SUPPORTING INFORMATION FOR

Reactions of *N*-heterocyclic Carbene-Based Chalcogenoureas with Halogens: A Diverse Range of Outcomes

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Contents

Cyclic voltammograms of [S(NHC)] scanned in the negative cathodic direction

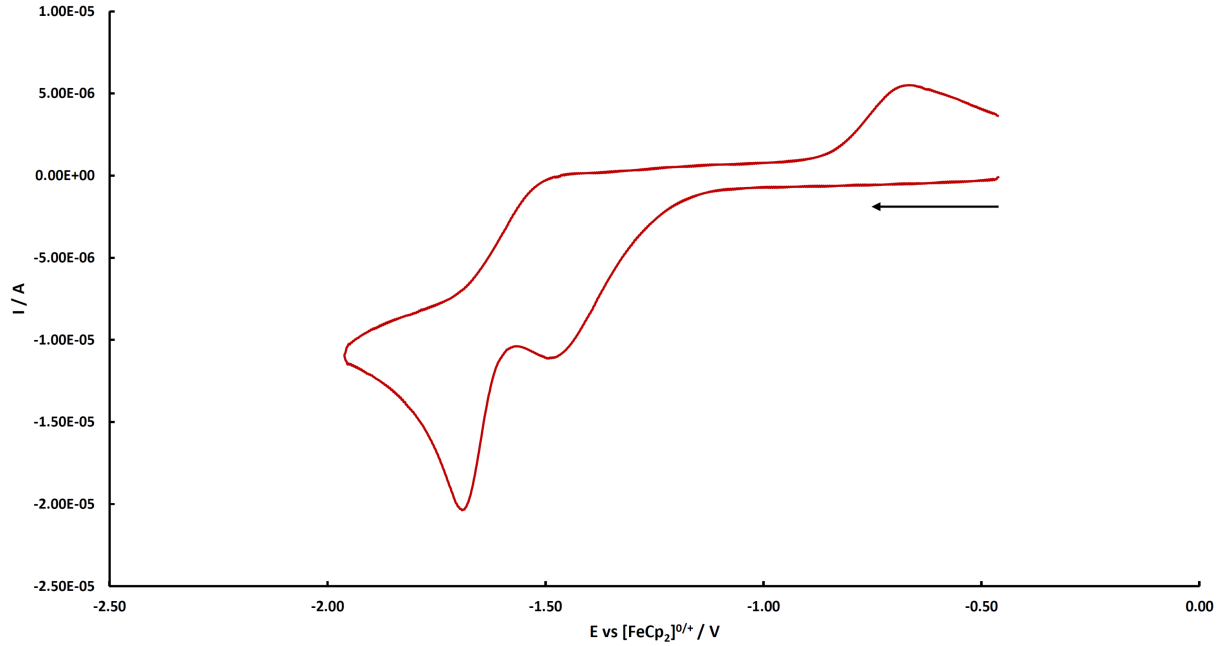


Figure S1. Cyclic voltammogram of [S(ICy)] scanned in the negative direction.

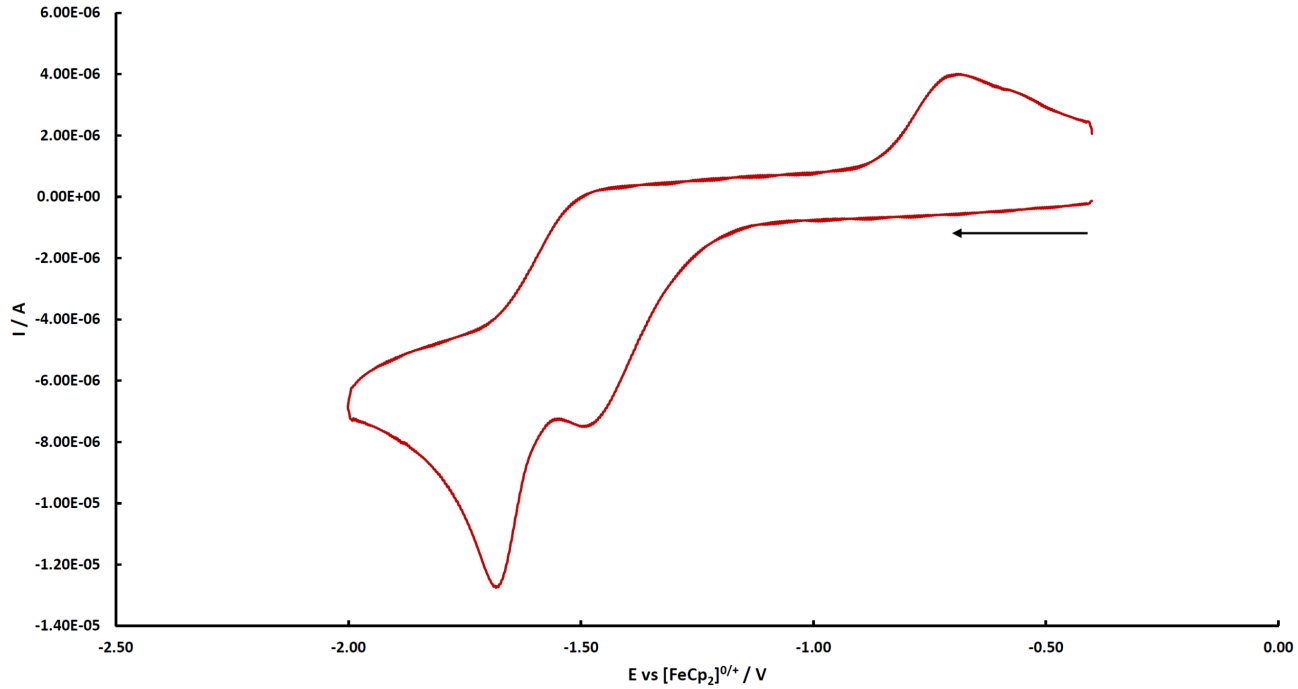


Figure S2. Cyclic voltammogram of [S(IPr)] scanned in the negative direction.*

Experimental section

General Information

NMR spectra were acquired on a Bruker AV3-400 spectrometer equipped with a liquid nitrogen cryoprobe, a Bruker AV400 spectrometer with a BBFO-z-ATMA probe or a Bruker Avance II 500MHz equipped with a 5mm triple channel probe head (TXO type). ^{1}H NMR spectra were referenced to residual solvent signals and ^{13}C{^{1}H} NMR spectra to the deuterated solvent signal, while chemical shifts are reported in ppm. ^{77}Se NMR spectra were referenced to external standards. [^{1}H, ^{1}H] COSY, [^{1}H, ^{13}C] HSQC and [^{1}H, ^{13}C] HMBC spectra were used to assign signals. X-ray intensity data were collected at 100 K, on a Rigaku Oxford Diffraction Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using ω scans and Cu Kα (λ = 1.54184 Å) radiation. The images were interpreted and integrated with the program CrysAlisPro. Using Olex the structures were solved by direct methods using the ShelXS/T structure solution program and refined by full-matrix least-squares on F^2 using the ShelXL program package. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). Bromine, Sulfuryl chloride and iodine were obtained from commercial sources and used as supplied. Chalcogenourea NHCs are prepared according to a known procedure.[1] Reagent grade solvents were always used as received unless otherwise stated. Crystallographic data underpinning this study can be downloaded from the Cambridge Structural Database (CSD) via the following link: https://www.ccdc.cam.ac.uk/structures/ (CCDC 2121842-2121867). See below for more details.

General procedure for the synthesis of NHC-based dibromo-chalcogenoureas

100 mg of seleno- or thiourea NHCs were dissolved in 3 mL of dichloromethane. 1.2 equiv. of bromine was then added to the solution and the mixture was stirred in an ice bath for 2-3 h. The product was then washed with pentane and dried in the vacuum oven.

Dibromo-selenoureas

[SeBr$_2$(IPr)]: m = 132.8 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.59 (t, J = 8 Hz, 2H, Ar CH), 7.50 (s, 2H, $N(CH)_2N$), 7.40 (d, J = 7.8 Hz, 4H, Ar CH), 2.91 (sept, J = 6.6 Hz, 4H, $CHMe_2$), 1.47 (d, J = 6.5 Hz, 12H, CH_3), 1.13 (d, J = 6.8 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 146.1 (Ar C), 142.4 (C-Se), 132.4 (Ar C), 132.0 (Ar CH), 126.3 ($N(CH)_2N$), 124.9 (Ar CH), 29.5 ($CHMe_2$), 26.5 (CH_3), 23.4 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 445.1.

[SeBr(SIPr)]Br$_3$: m = 132.6 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.54 (t, J = 7.8 Hz, 2H, Ar CH), 7.32 (d, J = 7.8 Hz, 4H, Ar CH), 4.64 (s, 4H, $N(CH_2)_2N$), 3.13 (sept., J = 6.6 Hz, 4H, $CHMe_2$), 1.45 (d, J = 6.7 Hz, 12H, CH_3), 1.39 (d, J = 6.7 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 163.3 (C-Se), 147.4 (Ar C), 132.4 (Ar CH), 129.6 (Ar C), 125.6 (Ar CH), 55.8 ($N(CH_2)_2N$), 29.8 ($CHMe_2$), 26.1 (CH_3), 24.1 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 627.9.

[SeBr$_2$(IMes)]: m = 138.8 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.43 (s, 2H, $N(CH)_2N$), 7.07 (s, 4H, Ar CH), 2.39 (s, 6H, CH_3), 2.33 (s, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 141.3 (C-Se), 141.2 (Ar C), 135.5

[1] M. Saab, D. J. Nelson, N. V. Tzouras, T. A. C. A. Bayrakdar, S. P. Nolan, F. Nahra, K. Van Hecke, *Dalton Trans.* **2020**, *49*,12068-12081

(Ar C), 132.3 (Ar C), 130.0 (Ar CH), 126.3 ($N(CH)_2N$), 21.4 (CH_3), 20.4 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 467.7.

[$SeBr_2$(SIMes)]: m = 130.1 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.00 (s, 4H, Ar C–H), 4.28 (s, 4H, $N(CH_2)_2N$), 2.55 (s, 12H, CH_3), 2.33 (s, 6H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 167.0 (C-Se), 140.3 (Ar C), 136.1 (Ar C), 132.3 (Ar C), 130.1 (Ar CH), 52.1 ($N(CH_2)_2N$), 21.3 (CH_3), 20.5 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 501.9.

[$SeBr_2$(IPr^{Me})]: m = 129.5 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.60 (t, J = 8 Hz, 2H, Ar CH), 7.42 (d, J = 7.8 Hz, 4H, Ar CH), 2.77 (sept, J = 6.6 Hz, 4H, $CHMe_2$), 2.19 (s, 6H, CH_3), 1.46 (d, J = 6.5 Hz, 12H, CH_3), 1.15 (d, J = 6.7 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** (CDCl3, 101 MHz): δ_C 146.7 (Ar C), 143.9 (C-Se), 133.0 (Ar C), 132.1 (Ar CH), 130.4 ($N(CH)_2N$), 125.7 (Ar CH), 29.4 ($CHMe_2$), 25.6 (CH_3), 25.4 (CH_3), 12.1 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 482.3.

[SeBr(IPr^{Cl})]Br_3: m = 128.4 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.67 (t, J = 7.8 Hz, 2H, Ar CH), 7.45 (d, J = 7.8 Hz, 4H, Ar CH), 2.75 (sept, J = 6.1 Hz, 4H, $CHMe_2$), 1.49 (d, J = 6.4 Hz, 12H, CH_3), 1.24 (d, J = 6.6 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 146.9 (Ar C), 141.0 (C-Se), 133.1 (Ar CH), 129.5 (Ar C), 126.0 (Ar CH), 124.3 ($N(CH)_2N$), 29.9 ($CHMe_2$), 25.5 (CH_3), 25.4 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 506.5.

[$SeBr_2$(ICy)]: m = 146.7 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.27 (s, 2H, $N(CH)_2N$), 5.02 (tt, 2H, J = 3.8 Hz, NCH), 2.43 (m, 4H, CH_2), 1.98–1.95 (m, 4H, CH_2), 1.85–1.82 (m, 2H, CH_2), 1.63–1.54 (m, 8H, CH_2), 1.27–1.25 (m, 2H, CH_2). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 Hz): δ_C 141.6 (C-Se), 120.0 ($N(CH)_2N$), 61.4 (NCH), 33.4 (CH_2), 25.5 (CH_2), 25.2 (CH_2). **CHN calculated for $C_{15}H_{24}Br_2N_2Se$:** C, 38.24; H, 5.13; N, 5.95. Found: C, 37.84; H, 5.03; N, 5.82. **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 298.6.

[Br_2{Se(IPr*)}]: m = 107.9 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.28 (d, J = 4.8 Hz, 8H, Ar CH), 7.11–7.06 (m, 24H, Ar CH), 6.84–6.69 (m, 12H, Ar CH), 5.76 (s, 4H, $CH(Ph)_2$), 4.96 (s, 2H, $N(CH_2)_2N$), 2.25(s, 6H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 144.2 (Ar C), 142.8 (Ar C), 141.6 (Ar C), 141.2 (C-Se), 140.6 (Ar C), 131.8 (Ar C), 131.2 (Ar CH), 130.8 (Ar CH), 129.4 (Ar CH), 128.5 (Ar CH), 128.3 (Ar CH), 126.7 (Ar CH), 126.6 (Ar CH), 124.7 (CH_{imid}), 51.0 ($CHPh_2$), 22.0 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 462.2.

Dibromo-thioureas

[(Br_2)·S(IPr)}]: m = 135.2 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.89 (s, 2H, $N(CH)_2N$), 7.64 (t, J = 7.8 Hz, 2H, Ar CH), 7.42 (d, J = 8 Hz, 4H, Ar CH), 2.37 (sept, J = 6.5 Hz, 4H, $CHMe_2$), 1.38 (d, J = 6.8 Hz, 12H, CH_3), 1.26 (d, J = 6.8 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 202.0 (C-S), 145.4 (Ar C), 132.7 (Ar C), 130.2 (Ar CH) (determined with HMBC), 129.7 ($N(CH)_2N$) (determined with HMBC), 125.3 (Ar CH), 29.8 ($CHMe_2$), 26.0 (CH_3), 23.6 (CH_3).

[(Br_2)·S(SIPr)}]: m = 132.8 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.47 (t, J = 7.8 Hz, 2H, Ar CH), 7.28 (d, J = 7.8 Hz, 4H, Ar CH), 4.23 (s, 4H, $N(CH_2)_2N$), 2.98 (sept., J = 6.8 Hz, 4H, $CHMe_2$), 1.39 (d, J = 6.8 Hz, 12H, CH_3), 1.35 (d, J = 6.9 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 177.8 (C-S) (determined with HMBC), 147.1 (Ar C), 131.9 (Ar C), 131.1 (Ar CH), 125.2 (Ar CH), 52.8 ($N(CH_2)_2N$), 29.5 ($CHMe_2$), 25.3 (CH_3), 24.2 (CH_3).

[(Br_2)·S(IMes)}]: m = 140.1 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.08 (s, 2H, $N(CH)_2N$), 7.05 (s, 4H, Ar CH), 2.36 (s, 6H, CH_3), 2.15 (s, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 141.0 (C-S), 137.9 (Ar C), 135.8 (Ar C), 134.8 (Ar C), 130.1 ($N(CH)_2N$), 129.9 (Ar CH), 21.4 (CH_3), 20.4 (CH_3).

[(Br_2)·S(SIMes)}]: m = 139.8 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.00 (s, 4H, Ar C-H), 4.20 (s, 4H, $N(CH_2)_2N$), 2.33 (s, 12H, CH_3), 2.32 (s, 6H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 173.9 (C-S), 140.3 (Ar C), 135.9 (Ar C), 132.2 (Ar C), 130.2 (Ar CH), 50.3 ($N(CH_2)_2N$), 21.3 (CH_3), 18.1 (CH_3).

[SBr·(IPr^{Me})]Br_3: m = 130.1 mg. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ_H 7.58 (t, J = 7.8 Hz, 2H, Ar CH), 7.41 (d, J = 7.8 Hz, 4H, Ar CH), 2.88 (sept, J = 8 Hz, 4H, $CHMe_2$), 2.15 (s, 6H, CH_3), 1.45 (d, J = 6.5 Hz, 12H, CH_3), 1.11 (d, J = 6.8 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 125 MHz): δ_C (C-S signal was not located), 147.2 (Ar C), 131.8 (Ar CH), 131.3 ($N(CH)_2N$) (HMBC), 130.4 (Ar C) (HMBC), 125.4 (Ar CH), 29.1 ($CHMe_2$), 25.5 (CH_3), 25.3 (CH_3), 11.8 (CH_3). The carbon attached to sulfur could not be located.

[(Br_2)·S(IPr^{Cl})]: m = 126.0 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.53(t, J = 7.8 Hz, 2H, Ar CH), 7.33 (d, J = 7.8 Hz, 4H, Ar CH), 2.65 (sept, J = 6.8 Hz, 4H, $CHMe_2$), 1.31 (d, J = 6.8 Hz, 12H, CH_3), 1.26 (d, J = 6.9 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 165.4 (C-S), 147.2 (Ar C), 131.1 (Ar CH), 130.4 (Ar C), 124.6 (Ar CH), 114.0 ($N(CH)_2N$), 29.6 ($CHMe_2$), 24.0 (CH_3), 24.0 (CH_3).

[SBr·(ICy)]Br: m = 152.4 mg. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.28 (s, 2H, $N(CH)_2N$), 4.96 (tt, 2H, J = 7.8 Hz, NCH), 2.44-2.42 (m, 4H, CH_2), 1.97–1.90 (m, 4H, CH_2), 1.84–1.80 (m, 2H, CH_2), 1.63–1.46 (m, 8H, CH_2), 1.29–1.22 (m, 2H, CH_2). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 Hz): δ_C (C-S signal was not located), 119.4 ($N(CH)_2N$), 59.6 (NCH), 32.9 (CH_2), 25.4 (CH_2), 25.2 (CH_2).

General procedure for the synthesis of NHC-based dichloro-chalcogenoureas

100 mg of seleno- or thiourea NHCs were dissolved in 3 mL of dichloromethane. 1.2 equiv. of SO_2Cl_2 was added to the solution and the mixture was stirred for 4 h at room temperature. The product was then washed with pentane and dried in the vacuum oven.

Dichloro-selenoureas

[$SeCl_2$(IPr)]: m = 112.8 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.58 (t, J = 7.8 Hz, 2H, Ar CH), 7.41 (s, 2H, $N(CH)_2N$), 7.40 (d, J = 7.8 Hz, 4H, Ar CH), 2.89 (sept, J = 8 Hz, 4H, $CHMe_2$), 1.44 (d, J = 6.6 Hz, 12H, CH_3), 1.13 (d, J = 6.9 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 150.6 (C-Se), 146.3 (Ar C), 132.4 (Ar C), 131.9 (Ar CH), 125.4 ($N(CH)_2N$), 124.8 (Ar CH), 29.3 ($CHMe_2$), 26.5 (CH_3), 23.1 (CH_3). **CHN calculated for $C_{27}H_{36}Cl_2N_2Se$:** C, 60.23; H, 6.74; N, 5.20. Found: C, 59.77; H, 6.67; N, 5.13. **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 526.7.

[$SeCl_2$(SIPr)]: m = 110.4 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.47 (t, J = 4 Hz, 2H, Ar CH), 7.32 (d, J = 7.8 Hz, 4H, Ar CH), 4.36 (s, 4H, $N(CH_2)_2N$), 3.29 (sept., J = 8 Hz, 4H, $CHMe_2$), 1.50 (d, J = 6.5 Hz, 12H, CH_3), 1.27 (d, J = 6.8 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 171.8 (C-Se) (determined by HMBC), 146.9 (Ar C), 132.9 (Ar C), 130.9 (Ar CH), 125.0 (Ar CH), 53.7 ($N(CH_2)_2N$), 29.5 ($CHMe_2$), 27.0 (CH_3), 23.8 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 197.3.

[$SeCl_2$(IMes)]: m = 109.1 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.38 (s, 2H, $N(CH)_2N$), 7.06 (s, 4H, Ar CH), 2.38 (s, 6H, CH_3), 2.31 (s, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 141.2 (Ar C), 135.7 (C-Se), 132.3 (Ar C), 130.8 (Ar C), 129.9 (Ar CH), 125.0 ($N(CH)_2N$), 21.4 (CH_3), 19.4 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 551.5 (a second unidentified Se signal was observed at 558.9 ppm).

[$SeCl_2$(SIMes)]: m = 112.4 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.00 (s, 4H, Ar CH), 4.31 (s, 4H, $N(CH_2)_2N$), 2.53 (s, 6H, CH_3), 2.33 (s, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 169.9 (C-Se), 140.2 (Ar C),

136.3 (Ar C), 132.4 (Ar C), 130.0 (Ar CH), 51.4 ($N(CH_2)_2N$), 21.3 (CH_3), 19.6 (CH_3). **CHN calculated for $C_{21}H_{26}Cl_2N_2Se$:** C, 55.28; H, 5.74; N, 6.14. Found: C, 54.74; H, 5.70; N, 6.04. **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 586.9.

[$SeCl_2$(IPr^{Me})]: m = 108.5 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.58 (t, J = 8 Hz, 2H, Ar CH), 7.41 (d, J = 7.8 Hz, 4H, Ar CH), 2.87 (sept, J = 8 Hz, 4H, CHMe2), 2.16 (s, 6H, CH_3), 1.45 (d, J = 6.5 Hz, 12H, CH3), 1.11 (d, J = 6.8 Hz, 12H, CH3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 147.0 (Ar C), 145.5 (C-Se), 132.2 (Ar CH), 130.5 (Ar C), 125.5 (Ar CH), 125.2 $N(CH)_2N$), 29.2 ($CHMe_2$), 25.4 (CH_3), 25.3 (CH_3), 11.8 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 554.3.

[$SeCl_2$(IPr^{Cl})]: m = 110.9 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.63 (t, J = 7.8 Hz, 2H, Ar CH), 7.43 (d, J = 7.8 Hz, 4H, Ar CH), 2.86 (sept, J = 6.6 Hz, 4H, $CHMe_2$), 1.47 (d, J = 6.5 Hz, 12H, CH_3), 1.20 (d, J = 6.8 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** (CDCl3, 101 MHz): 180.6 (C-Se), 147.2 (Ar C), 131.7 (Ar CH), 130.0 (Ar C) (HMBC), 128.4 ($N(CH)_2N$), 125.4 (Ar CH), 29.7 ($CHMe_2$), 25.6 (CH_3), 25.1 (CH_3). **CHN calculated for $C_{27}H_{34}Cl_4N_2Se$:** C, 53.40; H, 5.64; N, 4.61. Found: C, 52.74; H, 5.59; N, 4.48. **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 546.9.

[$SeCl_2$(ICy)]: m = 120.3 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.27 (s, 2H, $N(CH)_2N$), 5.05 (tt, 2H, J = 4 Hz, NCH), 2.39 (m, 4H, CH_2), 1.97–1.92 (m, 4H, CH_2), 1.84–1.77 (m, 2H, CH_2), 1.66–1.52 (m, 8H, CH_2), 1.29–1.19 (m, 2H, CH_2). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 Hz): δ_C 144.9 (C-Se), 119.1 ($N(CH)_2N$), 61.1 (NCH), 33.5 (CH_2), 25.4 (CH_2), 25.2 (CH_2). **CHN calculated for $C_{15}H_{24}Cl_2N_2Se$:** C, 47.14; H, 6.33; N, 7.33. Found: C, 46.75; H, 6.24; N, 7.10. **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 441.6.

[$SeCl_2$(IPr*)]: m = 101.7 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): 7.27 (d, J = 4.3 Hz, 8H, Ar CH), 7.24–7.01 (m, 24H, Ar CH), 6.78–6.65 (m, 12H, Ar CH), 5.89 (s, 4H, $CH(Ph)_2$), 4.85 (s, 2H, $N(CH_2)_2N$), 2.22 (s, 6H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δC 166.0 (C-Se), 145.4 (Ar C), 144.0 (Ar C), 143.2 (Ar C), 141.9 (Ar C), 140.5 (Ar C), 131.2 (Ar C), 130.6 (Ar CH), 129.4 (Ar CH), 128.5 (Ar CH), 128.3 (Ar CH), 126.7 (Ar CH), 126.6 (Ar CH), 124.2 (CH_{imid}), 50.7 ($CHPh_2$), 22.0 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 519.8.

General procedure for the synthesis of NHC-based diiodo-chalcogenoureas

100 mg of seleno- or thio-urea NHCs was dissolved in 3 mL of acetone. 1.2 equiv. of iodine was added to the solution and the mixture was stirred for 5 h at room temperature. The product was then washed with pentane and dried.

Diiodo-selenoureas

[(I_2)·Se(IPr)]: m = 146.5 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.58 (t, J = 7.8 Hz, 2H, Ar CH), 7.36 (d, J = 7.8 Hz, 4H, Ar CH), 7.27 (s, 2H, $N(CH)_2N$), 2.50 (sept, J = 6.8 Hz, 4H, $CHMe_2$), 1.41 (d, J = 6.8 Hz, 12H, CH_3), 1.19 (d, J = 6.9 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 150.5 (C-Se) (determined by HMBC), 145.7 (Ar C), 132.5 (Ar C), 131.8 (Ar CH), 125.0 (Ar CH), 124.4 ($N(CH)_2N$), 29.5 ($CHMe_2$), 25.4 (CH_3), 23.6 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 264.5. **CHN calculated for $C_{27}H_{36}I_2N_2Se$:** C, 44.96; H, 5.03; N, 3.88. Found: C, 45.18; H, 5.01; N, 4.01.

[{Se(SIPr)}$_2$(μ-I)]I_5: m = 146.3 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.50 (t, J = 7.8 Hz, 2H, Ar CH), 7.29 (d, J = 7.8 Hz, 4H, Ar CH), 4.14 (s, 4H, $N(CH_2)_2N$), 2.94 (sept., J = 6.6 Hz, 4H, $CHMe_2$), 1.42 (d, J = 6.7 Hz, 12H, CH_3), 1.31 (d, J = 6.7 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 175.0 (C-Se), 146.9 (Ar C), 132.9 (Ar C), 131.2 (Ar CH), 125.3 (Ar CH), 53.0 ($N(CH_2)_2N$), 29.5 ($CHMe_2$), 25.4 (CH_3), 24.3 (CH_3). **^{77}Se NMR** ($CDCl_3$,

76 MHz): δ_{Se} 339.9. **CHN calculated for $C_{27}H_{38}I_2N_2Se$:** C, 44.83; H, 5.30; N, 3.87. Found: C, 44.87; H, 5.27; N, 3.98.

[(I_2)·Se(IMes)]: m = 154.5 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.33 (s, 2H, $N(CH)_2N$), 7.10 (s, 4H, Ar CH), 2.41 (s, 6H, CH_3), 2.15 (s, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 160.2 (C-Se), 141.4 (Ar C), 134.8 (Ar C), 132.5 (Ar C), 130.1 (Ar CH), 124.4 ($N(CH)_2N$), 21.5 (CH_3), 18.6 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 262.7.

[(I_2)·Se(SIMes)]: yield = 91%, m = 150.9 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.02 (s, 4H, Ar C–H), 4.13 (s, 4H, $N(CH_2)_2N$), 2.36 (s, 12H, CH_3), 2.32 (s, 6H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 170.0 (C-Se), 140.7 (Ar C), 136.1 (Ar C), 132.7 (Ar C), 130.3 (Ar CH), 50.8 ($N(CH_2)_2N$), 21.4 (CH_3), 18.3 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 315.6.

[SeI(IPr^{Me})]I_3: m = 139.1 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.64 (t, J = 7.8 Hz, 2H, Ar CH), 7.39 (d, J = 7.8 Hz, 4H, Ar CH), 2.39 (sept, J = 4 Hz, 4H, $CHMe_2$), 2.06 (s, 6H, CH_3), 1.38 (d, J = 6.4 Hz, 12H, CH_3), 1.23 (d, J = 6.1 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C (C-S signal was not located), 146.1 (Ar C), 132.2 (Ar CH), 130.2 (Ar C), 128.4 ($N(CH)_2N$), 125.4 (Ar CH), 29.4 ($CHMe_2$), 24.4 (CH_3), 24.3 (CH_3), 10.3 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 327.7.

[(I_2)·Se(IPr^{Cl})]: m = 138.4 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.66 (t, J = 7.8 Hz, 2H, Ar CH), 7.40 (d, J = 7.8 Hz, 4H, Ar CH), 2.43 (sept, J = 6.8 Hz, 4H, $CHMe_2$), 1.38 (d, J = 6.8 Hz, 12H, CH_3), 1.26 (d, J = 6.9 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): 148.0 (C-Se), 146.5 (Ar C), 132.8 (Ar C), 129.4 (Ar CH), 125.4 (Ar CH), 119.4 ($N(CH)_2N$), 29.8 ($CHMe_2$), 24.3 (CH_3), 23.9 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 341.7.

[SeI_2(ICy)]: m = 168.8 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.33 (s, 2H, $N(CH)_2N$), 4.85 (tt, 2H, J = 3.7 Hz, NCH), 2.44-2.41 (m, 4H, CH_2), 2.00–1.96 (m, 4H, CH_2), 1.86–1.83 (m, 2H, CH_2), 1.65–1.47 (m, 8H, CH_2), 1.30–1.23 (m, 2H, CH_2). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 Hz): δ_C 137.5 (C-Se), 120.4 ($N(CH)_2N$), 61.6 (NCH), 32.8 (CH_2), 25.4 (CH_2), 25.2 (CH_2). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 98.4.

[(I_2)·Se(IPr*)]: m = 118.0 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.29 (d, J = 8 Hz, 8H, Ar CH), 7.25–7.08 (m, 24H, Ar CH), 6.89–6.76 (m, 12H, Ar CH), 5.33 (s, 4H, CH(Ph)2), 5.21 (s, 2H, $N(CH_2)_2N$), 2.29(s, 6H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 147.7 (C-Se), 143.0 (Ar C), 142.1 (Ar C), 141.5 (Ar C), 141.3 (Ar C), 132.0 (Ar C), 130.9 (Ar C), 130.3 (Ar CH), 129.3 (Ar CH), 128.7 (Ar CH), 128.5 (Ar CH), 126.1 (Ar CH), 126.9 ($CH_{imid)}$, 123.5 (Ar CH) (determined by HMBC), 52.1 ($CHPh_2$), 22.2 (CH_3). **^{77}Se NMR** ($CDCl_3$, 76 MHz): δ_{Se} 280.8.

Diiodo-thioureas

[(I_2)·S(IPr)]: m = 152.3 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.54 (t, J = 7.8 Hz, 2H, Ar CH), 7.35 (d, J = 7.8 Hz, 4H, Ar CH), 7.11 (s, 2H, $N(CH)_2N$), 2.58 (sept, J = 6.8 Hz, 4H, $CHMe_2$), 1.39 (d, J = 6.8 Hz, 12H, CH_3), 1.20 (d, J = 6.9 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 157.1 (C-S) (determined by HMBC), 146.0 (Ar C), 132.4 (Ar C), 131.3 (Ar CH), 124.8 (Ar CH), 122.2 ($N(CH)_2N$), 29.4 ($CHMe_2$), 25.3 (CH_3), 23.6 (CH_3). **CHN calculated for $C_{27}H_{36}I_2N_2S$:** C, 48.08; H, 5.38; N, 4.15. Found: C, 47.62; H, 5.25; N, 3.95.

[(I_2)·S(SIPr)]: m = 151.9 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.46 (t, J = 7.8 Hz, 2H, Ar CH), 7.29 (d, J = 7.8 Hz, 4H, Ar CH), 4.25 (s, 4H, $N(CH_2)_2N$), 3.01 (sept., J = 8 Hz, 4H, $CHMe_2$), 1.37 (d, J = 2.2 Hz, 12H, CH_3), 1.35 (d, J = 2.1 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 167.1 (C-S), 147.4 (Ar C), 130.8 (Ar CH), 126.0 (Ar C), 125.2 (Ar CH), 52.1 ($N(CH_2)_2N$), 29.4 ($CHMe_2$), 25.0 (CH_3), 24.5 (CH_3).

[(I$_2$)·S(IMes)]: m = 157.8 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.10 (s, 2H, $N(CH)_2N$), 7.06 (s, 4H, Ar CH), 2.38 (s, 6H, CH_3), 2.16 (s, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 153.5 (C-S), 140.7 (Ar C), 135.1 (Ar C), 132.4 (Ar C), 129.9 (Ar CH), 121.8 ($N(CH)_2N$), 21.4 (CH_3), 18.5 (CH_3). **CHN calculated for $C_{21}H_{24}I_2N_2S$:** C, 42.73; H, 4.10; N, 4.75. Found: C, 42.58; H, 4.05; N, 4.76.

[(I$_2$)·S(SIMes)]: m = 164.4 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.00 (s, 4H, Ar C–H), 4.05 (s, 4H, $N(CH_2)_2N$), 2.33 (s, 6H, CH_3), 2.32 (s, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 176.6 (C-S), 139.6 (Ar C), 136.4 (Ar C), 133.4 (Ar C), 130.0 (Ar CH), 49.0 ($N(CH_2)_2N$), 21.3 (CH_3), 18.1 (CH_3).

[(I$_2$)·S(IPr^{Me})]: m = 142.5 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.55 (t, J = 7.8 Hz, 2H, Ar CH), 7.35 (d, J = 7.8 Hz, 4H, Ar CH), 2.49 (sept, J = 6.7 Hz, 4H, $CHMe_2$), 1.97 (s, 6H, CH_3), 1.35 (d, J = 6.8 Hz, 12H, CH3), 1.21 (d, J = 6.9 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 176.6 (C-S), 146.4 (Ar C), 131.4 (Ar CH), 130.5 (Ar C), 125.4 ($N(CH)_2N$), 125.0 (Ar CH), 29.3 ($CHMe_2$), 24.3 (CH3), 24.2 (CH_3), 10.1 (CH_3).

[(I$_2$)·S(IPr^{Cl})]: m = 139.6 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.55(t, J = 8 Hz, 2H, Ar CH), 7.34 (d, J = 7.8 Hz, 4H, Ar CH), 2.59 (sept, J = 6.9 Hz, 4H, $CHMe_2$), 1.32 (d, J = 6.8 Hz, 12H, CH_3), 1.25 (d, J = 6.9 Hz, 12H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** (CDCl3, 101 MHz): δ_C 162.8 (C-S), 147.1 (Ar C), 131.5 (Ar CH), 130.0 (Ar C), 124.8 (Ar CH), 115.1 ($N(CH)_2N$), 29.6 ($CHMe_2$), 24.1 (CH_3), 24.0 (CH_3). **CHN calculated for $C_{27}H_{34}I_2Cl_2N_2Se$:** C, 43.63; H, 4.61; N, 3.77. Found: C, 43.81; H, 4.64; N, 3.96.

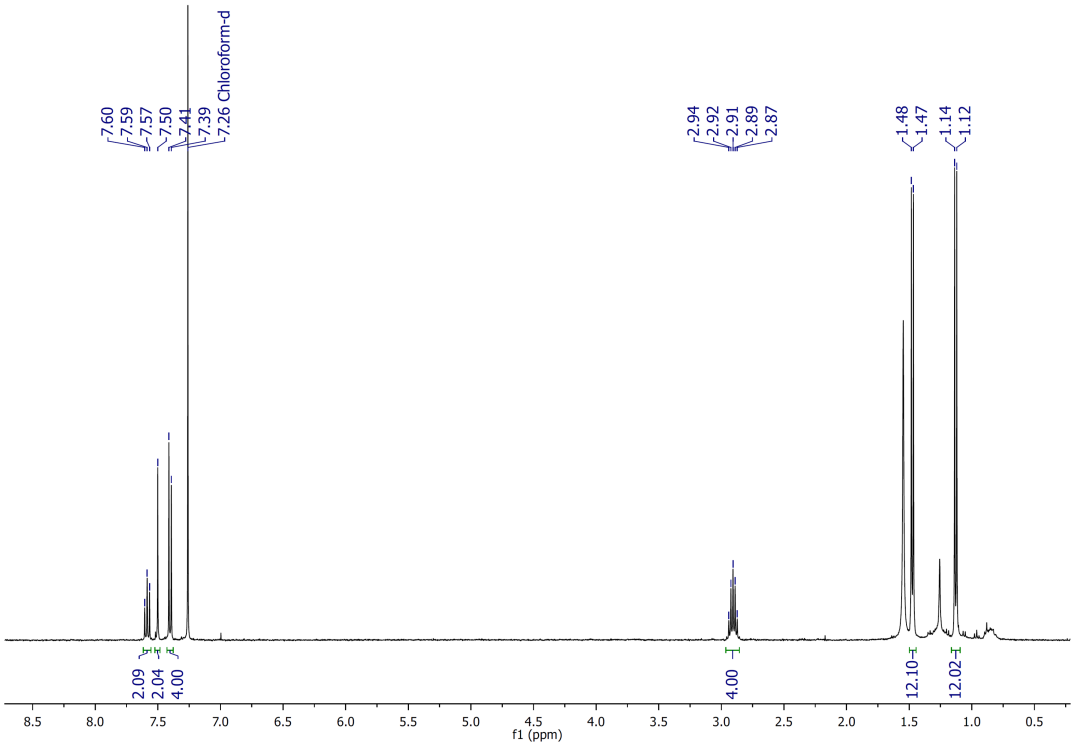
[(I$_2$)·S(ICy)]: m = 178.3 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.12 (s, 2H, $N(CH)_2N$), 4.69 (tt, 2H, J = 4 Hz, NCH), 2.17-2.15 (m, 4H, CH_2), 1.97–1.91 (m, 4H, CH_2), 1.82–1.79 (m, 2H, CH_2), 1.60–1.45 (m, 8H, CH_2), 1.29–1.19 (m, 2H, CH_2). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 Hz): δ_C 147.3 (C-S), 118.2 ($N(CH)_2N$), 58.4 (NCH), 33.2 (CH_2), 25.5 (CH_2), 25.2 (CH_2).

[(I$_2$)·S(IPr*)]: m = 114.1 mg. **^{1}H NMR** ($CDCl_3$, 400 MHz): 7.28 (d, J = 8 Hz, 8H, Ar CH), 7.25–7.18 (m, 24H, Ar CH), 6.82–6.79 (m, 12H, Ar CH), 5.37 (s, 4H, $CH(Ph)_2$), 5.24 (s, 2H, $N(CH_2)_2N$), 2.24 (s, 6H, CH_3). **^{13}C{^{1}H} DEPT Q NMR** ($CDCl_3$, 101 MHz): δ_C 160.8 (C-S) (determined by HMBC), 143.0 (Ar C), 141.7 (Ar C), 140.2 (Ar C), 139.4 (Ar C), 132.5 (Ar C), 130.6 (Ar C), 130.2 (Ar CH), 129.4 (Ar CH), 128.5 (Ar CH), 128.3 (Ar CH), 126.7 (Ar CH), 126.6 (Ar CH), 120.1 (CH_{imid}), 51.9 ($CHPh_2$), 22.1 (CH_3).

