

Supplementary Information

Si-Stereogenic Remote Alkenyl Monohydrosilanes Enabled by CuH-Catalyzed Enantioselective Hydrosilylation of Strained Methylenecyclopropanes

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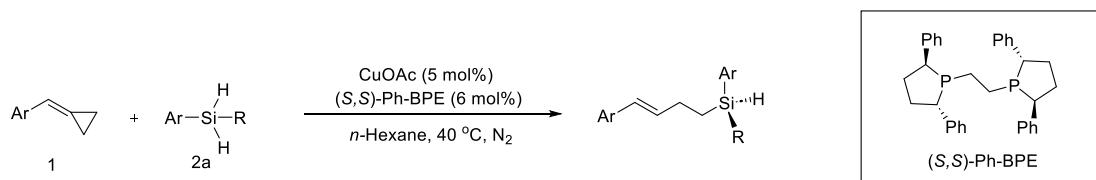
1. General Information

Commercially available chemicals were obtained from Adamas, Bide, Aldrich Chemical Co., and they were used as received unless otherwise stated. Anhydrous solvent, purchased from Acros Organics and *J&K* Chemical, were used as received. All reactions were carried out using Schlenk tube under N₂ atmosphere. NMR Spectra were recorded on 600 MHz and 400 MHz NMR spectrometers in the deuterated solvent indicated. The chemical shift is given in dimensionless δ values and is frequency referenced to TMS in ¹H and ¹³C NMR spectroscopy. HRMS data were obtained on a Thermo Scientific LTQ Orbitrap Discovery spectrometer (Bremen, Germany). GC-MS analysis was performed on Shimadzu GC-2010 gas chromatography coupled to a Shimadzu QP2010 mass selective detector. Column chromatography was performed on silica gel (200-300 mesh) using ethyl acetate/petroleum ether. The enantiomeric ratio (ee) of the products were determined by high-performance liquid chromatography (HPLC) with a chiral stationary phase in comparison with the authenticated racemate. All the chiral stationary phases including IC, IJ-3, AD-H, AD-3, OJ-H, OD-3 and OD-H used were purchased from Daicel Chiral Technologies.

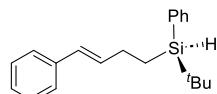
Dihydrosilanes,¹⁻³ *tert*-butyl(phenyl)silane-d₂⁴ and Methylenecyclopropanes^{5,6} were prepared according to published procedures.

2. Experimental Section

2.1 Substrate scope.



Procedure A: A 8 mL sealed tube reactor equipped with a magnetic stirrer bar was charged CuOAc (0.005 mmol, 5 mol%) and Ph-BPE (L, 0.006 mmol, 6 mol%) in dry *n*-Hexane (1 mL) under N₂ atmosphere in a glove box and stirred for 10 min, then the arylidene cyclopropane (0.1 mmol) and dihydrosilane (0.12 mmol) were added in the tube. The tube was capped, then removed from the glove box and stirred at 40 °C for 12 h. After the reaction completed, the reaction solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate to provide product. The enantiomeric excess was determined by chiral HPLC analysis. Corresponding racemic samples were obtained by carrying out the reactions at the identical conditions with (±)-Ph-BPE .



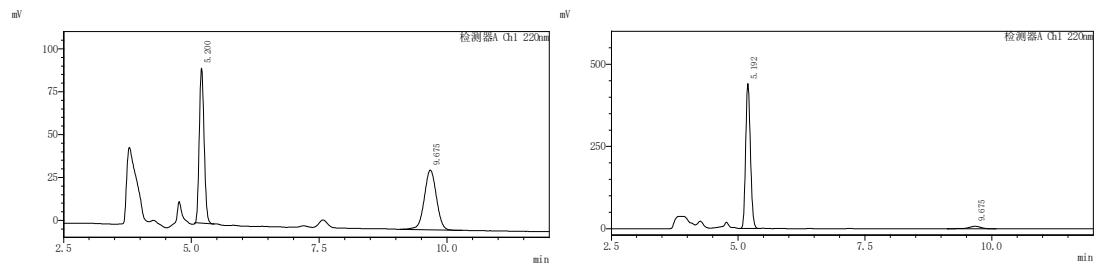
(*R,E*)-*tert*-butyl(phenyl)(4-phenylbut-3-en-1-yl)silane (3). Colourless oil (24.1 mg, 82%), *E/Z* = 17:1.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.43 (m, 2H), 7.32 – 7.24 (m, 3H), 7.21 – 7.16 (m, 4H), 7.13 – 7.07 (m, 1H), 6.23 (d, *J* = 16.0 Hz, 1H), 6.16 (dt, *J* = 15.7, 6.1 Hz, 1H), 4.03 (dd, *J* = 4.7, 3.0 Hz, 1H), 2.28 – 2.07 (m, 2H), 1.06 – 0.98 (m, 2H), 0.89 (s, 9H).

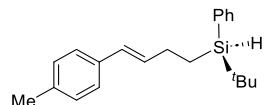
¹³C NMR (100 MHz, CDCl₃) δ 137.8, 135.4, 134.3, 133.0, 129.3, 128.7, 128.4, 127.7, 126.7, 125.9, 28.3, 27.2, 17.0, 8.9.

HRMS (EI) (m/z): Calcd for C₂₀H₂₆Si, ([M]⁺): 294.1804, found 294.1798. [α]_D²⁰ = +9.6 (c = 0.4, CHCl₃).

HPLC conditions: Daicel Chiraldpak IJ-3 column (90:10 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 5.2 min, tr (minor) = 9.7 min, 91% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	5.200	597473	51.042	1	5.192	286882	95.628
2	9.675	573070	48.958	2	9.675	131147	4.372



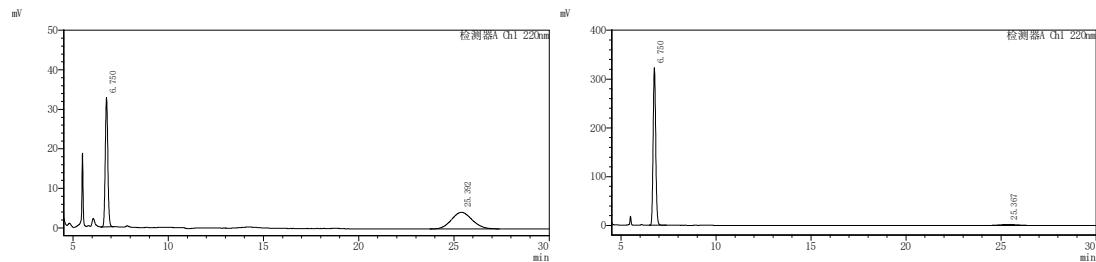
(R,E)-tert-butyl(phenyl)(4-(p-tolyl)but-3-en-1-yl)silane (4). Colourless oil (22.5 mg, 73%), E/Z = 10:1.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.55 – 7.44 (m, 2H), 7.34 – 7.25 (m, 3H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.04 – 6.96 (m, 2H), 6.20 (d, *J* = 15.7 Hz, 1H), 6.10 (dt, *J* = 15.7, 6.5 Hz, 1H), 4.03 (dd, *J* = 5.1, 2.7 Hz, 1H), 2.23 (s, 3H), 2.20 – 2.11 (m, 2H), 1.05 – 0.97 (m, 2H), 0.89 (s, 9H).

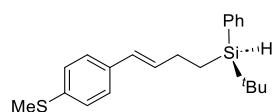
¹³C NMR (150 MHz, CDCl₃) δ 136.40, 135.41, 135.0, 134.3, 132.0, 129.2, 129.1, 128.5, 127.7, 125.8, 28.2, 27.2, 21.1, 17.0, 9.0.

GC-MS (EI) (m/z): Calcd for C₂₁H₂₈Si: 308.1960, found 308.20, [α]_D²⁰ = +6.7 (c = 0.4, CHCl₃).

HPLC conditions: Daicel Chiraldpak IJ-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 6.8 min, tr (minor) = 25.4 min, 91% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	6.750	314497	49.641	1	6.750	3128347	95.298
2	25.392	319042	50.359	2	25.367	154362	4.702

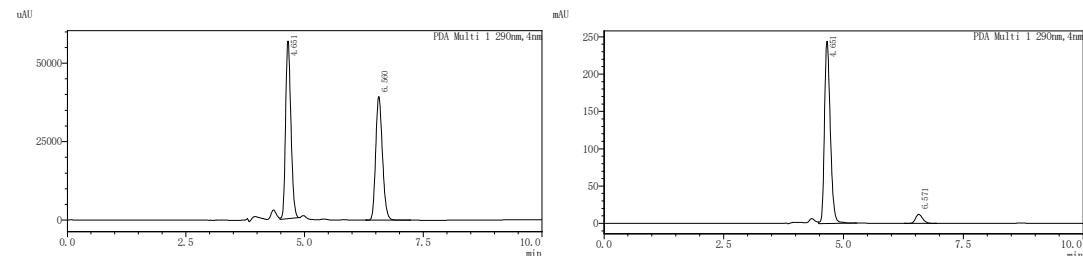


(R,E)-tert-butyl(4-(4-(methylthio)phenyl)but-3-en-1-yl)(phenyl)silane (5). Colourless oil (23.8 mg, 70%), $E/Z > 20:1$. ^1H NMR (400 MHz, Chloroform- d) δ 7.62 – 7.47 (m, 2H), 7.46 – 7.30 (m, 3H), 7.22 – 7.10 (m, 4H), 6.32 – 6.11 (m, 2H), 4.10 (dd, $J = 4.7, 2.9$ Hz, 1H), 2.46 (s, 3H), 2.33 – 2.15 (m, 2H), 1.13 – 1.02 (m, 2H), 0.96 (s, 9H).

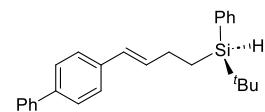
^{13}C NMR (100 MHz, CDCl₃) δ 136.5, 135.4, 135.0, 134.2, 132.6, 129.3, 128.1, 127.7, 126.9, 126.3, 28.3, 27.2, 17.0, 16.1, 8.9.

GC-MS: (EI) (m/z): Calcd for C₂₁H₂₈SSi: 340.1681, found 340.20. $[\alpha]_D^{20} = +15.6$ ($c = 0.3$, CHCl₃).

HPLC conditions: Daicel Chiraldak OD-H column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 290 nm); tr (major) = 4.7 min, tr (minor) = 6.6 min, 89% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	4.651	441348	53.127	1	4.651	2062711	94.304
2	6.560	389388	46.873	2	6.571	124599	5.696

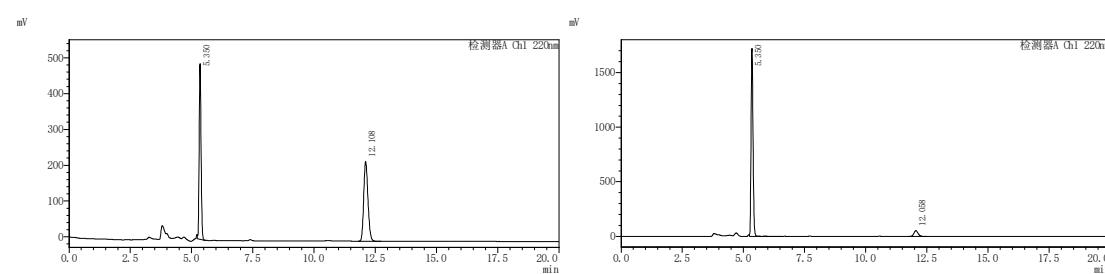


(R,E)-(4-(4-phenylbiphenyl)-4-yl)but-3-en-1-yl(tert-butyl)(phenyl)silane (6). White solid (24.1 mg, 65%), $E/Z > 20:1$. ^1H NMR (600 MHz, Chloroform- d) δ 7.61 – 7.54 (m, 4H), 7.52 – 7.49 (m, 2H), 7.44 – 7.29 (m, 8H), 6.36 – 6.31 (m, 1H), 6.31 – 6.23 (m, 1H), 4.19 – 4.07 (m, 1H), 2.34 – 2.23 (m, 2H), 1.15 – 1.09 (m, 2H), 0.97 (s, 9H).

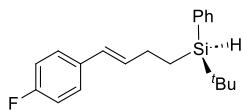
^{13}C NMR (150 MHz, CDCl₃) δ 140.9, 139.5, 136.9, 135.4, 134.3, 133.2, 129.3, 128.7, 128.3, 127.7, 127.11, 127.10, 126.9, 126.3, 28.3, 27.2, 17.0, 8.9.

HRMS (APCI) (m/z): Calcd for C₂₆H₃₁Si⁺, ([M + H]⁺): 371.2190, found 371.2196. $[\alpha]_D^{20} = +12.5$ ($c = 0.4$, CHCl₃).

HPLC conditions: Daicel Chiraldak OD-3 column (90: 10 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 5.4 min, tr (minor) = 12.1 min, 88% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	5.350	2608953	49.404	1	5.350	9637598	93.959
2	12.108	2671941	50.596	2	12.058	619669	6.041



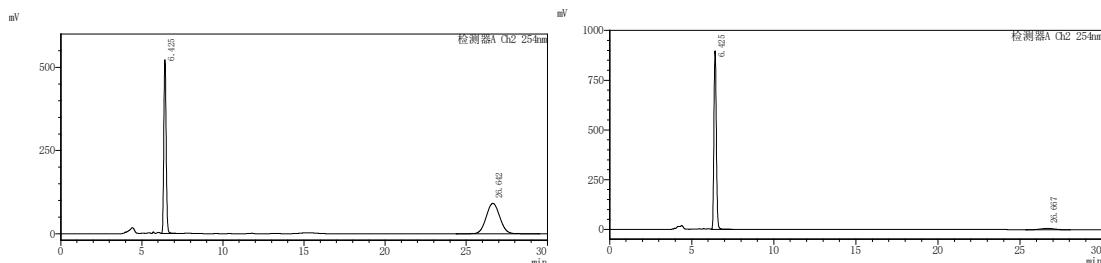
(*R,E*)-tert-butyl(4-(4-fluorophenyl)but-3-en-1-yl)(phenyl)silane (7). Colourless oil (20.6 mg, 66%), *E/Z* = 14:1. **¹H NMR** (600 MHz, Chloroform-*d*) δ 7.56 – 7.51 (m, 2H), 7.40 – 7.32 (m, 3H), 7.25 – 7.18 (m, 2H), 6.98 – 6.91 (m, 2H), 6.25 (d, *J* = 15.4 Hz, 1H), 6.17 – 6.07 (m, 1H), 4.10 (dd, *J* = 5.1, 2.6 Hz, 1H), 2.30 – 2.17 (m, 2H), 1.11 – 1.06 (m, 2H), 0.96 (s, 9H).

¹³C NMR (150 MHz, CDCl₃) δ 162.7, 161.0, 135.4, 134.2, 134.0, 133.9, 132.7, 129.3, 127.73, 127.6, 127.32, 127.27, 115.3, 115.2, 28.2, 27.2, 17.0, 8.9.

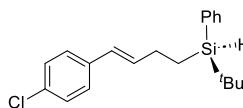
¹⁹F NMR (565 MHz, CDCl₃) δ -115.90.

HRMS (EI) (m/z): Calcd for C₂₀H₂₅FSi, ([M]⁺): 312.1710, found 312.1710. [α]_D²⁰ = +13.9 (c = 0.4, CHCl₃).

HPLC conditions: Daicel Chiraldak OJ-H column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 6.4 min, tr (minor) = 26.7 min, 92% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	6.425	5261206	49.691	1	6.425	9210144	95.850
2	26.642	5326641	50.309	2	26.667	398749	4.150

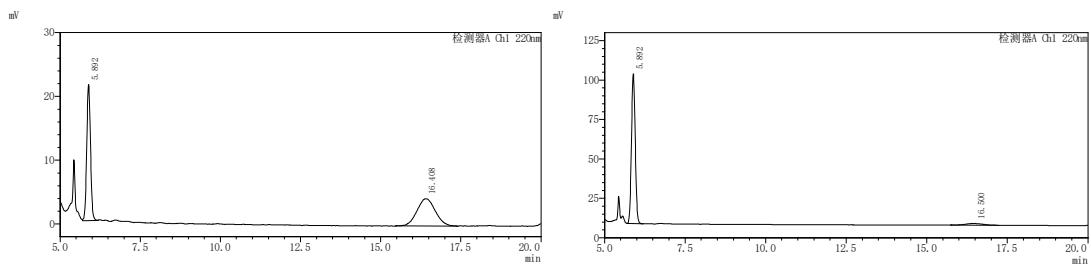


(*R,E*)-tert-butyl(4-(4-chlorophenyl)but-3-en-1-yl)(phenyl)silane (8). Colourless oil (26.0 mg, 79%), *E/Z* > 20:1. **¹H NMR** (600 MHz, Chloroform-*d*) δ 7.57 – 7.50 (m, 2H), 7.41 – 7.33 (m, 3H), 7.24 – 7.20 (m, 2H), 7.20 – 7.16 (m, 2H), 6.25 (d, *J* = 15.9 Hz, 1H), 6.22 – 6.16 (m, 1H), 4.10 (dd, *J* = 5.1, 2.5 Hz, 1H), 2.31 – 2.21 (m, 2H), 1.11 – 1.05 (m, 2H), 0.96 (s, 9H).

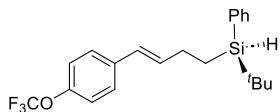
¹³C NMR (150 MHz, CDCl₃) δ 136.3, 135.4, 134.2, 133.7, 132.2, 129.3, 128.5, 127.7, 127.6, 127.1, 28.3, 27.2, 17.0, 8.8.

HRMS (APCI) (m/z): Calcd for C₂₀H₂₆ClSi⁺, ([M + H]⁺), 329.1487, found 329.1490. [α]_D²⁰ = +13.2 (c = 0.3, CH₂Cl₂).

HPLC conditions: Daicel Chiraldak IJ-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 5.9 min, tr (minor) = 16.5 min, 90% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	5.892	175264	50.711	1	5.892	774207	94.892
2	16.408	170352	49.289	2	16.500	41672	5.108



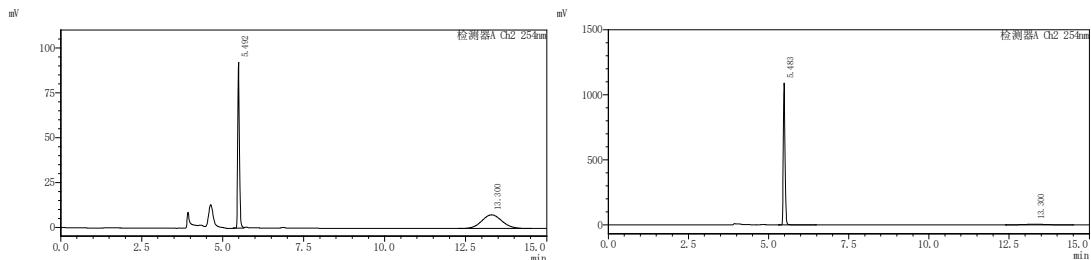
(R,E)-tert-butyl(phenyl)(4-(4-(trifluoromethoxy)phenyl)but-3-en-1-yl)silane (9). Colourless oil (29.9 mg, 79%), $E/Z > 20:1$. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 7.62 – 7.50 (m, 2H), 7.48 – 7.32 (m, 5H), 7.25 (d, J = 8.9 Hz, 2H), 6.42 – 6.22 (m, 2H), 4.08 (dd, J = 5.6, 2.0 Hz, 1H), 2.32 – 2.14 (m, 2H), 1.21 – 1.03 (m, 2H), 0.93 (s, 9H).

¹³C NMR (100 MHz, DMSO) δ 147.0, 136.7, 135.1, 134.0, 133.4, 129.5, 127.8, 127.3, 127.1, 123.9, 121.3, 121.0, 118.8, 116.2, 27.8, 27.0, 16.5, 8.1.

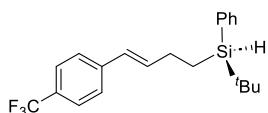
¹⁹F NMR (376 MHz, DMSO) δ -56.92.

GC-MS: (EI) (m/z): Calcd for C₂₁H₂₅F₃OSi: 378.1627, found 378.05. $[\alpha]_D^{20} = +14.7$ (*c* = 0.4, CHCl₃).

HPLC conditions: Daicel Chiraldak IJ-3 column (95:5 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 5.5 min, tr (minor) = 13.3 min, 90% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	5.492	341000	50.879	1	5.483	4086151	95.112
2	13.300	329213	49.121	2	13.300	209999	4.888



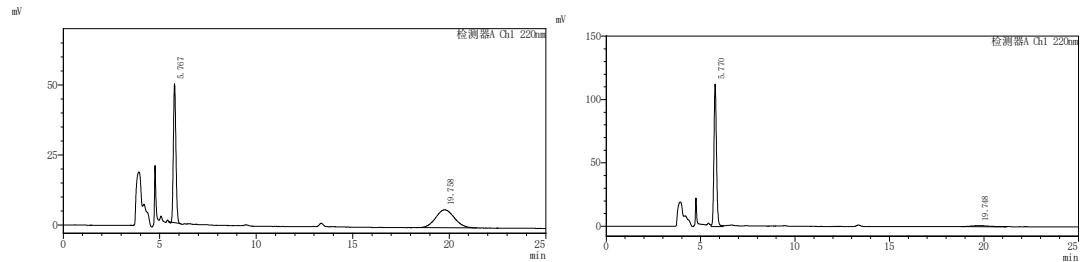
(R,E)-tert-butyl(phenyl)(4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)silane (10). Colourless oil (27.2 mg, 75%), $E/Z > 20:1$. **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.50 – 7.39 (m, 4H), 7.33 – 7.22 (m, 5H), 6.32 – 6.17 (m, 2H), 4.03 (dd, J = 4.8, 2.9 Hz, 1H), 2.27 – 2.14 (m, 2H), 1.08 – 0.98 (m, 2H), 0.89 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 141.3, 135.8, 135.4, 134.1, 129.3, 129.0, 128.7, 128.39, 128.36, 128.1, 127.8, 127.6, 126.0, 125.7, 125.41, 125.37, 125.34, 125.30, 123.0, 120.3, 28.3, 27.2, 17.0, 8.7.

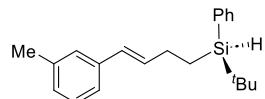
¹⁹F NMR (376 MHz, CDCl₃) δ -62.35.

HRMS (EI) (m/z): Calcd for C₂₁H₂₅F₃Si, ([M]⁺): 362.1678, found 362.1681. [α]_D²⁰ = +13.5 (c = 0.5, CHCl₃).

HPLC conditions: Daicel Chiralpak IJ-3 column (90: 10 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 5.8 min, tr (minor) = 19.7 min, 90% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	5.767	457366	51.363	1	5.770	1067330	95.050
2	19.758	433099	48.637	2	19.748	555582	4.950

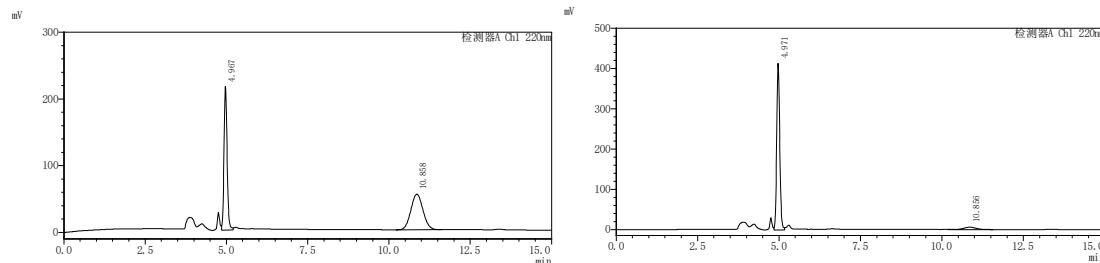


(R,E)-tert-butyl(phenyl)(4-(m-tolyl)but-3-en-1-yl)silane (11). Colourless oil (21.0 mg, 68%), E/Z > 20:1. **¹H NMR** (600 MHz, Chloroform-d) δ 7.61 – 7.51 (m, 2H), 7.40 – 7.33 (m, 3H), 7.17 – 7.14 (m, 1H), 7.08 (d, J = 9.7 Hz, 2H), 6.99 (d, J = 7.4 Hz, 1H), 6.27 (d, J = 15.8 Hz, 1H), 6.24 – 6.17 (m, 1H), 4.10 (dd, J = 5.0, 2.5 Hz, 1H), 2.31 (s, 3H), 2.29 – 2.22 (m, 2H), 1.12 – 1.05 (m, 2H), 0.96 (s, 9H).

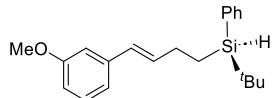
¹³C NMR (150 MHz, CDCl₃) δ 137.9, 137.8, 135.4, 134.3, 132.8, 129.3, 128.8, 128.3, 127.7, 127.5, 126.6, 123.1, 28.3, 27.2, 21.4, 17.0, 9.0.

HRMS (APCI) (m/z): Calcd for C₂₁H₂₉Si⁺, ([M + H]⁺), 309.2033, found 309.2035. [α]_D²⁰ = +12.3 (c = 0.4, CHCl₃).

HPLC conditions: Daicel Chiralpak IJ-3 column (90: 10 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 5.0 min, tr (minor) = 10.9 min, 87% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	4.967	1430126	50.834	1	4.971	2694573	93.333
2	10.858	1383219	49.166	2	10.856	192482	6.667

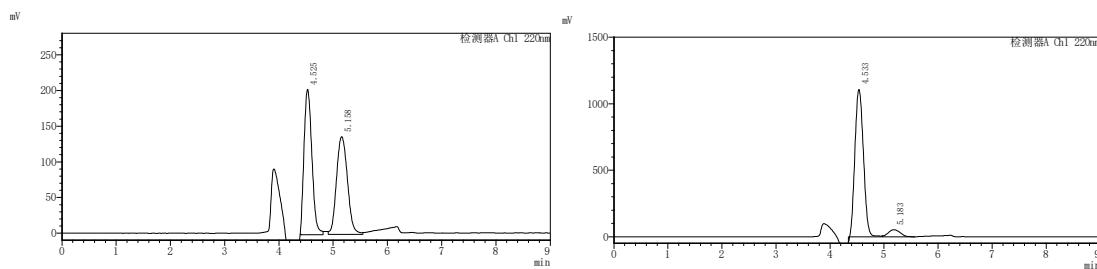


(R,E)-tert-butyl(4-(3-methoxyphenyl)but-3-en-1-yl)(phenyl)silane (12). Colourless oil (22.0 mg, 68%), $E/Z > 20:1$. **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 7.59 – 7.50 (m, 2H), 7.40 – 7.33 (m, 3H), 7.18 (t, $J = 7.9$ Hz, 1H), 6.91 – 6.86 (m, 1H), 6.86 – 6.80 (m, 1H), 6.76 – 6.71 (m, 1H), 6.34 – 6.16 (m, 2H), 4.10 (dd, $J = 4.8, 2.9$ Hz, 1H), 3.79 (s, 3H), 2.34 – 2.17 (m, 2H), 1.13 – 1.05 (m, 2H), 0.96 (s, 9H).

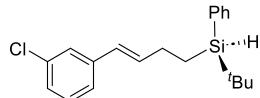
$^{13}\text{C NMR}$ (100 MHz, CDCl₃) δ 159.7, 139.3, 135.4, 134.2, 133.3, 129.4, 129.3, 128.6, 127.7, 118.6, 112.4, 111.2, 55.2, 28.2, 27.2, 17.0, 8.9.

GC-MS: (EI) (m/z): Calcd for C₂₁H₂₈OSi: 324.1909, found 324.20. $[\alpha]_D^{20} = +25.7$ (*c* = 0.4, CHCl₃).

HPLC conditions: Daicel Chiraldpak OD-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 4.5 min, tr (minor) = 5.2 min, 88% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	4.525	2060289	51.623	1	4.533	12106186	93.862
2	5.158	1930770	48.377	2	5.183	791614	6.138

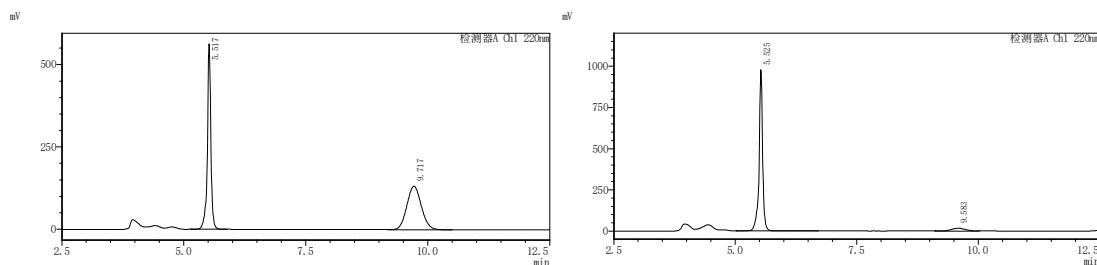


(R,E)-tert-butyl(4-(3-chlorophenyl)but-3-en-1-yl)(phenyl)silane (13). Colourless oil (25.6 mg, 78%), $E/Z > 20:1$. **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 7.55 – 7.52 (m, 2H), 7.40 – 7.33 (m, 3H), 7.25 – 7.23 (m, 1H), 7.18 – 7.10 (m, 3H), 6.25 – 6.21 (m, 2H), 4.10 (dd, $J = 4.8, 3.0$ Hz, 1H), 2.31 – 2.22 (m, 2H), 1.12 – 1.06 (m, 2H), 0.96 (s, 9H).

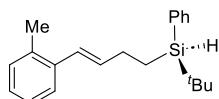
$^{13}\text{C NMR}$ (100 MHz, CDCl₃) δ 139.7, 135.4, 134.6, 134.3, 134.2, 129.6, 129.3, 127.8, 127.5, 126.7, 125.8, 124.2, 28.3, 27.2, 17.0, 8.8.

GC-MS: (EI) (m/z): Calcd for C₂₀H₂₅ClSi: 328.1414, found 328.15. $[\alpha]_D^{20} = +35.2$ (*c* = 0.3, CHCl₃).

HPLC conditions: Daicel Chiraldpak II-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 5.5 min, tr (minor) = 9.6 min, 87% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	5.517	2777116	50.354	1	5.525	4965611	93.405
2	9.717	2738014	49.646	2	9.583	350581	6.595



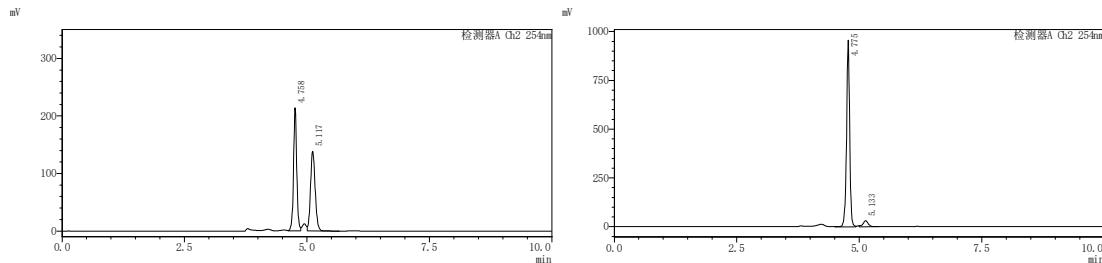
(*R,E*)-tert-butyl(phenyl)(4-(*o*-tolyl)but-3-en-1-yl)silane (14). Colourless oil (21.6 mg, 70%), *E/Z* = 10:1.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.59 – 7.52 (m, 2H), 7.40 – 7.34 (m, 3H), 7.33 – 7.30 (m, 1H), 7.13 – 7.08 (m, 3H), 6.54 – 6.43 (m, 1H), 6.09 (dt, *J* = 15.6, 6.7 Hz, 1H), 4.12 (dd, *J* = 5.2, 2.5 Hz, 1H), 2.33 – 2.26 (m, 5H), 1.14 – 1.08 (m, 2H), 0.97 (s, 9H).

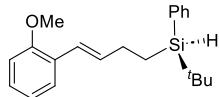
¹³C NMR (150 MHz, CDCl₃) δ 136.9, 135.4, 134.9, 134.30, 134.28, 130.1, 129.3, 127.7, 126.7, 126.6, 125.9, 125.4, 28.6, 27.3, 19.8, 17.0, 9.1.

HRMS (APCI) (m/z): Calcd for C₂₁H₂₉Si⁺, ([M + H]⁺), 309.2033, found 309.2037. [α]_D²⁰ = +13.8 (c = 0.4, CHCl₃).

HPLC conditions: Daicel Chiraldak IJ-3 column (90: 10 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 4.8 min, tr (minor) = 5.1 min, 89% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	4.758	964057	51.271	1	4.775	4220102	94.689
2	5.117	916254	48.729	2	5.133	236700	5.311

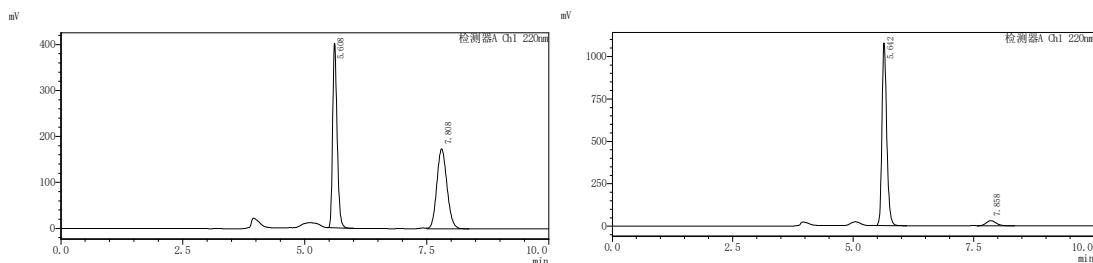


(*R,E*)-tert-butyl(4-(2-methoxyphenyl)but-3-en-1-yl)(phenyl)silane (15). Colourless oil (20.1 mg, 62%), *E/Z* = 11:1. **¹H NMR** (600 MHz, Chloroform-*d*) δ 7.66 – 7.50 (m, 2H), 7.40 – 7.30 (m, 4H), 7.19 – 7.13 (m, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.84 – 6.81 (m, 1H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.11 (dd, *J* = 5.0, 2.7 Hz, 1H), 3.82 (s, 3H), 2.34 – 2.23 (m, 2H), 1.13 – 1.08 (m, 2H), 0.96 (s, 9H).

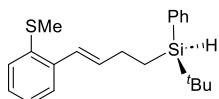
¹³C NMR (150 MHz, CDCl₃) δ 156.3, 135.4, 134.4, 133.8, 129.2, 127.74, 127.68, 126.9, 126.4, 123.2, 120.6, 110.7, 55.4, 28.7, 27.3, 17.0, 9.1.

GC-MS: (EI) (m/z): Calcd for C₂₁H₂₈O₂Si: 324.1909, found 324.20. [α]_D²⁰ = +15.7 (c = 0.4, CHCl₃).

HPLC conditions: Daicel Chiraldak IJ-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 5.6 min, tr (minor) = 7.9 min, 89% ee..



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	5.608	2562727	50.388	1	5.642	7417226	94.546
2	7.808	2523250	49.612	2	7.858	427837	5.454

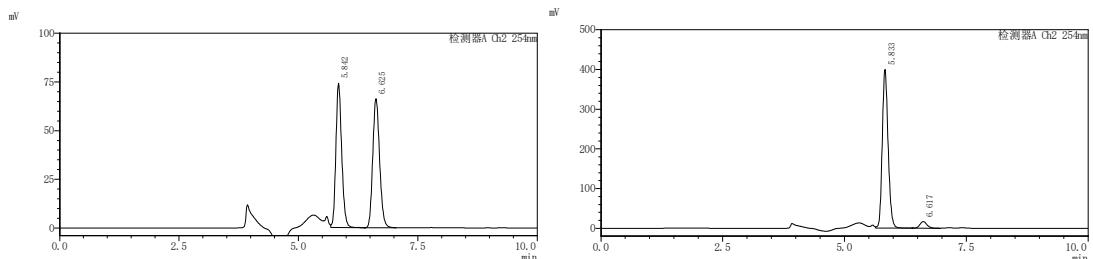


(R,E)-tert-butyl(4-(2-(methylthio)phenyl)but-3-en-1-yl)(phenyl)silane (16). Colourless oil (23.5 mg, 69%), $E/Z = 12:1$. $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 7.60 – 7.50 (m, 2H), 7.41 – 7.33 (m, 3H), 7.31 – 7.27 (m, 1H), 7.22 – 7.13 (m, 2H), 7.12 – 7.06 (m, 1H), 6.72 (d, $J = 15.6$ Hz, 1H), 6.15 (dt, $J = 15.6$, 6.6 Hz, 1H), 4.12 (dd, $J = 4.8$, 3.0 Hz, 1H), 2.42 (s, 3H), 2.36 – 2.26 (m, 2H), 1.17 – 1.08 (m, 2H), 0.97 (s, 9H).

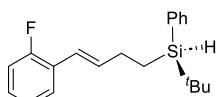
$^{13}\text{C NMR}$ (100 MHz, CDCl₃) δ 137.1, 135.9, 135.4, 135.3, 134.3, 129.3, 127.7, 127.3, 126.5, 125.98, 125.95, 125.4, 28.5, 27.2, 17.0, 16.2, 8.9.

HRMS (EI) (m/z): Calcd for C₂₁H₂₈SSi, ([M]⁺): 340.1681, found 340.1675. $[\alpha]_{D}^{20} = +19.3$ ($c = 0.4$, CHCl₃).

HPLC conditions: Daicel Chiraldak OJ-H column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 5.8 min, tr (minor) = 6.6 min, 90% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	5.842	628054	48.638	1	5.833	3327524	95.216
2	6.625	663225	51.362	2	6.617	167197	4.784



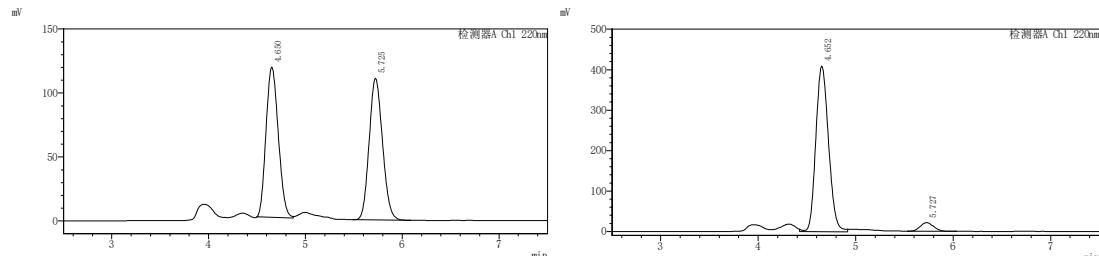
(R,E)-tert-butyl(4-(2-fluorophenyl)but-3-en-1-yl)(phenyl)silane (17). Colourless oil (23.7 mg, 76%), $E/Z > 20:1$. $^1\text{H NMR}$ (600 MHz, Chloroform- d) δ 7.58 – 7.50 (m, 2H), 7.41 – 7.30 (m, 4H), 7.16 – 7.10 (m, 1H), 7.03 (t, $J = 7.5$ Hz, 1H), 7.00 – 6.95 (m, 1H), 6.47 (d, $J = 15.8$ Hz, 1H), 6.30 (dt, $J = 15.9$, 6.6 Hz, 1H), 4.11 (dd, $J = 5.1$, 2.6 Hz, 1H), 2.34 – 2.24 (m, 2H), 1.15 – 1.07 (m, 2H), 0.96 (s, 9H).

¹³C NMR (150 MHz, CDCl₃) δ 160.7, 159.1, 135.7, 135.6, 135.4, 134.2, 129.3, 127.92, 127.87, 127.7, 127.01, 126.98, 125.6, 125.5, 123.93, 123.90, 121.08, 121.05, 115.6, 115.5, 28.7, 27.2, 17.0, 8.8.

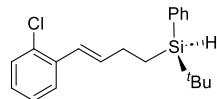
¹⁹F NMR (565 MHz, CDCl₃) δ -118.94.

HRMS (APCI) (m/z): Calcd for C₂₀H₂₆FSi⁺, ([M + H]⁺), 313.1782, found 313.1835. [α]_D²⁰ = +8.9 (c = 0.4, CHCl₃).

HPLC conditions: Daicel Chiraldak IJ-3 column (98: 2 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 4.7 min, tr (minor) = 5.7 min, 90% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	4.650	1036112	49.404	1	4.652	3723590	94.862
2	5.725	1061130	50.596	2	5.727	201680	5.138

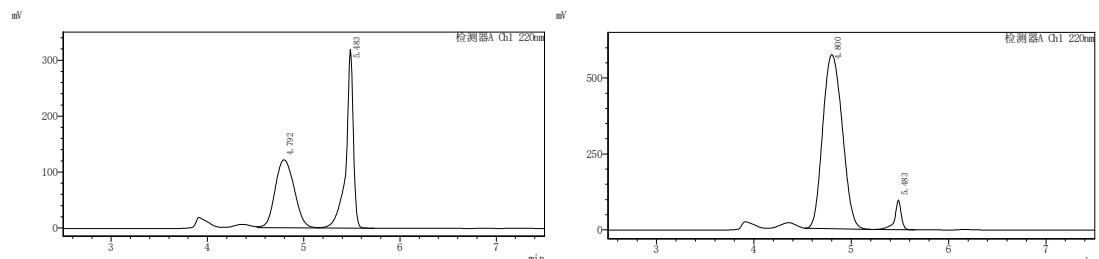


(R,E)-tert-butyl(4-(2-chlorophenyl)but-3-en-1-yl)(phenyl)silane (18). Colourless oil (22.3 mg, 68%), E/Z > 20:1. **¹H NMR** (600 MHz, Chloroform-d) δ 7.59 – 7.51 (m, 2H), 7.40 – 7.33 (m, 4H), 7.31 – 7.29 (m, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.12 – 7.08 (m, 1H), 6.69 (d, J = 15.7 Hz, 1H), 6.20 (dt, J = 15.5, 6.6 Hz, 1H), 4.12 (dd, J = 5.0, 2.6 Hz, 1H), 2.35 – 2.26 (m, 2H), 1.14 – 1.09 (m, 2H), 0.97 (s, 9H).

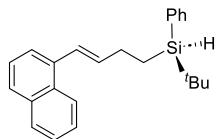
¹³C NMR (150 MHz, CDCl₃) δ 135.89, 135.85, 135.4, 134.2, 132.5, 129.5, 129.3, 127.8, 127.7, 126.7, 126.6, 125.0, 28.5, 27.2, 17.0, 8.8.

HRMS (APCI) (m/z): Calcd for C₂₀H₂₅NaSi⁺, ([M + Na]⁺), 351.1306, found 351.1311. [α]_D²⁰ = +11.1 (c = 0.4, CHCl₃).

HPLC conditions: Daicel Chiraldak IJ-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 4.8 min, tr (minor) = 5.5 min, 89% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	4.792	1671348	49.605	1	4.800	8019118	94.621
2	5.483	1697949	50.395	2	5.483	455891	5.379

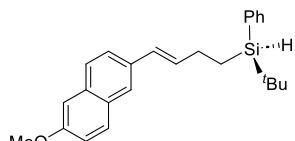
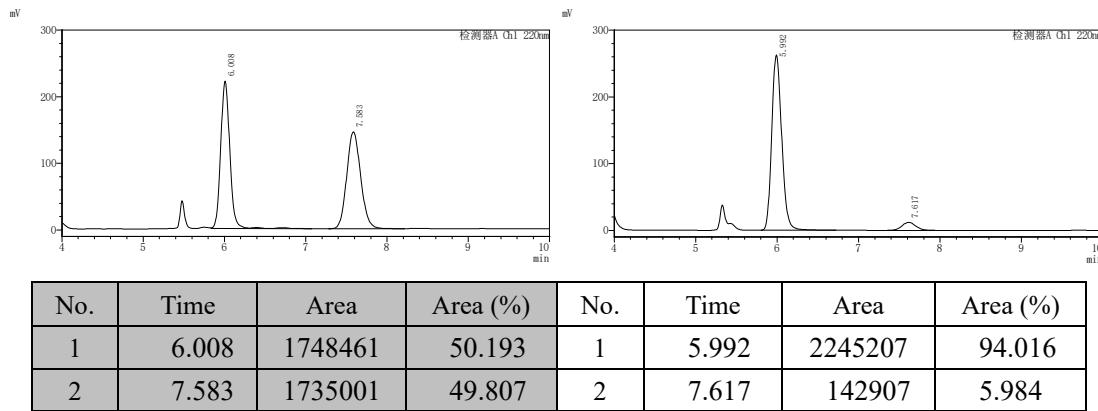


(*R,E*)-tert-butyl(4-(naphthalen-1-yl)but-3-en-1-yl)(phenyl)silane (19). Colourless oil (25.8 mg, 75%), *E/Z* = 11:1. **¹H NMR** (600 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.34 – 7.26 (m, 4H), 6.95 (d, *J* = 15.4 Hz, 1H), 6.25 – 6.08 (m, 1H), 4.08 (dd, *J* = 5.4, 2.5 Hz, 1H), 2.41 – 2.26 (m, 2H), δ 1.15 – 1.07 (m, 2H), 0.91 (s, 9H).

¹³C NMR (150 MHz, CDCl₃) δ 136.2, 135.6, 135.4, 134.3, 133.6, 131.1, 129.3, 128.4, 127.8, 127.2, 125.9, 125.7, 125.6, 125.6, 124.0, 123.5, 28.7, 27.3, 17.0, 9.0.

HRMS (APCI) (m/z): Calcd for C₂₄H₂₉Si⁺, ([M + H]⁺), 345.2033, found 345.2038. $[\alpha]_D^{20} = +21.5$ (*c* = 0.5, CHCl₃).

HPLC conditions: Daicel Chiraldak IJ-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 6.0 min, tr (minor) = 7.6 min, 88% ee.

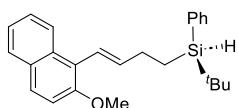
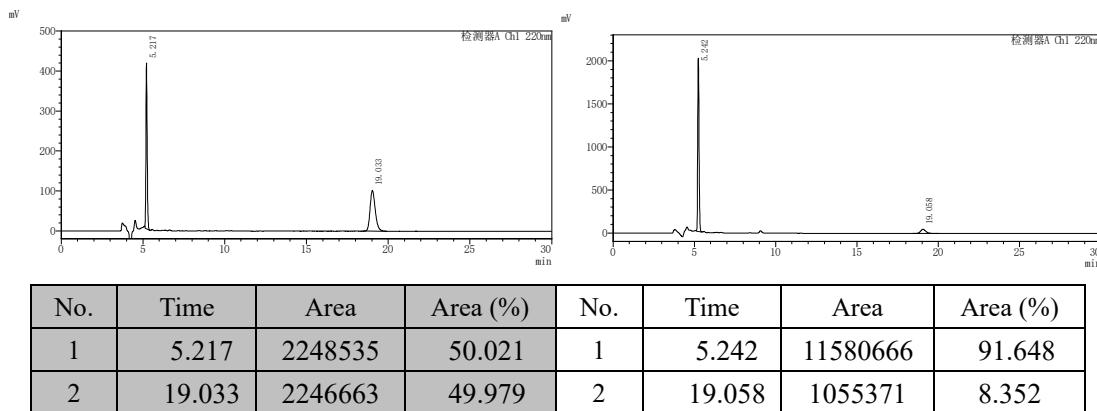


(*R,E*)-tert-butyl(4-(6-methoxynaphthalen-2-yl)but-3-en-1-yl)(phenyl)silane (20). Colourless oil (25.8 mg, 69%), *E/Z* > 20:1. **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (t, *J* = 9.4 Hz, 2H), 7.59 – 7.51 (m, 3H), 7.49 – 7.44 (m, 1H), 7.43 – 7.32 (m, 3H), 7.12 – 7.05 (m, 2H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.30 (dt, *J* = 15.7, 6.5 Hz, 1H), 4.13 (dd, *J* = 4.7, 3.0 Hz, 1H), 3.89 (s, 3H), 2.39 – 2.21 (m, 2H), 1.18 – 1.09 (m, 2H), 0.97 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 157.4, 135.4, 134.3, 133.7, 133.2, 132.4, 129.30, 129.25, 129.1, 128.8, 127.7, 126.9, 125.1, 124.2, 118.8, 105.8, 55.3, 28.4, 27.3, 17.0, 9.0.

HRMS (EI) (m/z): Calcd for C₂₅H₃₀OSi, ([M]⁺): 374.2066, found 374.2069. $[\alpha]_D^{20} = +15.9$ (*c* = 0.4, CHCl₃).

HPLC conditions: Daicel Chiraldak OD-3 column (90: 10 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 5.2 min, tr (minor) = 19.1 min, 83% ee.

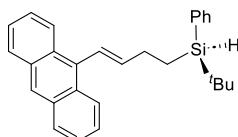
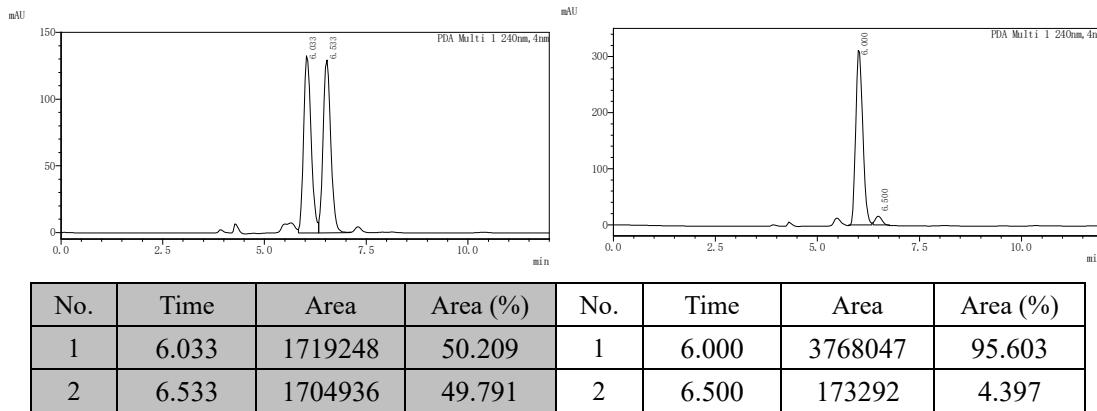


(R,E)-tert-butyl(4-(2-methoxynaphthalen-1-yl)but-3-en-1-yl)(phenyl)silane (21). Colourless oil (23.6 mg, 63%), $E/Z = 14:1$. $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 8.14 (d, $J = 7.9$ Hz, 1H), 7.79 – 7.68 (m, 2H), 7.63 – 7.54 (m, 2H), 7.44 – 7.35 (m, 4H), 7.34 – 7.29 (m, 1H), 7.24 (d, $J = 2.8$ Hz, 1H), 6.74 – 6.63 (m, 1H), 6.24 (dt, $J = 16.0, 6.5$ Hz, 1H), 4.18 (dd, $J = 4.5, 3.1$ Hz, 1H), 3.92 (s, 3H), 2.47 – 2.38 (m, 2H), 1.25 – 1.17 (m, 2H), 0.99 (s, 9H).

$^{13}\text{C NMR}$ (100 MHz, CDCl₃) δ 154.0, 139.4, 135.5, 134.4, 132.6, 129.29, 129.26, 128.2, 128.1, 127.7, 126.1, 124.5, 123.3, 121.4, 121.3, 113.4, 56.5, 29.2, 27.3, 17.0, 9.1.

HRMS (EI) (m/z): Calcd for C₂₅H₃₀OSi, ([M]⁺): 374.2066, found 374.2056. $[\alpha]_D^{20} = +27.8$ ($c = 0.4$, CHCl₃).

HPLC conditions: Daicel Chiralpak OD-H column (98: 2 hexane: *i*PrOH, 0.8 mL/min, 40 °C, 240 nm); tr (major) = 6.0 min, tr (minor) = 6.5 min, 91% ee.



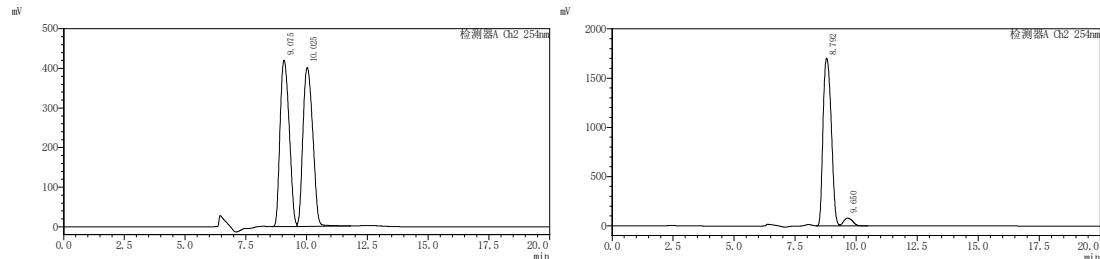
(R,E)-(4-(anthracen-9-yl)but-3-en-1-yl)(tert-butyl)(phenyl)silane (22). Yellow oil (26.4 mg, 67%), $E/Z > 20:1$. $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 8.24 (s, 1H), 8.24 – 8.15 (m, 2H), 7.98 – 7.78 (m, 2H),

7.59 – 7.49 (m, 2H), 7.41 – 7.25 (m, 7H), 6.96 (d, J = 16.0 Hz, 1H), 5.98 (dt, J = 16.0, 6.5 Hz, 1H), 4.15 (dd, J = 4.8, 2.9 Hz, 1H), 2.53 – 2.39 (m, 2H), 1.29 – 1.13 (m, 2H), 0.94 (s, 9H).

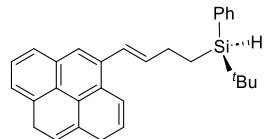
^{13}C NMR (100 MHz, CDCl_3) δ 141.3, 135.5, 134.2, 133.5, 131.5, 129.6, 129.4, 128.5, 127.8, 126.2, 125.8, 125.02, 124.99, 124.3, 28.9, 27.3, 17.1, 9.0.

HRMS (EI) (m/z): Calcd for $\text{C}_{28}\text{H}_{30}\text{Si}$, ([M] $^+$): 394.2117, found 394.2116. $[\alpha]_D^{20} = +12.1$ (c = 0.4, CHCl_3).

HPLC conditions: Daicel Chiralpak OD-3 column (98: 2 hexane: $^i\text{PrOH}$, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 8.8 min, tr (minor) = 9.6 min, 91% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	9.075	2150991	49.593	1	8.792	8508023	95.550
2	10.025	2186269	50.407	2	9.642	396231	4.450

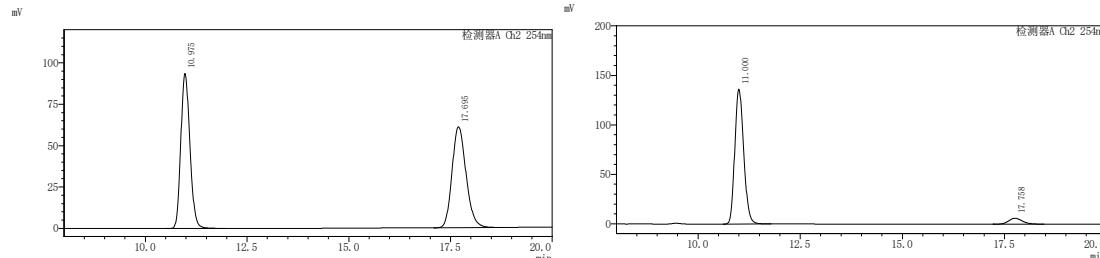


(R,E)-tert-butyl(4-(1,9-dihydropyren-4-yl)but-3-en-1-yl)(phenyl)silane (23). Yellow oil (24.8 mg, 59%), $E/Z > 20:1$. **^1H NMR** (400 MHz, Chloroform- d) δ 8.23 (d, J = 9.3 Hz, 1H), 8.05 (d, J = 7.6 Hz, 2H), 8.01 – 7.85 (m, 6H), 7.56 – 7.49 (m, 2H), 7.36 – 7.28 (m, 3H), 7.28 – 7.21 (m, 1H), 6.36 (dt, J = 15.4, 6.7 Hz, 1H), 4.12 (dd, J = 4.7, 2.9 Hz, 1H), 2.46 – 2.35 (m, 2H), 1.24 – 1.11 (m, 2H), 0.93 (s, 9H).

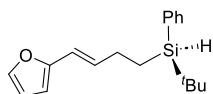
^{13}C NMR (100 MHz, CDCl_3) δ 136.6, 135.5, 134.3, 132.7, 131.5, 131.0, 130.2, 129.3, 127.8, 127.7, 127.4, 127.1, 126.8, 126.0, 125.8, 124.97, 124.95, 124.9, 124.7, 123.9, 123.3, 29.0, 27.3, 17.0, 9.0.

HRMS (EI) (m/z): Calcd for $\text{C}_{30}\text{H}_{32}\text{Si}$, ([M] $^+$): 420.2273, found 420.2120. $[\alpha]_D^{20} = +6.1$ (c = 0.4, CHCl_3).

HPLC conditions: Daicel Chiralpak OD-3 column (95: 5 hexane: $^i\text{PrOH}$, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 11.0 min, tr (minor) = 17.8 min, 88% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	10.975	1561867	49.953	1	11.000	2257115	93.807
2	17.692	1564796	50.047	2	17.767	149006	6.193

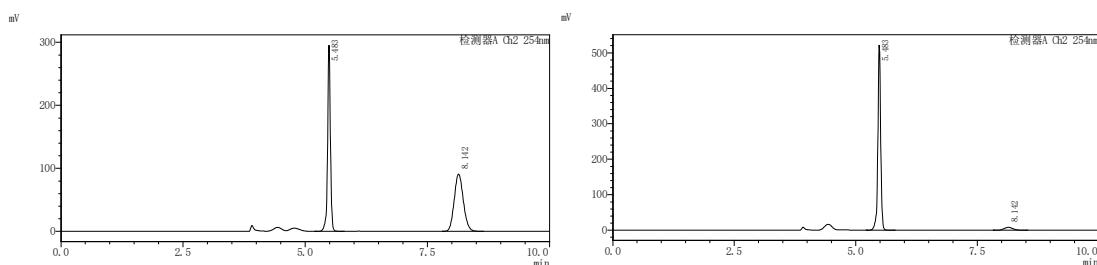


(R,E)-tert-butyl(4-(furan-2-yl)but-3-en-1-yl)(phenyl)silane (24). Colourless oil (20.7 mg, 73%), $E/Z = 10:1$. $^1\text{H NMR}$ (600 MHz, Chloroform- d) δ 7.55 – 7.50 (m, 2H), 7.40 – 7.33 (m, 3H), 7.28 (s, 1H), 6.35 – 6.30 (m, 1H), 6.20 (dt, $J = 15.9, 6.3$ Hz, 1H), 6.16 – 6.12 (m, 1H), 6.09 (d, $J = 3.4$ Hz, 1H), 4.09 (dd, $J = 5.3, 2.8$ Hz, 1H), 2.27 – 2.17 (m, 2H), 1.10 – 1.05 (m, 2H), 0.95 (s, 9H).

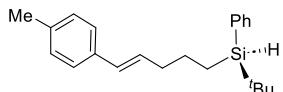
$^{13}\text{C NMR}$ (150 MHz, CDCl₃) δ 153.3, 141.2, 135.4, 134.1, 132.1, 129.3, 127.7, 117.5, 111.0, 106.0, 28.0, 27.2, 17.0, 8.8.

HRMS (APCI) (m/z): Calcd for C₁₈H₂₅OSi⁺, ([M + H]⁺): 285.1669, found 285.1669. $[\alpha]_D^{20} = +13.5$ ($c = 0.4$, CHCl₃).

HPLC conditions: Daicel Chiraldak IJ-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 5.5 min, tr (minor) = 8.1 min, 91% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	5.483	1195572	50.380	1	5.483	2131603	95.289
2	8.142	1177558	49.620	2	8.142	105376	4.711

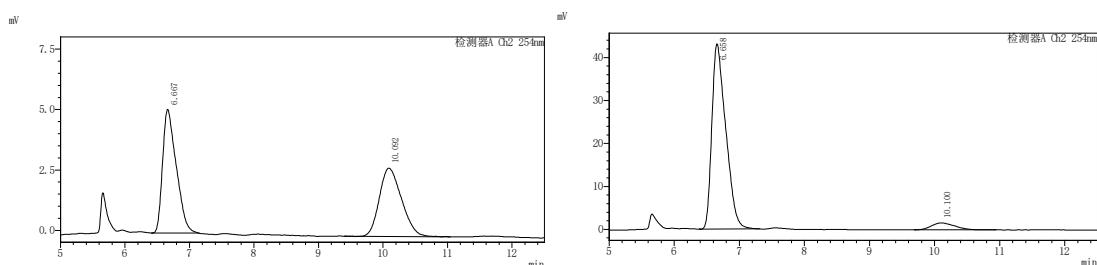


(R,E)-tert-butyl(phenyl)(5-(p-tolyl)pent-4-en-1-yl)silane (25). Colourless oil (16.4 mg, 51%), $E/Z > 20:1$. $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 7.49 – 7.42 (m, 2H), 7.33 – 7.24 (m, 3H), 7.17 – 7.12 (m, 2H), 7.06 – 6.99 (m, 2H), 6.29 – 6.17 (m, 1H), δ 6.03 (dt, $J = 15.7, 6.9$ Hz, 1H), 3.99 (dd, $J = 4.7, 2.9$ Hz, 1H), 2.24 (s, 3H), 2.21 – 2.09 (m, 2H), 1.54 – 1.40 (m, 2H), 0.96 – 0.79 (m, 11H).

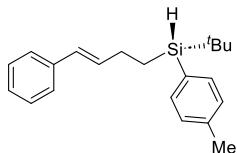
$^{13}\text{C NMR}$ (100 MHz, CDCl₃) δ 136.4, 135.4, 135.1, 134.6, 129.96, 129.55, 129.2, 129.1, 127.7, 125.8, 36.4, 27.3, 24.9, 21.1, 17.0, 8.7.

HRMS (EI) (m/z): Calcd for C₂₂H₃₀Si, ([M]⁺): 322.2117, found 322.2114. $[\alpha]_D^{20} = +12.9$ ($c = 0.4$, CHCl₃).

HPLC conditions: Daicel Chiraldak OJ-H column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 6.7 min, tr (minor) = 10.1 min, 88% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	6.667	75391	52.699	1	6.658	640386	94.065
2	10.092	67670	47.301	2	10.100	40408	5.935



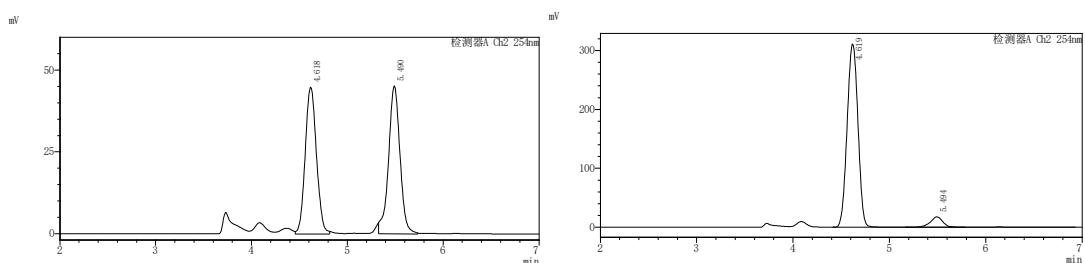
(R,E)-tert-butyl(4-phenylbut-3-en-1-yl)(p-tolyl)silane (26). Colourless oil (14.5 mg, 47%), $E/Z = 14:1$.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.49 – 7.41 (m, 2H), 7.28 – 7.23 (m, 4H), 7.20 – 7.16 (m, 3H), 6.35 – 6.26 (m, 1H), 6.22 (dt, $J = 15.8, 6.1$ Hz, 1H), 4.08 (dd, $J = 4.6, 3.1$ Hz, 1H), 2.36 (s, 3H), 2.32 – 2.19 (m, 2H), 1.11 – 1.04 (m, 2H), 0.95 (s, 9H).

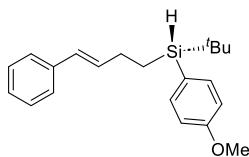
$^{13}\text{C NMR}$ (100 MHz, CDCl₃) δ 139.1, 137.9, 135.4, 133.1, 130.5, 128.63, 128.58, 128.4, 126.7, 125.9, 28.3, 27.2, 21.5, 17.0, 9.0.

HRMS (EI) (m/z): Calcd for C₂₁H₂₈Si, ([M]⁺): 308.1960, found 308.1958. $[\alpha]_D^{20} = +5.7$ (*c* = 0.5, CHCl₃).

HPLC conditions: Daicel Chiraldak IJ-3 column (90: 10 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 4.6 min, tr (minor) = 5.5 min, 88% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	4.618	366659	49.422	1	4.619	2444920	93.887
2	5.490	375233	50.578	2	5.494	159202	6.113

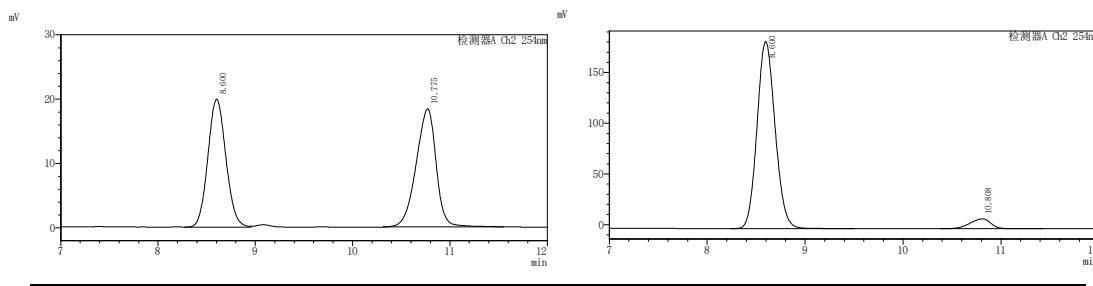


(R,E)-tert-butyl(4-methoxyphenyl)(4-phenylbut-3-en-1-yl)silane (27). Colourless oil (21.7 mg, 67%), $E/Z = 20:1$. **$^1\text{H NMR}$** (600 MHz, Chloroform-*d*) δ 7.52 – 7.44 (m, 2H), 7.30 – 7.23 (m, 4H), 7.19 – 7.15 (m, 1H), 6.91 (d, $J = 8.2$ Hz, 2H), 6.30 (d, $J = 15.8$ Hz, 1H), 6.23 (dt, $J = 15.7, 6.4$ Hz, 1H), 4.08 (t, $J = 3.9$ Hz, 1H), 3.81 (s, 3H), 2.30 – 2.20 (m, 2H), 1.10 – 1.04 (m, 2H), 0.95 (s, 9H).

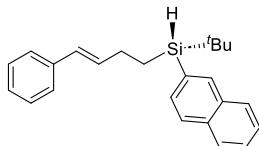
$^{13}\text{C NMR}$ (150 MHz, CDCl₃) δ 160.6, 137.9, 136.8, 133.1, 128.6, 128.4, 126.7, 125.9, 125.0, 113.5, 55.0, 28.3, 27.2, 17.0, 9.1.

HRMS (APCI) (m/z): Calcd for C₂₁H₂₉OSi⁺, ([M + H]⁺): 325.1982, found 325.1984. $[\alpha]_D^{20} = +13$ (*c* = 0.6, CHCl₃).

HPLC conditions: Daicel Chiraldak IJ-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 8.6 min, tr (minor) = 10.8 min, 88% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	8.600	256621	49.369	1	8.600	2365676	94.224
2	10.775	263177	50.631	2	10.808	145009	5.776

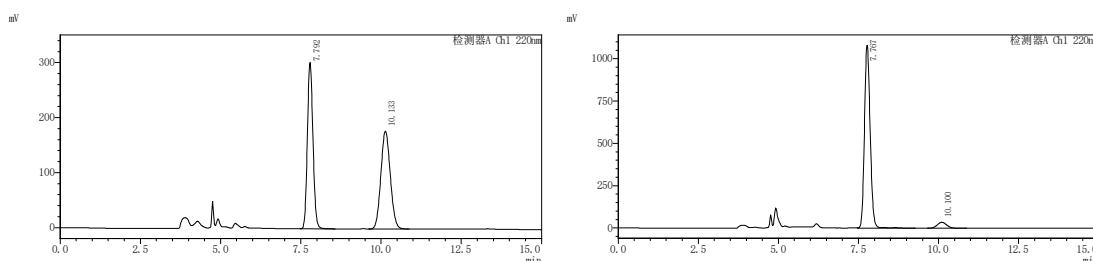


(R,E)-tert-butyl(naphthalen-2-yl)(4-phenylbut-3-en-1-yl)silane (28). Colourless oil (23.7 mg, 69%), $E/Z > 20:1$. **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.93 – 7.71 (m, 3H), 7.66 – 7.56 (m, 1H), 7.54 – 7.43 (m, 2H), 7.27 – 7.20 (m, 4H), 7.18 – 7.12 (m, 1H), 6.30 (d, $J = 15.8$ Hz, 1H), 6.23 (dt, $J = 15.7, 5.9$ Hz, 1H), 4.24 (dd, $J = 5.5, 2.2$ Hz, 1H), 2.38 – 2.20 (m, 2H), 1.27 – 1.11 (m, 2H), 1.00 (s, 9H).

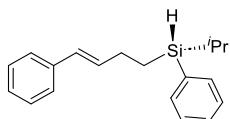
¹³C NMR (100 MHz, CDCl₃) δ 137.8, 136.4, 133.9, 132.9, 131.90, 131.89, 131.4, 128.8, 128.4, 128.1, 127.7, 126.9, 126.7, 126.4, 125.9, 28.3, 27.3, 17.2, 9.0.

