Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Additive-Modulated Switchable Reaction Pathway in the Addition of Alkynes with Organosilanes Catalyzed by a Supported Pd Nanoparticles: Hydrosilylation versus Semihydrogenation

Yanan Duan,[†] [a] Guijie Ji,[†a] Shaochun Zhang,*[a] Xiufang Chen[a] and Yong Yang*[a]

[a]CAS Key Laboratory of Bio-Based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

[‡]These authors contributed equally.

Corresponding author: Y. Yang (yangyong@qibebt.ac.cn)

1. General Considerations

Unless otherwise noted, all reagents were purchased commercially from Strem Chemicals, Sigma-Aldrich, J&K, Alfa-Aesar or Aladdin and used as received without further purification. All operations were carried out in an argon atmosphere using glovebox and Schlenk techniques unless otherwise specified. Anhydrous tetrahydrofuran (THF), hexanes, 1,4-dioxane and toluene were distilled from sodium under argon prior to use and anhydrous *N,N'*-dimethylformamide (DMF), acetonitrile (CH_3CN), dichloromethane (DCM), and dimethyl sulfoxide (DMSO) were distilled from CaH_2. Reactions were monitored by thin-layer chromatography (TLC) on 0.25 mm silica gel plates (60F-254) using UV light as the visualizing agent. Column chromatography was carried out on silica gel (200-300 mesh) by elution with appropriate solvents. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Gas chromatography analysis was performed on an Agilent HP-7890 instrument with a flame ionization detector (FID) and an HP-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thicknesses) using argon as the carrier gas. Gas chromatography-mass spectrometry analysis was carried out on an Agilent HP-7890 instrument with an Agilent HP-5975 with triple-axis detector and HP-5MS capillary column using argon carrier gas. NMR or in-situ NMR spectra were obtained from a Bruker DRX-400, or DRX-600 instrument and calibrated using residual non-deuterated solvent ($CDCl_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.00$ ppm, DMSO: $\delta_H = 2.50$ ppm, $\delta_C = 39.50$ ppm) as an internal reference. High resolution mass spectra (HRMS) were recorded on an Bruke Maxis UHR TOF (time of flight) mass spectrometer using ESI (electrospray ionization). The X-ray photoelectron spectroscopy (XPS) data was collected on an ESCALAB 250Xi (Thermo Scientific, UK) instrument equipped with a monochromatized Al Ka line source. All the binding energies obtained were calibrated based on the C 1s peak at 284.8 eV.

2. Preparation of the catalyst Pd@N,O-Carbon

The porous heteroatom doped carbon materials were prepared in two-steps including hydrothermal treatment and carbonization process. The fresh bamboo shoots were obtained from Anhui Taiping Test Centre, International Centre for Bamboo and Rattan, Anhui Province, China. The Bamboo shoots were firstly cut into slices and dried at 70 ℃ for 24 h. The dried bamboo shoots (2 g) were then ground into powders and transferred in a 100 mL Teflon-inner stainless-steel autoclave coupled with 20 ml of deionized water. The autoclave was then heated to 180 ℃ and maintained for 6 h. The resulting brown solids were filtered, washed by distilled water thoroughly to remove any residual of soluble metal ions such as Ca^{2+} or K^+ (detected by ion chromatography), dried at room temperature under vacuum for 24 h. After that, the hydrochars were calcined at 850 ^oC for 4 h in N_2 flow with a heating rate of 5 °C min^{-1}. The black powder heteroatom doped porous carbons were obtained and denoted as N.O-Carbon. The porous heteroatom doped carbon supported Pd materials with metal loading of 2.0 wt % were prepared by ultrasound-assisted reduction method. 0.15 g porous heteroatom doped carbon materials were dispersed in 100 mL deionized water under ultrasonic condition for 30 min. Then 3 g of 0.268 wt% of $Pd(NO_3)_2$ aqueous solution was added dropwise into the mixture and stirred vigorously for 1 h. After that, the pH value of solution was adjusted to 11 using ammonia solution. The resulting solution was put into 80oC oil bath with subsequent addition of 0.2 mL of hydrazine solution (85%), which was further stirred vigorously for another 4 h. Finally, the product was filtered and washed with deionized water and dried at 105 ℃ under vacuum for 12 h. The as - prepared sample was denoted as Pd@N,O-Carbon and the Pd loading was determined by ICP-AES to be 1.64 wt%.

3. Hydrosilylation of Alkynes

In a typical procedure, to a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with Pd@N,O-Carbon catalyst (5 mg, 0.15 mol%), tetrabutylammonium iodide (TBAI) (92.3 mg, 0.25 mmol), the alkyne (0.5 mmol), the hydrosilane (0.6 mmol), and anhydrous THF (1 mL) under argon. The tube was capped with rubber septum and stirred vigorously at room temperature. The reaction progress was monitored by GC-MS. After the completion of the reaction, the mixture was filtered and the yield and selectivity were recored using ^{1}H NMR or GC, then the crude product was purified by flash chromatography on silica gel to afford pure product for the analysis of ^{1}H/^{13}C NMR and HR-MS.

4. Transfer Semihydrogenation of Alkynes

In a typical procedure, to a sealable Schlenk reaction tube equipped with a magnetic stir bar was charged with 5 mg of Pd@N,O-Carbon catalyst (0.15 mol%). The tube was then sealed with a rubber septum and was evacuated for a while to remove air and was recharged with Ar gas. The alkyne (0.5 mmol), the hydrosilane (0.75 mmol), water (1.0 mmol) and anhydrous DMSO (1 mL) were injected via syringe into the tube and the reaction was stirred at 70^{o}C. The reaction was monitored by extracting an aliquot of the reaction mixture for GC analysis during the reaction period. After completion of the reaction, the reaction mixture was centrifuged. Finally, the products were identified by gas chromatograph coupled with a mass spectrometer (GC-MS, Shimadzu, 2010 plus).

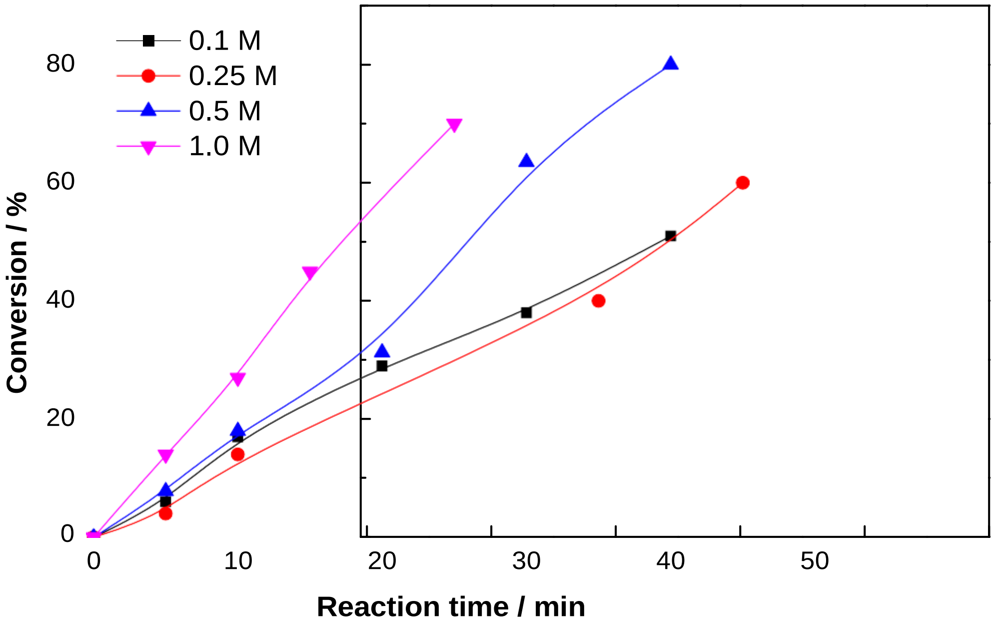


Figure S1. Effect of TBAI concentration on the reaction rate for phenylacetylene hydrosilylation with $PhMe_2SiH$.

Reaction conditions: phenylacetylene (0.5 mmol), $PhMe_2SiH$ (0.6 mmol), TBAI (0.1-1.0 mmol), Pd@N,O-Carbon (5 mg, 0.15 mol% of Pd), anhydrous THF (1mL), room temperature. Conversion was determined by GC-FID using dodecane as the internal standard.

Table S1. Temperature Effect on Transfer Semihydrogenation of Phenylacetylene

Entry	Temperature (^{o}C)	Time (min)	Conversion (%)[b]	Selectivity (**2a**/**3a**) (%)[b]
1	25	1320	65	100/0
2	40	240	100	100/0
3	50	150	100	100/0
4	60	70	100	100/0
5	70	20	100	100/0
6	80	10	100	76/24

[a] Reaction conditions: **1a** (0.5 mmol), $PhMe_2SiH$ (0.75 mmol), H_2O (1.0 mmol), Pd@N,O-Carbon (5 mg, 0.15 mol% of Pd), DMSO (1 mL), 70^{o}C. [b] determined by GC-FID using dodecane as the internal standard.

Table S2. Hydrosilane Concentration Effect on Transfer Semihydrogenation of Phenylacetylene

Entry	Conc.$_{PhMe2SiH}$ (mM)	Time (min)	Conversion (%)[b]	Selectivity (**2a**/**3a**) (%)[b]
1	0	720	0	-
2	0.5	180	76	100/0
3	0.75	20	100	100/0
4	1.0	20	100	92/8
5	1.5	10	100	90/10

[a] Reaction conditions: **1a** (0.5 mmol), $PhMe_2SiH$ (0-1.5 mmol), H_2O (1.0 mmol), Pd@N,O-Carbon (5 mg, 0.15 mol% of Pd), DMSO (1 mL), 70^{o}C. [b] determined by GC-FID using dodecane as the internal standard.

Table S3. H_2O Concentration Effect on Transfer Semihydrogenation of Phenylacetylene

Entry	H_2O (mmol)	Time (min)	Conversion (%)[b]	Selectivity (**2a**/**3a**) (%)[b]
1	0	720	0	-
2	0.5	40	100	100/0
3	0.75	30	100	100/0
4	1.0	20	100	100/0
5	1.5	20	100	100/0

[a] Reaction conditions: **1a** (0.5 mmol), $PhMe_2SiH$ (0.75 mmol), H_2O (0-1.5 mmol), Pd@N,O-Carbon (5 mg, 0.15 mol% of Pd), DMSO (1 mL), 70°C.
[b] determined by GC-FID using dodecane as the internal standard.

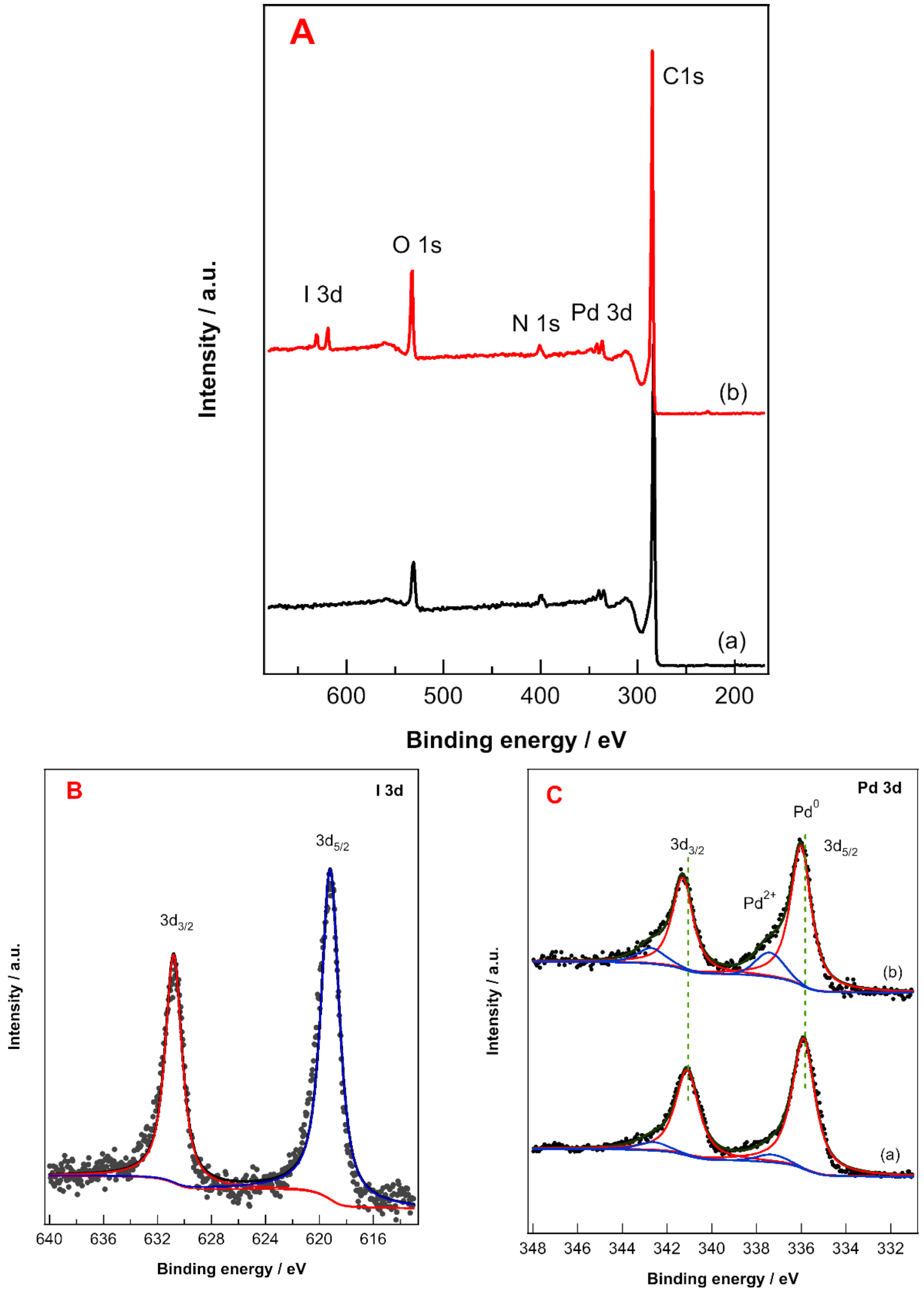
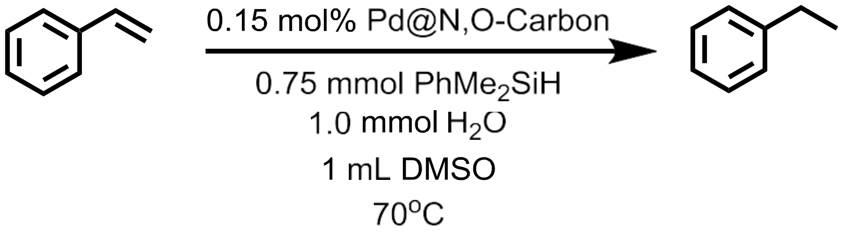


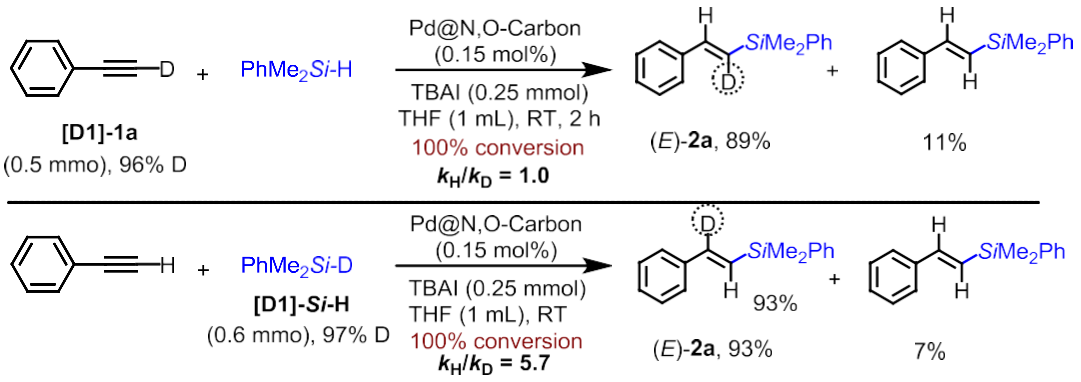
Figure S2. (A) XPS survey spectra for the catalyst (a) Pd@N,O-Carbon and (b) Iodide-modified Pd@N,O-Carbon. (B) I 3d XPS spectrum for the iodide-modified Pd@N,O-Carbon. (C) Pd 3d XPS spectra for the catalyst (a) Pd@N,O-Carbon and (b) iodide-modified Pd@N,O-Carbon.

