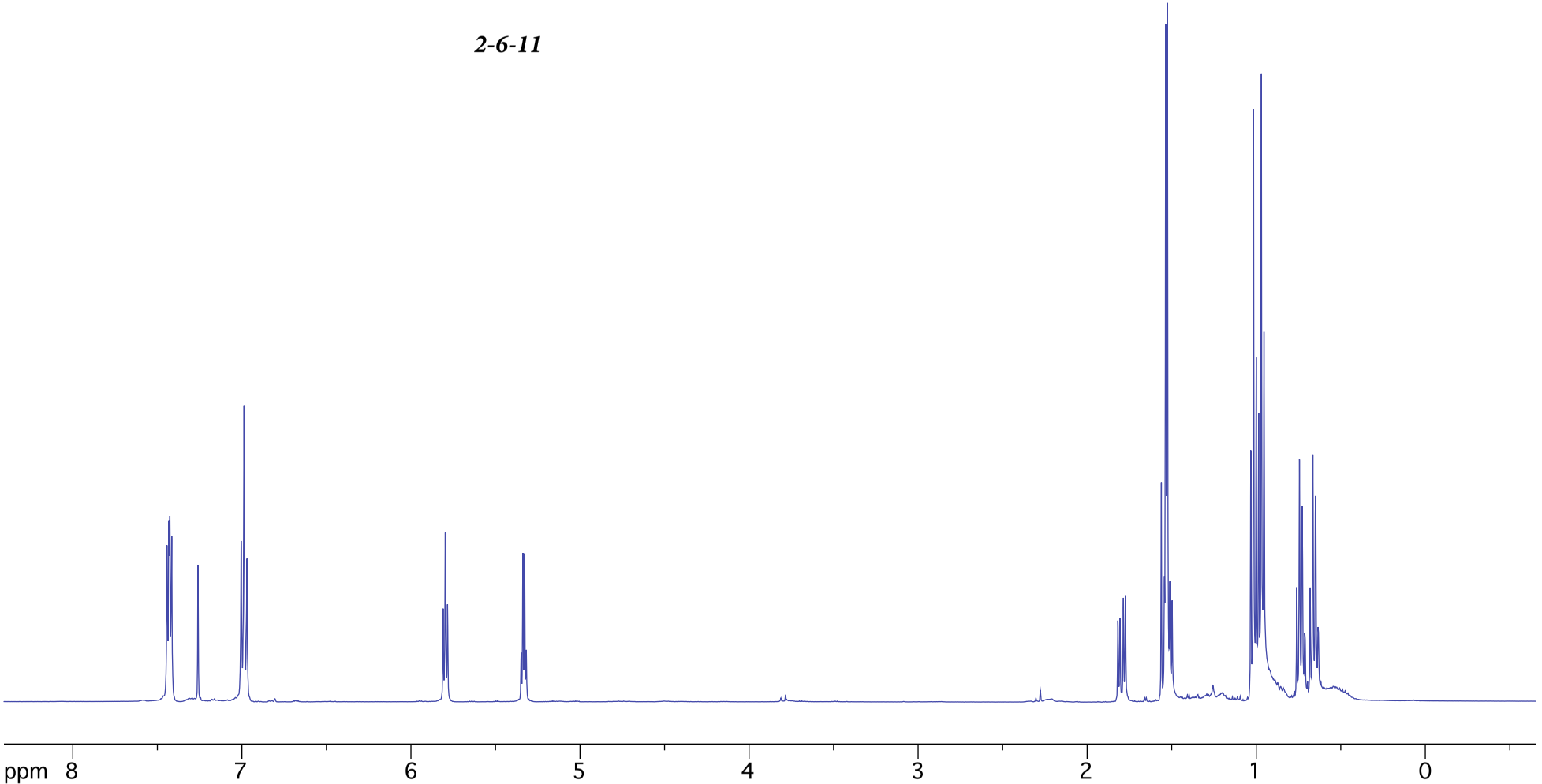


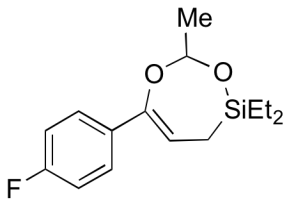


2-6-10

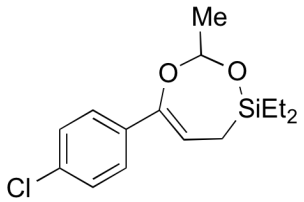


2-6-11

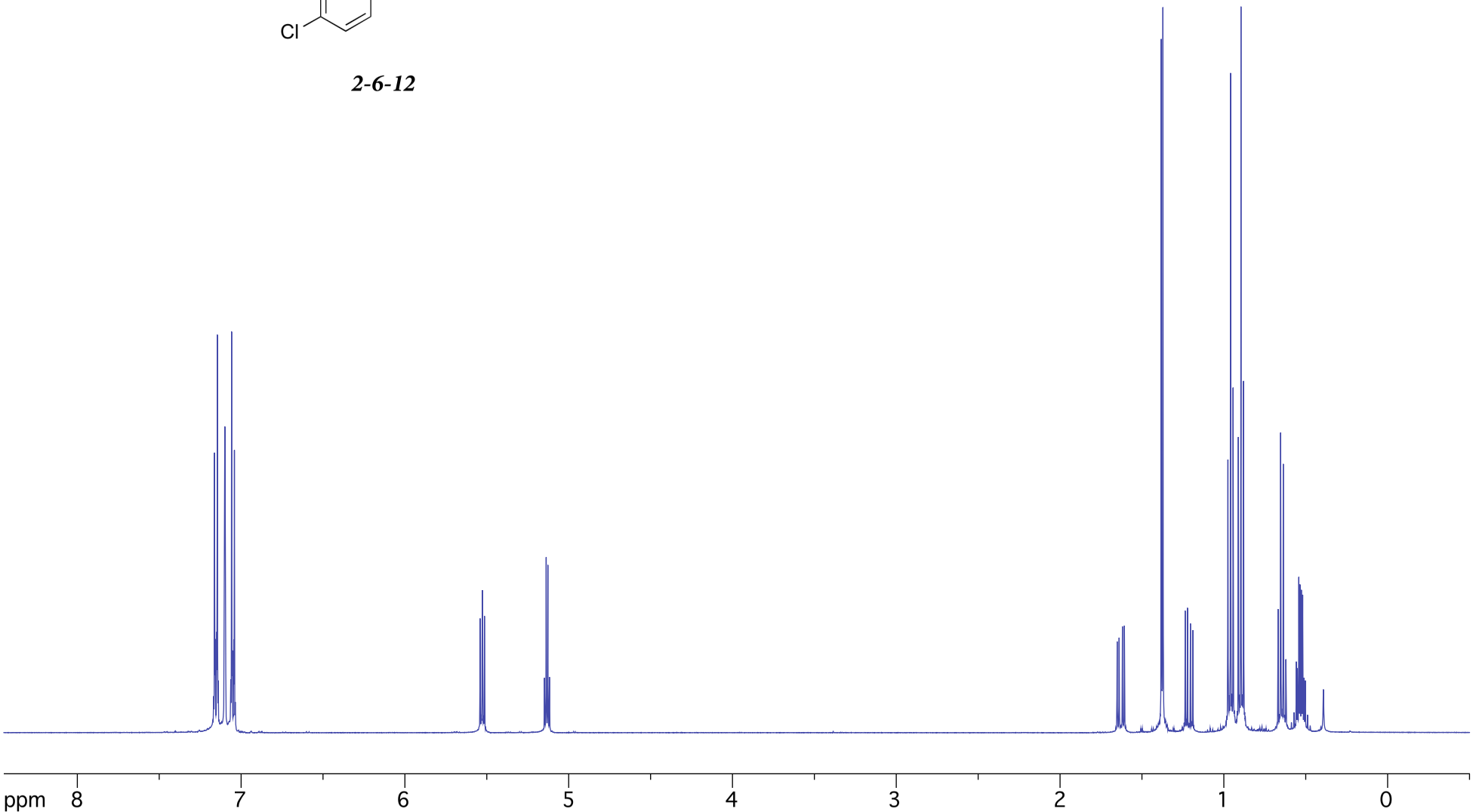


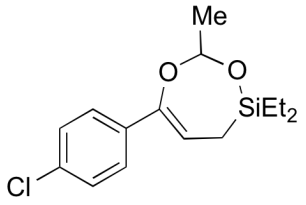


2-6-11

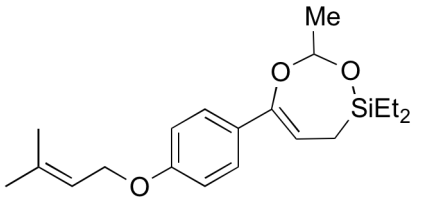


2-6-12

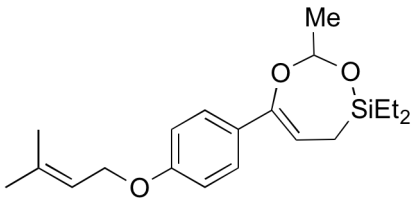




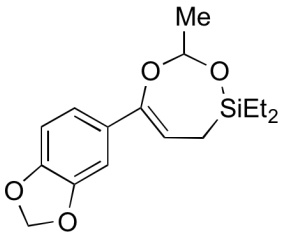
2-6-12



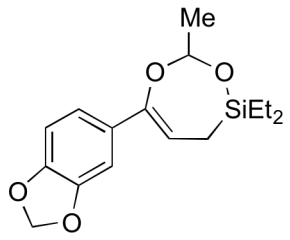
2-6-13



