

Pd-Catalyzed Modifiable Silanol-Directed Aromatic C–H Oxygenation

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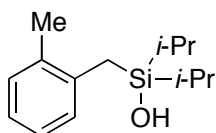
General Information

NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) or DPX-400 (400 MHz) instrument. LRMS and HRMS analyses were performed on Micromass 70 VSE mass spectrometer. GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle Silica-P flash silica gel (40-63 μm) and/or Florisil[®] (60-100 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. All manipulations with transition metal catalysts were conducted in oven-dried glassware under inert atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous solvents purchased from Aldrich were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system and/or stored over calcium hydride. All other starting materials were purchased from Strem Chemicals, Aldrich, Gelest Inc., Alfa Aesar, or TCI.

Part I. Preparation of Starting Material Silanols.

General Procedure of One-pot Preparation of Silanols

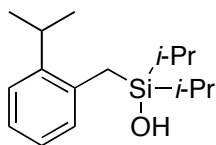
To a mixture of magnesium powder (220 mg, 9 mmol) and a crystal of iodine, anhydrous THF (6 mL) was added and the reaction stirred for 10 min at RT under argon atmosphere. Diisopropyldichlorosilane (1.35 mL, 7.5 mmol) was added to the mixture, followed by a dropwise addition of benzyl halide (3 mmol) in THF (10 mL). After stirring for 1.5 h at RT, the reaction mixture was cooled down to 0 °C and DMF (0.6 mL) and sat. aqeous NaHCO₃ (3 mL) was added. The mixture was stirred for additional 30 min at RT. The mixture was then diluted with diethyl ether and washed with sat. NH₄Cl and water. The organic extract dried over anhydrous Na₂SO₄, and concentrated under a reduced pressure. The residue was purified by flash column chromatography (silica gel, eluent: hexanes/EtOAc) to provide the silanol products.



1c:¹ 71%. Eluent: hexanes/AcOEt (10:1)

¹H NMR (500 MHz, CDCl₃) δ ppm 7.13 (d, *J* = 7.3 Hz, 1H), 7.07-7.10 (m, 2H), 7.02 (m, 1H), 3.32(s, 3H), 2.21 (s, 2H), 1.38 (s, 1H), 1.01-1.07 (m, 14H).

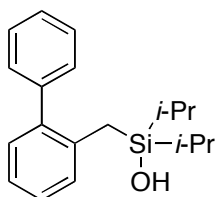
¹³C NMR (126 MHz, CDCl₃) δ ppm 137.8, 135.2, 130.3, 129.0, 125.9, 124.5, 20.4, 18.4, 17.4, 17.2, 13.1.



1g:² 61%. Eluent: hexanes/AcOEt (20:1)

¹H NMR (500 MHz, CDCl₃) δ ppm 7.24 (d, *J* = 7.3 Hz, 1H), 7.04-7.13 (m, 3H), 3.18 (sep, *J* = 6.9 Hz, 1H), 2.25 (s, 2H), 1.38 (s, 1H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.01-1.06 (m, 14H).

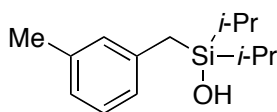
¹³C NMR (126 MHz, CDCl₃) δ ppm 145.7, 136.1, 129.4, 125.5, 125.2, 124.9, 29.1, 23.5, 17.9, 17.4, 17.3, 12.9.



1h:¹ 60%. Eluent: hexanes/AcOEt (10:1)

¹H NMR (500 MHz, CDCl₃) δ ppm 7.43-7.46 (m, 2H), 7.34-7.40 (m, 3H), 7.23-7.25 (m, 2H), 7.15-7.21 (m, 2H), 2.34 (s, 2H), 1.03 (s, 1H), 0.82-0.85 (m, 14H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 142.4, 140.8, 136.9, 130.4, 129.7, 129.5, 128.4, 127.4, 126.9, 124.5, 18.7, 17.02, 16.97, 12.8.



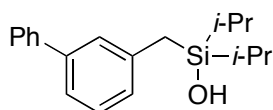
1i:² 94%. Eluent: hexanes/AcOEt (10:1)

¹H NMR (500 MHz, CDCl₃) δ ppm 7.13 (t, *J* = 8.8 Hz, 1H), 6.91-6.93 (m, 3H), 3.32(s, 3H), 2.18 (s, 2H), 1.44 (s, 1H), 1.01-1.04 (m, 14H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 139.1, 138.0, 129.2, 125.4, 125.0, 21.4, 21.1, 18.4, 17.3, 17.2, 12.7.

¹ Prepared from benzyl bromide.

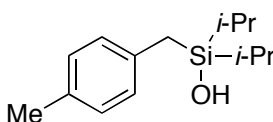
² Prepared from benzyl chloride.



1j:¹ 61%. Eluent: hexanes/AcOEt (10:1)

¹H NMR (500 MHz, CDCl₃) δ ppm 7.58-7.60 (m, 2H), 7.43-7.46 (m, 2H), 7.30-7.37 (m, 4H), 7.12 (dt, *J* = 7.1, 1.6 Hz, 1H), 2.29 (s, 2H), 1.49 (s, 1H), 1.03-1.06 (m, 14H).

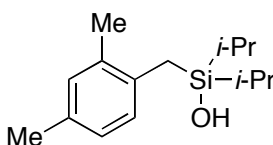
¹³C NMR (126 MHz, CDCl₃) δ ppm 141.4, 141.3, 139.8, 128.8, 128.7, 127.4, 127.3, 127.1, 123.3, 21.5, 17.3, 17.2, 12.7.



1k:¹ 52%. Eluent: hexanes/AcOEt (10:1)

¹H NMR (500 MHz, CDCl₃) δ ppm 7.05 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 2.30 (s, 3H), 2.17 (s, 2H), 1.44 (s, 1H), 0.95-1.04 (m, 14H).

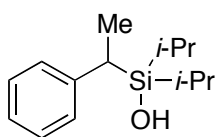
¹³C NMR (126 MHz, CDCl₃) δ ppm 135.9, 133.6, 129.1, 128.3, 20.9, 20.6, 17.3, 17.2, 12.7.



1l:² 85%. Eluent: hexanes/AcOEt (10:1)

¹H NMR (500 MHz, CDCl₃) δ ppm 6.98 (d, *J* = 7.7 Hz, 1H), 6.95 (s, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 2.28 (s, 3H), 2.27 (s, 3H), 2.16 (s, 2H), 1.37 (s, 1H), 1.02-1.07 (m, 14H).

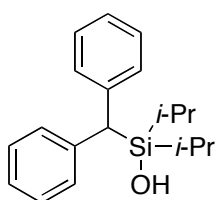
¹³C NMR (126 MHz, CDCl₃) δ ppm 134.9, 134.4, 133.7, 131.1, 128.9, 126.6, 20.8, 20.4, 17.7, 17.4, 17.3, 13.0.



1m:¹ 68%. Eluent: hexanes/AcOEt (10:1)

¹H NMR (500 MHz, CDCl₃) δ ppm 7.26-7.29 (m, 2H), 7.18 (m, 2H), 7.12 (m, 1H), 2.46 (q, *J* = 7.5 Hz, 1H), 1.46 (d, *J* = 7.7 Hz, 3H), 1.39 (s, 1H), 0.93-1.08 (m, 14H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 145.3, 128.3, 127.4, 124.7, 27.2, 17.8, 17.7, 17.4, 15.4, 12.4, 12.3.

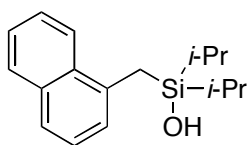


1n:² 82%. Eluent: hexanes/AcOEt (10:1)

¹H NMR (500 MHz, CDCl₃) δ ppm 7.43 (dd, *J* = 7.9, 1.0 Hz, 4H), 7.26-7.29 (m, 4H), 7.15 (m, 2H), 3.68 (s, 1H), 1.74 (s, 1H), 0.98 (m, 2H), 0.92 (m, 12H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 142.4, 129.0, 128.5, 125.4, 42.9, 17.6, 17.5, 13.1.

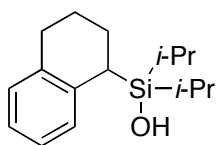
HRMS (EI) calcd. for C₁₉H₂₆OSi [M]⁺: 298.17530. Found: 298.17628.



1o:² 64%. Eluent: hexanes/AcOEt (20:1)

¹H NMR (500 MHz, CDCl₃) δ ppm 8.09 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.48-7.55 (m, 2H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.0 Hz, 1H), 2.70 (s, 2H), 1.50 (s, 1H), 1.03-1.08 (m, 14H).

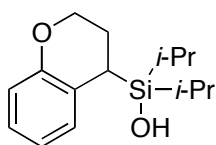
¹³C NMR (126 MHz, CDCl₃) δ ppm 136.1, 134.0, 131.9, 128.7, 125.9, 125.6, 125.5, 125.1, 124.4, 18.4, 17.4, 17.2, 13.0.



1p:² 73%. Eluent: hexanes/AcOEt (10:1)

¹H NMR (500 MHz, CDCl₃) δ ppm 7.15 (d, *J* = 7.0 Hz, 1H), 7.00-7.07 (m, 3H), 2.77 (q, *J* = 6.2 Hz, 2H), 2.68 (t, *J* = 6.4 Hz, 1H), 1.90-2.00 (m, 3H), 1.66-1.72 (m, 1H), 1.48 (s, 1H), 0.96-1.11 (m, 14H).

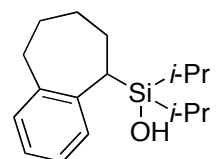
¹³C NMR (126 MHz, CDCl₃) δ ppm 138.4, 136.7, 129.4, 128.5, 125.3, 124.2, 29.9, 26.7, 24.2, 22.5, 17.72, 17.66, 17.5, 12.83, 12.69.



1q:² 68%. Eluent: hexanes/AcOEt (10:1)

¹H NMR (500 MHz, CDCl₃) δ ppm 7.15 (m, 1H), 7.03 (m, 1H), 6.80-6.84 (m, 2H), 4.33 (m, 1H), 4.09 (m, 1H), 2.64 (t, *J* = 6.7 Hz, 1H), 2.13-2.19 (m, 2H), 1.78 (s, 1H), 0.97-1.15 (m, 14H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 138.4, 136.7, 129.4, 128.5, 125.3, 124.2, 29.9, 26.7, 24.2, 22.5, 17.72, 17.66, 17.5, 12.83, 12.69.

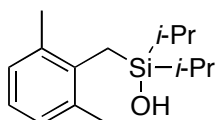


1r:²

55%. Eluent: hexanes/AcOEt (10:1)

¹H NMR (500 MHz, CDCl₃) δ ppm 7.03-7.13 (m, 4H), 3.18 (m, 1H), 2.72 (m, 1H), 2.62 (m, 1H), 1.81-2.02 (m, 5H), 1.55-1.60 (m, 2H), 1.13-1.24 (m, 7H), 0.92-0.97 (m, 7H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 143.5, 142.8, 129.9, 129.8, 125.7, 125.1, 35.7, 35.1, 29.5, 28.6, 28.2, 18.1, 17.9, 17.7, 17.5, 13.5, 13.2.



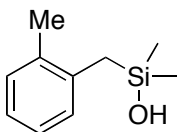
F:

¹H NMR (500 MHz, CDCl₃) δ ppm 6.92-7.00 (m, 3H), 2.33 (s, 6H), 2.24 (s, 2H), 1.48 (s, 1H), 1.07 (d, *J* = 7.3 Hz, 6H), 0.95-1.07 (m, 14H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 136.8, 135.2, 128.0, 124.0, 21.3, 17.3, 17.1, 16.1, 13.8.

Synthesis of 1a: To a mixture of magnesium powder (360 mg, 15 mmol) and a crystal of iodine in anhydrous THF (20 mL), a solution of 2-methyl benzylbromide (10 mmol) and Me₂SiHCl in THF (30 mL) was added dropwise using addition funnel. The resulted reaction mixture was stirred at RT for 5 h. The mixture was added with sat. aqueous NH₄Cl (0.5 mL) and dried over Na₂SO₄, filtered, and concentrated under a reduced pressure. The residue was purified by flash column chromatography (silica gel, eluent: hexanes) to provide dimethyl(2-methylbenzyl)silane 1.26 g (99% yield). ¹H NMR (500 MHz, CDCl₃) δ ppm 7.12 (dd, *J* = 16.4, 7.5 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 2H), 4.01-3.98 (m, 1H), 2.29 (s, 3H), 2.19 (d, *J* = 3.4 Hz, 2H), 0.12 (d, *J* = 3.7 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 138.5, 134.7, 130.1, 128.7, 125.8, 124.4, 21.5, 20.2, -4.2. To a solution of the resulted dimethyl(2-methylbenzyl)silane (460 mg, 2.8 mmol) in CH₃CN

(8.5 mL) was added catalyst $[\text{RuCl}_2(p\text{-cymene})]_2$ (52.5 mg, 3 mol %) and water (252 mg, 5 equiv). The reaction mixture was heated at 80 °C with an air balloon for 1.5 h. Solvents were removed under a reduced pressure and the residue was purified by flash column chromatography (silica gel, eluent: hexanes/EtOAc = 10:1) to provide silanol **1a** in 100% yield.

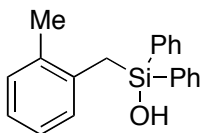


1a:

^1H NMR (500 MHz, CDCl_3) δ ppm 7.14-7.08 (m, 2H), 7.04-7.02 (m, 2H), 2.28 (s, 3H), 2.20 (s, 2H), 1.72 (s, 1H), 0.16 (s, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 137.5, 134.9, 130.3, 128.8, 125.9, 124.5, 25.0, 20.3, -0.2.

Synthesis of 1b: To a mixture of magnesium powder (360 mg, 15 mmol) and a crystal of iodine in anhydrous THF (20 mL), a solution of 2-methyl benzylbromide (10 mmol) and Ph_2SiHCl in THF (30 mL) was added dropwise via addition funnel. The resulted reaction mixture was stirred at RT for 18 h. The mixture was added with sat. aqeous NH_4Cl (0.5 mL) and dried over Na_2SO_4 , filtered, and concentrated under a reduced pressure. The residue was purified by purified by a Combiflash system (eluent: hexane) to provide (2-methylbenzyl)diphenylsilane 2.47 g (not pure, used directly for the next step). To a solution of the resulted (2-methylbenzyl)diphenylsilane (1.60 g) in CH_3CN (17 mL) was added catalyst $[\text{IrCl}(\text{COD})]_2$ (56 mg) and water (0.5 mL). The reaction mixture was heated at 80 °C for 4 h. Solvents were removed under a reduced pressure and the residue was purified by flash column chromatography (silica gel, eluent: hexanes/EtOAc = 10:1) to provide silanol **1b** in 56% yield over two steps.

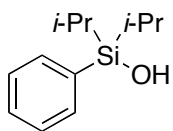


1b:

^1H NMR (500 MHz, CDCl_3) δ ppm 7.55-7.53 (m, 4H), 7.45-7.42 (m, 2H), 7.37 (tt, $J = 7.1, 0.9$ Hz, 4H), 7.08-6.95 (m, 4H), 2.71 (s, 2H), 2.15 (s, 1H), 2.07 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 136.0, 135.7, 135.6, 130.2, 130.0, 129.2, 127.9, 125.8, 124.9, 22.4, 20.2.

Synthesis of 1d: To a solution of $\text{PhSiH}^i\text{Pr}_2$ ³ (1.74 g, 9.06 mmol) in EtOH (27 mL), KOH pellets (2.03g, 4 equiv) were added. The reaction mixture was refluxed overnight and then cooled down to RT. A saturated NH_4Cl solution was added and the mixture was extracted with ethyl acetate. The combined organic extracts were washed with water and brine, dried over Mg_2SO_4 and concentrated. The residue was purified by flash column chromatography (eluent: hexane/EtOAc 9:1) to give silanol **1d** in 82% yield.



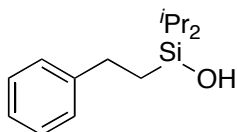
1d:

^1H NMR (500 MHz, CDCl_3) δ ppm 7.58-7.56 (m, 2H), 7.42-7.36 (m, 3H), 1.75 (s, 1H), 1.28-1.19 (m, 2H), 1.07 (d, $J=7.4$

³ H.-J. Knoelker, N. Foitzik, H. Goesmann, R. Graf, P. G. Jones, G. Wanzl, *Chem. Eur. J.* **1997**, *3*, 538-551.

Hz, 6H), 0.99 (d, $J=7.4$ Hz, 6H).
 ^{13}C NMR (126 MHz, CDCl_3) δ ppm 135.4, 134.0, 129.3, 127.6, 17.1, 16.9, 12.4.

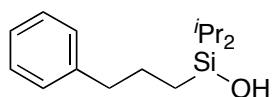
Synthesis of 1e: To a mixture of magnesium powder (105 mg, 4.37 mmol) and a crystal of iodine in anhydrous THF (1 mL), a solution of (2-bromoethyl)benzene (666 mg, 3.6 mmol) in THF (2.6 mL) was added and stirred at RT for 1 h under argon atmosphere. The resulted reaction mixture was transferred via cannula into a THF solution of diisopropylchlorosilane (0.52 mL, 3 mmol). The reaction was refluxed for 18 h, and then cooled down to RT. The mixture was then diluted with diethyl ether and washed with sat. aqeous NH_4Cl and water. The organic extract dried over anhydrous Na_2SO_4 , and concentrated under a reduced pressure. Flash column chromatography (silica gel, eluent: hexanes) provided diisopropyl(phenethyl)silane in 99% yield. ^1H NMR (500 MHz, CDCl_3) δ ppm 7.29 (t, $J = 7.4$ Hz, 2H), 7.23-7.16 (m, 3H), 3.51 (s, 1H), 2.74-2.69 (m, 2H), 1.07-0.96 (m, 16H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 145.2, 128.3, 127.7, 125.6, 31.5, 19.1, 18.7, 10.8, 10.6. The resulted diisopropyl(phenethyl)silane (656.6 mg) was dissolved in DCM (15 mL) and followed by addition of NBS (583.1 mg) over 30 min. The reaction mixture was stirred at room temperature for 2 h. To the mixture, DMF (0.5 mL) and sat. aqeous NaHCO_3 (0.5 mL) were added and the resulted mixture was stirred for additional 30 min at RT. The mixture was then diluted with diethyl ether and washed with sat. aqeous NH_4Cl and water. The organic extract dried over anhydrous Na_2SO_4 , and concentrated under a reduced pressure. Flash column chromatography (silica gel, eluent: hexanes/ $\text{EtOAc} = 10:1$) provided silanol **1e** in 88% yield.



1e:
 ^1H NMR (500 MHz, CDCl_3) δ ppm 7.32 (t, $J = 7.6$ Hz, 2H), 7.25 (d, $J = 7.4$ Hz, 2H), 7.21 (t, $J = 7.3$ Hz, 1H), 2.78-2.74 (m, 2H), 1.62 (s, 1H), 1.10-1.01 (m, 16H).
 ^{13}C NMR (126 MHz, CDCl_3) δ ppm 145.2, 128.4, 127.7, 125.7, 29.4, 17.4, 13.7, 13.0.

Synthesis of 1f: To a mixture of magnesium powder (140 mg, 5.76 mmol) and a crystal of iodine in anhydrous THF (1 mL), a solution of (3-bromopropyl)benzene (956 mg, 4.8 mmol) in THF (4 mL) was added and stirred at RT for 1 h under argon atmosphere. The resulted reaction mixture was transferred via cannula into a THF solution of diisopropylchlorosilane (0.69 mL, 4 mmol). The reaction was refluxed for 18 h, and then cooled down to RT. The mixture was then diluted with diethyl ether and washed with sat. aq. NH_4Cl and water. The organic extract dried over anhydrous Na_2SO_4 , and concentrated under a reduced pressure. Flash column chromatography (silica gel, eluent: hexanes) provided diisopropyl(3-phenylpropyl)silane in 92% yield. ^1H NMR (500 MHz, CDCl_3) δ ppm 7.29 (t, $J = 7.5$ Hz, 2H), 7.20-7.18 (m, 3H), 3.45 (s, 1H), 2.66 (t, $J = 7.7$ Hz, 2H), 1.76-1.69 (m, 2H), 1.03 (dd, $J = 8.4, 5.4$ Hz, 14H), 0.70-0.66 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 142.5, 128.5, 128.2, 125.6, 39.8, 27.4, 19.1, 18.7, 10.6,

8.3. The resulted diisopropyl(3-phenylpropyl)silane (860 mg) was dissolved in DCM (20 mL) and followed by addition of NBS (720 mg) over 30 min. The reaction mixture was stirred at room temperature for 2 h. To the mixture, DMF (0.5 mL) and sat. aqeous NaHCO_3 (0.5 mL) were added and the resulted mixture was stirred for additional 30 min at RT. The mixture was then diluted with diethyl ether and washed with sat. aq. NH_4Cl and water. The organic extract dried over anhydrous Na_2SO_4 , and concentrated under a reduced pressure. Flash column chromatography (silica gel, eluent: hexanes/ EtOAc = 10:1) provided silanol **1f** in 60% yield.

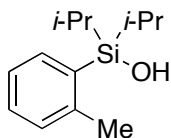


1f:

^1H NMR (500 MHz, CDCl_3) δ ppm 7.31 (t, J = 7.4 Hz, 2H), 7.22-7.19 (m, 3H), 2.67 (t, J = 7.6 Hz, 2H), 1.78-1.70 (m, 2H), 1.59 (s, 1H), 1.06-0.96 (m, 14H), 0.72-0.68 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 142.5, 128.5, 128.3, 125.7, 40.1, 25.4, 17.4, 12.9, 11.5.

Synthesis of D: To a solution of 2-bromotoluene (513 mg, 2 mmol) in THF (30 mL), *n*-BuLi (1 equiv) was added at -78 °C. The mixture was stirred for 2 h at that temperature and then was added $^i\text{Pr}_2\text{SiHCl}$ (520 μL , 1 equiv). After stirring for another 1 h at -78 °C, the mixture was quenched with water, extracted with Et_2O , dried over Na_2SO_4 , and concentrated. The resultant crude hydrosilane was dissolved in EtOH (9 mL). KOH pellets (672 mg, 4 equiv) were added. The reaction mixture was refluxed overnight and then cooled down to RT. A saturated NH_4Cl solution was added and the mixture was extracted with ethyl acetate. The combined organic extracts were washed with water and brine, dried over Mg_2SO_4 and concentrated. The residue was purified by flash column chromatography (eluent: hexane/ EtOAc 20:1) to give silanol **D** in 63% yield.



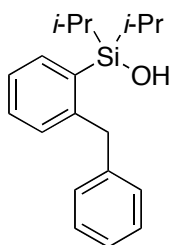
D:

^1H NMR (500 MHz, CDCl_3) δ ppm 7.55 (m, 1H), 7.29 (td, J = 7.4, 1.4 Hz, 1H), 7.17-7.20 (m, 2H), 2.49 (s, 3H), 1.70 (s, 1H), 1.29 (sep, J = 7.5 Hz, 2H), 1.10 (d, J = 7.5 Hz, 6H), 0.98 (d, J = 7.5 Hz, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 143.5, 135.1, 134.3, 130.0, 129.3, 124.6, 23.3, 17.6, 17.3, 13.5.

