

Supplementary Information

The Tethered Silanoxymercuration of Allylic Alcohols

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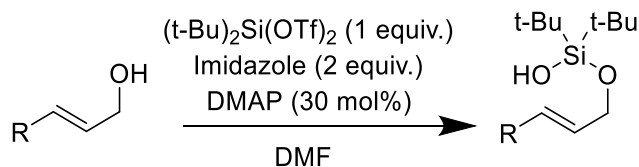
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I. General Considerations:

All reagents were obtained commercially unless otherwise noted. Solvents were purified by passage under 10 psi N₂ through activated alumina columns. Infrared (IR) spectra were recorded on a Thermo Scientific™ Nicolet™ iS™5 FT-IR Spectrometer; data are reported in frequency of absorption (cm⁻¹). NMR spectra were recorded on a Bruker Avance 400 operating at 400 and 100 MHz. ¹H NMR spectra were recorded at 400 MHz. Data are recorded as: chemical shift in ppm referenced internally using residue solvent peaks, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances), integration, coupling constant (Hz). ¹³C NMR spectra were recorded at 100 MHz. Exact mass spectra were recorded using an electrospray ion source (ESI) either in positive mode or negative mode and with a time-of-flight (TOF) analyzer on a Waters LCT Premier™ mass spectrometer and are given in m/z. TLC was performed on pre-coated glass plates (Merck) and visualized either with a UV lamp (254 nm) or by dipping into a solution of KMnO₄-K₂CO₃ in water followed by heating. Flash chromatography was performed on silica gel (230-400 mesh). Reversed phase HPLC was performed on a Hamilton PRP-1.7 μm, 21.2 x 250 mm, C18 column. Hg(OTf)₂ was purchased from either Alfa Aesar or Strem Chemicals. Di-*tert*-butylsilyl Bis(trifluoromethanesulfonate) was purchased from either TCI America or from Sigma-Aldrich.

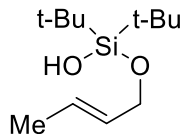
II. General Procedure for Substrate Preparation



A 100 mL round bottom flask with a magnetic stir bar was charged with imidazole (0.273 g, 4 mmol, 2 equiv.) and 20 ml of DMF. After the flask was cooled to 0 °C, di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (0.65 ml, 2 mmol, 1 equiv.) was added dropwise. Following addition, the flask was removed from the ice-water bath and the clear, colorless solution stirred for 30 minutes at room temperature. Following this time, the reaction flask was cooled to 0 °C and substrate (2 mmol, 1 equiv) was added dropwise followed by dimethylaminopyridine (0.073 g, 0.6 mmol, 0.3 equiv.). The reaction was warmed to room temperature over a period of 12 h. Following this time, the reaction mixture was diluted with ethyl acetate and transferred to a separatory funnel. The solution was washed once with 50 mL of 1M HCl (washing with 1M NaHCO₃ gives comparable results) and then with 200 mL of H₂O. The organic layer was collected, dried with MgSO₄, and concentrated under reduced pressure to yield a semi-solid residue. Chromatography on silica gel (0 to 100% ethyl acetate in hexanes) yielded purified product.

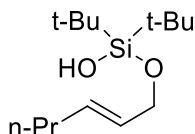
III. Characterization of Substrates

Note: The HRMS data is not within the 10 ppm acceptable error for compounds: 1, 2, 4, 8, 12, 18-21, 43, 44. Due to the low molecular weight (<400) of these compounds, our lab often sees mass errors around 15 ppm.



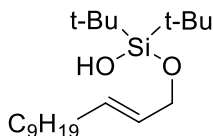
(*E*)-(but-2-en-1-yloxy)di-*tert*-butylsilanol

Compound 1: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 64% yield); ^1H NMR (400 MHz, CDCl_3) δ 5.75 – 5.64 (m, 1H), 5.63 – 5.48 (m, 1H), 4.28 (dp, $J = 5.1$, 1.3 Hz, 2H), 1.70 (dq, $J = 6.3$, 1.4 Hz, 3H), 1.02 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 130.7, 126.0, 64.3, 27.6, 20.6, 17.8. IR 2850, 1464, 1090, 833 cm^{-1} . HRMS calculated for $\text{C}_{12}\text{H}_{25}\text{O}_2\text{Si}^-$ 229.1629 Found 229.1666.



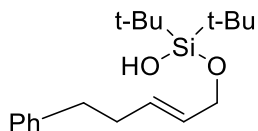
(*E*)-di-*tert*-butyl(hex-2-en-1-yloxy)silanol

Compound 2: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 48% yield); ^1H NMR (400 MHz, CDCl_3) δ 5.66 (dtt, $J = 15.6$, 6.4, 1.3 Hz, 1H), 5.55 (dtt, $J = 15.3$, 5.3, 1.2 Hz, 1H), 4.28 (dq, $J = 5.1$, 1.2 Hz, 2H), 2.04 – 1.94 (m, 2H), 1.39 (dq, $J = 14.8$, 7.4 Hz, 2H), 1.01 (s, 18H), 0.89 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 131.3, 129.6, 64.3, 34.4, 27.6, 22.5, 20.6, 13.8. IR 2872, 1471, 1100, 788 cm^{-1} . HRMS calculated for $\text{C}_{14}\text{H}_{29}\text{O}_2\text{Si}^-$ 257.1942 Found 257.1987.



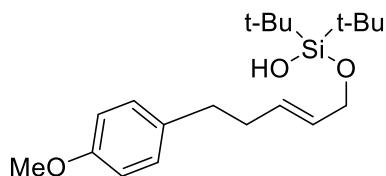
(*E*)-di-*tert*-butyl(dodec-2-en-1-yloxy)silanol

Compound 3: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 48% yield); ^1H NMR (400 MHz, CDCl_3) δ 5.67 (dtt, $J = 15.7$, 6.4, 1.3 Hz, 1H), 5.60 – 5.49 (m, 1H), 4.29 (dq, $J = 5.2$, 1.2 Hz, 2H), 2.10 – 1.93 (m, 2H), 1.44 – 1.18 (m, 14H), 1.02 (s, 18H), 0.94 – 0.80 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 131.5, 129.2, 64.2, 32.2, 31.9, 29.6, 29.5, 29.3, 29.26, 29.2, 27.4, 22.7, 20.4, 14.1. IR 2931, 1471, 1100, 835 cm^{-1} . HRMS calculated for $\text{C}_{20}\text{H}_{41}\text{O}_2\text{Si}^-$ 341.2881 Found 341.2889.



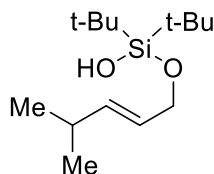
(*E*)-di-*tert*-butyl((5-phenylpent-2-en-1-yl)oxy)silanol

Compound 4: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 45% yield); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.39 – 7.28 (m, 2H), 7.28 – 7.09 (m, 3H), 5.85 – 5.75 (m, 1H), 5.74 – 5.56 (m, 1H), 4.36 (dt, $J = 5.1, 1.2$ Hz, 2H), 2.77 (dd, $J = 8.9, 6.7$ Hz, 2H), 2.51 – 2.37 (m, 2H), 1.09 (d, $J = 1.0$ Hz, 18H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.8, 130.08, 130.02, 128.4, 128.3, 125.8, 64.0, 35.7, 33.9, 27.4, 20.5. IR 2937, 1465, 1095, 835 cm^{-1} . HRMS calculated for $\text{C}_{19}\text{H}_{31}\text{O}_2\text{Si}^-$ 319.2099 Found 319.2033.



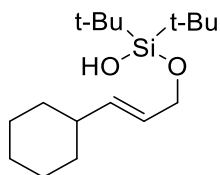
(*E*)-di-*tert*-butyl((5-(4-methoxyphenyl)pent-2-en-1-yl)oxy)silanol

Compound 5: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 54% yield); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.15 – 7.02 (m, 2H), 6.88 – 6.72 (m, 2H), 5.71 (dtd, $J = 15.8, 6.4, 1.4$ Hz, 1H), 5.65 – 5.51 (m, 1H), 4.29 (dq, $J = 5.3, 1.3$ Hz, 2H), 3.79 (s, 3H), 2.65 (dd, $J = 8.8, 6.6$ Hz, 2H), 2.43 – 2.21 (m, 2H), 1.02 (s, 18H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 157.9, 134.1, 130.3, 130.0, 129.4, 113.8, 64.1, 55.3, 34.8, 34.3, 27.5, 20.6. IR 2937, 1512, 1247, 829 cm^{-1} . HRMS calculated for $\text{C}_{20}\text{H}_{33}\text{O}_3\text{Si}^-$ 349.2204 Found 349.2226.



(*E*)-di-*tert*-butyl((4-methylpent-2-en-1-yl)oxy)silanol

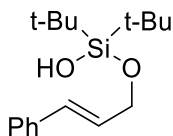
Compound 6: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 50% yield); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.64 (dtd, $J = 15.4, 6.3, 1.4$ Hz, 1H), 5.51 (dtd, $J = 15.4, 5.3, 1.2$ Hz, 1H), 4.29 (dt, $J = 5.4, 1.2$ Hz, 2H), 2.37 – 2.21 (m, 1H), 1.02 (s, 18H), 0.99 (d, $J = 6.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.4, 126.5, 64.4, 30.7, 27.5, 22.4, 20.6. IR 2943, 1471, 1044, 759 cm^{-1} . HRMS calculated for $\text{C}_{14}\text{H}_{29}\text{O}_2\text{Si}^-$ 257.1942 Found 257.1964.



(*E*)-di-*tert*-butyl((3-cyclohexylallyl)oxy)silanol

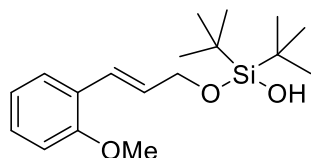
Compound 7: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 52% yield); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.65 (dtd, $J = 15.4, 6.3, 1.3$ Hz, 1H), 5.54 (dtd, $J = 15.5, 5.3, 1.1$ Hz, 1H), 4.32 (dt, $J = 5.2, 1.1$ Hz, 2H), 1.80 – 1.61 (m, 5H), 1.36 – 1.08 (m, 6H), 1.05 (s, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.2, 126.8, 64.3, 40.2, 32.8, 27.4, 26.1, 26.0, 20.4. IR 2913, 1472, 1065, 829 cm^{-1} . HRMS calculated for $\text{C}_{17}\text{H}_{33}\text{O}_2\text{Si}^-$ 297.2255 Found 297.2247.



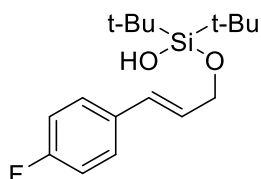
di-*tert*-butyl(cinnamyloxy)silanol

Compound 8: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 59% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.35 (m, 2H), 7.31 (ddd, $J = 7.8, 6.7, 1.2$ Hz, 2H), 7.28 – 7.19 (m, 1H), 6.64 (dt, $J = 15.9, 1.9$ Hz, 1H), 6.32 (dt, $J = 15.8, 5.1$ Hz, 1H), 4.53 (dd, $J = 5.1, 1.8$ Hz, 2H), 1.06 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.2, 129.5, 129.3, 128.6, 127.4, 126.5, 64.1, 27.6, 20.7. IR 2943, 1465, 1112, 829 cm^{-1} . HRMS calculated for $\text{C}_{17}\text{H}_{27}\text{O}_2\text{Si}^-$ 291.1786 Found 291.1843.



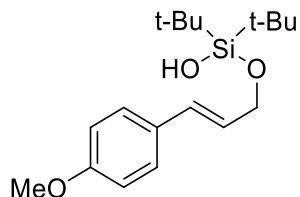
(*E*)-di-*tert*-butyl((3-(2-methoxyphenyl)allyl)oxy)silanol

Compound 9: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 61% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.43 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.22 (ddd, $J = 8.2, 7.4, 1.8$ Hz, 1H), 7.00 – 6.82 (m, 3H), 6.33 (dt, $J = 16.0, 5.2$ Hz, 1H), 4.55 (dd, $J = 5.2, 1.8$ Hz, 2H), 3.84 (s, 3H), 1.07 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.7, 129.9, 128.3, 126.9, 126.2, 124.4, 120.6, 110.9, 64.5, 55.4, 27.5, 20.5. IR 2931, 1465, 1059, 835 cm^{-1} . HRMS calcd for $\text{C}_{18}\text{H}_{30}\text{NaO}_3\text{Si}^+$ 345.1856 Found 345.1889.



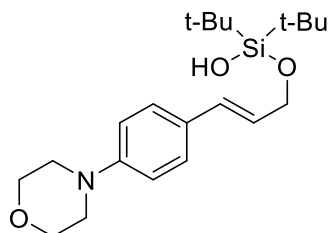
(*E*)-di-*tert*-butyl((3-(4-fluorophenyl)allyl)oxy)silanol

Compound 10: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 66% yield); ^1H NMR (400 MHz, CDCl_3) δ 1.1 (s, 18H), 1.8 (s, 1H), 4.5 (dd, $J = 5.1, 1.8$ Hz, 2H), 6.2 (dt, $J = 15.8, 5.0$ Hz, 1H), 6.6 (dt, $J = 15.8, 1.9$ Hz, 1H), 6.9 – 7.0 (m, 2H), 7.3 – 7.4 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ ^{13}C NMR (101 MHz, CDCl_3) δ 162.2 (d, $J = 246.3$ Hz), 133.2 (d, $J = 3.2$ Hz), 128.9 (d, $J = 2.2$ Hz), 128.2, 127.8 (d, $J = 8.0$ Hz), 115.4 (d, $J = 21.5$ Hz), 63.9, 27.4, 20.5. IR 3497, 2933, 2858, 1127, 825, 645 cm^{-1} ; HRMS calculated for $\text{C}_{17}\text{H}_{26}\text{FO}_2\text{Si}^-$ 309.1692 Found 309.1709.



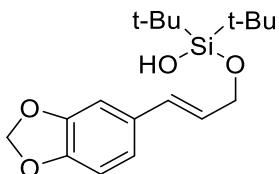
(*E*)-di-*tert*-butyl((3-(4-methoxyphenyl)allyl)oxy)silanol

Compound 11: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 55% yield); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 – 7.28 (m, 2H), 6.89 – 6.79 (m, 2H), 6.57 (dt, $J = 15.8$, 1.7 Hz, 1H), 6.18 (dt, $J = 15.8$, 5.3 Hz, 1H), 4.51 (dd, $J = 5.3$, 1.7 Hz, 2H), 3.81 (s, 3H), 1.06 (s, 18H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.2, 130.0, 129.1, 127.6, 127.1, 114.1, 64.3, 55.4, 27.6, 20.6. IR 2937, 1253, 1100, 971 cm^{-1} . HRMS calculated for $\text{C}_{18}\text{H}_{30}\text{NaO}_3\text{Si}^+$ 345.1856 Found 345.1830.



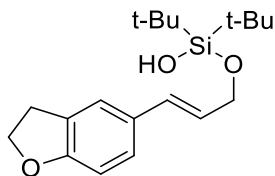
(*E*)-di-*tert*-butyl((3-(4-morpholinophenyl)allyl)oxy)silanol

Compound 12: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Light yellow solid, 39% yield); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.1 (s, 18H), 3.0 – 3.2 (m, 4H), 3.8 – 3.9 (m, 4H), 4.5 (dd, $J = 5.4$, 1.7 Hz, 2H), 6.2 (dt, $J = 15.8$, 5.3 Hz, 1H), 6.5 (dt, $J = 15.7$, 1.7 Hz, 1H), 6.8 – 6.9 (m, 2H), 7.3 – 7.3 (m, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 20.6, 27.5, 49.2, 64.3, 66.9, 115.6, 126.6, 127.3, 129.0, 129.2, 150.5; IR 3445, 2932, 2855, 1450, 645 cm^{-1} ; HRMS calculated for $\text{C}_{21}\text{H}_{36}\text{NO}_3\text{Si}^+$ 378.2459 Found 378.2408.



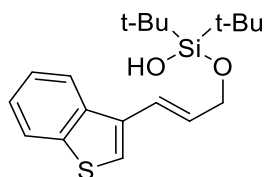
(*E*)-((3-(benzo[*d*][1,3]dioxol-5-yl)allyl)oxy)di-*tert*-butylsilanol

Compound 13: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless solid, 68% yield); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.1 (s, 18H), 1.9 (s, 1H), 4.5 (dd, $J = 5.2$, 1.7 Hz, 2H), 5.9 (s, 2H), 6.1 (dt, $J = 15.7$, 5.2 Hz, 1H), 6.5 (dt, $J = 15.8$, 1.8 Hz, 1H), 6.7 (d, $J = 8.0$ Hz, 1H), 6.8 (dd, $J = 8.0$, 1.7 Hz, 1H), 6.9 (d, $J = 1.6$ Hz, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 20.5, 27.5, 64.0, 101.0, 105.8, 108.3, 120.9, 127.5, 129.2, 131.6, 147.0, 148.0; IR 3484, 2936, 2855, 1440, 1275, 750 cm^{-1} ; HRMS calculated for $\text{C}_{18}\text{H}_{27}\text{O}_4\text{Si}^-$ 335.1684 Found 335.1678.



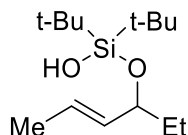
(*E*)-di-*tert*-butyl((3-(2,3-dihydrobenzofuran-5-yl)allyl)oxy)silanol

Compound 14: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Pale yellow oil, 56% yield); ^1H NMR (400 MHz, CDCl_3) δ 1.1 (s, 18H), 2.0 (s, 1H), 3.2 (t, $J = 8.7$ Hz, 2H), 4.5 (dd, $J = 5.4, 1.7$ Hz, 2H), 4.6 (t, $J = 8.7$ Hz, 2H), 6.1 (dt, $J = 15.8, 5.3$ Hz, 1H), 6.5 (dt, $J = 15.8, 1.7$ Hz, 1H), 6.7 (d, $J = 8.2$ Hz, 1H), 7.1 (dd, $J = 8.3, 1.9$ Hz, 1H), 7.2 – 7.3 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 20.5, 27.5, 29.6, 64.3, 71.4, 109.2, 122.6, 126.4, 126.8, 127.4, 129.5, 129.9, 159.7; IR 3456, 2932, 2857, 1491, 825, 646 cm^{-1} ; HRMS calculated for $\text{C}_{19}\text{H}_{29}\text{O}_3\text{Si}^-$ 333.1891 Found 333.1906.



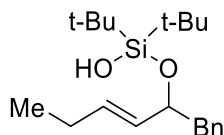
(*E*)-((3-(benzo[*b*]thiophen-3-yl)allyl)oxy)di-*tert*-butylsilanol

Compound 15: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Pale yellow oil, 51% yield); ^1H NMR (400 MHz, CDCl_3) δ 1.1 (s, 18H), 2.0 (s, 1H), 4.6 (dd, $J = 4.9, 1.9$ Hz, 2H), 6.4 (dt, $J = 15.9, 4.9$ Hz, 1H), 6.9 (dtd, $J = 15.8, 1.9, 0.8$ Hz, 1H), 7.3 – 7.5 (m, 3H), 7.8 – 8.0 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 20.3, 27.2, 63.7, 121.2, 121.6, 122.5, 123.9, 124.1, 130.6, 133.5, 137.5, 140.1; IR 3428, 2932, 2857, 1471, 1114, 759, 647 cm^{-1} ; HRMS calculated for $\text{C}_{19}\text{H}_{27}\text{O}_2\text{SSi}^-$ 347.1507 Found 347.1509.



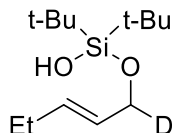
(*E*)-di-*tert*-butyl(hex-4-en-3-yloxy)silanol

Compound 16: Note: during synthesis, heated to 50 °C for 16 hours; (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 38% yield); ^1H NMR (400 MHz, CDCl_3) δ 5.58 (dq, $J = 15.3, 6.3, 0.8$ Hz, 1H), 5.45 (ddq, $J = 15.3, 7.3, 1.4$ Hz, 1H), 4.30 – 4.16 (m, 1H), 1.68 (ddd, $J = 6.3, 1.5, 0.5$ Hz, 3H), 1.64 – 1.41 (m, 2H), 1.02 (s, 9H), 0.99 (s, 9H), 0.86 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 134.88, 125.38, 75.31, 31.23, 27.47, 27.45, 20.57, 20.32, 17.53, 9.35. IR 2925, 1472, 1047, 823 cm^{-1} . HRMS calculated for $\text{C}_{14}\text{H}_{29}\text{O}_2\text{Si}^-$ 257.1942 Found 257.1964.



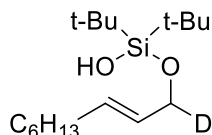
(*E*)-di-*tert*-butyl((1-phenylhex-3-en-2-yl)oxy)silanol

Compound 17: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Pale yellow oil, 30% yield); ^1H NMR (400 MHz, CDCl_3) δ 0.9 (s, 9H), 1.0 (m, 12H), 2.0 (qdd, $J = 7.9, 6.6, 1.4$ Hz, 2H), 2.8 (d, $J = 6.5$ Hz, 2H), 4.4 – 4.6 (m, 1H), 5.5 (ddt, $J = 15.5, 6.9, 1.4$ Hz, 1H), 5.6 (dtd, $J = 15.4, 6.2, 0.8$ Hz, 1H), 7.2 (ddd, $J = 9.2, 3.6, 2.4$ Hz, 3H), 7.2 – 7.3 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 13.9, 20.7, 20.8, 25.4, 27.8, 27.8, 45.8, 75.7, 126.5, 128.4, 130.3, 132.7, 132.9, 139.2; IR 3640, 2933, 2857, 1472, 825, 697 cm^{-1} ; HRMS calculated for $\text{C}_{20}\text{H}_{33}\text{O}_2\text{Si}^-$ 333.2255 Found 333.2265.



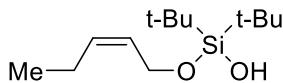
(*E*)-di-*tert*-butyl((pent-2-en-1-yl-1-*d*)oxy)silanol

Compound 18: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 54% yield); ^1H NMR (400 MHz, CDCl_3) δ 5.74 (dtd, $J = 15.3, 6.3, 1.5$ Hz, 1H), 5.65 – 5.52 (m, 1H), 4.30 (dq, $J = 5.3, 1.6$ Hz, 1H), 2.15 – 2.00 (m, 2H), 1.05 (s, 18H), 1.02 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.8, 128.2, 64.9 – 63.0 (t, $J = 22$ Hz, 1C), 27.4, 25.1, 20.4, 13.4. IR 2925, 1477, 1065, 829 cm^{-1} . HRMS calculated for $\text{C}_{13}\text{H}_{26}\text{DO}_2\text{Si}^-$ 244.1849 Found 244.1880.



(*E*)-di-*tert*-butyl((non-2-en-1-yl-1-*d*)oxy)silanol

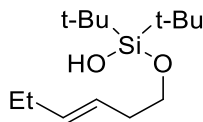
Compound 19: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 53% yield); ^1H NMR (400 MHz, CDCl_3) δ 5.70 (dtd, $J = 15.3, 6.5, 1.3$ Hz, 1H), 5.58 (ddt, $J = 15.3, 5.3, 1.2$ Hz, 1H), 4.30 (tq, $J = 4.4, 1.4$ Hz, 1H), 2.08 – 2.01 (m, 2H), 1.49 – 1.24 (m, 8H), 1.05 (s, 18H), 0.91 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 131.5, 129.1, 64.9 – 62.1 (t, $J = 21$ Hz, 1C), 32.1, 31.7, 29.2, 28.8, 27.4, 22.6, 20.4, 14.0. IR 2919, 1465, 1100, 829 cm^{-1} . HRMS calculated for $\text{C}_{17}\text{H}_{34}\text{DO}_2\text{Si}^-$ 300.2475 Found 300.2507.



(*Z*)-di-*tert*-butyl(pent-2-en-1-yloxy)silanol

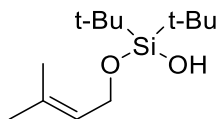
Compound 20: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 50% yield); ^1H NMR (400 MHz, CDCl_3) δ 5.55 (dtd, $J = 10.9, 5.9, 1.3$ Hz, 1H), 5.51 – 5.40 (m, 1H), 4.53 – 4.36 (m, 2H), 2.15 – 1.99 (m, 2H), 1.05 (s, 18H), 1.00 (t, $J = 7.5$ Hz, 3H). IR 2937, 1471,

1094, 823 cm^{-1} . ^{13}C NMR (101 MHz, CDCl_3) δ 132.5, 128.9, 59.5, 27.4, 20.8, 20.4, 14.2. HRMS calculated for $\text{C}_{17}\text{H}_{27}\text{O}_2\text{Si}^-$ 243.1786 Found 243.1841.



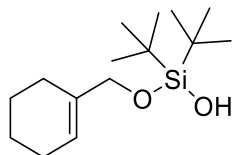
(*E*)-di-*tert*-butyl(hex-3-en-1-yloxy)silanol

Compound 21: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 40% yield); ^1H NMR (400 MHz, CDCl_3) δ 5.57 (dt, $J = 14.6, 5.9, 1.2$ Hz, 1H), 5.50 – 5.28 (m, 1H), 3.83 (t, $J = 6.7$ Hz, 2H), 2.27 (qq, $J = 6.7, 1.1$ Hz, 2H), 2.04 (ddtd, $J = 8.6, 7.3, 6.1, 1.1$ Hz, 2H), 1.12 – 0.91 (m, 21H). ^{13}C NMR (101 MHz, CDCl_3) δ 134.4, 125.7, 63.7, 36.5, 27.6, 25.8, 20.6, 13.9. IR 2943, 1471, 1094, 823 cm^{-1} . HRMS calculated for $\text{C}_{14}\text{H}_{31}\text{O}_2\text{Si}^+$ 259.2088 Found 259.2059.



di-*tert*-butyl((3-methylbut-2-en-1-yl)oxy)silanol

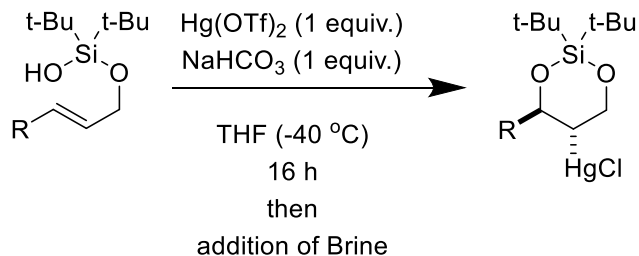
Compound 43: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 48% yield); ^1H NMR (400 MHz, CDCl_3) δ 5.34 (ddq, $J = 7.8, 5.0, 1.4$ Hz, 1H), 4.34 (dp, $J = 6.5, 0.9$ Hz, 2H), 2.01 (s, 1H), 1.72 (q, $J = 1.4$ Hz, 3H), 1.64 (d, $J = 1.3$ Hz, 3H), 1.02 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 133.7, 124.7, 60.6, 27.5, 25.7, 20.6, 18.1. IR 2937, 1471, 1100, 651 cm^{-1} . HRMS calculated for $\text{C}_{13}\text{H}_{27}\text{O}_2\text{Si}^-$ 243.1786 Found 243.1840.



di-*tert*-butyl(cyclohex-1-en-1-ylmethoxy)silanol

Compound 44: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 41% yield); ^1H NMR (400 MHz, CDCl_3) δ 5.68 (td, $J = 3.6, 1.8$ Hz, 1H), 4.17 (dtd, $J = 2.6, 1.8, 0.9$ Hz, 2H), 2.04 – 1.93 (m, 4H), 1.68 – 1.56 (m, 4H), 1.03 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.5, 121.5, 67.9, 27.6, 25.6, 25.0, 22.8, 22.7, 20.7. IR 2849, 1477, 1071, 829 cm^{-1} . HRMS calculated for $\text{C}_{15}\text{H}_{29}\text{O}_2\text{Si}^-$ 269.1942 Found 269.1982.

IV. General Procedure for Cyclization of Alkenyl Silanols into Silanediol Synthons



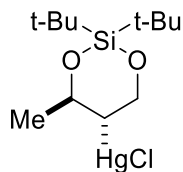
A 5 mL microwave vial was charged with NaHCO₃ (16.8 mg, 0.2 mmol, 1 equiv.) and Hg(OTf)₂ (100 mg, 0.2 mmol, 1 equiv.). 1 mL of anhydrous THF was added after which the reaction flask was immersed in a cooling bath set to -40 °C. Silanediol substrate (0.2 mmol, 1 equiv.) in 1 mL of THF was added dropwise to the cooled reaction flask after which the microwave vial was sealed. After 16 h at -40 °C (temperature maintained by a Brinkmann Lauda IC-6 immersion cooler chiller), 2 mL of saturated aqueous NaCl (brine) solution was added. The vial was removed from the cooling bath and allowed to warm to room temperature. The reaction mixture was diluted with ethyl acetate and transferred to a separatory funnel. After washing with H₂O, the organic layer was collected, dried with MgSO₄, and concentrated under reduced pressure. Chromatography on silica gel (0 to 100% ethyl acetate in hexanes) yielded purified product.



V. Characterization of Products

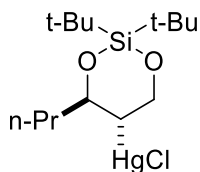
Note 1: In all cases, relative stereochemistry is shown.

Note 2: During ESI-MS, in almost all cases, we observed cleavage of the carbon mercury bond into a carbocation fragment. A representative mass spectrum of Compound 31 is given at the end of this section illustrating this phenomenon. A crystal structure of Compound 31 has been obtained, unequivocally establishing its structural assignment. This data is in Section VIII.



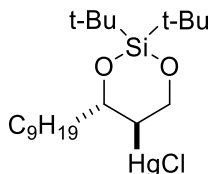
2,2-di-*tert*-butyl-4-methyl-1,3,2-dioxasilinan-5-yl)mercury(II) chloride

Compound 22: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 70% yield); ^1H NMR (400 MHz, CDCl_3) δ 4.41 (dq, $J = 11.1, 6.1$ Hz, 1H), 4.32 (dd, $J = 12.8, 11.1$ Hz, 1H), 4.16 (dd, $J = 11.2, 4.0$ Hz, 1H), 2.90 (ddd, $J = 12.7, 11.0, 4.1$ Hz, 1H), 1.30 (d, $J = 6.1$ Hz, 3H), 0.94 (d, $J = 18.9$ Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 72.8, 66.9, 61.1, 27.7, 27.4, 27.0, 22.8, 19.6. IR 2937, 1477, 1047, 825 cm^{-1} .



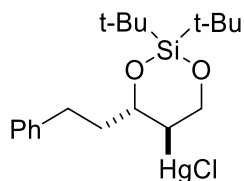
2,2-di-*tert*-butyl-4-propyl-1,3,2-dioxasilinan-5-yl)mercury(II) chloride

Compound 23: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 63% yield); ^1H NMR (400 MHz, CDCl_3) δ 4.39 (dd, $J = 12.7, 11.1$ Hz, 1H), 4.31 (td, $J = 6.5, 3.3$ Hz, 1H), 4.28 – 4.20 (m, 1H), 2.99 (ddd, $J = 12.7, 11.1, 4.1$ Hz, 1H), 1.64 – 1.52 (m, 4H), 1.03 (s, 9H), 0.98 (s, 9H), 0.94 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 75.8, 67.2, 59.9, 43.6, 27.4, 27.0, 22.9, 19.7, 18.4, 13.8. IR 2855, 1364, 1059, 823 cm^{-1} .



2,2-di-*tert*-butyl-4-nonyl-1,3,2-dioxasilinan-5-yl)mercury(II) chloride

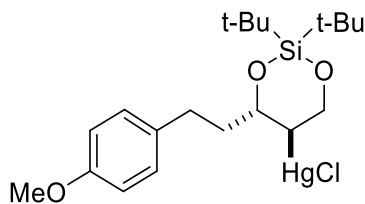
Compound 24: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 70% yield); ^1H NMR (400 MHz, CDCl_3) δ 4.32 (dd, $J = 12.7, 11.1$ Hz, 1H), 4.23 (td, $J = 7.2, 3.6$ Hz, 1H), 4.18 (dd, $J = 11.1, 4.2$ Hz, 1H), 2.92 (ddd, $J = 12.7, 11.0, 4.1$ Hz, 1H), 1.60 – 1.35 (m, 4H), 1.22 (d, $J = 6.7$ Hz, 12H), 0.96 (s, 9H), 0.91 (s, 9H), 0.85 – 0.77 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 76.1, 67.2, 59.9, 41.5, 31.9, 29.6, 29.5, 29.37, 29.30, 27.5, 27.1, 25.1, 22.8, 22.6, 19.7, 14.1. IR 2919, 1471, 1035, 823 cm^{-1} .



((*4S,5R*)-2,2-di-*tert*-butyl-4-phenethyl-1,3,2-dioxasilinan-5-yl)mercury(II) chloride

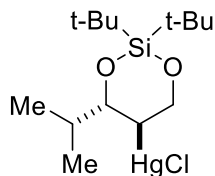
Compound 25: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 68% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 4.34 (dd, $J = 12.6, 11.1$ Hz, 1H), 4.27 (ddd, $J = 11.6, 8.4, 3.5$ Hz, 1H), 4.21 (dd, $J = 11.2, 4.1$ Hz, 1H), 3.08 – 2.85

(m, 2H), 2.79 (dt, $J = 13.8, 7.9$ Hz, 1H), 2.03 – 1.83 (m, 2H), 1.04 (d, $J = 8.5$ Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.8, 128.6, 128.6, 126.0, 75.2, 67.0, 59.7, 43.1, 31.2, 27.4, 27.1, 22.9, 19.7. IR 2860, 1465, 1024, 824 cm^{-1} .



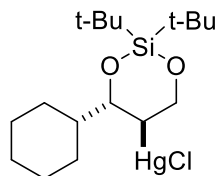
2,2-di-*tert*-butyl-4-(4-methoxyphenethyl)-1,3,2-dioxasilinan-5-ylmercury(II) chloride

Compound 26: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless oil, 61% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.13 – 6.98 (m, 2H), 6.83 – 6.68 (m, 2H), 4.26 (dd, $J = 12.6, 11.1$ Hz, 1H), 4.19 (ddd, $J = 11.5, 8.2, 3.6$ Hz, 1H), 4.13 (dd, $J = 11.1, 4.1$ Hz, 1H), 3.72 (s, 3H), 2.90 (ddd, $J = 12.6, 11.1, 4.1$ Hz, 1H), 2.79 (ddd, $J = 13.6, 7.6, 5.8$ Hz, 1H), 2.66 (dt, $J = 13.8, 7.8$ Hz, 1H), 1.90 – 1.70 (m, 2H), 0.97 (s, 9H), 0.95 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.1, 134.0, 129.6, 114.2, 75.3, 67.2, 59.9, 55.4, 43.5, 30.3, 27.5, 27.2, 23.0, 19.9. IR 2937, 1511, 1029, 825 cm^{-1} .



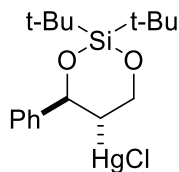
2,2-di-*tert*-butyl-4-isopropyl-1,3,2-dioxasilinan-5-ylmercury(II) chloride

Compound 27: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 54% yield); ^1H NMR (400 MHz, CDCl_3) δ 4.40 (dd, $J = 12.6, 10.9$ Hz, 1H), 4.30 (dd, $J = 10.9, 4.3$ Hz, 1H), 4.23 (dd, $J = 11.4, 2.2$ Hz, 1H), 3.07 (ddd, $J = 12.6, 11.3, 4.3$ Hz, 1H), 1.77 (pd, $J = 6.7, 2.1$ Hz, 1H), 1.08 (d, $J = 6.6$ Hz, 3H), 1.03 (s, 9H), 0.99 (s, 9H), 0.96 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 80.4, 67.7, 58.2, 38.0, 27.7, 27.2, 23.2, 20.2, 20.2, 14.9. IR 2961, 1472, 1071, 759 cm^{-1} .



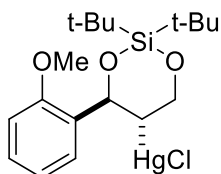
2,2-di-*tert*-butyl-4-cyclohexyl-1,3,2-dioxasilinan-5-ylmercury(II) chloride

Compound 28: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 62% yield); ^1H NMR (400 MHz, CDCl_3) δ 4.33 (dd, $J = 12.6, 11.0$ Hz, 1H), 4.23 (dd, $J = 10.9, 4.3$ Hz, 1H), 4.11 (dd, $J = 11.4, 1.7$ Hz, 1H), 3.04 (ddd, $J = 12.6, 11.3, 4.3$ Hz, 1H), 1.80 – 1.66 (m, 2H), 1.66 – 1.43 (m, 4H), 1.36 – 1.01 (m, 5H), 0.95 (s, 9H), 0.92 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 80.4, 67.7, 57.6, 48.2, 30.5, 27.7, 27.2, 26.52, 26.50, 26.3, 25.4, 23.1, 20.1. IR 919, 1472, 1112, 1012 cm^{-1} .



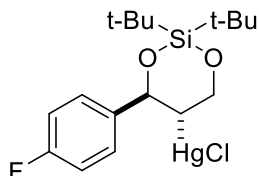
2,2-di-*tert*-butyl-4-phenyl-1,3,2-dioxasilinan-5-yl)mercury(II) chloride

Compound 29: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 60% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.38 (m, 2H), 7.36 – 7.29 (m, 2H), 7.27 – 7.21 (m, 1H), 5.29 (d, $J = 11.4$ Hz, 1H), 4.52 – 4.36 (m, 1H), 4.19 (dd, $J = 11.2, 4.2$ Hz, 1H), 3.16 (ddd, $J = 12.8, 11.3, 4.2$ Hz, 1H), 1.04 (s, 9H), 1.01 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.0, 129.4, 128.5, 125.4, 79.5, 67.5, 64.0, 27.5, 27.2, 23.0, 20.1. IR 2866, 1471, 1065, 829 cm^{-1} .



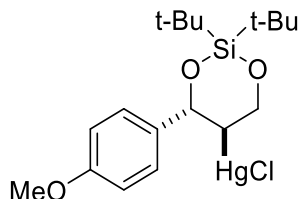
(2,2-di-*tert*-butyl-4-(2-methoxyphenyl)-1,3,2-dioxasilinan-5-yl)mercury(II) chloride

Compound 30: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 52% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.62 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.22 (ddd, $J = 8.2, 7.4, 1.8$ Hz, 1H), 7.00 (td, $J = 7.5, 1.1$ Hz, 1H), 6.82 (dd, $J = 8.3, 1.1$ Hz, 1H), 5.64 (d, $J = 10.8$ Hz, 1H), 4.49 (dd, $J = 12.9, 11.2$ Hz, 1H), 4.21 (dd, $J = 11.3, 4.1$ Hz, 1H), 3.84 (s, 3H), 2.85 (ddd, $J = 12.9, 10.8, 4.1$ Hz, 1H), 1.13 (s, 9H), 1.09 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 153.5, 133.0, 129.0, 126.6, 121.8, 110.4, 73.2, 67.9, 59.6, 55.2, 27.7, 27.4, 23.1, 20.3. IR 2949, 1489, 1094, 753 cm^{-1} .



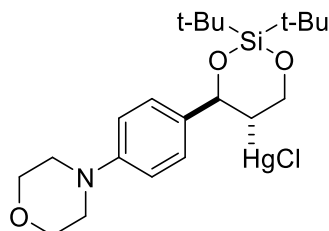
(2,2-di-*tert*-butyl-4-(4-fluorophenyl)-1,3,2-dioxasilinan-5-yl)mercury(II) chloride

Compound 31: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 59% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.38 (m, 2H), 7.15 – 7.01 (m, 2H), 5.34 (d, $J = 11.4$ Hz, 1H), 4.54 (dd, $J = 12.8, 11.2$ Hz, 1H), 4.28 (dd, $J = 11.2, 4.2$ Hz, 1H), 3.22 (ddd, $J = 12.7, 11.4, 4.2$ Hz, 1H), 1.10 (s, 9H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.5 (d, $J = 240$ Hz), 141.8, 127.1 (d, $J = 8.2$ Hz), 116.3 (d, $J = 21.6$ Hz), 78.9, 67.3, 63.8, 27.5, 27.2, 23.0, 20.1. IR 2943, 1377, 1035, 812 cm^{-1} .



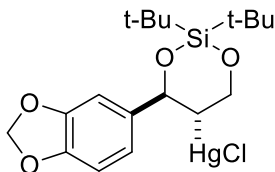
2,2-di-*tert*-butyl-4-(4-methoxyphenyl)-1,3,2-dioxasilinan-5-yl)mercury(II) chloride

Compound 32: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 43% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.34 (m, 2H), 6.96 – 6.87 (m, 2H), 5.31 (d, $J = 11.3$ Hz, 1H), 4.53 (dd, $J = 12.8, 11.2$ Hz, 1H), 4.27 (dd, $J = 11.1, 4.2$ Hz, 1H), 3.81 (s, 3H), 3.27 (ddd, $J = 12.8, 11.4, 4.2$ Hz, 1H), 1.09 (s, 9H), 1.08 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.7, 138.3, 126.7, 114.9, 79.2, 67.6, 64.3, 55.5, 27.7, 27.4, 23.2, 20.2. IR 2949, 1512, 1100, 829 cm^{-1} .



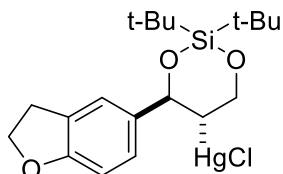
2,2-di-*tert*-butyl-4-(4-morpholinophenyl)-1,3,2-dioxasilinan-5-ylmercury(II) chloride

Compound 33: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless solid, 56% yield); ^1H NMR (400 MHz, CDCl_3) δ 1.08 (s, 9H), 1.09 (s, 9H), 3.1 – 3.2 (m, 4H), 3.3 (ddd, $J = 12.8, 11.4, 4.2$ Hz, 1H), 3.8 – 3.9 (m, 4H), 4.3 (dd, $J = 11.2, 4.2$ Hz, 1H), 4.5 – 4.6 (m, 1H), 5.3 (d, $J = 11.4$ Hz, 1H), 6.9 (d, $J = 8.8$ Hz, 2H), 7.4 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 19.8, 22.7, 26.9, 27.2, 48.8, 63.7, 66.5, 67.1, 78.7, 115.9, 126.0, 136.9, 150.9; IR 2930, 2856, 1515, 1068, 815, 650 cm^{-1} .



4-(benzo[*d*][1,3]dioxol-5-yl)-2,2-di-*tert*-butyl-1,3,2-dioxasilinan-5-ylmercury(II) chloride

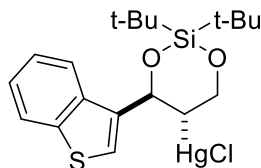
Compound 34: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless solid, 55% yield); ^1H NMR (400 MHz, CDCl_3) δ 1.08 (s, 9H), 1.09 (s, 9H), 3.2 – 3.3 (m, 1H), 4.3 (dd, $J = 11.2, 4.2$ Hz, 1H), 4.5 (dd, $J = 12.8, 11.2$ Hz, 1H), 5.3 (d, $J = 11.3$ Hz, 1H), 6.0 (s, 2H), 6.8 (d, $J = 7.9$ Hz, 1H), 6.9 (d, $J = 1.7$ Hz, 1H), 7.0 (d, $J = 1.7$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 20.1, 23.1, 27.3, 27.6, 64.0, 67.4, 79.3, 101.3, 105.8, 108.8, 118.9, 140.3, 147.7, 148.6; IR 2932, 2857, 1442, 1246, 825, 650 cm^{-1} .



2,2-di-*tert*-butyl-4-(2,3-dihydrobenzofuran-5-yl)-1,3,2-dioxasilinan-5-ylmercury(II) chloride

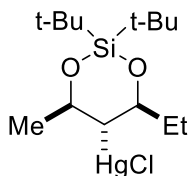
Compound 35: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless solid, 50% yield); ^1H NMR (400 MHz, CDCl_3) δ 0.9 – 1.2 (m, 18H), 3.1 – 3.4 (m, 3H), 4.3 (dd, $J = 11.1, 4.2$ Hz, 1H), 4.4 – 4.7 (m, 3H), 5.3 (d, $J = 11.4$ Hz, 1H), 6.8 (d, $J = 8.2$ Hz, 1H), 7.2 (dd, $J = 8.1, 2.0$ Hz, 1H), 7.2 – 7.4 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 19.8, 22.7, 26.9, 27.2, 29.4, 64.0, 67.2,

71.1, 79.0, 109.6, 121.7, 125.0, 128.1, 138.0, 159.9; IR ν_{max} = 2931, 2857, 1613, 1491, 1094, 764, 650 cm^{-1} .

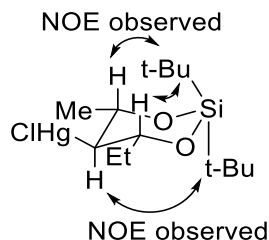


4-(benzo[*b*]thiophen-3-yl)-2,2-di-*tert*-butyl-1,3,2-dioxasilinan-5-ylmercury(II) chloride

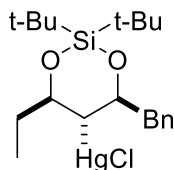
Compound 36: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless solid, 52% yield); ^1H NMR (400 MHz, CDCl_3) δ 1.11 (s, 9H), 1.12 (s, 9H), 3.3 (ddd, $J = 12.5, 11.0, 4.2$ Hz, 1H), 4.3 (dd, $J = 11.3, 4.2$ Hz, 1H), 4.5 – 4.7 (m, 1H), 5.8 (dd, $J = 11.2, 2.7$ Hz, 1H), 7.3 – 7.5 (m, 2H), 7.6 (d, $J = 2.4$ Hz, 1H), 7.9 (d, $J = 7.9$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 20.1, 23.1, 27.2, 27.5, 60.2, 67.7, 74.2, 121.1, 123.4, 123.7, 124.8, 125.0, 136.0, 140.1, 141.2; IR 2931, 2856, 1471, 1260, 1019, 764, 648 cm^{-1} .



2,2-di-*tert*-butyl-4-ethyl-6-methyl-1,3,2-dioxasilinan-5-ylmercury(II) chloride



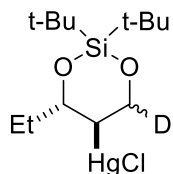
Compound 37: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White foam, 88% yield); ^1H NMR (400 MHz, CDCl_3) δ 4.40 (dq, $J = 11.1, 6.1$ Hz, 1H), 4.16 (ddd, $J = 11.2, 8.1, 3.0$ Hz, 1H), 2.60 (t, $J = 11.2$ Hz, 1H), 1.66 (dddd, $J = 14.7, 10.3, 6.8, 3.0$ Hz, 1H), 1.54 – 1.41 (m, 1H), 1.31 (d, $J = 6.1$ Hz, 3H), 0.96 (d, $J = 8.8$ Hz, 12H), 0.90 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 76.6, 72.5, 67.1, 34.9, 28.2, 27.6, 27.2, 22.9, 19.7, 9.5. IR 2902, 1477, 994, 823 cm^{-1} .



4-benzyl-2,2-di-*tert*-butyl-6-ethyl-1,3,2-dioxasilinan-5-ylmercury(II) chloride

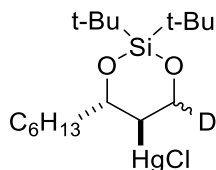
Compound 38: (Purified using a gradient of 0 to 100% EtOAc in hexanes, Colorless solid, 85% yield); ^1H NMR (400 MHz, CDCl_3) δ 0.9 – 1.1 (m, 21H), 1.4 – 1.6 (m, 1H), 1.6 – 1.8 (m, 1H), 2.3 (t, $J = 11.3$ Hz, 1H), 2.6 (dd, $J = 13.7, 9.8$ Hz, 1H), 3.3 (dd, $J = 13.7, 4.3$ Hz, 1H), 4.2 (ddd, $J =$

11.0, 8.0, 2.9 Hz, 1H), 4.6 (ddd, $J = 11.2, 9.7, 4.3$ Hz, 1H), 7.1 – 7.2 (m, 2H), 7.3 – 7.4 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 9.4, 19.7, 22.8, 27.1, 27.5, 35.7, 46.5, 60.6, 76.8, 78.4, 128.1, 129.2, 130.0, 137.8; IR 2931, 2856, 1471, 1041, 824, 696 cm^{-1} .



