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Photoexcited Cobalt Catalyzed Endo-Selective Alkyl Heck Reaction

Chenyang Wang,[†] Luis Miguel Azofra,[‡] Phong Dam,[†] Edelman J. Espinoza-Suárez,[†] Hieu Trung Do,[†] Jabor Rabeah,[†] Angelika Brückner,[†] and Osama El-Sepelgy[†]*

[†]Leibniz Institute for Catalysis e.V., Albert-Einstein-Str. 29a, 18059 Rostock, Germany

[‡]Instituto de Estudios Ambientales y Recursos Naturales (i-UNAT), Universidad de Las Palmas de Gran Canaria (ULPGC), Campus de Tafira, 35017 Las Palmas de Gran Canaria, Spain

Email: Osama.Elsepelgy@Catalysis.de.

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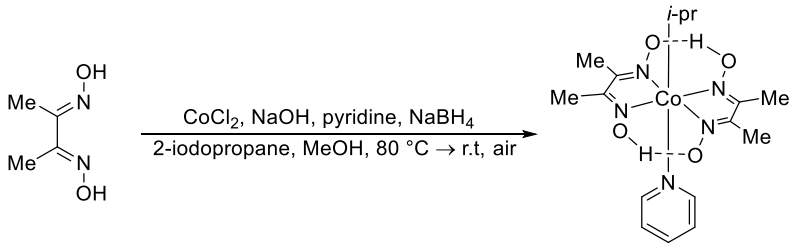
1. General information

Unless otherwise noted, all commercial reagents were purchased from commercial suppliers and used without further purification. And all solvents were treated according to the general methods. The reactions were monitored by thin layer chromatography (TLC) with aluminum sheets silica gel 60 F_{254} from Merck, and flash column chromatography purifications were performed using silica gel 60 (63-200 μm) from MACHEREY-NAGEL. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AV 300 (300 MHz), AV 400 (400 MHz) or Fourier 300 (300 MHz) NMR spectrometers. Chemical shifts (δ) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H NMR) and 77.16 ppm (^{13}C NMR). And all signals were reported in parts per million (ppm) and spin-spin coupling constants (J) are given in Hz, while multiplicities are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), br (broad), m (multiplet). All IR data were collected by attenuated total reflectance (ATR, Bruker Alpha FT-IR spectrometer) and wavenumbers ν are given in cm^{-1}. All measurements were carried out at room temperature unless otherwise stated.

2. General procedures

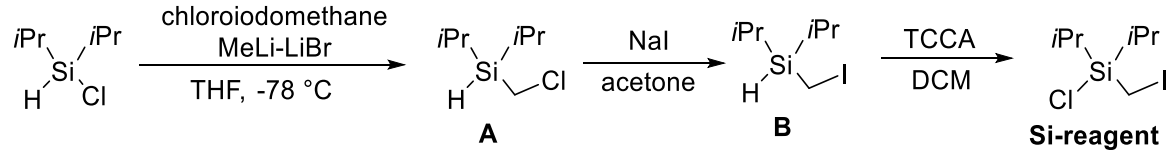
2.1 Synthesis of the cobalt catalyst [Co]-*i*-Pr[1]



The mixture of $CoCl_2$ (1.11 g, 8.6 mmol), MeOH (60 ml) and dimethylglyoxime (2.0 g, 17.2 mmol, 2.0 equiv.) was stirred for 10 min at room temperature resulting brown suspension. Pyridine (0.73 ml, 9.0 mmol, 1.1 equiv.) and NaOH (1.07 M in degassed H_2O, 16.2 ml, 17.3 mmol, 2.0 equiv.) were added, and the dark solution was stirred for another 10 min at room temperature before cooling to 0 °C. NaOH (1.07 M in degassed H_2O, 8.1 ml, 8.7 mmol, 1.0 equiv.) was added and $NaBH_4$ (0.65 g, 17.1 mmol, 2 equiv.) was added portion wise at 0 °C affording a deep blue, very dark mixture. 2-iodopropane (0.86 ml, 8.7 mmol) was added drop wise at 0 °C and the flask was removed from the cooling bath. The orange-red mixture was stirred for 90 min at room temperature and then diluted with H_2O (80 ml). The mixture was extracted with DCM (3 x 50 ml) and the combined, organic layers were dried over Na_2SO_4, filtrated and concentrated in vacuo. The brown residue was suspended in MeOH (18 ml) and stirred for 30 min at 70°C. The mixture was allowed to cool slowly to room temperature and let to stand for 3 h at room temperature. The precipitated orange solid was collected on a glass frit, rinsed with ice-cold MeOH (2 x 2 ml) and dried on high vacuum. After recrystallization (using DCM and hexane) to afford **[Co]-*i*-Pr** (1.80 g, 4.4 mmol, 51%) as an orange solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (m, 2H), 7.67 – 7.57 (m, 1H), 7.24 – 7.18 (m, 2H), 2.06 (s, 12H), 1.93 – 1.81 (m, 1H), 0.40 (m, 6H).

2.2 Synthesis of chloro(iodomethyl)diisopropylsilane (Si-reagent)[2]



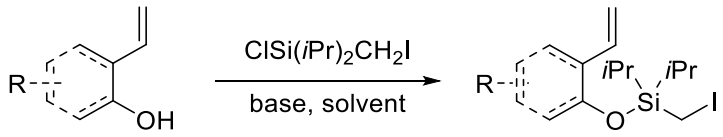
Chlorodiisopropylsilane (6.8 mL, 1 equiv., 40 mmol), chloroiodomethane (4.4 mL, 1.5 equiv, 60 mmol) were dissolved in THF (50 mL). The reaction mixture was cooled down to –78 °C and a solution of MeLi-LiBr complex (1.5 M in ether, 40 mL, 60 mmol) was added dropwise at the same temperature over 30 min. The reaction mixture was further stirred at –78 °C for 1 h and at room temperature for additional 2 h. Then the reaction was quenched with saturated ammonium chloride solution and extracted with hexane and the organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to produce the crude product (chloromethyl)diisopropylsilane (**A**). The crude **A** was then dissolved in acetone (60 mL) and NaI (18 g, 3 equiv., 120 mmol) was added to the reaction mixture, followed by refluxing at 85 °C for 1 h. Afterwards, the reaction mixture was allowed to cool to room temperature before quenching with saturated solution of $Na_2S_2O_3$. The aqueous layer was extracted with hexane and the combined organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo to give **B**. Then a solution of the crude product **B** in DCM (10 mL) was added dropwise to a solution of Trichloroisocyanuric acid (1.67 g, 0.36 equiv., 7.2 mmol) in DCM (60 mL) under argon at 0 °C. The reaction mixture was allowed to warm to room temperature, filtered through celite and concentrated *in vacuo*. The residue was then dissolved in hexanes and re-filtered through celite and then concentrated to give final product chloro(iodomethyl)diisopropylsilane (8.4 g, >90% purity, 65% overall-yield) as a yellow oil, which was used without further purification.

Note: for the synthesis of chloro(bromomethyl)diisopropylsilane, LiBr was used as halogen source, and the heat time is 4 h.

Chloro(iodomethyl)diisopropylsilane: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.19 (s, 2H), 1.47 – 1.34 (m, 2H), 1.11 (m, 6H), 1.09 (m, 6H).

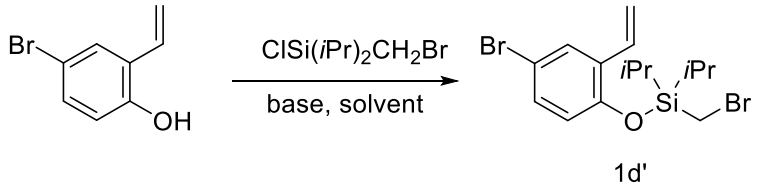
Chloro(bromomethyl)diisopropylsilane: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.62 (s, 2H), 1.42 – 1.28 (m, 2H), 1.09 (m, 6H), 1.06 (m, 6H).

2.4 Synthesis of silyl tethered phenols and alcohols[2]



For the phenols 1a-1m:

The Si-reagent (872 mg, 3 mmol, 1 equiv.) was added to a solution of imidazole (450 mg, 6.6 mmol, 2.2 equiv.) in THF (20 mL) at room temperature under argon atmosphere. Then a solution of phenol (**1a-1m**) (3.3 mmol, 1.1 equiv.) in THF (5 mL) was added. The reaction mixture was stirred overnight at room temperature. To this mixture, hexane (20 mL) was added and filtered. The filtrate was then concentrated and purified by column chromatography on silica gel using hexane as eluent.



1d'

Using the same procedure for substrate **1d'**:

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 2.6, 0.4 Hz, 1H), 7.25 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.07 – 6.91 (m, 1H), 6.75 (d, *J* = 8.6 Hz, 1H), 5.71 (dd, *J* = 17.7, 1.1 Hz, 1H), 5.33 (dd, *J* = 11.1, 1.1 Hz, 1H), 2.72 (s, 2H), 1.40 (ddt, *J* = 14.2, 8.3, 7.0 Hz, 2H), 1.14 (dd, *J* = 7.4, 3.0 Hz, 12H).

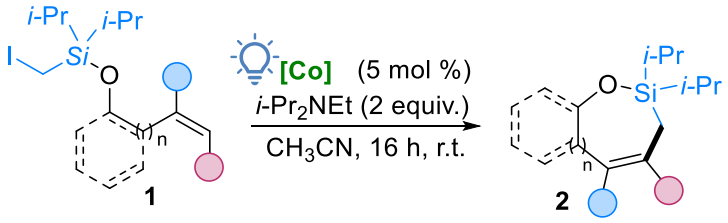
^{13}C NMR (75 MHz, $CDCl_3$) δ 151.34, 131.35, 130.99, 130.60, 130.54, 129.06, 120.98, 115.54, 114.39, 77.47, 77.05, 76.62, 25.48, 17.43, 17.29, 17.25, 17.20, 14.16, 13.67, 12.31, 12.08, 10.90.

For the alcohols 1n-1s:

Procedure A: To a stirred mixture of DMAP (18.3 mg, 0.15 mmol, 5 mol %), Si-reagent (872 mg, 3 mmol, 1 equiv.), triethylamine (0.3 mL, 3 mmol, 1 equiv.) DCM (10 mL), alcohol (**1n**, **1o**, **1q**, **1r**, **1s**) (3.3 mmol, 1.1 equiv.) in 5 mL of DCM was added at 0 °C under argon atmosphere. The mixture was stirred overnight. After completion the mixture was quenched with saturated NH_4Cl solution and extracted with DCM (3 x 50 mL). The combined organic layer was washed with brine. The organic layer was dried with Na_2SO_4, filtered, and evaporated. Then the residue was purified by column chromatography.

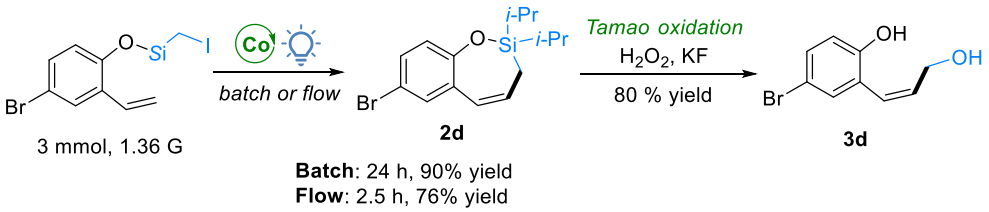
Procedure B: To a stirred mixture of alcohol (**1p**) (3.3 mmol, 1.1 equiv.) and THF (10 mL), MeLi (2.06 mL, 1.5 M, 3.3 mmol, 1.1 equiv.) was added dropwise at 0 °C under argon atmosphere. To this mixture, HMPA (0.57 mL, 3.3 mmol, 1.1 equiv.) was added, followed by, **P3** (872 mg, 3 mmol, 1 equiv.) in 5 mL of THF was added at 0 °C. The mixture was stirred until completion of the reaction by (1 h) GC. After completion the mixture was quenched with saturated NH_4Cl solution and extracted with DCM (3 x 50 mL). The combined organic layer was washed with brine. The organic layer was dried with $MgSO_4$, filtered, and then evaporated by rotary evaporator under reduced pressure. The residue was purified by column chromatography.

2.4 General Procedure for the intramolecular alkyl Heck reaction



In an oven dried 25 mL Schlenk tube equipped with a magnetic stir bar, substrates **1** (0.2 mmol), [**Co]-*i*Pr** (5 mol%, 3.7 mg) and *i*-Pr$_2$NEt (0.4 mmol, 70 µL) were added to degassed CH_3CN (2 mL) under the argon atmosphere. Then, the reaction mixture was stirred under blue-LED irradiation at room temperature for 16 h. The residue was then purified by column chromatography on silica gel using hexane as eluent to give pure cyclization products **2**.

2.5. scale up experiments and further functionalization



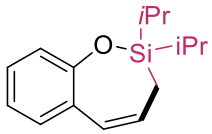
In Batch: In an oven dried 50 mL Schlenk tube equipped with a magnetic stir bar, substrates **1d** (3 mmol, 1.36 G), [**Co]-*i*-Pr** (5 mol%, 55.5 mg) and *i*-Pr$_2$NEt (6 mmol, 750 µL) were added to CH_3CN (25 mL) under the argon atmosphere. Then, the reaction mixture was stirred under blue-LED (19 W) irradiation at room temperature for 24 h. The residue was then purified by column chromatography on silica gel using hexane as eluent to give pure cyclization product **2d** (90%, 875 mg).

In flow: For liquid cooling a separate channel system was implemented above and below of the reaction channel. The LED array (105 x 125 mm) was dimensioned to irradiate the entire area of the reaction channel with 240 blue light LEDs with total 19.2 W. The LED wavelength maximum was 467 nm and the distance between the LED array and the microreactor was adjusted to 8 mm. Additionally, the LED array was cooled by using an air cooler. In an initial experiment, irradiation of the intramolecular alkyl Heck reaction of **1d** (3 mmol, 1.36 G), [**Co]-*i*-Pr** (5 mol%, 55.5 mg) and *i*-Pr$_2$NEt (6 mmol, 750 µL) using microflow reactor with residence time t_R = 2.5 h (flow rate = 0.2 mL min^{-1}) led to 85% conversion (detected by GC), and the desired product was isolated in 76% yield, 741 mg.

Tamao oxidation:[3] A 25 mL tube, containing a stirring bar, was charged with **2d** (452 mg, 1 mmol), $KHCO_3$ (1.0 g, 10 mmol), and DMF (6 mL) and 50%. H_2O_2 (800 µL) was added via syringes under argon atmosphere. The reaction mixture was heated at 70 °C for 12 h. The reaction was then cooled to room temperature, followed by addition of KF on Al_2O_3 (365 mg, 3 mmol). The reaction mixture was stirred for another 8h at room temperature. The product was purified by silica gel column chromatography (eluent: hexanes/AcOEt 4:1 – 1:1) to give **3d** as white solid.

3. Characterization data

2,2-diisopropyl-2,3-dihydrobenzo[*f*][1,2]oxasilepine (2a)[2]

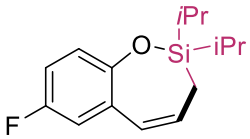


According to the general procedure for silyl methyl Heck reaction, **2a** was isolated in yield 99% (49 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (only hexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.06 (m, 2H), 7.02 – 6.92 (m, 2H), 6.32 – 6.25 (m, 1H), 6.14 – 6.05 (m, 1H), 1.64 (dd, *J* = 7.5, 0.9 Hz, 2H), 1.21 – 1.14 (m, 2H), 1.14 – 1.08 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.11, 130.93, 128.37, 128.16, 127.81, 126.09, 121.65, 120.98, 17.73, 17.46, 13.61, 12.34.

7-fluoro-2,2-diisopropyl-2,3-dihydrobenzo[*f*][1,2]oxasilepine (2b)



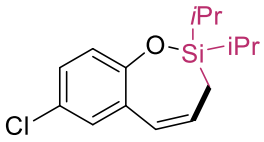
According to the general procedure for silyl methyl Heck reaction, **2b** was isolated in yield 90% (52 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (only hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 – 6.91 (m, 1H), 6.88 – 6.83 (m, 1H), 6.79 – 9.76 (m, 1H), 6.23 – 6.21 (m, 1H), 6.17 – 6.10 (m, 1H), 1.65 (dd, *J* = 7.3, 0.7 Hz, 2H), 1.21 – 1.14 (m, 2H), 1.12 – 1.08 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.28, 155.91, 150.13, 150.11, 129.51, 129.44, 125.14, 125.12, 122.43, 122.35, 116.35, 116.13, 114.49, 114.26, 17.71, 17.45, 13.56, 12.40.

^{19}F NMR (282 MHz, CDCl3) δ -123.89 (m).
HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{21}FOSi$ 264.1346; Found 264.1340.

7-chloro-2,2-diisopropyl-2,3-dihydrobenzo[*f*][1,2]oxasilepine (2c)[2]

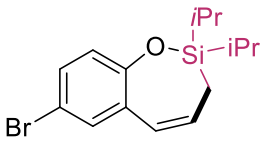


According to the general procedure for silyl methyl Heck reaction, **2c** was isolated in yield 94% (53 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (only hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.05 (m, 2H), 6.93 – 6.91 (m, 1H), 6.24 – 6.11 (m, 2H), 1.65 (dd, *J* = 7.3, 0.6 Hz, 2H), 1.23 – 1.14 (m, 2H), 1.13 – 1.07 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.76, 130.26, 129.89, 129.55, 127.63, 125.78, 124.95, 122.89, 17.69, 17.42, 13.59, 12.42.

7-bromo-2,2-diisopropyl-2,3-dihydrobenzo[*f*][1,2]oxasilepine (2d)



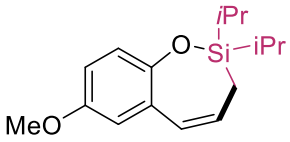
According to the general procedure for silyl methyl Heck reaction, **2d** was isolated in yield 95% (62 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (only hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 6.86 – 6.81 (m, 1H), 6.21 – 6.06 (m, 2H), 1.62 (dd, *J* = 7.3, 0.6 Hz, 2H), 1.19 – 1.11 (m, 2H), 1.09 – 1.05 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.23, 133.19, 130.49, 130.41, 129.53, 124.81, 123.32, 113.15, 17.63, 17.36, 13.53, 12.37.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{21}BrOSi$ 324.0540; Found 324.0541.

2,2-diisopropyl-7-methoxy-2,3-dihydrobenzo[*f*][1,2]oxasilepine (2e)



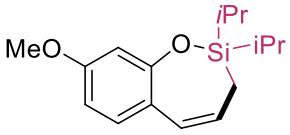
According to the general procedure for silyl methyl Heck reaction, **2e** was isolated in yield 97% (54 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (hexane/ethyl acetate = 100 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.70 (d, *J* = 8.8 Hz, 1H), 6.52 (dd, *J* = 8.8, 3.2 Hz, 1H), 6.40 (d, *J* = 3.1 Hz, 1H), 6.06 – 6.01 (m, 1H), 5.89 (dt, *J* = 10.8, 7.5 Hz, 1H), 3.57 (s, 3H), 1.42 (dd, *J* = 7.5, 0.9 Hz, 2H), 0.99 – 0.92 (m, 2H), 0.91 – 0.86 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.66, 148.13, 128.83, 128.75, 125.88, 122.18, 114.70, 113.99, 55.62, 17.78, 17.52, 13.59, 12.37.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{24}O_2Si$ 276.1540; Found 276.1534.

2,2-diisopropyl-8-methoxy-2,3-dihydrobenzo[f][1,2]oxasilepine (2f) [2]

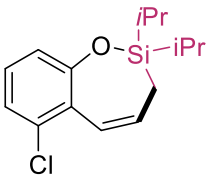


According to the general procedure for silyl methyl Heck reaction, **2f** was isolated in yield 95% (52 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (hexane/ethyl acetate = 100 : 1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 – 6.84 (m, 1H), 6.47 – 6.41 (m, 2H), 6.11 (dd, *J* = 10.8, 0.9 Hz, 1H), 5.87 (dt, *J* = 10.8, 7.4 Hz, 1H), 3.69 (s, 3H), 1.54 – 1.47 (m, 2H), 1.07 – 1.02 (m, 2H), 1.02 – 0.94 (m, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.52, 155.11, 131.64, 126.32, 125.95, 121.06, 107.57, 106.61, 55.31, 17.73, 17.69, 17.46, 17.42, 13.62, 13.60, 12.19.

6-chloro-2,2-diisopropyl-2,3-dihydrobenzo[f][1,2]oxasilepine (2g)



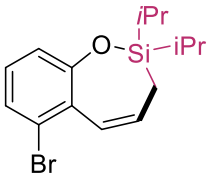
According to the general procedure for silyl methyl Heck reaction, **2g** was isolated in yield 95% (53 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (only hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.06 (m, 2H), 6.93 (m, 1H), 6.39 (dd, *J* = 10.9, 0.9 Hz, 1H), 6.25 (dt, *J* = 10.8, 7.7 Hz, 1H), 1.68 (dd, *J* = 7.7, 0.8 Hz, 2H), 1.24 – 1.16 (m, 2H), 1.15 – 1.09 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.05, 134.25, 129.52, 128.01, 127.20, 122.88, 122.39, 120.17, 17.75, 17.47, 13.56, 12.53.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{21}ClOSi$ 280.1045; Found 280.1049.

6-bromo-2,2-diisopropyl-2,3-dihydrobenzo[*f*][1,2]oxasilepine (2h)



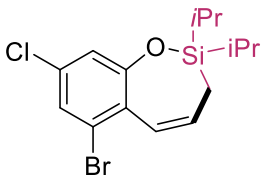
According to the general procedure for silyl methyl Heck reaction, **2h** was isolated in yield 98% (63 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (only hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.09 (m, 2H), 6.76 – 6.74 (m, 1H), 6.09 (d, *J* = 10.9, 1H), 6.02 (dt, *J* = 7,2, 10.9, 1H),1.55 – 1.50 (d, *J* = 6.8, 2H), 1.10 – 1.02 (m, 2H), 1.00 – 0.96 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.28, 133.25, 130.54, 130.47, 129.59, 124.86, 123.37, 113.21, 17.69, 17.42, 13.59, 12.43.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{21}BrOSi$ 324.0540; Found 324.0542.