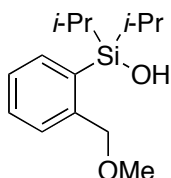
Synthesis of E: To a solution of 1-benzyl-2-bromobenzene (496 mg, 2 mmol) in THF/hexane (30 mL, 2:1), *n*-BuLi (1 equiv) was added at -78 °C. The mixture was stirred for 2 h at that temperature and then was added $^i\text{Pr}_2\text{SiHCl}$ (346.5 μL , 1 equiv). After stirring for another 1 h at -78 °C, the mixture was quenched with water, extracted with Et_2O , dried over Na_2SO_4 , and concentrated. The resultant crude hydrosilane was dissolved in EtOH (6 mL). KOH pellets (450 mg, 4 equiv) were added. The reaction mixture was refluxed overnight and then cooled down to RT. A saturated NH_4Cl solution was added and the mixture was extracted with ethyl acetate. The combined organic

extracts were washed with water and brine, dried over Mg_2SO_4 and concentrated. The residue was purified by flash column chromatography (eluent: hexane/EtOAc 20:1) to give silanol **E** in 59% yield.



E:
 ^1H NMR (500 MHz, CDCl_3) δ ppm 7.56 (dd, $J = 7.5, 0.9$ Hz, 1H), 7.21-7.35 (m, 5H), 7.10-7.12 (m, 3H), 4.25 (s, 2H), 1.62 (s, 1H), 1.25 (sep, $J = 7.3$ Hz, 2H), 1.07 (d, $J = 7.3$ Hz, 6H), 0.95 (d, $J = 7.3$ Hz, 6H).
 ^{13}C NMR (126 MHz, CDCl_3) δ ppm 146.3, 142.0, 135.1, 135.0, 130.7, 129.4, 128.8, 128.5, 126.0, 125.3, 42.0, 17.5, 17.2, 13.5.

Synthesis of G: To a solution of 1-bromo-2-(methoxymethyl)benzene (402 mg, 2 mmol) in THF/hexane (50 mL, 4:1), *n*-BuLi (1 equiv) was added at -78 °C. The mixture was stirred for 1.5 h at that temperature and then was added $^t\text{Pr}_2\text{SiHCl}$ (346.5 μL , 1 equiv). After stirring for another 1 h at -78 °C, the mixture was quenched with water, extracted with Et_2O , dried over Na_2SO_4 , and concentrated. The resultant crude hydrosilane was dissolved in MeOH (9 mL). KOH pellets (450 mg, 4 equiv) were added. The reaction mixture was refluxed overnight and then cooled down to RT. A saturated NH_4Cl solution was added and the mixture was extracted with ethyl acetate. The combined organic extracts were washed with water and brine, dried over Mg_2SO_4 and concentrated. The residue was purified by flash column chromatography (eluent: hexane/EtOAc 20:1) to give silanol **G** in 38% yield.

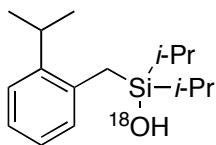


G:
 ^1H NMR (500 MHz, CDCl_3) δ ppm 7.51-7.49 (m, 1H), 7.36-7.31 (m, 2H), 7.28-7.26 (m, 1H), 4.76 (br. s, 1H), 4.56 (s, 2H), 3.32 (s, 3H), 1.23 (dq, $J = 14.9, 7.4$ Hz, 2H), 1.07 (d, $J = 7.3$ Hz, 6H), 0.96 (d, $J = 7.4$ Hz, 6H).
 ^{13}C NMR (126 MHz, CDCl_3) δ ppm 142.7, 137.0, 135.2, 128.8, 127.3, 76.5, 57.0, 17.3, 17.0, 13.2.

Preparation of ^{18}O -Labeled Silanol **4**

To a mixture of magnesium powder (108 mg, 4.5 mmol) and a crystal of iodine, anhydrous THF (5 mL) was added and stirred at RT for 10 min under argon atmosphere. A mixture of diisopropylchlorosilane (0.52 mL, 3 mmol) and 2-isopropylbenzyl chloride (506 mg, 3 mmol) in 10 dry THF (10 mL) was added to the reaction vessel. After stirring for 2h at RT, the reaction mixture was subjected to aqueous workup. Flash column chromatography (silica gel, eluent: Hexanes) gave the product diisopropyl(2-isopropylbenzyl)silane as a colorless oil (530 mg, 71%). ^1H NMR (500 MHz, CDCl_3) δ ppm 7.23 (dd, $J = 7.7, 1.1$ Hz, 1H), 7.03-7.12 (m, 3H), 3.60 (t, $J = 3.7$ Hz, 1H), 3.17 (sep, $J = 6.8$ Hz, 1H), 2.23 (d, $J = 4.6$ Hz, 2H), 1.25 (d, $J = 7.2$ Hz, 6H), 1.02-1.06 (m, 14H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 145.5, 137.2, 129.5, 125.3, 125.2, 124.8, 29.0, 23.6, 18.8, 15.5, 10.7. To a solution of diisopropyl(2-isopropylbenzyl)silane (510 mg, 2.18

mmol) in dry DCM (10 mL) NBS (427 mg, 2.40 mmol, 1.1 equiv) was added slowly at RT under argon atmosphere and stirred for 2 h at room temperature. TEA (0.6 ml) and H₂¹⁸O (65 μL) was added to the reaction mixture and stirred at RT for additional 30 min. The solvent was evaporated under reduced pressure. To the residue, hexane (20 ml) was added, stirred for 5 min at RT and filtered. The filtrate was then evaporated and the remaining oil was purified by Kugelrohr distillation (~1.3 Torr, 140°C) to give 520 mg pure product **4** (90%, ~75% ¹⁸O incorporation).

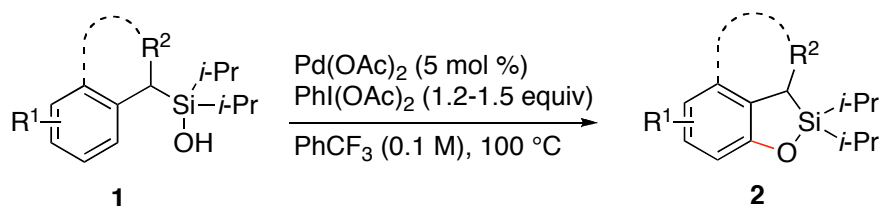


4:

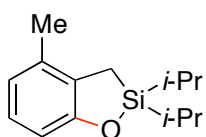
¹H NMR (500 MHz, CDCl₃) δ ppm 7.25 (d, *J* = 7.3 Hz, 1H), 7.03-7.12 (m, 3H), 3.18 (m, 1H), 2.26 (d, *J* = 2.2 Hz, 2H), 1.41 (d, *J* = 2.6 Hz, 1H), 1.24 (m, 6H), 1.01-1.06 (m, 14H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 145.7, 136.1, 129.5, 125.5, 125.2, 124.9, 29.2, 23.5, 17.9, 17.4, 17.2, 13.0.

Part II: Oxasilacycle Formation via Pd-Catalyzed Silanol-Directed C–H Oxygenation.



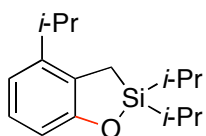
General procedure: An oven dried 10 mL Wheaton V-vial, containing a stirring bar, was charged with benzylsilanols (0.5 mmol), Pd(OAc)₂ (5.6 mg, 0.025 mmol), and PhI(OAc)₂ (0.6 – 0.75 mmol) under N₂ atmosphere. Dry α,α,α-trifluorotoluene (5 mL) was added via syringes and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 100 °C for 7 h. The resulting mixture was cooled down to room temperature and filtered through a short layer of celite plug with the aid of EtOAc. The filtrate was concentrated under a reduced pressure. The residue was purified by column chromatography on Florisil® (eluent: hexanes/EtOAc = 25:1) affording the corresponding cyclized products. **2i** and **2m** were purified by Kugelrohr distillation on a 1.5 mmol scale.



2c: 2,2-diisopropyl-4-methyl-2,3-dihydrobenzo[*d*][1,2]oxasilole

¹H NMR (500 MHz, CDCl₃) δ ppm 7.00 (t, *J*=7.79 Hz, 1 H), 6.75 (d, *J*=7.89 Hz, 1 H), 6.71 (d, *J*=7.52 Hz, 1 H), 2.29 (s, 3 H), 1.88 (s, 2 H), 1.18 - 1.28 (m, 2 H), 1.08 (dd, *J*=7.43, 2.84 Hz, 12 H);
¹³C NMR (126 MHz, CDCl₃) δ ppm 160.4, 137.9, 127.0, 126.7, 121.1, 111.5, 19.8, 16.7, 16.6, 12.4, 8.4.

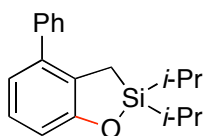
HRMS (EI) calcd. for C₁₄H₂₂OSi [M]⁺: 234.14400. Found: 234.14454.



2g: 2,2,4-triisopropyl-2,3-dihydrobenzo[*d*][1,2]oxasilole

¹H NMR (500 MHz, CDCl₃) δ ppm 7.10 (t, *J*=7.89 Hz, 1 H), 6.80 (d, *J*=7.70 Hz, 1 H), 6.76 (d, *J*=8.07 Hz, 1 H), 3.09 - 3.17 (m, 1 H), 1.97 (s, 2 H), 1.20 - 1.30 (m, 8 H), 1.09 (dd, *J*=7.34, 4.03 Hz, 12 H);
¹³C NMR (126 MHz, CDCl₃) δ ppm 160.4, 148.3, 127.4, 125.3, 116.3, 111.5, 30.7, 23.0, 16.8, 16.6, 12.4, 7.6.

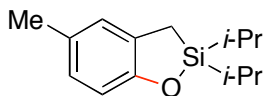
HRMS (EI) calcd. for C₁₆H₂₆OSi [M]⁺: 262.17530. Found: 262.17610.



2h: 2,2-diisopropyl-4-phenyl-2,3-dihydrobenzo[*d*][1,2]oxasilole

¹H NMR (500 MHz, CDCl₃) δ ppm 7.44 - 7.51 (m, 4 H), 7.35 - 7.42 (m, 1 H), 7.19 (t, *J*=7.79 Hz, 1 H), 6.95 (d, *J*=8.07 Hz, 1 H), 6.88 (d, *J*=7.52 Hz, 1 H), 2.03 (s, 2 H), 1.20 - 1.31 (m, 2 H), 1.10 (dd, *J*=12.93, 7.43 Hz, 12 H);

^{13}C NMR (126 MHz, CDCl_3) δ ppm 160.8, 142.5, 141.9, 128.9, 128.2, 127.4, 126.9, 125.8, 121.3, 113.3, 16.8, 16.6, 12.4, 9.5.

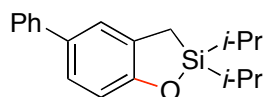


2i: 2,2-diisopropyl-5-methyl-2,3-dihydrobenzo[*d*][1,2]oxasilole

^1H NMR (500 MHz, CDCl_3) δ ppm 7.04 (s, 1 H), 6.87 (d, $J=7.52$ Hz, 1 H), 6.76 (d, $J=8.07$ Hz, 1 H), 2.26 (s, 3 H), 2.01 (s, 2 H), 1.14 - 1.25 (m, 2 H), 1.05 (dd, $J=7.43, 5.23$ Hz, 12 H);

^{13}C NMR (126 MHz, CDCl_3) δ ppm 158.3, 130.0, 129.1, 127.7, 127.3, 113.6, 20.7, 16.7, 16.6, 12.3, 9.8.

HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{22}\text{OSi}$ $[\text{M}]^+$: 234.14400. Found: 234.14447.



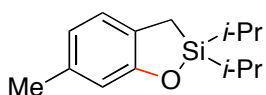
2j: 2,2-diisopropyl-5-phenyl-2,3-dihydrobenzo[*d*][1,2]oxasilole

Analytic sample was obtained by three columns of chromatography on Florisil[®].

^1H NMR (500 MHz, CDCl_3) δ ppm 7.54 - 7.60 (m, 2 H), 7.49 (s, 1 H), 7.42 (t, $J=7.70$ Hz, 2 H), 7.27 - 7.36 (m, 2 H), 6.96 (d, $J=8.44$ Hz, 1 H), 2.13 (s, 2 H), 1.21 - 1.33 (m, 2 H), 1.11 (dd, $J=7.43, 6.14$ Hz, 12 H);

^{13}C NMR (126 MHz, CDCl_3) δ ppm 160.3, 141.4, 133.4, 128.6, 128.2, 128.1, 126.8, 126.4, 126.3, 114.2, 16.8, 16.6, 12.4, 9.9.

HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{24}\text{OSi}$ $[\text{M}]^+$: 296.15965. Found: 296.15903.



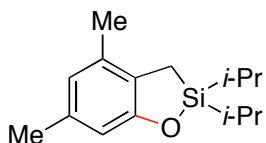
2k: 2,2-diisopropyl-6-methyl-2,3-dihydrobenzo[*d*][1,2]oxasilole

Analytic sample was obtained by three columns of chromatography on Florisil[®].

^1H NMR (500 MHz, CDCl_3) δ ppm 7.10 (d, $J=7.52$ Hz, 1 H), 6.71 (s, 1 H), 6.63 (d, $J=7.52$ Hz, 1 H), 2.29 (s, 3 H), 2.00 (s, 2 H), 1.15 - 1.26 (m, 2 H), 1.06 (dd, $J=7.34, 5.69$ Hz, 12 H);

^{13}C NMR (126 MHz, CDCl_3) δ ppm 160.5, 137.3, 128.9, 124.3, 120.8, 114.8, 21.3, 16.7, 16.6, 12.3, 9.3.

HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{22}\text{OSi}$ $[\text{M}]^+$: 234.14400. Found: 234.14504.

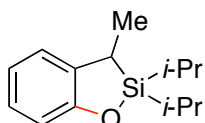


2l: 2,2-diisopropyl-4,6-dimethyl-2,3-dihydrobenzo[*d*][1,2]oxasilole

^1H NMR (500 MHz, CDCl_3) δ ppm 6.57 (s, 1 H), 6.53 (s, 1 H), 2.25 (s, 3 H), 2.24 (s, 3 H), 1.82 (s, 2 H), 1.15 - 1.25 (m, 2 H), 1.06 (dd, $J=7.34, 3.30$ Hz, 12 H);

^{13}C NMR (126 MHz, CDCl_3) δ ppm 160.4, 137.4, 136.9, 123.4, 122.0, 112.2, 21.3, 19.7, 16.7, 16.6, 12.3, 7.9.

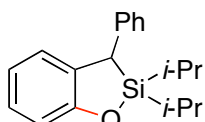
HRMS (EI) calcd. for $\text{C}_{15}\text{H}_{24}\text{OSi}$ $[\text{M}]^+$: 248.15965. Found: 248.15892.

**2m:** 2,2-diisopropyl-3-methyl-2,3-dihydrobenzo[*d*][1,2]oxasilole

^1H NMR (500 MHz, C_6D_6) δ ppm 7.27 (d, $J=7.52$ Hz, 1 H), 7.14 - 7.18 (m, 1 H), 7.11 (t, $J=7.61$ Hz, 1 H), 6.96 (td, $J=7.34$, 1.10 Hz, 1 H), 2.34 (q, $J=7.70$ Hz, 1 H), 1.35 (d, $J=7.70$ Hz, 3 H), 1.10 - 1.18 (m, 5 H), 1.05 - 1.10 (m, 6 H), 1.01 (d, $J=6.79$ Hz, 3 H);

^{13}C NMR (126 MHz, C_6D_6) δ ppm 159.9, 134.1, 128.1, 126.8, 120.5, 114.4, 18.1, 17.1, 17.0, 16.8, 16.5, 14.8, 12.0, 11.8.

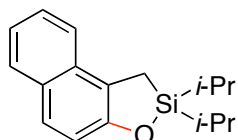
HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{22}\text{OSi}$ $[\text{M}]^+$: 234.14400. Found: 234.14295.

**2n:** 2,2-diisopropyl-3-phenyl-2,3-dihydrobenzo[*d*][1,2]oxasilole

^1H NMR (400 MHz, CDCl_3) δ ppm 7.22 - 7.28 (m, 2 H), 7.15 - 7.21 (m, 2 H), 7.10 - 7.15 (m, 1 H), 7.05 (dd, $J=7.82$, 1.24 Hz, 2 H), 6.99 (d, $J=8.04$ Hz, 1 H), 6.90 (td, $J=7.42$, 1.24 Hz, 1 H), 3.94 (s, 1 H), 1.30 - 1.41 (m, 1 H), 1.19 (d, $J=7.31$ Hz, 3 H), 1.13 (d, $J=7.31$ Hz, 3 H), 0.95 - 1.07 (m, 1 H), 0.89 (d, $J=7.45$ Hz, 3 H), 0.72 (d, $J=7.45$ Hz, 3 H);

^{13}C NMR (101 MHz, CDCl_3) δ ppm 160.4, 142.2, 131.0, 129.4, 128.4, 128.2, 127.7, 124.8, 120.8, 114.4, 34.2, 17.1, 16.9, 16.7, 16.5, 12.4, 12.2.

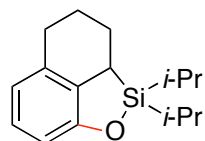
HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{24}\text{OSi}$ $[\text{M}]^+$: 296.15965. Found: 296.16059.

**2o:** 2,2-diisopropyl-1,2-dihydronaphtho[1,2-*d*][1,2]oxasilole

^1H NMR (500 MHz, CDCl_3) δ ppm 7.87 (d, $J=8.44$ Hz, 1 H), 7.83 (d, $J=8.25$ Hz, 1 H), 7.69 (d, $J=8.80$ Hz, 1 H), 7.54 (ddd, $J=8.21$, 6.92, 1.19 Hz, 1 H), 7.36 (ddd, $J=8.07$, 6.97, 1.10 Hz, 1 H), 7.25 (d, $J=8.80$ Hz, 1 H), 2.30 (s, 2 H), 1.27 - 1.38 (m, 2 H), 1.15 (dd, $J=7.43$, 1.74 Hz, 12 H);

^{13}C NMR (126 MHz, CDCl_3) δ ppm 158.1, 133.7, 129.0, 128.5, 128.2, 126.3, 123.5, 122.9, 119.9, 116.7, 16.8, 16.6, 12.4, 7.6.

HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{22}\text{OSi}$ $[\text{M}]^+$: 270.14400. Found: 270.14489.

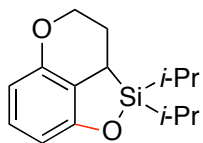
**2p:** 2,2-diisopropyl-2a,3,4,5-tetrahydro-2*H*-naphtho[1,8-*cd*][1,2]oxasilole

^1H NMR (500 MHz, CDCl_3) δ ppm 6.99 (td, $J=7.75$, 1.19 Hz, 1 H), 6.67 (d, $J=7.89$ Hz, 1 H), 6.63 (d, $J=7.70$ Hz, 1 H), 2.79 - 2.88 (m, 1 H), 2.65 - 2.74 (m, 1 H), 2.29 - 2.37 (m, 1 H), 2.02 - 2.16 (m, 2 H), 1.61 - 1.81 (m, 2 H), 1.32 - 1.42 (m, 1 H), 1.07 - 1.22 (m, 7 H), 0.98 (dd, $J=7.34$, 4.40 Hz, 6 H);

^{13}C NMR (126 MHz, CDCl_3) δ ppm 158.3, 136.3, 129.1, 126.7, 120.1, 110.5, 26.9, 25.4, 23.4, 22.7, 17.4, 17.1, 16.9, 16.8, 12.4, 11.4.

HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{24}\text{OSi}$ $[\text{M}]^+$: 260.15965. Found:

260.16007.

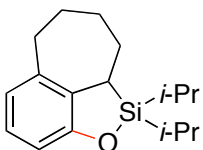


2q: 2,2-diisopropyl-2,2a,3,4-tetrahydro-[1,2]oxasilolo[3,4,5-*de*]chromene

^1H NMR (500 MHz, CDCl_3) δ ppm 6.96 (t, $J=8.16$ Hz, 1 H), 6.43 (d, $J=7.89$ Hz, 1 H), 6.35 (d, $J=8.25$ Hz, 1 H), 4.43 - 4.54 (m, 1 H), 4.00 - 4.12 (m, 1 H), 2.47 (dd, $J=12.47, 4.58$ Hz, 1 H), 2.09 - 2.16 (m, 1 H), 1.97 - 2.08 (m, 1 H), 1.33 - 1.44 (m, 1 H), 1.16 - 1.23 (m, 6 H), 1.09 - 1.16 (m, 1 H), 0.96 - 1.02 (m, 6 H);

^{13}C NMR (126 MHz, CDCl_3) δ ppm 159.1, 153.7, 128.1, 113.7, 107.6, 105.6, 68.2, 22.7, 18.8, 17.4, 17.1, 16.8, 16.6, 12.2, 11.4.

HRMS (EI) calcd. for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{Si}$ $[\text{M}]^+$: 262.13891. Found: 262.13987.



2r:

^1H NMR (500 MHz, CDCl_3) δ ppm 6.99 (t, $J=7.79$ Hz, 1 H), 6.75 (d, $J=8.07$ Hz, 1 H), 6.66 (d, $J=7.52$ Hz, 1 H), 2.74 - 2.88 (m, 2 H), 2.42 (d, $J=11.55$ Hz, 1 H), 2.18 (d, $J=13.57$ Hz, 1 H), 1.98 - 2.10 (m, 2 H), 1.58 - 1.70 (m, 1 H), 1.46 - 1.54 (m, 1 H), 1.36 - 1.45 (m, 1 H), 1.29 - 1.36 (m, 1 H), 1.21 - 1.28 (m, 1 H), 1.18 (dd, $J=7.34, 6.24$ Hz, 6 H), 1.06 (dd, $J=9.35, 7.34$ Hz, 6 H);

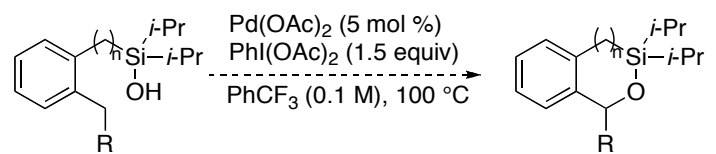
^{13}C NMR (126 MHz, CDCl_3) δ ppm 159.5, 145.0, 132.9, 127.2, 120.7, 112.1, 37.2, 34.7, 29.5, 28.4, 26.3, 17.6, 17.4, 16.8, 16.4, 12.4, 11.7.

HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{26}\text{OSi}$ $[\text{M}]^+$: 274.17530. Found: 274.17477.

