Alkali metal hydroxide–catalyzed C(*sp*)–H bond silylation

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Table of Contents

General information.

Unless otherwise stated, reactions were performed in oven-dried brand-new Fisherbrand scintillation vials in a nitrogen filled glove box or in flame-dried Schlenk flasks under argon connected on a Schlenk line using dry, degassed solvents and brand-new stirring bars. Solvents were dried by passage through an activated alumina column under argon.[1] Reaction progress was monitored by thin-layer chromatography (TLC) or GC-FID analyses. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, phosphomolybdic acid, or $KMnO_4$ staining. Silicycle SiliaFlash P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. ^1H NMR spectra were recorded on a Varian Inova 500 MHz in $CDCl_3$ or THF-d_8 and are reported relative to residual solvent peak at δ 7.26 ppm or δ 3.58 ppm respectively. ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (126 MHz) in $CDCl_3$ or THF-d_8 and are reported relative to residual solvent peak at δ 77.16 ppm or δ 67.21 ppm respectively. Data for ^1H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septet, m = multiplet, br s = broad singlet, br d = broad doublet, app = apparent. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). GC-FID analyses were obtained on an Agilent 6890N gas chromatograph equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). GC-MS analyses were obtained on an Agilent 6850 gas chromatograph equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). High resolution mass spectra (HRMS) were acquired from the California Institute of Technology Mass Spectrometry Facility. Note that the calculated mass of the quasi-molecular ion does not take into account the loss of the electron mass. ICP-MS analysis was conducted at the California Institute of Technology Mass Spectrometry Facility.

Silanes were purchased from Aldrich and distilled before use. KO*t*-Bu was purchased from Aldrich (sublimed grade, 99.99% trace metals basis) and used directly. KOH was purchased from Aldrich (semiconductor grade, pellets, 99.99% trace metals basis) and was pulverized (mortar and pestle) and heated (150 °C) under vacuum for 24 h prior to use.

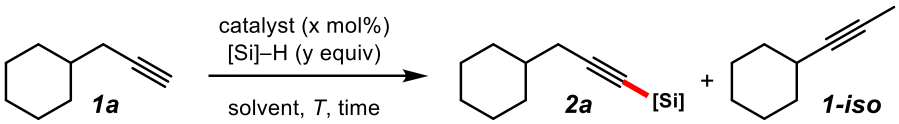
NaOH was purchased from Aldrich (semiconductor grade, pellets, 99.99% trace metals basis) and was pulverized (mortar and pestle) and heated (150 °C) under vacuum prior to use. Alkyne substrates were purchased from Aldrich, TCI, or Acros and used as received (unless noted).

Part I. Reaction optimizations, trace metal analysis, and preliminary mechanistic investigations.

1. Reaction optimization.

Procedure for reaction condition optimization: In a nitrogen-filled glovebox, catalyst and alkyne **1a** (0.1 mmol, 1 equiv) were added to a 2 dram scintillation vial equipped with a magnetic stirring bar. Next, hydrosilane and solvent (0.1 mL) were added. The vial was sealed and the mixture was stirred at the indicated temperature for the indicated time. The vial was then removed from the glovebox, diluted with diethyl ether (1 mL), and concentrated under reduced pressure. The yield was determined by ^{1}H NMR or GC analysis of the crude mixture using an internal standard.

Table 1. Condition optimization of direct C(*sp*)–H silylation.



entry	catalyst	[Si]–H	solvent	*T* (°C)	time (h)	yield *2a*^{1}	yield *1-iso*^{1}
1	KO*t*-Bu (20 mol%)	Et_3SiH	–	85	72	**22%**	**60%**
2	KO*t*-Bu (20 mol%)	Et_3SiH	THF	85	72	**94%**	**1%**
3	KO*t*-Bu (20 mol%)	Et_3SiH	1,4-dioxane	85	72	**88%**	–
4	KO*t*-Bu (20 mol%)	Et_3SiH	DME	85	72	**>99%**	–
5	KO*t*-Bu (20 mol%)	Et_3SiH	MTBE	85	72	**30%**	**53%**
6	KO*t*-Bu (20 mol%)	Et_3SiH	toluene	85	72	**27%**	**59%**
7	KO*t*-Bu (20 mol%)	Et_3SiH	CyMe	85	72	**15%**	**66%**
8	KO*t*-Bu (20 mol%)	Et_3SiH	Pentane	85	72	**13%**	**74%**
9	KO*t*-Bu (20 mol%)	Et_3SiH	Mesitylene	85	72	**26%**	**56%**
10	KO*t*-Bu (20 mol%)	Et_3SiH	DCM	85	72	–	–
11	KO*t*-Bu (20 mol%)	Et_3SiH	Et_2O	85	72	**23%**	**61%**
12	KO*t*-Bu (20 mol%)	Et_3SiH	2-Me-THF	85	72	**48%**	**51%**
13	KO*t*-Bu (40 mol%)	Et_3SiH	DME	85	48	**89%**	–
14	KO*t*-Bu (20 mol%)	Et_3SiH	DME	85	48	**99%**	–
15	KO*t*-Bu (10 mol%)	Et_3SiH	DME	85	48	**>99%**	–
16	KO*t*-Bu (5 mol%)	Et_3SiH	DME	85	48	**99%**	**<1%**
17	KO*t*-Bu (1 mol%)	Et_3SiH	DME	85	48	**97%**	**2%**
18	KO*t*-Bu (10 mol%)	Et_3SiH	DME	25	48	**7%**	**63%**
19	KO*t*-Bu (10 mol%)	Et_3SiH	DME	55	48	**59%**	**30%**

entry	catalyst	[Si]–H	solvent	*T* (°C)	time (h)	yield *2a*[1]	yield *1-iso*[1]
20	KH (20 mol%)	Et_3SiH	DME	85	72	**99%**	–
21	KHMDS (20 mol%)	Et_3SiH	DME	85	72	**99%**	**<1%**
22	NaO*t*-Bu (20 mol%)	Et_3SiH	DME	85	72	**51%**	**40%**
23	LiO*t*-Bu (20 mol%)	Et_3SiH	DME	85	72	**<1%**	**5%**
24	DABCO (20 mol%)	Et_3SiH	DME	85	72	**<1%**	–
25	NaOEt (20 mol%)	Et_3SiH	DME	85	72	**82%**	**<1%**
26	KOEt (20 mol%)	Et_3SiH	DME	85	72	**99%**	**<1%**
27	NaOAc (20 mol%)	Et_3SiH	DME	85	72	**<1%**	–
28	KOAc (20 mol%)	Et_3SiH	DME	85	72	**<1%**	–
29	KOMe (20 mol%)	Et_3SiH	DME	85	72	**98%**	**<1%**
30	NaOMe (20 mol%)	Et_3SiH	DME	85	72	**95%**	**3%**
31	KO*t*-Amyl (20 mol%)	Et_3SiH	DME	85	72	**>99%**	**<1%**
32	KOH (20 mol%)	Et_3SiH	DME	85	72	**94%**	**<1%**
33	K_2CO_3 (20 mol%)	Et_3SiH	DME	85	72	**<1%**	–
34	Cs_2CO_3 (20 mol%)	Et_3SiH	DME	85	72	–	–
35	KF (20 mol%)	Et_3SiH	DME	85	72	**<1%**	–
36	KO*t*-Bu (10 mol%)	Et_3SiH	DME	85	24	**89%**	**9%**
37	KH (10 mol%)	Et_3SiH	DME	85	24	**87%**	**11%**
38	NaO*t*-Bu (10 mol%)	Et_3SiH	DME	85	24	**46%**	**2%**
39	LiO*t*-Bu (10 mol%)	Et_3SiH	DME	85	24	**<1%**	–
40	KOEt (10 mol%)	Et_3SiH	DME	85	24	**96%**	**2%**
41	NaOEt (10 mol%)	Et_3SiH	DME	85	24	**91%**	**<1%**
42	KOMe (10 mol%)	Et_3SiH	DME	85	24	**96%**	**4%**
43	NaOMe (10 mol%)	Et_3SiH	DME	85	24	**83%**	**<1%**
44	KO*t*-Amyl (10 mol%)	Et_3SiH	DME	85	24	**91%**	**6%**
45	KOH (10 mol%)	Et_3SiH	DME	85	24	**95%**	**3%**
46	NaOH (10 mol%)	Et_3SiH	DME	85	24	**98%**	–
47	LiOH (10 mol%)	Et_3SiH	DME	85	24	**3%**	–
48	Et_3N (10 mol%)	Et_3SiH	DME	85	48	**4%**	–
49	Pyridine(10 mol%)	Et_3SiH	DME	85	48	**1%**	–
50	KOH (10 mol%)	Et_3SiH (1.0 eq)	DME	85	48	**71%**	**21%**
51	KOH (10 mol%)	Et_3SiH (1.5 eq)	DME	85	48	**92%**	**6%**
52	KOH (10 mol%)	Et_3SiH (2.0 eq)	DME	85	48	**93%**	**6%**
53	KOH (10 mol%)	Et_3SiH (2.5 eq)	DME	85	48	**97%**	**2%**
54	KOH (10 mol%)	Et_3SiH (3.0 eq)	DME	85	48	**98%**	**1%**
55	KOH (10 mol%)	Et_3SiH (3.5 eq)	DME	85	48	**99%**	**1%**
56	KOH (10 mol%)	Et_3SiH (4.0 eq)	DME	85	48	**97%**	**2%**

[1] Yields determined by GC analysis of the crude reaction mixture using an internal standard.

The results from Table 1 reveal that there is a high degree of tunability in the reaction conditions for the C(*sp*)–H silylation reaction. THF, dioxane, and DME all proved to be suitable solvents, with low amounts of the isomerized starting material produced (Entries 2, 3, 4 respectively). Low loadings of KO*t*-Bu (Entries 15–17), down to 1 mol% (Entry 17), could be employed without loss of efficiency, demonstrating turnover numbers (TON) of up to 97%. High temperatures (85 °C) proved necessary for silylation with triethylsilane (Entries 15, 18, 19); as seen in the silane screen in the text, the reaction proceeded at lower temperatures when employing various other silanes. The extensive base screen (Entries 20–35) with longer reaction times (72 h) showed that there are a number of good catalysts for the C–H silylation reaction. A refined base screen with lower catalyst loading (Entries 36–49) revealed that there were still several catalysts that performed with surprisingly high efficiency, but NaOH proved to be the most convenient and high-performing catalyst. No product was observed in the absence of catalyst, or when LiO*t*-Bu, NaOAc, KOAc, DABCO, K_2CO_3, Cs_2CO_3, or KF were employed (Entries 39, 27, 28, 24, 33, 34, 35 respectively).

2. Trace metal analysis by ICP-MS.

ICP-MS trace metal analysis of all the reaction components. To provide further support against involvement of adventitious trace metal species in the cross-dehydrogenative C(*sp*)–H silylation catalysis, inductively coupled plasma mass spectrometry was performed on samples of NaOH, KOH, 3-cyclohexyl-1-propyne starting material, dimethoxyethane (DME) solvent, $PhMe_2SiH$, and a standard reaction mixture that was run under optimized conditions in the glove box. The results from quantitative analysis revealed that most metal contaminants were present below the instrument's lowest limit of detection (i.e., in ppt range or lower). Microgram per liter (ppb) quantities of metal contaminants are given in Table 2.

ICP-MS trace metal analysis.

1000 mg samples each of NaOH (99.99% Aldrich), 3-cyclohexyl-1-propyne, $PhMe_2SiH$, 1,2-dimethoxyethane, and a standard reaction mixture (0.5 mmol scale mixture, prepared following the general procedure with 61.1 mg of 3-cyclohexyl-1-propyne, 2 mg of NaOH, 204.4 mg of $PhMe_2SiH$ in 0.5 mL of 1,2-dimethoxyethane (DME) and stirred in the glovebox for 48 h.) were analyzed (Table 2).

Each sample was added to a 50 mL DigiTUBE digestion tube (SCP Science) followed by addition of 3.0 mL of Plasma Pure nitric acid (SCP Science) and heating to 75 ^{o}C for 36 hours. After digestion, each sample was diluted using Milli Q water to 50 mL and subjected to trace metal analysis. Trace metal concentrations were determined by Inductively Coupled Plasma – Mass Spectrometry using an Agilent 8800. The sample introduction system consisted of a micromist nebulizer, scott type spray chamber and fixed injector quartz torch. A guard electrode was used and the plasma was operated at 1500 W. Elements were determined in single-quad mode with either no gas or helium (kinetic energy discrimination mode) in the collision cell. 33 elements were calibrated using external standard solutions ranging from 1 to 100 ppb (micrograms/L). Detection limits of trace elements of concern were below the 1 ppb standard. In addition Quick Scan data in helium mode data were calibrated semiquantitatively. LOD indicates that the analyte concentration is below the instrument's *Lowest Limit of Detection*. Values are in ppb unless otherwise stated.

Table 2. Trace-metal analysis of reactants in the alkyne silylation reaction.

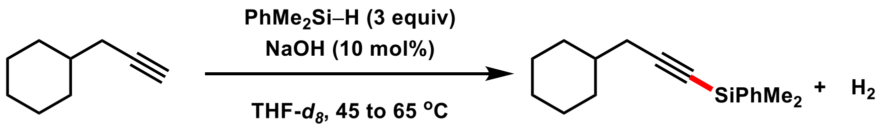
	Values in ng/g (ppb) unless otherwise stated*					
Element	**NaOH**	**KOH**	**3-cyclohexyl-1-propyne**	**1,2-DME**	**$PhMe_2SiH$**	**Reaction Mixture**
Ti	LOD	0.767*	0.324*	0.206*	0.545*	0.059*
Co	LOD	LOD	18.543	LOD	LOD	LOD
Cu	LOD	LOD	10.440	0.069*	3.048	0.116
Zn	LOD	0.682*	25.908*	1.787*	0.063*	0.320
Zr	LOD	LOD	LOD	LOD	0.232*	LOD
Mo	LOD	LOD	LOD	LOD	1.118*	LOD
Ru	LOD	21.248	1.576	LOD	41.188	18.692
Rh	LOD	0.165	LOD	LOD	0.908	LOD
Pd	LOD	1.834	0.612	7.950	7.339	0.612
Ag	LOD	LOD	LOD	LOD	LOD	LOD
Re	LOD	0.156	LOD	0.700	5.835	0.311
Os	LOD	LOD	LOD	LOD	LOD	LOD
Ir	LOD	0.063*	7.776*	0.253*	2.429*	0.604
Pt	LOD	0.406	0.135	0.813	1.490	0.271
Au	LOD	LOD	0.115	LOD	1.729	1.383

*****ppm

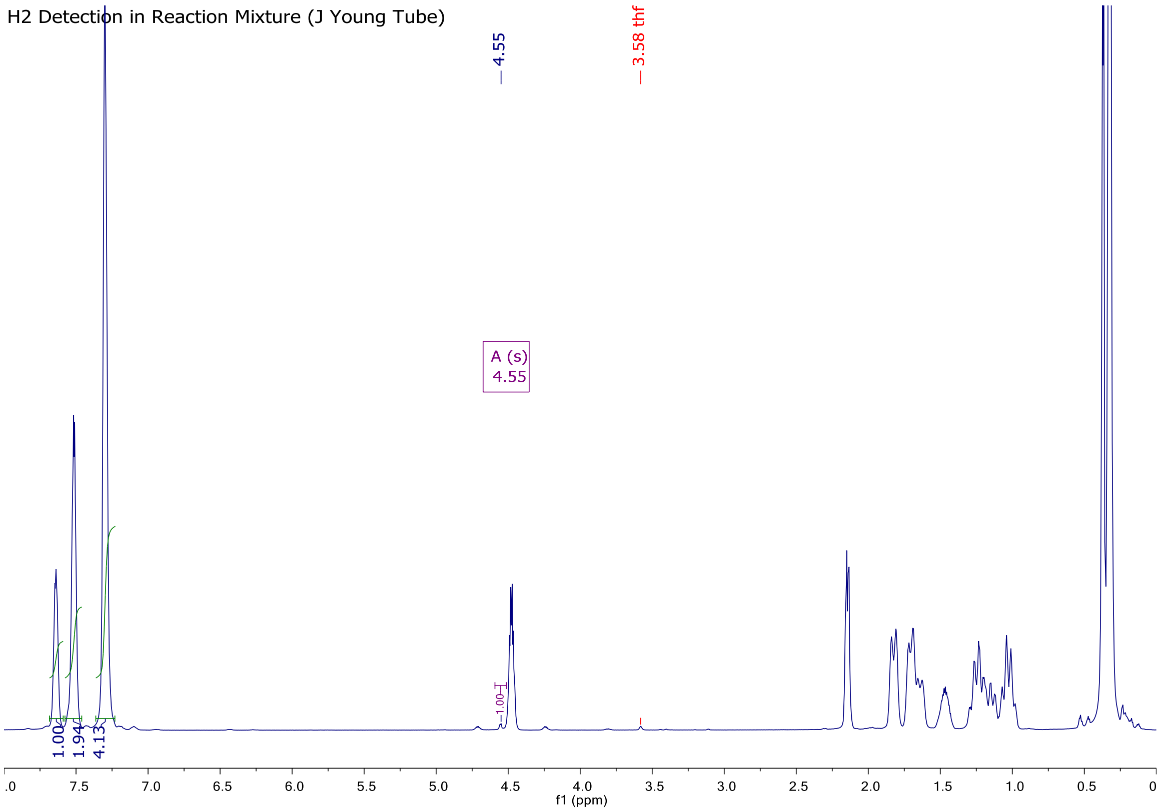
3. Confirmation of H_2 production.

The evolution of hydrogen gas during the alkyne silylation reaction was confirmed by ^{1}H NMR and headspace GC-TCD analysis.

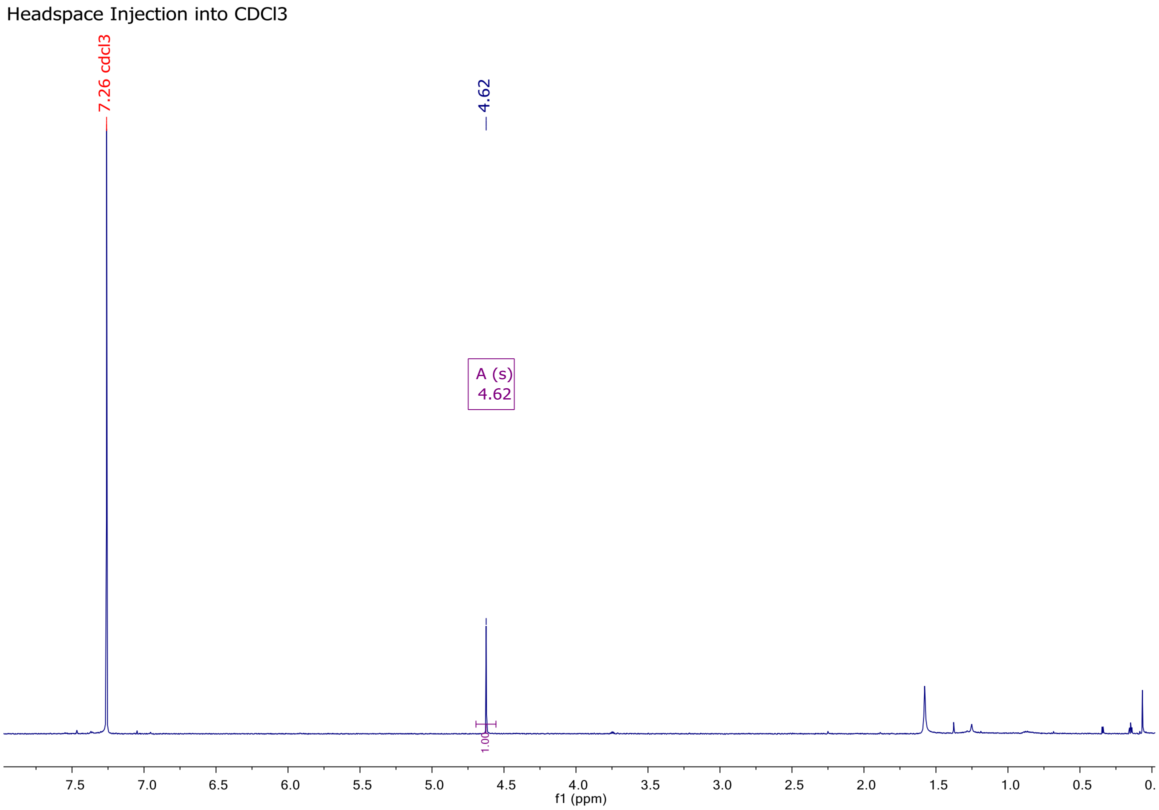
^{1}H NMR Detection of Hydrogen:



In a N_2-filled glove box, 3-cyclohexyl-1-propyne (36.7 mg, 0.3 mmol), dried NaOH (1.2 mg, 0.03 mmol), PhMe$_2$Si–H (122.6 mg, 0.9 mmol), and THF-d_8 (0.3 mL) were added to a J-Young tube and fitted with a Teflon cap. The tube was placed in a 45 °C oil bath for 48 h, after which time no change was observed by ^{1}H NMR. The oil bath was then heated to 55 °C for 48 h, after which time no change was observed by ^{1}H NMR. The oil bath was finally heated to 65 °C for 48 h, after which time the crude ^{1}H NMR indicated the presence of H_2 (see below; THF-d_8, 400 MHz, δ 4.55 ppm, s).



To further confirm the presence of H_2, the J-Young tube containing the reaction mixture was fitted with a septum and the headspace was transferred with a needle and syringe to freshly degassed $CDCl_3$ in a dry NMR tube with a septum cap. ^{1}H NMR clearly showed the presence of H_2 in the headspace (see below; $CDCl_3$, 500 MHz, δ 4.62 ppm, s).

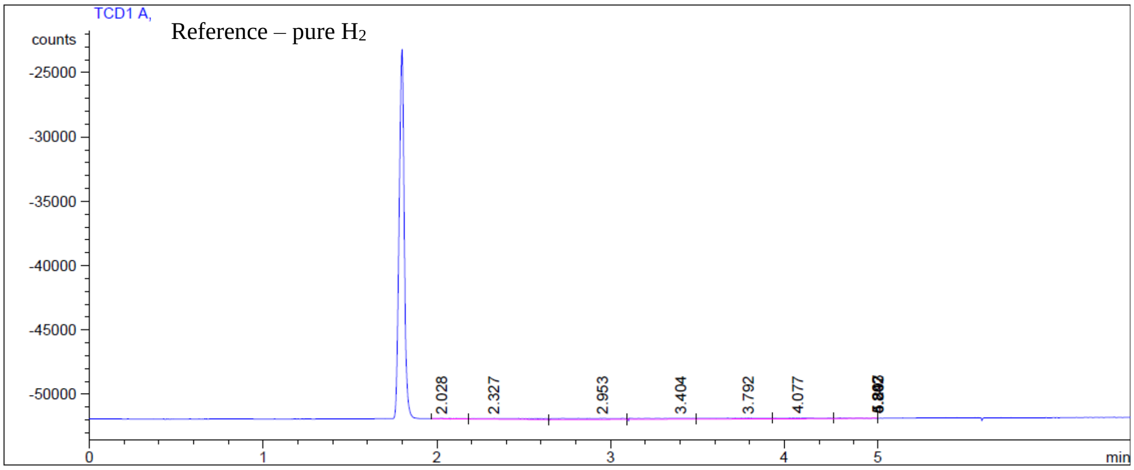


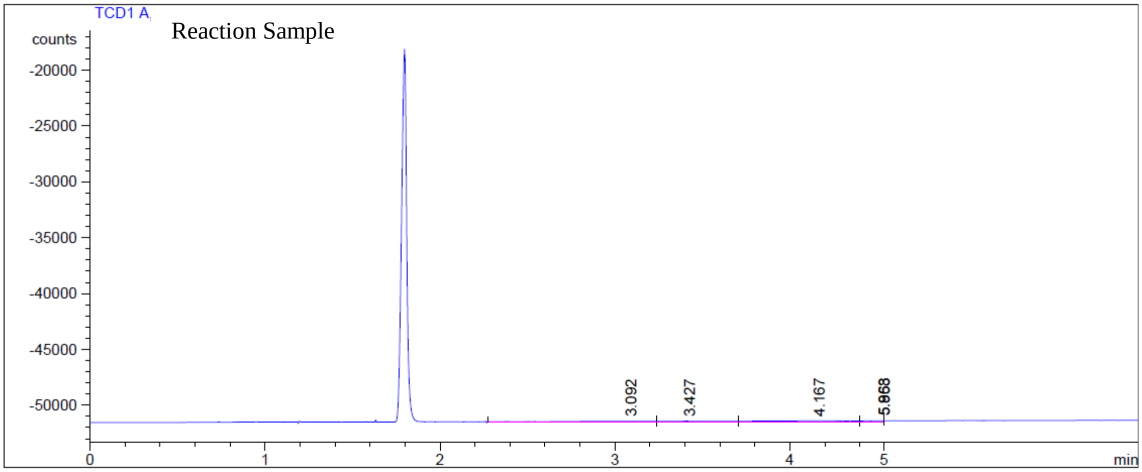
Note: raised temperatures were necessary for the experiment conducted in the J Young tube due to the lack of stirring in such a setup.

GC-TCD Detection of Hydrogen:

Hydrogen was analyzed by gas chromatography (GC) on a carbon-based molecular sieve column (HP MOLSIV 30m x 0.320mm ID, 12 micron) with thermal conductivity detection (TCD). A Hewlett-Packard 5890 GC with a split-splitless injector was operated in the splitless mode for 0.5 min at which point the injector was purged with a split flow of 20 mL/min. Ultra-high purity nitrogen was used for carrier gas, and the column was operated at a constant flow rate of 2.2 mL/min (37 cm/sec average linear velocity). Oven temperature was isothermal at 32 °C. Injections of 10 microliters were performed manually with a gastight syringe. The injector was maintained at 150 °C and the detector at 200 °C. Hydrogen eluted at approximately 1.8 minutes under these conditions (see chromatogram of injected pure H_2 reference standard below). Absence of interference from other gases that were expected to be in any injection mixture was tested empirically.

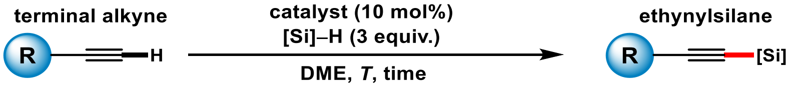
The reaction was performed according to the general procedure, with 0.5 mmol 3-cyclohexyl-1-propyne, 0.1 mmol (dried, powdered) KOH, 1.5 mmol $EtMe_2SiH$, and 0.5 mL DME and the reaction vial was sealed with a septumed cap. The reaction was heated to 45 °C for 24 h. Injection of the headspace of this showed a single signal at 1.8 min, which overlays very well with the H2 reference stardard, strongly corroborating the presence of H_2.





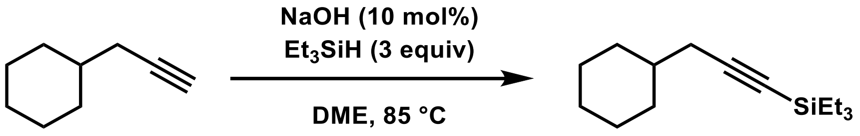
Part II. Experimental and analytics.

1. General procedure for cross-dehydrogenative C(*sp*)–H silylation and characterization data.

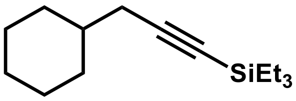


In a nitrogen-filled glove box, catalyst (0.05 mmol, 10 mol%) and alkyne (0.5 mmol, 1 equiv) were added to a 2 dram scintillation vial equipped with a magnetic stirring bar, followed by solvent (0.5 mL) and silane (1.5 mmol, 3 equiv). The vial was then sealed and the mixture was stirred at the indicated temperature for the indicated time. The vial was then removed from the glove box; the reaction mixture was diluted with diethyl ether (2 mL), filtered through a short pad of silica gel, and concentrated under reduced pressure. Volatiles were removed under high vacuum with heating as indicated and the resultant material was purified by silica gel flash chromatography if necessary to give the desired C(*sp*)–Si product.

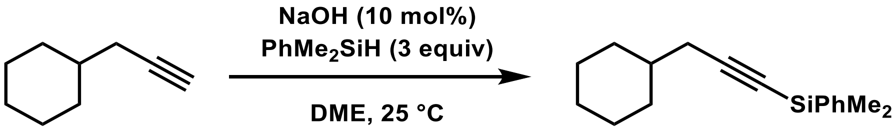
The reaction can likewise be comfortably performed outside of the glovebox using simple air free technique and non-degassed solvents under a nitrogen or argon atmosphere on both small and large (i.e., see SI-41, multi-gram scale synthesis of* ***4s**) scales. However, in the case of small scale preparations especially, particular care must be given to ensure that weighing of the hygroscopic catalysts in air is rapid such that moisture does not enter the system. If rigorous exclusion of moisture is not achieved, the presence of oxidized silanes is sometimes observed (i.e., silanols, siloxanes; only in the case of certain silanes), but this does not appear to impact the product yield.*



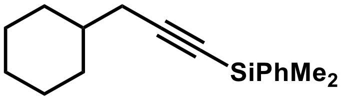
2a



(3-Cyclohexylprop-1-yn-1-yl)triethylsilane 2a: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), Et_3SiH (174 mg, 240 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 85 °C for 48 h. The desired product **2a** (111.9 mg, 95% yield) was obtained as a colorless oil in analytical purity after removal of volatiles under high vacuum (45 mtorr, 2 hours). ^1H NMR (500 MHz, $CDCl_3$) δ 2.13 (d, *J* = 6.6 Hz, 2H), 1.84 – 1.76 (m, 2H), 1.75 – 1.68 (m, 2H), 1.65 (dtt, *J* = 12.9, 3.4, 1.5 Hz, 1H), 1.47 (dddd, *J* = 14.8, 6.8, 4.7, 3.4 Hz, 1H), 1.24 (tdd, *J* = 15.9, 9.4, 3.4 Hz, 2H), 1.19 – 1.07 (m, 2H), 1.07 – 1.01 (m, 1H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.57 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 107.7, 82.4, 37.5, 32.7, 27.9, 26.5, 26.3, 7.7, 4.8. HRMS (EI+) calc'd for $C_{15}H_{27}Si$ [(M+H)–H_2]: 235.1882, found 235.1881.

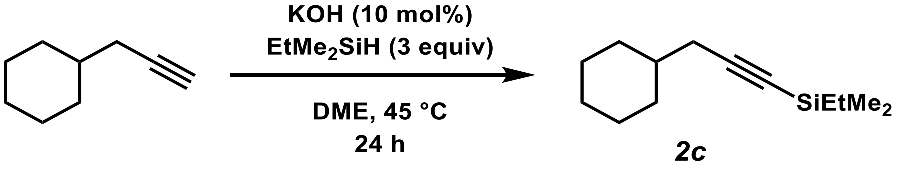


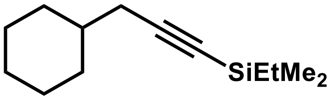
2b



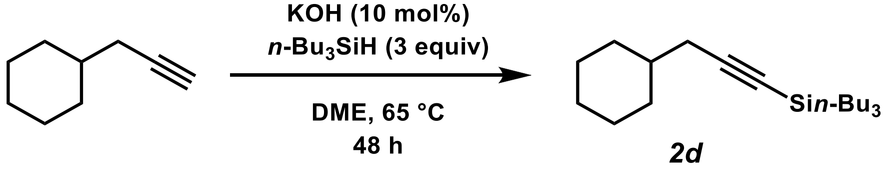
(3-Cyclohexylprop-1-yn-1-yl)dimethyl(phenyl)silane 2b: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 25 °C for 48 h. The desired product **2b** (113.6 mg, 89% yield) was obtained as a colorless oil after removal of volatiles by heating to 85°C at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100% hexanes). R_f = 0.67 (100% hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 2H), 7.40 – 7.34 (m, 3H), 2.19 (d, *J* = 6.6 Hz, 2H), 1.87 – 1.80

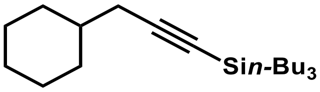
(m, 2H), 1.74 (dt, *J* = 12.8, 3.3 Hz, 2H), 1.67 (dddd, *J* = 11.3, 5.2, 3.3, 1.6 Hz, 1H), 1.53 (ddtd, *J* = 14.9, 11.5, 6.7, 3.5 Hz, 1H), 1.27 (dddd, *J* = 15.9, 12.6, 9.5, 3.3 Hz, 2H), 1.15 (qt, *J* = 12.7, 3.3 Hz, 1H), 1.08 – 0.98 (m, 2H), 0.41 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 133.8, 129.3, 127.9, 108.7, 83.2, 37.4, 32.8, 27.9, 26.4, 26.3, –0.4. HRMS (EI+) calc'd for $C_{17}H_{25}Si$ [M+H]: 257.1726, found 257.1720.





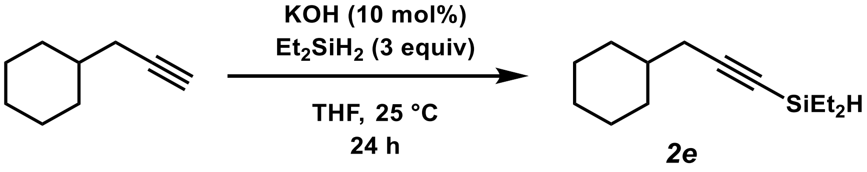
(3-Cyclohexylprop-1-yn-1-yl)(ethyl)dimethylsilane 2c: The general procedure was followed. The reaction was performed with KOH (2.8 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), $EtMe_2SiH$ (132 mg, 198 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 24 h. The desired product **2c** (95.1 mg, 91% yield) was obtained as a colorless oil in analytical purity after removal of volatiles under high vacuum (45 mtorr, 2 hours). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.12 (d, *J* = 6.6 Hz, 2H), 1.86 – 1.76 (m, 2H), 1.77 – 1.69 (m, 2H), 1.66 (dtd, *J* = 12.6, 3.3, 1.6 Hz, 1H), 1.53 – 1.40 (m, 1H), 1.32 – 1.19 (m, 2H), 1.20 – 1.07 (m, 2H), 1.06 – 0.94 (m, 4H), 0.57 (q, *J* = 7.9 Hz, 2H), 0.12 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 107.0, 84.3, 37.5, 32.8, 27.8, 26. 5, 26.3, 8.5, 7.5, –1.9. HRMS (EI+) calc'd for $C_{13}H_{23}Si$ [(M+H)–H_2]: 207.1569, found 207.1562.

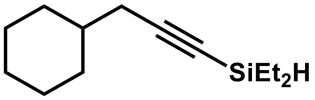




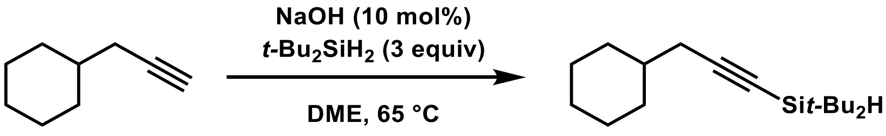
Tributyl(3-cyclohexylprop-1-yn-1-yl)silane 2d: The general procedure was followed. The reaction was performed with KOH (2.8 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne

(61 mg, 0.5 mmol, 1.0 equiv), *n*-Bu_3SiH (301 mg, 386 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **2d** (117.2 mg, 73% yield) was obtained as a colorless oil by silica gel flash chromatography (100% hexanes). $R_f = 0.78$ (100% hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 2.13 (d, J = 6.5 Hz, 2H), 1.80 (dddd, J = 12.3, 6.2, 3.1, 1.8 Hz, 2H), 1.72 (ddd, J = 14.0, 4.5, 2.3 Hz, 2H), 1.66 (dddt, J = 12.8, 5.1, 3.3, 1.5 Hz, 1H), 1.47 (dddt, J = 14.5, 7.9, 6.6, 3.2 Hz, 1H), 1.40 – 1.31 (m, 12H), 1.25 (qt, J = 12.6, 3.3 Hz, 2H), 1.14 (qt, J = 12.7, 3.3 Hz, 1H), 1.09 – 0.97 (m, 2H), 0.96 – 0.83 (m, 9H), 0.65 – 0.51 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 107.7, 83.2, 37.6, 32.7, 27.9, 26.6, 26.5, 26.4, 26.3, 14.0, 13.4. HRMS (EI+) calc'd for $C_{21}H_{40}Si$ [M+•]: 320.2899, found 320.2905.

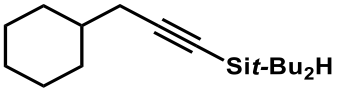




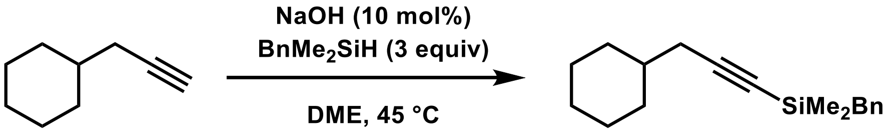
(3-Cyclohexylprop-1-yn-1-yl)diethylsilane 2e: The general procedure was followed. The reaction was performed with KOH (2.8 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), Et_2SiH_2 (132 mg, 194 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 24 h. The desired product **2e** (73.6 mg, 71% yield) was obtained in as a colorless oil after removal of volatiles under high vacuum at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100% hexanes). $R_f = 0.77$ (100% hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 3.92 (pt, *J* = 3.2, 1.2 Hz, 1H), 2.15 (dd, *J* = 6.7, 1.2 Hz, 2H), 1.85 – 1.78 (m, 2H), 1.72 (ddd, *J* = 13.9, 4.5, 2.2 Hz, 2H), 1.66 (dddt, *J* = 12.7, 5.1, 3.3, 1.5 Hz, 1H), 1.49 (ddtd, *J* = 14.9, 11.5, 6.8, 3.5 Hz, 1H), 1.31 – 1.20 (m, 2H), 1.15 (tt, *J* = 12.6, 3.2 Hz, 1H), 1.07 – 0.95 (m, 8H), 0.70 – 0.64 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 109.0, 80.2, 37.4, 32.8, 27.9, 26.4, 26.3, 8.1, 4.2. HRMS (EI+) calc'd for $C_{13}H_{23}Si$ [(M+H)-H_2]: 207.1569, found 207.1562.



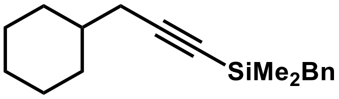
2f



Di-tert-butyl(3-cyclohexylprop-1-yn-1-yl)silane 2f: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), *t*-Bu_2SiH_2 (216 mg, 297 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **2f** (120.3 mg, 91% yield) was obtained as a colorless oil after removal of volatiles under high vacuum at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100% hexanes). R_f = 0.88 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.57 (t, J = 1.2 Hz, 1H), 2.17 (dd, J = 6.5, 1.2 Hz, 2H), 1.84 – 1.78 (m, 2H), 1.76 – 1.70 (m, 2H), 1.66 (dddt, J = 12.8, 5.1, 3.3, 1.5 Hz, 1H), 1.50 (dddt, J = 14.5, 7.8, 6.5, 3.1 Hz, 1H), 1.26 (qt, J = 12.7, 3.4 Hz, 3H), 1.19 – 1.09 (m, 2H), 1.06 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 108.9, 79.5, 37.5, 32.8, 28.3, 27.9, 26.4, 26.3, 18.6. HRMS (EI+) calc'd for $C_{17}H_{31}Si$ [(M+H)-H_2]: 263.2195, found 263.2206.

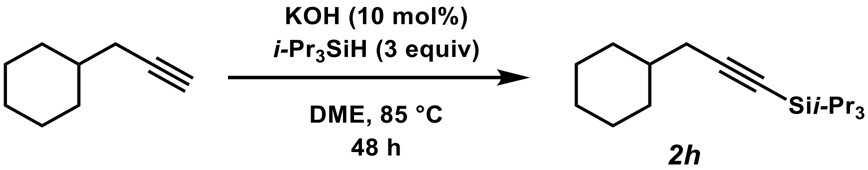


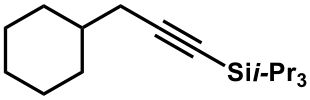
2g



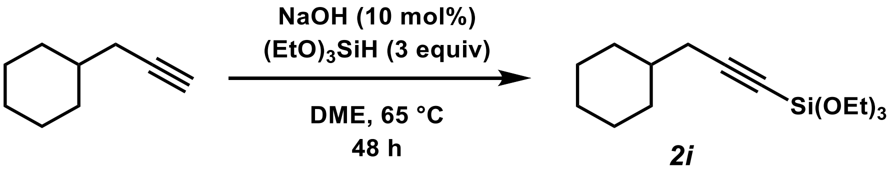
Benzyl(3-cyclohexylprop-1-yn-1-yl)dimethylsilane 2g: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), $BnMe_2SiH$ (150 mg, 238 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h. The desired product **2g** (101.9 mg, 75% yield) was obtained as a colorless oil by silica gel flash chromatography (100% hexanes). R_f = 0.51 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$)

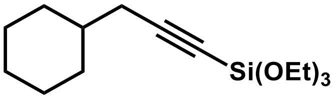
δ 7.25 – 7.21 (m, 2H), 7.12 – 7.08 (m, 3H), 2.18 (s, 2H), 2.12 (d, *J* = 6.8 Hz, 2H), 1.78 (ddd, *J* = 13.3, 3.5, 1.5 Hz, 2H), 1.72 (dt, *J* = 12.7, 3.2 Hz, 2H), 1.66 (dddd, *J* = 11.3, 5.3, 3.4, 1.7 Hz, 1H), 1.46 (tdt, *J* = 11.4, 6.7, 3.3 Hz, 1H), 1.25 (qt, *J* = 12.6, 3.3 Hz, 2H), 1.14 (qt, *J* = 12.7, 3.3 Hz, 1H), 1.04 – 0.92 (m, 2H), 0.11 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.5, 128.5, 128.2, 124.3, 108.1, 83.7, 37.4, 32.8, 27.9, 26.7, 26.4, 26.3, –1.7. HRMS (EI+) calc'd for $C_{18}H_{26}Si$ [M+•]: 270.1804, found 270.1810.



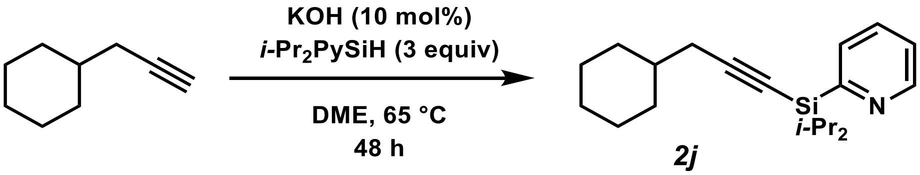


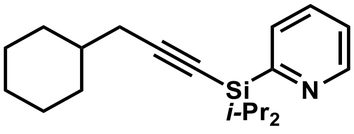
(3-Cyclohexylprop-1-yn-1-yl)triisopropylsilane 2h: The general procedure was followed. The reaction was performed with KOH (2.8 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), *i*-Pr_3SiH (238 mg, 307 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 85 °C for 48 h. The desired product **2h** (95.6 mg, 69% yield) was obtained as a colorless oil by silica gel flash chromatography (100% hexanes). R_f = 0.79 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.16 (d, *J* = 6.4 Hz, 2H), 1.84 – 1.77 (m, 2H), 1.73 (dt, *J* = 12.8, 3.4 Hz, 2H), 1.66 (dtd, *J* = 12.7, 3.3, 1.6 Hz, 1H), 1.48 (ddtd, *J* = 14.6, 11.2, 6.5, 3.4 Hz, 1H), 1.25 (qt, *J* = 12.6, 3.4 Hz, 2H), 1.15 (tt, *J* = 12.6, 3.3 Hz, 1H), 1.10 – 0.99 (m, 23H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 108.2, 80.9, 37.6, 32.7, 27.9, 26.5, 26.3, 18.8, 11.5. HRMS (EI+) calc'd for $C_{18}H_{33}Si$ [(M+H)-H_2]: 277.2352, found 277.2349.



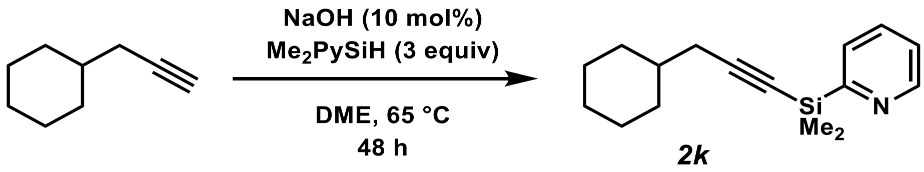


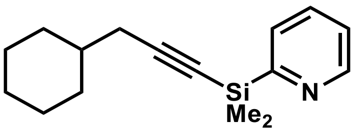
(3-Cyclohexylprop-1-yn-1-yl)triethoxysilane 2i: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), $(EtO)_3SiH$ (246 mg, 277 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **2i** (97.1 mg, 68% yield) was obtained as a colorless oil by silica gel flash chromatography (5% Et_2O in hexanes). R_f = 0.41 (5% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (q, *J* = 7.0 Hz, 6H), 2.16 (d, *J* = 6.6 Hz, 2H), 1.84 – 1.78 (m, 2H), 1.72 (dp, *J* = 12.6, 3.7 Hz, 2H), 1.66 (dddt, *J* = 12.8, 5.1, 3.3, 1.5 Hz, 1H), 1.52 (ddtd, *J* = 14.9, 11.5, 6.8, 3.5 Hz, 1H), 1.26 (t, *J* = 7.0 Hz, 9H), 1.24 – 1.19 (m, 2H), 1.14 (qt, *J* = 12.7, 3.3 Hz, 1H), 1.02 (qd, *J* = 12.7, 3.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 106.5, 76.8, 59.0, 37.1, 32.7, 27.5, 26.3, 26.2, 18.2. HRMS (EI+) calc'd for $C_{15}H_{29}O_3Si$ [M+H]: 285.1886, found 285.1889.



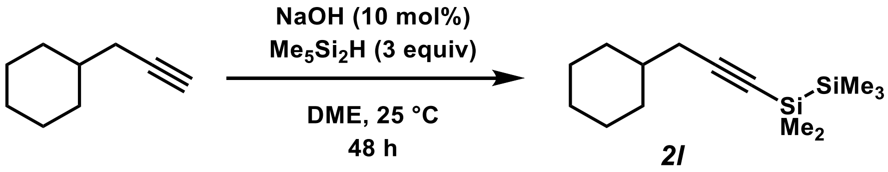


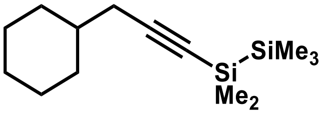
2-((3-Cyclohexylprop-1-yn-1-yl)diisopropylsilyl)pyridine 2j: The general procedure was followed. The reaction was performed with KOH (2.8 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), *i*-Pr_2(Pyr)SiH (290 mg, 322 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **2j** (122.5 mg, 78% yield) was obtained as a colorless oil by silica gel flash chromatography (10% EtOAc in hexanes). R_f = 0.47 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, THF-d_8) δ 8.65 (ddd, *J* = 4.8, 1.7, 1.1 Hz, 1H), 7.76 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.59 (td, *J* = 7.6, 1.8 Hz, 1H), 7.19 (ddd, *J* = 7.7, 4.8, 1.4 Hz, 1H), 2.26 (d, *J* = 6.4 Hz, 2H), 1.95 – 1.84 (m, 2H), 1.78 – 1.73 (m, 2H), 1.67 (dtt, J = 13.0, 3.4, 1.6 Hz, 1H), 1.55 (ddtd, *J* = 14.9, 11.4, 6.6, 3.5 Hz, 1H), 1.37 – 1.26 (m, 4H), 1.21 – 1.16 (m, 1H), 1.16 – 1.11 (m, 2H), 1.09 (d, *J* = 7.4 Hz, 6H), 0.99 (d, *J* = 7.3 Hz, 6H); ^{13}C NMR (126 MHz, THF-d_8) δ 164.8, 150.8, 134.4, 132.1, 123.7, 110.5, 80.3, 38.6, 33.7, 28.4, 27.4, 27.2, 18.5, 18.4, 12.7. HRMS (EI+) calc'd for $C_{20}H_{32}NSi$ [M+H]: 314.2304, found 314.2311.



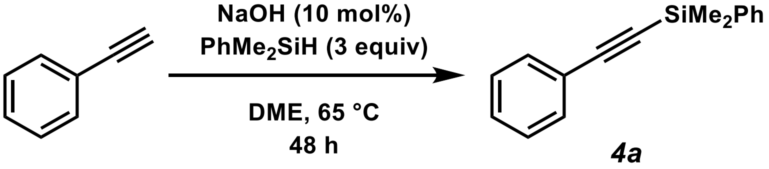


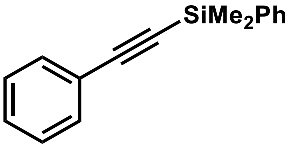
2-((3-Cyclohexylprop-1-yn-1-yl)dimethylsilyl)pyridine 2k: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), Me_2(Py)SiH (206 mg, 225 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **2k** (99.9 mg, 78% yield) was obtained as a colorless oil by silica gel flash chromatography (10% EtOAc in hexanes). R_f = 0.42 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, THF-d_8) δ 8.65 (ddd, *J* = 4.8, 1.8, 1.1 Hz, 1H), 7.74 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.59 (td, *J* = 7.6, 1.8 Hz, 1H), 7.18 (ddd, *J* = 7.7, 4.8, 1.4 Hz, 1H), 2.19 (d, *J* = 6.6 Hz, 2H), 1.88 – 1.81 (m, 2H), 1.73 – 1.70 (m, 2H), 1.66 (dddd, *J* = 12.7, 5.1, 3.2, 1.5 Hz, 1H), 1.50 (dddt, *J* = 14.7, 7.9, 6.7, 3.2 Hz, 1H), 1.27 (tdd, *J* = 16.0, 9.4, 3.4 Hz, 2H), 1.17 (qt, *J* = 12.7, 3.3 Hz, 1H), 1.06 (qd, *J* = 12.8, 3.4 Hz, 2H), 0.36 (s, 6H); ^{13}C NMR (126 MHz, THF-d_8) δ 166.5, 151.0, 134.7, 130.1, 123.8, 109.2, 83.6, 38.5, 33.7, 28.4, 27.3, 27.2, –1.0. HRMS (EI+) calc'd for $C_{16}H_{24}NSi$ [M+H]: 258.1678, found 258.1672.





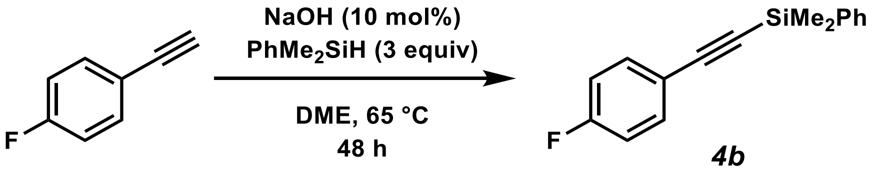
1-(3-Cyclohexylprop-1-yn-1-yl)-1,1,2,2,2-pentamethyldisilane 2l: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), Me_5Si_2H (246 mg, 277 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 25 °C for 48 h. The desired product **2l** (120.0 mg, 95% yield) was obtained in analytical purity as a cloudy, colorless oil after removal of volatiles at 85°C at 45 mtorr for 30 minutes. ^{1}H NMR (500 MHz, THF-*d*$_8$) δ 2.11 (d, *J* = 6.5 Hz, 2H), 1.81 (dddd, *J* = 13.1, 6.1, 3.1, 1.9 Hz, 2H), 1.72 – 1.69 (m, 2H), 1.65 (dddt, *J* = 12.7, 5.1, 3.2, 1.5 Hz, 1H), 1.44 (dddt, *J* = 14.6, 8.0, 6.7, 3.2 Hz, 1H), 1.33 – 1.21 (m, 2H), 1.17 (qt, *J* = 12.7, 3.2 Hz, 1H), 1.03 (qd, *J* = 12.8, 3.5 Hz, 2H), 0.15 (s, 6H), 0.11 (s, 9H); ^{13}C NMR (126 MHz, THF-*d*$_8$) δ 109.1, 84.1, 38.6, 33.6, 28.5, 27.4, 27.2, –2.2, –2.4. HRMS (EI+) calc'd for $C_{14}H_{28}Si_2$ [M+•]: 252.1730, found 252.1737.

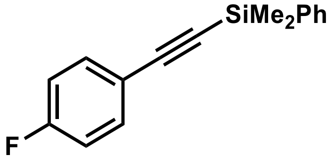




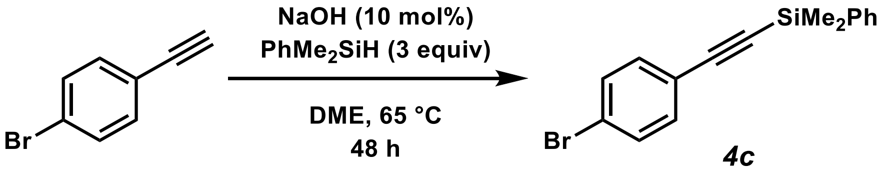
Dimethyl(phenyl)(phenylethynyl)silane 4a: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), ethynylbenzene (52 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **4a** (105.7 mg, 89% yield) was obtained as a colorless oil after removal of volatiles by heating to 85°C at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100%

hexanes). R_f = 0.38 (100% hexanes); ^{1}H NMR (500 MHz, THF-d_8) δ 7.71 – 7.65 (m, 2H), 7.49 – 7.44 (m, 2H), 7.38 – 7.28 (m, 6H), 0.46 (s, 6H). ^{13}C NMR (126 MHz, THF-d_8) δ 137.9, 134.7, 132.9, 130.3, 129.8, 129.3, 128.8, 124.2, 107.9, 92.5, –0.5. HRMS (EI+) calc'd for $C_{16}H_{17}Si$ [M+H]: 237.1100, found 237.1101.

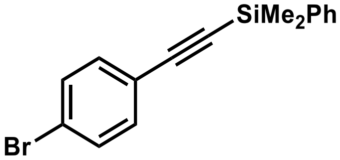




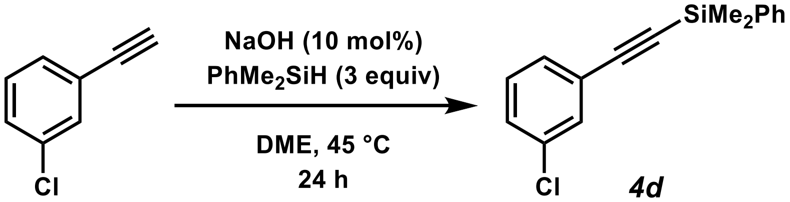
((4-Fluorophenyl)ethynyl)dimethyl(phenyl)silane 4b: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 1-ethynyl-4-fluorobenzene (60 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **4b** (111.9 mg, 88% yield) was obtained as a colorless oil after solvent removal at 85°C at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100% hexanes). R_f = 0.49 (100% hexanes); ^{1}H NMR (500 MHz, THF-d_8) δ 7.68 – 7.65 (m, 2H), 7.53 – 7.48 (m, 2H), 7.35 (dd, J = 4.9, 1.9 Hz, 3H), 7.09 (t, J = 8.8 Hz, 2H), 0.46 (s, 6H); ^{13}C NMR (126 MHz, THF-d_8) δ 163.9 (d, J = 249.1 Hz), 137.7, 135.1 (d, J = 8.5 Hz), 134.6, 130.4, 128.8, 120.4 (d, J = 3.8 Hz), 116.5 (d, J = 21.7 Hz), 106.7, 92.4, -0.6; ^{19}F NMR (282 MHz, THF-d_8) δ -113.63. HRMS (EI+) calc'd for $C_{16}H_{16}FSi$ [M+H]: 255.1005, found 255.1000.



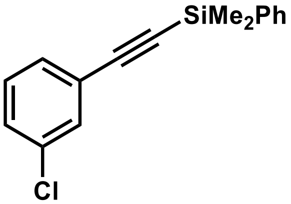
4c



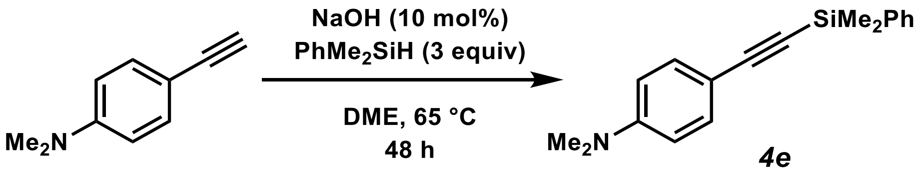
((4-Bromophenyl)ethynyl)dimethyl(phenyl)silane 4c: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 1-bromo-4-ethynylbenzene (90 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **4c** (81.3 mg, 52% yield) was obtained as colorless crystals after solvent removal at 85°C at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100% hexanes). R_f = 0.54 (100% hexanes); ^{1}H NMR (500 MHz, THF-d_8) δ 7.69 – 7.63 (m, 2H), 7.51 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.36 – 7.32 (m, 3H), 0.46 (s, 6H); ^{13}C NMR (126 MHz, THF-d_8) δ 137.6, 134.6, 134.5, 132.7, 130.4, 128.8, 123.9, 123.2, 106.5, 94.2, –0.7. HRMS (EI+) calc'd for $C_{16}H_{16}Si^{18}Br$ [M+H]: 317.0184, found 317.0180.

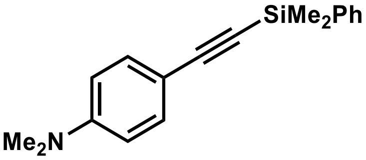


4d

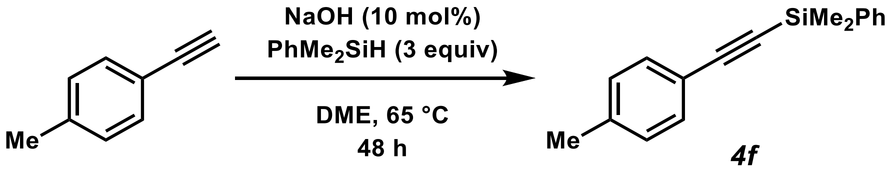


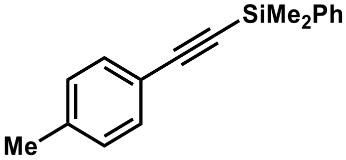
((3-Chlorophenyl)ethynyl)dimethyl(phenyl)silane 4d: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 1-chloro-3-ethynylbenzene (68 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 24 h. The desired product **4d** (121.6 mg, 90% yield) was obtained as a colorless oil after solvent removal at 85°C at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100% hexanes). R_f = 0.42 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 2H), 7.49 (ddd, *J* = 2.1, 1.5, 0.5 Hz, 1H), 7.40 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.38 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.31 (ddd, *J* = 8.1, 2.1, 1.2 Hz, 1H), 7.24 (ddd, *J* = 8.0, 7.6, 0.5 Hz, 1H), 0.51 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 134.2, 133.9, 132.1, 130.3, 129.7, 129.6, 129.1, 128.1, 124.8, 105.1, 93.8, –0.8. HRMS (EI+) calc'd for $C_{16}H_{16}ClSi$ [M+H]: 271.0710, found 271.0710.



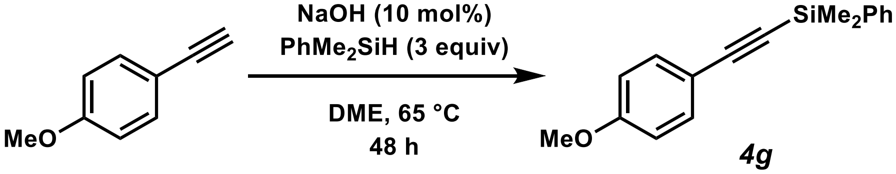


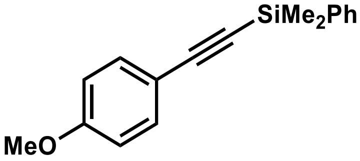
4-((Dimethyl(phenyl)silyl)ethynyl)-N,N-dimethylaniline 4e: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 4-ethynyl-N,N-dimethylaniline (73 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **4e** (139.4 mg, 100% yield) was obtained in analytical purity as colourless crystals after removal of volatiles at 85°C at 45 mtorr for 30 minutes. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.41 – 7.36 (m, 5H), 6.61 (d, *J* = 8.9 Hz, 2H), 2.98 (s, 6H), 0.48 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 137.9, 133.9, 133.4, 129.4, 127.9, 111.7, 109.8, 108.5, 89.2, 40.3, -0.4. HRMS (EI+) calc'd for $C_{18}H_{21}NSi$ [M+•]: 279.1443, found 279.1445.



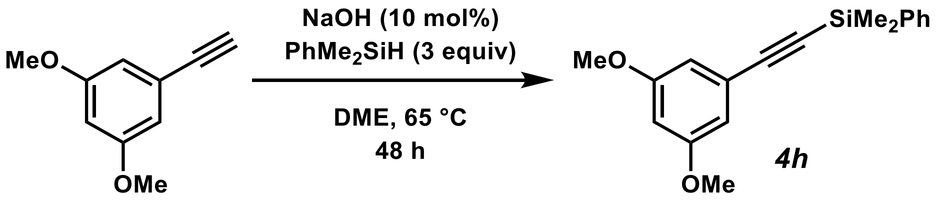


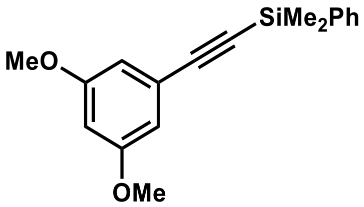
Dimethyl(phenyl)(*p*-tolylethynyl)silane 4f: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 1-ethynyl-4-methylbenzene (58 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **4f** (115.5 mg, 92% yield) was obtained in analytical purity as a pale yellow oil after removal of volatiles at 85°C at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100% hexanes). R_f = 0.46 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (ddd, *J* = 6.0, 2.4, 1.1 Hz, 2H), 7.43 (m, 5H), 7.16 – 7.12 (m, 2H), 2.37 (s, 3H), 0.52 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 137.3, 133.9, 132.1, 129.5, 129.1, 128.0, 120.0, 107.2, 91.3, 21.7, –0.6. HRMS (EI+) calc'd for $C_{17}H_{19}Si$ [M+H]: 251.1256, found 251.1257.



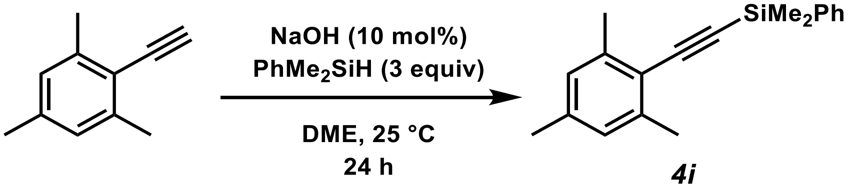


((4-Methoxyphenyl)ethynyl)dimethyl(phenyl)silane 4g: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 1-ethynyl-4-methoxybenzene (66 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **4g** (121.6 mg, 91% yield) was obtained as a yellow oil after removal of volatiles at 85°C at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100% hexanes → 5% EtOAc in hexanes). R_f = 0.27 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.46 (d, *J* = 8.9 Hz, 2H), 7.43 – 7.38 (m, 3H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 0.51 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 137.4, 133.9, 133.7, 129.5, 128.0, 115.2, 114.0, 107.0, 90.5, 55.4, -0.6. HRMS (EI+) calc'd for $C_{17}H_{18}OSi$ [M+•]: 266.1127, found 266.1135.

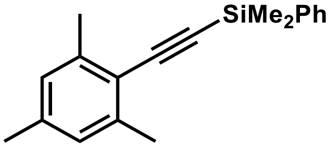




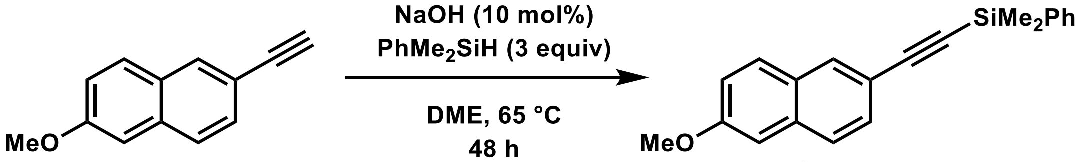
((3,5-Dimethoxyphenyl)ethynyl)dimethyl(phenyl)silane 4h: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 1-ethynyl-3,5-dimethoxybenzene (81 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **4h** (140.6 mg, 95% yield) was obtained in analytical purity as a light yellow oil after removal of volatiles at 85°C at 45 mtorr for 30 minutes. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (ddd, *J* = 5.5, 2.7, 1.2 Hz, 2H), 7.41 (dd, *J* = 4.6, 2.1 Hz, 3H), 6.67 (d, *J* = 2.3 Hz, 2H), 6.47 (t, *J* = 2.3 Hz, 1H), 3.79 (s, 6H), 0.52 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 137.0, 133.9, 129.6, 128.1, 124.3, 109.9, 106.8, 102.5, 91.7, 55.6, –0.7. HRMS (EI+) calc'd for $C_{18}H_{21}O_2Si$ [M+H]: 297.1311, found 297.1309.



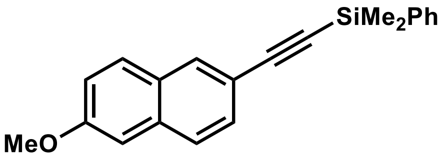
4i



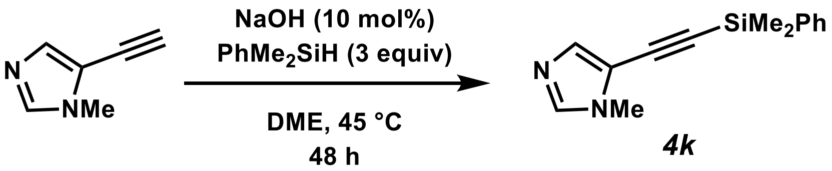
(Mesitylethynyl)dimethyl(phenyl)silane 4i: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 2-ethynyl-1,3,5-trimethylbenzene (72 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 25 °C for 24 h. The desired product **4i** (119.1 mg, 86% yield) was obtained in analytical purity as a colorless oil after removal of volatiles at 85 °C at 45 mtorr for 30 minutes. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.73 (ddt, *J* = 4.5, 3.2, 0.8 Hz, 3H), 7.40 (dd, *J* = 2.5, 0.8 Hz, 2H), 6.87 (dt, *J* = 1.4, 0.7 Hz, 2H), 2.42 (s, 6H), 2.29 (s, 3H), 0.52 (t, *J* = 0.7 Hz, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 140.9, 138.2, 137.7, 133.9, 129.4, 128.0, 127.7, 119.9, 105.0, 99.7, 21.5, 21.2, –0.3. HRMS (EI+) calc'd for $C_{19}H_{23}Si$ [M+H]: 279.1569, found 279.1561.

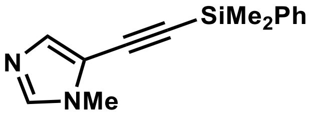


4j

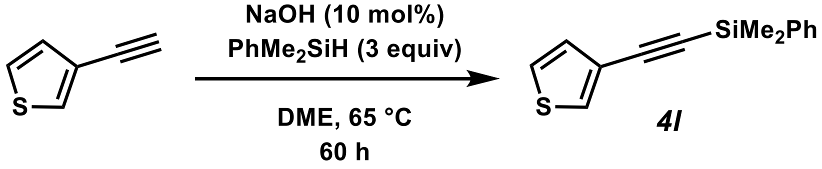


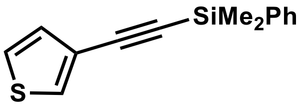
((6-Methoxynaphthalen-2-yl)ethynyl)dimethyl(phenyl)silane 4j: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 2-ethynyl-6-methoxynaphthalene (91 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **4j** (134.8 mg, 85% yield) was obtained in as a colorless oil after removal of volatiles at 85°C at 45 mtorr for 30 minutes and subsequent purification by alumina flash chromatography (gradient 2.5% Et_2O in hexanes → 10% Et_2O in hexanes). R_f = 0.36 (5% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.68 (dd, *J* = 9.0, 8.2 Hz, 2H), 7.51 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.15 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.10 (d, *J* = 2.6 Hz, 1H), 3.92 (s, 3H), 0.52 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 137.3, 134.5, 133.9, 132.2, 129.6, 129.5, 129.3, 128.4, 128.1, 126.8, 119.6, 117.9, 107.5, 105.9, 91.7, 55.5, –0.6. HRMS (EI+) calc'd for $C_{21}H_{20}OSi$ [M+•]: 316.1284, found 316.1296.



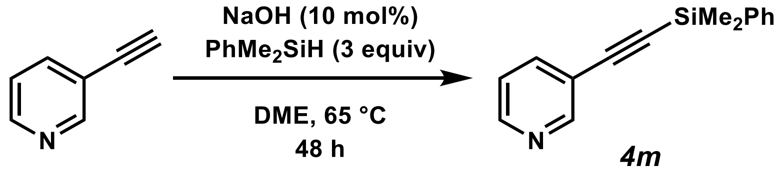


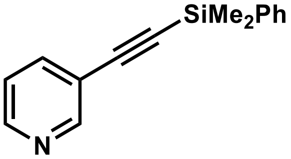
5-((Dimethyl(phenyl)silyl)ethynyl)-1-methyl-1*H*-imidazole 4k: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 5-ethynyl-1-methyl-1*H*-imidazole (53 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h. The desired product **4k** (98.7 mg, 82% yield) was obtained as a colorless oil after removal of volatiles at 85°C at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100% EtOAc). R_f = 0.45 (100% EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 2H), 7.40 (m, 4H), 7.31 (d, *J* = 1.0 Hz, 1H), 3.68 – 3.65 (d, *J* = 0.9 Hz, 3H), 0.52 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.4, 136.5, 135.3, 133.7, 129.7, 128.1, 116.3, 100.6, 94.1, 32.1, –0.8. HRMS (EI+) calc'd for $C_{14}H_{17}N_2Si$ [M+H]: 241.1161, found 241.1169.