HRMS (EI) (m/z): Calcd for C₂₄H₂₈Si, ([M]⁺): 344.1960, found 344.1958. $[\alpha]_D^{20} = +26.5$ (*c* = 0.5, CHCl₃).

HPLC conditions: Daicel Chiraldak IJ-3 column (90: 10 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 7.8 min, tr (minor) = 10.1 min, 90% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	7.792	3657903	50.156	1	7.767	13408452	94.985
2	10.133	3635211	49.844	2	10.100	707902	5.015



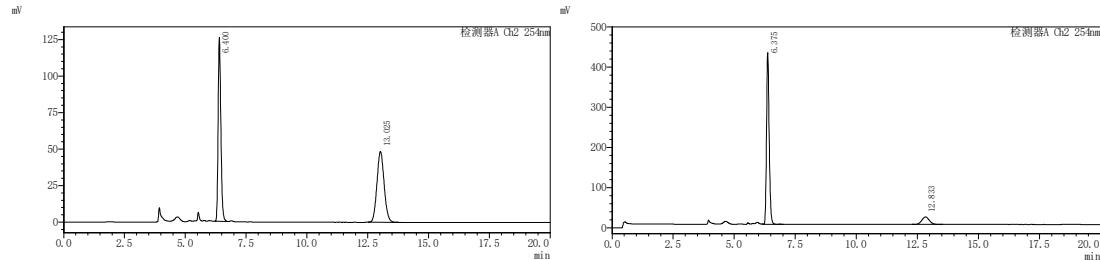
(R,E)-isopropyl(phenyl)(4-phenylbut-3-en-1-yl)silane (29). Colourless oil (21.9 mg, 78%), $E/Z = 17:1$.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.44 (m, 2H), 7.34 – 7.25 (m, 3H), 7.24 – 7.17 (m, 4H), 7.14 – 7.08 (m, 1H), 6.26 (d, $J = 15.7$ Hz, 1H), 6.17 (dt, $J = 15.7, 6.3$ Hz, 1H), 4.10 (q, $J = 3.4$ Hz, 1H), 2.26 – 2.17 (m, 2H), 1.12 – 1.03 (m, 1H), 1.02 – 0.96 (m, 5H), 0.96 – 0.92 (m, 3H).

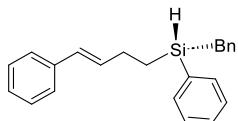
^{13}C NMR (100 MHz, CDCl_3) δ 137.8, 135.1, 134.6, 133.0, 129.3, 128.7, 128.4, 127.8, 126.8, 125.9, 28.0, 18.4, 18.3, 11.8, 10.0.

HRMS (EI) (m/z): Calcd for $\text{C}_{19}\text{H}_{14}\text{Si}$, ($[\text{M}]^+$): 280.1647, found 280.1642. $[\alpha]_{\text{D}}^{20} = +9.5$ ($c = 0.5$, CHCl_3).

HPLC conditions: Daicel Chiralpak IJ-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 6.4 min, tr (minor) = 12.8 min, 78% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	6.400	994834	49.920	1	6.375	3249742	89.105
2	13.025	998004	50.080	2	12.833	397346	10.895



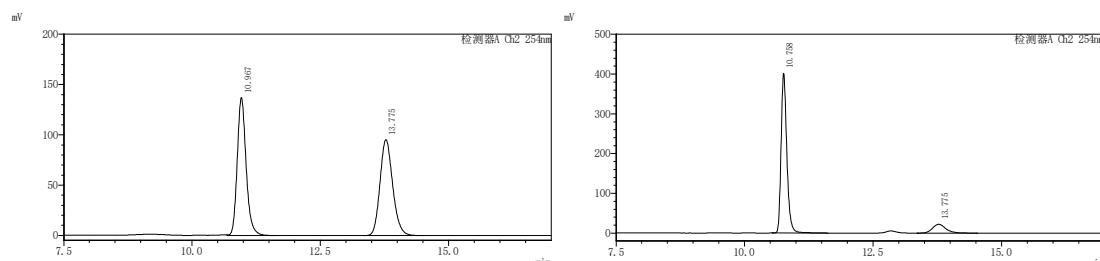
(R,E)-benzyl(phenyl)(4-phenylbut-3-en-1-yl)silane (30). Colourless oil (20.7 mg, 63%), $E/Z = 5:1$.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.36 (m, 2H), 7.31 – 7.24 (m, 3H), 7.20 – 7.17 (m, 4H), 7.13 – 7.08 (m, 3H), 7.03 – 6.98 (m, 1H), 6.97 – 6.92 (m, 2H), 6.24 – 6.16 (m, 1H), 6.14 – 6.01 (m, 1H), 4.38 – 4.31 (m, 1H), 2.40 – 2.31 (m, 2H), 2.20 – 2.09 (m, 2H), 0.98 – 0.90 (m, 2H).

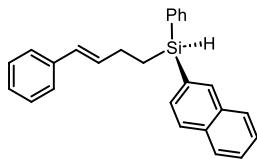
^{13}C NMR (100 MHz, CDCl_3) δ 139.1, 137.7, 134.7, 134.4, 132.6, 129.5, 128.9, 128.42, 128.39, 128.35, 127.9, 126.8, 125.9, 124.5, 27.7, 22.1, 11.1.

GC-MS (EI) (m/z): Calcd for $\text{C}_{23}\text{H}_{24}\text{Si}$: 328.1647, found 328.05. $[\alpha]_{\text{D}}^{20} = +10.3$ ($c = 0.3$, CHCl_3).

HPLC conditions: Daicel Chiralpak IJ-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 10.8 min, tr (minor) = 13.8 min, 77% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	10.958	1960776	49.869	1	10.758	3703068	88.542
2	13.775	1971082	50.131	2	13.775	479204	11.458



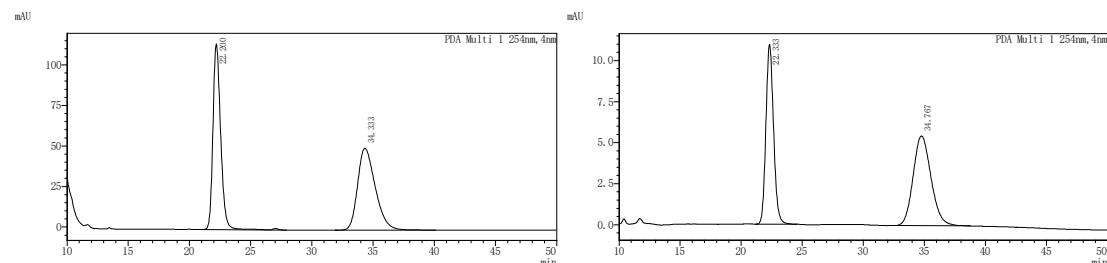
(*S,E*)-naphthalen-2-yl(phenyl)(4-phenylbut-3-en-1-yl)silane (31). Colourless oil (25.8 mg, 71%), *E/Z* = 15:1.

¹H NMR (600 MHz, CDCl₃) δ 8.03 (d, *J* = 1.1 Hz, 1H), 7.76 – 7.73 (m, 3H), 7.56 – 7.51 (m, 3H), 7.44 – 7.38 (m, 2H), 7.34 – 7.28 (m, 3H), 7.19 – 7.15 (m, 4H), 7.11 – 7.07 (m, 1H), 6.29 – 6.25 (m, 1H), 6.19 (dt, *J* = 15.7, 6.5 Hz, 1H), 4.97 (t, *J* = 3.7 Hz, 1H), 2.35 – 2.30 (m, 2H), 1.37 – 1.33 (m, 2H).

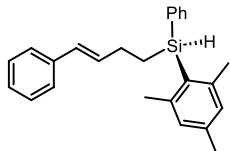
¹³C NMR (150 MHz, CDCl₃) δ 137.3, 135.9, 134.8, 133.8, 133.6, 132.6, 132.2, 131.2, 130.5, 129.3, 128.7, 128.0, 127.7, 127.7, 127.4, 126.9, 126.4, 126.3, 125.6, 125.5, 27.4, 11.6.

GC-MS (EI) (m/z): Calcd for C₂₆H₂₄Si: 364.1647, found 364.05, [α]_D²⁰ = +12.1 (c = 0.4, CHCl₃)

HPLC conditions: Daicel Chiraldak IJ-3 column (90: 10 hexane:¹PrOH, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 22.3 min, tr (minor) = 34.8 min, 8% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	22.200	5042120	49.869	1	22.333	478009	46.108
2	34.333	5068512	50.131	2	34.767	558713	53.892



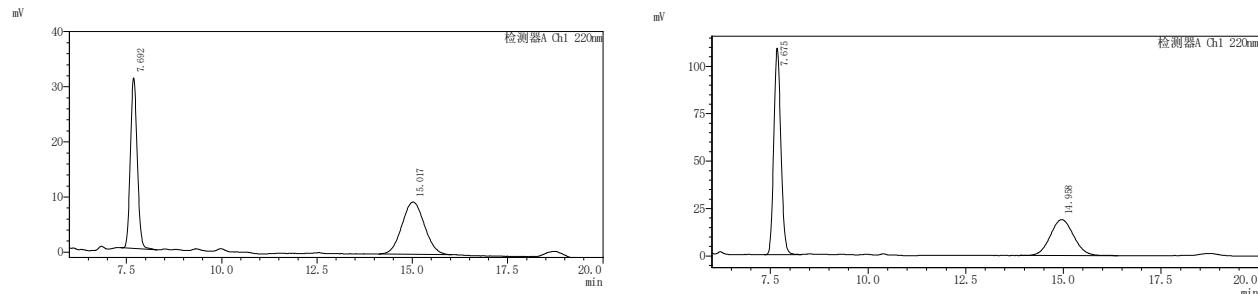
(*S,E*)-mesityl(phenyl)(4-phenylbut-3-en-1-yl)silane (32). Colourless oil (19.6 mg, 55%), *E/Z* = 20:1.

¹H NMR (600 MHz, CDCl₃) δ 7.45 – 7.42 (m, 2H), 7.28 – 7.22 (m, 3H), 7.20 – 7.19 (m, 3H), 7.18 (s, 1H), 7.12 – 7.08 (m, 1H), 6.78 (s, 2H), 6.29 – 6.24 (m, 1H), 6.20 (dt, *J* = 15.7, 6.4 Hz, 1H), 5.13 (dd, *J* = 5.0, 3.5 Hz, 1H), 2.36 – 2.28 (m, 8H), 2.21 (s, 3H), 1.44 – 1.38 (m, 1H), 1.33 – 1.27 (m, 1H).

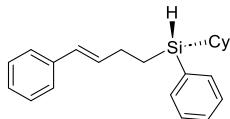
¹³C NMR (150 MHz, CDCl₃) δ 145.1, 139.6, 137.8, 135.4, 134.7, 132.7, 129.2, 129.0, 128.7, 128.4, 128.0, 127.9, 126.8, 126.0, 28.7, 24.3, 21.2, 12.6.

GC-MS (EI) (m/z): Calcd for C₂₄H₂₅Si: 356.1960, found 356.20. [α]_D²⁰ = +8.9 (c = 0.4, CHCl₃)

HPLC conditions: Daicel Chiraldak IJ-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 16.4 min, tr (minor) = 18.0 min, 28% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	7.692	274475	50.110	1	7.675	959944	63.743
2	15.017	273272	49.890	2	14.958	546015	36.257



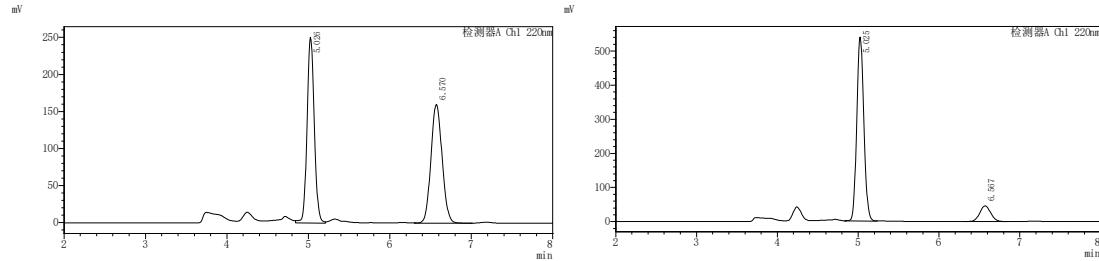
(R,E)-cyclohexyl(phenyl)(4-phenylbut-3-en-1-yl)silane (33). Colourless oil (22.7 mg, 71%), $E/Z = 17:1$.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.55 – 7.50 (m, 2H), 7.38 – 7.32 (m, 3H), 7.29 – 7.24 (m, 4H), 7.19 – 7.14 (m, 1H), 6.32 (d, $J = 15.8$ Hz, 1H), 6.23 (dt, $J = 15.7, 6.4$ Hz, 1H), 4.15 (q, $J = 3.5$ Hz, 1H), 2.35 – 2.19 (m, 2H), 1.81 – 1.74 (m, 1H), 1.71 – 1.65 (m, 4H), 1.28 – 1.13 (m, 6H), 1.07 – 1.02 (m, 2H).

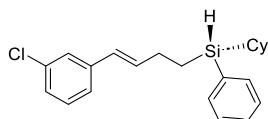
$^{13}\text{C NMR}$ (150 MHz, CDCl₃) δ 137.9, 135.1, 134.7, 133.0, 129.2, 128.7, 128.4, 127.8, 126.7, 125.9, 28.3, 28.3, 28.1, 27.9, 27.8, 26.8, 23.6, 9.9.

HRMS (EI) (m/z): Calcd for C₂₂H₂₈Si, ([M]⁺): 320.1960, found 320.1958. $[\alpha]_D^{20} = -4.3$ ($c = 0.2$, CHCl₃).

HPLC conditions: Daicel Chiralpak IJ-3 column (90: 10 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 5.0 min, tr (minor) = 6.6 min, 77% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	5.026	1542434	50.241	1	5.025	3287422	88.410
2	6.570	1527648	49.759	2	6.567	430959	11.590

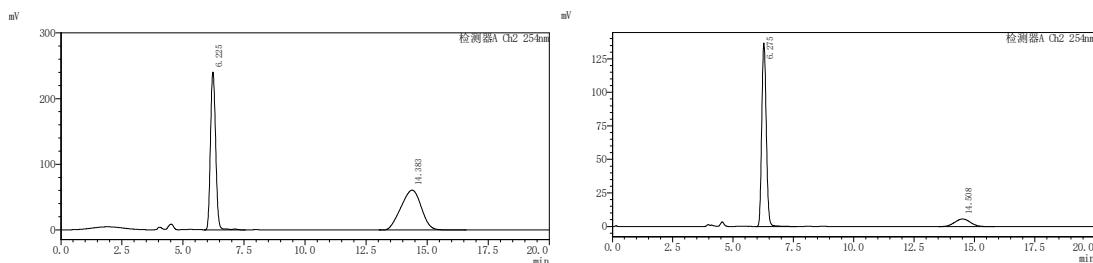


(R,E)-(4-(3-chlorophenyl)but-3-en-1-yl)(cyclohexyl)(phenyl)silane (34). Colourless oil (23.7 mg, 67%), $E/Z > 20:1$. **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 2H), 7.32 – 7.26 (m, 3H), 7.19 – 7.17 (m, 1H), 7.14 – 7.08 (m, 1H), 7.08 – 7.03 (m, 2H), 6.26 – 6.07 (m, 2H), 4.07 (q, $J = 3.4$ Hz, 1H), 2.27 – 2.11 (m, 2H), 1.76 – 1.67 (m, 1H), 1.65 – 1.57 (m, 4H), 1.21 – 1.08 (m, 6H), 0.98 – 0.93 (m, 2H).

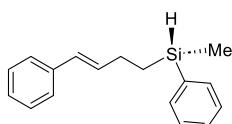
$^{13}\text{C NMR}$ (100 MHz, CDCl₃) δ 139.7, 135.1, 134.6, 134.5, 134.3, 129.6, 129.3, 127.8, 127.5, 126.6, 125.8, 124.1, 28.30, 28.26, 28.1, 27.81, 27.80, 26.7, 23.5, 9.7.

HRMS (EI) (m/z): Calcd for C₂₂H₂₇ClSi, ([M]⁺): 354.1571, found 354.1570. $[\alpha]_D^{20} = -3.5$ ($c = 0.2$, CHCl₃).

HPLC conditions: Daicel Chiralpak OJ-H column (95: 5 hexane: ⁱPrOH, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 6.3 min, tr (minor) = 14.5 min, 75% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	6.225	3556021	50.213	1	6.275	1786069	87.348
2	14.383	3525867	49.787	2	14.508	258716	12.652

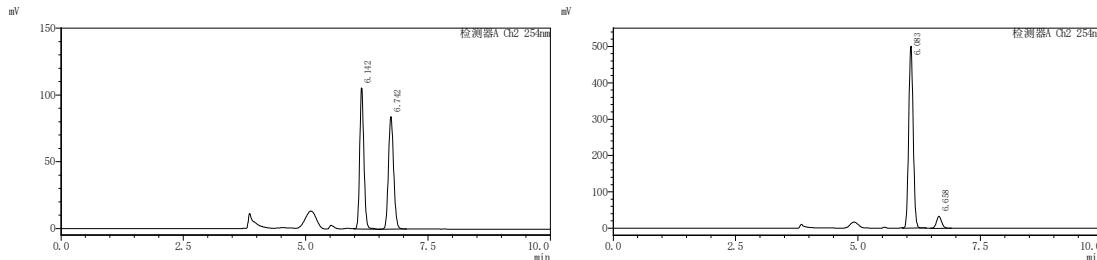


(S,E)-methyl(phenyl)(4-phenylbut-3-en-1-yl)silane (35). Colourless oil (18.9 mg, 75%), *E/Z* = 14:1. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.46 (m, 2H), 7.33 – 7.29 (m, 3H), 7.26 – 7.18 (m, 4H), 7.14 – 7.10 (m, 1H), 6.34 – 6.26 (m, 1H), 6.18 (dt, *J* = 15.7, 6.4 Hz, 1H), 4.43 – 4.29 (m, 1H), 2.29 – 2.21 (m, 2H), 1.05 – 0.91 (m, 2H), 0.32 (d, *J* = 3.8 Hz, 3H).

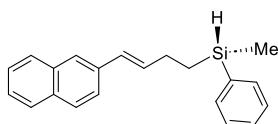
¹³C NMR (100 MHz, CDCl₃) δ 137.8, 136.2, 134.3, 132.8, 129.3, 128.8, 128.4, 127.9, 126.8, 125.9, 27.7, 13.1, -5.7.

HRMS (APCI) (m/z): Calcd for C₁₇H₂₁Si⁺, ([M + H]⁺): 253.1407, found 253.1409. [α]_D²⁰ = +1.3 (c = 0.4, CHCl₃).

HPLC conditions: Daicel Chiraldak IJ-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 6.1 min, tr (minor) = 6.7 min, 86% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	6.142	630393	50.257	1	6.083	3191958	92.953
2	6.742	623940	49.743	2	6.658	241992	7.047

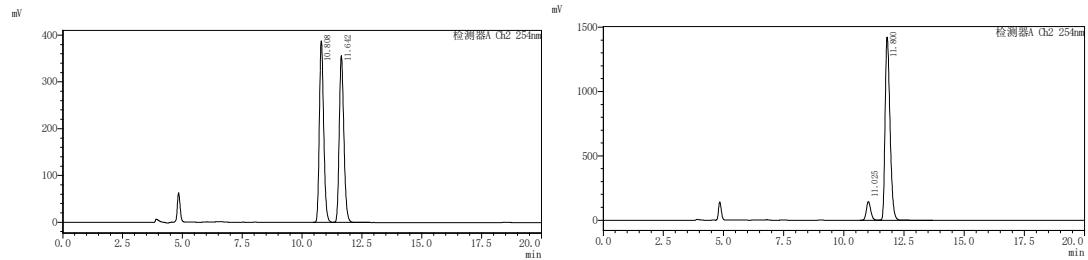


(S,E)-methyl(4-naphthalen-2-yl)but-3-en-1-yl(phenyl)silane (36). Colourless oil (20.8 mg, 69%), *E/Z* = 14:1. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.59 (m, 3H), 7.52 (s, 1H), 7.50 – 7.39 (m, 3H), 7.36 – 7.21 (m, 5H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.26 (dt, *J* = 15.7, 6.5 Hz, 1H), 4.54 – 4.13 (m, 1H), 2.35 – 2.12 (m, 2H), 1.03 – 0.89 (m, 2H), 0.30 (d, *J* = 3.8 Hz, 3H).

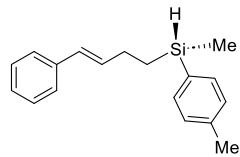
¹³C NMR (100 MHz, CDCl₃) δ 136.2, 135.3, 134.4, 133.7, 133.3, 132.6, 129.3, 129.0, 128.0, 127.9, 127.8, 127.6, 126.1, 125.4, 125.3, 123.6, 27.9, 13.2, -5.6.

GC-MS (EI) (m/z): Calcd for C₂₁H₂₂Si: 302.1491, found 302.15. [α]_D²⁰ = +9.4 (c = 0.3, CHCl₃).

HPLC conditions: Daicel Chiralpak OD-3 column (95: 5 hexane: ⁱPrOH, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 11.8 min, tr (minor) = 11.0 min, 83% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	10.808	4871081	50.450	1	11.025	1838800	8.378
2	11.642	4784186	49.550	2	11.800	20110467	91.622

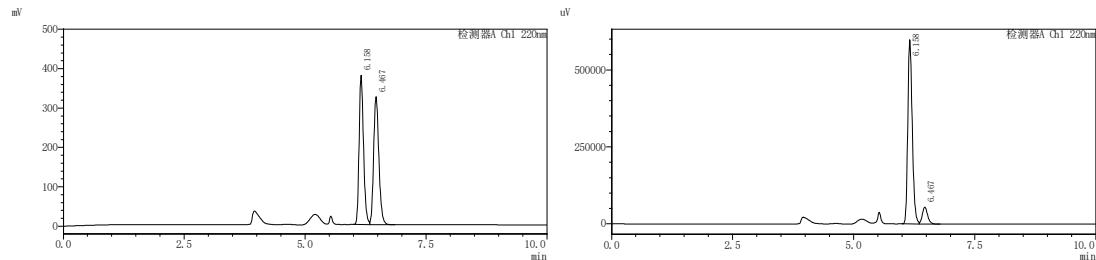


(S,E)-methyl(4-phenylbut-3-en-1-yl)(p-tolyl)silane (37). Colourless oil (20.2 mg, 76%), E/Z = 10:1. **¹H NMR** (400 MHz, Chloroform-d) δ 7.53 – 7.41 (m, 2H), 7.31 – 7.24 (m, 4H), 7.21 – 7.16 (m, 3H), 6.39 – 6.30 (m, 1H), 6.23 (dt, J = 15.8, 6.4 Hz, 1H), 4.44 – 4.36 (m, 1H), 2.35 (s, 3H), 2.33 – 2.25 (m, 2H), 1.07 – 0.95 (m, 2H), 0.35 (d, J = 3.8 Hz, 3H).

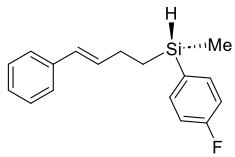
¹³C NMR (100 MHz, CDCl₃) δ 139.2, 137.8, 134.4, 132.9, 132.5, 128.74, 128.70, 128.4, 126.7, 125.9, 27.8, 21.5, 13.3, -5.6.

HRMS (EI) (m/z): Calcd for C₁₈H₂₂Si, ([M]⁺): 266.1491, found 266.1486. [α]_D²⁰ = +14.3 (c = 0.4, CHCl₃).

HPLC conditions: Daicel Chiralpak II-3 column (95: 5 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 6.2 min, tr (minor) = 6.5 min, 81% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	6.158	2411837	49.709	1	6.158	3832993	90.270
2	6.467	2440117	50.291	2	6.467	413167	9.730

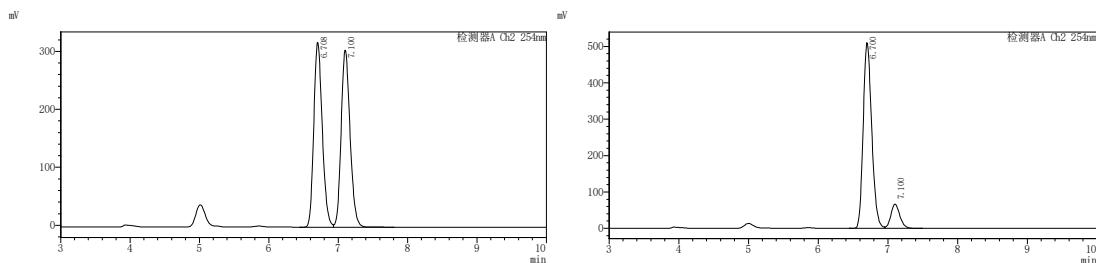


(*S,E*)-(4-fluorophenyl)(methyl)(4-phenylbut-3-en-1-yl)silane (38). Colourless oil (19.4 mg, 72%), $E/Z > 20:1$. $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.57 – 7.47 (m, 2H), 7.33 – 7.26 (m, 4H), 7.20 – 7.16 (m, 1H), 7.06 (t, $J = 8.9$ Hz, 2H), 6.34 (d, $J = 15.8$ Hz, 1H), 6.22 (dt, $J = 15.6, 6.5$ Hz, 1H), 4.46 – 4.35 (m, 1H), 2.32 – 2.25 (m, 2H), 1.06 – 0.98 (m, 2H), 0.37 (d, $J = 3.7$ Hz, 3H).

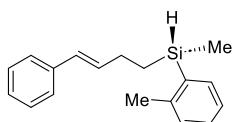
$^{13}\text{C NMR}$ (150 MHz, CDCl₃) δ 164.7, 163.1, 137.7, 136.3, 136.2, 132.6, 131.61, 131.59, 129.0, 128.5, 126.8, 125.9, 115.2, 115.0, 27.7, 13.3, -5.5.

HRMS (EI) (m/z): Calcd for C₁₇H₁₉FSi, ([M]⁺): 270.1240, found 270.1237. $[\alpha]_D^{20} = +3.1$ (*c* = 0.4, CHCl₃).

HPLC conditions: Daicel Chiraldak IJ-3 column (98: 2 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 6.7 min, tr (minor) = 7.1 min, 76% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	6.708	2726698	49.847	1	6.700	4367209	87.961
2	7.100	2743442	50.153	2	7.100	597711	12.039



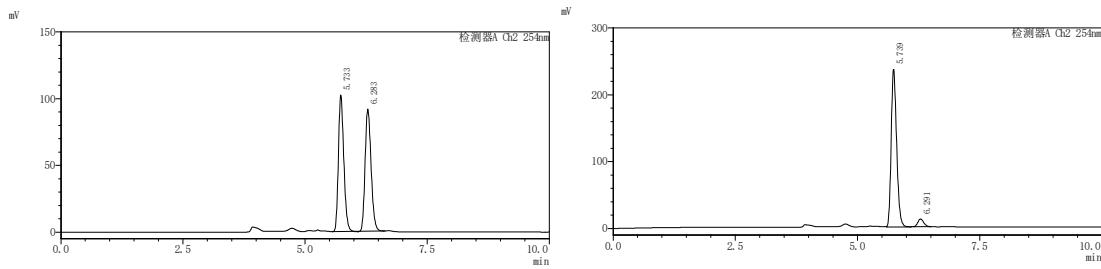
(*S,E*)-methyl(4-phenylbut-3-en-1-yl)(o-tolyl)silane (39). Colourless oil (20.0 mg, 75%), $E/Z > 20:1$.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.43 – 7.38 (m, 1H), 7.24 – 7.16 (m, 5H), 7.13 – 7.05 (m, 3H), 6.34 – 6.22 (m, 1H), 6.16 (dt, $J = 15.7, 6.4$ Hz, 1H), 4.51 – 4.37 (m, 1H), 2.38 (s, 3H), 2.26 – 2.16 (m, 2H), 1.07 – 0.90 (m, 2H), 0.31 (d, $J = 3.8$ Hz, 3H).

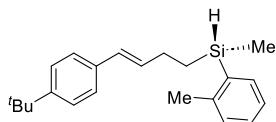
$^{13}\text{C NMR}$ (100 MHz, CDCl₃) δ 143.7, 137.8, 135.02, 134.96, 132.8, 129.6, 129.5, 128.8, 128.4, 126.8, 125.9, 125.0, 28.0, 22.5, 13.0, -5.3.

HRMS (EI) (m/z): Calcd for C₁₈H₂₂Si, ([M]⁺): 266.1491, found 266.1488. $[\alpha]_D^{20} = +15.1$ (*c* = 0.4, CHCl₃).

HPLC conditions: Daicel Chiraldak IJ-3 column (98: 2 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 5.5 min, tr (minor) = 6.1 min, 88% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	5.733	784991	50.076	1	5.533	2463553	94.028
2	6.283	782603	49.924	2	6.058	156468	5.972

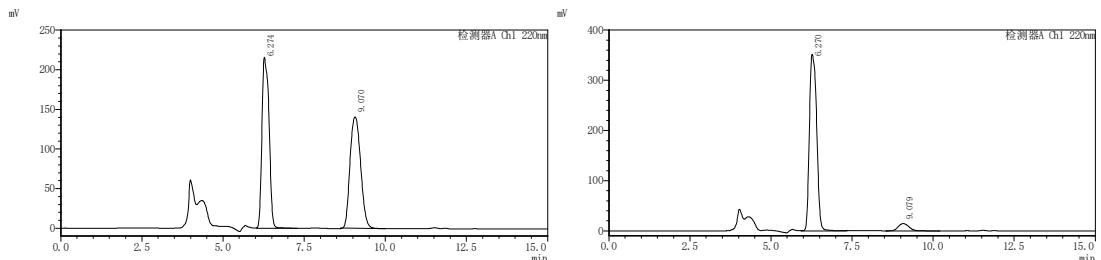


(*S,E*)-(4-(*tert*-butyl)phenyl)but-3-en-1-yl(methyl)(*o*-tolyl)silane (40**).** Colourless oil (22.6 mg, 70%), $E/Z = 10:1$. $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 7.51 – 7.45 (m, 1H), 7.34 – 7.26 (m, 3H), 7.26 – 7.21 (m, 2H), 7.20 – 7.14 (m, 2H), 6.32 (d, $J = 15.7$ Hz, 1H), 6.20 (dt, $J = 15.7, 6.5$ Hz, 1H), 4.55 – 4.46 (m, 1H), 2.46 (s, 3H), 2.33 – 2.23 (m, 2H), 1.30 (s, 9H), 1.14 – 0.97 (m, 2H), 0.38 (d, $J = 3.8$ Hz, 3H).

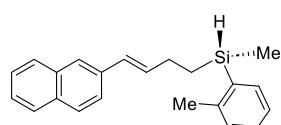
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 149.8, 143.7, 135.1, 135.0, 132.1, 129.6, 129.5, 128.5, 128.4, 125.6, 125.4, 125.0, 34.5, 31.3, 28.0, 22.5, 13.1, -5.3.

HRMS (EI) (m/z): Calcd for $\text{C}_{22}\text{H}_{30}\text{Si}$, ([M] $^+$): 322.2117, found 322.2120. $[\alpha]_D^{20} = +7.9$ ($c = 0.1$, CHCl_3).

HPLC conditions: Daicel Chiraldak IJ-3 column (95:5 hexane: ethanol, 0.8 mL/min, 40 °C, 220 nm); tr (major) = 6.3 min, tr (minor) = 9.1 min, 88% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	6.274	3304765	50.841	1	6.270	5515754	94.105
2	9.070	3195395	49.159	2	9.079	345504	5.895

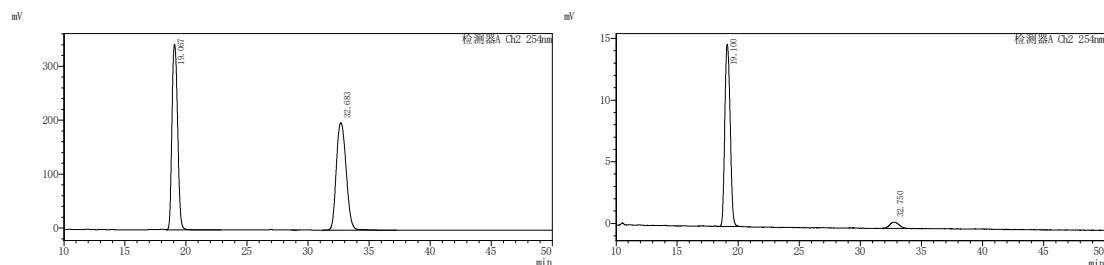


(*S,E*)-methyl(4-(naphthalen-2-yl)but-3-en-1-yl)(*o*-tolyl)silane (41**).** Colourless oil (21.5 mg, 68%), $E/Z > 20:1$. $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 7.77 – 7.71 (m, 3H), 7.61 (s, 1H), 7.55 – 7.47 (m, 2H), 7.44 – 7.35 (m, 2H), 7.33 – 7.27 (m, 1H), 7.21 – 7.15 (m, 2H), 6.49 (d, $J = 15.3$ Hz, 1H), 6.36 (dt, $J = 15.9, 6.6$ Hz, 1H), 4.57 – 4.50 (m, 1H), 2.47 (s, 3H), 2.39 – 2.29 (m, 2H), 1.17 – 1.02 (m, 2H), 0.40 (d, $J = 3.9$ Hz, 3H).

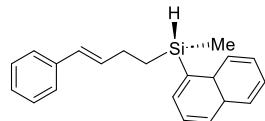
¹³C NMR (100 MHz, CDCl₃) δ 143.7, 135.3, 135.04, 134.96, 133.7, 133.3, 132.6, 129.6, 129.5, 129.0, 128.0, 127.8, 127.6, 126.1, 125.4, 125.3, 125.1, 123.6, 28.1, 22.5, 13.1, -5.3.

HRMS (EI) (m/z): Calcd for C₂₂H₂₄Si, ([M]⁺): 316.1647, found 316.1647. [α]_D²⁰ = +13.8 (c = 0.3, CHCl₃).

HPLC conditions: Daicel Chiralpak OD-H column (90: 10 hexane: ethanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 19.1 min, tr (minor) = 32.8 min, 89% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	19.067	11101420	49.873	1	19.100	450023	94.277
2	32.683	11158181	50.127	2	32.750	27317	5.723

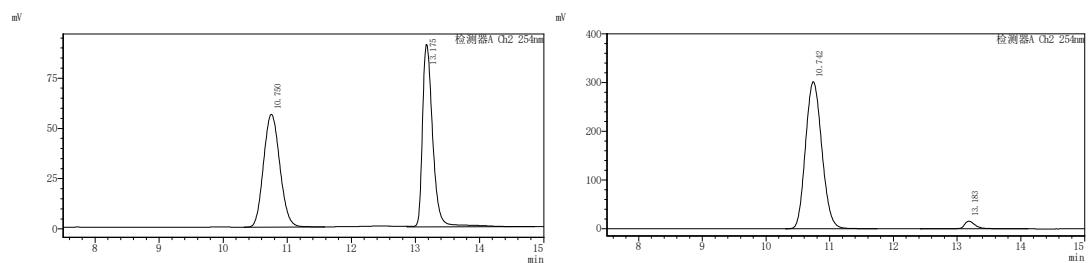


(1*S*)-(4a,8a-dihydronaphthalen-1-yl)(methyl)((E)-4-phenylbut-3-en-1-yl)silane (42). Colourless oil (18.1 mg, 60%), E/Z = 17:1. **¹H NMR** (600 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.6 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.76 – 7.71 (m, 1H), 7.53 – 7.43 (m, 3H), 7.30 – 7.23 (m, 4H), 7.18 – 7.14 (m, 1H), 6.34 – 6.29 (m, 1H), 6.26 – 6.17 (m, 1H), 4.87 – 4.80 (m, 1H), 2.35 – 2.27 (m, 2H), 1.26 – 1.13 (m, 2H), 0.52 (dd, *J* = 3.8, 1.9 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 137.8, 137.1, 134.5, 134.2, 133.2, 132.7, 130.1, 129.0, 128.9, 128.4, 127.6, 126.8, 126.0, 125.9, 125.6, 125.2, 28.1, 13.5, -5.0.

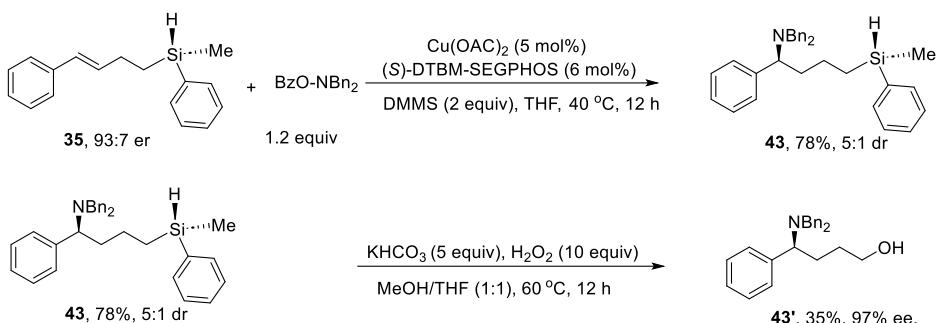
HRMS (EI) (m/z): Calcd for C₂₁H₂₂Si: 302.1491, found 302.15. [α]_D²⁰ = +8.2 (c = 0.3, CHCl₃).

HPLC conditions: Daicel Chiralpak OJ-H column (95: 5 hexane: ⁱPrOH, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 10.7 min, tr (minor) = 13.2 min, 93% ee.

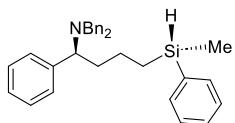


No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	10.750	994645	49.610	1	10.742	5377573	96.625
2	13.175	1010284	50.390	2	13.183	187816	3.375

2.2. Synthetic Applications



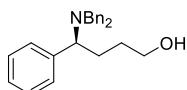
In a glove-box, Cu(OAc)_2 (0.9 mg, 5 mol%) and (*S*)-DTBM-SEGPHOS (7.1mg, 6 mol%) were added to a screw-cap test tube. The tube was then sealed and taken out from the glove-box and THF (2.0 mL, 0.5 M) was added. The mixture was stirred for 15 min, then DMMS (dimethoxymethylsilane, 21 mg, 25 μL , 2.0 equiv.) was added dropwise and the stirring was continued for another 10 min at rt before being added by asyringe to another screw-cap test tube containing **35** (25.2 mg, 0.1 mmol, 1.0 equiv.) and *O*-benzoyl-*N,N*-dibenzylhydroxylamine (38.1 mg, 1.2 mmol, 1.2 equiv.). The reaction tube was stirred at 40 $^\circ\text{C}$ for 36 h. The reaction mixture was diluted with EtOAc, quenched with 2 mL Na_2CO_3 solution. The product **43** was purified by chromatography onsilica gel (5-10% EtOAc/hexane). After the oxidation of **43** by using KHCO_3 (5.0 equiv) and H_2O_2 (10 equiv) in MeOH/THF (1:1, 2 mL) at 60 $^\circ\text{C}$ for 12 h, the mixture was washed with NH_4Cl (2 x 10.0 mL) and extracted with ethyl acetate (2 x 10.0 mL). Then the combined organic phases were dried over anhydrous Na_2SO_4 , filtered off and the solvent was evaporated under vacuum. The residue was purified by flash column chromatography on silica with a mixture of ethyl acetate and petroleum ether as eluent to obtain the product **43'**.



(*S*)-*N,N*-dibenzyl-4-((*S*)-methyl(phenyl)silyl)-1-phenylbutan-1-amine (43). Colourless oil (35.0 mg, 78%). **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 7.48 – 7.37 (m, 2H), 7.33 – 7.23 (m, 9H), 7.23 – 7.18 (m, 5H), 7.18 – 7.05 (m, 4H), 4.31 – 4.19 (m, 1H), 3.72 (s, 1H), 3.68 (s, 1H), 3.59 (t, $J = 7.4$ Hz, 1H), 3.03 (s, 1H), 3.00 (s, 1H), 2.09 – 1.97 (m, 1H), 1.73 – 1.61 (m, 1H), 1.57 – 1.47 (m, 1H), 1.39 – 1.25 (m, 1H), 0.73 – 0.63 (m, 2H), 0.22 (d, $J = 3.8$ Hz, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.4, 138.9, 136.6, 134.3, 129.2, 129.0, 128.8, 128.2, 127.9, 127.8, 126.9, 126.9, 61.3, 53.6, 34.7, 21.7, 13.3, -5.5.

HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{31}\text{H}_{36}\text{NSi}^+$, ($[\text{M} + \text{H}]^+$), 450.2612, found 450.2606. $[\alpha]_{D}^{20} = +15.1$ (c = 0.4, CHCl_3).



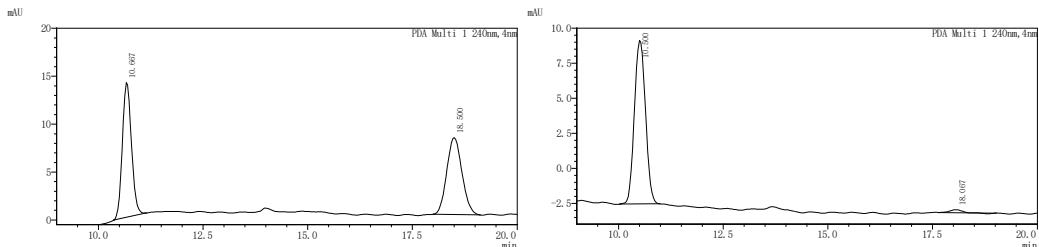
(*S*)-4-(dibenzylamino)-4-phenylbutan-1-ol (43'). Colourless oil (9.4 mg, 35%). **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 7.42 – 7.26 (m, 6H), 7.27 – 7.20 (m, 5H), 7.18 – 7.13 (m, 4H), 3.76 (d, $J = 13.7$ Hz, 2H), 3.69 – 3.58 (m, 1H), 3.50 (t, $J = 6.4$ Hz, 2H), 3.07 (d, $J = 13.8$ Hz, 2H), 2.15 – 2.00 (m, 1H), 1.84 – 1.73 (m, 1H), 1.70 – 1.62 (m, 1H), 1.48 – 1.41 (m, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.2, 138.6, 129.0, 128.8, 128.2, 128.0, 127.1, 126.8, 62.9, 61.7, 53.5, 30.2, 27.7.

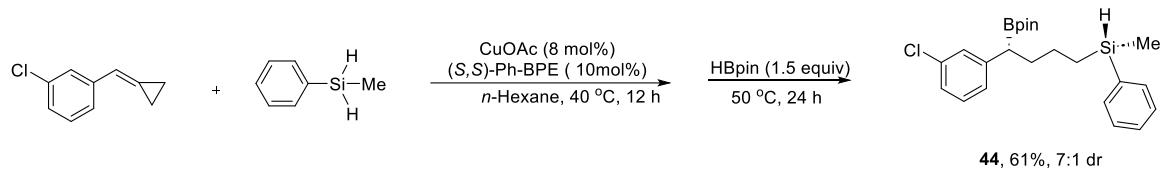
HRMS (ESI-TOF) (m/z): Calcd for C₂₄H₂₈NO⁺, ([M + H]⁺), 346.2165, found 346.2175. [α]_D²⁰ = -50 (c = 0.4, CHCl₃).

To confirm the absolute configuration of **41**, we compared the specific rotation of **41** with the known substances' specific rotation^{7,8}. We concluded that the stereogenic carbon center is *S*-configuration.

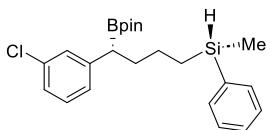
HPLC conditions: Daicel Chiralpak IC column (95:10 hexane: ⁱPrOH, 0.8 mL/min, 40 °C, 240 nm); tr (major) = 10.5 min, tr (minor) = 18.1 min, 97% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	10.667	212319	51.108	1	10.500	216063	98.557
2	18.500	203109	48.892	2	18.067	3164	1.443



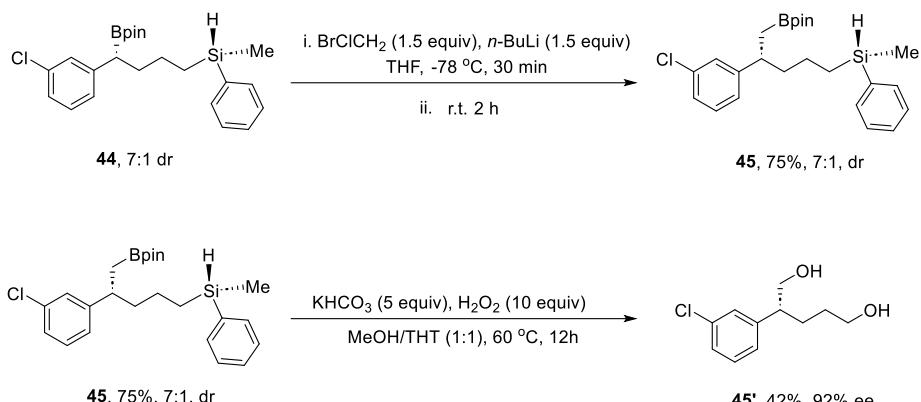
A 8 mL sealed tube reactor equipped with a magnetic stirrer bar was charged CuOAc (1.0 mg, 8 mol%) and (S,S)-Ph-BPE (5.1mg, 10 mol%) in dry *n*-Hexane (1 mL) under N₂ atmosphere in a glove box and stirred for 10 min, then the arylidene cyclopropane (0.1 mmol) and dihydrosilane (0.12 mmol) were added in the tube. The tube was capped, then removed from the glove box and the resulting mixture was stirred at 40 °C for 12 h prior adding HBpin (36.3 μL, 0.250 mmol) under N₂ atmosphere in a glove box. The tube was removed from the glove box, and the mixture was stirred at 50 °C for 24 h. After the reaction completed, the reaction solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate to provide product **44**.



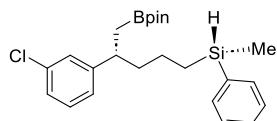
(*S*)-(*R*)-4-(3-chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl(methyl)(phenyl)silane (44**).** Colourless oil (25.3 mg, 61% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.46 (m, 2H), 7.37 – 7.30 (m, 3H), 7.19 – 7.12 (m, 2H), 7.11 – 7.07 (m, 1H), 7.07 – 7.02 (m, 1H), 4.39 – 4.23 (m, 1H), 2.29 (t, *J* = 7.9 Hz, 1H), 1.93 – 1.79 (m, 1H), 1.74 – 1.60 (m, 1H), 1.41 – 1.31 (m, 2H), 1.16 (d, *J* = 8.1 Hz, 12H), 0.93 – 0.75 (m, 2H), 0.30 (d, *J* = 3.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.5, 136.5, 134.3, 133.9, 129.4, 129.1, 128.3, 127.8, 126.5, 125.3, 83.4, 35.9, 24.6, 24.5, 23.9, 13.3, -5.7.(the resonance of the carbon with boron attached was not observed)

HRMS (EI) (m/z): Calcd for C₂₃H₃₂BClO₂Si: 414.1953, found 414.1938. [α]_D²⁰ = +9.3 (c = 0.4, CHCl₃).

¹¹B NMR (128 MHz, CDCl₃) δ 32.91.



To a solution of **44** (0.100 mmol, 41.4 mg) and BrClCH_2 (0.15 mmol, 9.7 μL) in 1 mL THF was added dropwise $n\text{-BuLi}$ (0.15 mmol, 2.5 M in n -hexane, 60 μL) at -78°C in 5 minutes under N_2 . The resulting mixture stirred at -78°C for 30 min. Then the mixture was warmed to room temperature and stirred for 2 h. After the reaction completed, the reaction solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate to provide product **45**. After the oxidation of **45** by using KHCO_3 (5.0 equiv) and H_2O_2 (10 equiv) in MeOH/THF (1:1, 2 mL) at 60°C for 12 h, the mixture was washed with NH_4Cl (2 \times 10.0 mL) and extracted with ethyl acetate (2 \times 10.0 mL). Then the combined organic phases were dried over anhydrous Na_2SO_4 , filtered off and the solvent was evaporated under vacuum. The residue was purified by flash column chromatography on silica with a mixture of ethyl acetate and petroleum ether as eluent to obtain product **45'**.

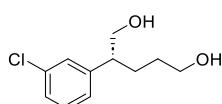


(S)-(R)-4-(3-chlorophenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl(methyl)(phenyl)silane (45**).** Colourless oil (32.1 mg, 75% yield). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.45 – 7.35 (m, 2H), 7.32 – 7.21 (m, 3H), 7.11 – 7.01 (m, 3H), 7.01 – 6.93 (m, 1H), 4.32 – 4.13 (m, 1H), 2.79 – 2.66 (m, 1H), 1.60 – 1.49 (m, 2H), 1.23 – 1.15 (m, 2H), 1.11 – 0.93 (m, 14H), 0.84 – 0.62 (m, 2H), 0.20 (d, $J = 3.8$ Hz, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 149.5, 136.5, 134.2, 133.7, 129.3, 129.1, 127.8, 127.7, 125.8, 125.5, 83.0, 42.4, 41.0, 24.7, 24.6, 22.3, 13.2, -5.7.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 33.26.

HRMS (EI) (m/z): Calcd for $\text{C}_{24}\text{H}_{34}\text{BClO}_2\text{Si}$: 428.2110, found 428.2106. $[\alpha]_D^{20} = +8.3$ ($c = 0.4$, CHCl_3).

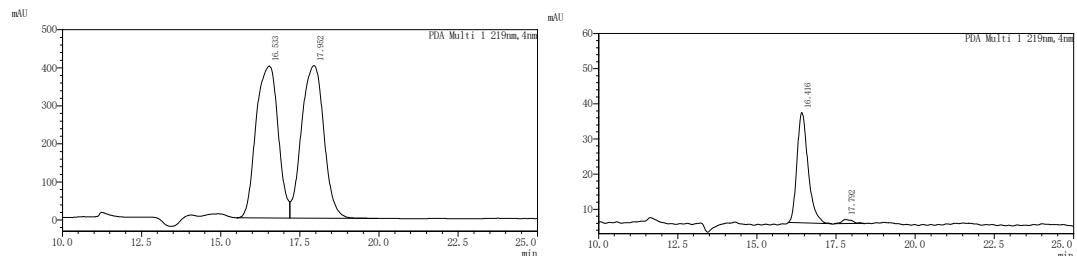


(R)-2-(3-chlorophenyl)pentane-1,5-diol (45'**).** Colourless oil (6.7 mg, 42% yield). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.22 – 7.13 (m, 3H), 7.06 – 7.00 (m, 1H), 3.74 – 3.61 (m, 2H), 3.54 (t, $J = 6.4$ Hz, 2H), 2.79 – 2.63 (m, 1H), 1.82 – 1.72 (m, 1H), 1.60 – 1.56 (m, 1H), 1.46 – 1.33 (m, 2H).

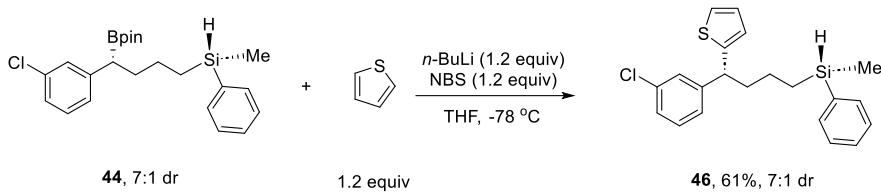
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 144.5, 134.5, 129.9, 128.1, 127.0, 126.3, 67.2, 62.7, 48.2, 30.3, 28.1

HRMS (ESI-TOF) (m/z): Calcd for $C_{11}H_{16}ClO_2^+$, ($[M + H]^+$), 215.0833, found 215.0835. $[\alpha]_D^{20} = +3.8$ (c = 0.4, $CHCl_3$).

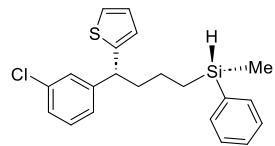
HPLC conditions: Daicel Chiralpak IC column (90: 10 hexane: iPrOH , 0.8 mL/min, 40 °C, 219 nm); tr (major) = 16.4 min, tr (minor) = 18.0 min, 93% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	16.533	19328449	49.512	1	16.416	770374	96.400
2	17.952	19709455	50.488	2	17.792	28767	3.600



To a solution of thiophene (0.12 mmol, 9.2 μ L) in 1 mL THF was added dropwise *n*-BuLi (0.12 mmol, 2.5 M in THF, 48 μ L) in 5 minutes at -78 °C under N_2 . The mixture was warmed to room temperature and stirred for 1 h. Then **44** (0.100 mmol, 41.4 mg) dissolved in 1 mL THF was injected into the solution at -78 °C. The resulting mixture stirred at -78 °C for 1 h following by adding NBS (0.12 mmol, 21.4 mg) in 1 mL THF, and reacted for another 1 h. After the reaction finished, 20% aqueous solution of $Na_2S_2O_3$ was added, and then the mixture was extracted with ethyl acetate (2 x 10 mL). The combined organic fractions were dried with anhydrous Na_2SO_4 . The solvent was removed under vacuum and the residue was purified by flash column chromatography with a mixture of hexane/ethyl acetate (100:1 to 50:1) as eluent. Compound **46** was obtained as colourless oil.

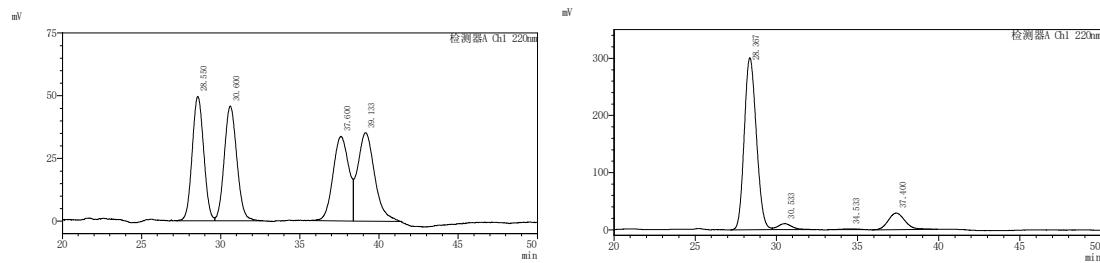


(S)-((R)-4-(3-chlorophenyl)-4-(thiophen-2-yl)butyl)(methyl)(phenyl)silane (46). Colourless oil (22.6 mg, 61% yield). **1H NMR** (400 MHz, Chloroform-*d*) δ 7.44 – 7.36 (m, 2H), 7.30 – 7.23 (m, 3H), 7.16 – 7.08 (m, 3H), 7.06 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.82 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.74 – 6.65 (m, 1H), 4.29 – 4.20 (m, 1H), 4.02 (t, *J* = 7.7 Hz, 1H), 2.12 – 1.89 (m, 2H), 1.41 – 1.22 (m, 2H), 0.89 – 0.66 (m, 2H), 0.21 (d, *J* = 3.8 Hz, 3H).

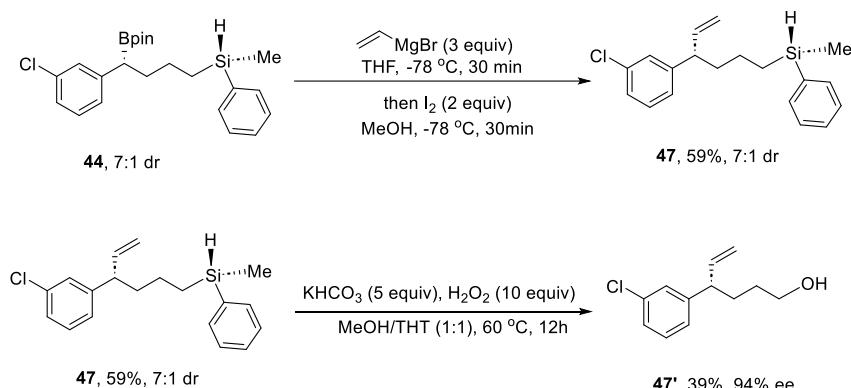
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 146.6, 136.2, 134.2, 129.7, 129.2, 127.9, 127.8, 126.7, 126.6, 125.8, 123.9, 123.6, 46.0, 40.4, 22.5, 13.1, -5.7.

HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{24}ClSSi^+$, ($[M + H]^+$), 371.1051, found 371.1047. $[\alpha]_D^{20} = +24.9$ (c = 0.4, $CHCl_3$).

HPLC conditions: Daicel Chiralpak OJ-H column (98: 2 hexane: $^i\text{PrOH}$, 0.6 mL/min, 40 °C, 220 nm); major isomer: tr (major) = 28.4 min, tr (minor) = 30.5 min, 92% ee.; minor isomer: tr (major) = 37.4 min, tr (minor) = 34.5 min, 96% ee.

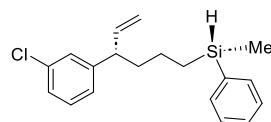


No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	28.550	2510785	25.030	1	28.367	15614391	84.529
2	30.600	2536737	25.288	2	30.533	654655	3.544
3	37.600	2343433	23.361	3	34.533	108566	0.588
4	39.133	2640275	26.321	4	37.400	2094594	11.339



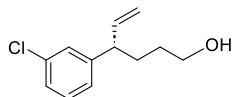
To a solution of **44** (41.4 mg, 0.1 mmol) in THF (1 mL) was added vinylmagnesium bromide solution (0.3 mL, 1.0 M in THF, 0.3 mmol) at -78 °C and the reaction mixture was stirred for 30 min at the same temperature. A solution of iodine (50.8 mg, 0.3 mmol in MeOH) was added. After the reaction mixture was stirred for 30 minutes, it was allowed react for additional 5 h at room temperature, and then quenched with saturated $\text{Na}_2\text{S}_2\text{O}_3$ and extracted with Et_2O . The combined organic layers were washed with brine and dried over Na_2SO_4 . The solvent was removed under reduced pressure. The crude product was purified flash column chromatography with a mixture of hexane/ethyl acetate as eluent. Compound **47** was obtained as a colourless oil (18.5 mg, 0.059 mmol, dr = 7:1).

After the oxidation of compound **47** by using KHCO_3 (5.0 equiv) and H_2O_2 (10 equiv) in MeOH/THF (1:1, 2 mL) at 60 °C for 12 h, the mixture was washed with NH_4Cl (2 x 10.0 mL) and extracted with ethyl acetate (2 x 10.0 mL). Then the combined organic phases were dried over anhydrous Na_2SO_4 , filtered off and the solvent was evaporated under vacuum. The residue was purified by flash column chromatography on silica with a mixture of ethyl acetate and petroleum ether as eluent to obtain the product **47'**.



(S)-((S)-4-(3-chlorophenyl)hex-5-en-1-yl)(methyl)(phenyl)silane (47). Colourless oil (18.5 mg, 59%, dr = 7:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.49 – 7.37 (m, 2H), 7.35 – 7.23 (m, 3H), 7.15 – 7.04 (m, 3H), 6.98 – 6.92 (m, 1H), 5.87 – 5.71 (m, 1H), 4.98 – 4.89 (m, 2H), 4.30 – 4.19 (m, 1H), 3.14 (q, *J* = 7.5 Hz, 1H), 1.73 – 1.58 (m, 2H), 1.37 – 1.17 (m, 2H), 0.84 – 0.67 (m, 2H), 0.23 (d, *J* = 3.7 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 146.5, 141.4, 136.4, 134.2, 134.2, 129.6, 129.2, 127.8, 127.7, 126.3, 125.8, 114.6, 49.2, 38.5, 22.1, 13.2, -5.7.

HRMS (EI) (m/z): Calcd for C₁₉H₂₃ClSi: 314.1258, found 314.1244. [α]_D²⁰ = -6 (c = 0.4, CHCl₃).

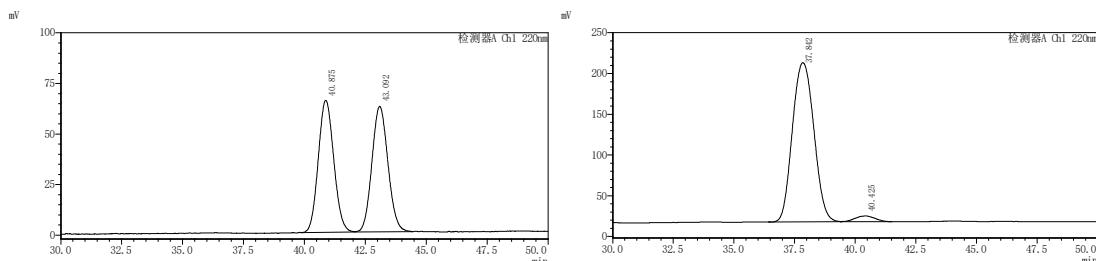


(S)-4-(3-chlorophenyl)hex-5-en-1-ol(47'). Colourless oil (4.8 mg, 39%). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.19 – 7.07 (m, 3H), 7.04 – 6.96 (m, 1H), 6.01 – 5.72 (m, 1H), 5.04 – 5.00 (m, 1H), 5.00 – 4.93 (m, 1H), 3.57 (t, *J* = 6.5 Hz, 2H), 3.27 – 3.08 (m, 1H), 1.81 – 1.65 (m, 2H), 1.45 – 1.27 (m, 2H).

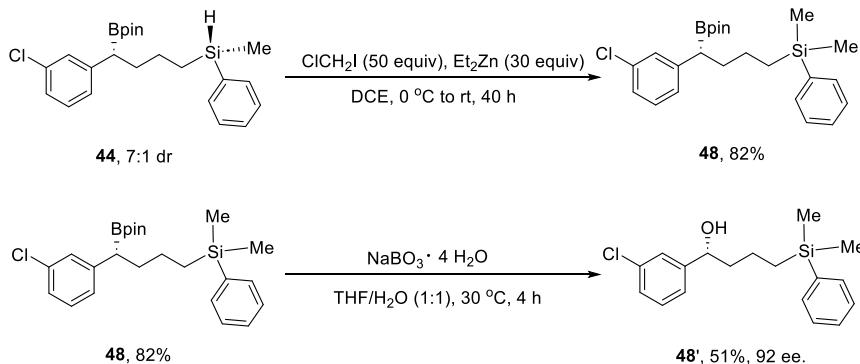
¹³C NMR (100 MHz, CDCl₃) δ 146.3, 141.3, 134.2, 129.7, 127.7, 126.4, 125.8, 114.9, 62.8, 49.3, 31.4 30.6.

HRMS (ESI-TOF) (m/z): Calcd for C₁₂H₁₆ClO⁺, ([M + H]⁺), 211.0884, found 211.0884. [α]_D²⁰ = -6.1 (c = 0.3, CHCl₃).

HPLC conditions: Daicel Chiraldak OD-3 column (98: 2 hexane: ⁱPrOH, 0.5 mL/min, 40 °C, 220 nm); tr (major) = 37.8 min, tr (minor) = 40.4 min, 93% ee.

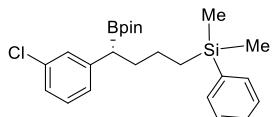


No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	40.875	2889895	50.429	1	37.842	12079727	96.697
2	43.092	2840691	49.571	2	40.425	412623	3.303



To a solution of **44** (0.100 mmol, 41.4 mg) and ClCH₂I (5 mmol, 383 μ L) in 1 mL THF was added dropwise Et₂Zn (2.0 M in toluene, 3 mmol, 1.5 ml) at 0 °C in 5 minutes under N₂. The mixture was

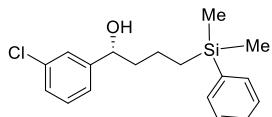
warmed to room temperature and stirred for 40 h. After the reaction finished, the combined filtrates were concentrated and crude product was purified by flash column chromatography with a mixture of hexane/ethyl acetate as eluent to give the corresponding product **48** as a colourless oil. Then the product **48** followed by 0.4 mmol of NaBO₃•4H₂O (4 equiv) under air. Then THF (1.5 mL) and H₂O (1.5 mL) was added. The reaction mixture was stirred at room temperature until full conversion by TLC. Then, the reaction mixture was extracted with EA/H₂O. The combined organic layers were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography to afford the product **48'**.



(R)-(4-(3-chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)dimethyl(phenyl)silane (48). Colourless oil (35.1 mg, 82%). ¹H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.20 (m, 2H), 7.14 – 7.07 (m, 3H), 6.96 – 6.94 (m, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.91 – 6.83 (m, 1H), 6.86 – 6.79 (m, 1H), 2.07 (t, *J* = 7.9 Hz, 1H), 1.66 – 1.56 (m, 1H), 1.47 – 1.37 (m, 1H), 1.14 – 1.04 (m, 2H), 0.94 (d, *J* = 8.5 Hz, 12H), 0.59 – 0.48 (m, 2H), 0.00 (d, *J* = 1.9 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 145.6, 139.5, 133.9, 133.5, 129.4, 128.7, 128.3, 127.7, 126.5, 125.3, 83.4, 36.3, 24.6, 24.5, 23.4, 15.6, -3.0, -3.2.

HRMS (ESI-TOF) (m/z): Calcd for C₂₄H₃₅BClO₂Si⁺, ([M + H]⁺), 429.2182, found 429.2020. [α]_D²⁰ = +15.9 (c = 0.4, CHCl₃).

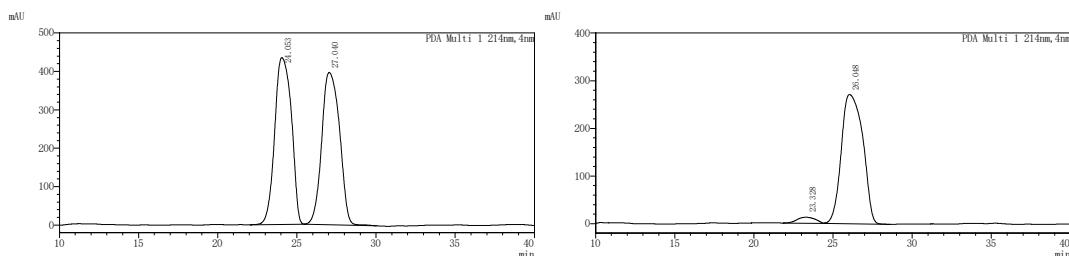


(R)-1-(3-chlorophenyl)-4-(dimethyl(phenyl)silyl)butan-1-ol (48'). Colourless oil (13.3 mg, 51%)
¹H NMR (400 MHz, Chloroform-d) δ 7.62 – 7.43 (m, 2H), 7.43 – 7.31 (m, 4H), 7.29 – 7.24 (m, 2H), 7.20 – 7.16 (m, 1H), 4.65 (dd, *J* = 8.0, 5.1 Hz, 1H), 1.84 – 1.63 (m, 2H), 1.59 – 1.32 (m, 1H), 1.44 – 1.33 (m, 1H), 0.86 – 0.74 (m, 2H), 0.28 (s, 6H).

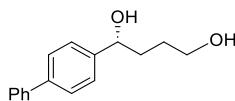
¹³C NMR (100 MHz, CDCl₃) δ 147.0, 139.3, 134.3, 133.5, 129.7, 128.9, 127.8, 127.5, 126.0, 123.9, 73.56, 42.8, 20.2, 15.5, -3.07, -3.11.

HRMS (ESI-TOF) (m/z): Calcd for C₁₈H₂₄ClOSi⁺, ([M + H]⁺), 318.1207, found 319.1279. [α]_D²⁰ = +24.9 (c = 0.4, CHCl₃).

HPLC conditions: Daicel Chiralpak IA column (98: 2 hexane: ⁱPrOH, 0.5 mL/min, 40 °C, 214 nm); tr (major) = 26.0 min, tr (minor) = 23.3 min, 92% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	24.053	31899050	50.642	1	23.328	1038421	3.884
2	27.040	31089772	49.358	2	26.048	25699813	96.116



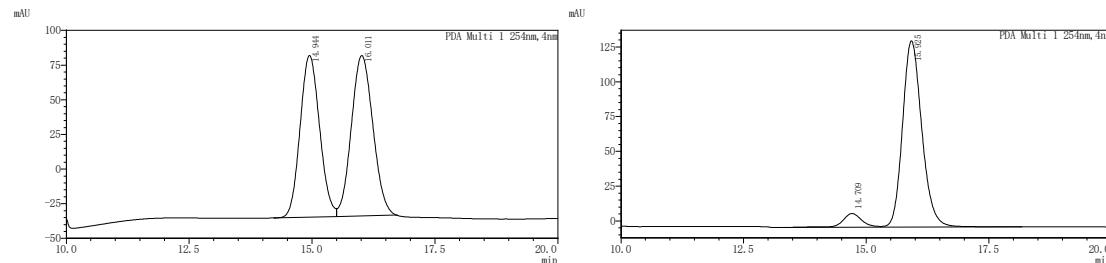
(R)-1-([1,1'-biphenyl]-4-yl)butane-1,4-diol (49).

To confirm the absolute configuration of the chiral carbon linked to borane, we compared the spectrum of HPLC with the known substance⁹, and we have determined the absolute configuration of **49** is *R*-configuration.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.45 (m, 4H), 7.42 – 7.31 (m, 4H), 7.31 – 7.22 (m, 1H), 4.71 (t, *J* = 6.3 Hz, 1H), 3.71 – 3.57 (m, 2H), 2.25 (s, 2H), 1.83 (q, *J* = 7.0 Hz, 2H), 1.72 – 1.57 (m, 2H).