Attempts on sp^3 C–H activation

We were also interested to verify whether this silanol-directed C–H oxygenation reaction could be extended to aliphatic C–H bonds. Thus, various silanols with both nonactivated and activated benzylic C–H bonds were prepared for model studies. Standard oxygenation conditions were applied to those substrates, and the reaction outcomes were listed in Tables S1 and S2. However, all attempts on aliphatic C–H activation failed, thus suggesting the current silanol-directed C–H oxygenation method is effective for aromatic C–H bond activation only.

Table S1. Attempts on sp^3 C–H activation (0.1 mmol scale).



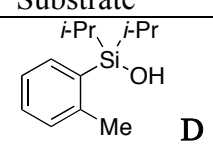
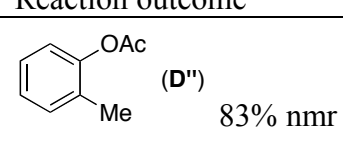
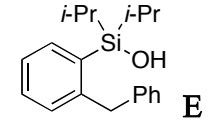
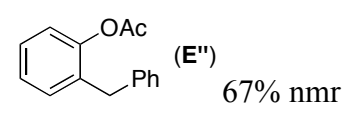
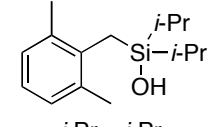
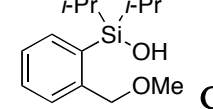
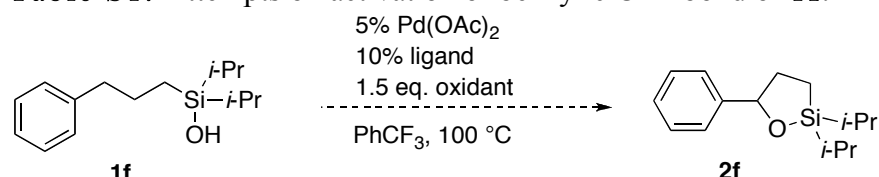
Entry	Substrate	Reaction outcome
1	 D	 (D'') 83% nmr
2	 E	 (E'') 67% nmr
3	 F	Slow decomposition of F without formation of desired cyclization product
4	 G	Slow decomposition of G without formation of desired cyclization product

Table S1. Attempts on activation of benzylic C–H bond of **1f**.



Entry	Ligand	Oxidant	Yield, %
1	none	PhI(OAc) ₂	0 (slow decomposition of 1f)
2	none	Oxone	0 (no reaction)
3	none	AcOO ^t Bu	0 (no reaction)
4	(+)-Menthyl(O ₂ C)-Leu-OH	PhI(OAc) ₂	0 (decomposition)
5	Boc-Val-OH	PhI(OAc) ₂	0 (decomposition)
6	1,10-phenanthroline	PhI(OAc) ₂	0 (decomposition)

Part III: Mechanistic Studies

GC Trace of the Reaction:

An oven dried 2.5 mL Wheaton V-vial, containing a stirring bar, was charged with silanol **1c** (47.2 mg, 0.2 mmol), Pd(OAc)₂ (2.2 mg, 5 mol%), tetradecane (26 μ L, 0.1 mmol, internal standard), and PhI(OAc)₂ (100 mg, 0.3 mmol) under N₂ atmosphere. 2 mL of dry PhCF₃ was added via syringes and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 100 °C. Aliquots (~10 μ L) were removed from the reaction mixture periodically and analyzed by GC/MS. Both starting material and products were calibrated with internal standard. The resulted reaction profile was strikingly different from our previous result, in which the reaction profile clearly involves acetoxyated product as an intermediate.⁴ Thus, a switched reaction pathway may be operative in this transformation.

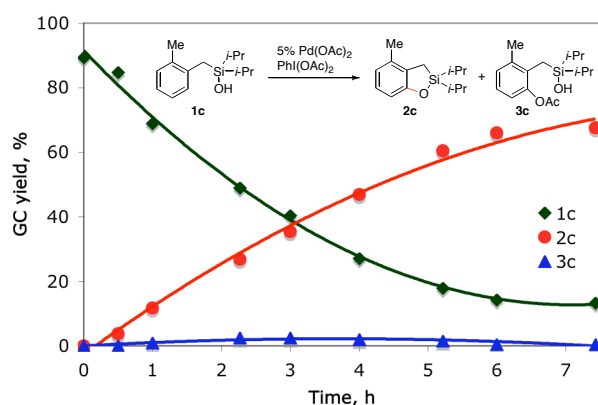
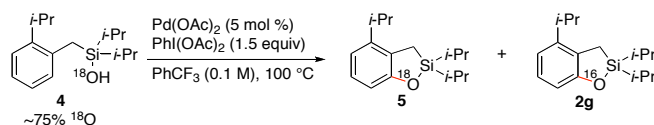


Figure S1. Reaction profile.

GC/MS trace of oxygenation of ¹⁸O-labeled silanol **4** and evaluation the effects of acidic and basic environments.



Three oven dried 2.5 ml Wheaton V-vials, containing stirring bars, were all charged with ¹⁸O-labeled silanol **4** (53.2 mg, 0.2 mmol), Pd(OAc)₂ (2.2 mg, 5 mol%), PhI(OAc)₂ (98 mg, 0.3 mmol), and PhCF₃ (2 ml) under N₂ atmosphere. Two of them were additionally charged with 2 equiv of HOAc or Li₂CO₃, respectively. The reaction mixtures were heated at 100 °C. The reactions were monitored by GC/MS periodically. During the reaction, the acetoxyated product was barely observed in all cases. The abundance of ¹⁸O in the starting silanol **4** remained unchanged during the reaction (shown in red). A mixture of cyclization products **5** with ¹⁸O label and **2g** without ¹⁸O label were formed. The abundance of ¹⁸O label in the products was lower than that of **4** and gradually decreased as the reaction proceeded. It was also found that the abundance of ¹⁸O label in

⁴ C. Huang, N. Ghavtadze, B. Chattopadhyay, V. Gevorgyan, *J. Am. Chem. Soc.* **2011**, *133*, 17630-17633.

the products was much lower in acidic conditions but higher in basic media compared to additive-free reaction conditions. The nmr yields of those reactions were 85% for neutral, 72% for acidic, and 54% for basic conditions, respectively.

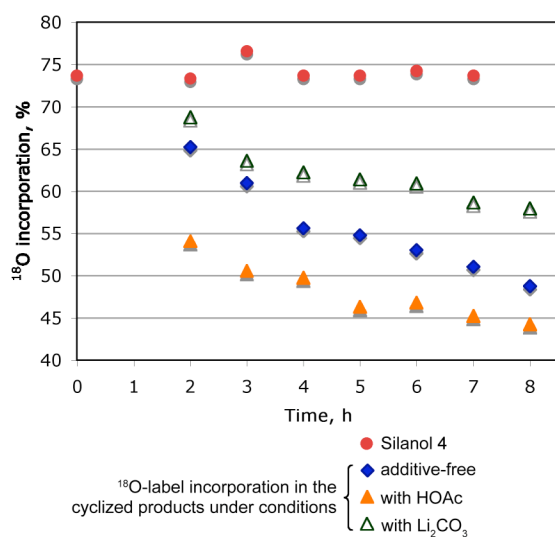
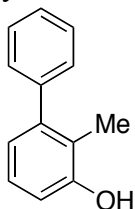


Figure S2. The abundance of ¹⁸O incorporation in the starting material shown in red, the abundance of ¹⁸O incorporation in the cyclized product (neutral conditions in blue; acidic conditions in solid orange; basic conditions in hollow green).

Part IV: Further Transformation of Silanol Directing Group

Desilylation of **2h**

A 0.5 mL Wheaton V-vial, containing a stirring bar, was charged with cyclic product **2h** (29.6 mg, 0.1 mmol), CsF (60.8 mg, 0.4 mmol) and DMF (0.3 mL) was added via syringes and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 80 °C for 2 h. The product was purified by silica gel column chromatography (eluent: hexanes/AcOEt 10:1) to give 2-methylbiphenyl-3-ol⁵ as a yellow solid (12.0 mg, 65%).



8:

¹H NMR (500 MHz, CDCl₃) δ ppm 7.41-7.44 (m, 2H), 7.32-7.37 (m, 3H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 4.78 (s, 1H), 2.17 (s, 3 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 154.0, 143.7, 141.6, 129.3, 128.0, 126.8, 126.2, 122.5, 121.5, 113.8, 13.0.

HRMS (EI) calcd. for C₁₃H₁₂O [M]⁺: 184.08882. Found: 184.08895.

Ring Opening of **2i** with Meerwein Salt

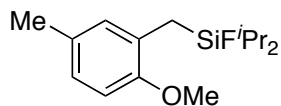
An oven dried 0.5 mL Wheaton V-vial, containing a stirring bar, was charged with oxasilacycle **2i** (234 mg, 1 mmol) and Me₃O⁺BF₄⁻ (296 mg, 2 mmol) under argon atmosphere. Dry DCE (0.5 mL) was added via syringes and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 50 °C for 48 h. After completion of the reaction, the mixture was cooled down to RT, transferred into 25 mL flask, diluted with DCM (10 mL) and treated with saturated aqueous solution of sodium bicarbonate. The reaction mixture was stirred for additional 30 min at RT. The aqueous layer was extracted with DCM and the organic phase was washed with water. The combined organic extracts dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexanes/AcOEt 50:1) to give fluorodiisopropyl(2-methoxy-5-methylbenzyl)silane **9** as a yellow oil (200 mg, 75%).

Semi-one-pot procedure (**1i**→**9**)

An oven dried 25 mL flask, containing a stirring bar, was charged with benzylsilanol **1i** (236 mg, 1.0 mmol), Pd(OAc)₂ (11.2 mg, 5 mol %), and PhI(OAc)₂ (392 mg, 1.2 mmol) under N₂ atmosphere. Dry PhCF₃ (10 mL) was added via syringes and the reaction was heated at 100 °C for 7 h. The resulting mixture was cooled down to RT and filtered through a short layer of Florisil plug with the aid of EtOAc. The filtrate was concentrated under a reduced pressure and further dried under vacuum. The resulted crude cyclic product was transferred into a 0.5 mL Wheaton V-vial. Then, Me₃O⁺BF₄⁻ (296 mg, 2 mmol) and Dry DCE (0.5 mL) was added and the reaction mixture was heated at 50 °C for 48 h. After completion of the reaction, the mixture was cooled down to RT, diluted with DCM (10 mL) and treated with saturated aqueous solution of sodium bicarbonate. The reaction mixture was stirred for additional 30 min at RT. The aqueous layer was

⁵ D. J. Krysan, A. Gurski, L. S. Leibeskind, *J. Am. Chem. Soc.* **1992**, *114*, 1412-1418.

extracted with DCM and the organic phase was washed with water. The combined organic extracts dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexanes/AcOEt 50:1) to give 136.8 mg of **9** (51%).



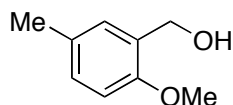
9:

¹H NMR (500 MHz, CDCl₃) δ ppm 6.94 (s, 1H), 6.90 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.71 (d, *J* = 8.1, 1H), 3.79 (s, 3H), 2.25-2.26 (m, 5 H), 1.01-1.07 (m, 14H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 154.5, 130.9, 126.2, 126.0, 109.9, 108.3, 55.0, 20.5, 16.72, 16.69, 14.2 (d, *J* = 12.9 Hz), 12.5 (d, *J* = 12.9 Hz).

HRMS (EI) calcd. for C₁₅H₂₅OSiF₂ [M]⁺: 268.16588. Found: 268.16576.

Tamao oxidation of 9: A 10 mL flask, containing a stirring bar, was charged with **9** (26.8 mg, 0.1 mmol), KF on Al₂O₃ (36.5 mg, 0.2 mmol), and DMF (1 mL) and 50% H₂O₂ (80 μL) was added via syringes under argon atmosphere. The reaction mixture was heated at 80 °C for 3 h. The product was purified by silica gel column chromatography (eluent: hexanes/AcOEt 5:1) to give (2-methoxy-5-methylphenyl)methanol (**10**) as a colorless oil (11.5 mg, 76%).



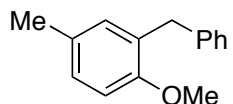
10:

¹H NMR (500 MHz, CDCl₃) δ ppm 7.07-7.09 (m, 2H), 6.79 (d, *J* = 7.7 Hz, 1H), 4.66 (d, *J* = 5.9 Hz, 2H), 3.85 (s, 3H), 2.32 (t, *J* = 6.2 Hz, 1H), 2.30 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 155.4, 129.9, 129.6, 129.1, 128.8, 110.2, 62.2, 55.4, 20.4.

HRMS (EI) calcd. for C₉H₁₂O₂ [M]⁺: 152.08373. Found: 152.081415.

Hiyama-Denmark coupling of 9: A 10 mL flask, containing a stirring bar, was charged with **9** (26.8 mg, 0.1 mmol), Pd(PPh₃)₄ (6 mg, 5 mol%), Ag₂O (25.5 mg, 0.11 mmol) and 0.4 mL of THF and PhI (14.5 μL, 0.13 mmol) was added via syringes under argon atmosphere. The reaction mixture was heated at 60 °C for 24 h.⁶ The product was purified by silica gel column chromatography (eluent: hexanes/AcOEt 5:1) to give (2-methoxy-5-methylphenyl)methanol (**11**) as a colorless oil (13.8 mg, 65%).



11:

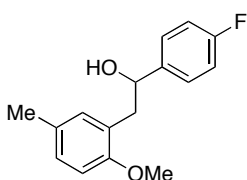
¹H NMR (500 MHz, CDCl₃) δ ppm 7.27-7.30 (m, 2H), 7.18-7.24 (m, 3H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.90 (s, 1H), 6.79 (d, *J* = 8.4, 1H), 3.96 (s, 2H), 3.81 (s, 3H), 2.26 (s, 3 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 155.3, 141.2, 131.1, 129.6,

⁶ This reaction was performed under reported conditions: K. Itami, M. Mineno, T. Kamei, J-i. Yoshida, *Org. Lett.* **2002**, *4*, 3635-3638.

129.4, 128.9, 128.2, 127.6, 125.7, 110.5, 55.5, 35.8, 20.5.
 HRMS (EI) calcd. for C₁₅H₁₆O [M]⁺: 212.12012. Found:
 212.12084.

Nucleophilic addition to 9: A 0.5 mL Wheaton V-vial, containing a stirring bar, was charged with compound **9** (26.8 mg, 0.1 mmol), CsF (30.4 mg, 0.2 mmol), *p*-F-benzaldehyde (22.8 mg, 0.2 mmol). DMF (0.3 mL) was added via syringes and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 60 °C for 2 h. The product was purified by silica gel column chromatography (eluent: hexanes/AcOEt 20:1) to give 1-(4-fluorophenyl)-2-(2-methoxy-5-methylphenyl)ethanol (**12**) as a yellow solid (23 mg, 88%).

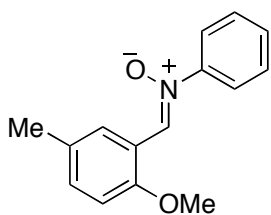


12:
¹H NMR (500 MHz, CDCl₃) δ ppm 7.34-7.37 (m, 2H), 7.01-7.05 (m, 3H), 6.89 (d, *J* = 2.2 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 4.94 (dt, *J* = 8.4, 3.3 Hz, 1H), 3.84 (s, 3H), 3.06 (dd, *J* = 13.6, 4.0 Hz, 1H), 2.91 (dd, *J* = 13.6, 8.8 Hz, 1H), 2.65 (d, *J* = 2.9 Hz, 1H), 2.27 (s, 3 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 162.0 (d, *J* = 244.1 Hz), 155.5, 140.3, 132.2, 130.0, 128.3, 127.3 (d, *J* = 7.4 Hz), 126.1, 114.9 (d, *J* = 20.4 Hz), 110.4, 73.8, 55.5, 41.4, 20.4.

HRMS (EI) calcd. for C₁₆H₁₇O₂F [M]⁺: 260.12126. Found: 260.12197.

C–N bond formation of 9: A 0.5 mL Wheaton V-vial, containing a stirring bar, was charged with compound **9** (53.6 mg, 0.2 mmol), CsF (60.8 mg, 0.4 mmol), and nitrosobenzene (66.0 mg, 0.6 mmol). DMF (0.5 mL) was added via syringes and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 60 °C for 2 h. The product was purified by silica gel column chromatography (eluent: hexanes/AcOEt 5:1) to give nitrone **13** as an orange oil (28 mg, 58%).



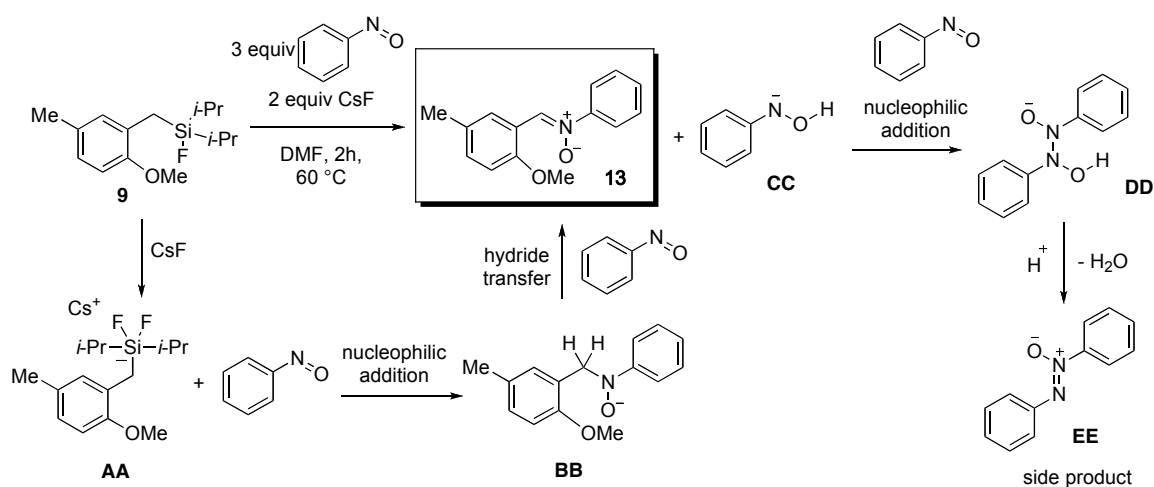
13:
¹H NMR (500 MHz, CDCl₃) δ ppm 9.32 (d, *J* = 2.2 Hz, 1H), 8.38 (s, 1H), 7.80 (m, 2H), 7.45-7.50 (m, 3H), 7.24 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 3.87 (s, 3H), 2.28 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 155.6, 149.6, 132.7, 130.1, 129.6, 129.4, 129.1, 129.0, 121.8, 119.6, 109.8, 55.7, 20.7.

HRMS (EI) calcd. for C₁₅H₁₅O₂N [M]⁺: 241.11028. Found: 241.10970.

Explanation of nitrene formation

The observed products of the reaction between **9** and nitrosobenzene were nitrene **13** and azoxybenzene **EE**. Based on this experimental fact, we propose the following mechanism for nitrene formation: fluoride anion attacks silicon atom forms pentavalent silicon anion **AA**. The formed nucleophile reacts with nitrosobenzene by generating intermediate anion **BB**, which transfers hydride to nitrosobenzene affording the nitrene product **13** and hydroxylamine anion **CC**. The latter adds to another molecule of nitrosobenzene and subsequent workup leads to the azoxybenzene **EE** side product.



Part V. Theoretical Investigations on the Mechanism of Meerwein Salt Mediated Ring Opening Process of Oxasilacycles

Quantum chemical calculations have been performed using the Gaussian 09 suite of programs.⁷ B3LYP⁸ functional with the 6-31G(d) basis set was used to compute the geometries and the normal mode vibration frequencies of the structures under study. For single-point energy calculations on B3LYP-optimized geometries the CPCM(UAKS)-M06-2X⁹ method with a dichloroethane solvent sphere and the 6-311G(d,p) basis set was applied.¹⁰ All energies discussed are 0 K energies including zero-point corrections. The character of the stationary points was verified on the basis of frequency analyses. The vibration related to the imaginary frequency of the transition structure corresponds to the nuclear motion along the reaction coordinate under study. An intrinsic reaction coordinate (IRC) calculation was performed in order to unambiguously connect the transition structure with the reactant and the product.

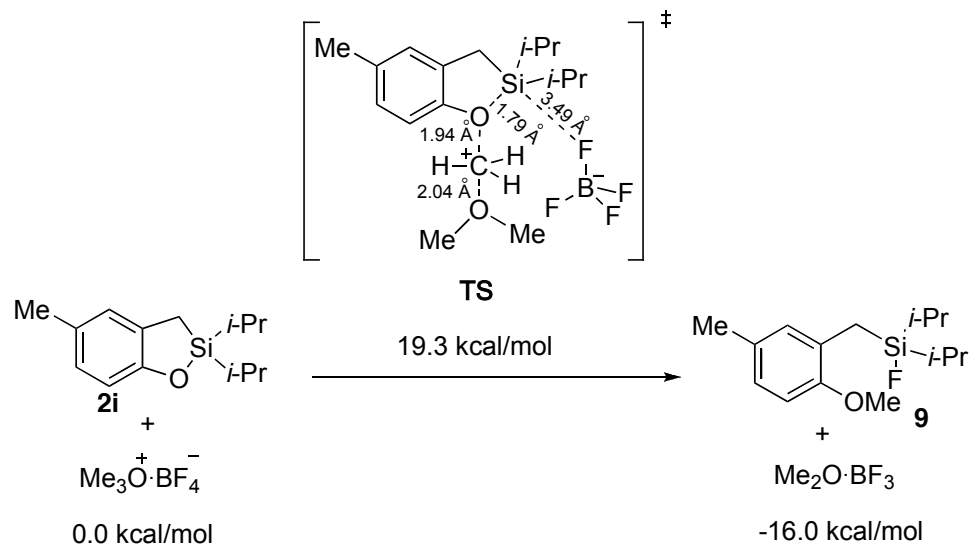
According to quantum chemical calculations the reaction proceeds through a concerted asynchronous mechanism via the transition structure TS, as shown in Scheme 1. Formation of the C–O bond precedes the transfer of the fluorine from the boron to the silicon atom. The activation barrier is calculated to be 19.3 kcal/mol and the reaction is exothermic by 16.0 kcal/mol (The energy of the starting structures is a sum of the energies of separately calculated the cyclic molecule and the Meerwein salt. Similarly, the energy of the products is a sum of the energies of the open ring structure and the BF₃ dimethyl etherate, calculated separately).

⁷ Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

⁸ (a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, **1988**, *37*, 785-789. (c) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200-1211. (d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623-11627.

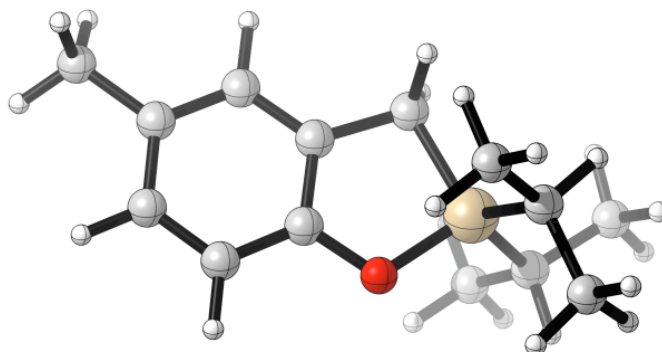
⁹ Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241.

