Supporting Information

A Direct, Versatile Route to Functionalized Trialkoxysilanes.

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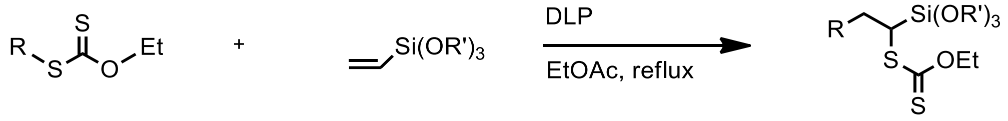
Contents :

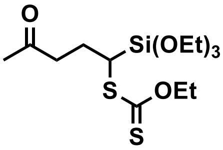
General experimental methods: All reactions requiring anhydrous conditions were conducted under an inert atmosphere. Reactions were monitored by TLC, using plates pre-coated with a 0.25 mm layer of silica containing a fluorescent indicator. Visualization of reaction components was achieved with 254 nm light, and with anisaldehyde reagent. Column chromatography was carried out on Kieselgel 60 (40-63 μm). Petroleum ether refers to the fraction of petroleum boiling between 40 °C and 60 °C. IR spectra were recorded as solutions in CCl_4. Absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}) and only selected peaks are reported. Melting points were recorded on a Kofler hot block, and are uncorrected. ^1H and ^{13}C NMR spectra of compounds were recorded in $CDCl_3$ at 25 °C. Chemical shifts (δ_H, δ_C) are quoted in parts per million (ppm) and are referenced to the residual solvent peak ($CDCl_3$: δ_H = 7.27 and δ_C = 77.14). Coupling constants (*J*) are given in Hz, multiplicities are given as multiplet (m), singlet (s), doublet (d), triplet (t), quartet (q), or broad (br). DEPT were use to aid spectral assignments. Low-resolution mass spectra (*m/z*) were recorded using HP 5989B, JMS-GCmateII and Micromass Autospec mass spectrometers and only report molecular species (M^+, $[M+H]^+$, $[M+NH_4]^+$, $[M+Na]^+$) and other major fragments, with intensities quoted as percentages of the base peak. High-resolution mass spectra were recorded by electron impact ionization (EI) on a JMS-GCmateII mass spectrometer. The quoted masses are accurate to ± 5 ppm. DLP corresponds to di-lauroyl peroxide (often sold under lauroyl peroxide or laurox).

General procedure



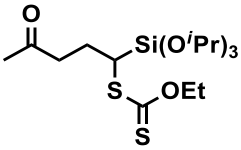
A magnetically stirred solution of xanthate derivative (1 equiv) and olefin (2 equiv) in ethyl acetate (1 mL/mmol of xanthate) was refluxed for 10 min. Dilauroyl peroxide (DLP) (5 or 10 mol%) was added every 60 min until total consumption of the xanthate. The mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to yield the desired compounds.

Compound 6a



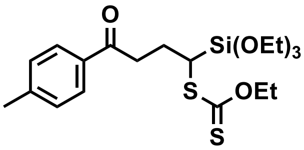
The radical addition was realized on 0.6 mmol of xanthate and 1.44 mmol of vinyl tri-ethoxysilane in ethyl acetate (1.2 mL) and 10% of DLP. The adduct **6a** was isolated as a colorless oil in 46% yield after purification on a silica gel column using petroleum ether/ ethyl acetate as the eluent (9:1). δ_H(400 MHz, $CDCl_3$) 4.64 (q, 2H, *J* = 7.9 Hz), 3.85 (q, 6H, *J* = 7.0 Hz), 3.32 (dd, 1H, *J* = 8.0, 5.2 Hz), 2.60-2.53 (m, 2H), 2.22-2.13 (m, 1H), 2.11 (s, 3H), 1.90-1.81 (1H, m), 1.41 (t, 3H, *J* = 7.0 Hz), 1.22 (t, 9H, *J* = 7.0 Hz). δ_C(100 MHz, $CDCl_3$) 215.8, 208.0, 70.3, 59.1, 41.5, 32.1, 29.8, 24.6, 18.0, 13.7. (ν_{max}/cm^{-1}, CH_2Cl_2) 3060, 2990, 1735, 1440, 1270. HRMS (EI) calcd for $C_{12}H_{22}O_4S_2Si$ [M-EtOH]$^{+\cdot}$ 322.0729, found 322.0734.

Compound 6b



The radical addition was realized on 0.3 mmol of xanthate and 0.6 mmol of vinyl tri-isopropylsilane in ethyl acetate (0.4 mL) and 15% of DLP. The adduct **6b** was isolated as a colorless oil in 73% yield yield after purification on a silica gel column using petroleum ether/ ethyl acetate as the eluent (9:1). δ_H(400 MHz, $CDCl_3$) 4.65 (q, 2H, *J* = 7.3 Hz), 4.26 (m, 3H), 3.26 (dd, 1H, *J* = 7.6, 5.2 Hz), 2.71-2.55 (m, 2H), 2.22-2,13 (m, 1H), 2.11 (s, 3H), 1.91-1.82 (m, 1H), 1.42 (t, 3H, *J* = 7.3 Hz), 1.19 (d, 9H, *J* = 6.2 Hz), 1.18 (d, 9H, *J* = 6.2 Hz). δ_C(100 MHz, $CDCl_3$) 216.3, 208.4, 70.2, 65.9, 41.7, 33.0, 29.8, 25.4, 25.3, 25.0, 13.7. (ν_{max}/cm^{-1}, CH_2Cl_2) 3060, 2990, 1715, 1465, 1440. HRMS (EI) calcd for $C_{14}H_{26}O_4S_2Si$ [M-^{i}PrOH]$^{+\cdot}$ 350.1042, found 350.1059.

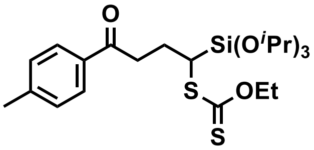
Compound 6c



The radical addition was realized on 0.4 mmol of xanthate and 0.8 mmol of vinyl tri-ethoxysilane in ethyl acetate (0.4mL) and 20% of DLP. The adduct **6c** was isolated as a colorless oil in 46% yield after purification on a silica gel column using petroleum ether/ ethyl acetate as the eluent (9:1). δ_H(400 MHz, $CDCl_3$) 7.85 (d, 2H, *J* = 8.0 Hz), 7.24 (d, 2H, *J* = 8.0 Hz), 4.67-4.53 (m, 2H), 3.89 (q, 6H, *J* = 8.0 Hz), 3.45 (dd, 1H, *J* = 8.0, 4.0 Hz), 3.24-3.06 (m, 2H), 2.40 (s, 3H), 2.38-2.31 (m, 1H), 2.09-2.01 (m, 1H), 1.38 (t, 3H, *J* = 7.2 Hz), 1.24 (t, 9H, *J* = 7.2

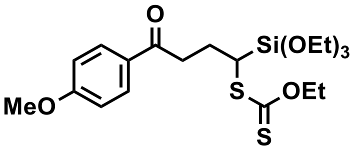
Hz). δ_C(100 MHz, $CDCl_3$) 215.6, 199.3, 143.5, 134.4, 129.1, 128.1, 70.4, 59.2, 36.6, 32.4, 25.5, 21.5, 18.2, 13.7. (ν_{max}/cm^{-1}, CH_2Cl_2) 3054, 2990, 1680, 1600, 1440, 1260. HRMS (EI) calcd for $C_{18}H_{26}O_4S_2Si$ [M-EtOH]$^{+\cdot}$ 398.1042, found 398.1041.

Compound 6d



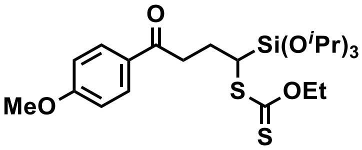
The radical addition was realized on 0.2 mmol of xanthate and 0.6 mmol of vinyl tri-isopropylsilane in ethyl acetate (0.4 mL) and 25% of DLP. The adduct **6d** was isolated as a colorless oil in 79% yield after purification on a silica gel column using petroleum ether/ ethyl acetate as the eluent (9:1). δ_H(400 MHz, $CDCl_3$) 7.86 (d, 2H, J = 8.0 Hz), 7.24 (d, 2H, J = 8.0 Hz), 4.68-4.53 (m, 2H), 4.28 (m, 3H), 3.37 (dd, 1H, J = 7.6, 5.2 Hz), 3.25-3.07 (m, 2H), 2.40 (s, 3H), 2.38-2.31 (m, 1H), 2.09-2.00 (m, 1H), 1.38 (t, 3H, J = 7.2 Hz), 1.21 (d, 9H, J = 6.0 Hz), 1.20 (d, 9H, J = 6.0 Hz). δ_C(100 MHz, $CDCl_3$) 216.2, 199.6, 143.5, 134.5, 129.1, 128.1, 70.2, 66.0, 36.8, 33.3, 25.9, 25.5, 25.4, 21.6, 13.8. (ν_{max}/cm^{-1}, CH_2Cl_2) 3065, 2980, 2930, 2870, 1680, 1610, 1430, 1280. HRMS (EI) calcd for $C_{20}H_{30}O_4S_2Si$ [M-^{i}PrOH]$^{+\cdot}$426.1355, found 426.1352.

Compound 6e



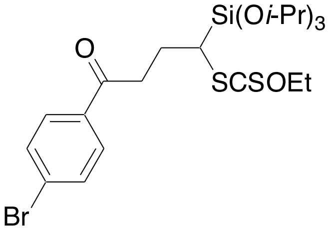
The radical addition was realized on 0.2 mmol of xanthate and 0.4 mmol of vinyl tri-ethoxysilane in ethyl acetate (0.4mL) and 30% of DLP. The adduct **6d** was isolated as a colorless oil in 33% yield after purification on a silica gel column using petroleum ether/ ethyl acetate as the eluent (9:1). δ_H(400 MHz, $CDCl_3$) 7.33 (d, 2H, J = 9.2 Hz), 6.92 (d, 2H, J = 9.2 Hz), 4.68-4.53 (m, 2H), 3.91-3.82 (m, 6H), 3.44 (dd, 1H, J = 7.8, 5.2 Hz), 3.17-3.08 (m, 2H), 2.39-2.30 (m, 1H), 2.09-1.99 (m, 1H), 1.39 (t, 3H, J = 7.2 Hz), 1.24 (t, 9H, J = 7.0). δ_C(100 MHz, $CDCl_3$) 215.7, 198.3, 163.2, 130.2, 130.0, 113.6, 70.4, 59.2, 55.4, 36.4, 32.4, 25.7, 18.2, 13.7. (ν_{max}/cm^{-1}, CH_2Cl_2) 3055, 2990, 2890, 1690. HRMS (EI) calcd for $C_{18}H_{26}O_5S_2Si$ [M-EtOH]$^{+\cdot}$ 414.0991, found 414.0996.

Compound 6f



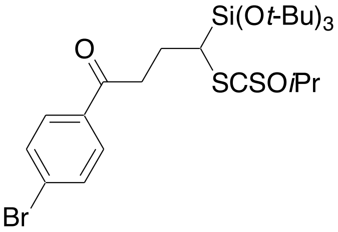
The radical addition was realized on 0.2 mmol of xanthate and 0.6 mmol of vinyl tri-isopropylsilane in ethyl acetate (0.4 mL) and 20% of DLP. The adduct **6f** isolated as a colorless oil in 62% yield after purification on a silica gel column using petroleum ether/ ethyl acetate as the eluent (9:1). δ_H(400 MHz, $CDCl_3$) 7.93 (d, 2H, *J* = 8.8 Hz), 6.91 (d, 2H, *J* = 8.8 Hz), 4.67-4.52 (m, 2H), 4.28 (m, 3H), 3.86 (s, 3H), 3,36 (dd, 1H, J = 7.6, 8.0 Hz), 3.21-3.04 (m, 2H), 2.37-2.28 (m, 1H), 2.08-2.00 (m, 1H), 1.38 (t, 3H, *J* = 7.2), 1.21 (d, 9H, *J* = 6.0 Hz), 1.20 (d, 9H, *J* = 6.0 Hz). δ_C(100 MHz, $CDCl_3$) 216.1, 198.5, 163.2, 130.2, 130.0, 113.5, 70.2, 66.0, 554, 36.6, 33.3, 25.9, 25.5, 25.4, 13.7. (ν_{max}/cm^{-1}, CH_2Cl_2) 3054, 2990, 2930, 1675, 1600, 1440, 1240. HRMS (EI) calcd for $C_{23}H_{38}O_6S_2Si$ 502.1879 $[M]^+$ found 502.1880. HRMS (EI) calcd for $C_{20}H_{30}O_5S_2Si$ [M-^{i}PrOH]$^{+\cdot}$ 442.1304, found 442.1316

Compound 6g



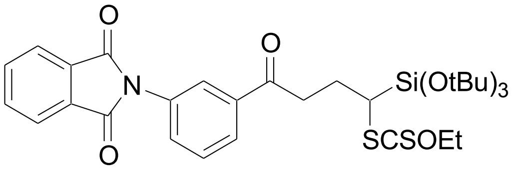
The radical addition was realized on 1 mmol of xanthate and 2 mmol of vinyl triisopropylsilane in ethyl acetate (1 mL) and 20% of DLP. The adduct **6g** was isolated as a colorless oil in 65% yield after purification on a silica gel column using petroleum ether/ diethyl ether as a gradient of elution (10:0 to 95:5). δ_H(400 MHz, $CDCl_3$) 7.83 (d, 2H, J=8.6Hz, 2CHAr), 7.59 (d, 2H, J=8.6Hz, 2CHAr), 4.61 (m, 2H, OCH_2CH_3), 4.29 (m, 3H, 3CHO), 3.37 (dd, 1H, J=5.2Hz, J=7.3Hz, CHS), 3.20 (m, 1H, C*H*HCO), 3.10 (m, 1H, CH*H*CO), 2.34 (m, 1H, C*H*HCHS), 2.05 (m, 1H, CH*H*CHS), 1.40 (t, 3H, J=7.1Hz, OCH_2CH_3), 1.21 (d, 9H, J=6.0Hz, $3CH_3$), 1.20 (d, 9H, J=6.1Hz, $3CH_3$). δ_C(100 MHz, $CDCl_3$) 216.3 (CS), 199.0 (ArCO), 135.7 (CqAr), 131.9 (2CHAr), 129.7 (2CHAr), 128.1 (CqAr), 70.5 (OCH_2), 66.2 (3CHO), 36.9 (CHS), 33.3 (CH_2CO), 25.7 (CH_2), 25.6, 25.5 ($6CH_3$), 13.9 (CH_3CH_2O). (ν_{max}/cm^{-1}, CCl_4) 1691 (OCO), 1220 (COS), 1049 (CS). m/z (CI, NH_3) 492, 494 (MH^+). HRMS (EI) calcd for $C_{19}H_{27}BrO_4S_2Si$ $(M-C_3H_8O)^{+\cdot}$ 490.0303; found 490.0312.

Compound 6h



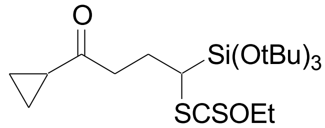
The radical addition was realized on 1 mmol of xanthate and 2 mmol of vinyl tri-*t*-butoxysilane in ethyl acetate (1 mL) and 15% of DLP. The adduct **6h** was isolated as a colorless oil in 88% yield after purification on a silica gel column using petroleum ether/diethyl ether as a gradient of elution (10:0 to 95:5). δ_H(400 MHz, $CDCl_3$) 7.82 (d, 1H, J=8.6Hz, 2CHAr), 7.58 (d, 1H, J=8.5Hz, 2CHAr), 5.75 (m, 1H, $OC\mathit{H}Me_2$), 3.23 (dd, 1H, J=4.4Hz, J=7.7Hz, CHS), 3.17 (m, 2H, CH_2CO), 2.37 (m, 1H, C*H*HCHS), 2.02 (m, 1H, CH*H*CHS), 1.37 (d, 3H, J=6.1Hz, CH_3), 1.35 (s, 27H, $3Me_3$), 1.33 (d, 3H, J=6.3H, CH_3). δ_C(100 MHz, $CDCl_3$) 216.3 (CS), 199.3 (ArCO), 135.9 (CqAr), 131.9 (2CHAr), 129.7 (2CHAr), 127.9 (CqAr), 78.0 ($O\mathit{C}HMe_2$), 73.9 (3SiOCq), 36.9 (CHS), 35.3 ($\mathit{C}H_2CO$), 31.8 ($3Me_3$), 26.1 (CH_2), 21.4, 21.3 ($2CH_3$). HRMS (EI) calcd for $C_{22}H_{33}BrO_4S_2Si$ $(M-C_4H_{10}O)^{+\cdot}$ 532.0773; found 532.0779.

Compound 6i



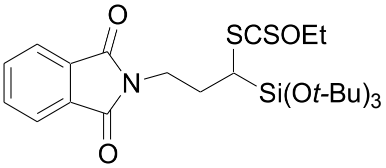
The radical addition was realized on 0.65 mmol of xanthate and 1.3 mmol of vinyl tri-*t*-butoxysilane in ethyl acetate (0.65 mL) and 1,2-dichloroethane (0.15 mL) and 10% of DLP. The adduct **6i** was isolated as a colorless oil in 90% yield after purification on a silica gel column using pentane/ethyl acetate as a gradient of elution (10:0 to 85:15). δ_H(400 MHz, $CDCl_3$) 8.05 (bs, 1H, CHAr), 7.98 (m, 3H, 3CHAr), 7.82 (m, 2H, 2CHAr), 7.61 (m, 2H, 2CHAr), 4.64 (m, 1H, $OC\mathit{H}HCH_3$), 4.53 (m, 1H, $OCH\mathit{H}CH_3$), 3.24 (m, 3H, CHS, CH_2CO), 2.42 (m, 1H, C*H*HCHS), 2.05 (m, 1H, , CH*H*CHS), 1.37, 1.35 (t, J=7.1Hz , +bs, 30H, OCH_2CH_3 + $9CH_3$). δ_C(100 MHz, $CDCl_3$) 216.9 (CS), 199.1 (Ar*C*O), 167.0 (2NCO), 138.1 (CqAr), 134.7 (2CHAr), 132.3 (2CqAr), 131.7 (CqAr), 130.8, 129.4, 127.6, 126.3 (4CHAr), 123.9 (2CHAr), 73.9 (3SiOCq), 70.2 ($O\mathit{C}H_2CH_3$), 36.9, 35.5 (CHS, CH_2), 31.8 ($9CH_3$), 25.9 (CH_2), 13.9 ($OCH_2\mathit{C}H_3$). (ν_{max}/cm^{-1}, CCl_4) 1782 (NCO), 1727 (NCO), 1694 (ArCO), 1388, 1366, 1211 (COS), 1066 (CS). HRMS (EI) calcd for $C_{33}H_{45}O_7NS_2Si$ 659.2407; found 659.2427.

Compound 6j



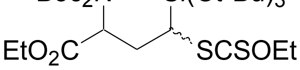
The radical addition was realized on 1.22 mmol of xanthate and 1.3 mmol of vinyl tri-*t*-butoxysilane in ethyl acetate (1.22 mL) and 10% of DLP. The adduct **6j** was isolated as a colorless oil in 75% yield after purification on a silica gel column using petroleum ether/diethyl ether as the gradient of elution (98:2 to 95:5). δ_H(400 MHz, $CDCl_3$) 4.66 (m, 2H, $OC\mathit{H}_2CH_3$), 3.14 (dd, 1H, J=4.4Hz, J=7.7Hz, CHS), 2.78 (m, 2H, CH_2CO), 2.23 (m, 1H, $C\mathit{H}HCHS$), 1.89 (m, 2H, $CH\mathit{H}CHS$, CHCO), 1.42 (t, 3H, J=7.1Hz, $OCH_2C\mathit{H}_3$), 1.33 (bs, 27H, $9CH_3$), 0.99 (m, 2H, CH_2), 0.83 (m, 2H, CH_2). δ_C(100 MHz, $CDCl_3$) 217.2 (CS), 211.0 (CO), 73.9 (3SiOCq), 70.1 ($O\mathit{C}H_2CH_3$), 41.5 (CH_2CO), 35.5 (CHS), 31.8 ($9CH_3$), 25.6 (CH_2), 20.5 (CHCO), 14.0 ($OCH_2\mathit{C}H_3$), 10.6, 10.5 ($2CH_2$). (ν_{max}/cm^{-1}, CCl_4) 1702 (CO), 1241 (COS), 1066 (CS). HRMS (EI) calcd for $C_{22}H_{42}O_5S_2Si$ 478.2243; found 478.2244.

Compound 6k



The radical addition was realized on 1 mmol of xanthate and 2 mmol of vinyl tri-*t*-butoxysilane in ethyl acetate (1 mL) and 10% of DLP. The adduct **6k** was isolated as white crystals in 82% yield after purification on a silica gel column using petroleum ether/ethyl acetate as a gradient of elution (10:0 to 9:1). Mp 96-98°C. δ_H(400 MHz, $CDCl_3$) 7.82 (m, 2H, 2CHPhth), 7.68 (m, 2H, 2CHPhth), 4.65 (m, 2H, $OC\mathit{H}_2CH_3$), 3.93 (ddd, 1H, J=5.5Hz, J=11.2Hz, J=13.2Hz, NCH_2), 3.82 (ddd, 1H, J=4.9Hz, J=11.2Hz, J=13.3Hz, NCH_2), 3.14 (dd, 1H, J=4.8Hz, J=7.7Hz, CHS), 2.27 (m, 1H, $C\mathit{H}HCHS$), 1.98 (m, 1H, $CH\mathit{H}CHS$), 1.41 (t, 3H, J=7.1Hz, OCH_2CH_3), 1.35 (bs, 27H, $9CH_3$). δ_C(100 MHz, $CDCl_3$) 217.1 (CS), 168.3 (2NCO), 133.8 (2CHPhth), 132.4 (2CqPhth), 123.2 (2CHPhth), 74.0 (3SiOCq), 70.2 ($O\mathit{C}H_2CH_3$), 37.15 (NCH_2), 33.8 (CHS), 31.8 ($9CH_3$), 30.8 (CH_2), 13.9 ($OCH_2\mathit{C}H_3$). (ν_{max}/cm^{-1}, CCl_4) 1775, 1717 (NCO), 1241, (COS), 1027 (CS). HRMS (EI) calcd for $C_{26}H_{41}O_6NS_2Si$ 555.2145 ; found 555.2158.

Compound 6l

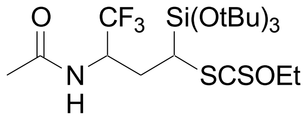


The radical addition was realized on 1 mmol of xanthate and 2 mmol of vinyl tri-*t*-butoxysilane in ethyl acetate (1 mL) and 35% of DLP. The ratio of the two diastereoisomer was evaluated to 2 : 1 in NMR spectrum. After purification on a silica gel column using petroleum ether/diethyl ether as a gradient of elution (10:0 to 9:1), we isolated 0.15g of a pure diastereoisomer and 0.23g of a mixture of the two diastereoisomers. The adduct **6l** was isolated as a colorless oil in 54% yield.

Major diastereoisomer. δ_H(400 MHz, $CDCl_3$) 5.17 (dd, 1H, J=3.7Hz, J=10.1Hz, CHN), 4.58 (m, 2H, OCH_2CH_3), 4.14 (q, 2H, J=7.2Hz, $CO_2CH_2CH_3$), 3.06 (dd, 1H, J=3.3Hz, J=13.2Hz, CHS), 2.57 (m, 1H, CHHCHS), 2.30 (m, 1H, CHHCHS), 1.47 (bs, 18H, $2NCO_2tBu$), 1.40 (t, 3H, J=7.1Hz, OCH_2CH_3), 1.31 (s, 27H, $9CH_3$), 1.21 (t, 3H, J=7.2Hz, $CO_2CH_2CH_3$). δ_C(100 MHz, $CDCl_3$) 214.5 (CS), 171.4 (CO_2), 152.6 (2NCO), 82.7 ($2CqCO_2CMe_3$), 73.7 (3SiOCq), 69.7 (OCH_2CH_3), 61.1 ($CO_2CH_2CH_3$), 57.2 ($CHCO_2CH_2CH_3$), 32.2 (CHS), 31.8 ($9CH_3$), 29.4 (CH_2), 28.1 ($6CH_3$), 14.2, 13.7 (OCH_2CH_3, $CO_2CH_2CH_3$).

Minor diastereoisomer 4.96 (dd, 1H, J=3.0Hz, J=8.6Hz, CHN), 4.60 (m, 2H, OCH_2CH_3), 4.18 (q, 2H, J=7.2Hz, J=14.6Hz, $CO_2CH_2CH_3$), 3.37 (dd, 1H, J=3.3Hz, J=12.1Hz, CHS), 3.05 (m, 2H, CH_2CHS), 1.48 (bs, 18H, $2CO_2tBu$), 1.37 (t, 3H, J=7.2Hz, OCH_2CH_3), 1.33 (s, 27H, $9CH_3$), 1.27 (t, 3H, J=7.1Hz, $CO_2CH_2CH_3$). δ_C(100 MHz, $CDCl_3$) 217.0 (CS), 170.8 (CO_2), 152.5 (2NCO), 82.9 ($2CqCO_2CMe_3$), 73.7 (SiOCq), 69.9 (OCH_2CH_3), 61.0 ($CO_2CH_2CH_3$), 57.0 ($CHCO_2CH_2CH_3$), 34.6 (CHS), 32.1 (CH_2), 31.8 ($9CH_3$), 28.0 (6CH), 14.3, 13.8 (OCH_2CH_3, $CO_2CH_2CH_3$). (ν_{max}/cm^{-1}, CCl_4) 1744, 1702 (CO), 1241 (COS), 1046 (CS). HRMS (EI) calcd for $C_{31}H_{59}O_{10}NS_2Si$ 697.3349 ; found 697.3346.

Compound 6m



The radical addition was realized on 1. mmol of xanthate and 2 mmol of vinyl tri-*t*-butoxysilane in ethyl acetate (1 mL) and 20% of DLP. Adduct **6m** was isolated as a 2:3 mixture of two diastereoisomers and as white solids in 60% yield after purification on a silica gel column using pentane/diethyl ether as the gradient of elution (10:0 to7:3).

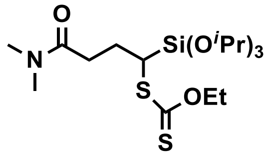
Major isomer (0.194 g) Mp 104-105°C (pentane) δ_H(400 MHz, $CDCl_3$) 6.19 (d, 1H, J=8.4Hz, NH), 5.03 (m, 1H, $CHCF_3$), 4.66 (m, 2H, OCH_2CH_3), 2.89 (dd, 1H, J=2.7Hz, J=10.8Hz, CHS), 2.41 (ddd, 1H, J=2.6Hz, J=10.8Hz, J=13.8Hz, CHHCHS), 2.11 (s, 3H, $COCH_3$), 1.72 (ddd, 1H, J=2.8Hz, J=12.0Hz, J=14.5Hz, CHHCHS), 1.44 (t, 3H, J=7.1Hz, OCH_2CH_3), 1.35 (bs, 27H, $9CH_3$). δ_C(100 MHz, $CDCl_3$) 218.3 (CS), 170.2 (NCO), 125.3 (q, J=282Hz, CF_3) 74.6 (3SiOCq), 70.8

(OCH_2CH_3), 49.9 (q, J=30.1Hz, $CHCF_3$), 31.8 ($9CH_3$), 31.3, 31.0 (CHS, CH_2), 23.3 ($COCH_3$), 13.9 (OCH_2CH_3).

Minor isomer (0.126 g) Mp 151-152°C (pentane:diethyl ether). δ_H(400 MHz, $CDCl_3$) 5.92 (d, 1H, J=8.7Hz, NH), 4.84 (m, 1H, $CHCF_3$), 4.67 (m, 2H, OCH_2CH_3), 3.14 (dd, 1H, J=4.3Hz, J=7.6Hz, CHS), 2.23 (ddd, 1H, J=4.3Hz, J=11.2Hz, J=15.3Hz, *CH*HCHS), 2.06 (m, 1H, CH*H*CHS), 2.02 (s, 3H, $COCH_3$), 1.41 (t, 3H, J=7.1Hz, OCH_2CH_3), 1.35 (s, 27H, $9CH_3$). δ_C(100 MHz, $CDCl_3$) 215.8 (CS), 169.9 (NCO), 125.4 (q, J=282Hz, CF_3), 74.5 (3SiOCq), 70.7 (OCH_2CH_3), 49.9 (q, J=29.1Hz, $CHCF_3$), 31.8 ($9CH_3$), 30.5, 29.9 (CHS, CH_2), 23.4 ($COCH_3$), 13.9 (OCH_2CH_3).

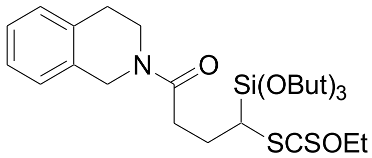
(ν_{max}/cm^{-1}, CCl_4) 3391 (NH), 1703 (NCO), 1242 (COS), 1044 (CS). HRMS (EI) calcd for $C_{21}H_{40}O_5NS_2SiF_3$ 535.2069; found 535.2077.

Compound 6n



The radical addition was realized on 0.3 mmol of xanthate and 0.75 mmol of vinyl tri-isopropylsilane in ethyl acetate (0.6 mL) and 25% of DLP. The adduct **6n** was isolated as a colorless oil in 53% yield after purification on a silica gel column using petroleum ether/ ethyl acetate as the eluent (1:1). δ_H(400 MHz, $CDCl_3$) 4.68-4.61 (m, 2H), 4.26 (m, 3H), 3.32 (dd, 1H, *J* = 7.4, 4.8 Hz), 2.97 (s, 3H), 2.92 (s, 3H), 2.57-2.43 (m, 2H), 2.27-2.21 (m, 1H), 1.99-1.91 (m, 1H), 1.41 (t, 3H, *J* = 8.0 Hz), 1.20 (d, 9H, *J* = 4.0 Hz), 1.18 (d, 9H, *J* = 4.0 Hz). δ_C(100 MHz, $CDCl_3$) 216.2, 172.4, 70.1, 65.9, 37.05, 35.2, 33.4, 31.6, 26.6, 25.4, 25.3, 13.7. (ν_{max}/cm^{-1}, CCl_4) 3055, 2970, 2932, 1712, 1639. HRMS (EI) calcd for $C_{18}H_{37}NO_5S_2Si$ $[M]^+$ 439.1882, found 439.1883; calcd for $C_{15}H_{29}NO_4S_2Si$ $[M-EtOH]^{+\cdot}$ 379.1307, found 379.1307.

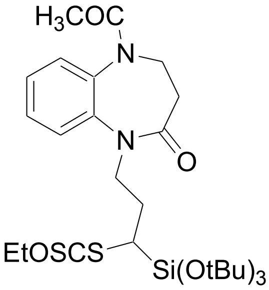
Compound 6o



The radical addition was realized on 1 mmol of xanthate and 2 mmol of vinyl tri-*t*-butoxysilane in ethyl acetate (1 mL) and 4x10% of DLP. The adduct **6o** was isolated as a colorless oil in 58% yield and after purification on a silica gel column using pentane/ethyl acetate as a gradient of elution (10:0 to 8:2). δ_H(400

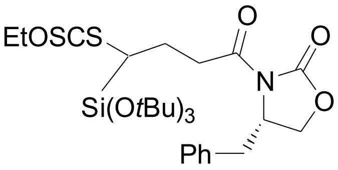
MHz, $CDCl_3$) 7.11 (m, 4H, 4CHAr), 4.61 (m, 2H, $OC\textit{H}_2CH_3$), 3.75 (m, 2H, NCH_2), 3.14 (dd, 1H, J=4.1Hz, J=7.2Hz, CHS), 2.70 (m, 4H, $2CH_2$), 2.33 (m, 1H, C*H*HCHS), 1.97 (m, 3H, CH*H*CHS, CH_2), 1.37 (t, 3H, J=7.2Hz, $OCH_2C\textit{H}_3$), 1.30 (s, 27H, $9CH_3$). δ_C(100 MHz, $CDCl_3$) 217.1 (CS), 172.8 (NCO), 139.2, 128.5, 126.1, 124.9, 124.8 (CqAr, CHAr), 73.8 (OSiCq), 69.9 ($O\textit{C}H_2CH_3$), 43.2 (m), 35.8, 33.2, 31.7, ($9CH_3$), 31.3, 27.6, 26.9, 24.2, 13.9 ($OCH_2\textit{C}H_3$). (ν_{max}/cm^{-1}, CCl_4) 1656 (NCO), 1388, 1365, 1240 (COS), 1046 (CS). HRMS (EI) calcd for $C_{28}H_{47}O_5NS_2Si$ 569.2665; found 569.2650.