6-bromo-8-chloro-2,2-diisopropyl-2,3-dihydrobenzo[*f*][1,2]oxasilepine (2i)



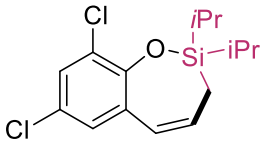
According to the general procedure for silyl methyl Heck reaction, **2i** was isolated in yield 99% (71 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (only hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 2.6, 1H), 7.02 (d, *J* = 2.6, 1H), 6.19 – 6.15 (m, 2H), 1.67 (dd, *J* = 4.8, 1.8 Hz, 2H), 1.27 – 1.18 (m, 2H), 1.12 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ149.33, 130.71, 130.41, 129.83, 125.70, 124.66, 116.68, 17.55, 17.17, 13.67, 12.60.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{20}BrClOSi$ 358.0150; Found 358.0150.

7,9-dichloro-2,2-diisopropyl-2,3-dihydrobenzo[*f*][1,2]oxasilepine (2j)



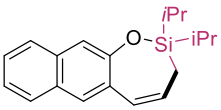
According to the general procedure for silyl methyl Heck reaction, **2j** was isolated in yield 99% (62 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (only hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 2.7, 1H), 6.76 (d, *J* = 2.7, 1H), 5.97 – 5.94 (m, 2H), 1.44 (dd, *J* = 4.8, 1.9 Hz, 2H), 1.02 – 0.94 (m, 2H), 0.90 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.48, 130.76, 130.46, 128.99, 127.78, 126.92, 125.38, 124.53, 17.49, 17.15, 13.64, 12.69.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{20}Cl_2OSi$ 314.0655; Found 314.0656.

2,2-diisopropyl-2,3-dihydronaphtho[2,3-*f*][1,2]oxasilepine (2k)

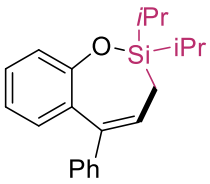


According to the general procedure for silyl methyl Heck reaction, **2k** was isolated in yield 99% (59 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (only hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 1H), 7.69 – 7.67 (m, 1H), 7.59 – 7.57 (m, 1H), 7.39-7.34 (m, 1H), 7.30-7.24 (m, 1H), 7.12 – 7.09 (m, 1H), 6.61 (d, *J* = 10.7 Hz, 1H), 6.24 (dt, *J* = 10.8, 7.7 Hz, 1H), 1.59 (dd, *J* = 7.8, 0.9 Hz, 2H), 1.16 – 1.06 (m, 2H), 1.05 – 1.00 (m, 12H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.78, 133.48, 129.49, 129.45, 128.48, 128.11, 126.03, 123.95, 123.74, 123.02, 122.31, 121.07, 17.87, 17.56, 13.71, 12.82.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{24}OSi$ 296.1591; Found 296.1592.

2,2-diisopropyl-5-phenyl-2,3-dihydrobenzo[*f*][1,2]oxasilepine (2l) [2]

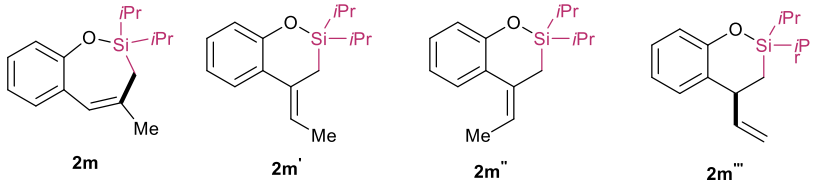


According to the general procedure for silyl methyl Heck reaction, **2l** was isolated in yield 98% (63 mg, colorless oil, Endo: Exo >20:1), purification by chromatography (only hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.07 (m, 6H), 6.98 – 6.94 (m, 1H), 6.87 – 6.79 (m, 2H), 6.24 (t, *J* = 8.1 Hz, 1H), 1.63 (d, *J* = 8.1 Hz, 2H), 1.14 – 1.05 (m, 2H), 1.01 – 0.97 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.88, 143.89, 137.08, 132.01, 130.72, 128.34, 128.03, 126.54, 126.04, 121.63, 121.29, 17.81, 17.55, 13.56, 13.44.

2,2-diisopropyl-4-methyl-2,3-dihydrobenzo[*f*][1,2]oxasilepine (2m, and other isomers, **2m'**, **2m"**, **2m"')** [2]



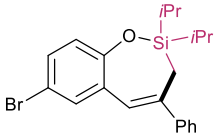
6.4:1:1.6:1.6

According to the general procedure for silyl methyl Heck reaction, **2m,** and other isomers, **2m'**, **2m"**, **2m"'** were obtained in 91% NMR yield (Ratio = 6.4:1:1.6:1.6), purification by chromatography (only hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm only olefinic proton were analyzed: 2m = 6.10 (s, 6.4H), 2m'= 5.66-5.71 (q, 1H), 2m''=5.50 – 5.55 (q, 1.6H), 2m'''= 5.08-5.17 (dd, 3.2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.03, 155.00, 154.15, 154.00, 151.73, 142.40, 137.19, 134.01, 132.86, 131.62, 131.46, 130.71, 129.59, 129.54, 129.37, 129.05, 128.52, 128.42, 128.29, 127.92, 127.84, 127.76, 127.63, 127.28, 127.24, 126.33, 126.15, 126.06, 125.58, 121.89, 121.85, 121.64, 121.27, 121.25, 121.12, 121.01, 120.67, 120.60, 120.58, 120.13, 119.72, 119.62, 119.40, 119.27, 119.02, 114.44, 40.59, 34.27, 30.37, 27.71, 19.07, 18.89, 17.76, 17.72, 17.69, 17.65, 17.51, 17.46, 17.42, 17.38, 17.33, 17.17, 17.15, 17.10, 17.04, 17.00, 16.93, 16.89, 15.31, 14.07, 13.84, 13.66, 13.53, 13.27, 13.23, 12.95, 12.89, 12.76, 12.69, 12.57, 10.40.

2,2-diisopropyl-4-phenyl-2,3-dihydrobenzo[*f*][1,2]oxasilepine (2n)

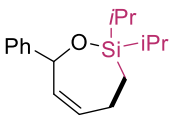


According to the general procedure for silyl methyl Heck reaction, **2n** was isolated in yield 90% (72 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (hexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.12 (m, 4H), 7.12 – 7.03 (m, 3H), 6.84 (d, *J* = 8.6 Hz, 1H), 6.46 (d, *J* = 1.6 Hz, 1H), 2.00 (d, *J* = 1.5 Hz, 2H), 1.25 – 1.12 (m, 3H), 1.11 – 1.04 (m, 13H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.46, 137.22, 133.65, 132.36, 131.89, 129.96, 129.02, 128.13, 126.50, 126.44, 121.32, 112.11, 29.74, 20.17, 17.10, 16.84, 12.89.

2,2-diisopropyl-7-phenyl-2,3,4,7-tetrahydro-1,2-oxasilepine (2o)[2]

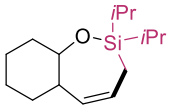


According to the general procedure for silyl methyl Heck reaction, **2o** was isolated in yield 78% (43 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (hexane/ethyl acetate = 100 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.42 – 7.40 (m, 2H), 7.32 – 7.28 (m, 1H), 6.02 – 6.00 (m, 1H), 5.67 – 5.57 (m, 1H), 5.19 – 5.16 (dd, J = 9.0, 2.4 Hz, 1H), 2.70 – 2.48 (m, 2H), 1.89 – 1.70 (m, 2H), 1.28 – 1.09 (m, 14H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.85, 128.19, 128.06, 126.74, 125.79, 125.29, 74.33, 40.10, 17.83, 17.74, 17.72, 17.64, 13.12, 12.94, 11.63.

2,2-diisopropyl-2,3,5a,6,7,8,9,9a-octahydrobenzo[*f*][1,2]oxasilepine (2p)[2]

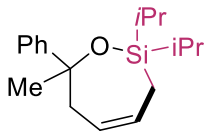


According to the general procedure for silyl methyl Heck reaction, **2p** was isolated in yield 89% (45 mg, colorless oil, Endo:Exo > 20:1), purification by chromatography (hexane/ethyl acetate = 100 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 – 5.71 (m, 1H), 5.15 – 5.10 (m, 1H), 3.60 (m, 1H), 2.22 (m, 1H), 1.99 (m, 1H), 1.76 – 1.47 (m, 5H), 1.37 – 1.07 (m, 4H), 1.03 – 0.92 (m, 14H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.54, 125.20, 46.43, 36.42, 32.60, 25.53, 25.08, 17.83, 17.67, 17.50, 13.50, 13.25, 11.27.

2,2-diisopropyl-7-methyl-7-phenyl-2,3,6,7-tetrahydro-1,2-oxasilepine (2q)



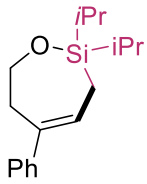
According to the general procedure for silyl methyl Heck reaction, **2q** was isolated in yield 75% (43 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (hexane/ethyl acetate = 100:0 to 100:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.36 – 7.28 (m, 2H), 7.24 – 7.17 (m, 1H), 5.96 – 5.90 (m, 1H), 5.45 – 5.42 (m, 1H), 2.80 – 2.60 (m, 2H), 1.76 – 1.57 (m, 2H), 1.53 (s, 3H), 1.13 – 0.97 (m, 14H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.59, 129.51, 127.75, 126.10, 124.86, 124.42, 40.94, 31.73, 29.72, 18.02, 17.83, 17.68, 17.62, 14.34, 13.78, 11.84.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{28}OSi$ 288.1909; Found 288.1910.

2,2-diisopropyl-5-phenyl-2,3,6,7-tetrahydro-1,2-oxasilepine (2r)[2]

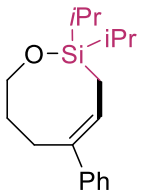


According to the general procedure for silyl methyl Heck reaction, **2r** was isolated in yield 89% (49 mg, colorless oil, Endo:Exo>20:1), purification by chromatography (hexane/ethyl acetate = 100 : 1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 5H), 6.14 (t, *J* = 7.5, 1H), 4.01 – 3.95 (m, 2H), 2.81 – 2.75 (m, 2H), 1.74 (d, *J* = 7.5 Hz, 2H), 0.97 (m, *J* = 3.3, 1.8 Hz, 14H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.53, 137.43, 128.34, 128.30, 126.30, 126.08, 125.52, 63.58, 34.88, 17.68, 17.59, 13.36, 13.04.

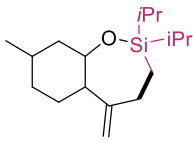
(*E*)-2,2-diisopropyl-5-phenyl-3,6,7,8-tetrahydro-2H-1,2-oxasilocine (2s)[2]



According to the general procedure for silyl methyl Heck reaction, **2s** was produced in 78% (NMR yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.20 (m, 5H), 6.22 (t, *J* = 8.24, 1H), 3.76 – 3.73 (m, 2H), 2.74 (m, 2H), 1.83 (d, *J* = 8.2 Hz, 2H), 1.77 (m, 2H), 1.13 (m, 14H).

2,2-diisopropyl-8-methyl-5-methylenedecahydrobenzo[*f*][1,2]oxasilepine (2t)[2]

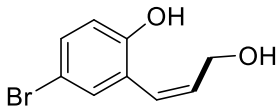


According to the general procedure for silyl methyl Heck reaction, **2t** was isolated in yield 80% (45 mg, colorless oil, Endo:Exo >20:1), purification by chromatography (hexane/ethyl acetate = 100:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 – 4.72 (m, 2H), 3.52 – 3.55 (m, 1H), 2.32 – 2.36 (m, 1H), 2.27 – 2.20 (m, 1H), 2.06 – 1.92 (m, 2H), 1.62 – 1.57 (m, 2H), 1.44 – 1.46 (m, 1H), 1.38 – 1.25 (m, 1H), 1.13 – 0.86 (m, 19H), 0.84 – 0.77 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.35, 111.76, 74.98, 53.37, 44.68, 34.51, 31.89, 31.78, 29.54, 22.15, 17.93, 17.49, 17.36, 13.68, 12.77, 11.87.

(*Z*)-4-bromo-2-(3-hydroxyprop-1-en-1-yl)phenol



According to the general procedure for the Tamao oxidation of **2d**, **3d** was isolated in yield 80% (182 mg, white solid).

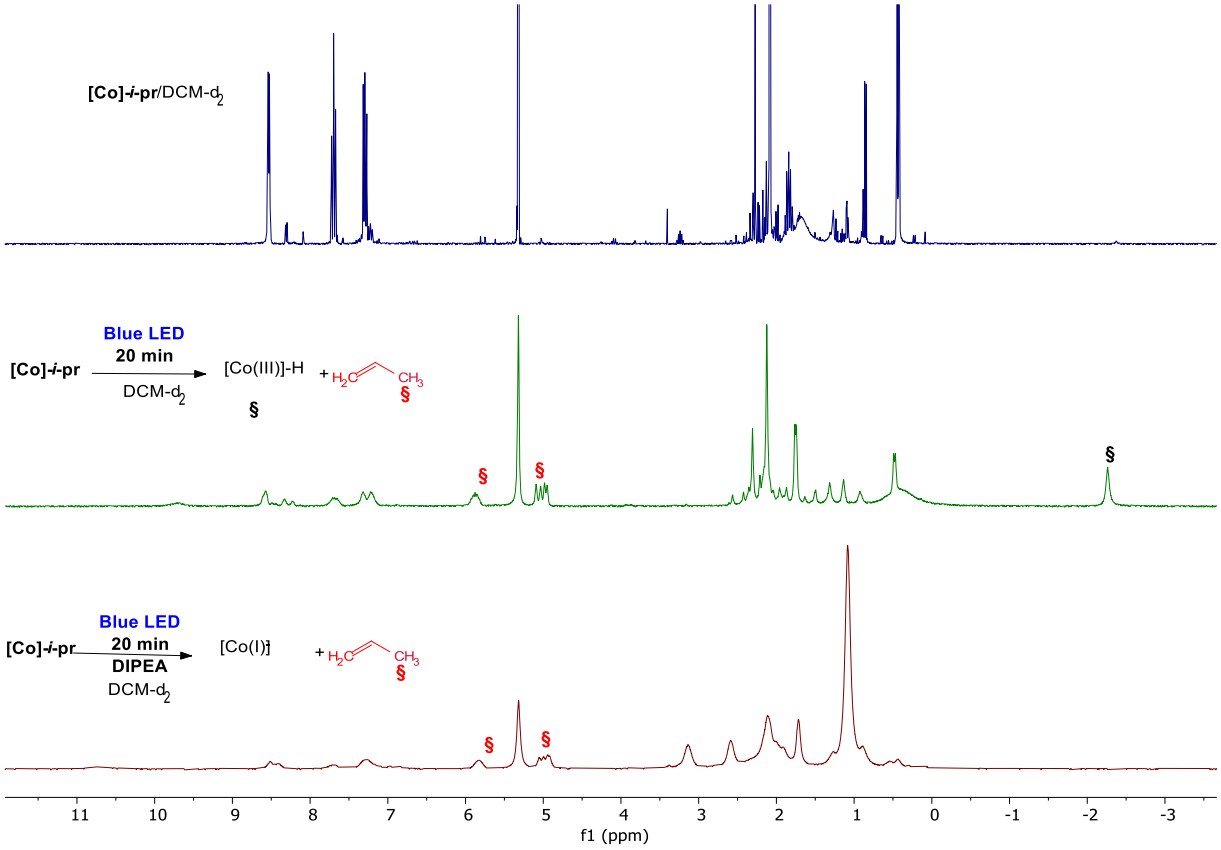
^{1}H NMR (300 MHz, MeOD) δ 7.31 – 7.13 (m, 2H), 6.81 – 6.67 (m, 1H), 6.60 – 6.55 (m, 1H), 5.87 (dt, *J* = 6.5, 11.7, 1H), 4.27 – 4.23 (dd, *J* = 1.7, 6.5, 2H).

^{13}C NMR (75 MHz, MeOD) δ 154.10, 132.09, 131.52, 130.86, 125.84, 124.73, 116.60, 110.27, 58.47.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_{11}O_2Br$ 228.9859; Found 288.1910.

4. NMR Study

This NMR study has been reported before by us.[4] we present it here again for the convince of the readers.



5. Computational information

The reaction mechanism for the light-driven desaturation process of amines has been studied using density functional theory (DFT). In a first stage, the initial guess structures were optimized using the BP86 functional[5,6] and the Pople's 6-31G basis set,[7] using the split-valence double-ξ SVP basis set for Sn and I. To simulate the solvent effect, the conductor-like screening solvation model (COSMO)[8,9] was used with the standard parameters for acetonitrile (ε = 35.688). At this stage, frequency calculations were performed to confirm the nature of the stationary points (minima or first-order TSs with one imaginary frequency). In a second stage, single-point energy refinement calculations were carried out using the PBE96 functional[10,11] and the split-valence triple-ξ TZVP basis set[12] in acetonitrile solution. All calculations were carried out through the facilities provided by the NWChem package (version 6.8.1).[13] The visualization programs CYLview and Jmol were used for drawing the optimized structures.

6. UV-vis measurement information

UV-vis spectra were recorded by a fiberoptical spectrometer (AvaSpec-2048, Avantes) with a probe consisting of a quartz fiber and a 1-mm-probe tip. The measurements were conducted in a 25-ml-Schlenk tube under argon after three times argon purging/ evacuation.

7. EPR measurements information

EPR measurements were performed on a Bruker EMX CW-micro X-band spectrometer with a microwave power ≈ 6.9 mW, a modulation frequency of 100 kHz and modulation amplitude up to 5 G. The EPR spectrometer is equipped with a variable temperature control unit including a liquid N_2 cryostat and a temperature controller for recording the EPR spectra at low temperature down to 100 K. g values were calculated using the equation $h\nu = g\beta B_0$ with β, B_0 and ν being the Bohr magneton, resonance field and frequency, respectively. Calibration of the g values was performed using a DPPH standard (g = 2.0036 ± 0.0004).

Rapid scan EPR spectra were obtained on an ELEXYS 500 cw-EPR spectrometer (Bruker) using a Bruker ER4125RS Vers. M1 resonator. For the measurement, 200 µl of the Co-*i*-Pr 5 mM was filled to an EPR flat cell, followed by injecting 10 µl of DMPO under Ar. The simulated spectrum was acquired by using software package Easyspin [14]

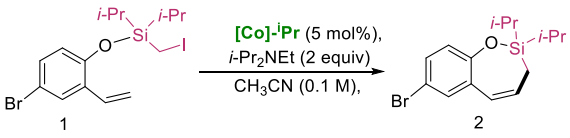
8. Photoflow reactor information[4]

The channel of the microreactor (XXL series, Little Things Factory, Germany) has a total length of about 3000 mm with a cross-section of 2.2 x 2.2 mm giving a total volume of 8 mL and was arranged on an area of 150 x 150 mm. For liquid cooling a separate channel system was implemented above and below of the reaction channel, and the LED array (105 x 125 mm) was dimensioned to irradiate the entire area of the reaction channel with 240 blue light LEDs with total 19.2 W. The LED wavelength maximum was 467 nm and the distance between the LED

array and the microreactor was adjusted to 8 mm. Additionally, the LED array was cooled by using an air cooler.

9. Determination of initial rate and quantum yield

Cyclization of alcohol



Reaction profile

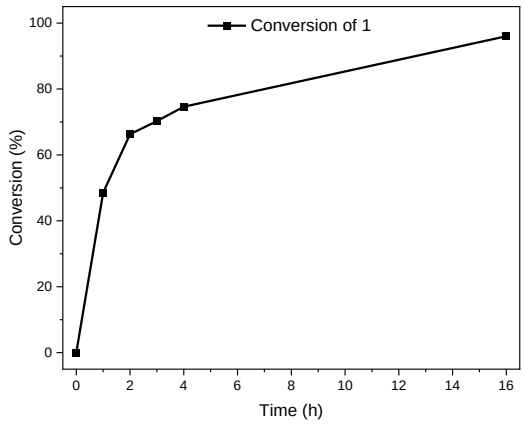
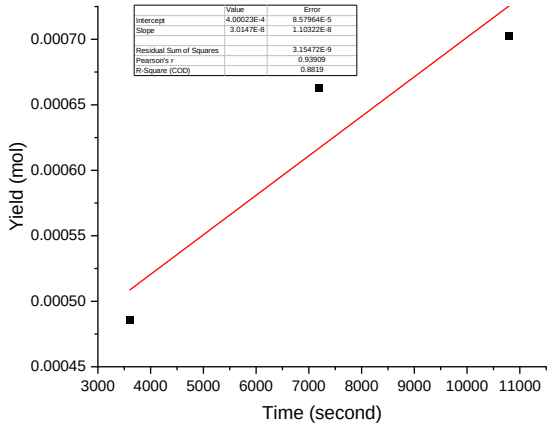


Figure 1. Reaction profile experiment was conducted under the standard conditions (1 = 0.1 mmol, [Co] = 0.005 mmol, $^{i}Pr_2NEt$ = 0.2 mmol, CH_3CN = 1 ml).

The conversion was determined using n-dodecane as an internal standard.

Determination of Initial rate

Time (s)	3600	7200	10800
Product (%)	48.56	66.29	70.26
Product (mol × 10^{-4})	4.856	6.629	7.026



From the slope of the plot, the initial rate of this reaction is determined as 3.014 × 10^{-8} mol/s.

Determination of Quantum yield

The quantum yield was determined in similar procedure to the literature.[15-17]

Preparation of potassium ferrioxalate solution:

118 mg of solid potassium ferrioxalate trihydrate, and 56 µL of H_2SO_4 were diluted with H_2O to a finale volume of 20 mL.

Preparation of buffer solution:

2.48 g of NaOAc and 0.5 ml of H_2SO_4 were diluted with H_2O to a finale volume of 50 mL.

Using the same setup as for catalytic reactions, 2 mL of the potassium ferrioxalate solution were irradiated for 10 sec. The sample solution was added to of 4 mL of the buffer solution containing 2 mg 1,10-phenanthroline and diluted with H_2O to a finale volume of 10 mL.

Subsequently the absorbance of this solution was determined at 510 nm by Avantes with a 1-xmm-tip. The same procedure was followed for an unirradiated sample.