¹⁰ (a) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995-2001. (b) V. Barone, M. Cossi, J. Tomasi, *J. Comput. Chem.* **1998**, *19*, 404-417. (c) Y. Takano, K. N. Houk, *J. Chem. Theory Comput.* **2005**, *1*, 70-77.



Scheme S1. Calculated relative energies of the starting structures, TS and Products for the Meerwein salt mediated ring opening process (CPCM(UAKS)-M06-2X/6-311G(d,p)//B3LYP/6-31G(d) including zero-point correction (ZPE)) (kcal/mol).

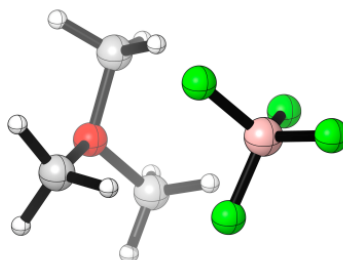
Cartesian coordinates, CPCM(UAKS)-M06-2X/6-311G(d,p)//B3LYP/6-31G(d)+ZPE energies and numbers of imaginary frequencies (in parenthesis) for the calculated structures



-911.0845503 (0)

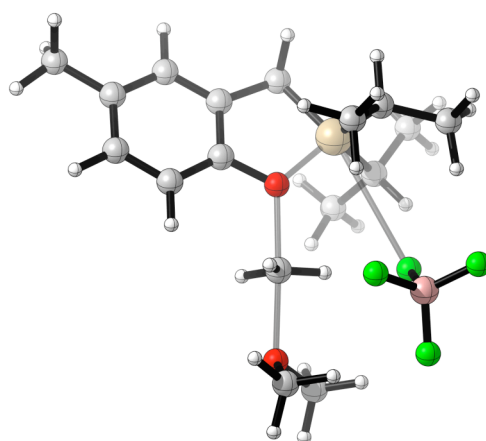
C	-3.70710700	-0.07153900	-0.18762800
C	-2.61448700	-0.28724700	-1.04069500
C	-1.30137500	-0.16089100	-0.58837200
C	-1.08020000	0.18849700	0.75642100
C	-2.14425500	0.40528000	1.62794500
C	-3.44754300	0.27179900	1.14587900
C	-0.03596300	-0.37102800	-1.40743400

O	0.22737900	0.30111000	1.17642600
Si	1.31766300	-0.01748000	-0.10680300
C	2.38798000	-1.51764900	0.34873700
C	2.35089500	1.54013400	-0.44779500
C	1.53370700	-2.73632500	0.74619800
C	3.38129700	-1.87272100	-0.77600000
C	3.34099200	1.85199200	0.69285900
C	1.45730000	2.76104000	-0.74282400
H	-2.79423300	-0.56120100	-2.07923200
H	-1.94743700	0.66833900	2.66263800
H	-4.28143800	0.43750200	1.82464900
H	0.00755300	0.30845600	-2.26837700
H	0.01599200	-1.38942800	-1.81467200
H	2.97146100	-1.21944100	1.23308200
H	2.93845200	1.32363600	-1.35520800
H	2.17119800	-3.57050200	1.06829900
H	0.93043800	-3.09726800	-0.09643900
H	0.84934200	-2.50022800	1.56775300
H	4.00943500	-2.72626300	-0.48855700
H	4.05200700	-1.03956800	-1.01778400
H	2.85846400	-2.15580500	-1.69910200
H	3.93142700	2.74850900	0.46113800
H	4.04681400	1.03173900	0.86808900
H	2.81268900	2.04406100	1.63468900
H	2.06831000	3.64145500	-0.98223400
H	0.83807300	3.01485200	0.12533500
H	0.78376700	2.58769000	-1.59001400
C	-5.12489600	-0.18208000	-0.70221000
H	-5.82694700	-0.41314500	0.10627000
H	-5.46219200	0.75488600	-1.16656100
H	-5.21756600	-0.96799400	-1.46041200



-619.1882720 (0)

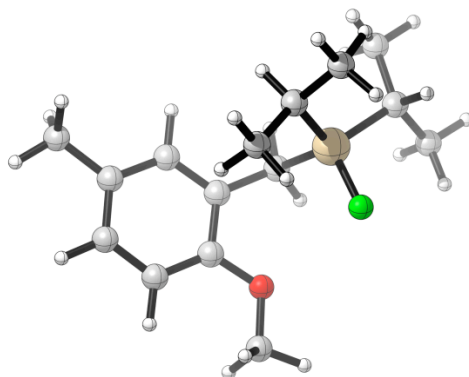
C	-1.44228400	0.00000000	-1.67592200
O	0.00000000	0.00000000	-2.05027800
C	0.72114200	1.24905500	-1.67592200
C	0.72114200	-1.24905500	-1.67592200
B	0.00000000	0.00000000	1.53892700
F	-0.58964100	1.18510500	1.01007600
F	0.00000000	0.00000000	2.90651800
F	-0.73151100	-1.10319700	1.01007600
F	1.32115200	-0.08190800	1.01007600
H	-1.90036100	-0.74299100	-2.32840500
H	-1.80337900	1.00016500	-1.90754600
H	-1.52289200	-0.24224600	-0.61622400
H	0.55165500	1.43998600	-0.61622400
H	0.30673100	2.01725600	-2.32840500
H	1.76785800	1.06169000	-1.90754600



-1530.2420030 (1)

C	-4.78610300	1.24942300	-0.33499600
C	-4.38436600	-0.06436000	-0.04833100
C	-3.03947200	-0.40729600	0.07591000
C	-2.07508300	0.59688500	-0.09375300
C	-2.43450600	1.90721600	-0.38957100
C	-3.79289200	2.21945200	-0.50162800
C	-2.49144100	-1.78867200	0.36889000
O	-0.74309200	0.18974200	0.04146500
Si	-0.60213000	-1.59408500	0.16271500
C	0.34479800	-2.05980300	1.73566900
C	-0.00757800	-2.31751300	-1.49468800
C	-0.01559100	-1.17713100	2.94576700
C	0.09044000	-3.54791300	2.06780800
C	1.33361700	-3.07885300	-1.46345700
C	-0.00958700	-1.26162500	-2.62339400
C	0.57708200	1.56310400	0.41043900
O	1.88863900	3.05896100	0.86106600
C	2.60044500	3.60480500	-0.26845400
C	2.78444000	2.66681600	1.91924800
F	2.68933900	-0.46273400	0.41497500
B	3.46033200	0.02519700	-0.70428300
F	4.42003400	0.92035000	-0.20785700
F	4.03281500	-1.04141500	-1.36399000
F	2.56247000	0.72877200	-1.54697600
H	-5.13812500	-0.83906300	0.08026300
H	-1.68789000	2.67753100	-0.54419500
H	-4.07768300	3.24305400	-0.73150200
H	-2.91250300	-2.53695300	-0.31335800
H	-2.75730000	-2.10973100	1.38526300
H	1.40878500	-1.92587700	1.51313300
H	-0.79804700	-3.05085500	-1.72855200
H	0.53144400	-1.51330300	3.83608300
H	-1.08554200	-1.22514100	3.18727100

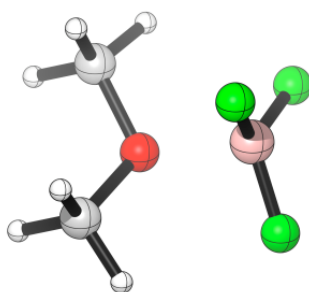
H	0.24110300	-0.12523200	2.78375800
H	0.67888300	-3.84418400	2.94540800
H	0.37269100	-4.21853800	1.24900400
H	-0.96408300	-3.73693900	2.30751200
H	1.49849200	-3.56318600	-2.43480200
H	1.34704000	-3.86872300	-0.70374000
H	2.18299000	-2.41675700	-1.28159700
H	0.18243100	-1.75095200	-3.58676400
H	0.77968900	-0.52099100	-2.46364600
H	-0.96960800	-0.73751500	-2.70669400
H	-0.06755600	2.01468000	1.14764800
H	1.31843000	0.82028400	0.66822500
H	1.85171900	3.84763300	-1.02502600
H	3.31722900	2.88012900	-0.65722700
H	3.10371200	4.52497000	0.05156900
H	2.16574100	2.25612800	2.72046100
H	3.30700000	3.55766100	2.28745000
H	3.49838600	1.92288000	1.55696200
H	0.55531600	1.90230400	-0.61125900
C	-6.25108400	1.59353900	-0.47657600
H	-6.40146600	2.67507000	-0.55069800
H	-6.68478700	1.13763100	-1.37589100
H	-6.83333800	1.23238500	0.37942600



-1050.8036060 (0)

C	3.15246200	-1.34432700	-0.63061300
C	1.82365900	-1.10077700	-1.01331800
C	1.17488000	0.11012000	-0.76999500
C	1.90537700	1.13312500	-0.12435200
C	3.22841000	0.91797100	0.26344300
C	3.83930500	-0.31548100	0.01217200
C	-0.26018100	0.33412600	-1.17590900
O	1.22484000	2.30491300	0.06978300
Si	-1.61012300	0.07619900	0.14159800
C	-3.30589600	0.11108200	-0.71601400
C	-1.34666200	-1.48834300	1.18979000
C	-3.57856100	1.46692600	-1.39709000
C	-3.49954300	-1.05196400	-1.70914600
C	-2.64533500	-1.95955200	1.87586000
C	-0.22978600	-1.29845100	2.23831400
C	1.87453400	3.35611600	0.76261600
F	-1.60660600	1.34125700	1.17820400
H	1.27073300	-1.88744800	-1.52546800
H	3.79358300	1.69953800	0.75866300
H	4.87102300	-0.46600300	0.32161800
H	-0.50946900	-0.34700700	-2.00122200
H	-0.38983100	1.35350600	-1.55925100
H	-4.04577000	-0.00869400	0.09015900
H	-1.02408500	-2.28003600	0.49468100
H	-4.59197300	1.49616200	-1.81983100
H	-2.87921700	1.64913900	-2.22291800
H	-3.48648100	2.30140800	-0.69343900
H	-4.51421600	-1.04319100	-2.12892000
H	-3.34783200	-2.03248400	-1.24174300
H	-2.80343900	-0.97765700	-2.55427400
H	-2.46151200	-2.86312300	2.47243100
H	-3.43827300	-2.19674300	1.15778100
H	-3.03515800	-1.19547300	2.56034200
H	-0.08677600	-2.22076600	2.81752800

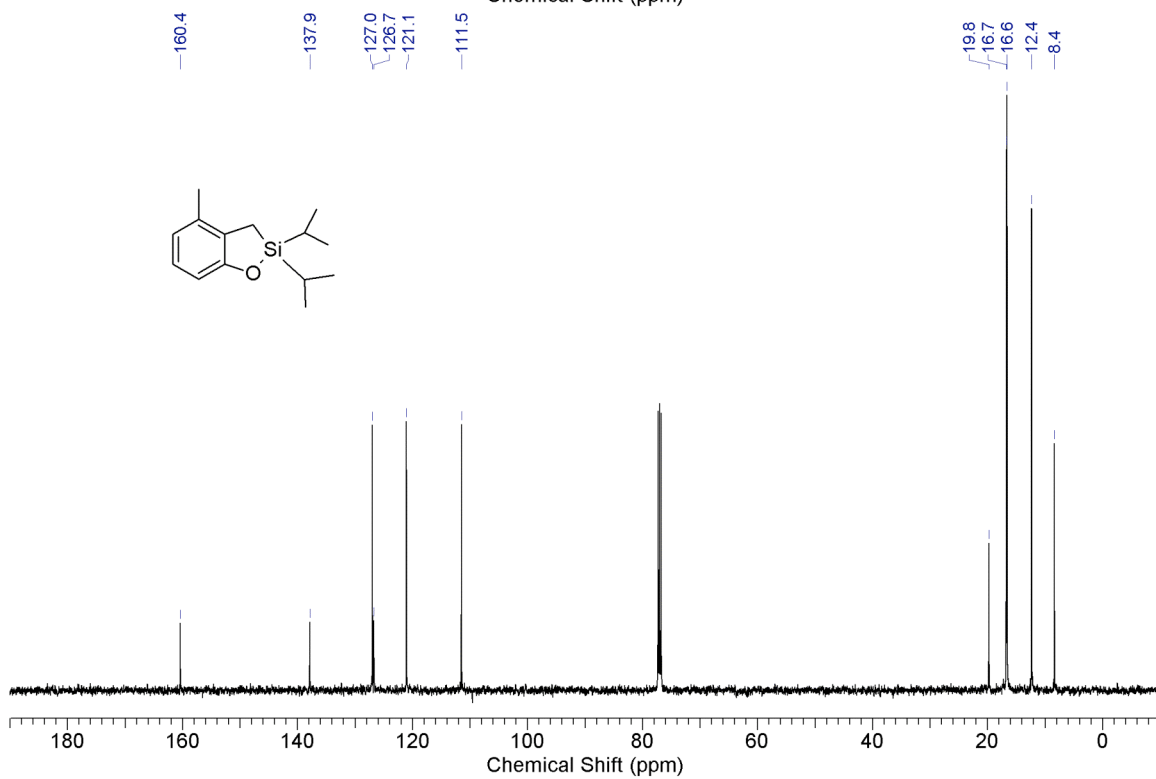
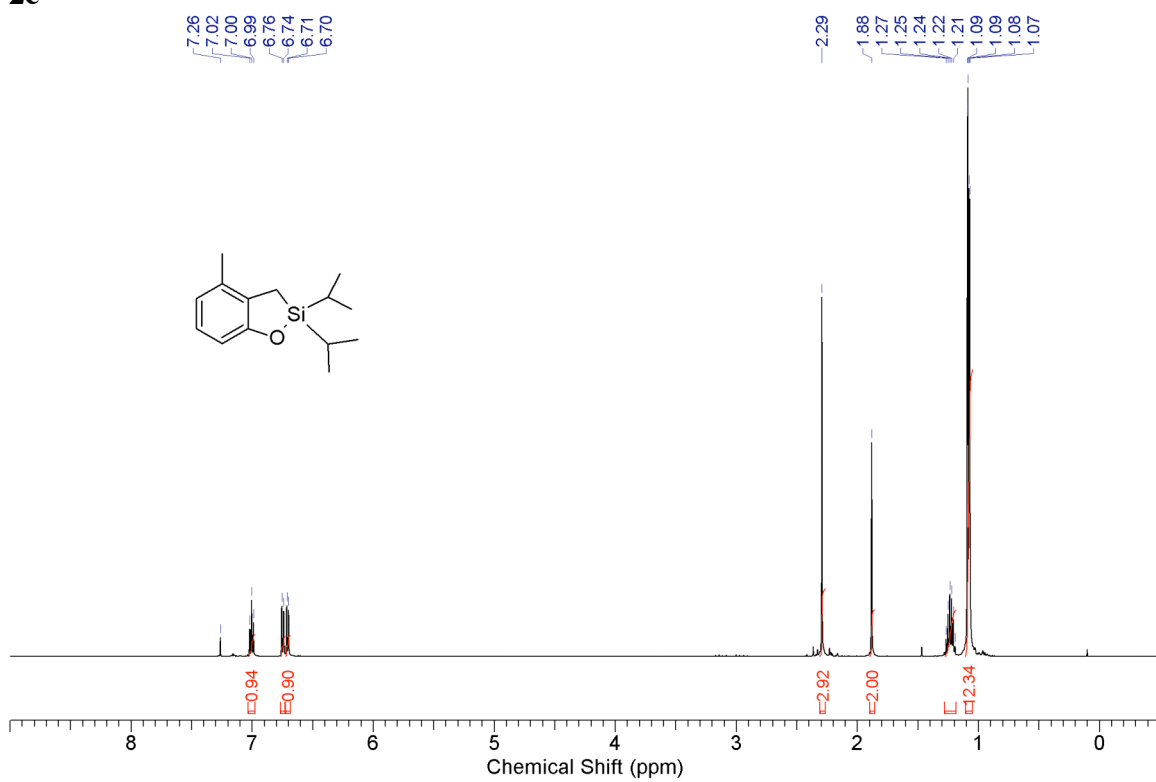
H	-0.48793700	-0.50133300	2.94497400
H	0.72909900	-1.04050900	1.77926900
H	2.76228900	3.70980400	0.22074300
H	1.14560600	4.16569100	0.82988100
H	2.16978600	3.04923900	1.77464600
C	3.80552300	-2.67763100	-0.91405700
H	4.85061200	-2.68504400	-0.58791900
H	3.29194600	-3.49856200	-0.39709100
H	3.79064900	-2.91545800	-1.98529600



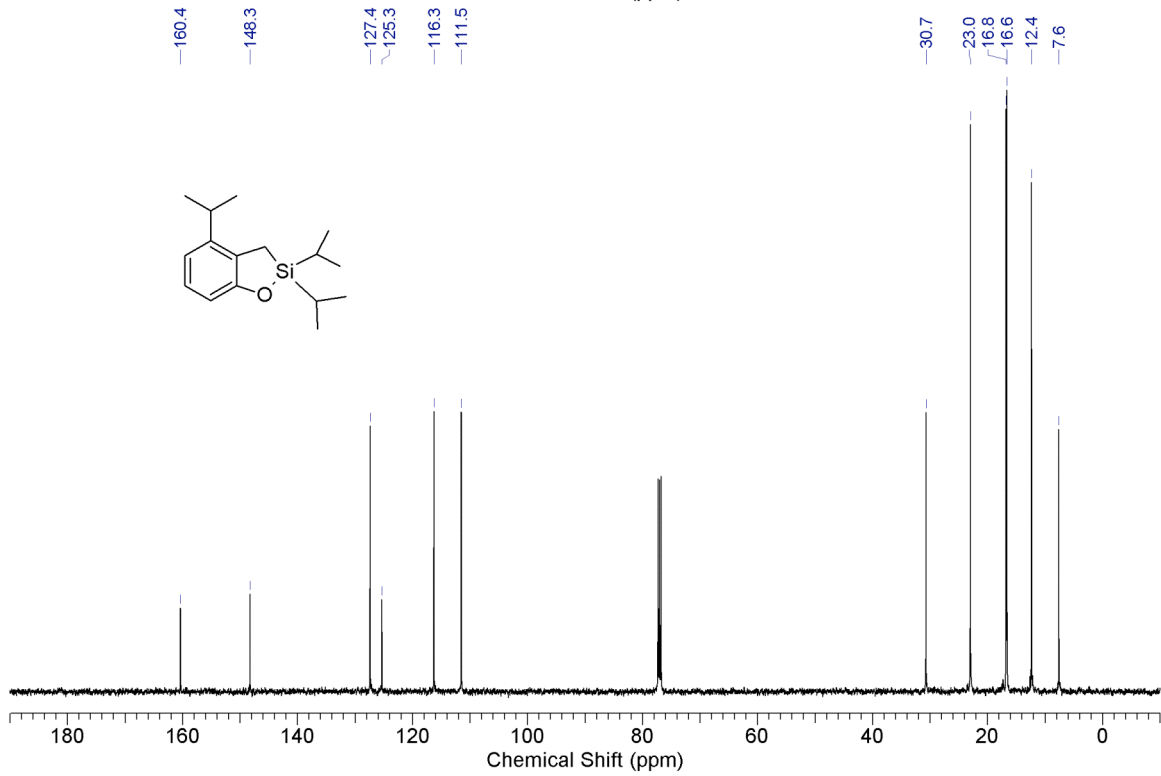
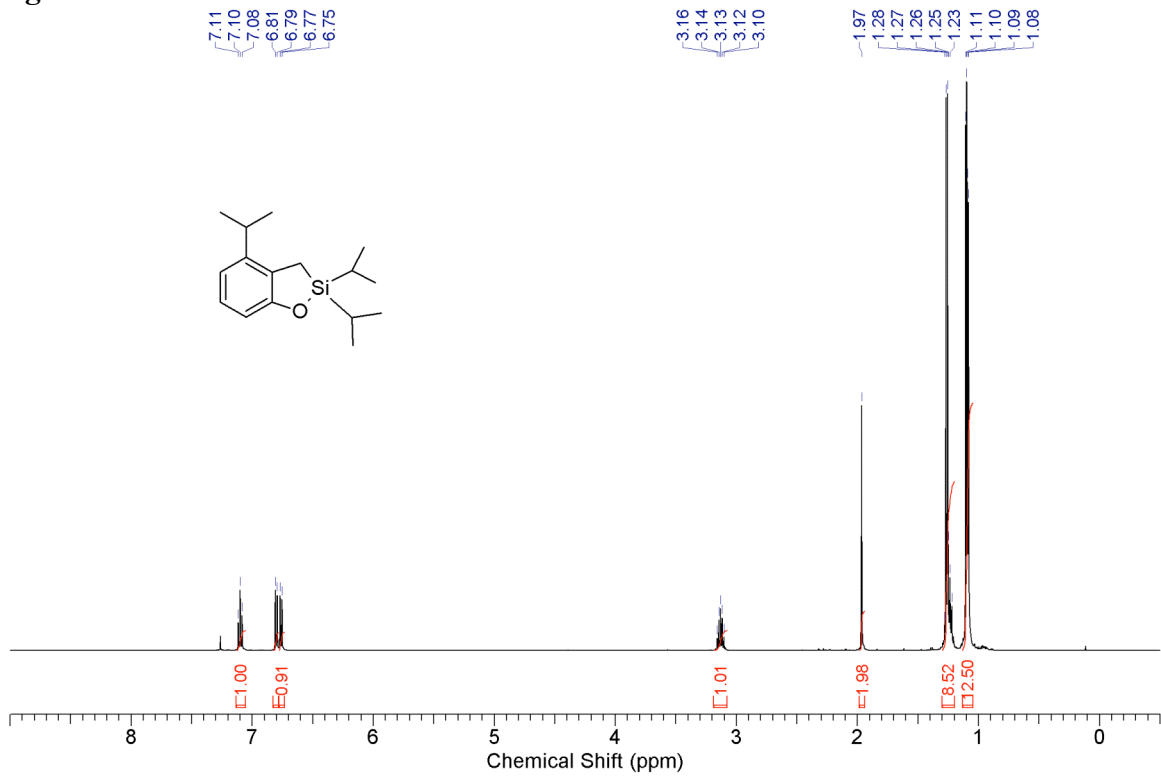
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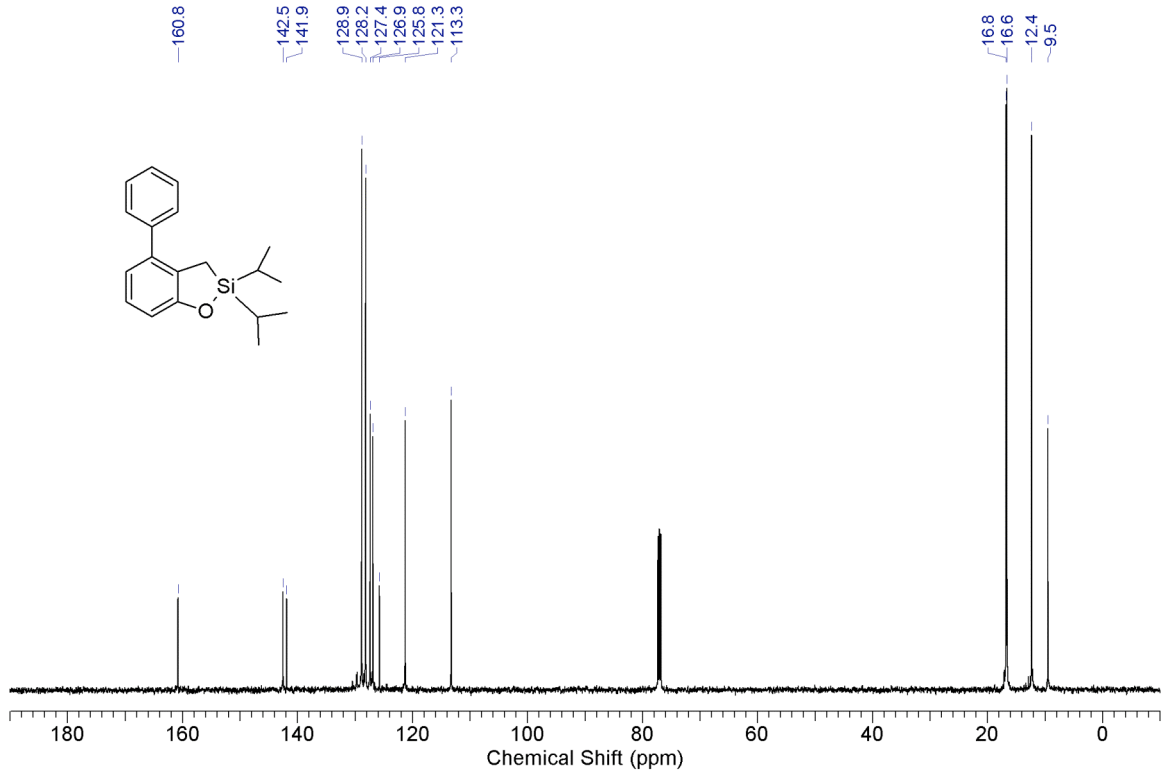
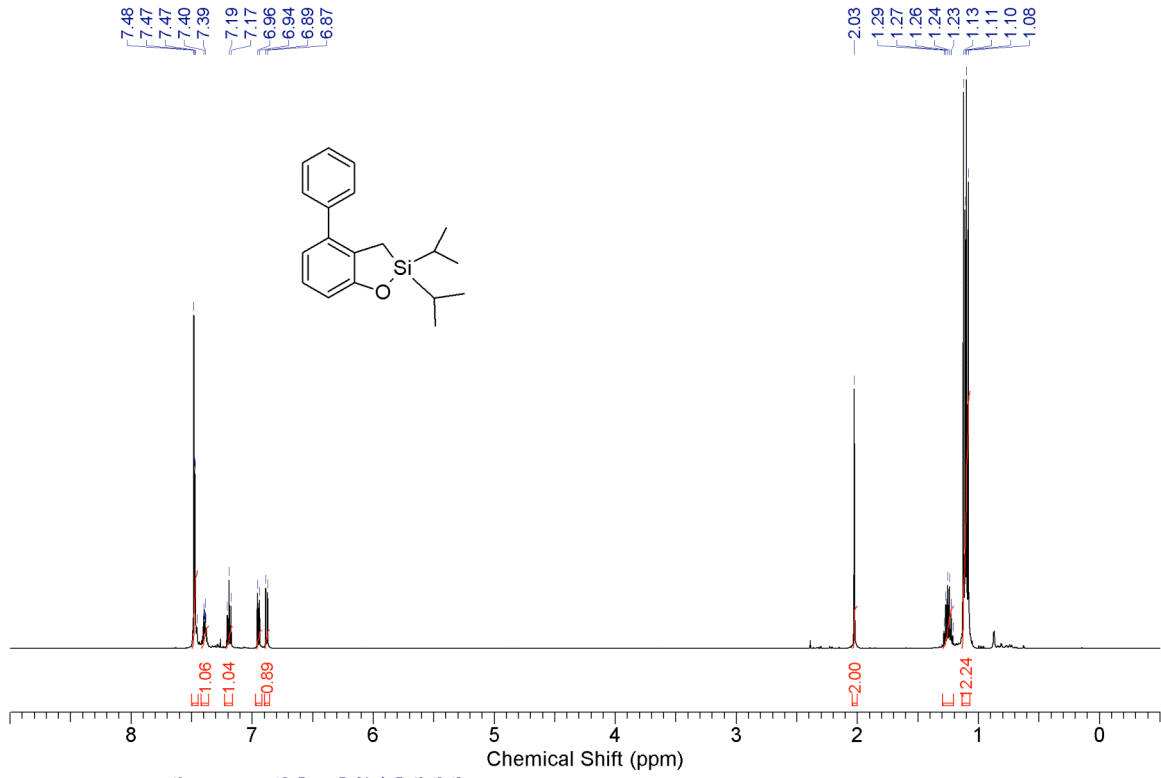
C	-0.29519900	1.48823200	1.20462200
O	-0.53914300	0.73460500	0.00000000
C	-0.29519900	1.48823200	-1.20462200
B	0.19212200	-0.84617600	0.00000000
F	-0.29519900	-1.36467900	1.15306900
F	-0.29519900	-1.36467900	-1.15306900
F	1.51888400	-0.54346700	0.00000000
H	-0.95368900	2.36102400	1.21104300
H	0.75515500	1.79389400	1.24966900
H	-0.53218800	0.82041800	2.02994300
H	-0.95368900	2.36102400	-1.21104300
H	-0.53218800	0.82041800	-2.02994300
H	0.75515500	1.79389400	-1.24966900