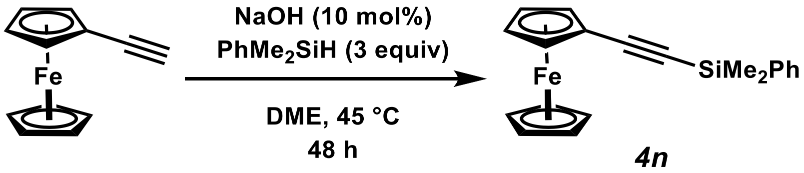
Dimethyl(phenyl)(thiophen-3-ylethynyl)silane 4l: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 3-ethynylthiophene (54 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 60 h. The desired product **4l** (113.2 mg, 93% yield) was obtained as a colorless oil after removal of volatiles at 85°C at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100% hexanes). $R_f = 0.39$ (100% hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 2H), 7.53 (dd, $J = 3.0$, 1.2 Hz, 1H), 7.43 – 7.39 (m, 3H), 7.27 – 7.24 (m, 1H), 7.17 (dd, $J = 5.0$, 1.2 Hz, 1H), 0.51 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1, 133.9, 130.3, 130.1, 129.6, 128.0, 125.4, 122.3, 101.7, 91.9, –0.7. HRMS (EI+) calc'd for $C_{14}H_{14}SSi$ [M+•]: 242.0586, found 242.0576.

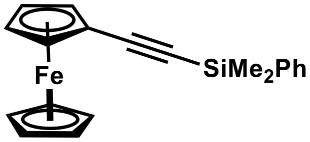




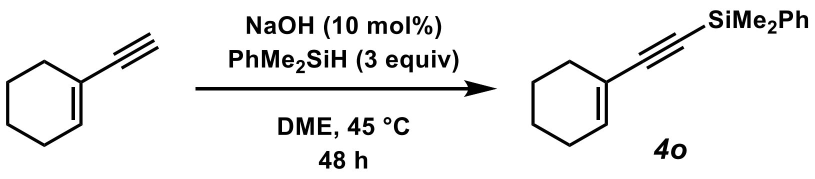
3-((Dimethyl(phenyl)silyl)ethynyl)pyridine 4m: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 3-ethynylpyridine (52 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **4m** (91.8 mg, 77% yield) was obtained as a colorless oil after removal of volatiles at 85°C at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100%

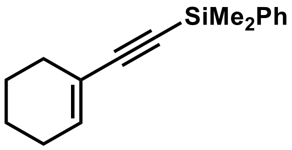
hexanes). $R_f = 0.31$ (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (dd, *J* = 2.1, 0.9 Hz, 1H), 8.54 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.77 (ddd, *J* = 7.9, 2.1, 1.7 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.44 – 7.40 (m, 3H), 7.24 (ddd, *J* = 7.9, 4.9, 0.9 Hz, 1H), 0.54 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 149.0, 139.0, 136.5, 133.8, 129.7, 128.1, 123.0, 120.2, 103.1, 96.3, –0.9. HRMS (EI+) calc'd for $C_{15}H_{16}NSi$ [M+H]: 238.1052, found 238.1049.



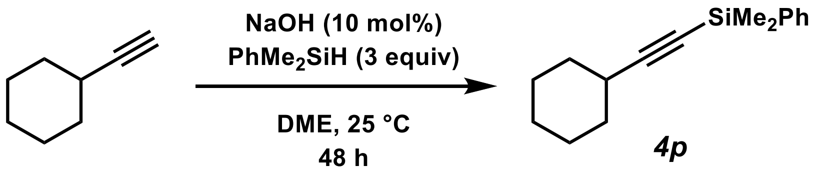


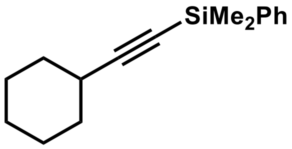
((Dimethyl(phenyl)silyl)ethynyl)ferrocene 4n: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), ethynylferrocene (105 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h. The desired product **4n** (170.1 mg, 99% yield) was obtained in analytical purity as an orange crystalline solid after removal of volatiles at 85°C at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (gradient 100% hexanes → 5% EtOAc in hexanes). $R_f = 0.45$ (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, J = 6.1, 3.1 Hz, 2H), 7.43 – 7.39 (m, 3H), 4.49 (t, J = 1.7 Hz, 2H), 4.22 (s, 5H), 4.22 – 4.20 (m, 2H), 0.47 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 133.9, 129.4, 128.0, 106.3, 88.5, 72.1, 70.3, 69.0, 64.7, –0.4. HRMS (EI+) calc'd for $C_{20}H_{20}FeSi$ [M+•]: 344.0684, found 344.0696.



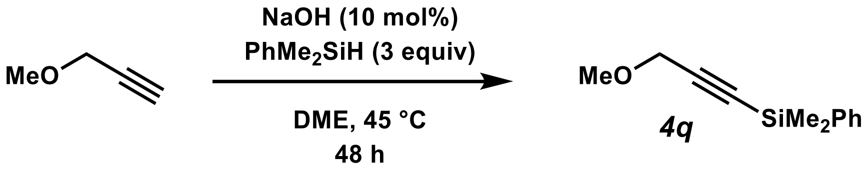


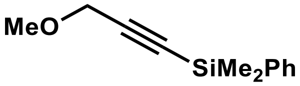
(Cyclohex-1-en-1-ylethynyl)dimethyl(phenyl)silane 4o: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 1-ethynylcyclohex-1-ene (53 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h. The desired product **4o** (102.7 mg, 85% yield) was obtained as a colorless oil after removal of volatiles at 85°C at 45 mtorr for 15 minutes and subsequent purification by silica gel flash chromatography (100% hexanes). $R_f = 0.50$ (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 2H), 7.39 – 7.36 (m, 3H), 6.24 (tt, J = 3.9, 1.8 Hz, 1H), 2.17 (tdd, J = 6.0, 2.7, 1.8 Hz, 2H), 2.11 (tdd, J = 6.4, 4.6, 2.5 Hz, 2H), 1.68 – 1.55 (m, 4H), 0.43 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 136.9, 133.8, 129.4, 127.9, 120.8, 109.2, 88.8, 29.1, 25.8, 22.3, 21.5, –0.5. HRMS (EI+) calc'd for $C_{16}H_{21}Si$ [M+H]: 241.1413, found 241.1402.



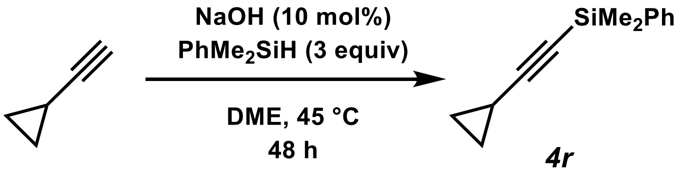


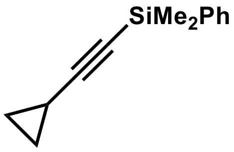
(Cyclohexylethynyl)dimethyl(phenyl)silane 4p: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), ethynylcyclohexane (54 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 25 °C for 48 h. The desired product **4p** (97.4 mg, 80% yield) was obtained as a colorless oil after removal of volatiles at 85°C at 45 mtorr for 15 minutes and subsequent purification by silica gel flash chromatography (100% hexanes). R$_f$ = 0.53 (100% hexanes); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.65 (ddd, *J* = 5.4, 2.4, 1.7 Hz, 2H), 7.38 (ddq, *J* = 4.0, 1.9, 0.8 Hz, 3H), 2.46 (tt, *J* = 9.0, 3.8 Hz, 1H), 1.89 – 1.79 (m, 2H), 1.73 (ddd, *J* = 9.8, 6.2, 3.1 Hz, 2H), 1.51 (td, *J* = 9.7, 9.2, 3.8 Hz, 3H), 1.38 – 1.26 (m, 3H), 0.39 (d, J = 1.0 Hz, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 138.0, 133.8, 129.3, 127.9, 113.9, 81.7, 32.7, 30.2, 26.0, 24.9, -0.3. HRMS (EI+) calc'd for $C_{16}H_{21}Si$ [(M+H)-H$_2$]: 241.1413, found 241.1419.



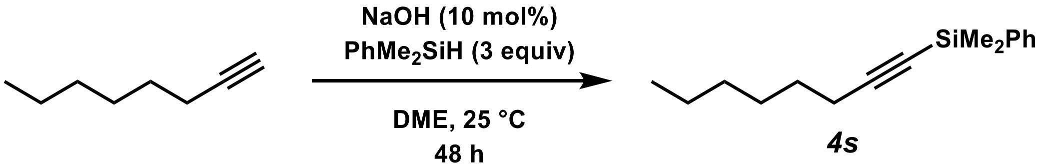


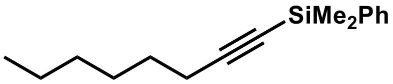
(3-Methoxyprop-1-yn-1-yl)dimethyl(phenyl)silane 4q: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 3-methoxyprop-1-yne (35 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h. The desired product **4q** (61.0 mg, 60% yield) was obtained as a colorless oil after removal of volatiles at 85°C at 45 mtorr for 15 minutes (careful heating is necessary, as the product is volatile under these conditions) and subsequent purification by silica gel flash chromatography (1:1 DCM:hexanes). R$_f$ = 0.38 (1:1 DCM:hexanes); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.65 – 7.62 (m, 2H), 7.41 – 7.36 (m, 3H), 4.16 (s, 2H), 3.41 (s, 3H), 0.45 (s, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 136.6, 133.7, 129.5, 127.9, 103.1, 89.5, 60.5, 57.7, –1.0. HRMS (EI+) calc'd for $C_{12}H_{16}OSi$ [M+•]: 204.0971, found 204.0977.





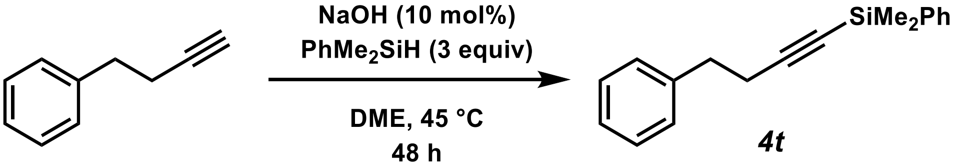
(Cyclopropylethynyl)dimethyl(phenyl)silane 4r: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), ethynylcyclopropane (33 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h. The desired product **4r** (70.1 mg, 70% yield) was obtained as a colorless oil after removal of volatiles at 85°C at 45 mtorr for 30 minutes (careful heating is necessary, as this product is volatile under these conditions) and subsequent purification by silica gel flash chromatography (100% hexanes). R$_f$ = 0.38 (100% hexanes); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.64 – 7.61 (m, 2H), 7.39 – 7.36 (m, 3H), 1.40 – 1.30 (m, 1H), 0.87 – 0.75 (m, 4H), 0.40 (s, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.8, 133.8, 129.4, 127.9, 112.4, 77.6, 9.0, 0.7, –0.5. HRMS (EI+) calc'd for $C_{13}H_{16}Si$ [M+•]: 200.1021, found 200.1031.



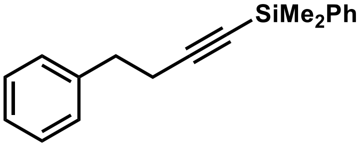


Dimethyl(oct-1-yn-1-yl)(phenyl)silane 4s: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), oct-1-yne (55 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 25 °C for 48 h. The desired product **4s** (101.0 mg, 83% yield) was as a colorless oil after removal of volatiles at 85°C at 45 mtorr for 15 minutes and subsequent purification by silica gel flash chromatography (100% hexanes). R$_f$ = 0.53

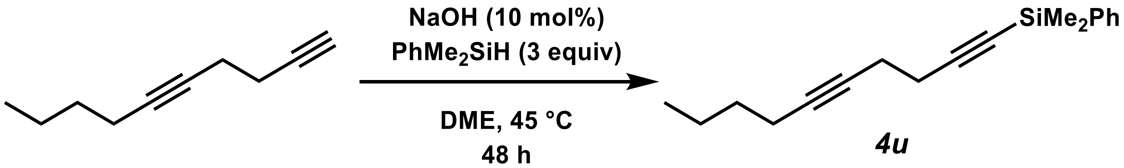
(100% hexanes); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.67 – 7.62 (m, 2H), 7.40 – 7.35 (m, 3H), 2.28 (t, J = 7.1 Hz, 2H), 1.59 – 1.53 (m, 2H), 1.47 – 1.39 (m, 2H), 1.35 – 1.27 (m, 4H), 0.91 (t, J = 6.9 Hz, 3H), 0.40 (s, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.9, 133.8, 129.4, 127.9, 109.9, 82.3, 31.4, 28.7, 28.6, 22.7, 20.1, 14.2, –0.4. HRMS (EI+) calc'd for $C_{16}H_{23}Si$ [M+H]: 245.1726, found 245.1727.

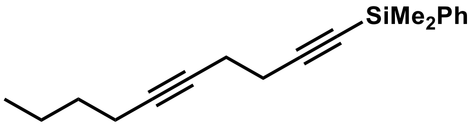


4t

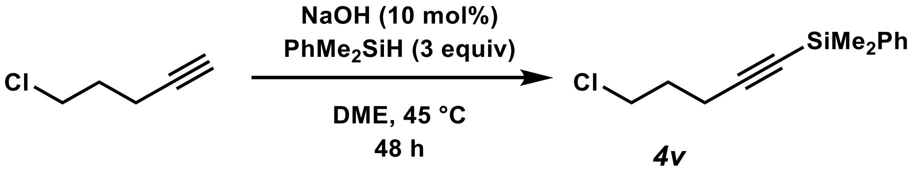


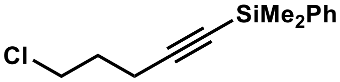
Dimethyl(phenyl)(4-phenylbut-1-yn-1-yl)silane 4t: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), but-3-yn-1-ylbenzene (65 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h. The desired product **4t** (130.0 mg, 98% yield) was obtained in analytical purity as a pale yellow oil after removal of volatiles at 85°C at 45 mtorr for 30 minutes. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.64 – 7.59 (m, 2H), 7.42 – 7.37 (m, 3H), 7.31 (dd, J = 8.0, 6.8 Hz, 2H), 7.28 – 7.23 (m, 3H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.60 (t, *J* = 7.5 Hz, 2H), 0.42 (d, *J* = 0.6 Hz, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 140.6, 137.6, 133.8, 129.4, 128.7, 128.5, 127.9, 126.4, 108.6, 83.4, 35.1, 22.4, –0.6. HRMS (EI+) calc'd for $C_{18}H_{19}Si$ [(M+H)-H$_2$]: 263.1256, found 263.1258.



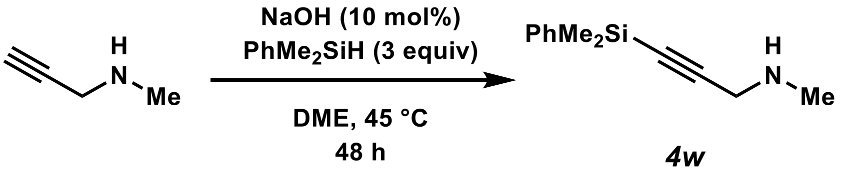


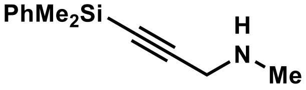
Deca-1,5-diyn-1-yldimethyl(phenyl)silane 4u: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), deca-1,5-diyne (67 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h. The desired product **4u** (131.3 mg, 98% yield) was obtained in analytical purity as a colorless oil after removal of volatiles at 85°C at 45 mtorr for 30 minutes. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2H), 7.38 (dd, *J* = 5.0, 1.9 Hz, 3H), 2.49 (ddd, *J* = 7.7, 6.1, 1.7 Hz, 2H), 2.46 – 2.39 (m, 2H), 2.18 (tt, *J* = 7.0, 2.3 Hz, 2H), 1.52 – 1.39 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.42 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 133.8, 129.4, 127.9, 107.8, 83.3, 81.6, 78.3, 31.2, 22.0, 20.8, 19.2, 18.5, 13.8, –0.5. HRMS (EI+) calc'd for $C_{18}H_{23}Si$ [(M+H)-H_2]: 267.1569, found 267.1565.



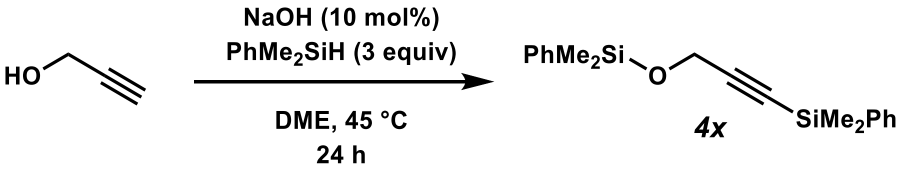


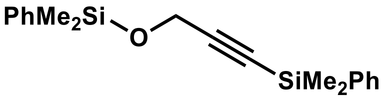
(5-Chloropent-1-yn-1-yl)dimethyl(phenyl)silane 4v: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 5-chloropent-1-yne (51 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h. The desired product **4v** (93.3 mg, 79% yield) was obtained as a colorless oil after removal of volatiles at 85°C at 45 mtorr for 15 minutes (careful heating is necessary, as this product is volatile under these conditions) and subsequent purification by silica gel flash chromatography (100% hexanes). R$_f$ = 0.31 (100% hexanes); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.65 – 7.60 (m, 2H), 7.38 (dd, *J* = 4.9, 1.9 Hz, 3H), 3.67 (t, *J* = 6.4 Hz, 2H), 2.49 (t, *J* = 6.8 Hz, 2H), 2.01 (p, *J* = 6.6 Hz, 2H), 0.41 (s, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.5, 133.7, 129.5, 128.0, 107.2, 83.8, 43.8, 31.4, 17.6, –0.6. HRMS (EI+) calc'd for $C_{13}H_{16}ClSi$ [(M+H)-H$_2$]: 235.0710, found 235.0713.



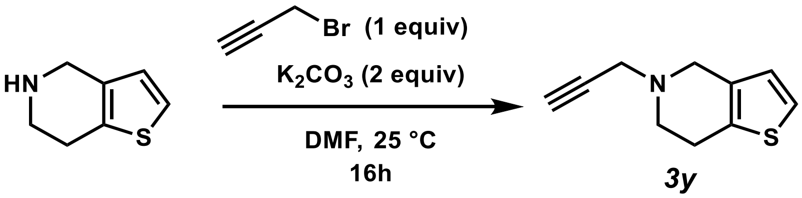


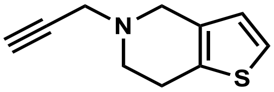
3-(Dimethyl(phenyl)silyl)-*N*-methylprop-2-yn-1-amine 4w: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), *N*-methylprop-2-yn-1-amine (69 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h. The desired product **4w** (81.8 mg, 80% yield) was obtained as a colorless oil after removal of volatiles at 85°C at 45 mtorr for 15 minutes (careful heating is necessary, as the product is volatile under these conditions) and subsequent purification by silica gel flash chromatography (100% EtOAc). R$_f$ = 0.32 (100% EtOAc); ^{1}H NMR (500 MHz, THF-d_8) δ 7.63 – 7.59 (m, 2H), 7.33 – 7.29 (m, 3H), 3.36 (s, 2H), 2.39 (s, 3H), 0.36 (s, 6H); ^{13}C NMR (126 MHz, THF-d_8) δ 138.3, 134.6, 130.2, 128.7, 108.5, 85.4, 41.7, 35.6, –0.3. HRMS (EI+) calc'd for $C_{12}H_{18}NSi$ [M+H]: 204.1208, found 204.1214.



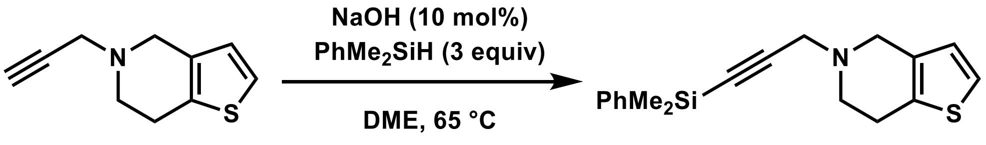


(3-((Dimethyl(phenyl)silyl)oxy)prop-1-yn-1-yl)dimethyl(phenyl)silane 4x: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), prop-2-yn-1-ol (28 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 24 h. The desired product **4x** (142.9 mg, 88% yield) was obtained in analytical purity as a colorless oil after removal of volatiles at 85°C at 45 mtorr for 30 minutes (careful heating is necessary, as the product is volatile under these conditions). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.62 (ddt, *J* = 6.4, 1.8, 0.9 Hz, 4H), 7.44 – 7.36 (m, 6H), 4.35 (s, 2H), 0.48 (s, 6H), 0.43 (s, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.1, 136.8, 133.8, 133.7, 129.9, 129.6, 128.0, 128.0, 105.8, 88.2, 52.3, –0.9, –1.4. HRMS (EI+) calc'd for $C_{19}H_{23}OSi_2$ [(M+H)–H$_2$]: 323.1288, found 323.1297.

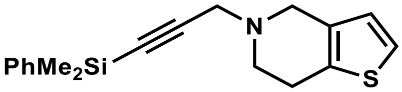




5-(Prop-2-yn-1-yl)-4,5,6,7-tetrahydrothieno[3,2-c]pyridine 3y: To a mixture of tetrahydrothieno[3,2-*c*]pyridine hydrochloride (1.40 g, 10 mmol, 1 equiv) and K$_2$CO$_3$ (2.76 g, 20 mmol, 2 equiv) in DMF (30 ml), was added 1-propyne-3-bromide (1.18 g, 10 mmol, 1 equiv) and the mixture was stirred at room temperature for 16 h. The mixture was filtered and solvent was removed under reduced pressure to give a brown oil. This oil was diluted with 20 mL of diethyl ether and washed with 20 mL of water, then 20 mL brine, then dried over anhydrous Na$_2$SO$_4$. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (10:1 hexanes:Et_2O) yielding the product **3y** as a yellow liquid (1.27 g, 72% yield). $R_f = 0.35$ (10% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.08 (dt, *J* = 5.1, 0.7 Hz, 1H), 6.73 (d, *J* = 5.1 Hz, 1H), 3.69 (t, *J* = 1.7 Hz, 2H), 3.53 (d, *J* = 2.4 Hz, 2H), 2.95 – 2.91 (m, 2H), 2.91 – 2.88 (m, 2H), 2.29 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.5, 132.9, 125.2, 122.8, 78.8, 73.4, 51.5, 49.7, 46.4, 25.6. HRMS (EI+) calc'd for $C_{10}H_{12}NS$ [M+H]: 178.0690, found 178.0689.

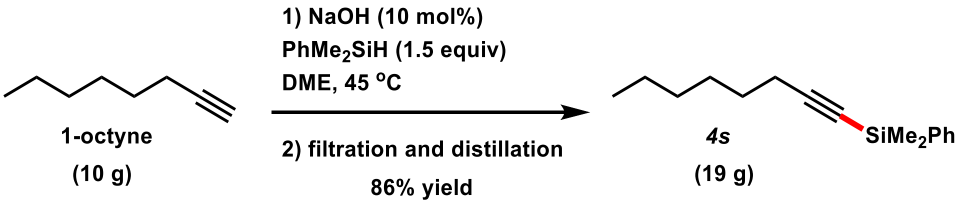


4y



5-(3-(Dimethyl(phenyl)silyl)prop-2-yn-1-yl)-4,5,6,7-tetrahydrothieno[3,2-c]pyridine 4y: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 5-(prop-2-yn-1-yl)-4,5,6,7-tetrahydrothieno[3,2-c]pyridine (89 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **4y** (120.4 mg, 77% yield) was obtained as a yellow oil after removal of volatiles at 85 °C at 45 mtorr for 15 minutes and subsequent purification by silica gel flash chromatography (10% EtOAc in hexanes). $R_f = 0.40$ (10% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.43 – 7.34 (m, 3H), 7.10 (dd, *J* = 5.1, 0.8 Hz, 1H), 6.75 (d, *J* = 5.1 Hz, 1H), 3.76 (t, *J* = 1.6 Hz, 2H), 3.64 (d, *J* = 0.7 Hz, 2H), 2.96 (s, 4H), 0.42 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1, 133.8, 133.2, 133.1, 129.5, 128.0, 125.4, 122.9, 102.7, 88.4, 51.7, 49.9, 47.6, 25.7, –0.6. HRMS (EI+) calc'd for $C_{18}H_{20}NSSi$ [(M+H)-H_2]: 310.1086, found 310.1087.

2. Multi-gram scale synthesis of *4s*.



Dimethyl(oct-1-yn-1-yl)(phenyl)silane 4s: A 500 mL oven-dried Schlenk flask equipped with a stir bar and stoppered with a rubber septum was evacuated and refilled once with argon. NaOH (364 mg, 9.1 mmols, 10 mol%) was weighed out on the bench and added to the flask under a strong flow of argon. The charged flask was then evacuated and heated under vacuum for 2 minutes with a heat gun, then refilled with argon. 1,2-dimethoxyethane (DME) (90 mL), 1-octyne (13.4 mL, 90.7 mmol, 1.0 equiv) and $PhMe_2SiH$ (20.9 mL, 136.1 mmol, 1.5 equiv) were added through the septum by syringe. The flask was then heated with a heating mantle set at 45 °C and stirred for 60 hours. The flask with the resultant cloudy brown-tan solution was removed from heating and allowed to cool to room temperature, diluted with anhydrous Et_2O (50 mL), and filtered through a short pad of silica to remove solid residue. After the solvent was removed *in vacuo*, a stirbar was added and the transparent deep amber solution was stirred under high vacuum (100 millitorr) for several hours to remove remaining volatiles. The mixture was then subjected to distillation under vacuum:

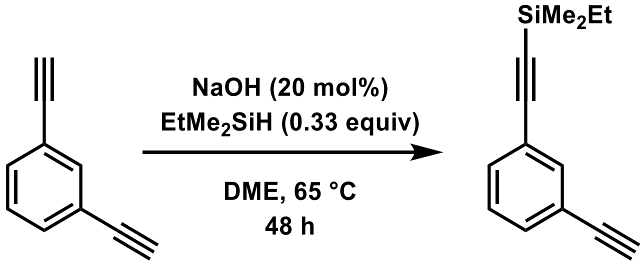
a) Heating bath to 80 °C, vacuum stabilizes at 200 millitorr as a small amount of droplets condense into the forerun. Forerun comes off as a colorless liquid. Thermometer reads 22 °C.

b) Vacuum stays at 200 millitorr. Heating bath set to 85 °C as the last of the remaining silane boils off.

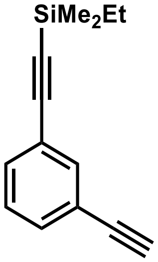
c) Heating bath temperature increased to 125 °C. The solution starts to boil slowly. Thermometer reads 60 °C. Vacuum stays at 200 millitorr.

d) Increase temperature to 130 °C, vacuum at 200 millitorr to distill over the desired dimethyl(oct-1-yn-1-yl)(phenyl)silane (colorless oil). Thermometer reads 85 °C. The desired product ***4s*** is obtained as a colorless oil (19.0 g, 86% yield).

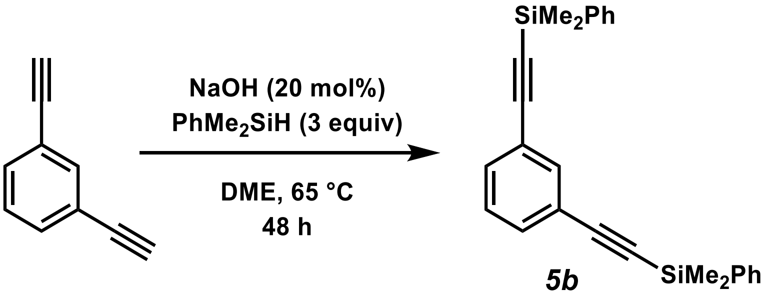
3. Optimization and synthesis of *mono*- and *bis*-silylated diynes.

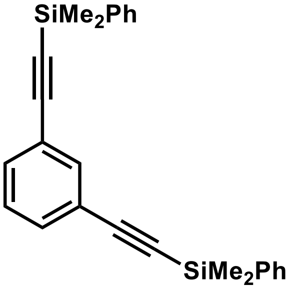


5a



Ethyl((3-ethynylphenyl)ethynyl)dimethylsilane 5a: The general procedure was followed. The reaction was performed with NaOH (4.0 mg, 0.1 mmol, 20 mol%), 1,3-diethynylbenzene (189 mg, 1.5 mmol, 3.0 equiv), EtMe$_2$SiH (44 mg, 66 µL, 0.5 mmol, 1.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **5a** (68.9 mg, 65% yield; based on silane) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). The bis-silylated product was also obtained in 4% yield. R$_f$ = 0.33 (100% hexanes); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.60 (t, J = 1.7 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.26 (t, J = 7.8 Hz, 1H), 3.07 (s, 1H), 1.04 (t, J = 7.9 Hz, 3H), 0.67 (q, J = 7.9 Hz, 2H), 0.21 (s, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 135.66, 132.32, 132.11, 128.43, 123.66, 122.44, 104.41, 94.44, 82.85, 77.87, 8.16, 7.49, -2.15. HRMS (EI+) calc'd for $C_{14}H_{17}Si$ [M+H]: 213.1100, found 213.1089.

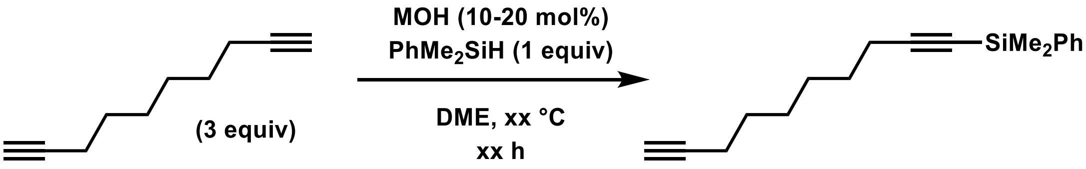




1,3-bis((dimethyl(phenyl)silyl)ethynyl)benzene 5b: The general procedure was followed. The reaction was performed with NaOH (4.0 mg, 0.1 mmol, 20 mol%), 1,3-diethynylbenzene (63 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **5b** (173.5 mg, 88% yield) was obtained as a light yellow oil after removal of volatiles at 85 °C at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100% hexanes → 3% EtOAc in hexanes). R$_f$ = 0.26 (100% hexanes); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.73 – 7.70 (m, 4H), 7.69 (t, J = 1.7 Hz, 1H), 7.47 (dd, J = 7.8, 1.7 Hz, 2H), 7.44 – 7.41 (m, 6H), 7.28 (ddd, J = 8.0, 7.4, 0.5 Hz, 1H), 0.53 (s, 12H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 136.9, 135.7, 133.9, 132.3, 129.6, 128.4, 128.1, 123.3, 105.7, 93.1, –0.7. HRMS (EI+) calc'd for $C_{26}H_{27}Si_2$ [M+H]: 395.1651, found 395.1659.

Optimization of 1,9-decadiyne monosilylation:

Table 4 details the optimization for the *mono*-silylation of 1,9-decadiyne. Yields are based on silane and are determined by GC analysis. Isolated yields are also provided for many cases.



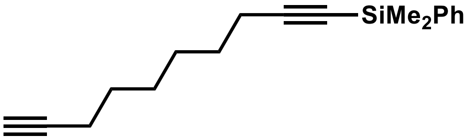
6a

Table 4. Optimization of 1,9-decadiyne *mono*-silylation.

Conditions	Time (days)	Yield *Mono* (%)[1]	Yield *Bis* (%)[1]	*Mono*:*bis*[1]	Isolated Yield (*mono*, %)	Isolated Yield (*bis*, %)
0.1 equiv **NaOH**, 45 °C	2	18.6	0.2	119.4	-	-
	5	38.2	0.5	70.5	-	-
	7	47.6	0.9	51.3	-	-
	9	54.2	1.4	39.5	-	-
	12	61.2	1.9	32.4	-	-
	14	64.6	2.2	29.1	-	-
	16	64.3	1.8	35.6	-	-
0.1 equiv **NaOH**, 65 °C	2	24.1	0.0	-	-	-
	5	43.2	0.8	57.4	-	-
	7	50.6	1.0	49.9	-	-
	9	56.6	1.4	39.2	-	-
	12	61.1	1.9	32.6	-	-
	14	65.5	2.1	31.9	-	-
	16	64.8	2.0	32.6	-	-

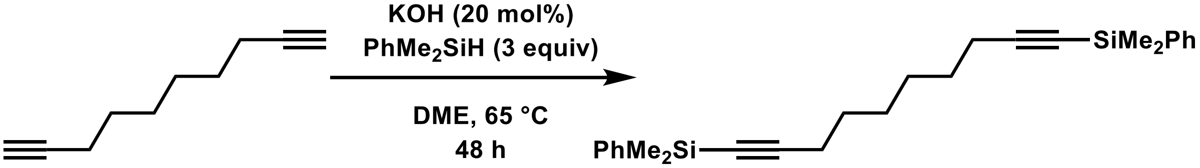
Conditions	**Time (days)**	**Yield *Mono* (%)**[1]	**Yield *Bis* (%)**[1]	***Mono* :*bis***[1]	**Isolated Yield (*mono* , %)**	**Isolated Yield (*bis* , %)**
0.1 equiv **KOH**, 45 °C	**2**	**59.6**	**1.7**	**35.9**	**46**	**1**
	5	**78.2**	**3.2**	**24.5**	**60**	**0**
	7	**82.8**	**4.0**	**20.5**	**65**	**2**
	9	86.2	4.3	20.2	-	-
	12	88.7	4.8	18.5	-	-
	14	90.0	5.0	17.9	-	-
	16	90.6	4.6	19.8	-	-
0.1 equiv **KOH**, 65 °C	**2**	**75.3**	**3.5**	**21.3**	**63**	**1**
	5	**84.1**	**4.2**	**19.8**	**68**	**4**
	7	**82.5**	**4.2**	**19.6**	**71**	**4**
	9	79.2	4.0	20.0	-	-
	12	85.6	4.3	20.1	-	-
	14	92.6	5.1	18.3	-	-
	16	97.1	5.3	18.4	-	-
0.2 equiv **NaOH**, 45 °C	1	23.8	0.0	-	-	-
	2	39.4	0.0	-	-	-
	5	54.8	1.2	45.0	-	-
	7	58.7	1.5	38.2	-	-
	9	61.1	1.9	33.0	-	-
0.2 equiv **NaOH**, 65 °C	**1**	**52.5**	**1.1**	**46.1**	**32**	**0**
	2	**68.7**	**2.1**	**33.4**	**57**	**2**
	5	**84.7**	**3.9**	**21.7**	**66**	**5**
	7	**87.1**	**4.8**	**18.3**	**73**	**5**
	9	88.9	5.2	17.2	-	-
0.2 equiv **KOH**, 45 °C	1	16.3	0.0	-	-	-
	2	24.9	0.0	-	-	-
	5	32.8	0.0	-	-	-
	7	35.0	0.0	-	-	-
	9	35.6	0.5	66.1	-	-
0.2 equiv **KOH**, 65 °C	1	28.1	0.0	-	-	-
	2	26.8	0.0	-	-	-
	5	27.3	0.0	-	-	-
	7	30.5	0.0	-	-	-
	9	34.2	0.0	-	-	-

[1] Yields and selectivities determined by GC-FID. Several experiments were also isolated via column chromatography as shown in the table (1:30 CH_2Cl_2:hexanes). The difference between GC-FID and the isolated yields are believed to be due primarily to volatility of the *mono*-silylated product under high vacuum and challenging separation of the mono and bis silylated products from each other on the column.

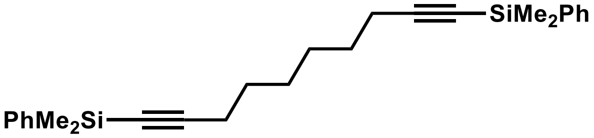


Deca-1,9-diyn-1-yldimethyl(phenyl)silane 6a: The general procedure was followed. The reaction was performed with either KOH or NaOH (10–20 mol%), deca-1,9-diyne (201 mg, 1.5 mmol, 3.0 equiv), $PhMe_2SiH$ (68 mg, 77 µL, 0.5 mmol, 1.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at either 45 °C or 65 °C for the specified amount of time (see yields in Table 4). The desired product **6a** was obtained as a colorless oil after purification by silica gel flash chromatography (gradient 1:30 dichloromethane : hexanes → 1:10 dichloromethane : hexanes). $R_f = 0.31$ (10% dichloromethane in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.40 – 7.35 (m, 3H), 2.29 (t, *J* = 7.1 Hz, 2H), 2.20 (td, *J* = 7.1, 2.6 Hz, 2H), 1.96 (t, *J* = 2.6 Hz, 1H), 1.57 (dtd, *J* = 9.6, 7.1, 4.5 Hz, 4H), 1.47 – 1.42 (m, 4H), 0.40 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 133.8, 129.4, 127.9, 109.6, 84.7, 82.5, 68.3, 28.51, 28.45, 28.39, 28.31, 20.0, 18.5, –0.5. HRMS (EI+) calc'd for $C_{18}H_{23}Si$ [(M+H)-H_2]: 267.1569, found 267.1556.

Bis-silylation of 1,9-decadiyne:



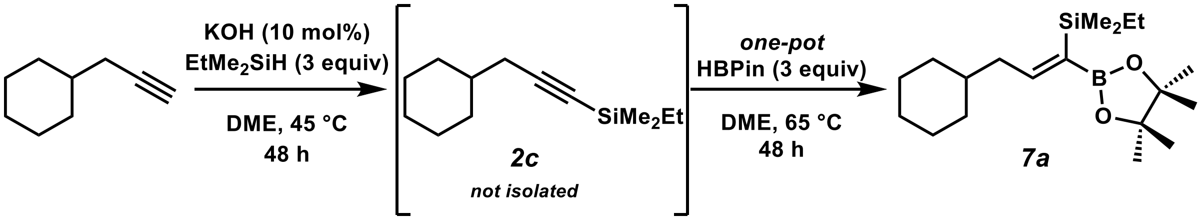
6b

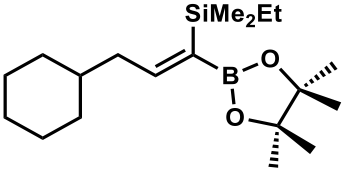


1,10-Bis(dimethyl(phenyl)silyl)deca-1,9-diyne 6b: The general procedure was followed. The reaction was performed with KOH (5.6 mg, 0.1 mmol, 20 mol%), deca-1,9-diyne (67 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h. The desired product **6b** (189.3 mg, 93% yield) was obtained as a colorless oil after removal of volatiles at 85 °C at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (gradient 1:30

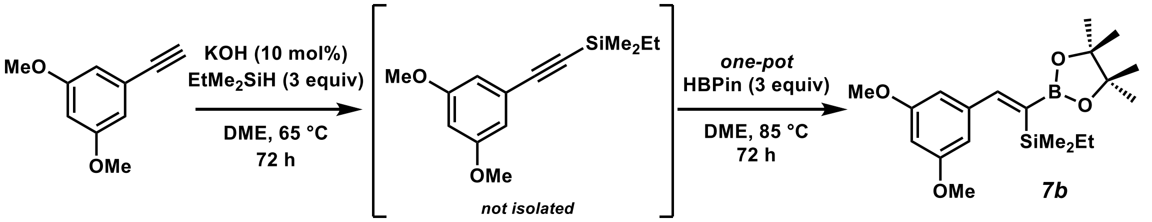
dichloromethane : hexanes → 1:10 dichloromethane : hexanes). R*f* = 0.28 (10% dichloromethane in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (ddt, *J* = 5.4, 3.0, 1.4 Hz, 4H), 7.38 (ddt, *J* = 4.4, 2.2, 1.1 Hz, 6H), 2.30 (td, *J* = 7.2, 1.1 Hz, 4H), 1.59 (t, *J* = 6.8 Hz, 4H), 1.49 – 1.42 (m, 4H), 0.42 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 133.8, 129.4, 127.9, 109.6, 82.5, 28.5, 28.4, 20.0, –0.4. HRMS (EI+) calc'd for $C_{26}H_{33}Si_2$ [(M+H)-H_2]: 401.2121, found 401.2120.

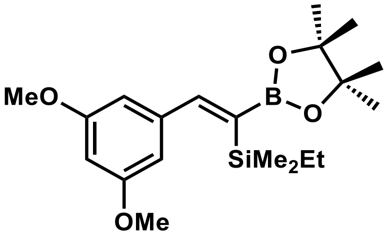
4. *Geminal* one-pot silaboration of alkynes.



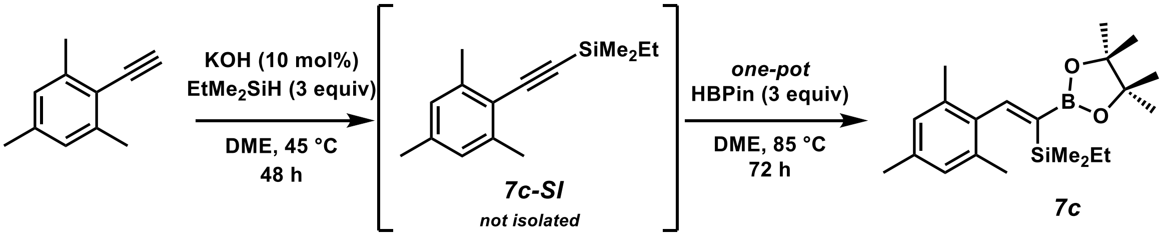


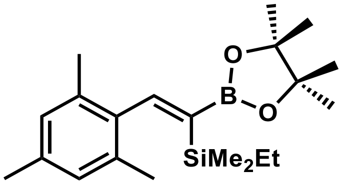
(Z)-(3-cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)(ethyl)dimethylsilane 7a: The general procedure was followed for the silylation portion of the reaction. The reaction was performed with KOH (2.8 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), $EtMe_2SiH$ (132 mg, 198 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h to yield the intermediate **2c**. HBPin (192 mg, 218 µL, 1.5 mmol, 3.0 equiv) was then added and the reaction mixture was stirred for a further 48 h at 65 °C. The desired product **7a** (107.6 mg, 64% yield) was obtained as a colorless oil by silica gel flash chromatography (2.5% EtOAc in hexanes). Note: product is somewhat unstable on silica gel, likely contributing to the lower isolated yield. R*f* = 0.24 (2.5% EtOAc in hexanes); ^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.57 (t, J = 7.2 Hz, 1H), 2.23 (t, J = 7.0 Hz, 2H), 1.72 (ddd, J = 14.7, 5.0, 2.6 Hz, 2H), 1.67 – 1.51 (m, 4H), 1.34 (dddq, J = 14.6, 11.0, 7.0, 3.5 Hz, 1H), 1.14 (td, J = 7.9, 0.7 Hz, 3H), 1.09 (d, J = 0.6 Hz, 12H), 1.08 – 1.04 (m, 2H), 0.93 (q, J = 8.0 Hz, 2H), 0.89 – 0.84 (m, 2H), 0.42 (s, 6H); ^{13}C NMR (126 MHz, Benzene-*d*$_6$) δ 163.1, 82.8, 43.2, 38.6, 33.7, 26.9, 26.8, 26.7, 24.9, 9.4, 8.1, -0.5. HRMS (EI+) calc'd for $C_{19}H_{36}BSiO_2$ [(M+H)-H_2]: 335.2578, found 335.2577. Olefin geometry was confirmed by 2D-NOESY.



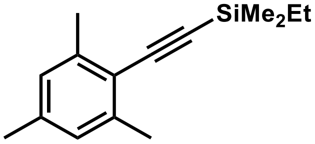


(Z)-(2-(3,5-dimethoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)(ethyl)dimethylsilane 7b: The general procedure was followed for the silylation portion of the reaction. The reaction was performed with KOH (2.8 mg, 0.05 mmol, 10 mol%), 1-ethynyl-3,5-dimethoxybenzene (81 mg, 0.5 mmol, 1.0 equiv), $EtMe_2SiH$ (132 mg, 198 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 72 h to yield the silylated alkyne intermediate. HBPin (192 mg, 218 μL, 1.5 mmol, 3.0 equiv) was then added and the reaction mixture was stirred for a further 72 h at 85 °C. The desired product **7b** (56.5 mg, 30% yield) was obtained as a colorless oil by silica gel flash chromatography (10% EtOAc in hexanes). Note: product is somewhat unstable on silica gel, likely contributing to the lower isolated yield. $R_f = 0.49$ (10% EtOAc in hexanes); ^1H NMR (500 MHz, Benzene-d_6) δ 8.59 (s, 1H), 6.60 (dt, J = 2.3, 0.6 Hz, 2H), 6.52 (t, J = 2.3 Hz, 1H), 3.30 (s, 6H), 1.12 (s, 12H), 1.06 (t, J = 7.6 Hz, 3H), 0.90 (q, J = 7.8 Hz, 2H), 0.30 (s, 6H); ^{13}C NMR (126 MHz, Benzene-d_6) δ 161.0, 159.7, 144.1, 106.5, 100.8, 83.2, 54.9, 24.9, 9.4, 8.1, -0.9. HRMS (EI+) calc'd for $C_{20}H_{34}BSiO_4$ [M+H]: 377.2320, found 377.2318. Olefin geometry was confirmed by 2D-NOESY.

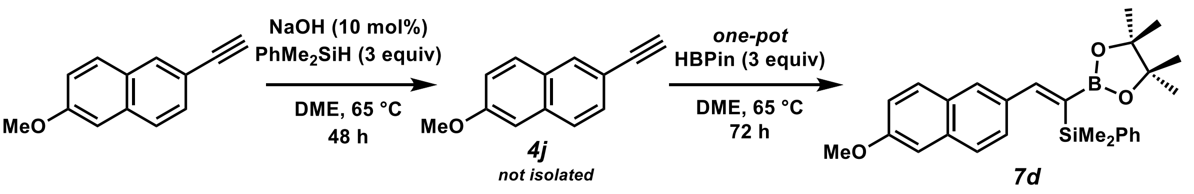


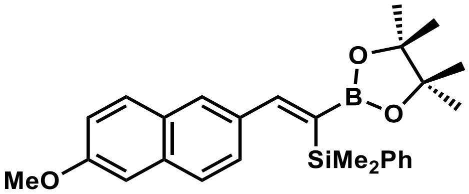


(Z)-ethyl(2-mesityl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethyl silane 7c: The general procedure was followed for the silylation portion of the reaction. The reaction was performed with KOH (2.8 mg, 0.05 mmol, 10 mol%), 2-ethynyl-1,3,5-trimethylbenzene (72 mg, 0.5 mmol, 1.0 equiv), EtMe$_2$SiH (132 mg, 198 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h to yield the intermediate **7c-SI**. HBPin (192 mg, 218 µL, 1.5 mmol, 3.0 equiv) was then added and the reaction mixture was stirred for a further 72 h at 85 °C. The desired product **7c** (57.3 mg, 32% yield) was obtained as a yellow gel by silica gel flash chromatography (2.5% EtOAc in hexanes). Note: product is somewhat unstable on silica gel, likely contributing to the lower isolated yield. R$_f$ = 0.25 (2.5% EtOAc in hexanes); ^{1}H NMR (500 MHz, Benzene-*d$_6$*) δ 8.36 (s, 1H), 6.73 (s, 2H), 2.21 (s, 6H), 2.13 (s, 3H), 1.11 (s, 12H), 1.03 (t, J = 7.9 Hz, 3H), 0.77 (q, J = 7.9 Hz, 2H), 0.07 (s, 6H); ^{13}C NMR (126 MHz, Benzene-*d$_6$*) δ 159.6, 138.9, 136.1, 134.4, 128.2, 83.1, 24.9, 21.2, 20.7, 8.4, 8.1, -2.3. HRMS (EI+) calc'd for $C_{21}H_{35}BSiO_2$ [M+•]: 358.2499, found 358.2495. Olefin geometry was confirmed by 2D-NOESY.

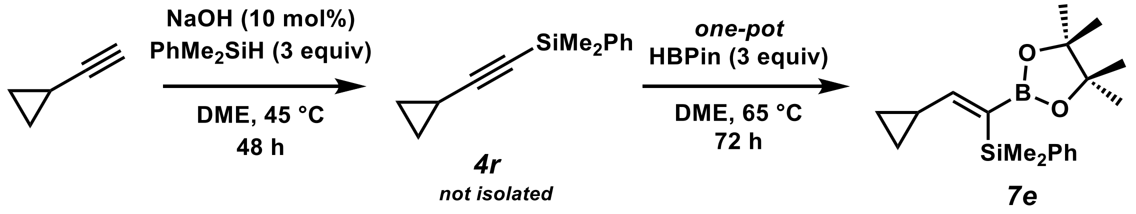


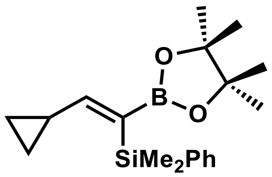
Ethyl(mesitylethynyl)dimethylsilane 7c-SI: Also isolated from the column was **7c-SI** (50.7 mg, 44% yield) as a colourless oil. R$_f$ = 0.63 (2.5% EtOAc in hexanes); ^{1}H NMR (500 MHz, Benzene-*d$_6$*) δ 6.67 (s, 2H), 2.47 (s, 6H), 2.05 (s, 3H), 1.13 (t, J = 7.9 Hz, 3H), 0.69 (q, J = 7.9 Hz, 2H), 0.26 (s, 6H); ^{13}C NMR (126 MHz, Benzene-*d$_6$*) δ 140.7, 138.0, 128.0, 120.8, 104.5, 101.0, 21.3, 21.2, 8.7, 7.8, -1.8. HRMS (EI+) calc'd for $C_{15}H_{22}Si$ [M+•]: 230.1491, found 230.1495.





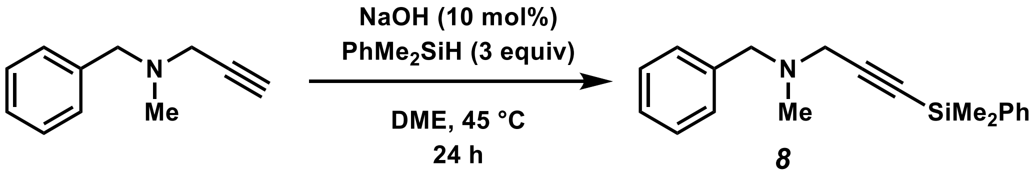
(Z)-(2-(6-methoxynaphthalen-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) vinyl)dimethyl(phenyl)silane 7d: The general procedure was followed for the silylation portion of the reaction. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 2-ethynyl-6-methoxynaphthalene (91 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 48 h to yield the intermediate **4j**. HBPin (192 mg, 218 µL, 1.5 mmol, 3.0 equiv) was then added and the reaction mixture was stirred for a further 72 h at 65 °C. The desired product **7d** (73.4 mg, 33% yield) was obtained as a colorless gel by silica gel flash chromatography (gradient 2.5% EtOAc in hexanes → 10% EtOAc in hexanes). Note: product is somewhat unstable on silica gel, likely contributing to the lower isolated yield. Also isolated was the silylated intermediate **4j** (13.5 mg, 4% yield). $R_f = 0.49$ (10% EtOAc in hexanes); ^1H NMR (500 MHz, Benzene-d_6) δ 8.76 (d, J = 1.0 Hz, 1H), 7.81 (dd, J = 8.0, 1.4 Hz, 2H), 7.63 (d, J = 1.4 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.25 (tt, J = 7.8, 1.3 Hz, 2H), 7.19 (tt, J = 7.5, 1.5 Hz, 1H), 7.09 (dd, J = 8.9, 2.5 Hz, 1H), 6.80 (d, J = 2.5 Hz, 1H), 3.33 (s, 3H), 1.12 (s, 12H), 0.47 (s, 6H); ^{13}C NMR (126 MHz, Benzene-d_6) δ 160.5, 158.6, 141.6, 136.6, 134.8, 134.5, 130.2, 128.84, 128.82, 128.5, 127.4, 126.5, 119.5, 106.0, 83.3, 54.8, 24.9, 0.2. HRMS (EI+) calc'd for $C_{27}H_{33}BSiO_3$ [M+•]: 444.2292, found 444.2304. Olefin geometry was confirmed by 2D-NOESY.

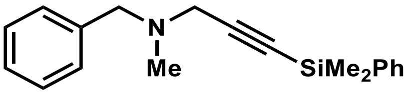




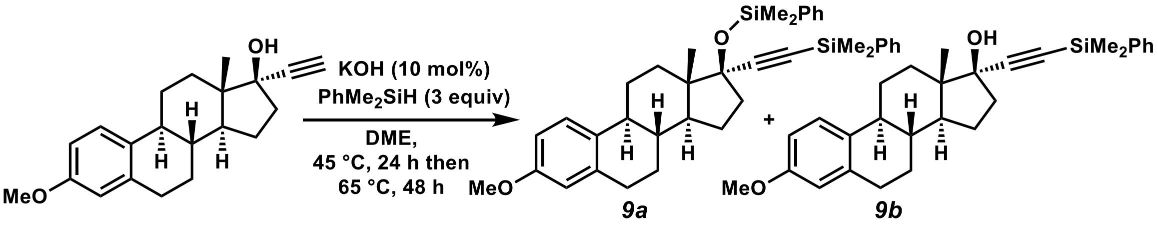
(Z)-(2-cyclopropyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethyl (phenyl)silane 7e: The general procedure was followed for the silylation portion of the reaction. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), cyclopropylacetylene (33 mg, 0.5 mmol, 1.0 equiv), PhMe$_2$SiH (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h to yield the intermediate **4r**. HBPin (192 mg, 218 μL, 1.5 mmol, 3.0 equiv) was then added and the reaction mixture was stirred for a further 72 h at 65 °C. The desired product **7e** (94.6 mg, 58% yield) was obtained as a colorless oil by silica gel flash chromatography (2.5% EtOAc in hexanes). Note: product is somewhat unstable on silica gel, likely contributing to the lower isolated yield. $R_f = 0.38$ (2.5% EtOAc in hexanes); ^{1}H NMR (500 MHz, Benzene-*d$_6$*) δ 7.77 – 7.72 (m, 2H), 7.29 – 7.22 (m, 3H), 6.83 (d, J = 10.5 Hz, 1H), 1.58 – 1.48 (m, 1H), 1.07 (s, 12H), 0.69 (s, 6H), 0.41 – 0.36 (m, 2H), 0.28 (dt, J = 6.9, 4.2 Hz, 2H); ^{13}C NMR (126 MHz, Benzene-*d$_6$*) δ 169.8, 141.3, 134.4, 128.8, 128.0, 82.7, 24.9, 17.5, 8.9, 0.6, -1.5. HRMS (EI+) calc'd for $C_{19}H_{29}BSiO_2$ [M+•]: 328.2030, found 328.2037. Olefin geometry was confirmed by 2D-NOESY.

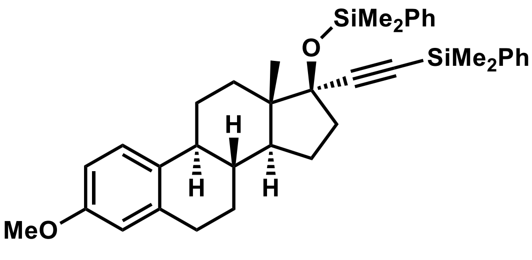
5. Late-stage silylation of pharmaceuticals.





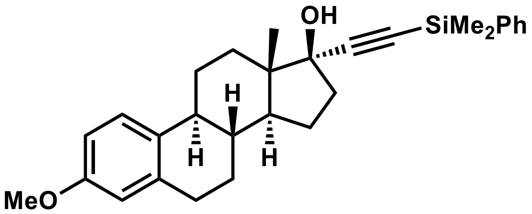
N-benzyl-3-(dimethyl(phenyl)silyl)-N-methylprop-2-yn-1-amine 8: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), Pargyline (N-benzyl-N-methylprop-2-yn-1-amine) (80 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 24 h. The desired product **8** (140.4 mg, 96% yield) was obtained in analytical purity as a pale yellow oil after removal of volatiles at 85 °C at 45 mtorr for 30 minutes. ^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (dq, *J* = 6.8, 3.4, 2.7 Hz, 2H), 7.40 (dt, *J* = 4.3, 2.1 Hz, 3H), 7.35 – 7.31 (m, 4H), 7.30 – 7.26 (m, 1H), 3.60 (d, *J* = 3.0 Hz, 2H), 3.38 (d, *J* = 3.1 Hz, 2H), 2.38 (d, *J* = 3.2 Hz, 3H), 0.47 (d, *J* = 3.4 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 137.3, 133.8, 129.5, 129.4, 128.4, 128.0, 127.4, 102.9, 88.4, 60.2, 46.1, 42.1, –0.5. HRMS (EI+) calc'd for $C_{19}H_{24}NSi$ [M+H]: 294.1678, found 294.1689.



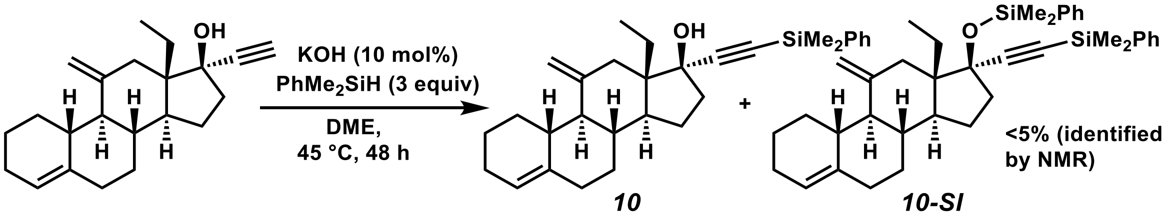


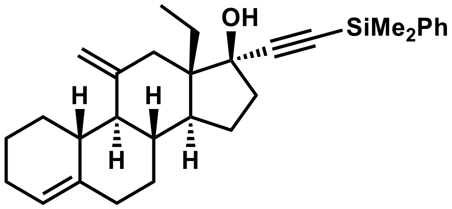
(((8R,9S,13S,14S,17S)-17-((dimethyl(phenyl)silyl)ethynyl)-3-methoxy-13-methyl-7,8, 9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)oxy)dimethyl

(phenyl)silane 9a: The general procedure was followed. The reaction was performed with KOH (2.8 mg, 0.05 mmol, 10 mol%), mestranol ((8R,9S,13S,14S,17R)-17-ethynyl-3-methoxy-13-methyl- 7,8,9,11,12,13,14,15,16,17- decahydro -6H-cyclopenta[a]phenanthren-17-ol) (155 mg, 0.5 mmol, 1.0 equiv), $PhMe_2SiH$ (204 mg, 230 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 24 h then 65 °C for 48 h. The product **9a** (185.5 mg, 64% yield) was obtained as a colorless oil by silica gel flash chromatography (1% → 5% EtOAc in hexanes). R_f = 0.50 (5% EtOAc in hexanes); ^1H NMR (500 MHz, THF-d_8) δ 7.59 (ddd, *J* = 7.6, 3.6, 2.1 Hz, 4H), 7.34 – 7.26 (m, 6H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.63 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.57 (d, *J* = 2.7 Hz, 1H), 3.70 (s, 3H), 2.87 – 2.79 (m, 2H), 2.36 (dq, *J* = 13.4, 3.9 Hz, 1H), 2.30 (ddd, *J* = 13.3, 9.2, 5.3 Hz, 1H), 2.16 (ddd, *J* = 14.6, 7.7, 2.8 Hz, 1H), 2.02 (dtd, *J* = 26.4, 12.8, 4.1 Hz, 2H), 1.88 (ddt, *J* = 12.7, 5.6, 2.5 Hz, 1H), 1.83 – 1.74 (m, 3H), 1.51 – 1.37 (m, 3H), 1.35 – 1.26 (m, 1H), 0.93 (s, 3H), 0.45 (s, 3H), 0.43 (s, 3H), 0.34 (s, 6H); ^{13}C NMR (126 MHz, THF-d_8) δ 158.9, 140.8, 138.4, 137.9, 134.7, 134.4, 133.1, 130.3, 130.0, 128.7, 128.4, 127.1, 114.5, 112.9, 112.4, 90.5, 82.7, 55.3, 49.9, 49.5, 45.2, 41.7, 41.0, 34.2, 30.9, 28.6, 27.7, 24.0, 13.8, 1.41, 1.36, -0.63, -0.65. HRMS (EI+) calc'd for $C_{37}H_{47}O_2Si_2$ [M+H]: 579.3115, found 579.3109.



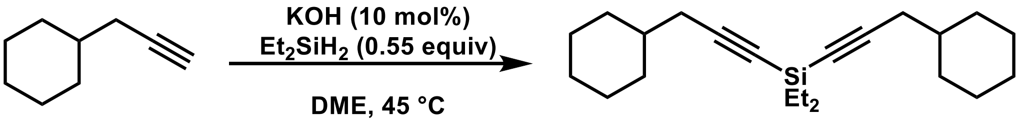
(8R,9S,13S,14S,17S)-17-((dimethyl(phenyl)silyl)ethynyl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17- decahydro- 6H- cyclopenta[a]phenanthren- 17- ol 9b: The desired product **9b** (40.0 mg, 18% yield) was also obtained from this reaction as a white solid foam by silica gel flash chromatography (1% → 5% EtOAc in hexanes) in a 9:1 mixture with **9a**. R_f = 0.39 (5% EtOAc in hexanes); ^1H NMR (500 MHz, THF-d_8) δ 7.61 – 7.56 (m, 2H), 7.35 – 7.30 (m, 3H), 7.13 (dd, *J* = 8.7, 1.1 Hz, 1H), 6.62 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.58 – 6.53 (m, 1H), 3.69 (s, 3H), 2.85 – 2.77 (m, 2H), 2.27 (dtd, *J* = 13.5, 4.2, 2.7 Hz, 1H), 2.11 (td, *J* = 11.2, 4.3 Hz, 1H), 1.91 – 1.84 (m, 4H), 1.66 – 1.61 (m, 1H), 1.57 – 1.47 (m, 1H), 1.46 – 1.38 (m, 2H), 1.36 – 1.30 (m, 1H), 1.17 – 1.09 (m, 2H), 0.80 (d, *J* = 0.7 Hz, 3H), 0.36 – 0.32 (m, 6H); ^{13}C NMR (126 MHz, THF-d_8) δ 158.9, 140.9, 138.4, 134.2, 132.9, 130.0, 128.6, 127.3, 114.5, 112.5, 91.1, 82.9, 55.4, 50.0, 49.5, 45.2, 40.9, 40.8, 34.2, 30.9, 28.6, 27.8, 24.0, 14.2, 1.6, 1.5. HRMS (EI+) calc'd for $C_{29}H_{37}O_2Si$ [M+H]: 445.2563, found 445.2575.



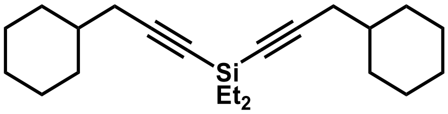


(8S,9S,10R,13S,14S,17S)-17-((dimethyl(phenyl)silyl)ethynyl)-13-ethyl-11-methylene-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-ol 10: The general procedure was followed. The reaction was performed with KOH (1.1 mg, 0.02 mmol, 10 mol%), desogestrel ((8S,9S,10R,13S,14S,17R)-13-ethyl-17-ethynyl-11-methylene-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-ol) (62 mg, 0.2 mmol, 1.0 equiv), $PhMe_2SiH$ (82 mg, 92 μL, 0.6 mmol, 3.0 equiv), and 0.2 mL of 1,2-dimethoxyethane (DME) at 45 °C for 48 h. The product **10** (53.4 mg, 60% yield) was obtained as a colorless solid by silica gel flash chromatography (2.5% Et_2O in hexanes). Also observed were what appear to be <5% of the *bis*-silylated product **10-SI** and <5% of the *mono*-O-silylated desogestrel. $R_f = 0.28$ (2.5% Et_2O in hexanes); ^1H NMR (500 MHz, THF-d_8) δ 7.63 – 7.54 (m, 2H), 7.33 – 7.28 (m, 3H), 5.44 (dt, J = 4.2, 2.4 Hz, 1H), 4.99 (s, 1H), 4.76 (s, 1H), 2.67 (d, J = 12.4 Hz, 1H), 2.24 (q, J = 7.7, 7.1 Hz, 2H), 2.17 (ddt, J = 13.8, 7.0, 3.8 Hz, 2H), 2.13 – 2.01 (m, 2H), 1.96 – 1.90 (m, 3H), 1.88 – 1.77 (m, 1H), 1.67 – 1.54 (m, 2H), 1.49 – 1.37 (m, 4H), 1.35 – 1.28 (m, 4H), 1.01 (t, J = 7.3 Hz, 3H), 0.93-0.86 (m, 1H), 0.38 (s, 3H), 0.37 (s, 6H); ^{13}C NMR (126 MHz, THF-d_8) δ 149.1, 140.7, 134.2, 130.1, 128.7, 122.2, 109.0, 91.3, 83.9, 56.2, 53.0, 52.2, 43.9, 41.63, 41.58, 37.6, 36.6, 33.0, 30.3, 26.7, 26.0, 23.1, 23.0, 21.4, 10.0, 1.6, 1.2. HRMS (EI+) calc'd for $C_{30}H_{41}OSi$ [M+H]: 445.2927, found 445.2931.

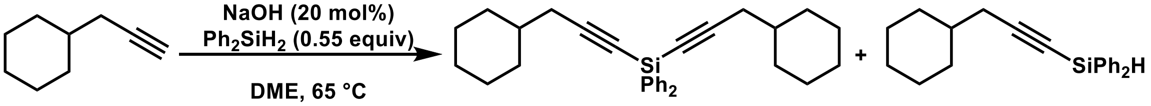
6. Synthesis of symmetric and unsymmetric diethynylsilanes.



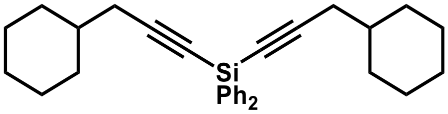
11a



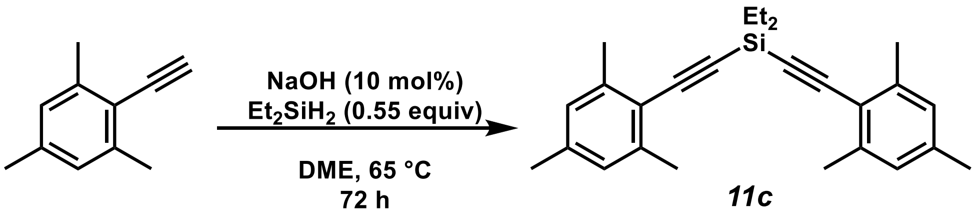
Bis(3-cyclohexylprop-1-yn-1-yl)diethylsilane 11a: The general procedure was followed. The reaction was performed with KOH (2.8 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), Et_2SiH_2 (24 mg, 36 μL, 0.275 mmol, 0.55 equiv), and 0.5 mL of tetrahydrofuran (THF) at 45 °C for 48 h. The desired product **11a** (62.5 mg, 76% yield) was obtained as a colorless oil after removal of volatiles under high vacuum at 45 mtorr for 30 minutes and subsequent purification by silica gel flash chromatography (100% hexanes). R_f = 0.51 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.15 (d, *J* = 6.6 Hz, 4H), 1.81 (ddd, *J* = 13.6, 4.0, 1.8 Hz, 4H), 1.72 (dt, *J* = 12.7, 3.2 Hz, 4H), 1.65 (dddt, *J* = 12.7, 5.1, 3.3, 1.5 Hz, 2H), 1.49 (dddt, *J* = 14.6, 8.0, 6.7, 3.2 Hz, 2H), 1.25 (qt, *J* = 12.7, 3.4 Hz, 4H), 1.15 (tt, *J* = 12.6, 3.2 Hz, 2H), 1.08 – 0.98 (m, 10H), 0.67 (q, *J* = 7.8 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 108.0, 80.7, 37.4, 32.8, 27.9, 26.4, 26.3, 7.5, 7.0. HRMS (EI+) calc'd for $C_{22}H_{37}Si$ [M+H]: 329.2665, found 329.2661.