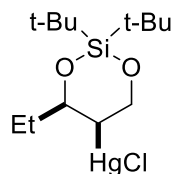
2,2-di-*tert*-butyl-4-ethyl-1,3,2-dioxasilinan-5-yl-6-*d*)mercury(II) chloride

Compound 39: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 57% yield); 1:1 mixture of diastereomers; ^1H NMR (400 MHz, CDCl_3) δ 4.37 (d, $J = 12.9$ Hz, 1H), 4.28 – 4.19 (m, 3H), 3.05 – 2.95 (m, 2H), 1.70 (dtd, $J = 14.5, 7.3, 3.0$ Hz, 2H), 1.63 – 1.52 (m, 2H), 1.07 – 1.04 (m, 6H), 1.03 (s, 18H), 0.98 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 77.4, 66.8 (t, $J = 20.5$ Hz), 59.4, 34.6, 27.6, 27.2, 23.0, 19.9, 9.7. IR 2949, 1353, 1205, 1065 cm^{-1} .



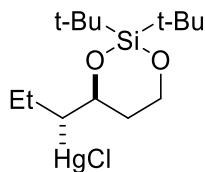
2,2-di-*tert*-butyl-4-hexyl-1,3,2-dioxasilinan-5-yl-6-*d*)mercury(II) chloride

Compound 40: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 74% yield); 1:1 mixture of diastereomers; ^1H NMR (400 MHz, CDCl_3) δ 4.39 (d, $J = 12.8$ Hz, 1H), 4.32 (ddd, $J = 11.2, 7.3, 4.0$ Hz, 2H), 4.25 (d, $J = 4.0$ Hz, 1H), 3.08 – 2.90 (m, 2H), 1.68 – 1.43 (m, 8H), 1.33 (pt, $J = 7.5, 3.8$ Hz, 12H), 1.06 (s, 18H), 1.01 (s, 18H), 0.95 – 0.86 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 76.1, 66.7, 59.8, 41.5, 31.8, 29.0, 27.4, 27.0, 25.1, 22.8, 22.6, 19.7, 14.0. IR 2931, 1459, 1053, 736 cm^{-1} .



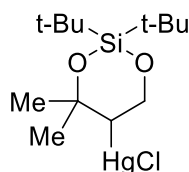
2,2-di-*tert*-butyl-4-ethyl-1,3,2-dioxasilinan-5-yl)mercury(II) chloride

Compound 41: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 43% yield); ^1H NMR (400 MHz, CDCl_3) δ 4.63 (dd, $J = 12.5, 2.2$ Hz, 1H), 4.44 (ddd, $J = 7.4, 4.7, 2.2$ Hz, 1H), 4.21 (dd, $J = 12.4, 2.2$ Hz, 1H), 3.00 (q, $J = 2.2$ Hz, 1H), 1.68 – 1.54 (m, 1H), 1.54 – 1.41 (m, 1H), 1.09 (d, $J = 4.8$ Hz, 18H), 0.99 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 79.3, 68.9, 62.4, 35.2, 28.6, 27.9, 23.2, 19.4, 9.9. IR 2933, 1471, 994, 650 cm^{-1} .



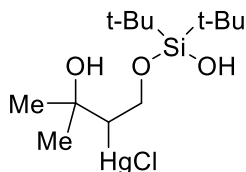
2,2-di-*tert*-butyl-1,3,2-dioxasilinan-4-yl)propyl)mercury(II) chloride

Compound 42: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 18% yield); ^1H NMR (400 MHz, CDCl_3) δ 4.41 (ddd, $J = 10.9, 5.2, 1.9$ Hz, 1H), 4.13 – 3.98 (m, 2H), 2.98 (dt, $J = 11.1, 5.0$ Hz, 1H), 1.89 – 1.73 (m, 2H), 1.73 – 1.55 (m, 2H), 1.03 (t, $J = 7.2$ Hz, 3H), 0.96 (d, $J = 3.7$ Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 76.6, 68.7, 64.4, 39.0, 27.5, 26.9, 23.4, 22.7, 19.7, 16.5. IR 2949, 1472, 1106, 826 cm^{-1} .



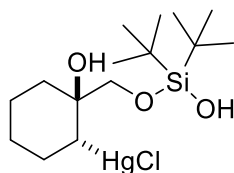
(2,2-di-*tert*-butyl-4,4-dimethyl-1,3,2-dioxasilinan-5-yl)mercury(II) chloride

Compound 45: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 30% yield); ^1H NMR (400 MHz, CDCl_3) δ 4.38 (t, $J = 11.9$ Hz, 1H), 4.13 (dd, $J = 11.7, 3.6$ Hz, 1H), 3.21 – 3.01 (m, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 0.94 (d, $J = 7.0$ Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 74.9, 65.1, 63.4, 34.4, 32.7, 27.5, 27.4, 21.4, 20.3. IR 2849, 1477, 1065, 648 cm^{-1} .



(1-((di-*tert*-butyl(hydroxy)silyl)oxy)-3-hydroxy-3-methylbutan-2-yl)mercury(II) chloride

Compound 46: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 35% yield); ^1H NMR (400 MHz, CDCl_3) δ 4.34 (dd, $J = 11.2, 4.8$ Hz, 1H), 4.20 (dd, $J = 11.2, 4.9$ Hz, 1H), 2.88 (t, $J = 4.8$ Hz, 1H), 1.33 (d, $J = 1.9$ Hz, 6H), 0.98 (d, $J = 1.9$ Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 73.9, 71.9, 64.5, 33.2, 29.8, 27.7, 27.6, 20.4, 20.1. IR 2866, 1465, 1082, 818 cm^{-1} .

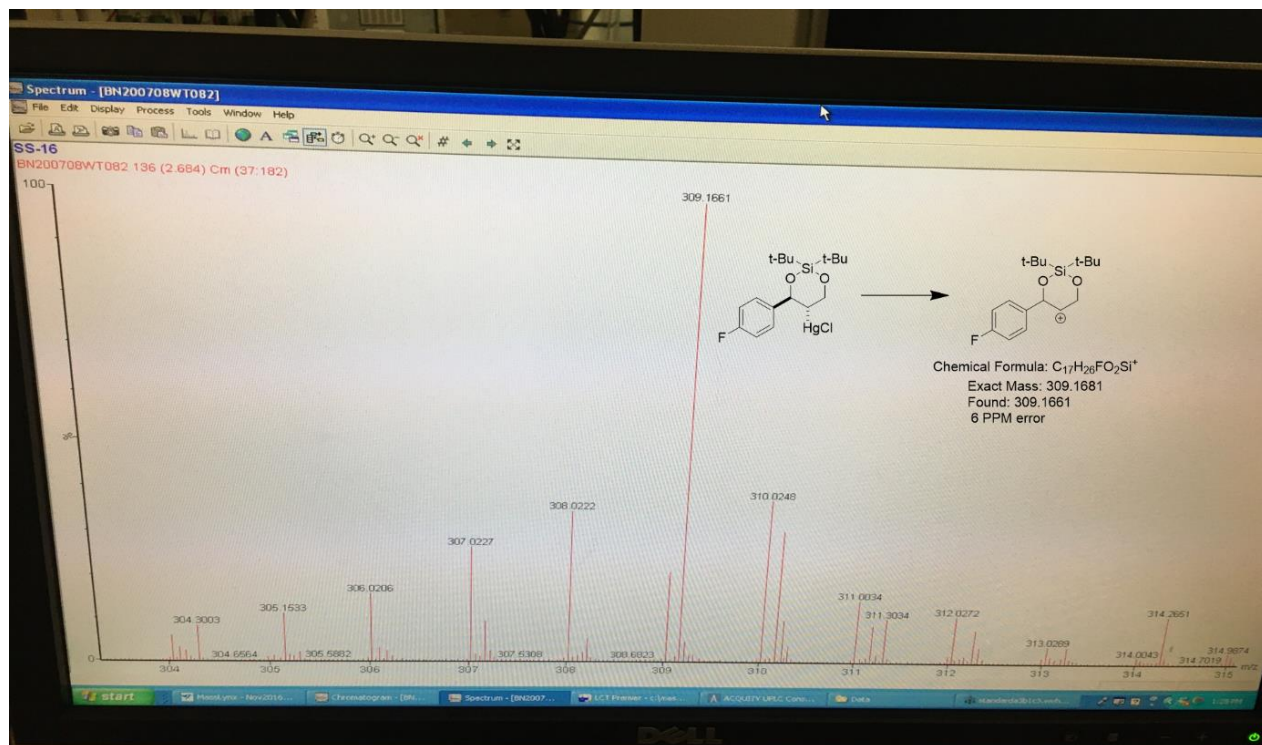


(2-(((di-*tert*-butyl(hydroxy)silyl)oxy)methyl)-2-hydroxycyclohexyl)mercury(II) chloride

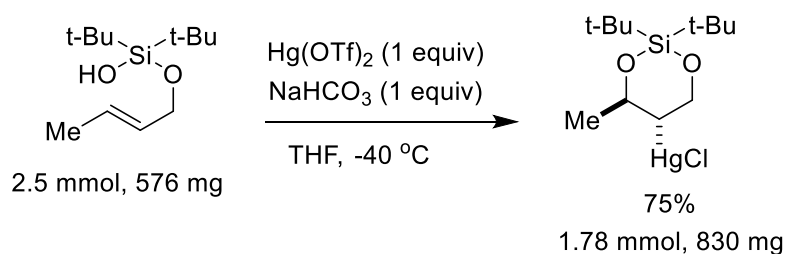
Compound 47: (Purified using a gradient of 0 to 100% EtOAc in hexanes, White solid, 73% yield); ^1H NMR (400 MHz, CDCl_3) δ 3.87 (q, $J = 10.3$ Hz, 2H), 2.78 (dd, $J = 9.1, 3.8$ Hz, 1H), 2.18 (ddt, $J = 14.4, 6.9, 3.7$ Hz, 1H), 1.92 – 1.65 (m, 3H), 1.65 – 1.36 (m, 4H), 1.09 (s, 18H). ^{13}C

NMR (101 MHz, CDCl_3) δ 74.6, 71.3, 59.2, 36.9, 29.3, 28.3, 27.8, 27.7, 22.2, 20.8, 20.7. IR 3520, 2943, 1465, 1365 cm^{-1} .

Mass Spectrum of **Compound 31** showing a characteristic fragmentation in ESI-positive mode. See Section VIII for crystallographic data establishing the structure of **Compound 31**.



VI. Scale-up Reaction

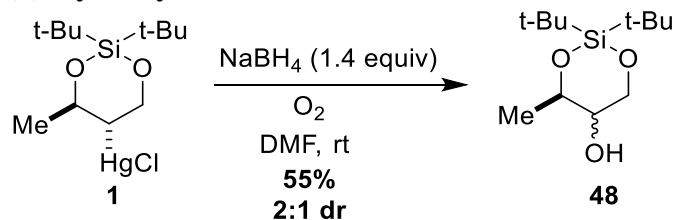


A 50 mL round-bottom flask was charged with a mixture of $\text{Hg}(\text{OTf})_2$ (1.248 g, 2.5 mmol, 1 equiv), NaHCO_3 (210 mg, 2.5 mmol, 1 equiv) and dry THF (15 mL). The flask was immersed into a cooling bath set to $-40 \text{ }^\circ\text{C}$. Following this, a solution of allylic silanediol (576 mg, 2.5 mmol) in dry THF (10 mL) was added dropwise. After 16 hours at $-40 \text{ }^\circ\text{C}$, 5 mL of saturated aqueous NaCl was added dropwise. The mixture was warmed to room temperature and transferred to a separatory funnel with ethyl acetate. The organic layer was collected, and the aqueous layer was extracted with additional ethyl acetate. The organic fractions were combined, dried with Na_2SO_4 , and concentrated under reduced pressure. The resulting residue was purified by chromatography on

silica gel (gradient of 3 to 5% ethyl acetate in hexanes) to furnish silanediol product (830 mg, 1.78 mmol) as a white solid.

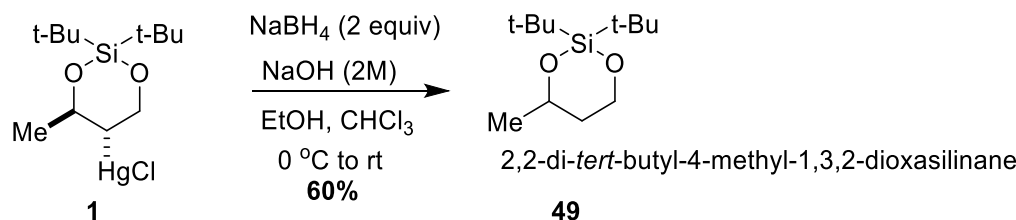
VII. Derivatization of Silanediol Organomercurial Products

(a) Hydroxylation



Oxygen gas (O₂) was bubbled into a well-stirred solution of NaBH₄ (11 mg, 0.29 mmol, 1.4 equiv) in DMF (1.5 mL) at room temperature for 15 min. Following this time, a solution of **1** (93.1 mg, 0.2 mmol) in DMF (4 mL) was added dropwise. During and after addition, O₂ was continuously bubbled. After 2 h at room temperature, the mixture was diluted with ethyl acetate, filtered through a pad of celite, transferred to a separatory funnel, and washed with water and brine. The organic layer was collected, dried over anhydrous MgSO₄, and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel (gradient of 15 to 20% ethyl acetate in hexanes) to yield **48** (26.9 mg, 55%) as a 2:1 mixture of diastereomers as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 0.9 – 1.0 (m, 27H), 1.2 (d, *J* = 6.4 Hz, 1.5H), 1.3 (d, *J* = 6.1 Hz, 3H), 3.4 (ddd, *J* = 10.1, 8.7, 4.6 Hz, 1.5H), 3.7 (t, *J* = 10.3 Hz, 1H), 3.9 (dq, *J* = 8.7, 6.0 Hz, 1H), 3.9 – 4.1 (m, 1.5H), 4.2 (dd, *J* = 12.0, 1.7 Hz, 0.5H), 4.3 (qd, *J* = 6.4, 1.6 Hz, 0.5H); ¹³C NMR (101 MHz, CDCl₃) δ 19.6, 19.8, 20.3, 20.9, 22.2, 22.8, 26.7, 26.8, 27.2, 27.6, 68.1, 69.3, 71.3, 71.9, 72.0, 74.5; IR 3437, 2933, 2859, 1473, 1053, 824, 650 cm⁻¹; HRMS calculated for C₁₂H₂₅O₃Si 245.1578 Found 245.1595.

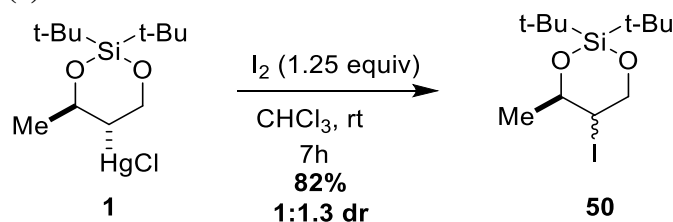
(b) Demercuration



A reaction flask was charged with **1** (93.1 mg, 0.2 mmol), 2M NaOH (0.2 mL), EtOH (1.5 mL), and CHCl₃ (1.5 mL). This mixture was cooled to 0 °C using an ice-water bath. At this temperature, NaBH₄ (15.2 mg, 0.4 mmol) was added in one portion. After stirring for 30 min at room temperature, the mixture was acidified with 3M HCl, transferred to a separatory funnel, and extracted with CHCl₃ (3 x 5 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude residue was purified by chromatography on silica gel (hexanes) to yield purified **49** (28 mg, 61%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 1.0 (s, 9H), 1.0 (s, 9H), 1.2 (d, *J* = 6.1 Hz, 3H), 1.6 (dq, *J* = 14.2, 2.6 Hz, 1H), 1.8 (dddd, *J* = 14.2, 10.4, 8.7, 7.5 Hz, 1H), 4.1 (d, *J* = 2.6 Hz, 1H), 4.1 (dd, *J* = 2.7, 1.3 Hz, 1H), 4.2 (dq, *J* = 12.3, 6.1, 2.7 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 19.5, 22.2, 24.4,

26.8, 27.1, 37.8, 63.8, 70.0; IR 2932, 2858, 1473, 1113, 969, 824, 648 cm^{-1} ; HRMS calculated for $\text{C}_{12}\text{H}_{25}\text{O}_2\text{Si}^-$ 229.1629 Found 229.1645.

(c) Iodination



I_2 (63.5 mg, 0.25 mmol, 1.25 equiv) was added to a solution of **1** (93.1 mg, 0.2 mmol) in 3 mL of CHCl_3 . After being stirred for 7 h, the mixture was diluted with dichloromethane and quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) solution. In a separatory funnel, the organic layer was separated, collected, dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure. The resulting residue (containing a 1:1.3 mixture of diastereomers of **50**) was purified by chromatography on silica gel (hexanes) to yield 47% of one diastereomer and 35% of the other.

Data for major diastereomer:

(Colorless liquid, 47% yield); ^1H NMR (400 MHz, CDCl_3) δ 0.98 (s, 9H), 1.03 (s, 9H), 1.5 (d, $J = 6$ Hz, 3H), 4.0 (td, $J = 10.5, 5.2$ Hz, 1H), 4.1 – 4.2 (m, 2H), 4.2 – 4.3 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 19.8, 22.8, 24.9, 26.9, 27.4, 34.2, 71.1, 75.8; IR 2932, 2858, 1473, 1135, 1044, 746 cm^{-1} .

Data for minor diastereomer:

(Colorless solid, 35% yield); ^1H NMR (400 MHz, CDCl_3) δ 1.04 (s, 9H), 1.07 (s, 9H), 1.4 (d, $J = 6.3$ Hz, 3H), 4.1 (qd, $J = 6.2, 3.8$ Hz, 1H), 4.3 – 4.4 (m, 2H), 4.5 (dt, $J = 6.8, 3.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 20.6, 21.6, 23.4, 27.4, 27.6, 33.5, 68.1, 71.2; IR 2930, 2857, 1471, 1121, 1057, 765 cm^{-1} .

VIII. X-ray Crystallographic Study for Compound 31: $\text{Hg}(\text{Cl})(\text{C}_{17}\text{H}_{26}\text{O}_2\text{FSi})$ [q63k, (1)].

A complete set of unique reflections was collected with monochromated $\text{CuK}\alpha$ radiation for a single-domain crystal of **1**. A total of 4521 1.0° -wide ω - or ϕ -scan frames with counting times of 4-6 seconds were collected on a Bruker Apex II CCD area detector. X-rays were provided by a Bruker MicroStar microfocus rotating anode operating at 45kV and 60 mA and equipped with Helios multilayer x-ray optics. Preliminary lattice constants were obtained with the Bruker program SMART.[S1] Integrated reflection intensities were produced using the Bruker program SAINT.[S2] The data set was corrected for variable absorption effects using a numerical face-indexed procedure. The Bruker software package SHELXTL was used to solve the structure using “direct methods” techniques. All stages of weighted full-matrix least-squares refinement were conducted using Fo^2 data with the SHELXTL v2014 software package.[S3]

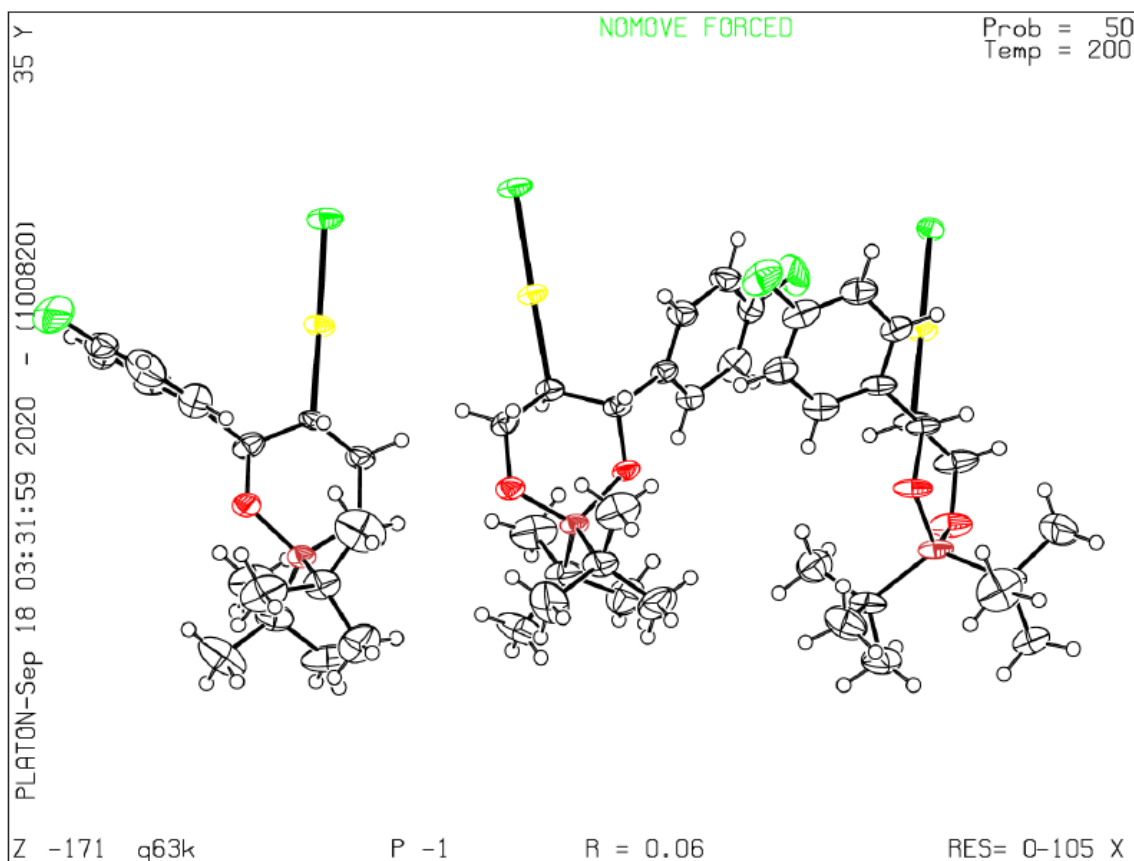
The final structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Hydrogen atoms were fixed at idealized riding-model sp^2 - or sp^3 -hybridized positions with C-H bond lengths of 0.95 – 1.00 Å. The eighteen methyl groups were

included in the structural model as idealized rigid rotors (with a C-H bond length of 0.98 Å) that were allowed to rotate freely about their C-C bonds in least-squares refinement cycles. Isotropic thermal parameters of the idealized hydrogen atoms were fixed at values 1.2 (non-methyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded. The relevant crystallographic and structure refinement data are given in Table S-1.

Note: Crystals were grown from pentane *via* slow evaporation.

CCDC: 2032765 (1)

Datablock q63k - ellipsoid plot



All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn at the 50% probability level.

Table S1. Crystal and Refinement Data for **Hg(Cl)(C₁₇H₂₆O₂FSi) (1)**.

	1
Empirical formula	C ₁₇ H ₂₆ ClFHgO ₂ Si
Formula weight	545.51
Temperature	200(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1 - Ci ¹ (No. 2)
<i>a</i>	12.3430(7) Å
<i>b</i>	13.6880(8) Å
<i>c</i>	20.8227(11) Å
α	105.8493(19)°
β	94.109(2)°
γ	113.192(2)°
Volume	3046.2(3) Å ³
Z	6
Density (calculated)	1.784 g/cm ³
Absorption coefficient	15.493 mm ⁻¹
F(000)	1584
Crystal size	0.093 x 0.077 x 0.055 mm ³
Theta range	2.25 to 70.46°
Index ranges	-13 ≤ <i>h</i> ≤ 14, -16 ≤ <i>k</i> ≤ 16, -24 ≤ <i>l</i> ≤ 24
Reflections collected	40728
Independent reflections	10681 [R _{int} = 0.055]
Completeness to $\theta = 66.00^\circ$	95.9 %
Absorption correction	Numerical face-indexed
Max. and min. transmission	1.000 and 0.579
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10681/0/640

Goodness-of-fit on F^2	1.117
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.059$, $wR_2 = 0.150$
R indices (all data)	$R_1 = 0.065$, $wR_2 = 0.160$
Largest diff. peak and hole	3.49 and $-2.67 \text{ e}^-/\text{\AA}^3$

References

[S1] Data Collection: SMART Software in APEX2 v2014.11-0 Suite. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

[S2] Data Reduction: SAINT Software in APEX2 v2014.11-0 Suite. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

[S3] Refinement: SHELXTL Software in APEX2 v2014.11-0 Suite. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) q63k

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: q63k

Bond precision: C-C = 0.0164 A Wavelength=1.54178

Cell: a=12.3430(7) b=13.6880(8) c=20.8227(11)

alpha=105.8493(19) beta=94.109(2) gamma=113.192(2)

Temperature: 200 K

Calculated Reported

Volume 3046.2(3) 3046.2(3)

Space group P -1 P -1

Hall group -P 1 -P 1

Moiety formula C17 H26 Cl F Hg O2 Si ?

Sum formula C17 H26 Cl F Hg O2 Si C17 H26 Cl F Hg O2 Si

Mr 545.51 545.51

$D_x, g \text{ cm}^{-3}$ 1.784 1.784

Z 6 6

μ (mm⁻¹) 15.494 15.493

F000 1584.0 1584.0

F000' 1565.38

h, k, lmax 15, 16, 25 14, 16, 24

Nref 11664 10681

Tmin, Tmax 0.275, 0.427 0.364, 0.629

Tmin' 0.206

Correction method= # Reported T Limits: Tmin=0.364 Tmax=0.629
AbsCorr = 'N
Data completeness= 0.916 Theta(max)= 70.464
R(reflections)= 0.0590(9584) wR2(reflections)= 0.1600(10681)
S = 1.117 Npar= 640

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level B

PLAT029_ALERT_3_B _diffn_measured_fraction_theta_full value Low . 0.959 Why?

Author Response: The crystal utilizes a low-symmetry triclinic unit cell and the data w

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 1.12A From Hg1A 3.47 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 1.19A From Cl1C 3.17 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 0.93A From C2B 3.14 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 1.04A From C2A 3.13 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 0.93A From Hg1B 3.04 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 1.10A From Cl1B 2.93 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 0.98A From C2C 2.77 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT972_ALERT_2_B Check Calcd Resid. Dens. 0.84A From Hg1C -2.51 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT973_ALERT_2_B Check Calcd Positive Resid. Density on Hg1A 1.64 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT973_ALERT_2_B Check Calcd Positive Resid. Density on Hg1B 1.60 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field.

Absorption correction given as numerical face-indexed

PLAT027_ALERT_3_C _diffn_reflns_theta_full value (too) Low 66.00 Degree

PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C10A Check

PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C14A Check

PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C14C Check

PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ... 2.1 Note

PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ... 2.1 Note

PLAT334_ALERT_2_C Small Aver. Benzene C-C Dist C4A -C9A 1.37 Ang.

PLAT334_ALERT_2_C Small Aver. Benzene C-C Dist C4C -C9C 1.37 Ang.

PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds 0.01636 Ang.

PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 556 Report

PLAT971_ALERT_2_C Check Calcd Resid. Dens. 1.08A From C3A 1.83 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT971_ALERT_2_C Check Calcd Resid. Dens. 2.34A From Cl1B 1.59 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.95A From Hg1B -2.50 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.92A From Hg1A -2.47 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.90A From Hg1A -2.20 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb

PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.82A From Hg1C -2.17 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.84A From Hg1C -2.07 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.72A From Hg1B -2.05 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.97A From Hg1B -2.05 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.95A From Hg1A -2.04 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.77A From Hg1A -1.98 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.53A From Hg1C -1.93 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 1.26A From Hg1C -1.87 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.69A From Hg1C -1.66 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.72A From Hg1B -1.63 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 1.85A From Hg1B -1.57 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 1.83A From Hg1B -1.54 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.72A From Hg1A -1.52 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 1.75A From Cl1A -1.51 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT973_ALERT_2_C Check Calcd Positive Resid. Density on Hg1C 1.44 eA-3

Author Response: The crystal contains several very heavy Hg atoms that strongly absorb
PLAT977_ALERT_2_C Check Negative Difference Density on H8AA -0.52 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H1BA -0.36 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H5BA -0.36 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H2CA -0.79 eA-3
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Alert level G

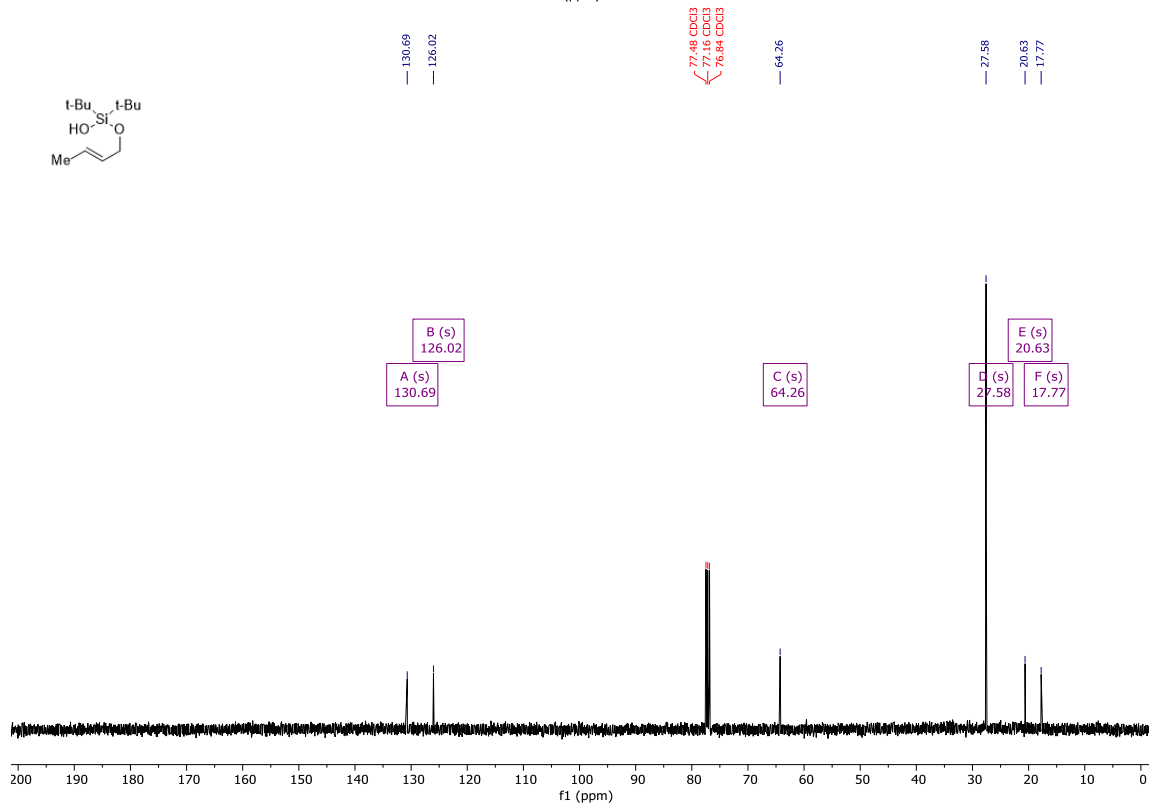
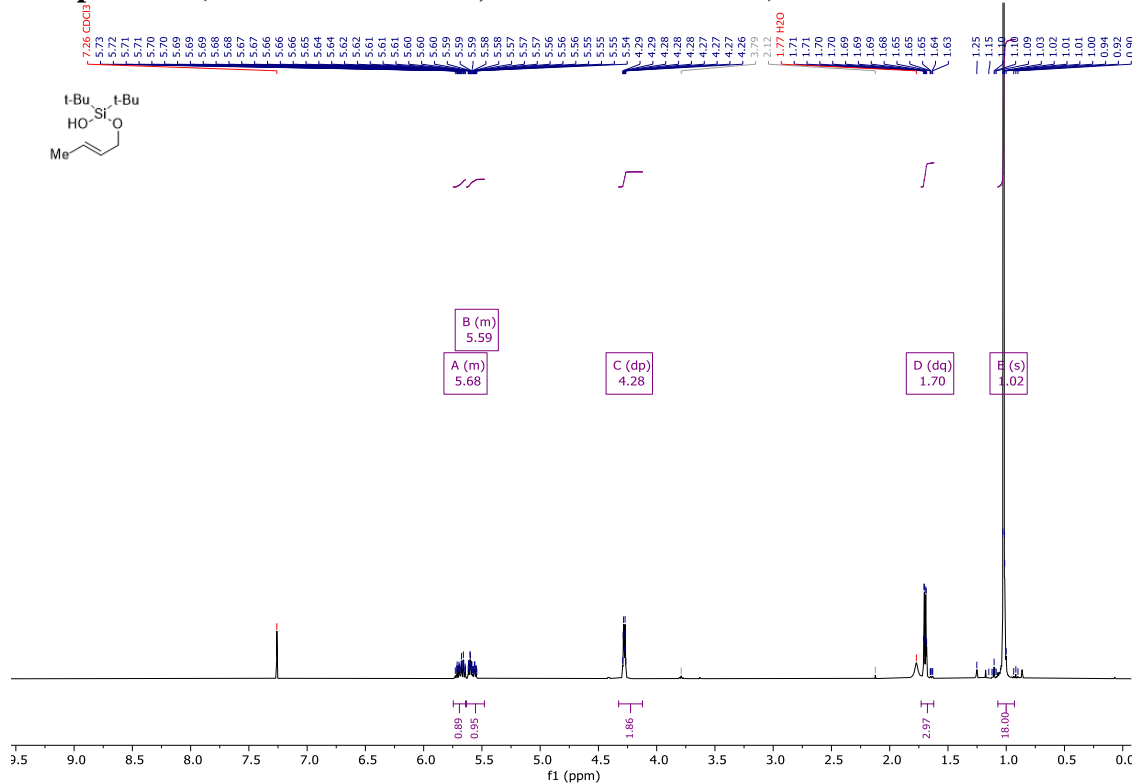
ABSTY01_ALERT_1_G Extra text has been found in the _exptl_absorpt_correction_type field, which should be only a single keyword. A literature citation should be included in the _exptl_absorpt_process_details field.

PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 14.48 Why ?
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 24 Note
PLAT793_ALERT_4_G Model has Chirality at C2A (Centro SPGR) R Verify
PLAT793_ALERT_4_G Model has Chirality at C2B (Centro SPGR) R Verify
PLAT793_ALERT_4_G Model has Chirality at C2C (Centro SPGR) S Verify
PLAT793_ALERT_4_G Model has Chirality at C3A (Centro SPGR) S Verify
PLAT793_ALERT_4_G Model has Chirality at C3B (Centro SPGR) S Verify
PLAT793_ALERT_4_G Model has Chirality at C3C (Centro SPGR) R Verify
PLAT802_ALERT_4_G CIF Input Record(s) with more than 80 Characters 4 Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 389 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity 3.8 Low
PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged Please Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 0 Info
0 **ALERT level A** = Most likely a serious problem - resolve or explain
11 **ALERT level B** = A potentially serious problem, consider carefully
36 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
15 **ALERT level G** = General information/check it is not something unexpected
3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
45 ALERT type 2 Indicator that the structure model may be wrong or deficient

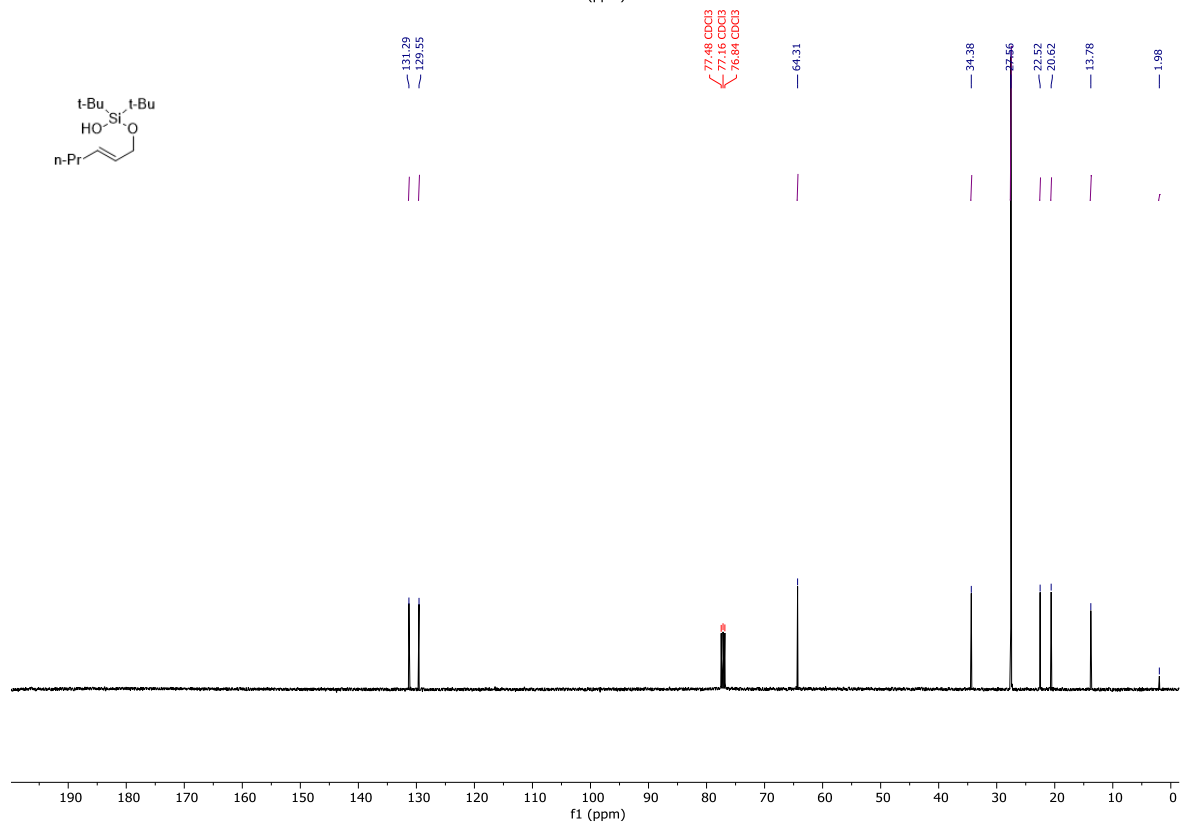
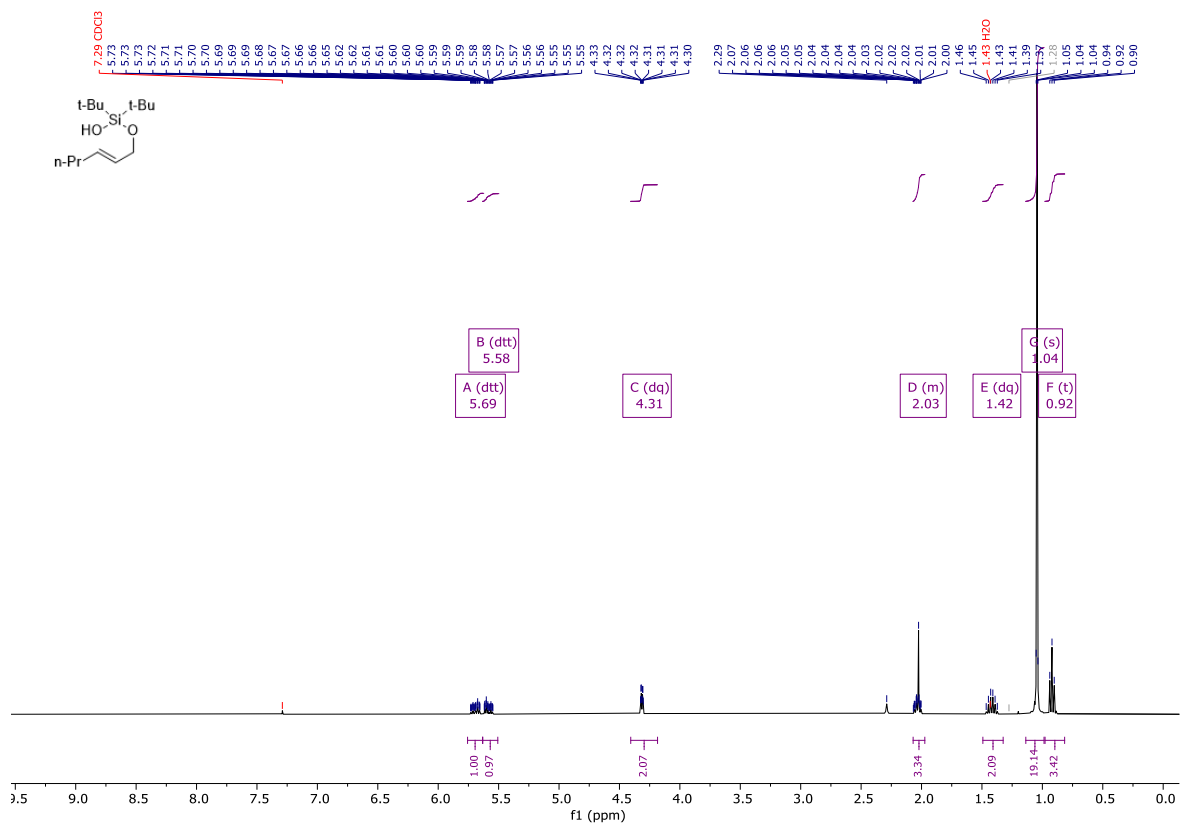
5 ALERT type 3 Indicator that the structure quality may be low
9 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

IX. NMR Spectra

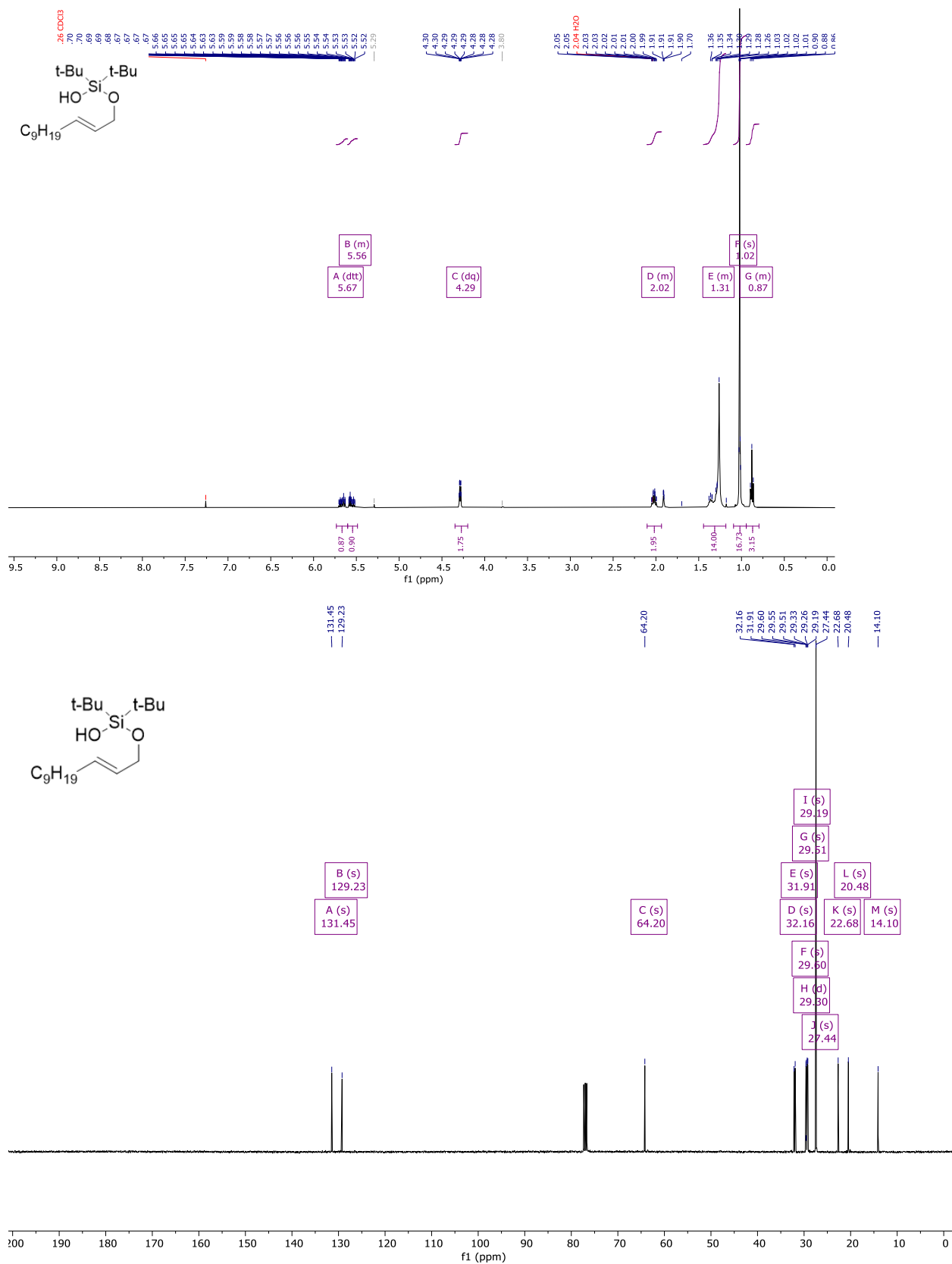
Compound 1 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz)