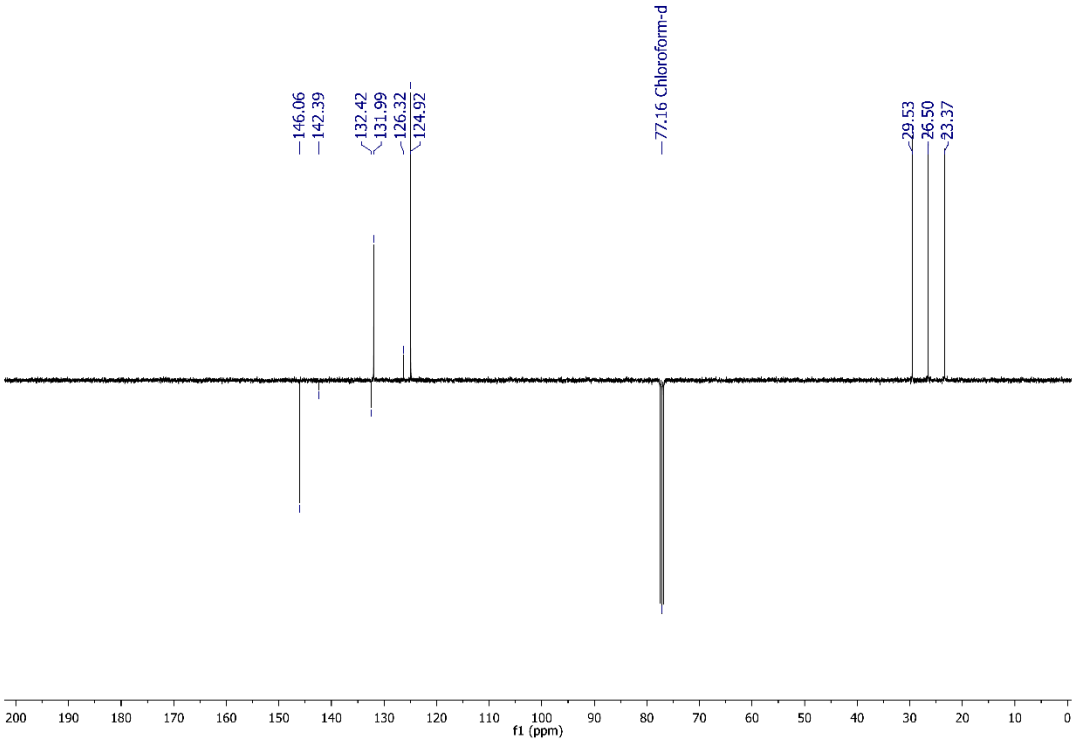
NMR spectra

[$SeBr_2$(IPr)]

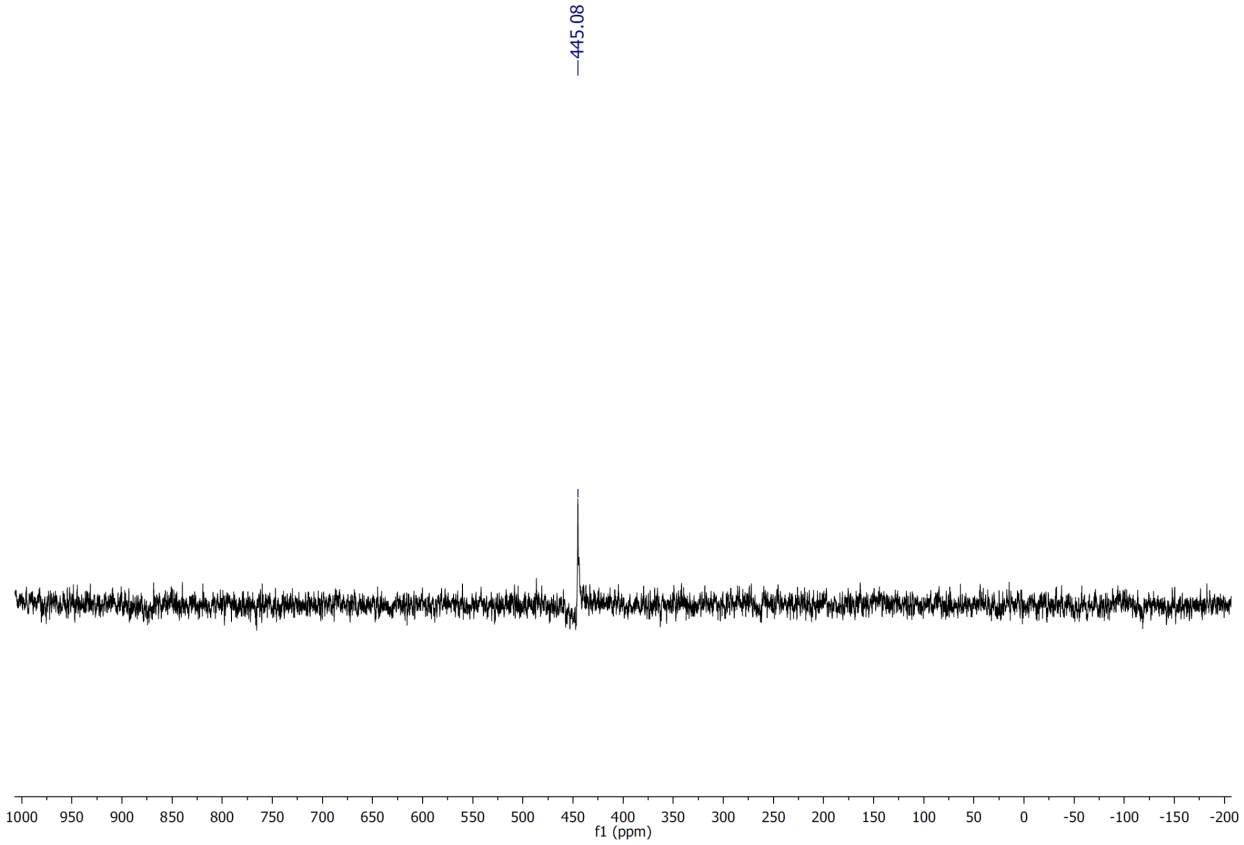
^{1}H NMR



$^{13}C\{^1H\}$ DEPT Q NMR



^{77}Se NMR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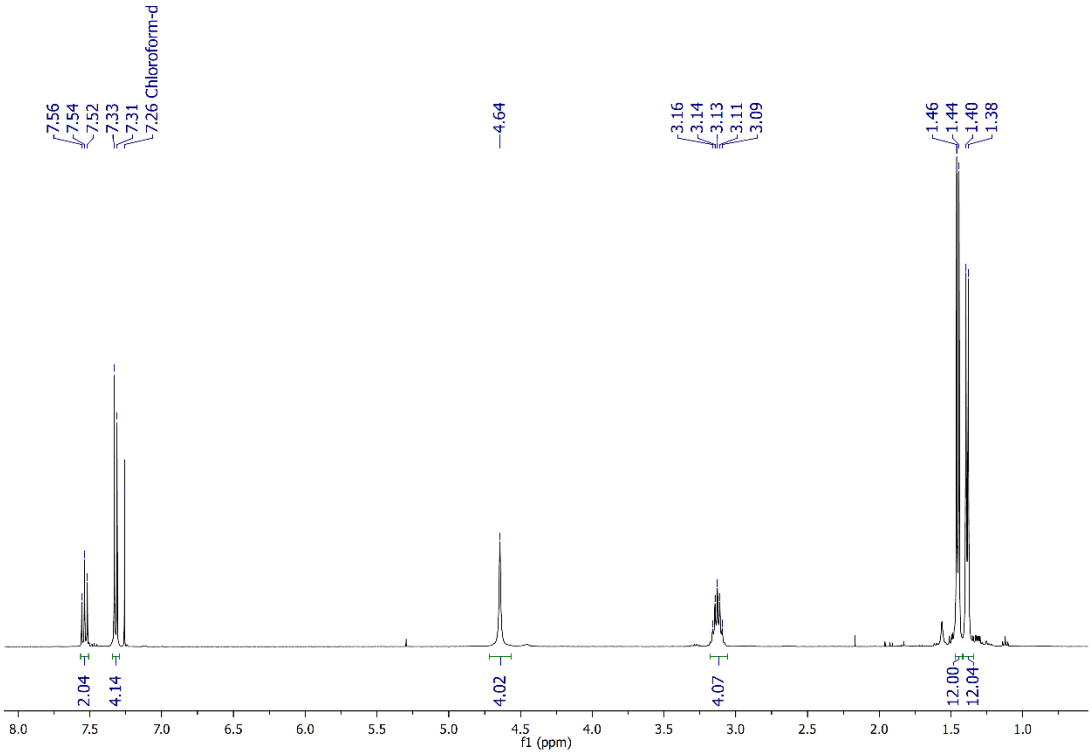
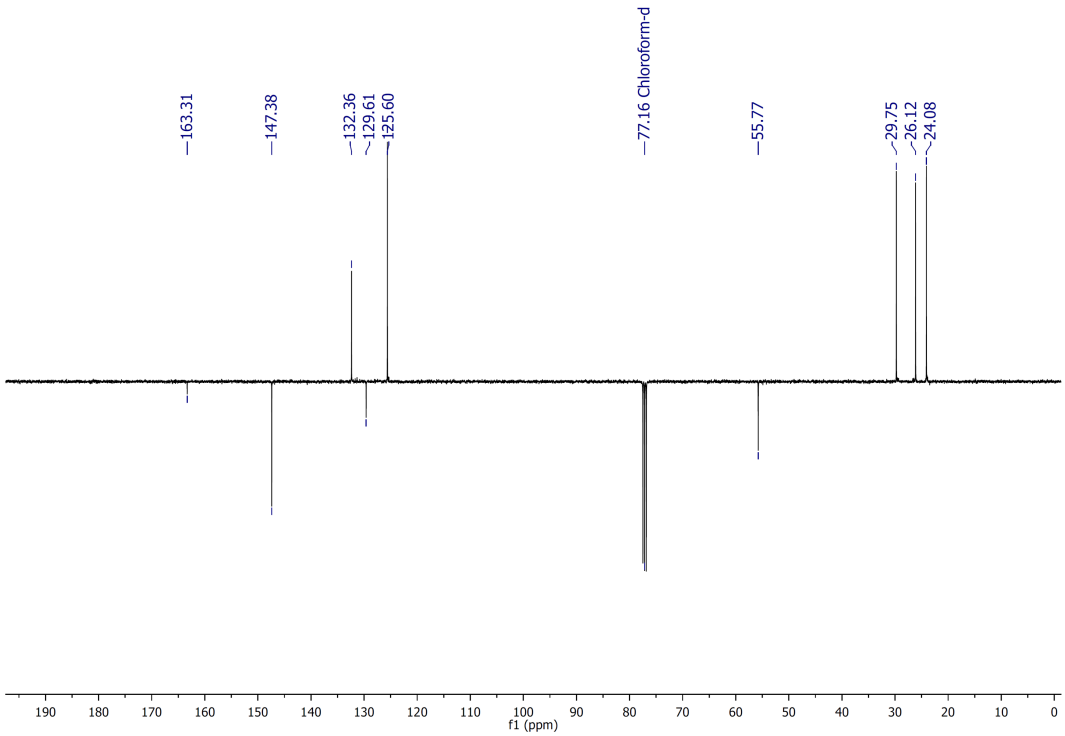
f1 (ppm)

[SeBr(SIPr)]Br_3

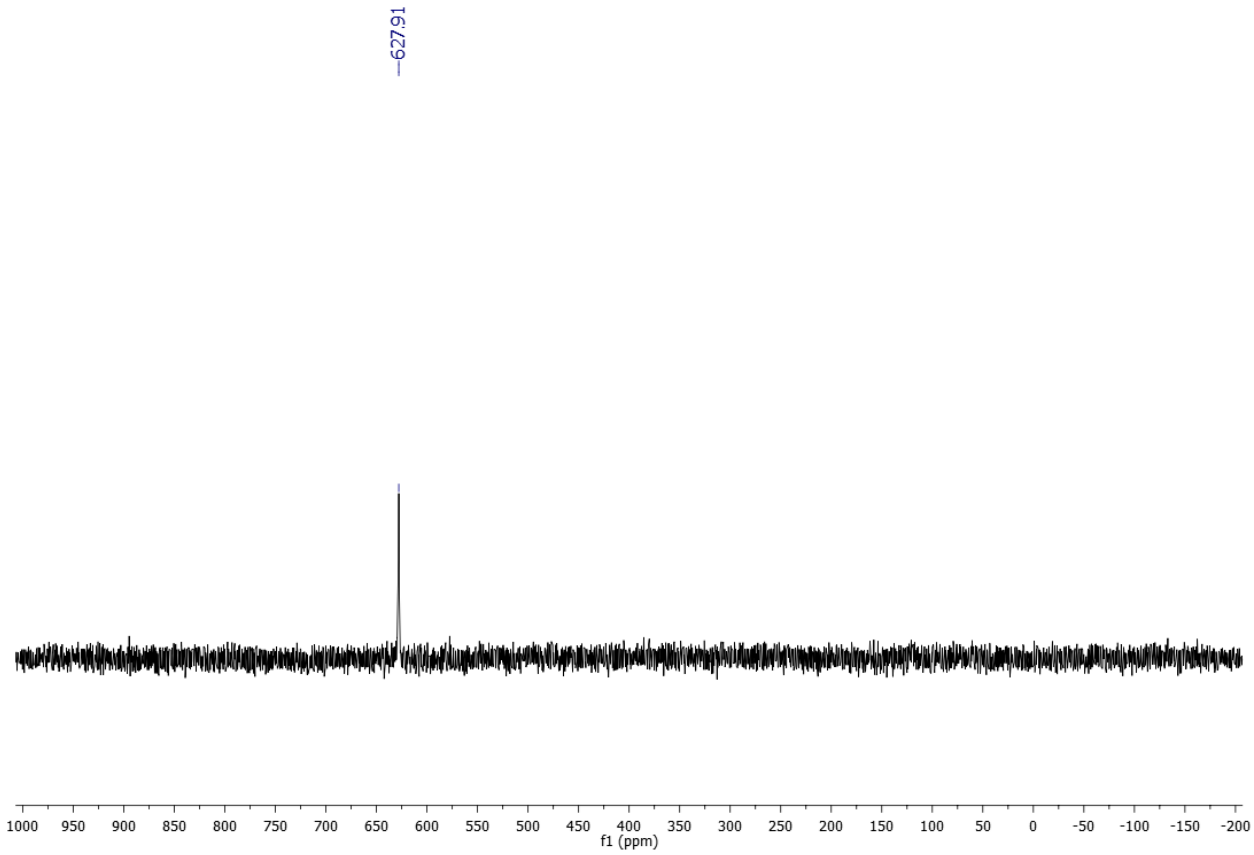
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR



^{77}Se NMR


627.91
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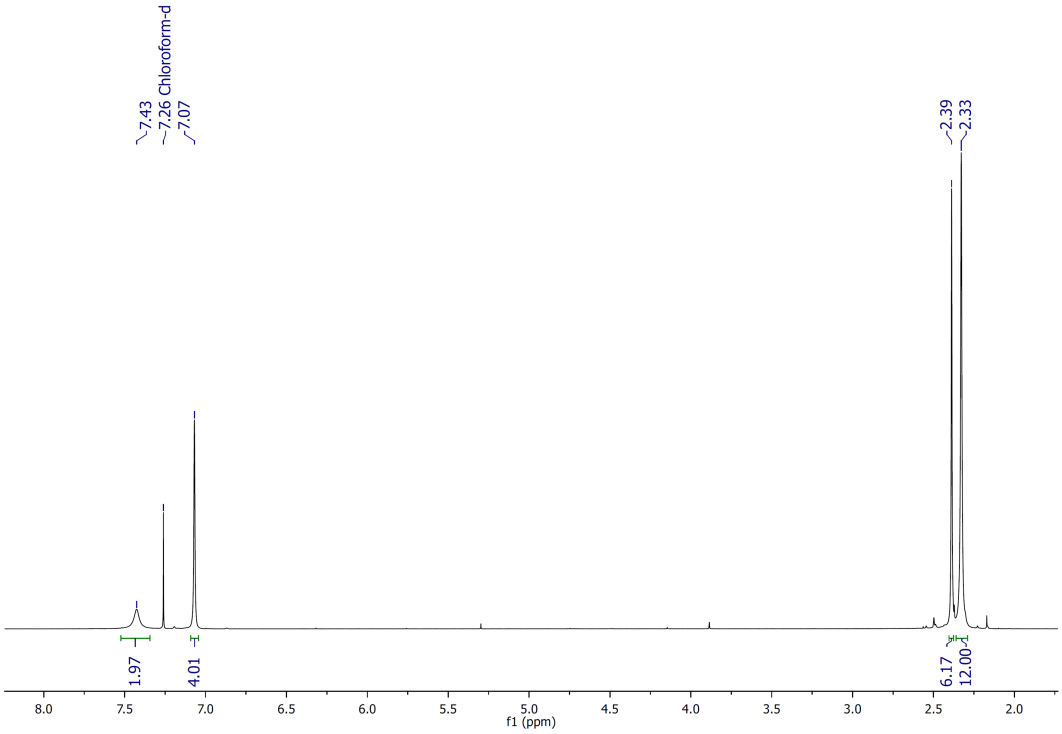
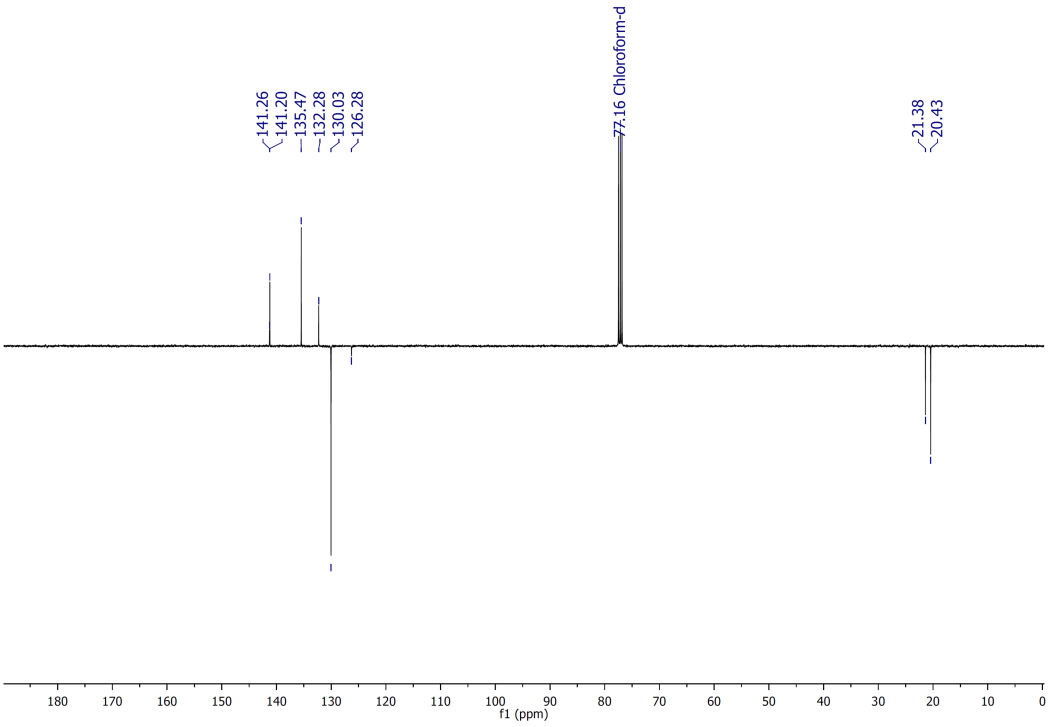
f1 (ppm)

[$SeBr_2$(IMes)]

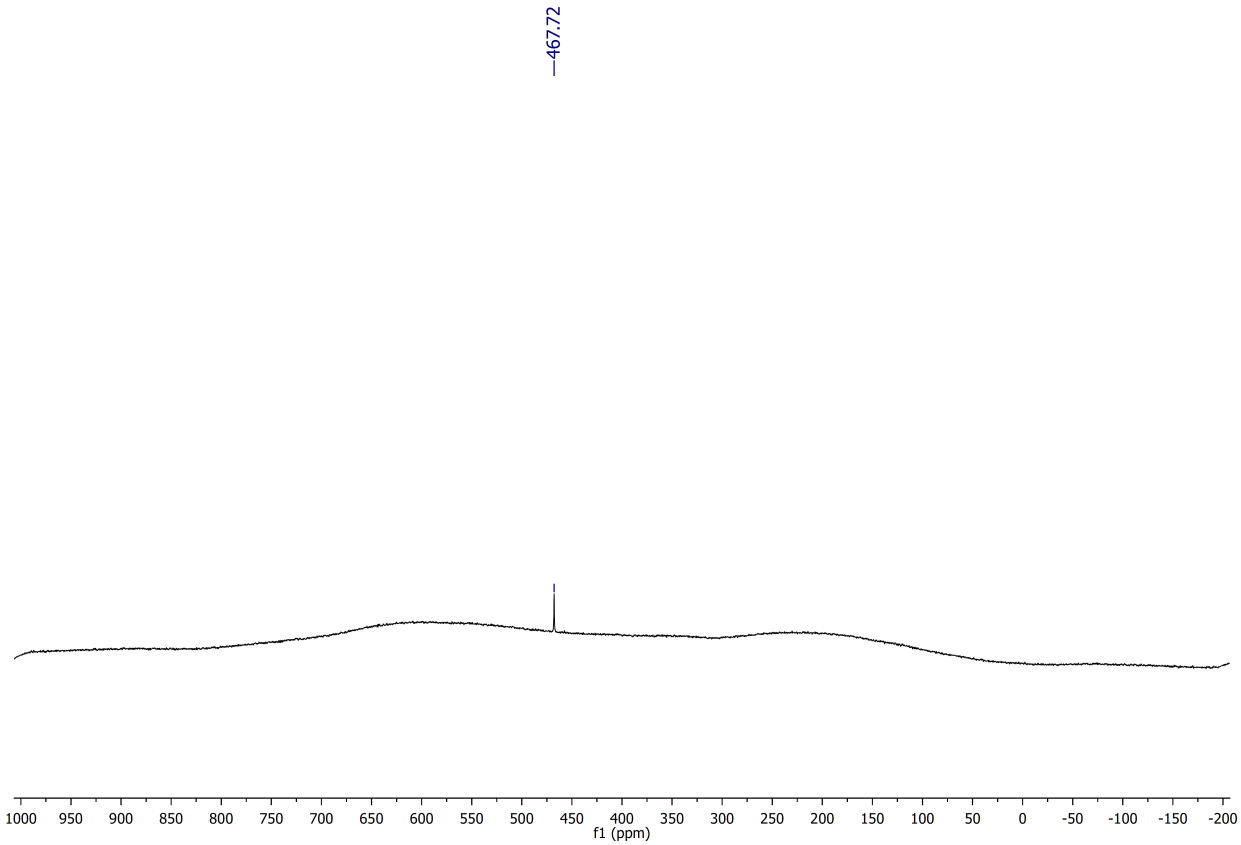
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR



^{77}Se NMR


467.72
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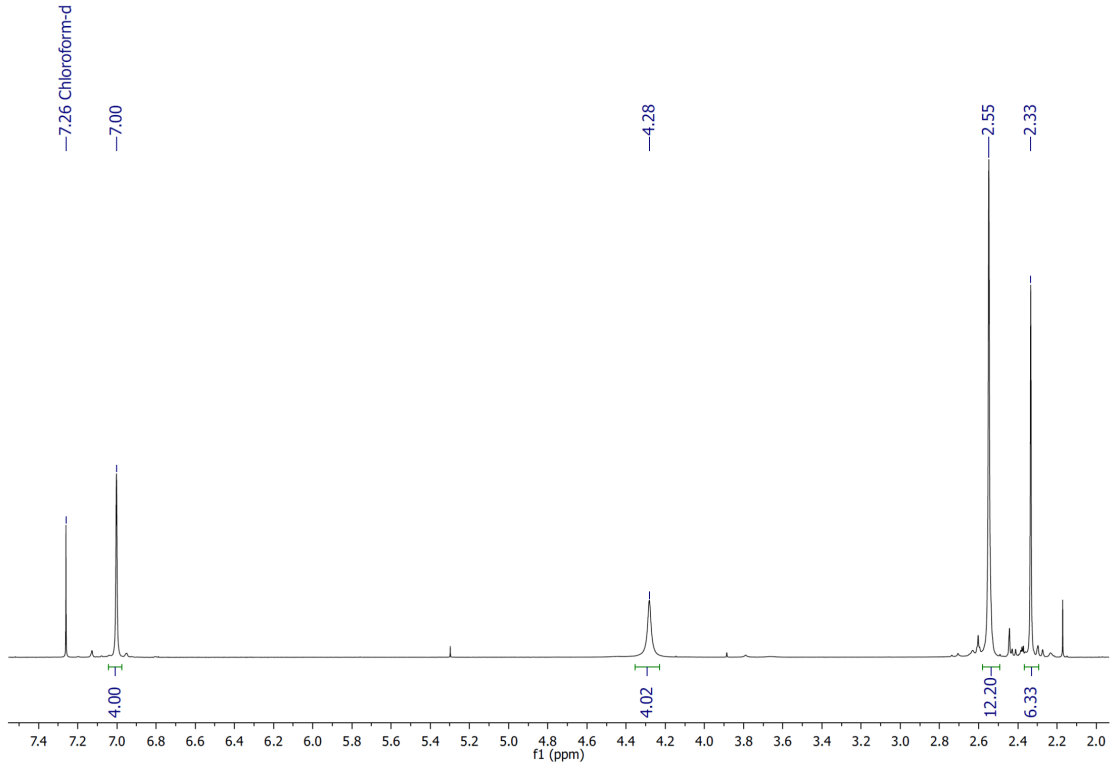
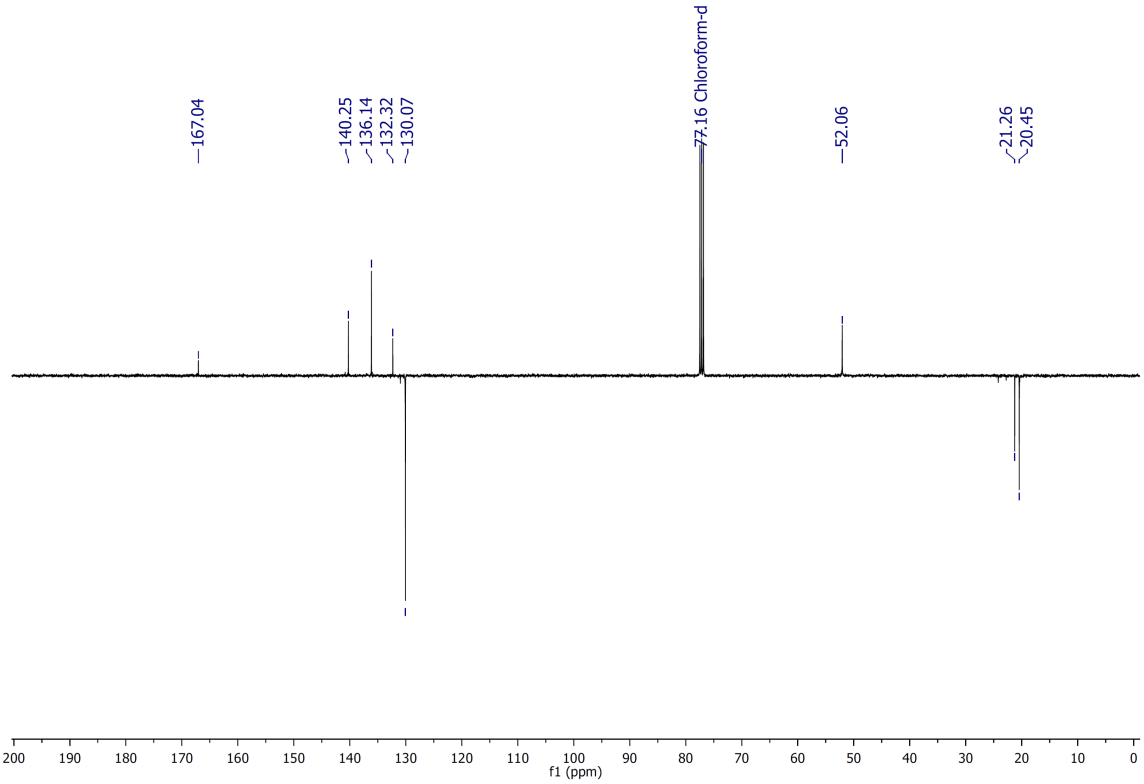
f1 (ppm)

[$SeBr_2$(SIMes)]

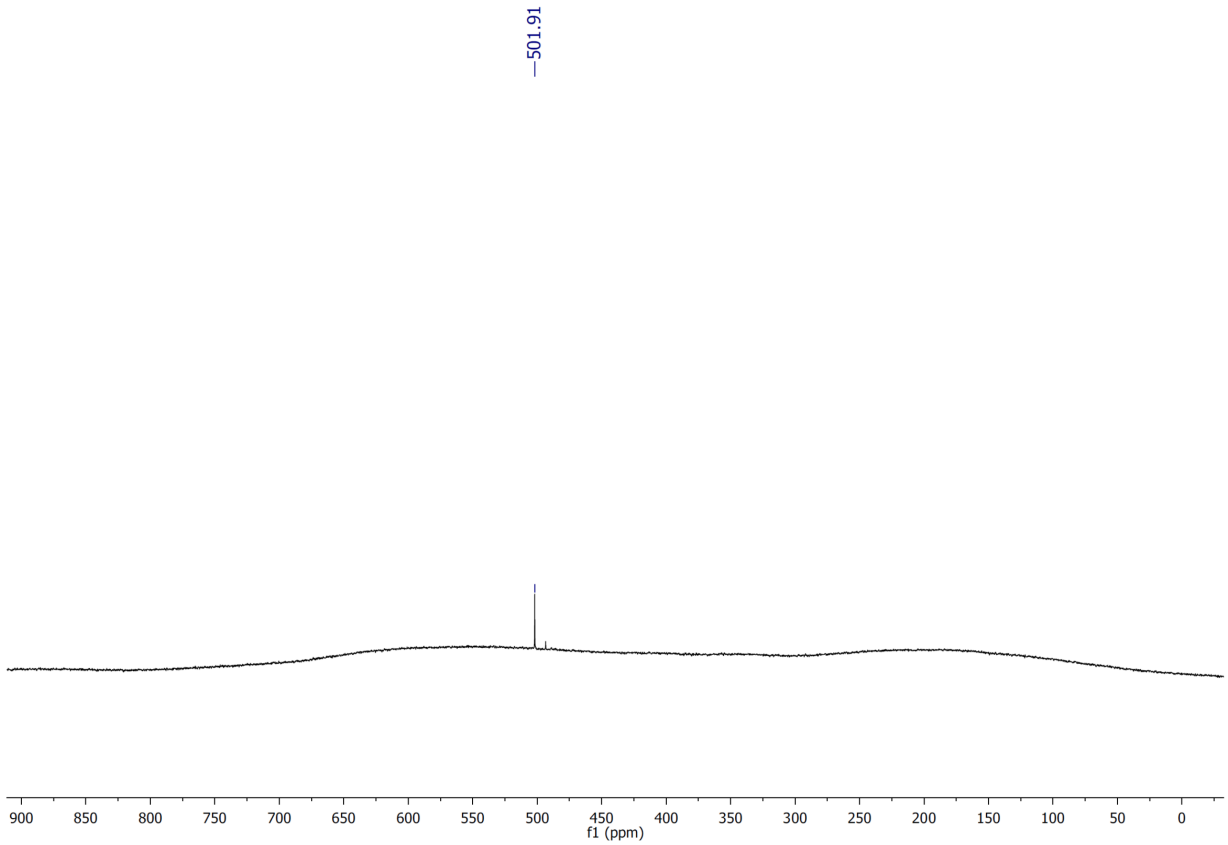
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR



^{77}Se NMR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650
600
550
500
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400
350
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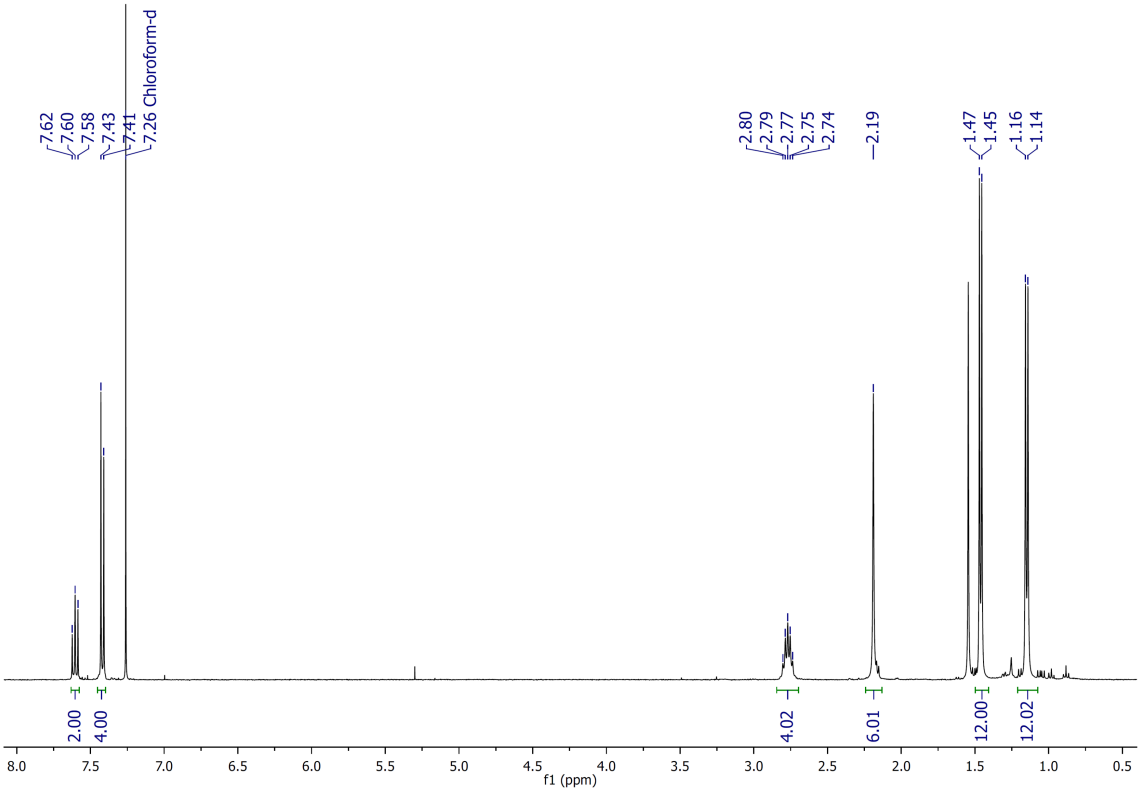
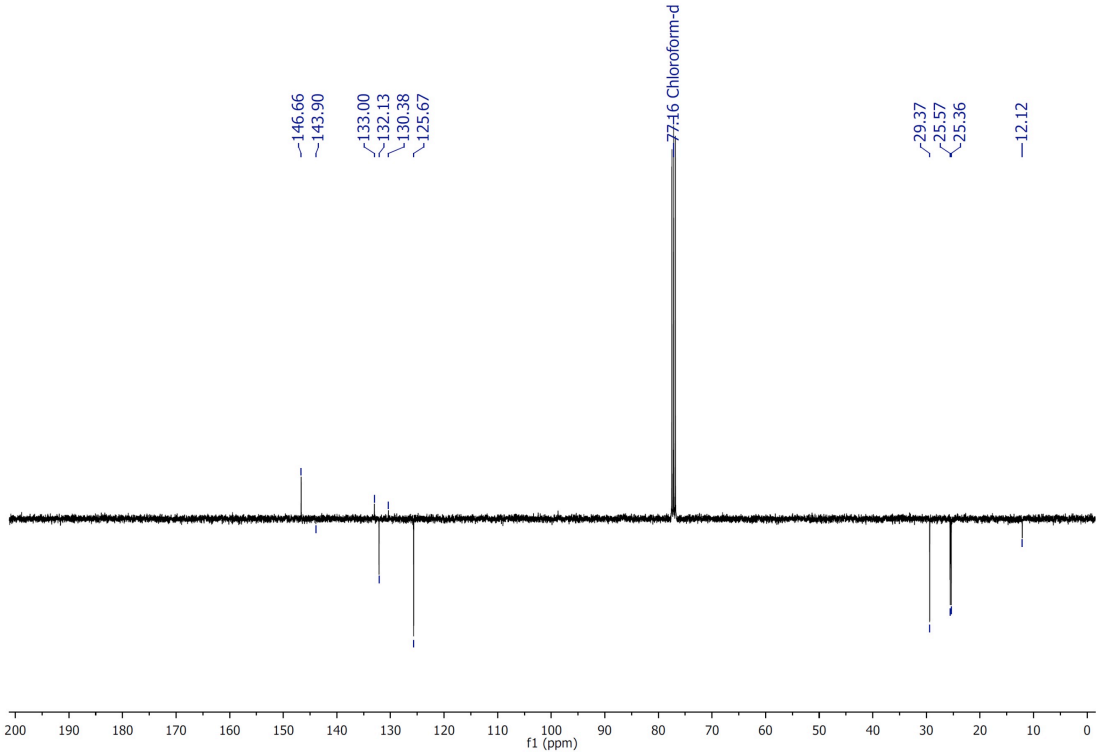
250
200
150
100
50
0
f1 (ppm)

[$SeBr_2(IPr^{Me})$]

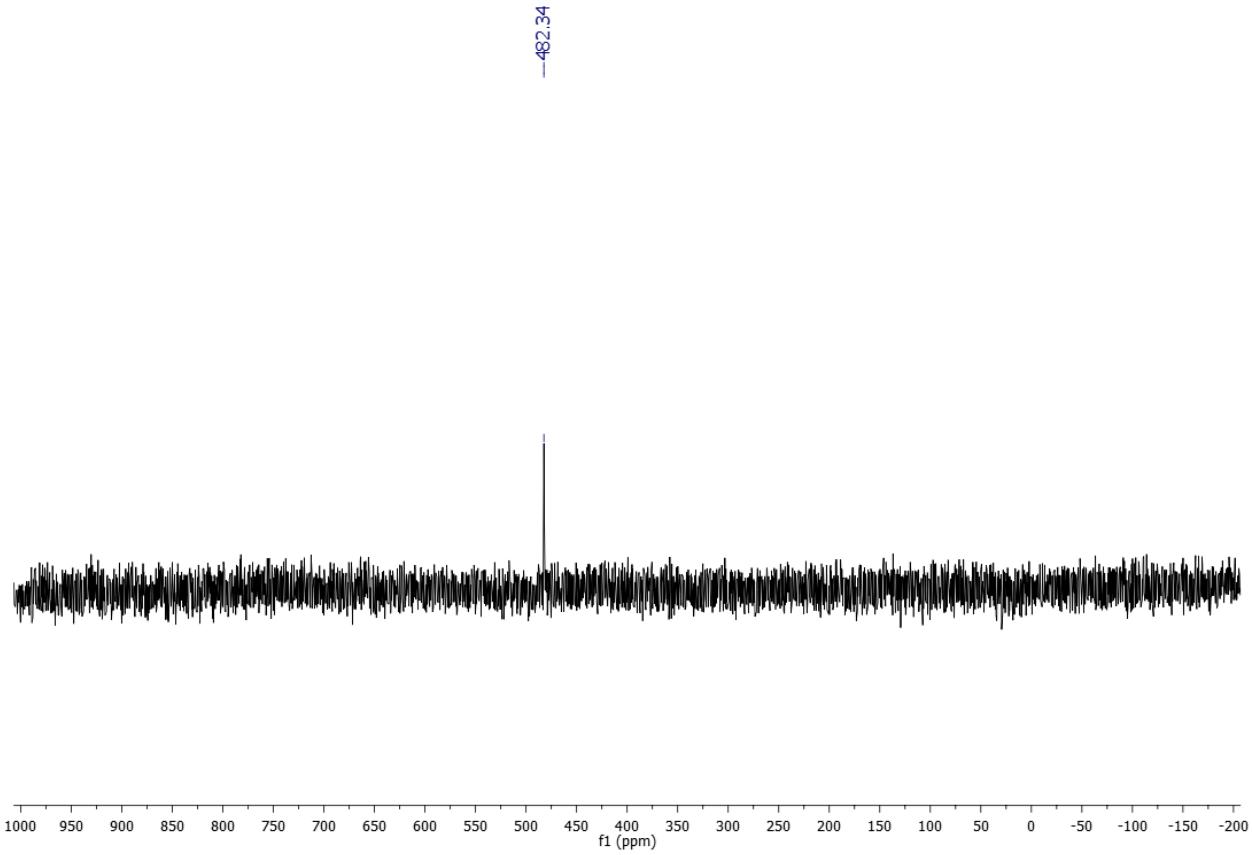
^1H NMR



$^{13}C\{^1H\}$ DEPT Q NMR



^{77}Se NMR


482.34
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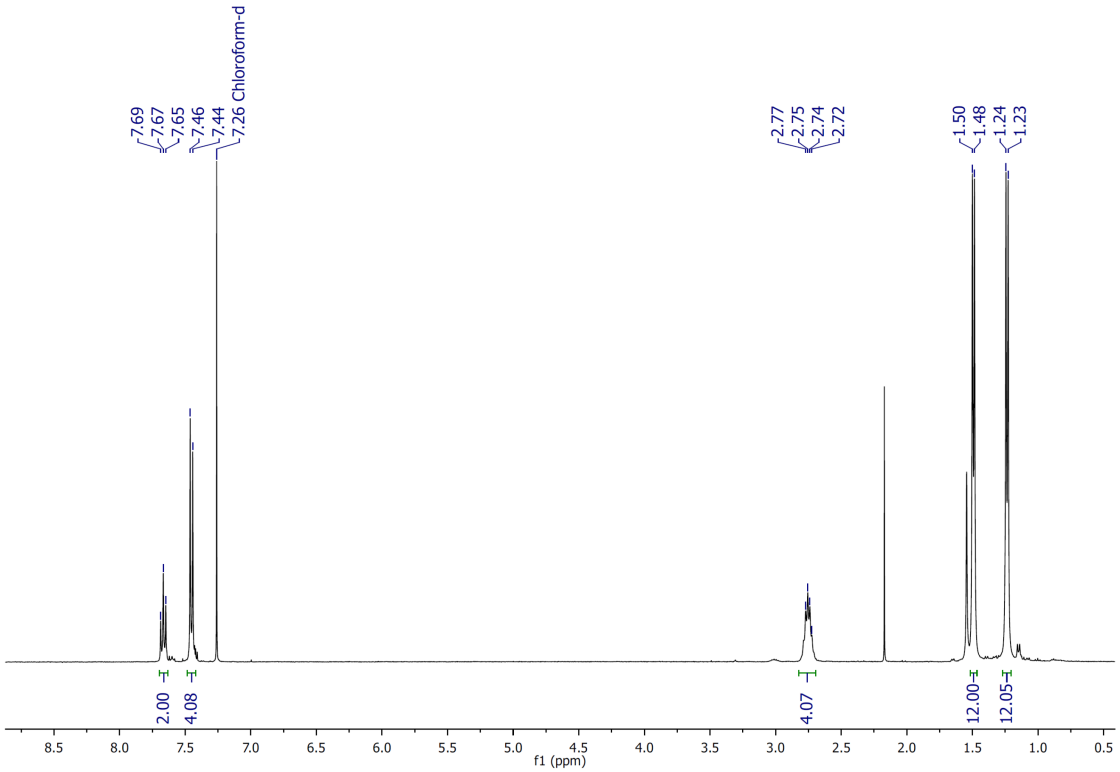
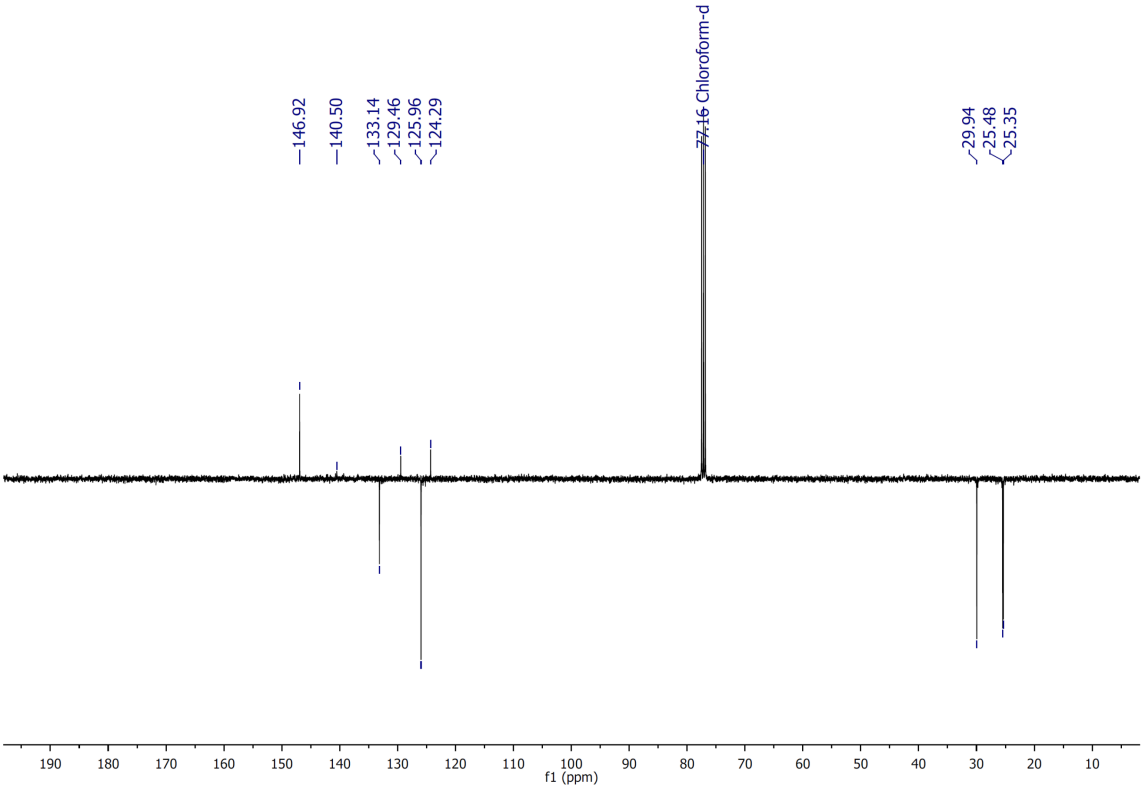
f1 (ppm)