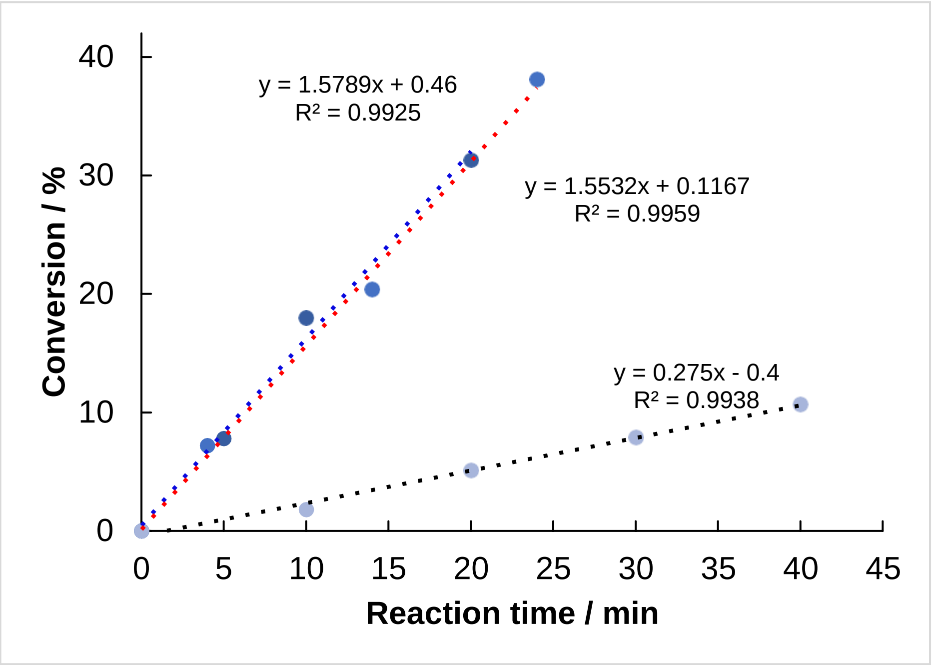
Scheme S1. Demonstration of Perfect selectivity to alkyne over the catalyst Pd@N,O-Carbon



Reaction time (min)	conversion (%)
20	0
60	2
90	2

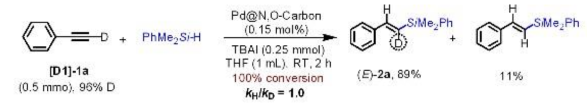
5. Kinetic Isotope Effect Experiments

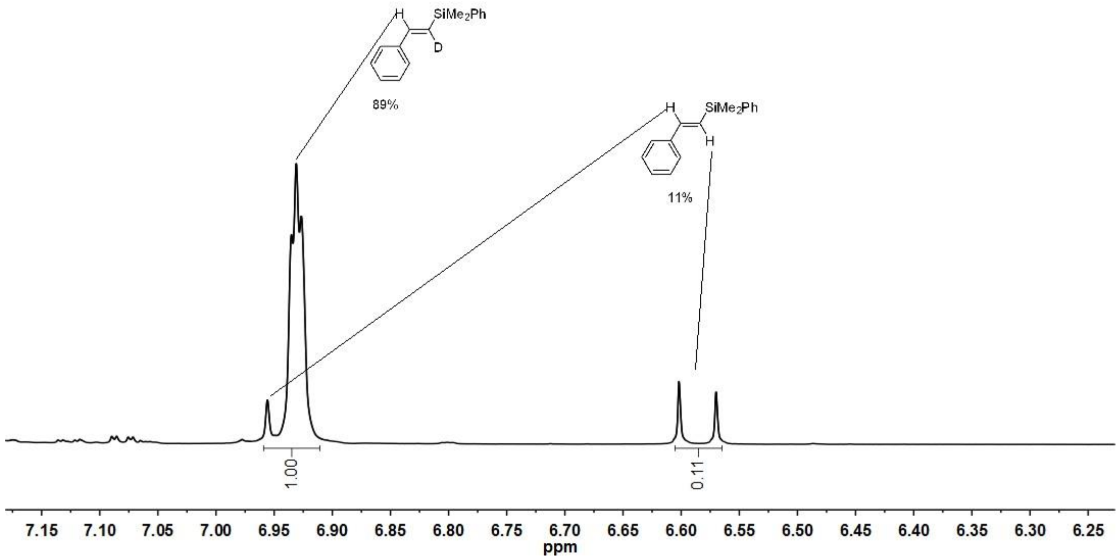


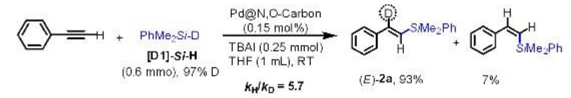


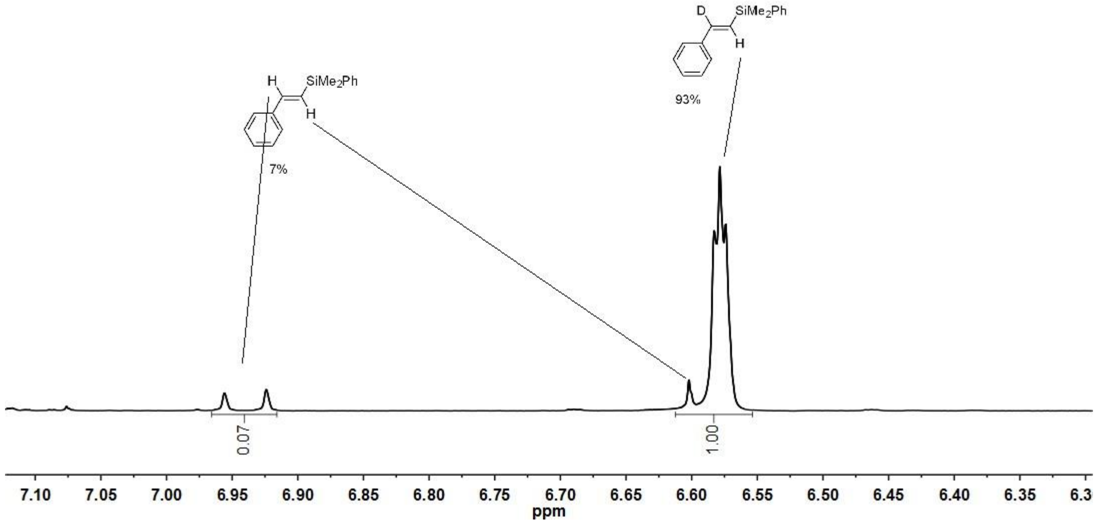
Substrates	***K*$_{\text{initial}}$ (mmol/min)[a]**	**KIE (*K*$_H$/*K*$_D$)**
PhC≡C-H + $PhMe_2Si$-H	1.5789	For comparison
PhC≡C-D + $PhMe_2Si$-H	1.5532	1.0
PhC≡C-H + $PhMe_2Si$-D	0.2750	5.7

Reaction conditions: PhC≡C-H or PhC≡C-D (0.5 mmol), $PhMe_2Si$-H or $PhMe_2Si$-D (0.6 mmol), anhydrous THF (1 mL), Pd@N,O-Carbon (5 mg, 0.15 mol% of Pd), room temperature. [a]*K*$_{\text{initial}}$ represents the initial reaction rate was determined according the maximum level of conversion was approximately 40%.


D
+
PhMe2Si-H
[D1]-1a
(0.5 mmo), 96% D
Pd@N,O-Carbon
(0.15 mol%)
TBAI (0.25 mmol)
THF (1 mL), RT, 2 h
100% conversion
k_H/k_D = 1.0
H
SiMe2Ph
D
(E)-2a, 89%
+
H
SiMe2Ph
H
11%


H
SiMe2Ph
D
89%
H
SiMe2Ph
H
11%
1.00
0.11
7.15
7.10
7.05
7.00
6.95
6.90
6.85
6.80
6.75
6.70
6.65
6.60
6.55
6.50
6.45
6.40
6.35
6.30
6.25
ppm


H
+
PhMe2Si-D
[D1]-Si-H
(0.6 mmo), 97% D
Pd@N,O-Carbon
(0.15 mol%)
TBAI (0.25 mmol)
THF (1 mL), RT
k_H/k_D = 5.7
D
SiMe2Ph
H
(E)-2a, 93%
+
H
H
SiMe2Ph
7%


D
SiMe2Ph
H
93%
H
SiMe2Ph
H
7%
0.07
1.00
7.10
7.05
7.00
6.95
6.90
6.85
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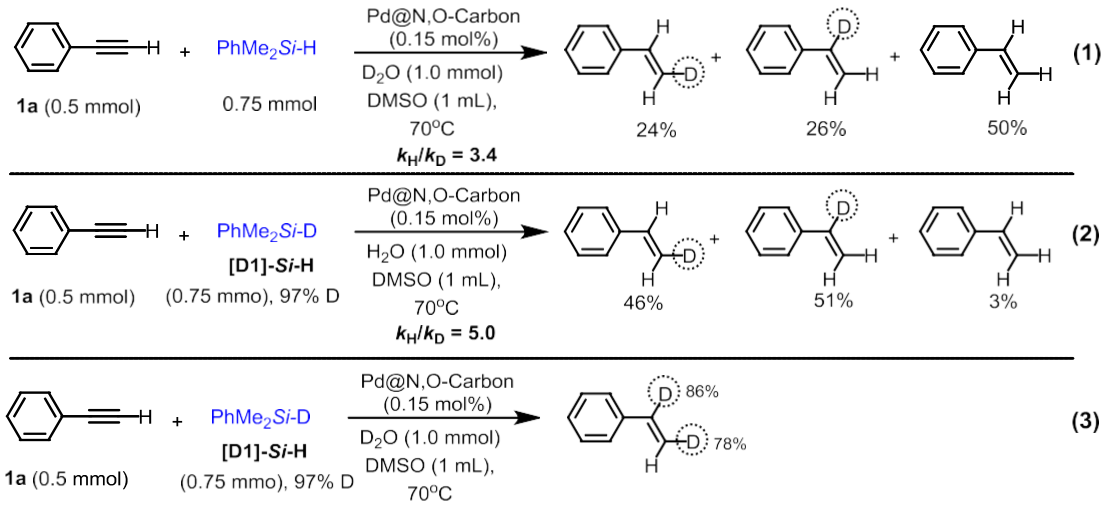
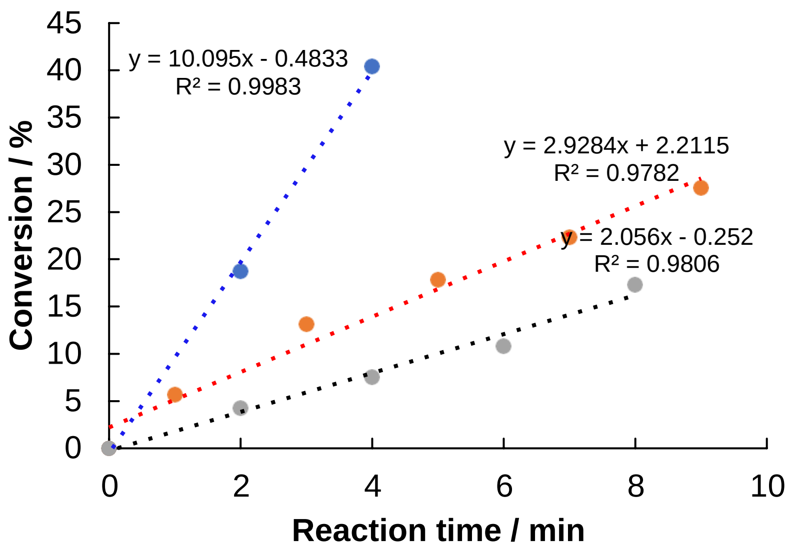
6.40
6.35
6.3
ppm





Substrates	K_{initial} (mmol/min)[a]	KIE (K_H/K_D)
PhC≡C-H + $PhMe_2Si$-H + H_2O	10.095	For comparison
PhC≡C-H + $PhMe_2Si$-H + D_2O	2.9284	3.4
PhC≡C-H + $PhMe_2Si$-D + H_2O	2.0560	5.0

Reaction conditions: PhC≡C-H or PhC≡C-D (0.5 mmol), $PhMe_2Si$-H or $PhMe_2Si$-D (0.75 mmol), H_2O or D_2O (1.0 mmol), anhydrous DMSO (1 mL), Pd@N,O-Carbon (5 mg, 0.15 mol% of Pd), 70°C. [a]K_{initial} represents the initial reaction rate was determined according the maximum level of conversion was approximately 40%.

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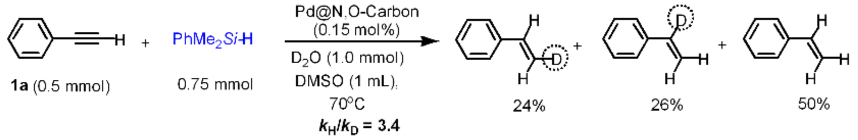
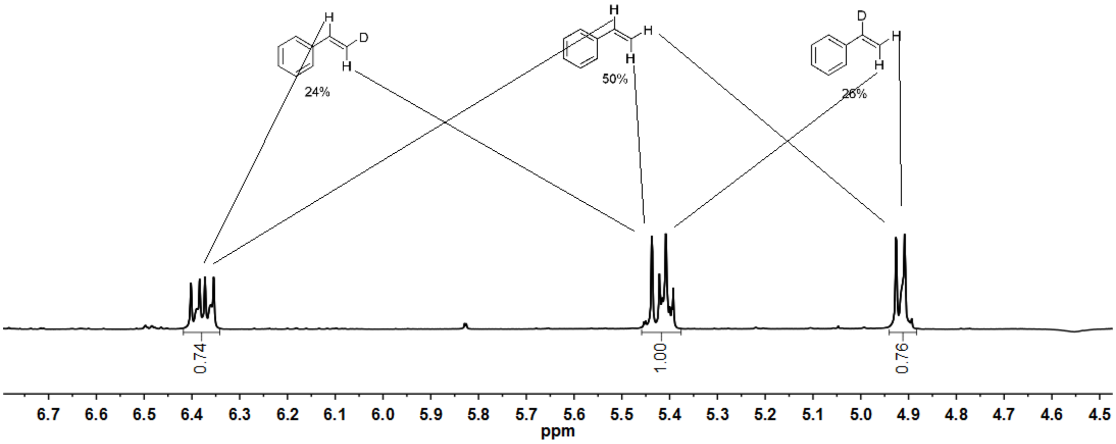
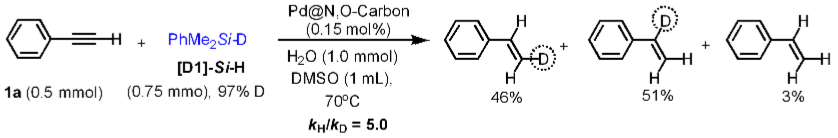
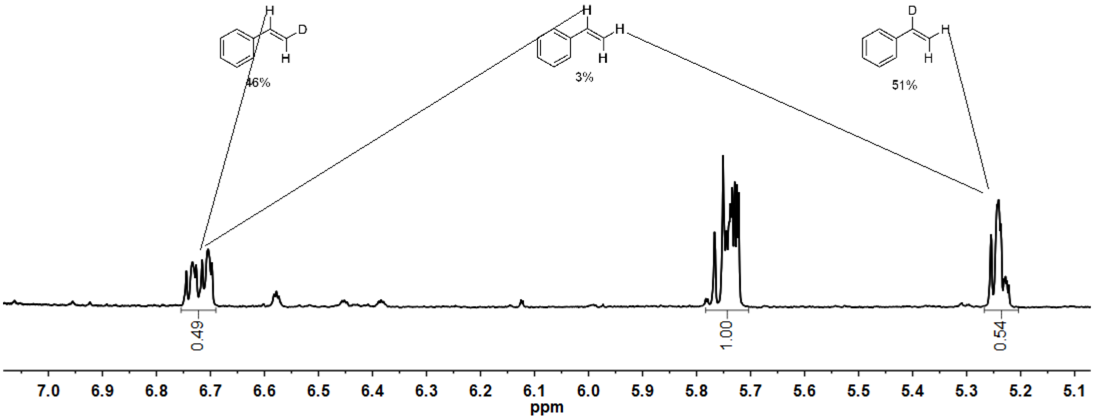
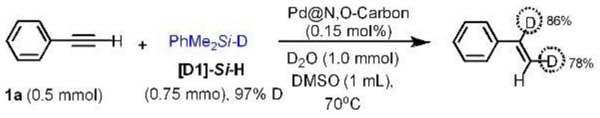
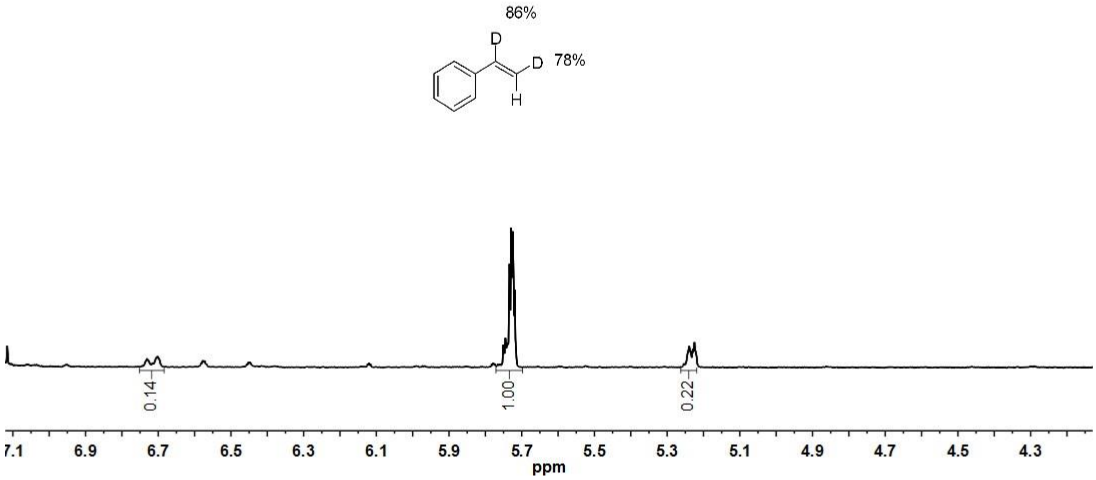









1a (0.5 mmol)
PhMe2Si-D
[D1]-Si-H
(0.75 mmo), 97% D
Pd@N,O-Carbon
(0.15 mol%)
D2O (1.0 mmol)
DMSO (1 mL),
70oC
D 86%
D 78%
H


86%
D
D 78%
H
0.14
1.00
0.22
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
5.5
5.3
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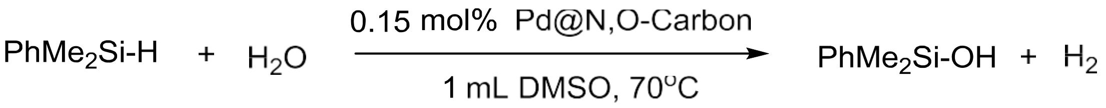
4.9
4.7
4.5
4.3
ppm



$$PhMe_2Si\text{-}H + H_2O \xrightarrow[\text{1 mL DMSO, 70}^{o}\text{C}]{\text{0.15 mol\% Pd@N,O-Carbon}} PhMe_2Si\text{-}OH + H_2$$

