Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Unusual Rearrangement-Remercuration Reactions of Allylic Silanols

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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). ^{13}C 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 PremierTM 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 $KMnO_4$–K_2CO_3 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.

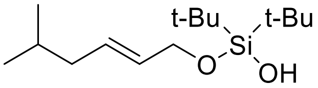
II. Characterization of Allylic Silanol Substrates

Note 1: Substrates were synthesized according to previously reported procedures. See Org. Lett. 2020, 22, 21, 8665–8669.

Compound 1: Previously characterized in *Org. Lett*. **2020**, *22*, 8665–8669

Compound 2: Previously characterized in *Org. Lett*. **2020**, *22*, 8665–8669

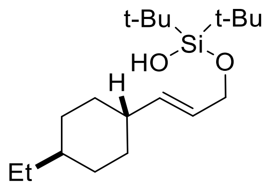
Compound 3: Previously characterized in *Org. Lett*. **2020**, *22*, 8665–8669



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

Compound 4: Purified using a gradient of 0 to 0.2% acetone/DCM on silica gel; (light yellow oil, 272 mg, 50% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 5.69 (dtt, *J* = 15.0, 6.7, 1.3 Hz, 1H), 5.58 (dtt, *J* = 15.3, 5.3, 1.1 Hz, 1H), 4.33 (dq, *J* = 5.1, 1.2 Hz, 2H), 1.95 (tq, *J* = 6.9, 1.1 Hz, 2H), 1.64 (dq, *J* = 13.3, 6.7 Hz, 1H), 1.05 (s, 18H), 0.91 (d, *J* = 6.7 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 130.4, 129.9, 64.1, 41.5, 28.3, 27.4, 22.2, 20.4.; IR 3393, 2895, 1467, 826 cm^{-1}.; HRMS (ESI) calculated for $C_{15}H_{32}NaO_2Si^+$ 295.2064 Found 295.2048 (MNa^+).

Compound 5: Previously characterized in *Org. Lett*. **2020**, *22*, 8665–8669

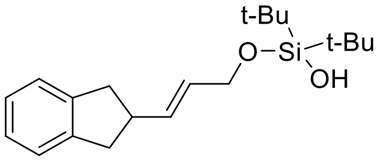


di-*tert*-butyl(((*E*)-3-(4-ethylcyclohexyl)allyl)oxy)silanol

Compound 6: Purified using a gradient of 0 to 0.2% Acetone/DCM on silica gel; (light yellow oil, 312 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (ddt, *J* = 15.4, 6.2, 1.2 Hz, 1H), 5.55 (dtd, *J* = 15.4, 5.2, 1.0 Hz, 1H), 4.32 (dt, *J* = 5.2, 1.1 Hz, 2H), 1.98 – 1.83 (m, 2H), 1.83 – 1.72 (m, 3H), 1.28 – 1.19 (m, 2H), 1.11 (ddt, *J* = 12.4, 8.8, 3.7 Hz, 3H), 1.05 (s, 18H), 1.00 – 0.83 (m, 5H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 137.1, 126.8, 64.3, 40.5, 39.0, 32.8, 32.5, 29.9, 27.4, 20.4, 11.5. IR 3491, 2899, 1470, 1103 cm^{-1}.; HRMS (APCI) calculated for $C_{19}H_{39}O_2Si^+$ 327.2719 Found 327.2705 (MH^+).

Compound 7: Previously characterized in *Molecules* **2021**, *26*, 3829

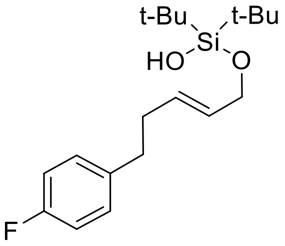
Compound 8: Previously characterized in *J. Org. Chem.* **2021** DOI:10.1021/acs.joc.1c00872



(*E*)-di-*tert*-butyl((3-(2,3-dihydro-1*H*-inden-2-yl)allyl)oxy)silanol

Compound 9: Purified using a gradient of 0 to 0.2% Acetone/DCM on silica gel; (light yellow oil, 300 mg, 45% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.09 (m, 4H), 6.00 – 5.83 (m, 1H), 5.83 – 5.66 (m, 1H), 4.39 (ddt, *J* = 5.2, 3.3, 1.9 Hz, 2H), 3.25 – 3.04 (m, 3H), 2.92 – 2.73 (m, 2H), 1.10 (dd, *J* = 4.7, 2.2 Hz, 18H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.1, 134.3, 128.7, 126.2, 124.3, 64.0, 42.9, 39.4, 27.5, 20.5. IR 3494, 2940, 1467, 1221, 970 cm^{-1}.; HRMS (APCI) Calculated for $C_{20}H_{31}O_2Si^-$ 331.2099 Found 331.2078 (M^-).

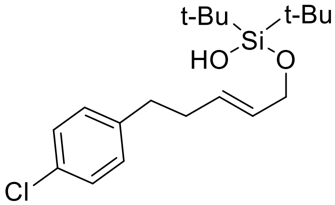
Compound 10: Previously characterized in *Org. Lett*. **2020**, *22*, 8665–8669



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

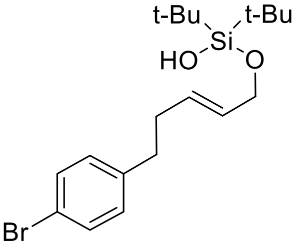
Compound 11: Purified using a gradient of 0 to 0.2% acetone/DCM on silica gel; (light yellow oil, 324 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.06 (m, 2H), 7.04 – 6.87 (m, 2H), 5.73 (dtt, *J* = 15.6, 6.3, 1.4 Hz, 1H), 5.62 (dtt, *J* = 15.3, 5.2, 1.2 Hz, 1H), 4.32 (dq, *J* = 5.0, 1.3 Hz, 2H), 2.70 (dd, *J* = 8.7, 6.7 Hz, 2H), 2.37 (dtd, *J* = 8.7, 6.3, 1.3 Hz, 2H), 1.05 (s, 18H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.2 (d, *J* = 243.1 Hz), 137.4

(d, *J* = 3.2 Hz), 130.2, 129.7 (d, *J* = 7.7 Hz), 129.6, 115.0 (d, *J* = 21.0 Hz), 63.9, 34.8, 34.0, 27.4, 20.5. IR 3982, 2860, 1604, 1473, 1195, 645 cm^{-1}.; HRMS (APCI) calculated for $C_{19}H_{30}FO_2Si^-$ 337.2005 Found 337.1990 (M$^-$).



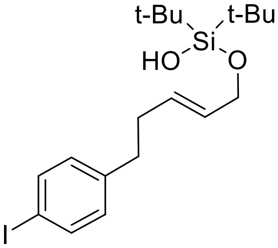
(*E*)-di-*tert*-butyl((5-(4-chlorophenyl)pent-2-en-1-yl)oxy)silanol

Compound 12: Purified using a gradient of 0 to 10% EtOAc in hexanes on silica gel; (white semi-solid, 390 mg, 55%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 5.69 (dtt, *J* = 14.2, 6.4, 1.4 Hz, 1H), 5.63 – 5.54 (m, 1H), 4.29 (dd, *J* = 5.0, 1.3 Hz, 2H), 2.68 (dd, *J* = 8.6, 6.8 Hz, 2H), 2.41 – 2.28 (m, 2H), 1.02 (s, 18H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 140.24, 131.51, 130.29, 129.80, 129.50, 128.37, 63.89, 34.97, 33.74, 27.40, 20.45; IR 2857, 1457, 1170 cm^{-1}.; HRMS (APCI) calculated for $C_{19}H_{30}ClO_2Si^-$ 353.1704, found 353.1674 (M$^-$).



(E)-((5-(4-bromophenyl)pent-2-en-1-yl)oxy)di-tert-butylsilanol

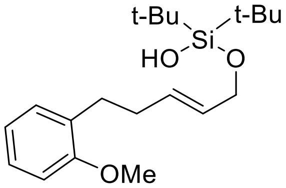
Compound 13: Purified using a gradient of 0 to 2% acetone/CH_2Cl_2 on silica gel; (colorless oil, 400 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.09 – 7.01 (m, 2H), 5.68 (dtt, *J* = 15.5, 6.2, 1.3 Hz, 1H), 5.57 (dtt, *J* = 15.4, 5.2, 1.1 Hz, 1H), 4.28 (dq, *J* = 4.8, 1.2 Hz, 2H), 2.65 (dd, *J* = 8.6, 6.7 Hz, 2H), 2.34 (dtd, *J* = 8.7, 6.4, 1.3 Hz, 2H), 1.01 (s, 18H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 140.9, 131.5, 130.5, 130.4, 129.6, 119.7, 64.0, 35.2, 33.8, 27.6, 20.6. IR 3520, 2860, 1470, 1100 cm^{-1}. HRMS (APCI) calculated for $C_{19}H_{30}BrO_2S^-$ 397.1198 Found 397.1203 (M$^-$).



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

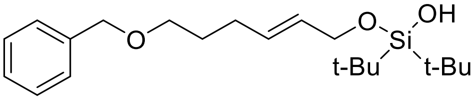
Compound 14: Purified using a gradient of 0 to 0.2% acetone/DCM on silica gel; (colorless oil, 338 mg, 38% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.54 (m, 2H), 7.03 – 6.88 (m, 2H), 5.71 (dtt, *J* = 14.8, 6.6, 1.5 Hz, 1H), 5.61 (dtt, *J* = 15.3, 5.1, 1.3 Hz, 1H), 4.31 (dt, *J* = 5.0, 1.3 Hz, 2H), 2.67 (dd, *J* = 8.6, 6.8 Hz, 2H), 2.43

– 2.30 (m, 2H), 1.12 – 0.95 (m, 18H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 141.4, 137.3, 130.6, 130.3, 129.4, 90.9, 63.9, 35.1, 33.7, 27.4, 20.5. IR 3499, 1473, 1124, 970, 645 cm^{-1}.; HRMS (APCI) calculated for $C_{19}H_{30}IO_2Si^-$ 445.1065 Found 445.1062 (M^-).



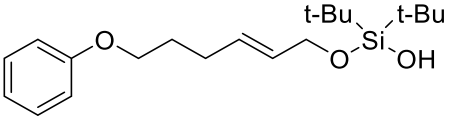
(*E*)-di-*tert*-butyl((5-(2-methoxyphenyl)pent-2-en-1-yl)oxy)silanol

Compound 15: Purification 0 to 10% EtOAc in hexanes under flash chromatography (oil, 518 mg, 74%);^1H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.09 (m, 2H), 6.93 – 6.81 (m, 2H), 5.79 – 5.66 (m, 1H), 5.65-5.55 (m, 1H), 4.30 (dd, *J* = 5.2, 1.3 Hz, 2H), 3.83 (s, 3H), 2.73-2.69 (m, 2H), 2.37-2.31 (m, 2H), 1.03 (s, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.4, 130.8, 130.2, 129.8, 129.5, 127.0, 120.3, 110.3, 64.1, 55.2, 32.2, 30.0, 27.4, 20.4. IR 2857, 1494, 1161 cm^{-1}. HRMS (APCI) calculated for $C_{20}H_{33}O_3Si^-$ 349.2199, found mass 349.2193 (M^-).



(*E*)-((6-(benzyloxy)hex-2-en-1-yl)oxy)di-*tert*-butylsilanol

Compound 16: Purified using a gradient of 0 to 5% acetone/DCM on silica gel; (light yellow oil, 370 mg, 50% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.20 (m, 5H), 5.71 (dddd, *J* = 15.6, 7.6, 4.6, 1.3 Hz, 1H), 5.66 – 5.55 (m, 1H), 4.53 (d, *J* = 1.3 Hz, 2H), 4.32 (dq, *J* = 5.1, 1.3 Hz, 2H), 3.51 (td, *J* = 6.5, 1.2 Hz, 2H), 2.21 – 2.12 (m, 2H), 1.74 (qd, *J* = 7.4, 5.8 Hz, 2H), 1.05 (d, *J* = 1.9 Hz, 18H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.6, 130.4, 129.8, 128.3, 127.6, 127.5, 72.9, 69.7, 64.0, 29.3, 28.8, 27.4, 20.5. IR 3460, 2860, 1473, 1364, 970, 736 cm^{-1}.; HRMS (APCI) calculated for $C_{21}H_{35}O_3Si^-$ 363.2361 Found 363.2356 (M^-).

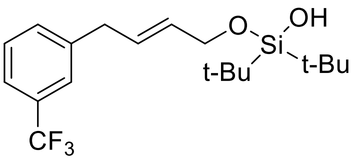


(*E*)-di-*tert*-butyl((6-phenoxyhex-2-en-1-yl)oxy)silanol

Compound 17: Purified using a gradient of 0 to 5% acetone/DCM on silica gel; (light yellow oil, 421 mg, 60% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (ddt, *J* = 8.7, 6.5, 0.9 Hz, 2H), 7.01 – 6.89 (m, 3H), 5.81 – 5.71 (m, 1H), 5.71 – 5.61 (m, 1H), 4.34 (dh, *J* = 5.1, 1.3 Hz, 2H), 4.00 (ddd, *J* = 7.3, 6.1, 1.0 Hz, 2H), 2.27 (dddd, *J* = 10.1, 6.6, 2.4, 1.3 Hz, 2H), 1.97 – 1.86 (m, 2H), 1.13 – 1.00 (m, 18H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.0, 130.2, 129.8, 129.4, 120.5, 114.5, 67.1, 64.0, 28.8, 28.6, 27.4, 20.5. IR 3499, 2860, 1598, 1364, 970, 690 cm^{-1}.; HRMS (APCI) calculated for $C_{20}H_{33}O_3Si^-$ 349.2204 Found 349.2191 (M^-).

Compound 18: Previously characterized in *Org. Lett*. **2020**, *22*, 8665–8669

Compound 19: Previously characterized in *Molecules* **2021**, *26*, 3829



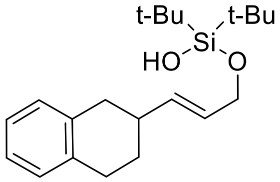
(*E*)-di-*tert*-butyl((4-(3-(trifluoromethyl)phenyl)but-2-en-1-yl)oxy)silanol

Compound 20: Purified using a gradient of 0 to 0.2% acetone/DCM; (light yellow oil, 361 mg, 50% yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 – 7.32 (m, 4H), 5.88 (dtt, *J* = 15.1, 6.7, 1.5 Hz, 1H), 5.69 (dtt, *J* = 15.3, 5.1, 1.4 Hz, 1H), 4.38 (dq, *J* = 5.1, 1.3 Hz, 2H), 3.47 (dd, *J* = 6.8, 1.5 Hz, 2H), 1.05 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 141.2, 131.9 (d, *J* = 1.5 Hz), 131.6, 131.1 – 130.1 (q, *J* = 34 Hz), 128.7, 128.3, 125.5 (q, *J* = 275 Hz), 125.2 (q, *J* = 3.8 Hz), 122.9 (q, *J* = 4.0 Hz), 63.7, 38.2, 27.3, 20.4. IR 3477, 1473, 1330, 1073, 970, 650 cm^{-1}.; HRMS (APCI) calculated for $C_{19}H_{28}F_3O_2Si^-$ 373.1816 Found 373.1798 (M^-).

Compound 21: Previously characterized in *Molecules* **2021**, *26*, 3829

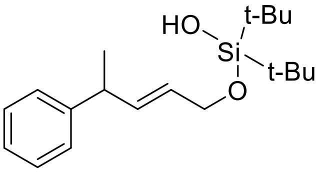
Compound 22: Previously characterized in *Molecules* **2021**, *26*, 3829

Compound 23: Previously characterized in *Molecules* **2021**, *26*, 3829



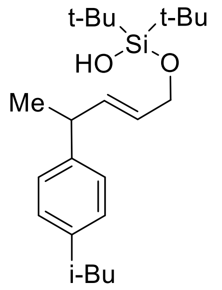
(*E*)-di-*tert*-butyl((3-(1,2,3,4-tetrahydronaphthalen-2-yl)allyl)oxy)silanol

Compound 24: Purified using a gradient of 0 to 0.2% acetone/DCM on silica gel; (light yellow oil, 265 mg, 49% yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.09 (dq, *J* = 4.6, 2.2 Hz, 4H), 5.82 – 5.69 (m, 1H), 5.65 (dtd, *J* = 15.5, 5.1, 1.1 Hz, 1H), 4.34 (dt, *J* = 5.1, 1.2 Hz, 2H), 2.95 – 2.75 (m, 3H), 2.61 (dd, *J* = 16.3, 10.5 Hz, 1H), 2.45 (d, *J* = 10.4 Hz, 1H), 2.03 – 1.93 (m, 1H), 1.64 – 1.49 (m, 1H), 1.03 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 136.4, 136.2, 135.3, 129.1, 128.9, 128.1, 125.6, 125.5, 64.2, 36.8, 35.6, 29.3, 28.8, 27.5, 20.5. IR 3507, 2857, 1463, 1099 cm^{-1}.; HRMS (APCI) calculated for $C_{21}H_{33}O_2Si^-$ 345.2250 Found 345.2248 (M^-).



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

Compound 25: Purified using a gradient of 0 to 0.2% acetone/DCM; (light yellow oil, 320 mg, 50% yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 – 7.27 (m, 3H), 7.22 (ddd, *J* = 7.2, 5.4, 3.0 Hz, 2H), 5.90 (ddt, *J* = 15.4, 6.7, 1.5 Hz, 1H), 5.62 (dtd, *J* = 15.4, 5.4, 1.4 Hz, 1H), 4.36 (dt, *J* = 5.4, 1.3 Hz, 2H), 3.51 (p, *J* = 7.0 Hz, 1H), 1.40 (d, *J* = 7.1 Hz, 3H), 1.04 (2 overlapping singlets, 18H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 145.8, 135.6, 128.4, 128.2, 127.2, 126.1, 64.0, 41.8, 27.4, 21.2, 20.5. IR 3360, 2940, 1474, 1013, 826 cm^{-1}. HRMS (ESI) calculated for $C_{19}H_{32}O_2SiNa^+$ 343.2064 Found 343.2042 (MNa^+).



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

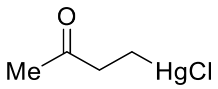
Compound 26: Purified using a gradient of 0-10% EtOAc/Hexanes on silica gel; (white solid, 301 mg, 40% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 5.86 (ddt, *J* = 15.4, 6.7, 1.5 Hz, 1H), 5.59 (dtd, *J* = 15.3, 5.4, 1.4 Hz, 1H), 4.33 (dt, *J* = 5.4, 1.3 Hz, 2H), 3.46 (p, *J* = 6.8 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.85 (m, 1H), 1.36 (d, *J* = 7.0 Hz, 3H), 1.03 (s, 9H), 1.01 (s, 9H), 0.90 (d, *J* = 6.6 Hz, 6H).; ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 143.0, 139.3, 136.0, 129.1, 128.0, 126.8, 64.1, 45.0, 41.4, 30.2, 27.8, 27.4, 22.3, 21.2, 20.4.; IR 3497, 2959, 1468, 1070, 826 cm^{-1}. HRMS (ESI) calculated for $C_{23}H_{39}O_2Si^-$ 375.2719 found 375.2740 (M$^-$).

III. General Procedures for Formation of Ketone Organomercurial Products

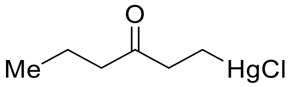
Protocol A: A 5 mL microwave vial was charged with a stir bar, CF_3CO_2Na (0.15 mmol, 20 mg, 1.5 equiv.) and $Hg(OTf)_2$ (0.15 mmol, 75 mg, 1.5 equiv.). 1 mL of NO_2Me was added, and the reaction flask was cooled to 0 °C with an ice-water bath. Allylic silanol (0.1 mmol) was dissolved in 1 mL of NO_2Me and added to the reaction flask. Following addition, the flask was sealed, and the reaction was kept for 2h at 0°C with magnetic stirring. Following this period, the seal was broken, and 2 mL of brine (saturated aqueous NaCl) solution was slowly added. The heterogenous mixture was allowed to stir for 5 minutes and then transferred to a separatory funnel. An additional 10 mL of brine were added followed by 10 mL of CH_2Cl_2. The organic portion was collected, and the aqueous layer was extracted with two additional portions of CH_2Cl_2. The organic fractions were pooled, dried with $MgSO_4$, and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel (specific conditions are associated with each compound).

Protocol B: A 5 mL microwave vial was charged with a stir bar, CF_3CO_2Na (0.15 mmol, 20 mg, 1.5 equiv.) and $Hg(OTf)_2$ (0.15 mmol, 75 mg, 1.5 equiv.). 1 mL of THF was added, and the reaction flask was cooled to 0 °C with an ice-water bath. Allylic silanol (0.1 mmol) was dissolved in 1 mL of THF and added to the reaction flask. Following addition, the flask was sealed, and the reaction warmed to room temperature over a period of 12h with magnetic stirring. Following this period, the seal was broken, and 2 mL of brine (saturated aqueous NaCl) solution was slowly added. The heterogenous mixture was allowed to stir for 5 minutes and then transferred to a separatory funnel. An additional 10 mL of brine were added followed by 10 mL of CH_2Cl_2. The organic portion was collected, and the aqueous layer was extracted with two additional portions of CH_2Cl_2. The organic fractions were pooled, dried with $MgSO_4$, and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel (specific conditions are associated with each compound).

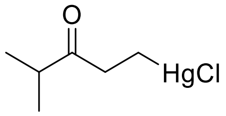
IV. Characterization of Ketone Organomercurial Products


(3-oxobutyl)mercury(II) chloride

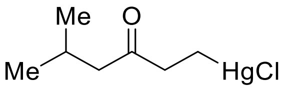
Compound 27: Synthesized using Protocol A; Purified using a gradient of 0 to 2% acetone/CH_2Cl_2 on silica gel; (white solid, 21 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (td, *J* = 6.7, 0.6 Hz, 2H), 2.20 (s, 3H), 1.70 (t, *J* = 6.7 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.7, 41.7, 30.2, 20.7. IR 1704, 1651, 1361, 1174 cm^{-1}.


(3-oxohexyl)mercury(II) chloride

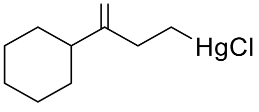
Compound 28: Synthesized using Protocol A; Purified using a gradient of 5 to 15% ethyl acetate/hexanes on silica gel; (white solid, 26 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (t, *J* = 6.7 Hz, 2H), 2.42 (t, *J* = 7.3 Hz, 2H), 1.73 – 1.58 (m, 4H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.1, 45.1, 40.7, 20.6, 17.5, 13.9. IR 1704, 1651, 1361, 1174 cm^{-1}.


(4-methyl-3-oxopentyl)mercury(II) chloride

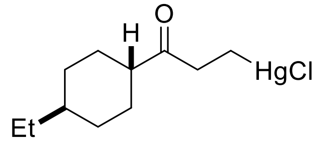
Compound 29: Synthesized using Protocol A; Purified using a gradient of 0 to 2% acetone/DCM on silica gel; (light yellow oil, 23 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (t, *J* = 6.7 Hz, 2H), 2.67 – 2.58 (m, 1H), 1.71 (t, *J* = 6.7 Hz, 2H), 1.12 (dd, *J* = 7 Hz, 1.3 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 215.8, 41.4, 38.4, 20.9, 18.5. IR 1699, 1487, 1057, 904 cm^{-1}.


(5-methyl-3-oxohexyl)mercury(II) chloride

Compound 30: Synthesized using Protocol A; Purified using a gradient of 0 to 20% acetone/hexanes on silica gel; (light yellow oil, 30 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (t, *J* = 6.7 Hz, 2H), 2.35 (d, *J* = 7.0 Hz, 2H), 2.24 – 2.12 (m, 1H), 1.72 (t, *J* = 6.7 Hz, 2H), 0.95 (d, *J* = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 211.6, 52.0, 41.1, 24.8, 22.6, 20.4. IR 2957, 1701, 1364 cm^{-1}.; HRMS (APCI) calculated for $C_7H_{14}ClHgO^+$ 351.0434 Found 350.0350 (M+).

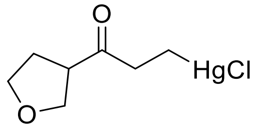

(3-cyclohexyl-3-oxopropyl)mercury(II) chloride

Compound 31: Synthesized using Protocol B; Purified using a gradient of 0 to 2% acetone/CH_2Cl_2 on silica gel; (light yellow oil, 26 mg, 70% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 2.96 (t, *J* = 6.7 Hz, 2H), 2.35 (tt, *J* = 11.3, 3.5 Hz, 1H), 1.85 – 1.77 (m, 4H), 1.70 (d, *J* = 6.7 Hz, 2H), 1.41 – 1.19 (m, 6H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 215.1, 51.3, 38.7, 28.7, 25.9, 25.7, 20.8. IR 1665, 1540, 1147, 1064 cm^{-1}. HRMS (APCI) calculated for $C_9H_{16}ClHgO^+$ 377.0596 Found 377.0604 (MH^+).



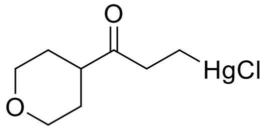
(3-(4-ethylcyclohexyl)-3-oxopropyl)mercury(II) chloride

Compound 32: Synthesized using Protocol B; Purified using a gradient of 0 to 1% acetone/CH_2Cl_2 on silica gel; (white solid, 30 mg, 78% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 2.97 (t, *J* = 6.6 Hz, 2H), 2.30 (tt, *J* = 12.2, 3.3 Hz, 1H), 1.86 (ddq, *J* = 11.1, 6.3, 2.8 Hz, 4H), 1.69 (t, *J* = 6.7 Hz, 2H), 1.47 – 1.18 (m, 4H), 1.18 – 1.00 (m, 1H), 1.00 – 0.91 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 210.7, 139.8, 131.8, 130.3, 120.2, 44.3, 41.2, 29.3, 20.6. IR 2930, 1698, 1540, 1103 cm^{-1}.



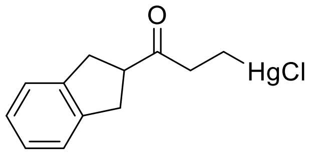
(3-oxo-3-(tetrahydrofuran-3-yl)propyl)mercury(II) chloride

Compound 33: Synthesized using Protocol B; Purified using a gradient of 0 to 0.2% MeOH/DCM on silica gel; (white semi-solid, 17 mg, 48% yield); ^1H NMR (400 MHz, Chloroform-*d*) δ 4.01 – 3.74 (m, 4H), 3.28-3.19 (m, 1H), 3.10-2.95 (m, 2H), 2.15-2.10 (m, 2H), 1.74 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.2, 69.4, 68.3, 51.2, 40.1, 28.9, 20.6. IR 2870, 1471, 1732, 1153 cm^{-1}. HRMS (APCI) calculated for $C_7H_{12}ClHgO_2^+$ 365.0232, Found 365.0273 (MH+).



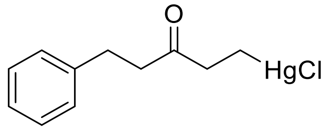
(3-oxo-3-(tetrahydro-2*H*-pyran-4-yl)propyl)mercury(II) chloride

Compound 34: Synthesized using Protocol B; Purified using a gradient of 0 to 2% acetone/CH_2Cl_2 on silica gel; (light yellow oil, 18 mg, 50% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 4.01 (ddd, *J* = 11.4, 3.8, 2.5 Hz, 2H), 3.48 – 3.40 (m, 2H), 2.99 (t, *J* = 6.6 Hz, 2H), 2.60 – 2.53 (m, 1H), 1.76 – 1.68 (m, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 213.0, 67.3, 48.1, 38.4, 28.4, 20.7. IR 2946, 2847, 1714, 1455 cm^{-1}. HRMS (APCI) calculated for $C_8H_{14}ClHgO^+$ 379.0389 Found 379.0419 (MH^+).



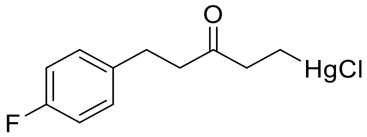
(3-(2,3-dihydro-1*H*-inden-2-yl)-3-oxopropyl)mercury(II) chloride

Compound 35: Synthesized using Protocol A; Purified using a gradient of 0 to 2% acetone/CH_2Cl_2 on silica gel; (white solid, 28 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 4H), 3.45 (dd, *J* = 9.1, 8.0 Hz, 1H), 3.22 – 3.19 (m, 2H), 3.18 (d, *J* = 2.6 Hz, 2H), 3.07 (t, *J* = 6.7 Hz, 2H), 1.75 (t, *J* = 6.7 Hz, 2H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.7, 141.3, 126.9, 124.6, 51.6, 39.5, 35.4, 20.9. IR 2923, 2853, 1704, 1455, 1065 cm^{-1}.



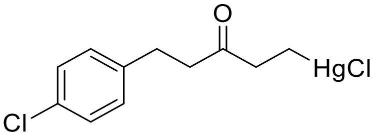
(3-oxo-5-phenylpentyl)mercury(II) chloride

Compound 36: Synthesized using Protocol B; Purified using a gradient of 0 to 2% acetone/CH_2Cl_2 on silica gel; (colorless oil, 18 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 7.2, 1.1 Hz, 2H), 7.22 – 7.15 (m, 3H), 2.96 – 2.84 (m, 4H), 2.77 (dd, *J* = 7.2, 0.8 Hz, 2H), 1.67 (t, *J* = 6.7 Hz, 2H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 211.2, 140.7, 128.8, 128.4, 126.5, 44.6, 41.2, 30.1, 20.6. IR 2930, 2857, 1717, 1488, 1003 cm^{-1}.



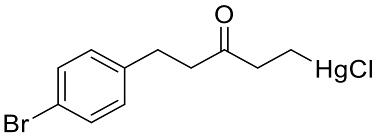
(5-(4-fluorophenyl)-3-oxopentyl)mercury(II) chloride

Compound 37: Synthesized using Protocol A; Purified using a gradient of 0 to 0.2% acetone/DCM on silica gel; (white solid, 22 mg, 58% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 – 7.03 (m, 2H), 6.94 – 6.87 (m, 2H), 2.86 – 2.78 (m, 4H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.61 (t, *J* = 6.6 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 210.8, 161.4 (d, *J* = 244.3 Hz), 136.2 (d, *J* = 3.0 Hz), 129.7 (d, *J* = 7.8 Hz), 115.4 (d, *J* = 21.4 Hz), 44.5, 41.0, 29.0, 20.4. IR 2929, 1701, 1507, 1404, 1079, 827 cm^{-1}.



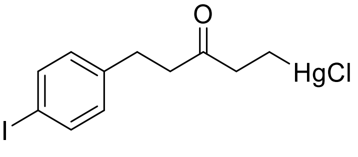
(5-(4-chlorophenyl)-3-oxopentyl)mercury(II) chloride

Compound 38: Synthesized using Protocol A; Purified using a gradient of 0 to 0.2% MeOH/DCM on silica gel; (white semi-solid, 21 mg, 49% yield); Purification 0 to 0.2% MeOH in dichloromethane under flash chromatography (White semi-solid, 49%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 2.93-2.86 (m, 4H), 2.75 (t, *J* = 7.4 Hz, 2H), 1.69 (t, *J* = 6.7 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 210.6, 139.0, 132.0, 129.6, 128.7, 44.2, 41.0, 29.1, 20.4. IR 2856, 1455, 1704, 1091 cm^{-1}.



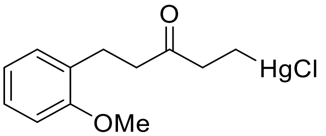
(5-(4-bromophenyl)-3-oxopentyl)mercury(II) chloride

Compound 39: Synthesized using Protocol A; Purified using a gradient of 0 to 1% acetone/CH_2Cl_2 on silica gel; (white solid, 33 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 2.91 – 2.85 (m, 4H), 2.76 – 2.72 (m, 2H), 1.68 (t, *J* = 6.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 210.7, 139.8, 131.8, 130.3, 120.2, 44.3, 41.1, 29.3, 20.6. IR 2931, 2860, 1704, 1071 cm^{-1}.



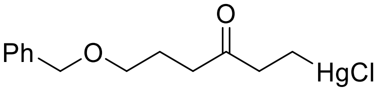
(5-(4-iodophenyl)-3-oxopentyl)mercury(II) chloride

Compound 40: Synthesized using Protocol A; Purified using a gradient of 0 to 0.2% acetone/CH_2Cl_2 on silica gel; (white solid, 42 mg, 80% yield); ^1H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.46 (m, 2H), 6.91 – 6.78 (m, 2H), 2.88 – 2.73 (m, 4H), 2.67 (t, *J* = 7.4 Hz, 2H), 1.61 (t, *J* = 6.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 210.6, 140.3, 137.6, 130.4, 91.4, 44.1, 41.0, 29.2, 20.5. IR 2934, 2860, 1695, 1507, 1364, 1004 cm^{-1}.; HRMS (APCI) calculated for $C_{11}H_{13}ClHgIO^+$ 523.9328 Found 523.9285 (M^+).



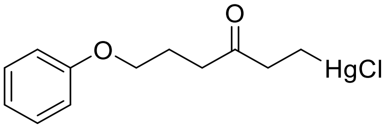
(5-(2-methoxyphenyl)-3-oxopentyl)mercury(II) chloride

Compound 41: Synthesized using Protocol B; Purified using a gradient of 0 to 0.2% MeOH/DCM on silica gel; (white semi-solid, 15 mg, 35% yield); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.21 (td, *J* = 7.8, 1.8 Hz, 1H), 7.12 (dd, *J* = 7.3, 1.8 Hz, 1H), 6.94 – 6.81 (m, 2H), 3.83 (s, 3H), 2.94-2.87 (m, 4H), 2.76-2.72 (m, 2H), 1.68 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.60, 157.38, 130.02, 128.82, 127.69, 120.65, 110.35, 55.25, 42.87, 40.76, 25.31, 20.44. IR 2857, 1684, 1471 cm^{-1}. HRMS (APCI) calculated for $C_{12}H_{15}ClHgO_2^+$ 428.0467, Found 428.0464 (M^+).



(6-(benzyloxy)-3-oxohexyl)mercury(II) chloride

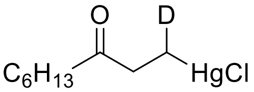
Compound 42: Synthesized using Protocol B; Purified using a gradient of 0 to 1% acetone/CH_2Cl_2 on silica gel; (light yellow oil, 26 mg, 60% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 5H), 4.49 (s, 2H), 3.52 (t, *J* = 5.9 Hz, 2H), 2.93 (t, *J* = 6.7 Hz, 2H), 2.57 (t, *J* = 7.1 Hz, 2H), 2.01 – 1.89 (m, 2H), 1.65 (d, *J* = 6.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 211.6, 138.2, 128.5, 127.8, 127.7, 72.9, 69.2, 40.6, 39.8, 24.1, 20.2. IR 3031, 2934, 1701, 1507, 1221, 742 cm^{-1}.



(3-oxo-6-phenoxyhexyl)mercury(II) chloride

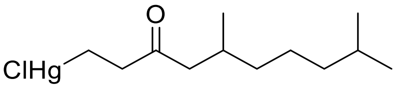
Compound 43: Synthesized using general procedure B; Purified using a gradient of 0 to 3% acetone/DCM on silica gel; (colorless oil, 21 mg, 50% yield); ^1H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 2H), 6.88 (tt, *J* =

7.3, 1.1 Hz, 1H), 6.82 – 6.78 (m, 2H), 3.91 (t, *J* = 5.9 Hz, 2H), 2.90 (t, *J* = 6.7 Hz, 2H), 2.60 (t, *J* = 7.1 Hz, 2H), 2.03 (tt, *J* = 7.1, 5.9 Hz, 2H), 1.64 (t, *J* = 6.7 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 211.2, 158.7, 129.5, 120.8, 114.4, 66.5, 40.7, 39.4, 23.4, 20.4. IR 293, 1701, 1598, 1495, 1039, 759 cm^{-1}.



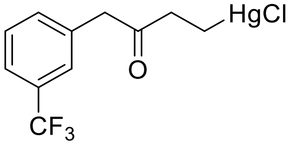
(3-oxononyl-1-*d*)mercury(II) chloride

Compound 44: Synthesized using general procedure A; purified using a gradient of 0 to 20% acetone/hexanes on silica gel; (light yellow solid, 80% yield); ^{1}H NMR (600 MHz, CDCl$_3$) δ 2.96 (d, *J* = 6.7 Hz, 2H), 2.46 (t, *J* = 7.5 Hz, 2H), 1.74 – 1.68 (m, 1H), 1.65 – 1.58 (m, 2H), 1.36 – 1.25 (m, 6H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 212.0, 43.1, 40.4, 31.5, 28.9, 23.8, 22.4, 20.5 – 19.7 (m), 14.0. IR 2951, 2860, 1707, 1467, 1267, 736 cm^{-1}.; HRMS (APCI) calculated for $C_9H_{15}DClHgO^-$ 378.0664 Found 378.0665 (M$^-$).



(5,9-dimethyl-3-oxodecyl)mercury(II) chloride

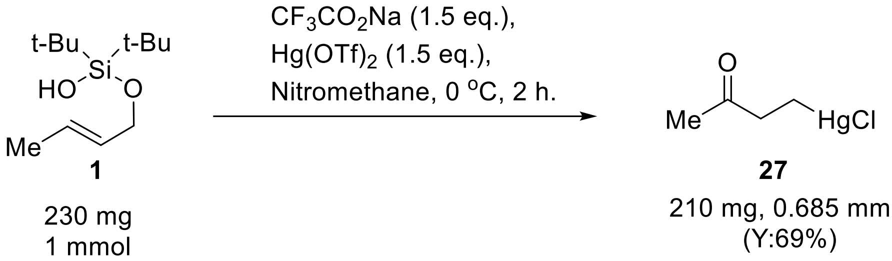
Compound 45: Synthesized using general procedure A; purified using a gradient of 0 to 20% acetone/hexanes on silica gel; (light yellow oil, 30 mg, 72% isolated yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.94 (q, *J* = 6.4 Hz, 2H), 2.44 (dd, *J* = 15.8, 5.7 Hz, 1H), 2.27 (dd, *J* = 15.7, 8.1 Hz, 1H), 2.09 – 1.97 (m, 1H), 1.72 (t, *J* = 6.7 Hz, 2H), 1.54 (dp, *J* = 13.2, 6.6 Hz, 1H), 1.35 – 1.21 (m, 3H), 1.21 – 1.12 (m, 3H), 0.98 – 0.76 (m, 9H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 211.9, 50.5, 41.2, 39.0, 37.1, 29.5, 27.9, 24.7, 22.6, 22.5, 20.4, 19.9. IR 2951, 2929, 1701, 1461, 1141, 799 cm^{-1}.; HRMS (APCI) calculated for $C_{12}H_{22}ClHgO^-$ 419.1071 Found 419.1076 (M$^-$).



(3-oxo-4-(3-(trifluoromethyl)phenyl)butyl)mercury(II) chloride

Compound 46: Synthesized using general procedure B; Purified using a gradient of 0 to 20% acetone/hexanes on silica gel followed by preparative TLC (1% acetone/DCM); (light yellow oil, 19 mg, 42% yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 – 7.57 (m, 1H), 7.58 – 7.46 (m, 2H), 7.46 – 7.40 (m, 1H), 3.83 (s, 2H), 3.06 (t, *J* = 6.7 Hz, 2H), 1.73 (d, *J* = 6.7 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 208.2, 134.4, 132.9, 131.1 (q, *J* = 32.3 Hz), 129.2, 126.2 (q, *J* = 3.8 Hz), 125.3 (q, *J* = 270 Hz), 124.2 (q, *J* = 3.8 Hz), 49.5, 40.5, 20.6. IR 2929, 1707, 1450, 1330, 1124, 805 cm^{-1}.; HRMS (APCI) calculated for $C_{11}H_{11}ClF_3HgO^+$ 453.0157 Found 453.0190 (MH$^+$).

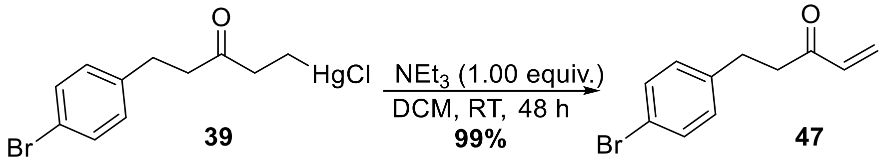
V. Scale-Up Procedure for Formation of 27



A 50 mL single-neck round-bottom flask was charged with **1** (230 mg, 1 mmol, 1 equiv.), CF_3CO_2Na (204 mg, 1.5 mmol, 1.5 equiv.), and nitromethane (20 mL). The flask was cooled to 0 °C in an ice-water bath, and $Hg(OTf)_2$ (750 mg, 1.5 mmol, 1.5 equiv.) was added in a single portion. The reaction mixture was stirred for 2 h at 0 °C. Then, the reaction was carefully quenched with brine (saturated aqueous NaCl) solution (20 mL) and stirred for 10 mins at 0 °C. The mixture was transferred to a separatory funnel. An additional 20 mL brine and DCM were added. The organic layer was separated, and then the aqueous layer was extracted with DCM (2 x 50 mL). The combined organic layers were washed with brine solution (50 mL), dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was purified using a gradient of 0 to 0.2% acetone/DCM (column chromatography, silica gel) to afford 210 mg (0.69 mmol, 69%) of **27** as a white solid.

VI. Derivatization Reactions of Ketone Organomercurial Compounds

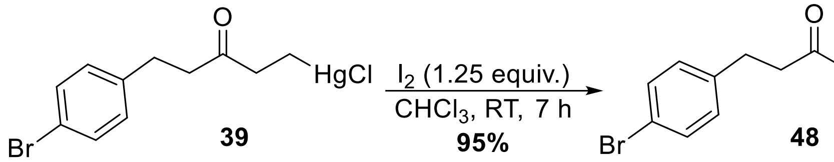
a) Elimination



Triethylamine (3 µl, 0.02 mmol, 1.00 equiv) was added to a solution of **39** (10 mg, 0.02 mmol) in 1.5 mL of DCM. After being stirred for 48 h, the mixture was diluted with dichloromethane, transferred to a separatory funnel, and washed with water. The organic layer was collected, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel (gradient of 0 to 10% ethyl acetate in hexanes) to provide **47** (5 mg, 0.02 mmol, 99%) as an oil.

Compound 47: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.36 (dd, *J* = 17.7, 10.4 Hz, 1H), 6.22 (dd, *J* = 17.7, 1.1 Hz, 1H), 5.85 (dd, *J* = 10.5, 1.1 Hz, 1H), 2.93-2.90 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.31, 140.05, 136.39, 131.54, 130.16, 128.40, 119.90, 40.88, 29.09. IR 2857, 1457, 1684, 1173 cm^{-1}. HRMS (APCI) calculated for $C_{11}H_{12}BrO^+$ 239.0072, Found 239.0058 (MH$^+$).

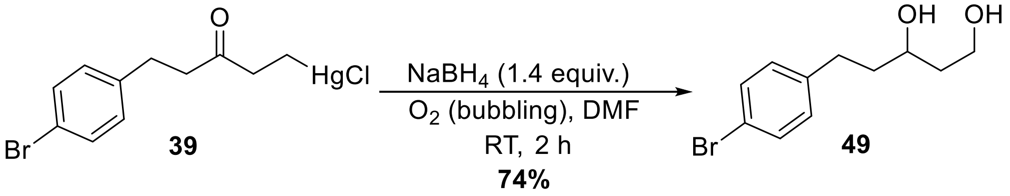
b) Iodination



I_2 (13.3 mg, 0.05 mmol, 1.25 equiv.) was added to a solution of **39** (20 mg, 0.04 mmol, 1 equiv.) in $CHCl_3$ (1.5 mL). After stirring for 7 h, the mixture was diluted with dichloromethane and quenched with saturated aqueous $Na_2S_2O_3$ (2 mL) solution. In a separatory funnel, the organic layer was separated, collected, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to provide **48** (14.6 mg, 0.039 mmol, >95%) as a light-yellow solid, which was deemed pure without chromatography.

Compound 48: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.29 (t, *J* = 6.9 Hz, 2H), 3.06 (t, *J* = 6.9 Hz, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.74, 139.65, 131.59, 130.12, 120.01, 46.30, 44.12, 28.75, -4.77. IR 2857, 1457, 1730 1173 cm^{-1}. HRMS (APCI) calculated for C11H13BrIO$^+$ 366.9195, Found 366.9184 (MH$^+$).

c) Hydroxylation-Reduction



$NaBH_4$ (2.2 mg, 0.06 mmol, 1.4 equiv) was dissolved in DMF (0.5 mL), and the solution was sparged with O_2 gas for 15 minutes. Following this time, a solution of **39** (20 mg, 0.04 mmol) in DMF (0.5 mL) was added dropwise. During and after addition, O_2 gas 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 $MgSO_4$, and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel (gradient of 0 to 50% ethyl acetate in hexanes) to yield **49** (8 mg, 0.031 mmol, 74%) as a white semi-solid.

Compound 49: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 3.99 – 3.79 (m, 3H), 2.79-2.72 (m, 1H), 2.69 – 2.61 (m, 1H), 1.88 – 1.66 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.9, 131.4, 130.2, 119.5, 71.3, 61.8, 39.1, 38.3, 31.2. IR 2926, 1455, 1002 cm^{-1}. HRMS (ESI) calculated for $C_{11}H_{14}BrO_2^-$ 257.0177, Found 257.0180 (M$^-$).

VII. General Procedures for Formation of Cyclic Silanediol Organomercurial Products

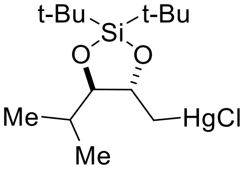
Protocol A: A 5 mL microwave vial was charged with a stir bar, $NaHCO_3$ (0.1 mmol, 8 mg, 1 equiv.) and $Hg(OTf)_2$ (0.175 mmol, 93 mg, 1.75 equiv.). 1 mL of THF was added, and the reaction flask was cooled to 0 °C with an ice-water bath. Allylic silanol (0.1 mmol) was dissolved in 1 mL of THF and added to the reaction flask. Following addition, the flask was sealed, and the reaction was kept for 40 minutes at 0°C with magnetic stirring. Following this period, the seal was broken, and 2 mL of brine (saturated aqueous NaCl) solution was slowly added. The heterogenous mixture was allowed to stir for 5 minutes and then transferred to a separatory funnel. An additional 10 mL of brine were added followed by 10 mL of CH_2Cl_2. The organic portion was collected, and the aqueous layer was extracted with two additional portions of CH_2Cl_2. The organic fractions were pooled, dried with $MgSO_4$, and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel (specific conditions are associated with each compound).

Protocol B: A 5 mL microwave vial was charged with a stir bar, $NaHCO_3$ (0.1 mmol, 8 mg, 1 equiv.) and $Hg(OTf)_2$ (0.25 mmol, 125 mg, 2.5 equiv.). 1 mL of THF was added, and the reaction flask was cooled to 0 °C with an ice-water bath. Allylic silanol (0.1 mmol) was dissolved in 1 mL of THF and added to the reaction flask. Following addition, the flask was sealed, and the reaction was kept for 40 minutes at 0°C with magnetic stirring. Following this period, the seal was broken, and 2 mL of brine (saturated aqueous NaCl) solution was slowly added. The heterogenous mixture was allowed to stir for 5 minutes and then transferred to a separatory funnel. An additional 10 mL of brine were added followed by 10 mL of CH_2Cl_2. The organic portion was collected, and the aqueous layer was extracted with two additional portions of CH_2Cl_2. The organic fractions were pooled, dried with $MgSO_4$, and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel (specific conditions are associated with each compound).

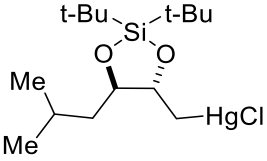
Protocol C: A 5 mL microwave vial was charged with a stir bar, CF_3CO_2Na (0.15 mmol, 20 mg, 1.5 equiv.) and $Hg(OTf)_2$ (0.15 mmol, 75 mg, 1.5 equiv.). 1 mL of THF was added, and the reaction flask was cooled to 0 °C with an ice-water bath. Allylic silanol (0.1 mmol) was dissolved in 1 mL of THF and added to the reaction flask. Following addition, the flask was sealed, and the reaction was kept for 2h at 0°C with magnetic stirring. Following this period, the seal was broken, and 2 mL of brine (saturated aqueous NaCl) solution was slowly added. The heterogenous mixture was allowed to stir for 5 minutes and then transferred to a separatory funnel. An additional 10 mL of brine were added followed by 10 mL of CH_2Cl_2. The organic portion was collected, and the aqueous layer was extracted with two additional portions of CH_2Cl_2. The organic fractions were pooled, dried with $MgSO_4$, and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel (specific conditions are associated with each compound).

Protocol D: A 5 mL microwave vial was charged with a stir bar, $NaHCO_3$ (0.15 mmol, 13 mg, 1.5 equiv.) and $Hg(OTf)_2$ (0.15 mmol, 75 mg, 1.5 equiv.). 0.75 mL of THF was added, and the reaction flask was cooled to -40 °C with an ice-water bath. Allylic silanol (0.1 mmol) was dissolved in 0.75 mL of THF and added to the reaction flask. Following addition, the flask was sealed, and the reaction was kept for 16h at -40°C with magnetic stirring. Following this period, the flask was removed from the cooling bath and allowed to warm to room temperature over a period 6 hours. Following this period, the seal was broken, and 2 mL of brine (saturated aqueous NaCl) solution was slowly added. The heterogenous mixture was allowed to stir for 5 minutes and then transferred to a separatory funnel. An additional 10 mL of brine were added followed by 10 mL of CH_2Cl_2. The organic portion was collected, and the aqueous layer was extracted with two additional portions of CH_2Cl_2. The organic fractions were pooled, dried with $MgSO_4$, and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel (specific conditions are associated with each compound).

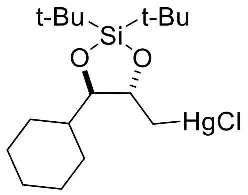
VIII. Characterization of Cyclic Silanediol Organomercurial Products


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

Compound 50: Synthesized using Protocol A; Purified using a gradient of 0 to 20% EtOAc/hexanes on Florisil; single diastereomer; (light yellow oil, 32 mg, 66% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.16 (ddd, *J* = 8.3, 6.9, 4.5 Hz, 1H), 3.28 (dd, *J* = 8.4, 4.8 Hz, 1H), 2.41 (dd, *J* = 12.2, 4.5 Hz, 1H), 2.13 (dd, *J* = 12.2, 6.9 Hz, 1H), 1.74 (pd, *J* = 6.8, 4.9 Hz, 1H), 1.09 (s, 9H), 1.06 (s, 9H), 1.03 – 0.98 (m, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 88.7, 76.9, 38.1, 31.6, 27.3, 27.1, 20.8, 20.7, 20.0, 17.7. IR 2944, 2857, 1473, 1366, 993 cm^{-1}.; HRMS (ESI) calculated for $C_{14}H_{30}ClHgO_2Si^+$ 495.1410 Found 495.1420 (MH^+).

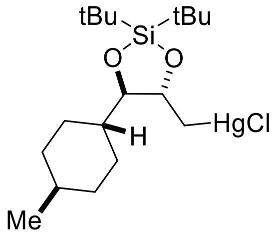

((2,2-di-*tert*-butyl-5-isobutyl-1,3,2-dioxasilolan-4-yl)methyl)mercury(II) chloride

Compound 51: Synthesized using Protocol A; Purified using a gradient of 0 to 30% EtOAc/hexanes on silica gel; single diastereomer; (light yellow oil, 24 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (ddd, *J* = 8.4, 6.1, 4.9 Hz, 1H), 3.51 (ddd, *J* = 9.6, 8.4, 2.7 Hz, 1H), 2.40 (dd, *J* = 12.2, 4.9 Hz, 1H), 2.09 (dd, *J* = 12.2, 6.1 Hz, 1H), 1.93 (dpd, *J* = 8.7, 6.7, 5.1 Hz, 1H), 1.46 (ddd, *J* = 13.7, 9.6, 5.1 Hz, 1H), 1.24 (ddd, *J* = 13.8, 8.7, 2.7 Hz, 1H), 1.09 (s, 9H), 1.05 (s, 9H), 1.02 – 0.97 (m, 3H), 0.96 (d, *J* = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 82.3, 79.6, 43.8, 36.8, 27.3, 27.0, 25.2, 23.5, 22.0, 20.7, 20.5. IR 2968, 2851, 1473, 1076, 1003 cm^{-1}.; HRMS (ESI) calculated for $C_{15}H_{32}ClHgO_2Si^+$ 509.1566 Found 509.1577 (MH^+).



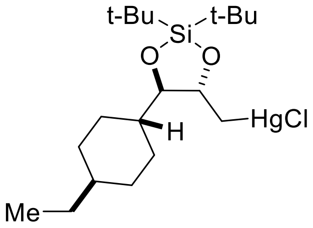
((2,2-di-*tert*-butyl-5-cyclohexyl-1,3,2-dioxasilolan-4-yl)methyl)mercury(II) chloride

Compound 52: Synthesized using Protocol A; Purified using a gradient of 0 to 20% EtOAC/hexanes on Florisil; single diastereomer; (light yellow oil, 43 mg, 80% yield); ^{1}H NMR (600 MHz, CDCl$_3$) δ 4.25 – 4.17 (m, 1H), 3.27 (dd, *J* = 8.4, 4.8 Hz, 1H), 2.41 (dd, *J* = 12.2, 4.5 Hz, 1H), 2.13 (dd, *J* = 12.2, 6.8 Hz, 1H), 1.89 – 1.76 (m, 3H), 1.71-1.68 (m, 1H), 1.65-1.59 (m, 1H), 1.46 – 1.37 (m, 1H), 1.35 – 1.14 (m, 5H), 1.08 (s, 9H), 1.05 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 88.3, 76.4, 41.5, 38.2, 30.3, 28.2, 27.3, 27.1, 26.3, 26.1, 20.8, 20.6. IR 2941, 2854, 1473, 1076 cm^{-1}.; HRMS (ESI) calculated for $C_{17}H_{34}ClHgO_2Si^+$ 535.1723 Found 535.1736 (MH$^+$).