Calculation Number of Photons:

Abs of Fe^{2+} (at 510 nm) = 0.6670 (after irradiation of 10 sec)

Abs of Fe^{2+} (at 510 nm) = 0.1225 (no irradiation)

Abs of Fe^{2+} (at 510 nm) = 0.6670 - 0.1225 = 0.5445

Mol of Fe^{2+}:

$$n_{Fe^{2+}} = \frac{\text{Abs of } Fe^{2+}(\text{at 510 nm}) \times V}{\varepsilon_{510\,nm} \times l} = \frac{0.5445 \times 0.01\ L}{11100\ M^{-1}cm^{-1} \times 0.1\ cm} = 4.905 \times 10^{-6}\ mol$$

With quantum yield of 0.805 for the absorption of ferrioxalate actinometer [1], number of photons generated by the Blue LED:

$$n_{(photons)} = \frac{n_{Fe^{2+}}}{\phi} = \frac{4.905 \times 10^{-6}\ mol}{0.805} = 6.093 \times 10^{-6}\ mol$$

The photon flux of the Blue LED:

$$n_{(photons/s)} = \frac{n_{(photons)}}{t} = \frac{6.093 \times 10^{-6}\ mol}{10} = 6.093 \times 10^{-7}\ mol/s$$

The initial rate of the desaturation of amine was determined to be 3.014×10^{-8} mol/s. Therefore, quantum yield for desaturation reaction:

$$\phi = \frac{n_{product/s}}{photons/s} = \frac{3.014 \times 10^{-8}\ mol/s}{6.093 \times 10^{-7}\ mol/s} = 0.049$$

10. References

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(3) Wang, C.; Azofra, L. M.; Dam, P.; Sebek, M.; Steinfeldt, N.; Rabeah, J.; El-Sepelgy, O. Catalytic Desaturation of Aliphatic Amides and Imides Enabled by Excited-State Base-Metal Catalysis. *ACS Catal* **2022**, *12*, 8868-8876.

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(5) Becke, A. D. A Multicenter Numerical Integration Scheme for Polyatomic Molecules. *J. Chem. Phys.* **1988**, *88* (4), 2547–2553.

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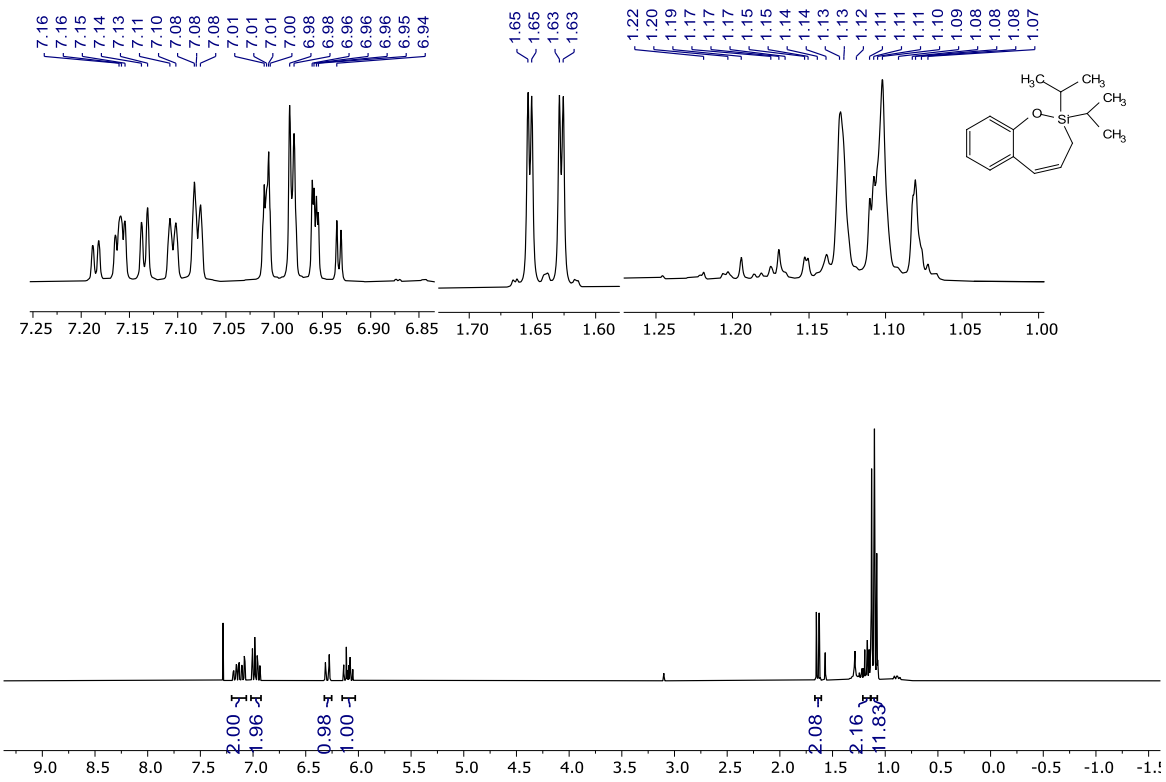
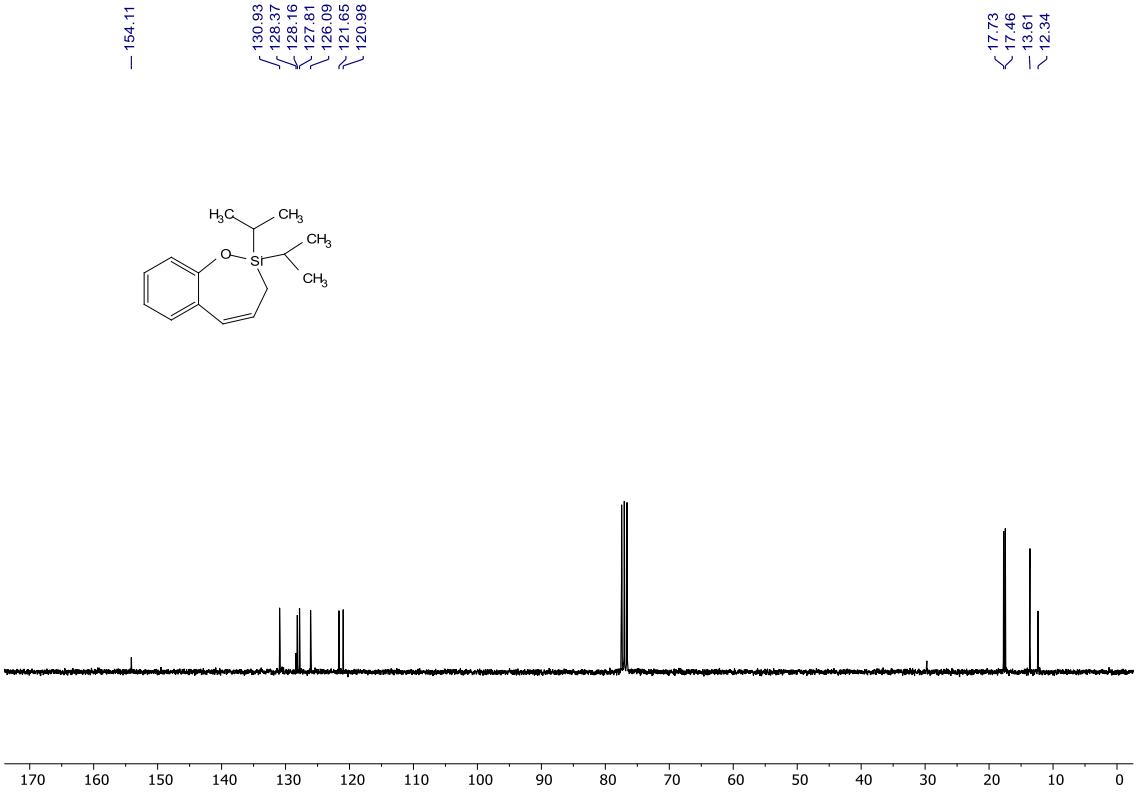
9. NMR spectra NMR spectra



^{1}H NMR spectrum of compound **2a** (300 MHz, $CDCl_3$)



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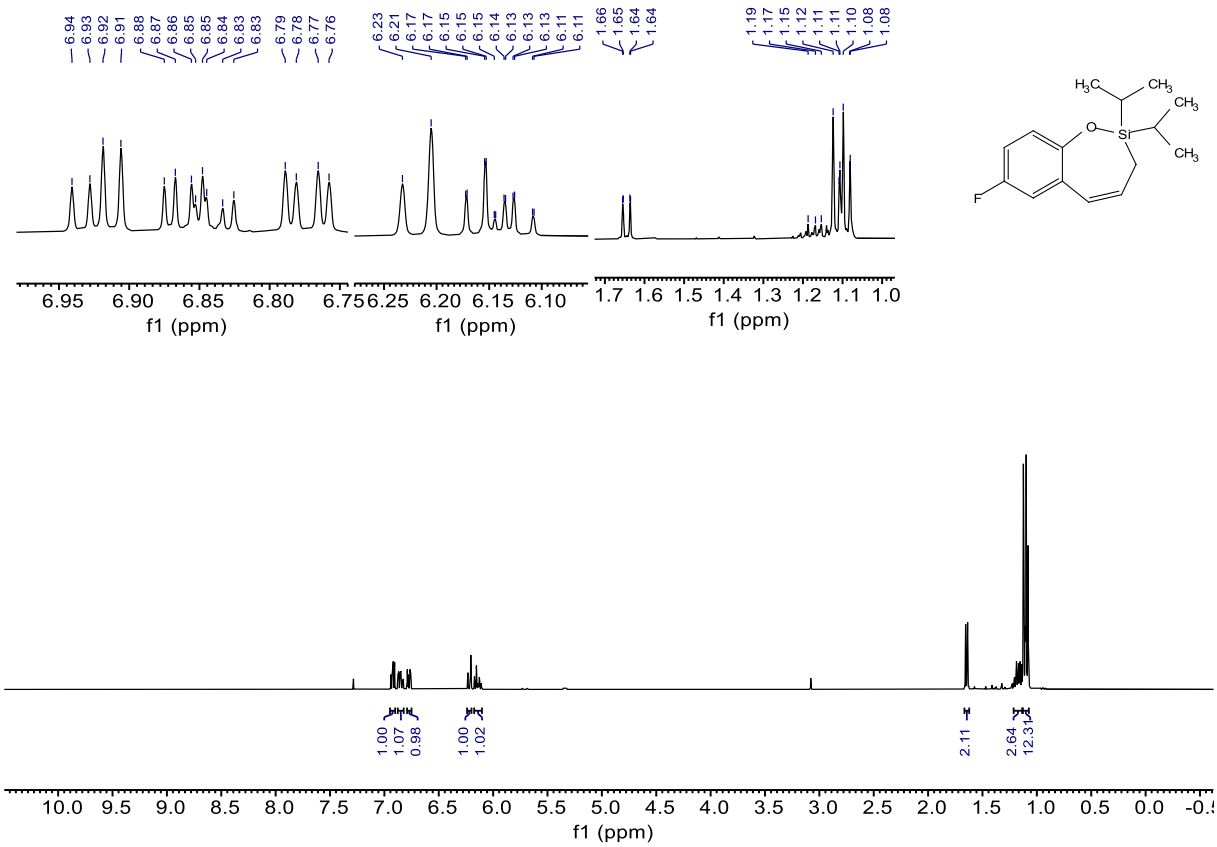

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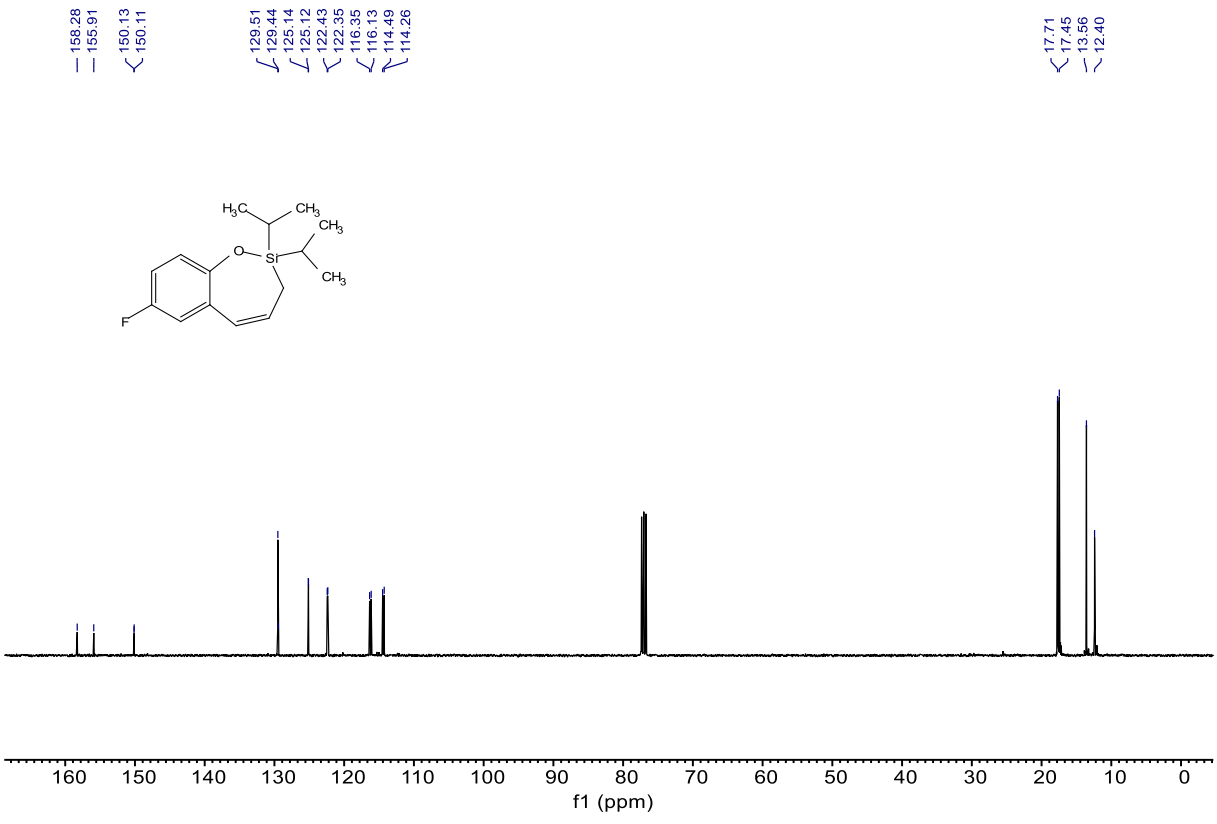
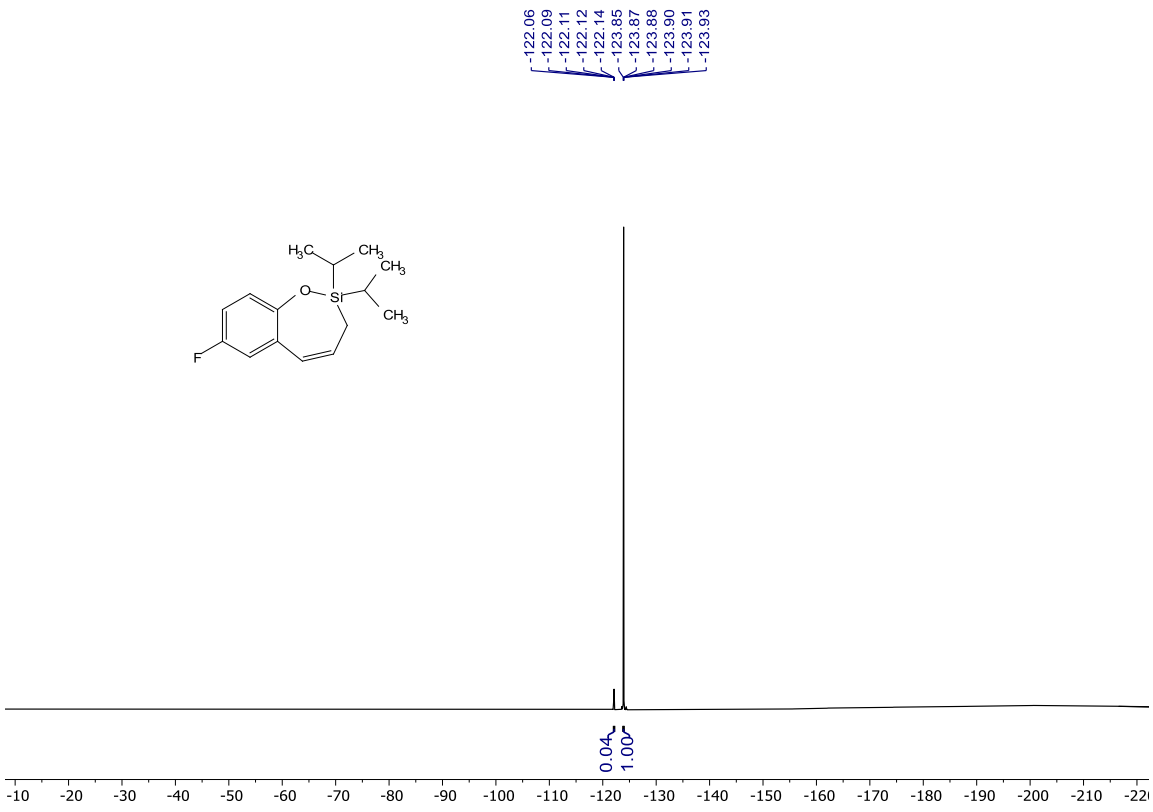
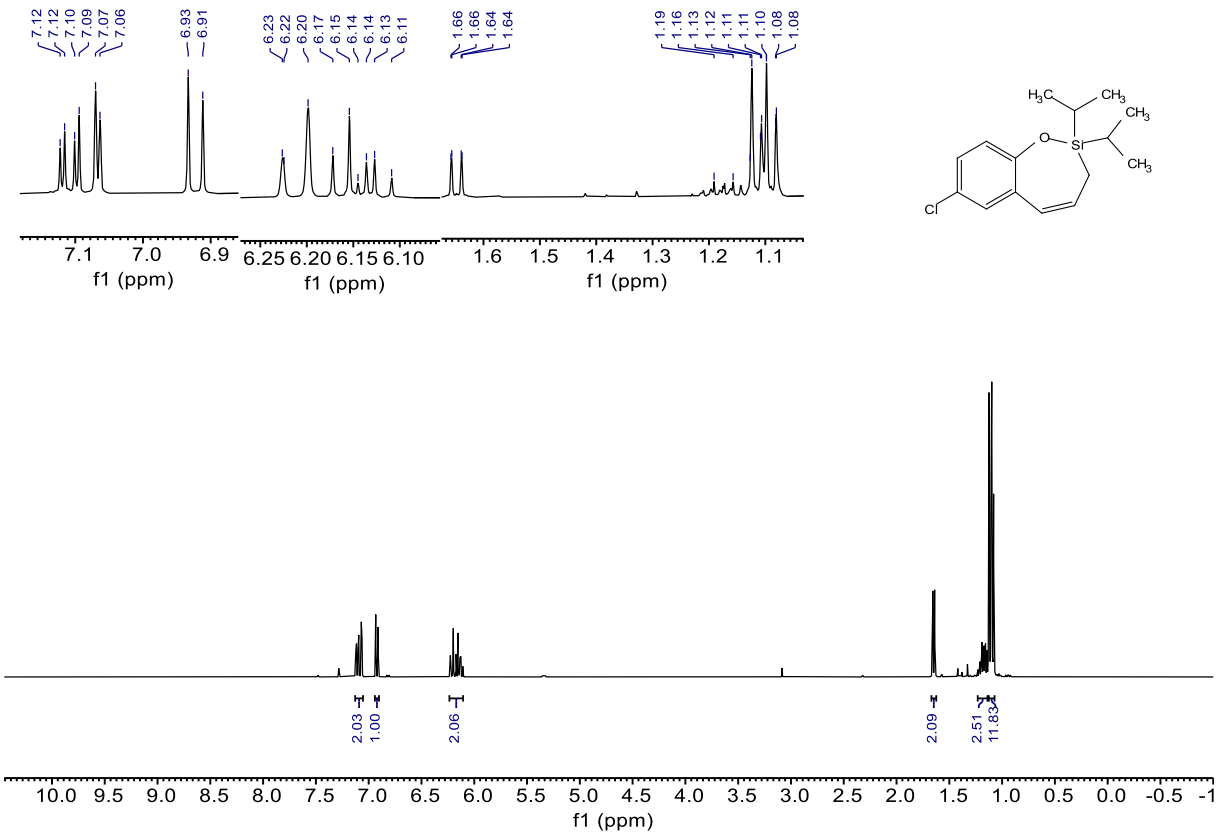


^{13}C NMR spectrum of compound **2b** (101 MHz, $CDCl_3$)



^{19}F NMR spectrum of compound **2b** (282 MHz, $CDCl_3$)