Compound 6p

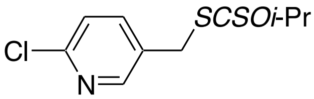


The radical addition was realized on 0.88 mmol of xanthate and 1.76 mmol of vinyl tri-*t*-butoxysilane in ethyl acetate (0.9 mL) and 1,2-dichloroethane (0.3 mL) and 10% of DLP. The adduct **6p** was isolated as a colorless oil in 76% yield after purification on a silica gel column using pentane/ethyl acetate as a gradient of elution. δ_H(400 MHz, $CDCl_3$) (mixture of rotamers) 7.45-7.24 (m, 3H, 3CHAr), 7.16 (d, 1H, J=7.8Hz, CHAr), 4.88 (dt, 1H, J=5.5Hz, J=13.8Hz, NC*H*H), 4.68 (dq, 1H, J=7.1Hz, $OC\textit{H}HCH_3$), 4.61 (m, 1H, $OCH\textit{H}CH_3$), 4.44 (dtd, 1H, J=5.1Hz, J=12.9Hz, J=17.9Hz, NCH*H*), 3.58 (m, 1H, C*H*H), 3.45 (dd, 1H, J=6.3Hz, J=12.7Hz, CH*H*), 3.04 (m, 1H, CHS), 2.48 (m, 2H), 2.13, 2.00 (2m, 1H, C*H*H), 1.83 (s, 1.5H, $COCH_3$), 1.82 (s, 1.5H, $COCH_3$), 1.83, 1.64 (2m, 1H, CH*H*), 1.44 (t, 1.5H, J=7.1Hz, $OCH_2C\textit{H}_3$), 1.38 (t, 1.5H, J=7.1Hz, $OCH_2C\textit{H}_3$), 1.29, 1.28 (2s, 27H, $9CH_3$). δ_C(100 MHz, $CDCl_3$) 217.2, 216.8 (CS), 170.5, 170.4, 170.3, 170.1 (2NCO), 140.4, 140.2 (CqAr), 135.4 (CqAr), 129.61, 129.57, 129.47, 129.39 (2CHAr), 126.97, 126.86 (CHAr), 124.2, 123.9 (CHAr), 74.0 (3SiOCq), 70.3, 70.2 ($O\textit{C}H_2CH_3$), 48.29, 45.9, 45.6, 34.1, 33.8, 33.75, 33.69, 31.8 ($9CH_3$), 30.5, 30.49, 29.7-29.22 (m), 22.76, 22.73 ($NCO\textit{C}H_3$), 14.0 ($OCH_2\textit{C}H_3$). (ν_{max}/cm^{-1}, CCl_4) 1681 (NCO), 1241 (COS), 1045 (CS). HRMS (EI) calcd for $C_{29}H_{48}O_6N_2S_2Si$ 612.2723; found 612.2721.

Compound 6q

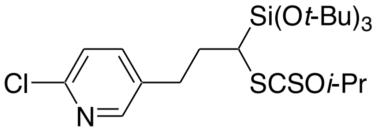


The radical addition was realized on 0.74 mmol of xanthate and 1.48 mmol of vinyl tri-*t*-butoxysilane in ethyl acetate (0.74 mL) and 10% of DLP. The adduct \$ was isolated as a colorless oil in 89% yield and as a 1:1 mixture of diastereoisomers after purification on a silica gel column using pentane/ethyl acetate as a gradient of elution (10:0 to 9:1). δ_H(400 MHz, $CDCl_3$) 7.34-7.20 (m, 5H, 5CHAr), 4.66 (m, 3H, OCH_2CH_3, CHN), 4.14 (m, 2H, CH_2OCO), 3.39-3.17 (m, 3H), 3.05 (m, 1H), 2.78 (dd, 0.5H, J=7.0Hz, J=10.9Hz), 2.73 (dd, 0.5H, J=7.3Hz, J=10.8Hz), 2.40 (m, 1H, C*H*HCHS), 1.98 (m, 1H, CH*H*CHS), 1.43, 1.42 (2t, 3H, J=7.1Hz, OCH_2CH_3), 1.36 (2s, 1H, 27H, $9CH_3$). δ_C(100 MHz, $CDCl_3$) 217.6, 217.2 (CS), 173.3 (OCO), 153.43, 153.39 (NCO), 135.7, 135.5 (CqPh), 129.5 (2CHPh), 128.9 (2CHPh), 127.3 (CHPh), 73.9 (3SiOCq), 70.2 (O*C*H_2CH_3), 66.2 (*C*H_2OCO), 55.3, 55.2 (CHN), 37.9, 35.4 (CHS, CH_2), 34.1, 33.8 (CH_2), 31.8 ($9CH_3$), 25.9, 25.8 (CH_2), 13.9 (OCH_2*C*H_3). (ν_{max}/cm^{-1}, CCl_4) 1791 (COO), 1702 (NCO), 13.81, 1365, 1211 (COS), 1066, 1046 (CS). HRMS (EI) calcd for $C_{29}H_{47}O_7NS_2Si$ 613.2563; found 613.2575.

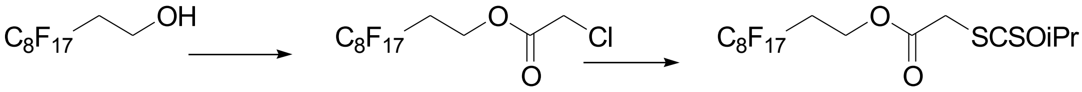


To a solution of the commercially available halogeno derivative (6.2 mmol) in acetone (12 mL) was added under nitrogen and portion-wise potassium O-isopropyl xanthogenate (6.8 mmol, 1.1 eq.). After addition of ice water, the precipitate was filtered off and dried to afford the desired xanthate as yellow crystals, which were recrystallised from diethyl ether/pentane and in 81% yield. Mp 62-63°C. δ_H(400 MHz, $CDCl_3$) 8.37 (d, 1H, J=2.5Hz, CHAr), 7.66 (dd, 1H, J=2.6Hz, J=8.2Hz, CHAr), 7.28 (d, 1H, J=8.3Hz, CHAr), 5.73 (m, 1H, CHO), 4.29 (s, 2H, CH_2S), 1.38 (s, 3H, CH_3), 1.36 (s, 3H, CH_3). δ_C(100 MHz, $CDCl_3$) 211.8 (CS), 150.4 (CqAr), 149.9 (CHAr), 139.2 (CHAr), 131.4 (CqAr), 124.1 (CHAr), 78.6 (CHO), 36.2 (CH_2S), 21.2 ($2CH_3$). (ν_{max}/cm^{-1}, CCl_4) 1587, 1563, 1461, 1375, 1235 (COS), 1139, 1109, 1092, 1043 (CS), 1022. *m/z* (CI, NH_3) 262, 264 (MH^+), HRMS (EI) calcd for C10H12NClOS$_2$ 261.0049; found 261.0048.

Compound 6r



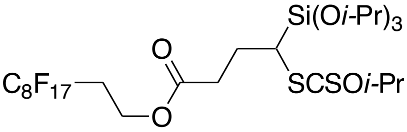
A solution of the above xanthate (1 mmol) and olefin (2 mmol) in ethyl acetate (1 mL) was refluxed under nitrogen for 10 min. Then dilauroyl peroxide (DLP) was added portion-wise (3x10 mol% and 2x5 mol%) every hour. After evaporation of the solvent, the residue was purified by silica gel column chromatography using a gradient of elution (diethyl ether/pentane, 95-5) affording the addition product as a colorless oil and in 68% yield. δ_H(400 MHz, CDCl$_3$) 8.21 (d, 1H, J=2.3Hz, CHAr), 7.46 (dd, 1H, J=2.5Hz, J=8.1Hz, CHAr),7.22 (d, 1H, J=8.1Hz, CHAr), 5.79 (m, 1H, CHO), 3.18 (dd, 1H, J=4.6Hz, J=7.2Hz, CHS), 2.85 (ddd, 1H, J=5.0Hz, J=12.0Hz, J=13.7Hz, C*H*HAr), 2.73 (ddd, 1H, J=5.3Hz, J=11.9Hz, J=13.9Hz, CH*H*Ar), 2.13 (m, 1H, C*H*HCHS), 1.89 (m, 1H, CH*H*CHS), 1.39 (d, 3H, J=6.2Hz, CH$_3$), 1.37 (d, 3H, J=6.2Hz, CH$_3$), 1.33 (s, 27H, 9CH$_3$). δ_C(100 MHz, CDCl$_3$) 216.2 (CS), 149.7 (CHAr), 148.9 (CqAr), 138.9 (CHAr), 137.2 (CqAr), 123.9 (CHAr), 78.0 (CHO), 73.9 (O*Cq*Me$_3$), 35.6, 33.9 (CHS, CH$_2$), 31.8 (9 CH$_3$), 30.5 (CH$_2$), 21.5, 21.4 (2CH$_3$). (ν_{max}/cm^{-1}, CCl$_4$) 1459, 1388, 1365, 1228 (COS), 1071, 1037 (CS). HRMS (EI) calcd for $C_{24}H_{42}NClO_4S_2Si$ 535.2013; found 535.2005.



To a solution of Foralkyl-OH-8 (43 mmol) and pyridine (86 mmol) in diethyl ether (300 mL) was added dropwise chloroacetyl chloride (1.2 equiv, 51.7 mmol) at 0°C. The reaction mixture was stirred at room temperature for 4 h, evaporated under reduced pressure and filered over a pad of silica gel with ethyl acetate as the eluent. The chloride derivative was obtained as a white solid in 90% yield. Mp 39-40°C. δ_H(400 MHz, CDCl$_3$) 4.50 (t, 2H, *J* = 8.0 Hz, CH$_2$OCO), 4.08 (s, 2H, CH$_2$Cl), 2.59-2.47 (m, 2H, *CH$_2$*CH$_2$OCO). δ_C(100 MHz, CDCl$_3$) 166.96, 57.93, 40.48, 30.43. (ν_{max}/cm^{-1}, CH$_2$Cl$_2$) 1774 , 1752 , 1558, 1555, 1242 , 1153. HRMS (EI) calcd for $C_{12}H_6F_{17}O_2$ $[M]^{+\cdot}$ 539.9785, found 539.9780.

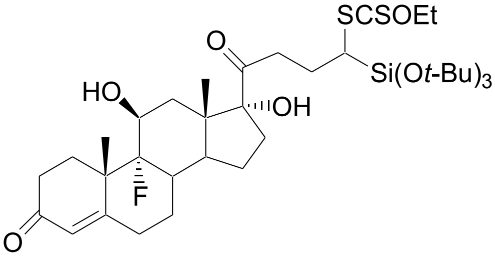
To a solution of the above chloride derivative (1.85 mmol) in acetone was added under nitrogen and portion-wise potassium O-isopropyl xanthogenate (2.03 mmol, 1.1 eq.). The pure xanthate was isolated as a white solid in 96% yield after extraction with dichloromethane and evaporation of the solvent under reduced pressure. Mp 31-32°C. δ_H(400 MHz, CDCl$_3$). 5.73 (sept., 1H, CHO), 4.47 (t, 2H, J=6.5Hz, CH$_2$O), 3.92 (s, 2H, CH$_2$S), 2.51 (m, 2H CH$_2$),1.40 (s, 3H, CH$_3$), 1.39 (s, 3H, CH$_3$). δ_C(100 MHz, CDCl$_3$) 211.7 (CS), 167.8 (CO), 79.1 (CHO), 57.7 (*CH$_2$*OCO), 37.6 (CH_2S), 30.6 (t, CH_2CH_2O). 21.3 ($2CH_3$). HRMS (EI) calcd for $C_{16}H_{13}F_{17}S_2O_3$ 640.0035; found 640.0005

Compound 6s



The radical addition was realized on 1 mmol of xanthate and 3 mmol of vinyl tri-*t*-butoxysilane in ethyl acetate (1 mL) and 10% of DLP. The adduct **6p** was isolated as a colorless oil in 55% yield after purification on a silica gel column using petroleum ether/toluene as a gradient of elution (10:0 to 0:10). δ_H(400 MHz, $CDCl_3$) 5.77 (m, 1H, CHO), 4.37 (t, 2H, J=6.6Hz, CH_2OCO), 4.26 (m, 3H, $3OCHMe_2$), 3.28 (dd, 1H, J=5.1Hz, J=7.8Hz, CHS), 2.48 (m, 4H, $2CH_2$), 2.22 (m, 1H, CHHCHS), 1.94 (m, 1H, CHHCHS), 1.39 (tapp, 6H, J=6.4Hz, $OCHMe_2$), 1.20 (d, 9H, J=6.1Hz, $3CH_3$), 1.19 (d, 9H, J=6.1Hz, $3CH_3$). δ_C(100 MHz, $CDCl_3$) 215.5 (CS), 173.2 (OCO), 78.4 (CHO), 66.2 (CHO), 56.2 (CH_2OCO), 32.9 (CH_2), 32.4 (CH_2), 30.6 (t, J=21.7Hz, CH_2CF_2), 26.5 (CH_2), 25.5, 25.4 ($6CH_3$), 21.4, 21.3 ($2CH_3$). (ν_{max}/cm^{-1}, CCl_4) 1745 (OCO), 1242 (COS), 1046 (CS).

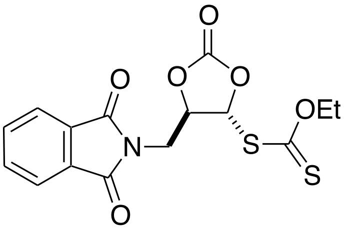
Compound 6t



The radical addition was realized on 0.62 mmol of xanthate and 1.24 mmol of vinyl tri-*t*-butoxysilane in a 1:1 mixture of 1,2-dichloroethane and acetonitrile (1.24 mL) and needed 20% of DLP. The adduct **6t** was isolated as a 1:1 mixture of diastereoisomers and as a white solid in 86% yield after purification on a silica gel column using petroleum ether/ethyl acetate as a gradient of elution (10:0 to 7:3). δ_H(400 MHz, $CDCl_3$) 5.76 (s, 1H, CHC=O), 4.63 (m, 2H, OCH_2CH_3), 4.31 (m, 1H, CHOH), 3.12 (m, 1H, CHS), 3.06-1.34 (several multiplets), 1.51 (s, 3H, CH_3), 1.40 (t, 3H, J=7.1Hz, OCH_2CH_3), 1.31 (bs, 27H, $9CH_3$), 0.91 (s, 1.5H, CH_3), 0.89 (s, 1.5H, CH_3). δ_C(100 MHz, $CDCl_3$) 217.6, 217.0 (CS), 213.53, 213.18 (CO), 199.5, 199.5 (C=CH-CO), 169.7 (CH=C), 124.8 (CH=C), 99.5 (d, J=173.4Hz, CF), 89.4 (COH), 73.90 (3SiOCq), 70.7 (d, J=38.1Hz, CHOH), 70.3 (OCH_2CH_3), 46.9, 46.8

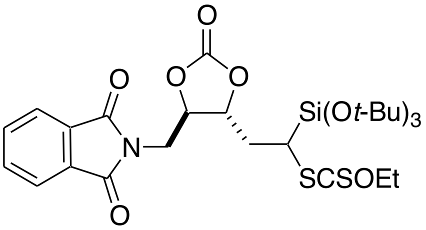
(C), 45.0, 44.9 (CH), 43.9 (d, 1H, J=20.1Hz, *C*-CF), 38.2, 38.05 (CH_2), 36.3 (CH_2), 35.6, 35.4 (CHS), 34.2 (d, J=20.0Hz, *CH*-CF), 33.9 (CH_2), 33.4, 33.0 (CH_2), 31.8 ($9CH_3$), 31.0 (CH_2), 28.5 (CH_2), 26.08 (CH_2), 25.3, 25.0 (CH_2), 23.9 (CH_2), 21.9 (CH_3), 17.3 (CH_3), 13.9 (OCH_2CH_3). (ν_{max}/cm^{-1}, CCl_4) 3620, 3487 (OH), 1708 (CO), 1677 (CO), 1240 (COS), 1045 (CS). HRMS (EI) calcd for $C_{38}H_{63}O_8S_2SiF$ 758.3717 ; found 758.3713

Compound 8



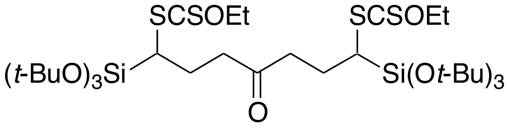
See "Radical aminomethylation of unactivated alkenes." Quiclet-Sire, B. and Zard, S.Z. *Org. Lett.* **2008**,*10*, 3279-3282.

Compound 6u



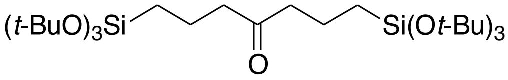
A solution of xanthate (0.24 mmol) and olefin (1.05 mmol) in ethyl acetate (0.5 mL) was refluxed under nitrogen for 10 min. Then dilauroyl peroxide (DLP) was added portion-wise (10 mol%). After 30 min the solvent was evaporated and the residue was purified by silica gel column chromatography using a gradient of elution (pentane/ethyl acetate, 8-2) affording the addition product as a white solid and about a 1 : 1 mixture of diastereoisomers and in 81% yield. δ_H(400 MHz, $CDCl_3$) 7.87 (m, 2H, 2CHAr), 7.75 (m, 2H, 2CHAr), 4.72 (m, 4H, 2CHO, (O*CH*$_2$CH$_3$), 3.98 (m, 2H, NCH_2), 3.22 (dd, 0.55H, J=3.5Hz, J=10.4Hz), 3.15 (dd, 0.45H, J=5.0Hz, J=8.8Hz), 2.36, 2.10, 1.75 (3m, 2H, CH_2), 1.45, 1.44 (2t, 3H, J=7.1Hz, OCH$_2$*CH*$_3$), 1.33, 1.30 (2s, 27H, $9CH_3$). δ_C(100 MHz, $CDCl_3$) 216.7, 214.9 (CS), 167.8, 167.7 (2NCO), 153.9, 153.7 (CO), 134.5, 134.4 (2CHAr), 131.8, 131.7 (2CqAr), 123.8, 123.7 (2CHAr), 78.5, 78.3, 78.2, 78.0 (2CHO), 74.4, 74.2 (3SiO*C*q), 70.9, 70.6 (O*C*H$_2$CH$_3$), 40.2, 39.8, 37.6, 35.9 (CHS, CH_2), 31.8, 31.7 ($9CH_3$), 31.2 (CH_2), 13.9, 13.8 (OCH$_2$*C*H$_3$). (ν_{max}/cm^{-1}, CCl_4) 1824 (OC(O)O), 1780, 1726 (NCO), 1390, 1366, 1220 (COS), 1070 (CS). HRMS (EI) calcd for $C_{29}H_{43}O_9NS_2Si$ 641.2148; found 641.2140.

Compound 6v



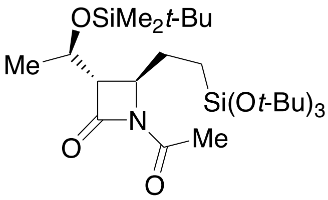
The radical addition was realized on 1 mmol of xanthate and 4 mmol of vinyl tri-*t*-butoxysilane in ethyl acetate (1 mL) and 10% of DLP. The adduct **6r** was isolated as a colorless oil in 82% yield after purification on a silica gel column using petroleum ether/diethyl ether as a gradient of elution (10:0 to 98:2). δ_H(400 MHz, $CDCl_3$) 4.63 (m, 4H, CH_3CH_2O), 3.11 (m, 2H, 2CHS), 2.60 (m, 4H, CH_2CO), 2.18 (m, 2H, 2C*H*HCHS), 1.84 (m, 2H, 2CH*H*CHS), 1.40 (t, 6H, J=7.1Hz, CH_3CH_2O), 1.31 (s, 54H, 2(Me_3)$_3$). δ_C(100 MHz, $CDCl_3$) 217.14, 217.07 (2CS), 210.9 (CO), 73.8 (6SiO*Cq*), 70.1 (2OCH_2CH_3), 41.0, 40.9 (2CHS), 35.4 (2CH_2CO), 31.8 (2x9CH_3), 25.5, 25.4 (2CH_2CHS),13.9 (2OCH_2CH_3). (ν_{max}/cm^{-1}, CCl_4) 1715 (CO), 1211 (COS), 1063 (CS). . HRMS (EI) calcd for $C_{37}H_{74}O_9S_4Si_2$ 846.3754; found 846.3804.

Compound 10



The reduction of the xanthate group of compound 6v (0.14 mmol) was carried out using tristrimethylsilylsilane (3 equiv) and AIBN (0.1 equiv) in 1 mL of a refluxing solution of cyclohexane : toluene (1:1) under nitrogen. The reduced product **10** was isolated as a colorless oil in 70% yield after purification on a silica gel column using petroleum ether/diethyl ether as a gradient of elution (10:0 to 98:2). δ_H(400 MHz, $CDCl_3$) 2.45 (t, 4H, J=7.4Hz, 2CH_2CO), 1.69 (m, 4H, CH_2CH_2CO), 1.29 (s, 54H, 2x9CH_3), 0.48 (m, 4H, 2CH_2Si). δ_C(100 MHz, $CDCl_3$) 212.6 (CO), 72.3 (6SiO*Cq*), 46.1 (2CH_2CO), 31.8 (2x9CH_3), 18.7 (2CH_2), 17.1 (2CH_2Si). (ν_{max}/cm^{-1}, CCl_4) 1713 (CO), 13.88, 1364, 1241, 1192, 1058, 1026. HRMS (EI) calcd for $C_{31}H_{66}O_7Si_2$ 606.4347; found 606.4366.

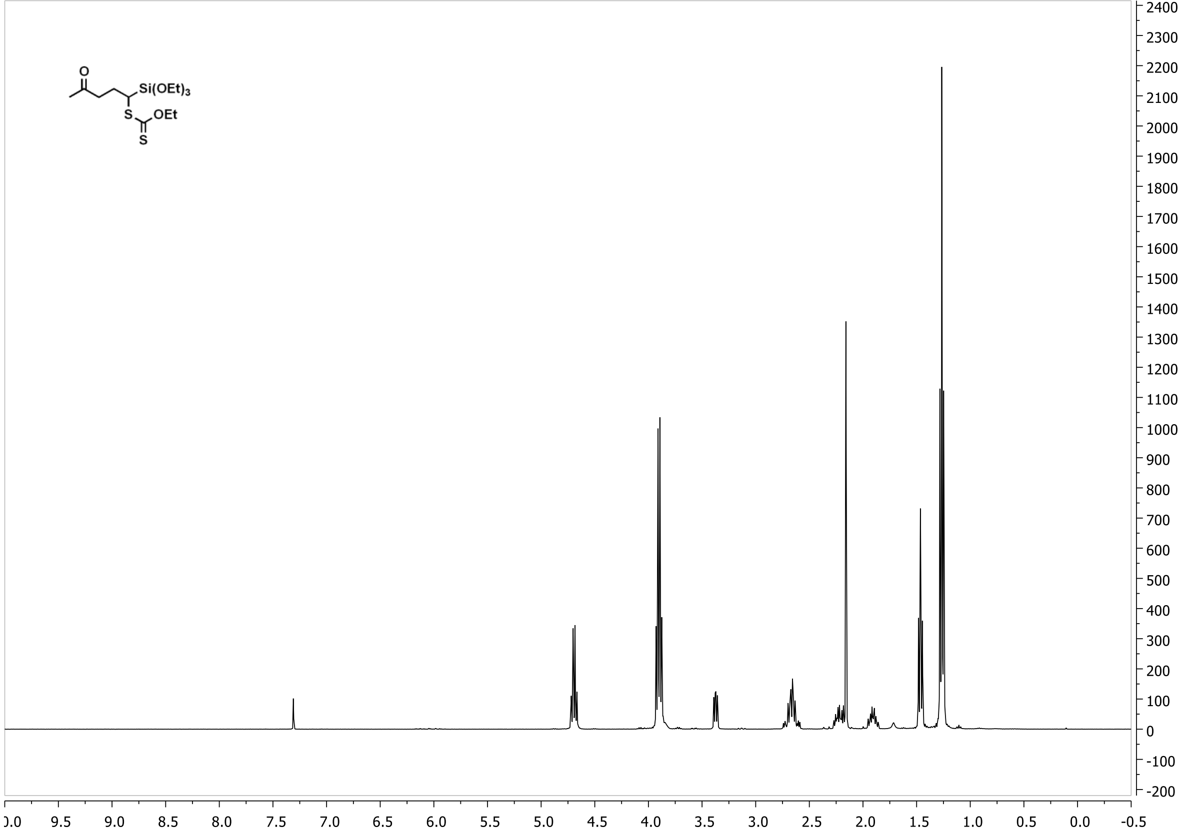
Compound 12

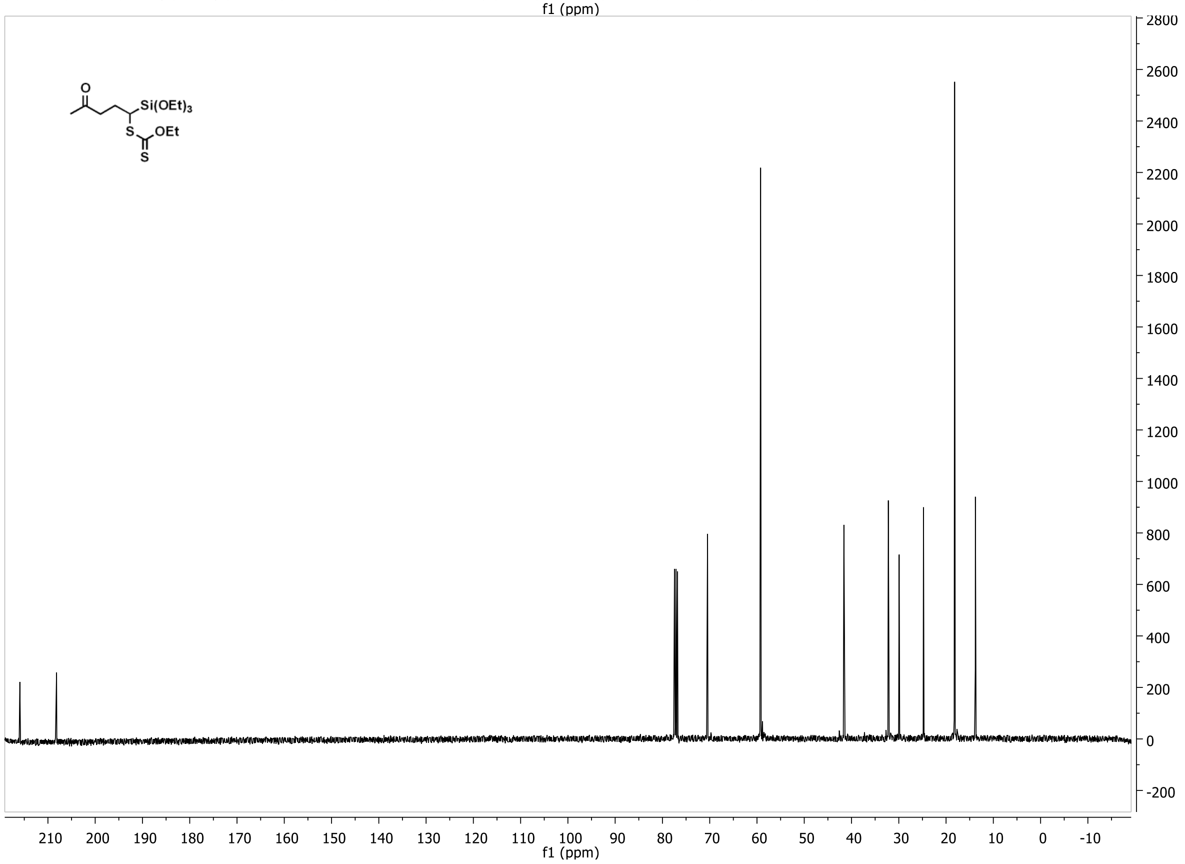


The radical addition was realized on 0.76 mmol of xanthate **11** and 2 mmol of vinyl tri-*t*-butoxysilane in ethyl acetate (0.8 mL) and 12.5% of DLP. After evaporation of the solvent, the addition product **6w** was purified by flash chromatography on silica gel (pentane/ diethyl ether, 95:5) and the xanthate group was directly reduced using tristrimethylsilylsilane (1.5 eq), AIBN (0.1 equi) in 7 mL of a 1:1 mixture of toluene/cyclohexane at reflux and under nitrogen. The reduced product **12** was obtained as crystals in 61% yield after purification on a silica gel column using pentane/ diethyl ether as a gradient of elution (10:0 to 9:1). Mp 70-71°C (MeOH). δ_H(400 MHz, $CDCl_3$) 4.27 (m, 1H, $CH_3\mathit{CHO}$), 4.11 (td, 1H, J=3.1Hz, J=9.0Hz, CHN), 2.80 (t, 1H, J=3.2Hz, *CHCO*), 2.34 (s, 3H, CH_3CO), 2.26 (m, 1H, $C\mathit{H}HCH_2Si$), 1.61 (m, 1H, $CH\mathit{H}CH_2Si$), 1.29 (s, 27H, $9CH_3$), 1.23 (d, 3H, J=6.3Hz, $\mathit{CH_3}CH$), 0.84 (s, 9H, $OSiCMe_3$), 0.44 (m, 2H, CH_2Si), 0.07 (s, 3H, SiMe), 0.05 (s, 3H, SiMe). δ_C(100 MHz, $CDCl_3$) 167.9, 167.4 (2NCO), 72.5 (3SiOCq), 65.0, 62.1, 54.9 (3CH), 31.7 ($SiO(\mathit{Me_3})_3$), 26.2 (CH_2), 25.7 ($OSiC\mathit{Me_3}$), 24.1, 22.6 ($2CH_3$), 17.9 ($Si\mathit{Cq}Me_3$), 12.5 (CH_2Si), -4.1, -5.1 ($Si\mathit{Me_2}$). HRMS (EI) calcd for $C_{27}H_{55}O_6NSi_2$ 545.3568; found 545.3549.