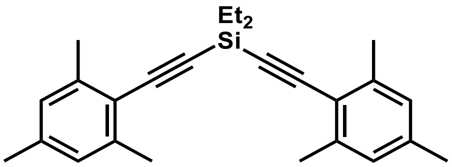


11b (<10%)



Bis(3-cyclohexylprop-1-yn-1-yl)diphenylsilane 11b: The general procedure was followed. The reaction was performed with NaOH (4.0 mg, 0.1 mmol, 20 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), Ph_2SiH_2 (51 mg, 51 μL, 0.275 mmol, 0.55 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 72 h. The desired product **11b** (71.5 mg, 67% yield) was obtained as a colorless oil via silica gel flash chromatography (gradient 100% hexanes → 2.5% Et_2O in hexanes); less than 10% of the monoalkynylhydrosilane was observed by GC-MS. R_f = 0.21 (2.5% Et_2O in hexanes); ^1H NMR (500 MHz, THF-*d*$_8$) δ 7.72 – 7.67 (m, 4H), 7.38 – 7.28 (m, 6H), 2.25 (d, J = 6.6 Hz, 4H), 1.86 (dd, J = 13.9, 1.8 Hz, 4H), 1.72 (ddt, J = 9.2, 7.1, 3.5 Hz, 4H), 1.65 (dtd, J = 11.1, 3.4, 1.8 Hz, 2H), 1.55 (dddd, J = 14.5, 11.4, 6.6, 3.2 Hz, 2H), 1.28 (qt, J = 12.6, 3.3 Hz, 4H), 1.18 (tt, J = 12.6, 3.3 Hz, 2H), 1.08 (qd, J = 12.1, 3.3 Hz, 4H); ^{13}C NMR (126 MHz, THF-*d*$_8$) δ 135.60, 135.58, 130.6, 128.7, 111.0, 80.7, 38.4, 33.7, 28.5, 27.3, 27.2. HRMS (EI+) calc'd for $C_{30}H_{37}Si$ [M+H]: 425.2665, found 425.2663.





Diethylbis(mesitylethynyl)silane 11c: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 2-ethynyl-1,3,5-trimethylbenzene (72 mg, 0.5 mmol, 1.0 equiv), Et_2SiH_2 (24 mg, 36 μL, 0.275 mmol, 0.55 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 65 °C for 72 h. The desired product **11c** (78.3 mg, 84% yield) was obtained as a colorless oil via silica gel flash chromatography (2.5% Et_2O in hexanes). R_f = 0.38 (2.5% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 6.86 (dd, J = 1.4, 0.7 Hz, 4H), 2.43 (t, J = 0.6 Hz, 12H), 2.28 (s, 6H), 1.19 (t, J = 7.8 Hz, 6H), 0.92 – 0.84 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 138.3, 127.6, 119.9, 104.4, 97.0, 21.5, 21.1, 7.6, 7.1. HRMS (EI+) calc'd for $C_{26}H_{33}Si$ [M+H]: 373.2352, found 373.2351.

Optimization of unsymmetric tethered diyne synthesis:

Table 5 details the practical considerations, product distribution, and other factors that were observed during our optimization efforts in the development of a protocol for the synthesis of Si-tethered diynes. A protocol for obtaining the product in moderate yield (i.e., with the desired selectivity) is presented. Products are readily separated by conventional silica gel column chromatography.

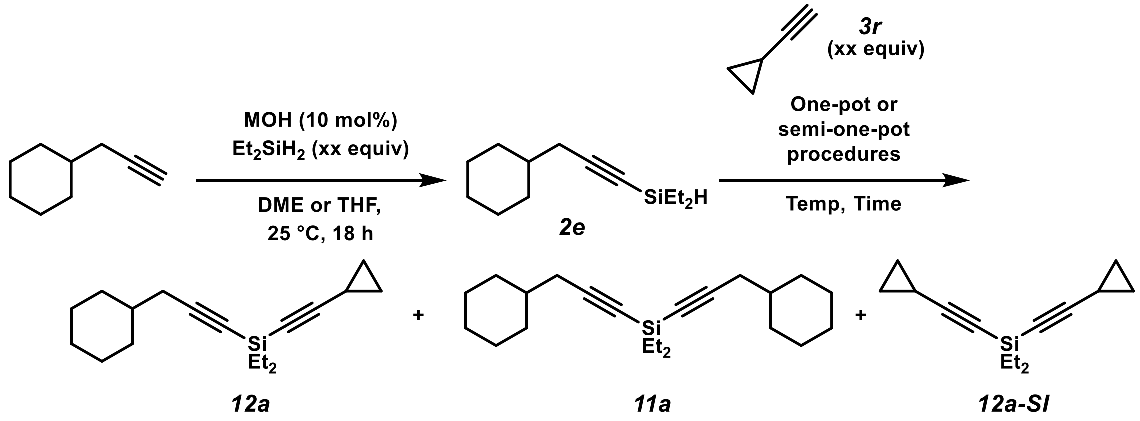
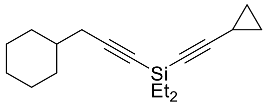
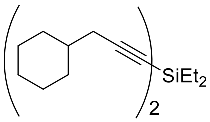
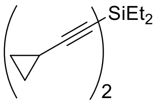
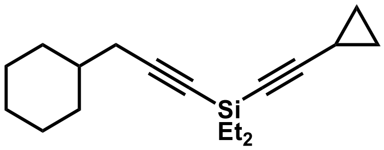


Table 5. Study of reaction conditions for unsymmetrical tethered diynes.

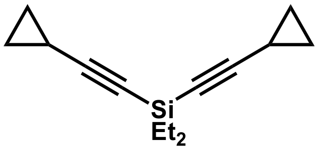
Entry	**Reaction Conditions** *Reactions done on a 0.5 mmol scale.*	 **Yield 12a** GC-FID; (Isolated)	 **Yield 11a** GC-FID; (Isolated)	 **Yield 12a-SI** GC-FID; (Isolated)
1	*"Semi-one-pot":* 1. **1**, KOH (10 mol%), Et_2SiH_2 (3.0 equiv) THF, 25 °C, 18 h 2. filtration, removal of volatiles 3. **3r** (1.2 equiv), NaOH (10 mol%) DME, 45 °C, 24 h then 65 °C, 48 h	**52%** (30%)	**18%** (14%)	**23%** (7%) *this product is volatile and is removed easily on high-vacuum*
2	*One-pot:* 1. **1**, NaOH (10 mol%), Et_2SiH_2 (1.5 equiv) DME, 25 °C, 18 h 2. **3r** (1.2 equiv) 45 °C, 24 h then 65 °C, 48 h	**53%** (51%)	**21%** (13%)	**25%** (14%)
3	*Excess of second alkyne:* 1. **1**, KOH (10 mol%), Et_2SiH_2 (3.0 equiv) DME, 25 °C, 18 h 2. **3r** (5.0 equiv) 45 °C, 24 h then 65 °C, 48 h	**66%** (62%)	**8%** (4%)	**0.82 mmol** (0.65 mmol) *due to excess **3r**, a large amount of **12a-SI** is produced.*

Yields and selectivities determined by GC-FID; isolated yields are shown in parentheses. The difference between GC-FID and the isolated yields are due to volatility of ***12a*** and ***12a-SI*** under high vacuum.

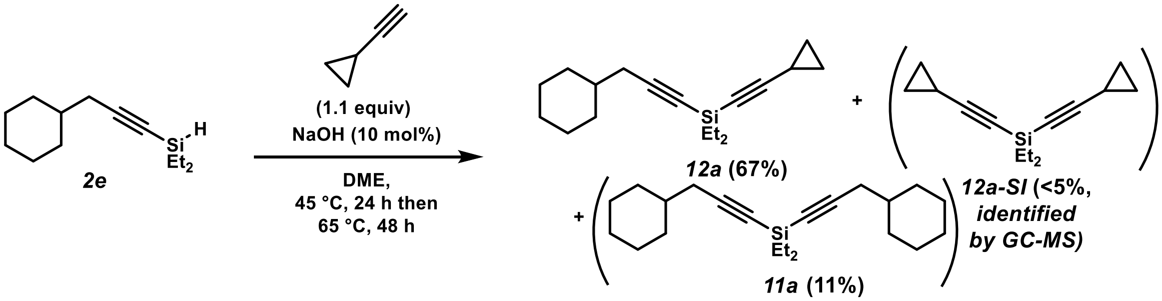
The conditions given in Table 5, Entry 3 proved to be the most appropriate for the synthesis of unsymmetrical Si-tethered diyne **12a**. For Entry 3, KOH, which generally catalyzes the dehydrocoupling to a lesser rate than NaOH, was used along with an excess of diethylsilane in order to minimize production of **11a** in the first step. For the second step, an excess (5.0 equivalents) of cyclopropylacetylene (**3r**) were added in a one-pot protocol. This reaction setup had the highest yield of the desired unsymmetrical dialkynylsilane **12a** (62% isolated yield) along with minimal production of **7** (4% isolated yield). An excess of **12a-SI** was also isolated (0.65 mmol), as expected, and could be readily separated from the desired product by standard silica gel chromatography. A two-step process involving isolation of **2e** provides the product in comparable yield (see SI-53).



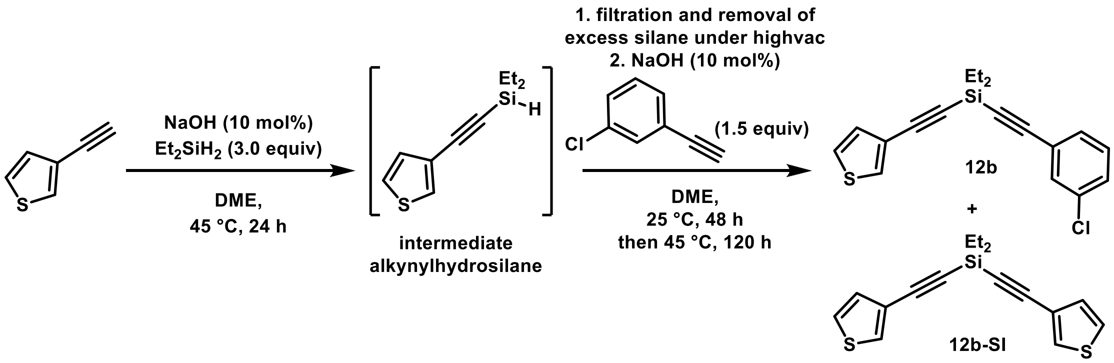
(3-Cyclohexylprop-1-yn-1-yl)(cyclopropylethynyl)diethylsilane 12a: *The procedure written is for the one-pot reaction using excess of the second alkyne (Entry 3 in Table 5).* The general procedure was followed. The reaction was performed with KOH (2.8 mg, 0.05 mmol, 10 mol%), cyclohexylpropyne (61 mg, 0.5 mmol, 1.0 equiv), Et_2SiH_2 (132 mg, 194 μL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 25 °C for 18 h, after which time cyclopropylacetylene (165 mg, 2.5 mmol, 5.0 equiv) was added. The reaction was stirred at 45 °C for 24 h then 65 °C for 48 h. The desired product **12a** (84.4 mg, 62% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). Also isolated was <5% yield of the homocoupled 3-cyclohexyl-1-propyne product **11a** and the expected homocoupled cyclopropylacetylene **12a-SI** (see below). R_f = 0.34 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (d, *J* = 6.6 Hz, 2H), 1.83 – 1.77 (m, 2H), 1.71 (dt, *J* = 12.7, 3.2 Hz, 2H), 1.65 (dddt, *J* = 12.8, 5.1, 3.3, 1.5 Hz, 1H), 1.48 (ddtd, *J* = 15.0, 11.6, 6.8, 3.6 Hz, 1H), 1.33 – 1.28 (m, 1H), 1.28 – 1.19 (m, 2H), 1.14 (qt, *J* = 12.8, 3.3 Hz, 1H), 1.03 (t, *J* = 7.9 Hz, 6H), 1.01 – 0.95 (m, 2H), 0.81 – 0.73 (m, 4H), 0.65 (q, *J* = 7.9 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 111.8, 108.1, 80.6, 75.1, 37.3, 32.8, 27.9, 26.4, 26.3, 9.0, 7.4, 7.0, 0.7. HRMS (EI+) calc'd for $C_{18}H_{29}Si$ [M+H]: 273.2039, found 273.2025.

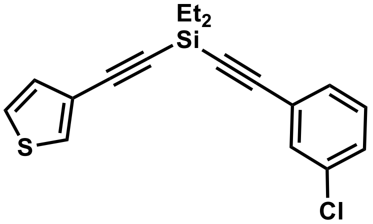


Bis(cyclopropylethynyl)diethylsilane 12a-SI: Also isolated from the column was **12a-SI** (140.7 mg, 0.65 mmol = 65% yield from excess cyclopropylacetylene added) as a colourless oil. R$_f$ = 0.21 (100% hexanes); ^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 1.33 – 1.25 (m, 2H), 1.00 (t, J = 7.9 Hz, 6H), 0.79 – 0.72 (m, 8H), 0.62 (q, J = 7.5 Hz, 4H); ^{13}C NMR (126 MHz, Benzene-*d*$_6$) δ 111.9, 75.0, 8.9, 7.4, 6.9, 0.7. HRMS (EI+) calc'd for $C_{14}H_{20}Si$ [M+•]: 216.1334, found 216.1337.

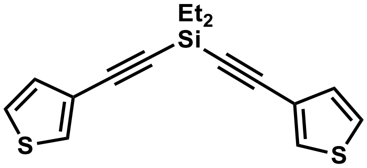


(3-Cyclohexylprop-1-yn-1-yl)(cyclopropylethynyl)diethylsilane 12a: This product is also prepared in comparable yield (91.3 mg, 67% yield) in a 2-step process by first obtaining the silylated cyclohexylpropyne **2e** and then following the general procedure, combining the pre-silylated product **2e** (104 mg, 0.5 mmol) with NaOH (2.0 mg, 0.05 mmol, 10 mol%), cyclopropylacetylene (36 mg, 0.55 mmol, 1.1 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 24 h, then 65 °C for 48 h.



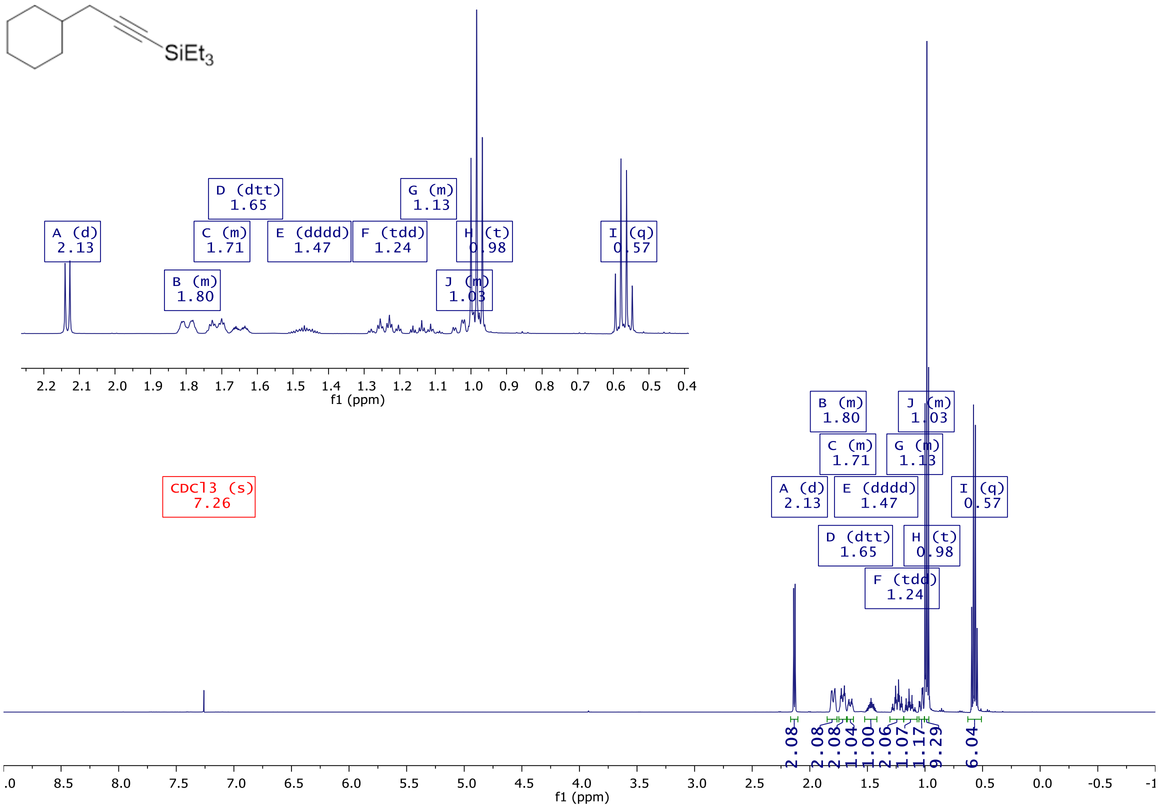


((3-Chlorophenyl)ethynyl)diethyl(thiophen-3-ylethynyl)silane 12b: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 3-ethynylthiophene (54 mg, 0.5 mmol, 1.0 equiv), Et_2SiH_2 (132 mg, 195 µL, 1.5 mmol, 3.0 equiv), and 0.5 mL of 1,2-dimethoxyethane (DME) at 45 °C for 24 h. The remaining silane and solvent were removed from the reaction mixture under high vacuum after removal of NaOH via filtration through a pad of silica, yielding the crude intermediate diethyl(thiophen-3-ylethynyl)silane. The intermediate alkynylhydrosilane was then resubjected to the reaction conditions to accomplish the second silylation without further isolation in a semi-one-pot procedure. The second step was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol%), 3-chloroethynylbenzene (102 mg, 0.75 mmol, 1.5 equiv), and 0.5 mL of DME at 25 °C for 48 h, then 45 °C for 120 h. The desired product **12b** (95.4 mg, 58% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). R_f = 0.28 (100% hexanes); ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.38 (t, J = 1.9 Hz, 1H), 7.14 (dd, J = 3.0, 1.2 Hz, 1H), 7.08 (dt, J = 7.7, 1.3 Hz, 1H), 6.95 (dd, J = 5.0, 1.2 Hz, 1H), 6.87 (ddd, J = 8.1, 2.2, 1.0 Hz, 1H), 6.54 – 6.52 (m, 2H), 1.25 (t, J = 7.9 Hz, 6H), 0.91 (q, J = 7.9 Hz, 4H); ^{13}C NMR (126 MHz, Benzene-d_6) δ 134.4, 132.3, 130.8, 130.4, 130.3, 129.7, 129.3, 125.6, 124.9, 122.4, 105.7, 102.7, 91.0, 88.8, 7.7, 7.0. HRMS (EI+) calc'd for $C_{18}H_{18}SSiCl$ [M+H]: 329.0587, found 329.0580.

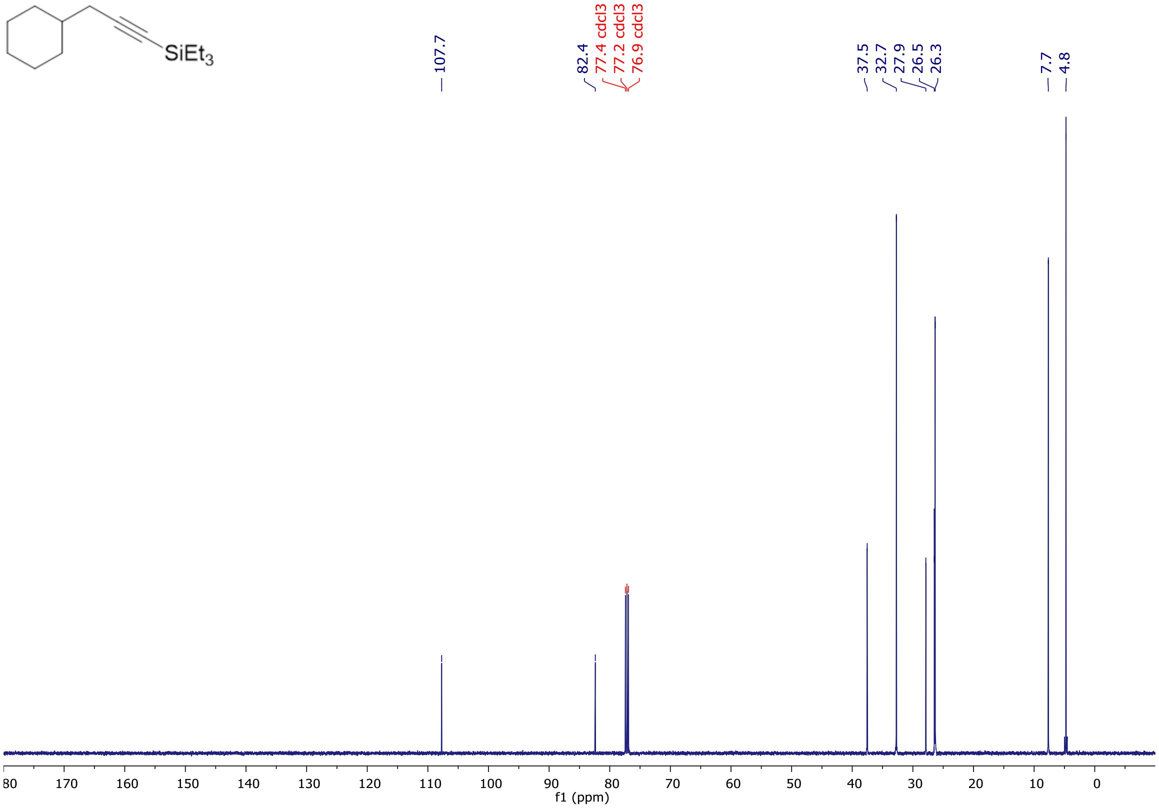


Diethylbis(thiophen-3-ylethynyl)silane 12b-SI: Also isolated from the column was **12b-SI** (13.7 mg, 18% yield) as a light yellow oil. R*f* = 0.20 (100% hexanes); ^{1}H NMR (500 MHz, Benzene-*d6*) δ 7.11 (dd, J = 3.0, 1.2 Hz, 2H), 6.93 (dd, J = 5.0, 1.2 Hz, 2H), 6.54 (dd, J = 5.0, 3.0 Hz, 2H), 1.27 (t, J = 7.9 Hz, 6H), 0.93 (q, J = 7.9 Hz, 4H); ^{13}C NMR (126 MHz, Benzene-*d6*) δ 130.6, 130.3, 125.4, 122.5, 102.4, 89.2, 7.7, 7.1. HRMS (EI+) calc'd for $C_{16}H_{17}S_2Si$ [M+H]: 301.0541, found 301.0547.

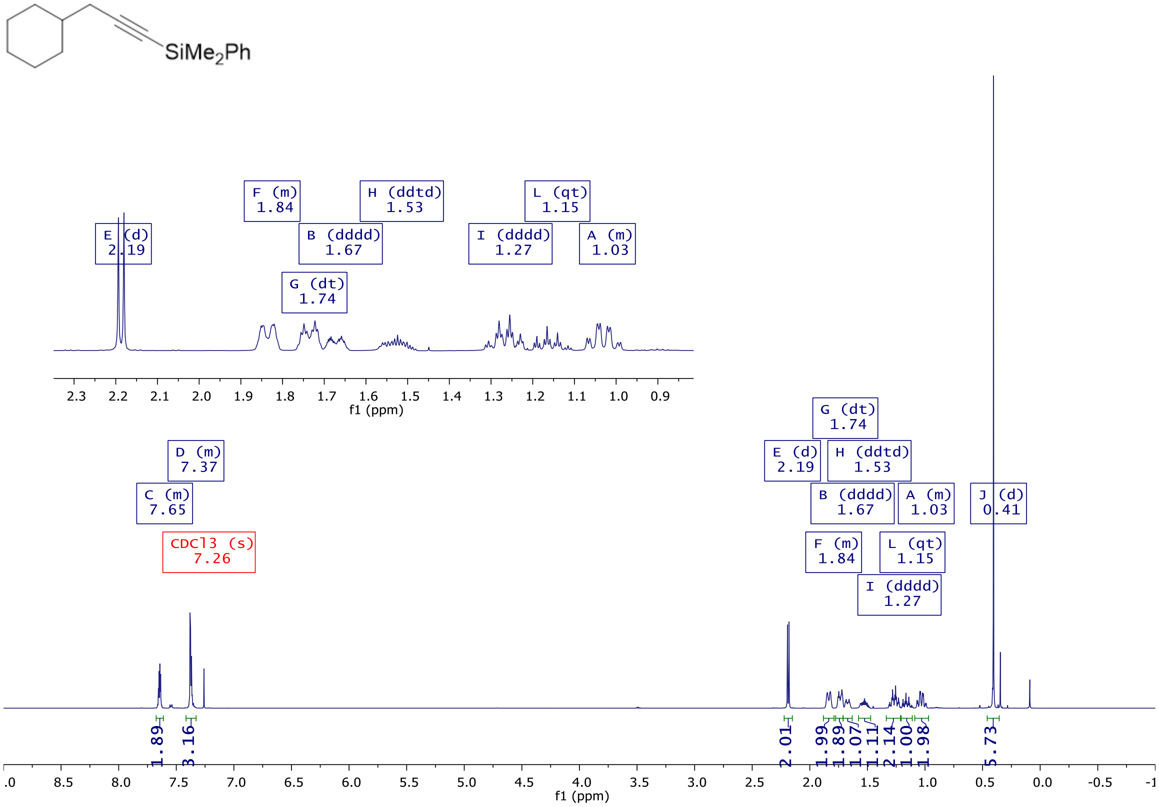
Part III. ^{1}H NMR and ^{13}C NMR Spectra of New Compounds



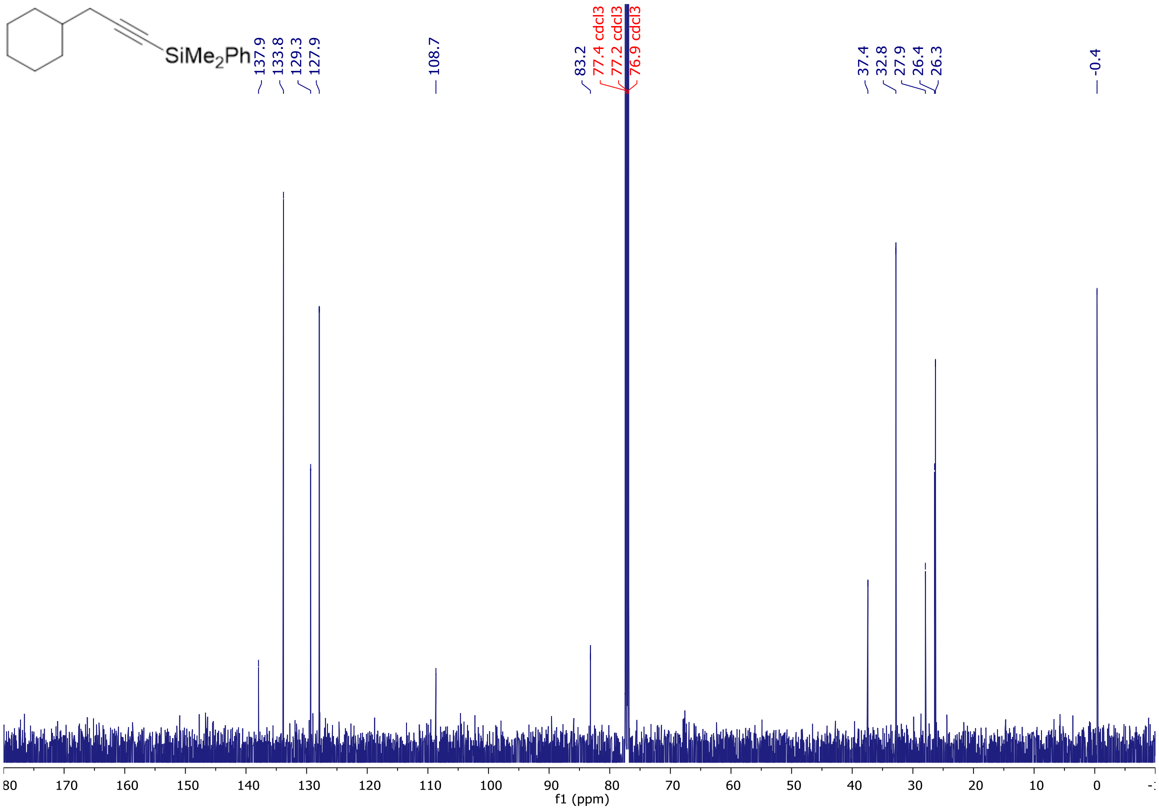
^{1}H NMR (500 MHz, CDCl$_3$) of compound **2a**.



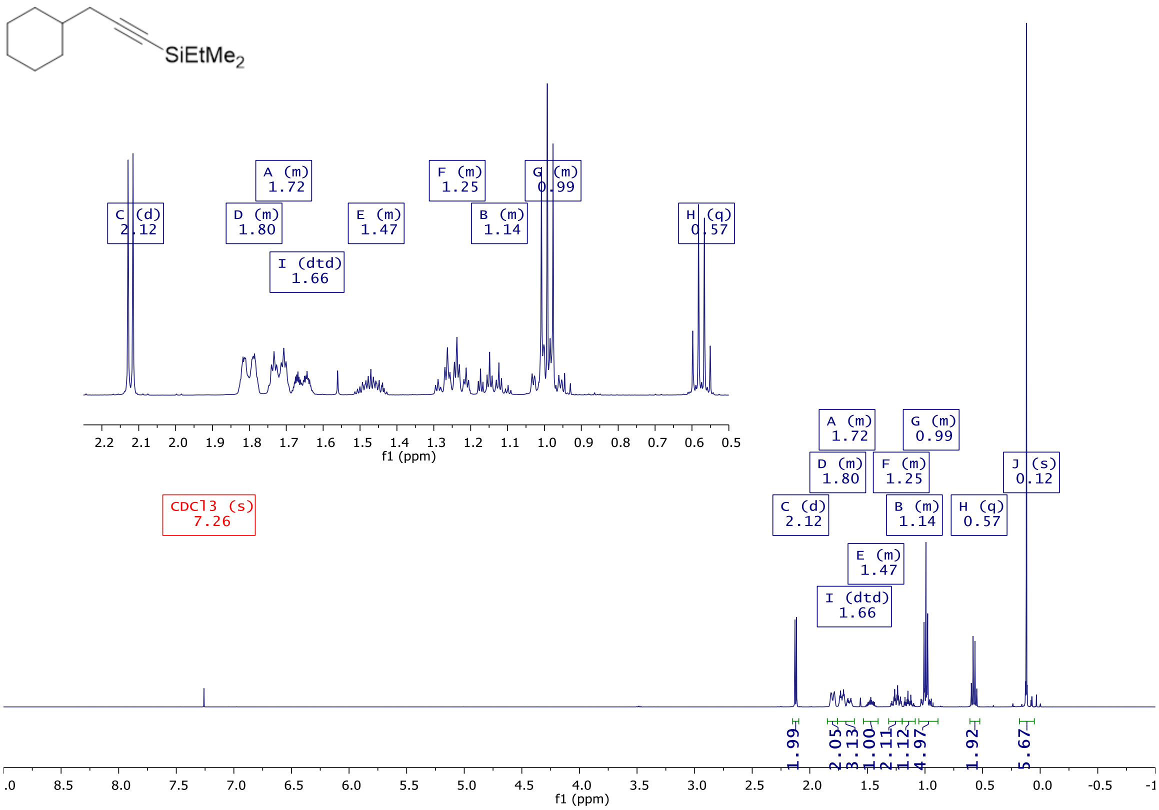
^{13}C NMR (126 MHz, CDCl$_3$) of compound **2a.**



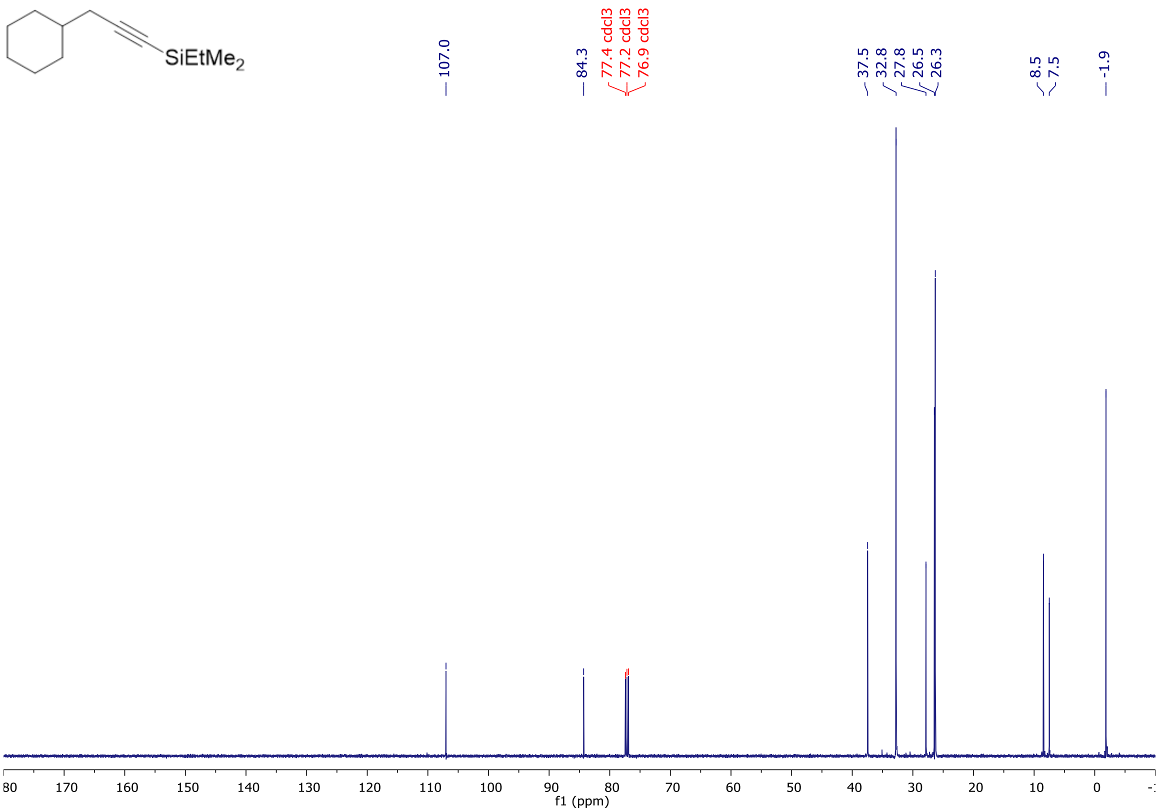
^{1}H NMR (500 MHz, CDCl$_3$) of compound **2b.**



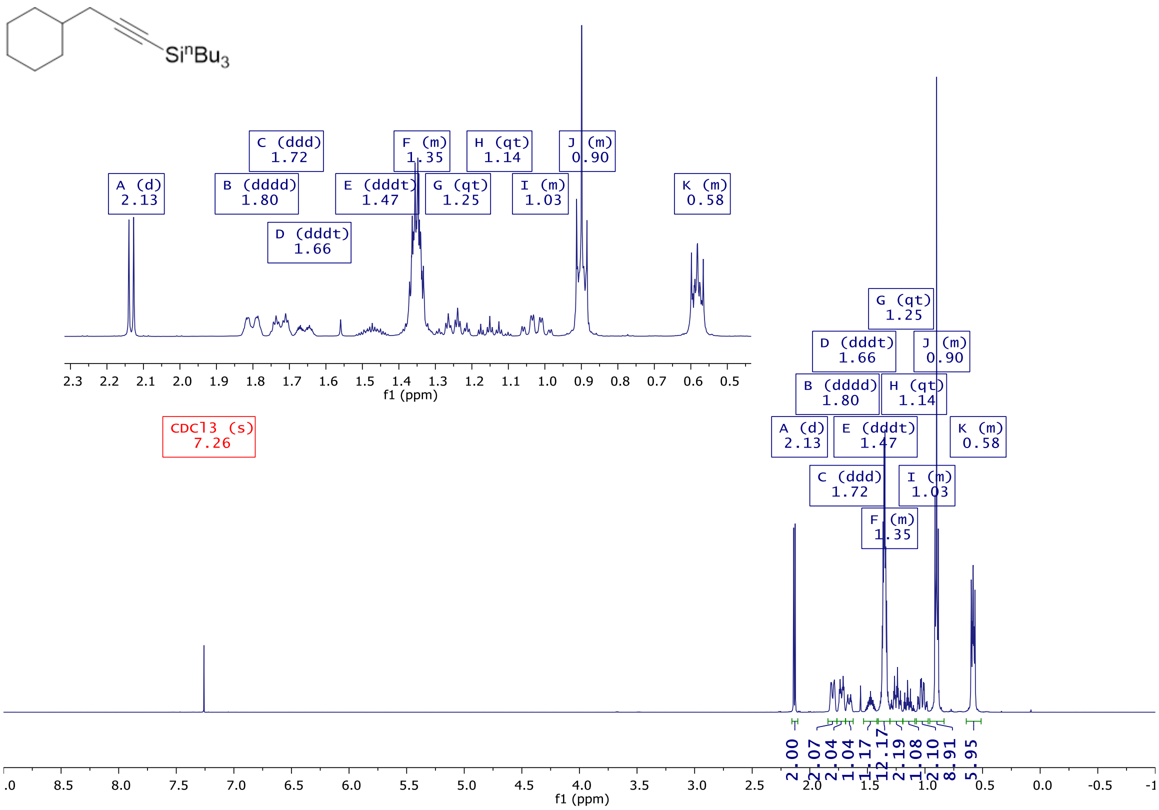
^{13}C NMR (126 MHz, CDCl$_3$) of compound **2b.**



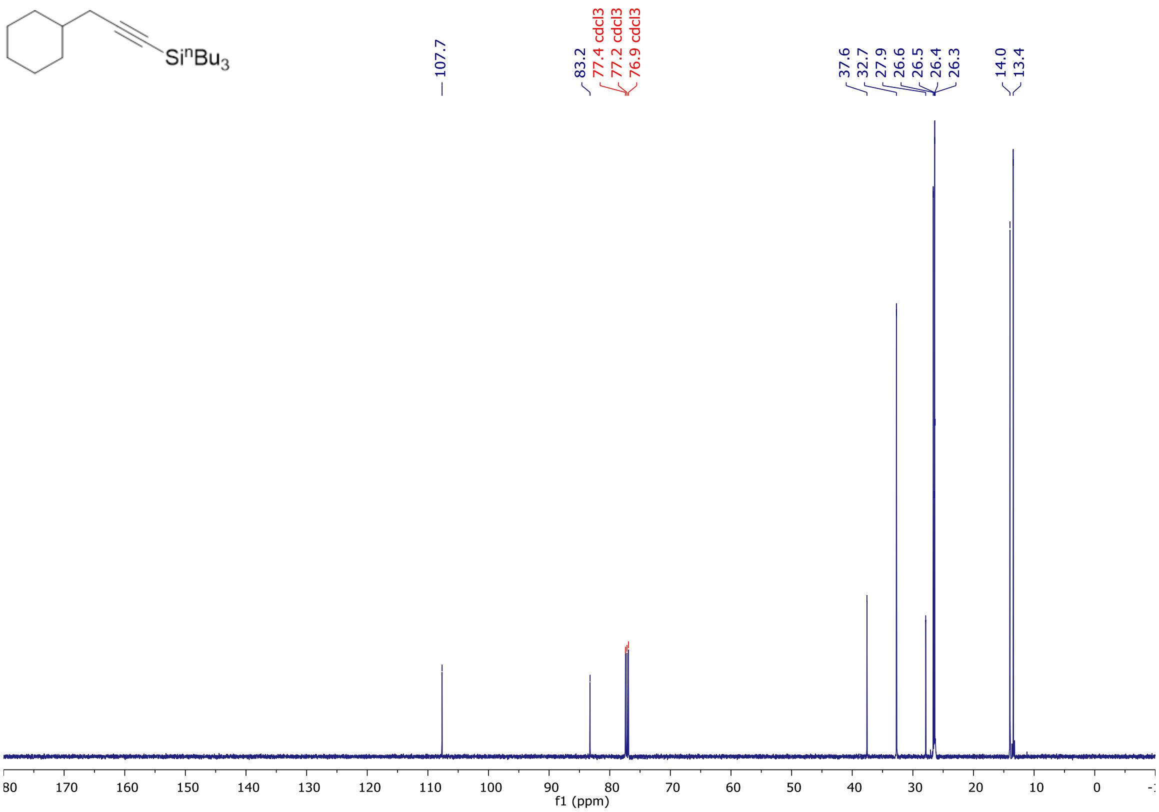
^{1}H NMR (500 MHz, CDCl$_3$) of compound **2c.**



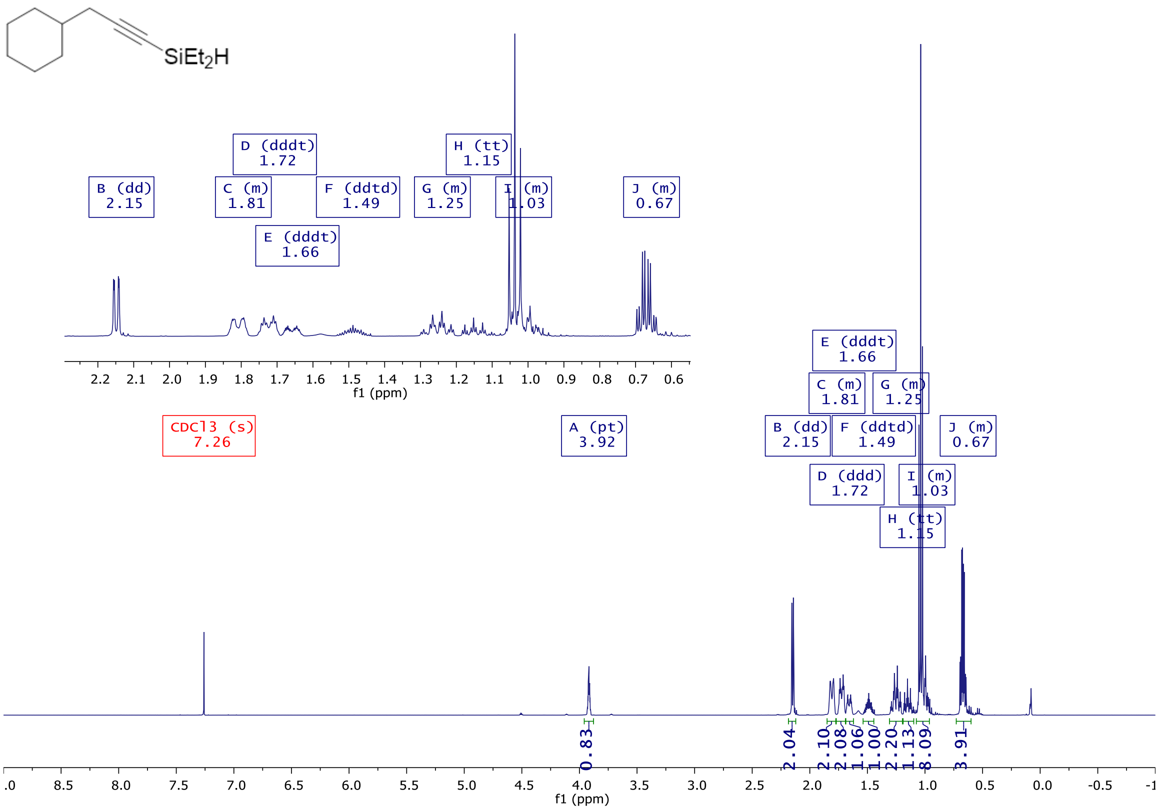
^{13}C NMR (126 MHz, CDCl$_3$) of compound **2c.**



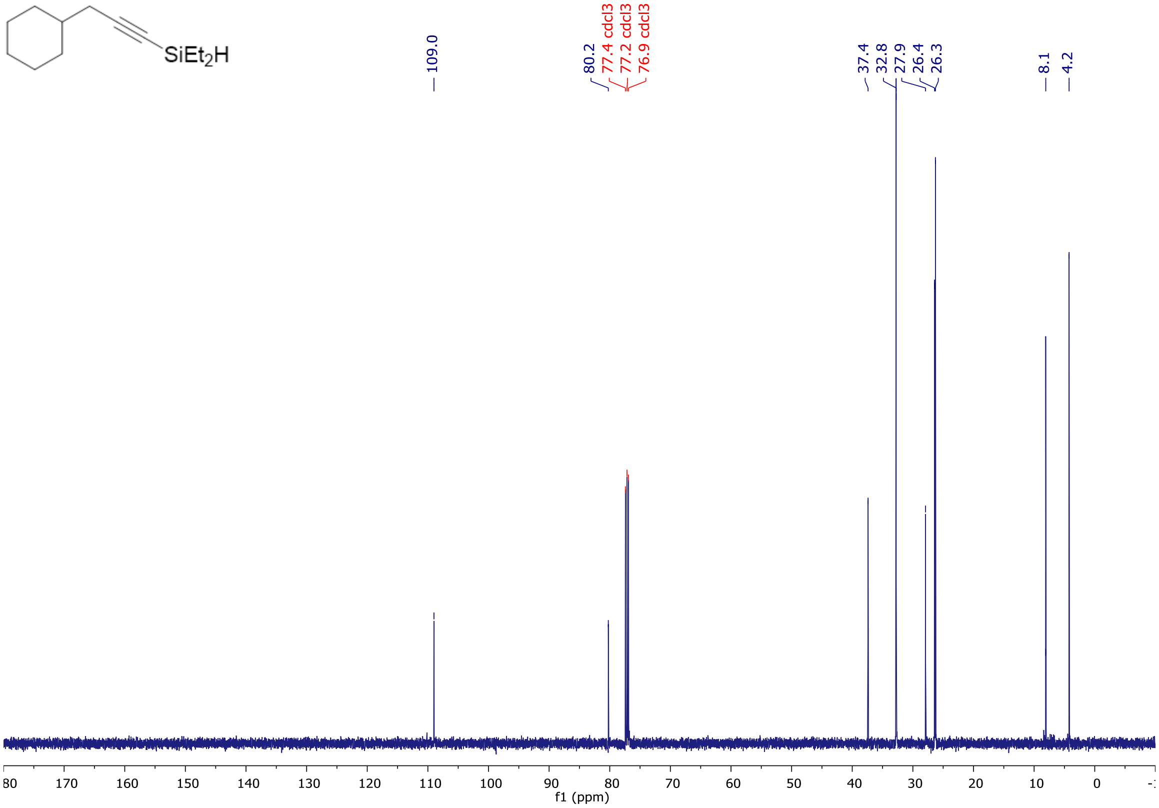
^{1}H NMR (500 MHz, CDCl$_3$) of compound **2d.**



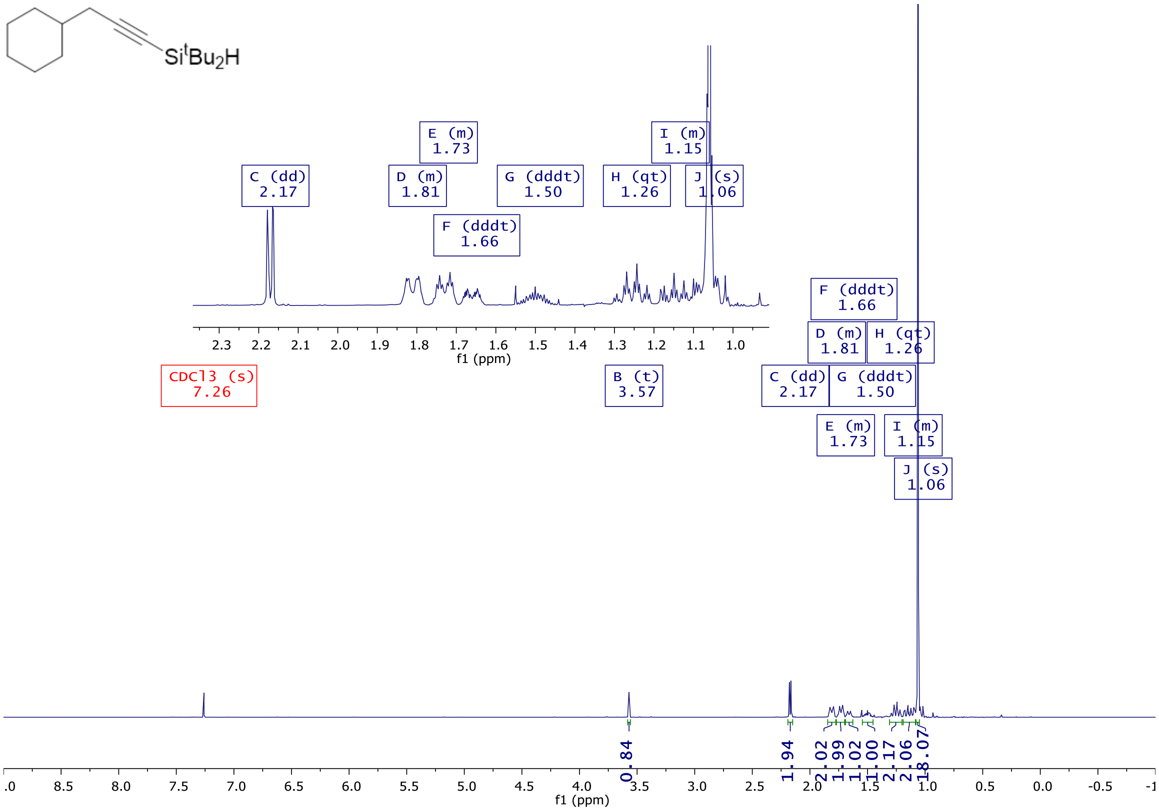
^{13}C NMR (126 MHz, CDCl$_3$) of compound **2d.**



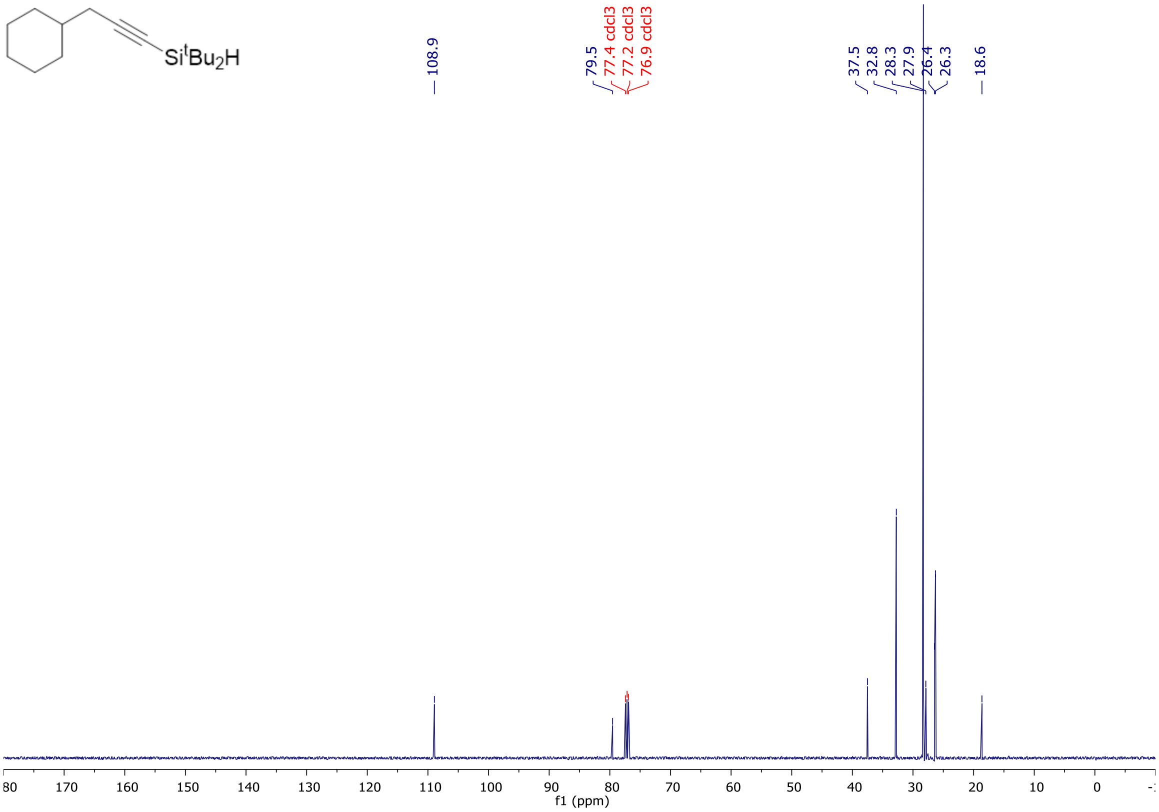
^{1}H NMR (500 MHz, CDCl$_3$) of compound **2e.**



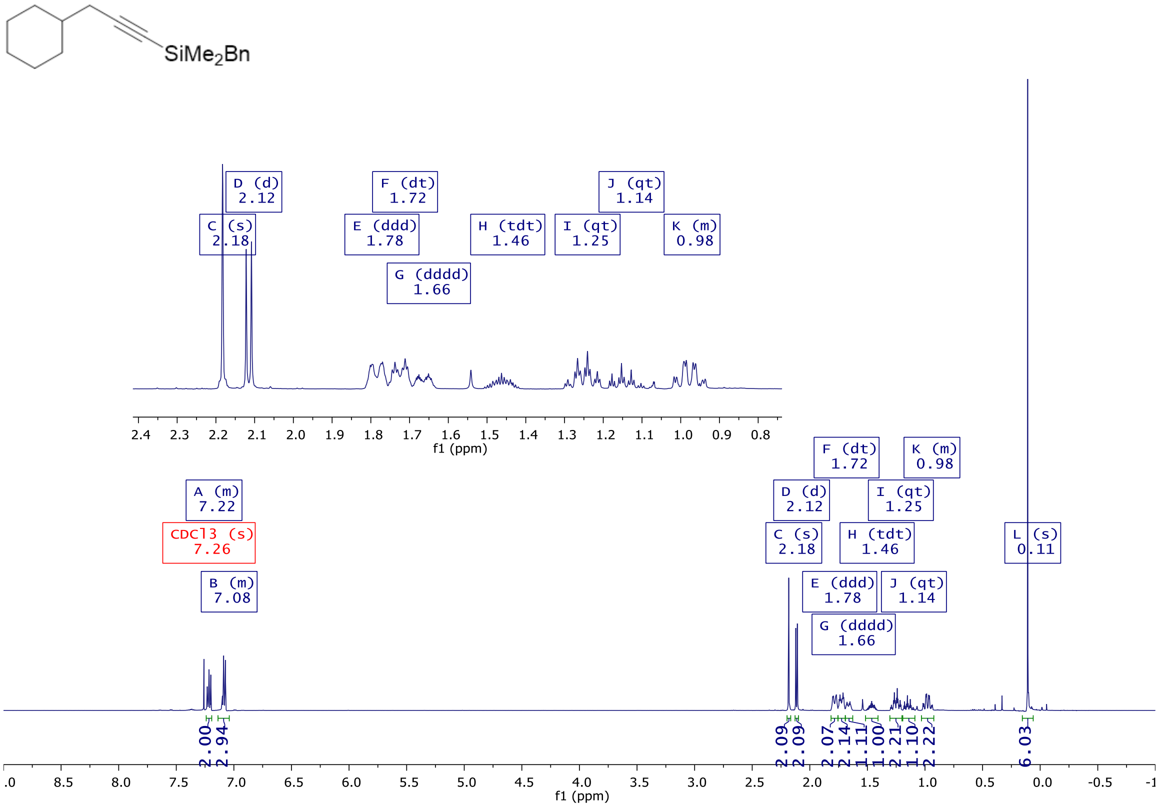
^{13}C NMR (126 MHz, CDCl$_3$) of compound **2e.**



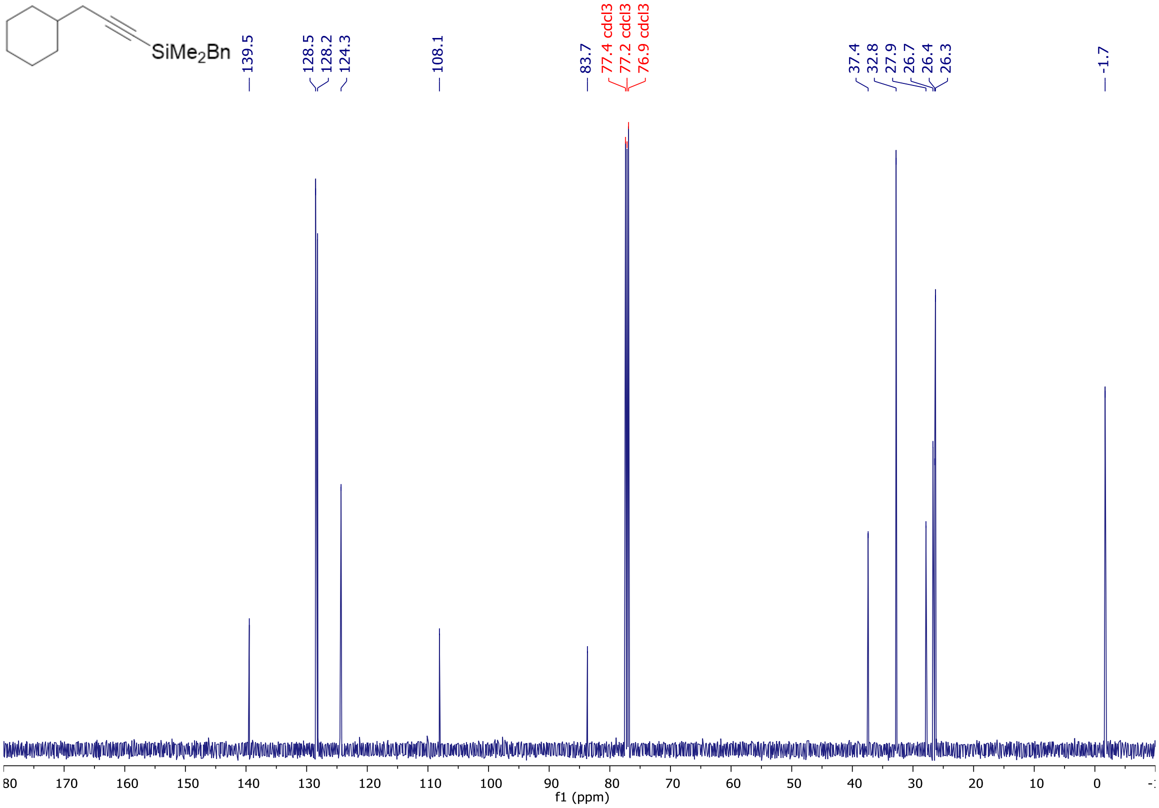
^{1}H NMR (500 MHz, CDCl$_3$) of compound **2f.**



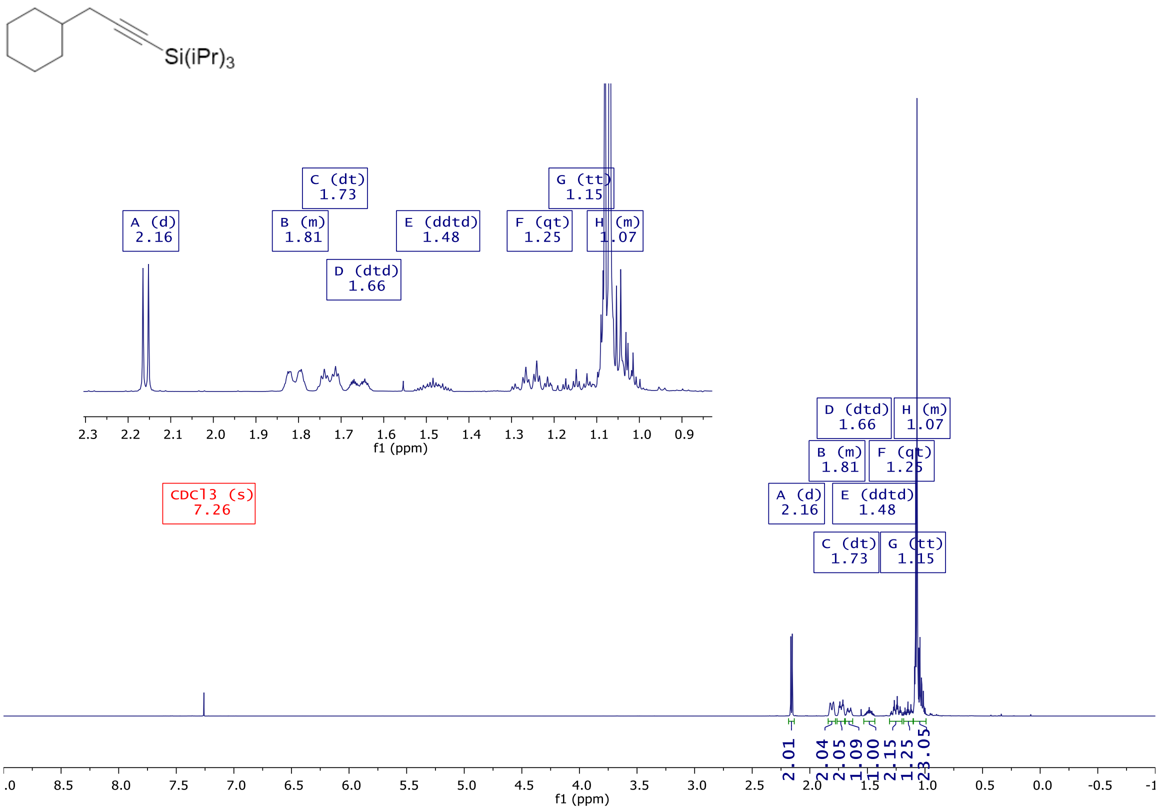
^{13}C NMR (126 MHz, CDCl$_3$) of compound **2f.**



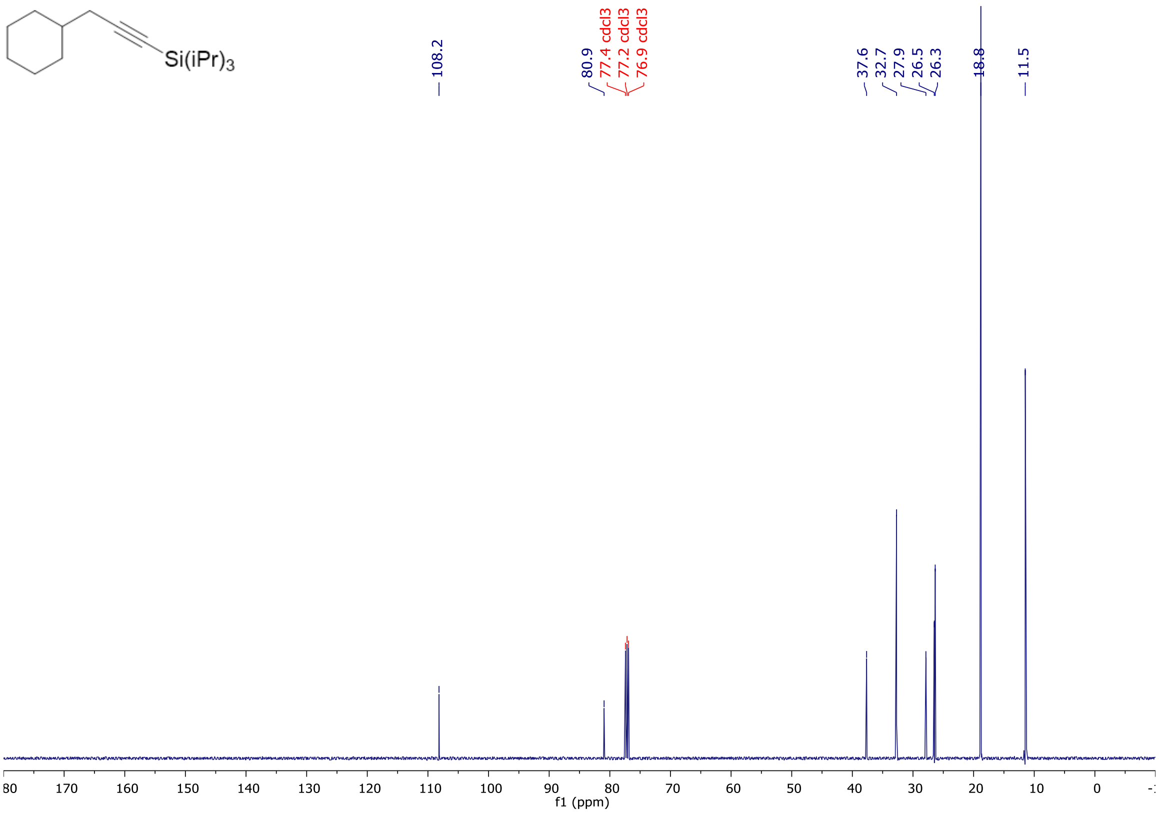
^{1}H NMR (500 MHz, CDCl$_3$) of compound **2g.**



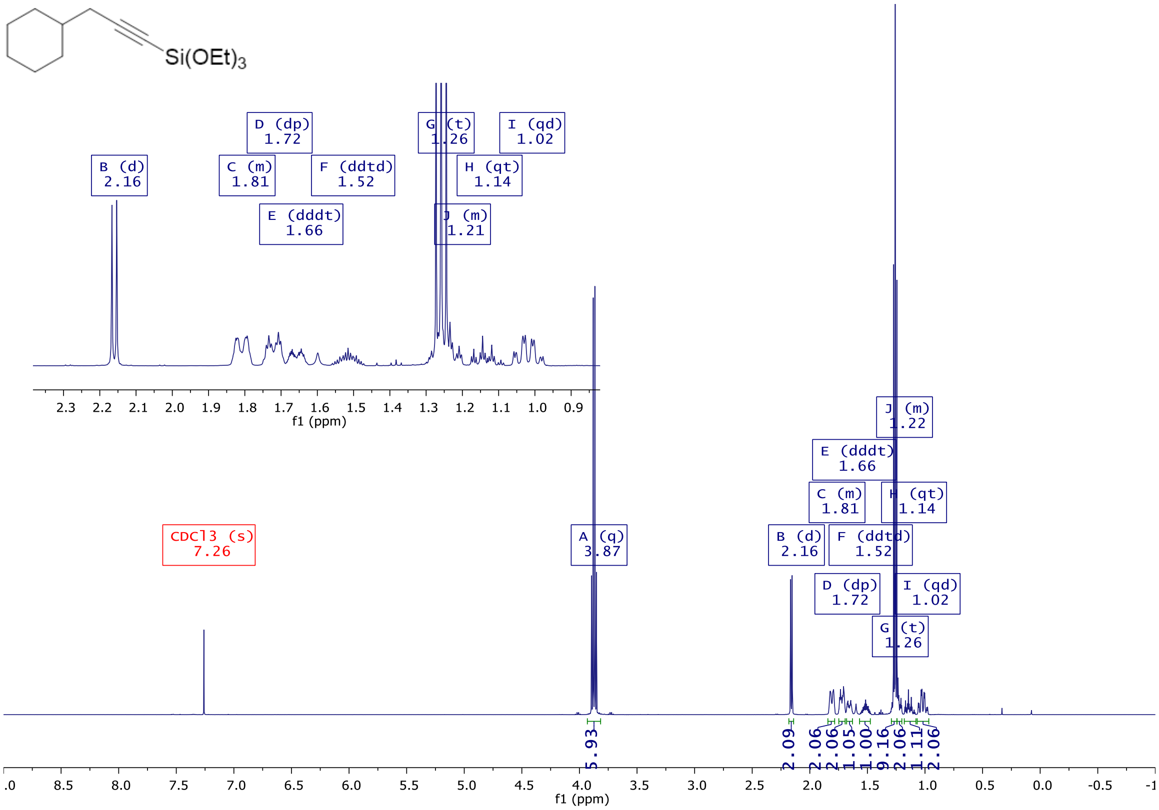
^{13}C NMR (126 MHz, CDCl$_3$) of compound **2g.**



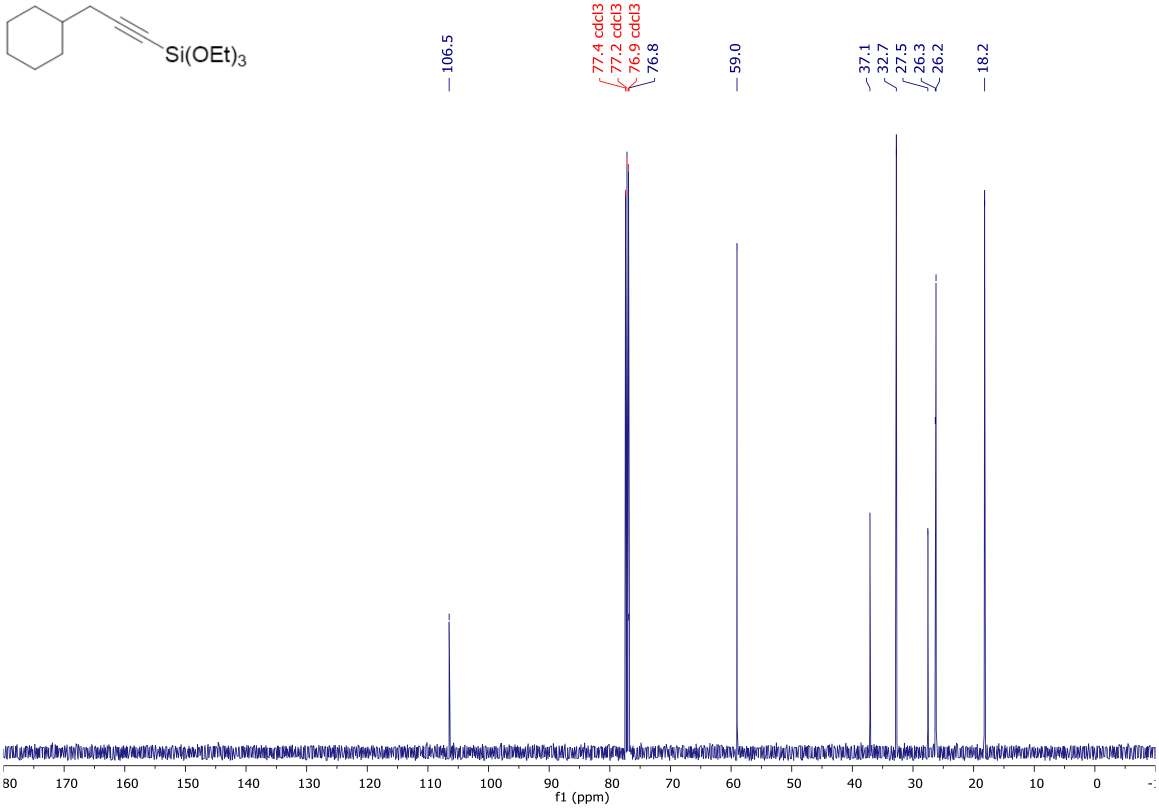
^{1}H NMR (500 MHz, CDCl$_3$) of compound **2h.**