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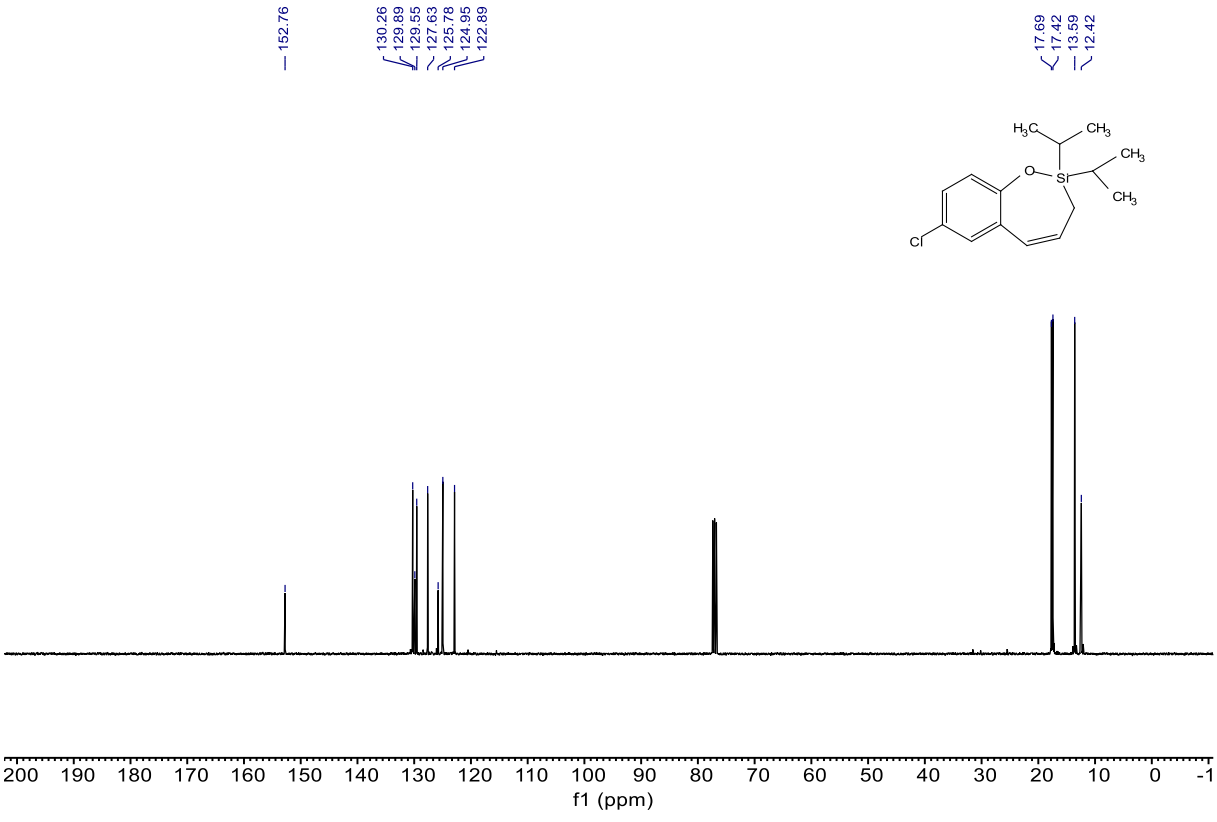
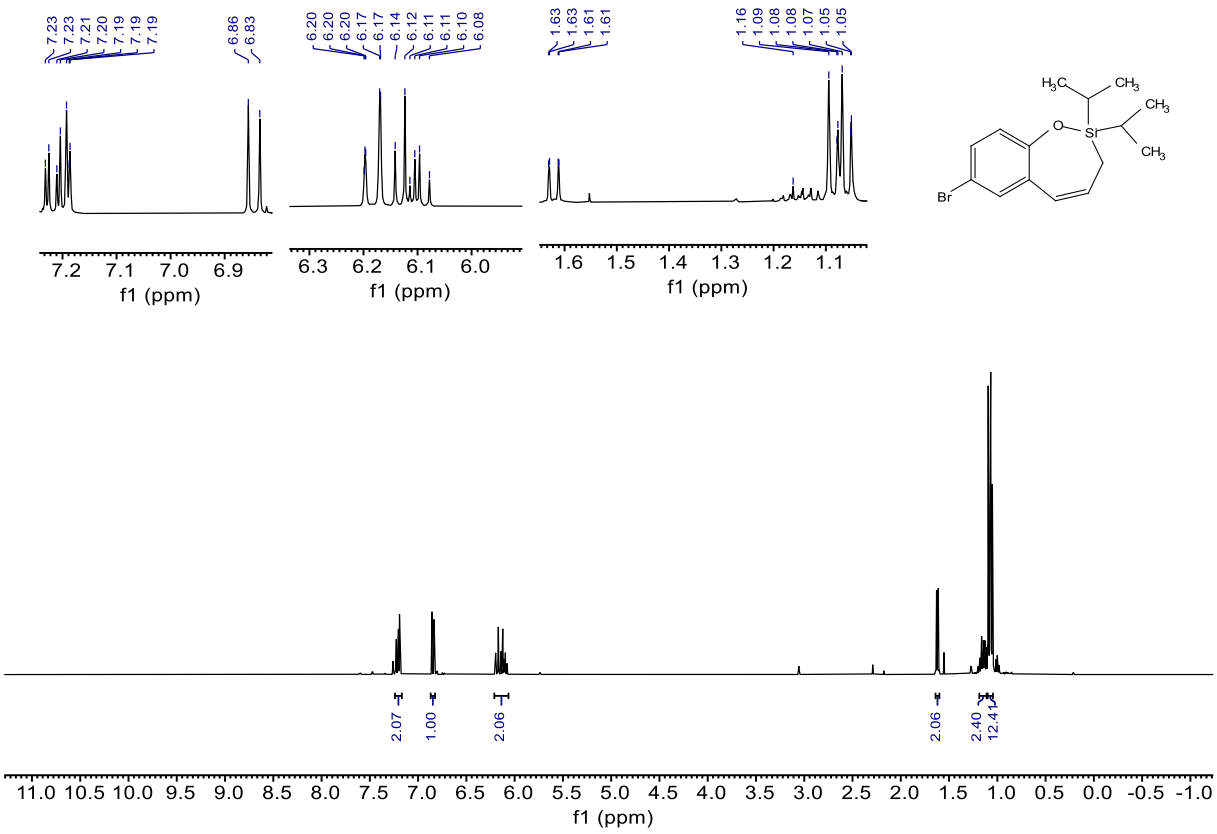
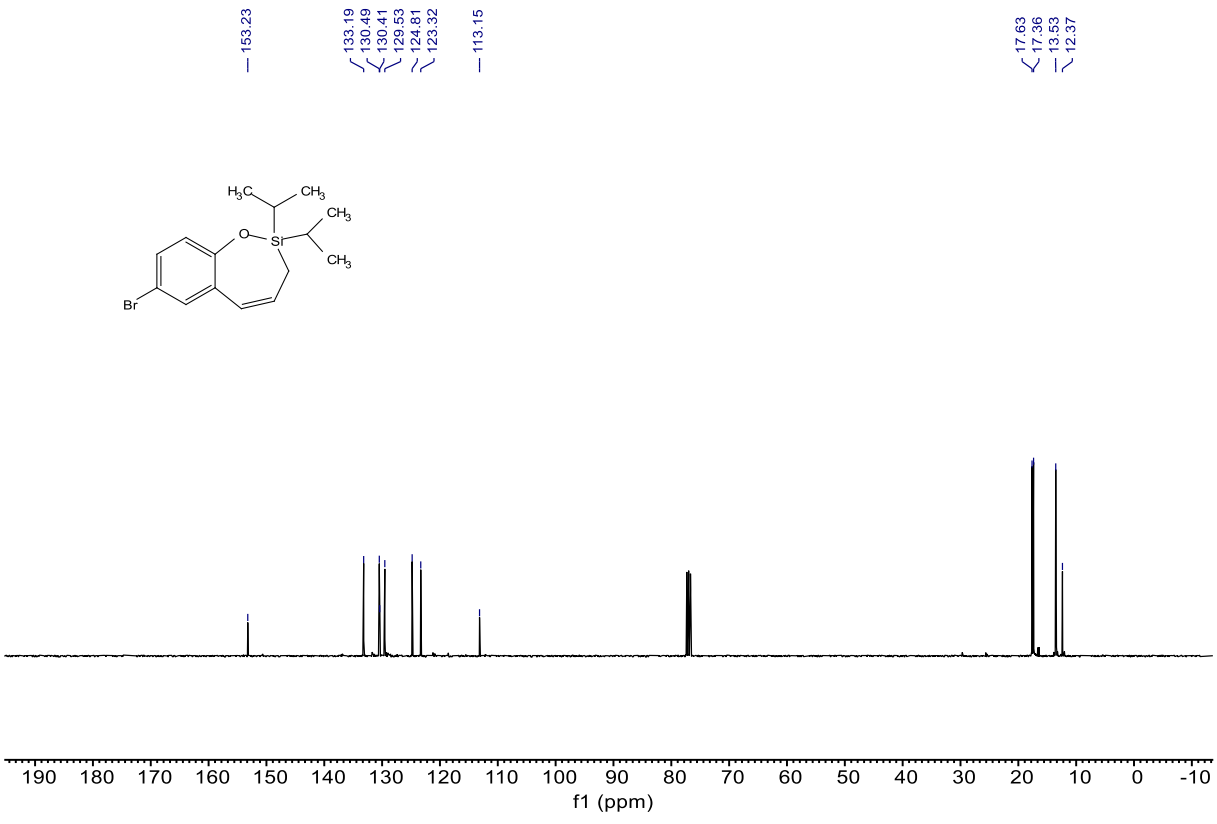


^{13}C NMR spectrum of compound **2c** (101 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **2d** (400 MHz, $CDCl_3$)



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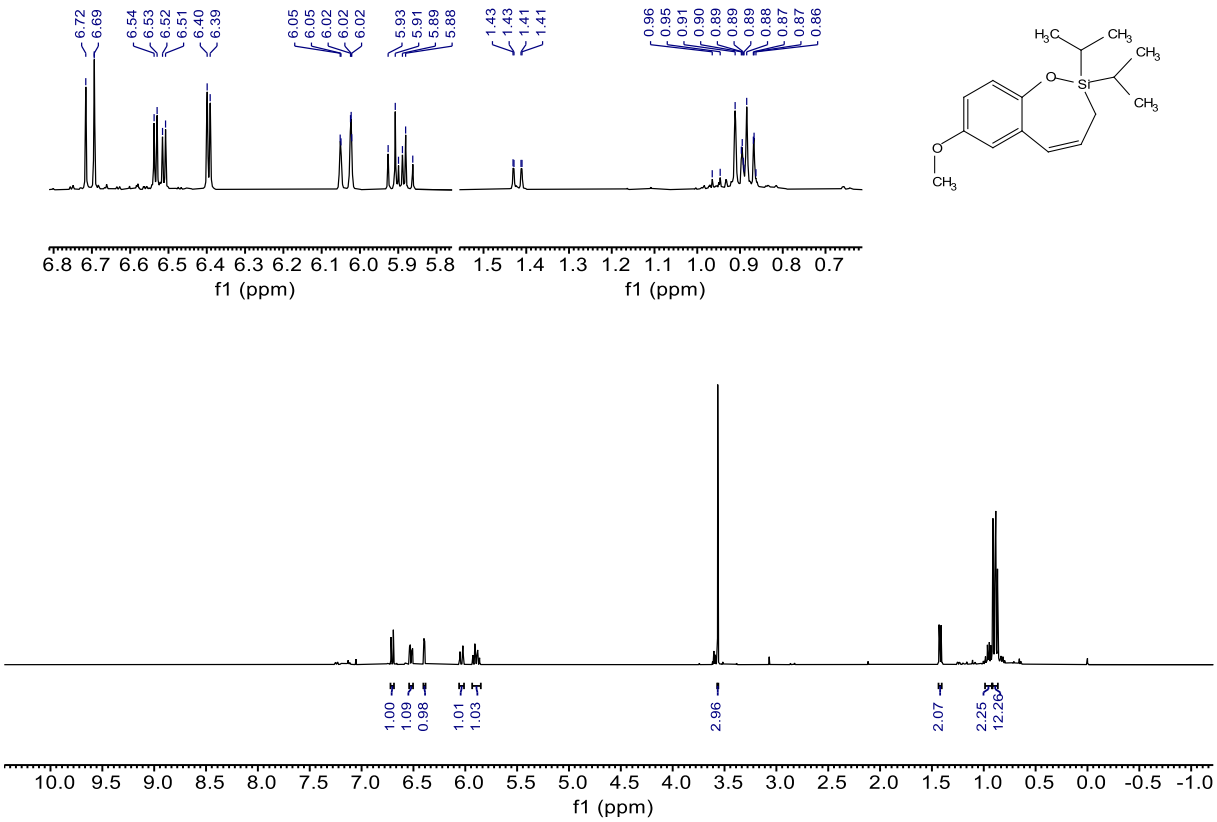

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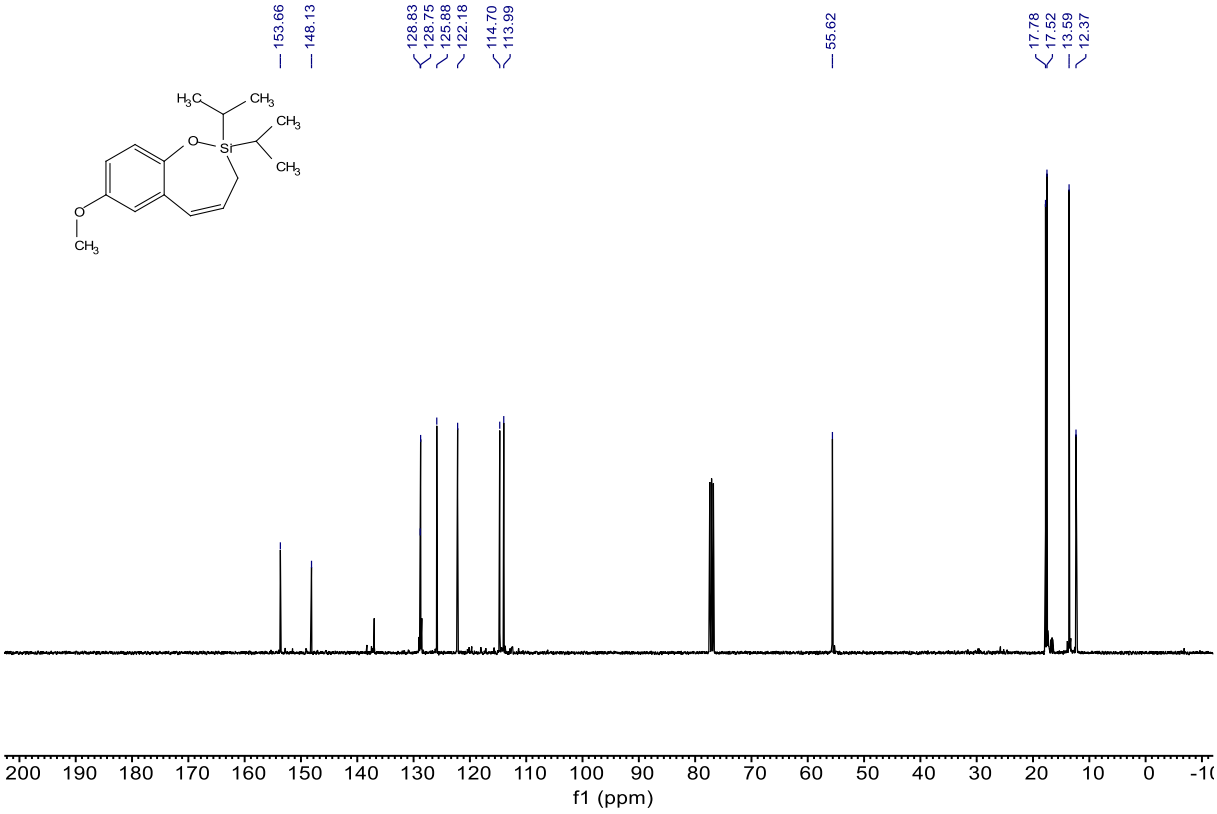

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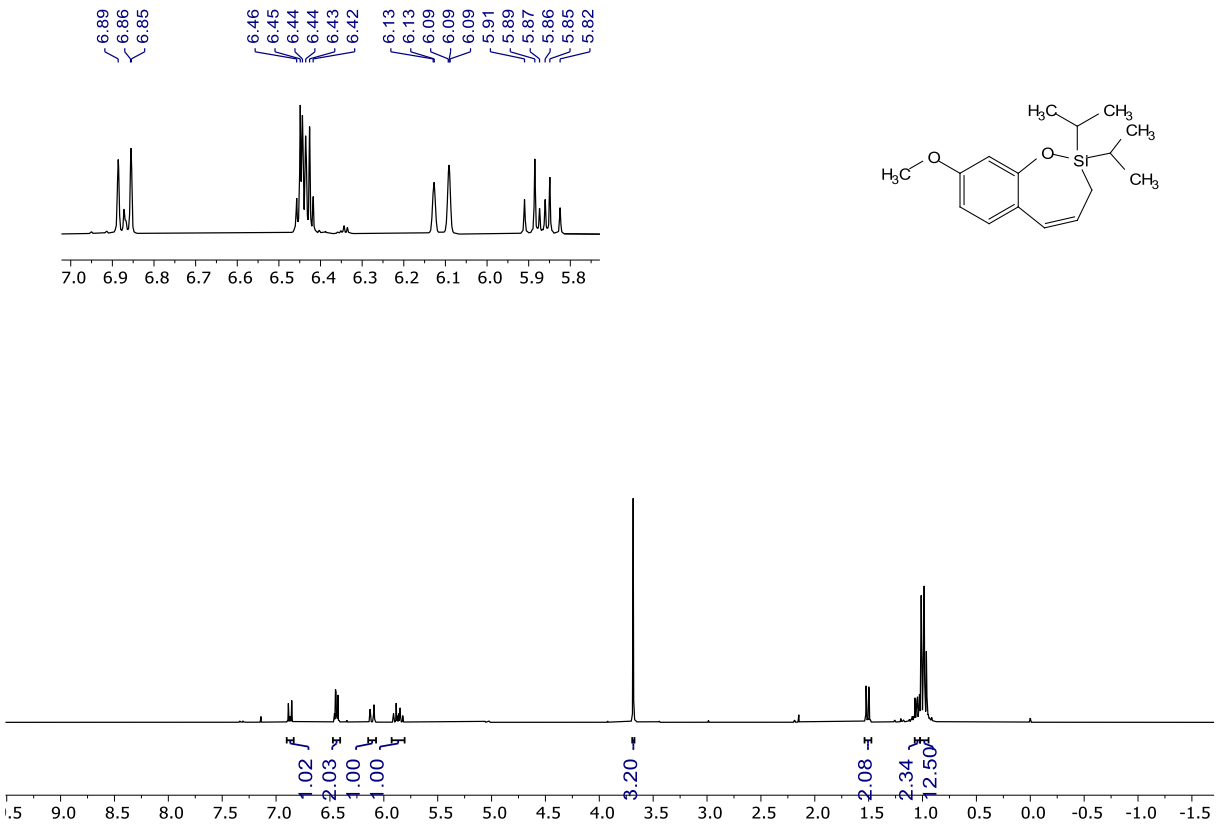
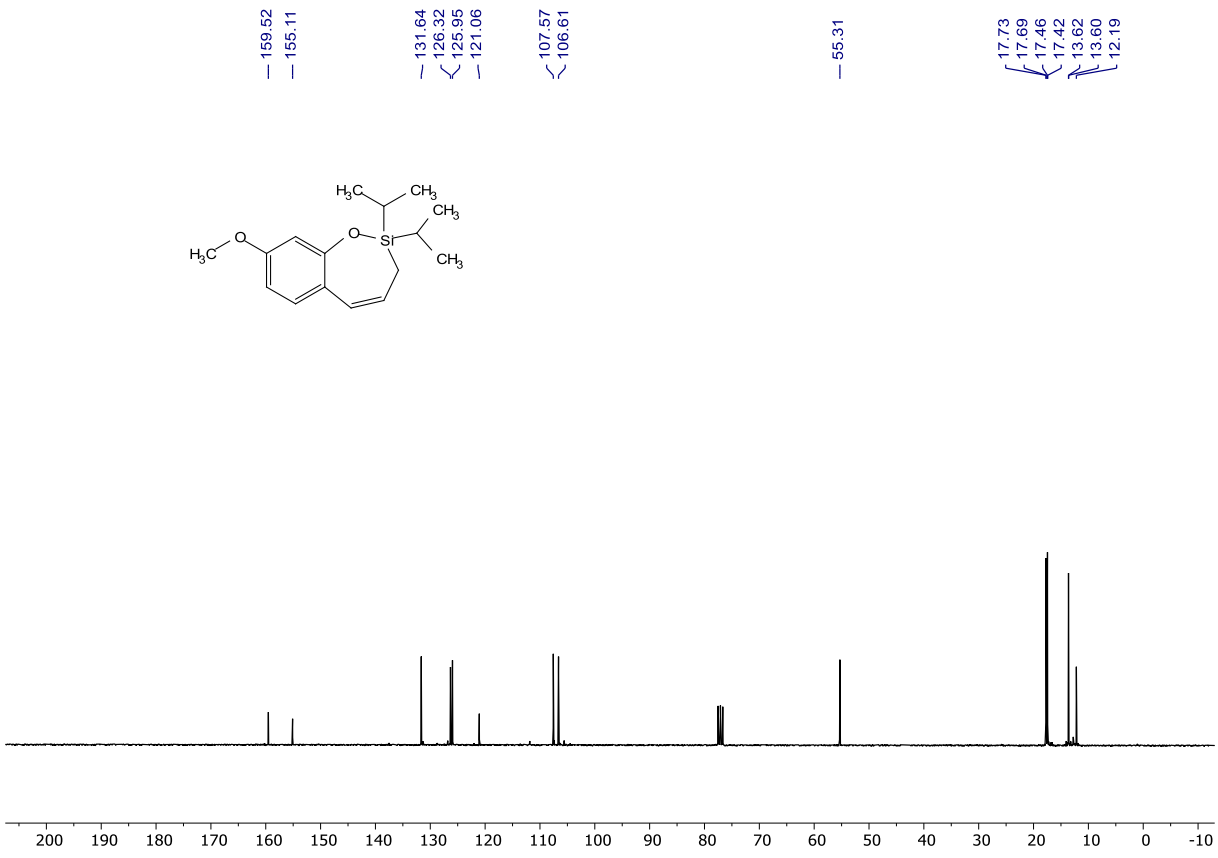


^{1}H NMR spectrum of compound **2f** (300 MHz, $CDCl_3$)



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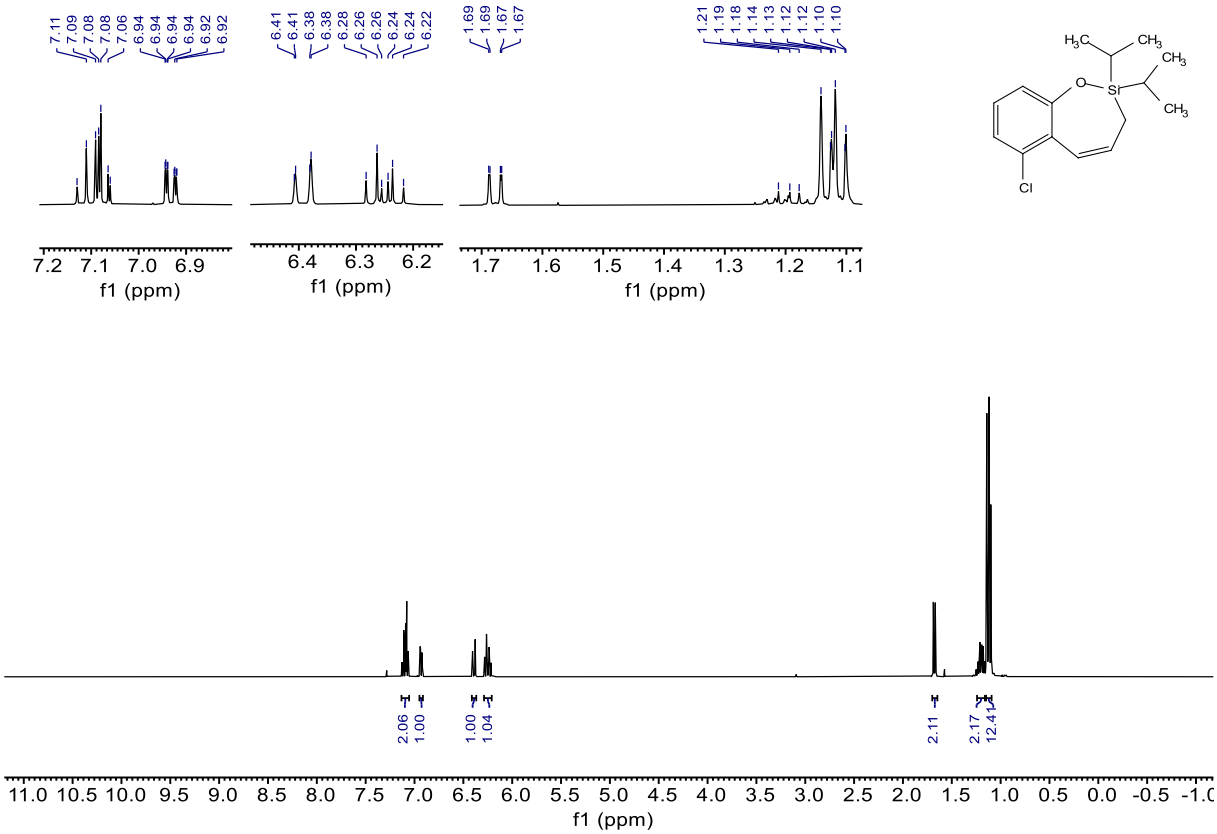