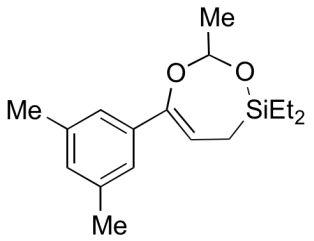
2-6-13



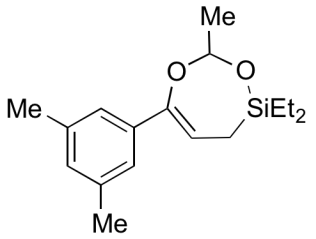
2-6-14



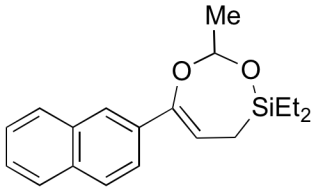
2-6-14



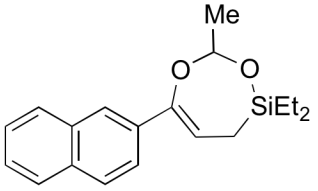
2-6-15



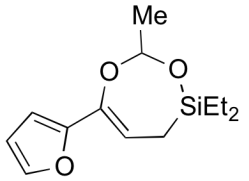
2-6-15



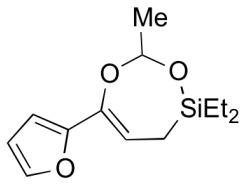
2-6-16



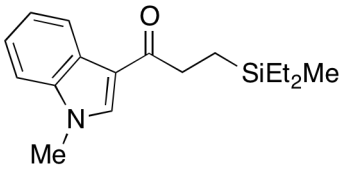
2-6-16



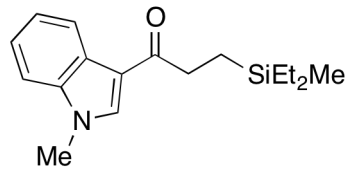
2-6-17



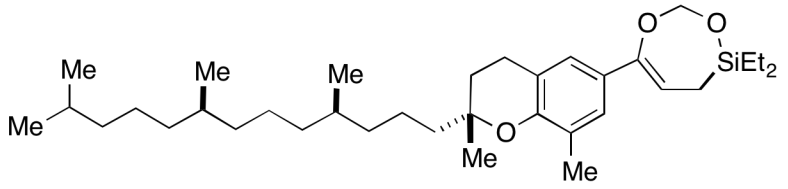