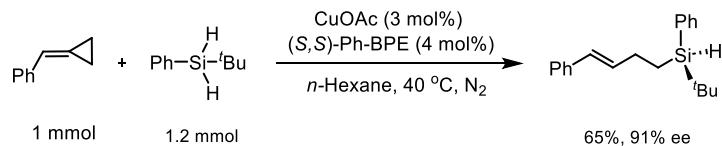
¹³C NMR 100 MHz, CDCl₃) δ 143.7, 140.8, 140.4, 128.8, 127.3, 127.2, 127.1, 126.2, 74.1, 62.9, 36.2, 29.2.

HPLC conditions: Daicel Chiraldak OD-H column (90: 10 hexane: ¹PrOH, 1 mL/min, 40 °C, 254 nm); tr (major) = 15.9 min, tr (minor) = 14.7 min, 86% ee.



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	14.944	3222997	47.677	1	14.709	279149	7.069
2	16.011	3537013	52.323	2	15.925	3669942	92.931

2.3 Scale-up experiment



A 25 mL sealed tube reactor equipped with a magnetic stirrer bar was charged CuOAc (0.03 mmol, 3 mol%) and (*S,S*)-Ph-BPE (L, 0.04 mmol, 4 mol%) in dry n-Hexane (6 mL) under N₂ atmosphere in a glove box and stirred for 10 min, then the arylidene cyclopropane (1 mmol) and dihydrosilane (1.2 mmol) were added in the tube. The tube was capped, then removed from the glove box and stirred at 40 °C for 16 h. After the reaction completed, the reaction solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate to provide product. The enantiomeric excess was determined by chiral HPLC analysis. Corresponding racemic samples were obtained by carrying out the reactions at the identical conditions with (\pm)-Ph-BPE

2.4 Determination of the absolute configuration of (*R*)-13.

All density functional theory (DFT)¹⁰ calculations were performed using the Gaussian 16 package¹¹. Geometry optimizations and frequency calculations were done at the CAM-B3LYP/Def2SVP level of theory¹²⁻¹⁶. Solvent effects (trichloromethane) were included in the calculations by the use of the polarized continuum model (PCM) implementation¹⁵ in Gaussian 16. The stationary points were ascertained by vibrational frequency analysis with no imaginary frequency. The electronic circular dichroism (ECD) simulations were carried out using the time-dependent DFT calculations on the optimized geometries at the CAM-B3LYP/Def2TZVPP level of theory^{13,14}. Finally, the Boltzmann-averaged ECD spectra of **13** was obtained with Multiwfn software¹⁶. The good consistence between simulation and experimental spectrum supported the assignment of the absolute configuration of **13** to be (*R*) as given in the manuscript.

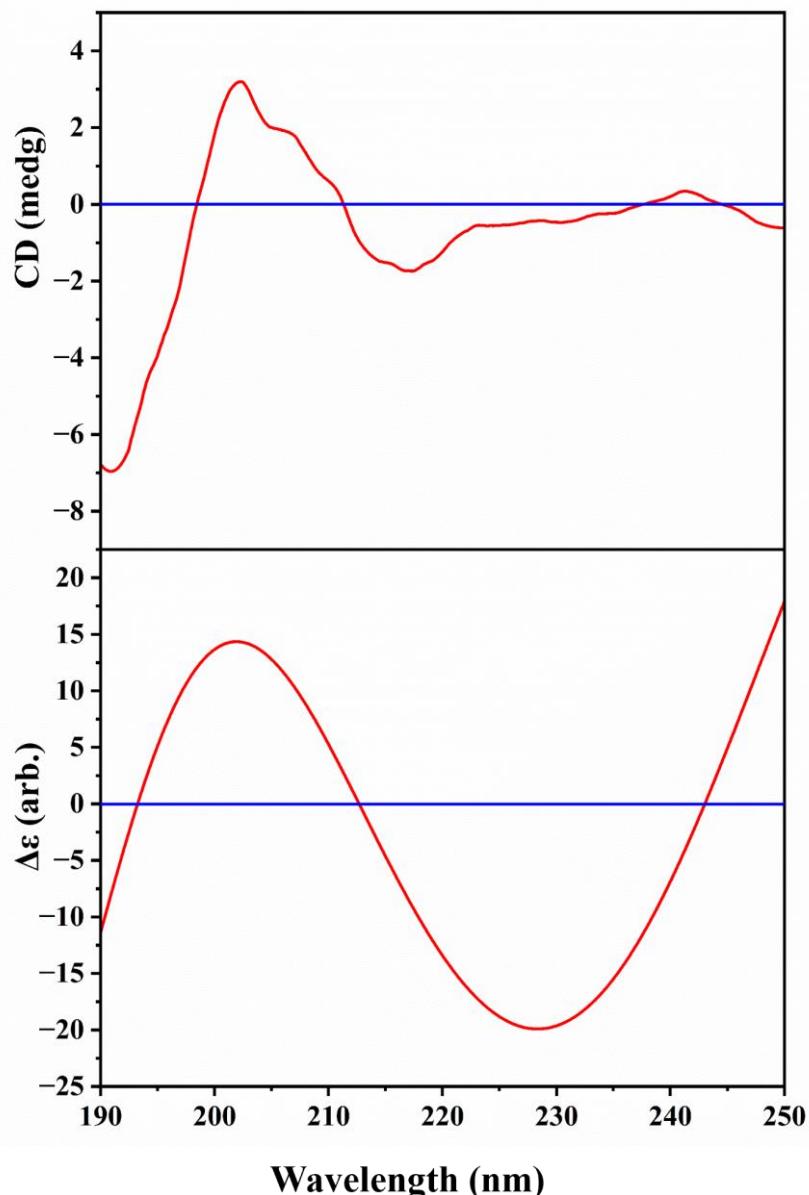
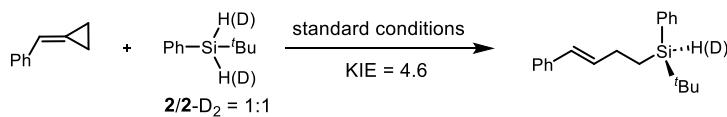


Figure S-1. Comparison between simulation ECD spectrum and experimental for **13**.

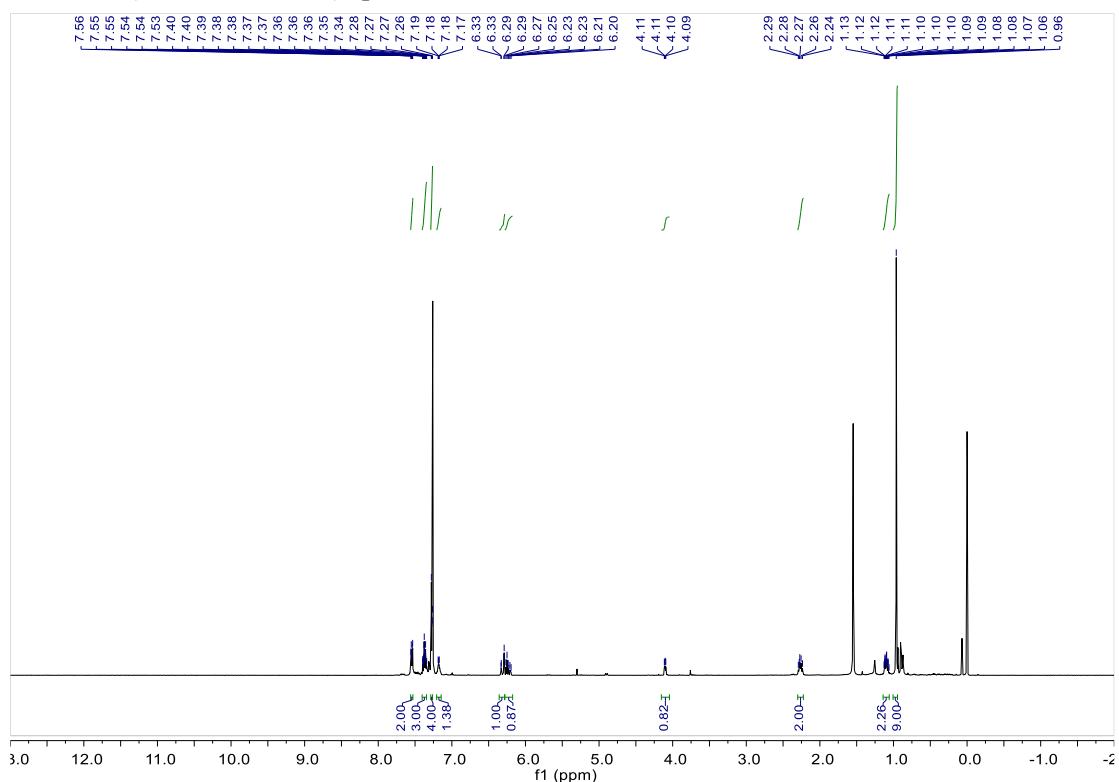
3. Mechanistic Studies

3.1 KIE experiments

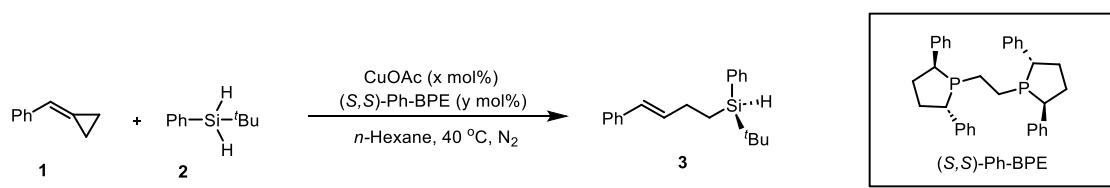


In two 8 mL sealed tube reactors equipped with the magnetic stirrer bar were charged CuOAc (0.005 mmol, 5 mol%) and (*S,S*)-Ph-BPE (0.006 mmol, 6 mol%) in dry *n*-Hexane (1 mL) under N₂ atmosphere in a glove box and stirred for 10 min, then the arylidenecyclopropanes **1** (0.1 mmol), silane **2a-D₂** (1.2 equiv) were added in one tube **A**, and reaction system **B** (arylidene cyclopropane **1**, silane **2a-D₂**) were added to the tube **B**. The tubes were capped, the removed from the glove box and stirred at 40 °C for 10 min. Then, the reaction mixture of tube **A** and tube **B** was filtered through a plug of celite with CH₂Cl₂. The filtrate was concentrated under reduced pressure. The KIE_(SiH) = [SiH]/[SiD] = 4.6.

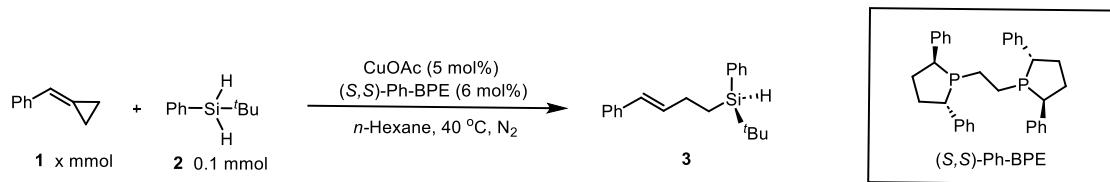
¹H NMR (400MHz, CDCl₃) spectrum of the mixture of **3** and **3-D**



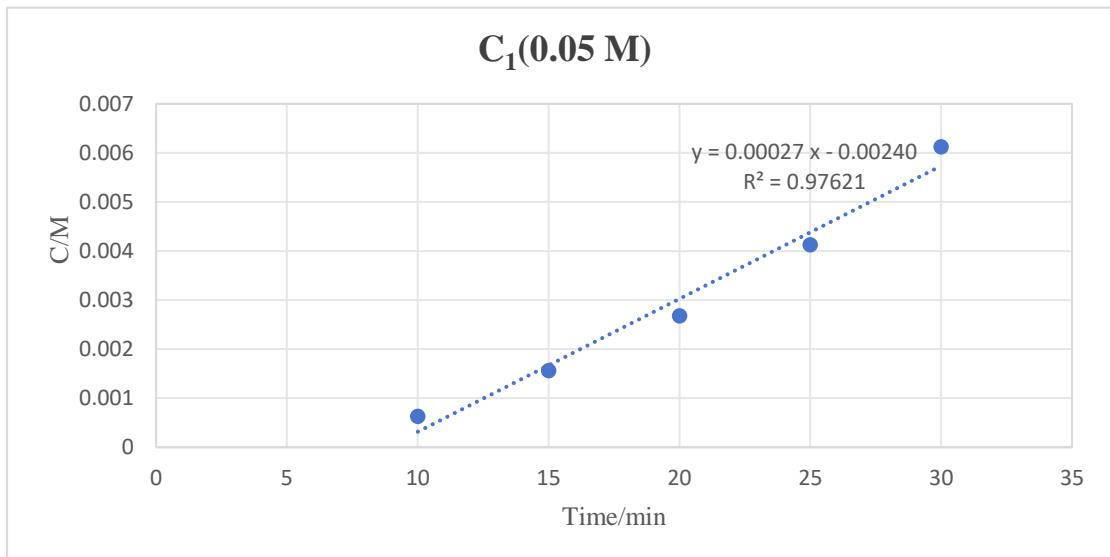
3.2 Kinetic Studies



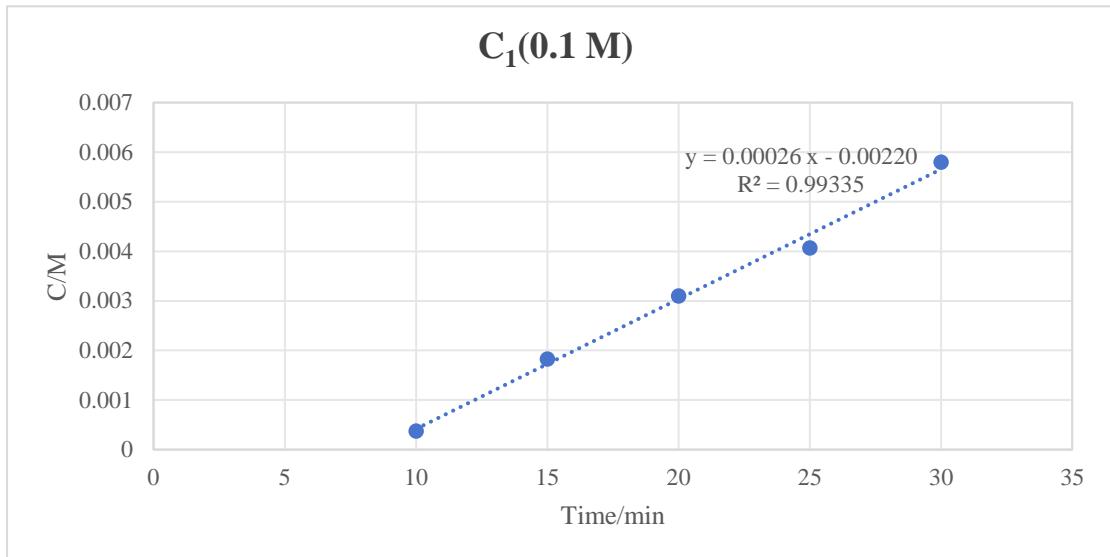
Several 8 mL sealed tube reactors equipped with the magnetic stirrer bar were charged CuOAc and (*S,S*)-Ph-BPE in dry *n*-Hexane (1 mL) under N₂ atmosphere in a glove box and stirred for 10 min, then the arylidene cyclopropane and dihydrosilane were added in the tube. The tube were capped, then removed from the glove box and stirred at 40 °C. Then the reactions were stopped at specific time. The reaction yields were determined by GC-MS using CH₂Br₂ as internal standard.



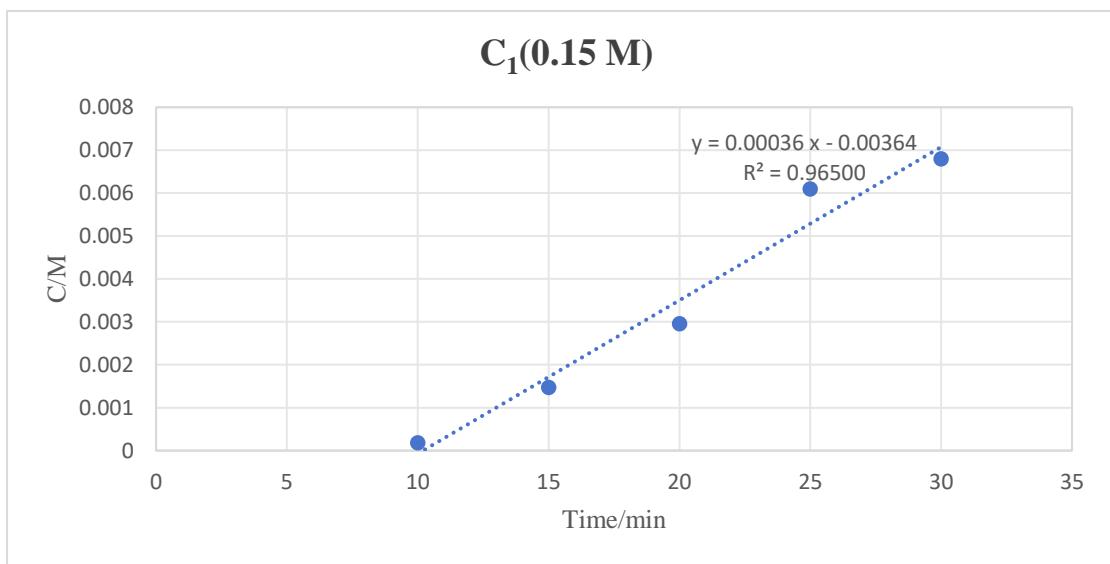
The concentrations of **1** used: 0.05 M, 0.1 M, 0.15 M, 0.2 M.



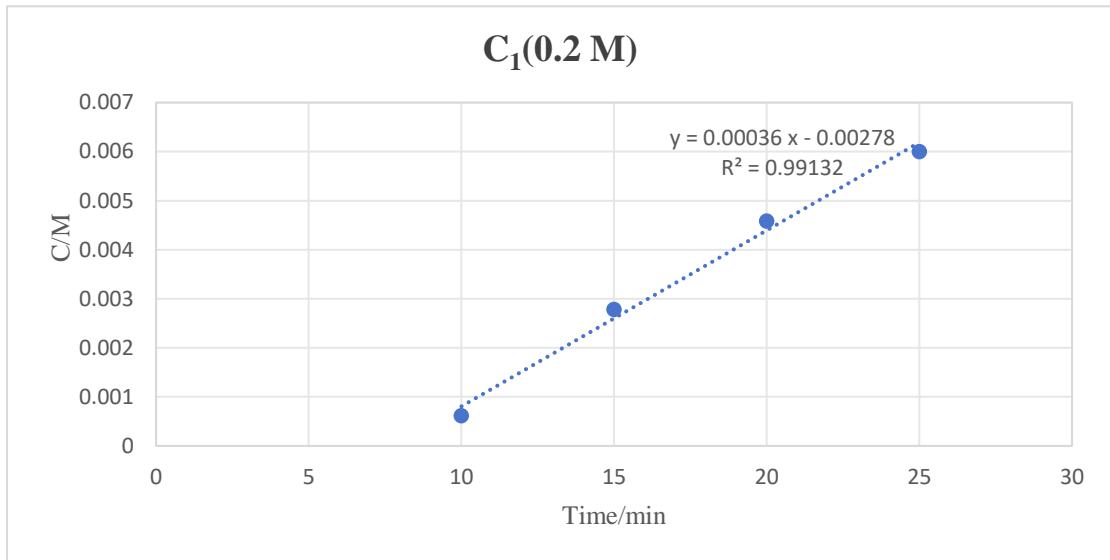
The plots of the concentrations of **3** depending on the time for the reactions with the concentration **1** at 0.05 M.



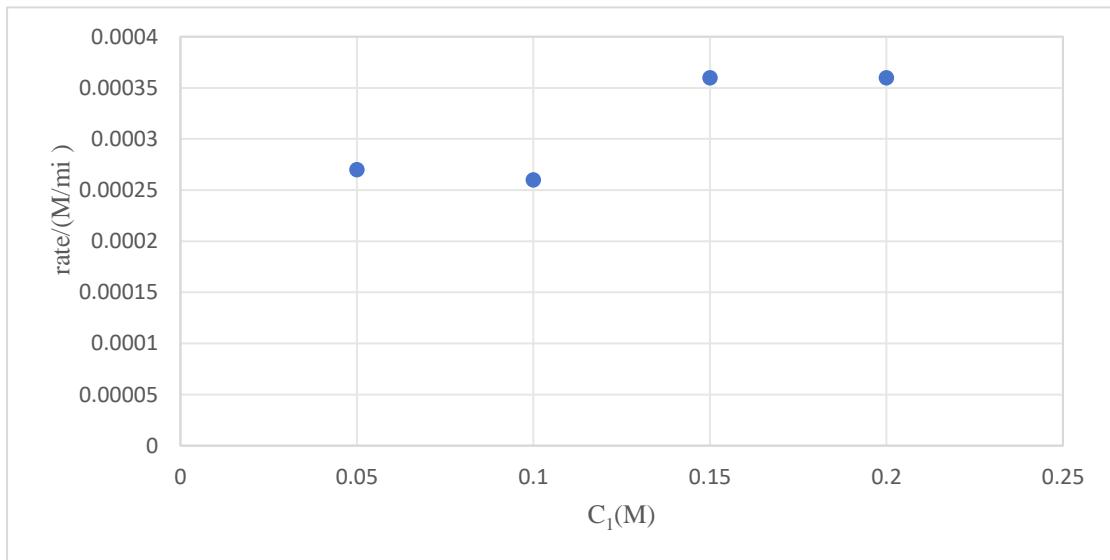
The plots of the concentrations of **3** depending on the time for the reactions with the concentration of **1** at 0.1 M.



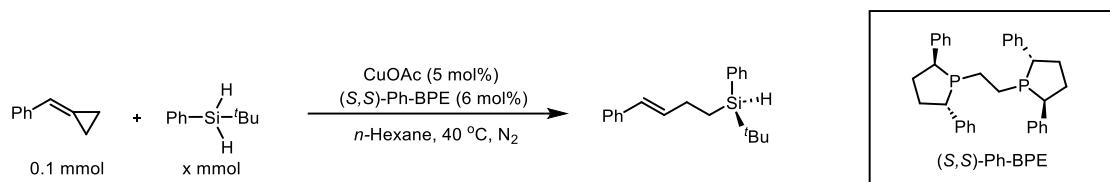
The plots of the concentrations of **3** depending on the time for the reactions with the concentration of **1** at 0.15 M.



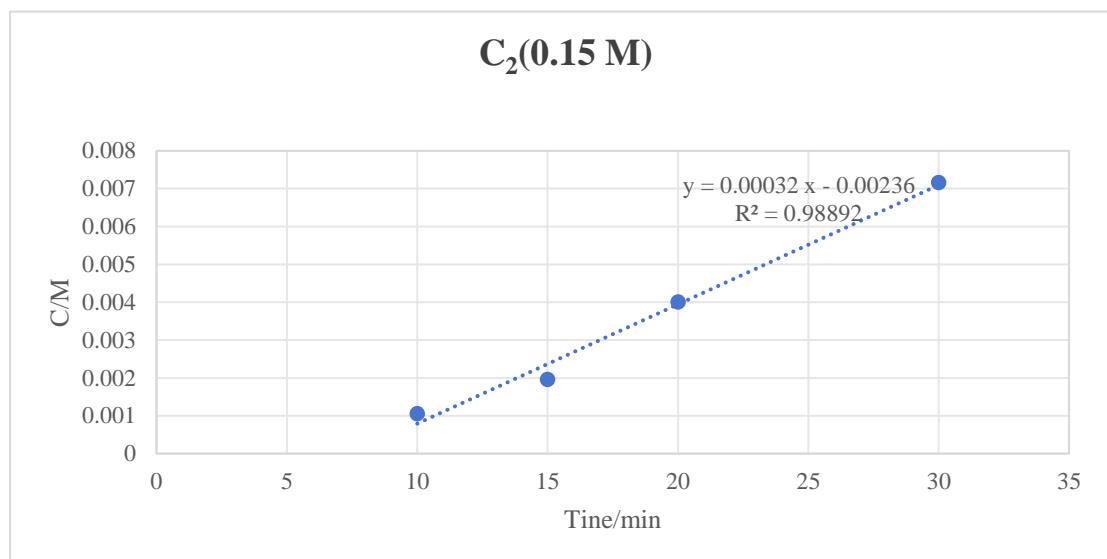
The plots of the concentrations of **3** depending on the time for the reactions with the concentration of **1** at 0.2 M.



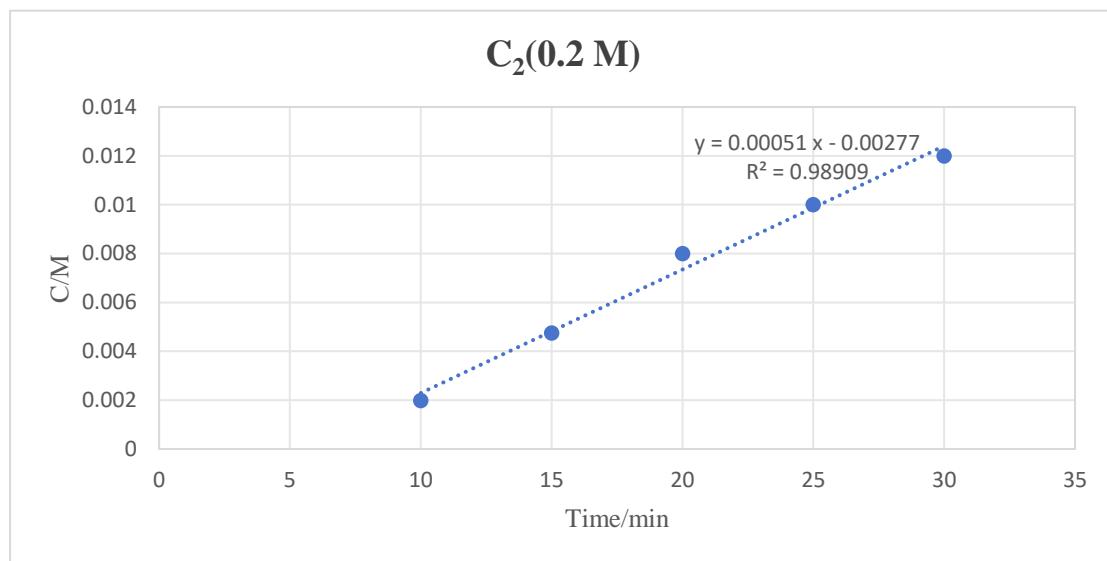
The zeroth order dependence of the reaction rate with respect to the concentration of **1**



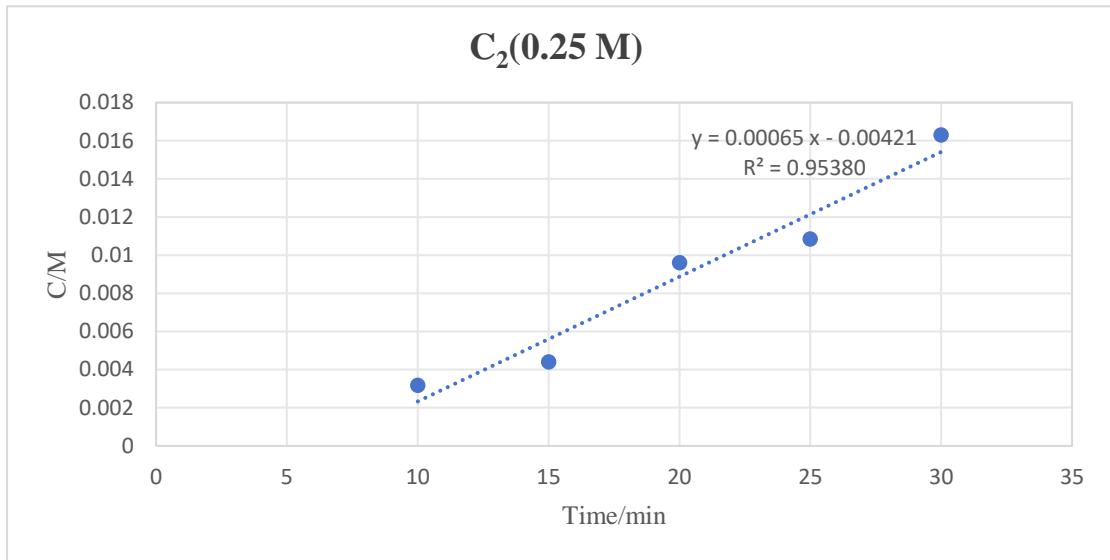
The concentrations of **1** used: 0.15 M, 0.2 M, 0.25 M, 0.3 M, 0.35 M.



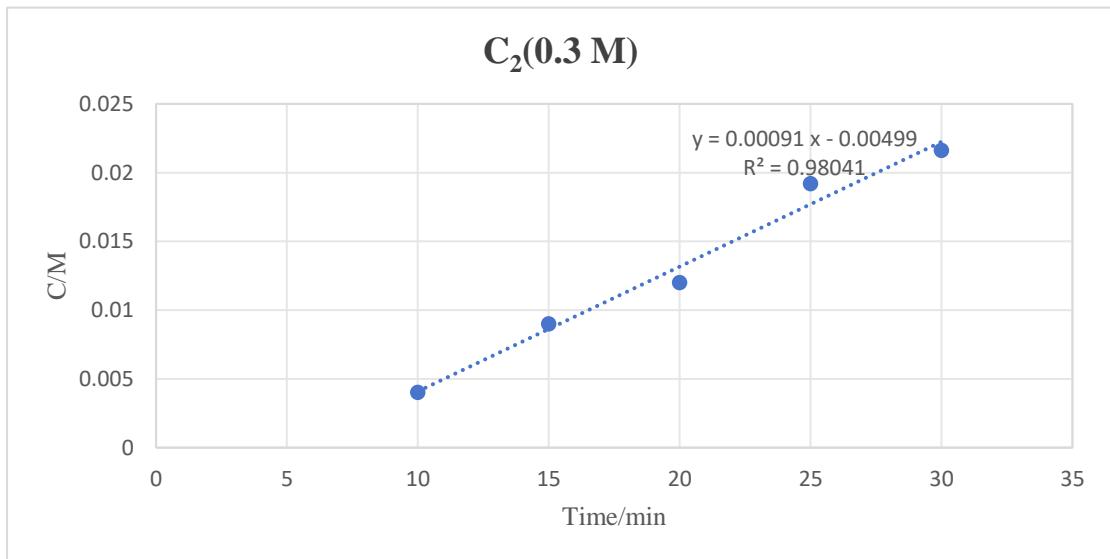
The plots of the concentrations of **3** depending on the time for the reactions with the concentration of **2** at 0.15 M.



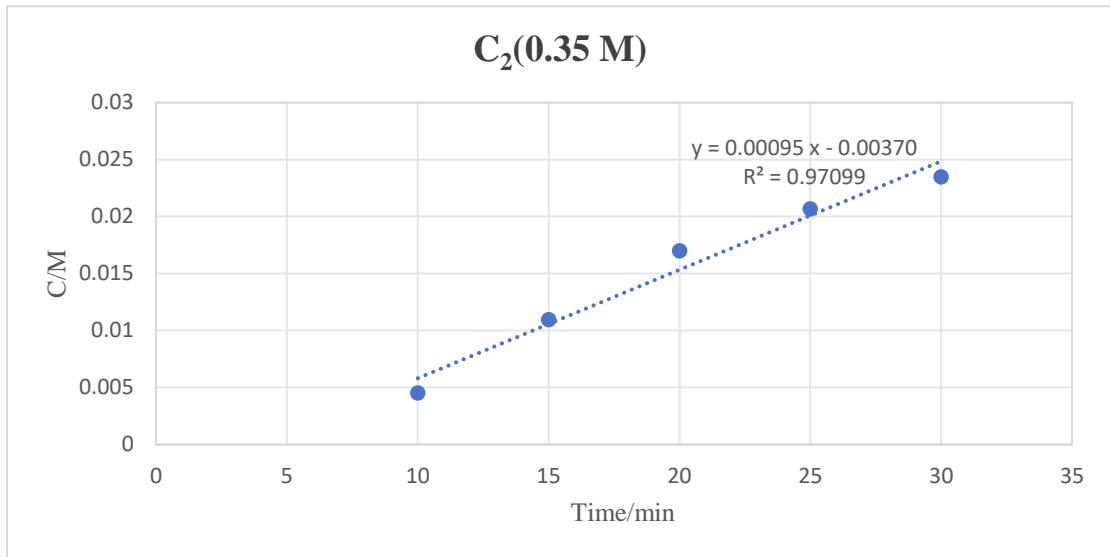
The plots of the concentrations of **3** depending on the time for the reactions with the concentration of **2** at 0.2 M.



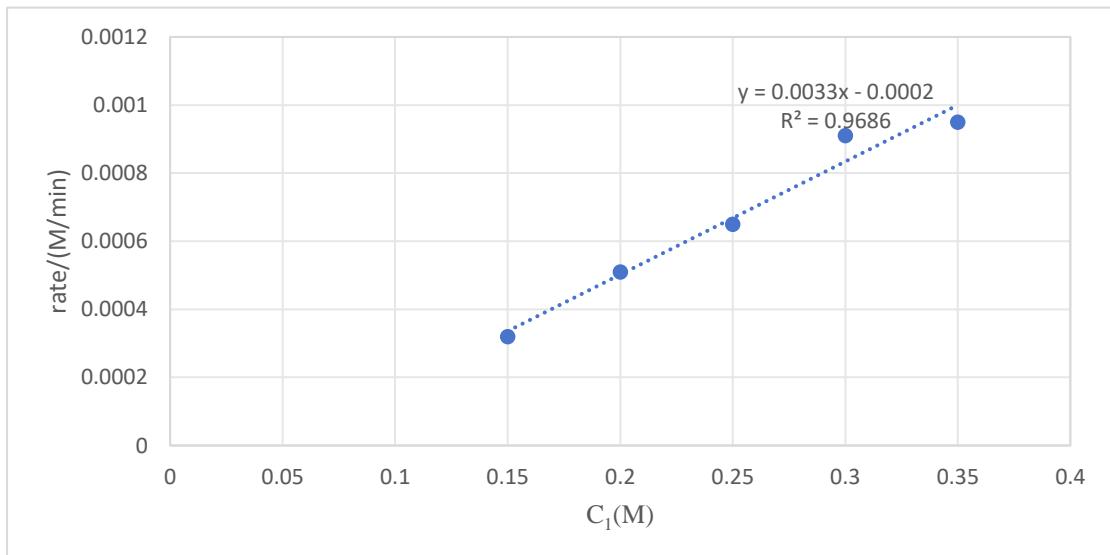
The plots of the concentrations of **3** depending on the time for the reactions with the concentration of **2** at 0.25 M.



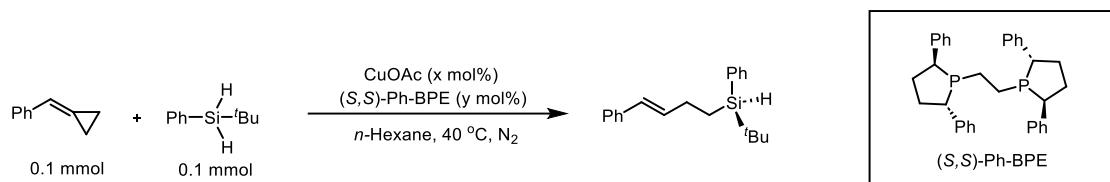
The plots of the concentrations of **3** depending on the time for the reactions with the concentration of **2** at 0.3 M.



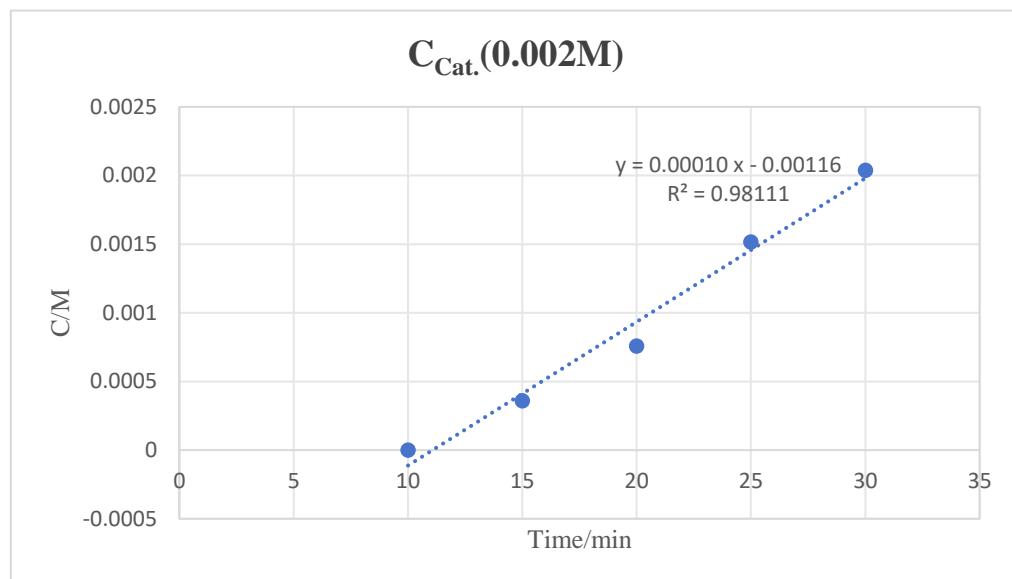
The plots of the concentrations of **3** depending on the time for the reactions with the concentration of **2** at 0.35 M.



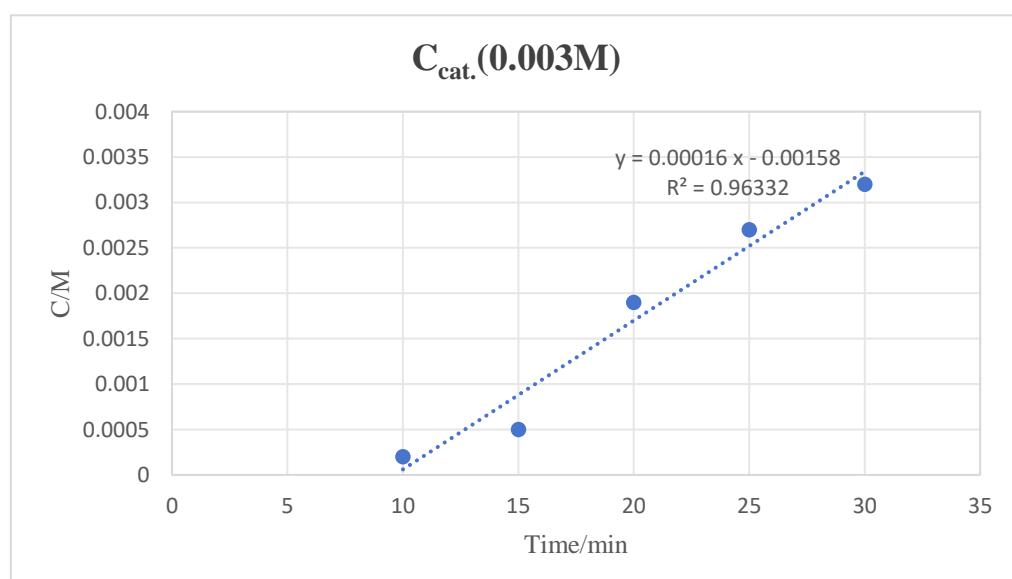
The first-order dependence of the reaction rate with respect to the concentration of **2**.



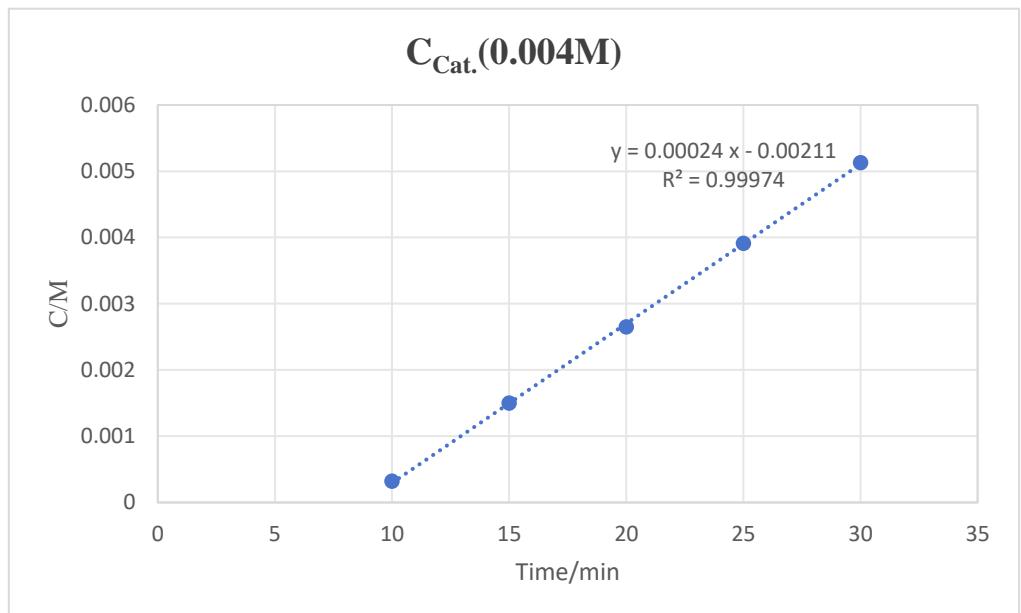
The concentrations of CuOAc-Ligand used: 0.002 M, 0.003 M, 0.004 M, 0.005 M.



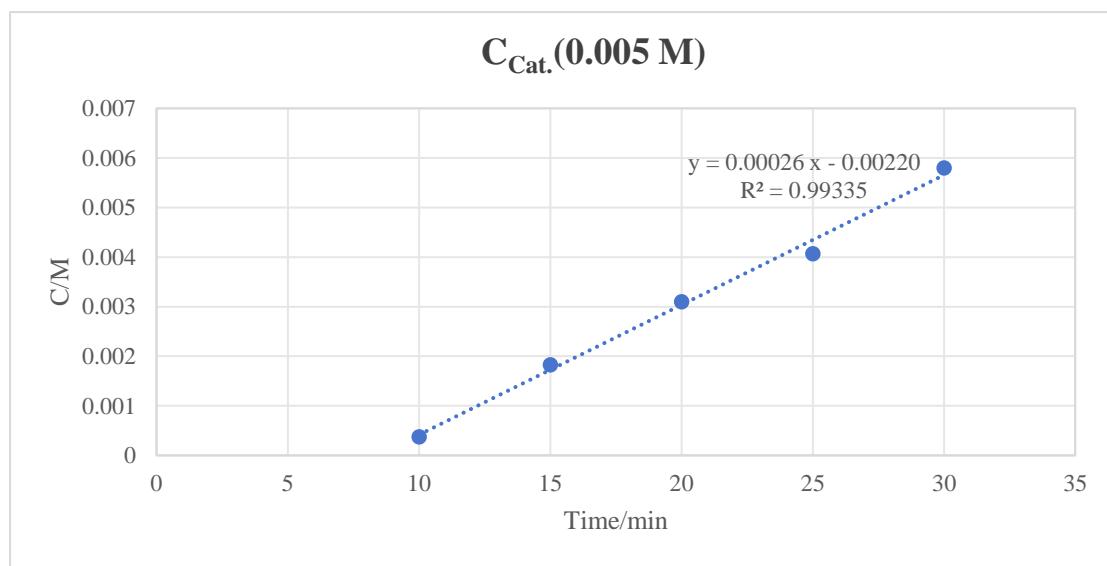
The plots of the concentrations of **3** depending on the time for the reactions with the concentration of CuOAc-Ligand at 0.002 M.



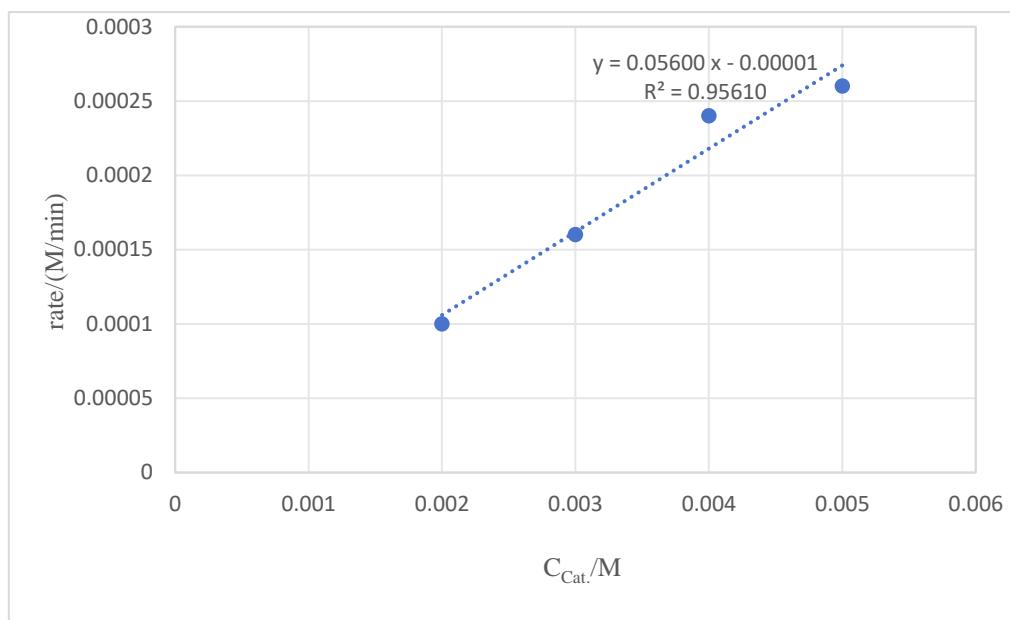
The plots of the concentrations of **3** depending on the time for the reactions with the concentration of CuOAc-Ligand at 0.003 M.



The plots of the concentrations of **3** depending on the time for the reactions with the concentration of CuOAc-Ligand at 0.004 M.

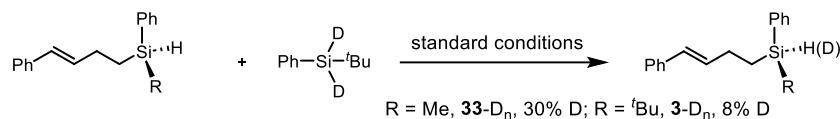


The plots of the concentrations of **3** depending on the time for the reactions with the concentration of CuOAc-Ligand at 0.005 M.



The first-order dependence of the reaction rate with respect to the concentration of CuOAc-Ligand.

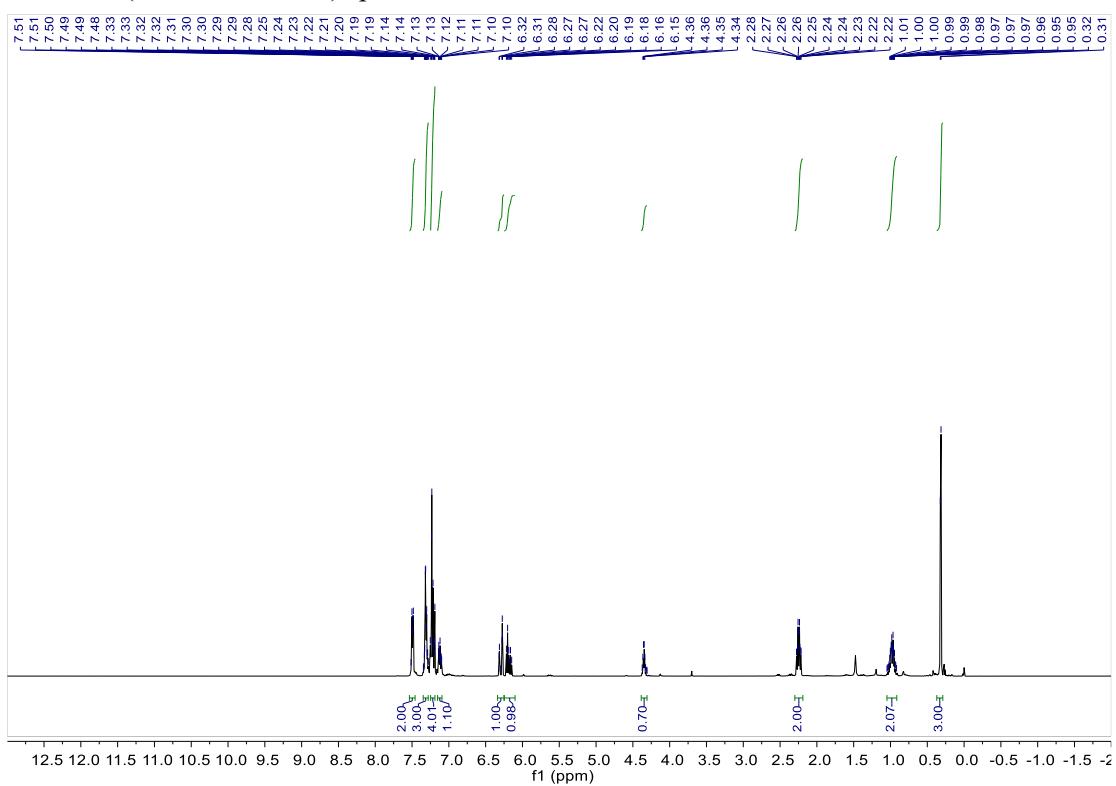
3.3



In two 8 mL sealed tube reactors equipped with the magnetic stirrer bar were charged CuOAc (0.005 mmol, 5 mol%) and (\pm)-Ph-BPE (0.006 mmol, 6 mol%) in dry *n*-Hexane (1 mL) under N₂ atmosphere in a glove box and stirred for 10 min, then the product **3** (0.1 mmol), silane **2a-D₂** (1.2 equiv) were added in one tube **A**, and reaction system **B** (product **35**, silane **2a-D₂**) were added to the tube **B**. The tubes were capped, removed from the glove box and stirred at room temperature for 12 h. After the reaction completed, reactions filtered through a plug of celite with CH₂Cl₂. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel

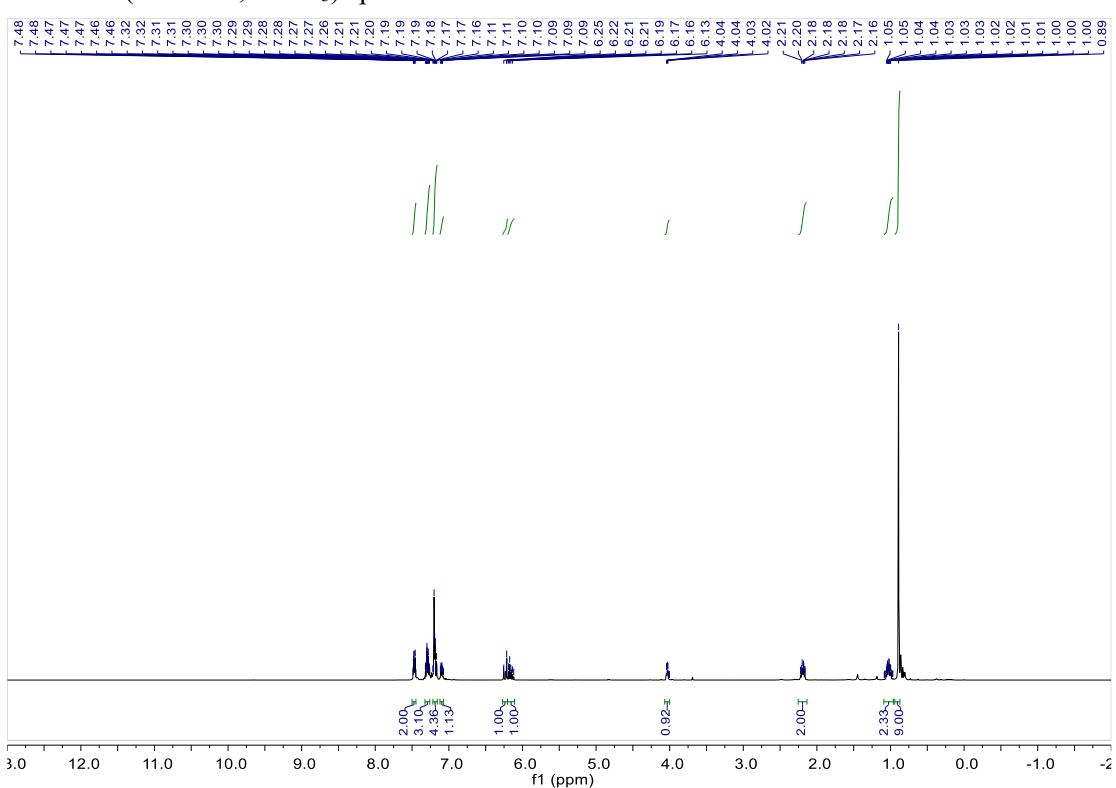
¹H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.46 (m, 2H), 7.35 – 7.28 (m, 3H), 7.25 – 7.19 (m, 4H), 7.15 – 7.09 (m, 1H), 6.34 – 6.25 (m, 1H), 6.18 (dt, *J* = 15.7, 6.4 Hz, 1H), 4.39 – 4.31 (m, 0.7 H), 2.30 – 2.19 (m, 2H), 1.05 – 0.92 (m, 2H), 0.32 (d, *J* = 3.9 Hz, 3H).

^1H NMR (400MHz, CDCl_3) spectrum of the mixture of **D-35** and **35**



^1H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.44 (m, 2H), 7.33 – 7.26 (m, 3H), 7.22 – 7.16 (m, 4H), 7.12 – 7.07 (m, 1H), 6.27 – 6.20 (m, 1H), 6.15 (dt, J = 15.8, 6.1 Hz, 1H), 4.03 (dd, J = 4.8, 3.0 Hz, 0.92H), 2.26 – 2.13 (m, 2H), 1.09 – 0.96 (m, 2H), 0.89 (s, 9H).

^1H NMR (400MHz, CDCl_3) spectrum of the mixture of **D-3** and **3**



4. DFT Calculation Studies

All calculations were performed with Gaussian 16¹². The hybrid functional B3LYP¹⁷ was combined with the dispersion correction D3(BJ)¹⁸ to improve computational accuracy. Structures were optimized and characterized by frequency calculations to be energy minima (zero imaginary frequencies) or transition states (only one imaginary frequency) at the B3LYP-D3(BJ)/def2-SVP¹⁵level in the gas phase. The energies were then refined by B3LYP-D3(BJ) /def2-TZVP¹⁵ //B3LYP - D3(BJ)/def2-SVP single-point energy calculations with the solvent (*n*-Hexane) effects included using the SMD solvation model¹⁹. The refined energies were converted to zero-point energy-corrected Gibbs free energies at 298.15 K and 1 atm, using the B3LYP-D3(BJ)/def2-SVP harmonic frequencies.

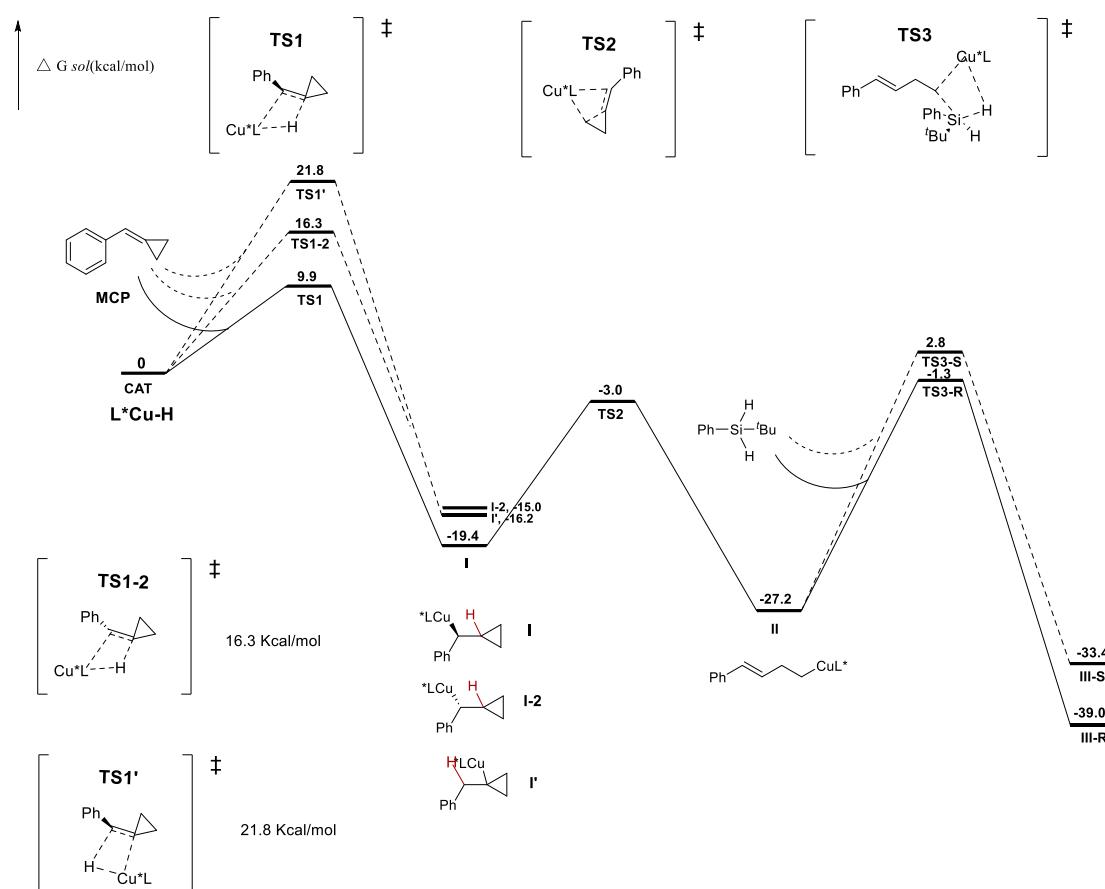


Figure S-2. The free energy profile depicting the regioselectivity of MCP insertion into Cu–H and the enantioselectivity of Si-stereogenic monohydrosilane.

Calculated Cartesian Coordinates

CAT

Cu	0.00066	-0.00023	1.59116
P	1.15043	1.08303	-0.10932
P	-1.15059	-1.08298	-0.10917
C	-2.9105	-1.67716	-0.44957
H	-3.11568	-1.42241	-1.5016
C	0.43634	2.83204	-0.15576
H	0.44281	3.12963	0.90571
C	-0.99219	2.82294	-0.62874
C	-1.3632	3.17287	-1.93402
H	-0.61389	3.54771	-2.63355
C	-2.69027	3.0376	-2.35862
H	-2.9598	3.31058	-3.38203
C	-3.66557	2.5583	-1.48146
H	-4.70093	2.44768	-1.81175
C	-3.31038	2.22402	-0.16984
H	-4.06427	1.85453	0.52561
C	-1.98714	2.35325	0.24831
H	-1.712	2.06514	1.26787
C	1.48696	3.67251	-0.88762
H	1.45202	3.48142	-1.97329
H	1.31444	4.75174	-0.74356
C	2.84106	3.22006	-0.33458
H	2.92174	3.50467	0.72769
H	3.69217	3.68517	-0.85636
C	2.91038	1.67715	-0.4495
H	3.11561	1.42254	-1.50156
C	3.97152	1.03319	0.41029
C	5.21944	0.71472	-0.14467
H	5.40242	0.92054	-1.20308
C	6.21984	0.12164	0.62948
H	7.18299	-0.1266	0.17664
C	5.98412	-0.16198	1.97775
H	6.76075	-0.63382	2.58441
C	4.74498	0.15652	2.54273
H	4.54502	-0.07074	3.59254
C	3.74749	0.75103	1.76717
H	2.76693	0.94647	2.20929
C	0.68788	0.34099	-1.75895
H	0.74238	1.10064	-2.55532
H	1.47785	-0.39937	-1.95817

C	-0.68821	-0.34072	-1.75879
H	-0.74291	-1.10032	-2.55521
H	-1.47823	0.39964	-1.95782
C	-2.84112	-3.22007	-0.33482
H	-2.92182	-3.50481	0.72742
H	-3.6922	-3.68515	-0.85667
C	-1.487	-3.67238	-0.8879
H	-1.45208	-3.48115	-1.97355
H	-1.31445	-4.75163	-0.74398
C	-0.4364	-2.83197	-0.15595
H	-0.44279	-3.12975	0.90547
C	0.99209	-2.82274	-0.62904
C	1.98713	-2.3533	0.24805
H	1.71213	-2.0655	1.26774
C	3.31034	-2.22398	-0.17019
H	4.06429	-1.8547	0.52529
C	3.6654	-2.5579	-1.48194
H	4.70073	-2.44719	-1.81229
C	2.69002	-3.03695	-2.35914
H	2.95945	-3.30967	-3.38265
C	1.36299	-3.17232	-1.93445
H	0.61362	-3.54698	-2.63401
C	-3.97171	-1.03335	0.41026
C	-3.74772	-0.7514	1.7672
H	-2.76719	-0.94699	2.20931
C	-4.74522	-0.15699	2.54283
H	-4.54531	0.07009	3.59269
C	-5.98433	0.16164	1.97784
H	-6.76096	0.63339	2.58456
C	-6.22001	-0.12176	0.62953
H	-7.18312	0.12658	0.17667
C	-5.21958	-0.71476	-0.14469
H	-5.40254	-0.92038	-1.20314
H	0.00179	0.00042	3.14713

SM1

C	0.9959	-0.97688	-0.00065
C	2.13158	-0.27877	-0.00012
C	2.80615	1.023	0.00079
C	3.59646	-0.294	0.00006
H	2.80012	1.62092	0.92041
H	2.80031	1.622	-0.91813
H	4.12387	-0.57524	-0.91949

H	4.12366	-0.57643	0.91935
C	-0.36815	-0.43044	-0.00035
C	-0.6338	0.95394	-0.0006
C	-1.46298	-1.31476	0.00018
C	-1.94375	1.42845	-0.00029
H	0.1985	1.65864	-0.00105
C	-2.77519	-0.83936	0.00051
H	-1.27509	-2.39191	0.00037
C	-3.02208	0.53564	0.00026
H	-2.1282	2.50575	-0.0005
H	-3.60886	-1.54596	0.00092
H	-4.04793	0.9116	0.00051
H	1.06886	-2.07039	-0.00119

TS1

Cu	0.06404	0.03004	-1.05984
P	0.98074	-1.80796	-0.02535
P	-1.04662	0.51449	0.894
C	-2.83721	0.96212	1.28
H	-3.10198	0.35996	2.16478
C	0.22256	-3.43808	-0.61645
H	0.2154	-3.32512	-1.71258
C	-1.20121	-3.57354	-0.14464
C	-1.5581	-4.32968	0.98135
H	-0.80816	-4.93165	1.4977
C	-2.87134	-4.31471	1.4644
H	-3.1286	-4.90745	2.34591
C	-3.84798	-3.54449	0.82836
H	-4.87087	-3.52341	1.2118
C	-3.50868	-2.80324	-0.30864
H	-4.2609	-2.19593	-0.81428
C	-2.2009	-2.82361	-0.79112
H	-1.93304	-2.21313	-1.65586
C	1.25592	-4.5069	-0.24628
H	1.22031	-4.72354	0.83436
H	1.06255	-5.45679	-0.77118
C	2.62452	-3.91736	-0.59941
H	2.70606	-3.8058	-1.69342
H	3.45942	-4.5614	-0.28164
C	2.73047	-2.52128	0.0607
H	2.95925	-2.65569	1.12943
C	3.76381	-1.60492	-0.54536
C	4.92458	-1.26496	0.16226

H	5.07766	-1.674	1.16456
C	5.87765	-0.4038	-0.39073
H	6.77384	-0.14733	0.1797
C	5.68212	0.13004	-1.66653
H	6.42153	0.80822	-2.09879
C	4.53079	-0.20775	-2.38582
H	4.3624	0.20994	-3.38097
C	3.58217	-1.06612	-1.82979
H	2.67273	-1.29355	-2.39055
C	0.50495	-1.71042	1.77303
H	0.46531	-2.71681	2.21898
H	1.32774	-1.16606	2.25937
C	-0.82167	-0.97397	1.99393
H	-0.92514	-0.67855	3.04992
H	-1.66822	-1.6338	1.75149
C	-2.76064	2.43513	1.73806
H	-2.63033	3.08762	0.86037
H	-3.69609	2.73459	2.23661
C	-1.54005	2.54905	2.65611
H	-1.72868	1.96757	3.57401
H	-1.3434	3.58889	2.96183
C	-0.35162	1.97365	1.87563
H	-0.07994	2.69633	1.0949
C	0.90508	1.5846	2.60705
C	2.08107	1.37783	1.8617
H	2.05628	1.5305	0.78361
C	3.25407	0.9387	2.47403
H	4.14759	0.78147	1.86722
C	3.27782	0.69074	3.851
H	4.19503	0.34561	4.33446
C	2.11882	0.89369	4.60341
H	2.12556	0.70807	5.68048
C	0.94411	1.33912	3.98675
H	0.05101	1.49409	4.59457
C	-3.85297	0.66658	0.20365
C	-3.56954	0.82966	-1.16037
H	-2.56764	1.12622	-1.46848
C	-4.53757	0.55514	-2.12857
H	-4.2885	0.67346	-3.18603
C	-5.81089	0.11865	-1.75129
H	-6.56619	-0.09999	-2.50997
C	-6.10794	-0.04218	-0.39458
H	-7.09801	-0.38755	-0.08667
C	-5.13476	0.22755	0.57013

H	-5.36744	0.08451	1.62917
H	-0.65229	-0.37445	-2.40281
C	1.23344	1.69201	-1.8991
C	0.53153	0.9282	-2.85497
C	-0.17824	1.3241	-4.1024
C	0.9864	0.34108	-4.14534
H	-0.00177	2.3437	-4.46001
H	-1.17978	0.93519	-4.29997
H	0.7553	-0.70459	-4.36274
H	1.9421	0.69391	-4.54652
C	0.7456	2.9509	-1.35007
C	-0.59083	3.39002	-1.5139
C	1.60565	3.7798	-0.59312
C	-1.04147	4.56991	-0.92592
H	-1.28294	2.78246	-2.0969
C	1.1497	4.95699	-0.0011
H	2.64817	3.47932	-0.46285
C	-0.18113	5.3612	-0.15386
H	-2.08182	4.87522	-1.06845
H	1.84095	5.56425	0.58925
H	-0.54036	6.28121	0.31239
H	2.27865	1.43835	-1.70351

TS1-2

Cu	0.24475	-0.22943	-1.00951
P	-0.55825	1.71189	0.06471
P	1.31603	-0.71849	0.94605
C	3.01735	-1.451	1.29716
H	3.43354	-0.873	2.13826
C	0.44162	3.19109	-0.58856
H	0.33196	3.10812	-1.68235
C	1.90863	3.09775	-0.24895
C	2.47823	3.79676	0.82628
H	1.87723	4.49934	1.40533
C	3.81645	3.59629	1.18312
H	4.23724	4.14697	2.02827
C	4.6092	2.69613	0.46758
H	5.65075	2.5287	0.75208
C	4.0611	2.01567	-0.62468
H	4.66924	1.3125	-1.19552
C	2.72931	2.22133	-0.98097
H	2.29775	1.66245	-1.81302
C	-0.32909	4.42354	-0.10479

H	-0.15781	4.58714	0.9715
H	0.00791	5.33642	-0.62288
C	-1.80895	4.13706	-0.34388
H	-2.00774	4.12816	-1.42754
H	-2.46608	4.90663	0.09085
C	-2.14917	2.74159	0.23861
H	-2.32964	2.83452	1.32036
C	-3.36332	2.12252	-0.40608
C	-4.54601	1.93214	0.32101
H	-4.56558	2.18777	1.38365
C	-5.69591	1.43047	-0.29568
H	-6.60837	1.29028	0.28898
C	-5.67955	1.11388	-1.65579
H	-6.57746	0.72522	-2.14174
C	-4.50175	1.28781	-2.38999
H	-4.47332	1.02431	-3.44989
C	-3.35508	1.78164	-1.7684
H	-2.43386	1.89255	-2.34689
C	0.01204	1.63028	1.84359
H	0.17958	2.6466	2.2341
H	-0.83257	1.20305	2.40205
C	1.2706	0.77325	2.04708
H	1.36341	0.47579	3.10367
H	2.17128	1.34694	1.78438
C	2.71272	-2.87848	1.80724
H	2.49138	-3.53152	0.94603
H	3.59163	-3.30477	2.3159
C	1.48783	-2.78441	2.72086
H	1.75812	-2.20922	3.62176
H	1.14101	-3.77339	3.06186
C	0.39925	-2.05926	1.91983
H	0.03356	-2.73887	1.13581
C	-0.7998	-1.49666	2.63952
C	-1.96027	-1.21304	1.89778
H	-1.99635	-1.46371	0.84009
C	-3.06207	-0.60049	2.49268
H	-3.94548	-0.39599	1.8853
C	-3.0259	-0.25059	3.84682
H	-3.88631	0.23246	4.3166
C	-1.88269	-0.5353	4.59805
H	-1.8455	-0.27582	5.6591
C	-0.78072	-1.15693	4.00004
H	0.10073	-1.37123	4.60708
C	3.98707	-1.37927	0.14295