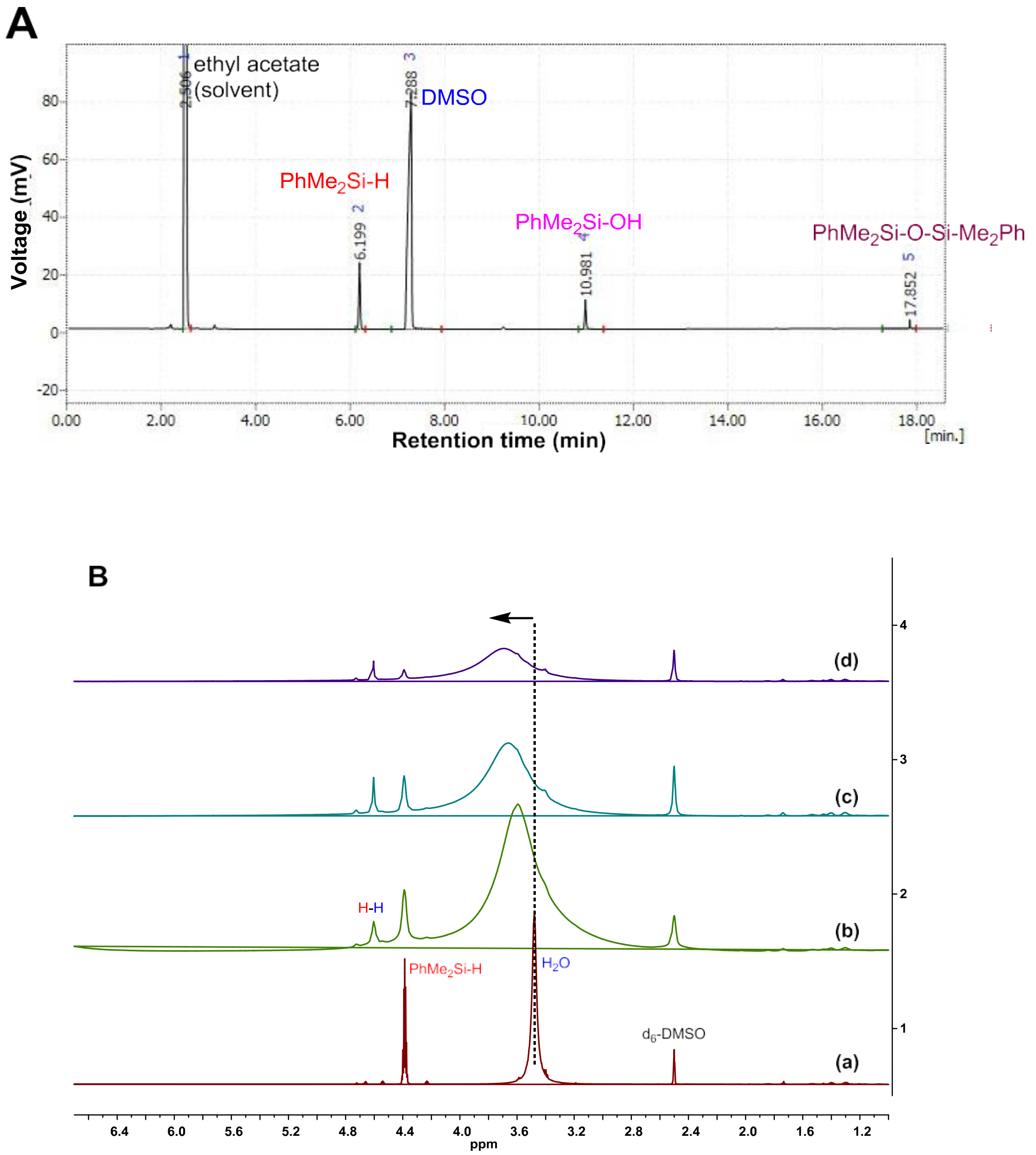
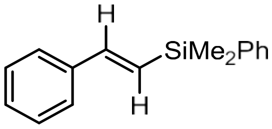


Figure S3. (A)GC analysis spectrum for $PhMe_2SiH$ oxidation with H_2O catalyzed by Pd@N,O-Carbon after 3 min. (B) In-situ NMR for $PhMe_2SiH$ oxidation with H_2O catalyzed by Pd@N,O-Carbon. (a) the mixture of $PhMe_2SiH$ and H_2O in d_6-DMSO. (b) Upon addition of the catalyst Pd@N,O-Carbon into the reaction mixture at 1 min. (c) at 10 min. (d) at 20 min. Reaction conditions: $PhMe_2SiH$ (0.75 mmol), H_2O (1.0 mmol), Pd@N,O-Carbon (5 mg, 0.15 mol% of Pd), d_6-DMSO (1 mL), 70^{o}C.

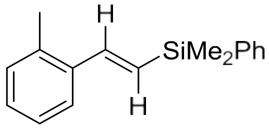
Upon addition of the catalyst Pd@N,O-Carbon into the reaction mixture of $PhMe_2SiH$ and H_2O in d_6-DMSO, the ^1H NMR peak of H_2O shifted to low magnetic field, and such trend keep gradually going on. Meanwhile, the H_2 gas was generated instantly and its intensity also increased gradually. Such observation indicates that H_2O indeed interacts with Pd NPs and silane oxidation was enabled efficiently.

6. ^{1}H and ^{13}C NMR spectra for vinylsilanes



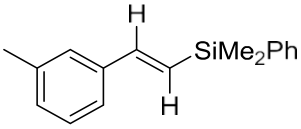
(E)-dimethyl(phenyl)(styryl)silane (2a):

The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.35 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.23 (m, 1H), 6.94 (d, *J* = 19.1 Hz, 1H), 6.59 (d, *J* = 19.1 Hz, 1H), 0.43 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.27, 138.57, 138.15, 133.92, 129.04, 128.52, 128.15, 127.81, 127.11, 126.49, -2.54. HRMS-(ESI-TOF) for $C_{16}H_{18}SiNa$ $[M+Na]^+$: calculated: 261.1075, found: 261.1073.



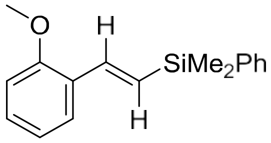
(E)-dimethyl(2-methylstyryl)(phenyl)silane (2b):

The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.55 (m, 2H), 7.55 – 7.51 (m, 1H), 7.39 – 7.34 (m, 3H), 7.23 – 7.08 (m, 4H), 6.49(d, *J* = 19.0 Hz, 1H), 2.35 (s, 3H), 0.44 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.14, 138.68, 137.47, 135.38, 133.91, 130.31, 129.01, 128.87, 127.89, 127.80, 126.08, 125.36, 19.57, -2.46. HRMS-(ESI-TOF) for $C_{17}H_{20}SiNa$ $[M+Na]^+$: calculated: 275.1232, found: 275.1228.

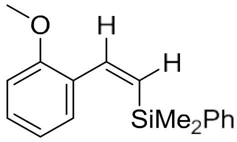


(E)-dimethyl(3-methylstyryl)(phenyl)silane (2c):

The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.38 – 7.33 (m, 3H), 7.30 – 7.18 (m, 3H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 19.1 Hz, 1H), 6.57 (d, *J* = 19.1 Hz, 1H), 2.34 (s, 3H), 0.42 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.40, 138.63, 138.10, 138.05, 133.91, 129.00, 128.94, 128.41, 127.79, 127.17, 126.79, 123.69, 21.35, -2.53. HRMS-(ESI-TOF) for $C_{17}H_{20}SiNa$ $[M+Na]^+$: calculated: 275.1232, found: 275.1225. HRMS-(ESI-TOF) for $C_{17}H_{20}SiNa$ $[M+Na]^+$: calculated: 275.1232, found: 275.1225.



2e-E



2e-Z

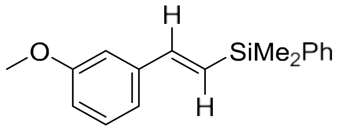
The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes), (E:Z = 1:0.8). HRMS-(ESI-TOF) for $C_{17}H_{20}OSiNa$ $[M+Na]^+$: calculated: 291.1181, found: 291.1178.

(E)-(2-methoxystyryl)dimethyl(phenyl)silane (2e-E):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.55 (s, 1H), 7.39 (d, *J* = 19.8 Hz, 1H), 7.37 – 7.36 (m, 3H), 7.26 – 7.23 (m, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 19.3 Hz, 1H), 3.85 (s, 3H), 0.44 (s, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 156.69, 139.55, 139.04, 133.92, 129.73, 129.19, 129.00, 127.74, 127.32, 127.31, 120.58, 110.93, 55.47, -2.45.

(Z)-(2-methoxystyryl)dimethyl(phenyl)silane (2e-Z):

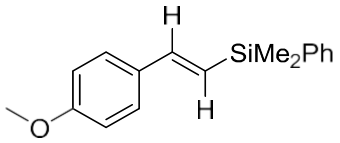
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, 1H), 7.54 -7.49 (m, 2H), 7.34 – 7.30 (m, 3H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.77 (d, *J* = 7.4 Hz, 1H), 6.06 (d, *J* = 15.0 Hz, 1H), 3.80 (s, 3H), 0.21 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.85, 143.95, 139.93, 133.68, 130.31, 128.97, 128.89, 128.66, 127.67, 126.34, 119.82, 109.98, 55.31, -1.26.



(E)-(3-methoxystyryl)dimethyl(phenyl)silane (2f):

The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes:DCM = 4:1).

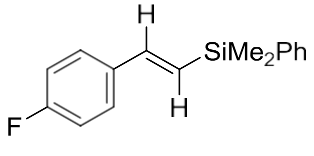
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.39 – 7.35 (m, 3H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 1.8 Hz, 1H), 6.91 (d, *J* = 19.1 Hz, 1H), 6.82 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.57 (d, *J* = 19.1 Hz, 1H), 3.82 (s, 3H), 0.43 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.84, 145.11, 139.63, 138.51, 133.92, 129.48, 129.05, 127.82, 127.48, 119.26, 114.12, 111.36, 55.24, -2.55. HRMS-(ESI-TOF) for $C_{17}H_{20}OSiNa$ $[M+Na]^+$: calculated: 291.1181, found: 291.1177.



(E)-(4-methoxystyryl)dimethyl(phenyl)silane (2g):

The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes).

^{1}H NMR (600 MHz, CDCl3) δ 7.58 – 7.55 (m, 2H), 7.40 – 7.37 (m, 2H), 7.37 – 7.35 (m, 3H), 6.88 (d, J = 19.1 Hz, 1H), 6.87-6.85 (m, 2H), 6.41 (d, J = 19.1 Hz, 1H), 3.81 (s, 3H), 0.42 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.68, 144.70, 138.87, 133.92, 131.17, 128.96, 127.77, 127.75, 124.19, 113.89, 55.30, -2.46. HRMS-(ESI-TOF) for $C_{17}H_{20}OSiNa$ $[M+Na]^+$: calculated: 291.1181, found: 291.1175.

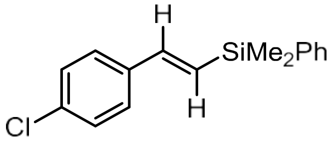


(E)-(4-fluorostyryl)dimethyl(phenyl)silane (2h):

The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes).

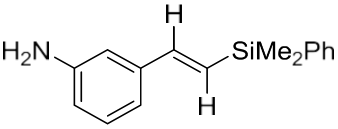
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.41 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.38 – 7.35 (m, 3H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 19.1 Hz, 1H), 6.48 (d, *J* = 19.1 Hz, 1H), 0.43 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.93, 133.89, 129.08, 128.08, 128.00, 127.84, 127.80, 126.87, 115.51, 115.29, -2.57. HRMS-(ESI-TOF) for $C_{16}H_{17}FSiNa$ $[M+Na]^+$: calculated: 279.0981, found:

279.0983.



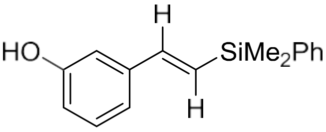
(E)-(4-chlorostyryl)dimethyl(phenyl)silane (2i):

The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes).
^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.39 – 7.33 (m, 5H), 7.31 – 7.22 (m, 2H), 6.87 (d, *J* = 19.1 Hz, 1H), 6.55 (d, *J* = 19.1 Hz, 1H), 0.43 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.00, 137.41, 135.80, 133.04, 132.14, 128.28, 127.82, 127.27, 127.01, 126.85, -0.00, -3.45. HRMS-(ESI-TOF) for $C_{16}H_{17}ClSiNa$ $[M+Na]^+$: calculated: 295.0686, found: 295.0684.



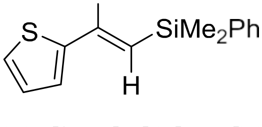
(E)-3-(2-(dimethyl(phenyl)silyl)vinyl)aniline (2j):

The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes:DCM = 1: 0.7).
^1H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.38 – 7.35 (m, 3H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.98 (s, 1H), 6.86 (d, *J* = 19.1 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.56 (d, *J* = 19.1 Hz, 1H), 0.42 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.34, 139.77, 138.29, 133.90, 129.74, 129.08, 128.53, 127.94, 127.83, 121.76, 118.54, 116.62, -2.60. HRMS-(ESI-TOF) for $C_{16}H_{20}NSi$ $[M+H]^+$: calculated: 254.1365, found: 254.1364.



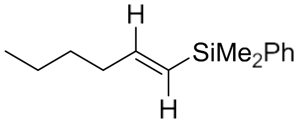
(E)-3-(2-(dimethyl(phenyl)silyl)vinyl)phenol (2k):

The products were isolated as a colorless oil following column chromatography (SiO_2, DCM).
^1H NMR (600 MHz, $CDCl_3$) δ 7.59-7.53 (m, 2H), 7.39 – 7.34 (m, 3H), 7.20 (t, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.92 (s, 1H), 6.87 (d, *J* = 19.1 Hz, 1H), 6.74 (dd, *J* = 8.0, 2.3 Hz, 1H), 6.56 (d, *J* = 19.1 Hz, 1H), 4.71 (s, 1H), 0.43 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.73, 133.90, 129.73, 129.07, 127.82, 119.46, 115.15, 112.89, -2.57. HRMS-(ESI-TOF) for $C_{16}H_{18}OSiNa$ $[M+Na]^+$: calculated: 277.1025, found: 277.1020.



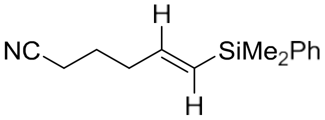
(E)-dimethyl(phenyl)(2-(thiophen-2-yl)vinyl)silane (2m):

The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes).
^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.40 – 7.35 (m, 3H), 7.21 – 7.17 (m, 1H), 6.99 (d, *J* = 18.8Hz, 1H), 6.99-6.95 (m, 2H), 6.32 (d, *J* = 18.8 Hz, 1H), 0.41 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.04, 137.73, 133.92, 132.98, 129.09, 127.83, 127.46, 126.83, 125.95, 125.05, -2.56. HRMS-(ESI-TOF) for $C_{14}H_{16}SSiNa$ $[M+Na]^+$: calculated: 267.0640, found: 267.0644.



(E)-hex-1-en-1-yldimethyl(phenyl)silane (2n):

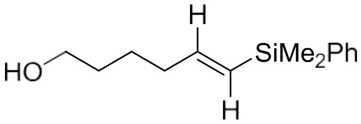
The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes). ^1H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.38 – 7.33 (m, 3H), 6.13 (dt, *J* = 18.5, 6.3 Hz, 1H), 5.76 (d, *J* = 18.5 Hz, 1H), 2.16 (td, *J* = 7.2, 6.6 Hz, 2H), 1.44 – 1.37 (m, 2H), 1.37 – 1.29 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.32 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.45, 139.40, 133.81, 128.77, 127.67, 127.14, 36.50, 30.81, 22.26, 13.96, -2.44. HRMS-(ESI-TOF) for $C_{14}H_{22}SiNa$ $[M+Na]^+$: calculated: 241.1388, found: 241.1383.



(E)-6-(dimethyl(phenyl)silyl)hex-5-enenitrile (2o):

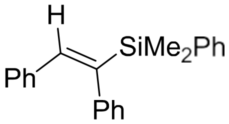
The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes:EA = 4:1).

^1H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.37 – 7.34 (m, 3H), 6.02 (dt, *J* = 18.5, 6.2 Hz, 1H), 5.86 (d, *J* = 18.6 Hz, 1H), 2.37 – 2.26 (m, 4H), 1.79 (p, *J* = 7.2 Hz, 2H), 0.33 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.69, 138.64, 133.75, 130.46, 128.99, 127.79, 35.22, 24.23, 16.45, -2.59. HRMS-(ESI-TOF) for $C_{14}H_{20}NSi$ $[M+H]^+$: calculated: 230.1365, found: 230.1360; for $C_{14}H_{19}NSiNa$ $[M+Na]^+$: calculated: 252.1184, found: 252.1185.



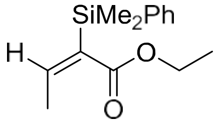
(E)-6-(dimethyl(phenyl)silyl)hex-5-en-1-ol (2p):

The products were isolated as a colorless oil following column chromatography (SiO_2, DCM). ^1H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.37 – 7.31 (m, 3H), 6.11 (dt, *J* = 18.5, 6.2 Hz, 1H), 5.78 (d, *J* = 18.5 Hz, 1H), 3.67 – 3.62 (m, 2H), 2.22 – 2.16 (m, 2H), 1.62 – 1.56 (m, 2H), 1.53 – 1.46 (m, 2H), 0.32 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.74, 139.22, 133.79, 128.82, 127.81, 127.70, 62.87, 36.41, 32.27, 24.74, -2.48. HRMS-(ESI-TOF) for $C_{14}H_{22}NaOSi$ $[M+Na]^+$: calculated: 257.1338, found: 257.1338.