((2,2-di-*tert*-butyl-5-((1*r*,4*R*)-4-methylcyclohexyl)-1,3,2-dioxasilolan-4-yl)methyl)mercury(II) chloride

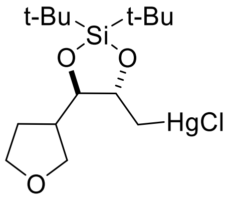
Compound 53: Synthesized using Protocol A; Purified using a gradient of 0 to 20% EtOAc/hexanes on Florisil; Single diastereomer; (light yellow oil, 32 mg, 58% yield); ^{1}H NMR (600 MHz, CDCl$_3$) δ 4.21 (ddd, *J* = 8.4, 6.8, 4.6 Hz, 1H), 3.28 (dd, *J* = 8.4, 4.7 Hz, 1H), 2.41 (dd, *J* = 12.2, 4.5 Hz, 1H), 2.13 (dd, *J* = 12.2, 6.8 Hz, 1H), 1.85 (dt, *J* = 13.0, 3.0 Hz, 1H), 1.78 (m, 2H), 1.62 (dt, *J* = 12.4, 2.9 Hz, 1H), 1.35 (ddt, *J* = 15.1, 7.9, 3.3 Hz, 2H), 1.31 – 1.25 (m, 2H), 1.25 – 1.16 (m, 1H), 1.08 (s, 9H), 1.05 (s, 9H), 0.90 (m, 4H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 88.2, 76.5, 41.2, 38.2, 35.0, 34.8, 32.5, 30.2, 28.0, 27.3, 27.1, 22.6, 20.8, 20.6. IR 2929, 2860, 1474, 1000 cm^{-1}.; HRMS (ESI) calculated for $C_{18}H_{36}ClHgO_2Si^+$ 549.1879 Found 549.1898 (MH$^+$).



((2,2-di-*tert*-butyl-5-((1*r*,4*R*)-4-ethylcyclohexyl)-1,3,2-dioxasilolan-4-yl)methyl)mercury(II) chloride

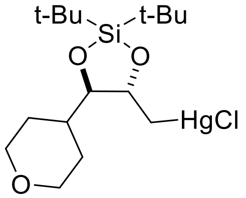
Compound 54: Synthesized using Protocol A; Purified using a gradient of 0 to 30% EtOAc/hexanes on silica gel; Single diastereomer; (light yellow oil, 40 mg, 70% yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.21 (ddd, *J* = 8.4, 6.8, 4.5 Hz, 1H), 3.28 (dd, *J* = 8.4, 4.6 Hz, 1H), 2.41 (dd, *J* = 12.2, 4.5 Hz, 1H), 2.13 (dd, *J* = 12.2, 6.8 Hz, 1H), 1.85 (tdd, *J* = 12.3, 5.4, 3.0 Hz, 3H), 1.65 (dt, *J* = 12.2, 2.7 Hz, 1H), 1.37 (tdd, *J* = 10.7, 8.5, 3.8 Hz, 1H), 1.31

– 1.11 (m, 5H), 1.08 (s, 9H), 1.05 (s, 9H), 0.94 – 0.86 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 88.2, 76.5, 41.7, 39.3, 38.2, 32.6, 32.4, 30.2, 29.9, 28.0, 27.3, 27.1, 20.8, 20.6, 11.5. IR 2935, 2854, 1471, 1076, 926 cm^{-1}.; HRMS (APCI) calculated for $C_{19}H_{37}ClHgO_2Si^+$ 562.1958 Found 562.1995 (M$^+$).



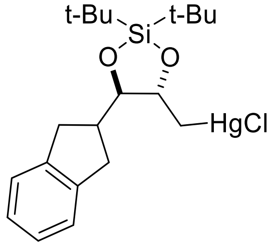
((2,2-di-*tert*-butyl-5-(tetrahydrofuran-3-yl)-1,3,2-dioxasilolan-4-yl)methyl)mercury(II) chloride

Compound 55: Synthesized using Protocol A; Purified using a gradient of 0 to 100% EtOAc/hexanes on silica gel; single diastereomer; (light yellow oil, 21 mg, 40% yield);^{1}H NMR (600 MHz, CDCl$_3$) δ 4.11 (tt, *J* = 7.7, 4.5 Hz, 1H), 3.99 (t, *J* = 8.2 Hz, 1H), 3.93 (qd, *J* = 7.6, 3.7 Hz, 1H), 3.80 (td, *J* = 8.3, 6.9 Hz, 1H), 3.75 (t, *J* = 8.3 Hz, 1H), 3.50 (t, *J* = 7.7 Hz, 1H), 2.41 (dd, *J* = 12.2, 4.3 Hz, 1H), 2.35 (h, *J* = 7.9 Hz, 1H), 2.15 (dd, *J* = 12.2, 7.3 Hz, 1H), 1.97 (dtd, *J* = 11.9, 7.5, 3.9 Hz, 1H), 1.74 (dq, *J* = 11.9, 8.5 Hz, 1H), 1.08 (s, 9H), 1.05 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 85.85, 78.75, 70.54, 68.34, 43.72, 37.63, 29.10, 27.23, 27.03, 20.79, 20.63. IR 2960, 2938, 1474, 1030 cm^{-1}.; HRMS (ESI) calculated for $C_{15}H_{30}ClHgO_3Si^+$ 523.1359 Found 523.1383 (MH$^+$).



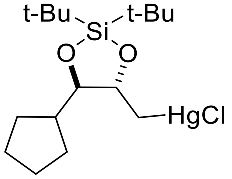
((2,2-di-*tert*-butyl-5-(tetrahydro-2*H*-pyran-4-yl)-1,3,2-dioxasilolan-4-yl)methyl)mercury(II) chloride

Compound 56: Synthesized using Protocol B; Purified using a gradient of 0 to 50% EtOAc/hexanes on silica gel; single diastereomer; (Colorless oil, 24 mg, 45% yield); ^{1}H NMR (600 MHz, CDCl$_3$) δ 4.19 (td, *J* = 7.7, 4.4 Hz, 1H), 4.04 (dt, *J* = 10.7, 5.5 Hz, 2H), 3.40 (tdd, *J* = 11.7, 7.3, 2.3 Hz, 2H), 3.30 (dd, *J* = 8.4, 4.7 Hz, 1H), 2.39 (dd, *J* = 12.2, 4.4 Hz, 1H), 2.12 (dd, *J* = 12.2, 7.2 Hz, 1H), 1.76 – 1.71 (m, 1H), 1.69 – 1.56 (m, 3H), 1.48 (dt, *J* = 11.8, 2.3 Hz, 1H), 1.08 (s, 9H), 1.05 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 87.4, 76.4, 67.9, 67.7, 39.2, 38.0, 29.9, 28.5, 27.2, 27.0, 20.8, 20.6. IR 2932, 2857, 1473, 1086, 1002 cm^{-1}.; HRMS (ESI) calculated for $C_{16}H_{32}ClHgO_3Si^+$ 537.1516 Found 537.1526 (MH$^+$).



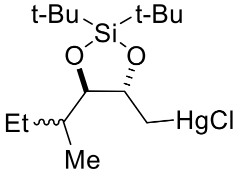
((2,2-di-*tert*-butyl-5-(2,3-dihydro-1*H*-inden-2-yl)-1,3,2-dioxasilolan-4-yl)methyl)mercury(II) chloride

Compound 57: Synthesized using Protocol B; Purified using a gradient of 0 to 30% EtOAc/hexanes; single diastereomer; (white solid, 27 mg, 48% yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 – 7.20 (m, 2H), 7.20 – 7.15 (m, 2H), 4.20 (ddd, *J* = 8.3, 6.9, 4.4 Hz, 1H), 3.65 (dd, *J* = 8.4, 5.8 Hz, 1H), 3.04 (dd, *J* = 8.8, 6.7 Hz, 2H), 2.94 (d, *J* = 9.0 Hz, 2H), 2.67 – 2.56 (m, 1H), 2.46 (dd, *J* = 12.2, 4.4 Hz, 1H), 2.18 (dd, *J* = 12.2, 7.0 Hz, 1H), 1.11 (s, 9H), 1.08 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 142.8, 142.5, 126.3, 126.2, 124.4, 124.2, 86.4, 78.2, 44.3, 37.5, 35.9, 34.8, 27.3, 27.1, 20.8, 20.7. IR 2941, 2860, 1470, 1364, 1065 cm^{-1}.; HRMS (ESI) calculated for $C_{20}H_{32}ClHgO_2Si^+$ 569.1566 Found 569.1544 (MH$^+$).



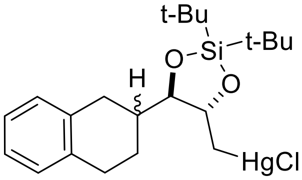
((2,2-di-*tert*-butyl-5-cyclopentyl-1,3,2-dioxasilolan-4-yl)methyl)mercury(II) chloride

Compound 58: Synthesized using Protocol A; Purified using a gradient of 0 to 30% EtOAc/hexanes on silica gel; single diastereomer; (colorless oil, 29 mg, 57% yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.13 (ddd, *J* = 8.4, 6.6, 4.5 Hz, 1H), 3.42 (dd, *J* = 8.4, 5.6 Hz, 1H), 2.43 (dd, *J* = 12.2, 4.5 Hz, 1H), 2.15 (dd, *J* = 12.2, 6.6 Hz, 1H), 1.96 – 1.84 (m, 1H), 1.79 – 1.63 (m, 4H), 1.62 – 1.47 (m, 3H), 1.43 – 1.32 (m, 1H), 1.09 (s, 9H), 1.06 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 87.3, 78.4, 43.8, 37.6, 29.6, 28.1, 27.3, 27.1, 25.4, 25.1, 20.8, 20.6. IR 2974, 2869, 1471, 1364, 1007 cm^{-1}.; HRMS (ESI) calculated for $C_{16}H_{32}ClHgO_2Si^+$ 521.1566 Found 521.1568 (MH$^+$).



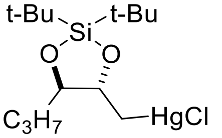
((5-(*sec*-butyl)-2,2-di-*tert*-butyl-1,3,2-dioxasilolan-4-yl)methyl)mercury(II) chloride

Compound 59: Synthesized using Protocol B; Purified using a gradient of 0 to 30% EtOAc/hexanes on silica gel; 1.5:1 mixture of diastereomers; (light yellow oil, 37 mg, 72% yield); ^{1}H NMR (400 MHz, CDCl$_3$) (Note: for major diastereomer) δ 4.18 (ddd, *J* = 8.3, 7.2, 4.4 Hz, 1H), 3.34 (dd, *J* = 8.2, 5.8 Hz, 1H), 2.41 (dd, *J* = 12.2, 4.4 Hz, 1H), 2.16 (dd, *J* = 12.2, 7.3 Hz, 1H), 1.65 (dtd, *J* = 15.0, 7.5, 3.4 Hz, 1H), 1.54 (dtd, *J* = 9.4, 6.2, 3.2 Hz, 1H), 1.35-1.25 (m, 1H), 1.09 (s, 9H), 1.07 – 1.02 (m, 9H), 0.99 – 0.90 (m, 6H).; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) (Note: for mixture of diastereomers) δ 88.2, 86.6, 77.0, 76.2, 38.8, 38.5, 37.4, 37.3, 27.33, 27.30, 27.2, 27.1, 24.9, 20.9, 20.8, 20.7, 20.6, 15.8, 13.8, 11.8, 11.4. IR 2965, 2866, 1473, 1364, 984 cm^{-1}.; HRMS (ESI) calculated for $C_{15}H_{32}ClHgO_2Si^+$ 509.1566 Found 509.1566 (MH$^+$).



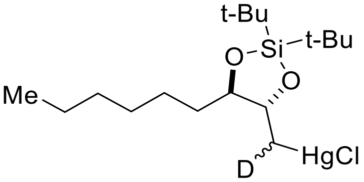
((2,2-di-*tert*-butyl-5-(1,2,3,4-tetrahydronaphthalen-2-yl)-1,3,2-dioxasilolan-4-yl)methyl)mercury(II) chloride

Compound 60: Purified using a gradient of 0 to 30% EtOAc/hexanes on silica gel; (colorless oil, 29 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (q, *J* = 4.3 Hz, 4H), 4.30 (td, *J* = 7.6, 4.4 Hz, 1H), 3.45 (dt, *J* = 8.7, 4.7 Hz, 1H), 2.96 – 2.66 (m, 4H), 2.43 (dd, *J* = 12.2, 4.4 Hz, 1H), 2.22 – 2.04 (m, 1H), 1.94 – 1.78 (m, 2H), 1.76 – 1.58 (m, 1H), 1.08 (d, *J* = 0.9 Hz, 9H), 1.05 (d, *J* = 1.4 Hz, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 136.6, 136.2, 136.1, 135.8, 129.3, 129.1, 128.8, 128.7, 125.8, 125.7, 125.6, 87.9, 87.0, 76.8, 38.5, 38.4, 38.1, 33.3, 31.2, 29.2, 29.0, 27.3, 27.1, 27.0, 24.7, 20.8, 20.7. IR 2932, 2869, 1471, 1064, 1000 cm^{-1}.; HRMS (ESI) calculated for $C_{21}H_{34}ClHgO_2Si^+$ 583.1723 Found 583.1740 (MH$^+$).



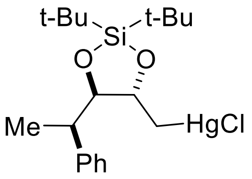
((2,2-di-*tert*-butyl-5-propyl-1,3,2-dioxasilolan-4-yl)methyl)mercury(II) chloride

Compound 61: Synthesized using general procedure C; purified using a gradient of 0 to 30% EtOAc/hexanes on silica gel; single diastereomer; (light white solid, 25 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.06 (ddd, *J* = 8.5, 6.1, 4.8 Hz, 1H), 3.48 (ddd, *J* = 8.6, 6.8, 4.3 Hz, 1H), 2.41 (dd, *J* = 12.2, 4.8 Hz, 1H), 2.10 (dd, *J* = 12.2, 6.1 Hz, 1H), 1.66 – 1.42 (m, 4H), 1.08 (d, *J* = 14.1 Hz, 18H), 1.01 – 0.93 (m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 83.8, 79.1, 37.0, 36.7, 27.3, 27.0, 20.7, 20.5, 19.2, 14.1. IR 2962, 2860, 2364, 1473 cm^{-1}.; HRMS (ESI) calculated for $C_{14}H_{30}ClHgO_2Si^+$ 495.1410 Found 495.1422 (MH$^+$).



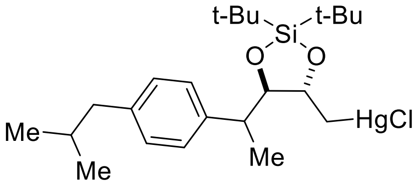
((2,2-di-*tert*-butyl-5-hexyl-1,3,2-dioxasilolan-4-yl)methyl-*d*)mercury(II) chloride

Compound 62: Synthesized using Protocol C; purified using a gradient of 0 to 30% EtOAc/hexanes on silica gel; 1:1 mixture of diastereomers; (colorless oil, 19 mg, 35% yield); ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of diastereomers) δ 4.10 – 3.99 (m, 2H), 3.46 (dq, *J* = 8.4, 3.4 Hz, 2H), 2.39 (d, *J* = 4.7 Hz, 1 H), 2.09 (d, *J* = 6.1 Hz, 1 H), 1.63 – 1.29 (m, 20 H), 1.09 (s, 18H), 1.06 (s, 18H), 0.95 – 0.90 (m, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 84.1, 79.1, 37.0 – 36.5 (m), 34.6, 31.7, 29.3, 27.3, 27.0, 25.9, 22.6, 20.7, 20.5, 14.0. IR 2938, 2884, 1470, 1028 cm^{-1}.; HRMS (ESI) calculated for $C_{17}H_{35}DClHgO_2Si^+$ 538.1942 Found 538.1953 (MH$^+$).



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

Compound 63: Synthesized using Protocol D; Purified using a gradient of 0 to 30% EtOAc/hexanes on silica gel; single diastereomer, relative stereochemistry determined through X-ray diffraction (CCDC: 2084035); (white solid, 27 mg, 49% yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.27 (m, 2H), 7.27 – 7.21 (m, 3H), 3.96 (ddd, *J* = 8.8, 6.3, 4.5 Hz, 1H), 3.63 (dd, *J* = 8.8, 3.4 Hz, 1H), 2.98 (qd, *J* = 7.2, 3.4 Hz, 1H), 2.27 (dd, *J* = 12.2, 4.5 Hz, 1H), 2.01 (dd, *J* = 12.2, 6.3 Hz, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.08 (s, 9H), 0.83 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 141.4, 129.0, 128.1, 126.7, 87.5, 75.8, 41.8, 37.0, 27.2, 26.7, 20.8, 20.6, 18.1. IR 2938, 2857, 1468, 1080, 997 cm^{-1}.; HRMS (ESI) calculated for $C_{19}H_{32}ClHgO_2Si^+$ 557.1566 Found 557.1585 (MH$^+$).

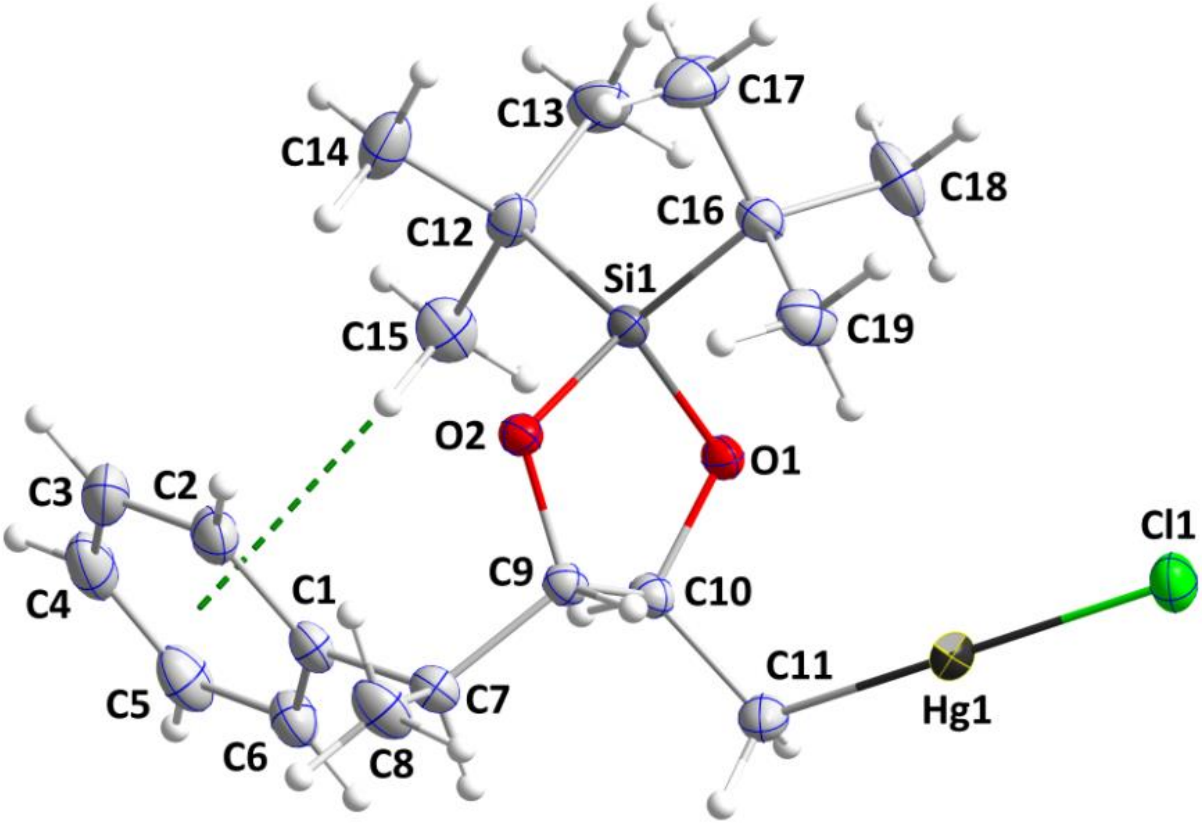


((2,2-di-*tert*-butyl-5-(1-(4-isobutylphenyl)ethyl)-1,3,2-dioxasilolan-4-yl)methyl)mercury(II) chloride

Compound 64: Synthesized using Protocol D; Purified using a gradient of 0 to 30% EtOAc/hexanes on silica gel; single diastereomer; (light yellow oil, 29 mg, 48% yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 – 7.13 (m, 2H), 7.11 – 7.06 (m, 2H), 3.95 (ddd, *J* = 8.9, 6.2, 4.5 Hz, 1H), 3.61 (dd, *J* = 8.9, 3.0 Hz, 1H), 2.96 (qd, *J* = 7.2, 3.0 Hz, 1H), 2.47 (d, *J* = 7.1 Hz, 2H), 2.27 (dd, *J* = 12.2, 4.5 Hz, 1H), 2.01 (dd, *J* = 12.2, 6.2 Hz, 1H), 1.85 (dq, *J* = 13.5, 6.7 Hz, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.08 (s, 9H), 0.91 (d, *J* = 6.6 Hz, 6H), 0.80 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 140.1, 138.3, 128.9, 128.8, 87.6, 75.6, 45.0, 41.2, 36.9, 30.2, 27.2, 26.7, 22.5, 22.4, 20.8, 20.6, 18.1. IR 2962, 2863, 1471, 1364, 977 cm^{-1}.; HRMS (ESI) calculated for $C_{23}H_{40}ClHgO_2Si^+$ 613.2192 Found 613.2191 (MH$^+$).

IX. Crystallographic Information for Compound 63 (CCDC 2084035)

Crystals suitable for X-ray diffraction grown from Ethanol.



Note: Ellipsoid contour probability levels are 50%.

Crystal Structure Report for JTM1445

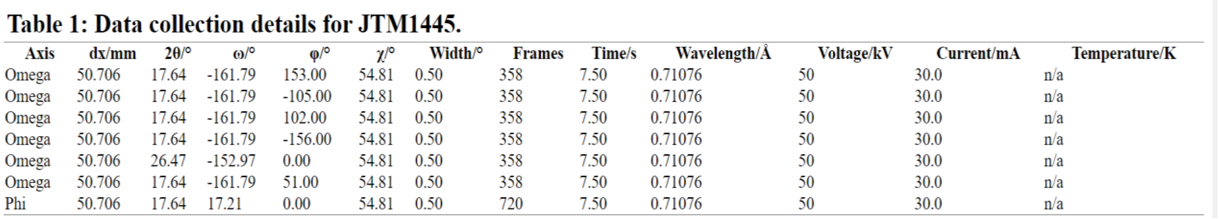


Table 1: Data collection details for JTM1445.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	50.706	17.64	-161.79	153.00	54.81	0.50	358	7.50	0.71076	50	30.0	n/a
Omega	50.706	17.64	-161.79	-105.00	54.81	0.50	358	7.50	0.71076	50	30.0	n/a
Omega	50.706	17.64	-161.79	102.00	54.81	0.50	358	7.50	0.71076	50	30.0	n/a
Omega	50.706	17.64	-161.79	-156.00	54.81	0.50	358	7.50	0.71076	50	30.0	n/a
Omega	50.706	26.47	-152.97	0.00	54.81	0.50	358	7.50	0.71076	50	30.0	n/a
Omega	50.706	17.64	-161.79	51.00	54.81	0.50	358	7.50	0.71076	50	30.0	n/a
Phi	50.706	17.64	17.21	0.00	54.81	0.50	720	7.50	0.71076	50	30.0	n/a

A colorless column-like specimen of $C_{19}H_{31}ClHgO_2Si$, approximate dimensions 0.032 mm x 0.079 mm x 0.268 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 QUEST PHOTON 3 diffractometer system equipped with a fine-focus sealed tube (MoKα, λ = 0.71073 Å) and a graphite monochromator.

A total of 2868 frames were collected. The total exposure time was 5.97 hours. The frames were integrated with the Bruker SAINT software package using a Bruker *SAINT*(Bruker, 2020) algorithm. The integration of the data using a monoclinic unit cell yielded a total of 75730 reflections to a maximum θ angle of 30.54° (0.70 Å resolution), of which 6529 were independent (average redundancy 11.599, completeness = 99.8%, R_{int} = 3.30%, R_{sig} = 1.78%) and 5798 (88.80%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 6.2377(4) Å, $\underline{b}$ = 21.9140(12) Å, $\underline{c}$ = 15.9493(9) Å, β = 101.061(2)°, volume = 2139.7(2) Å^3, are based upon the refinement of the XYZ-centroids of 9591 reflections above 20 σ(I) with 5.205° < 2θ < 61.02°. Data were corrected for absorption effects using the Numerical mu Calculated method (SADABS). The ratio of minimum to maximum apparent transmission was 0.404. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2420 and 0.7980.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, $C_{19}H_{31}ClHgO_2Si$. The final anisotropic full-matrix least-squares refinement on F^2 with 224 variables converged at R1 = 2.03%, for the observed data and wR2 = 4.24% for all data. The goodness-of-fit was 1.137. The largest peak in the final difference electron density synthesis was 0.598 $e^-/Å^3$ and the largest hole was -0.567 $e^-/Å^3$ with an RMS deviation of 0.096 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.725 g/cm^3 and F(000), 1088 e^-.

Table 2. Sample and crystal data for JTM1445.

Identification code	JTM1445	
Chemical formula	$C_{19}H_{31}ClHgO_2Si$	
Formula weight	555.57 g/mol	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal size	0.032 x 0.079 x 0.268 mm	
Crystal habit	colorless column	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 6.2377(4) Å	α = 90°
	b = 21.9140(12) Å	β = 101.061(2)°
	c = 15.9493(9) Å	γ = 90°
Volume	2139.7(2) Å^3	
Z	4	
Density (calculated)	1.725 g/cm^3	
Absorption coefficient	7.383 mm^{-1}	
F(000)	1088	

Table 3. Data collection and structure refinement for JTM1445.

Diffractometer	Bruker D8 QUEST PHOTON 3 diffractometer	
Radiation source	fine-focus sealed tube (MoKα, λ = 0.71073 Å)	
Theta range for data collection	2.60 to 30.54°	
Index ranges	-8<=h<=8, -31<=k<=31, -22<=l<=22	
Reflections collected	75730	
Independent reflections	6529 [R(int) = 0.0330]	
Coverage of independent reflections	99.8%	
Absorption correction	Numerical mu Calculated	
Max. and min. transmission	0.7980 and 0.2420	
Structure solution technique	direct methods	
Structure solution program	*SHELXT/5* (Sheldrick, 2015*a*)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	*SHELXL 2018/3* (Sheldrick, 2015*b*)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6529 / 0 / 224	
Goodness-of-fit on F^2	1.137	
Δ/σ_{max}	0.003	
Final R indices	5798 data; I>2σ(I)	R1 = 0.0203, wR2 = 0.0407
	all data	R1 = 0.0255, wR2 = 0.0424
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0139P)^2+1.9168P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.598 and -0.567 eÅ^{-3}	
R.M.S. deviation from mean	0.096 eÅ^{-3}	

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for JTM1445.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
Hg1	0.73538(2)	0.45938(2)	0.93348(2)	0.02121(3)
Cl1	0.70171(10)	0.56102(3)	0.97257(4)	0.02775(12)
Si1	0.33919(9)	0.40382(3)	0.69733(4)	0.01713(11)
O1	0.5913(2)	0.40670(7)	0.75580(10)	0.0192(3)
O2	0.2430(2)	0.34992(7)	0.75389(9)	0.0184(3)

	x/a	y/b	z/c	U(eq)
C1	0.3999(4)	0.22468(10)	0.78045(14)	0.0208(4)
C2	0.2163(4)	0.21370(11)	0.71691(17)	0.0280(5)
C3	0.2277(5)	0.17563(12)	0.64840(17)	0.0355(6)
C4	0.4239(5)	0.14788(12)	0.64236(18)	0.0372(6)
C5	0.6062(5)	0.15729(11)	0.70493(18)	0.0335(6)
C6	0.5937(4)	0.19509(10)	0.77355(16)	0.0261(5)
C7	0.3911(4)	0.26781(10)	0.85419(14)	0.0203(4)
C8	0.1951(4)	0.25510(11)	0.89629(17)	0.0300(5)
C9	0.4013(3)	0.33545(9)	0.82957(13)	0.0176(4)
C10	0.6262(3)	0.35493(10)	0.81273(14)	0.0187(4)
C11	0.7880(4)	0.37139(10)	0.89358(15)	0.0238(4)
C12	0.3377(4)	0.37350(11)	0.58628(14)	0.0238(4)
C13	0.4030(4)	0.42253(13)	0.52664(16)	0.0322(6)
C14	0.1106(4)	0.34790(13)	0.54703(17)	0.0352(6)
C15	0.5048(5)	0.32111(12)	0.59408(17)	0.0324(6)
C16	0.2082(4)	0.48073(10)	0.70635(15)	0.0227(4)
C17	0.9880(5)	0.48736(14)	0.64503(19)	0.0388(6)
C18	0.3635(5)	0.53257(11)	0.6909(2)	0.0392(7)
C19	0.1667(4)	0.48651(12)	0.79768(16)	0.0307(5)

Table 5. Bond lengths (Å) for JTM1445.

Hg1-C11	2.076(2)	Hg1-Cl1	2.3333(6)
Si1-O2	1.6663(16)	Si1-O1	1.6684(16)
Si1-C12	1.890(2)	Si1-C16	1.891(2)
O1-C10	1.443(2)	O2-C9	1.440(2)
C1-C6	1.395(3)	C1-C2	1.397(3)
C1-C7	1.518(3)	C2-C3	1.387(4)
C2-H2	0.95	C3-C4	1.386(4)
C3-H3	0.95	C4-C5	1.377(4)
C4-H4	0.95	C5-C6	1.387(3)
C5-H5	0.95	C6-H6	0.95
C7-C8	1.529(3)	C7-C9	1.538(3)
C7-H7	1.0	C8-H8A	0.98
C8-H8B	0.98	C8-H8C	0.98
C9-C10	1.539(3)	C9-H9	1.0
C10-C11	1.521(3)	C10-H10	1.0
C11-H11A	0.99	C11-H11B	0.99

C12-C15	1.540(4)	C12-C13	1.540(3)
C12-C14	1.541(3)	C13-H13A	0.98
C13-H13B	0.98	C13-H13C	0.98
C14-H14A	0.98	C14-H14B	0.98
C14-H14C	0.98	C15-H15A	0.98
C15-H15B	0.98	C15-H15C	0.98
C16-C17	1.532(3)	C16-C19	1.533(3)
C16-C18	1.543(3)	C17-H17A	0.98
C17-H17B	0.98	C17-H17C	0.98
C18-H18A	0.98	C18-H18B	0.98
C18-H18C	0.98	C19-H19A	0.98
C19-H19B	0.98	C19-H19C	0.98

Table 6. Bond angles (°) for JTM1445.

C11-Hg1-Cl1	174.92(7)	O2-Si1-O1	97.05(8)
O2-Si1-C12	108.71(9)	O1-Si1-C12	111.82(10)
O2-Si1-C16	112.64(9)	O1-Si1-C16	107.36(9)
C12-Si1-C16	117.40(11)	C10-O1-Si1	109.53(12)
C9-O2-Si1	110.47(12)	C6-C1-C2	117.7(2)
C6-C1-C7	120.7(2)	C2-C1-C7	121.5(2)
C3-C2-C1	121.1(2)	C3-C2-H2	119.5
C1-C2-H2	119.5	C4-C3-C2	119.9(3)
C4-C3-H3	120.1	C2-C3-H3	120.1
C5-C4-C3	120.1(2)	C5-C4-H4	120.0
C3-C4-H4	120.0	C4-C5-C6	119.9(2)
C4-C5-H5	120.1	C6-C5-H5	120.1
C5-C6-C1	121.4(2)	C5-C6-H6	119.3
C1-C6-H6	119.3	C1-C7-C8	112.18(19)
C1-C7-C9	113.14(17)	C8-C7-C9	111.29(18)
C1-C7-H7	106.6	C8-C7-H7	106.6
C9-C7-H7	106.6	C7-C8-H8A	109.5
C7-C8-H8B	109.5	H8A-C8-H8B	109.5
C7-C8-H8C	109.5	H8A-C8-H8C	109.5
H8B-C8-H8C	109.5	O2-C9-C7	111.77(17)
O2-C9-C10	107.10(16)	C7-C9-C10	113.30(17)
O2-C9-H9	108.2	C7-C9-H9	108.2
C10-C9-H9	108.2	O1-C10-C11	110.03(17)
O1-C10-C9	107.17(16)	C11-C10-C9	113.37(18)

O1-C10-H10	108.7	C11-C10-H10	108.7
C9-C10-H10	108.7	C10-C11-Hg1	111.23(14)
C10-C11-H11A	109.4	Hg1-C11-H11A	109.4
C10-C11-H11B	109.4	Hg1-C11-H11B	109.4
H11A-C11-H11B	108.0	C15-C12-C13	108.4(2)
C15-C12-C14	108.5(2)	C13-C12-C14	109.5(2)
C15-C12-Si1	107.75(16)	C13-C12-Si1	112.28(17)
C14-C12-Si1	110.34(16)	C12-C13-H13A	109.5
C12-C13-H13B	109.5	H13A-C13-H13B	109.5
C12-C13-H13C	109.5	H13A-C13-H13C	109.5
H13B-C13-H13C	109.5	C12-C14-H14A	109.5
C12-C14-H14B	109.5	H14A-C14-H14B	109.5
C12-C14-H14C	109.5	H14A-C14-H14C	109.5
H14B-C14-H14C	109.5	C12-C15-H15A	109.5
C12-C15-H15B	109.5	H15A-C15-H15B	109.5
C12-C15-H15C	109.5	H15A-C15-H15C	109.5
H15B-C15-H15C	109.5	C17-C16-C19	107.7(2)
C17-C16-C18	110.0(2)	C19-C16-C18	108.5(2)
C17-C16-Si1	112.54(18)	C19-C16-Si1	107.47(15)
C18-C16-Si1	110.51(17)	C16-C17-H17A	109.5
C16-C17-H17B	109.5	H17A-C17-H17B	109.5
C16-C17-H17C	109.5	H17A-C17-H17C	109.5
H17B-C17-H17C	109.5	C16-C18-H18A	109.5
C16-C18-H18B	109.5	H18A-C18-H18B	109.5
C16-C18-H18C	109.5	H18A-C18-H18C	109.5
H18B-C18-H18C	109.5	C16-C19-H19A	109.5
C16-C19-H19B	109.5	H19A-C19-H19B	109.5
C16-C19-H19C	109.5	H19A-C19-H19C	109.5
H19B-C19-H19C	109.5		

Table 7. Torsion angles (°) for JTM1445.

O2-Si1-O1-C10	12.76(14)	C12-Si1-O1-C10	-100.67(15)
C16-Si1-O1-C10	129.19(14)	O1-Si1-O2-C9	6.43(14)
C12-Si1-O2-C9	122.37(14)	C16-Si1-O2-C9	-105.74(14)
C6-C1-C2-C3	-1.3(3)	C7-C1-C2-C3	178.0(2)
C1-C2-C3-C4	-0.1(4)	C2-C3-C4-C5	1.1(4)
C3-C4-C5-C6	-0.7(4)	C4-C5-C6-C1	-0.7(4)
C2-C1-C6-C5	1.7(3)	C7-C1-C6-C5	-177.6(2)

C6-C1-C7-C8	-132.3(2)	C2-C1-C7-C8	48.4(3)
C6-C1-C7-C9	100.8(2)	C2-C1-C7-C9	-78.5(3)
Si1-O2-C9-C7	-146.86(14)	Si1-O2-C9-C10	-22.21(19)
C1-C7-C9-O2	51.0(2)	C8-C7-C9-O2	-76.4(2)
C1-C7-C9-C10	-70.1(2)	C8-C7-C9-C10	162.52(19)
Si1-O1-C10-C11	-150.35(15)	Si1-O1-C10-C9	-26.66(19)
O2-C9-C10-O1	30.9(2)	C7-C9-C10-O1	154.62(17)
O2-C9-C10-C11	152.53(17)	C7-C9-C10-C11	-83.8(2)
O1-C10-C11-Hg1	39.6(2)	C9-C10-C11-Hg1	-80.41(19)
O2-Si1-C12-C15	-66.35(17)	O1-Si1-C12-C15	39.62(18)
C16-Si1-C12-C15	164.35(16)	O2-Si1-C12-C13	174.39(16)
O1-Si1-C12-C13	-79.64(19)	C16-Si1-C12-C13	45.1(2)
O2-Si1-C12-C14	51.9(2)	O1-Si1-C12-C14	157.86(17)
C16-Si1-C12-C14	-77.4(2)	O2-Si1-C16-C17	-82.83(19)
O1-Si1-C16-C17	171.53(17)	C12-Si1-C16-C17	44.6(2)
O2-Si1-C16-C19	35.64(19)	O1-Si1-C16-C19	-70.01(18)
C12-Si1-C16-C19	163.06(16)	O2-Si1-C16-C18	153.80(17)
O1-Si1-C16-C18	48.2(2)	C12-Si1-C16-C18	-78.8(2)

Table 8. Anisotropic atomic displacement parameters (Å^2) for JTM1445.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg1	0.02149(4)	0.02099(4)	0.01980(4)	-0.00195(3)	0.00054(3)	-0.00205(3)
Cl1	0.0330(3)	0.0219(3)	0.0286(3)	-0.0041(2)	0.0066(2)	-0.0038(2)
Si1	0.0179(3)	0.0165(3)	0.0168(3)	0.0014(2)	0.0026(2)	-0.0014(2)
O1	0.0184(7)	0.0172(7)	0.0213(7)	0.0033(6)	0.0023(6)	-0.0030(6)
O2	0.0167(7)	0.0181(7)	0.0197(7)	0.0028(6)	0.0017(6)	-0.0011(6)
C1	0.0245(11)	0.0151(10)	0.0242(11)	0.0023(8)	0.0080(9)	-0.0005(8)
C2	0.0275(12)	0.0209(11)	0.0350(13)	0.0002(9)	0.0044(10)	-0.0047(9)
C3	0.0455(16)	0.0252(12)	0.0328(14)	-0.0042(10)	0.0000(12)	-0.0096(11)
C4	0.0607(19)	0.0200(12)	0.0329(14)	-0.0039(10)	0.0141(13)	-0.0033(12)
C5	0.0425(15)	0.0207(11)	0.0408(15)	-0.0017(10)	0.0165(12)	0.0051(10)
C6	0.0259(12)	0.0185(11)	0.0344(13)	-0.0001(9)	0.0069(10)	0.0009(9)
C7	0.0216(10)	0.0184(10)	0.0214(10)	0.0025(8)	0.0052(8)	0.0011(8)
C8	0.0366(14)	0.0245(12)	0.0336(13)	0.0062(10)	0.0184(11)	0.0017(10)
C9	0.0190(10)	0.0165(9)	0.0176(9)	0.0002(7)	0.0039(8)	0.0016(8)

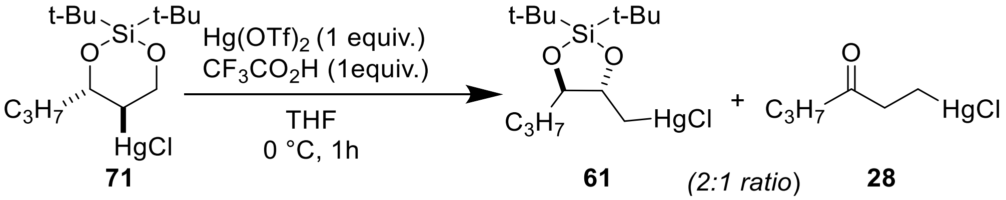
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10	0.0178(10)	0.0168(9)	0.0213(10)	0.0016(8)	0.0032(8)	0.0018(8)
C11	0.0215(11)	0.0216(11)	0.0262(11)	-0.0003(9)	-0.0008(9)	0.0019(9)
C12	0.0271(11)	0.0267(11)	0.0182(10)	-0.0014(9)	0.0059(8)	-0.0060(9)
C13	0.0363(14)	0.0396(14)	0.0210(12)	0.0069(10)	0.0066(10)	-0.0062(11)
C14	0.0357(14)	0.0413(15)	0.0278(13)	-0.0099(11)	0.0042(11)	-0.0130(12)
C15	0.0418(15)	0.0311(13)	0.0285(13)	-0.0028(10)	0.0174(11)	0.0022(11)
C16	0.0247(11)	0.0182(10)	0.0249(11)	0.0042(8)	0.0043(9)	0.0014(9)
C17	0.0325(14)	0.0427(16)	0.0371(15)	0.0014(12)	-0.0032(12)	0.0141(12)
C18	0.0486(17)	0.0171(12)	0.0552(18)	0.0048(11)	0.0183(14)	-0.0049(11)
C19	0.0373(14)	0.0253(12)	0.0306(13)	-0.0012(10)	0.0091(11)	0.0088(10)

Table 9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for JTM1445.

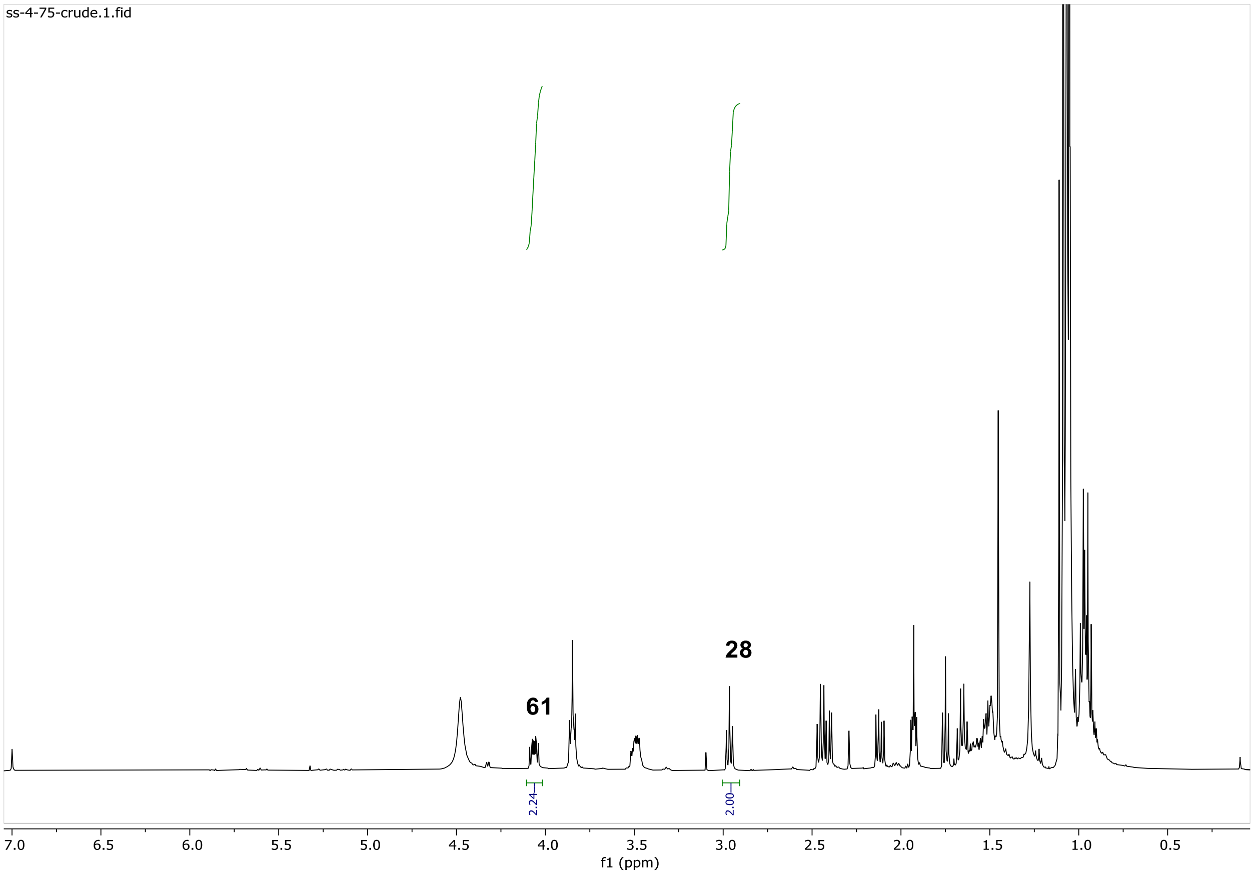
	x/a	y/b	z/c	U(eq)
H2	0.0814	0.2326	0.7207	0.034
H3	0.1014	0.1686	0.6057	0.043
H4	0.4326	0.1223	0.5950	0.045
H5	0.7402	0.1379	0.7011	0.04
H6	0.7198	0.2010	0.8168	0.031
H7	0.5247	0.2595	0.8985	0.024
H8A	0.2062	0.2801	0.9479	0.045
H8B	0.1935	0.2118	0.9117	0.045
H8C	0.0600	0.2652	0.8563	0.045
H9	0.3679	0.3607	0.8777	0.021
H10	0.6882	0.3207	0.7834	0.022
H11A	0.9386	0.3681	0.8827	0.029
H11B	0.7731	0.3422	0.9394	0.029
H13A	0.5465	0.4392	0.5521	0.048
H13B	0.2943	0.4554	0.5187	0.048
H13C	0.4096	0.4042	0.4712	0.048
H14A	0.0027	0.3809	0.5405	0.053
H14B	0.0701	0.3163	0.5846	0.053
H14C	0.1145	0.3302	0.4909	0.053
H15A	0.4641	0.2891	0.6310	0.049
H15B	0.6504	0.3367	0.6189	0.049
H15C	0.5063	0.3042	0.5373	0.049

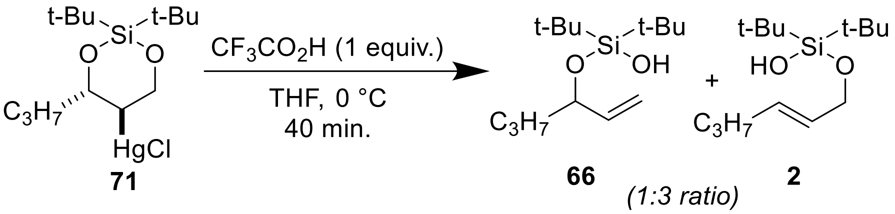
	x/a	y/b	z/c	U(eq)
H17A	-0.0752	0.5273	0.6533	0.058
H17B	-0.1113	0.4551	0.6566	0.058
H17C	0.0098	0.4839	0.5860	0.058
H18A	0.5017	0.5290	0.7319	0.059
H18B	0.2960	0.5721	0.6984	0.059
H18C	0.3915	0.5296	0.6326	0.059
H19A	0.3052	0.4823	0.8384	0.046
H19B	0.0658	0.4544	0.8081	0.046
H19C	0.1027	0.5265	0.8050	0.046

X. Mechanistic Experiments

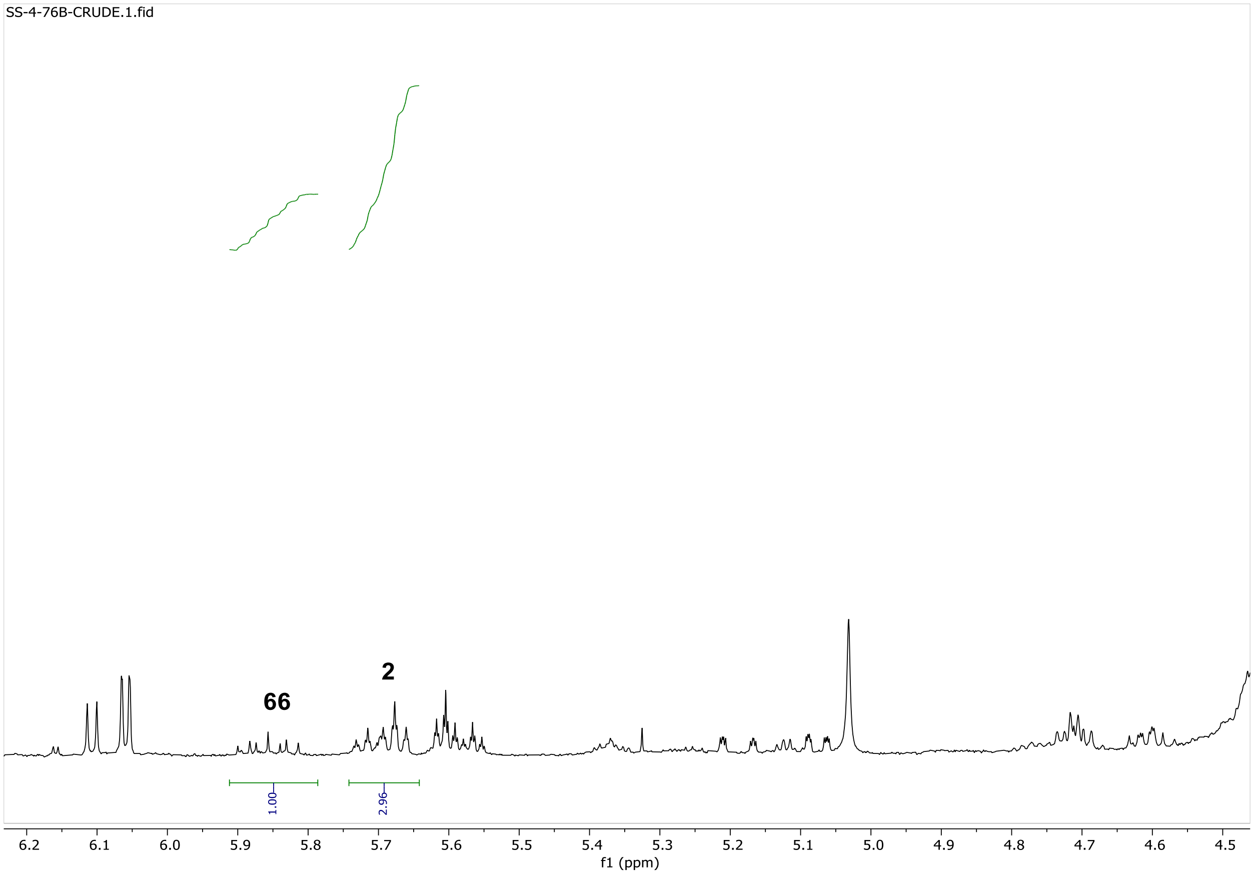


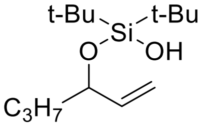
A 10 mL recovery flask with stir bar was charged with **71** (0.1 mmol, 49 mg, 1 equiv.), $Hg(OTf)_2$ (0.1 mmol, 49 mg, 1 equiv.), and 1 mL of THF. The flask was cooled to 0 °C using an ice-water bath. Subsequently, CF_3CO_2H (0.1 mmol, 12 mg, 1 equiv.) was added, and the reaction was allowed to stir for 1h. Following this time, 1 mL of brine solution was added, and the contents of the reaction flask were transferred to a separatory funnel. An additional 10 mL of brine were added followed by 10 mL of CH_2Cl_2. The organic portion was collected, and the aqueous layer was extracted with two additional portions of CH_2Cl_2. The organic fractions were pooled, dried with $MgSO_4$, and concentrated under reduced pressure. ^1H NMR (400 MHz, $CDCl_3$) analysis of the crude residue revealed:





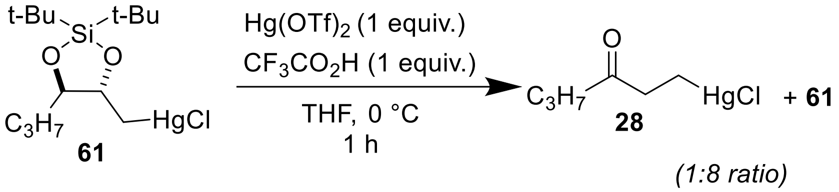
A 10 mL recovery flask with stir bar was charged with **71** (0.1 mmol, 49 mg, 1 equiv.) and 1 mL of THF. The flask was cooled to 0 °C using an ice-water bath. Subsequently, CF_3CO_2H (0.1 mmol, 12 mg, 1 equiv.) was added, and the reaction was allowed to stir for 1h. Following this time, 1 mL of brine solution was added, and the contents of the reaction flask were transferred to a separatory funnel. An additional 10 mL of brine were added followed by 10 mL of CH_2Cl_2. The organic portion was collected, and the aqueous layer was extracted with two additional portions of CH_2Cl_2. The organic fractions were pooled, dried with $MgSO_4$, and concentrated under reduced pressure. ^1H NMR (400 MHz, $CDCl_3$) analysis of the crude residue revealed:



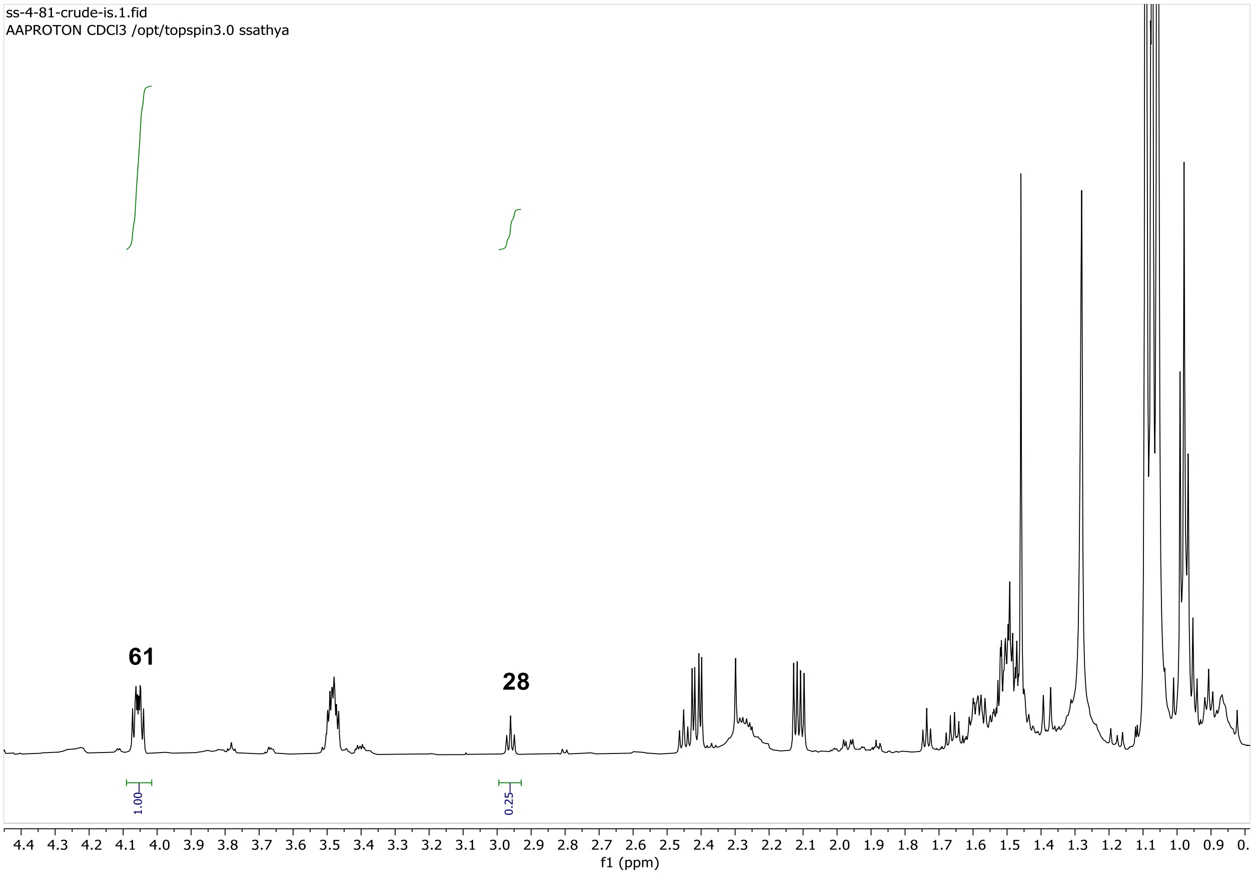


di-*tert*-butyl(hex-1-en-3-yloxy)silanol

Compound 61: ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.86 (ddd, *J* = 17.2, 10.3, 6.8 Hz, 1H), 5.19 (ddd, *J* = 17.3, 1.9, 1.2 Hz, 1H), 5.08 (ddd, *J* = 10.4, 1.9, 1.0 Hz, 1H), 4.41 (dtd, *J* = 6.7, 5.6, 1.1 Hz, 1H), 1.60 (dddd, *J* = 13.0, 8.6, 7.5, 5.6 Hz, 1H), 1.55 – 1.45 (m, 1H), 1.43 – 1.32 (m, 2H), 1.06 (s, 9H), 1.02 (s, 9H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.0, 113.9, 74.3, 40.4, 27.5, 27.4, 20.5, 20.3, 18.1, 14.1. IR 3503, 2932, 1471, 1071 cm^{-1}.; HRMS calculated for $C_{14}H_{31}O_2Si^+$ 259.2093 Found 259.2079 (MH$^+$).