2-6-17



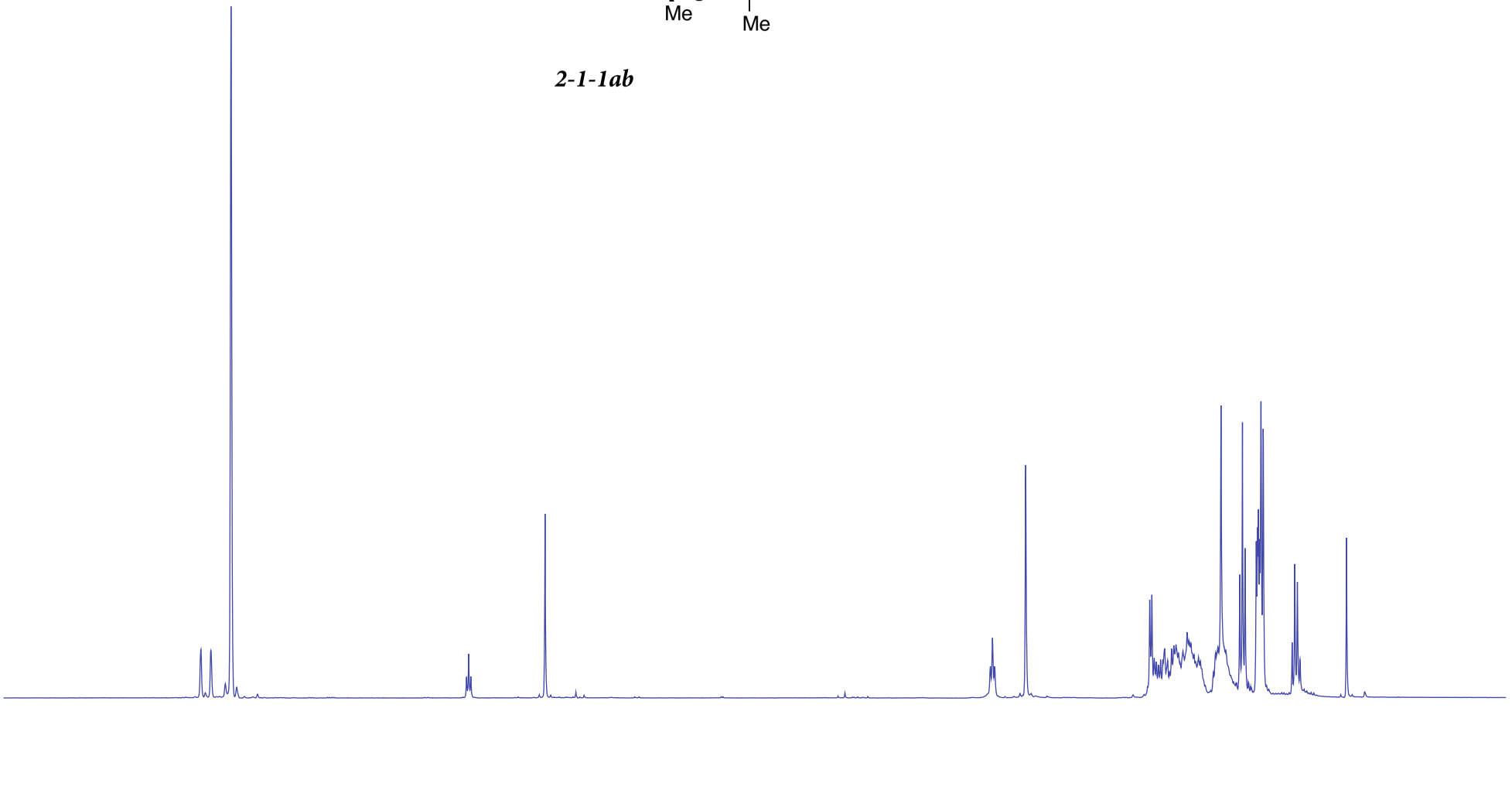
2-6-1aa

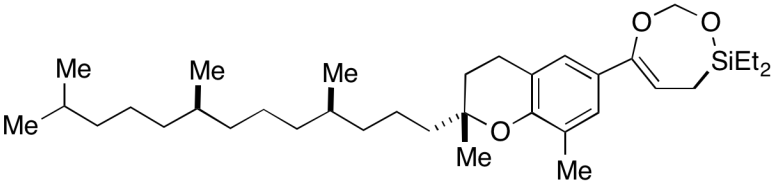


2-6-1aa

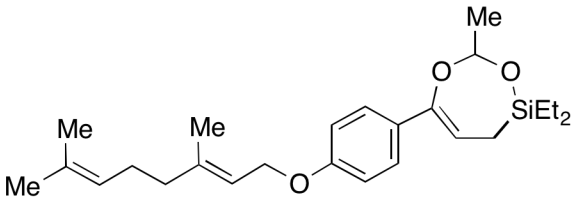


2-1-1ab

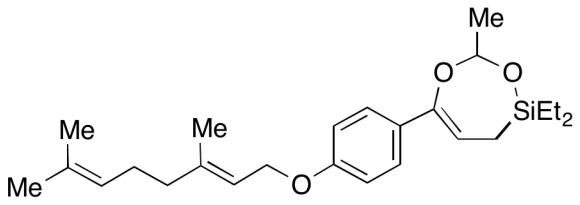




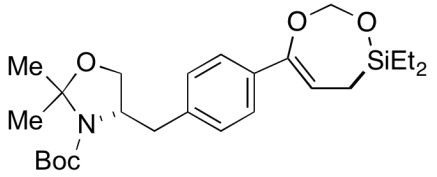
2-1-1ab



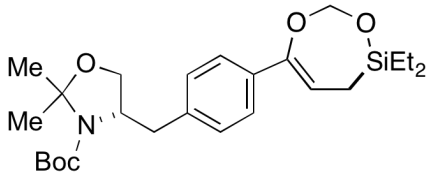
2-1-1ac



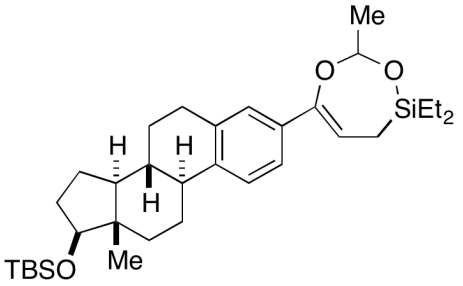
2-1-1ac



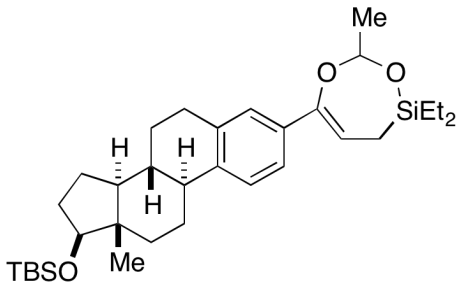
2-6-1ad



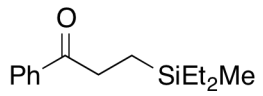