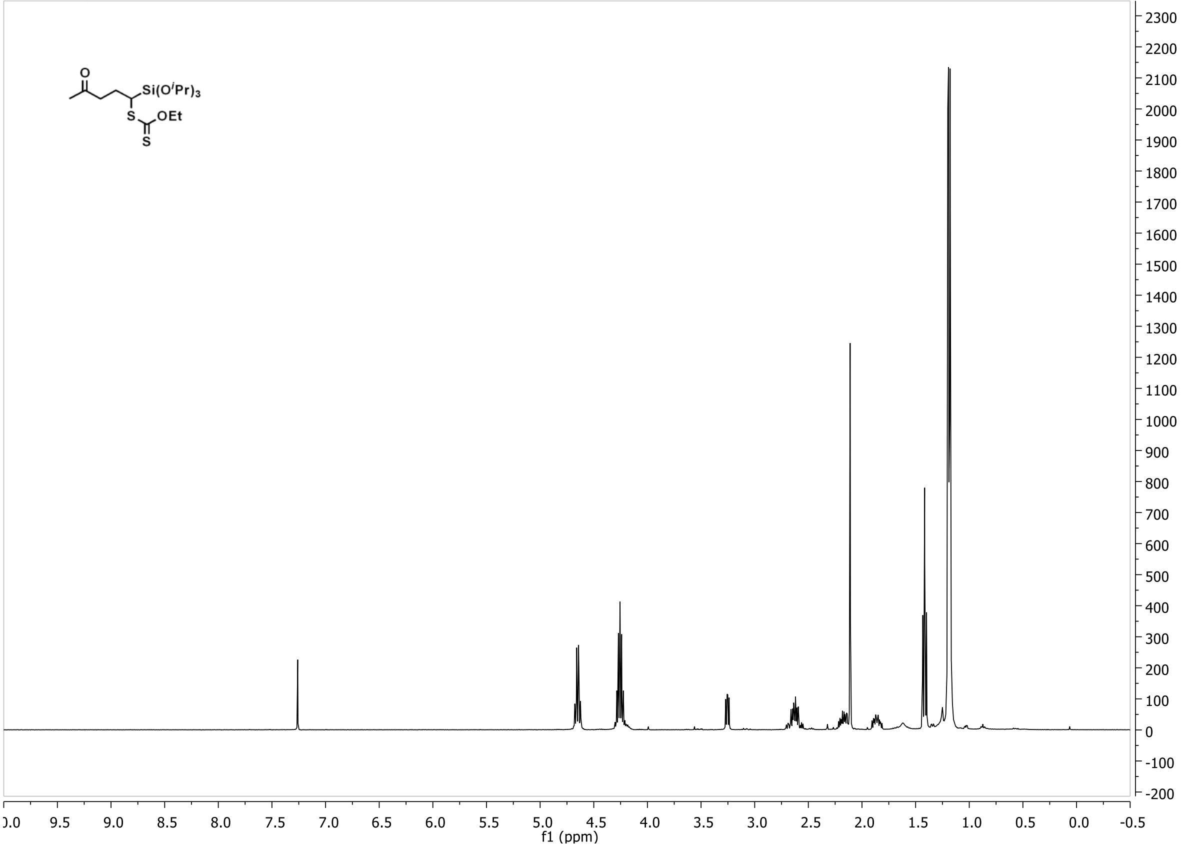
NMR SPECTRA

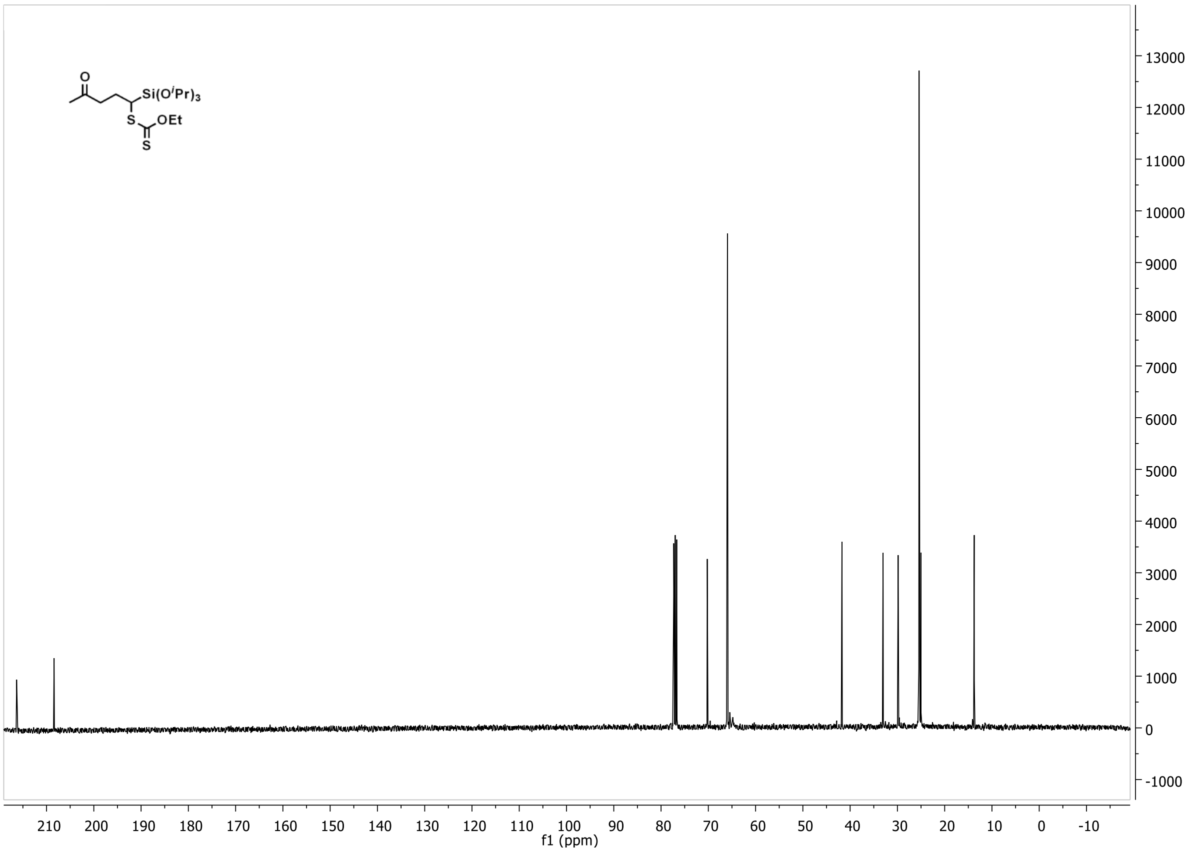
Compound 6a



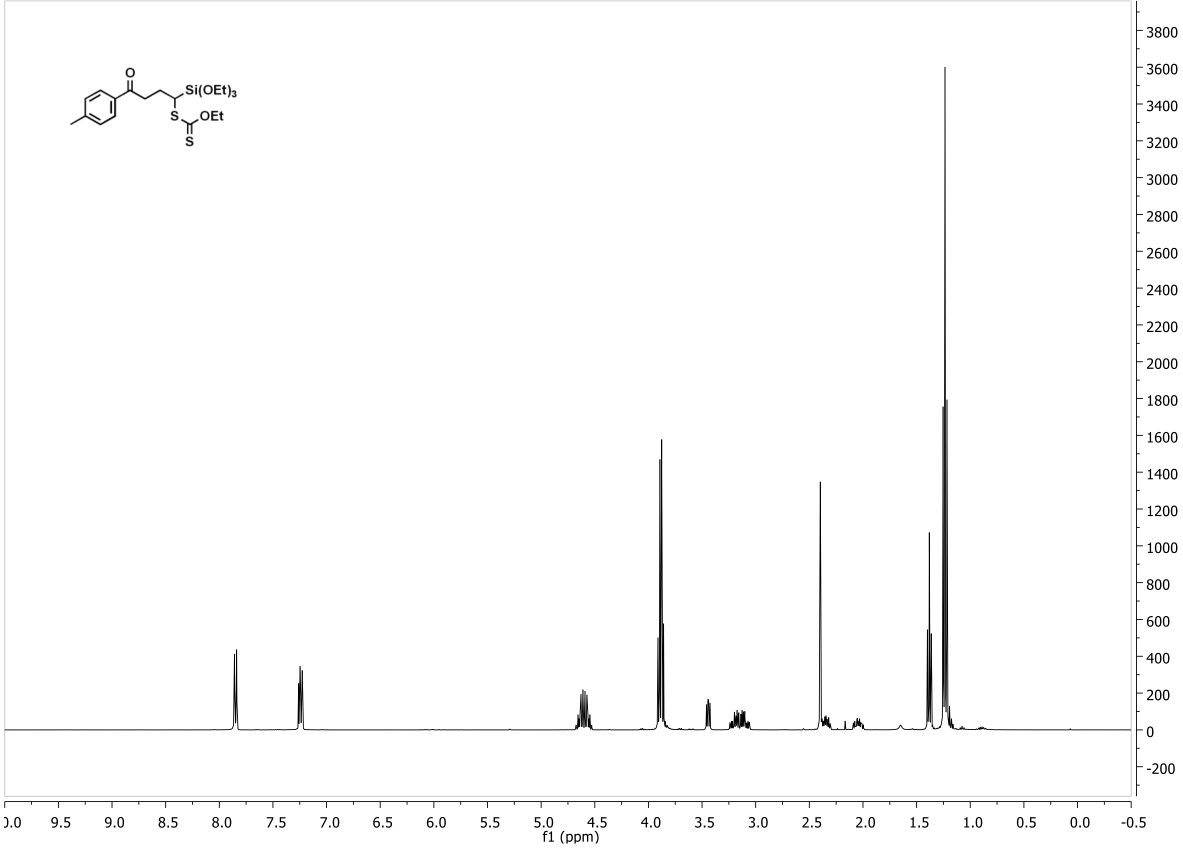


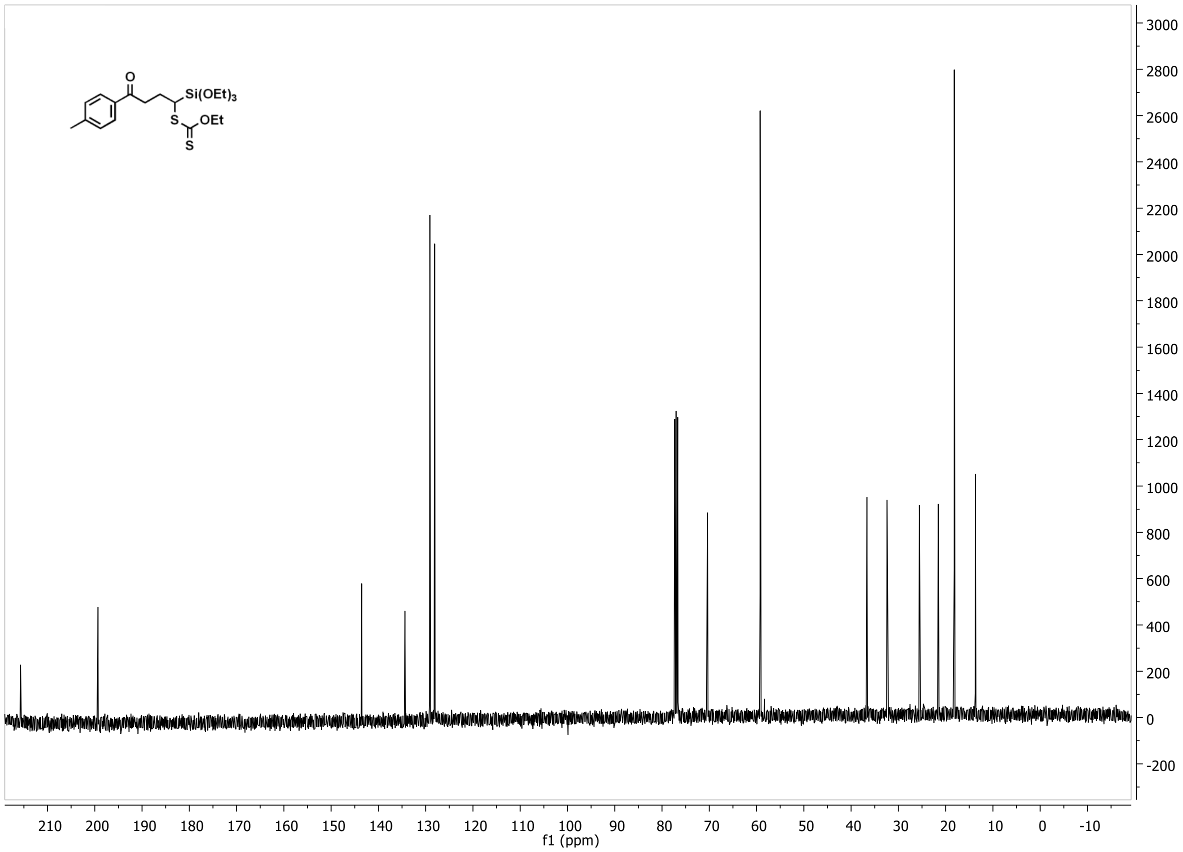
Compound 6b


O
Si(O^{i}Pr)$_3$
S
OEt
S
f1 (ppm)
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200


O
Si(O^{i}Pr)$_3$
S
OEt
S
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

Compound 6c


O
Si(OEt)3
S
OEt
S
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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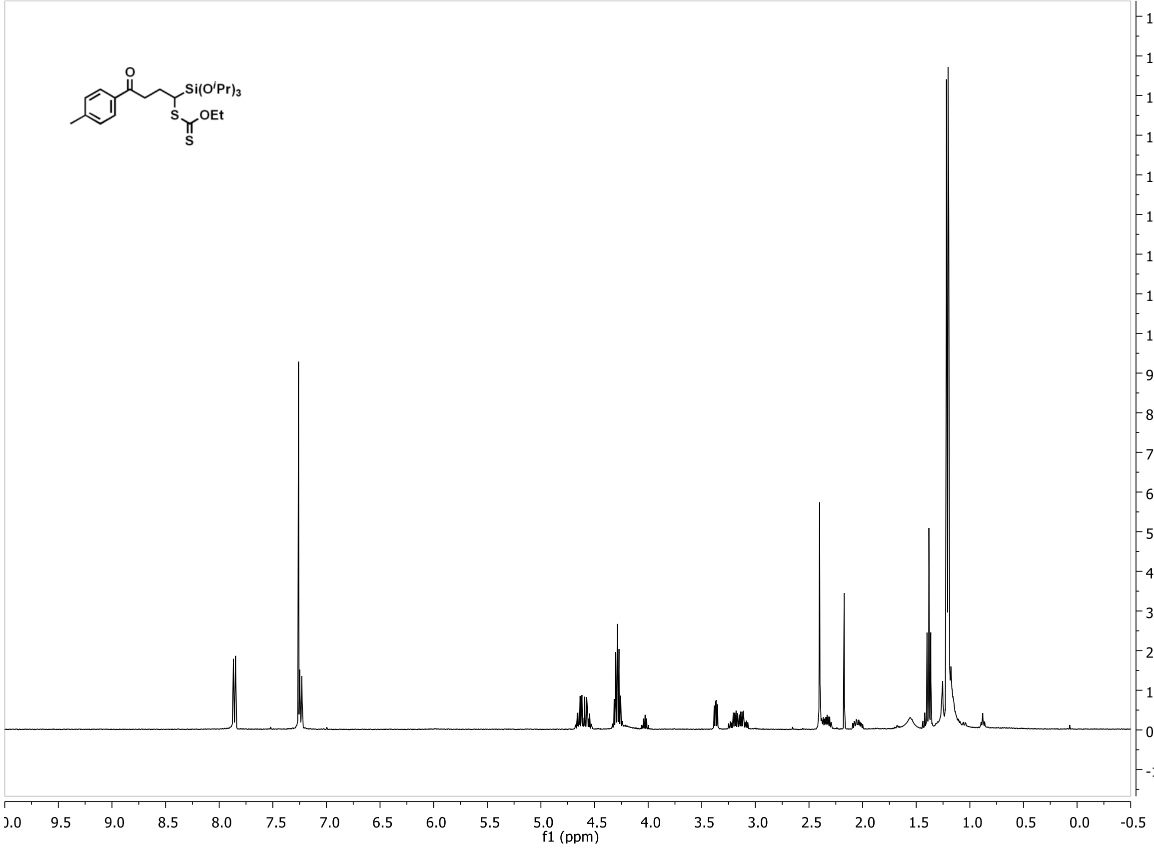
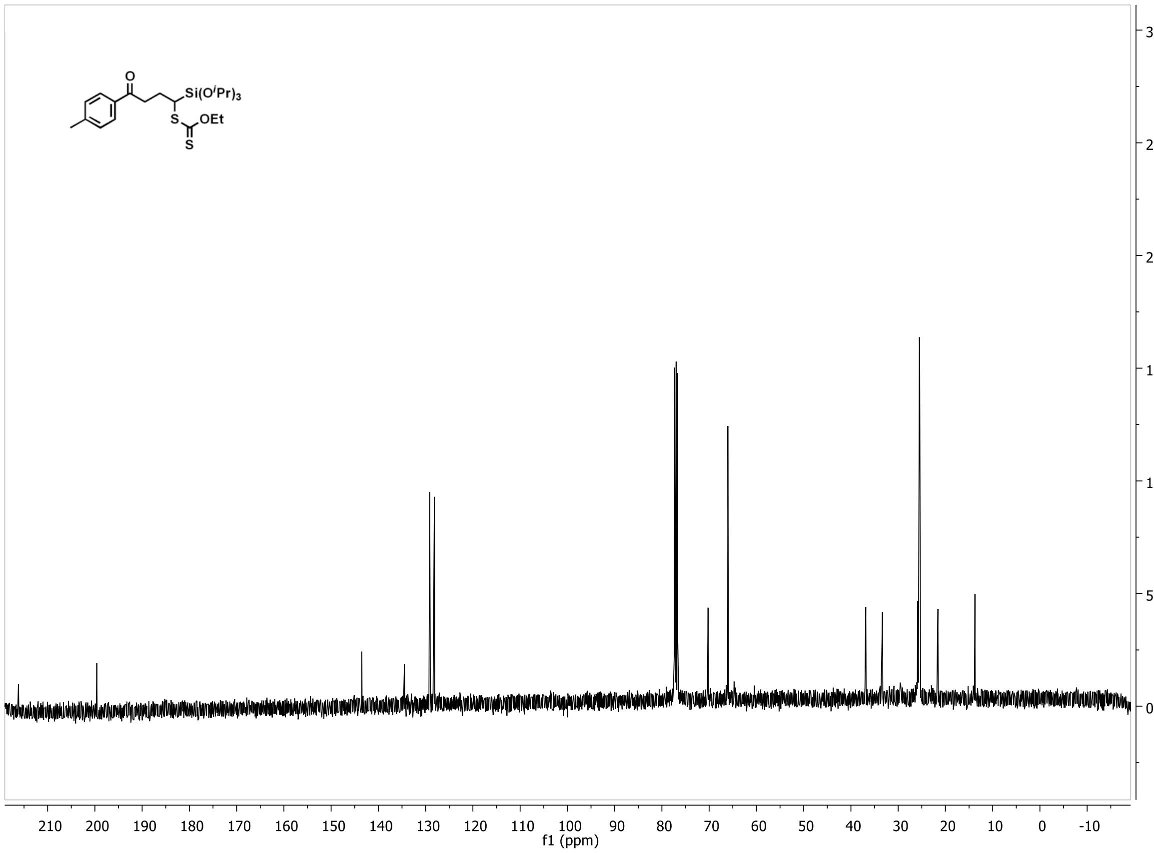
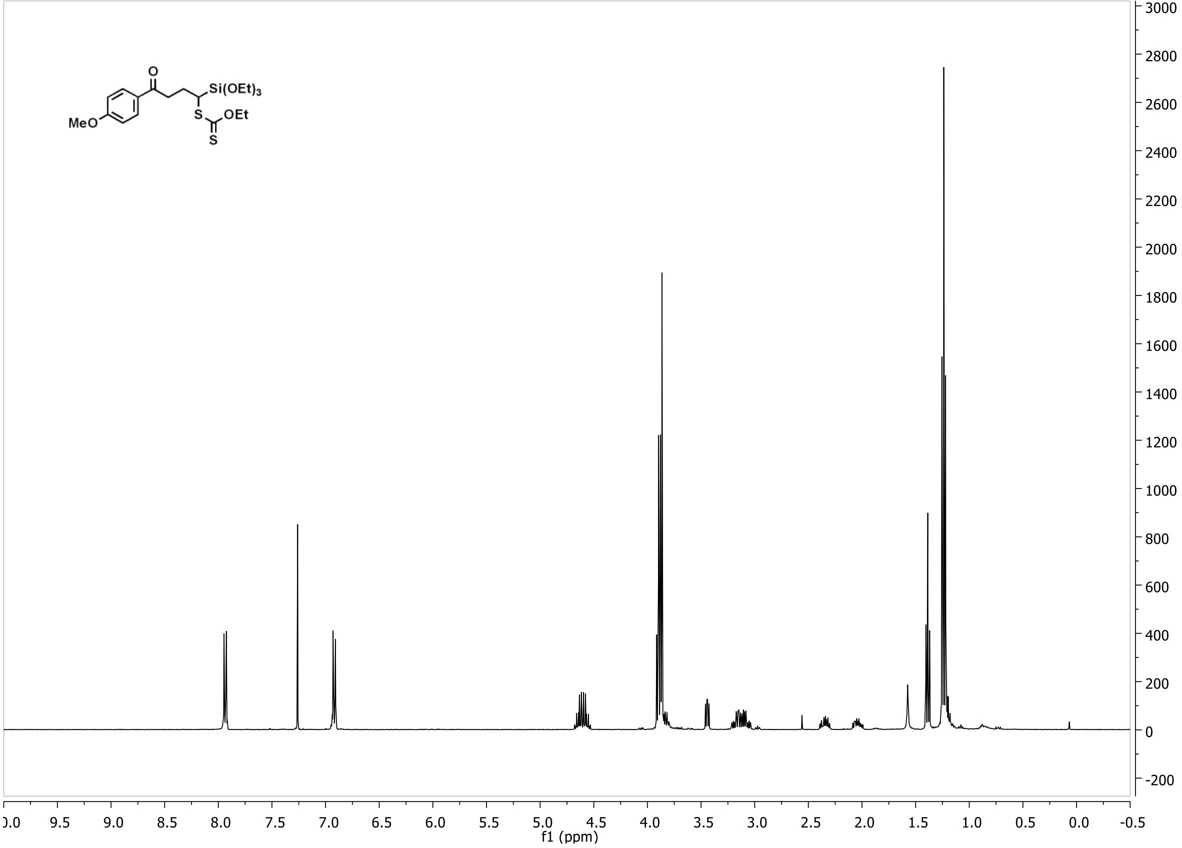
Si(OEt)3
S
OEt
S
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