C	3.58244	-1.64062	-1.17574
H	2.53533	-1.85937	-1.38853
C	4.49587	-1.57416	-2.22899
H	4.15375	-1.76605	-3.24873
C	5.83431	-1.25233	-1.98252
H	6.54796	-1.19551	-2.80792
C	6.25141	-0.99926	-0.67265
H	7.29412	-0.7437	-0.46851
C	5.33235	-1.06072	0.37788
H	5.65978	-0.84476	1.39862
H	0.72183	0.26344	-2.43443
C	-0.40736	-2.2434	-1.77735
C	-0.06607	-1.30032	-2.7671
C	0.66838	-1.49527	-4.05074
C	-0.74729	-0.92982	-4.03688
H	0.79926	-2.52855	-4.38895
H	1.48477	-0.81588	-4.30779
H	-0.87135	0.1269	-4.28469
H	-1.56884	-1.57673	-4.36024
C	-1.74239	-2.57553	-1.30429
C	-1.9357	-3.74758	-0.53468
C	-2.88203	-1.77367	-1.54952
C	-3.18564	-4.08476	-0.01773
H	-1.0778	-4.3978	-0.34021
C	-4.12916	-2.11506	-1.03369
H	-2.77114	-0.84988	-2.11483
C	-4.29599	-3.26985	-0.25799
H	-3.29258	-4.99208	0.58294
H	-4.97877	-1.45769	-1.22727
H	-5.27431	-3.5263	0.15424
H	0.37787	-2.95077	-1.48521

TS1'

Cu	0.21964	0.67117	-0.41573
P	-0.81531	-0.42052	1.33183
P	1.47883	-1.16817	-0.78526
C	3.33012	-1.33616	-1.1296
H	3.73502	-1.98015	-0.33367
C	-0.24177	0.30113	2.99686
H	-0.20055	1.38113	2.78935
C	1.15016	-0.15673	3.34444
C	1.3999	-1.27973	4.14832
H	0.57176	-1.80655	4.62591

C	2.70367	-1.74589	4.34435
H	2.87452	-2.62362	4.97274
C	3.78313	-1.09482	3.74152
H	4.80138	-1.46116	3.89378
C	3.54871	0.03568	2.95173
H	4.37917	0.55881	2.47377
C	2.24757	0.50029	2.75886
H	2.06647	1.36023	2.1113
C	-1.38786	0.04157	3.98348
H	-1.33169	-0.98248	4.38692
H	-1.33594	0.72882	4.84339
C	-2.6924	0.18718	3.19535
H	-2.82667	1.232	2.86577
H	-3.58017	-0.07709	3.79138
C	-2.57146	-0.73146	1.96113
H	-2.57334	-1.7708	2.32848
C	-3.67808	-0.59575	0.94641
C	-4.72862	-1.52617	0.94032
H	-4.71	-2.35682	1.65132
C	-5.78586	-1.41393	0.03444
H	-6.59081	-2.15301	0.04365
C	-5.80805	-0.3623	-0.88604
H	-6.63027	-0.27259	-1.59994
C	-4.76692	0.57111	-0.88925
H	-4.76842	1.3948	-1.60633
C	-3.71083	0.4548	0.01704
H	-2.89203	1.17237	-0.02334
C	-0.16471	-2.16713	1.28809
H	-0.18607	-2.60543	2.29806
H	-0.89424	-2.71767	0.67484
C	1.23796	-2.28755	0.68205
H	1.45438	-3.33472	0.41676
H	1.99566	-1.9684	1.41343
C	3.42434	-2.09156	-2.47902
H	3.36431	-1.36195	-3.30324
H	4.39755	-2.59813	-2.57303
C	2.24239	-3.06196	-2.57467
H	2.36691	-3.86833	-1.83258
H	2.1789	-3.5427	-3.56476
C	0.99266	-2.23406	-2.26457
H	0.85836	-1.49535	-3.07192
C	-0.32641	-2.91363	-2.01772
C	-1.4953	-2.12989	-2.02331
H	-1.41954	-1.06576	-2.24665

C	-2.73066	-2.68079	-1.68796
H	-3.62058	-2.05057	-1.68565
C	-2.82311	-4.03249	-1.33895
H	-3.78999	-4.46259	-1.06741
C	-1.6729	-4.82515	-1.34283
H	-1.73609	-5.88422	-1.08014
C	-0.43337	-4.27029	-1.68174
H	0.45511	-4.90437	-1.67552
C	4.04313	-0.00819	-1.09154
C	3.57674	1.07646	-1.85271
H	2.6812	0.96039	-2.46842
C	4.2231	2.31113	-1.80735
H	3.84023	3.14494	-2.40093
C	5.34858	2.48712	-0.99523
H	5.85051	3.45663	-0.95371
C	5.82306	1.41612	-0.23507
H	6.70158	1.54275	0.40263
C	5.17326	0.1787	-0.28566
H	5.54284	-0.65529	0.31693
H	0.96658	1.9469	0.1832
C	0.12605	2.57039	-1.2748
C	-0.53757	1.58924	-2.07338
C	-1.81369	1.61969	-2.82256
C	-0.49061	1.32144	-3.53178
H	-2.28721	2.58936	-3.02624
H	-2.5323	0.79872	-2.71778
H	-0.33235	0.30034	-3.90371
H	-0.0967	2.09339	-4.20686
C	-0.68699	3.63525	-0.61498
C	-1.44965	3.40291	0.53761
C	-0.75062	4.90478	-1.21087
C	-2.2691	4.39847	1.07203
H	-1.37131	2.42837	1.01832
C	-1.56348	5.90712	-0.67513
H	-0.1584	5.10578	-2.10786
C	-2.33077	5.65663	0.46632
H	-2.85605	4.19288	1.97112
H	-1.5979	6.88978	-1.15258
H	-2.96712	6.43996	0.885
H	1.09845	2.91867	-1.64026

I

Cu	-0.00677	-0.20327	0.85714
P	1.28318	1.54131	0.13008
P	-0.94744	-0.26502	-1.25824
C	-2.62632	-0.59458	-2.06019
H	-2.69304	0.09196	-2.91968
C	0.58437	3.05057	1.02182
H	0.5352	2.71704	2.07165
C	-0.81687	3.33557	0.55541
C	-1.11809	4.32414	-0.39035
H	-0.3349	4.99481	-0.74881
C	-2.41813	4.45566	-0.89308
H	-2.63493	5.23027	-1.63296
C	-3.43178	3.60004	-0.45696
H	-4.44373	3.69063	-0.85746
C	-3.14625	2.62168	0.50195
H	-3.93114	1.94927	0.84935
C	-1.85312	2.49614	1.00506
H	-1.63435	1.72355	1.74887
C	1.68006	4.11451	0.91535
H	1.71386	4.54035	-0.10151
H	1.50279	4.95105	1.61094
C	2.9934	3.3828	1.20978
H	3.00437	3.0546	2.26241
H	3.87923	4.02068	1.06439
C	3.06657	2.13422	0.2938
H	3.36397	2.46525	-0.71392
C	4.04592	1.07952	0.75382
C	5.35902	1.08792	0.26151
H	5.65333	1.85094	-0.46455
C	6.28469	0.12317	0.66682
H	7.30055	0.14159	0.2645
C	5.90743	-0.87114	1.5739
H	6.62506	-1.63433	1.88391
C	4.60372	-0.88329	2.07961
H	4.29589	-1.65769	2.78648
C	3.68309	0.08664	1.67737
H	2.65777	0.0456	2.05303
C	0.94216	1.842	-1.6789
H	1.01832	2.91544	-1.9157
H	1.76625	1.33328	-2.20152
C	-0.40672	1.28036	-2.15302
H	-0.3876	1.11057	-3.24128

H	-1.21202	2.00341	-1.94732
C	-2.50074	-2.03476	-2.60525
H	-2.60665	-2.75147	-1.77417
H	-3.30647	-2.24632	-3.32566
C	-1.10608	-2.16597	-3.2205
H	-1.04026	-1.5188	-4.11076
H	-0.88995	-3.19538	-3.54853
C	-0.11188	-1.71791	-2.14166
H	-0.08245	-2.49803	-1.36496
C	1.30436	-1.38881	-2.53202
C	2.31324	-1.49196	-1.55854
H	2.05782	-1.88347	-0.5738
C	3.62227	-1.09765	-1.83133
H	4.38482	-1.18749	-1.05706
C	3.95072	-0.58435	-3.0905
H	4.9744	-0.26845	-3.30512
C	2.96184	-0.49054	-4.07344
H	3.20988	-0.10225	-5.06456
C	1.65058	-0.89348	-3.79783
H	0.89322	-0.81059	-4.57939
C	-3.80568	-0.3511	-1.15581
C	-3.85665	-0.93219	0.12006
H	-3.02052	-1.54407	0.45928
C	-4.94775	-0.71468	0.9613
H	-4.96311	-1.16999	1.95465
C	-6.01211	0.0904	0.53905
H	-6.86548	0.26518	1.19846
C	-5.97376	0.67127	-0.73121
H	-6.79868	1.30291	-1.07011
C	-4.87683	0.45134	-1.56998
H	-4.84632	0.91809	-2.55827
H	-2.42054	-0.8674	2.62843
C	-0.27119	-1.35984	2.49011
C	-1.51518	-0.95889	3.23835
C	-1.76517	-1.38882	4.67089
C	-1.42086	0.04843	4.35264
H	-0.99448	-2.0042	5.1444
H	-2.78637	-1.61655	4.99343
H	-2.20461	0.80552	4.45409
H	-0.42	0.40602	4.61693
C	-0.26755	-2.65518	1.78585
C	-1.44946	-3.35768	1.4392
C	0.9512	-3.22704	1.33143
C	-1.42002	-4.4813	0.61057

H	-2.40589	-3.01498	1.83582
C	0.97998	-4.35465	0.51617
H	1.89092	-2.74289	1.61541
C	-0.20962	-4.98382	0.12091
H	-2.35955	-4.98112	0.35566
H	1.94283	-4.74576	0.17506
H	-0.18871	-5.86216	-0.52781
H	0.6204	-1.25464	3.13019

I-2

Cu	0.08653	-0.31469	-0.87408
P	-0.91377	1.66602	-0.28039
P	1.24446	-0.21085	1.11718
C	2.97902	-0.65849	1.69268
H	3.26469	0.09896	2.44095
C	-0.18584	2.97026	-1.43809
H	-0.25504	2.49368	-2.42957
C	1.26887	3.19667	-1.12611
C	1.72402	4.28012	-0.36268
H	1.02762	5.06076	-0.05114
C	3.06808	4.36914	0.01787
H	3.40363	5.2191	0.61732
C	3.97563	3.37769	-0.36148
H	5.02263	3.43982	-0.05651
C	3.53709	2.3016	-1.14082
H	4.23682	1.52307	-1.44537
C	2.1986	2.21687	-1.5195
H	1.85868	1.36332	-2.11427
C	-1.18279	4.13281	-1.40158
H	-1.07424	4.71003	-0.4682
H	-1.01863	4.83328	-2.23663
C	-2.57325	3.49143	-1.443
H	-2.72578	2.99556	-2.41627
H	-3.38538	4.22619	-1.32734
C	-2.63798	2.42815	-0.31871
H	-2.75154	2.95701	0.64126
C	-3.77393	1.44016	-0.45059
C	-4.99442	1.6982	0.19099
H	-5.09977	2.60254	0.79701
C	-6.06519	0.80725	0.08384
H	-7.00491	1.02276	0.59837
C	-5.92993	-0.36249	-0.66964
H	-6.76179	-1.06645	-0.74732

C	-4.72093	-0.62625	-1.32027
H	-4.59754	-1.53768	-1.90955
C	-3.65447	0.26918	-1.21464
H	-2.70795	0.03101	-1.70224
C	-0.31867	2.15072	1.42163
H	-0.25399	3.24712	1.50724
H	-1.1174	1.81687	2.10068
C	1.01622	1.50108	1.81676
H	1.1262	1.49231	2.91254
H	1.85789	2.07973	1.40505
C	2.78124	-2.00381	2.42768
H	2.6549	-2.80895	1.68554
H	3.66876	-2.249	3.03195
C	1.50899	-1.87444	3.26961
H	1.68062	-1.13882	4.07275
H	1.2304	-2.82539	3.75126
C	0.39871	-1.40271	2.31977
H	0.12071	-2.25294	1.67968
C	-0.8633	-0.81093	2.88935
C	-2.03925	-0.86694	2.12094
H	-2.02487	-1.40553	1.17385
C	-3.20954	-0.23913	2.54546
H	-4.10572	-0.29593	1.92634
C	-3.22723	0.46541	3.75397
H	-4.14105	0.96293	4.08771
C	-2.06984	0.51783	4.53535
H	-2.07508	1.05637	5.48643
C	-0.89897	-0.11813	4.10843
H	-0.00591	-0.06321	4.73368
C	4.01522	-0.66643	0.59708
C	3.75343	-1.26794	-0.64406
H	2.77058	-1.70191	-0.83002
C	4.72043	-1.27886	-1.65003
H	4.49218	-1.74409	-2.61202
C	5.96966	-0.68691	-1.43319
H	6.72513	-0.69055	-2.2225
C	6.24207	-0.08605	-0.20116
H	7.21302	0.38253	-0.02242
C	5.2702	-0.07697	0.80356
H	5.48457	0.40399	1.76193
H	-1.43034	-0.45062	-3.48361
C	-0.04495	-1.74731	-2.30308
C	-1.08987	-1.48755	-3.3789
C	-1.02168	-2.21043	-4.70962

C	-2.14983	-2.50044	-3.76101
H	-0.24464	-2.97416	-4.81271
H	-1.23252	-1.65289	-5.62771
H	-3.15032	-2.13519	-4.01444
H	-2.1434	-3.46279	-3.24421
C	-0.2609	-2.83149	-1.32394
C	0.81371	-3.64959	-0.88172
C	-1.51373	-3.06744	-0.69588
C	0.66584	-4.57864	0.14574
H	1.78642	-3.54053	-1.36825
C	-1.66395	-4.01115	0.31993
H	-2.37523	-2.47122	-1.00055
C	-0.5753	-4.76748	0.769
H	1.52791	-5.17739	0.45484
H	-2.64615	-4.14374	0.78251
H	-0.69398	-5.49842	1.57161
H	0.95221	-1.85267	-2.76103

I'

Cu	-0.01309	0.08176	-0.91244
P	-1.07657	0.2131	1.10802
P	1.27136	-1.6065	0.03905
C	3.06931	-2.17853	-0.00216
H	3.34553	-2.4068	1.03946
C	-0.40866	1.74228	1.9841
H	-0.41018	2.50326	1.19009
C	1.01369	1.53492	2.42717
C	1.36694	1.21796	3.74581
H	0.60285	1.19165	4.52491
C	2.6948	0.92318	4.07729
H	2.95022	0.67313	5.11017
C	3.68976	0.94916	3.09701
H	4.72572	0.71722	3.35527
C	3.35205	1.28292	1.78049
H	4.11888	1.31334	1.00594
C	2.02816	1.56864	1.45332
H	1.76553	1.81242	0.42244
C	-1.4885	2.12707	2.99987
H	-1.45233	1.46865	3.88426
H	-1.34887	3.16078	3.35613
C	-2.82622	1.94137	2.27768
H	-2.90291	2.67352	1.45846
H	-3.69347	2.09706	2.93847

C	-2.84817	0.51308	1.68037
H	-3.0281	-0.19911	2.5017
C	-3.89505	0.28928	0.61571
C	-5.1099	-0.32991	0.94133
H	-5.28311	-0.66212	1.96878
C	-6.09063	-0.54351	-0.03144
H	-7.02836	-1.03435	0.24072
C	-5.86773	-0.13937	-1.35077
H	-6.62863	-0.31326	-2.11534
C	-4.66043	0.4831	-1.68594
H	-4.46749	0.79317	-2.71572
C	-3.68473	0.697	-0.71108
H	-2.73039	1.14424	-0.9916
C	-0.56935	-1.23385	2.17438
H	-0.63613	-0.96924	3.24191
H	-1.33437	-2.00102	1.97789
C	0.82781	-1.784	1.84324
H	0.91751	-2.83162	2.17275
H	1.59807	-1.20581	2.37639
C	3.05685	-3.50283	-0.80861
H	3.11802	-3.26492	-1.88342
H	3.94069	-4.11317	-0.56541
C	1.73842	-4.2271	-0.52159
H	1.72404	-4.56783	0.52733
H	1.60624	-5.12051	-1.15393
C	0.63773	-3.19185	-0.76941
H	0.64304	-2.94157	-1.84335
C	-0.78251	-3.47449	-0.36276
C	-1.81047	-2.70199	-0.93375
H	-1.56459	-1.97528	-1.71364
C	-3.13001	-2.83098	-0.50475
H	-3.90855	-2.21378	-0.95376
C	-3.44975	-3.74344	0.5068
H	-4.48255	-3.83816	0.84959
C	-2.44275	-4.5322	1.06747
H	-2.68504	-5.25595	1.84976
C	-1.11818	-4.40022	0.63432
H	-0.34259	-5.01993	1.08803
C	4.02517	-1.13634	-0.53554
C	3.66577	-0.28521	-1.59392
H	2.66456	-0.34394	-2.02882
C	4.55948	0.679	-2.06457
H	4.25459	1.34029	-2.87923
C	5.82987	0.80458	-1.49294

H	6.52524	1.5641	-1.85815
C	6.20297	-0.04795	-0.45014
H	7.1929	0.04137	0.00414
C	5.30525	-1.00914	0.02215
H	5.59451	-1.66093	0.85132
H	1.70457	2.18139	-2.67363
C	0.61246	2.23264	-2.8269
C	0.01343	0.83088	-2.74072
C	-1.11216	0.53637	-3.71599
C	0.26245	-0.03981	-3.95461
H	-1.43354	1.32308	-4.41293
H	-1.93115	-0.13033	-3.42061
H	0.4196	-1.1181	-3.82877
H	0.82456	0.37491	-4.80274
C	0.03884	3.19719	-1.81208
C	0.86537	3.93199	-0.95013
C	-1.35143	3.36212	-1.68495
C	0.33007	4.7926	0.01513
H	1.95001	3.81968	-1.03083
C	-1.89327	4.22026	-0.72746
H	-2.00954	2.80078	-2.34923
C	-1.05374	4.93916	0.13267
H	0.99898	5.34227	0.68212
H	-2.97846	4.32772	-0.65003
H	-1.47692	5.60706	0.88697
H	0.47096	2.66245	-3.84373

TS2

Cu	0.06187	0.01504	-1.08398
P	0.8568	-1.80339	0.05466
P	-1.01673	0.69085	0.82439
C	-2.75732	1.29625	1.22333
H	-3.04515	0.78706	2.15768
C	0.00101	-3.43733	-0.38329
H	-0.03228	-3.43314	-1.4864
C	-1.41416	-3.45425	0.12888
C	-1.79155	-4.12873	1.29872
H	-1.06897	-4.75119	1.82931
C	-3.08956	-4.00563	1.80678
H	-3.36225	-4.53557	2.72286
C	-4.03196	-3.20926	1.15137
H	-5.04262	-3.10591	1.55315
C	-3.67382	-2.54804	-0.02806

H	-4.39806	-1.92201	-0.55092
C	-2.38013	-2.67306	-0.5317
H	-2.10424	-2.1332	-1.43669
C	0.98663	-4.52573	0.05342
H	0.96428	-4.65078	1.14864
H	0.73327	-5.50381	-0.38759
C	2.37503	-4.03947	-0.37076
H	2.43771	-4.0173	-1.47167
H	3.18228	-4.70107	-0.01963
C	2.56734	-2.60541	0.1774
H	2.79947	-2.67091	1.25181
C	3.64852	-1.80395	-0.50261
C	4.8368	-1.48879	0.16965
H	4.97338	-1.82943	1.19943
C	5.8378	-0.73683	-0.45309
H	6.75479	-0.49721	0.0909
C	5.66349	-0.28889	-1.76451
H	6.44038	0.30507	-2.2514
C	4.48565	-0.60457	-2.44995
H	4.33695	-0.25452	-3.47418
C	3.49011	-1.3542	-1.82332
H	2.56289	-1.57075	-2.35797
C	0.41957	-1.54411	1.84528
H	0.33574	-2.51316	2.36207
H	1.2791	-1.01269	2.27857
C	-0.86094	-0.72235	2.0294
H	-0.92612	-0.34469	3.06185
H	-1.74678	-1.34917	1.85024
C	-2.55976	2.79109	1.55553
H	-2.40724	3.35811	0.62397
H	-3.45539	3.2016	2.04835
C	-1.30743	2.88803	2.43274
H	-1.51471	2.40788	3.40362
H	-1.02404	3.93253	2.63723
C	-0.18337	2.15819	1.68502
H	0.13306	2.79381	0.84936
C	1.04782	1.72123	2.43127
C	2.20776	1.42334	1.69217
H	2.1962	1.56955	0.61241
C	3.35148	0.92912	2.31803
H	4.23514	0.70661	1.7177
C	3.35988	0.71363	3.70065
H	4.25426	0.32492	4.1939
C	2.21661	1.009	4.44704

H	2.21267	0.85183	5.52867
C	1.07235	1.5115	3.81747
H	0.19125	1.73877	4.42029
C	-3.80652	0.98643	0.18452
C	-3.53394	1.0526	-1.19067
H	-2.52627	1.30154	-1.52209
C	-4.52201	0.75727	-2.13184
H	-4.28396	0.80487	-3.19743
C	-5.8073	0.39599	-1.71572
H	-6.57928	0.16073	-2.45217
C	-6.09516	0.33644	-0.34922
H	-7.09525	0.05377	-0.01134
C	-5.10106	0.62681	0.58856
H	-5.32763	0.56182	1.65639
H	-0.87857	1.52668	-3.22393
C	1.07194	1.47945	-2.28082
C	0.03418	0.93329	-3.12274
C	0.17902	-0.08803	-4.18043
C	-0.63014	-0.79409	-3.11734
H	1.1997	-0.4724	-4.30325
H	-0.29313	0.11072	-5.15066
H	-1.71191	-0.84128	-3.27264
H	-0.18831	-1.71739	-2.73573
C	0.93332	2.78	-1.64963
C	-0.29433	3.48837	-1.54125
C	2.06998	3.41759	-1.08552
C	-0.37553	4.72033	-0.89399
H	-1.20842	3.06337	-1.95923
C	1.97995	4.63984	-0.42602
H	3.04054	2.92056	-1.16865
C	0.75363	5.3082	-0.31236
H	-1.34314	5.22776	-0.83754
H	2.88232	5.07981	0.00778
H	0.68344	6.26799	0.20344
H	2.09631	1.15458	-2.48315

II

Cu	0.02594	-0.44113	1.19816
P	-1.45456	-1.71475	-0.11158
P	1.11052	-0.00745	-0.78478
C	2.92451	0.19468	-1.27014
H	3.06471	-0.41532	-2.17664
C	-1.02287	-3.48395	0.39703

H	-1.04463	-3.4345	1.49839
C	0.37651	-3.83956	-0.02658
C	0.65671	-4.60684	-1.16521
H	-0.15811	-5.05562	-1.73636
C	1.97732	-4.79529	-1.5903
H	2.17637	-5.39262	-2.48368
C	3.0354	-4.22177	-0.88146
H	4.06558	-4.35942	-1.2179
C	2.76908	-3.47235	0.27003
H	3.58664	-3.02286	0.8349
C	1.45378	-3.28808	0.69163
H	1.25089	-2.68494	1.58201
C	-2.2126	-4.33072	-0.06268
H	-2.18887	-4.47603	-1.1558
H	-2.20069	-5.33283	0.39701
C	-3.46113	-3.53122	0.32112
H	-3.54353	-3.48379	1.41965
H	-4.39168	-3.98908	-0.04973
C	-3.30218	-2.09195	-0.23212
H	-3.54448	-2.10454	-1.30663
C	-4.17912	-1.06399	0.444
C	-5.40958	-0.70732	-0.12564
H	-5.71761	-1.1713	-1.06678
C	-6.23214	0.24692	0.479
H	-7.1834	0.51771	0.01416
C	-5.83252	0.86213	1.66865
H	-6.46811	1.61641	2.13858
C	-4.61148	0.50713	2.25148
H	-4.28534	0.98445	3.17877
C	-3.79404	-0.44999	1.64719
H	-2.82489	-0.68858	2.09278
C	-0.96011	-1.61564	-1.90885
H	-1.14999	-2.57007	-2.42599
H	-1.64055	-0.86657	-2.34245
C	0.5	-1.17884	-2.10456
H	0.63969	-0.73406	-3.10301
H	1.16946	-2.04986	-2.03723
C	3.06489	1.68576	-1.66402
H	3.20563	2.28939	-0.75352
H	3.95664	1.83659	-2.2926
C	1.7695	2.11707	-2.3563
H	1.6792	1.60366	-3.32885
H	1.74499	3.20139	-2.54804
C	0.64059	1.70469	-1.40786

H	0.72724	2.32451	-0.50607
C	-0.79074	1.75644	-1.86209
C	-1.80278	1.73397	-0.88515
H	-1.52124	1.7313	0.16974
C	-3.14872	1.69481	-1.24307
H	-3.91471	1.67546	-0.46735
C	-3.51182	1.66954	-2.5946
H	-4.56635	1.62989	-2.87746
C	-2.51772	1.70117	-3.57525
H	-2.79179	1.69061	-4.6333
C	-1.16642	1.74912	-3.21169
H	-0.40251	1.77508	-3.99089
C	3.90603	-0.2746	-0.22443
C	3.70441	-0.00825	1.1394
H	2.79725	0.50809	1.46005
C	4.61706	-0.45609	2.09592
H	4.43076	-0.25482	3.15358
C	5.75387	-1.17167	1.70553
H	6.46466	-1.52743	2.45519
C	5.97117	-1.43249	0.34977
H	6.85473	-1.99263	0.03369
C	5.0522	-0.98707	-0.60419
H	5.21703	-1.20913	-1.66219
H	1.4621	2.11603	2.81209
C	-0.19627	3.17468	2.0512
C	0.36926	2.21852	2.80928
C	-0.36035	1.18747	3.6145
C	0.06312	-0.23254	3.17972
H	-1.44653	1.33198	3.4728
H	-0.16496	1.37217	4.69367
H	1.09071	-0.42013	3.55058
H	-0.57541	-0.97111	3.70149
C	0.4947	4.09497	1.13805
C	1.89804	4.23324	1.10111
C	-0.25984	4.8257	0.19987
C	2.51504	5.04461	0.15092
H	2.51332	3.69123	1.82177
C	0.35728	5.63618	-0.75402
H	-1.34801	4.72721	0.20461
C	1.74979	5.7468	-0.78834
H	3.6046	5.13079	0.14135
H	-0.25393	6.17913	-1.47917
H	2.2365	6.37909	-1.53459
H	-1.29014	3.24829	2.0472

PhSiH₂'Bu

C	-0.90672	0.00017	-0.56086
C	-1.58029	1.20622	-0.29112
C	-1.58018	-1.20607	-0.29181
C	-2.87601	1.20906	0.23178
H	-1.08712	2.16107	-0.49562
C	-2.8759	-1.2093	0.2311
H	-1.08693	-2.16076	-0.49688
C	-3.52587	-0.00023	0.49473
H	-3.38169	2.15707	0.43215
H	-3.38147	-2.15747	0.43097
H	-4.54002	-0.0004	0.90201
Si	0.87142	0.00081	-1.17421
H	1.10354	1.22116	-2.00541
H	1.10396	-1.21818	-2.00731
C	2.10643	-0.00016	0.28778
C	1.87998	1.25692	1.14467
H	2.03803	2.18128	0.56476
H	0.85992	1.28931	1.55987
H	2.58574	1.27536	1.99464
C	3.53806	0.00029	-0.27468
H	4.27575	-0.00028	0.54813
H	3.73485	-0.88997	-0.89447
H	3.73478	0.89146	-0.89317
C	1.88001	-1.25847	1.14287
H	0.85994	-1.29146	1.55799
H	2.03811	-2.182	0.56166
H	2.58571	-1.2781	1.99286

TS3-S

C	3.54896	-0.87931	1.59378
C	3.83121	-2.13793	1.0353
C	4.50741	0.13305	1.40082
C	5.01238	-2.38008	0.32421
H	3.11566	-2.95525	1.14443
C	5.69002	-0.09533	0.69328
H	4.31754	1.1326	1.80468
C	5.94728	-1.35757	0.14781
H	5.19934	-3.37099	-0.09847
H	6.41098	0.71553	0.56032
H	6.86878	-1.54091	-0.41022

Si	1.90099	-0.40338	2.49102
H	1.77258	0.78316	1.30241
H	2.20925	0.71576	3.44648
C	1.77598	-1.86698	3.83904
Cu	0.51426	0.05157	0.55351
P	1.08824	-0.82117	-1.50548
P	-0.73174	1.66221	-0.6068
C	-0.88766	3.5224	-0.33549
H	-0.83459	3.97765	-1.3377
C	2.89386	-0.45939	-1.93635
H	3.41547	-0.61909	-0.98587
C	3.08158	0.9807	-2.33544
C	3.13969	1.40344	-3.67139
H	3.13397	0.66942	-4.47921
C	3.20103	2.7647	-3.98969
H	3.24325	3.07242	-5.0376
C	3.2092	3.72621	-2.97631
H	3.25387	4.78919	-3.22573
C	3.16829	3.31618	-1.6392
H	3.17201	4.05299	-0.83479
C	3.10704	1.95934	-1.32545
H	3.04688	1.64579	-0.28355
C	3.31418	-1.57486	-2.90315
H	2.99015	-1.3486	-3.93246
H	4.41057	-1.67837	-2.92075
C	2.62123	-2.85791	-2.43499
H	3.02516	-3.16709	-1.45986
H	2.77025	-3.69743	-3.1324
C	1.11817	-2.53596	-2.28895
H	0.71229	-2.39938	-3.30433
C	0.28993	-3.59189	-1.59904
C	-0.39761	-4.54211	-2.36997
H	-0.33793	-4.48821	-3.4606
C	-1.16569	-5.54103	-1.76691
H	-1.69728	-6.26683	-2.38725
C	-1.26089	-5.60447	-0.37406
H	-1.86678	-6.37868	0.10231
C	-0.57584	-4.66806	0.40553
H	-0.64161	-4.70691	1.49452
C	0.19359	-3.6729	-0.20137
H	0.69954	-2.93151	0.41774
C	0.10769	0.10392	-2.80121
H	0.67367	0.11075	-3.74549
H	-0.79384	-0.50414	-2.96178

C	-0.28282	1.53175	-2.40189
H	-1.1063	1.89988	-3.03454
H	0.57199	2.21223	-2.53589
C	-2.32937	3.70936	0.19091
H	-2.36561	3.44491	1.26129
H	-2.63644	4.76368	0.10974
C	-3.23216	2.76541	-0.60745
H	-3.26722	3.10064	-1.65811
H	-4.26723	2.75244	-0.22954
C	-2.59342	1.37707	-0.50409
H	-2.73464	1.02489	0.53058
C	-3.08071	0.27657	-1.40923
C	-2.59841	-1.03037	-1.21471
H	-1.85584	-1.21261	-0.43647
C	-3.04046	-2.09012	-2.00418
H	-2.64914	-3.09288	-1.82649
C	-3.97555	-1.8607	-3.02034
H	-4.32707	-2.68808	-3.64137
C	-4.45348	-0.5663	-3.23406
H	-5.18456	-0.37569	-4.0237
C	-4.01145	0.49276	-2.43312
H	-4.41701	1.49139	-2.60016
C	0.20105	4.12289	0.51884
C	0.58891	3.53232	1.73216
H	0.11357	2.60945	2.06397
C	1.6076	4.08942	2.50584
H	1.90637	3.5967	3.43381
C	2.2503	5.25846	2.08612
H	3.05108	5.6927	2.68941
C	1.86275	5.86587	0.88881
H	2.35743	6.78027	0.55186
C	0.84915	5.2977	0.11207
H	0.56367	5.76533	-0.83424
H	-3.10066	0.10918	3.27001
C	-3.94462	-1.00317	1.68136
C	-2.97173	-0.72183	2.56547
C	-1.60924	-1.35331	2.56809
C	-0.53546	-0.25159	2.42742
H	-1.55712	-2.09804	1.75857
H	-1.45359	-1.91336	3.50455
H	-1.01994	0.63227	1.98025
H	-0.2621	0.12776	3.42361
C	-5.17496	-0.24003	1.43637
C	-5.58117	0.8513	2.23052

C	-5.94811	-0.5534	0.3024
C	-6.70912	1.59909	1.89769
H	-5.00456	1.11942	3.11822
C	-7.07689	0.19544	-0.03229
H	-5.63597	-1.38103	-0.3387
C	-7.46343	1.27747	0.76232
H	-7.00522	2.44072	2.52915
H	-7.65211	-0.06387	-0.92454
H	-8.34582	1.86714	0.50249
H	-3.78034	-1.83345	0.98946
C	1.23887	-3.20651	3.3178
H	0.23118	-3.11095	2.89559
H	1.88511	-3.64033	2.54128
H	1.18416	-3.94911	4.13608
C	0.94044	-1.41613	5.05175
H	1.05791	-2.14056	5.87834
H	1.27265	-0.43496	5.42856
H	-0.13412	-1.34959	4.84071
C	3.21427	-2.06878	4.36072
H	3.8749	-2.53317	3.61795
H	3.67761	-1.11489	4.66359
H	3.19996	-2.72305	5.25162

TS3-R

Si	1.76589	2.02236	-1.74216
H	2.23074	0.58893	-0.993
H	2.23356	1.60574	-3.10086
Cu	0.81201	0.21048	-0.29521
P	0.90236	0.07838	2.00698
P	0.14112	-2.03116	-0.26767
C	0.66197	-3.45427	-1.38897
H	0.83973	-4.3193	-0.72992
C	2.71537	0.08696	2.56673
H	3.19617	0.78425	1.86781
C	3.35828	-1.26569	2.38642
C	3.51018	-2.18162	3.43775
H	3.22568	-1.90241	4.4536
C	4.02421	-3.46181	3.20555
H	4.13179	-4.15903	4.0402
C	4.40251	-3.84702	1.91746
H	4.80616	-4.84632	1.73763
C	4.26717	-2.93938	0.86187

H	4.55487	-3.22025	-0.15204
C	3.7479	-1.66634	1.09529
H	3.61603	-0.98043	0.25719
C	2.70762	0.73646	3.95964
H	2.46332	-0.00752	4.7349
H	3.6996	1.14647	4.20764
C	1.61589	1.81164	3.95444
H	1.88507	2.63181	3.269
H	1.46208	2.25945	4.9488
C	0.32378	1.125	3.4613
H	0.02083	0.40659	4.24086
C	-0.8487	2.03871	3.19428
C	-1.77386	2.29298	4.21903
H	-1.64101	1.81089	5.19167
C	-2.86573	3.13843	4.00845
H	-3.5774	3.31759	4.81809
C	-3.05267	3.74554	2.76287
H	-3.90982	4.40113	2.59292
C	-2.13654	3.50438	1.73526
H	-2.26734	3.96951	0.75587
C	-1.04628	2.65872	1.95252
H	-0.35571	2.45093	1.1352
C	0.26235	-1.59995	2.51906
H	0.76286	-1.9098	3.44911
H	-0.79842	-1.43432	2.75349
C	0.40249	-2.68998	1.44753
H	-0.29086	-3.52137	1.65079
H	1.42453	-3.09736	1.45055
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III-S

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III-R

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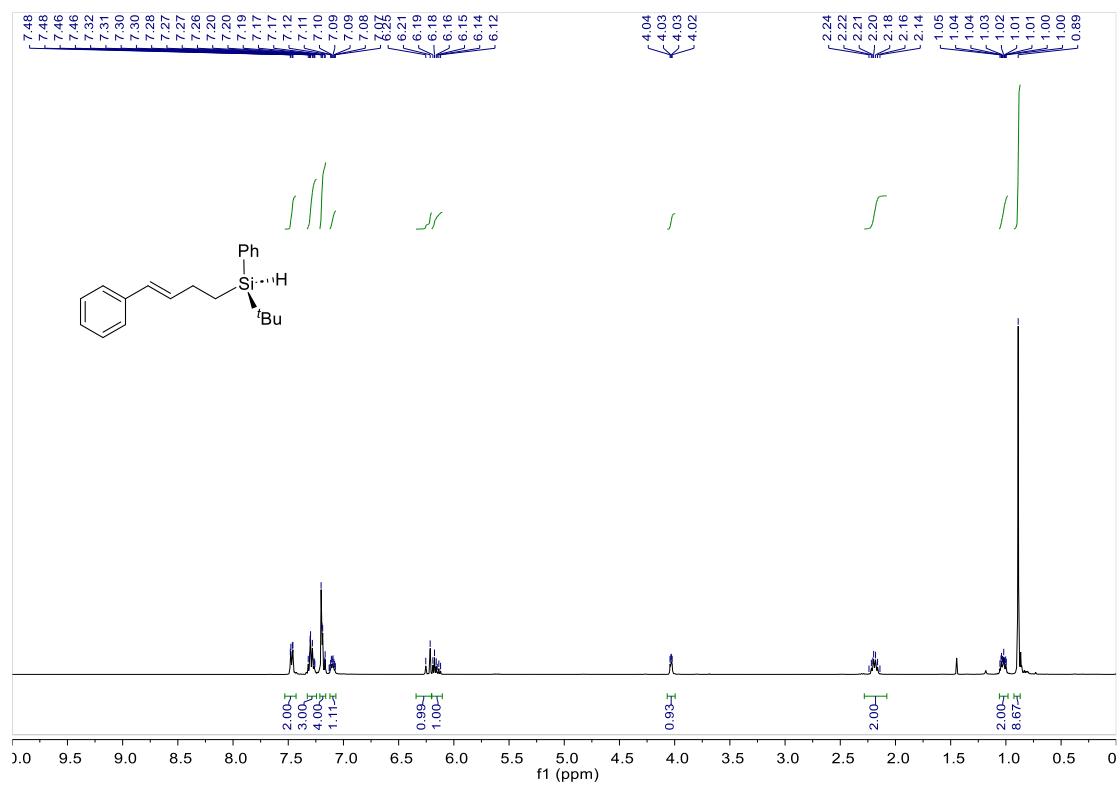
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5. References

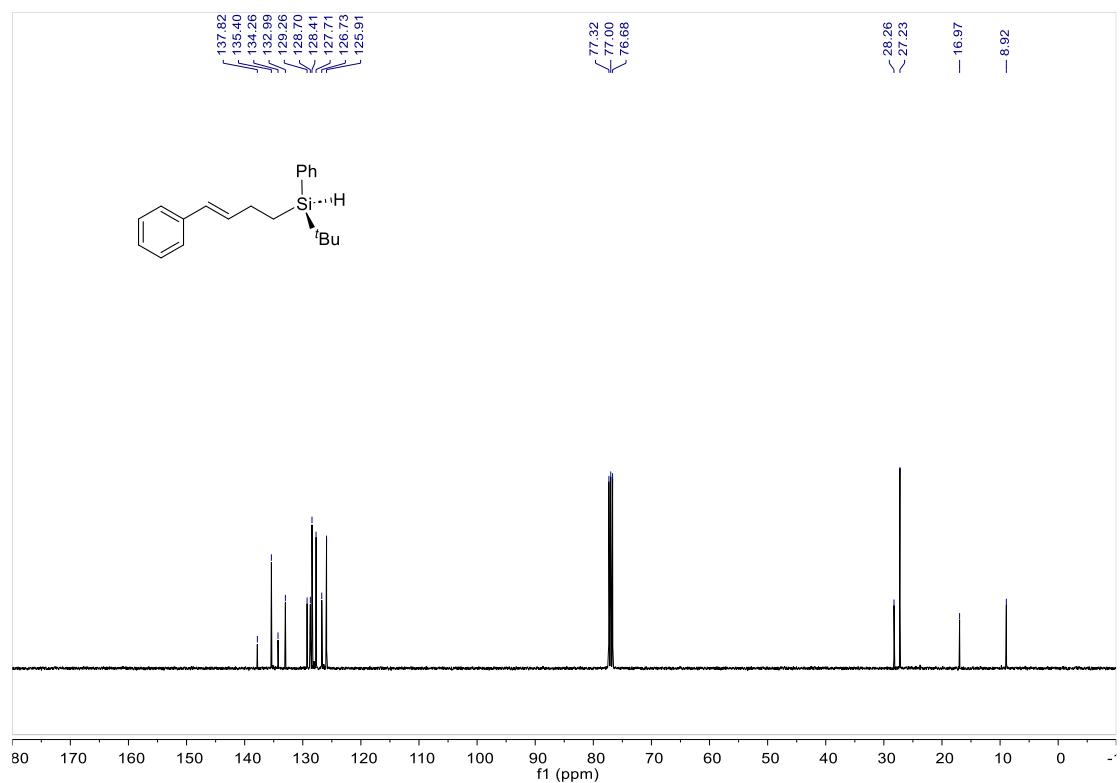
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5. NMR Spectra

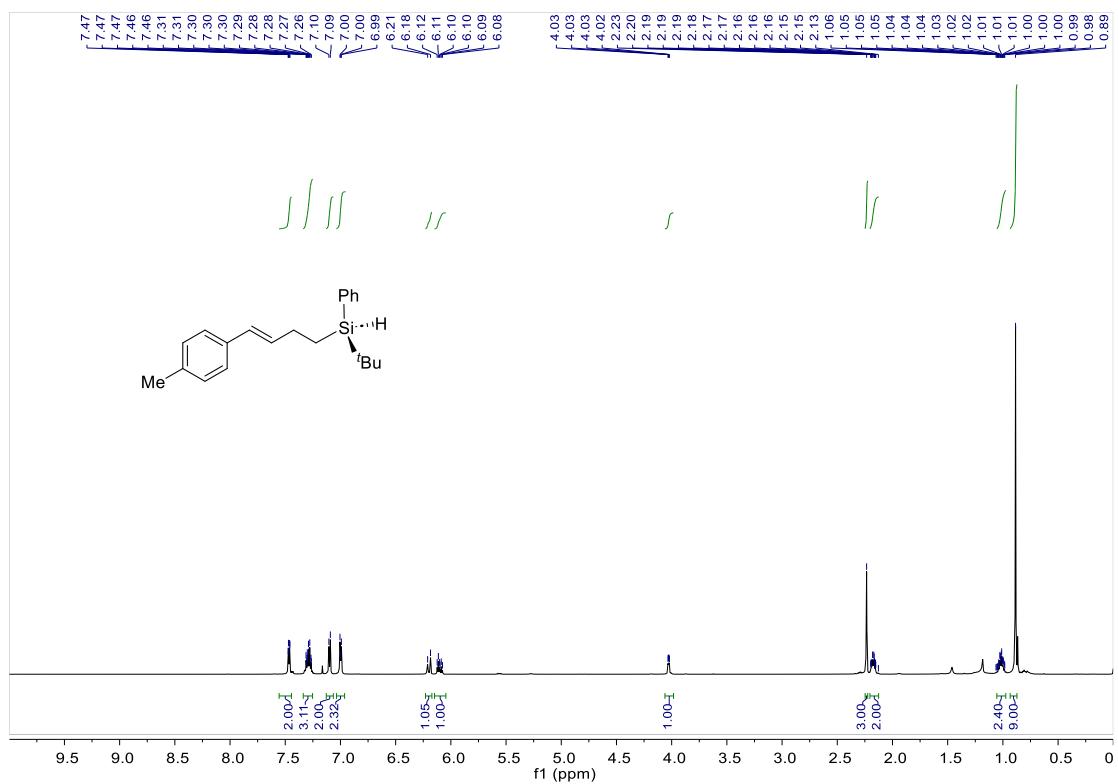
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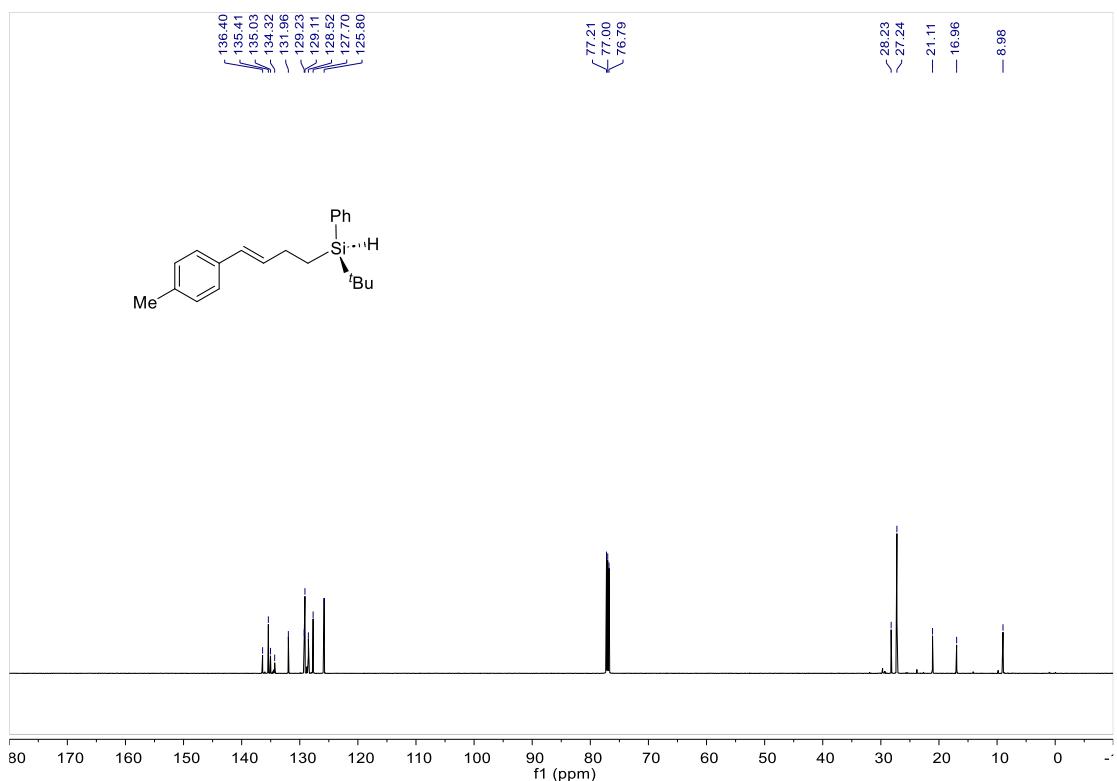
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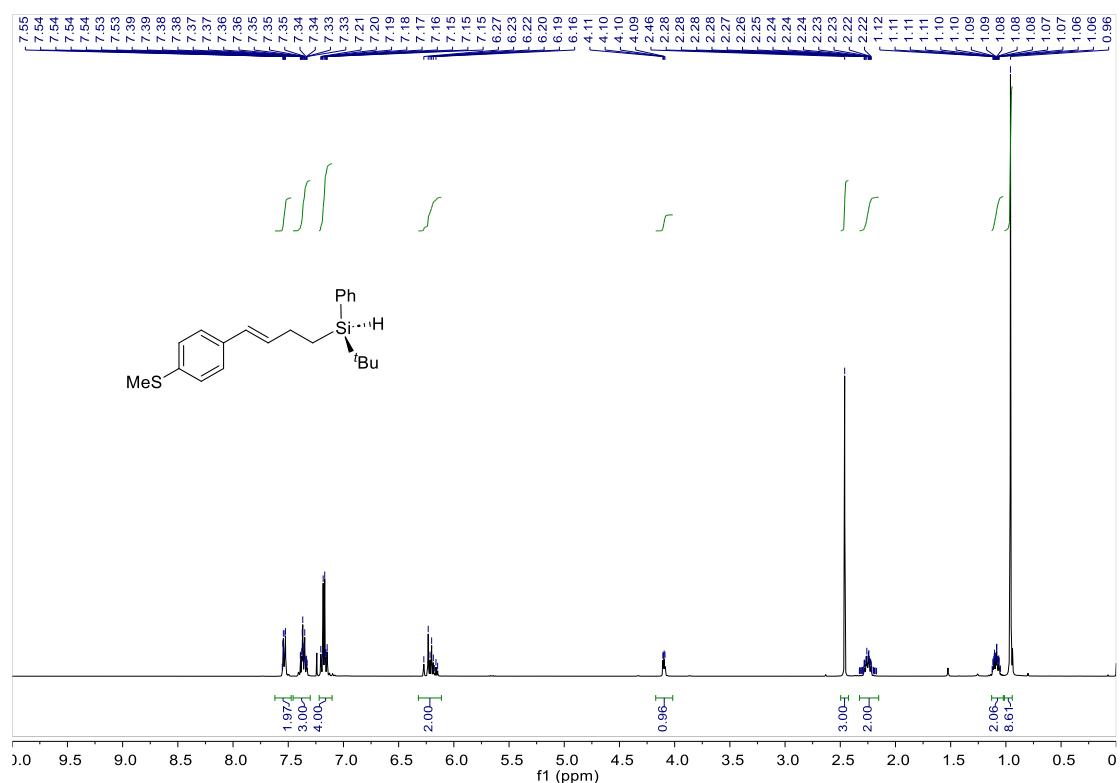
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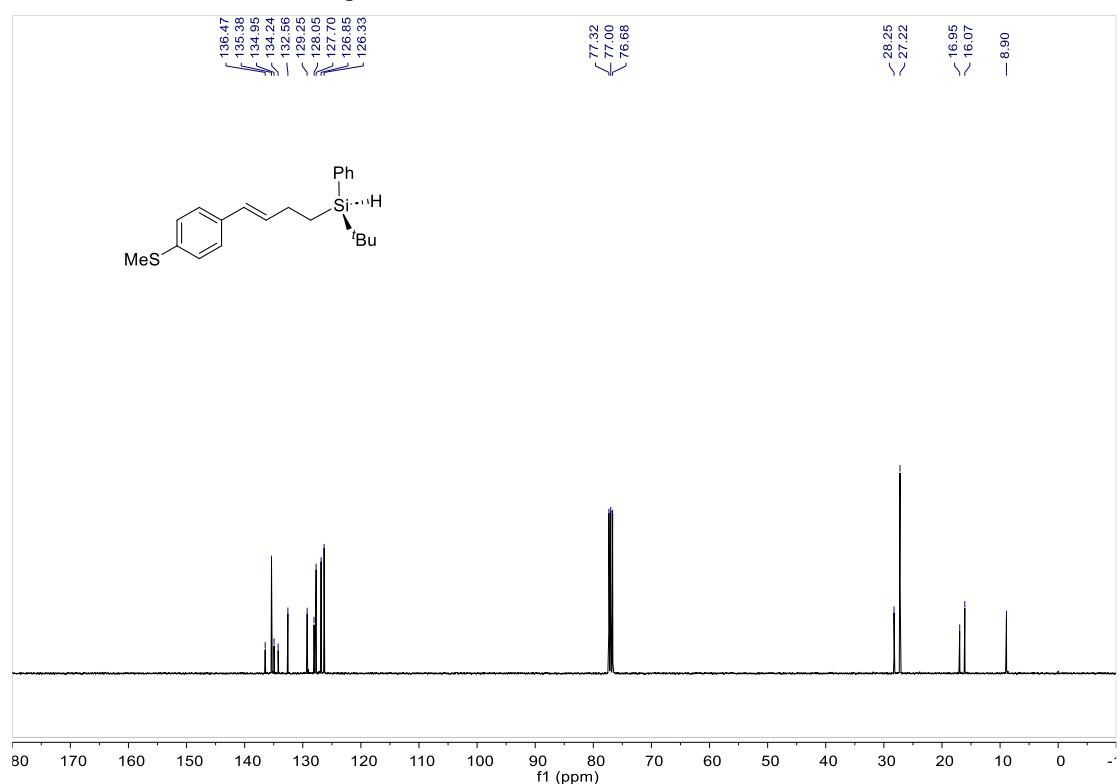
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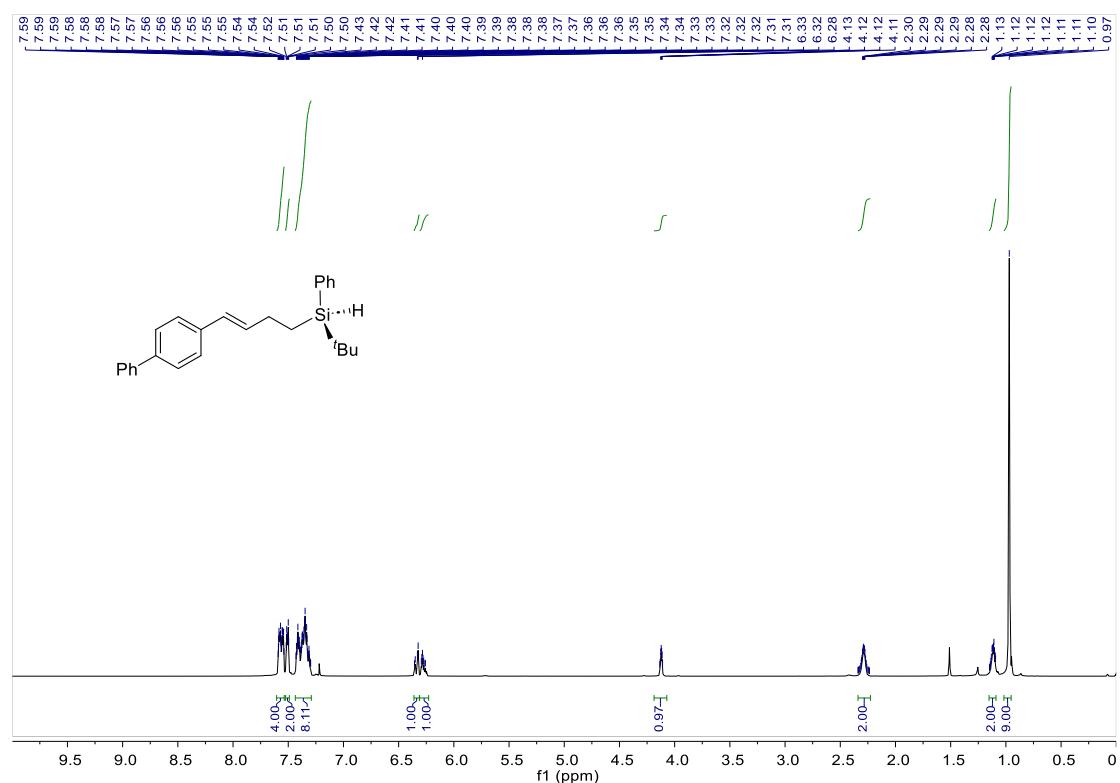
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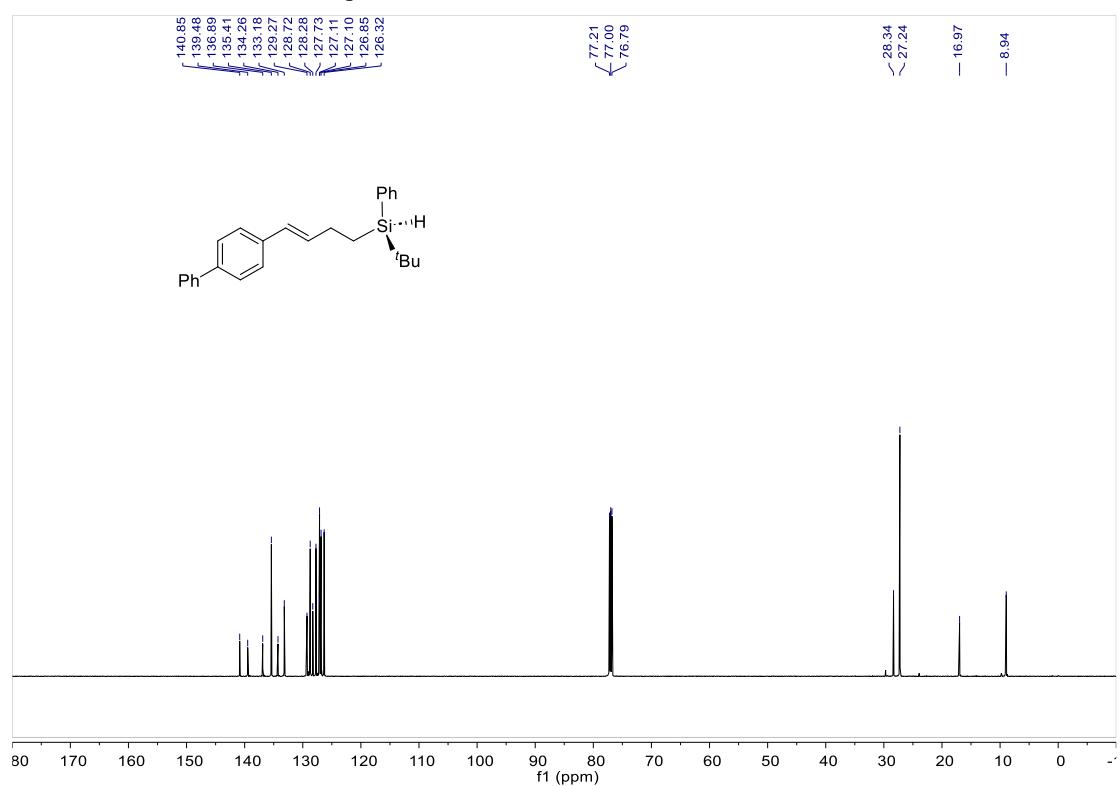
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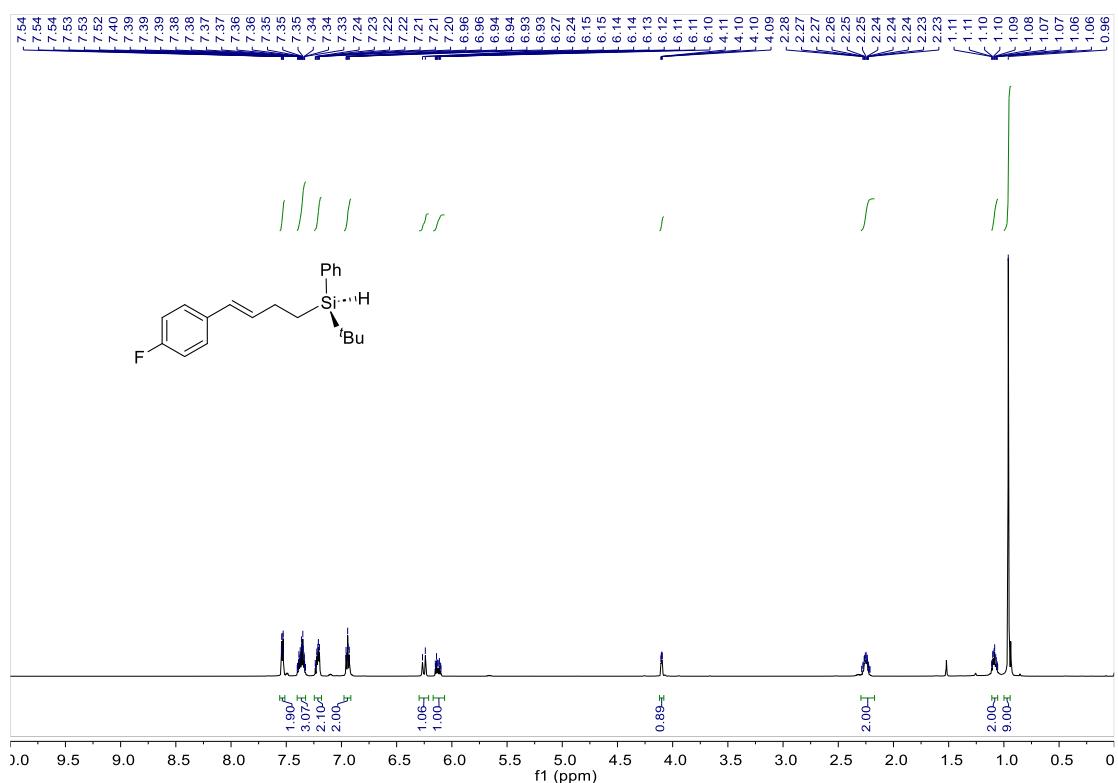
¹H NMR (600 MHz, CDCl₃) spectrum of 6



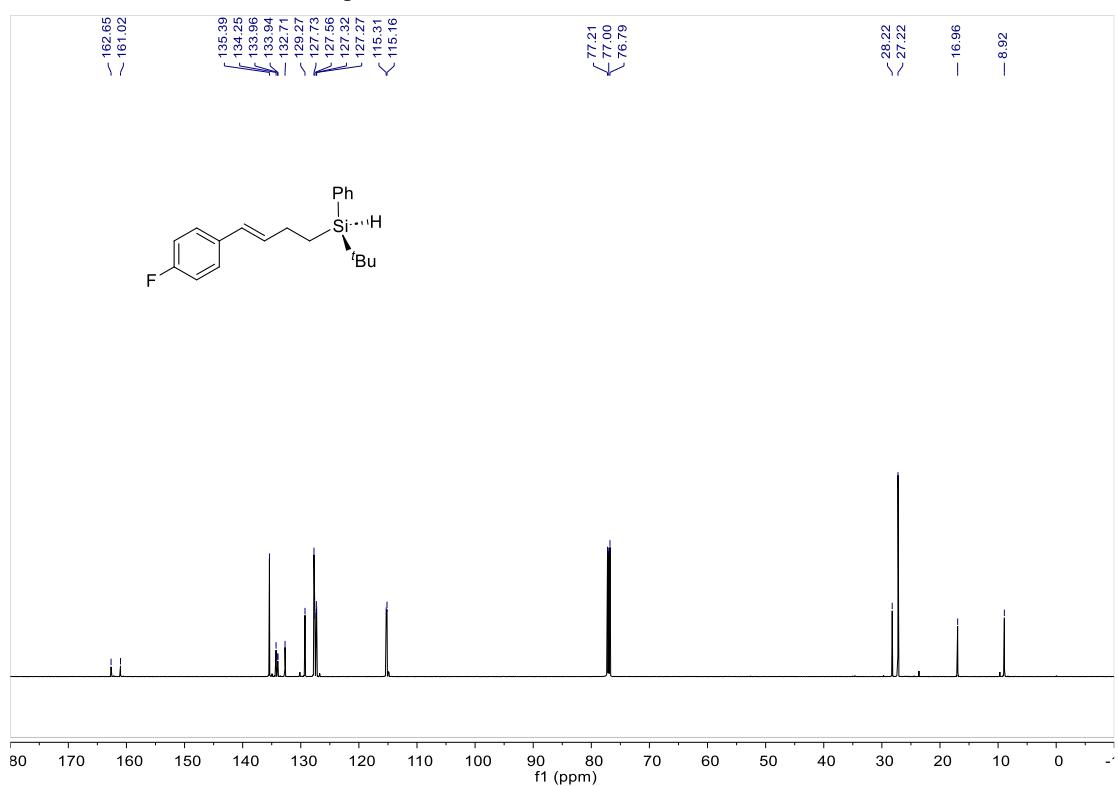
¹³C NMR (150 MHz, CDCl₃) spectrum of 6



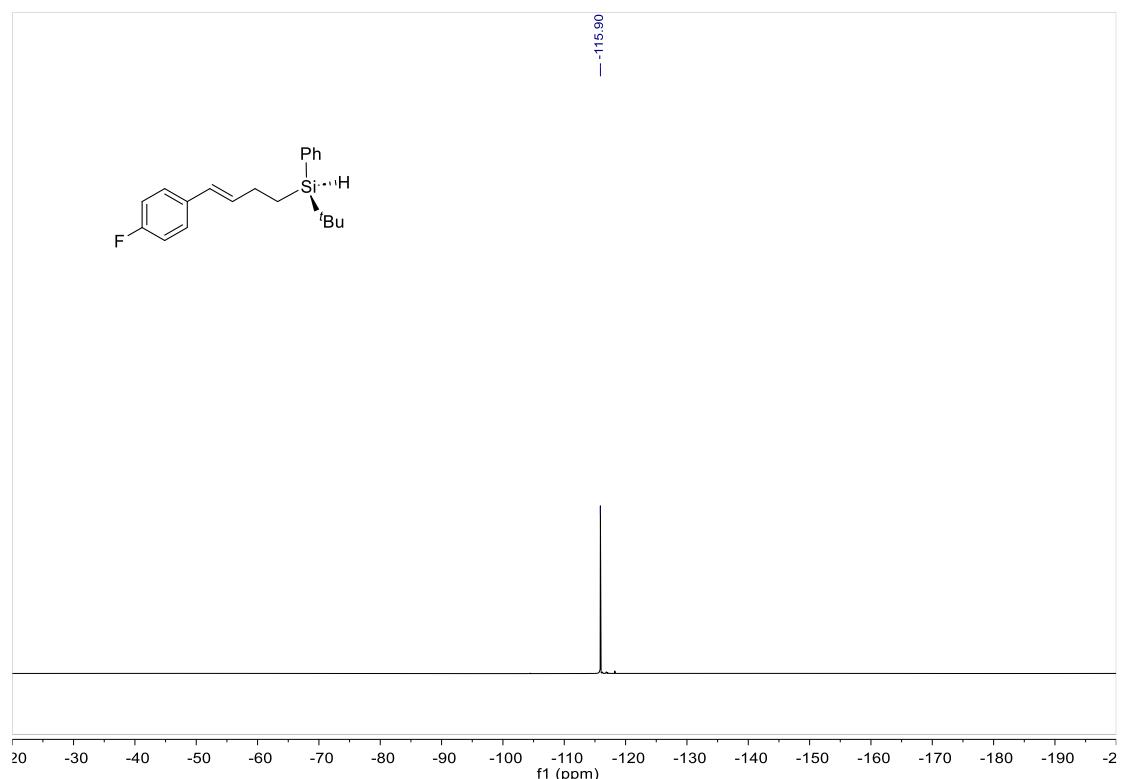
¹H NMR (600 MHz, CDCl₃) spectrum of 7



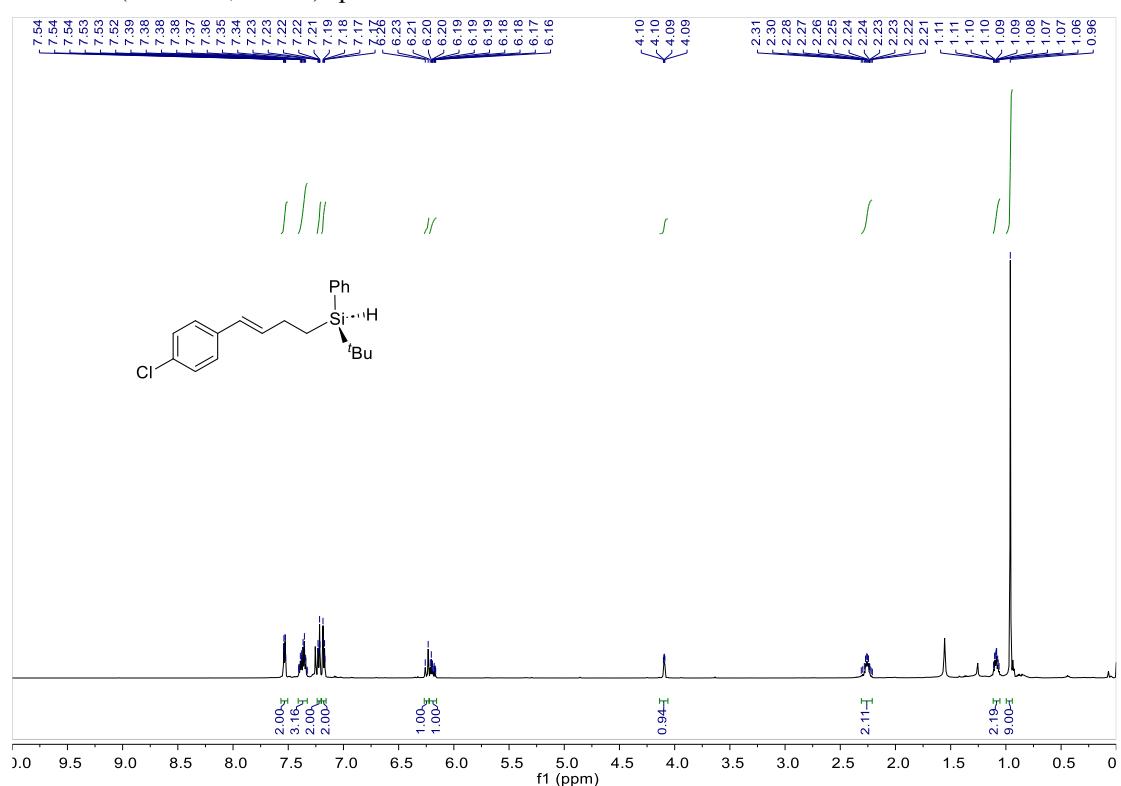
¹³C NMR (150 MHz, CDCl₃) spectrum of 7



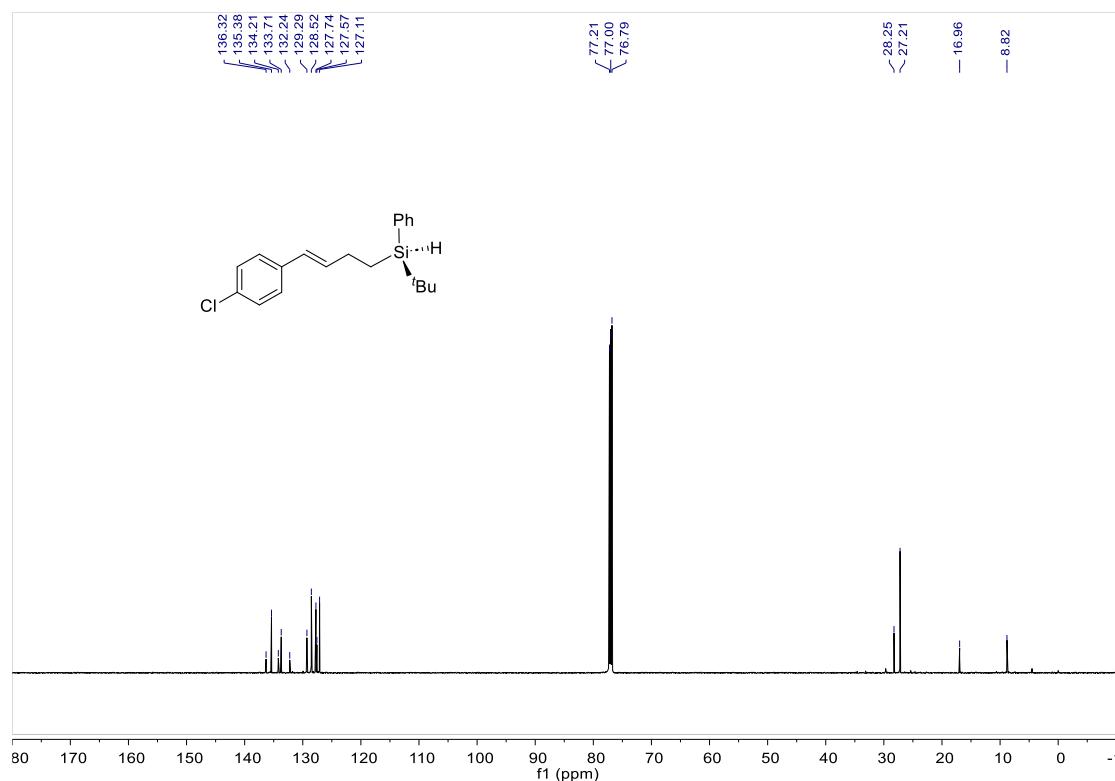
¹⁹F NMR (565 MHz, CDCl₃) spectrum of **7**