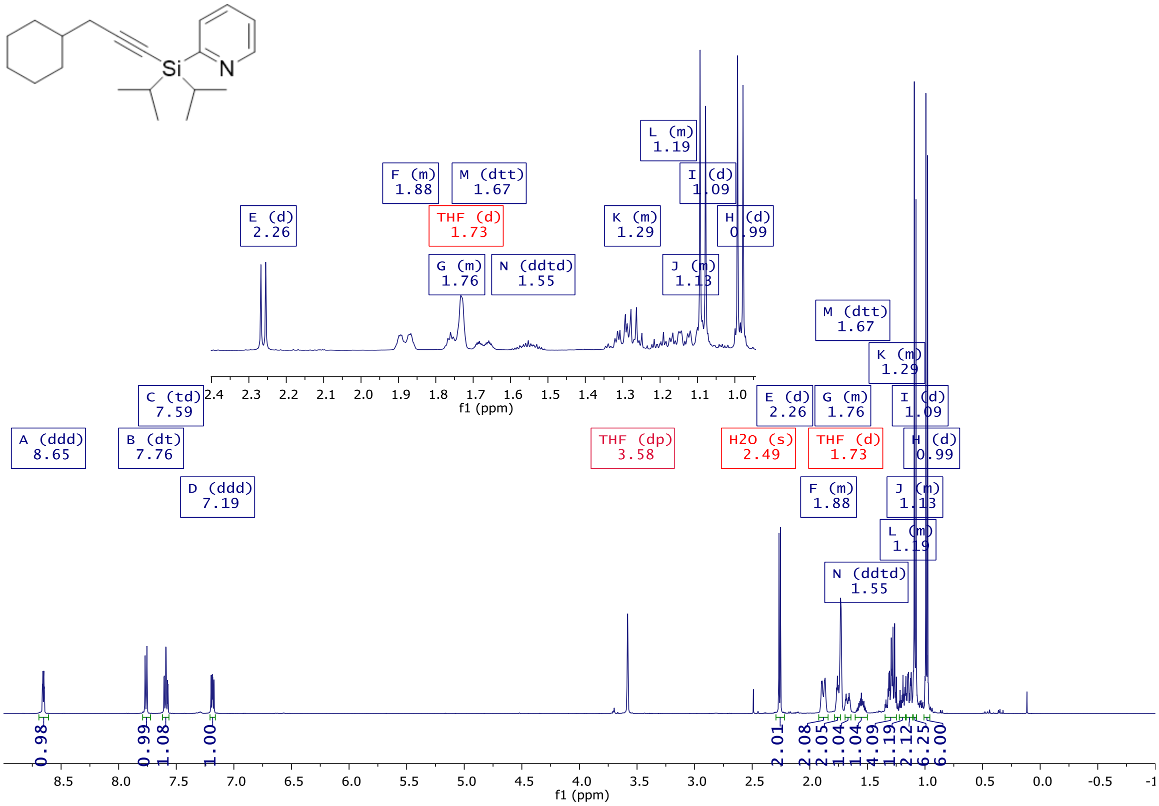
^{13}C NMR (126 MHz, CDCl$_3$) of compound **2h.**



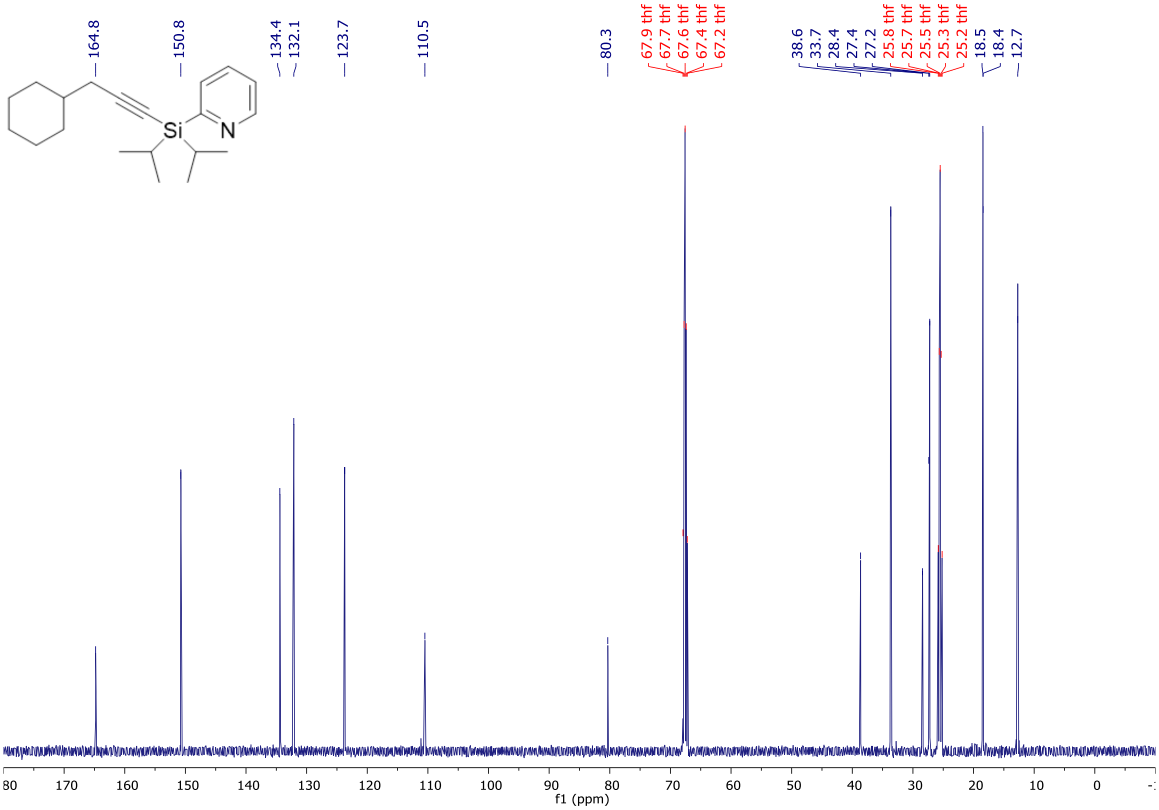
^{1}H NMR (500 MHz, CDCl$_3$) of compound **2i.**



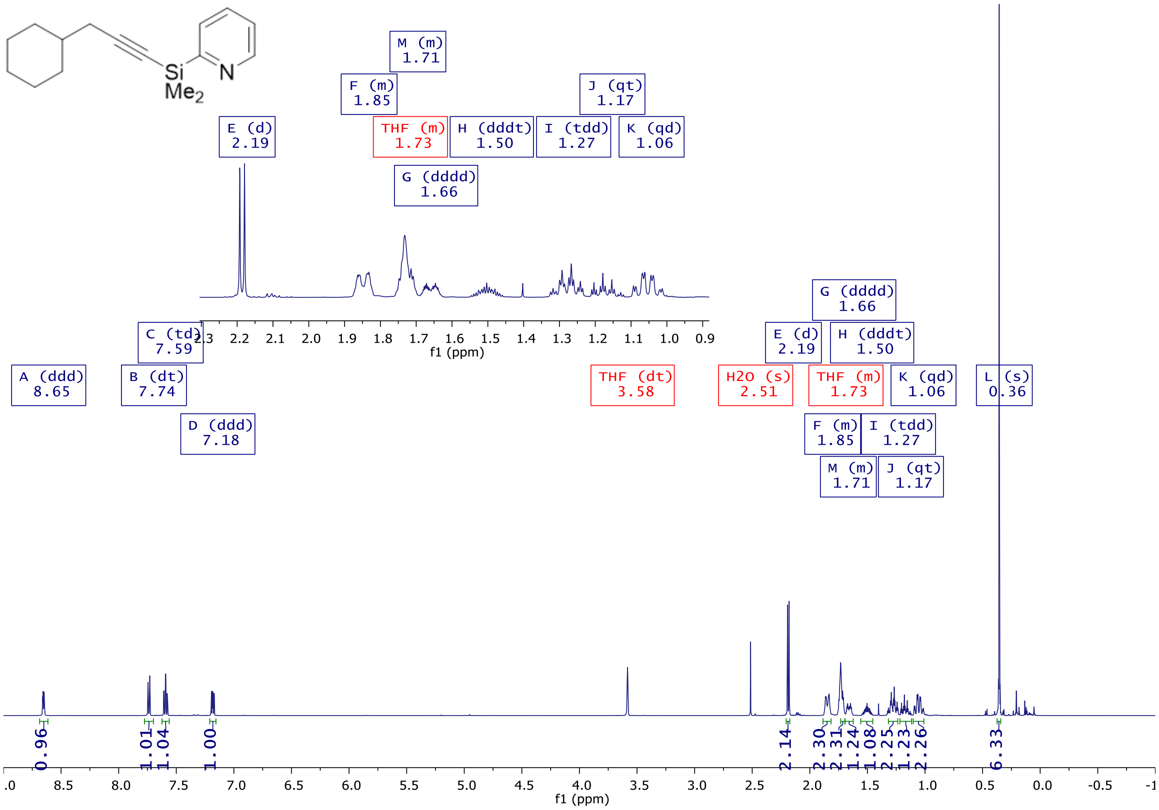
^{13}C NMR (126 MHz, CDCl$_3$) of compound **2i.**



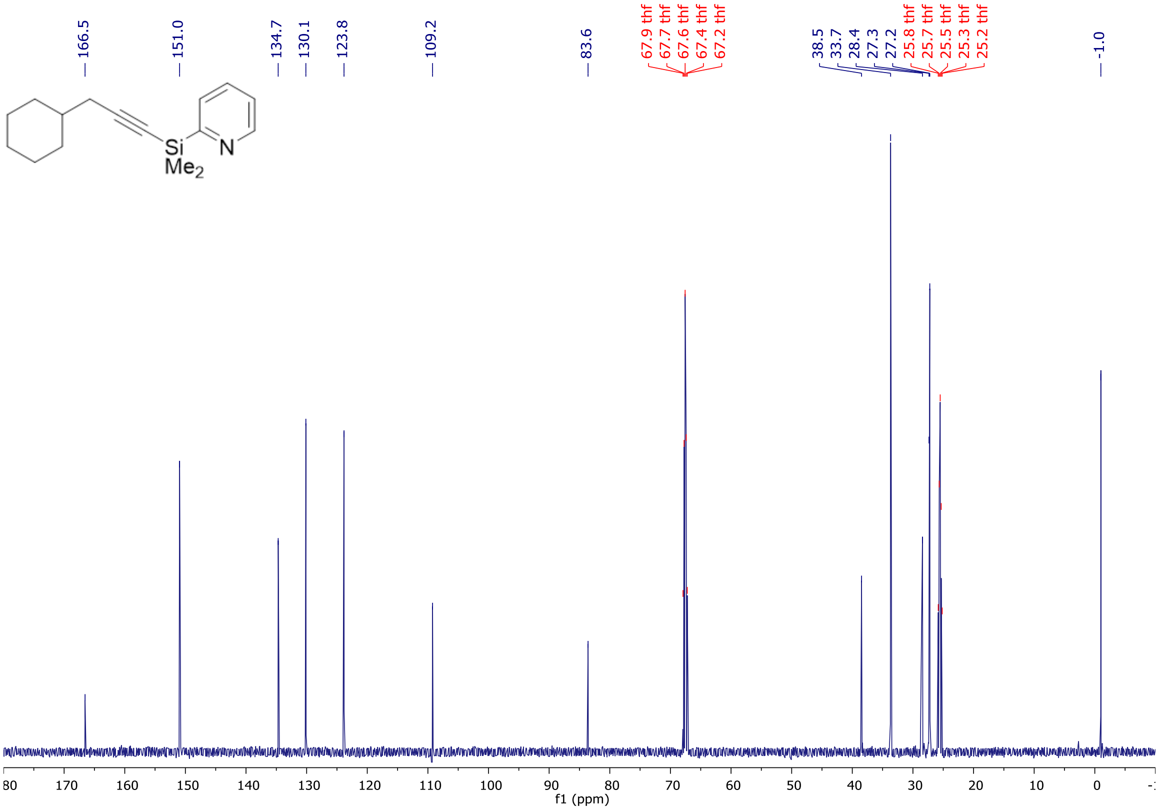
^{1}H NMR (500 MHz, THF-d_8) of compound **2j.**



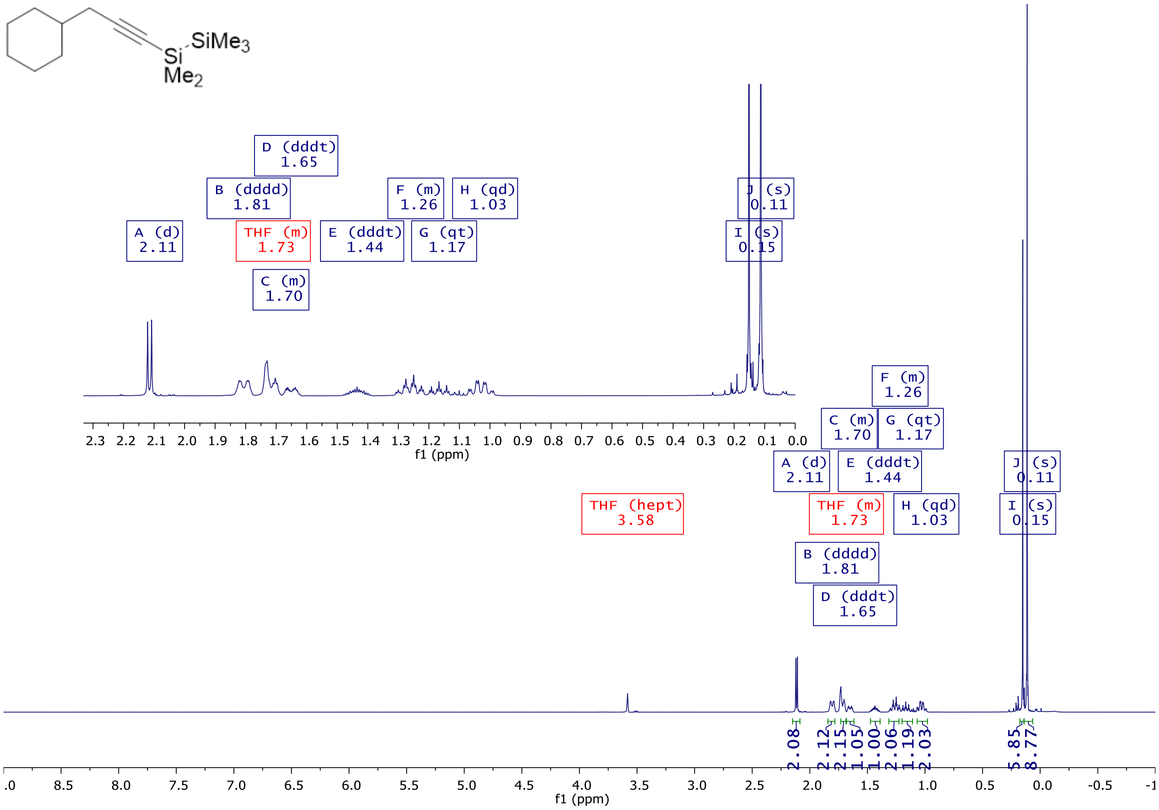
^{13}C NMR (126 MHz, THF-d_8) of compound **2j.**



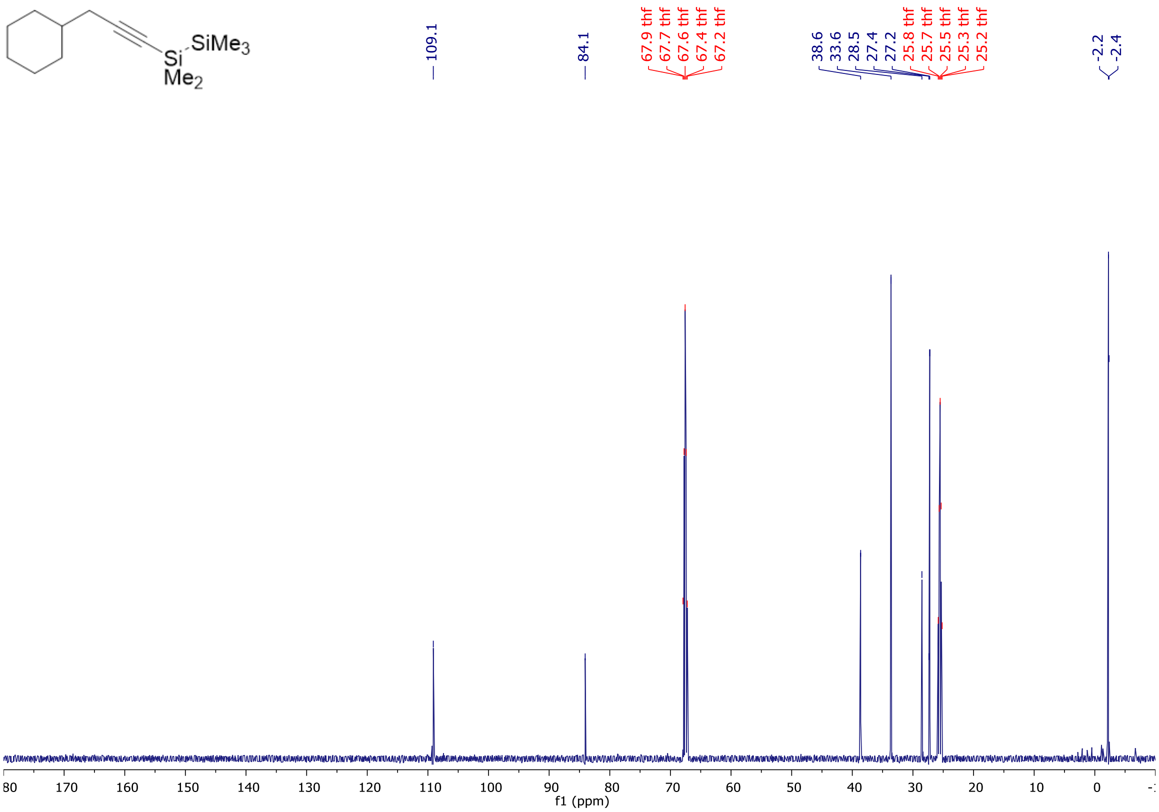
^{1}H NMR (500 MHz, THF-d_8) of compound **2k.**



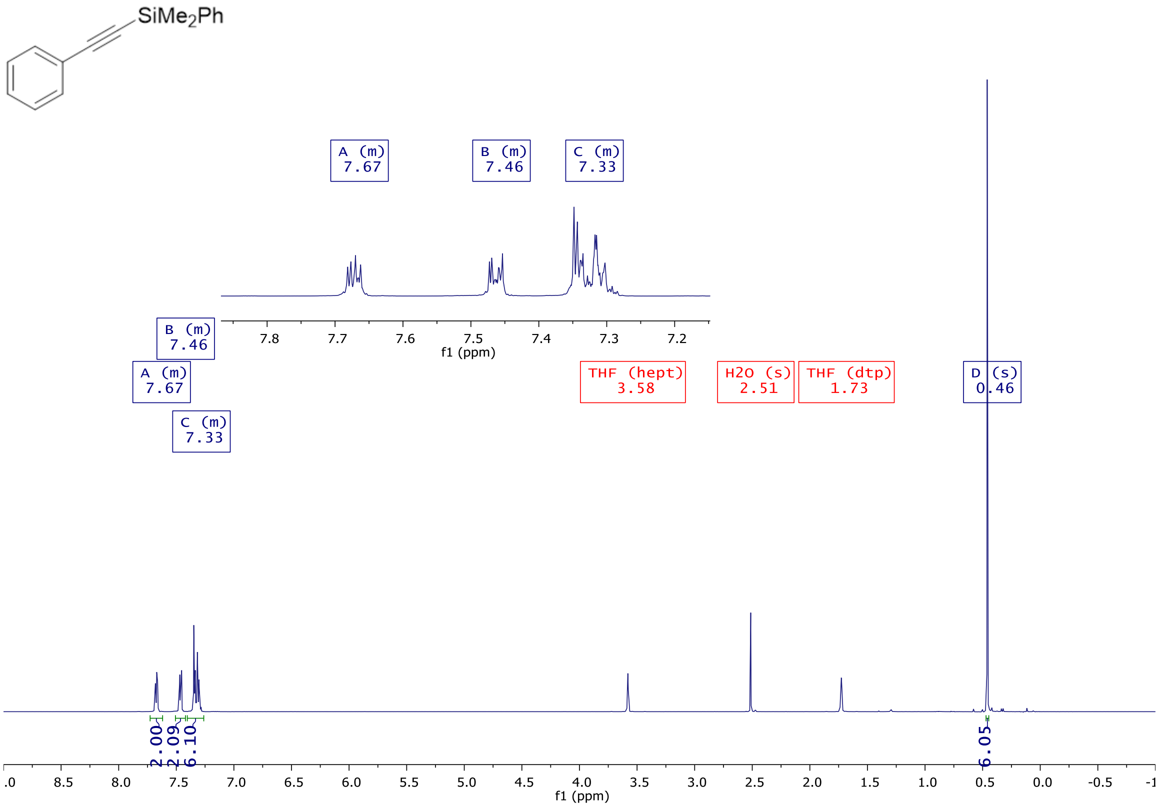
^{13}C NMR (126 MHz, THF-d_8) of compound **2k.**



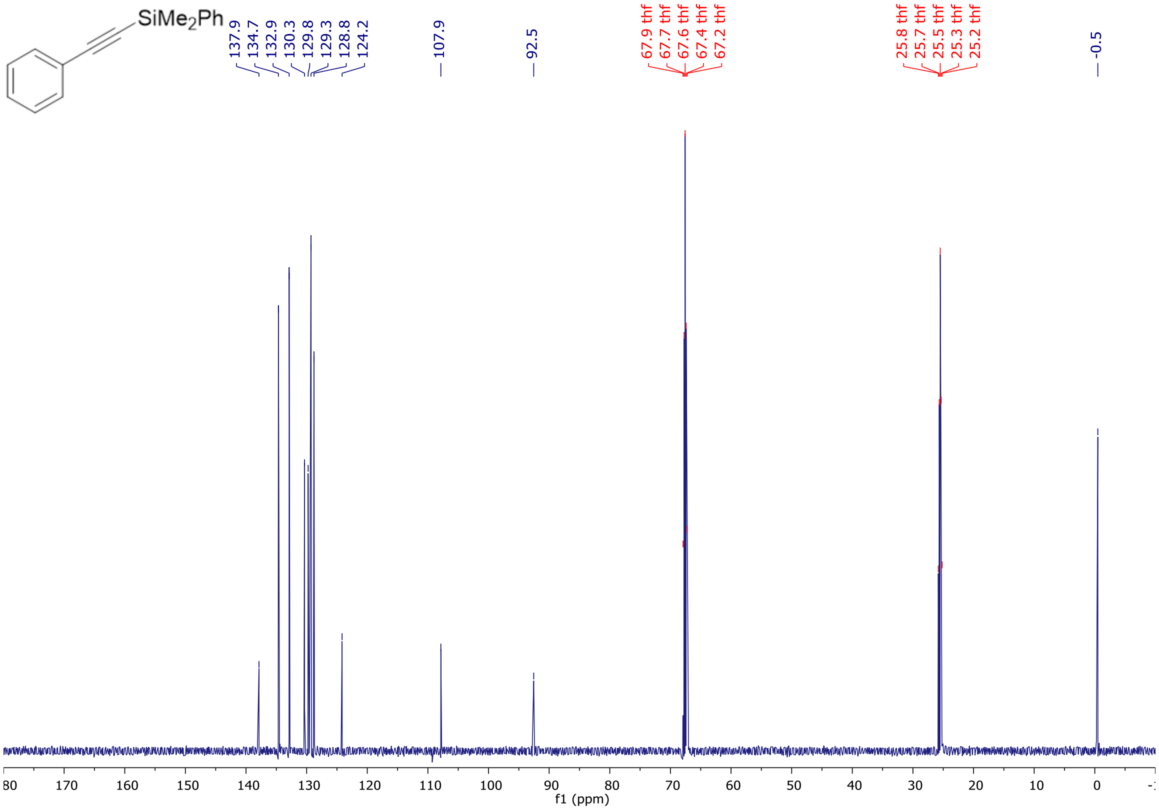
^{1}H NMR (500 MHz, THF-d_8) of compound **2l.**



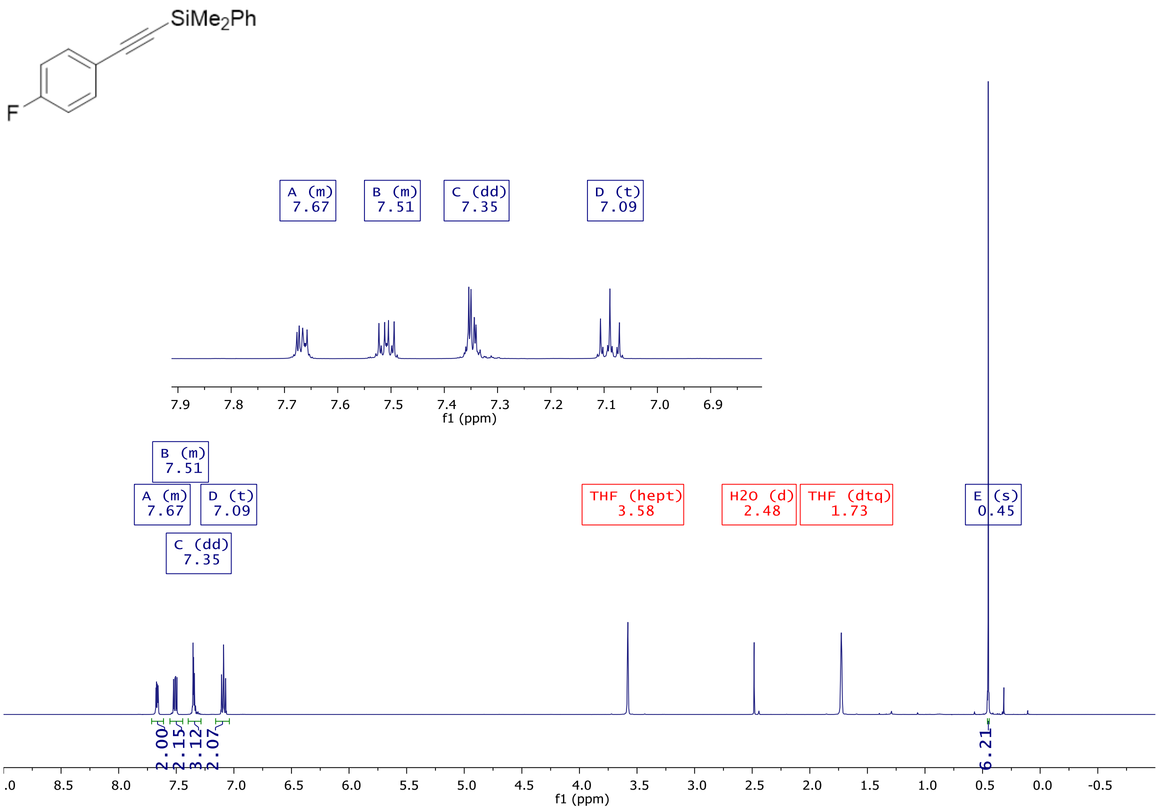
^{13}C NMR (126 MHz, THF-d_8) of compound **2l.**



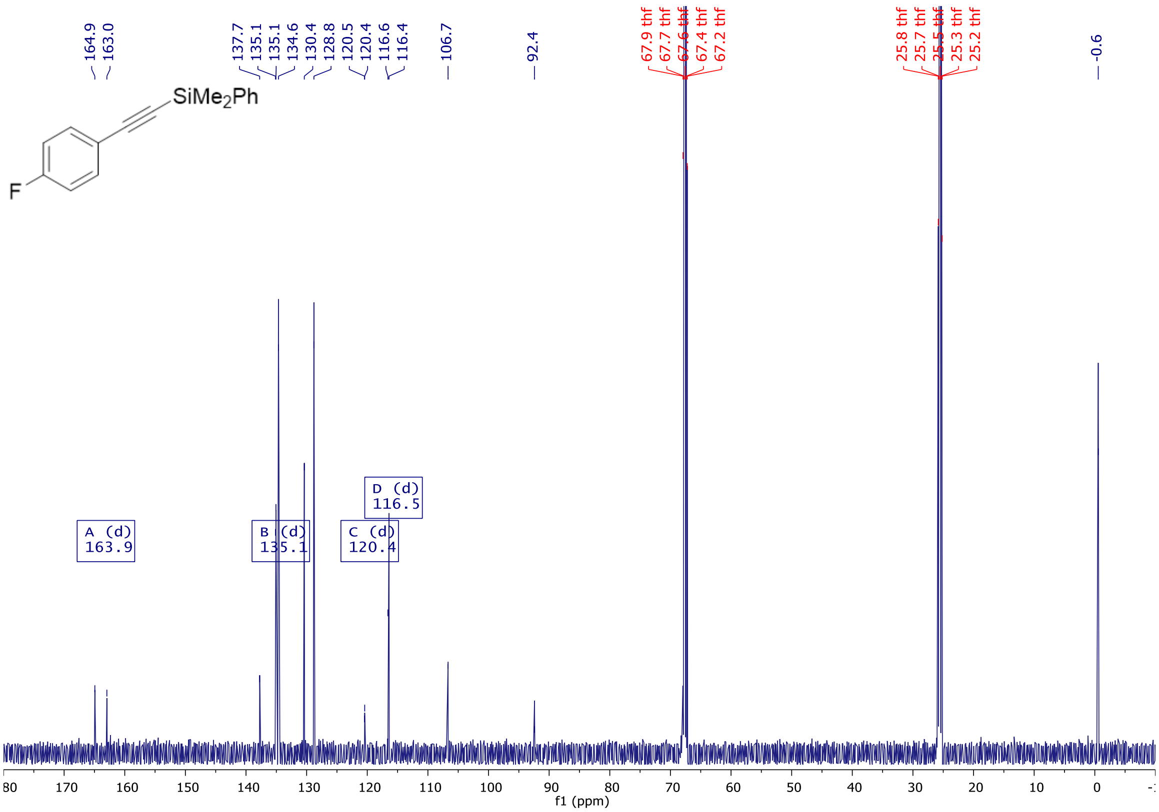
^{1}H NMR (500 MHz, THF-d_8) of compound **4a.**



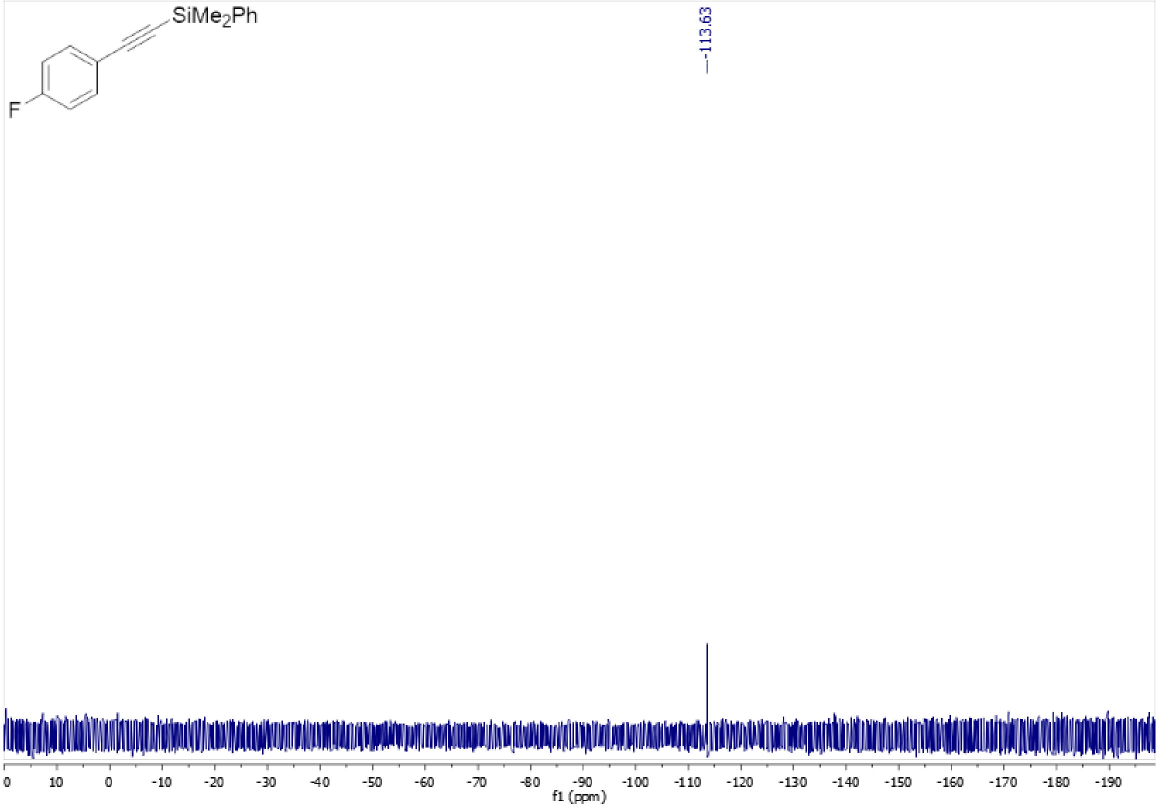
^{13}C NMR (126 MHz, THF-d_8) of compound **4a.**



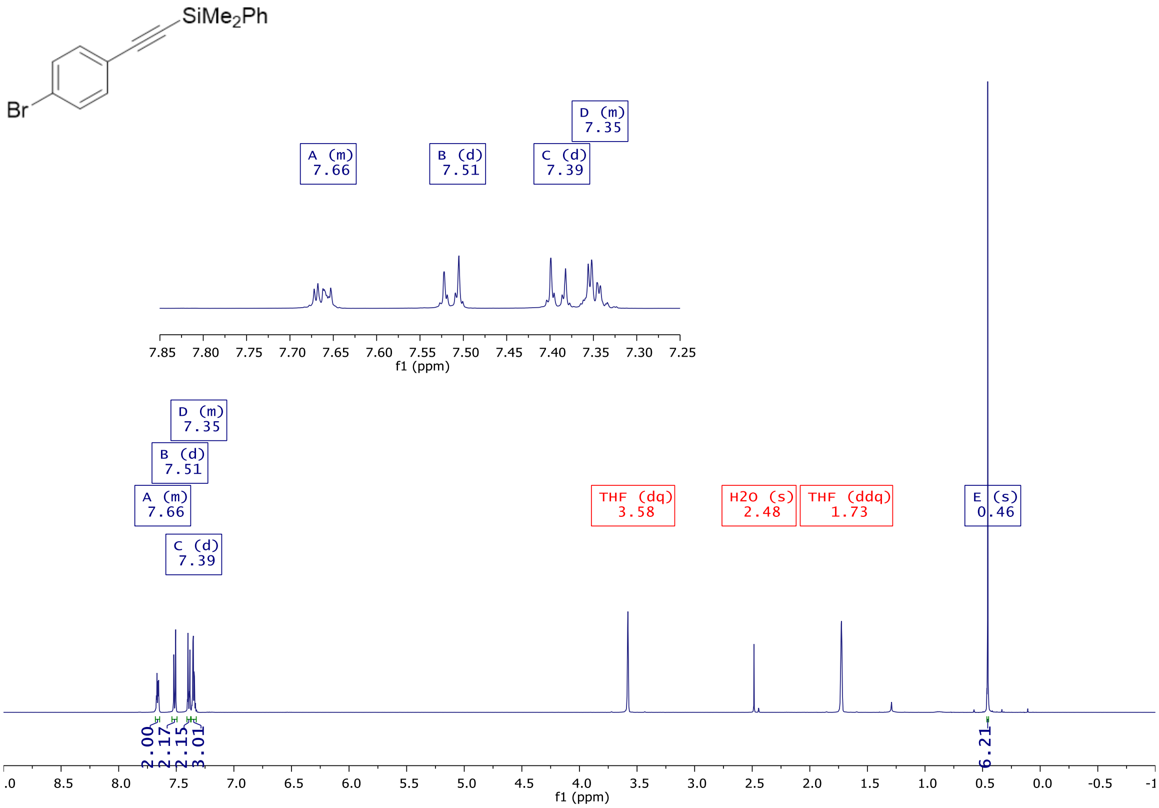
^{1}H NMR (500 MHz, THF-d_8) of compound **4b.**



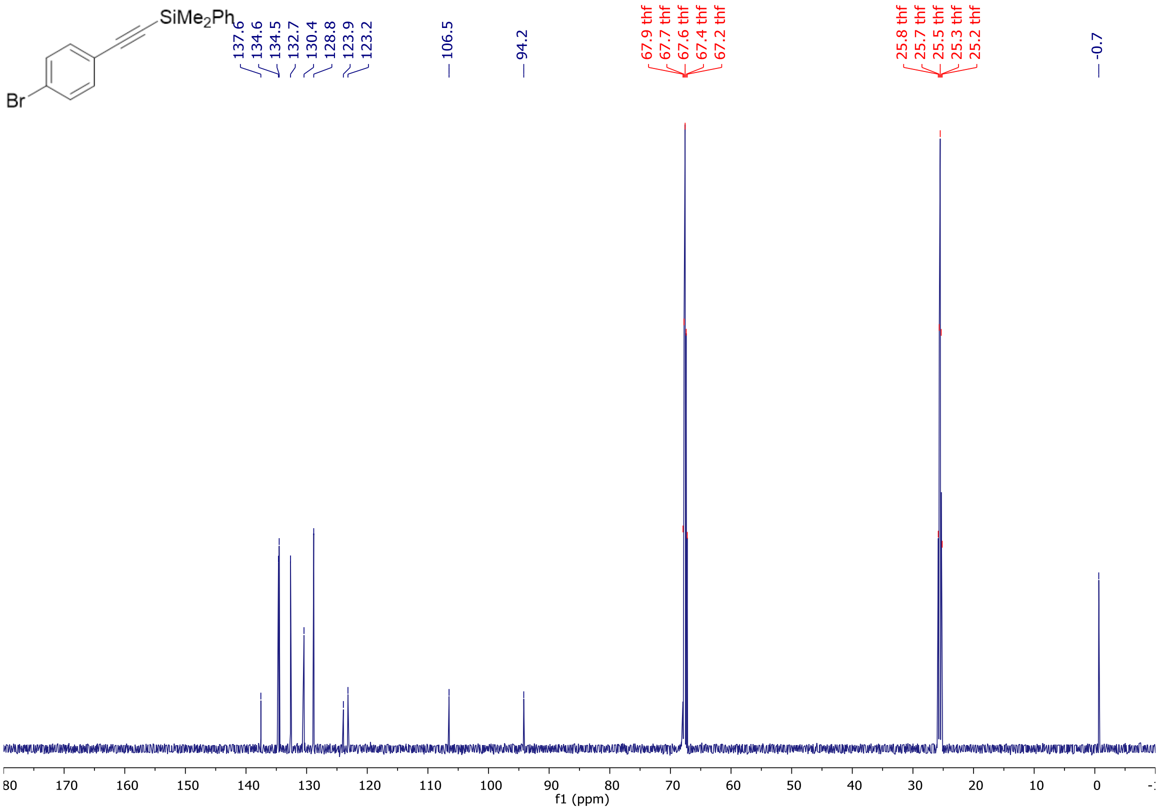
^{13}C NMR (126 MHz, THF-d_8) of compound **4b.**



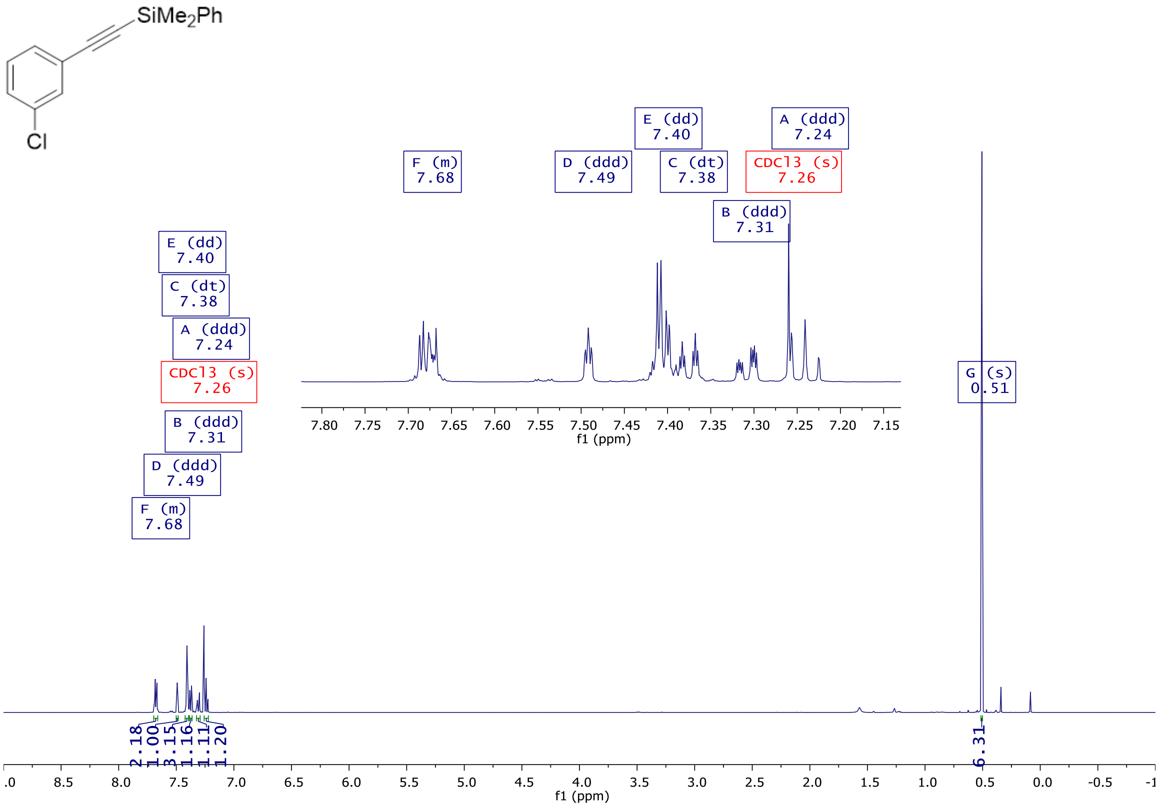
^{19}F NMR (282 MHz, THF-*d*$_8$) of compound **4b.**



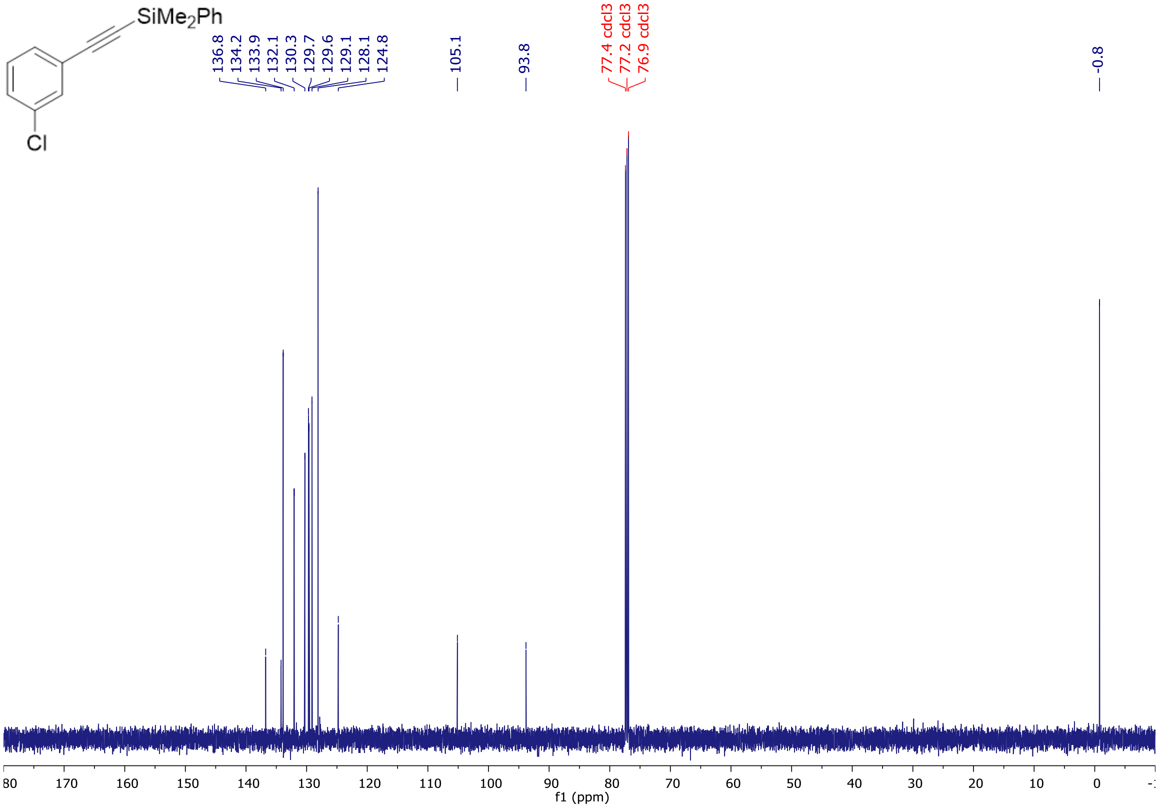
^{1}H NMR (500 MHz, THF-d_8) of compound **4c.**



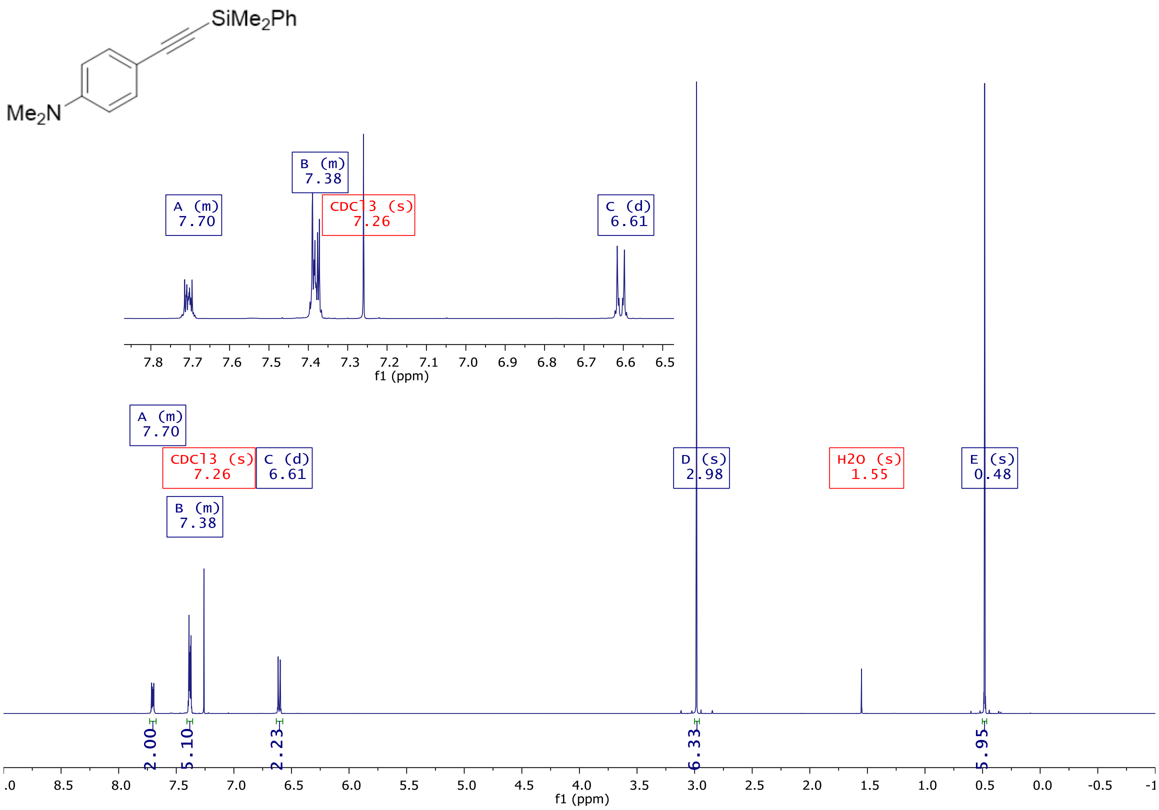
^{13}C NMR (126 MHz, THF-d_8) of compound **4c.**



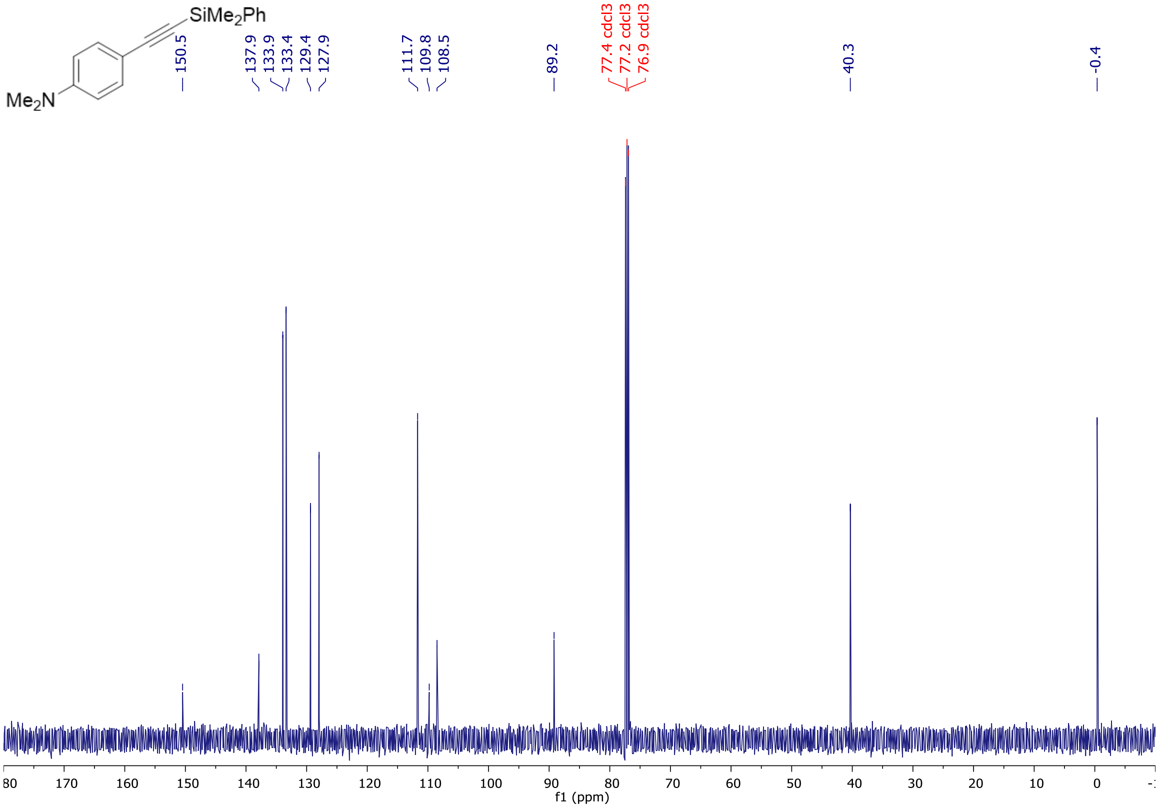
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4d.**



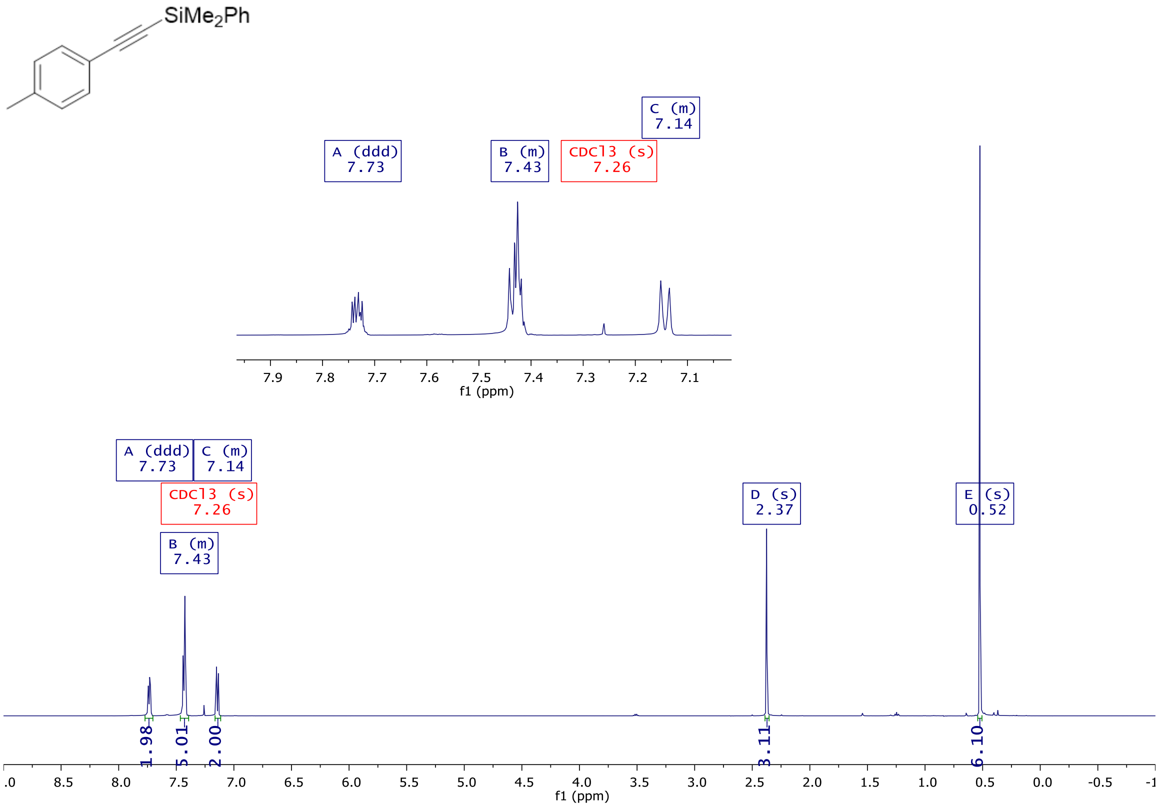
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4d.**



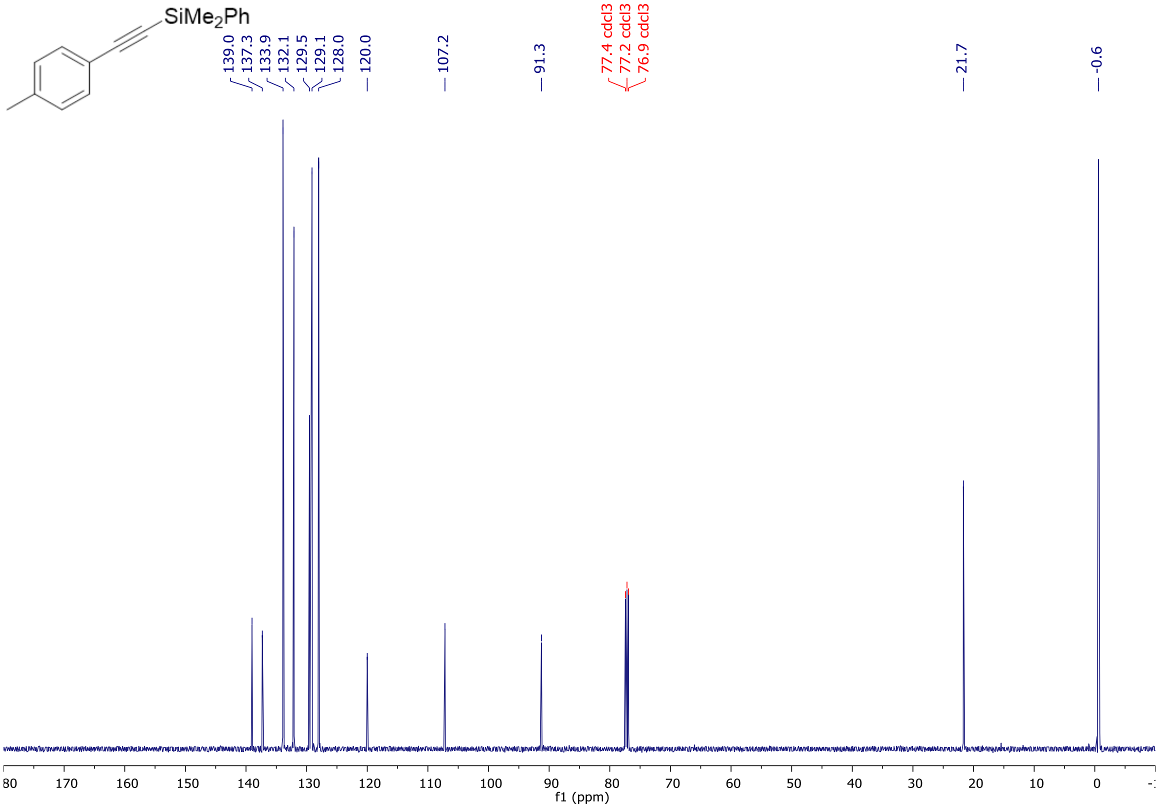
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4e.**



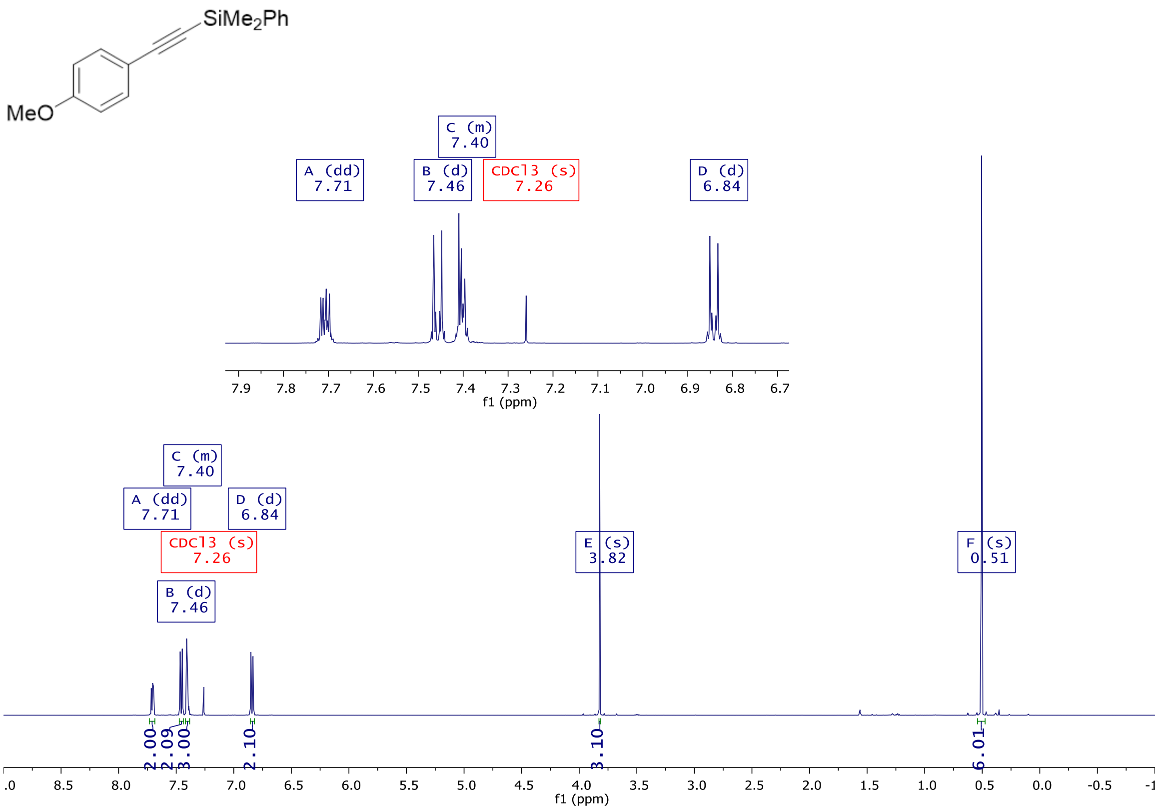
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4e.**



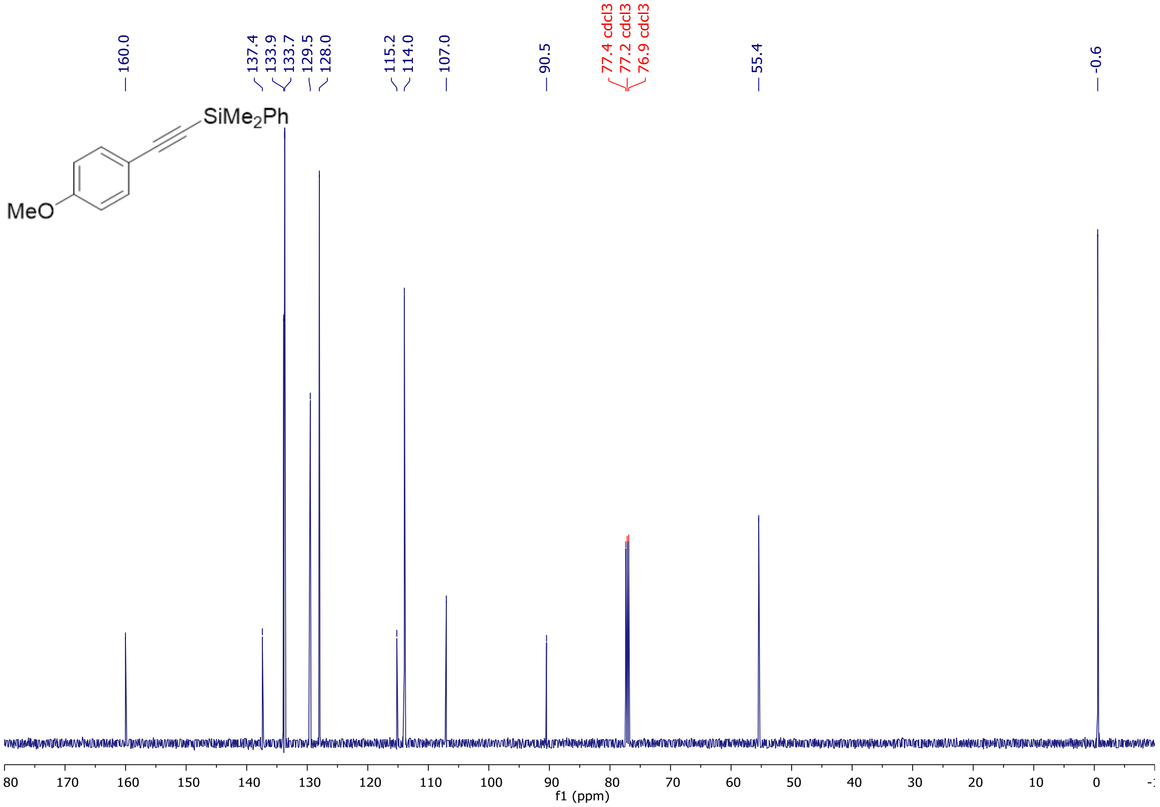
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4f.**



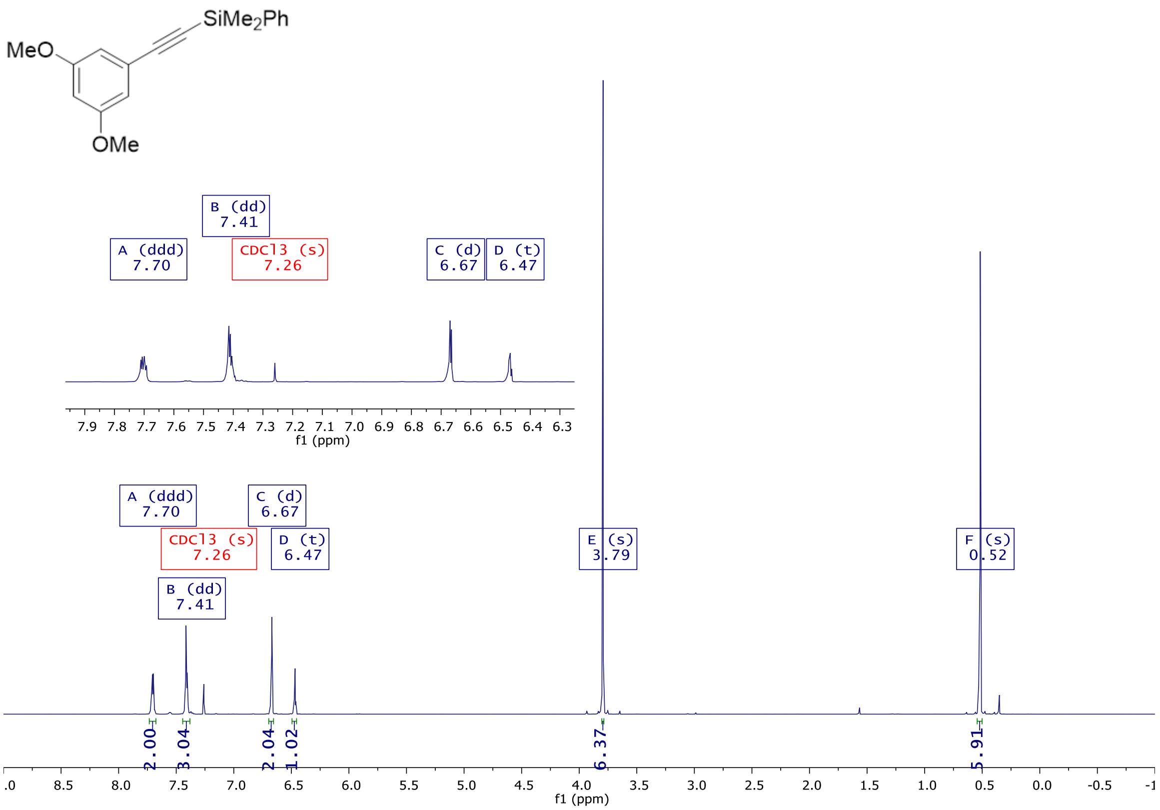
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4f.**



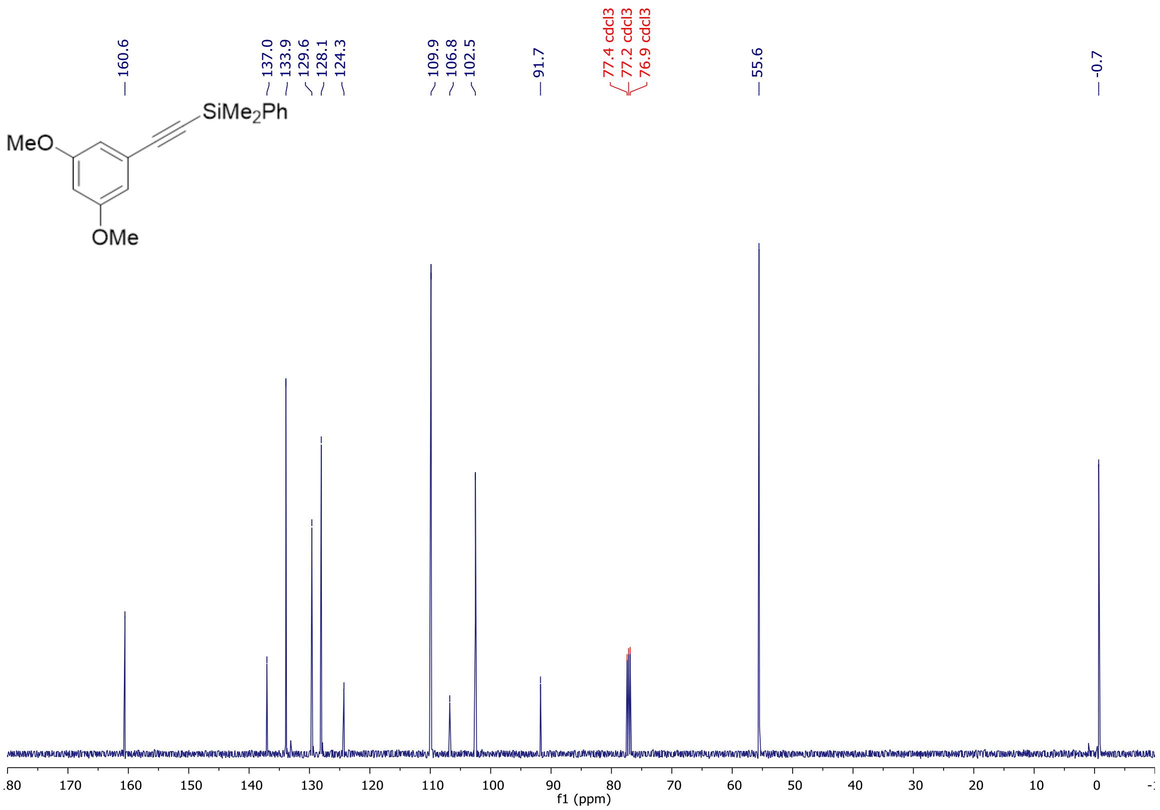
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4g.**