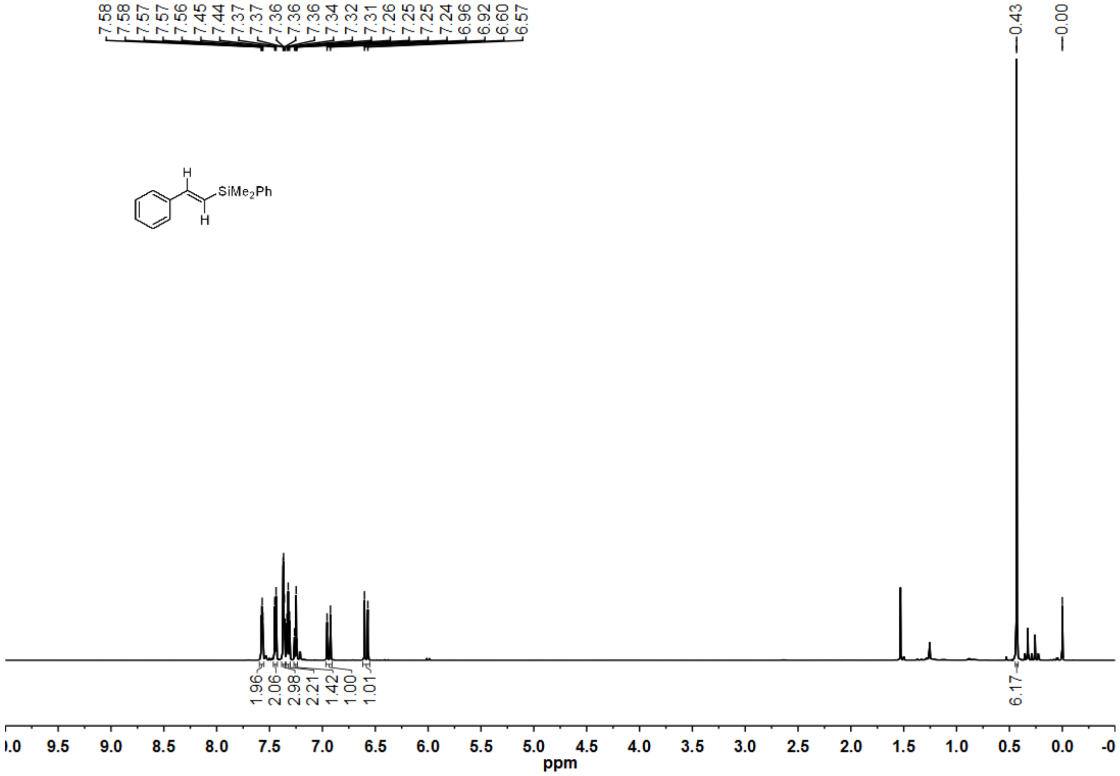
(E)-(1,2-diphenylvinyl)dimethyl(phenyl)silane (2q):

The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 2H), 7.38 – 7.31 (m, 3H), 7.26 – 7.12 (m, 3H), 7.08 – 7.04 (m, 3H), 6.95 – 6.91 (m, 2H), 6.91 – 6.87 (m, 2H), 6.82 (s, 1H), 0.39 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.98, 142.26, 139.15, 137.68, 137.20, 134.26, 129.52, 129.08, 128.50, 127.86, 127.72, 127.62, 127.14, 125.68, -3.10. HRMS-(ESI-TOF) for $C_{22}H_{22}NaSi$ $[M+Na]^+$: calculated: 337.1388, found: 337.1379.

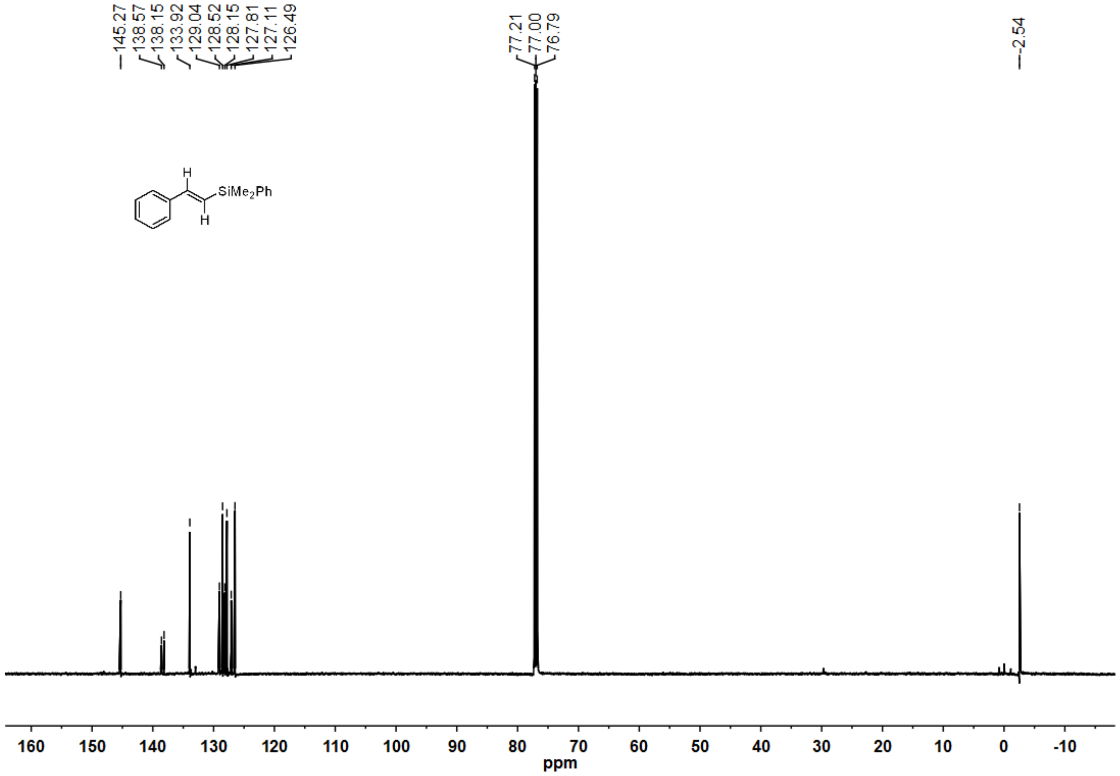


ethyl (E)-2-(dimethyl(phenyl)silyl)but-2-enoate (2r):

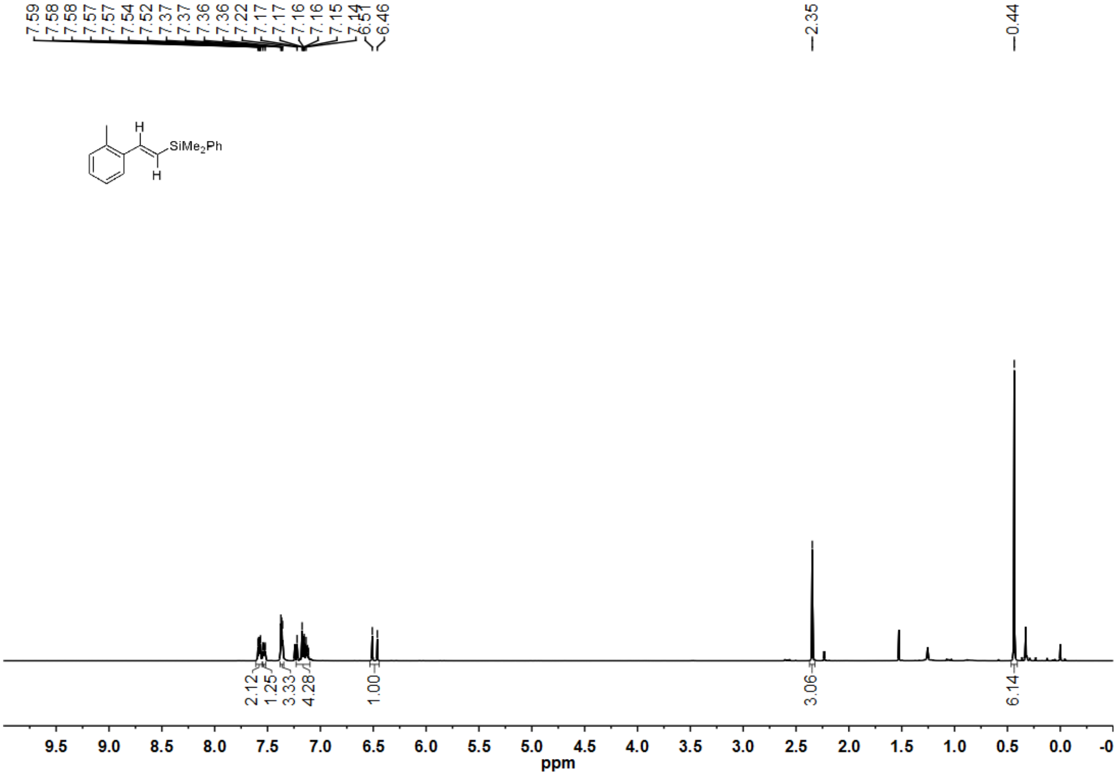
The products were isolated as a colorless oil following column chromatography (SiO_2, hexanes). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.38 – 7.32 (m, 3H), 6.30 (q, *J* = 6.8 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.99 (d, *J* = 6.9 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.43 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.00, 149.23, 137.46, 135.46, 134.02, 129.10, 127.69, 59.95, 17.81, 14.17, -2.59. HRMS-(ESI-TOF) for $C_{14}H_{20}O_2SiNa$ $[M+Na]^+$: calculated: 271.1130, found: 271.1134.



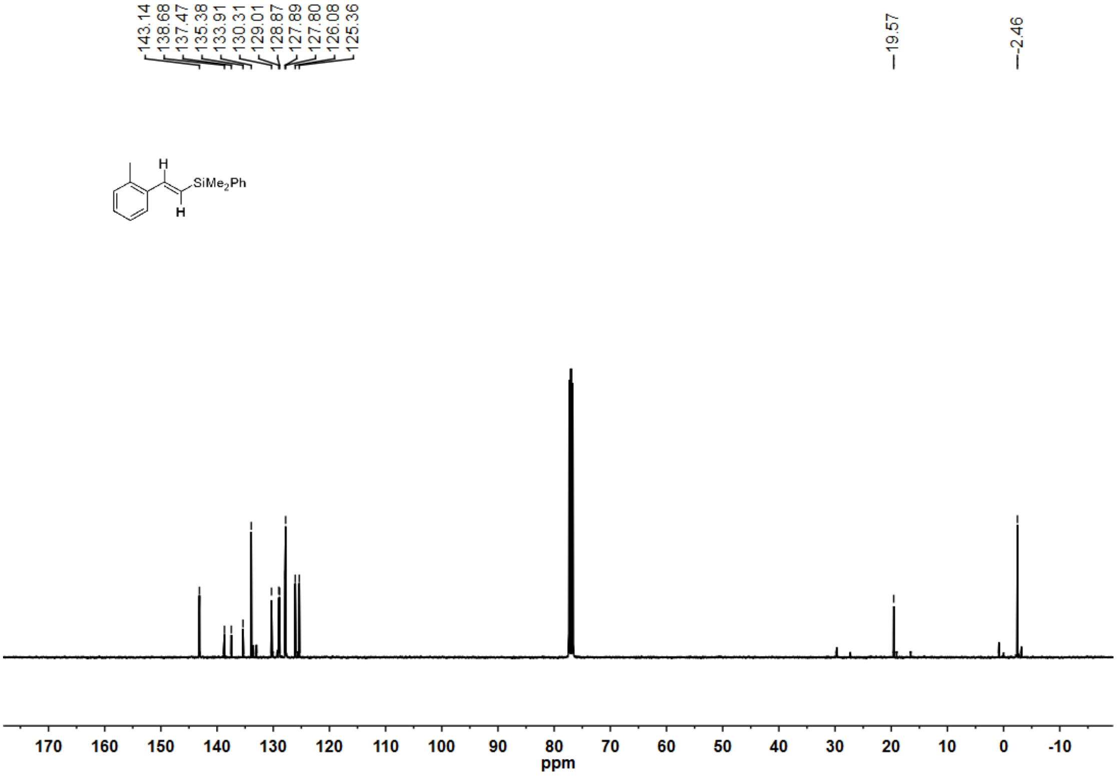
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **2a**



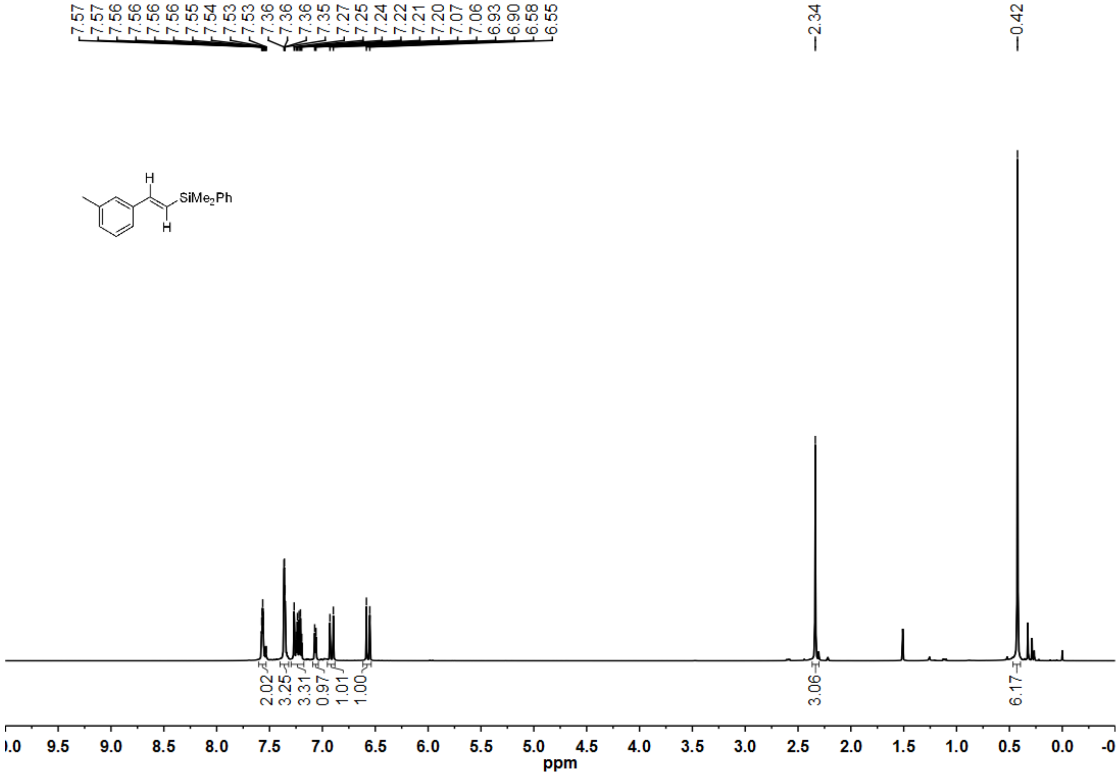
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2a**



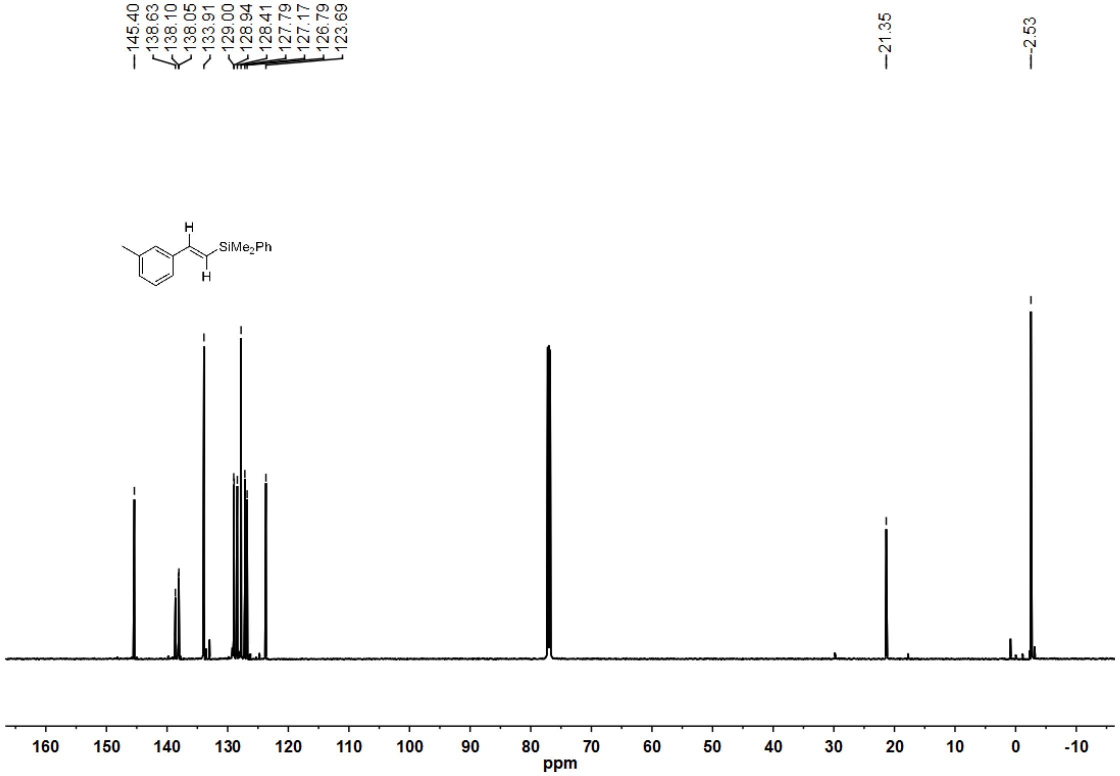
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **2b**



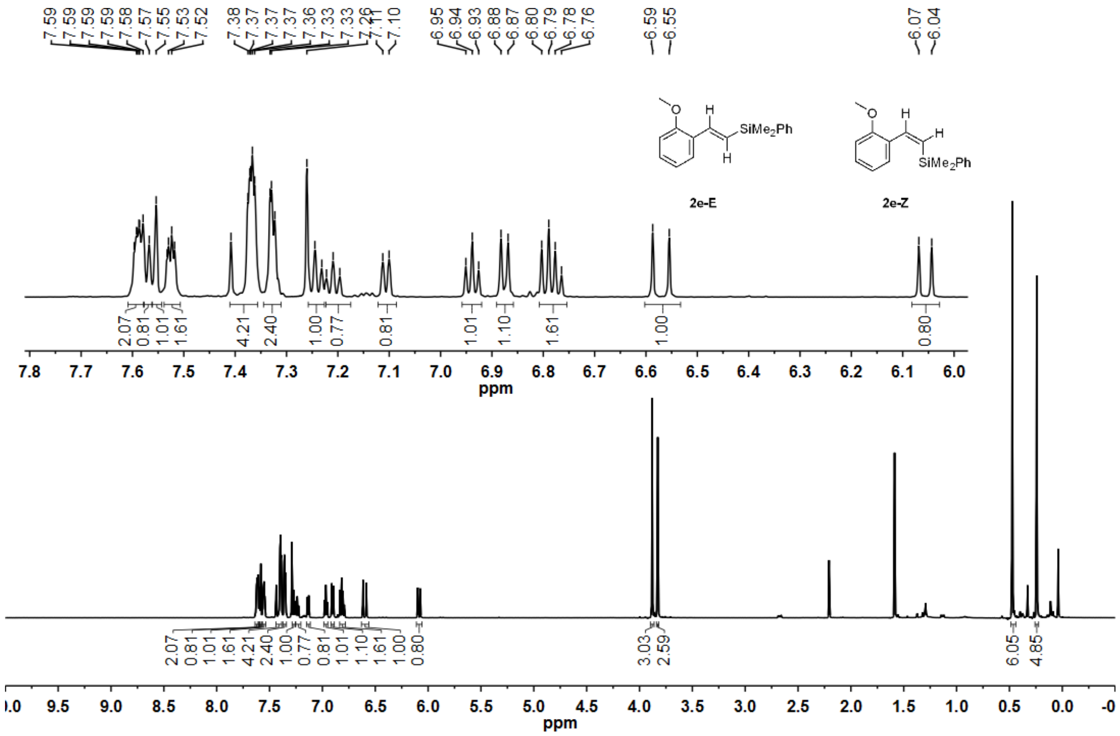
^{13}C NMR (101 MHz, CDCl$_3$) spectrum of **2b**