2c

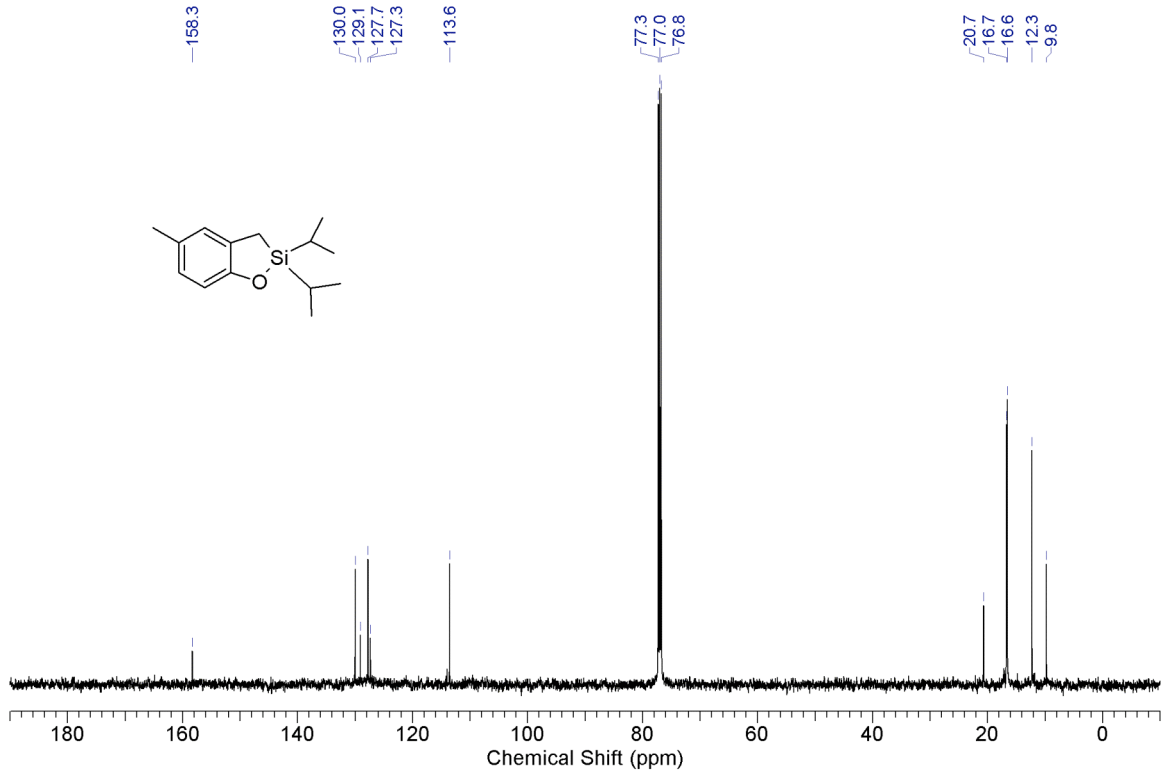
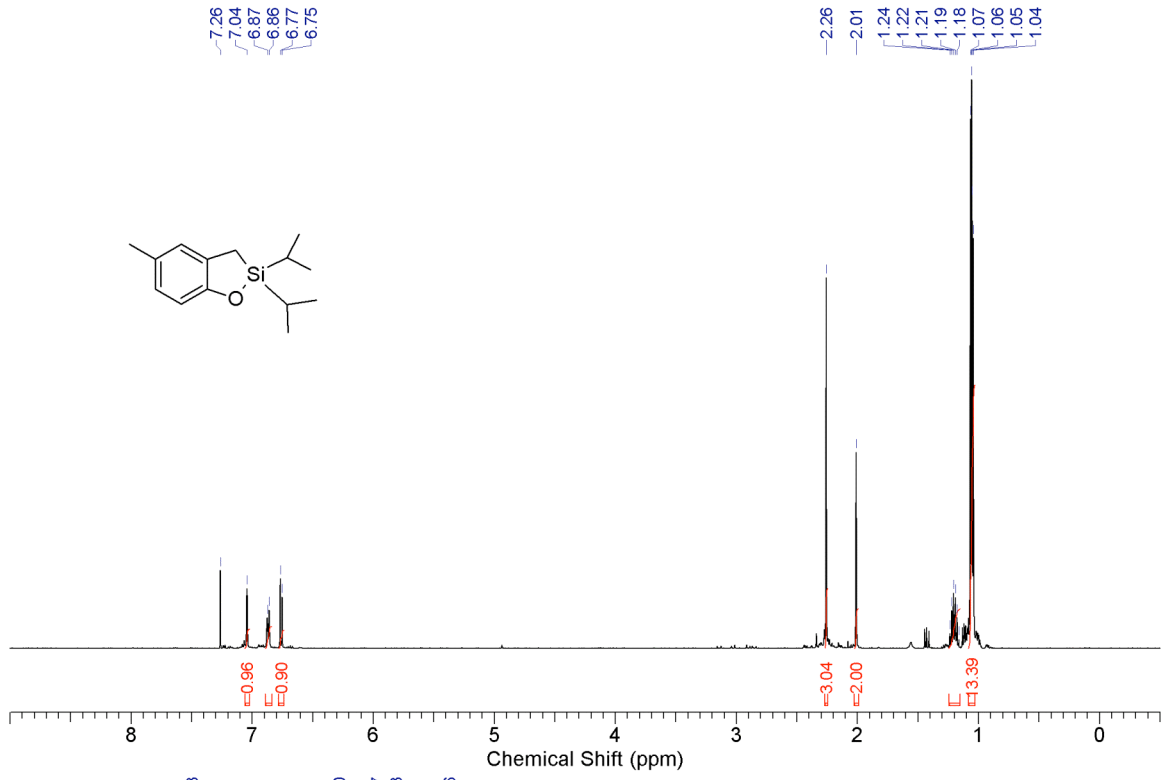


2g

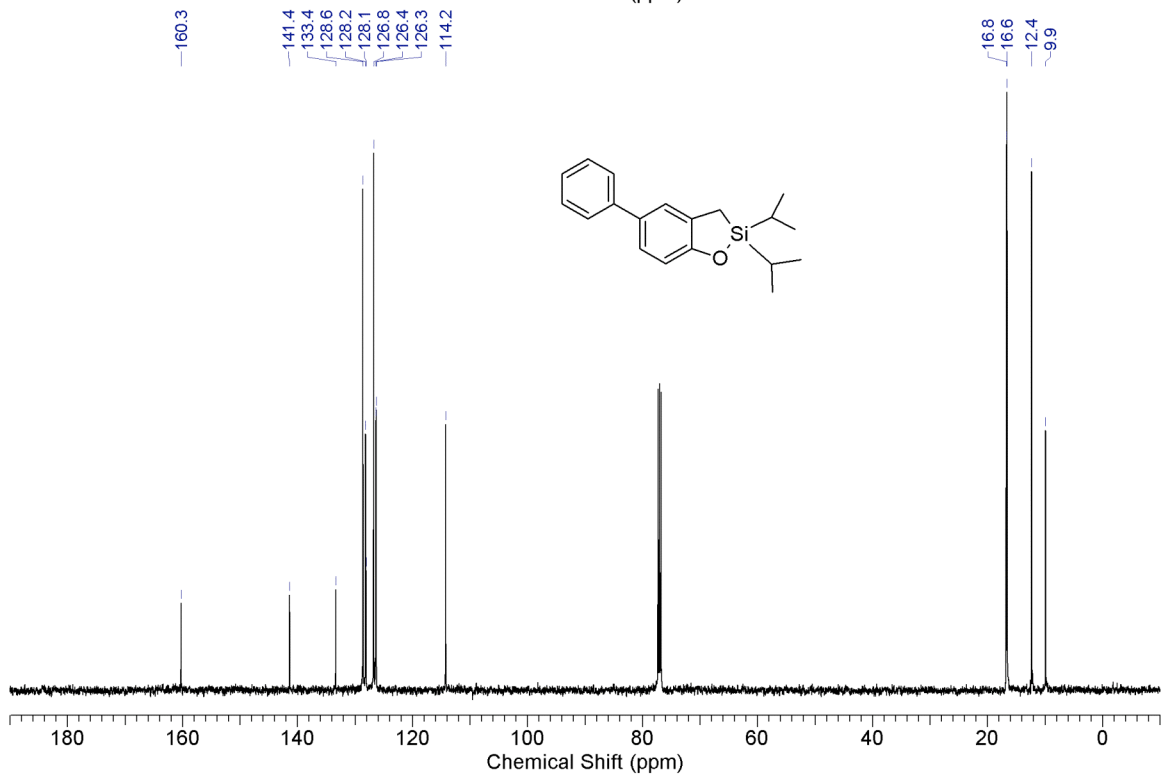
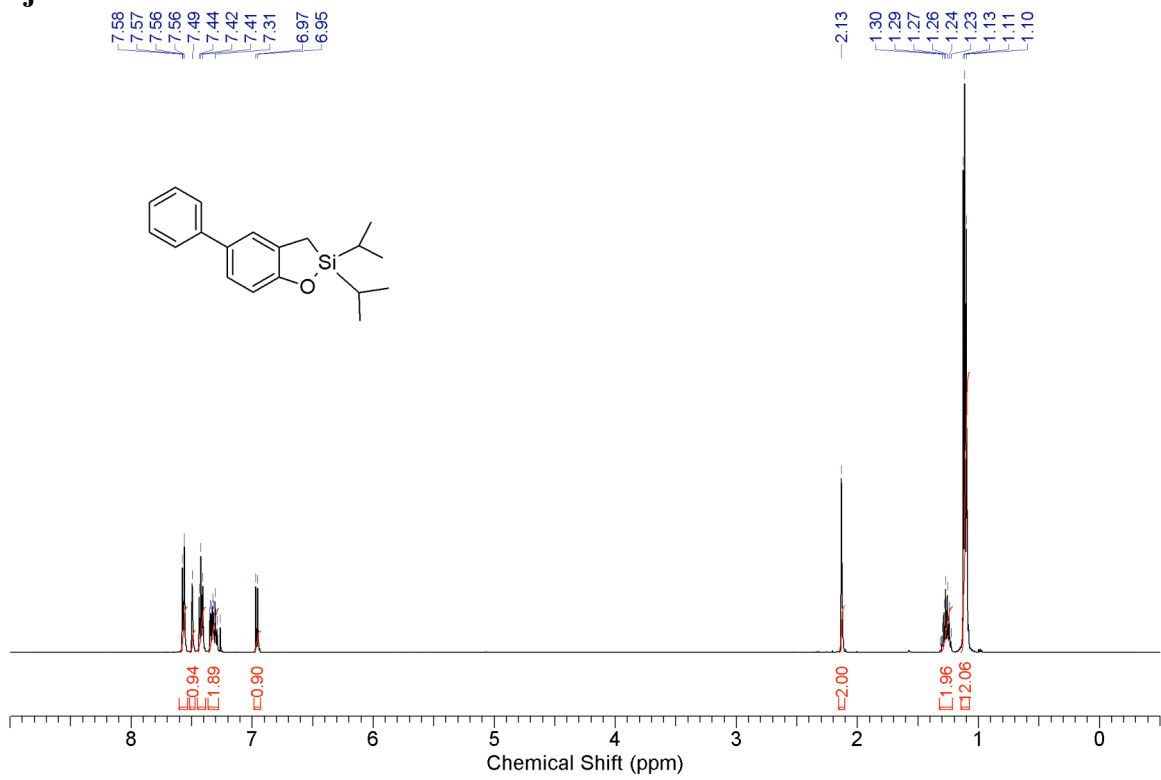