A 10 mL recovery flask with stir bar was charged with **A** (0.05 mmol, 22 mg, 1 equiv.), Hg(OTf)$_2$ (0.05 mmol, 22 mg, 1 equiv.), and 1 mL of THF. The flask was cooled to 0 °C using an ice-water bath. Subsequently, CF$_3$CO$_2$H (0.05 mmol, 5 mg, 1 equiv.) was added, and the reaction was allowed to stir for 1h. Following this time, 1 mL of brine solution was added, and the contents of the reaction flask were transferred to a separatory funnel. An additional 10 mL of brine were added followed by 10 mL of CH_2Cl_2. The organic portion was collected, and the aqueous layer was extracted with two additional portions of CH_2Cl_2. The organic fractions were pooled, dried with $MgSO_4$, and concentrated under reduced pressure. ^1H NMR (400 MHz, $CDCl_3$) analysis of the crude residue revealed:



XI. Computational Procedures and Results

Calculations were performed at home on a desktop gaming PC running Windows 10 with an Intel® Core™ i7-8700K CPU @ 3.70 GHz (6 CPUs) and 16 GB of RAM. The ORCA DFT package[1,2] was used for all DFT calculations. Calculation inputs were prepared using Avogadro[3], and when multiple conformers were possible, a systematic rotor search was performed to identify the lowest energy conformer as a starting point. DFT outputs were analyzed and visualized using Chemcraft[4]. DFT calculations were performed using the B3LYP[5,6] functional with the RIJCOSX approximation and D3BJ[7,8] dispersion correction using the def2-TZVP[9] basis set and def2/J[10] auxiliary basis set for RIJCOSX. For calculations involving mercury, the DEF2-ECP was automatically applied by ORCA, replacing 60 core electrons.[11] The SMD solvation module[12] was used to model implicit THF solvation. The larger solvent accessible surface (SAS) was used instead of the default smaller solvent excluded surface (SES) on account of geometry convergence issues with the latter.

Example ORCA Input card for a groundstate opt-freq job:

```
! RKS RIJCOSX B3LYP D3BJ def2-TZVP def2/J        #Level of theory
! Grid5 FinalGrid6 GridX7 tightSCF slowconv      #Tight grids lead to best results
! OPT FREQ
! pal6                                           #6 CPUs used on local machine
%maxcore 2048                                    #2GB RAM allocated per CPU
! CPCM(THF)                                      #Implicit water solvation
%cpcm
smd true SMDsolvent "THF"
surfacetype gepol_sas                            #Solvent accessible surface (SAS) used
end

* xyz 0 1
#Atomic coordinates go here
*
```

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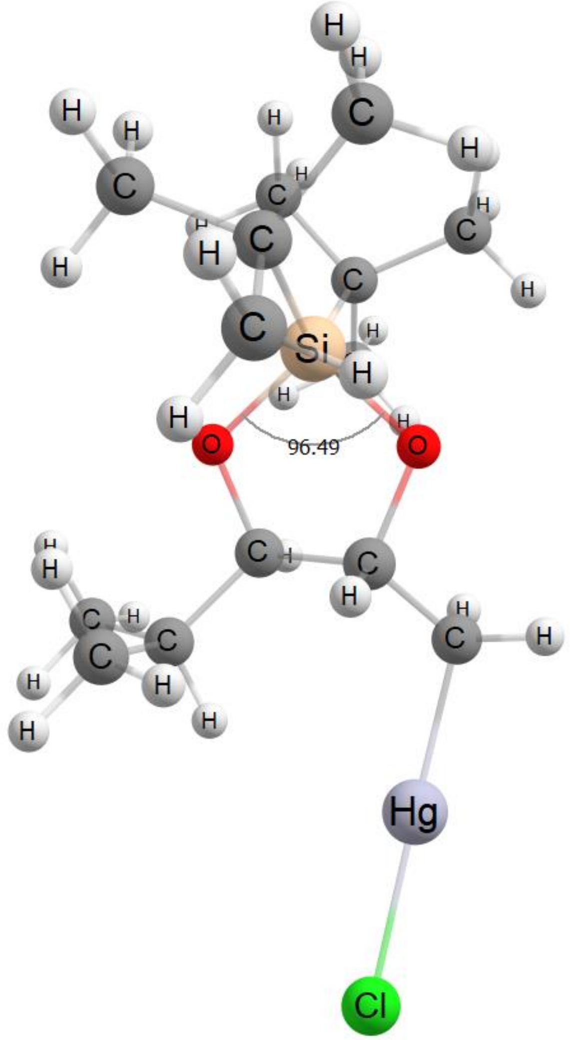
5-exo cyclized mercuric chloride

Level of theory: B3LYP D3BJ RIJCOSX def2/TZVP SMD THF (SAS)



Electronic Energy (Hartree): -1604.560063

Gibbs Free Energy (Hartree): -1604.200279

Negative Frequencies (cm^{-1}): None

Molecular Dipole (Debye): 3.83

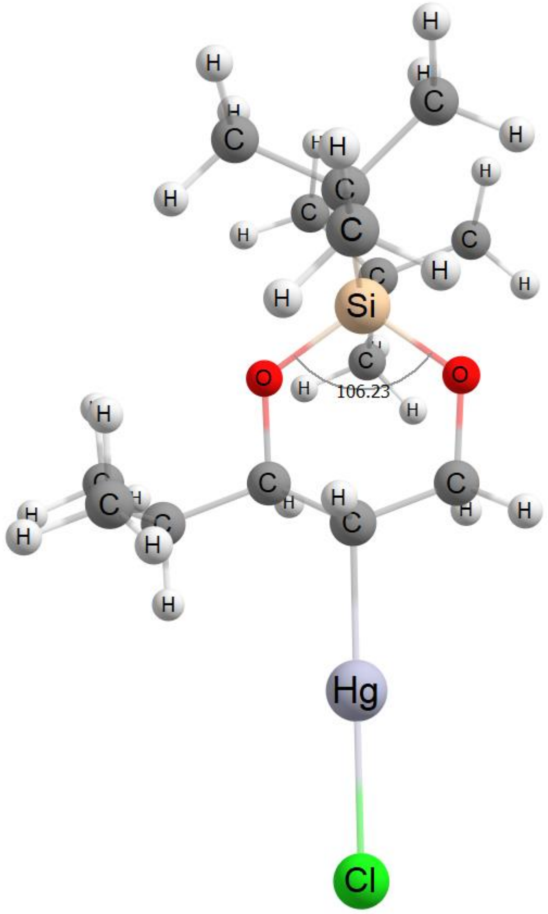
HOMO Energy (Hartree): -0.250261

LUMO Energy (Hartree): -0.035868

Coordinates (Charge 0, Multiplicity 1):

Hg	0.13735	-1.00643	-3.21448
Cl	-0.64129	-2.25609	-5.03330
Si	0.56187	0.22441	2.20116
O	1.35414	0.26501	0.73228
O	-0.80666	-0.55765	1.65580
C	-0.82269	-0.59885	0.22353
C	0.65522	-0.52812	-0.24349
C	0.86083	0.12297	-1.59574
C	0.19958	2.00810	2.72654
C	1.43801	-0.90101	3.44745
C	-1.64084	-1.80330	-0.25006
C	-1.08211	-3.14611	0.21516
C	-3.09927	-1.64142	0.17926
H	1.09743	-1.52804	-0.23599
H	1.92628	0.25379	-1.78112
H	0.38393	1.10267	-1.63431
H	-1.62263	-1.78621	-1.34700
H	-1.70328	-3.96193	-0.15908
H	-0.06634	-3.32556	-0.14022
H	-1.07646	-3.20423	1.30393
H	-3.51944	-0.70089	-0.18468
H	-3.18118	-1.64634	1.26711
H	-3.71278	-2.45483	-0.21257
H	-1.32330	0.30847	-0.13958
C	-0.79042	2.59639	1.70592
C	1.48931	2.84518	2.69411
C	-0.43102	2.08191	4.12430
C	1.93771	-2.13752	2.67967
C	0.45131	-1.36160	4.53329
C	2.64232	-0.21045	4.10337
H	-0.37954	2.59262	0.69451
H	-1.01334	3.63759	1.96226
H	-1.73518	2.05007	1.69314
H	-1.34258	1.48379	4.19626
H	-0.70279	3.11709	4.35806
H	0.25383	1.74697	4.90470
H	1.97254	2.80303	1.71608
H	2.21575	2.52081	3.44007
H	1.25735	3.89525	2.90349
H	-0.42705	-1.84626	4.10302
H	0.10443	-0.53693	5.15722
H	0.93739	-2.08639	5.19556
H	3.36047	0.15277	3.36443
H	3.17212	-0.91866	4.74977
H	2.34605	0.63334	4.72807
H	2.65762	-1.87036	1.90402
H	1.11864	-2.68288	2.20931
H	2.43509	-2.82729	3.36984

6-endo cyclized mercuric chloride
Level of theory: B3LYP D3BJ RIJCOSX
def2/TZVP SMD THF (SAS)

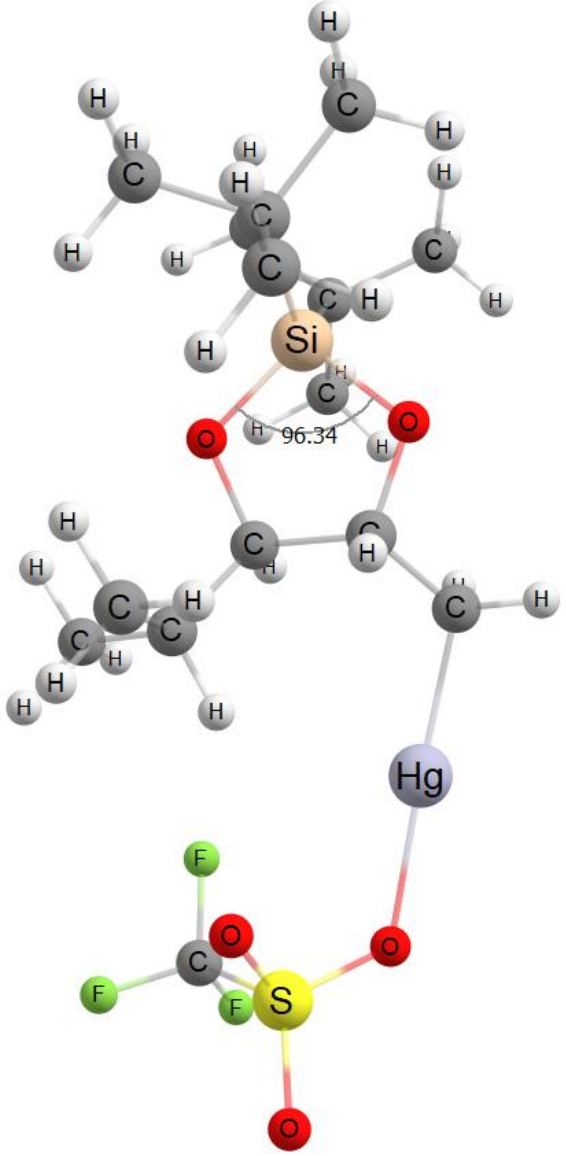


Electronic Energy (Hartree): -1604.560123
Gibbs Free Energy (Hartree): -1604.199463
Negative Frequencies (cm^{-1}): None
Molecular Dipole (Debye): 3.19
HOMO Energy (Hartree): -0.245635
LUMO Energy (Hartree): -0.041196
Coordinates (Charge 0, Multiplicity 1):

Hg	0.08554	-1.30694	-2.80936
Cl	-0.29007	-1.73791	-5.07979
Si	0.71978	0.26463	2.00863
O	1.75427	0.50162	0.73584
O	-0.56974	-0.58250	1.40568
C	-0.86053	-0.70528	0.00985
C	0.44489	-0.93450	-0.75512
C	1.40972	0.24028	-0.62058
C	0.13884	1.97116	2.60261
C	1.56169	-0.87168	3.26940
C	-1.93048	-1.79447	-0.15454
C	-1.43508	-3.17985	0.25508
C	-3.19320	-1.41325	0.61623
H	0.93107	-1.83775	-0.38462
H	2.34143	0.03361	-1.15121
H	0.97493	1.14545	-1.05952
H	-2.18928	-1.81892	-1.22069
H	-2.22937	-3.91885	0.13594
H	-0.58874	-3.51776	-0.34607
H	-1.12898	-3.18492	1.30202
H	-3.56437	-0.43161	0.31194
H	-2.99610	-1.37973	1.68827
H	-3.98880	-2.13934	0.43888
H	-1.29751	0.24102	-0.33510
C	-0.76300	2.54984	1.49683
C	1.33281	2.91862	2.80038
C	-0.67327	1.88818	3.90230
C	2.16690	-2.05320	2.49137
C	0.53604	-1.42502	4.27205
C	2.68513	-0.14991	4.02714
H	-0.23786	2.63896	0.54290
H	-1.09518	3.55603	1.77454
H	-1.65608	1.94240	1.34076
H	-1.51076	1.19132	3.82080
H	-1.09006	2.87115	4.14871
H	-0.05953	1.57979	4.75005
H	1.94219	2.99368	1.89803
H	1.98467	2.60155	3.61535
H	0.97516	3.92499	3.04519
H	-0.28771	-1.93301	3.76761
H	0.10896	-0.64622	4.90444
H	1.01754	-2.15237	4.93489
H	3.42046	0.29105	3.35024
H	3.21817	-0.85744	4.67176
H	2.30190	0.64341	4.67085
H	2.91881	-1.72488	1.77221
H	1.40278	-2.61547	1.95107
H	2.65099	-2.74752	3.18654

5-exo cyclized mercuric triflate

Level of theory: B3LYP D3BJ RIJCOSX def2/TZVP SMD THF (SAS)



Electronic Energy (Hartree): -2105.868276

Gibbs Free Energy (Hartree): -2105.487946

Negative Frequencies (cm^{-1}): None

Molecular Dipole (Debye): 7.60

HOMO Energy (Hartree): -0.253532

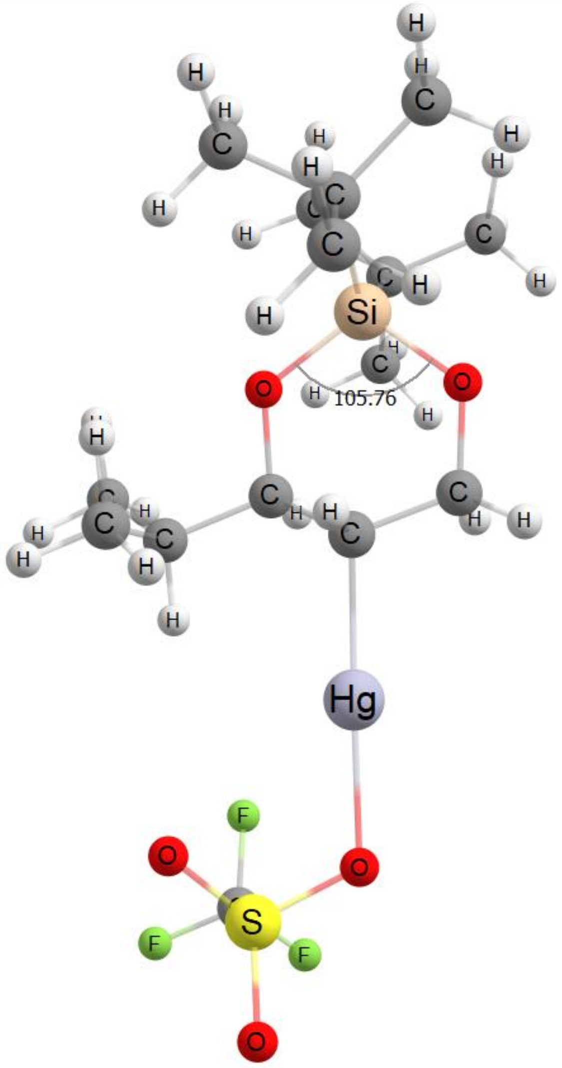
LUMO Energy (Hartree): -0.062637

Coordinates (Charge 0, Multiplicity 1):

Hg	0.94606	-0.39908	-3.71972
Si	0.55932	0.04236	1.74013
O	1.61465	0.28683	0.46523
O	-0.52549	-0.90464	0.90214
C	-0.27875	-0.84780	-0.50471
C	1.21482	-0.45378	-0.69314
C	1.47944	0.44598	-1.88695
C	-0.18904	1.71563	2.21974
C	1.34339	-0.99942	3.11145
C	-0.71181	-2.15640	-1.16996
C	-0.03648	-3.39362	-0.58385
C	-2.23317	-2.29185	-1.12353
H	1.83580	-1.35131	-0.75580
H	2.53893	0.68221	-1.96497
H	0.91531	1.37442	-1.80645
H	-0.42393	-2.09538	-2.22560
H	-0.35033	-4.28246	-1.13304
H	1.05166	-3.34694	-0.64586
H	-0.31389	-3.52664	0.46212
H	-2.72657	-1.42944	-1.57677
H	-2.57918	-2.37220	-0.09146
H	-2.55868	-3.18272	-1.66290
H	-0.88955	-0.03738	-0.92476
C	-1.03865	2.20096	1.03224
C	0.92308	2.74582	2.47805
C	-1.09266	1.60650	3.45644
C	2.18932	-2.09314	2.43651
C	0.24542	-1.67382	3.95170
C	2.25225	-0.16564	4.02567
H	-0.43926	2.32728	0.12846
H	-1.47983	3.17587	1.26464
H	-1.85653	1.51413	0.80796
H	-1.88745	0.86915	3.32084
H	-1.57444	2.57024	3.65370
H	-0.53397	1.33842	4.35415
H	1.59222	2.84086	1.62062
H	1.52993	2.49529	3.34871
H	0.48231	3.73137	2.66373
H	-0.43000	-2.26836	3.33391
H	-0.35722	-0.95286	4.50545
H	0.70062	-2.34714	4.68608
H	3.03719	0.34967	3.46708
H	2.74705	-0.81763	4.75352
H	1.69539	0.58199	4.59216
H	2.99721	-1.67054	1.83665
H	1.58677	-2.73293	1.79093
H	2.64321	-2.73419	3.19967
S	-0.21570	-2.53439	-5.68638
C	-2.02241	-2.10580	-5.55122
O	-0.04933	-3.14079	-6.97017
O	0.40310	-1.14745	-5.63374
O	0.07470	-3.28169	-4.48691
F	-2.75702	-3.21585	-5.48964
F	-2.42430	-1.37800	-6.59259
F	-2.23652	-1.39270	-4.42969

6-endo cyclized mercuric triflate

Level of theory: B3LYP D3BJ RIJCOSX
def2/TZVP SMD THF (SAS)

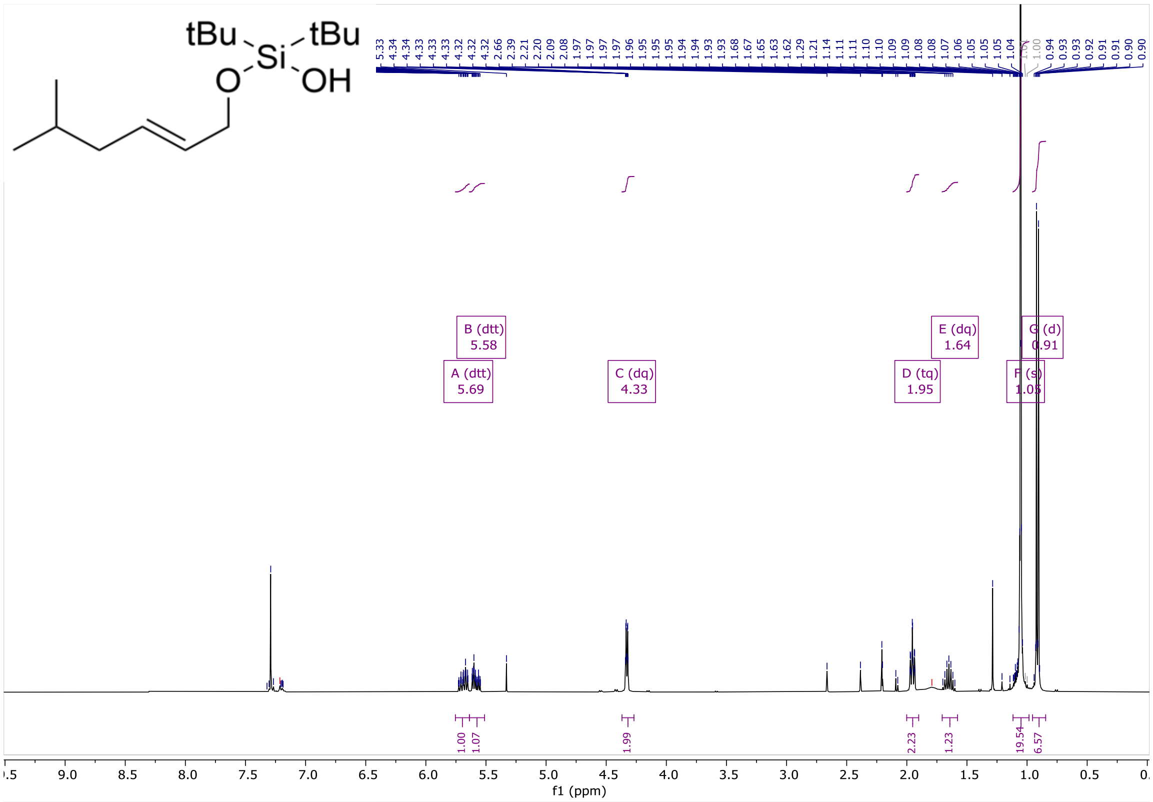


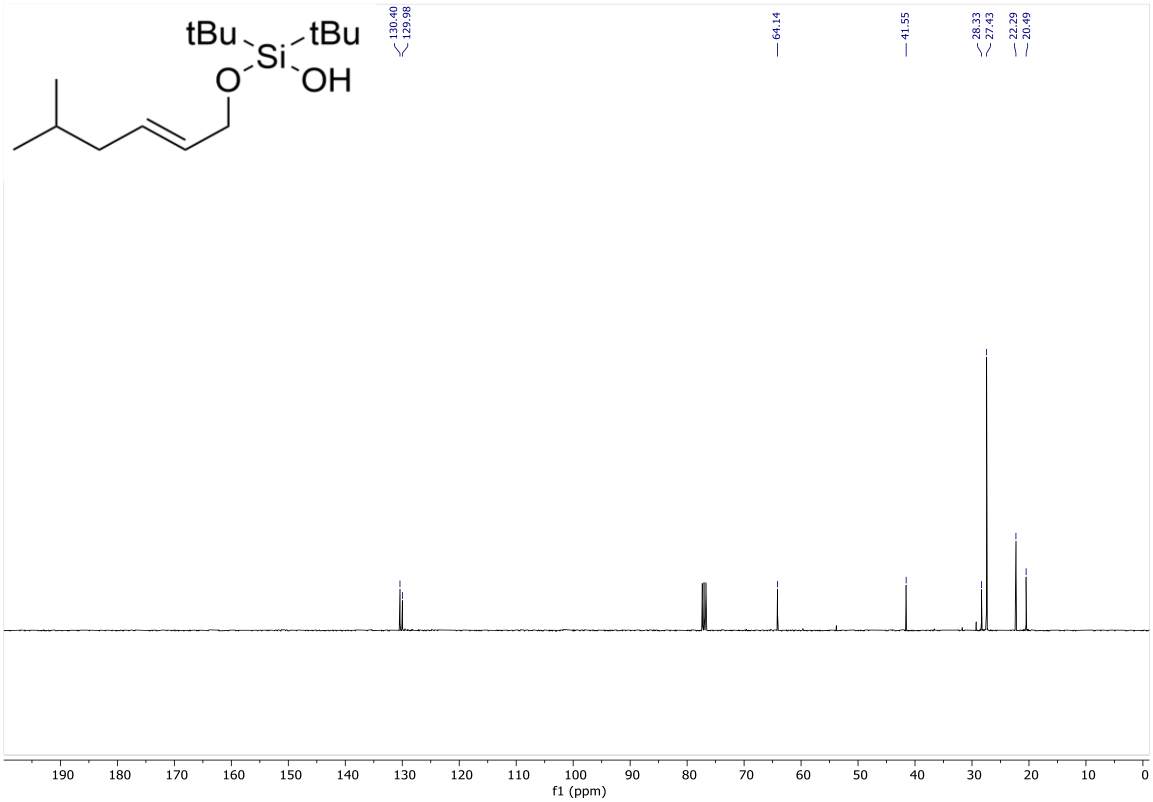
Electronic Energy (Hartree): -2105.866730
Gibbs Free Energy (Hartree): -2105.484855
Negative Frequencies (cm^{-1}): None
Molecular Dipole (Debye): 7.36
HOMO Energy (Hartree): -0.251196
LUMO Energy (Hartree): -0.067290
Coordinates (Charge 0, Multiplicity 1):

Hg	1.21151	-1.20659	-3.08408
Si	0.88291	0.32398	1.75318
O	2.07122	0.71721	0.66197
O	-0.16998	-0.66482	0.93618
C	-0.22763	-0.76903	-0.48561
C	1.20849	-0.81830	-1.01770
C	1.98511	0.46490	-0.73169
C	-0.00157	1.92649	2.24845
C	1.65409	-0.73364	3.12050
C	-1.11778	-1.96620	-0.84810
C	-0.53274	-3.30264	-0.39741
C	-2.52288	-1.76110	-0.28495
H	1.73591	-1.66751	-0.58332
H	3.00608	0.39013	-1.11088
H	1.50894	1.31822	-1.22790
H	-1.20155	-1.97755	-1.94209
H	-1.20648	-4.11833	-0.66350
H	0.42883	-3.52110	-0.86592
H	-0.39573	-3.31941	0.68460
H	-2.95424	-0.81589	-0.62339
H	-2.50598	-1.75152	0.80540
H	-3.18756	-2.56394	-0.60827
H	-0.70838	0.13380	-0.88387
C	-0.78344	2.41375	1.01467
C	1.01221	3.01253	2.64242
C	-0.99284	1.70557	3.39970
C	2.51158	-1.81444	2.43858
C	0.56238	-1.43085	3.94873
C	2.55078	0.09914	4.04773
H	-0.13046	2.59264	0.15723
H	-1.28117	3.36290	1.24011
H	-1.55646	1.70378	0.71573
H	-1.70787	0.90905	3.18124
H	-1.56869	2.62005	3.57940
H	-0.48719	1.45774	4.33412
H	1.73959	3.19406	1.84920
H	1.56474	2.75694	3.54712
H	0.49108	3.95624	2.83745
H	-0.10889	-2.01899	3.32051
H	-0.04533	-0.72505	4.51538
H	1.02278	-2.11396	4.67071
H	3.32120	0.64292	3.49626
H	3.06168	-0.55556	4.76198
H	1.97859	0.82301	4.63001
H	3.32050	-1.38108	1.84843
H	1.91419	-2.45156	1.78324
H	2.96353	-2.46272	3.19661
S	0.32217	-2.68137	-5.66217
O	1.24469	-1.57269	-5.18320
O	0.80944	-3.30769	-6.85140
O	-0.13696	-3.48294	-4.55198
C	-1.16429	-1.68942	-6.18074
F	-2.14189	-2.50235	-6.58056
F	-0.86109	-0.85641	-7.17592
F	-1.61230	-0.96316	-5.14127

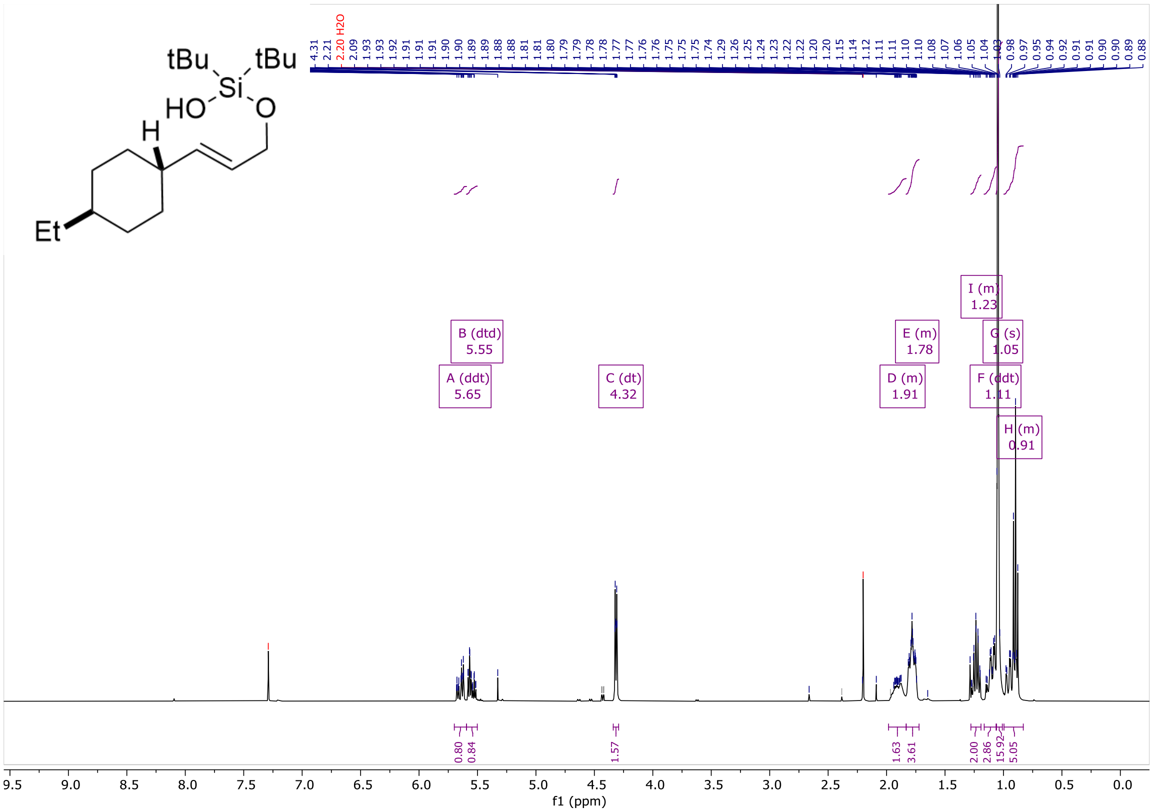
XII. NMR Spectra

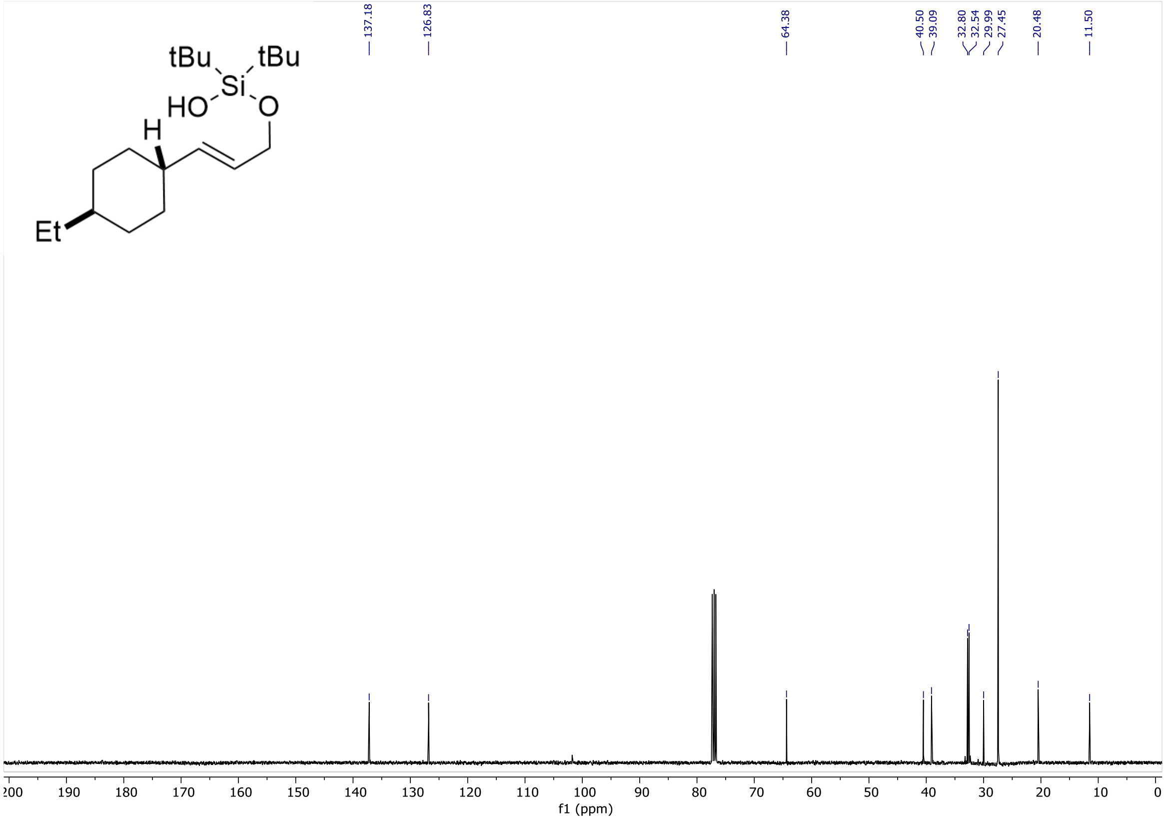
Compound 4 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



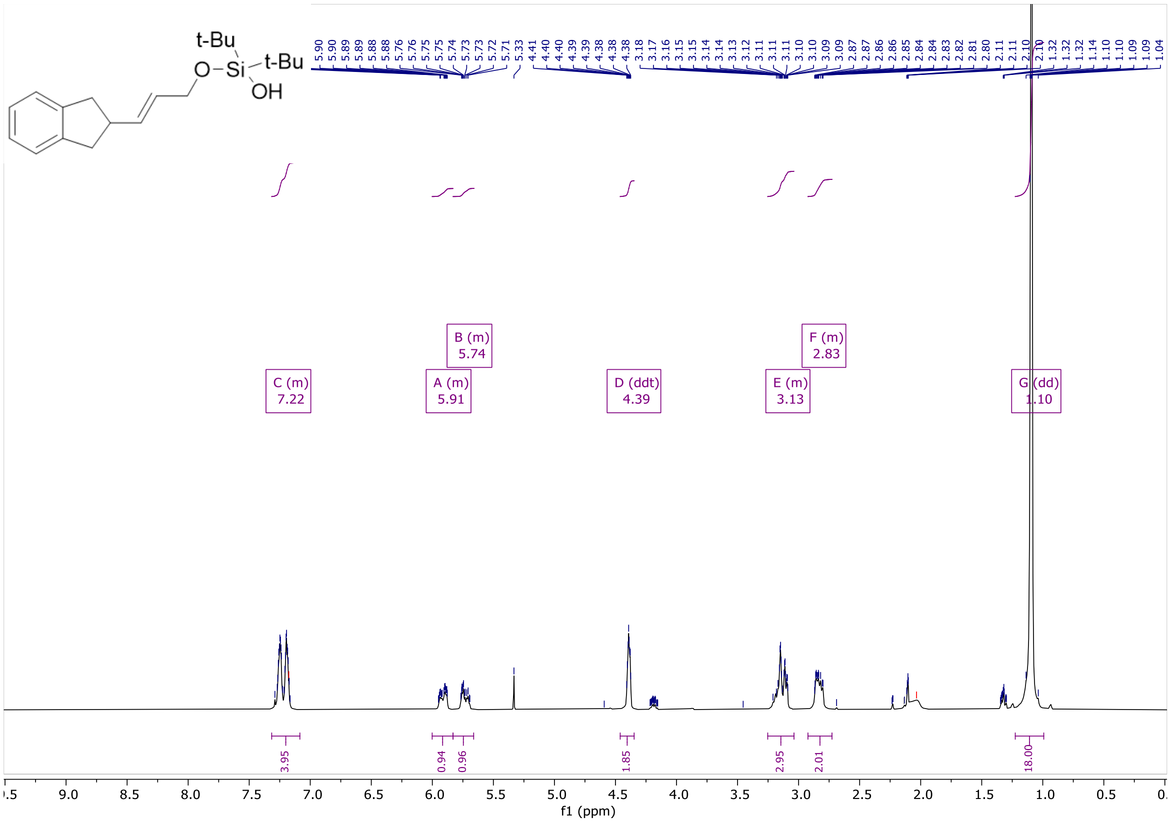


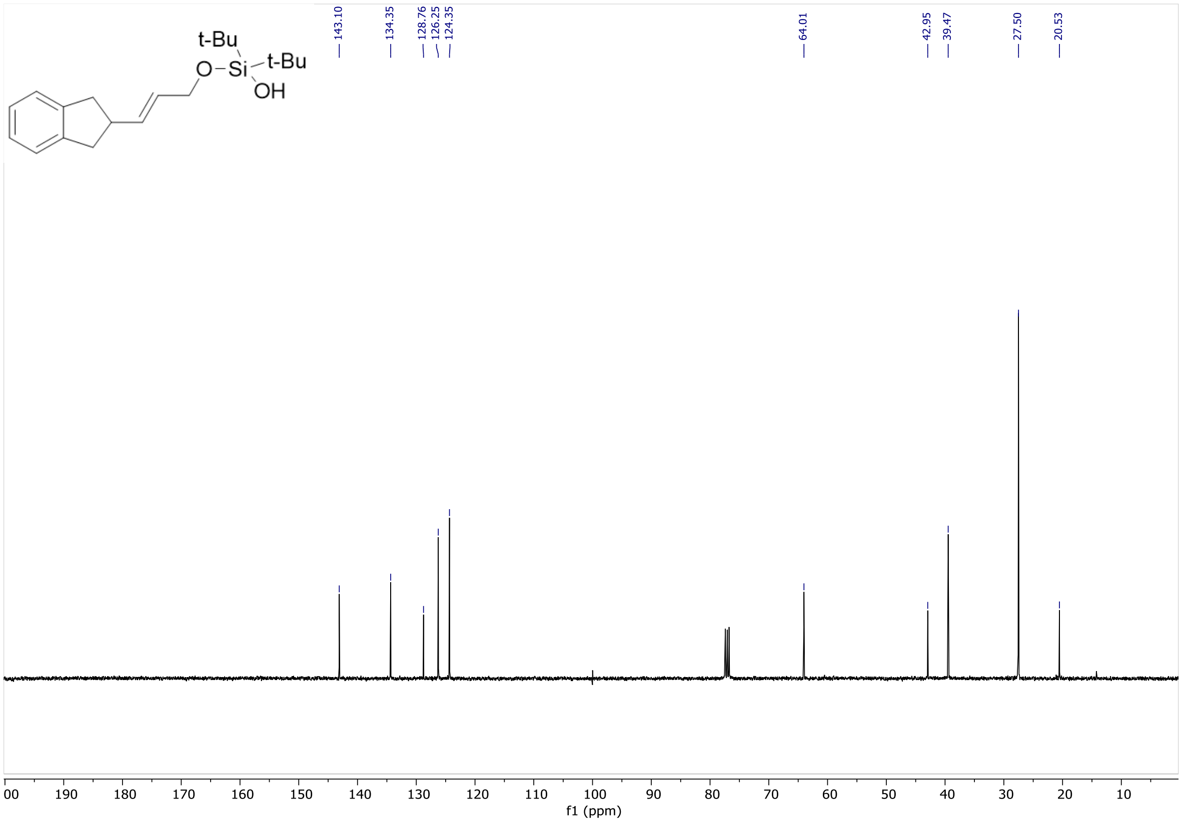
Compound 6 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



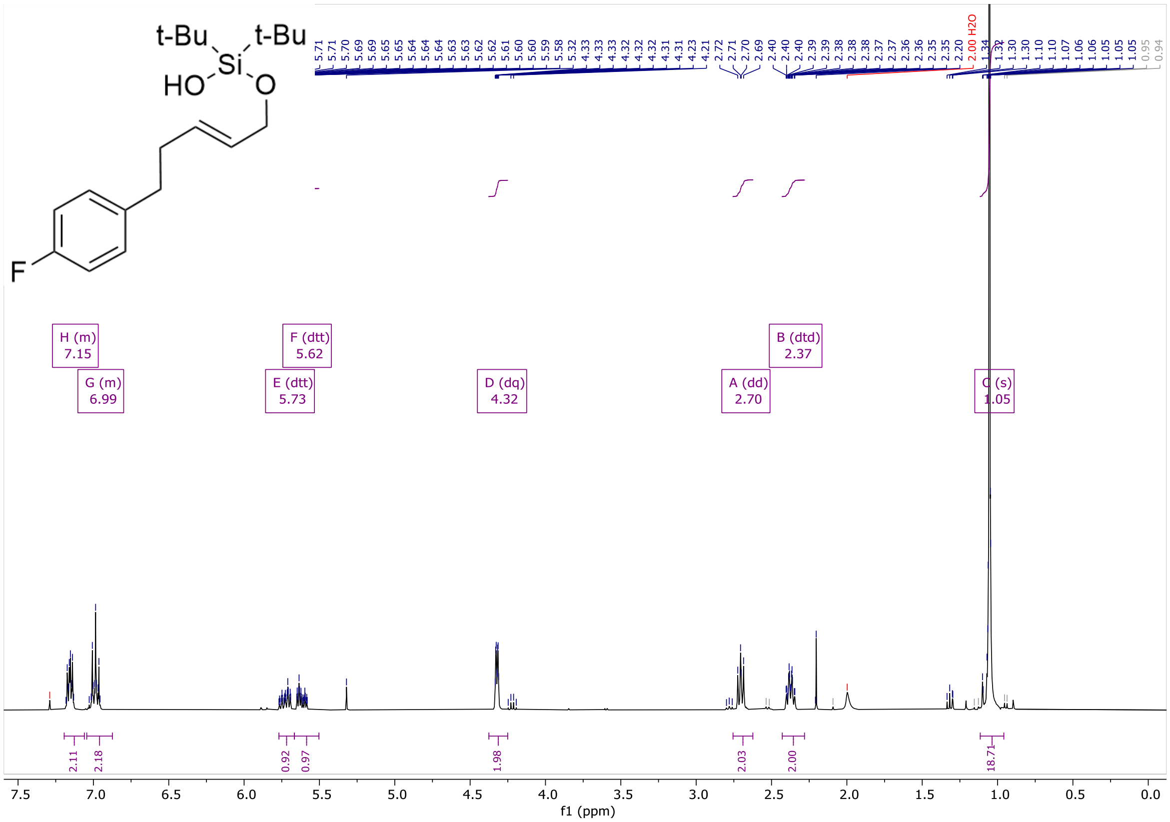


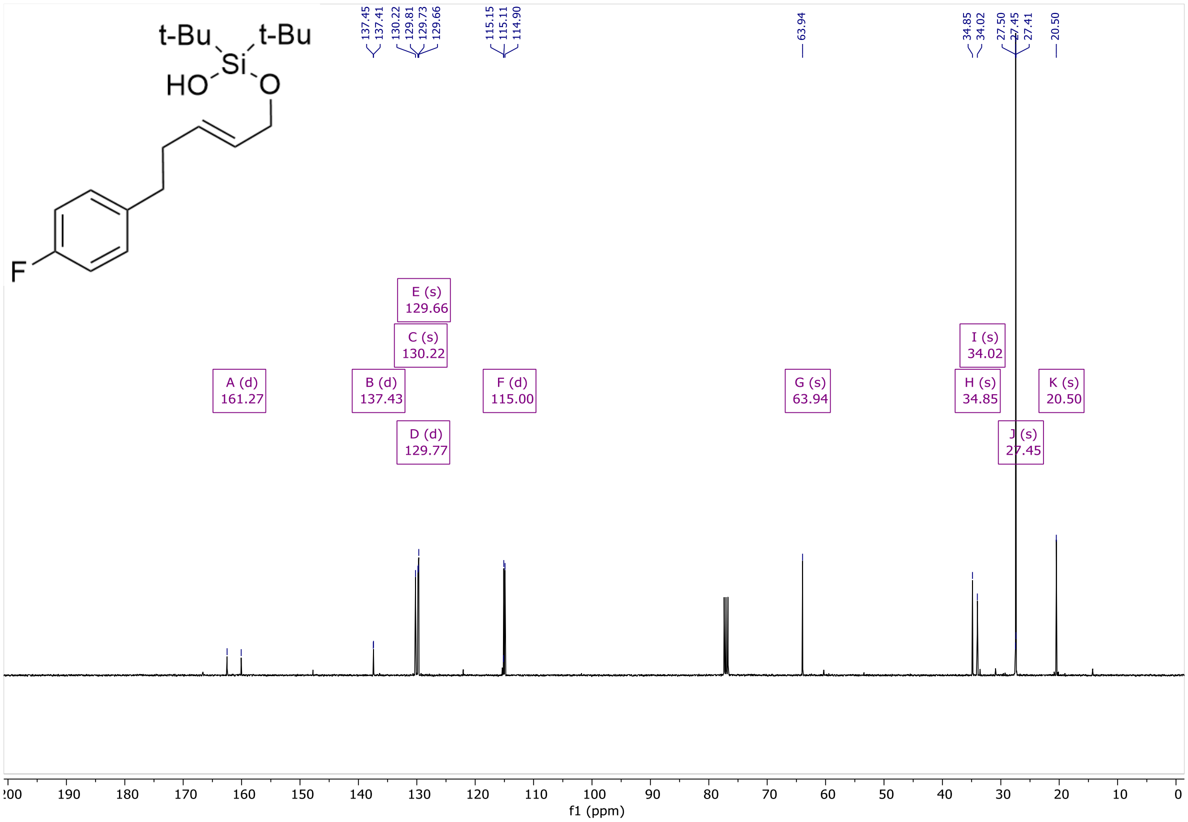
Compound 9 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



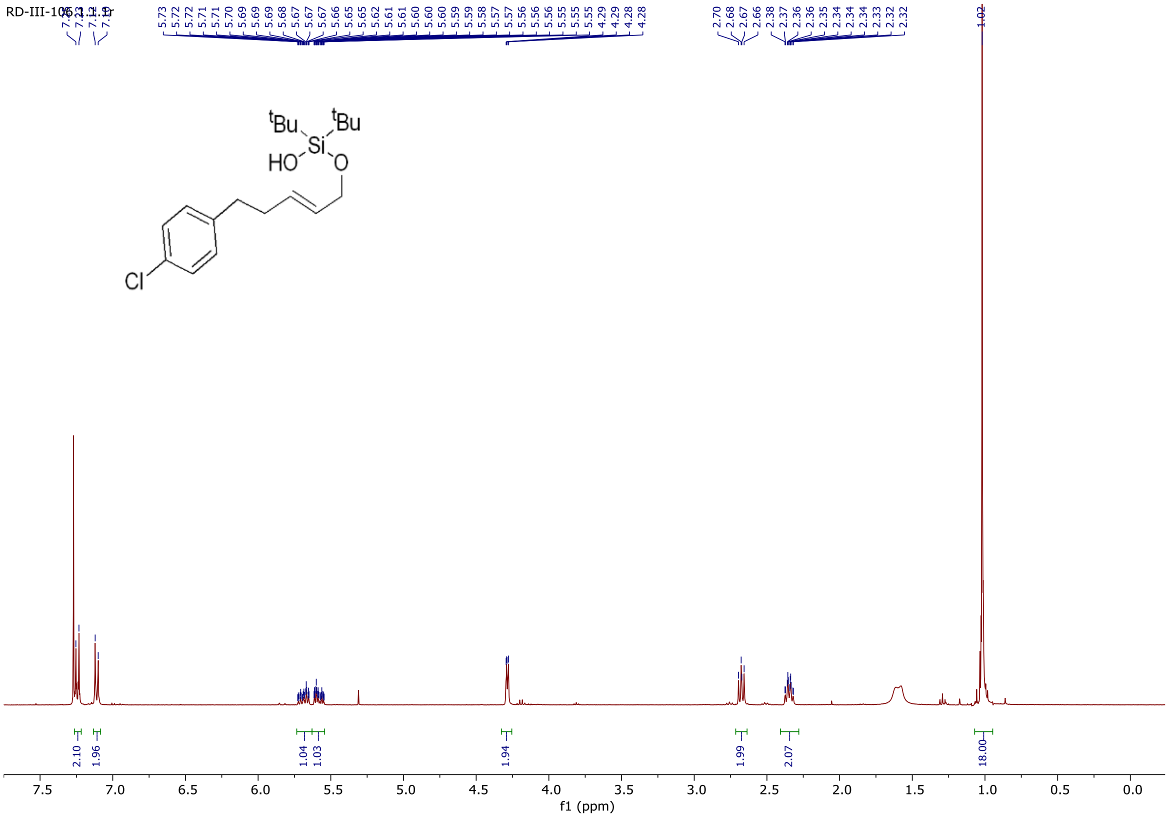


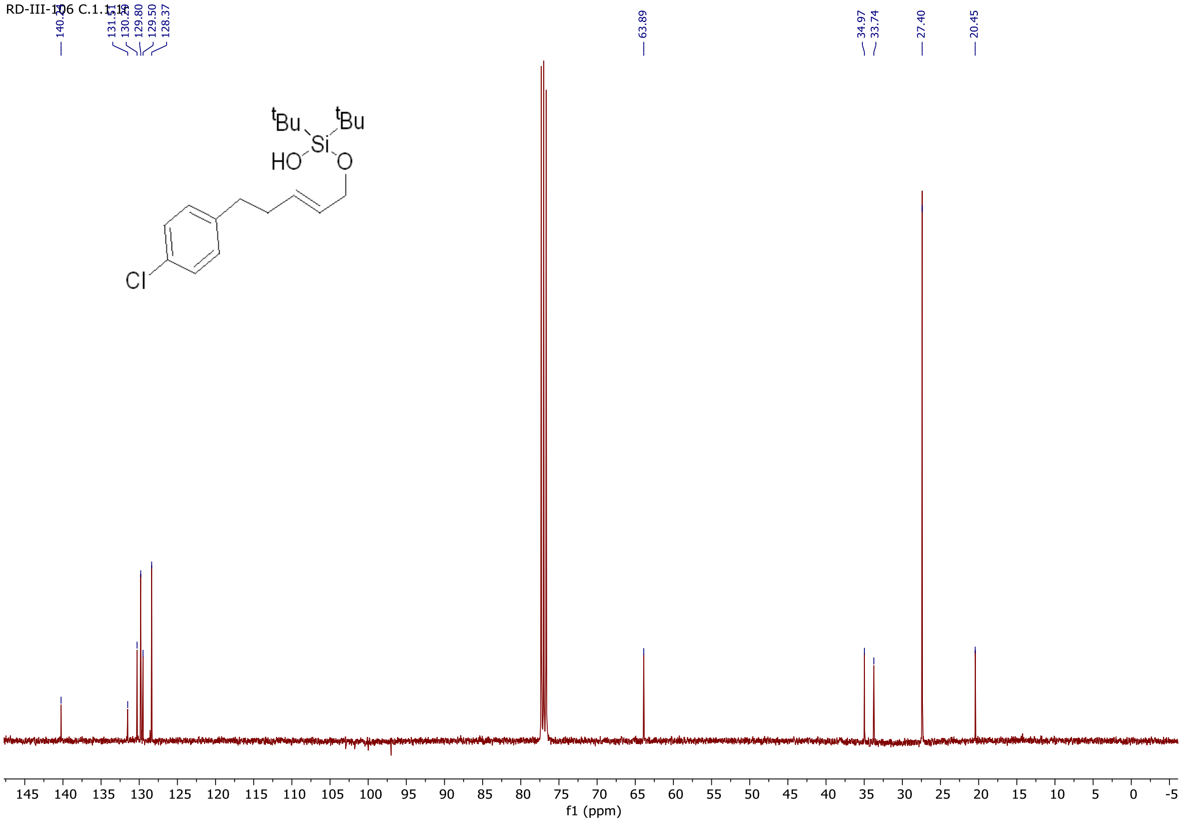
Compound 11 (^1H NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 100 MHz)