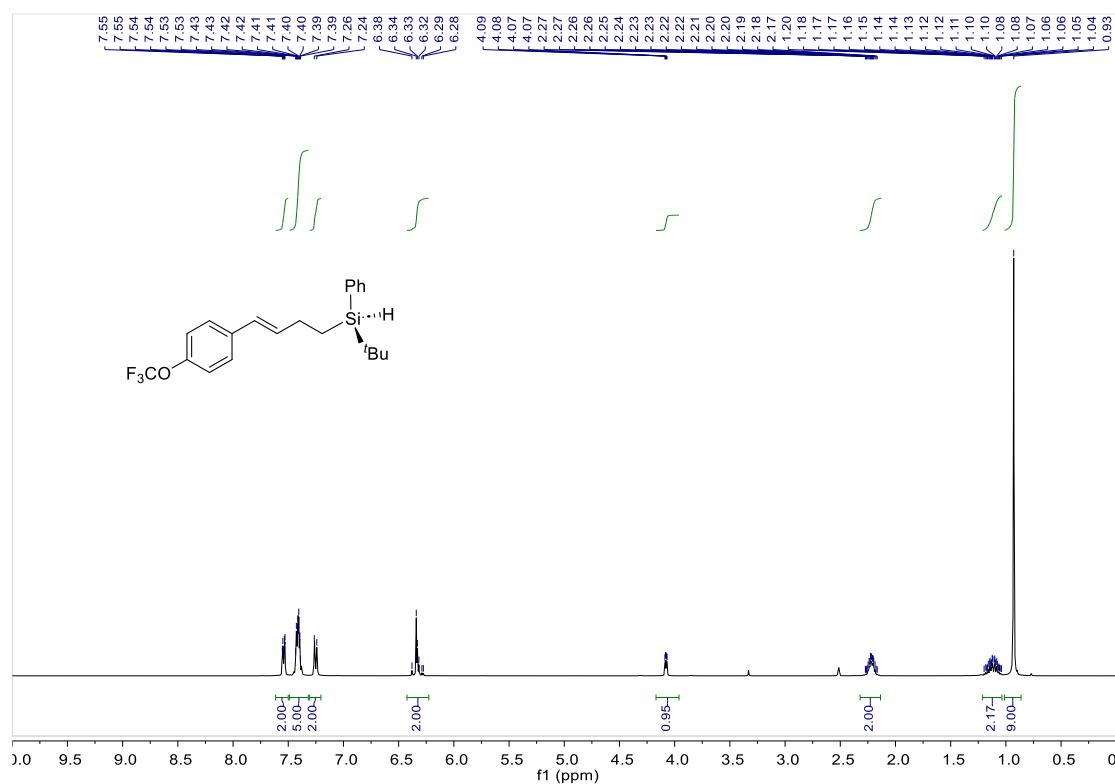
¹H NMR (600 MHz, CDCl₃) spectrum of **8**



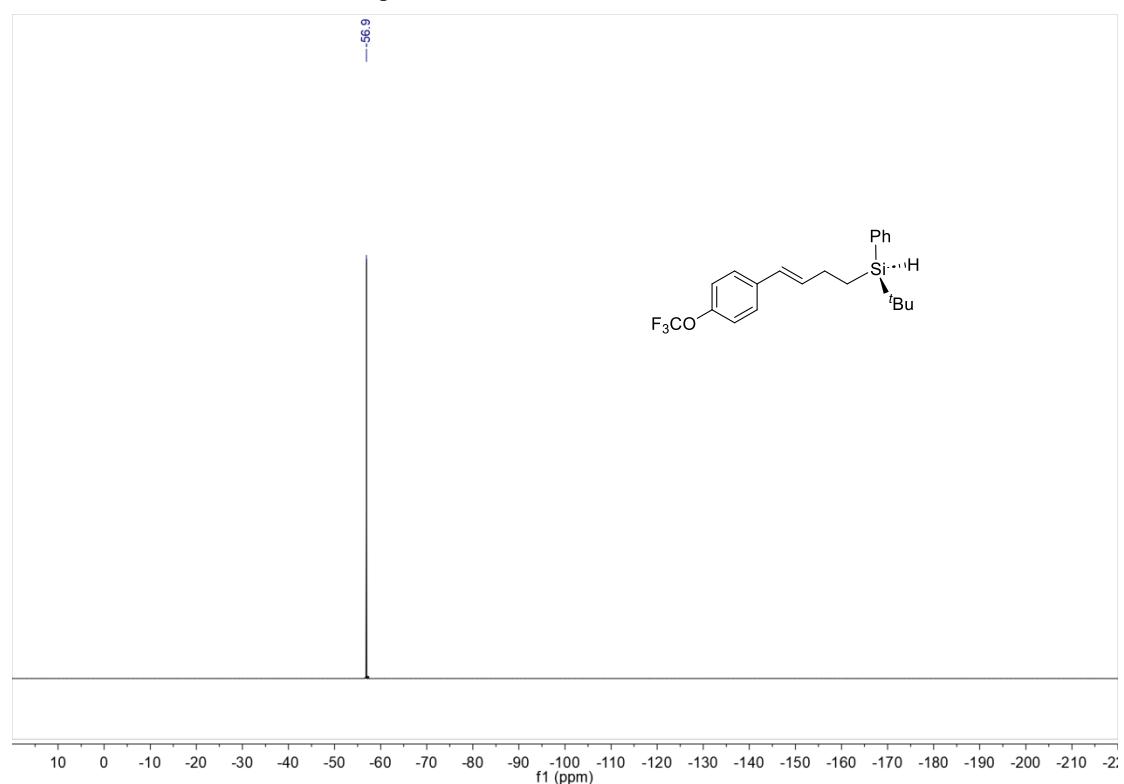
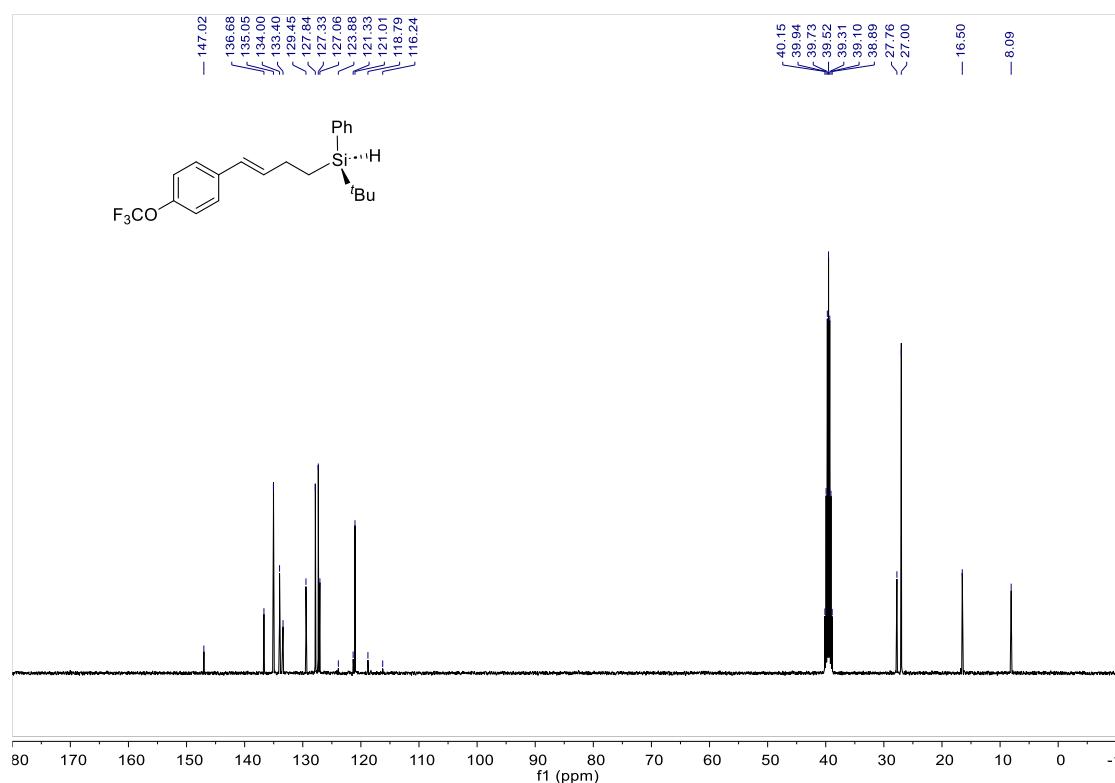
¹³C NMR (150 MHz, CDCl₃) spectrum of **8**



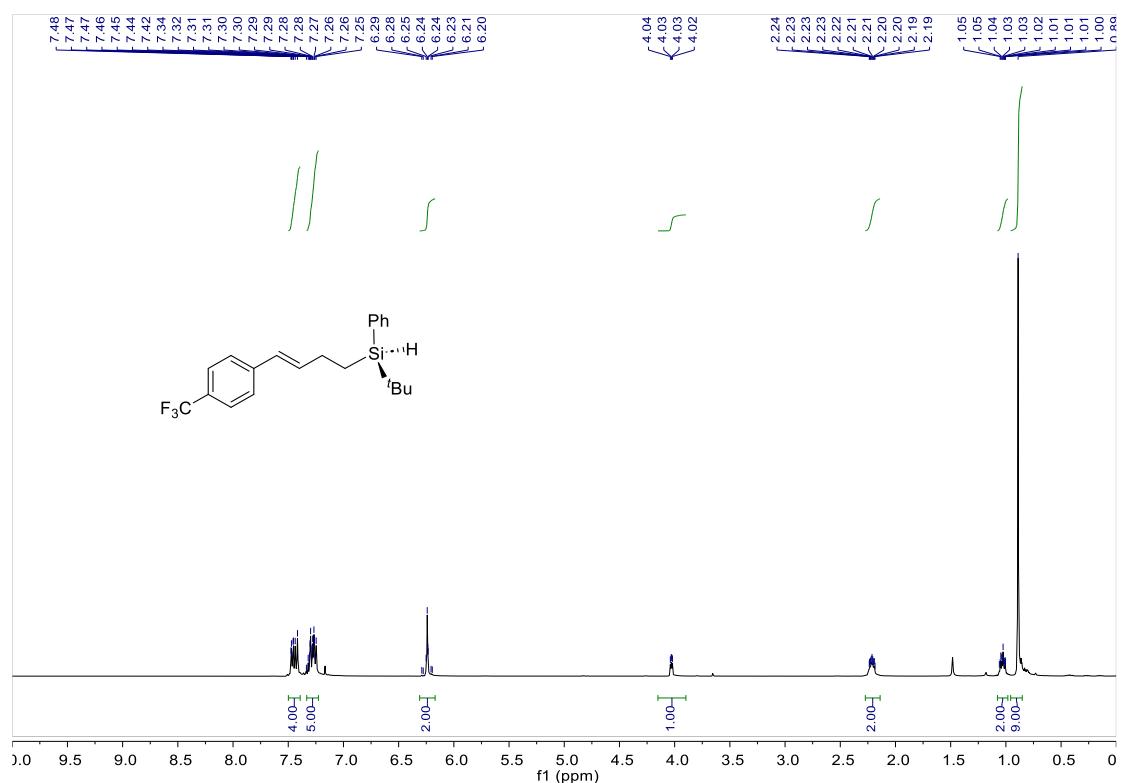
¹H NMR (400 MHz, DMSO-d₆) spectrum of **9**



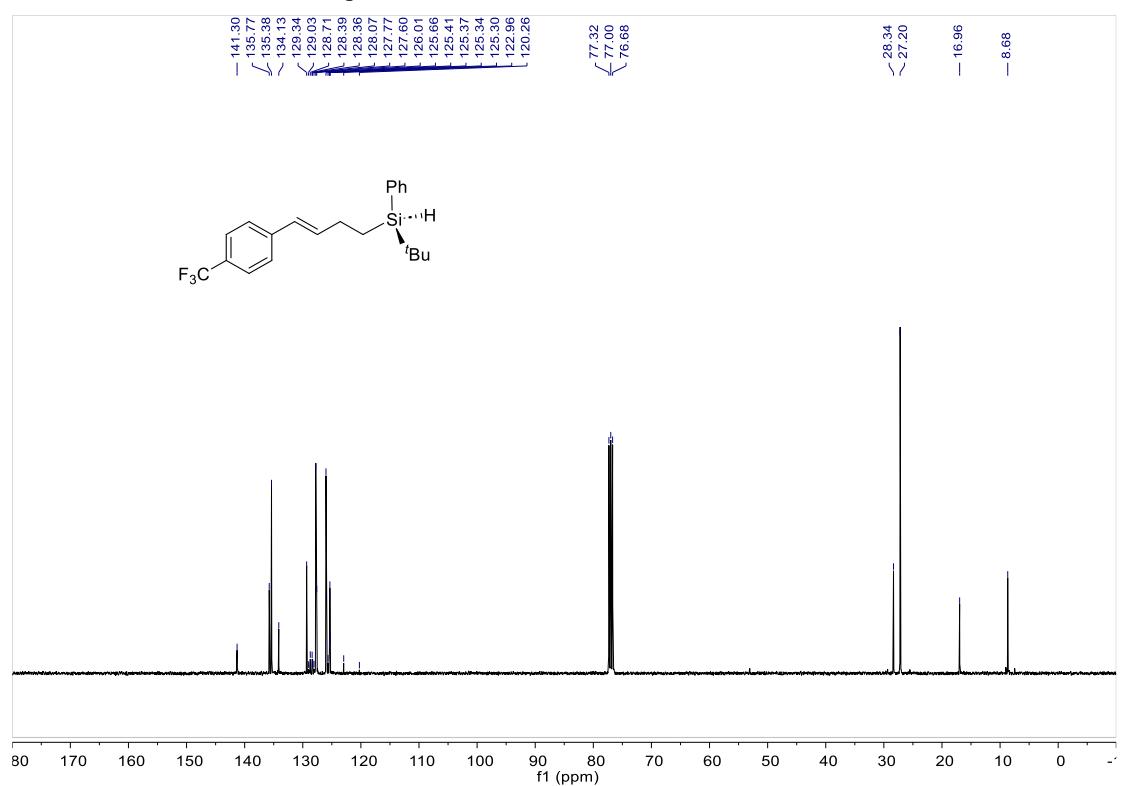
¹³C NMR (100 MHz, DMSO-*d*₆) spectrum of **9**



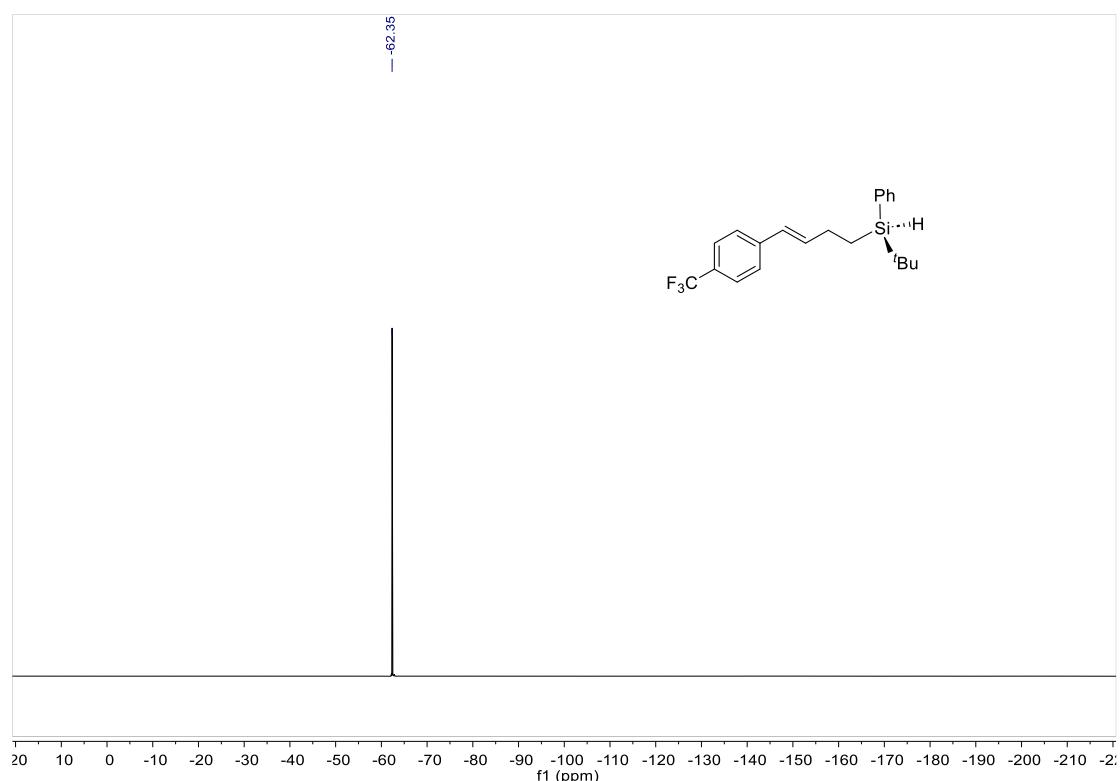
¹H NMR (400 MHz, CDCl₃) spectrum of **10**



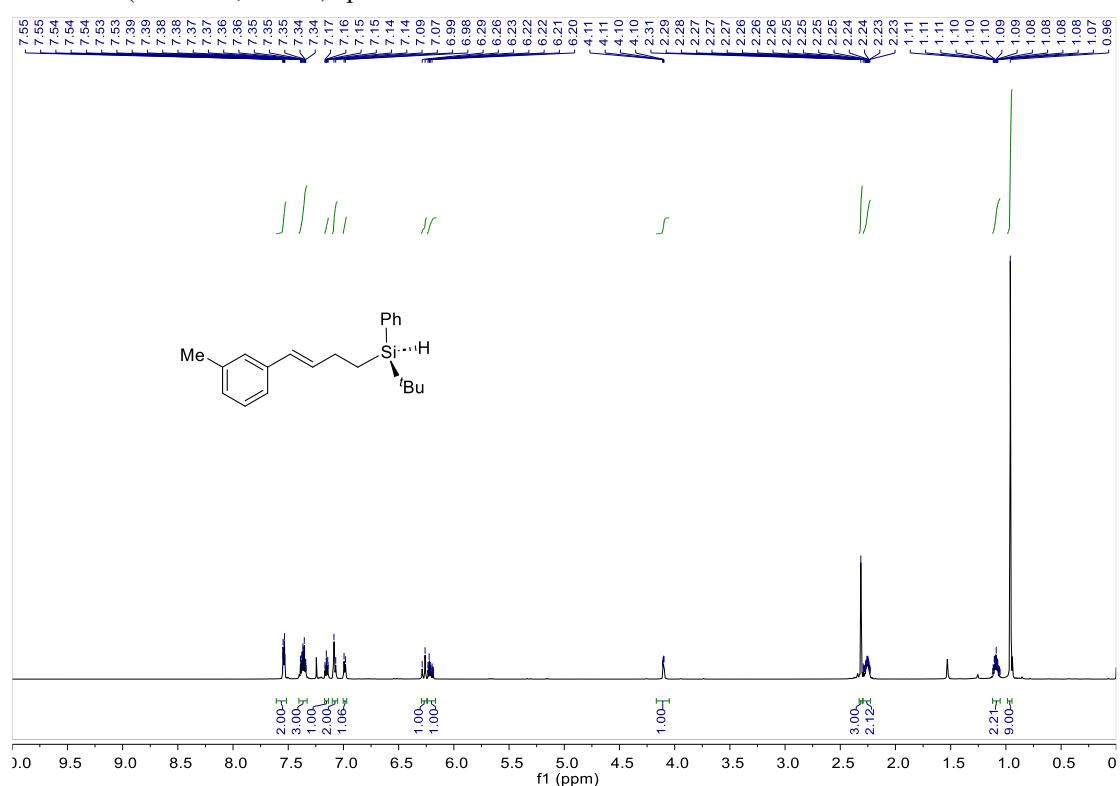
¹³C NMR (100 MHz, CDCl₃) spectrum of **10**



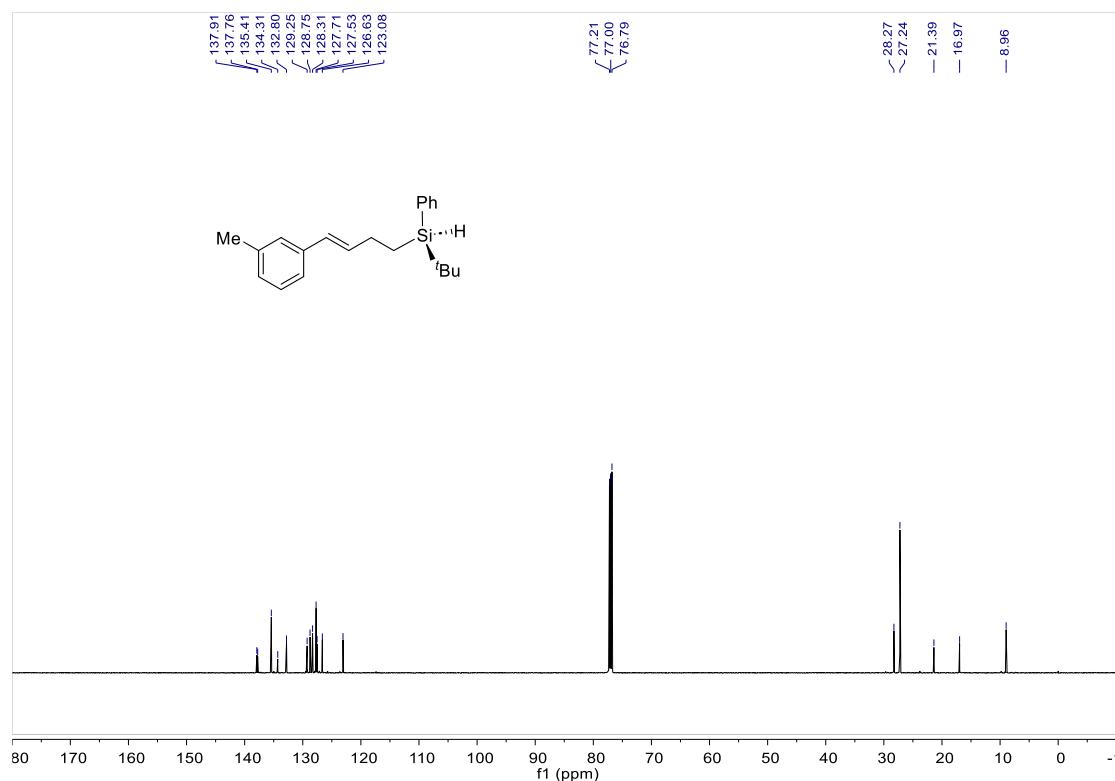
¹⁹F NMR (376 MHz, CDCl₃) spectrum of **10**



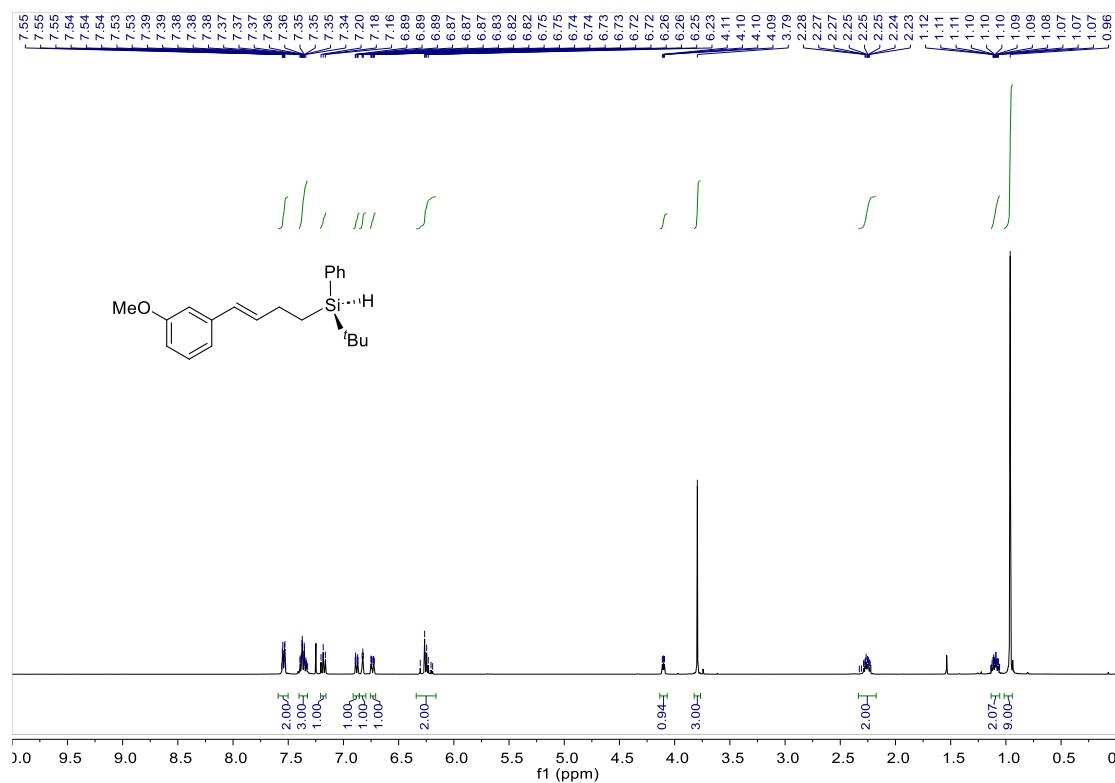
¹¹H NMR (600 MHz, CDCl₃) spectrum of **11**



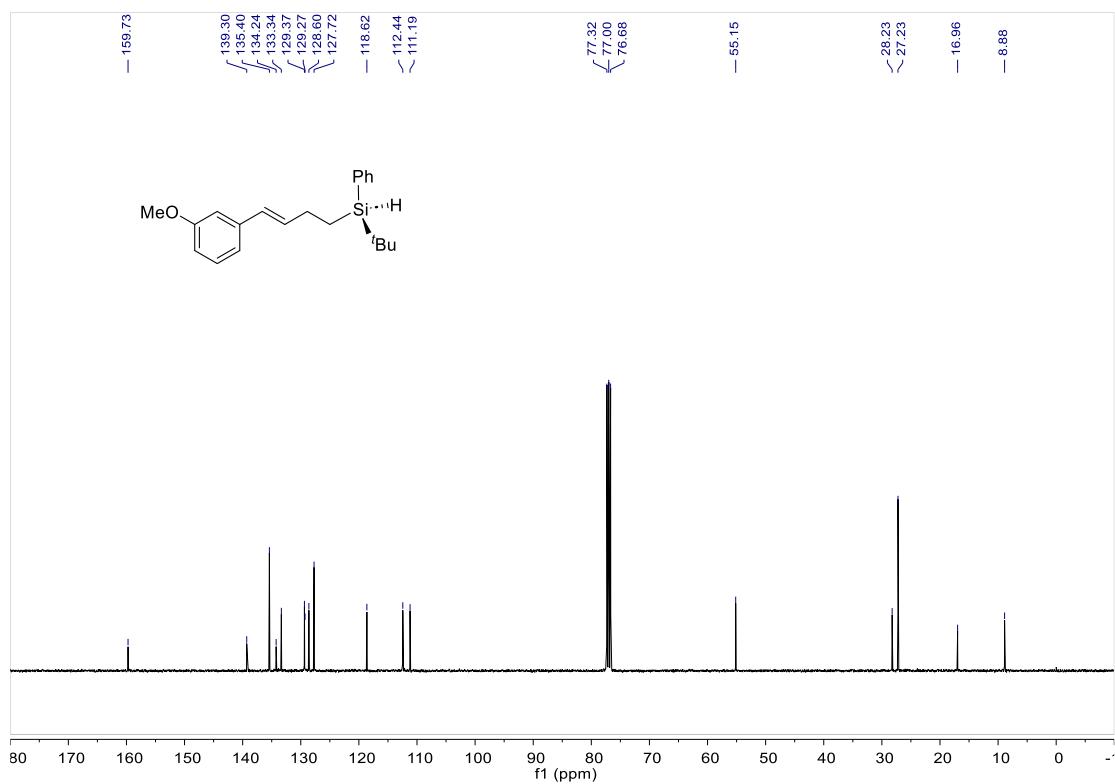
¹³C NMR (150 MHz, CDCl₃) spectrum of **11**



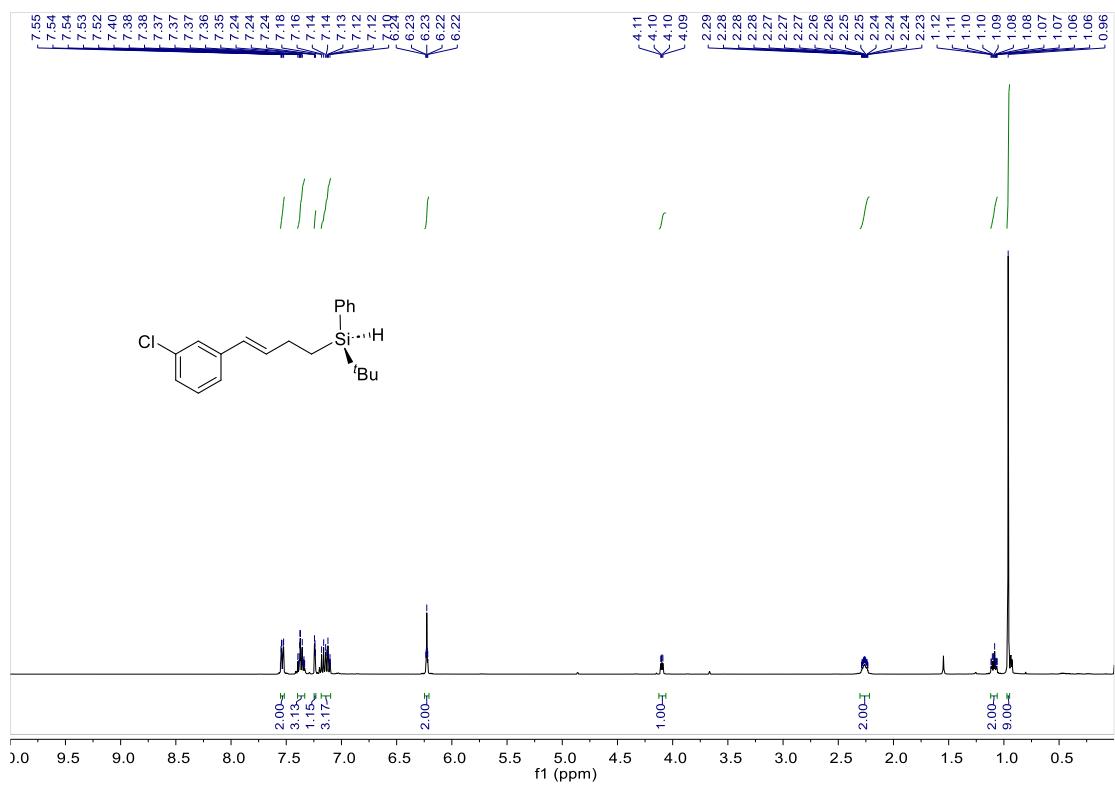
¹H NMR (400 MHz, CDCl₃) spectrum of **12**



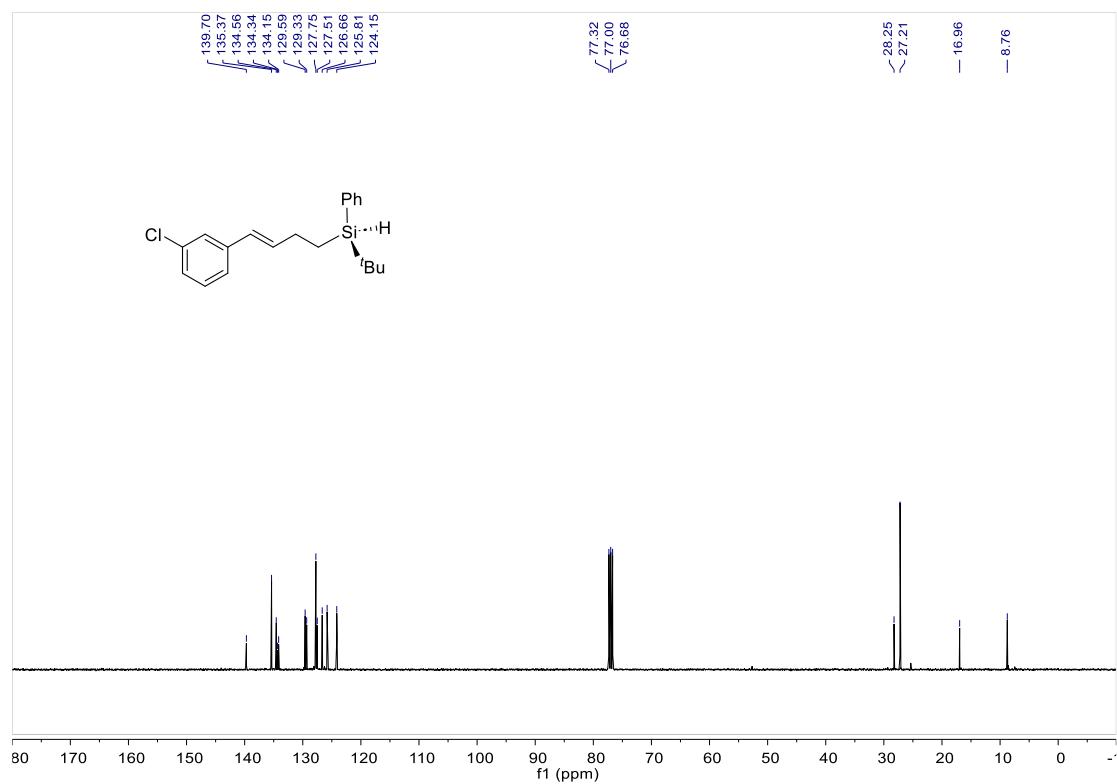
¹³C NMR (100 MHz, CDCl₃) spectrum of **12**



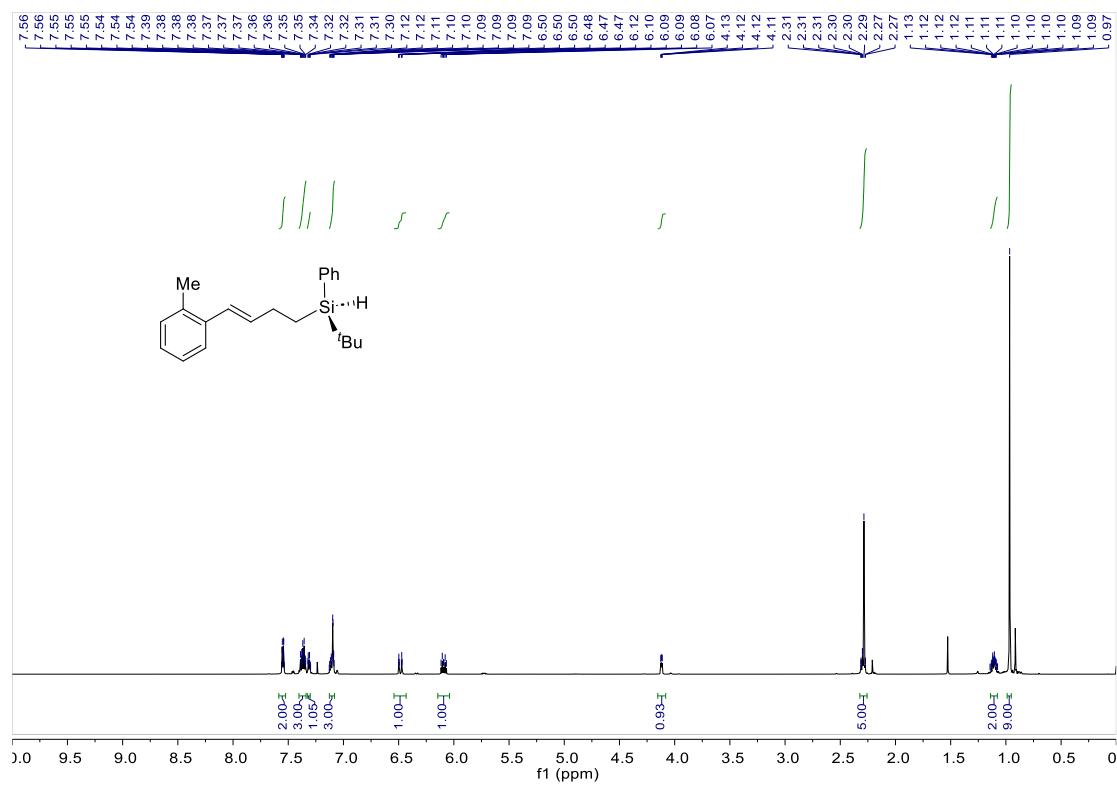
¹H NMR (400 MHz, CDCl₃) spectrum of **13**



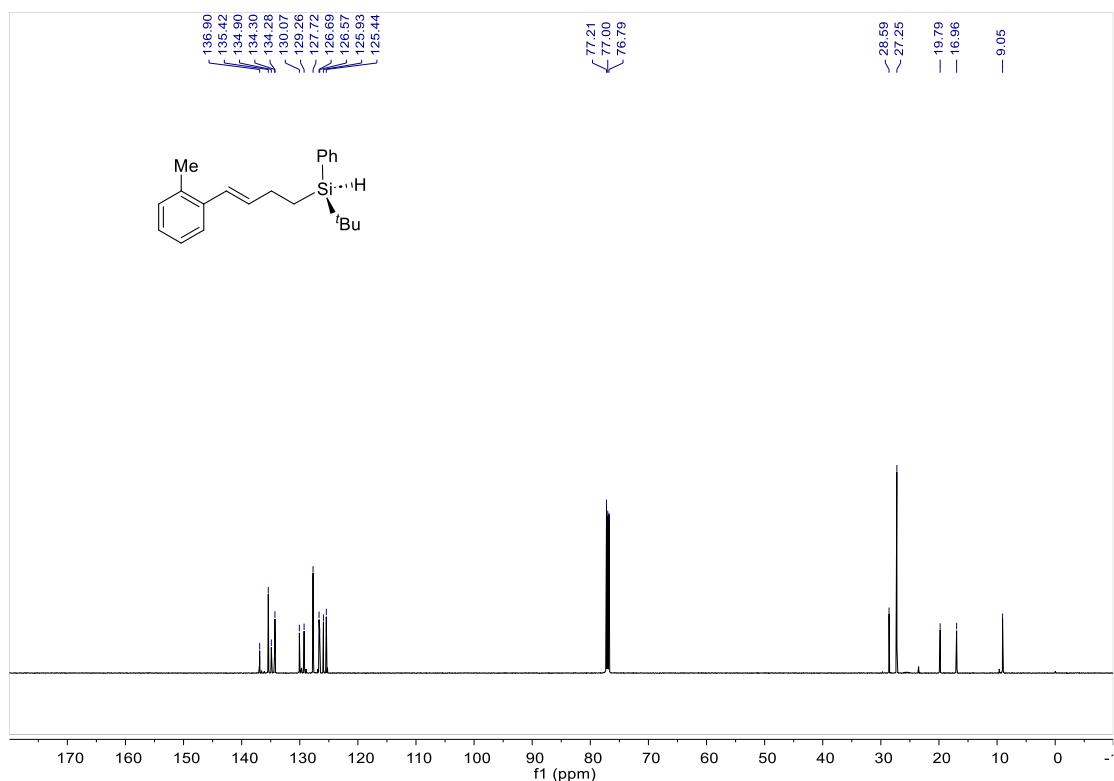
¹³C NMR (100 MHz, CDCl₃) spectrum of 13



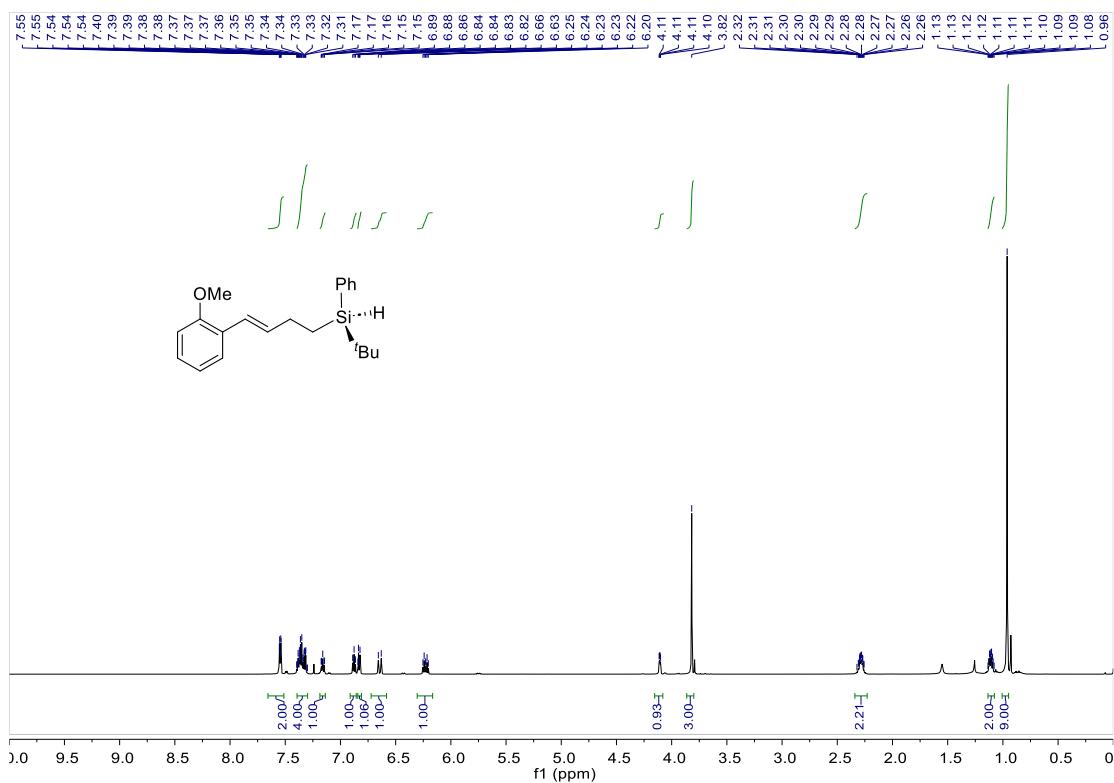
¹H NMR (600 MHz, CDCl₃) spectrum of 14



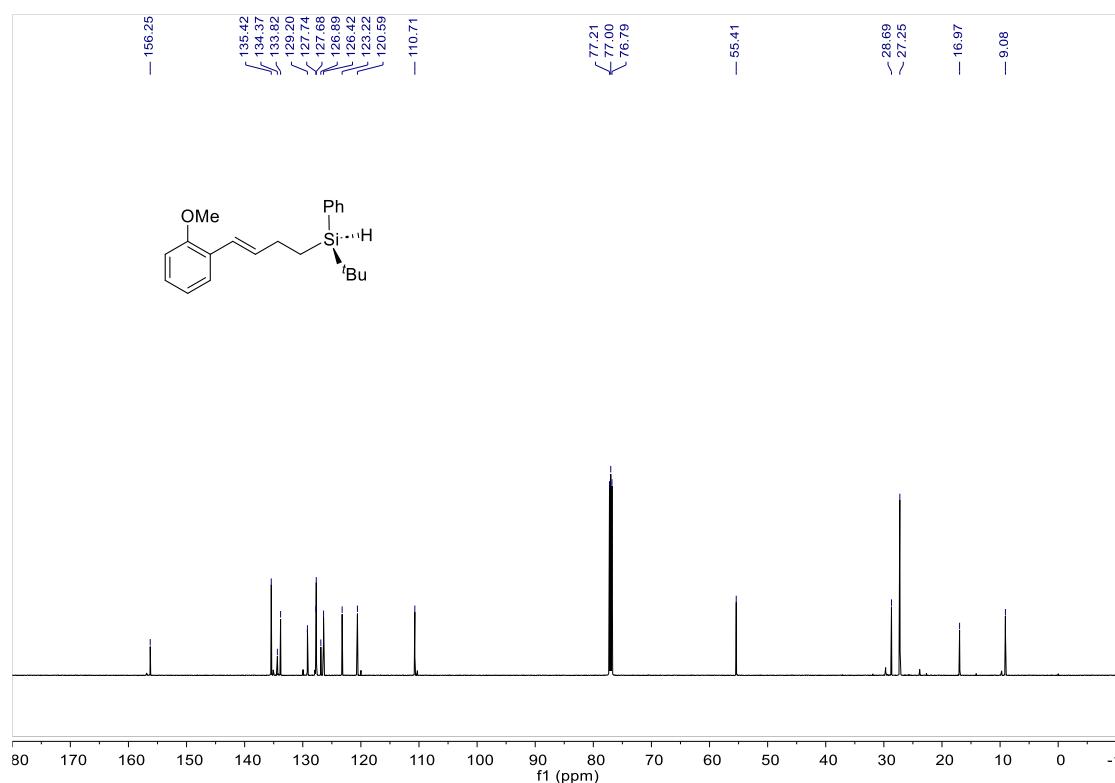
¹³C NMR (150 MHz, CDCl₃) spectrum of **14**



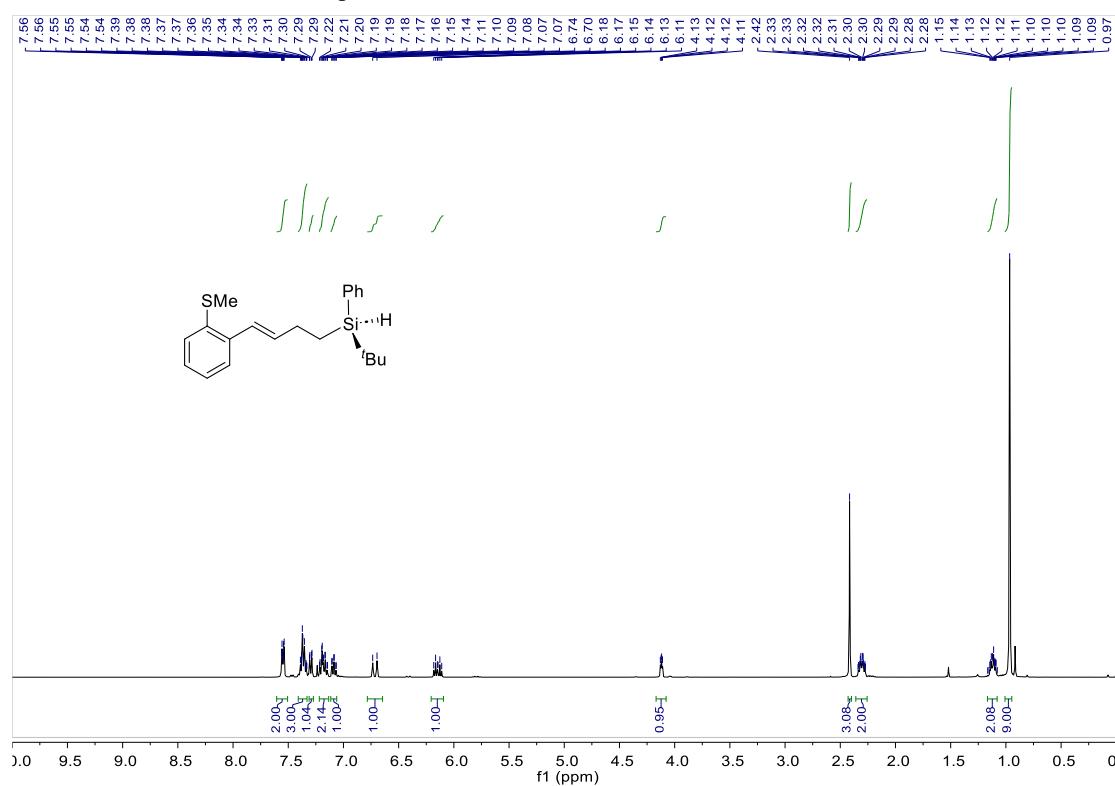
¹H NMR (600 MHz, CDCl₃) spectrum of **15**



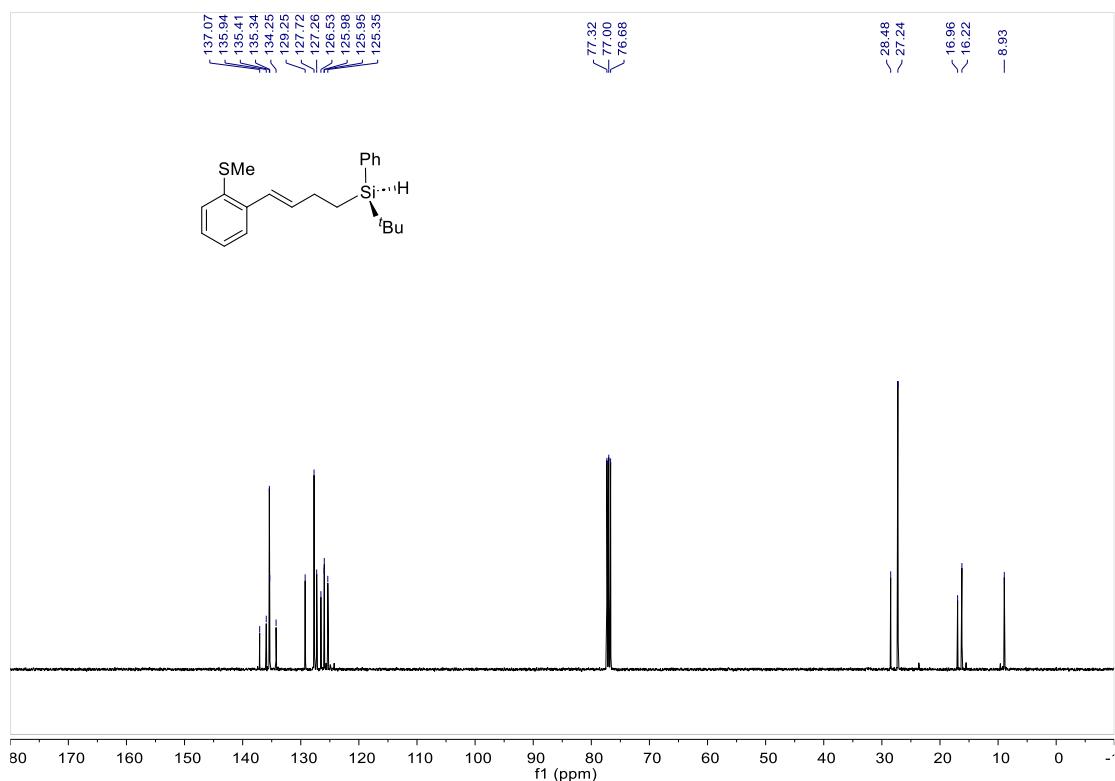
¹³C NMR (150 MHz, CDCl₃) spectrum of **15**



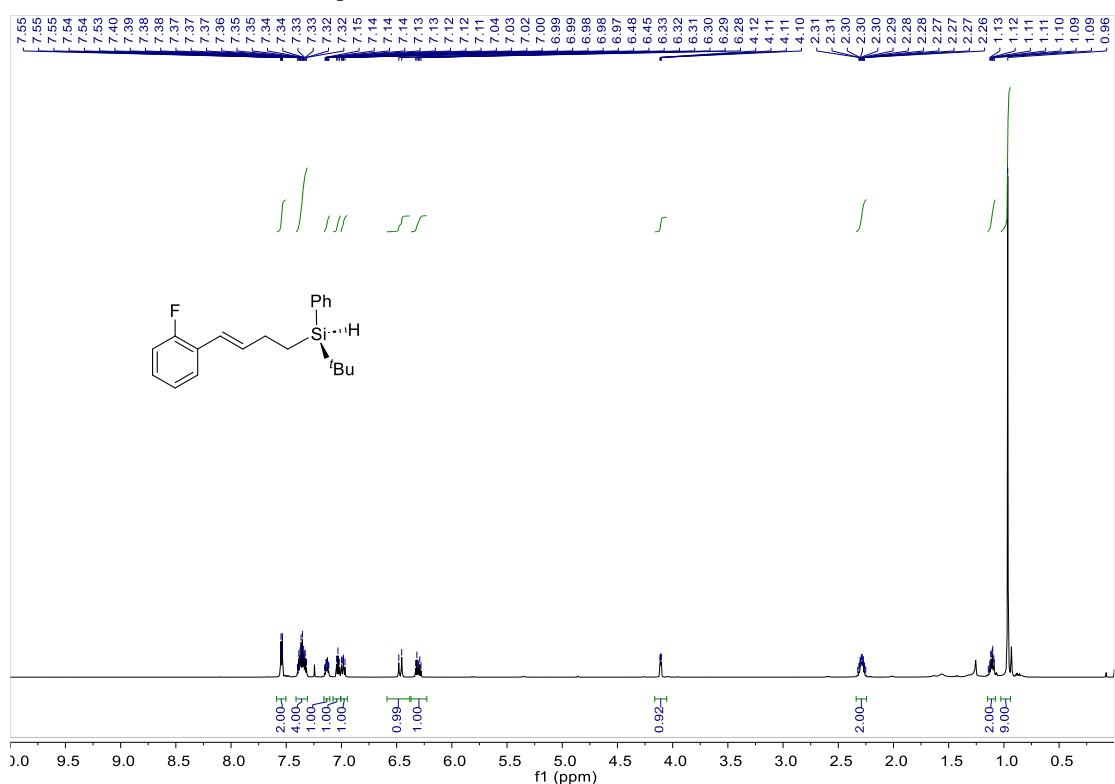
¹H NMR (400 MHz, CDCl₃) spectrum of **16**



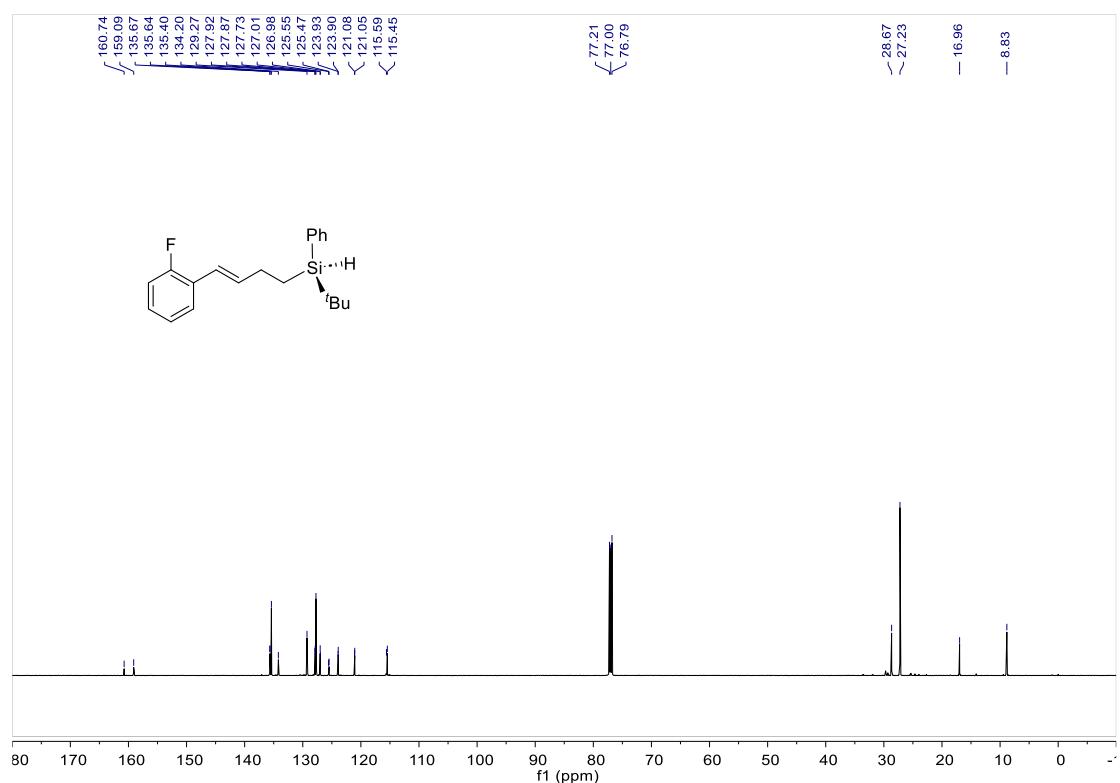
¹³C NMR (100 MHz, CDCl₃) spectrum of 16



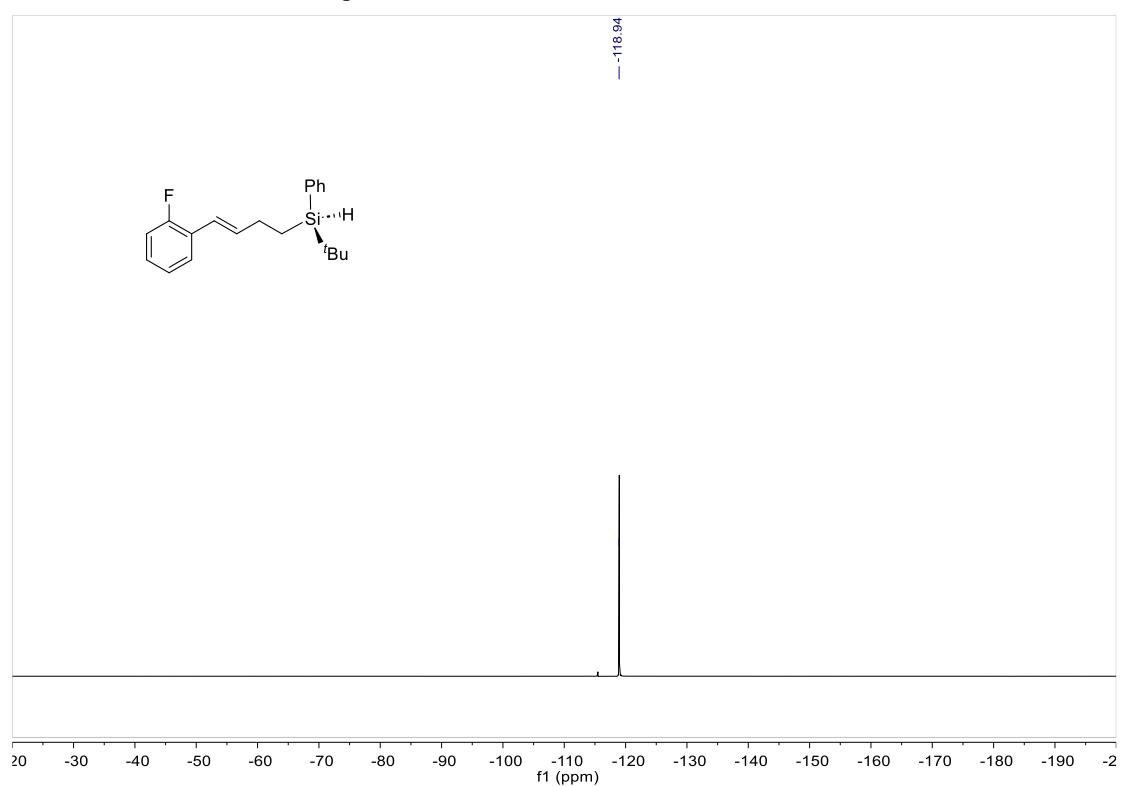
¹H NMR (600 MHz, CDCl₃) spectrum of 17



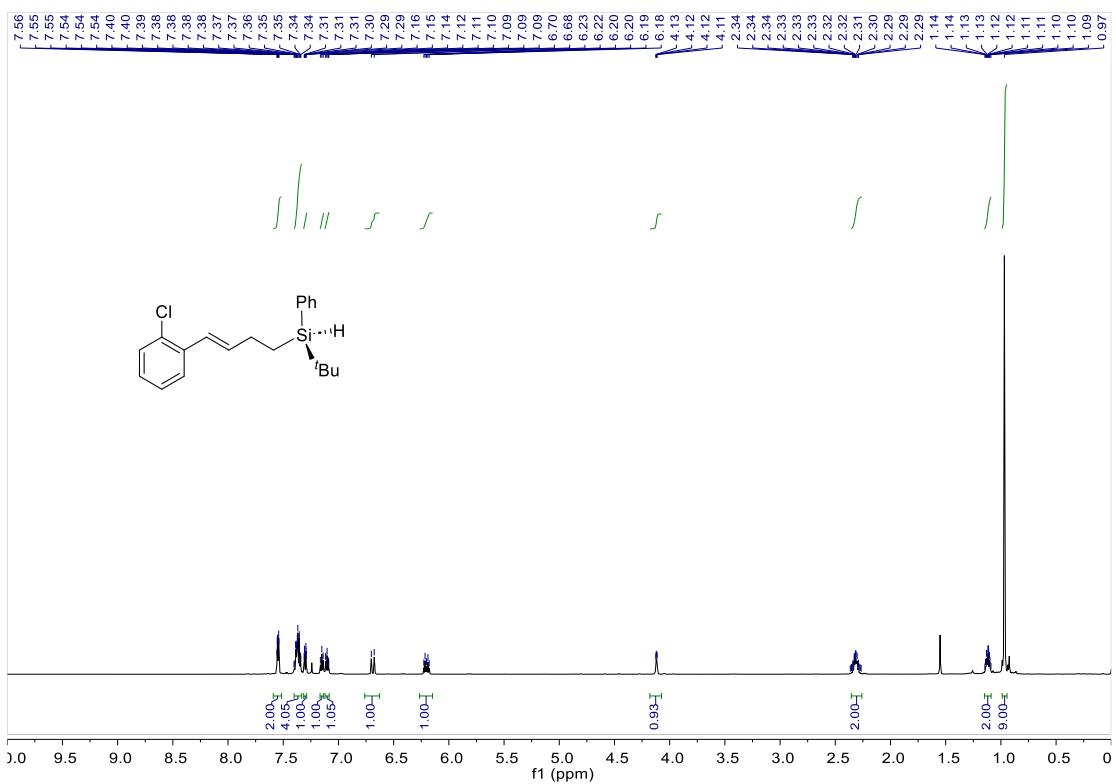
¹³C NMR (150 MHz, CDCl₃) spectrum of **17**



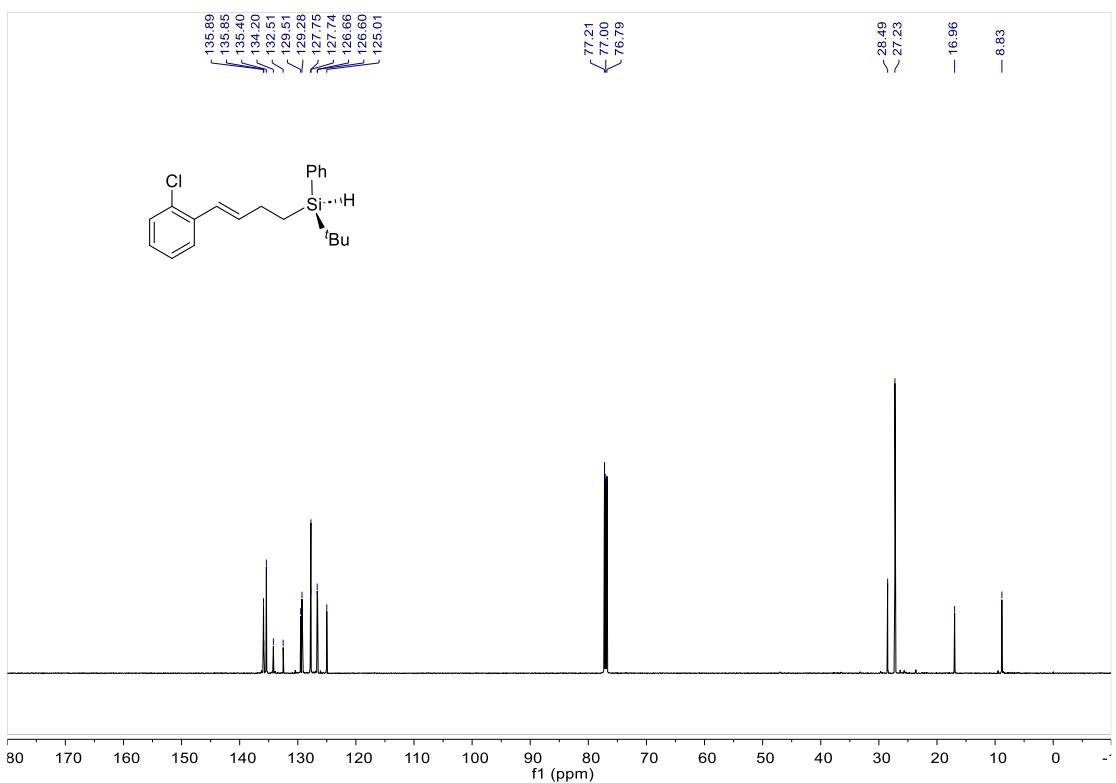
¹⁹F NMR (565 MHz, CDCl₃) spectrum of **17**



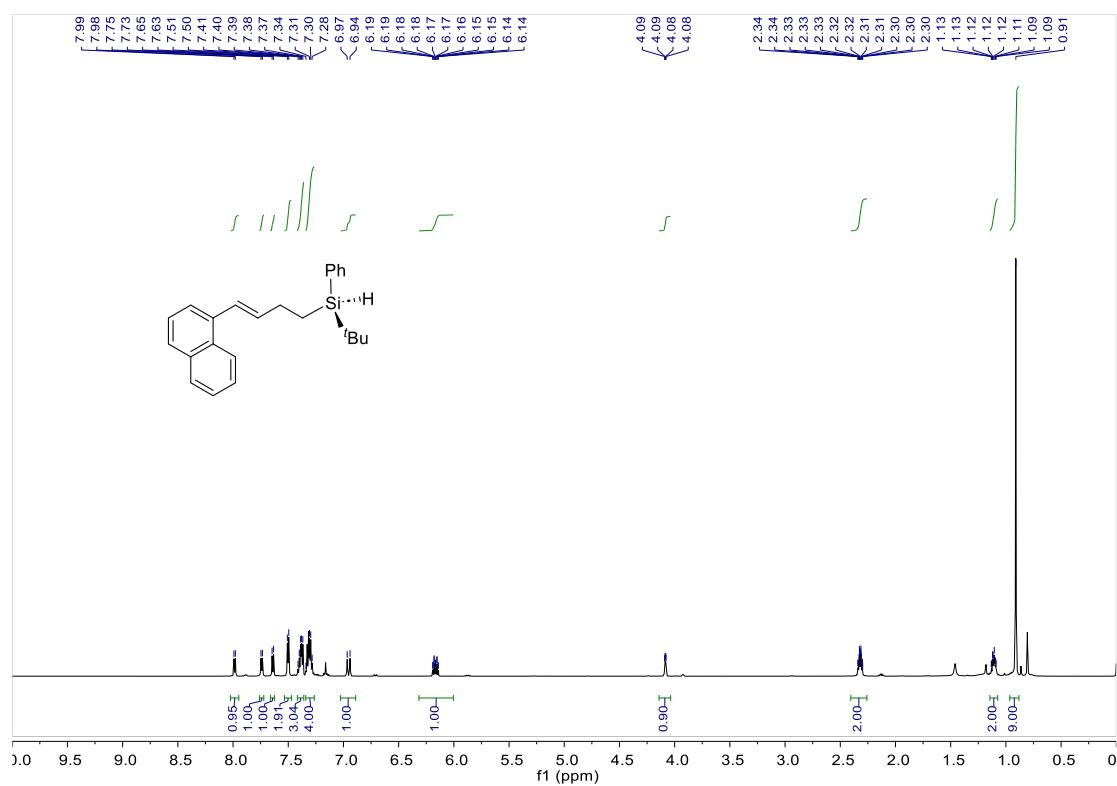
¹H NMR (600 MHz, CDCl₃) spectrum of **18**