[SeBr(IPr^{Cl})]Br$_3$

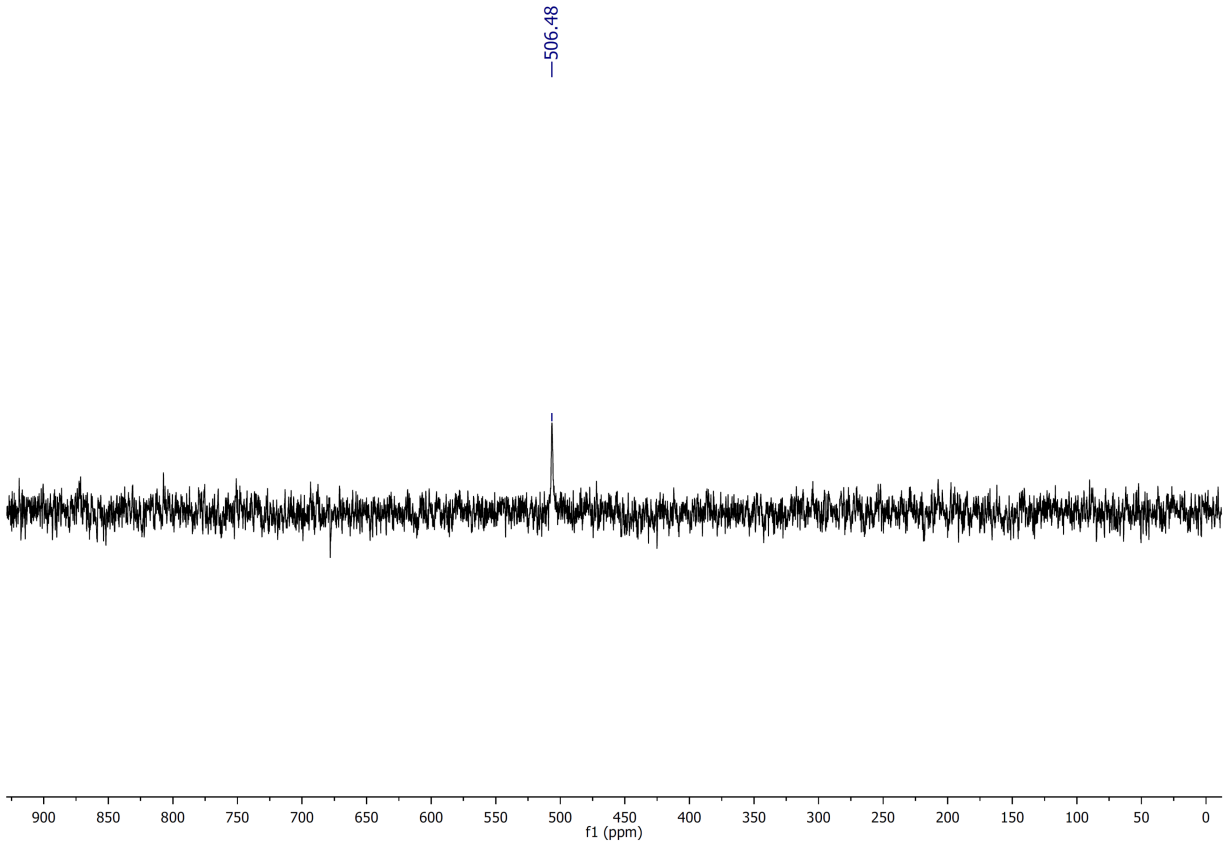
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR



^{77}Se NMR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900
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250
200
150
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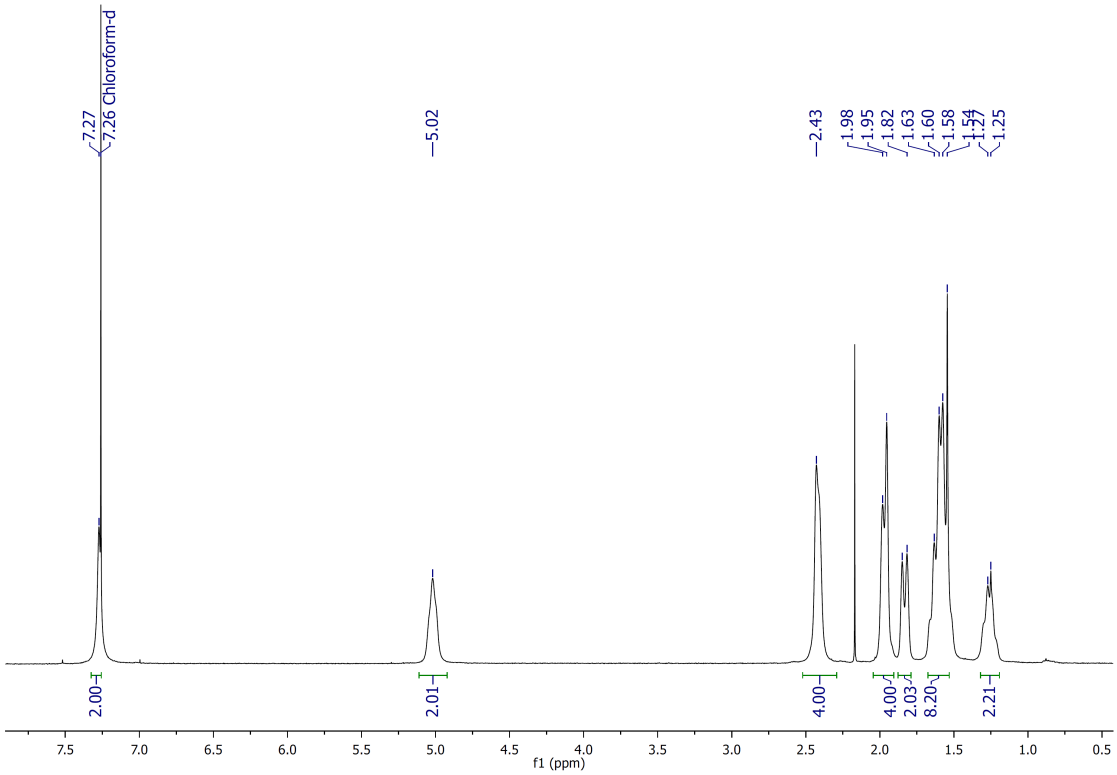
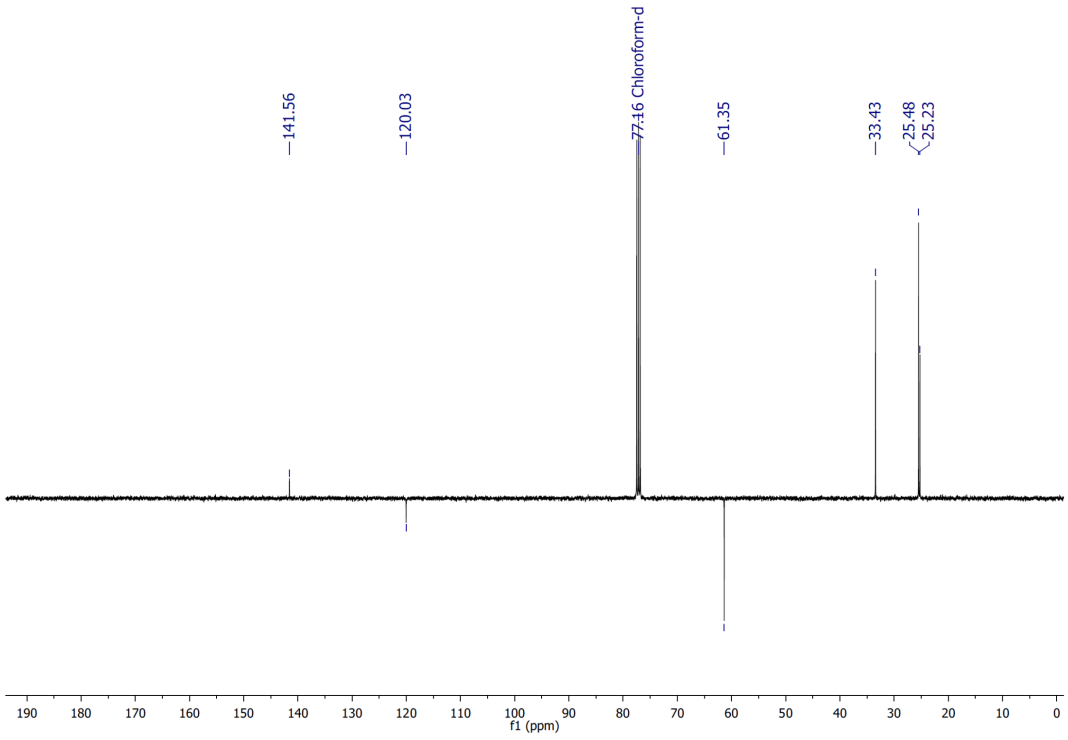
50
0
f1 (ppm)

[$SeBr_2$(ICy)]

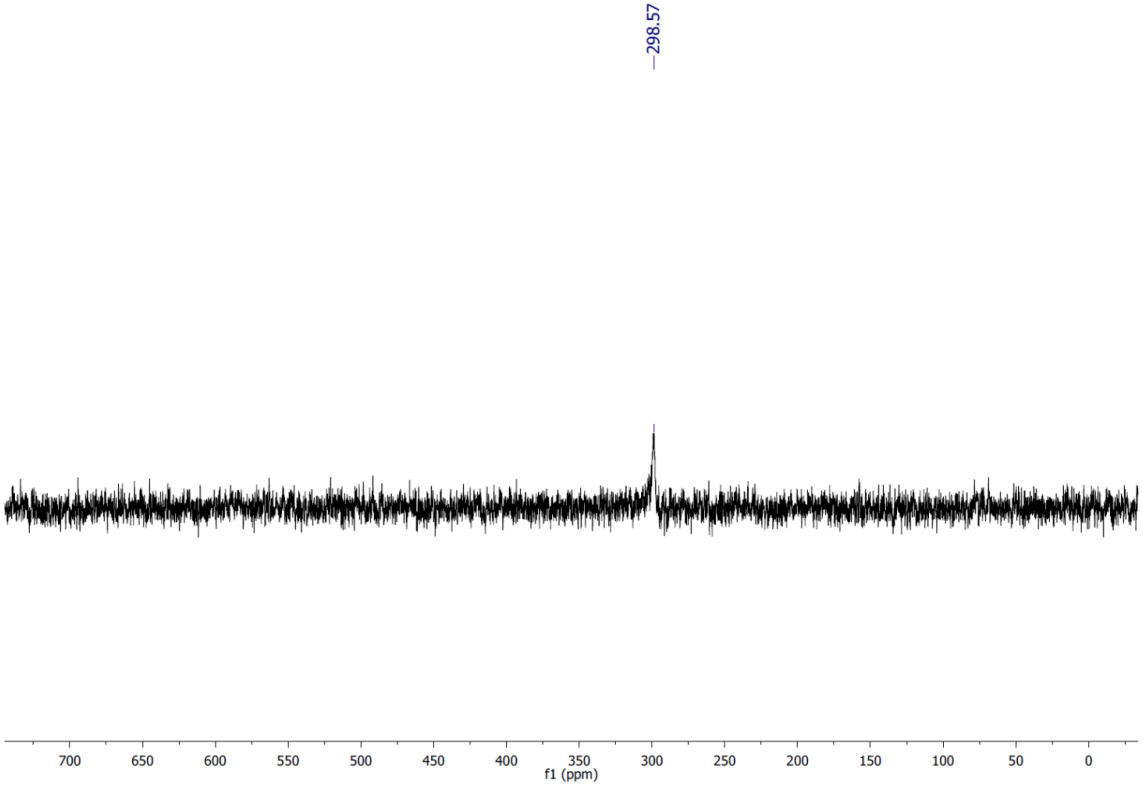
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

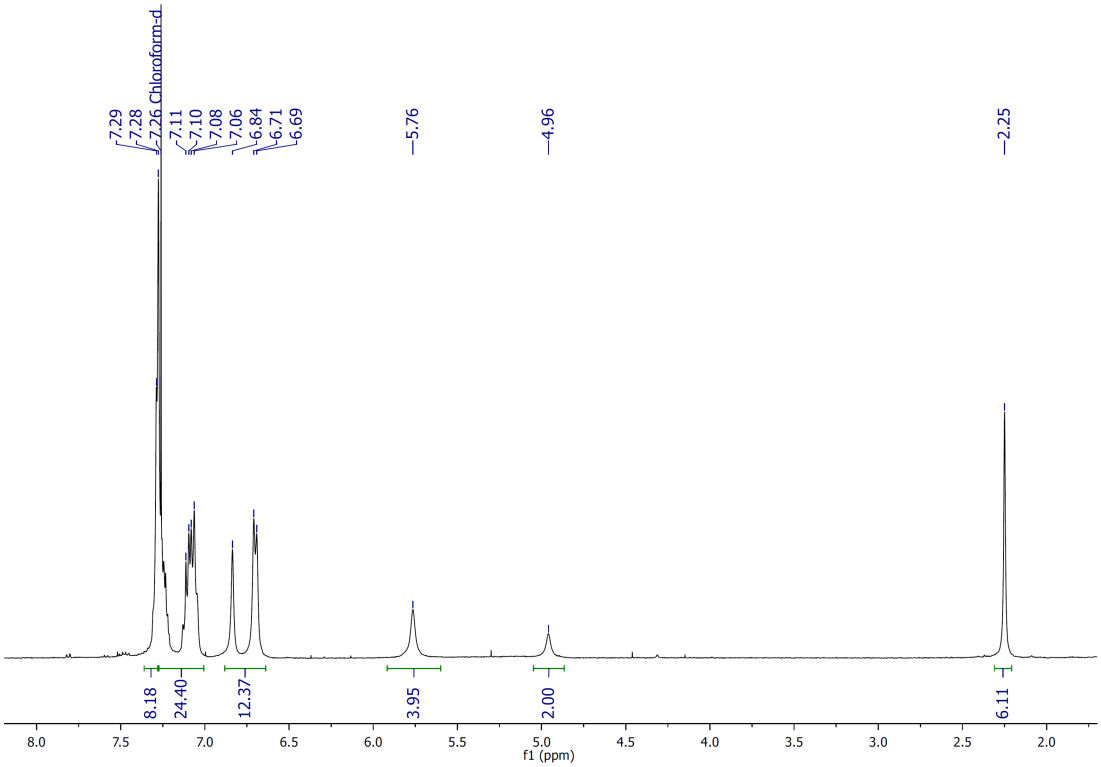


^{77}Se NMR

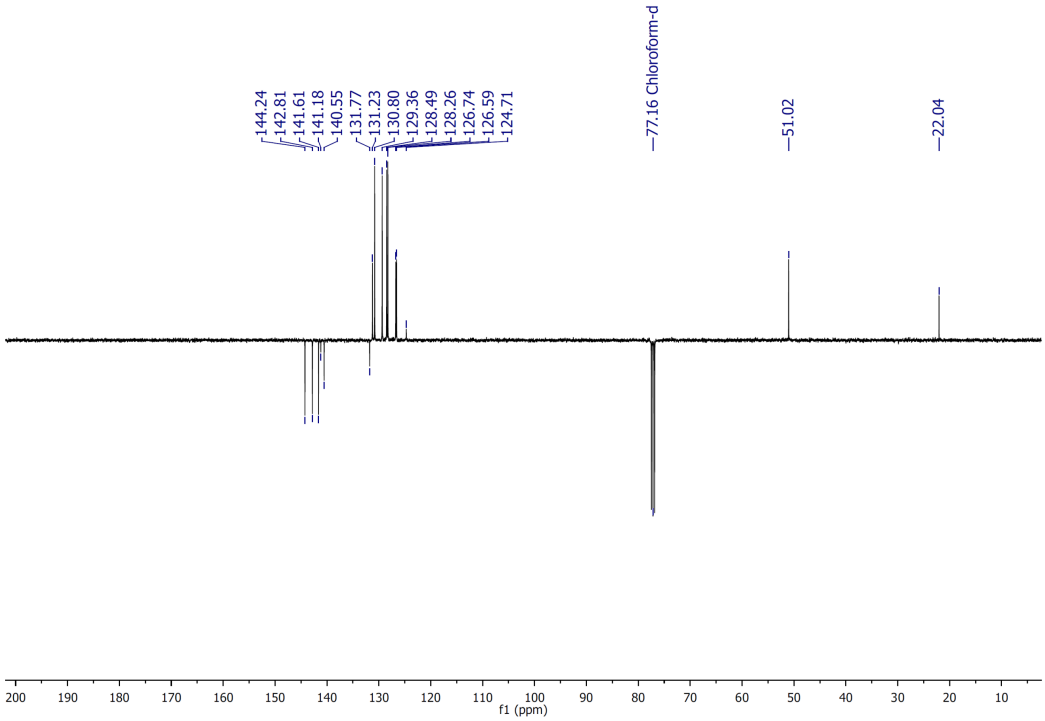

298.57
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
f1 (ppm)

[$SeBr_2$(IPr*)]

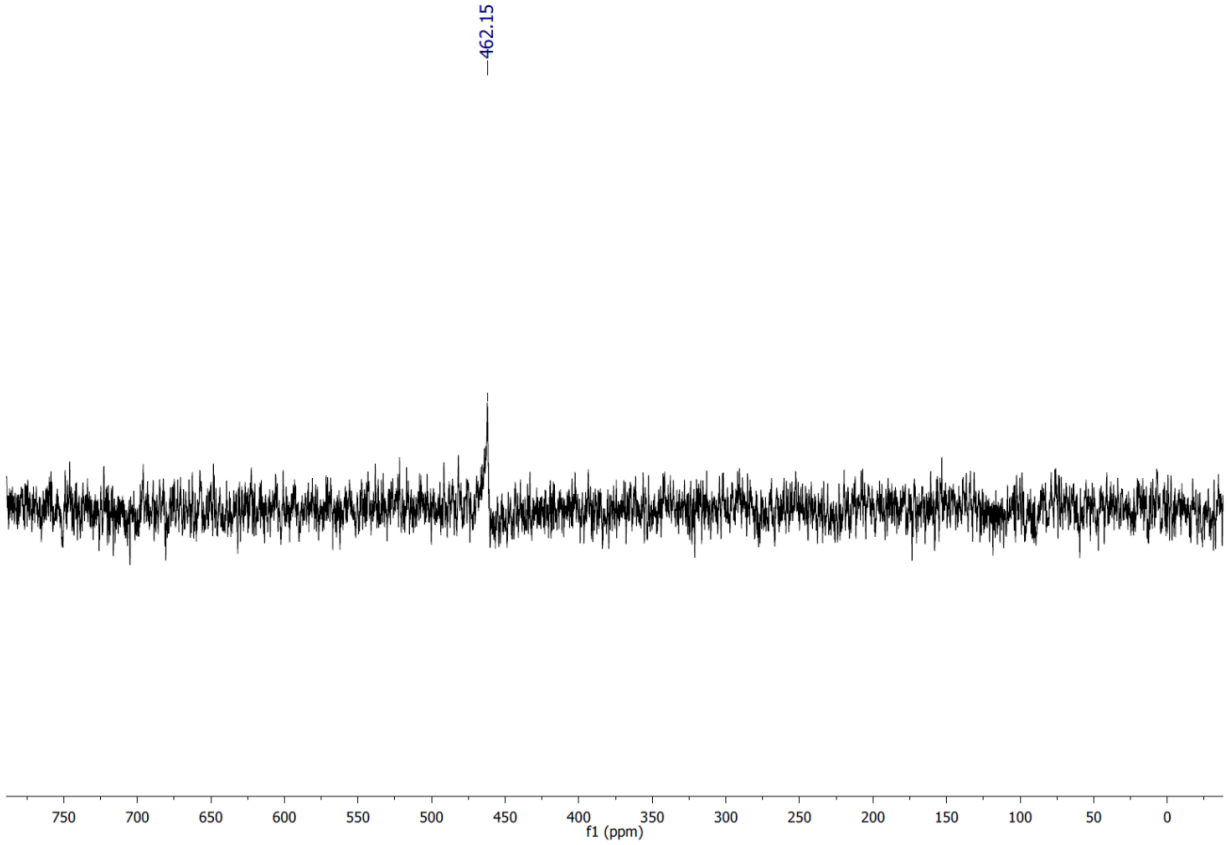
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

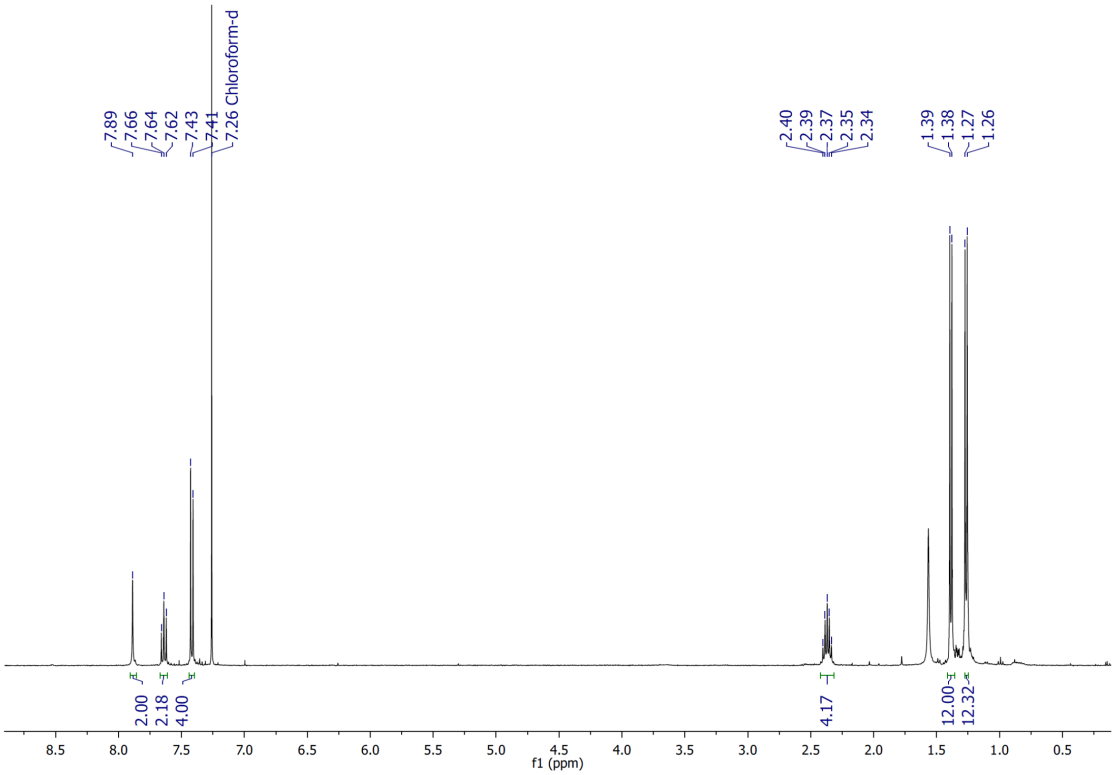


^{77}Se NMR

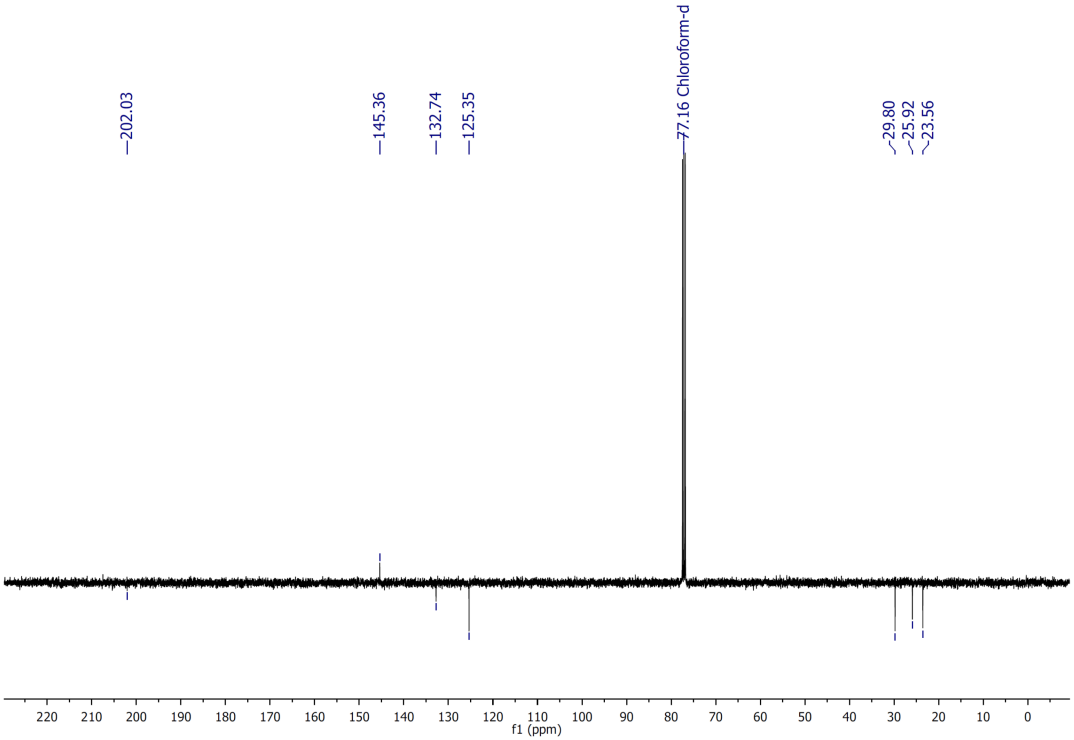

462.15
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
f1 (ppm)

[(Br$_2$)·S(IPr)}]

^{1}H NMR

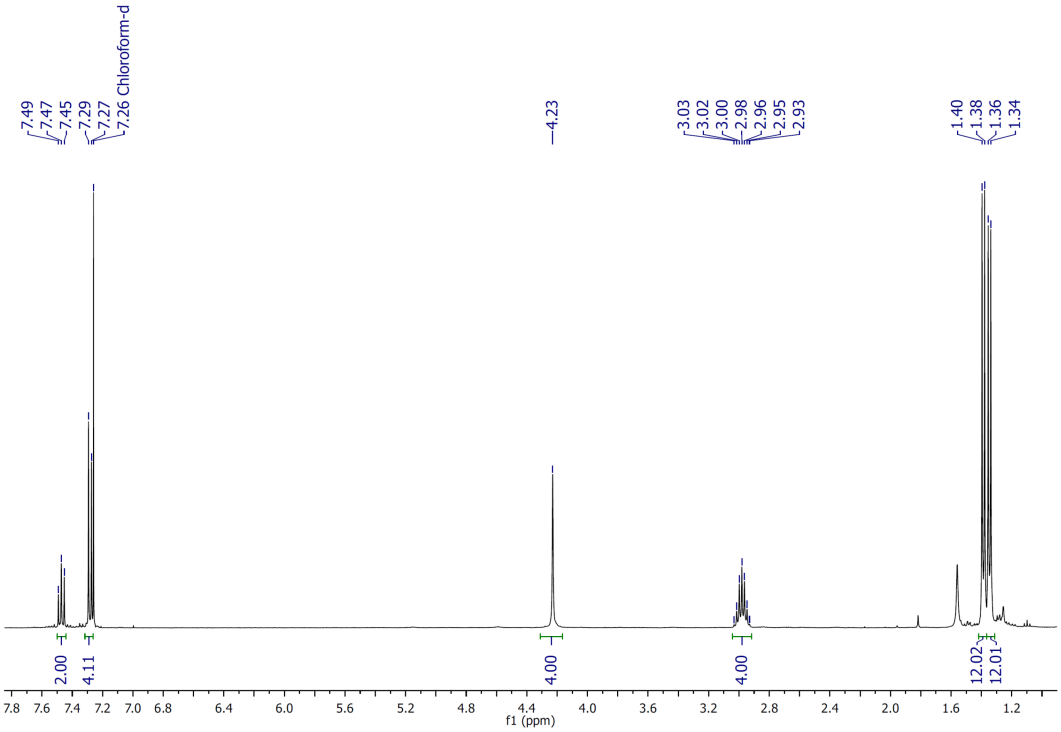


^{13}C{^{1}H} DEPT Q NMR

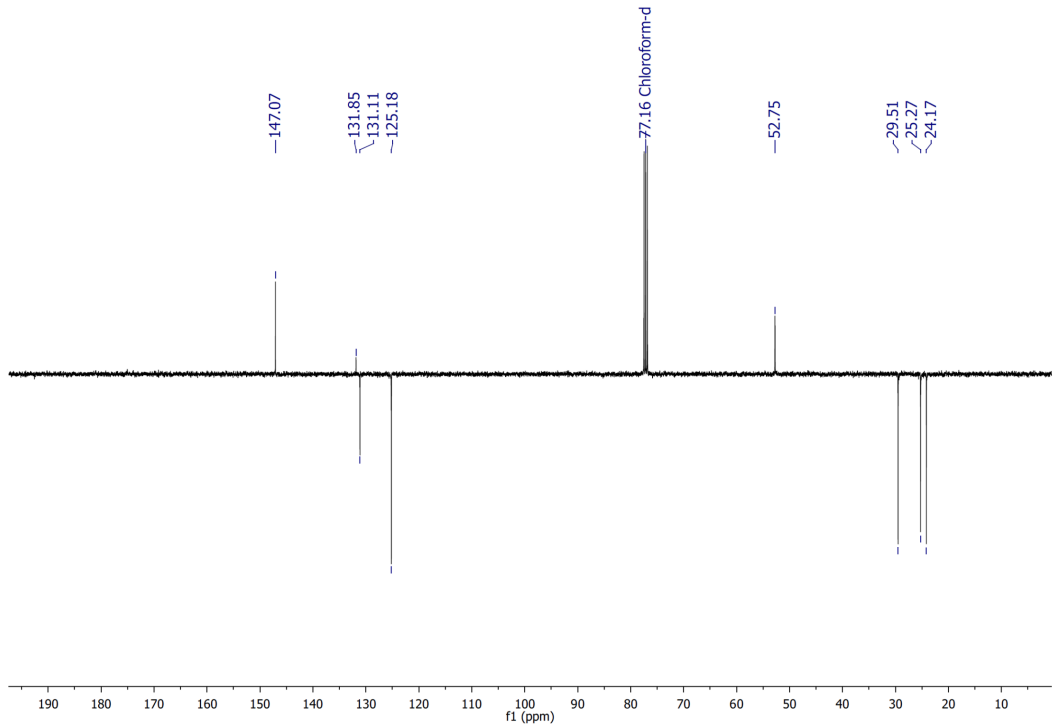


[(Br$_2$)·S(SIPr)}]

^{1}H NMR

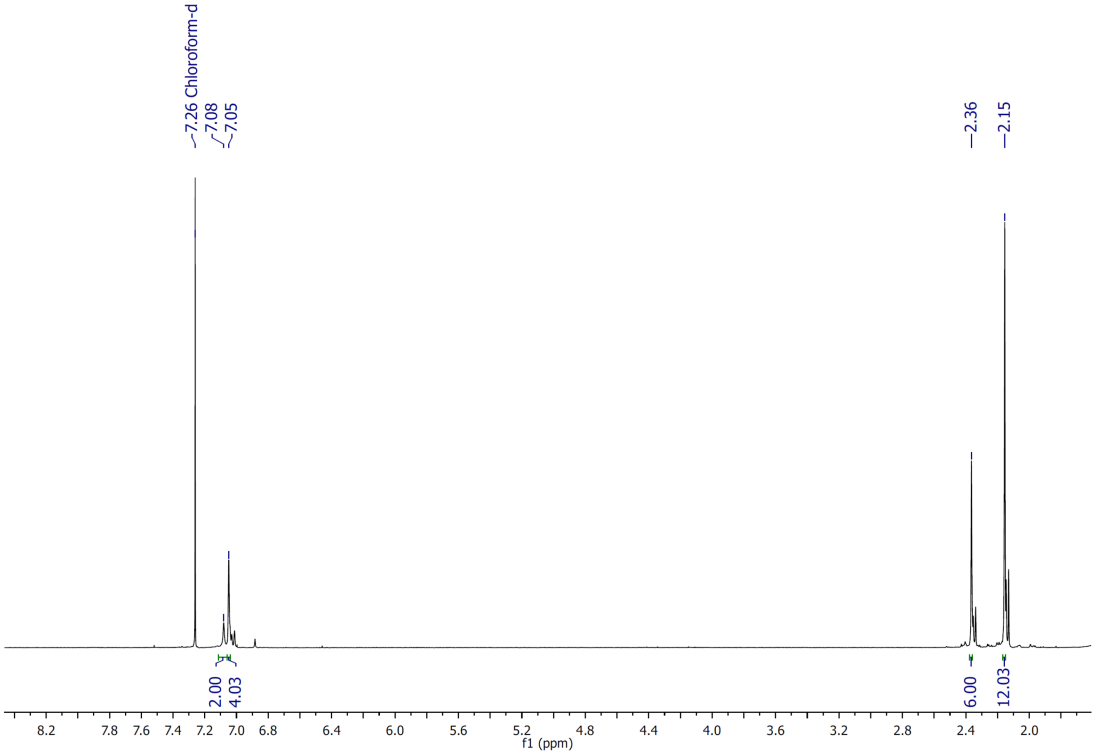


^{13}C{^{1}H} DEPT Q NMR

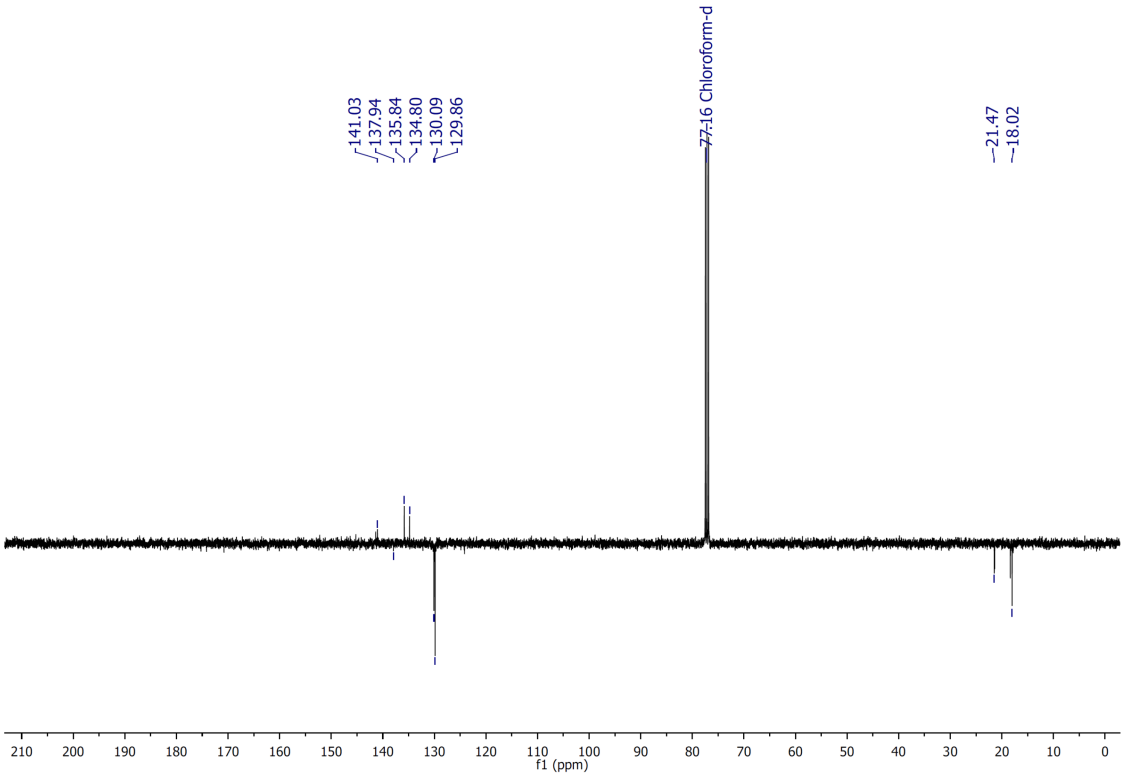


[(Br$_2$)·S(IMes)}]