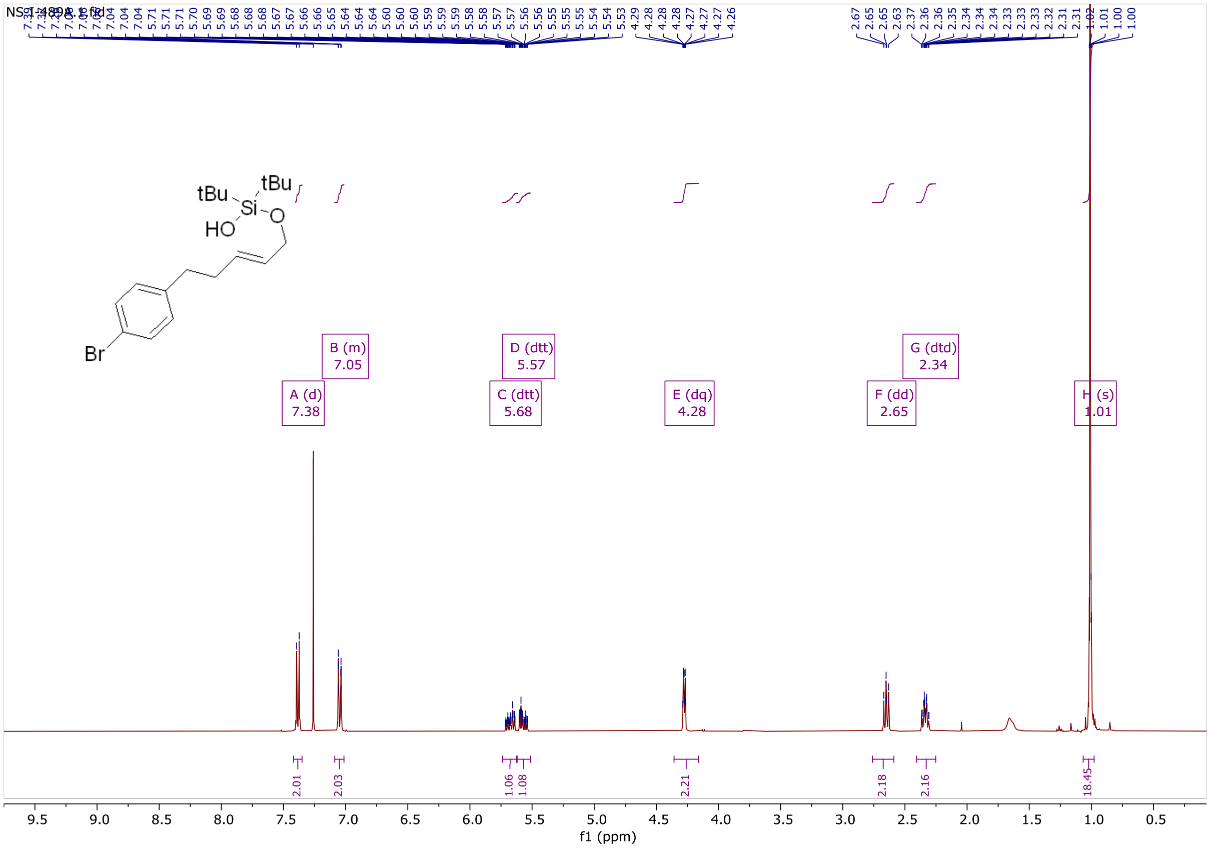


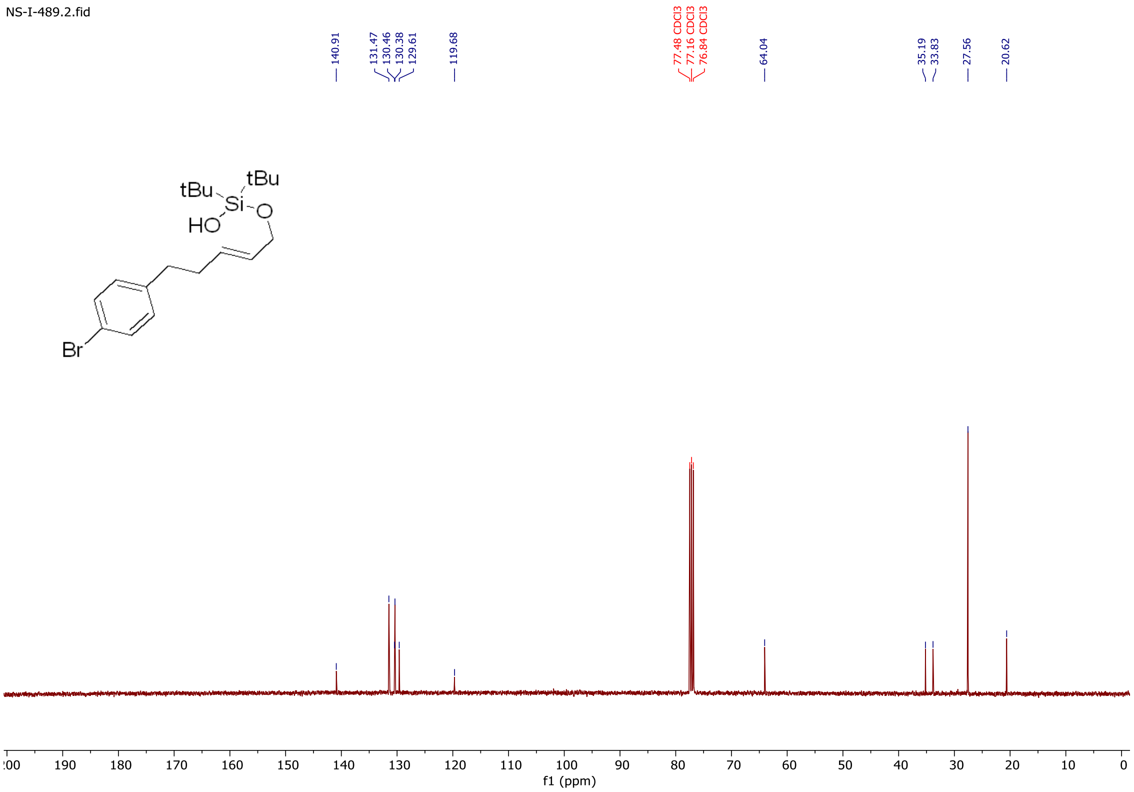
Compound 12 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



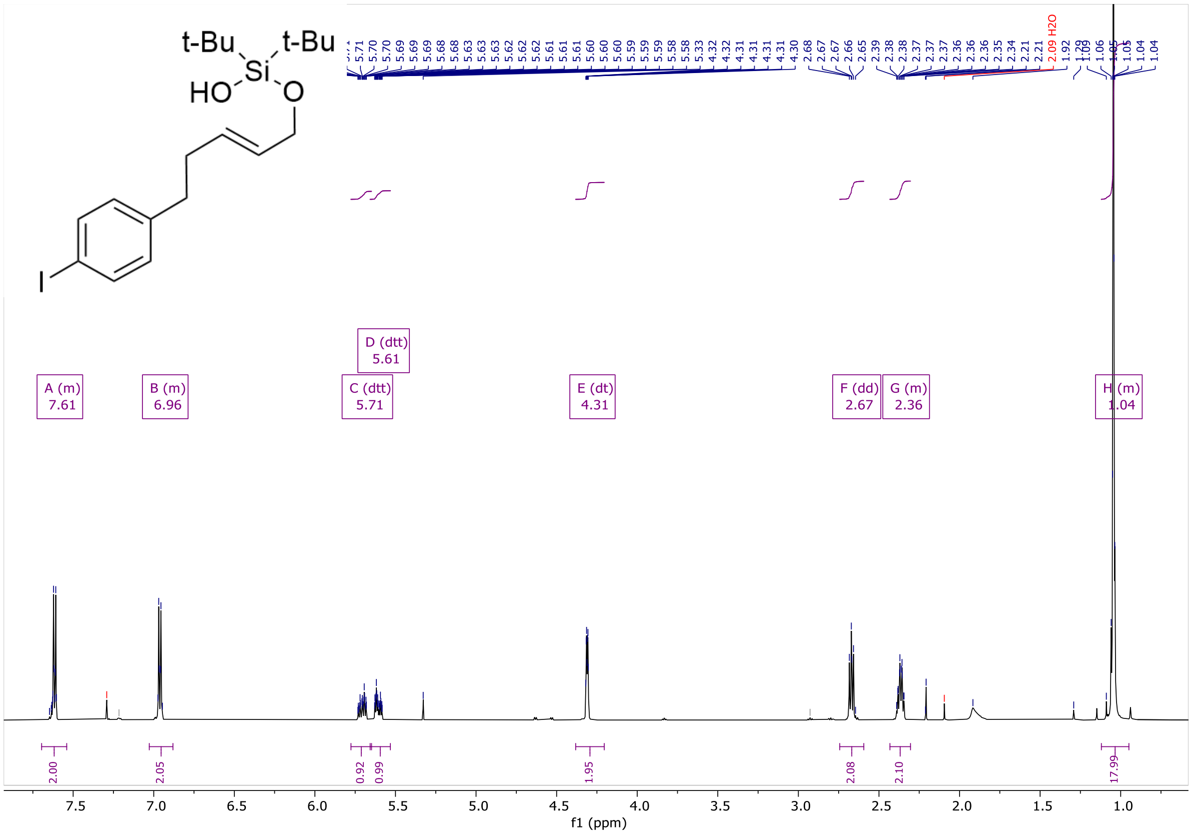


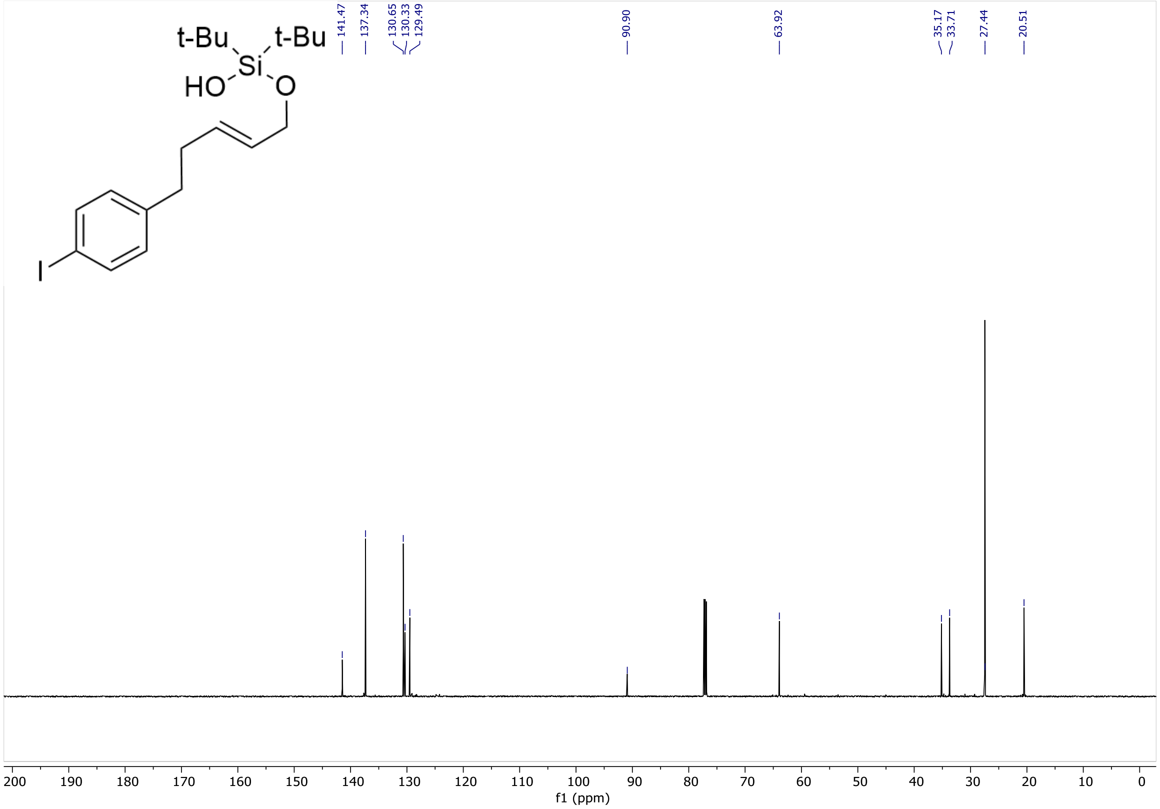
Compound 13 (^{1}H NMR: 400 MHz, $^{13}C\{^{1}H\}$ NMR: 100 MHz)



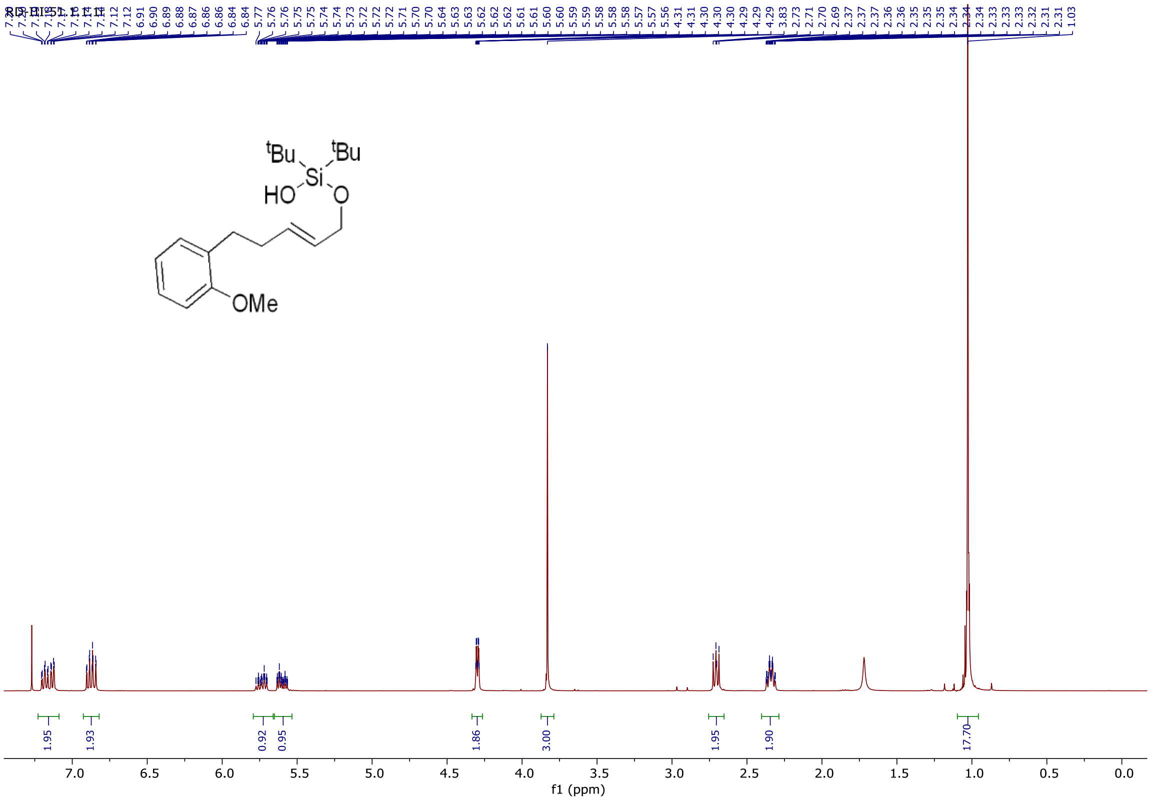


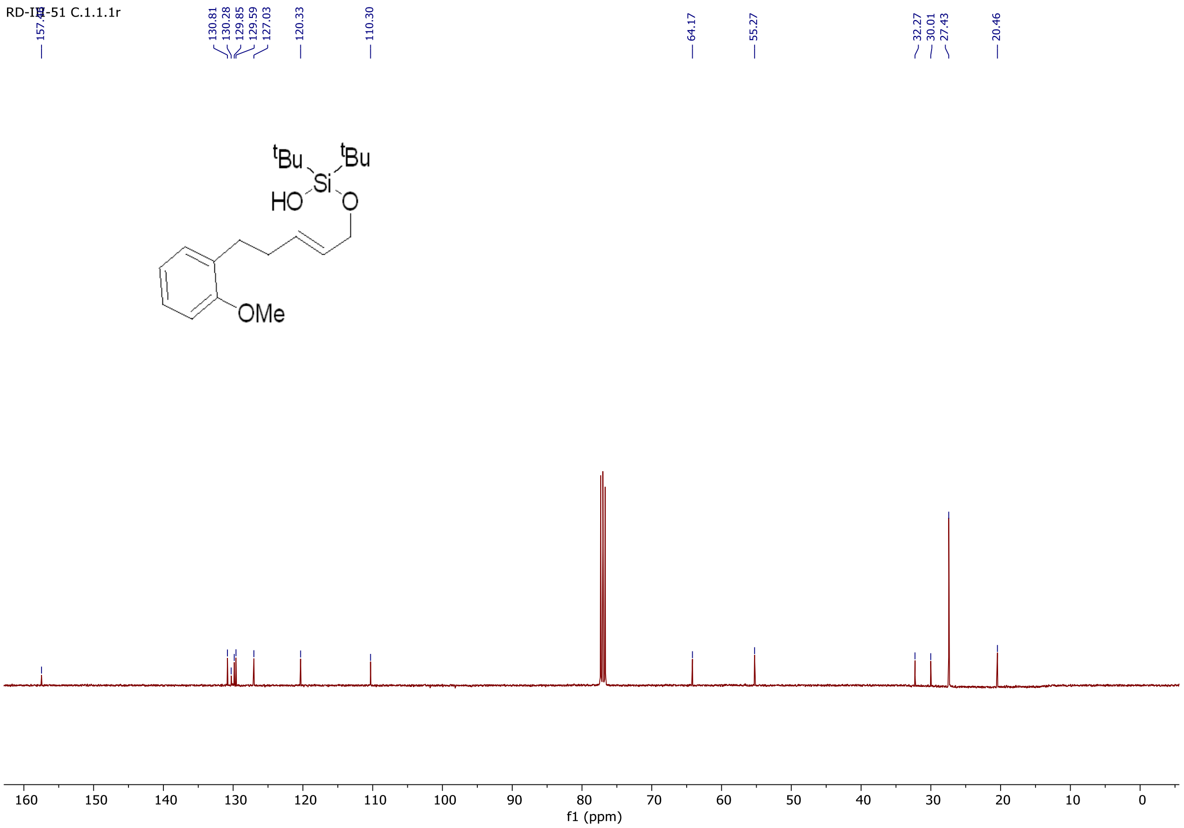
Compound 14 (^{1}H NMR: 600 MHz, ^{13}C{^{1}H} NMR: 150 MHz)



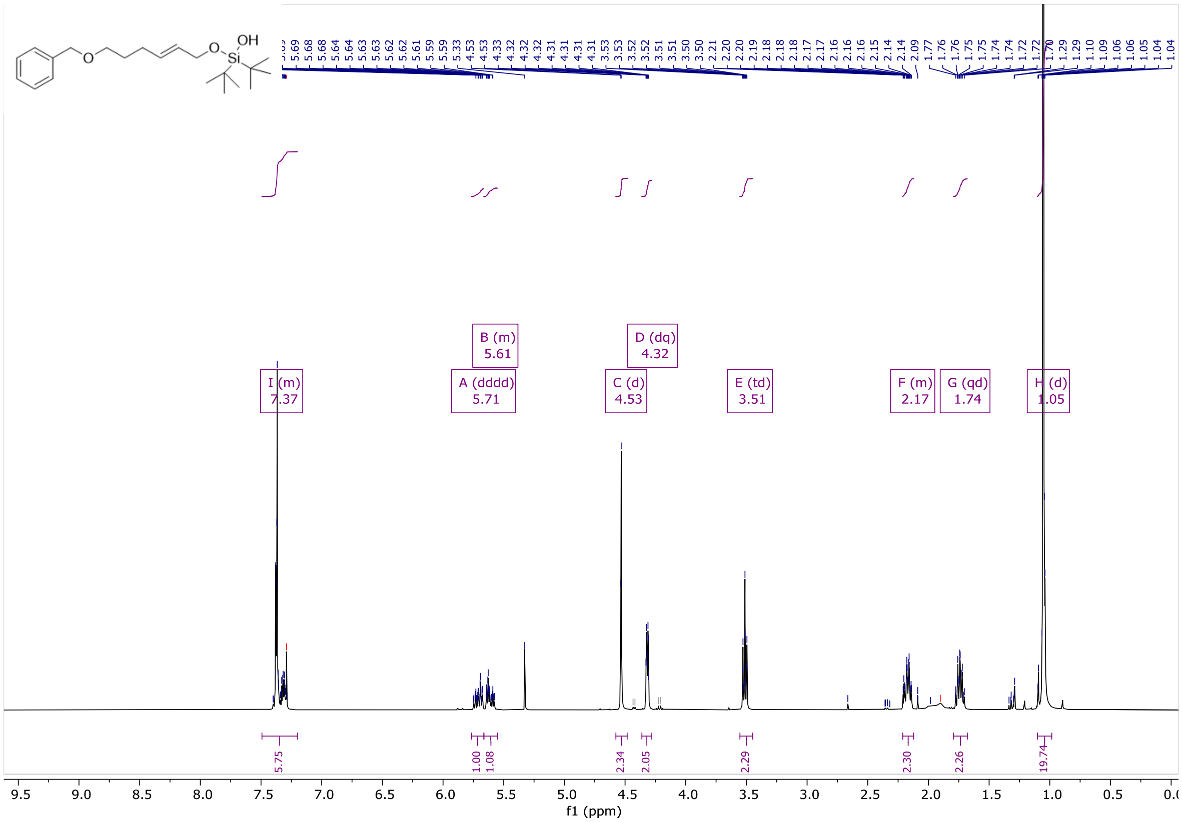


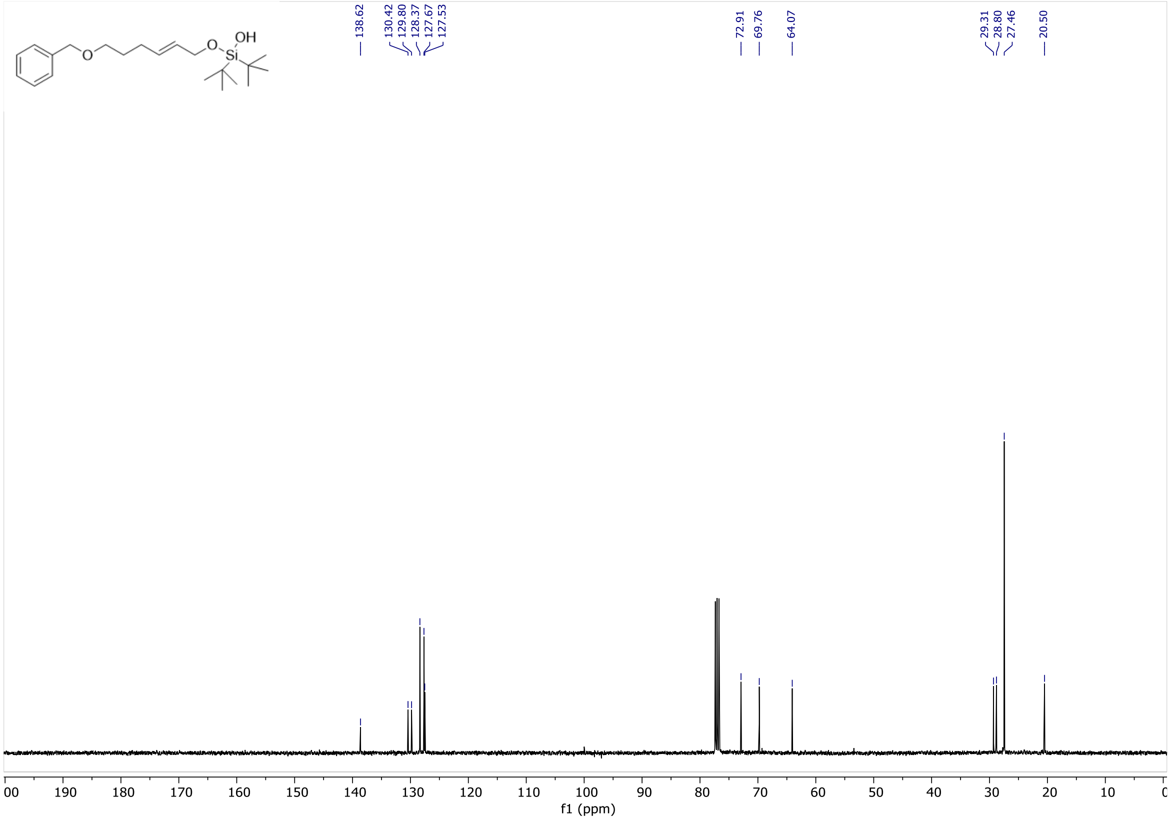
Compound 15 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



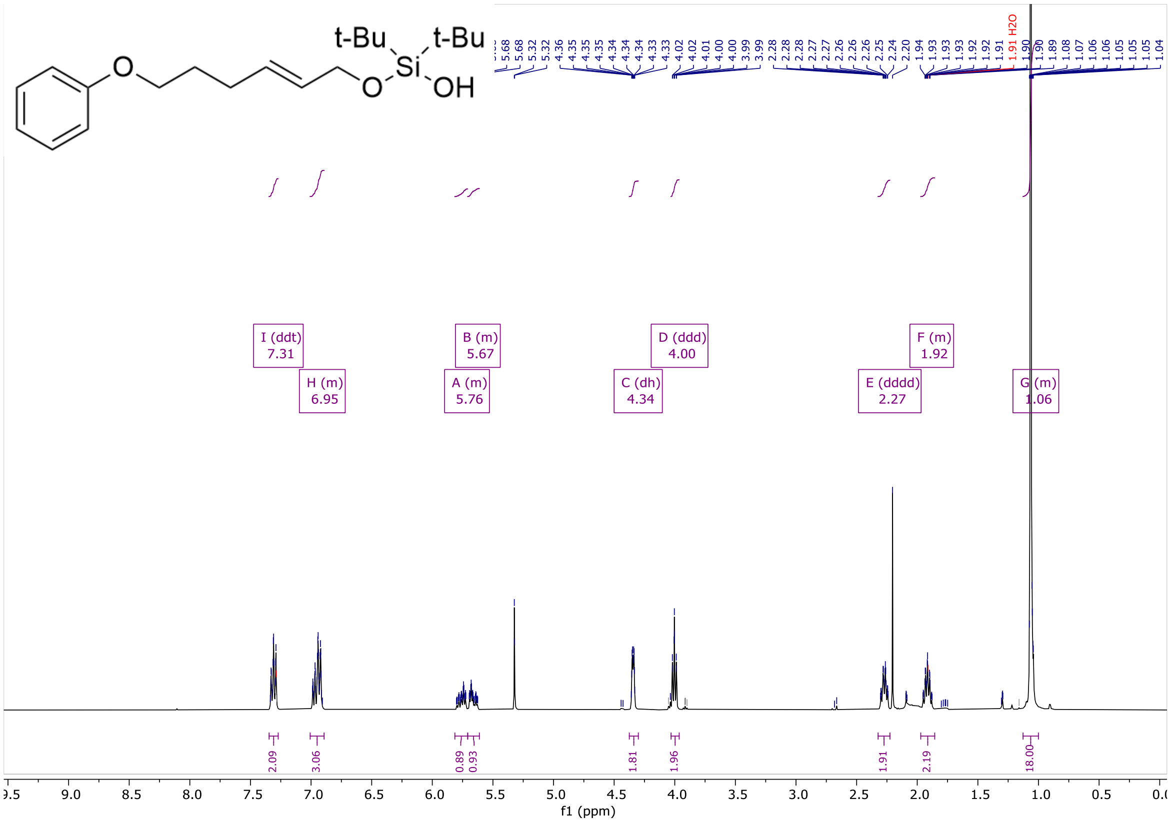


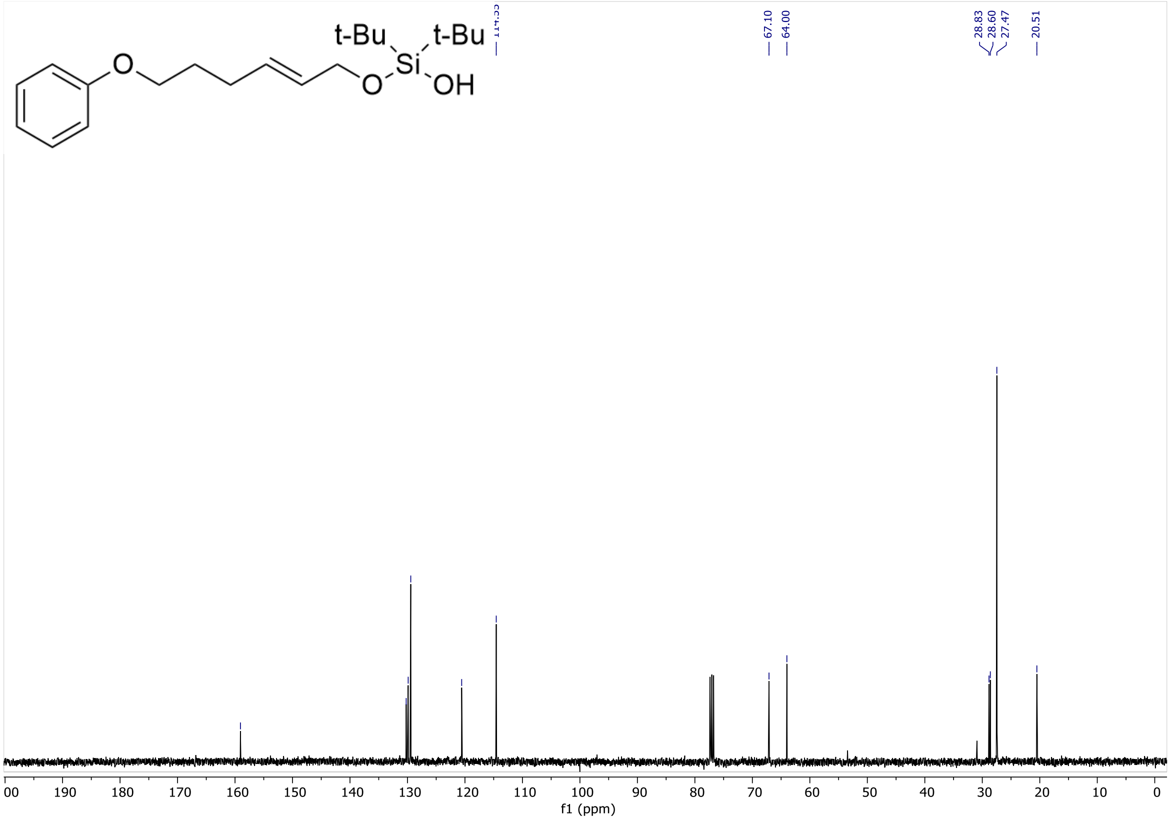
Compound 16 (^{1}H NMR: 400 MHz, $^{13}C\{^{1}H\}$ NMR: 100 MHz)



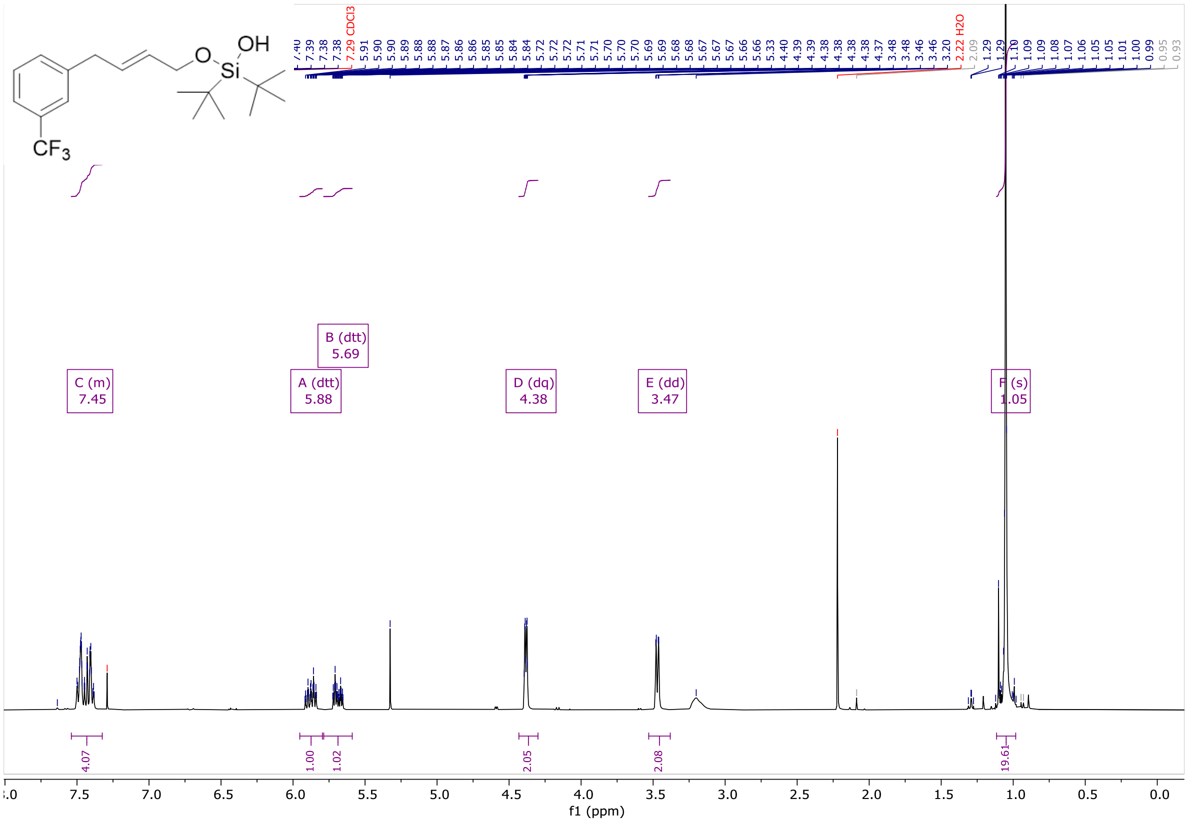


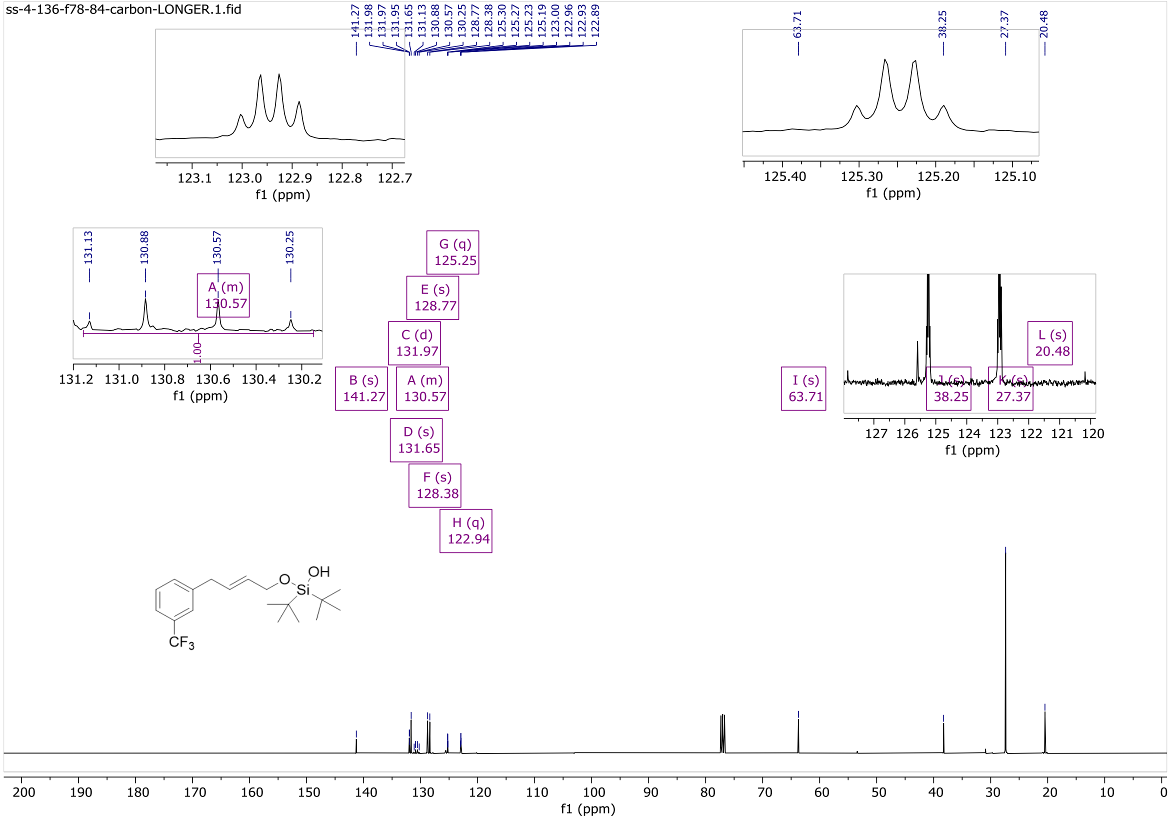
Compound 17 (^1H NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 100 MHz)



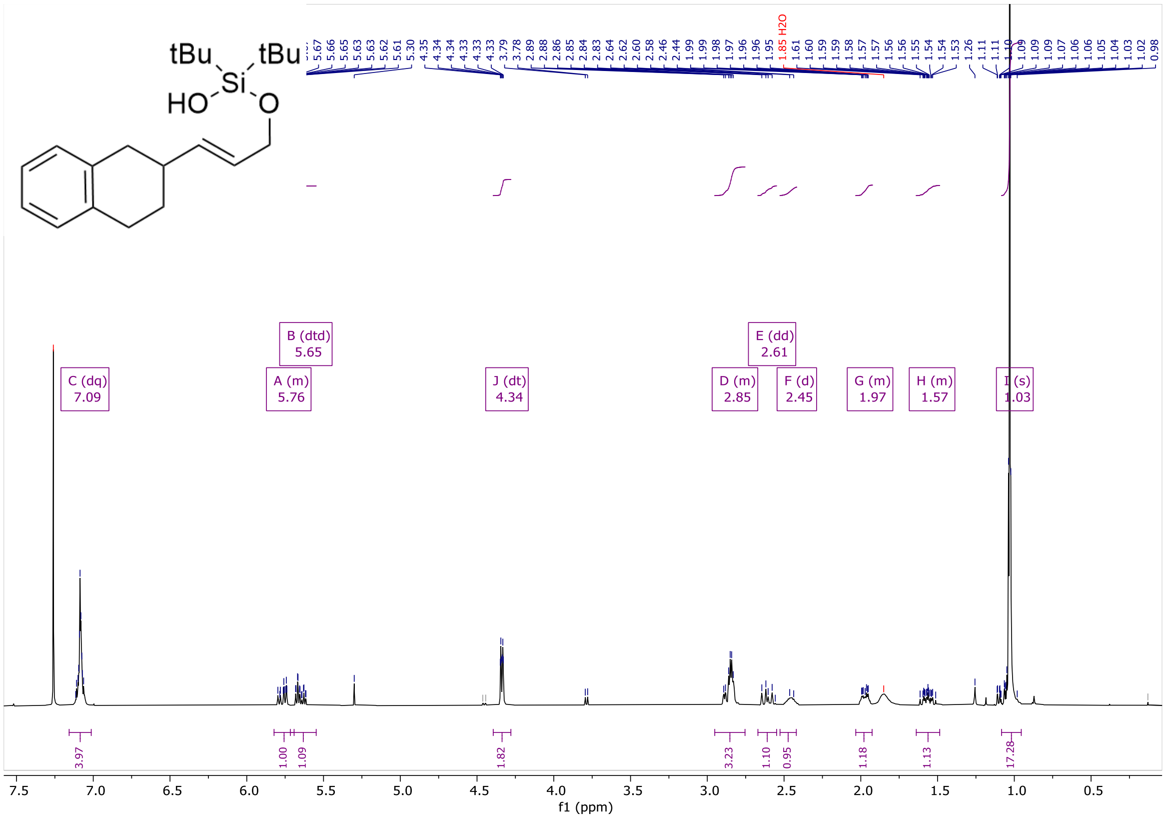


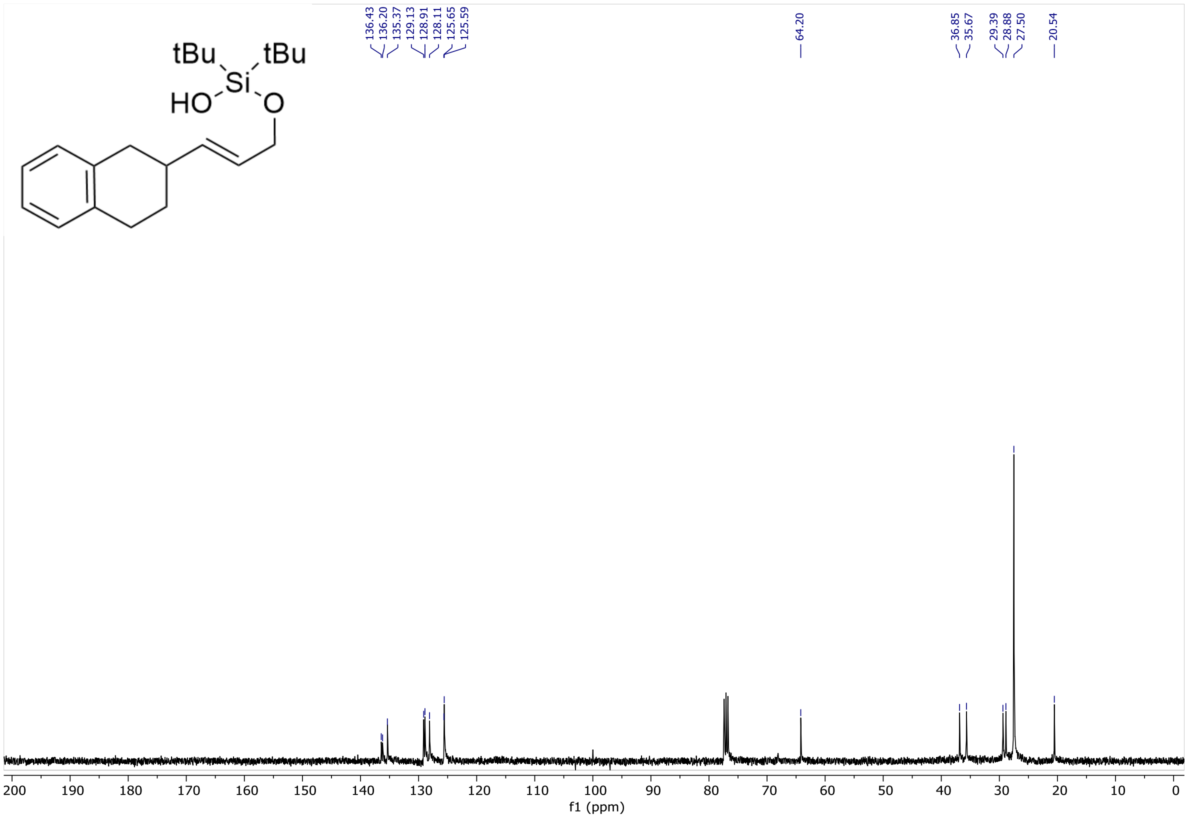
Compound 20 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



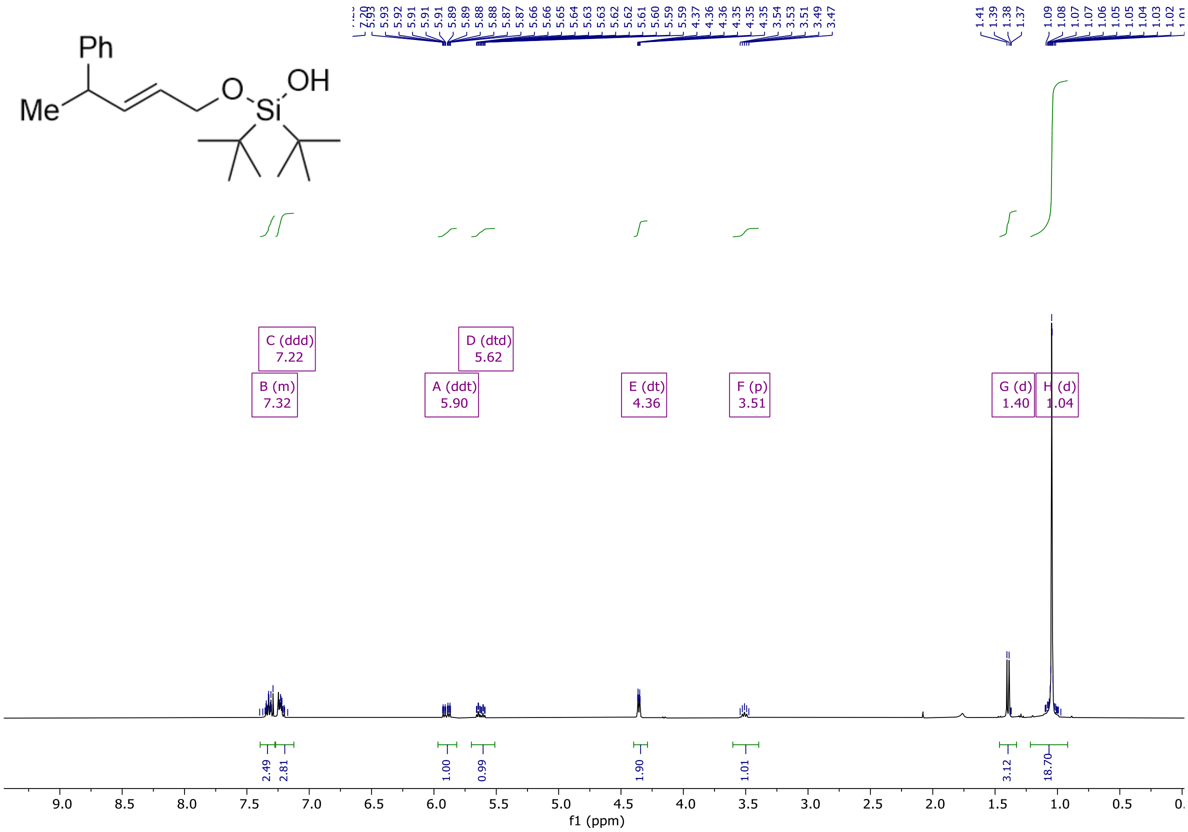


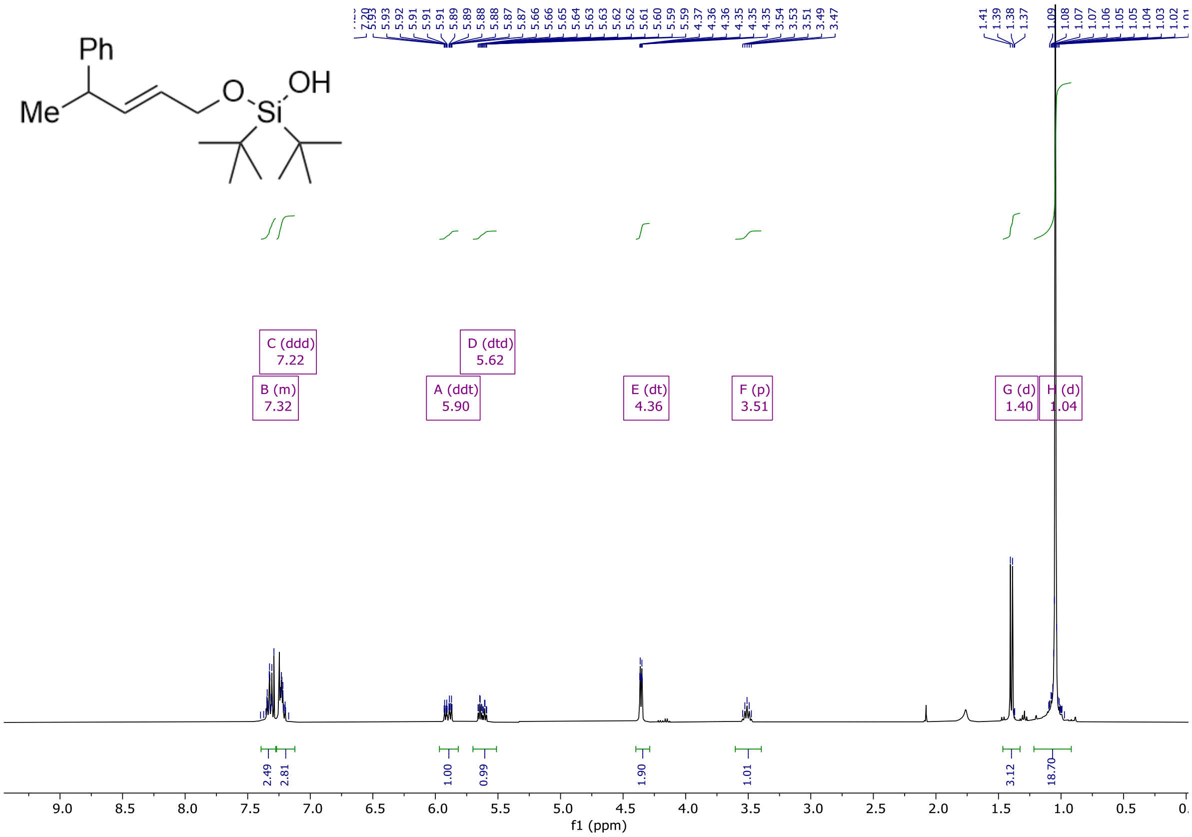
Compound 24 (^{1}H NMR: 400 MHz, $^{13}C\{^{1}H\}$ NMR: 100 MHz)



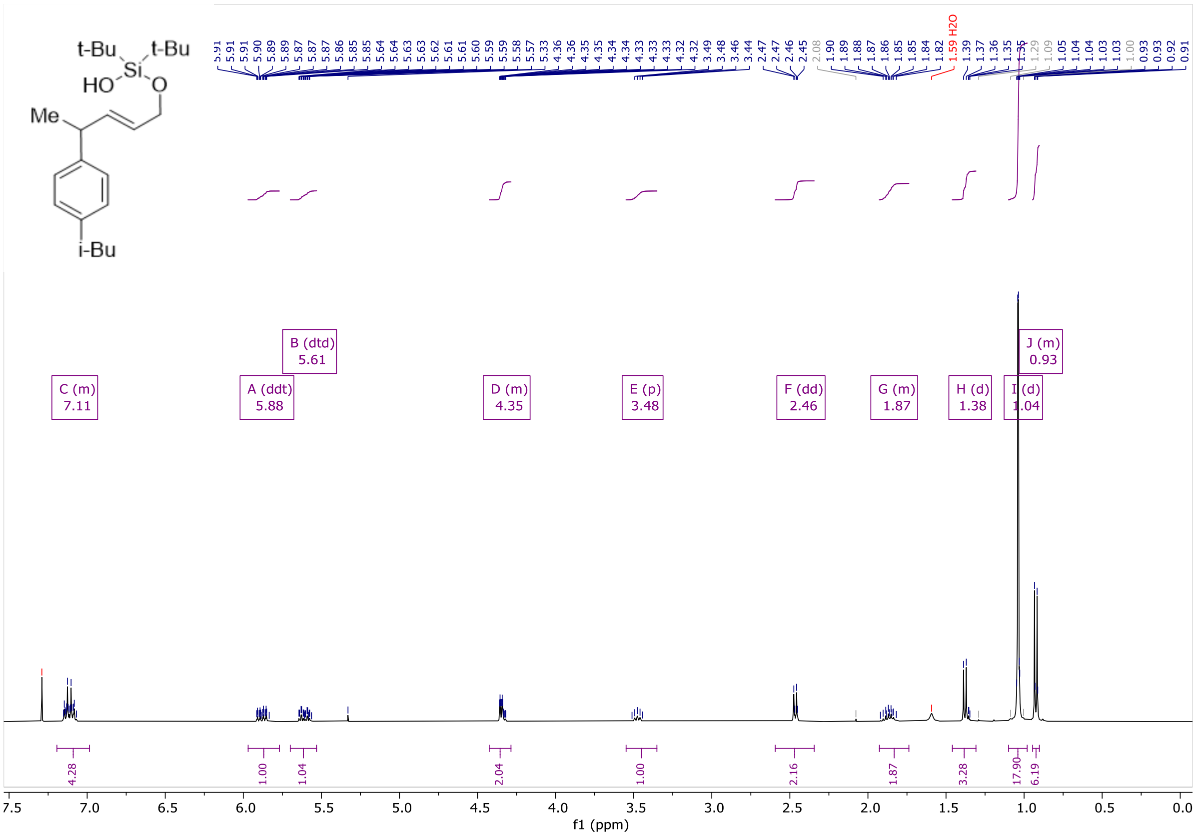


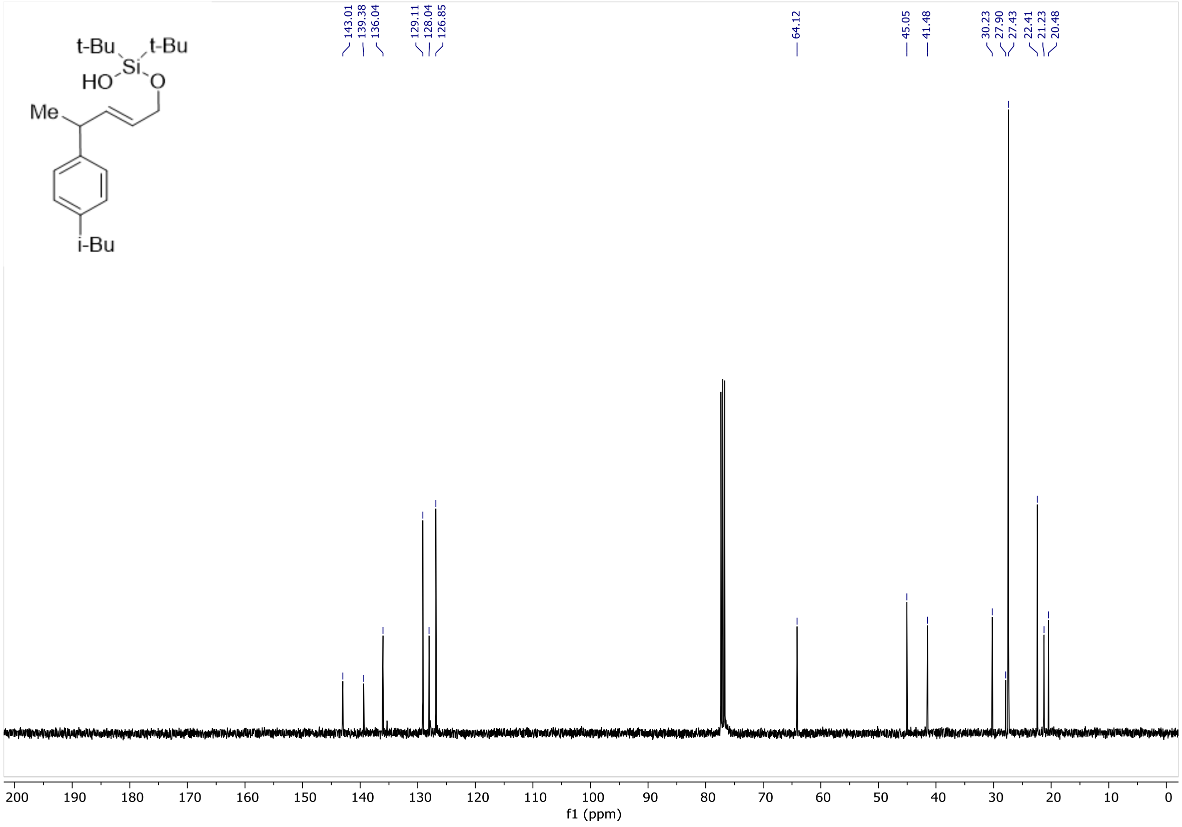
Compound 25 (^{1}H NMR: 400 MHz, $^{13}C\{^{1}H\}$ NMR: 100 MHz)