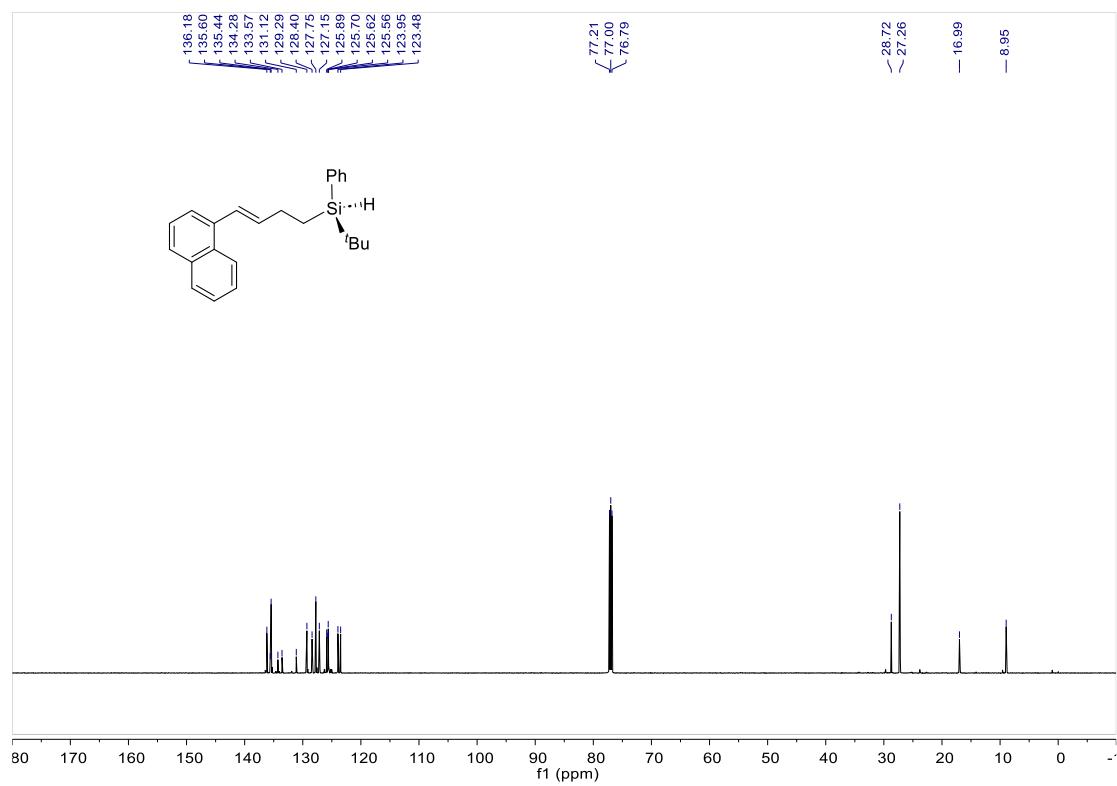
¹³C NMR (150 MHz, CDCl₃) spectrum of **18**



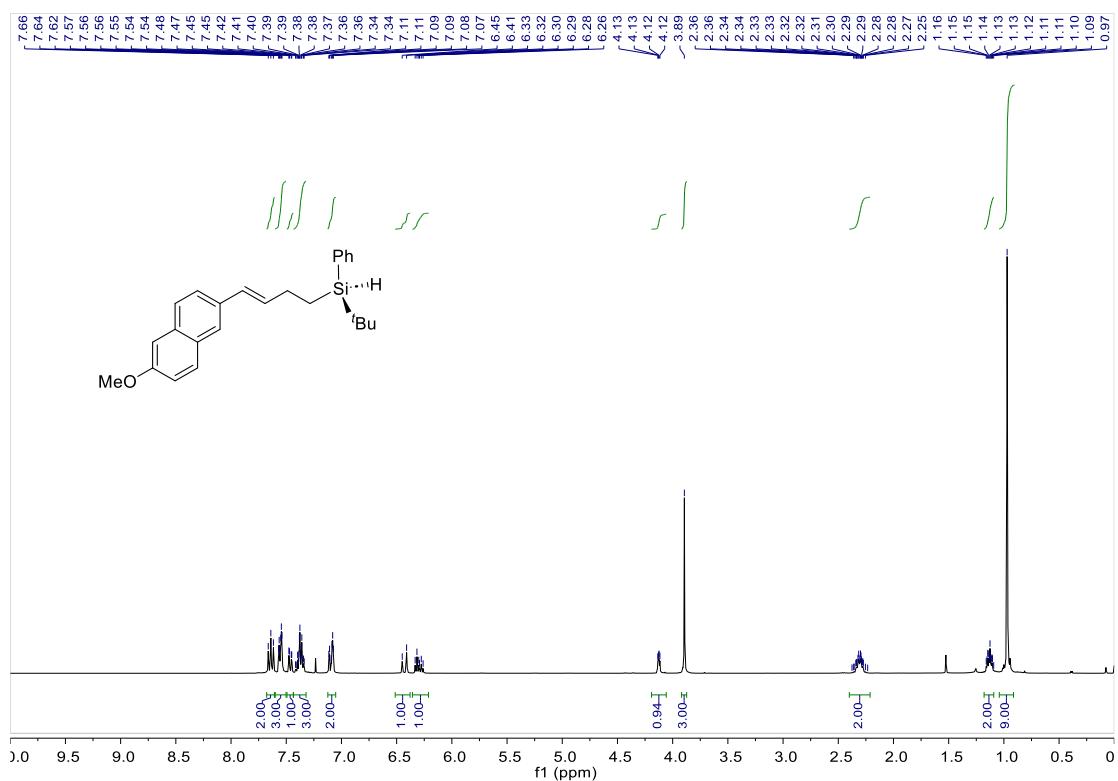
¹H NMR (600 MHz, CDCl₃) spectrum of **19**



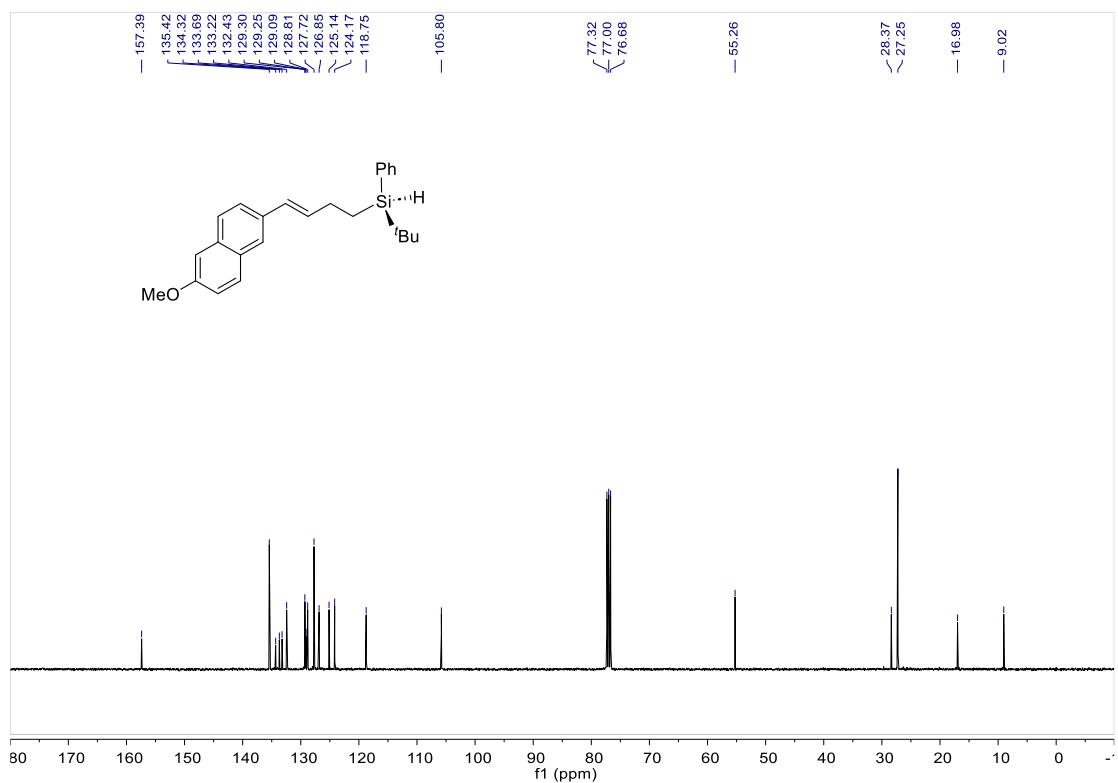
¹³C NMR (150 MHz, CDCl₃) spectrum of **19**



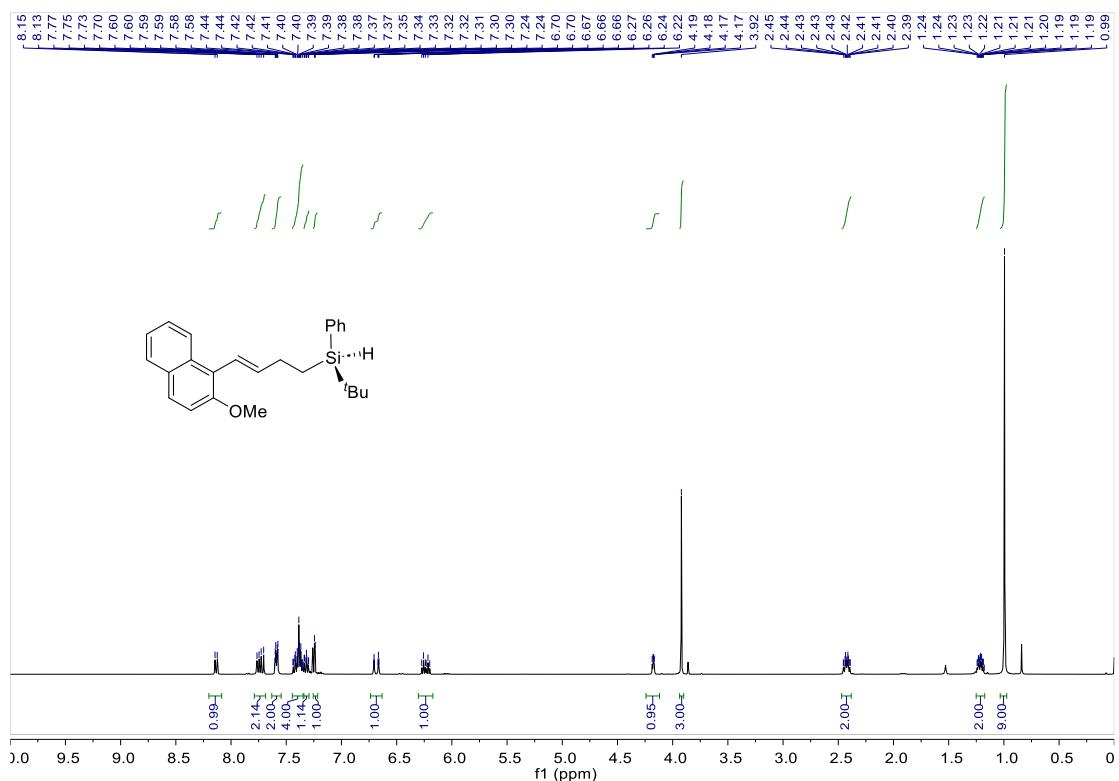
¹H NMR (400 MHz, CDCl₃) spectrum of **20**



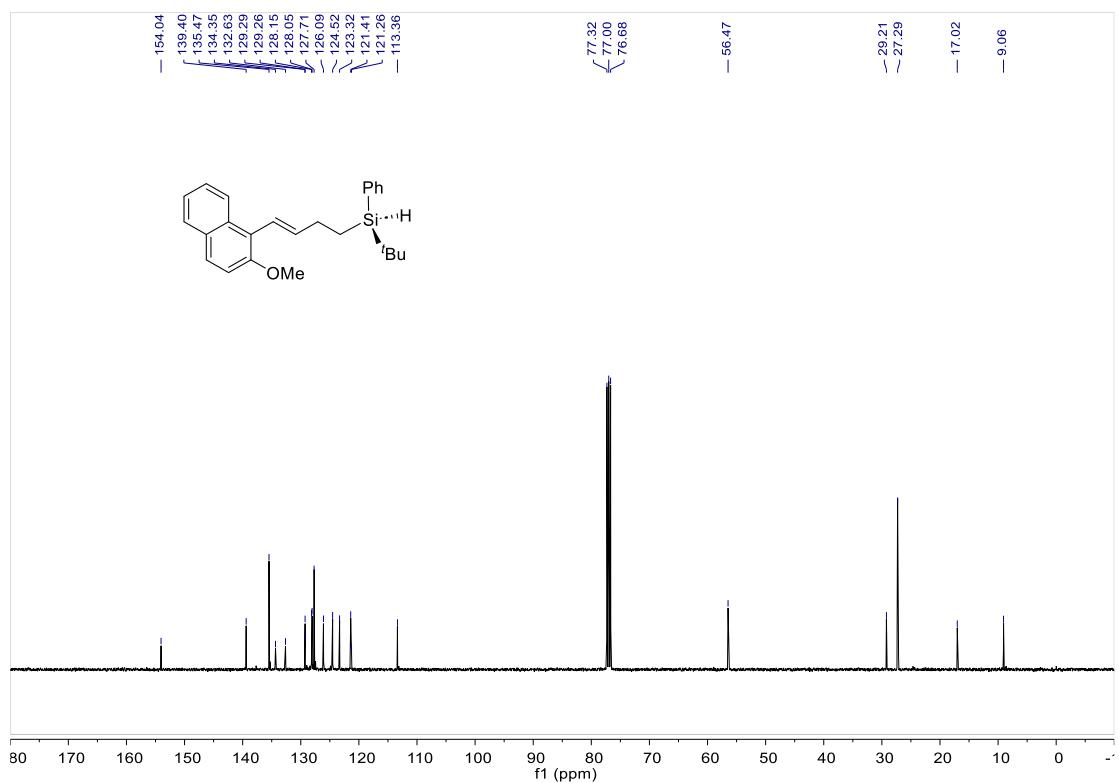
¹³C NMR (100 MHz, CDCl₃) spectrum of **20**



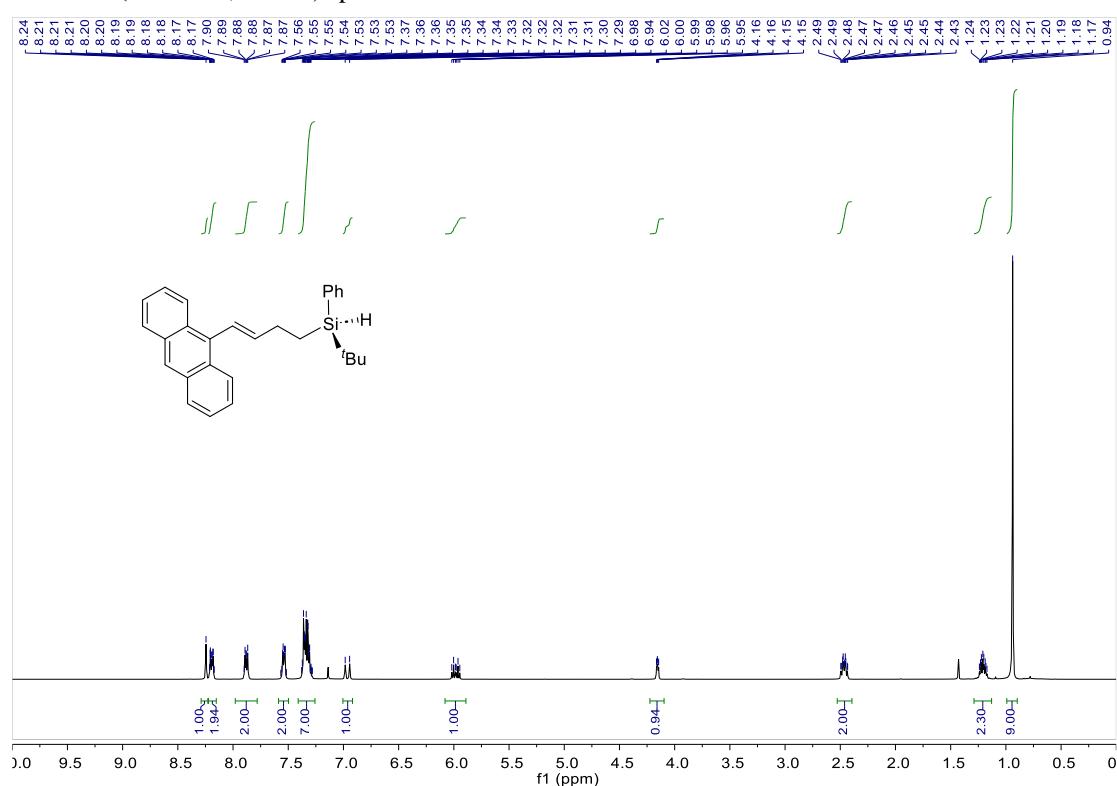
¹H NMR (400 MHz, CDCl₃) spectrum of **21**



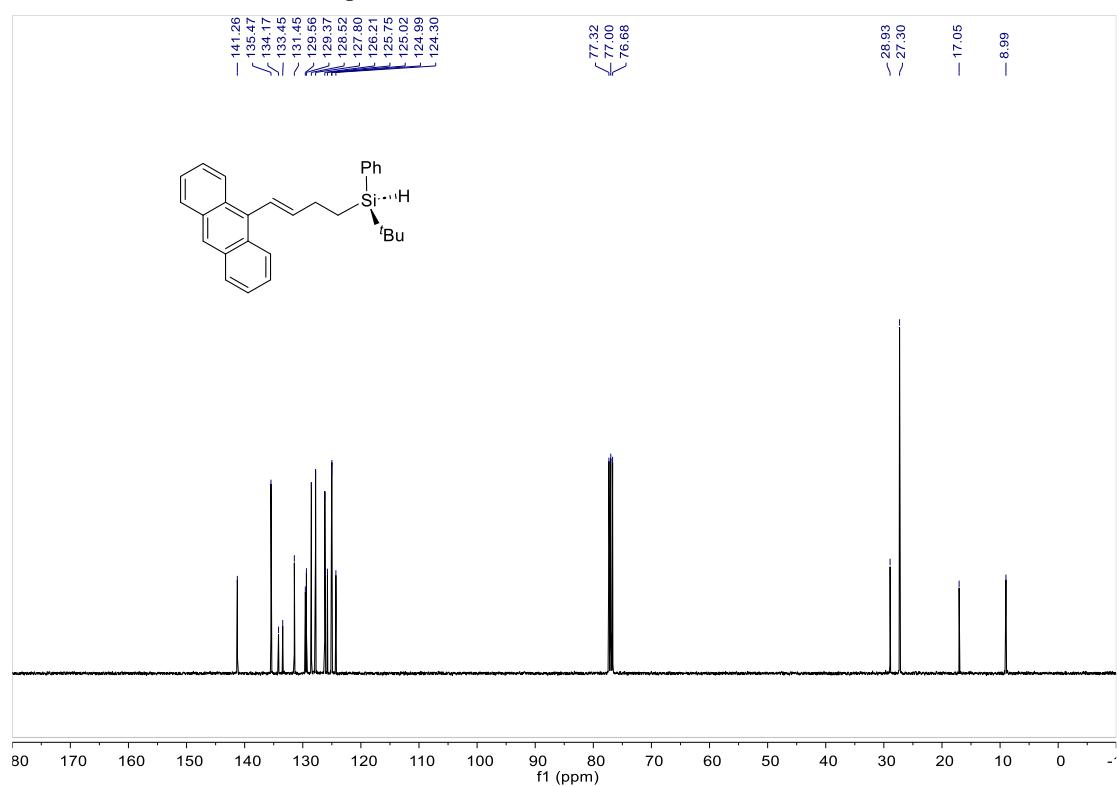
¹³C NMR (100 MHz, CDCl₃) spectrum of **21**



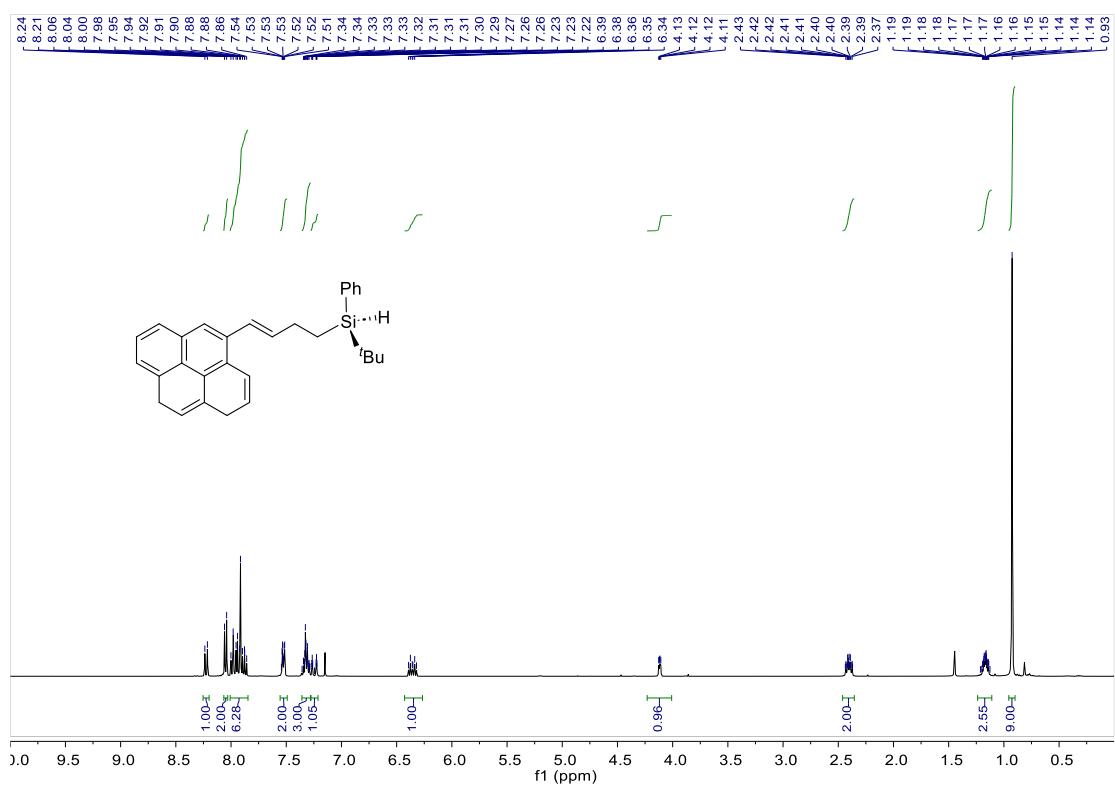
¹H NMR (400 MHz, CDCl₃) spectrum of 22



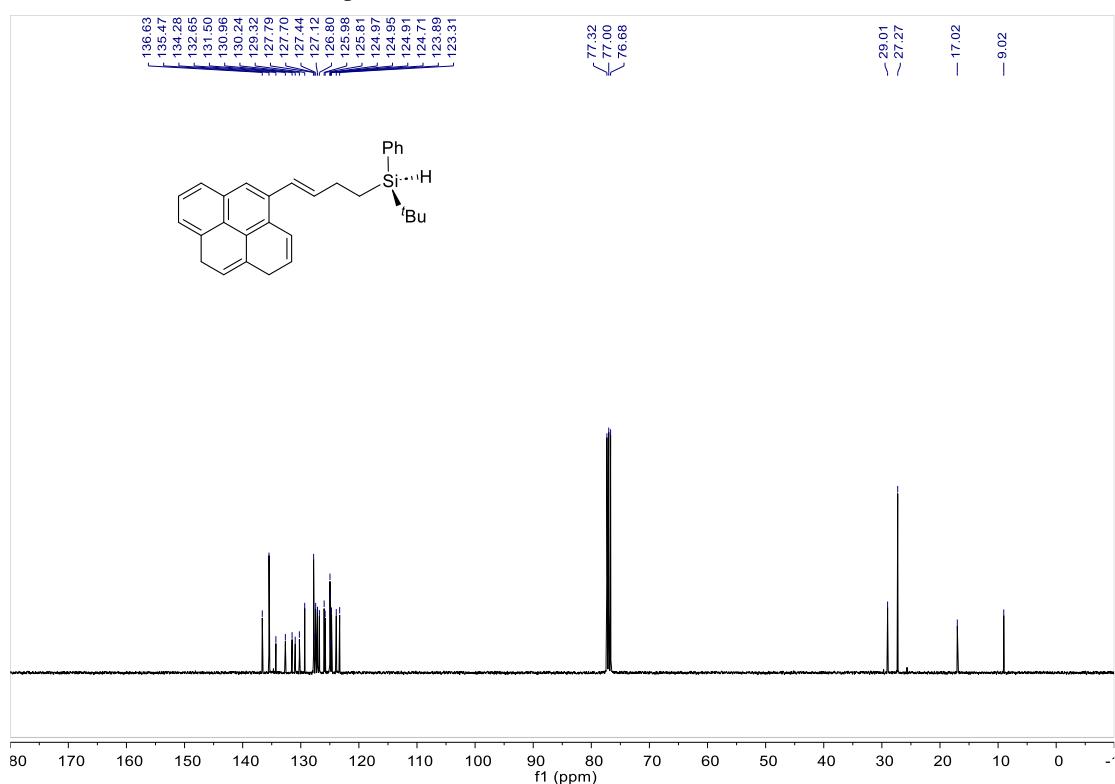
¹³C NMR (100 MHz, CDCl₃) spectrum of 22



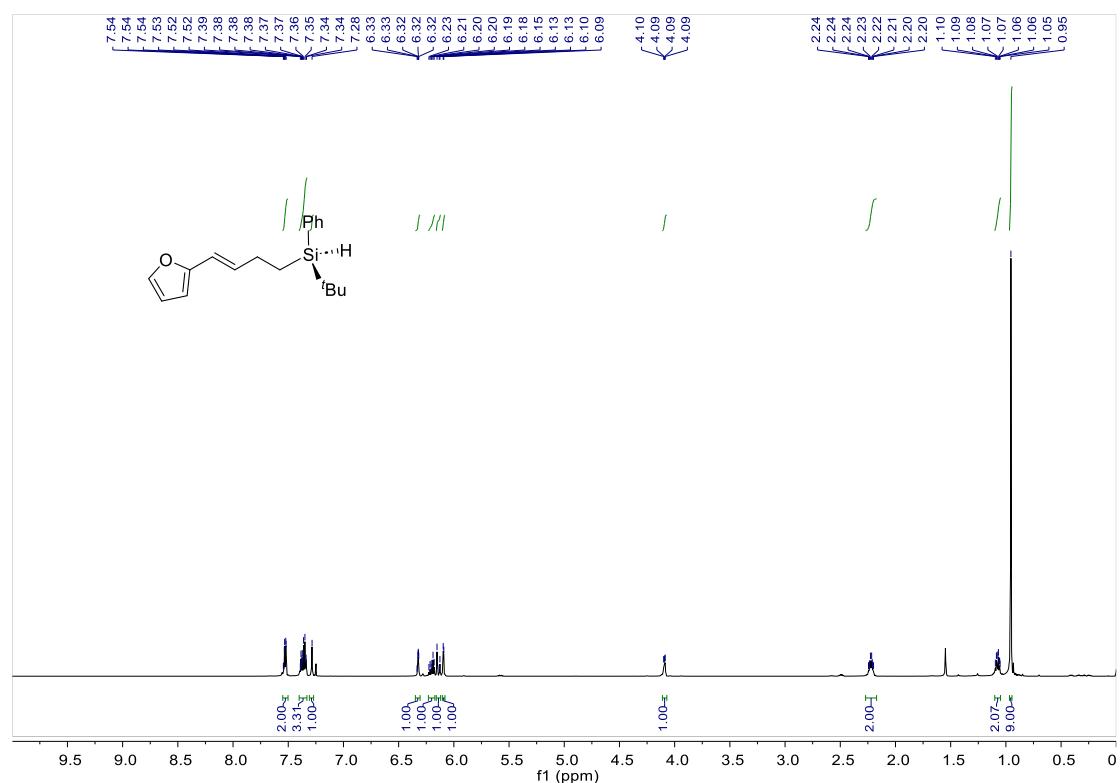
¹H NMR (400 MHz, CDCl₃) spectrum of **23**



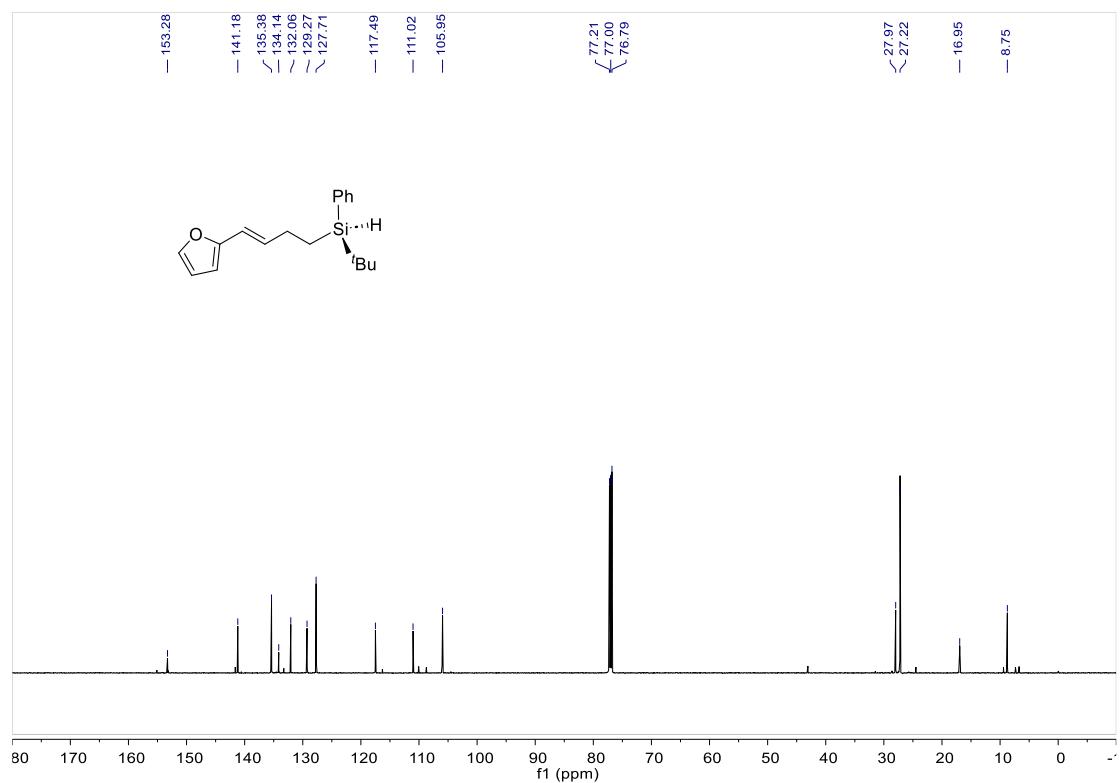
¹³C NMR (100 MHz, CDCl₃) spectrum of **23**



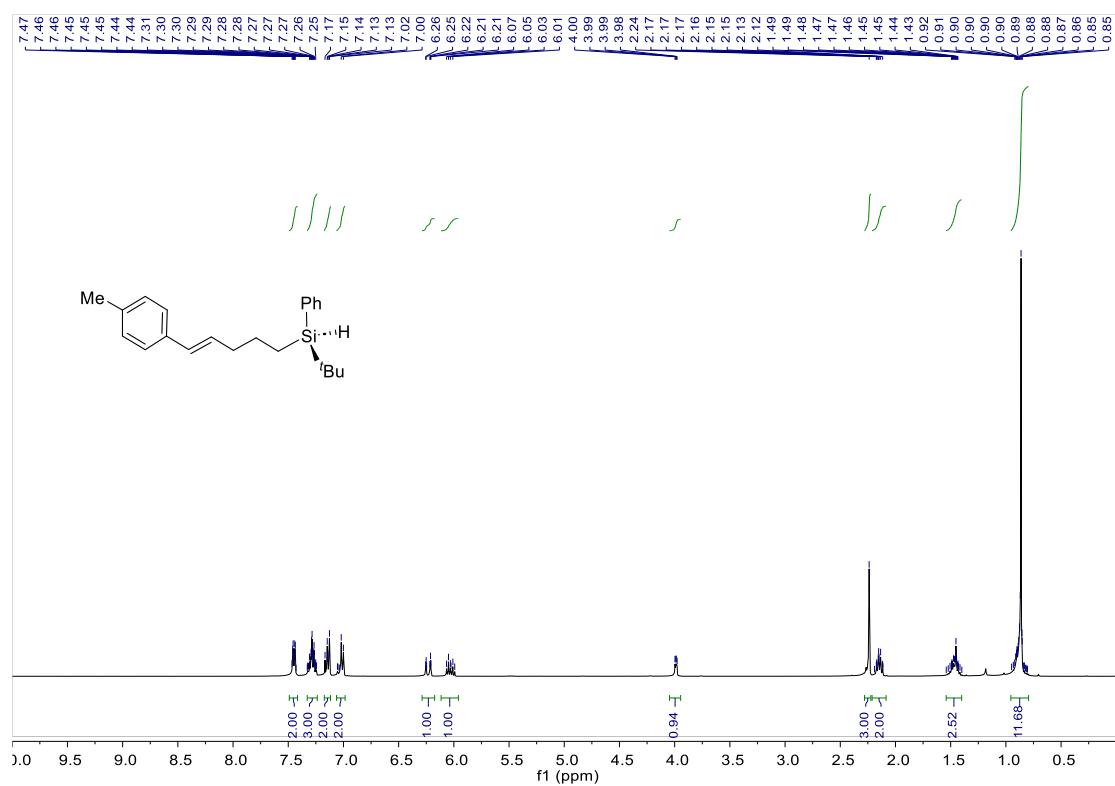
¹H NMR (600 MHz, CDCl₃) spectrum of **24**



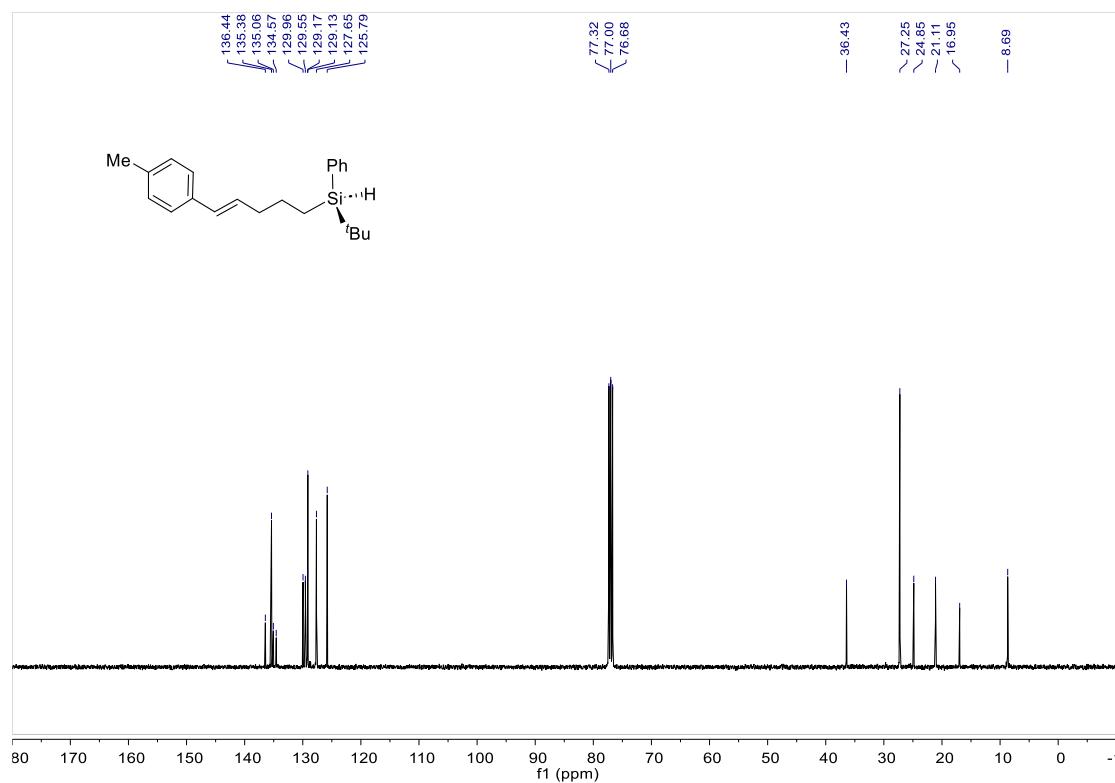
¹³C NMR (150 MHz, CDCl₃) spectrum of **24**



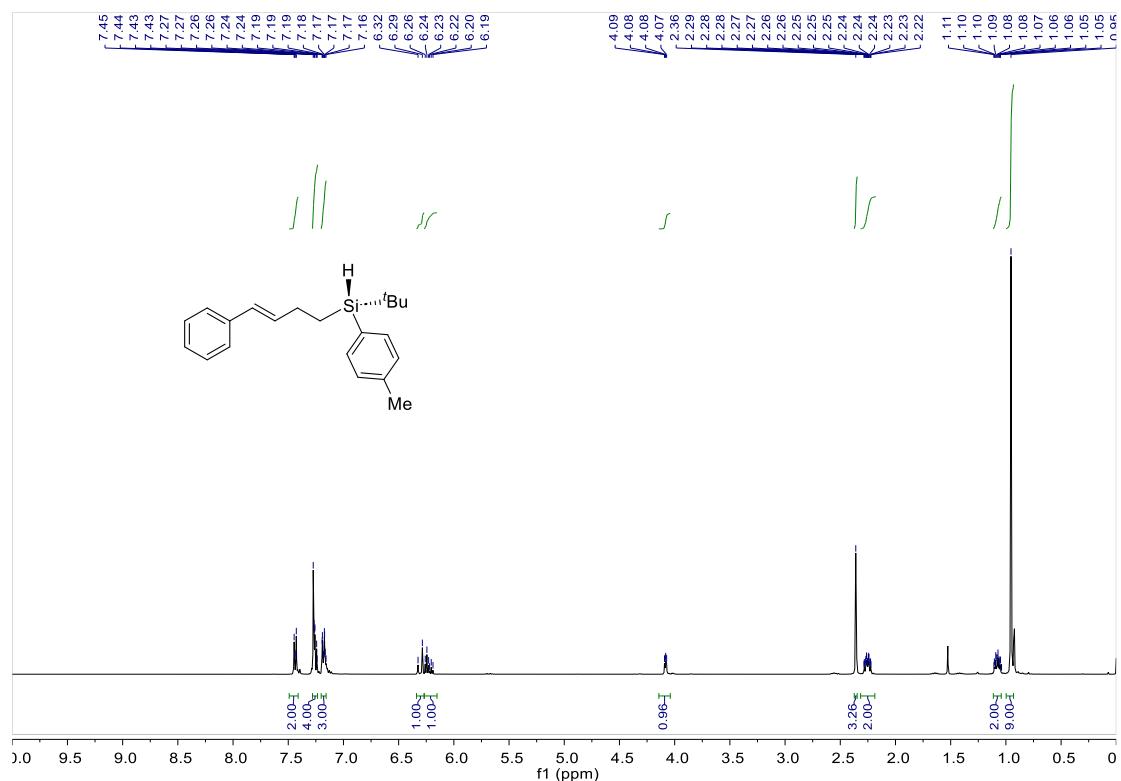
¹H NMR (400 MHz, CDCl₃) spectrum of **25**



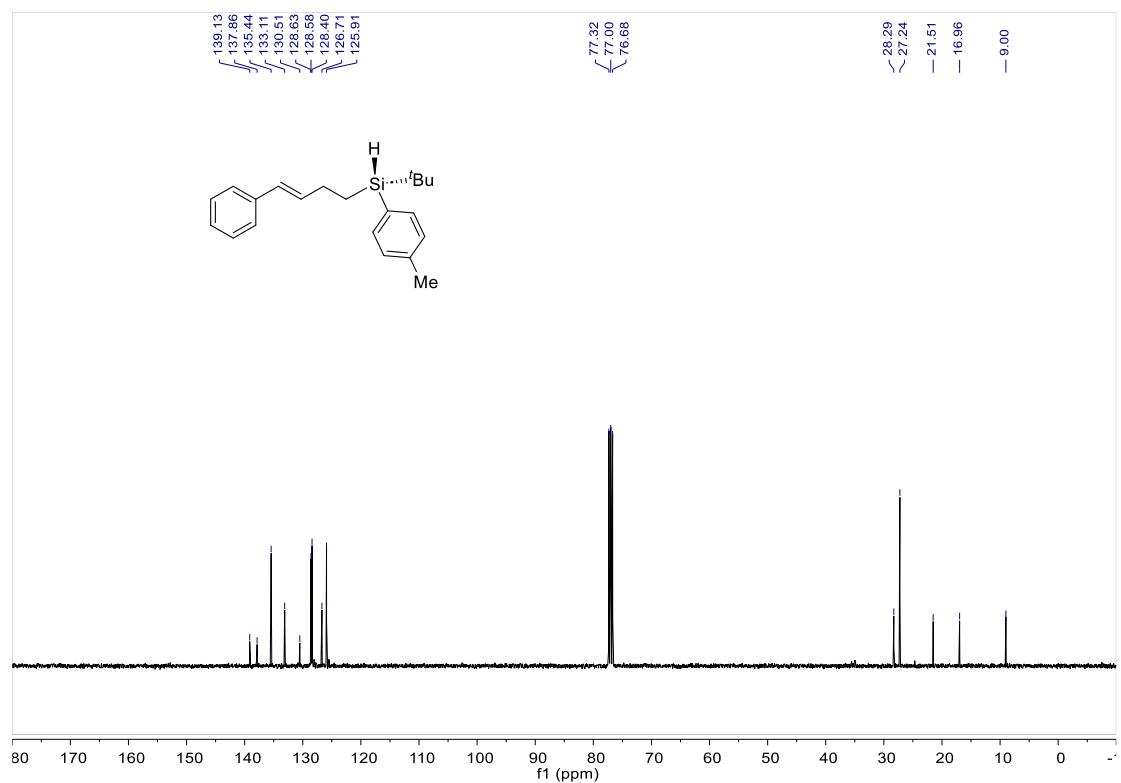
¹³C NMR (100 MHz, CDCl₃) spectrum of **25**



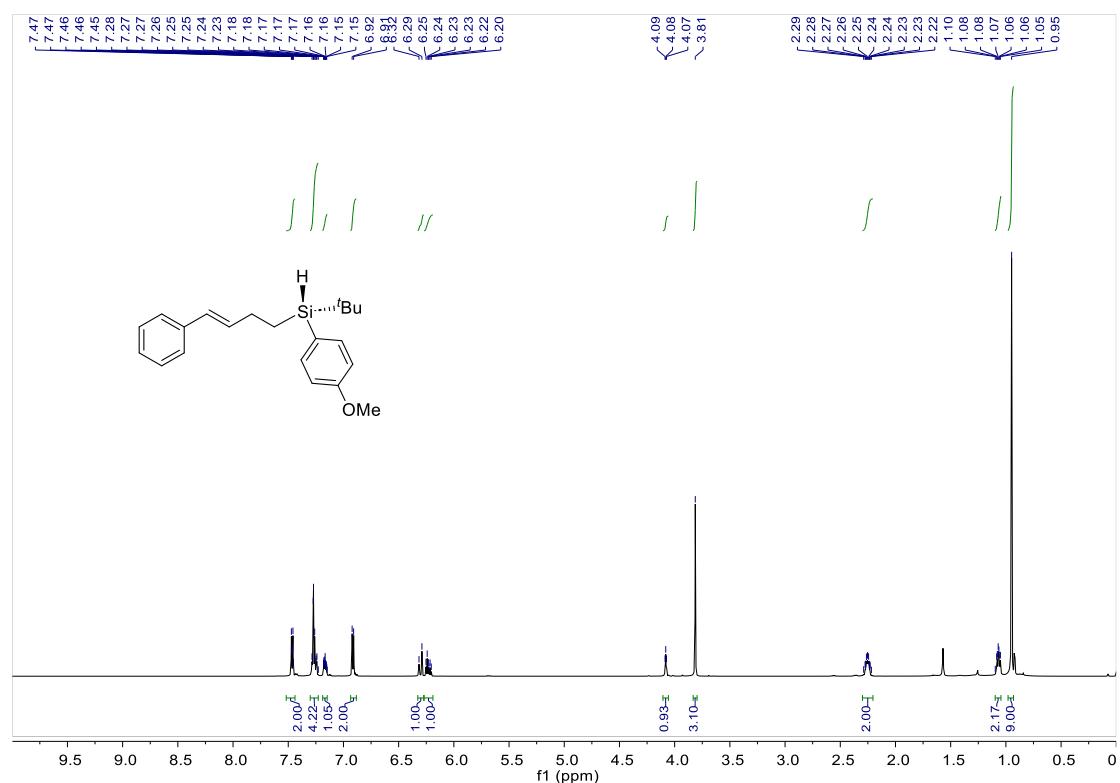
¹H NMR (400 MHz, CDCl₃) spectrum of **26**



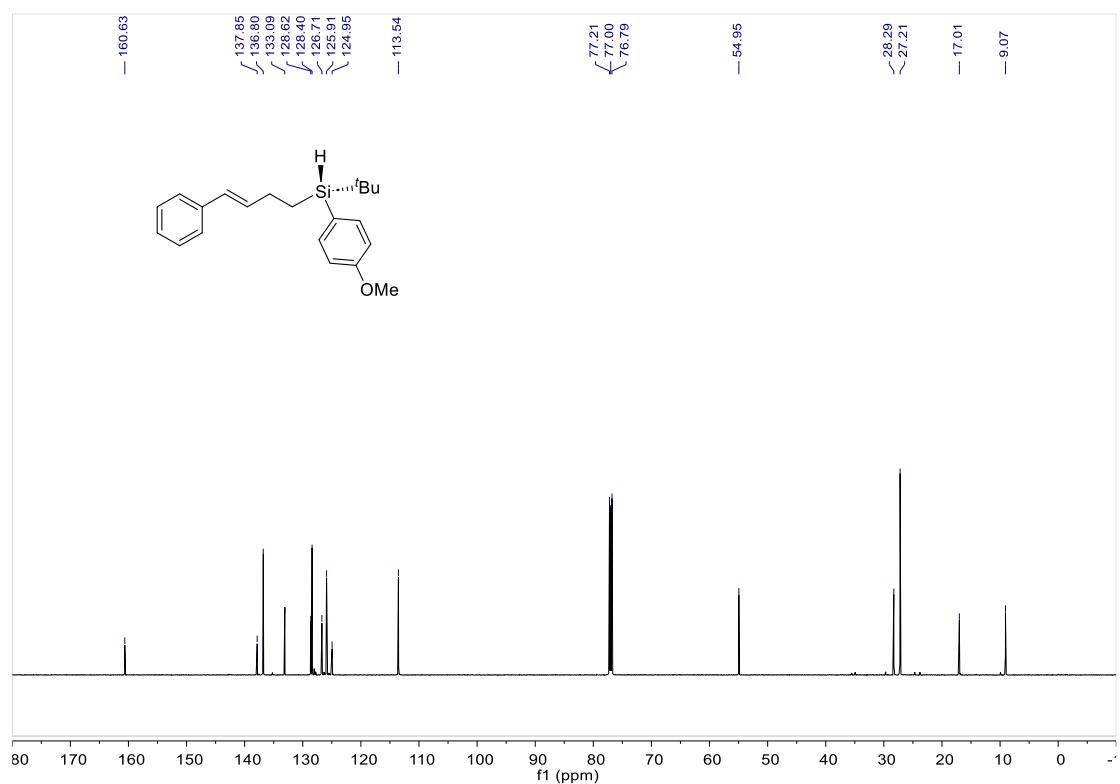
¹³C NMR (100 MHz, CDCl₃) spectrum of **26**



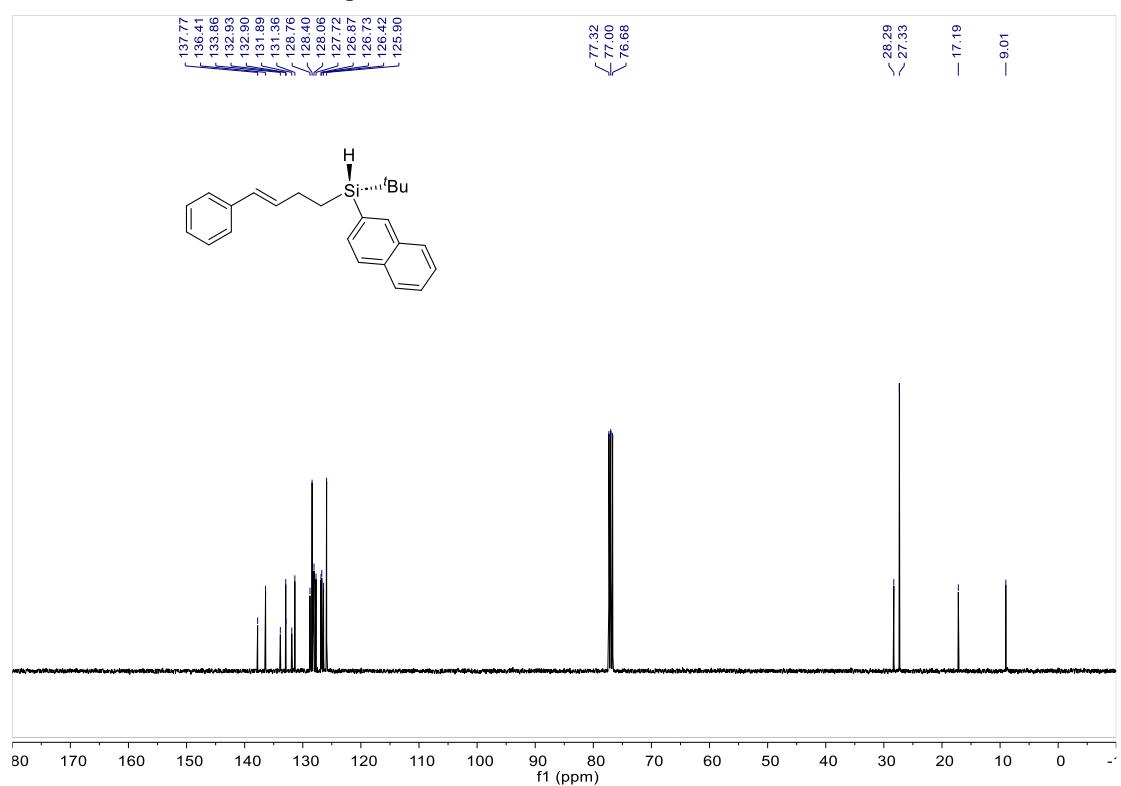
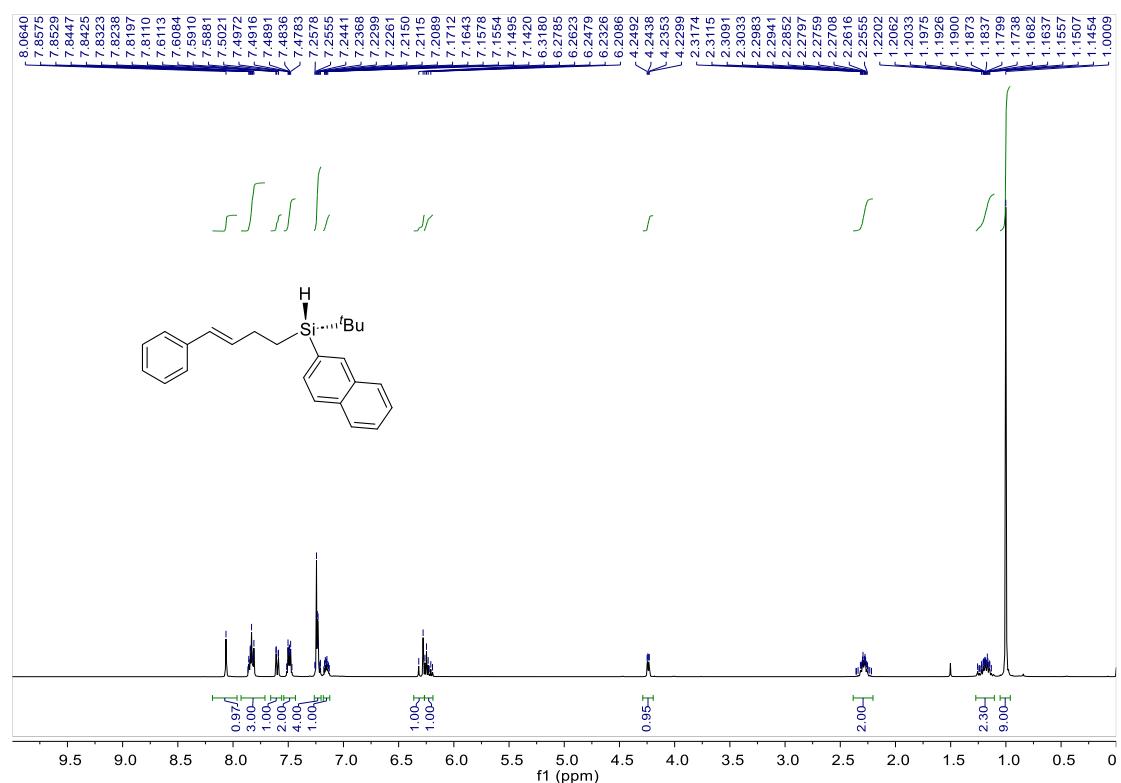
¹H NMR (600 MHz, CDCl₃) spectrum of 27



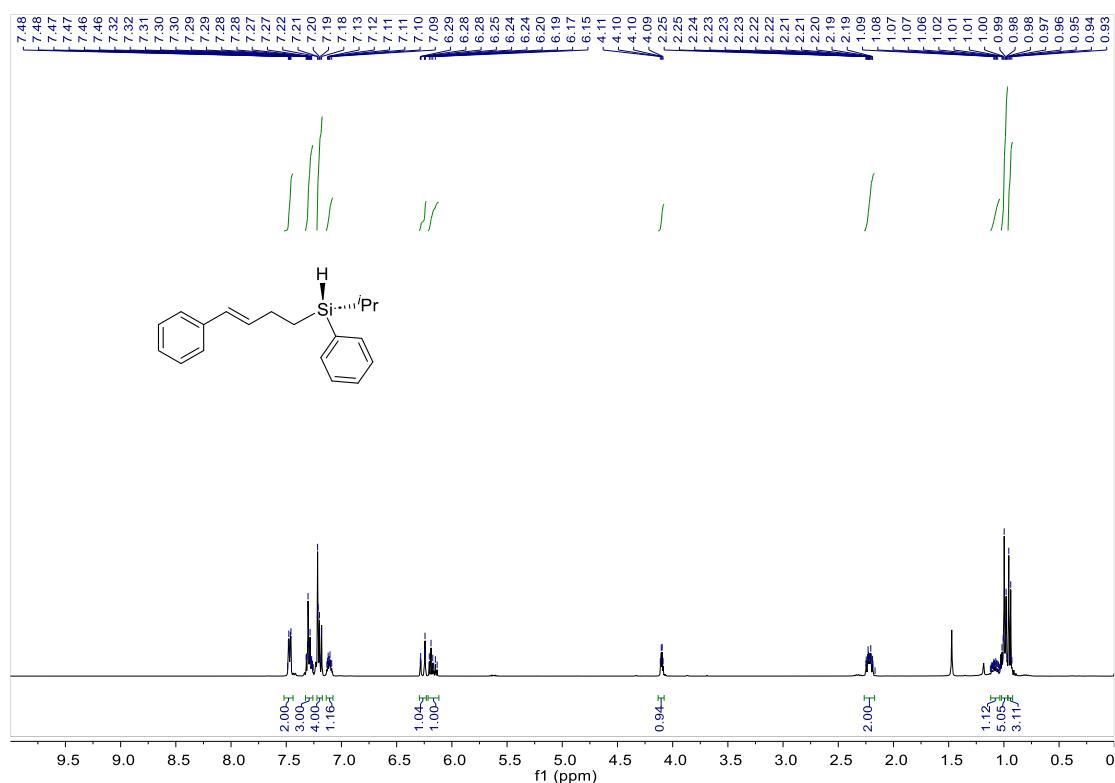
¹³C NMR (150 MHz, CDCl₃) spectrum of 27



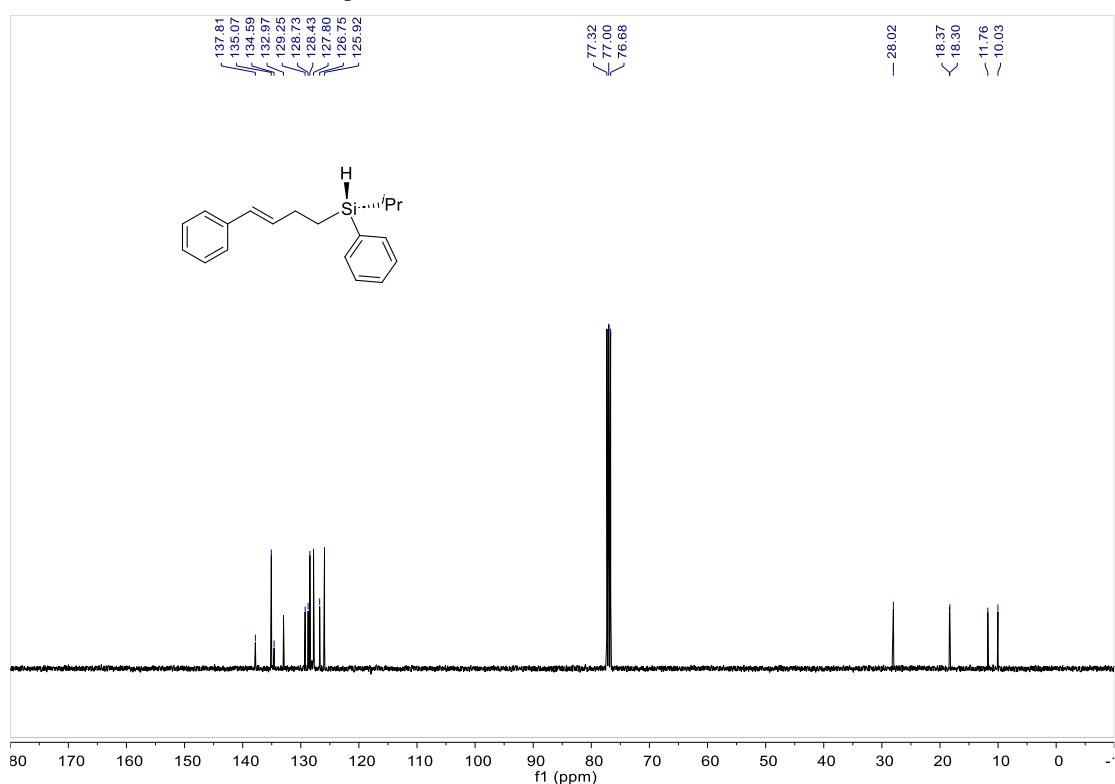
¹H NMR (400 MHz, CDCl₃) spectrum of 28



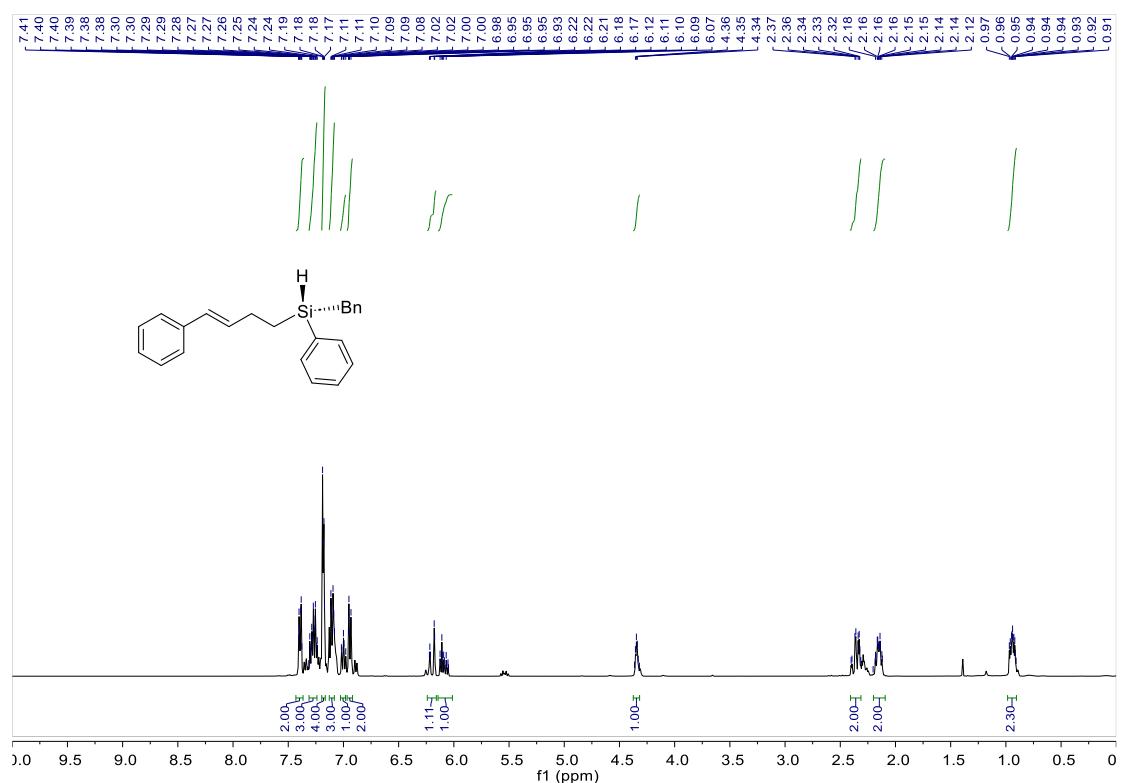
¹H NMR (400 MHz, CDCl₃) spectrum of **29**



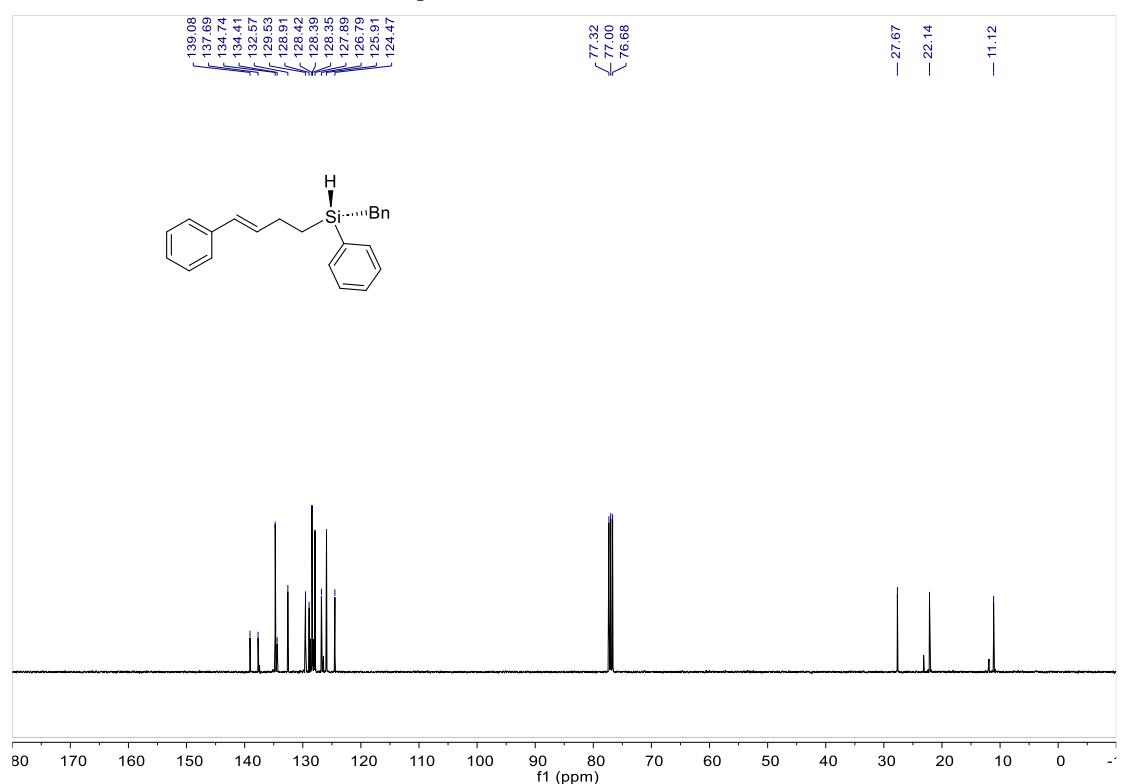
¹³C NMR (100 MHz, CDCl₃) spectrum of **29**



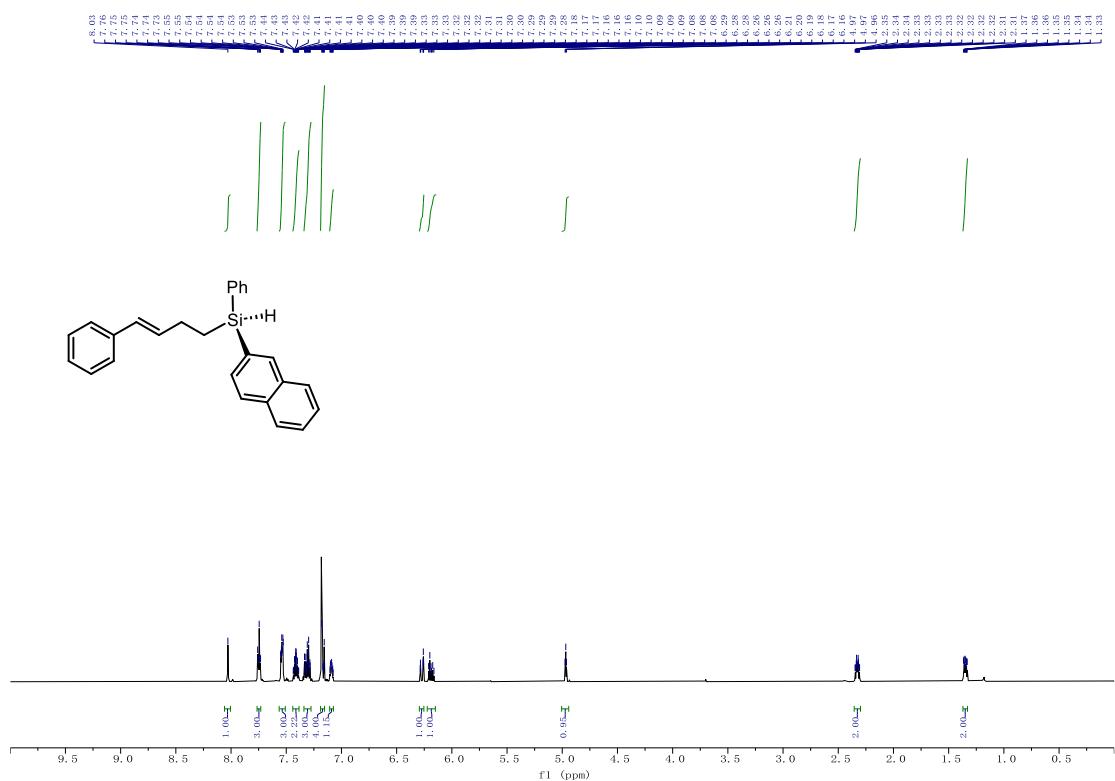
¹H NMR (400 MHz, CDCl₃) spectrum of **30**



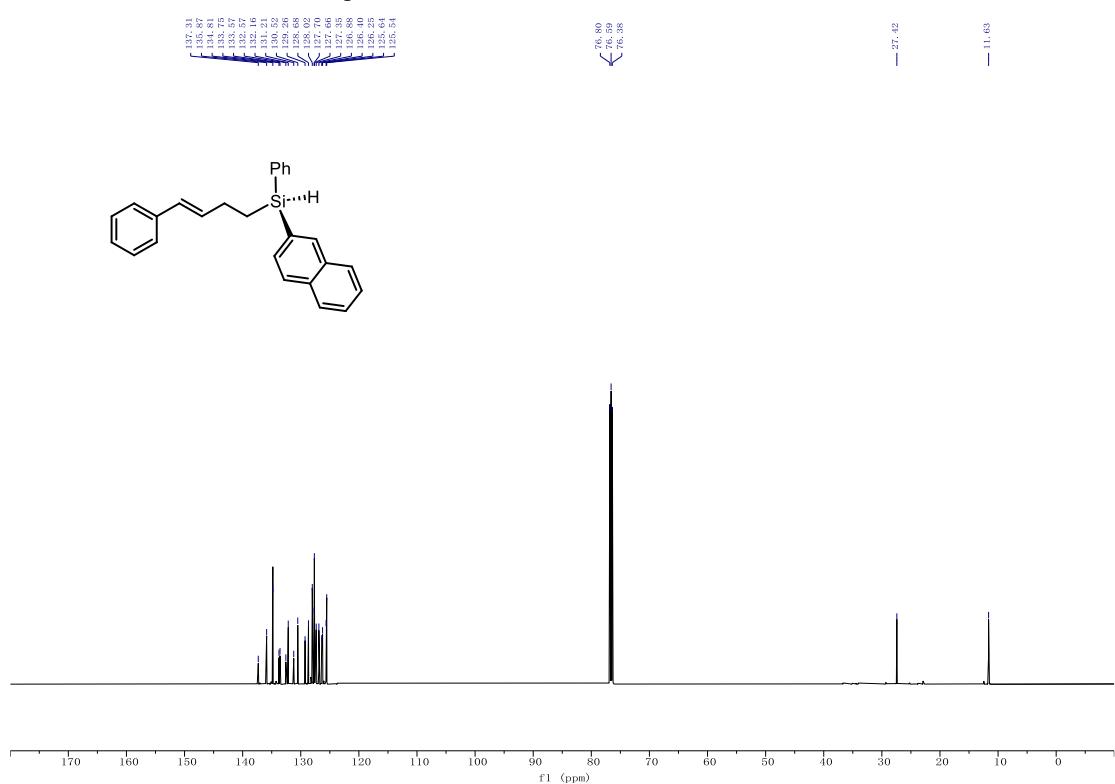
¹³C NMR (100 MHz, Chloroform-*d*) spectrum of **30**