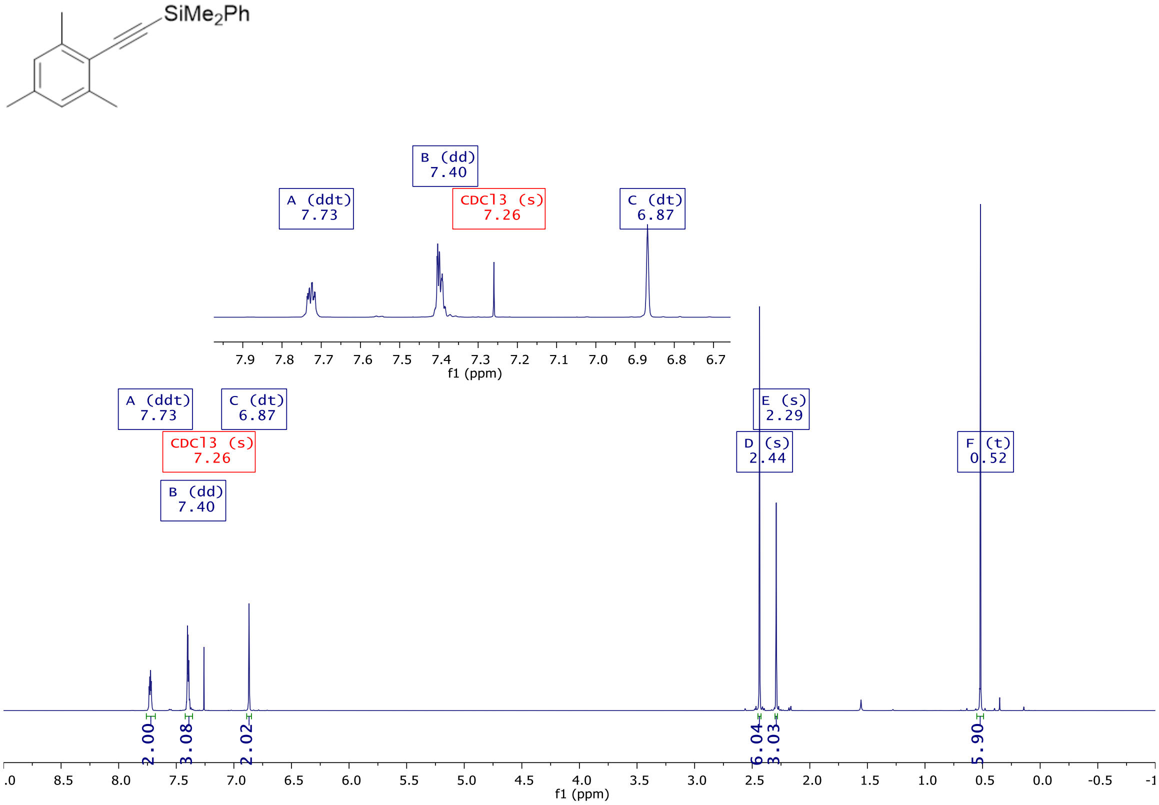
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4g.**



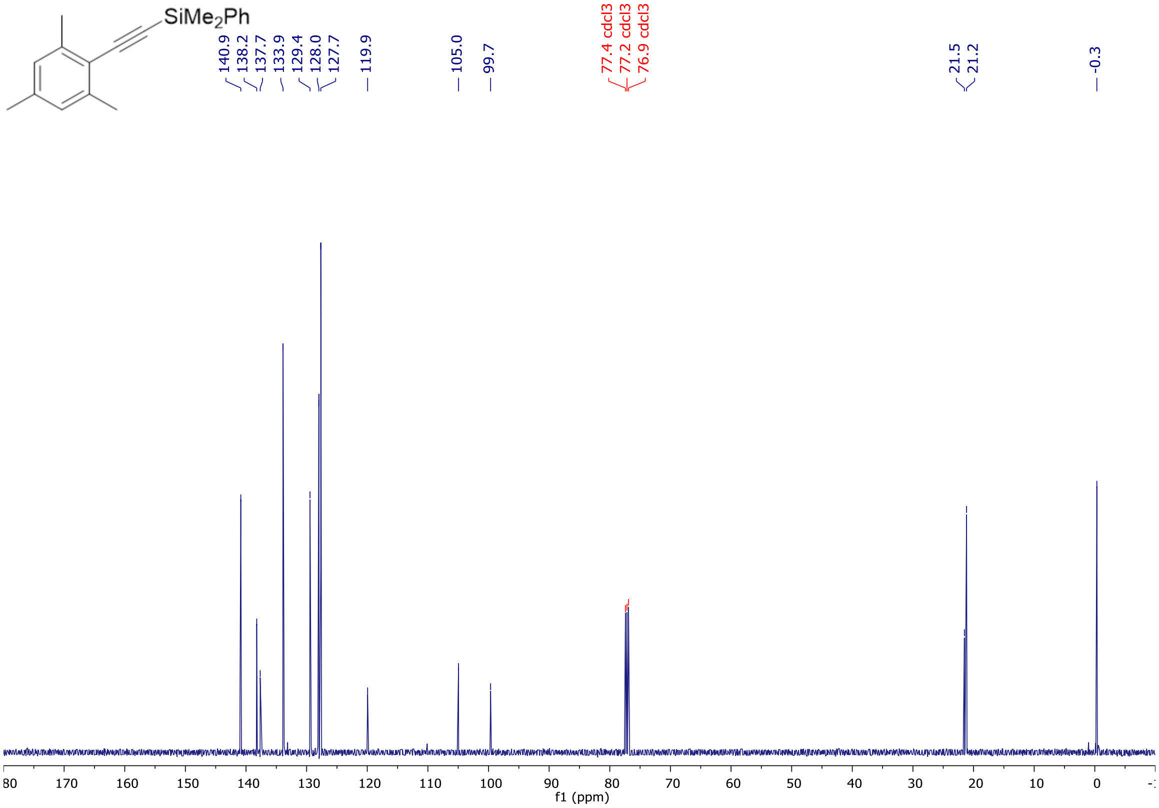
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4h.**



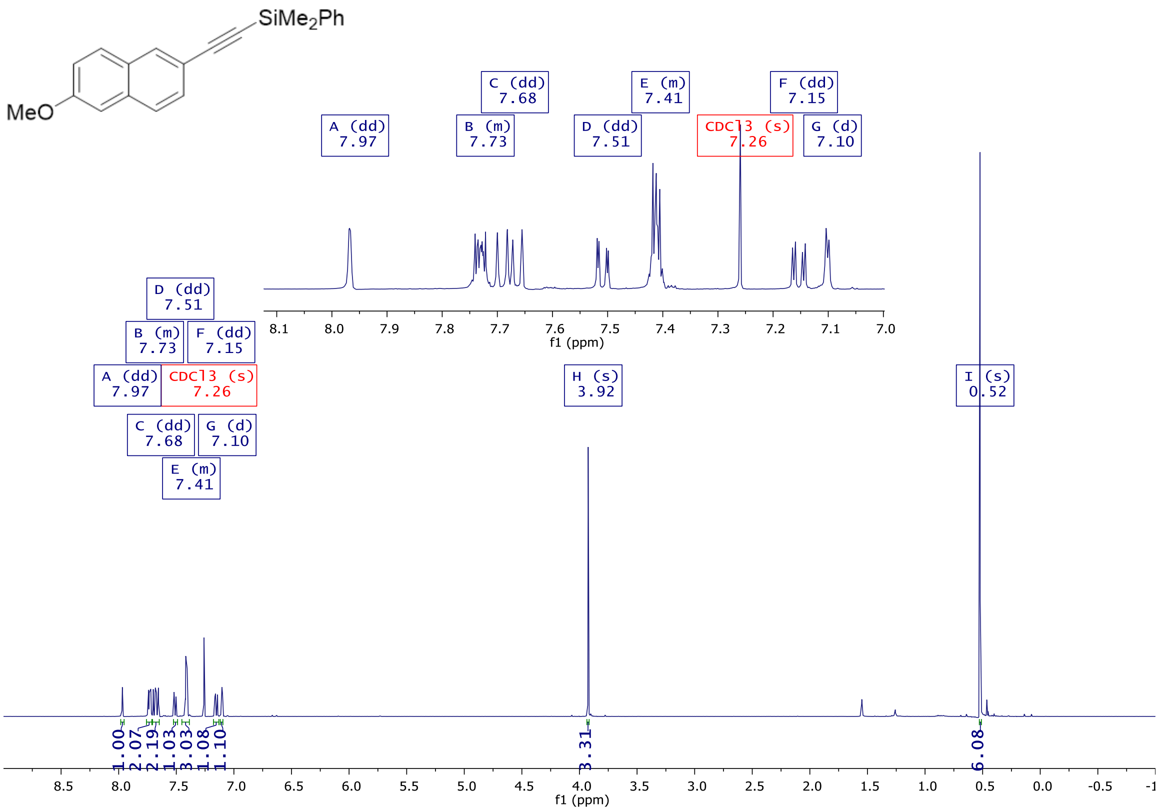
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4h.**



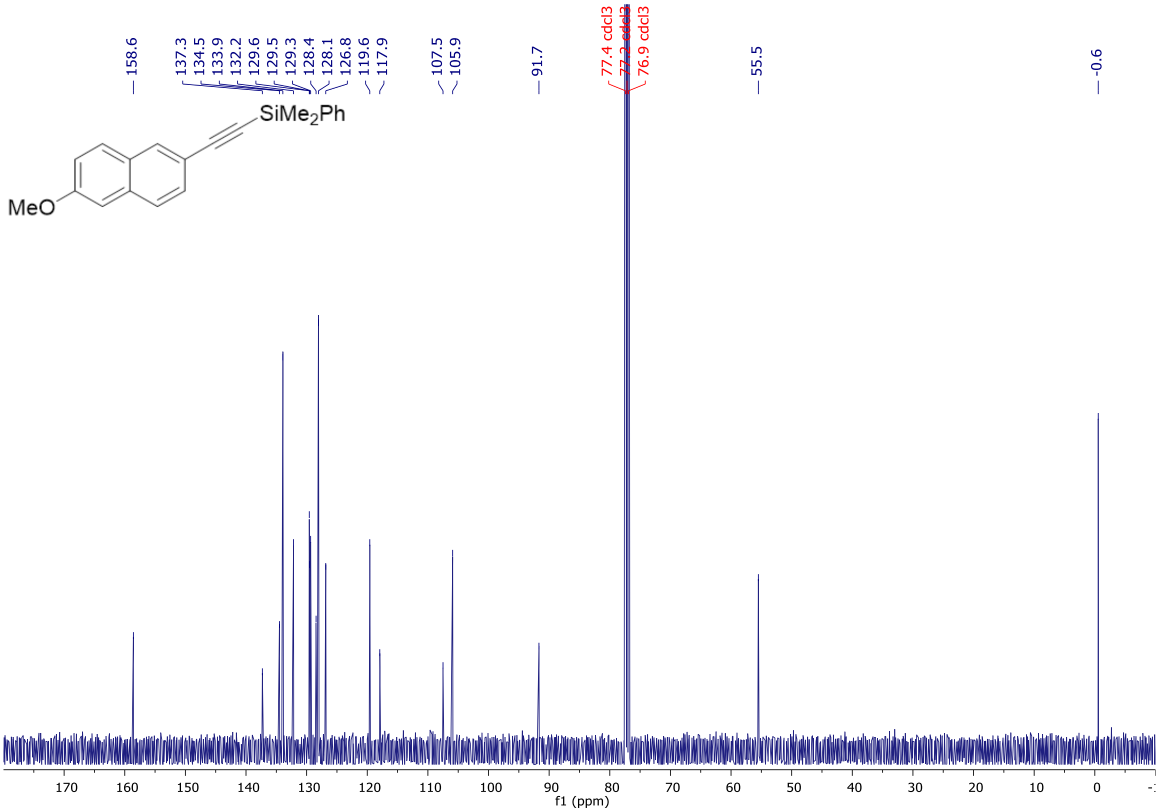
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4i.**



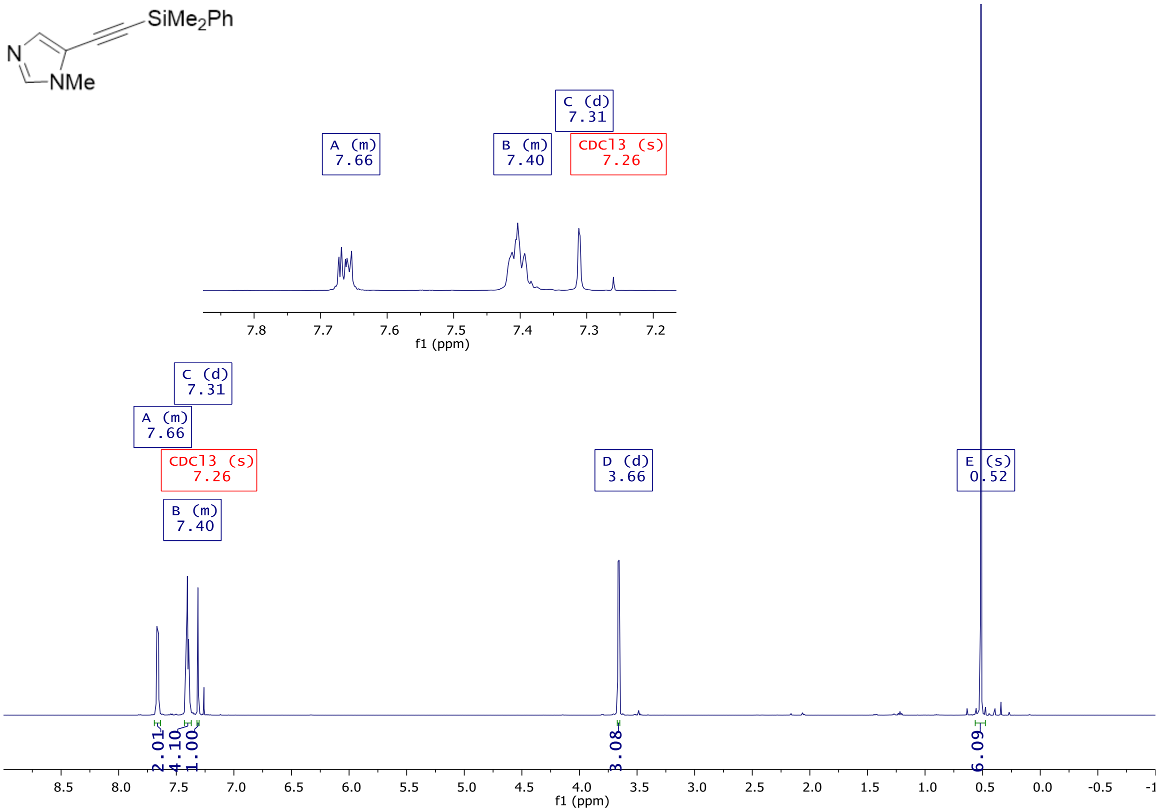
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4i.**



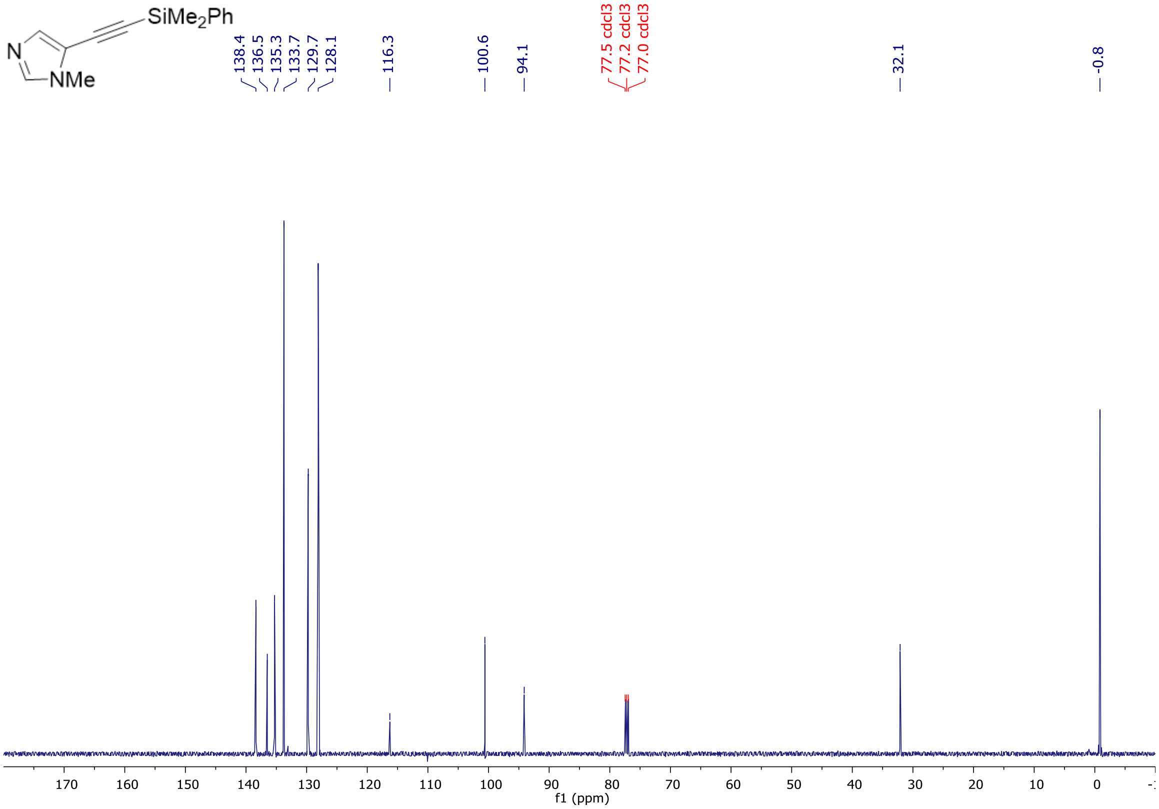
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4j.**



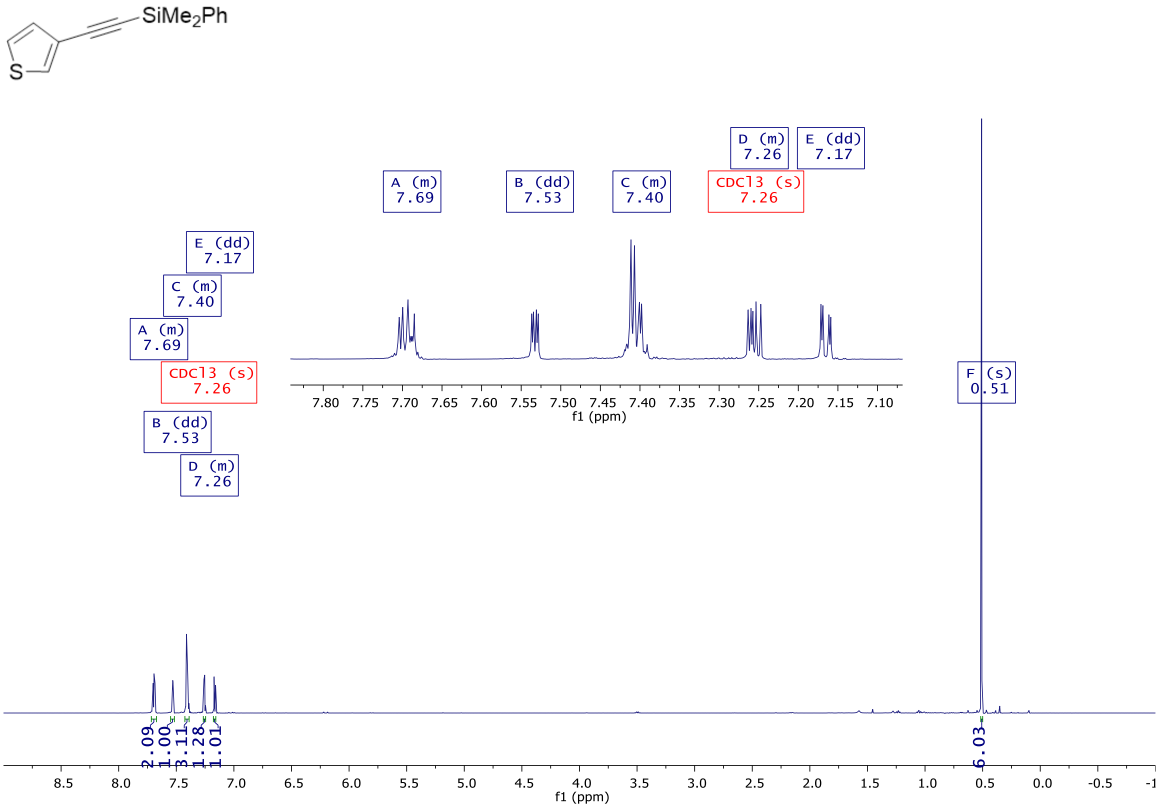
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4j.**



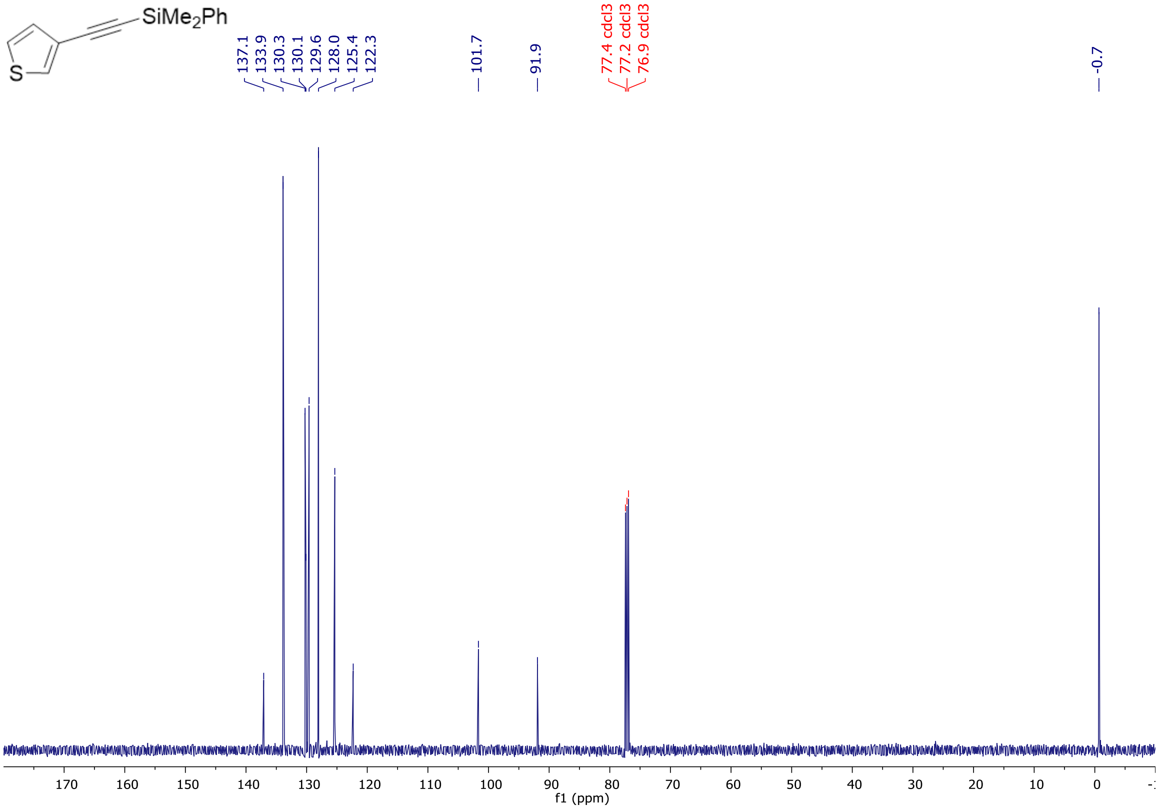
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4k.**



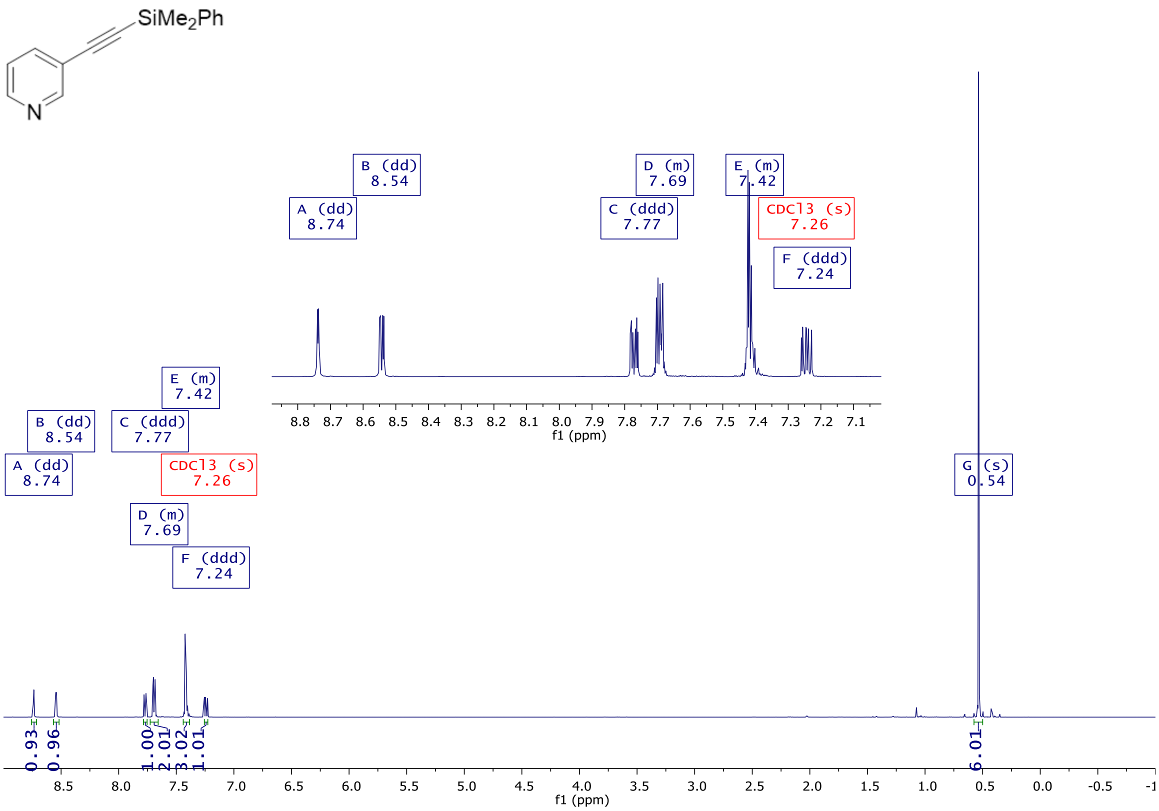
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4k.**



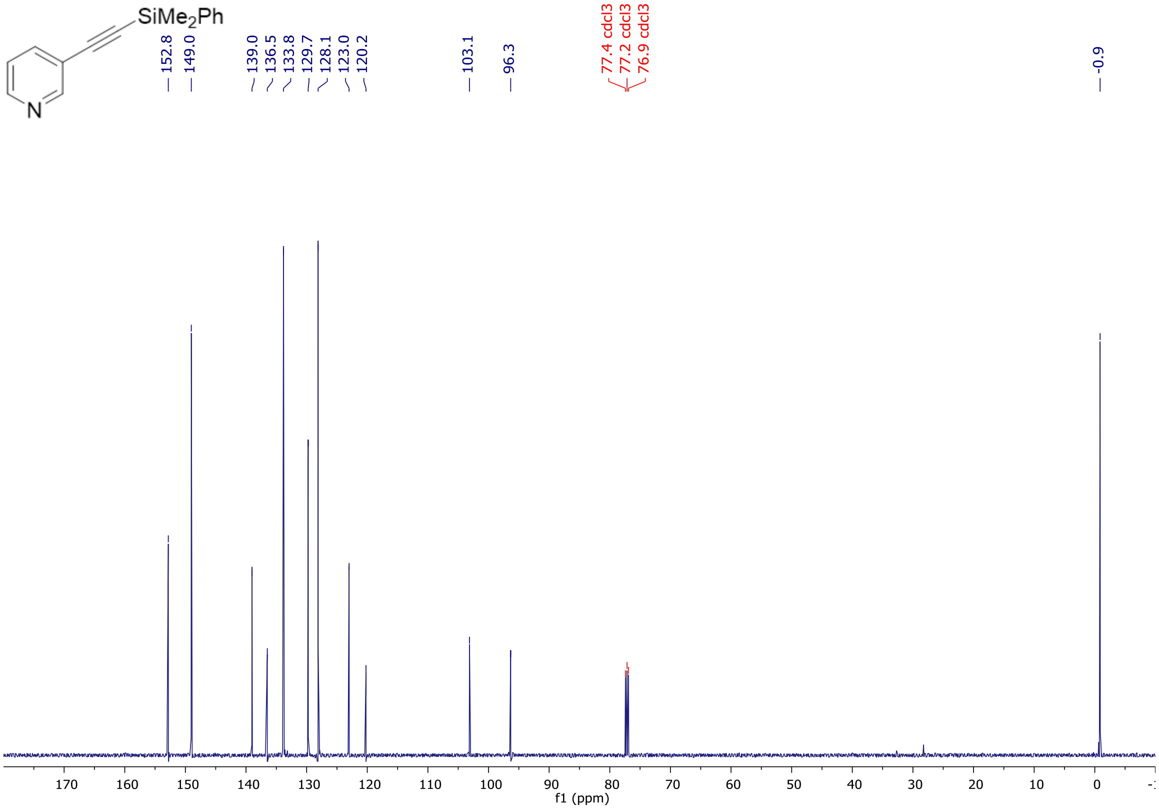
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4l.**



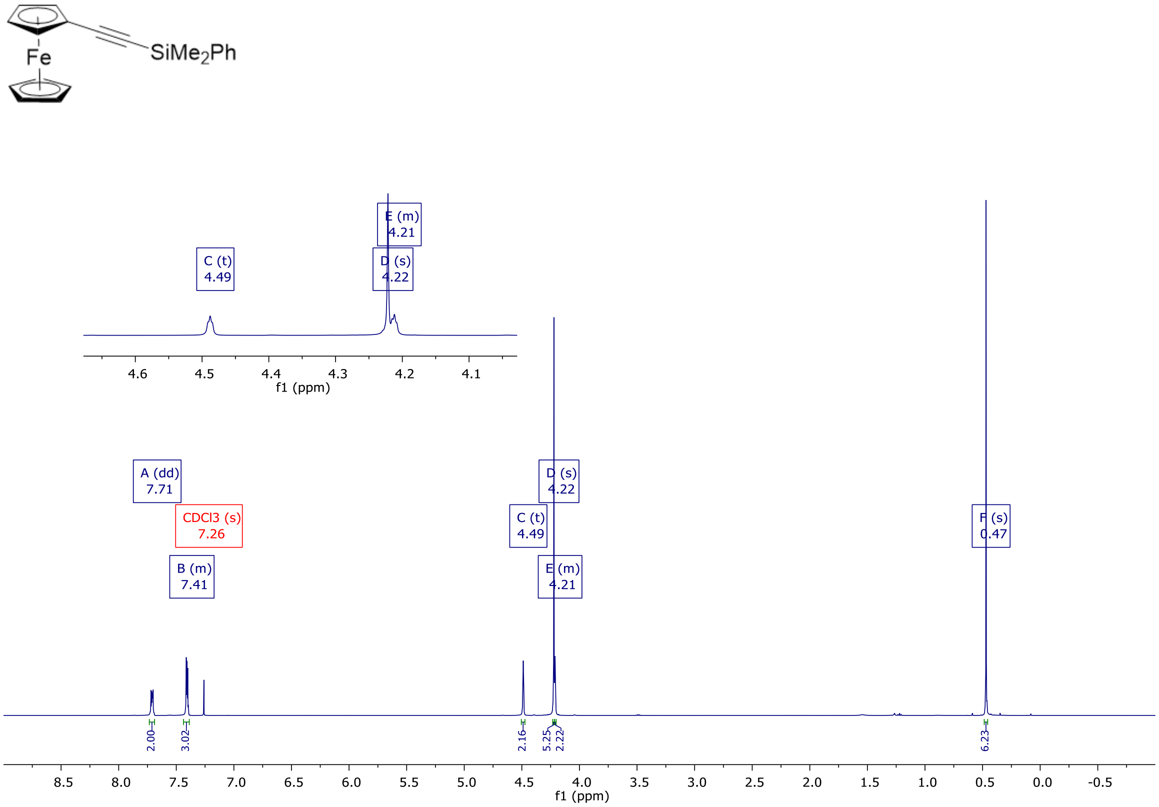
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4l.**



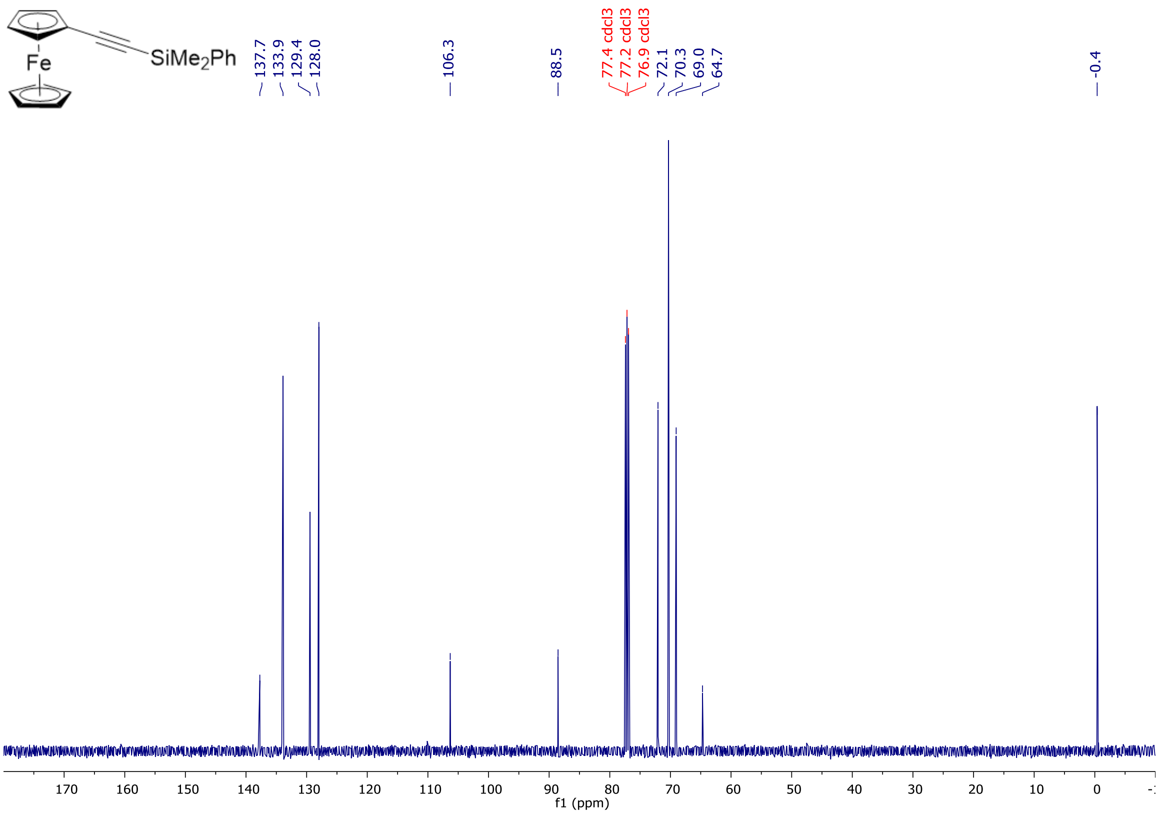
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4m.**



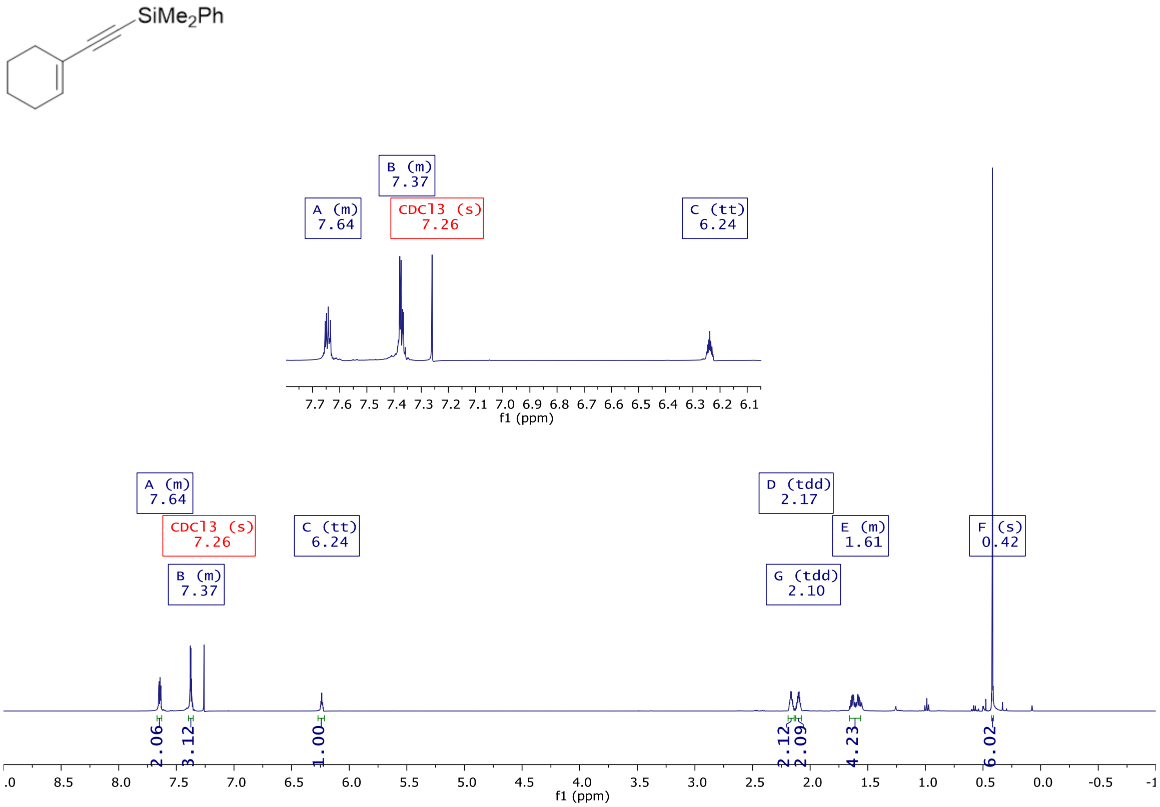
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4m.**



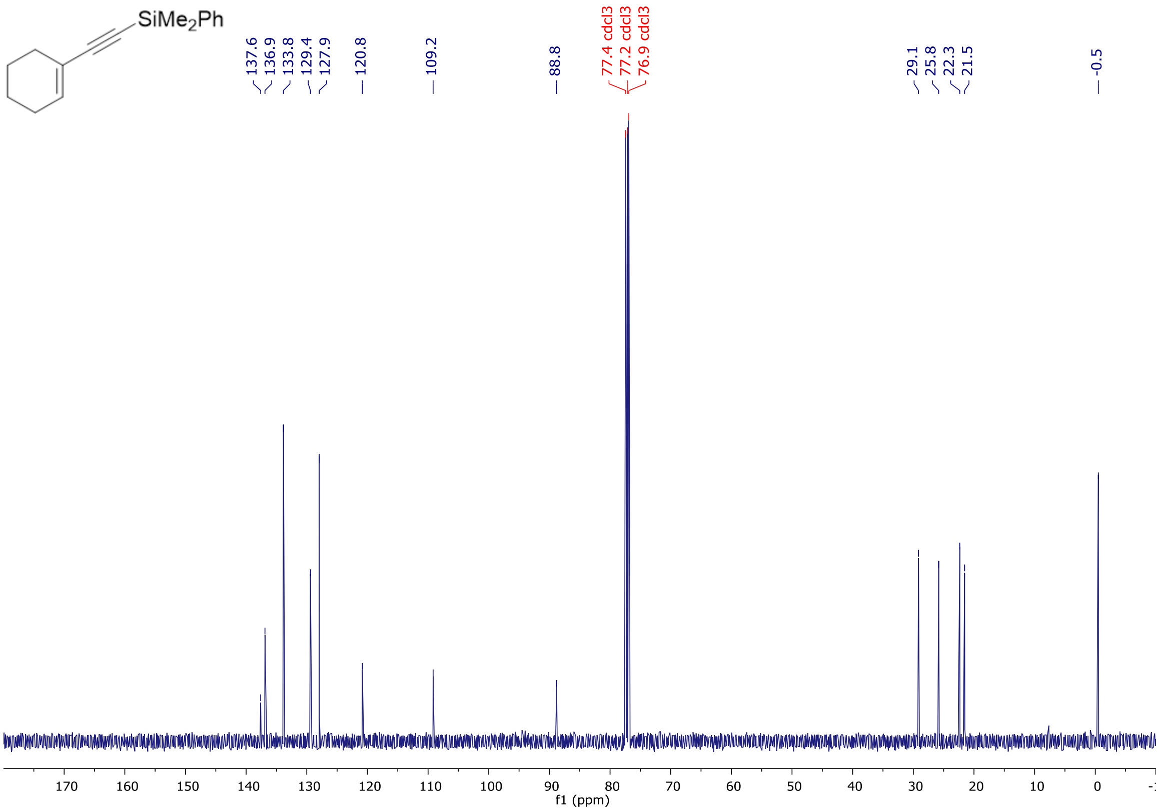
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4n.**



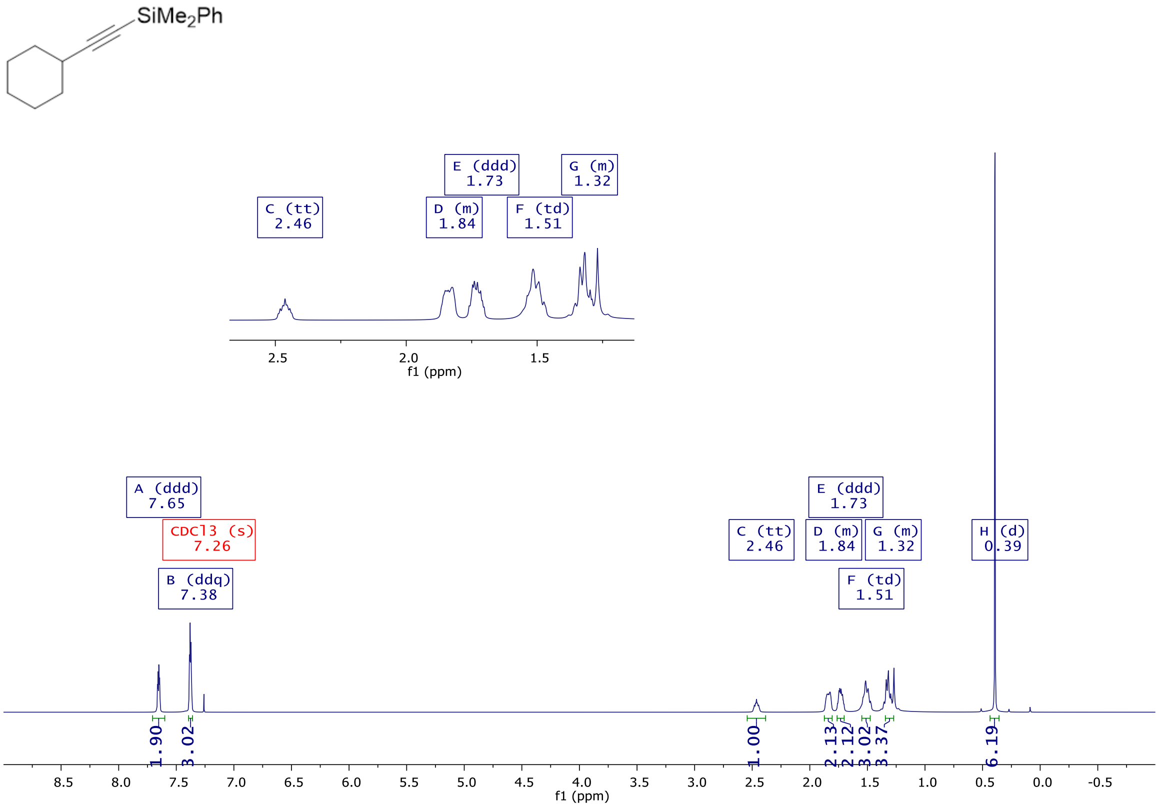
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4n.**



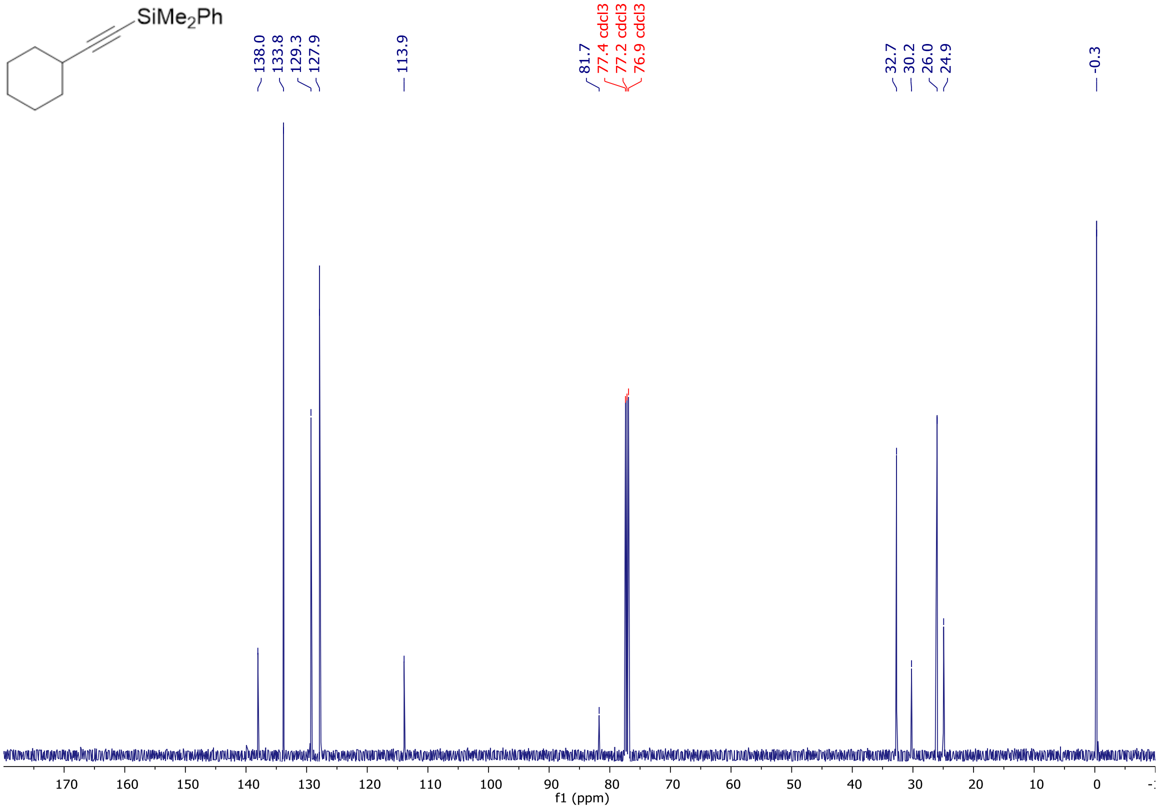
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4o.**



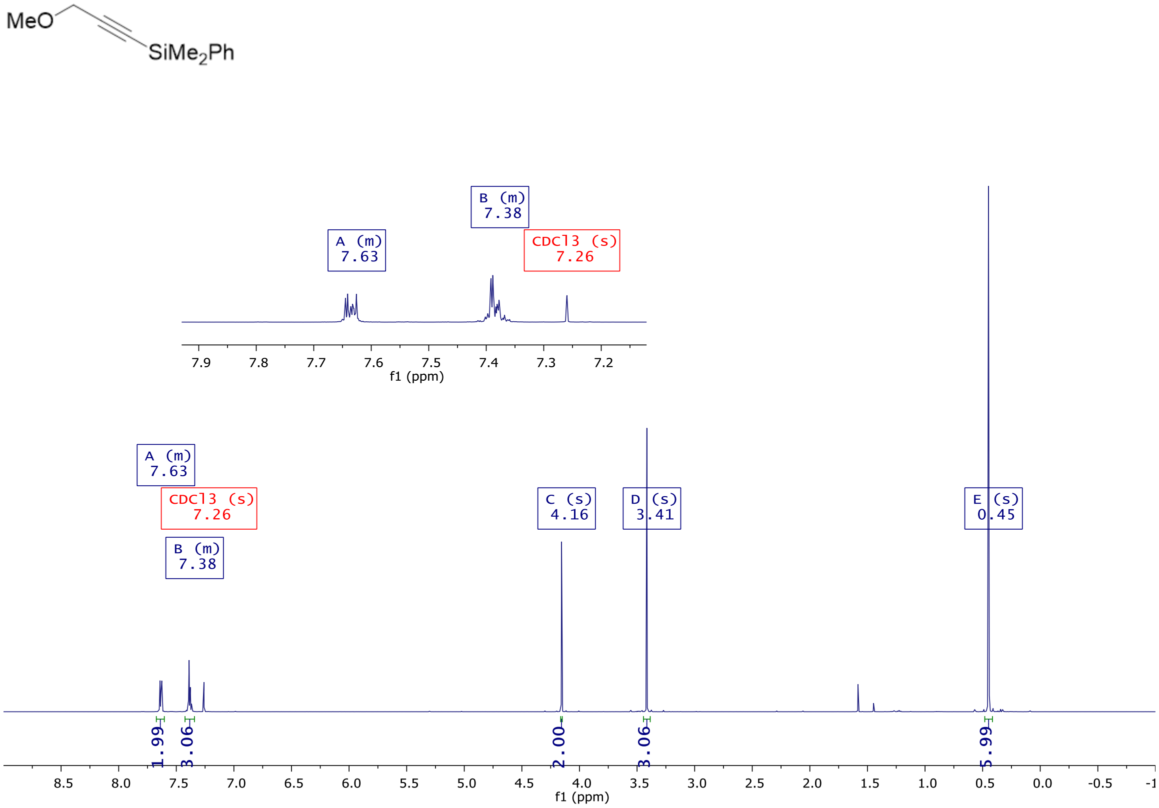
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4o.**



^{1}H NMR (500 MHz, CDCl$_3$) of compound **4p.**



^{13}C NMR (126 MHz, CDCl$_3$) of compound **4p.**



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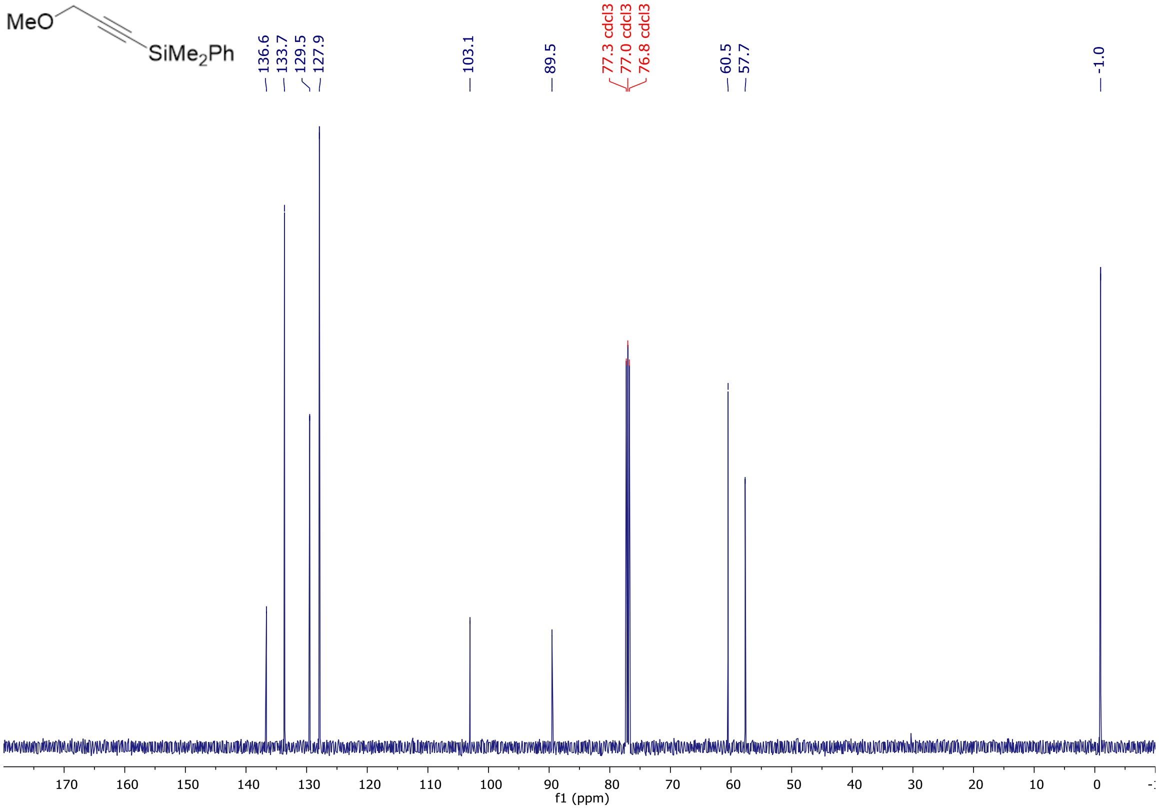
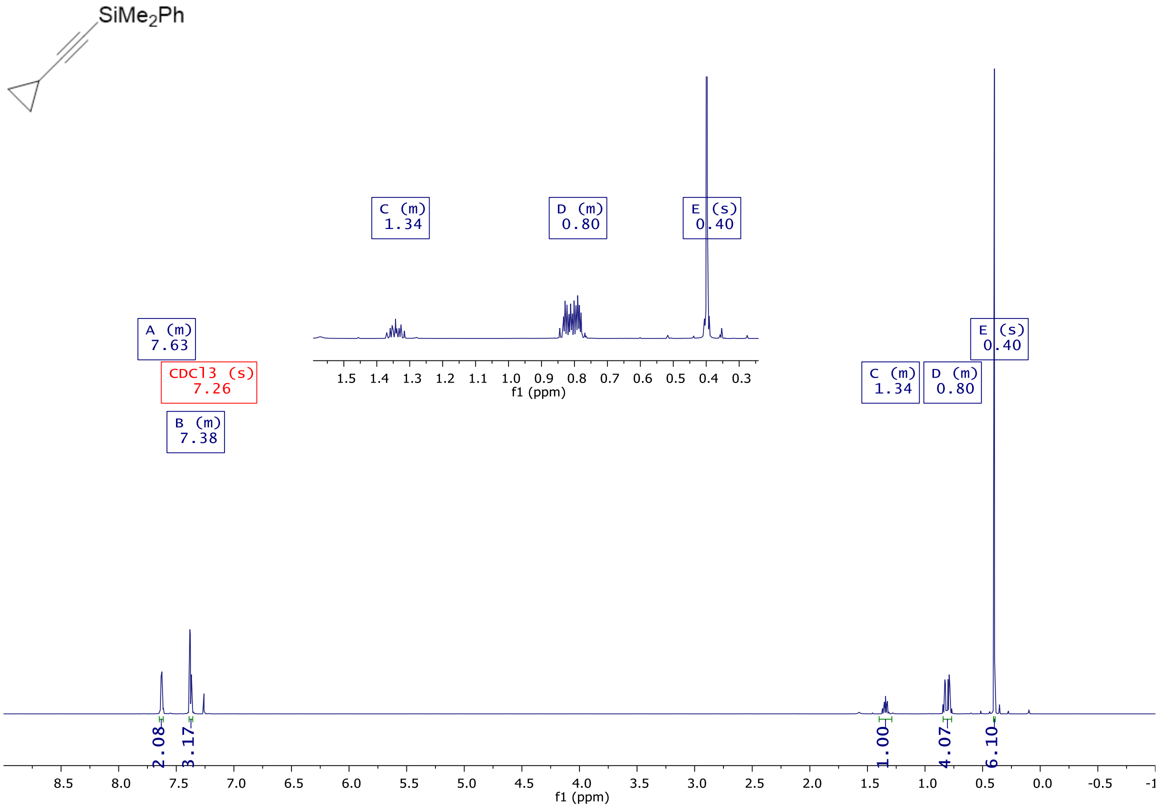
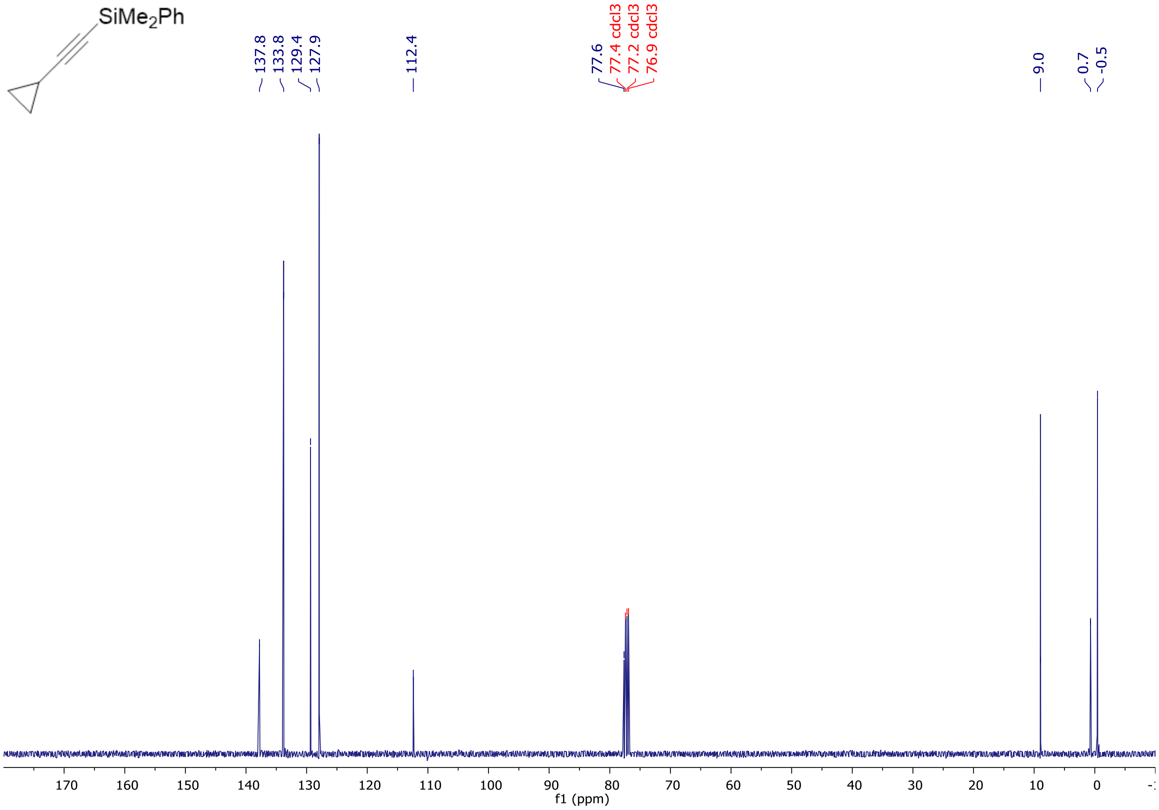


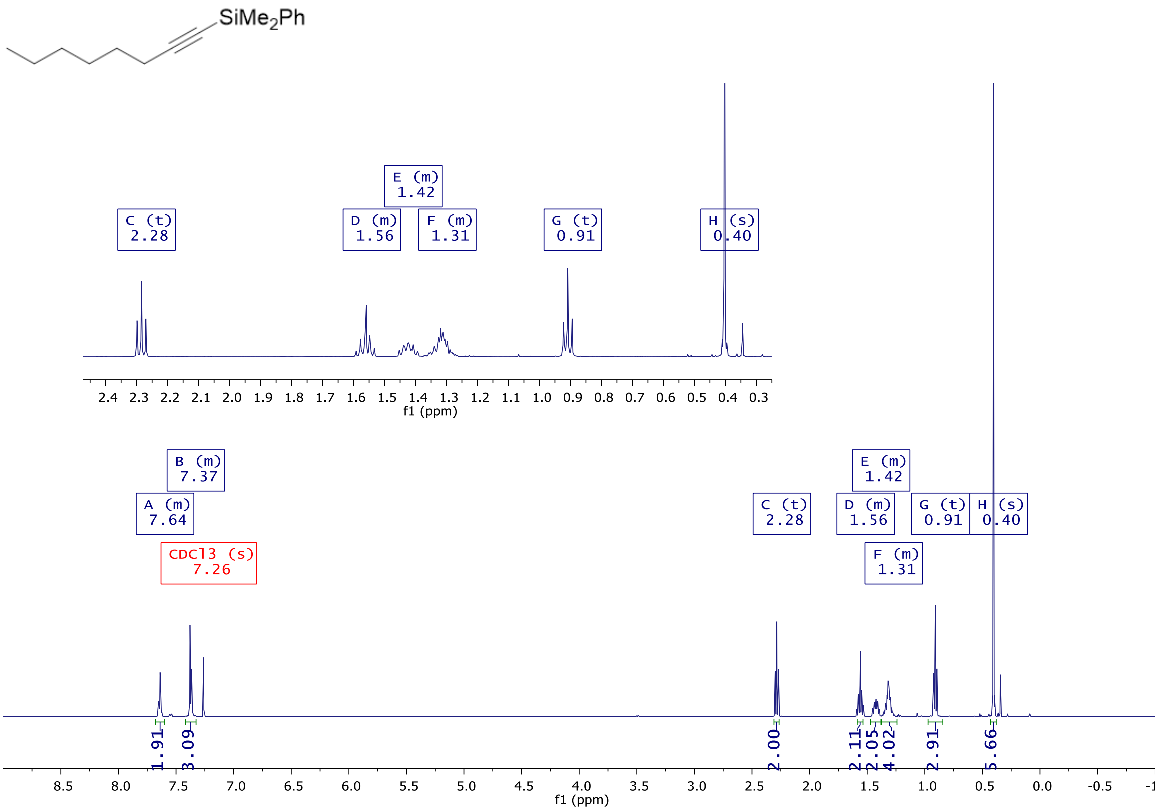
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4q.**



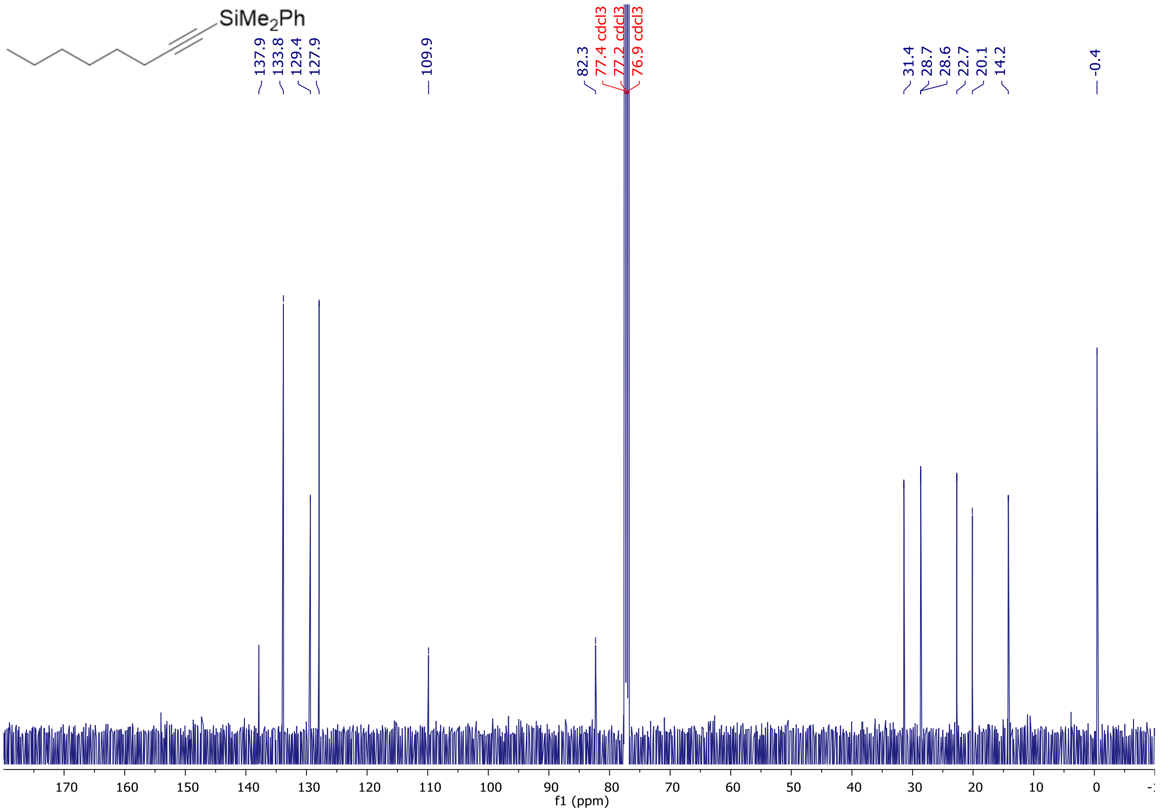
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4r.**



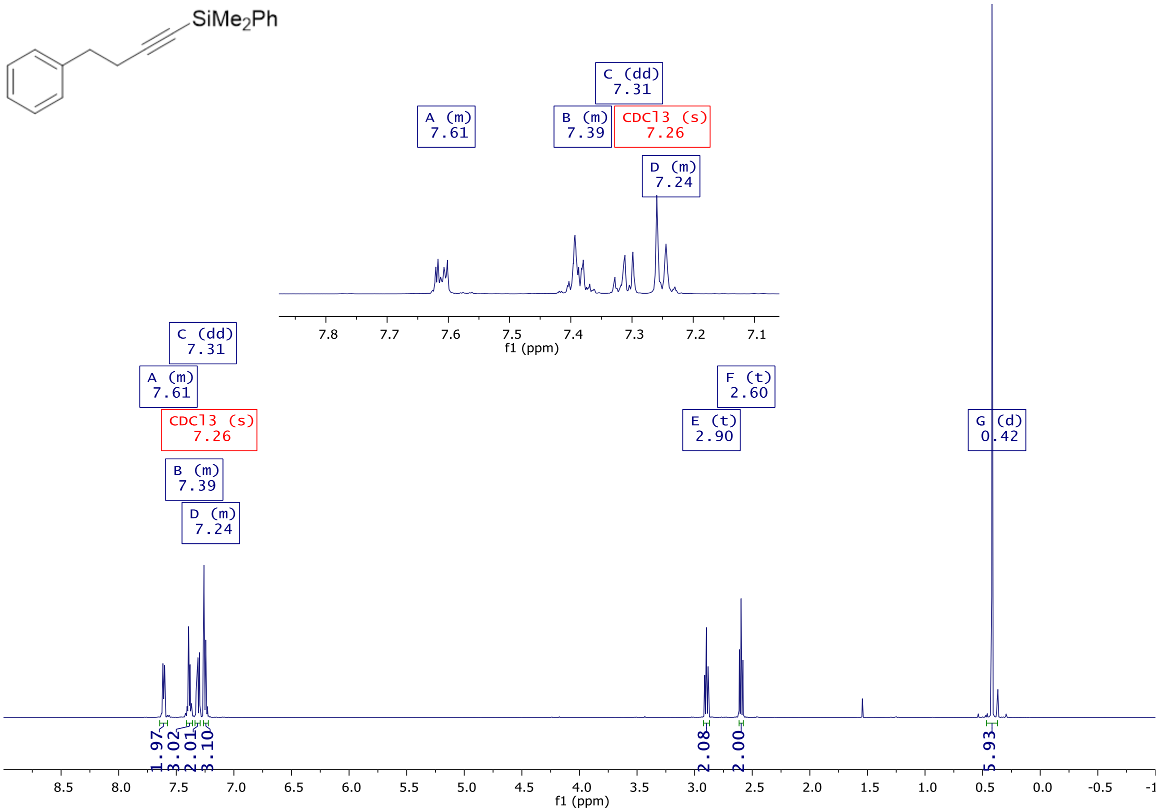
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4r.**