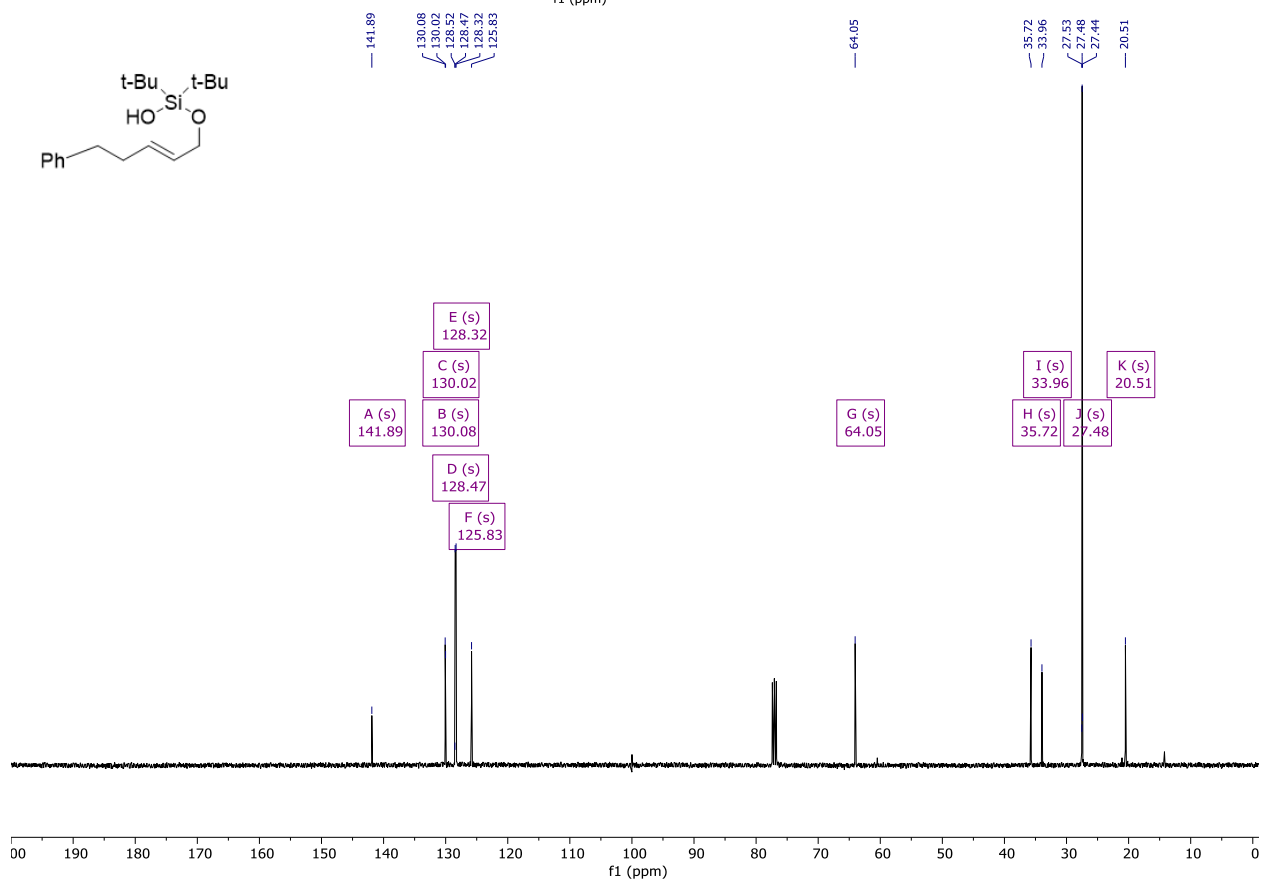
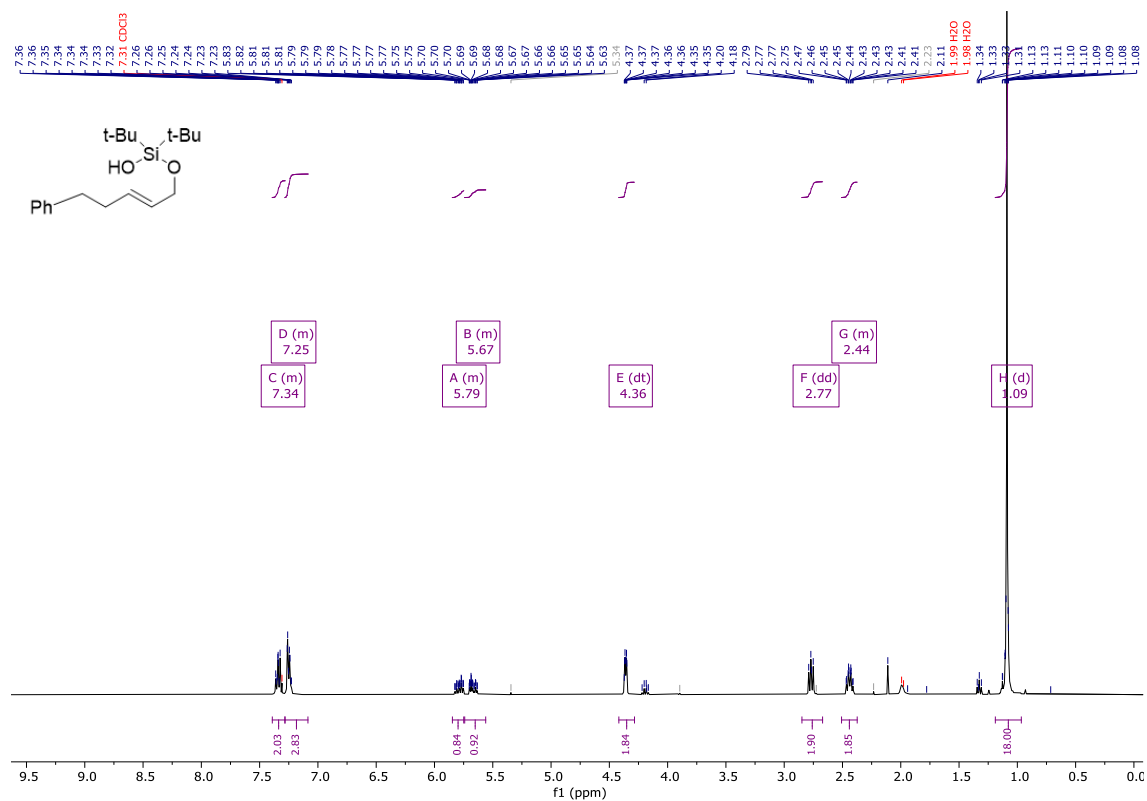
Compound 2 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



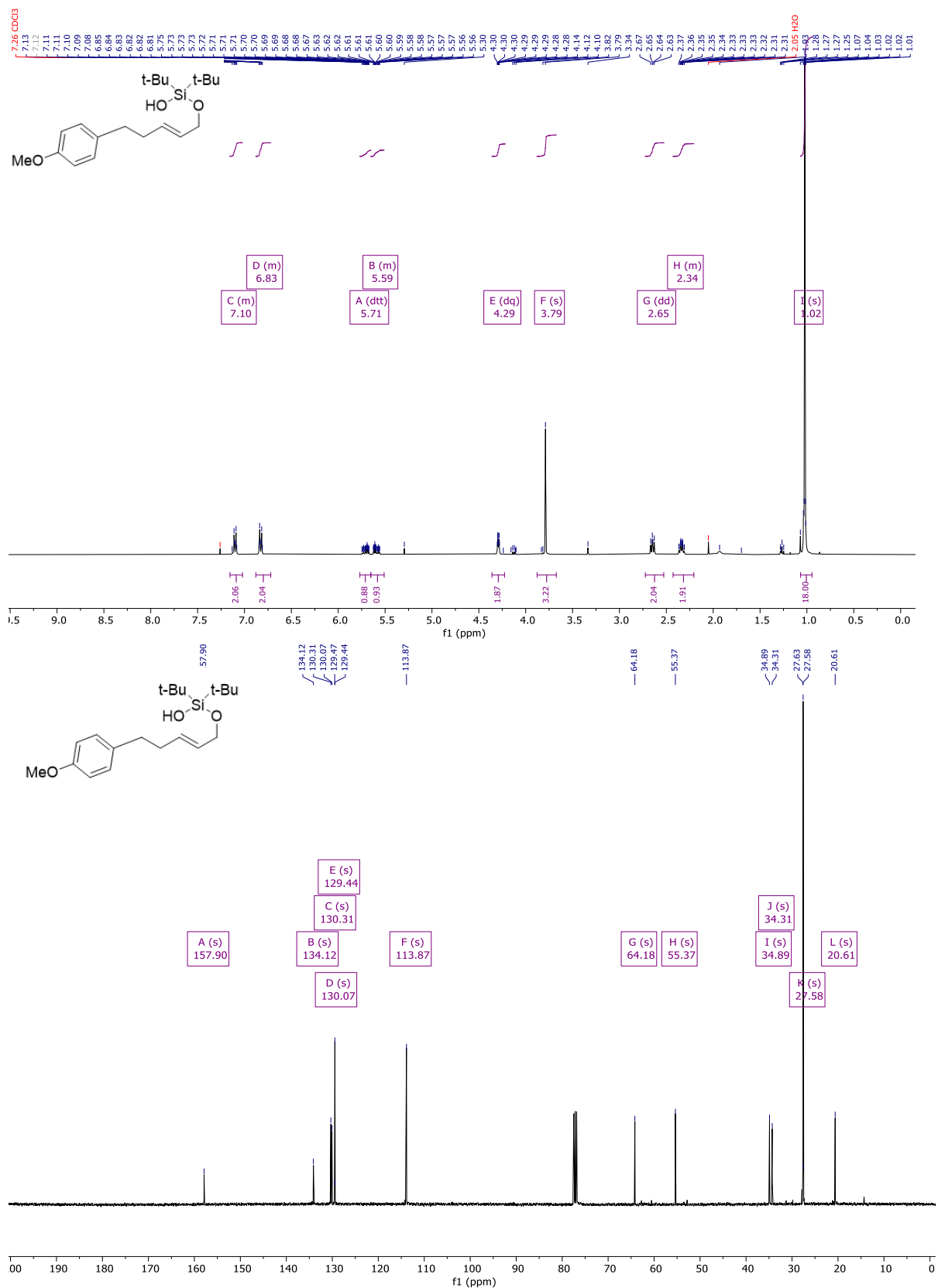
Compound 3 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz)



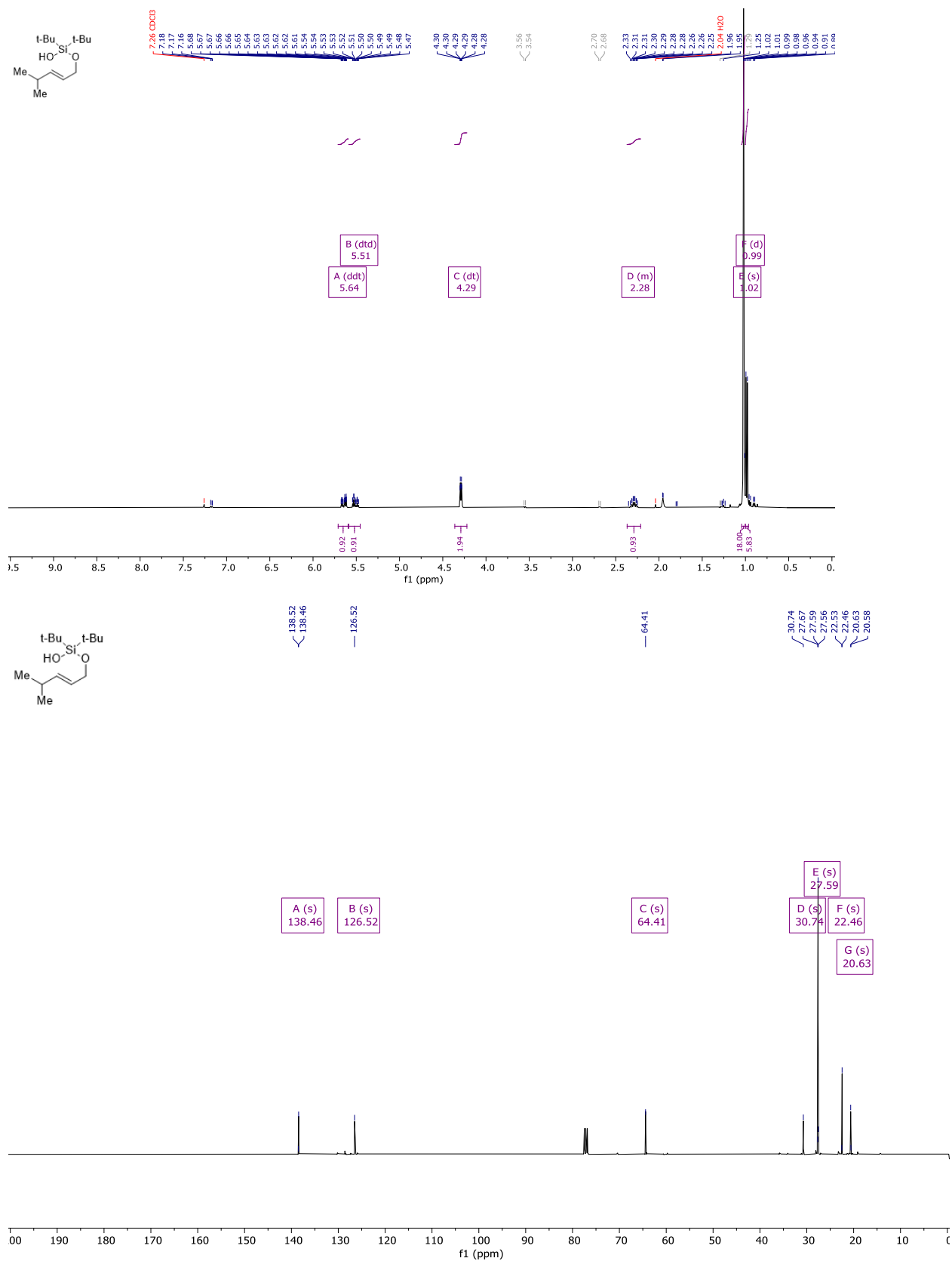
Compound 4 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



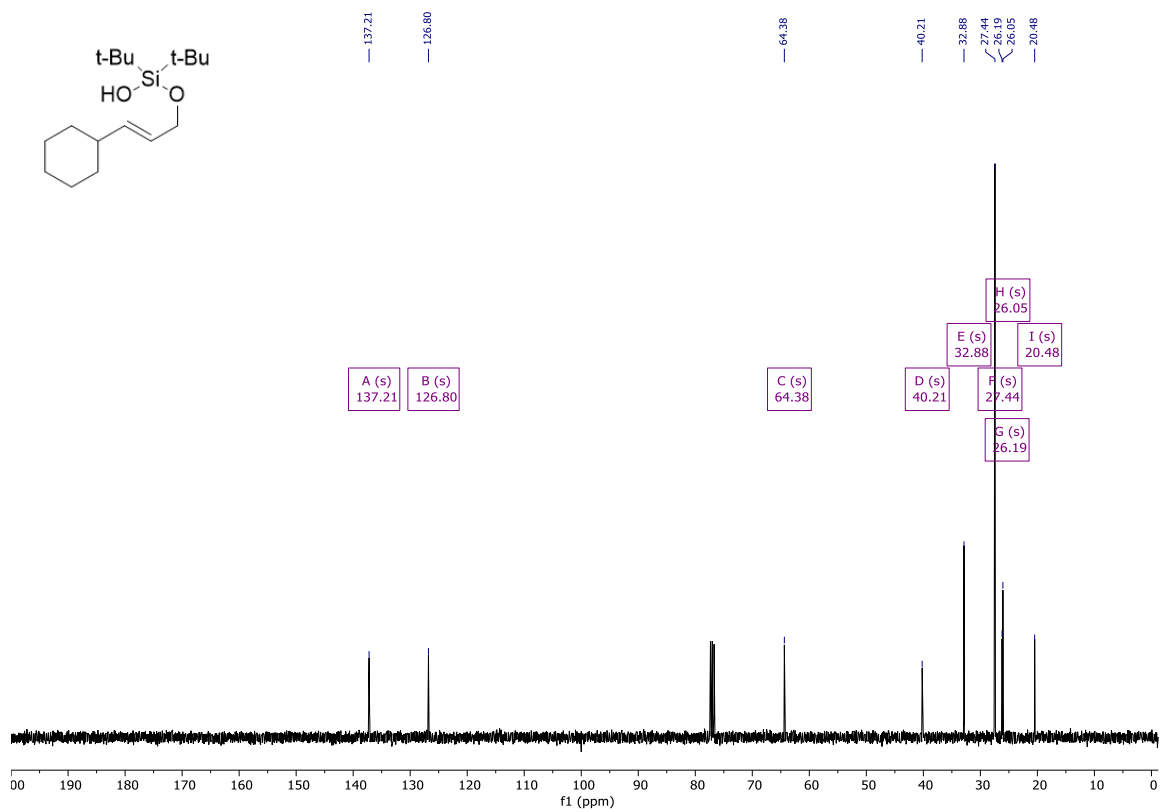
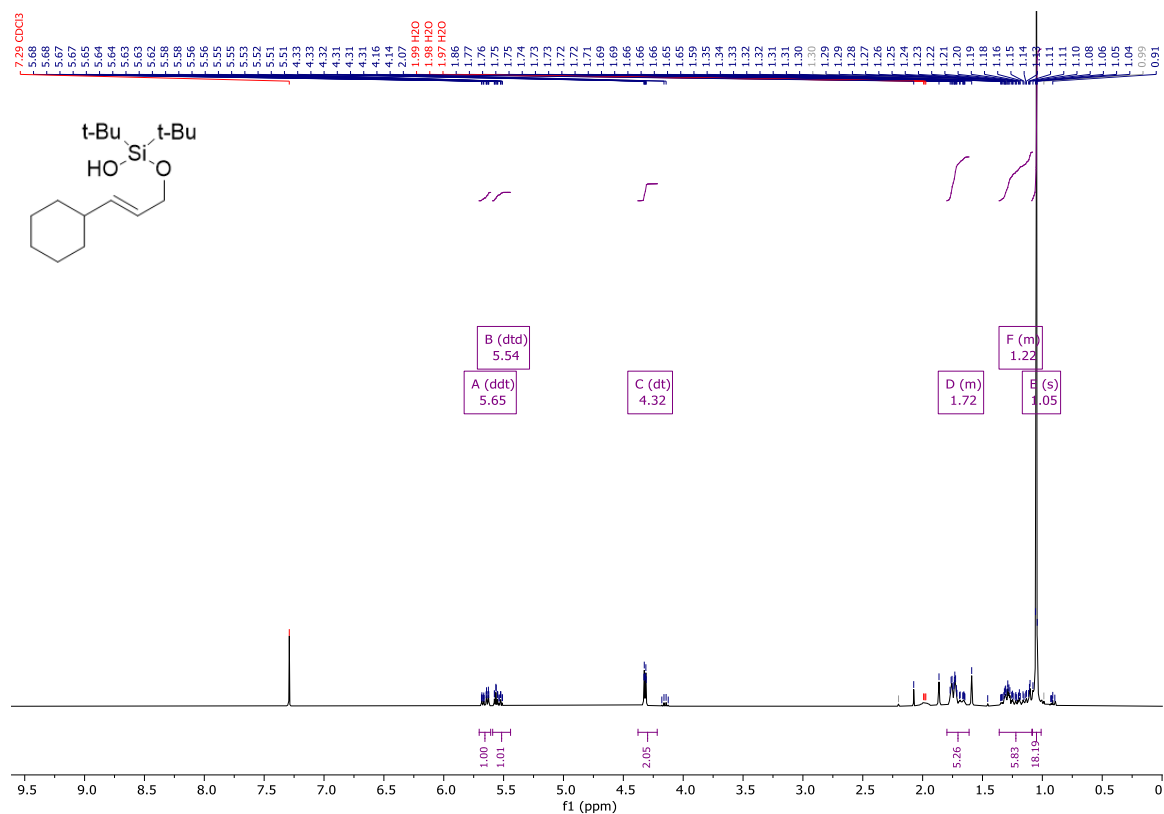
Compound 5 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



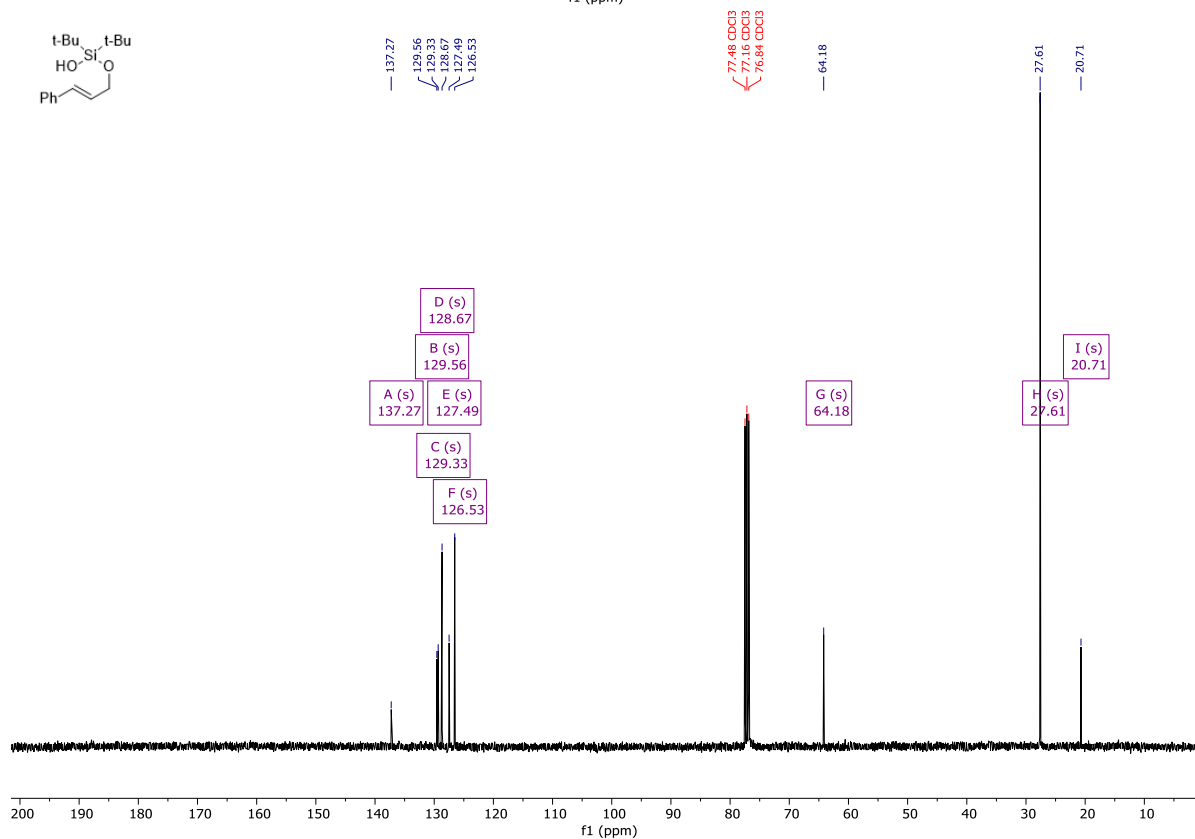
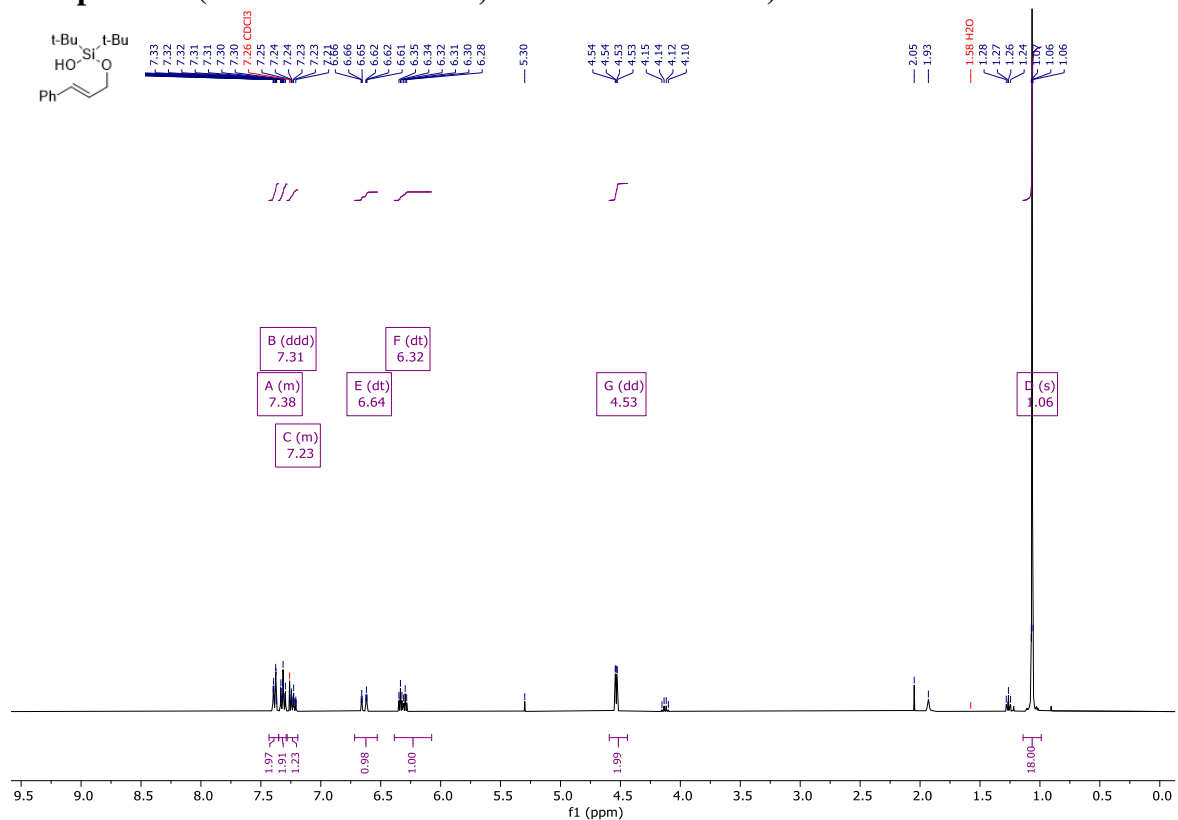
Compound 6 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz)



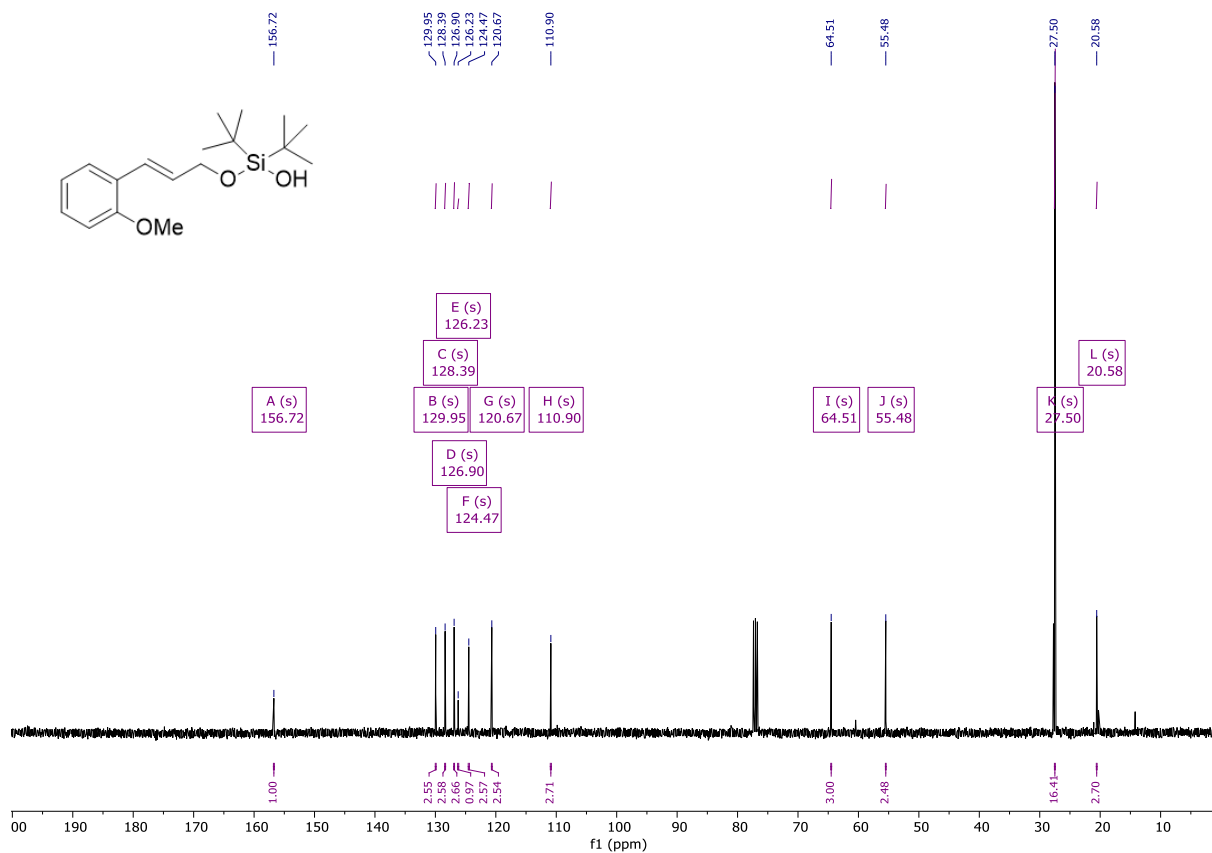
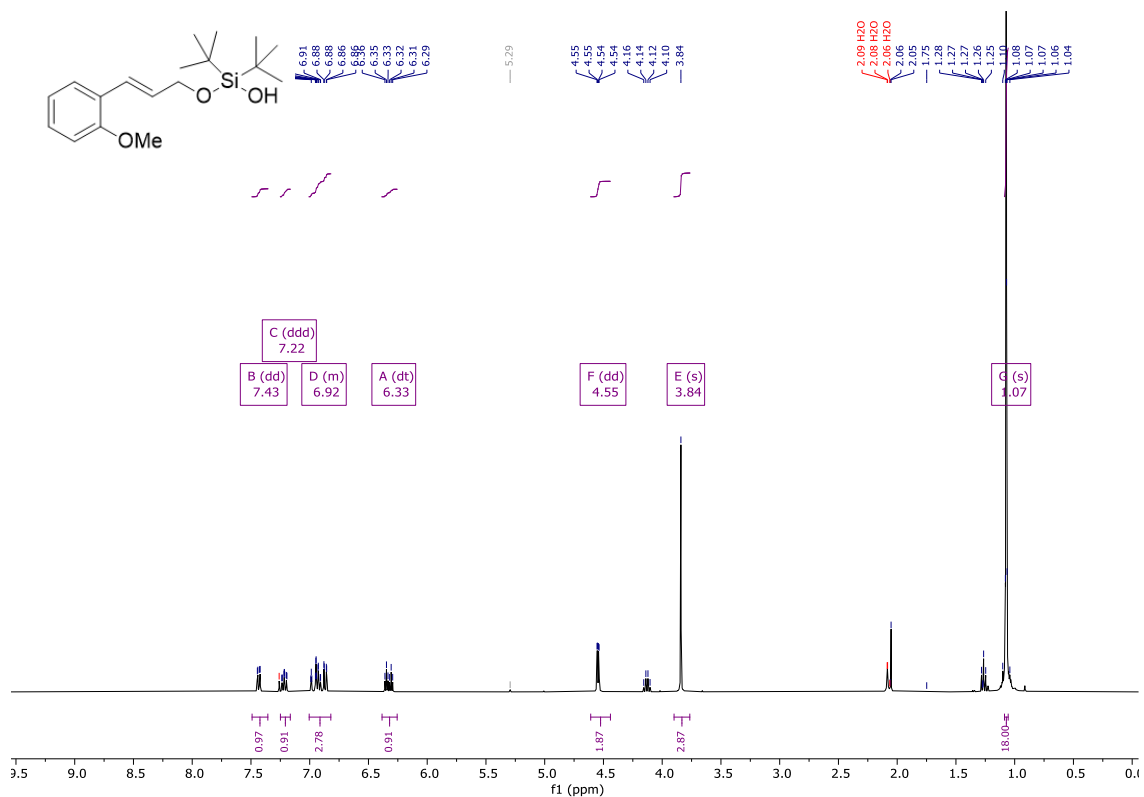
Compound 7 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz)



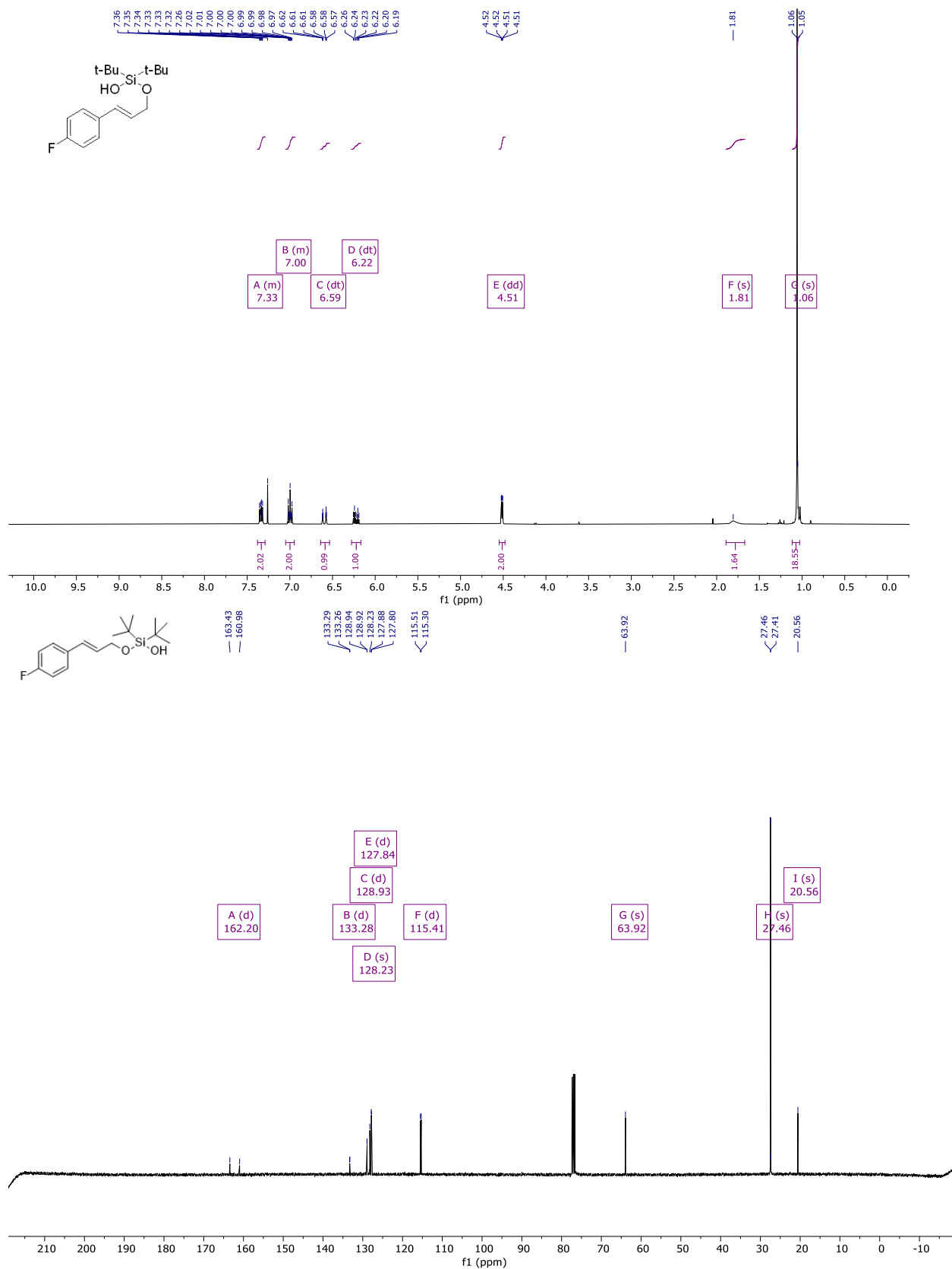
Compound 8 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



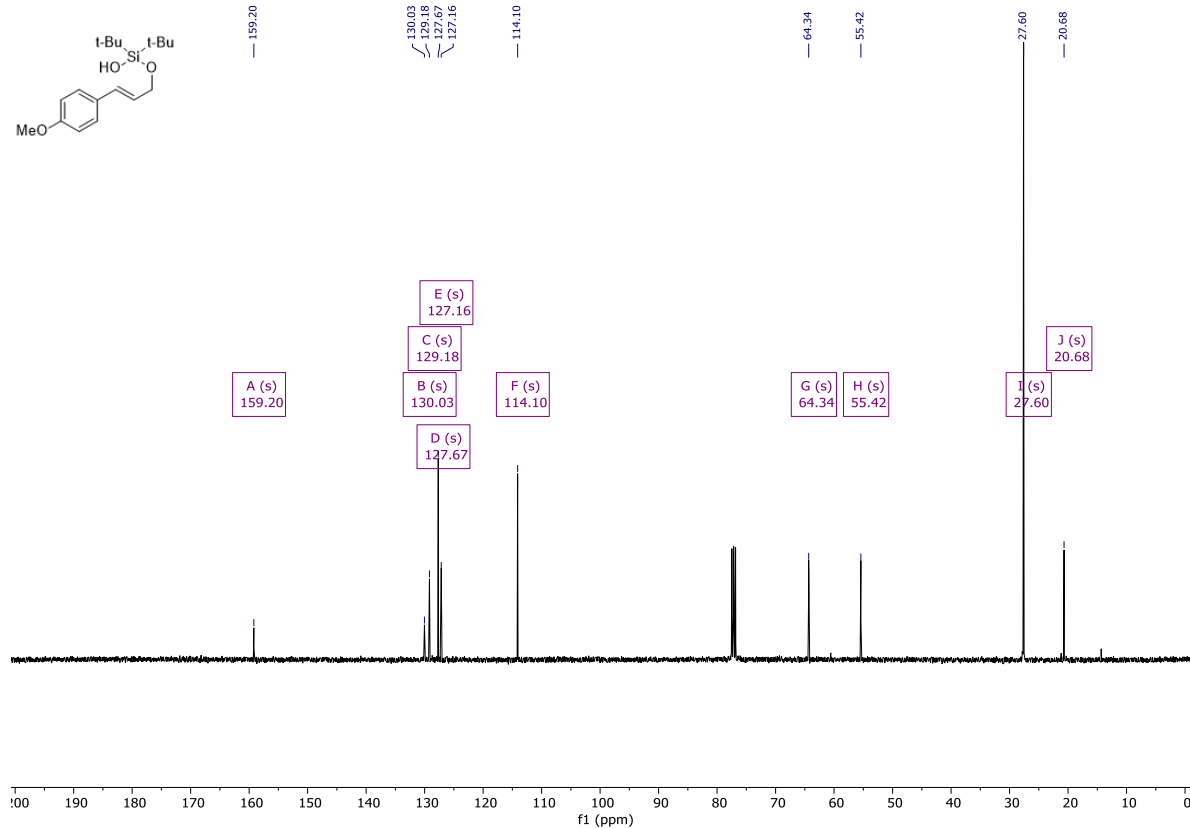
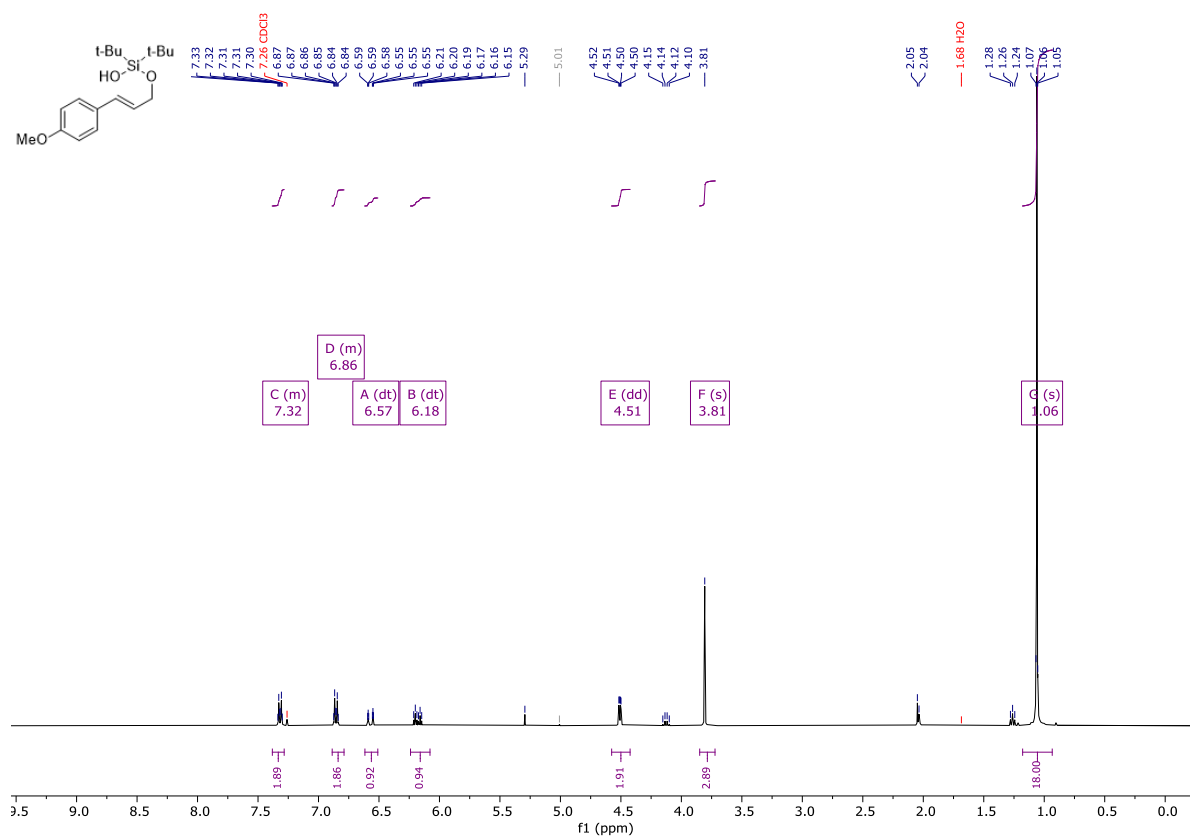
Compound 9 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz)



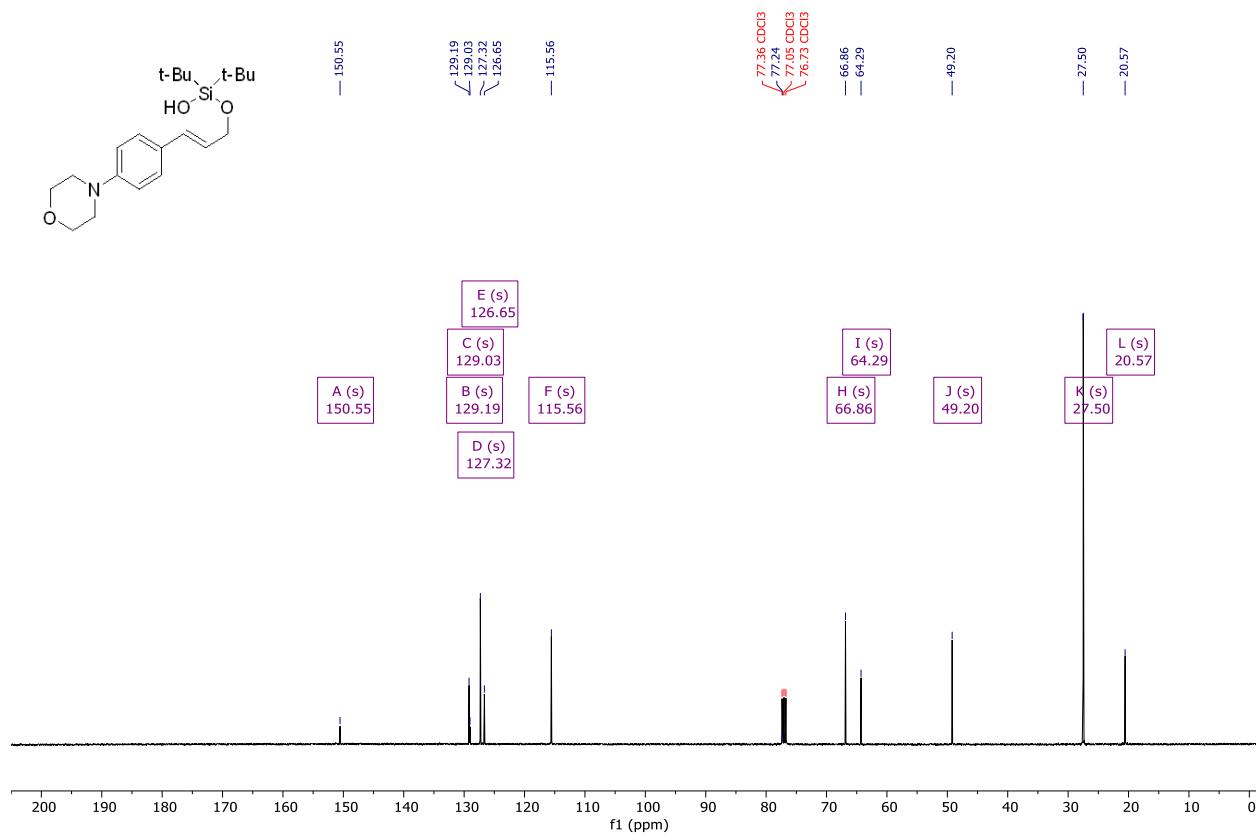
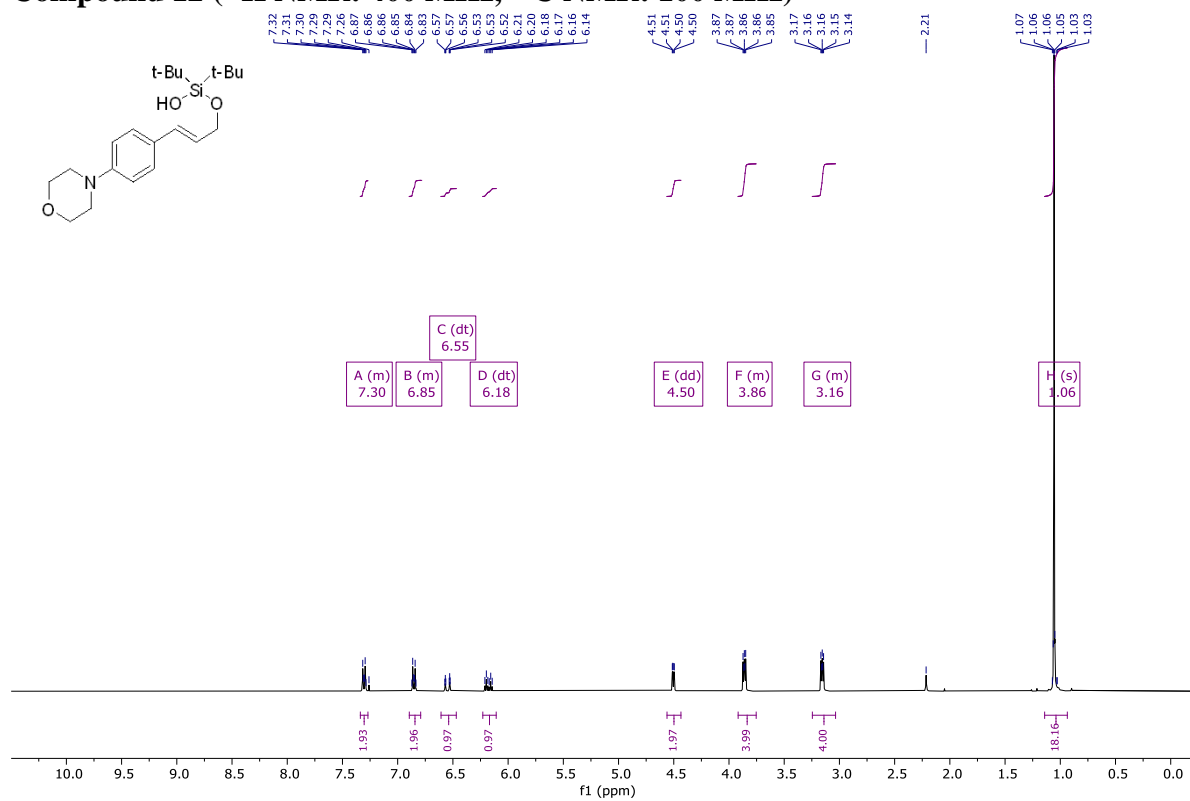
Compound 10 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