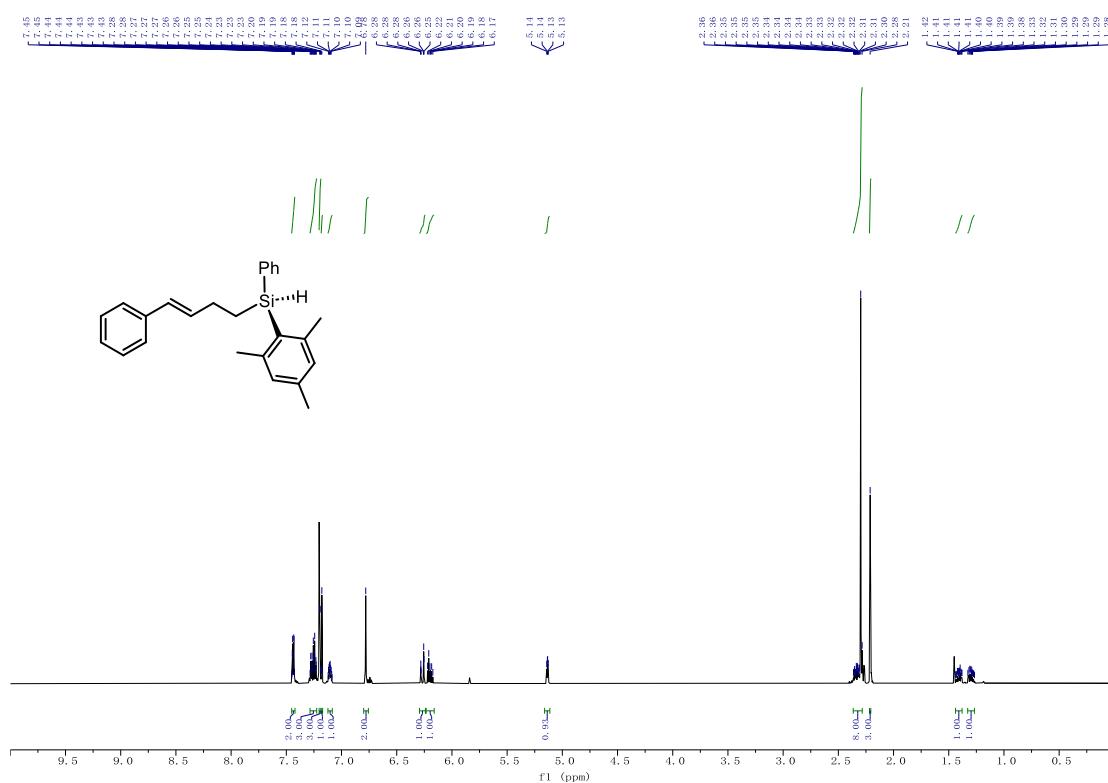
¹H NMR (600 MHz, CDCl₃) spectrum of 31



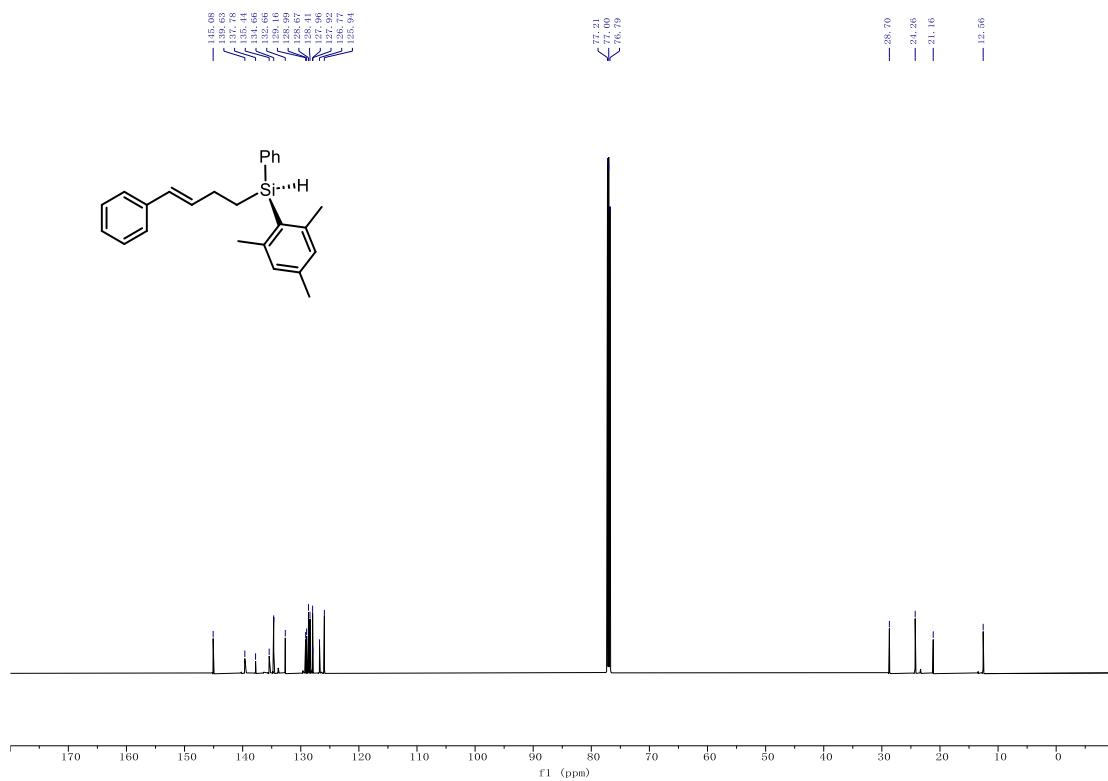
¹³C NMR (150 MHz, CDCl₃) spectrum of 31



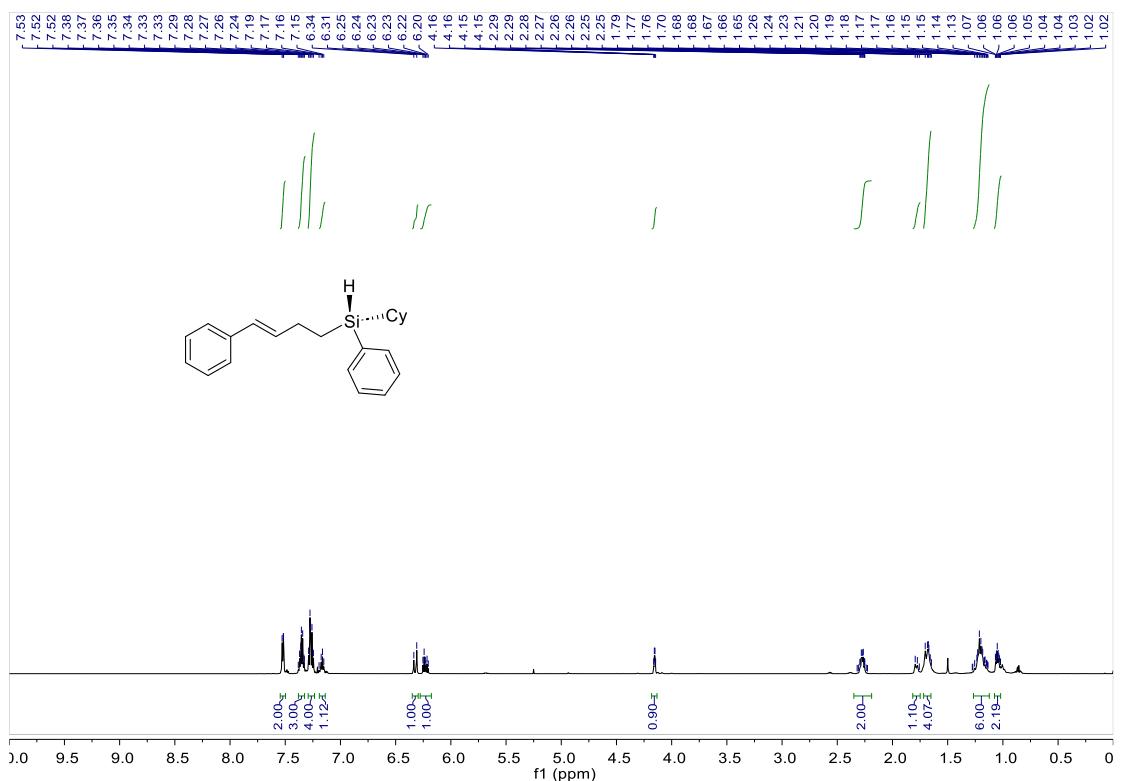
¹H NMR (600 MHz, CDCl₃) spectrum of **32**



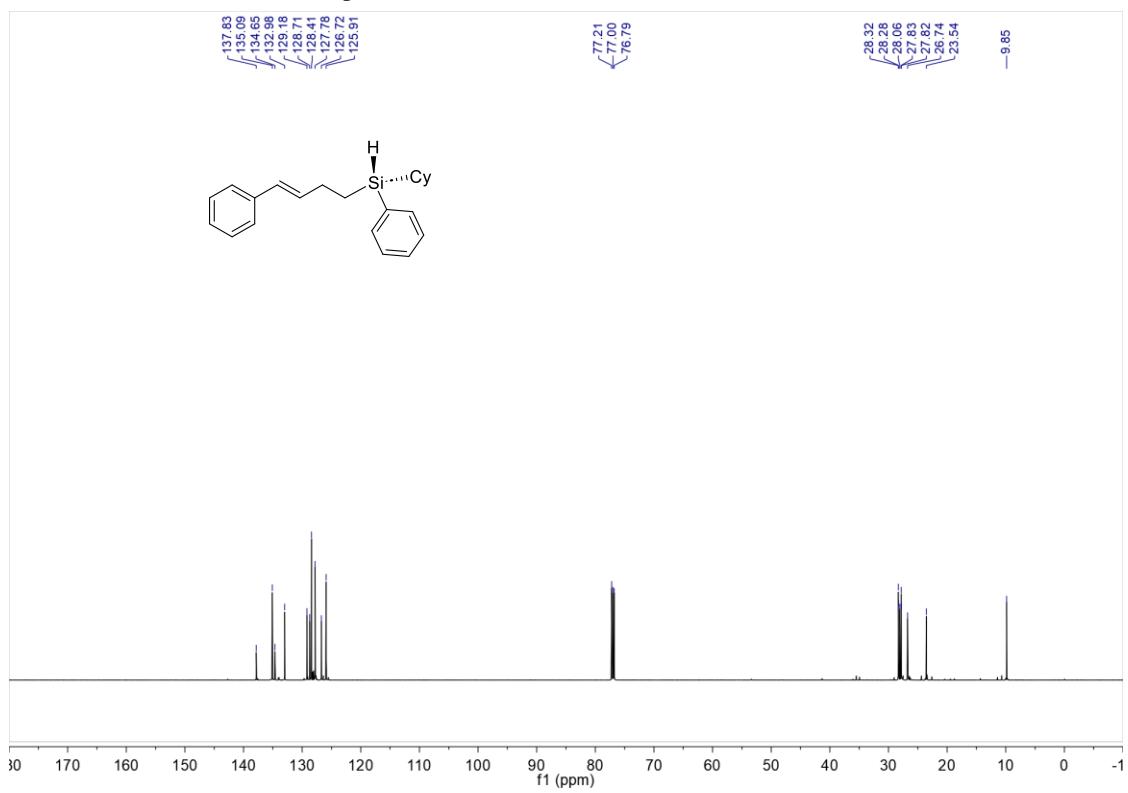
¹³C NMR (150 MHz, CDCl₃) spectrum of **32**



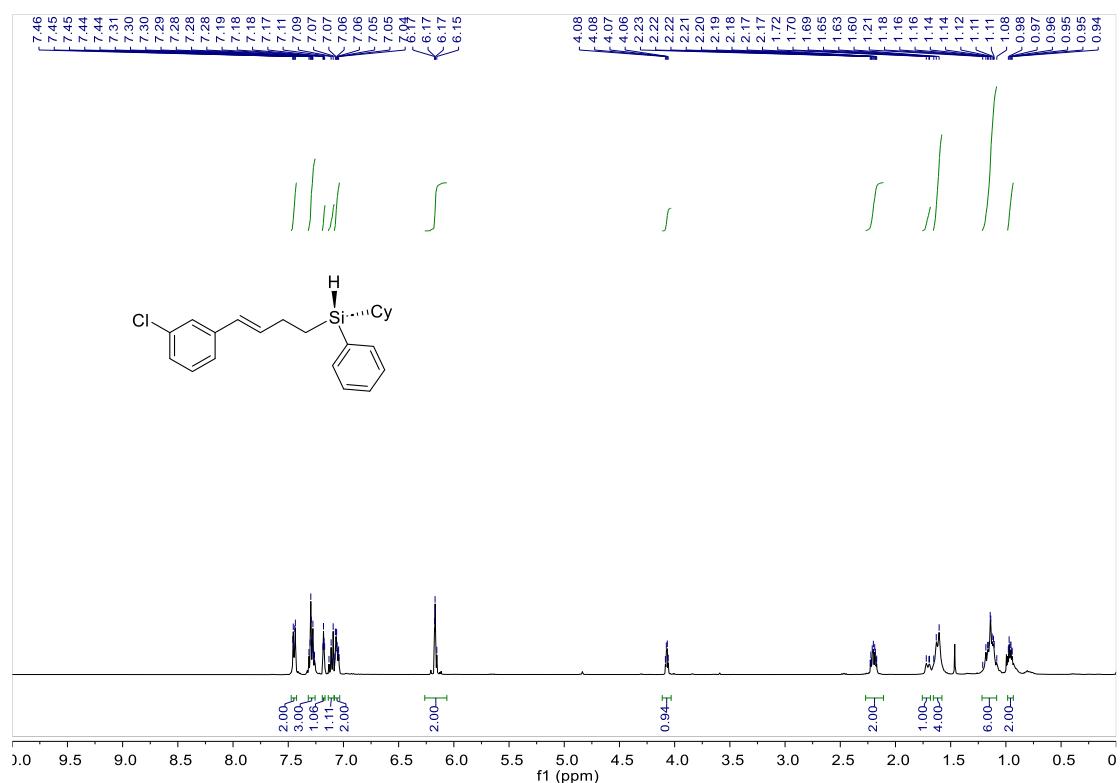
¹H NMR (600 MHz, CDCl₃) spectrum of **33**



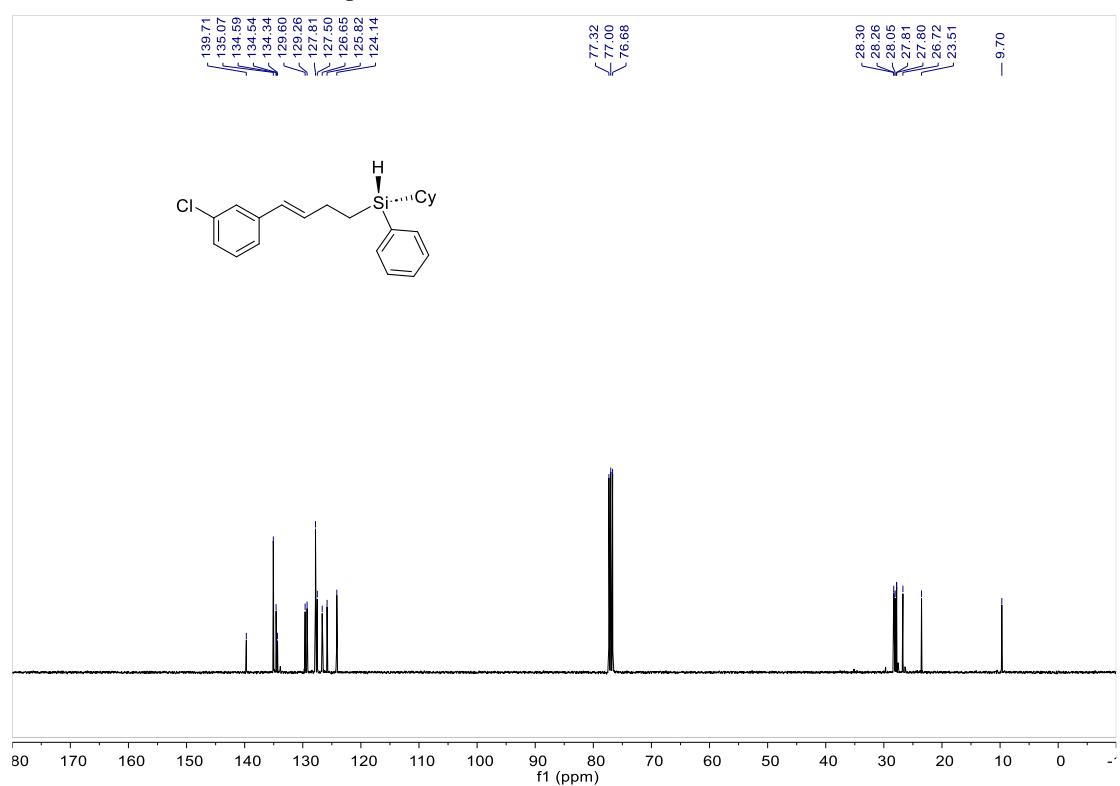
¹³C NMR (150 MHz, CDCl₃) spectrum of **33**



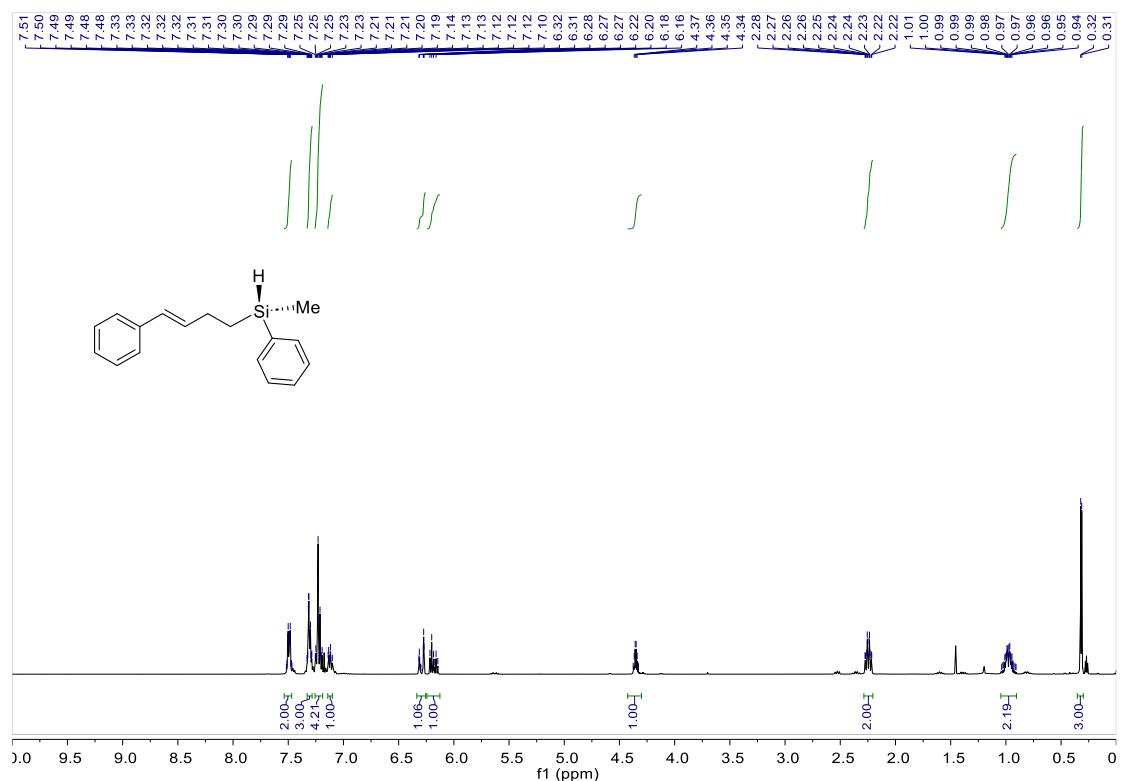
¹H NMR (400 MHz, CDCl₃) spectrum of **34**



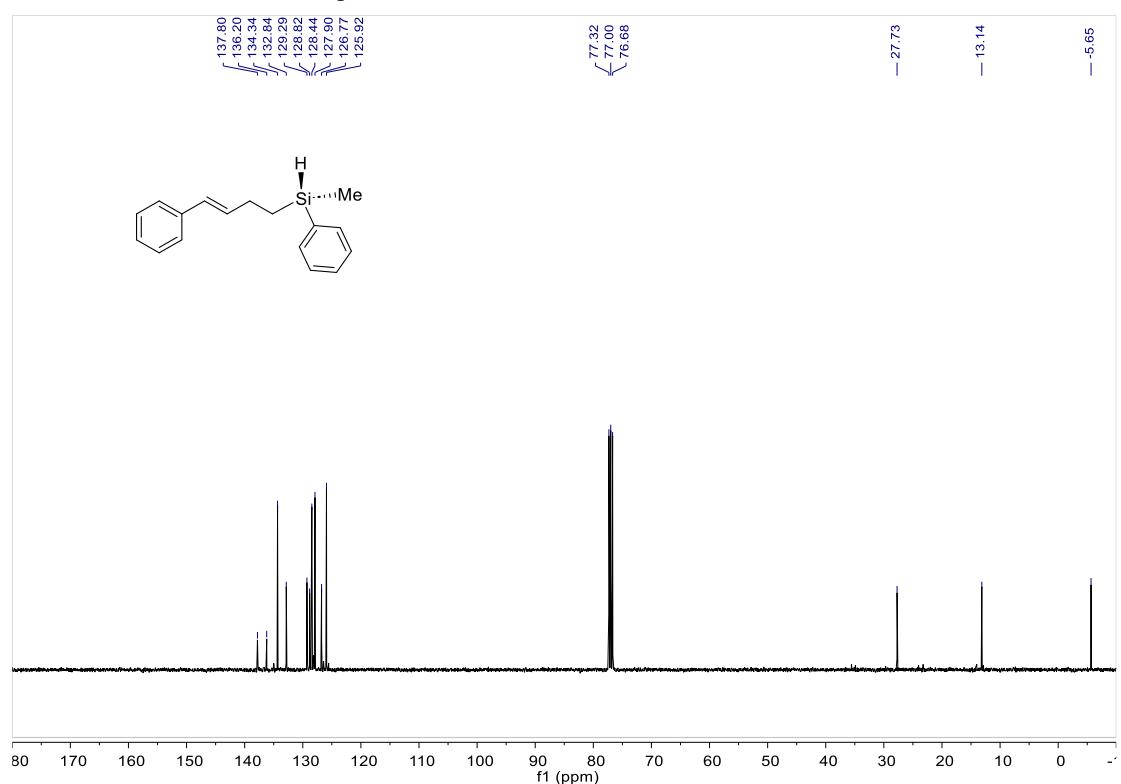
¹³C NMR (100 MHz, CDCl₃) spectrum of **34**



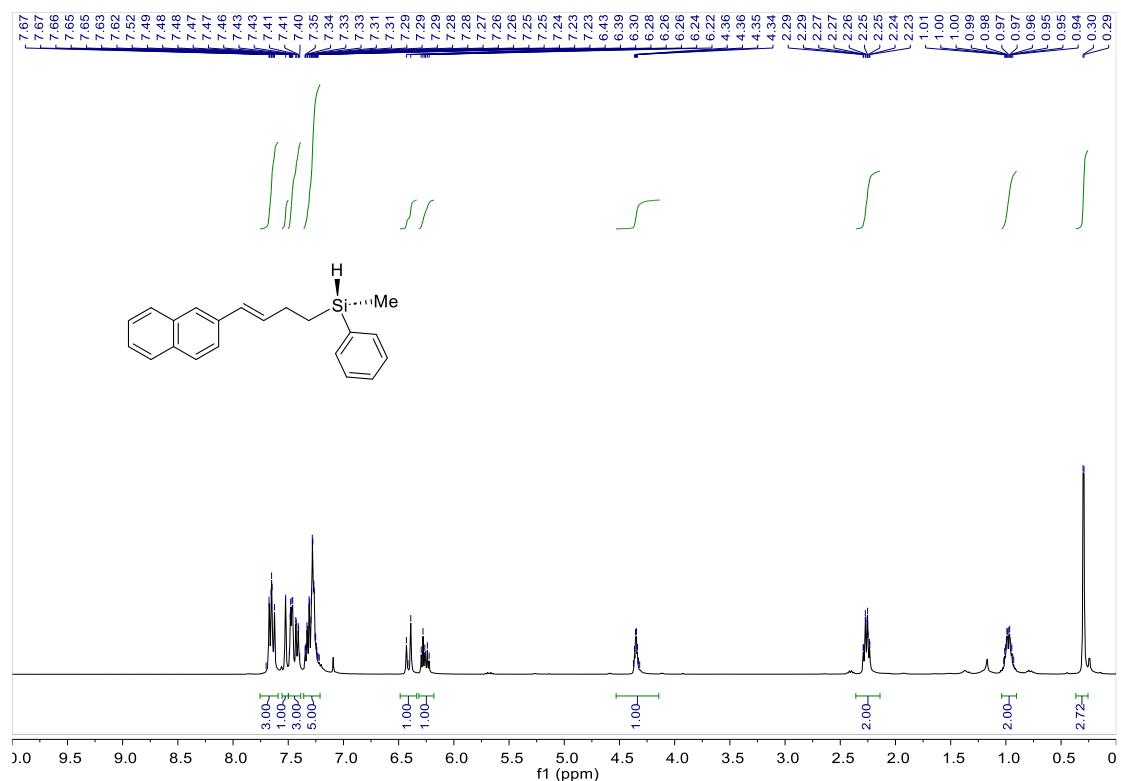
¹H NMR (400 MHz, CDCl₃) spectrum of **35**



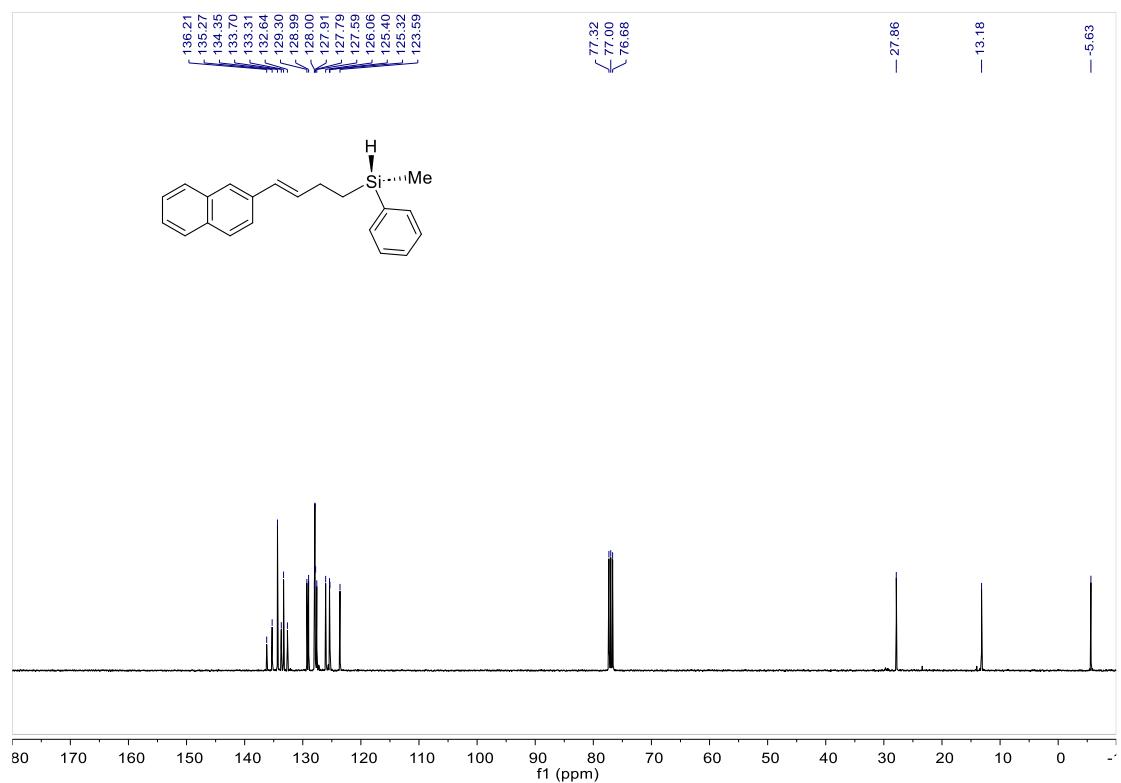
¹³C NMR (100 MHz, CDCl₃) spectrum of **35**



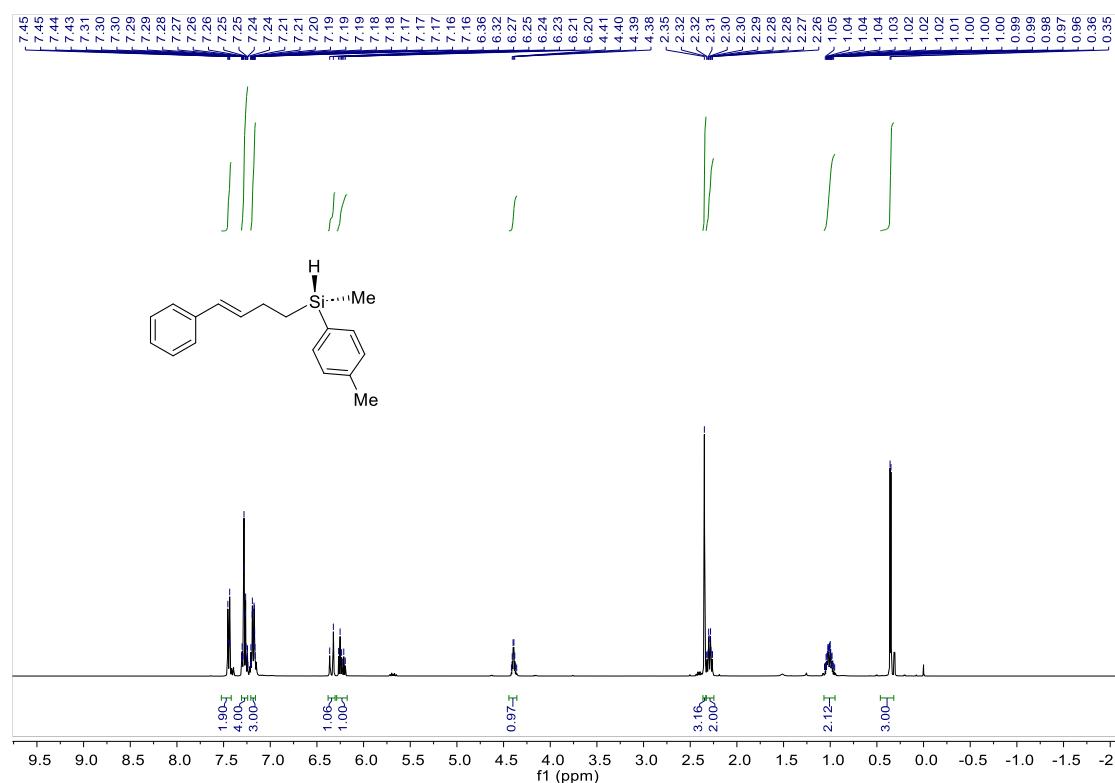
¹H NMR (400 MHz, CDCl₃) spectrum of **36**



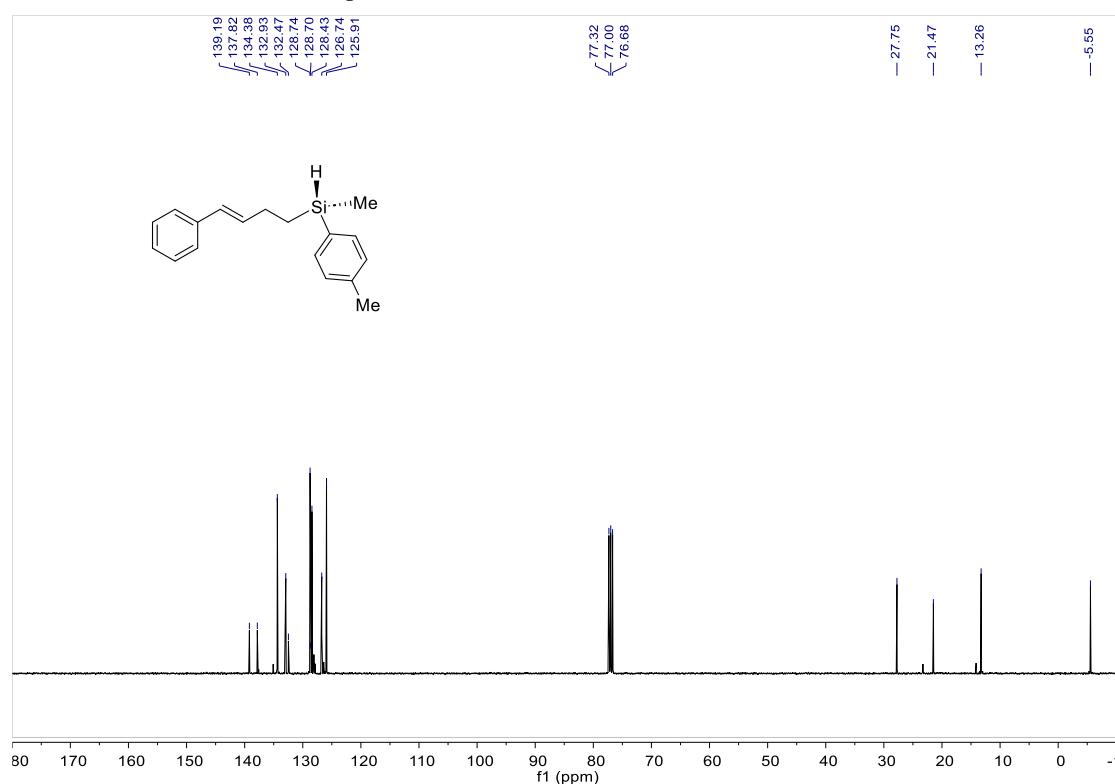
¹³C NMR (100 MHz, CDCl₃) spectrum of **36**



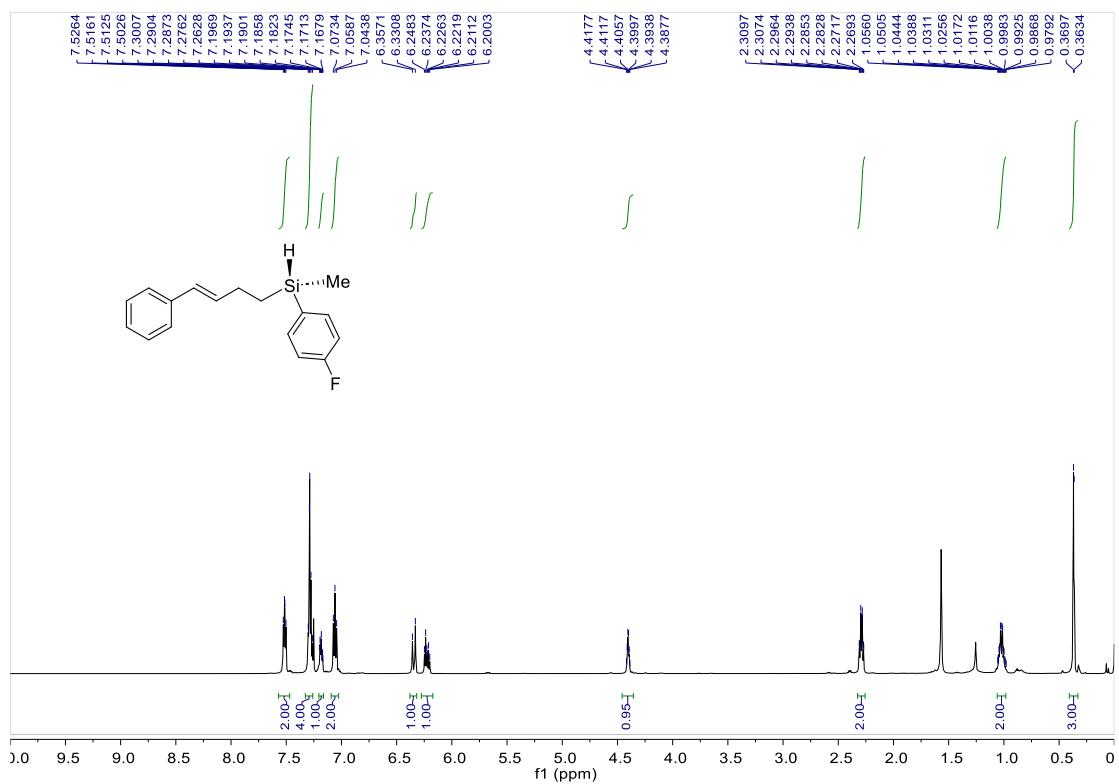
¹H NMR (400 MHz, CDCl₃) spectrum of **37**



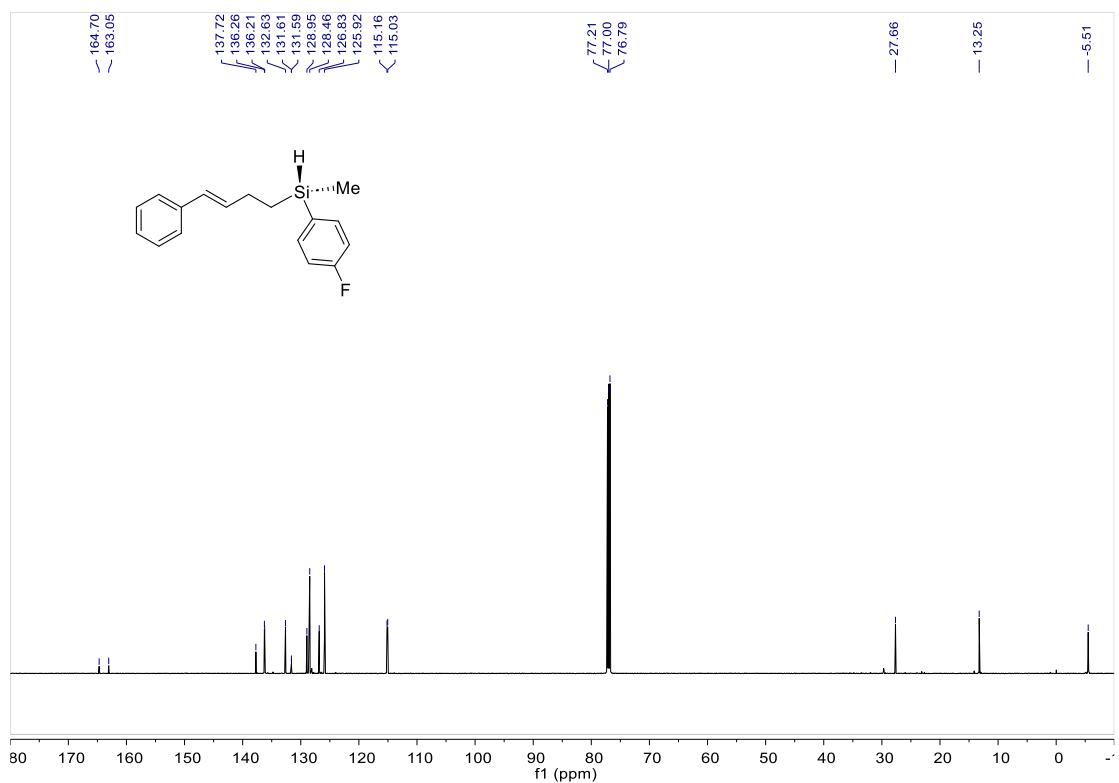
¹³C NMR (100 MHz, CDCl₃) spectrum of **37**



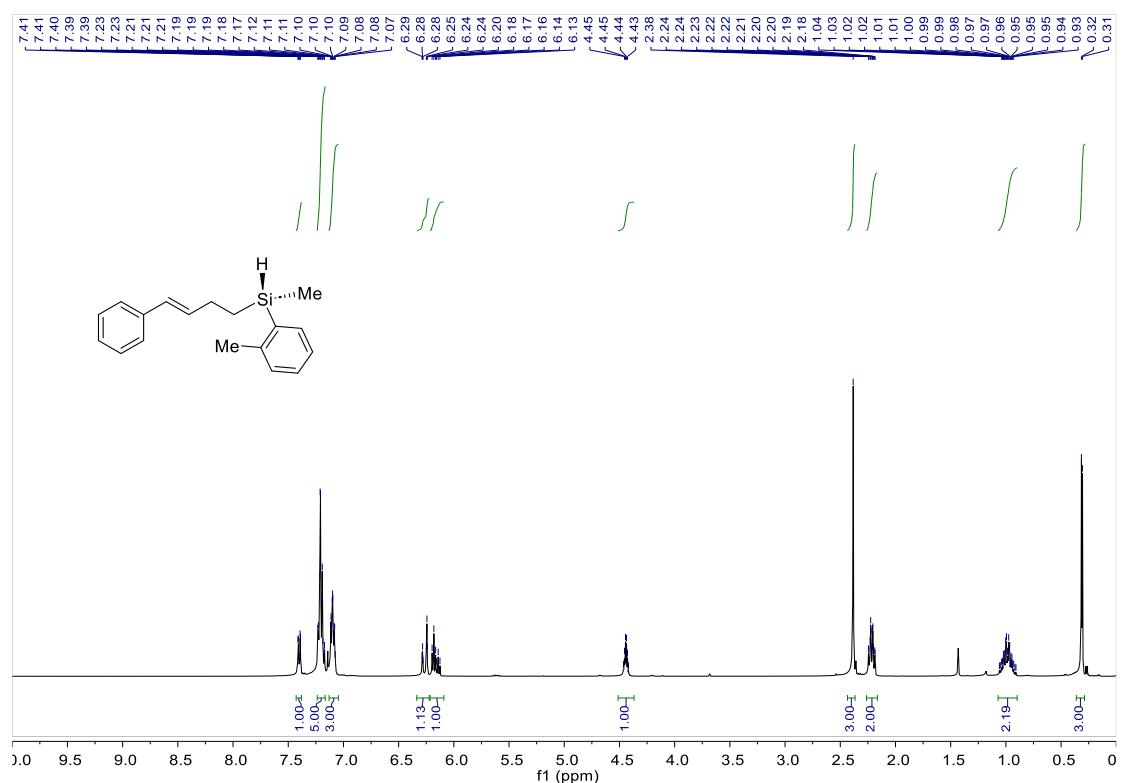
¹H NMR (600 MHz, CDCl₃) spectrum of **38**



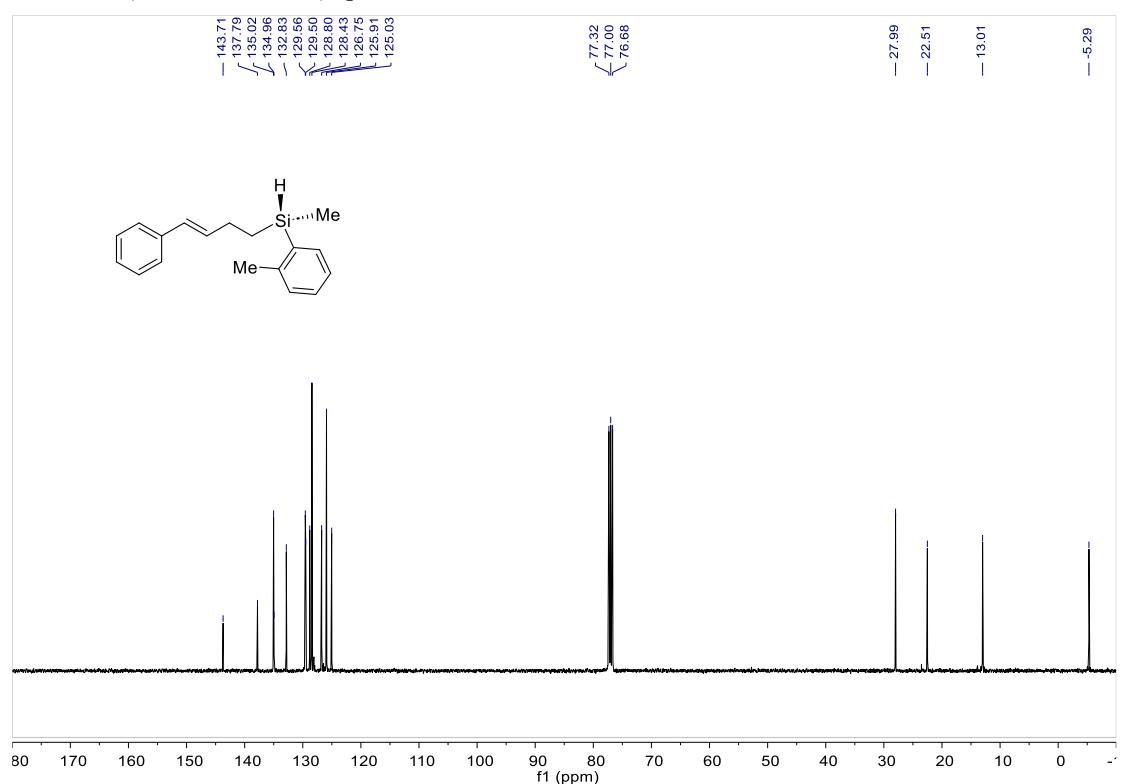
¹³C NMR (150 MHz, CDCl₃) spectrum of **38**



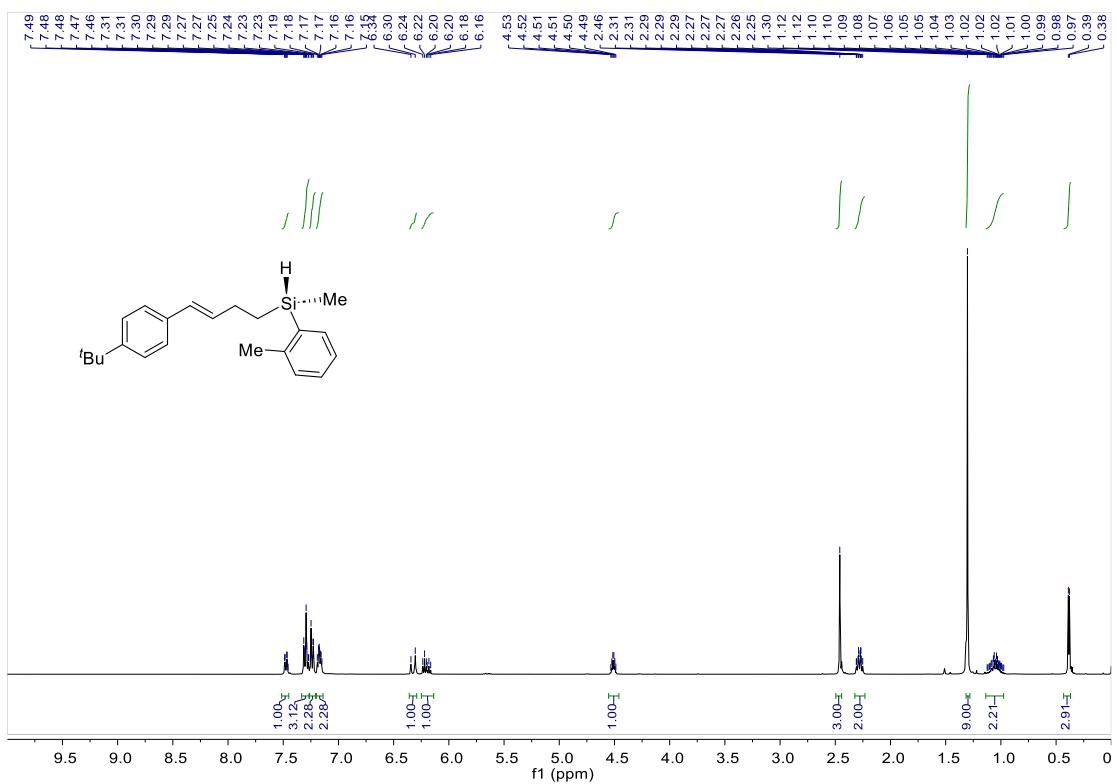
¹H NMR (400 MHz, CDCl₃) spectrum of **39**



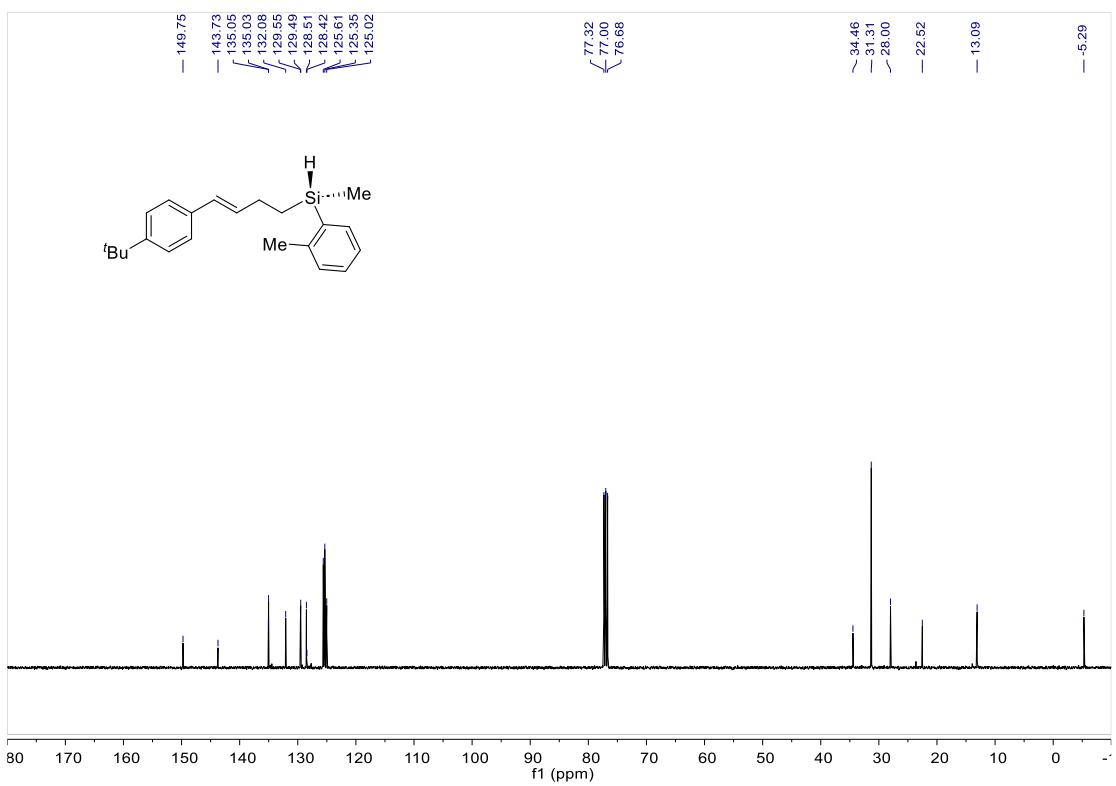
¹³C NMR (100 MHz, CDCl₃) spectrum of **39**



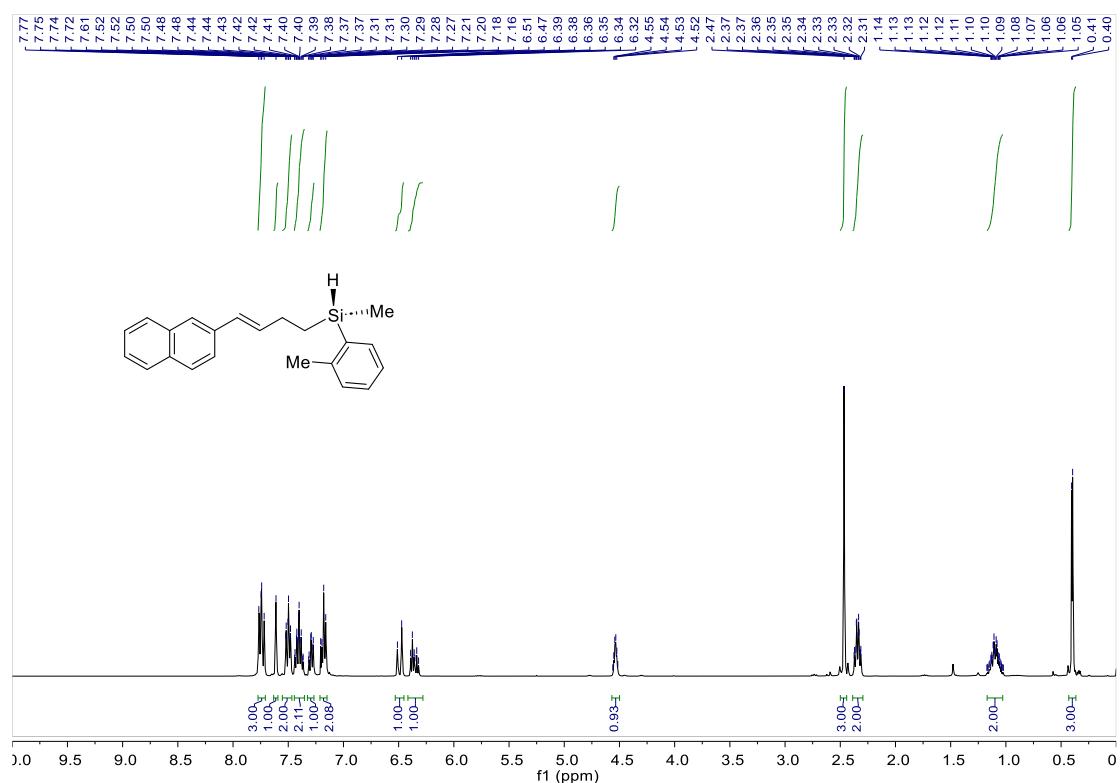
¹H NMR (400 MHz, CDCl₃) spectrum of **40**



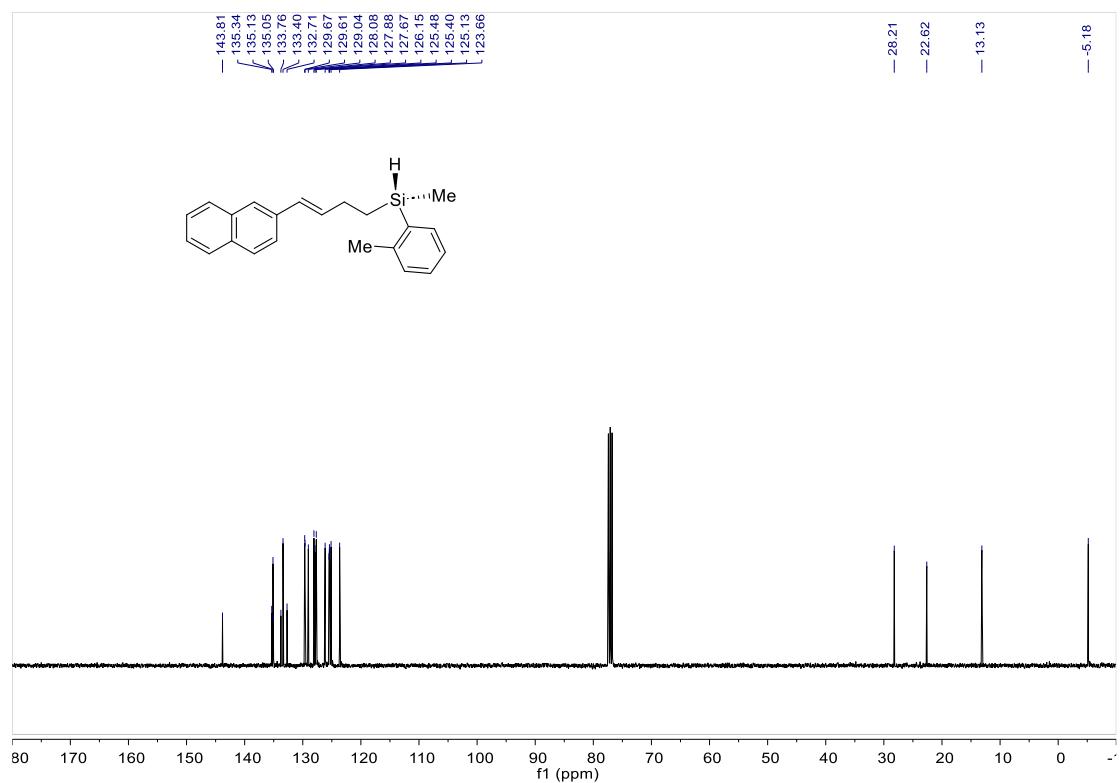
¹³C NMR (100 MHz, CDCl₃) spectrum of **40**



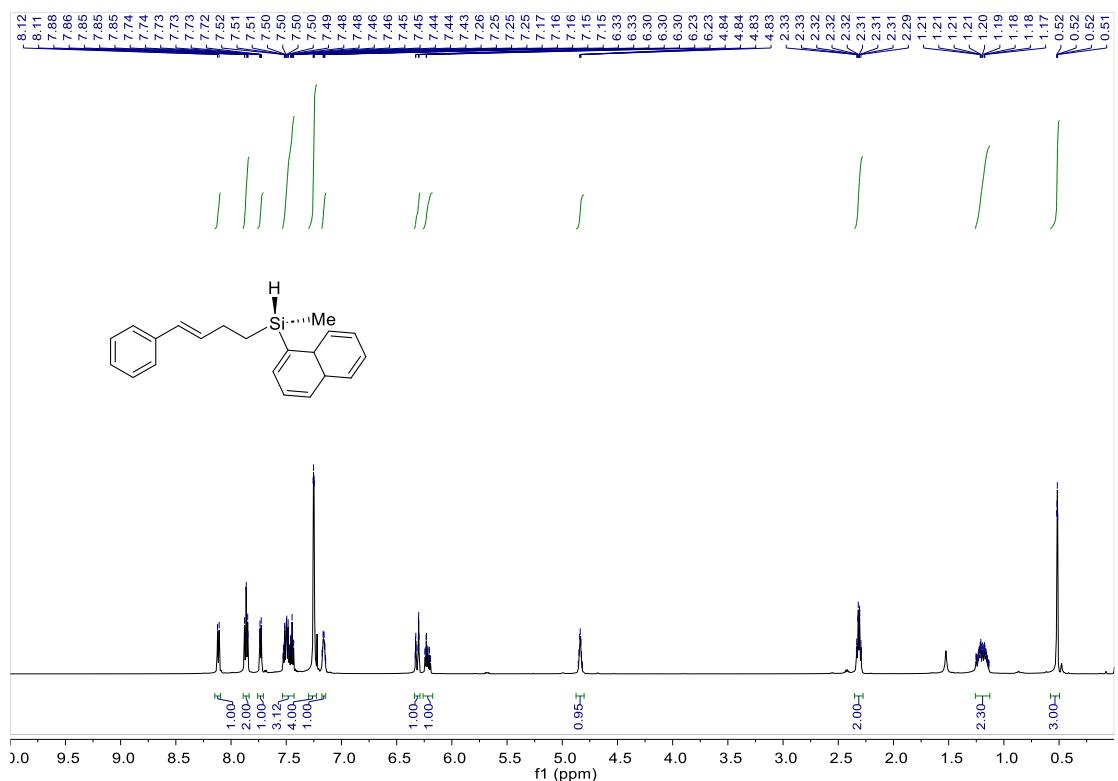
¹H NMR (400 MHz, CDCl₃) spectrum of **41**



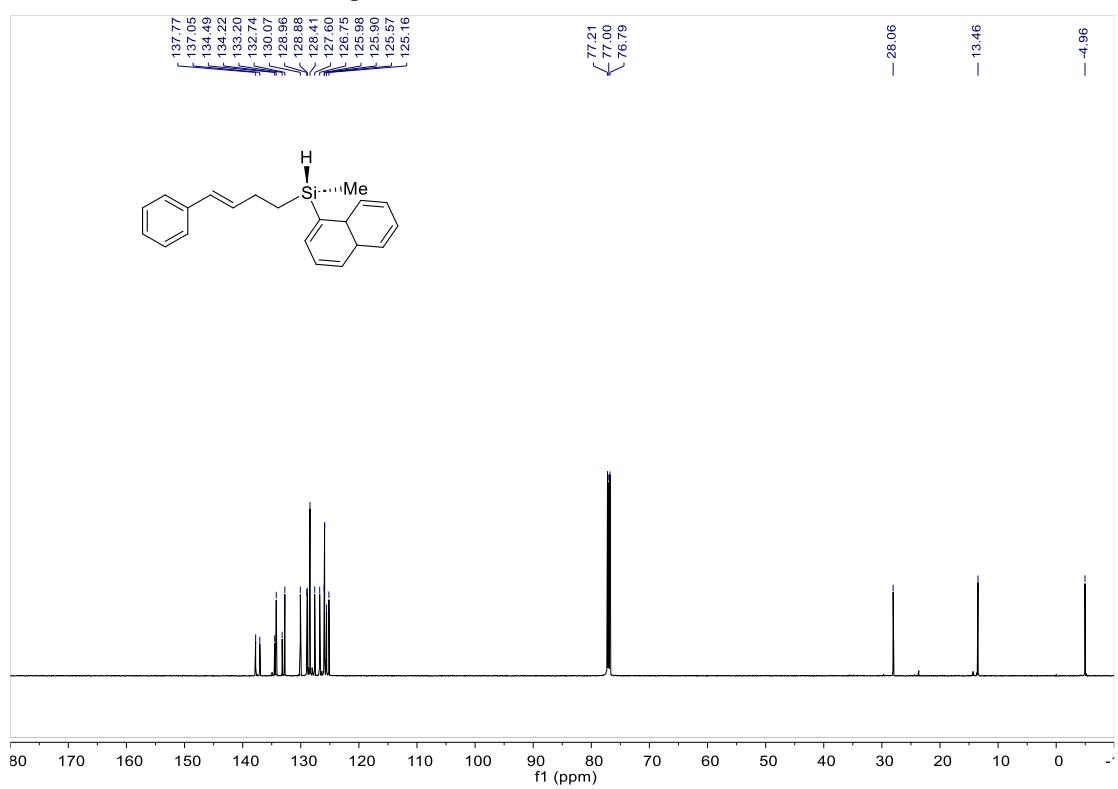
¹³C NMR (100 MHz, CDCl₃) spectrum of **41**



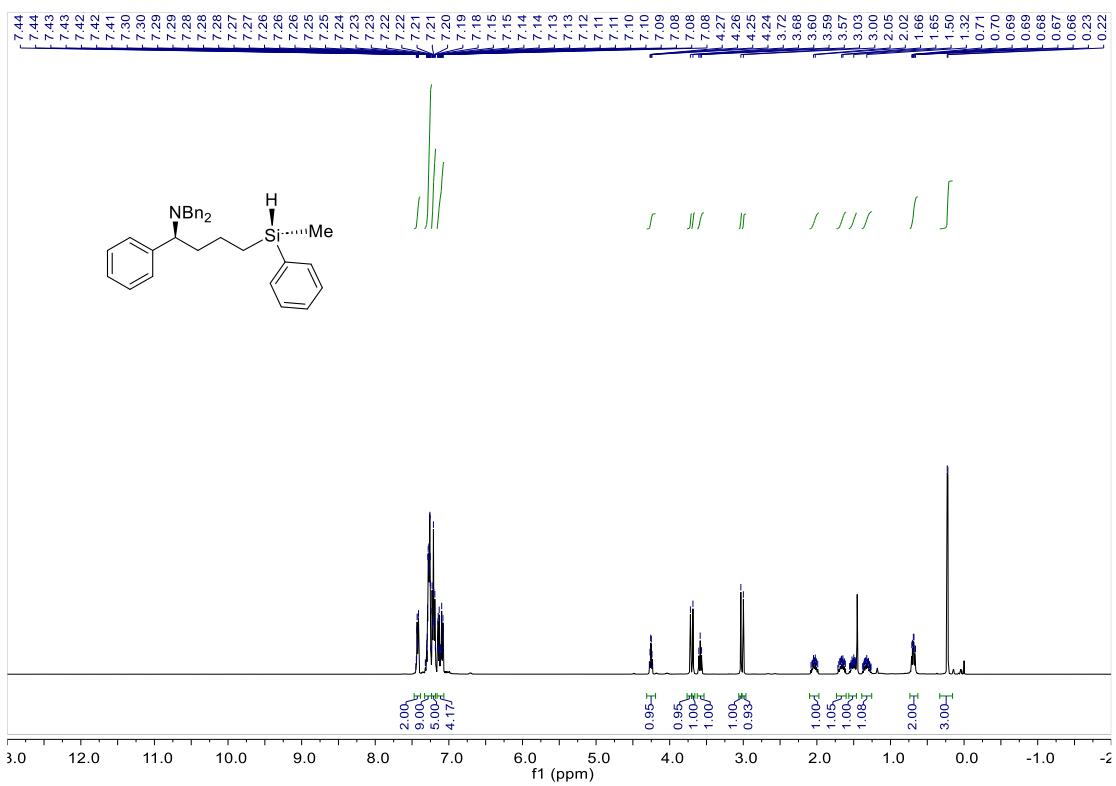
¹H NMR (600 MHz, CDCl₃) spectrum of **42**



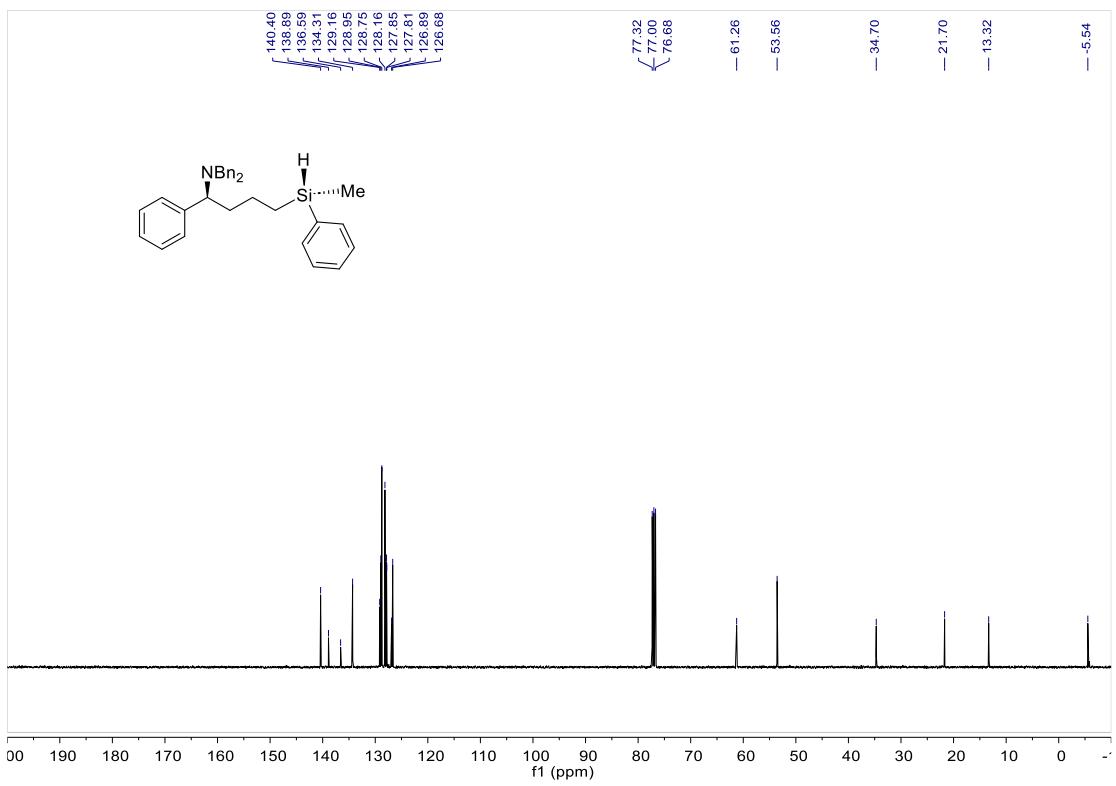
¹³C NMR (150 MHz, CDCl₃) spectrum of **42**



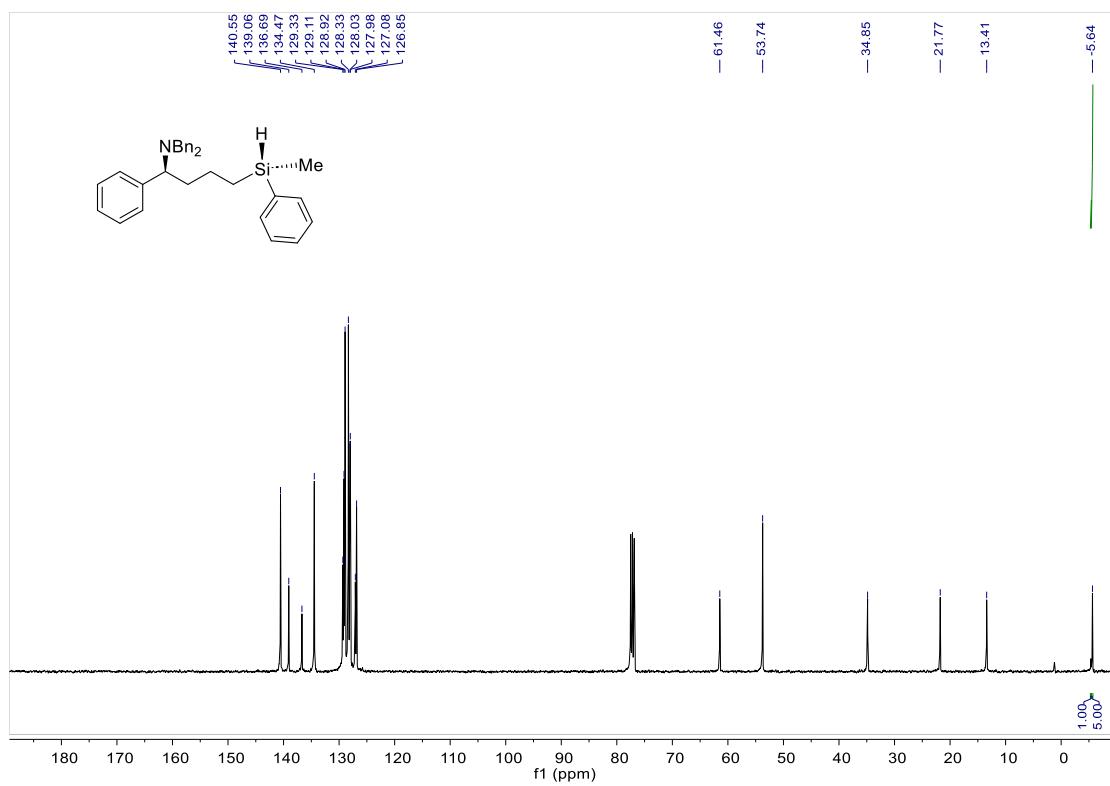
¹H NMR (400 MHz, CDCl₃) spectrum of **43**