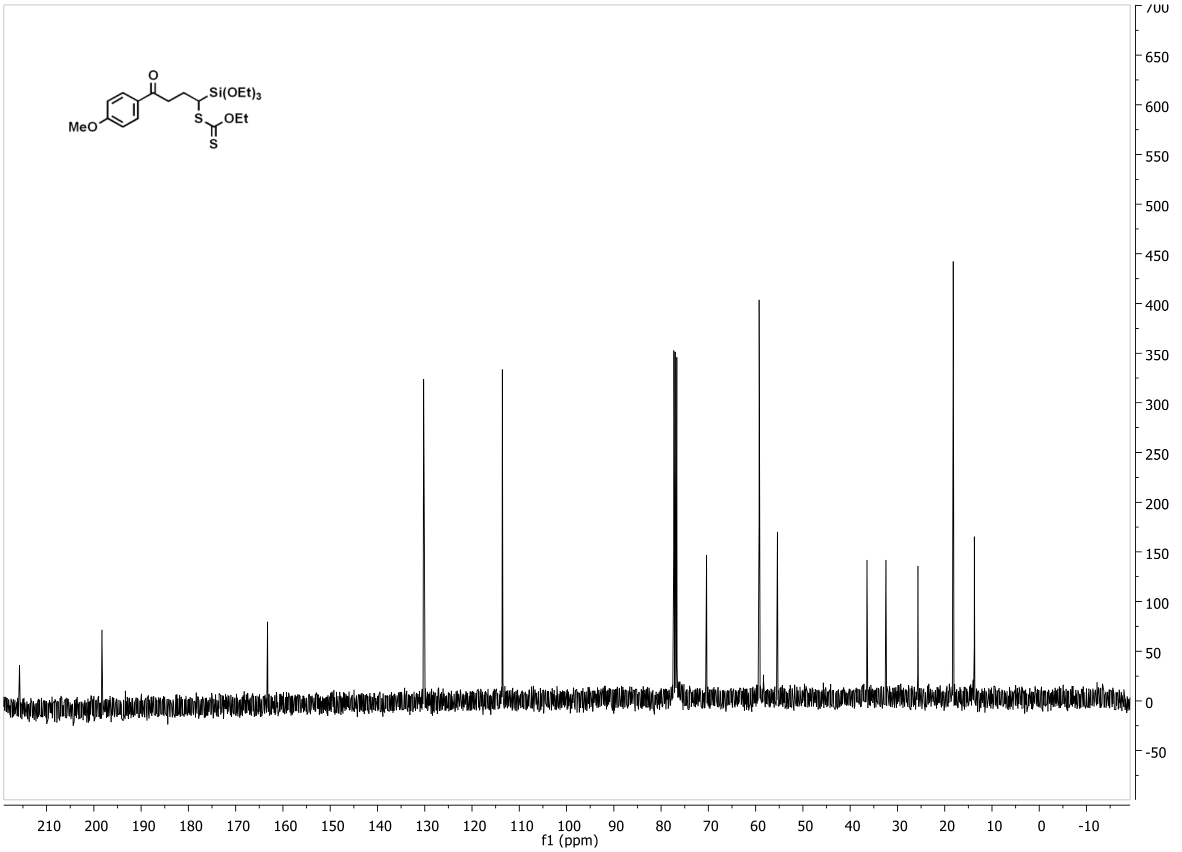
Compound 6d


O
Si(O^{i}Pr)$_3$
S
OEt
S
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

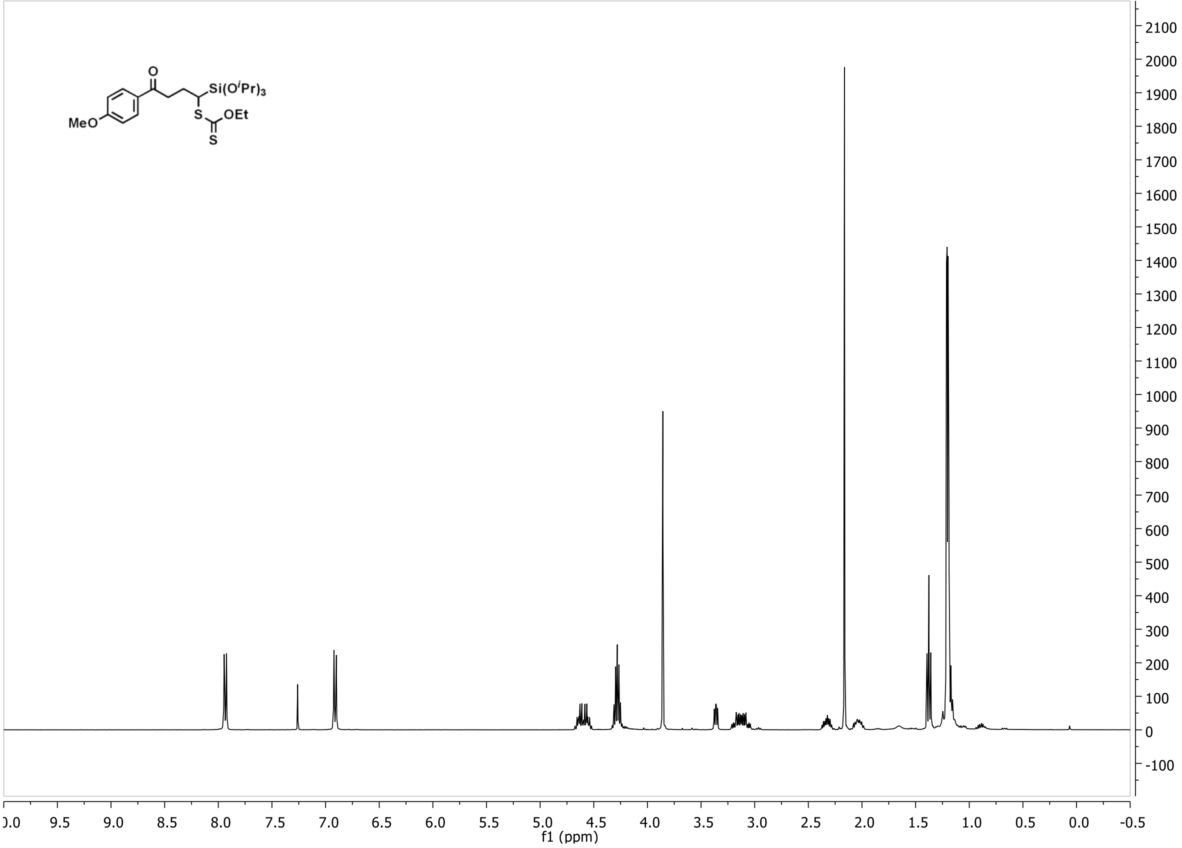

O
Si(O^{i}Pr)$_3$
S
OEt
S
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

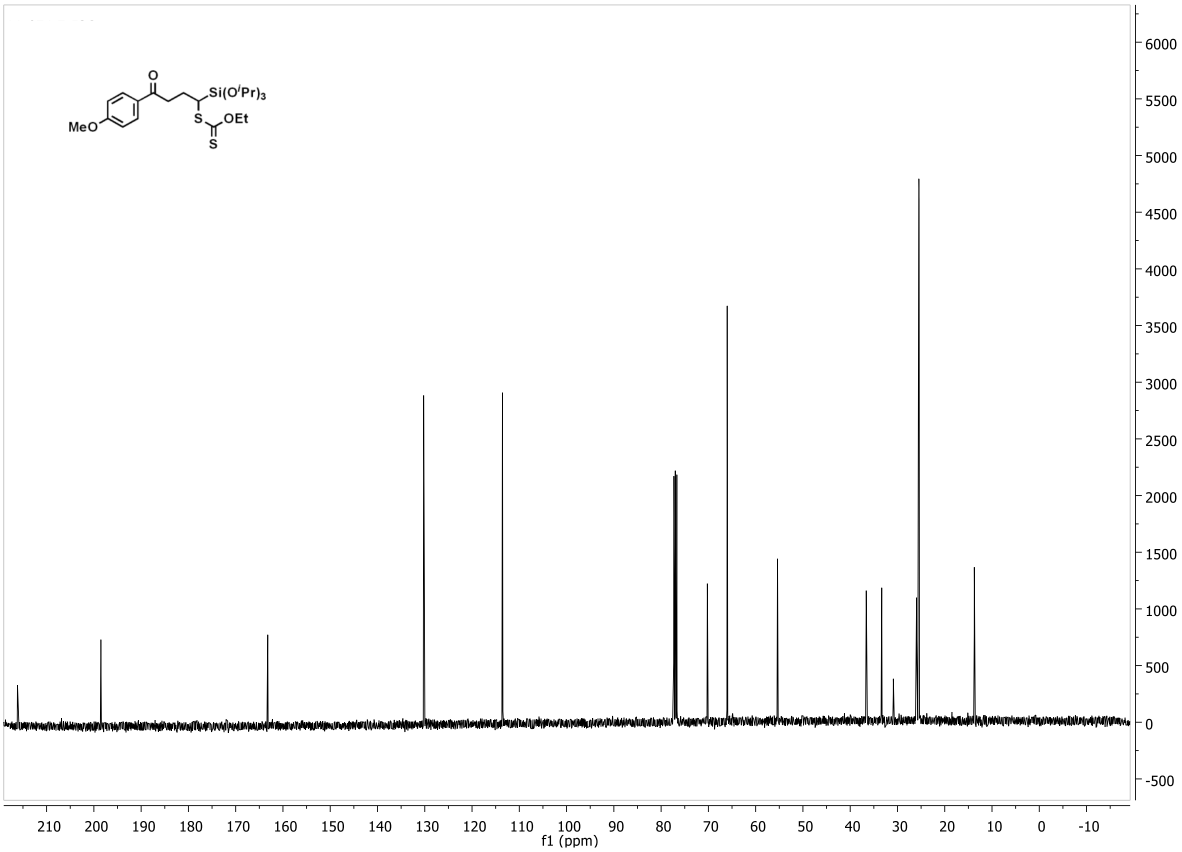
Compound 6e



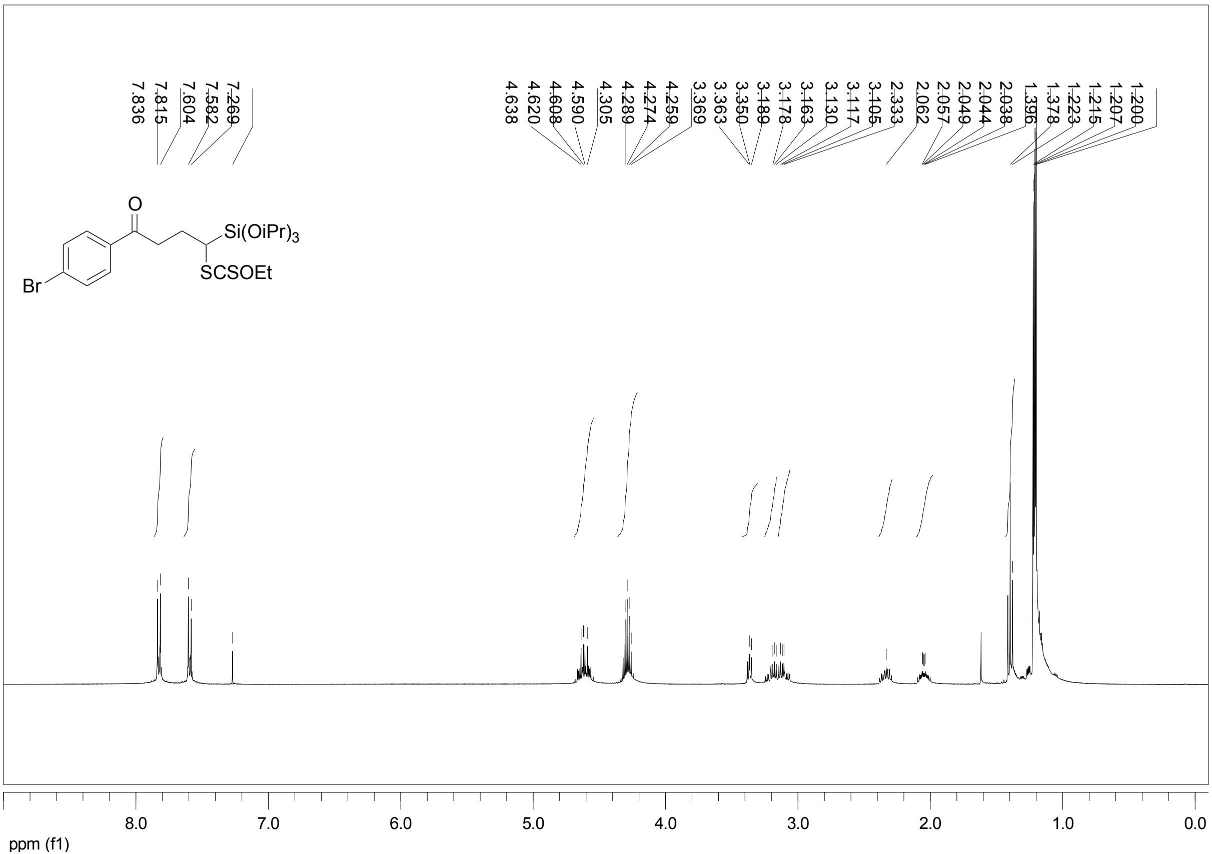


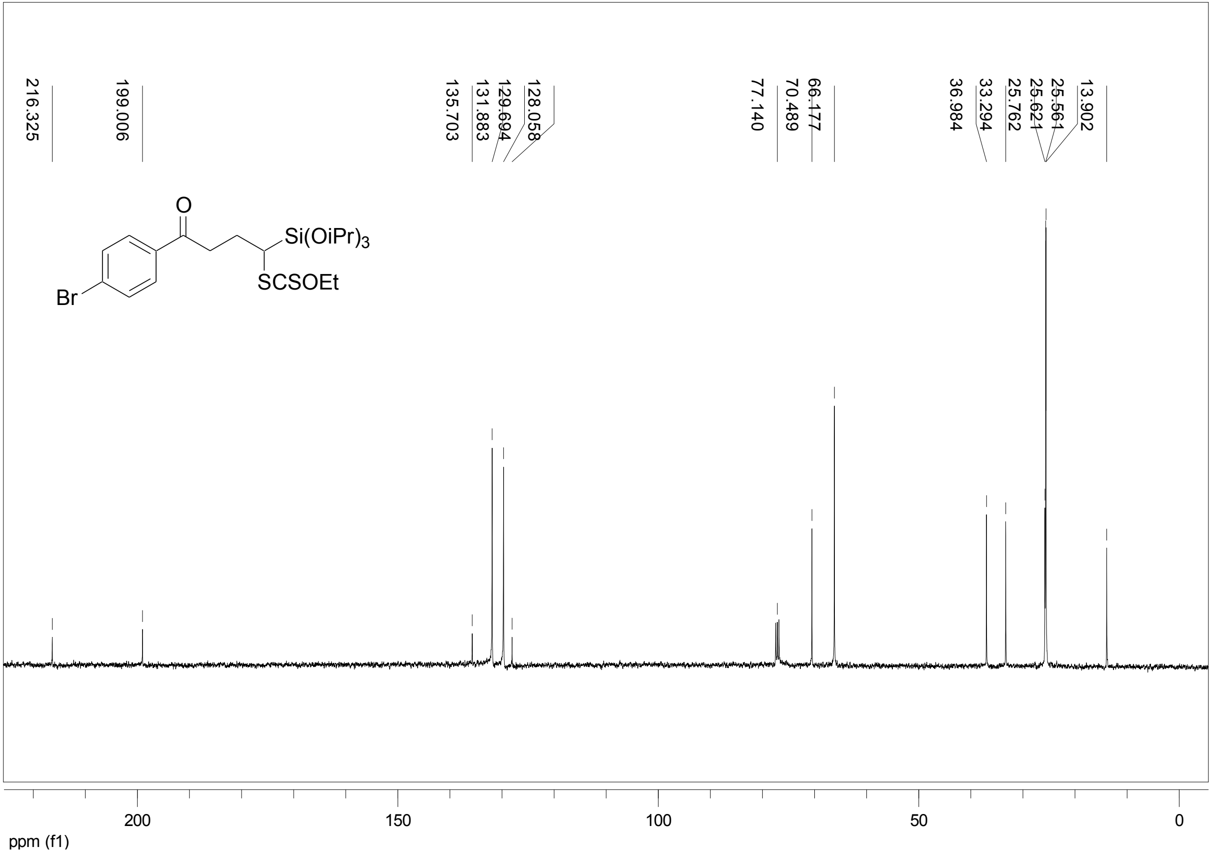
Compound 6f


O
Si(O^{i}Pr)$_3$
MeO
S
OEt
S
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

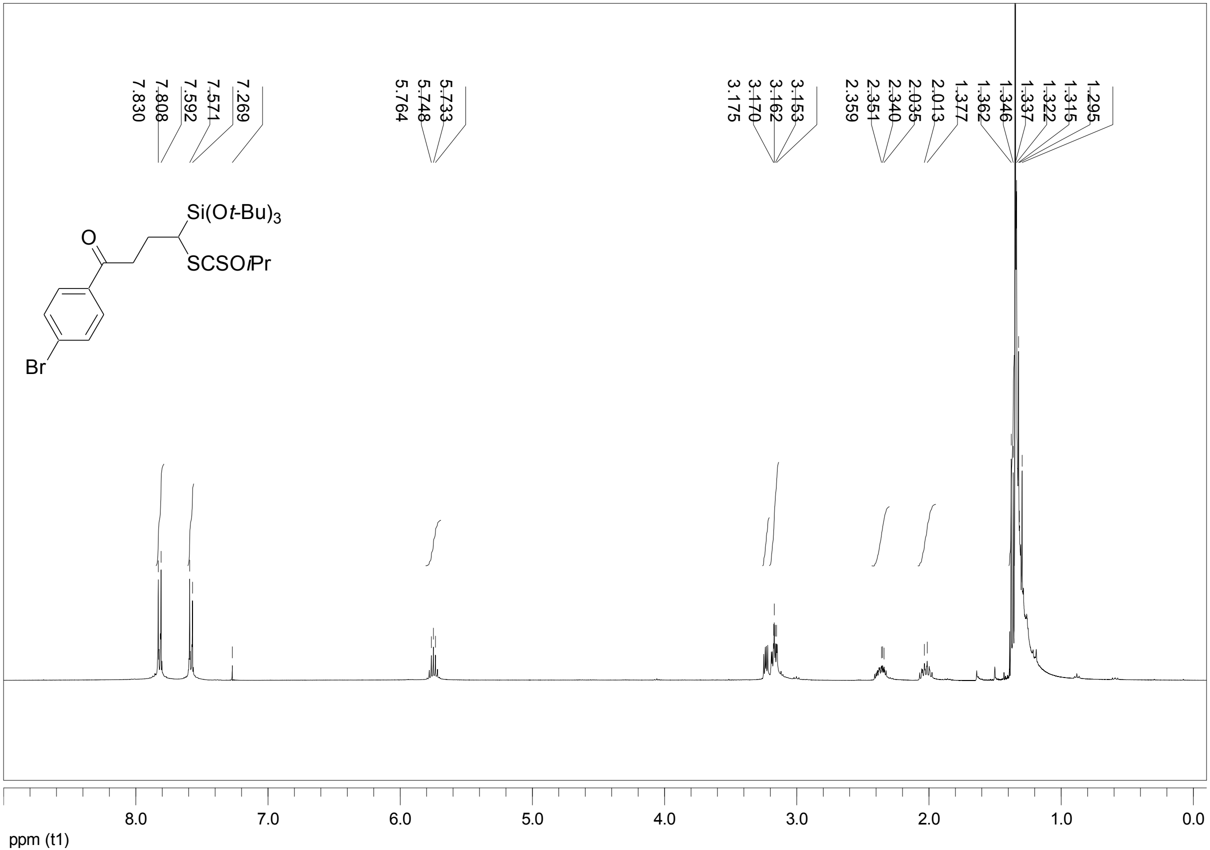

O
Si(O^{i}Pr)$_3$
MeO
S
OEt
S
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

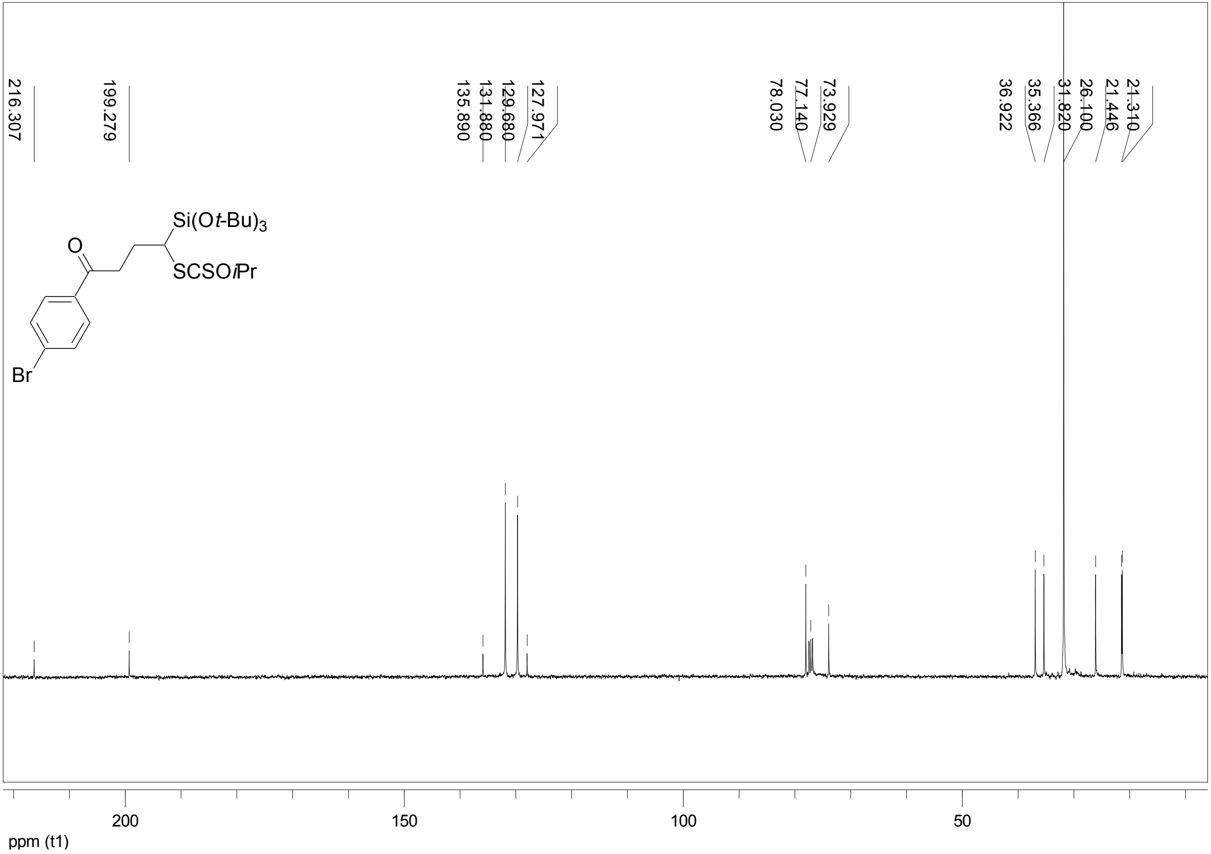
Compound 6g


7.836
7.815
7.604
7.582
7.269
4.638
4.620
4.608
4.590
4.305
4.289
4.274
4.259
3.369
3.363
3.350
3.189
3.178
3.163
3.130
3.117
3.105
2.333
2.062
2.057
2.049
2.044
2.038
1.396
1.378
1.223
1.215
1.207
1.200
O
Si(OiPr)3
SCSOEt
Br
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

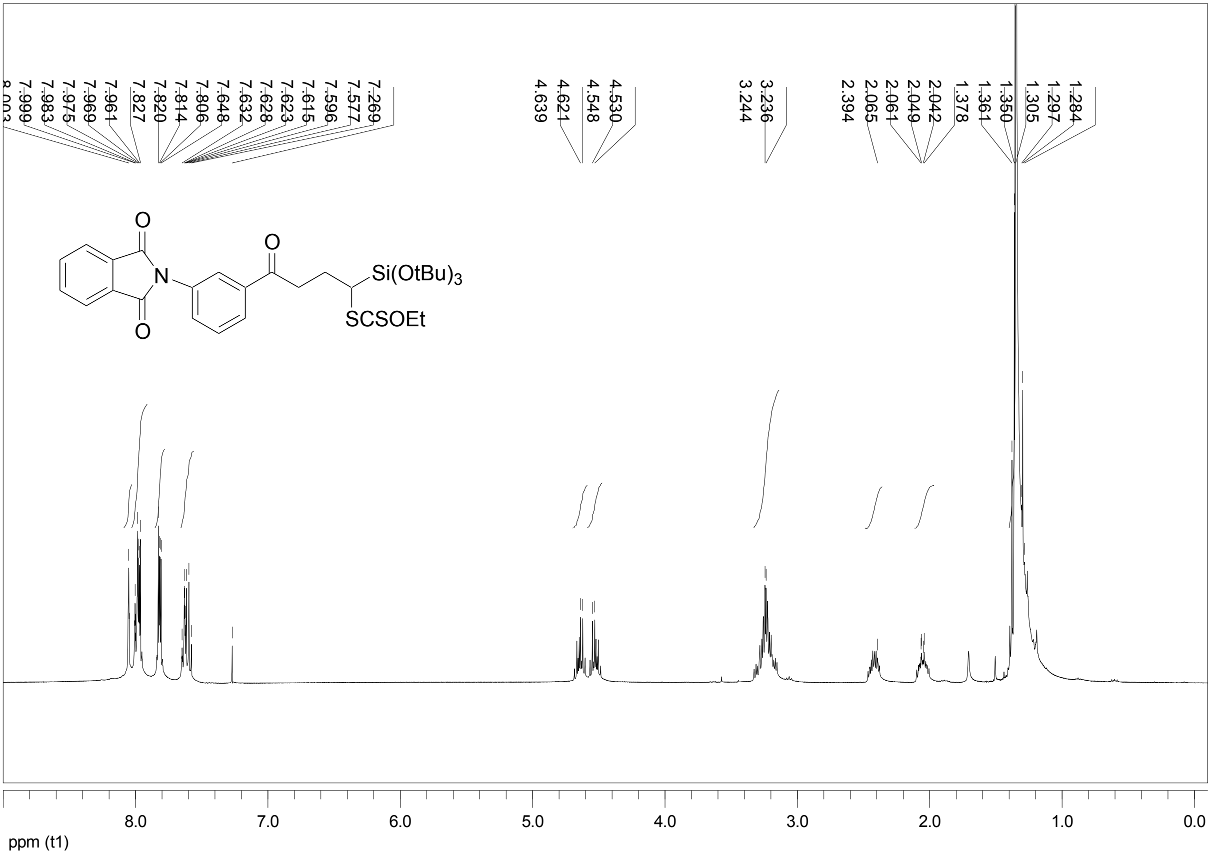

216.325
199.006
135.703
131.883
129.694
128.058
77.140
70.489
66.177
36.984
33.294
25.762
25.621
25.561
13.902
O
Si(OiPr)3
SCSOEt
Br
200
150
100
50
0
ppm (f1)

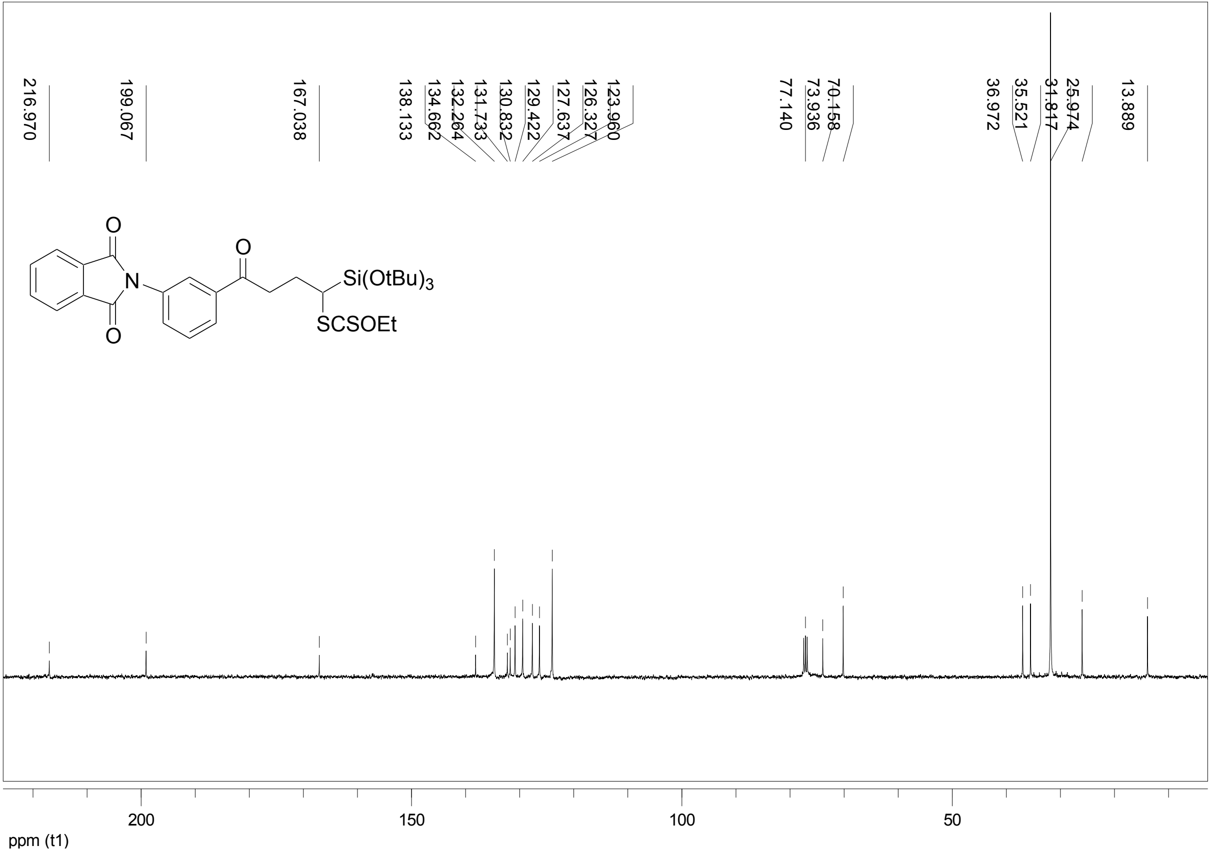
Compound 6h


7.830
7.808
7.592
7.571
7.269
5.764
5.748
5.733
3.175
3.170
3.162
3.153
2.359
2.351
2.340
2.035
2.013
1.377
1.362
1.346
1.337
1.322
1.315
1.295
O
Si(Ot-Bu)3
SCSOiPr
Br
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

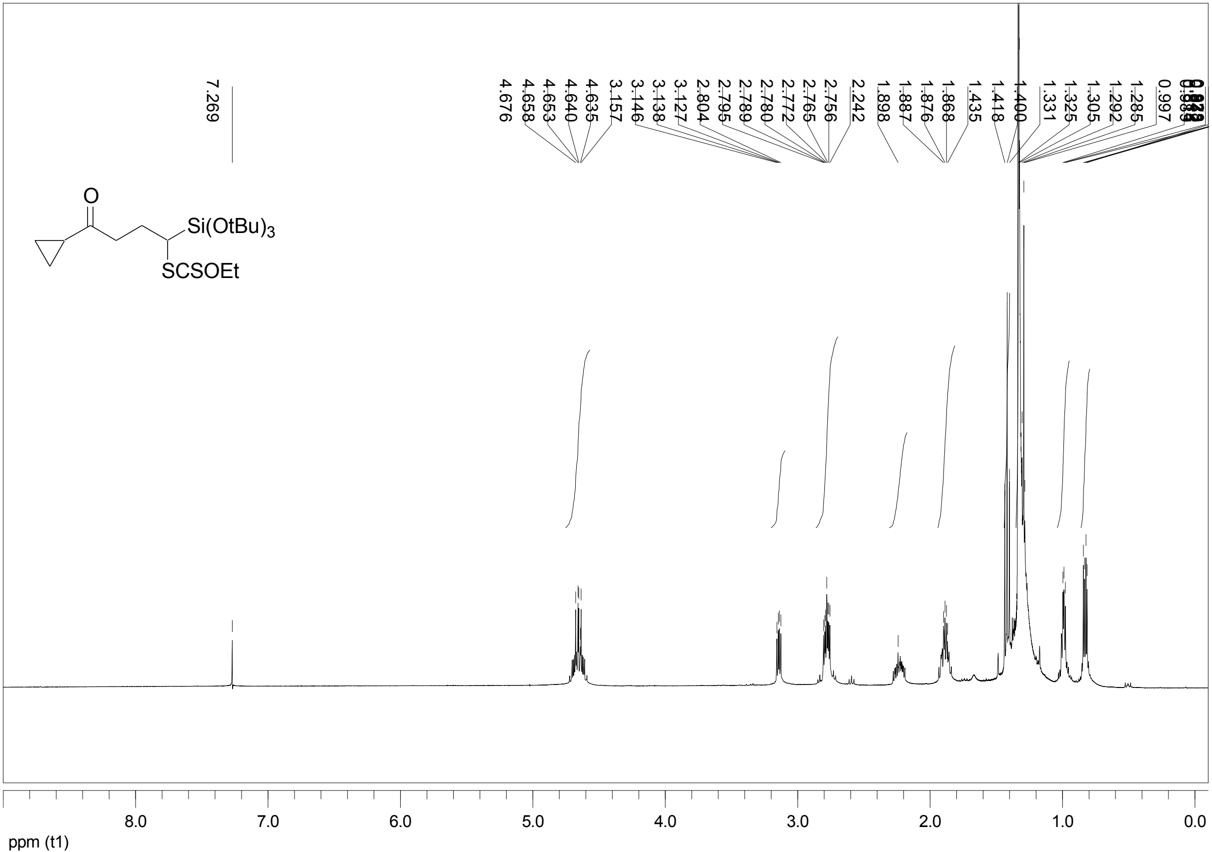

216.307
199.279
135.890
131.880
129.680
127.971
78.030
77.140
73.929
36.922
35.366
31.820
26.100
21.446
21.310
O
Si(Ot-Bu)3
SCSOiPr
Br
200
150
100
50
ppm (t1)

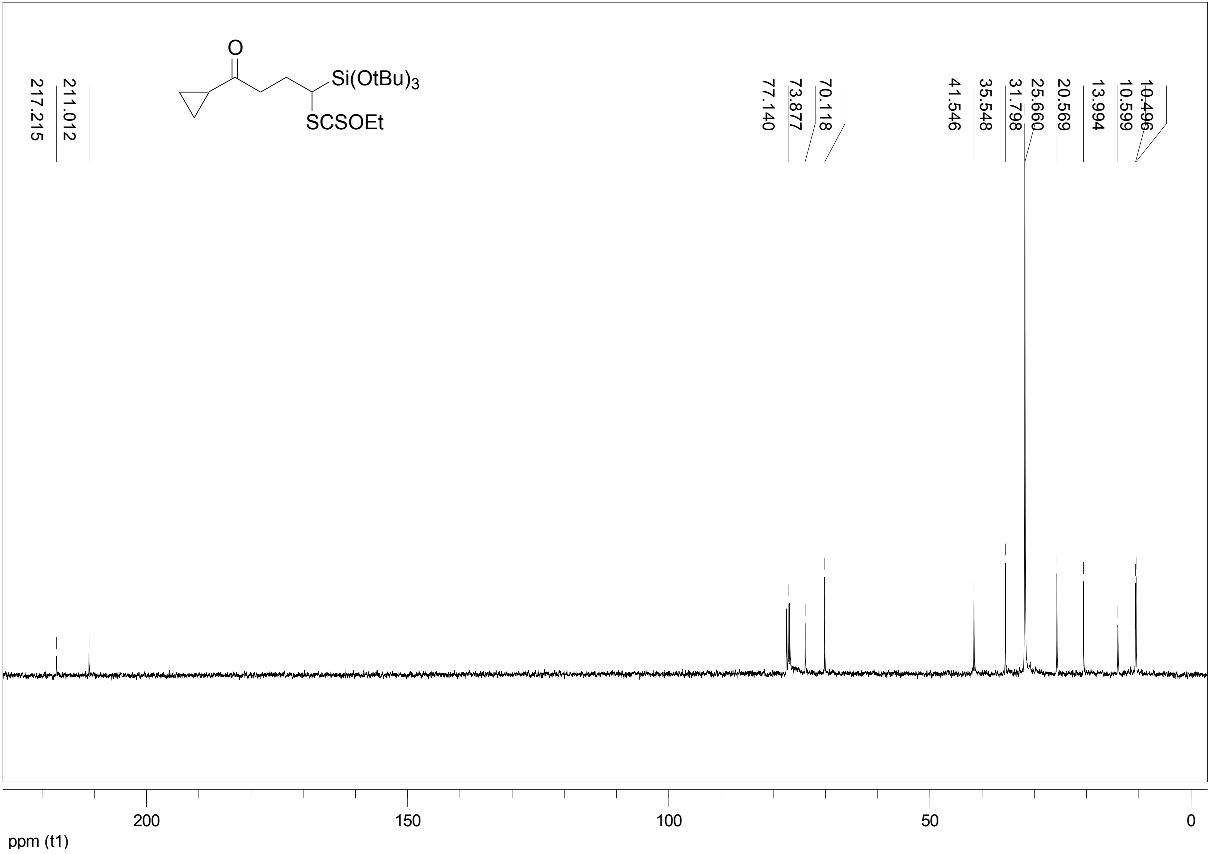
Compound 6i


7.999
7.983
7.975
7.969
7.961
7.827
7.820
7.814
7.806
7.648
7.632
7.628
7.623
7.615
7.596
7.577
7.269
4.639
4.621
4.548
4.530
3.244
3.236
2.394
2.065
2.061
2.049
2.042
1.378
1.361
1.350
1.305
1.297
1.284
O
N
O
O
Si(OtBu)3
SCSOEt
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

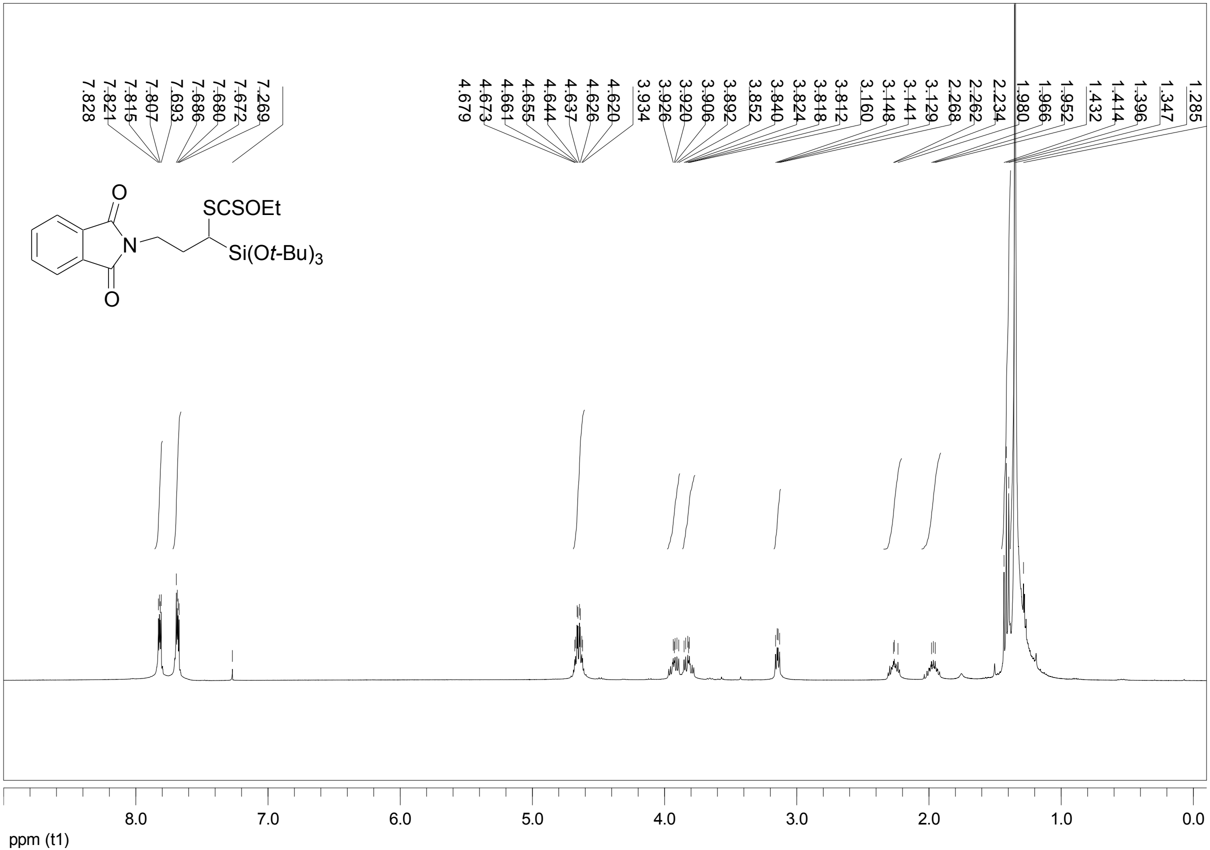

216.970
199.067
167.038
138.133
134.662
132.264
131.733
130.832
129.422
127.637
126.327
123.960
77.140
73.936
70.158
36.972
35.521
31.817
25.974
13.889
O
N
O
O
Si(OtBu)3
SCSOEt
200
150
100
50
ppm (t1)

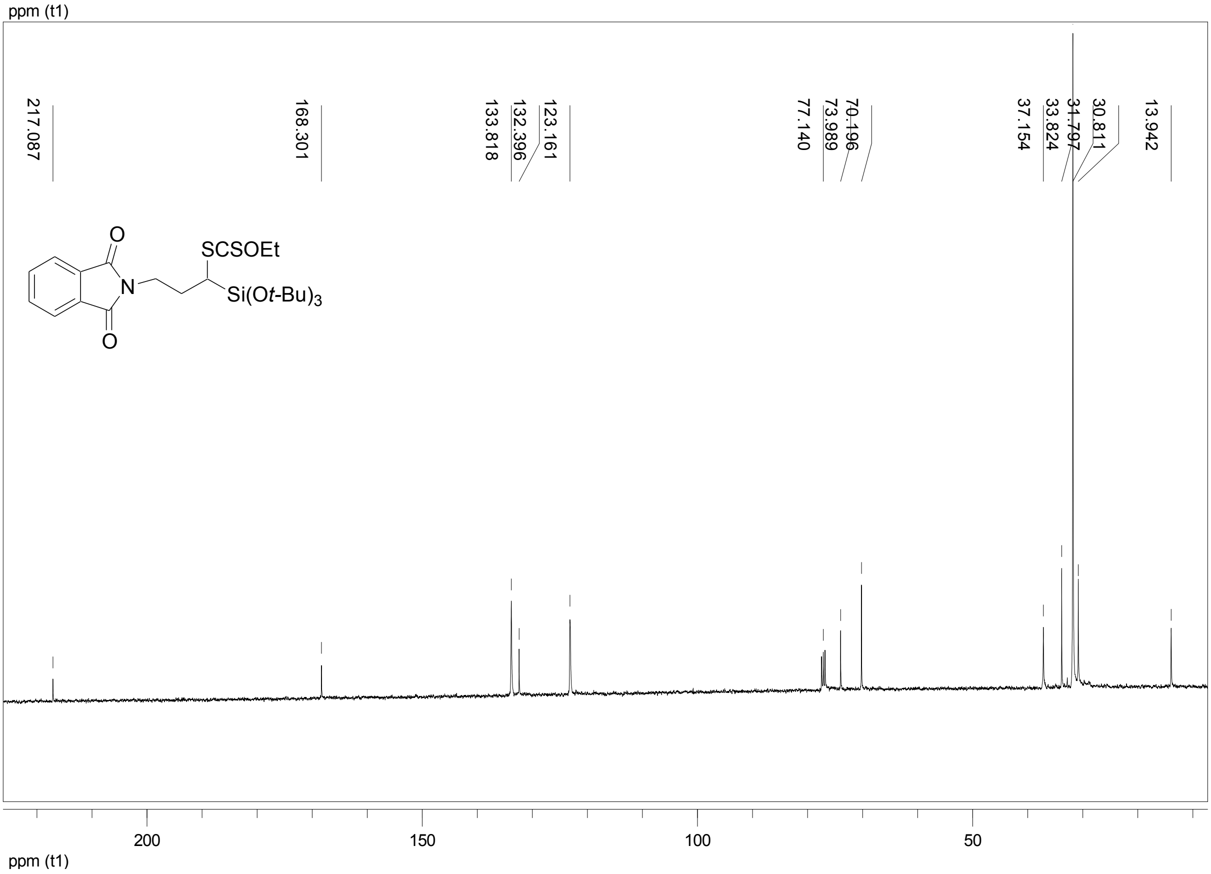
Compound 6j


7.269
4.676
4.658
4.653
4.640
4.635
3.157
3.146
3.138
3.127
2.804
2.795
2.789
2.780
2.772
2.765
2.756
2.242
1.898
1.887
1.876
1.868
1.435
1.418
1.400
1.331
1.325
1.305
1.292
1.285
0.997
O
Si(OtBu)3
SCSOEt
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