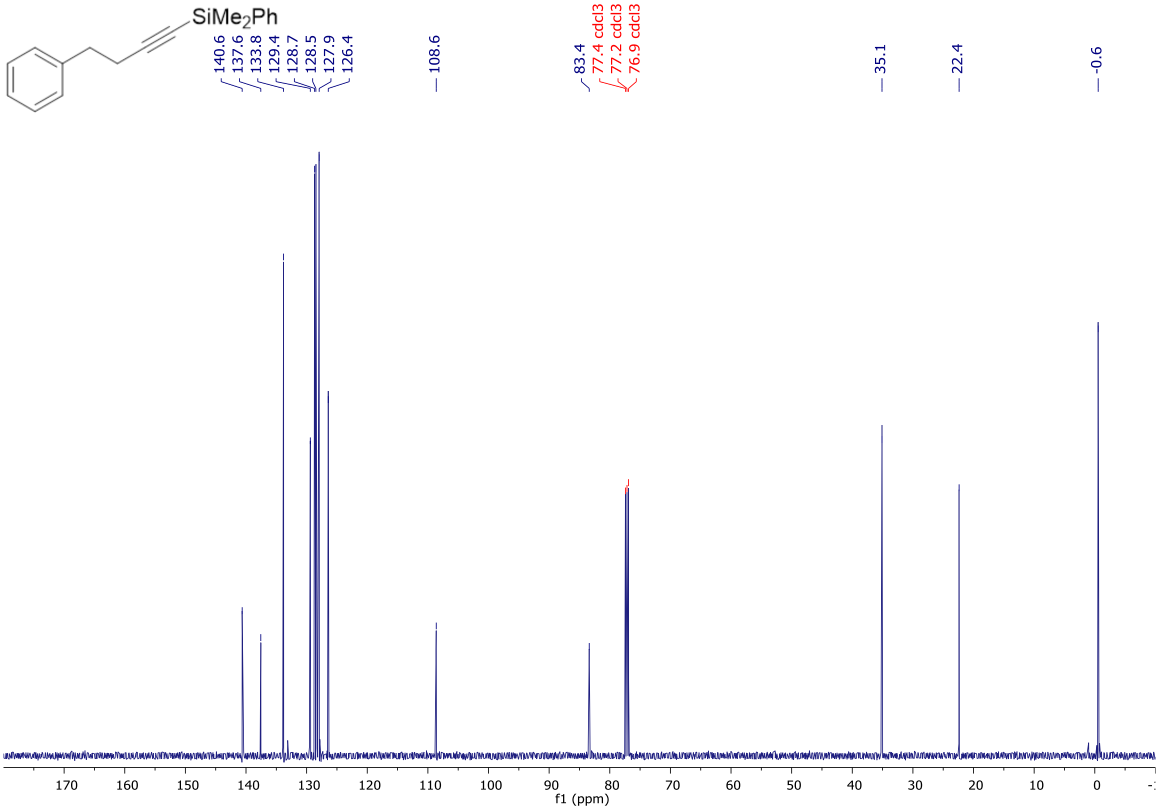
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4s.**



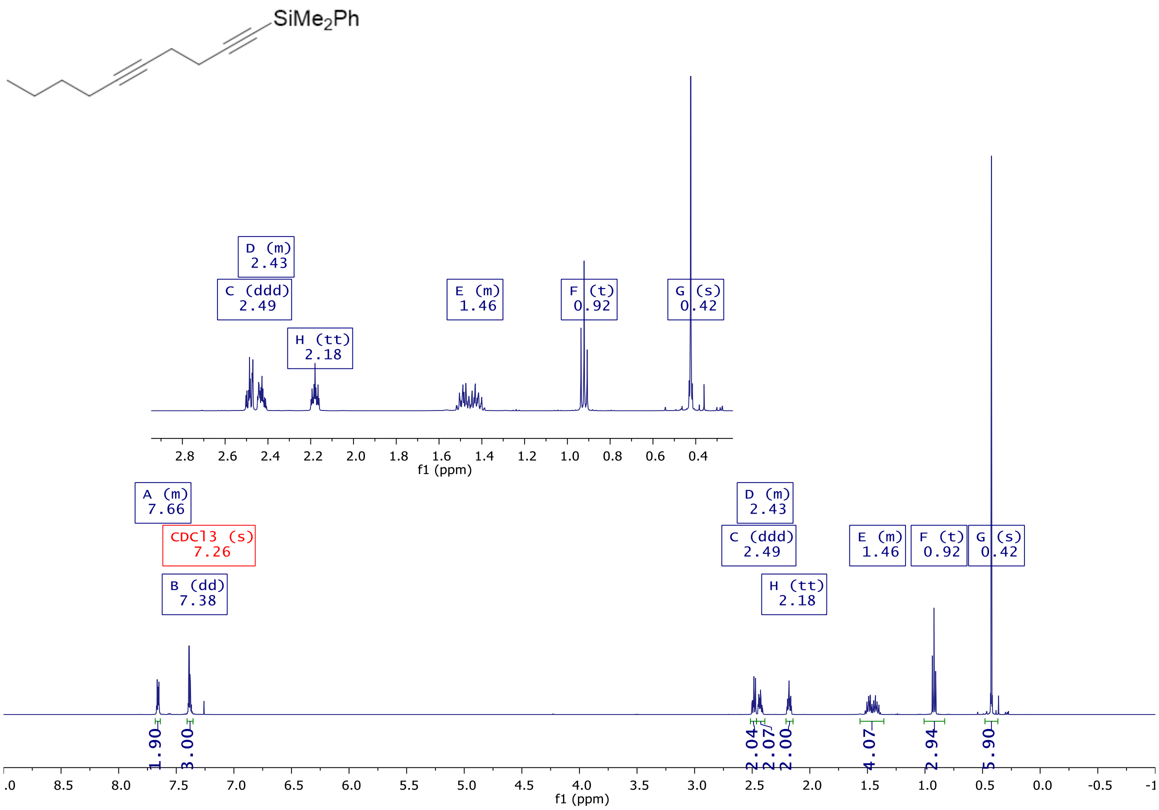
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4s.**



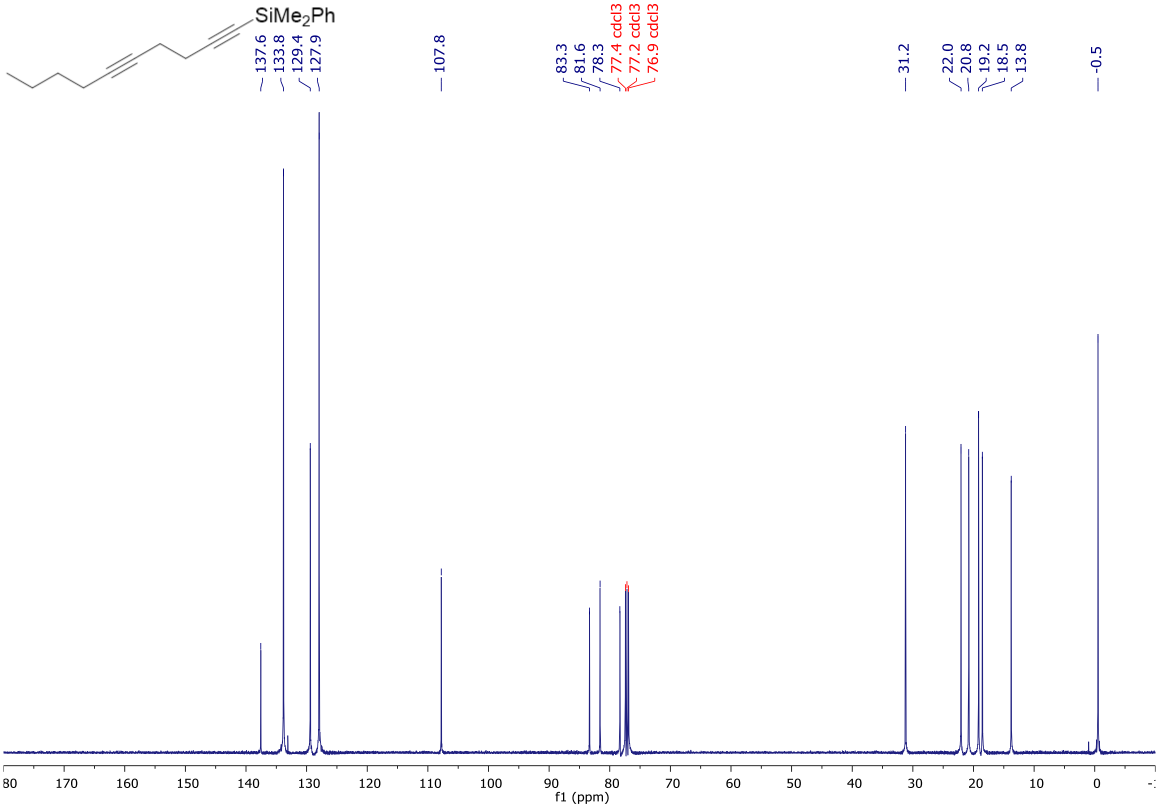
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4t.**



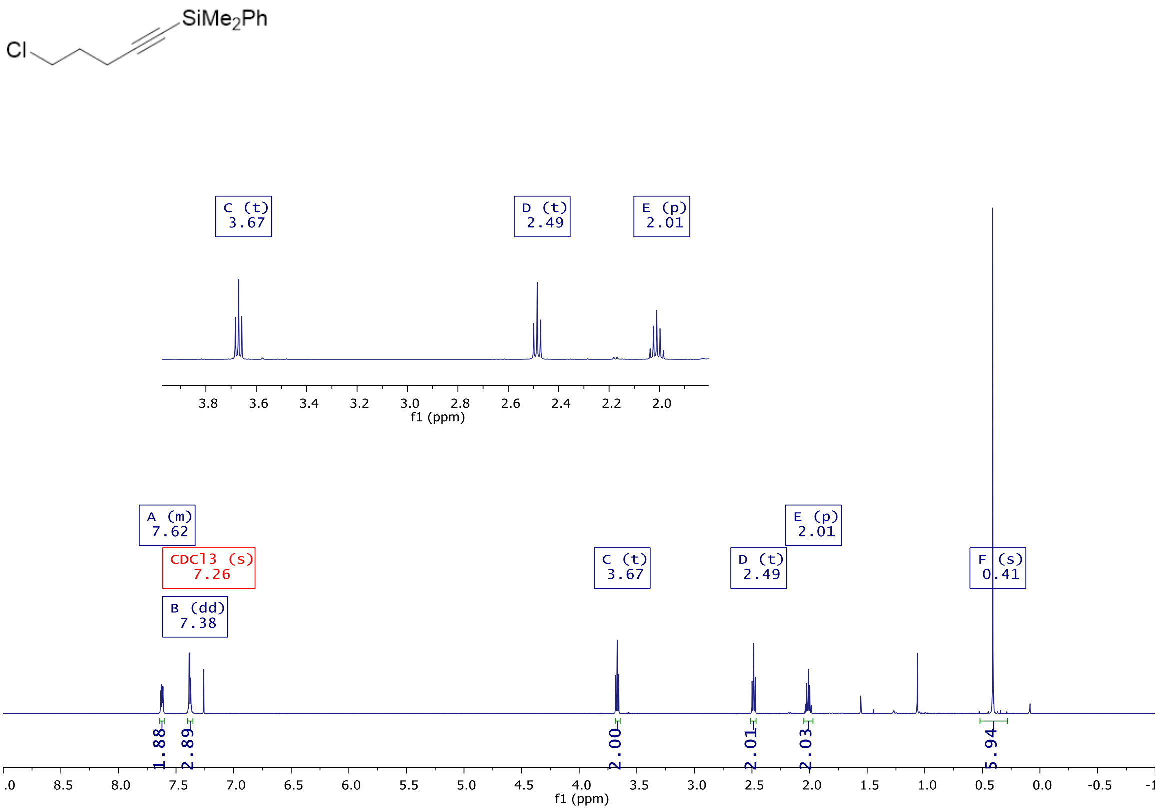
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4t.**



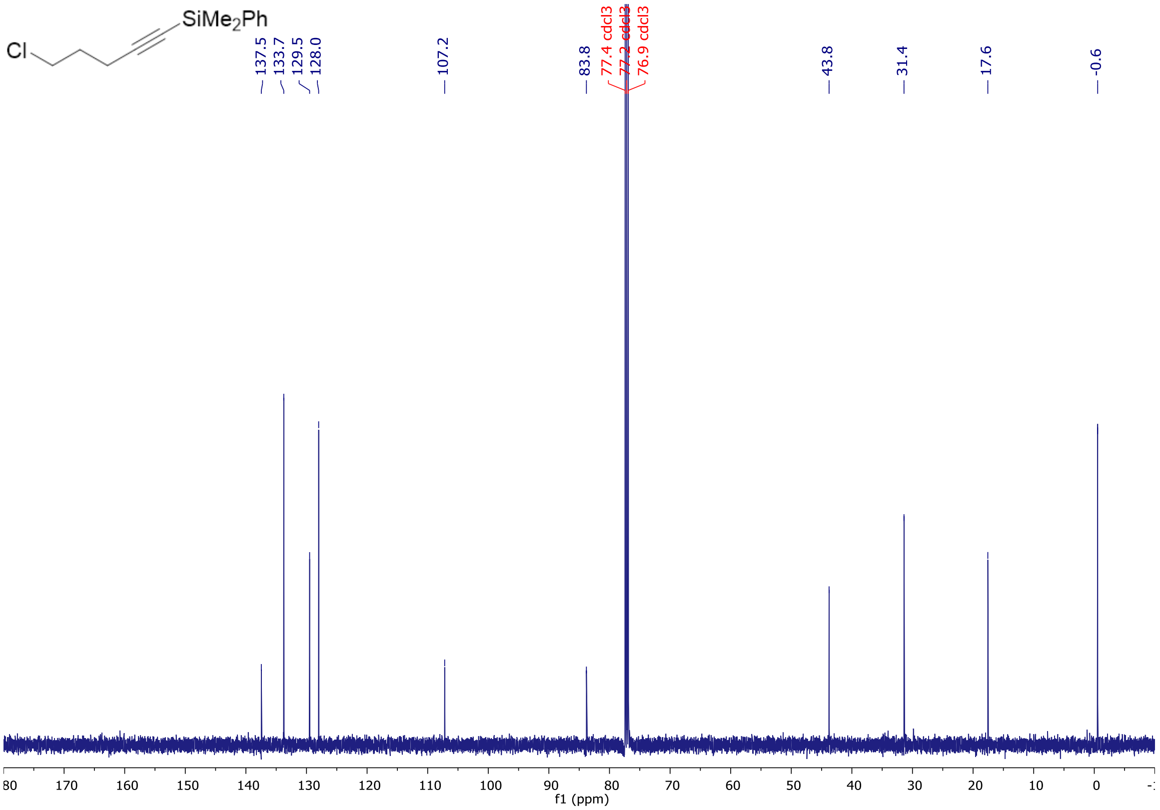
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4u.**



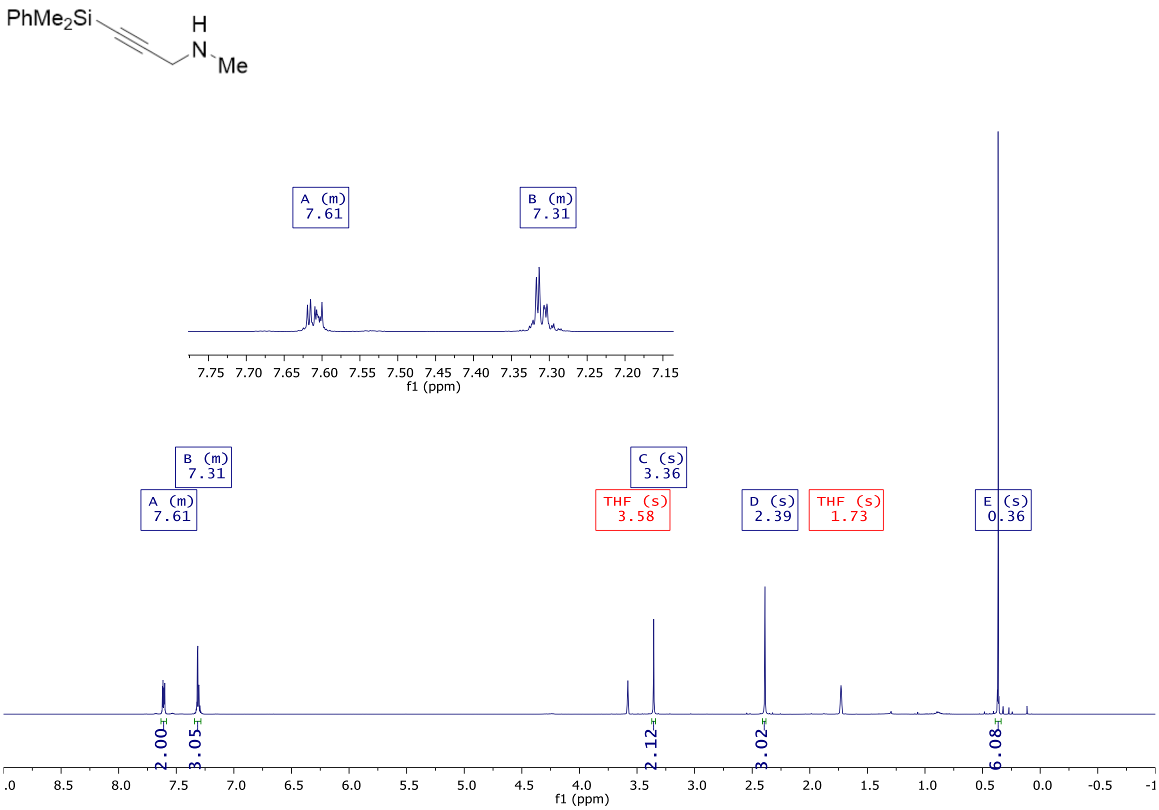
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4u.**



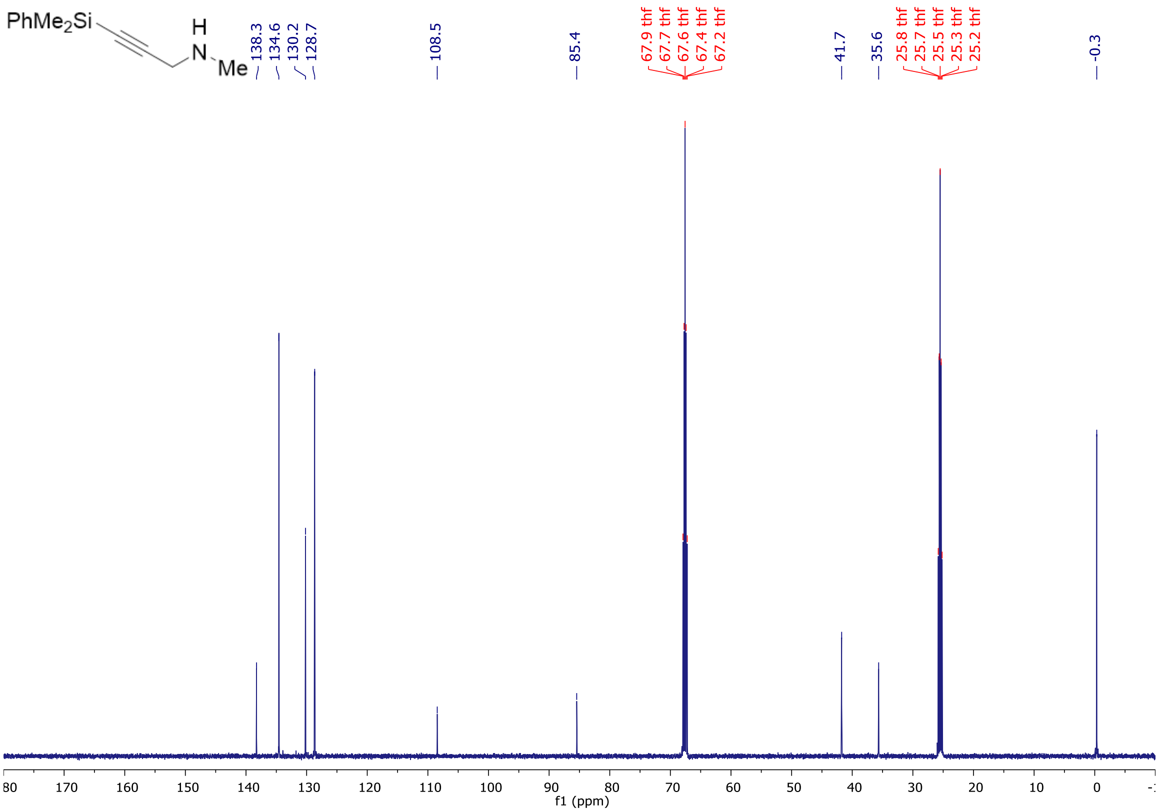
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4v.**



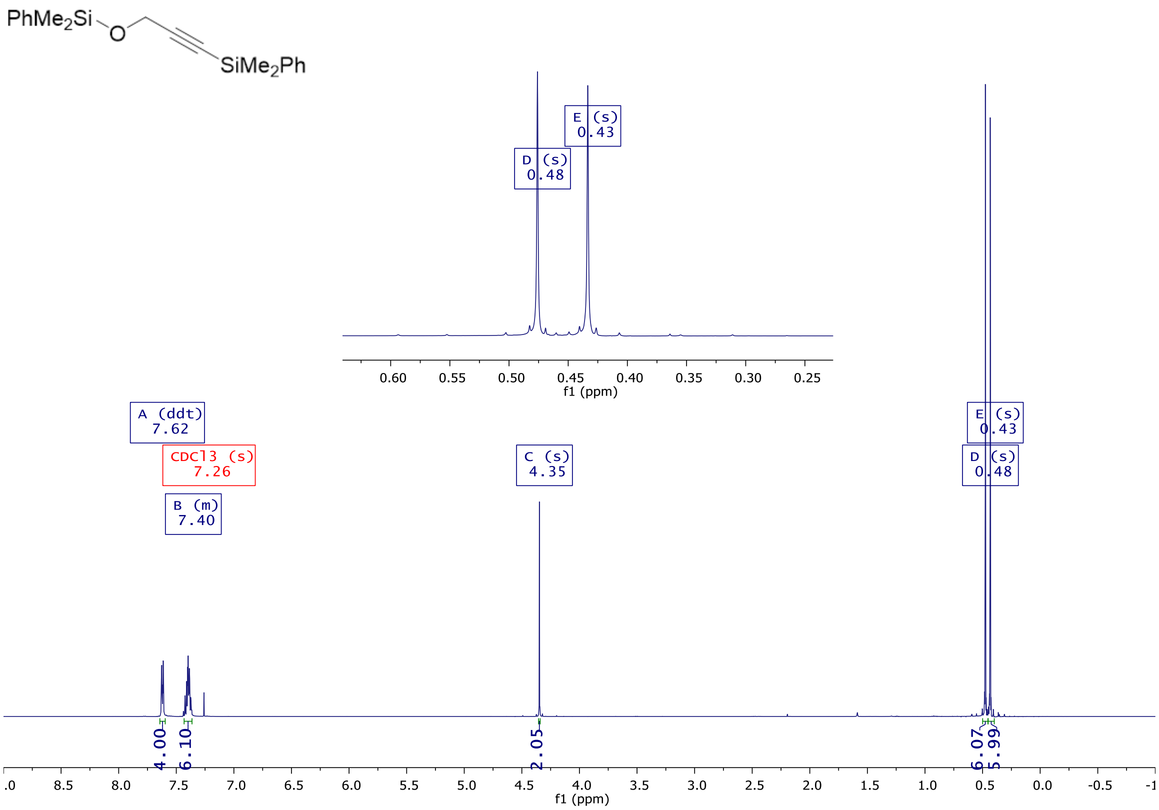
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4v.**



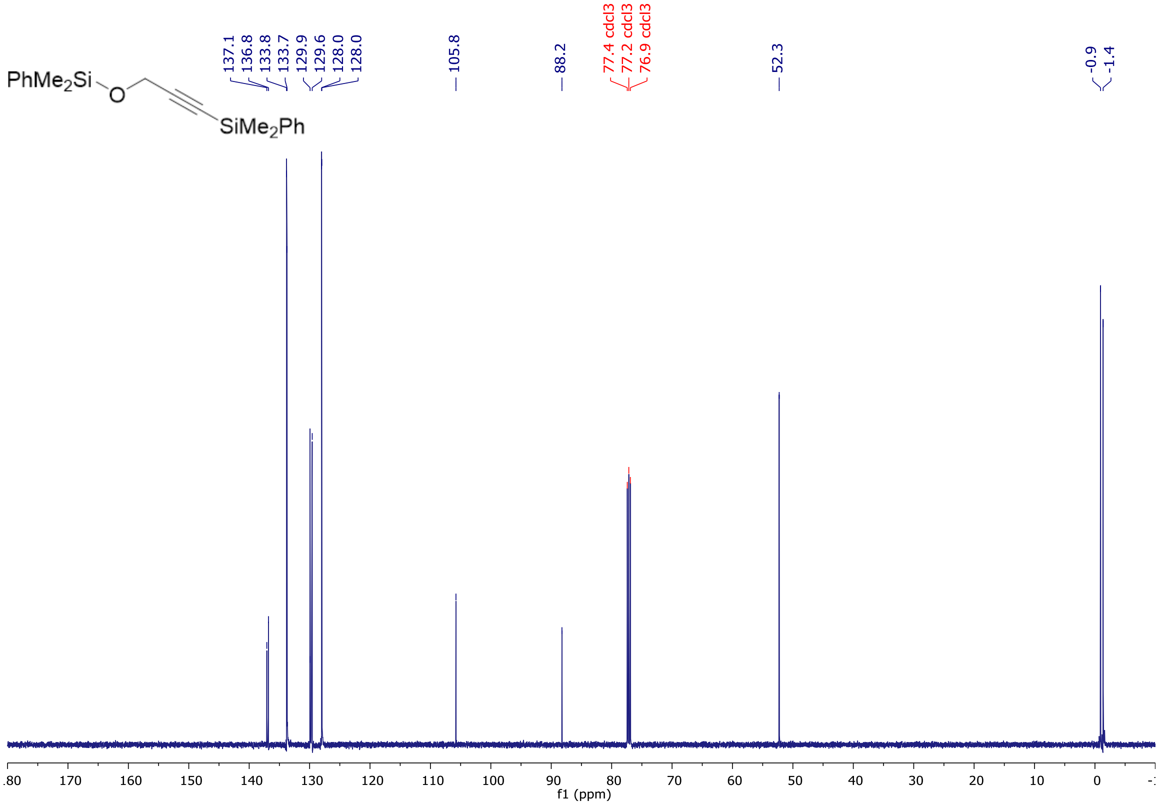
^{1}H NMR (500 MHz, THF-d_8) of compound **4w.**



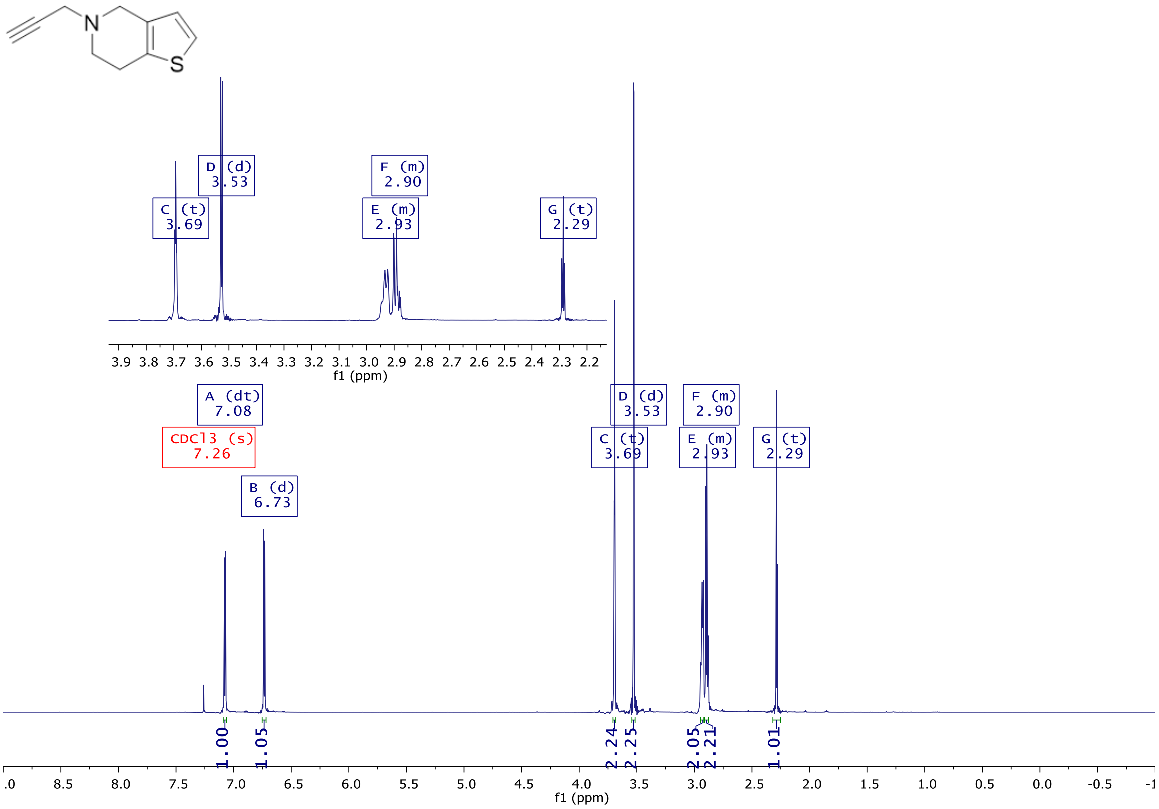
^{13}C NMR (126 MHz, THF-d_8) of compound **4w.**



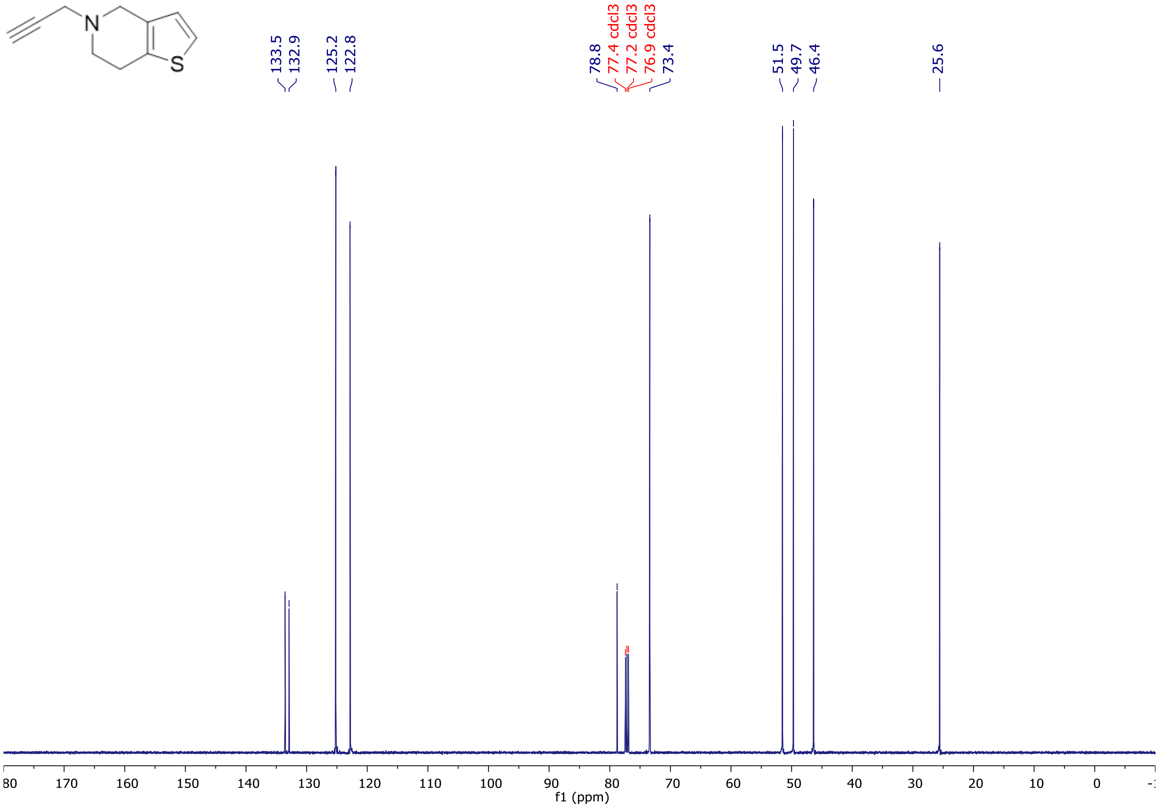
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4x.**



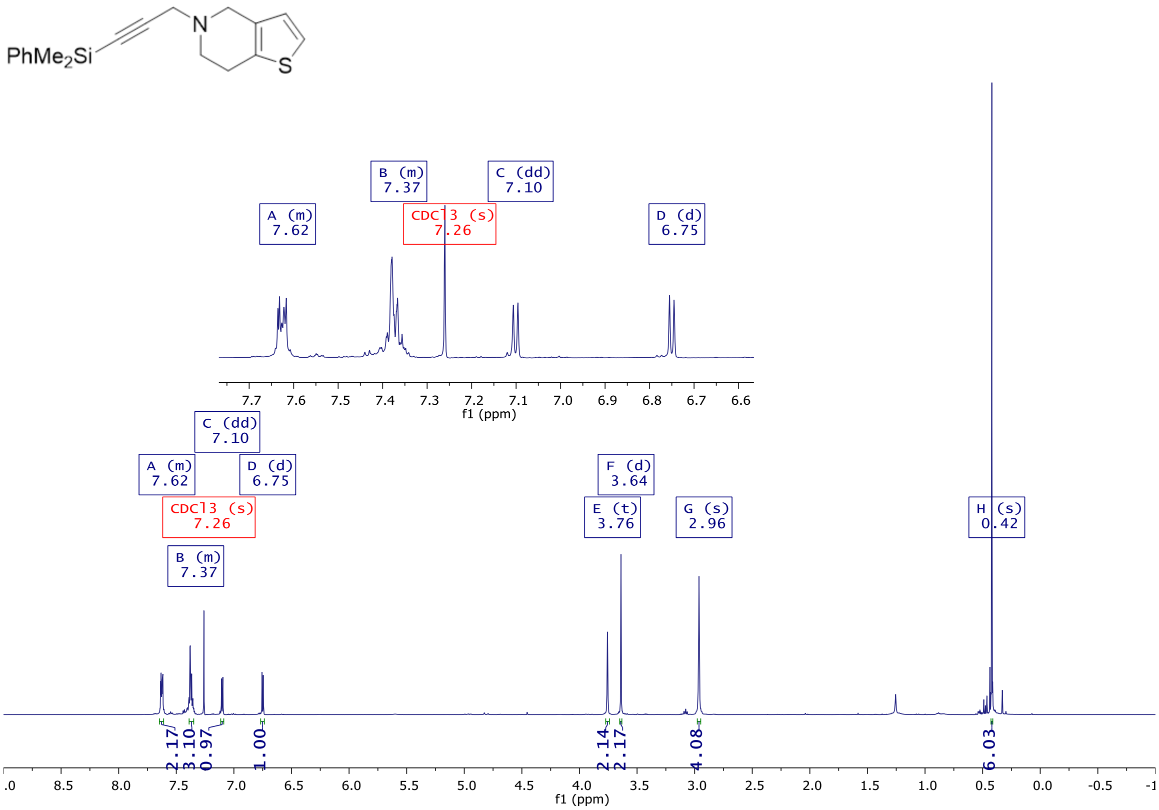
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4x.**



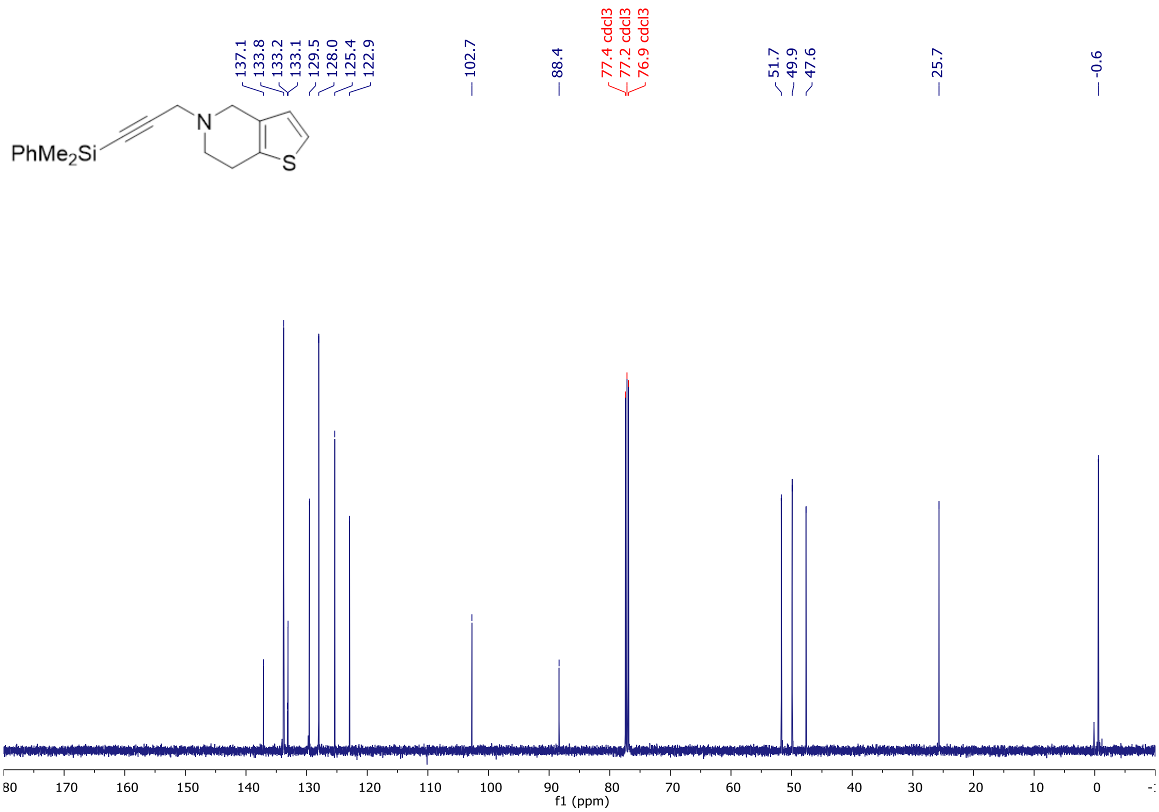
^{1}H NMR (500 MHz, CDCl$_3$) of compound **3y.**



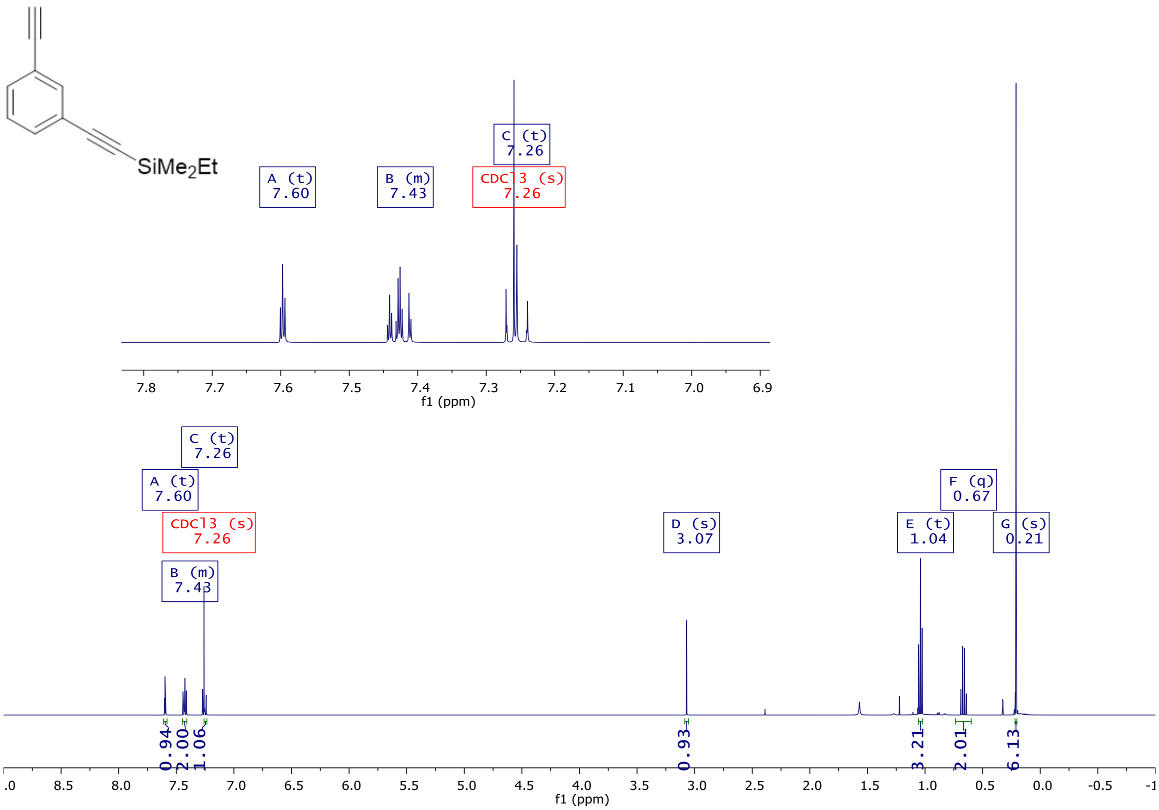
^{13}C NMR (126 MHz, CDCl$_3$) of compound **3y.**



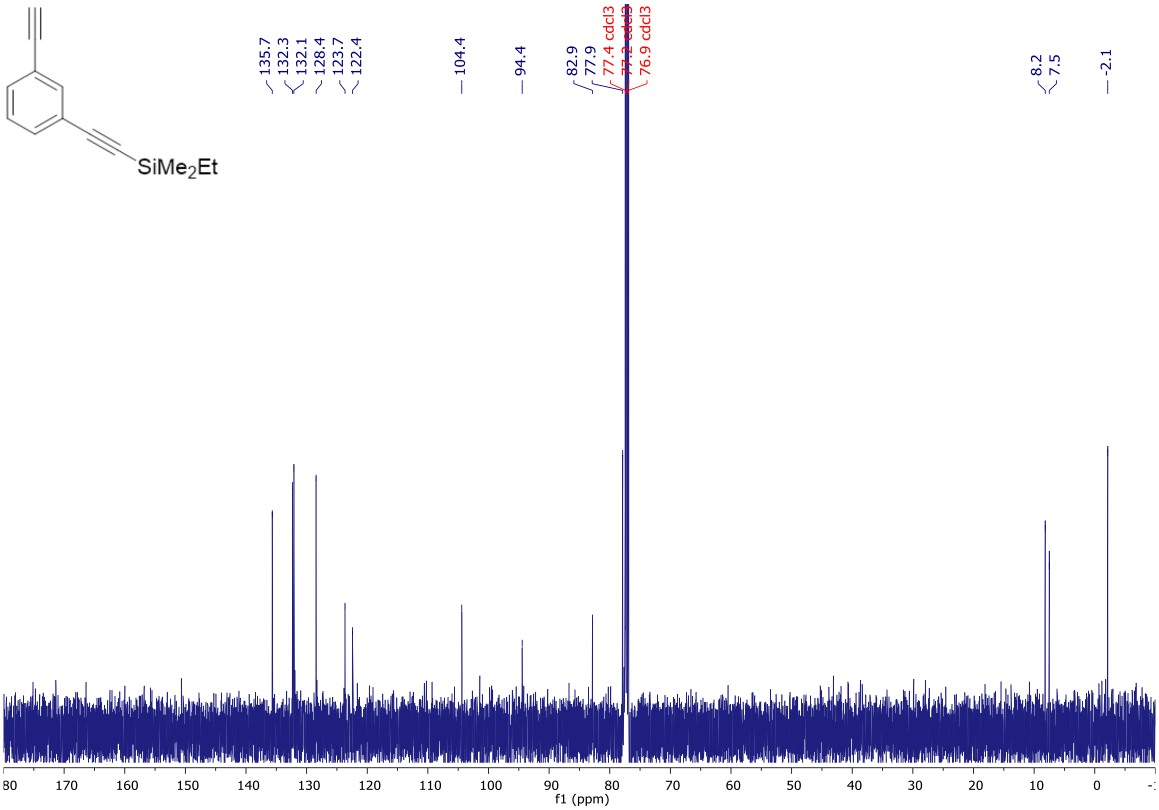
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4y.**



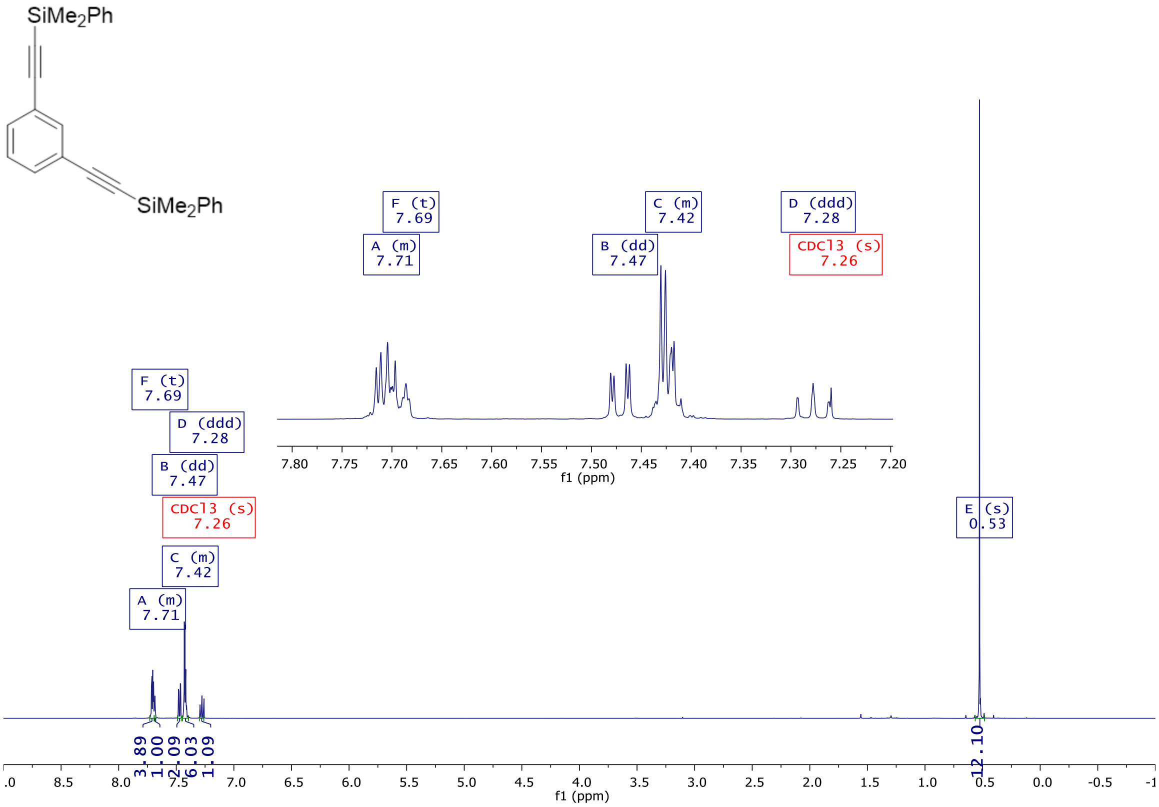
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4y.**



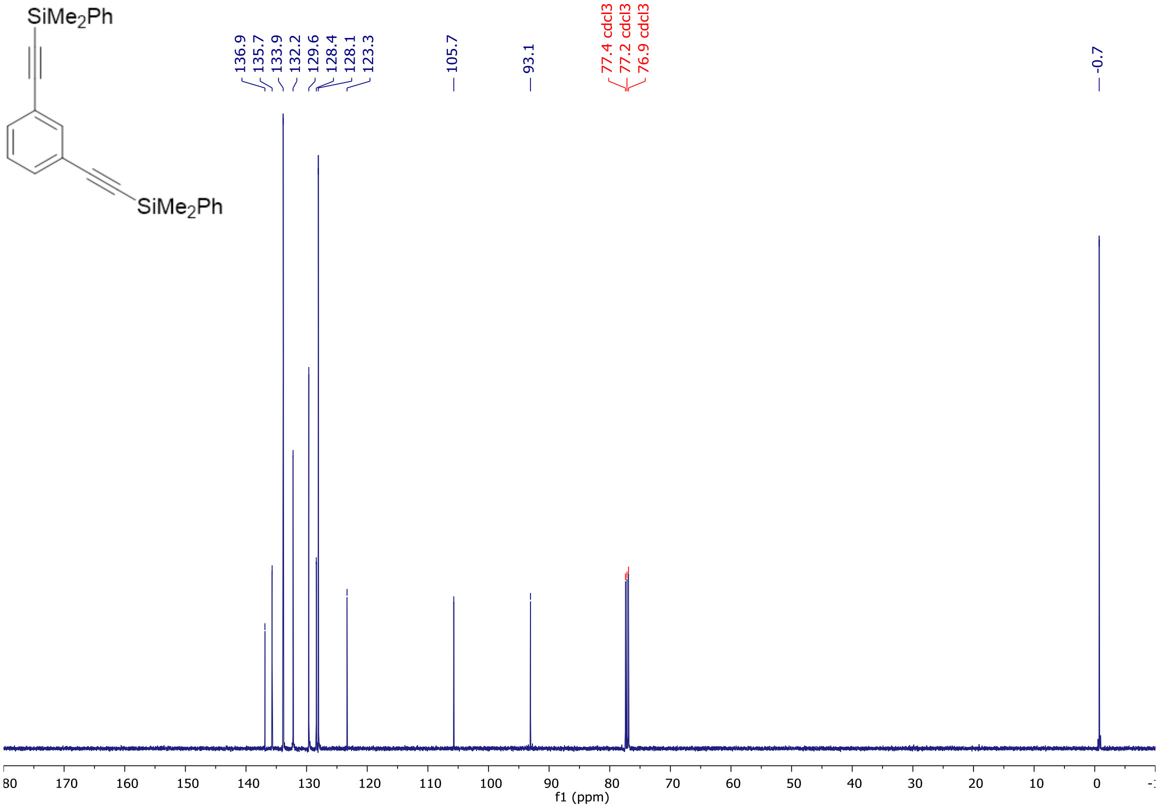
^{1}H NMR (500 MHz, CDCl$_3$) of compound **5a.**



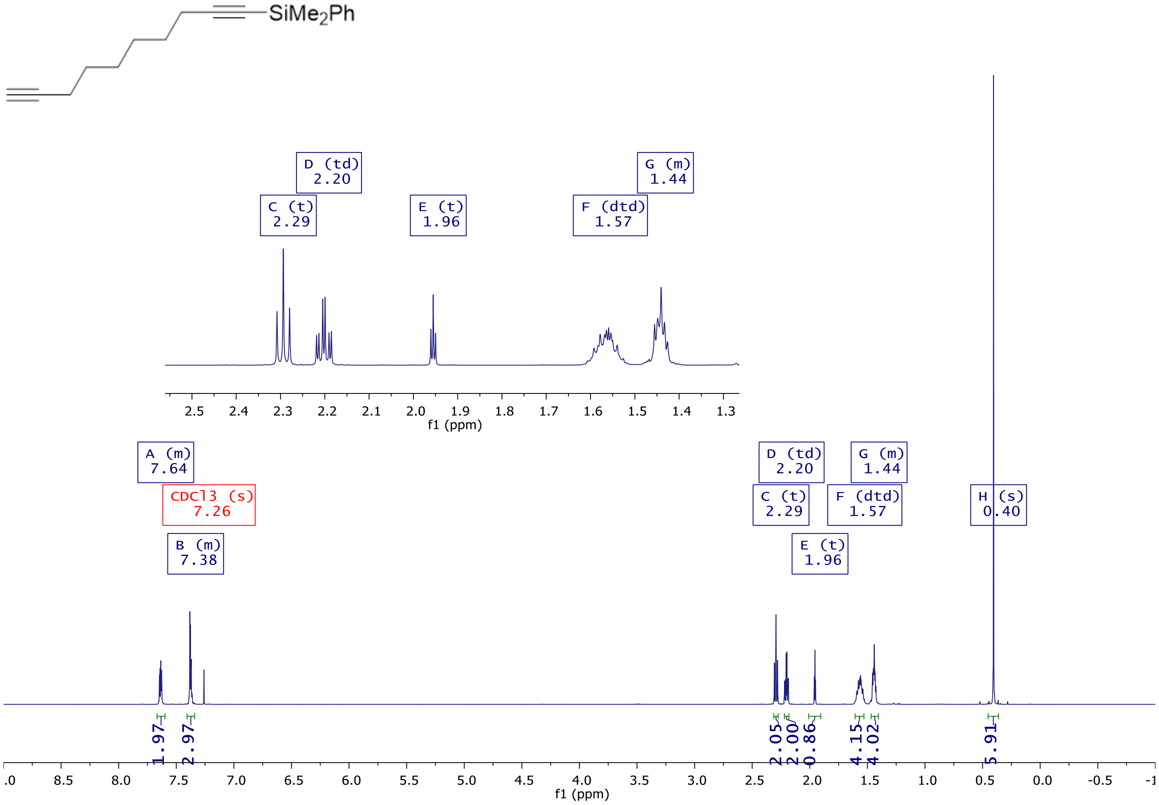
^{13}C NMR (126 MHz, CDCl$_3$) of compound **5a.**



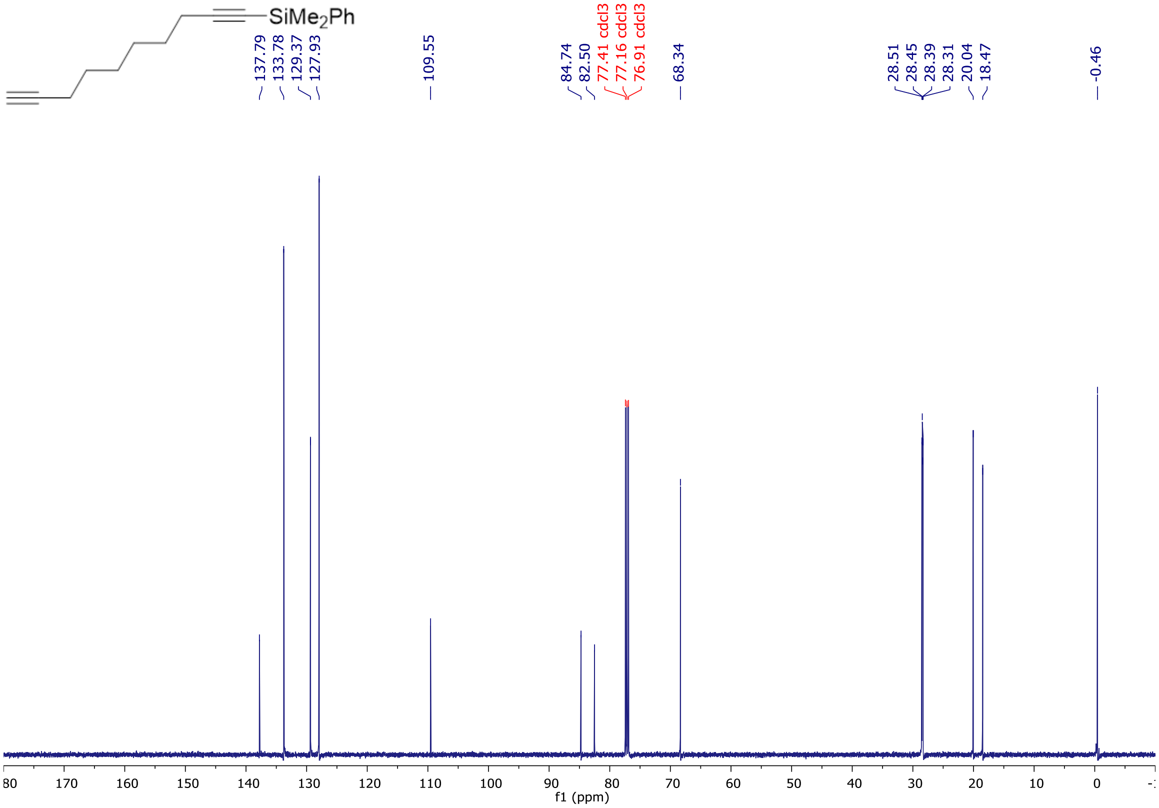
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5b.**



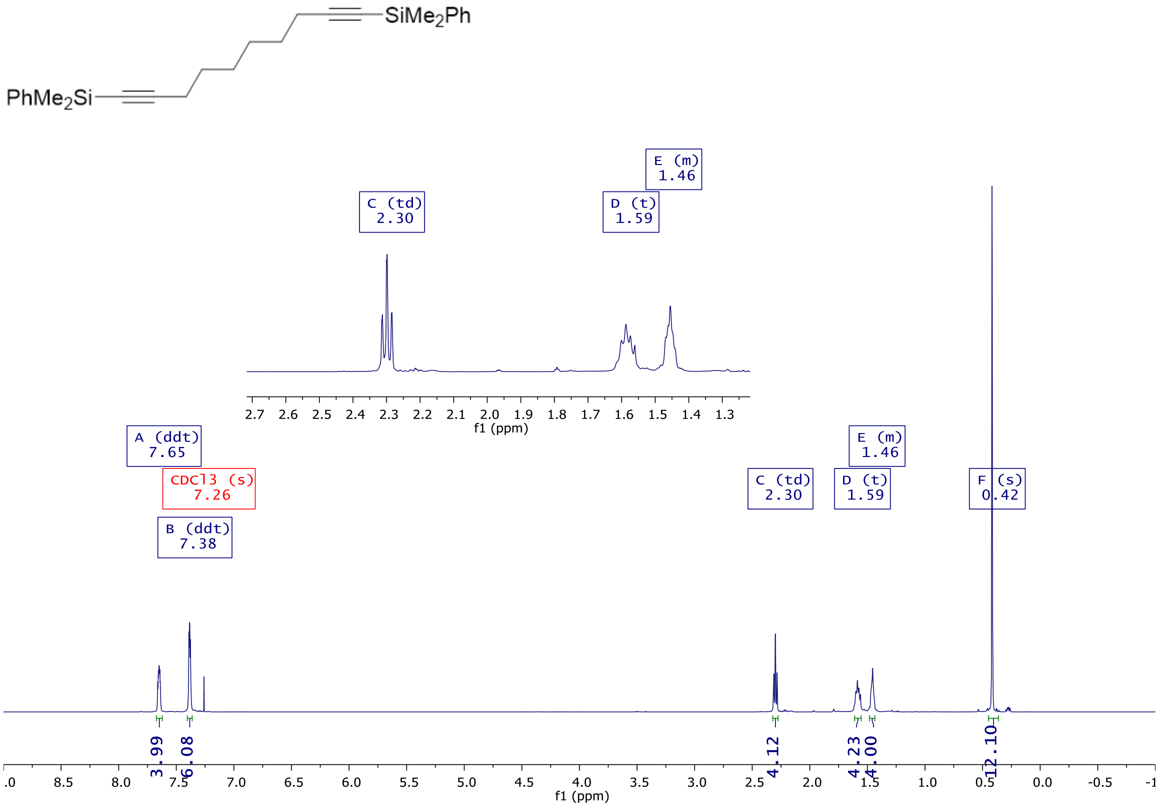
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5b.**



^{1}H NMR (500 MHz, CDCl$_3$) of compound **6a.**



^{13}C NMR (126 MHz, CDCl$_3$) of compound **6a.**



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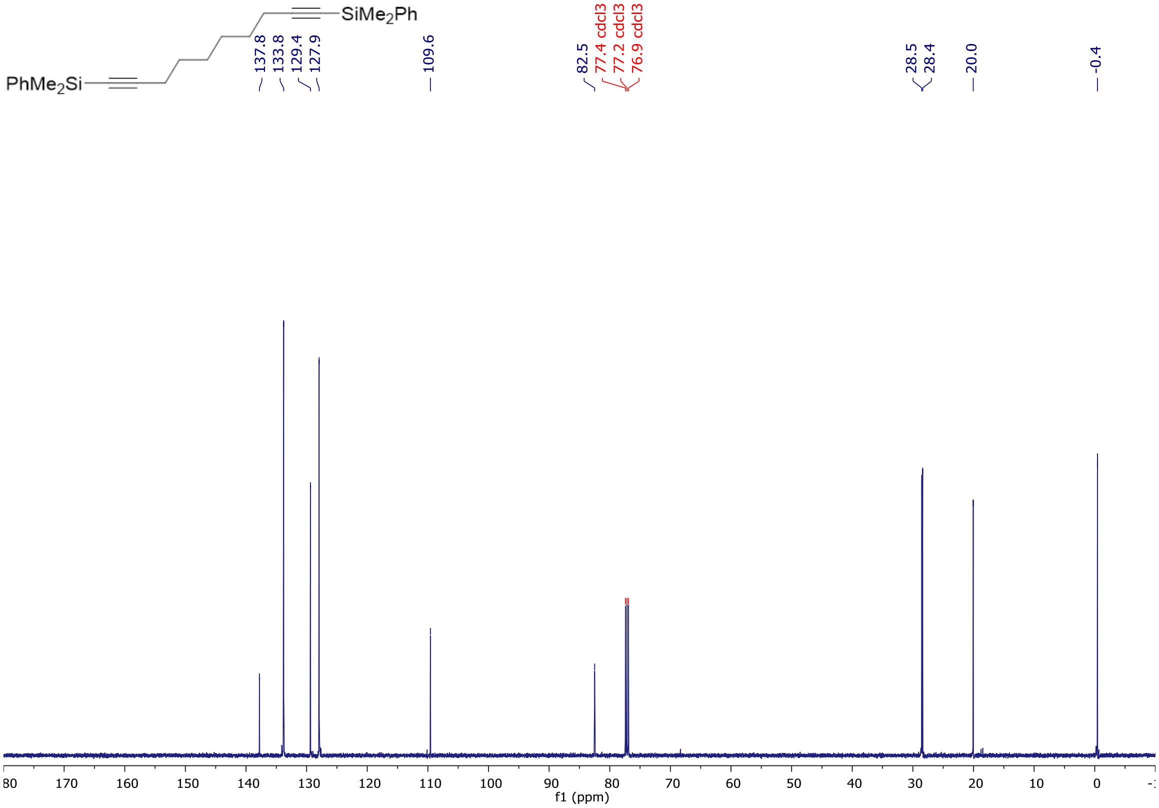

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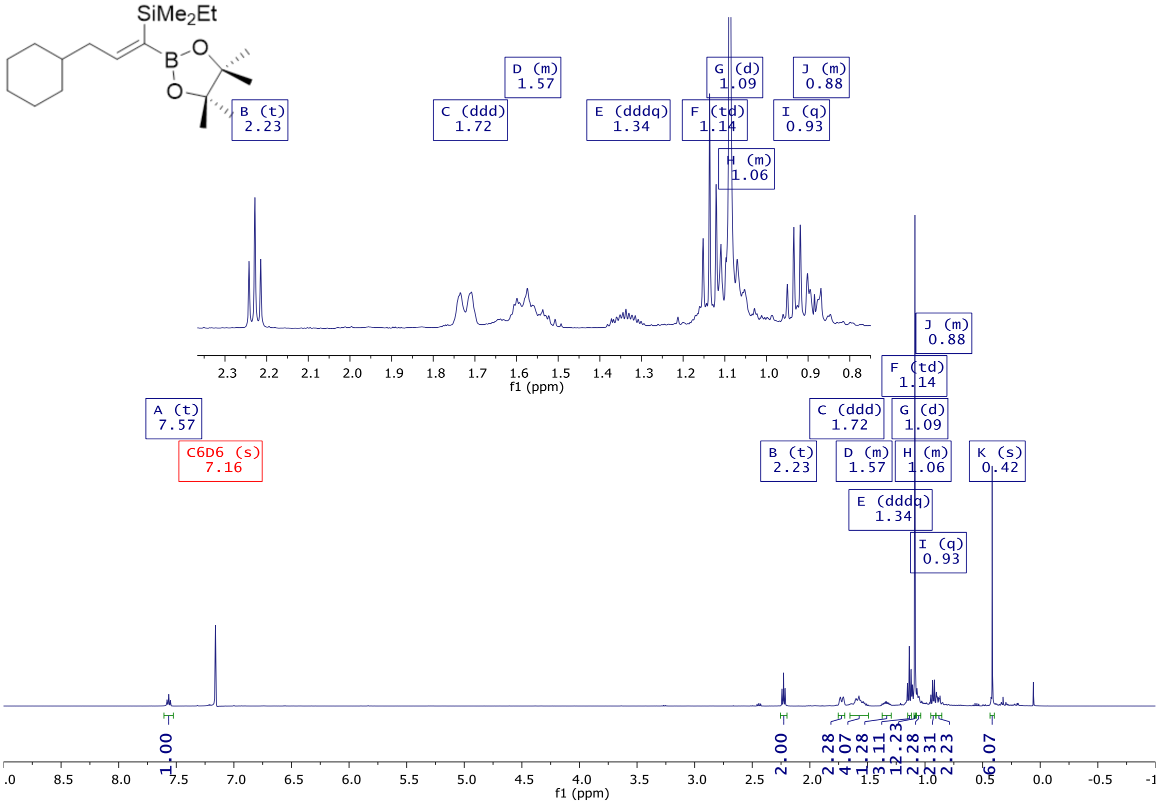
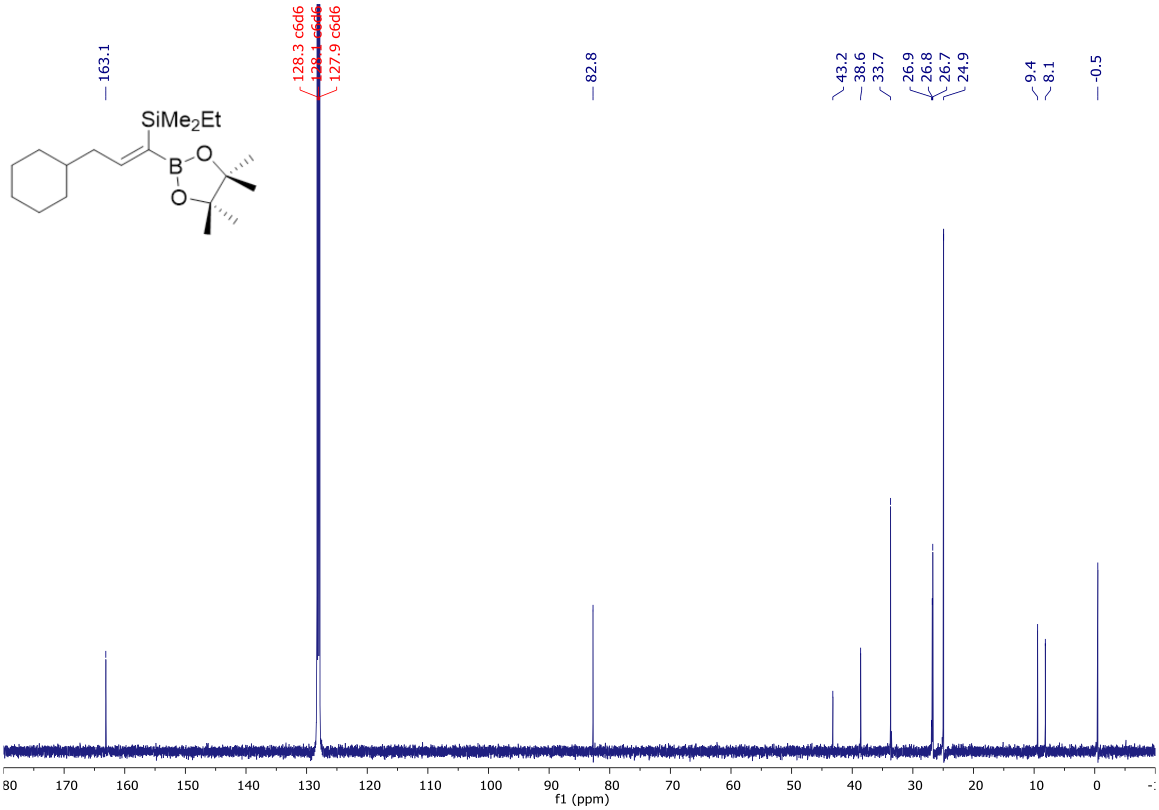
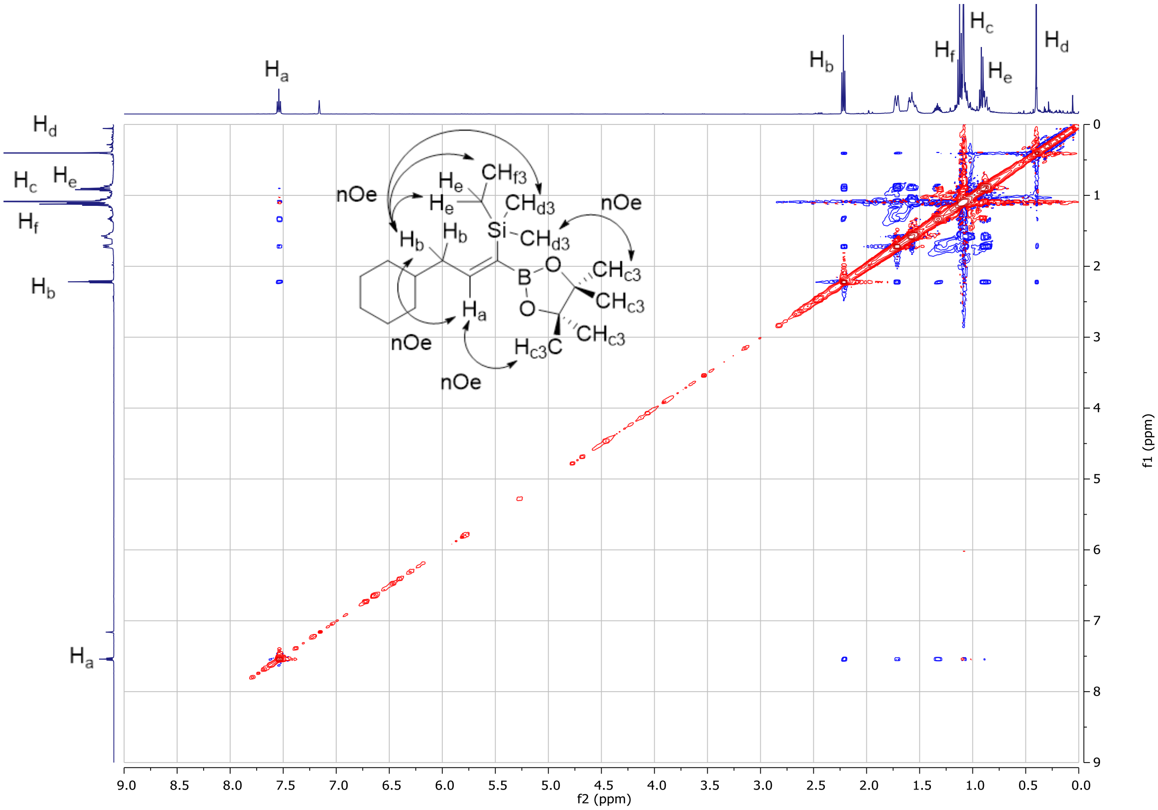