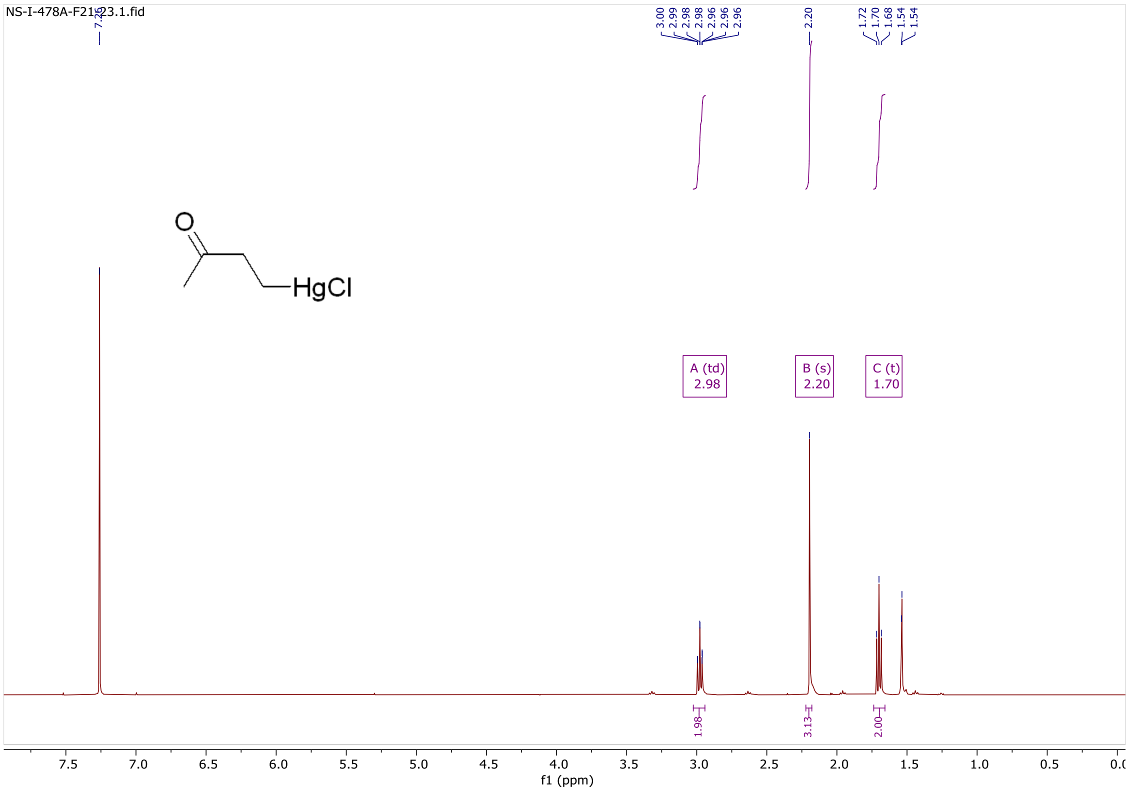


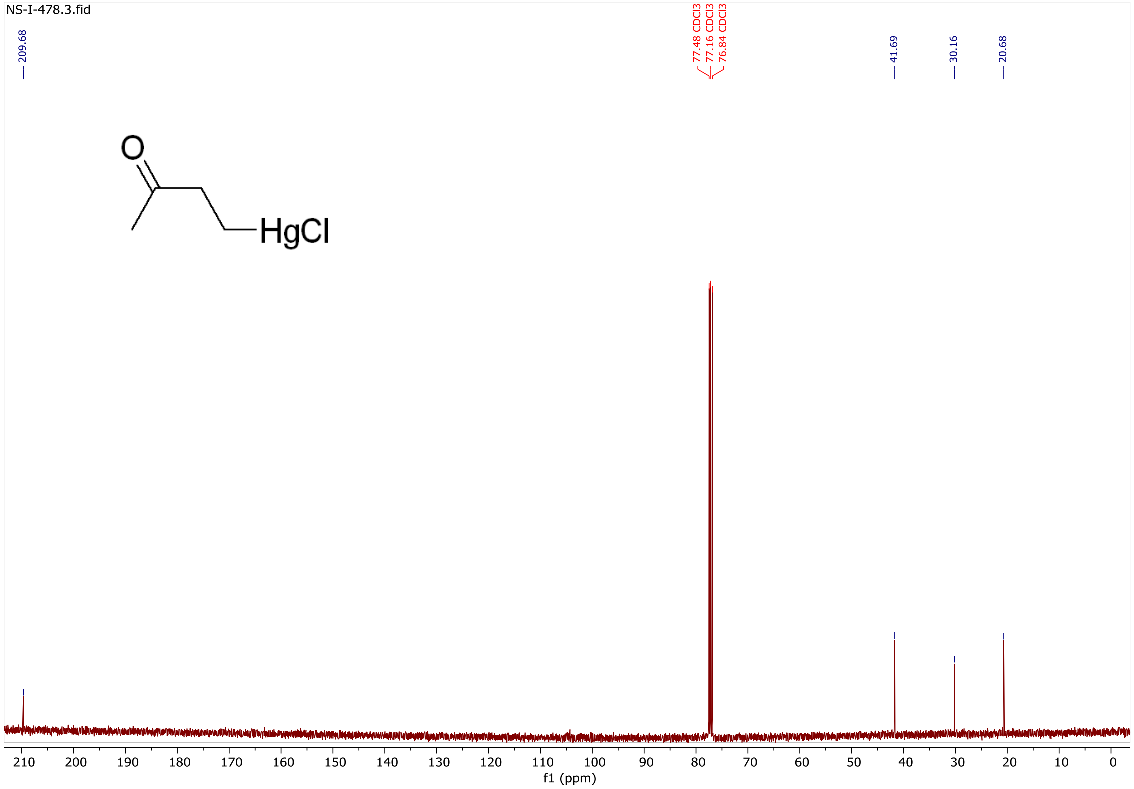
Compound 26 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



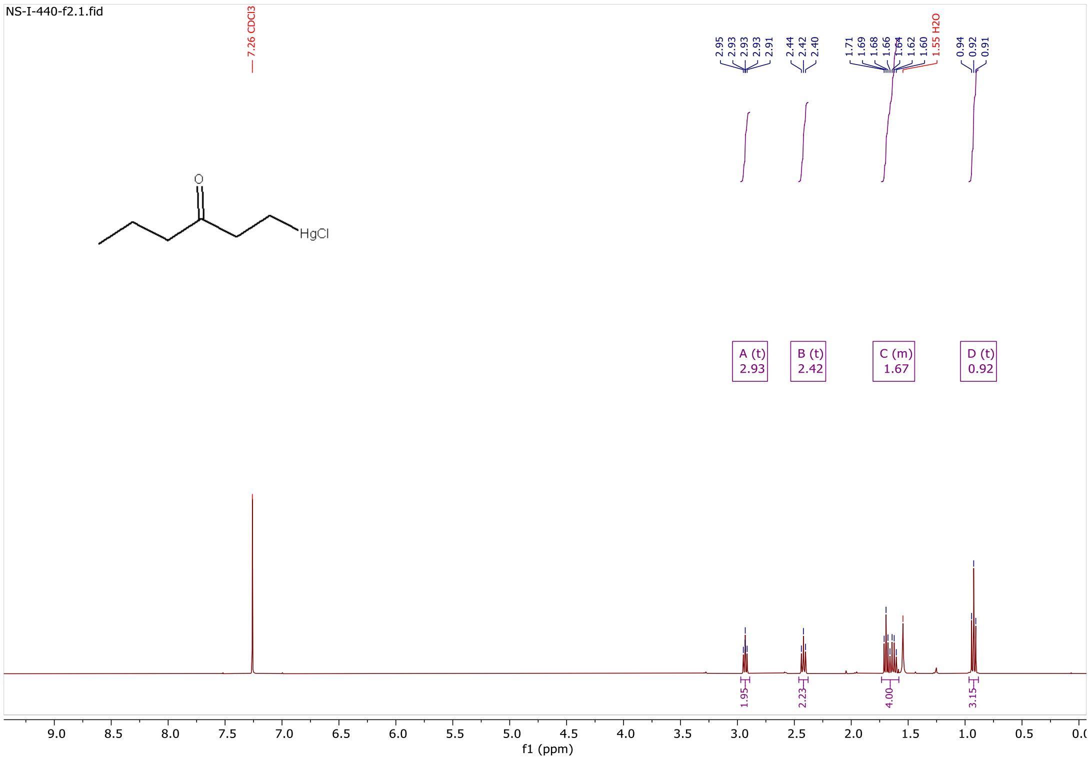


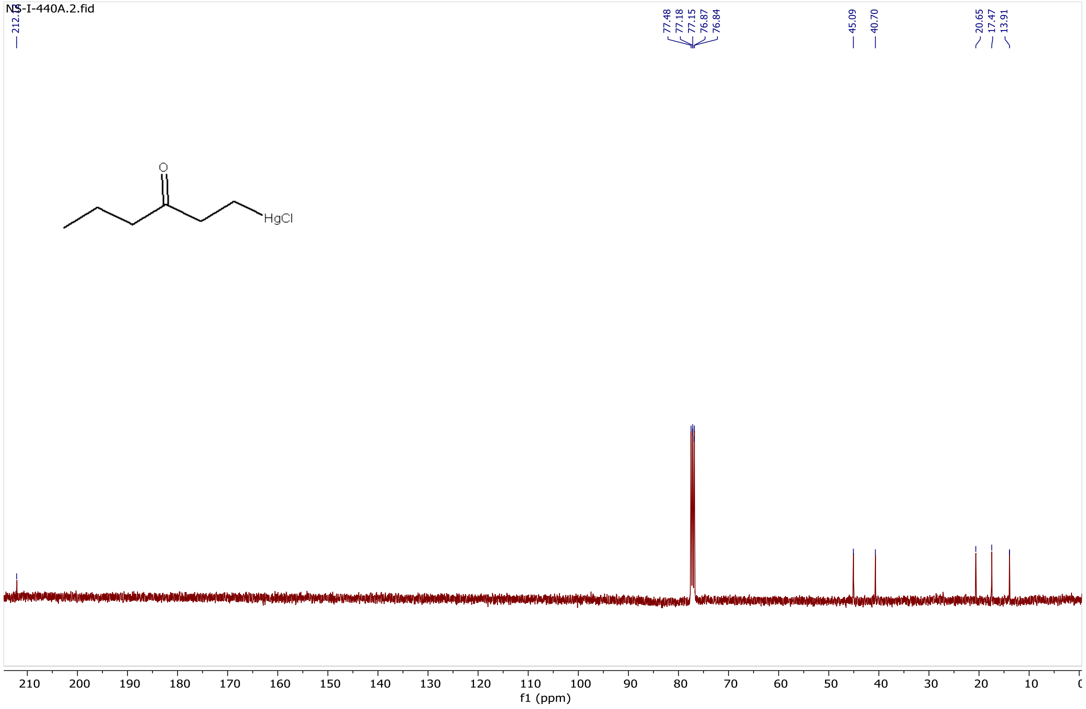
Compound 27 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



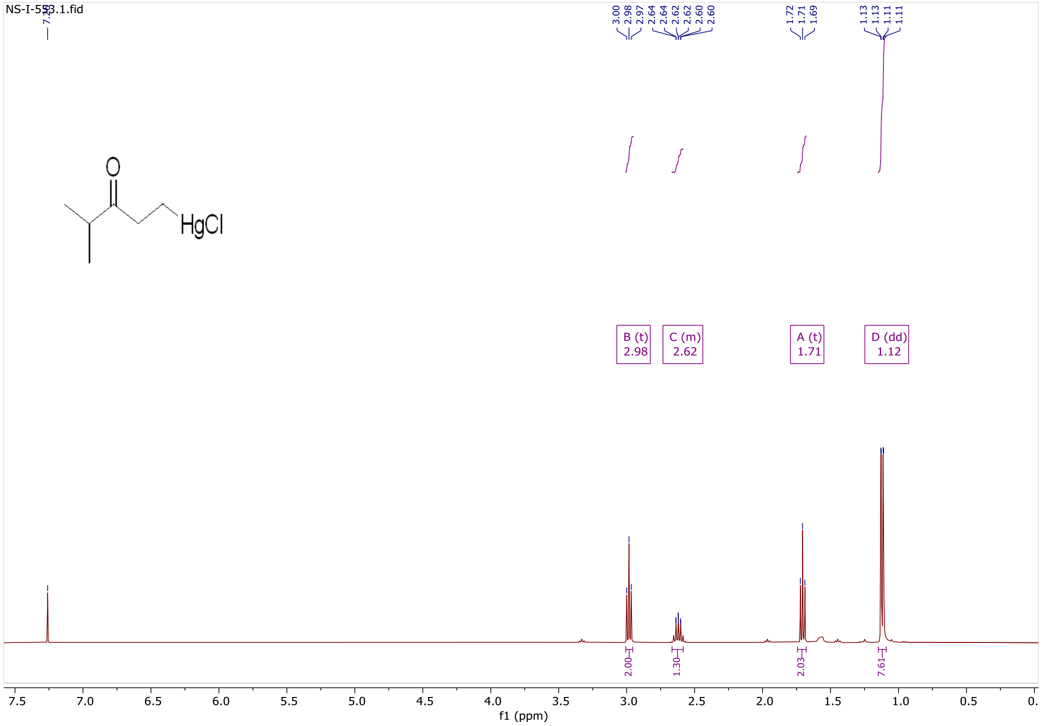


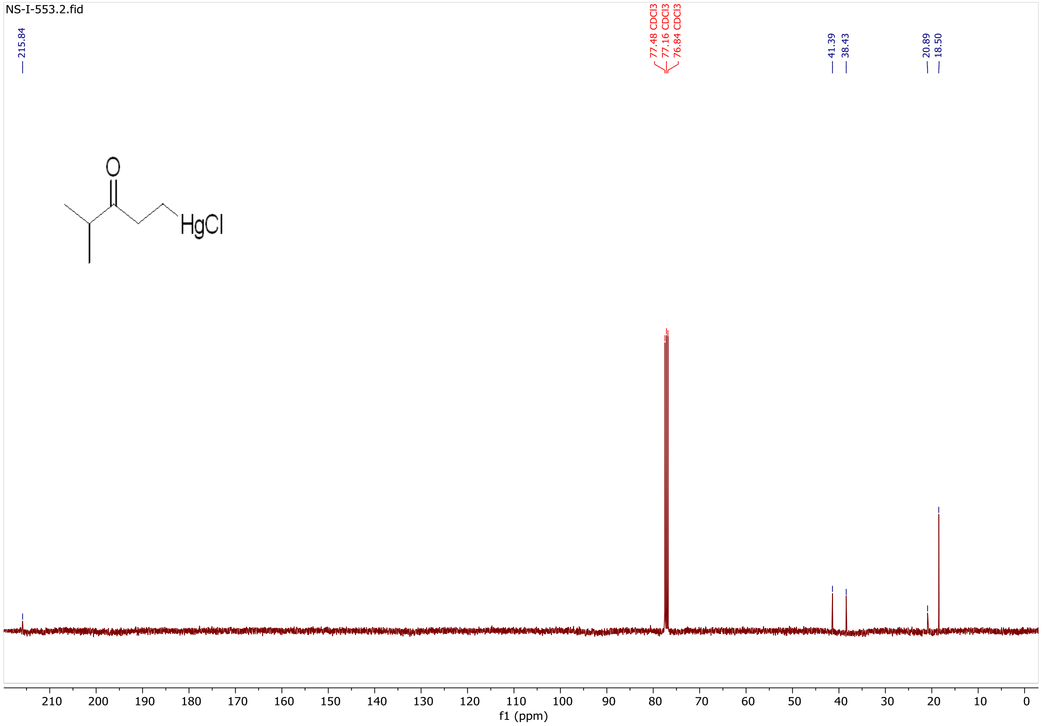
Compound 28 (^{1}H NMR: 400 MHz, $^{13}C\{^{1}H\}$ NMR: 100 MHz)



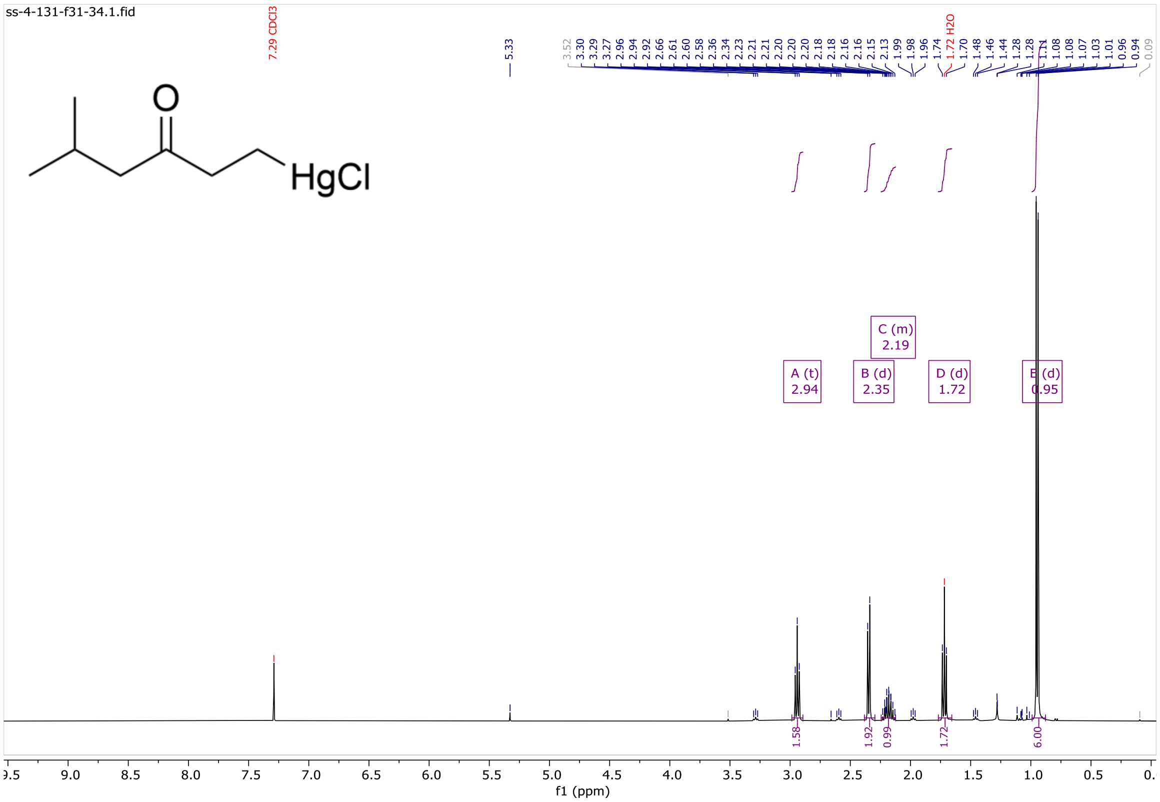


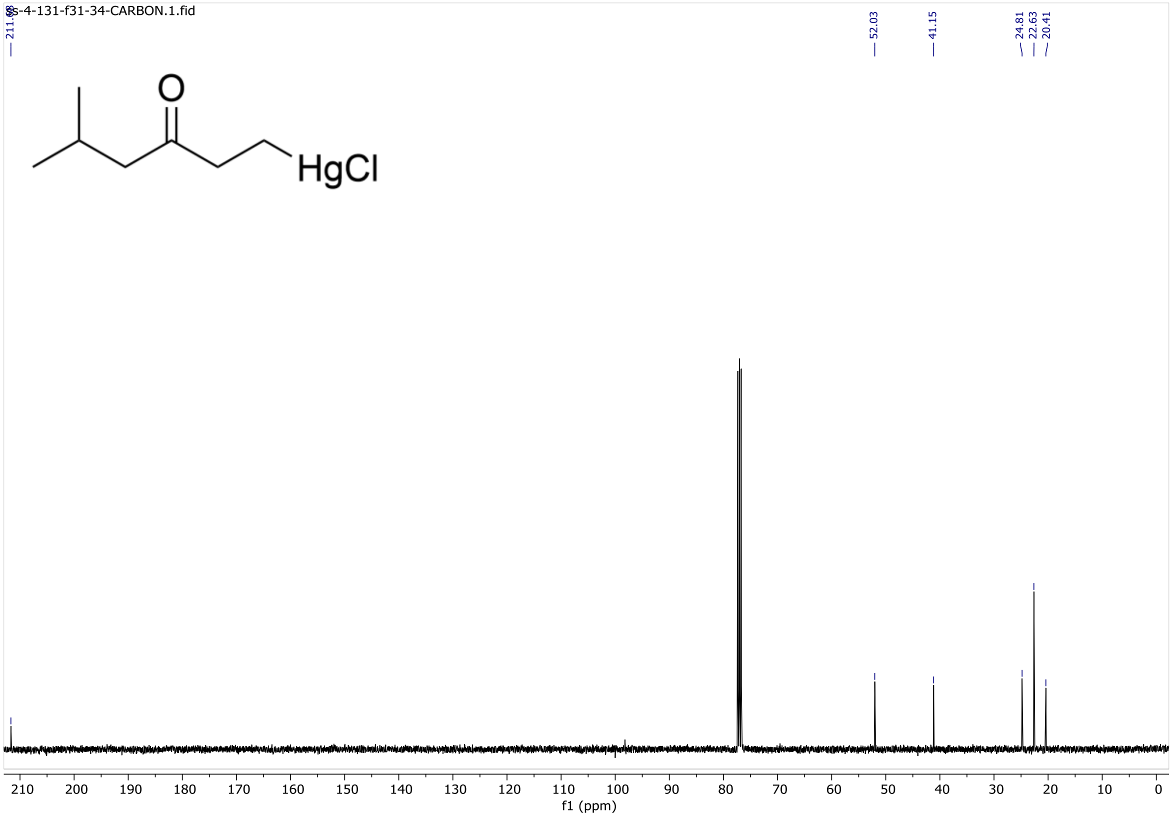
Compound 29 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



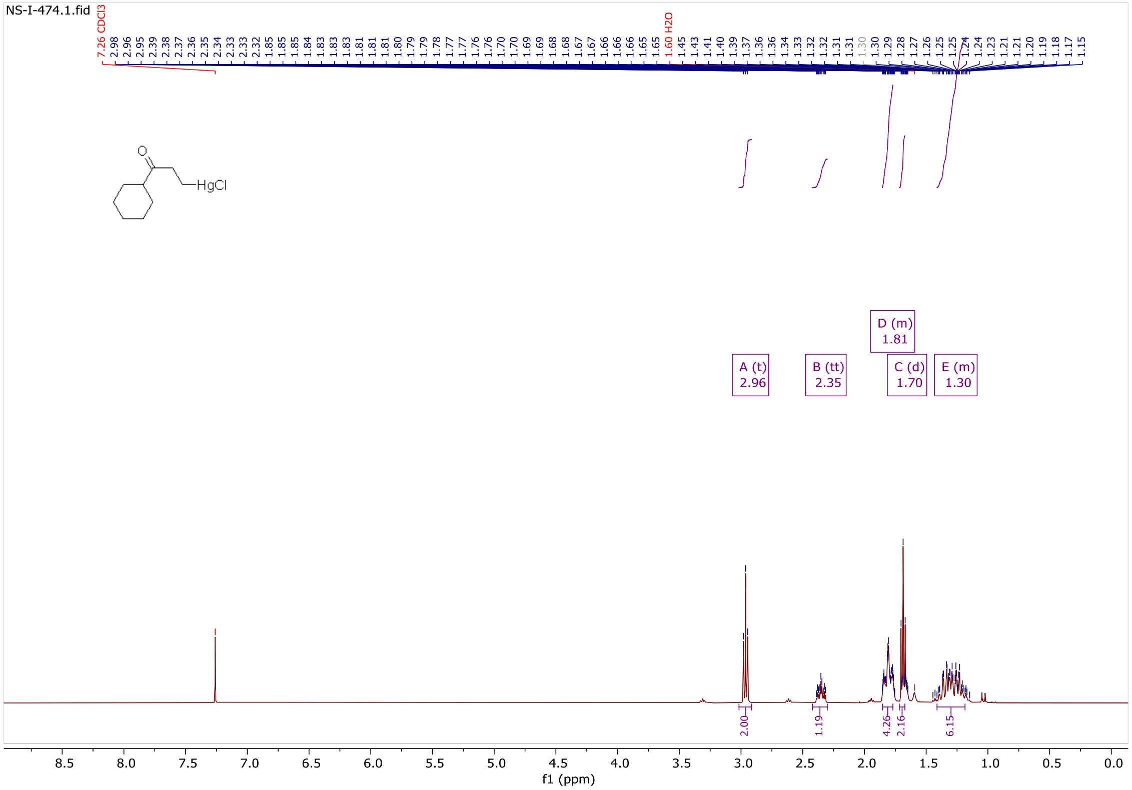


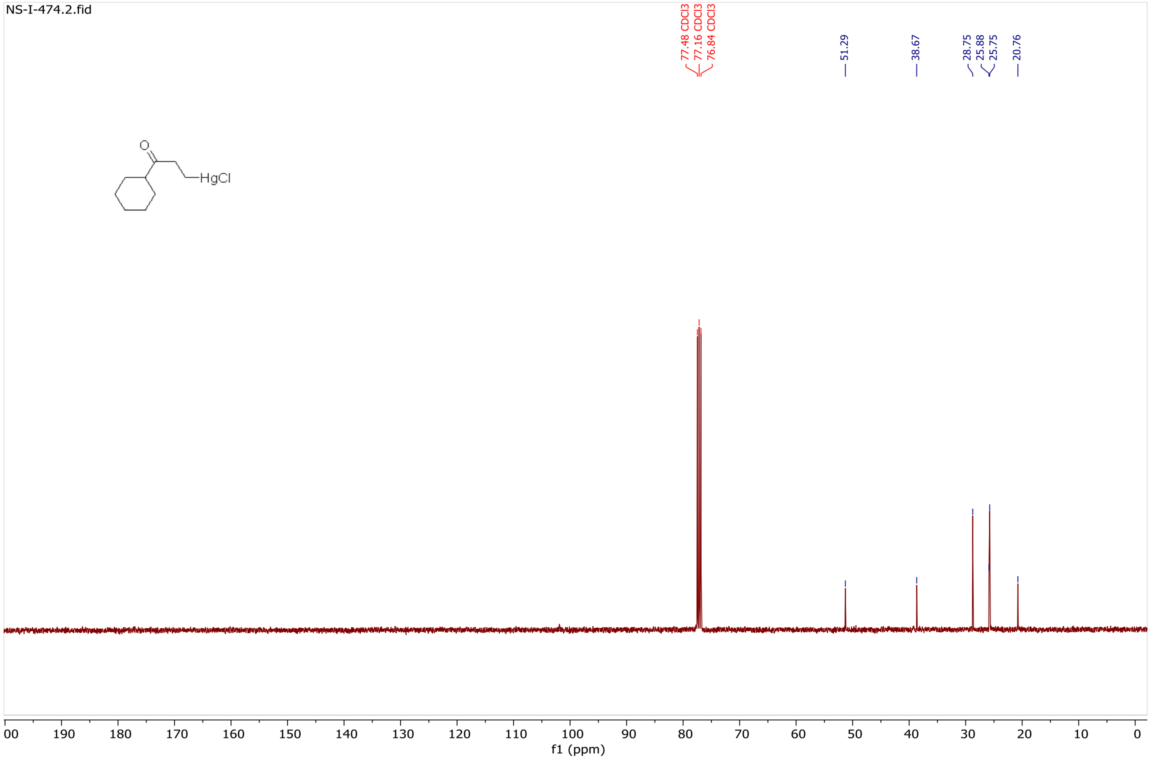
Compound 30 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



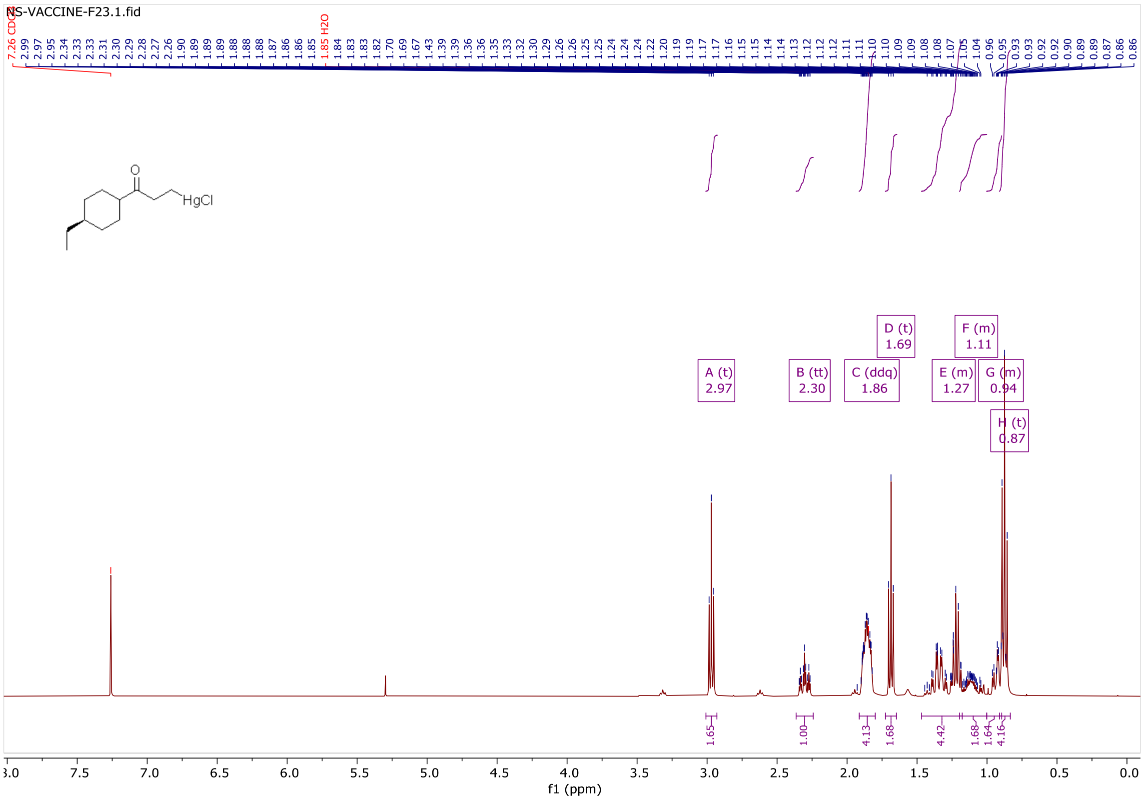


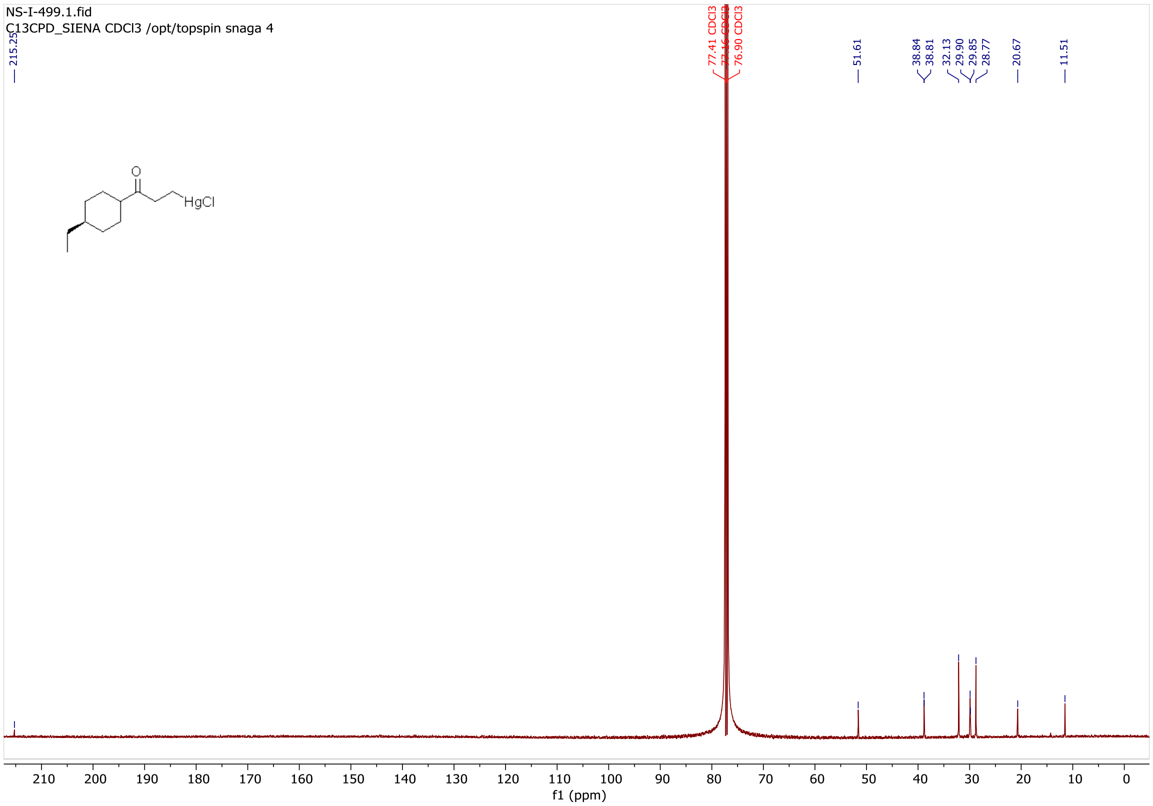
Compound 31 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



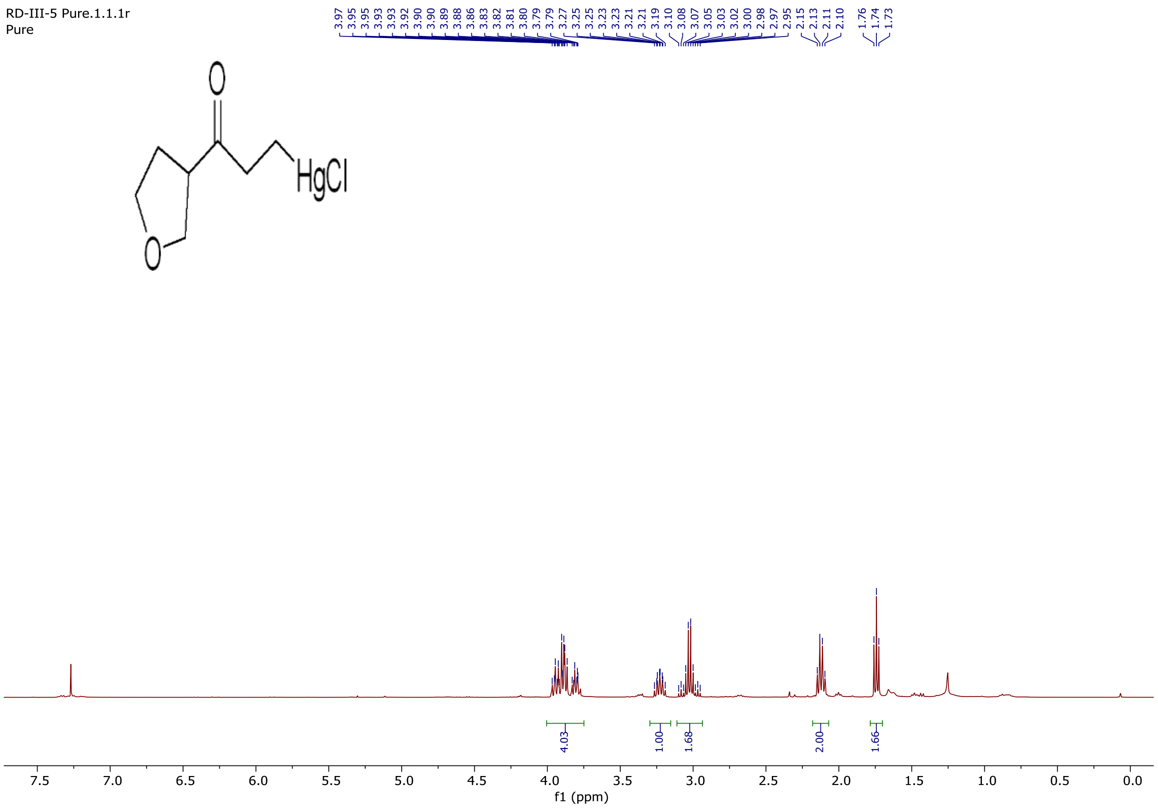


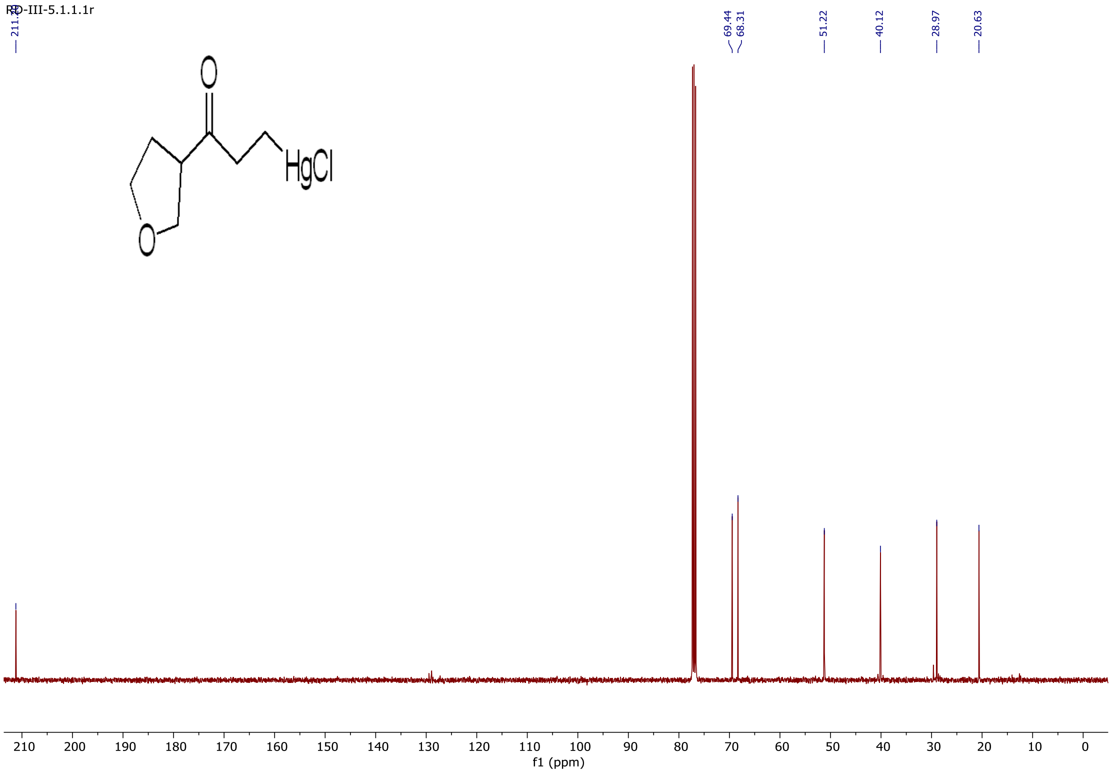
Compound 32 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



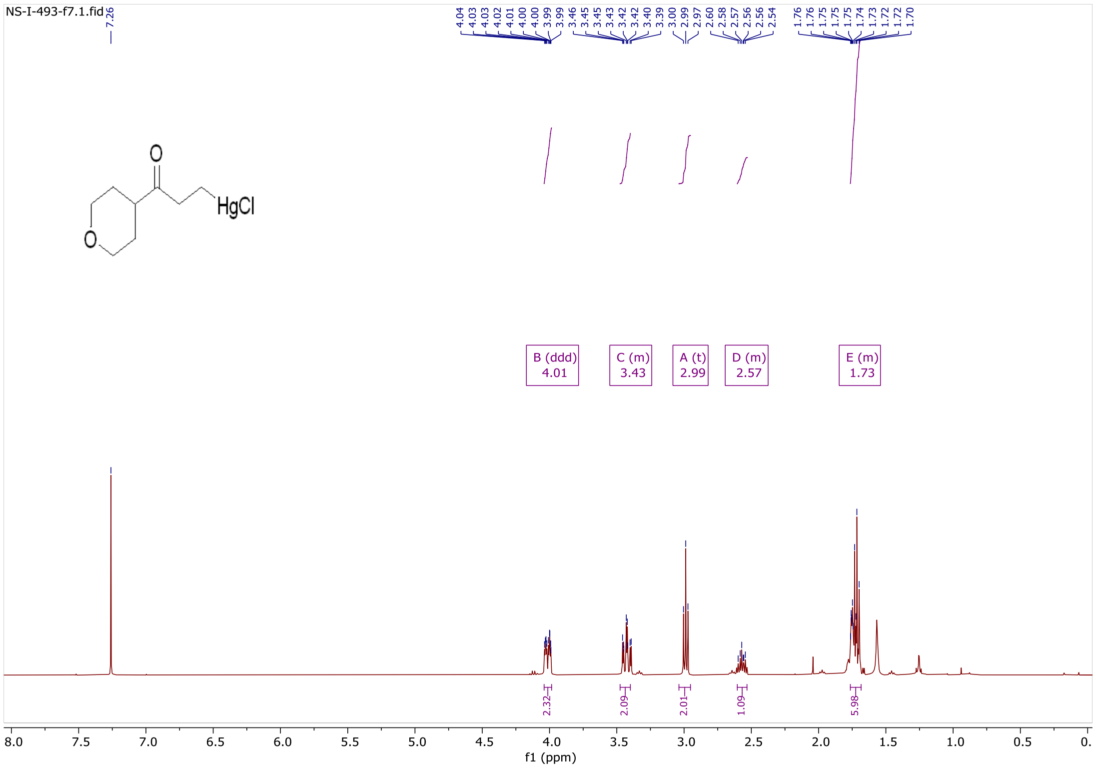


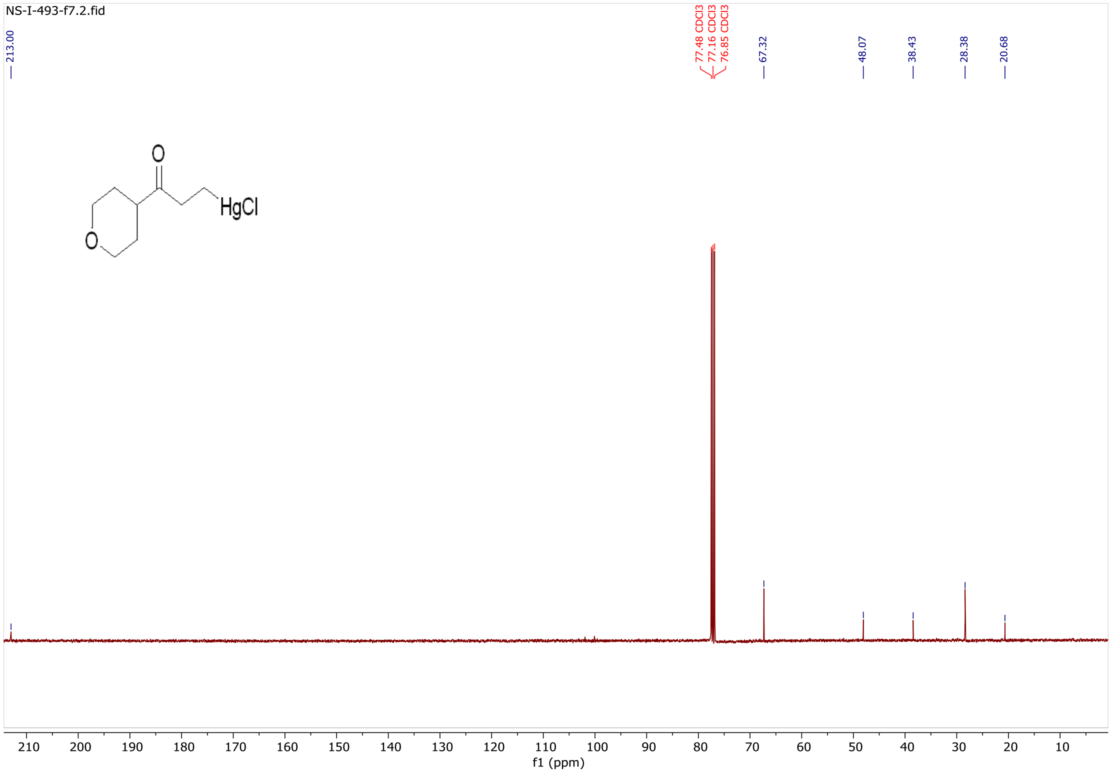
Compound 33 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



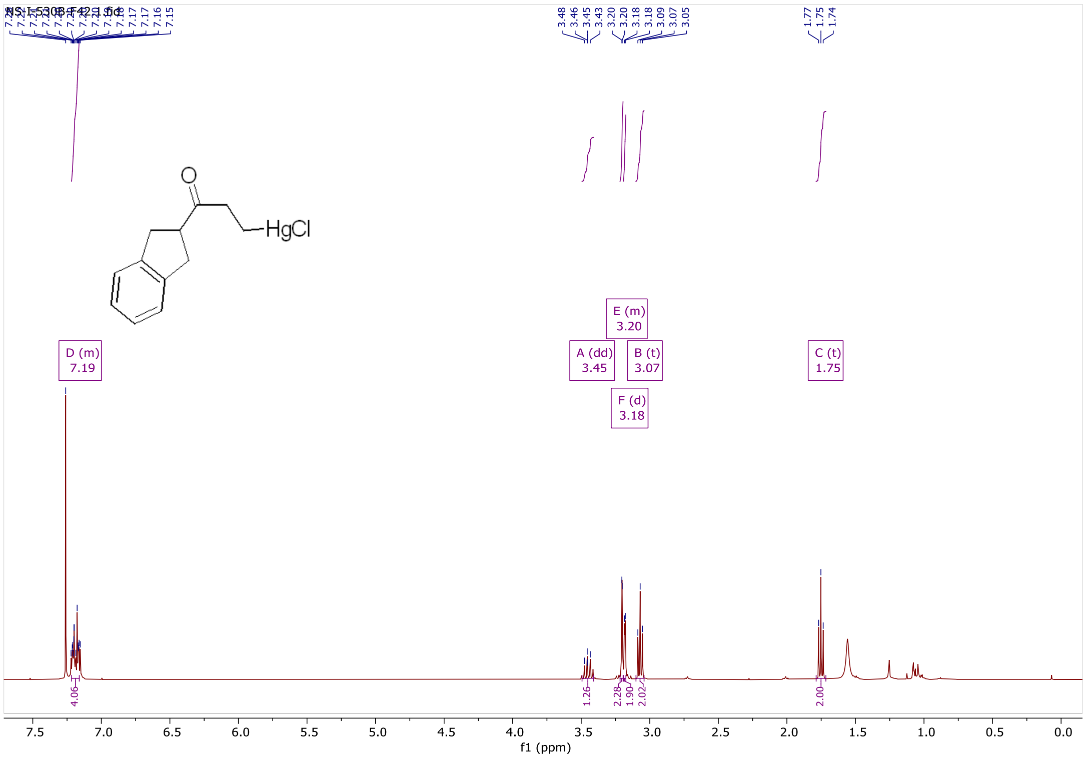


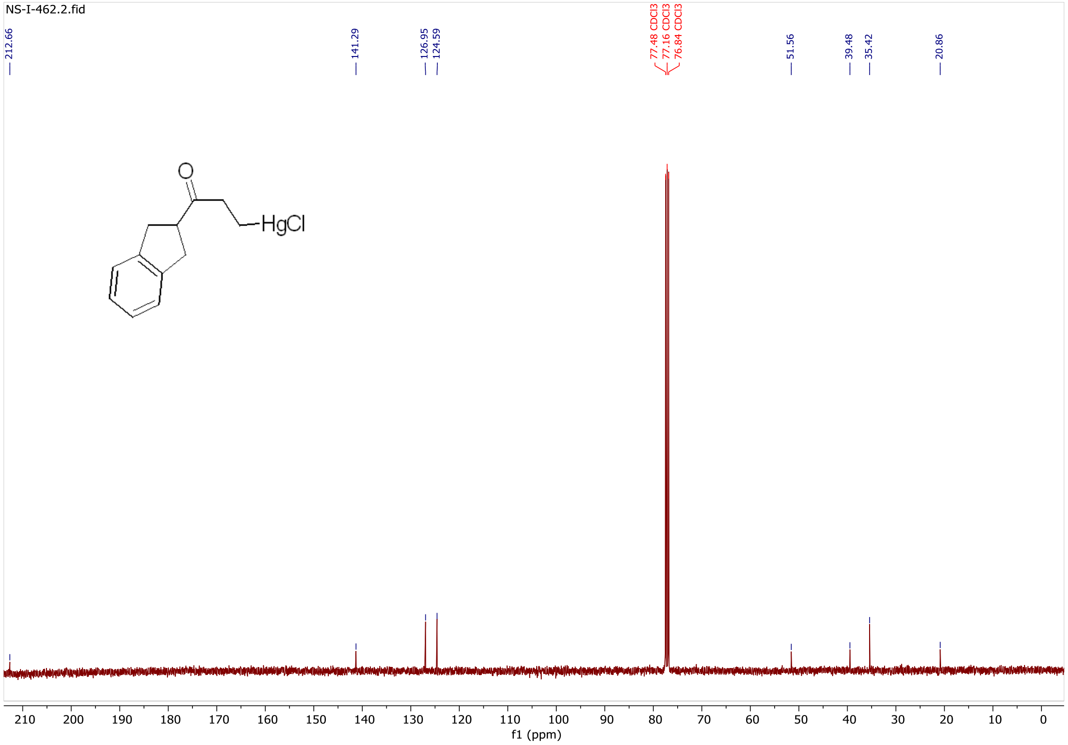
Compound 34 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



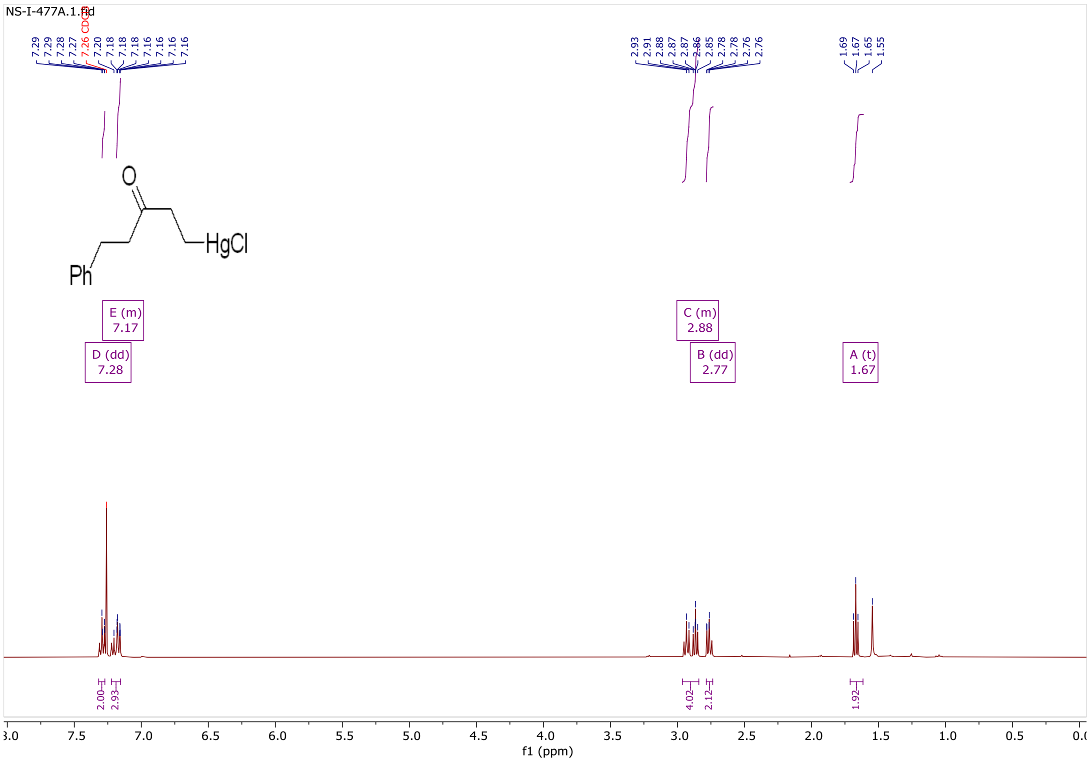


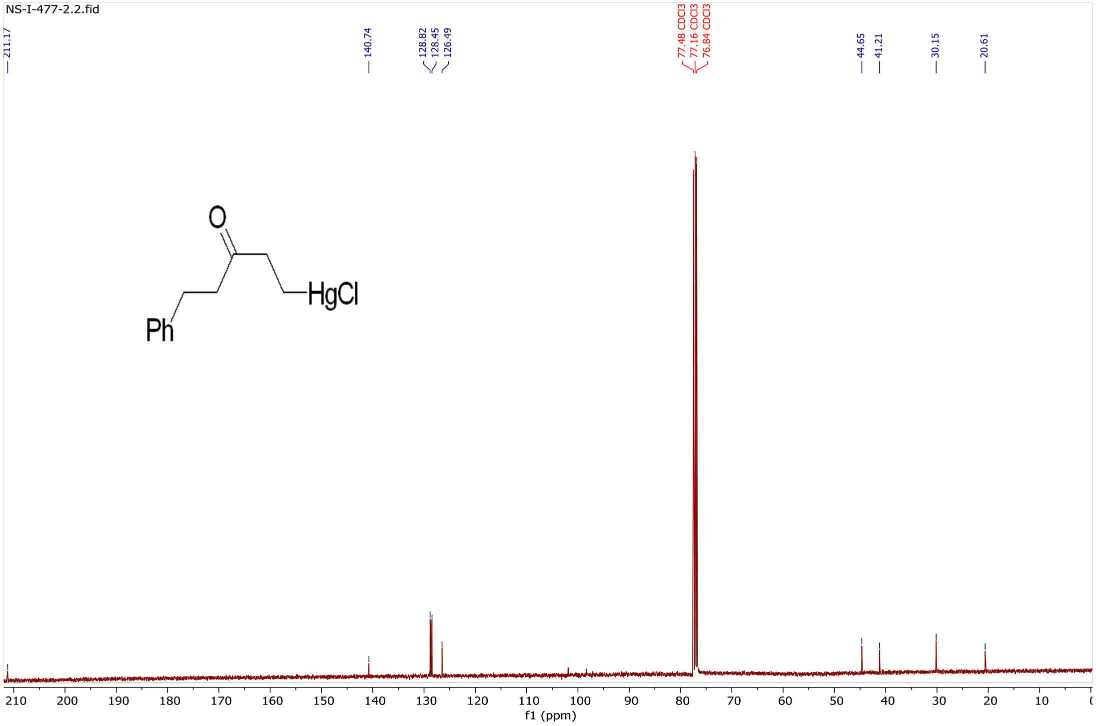
Compound 35 (^{1}H NMR: 400 MHz, $^{13}C\{^{1}H\}$ NMR: 100 MHz)