2-6-1ad



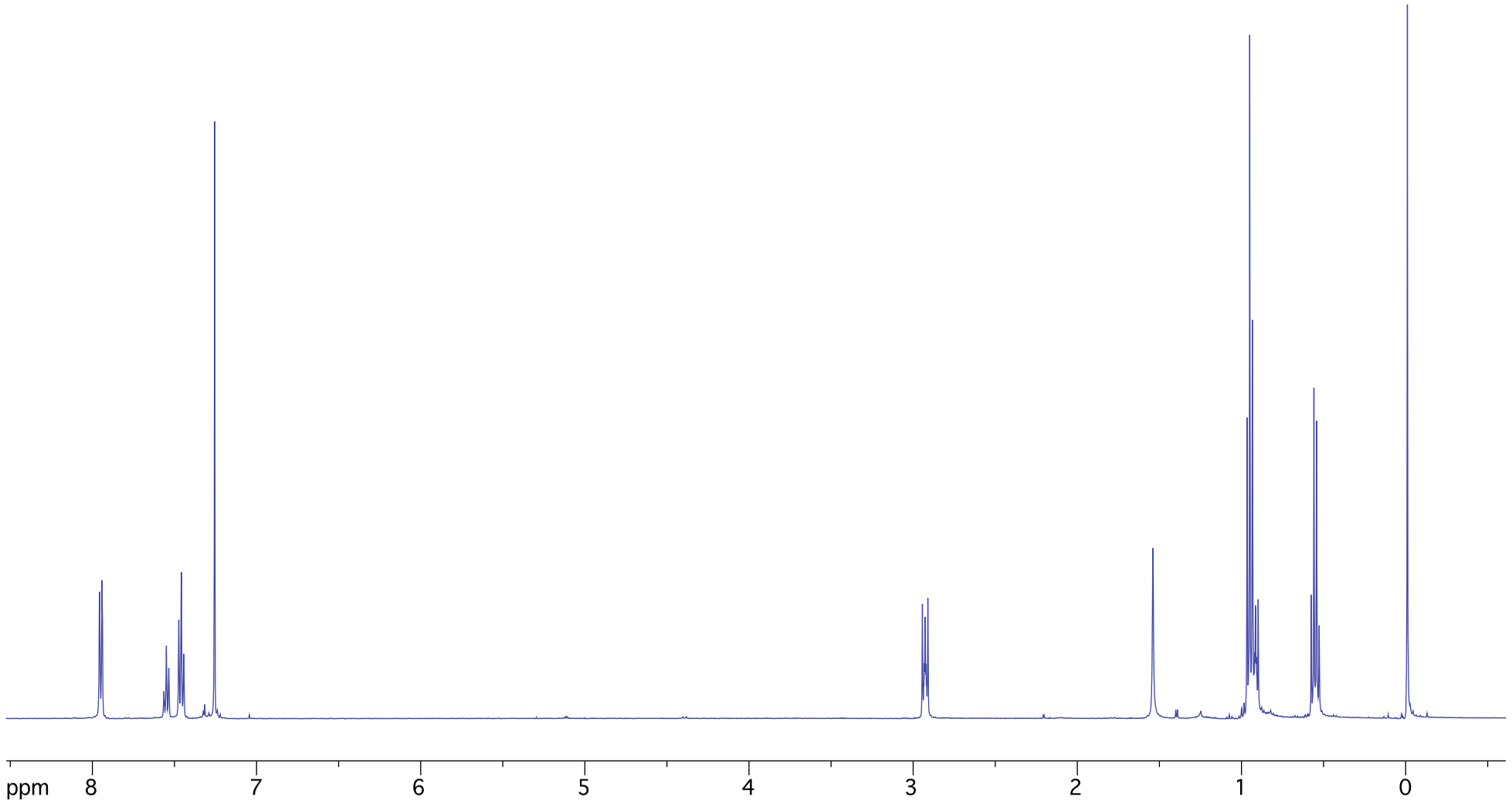
2-6-1ae

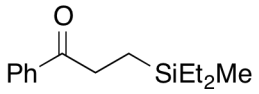


2-6-1ae

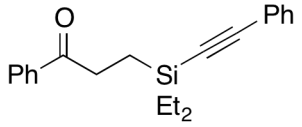


2-21

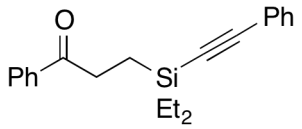




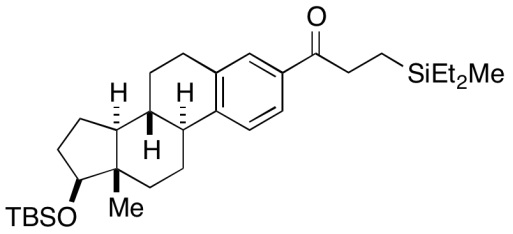
2-21



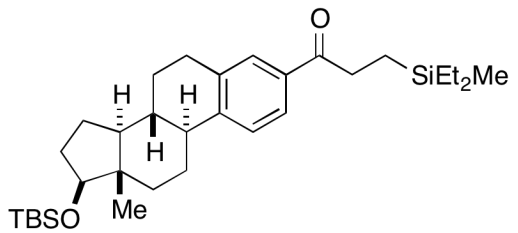
2-22



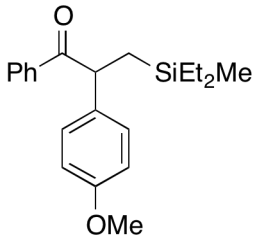
2-22



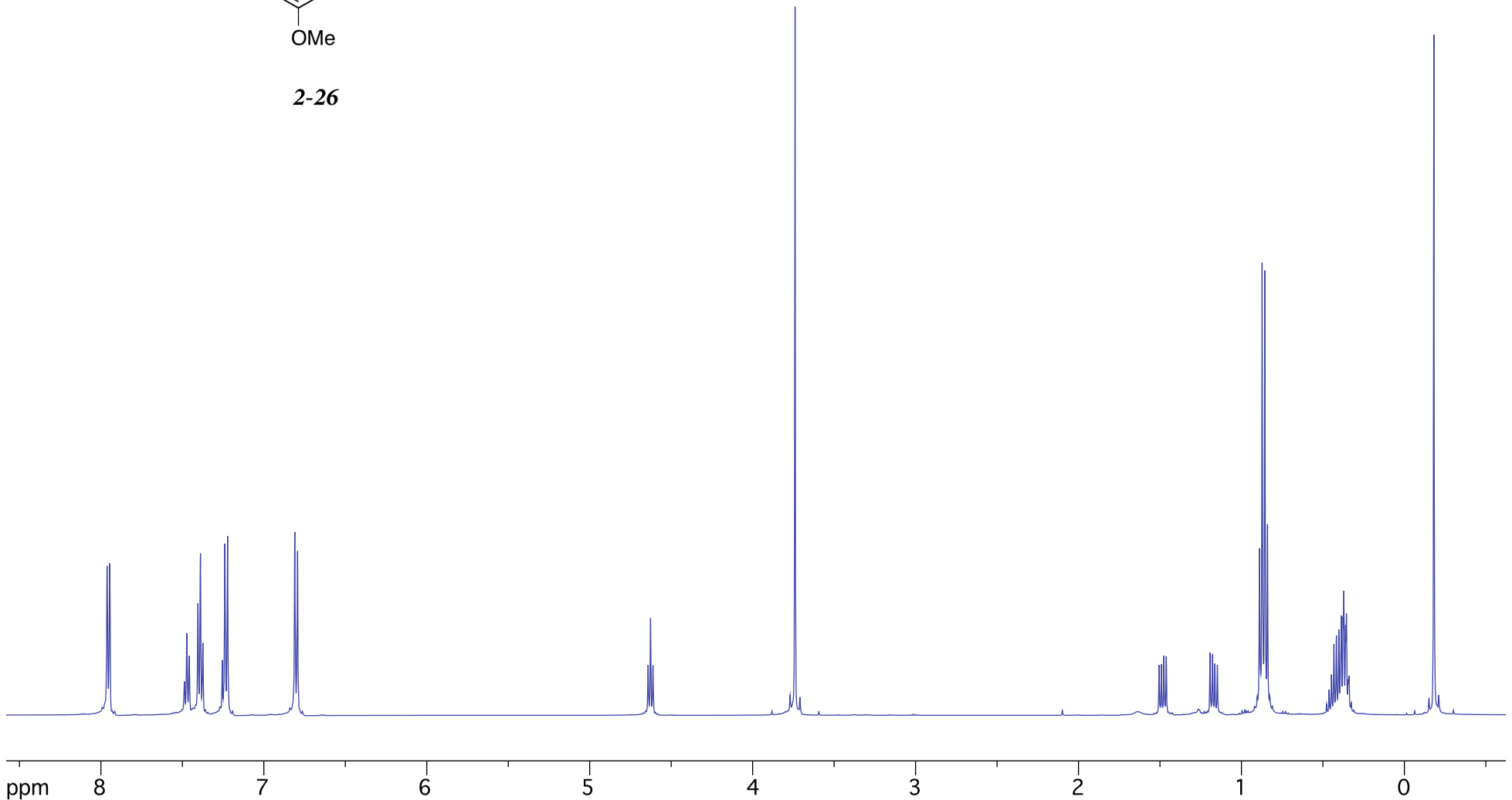
2-23

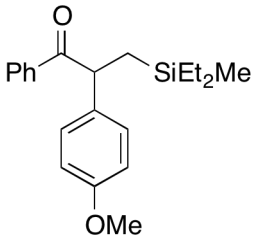