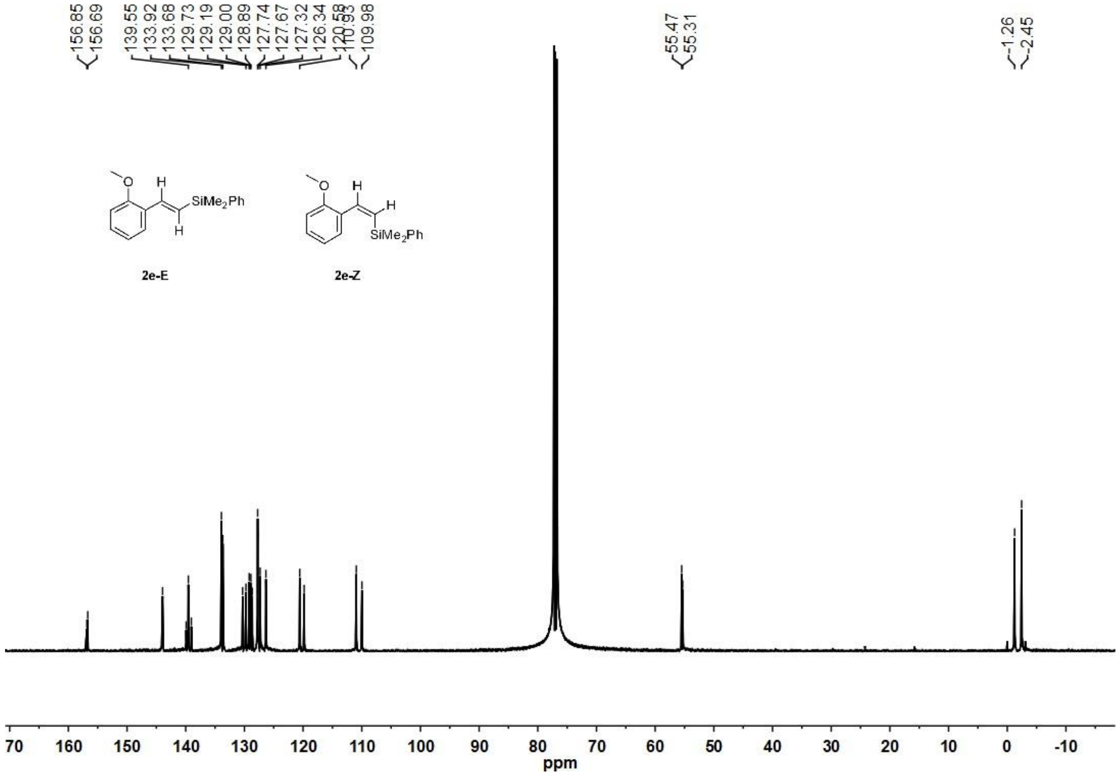
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2c**



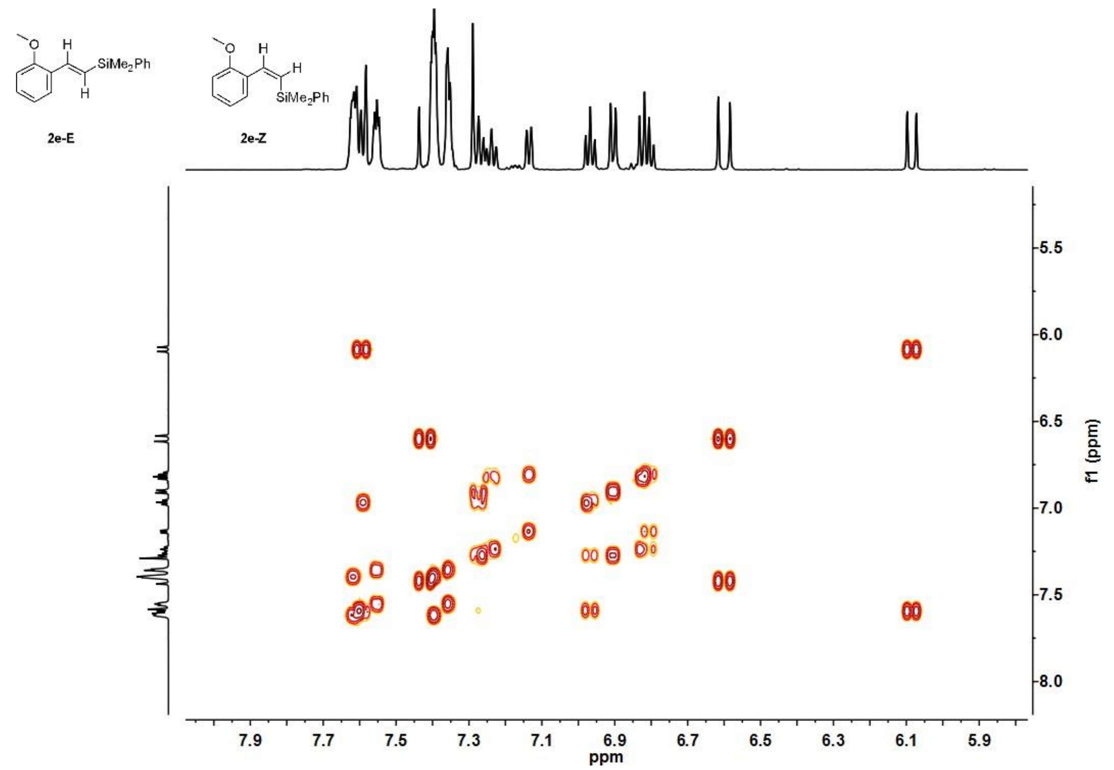
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2c**



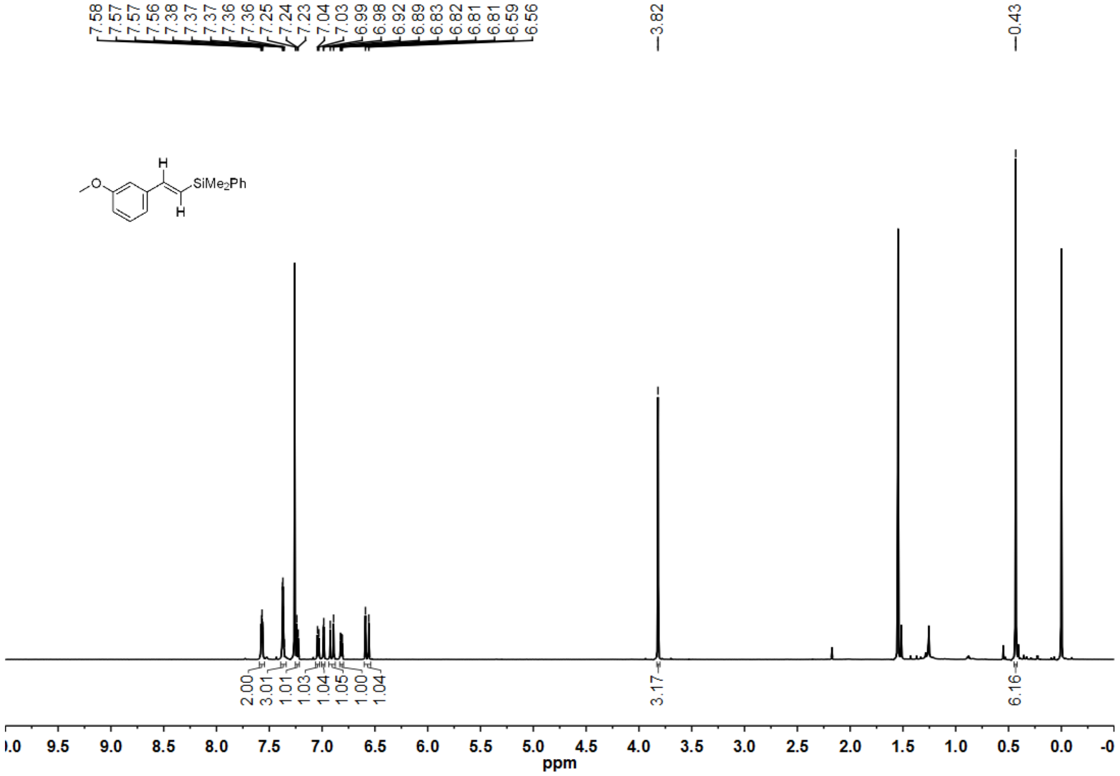
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **2e**



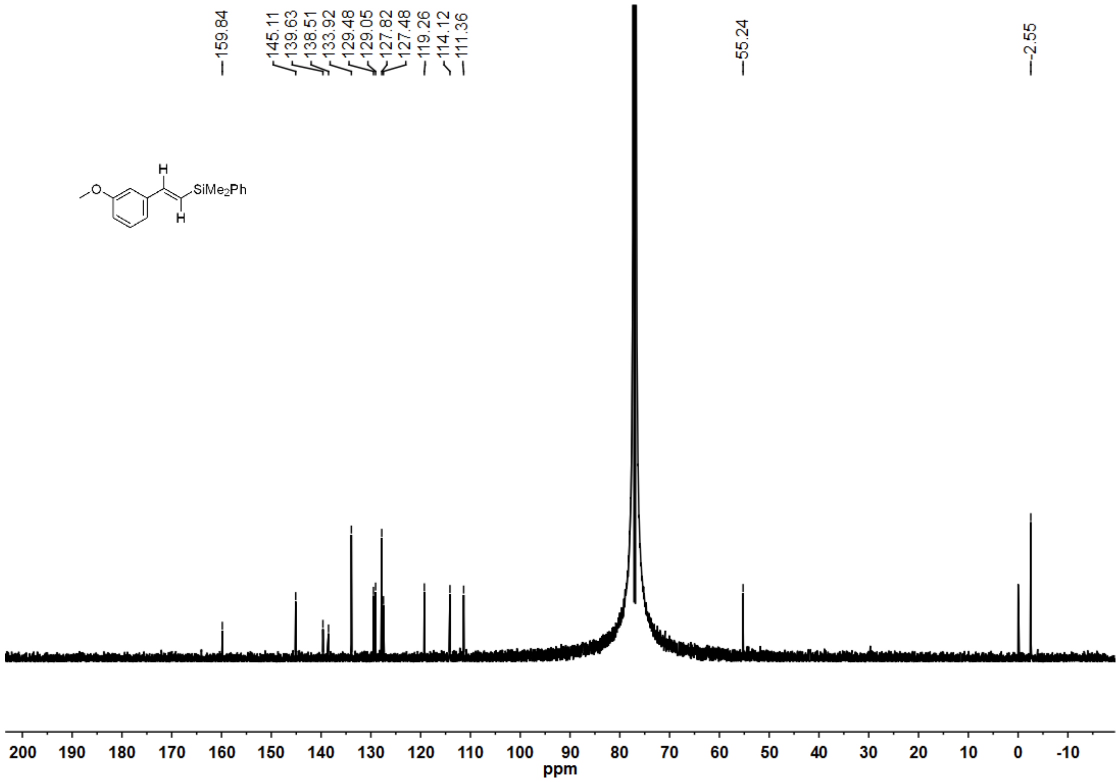
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2e**



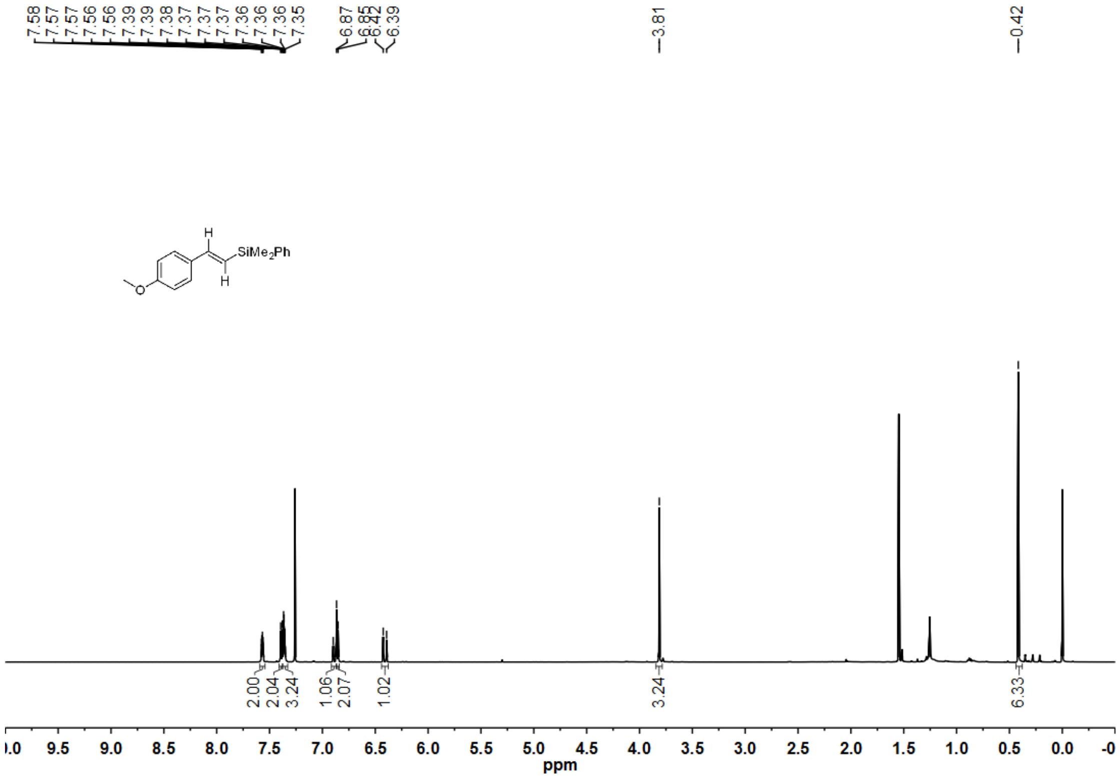
^{1}H - ^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **2e**



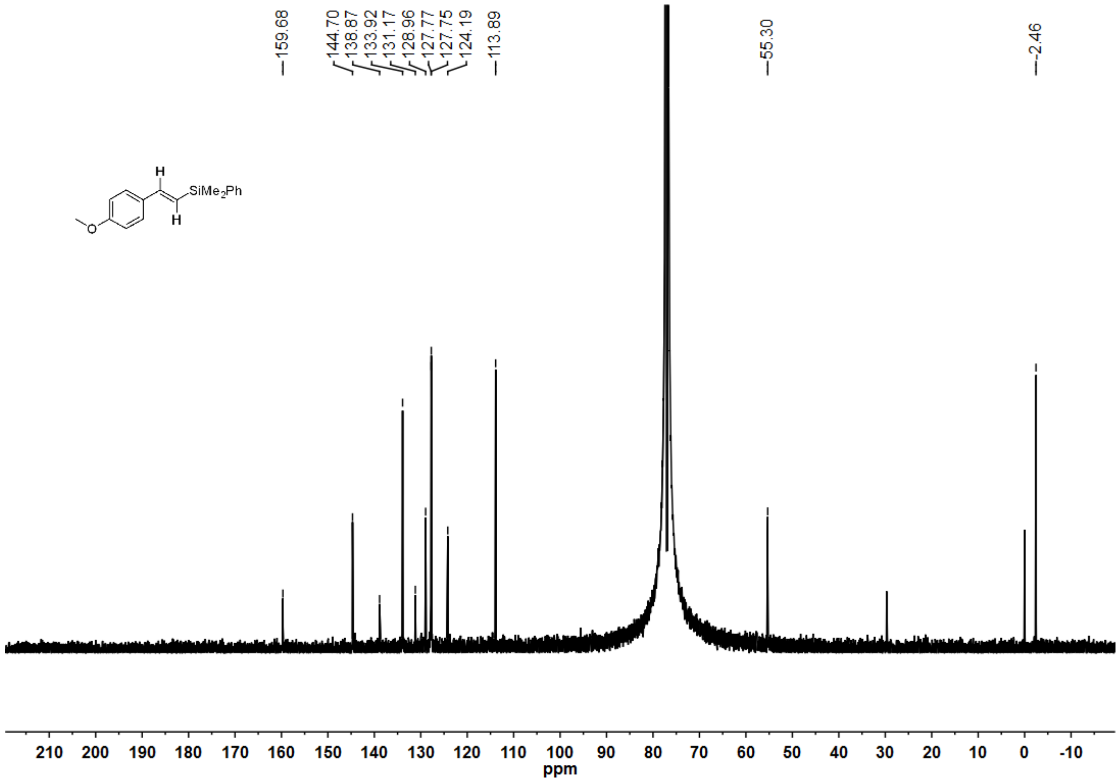
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2f**