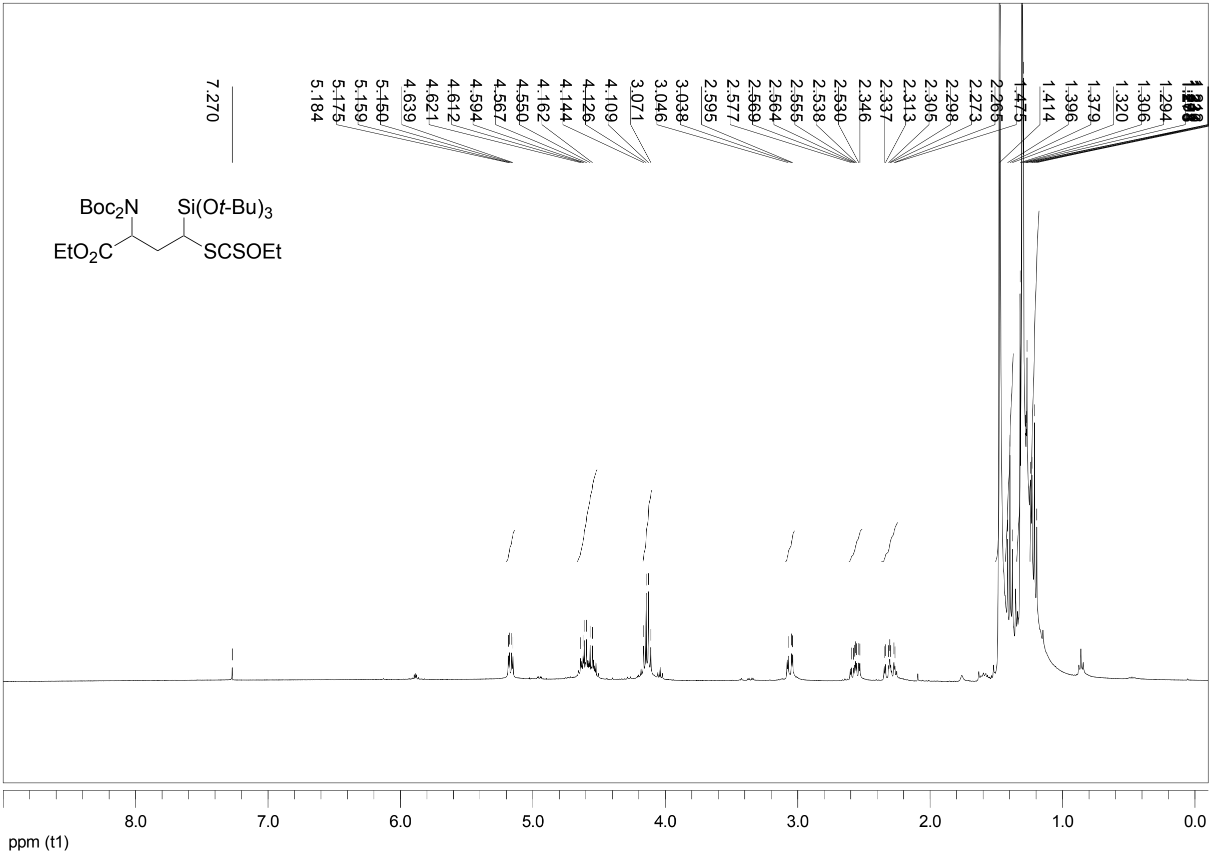

217.215
211.012
O
Si(OtBu)3
SCSOEt
77.140
73.877
70.118
41.546
35.548
31.798
25.660
20.569
13.994
10.599
10.496
200
150
100
50
0
ppm (t1)

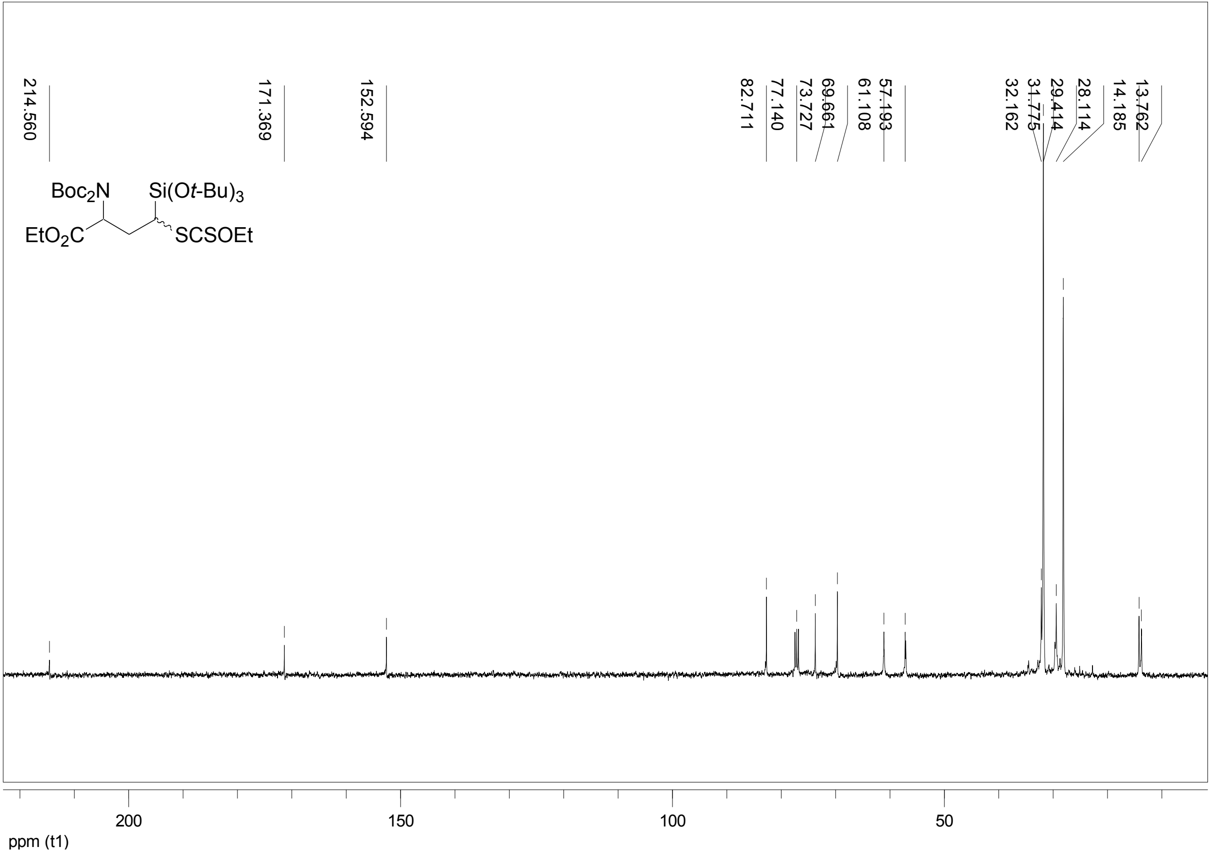
Compound 6k


7.828
7.821
7.815
7.807
7.693
7.686
7.680
7.672
7.269
4.679
4.673
4.661
4.655
4.644
4.637
4.626
4.620
3.934
3.926
3.920
3.906
3.892
3.852
3.840
3.824
3.818
3.812
3.160
3.148
3.141
3.129
2.268
2.262
2.234
1.980
1.966
1.952
1.432
1.414
1.396
1.347
1.285
O
N
O
SCSOEt
Si(Ot-Bu)3
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

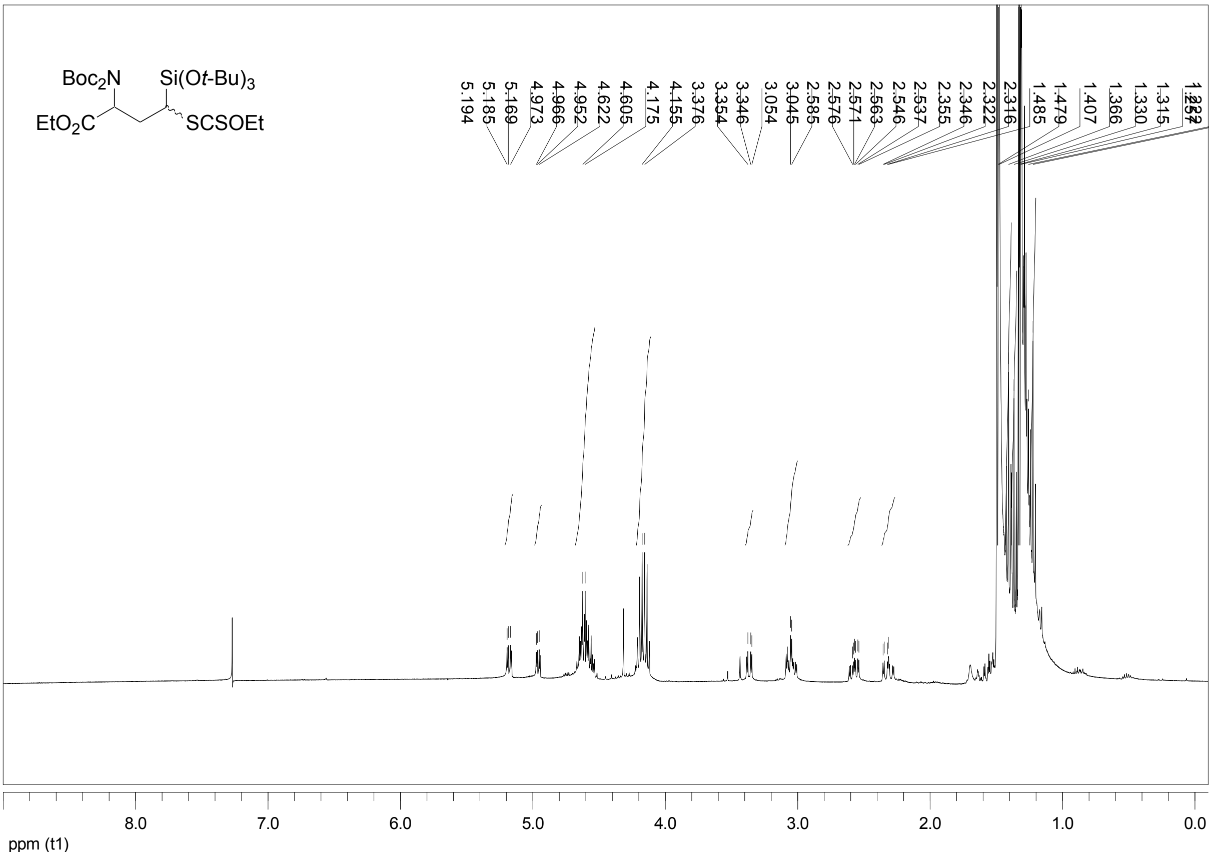

217.087
168.301
133.818
132.396
123.161
77.140
73.989
70.196
37.154
33.824
31.797
30.811
13.942
O
N
O
SCSOEt
Si(Ot-Bu)3
200
150
100
50
ppm (t1)

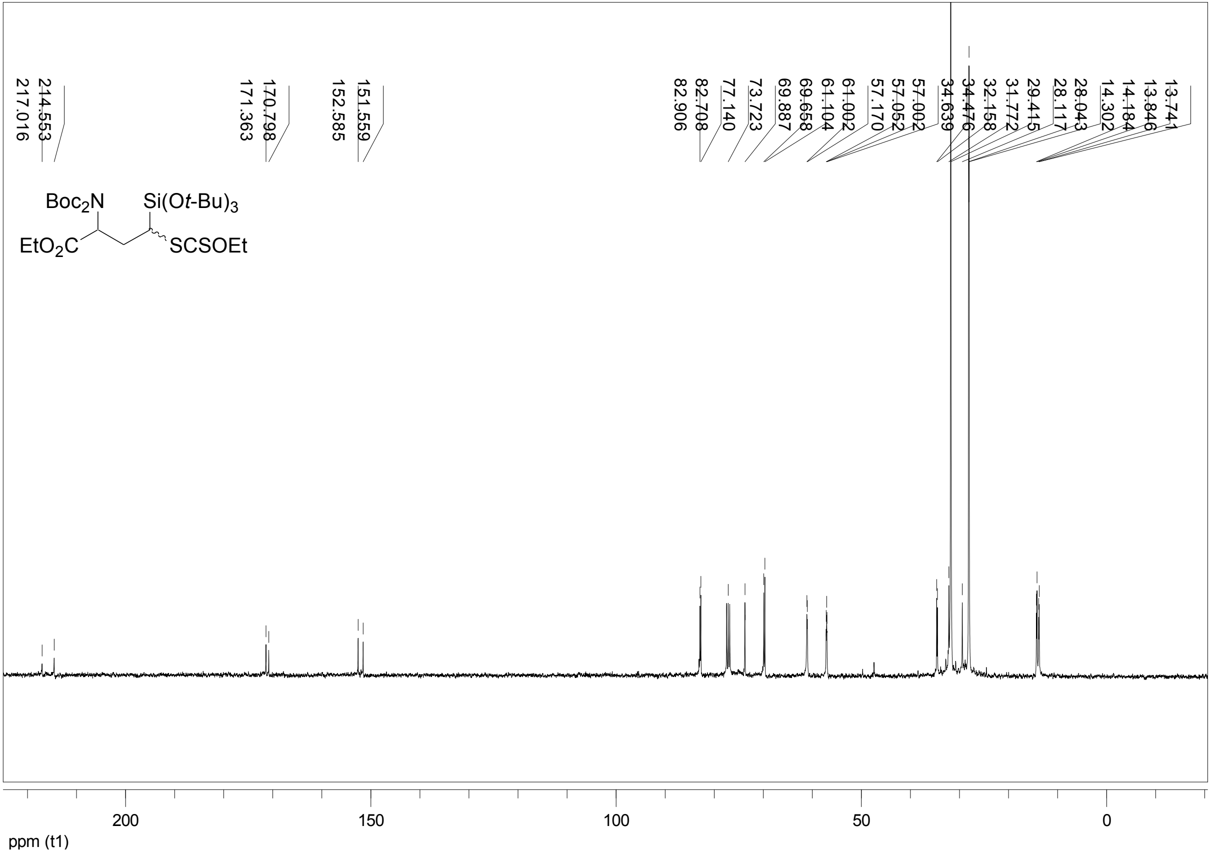
Compound 6l (major diastereoisomer)



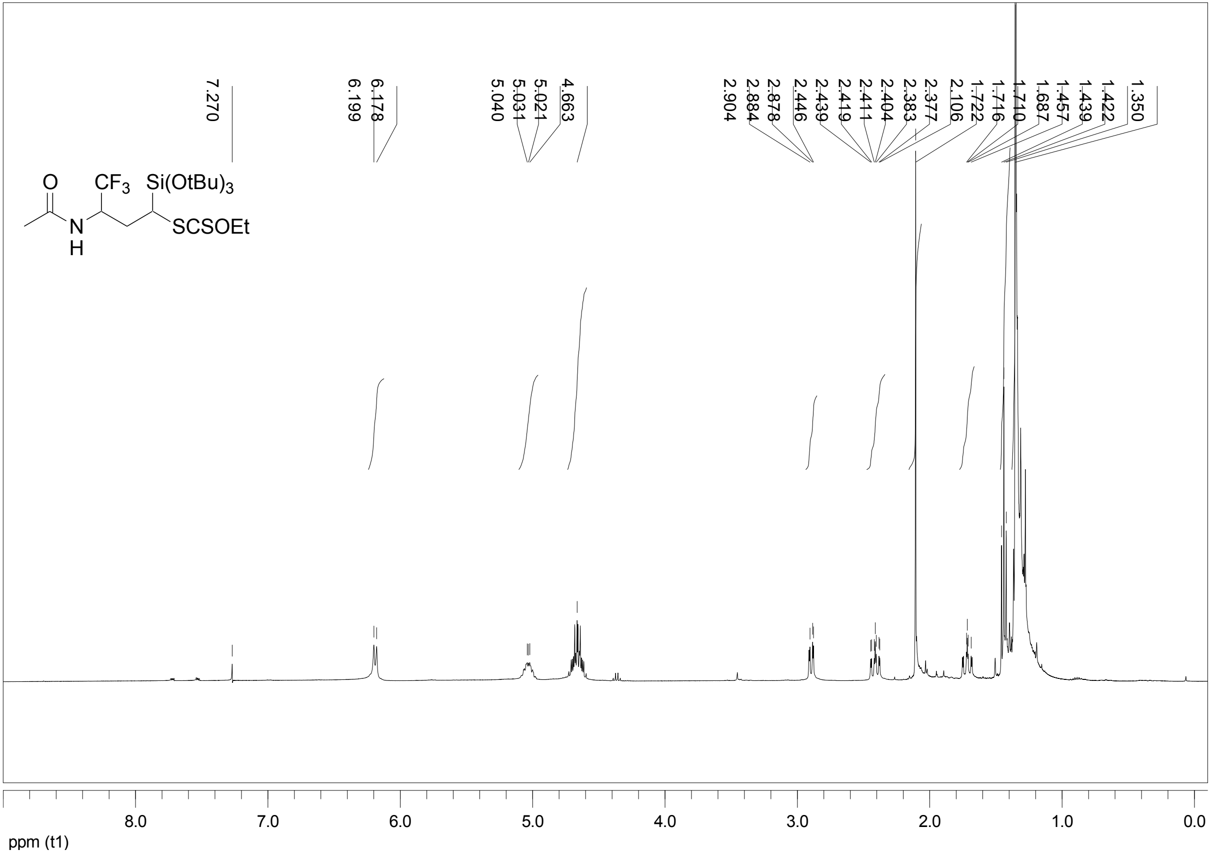


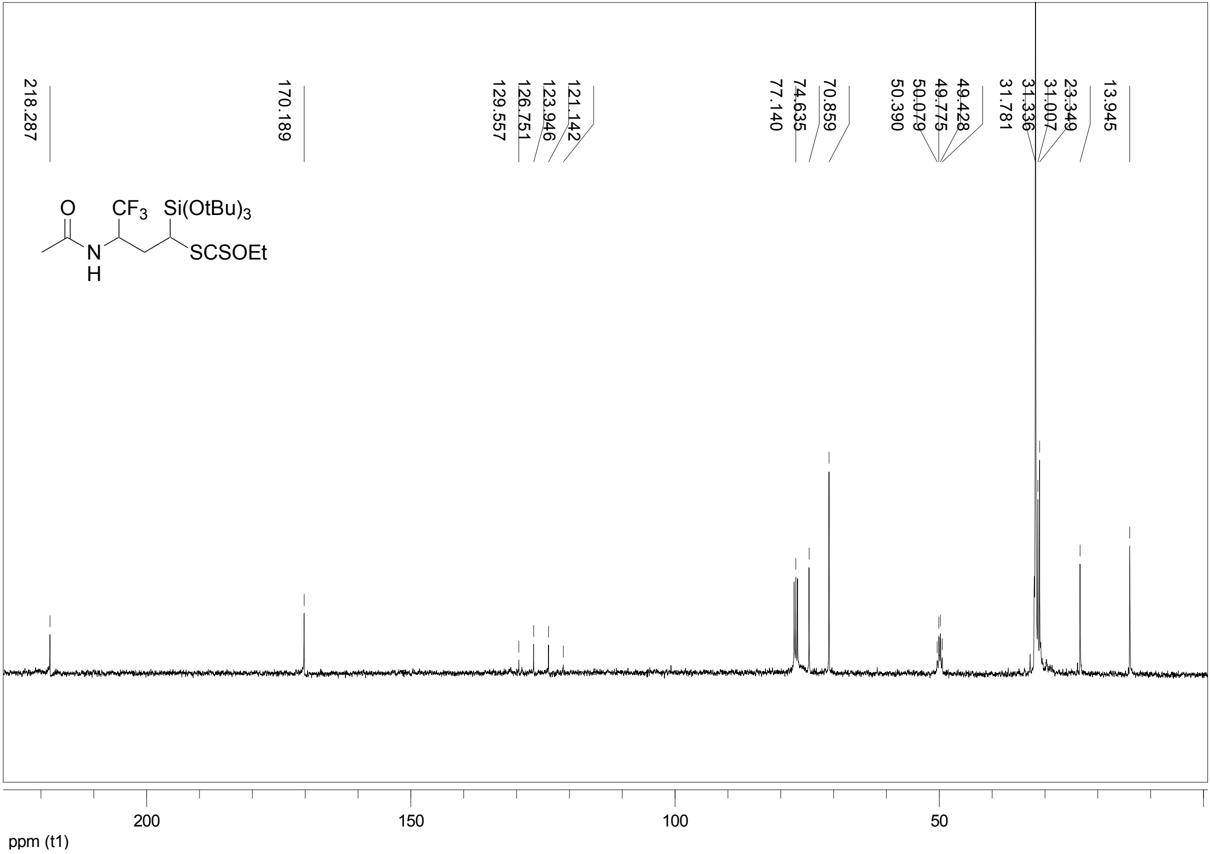
Compound 6l (mixture of 2 diastereoisomers)



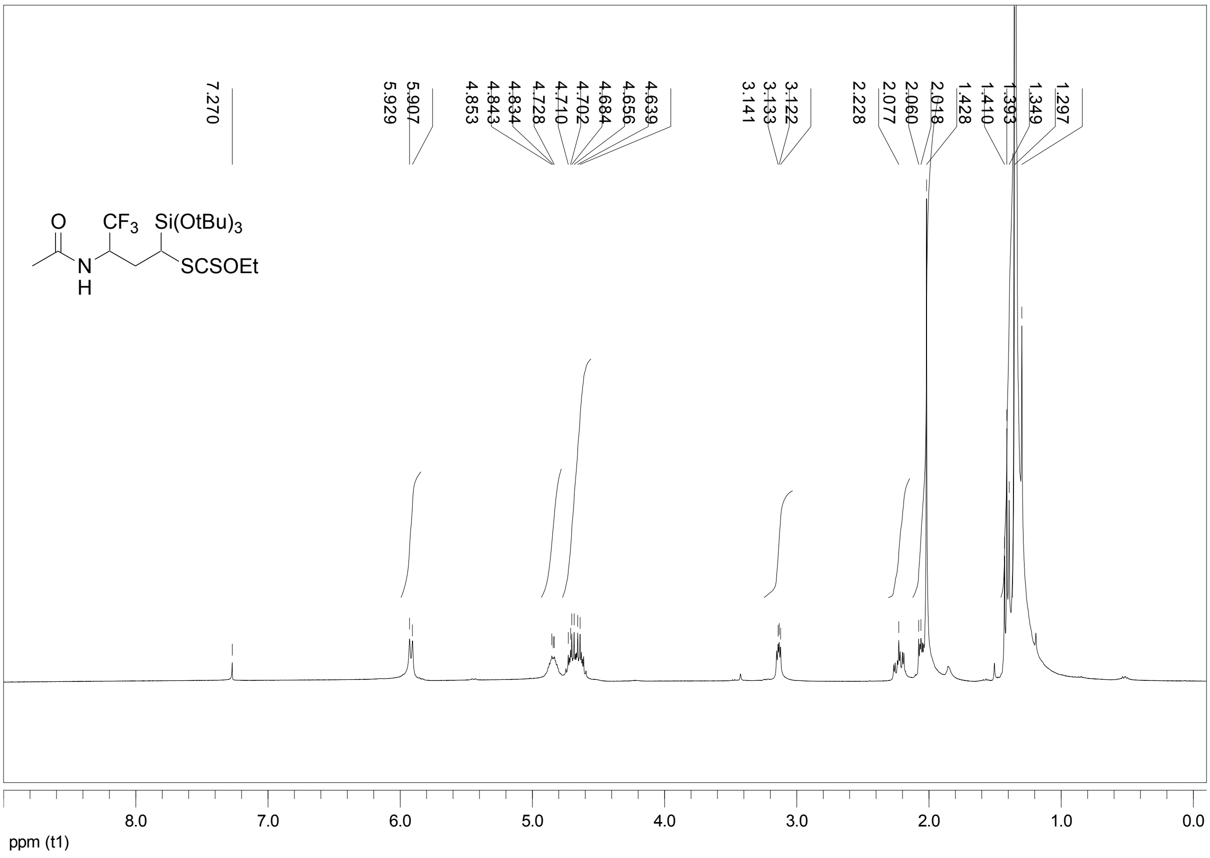


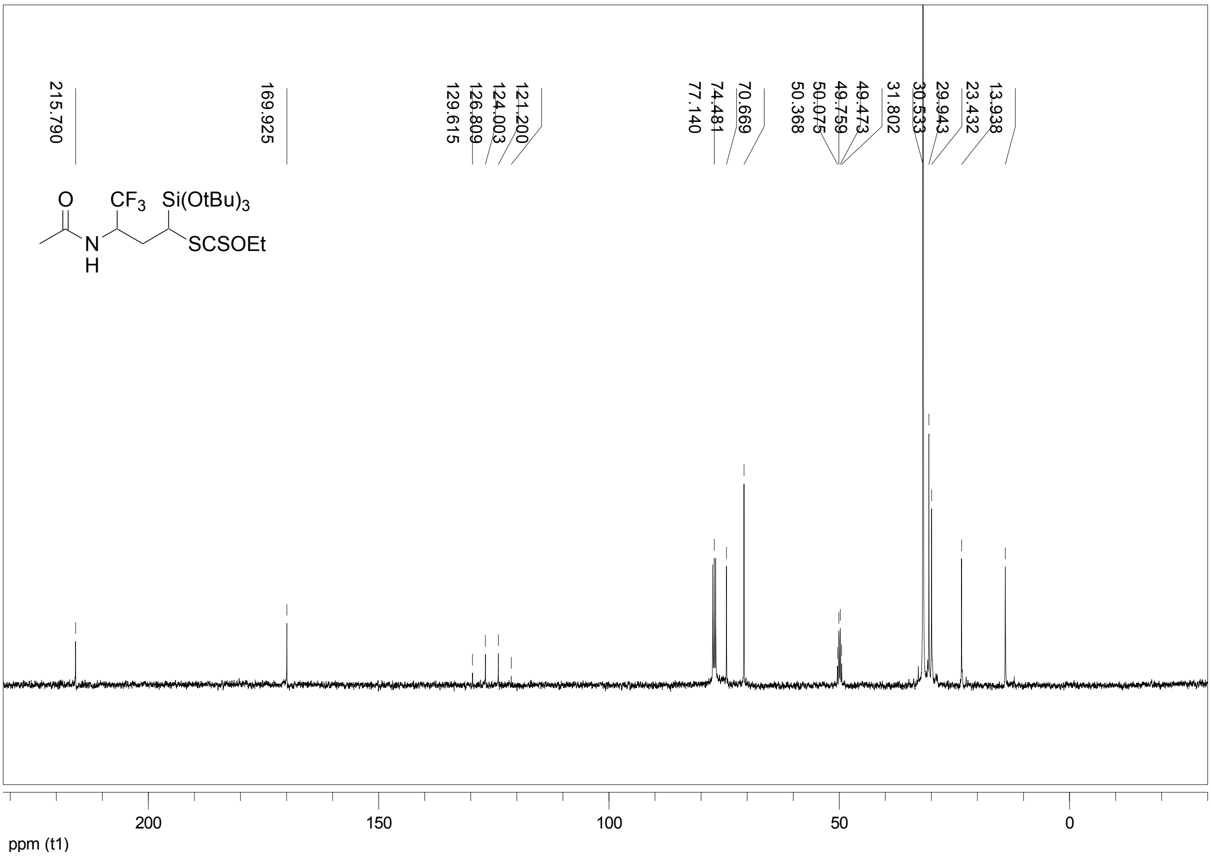
Compound 6m (major isomer)