2-23

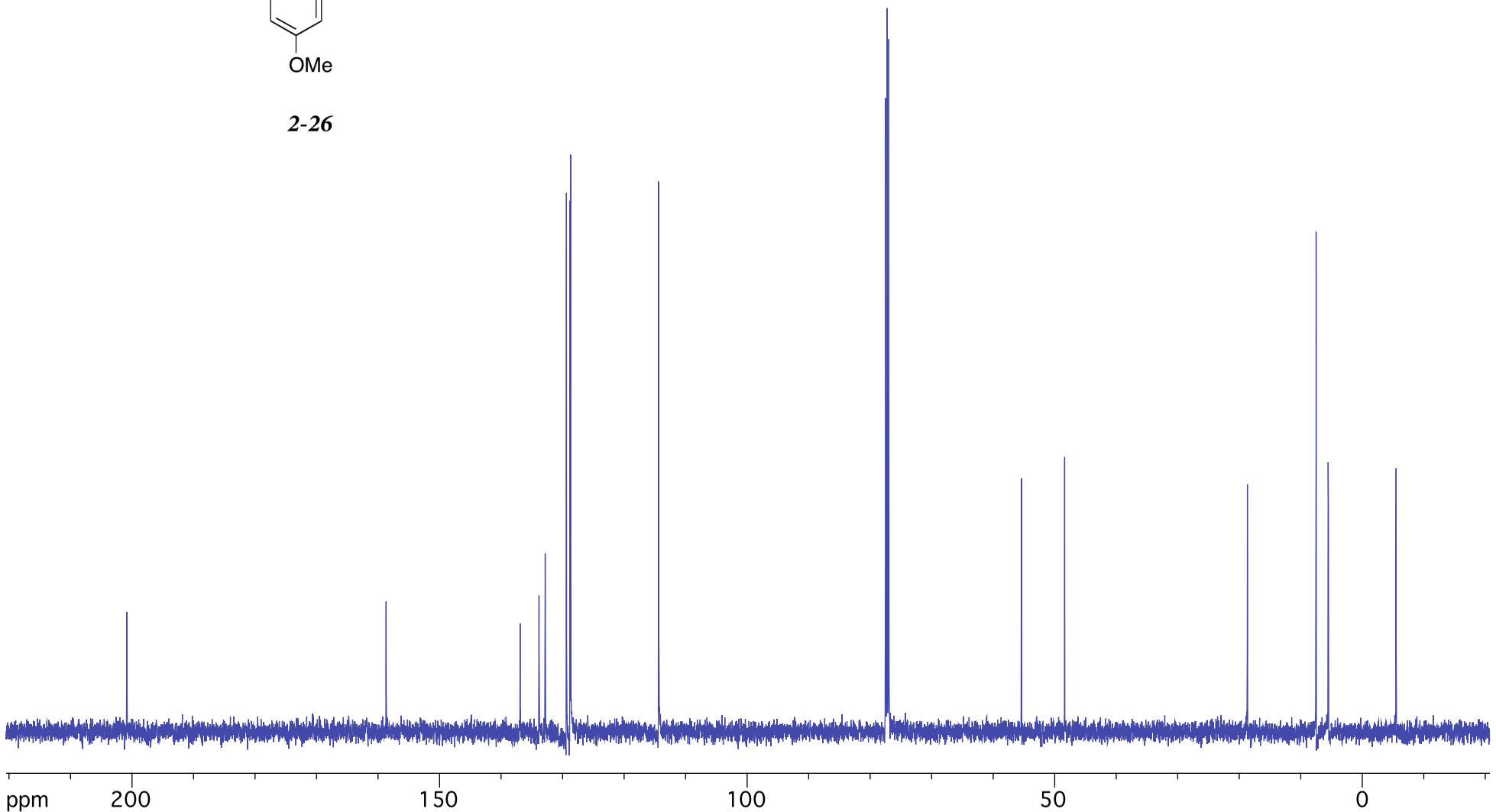


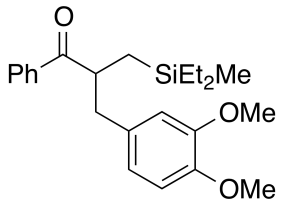
2-26



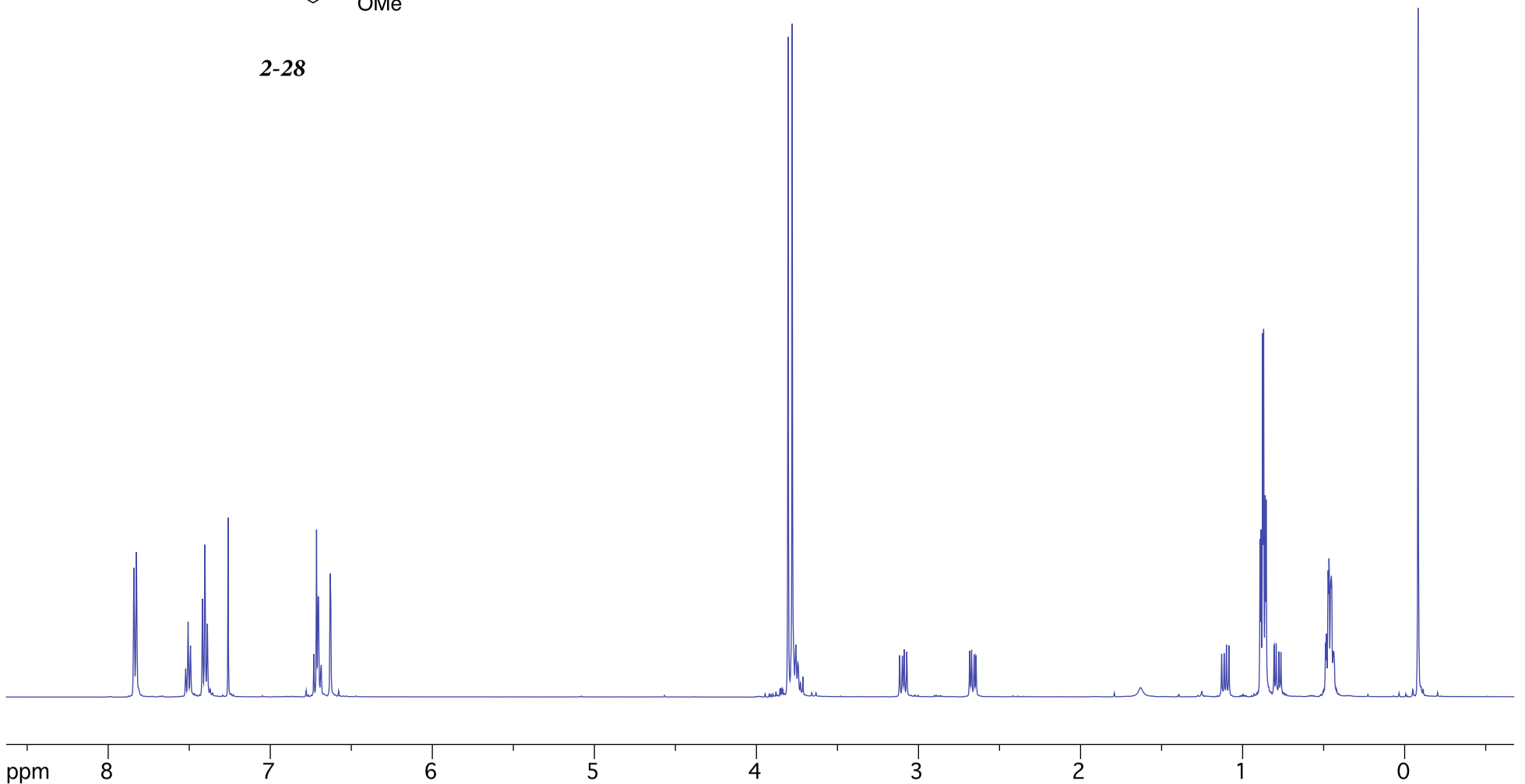


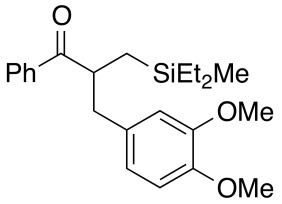
2-26



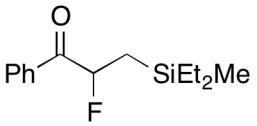


2-28

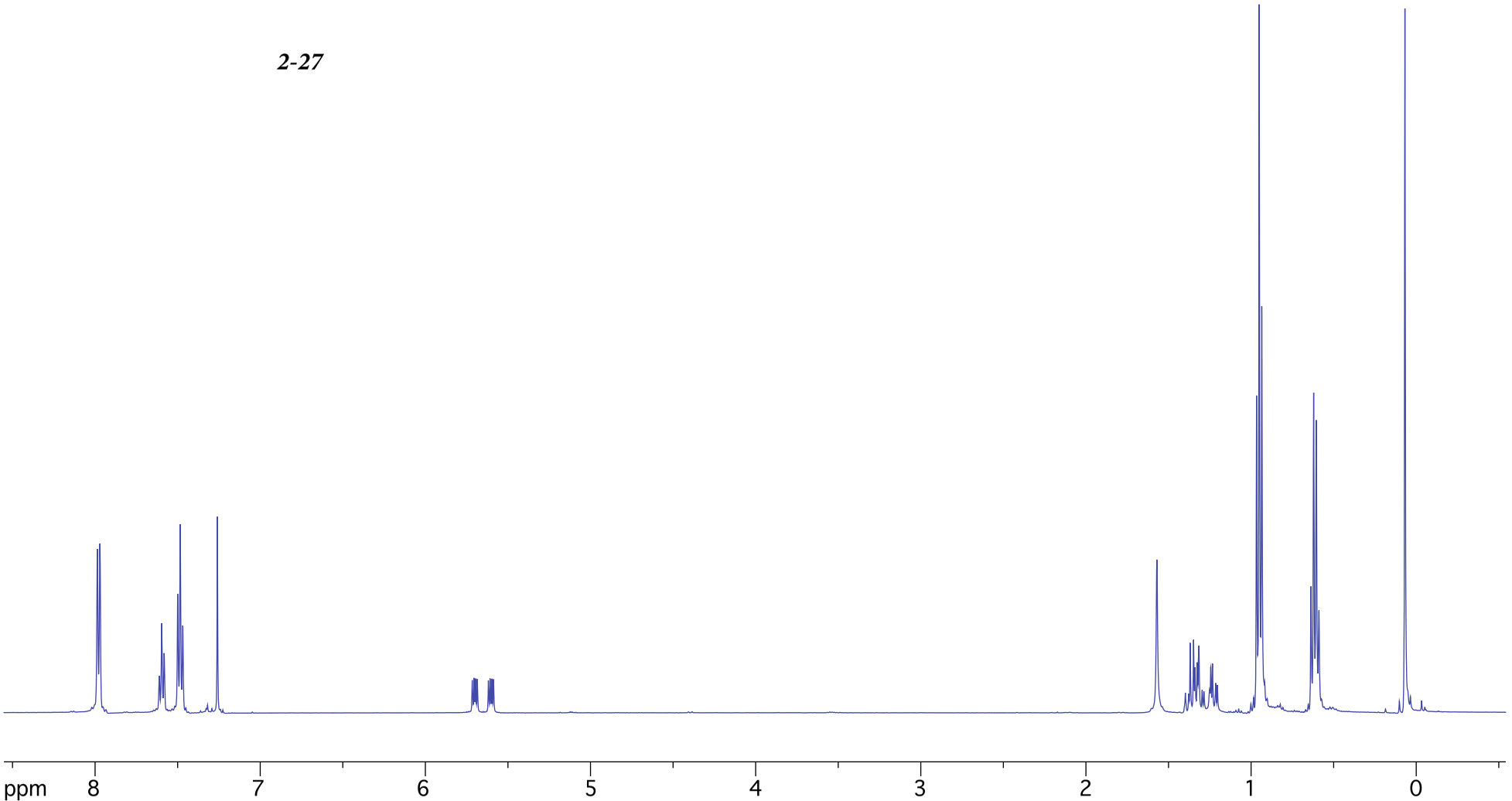


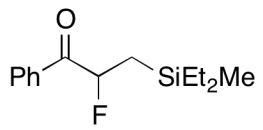


2-28

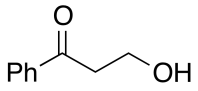


2-27

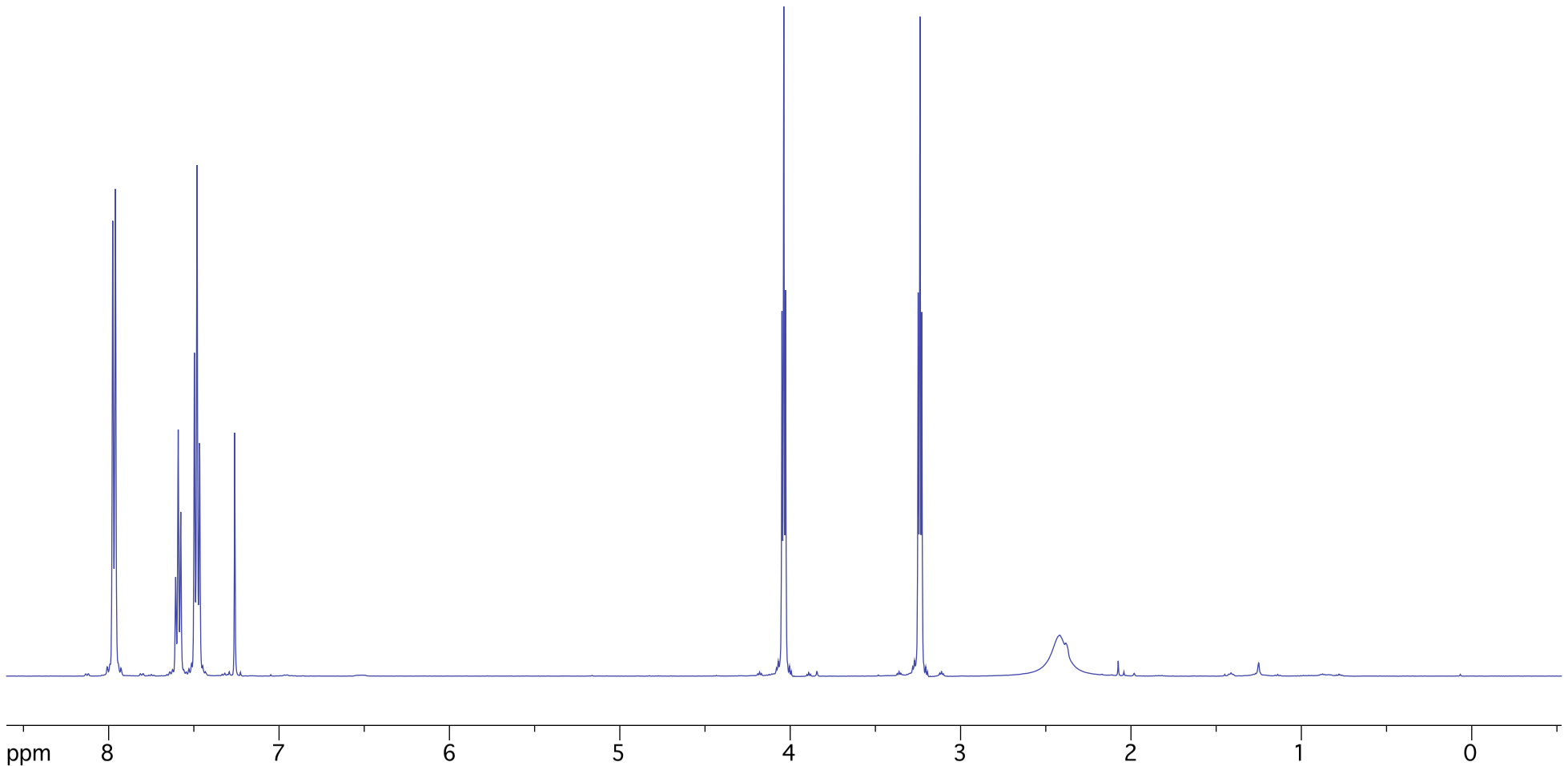