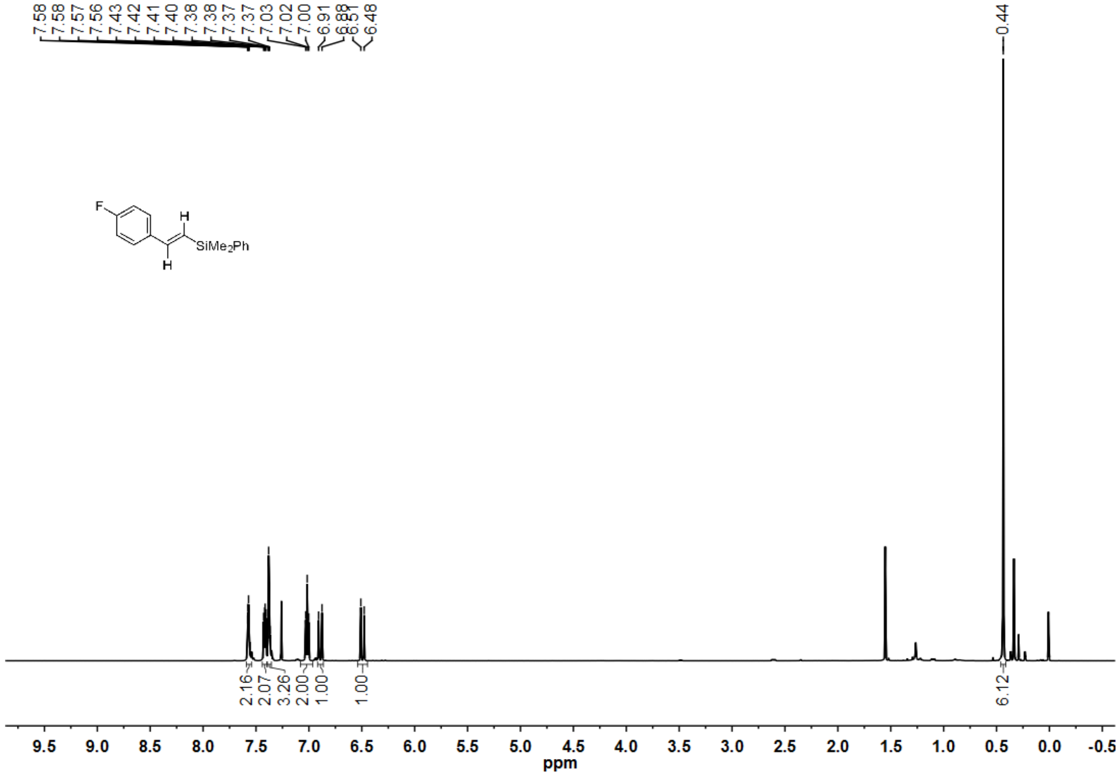
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2f**



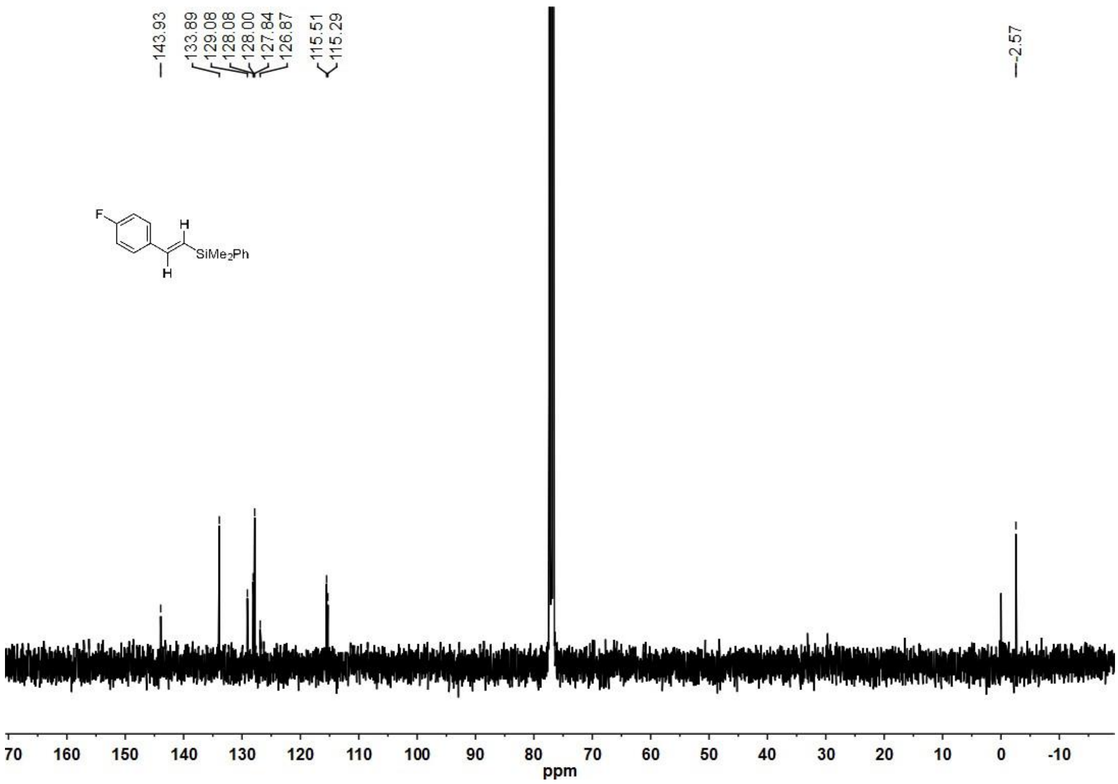
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **2g**



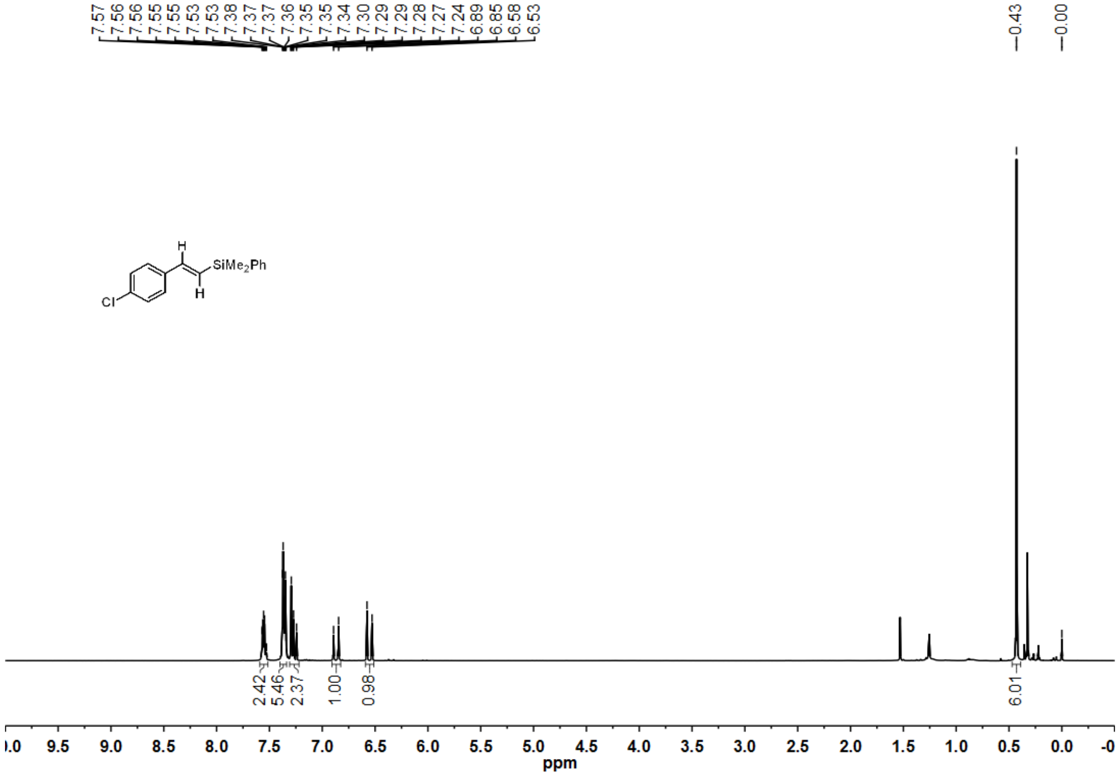
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2g**



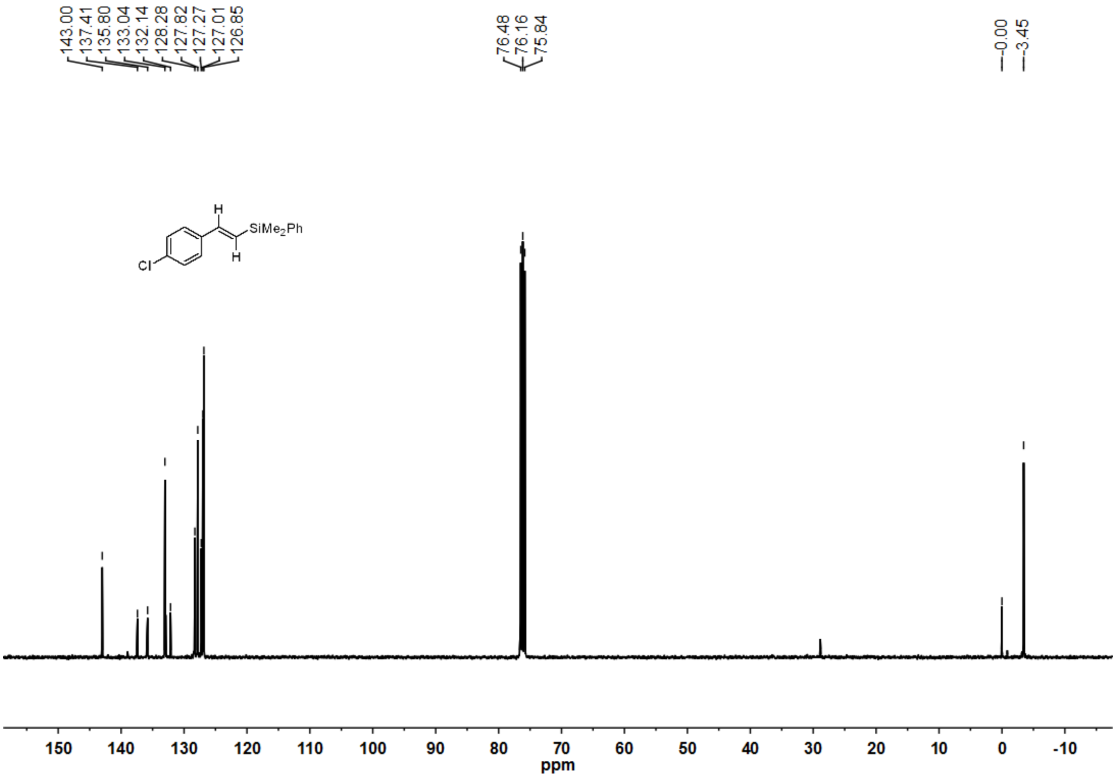
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **2h**



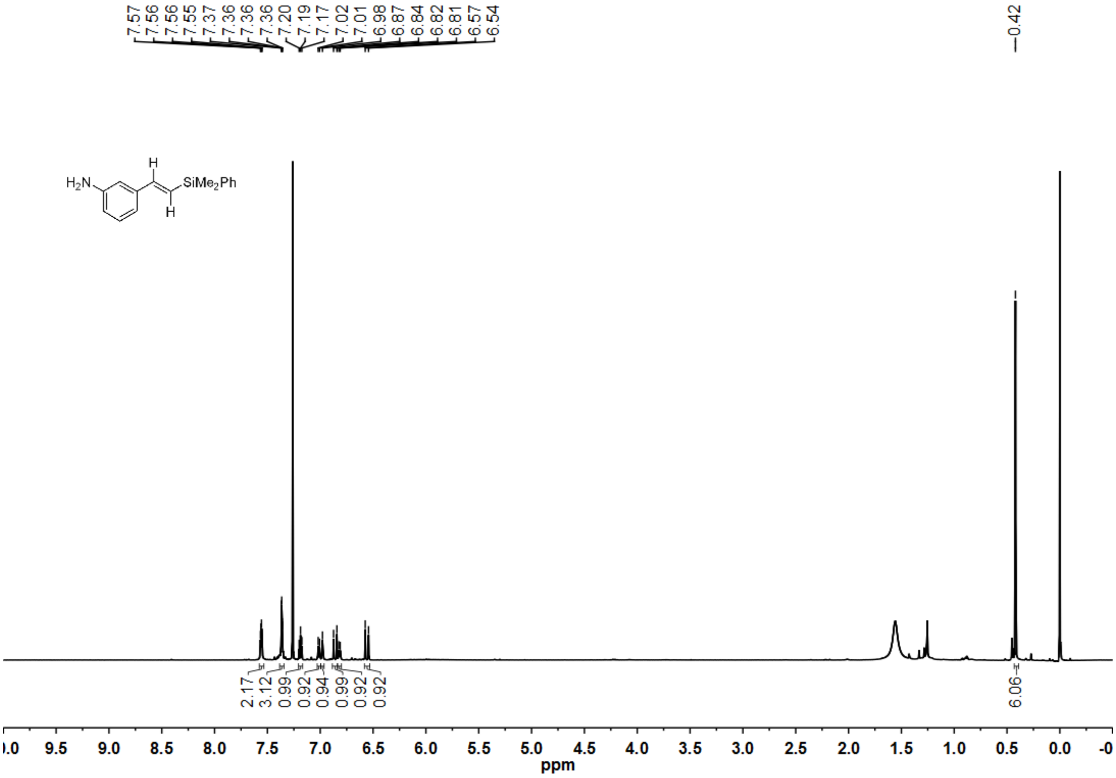
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2h**



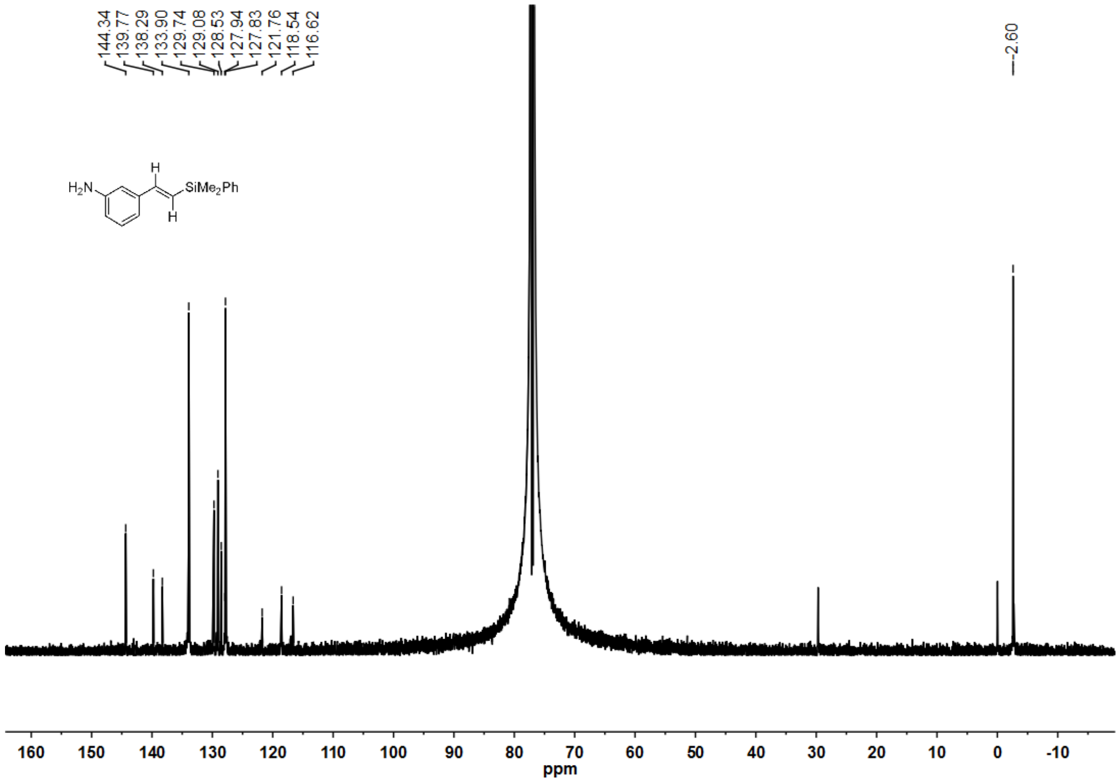
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **2i**



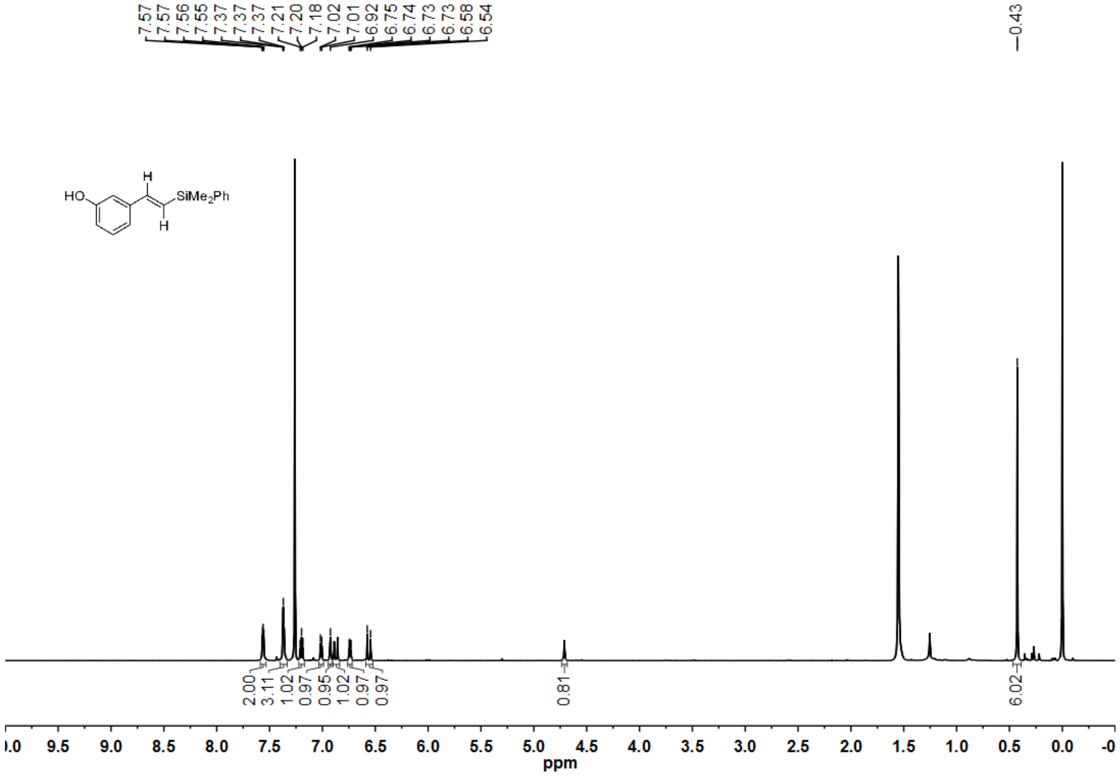
^{13}C NMR (101 MHz, CDCl$_3$) spectrum of **2i**