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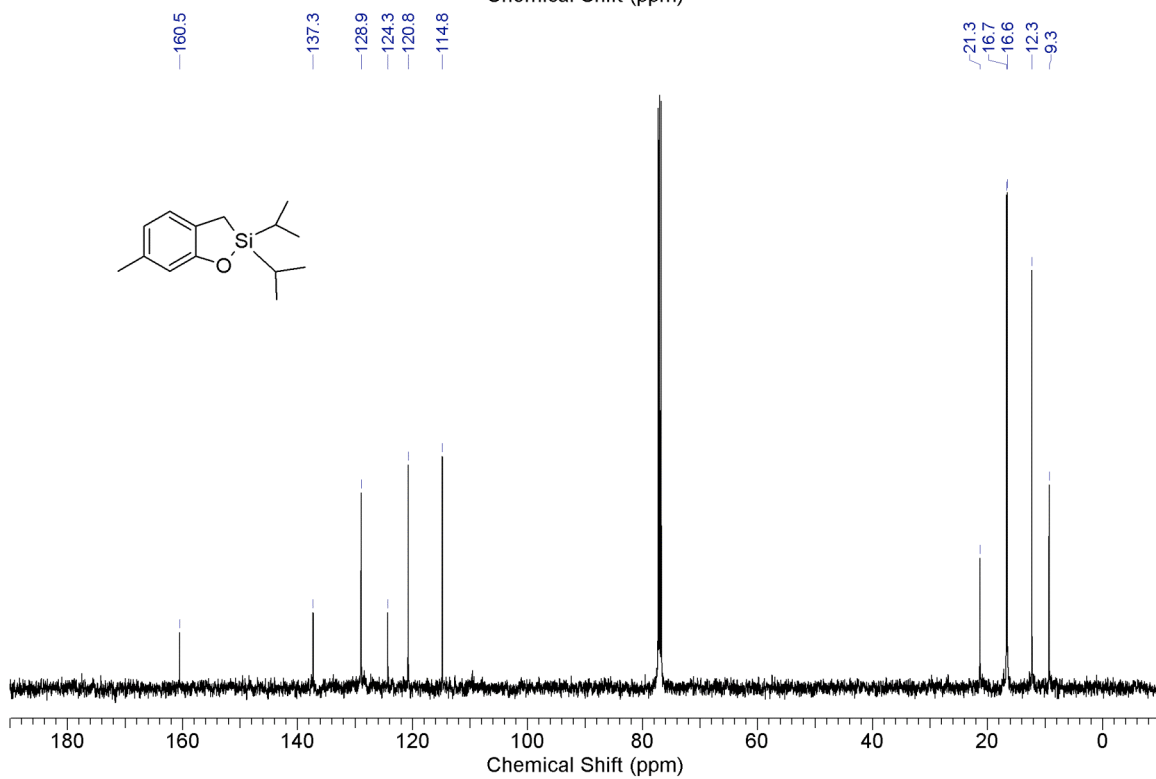
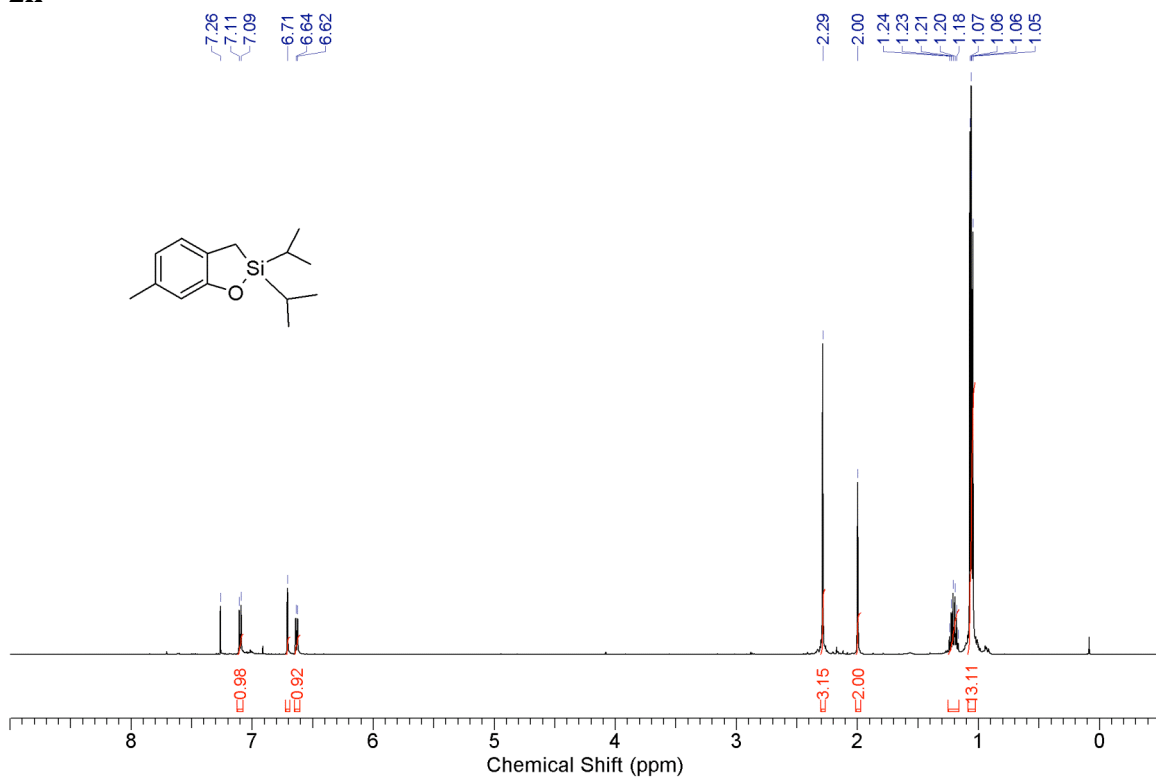
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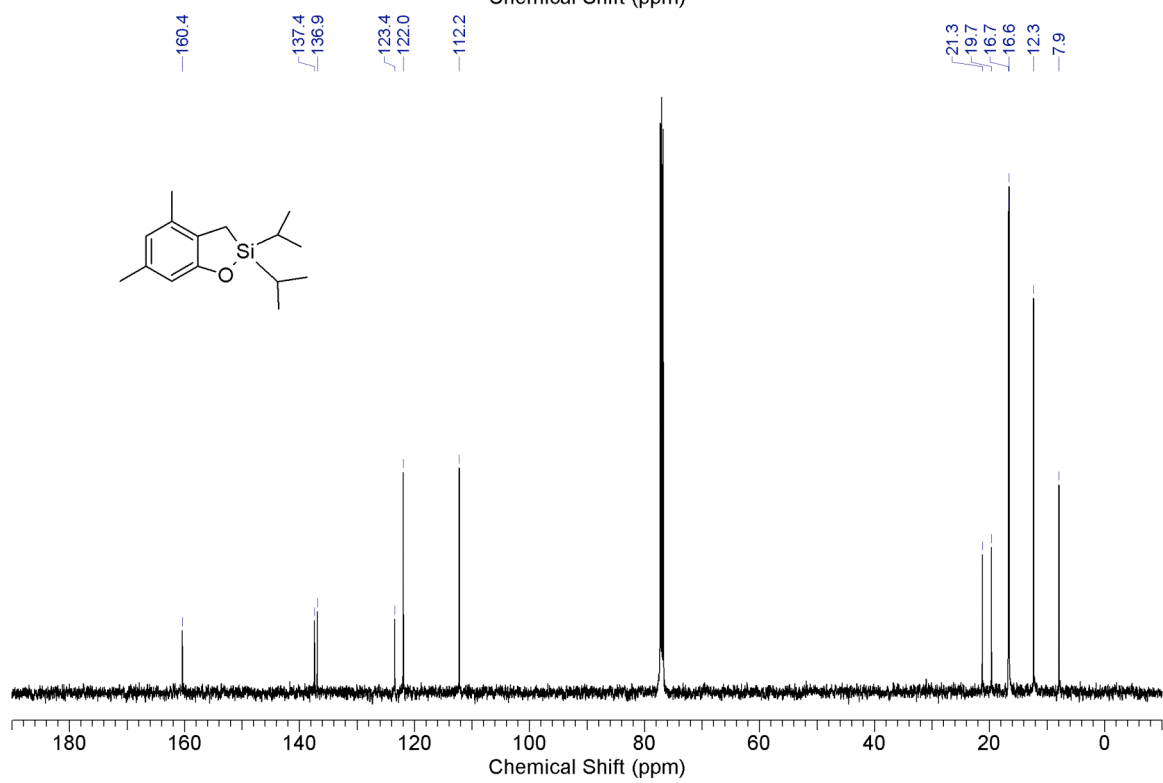
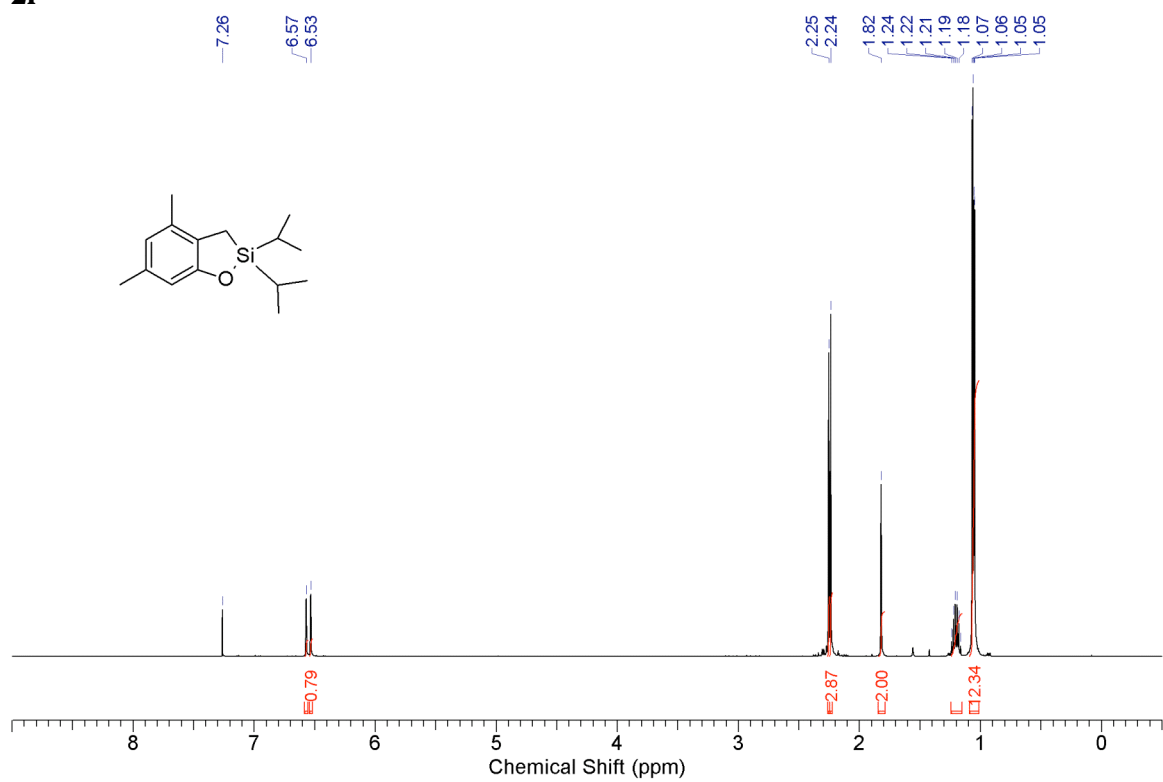
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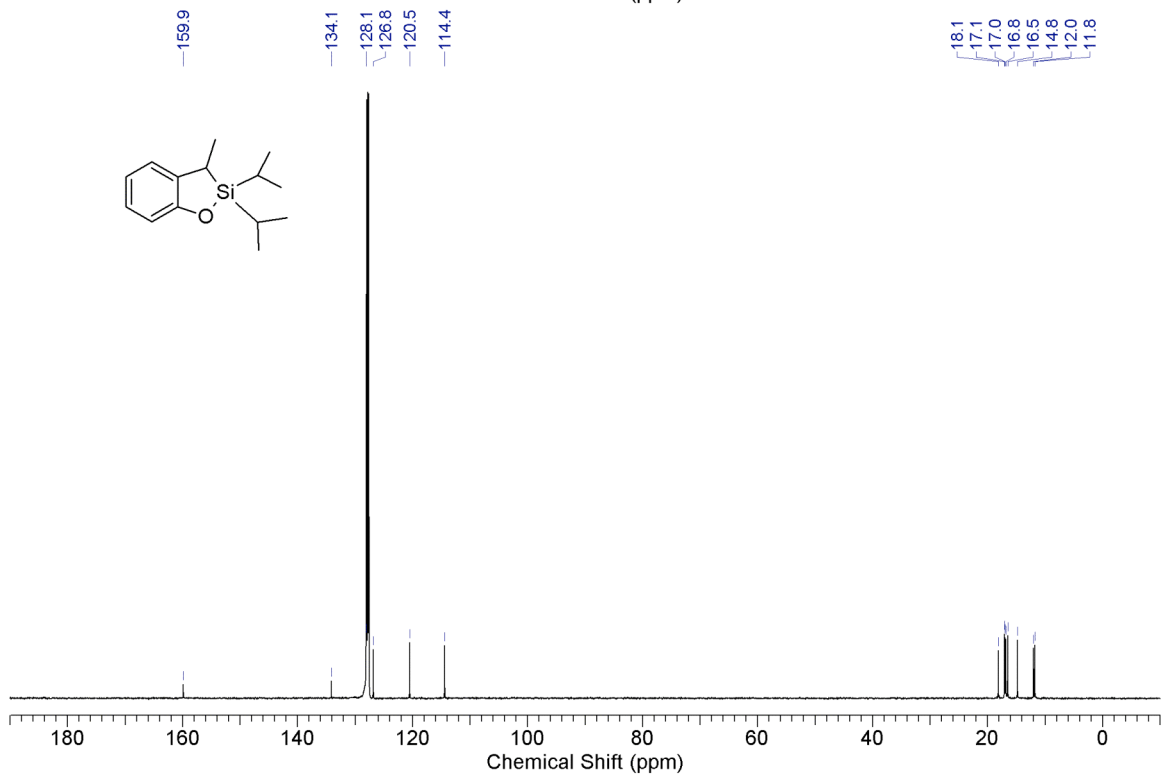
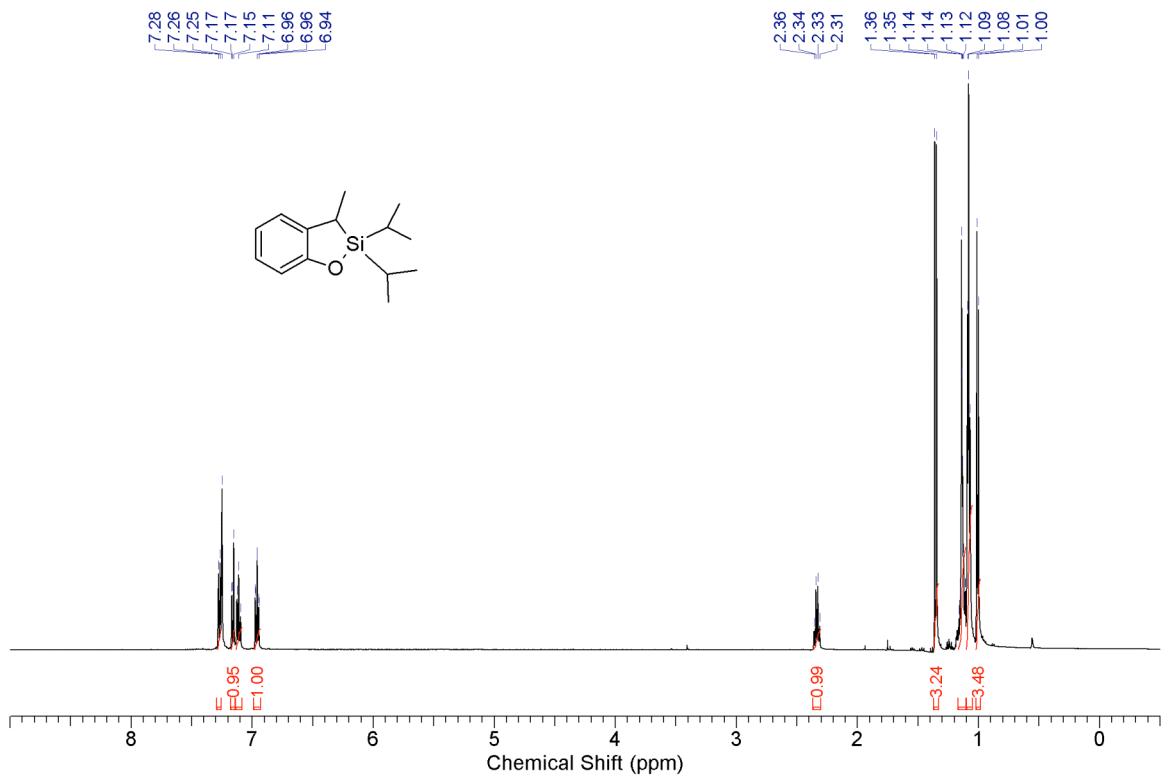
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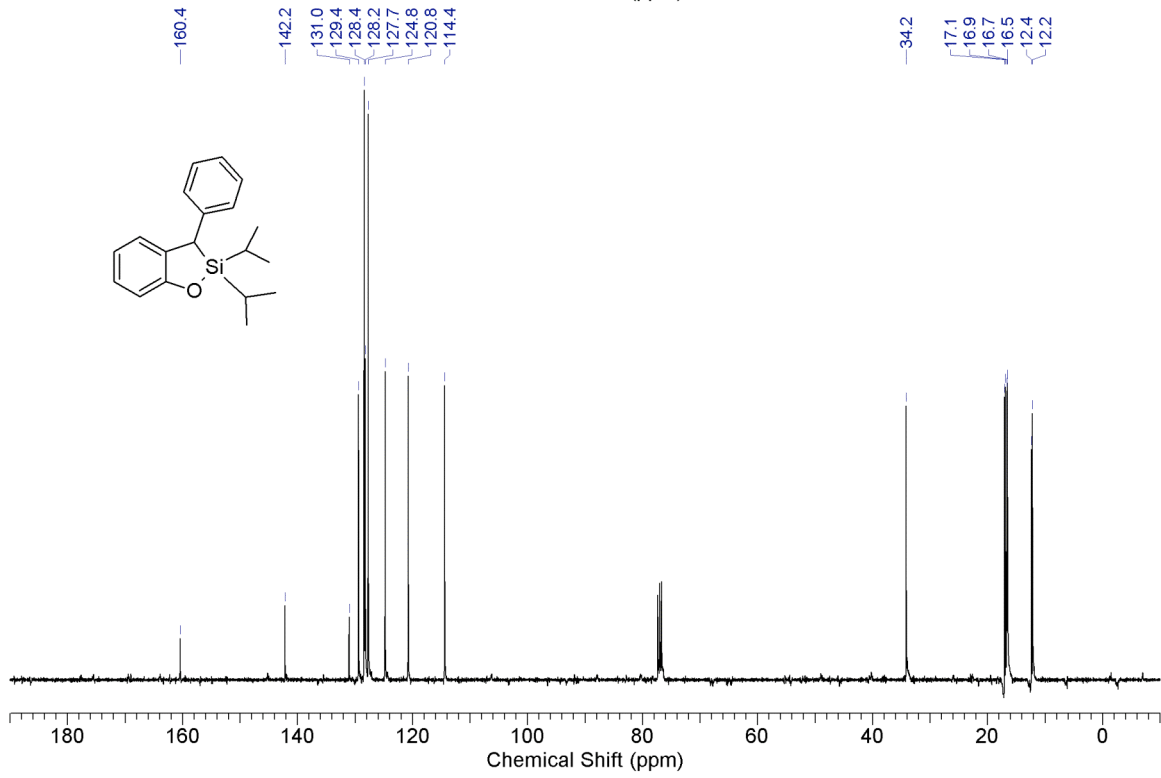
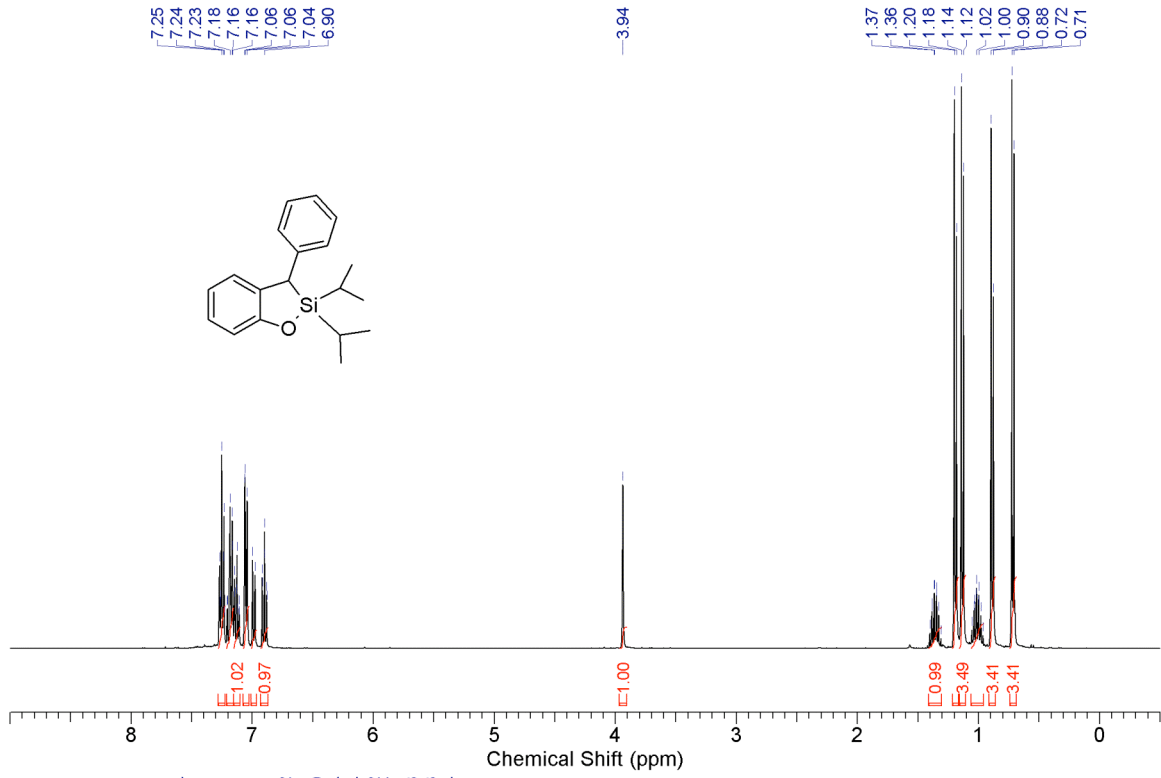


21

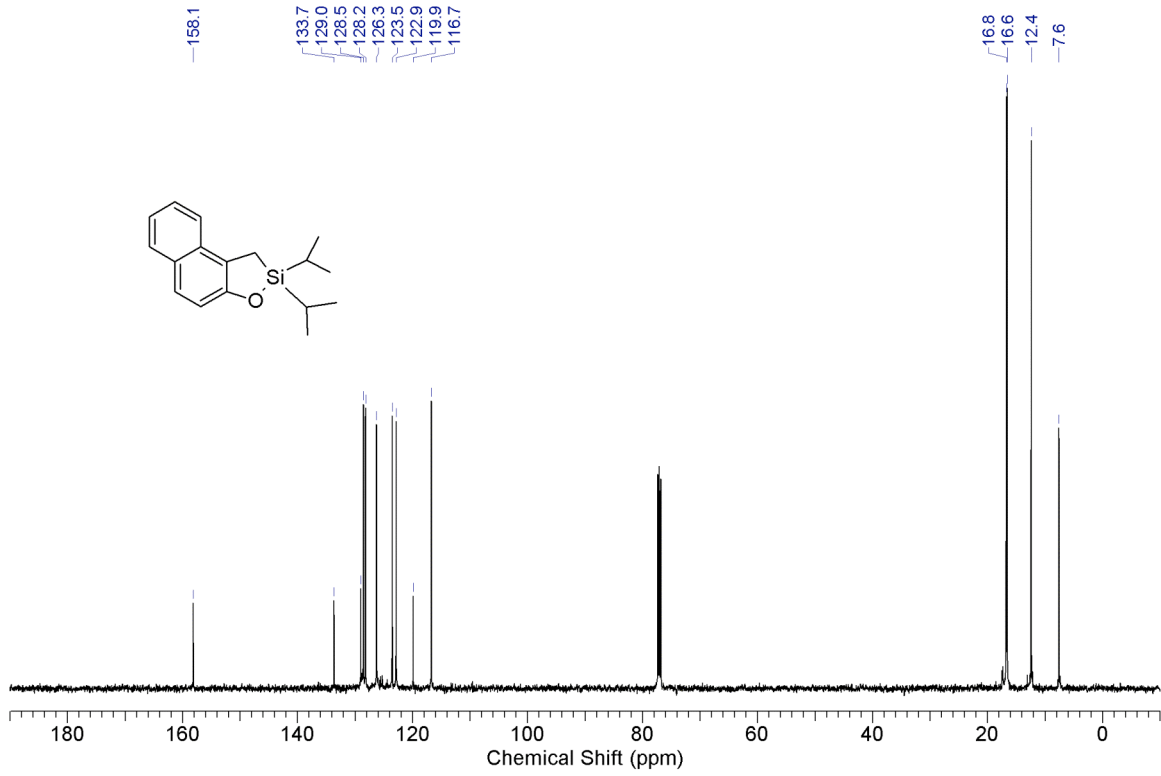
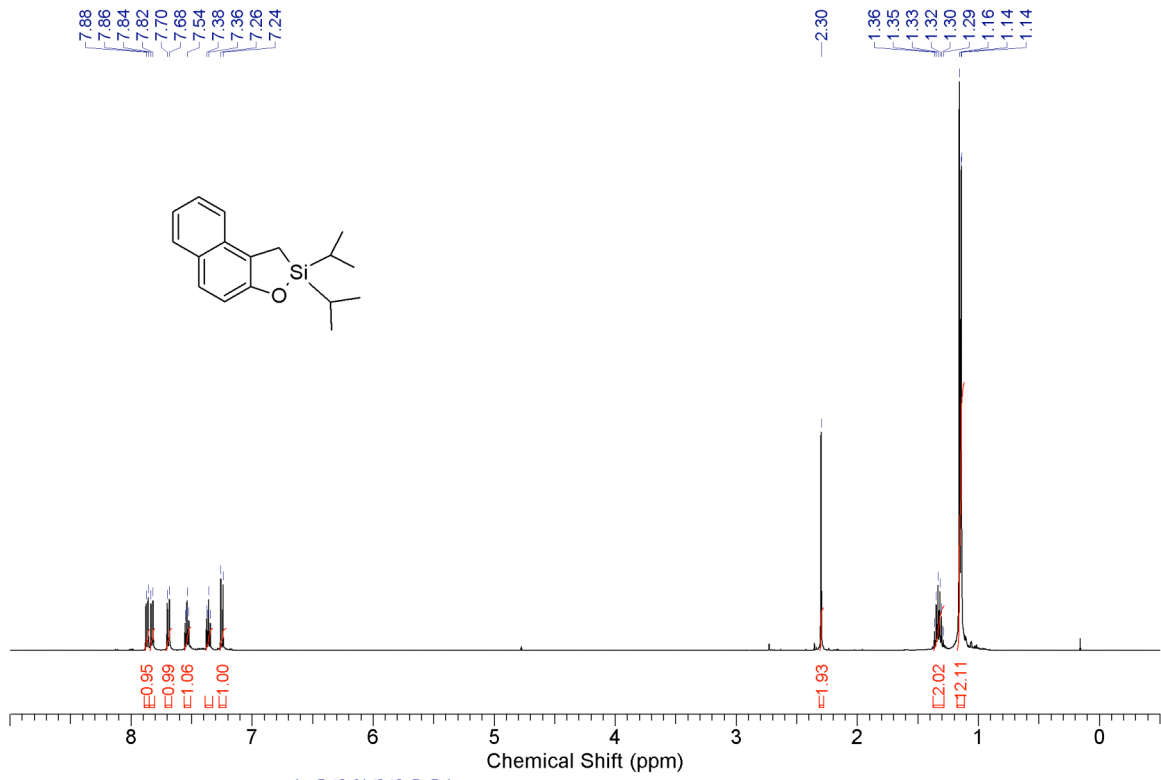