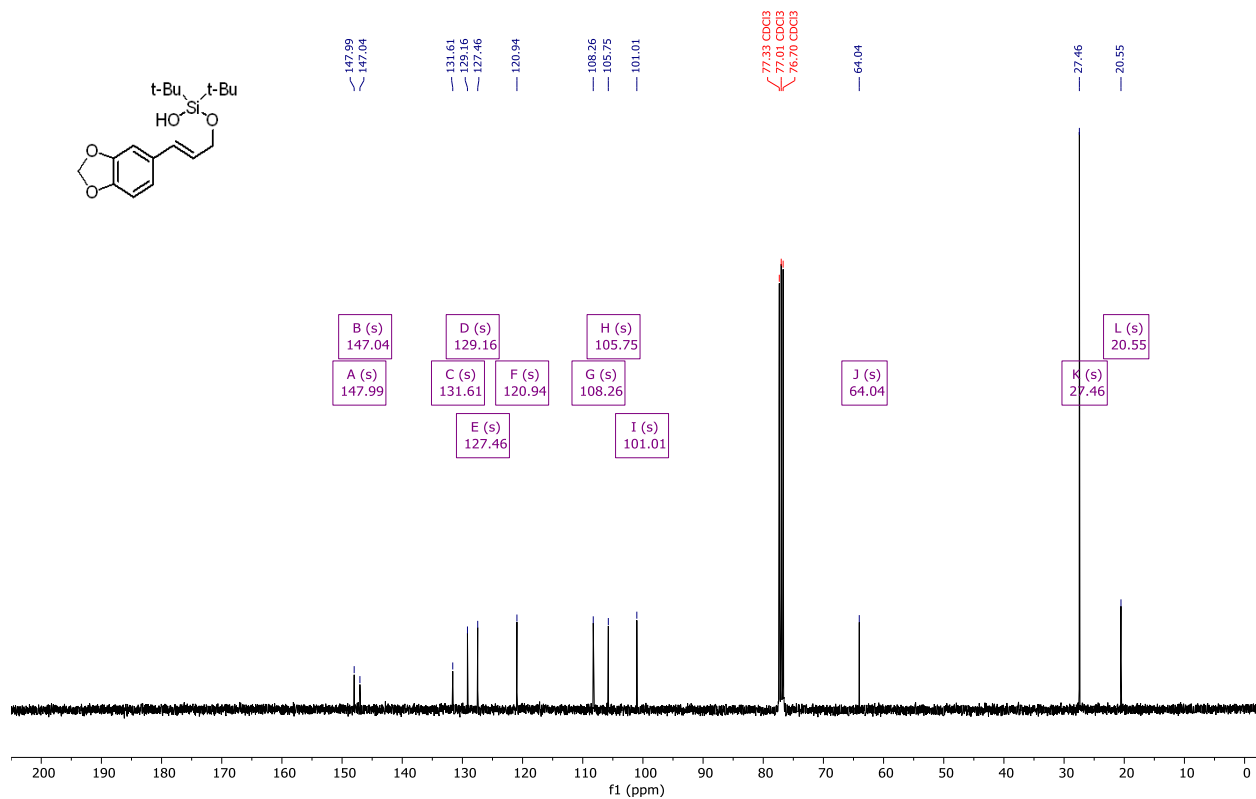
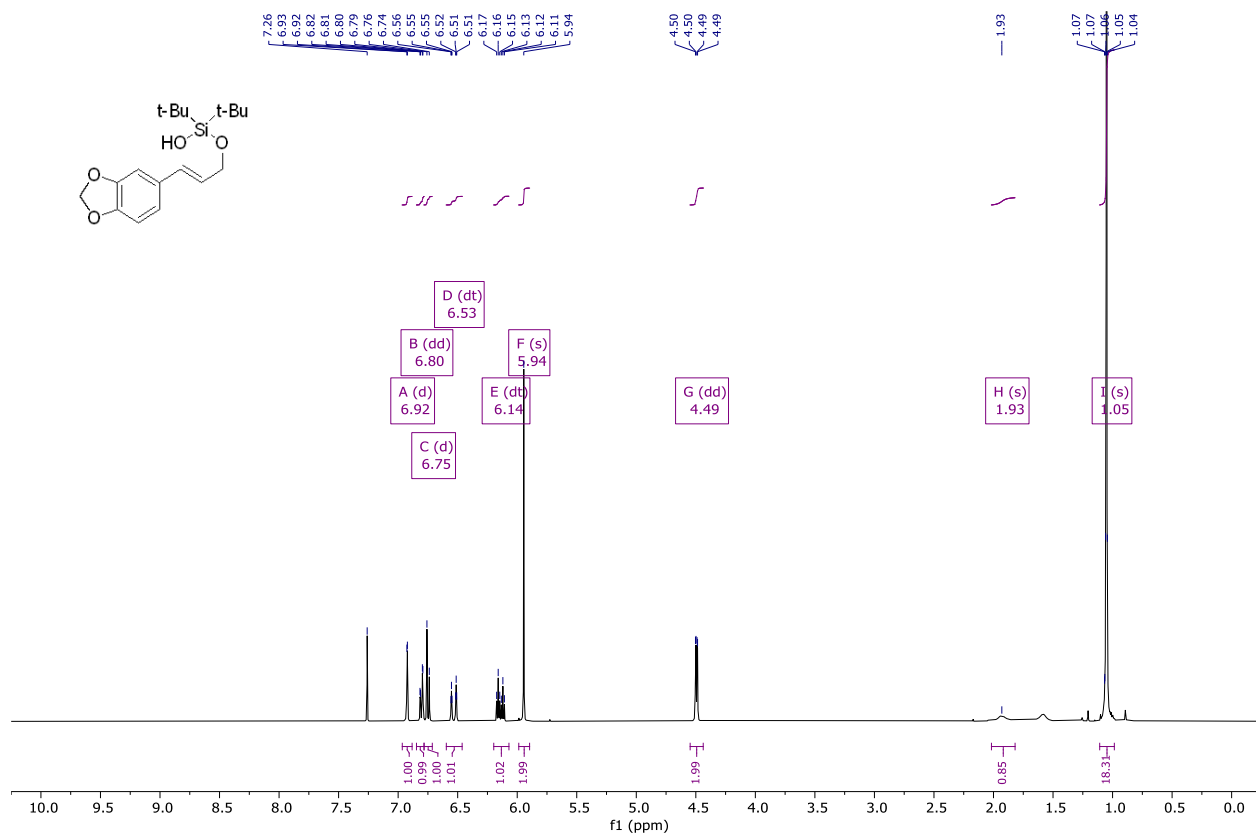
Compound 11 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



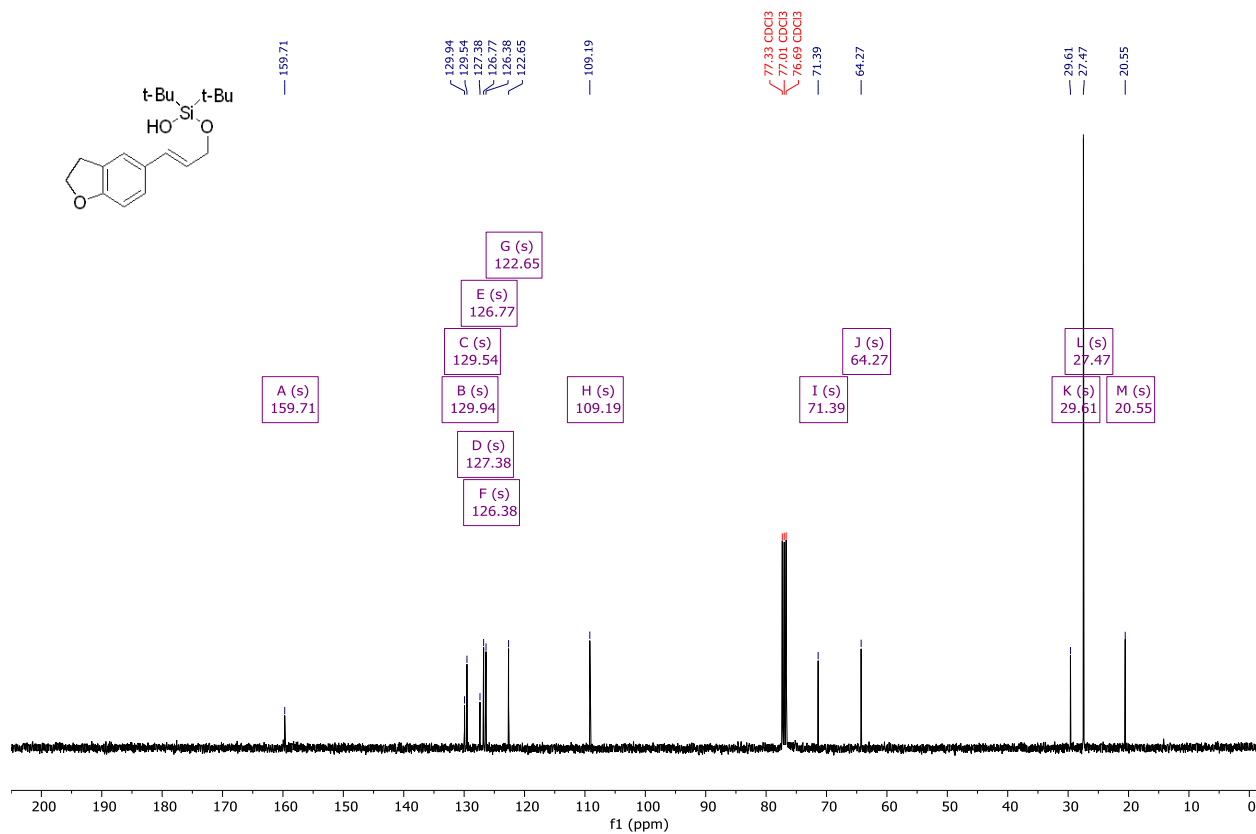
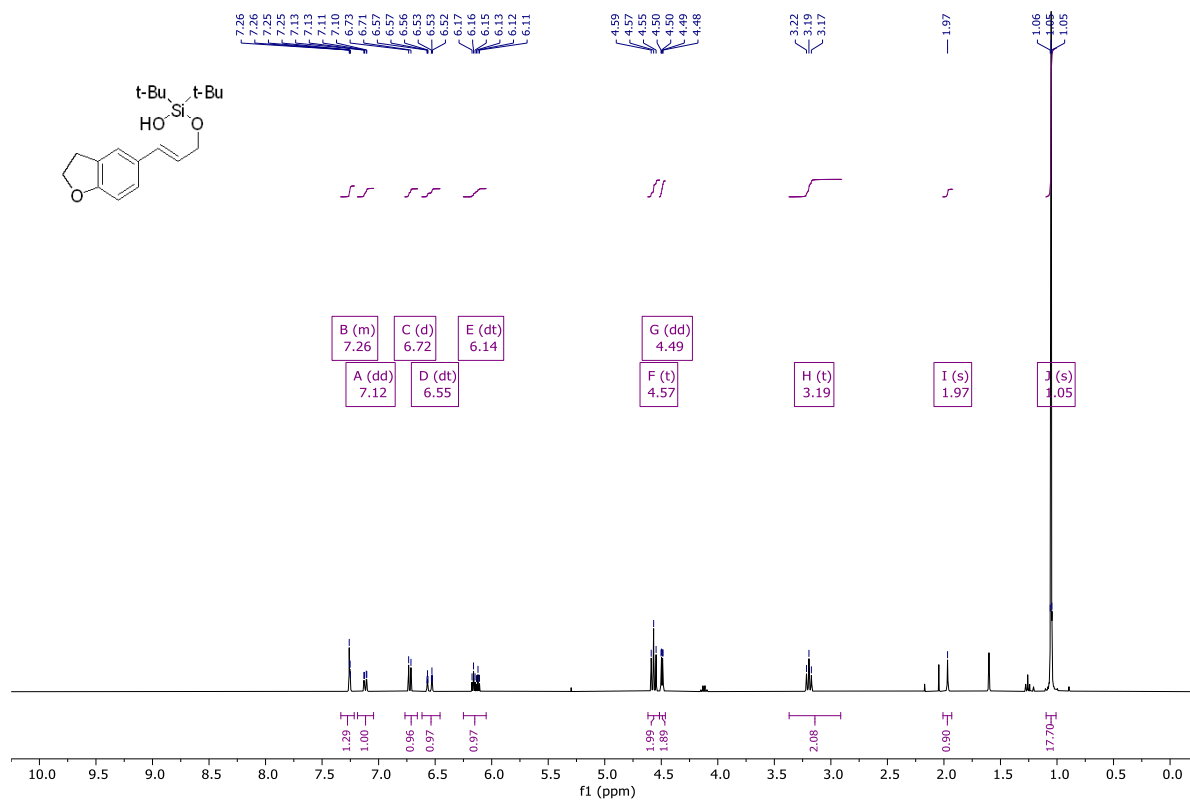
Compound 12 ($^1\text{H NMR}$: 400 MHz, $^{13}\text{C NMR}$: 100 MHz)



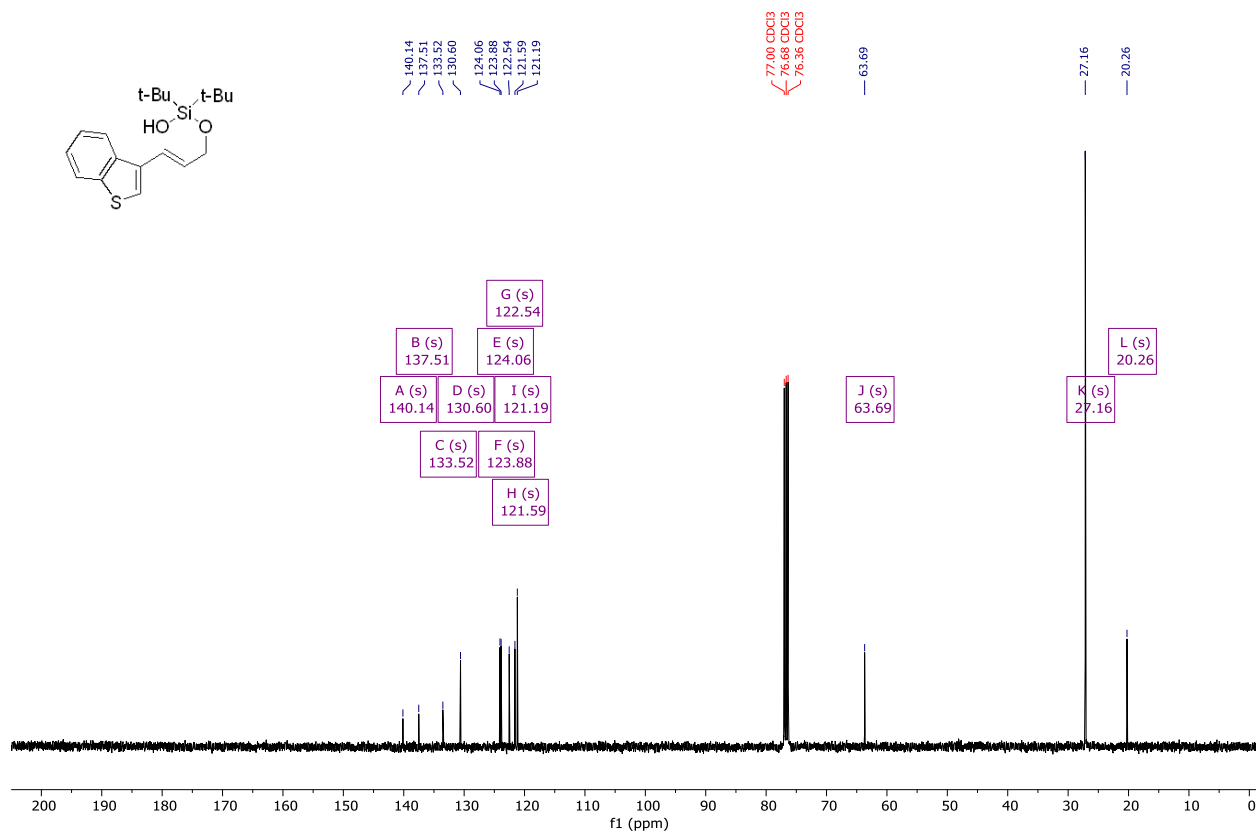
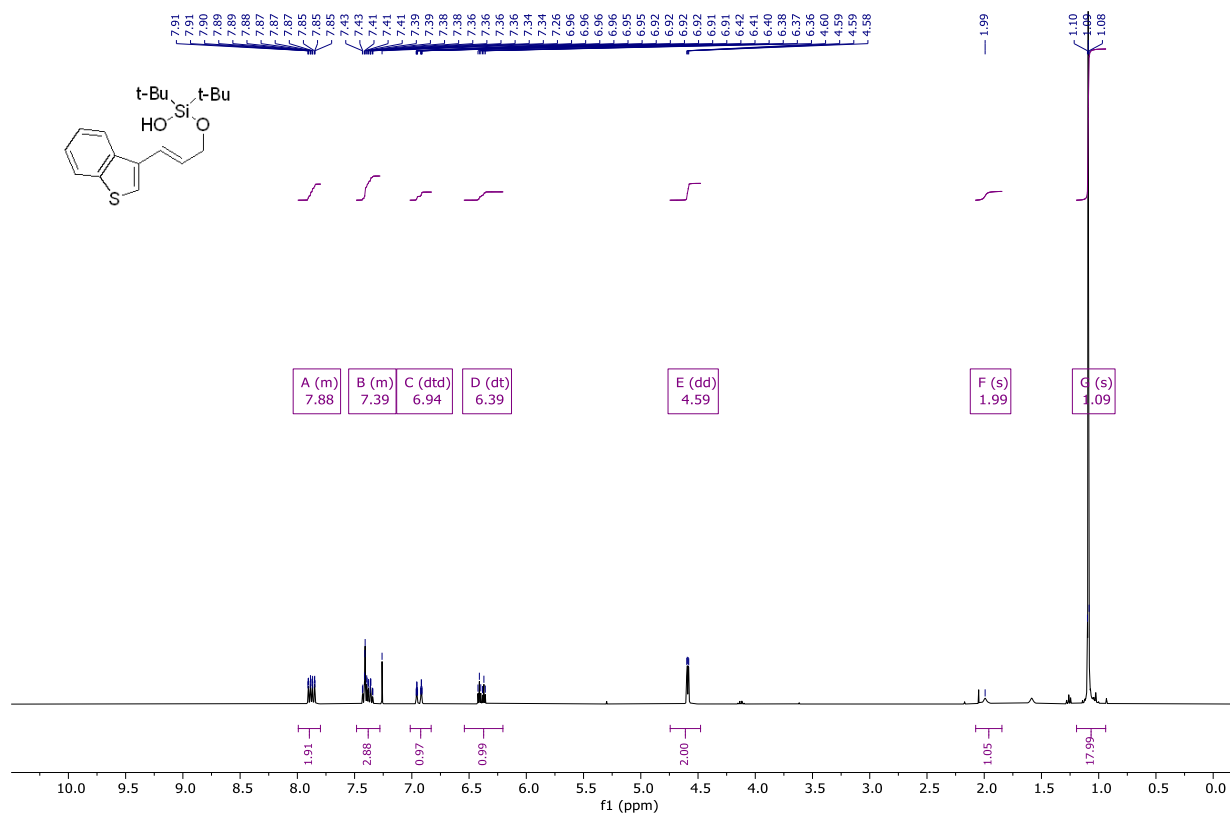
Compound 13 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



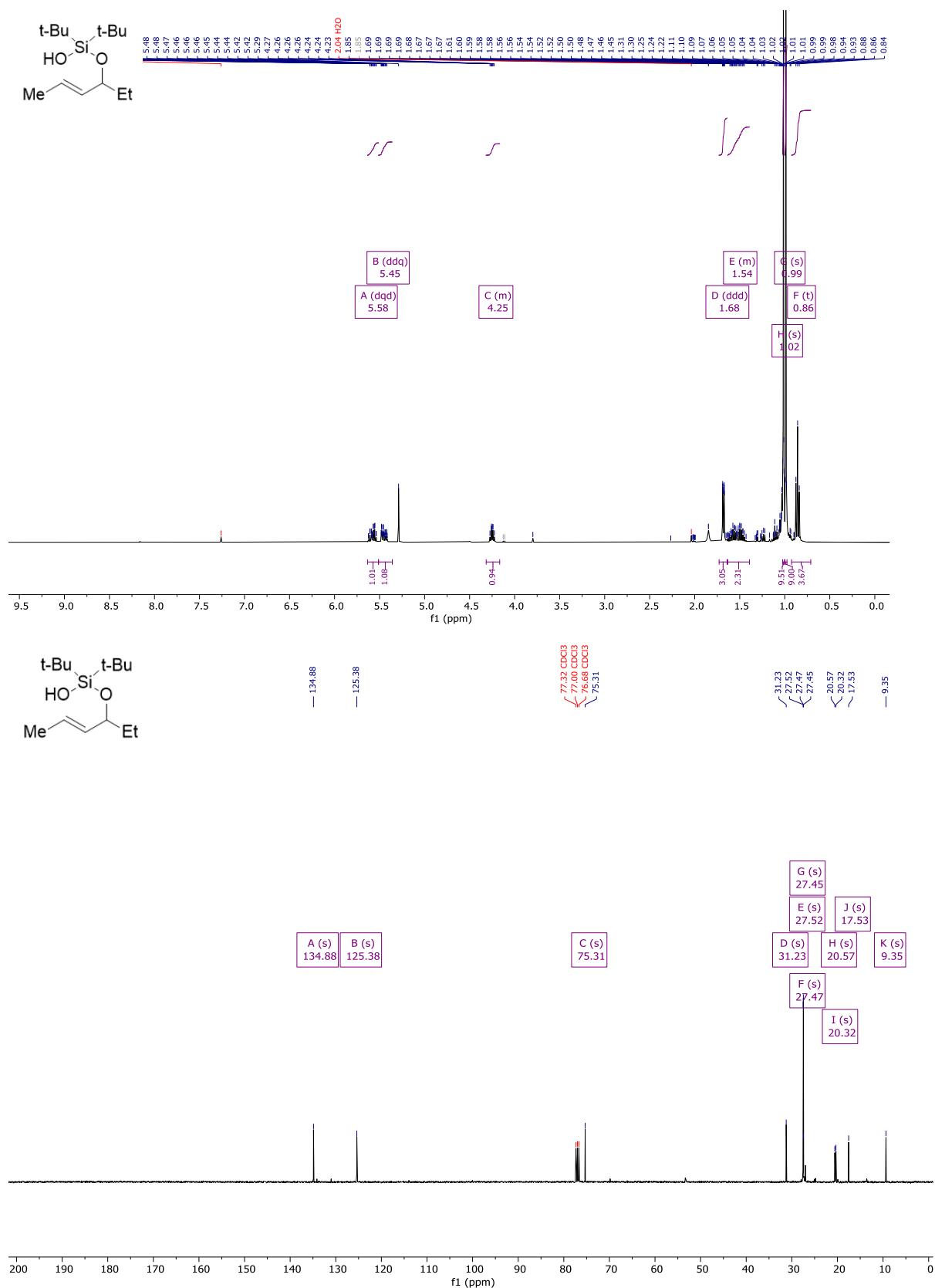
Compound 14 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



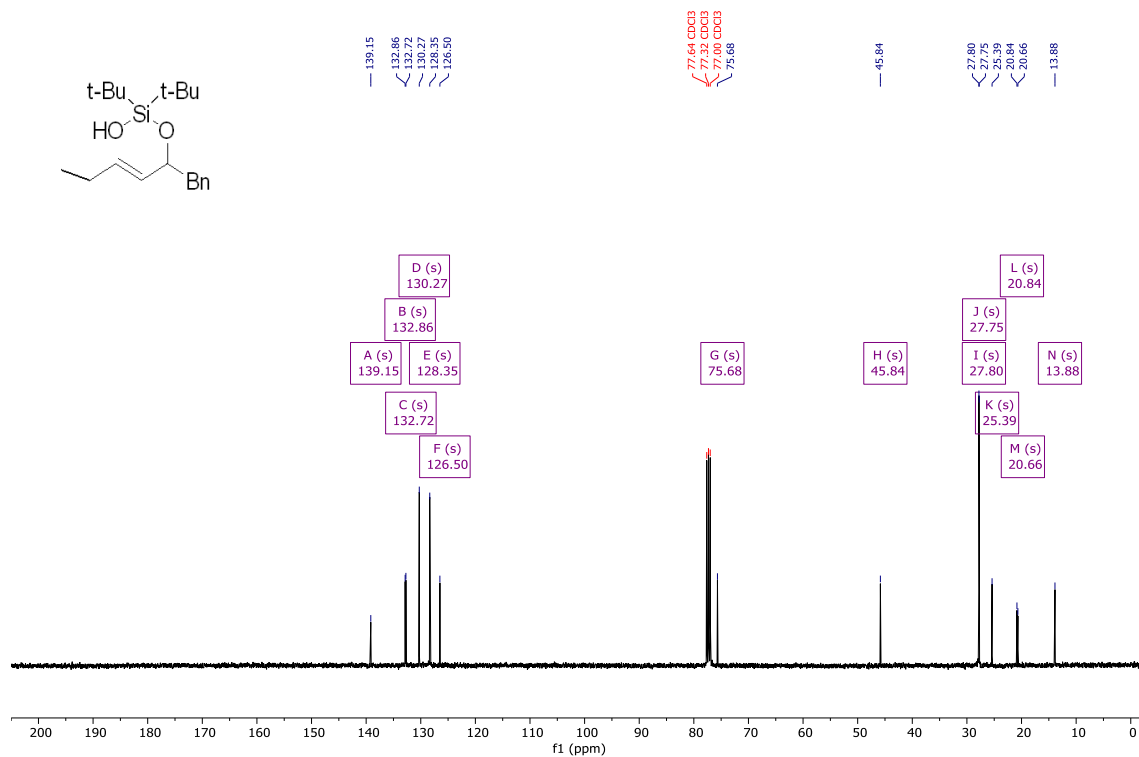
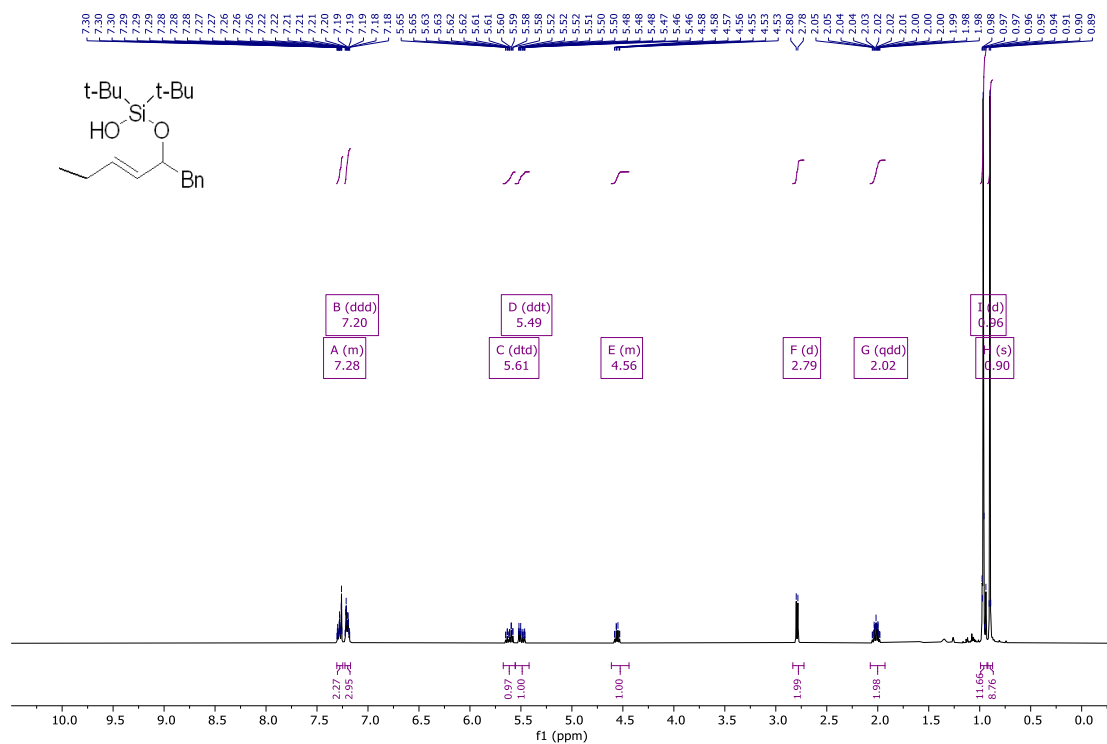
Compound 15 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



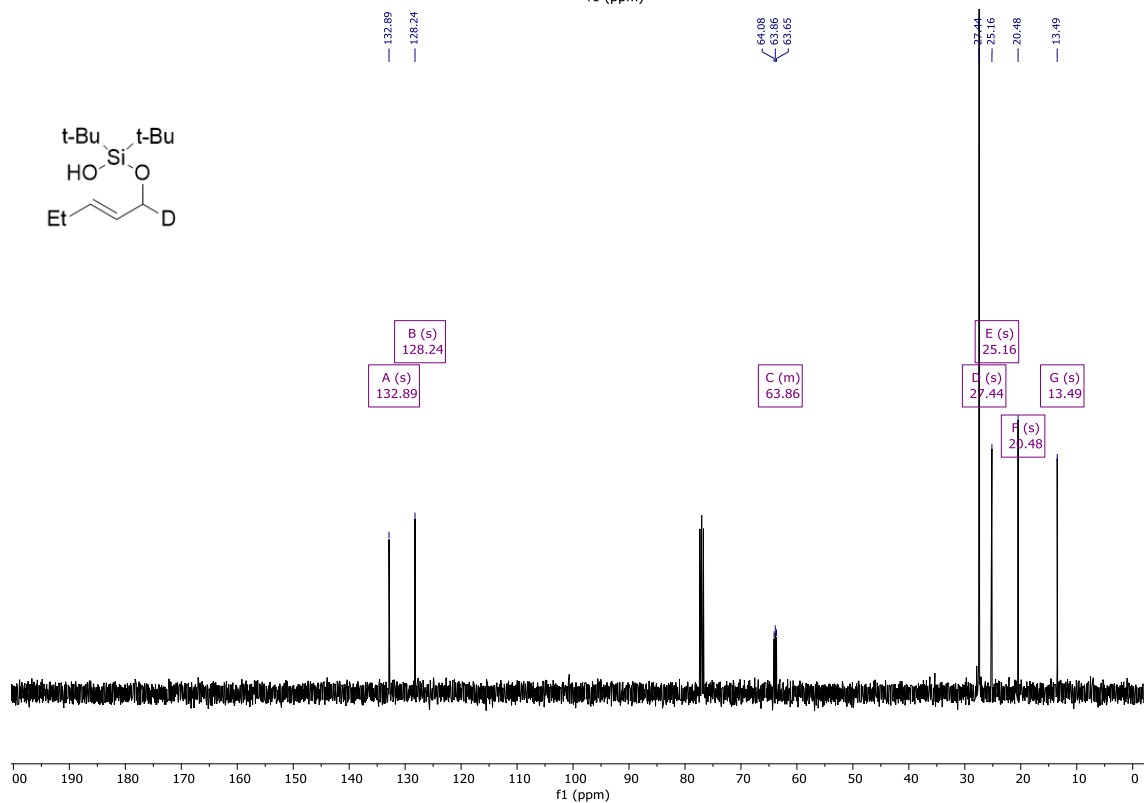
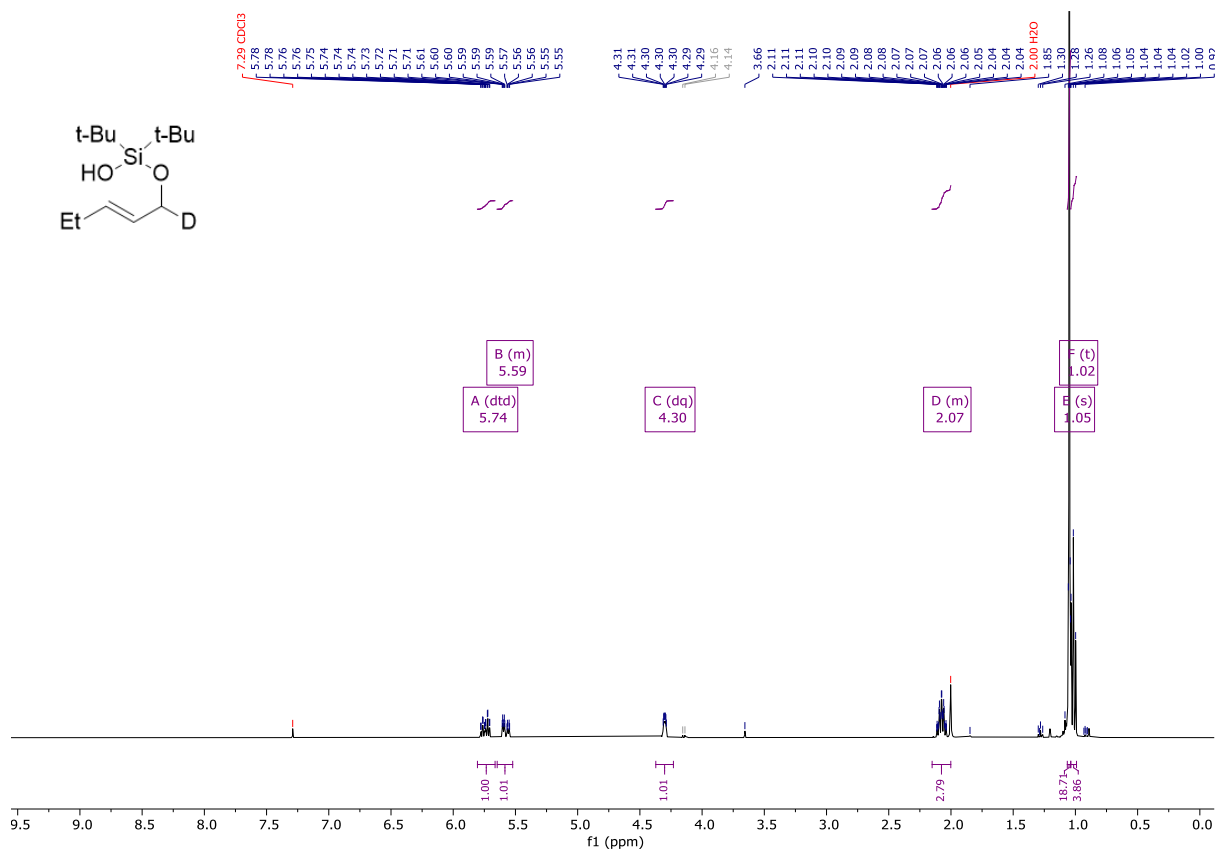
Compound 16 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



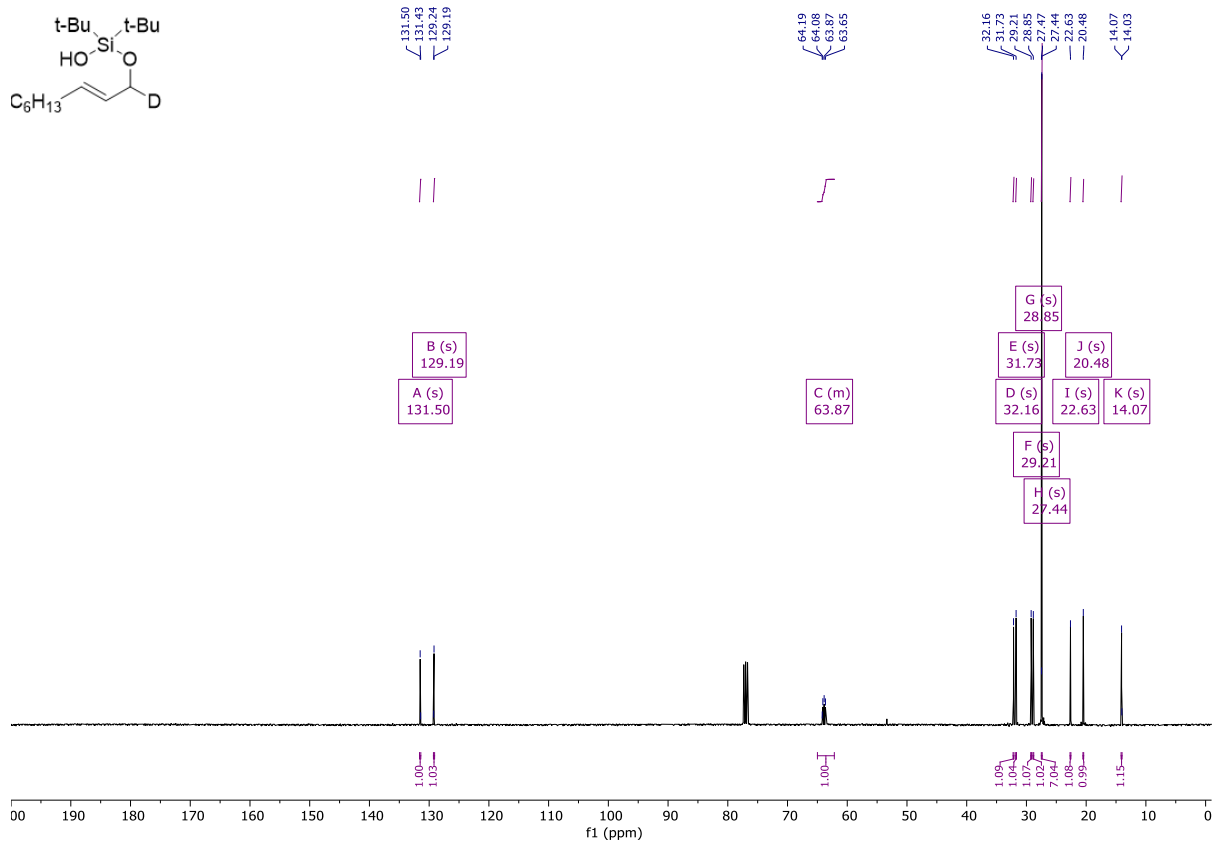
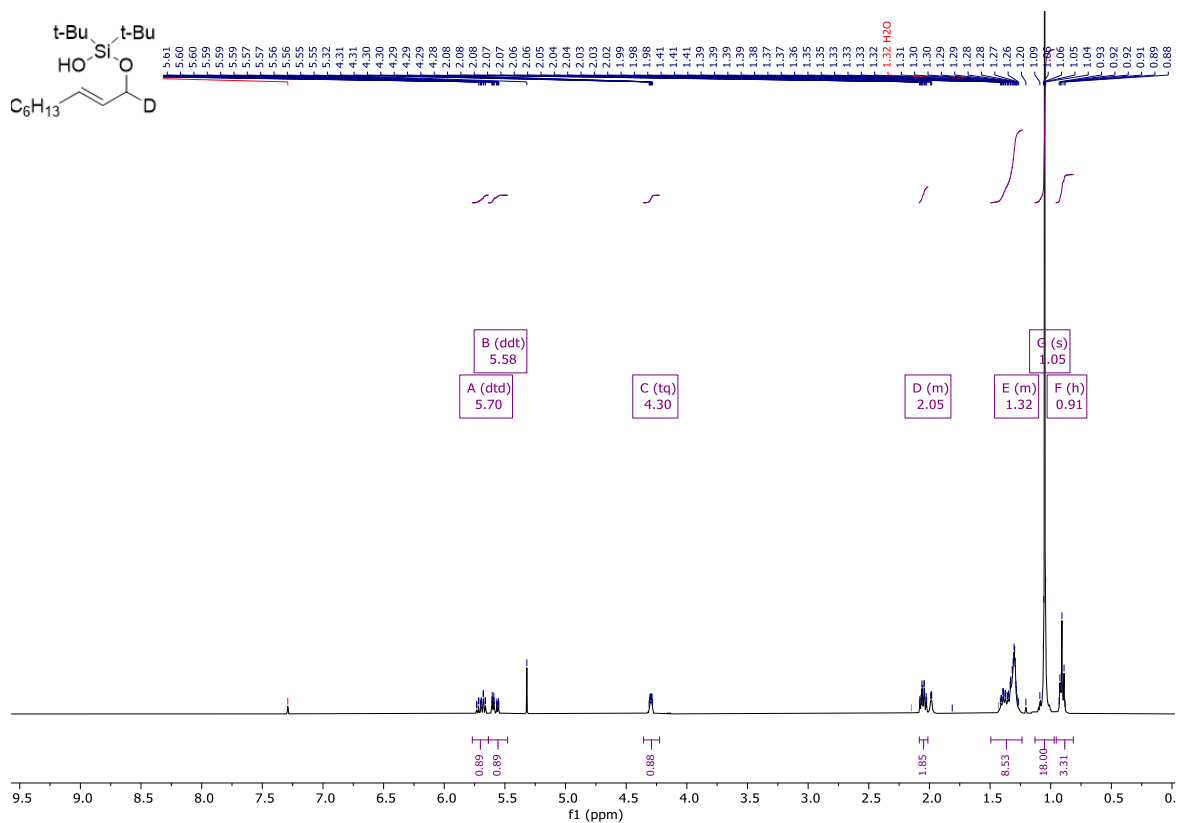
Compound 17 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz)



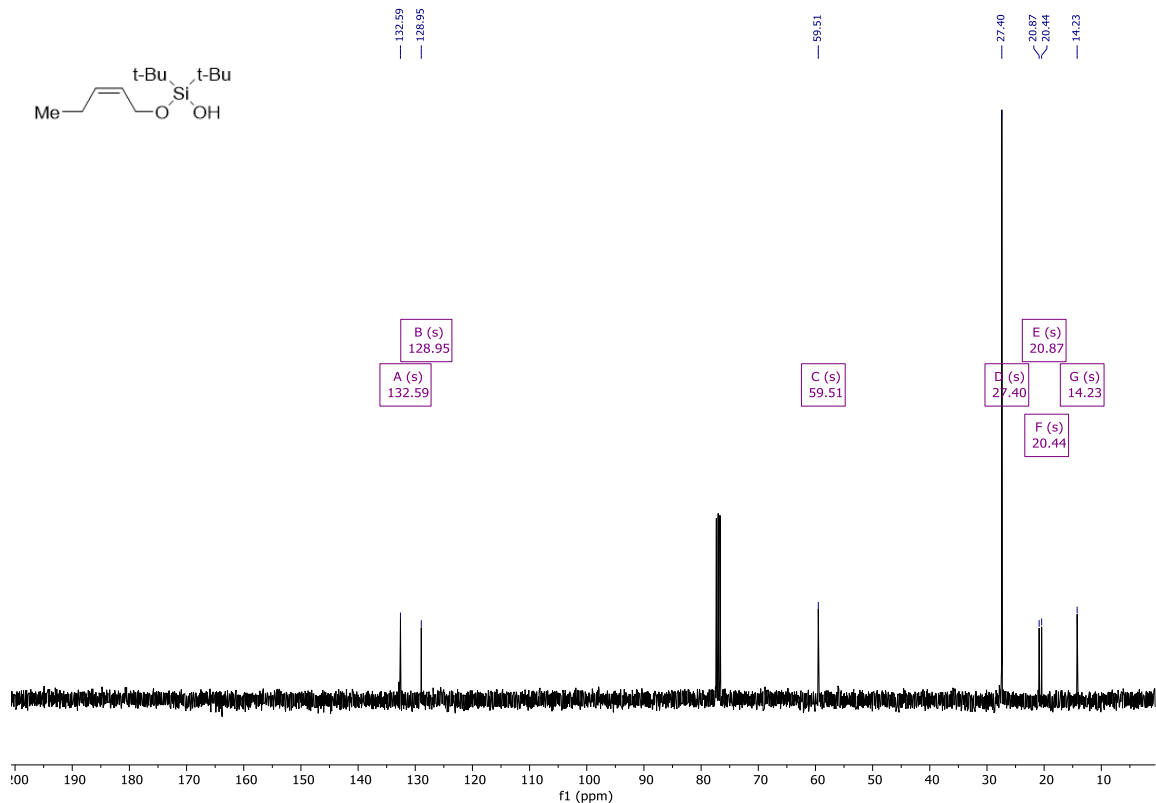
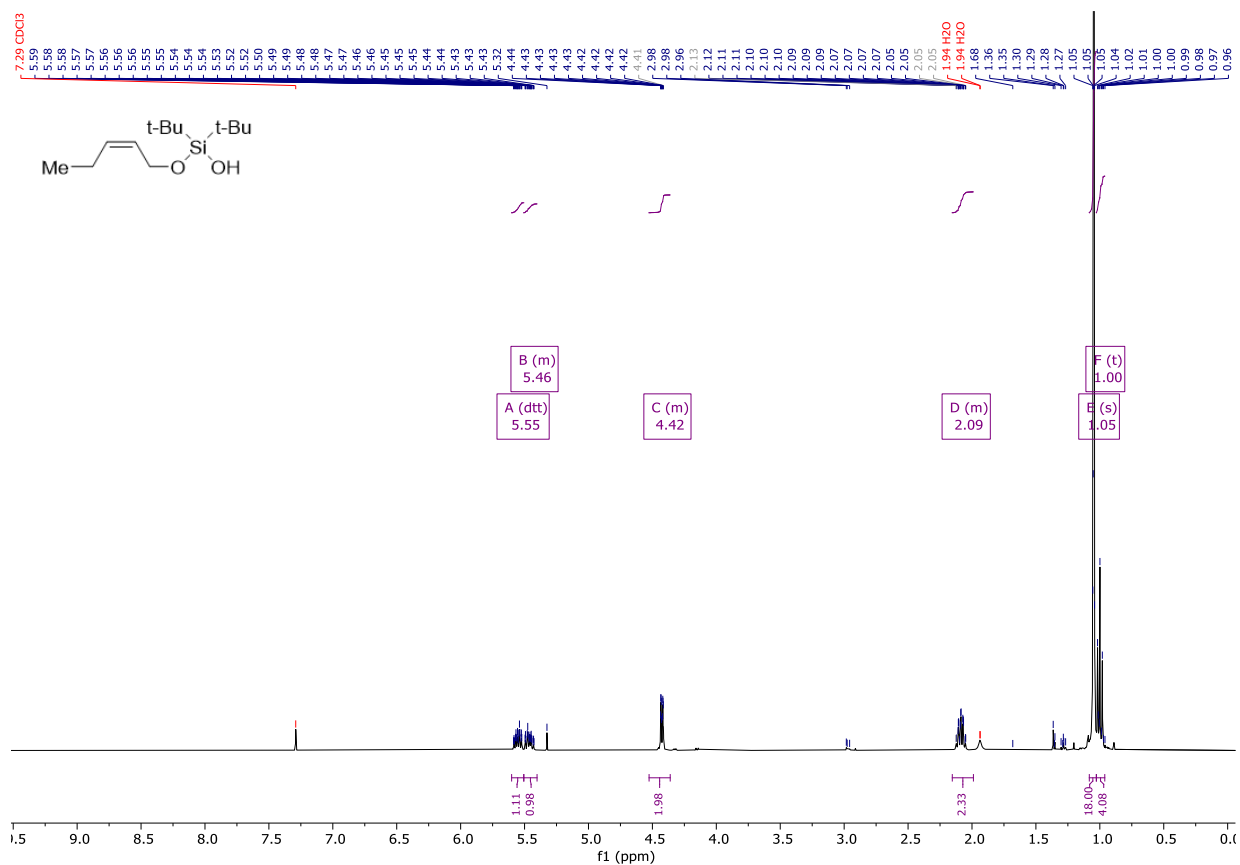
Compound 18 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