^{1}H NMR

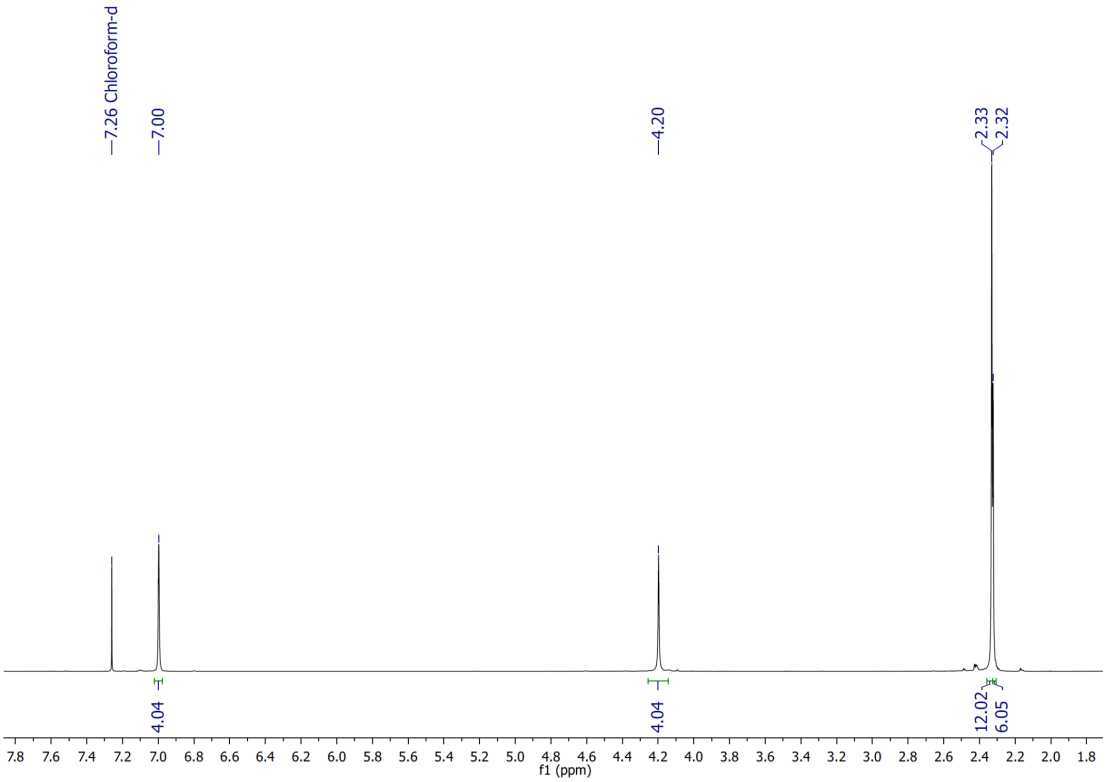


^{13}C{^{1}H} DEPT Q NMR

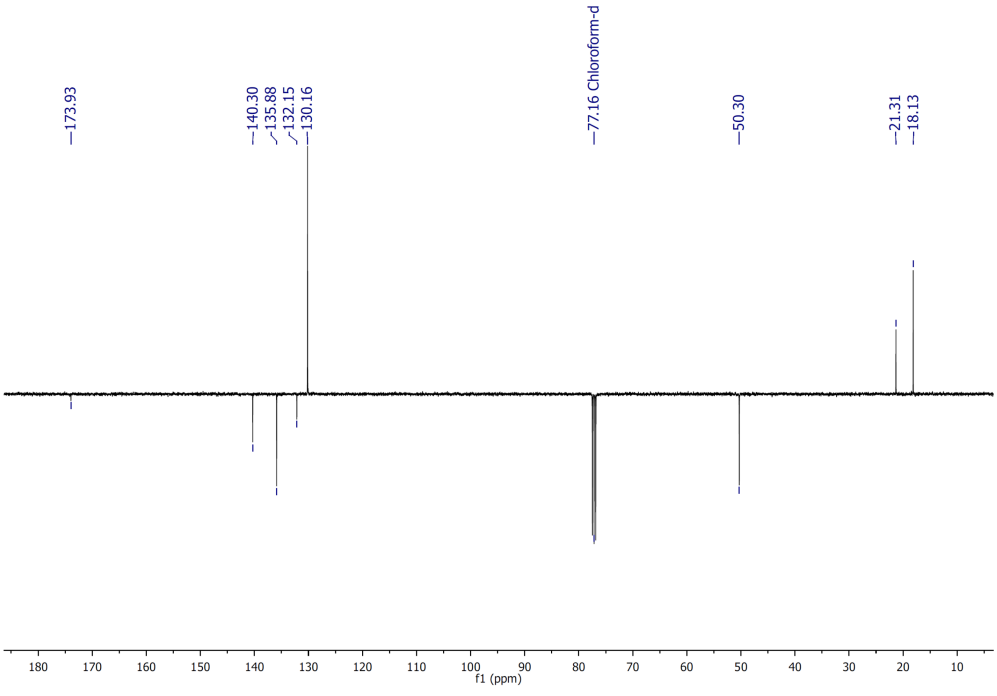


[(Br$_2$)·S(SIMes)}]

^{1}H NMR

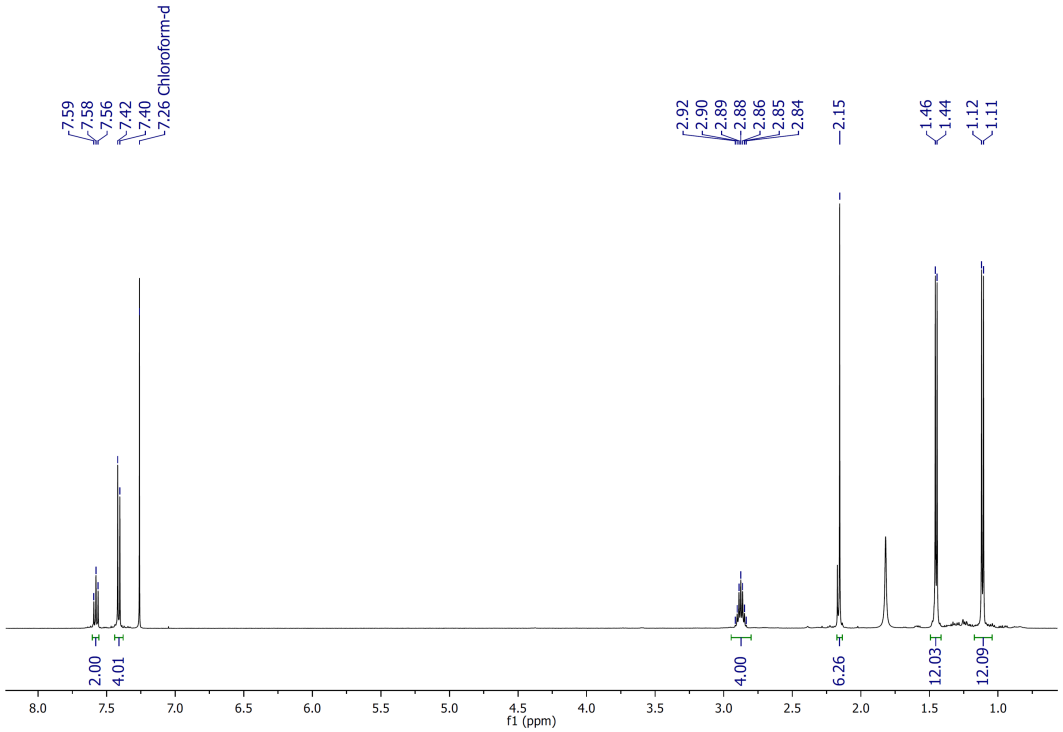


^{13}C{^{1}H} DEPT Q NMR

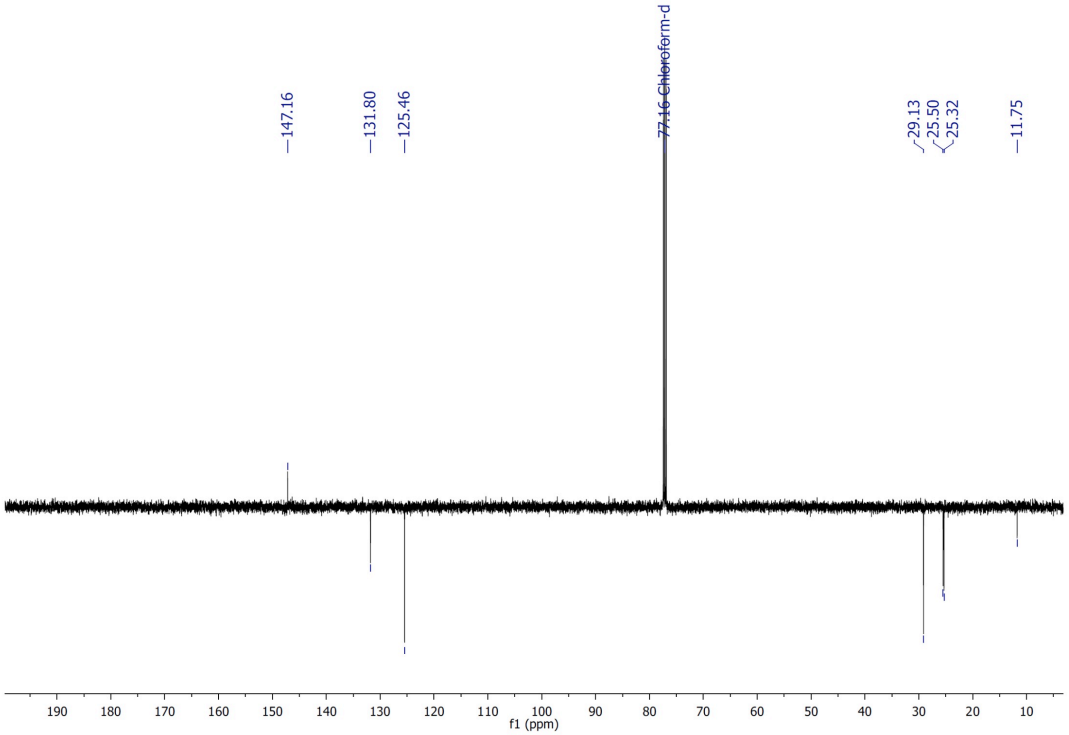


[SBr·(IPr^{Me})]Br$_3$

^{1}H NMR

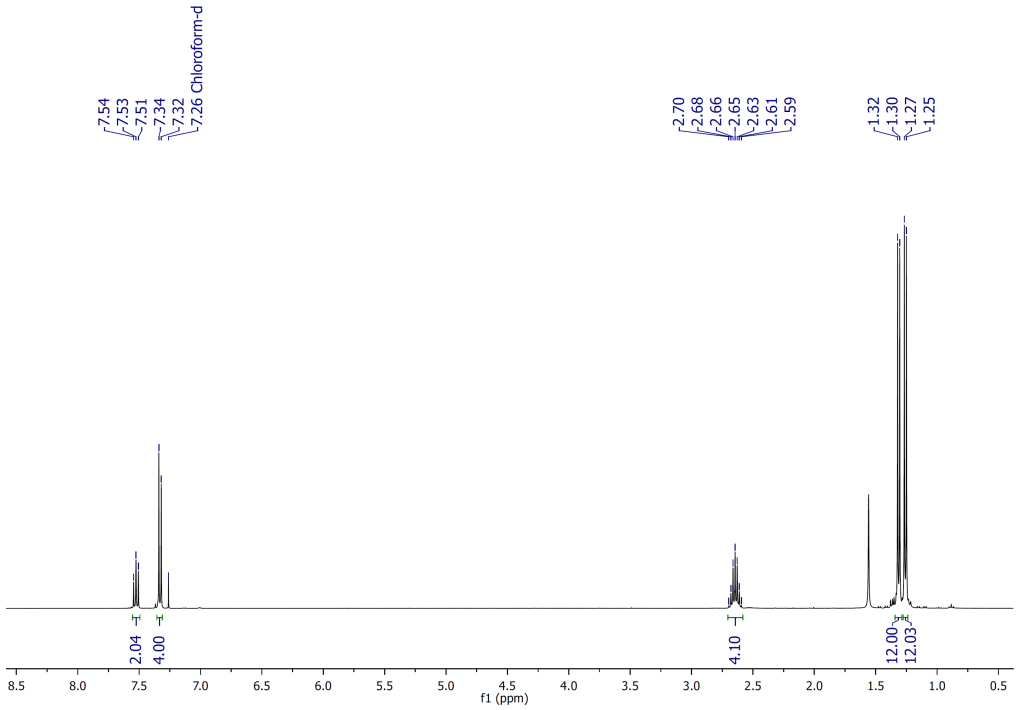


^{13}C{^{1}H} DEPT Q NMR

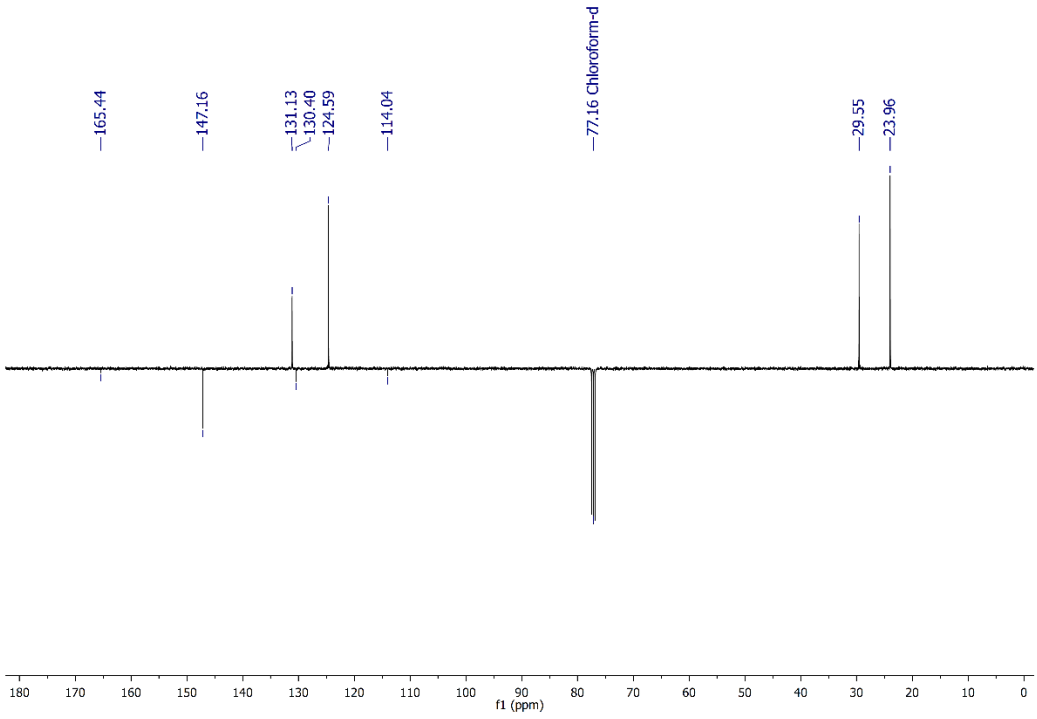


[(Br_2)·S(IPr^{Cl})]

^{1}H NMR

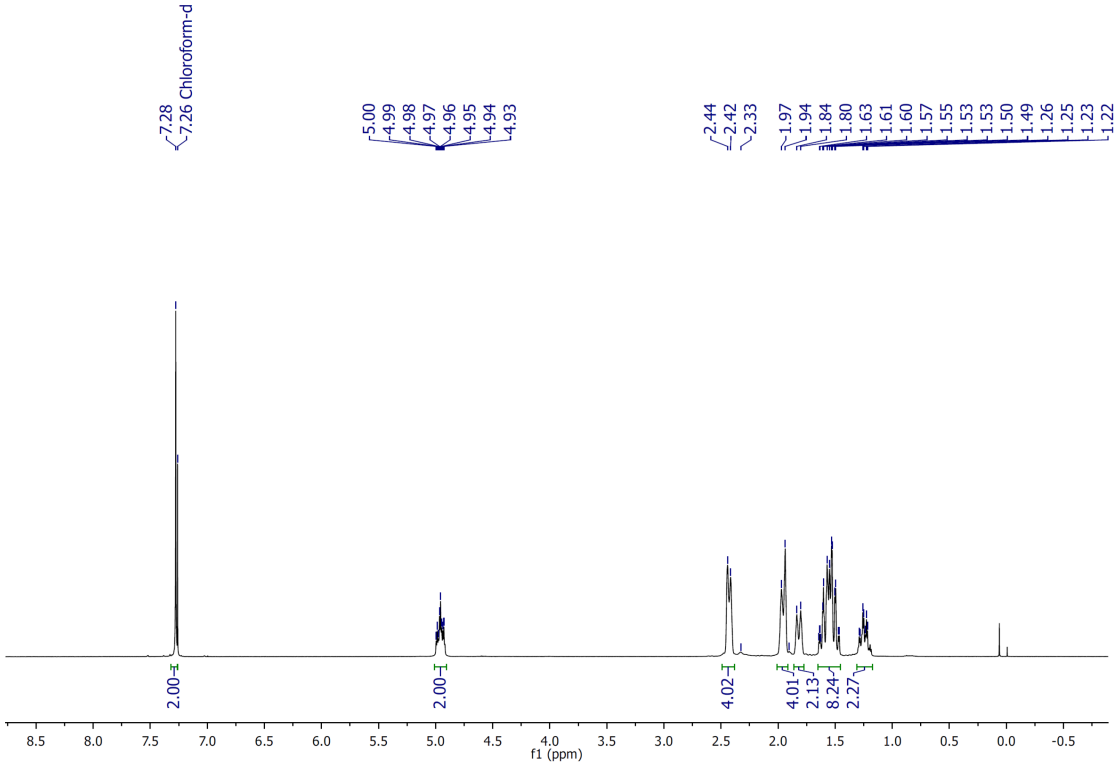


^{13}C{^{1}H} DEPT Q NMR

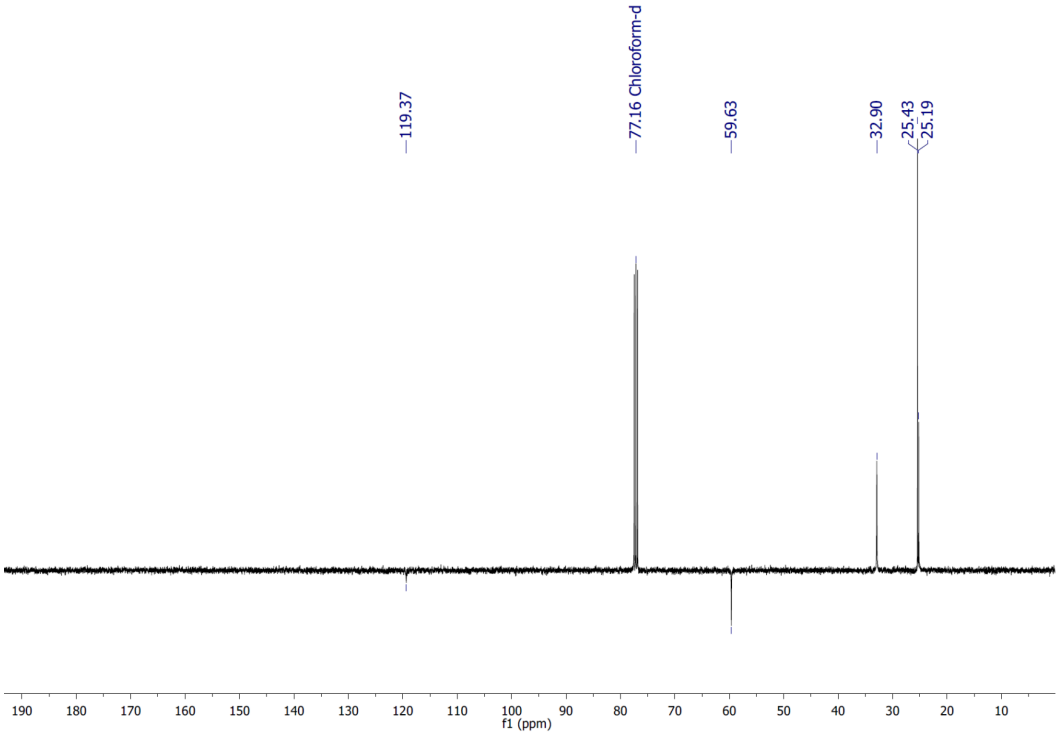


[SBr·(ICy)]Br

^{1}H NMR

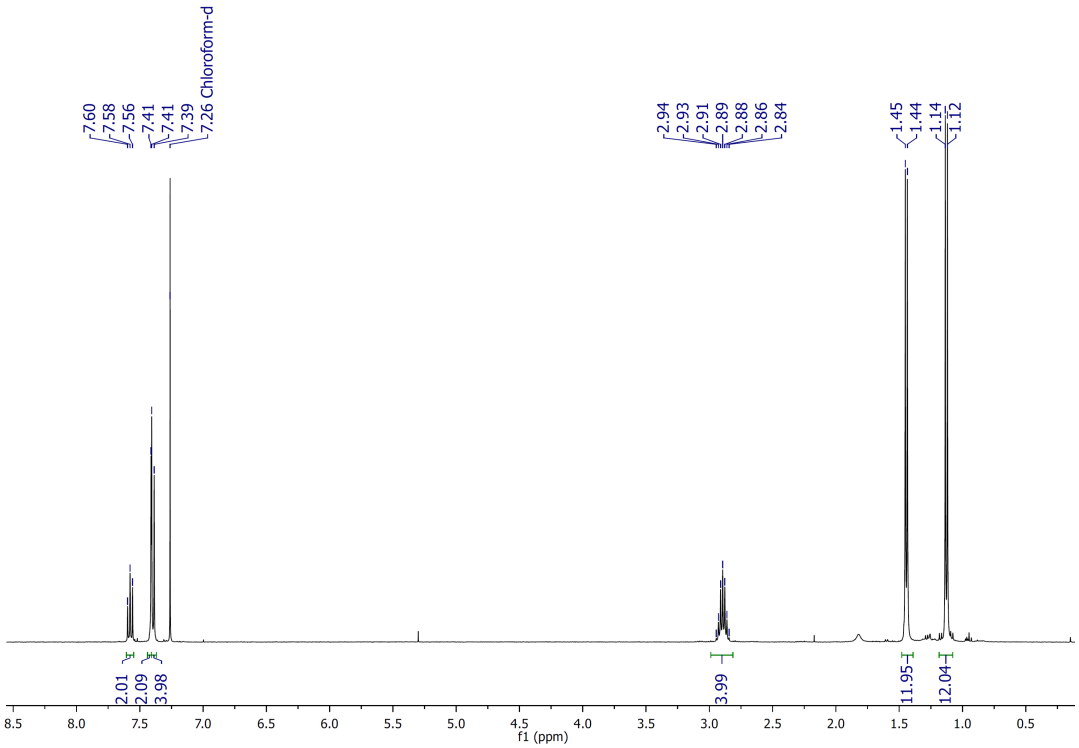


^{13}C{^{1}H} DEPT Q NMR

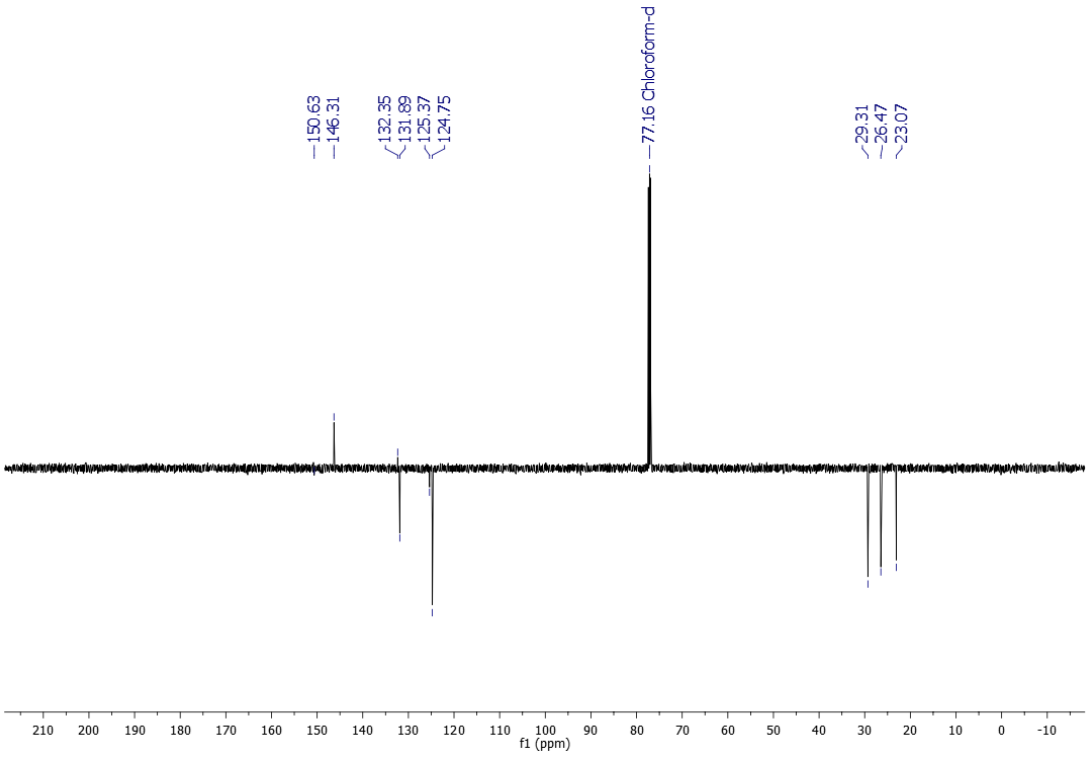


[$SeCl_2$(IPr)]

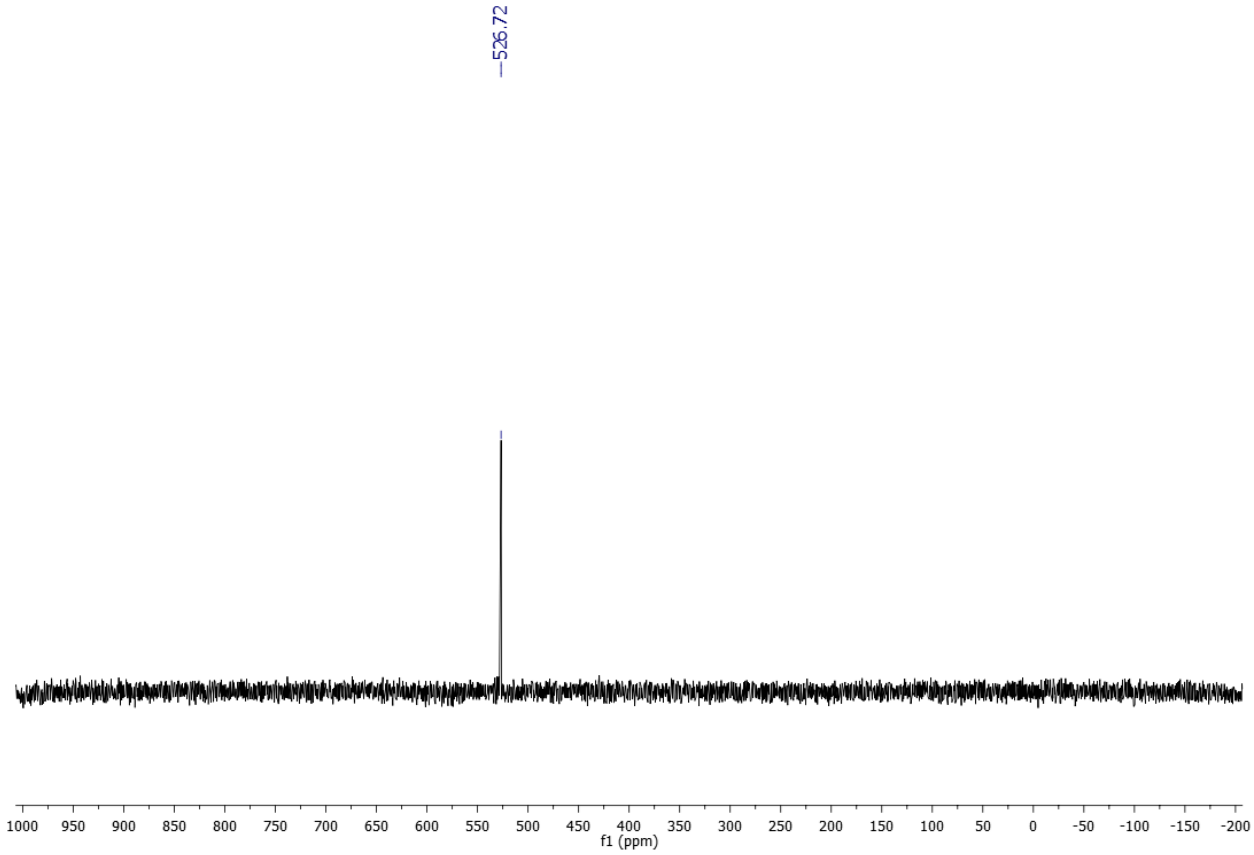
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

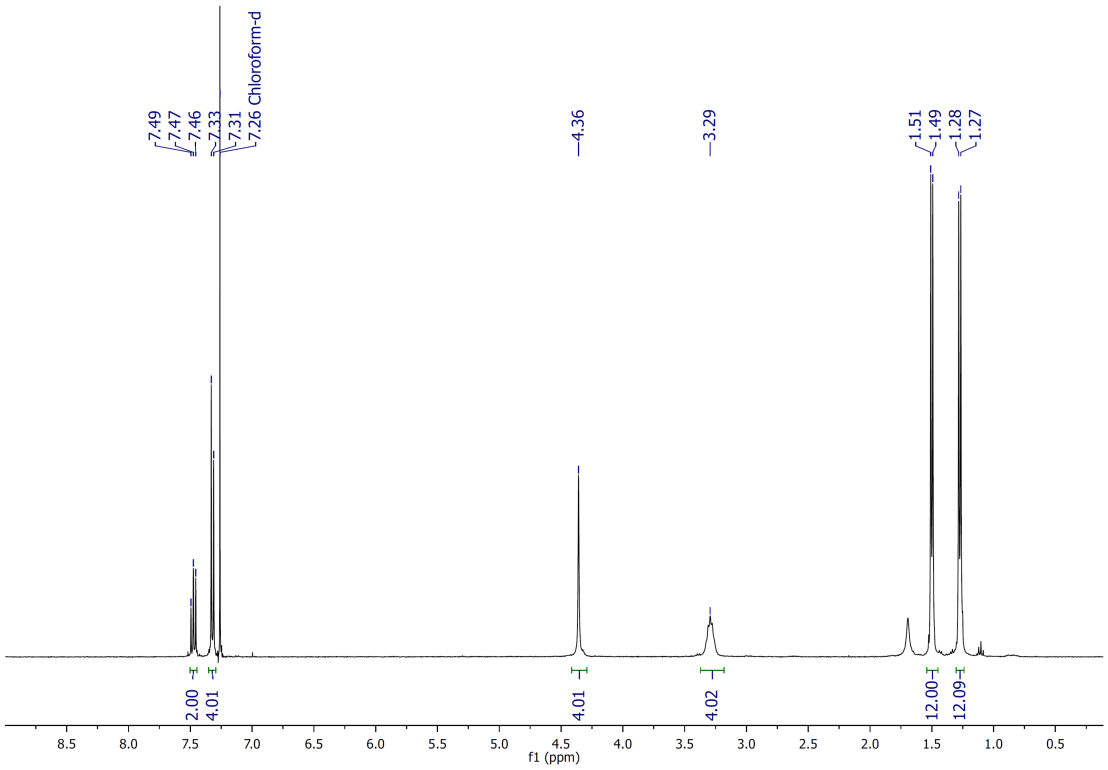


^{77}Se NMR

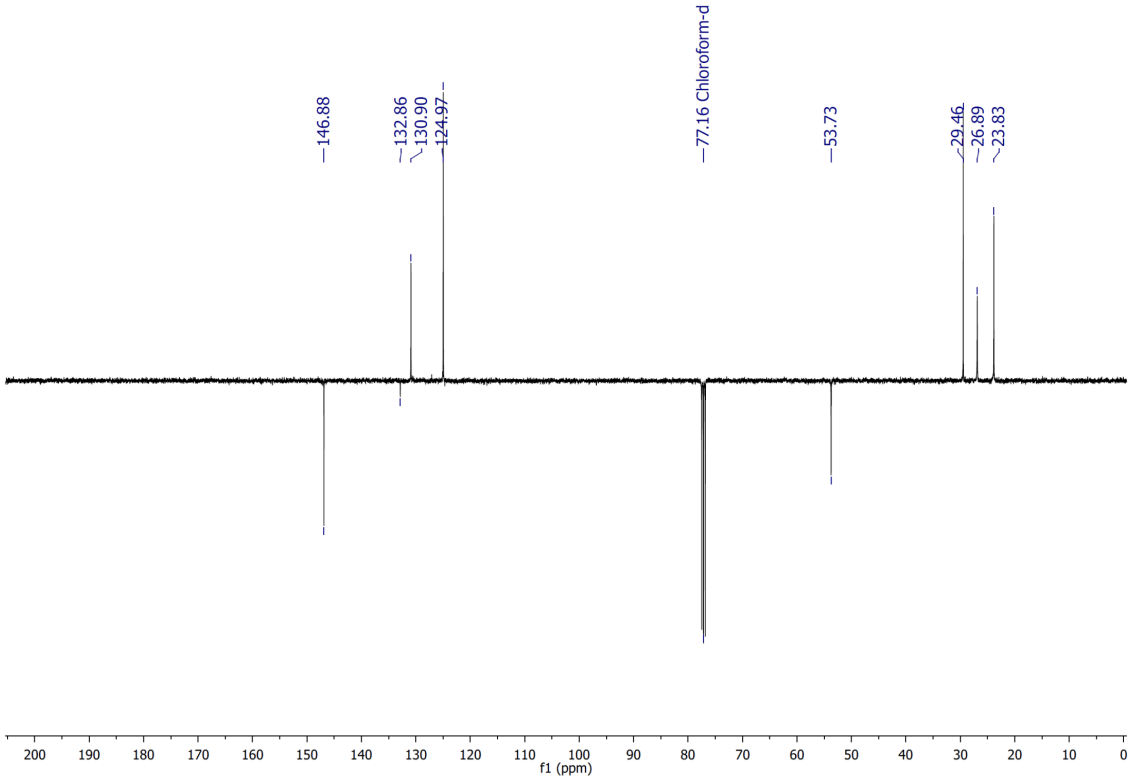

526.72
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

[$SeCl_2$(SIPr)]

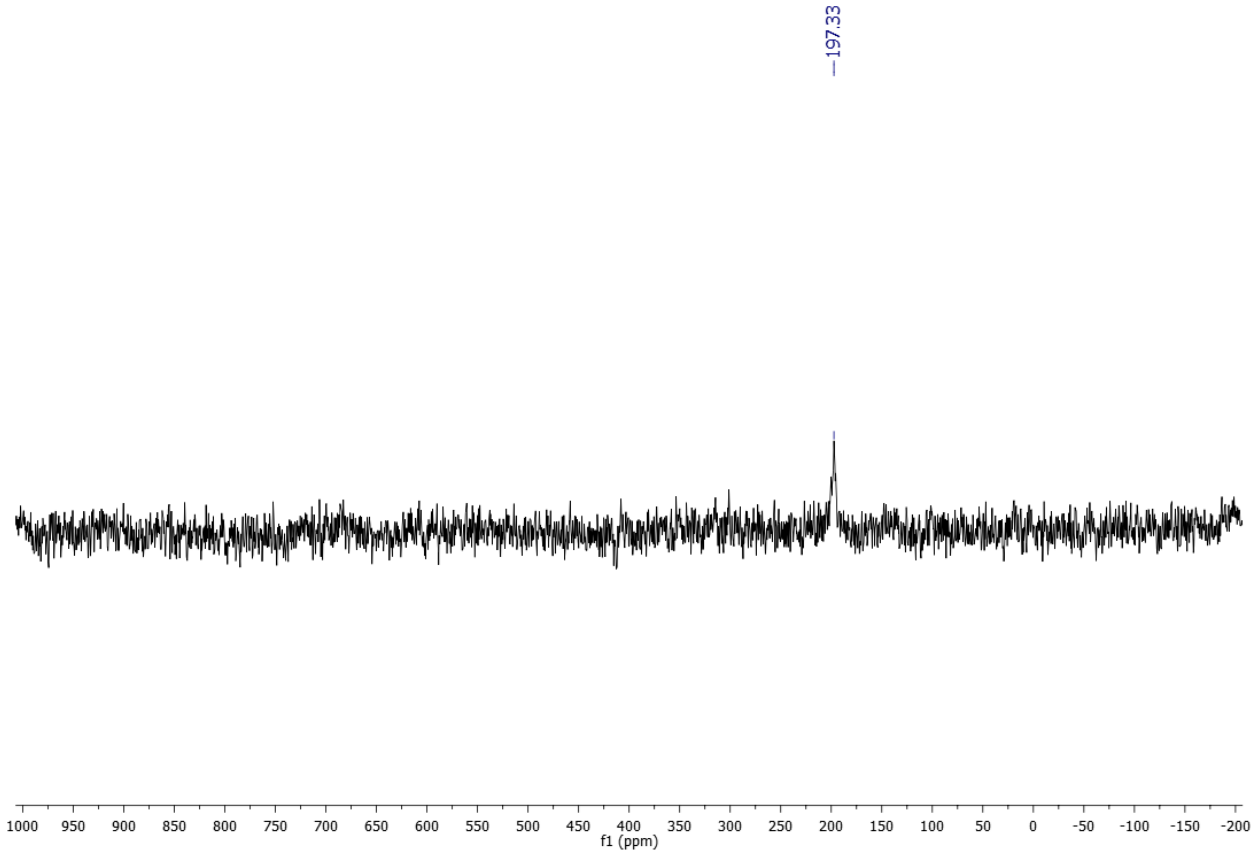
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

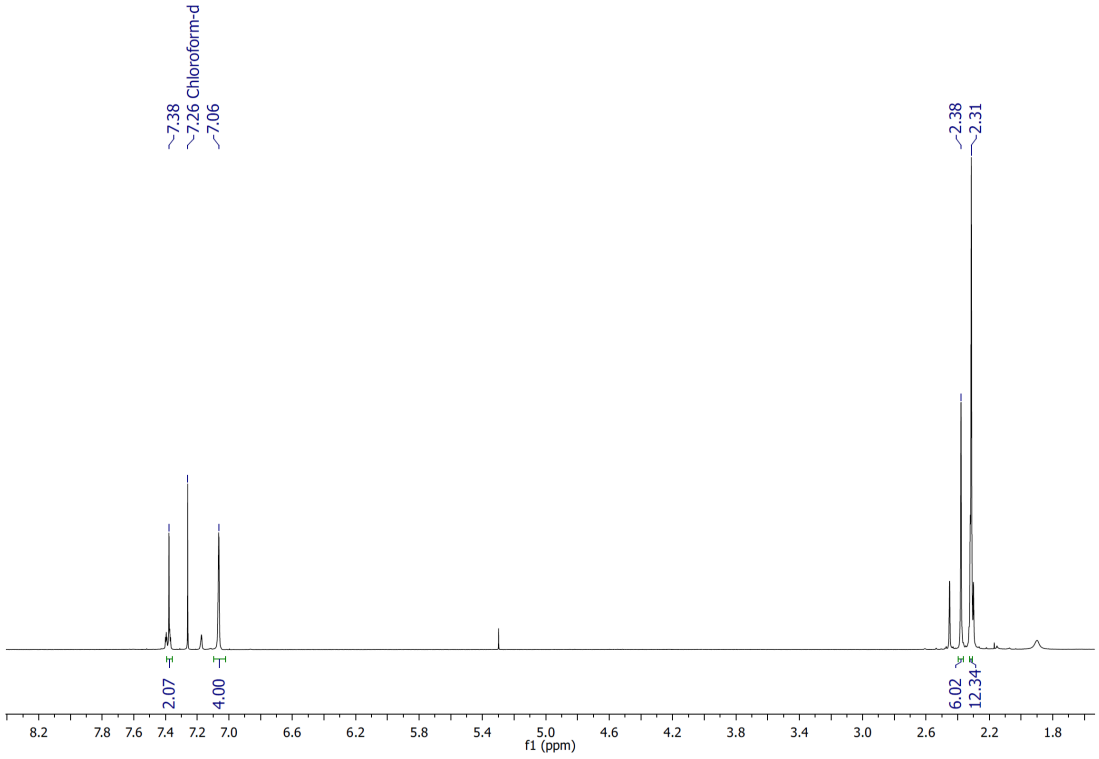


^{77}Se NMR

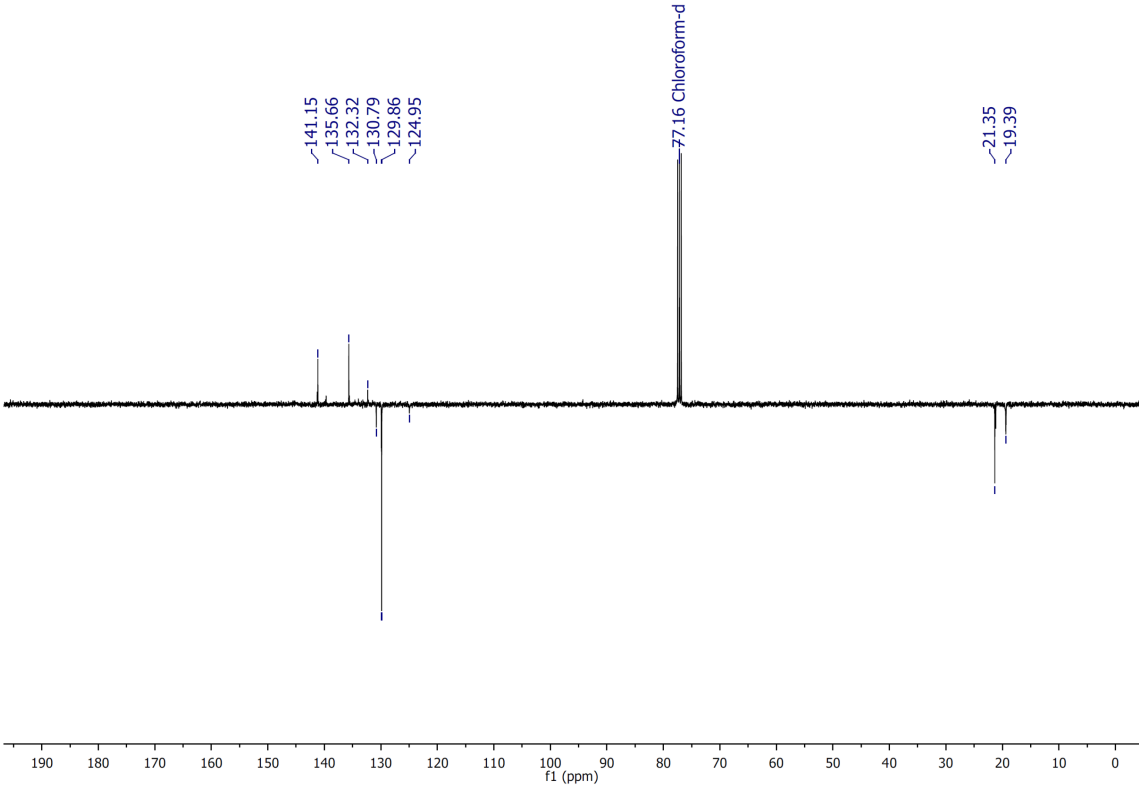

197.33
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

[$SeCl_2$(IMes)]