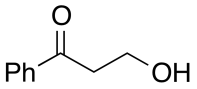


2-27

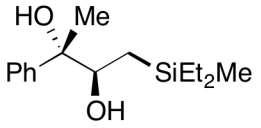


2-29

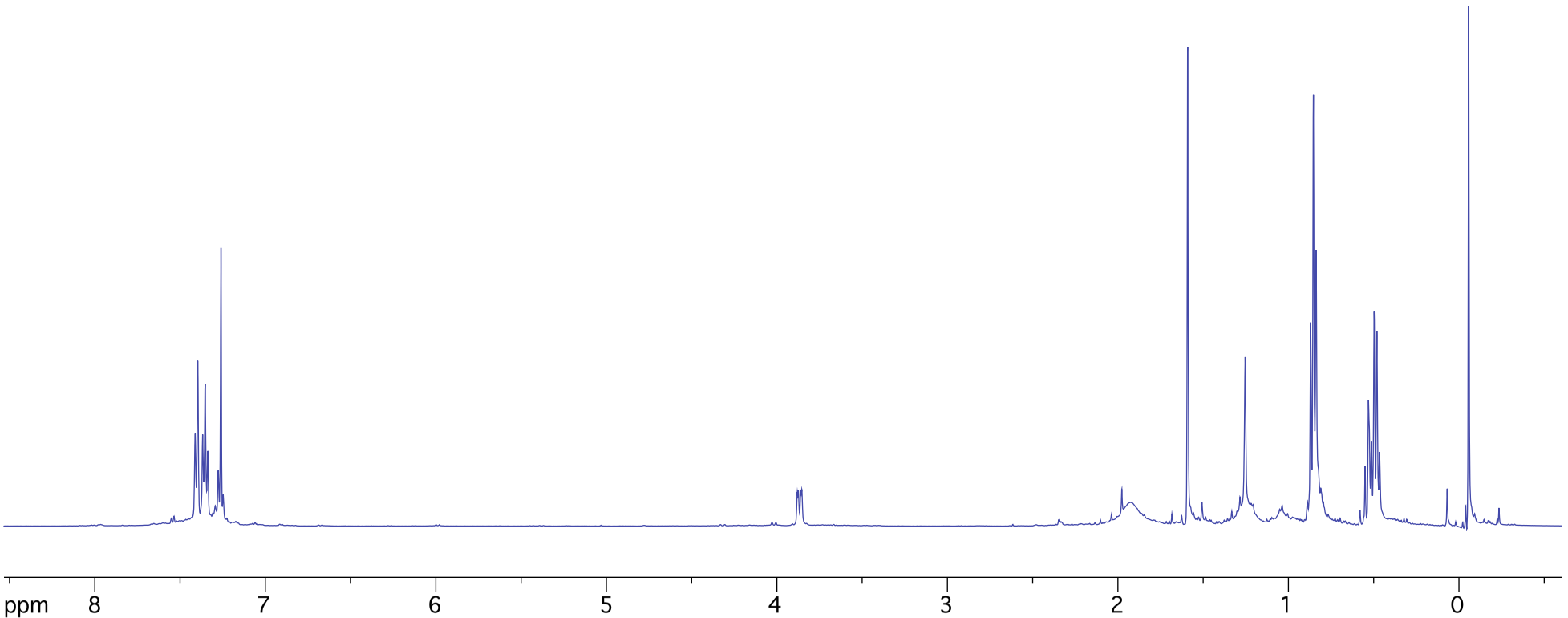


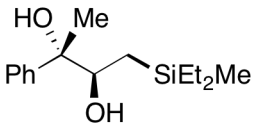


2-29

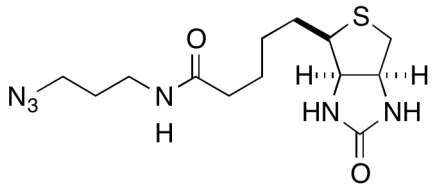


2-30

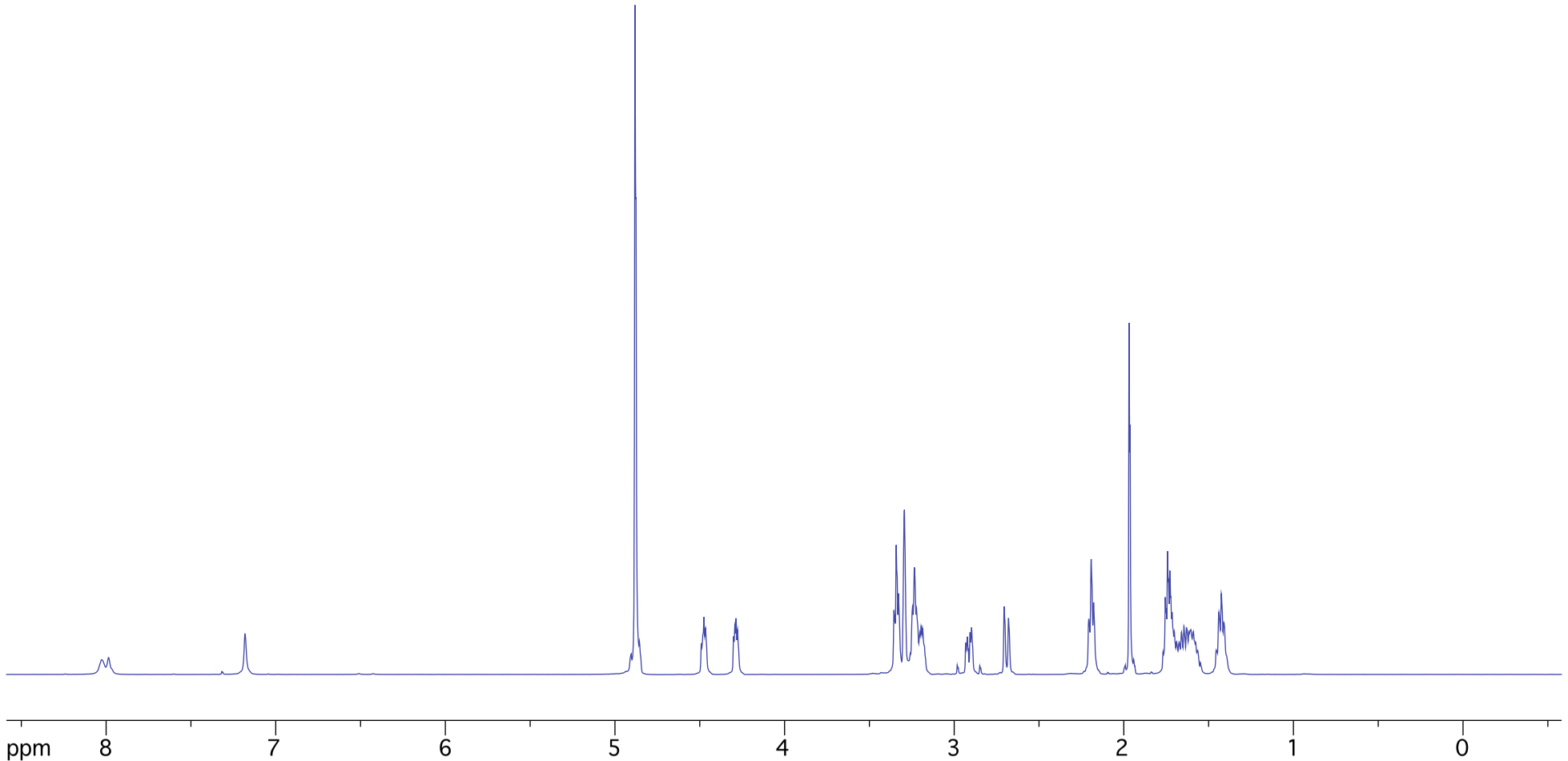


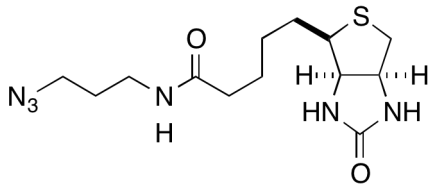


2-30

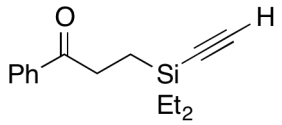


biotin-N3

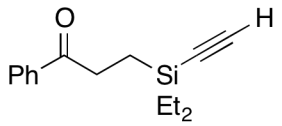