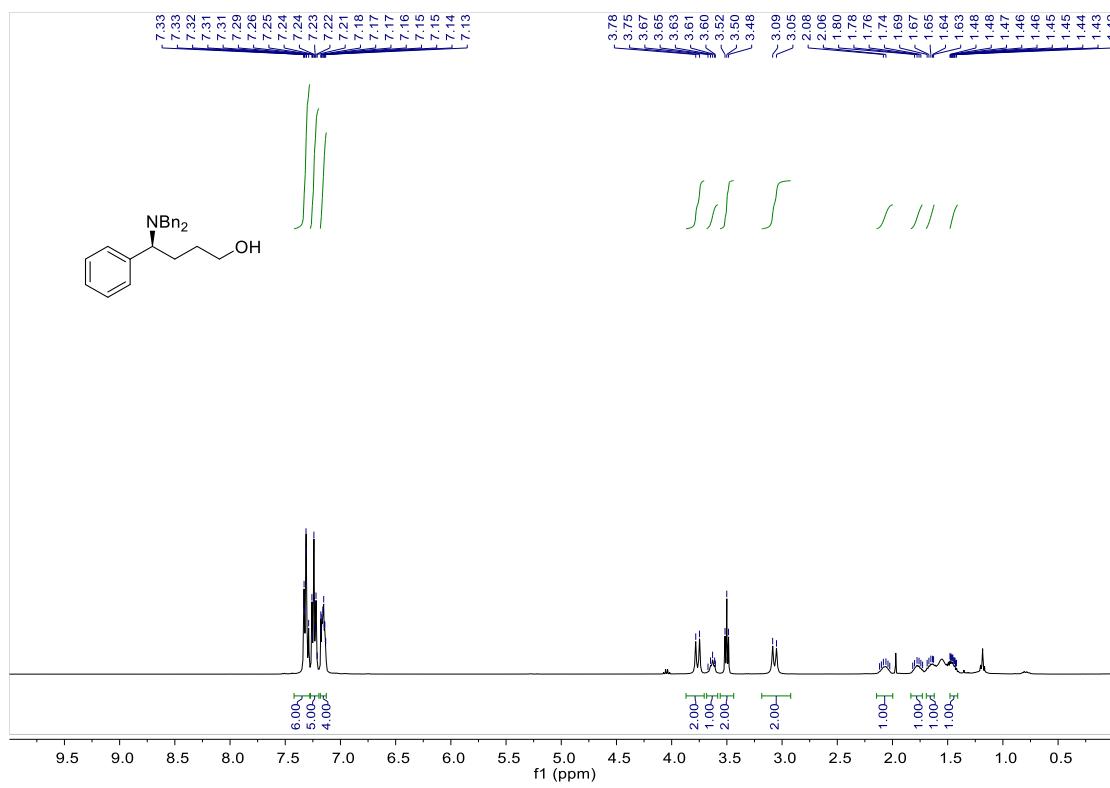
¹³C NMR (100 MHz, CDCl₃) spectrum of **43**



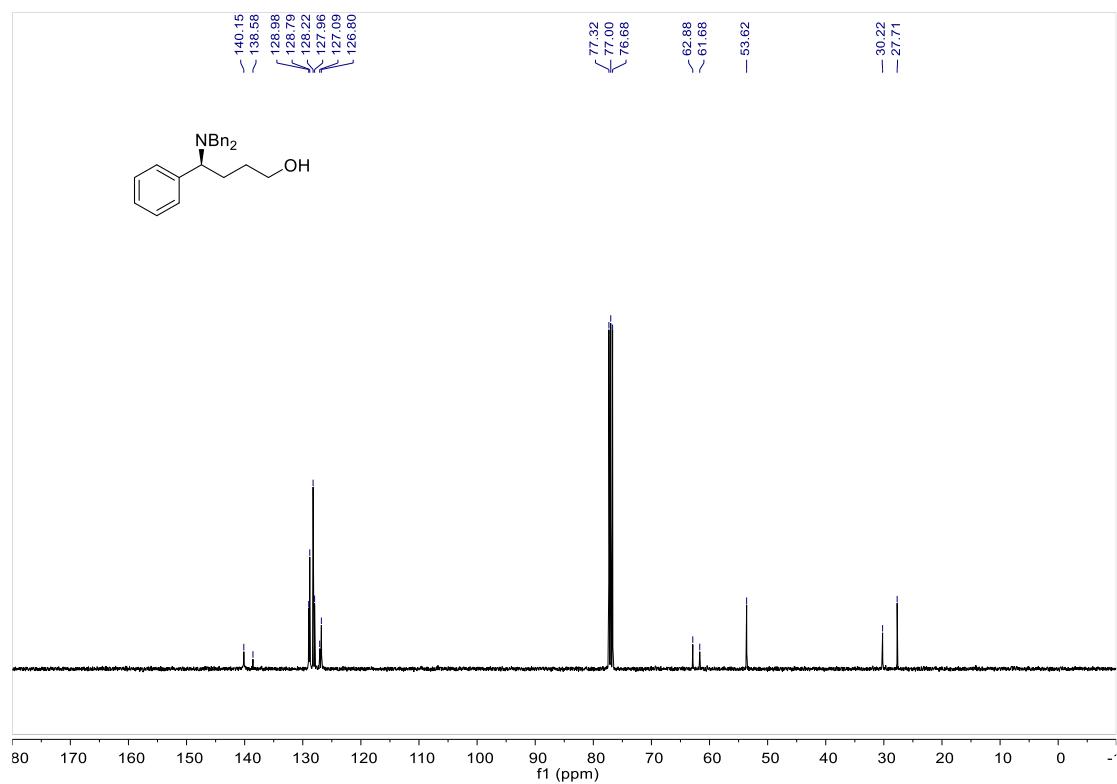
¹³C NMR (100 MHz, CDCl₃) spectrum of **43** (定量碳谱)



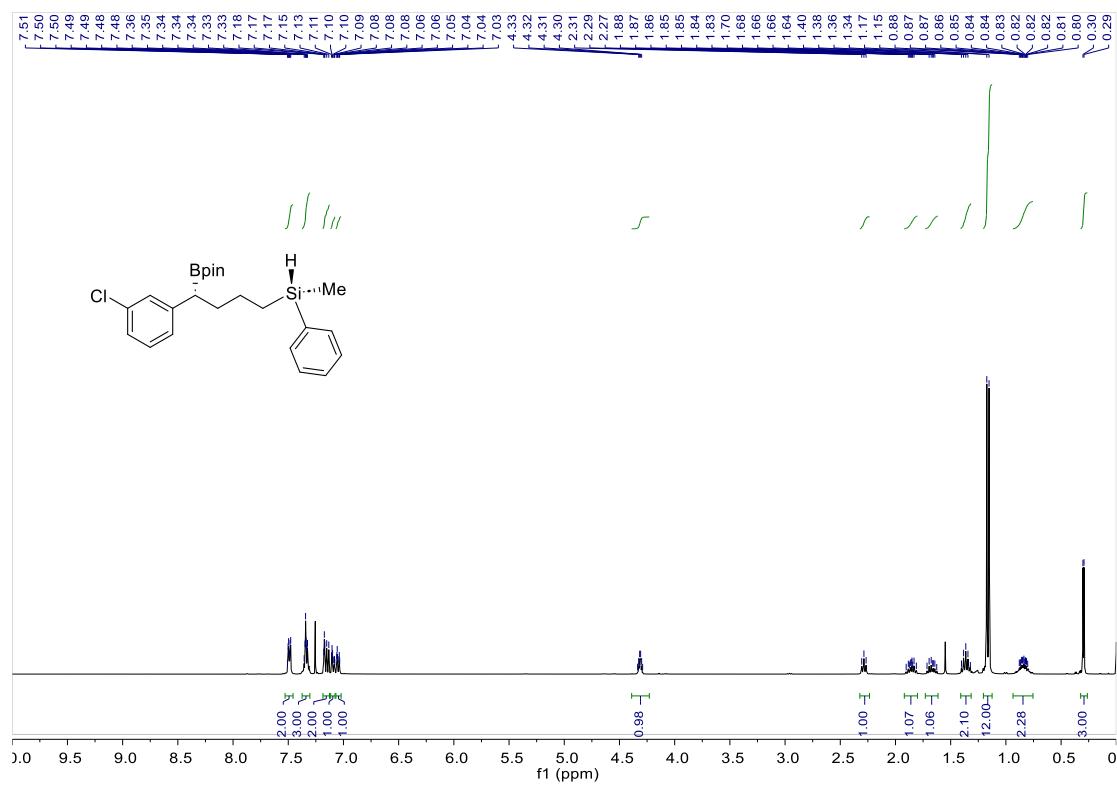
¹H NMR (400 MHz, CDCl₃) spectrum of **43'**



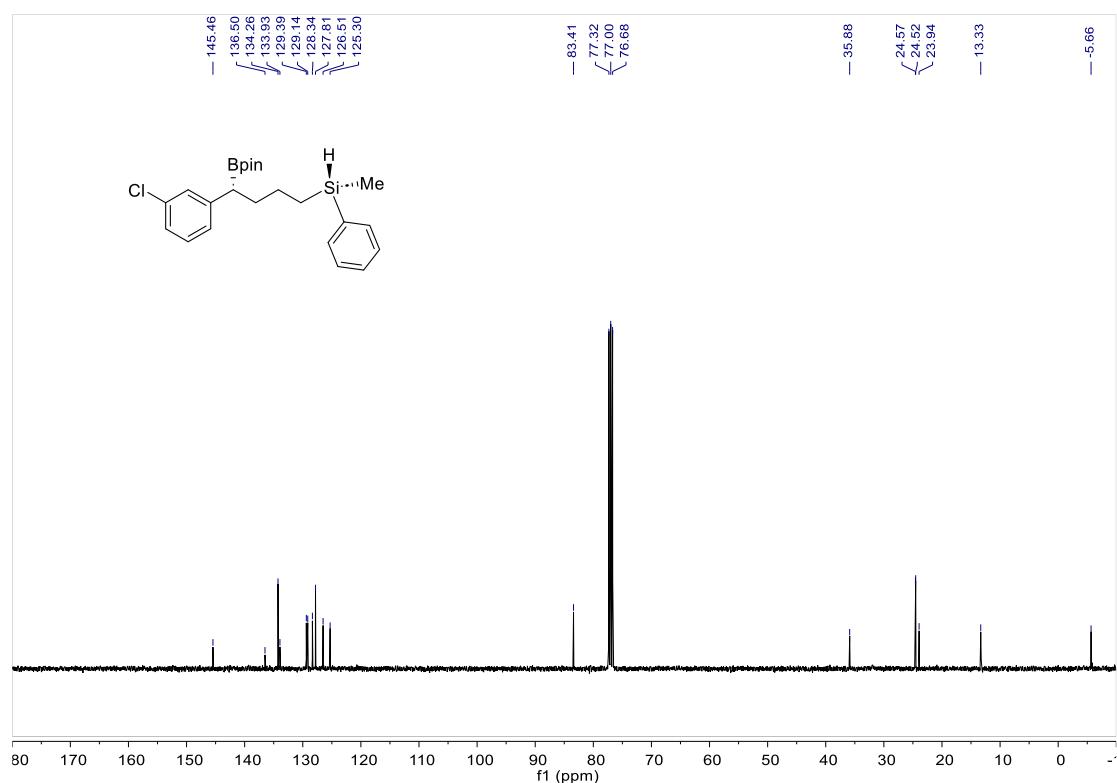
¹³C NMR (100 MHz, CDCl₃) spectrum of **43'**



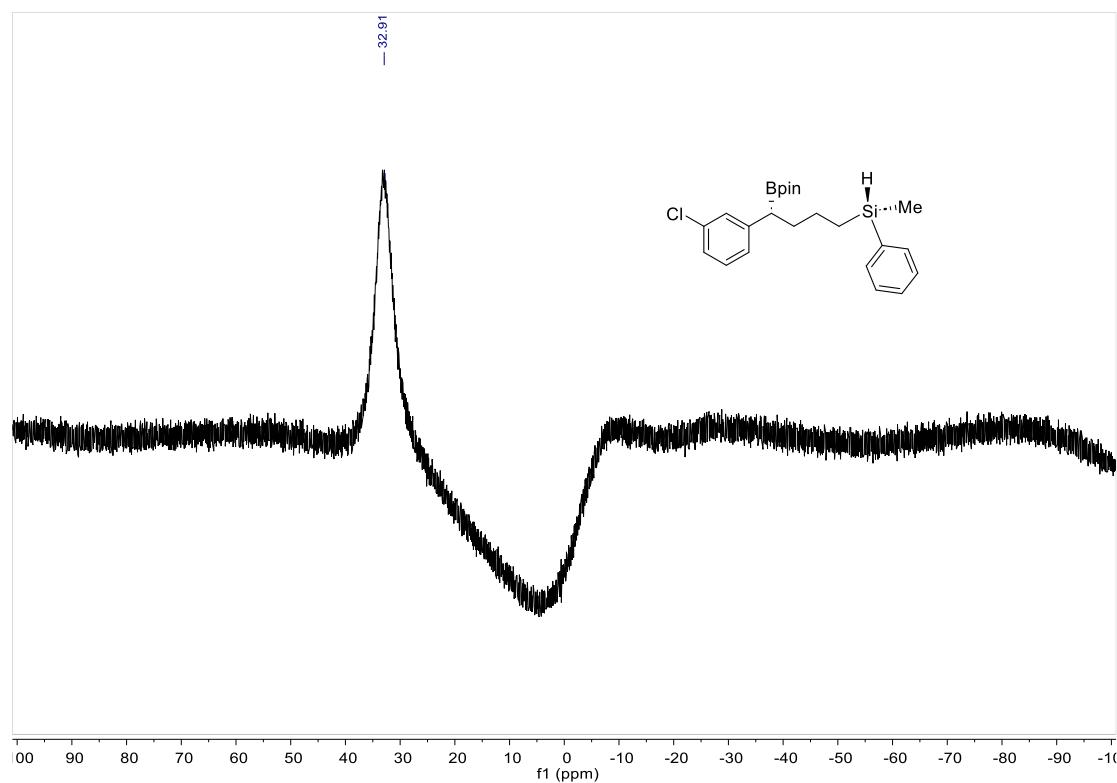
¹H NMR (400 MHz, CDCl₃) spectrum of **44**



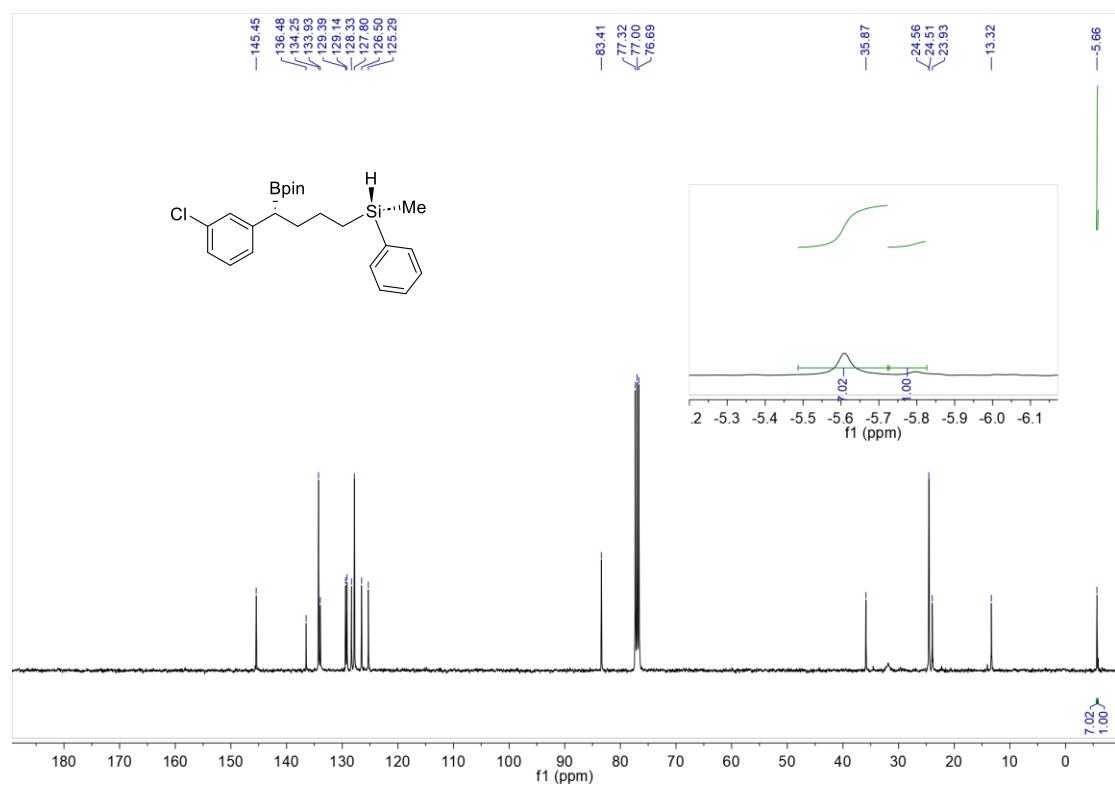
¹³C NMR (100 MHz, CDCl₃) spectrum of **44**



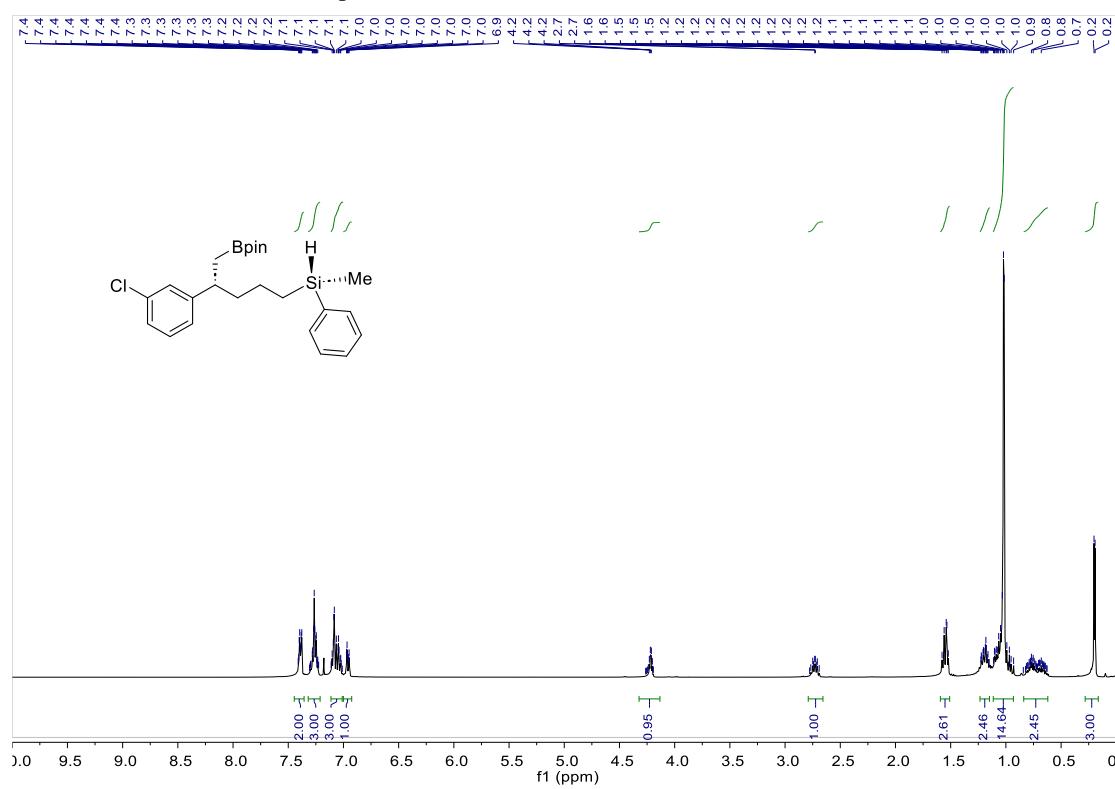
¹¹B NMR (128 MHz, CDCl₃) spectrum of **44**



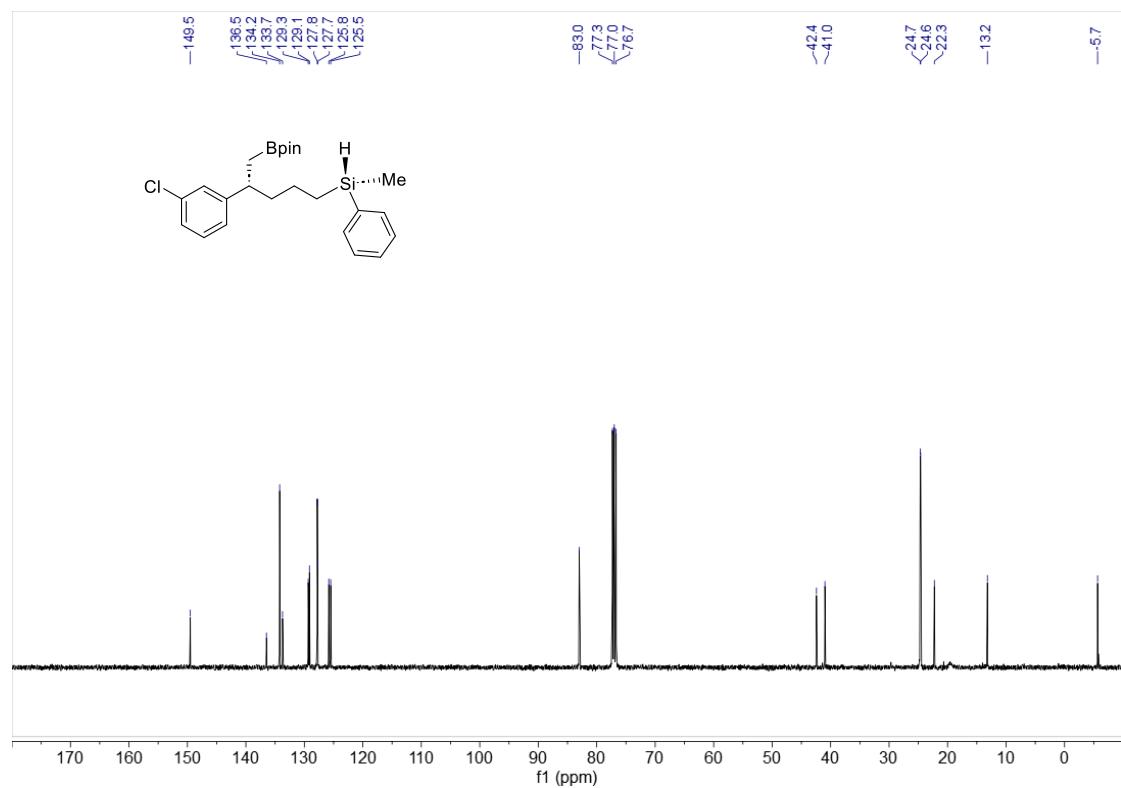
¹³C NMR (100 MHz, CDCl₃) spectrum of **44** (定量碳谱)



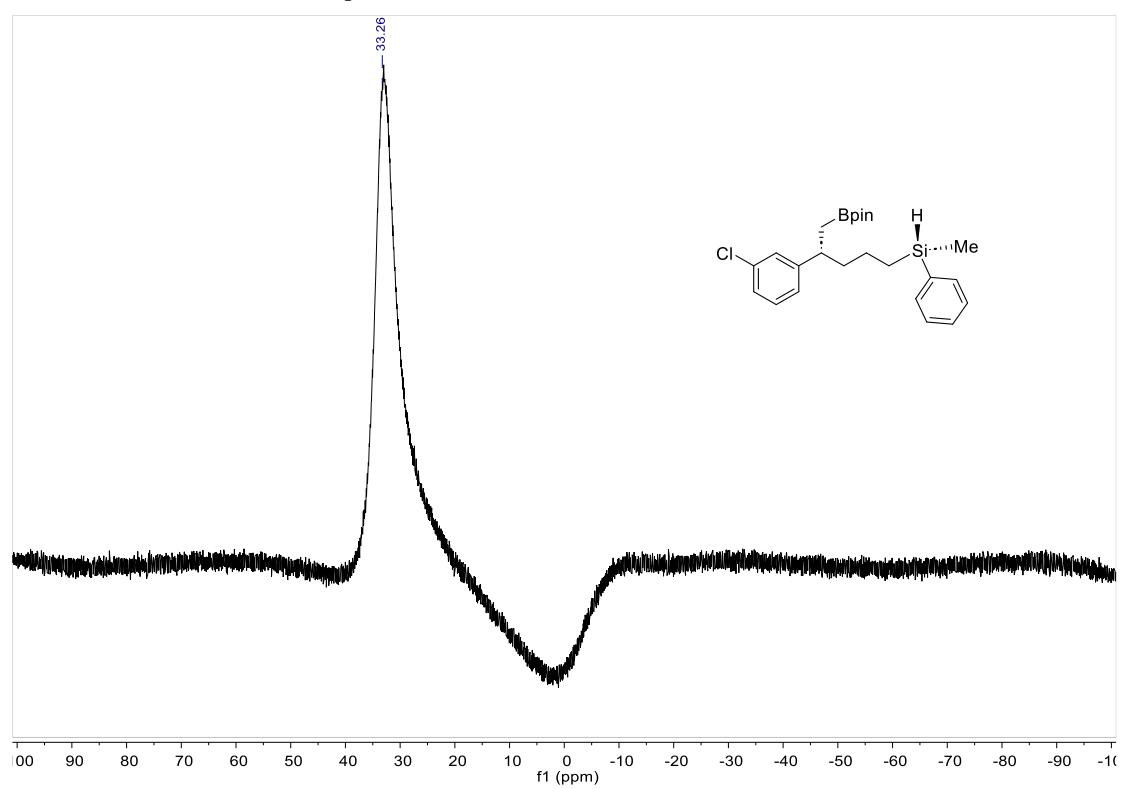
¹H NMR (400 MHz, CDCl₃) spectrum of **45**



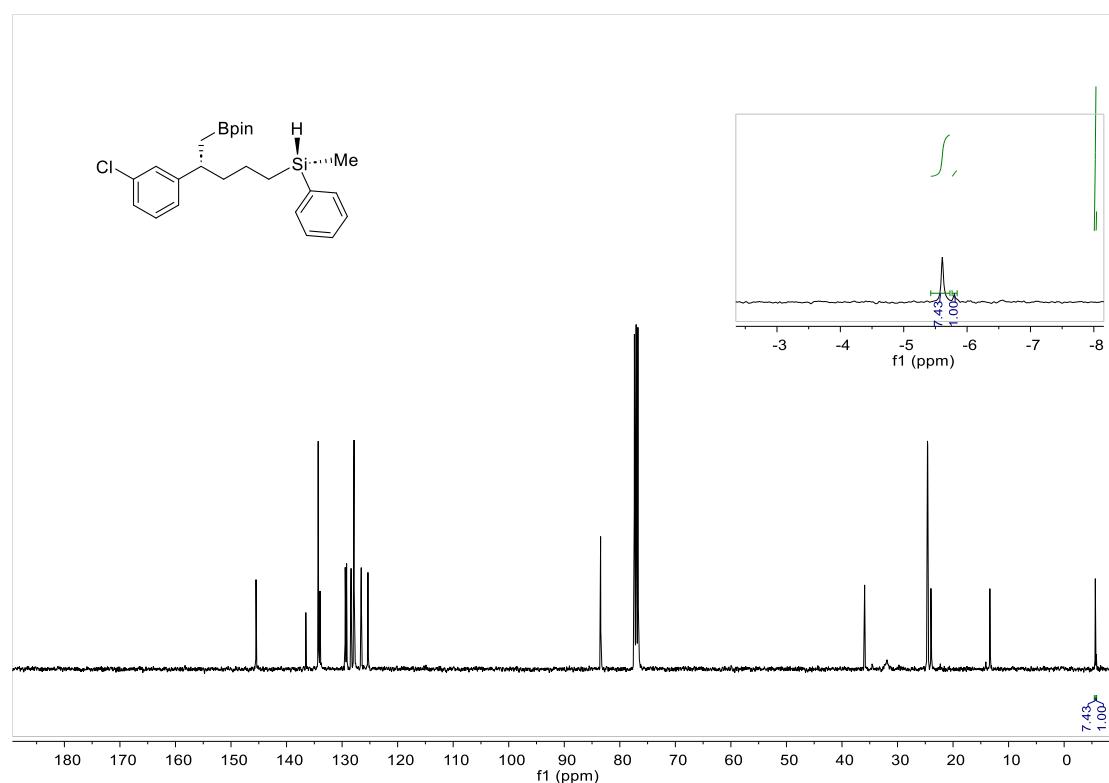
¹³C NMR (100 MHz, CDCl₃) spectrum of **45**



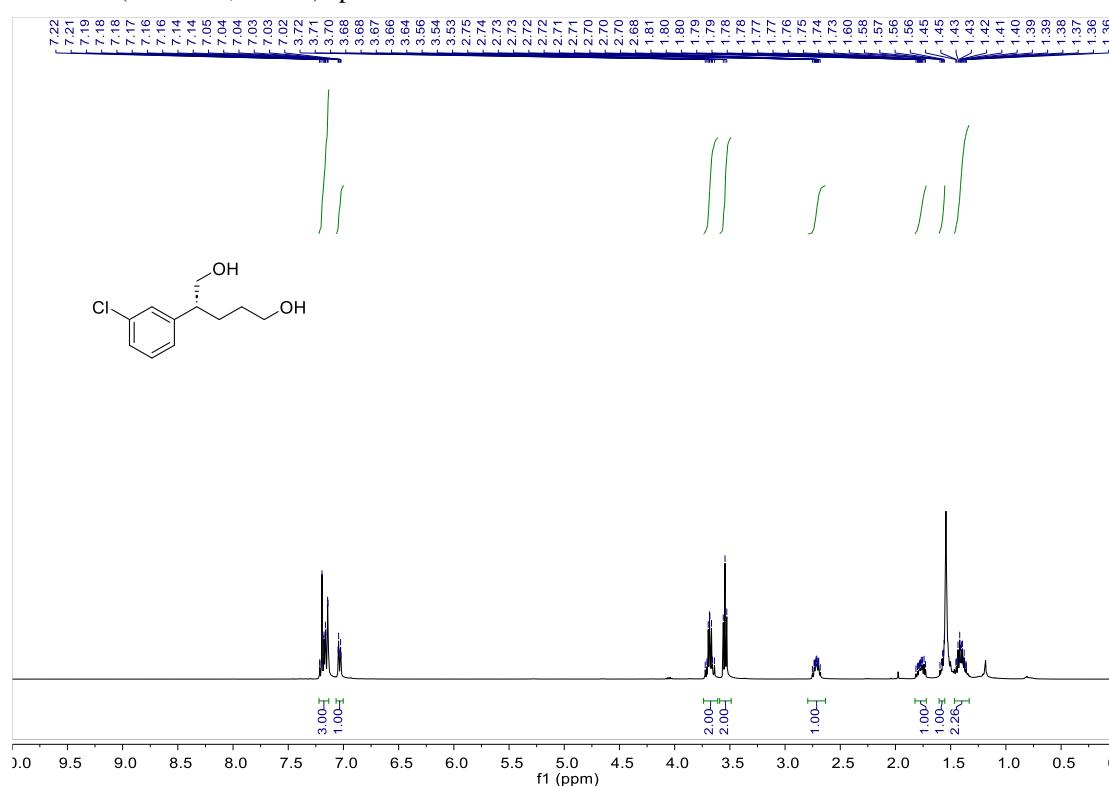
¹¹B NMR (128 MHz, CDCl₃) spectrum of **45**



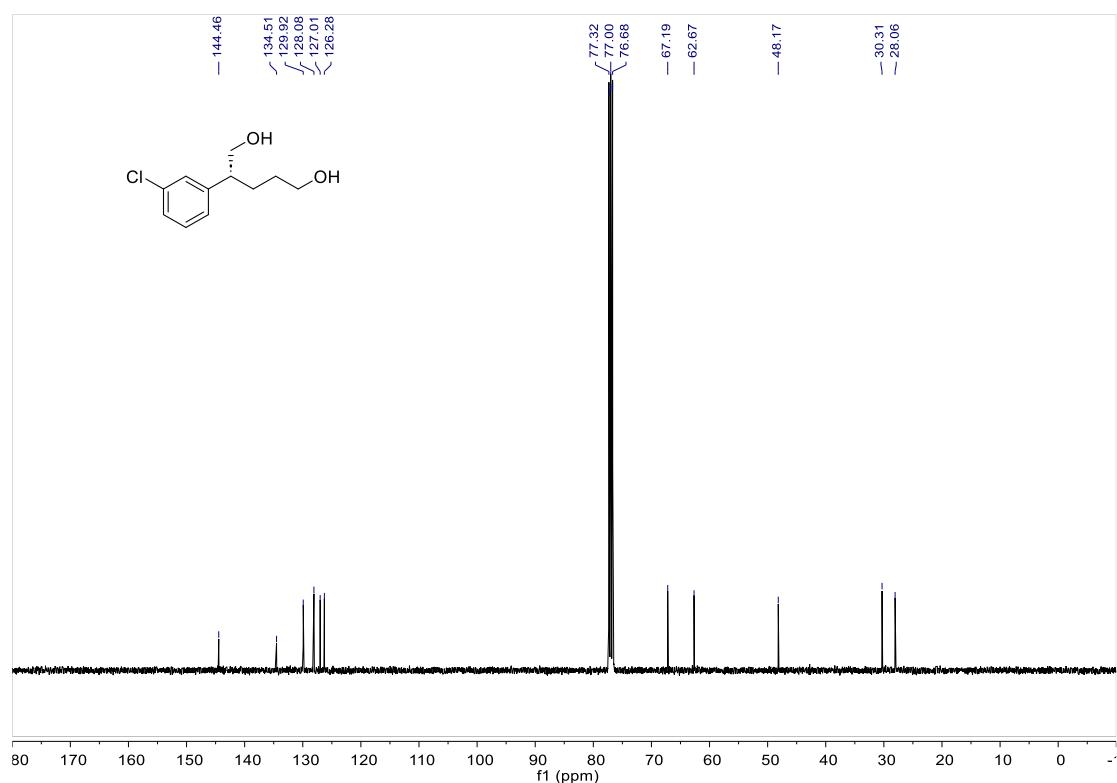
^{13}C NMR (100 MHz, CDCl_3) spectrum of **45** (定量碳谱)



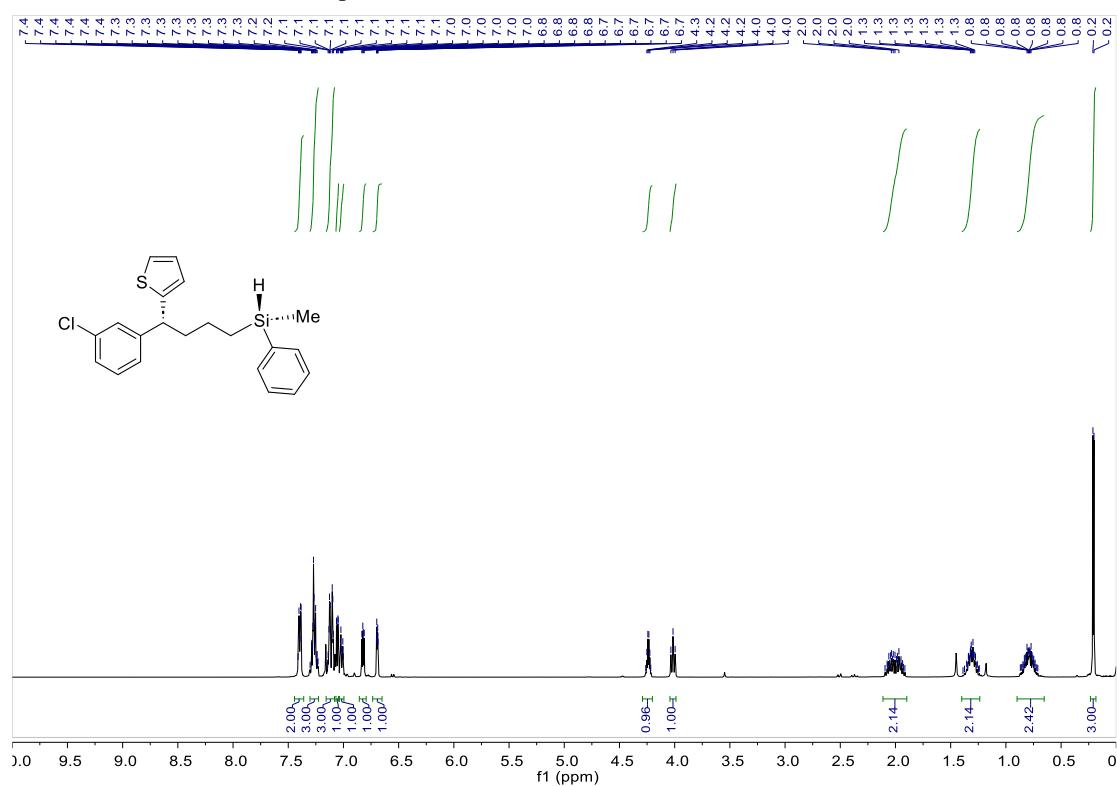
^1H NMR (400 MHz, CDCl_3) spectrum of **45'**



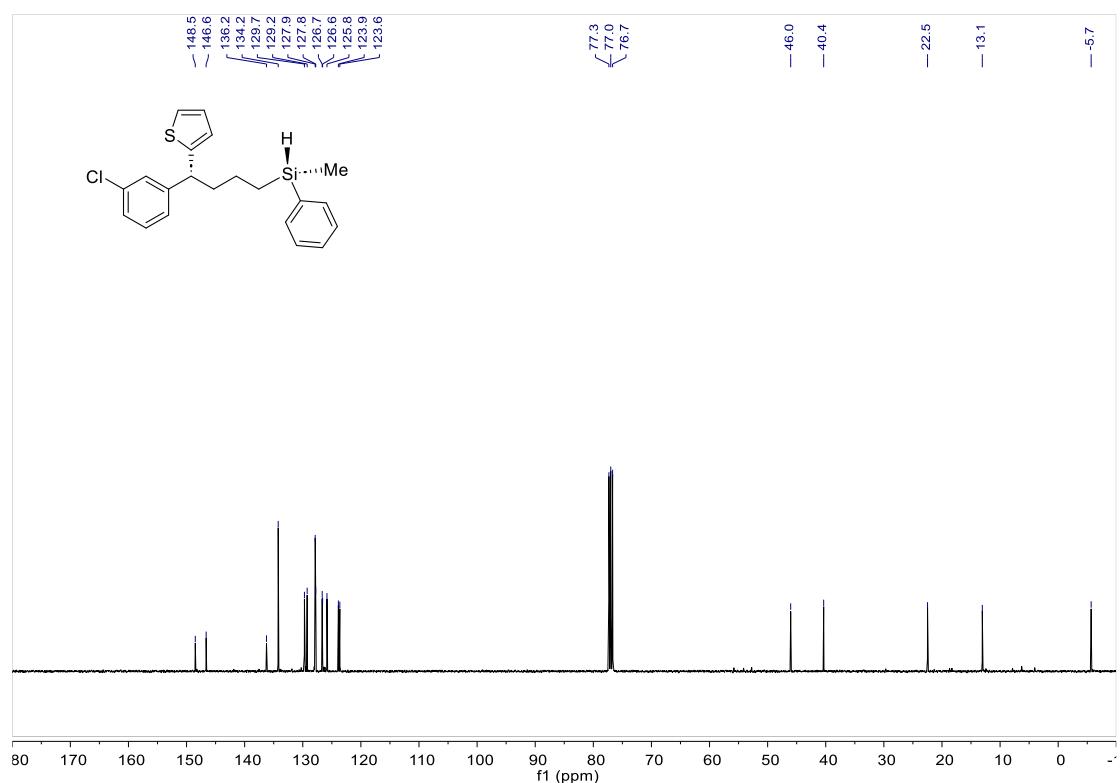
¹³C NMR (100 MHz, CDCl₃) spectrum of **45'**



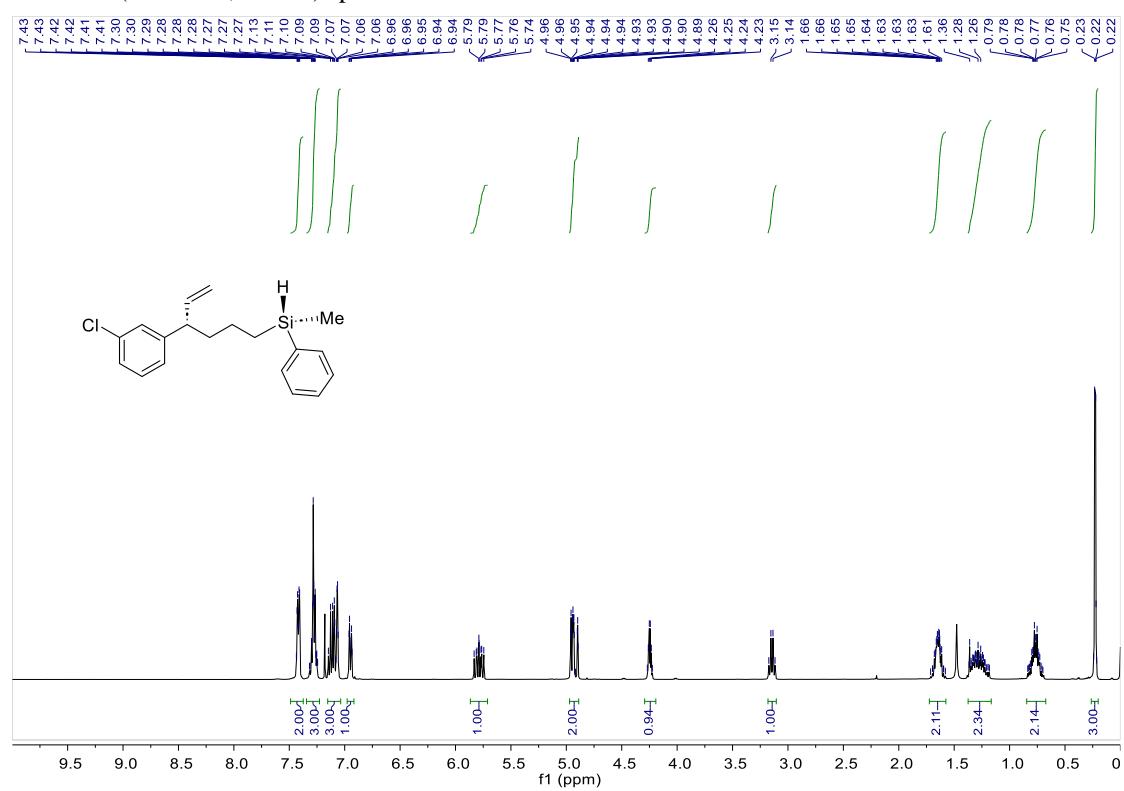
¹H NMR (400 MHz, CDCl₃) spectrum of **46**



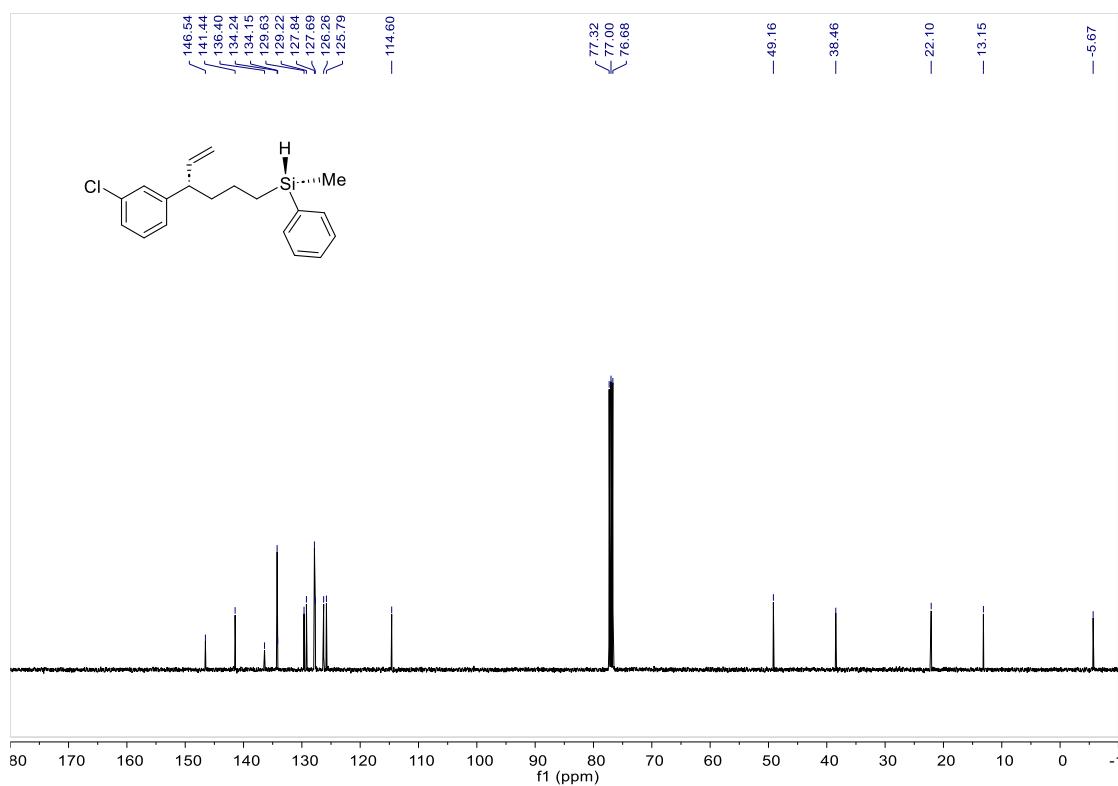
¹³C NMR (100 MHz, CDCl₃) spectrum of **46**



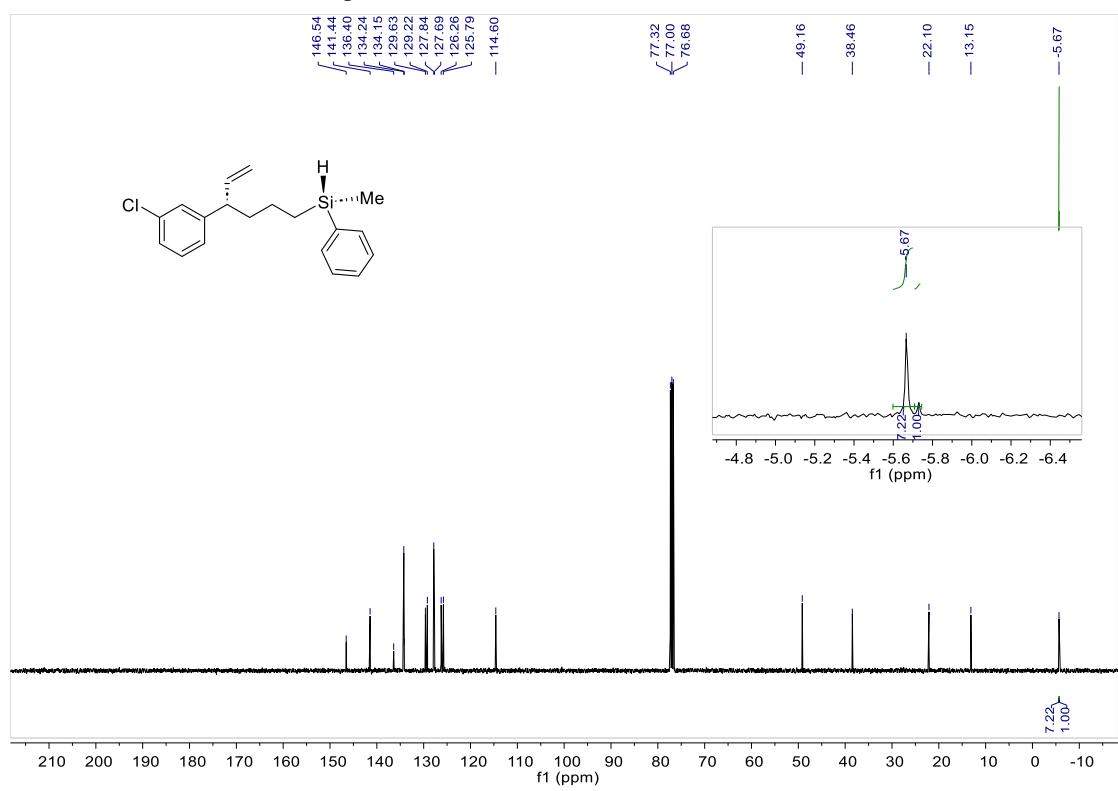
¹H NMR (400 MHz, CDCl₃) spectrum of **47**



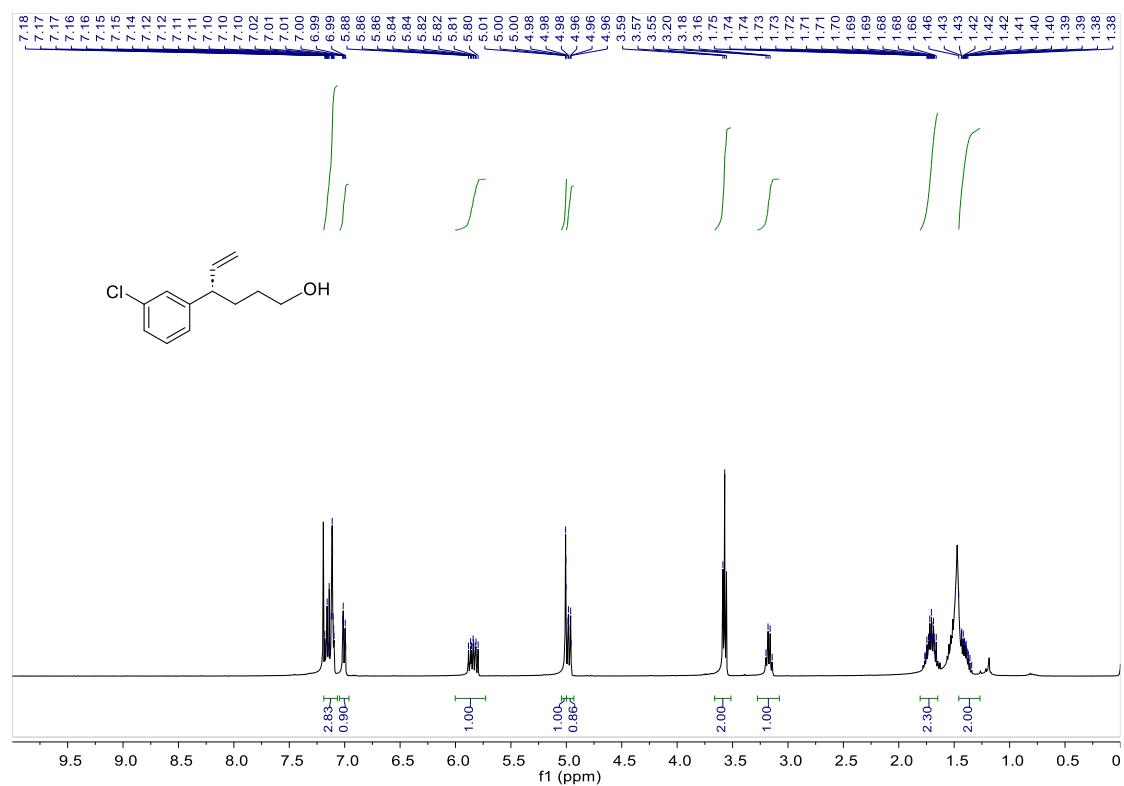
¹³C NMR (100 MHz, CDCl₃) spectrum of **47**



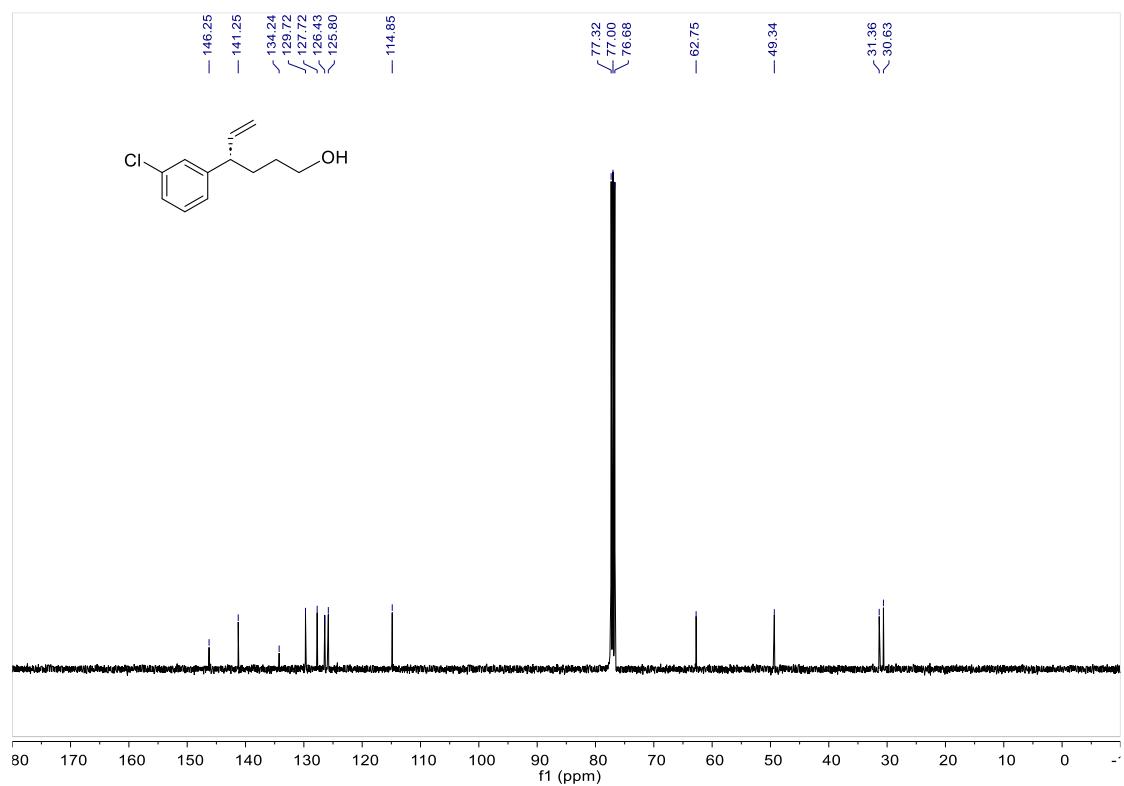
¹³C NMR (100 MHz, CDCl₃) spectrum of **47** (定量碳谱)



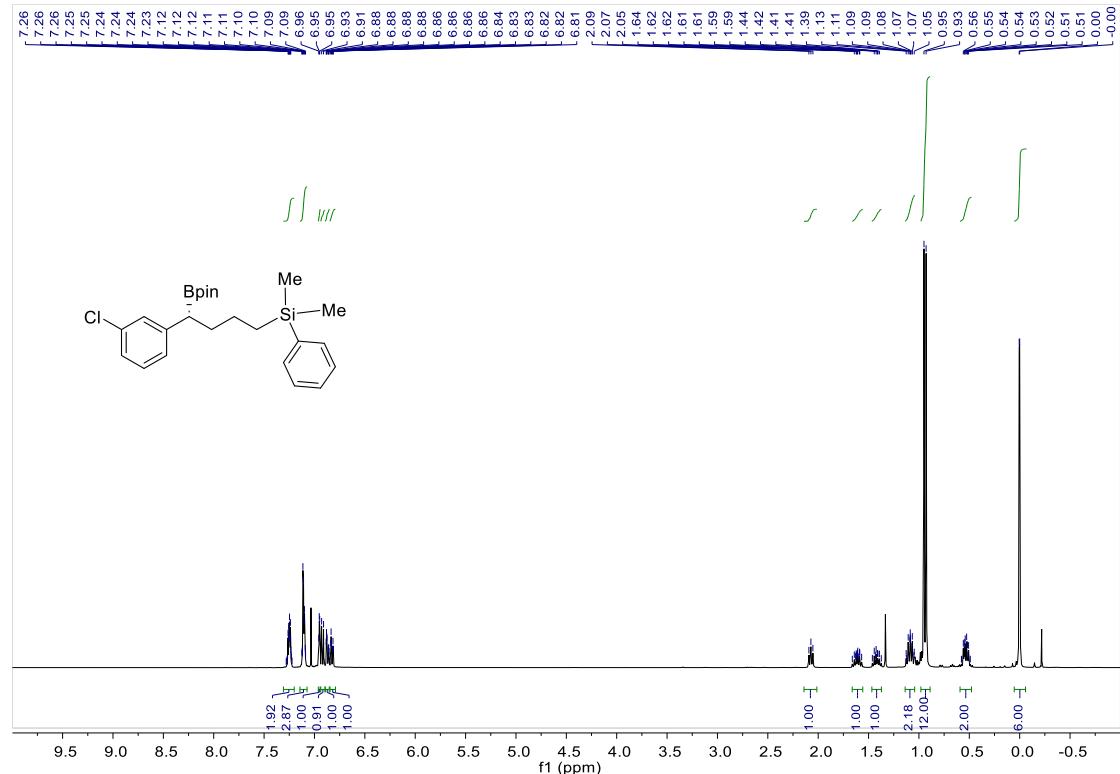
¹H NMR (400 MHz, CDCl₃) spectrum of **47'**



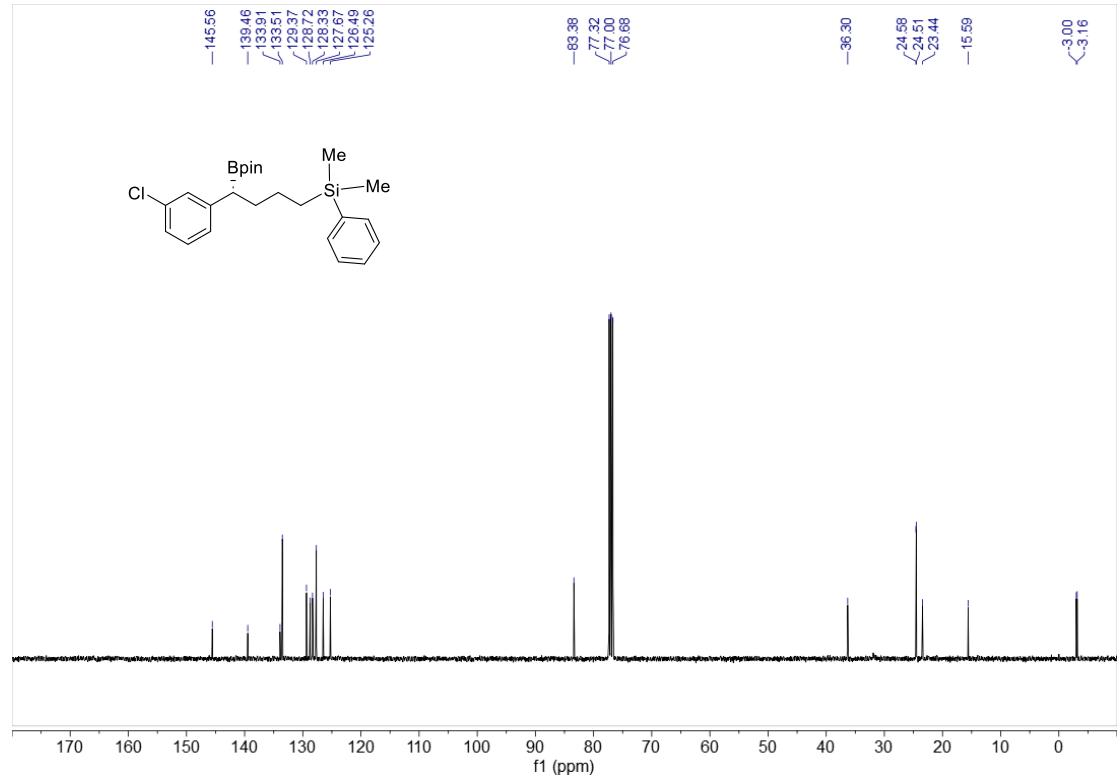
¹³C NMR (100 MHz, CDCl₃) spectrum of **47'**



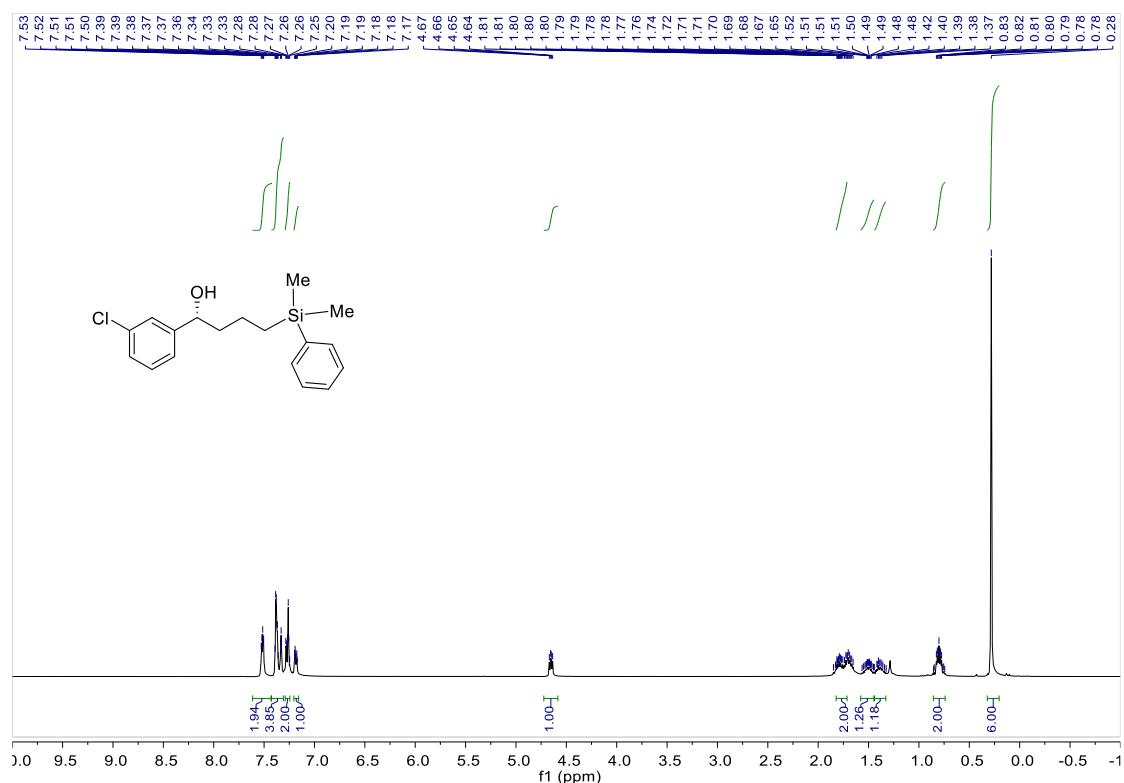
¹H NMR (400 MHz, CDCl₃) spectrum of **48**



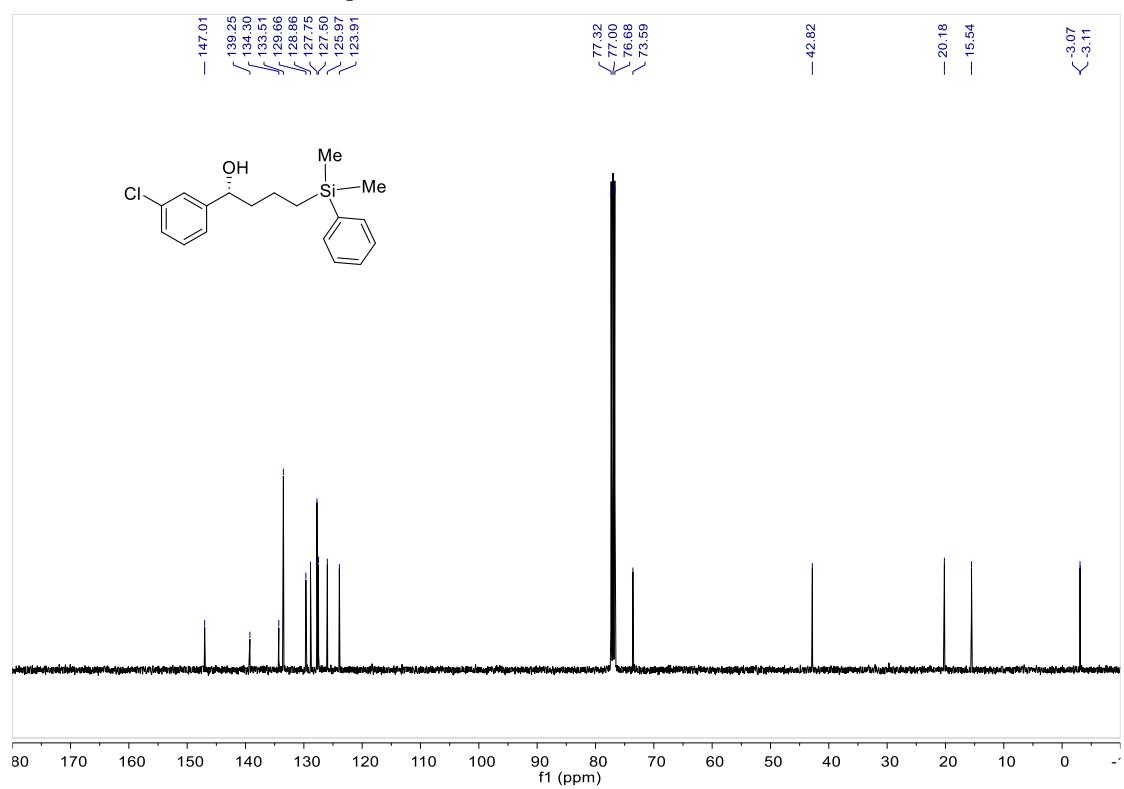
¹³C NMR (100 MHz, CDCl₃) spectrum of **48**



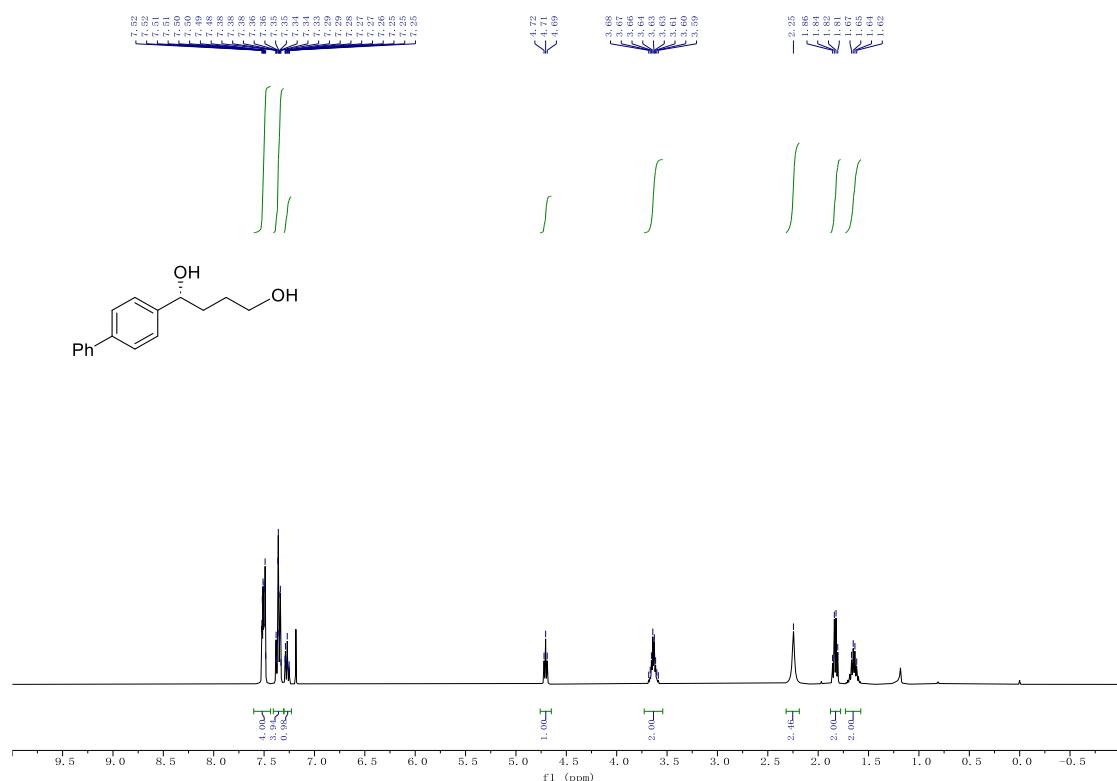
¹H NMR (400 MHz, CDCl₃) spectrum of **48'**



¹³C NMR (100 MHz, CDCl₃) spectrum of **48'**



¹H NMR (400 MHz, CDCl₃) spectrum of **49**



¹³C NMR (100 MHz, CDCl₃) spectrum of **49**