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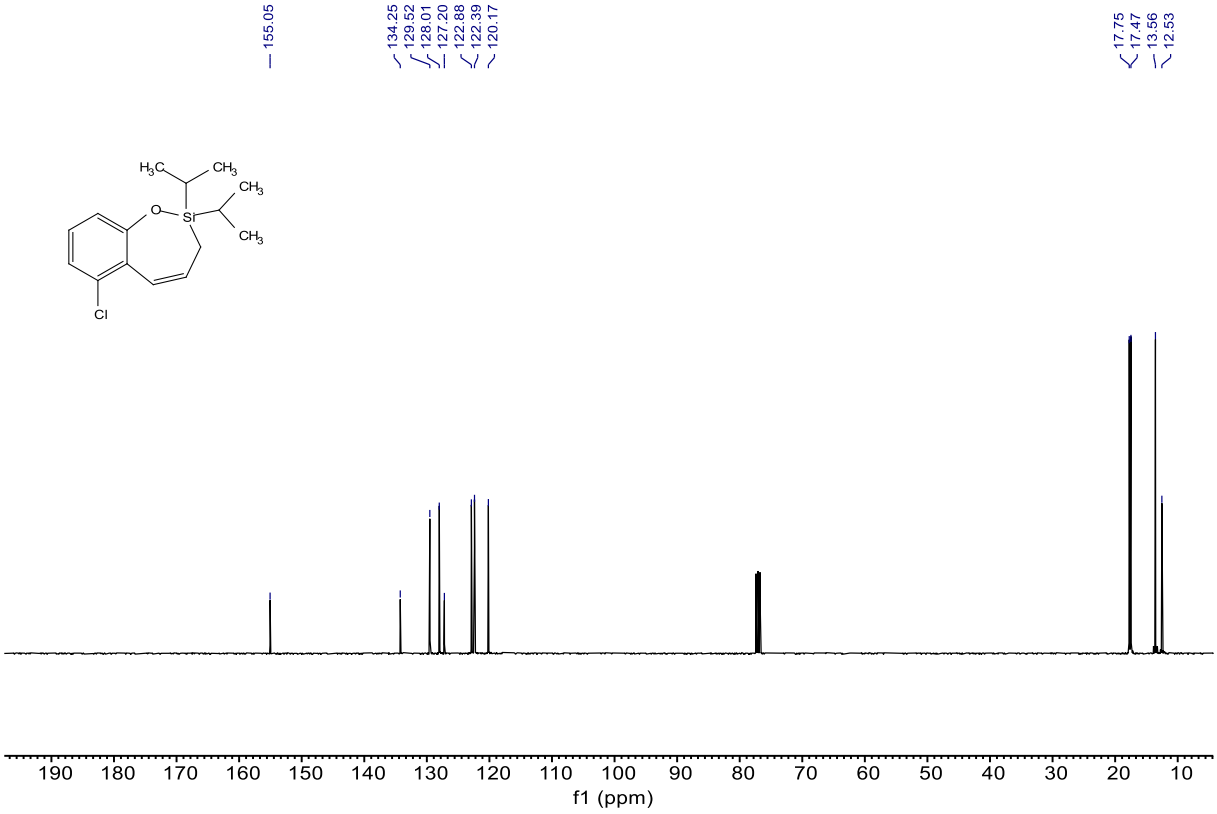

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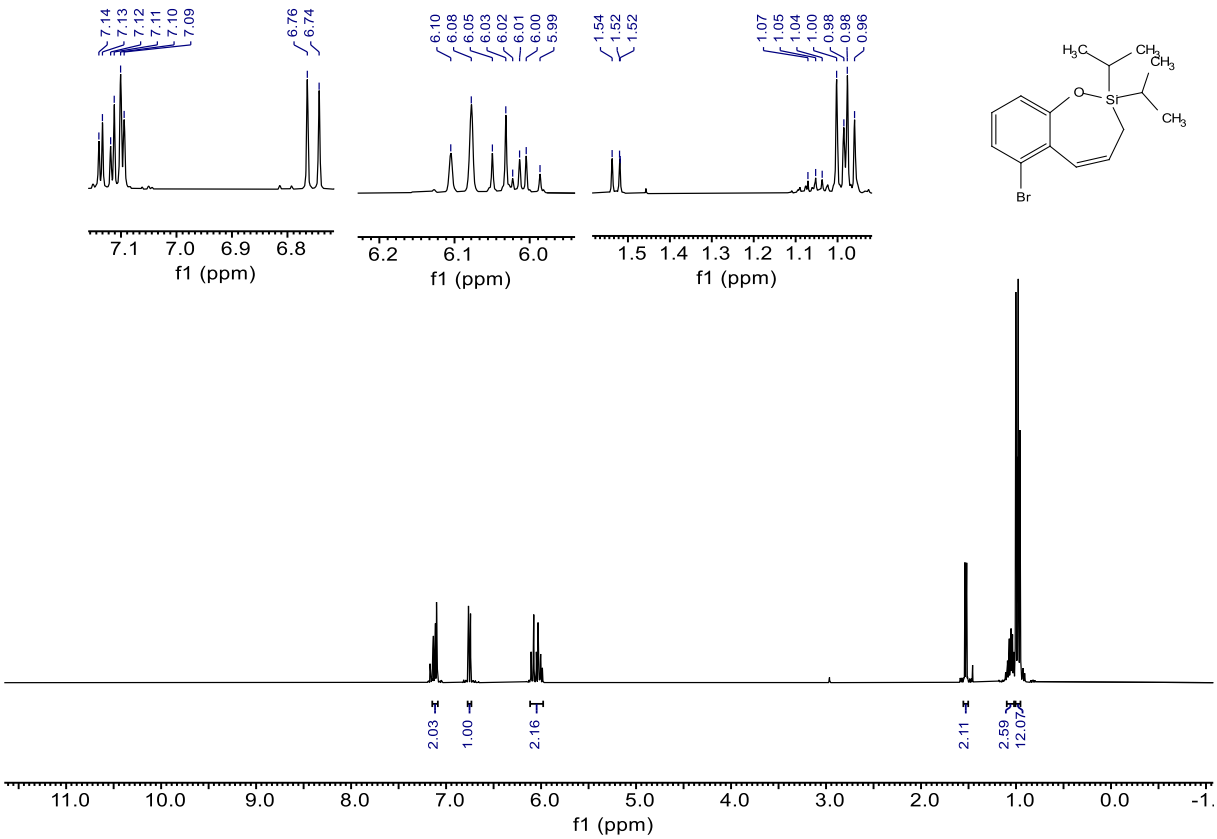
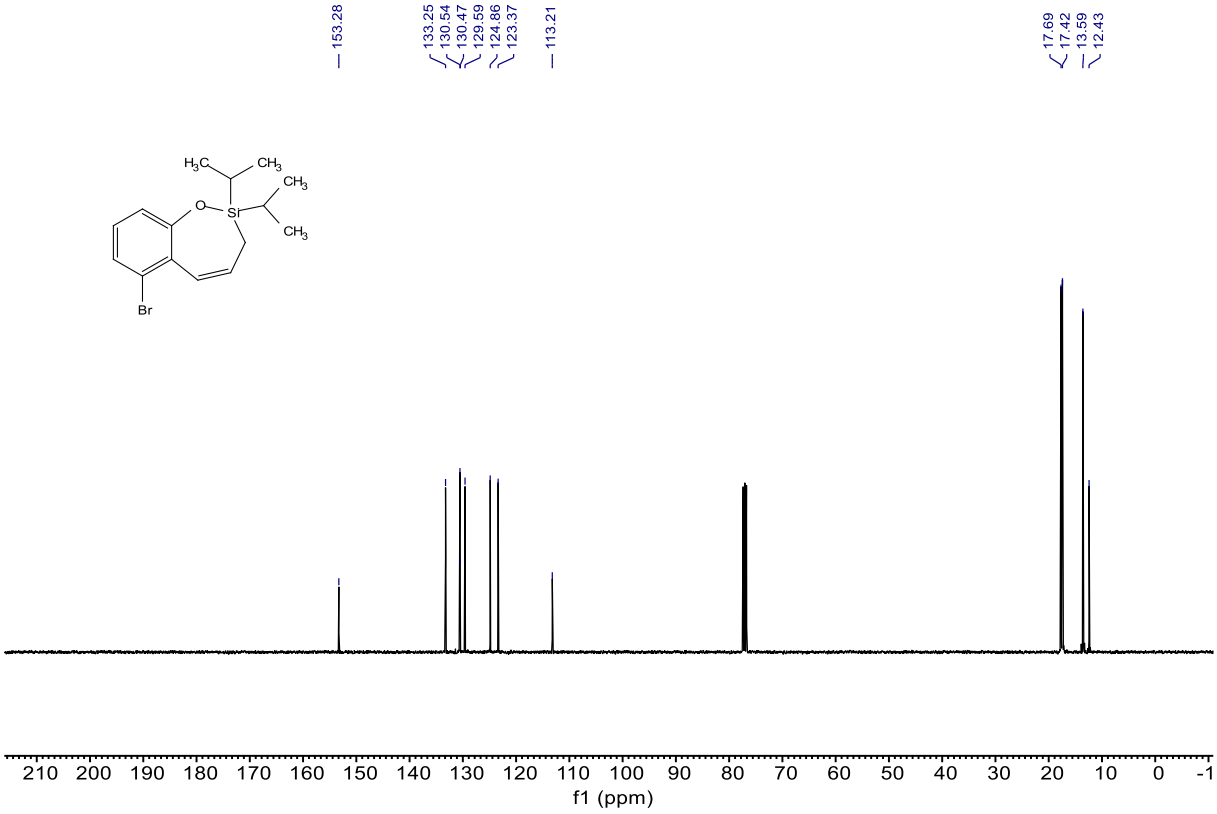


^{1}H NMR spectrum of compound **2h** (400 MHz, $CDCl_3$)



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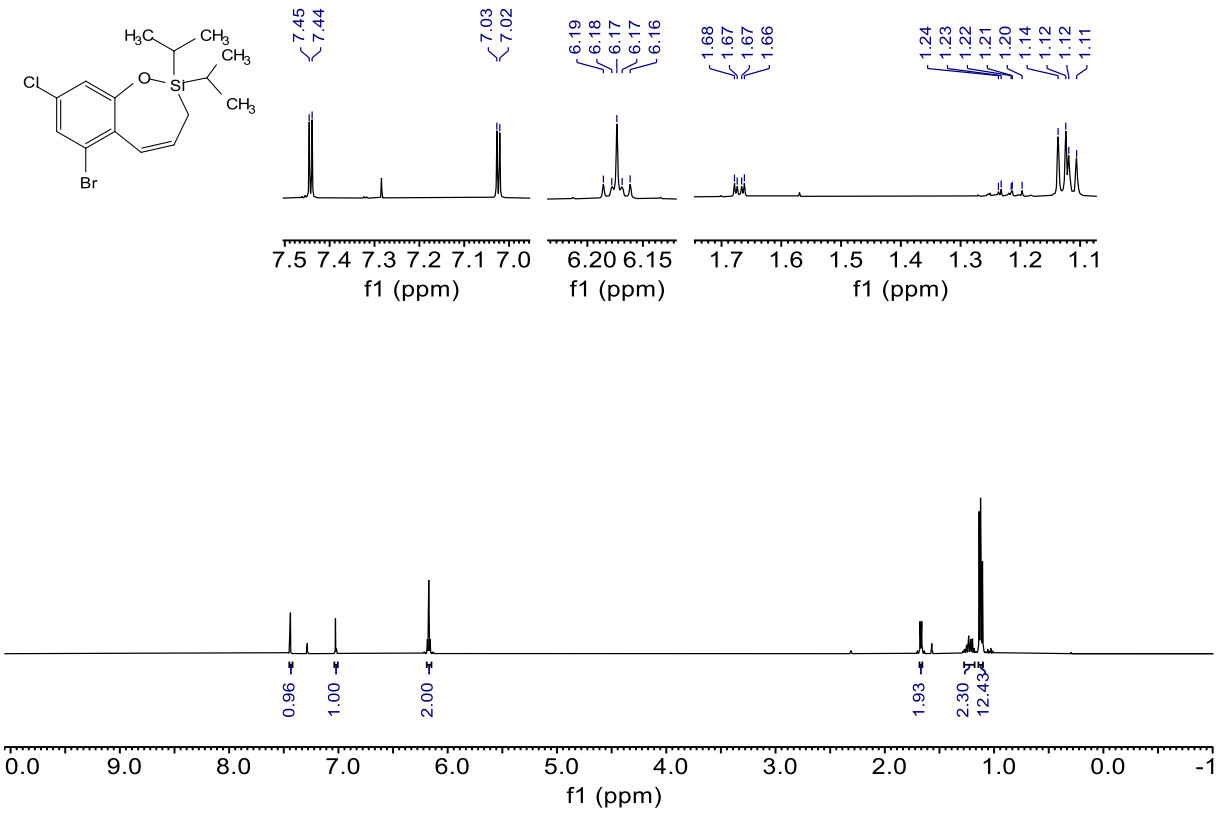
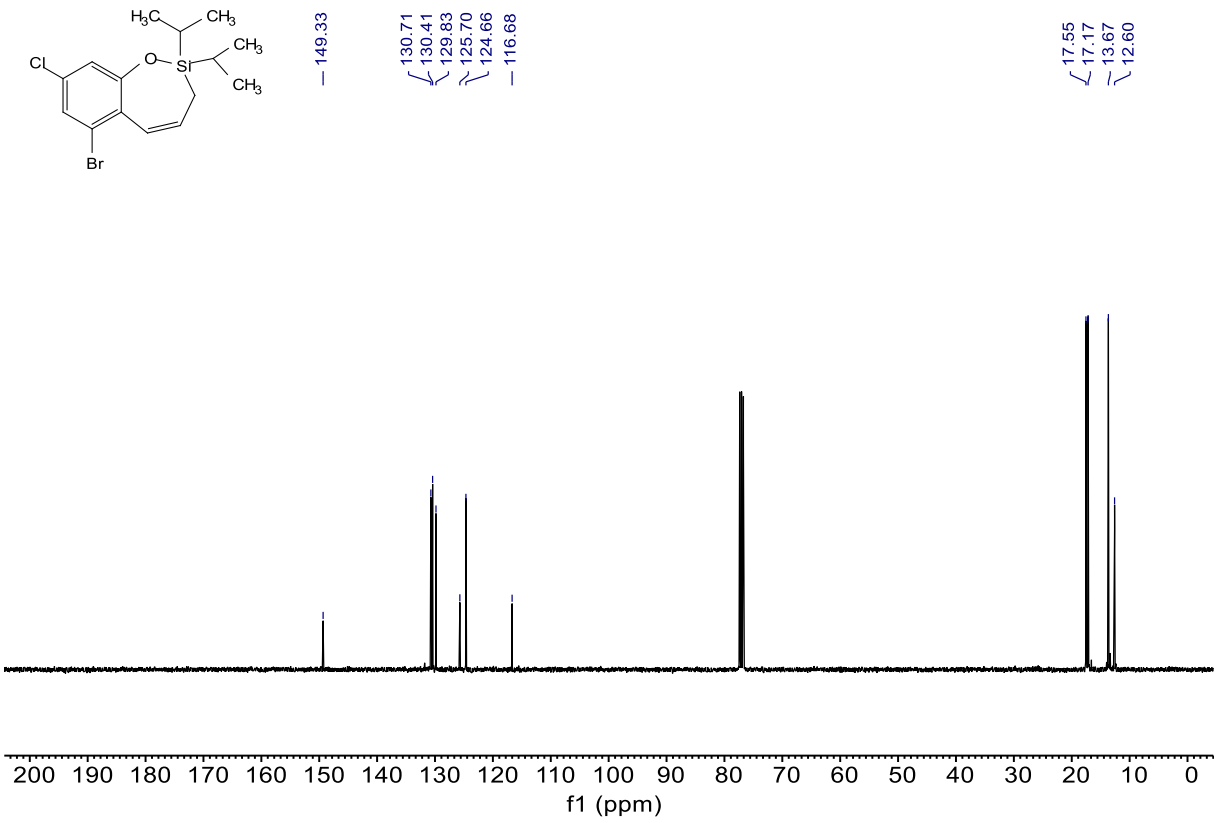


^{1}H NMR spectrum of compound **2i** (400 MHz, $CDCl_3$)



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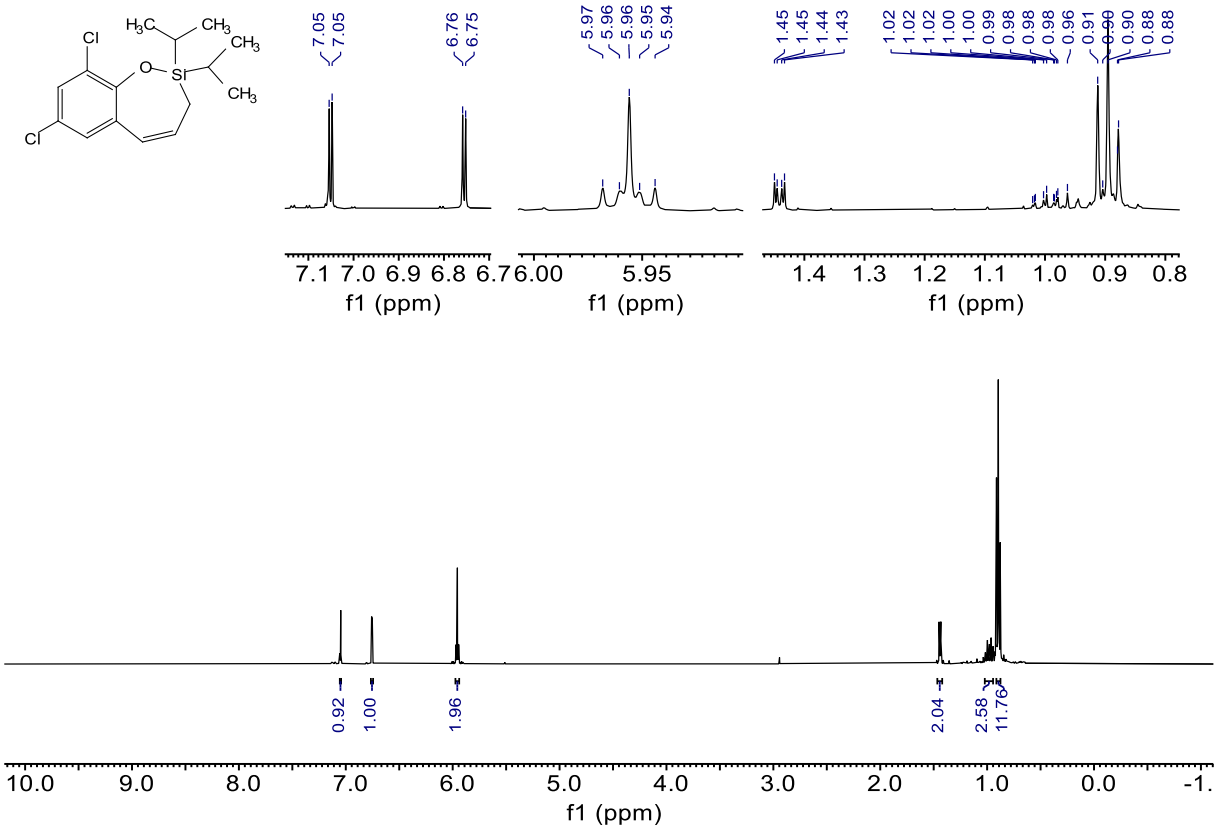

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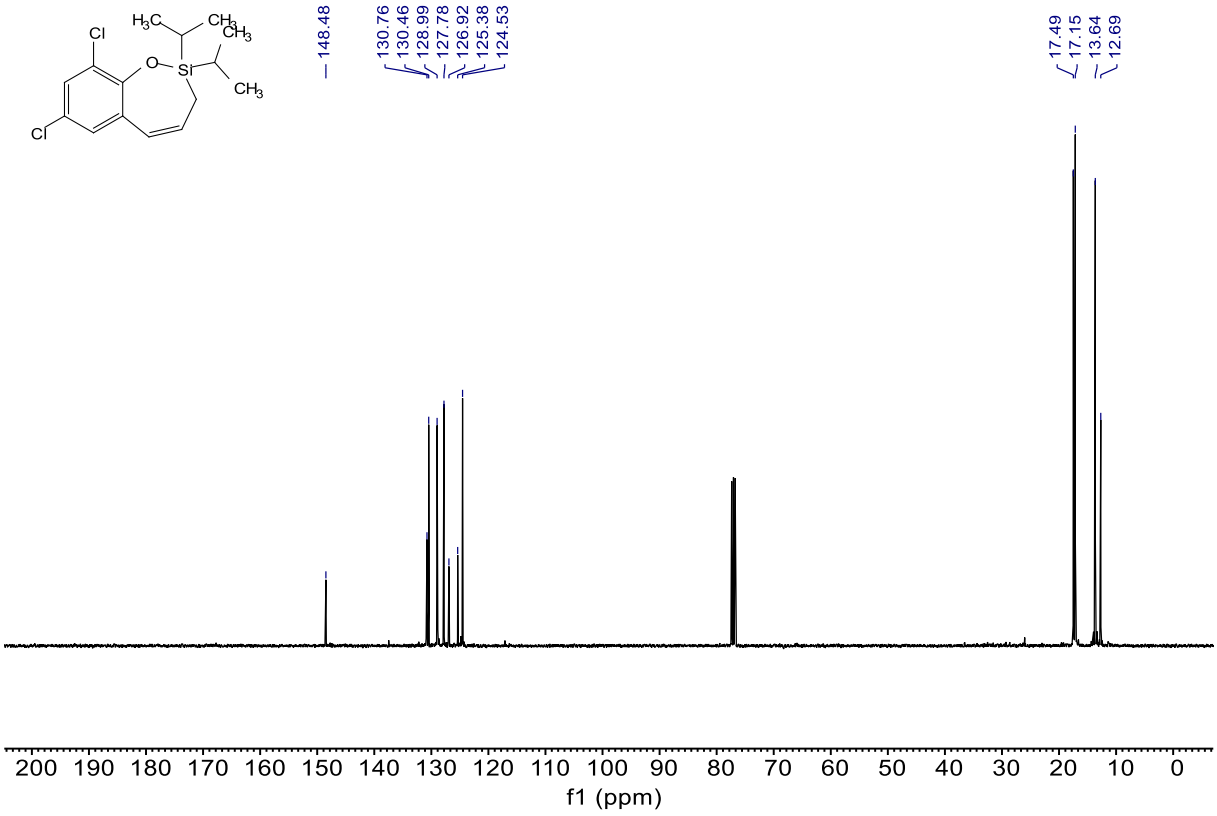