2m

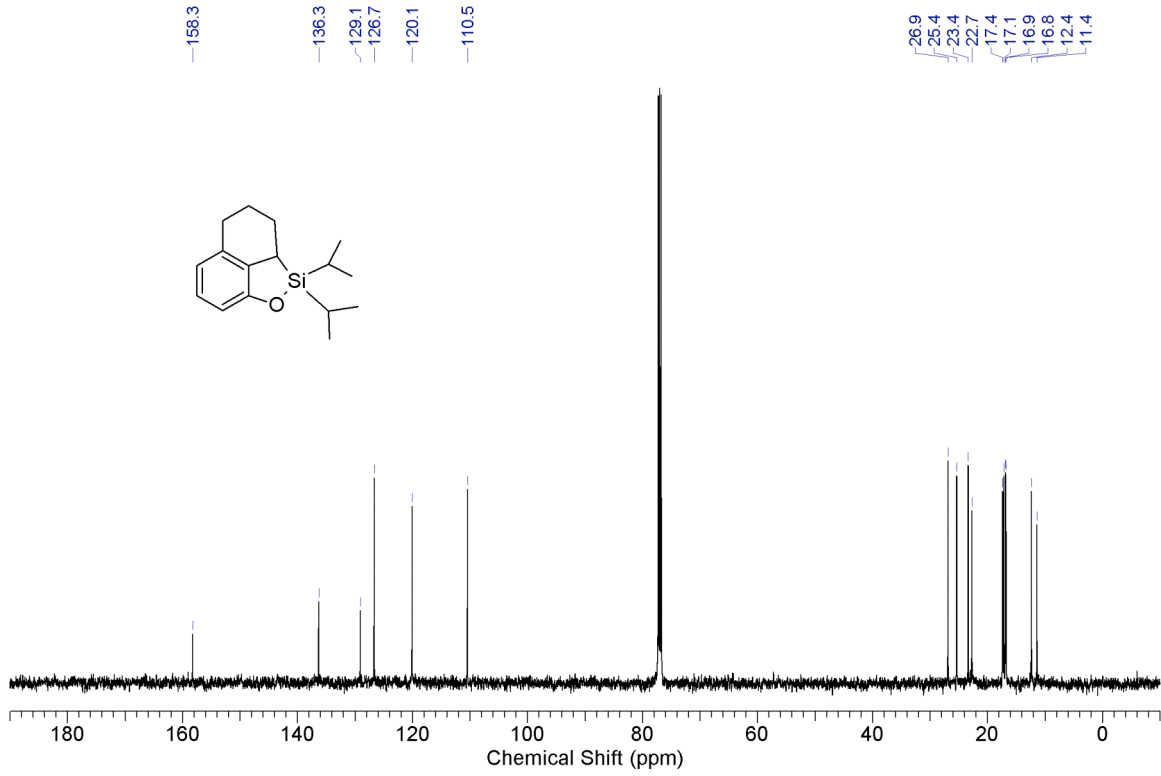
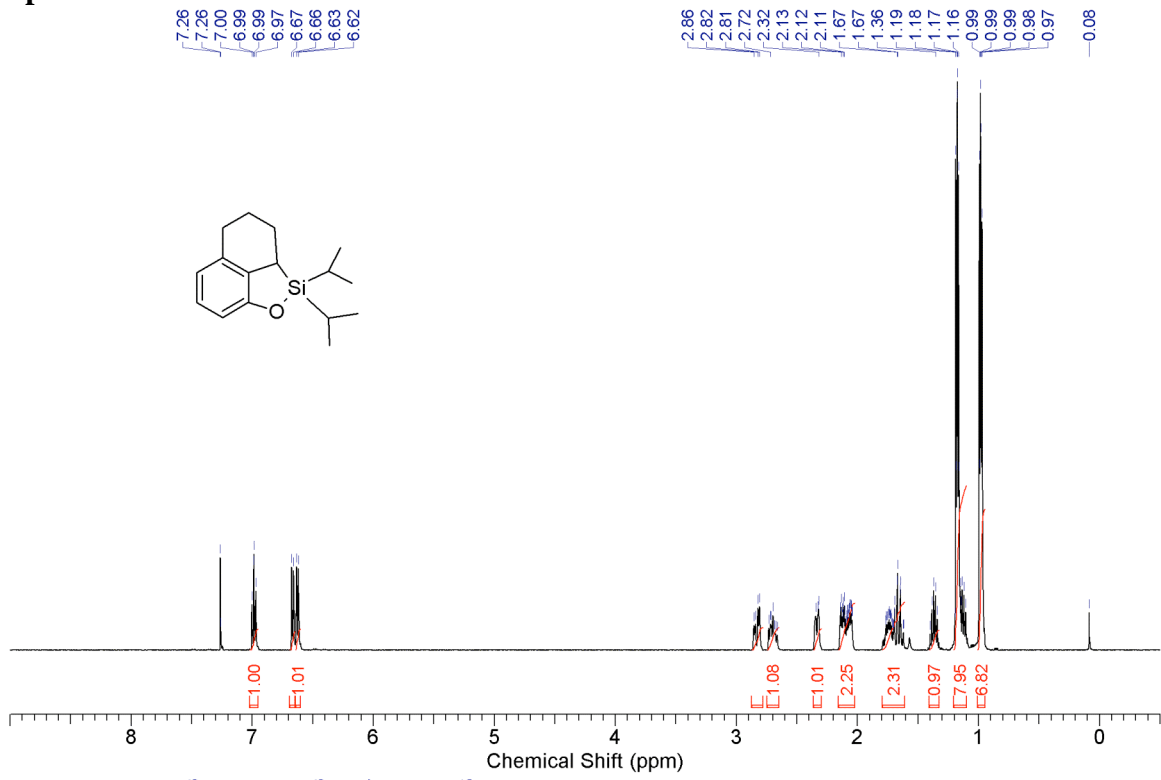