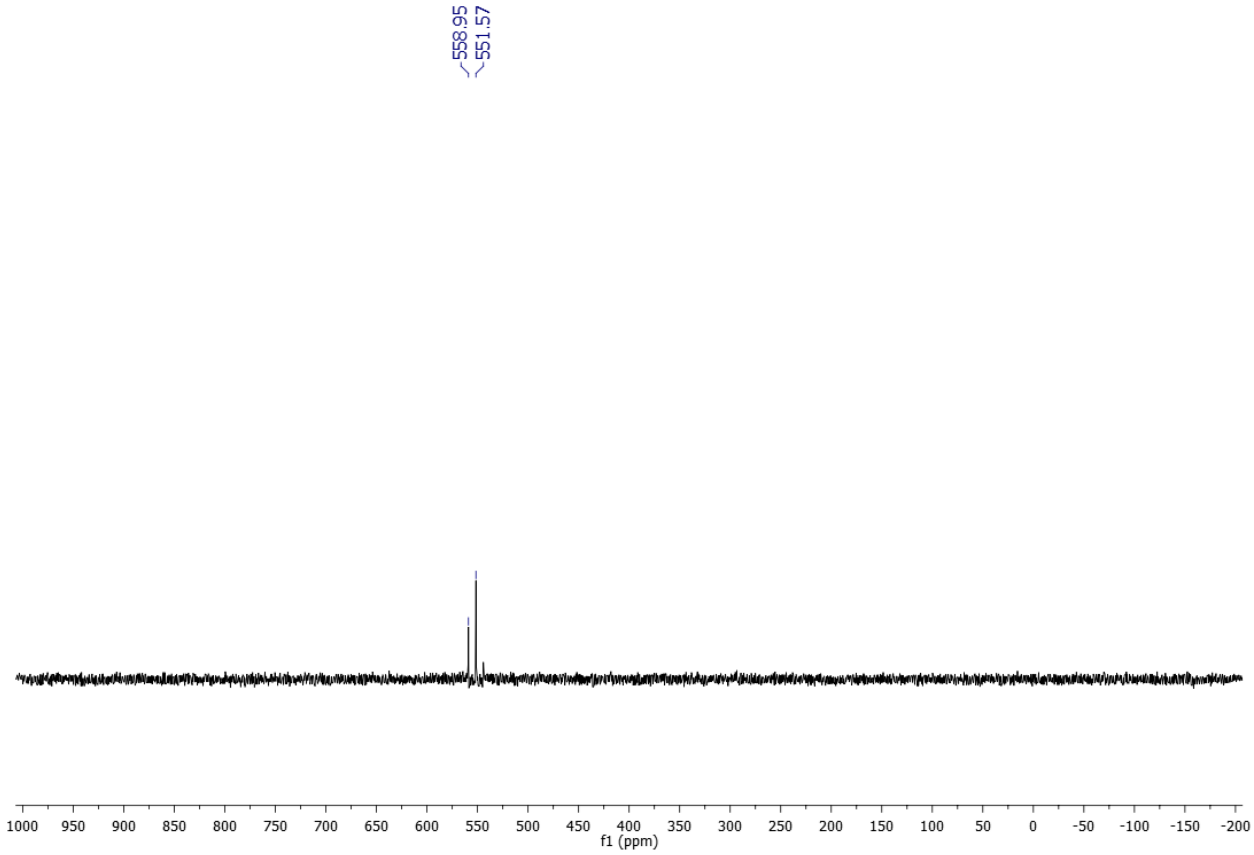
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

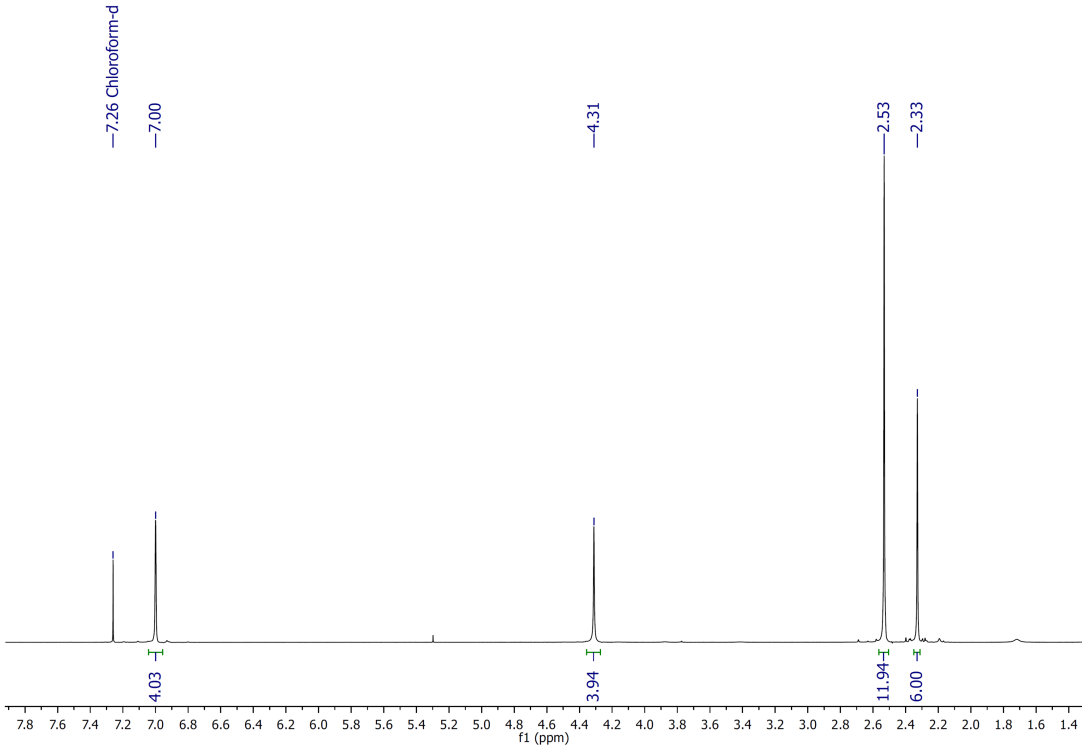


^{77}Se NMR

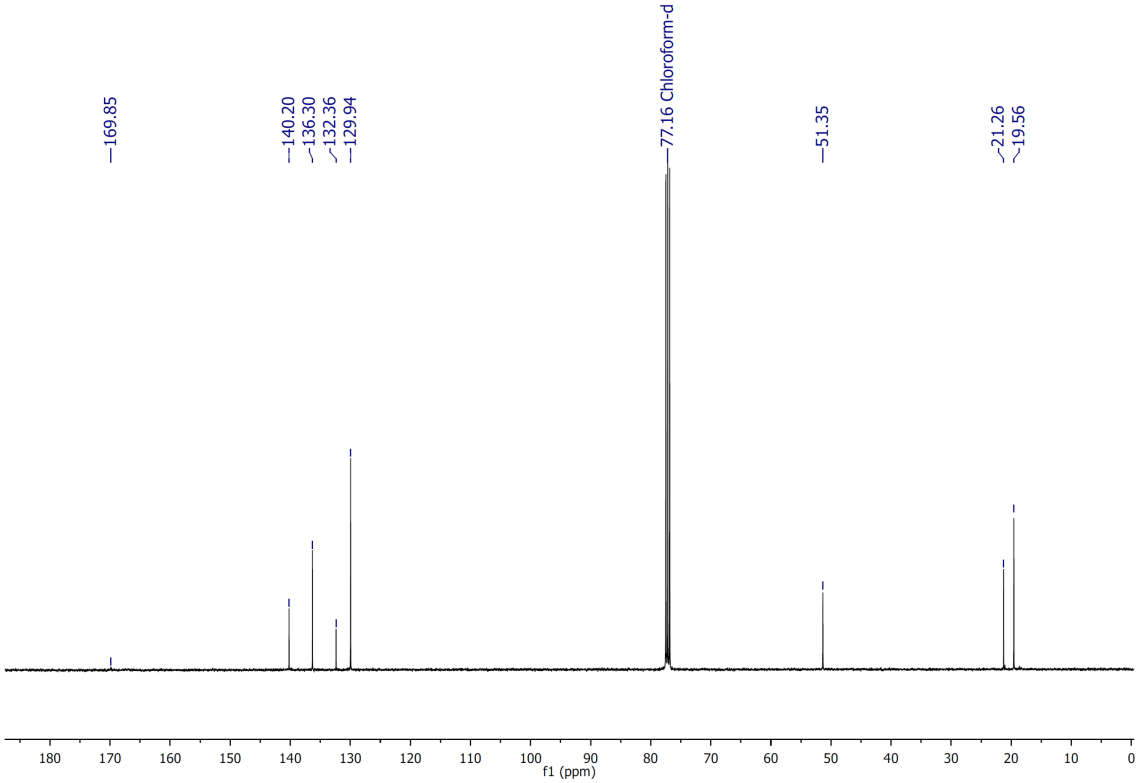

558.95
551.57
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

[$SeCl_2$(SIMes)]

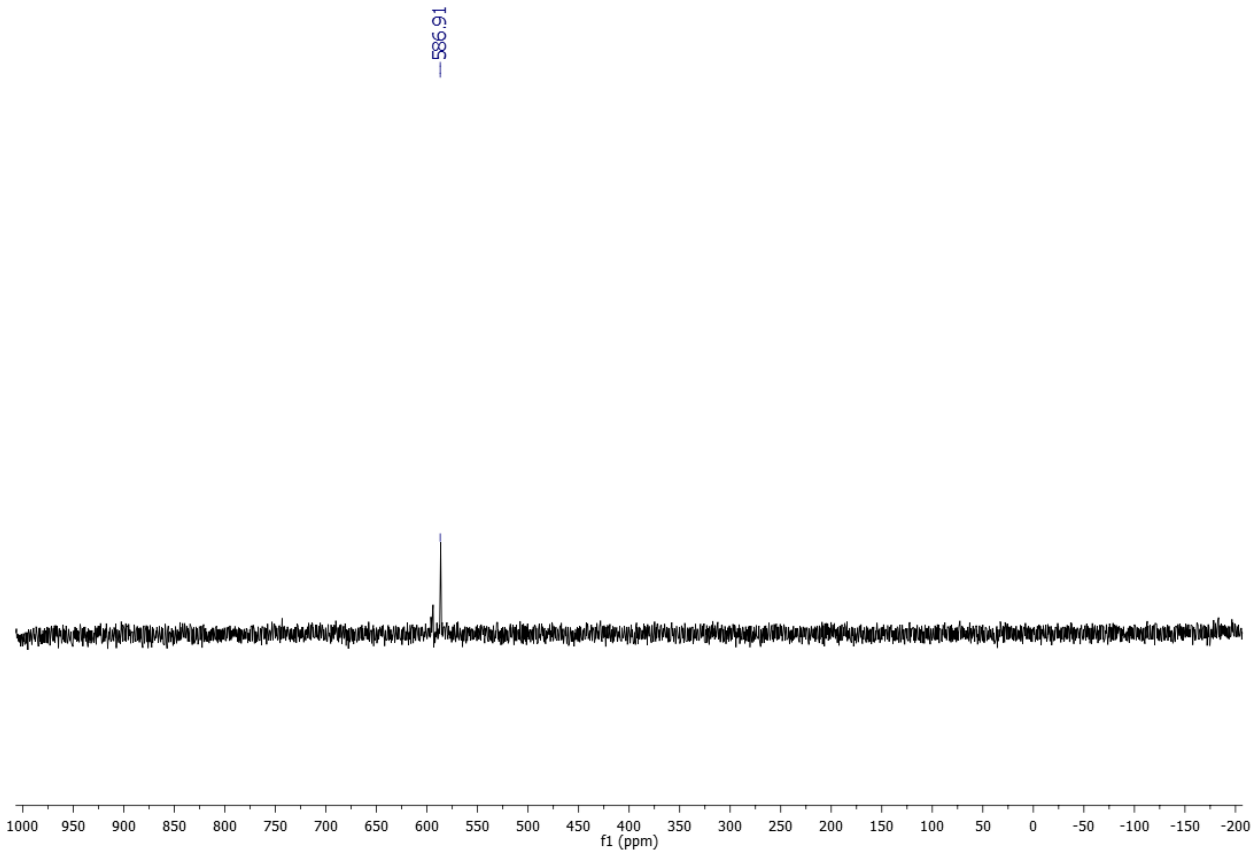
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

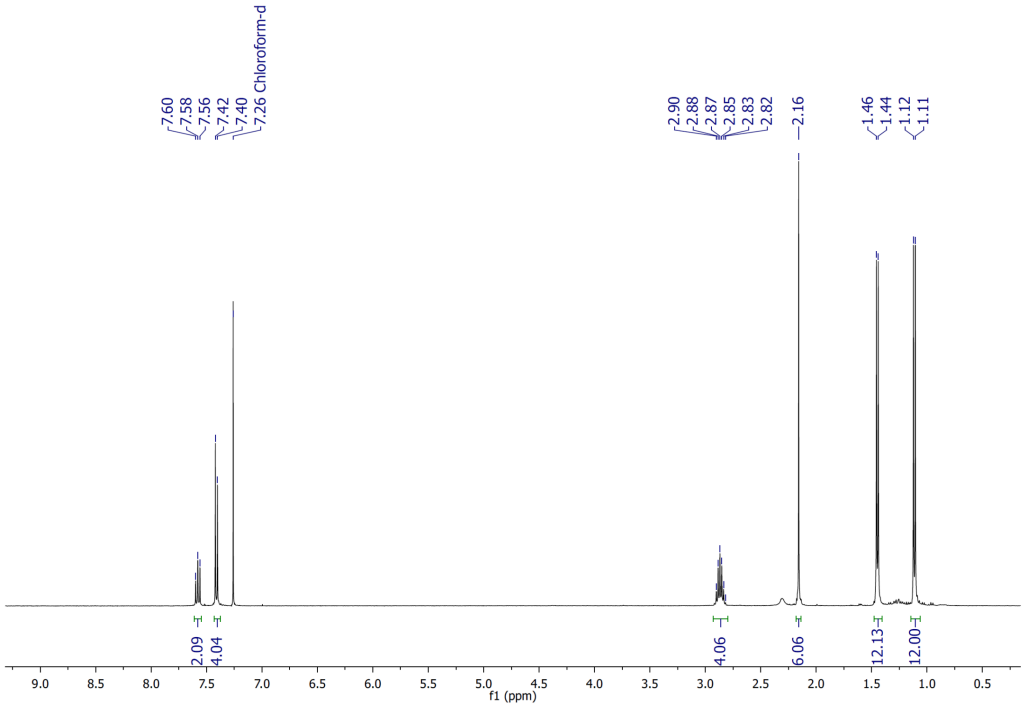


^{77}Se NMR

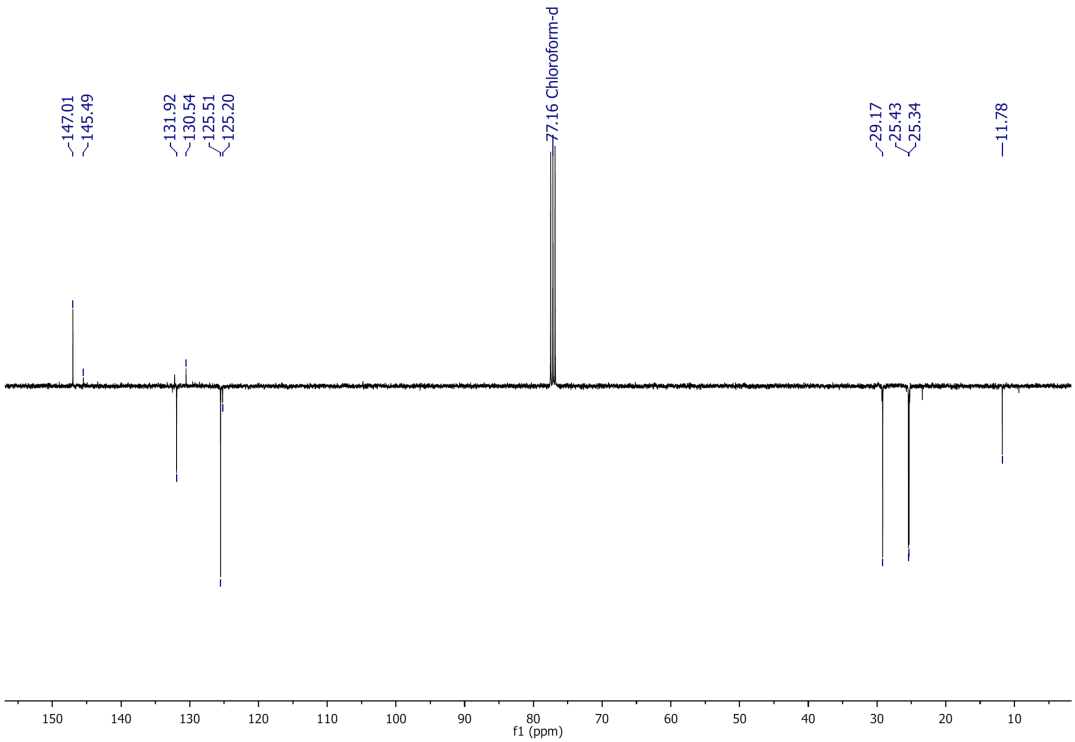

586.91
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

[$SeCl_2(IPr^{Me})$]

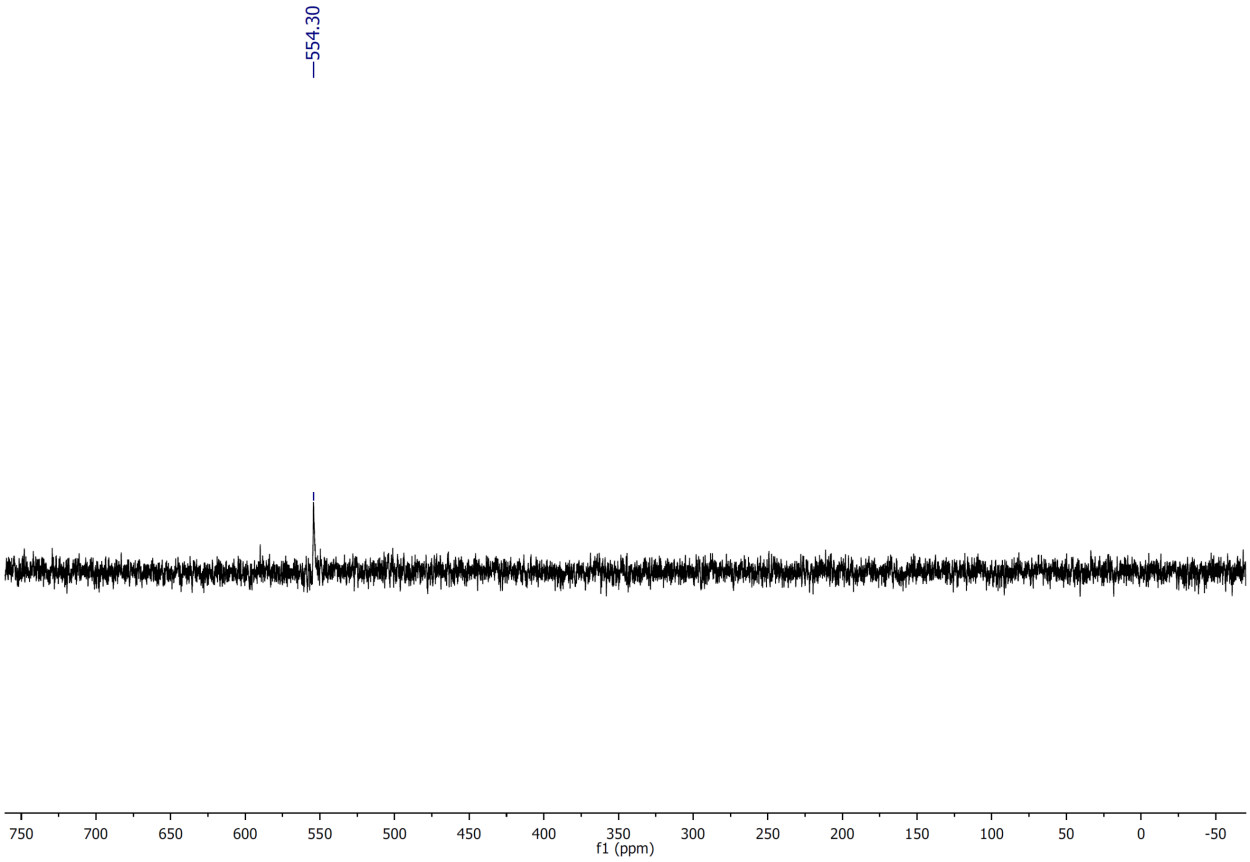
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

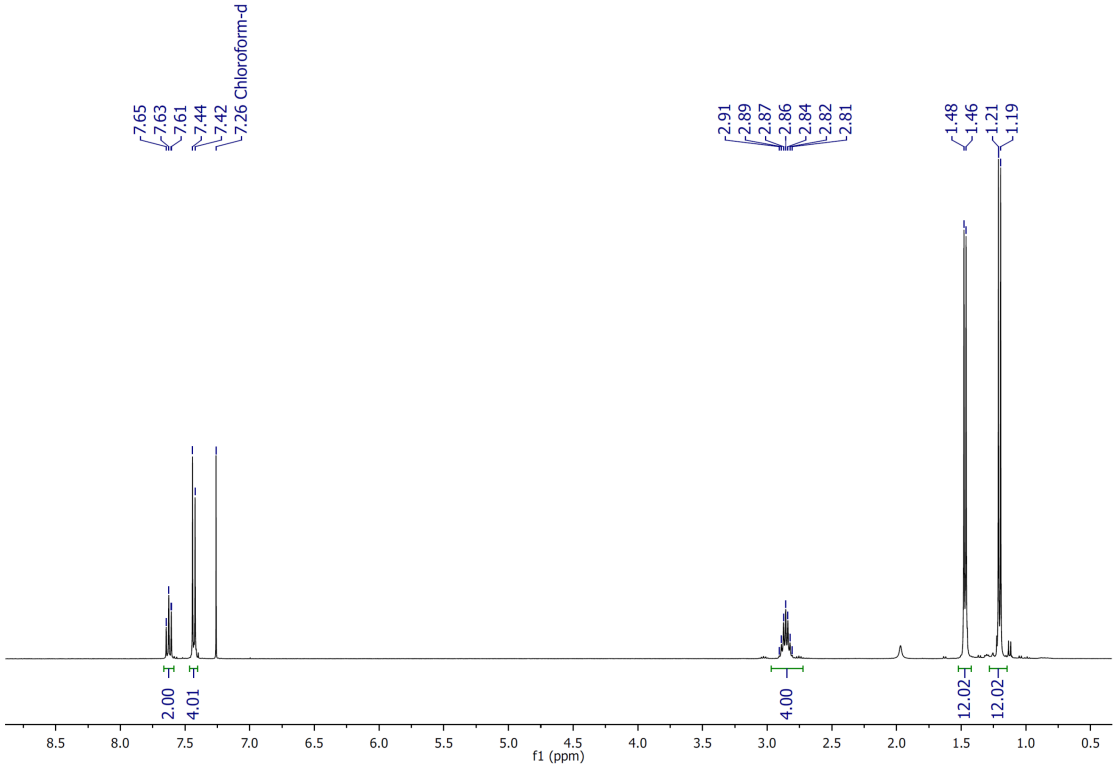


^{77}Se NMR

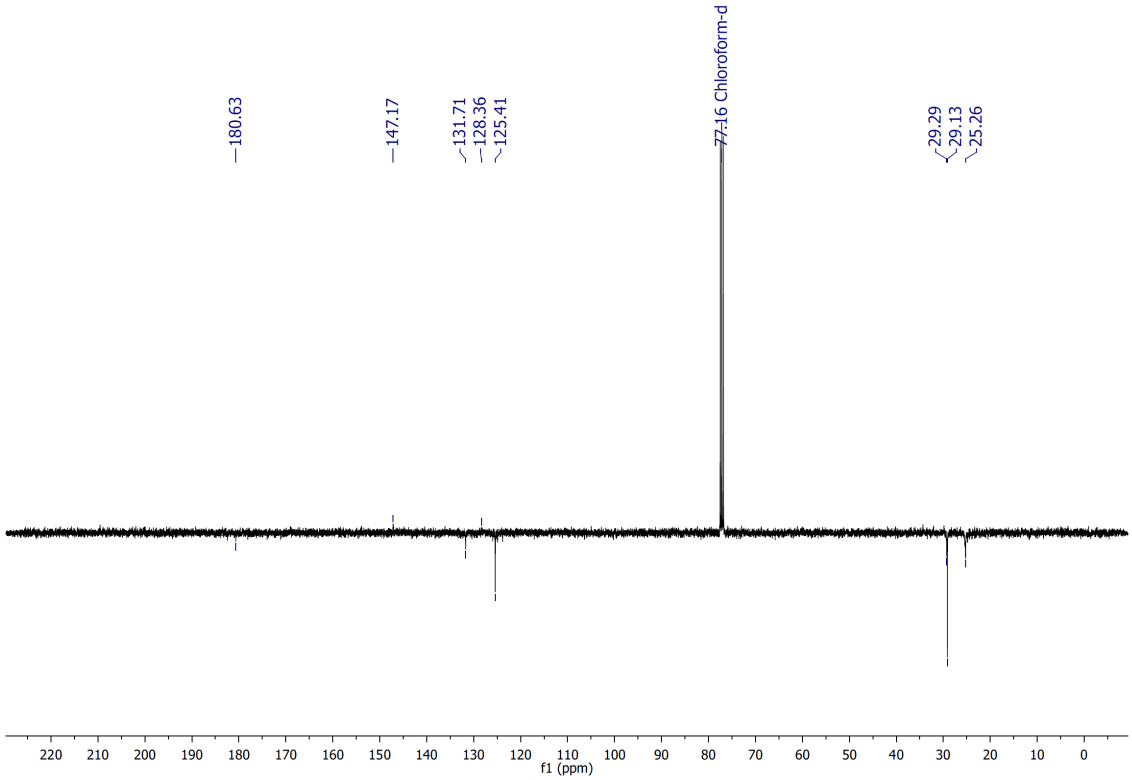

554.30
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
f1 (ppm)

[$SeCl_2(IPr^{Cl})$]

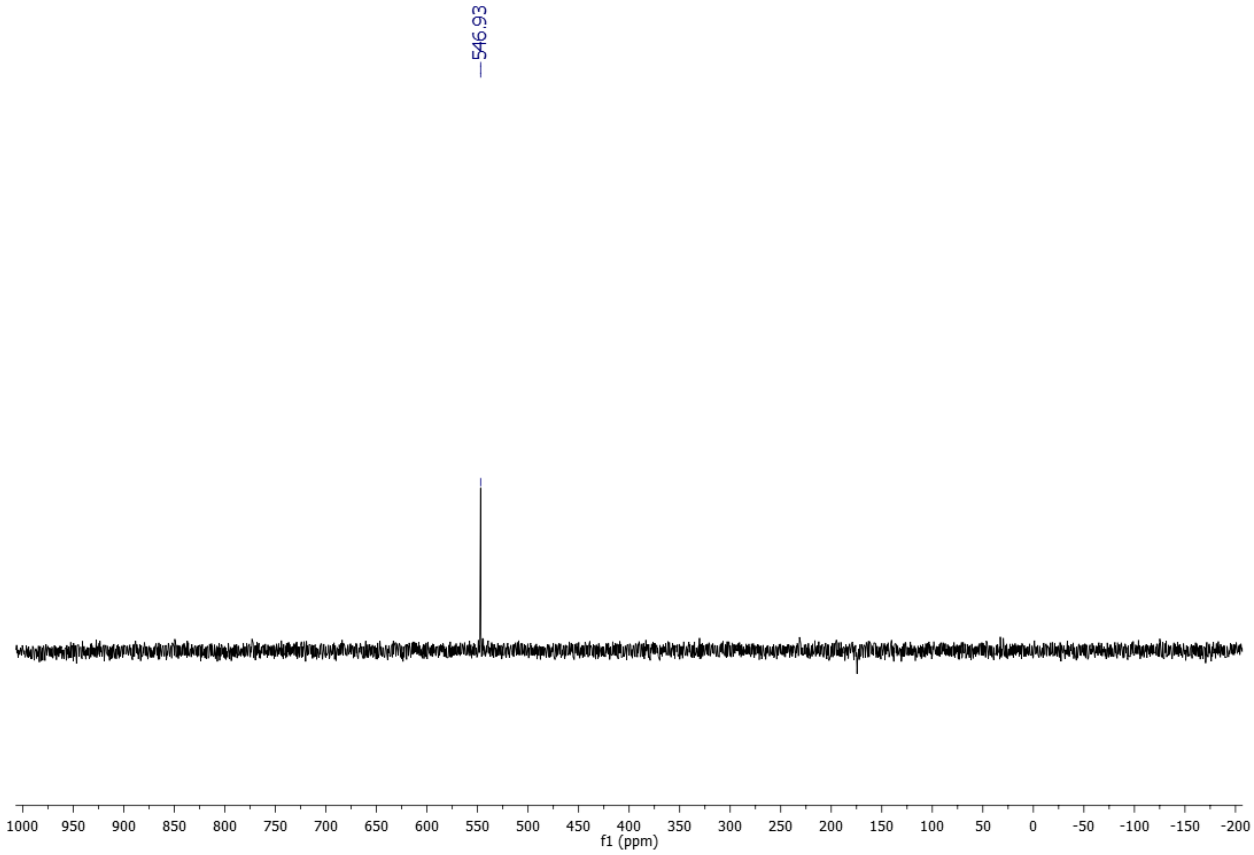
^1H NMR



$^{13}C\{^1H\}$ DEPT Q NMR

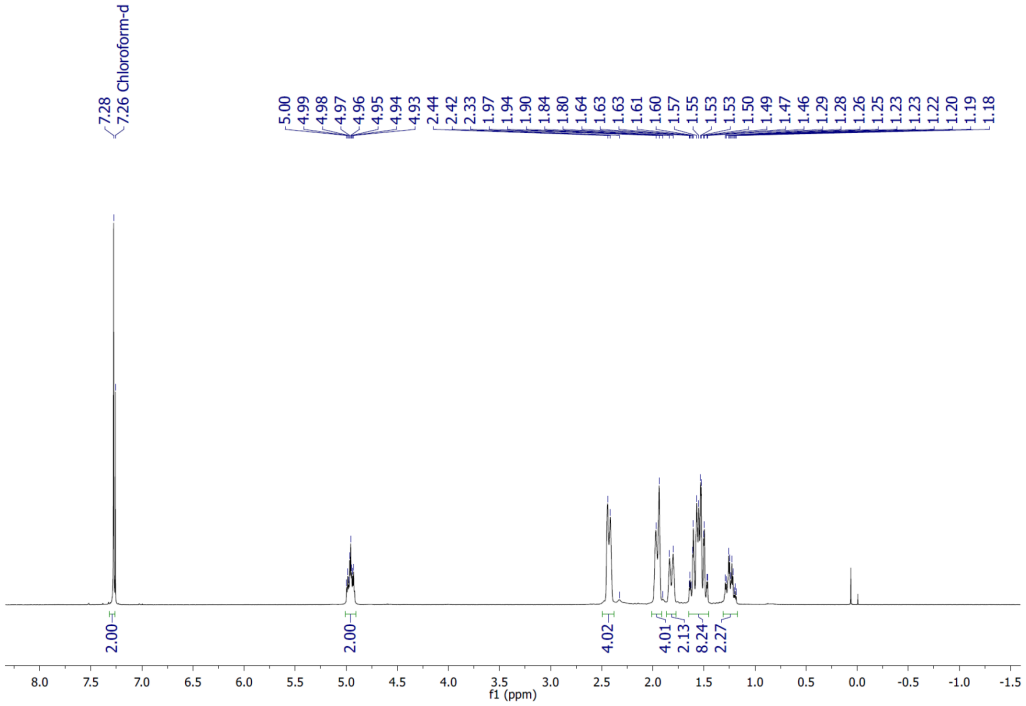


^{77}Se NMR

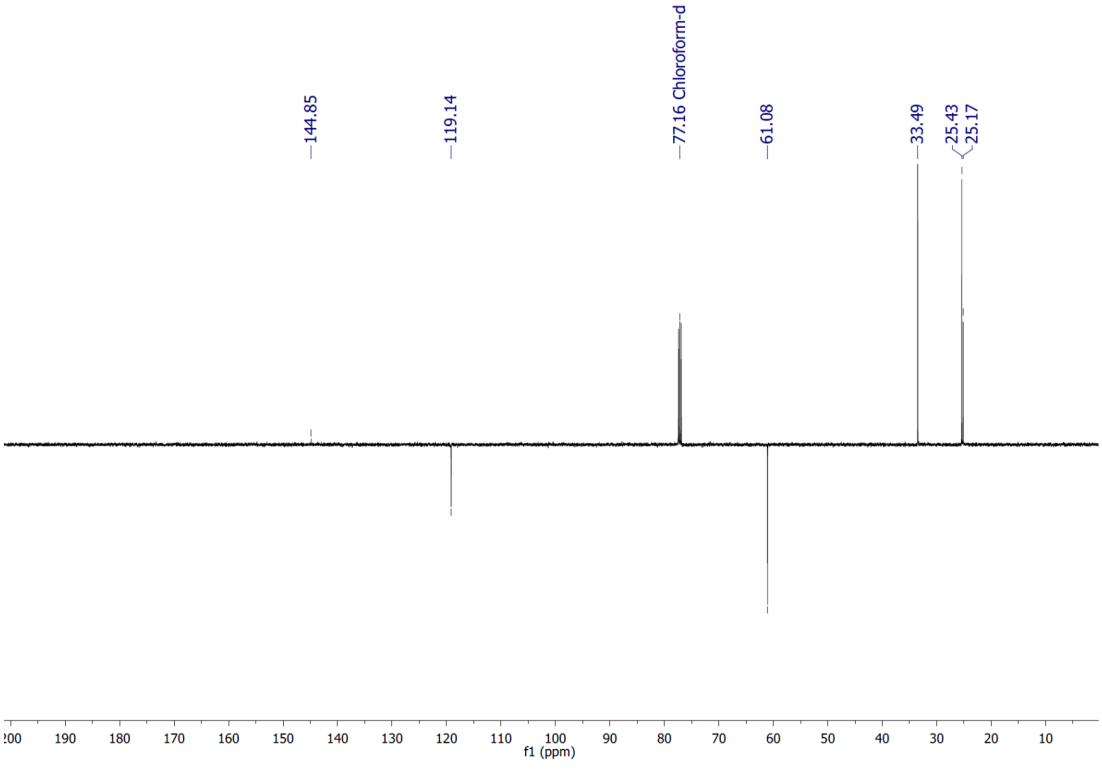

546.93
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

[$SeCl_2$(ICy)]

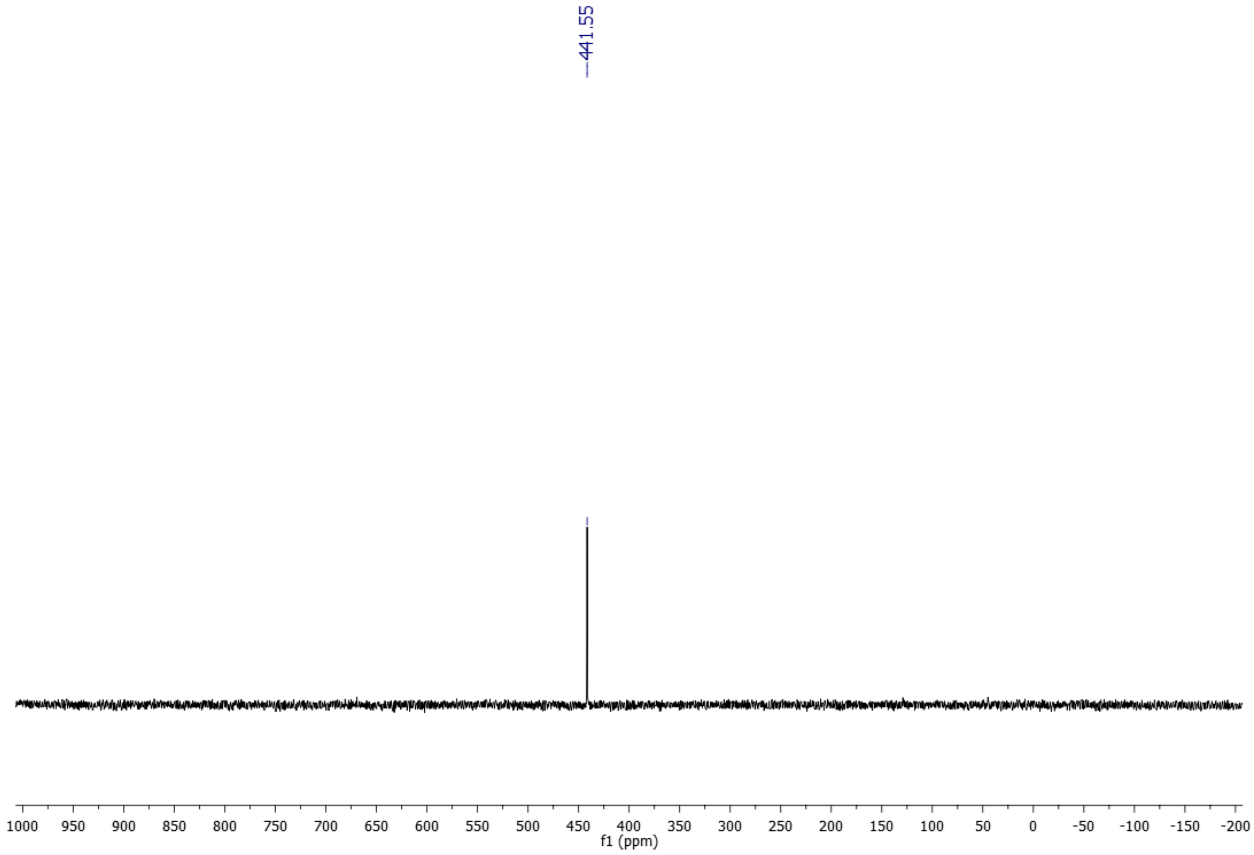
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