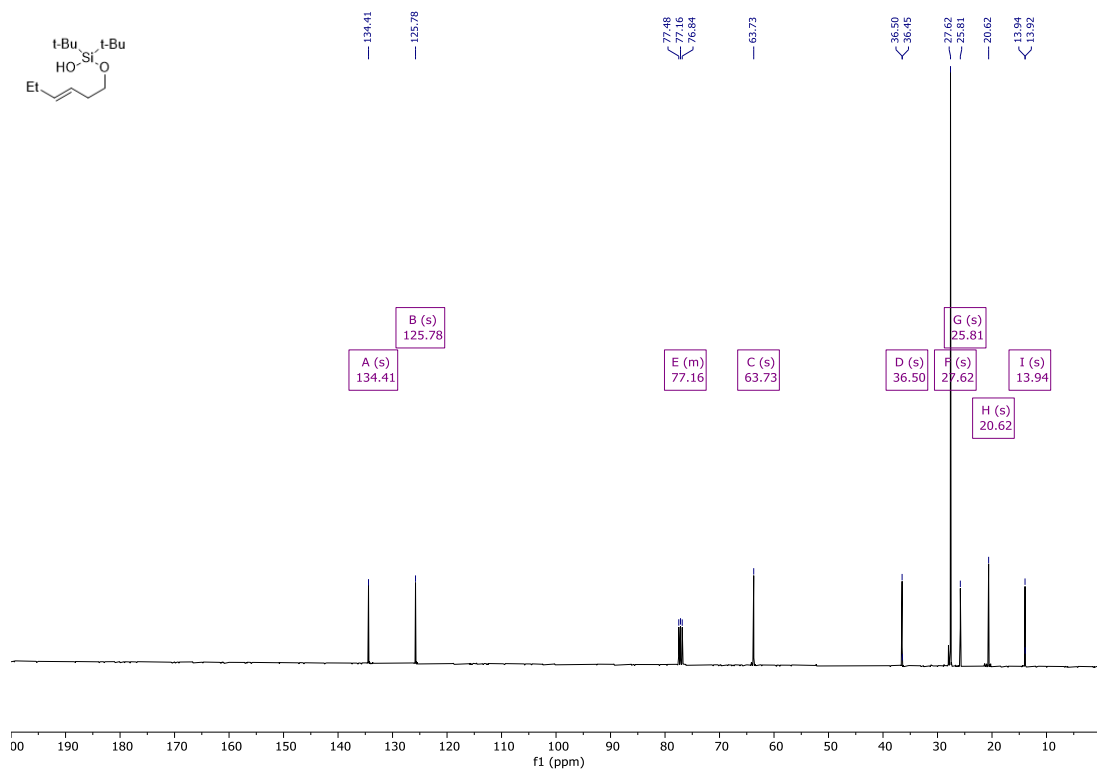
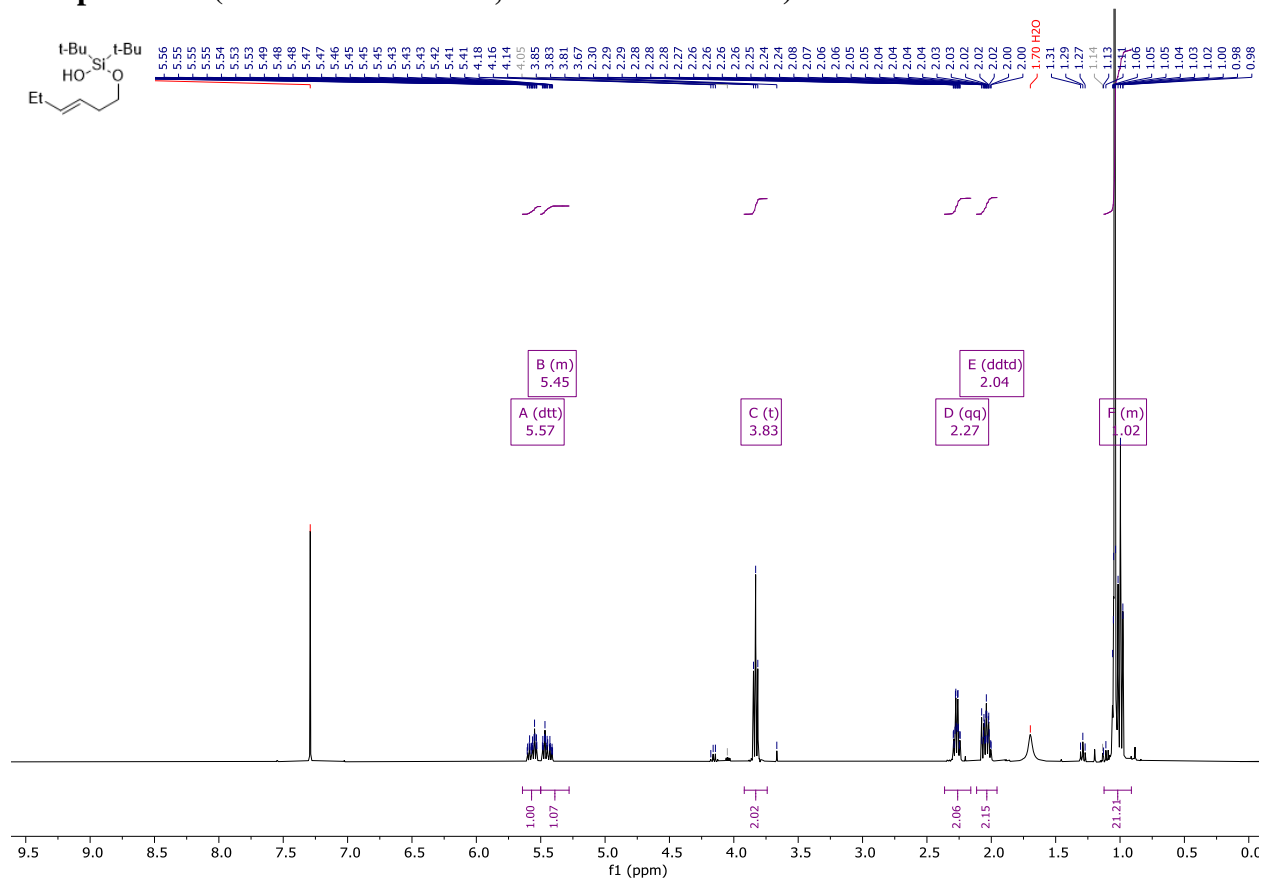
Compound 19 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz)



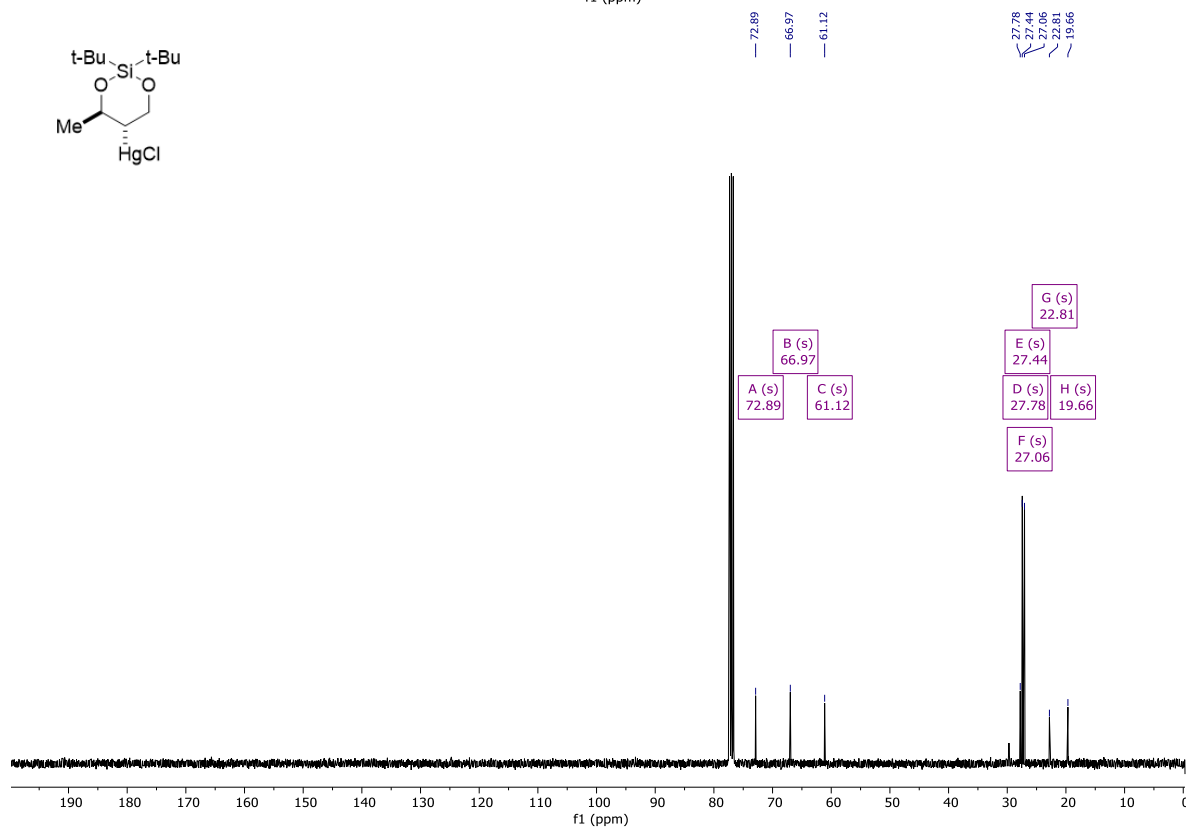
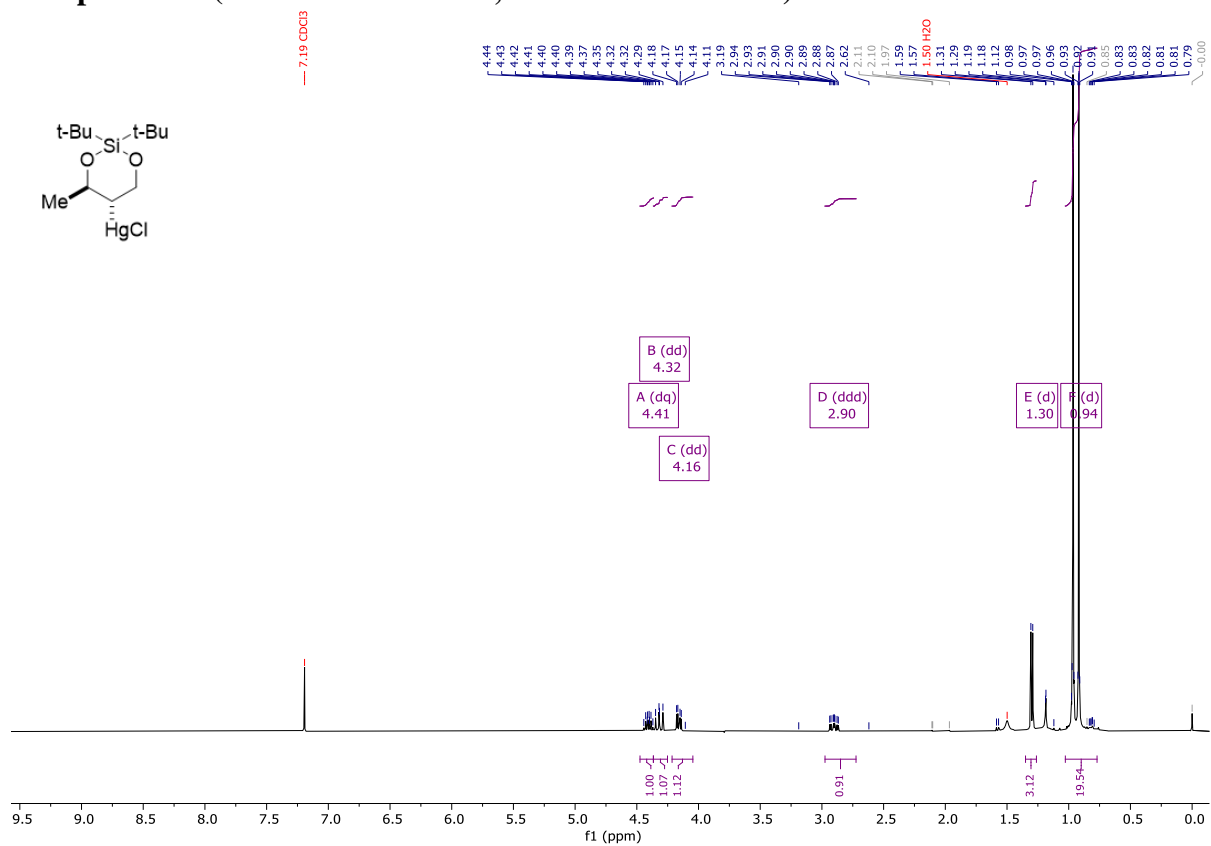
Compound 20 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



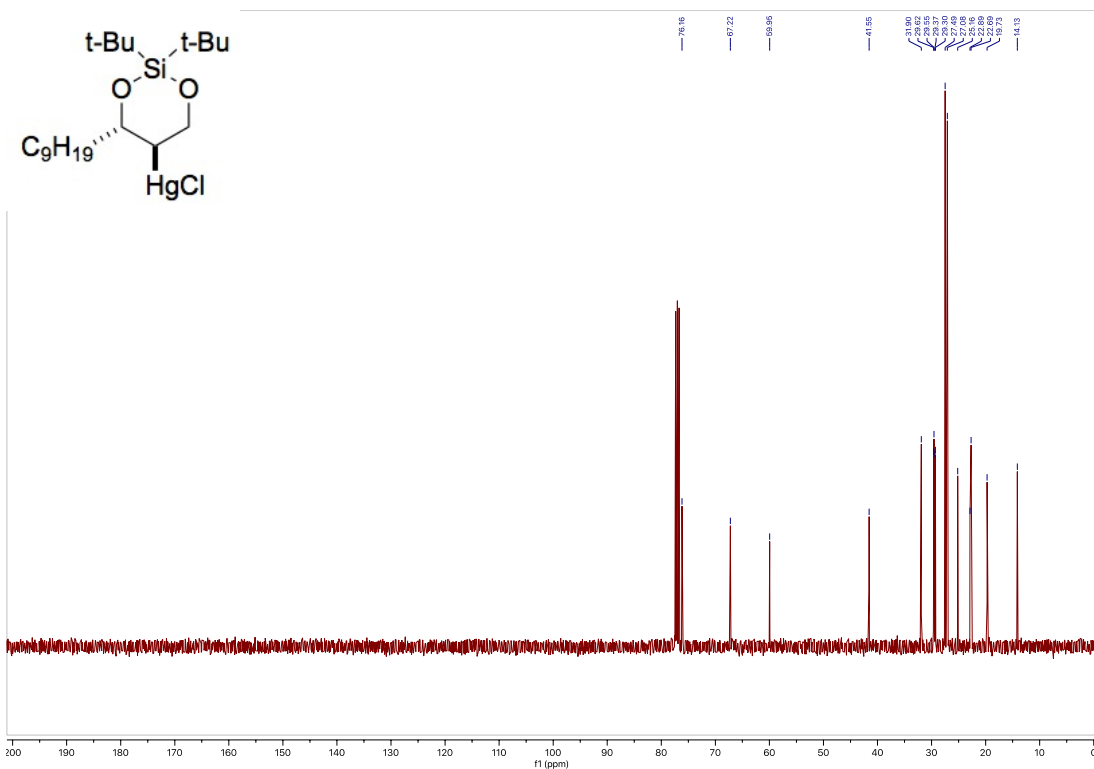
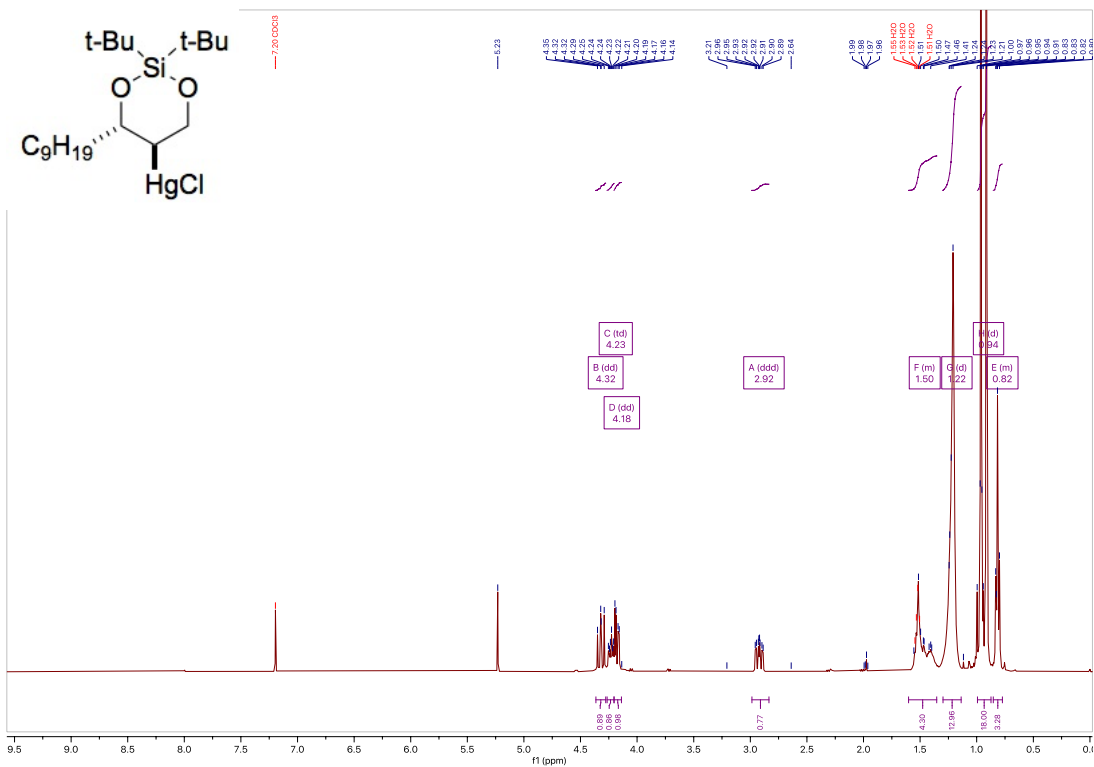
Compound 21 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



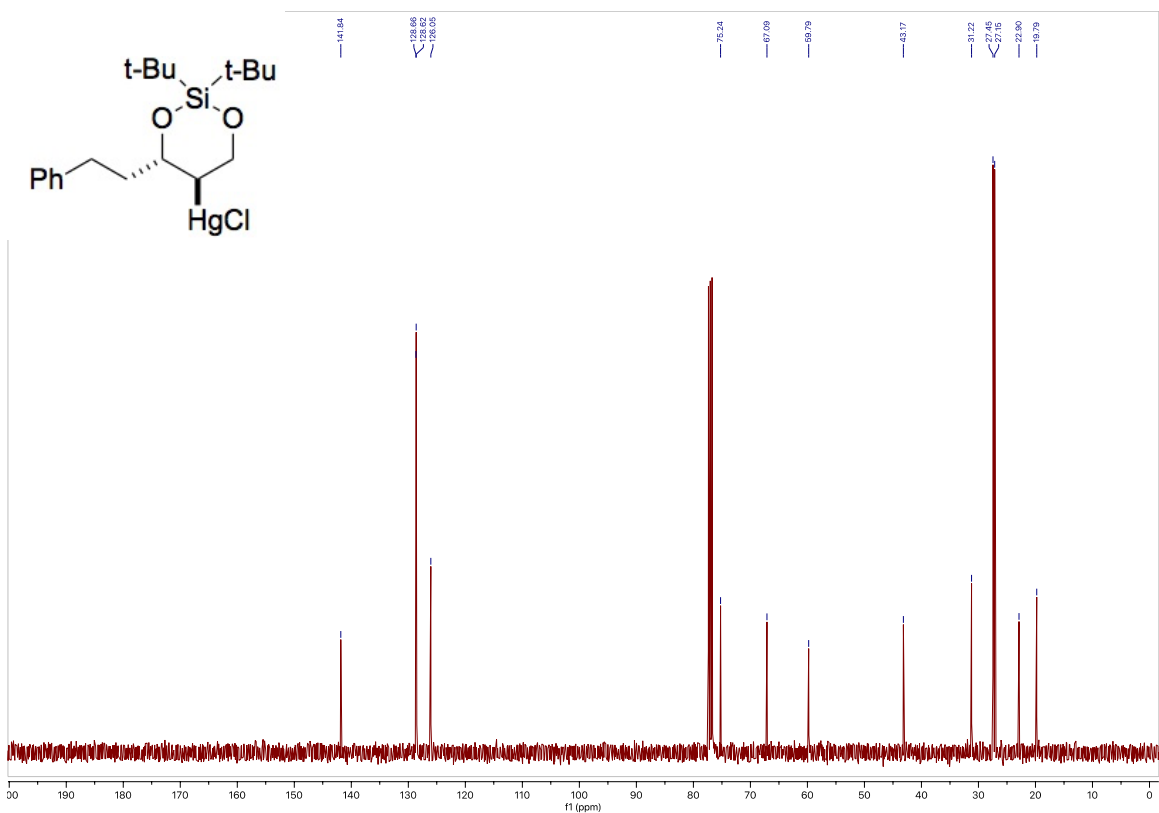
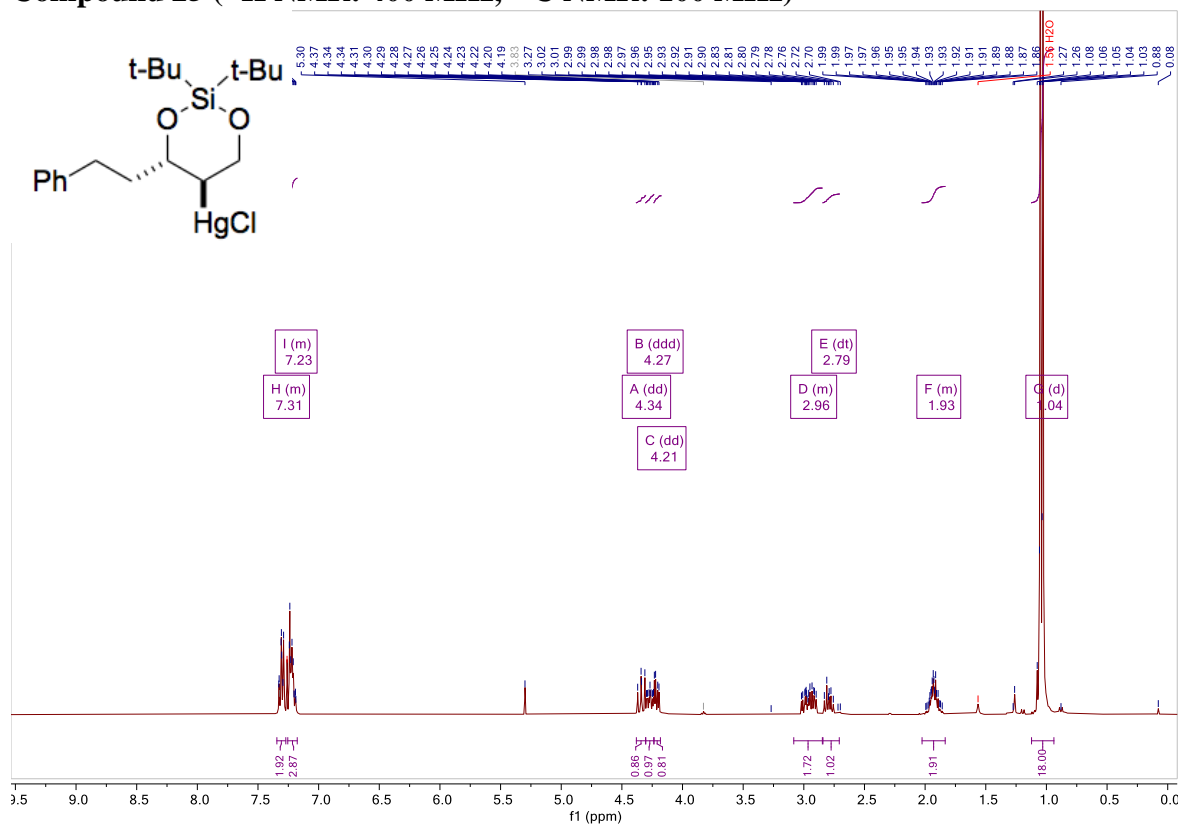
Compound 22 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



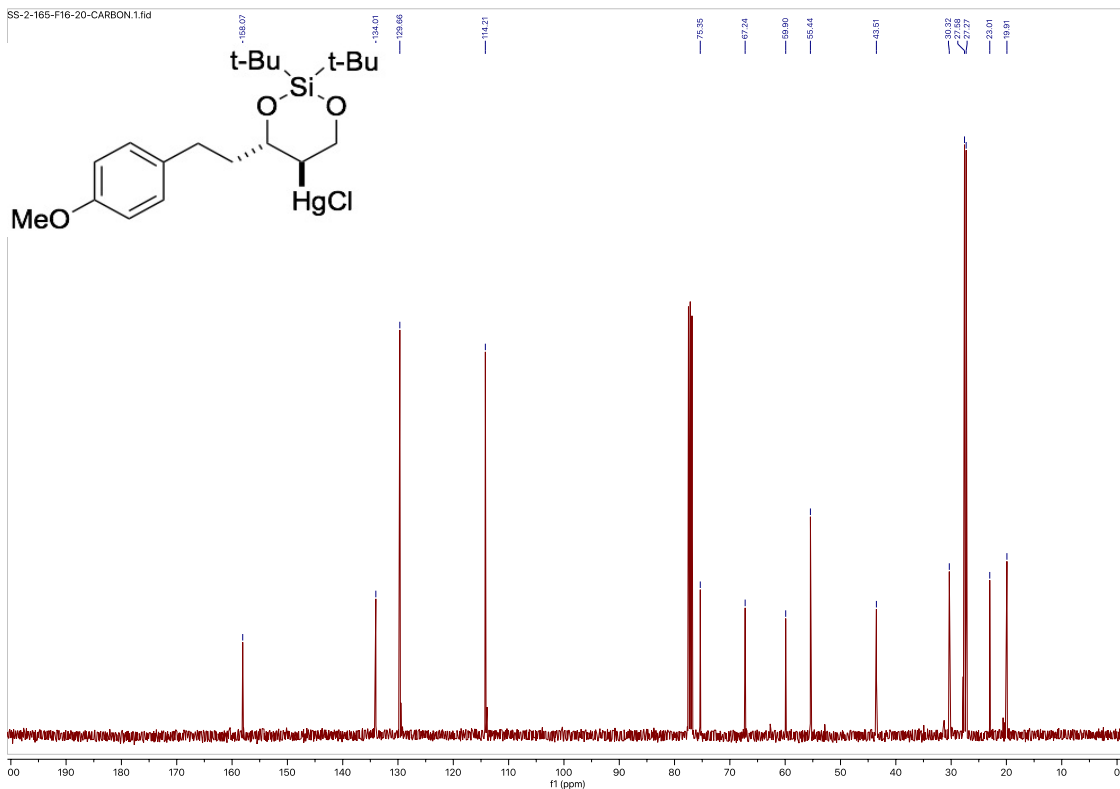
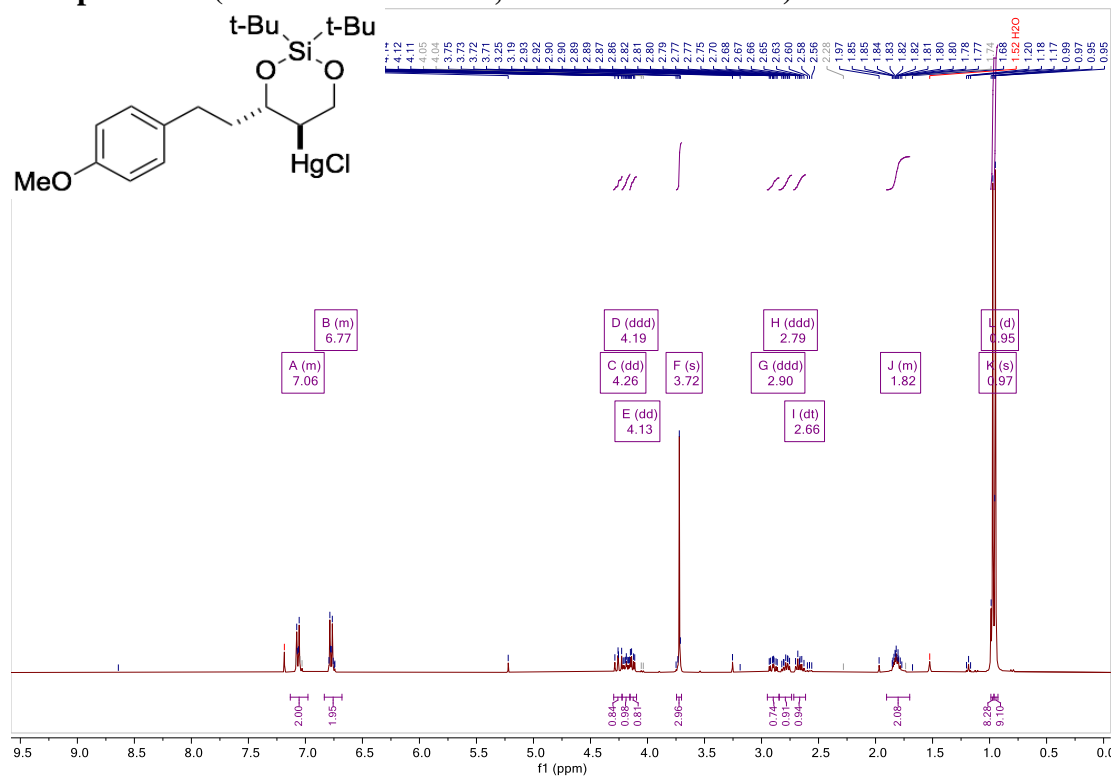
Compound 24 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



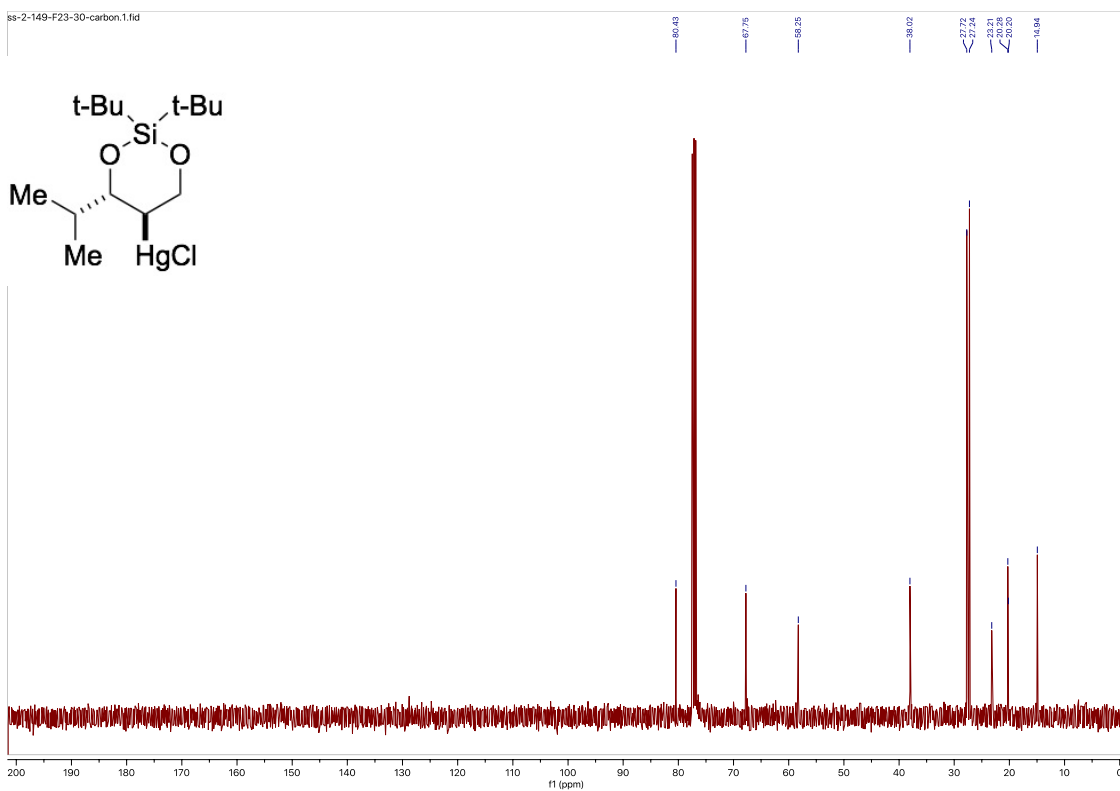
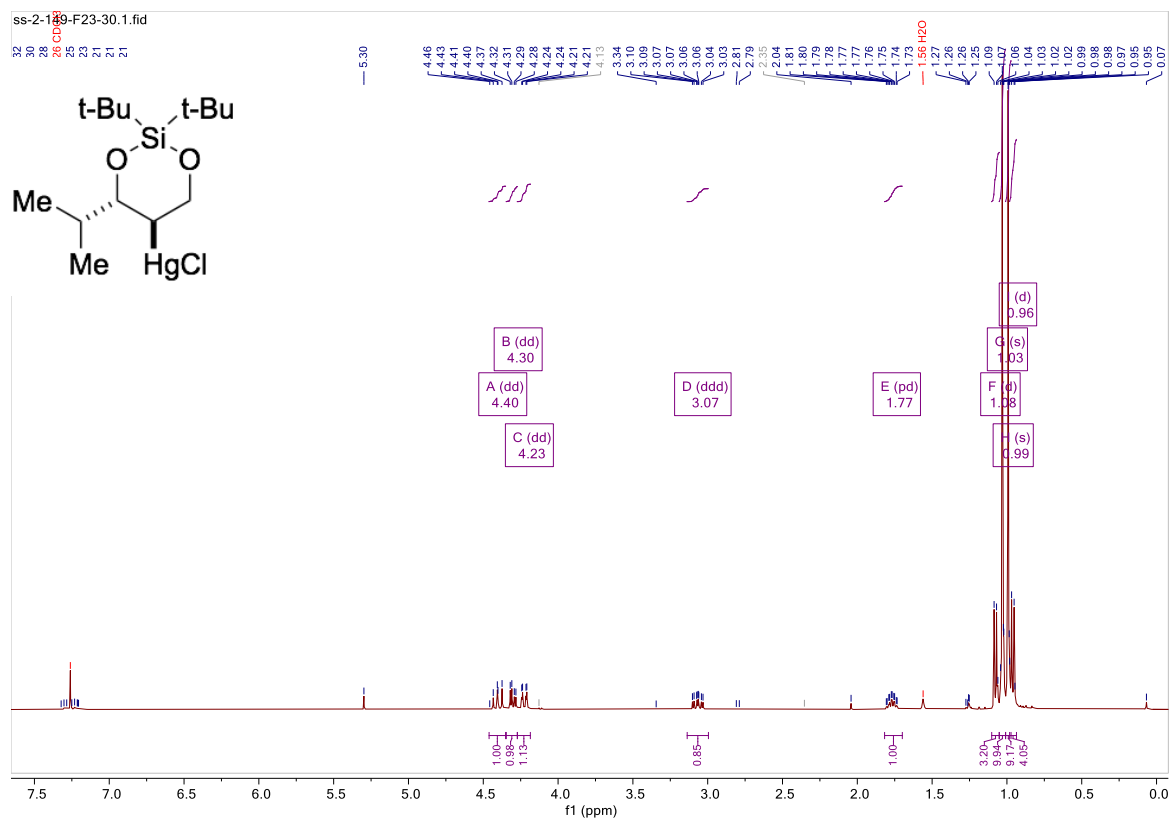
Compound 25 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



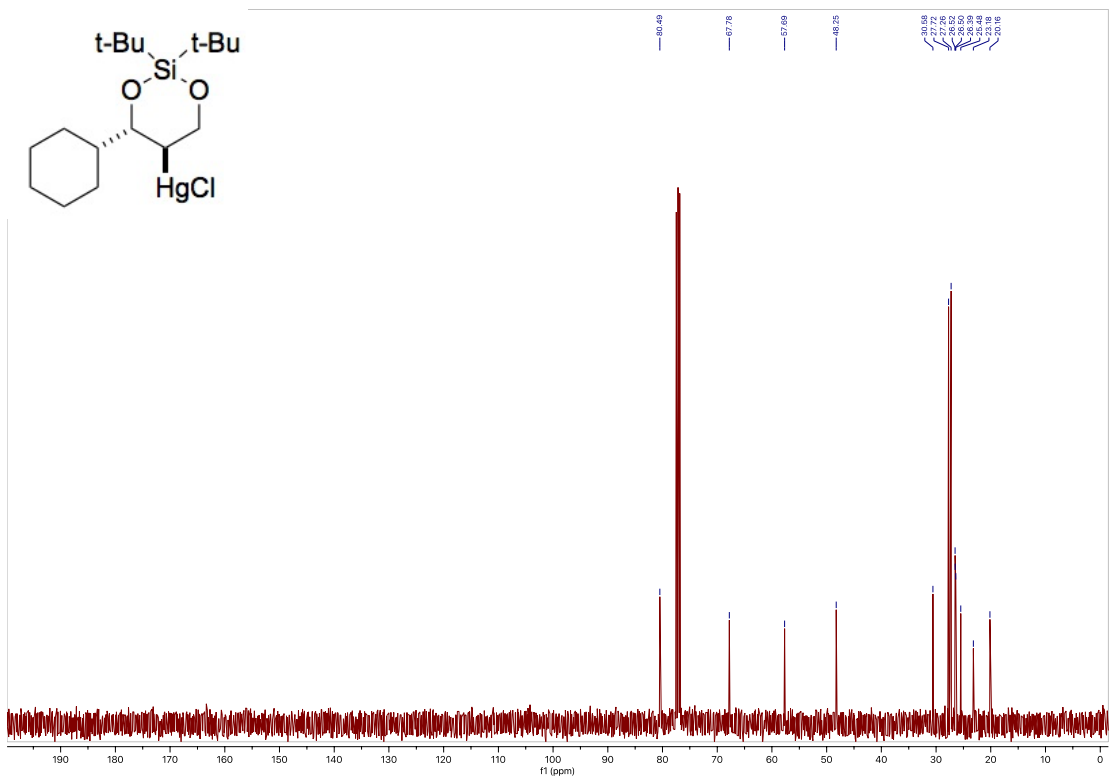
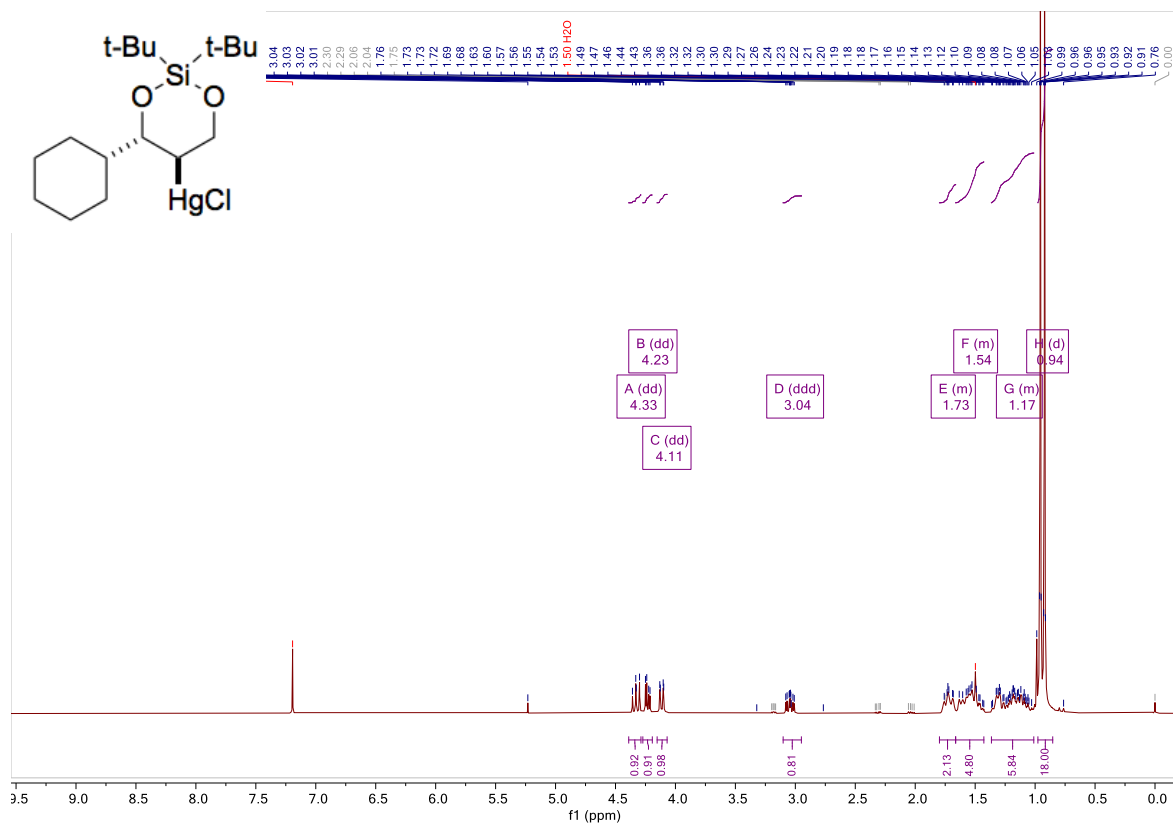
Compound 26 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



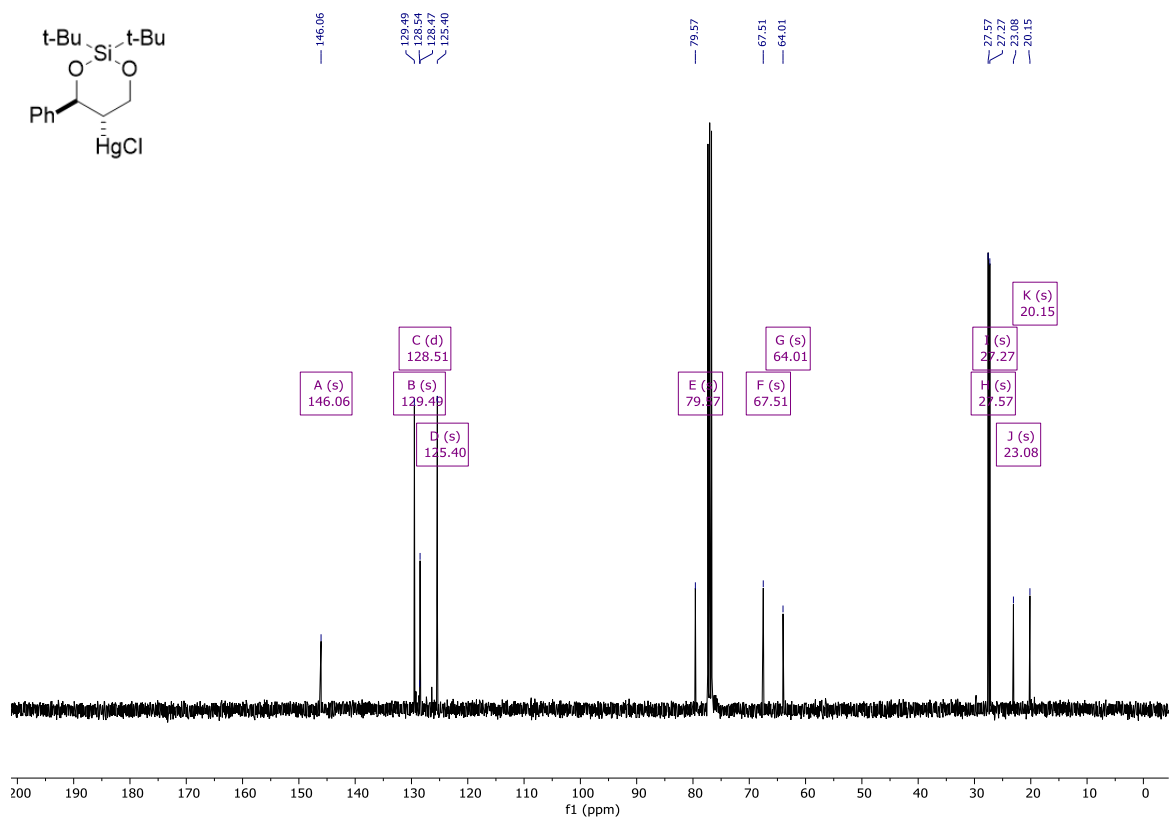
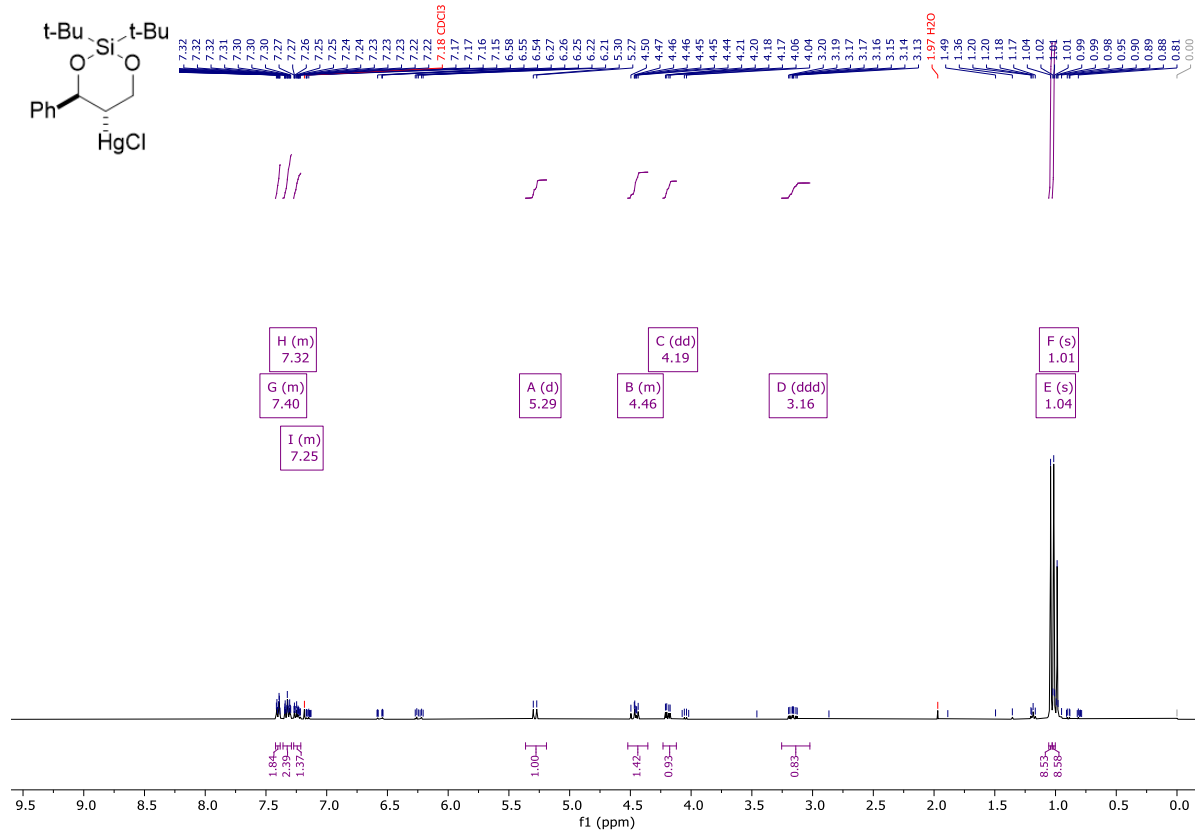
Compound 27 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