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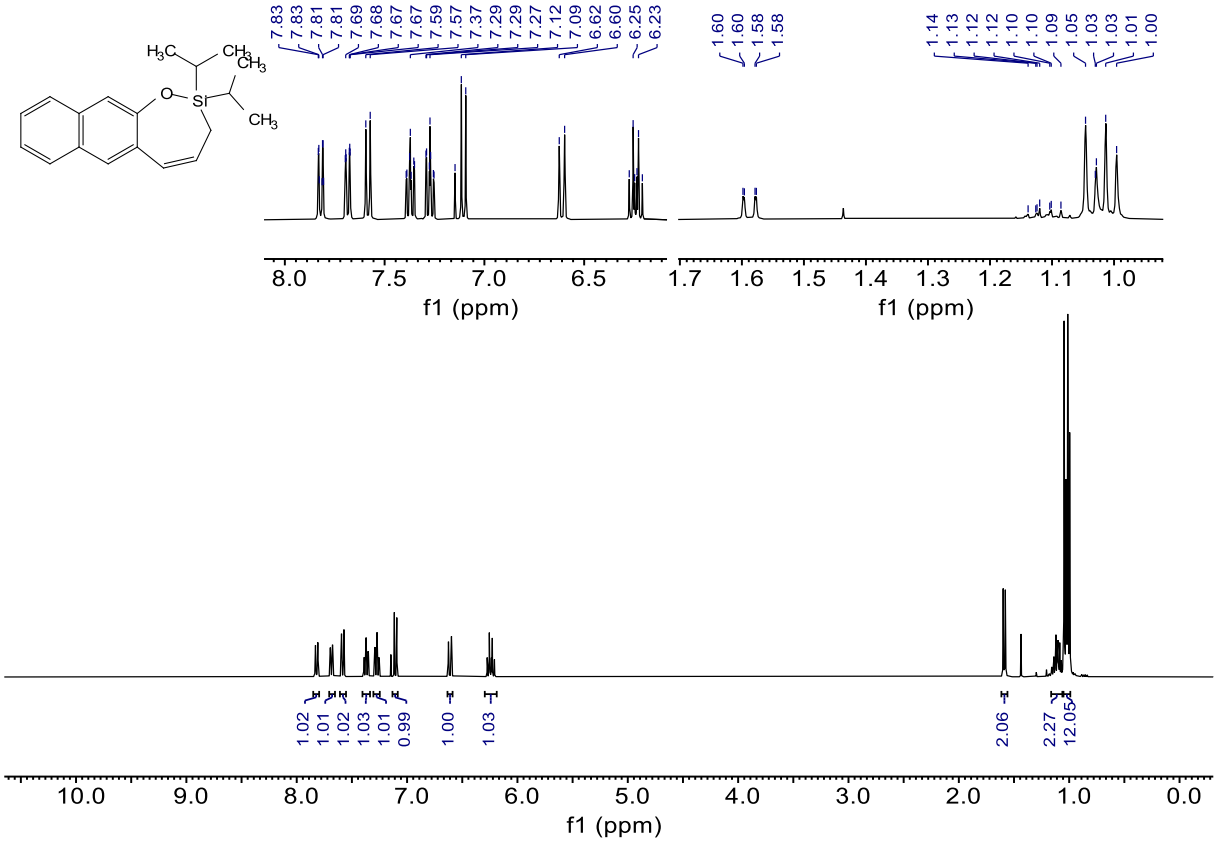

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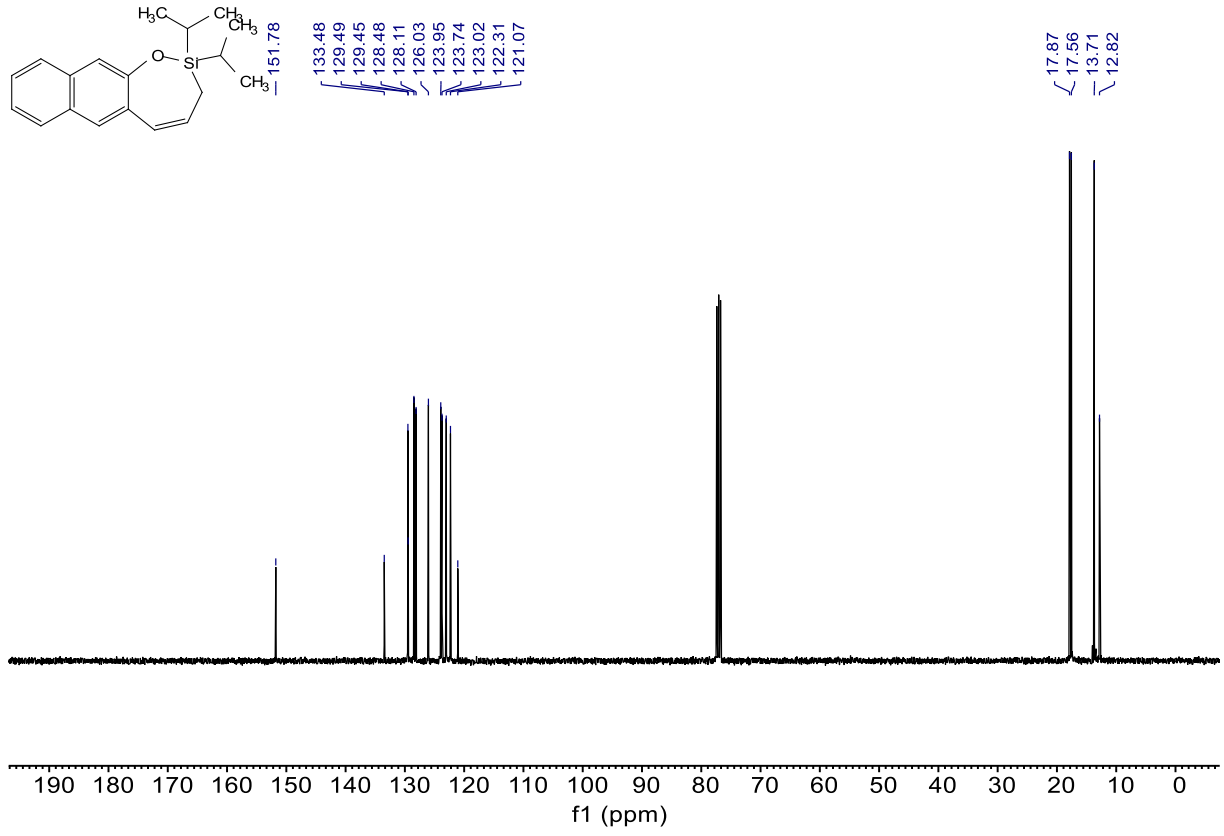

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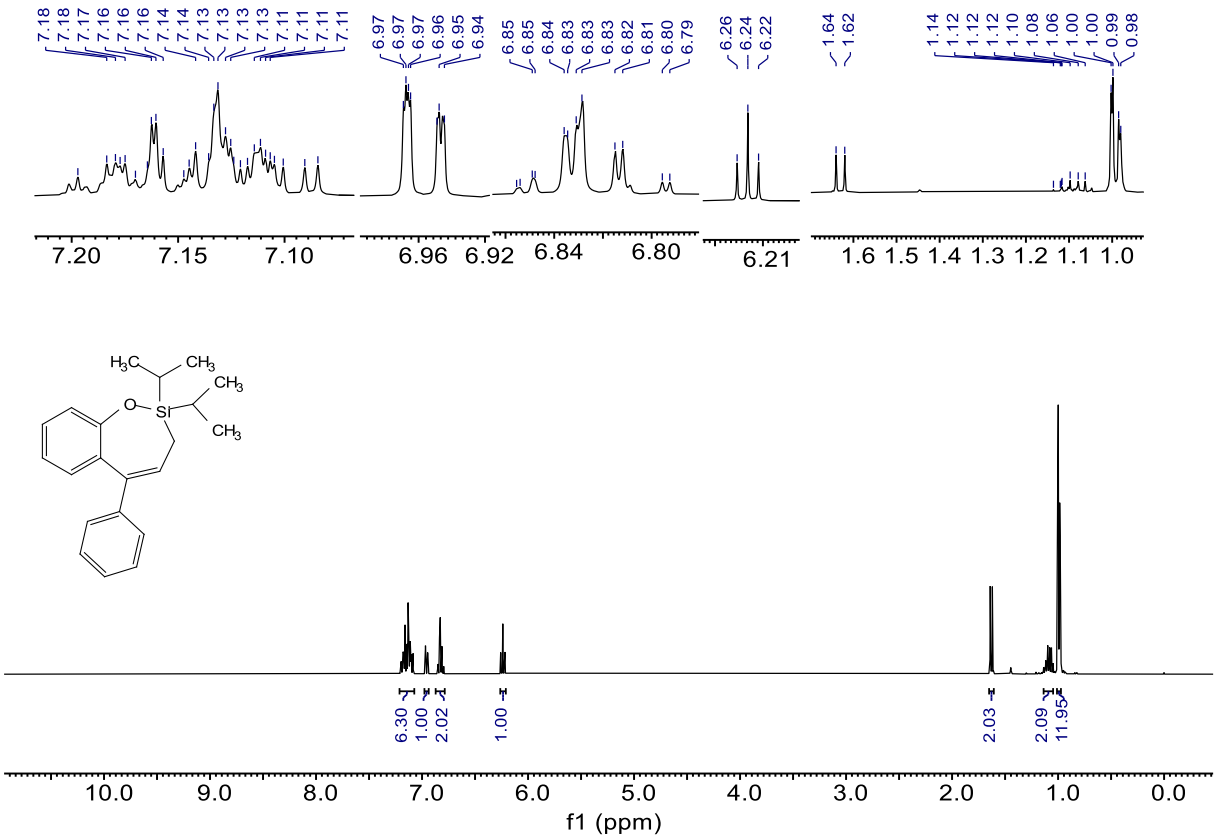

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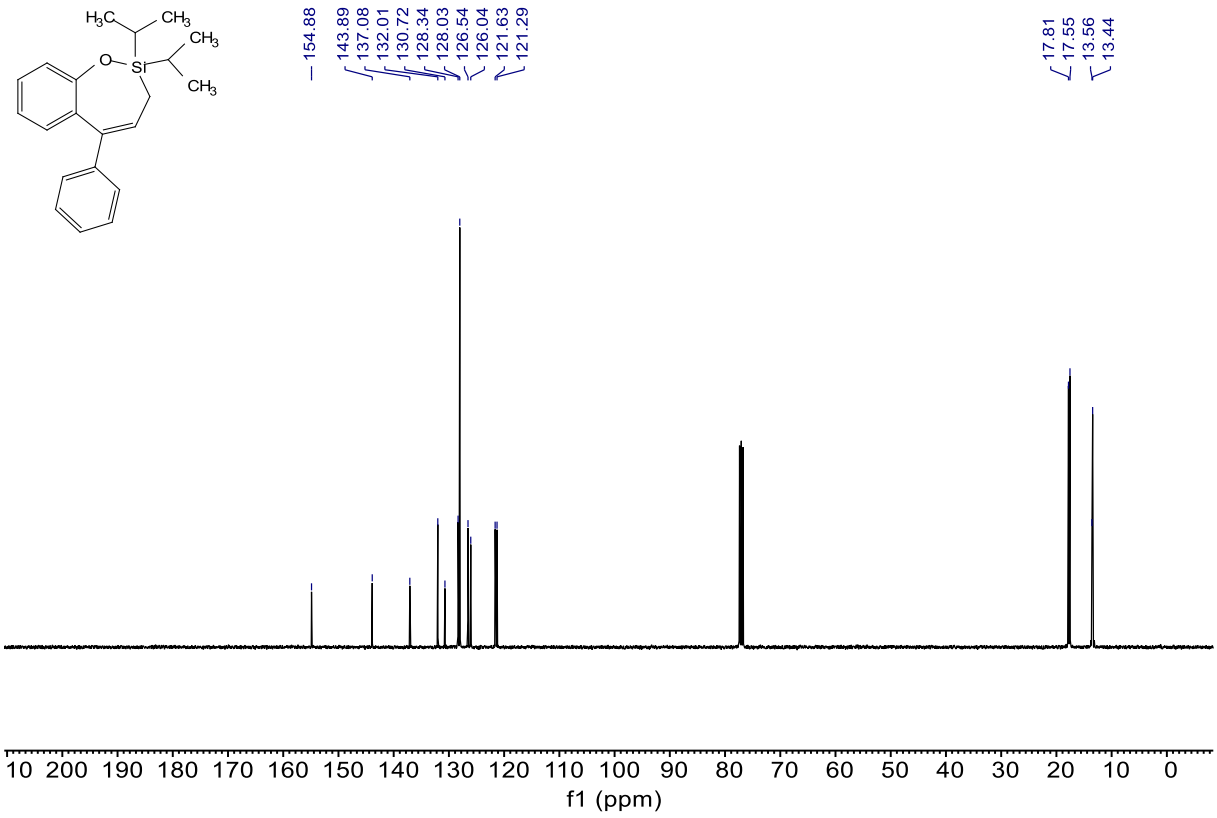

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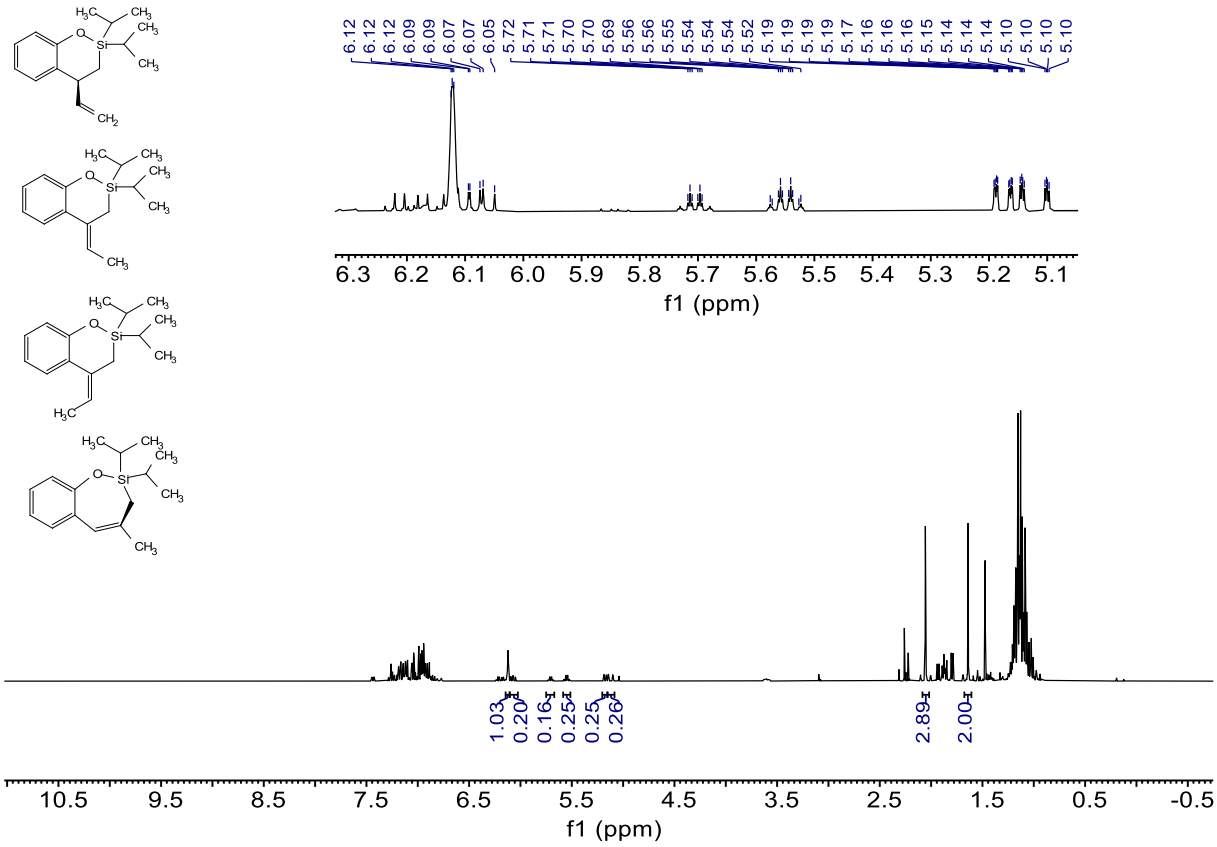
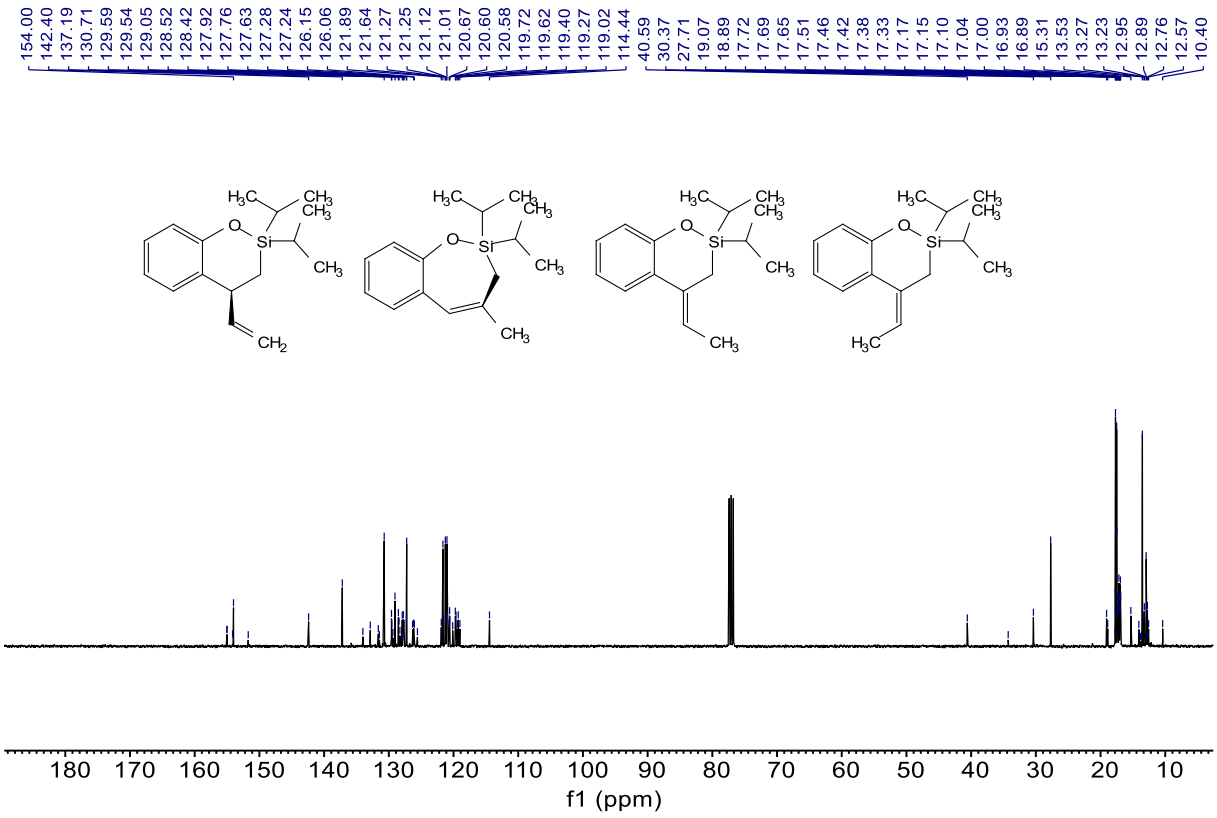


^{1}H NMR spectrum of compound **2m, 2m'**, **2m"** and **2m"'** (400 MHz, $CDCl_3$)



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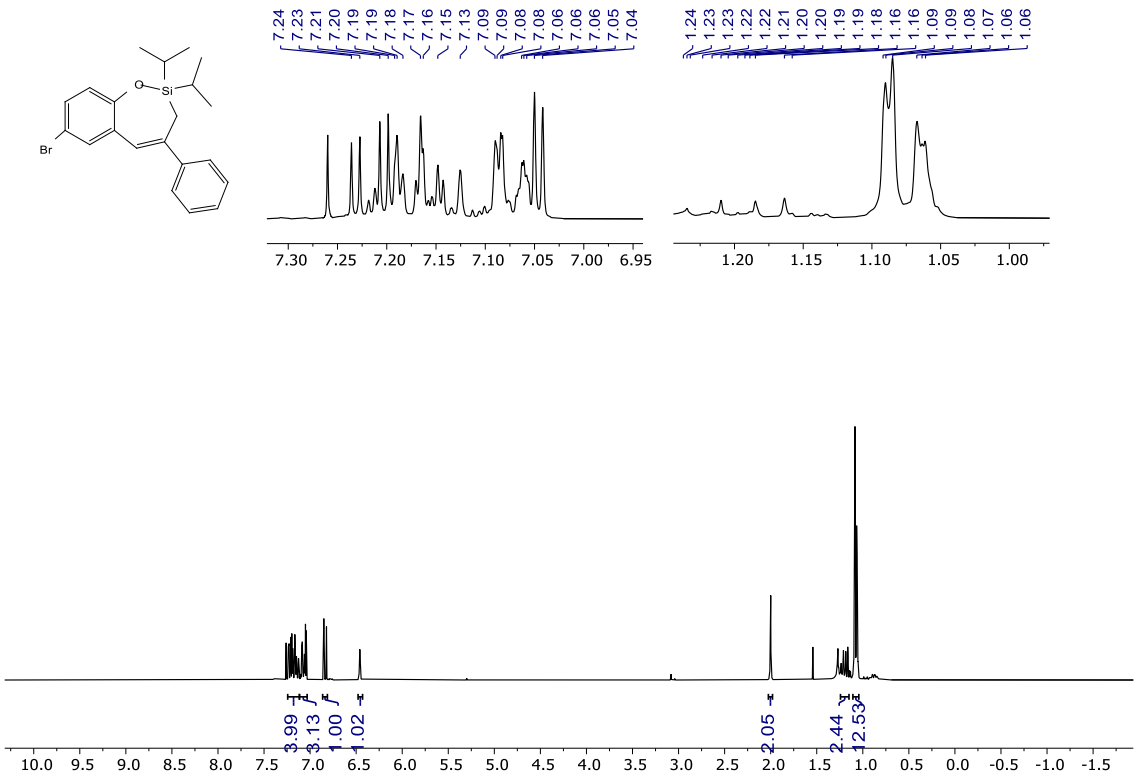