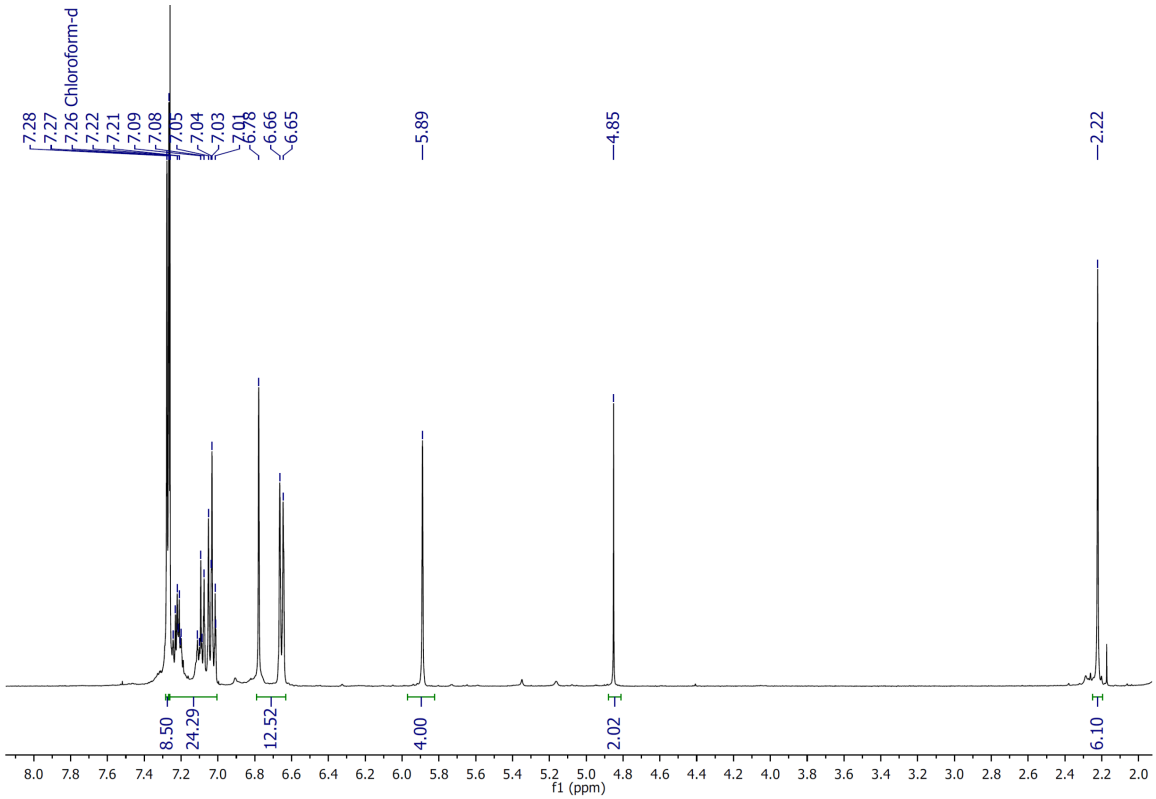


^{77}Se NMR

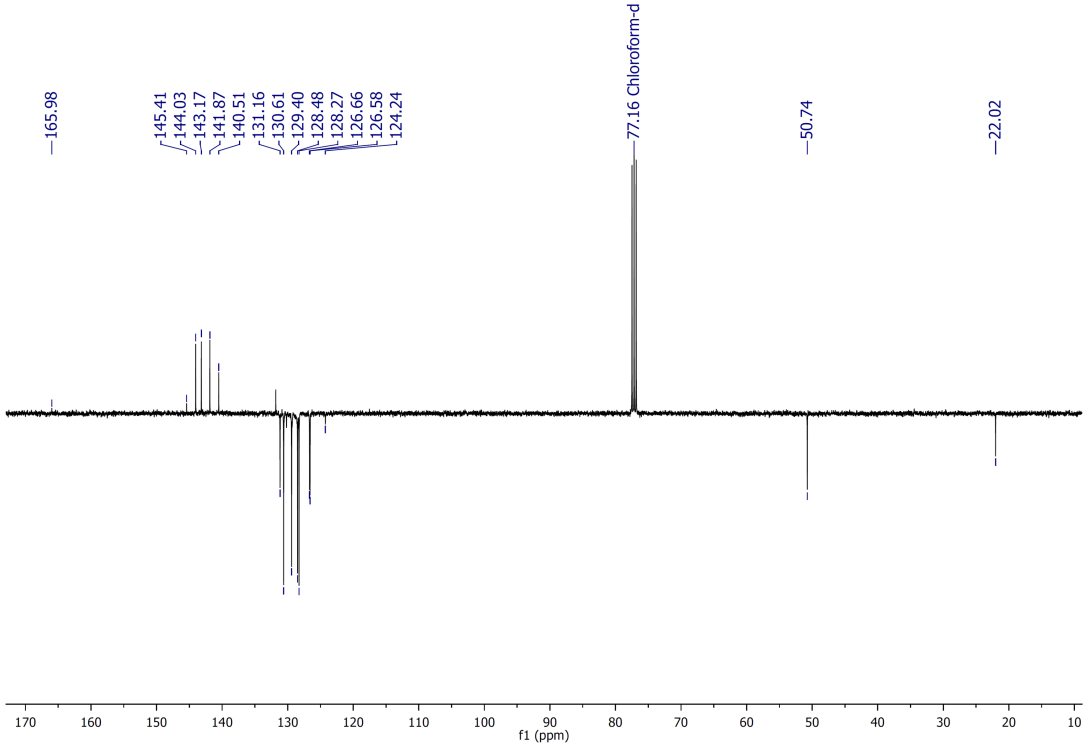

441.55
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

[$SeCl_2$(IPr*)]

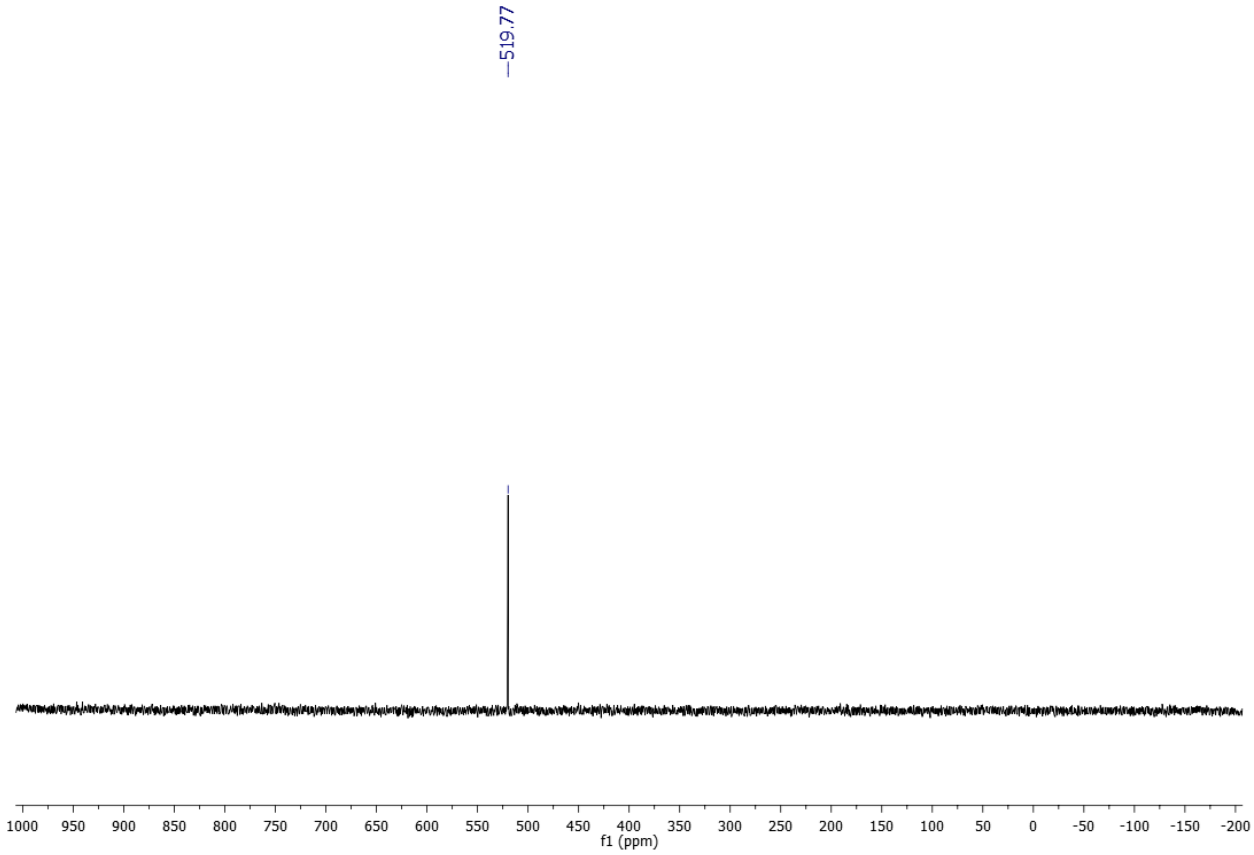
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

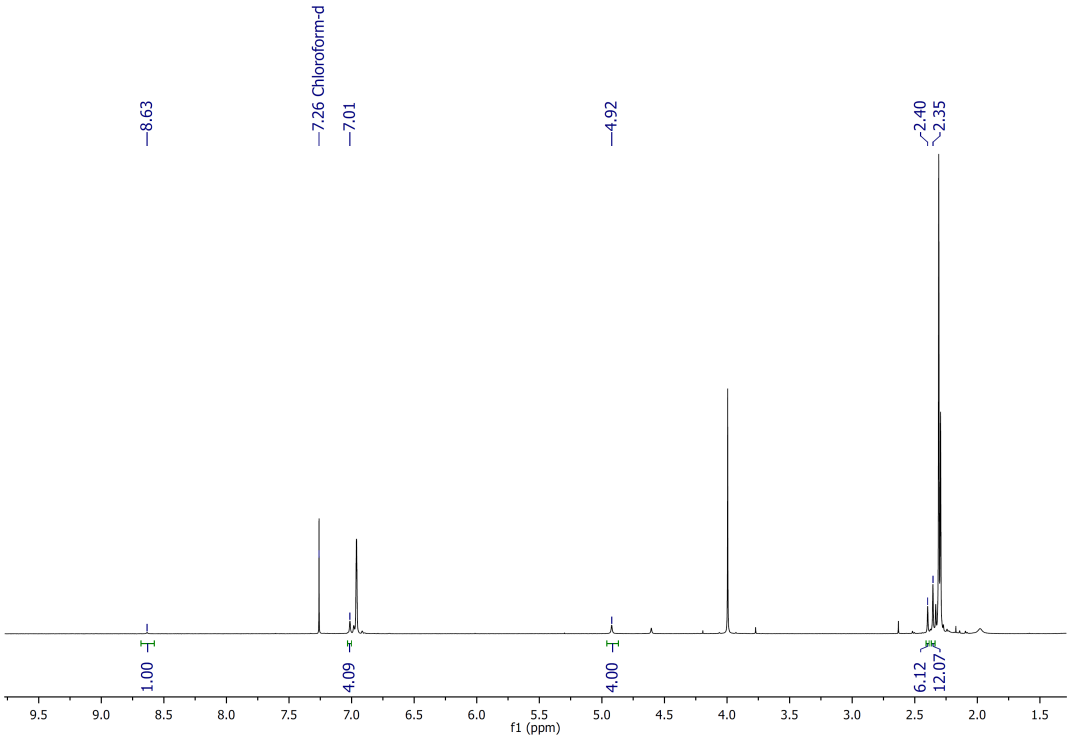


^{77}Se NMR


519.77
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

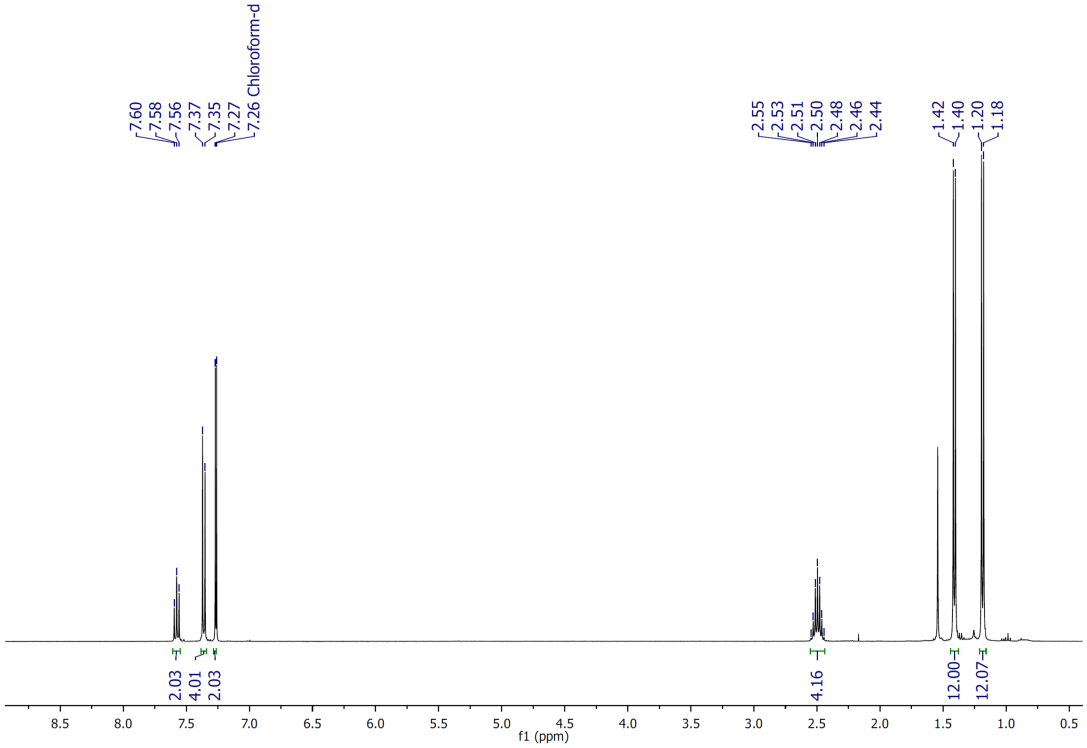
Reaction of [S(SIMes)] with SO_2Cl_2

^{1}H NMR

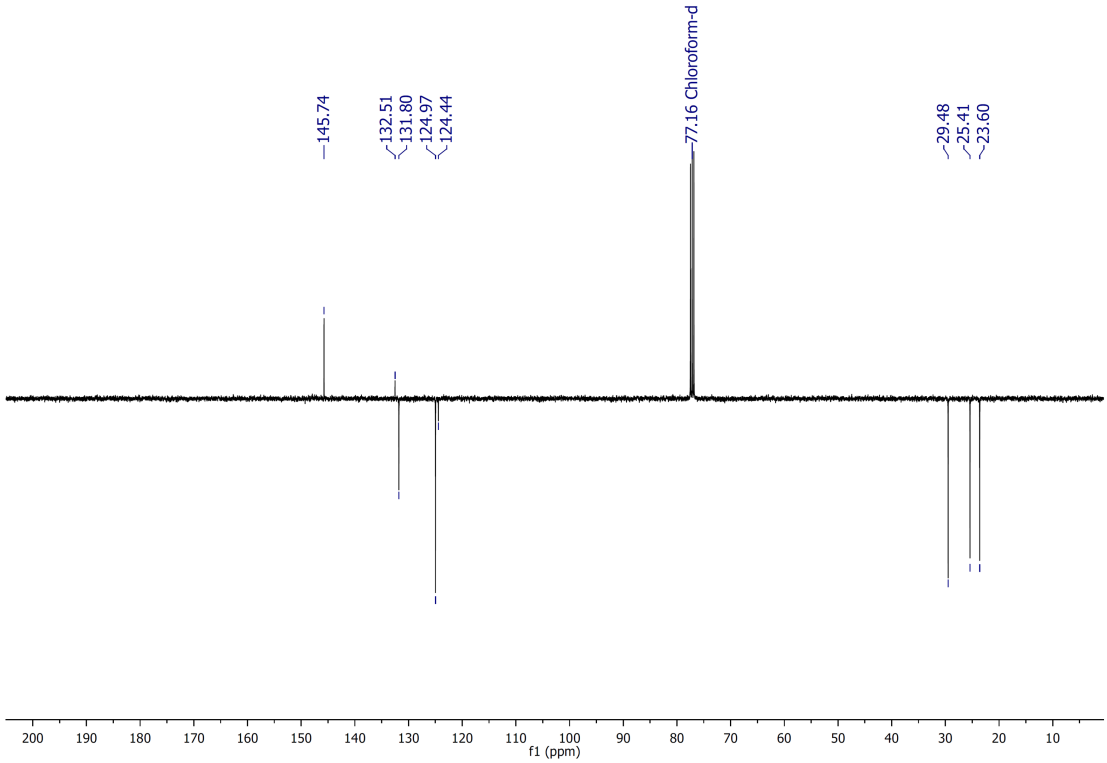


[(I_2)·Se(IPr)]

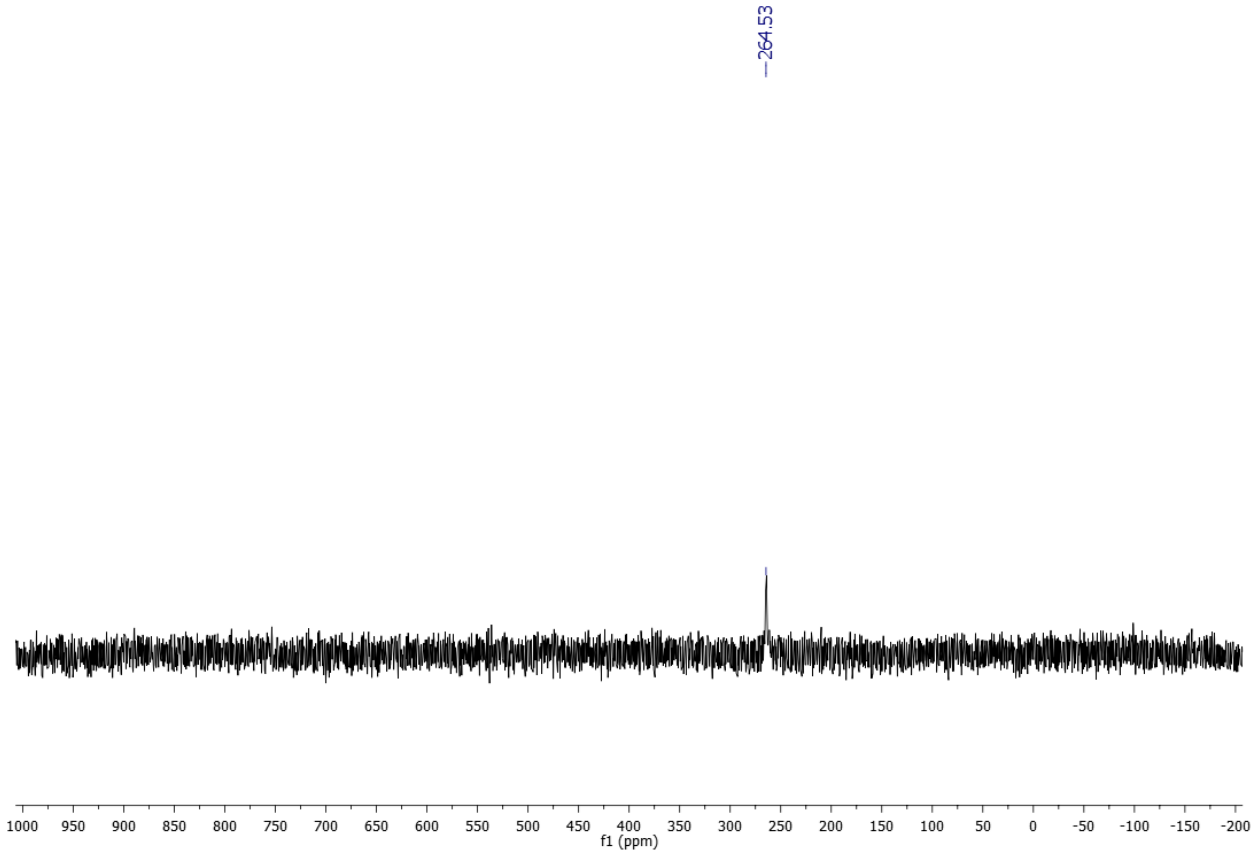
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

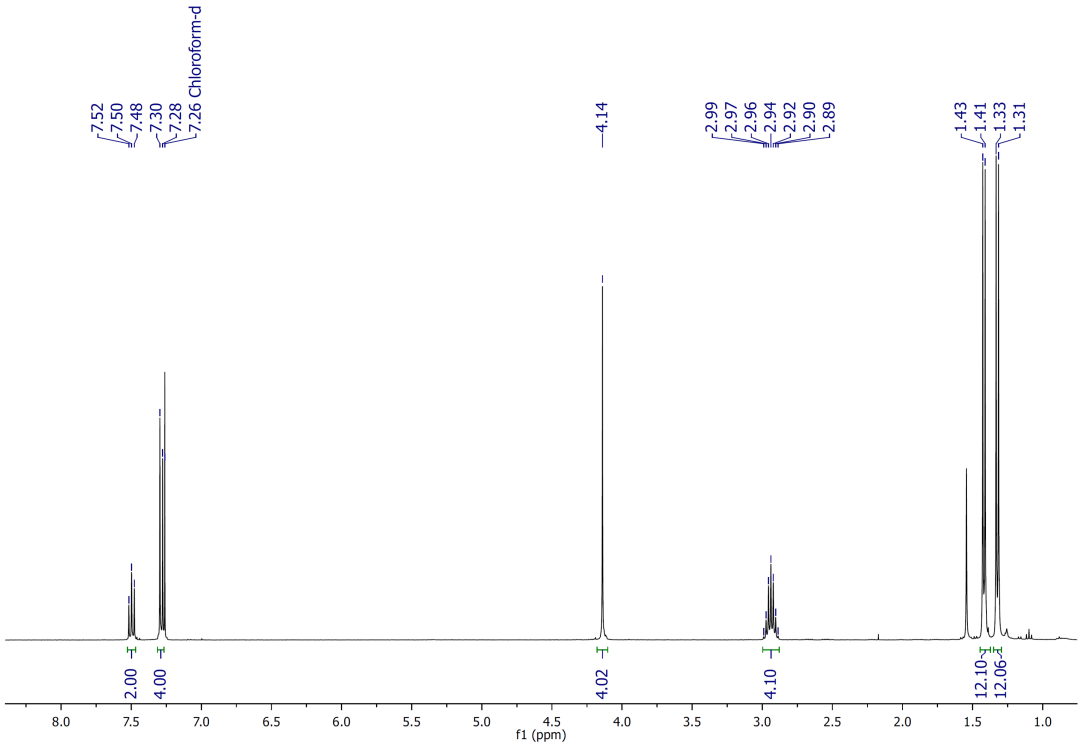


^{77}Se NMR

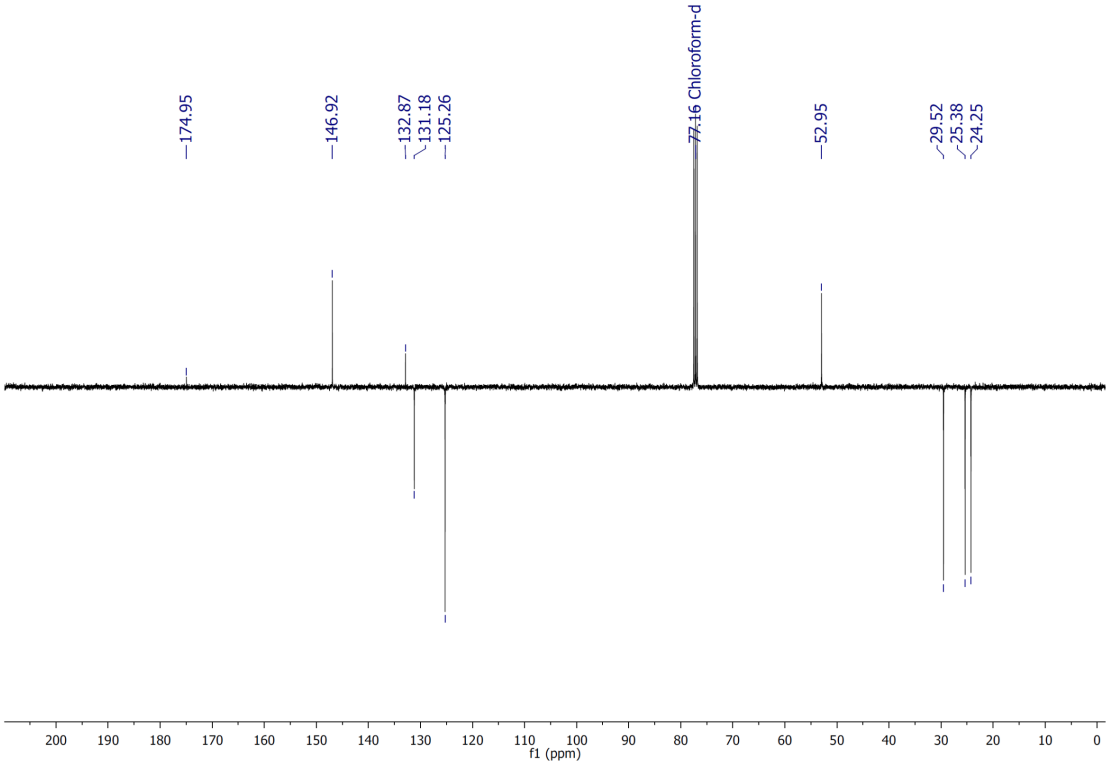

264.53
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

[{Se(SIPr)}$_2$(μ-I)]I$_5$

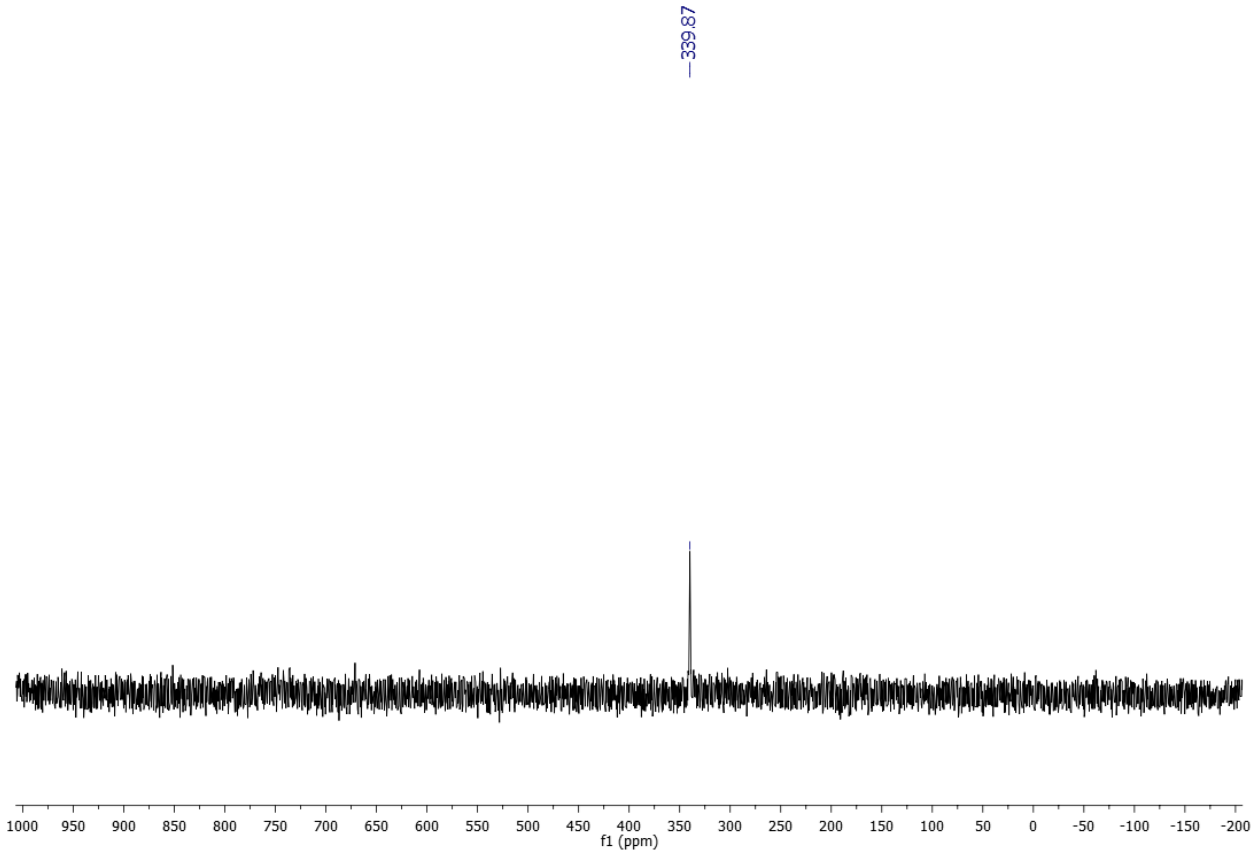
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

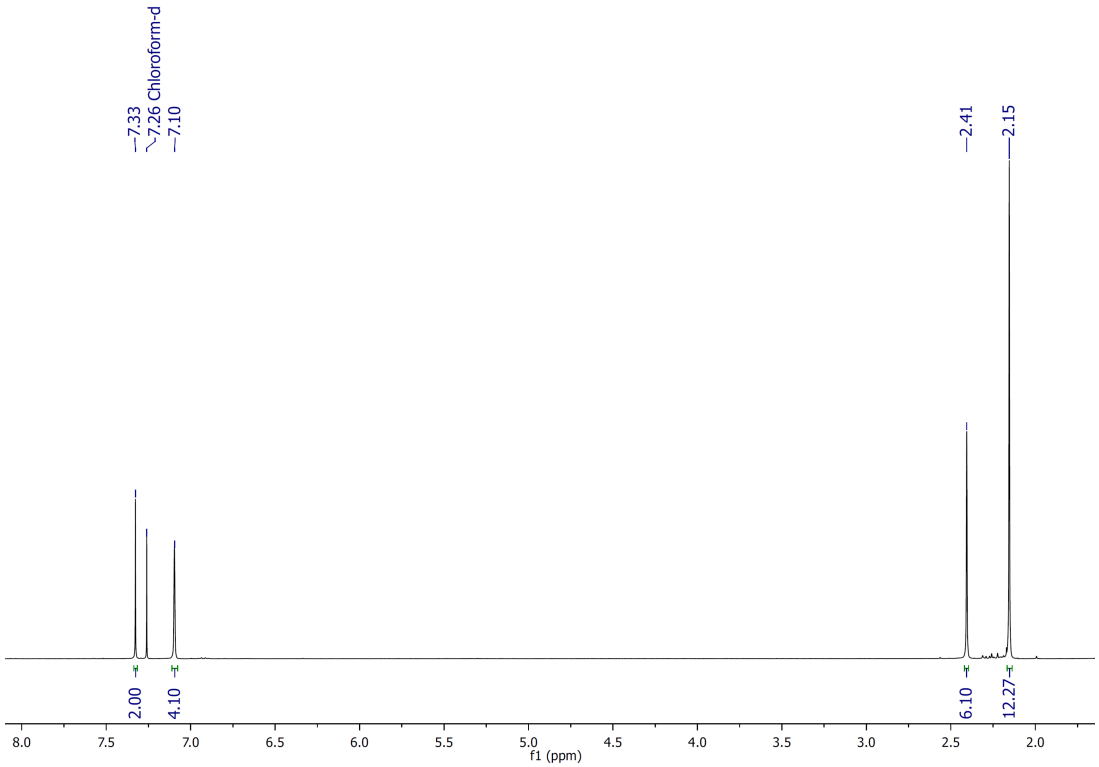


^{77}Se NMR

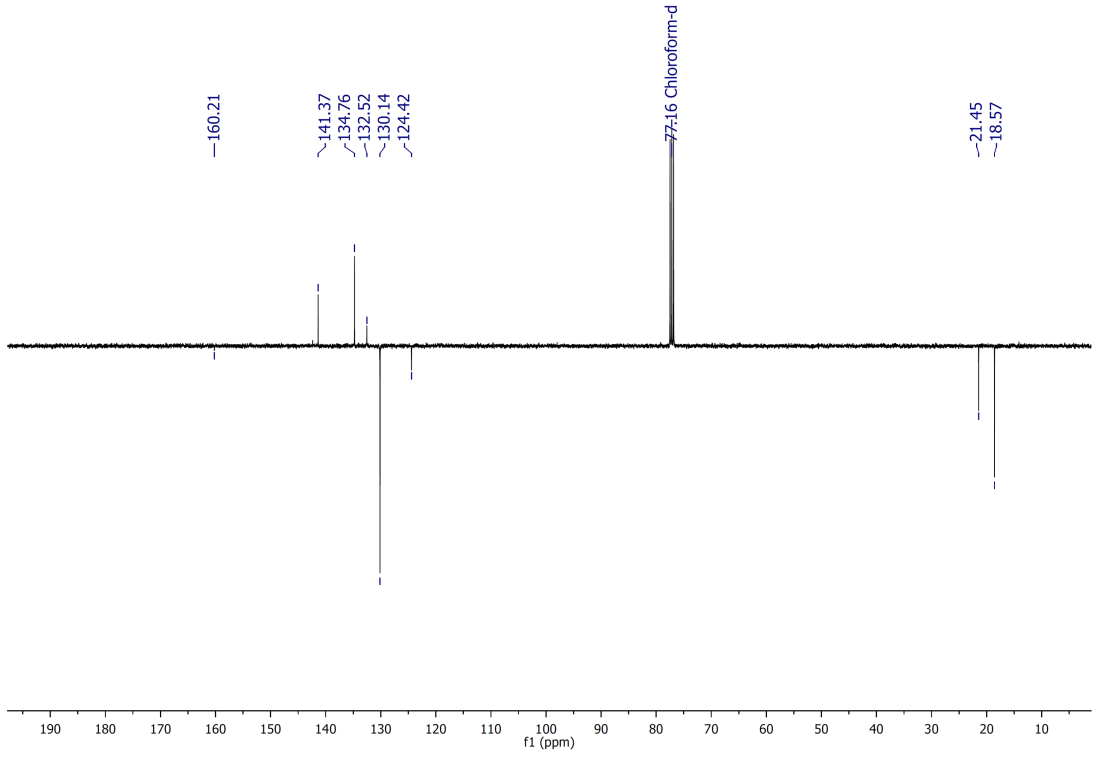

339.87
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

[(I_2)·Se(IMes)]

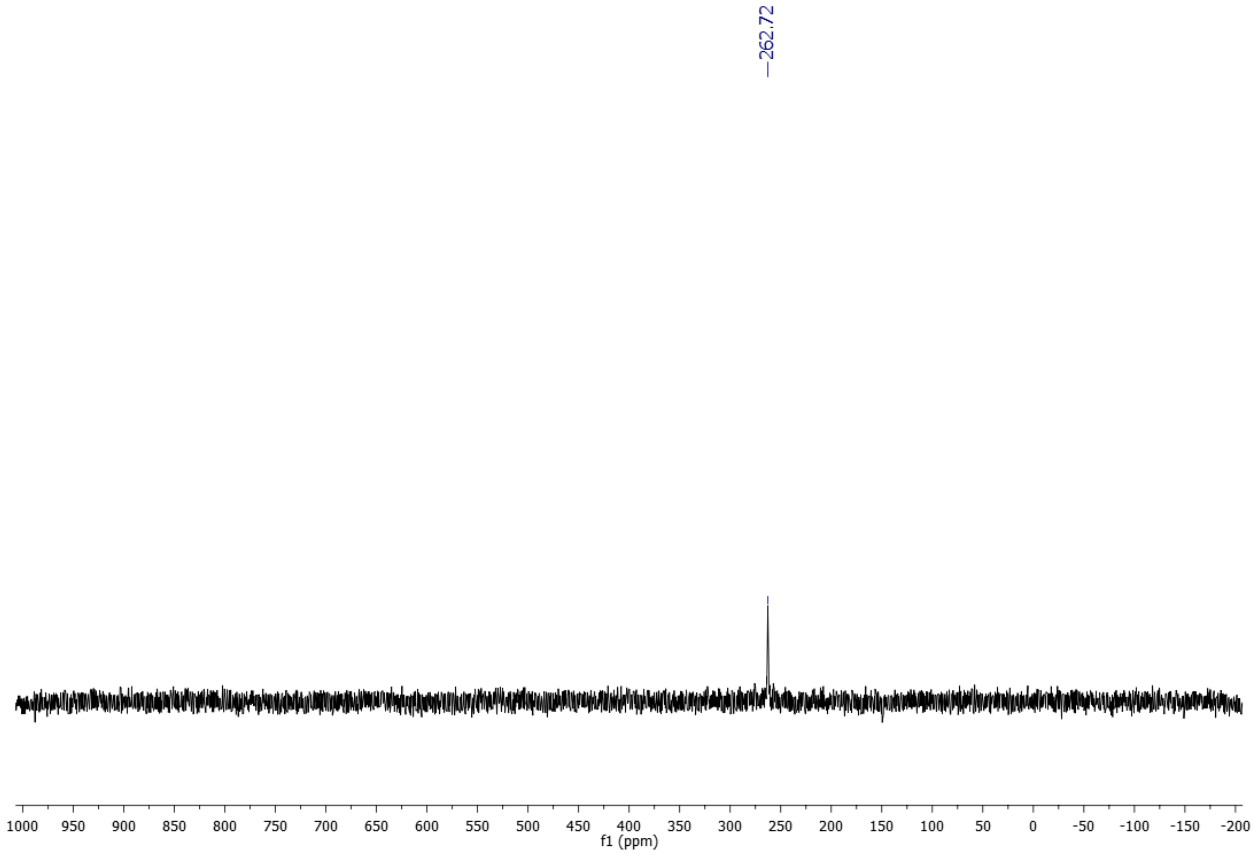
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

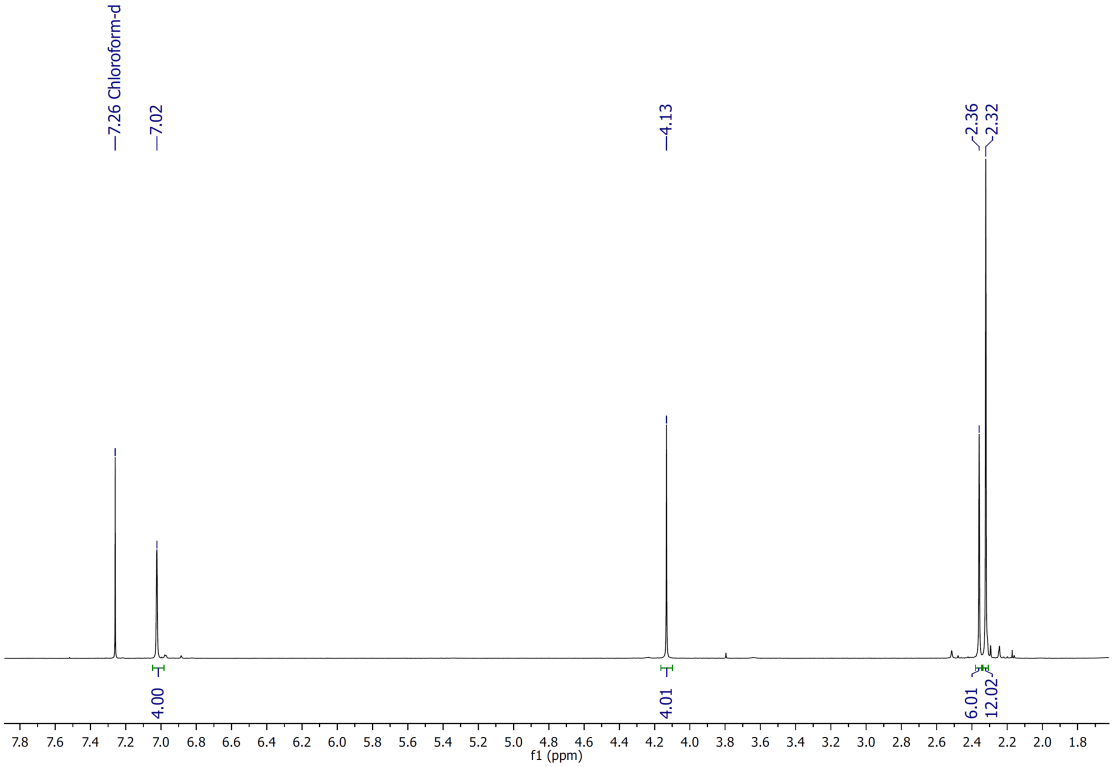


^{77}Se NMR

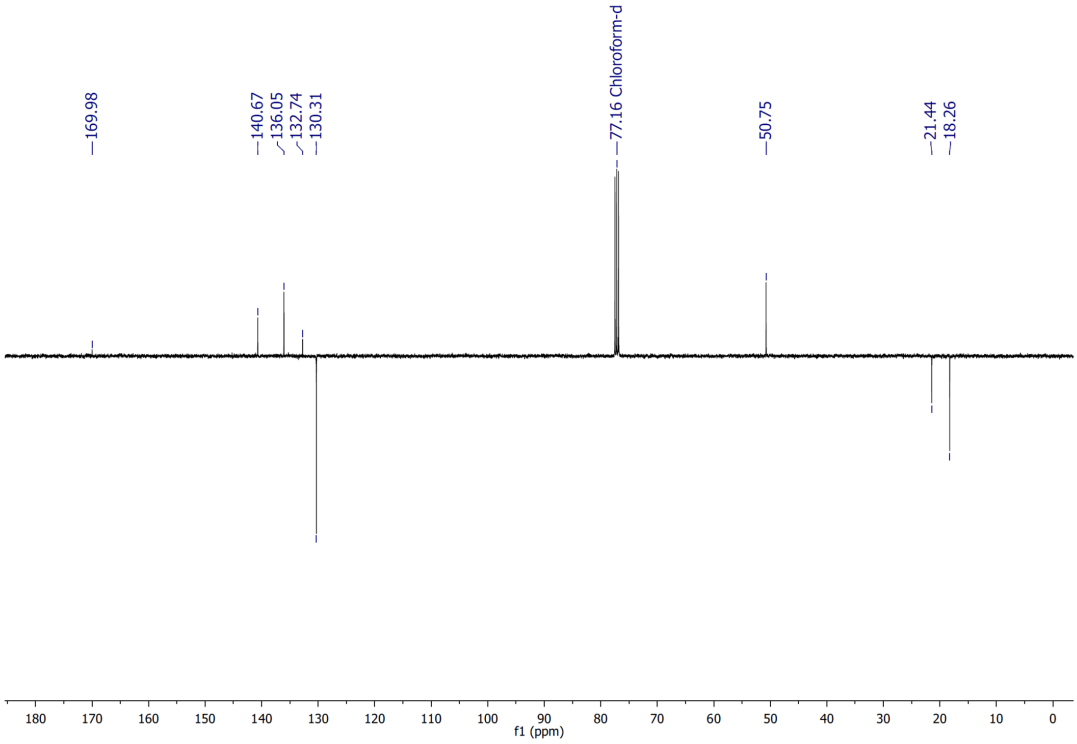

262.72
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

[(I_2)·Se(SIMes)]