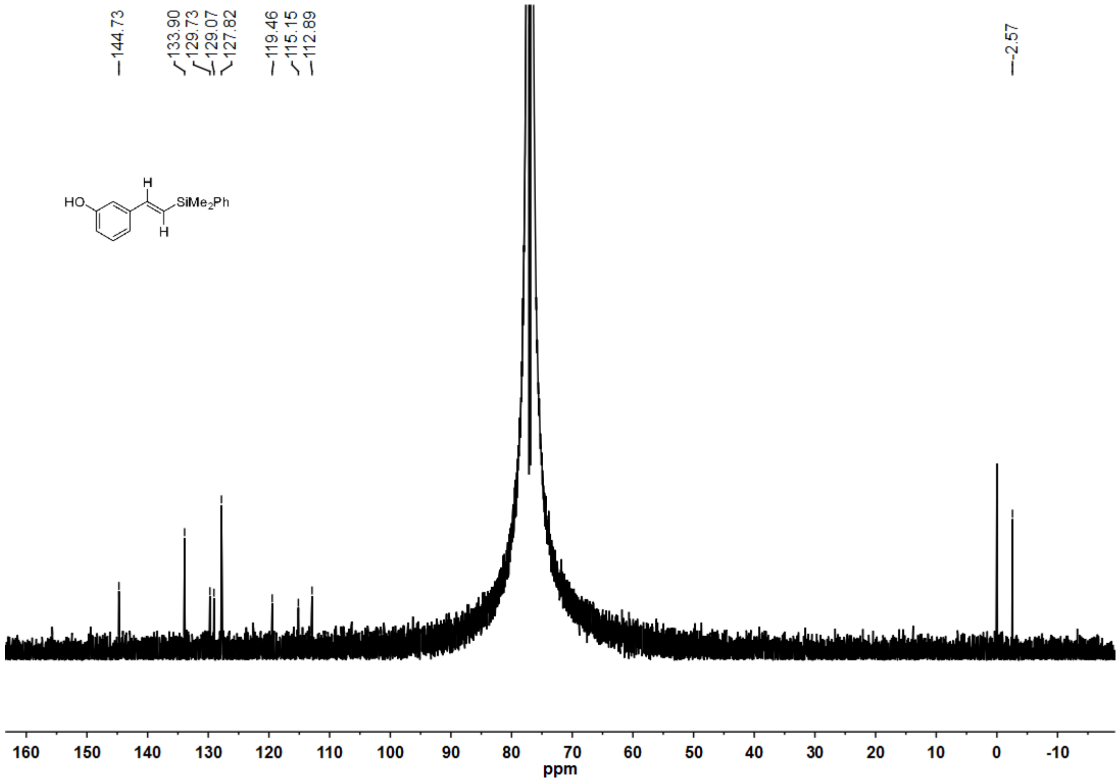
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **2j**



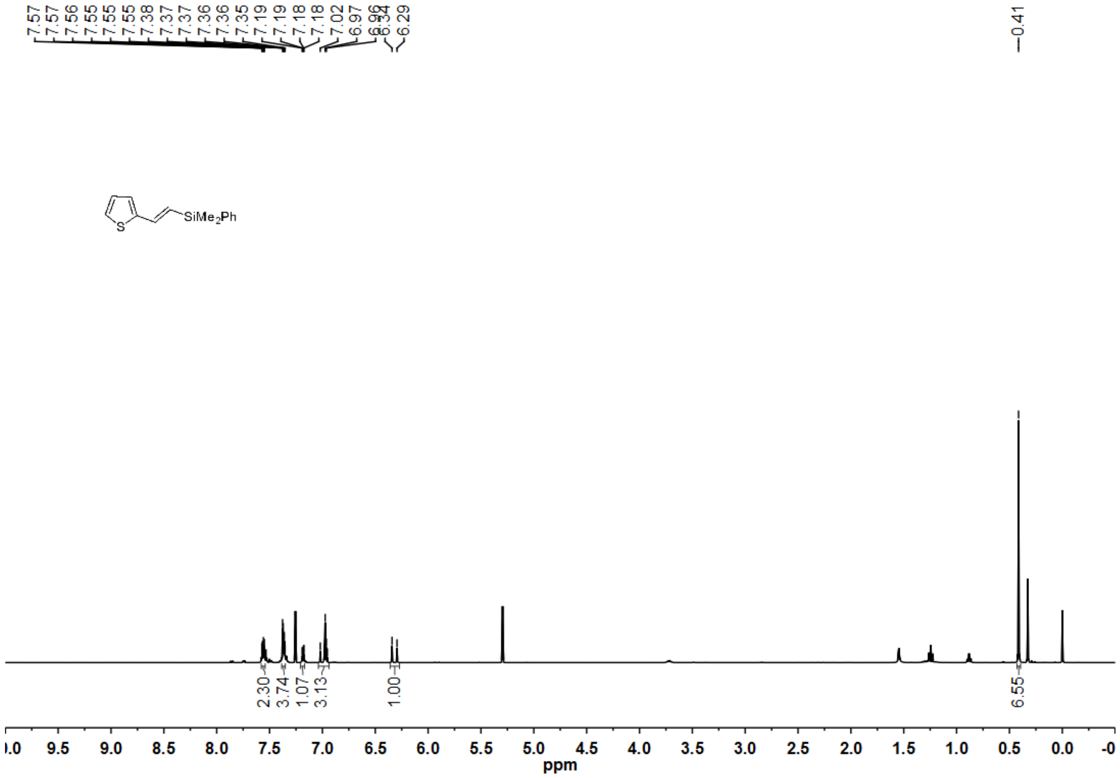
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2j**



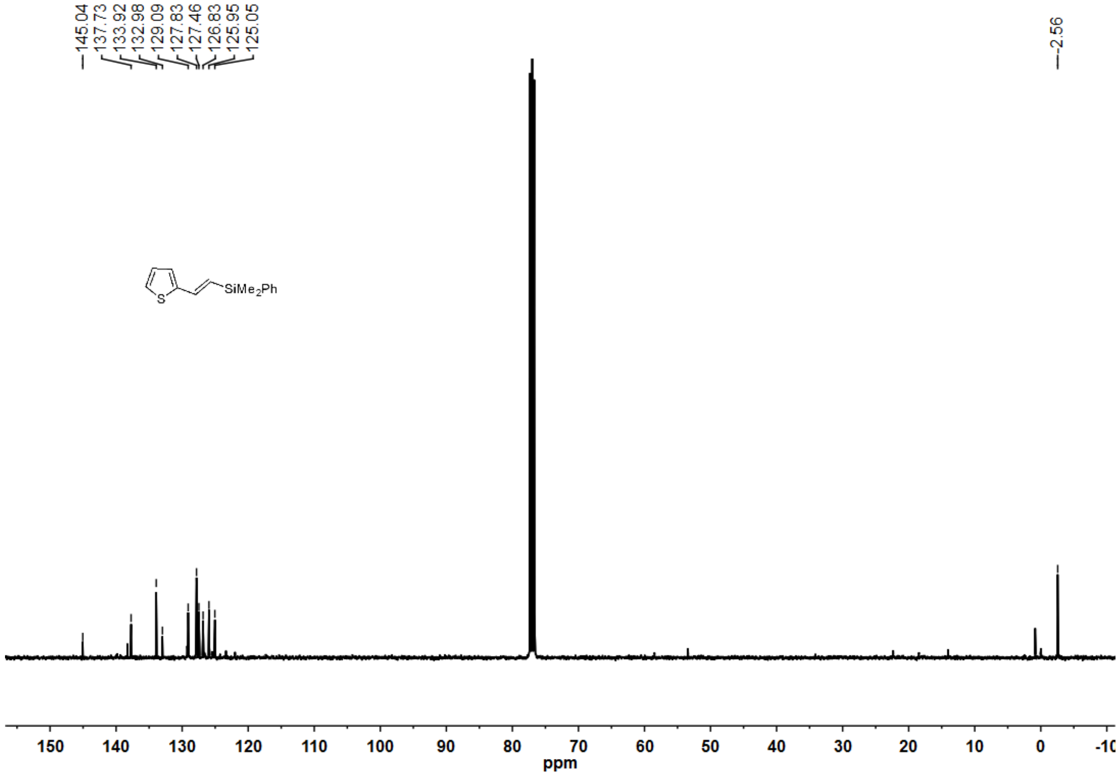
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **2k**



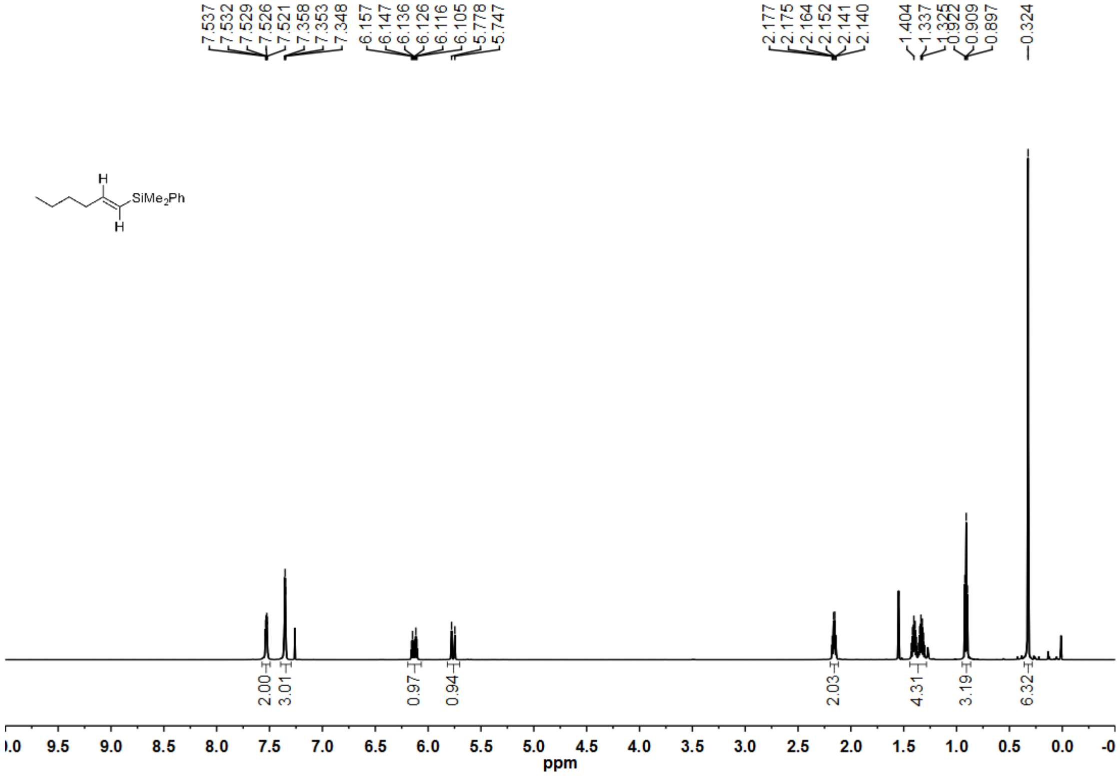
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2k**



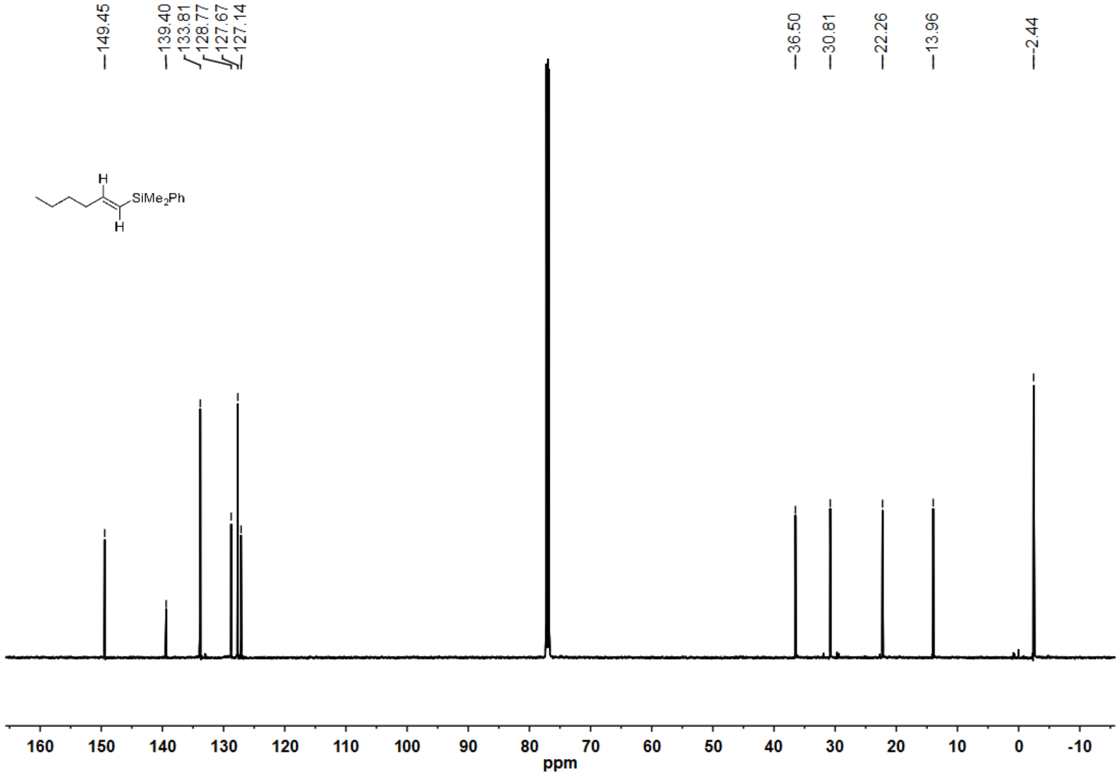
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **2m**



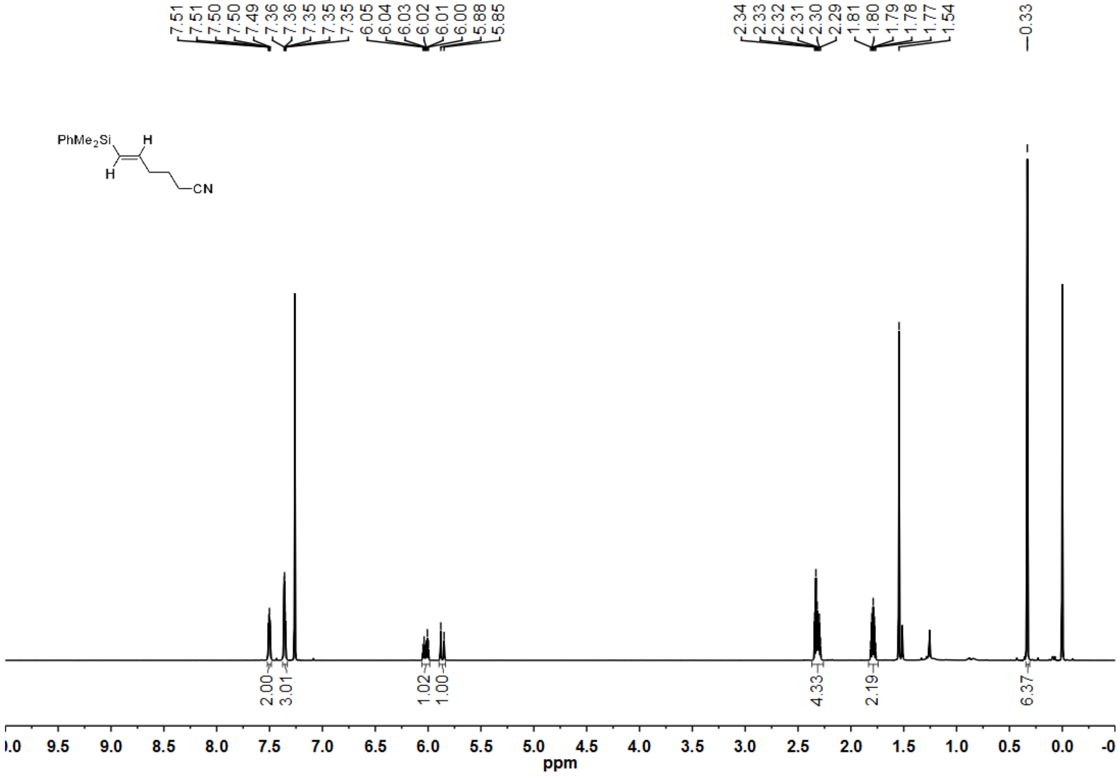
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **2m**