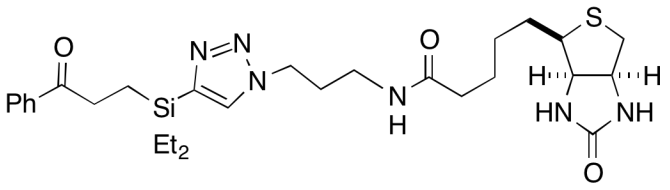
biotin-N3



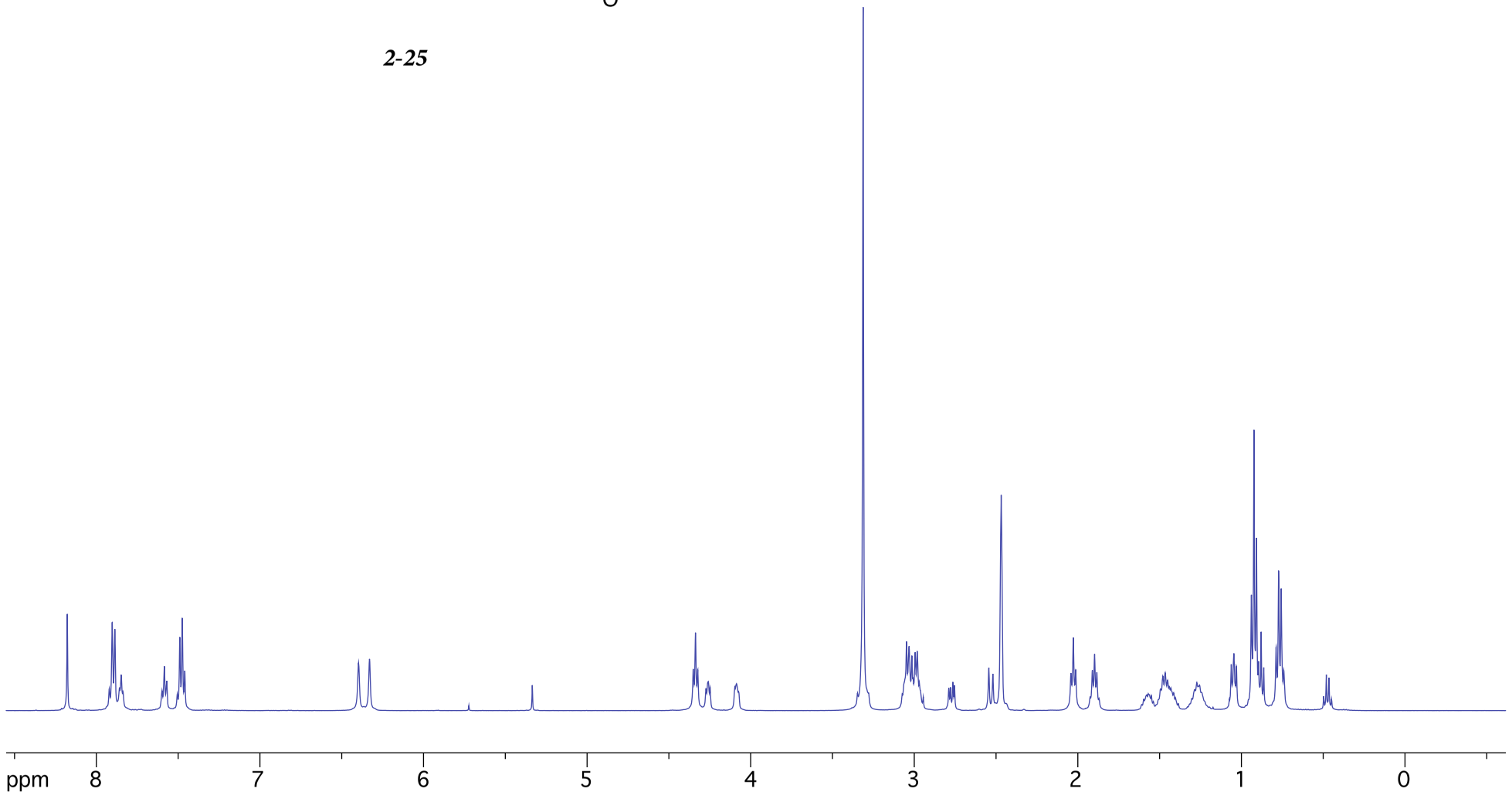
2-24

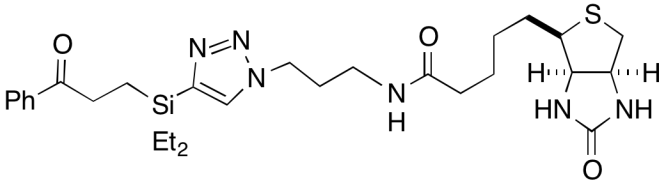


2-24



2-25





2-25

Biographical Information

Thirupataiah Avullala earned a Bachelor of Science in Chemistry from Osmania University, located in Hyderabad, TG, India in 2005. He got his Master of Science in Chemistry with specialization in Organic Chemistry form the Indian Institute of Technology Bombay in 20011. He worked as a research assistant in chemical engineering at Indian Institute of Technology Bombay for one year. In 2014, Thirupataiah Avullala his doctoral studies under the supervision of Dr. Junha Jeon at the Univeristy of Texas at Arlington (UTA). Thirupataiah has worked on various projects with emphasis on catalytic C–C activation reactions. Thirupataiah plans to continue his career in industry after receiving his degree from UTA.