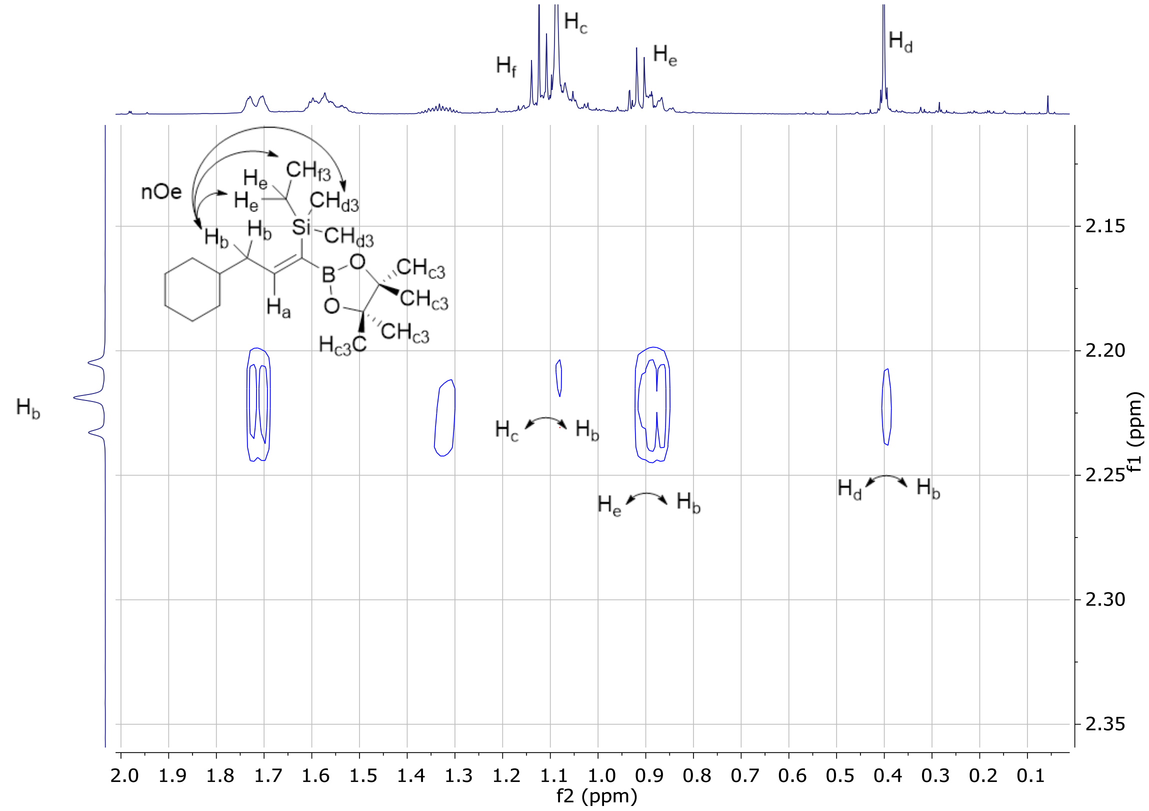
^{1}H NMR (500 MHz, C_6D_6) of compound **7a.**

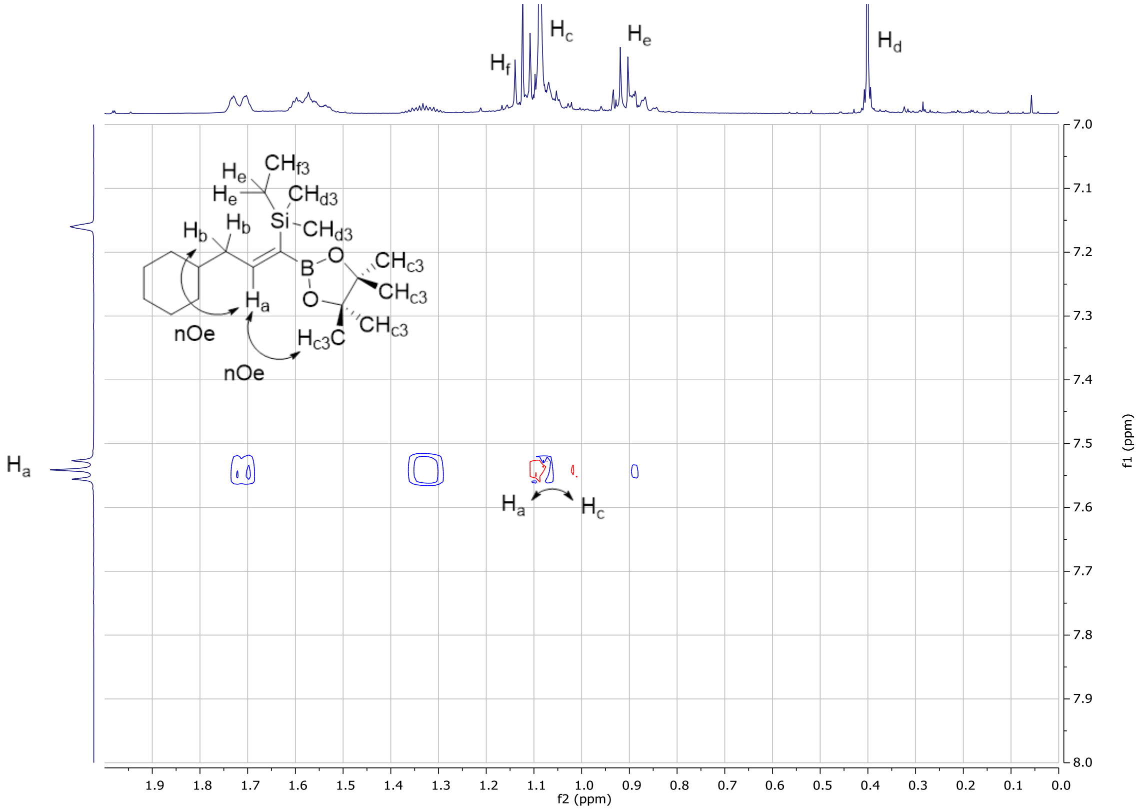


^{13}C NMR (126 MHz, C_6D_6) of compound **7a.**

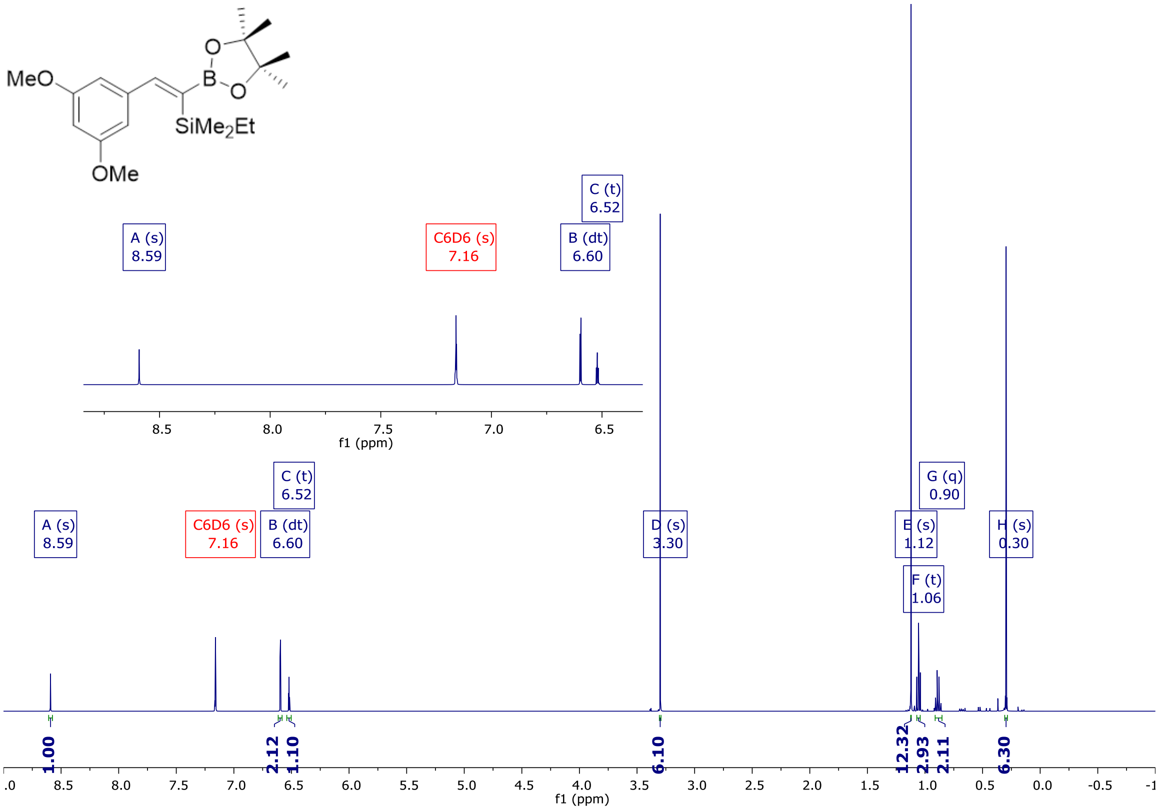


NOESY (500 MHz, C_6D_6) of compound **7a.**





NOESY (500 MHz, C_6D_6) of compound **7a.**



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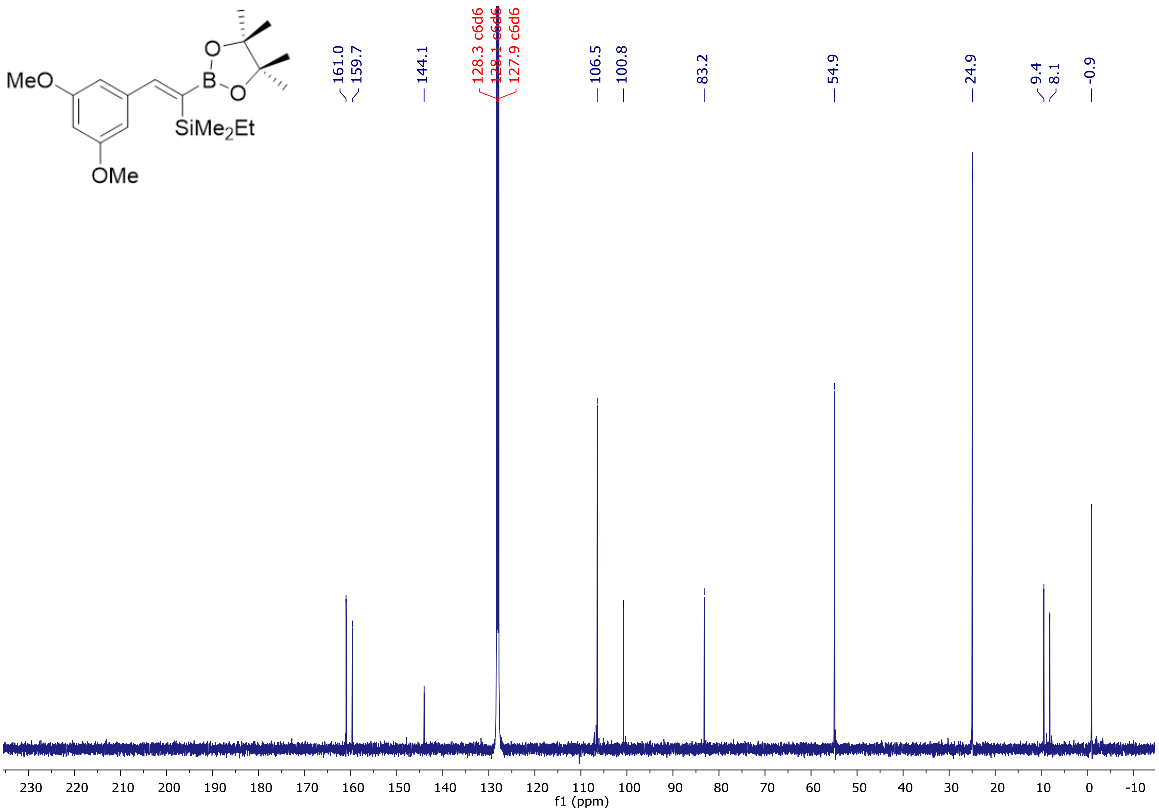
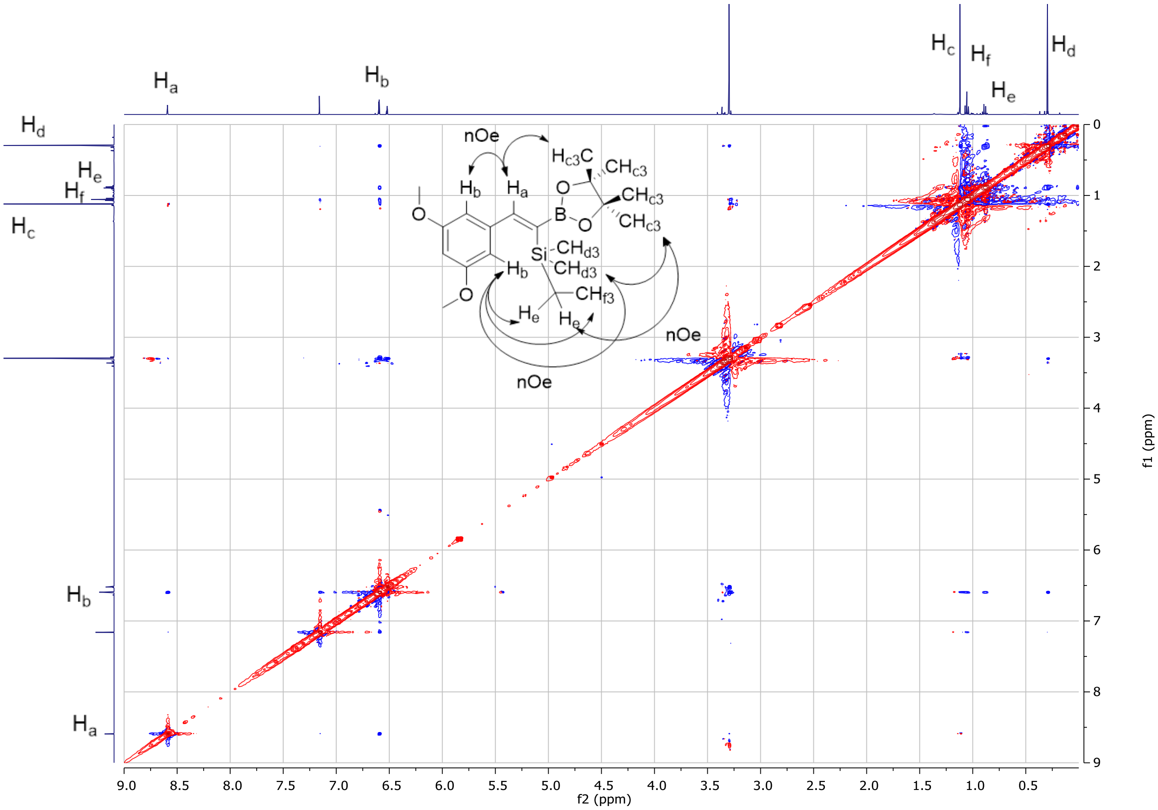
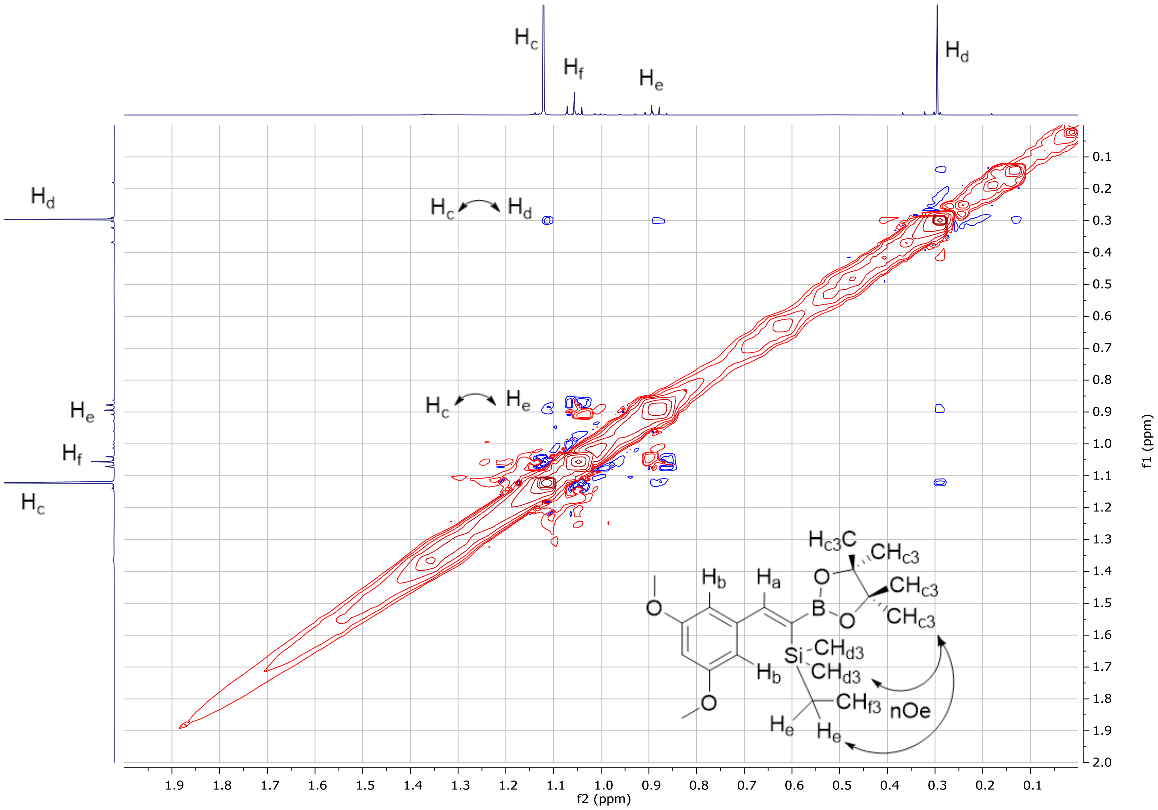
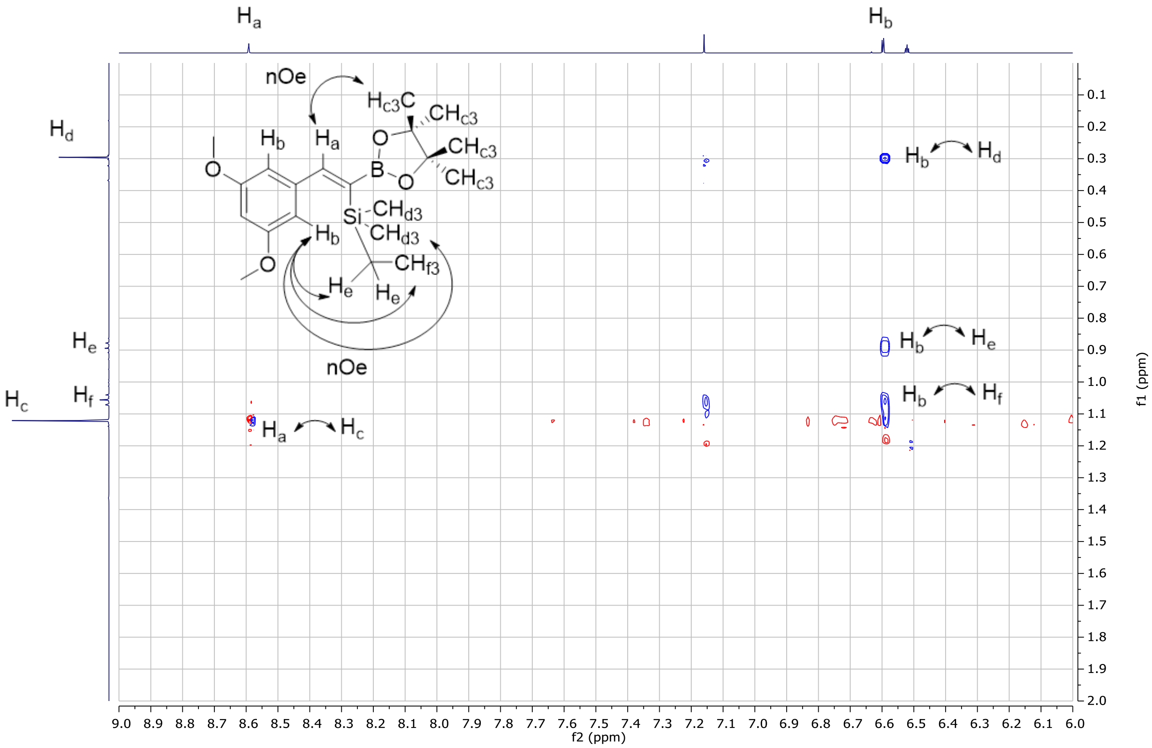


^{13}C NMR (126 MHz, C_6D_6) of compound **7b.**

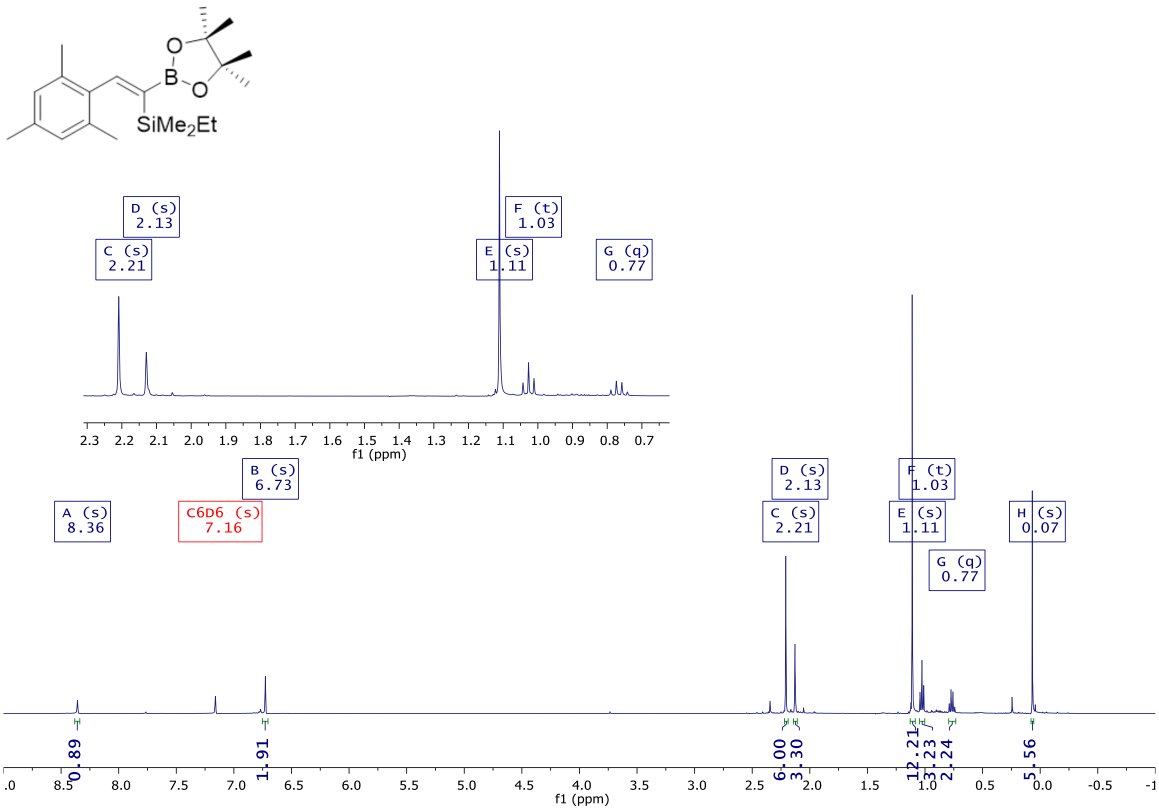


NOESY (500 MHz, C_6D_6) of compound **7b.**

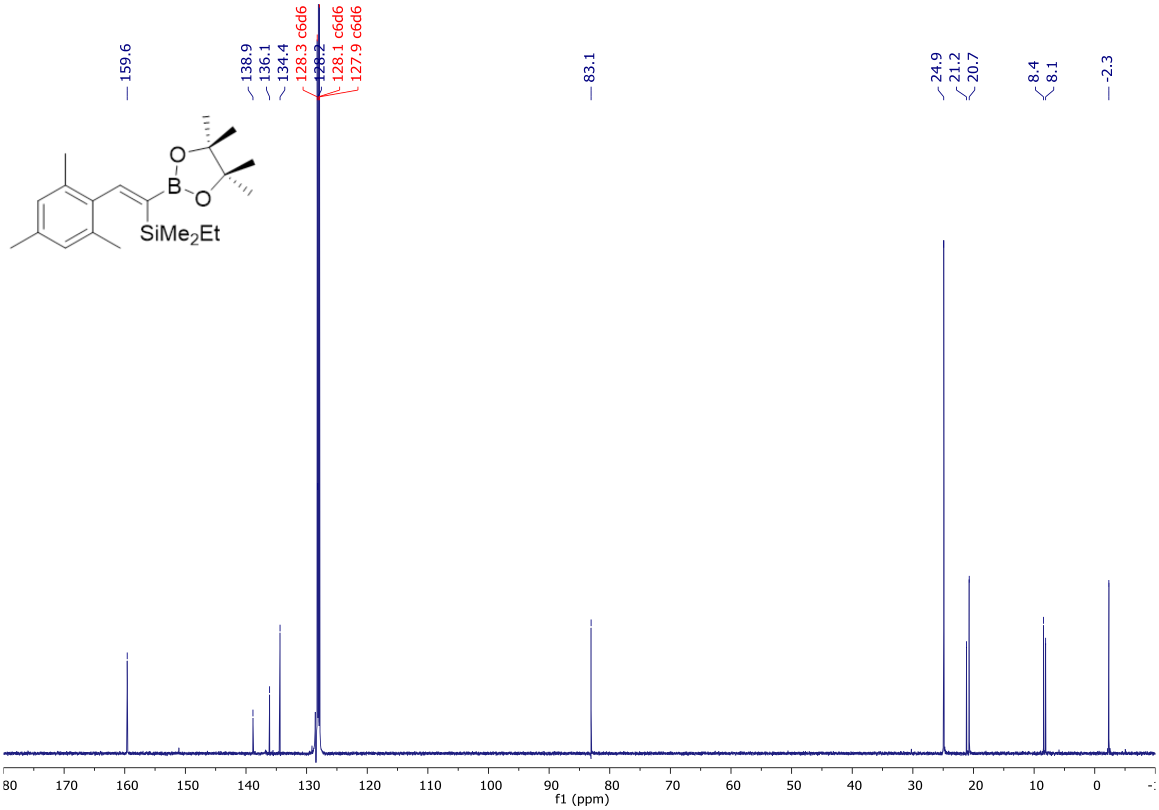




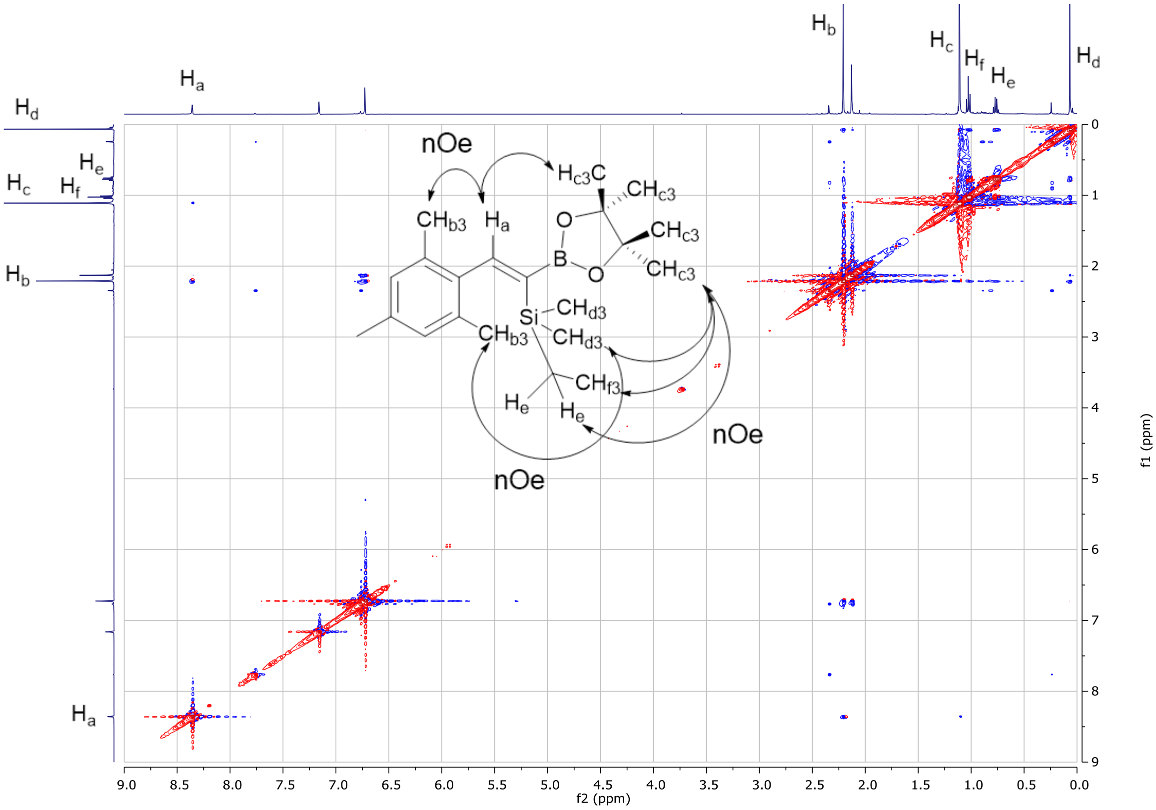
NOESY (500 MHz, C_6D_6) of compound **7b.**



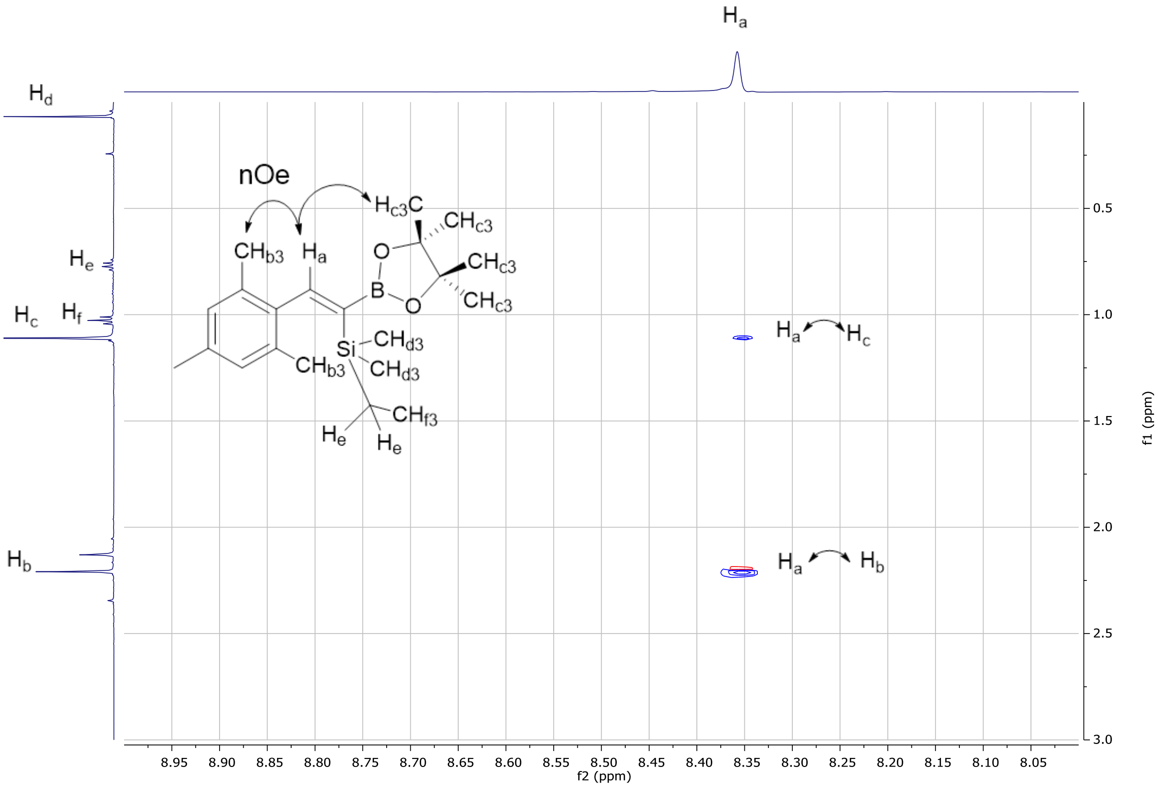
^{1}H NMR (500 MHz, C_6D_6) of compound **7c.**

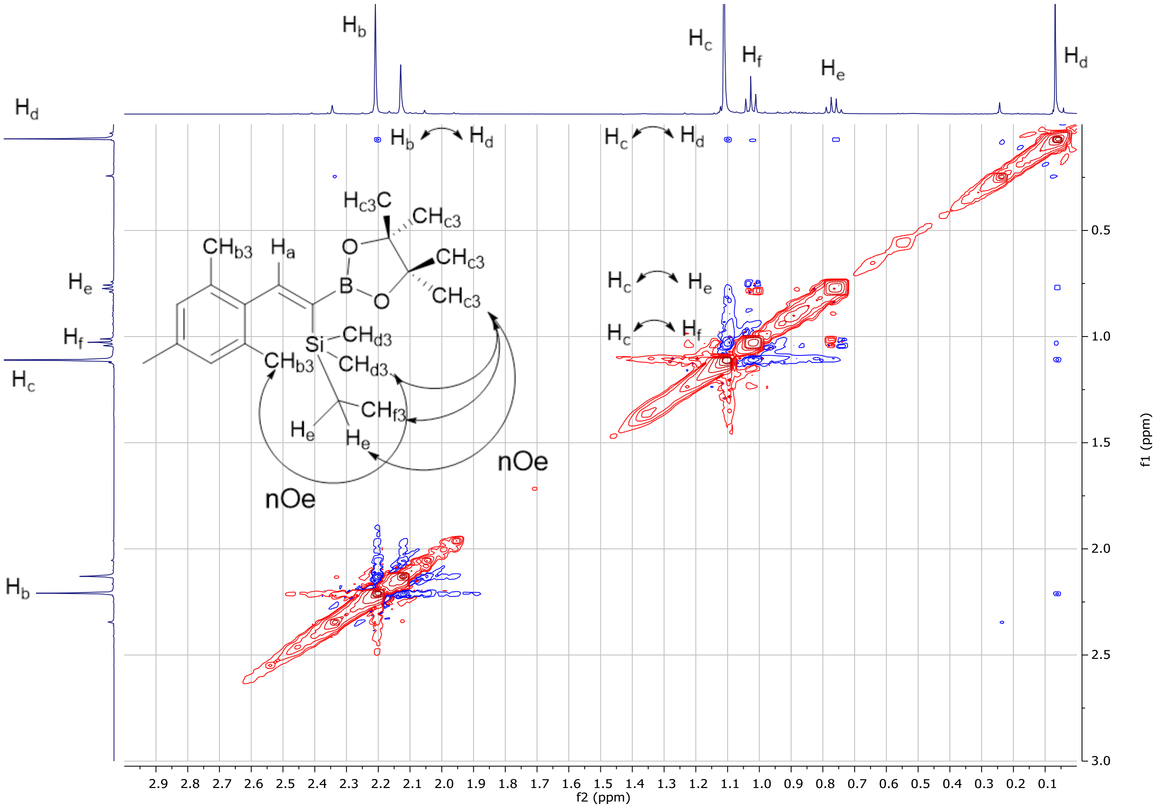


^{13}C NMR (126 MHz, C_6D_6) of compound **7c.**

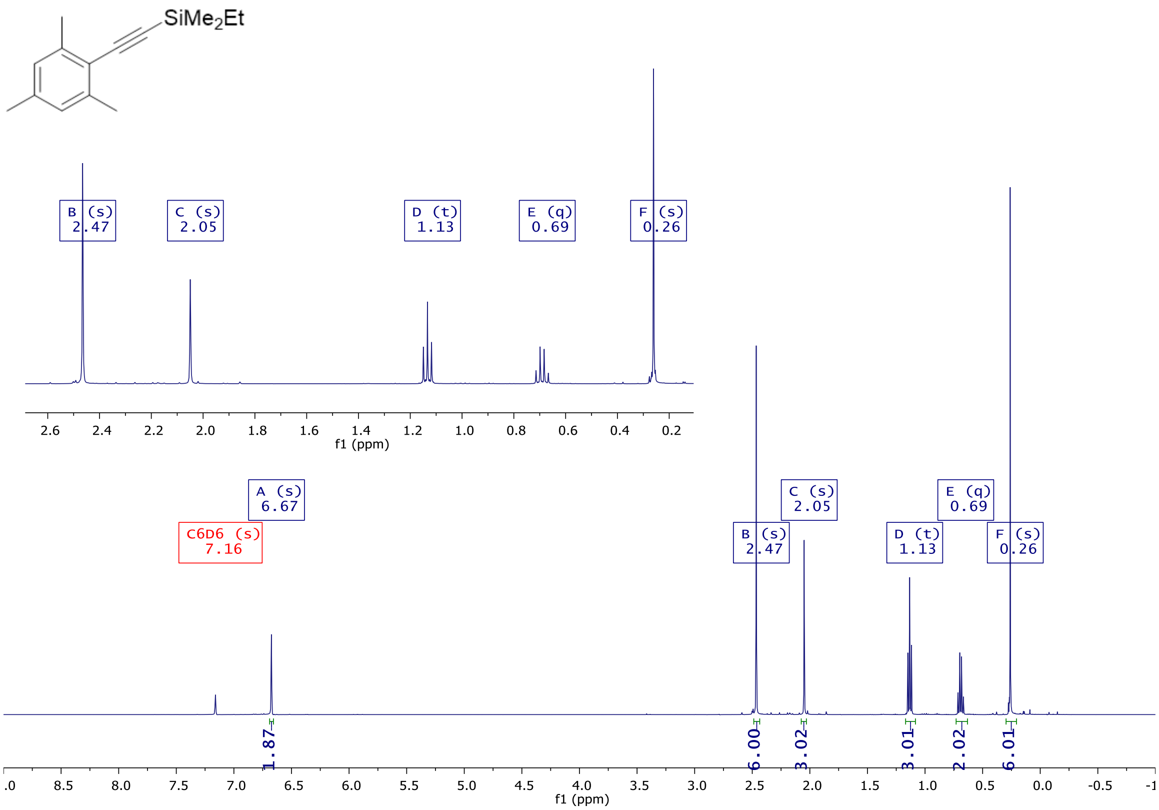


NOESY (500 MHz, C_6D_6) of compound **7c.**

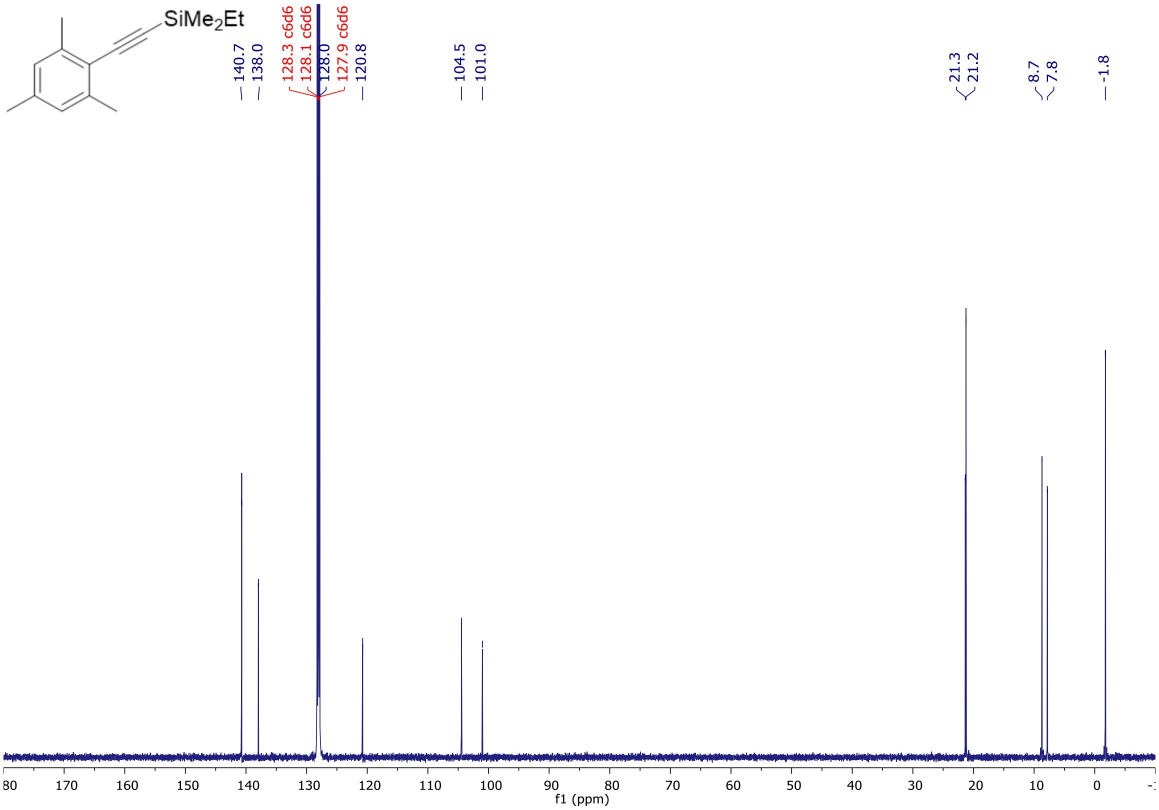




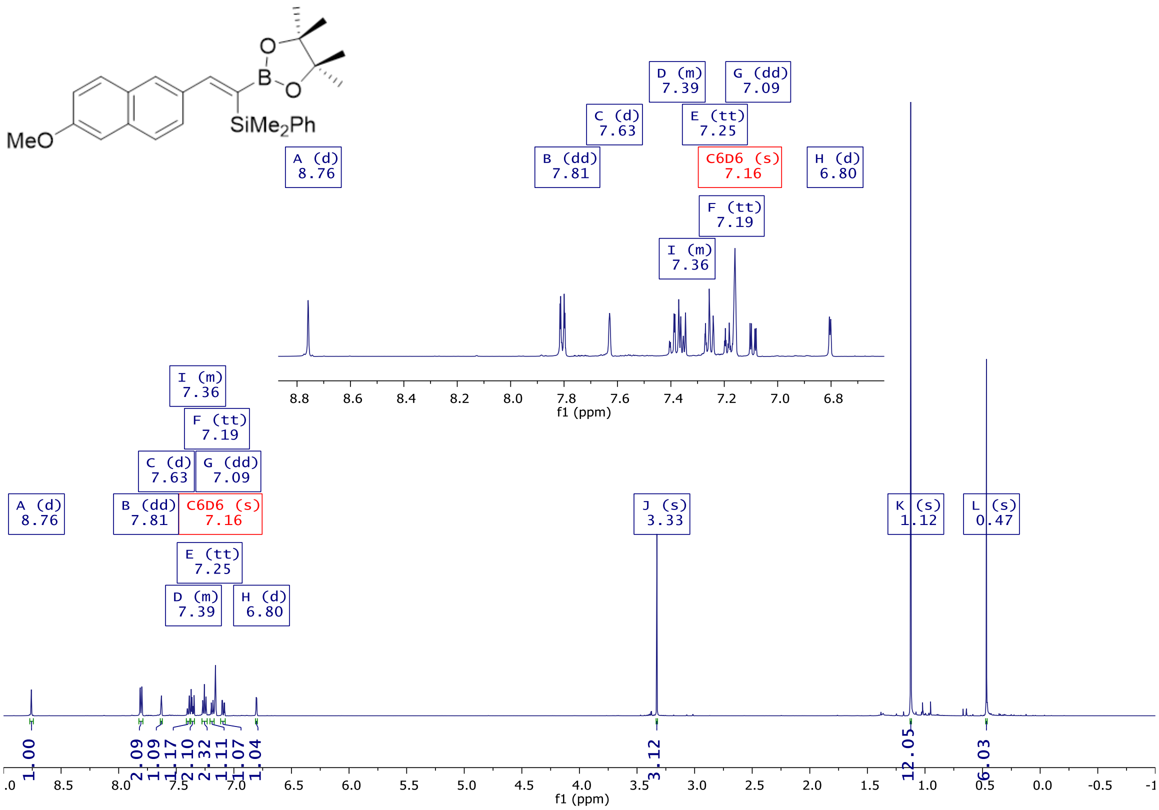
NOESY (500 MHz, C_6D_6) of compound **7c.**



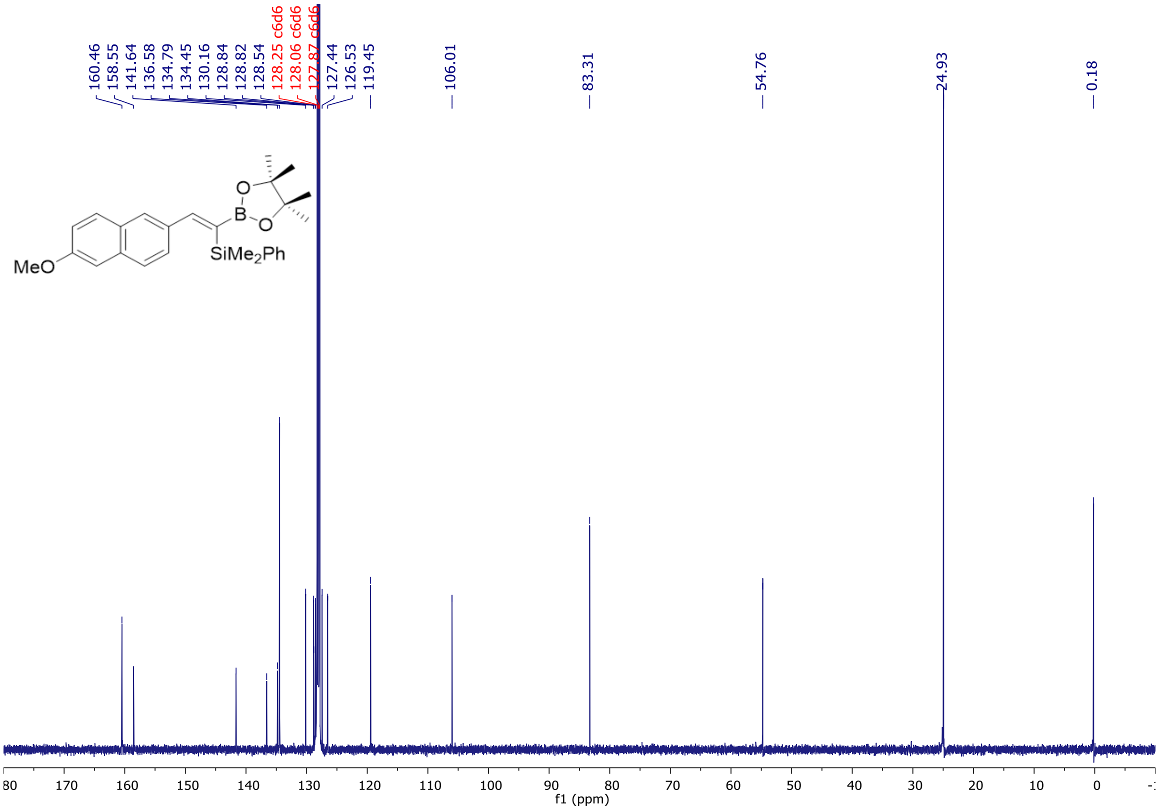
^{1}H NMR (500 MHz, C$_6$D$_6$) of compound **7c-SI.**



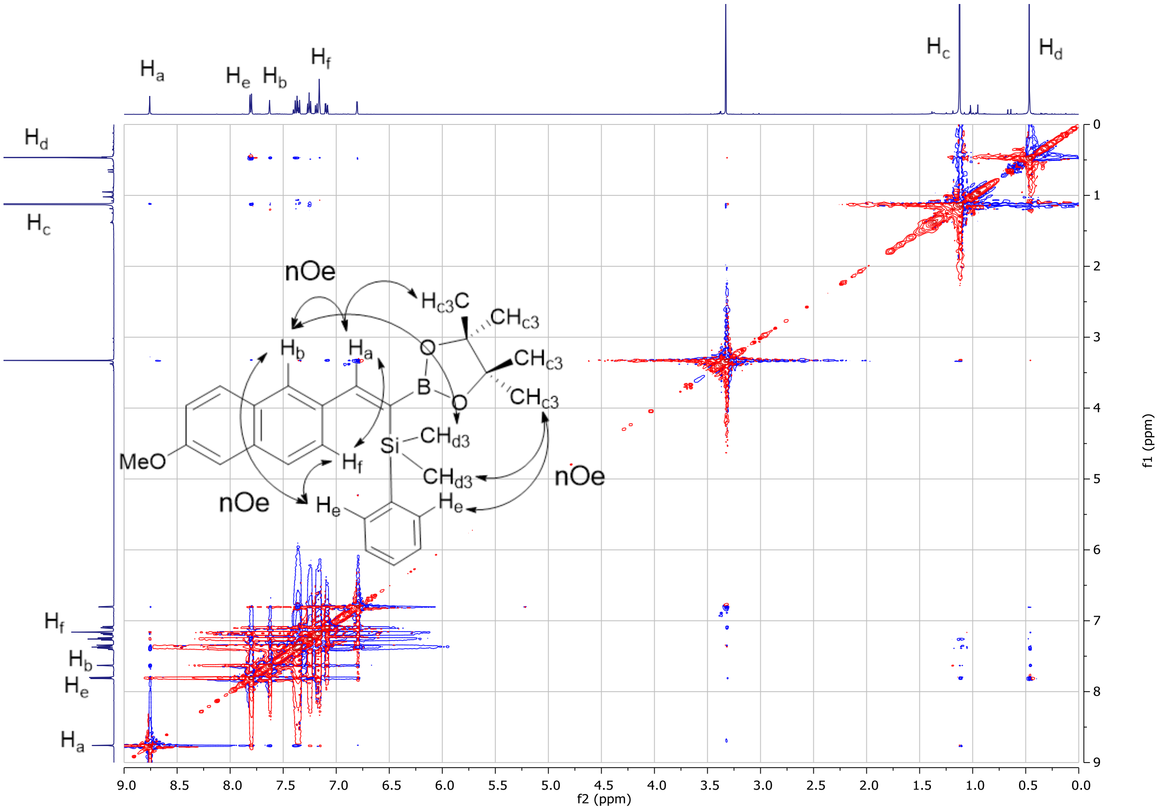
^{13}C NMR (126 MHz, C$_6$D$_6$) of compound **7c-SI.**



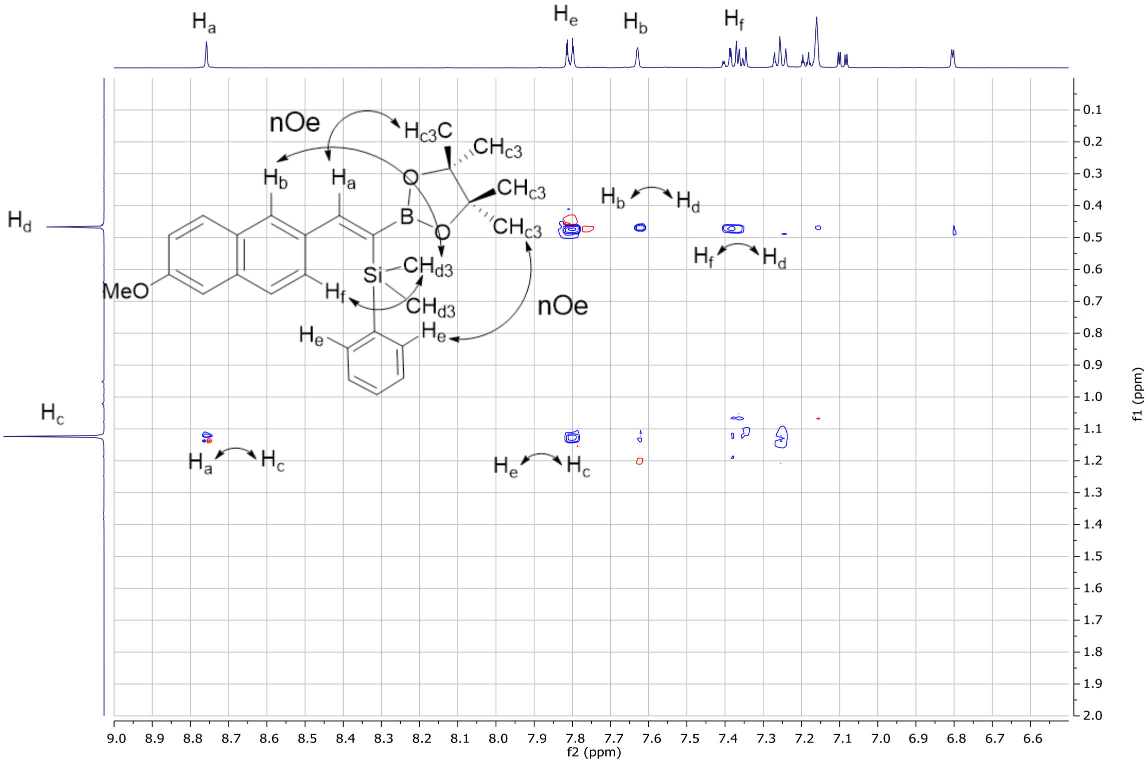
^{1}H NMR (500 MHz, C_6D_6) of compound **7d.**

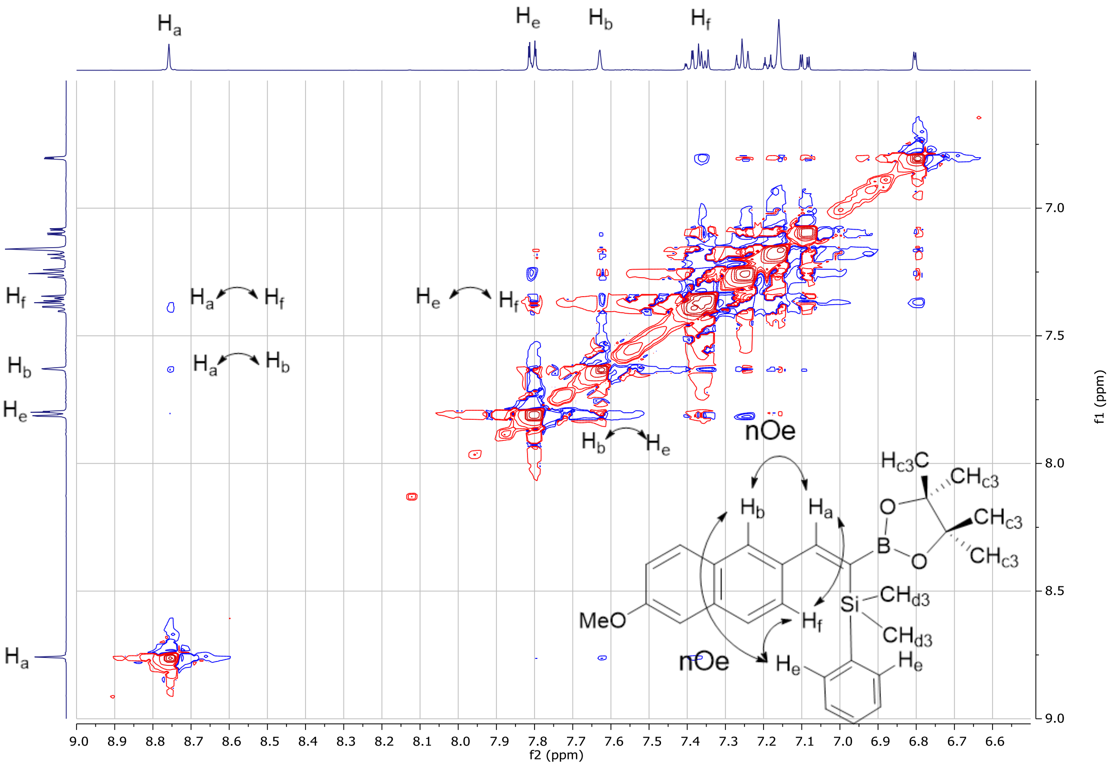


^{13}C NMR (126 MHz, C_6D_6) of compound **7d.**

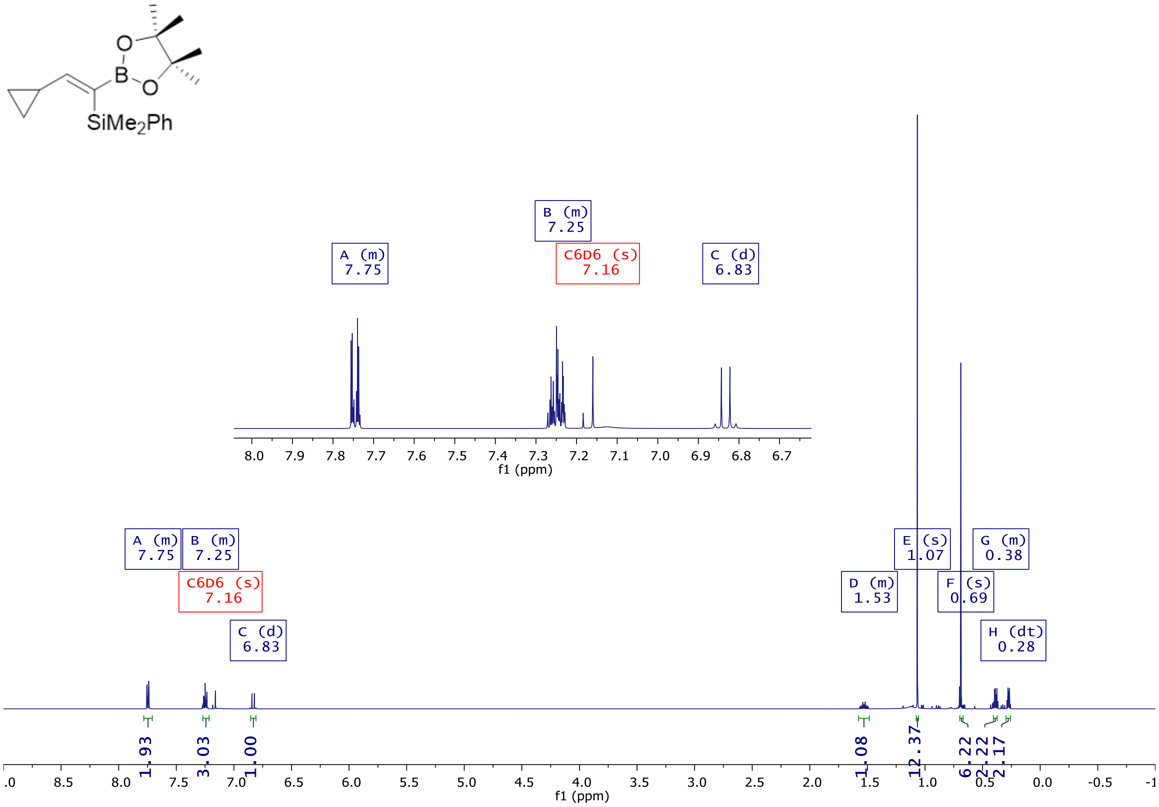


NOESY (500 MHz, C_6D_6) of compound **7d.**





NOESY (500 MHz, C_6D_6) of compound **7d.**



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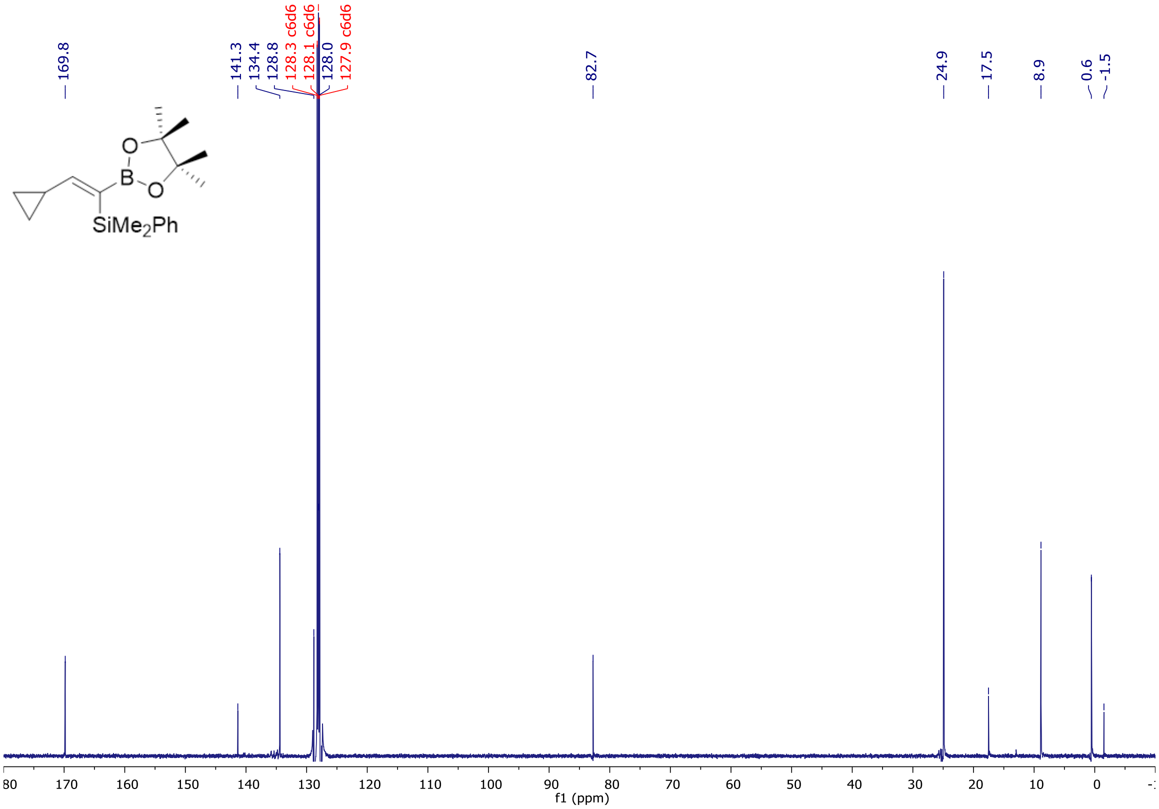
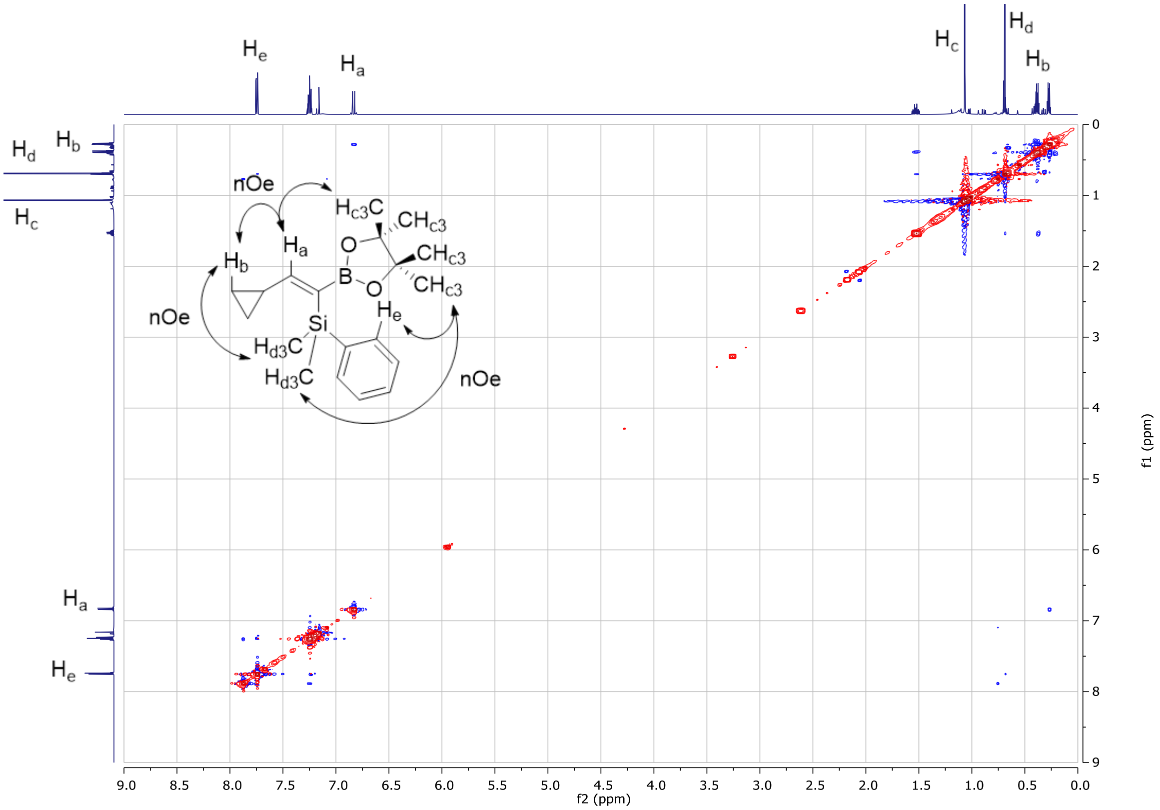
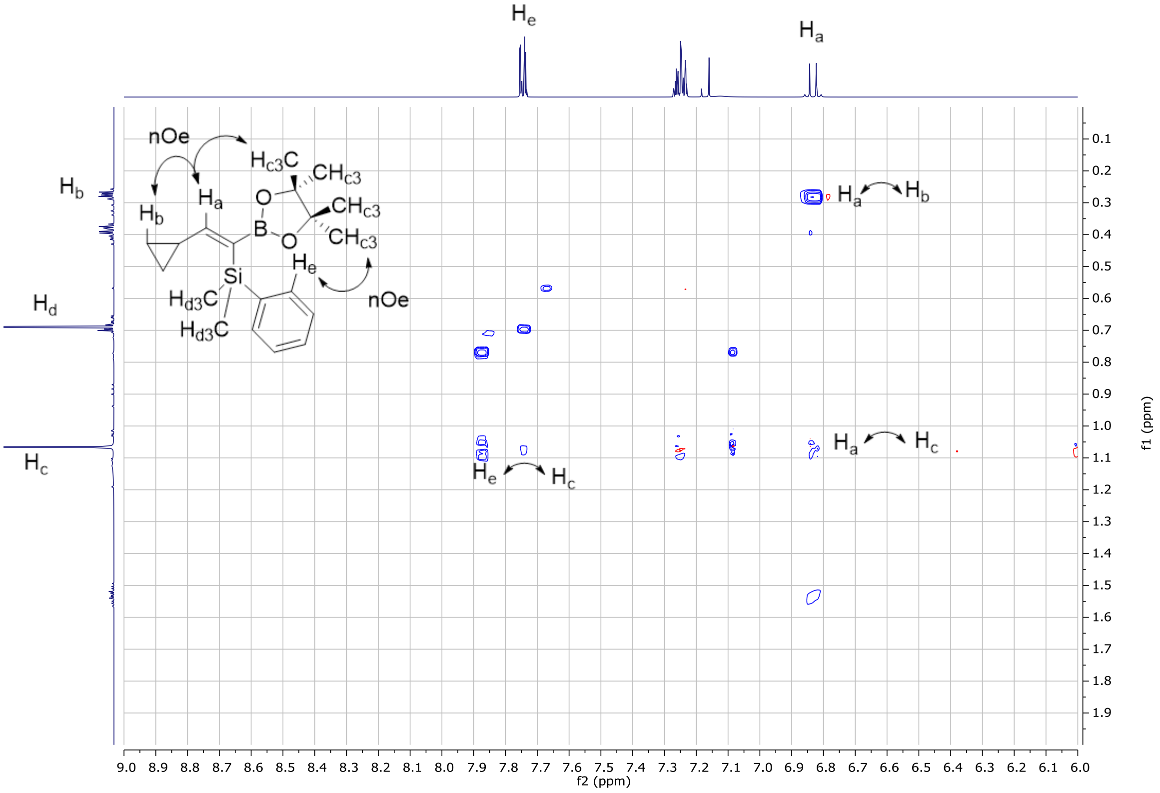
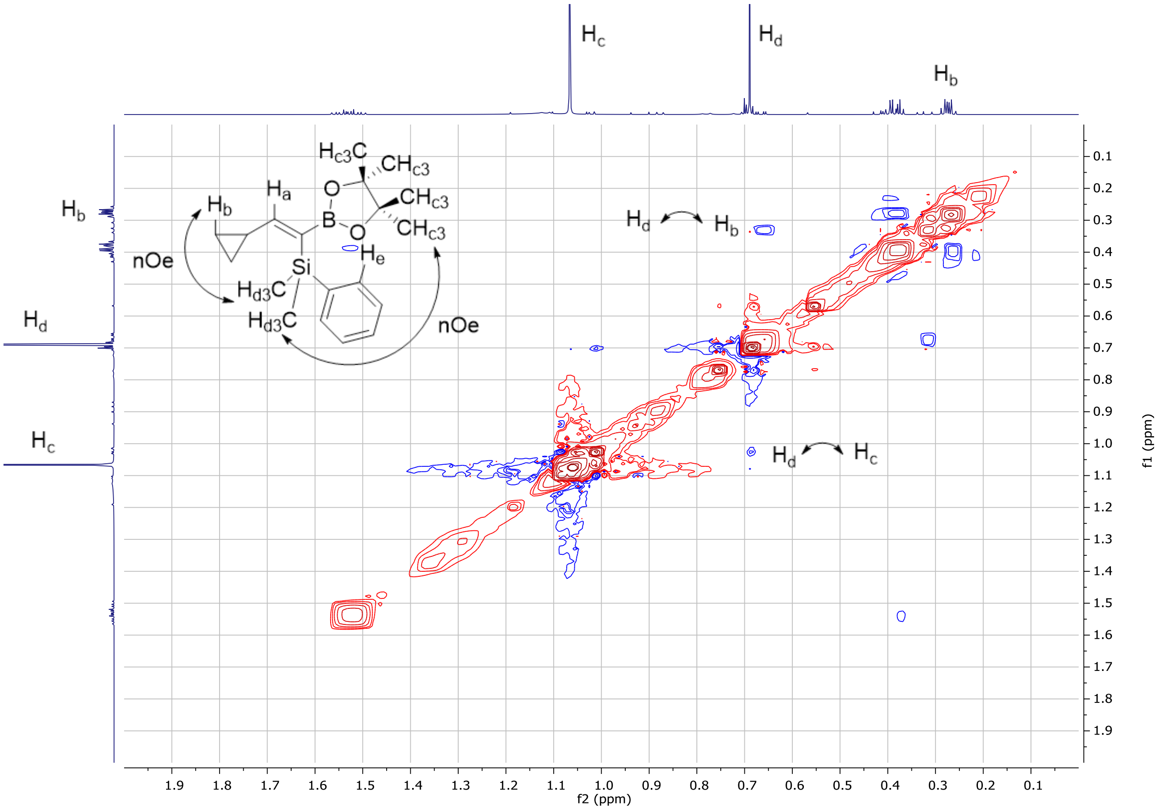