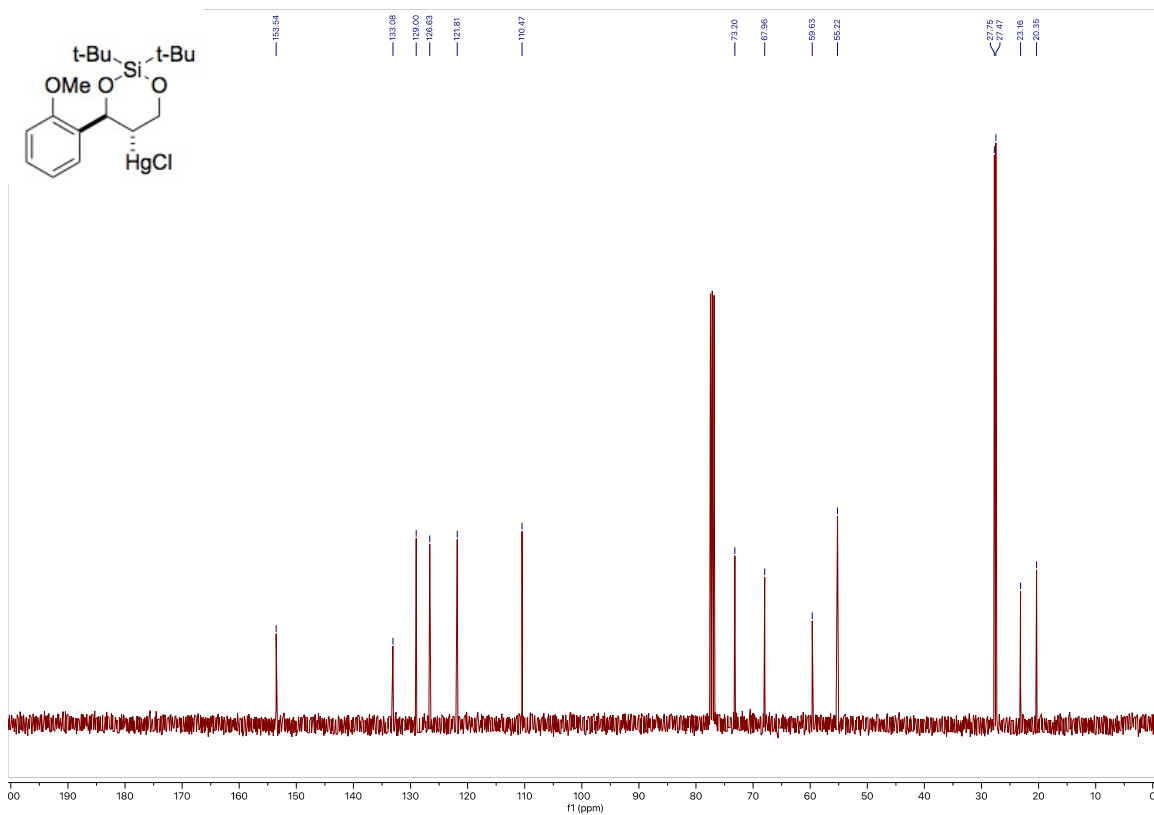
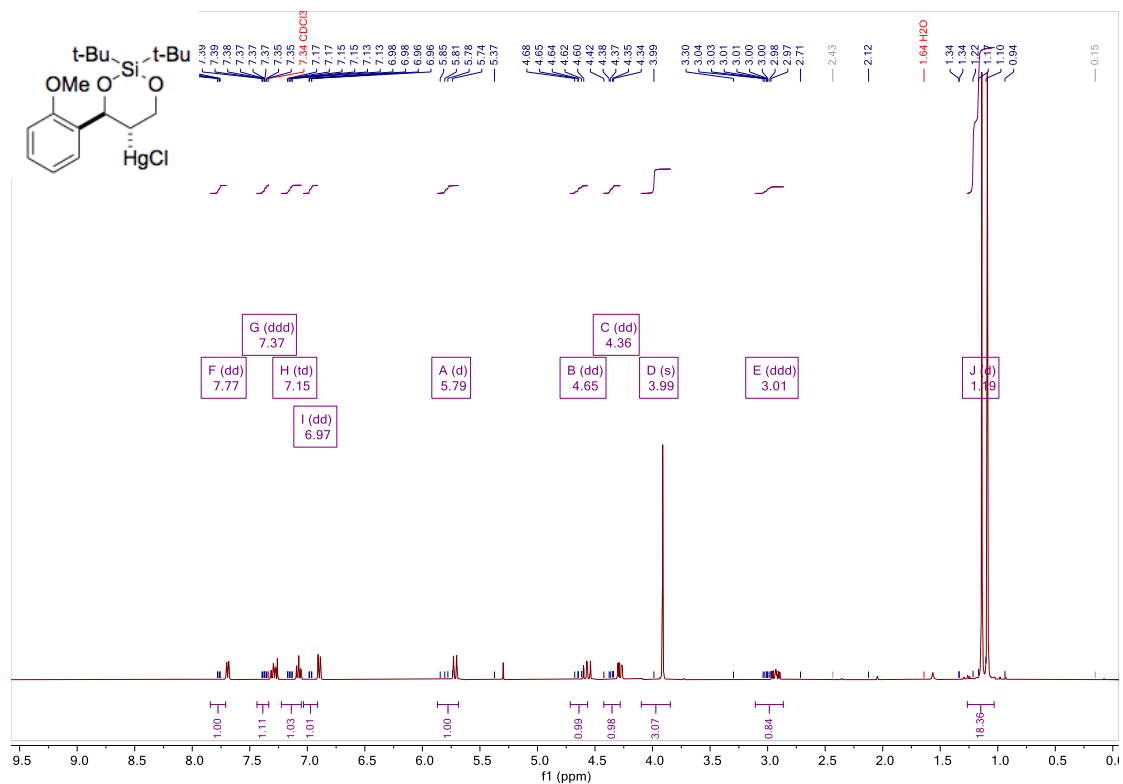
Compound 28 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



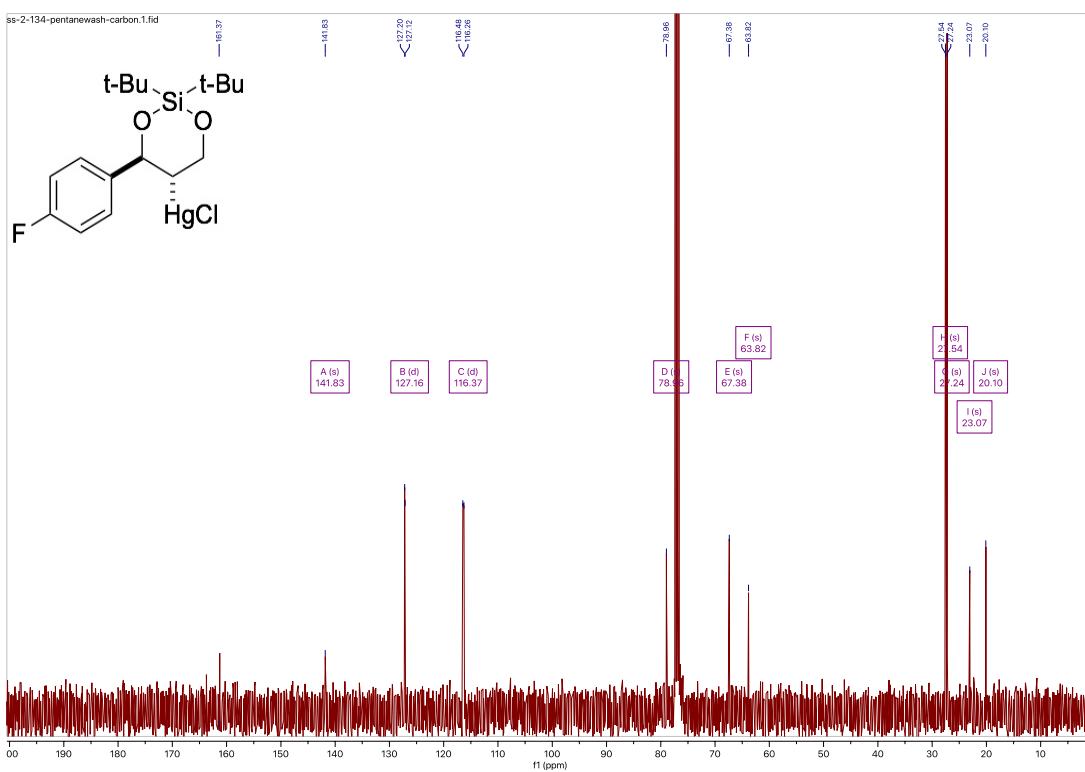
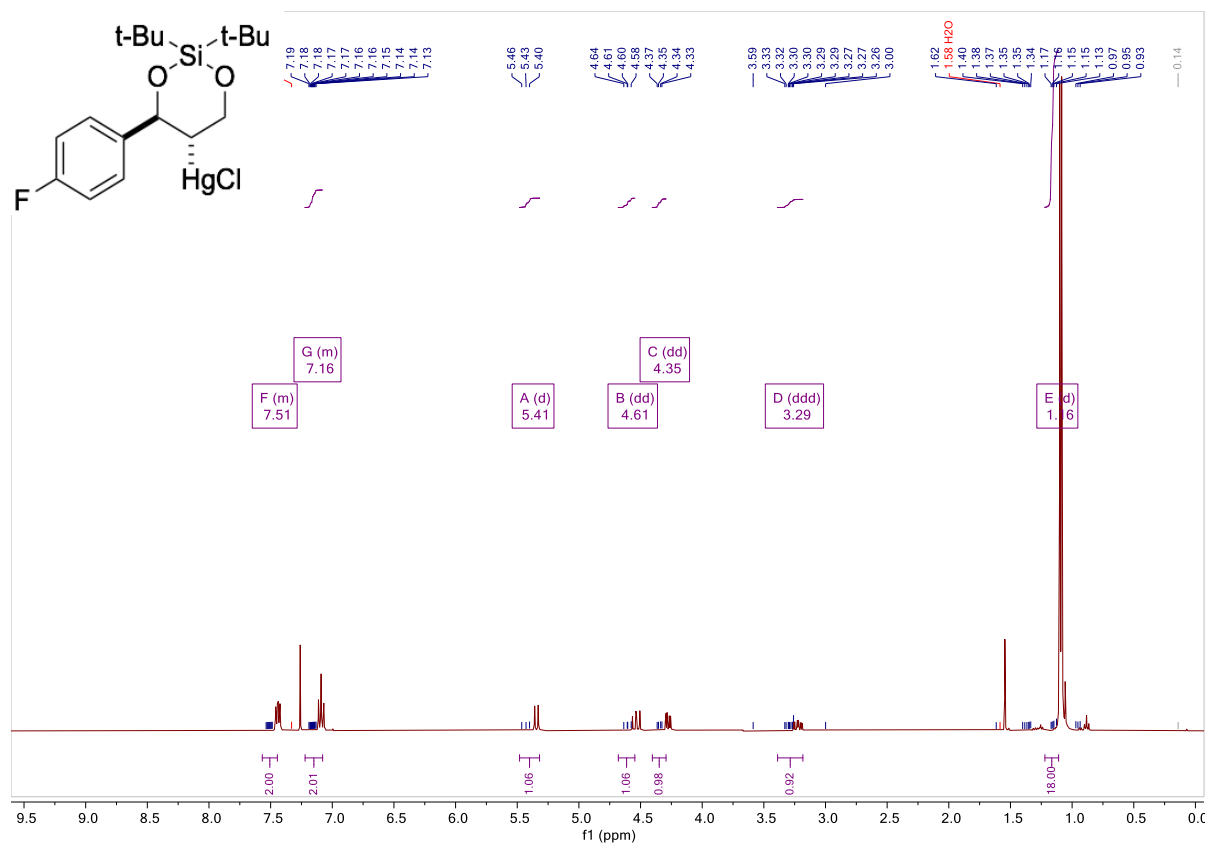
Compound 29 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



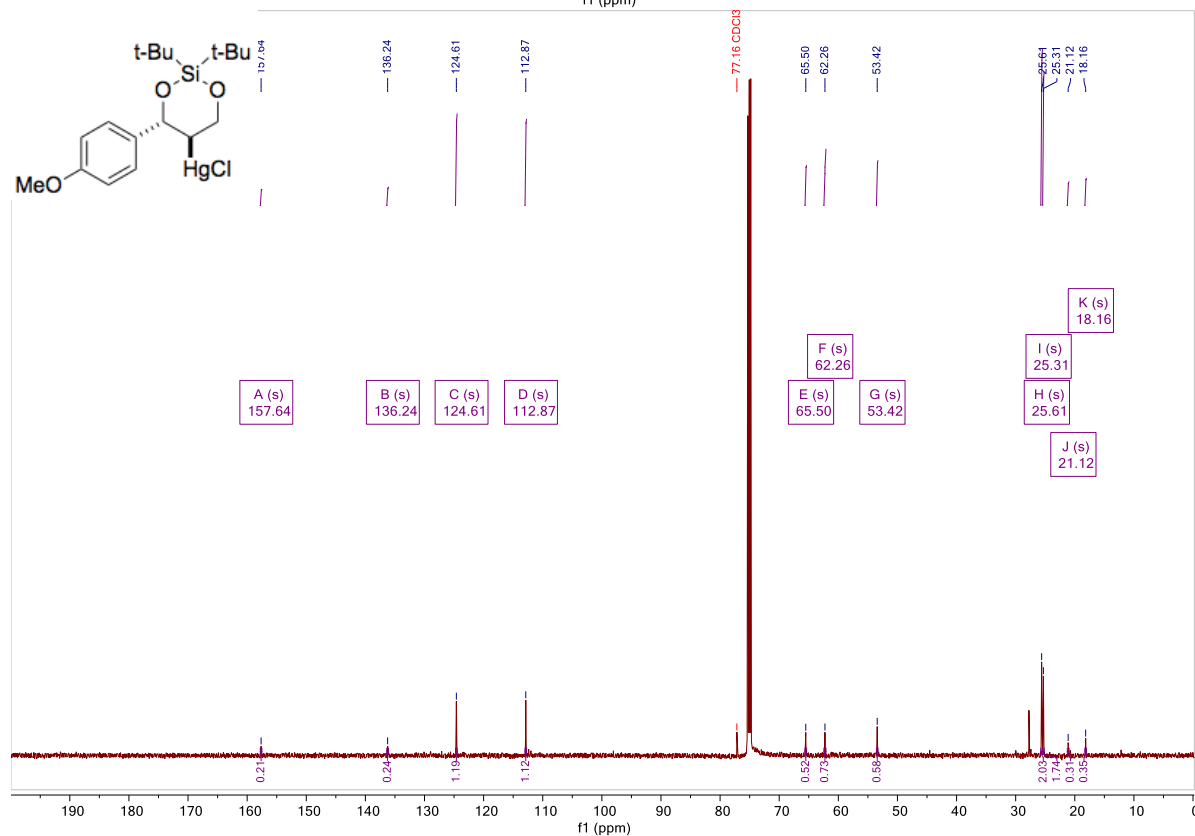
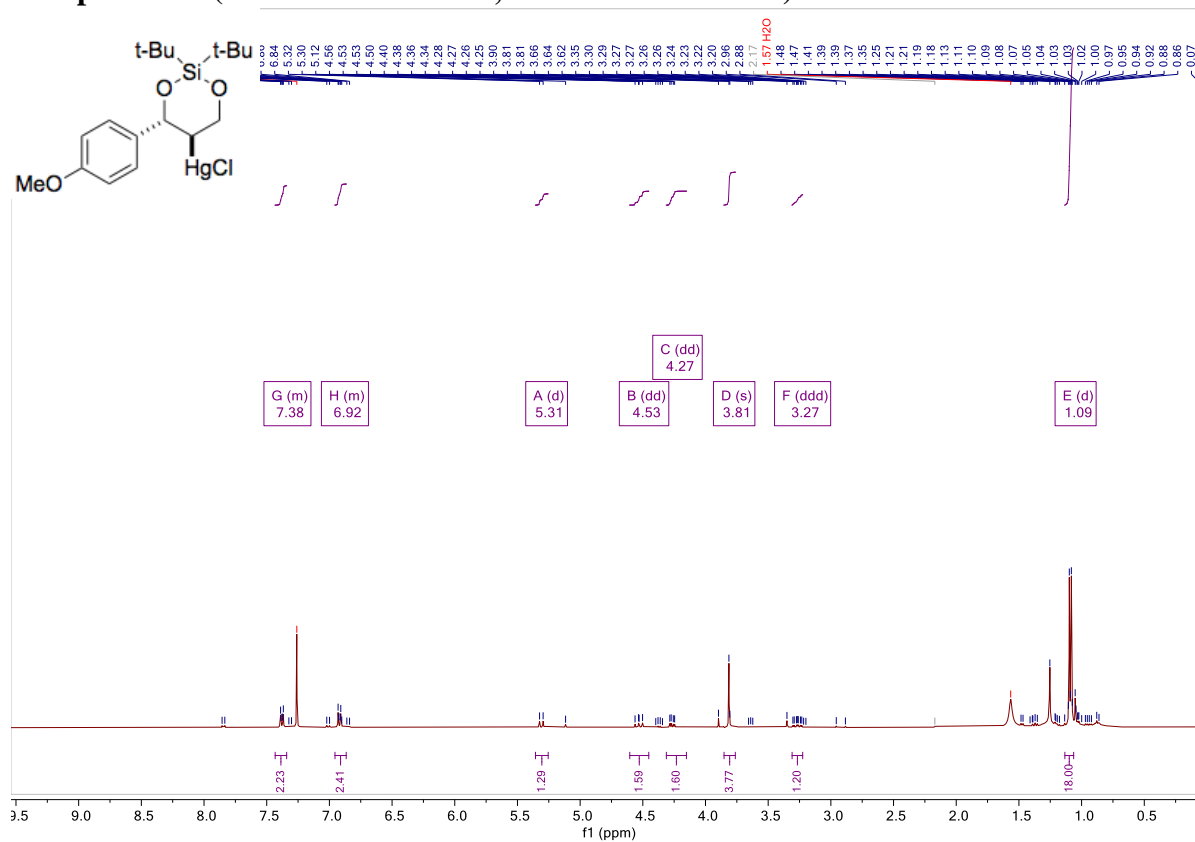
Compound 30 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



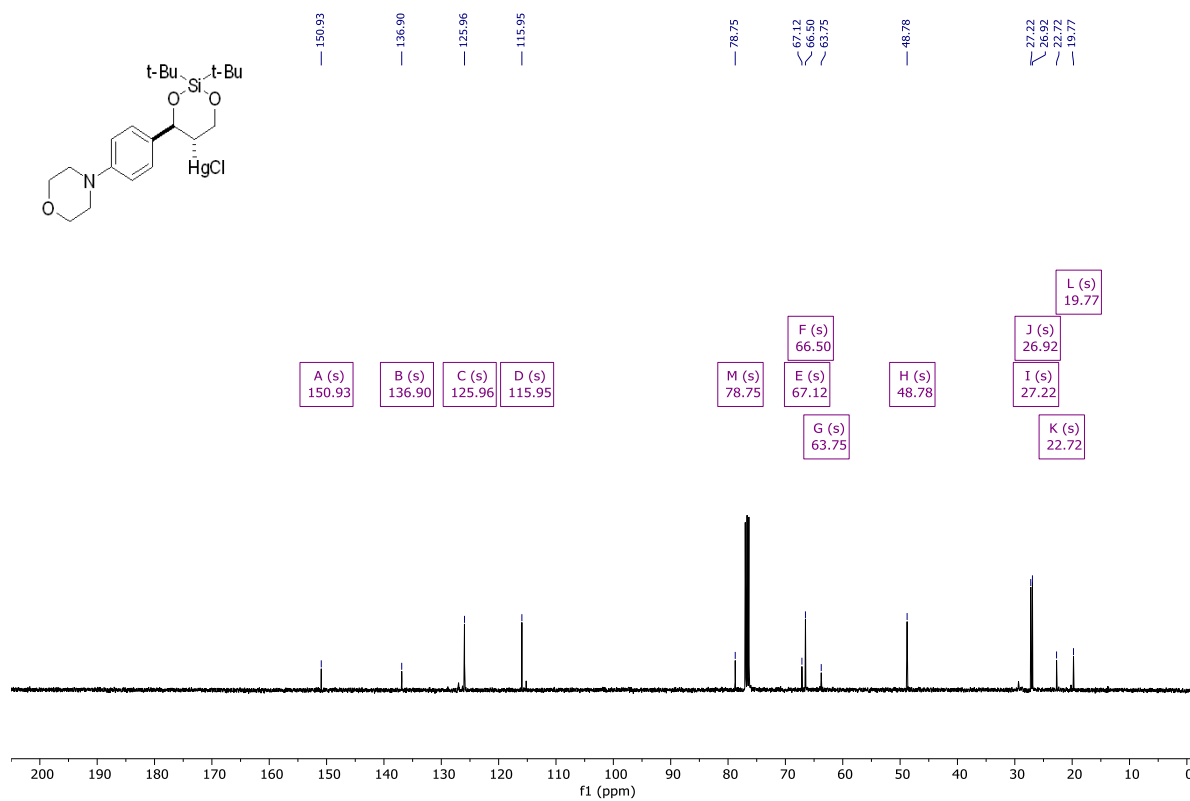
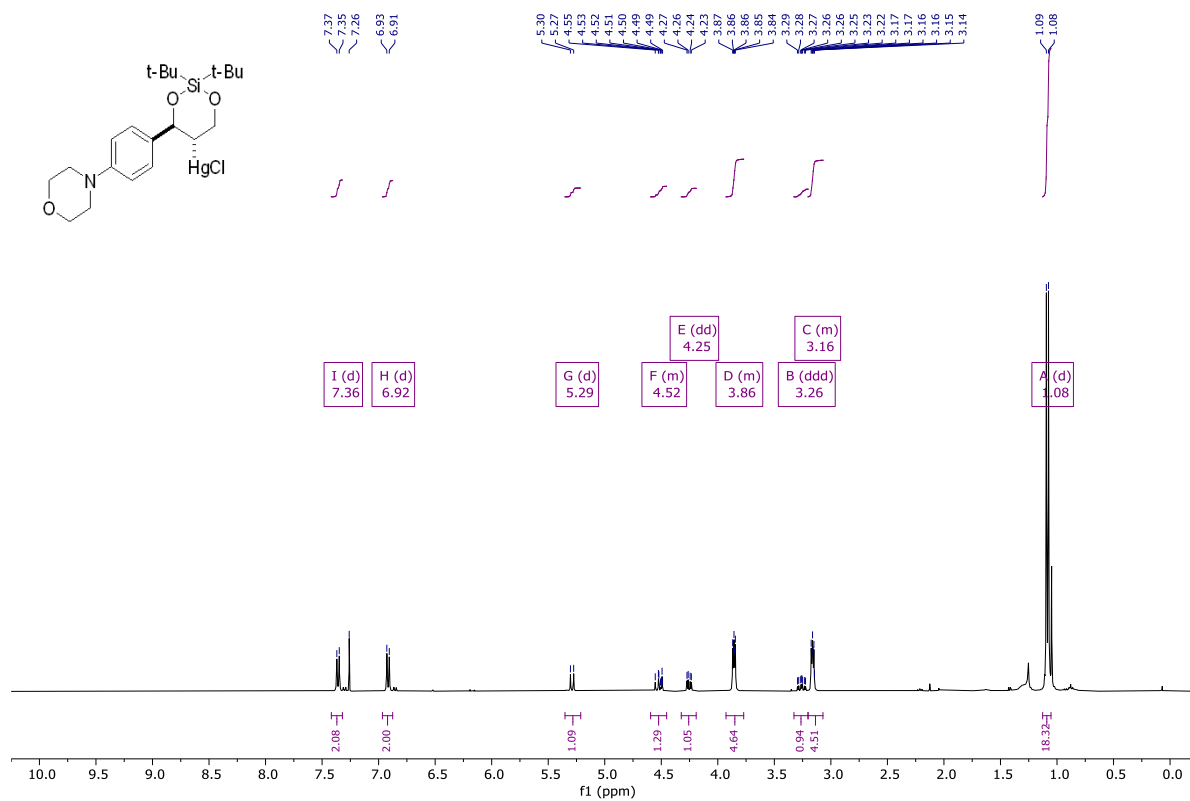
Compound 31 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



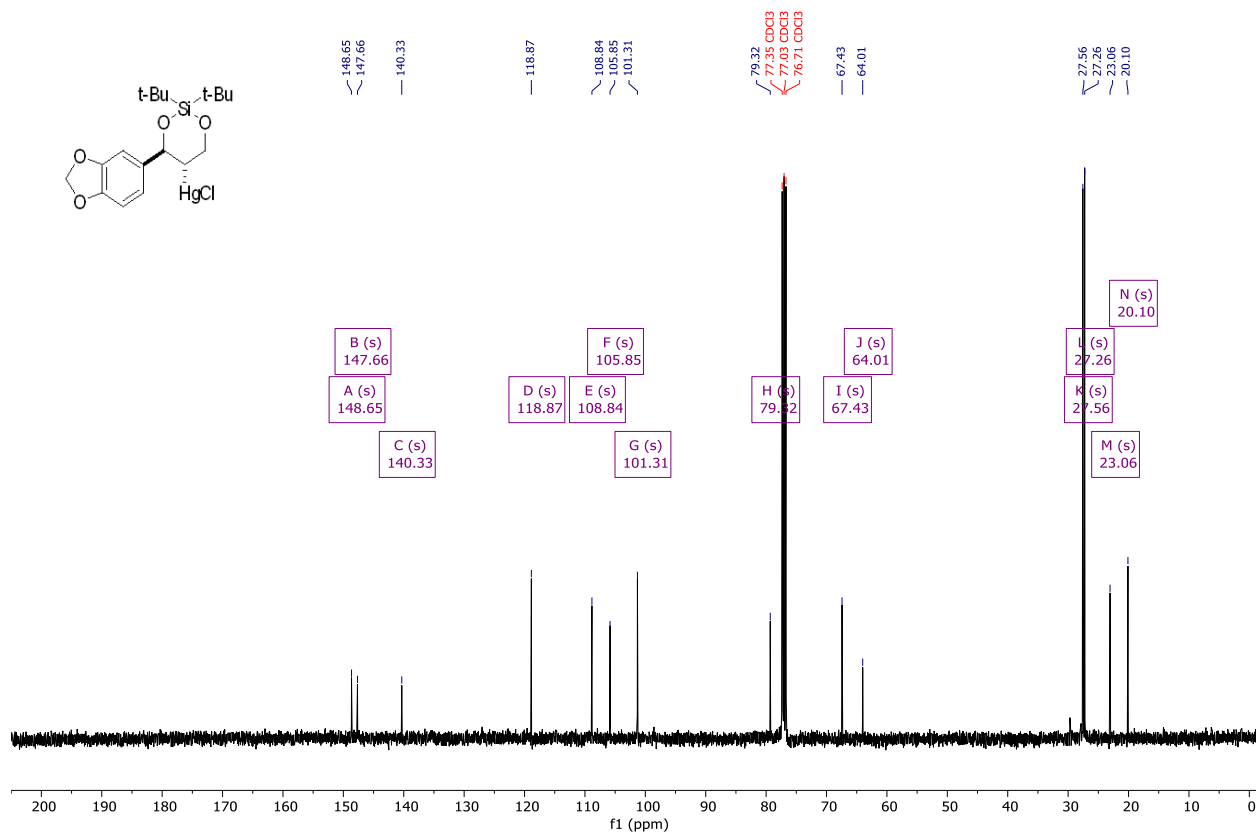
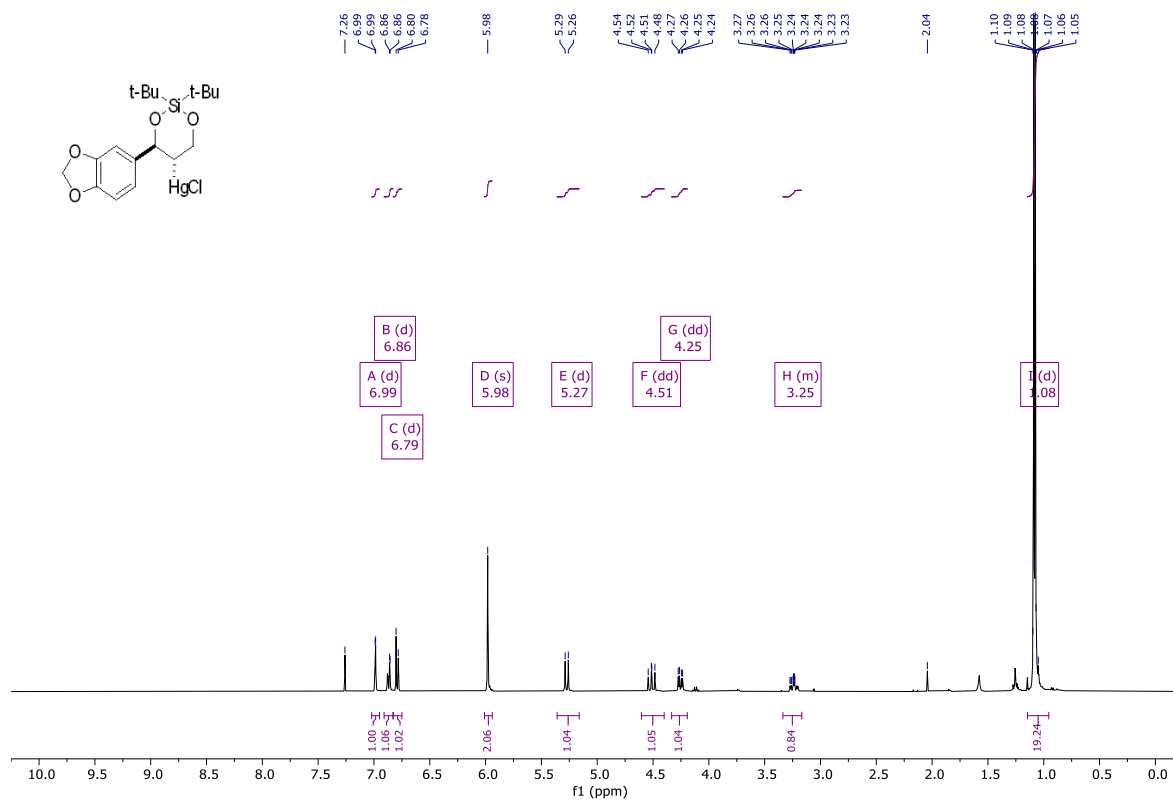
Compound 32 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



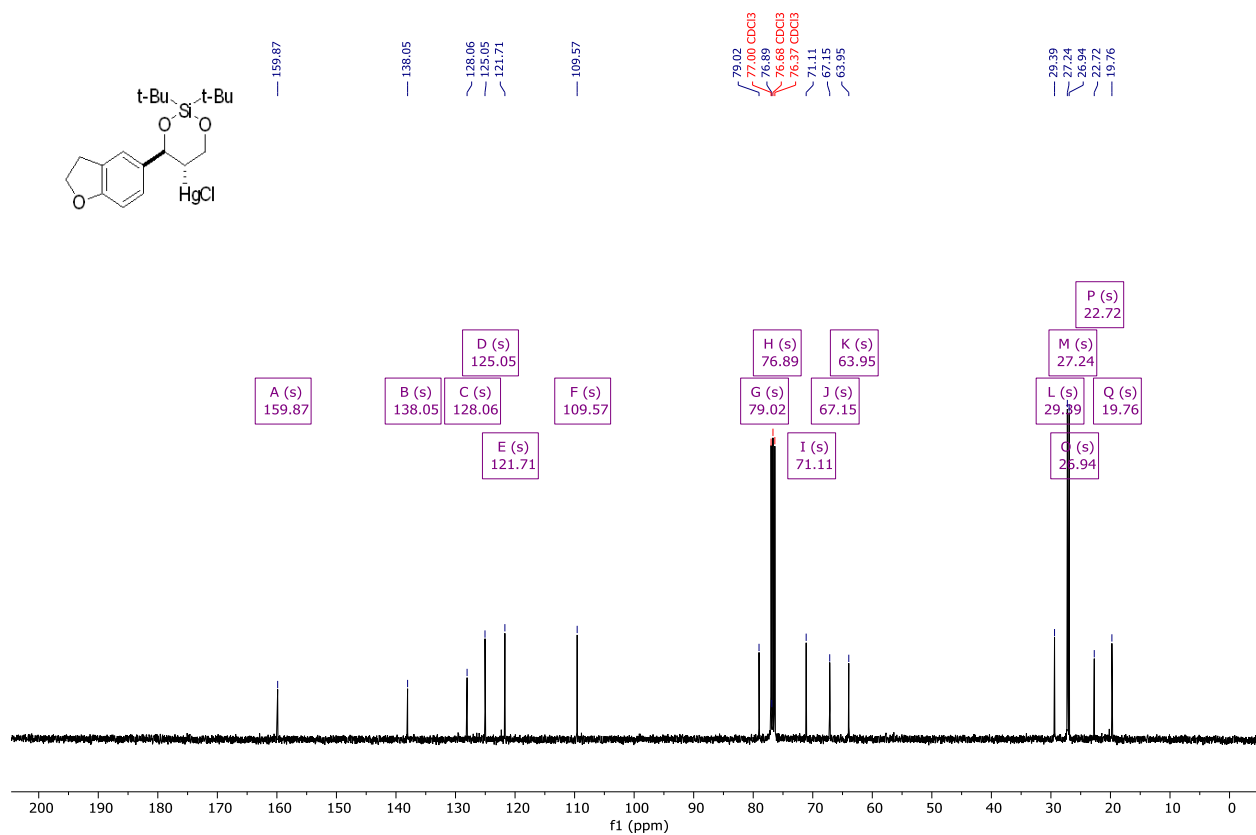
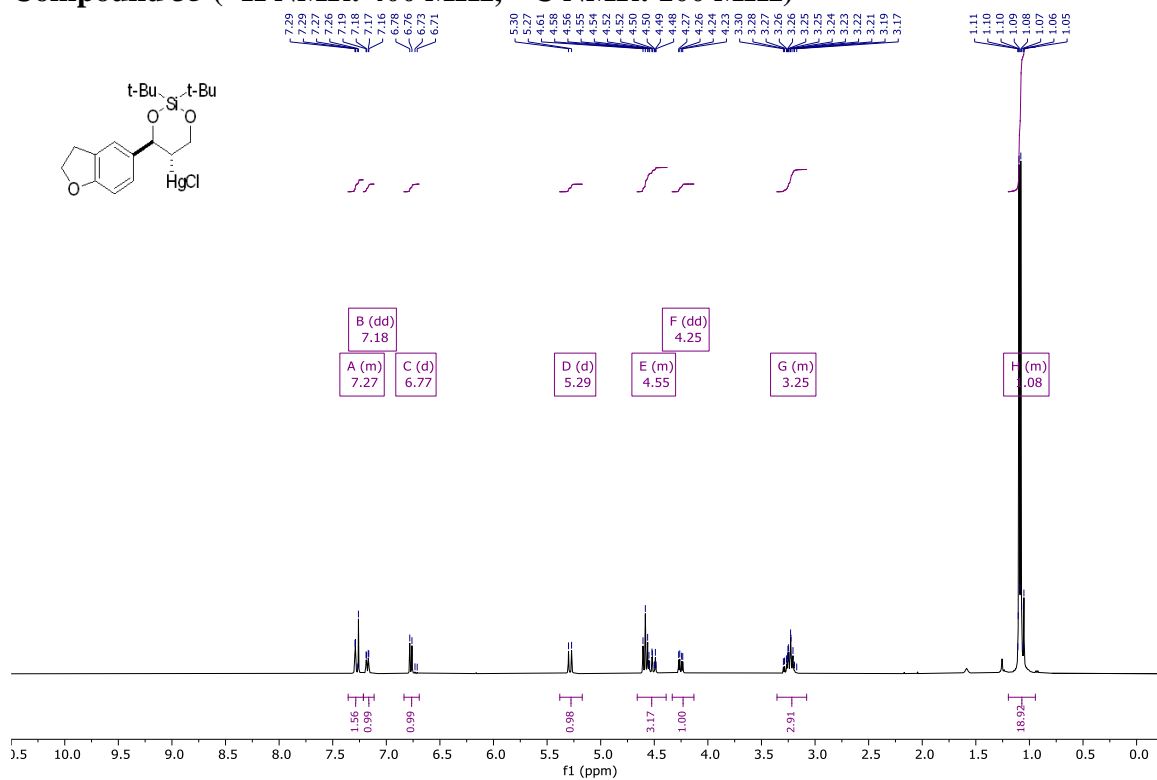
Compound 33 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz)



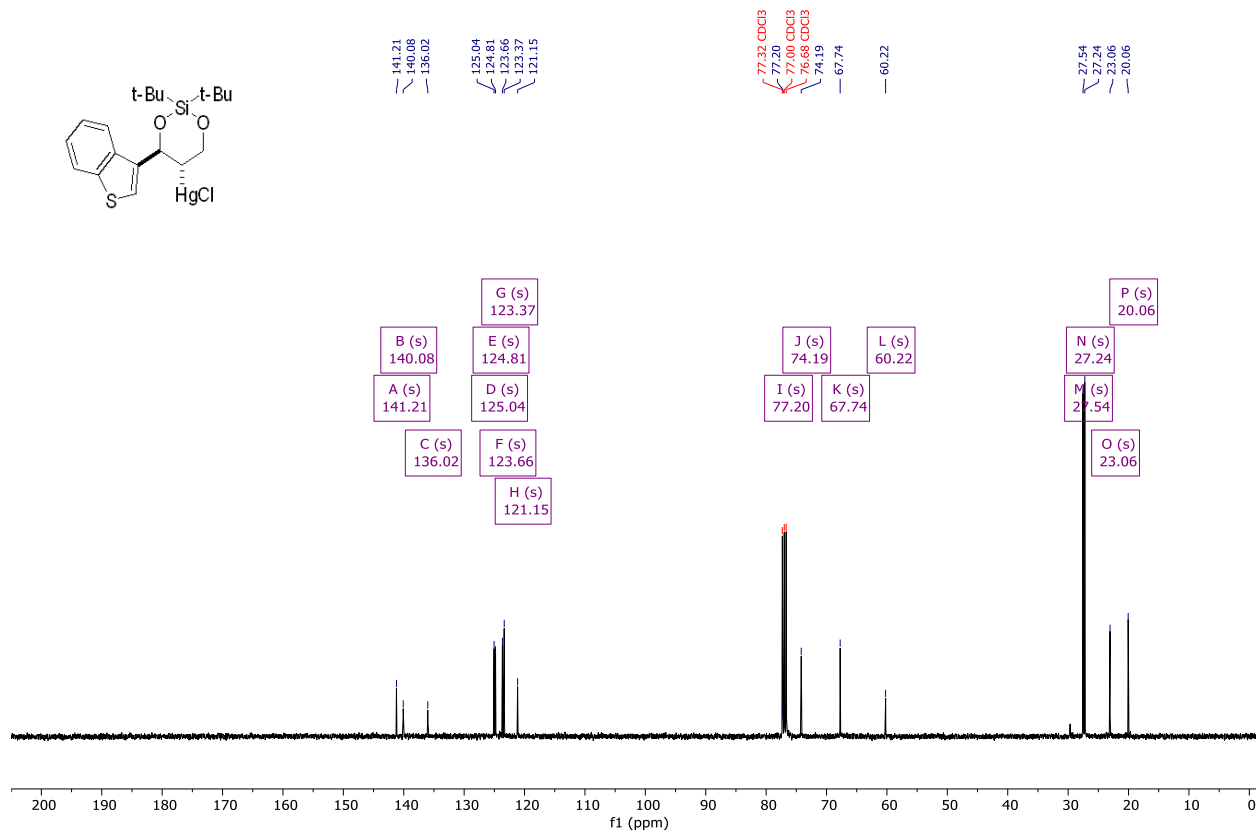
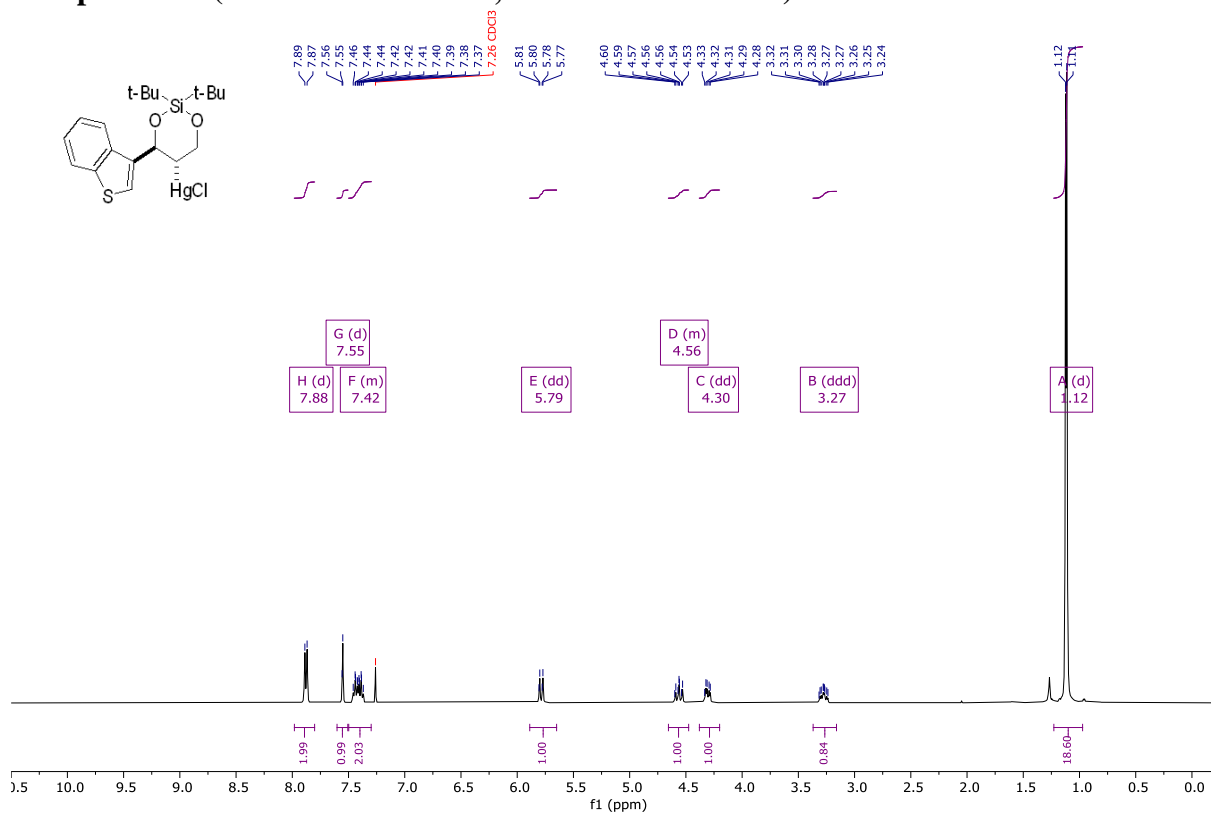
Compound 34 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



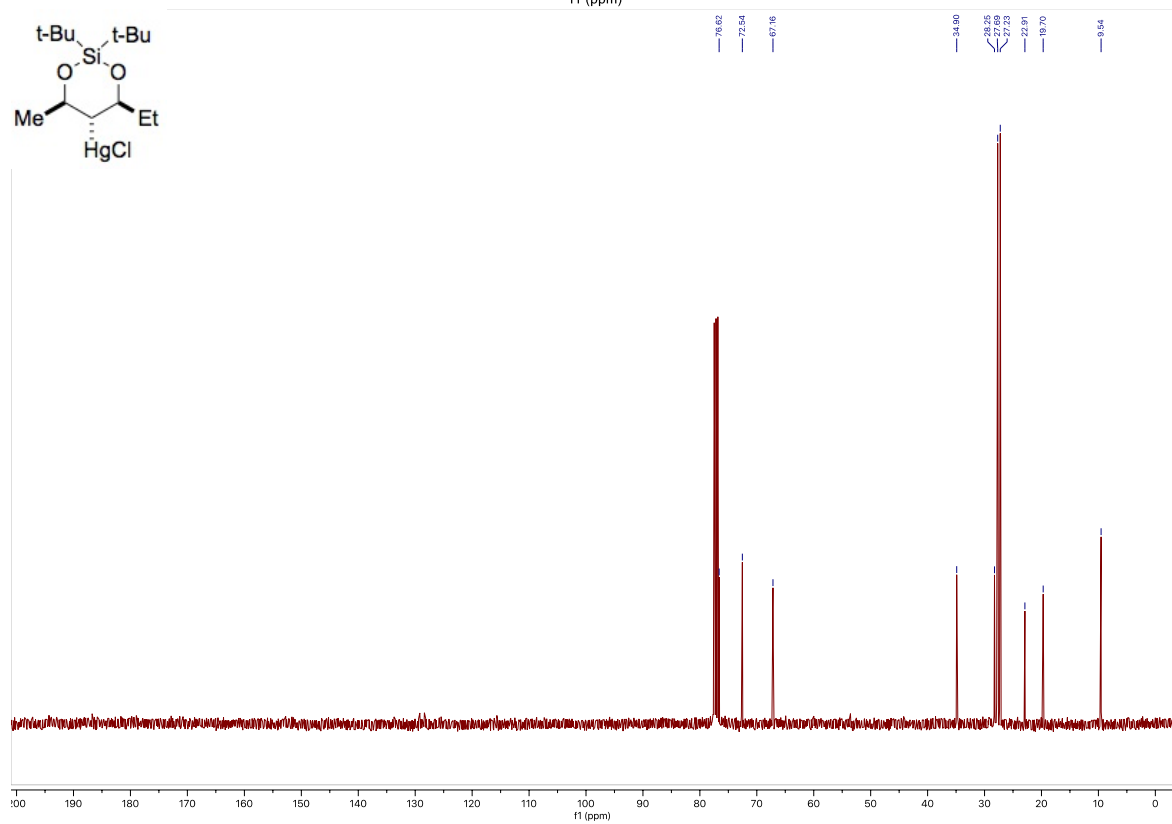
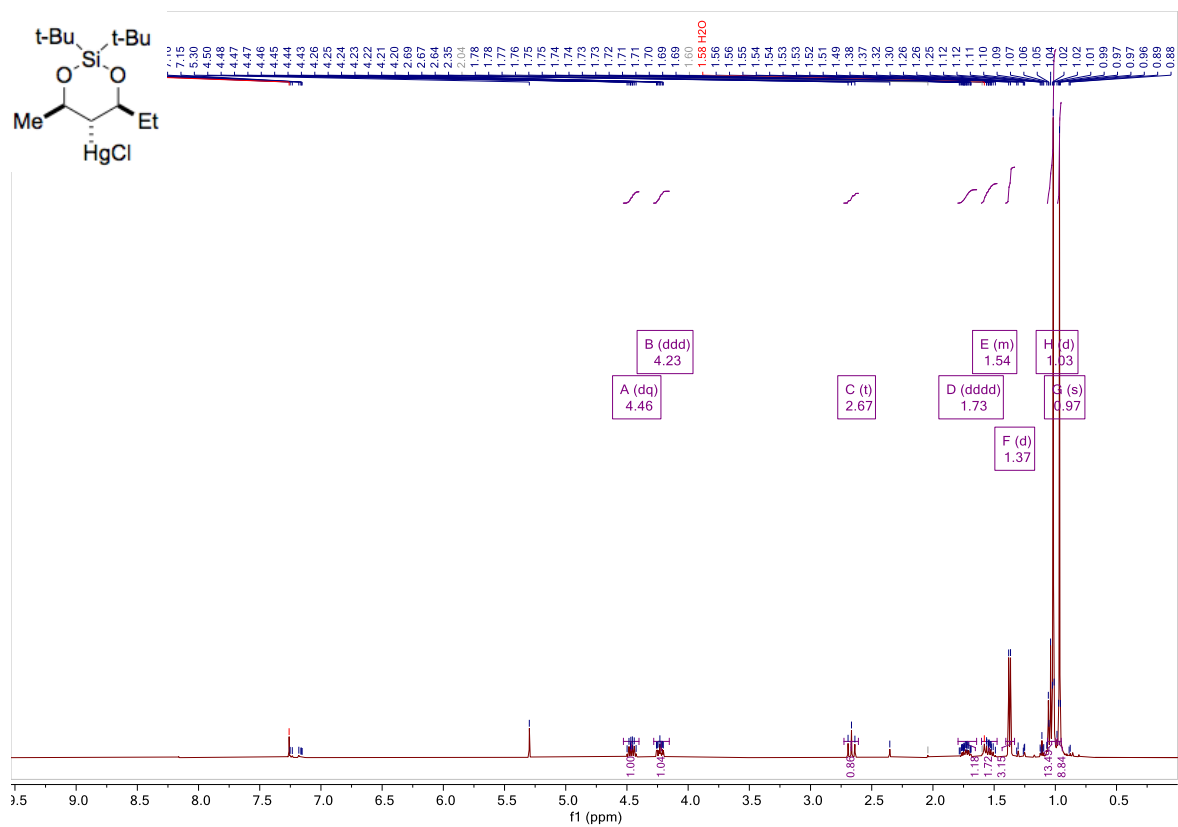
Compound 35 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz)