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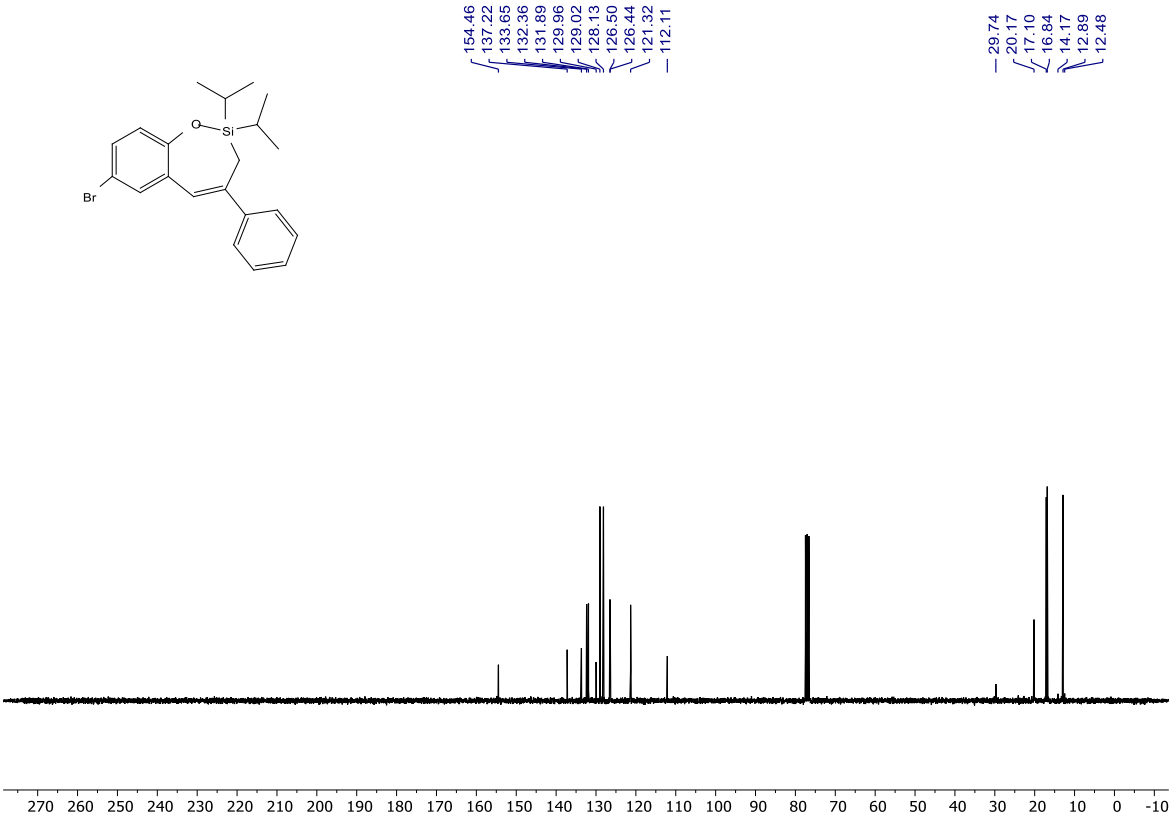

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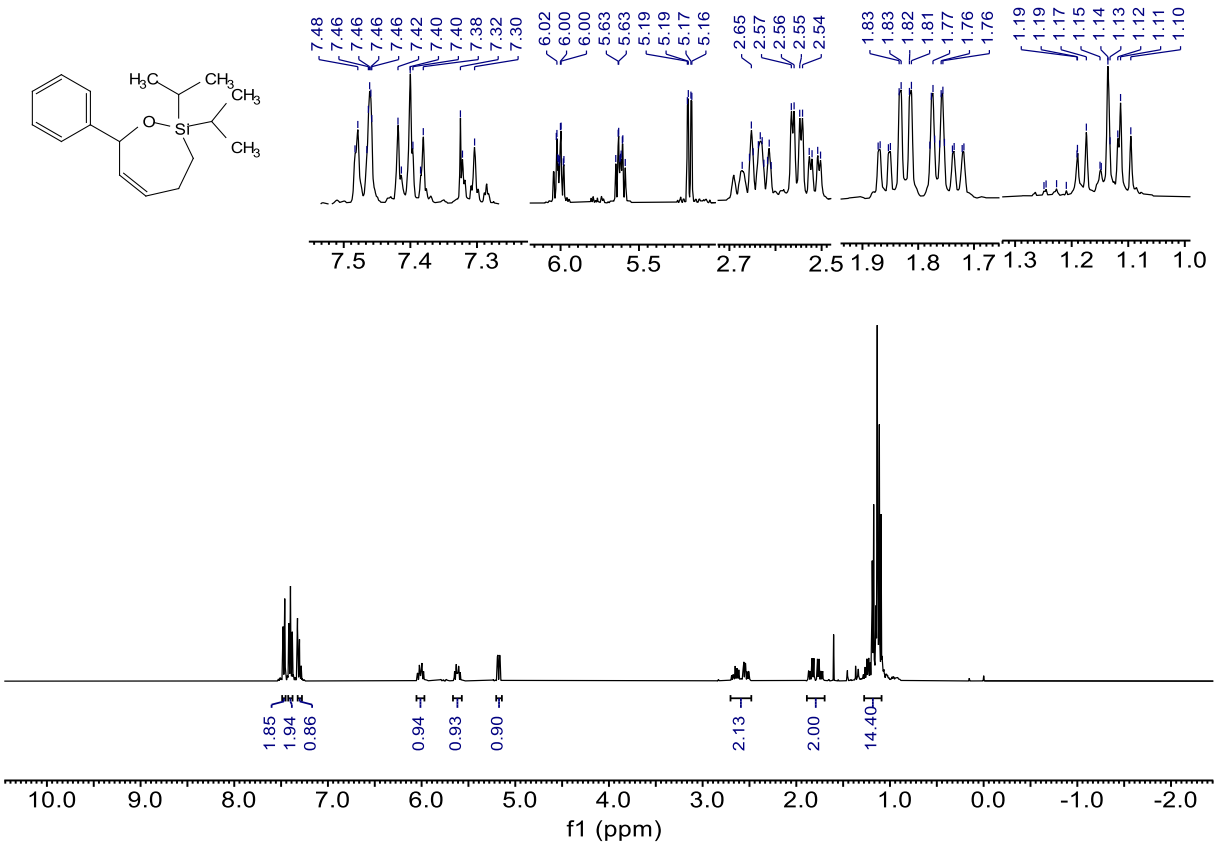

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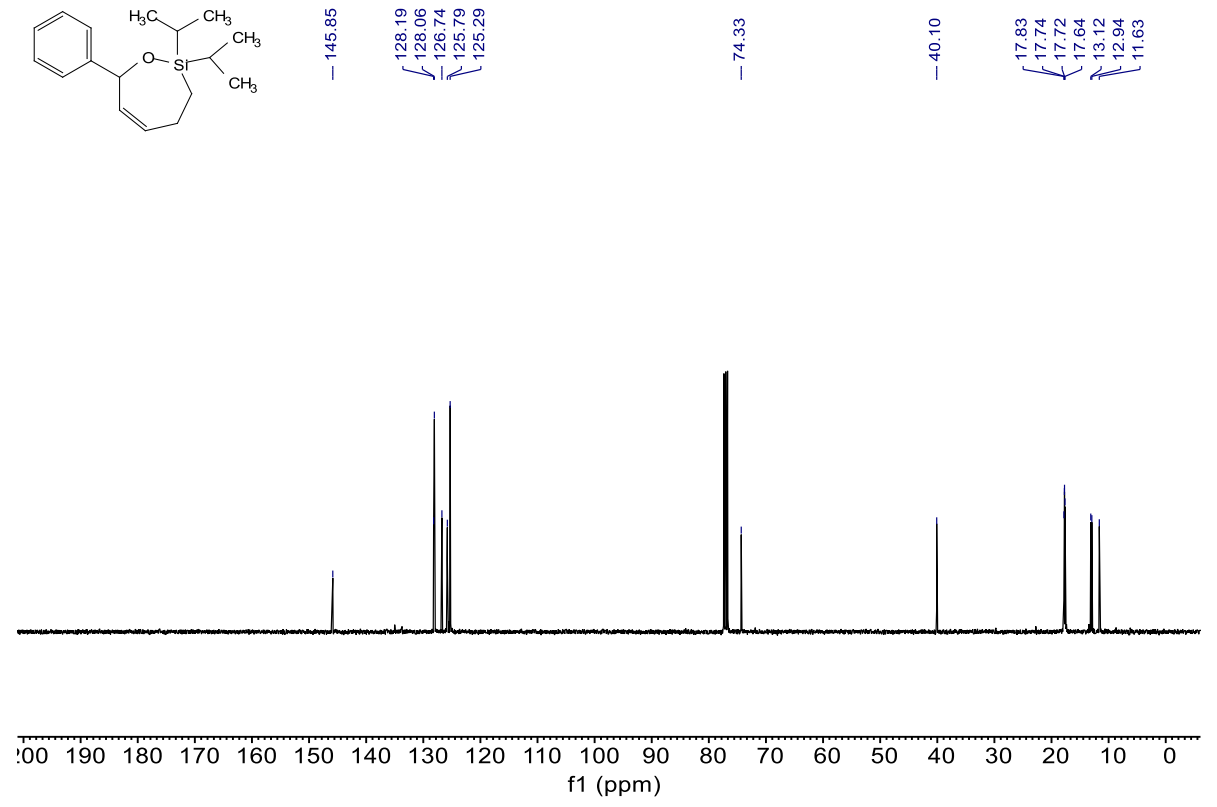

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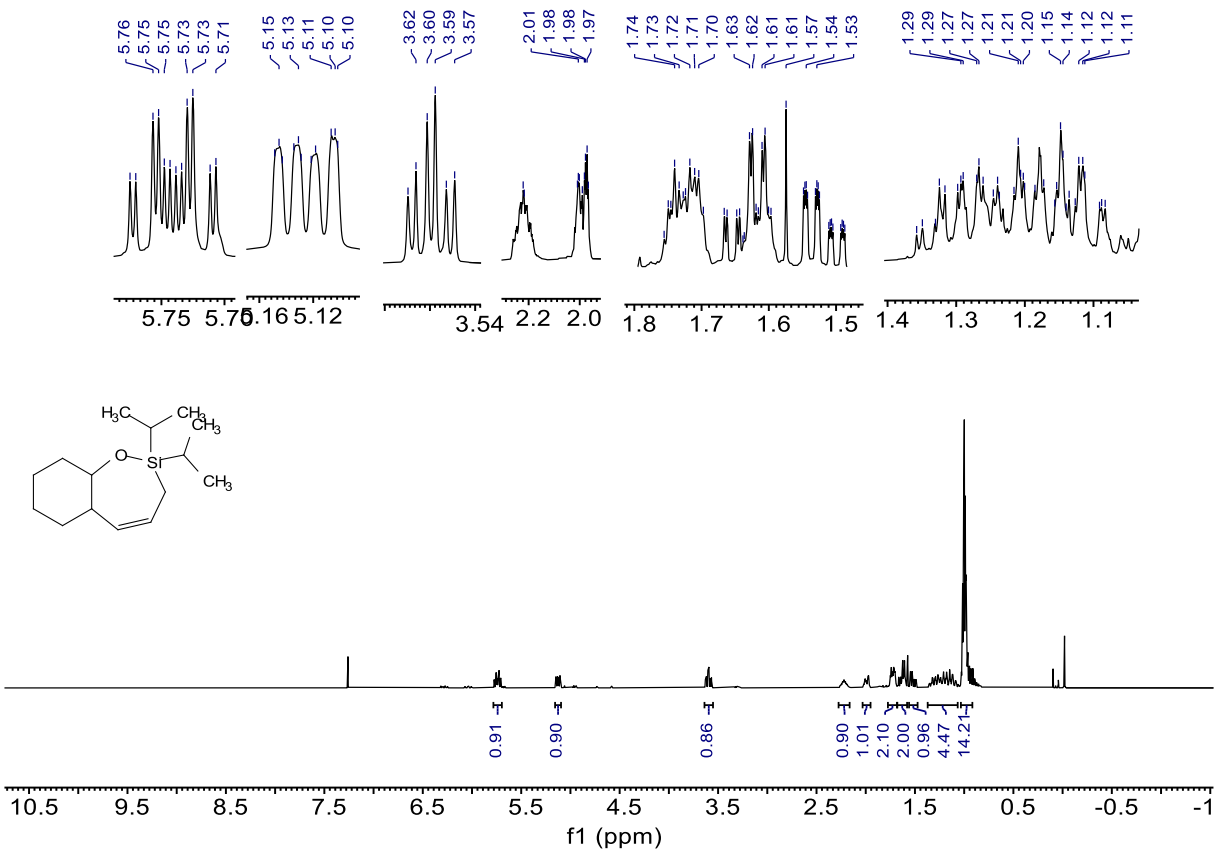
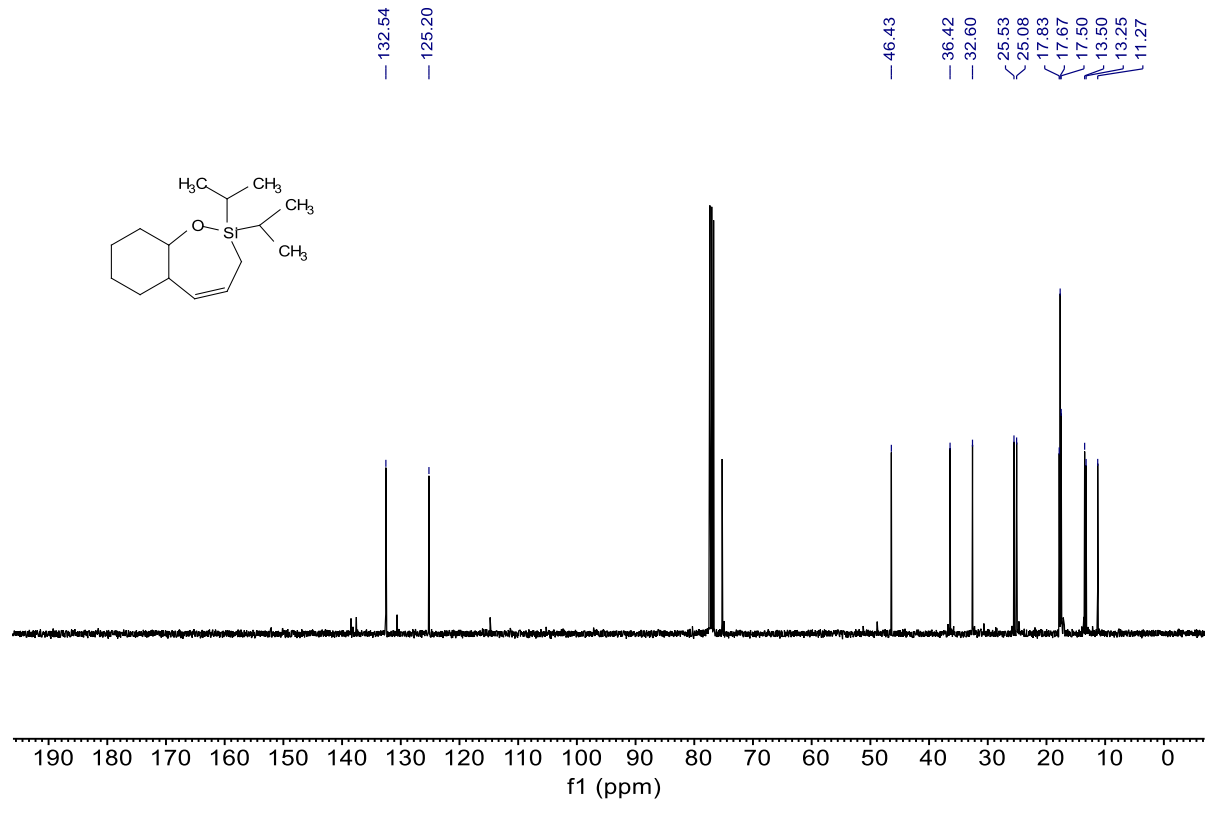


^{1}H NMR spectrum of compound **2p** (400 MHz, $CDCl_3$)



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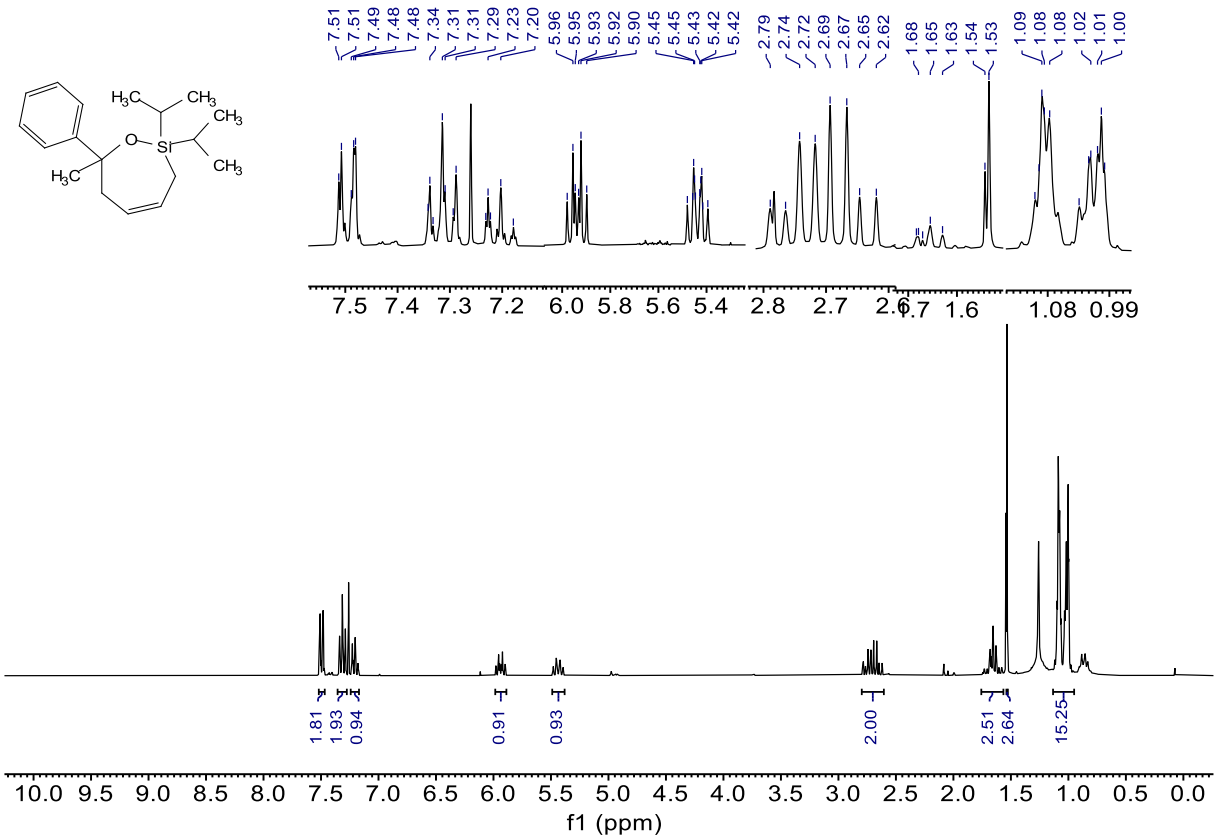