^{13}C NMR (126 MHz, C_6D_6) of compound **7e.**

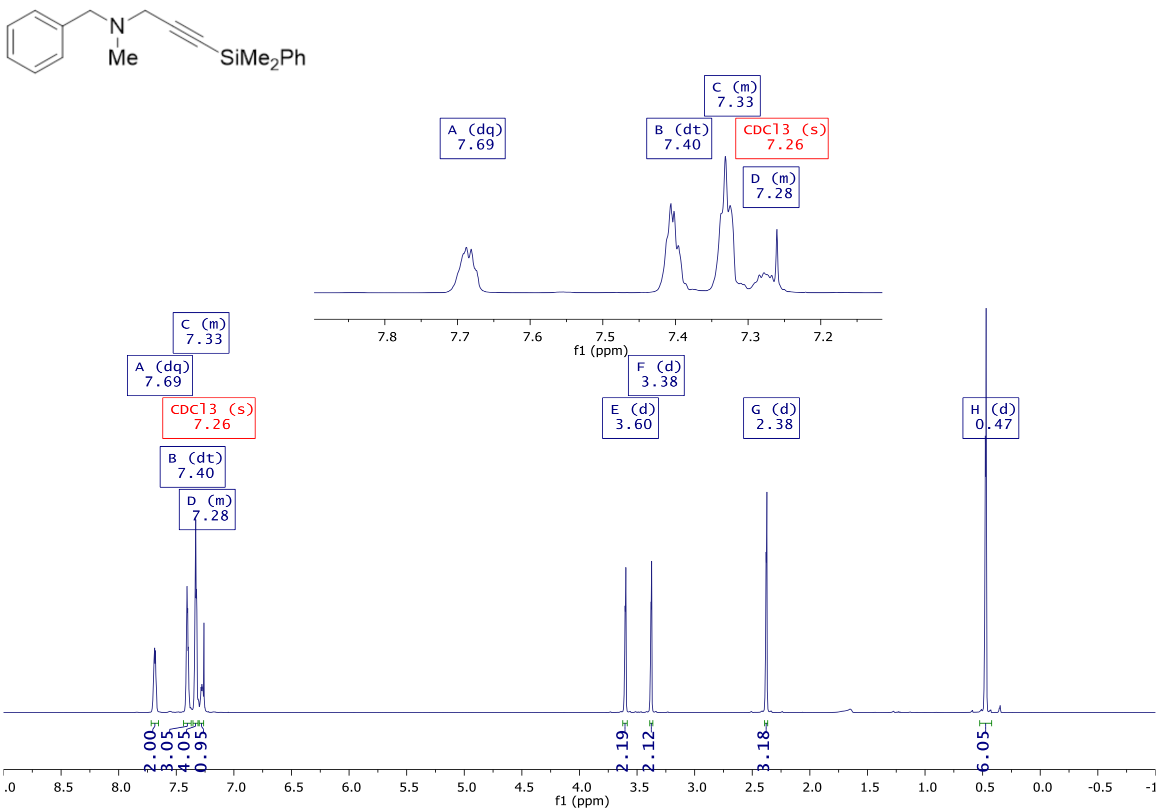


NOESY (500 MHz, C_6D_6) of compound **7e.**

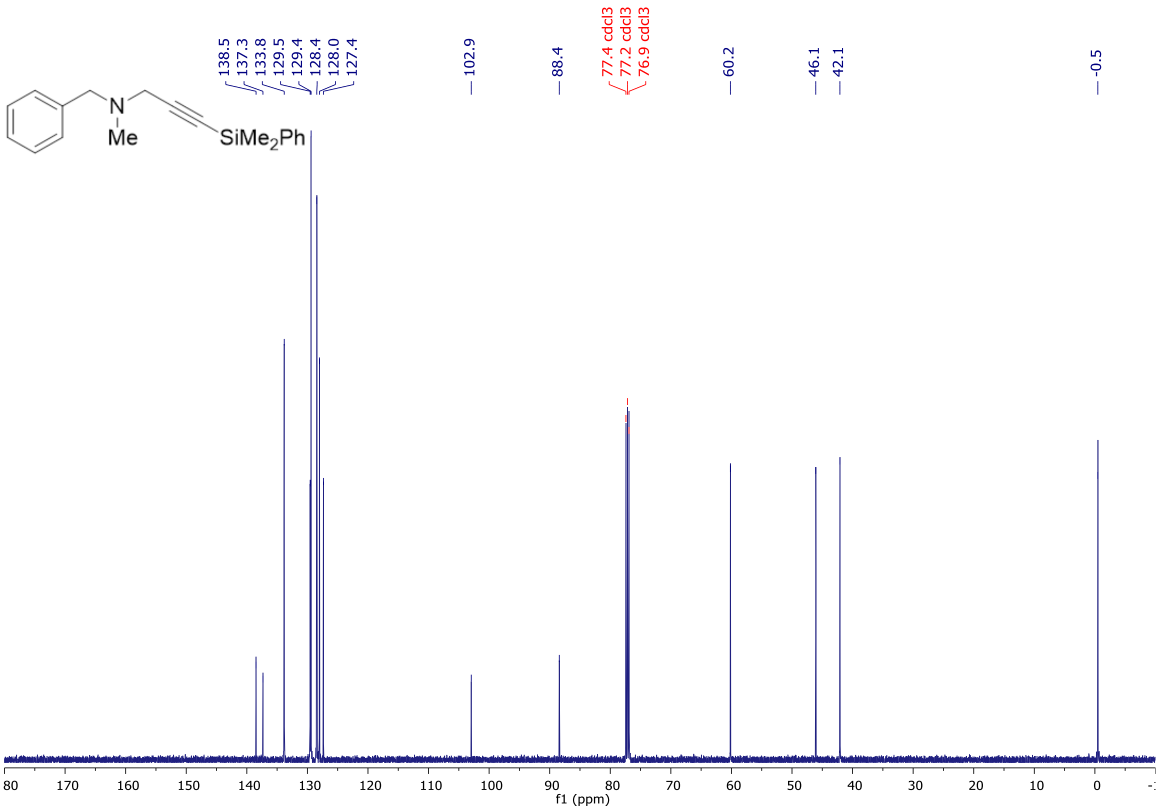




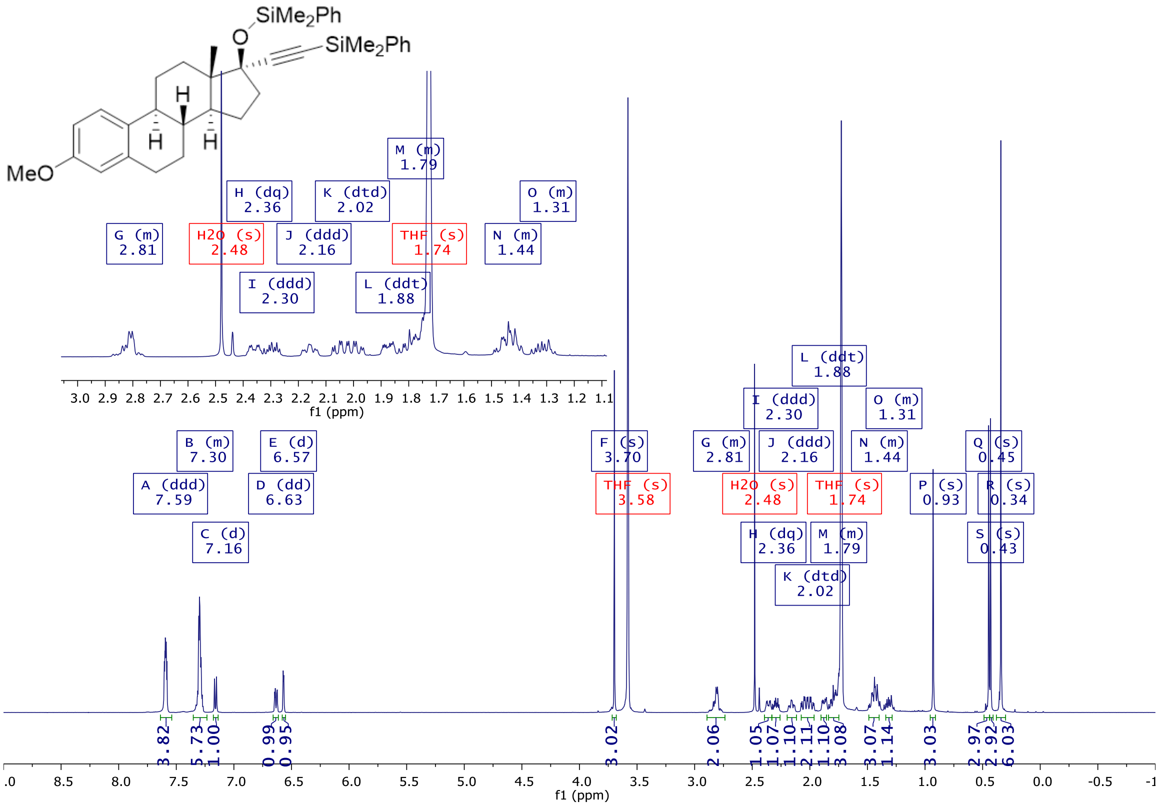
NOESY (500 MHz, C_6D_6) of compound **7e.**



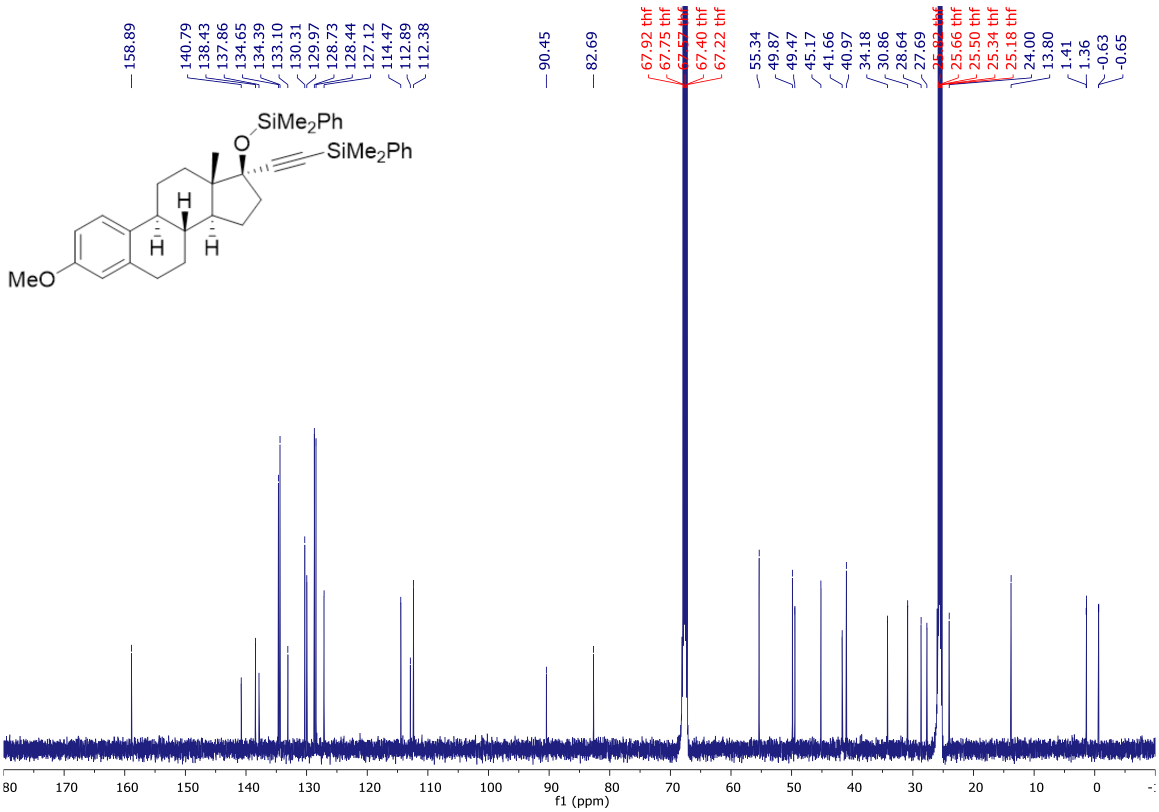
^{1}H NMR (500 MHz, CDCl$_3$) of compound **8.**



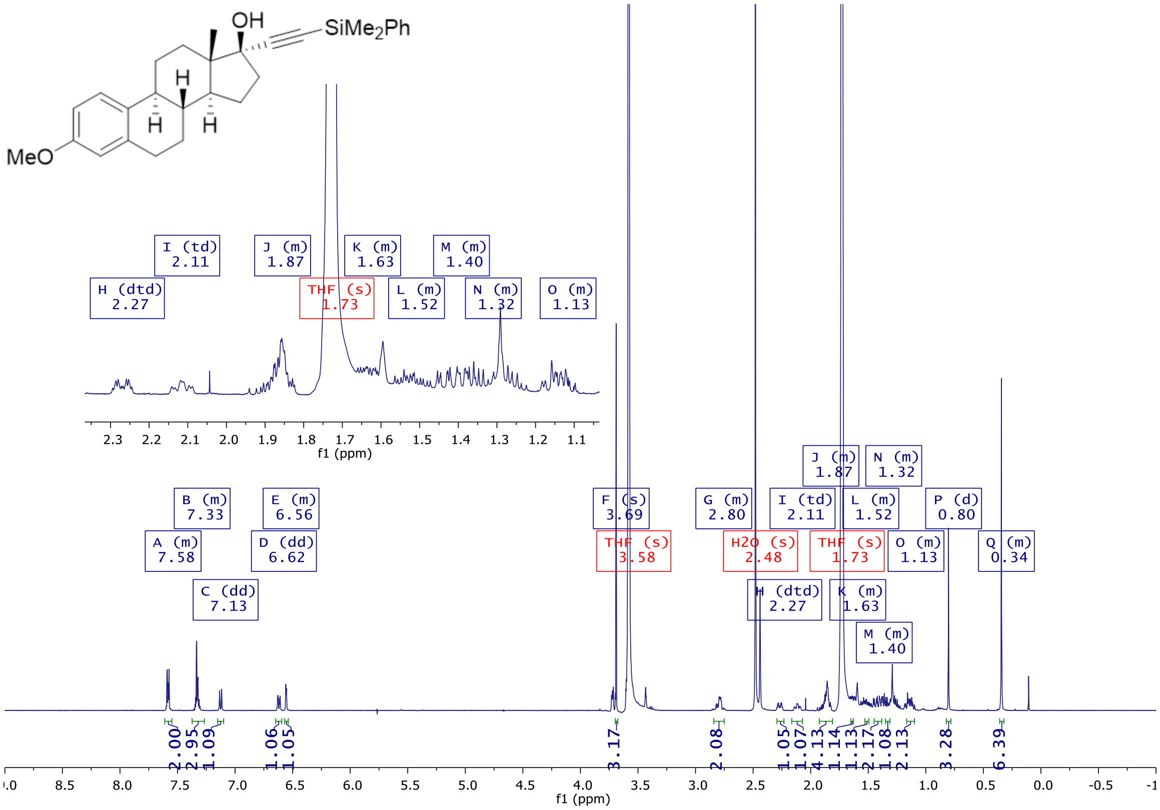
^{13}C NMR (126 MHz, CDCl$_3$) of compound **8.**



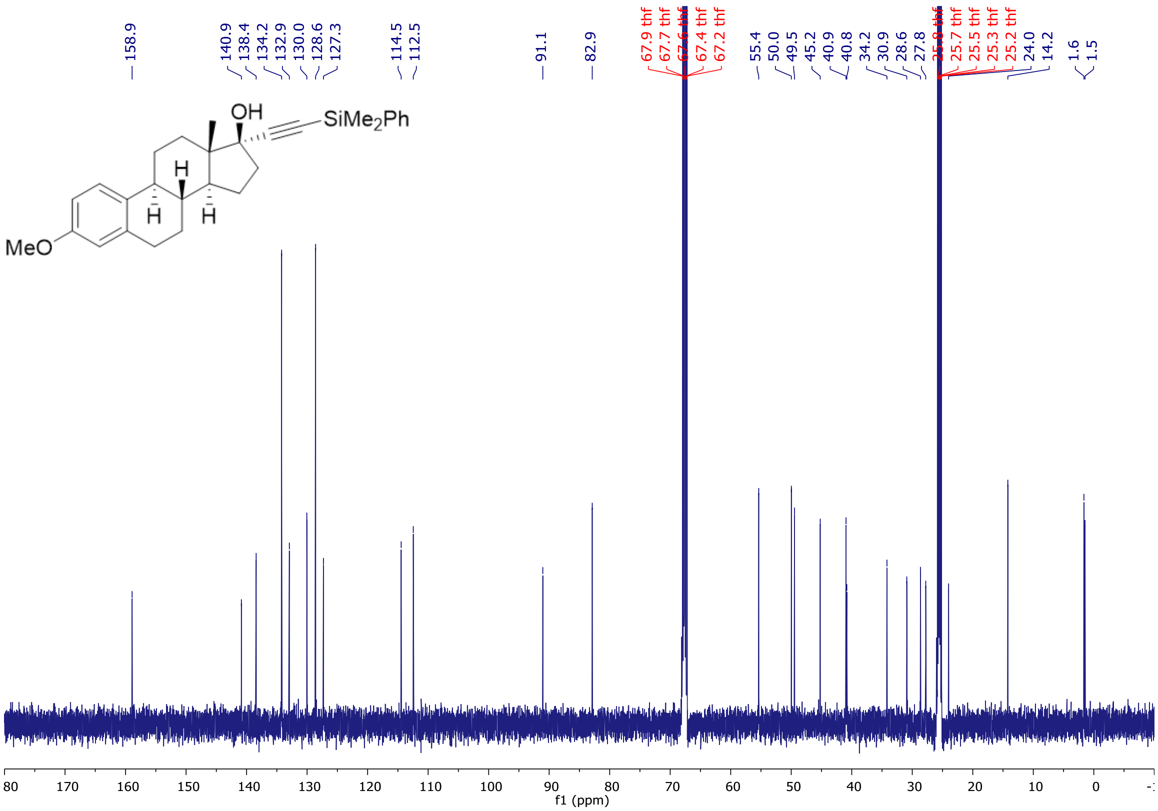
^{1}H NMR (500 MHz, THF-d_8) of compound **9a.**



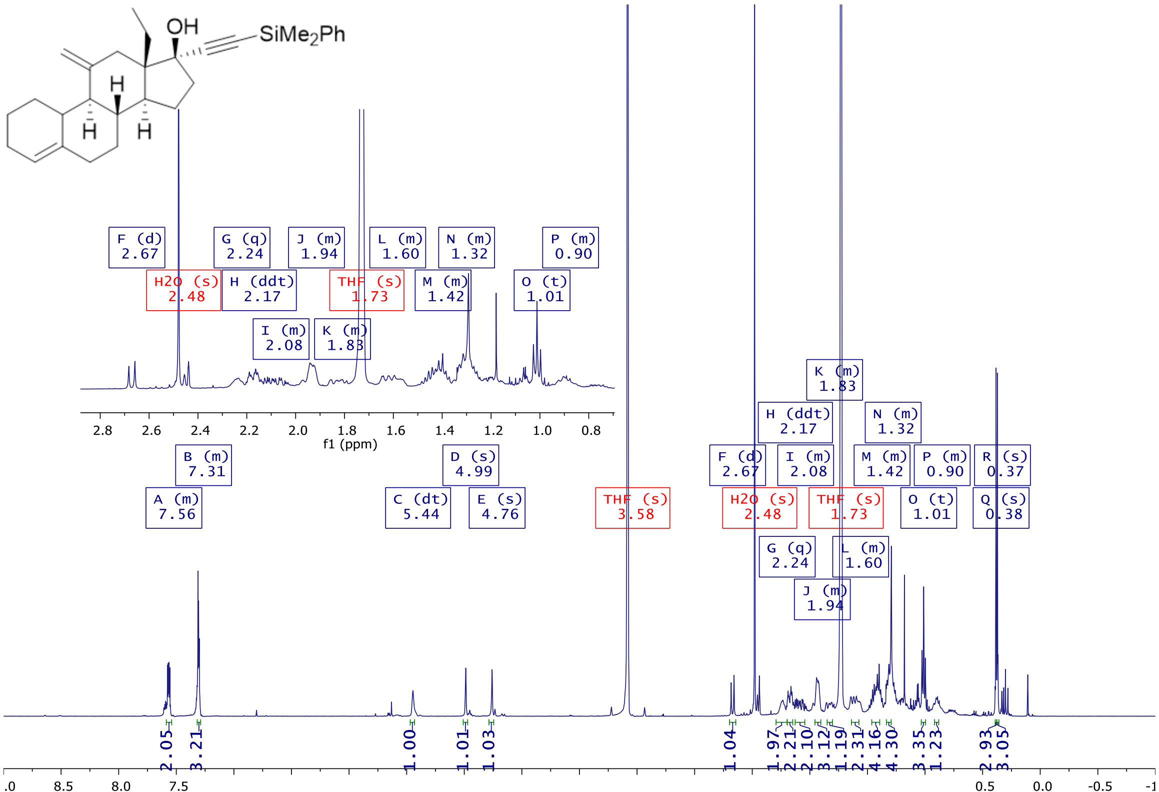
^{13}C NMR (126 MHz, THF-d_8) of compound **9a.**



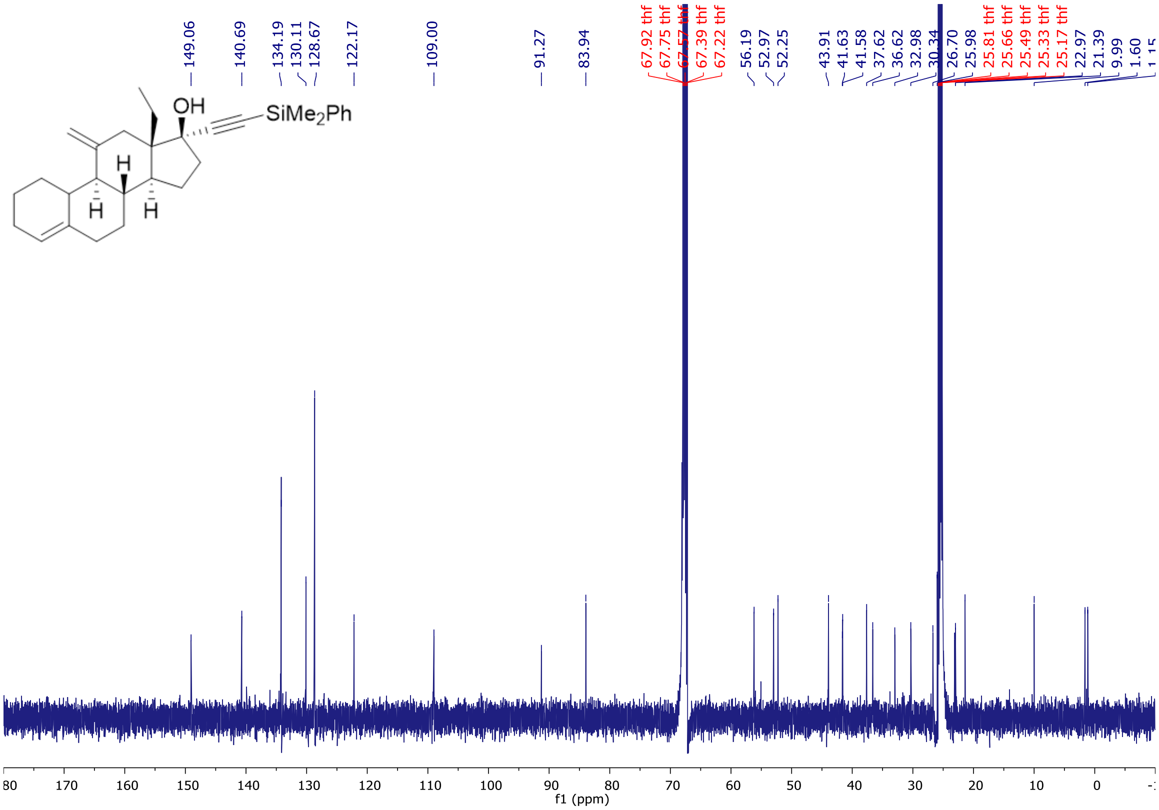
^{1}H NMR (500 MHz, THF-d_8) of compound **9b.**



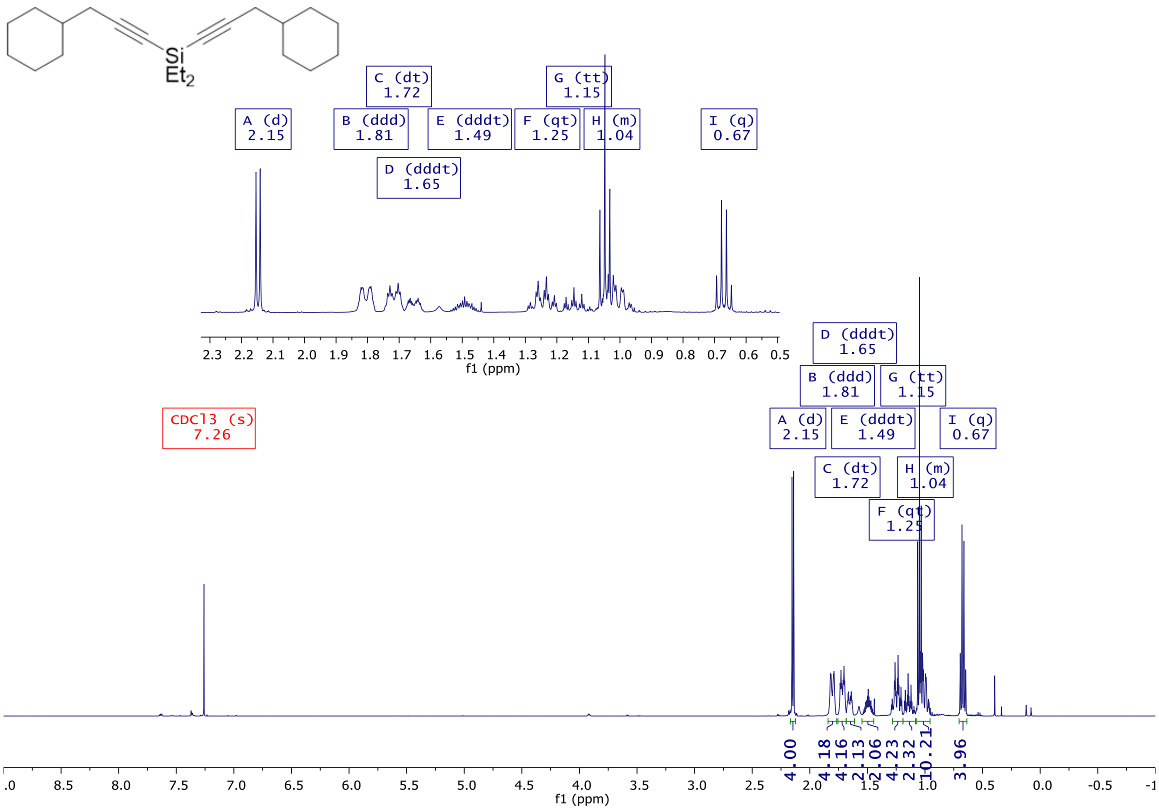
^{13}C NMR (126 MHz, THF-d_8) of compound **9b.**



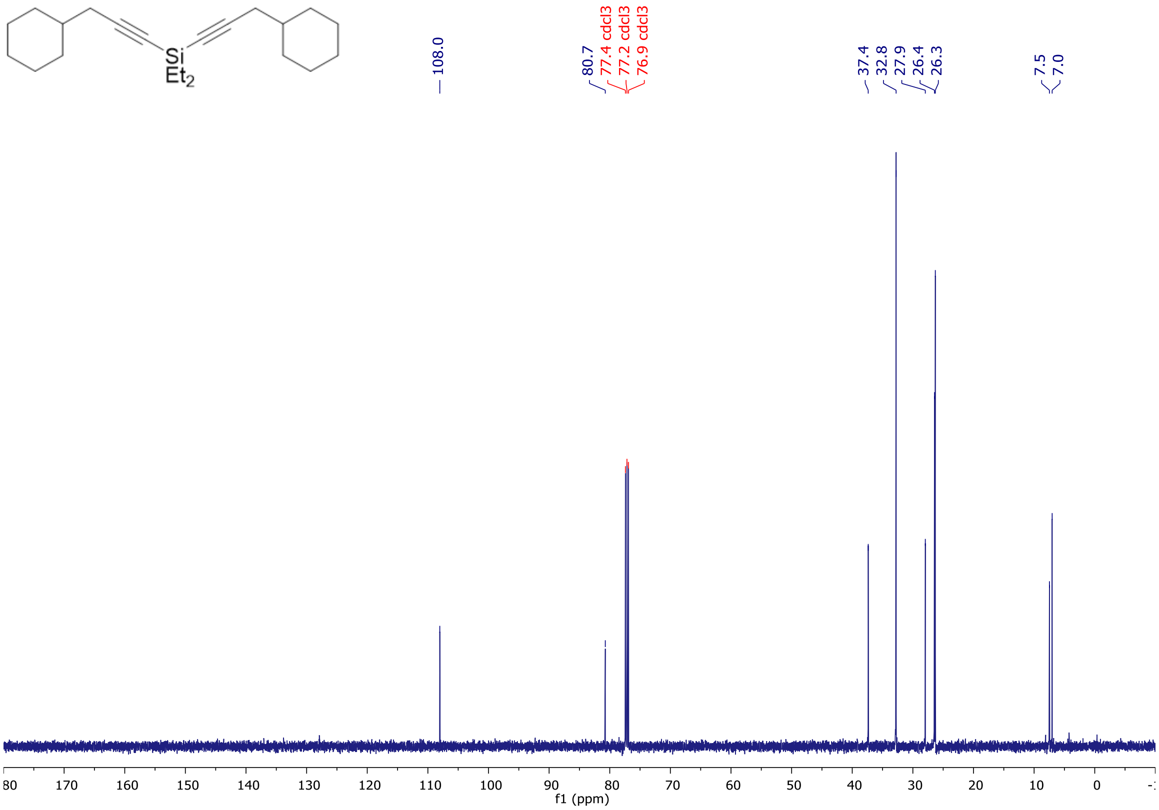
^{1}H NMR (500 MHz, THF-d_8) of compound **10.**



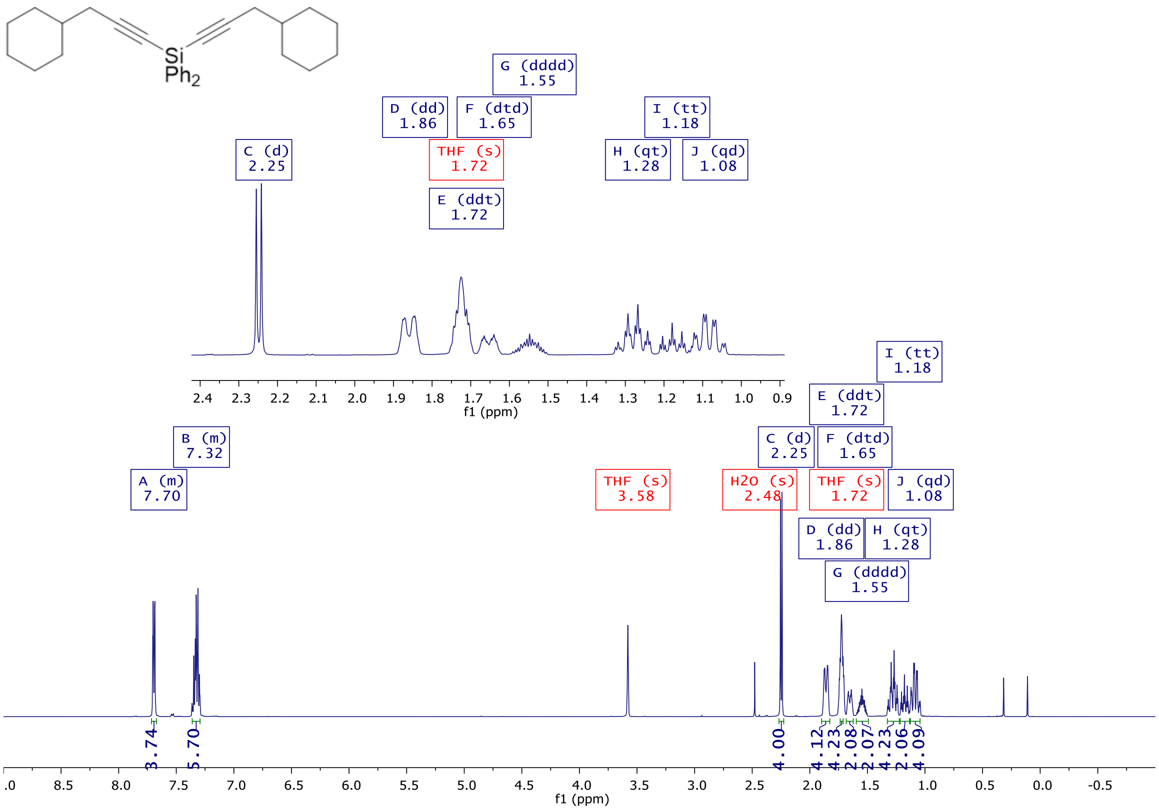
^{13}C NMR (126 MHz, THF-d_8) of compound **10.**



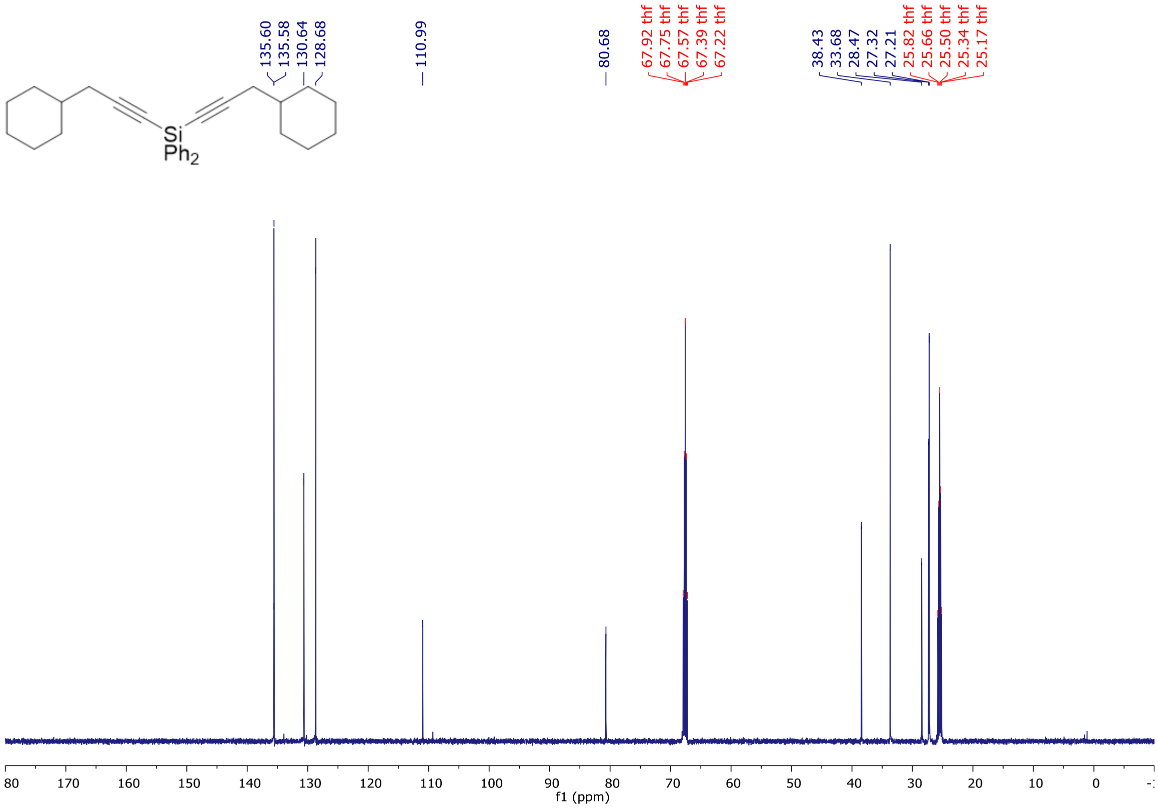
^{1}H NMR (500 MHz, $CDCl_3$) of compound **11a.**



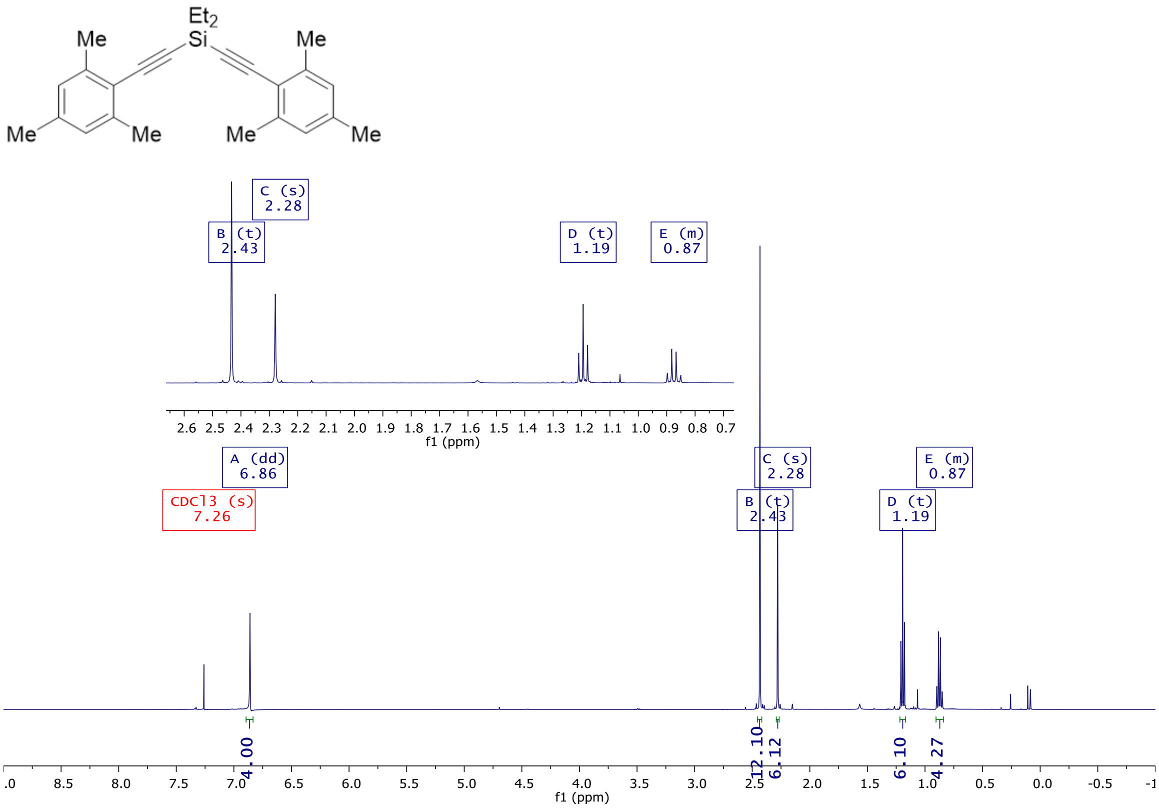
^{13}C NMR (126 MHz, $CDCl_3$) of compound **11a.**



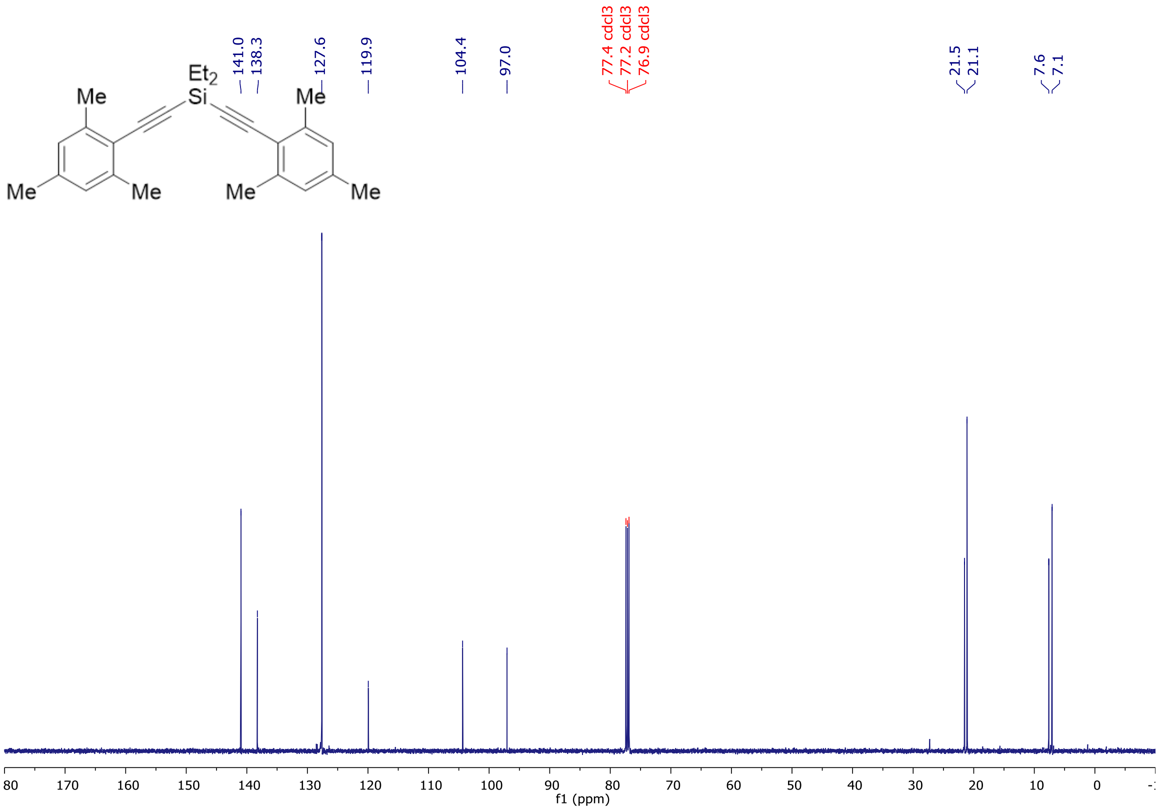
^{1}H NMR (500 MHz, THF-d_8) of compound **11b.**



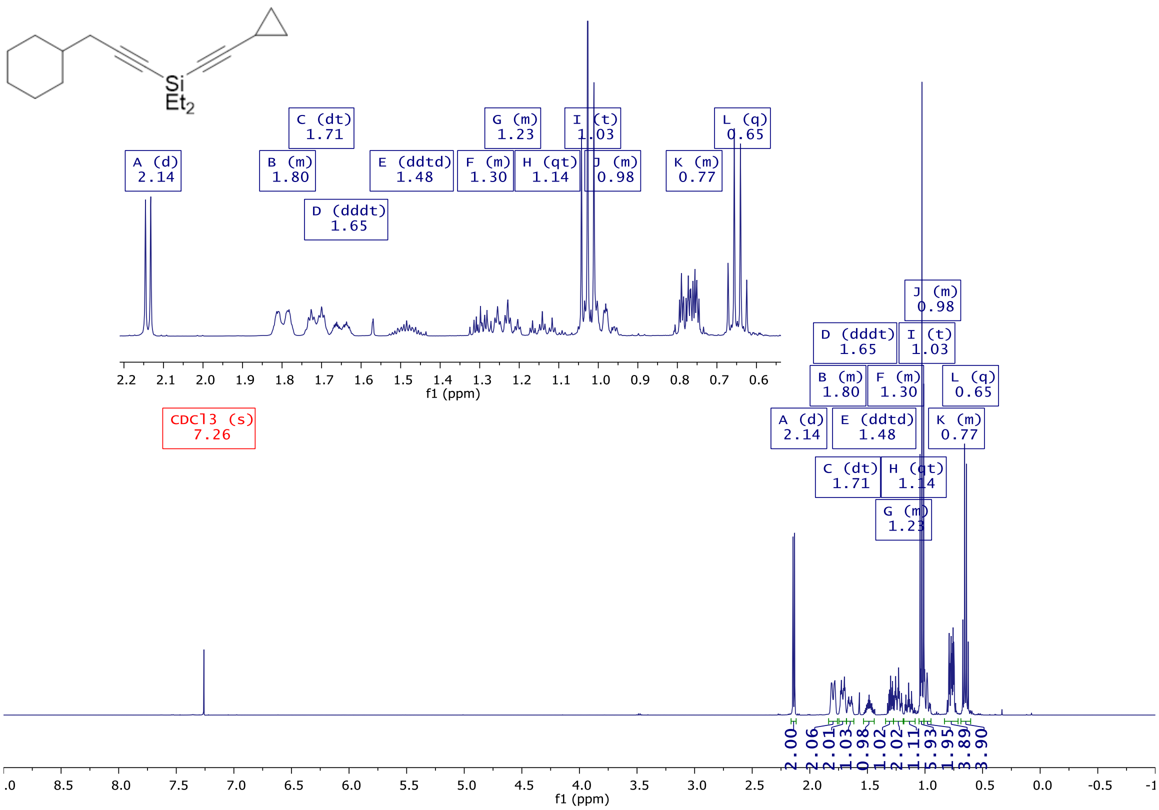
^{13}C NMR (126 MHz, THF-d_8) of compound **11b.**



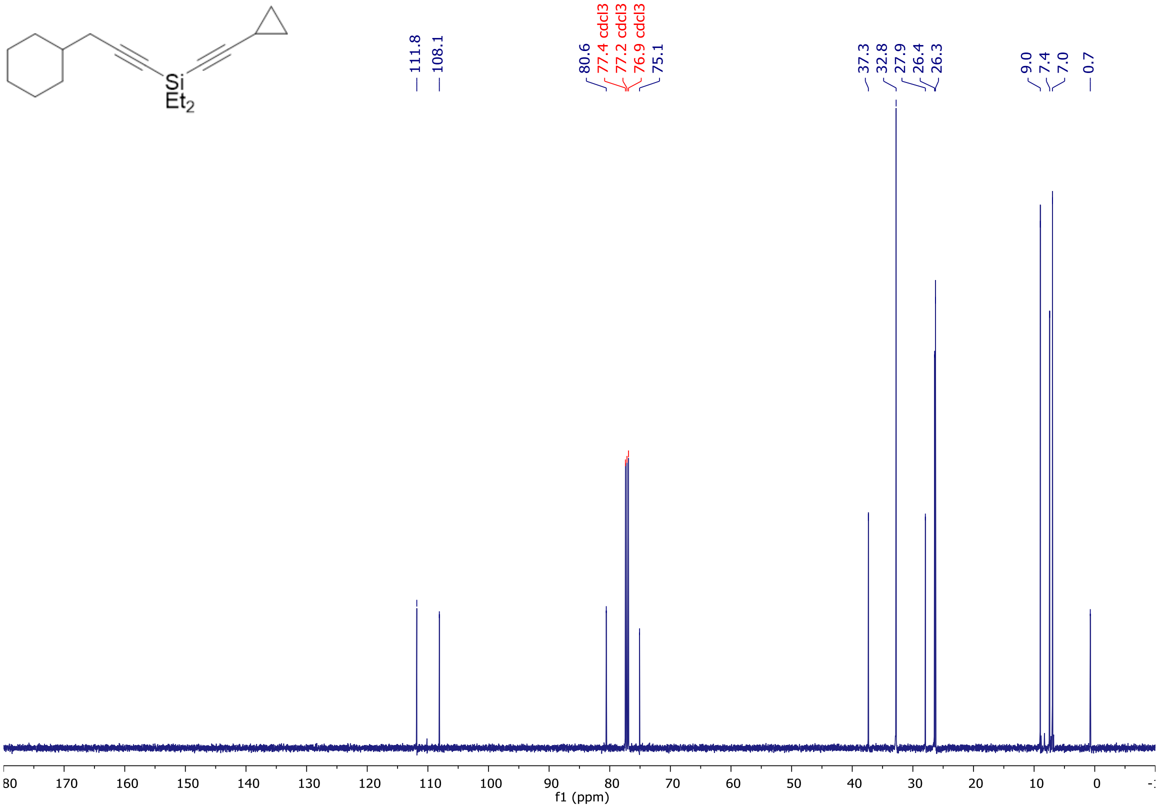
^{1}H NMR (500 MHz, CDCl$_3$) of compound **11c.**



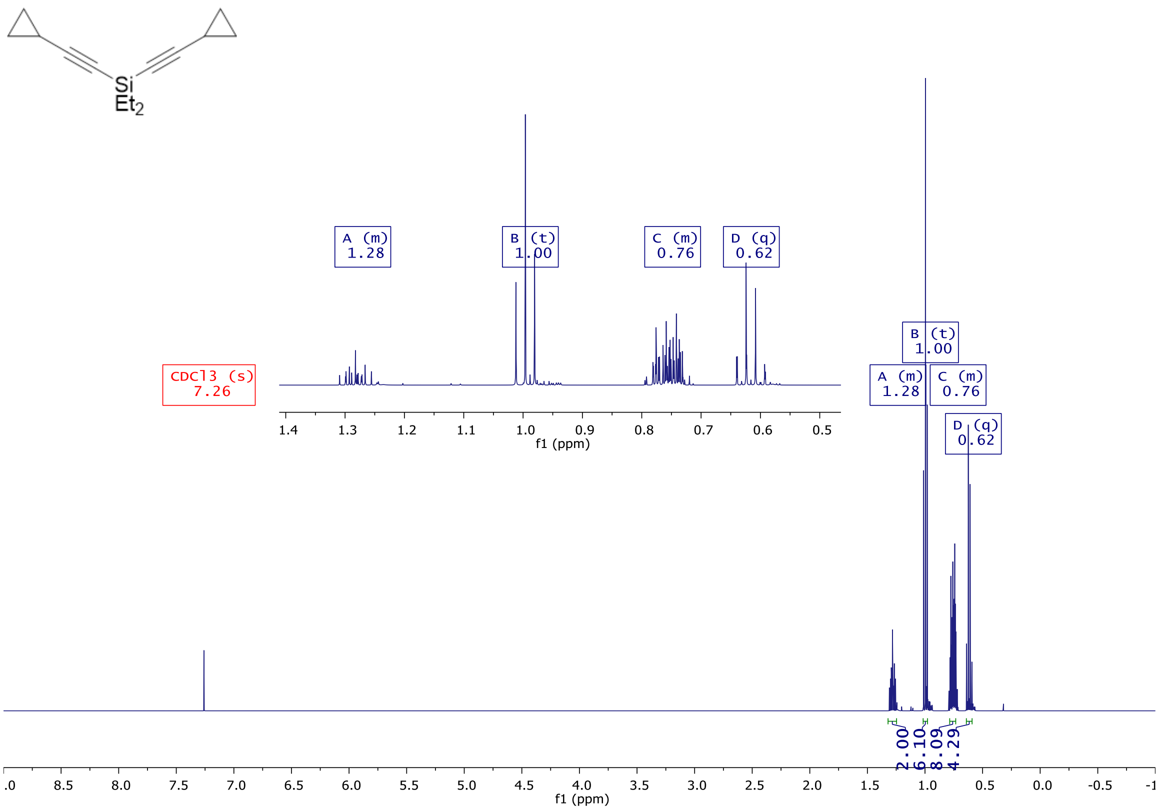
^{13}C NMR (126 MHz, CDCl$_3$) of compound **11c.**



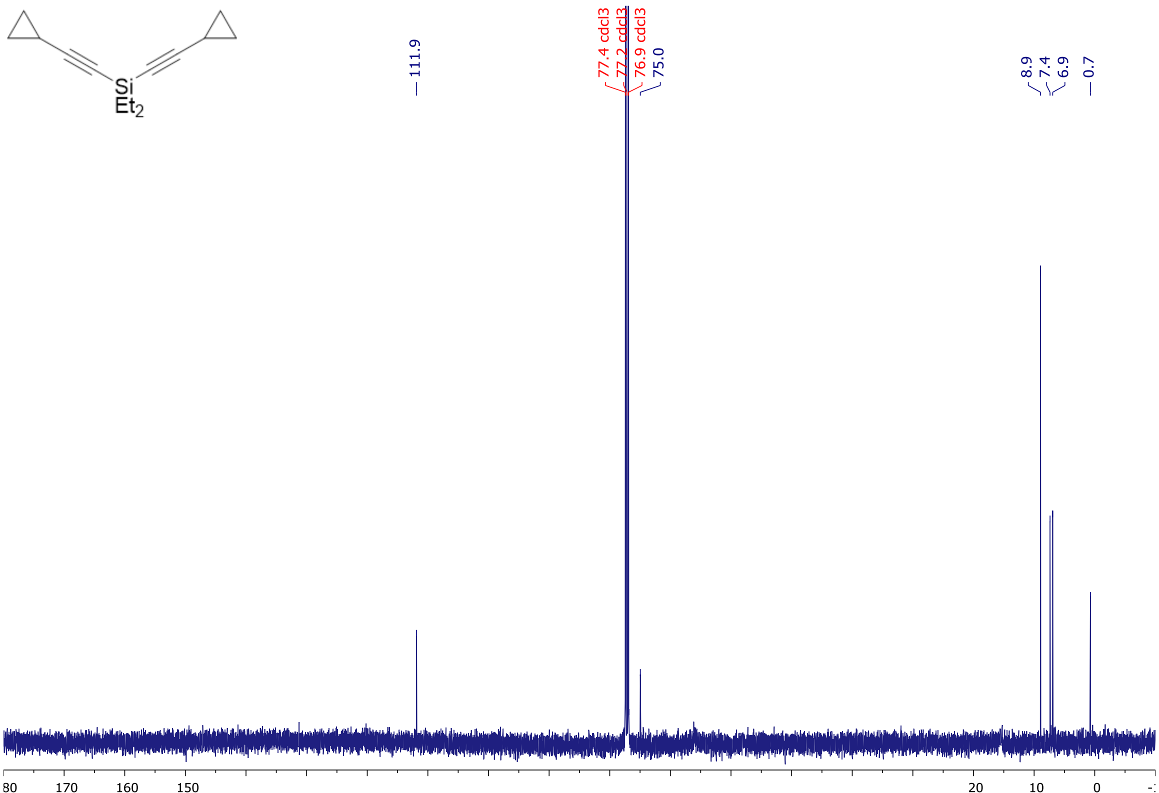
^{1}H NMR (500 MHz, CDCl$_3$) of compound **12a.**



^{13}C NMR (126 MHz, CDCl$_3$) of compound **12a.**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **12a-SI.**



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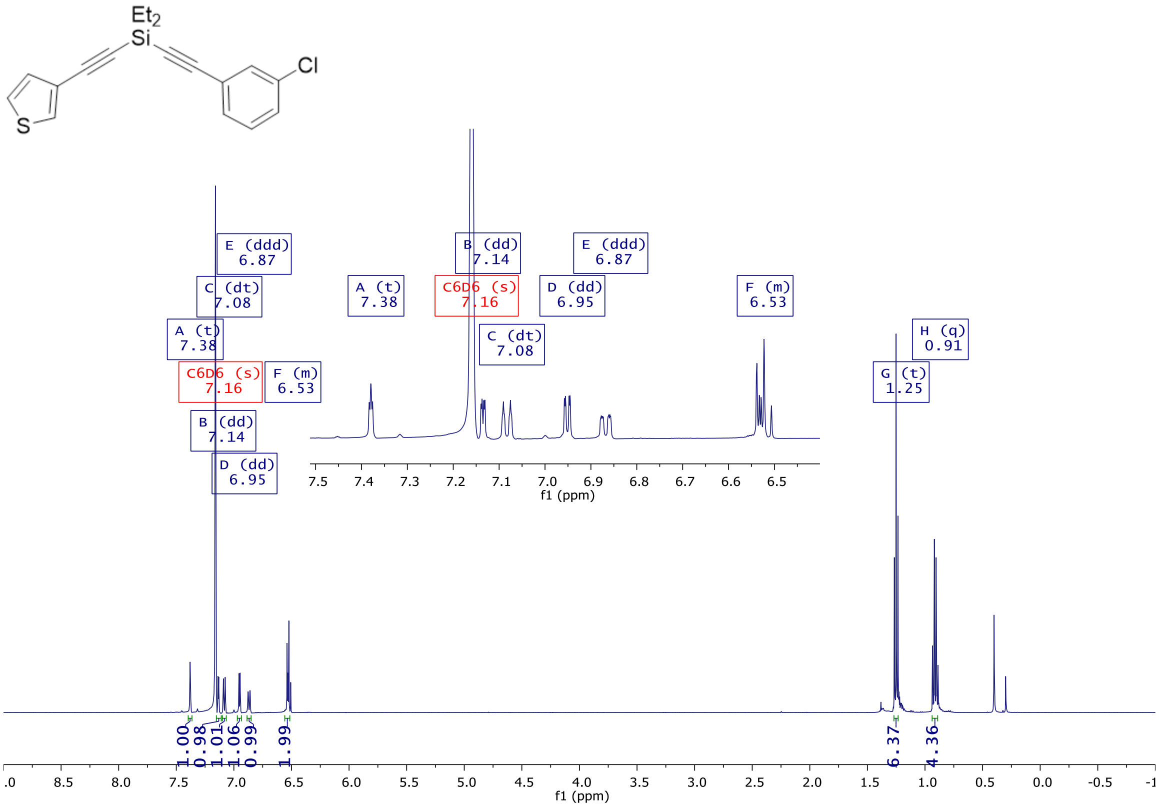
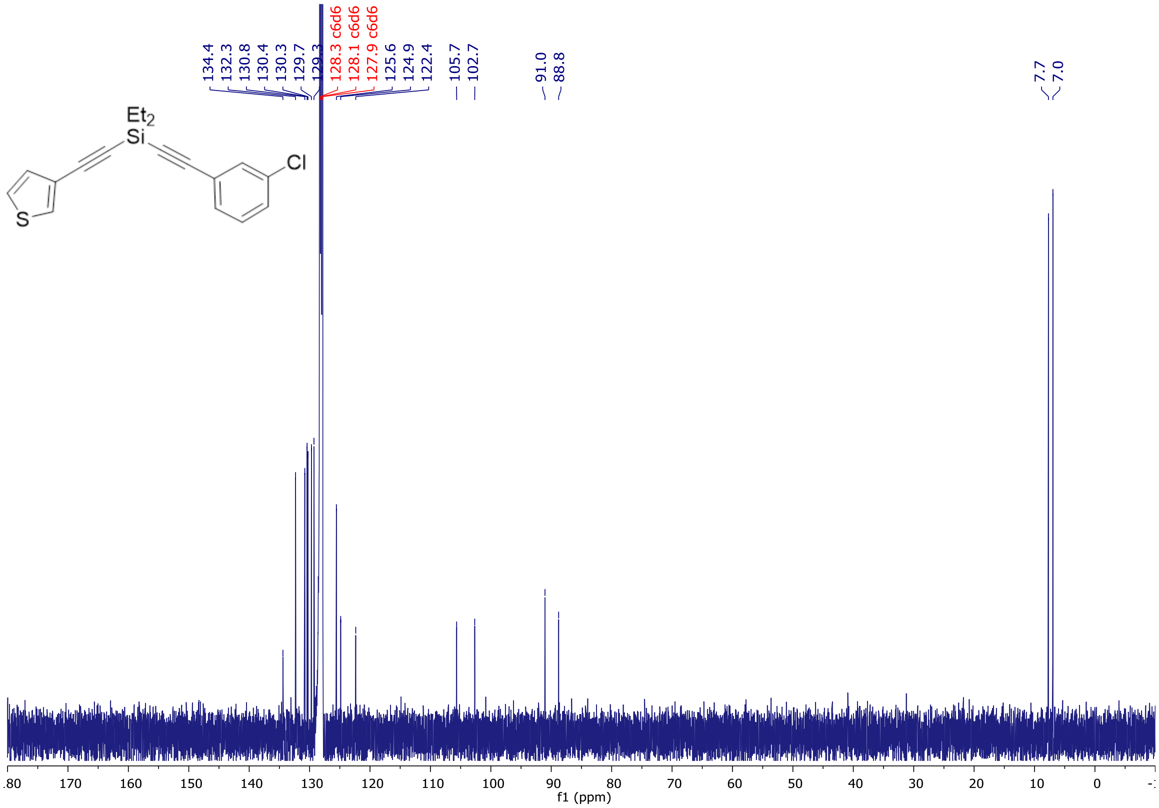
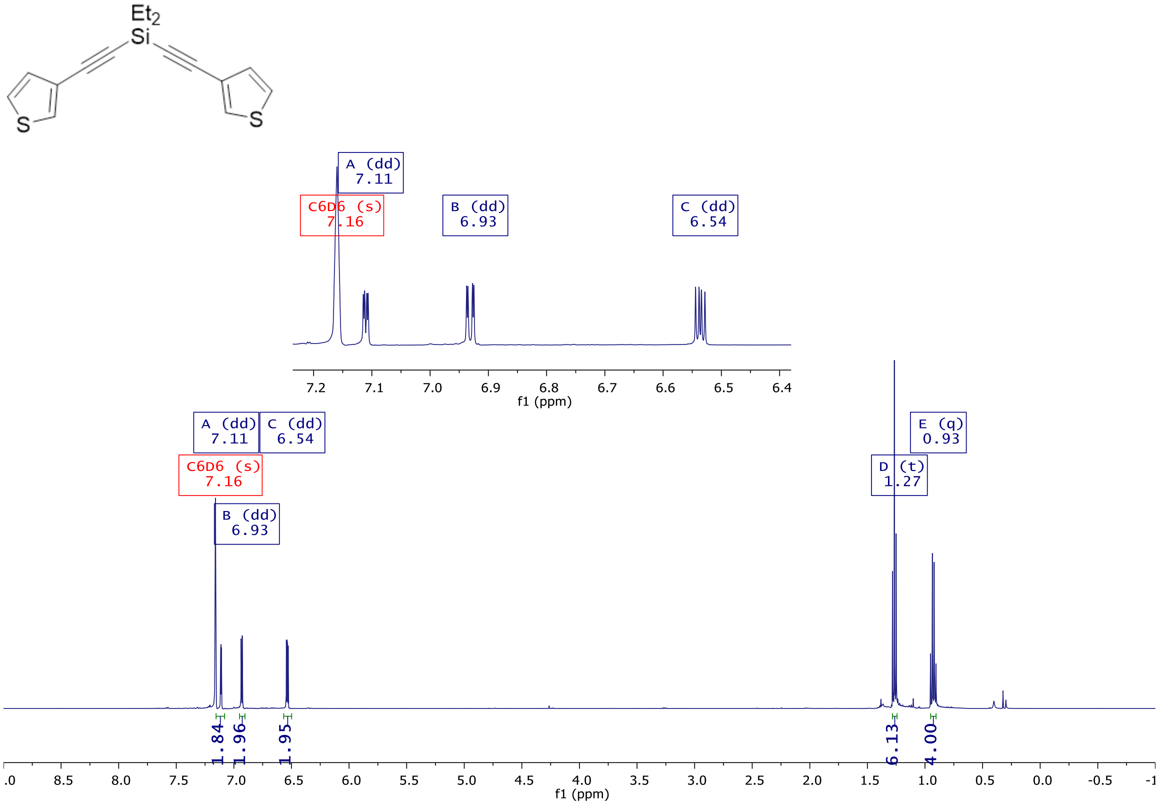


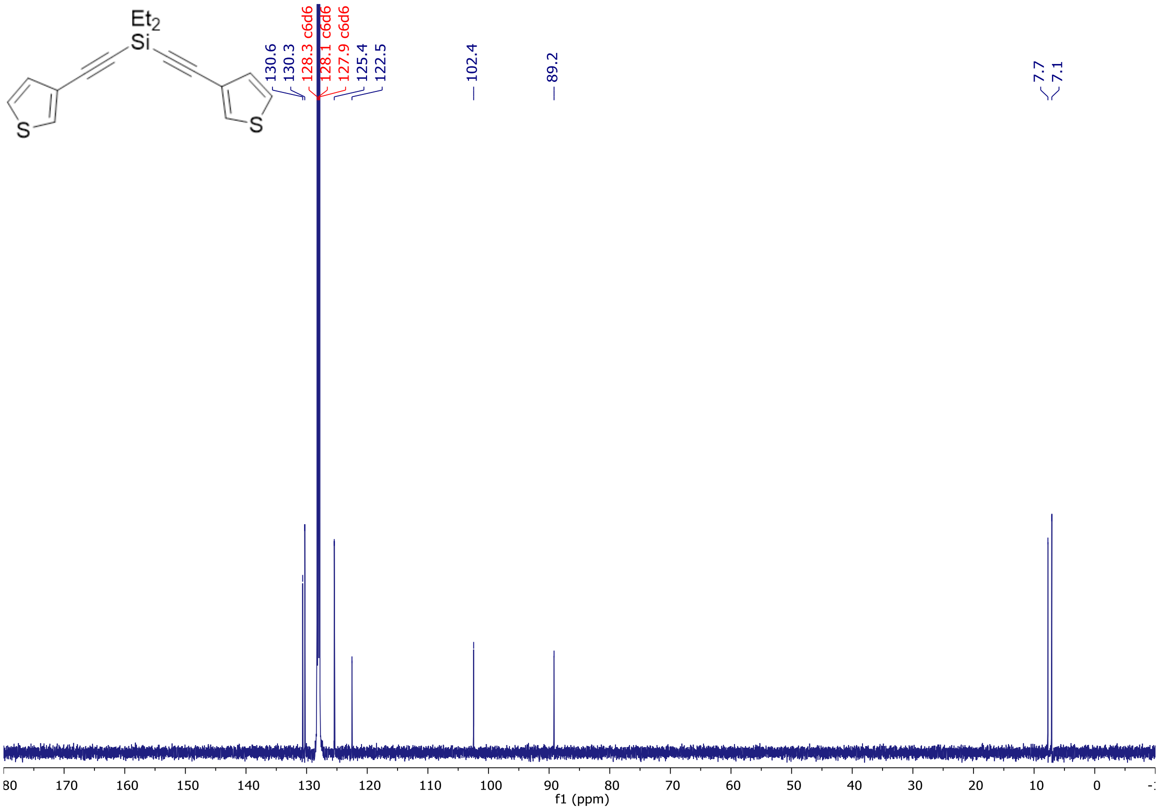
^{1}H NMR (500 MHz, C_6D_6) of compound **12b.**



^{13}C NMR (126 MHz, C_6D_6) of compound **12b.**



^{1}H NMR (500 MHz, C_6D_6) of compound **12b-SI.**



^{13}C NMR (126 MHz, C_6D_6) of compound **12b-SI.**

References:

(1) Pangborn, A. M.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.