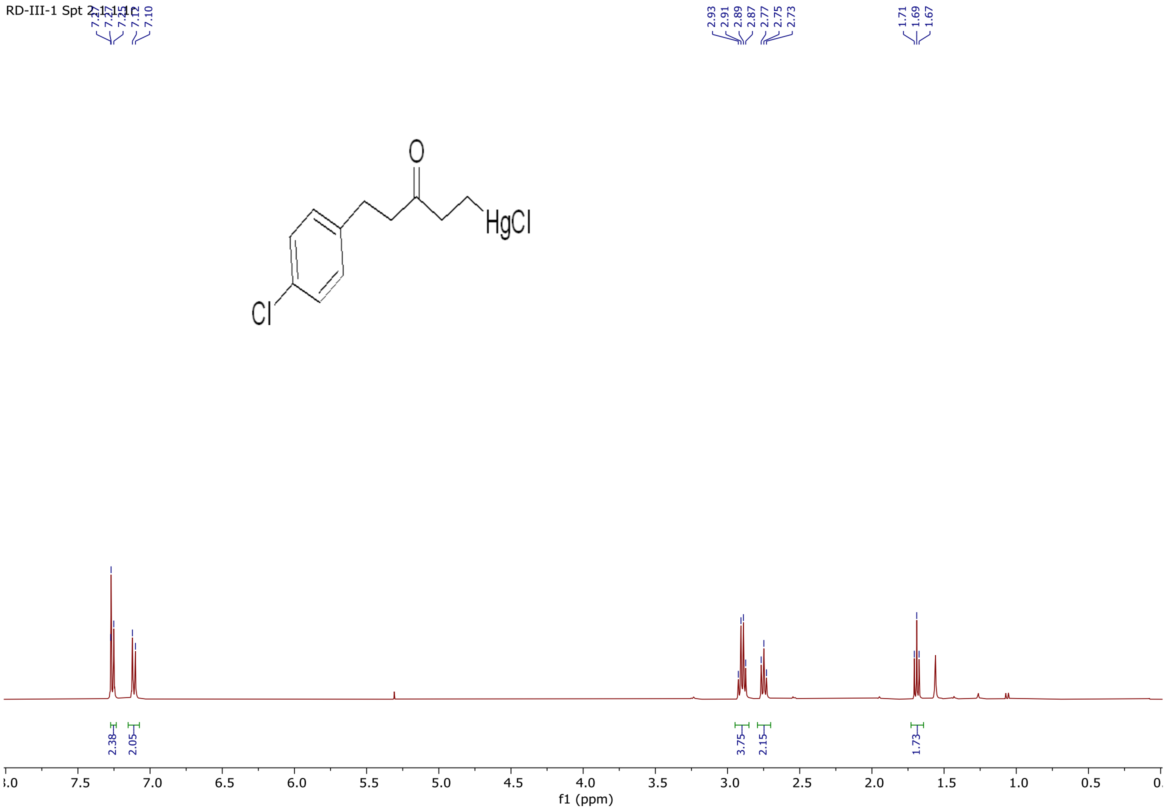
Compound 36 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)

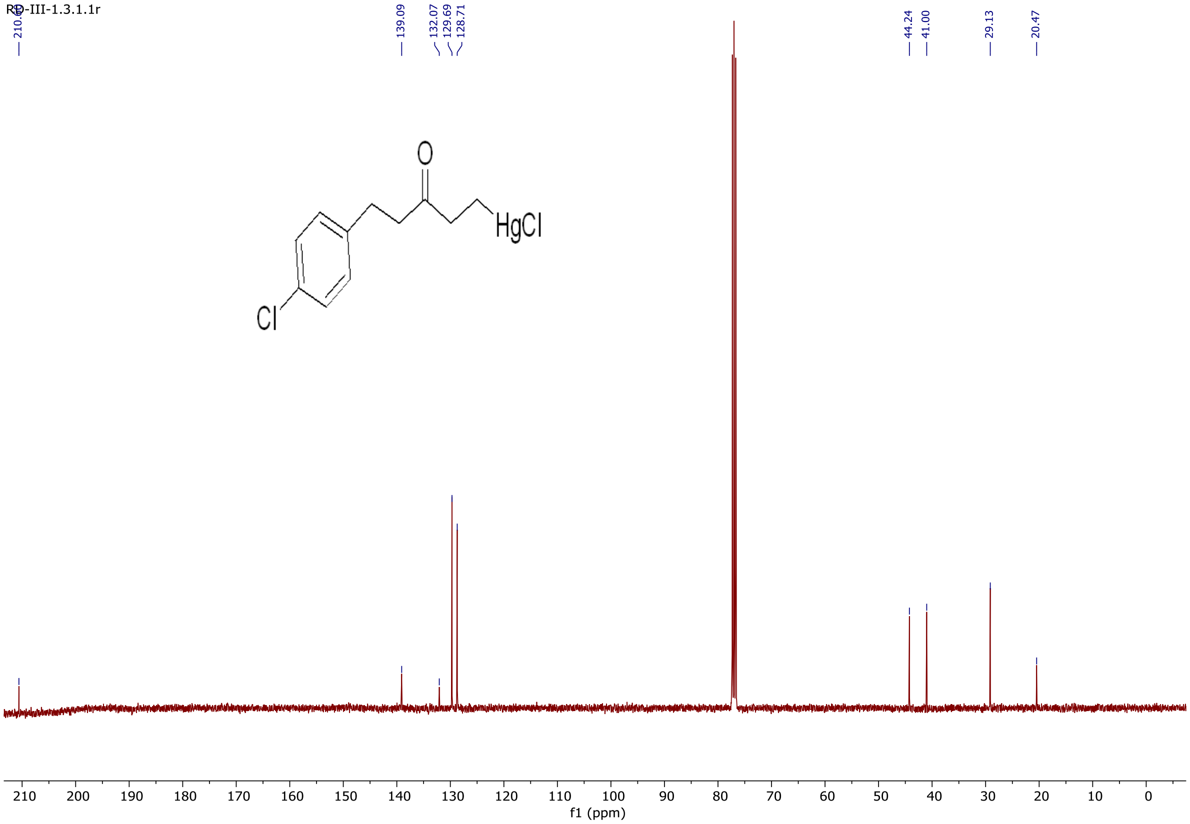




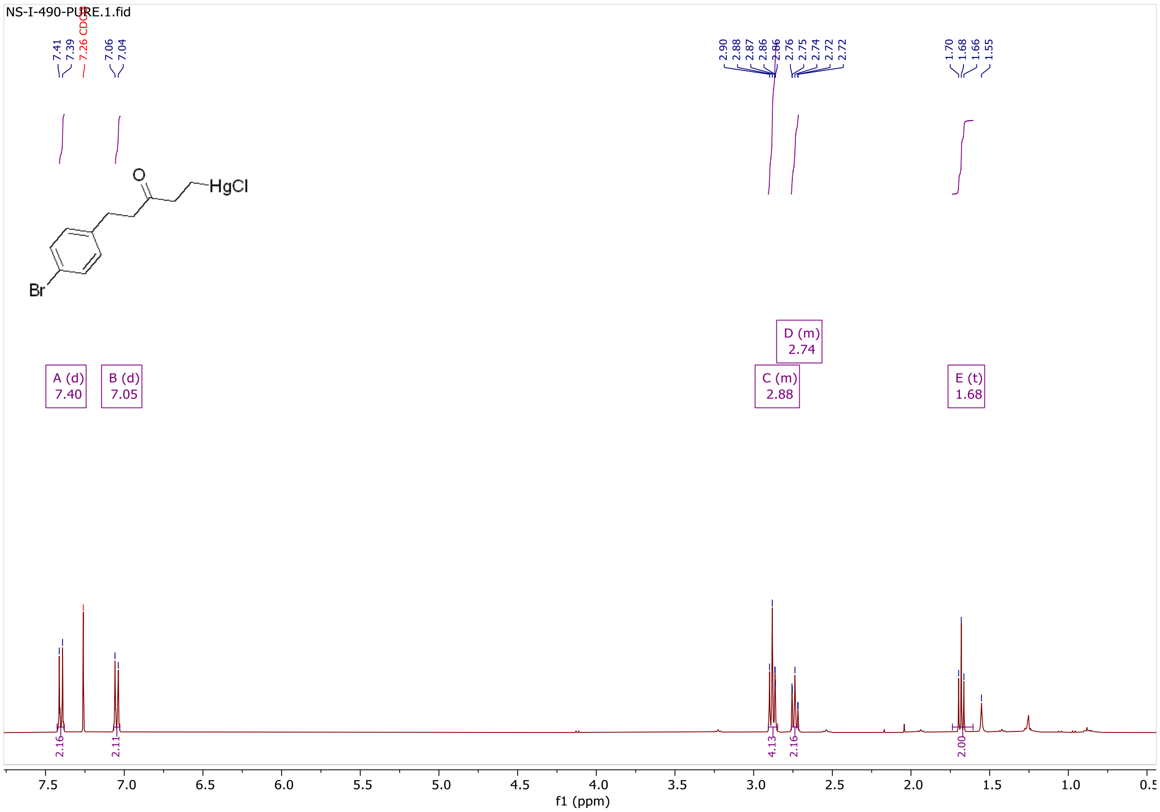
Compound 37 (^{1}H NMR: 600 MHz, ^{13}C{^{1}H} NMR: 150 MHz)

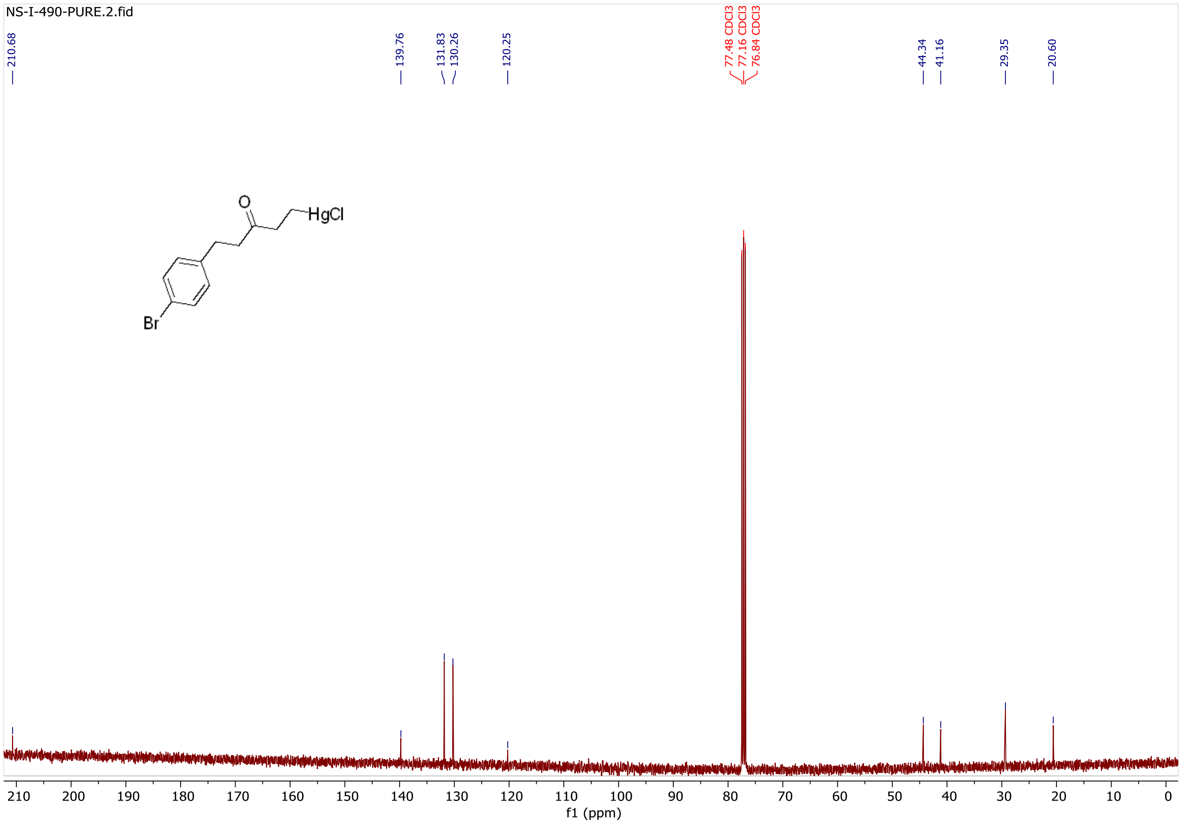
Compound 38 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



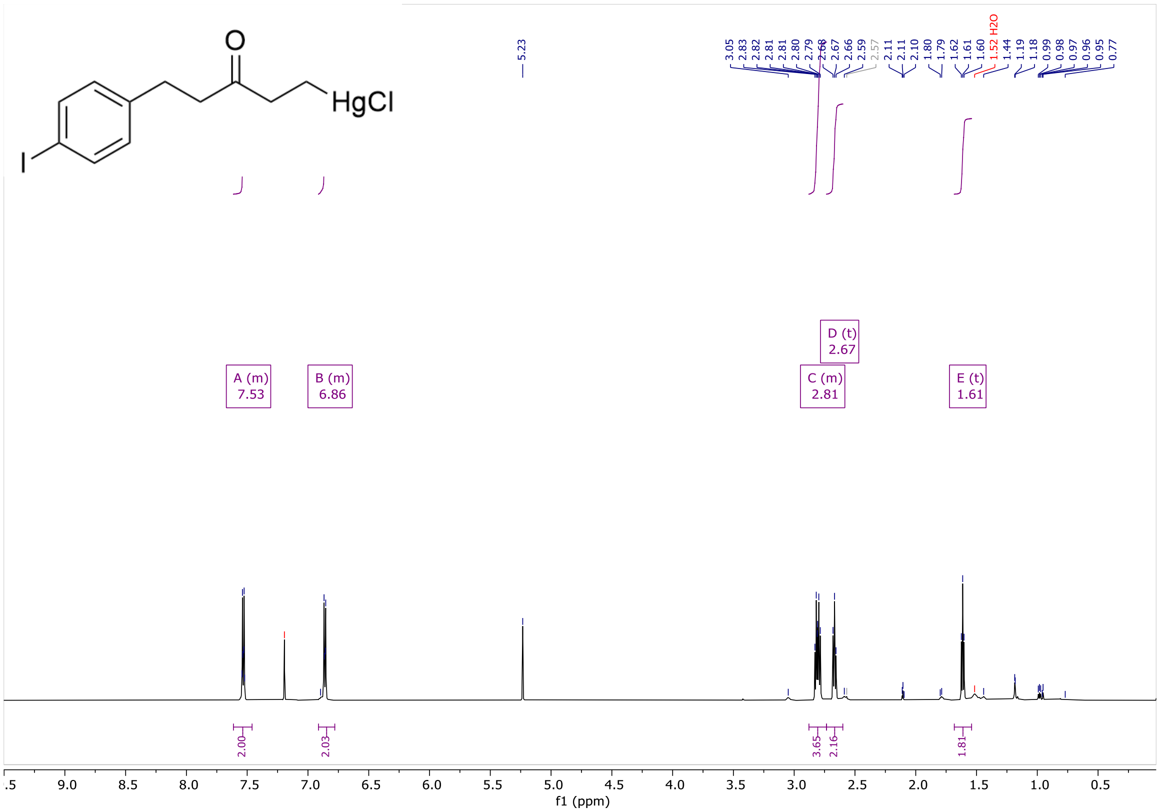


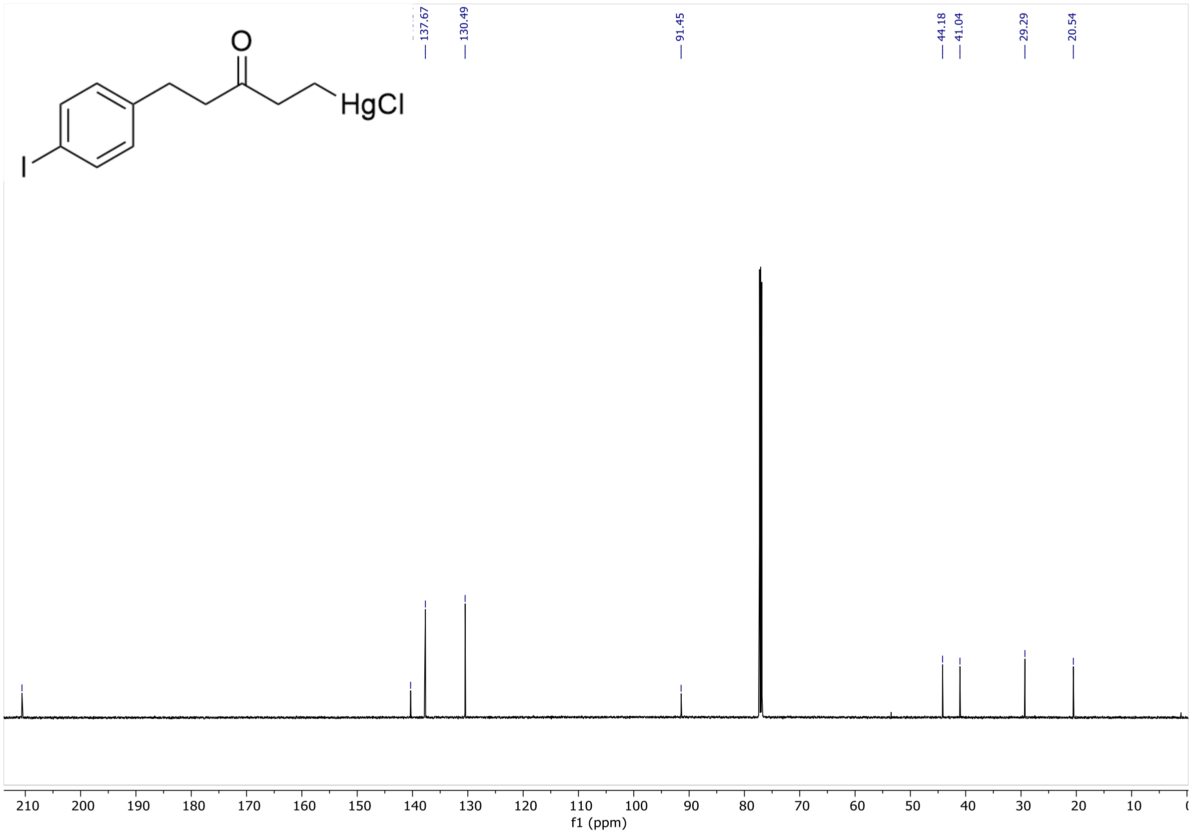
Compound 39 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



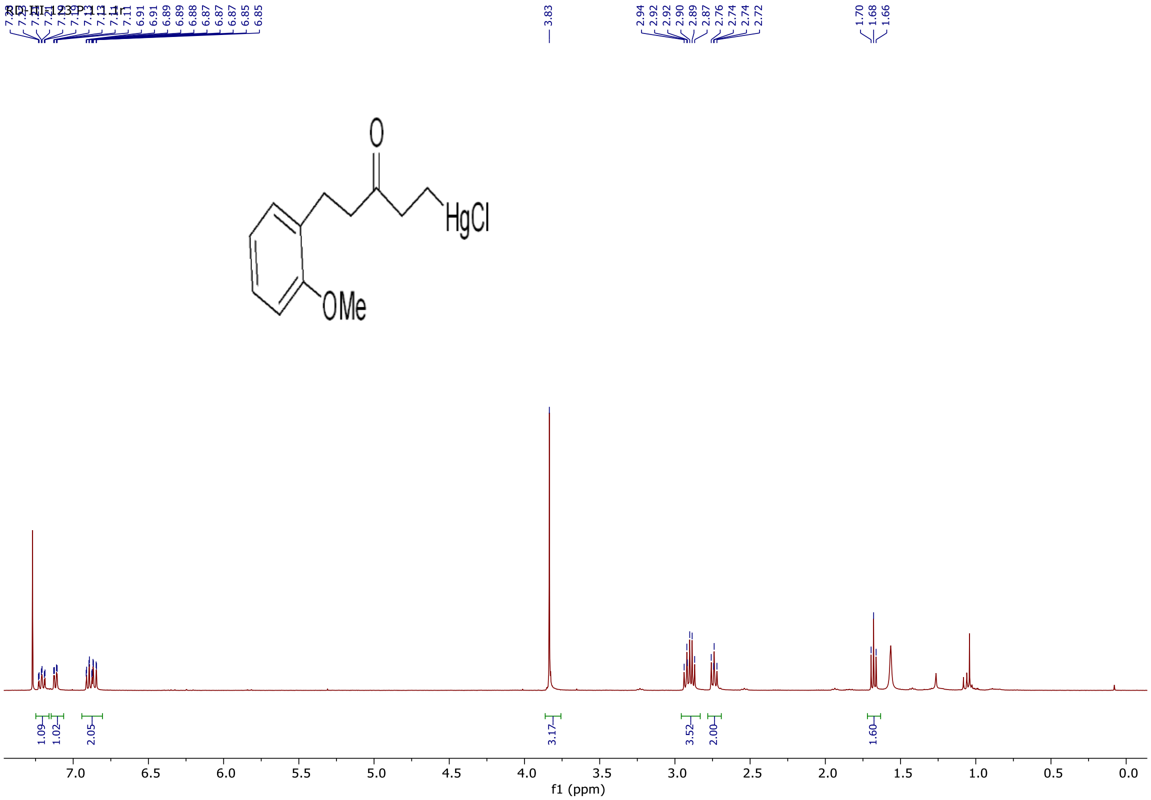


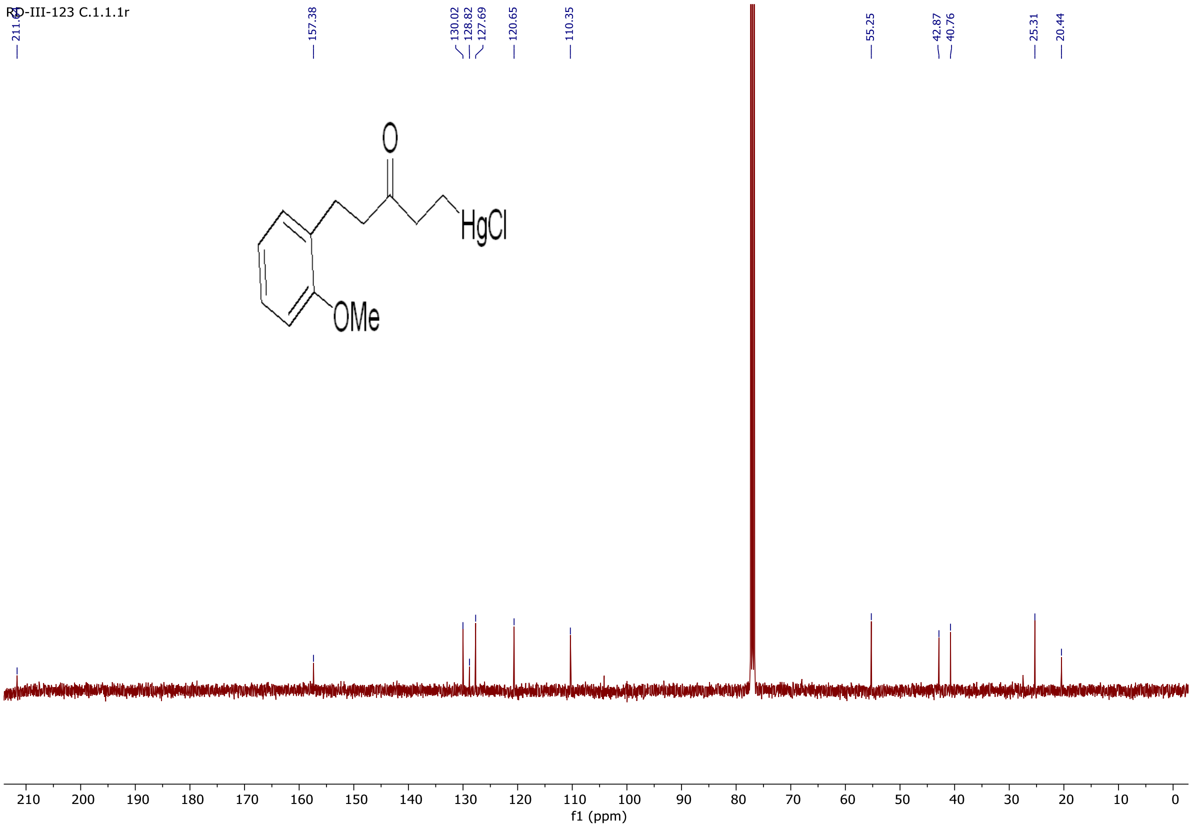
Compound 40 (^{1}H NMR: 600 MHz, ^{13}C{^{1}H} NMR: 150 MHz)



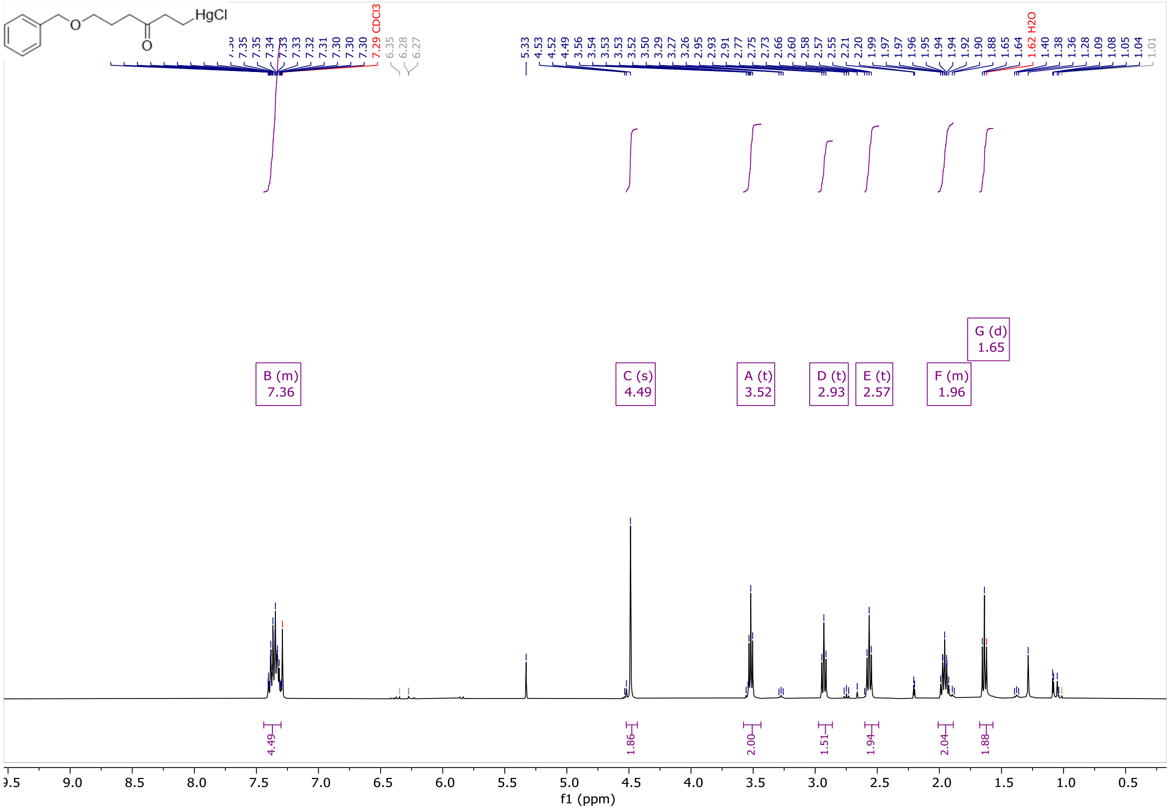


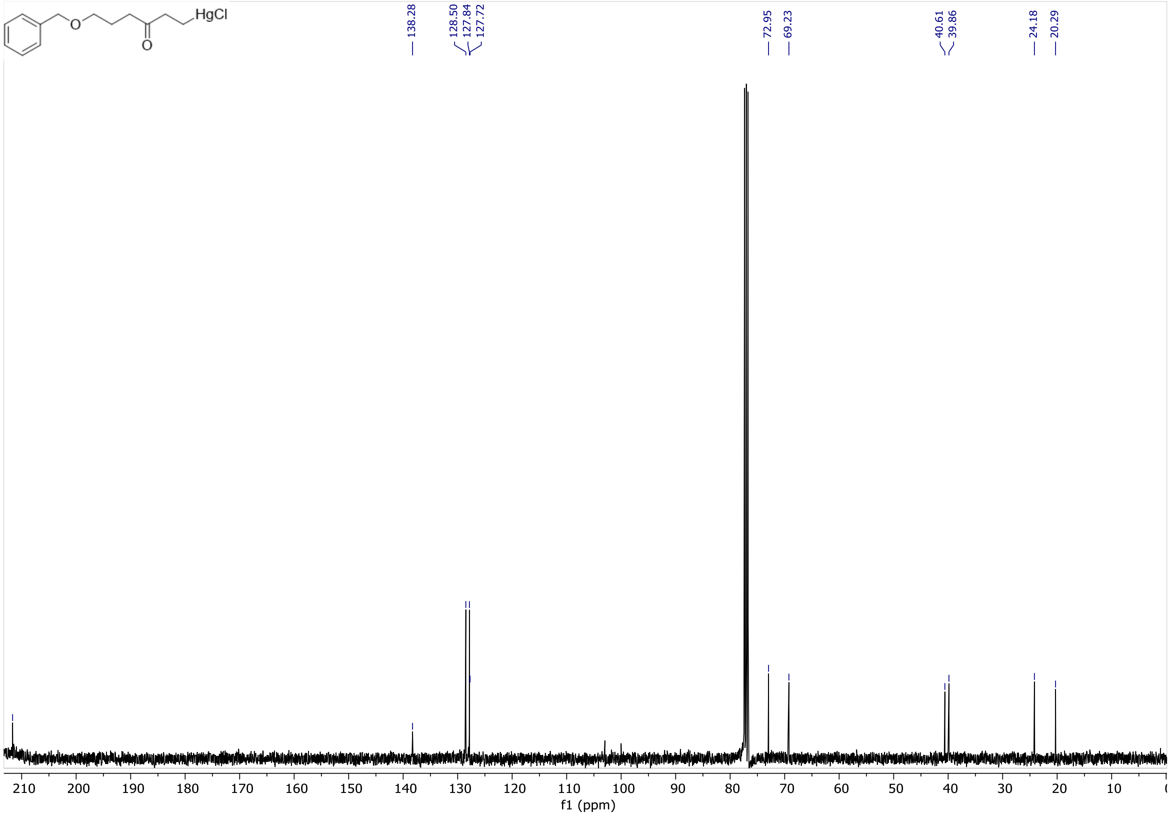
Compound 41 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



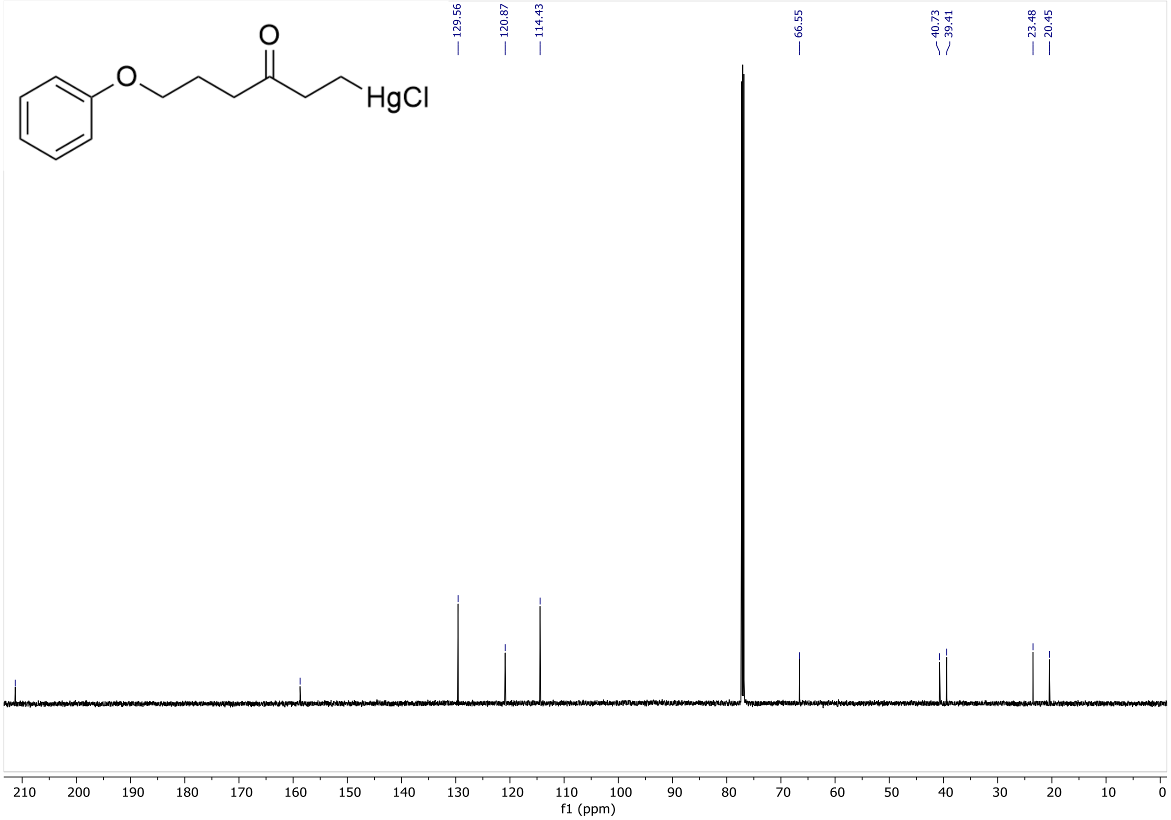


Compound 42 (^{1}H NMR: 400 MHz, $^{13}C\{^{1}H\}$ NMR: 100 MHz)

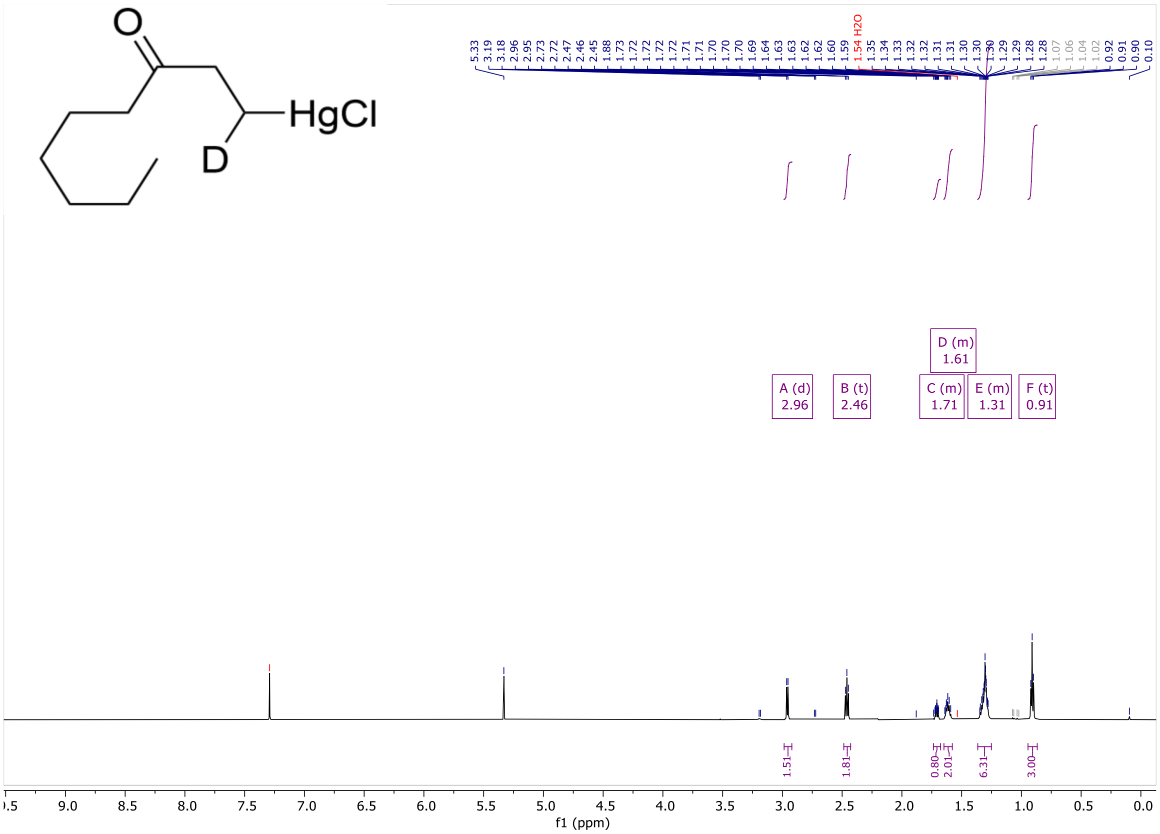


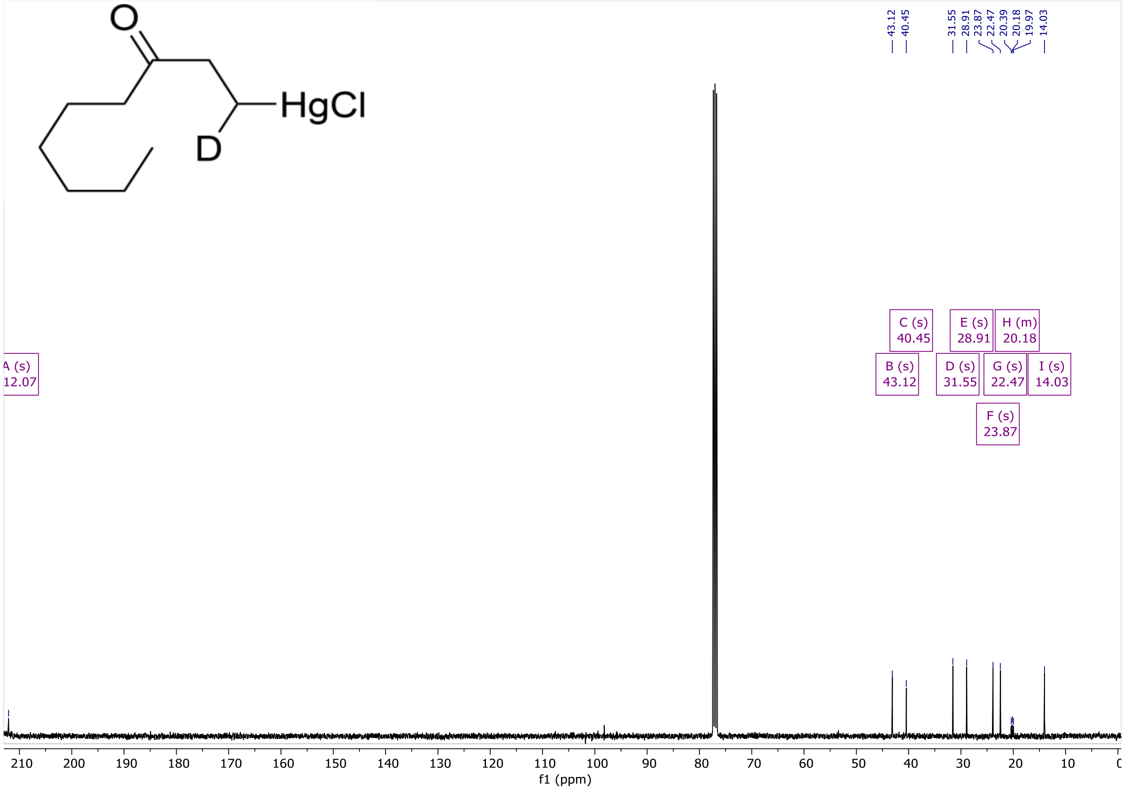


Compound 43 (^{1}H NMR: 600 MHz, ^{13}C{^{1}H} NMR: 150 MHz)

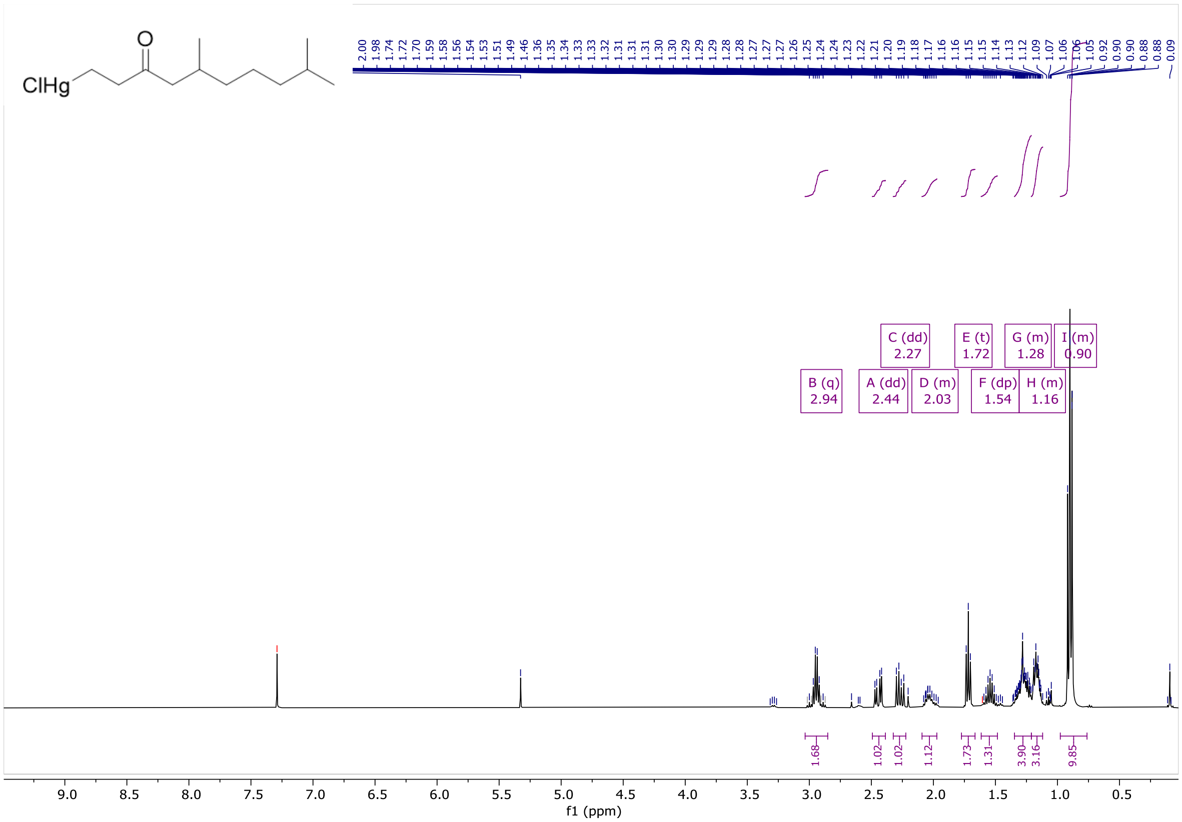


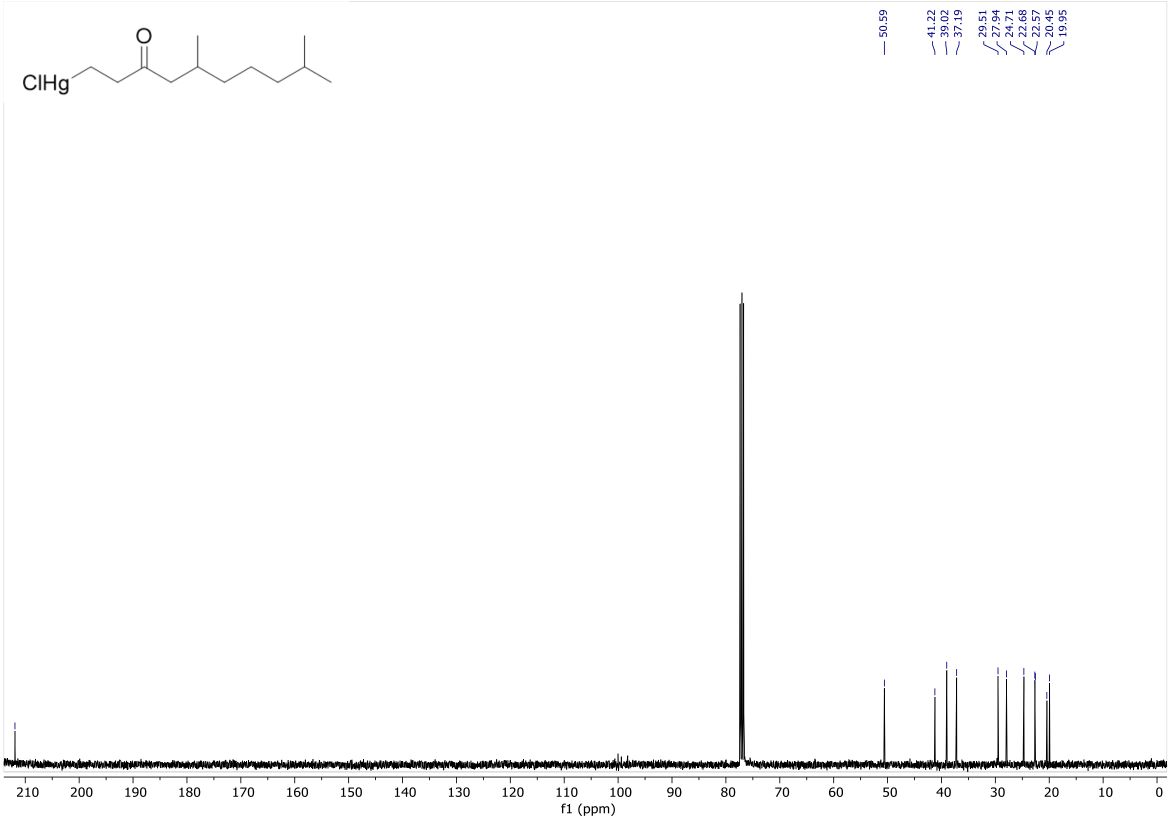
Compound 44 (^{1}H NMR: 600 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



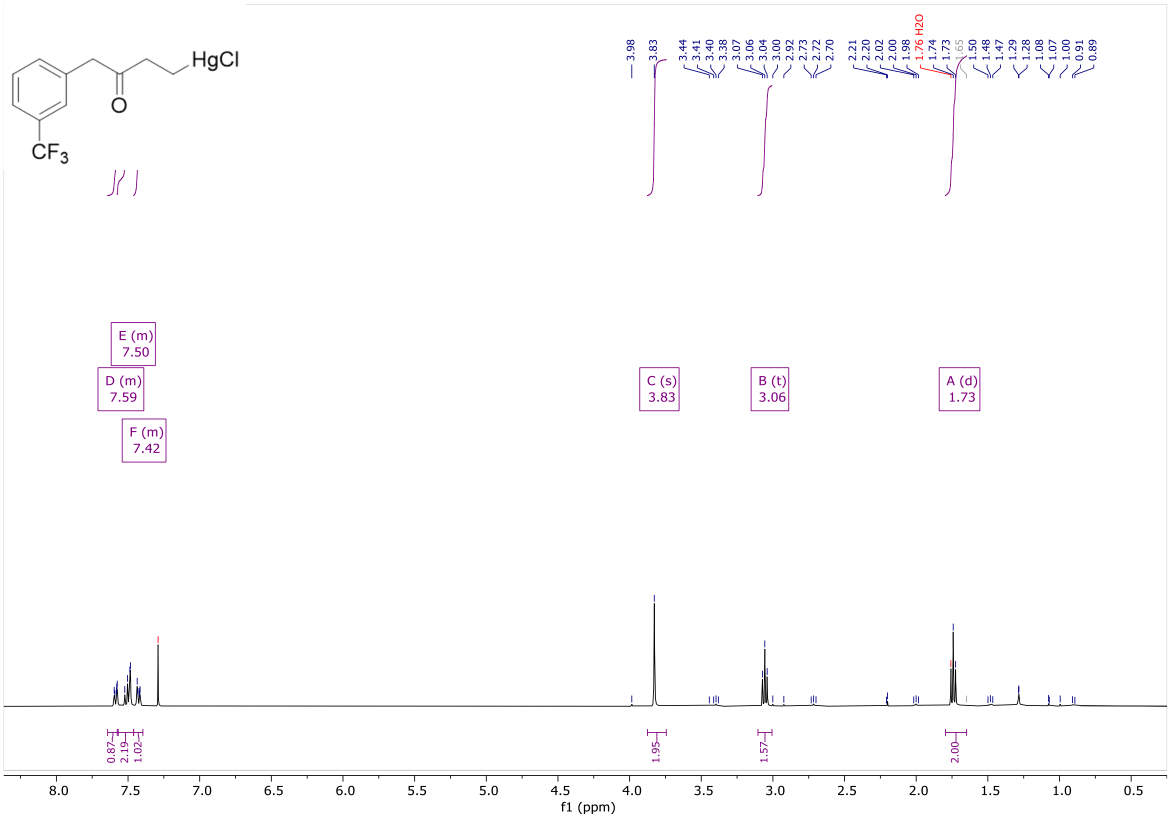


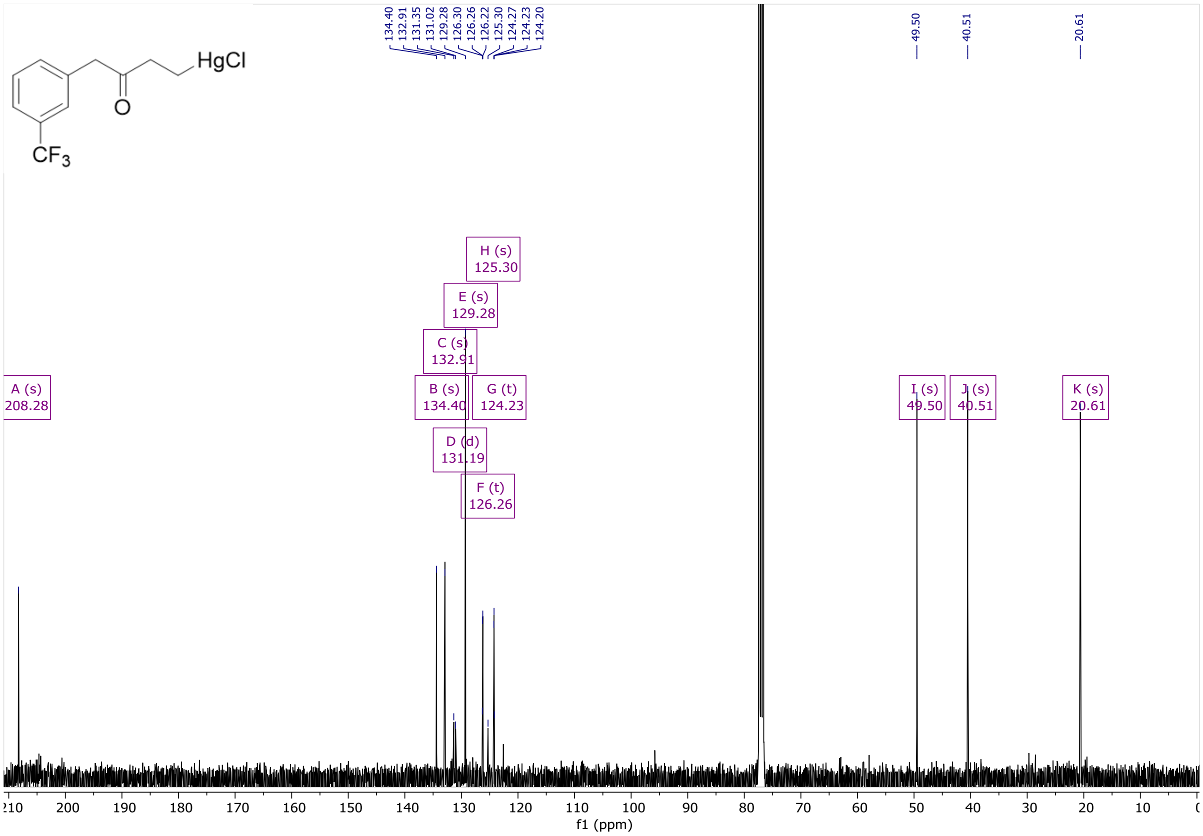
Compound 45 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