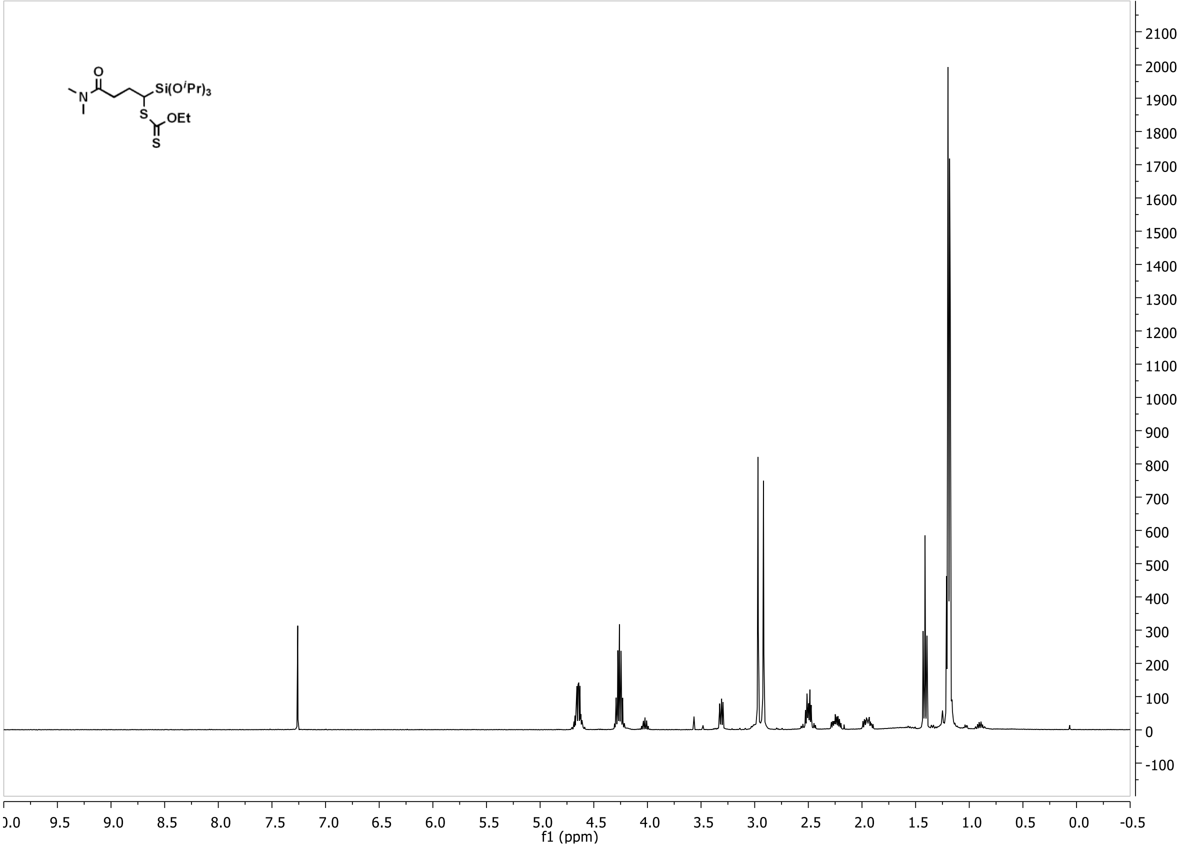


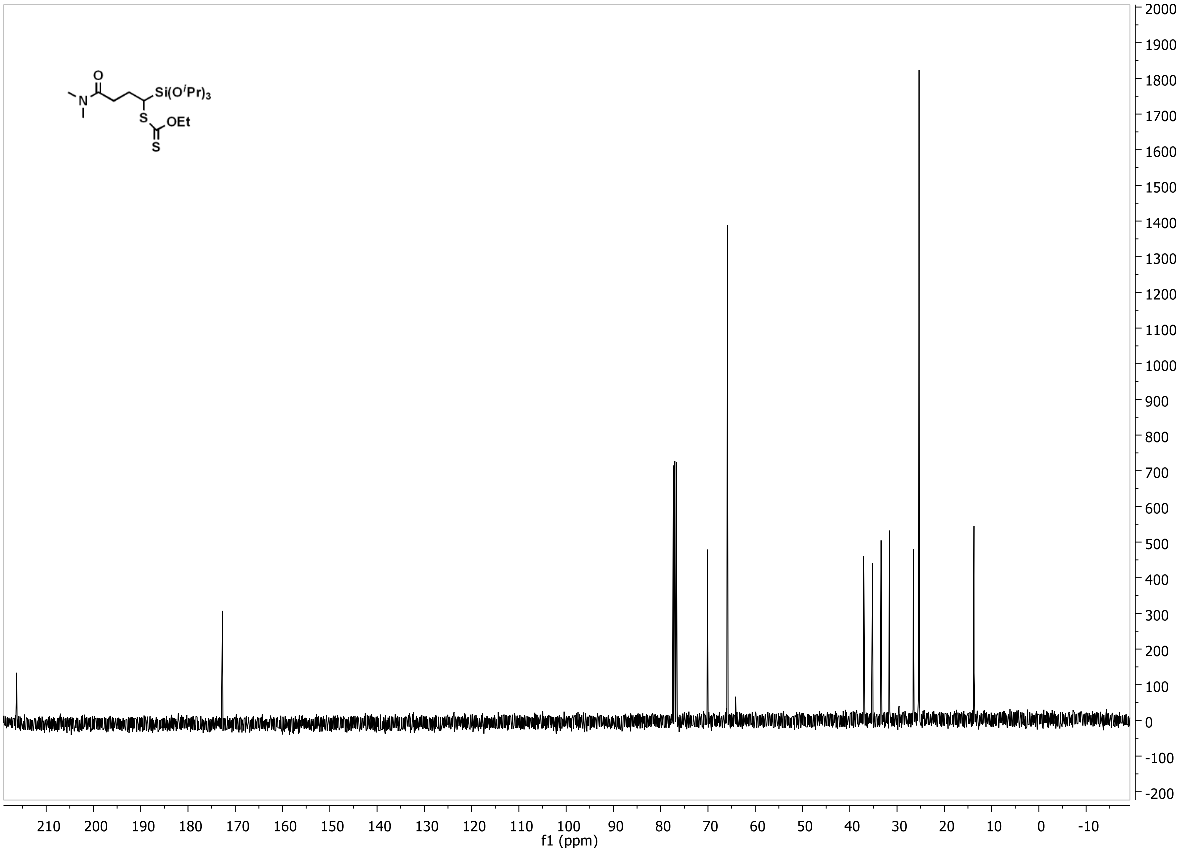
Compound 6m (minor isomer)



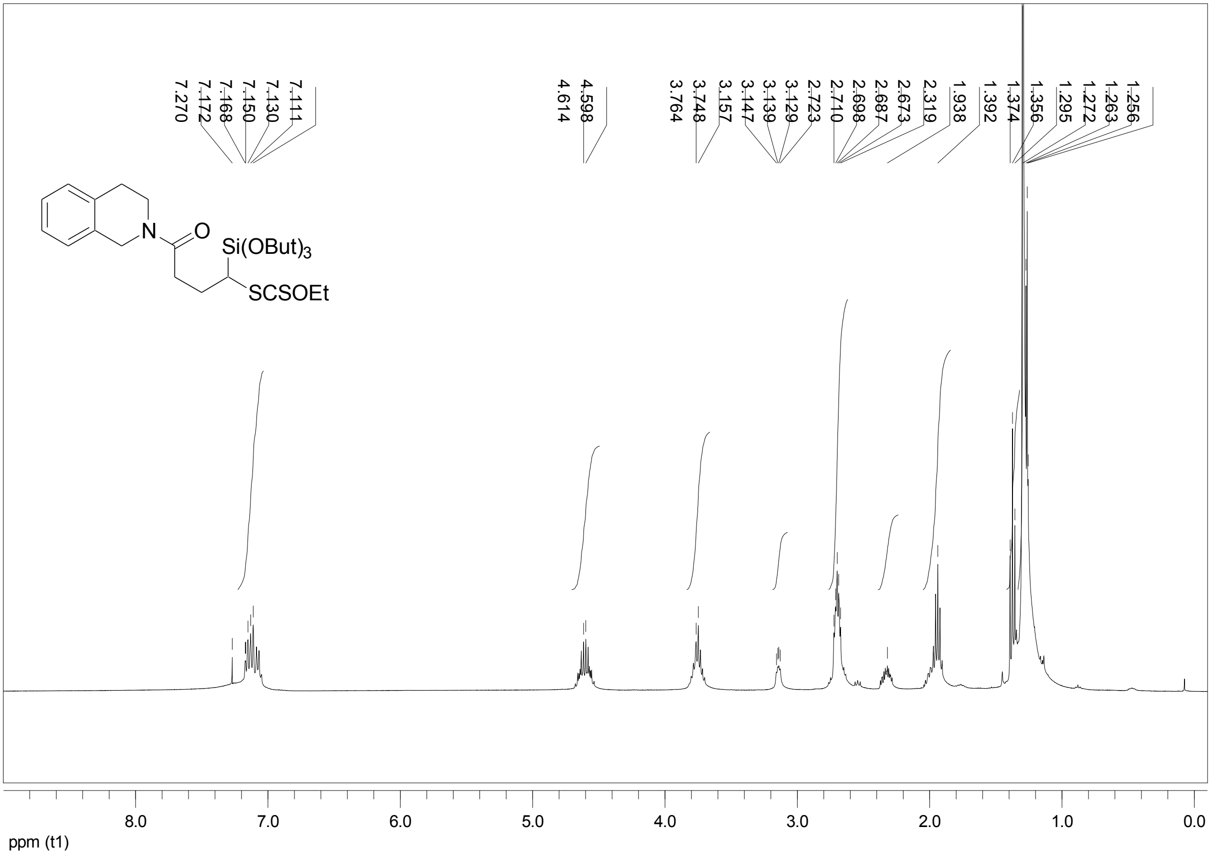


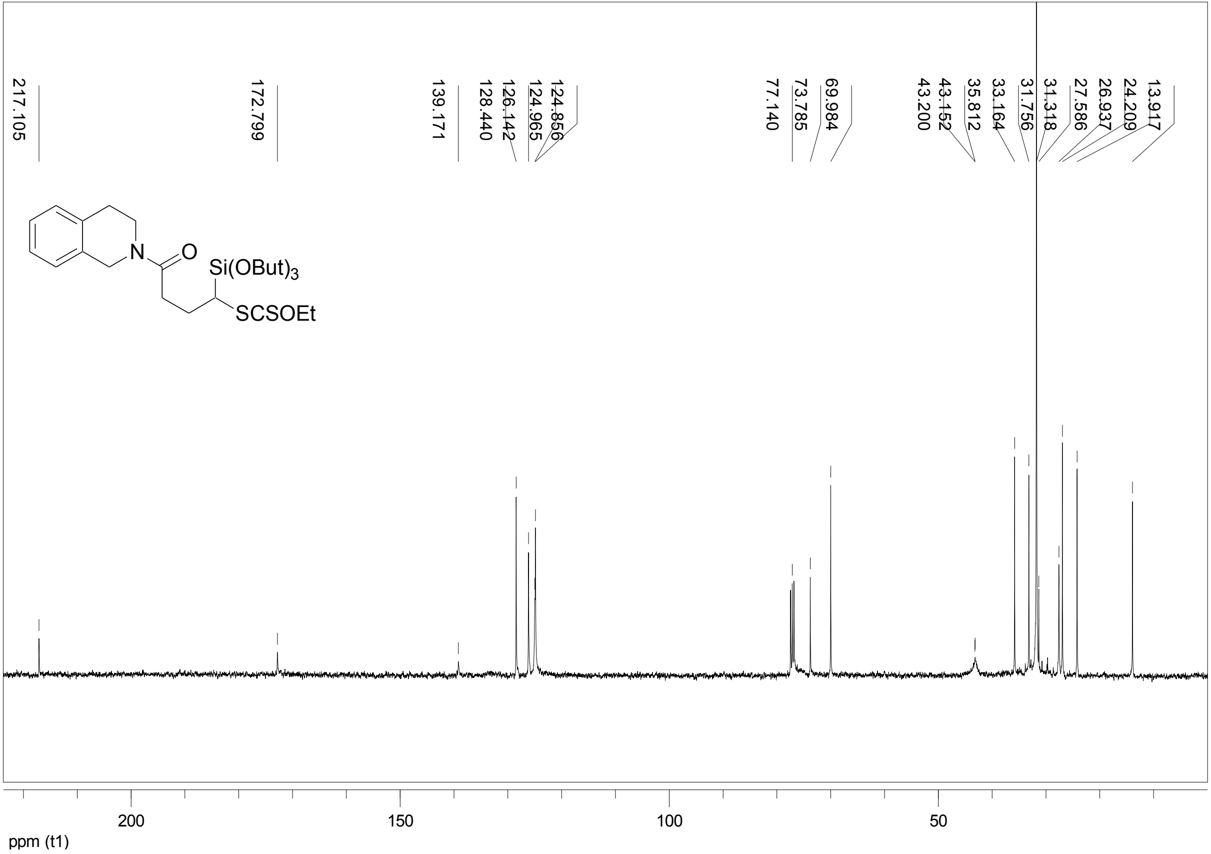
Compound 6n


O
N
Si(O^{i}Pr)$_3$
S
OEt
S
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

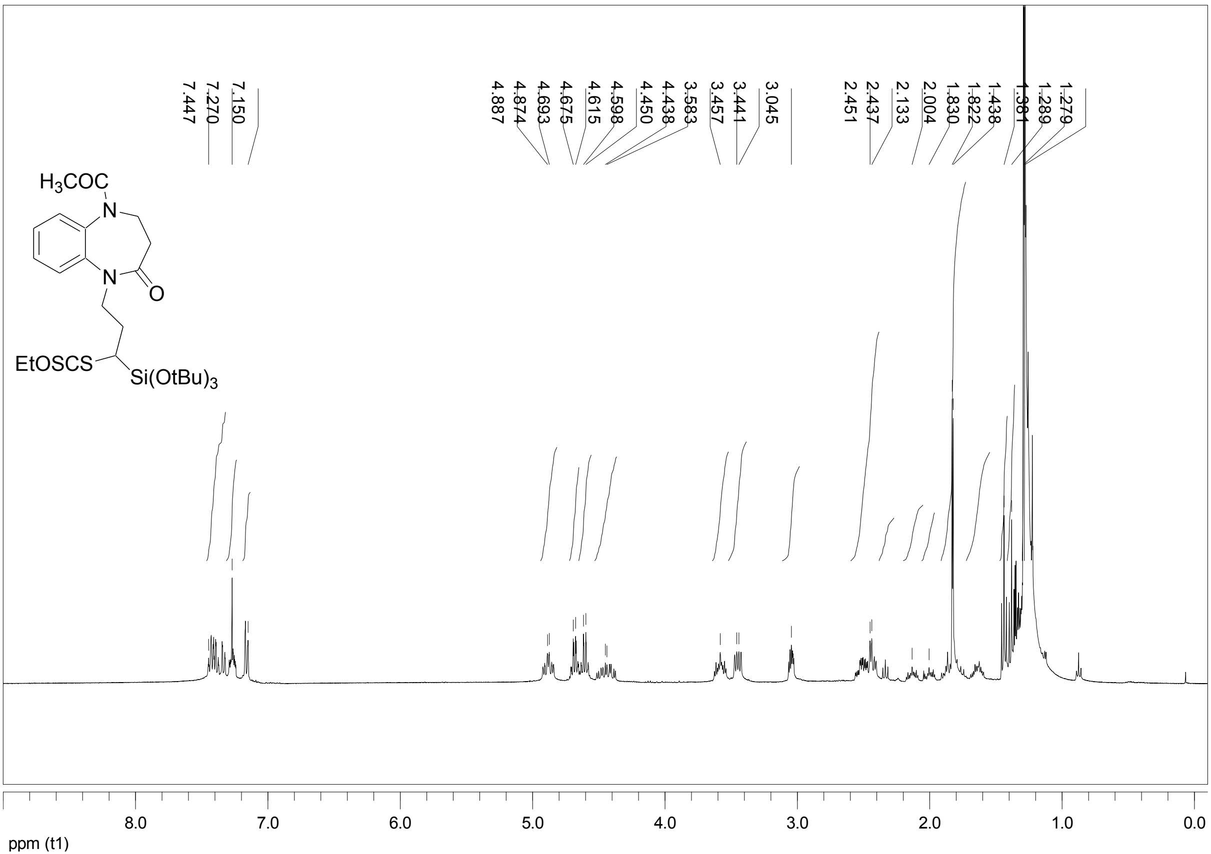

O
N
Si(O^{i}Pr)$_3$
S
OEt
S
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

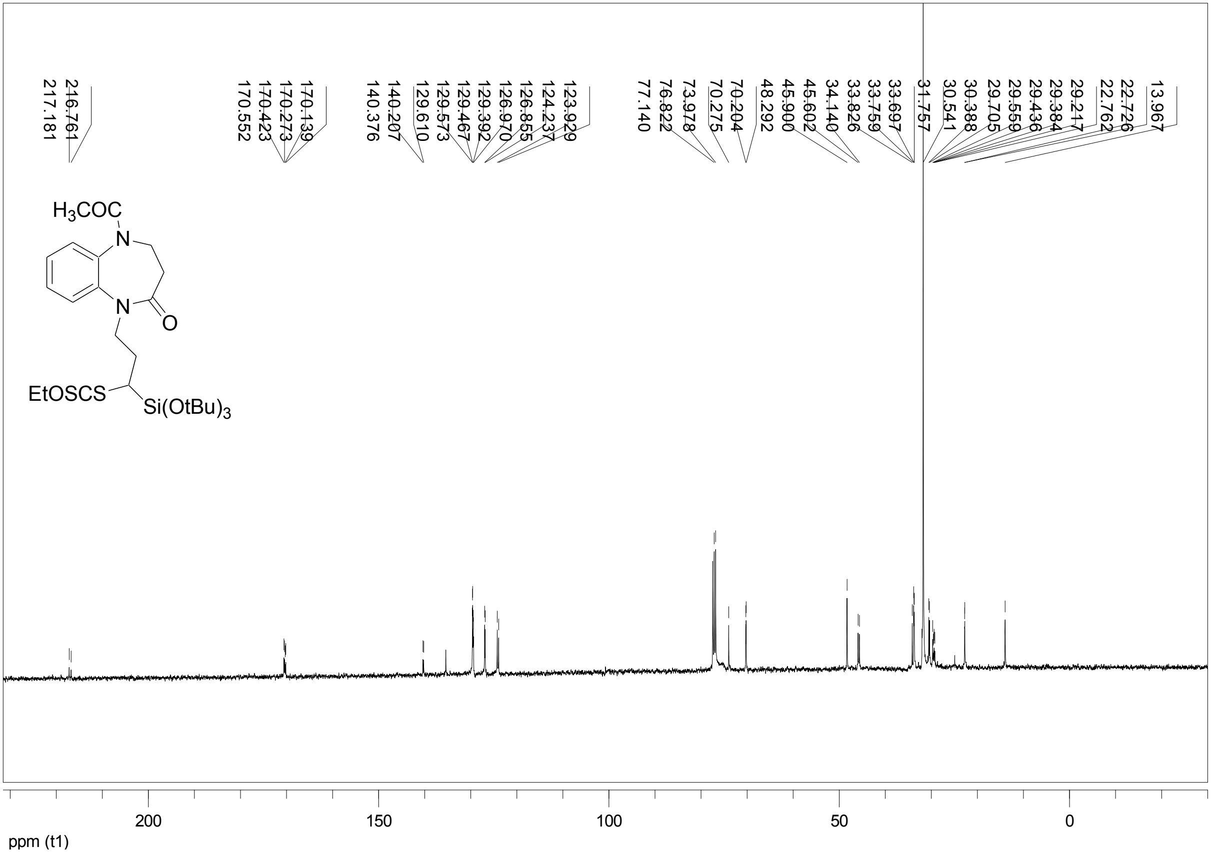
Compound 6o


7.270
7.172
7.168
7.150
7.130
7.111
4.614
4.598
3.764
3.748
3.157
3.147
3.139
3.129
2.723
2.710
2.698
2.687
2.673
2.319
1.938
1.392
1.374
1.356
1.295
1.272
1.263
1.256
N
O
Si(OBut)3
SCSOEt
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

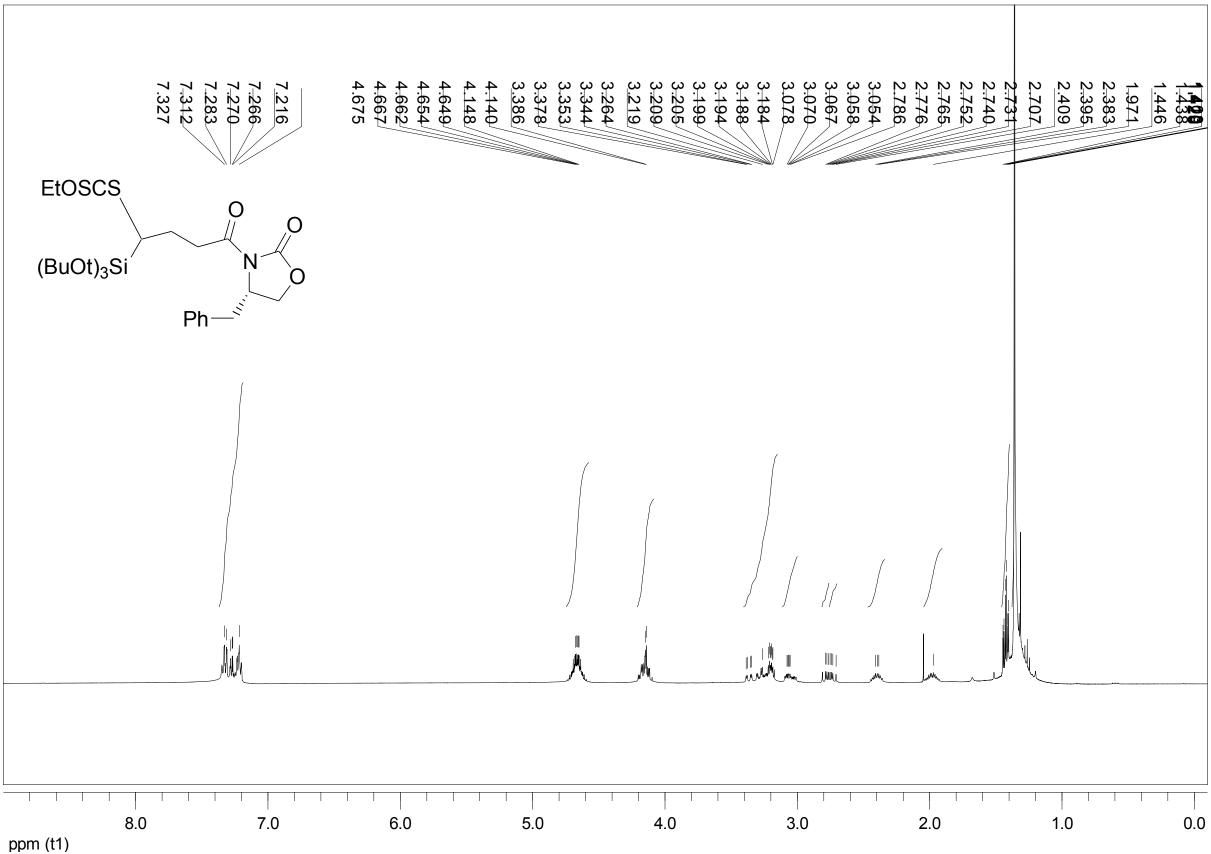

217.105
172.799
139.171
128.440
126.142
124.965
124.856
77.140
73.785
69.984
43.200
43.152
35.812
33.164
31.756
31.318
27.586
26.937
24.209
13.917
N
O
Si(OBut)3
SCSOEt
200
150
100
50
ppm (t1)

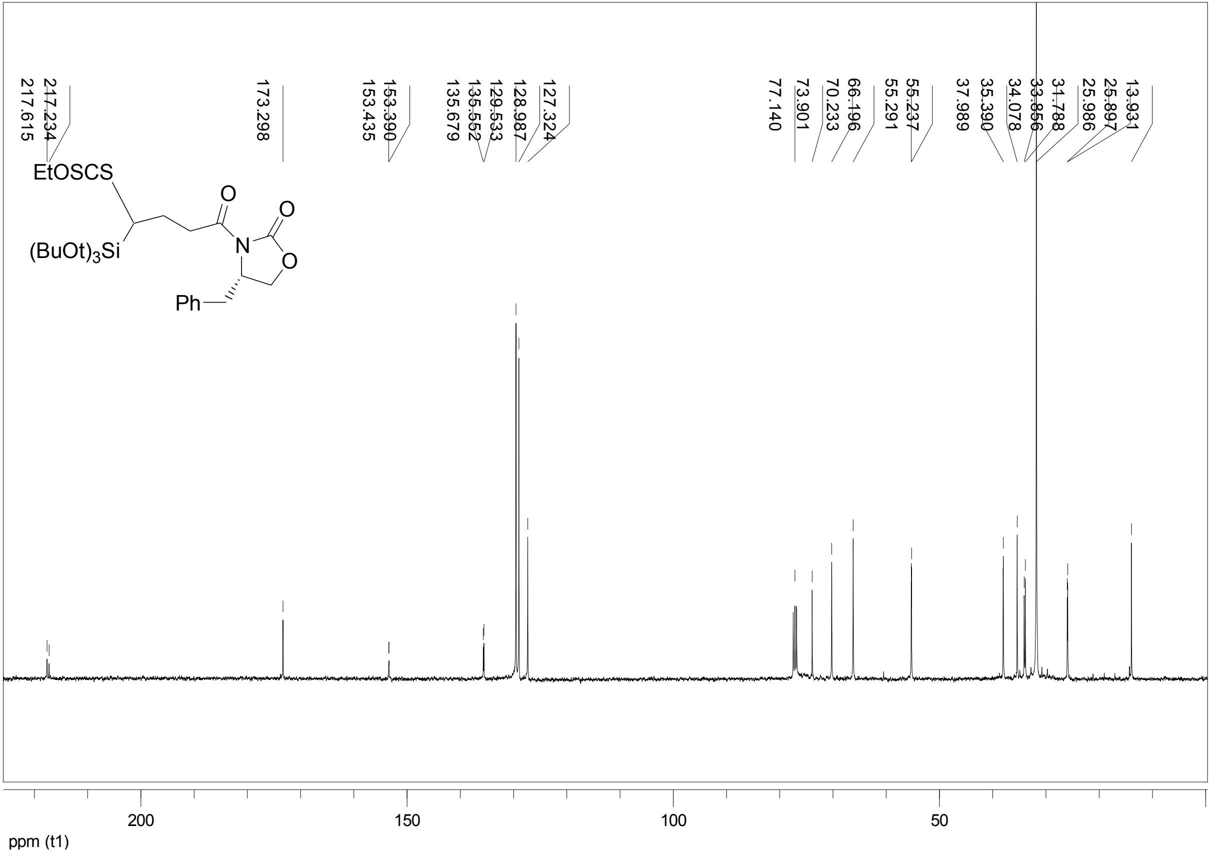
Compound 6p

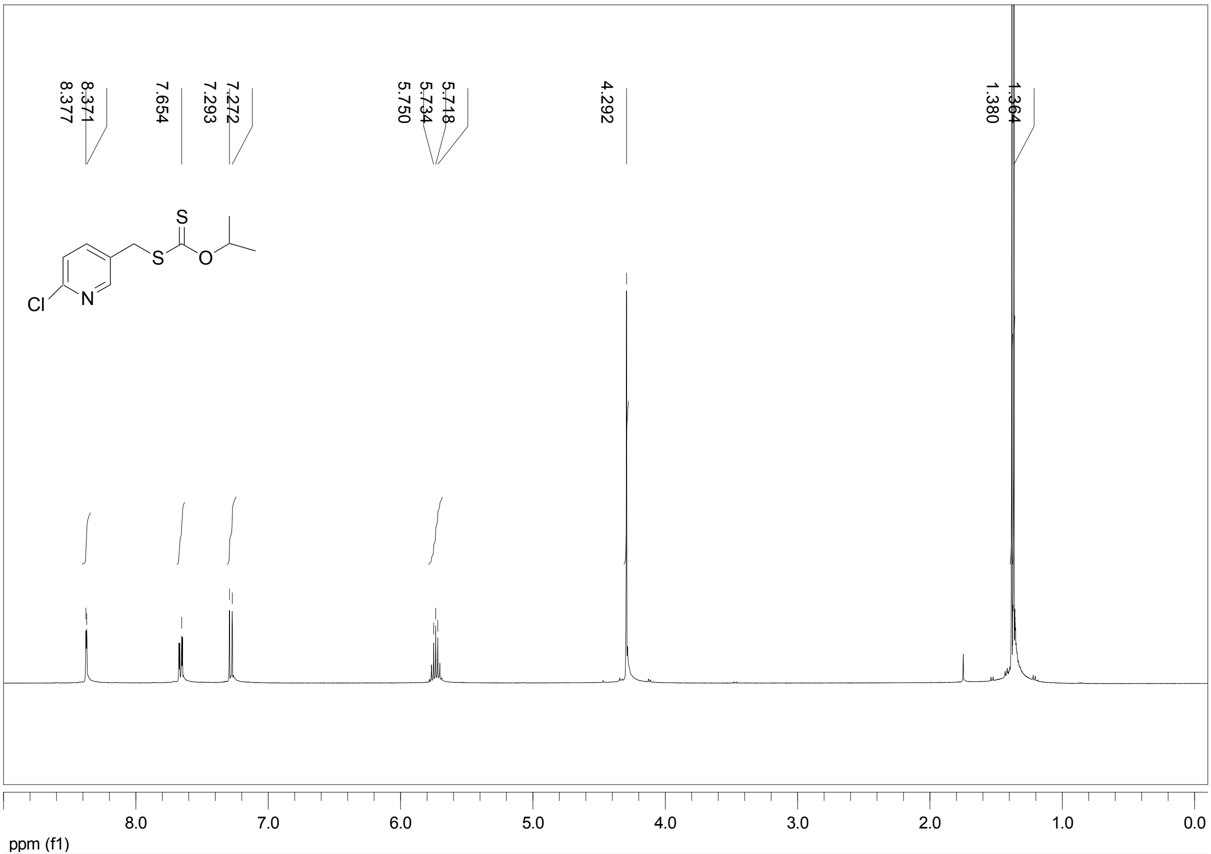

7.447
7.270
7.150
4.887
4.874
4.693
4.675
4.615
4.598
4.450
4.438
3.583
3.457
3.441
3.045
2.451
2.437
2.133
2.004
1.830
1.822
1.438
1.381
1.289
1.279
H_3COC
N
N
O
EtOSCS
$Si(OtBu)_3$
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

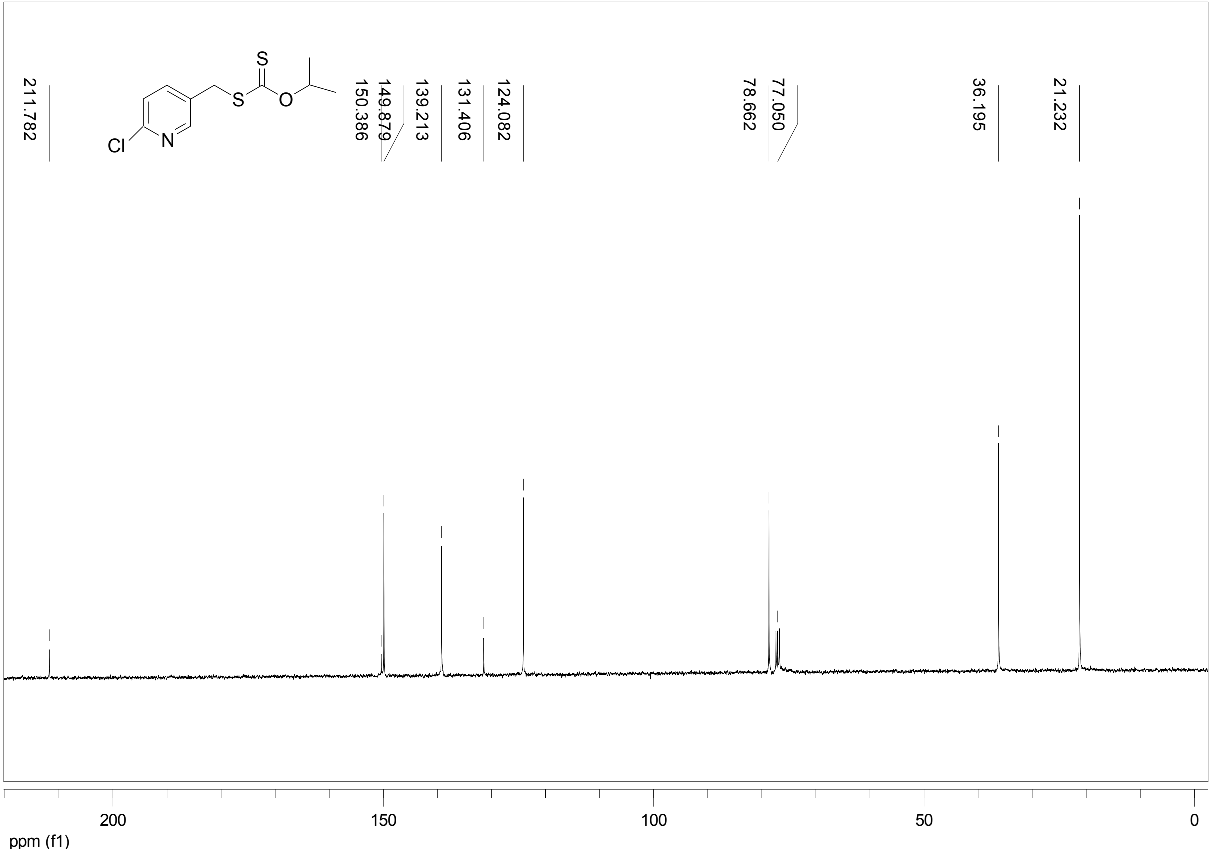

217.181
216.761
170.552
170.423
170.273
170.139
140.376
140.207
129.610
129.573
129.467
129.392
126.970
126.855
124.237
123.929
77.140
76.822
73.978
70.275
70.204
48.292
45.900
45.602
34.140
33.826
33.759
33.697
31.757
30.541
30.388
29.705
29.559
29.436
29.384
29.217
22.762
22.726
13.967
H_3COC
N
N
O
EtOSCS
$Si(OtBu)_3$
200
150
100
50
0
ppm (t1)