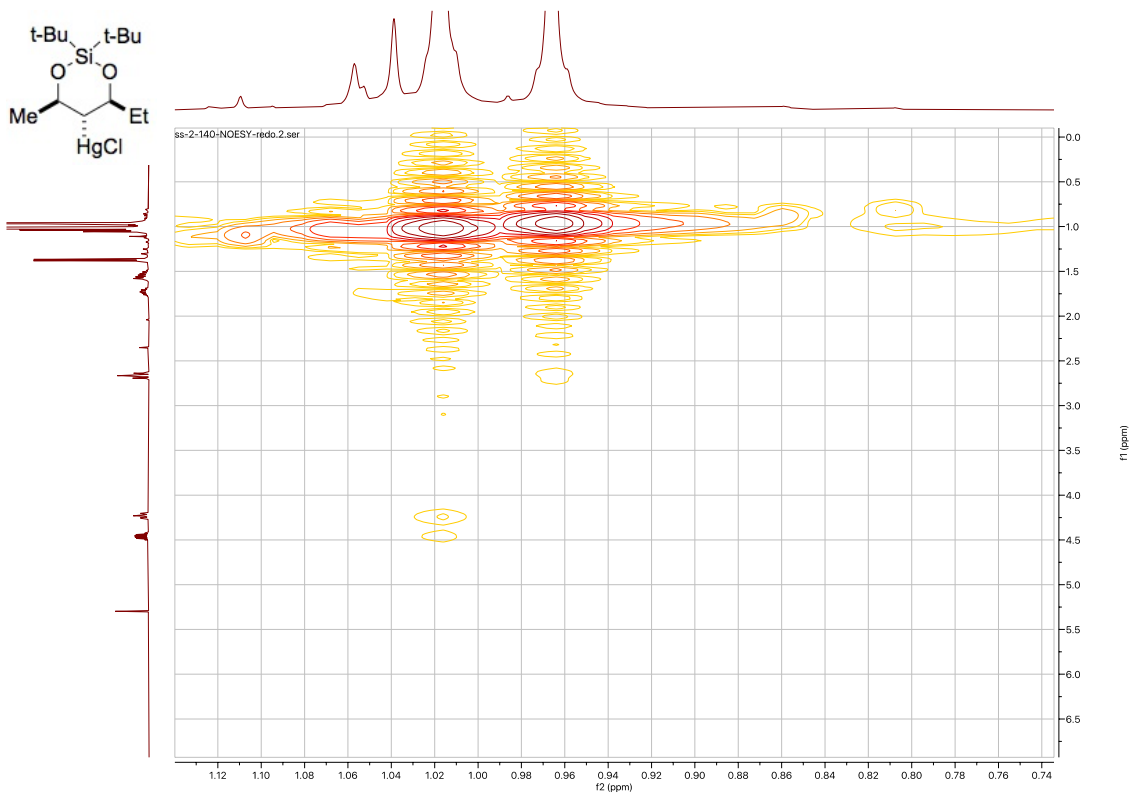
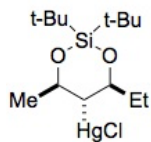
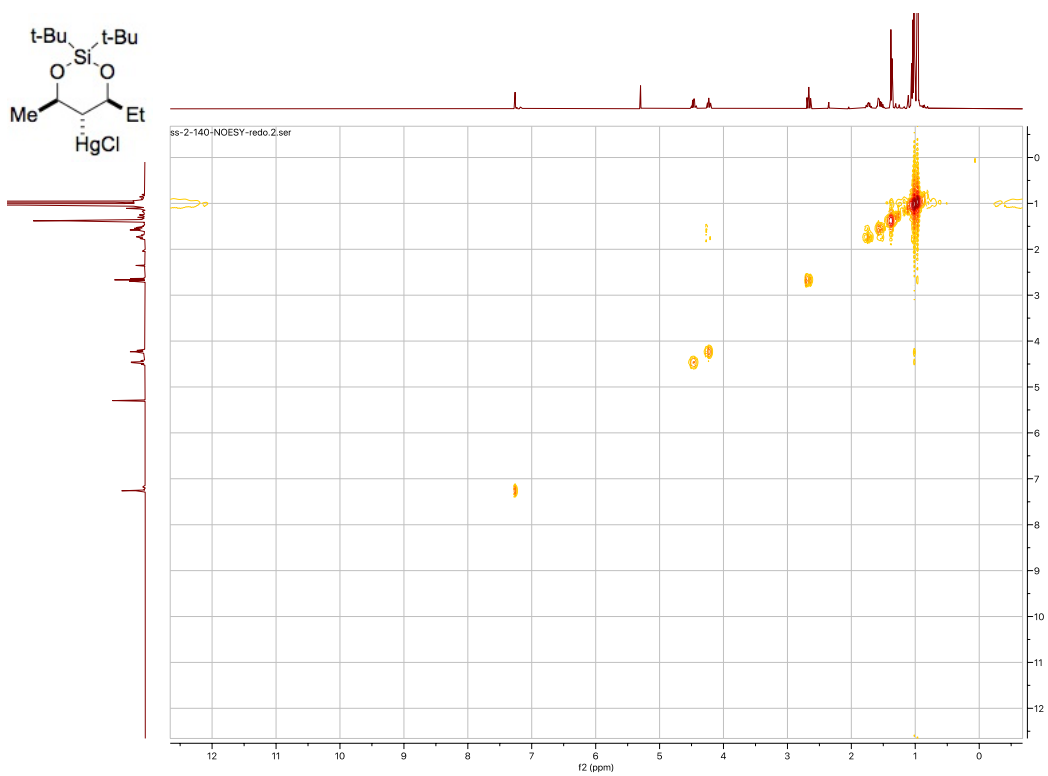
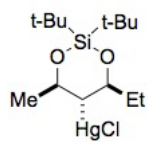
Compound 36 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



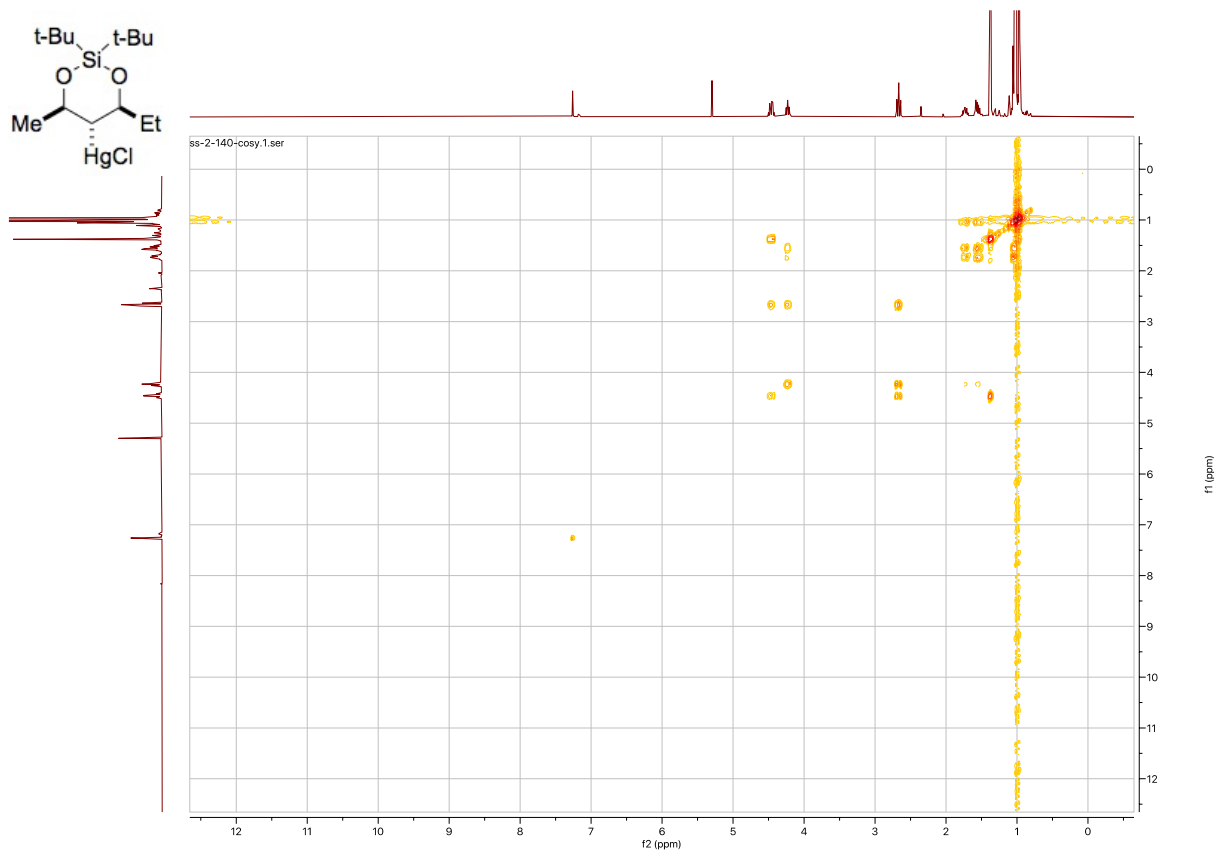
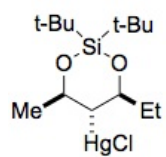
Compound 37 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz)



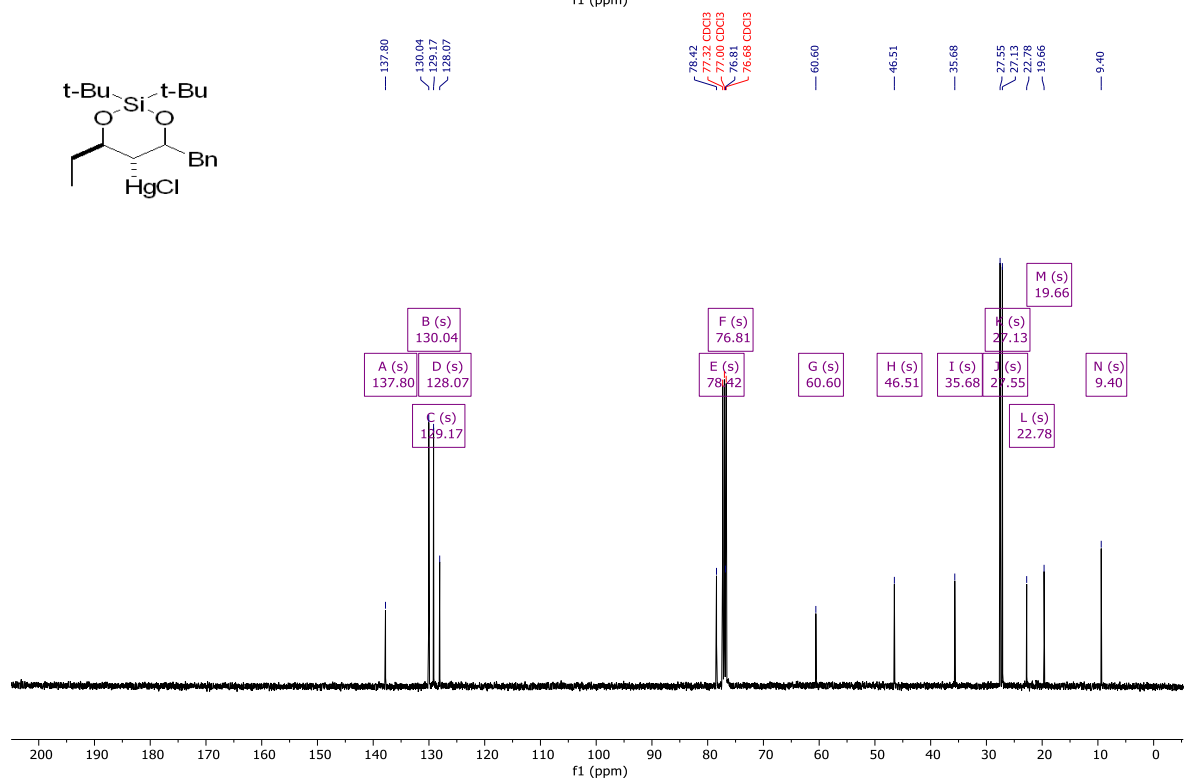
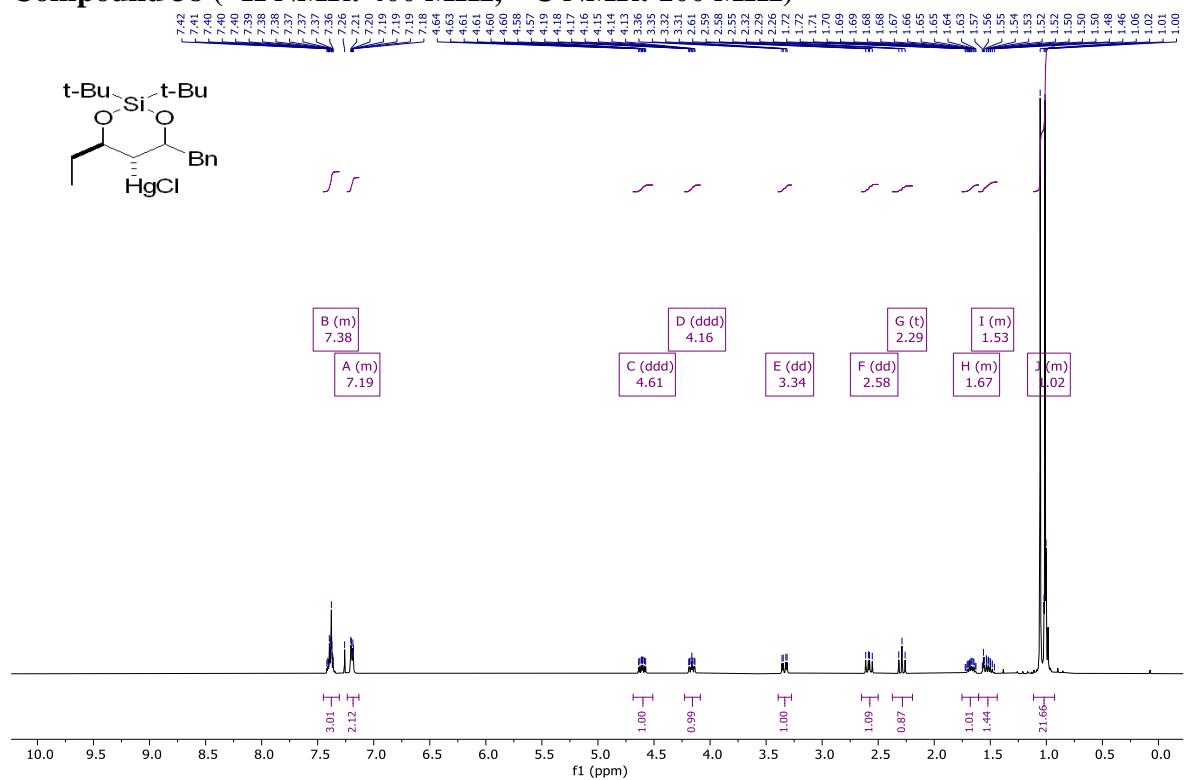
NOESY



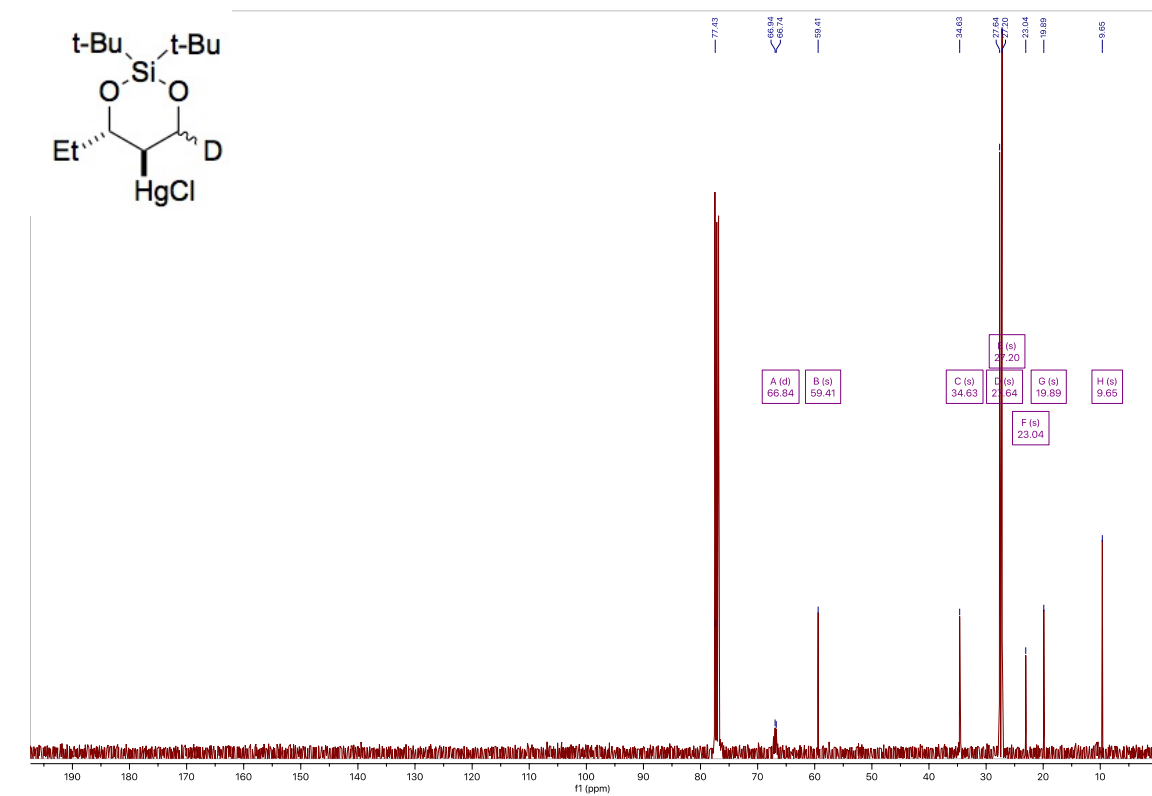
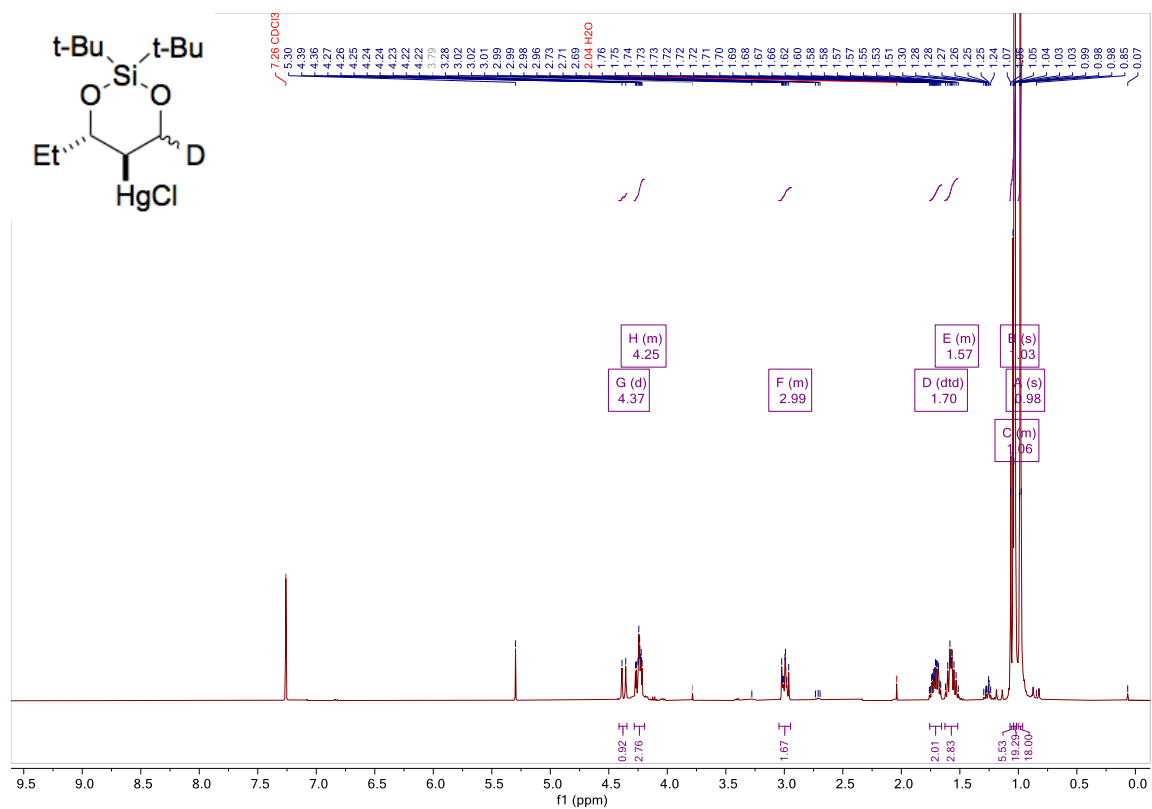
COSY



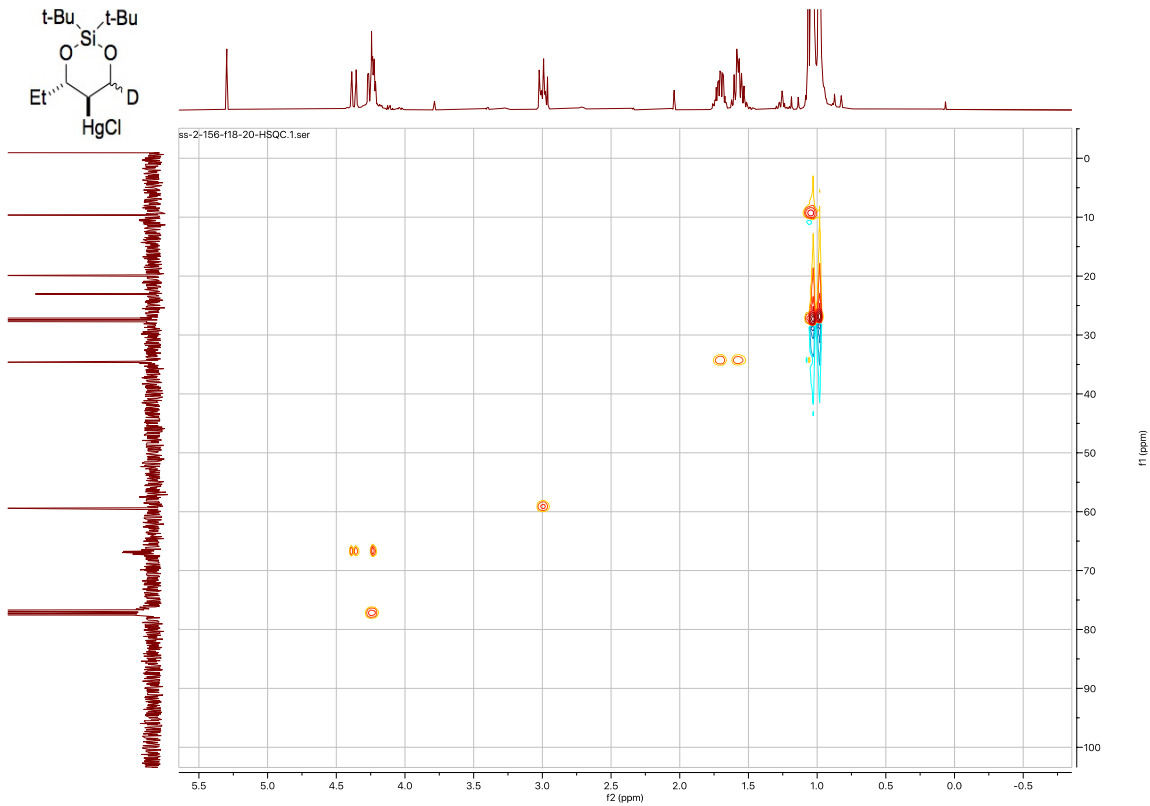
Compound 38 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz)



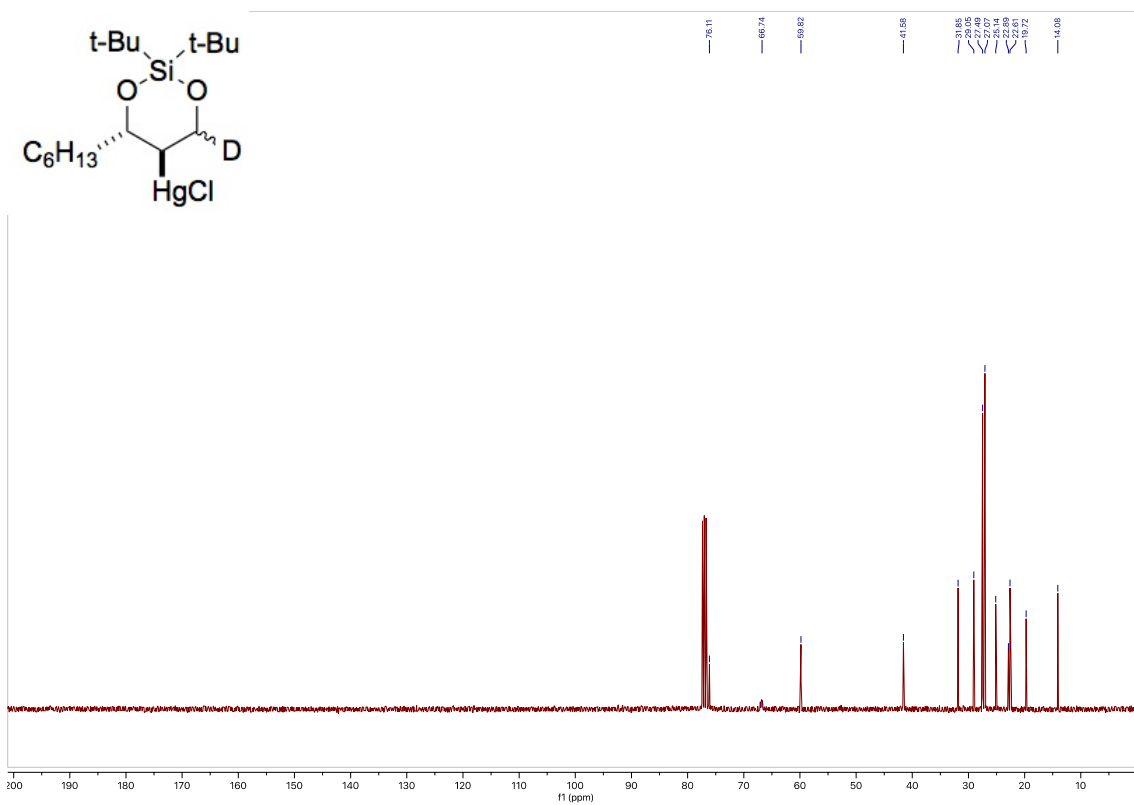
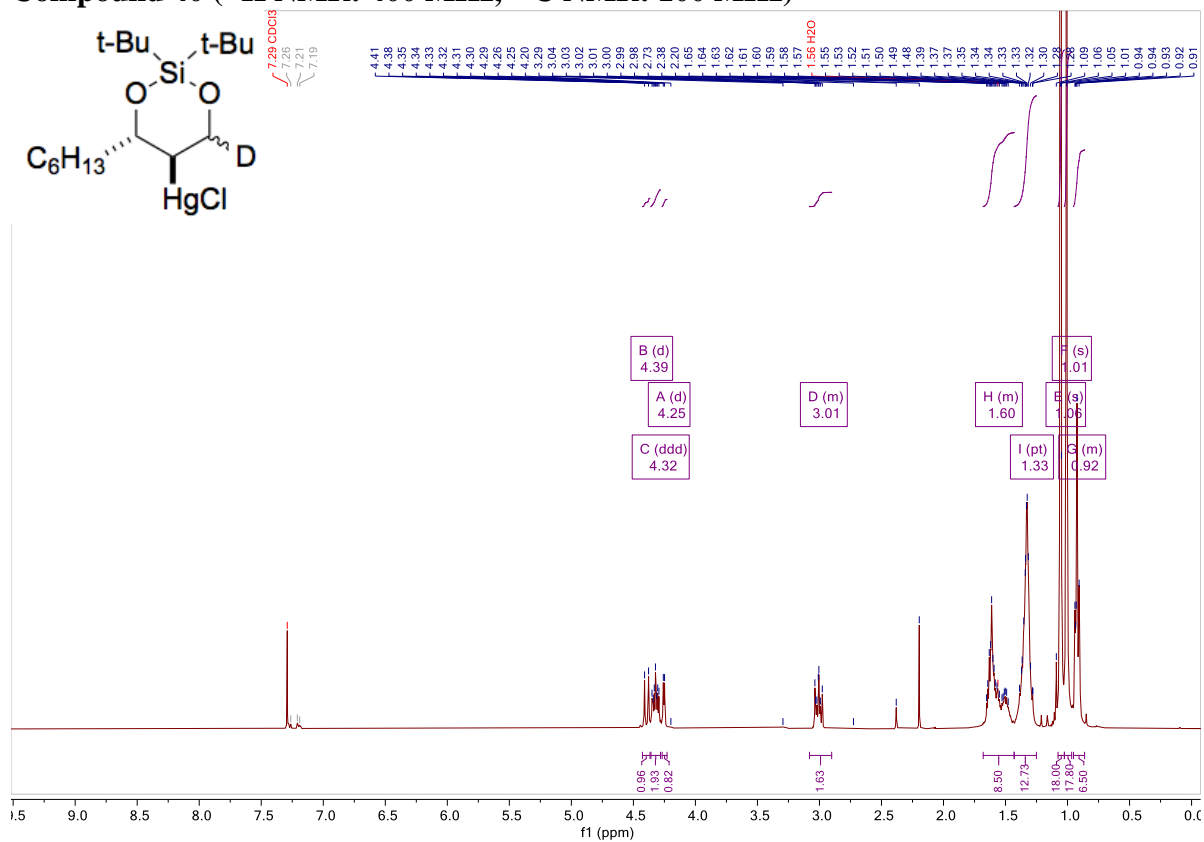
Compound 39 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



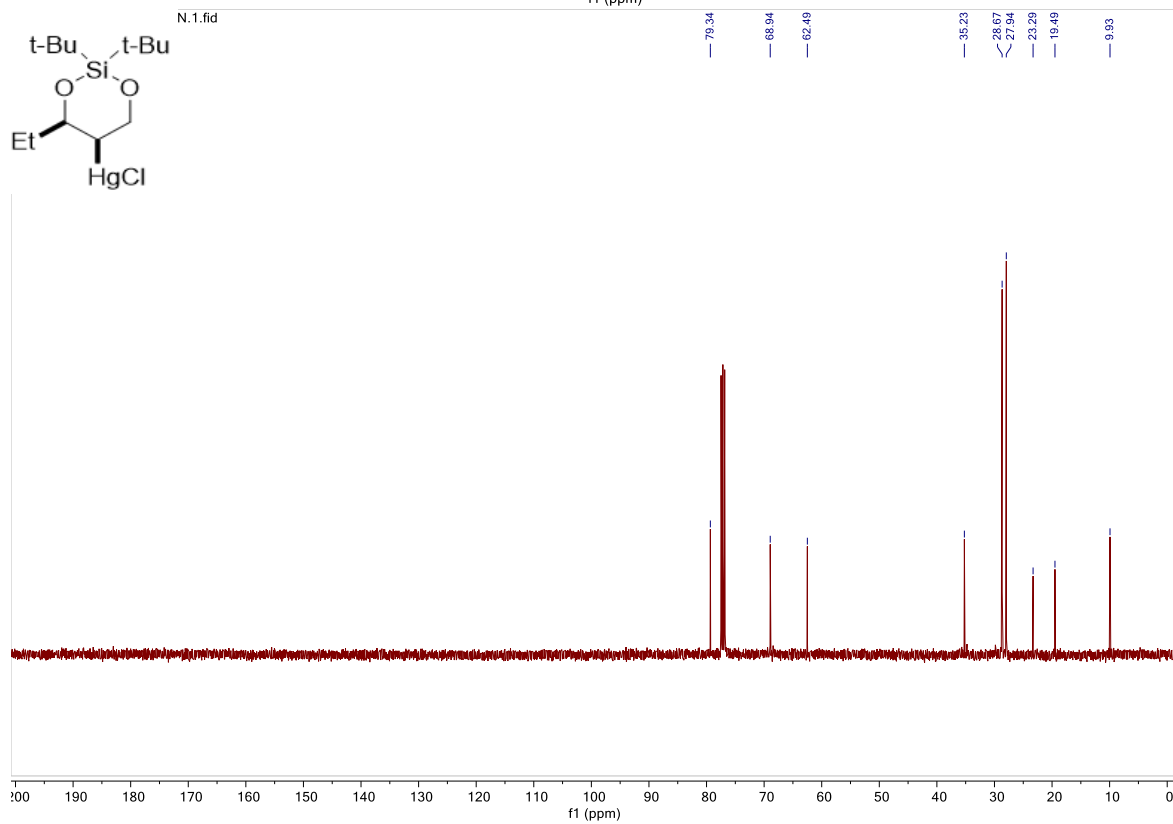
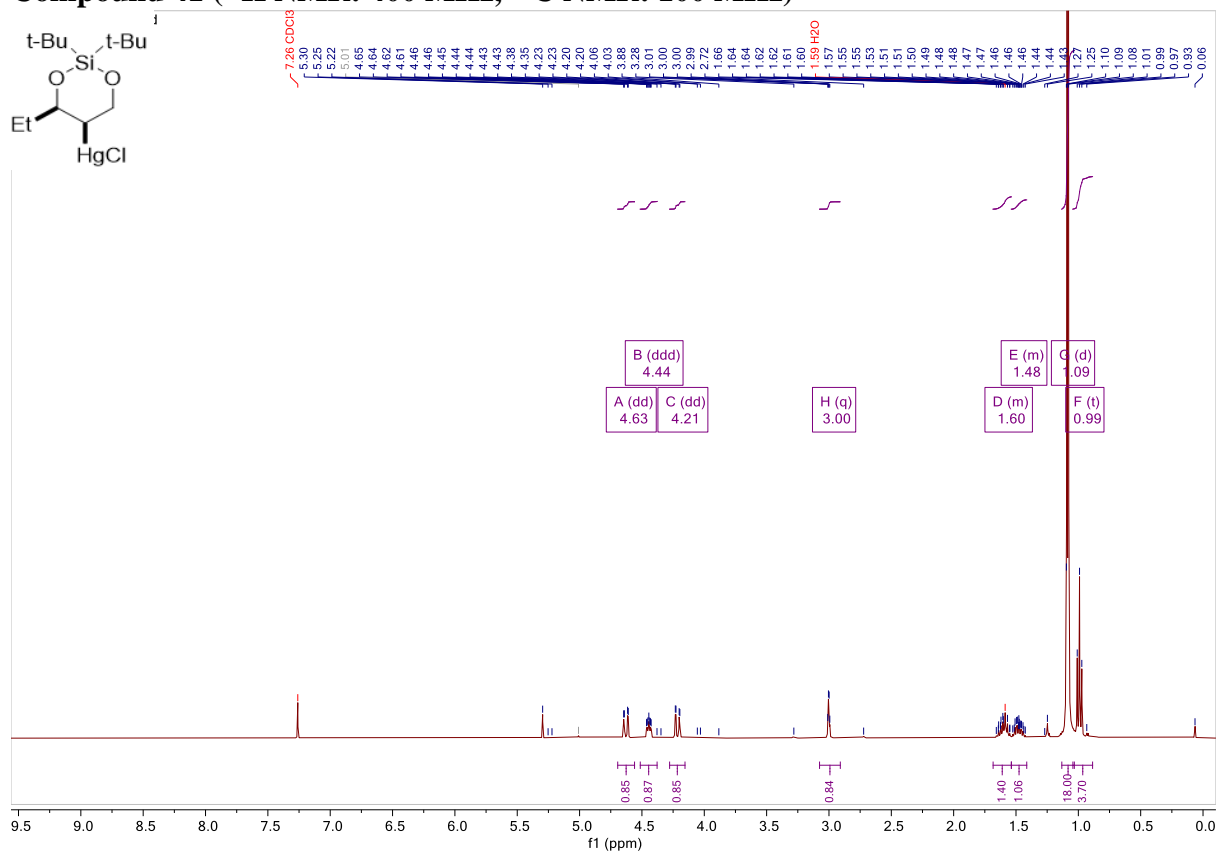
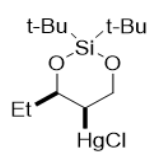
HSQC



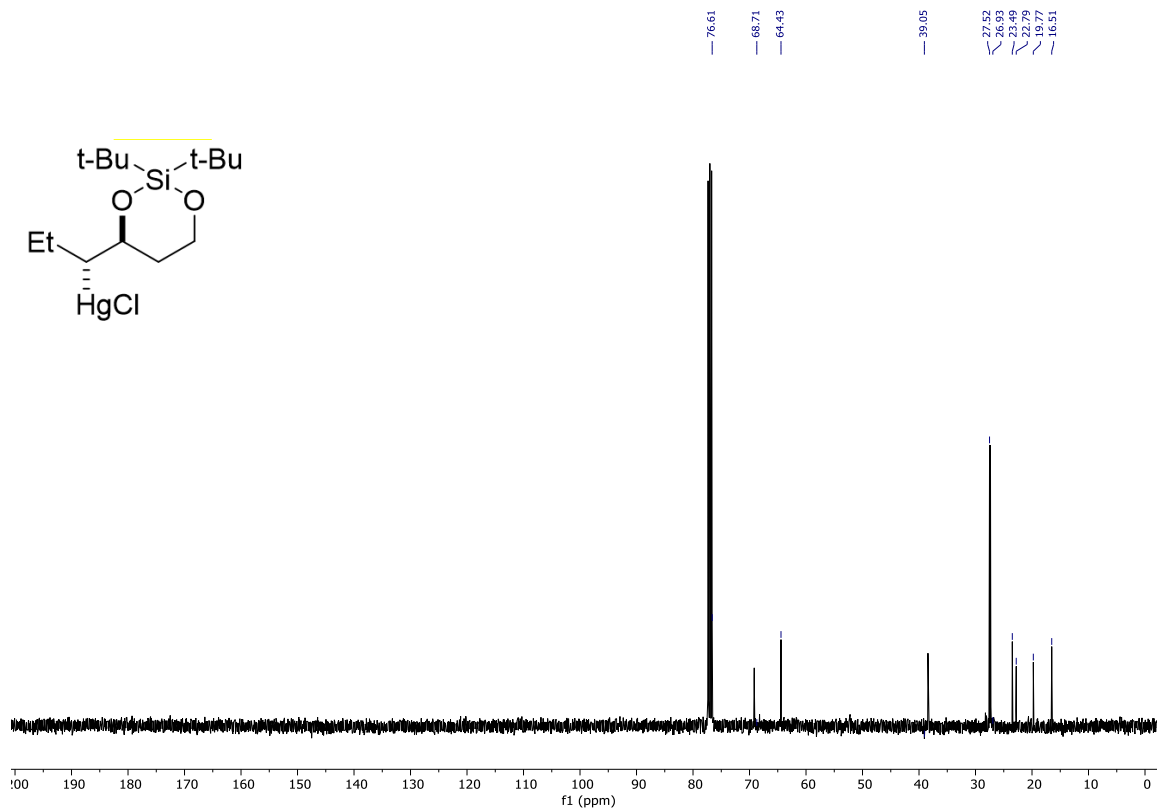
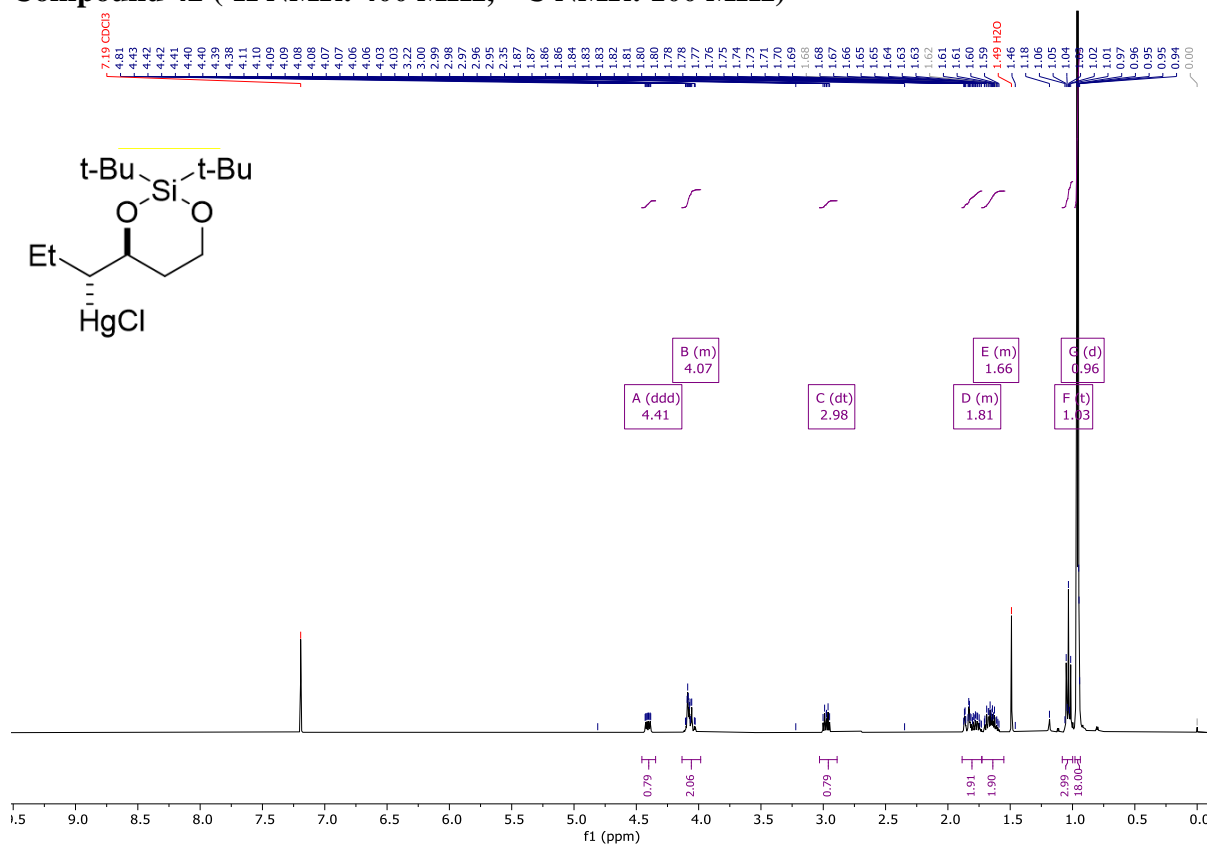
Compound 40 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



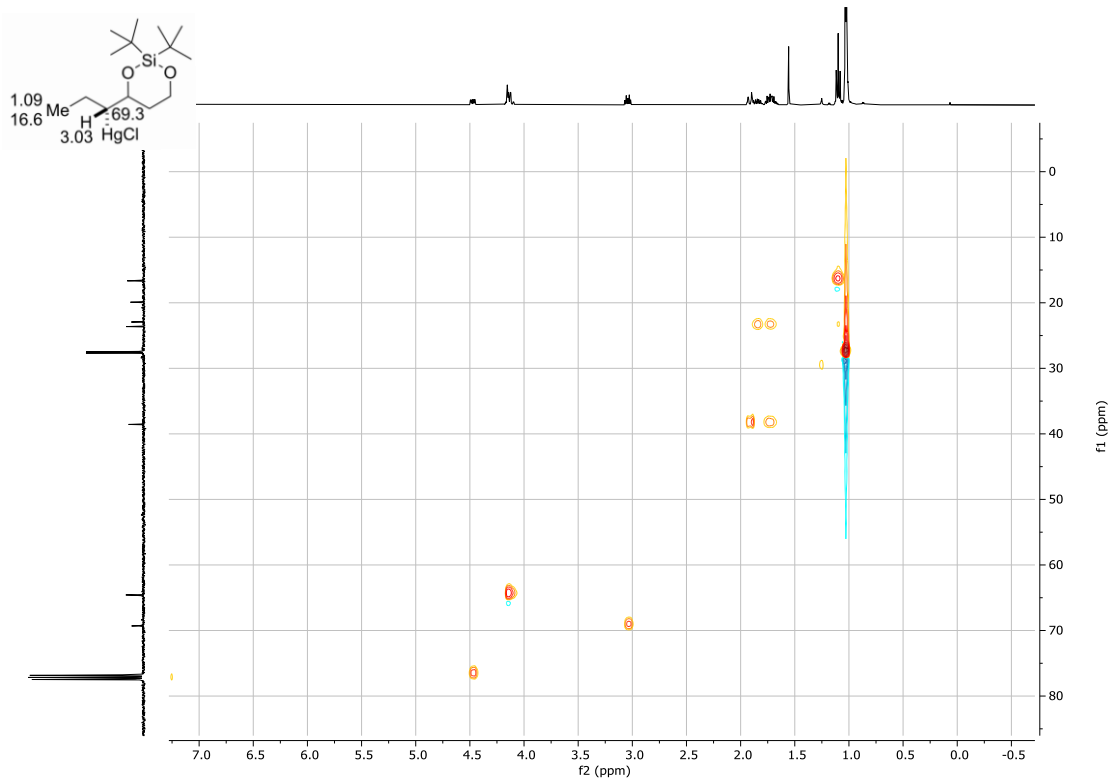
Compound 41 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



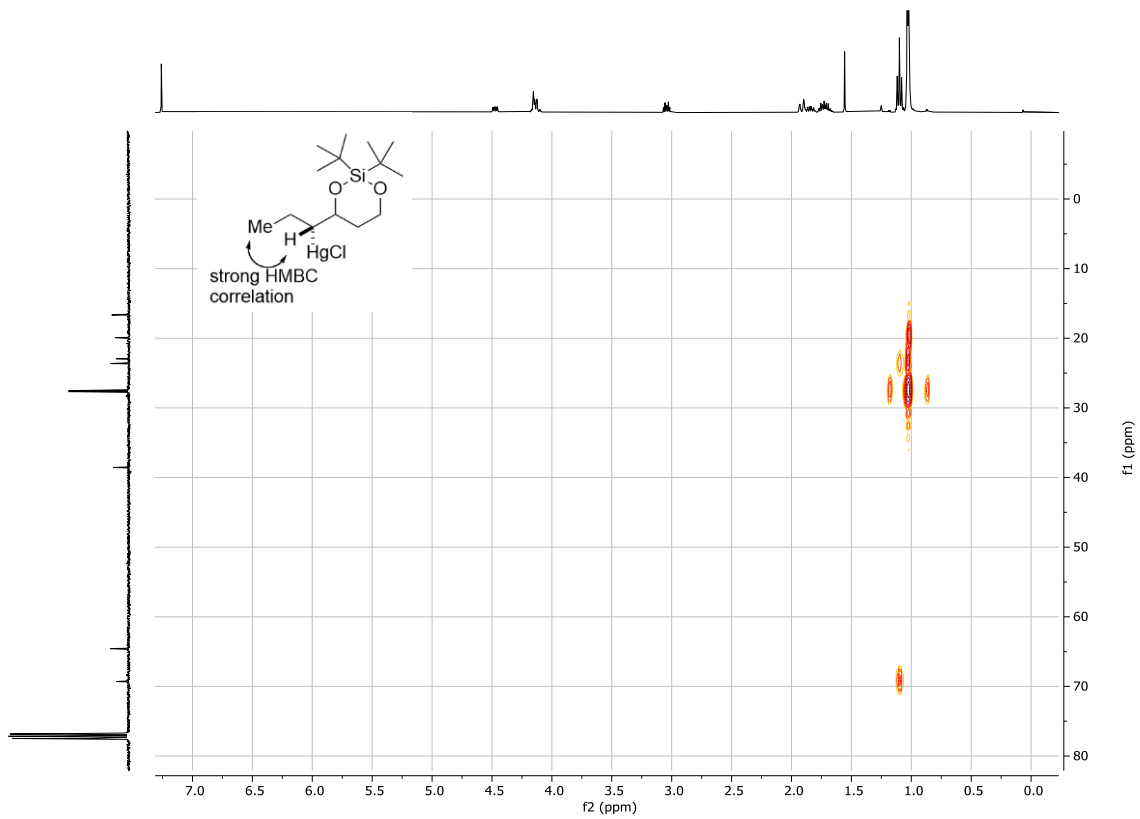
Compound 42 (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz)