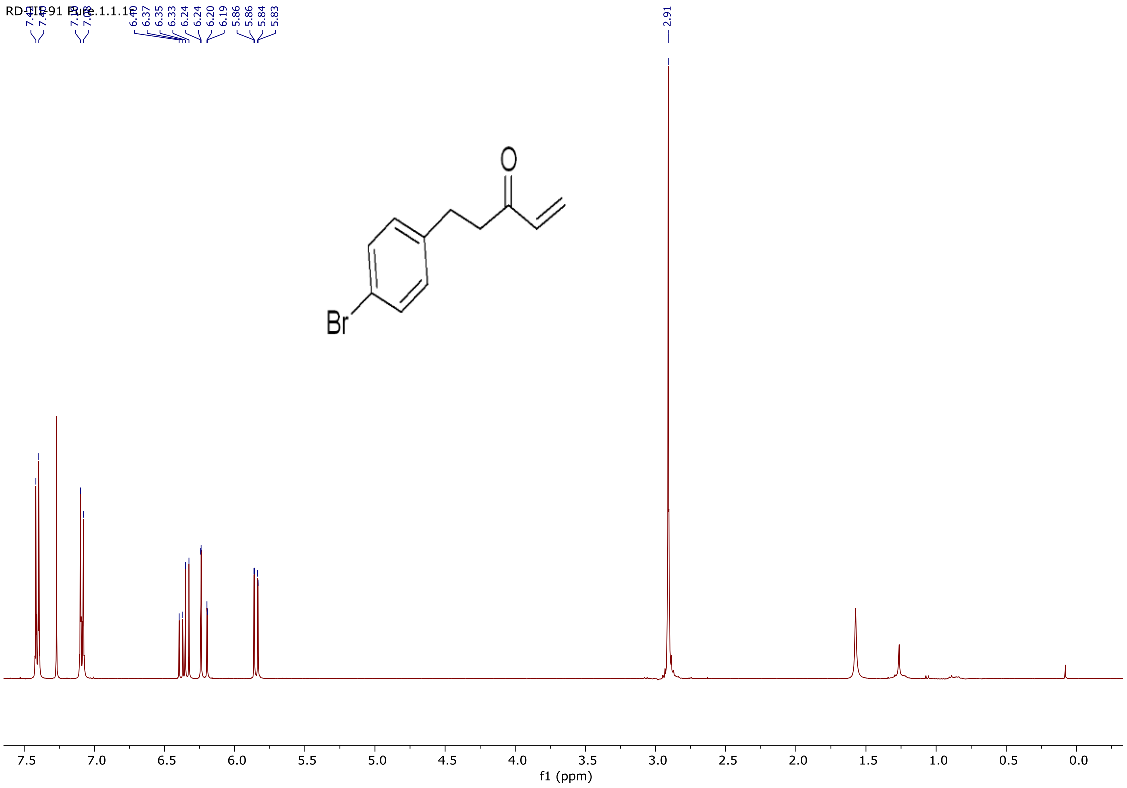


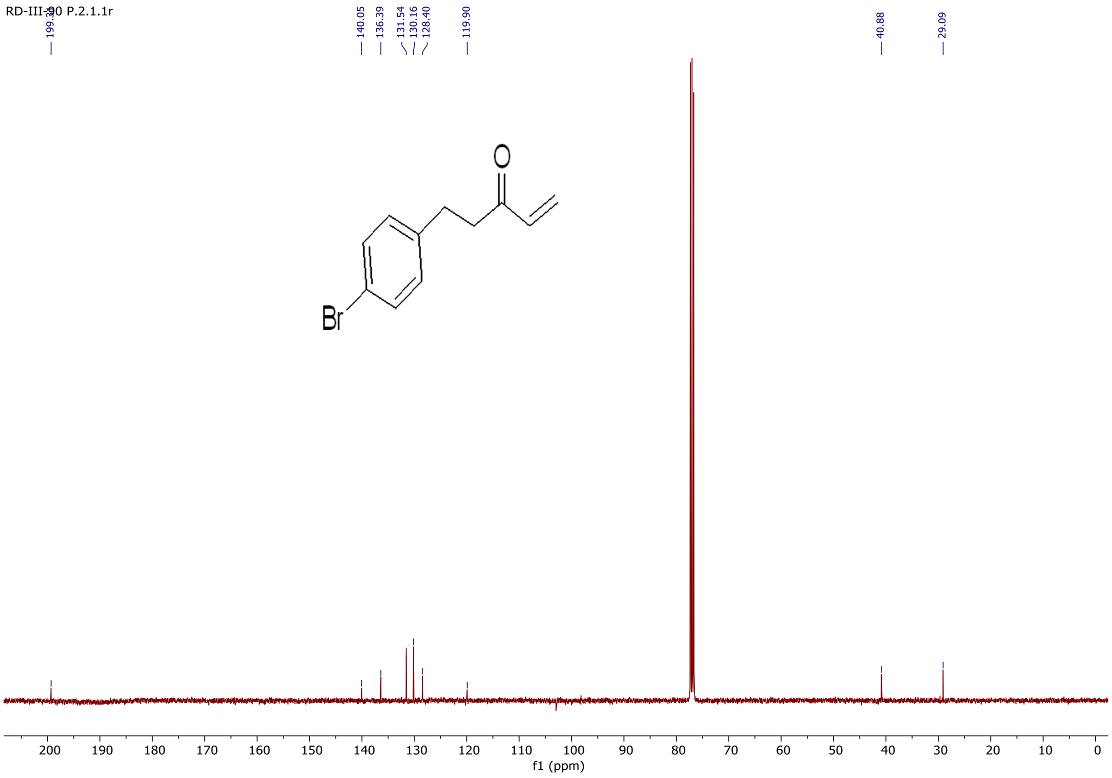
Compound 46 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



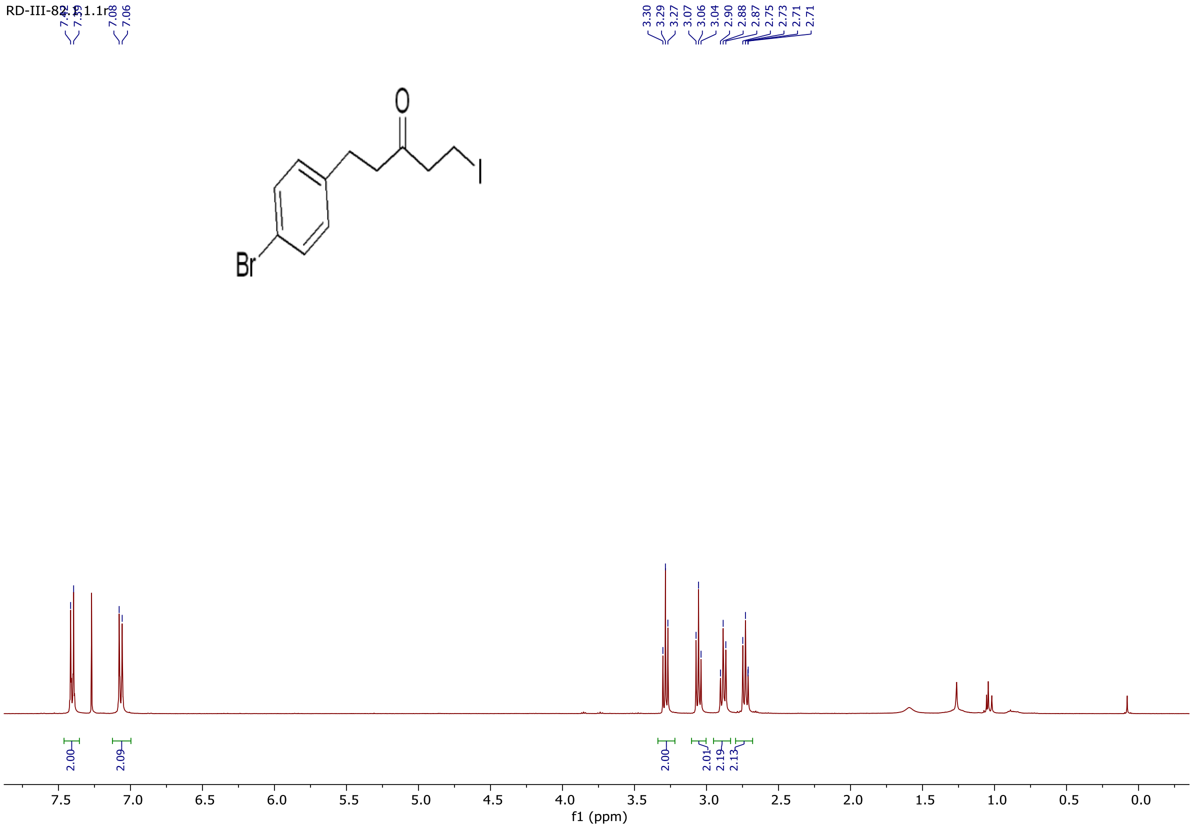


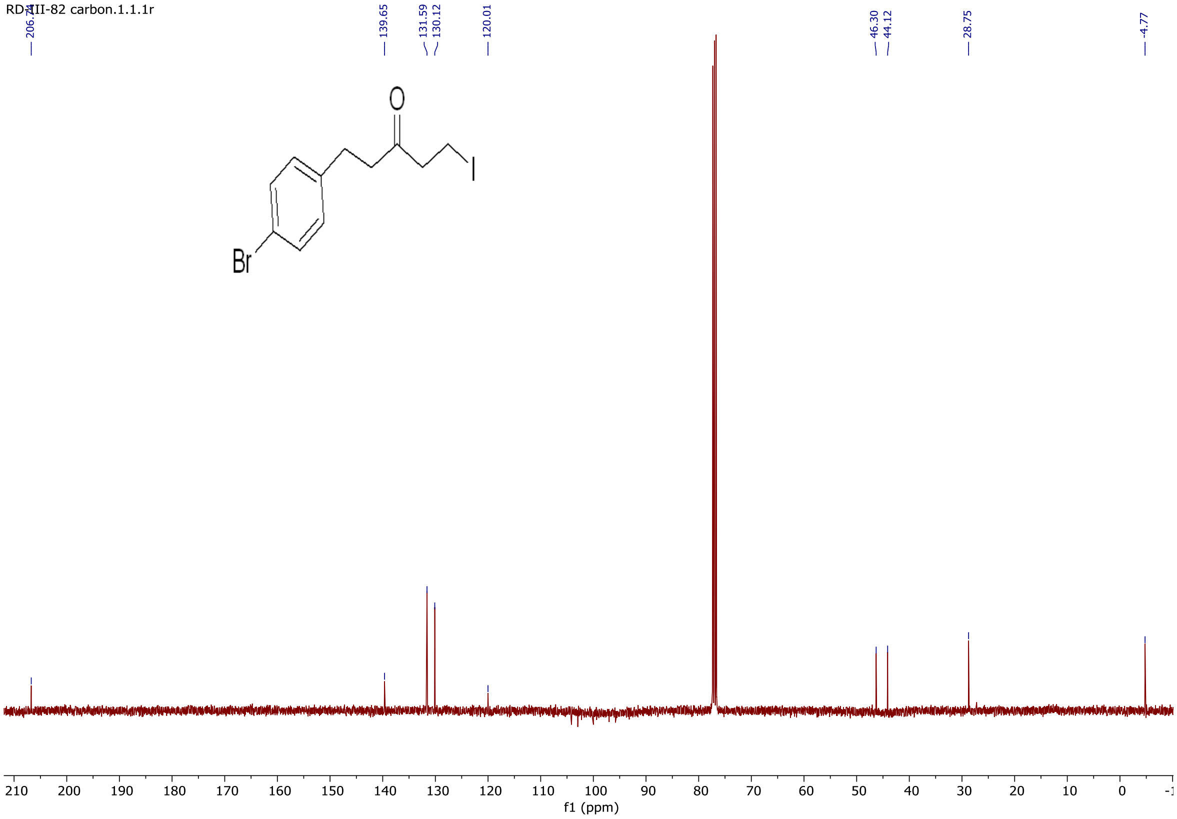
Compound 47 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



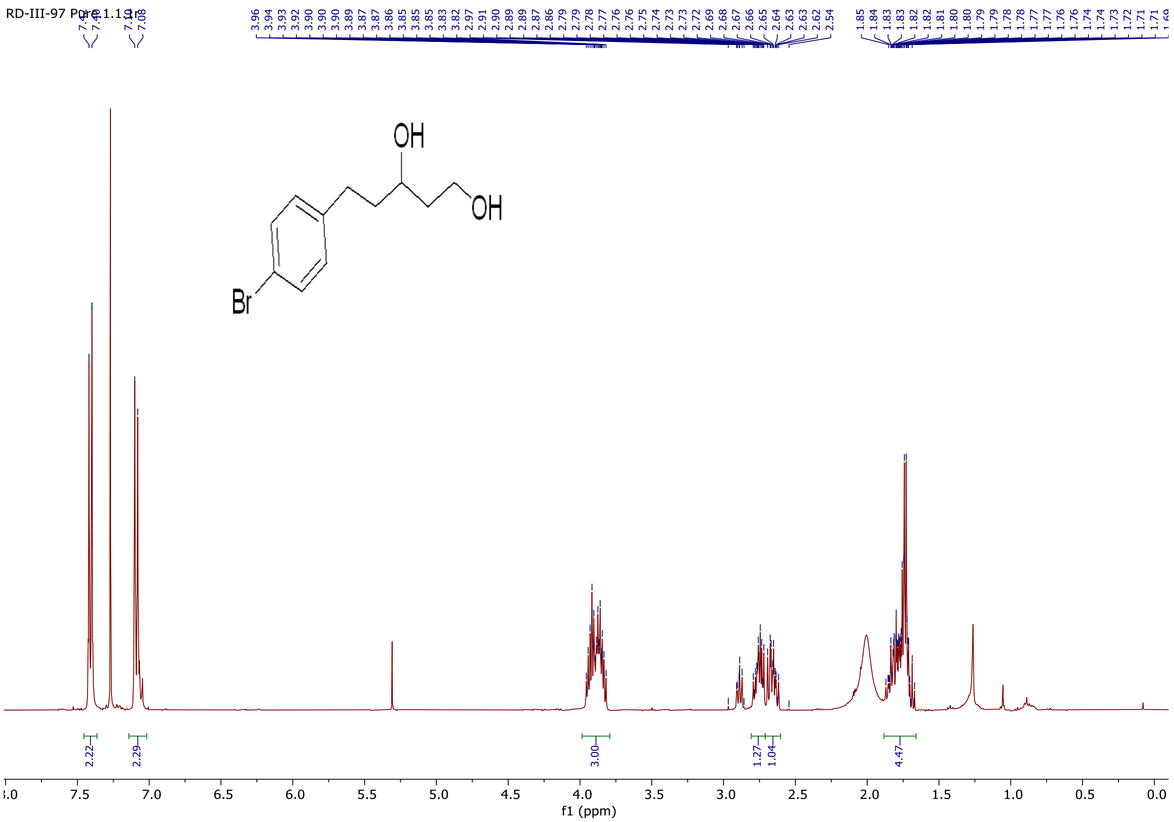


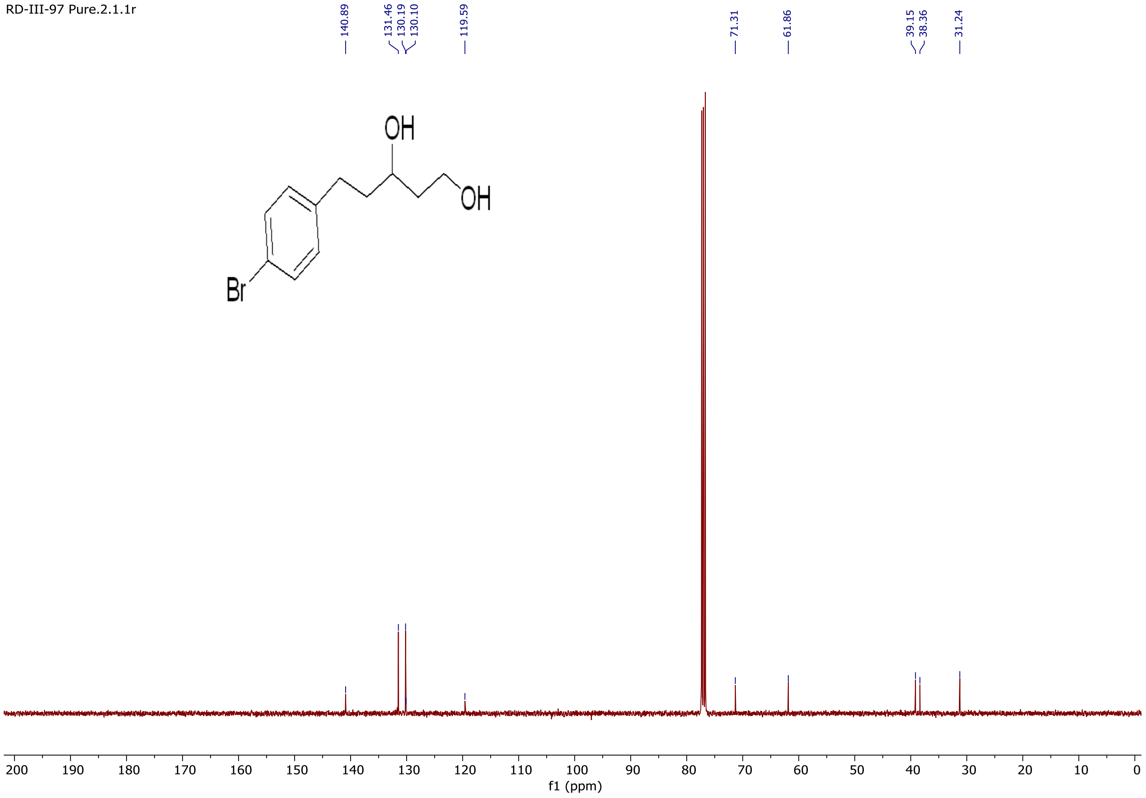
Compound 48 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



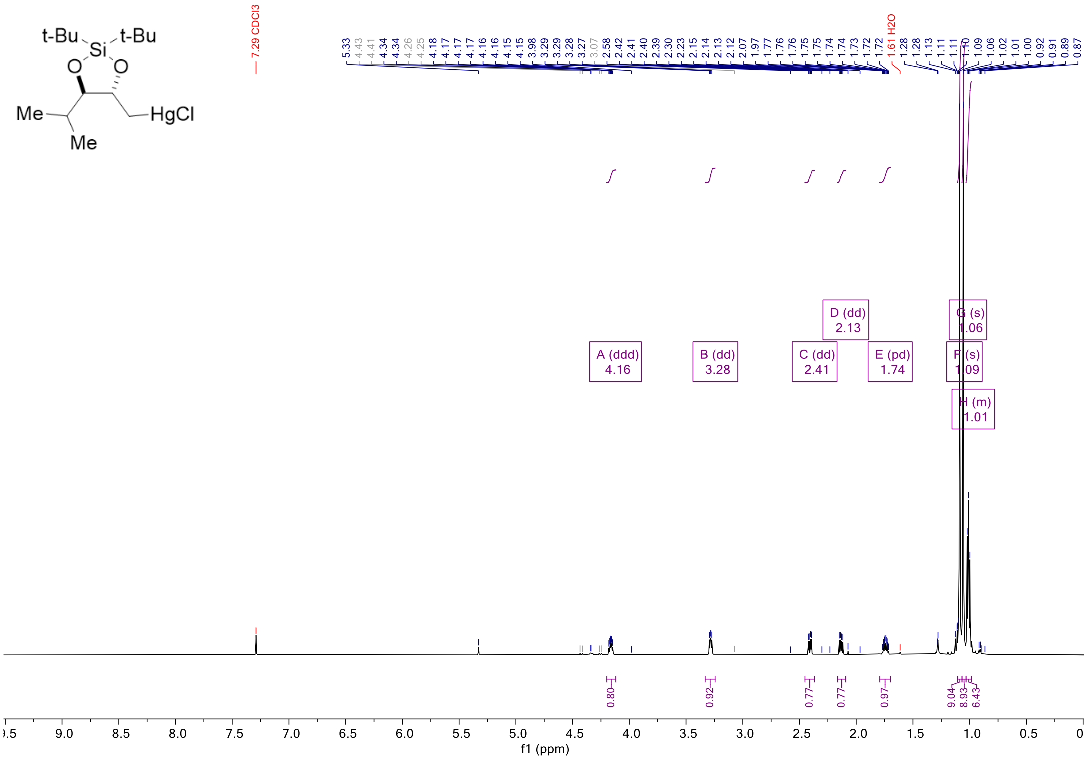


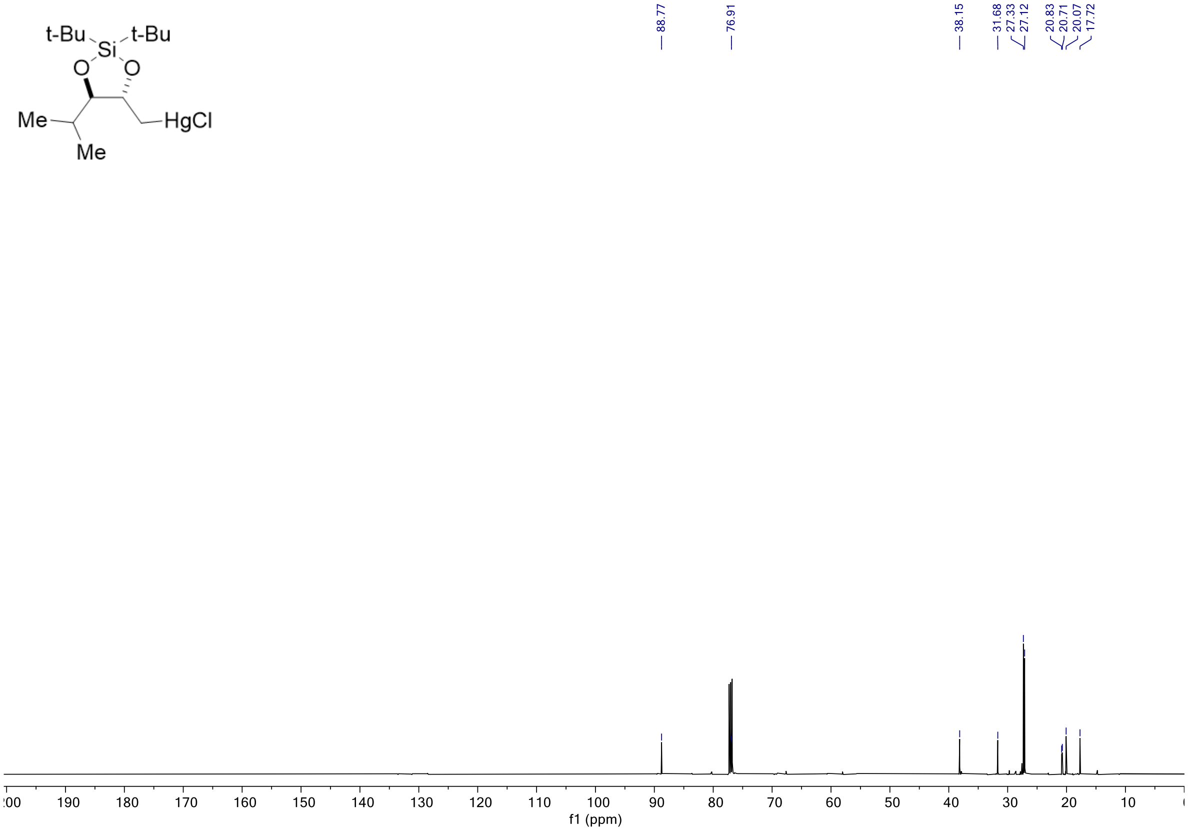
Compound 49 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



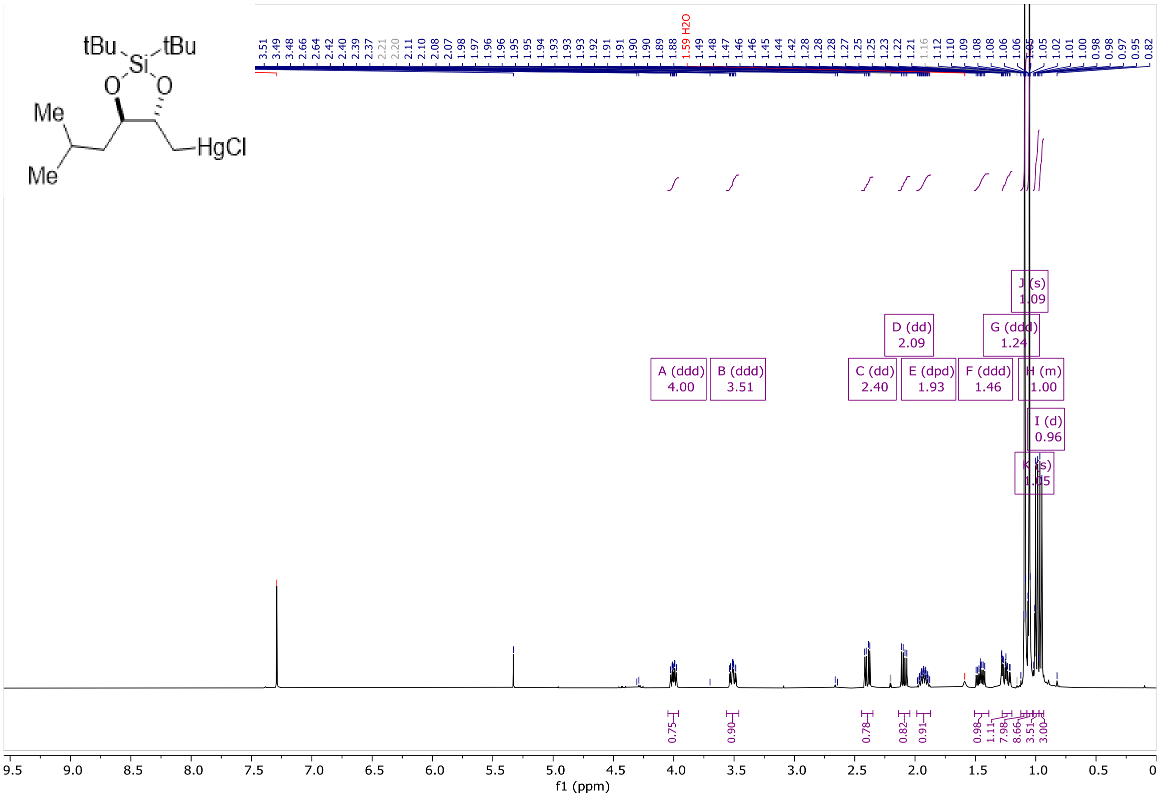


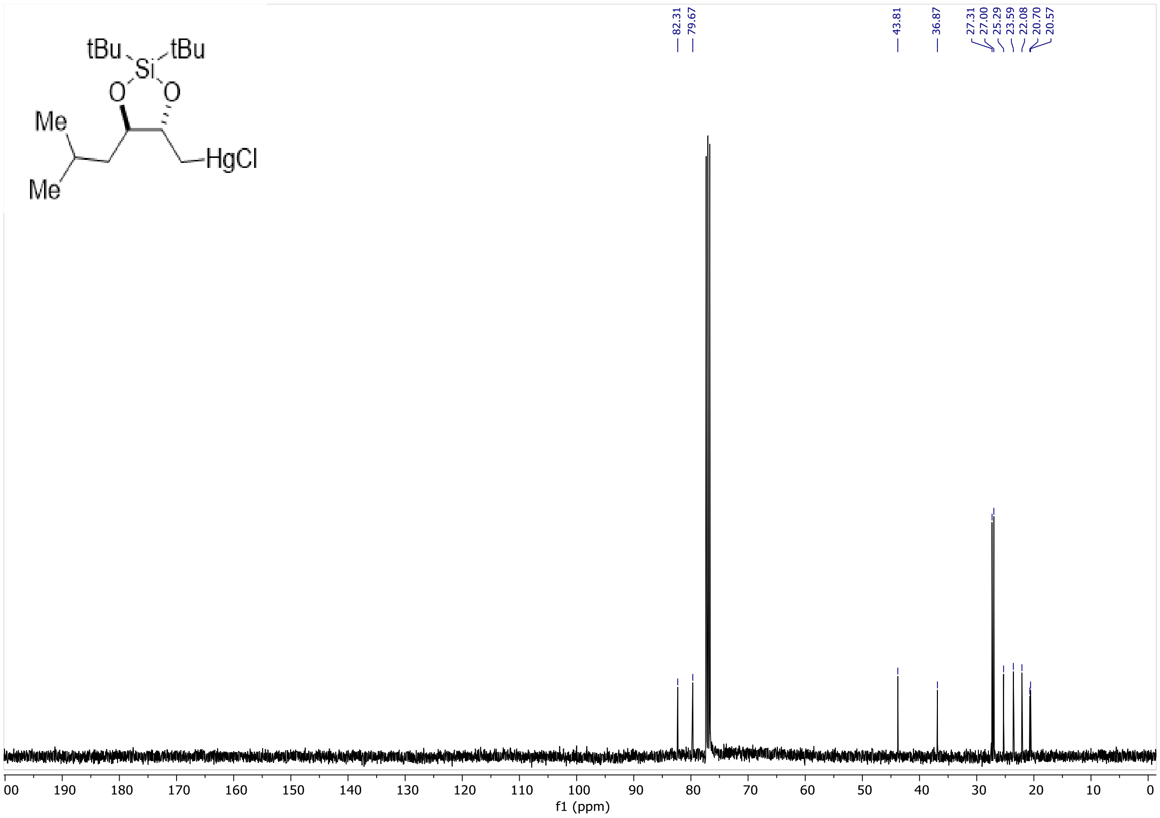
Compound 50 (^{1}H NMR: 600 MHz, ^{13}C{^{1}H} NMR: 125 MHz)



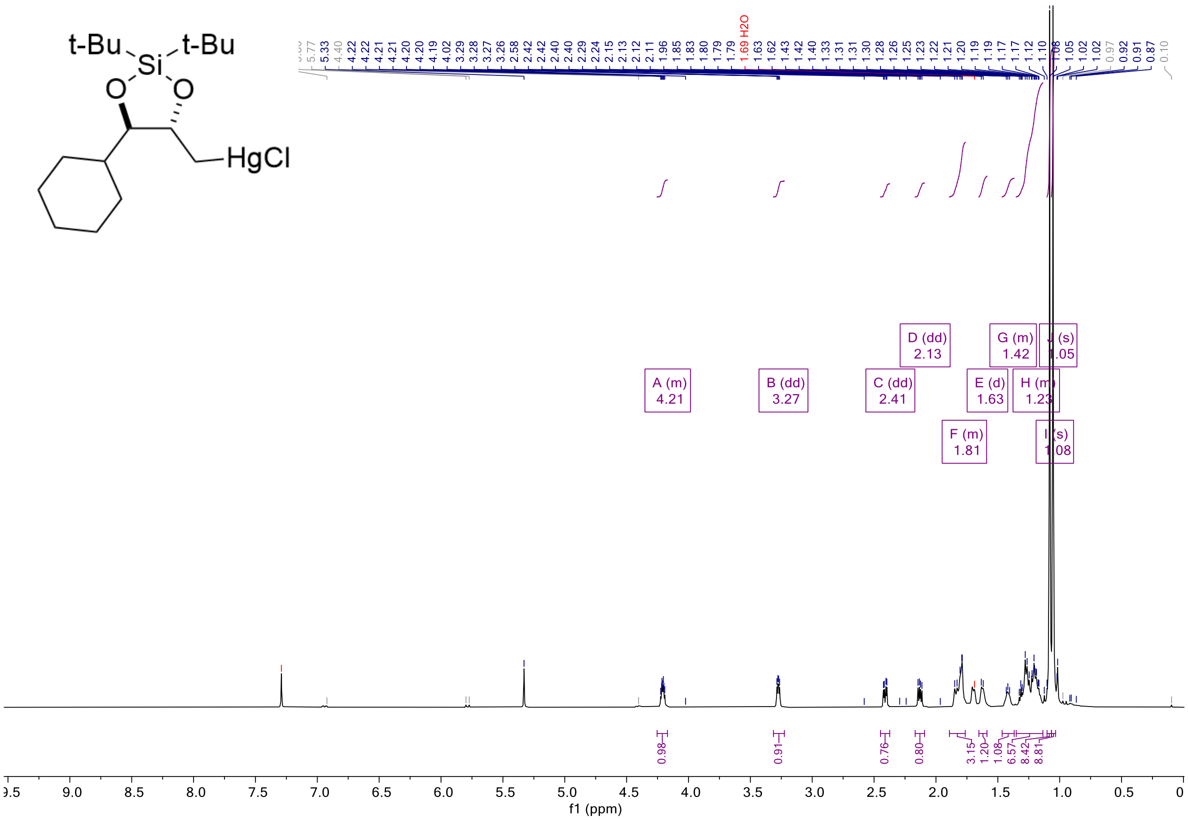


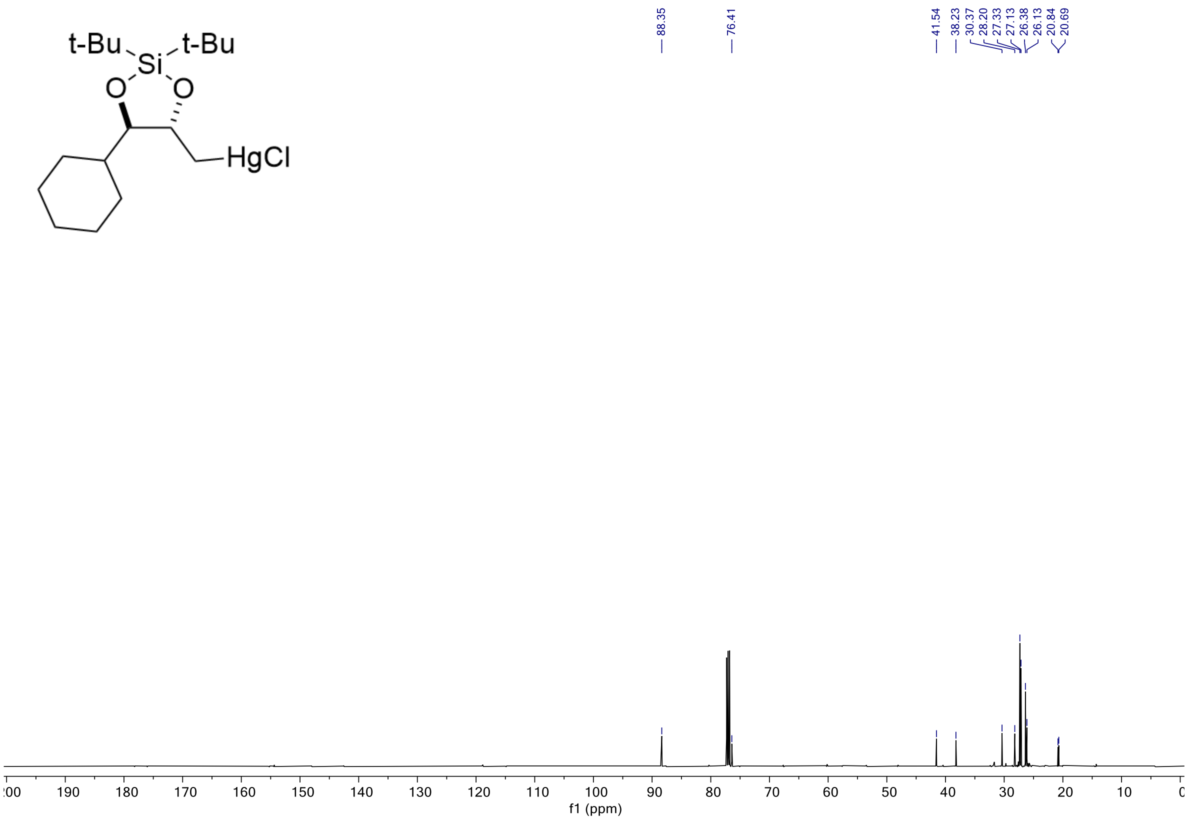
Compound 51 (^{1}H NMR: 400 MHz, $^{13}C\{^{1}H\}$ NMR: 100 MHz)



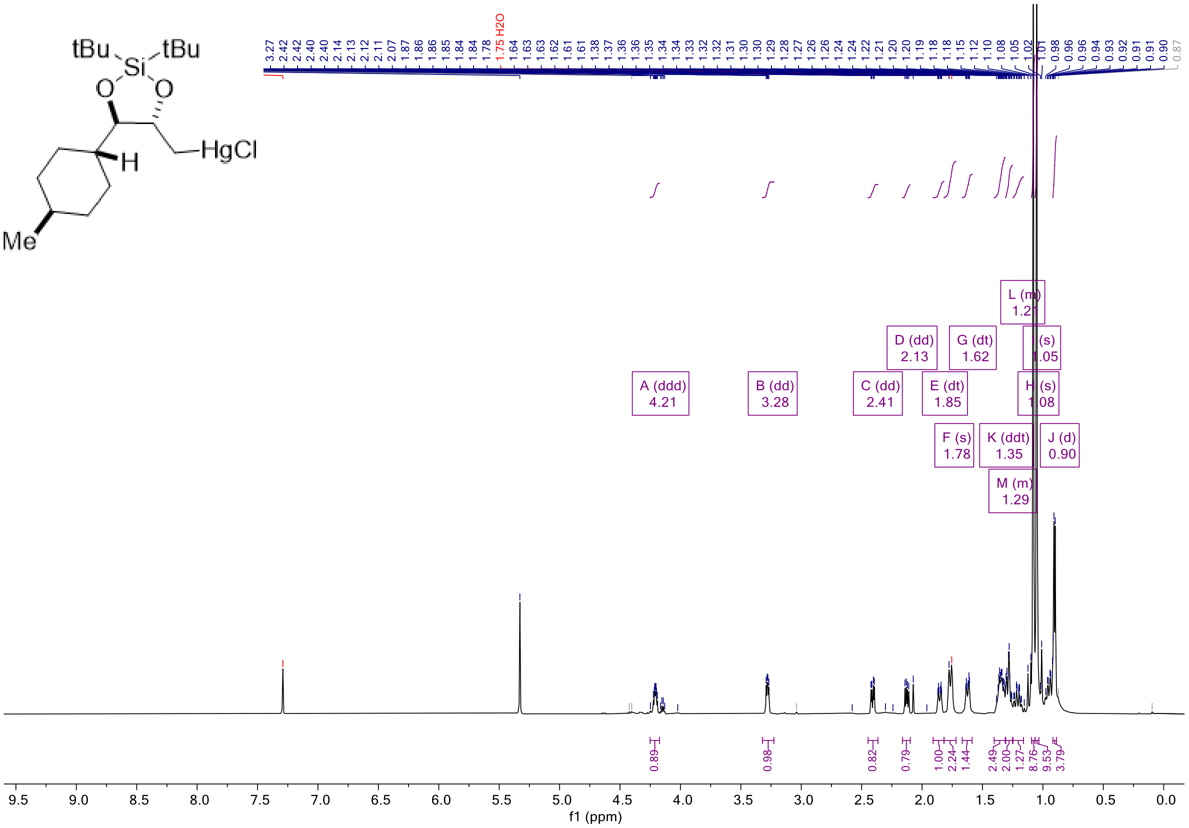


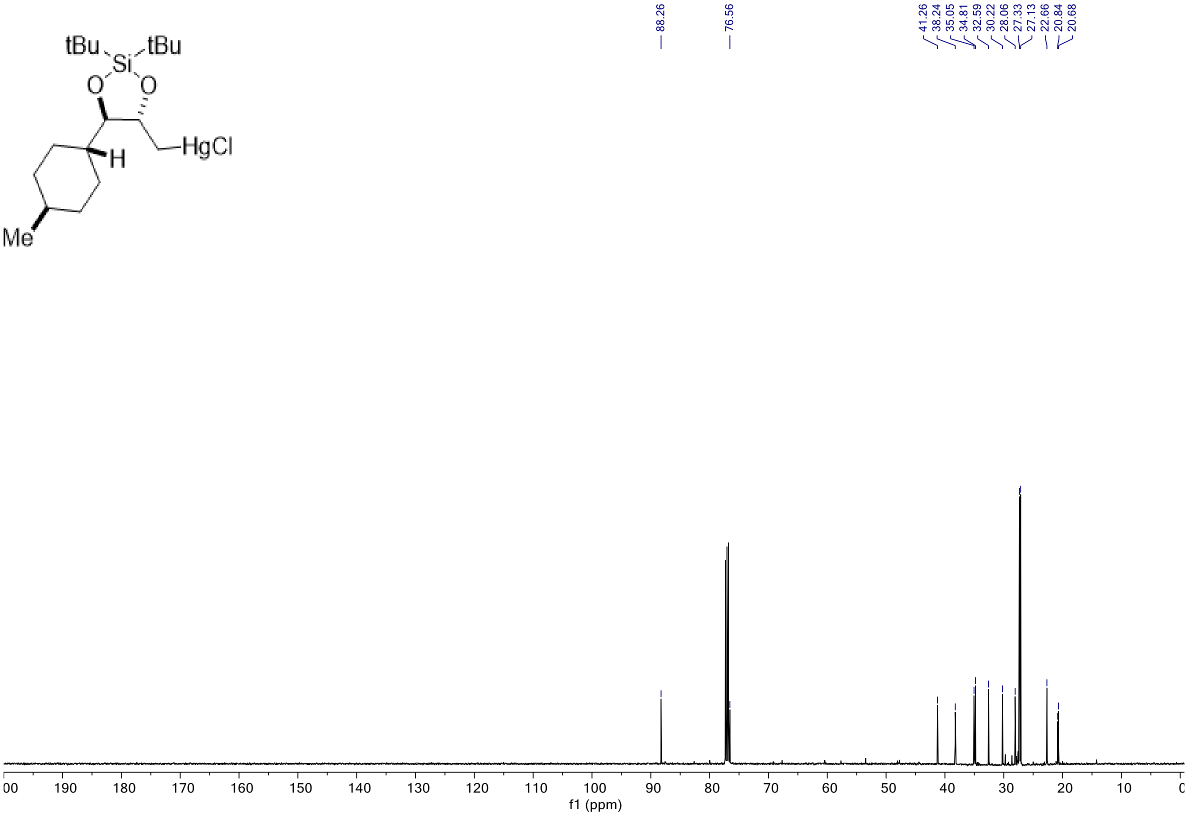
Compound 52 (^{1}H NMR: 600 MHz, ^{13}C{^{1}H} NMR: 125 MHz)



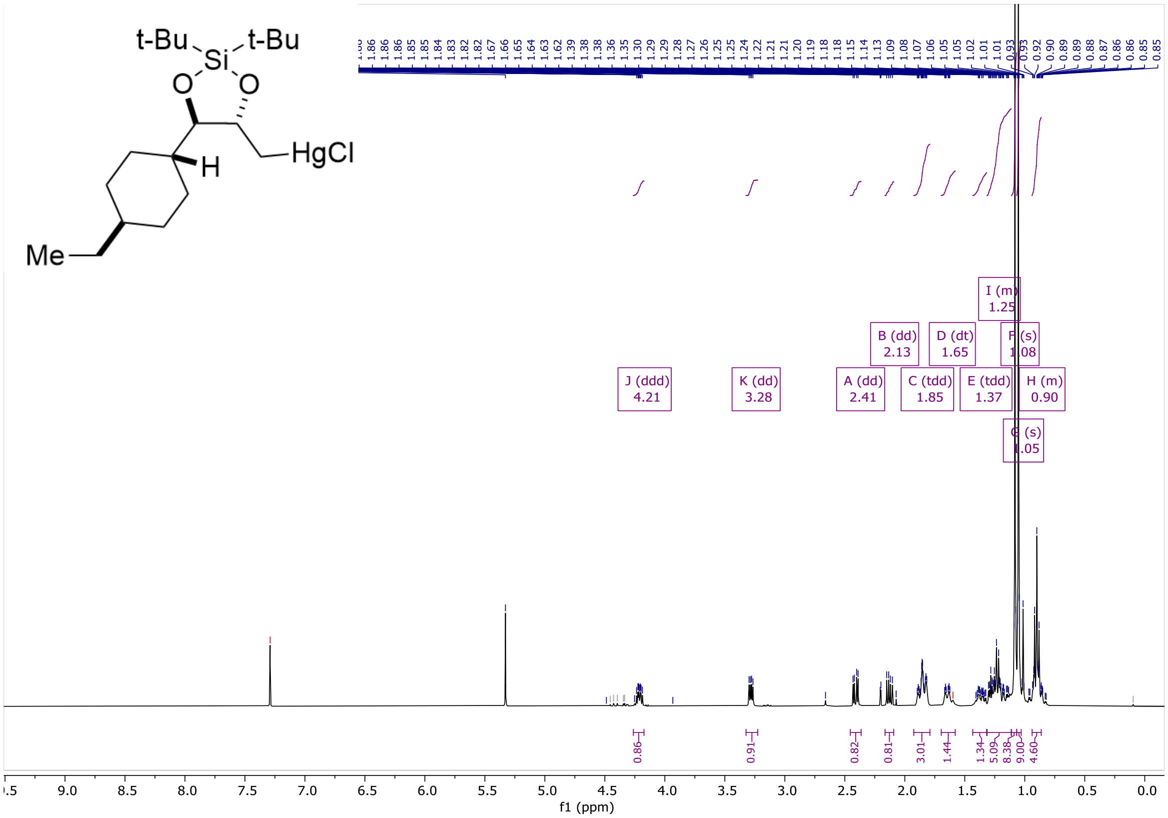


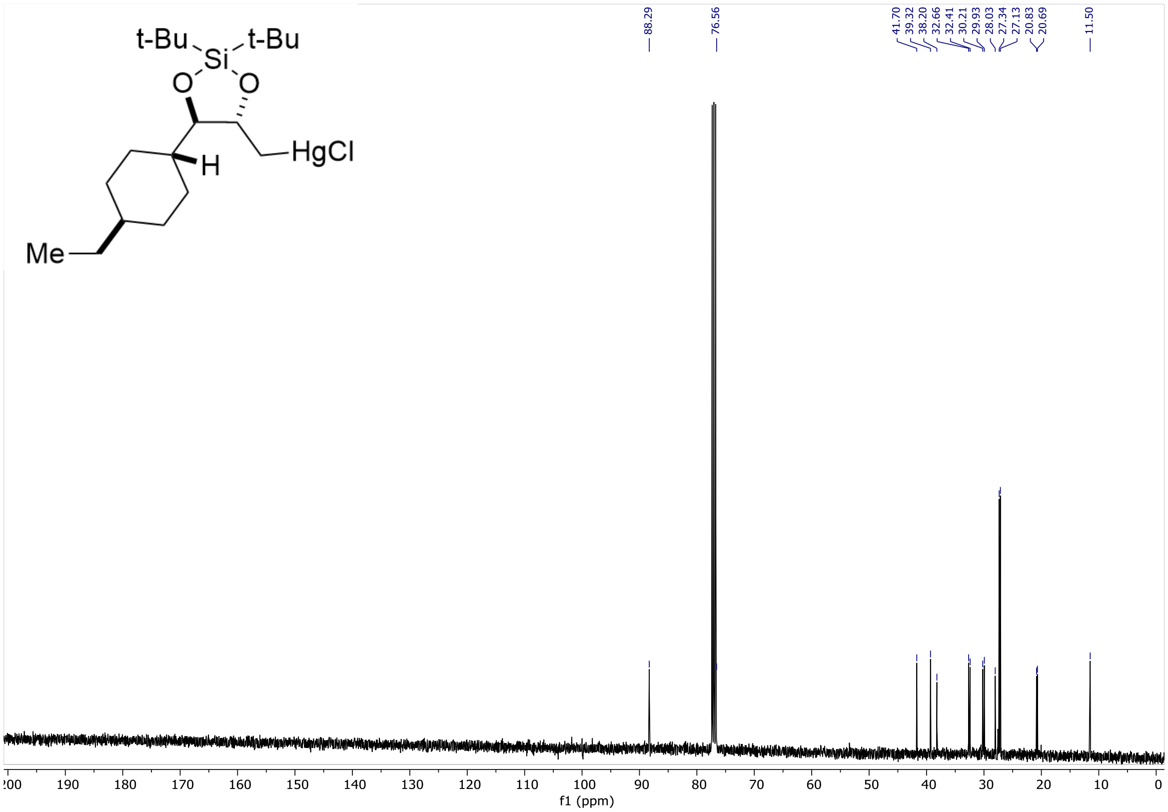
Compound 53 (^1H NMR: 600 MHz, $^{13}C\{^1H\}$ NMR: 125 MHz)



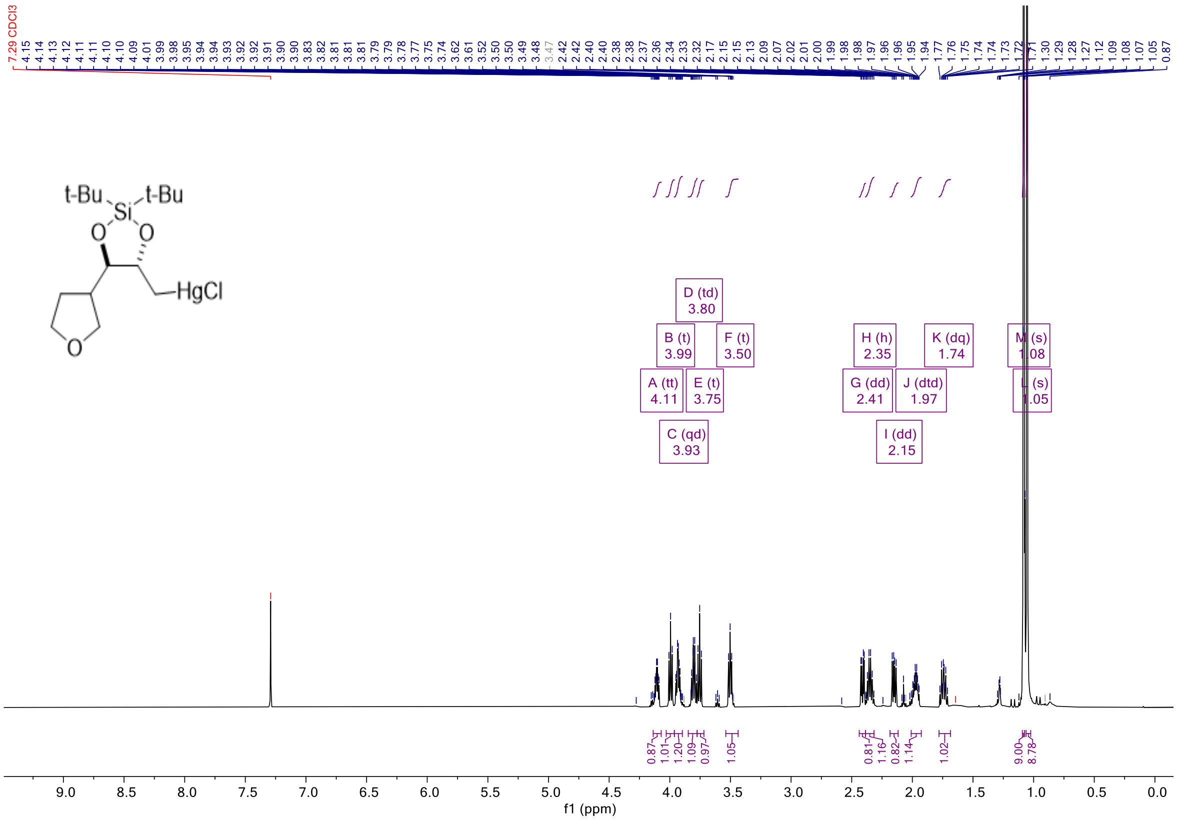


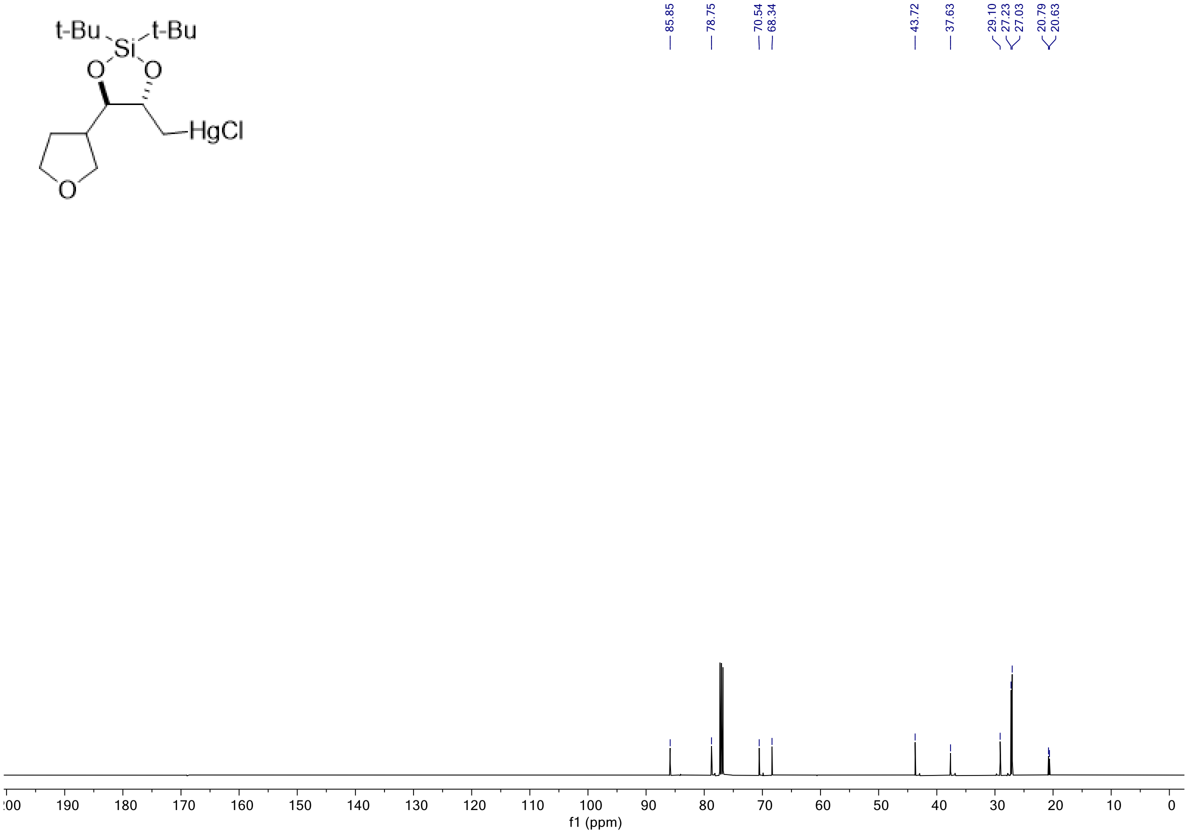
Compound 54 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