Compound 6q

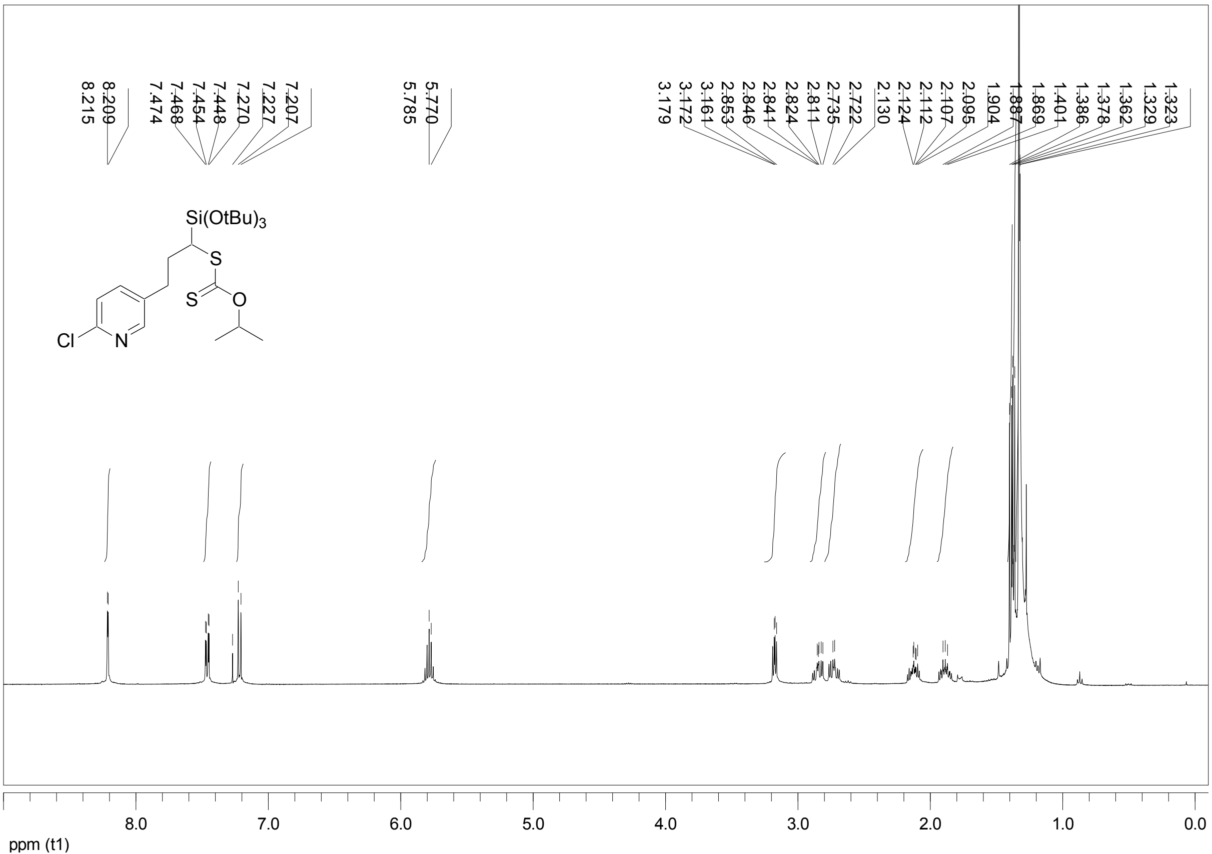

7.327
7.312
7.283
7.270
7.266
7.216
4.675
4.667
4.662
4.654
4.649
4.148
4.140
3.386
3.378
3.353
3.344
3.264
3.219
3.209
3.205
3.199
3.194
3.188
3.184
3.078
3.070
3.067
3.058
3.054
2.786
2.776
2.765
2.752
2.740
2.731
2.707
2.409
2.395
2.383
1.971
1.446
1.438
EtOSCS
O
O
N
O
(BuOt)3Si
Ph
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

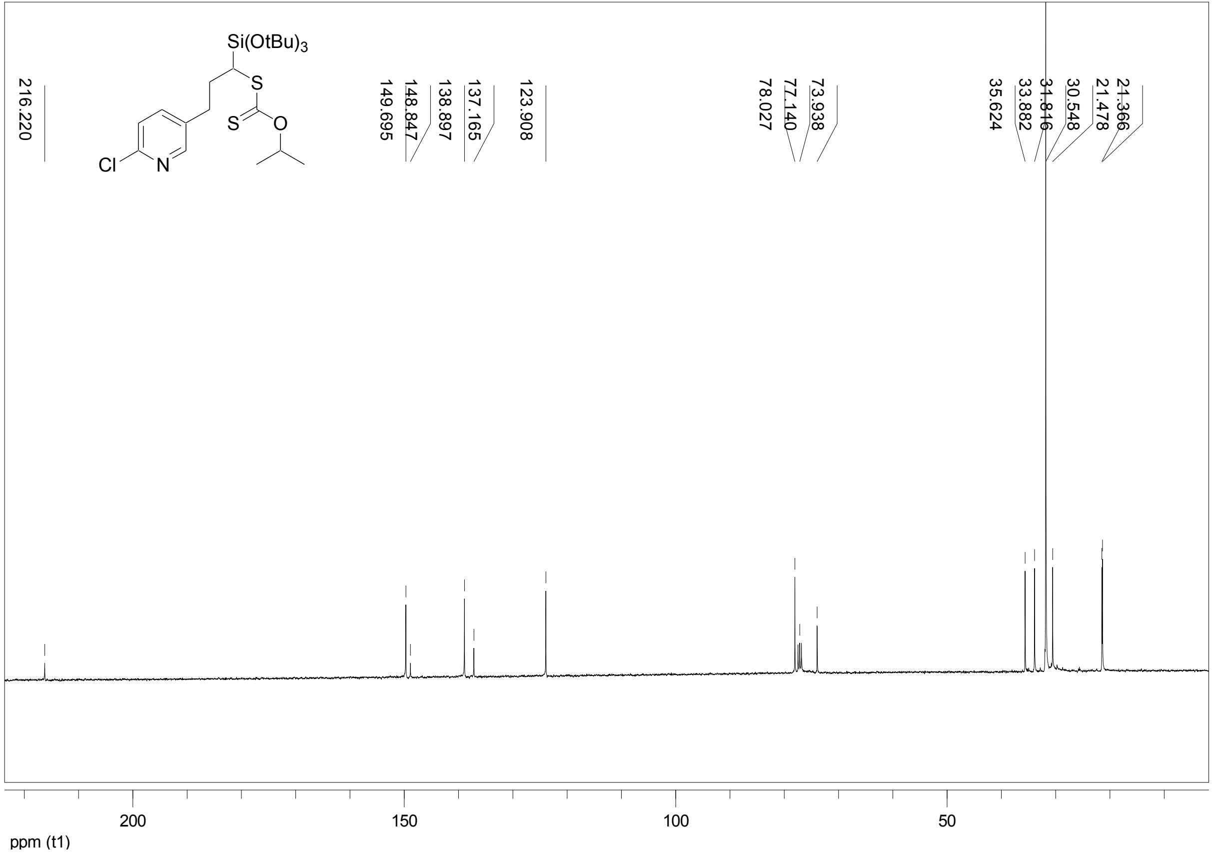

217.615
217.234
173.298
153.435
153.390
135.679
135.552
129.533
128.987
127.324
77.140
73.901
70.233
66.196
55.291
55.237
37.989
35.390
34.078
33.856
31.788
25.986
25.897
13.931
EtOSCS
O
O
N
O
(BuOt)3Si
Ph
200
150
100
50
ppm (t1)

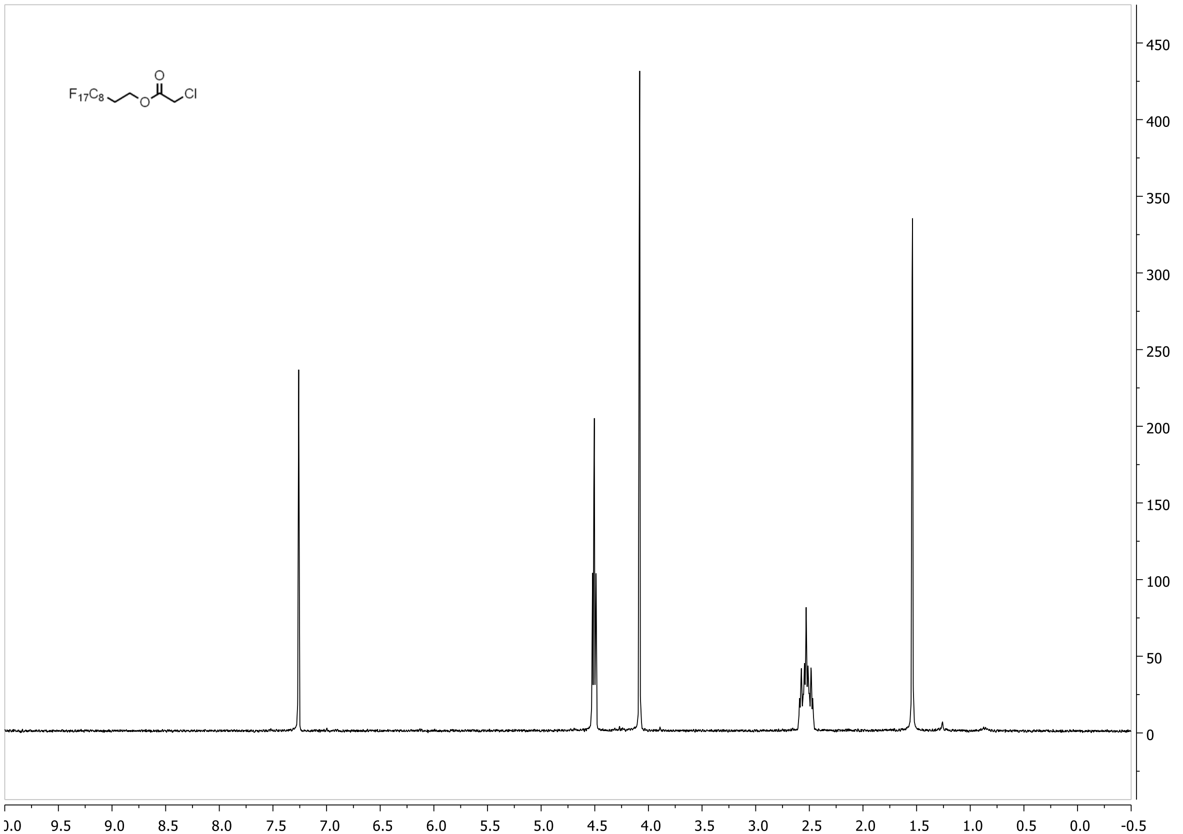

8.377
8.371
7.654
7.293
7.272
5.750
5.734
5.718
4.292
1.380
1.364
S
S
O
Cl
N
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

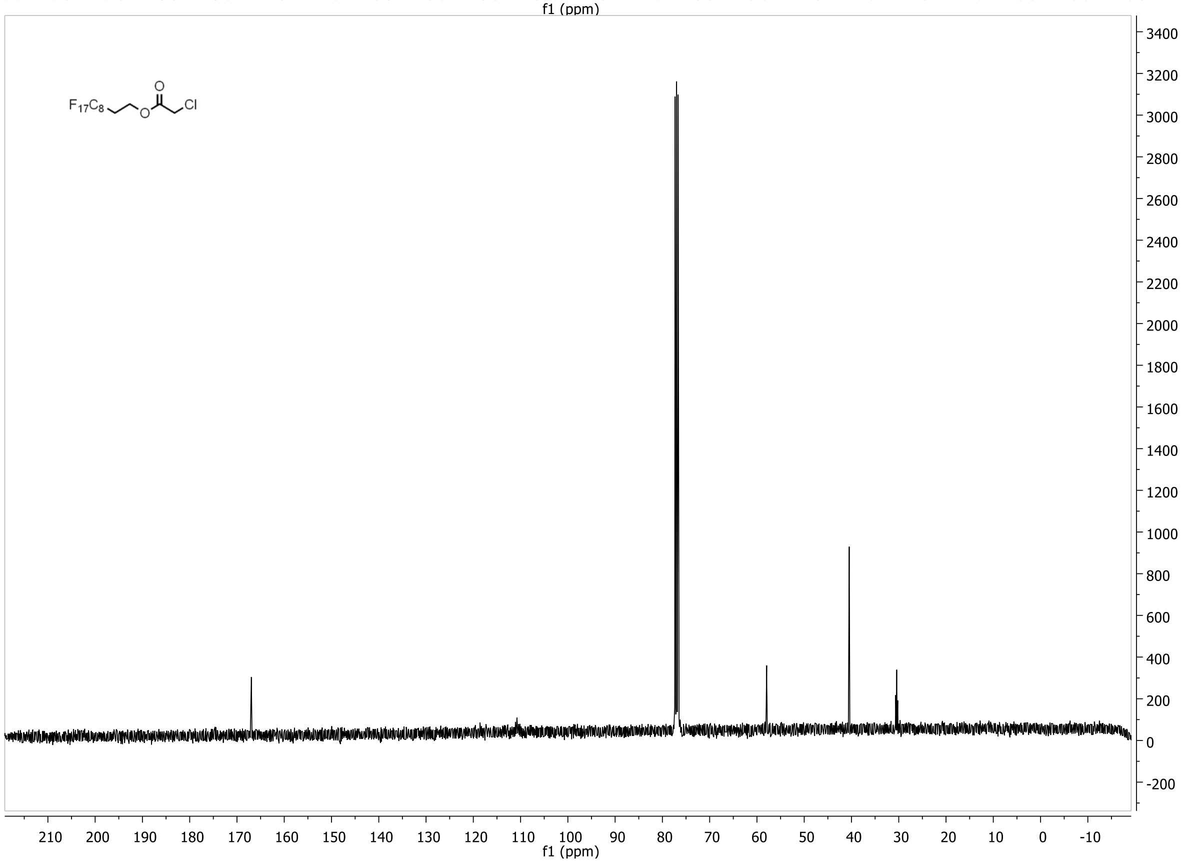

211.782
150.386
149.879
139.213
131.406
124.082
78.662
77.050
36.195
21.232
S
S
O
Cl
N
200
150
100
50
0
ppm (f1)

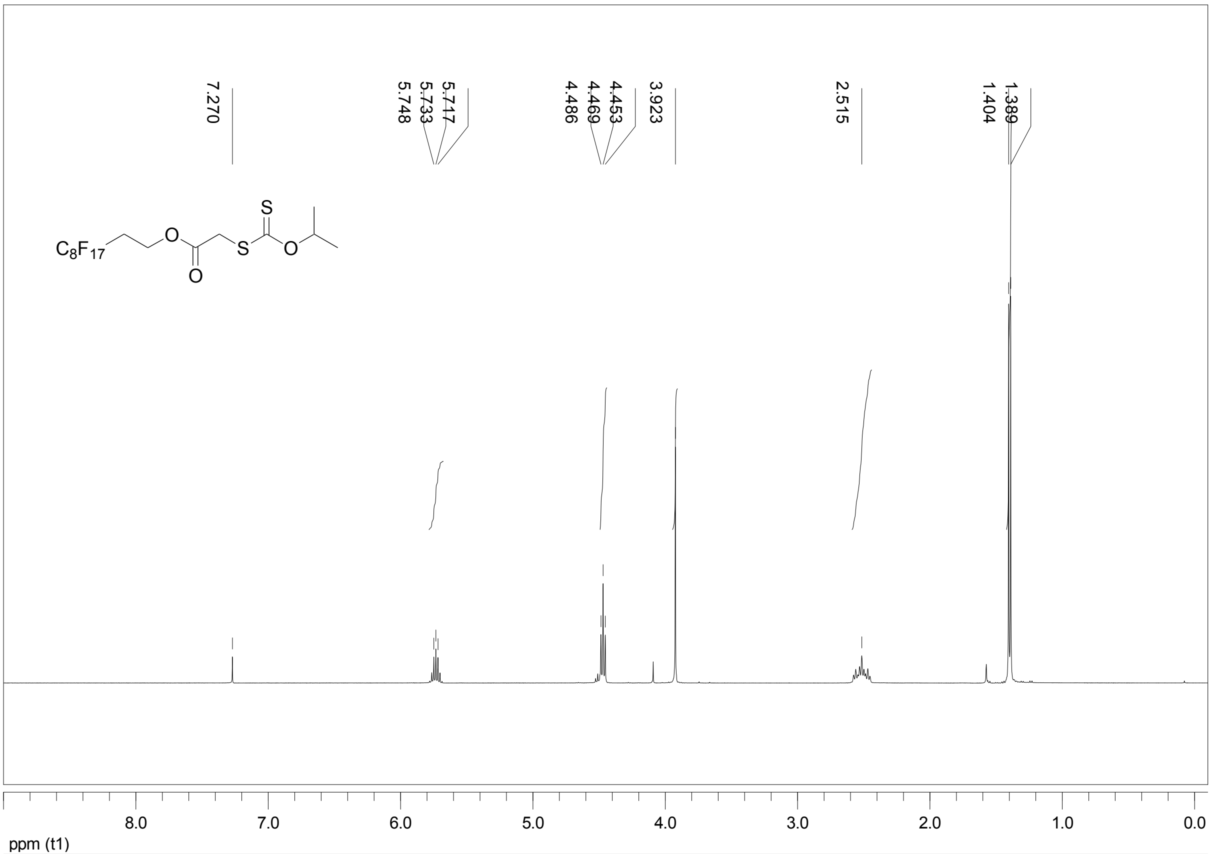
Compound 6r

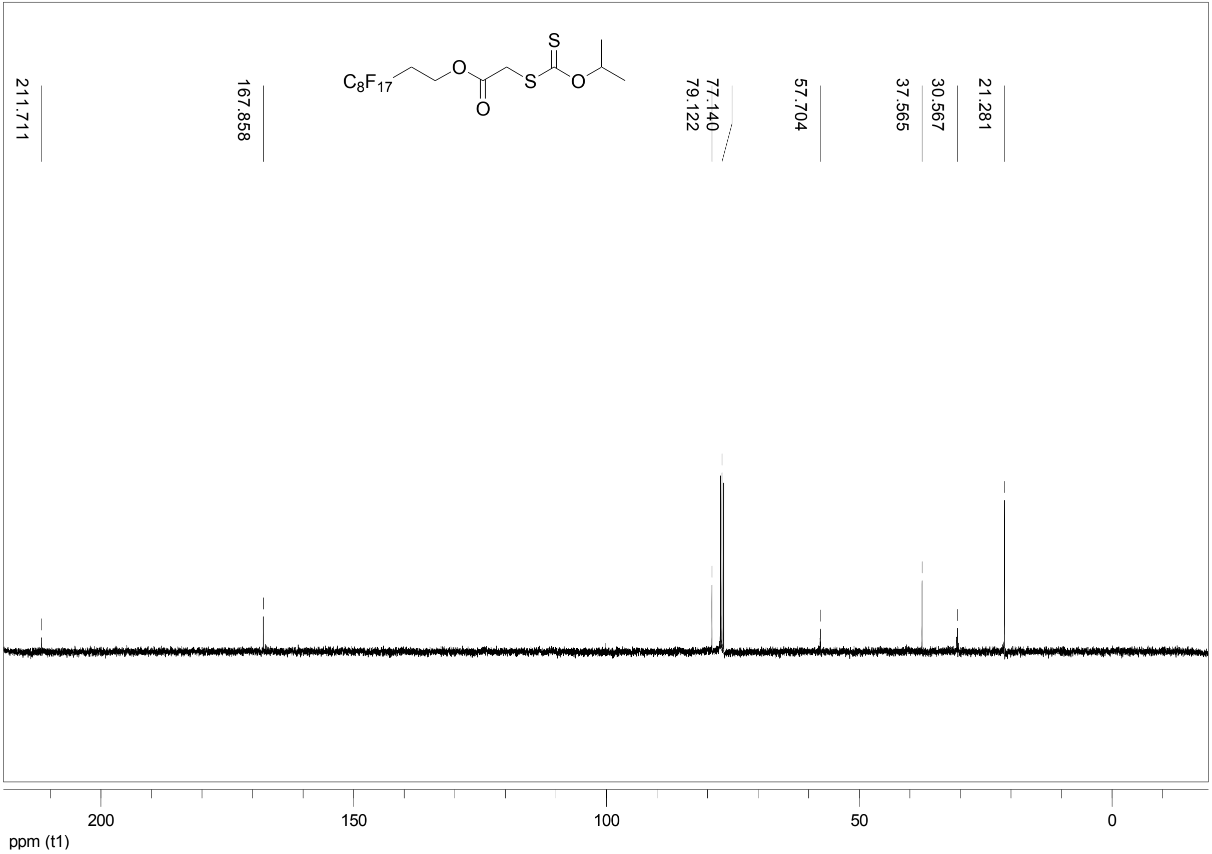

8.215
8.209
7.474
7.468
7.454
7.448
7.270
7.227
7.207
5.785
5.770
3.179
3.172
3.161
2.853
2.846
2.841
2.824
2.811
2.735
2.722
2.130
2.124
2.112
2.107
2.095
1.904
1.887
1.869
1.401
1.386
1.378
1.362
1.329
1.323
Si(OtBu)3
S
S
O
Cl
N
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


Si(OtBu)3
S
S
O
Cl
N
216.220
149.695
148.847
138.897
137.165
123.908
78.027
77.140
73.938
35.624
33.882
31.816
30.548
21.478
21.366
200
150
100
50
ppm (t1)

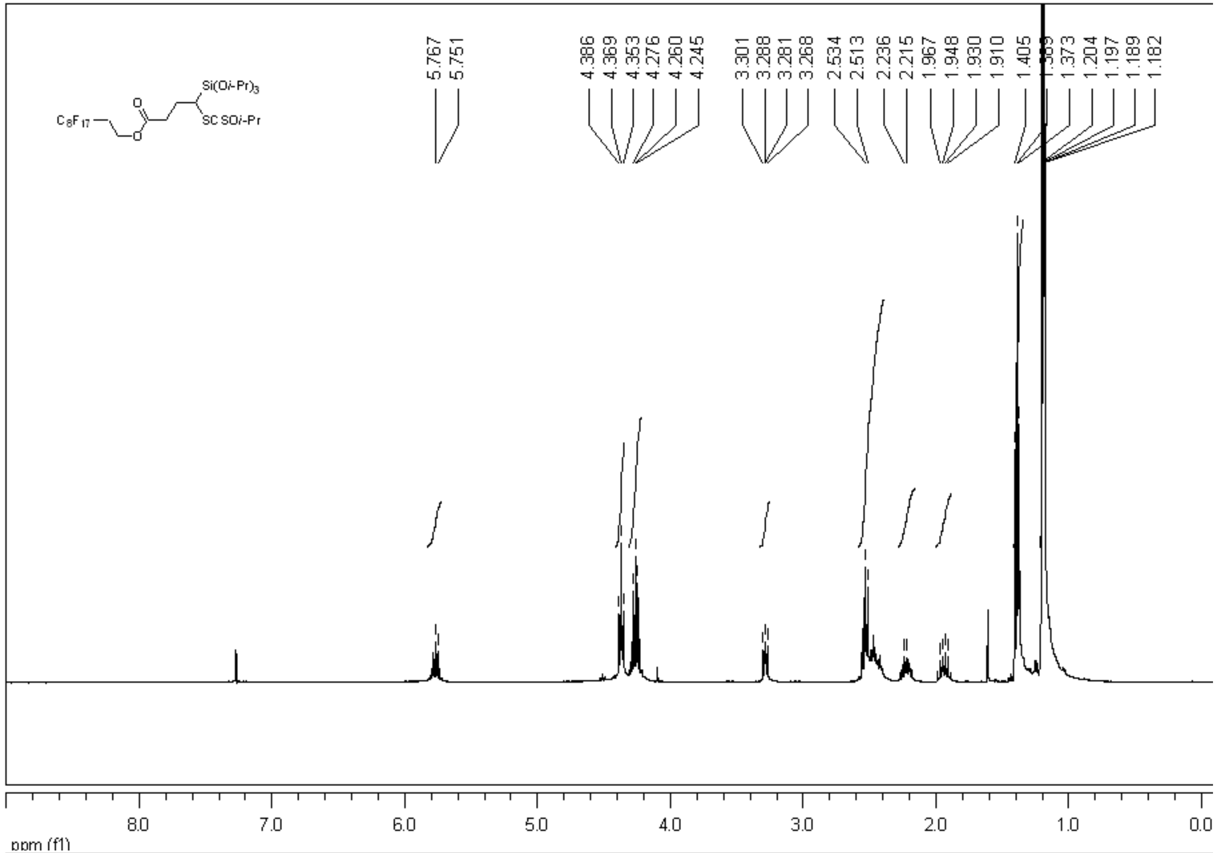

F17C8 O O Cl
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
450 400 350 300 250 200 150 100 50 0

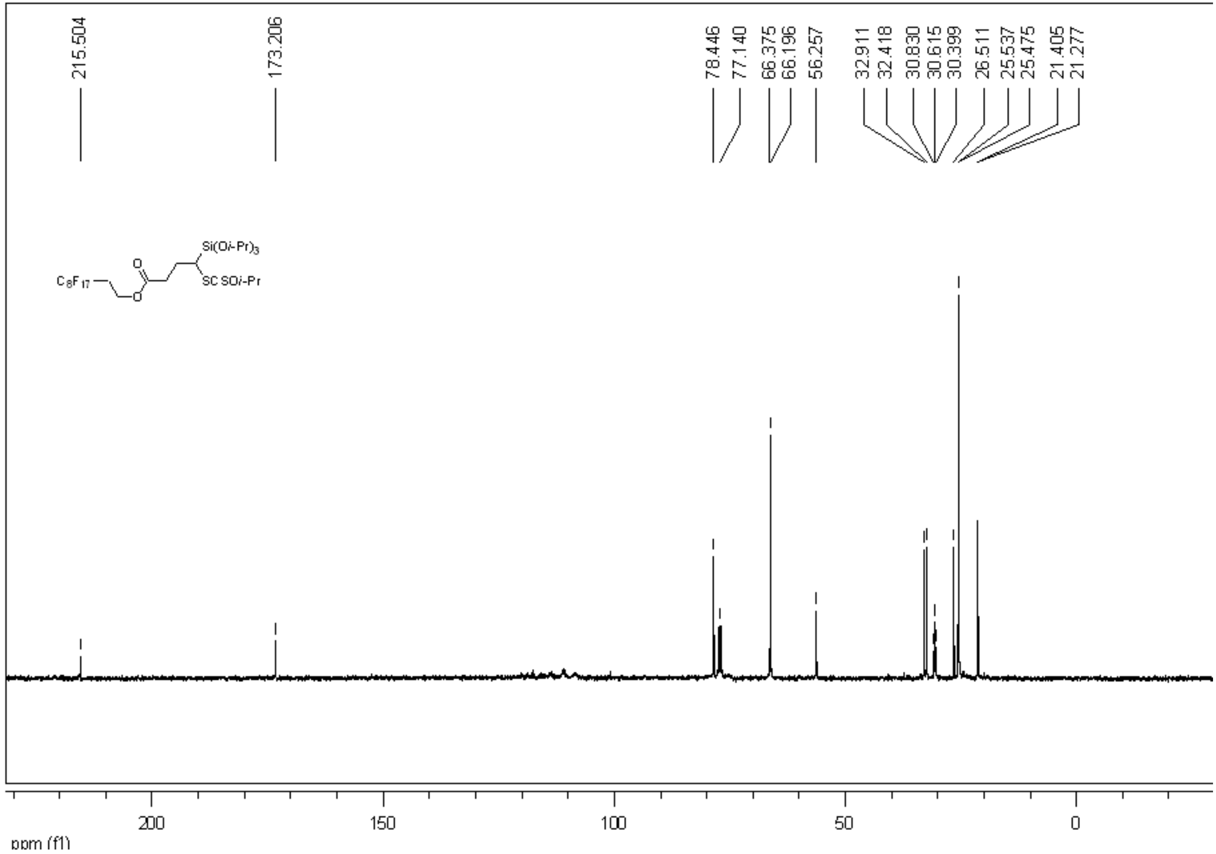

F17C8 O O Cl
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200


7.270
5.748
5.733
5.717
4.486
4.469
4.453
3.923
2.515
1.404
1.389
C_8F_{17}
O
O
S
S
O
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

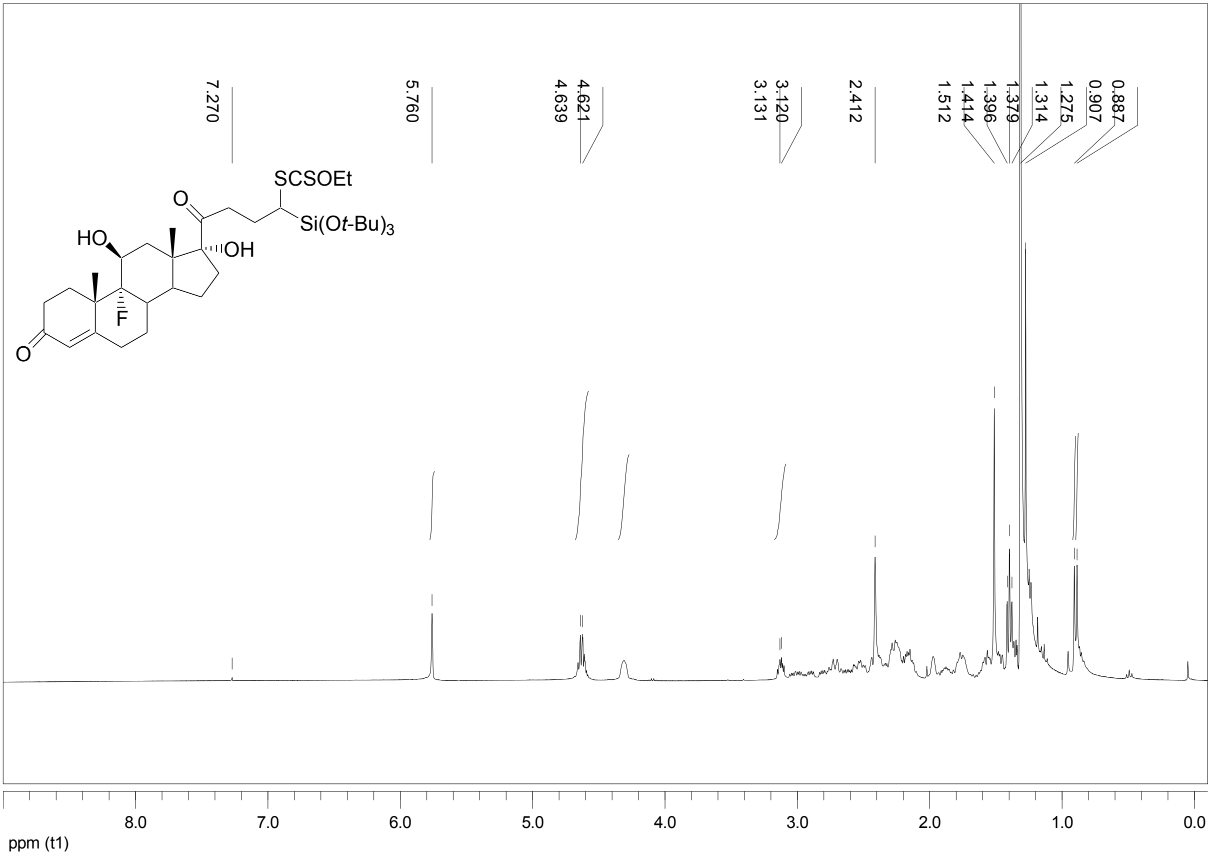

211.711
167.858
C_8F_{17}
O
O
S
S
O
79.122
77.140
57.704
37.565
30.567
21.281
200
150
100
50
0
ppm (t1)