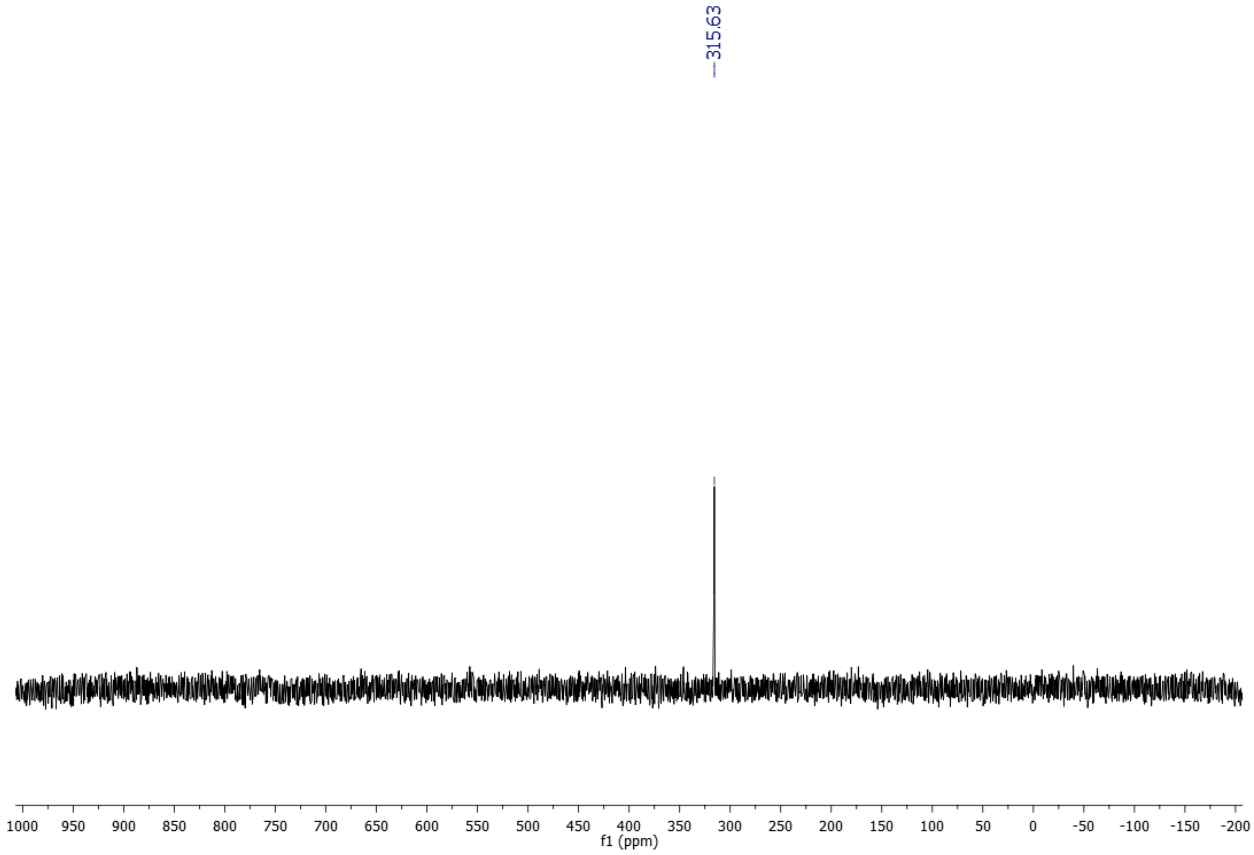
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

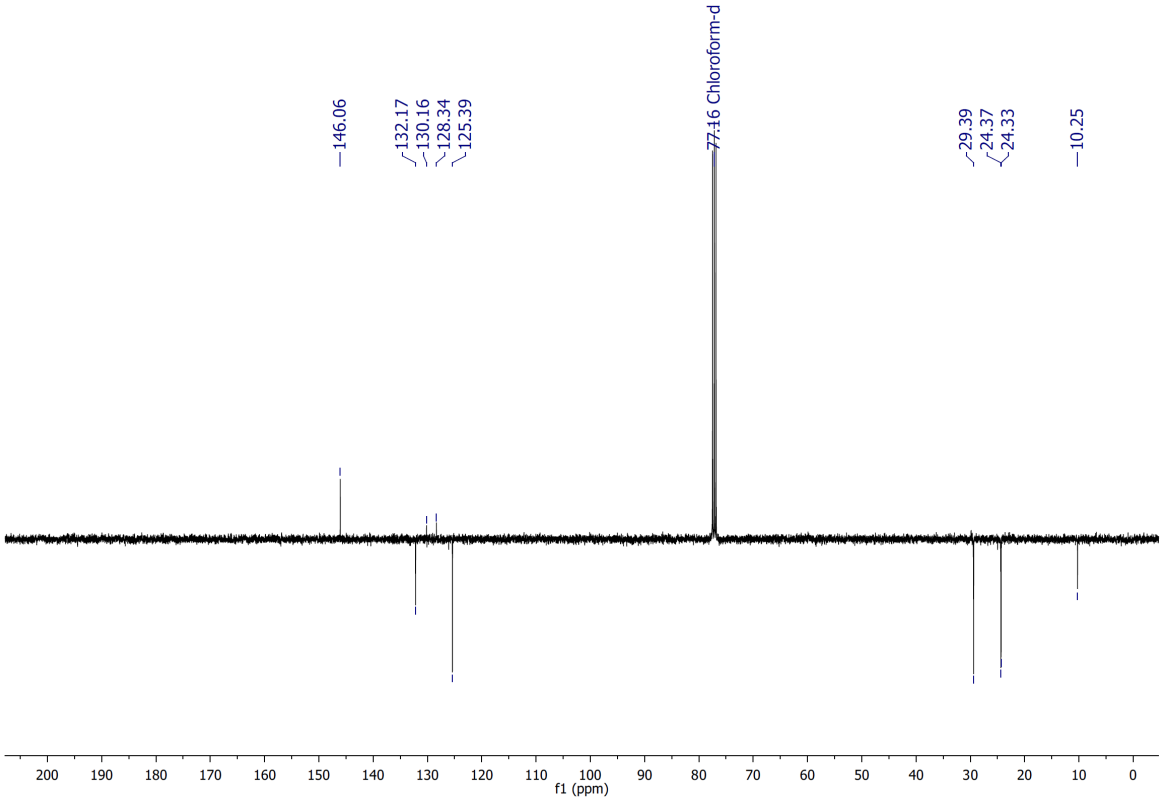


^{77}Se NMR

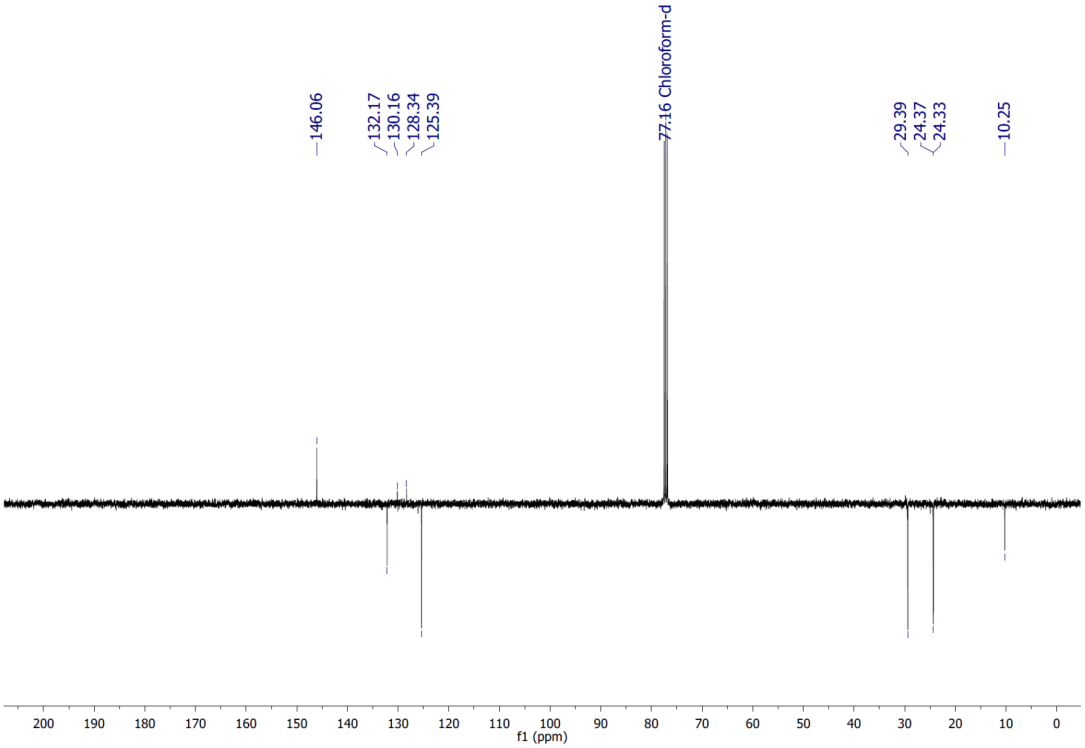

315.63
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

[SeI(IPr^{Me})]I$_3$

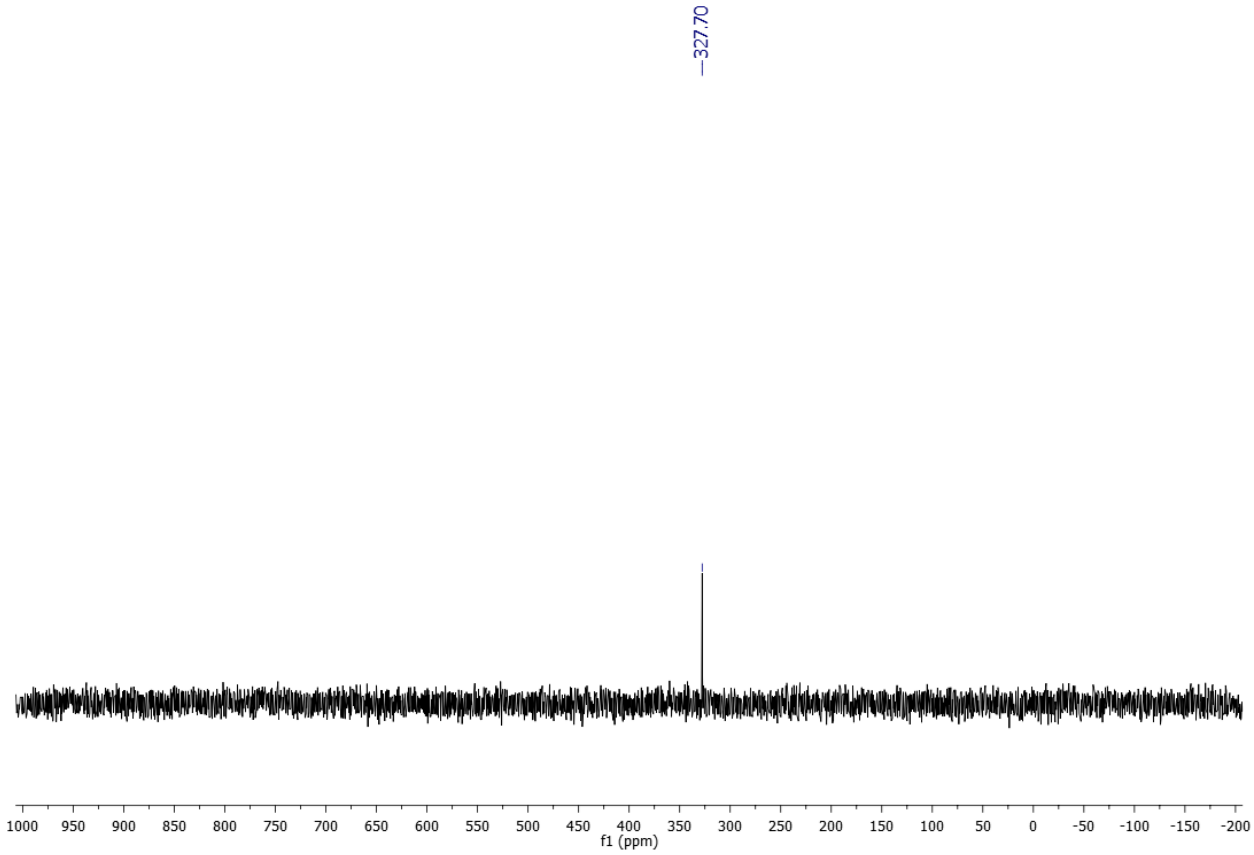
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

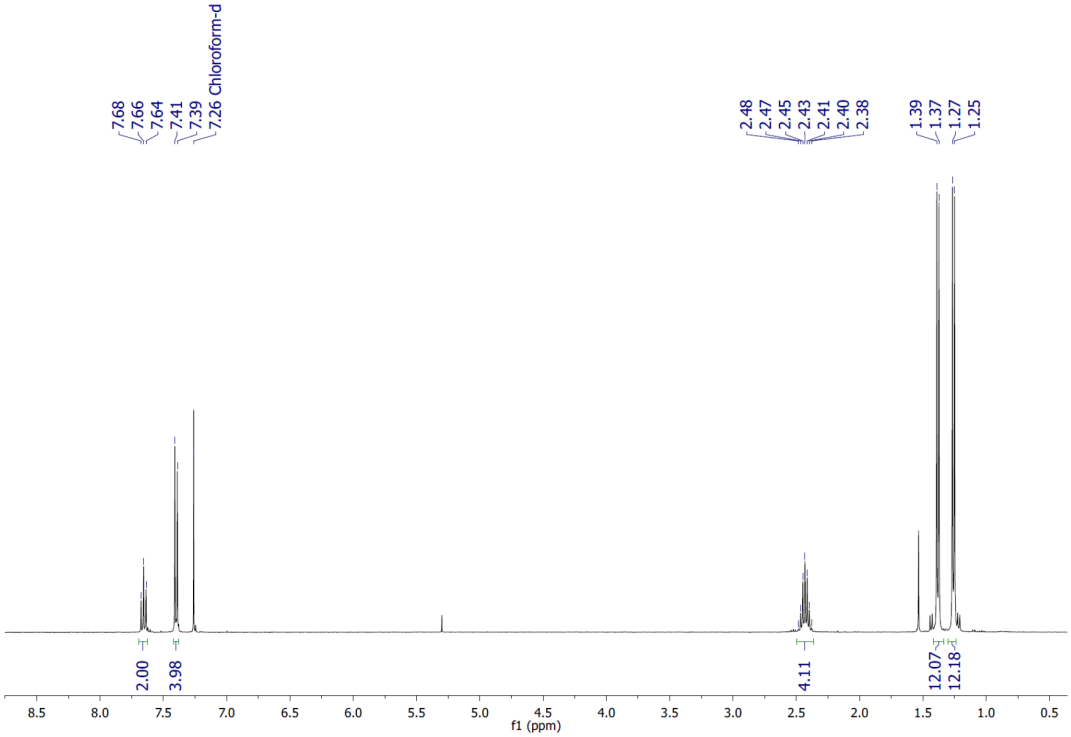


^{77}Se NMR

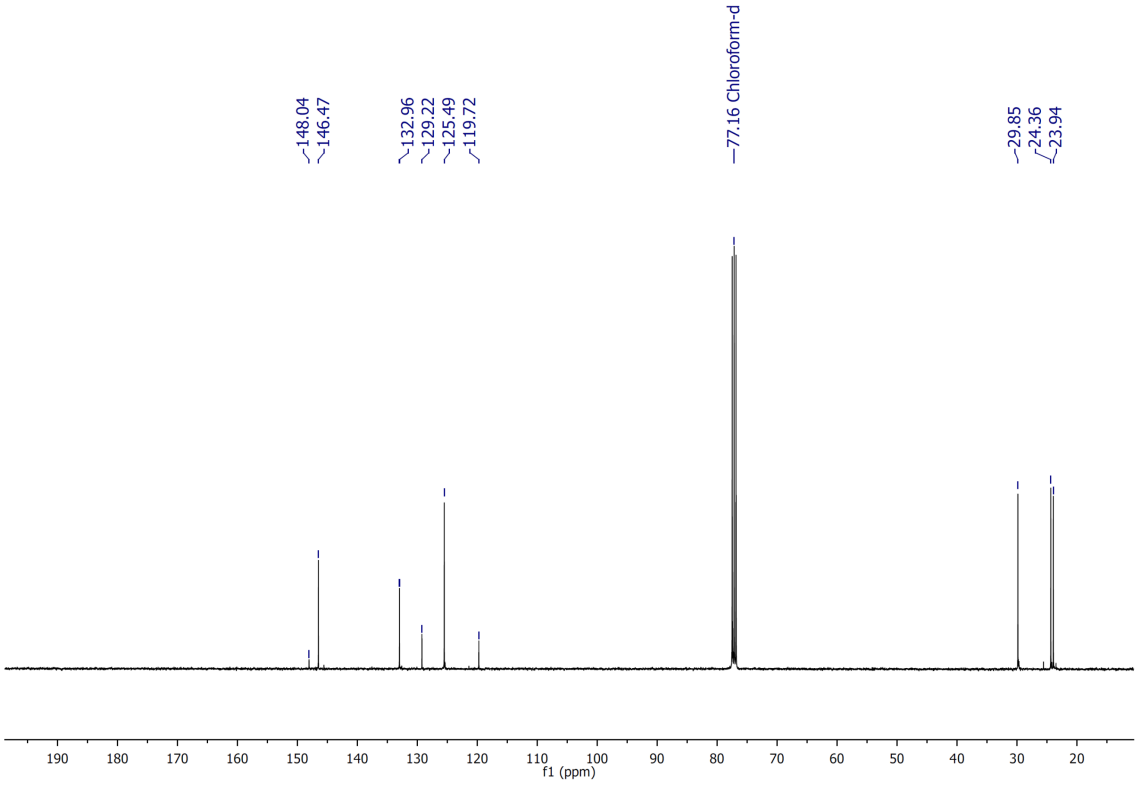

327.70
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

[(I$_2$)·Se(IPr^{Cl})]

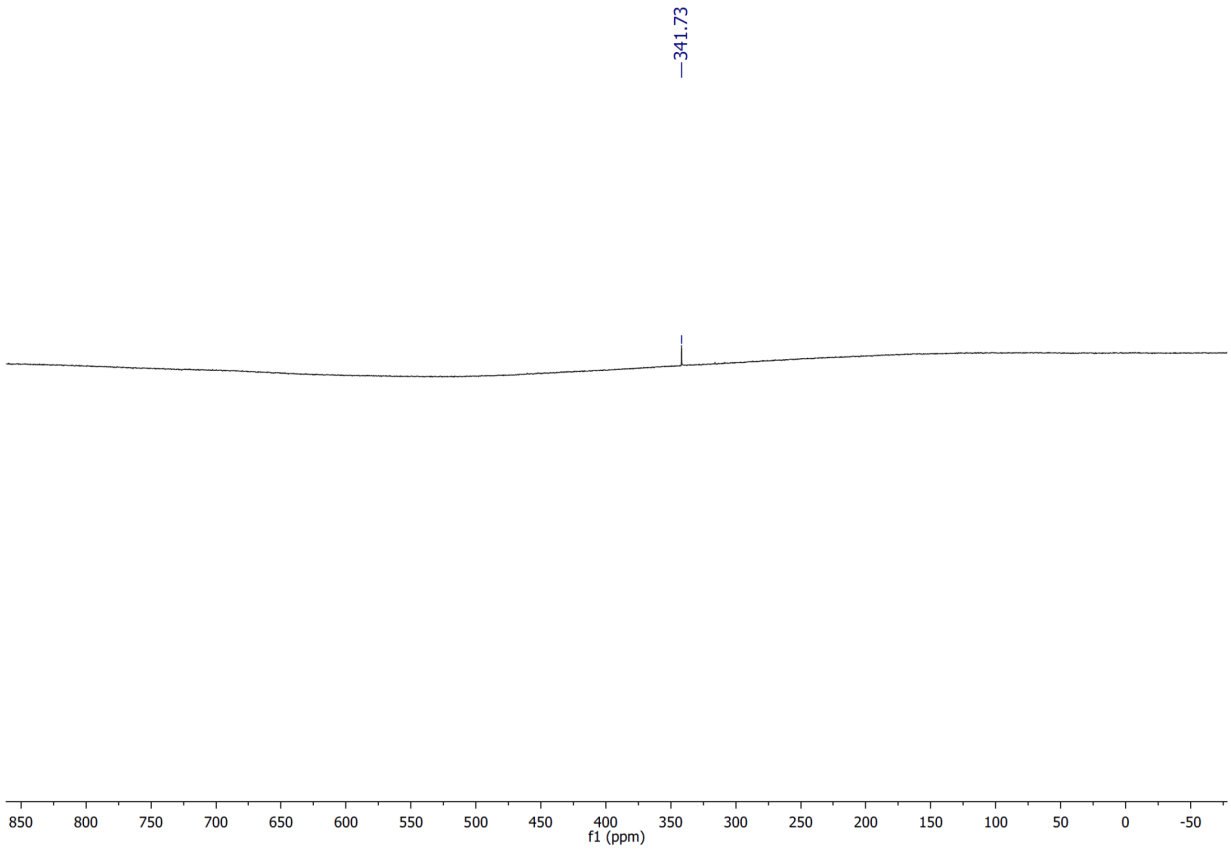
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

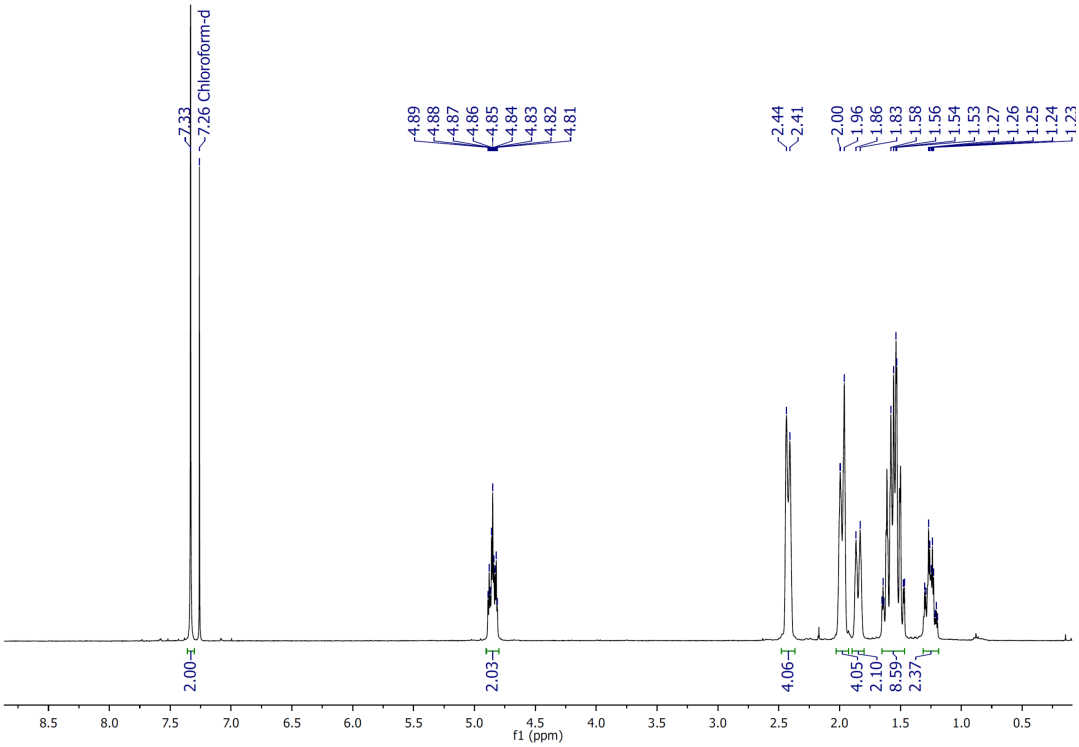


^{77}Se NMR

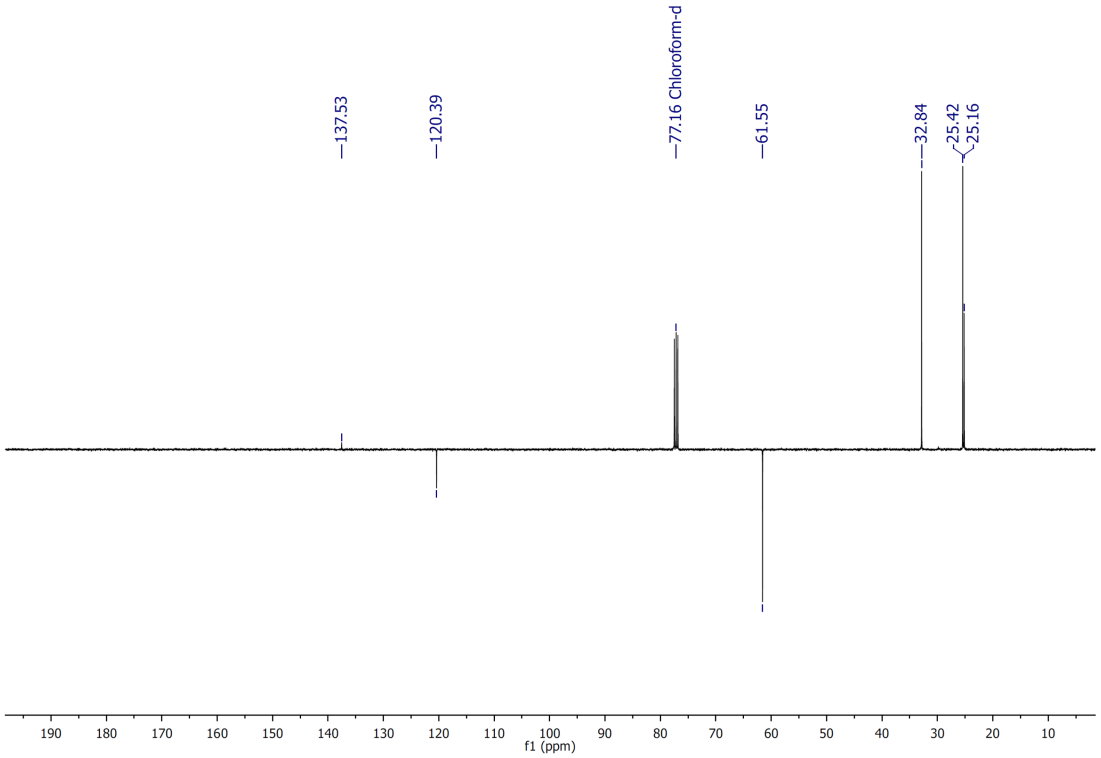

341.73
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
f1 (ppm)

[SeI_2(ICy)]

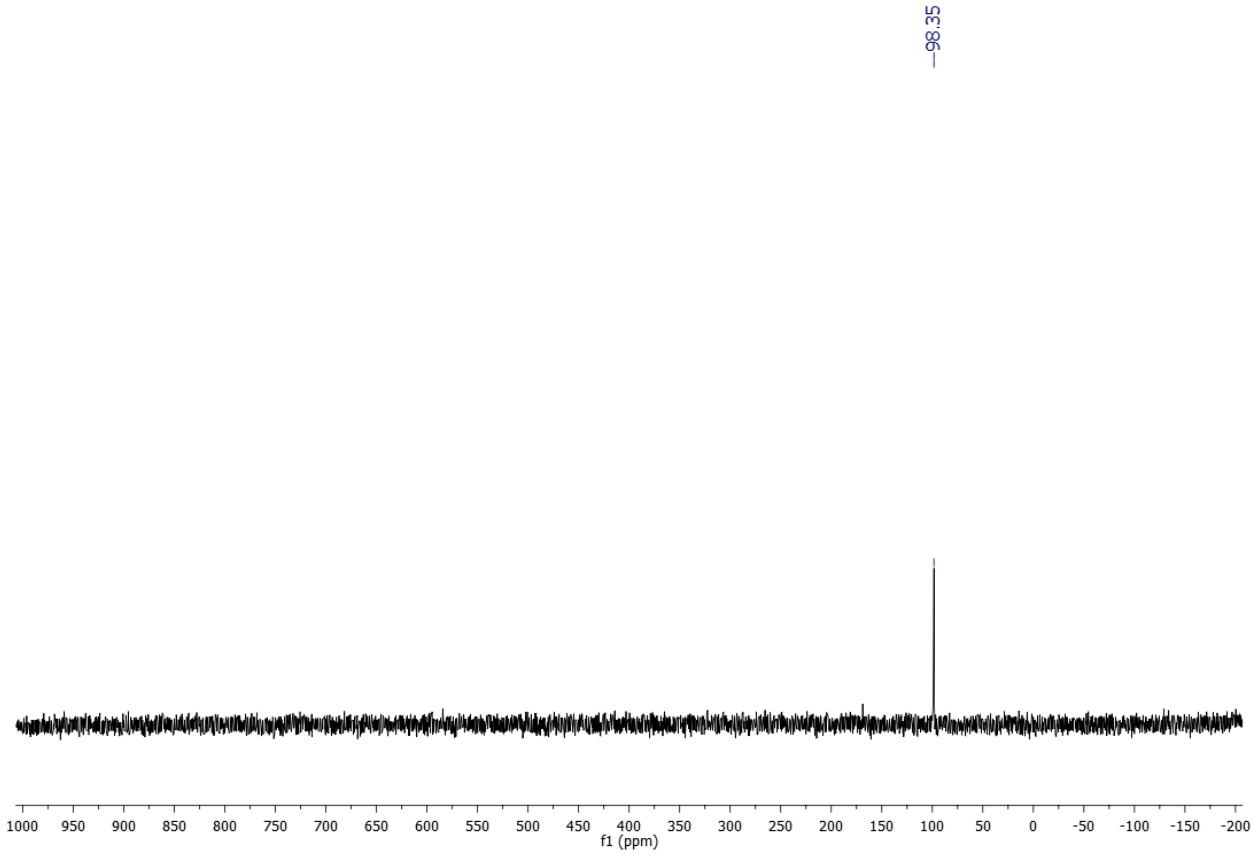
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

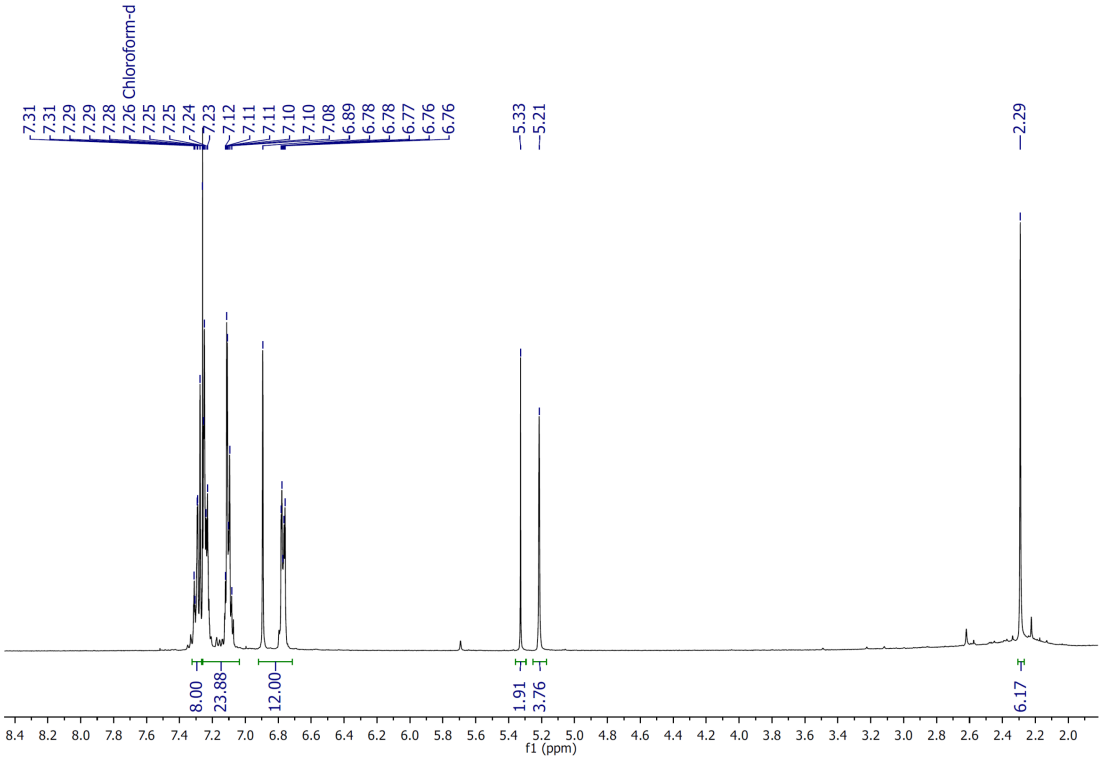


^{77}Se NMR

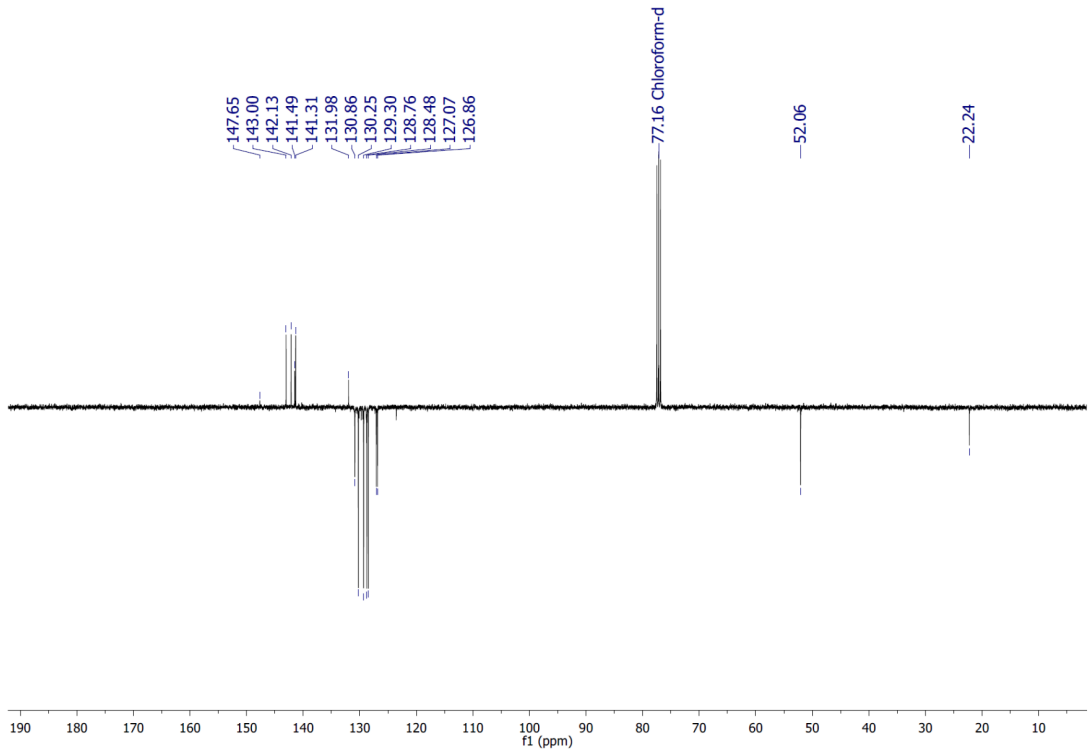

98.35
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

[(I$_2$)·Se(IPr*)]

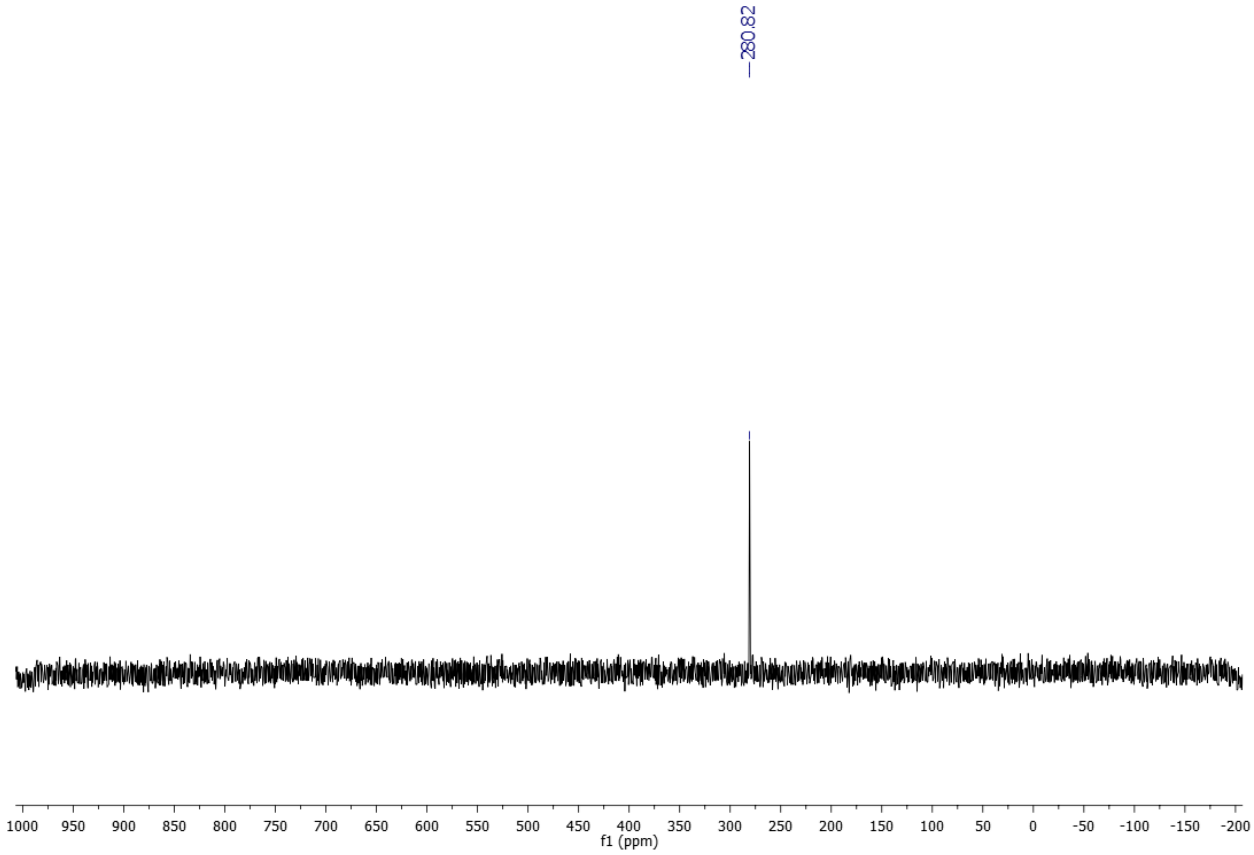
^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR

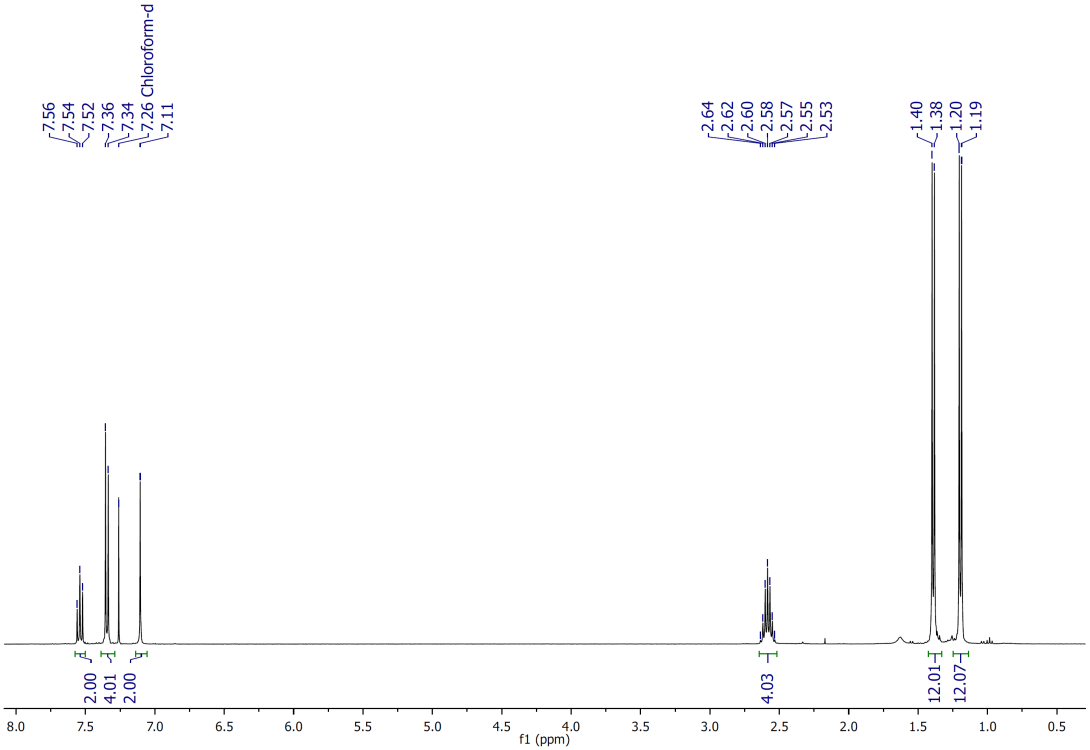


^{77}Se NMR

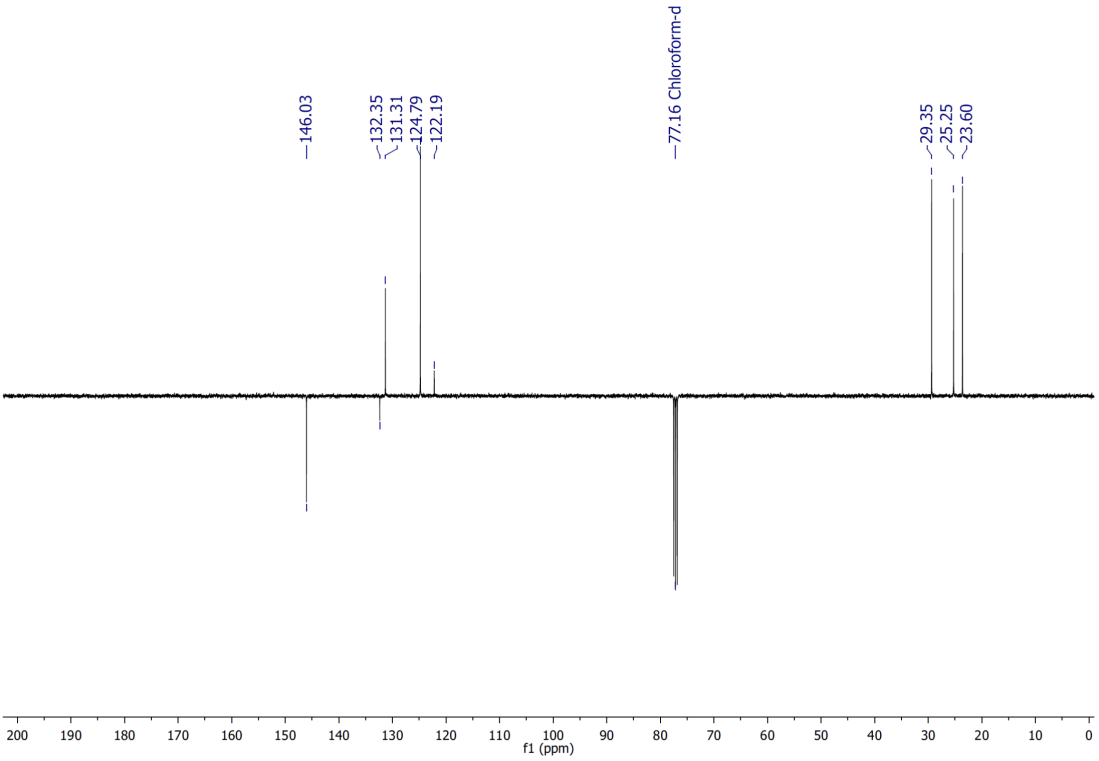

280.82
1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

[(I_2)·S(IPr)]