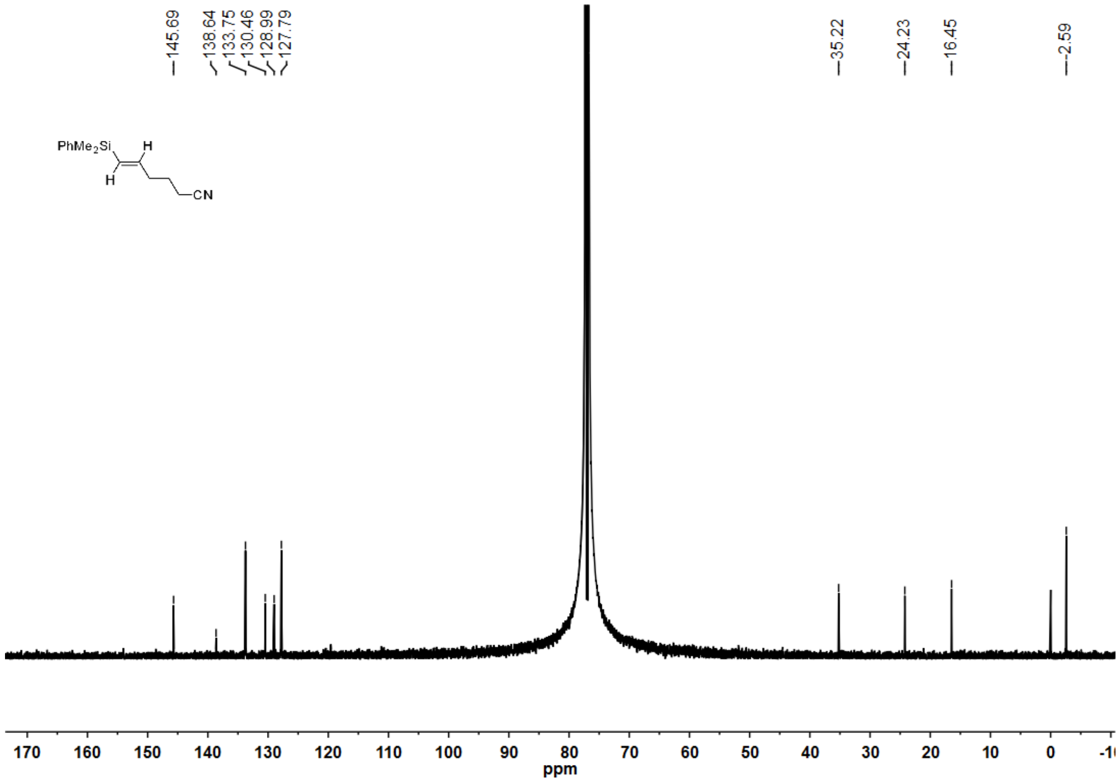
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2n**



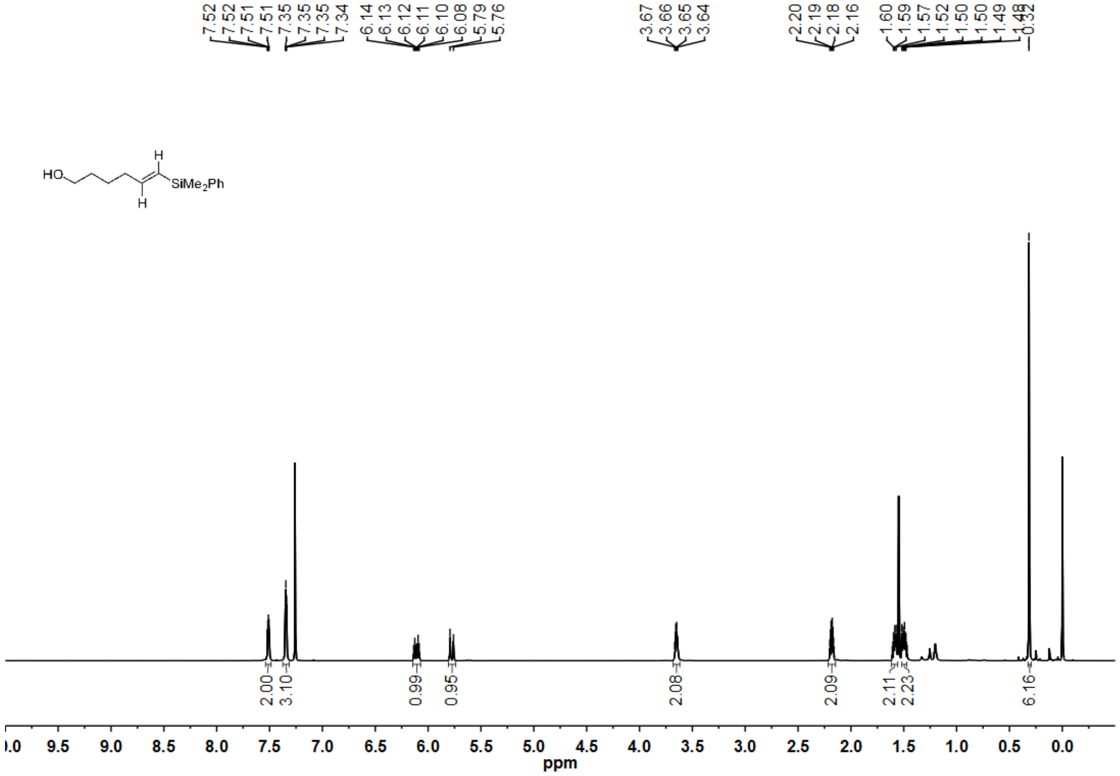
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2n**



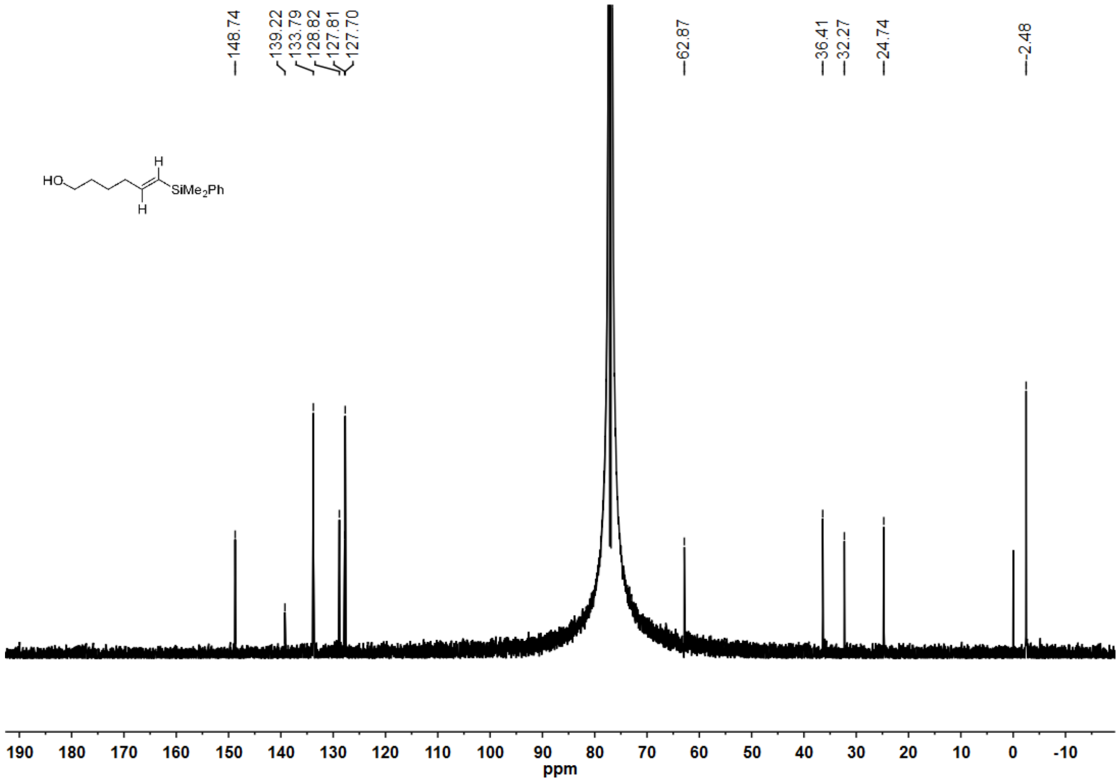
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **2o**



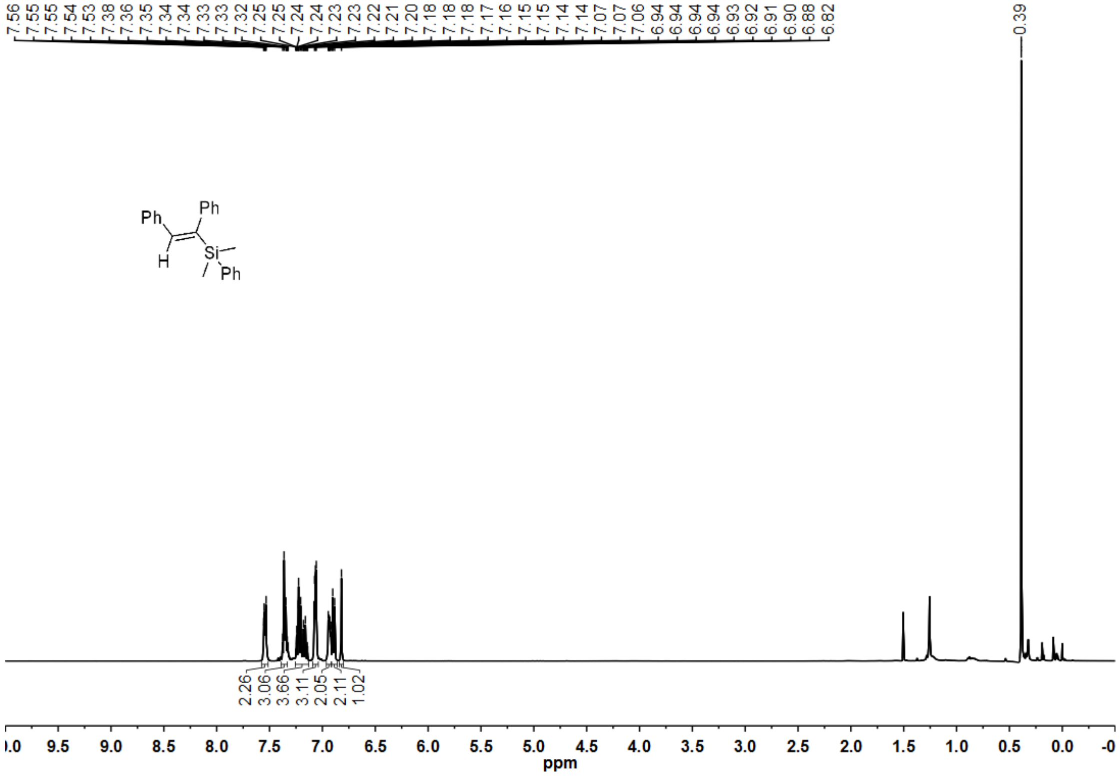
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2o**



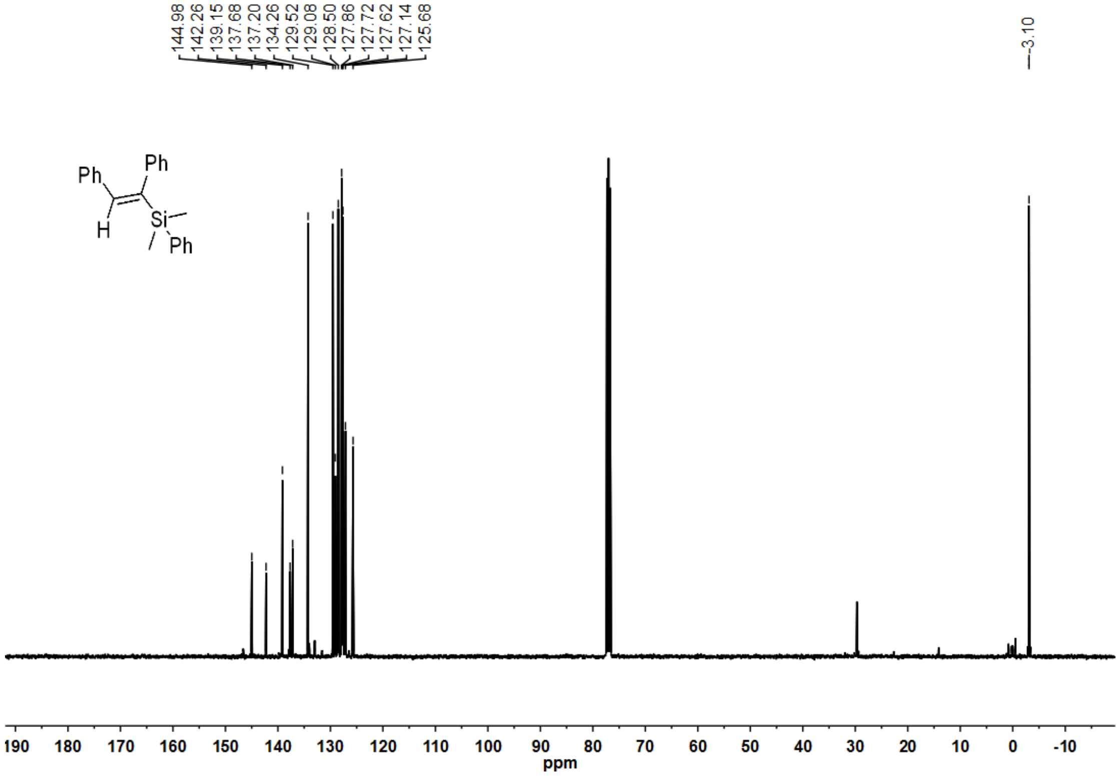
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **2p**



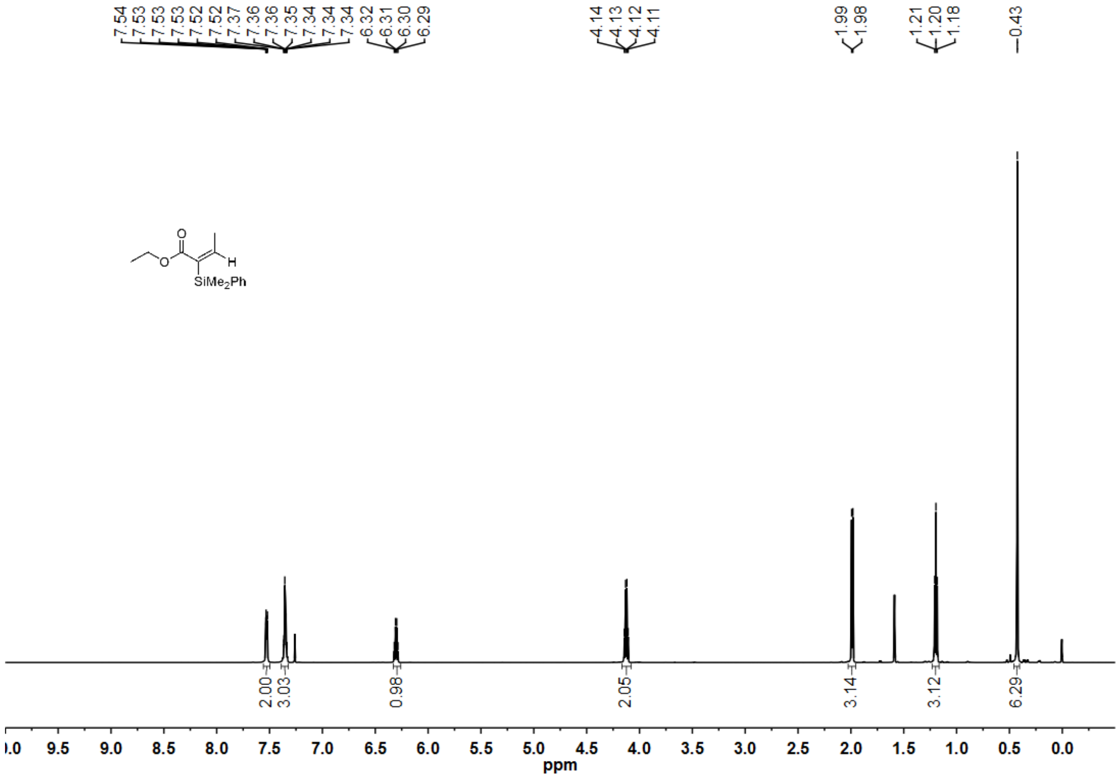
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2p**



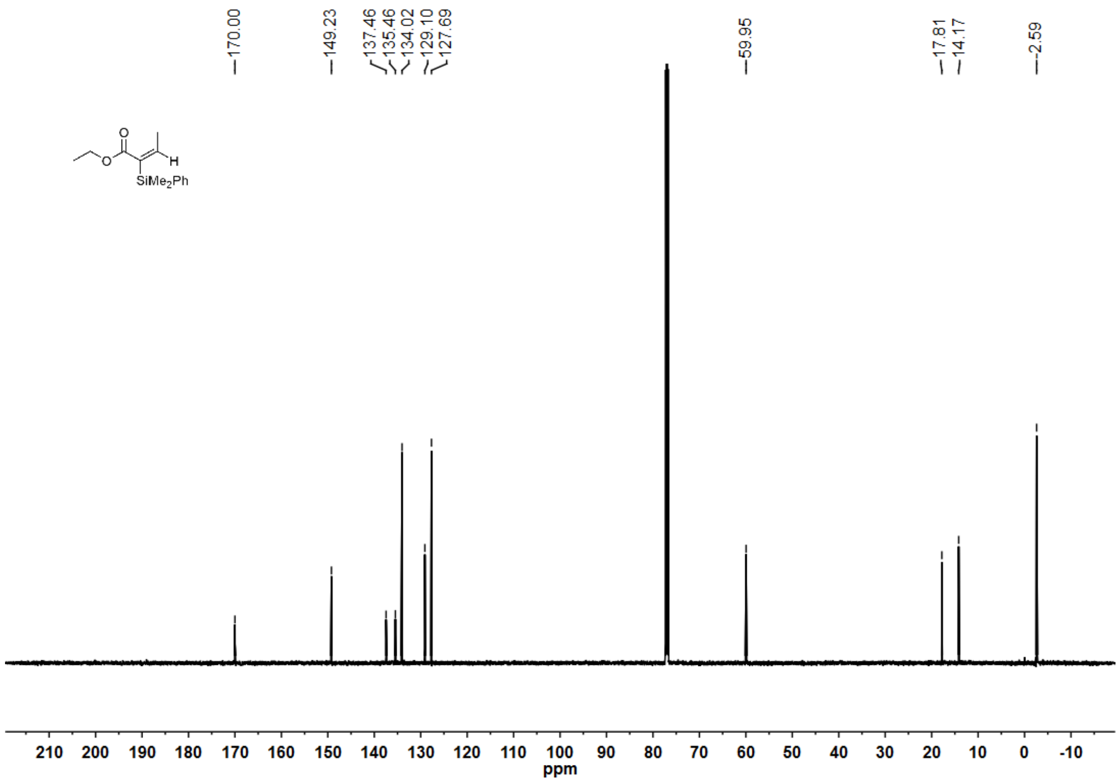
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **2q**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **2q**



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2r**



^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2r**