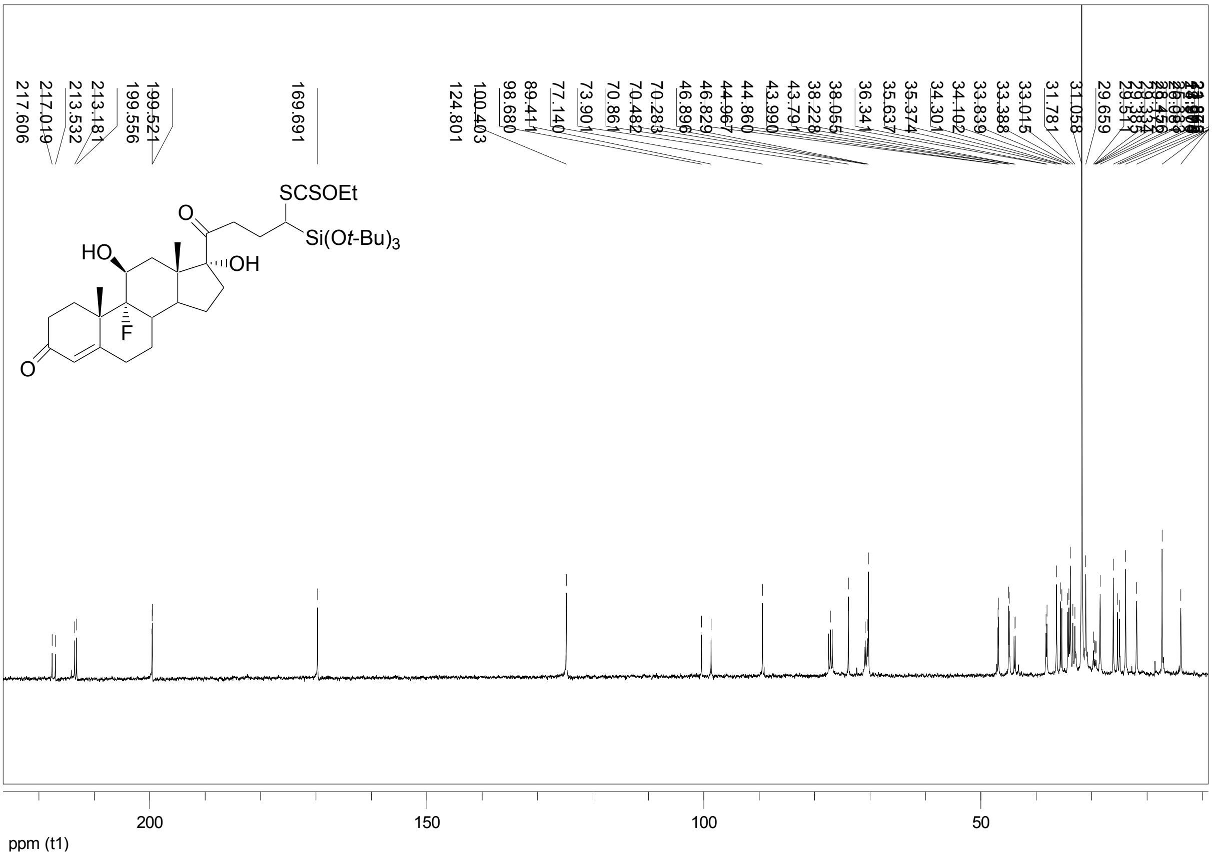
Compound 6s


5.767
5.751
4.386
4.369
4.353
4.276
4.260
4.245
3.301
3.288
3.281
3.268
2.534
2.513
2.236
2.215
1.967
1.948
1.930
1.910
1.405
1.389
1.373
1.204
1.197
1.189
1.182
Si(Oi-Pr)3
O
C8F17
O
SC SOi-Pr
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

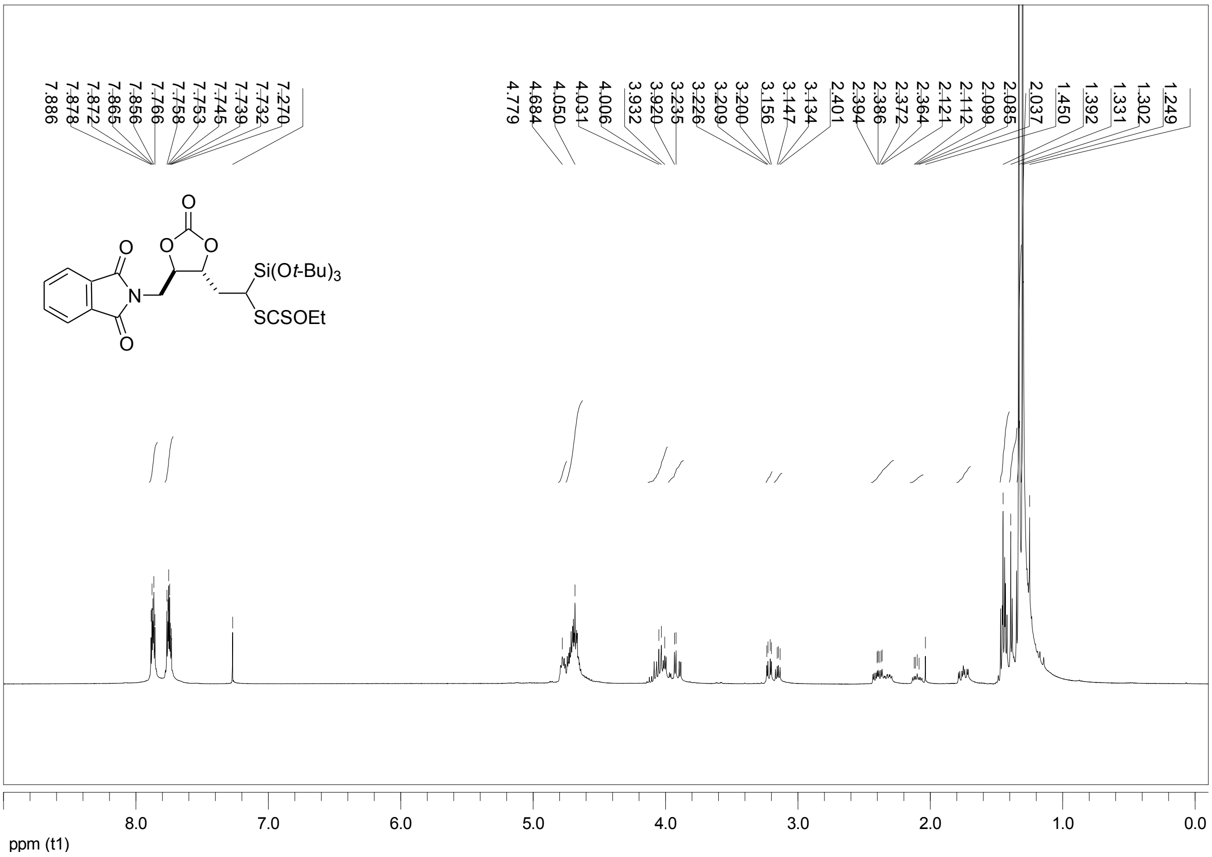

215.504
173.206
78.446
77.140
66.375
66.196
56.257
32.911
32.418
30.830
30.615
30.399
26.511
25.537
25.475
21.405
21.277
Si(Oi-Pr)3
O
C8F17
O
SC SOi-Pr
200
150
100
50
0
ppm (f1)

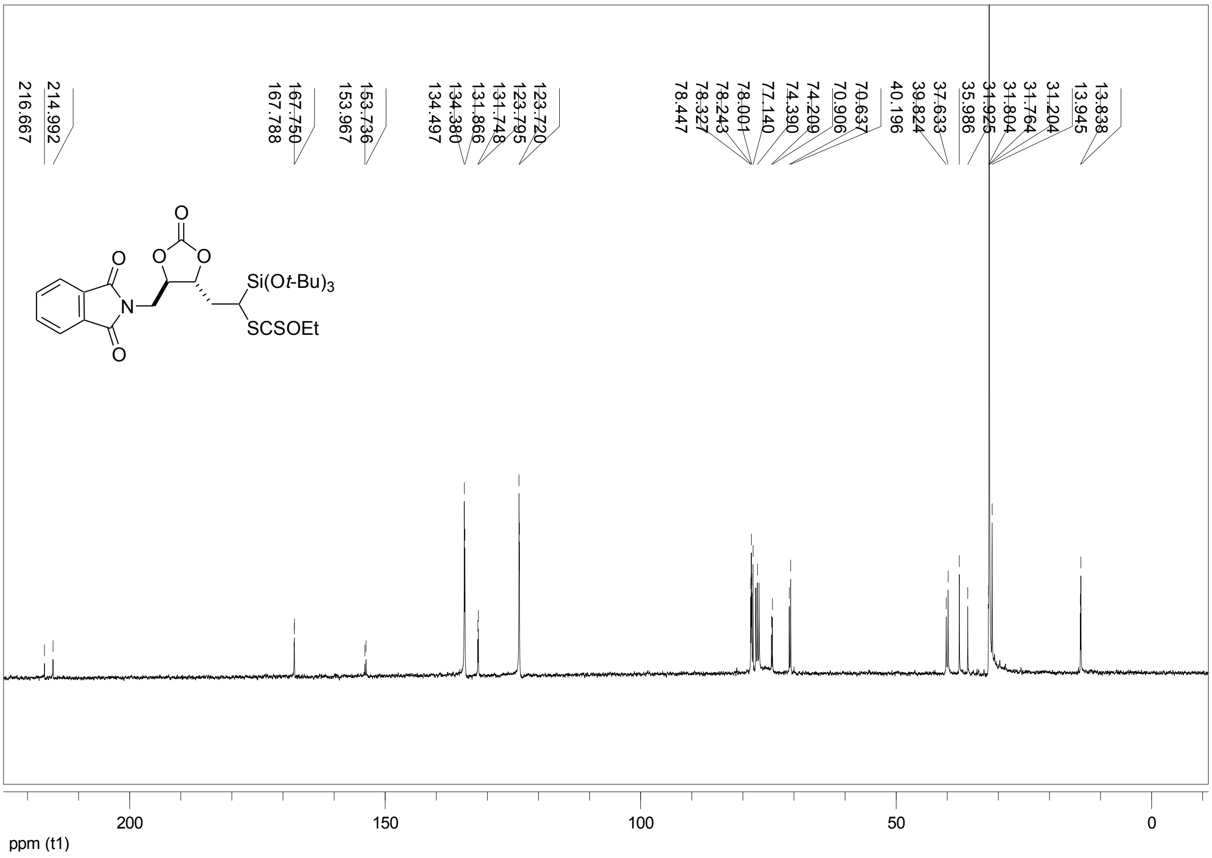
Compound 6t


7.270
5.760
4.621
4.639
3.120
3.131
2.412
1.512
1.414
1.396
1.379
1.314
1.275
0.907
0.887
SCSOEt
O
Si(Ot-Bu)3
HO
OH
F
O
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

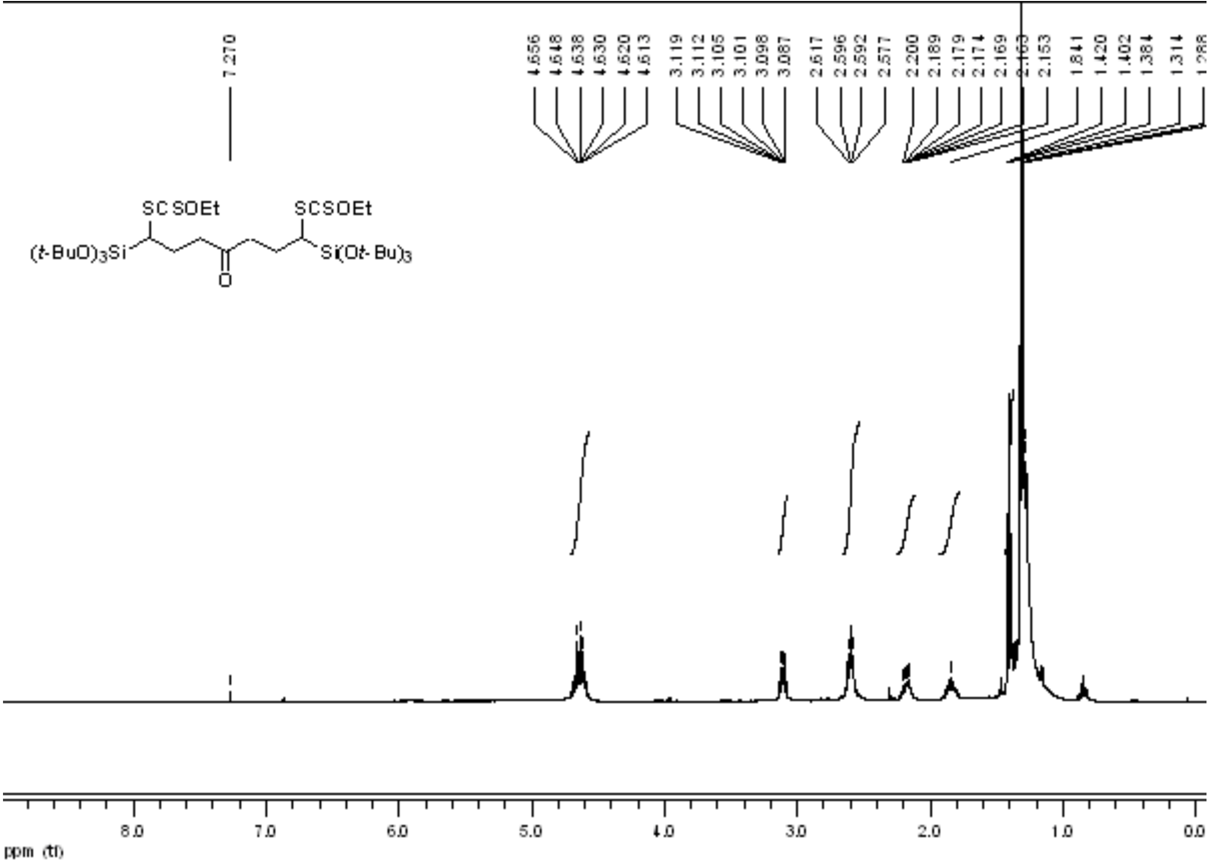

217.606
217.019
213.532
213.181
199.556
199.521
169.691
124.801
100.403
98.680
89.411
77.140
73.901
70.861
70.482
70.283
46.896
46.829
44.967
44.860
43.990
43.791
38.228
38.055
36.341
35.637
35.374
34.301
34.102
33.839
33.388
33.015
31.781
31.058
29.659
29.511
29.385
29.334
28.456
SCSOEt
O
Si(Ot-Bu)3
HO
OH
F
O
200
150
100
50
ppm (t1)

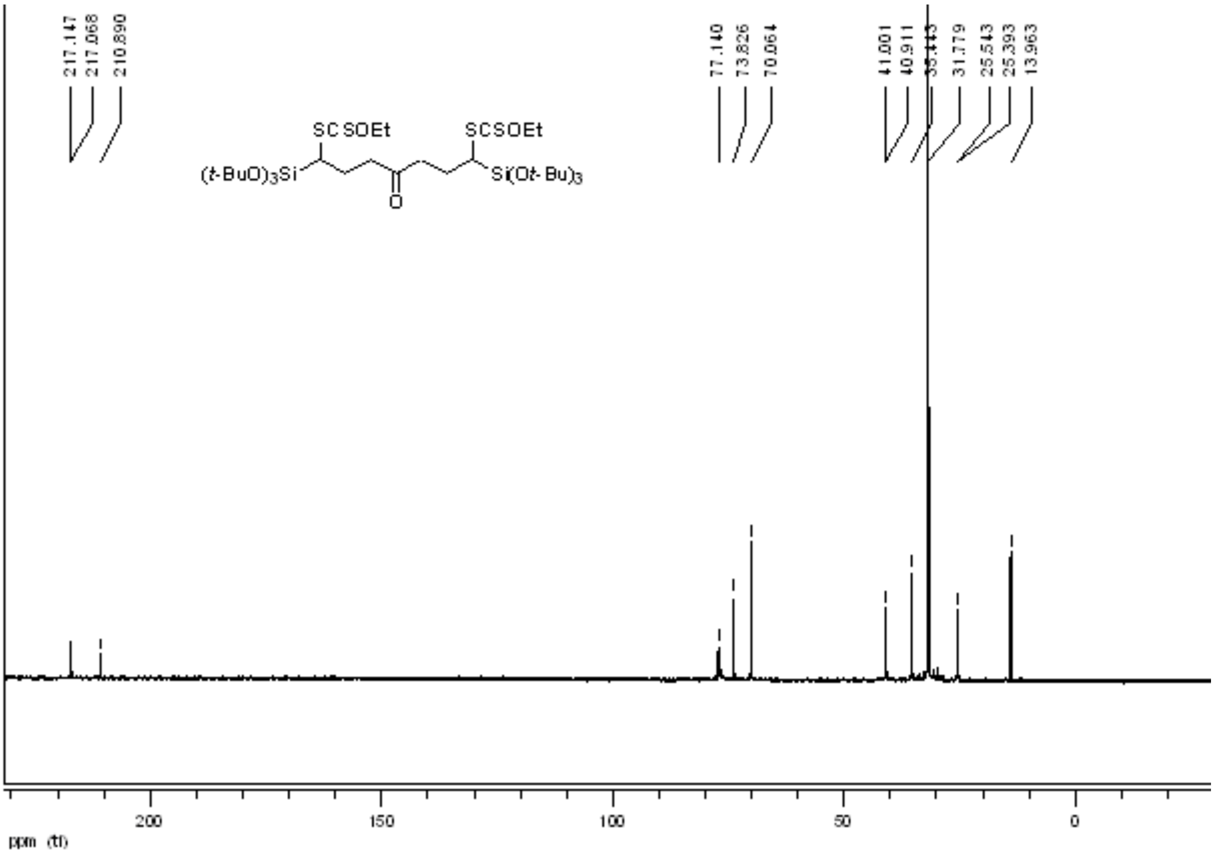
Compound 6u


7.886
7.878
7.872
7.865
7.856
7.766
7.758
7.753
7.745
7.739
7.732
7.270
4.779
4.684
4.050
4.031
4.006
3.932
3.920
3.235
3.226
3.209
3.200
3.156
3.147
3.134
2.401
2.394
2.386
2.372
2.364
2.121
2.112
2.099
2.085
2.037
1.450
1.392
1.331
1.302
1.249
O
O
O
O
N
Si(O*t*-Bu)$_3$
SCSOEt
O
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

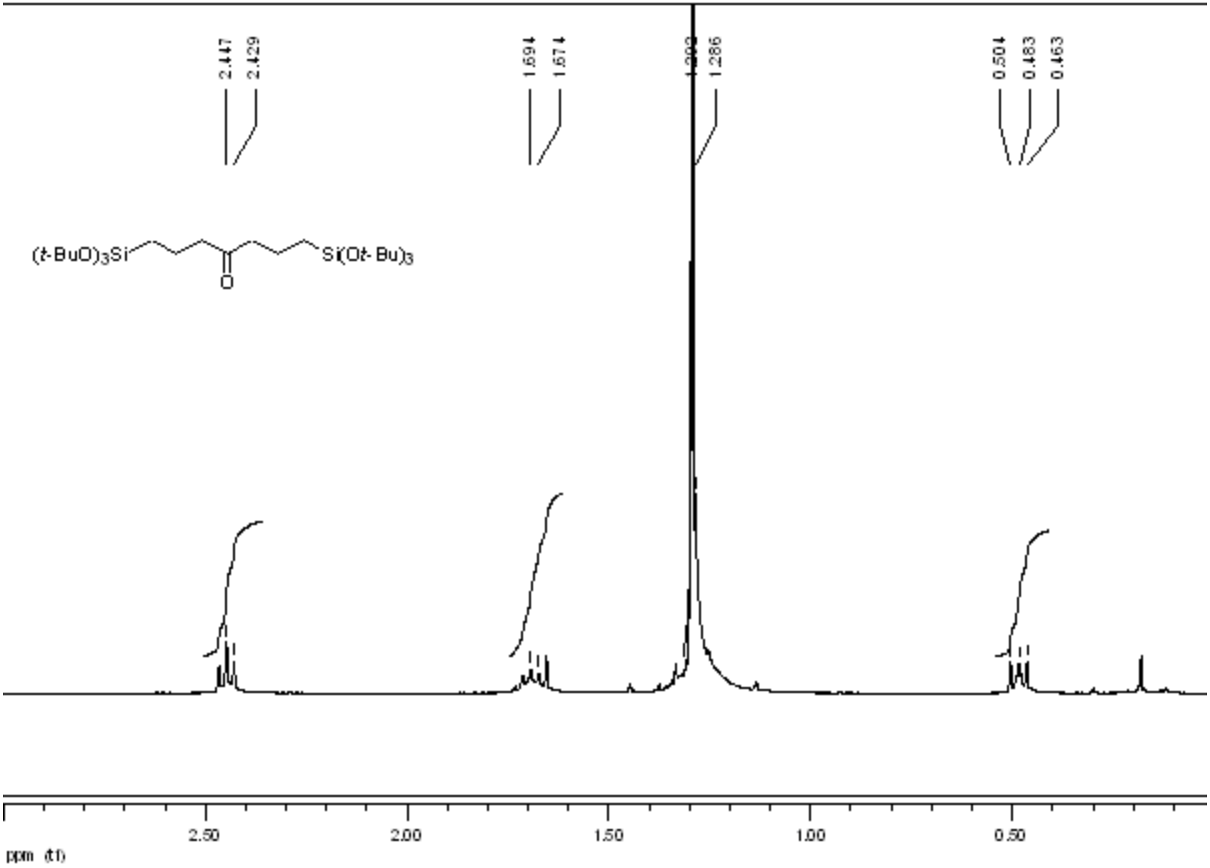

216.667
214.992
167.788
167.750
153.967
153.736
134.497
134.380
131.866
131.748
123.795
123.720
78.447
78.327
78.243
78.001
77.140
74.390
74.209
70.906
70.637
40.196
39.824
37.633
35.986
31.925
31.804
31.764
31.204
13.945
13.838
O
O
O
O
N
Si(O*t*-Bu)$_3$
SCSOEt
O
200
150
100
50
0
ppm (t1)

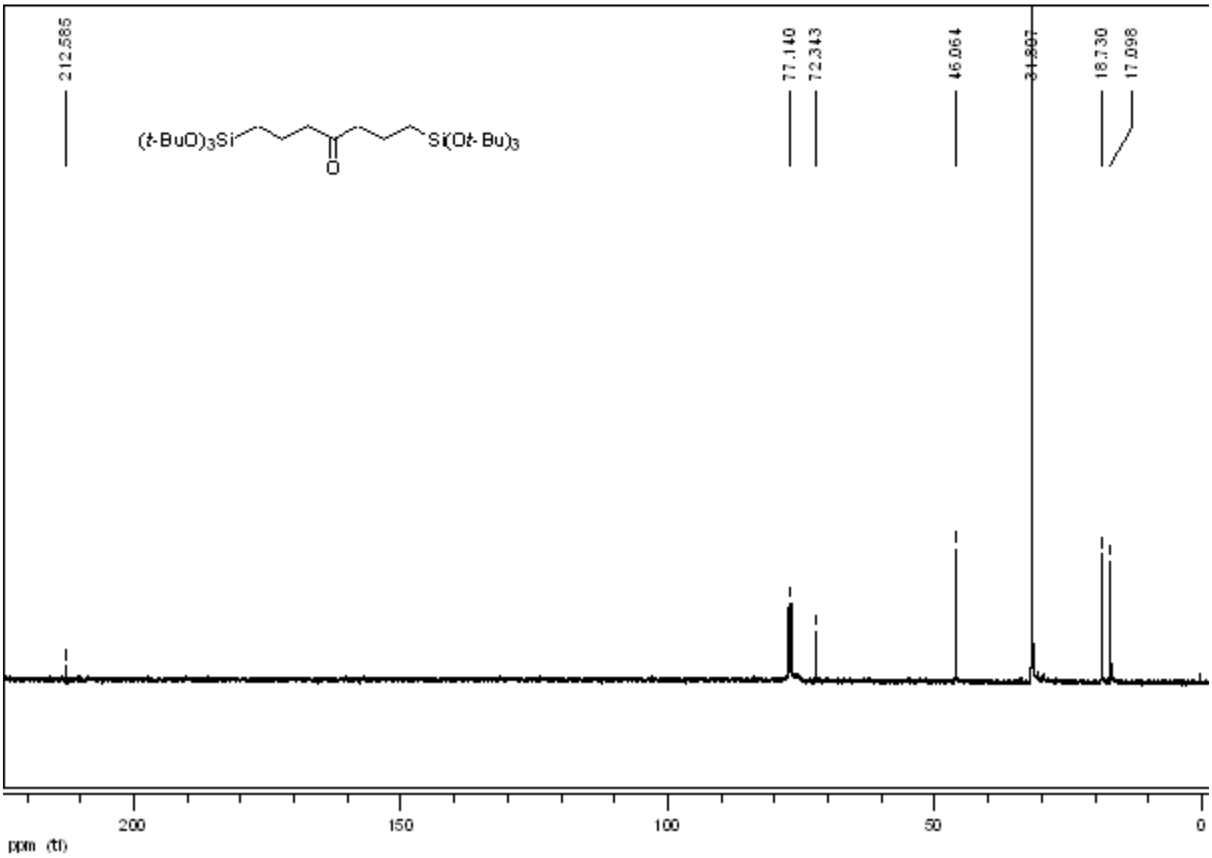
Compound 6v


7.270
4.656
4.648
4.638
4.630
4.620
4.613
3.119
3.112
3.105
3.101
3.098
3.087
2.617
2.596
2.592
2.577
2.200
2.189
2.179
2.174
2.169
2.163
2.153
1.841
1.420
1.402
1.384
1.314
1.288
SCSOEt
SCSOEt
(t-BuO)3Si
Si(Ot-Bu)3
O
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

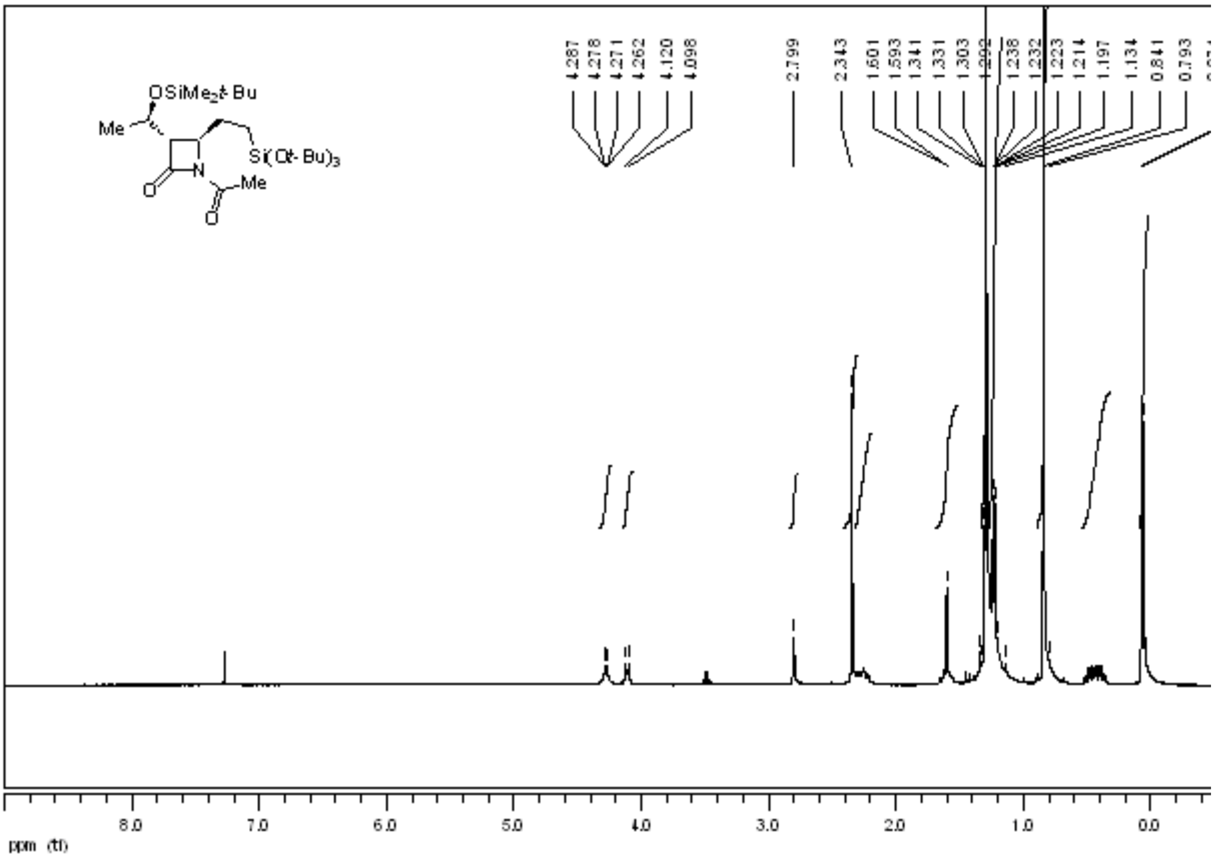

217.147
217.068
210.890
77.140
73.826
70.064
41.001
40.911
35.443
31.779
25.543
25.393
13.963
SCSOEt
SCSOEt
(t-BuO)3Si
Si(Ot-Bu)3
O
200
150
100
50
0
ppm (t1)

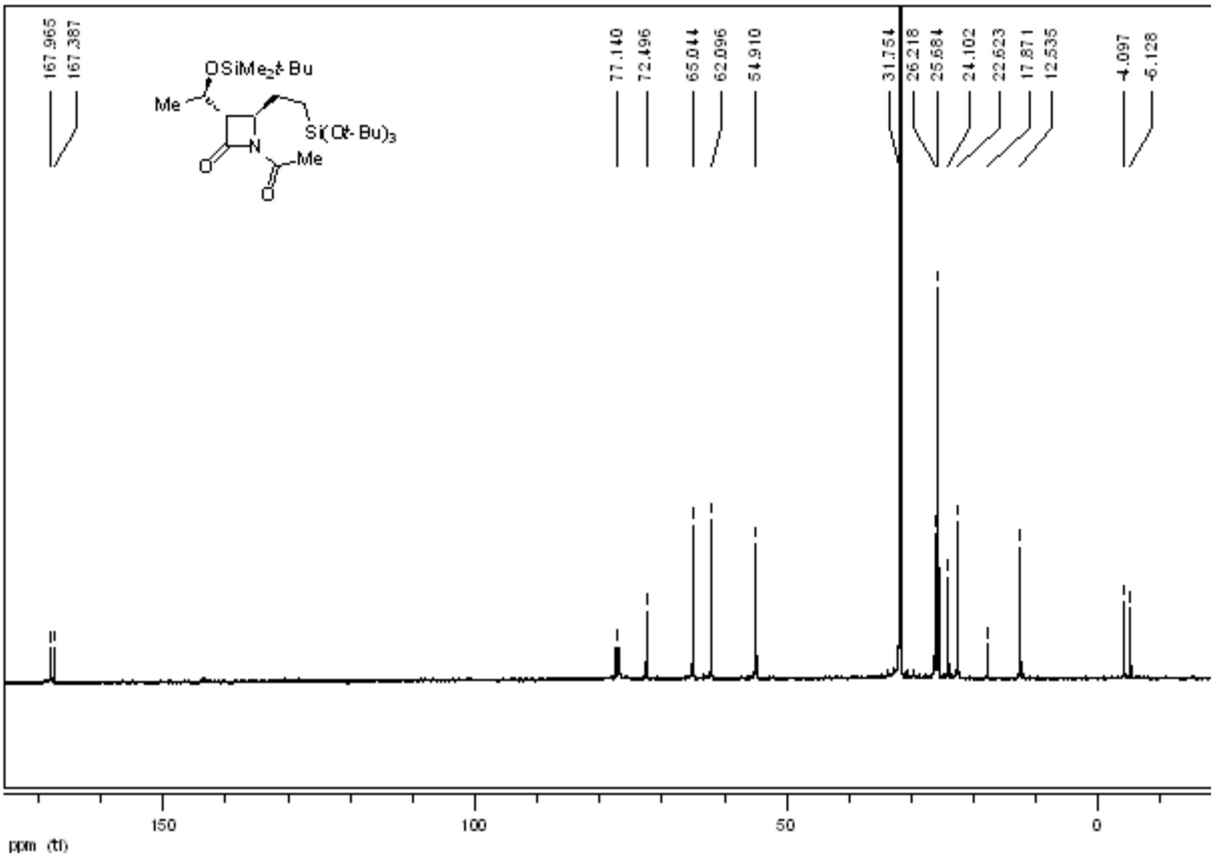
Compound 10


2.447
2.429
1.694
1.674
1.303
1.286
0.504
0.483
0.463
(t-BuO)3Si
Si(Ot-Bu)3
O
2.50
2.00
1.50
1.00
0.50
ppm (t1)


212.585
77.140
72.343
46.064
31.807
18.730
17.098
(t-BuO)3Si
Si(Ot-Bu)3
O
200
150
100
50
0
ppm (t1)

Compound 12


OSiMe2t-Bu
Me
Si(Ot-Bu)3
N
Me
O
O
4.287
4.278
4.271
4.262
4.120
4.098
2.799
2.343
1.601
1.593
1.341
1.331
1.303
1.292
1.238
1.232
1.223
1.214
1.197
1.134
0.841
0.793
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


167.965
167.387
OSiMe2t-Bu
Me
Si(Ot-Bu)3
N
Me
O
O
77.140
72.496
65.044
62.096
54.910
31.754
26.218
25.684
24.102
22.623
17.871
12.535
-4.097
-5.128
150
100
50
0
ppm (t1)