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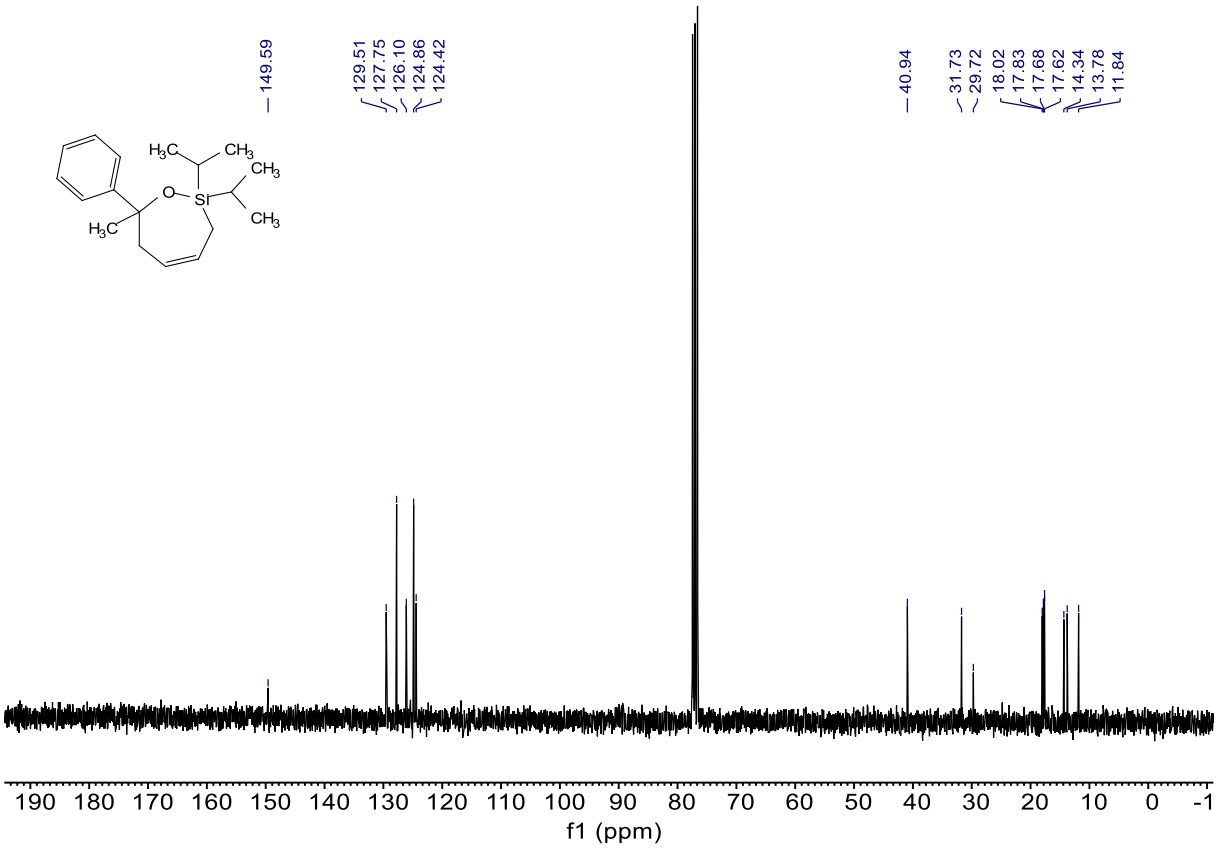
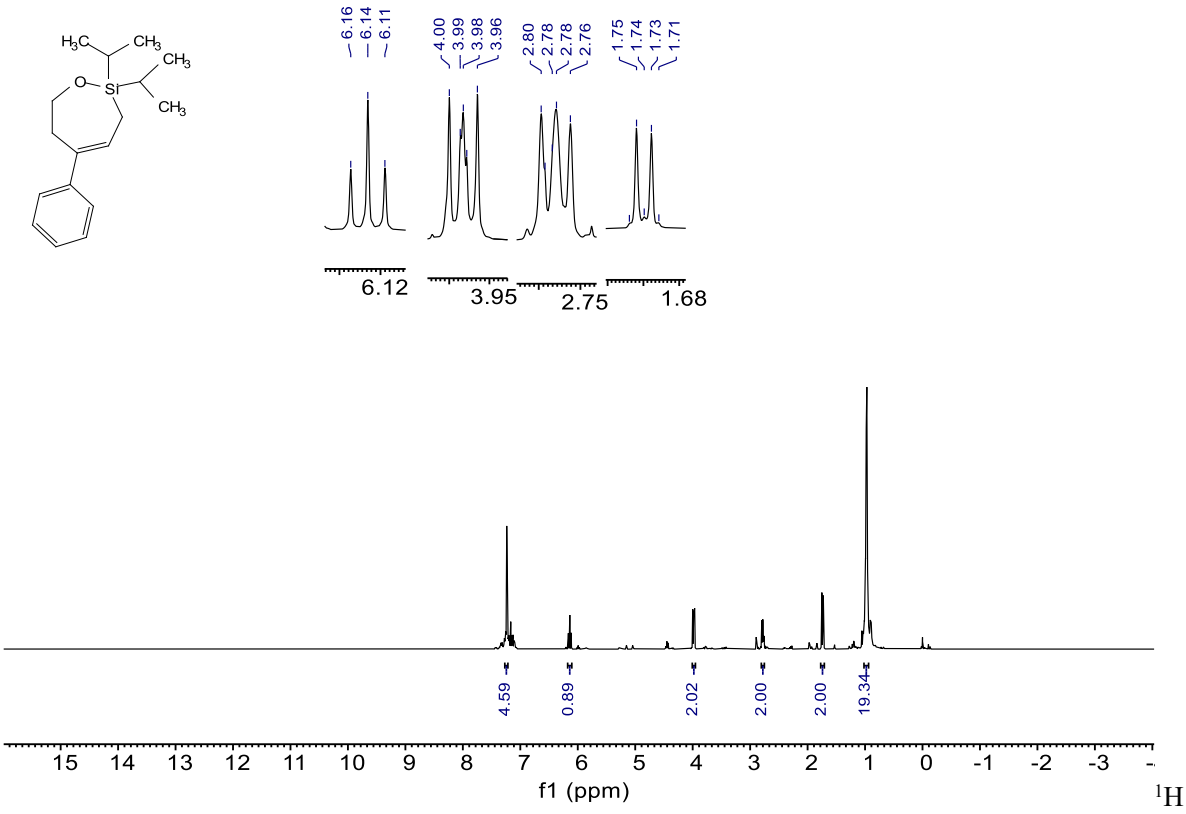
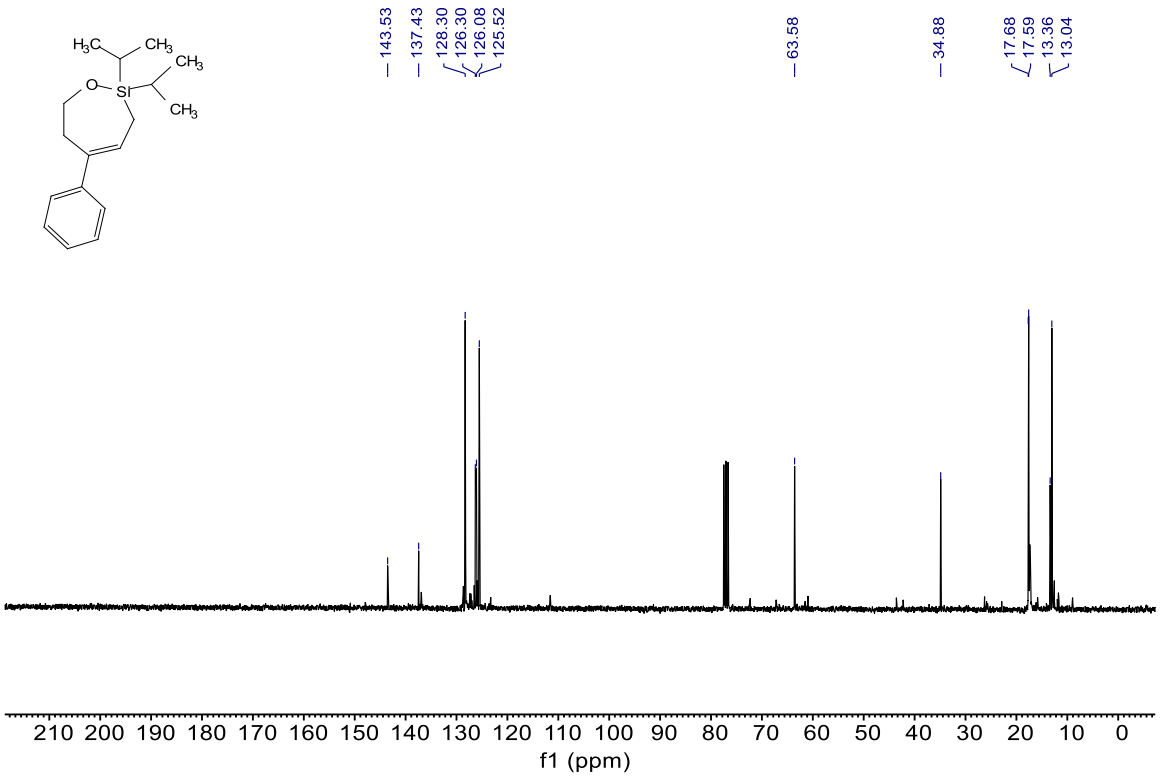


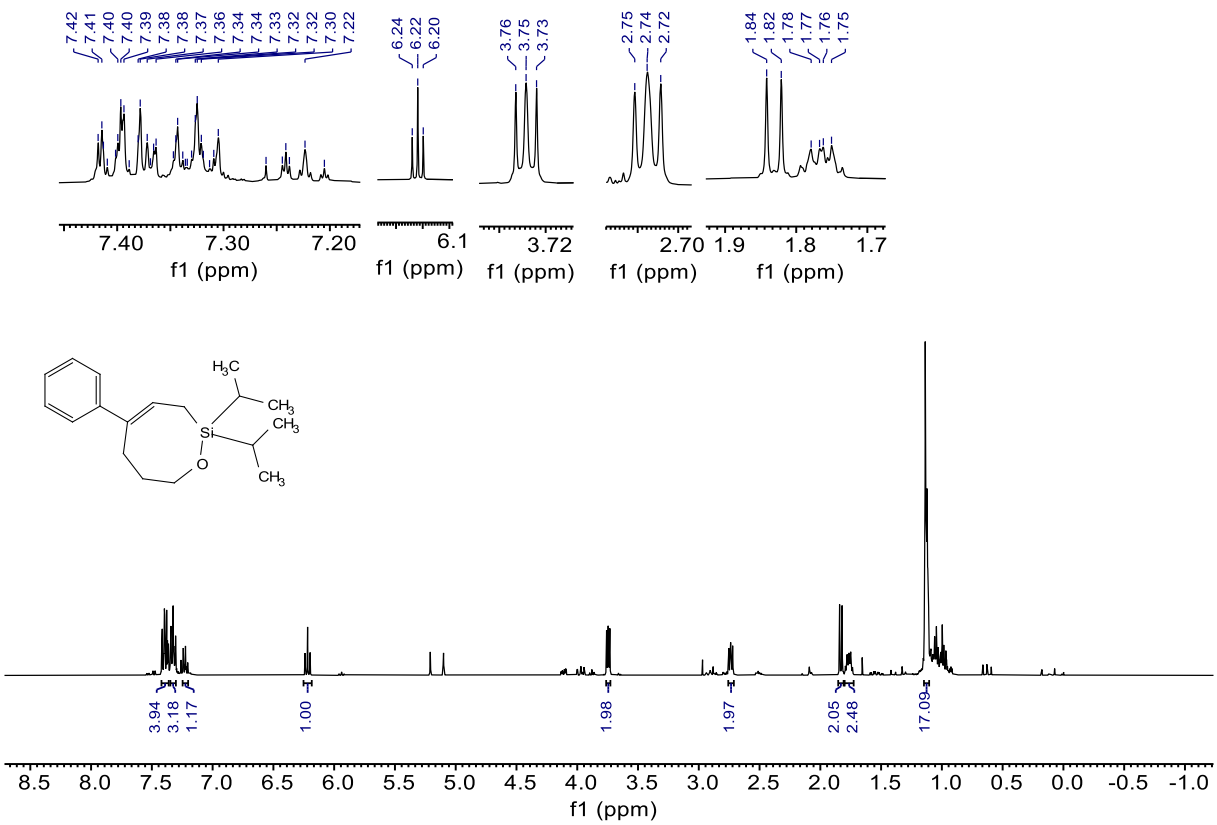
^{13}C NMR spectrum of compound **2q** (101 MHz, $CDCl_3$)



NMR spectrum of compound **2r** (300 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **2r** (75 MHz, $CDCl_3$)



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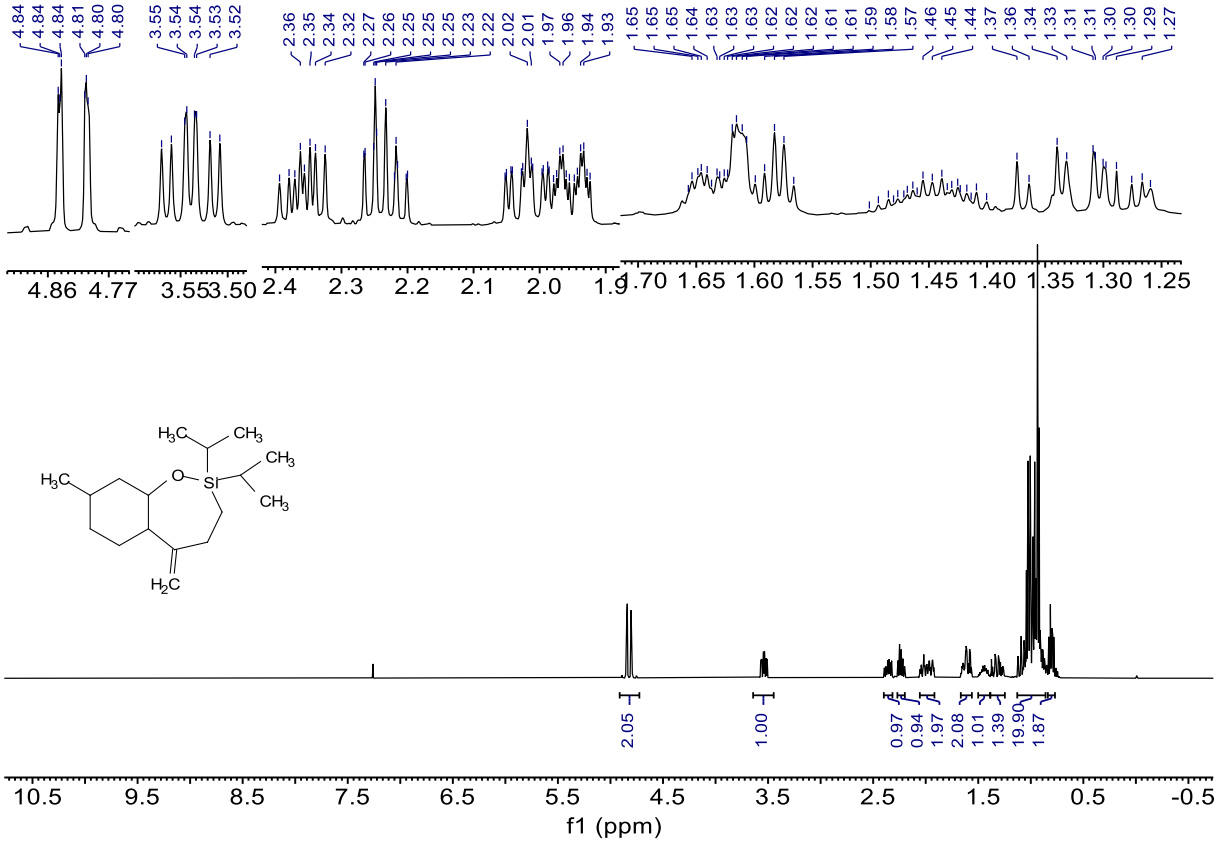

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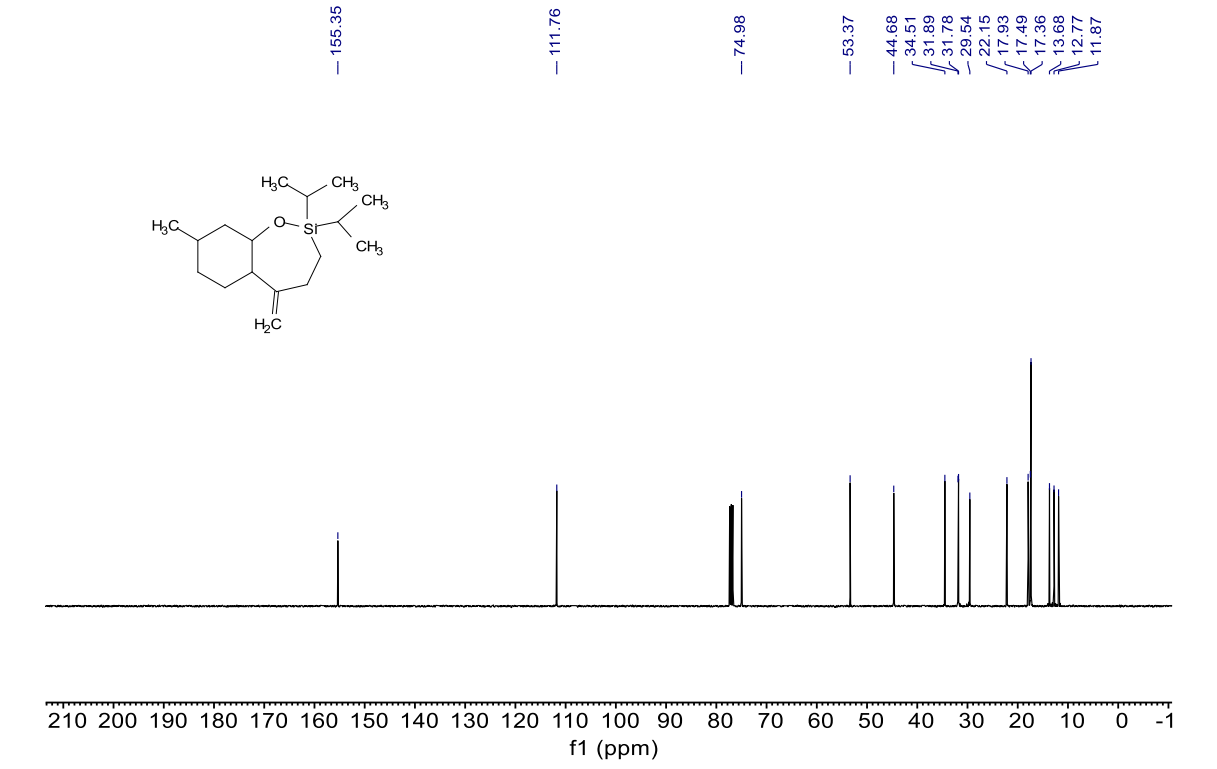

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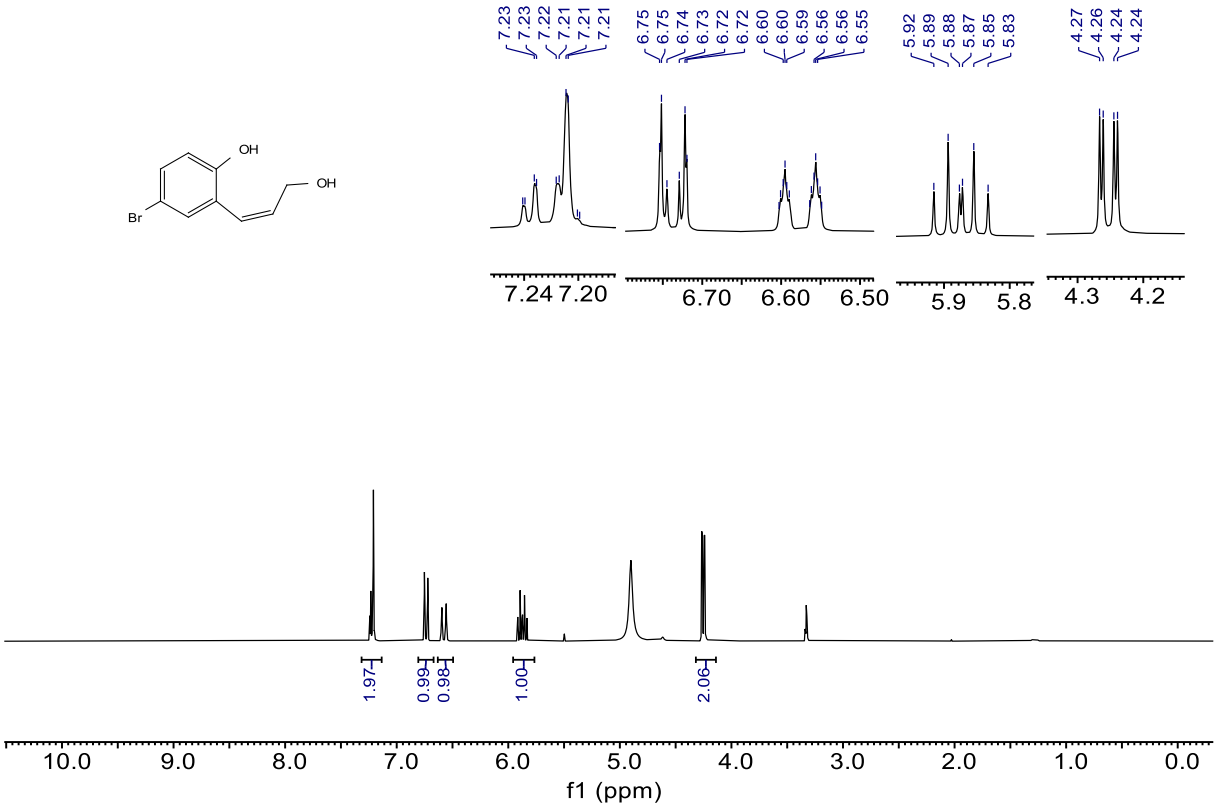

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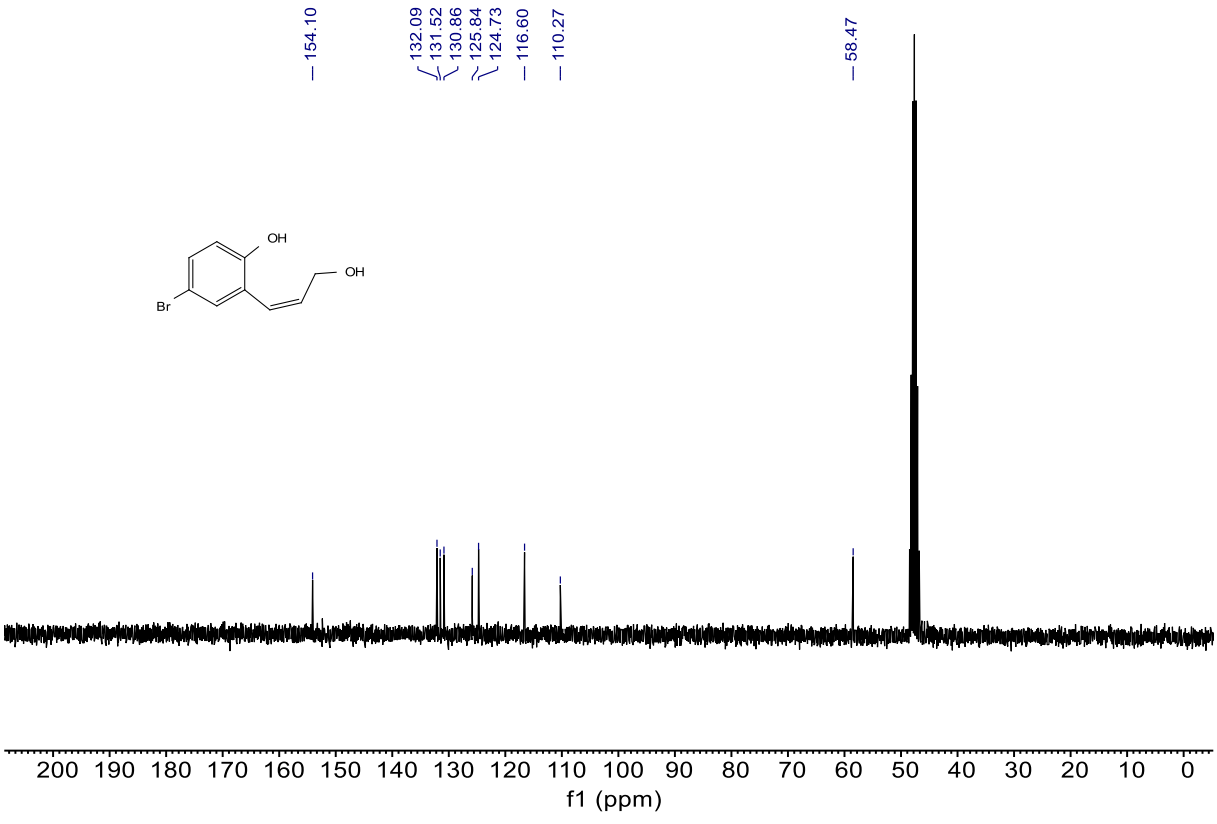

^{13}C NMR spectrum of compound **3d** (75 MHz, CD_3OD)