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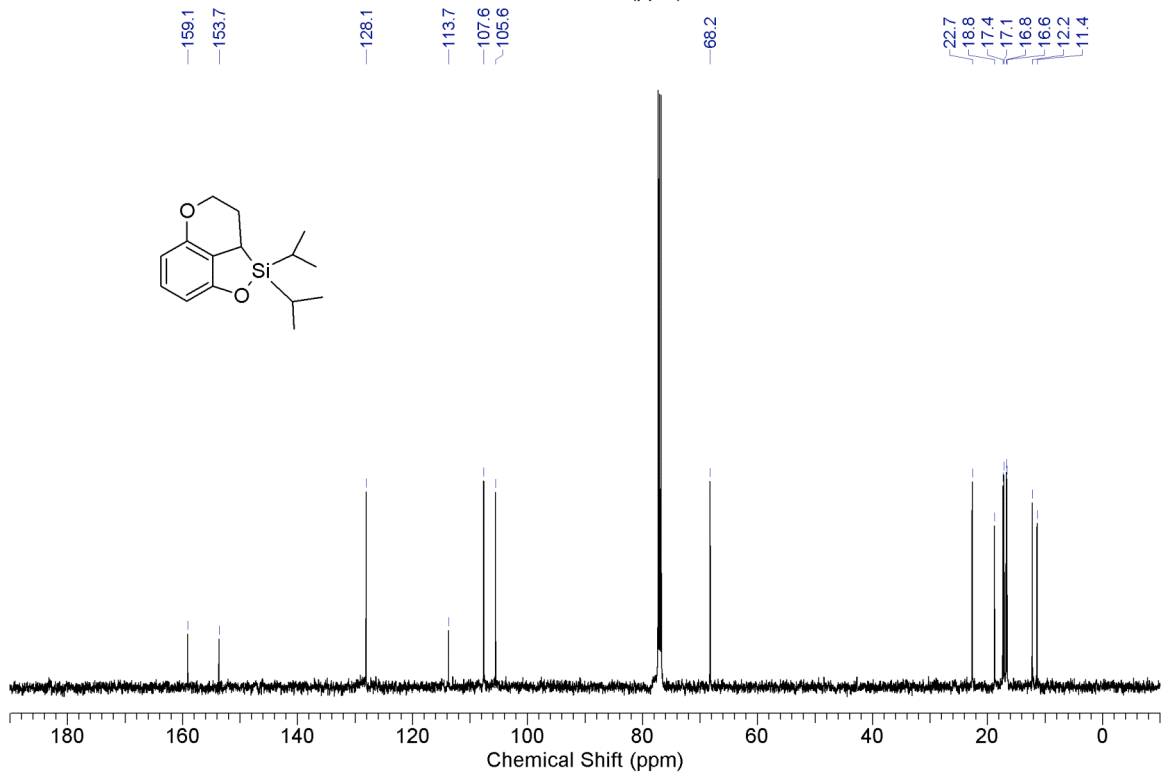
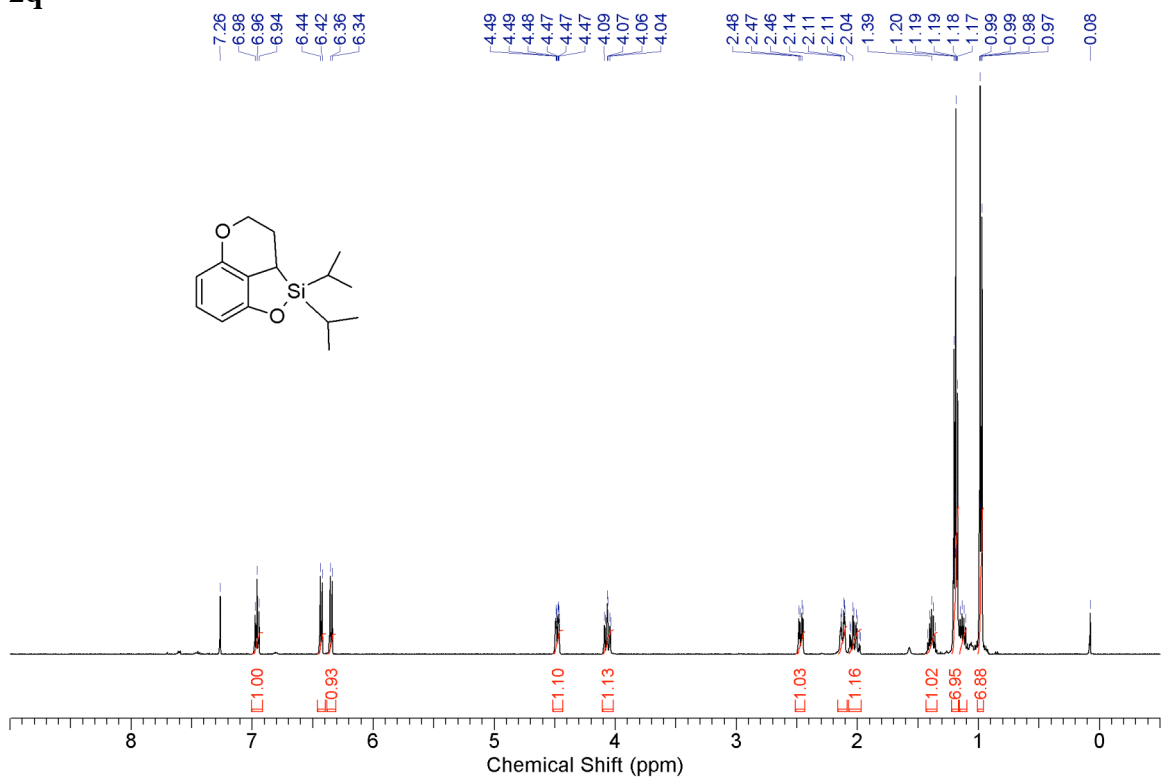
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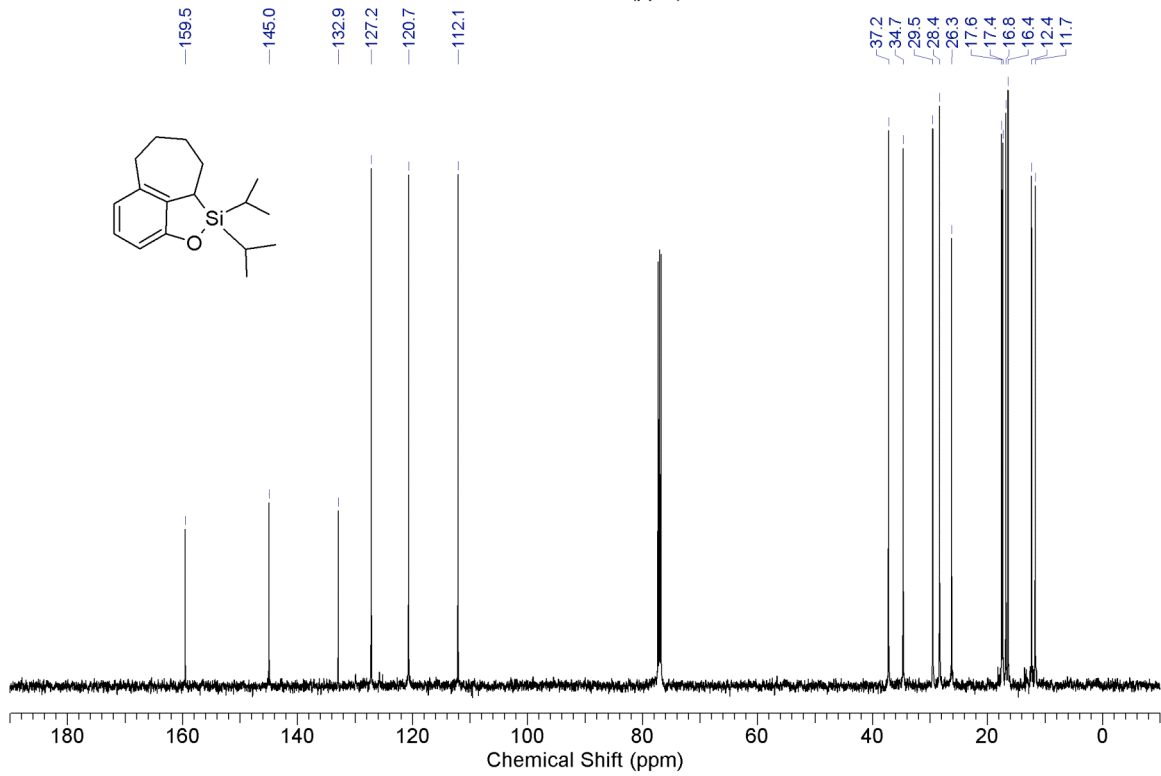
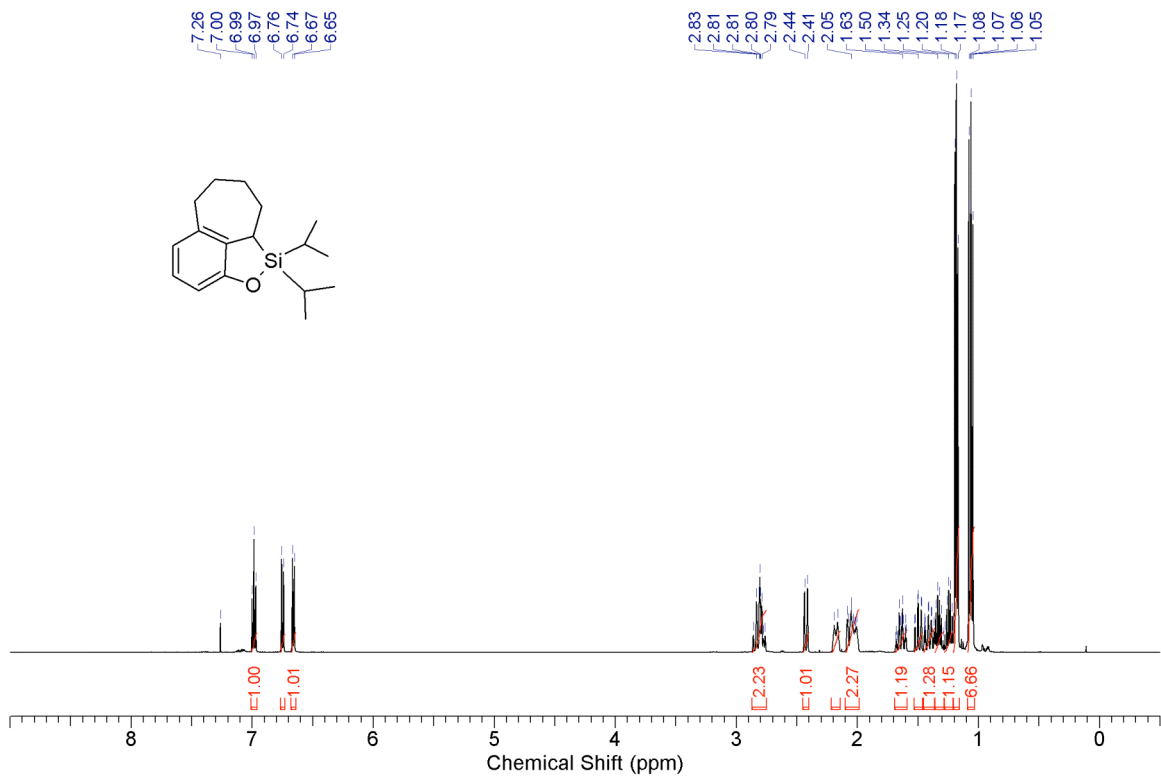
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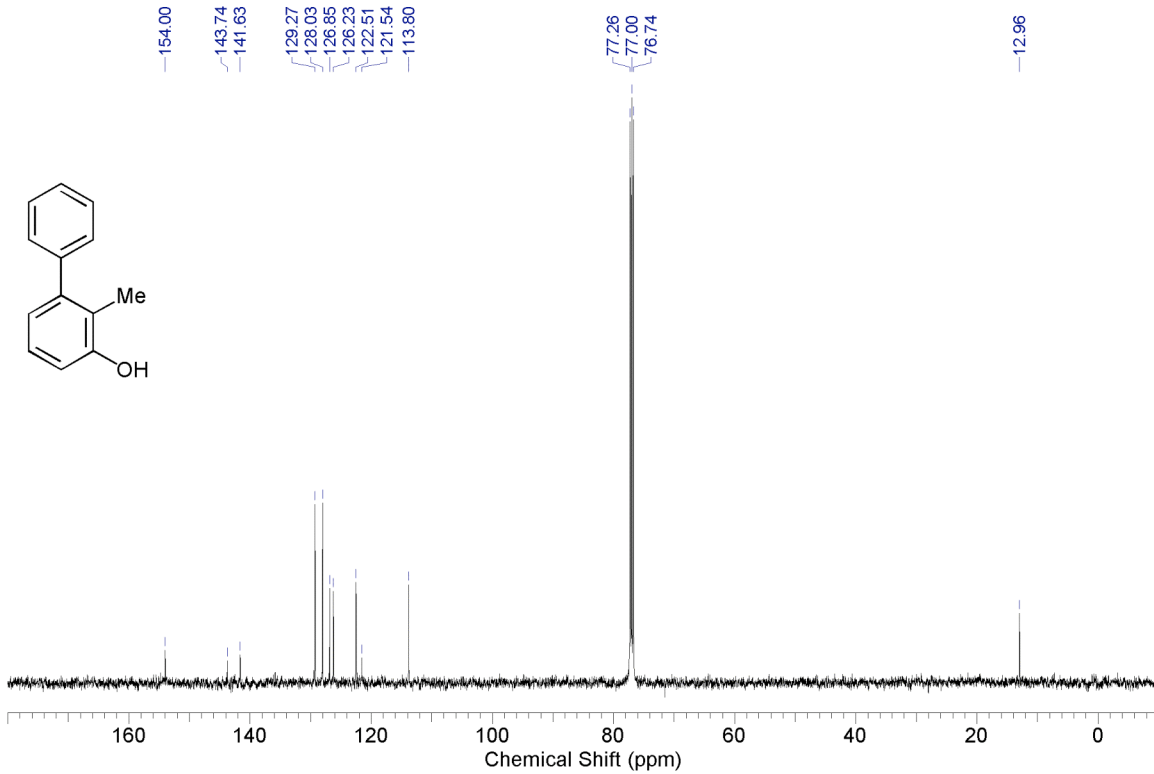
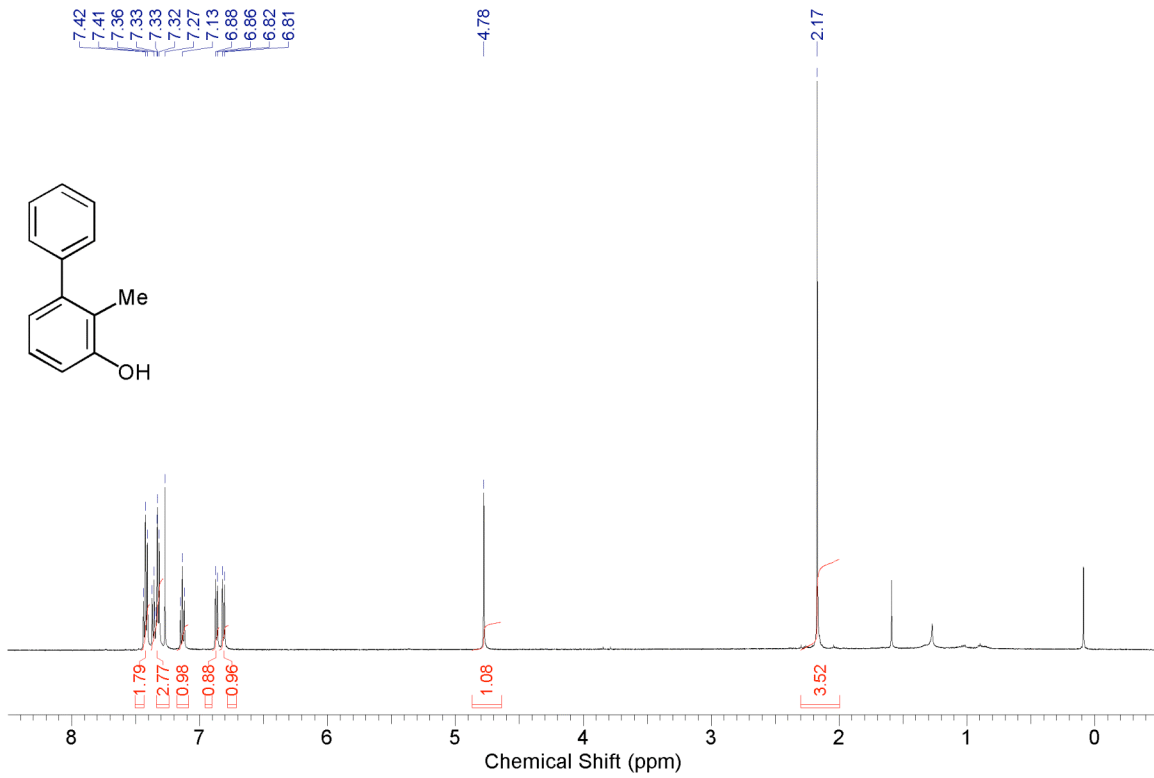
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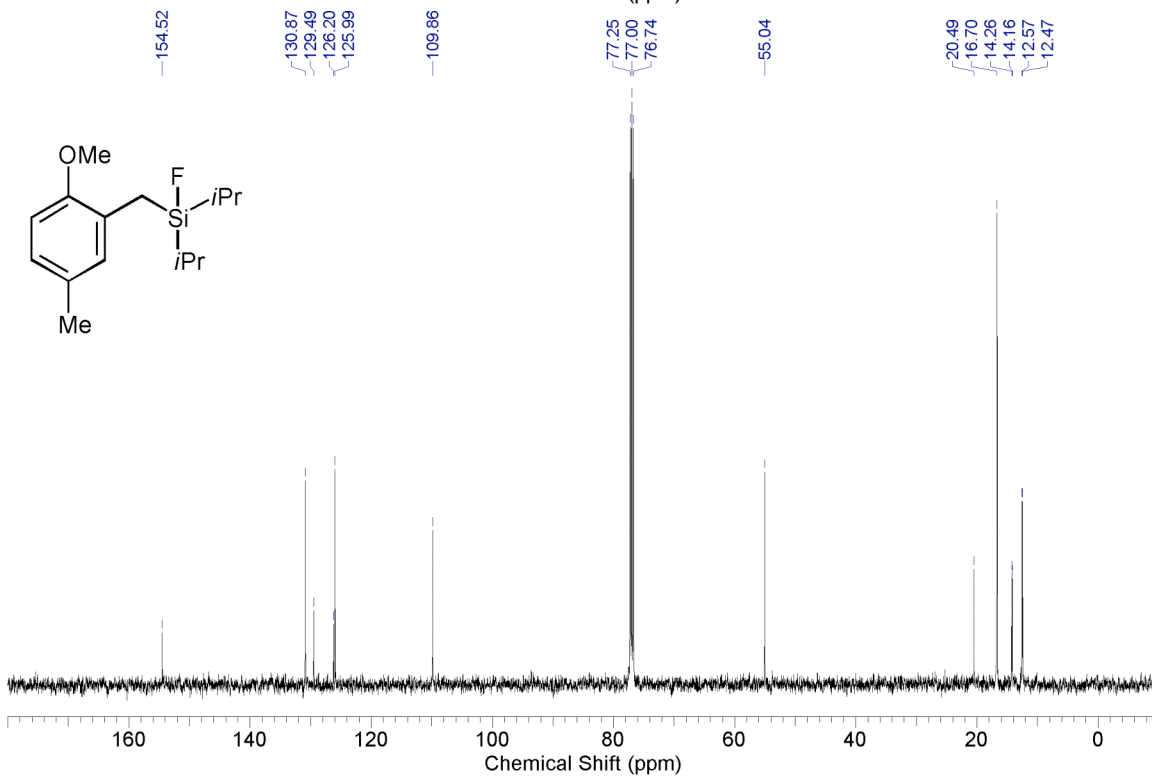
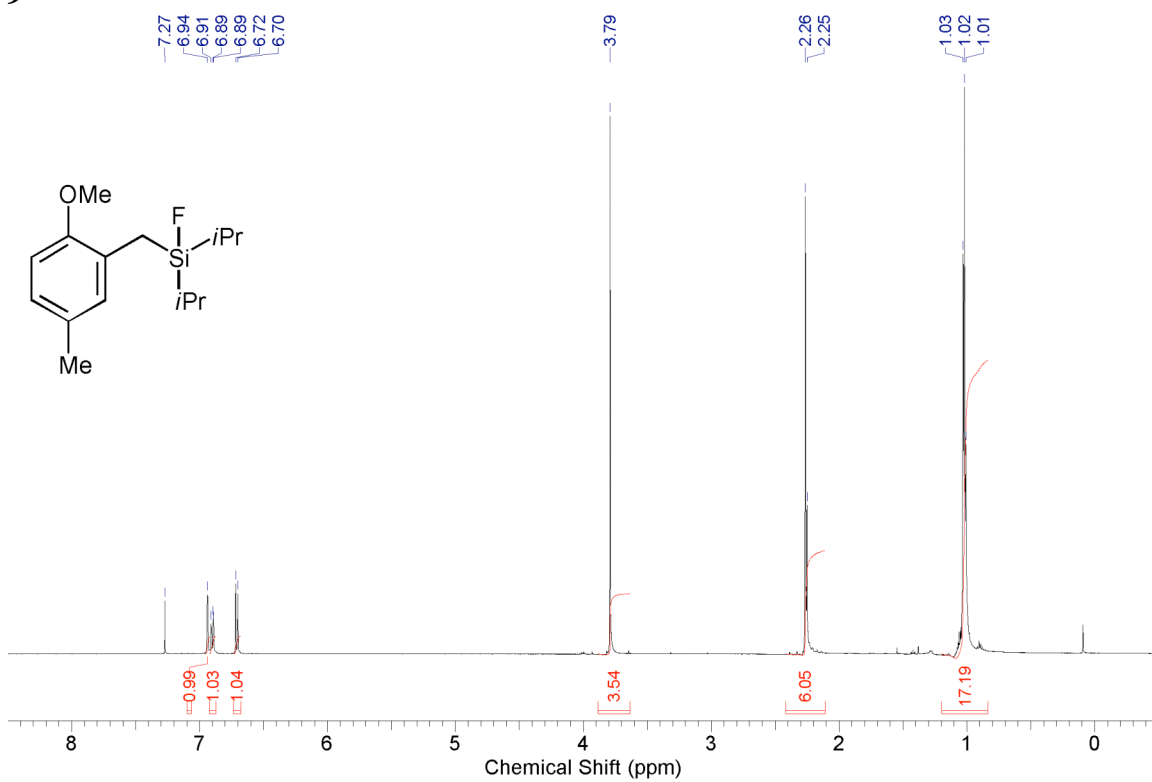
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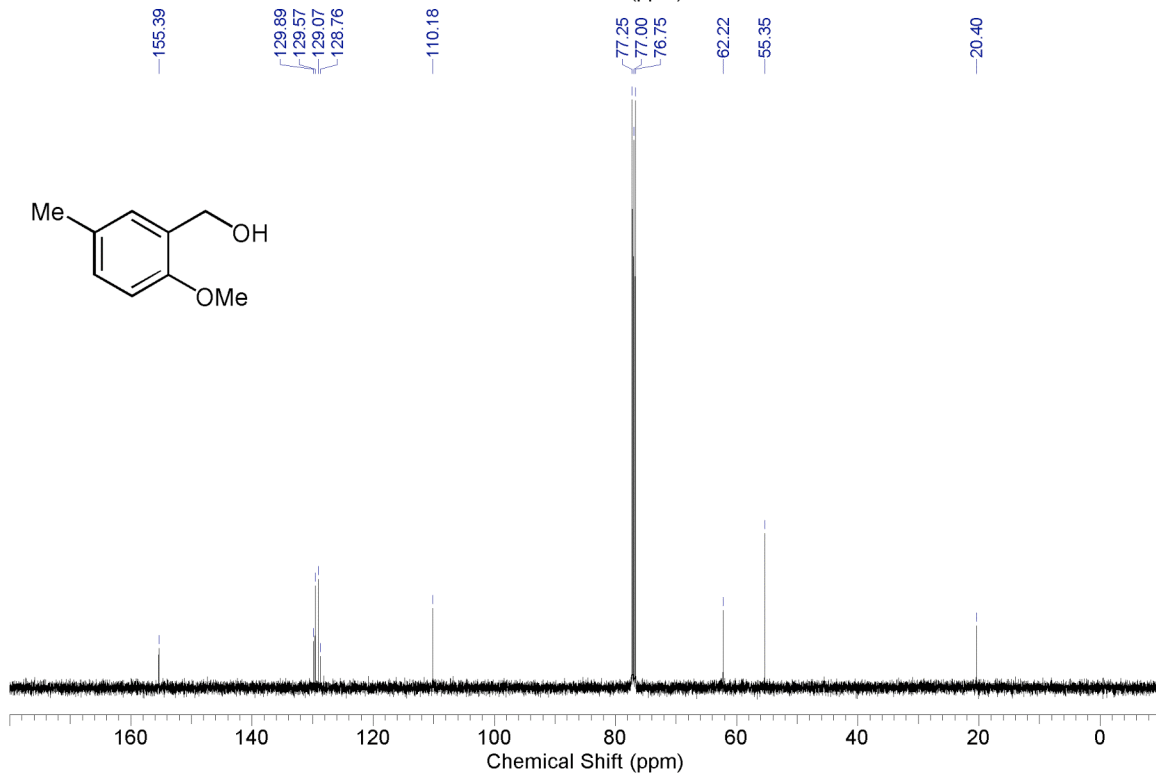
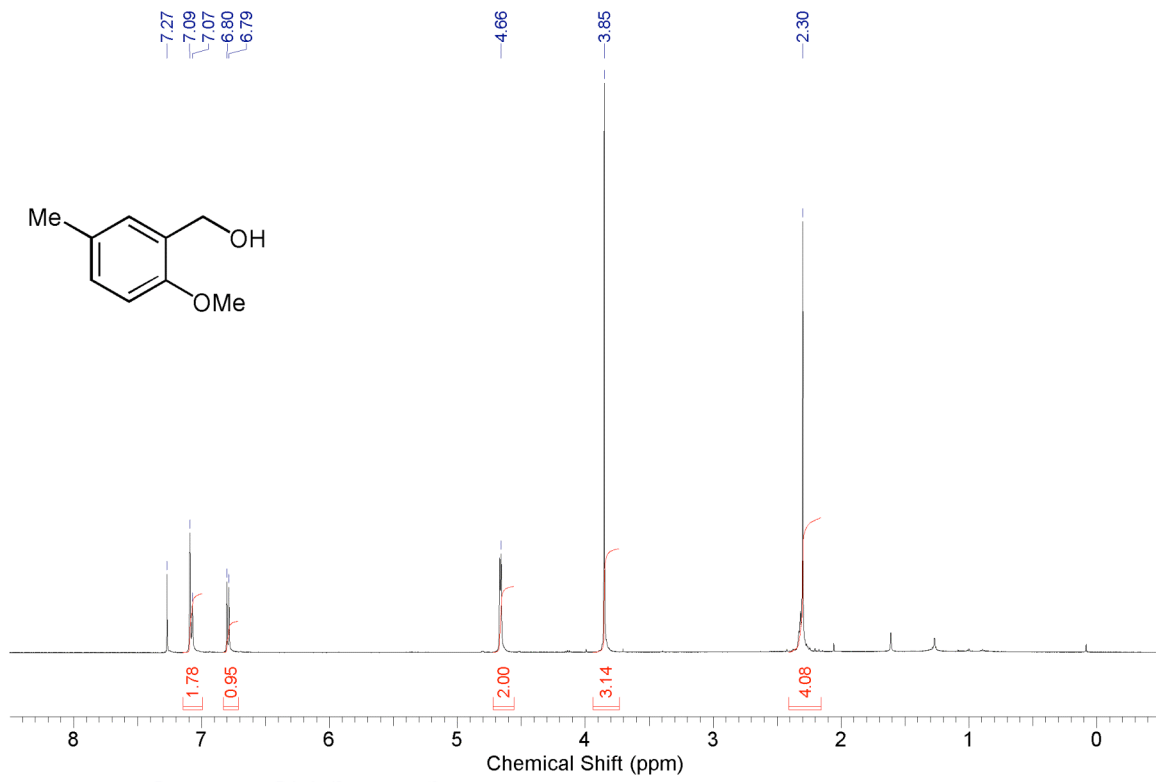
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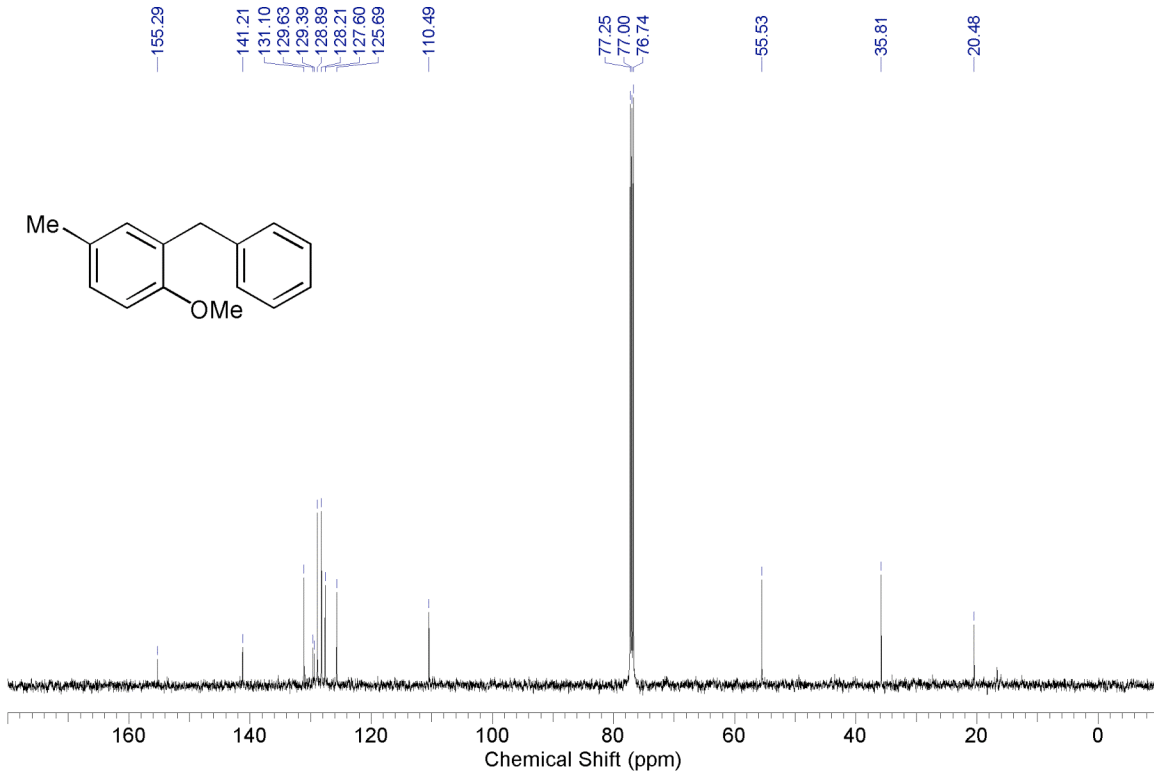
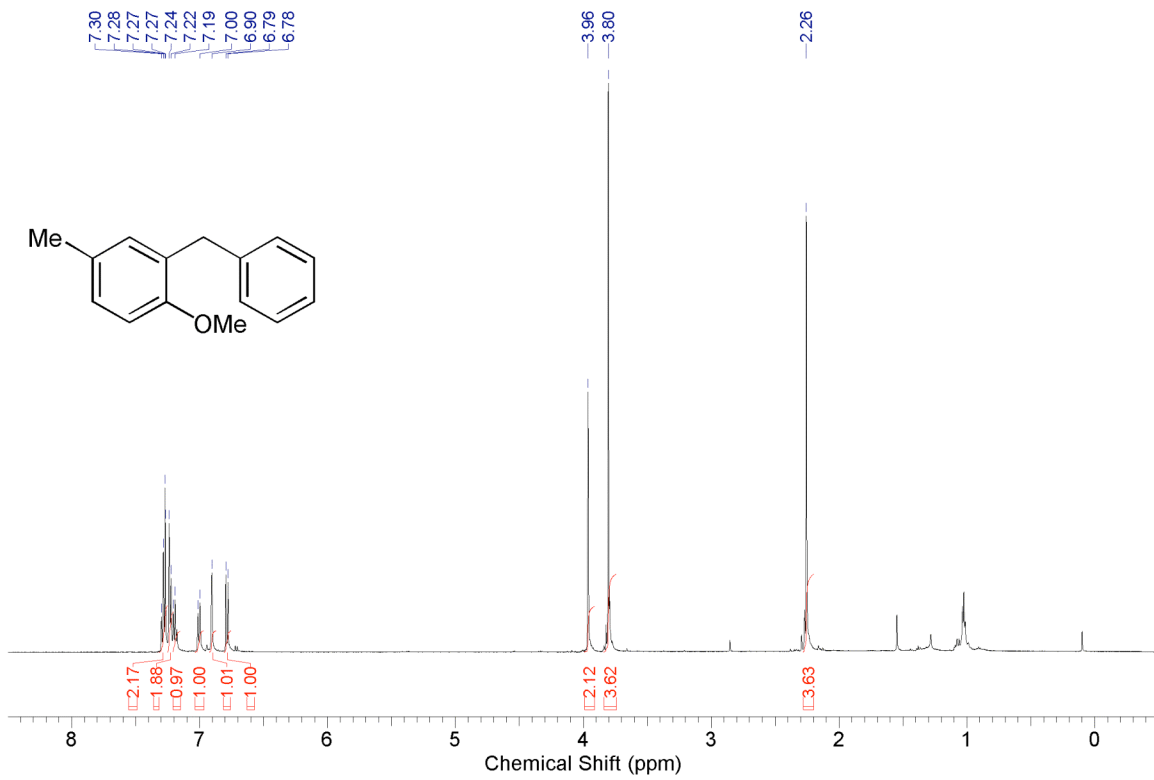
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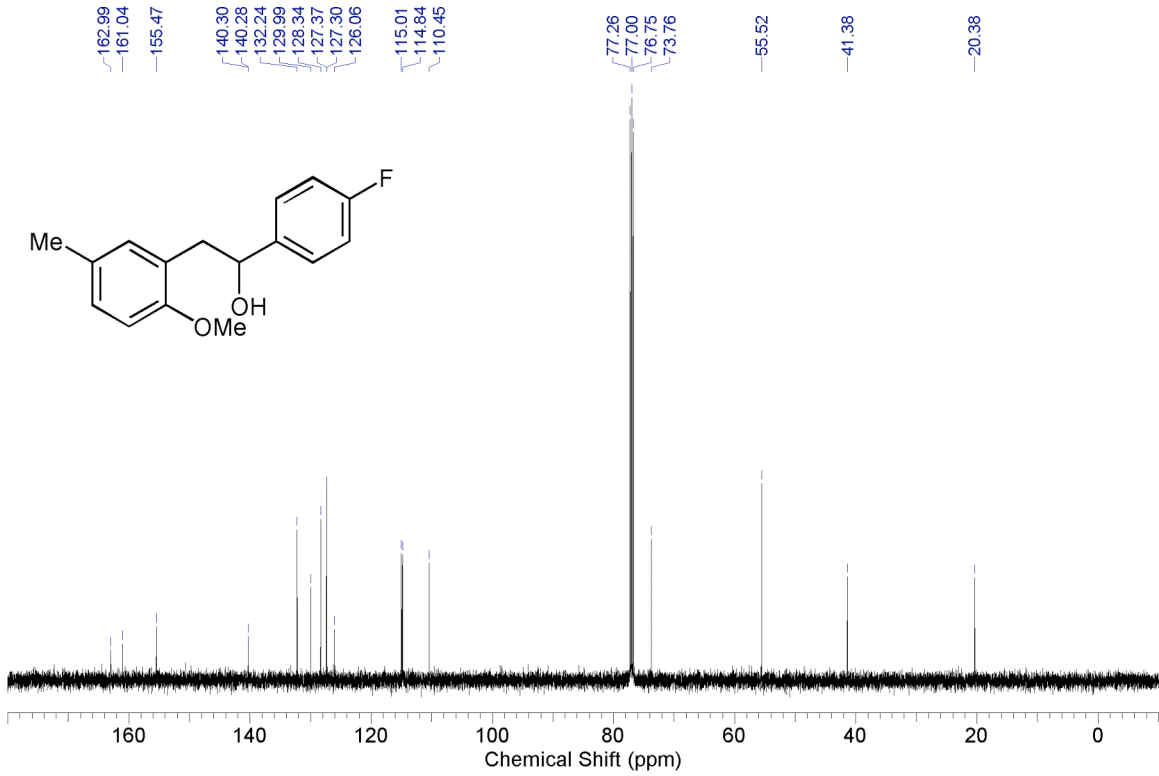
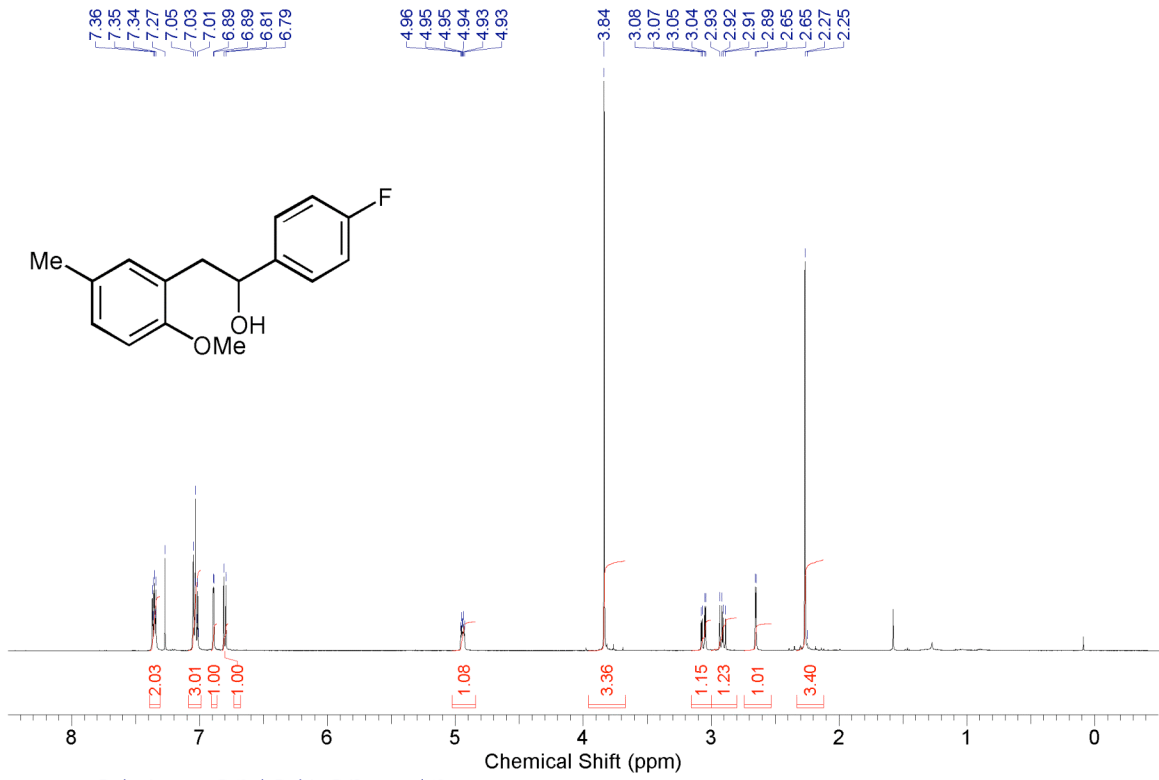
10



11



12



13