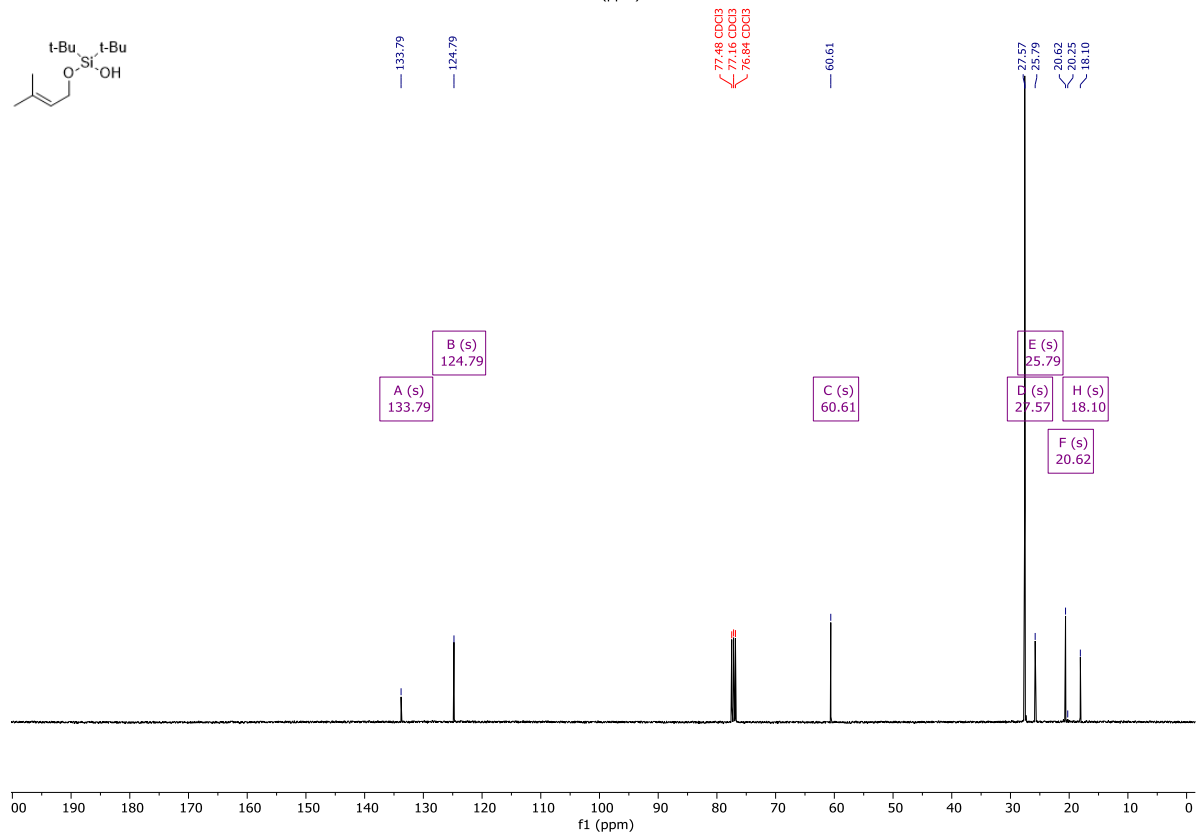
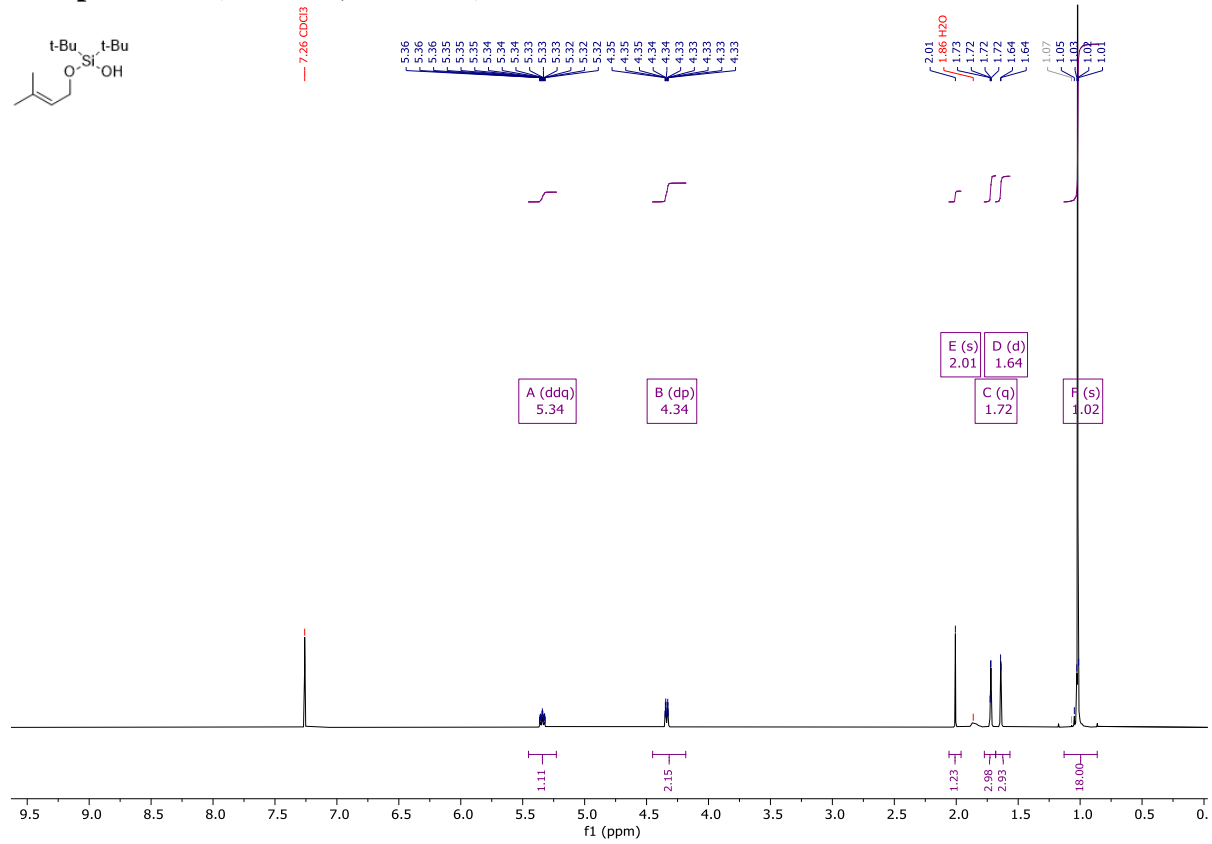
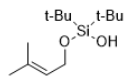
HSQC



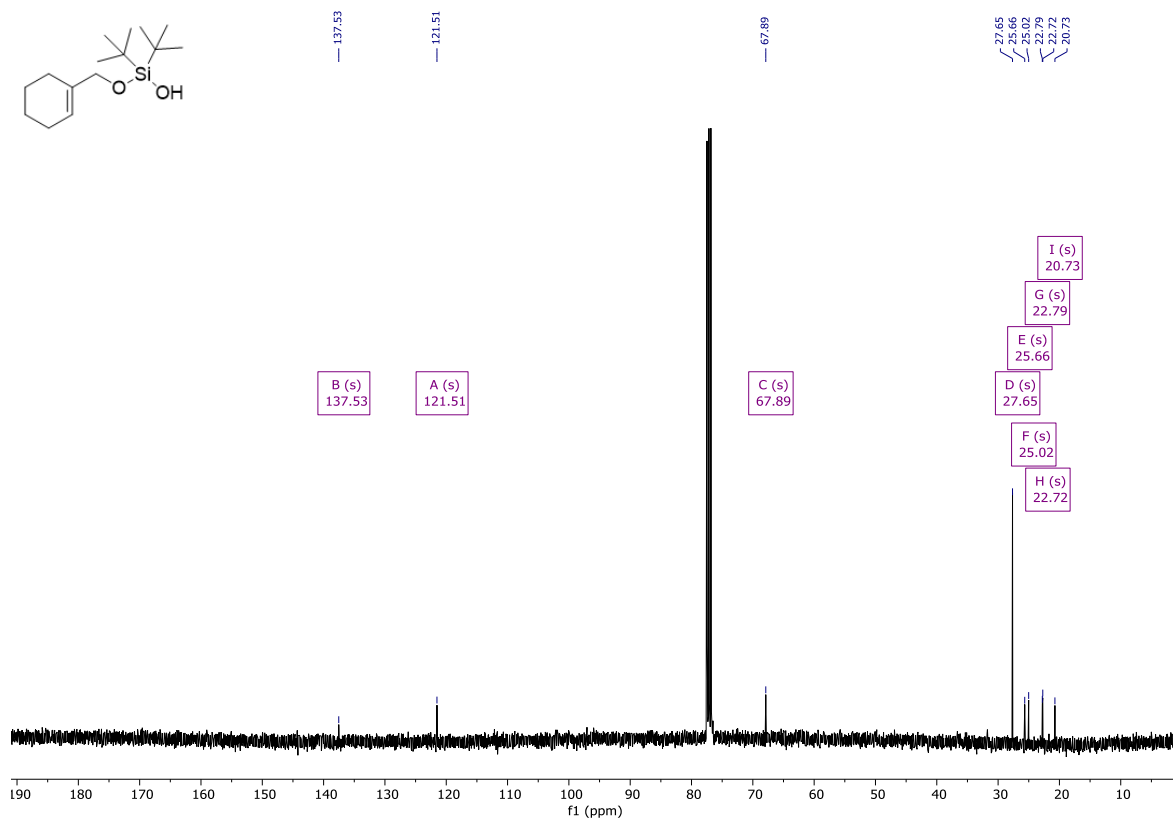
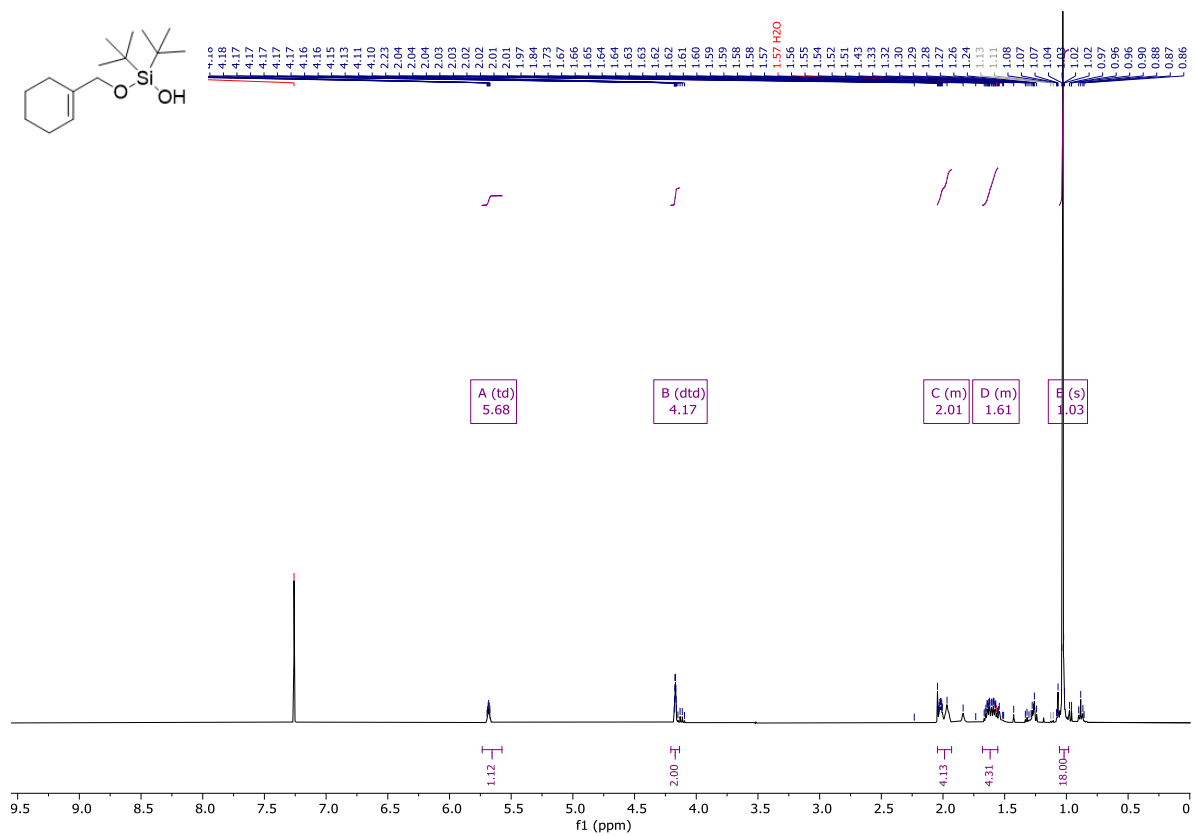
HMBC



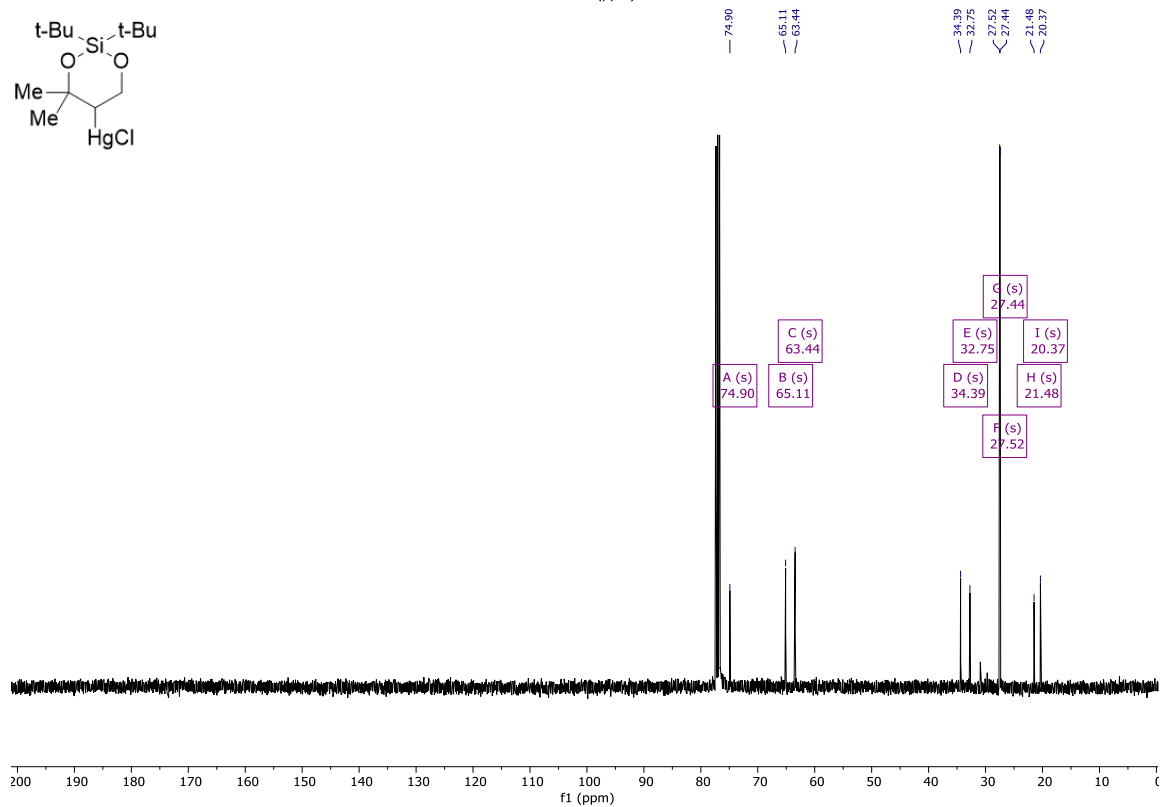
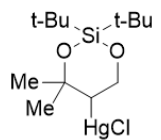
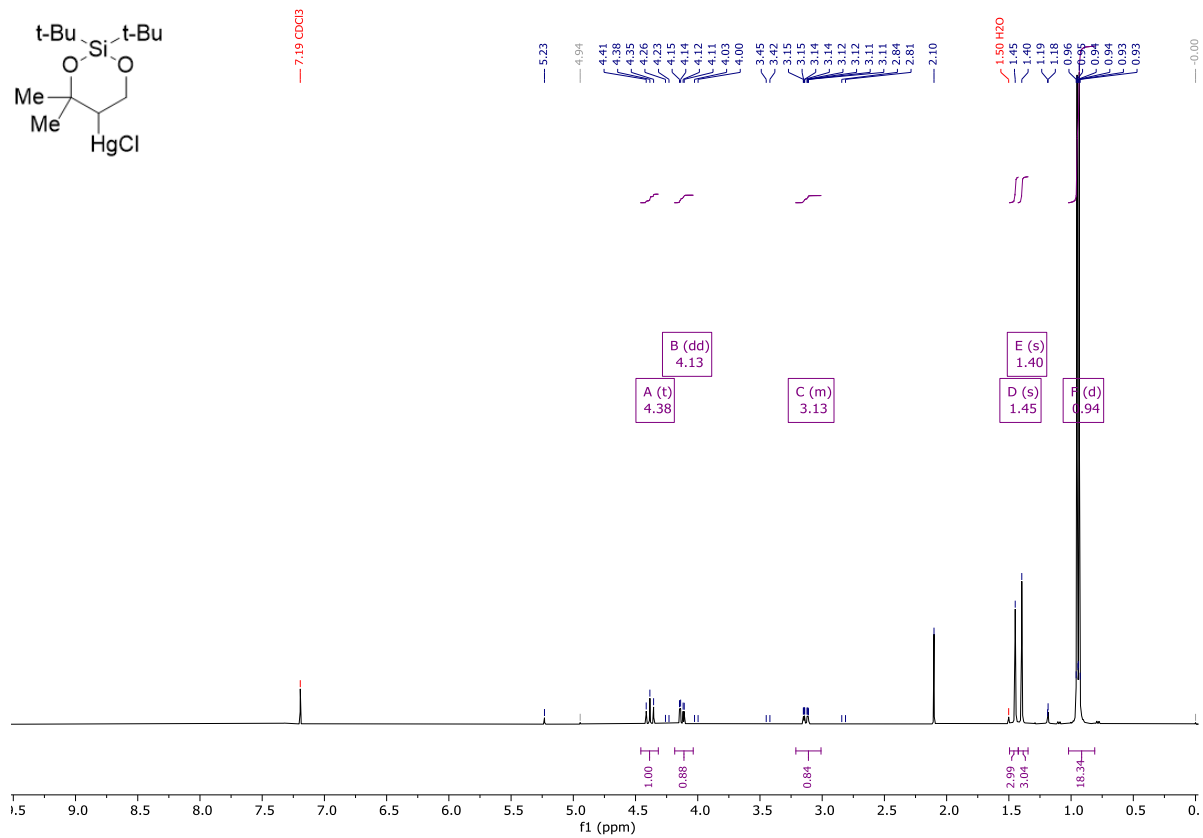
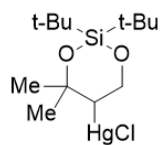
Compound 43 (400 Mhz, 100 Mhz)



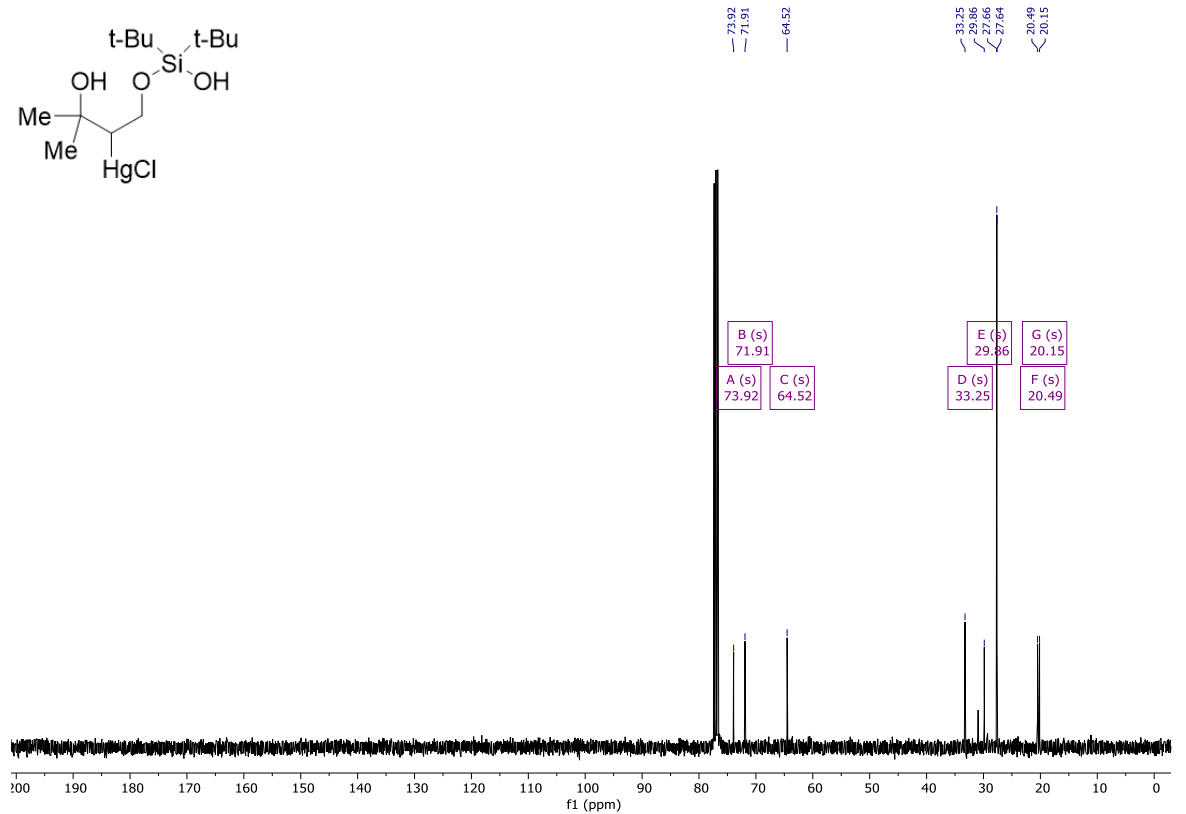
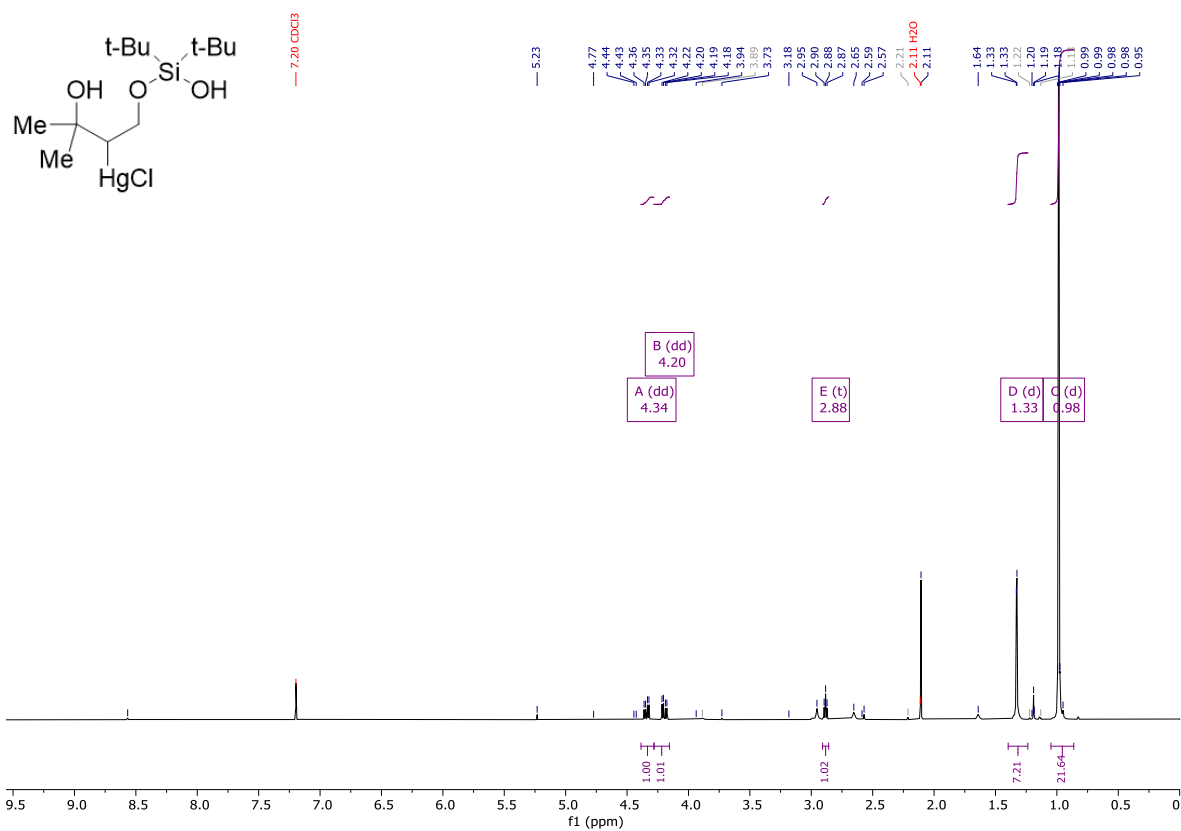
Compound 44 (400 Mhz, 100 Mhz)



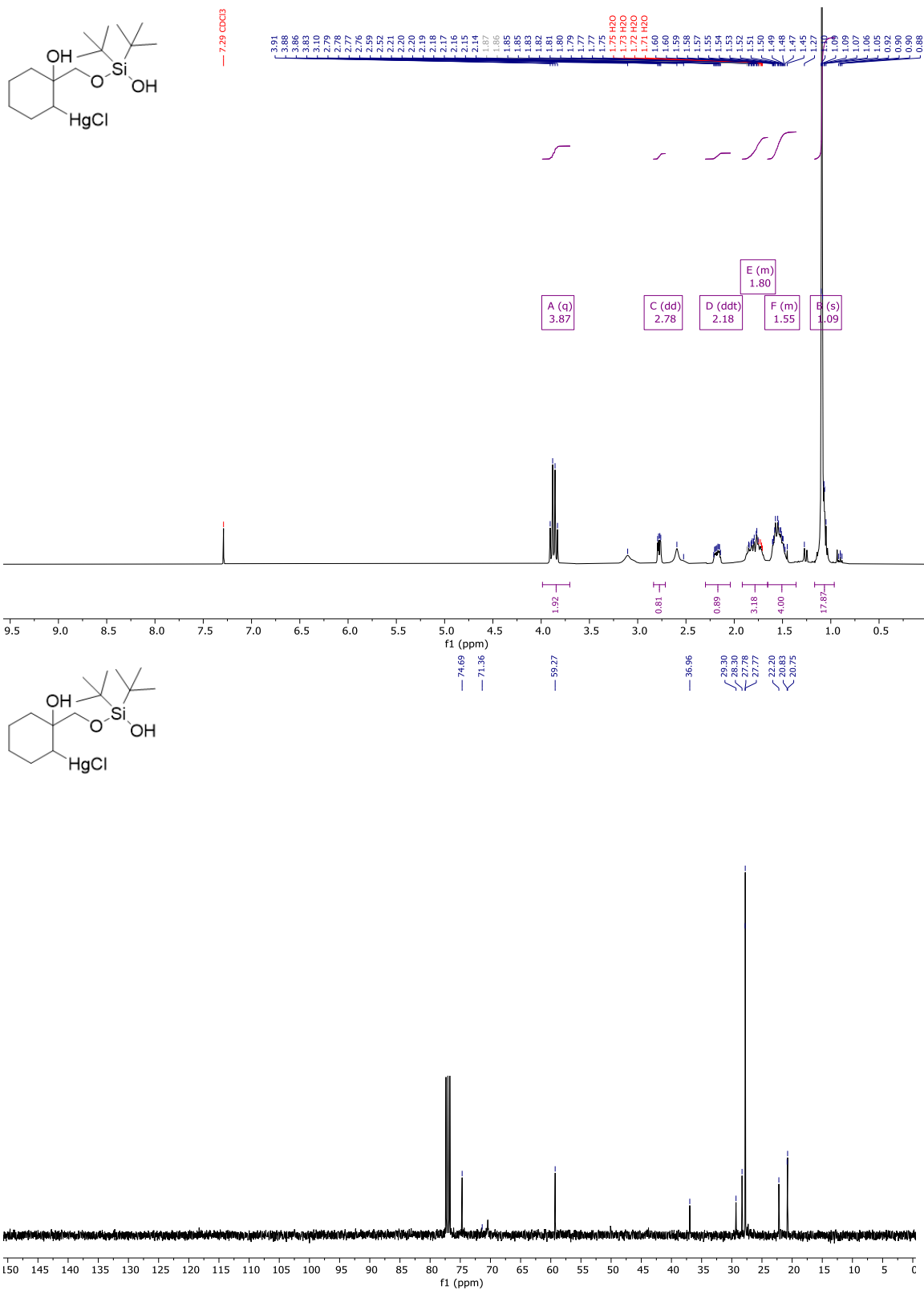
Compound 45 (400 Mhz, 100 Mhz)



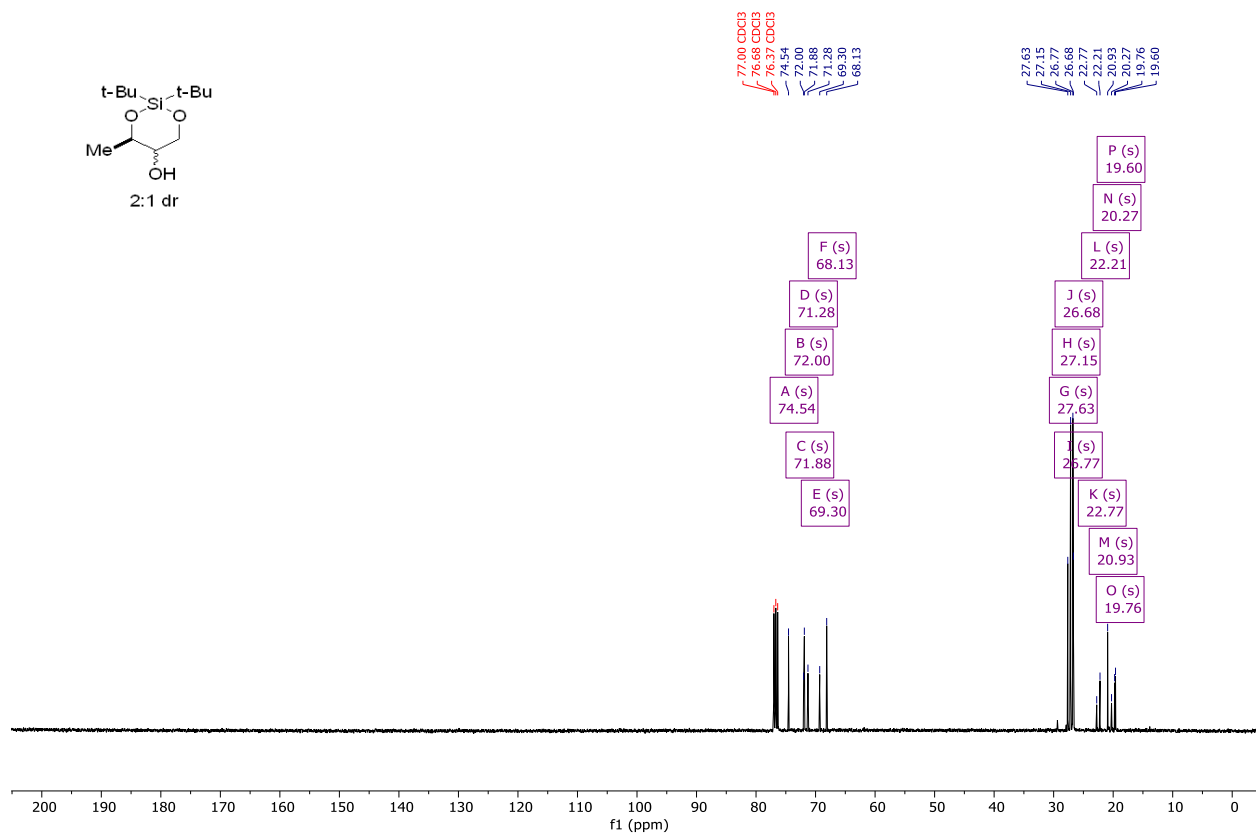
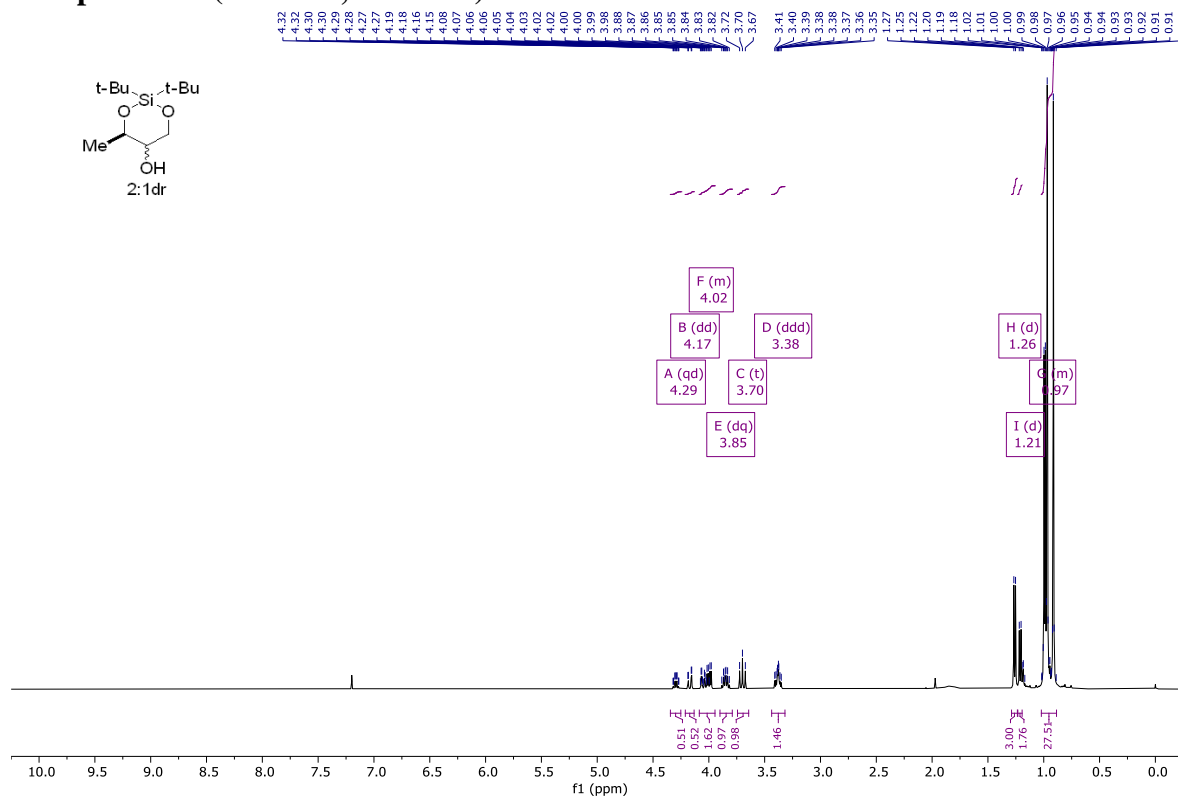
Compound 46 (400 Mhz, 100 Mhz)



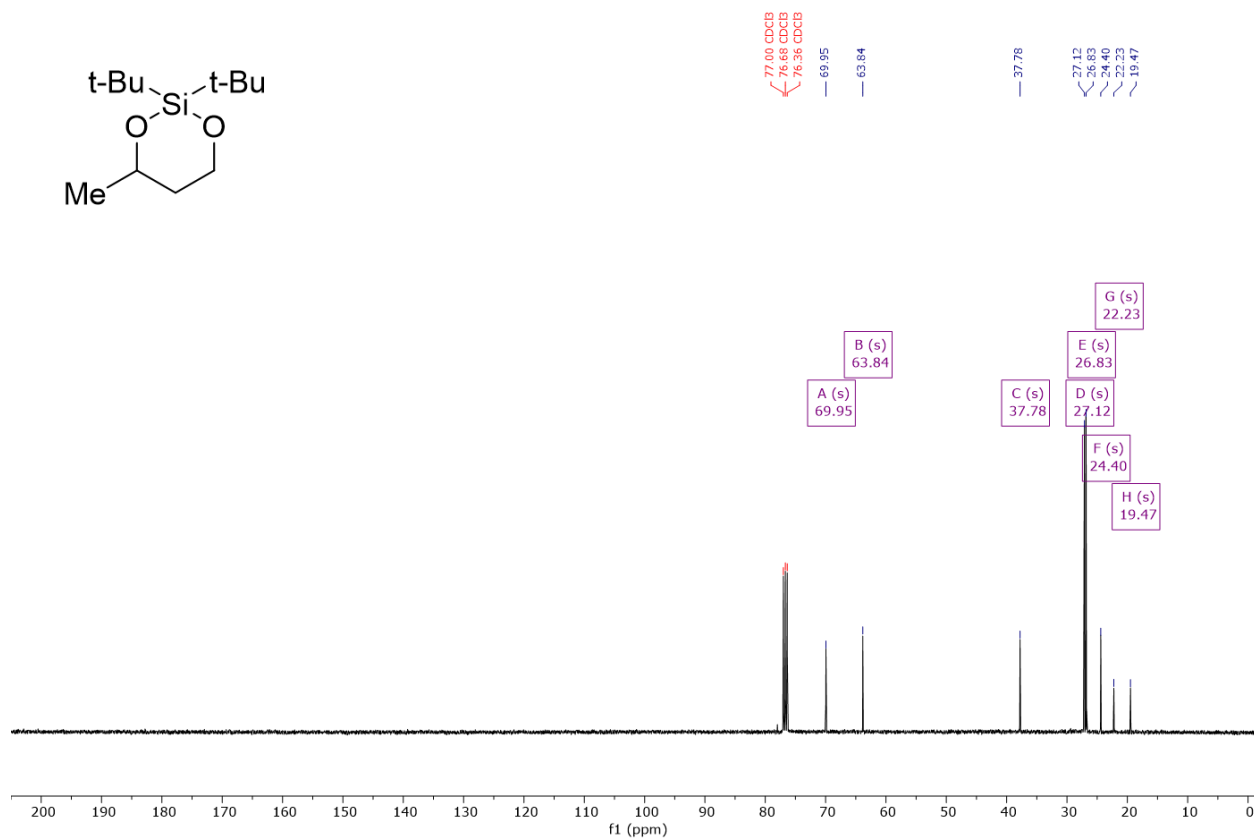
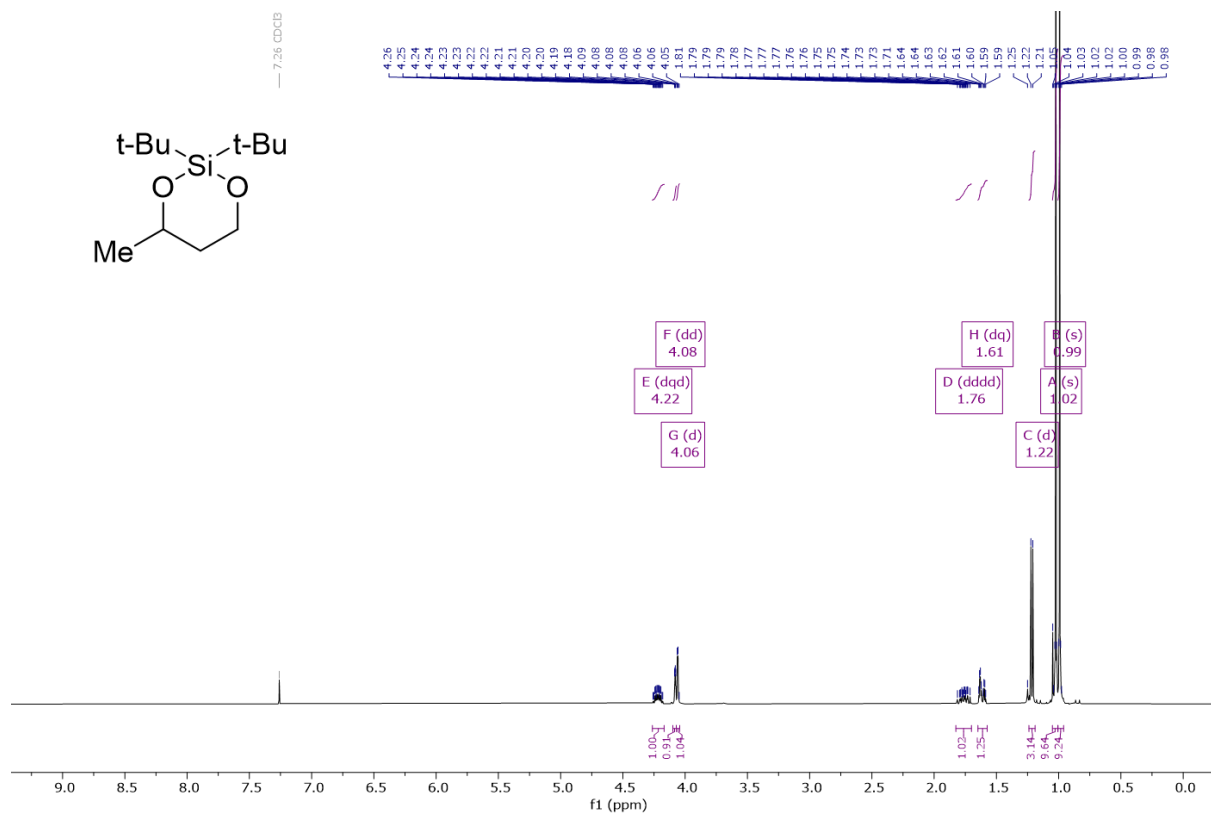
Compound 47 (400 Mhz, 100 Mhz)



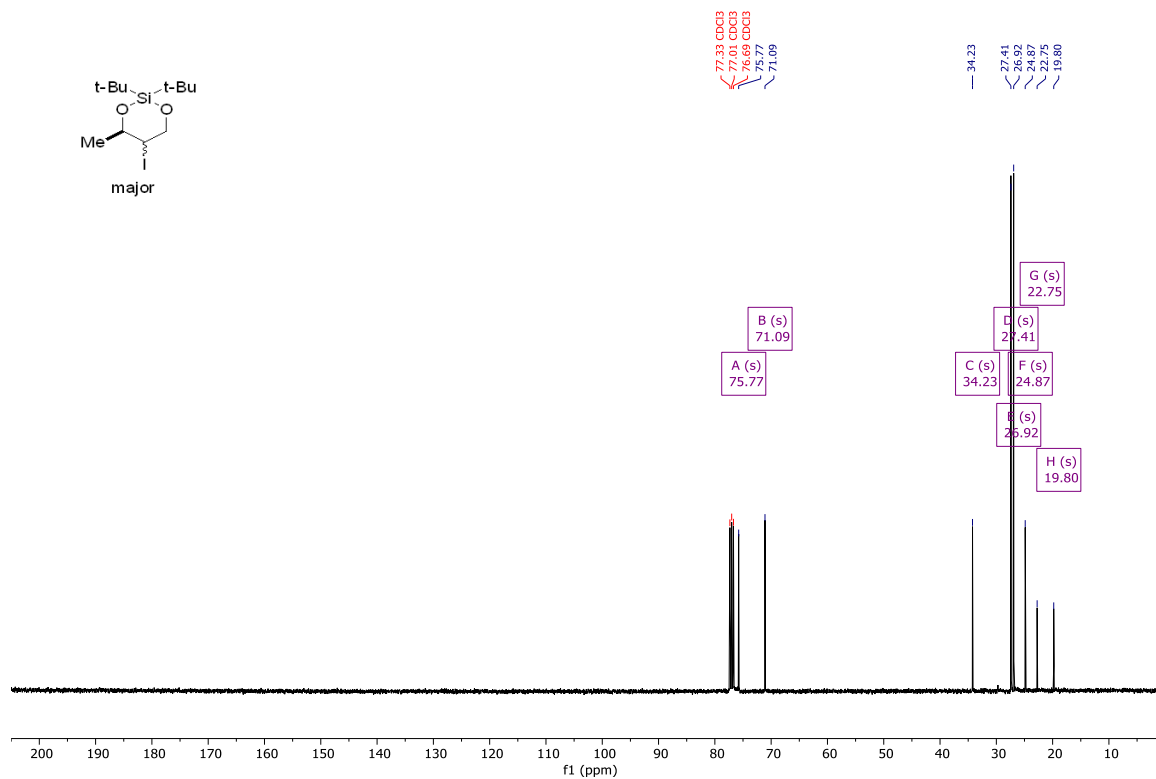
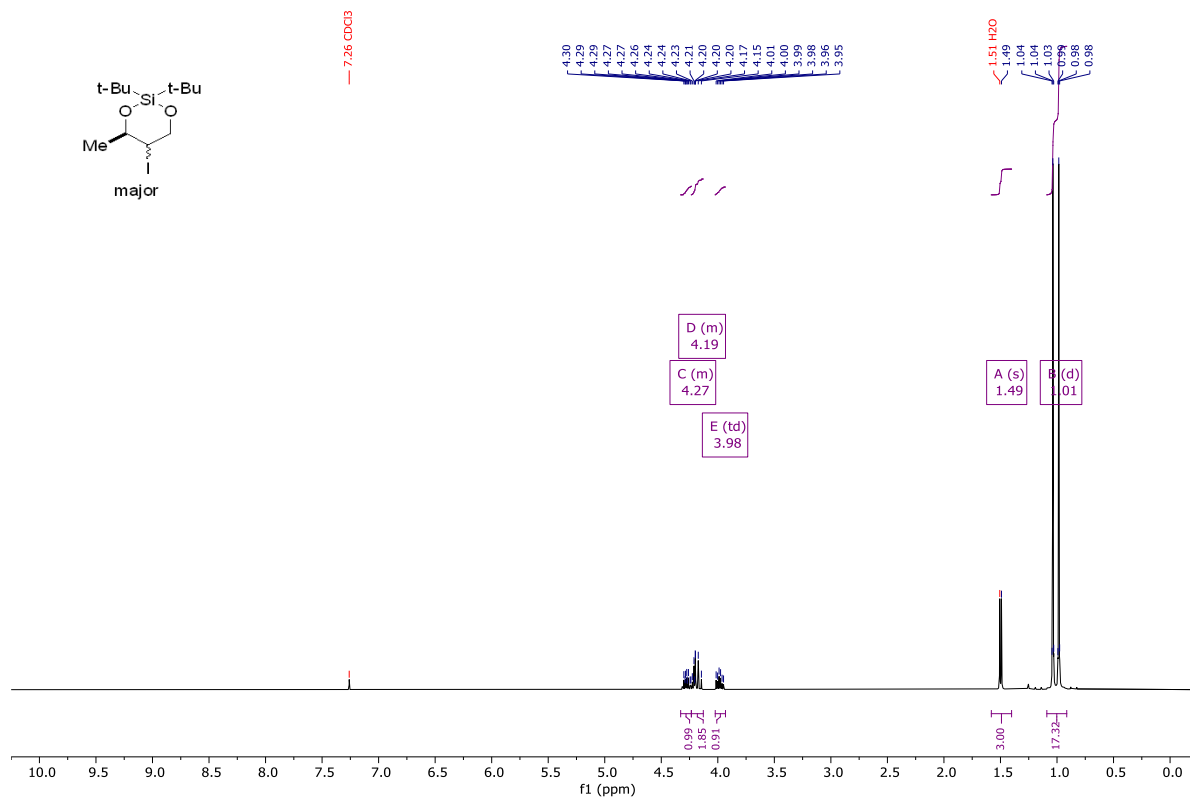
Compound 48 (400 Mhz, 100 Mhz)



Compound 49 (400 Mhz, 100 Mhz)



Compound 50 major diastereomer (400 Mhz, 100 Mhz)



Compound 50, minor diastereomer (400 Mhz, 100 Mhz)