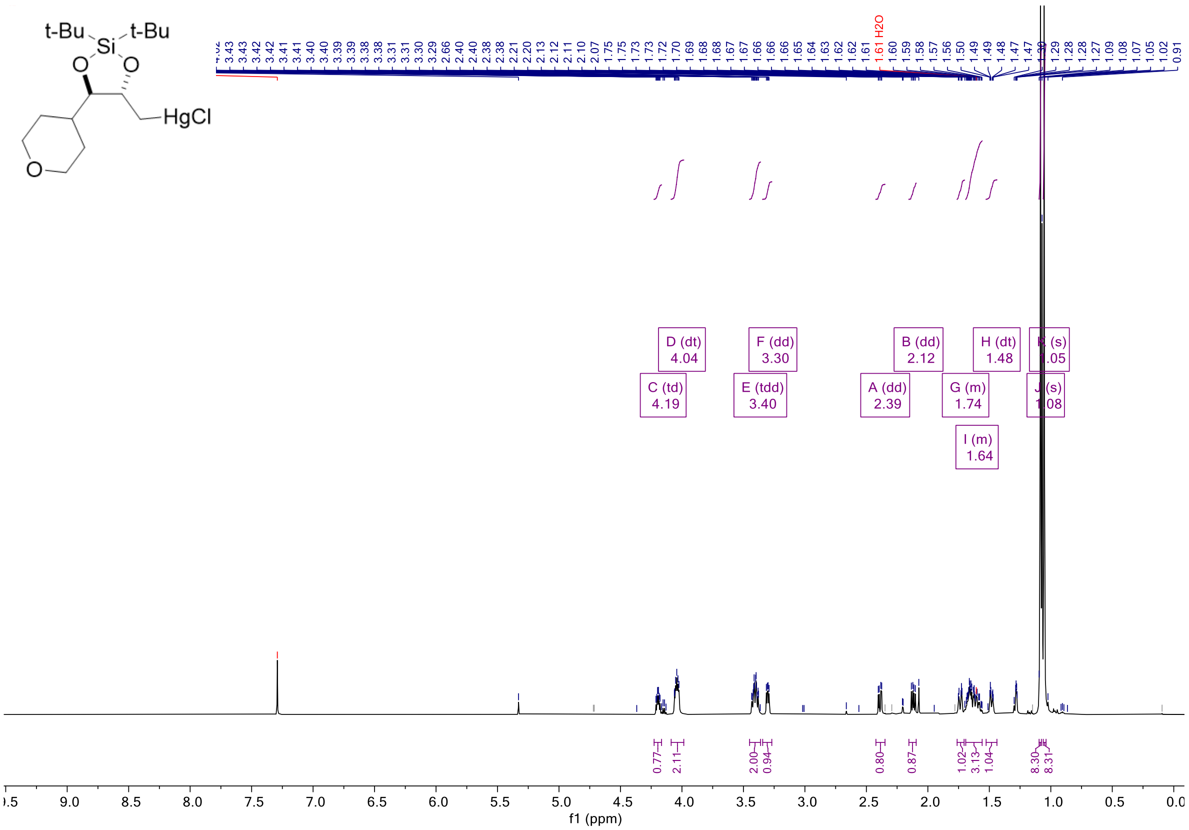


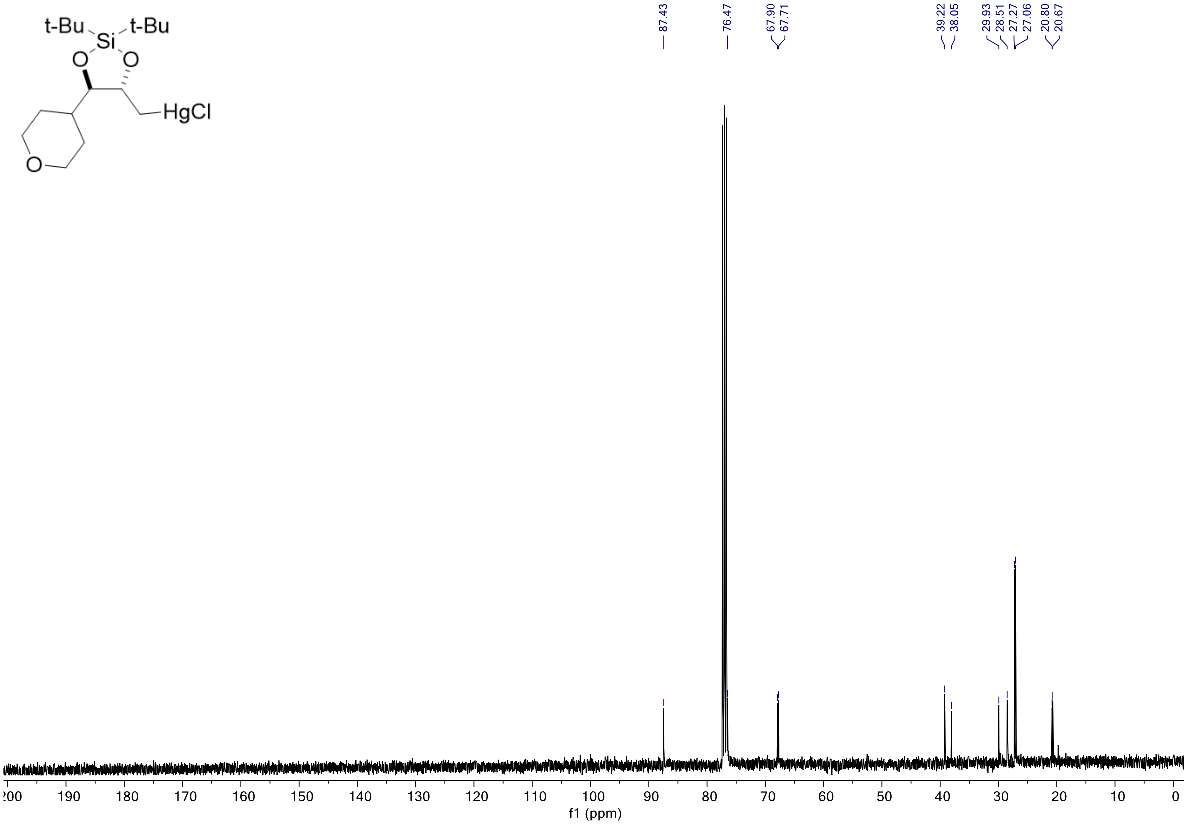
Compound 55 (^{1}H NMR: 600 MHz, ^{13}C{^{1}H} NMR: 125 MHz)



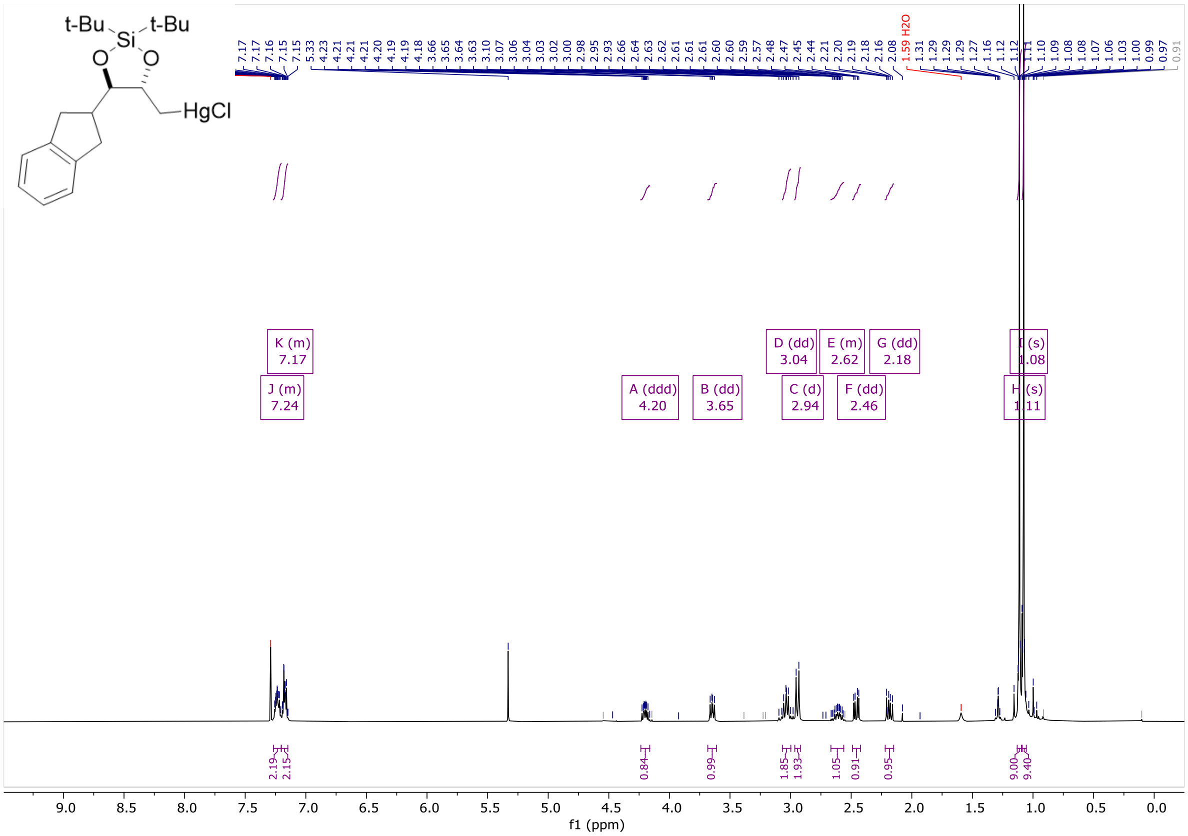


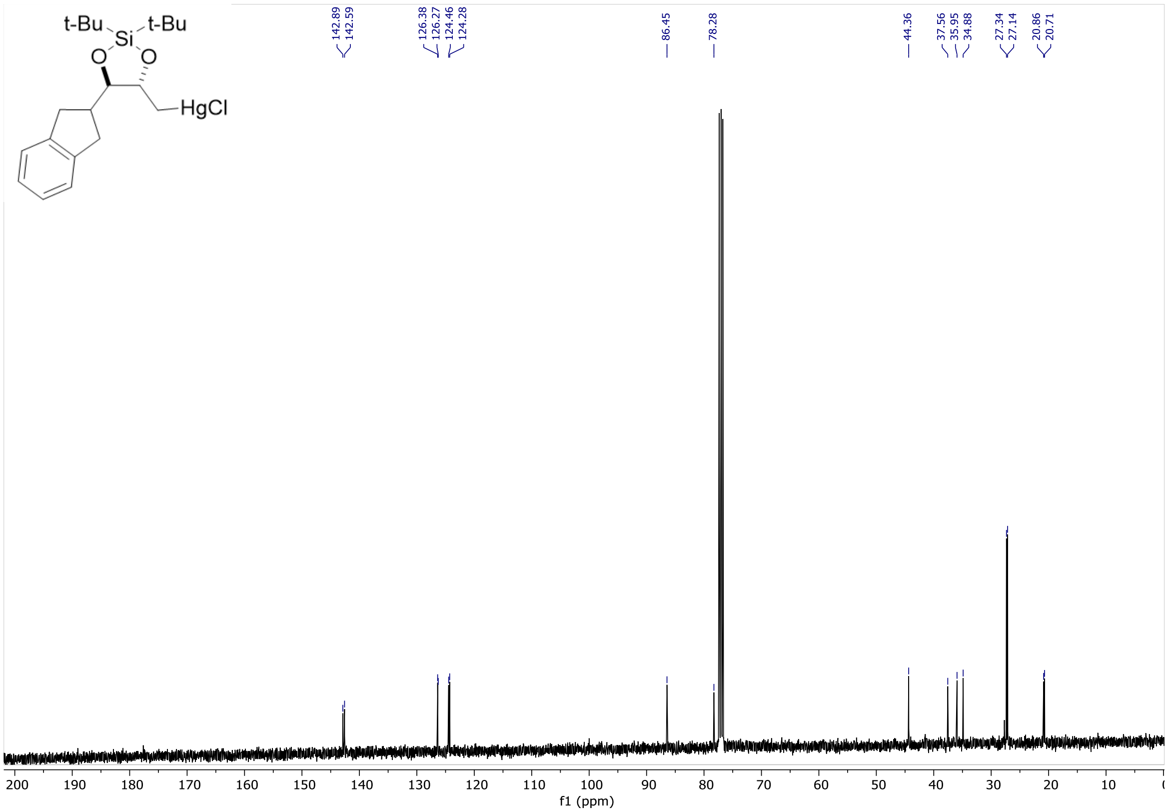
Compound 56 (^{1}H NMR: 600 MHz, $^{13}C\{^{1}H\}$ NMR: 100 MHz)



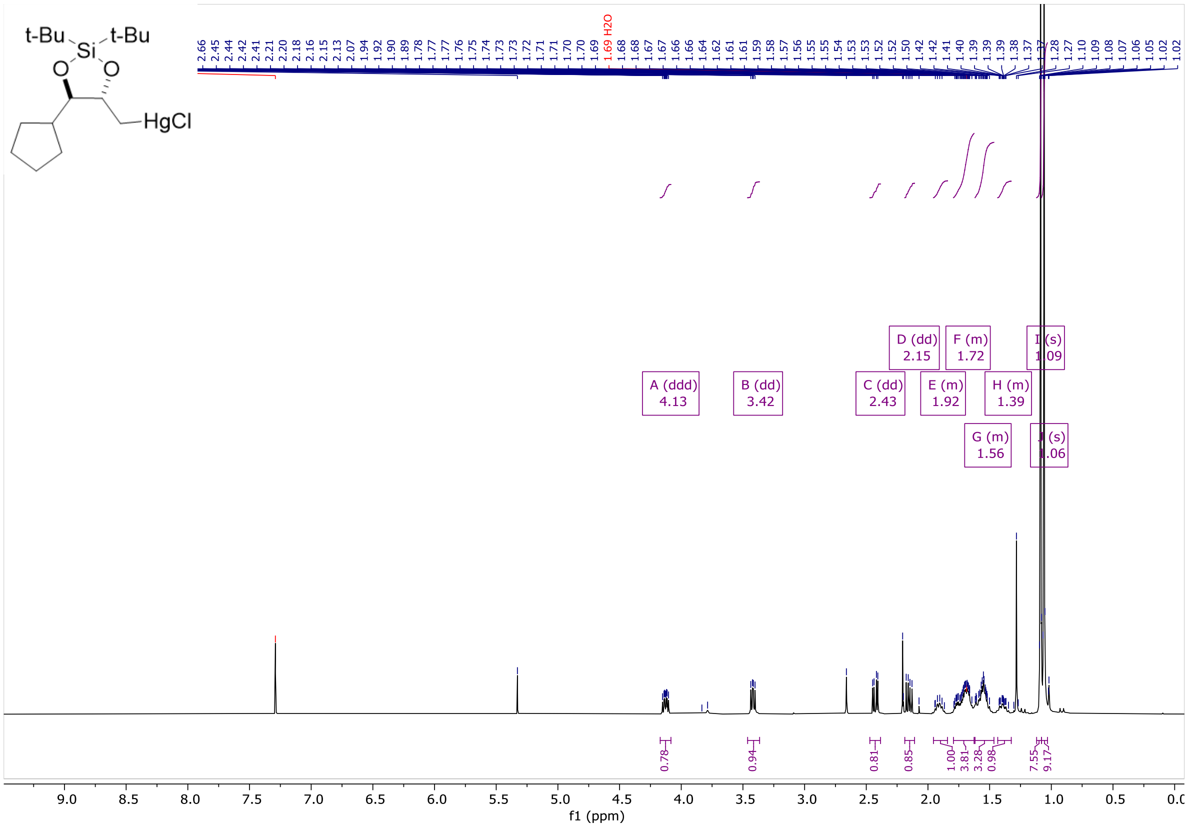


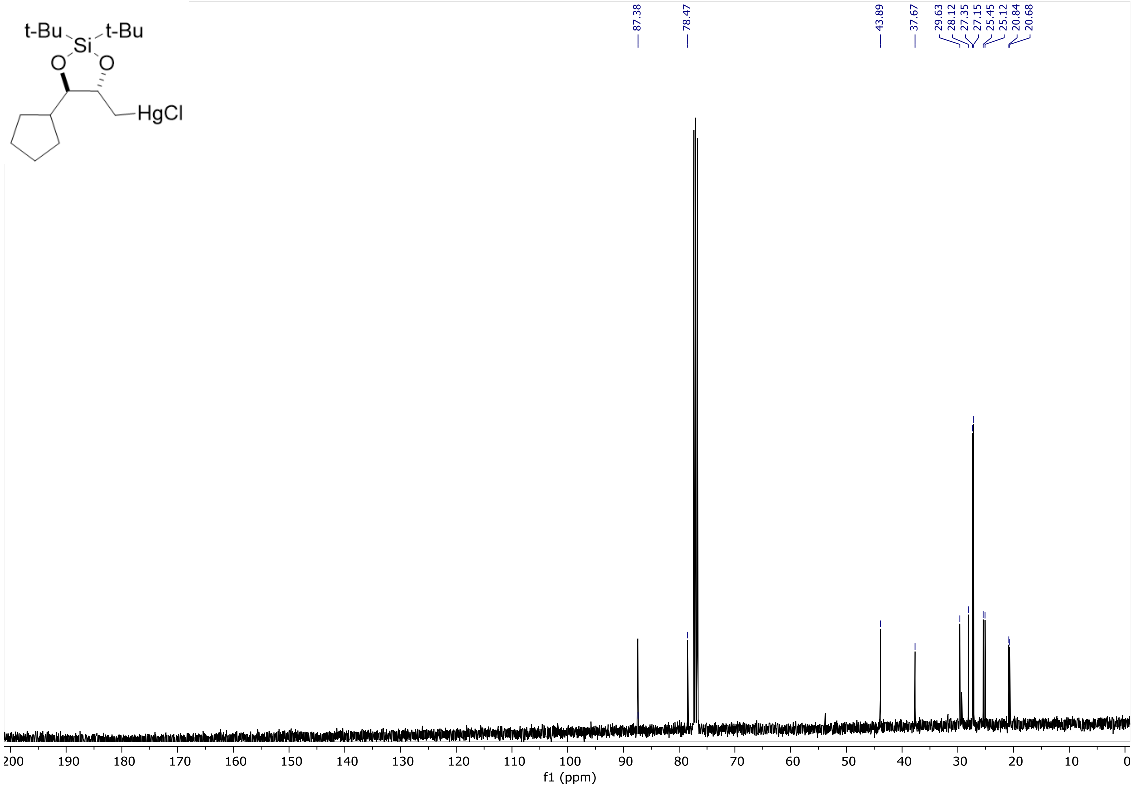
Compound 57 (^{1}H NMR: 400 MHz, $^{13}C\{^{1}H\}$ NMR: 100 MHz)



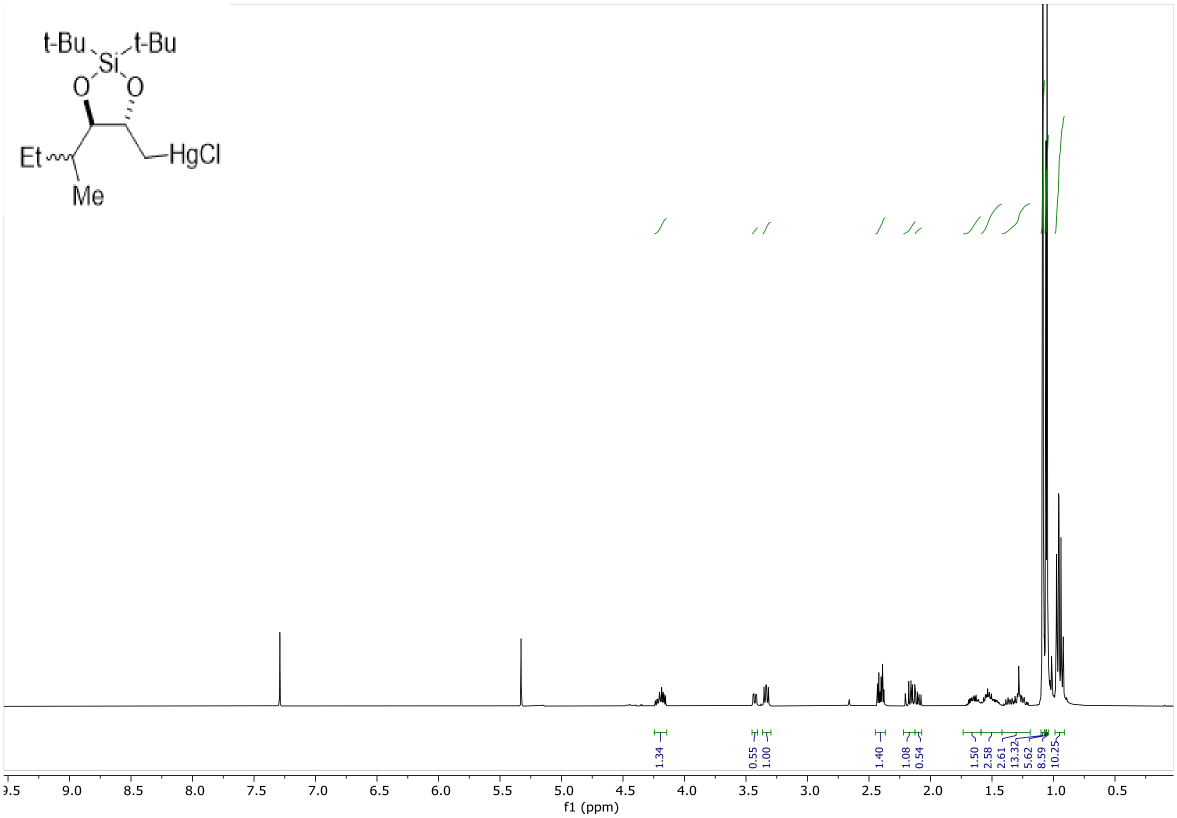


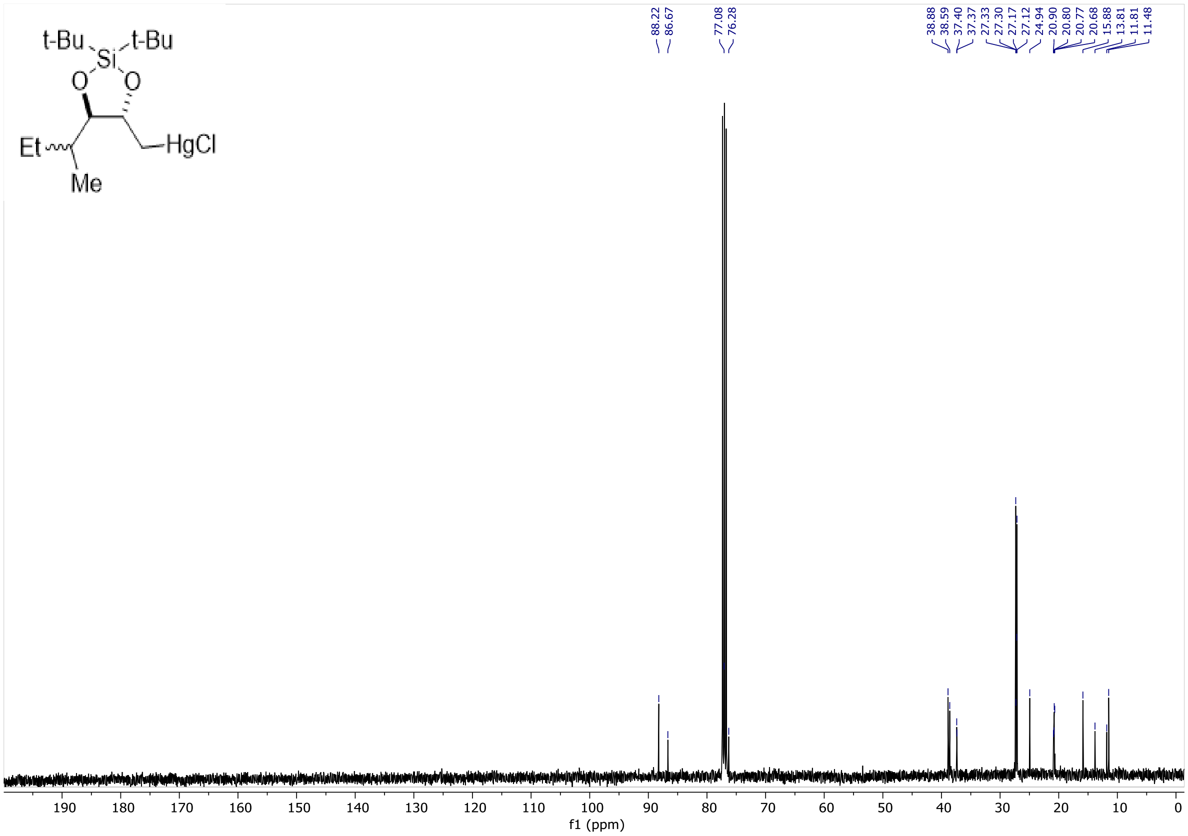
Compound 58 (^1H NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 100 MHz)



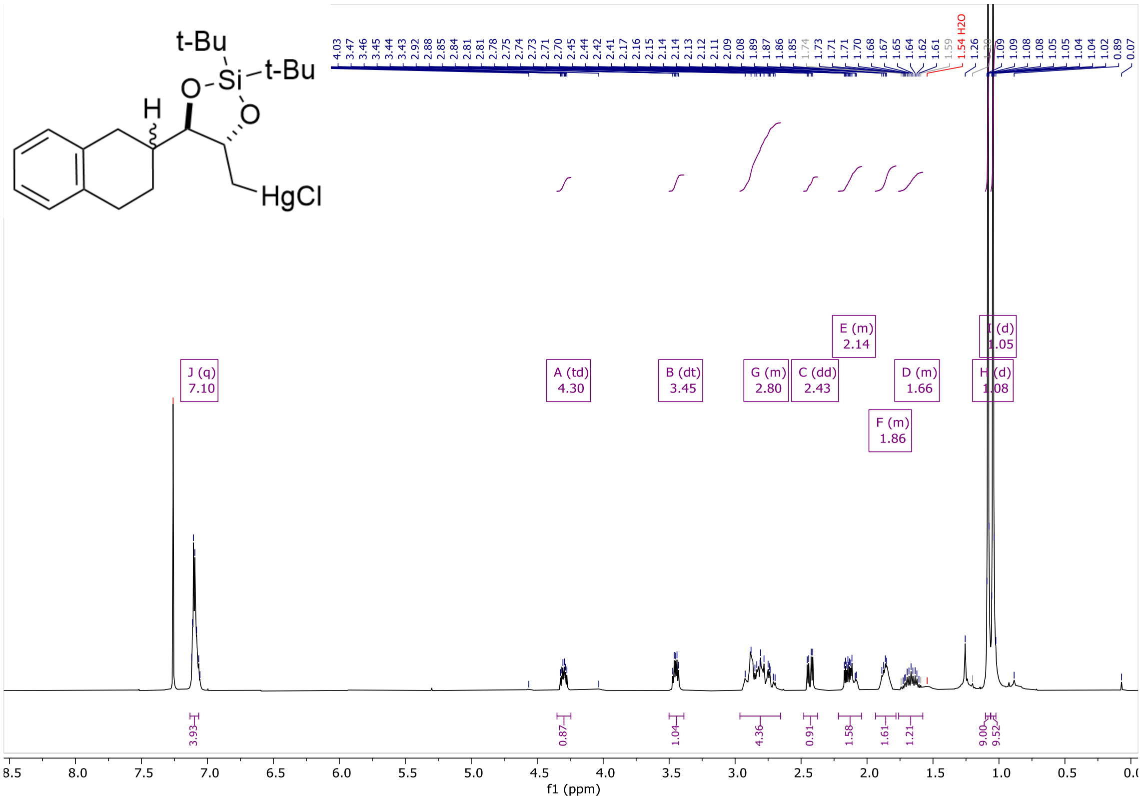


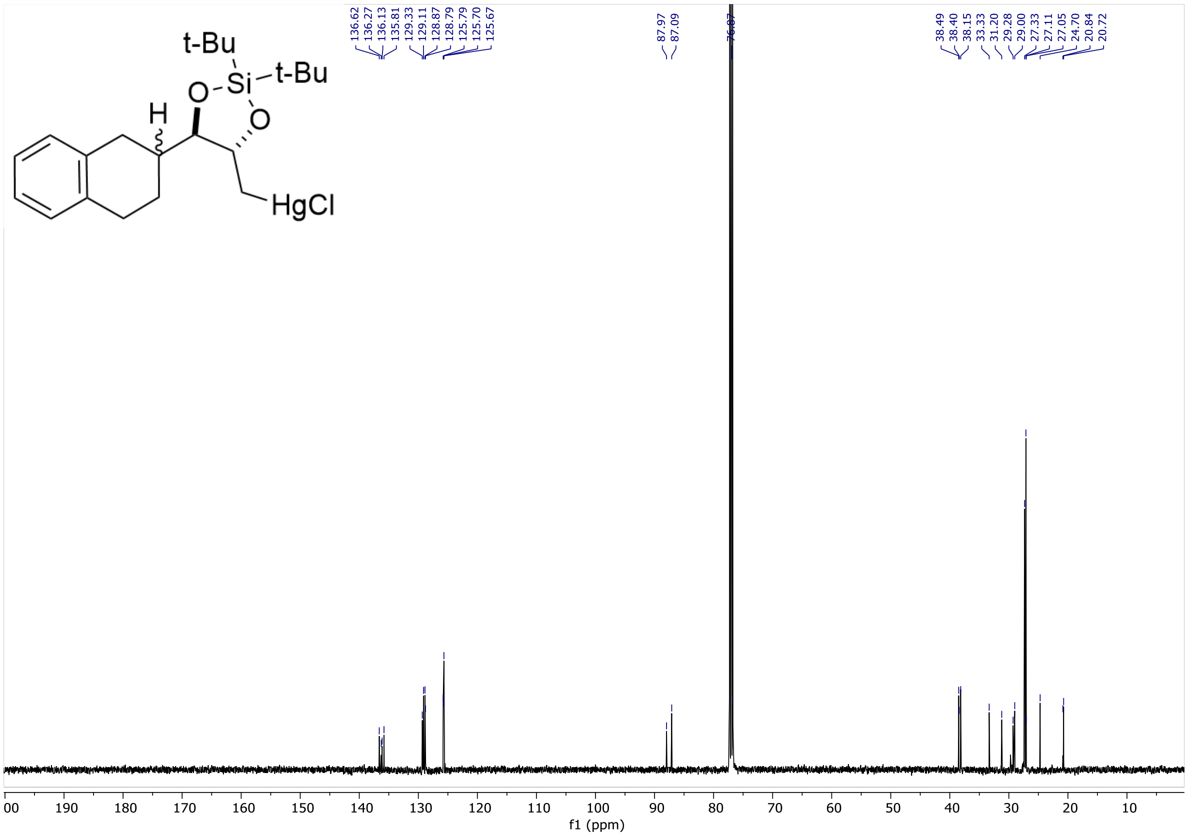
Compound 59 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



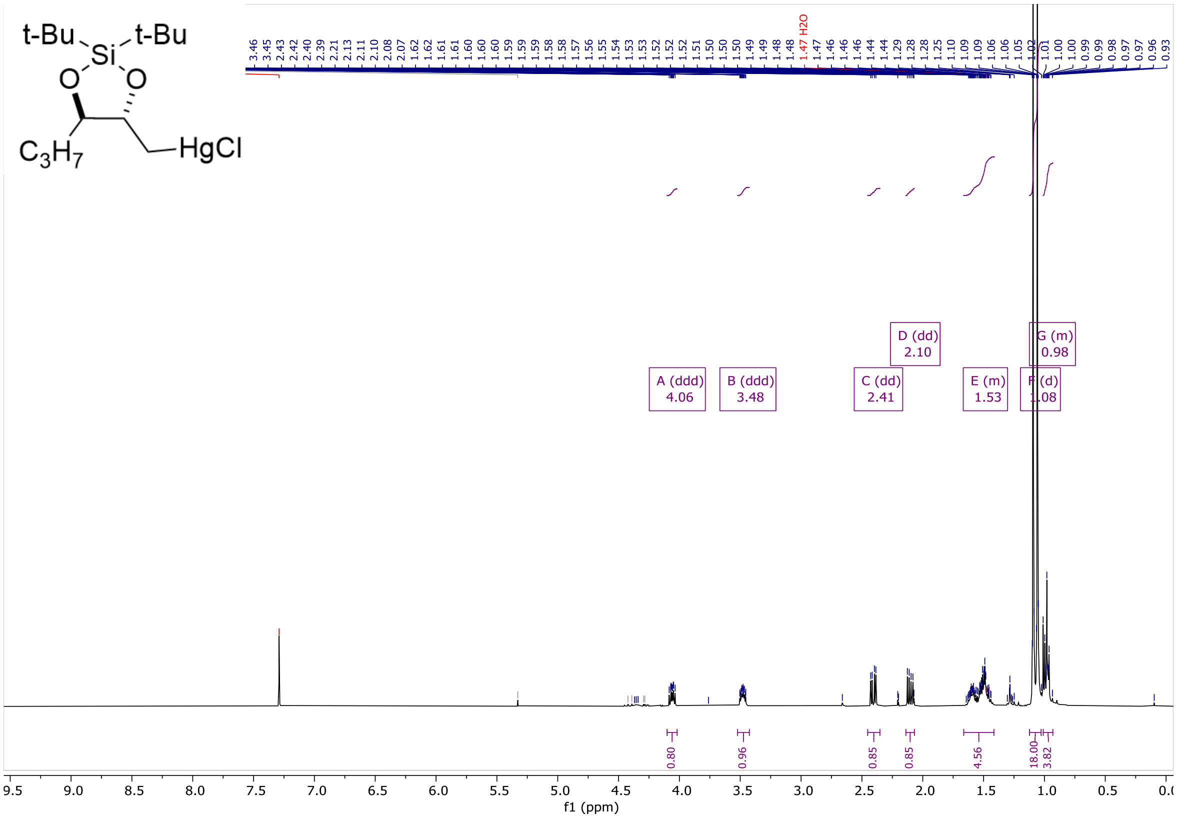


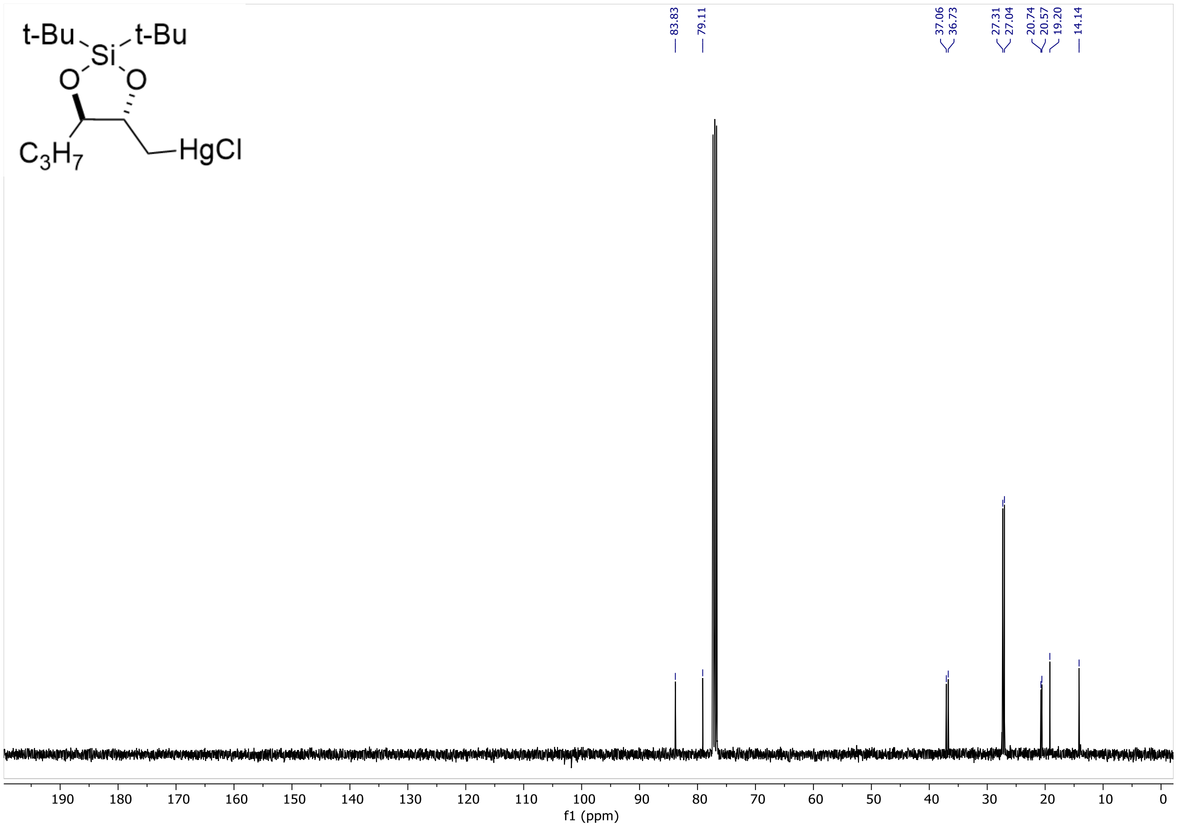
Compound 60 (^{1}H NMR: 600 MHz, ^{13}C{^{1}H} NMR: 125 MHz)



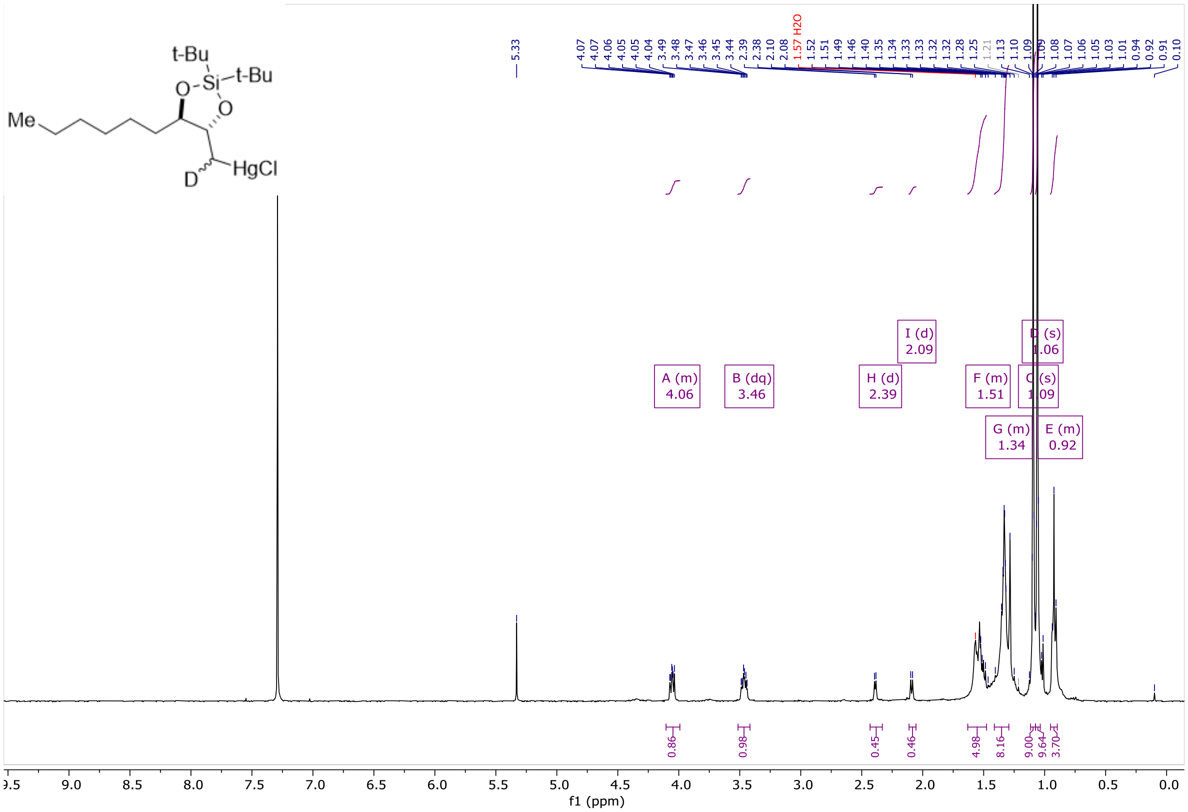


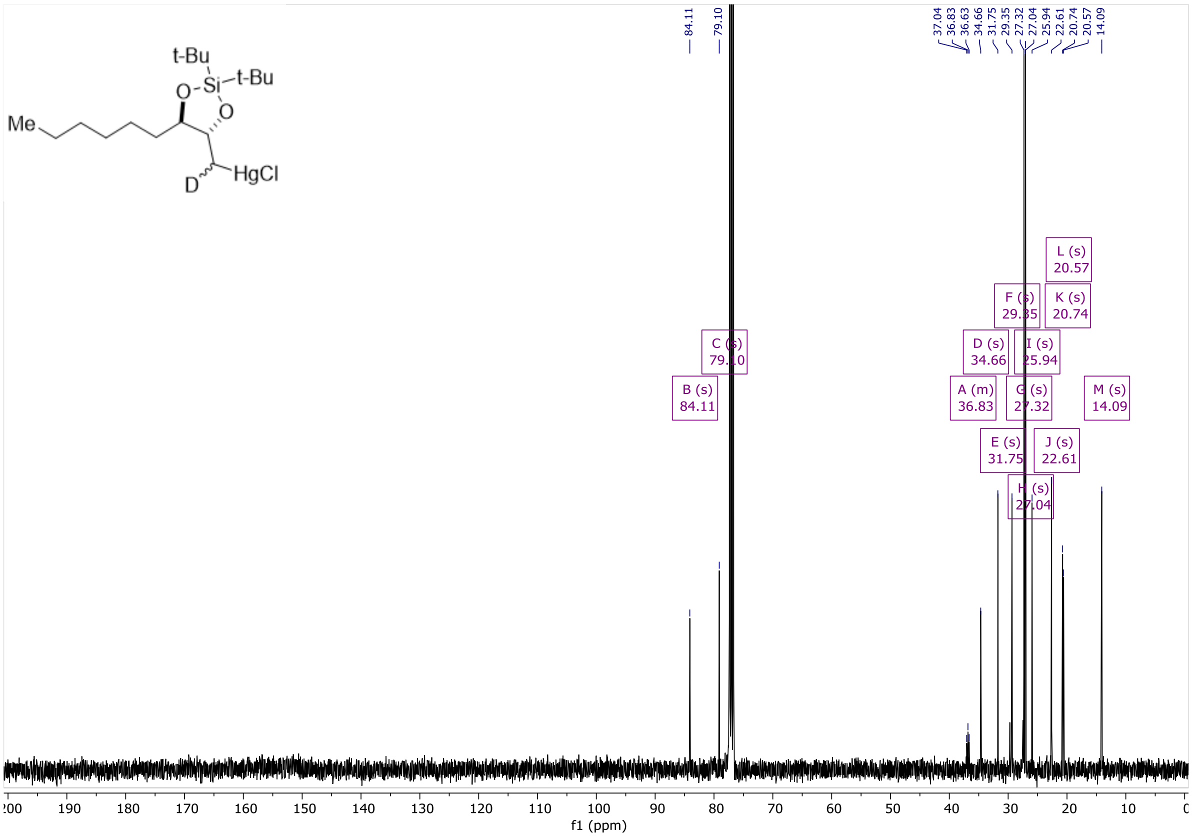
Compound 61 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)



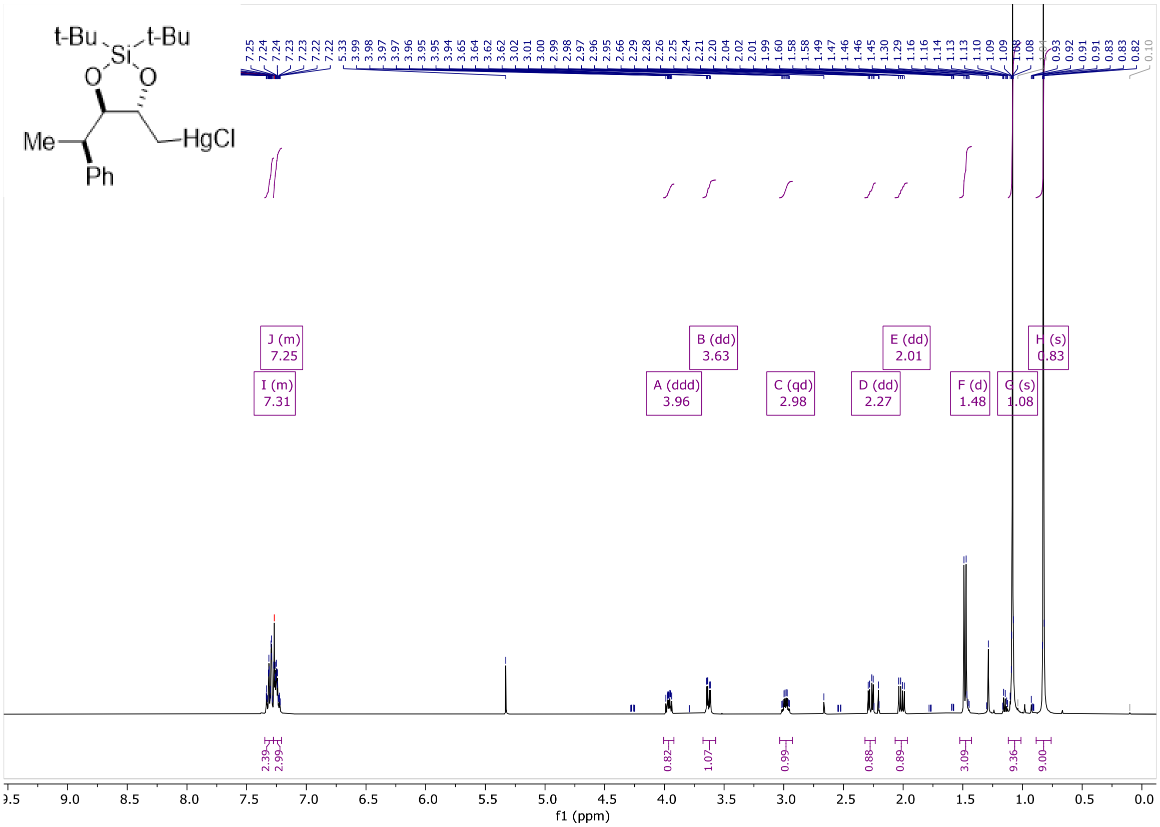


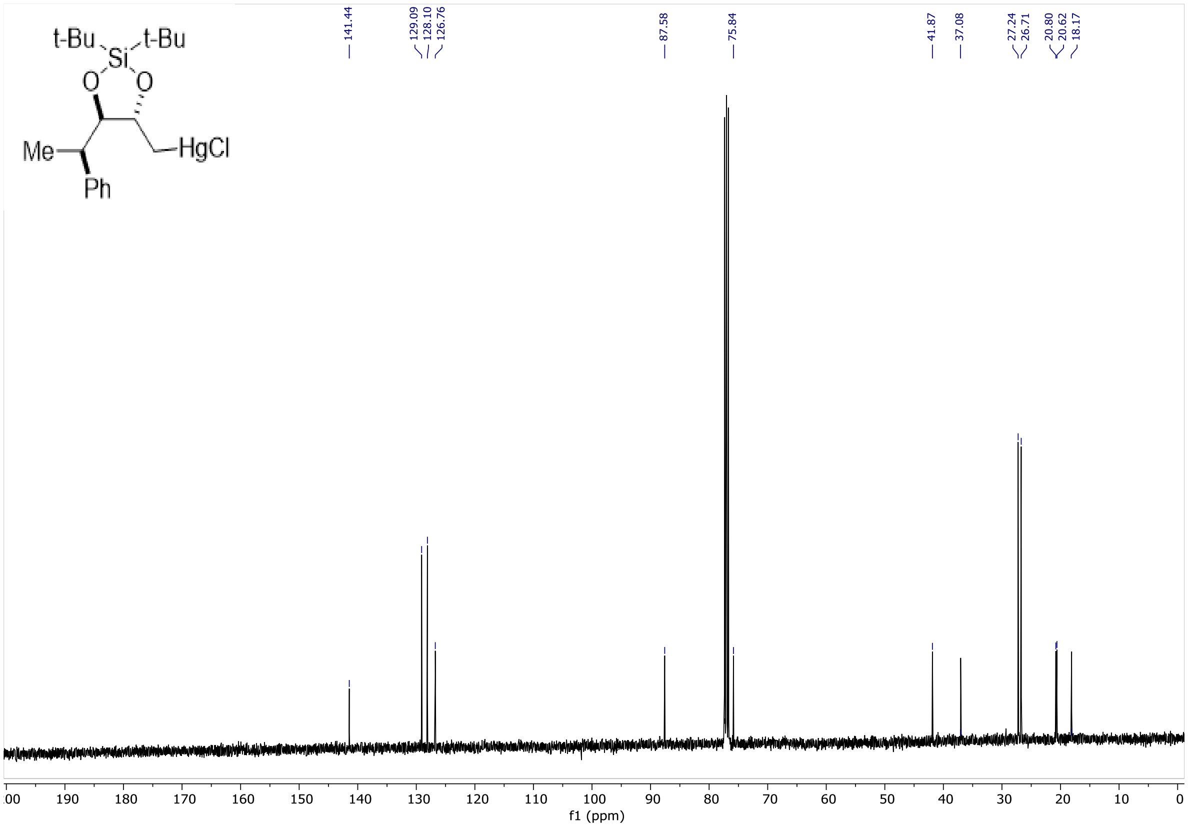
Compound 62 (^{1}H NMR: 400 MHz, $^{13}C\{^{1}H\}$ NMR: 100 MHz)



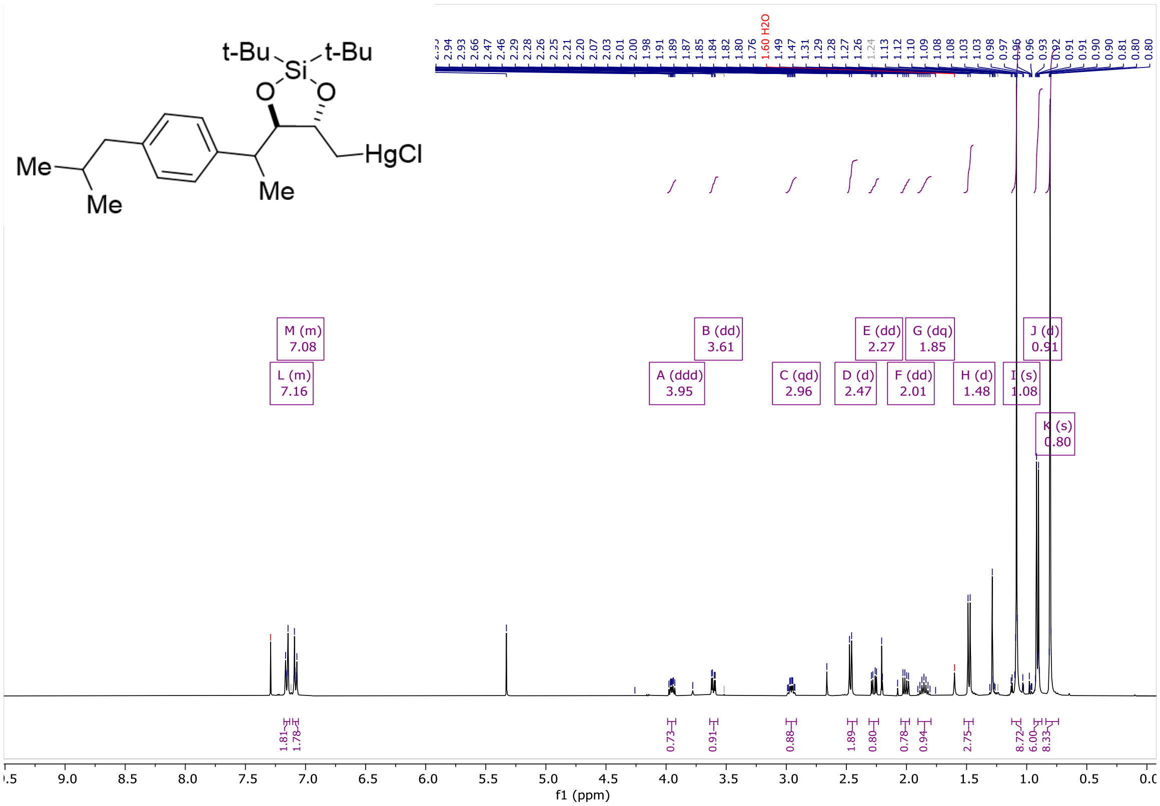


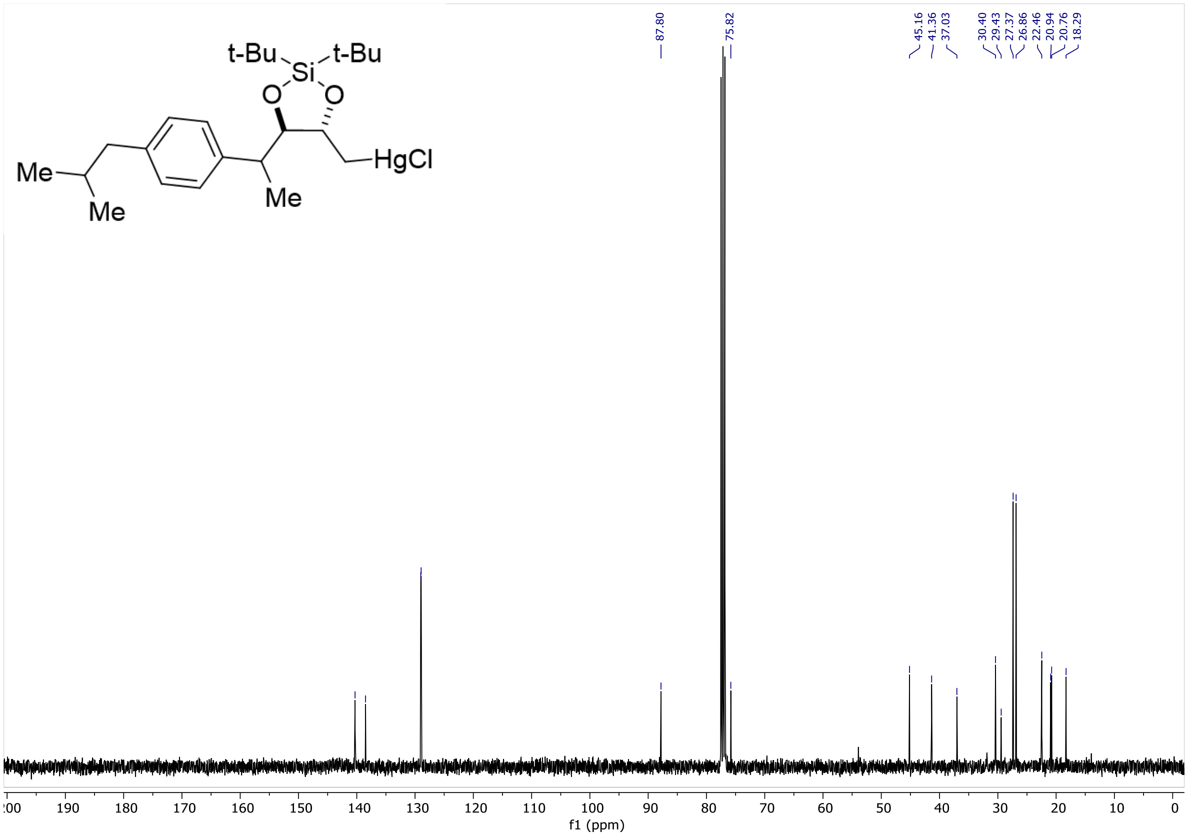
Compound 63 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)





Compound 64 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)





Compound 66 (^{1}H NMR: 400 MHz, ^{13}C{^{1}H} NMR: 100 MHz)