^{1}H NMR

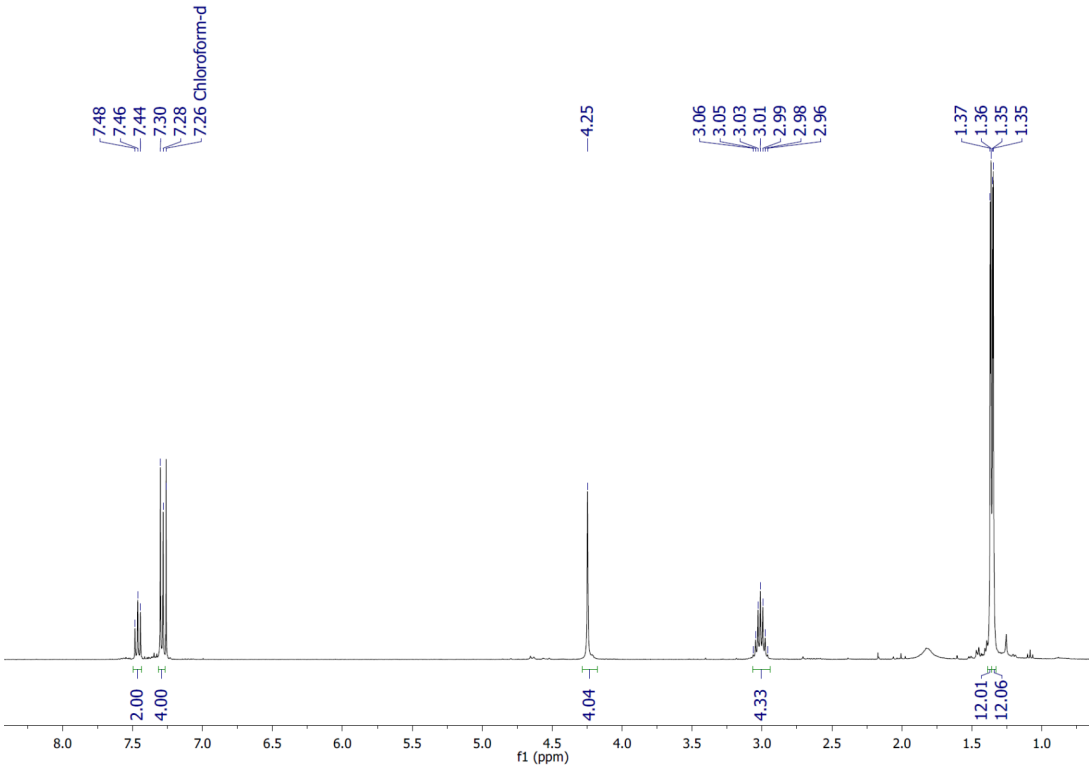


^{13}C{^{1}H} DEPT Q NMR

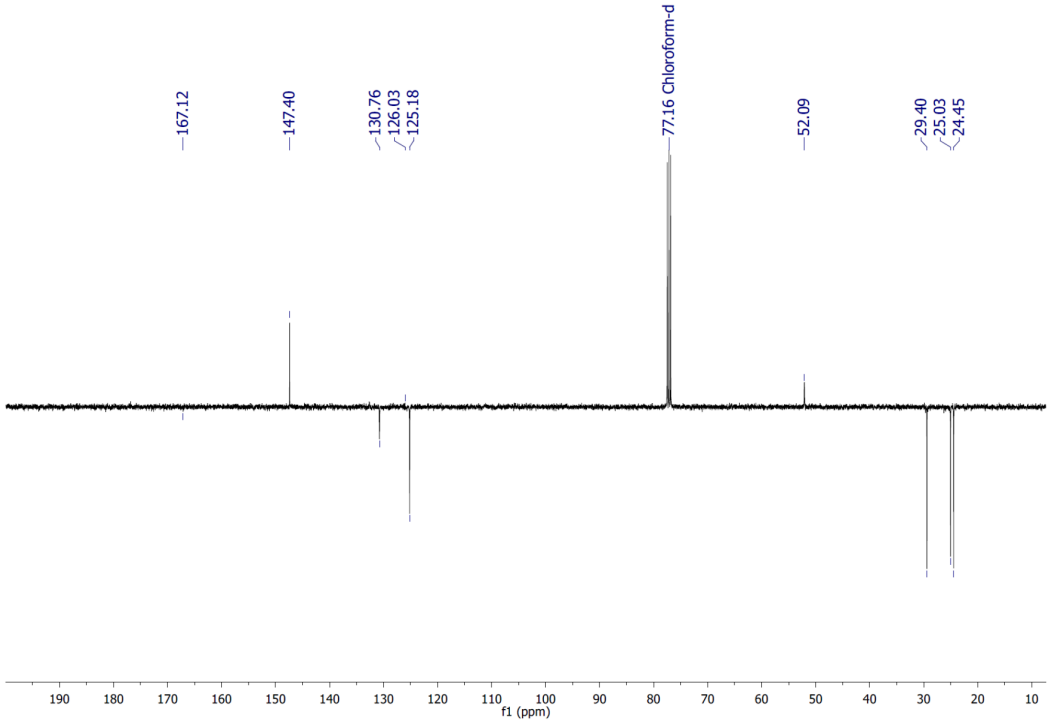


[(I_2)·S(SIPr)]

^{1}H NMR

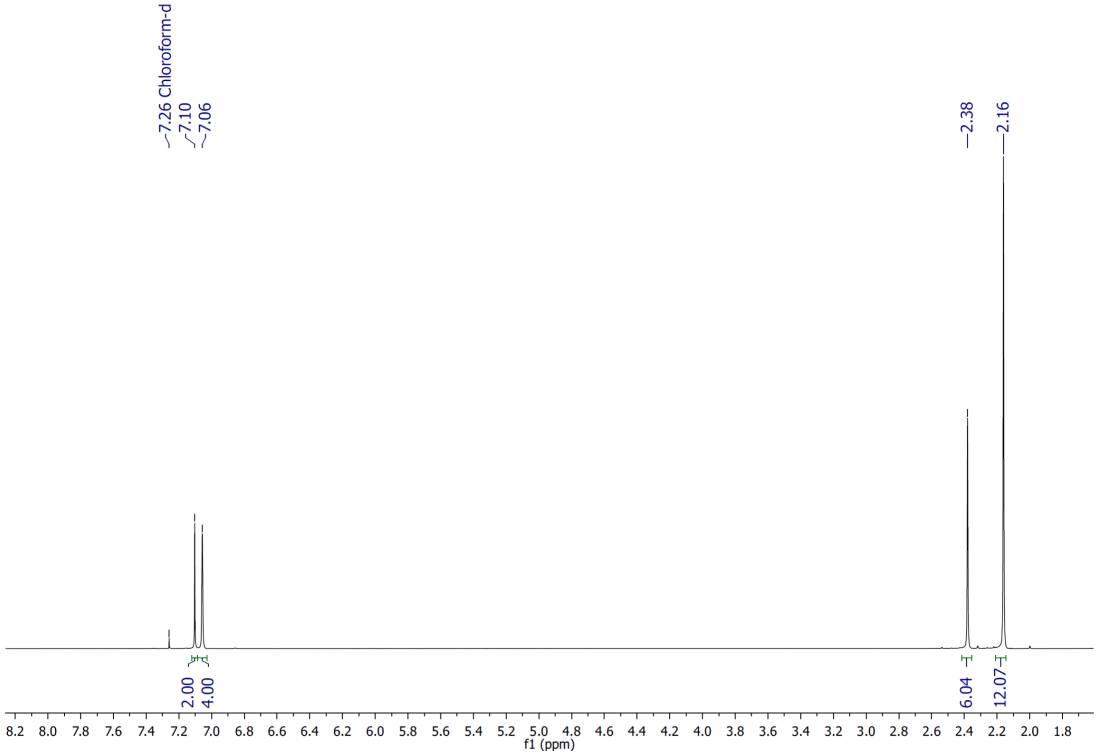


^{13}C{^{1}H} DEPT Q NMR

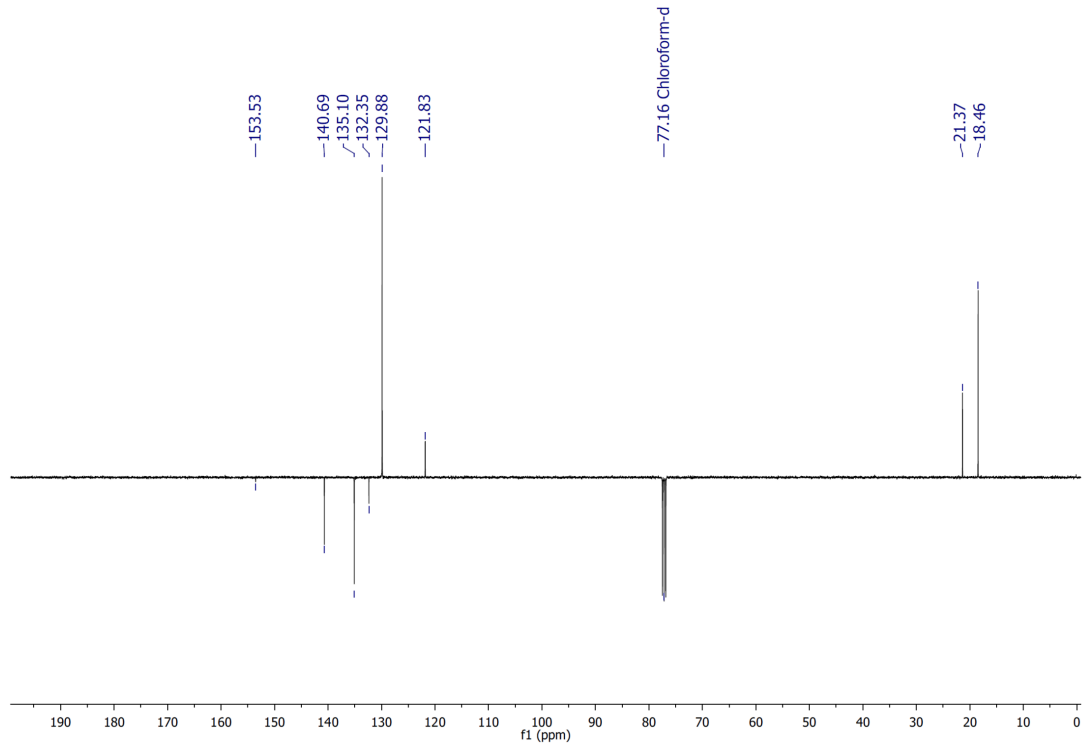


[(I_2)·S(IMes)]

^{1}H NMR

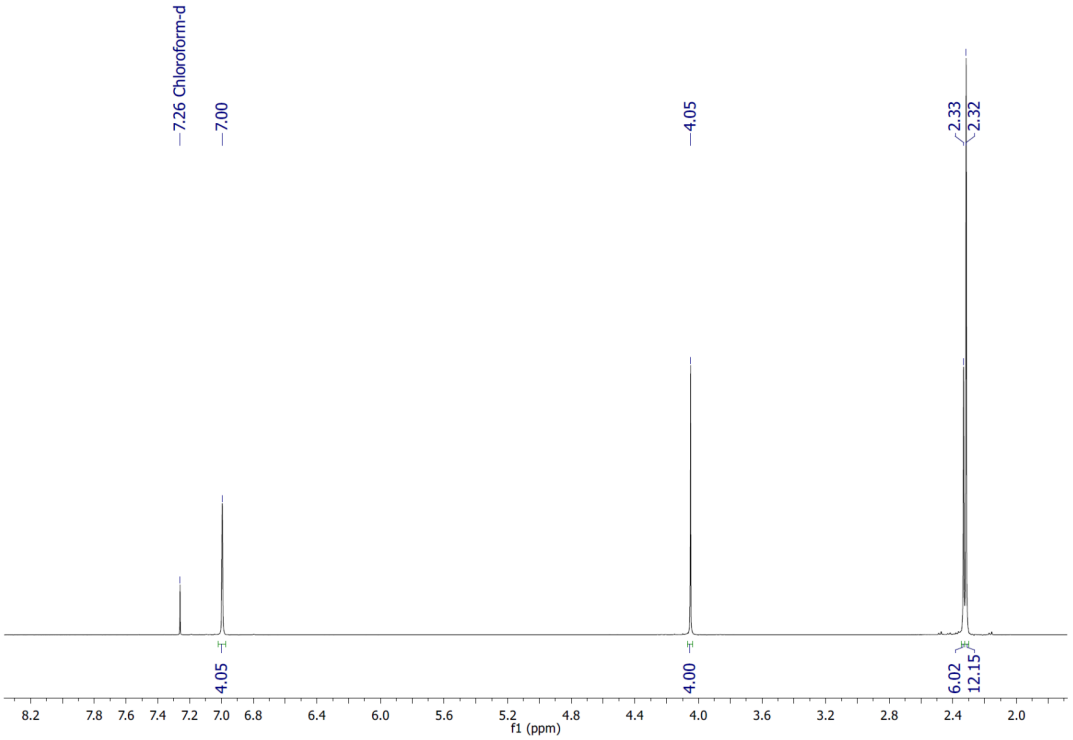


^{13}C{^{1}H} DEPT Q NMR

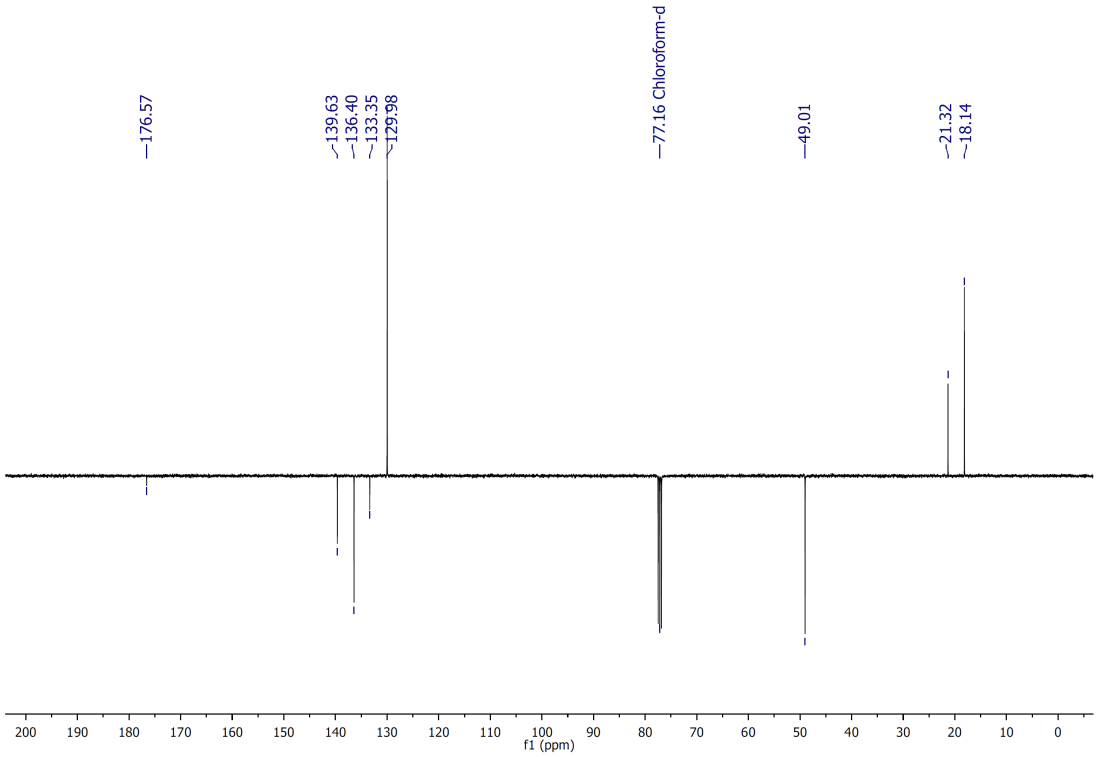


[(I_2)·S(SIMes)]

^{1}H NMR

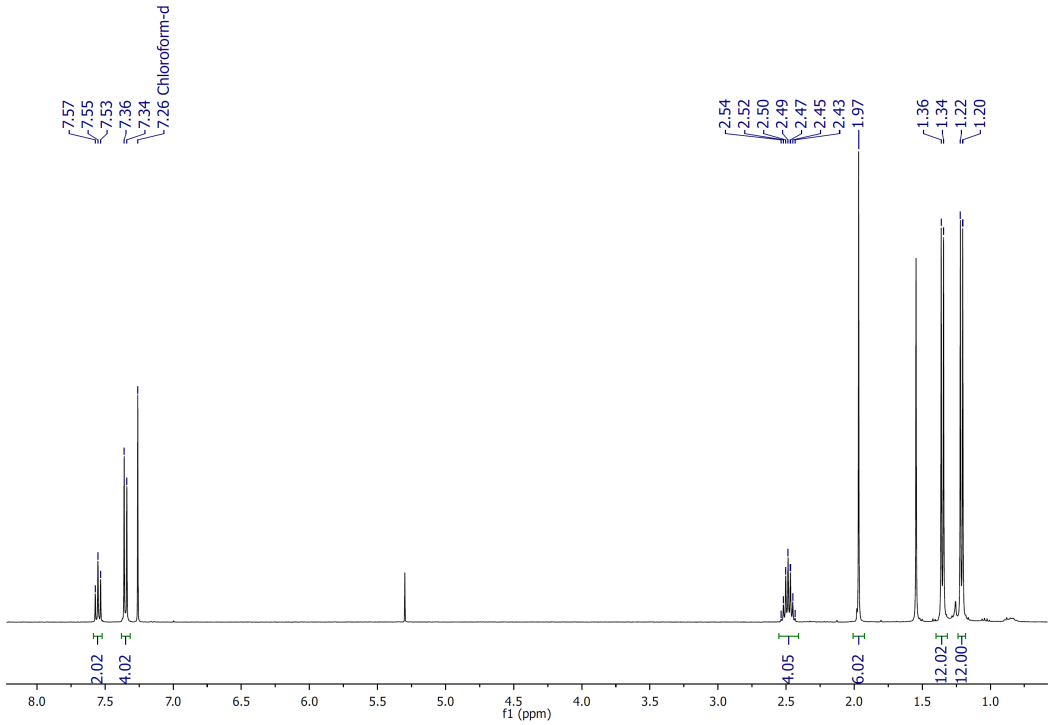


^{13}C{^{1}H} DEPT Q NMR

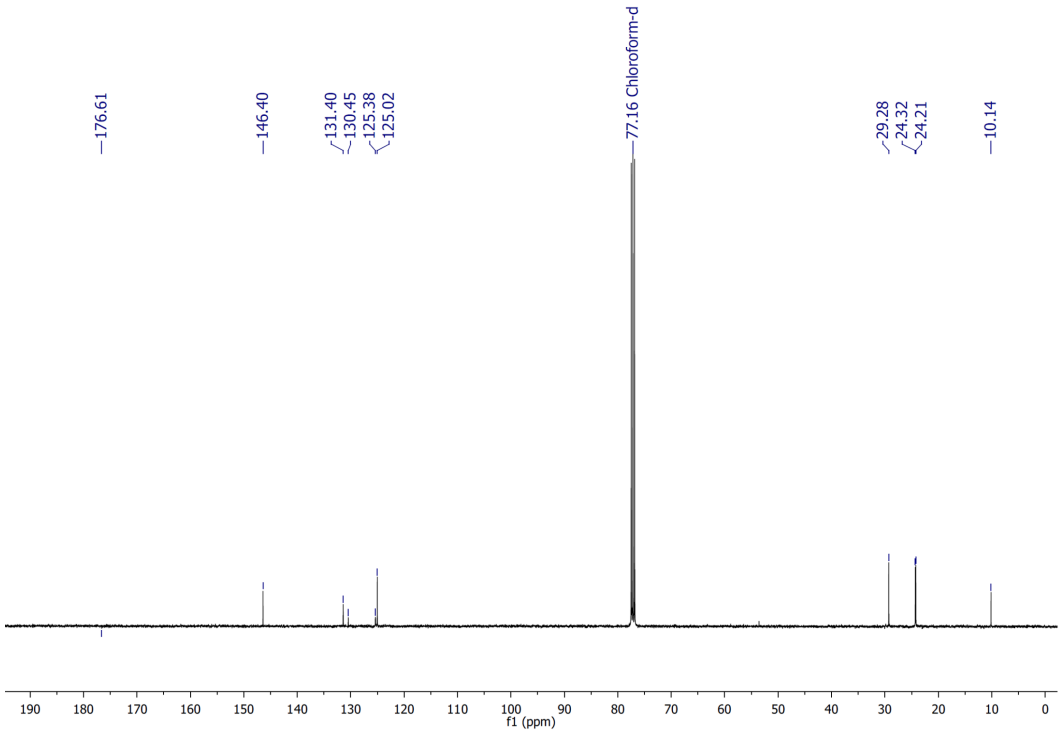


[(I$_2$)·S(IPr^{Me})]

^{1}H NMR

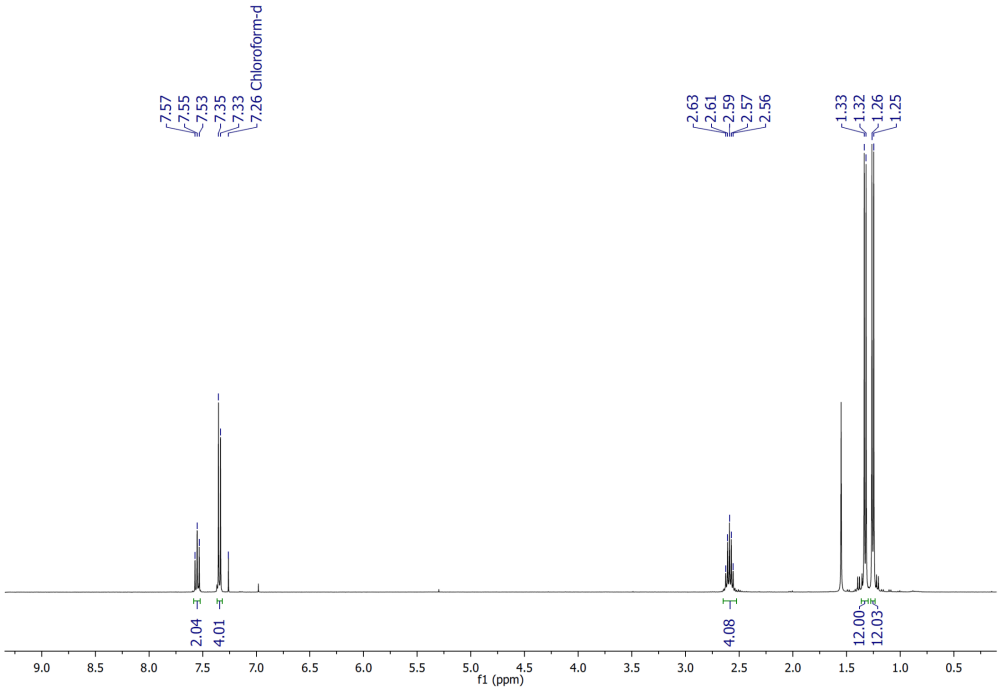


^{13}C{^{1}H} DEPT Q NMR

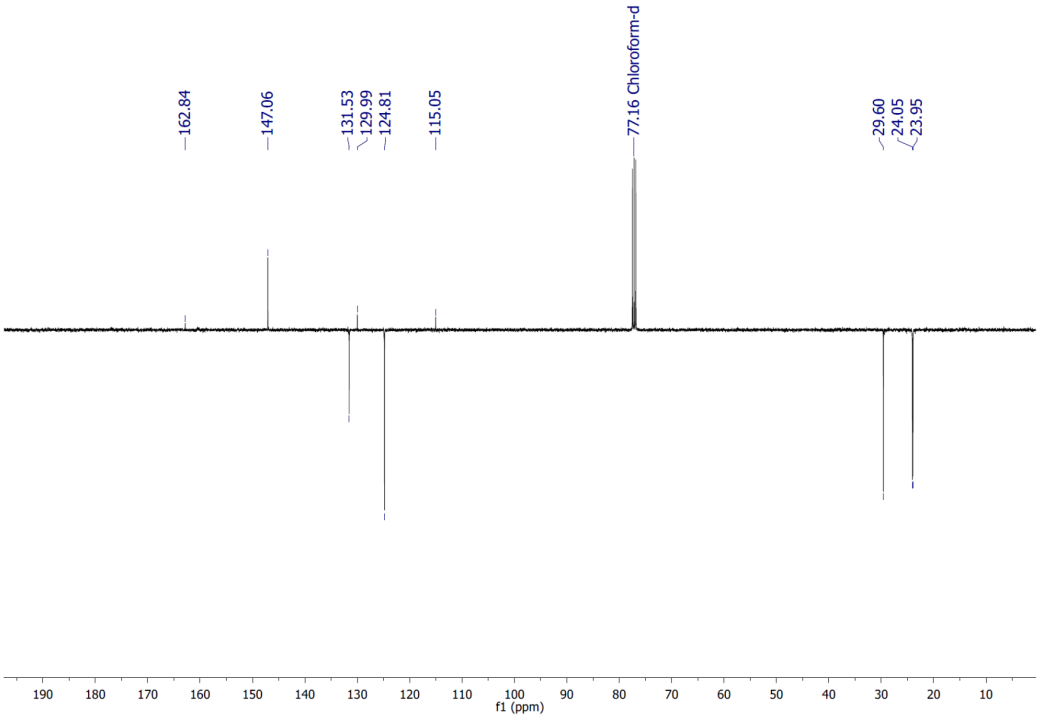


[(I$_2$)·S(IPr^{Cl})]

^{1}H NMR

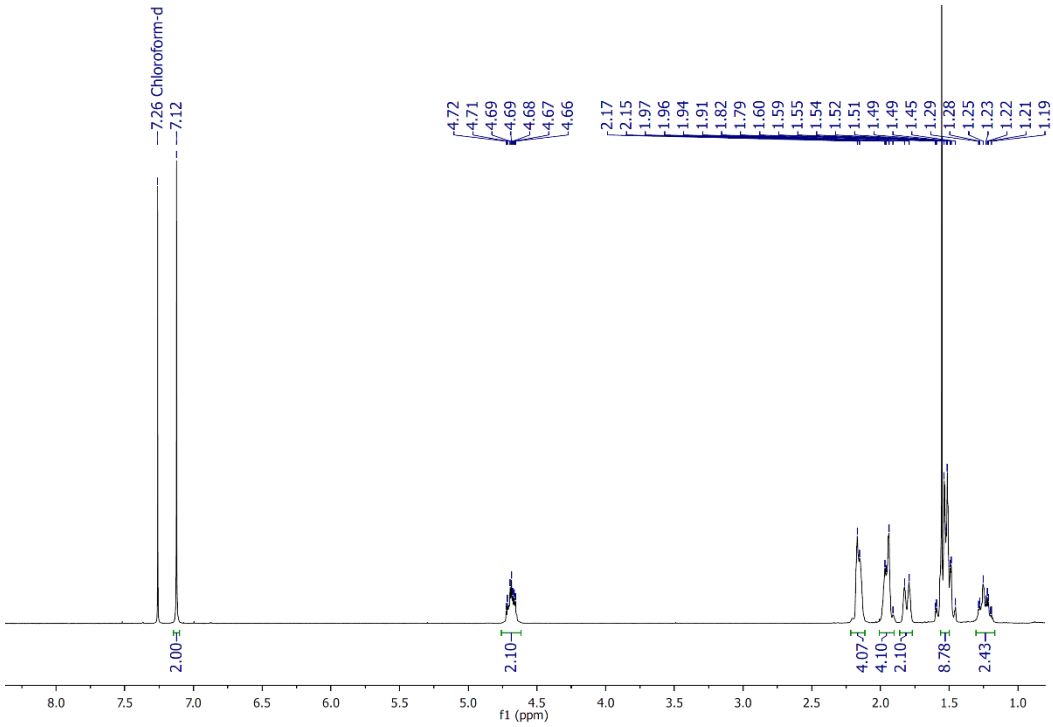


^{13}C{^{1}H} DEPT Q NMR

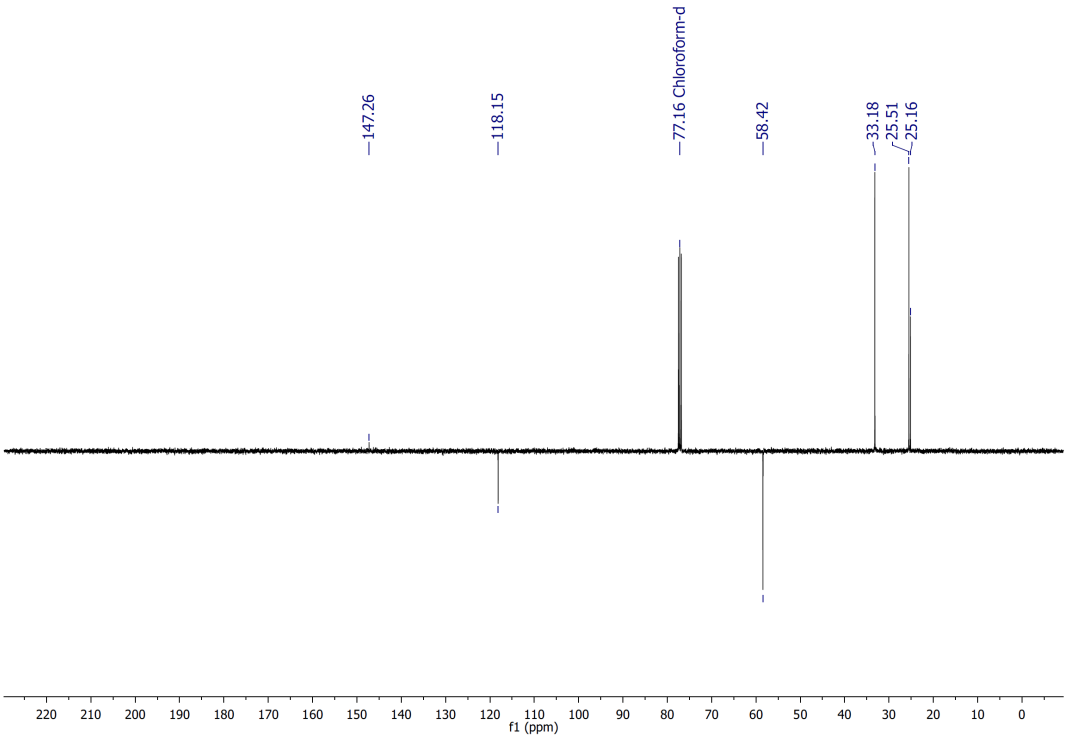


[(I_2)·S(ICy)]

^{1}H NMR

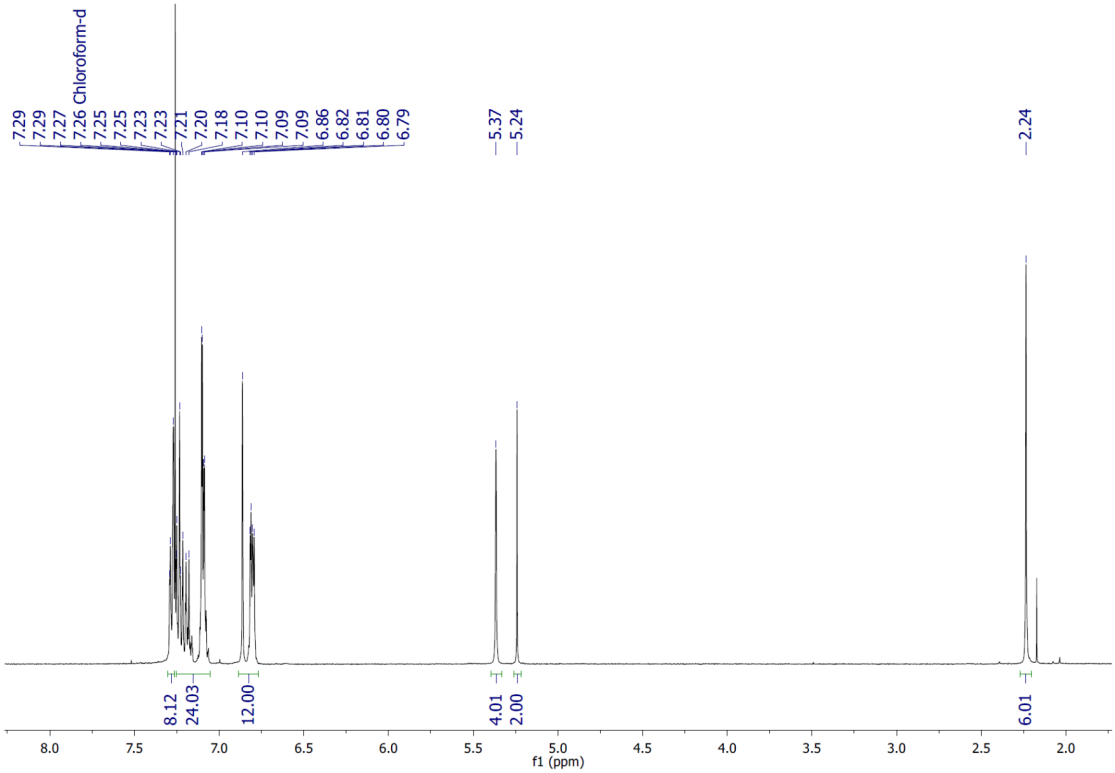


^{13}C{^{1}H} DEPT Q NMR

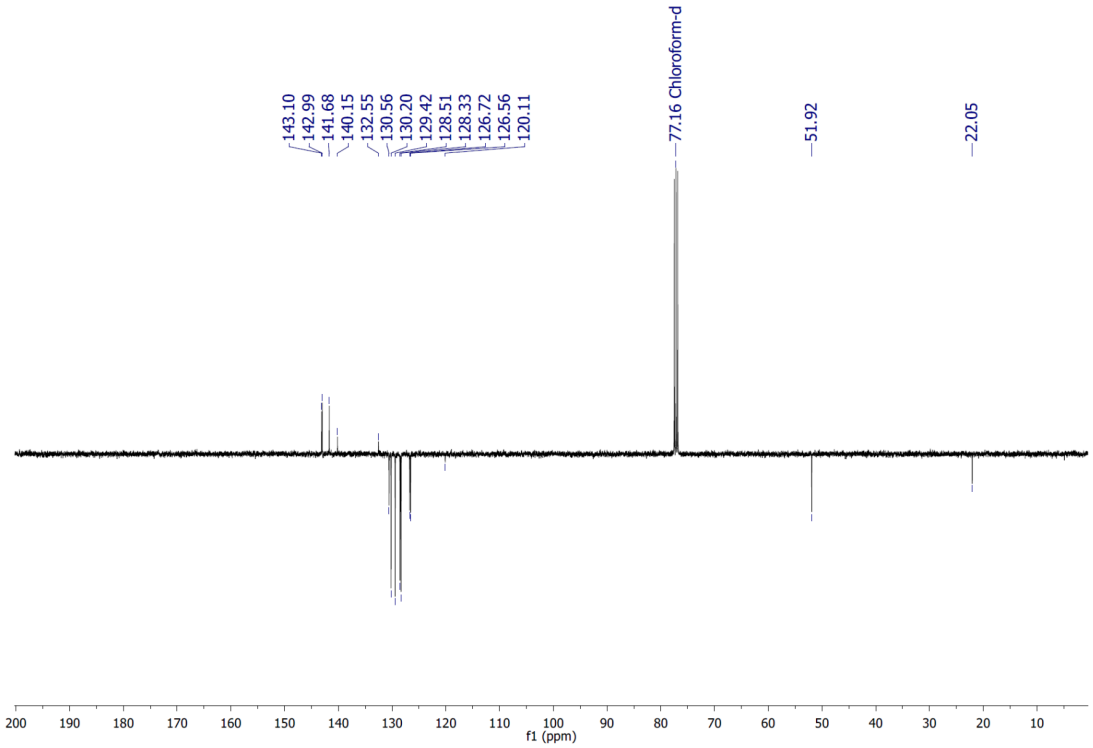


[(I_2)·S(IPr*)]

^{1}H NMR



^{13}C{^{1}H} DEPT Q NMR



Crystallographic data

	$[SeBr_2(IPr)]$	**$[SeBr(SIPr)]Br_3$**	**$[SeBr_2(IMes)]$**	**$[SeBr_2(SIMes)]$**
CCDC no.	2121842	2121843	2121844	2121845
Empirical formula	$C_{27}H_{36}Br_2N_2Se$	$C_{27}H_{38}Br_4N_2Se$	$C_{21}H_{24}Br_2N_2Se$	$C_{21}H_{26}Br_2N_2Se$
Formula weight (g mol^{-1})	627.34	789.15	543.18	545.20
T (K)	100	100	100	100
λ (Å)	1.54184	1.54184	1.54184	1.54184
Crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic
Space group	Pnma	$P2_1/n$	Pnma	Aea2
a (Å)	12.3667(2)	9.72480(10)	19.6139(4)	18.5263(6)
b (Å)	20.3331(4)	18.3045(2)	14.3164(3)	15.6201(6)
c (Å)	10.4430(2)	17.8287(3)	7.58200(10)	7.3666(2)
α (°)	90	90	90	90
β (°)	90	98.1660(10)	90	90
γ (°)	90	90	90	90
V ($Å^3$)	2625.93(8)	3141.47(7)	2129.03(7)	2131.77(12)
Z	4	4	4	4
ρ_{calc} (g cm^{-3})	1.587	1.669	1.695	1.699
μ (mm^{-1})	5.620	7.703	6.829	6.821
F (000)	1264.0	1552.0	1072.0	1080.0
Crystal dimensions (mm^3)	0.095 × 0.061 × 0.039	0.209 × 0.085 × 0.061	0.181 × 0.127 × 0.052	0.16 × 0.12 × 0.11
2θ max (°)	147.572	147.848	147.736	147.798
Reflections collected	12990	30317	10733	5586
Independent reflections	2675	6259	2137	2000
Parameters refined	155	315	122	122
Final R indexes [$I_0>2\sigma(I_0)$]	R_1 = 0.0294, wR_2 = 0.0584	R_1 = 0.0290, wR_2 = 0.0567	R_1 = 0.0255, wR_2 = 0.0601	R_1 = 0.0392, wR_2 = 0.0958
R indexes (all data)	R_1 = 0.0433, wR_2 = 0.0636	R_1 = 0.0428, wR_2 = 0.0617	R_1 = 0.0331, wR_2 = 0.0635	R_1 = 0.0471, wR_2 = 0.1008
Goodness-of-fit on F^2	1.015	1.067	1.044	1.034

	$[SeBr_2(IPr^{Me})]$	**$[SeBr(IPr^{Cl})]Br_3$**	**$[SeBr_2(ICy)]$**	**$[(Br_2)\cdot S(IMes)\}]$**
CCDC no.	2121846	2121847	2121848	2121849
Empirical formula	$C_{30}H_{42}Br_2Cl_2N_2Se$	$C_{27}H_{34}Br_4Cl_2N_2Se$	$C_{15}H_{24}Br_2N_2Se$	$C_{21}H_{24}Br_2N_2S$
Formula weight (g mol^{-1})	740.32	856.02	471.12	496.28
T (K)	100	100	100	100
λ (Å)	1.54184	1.54184	1.54184	1.54184
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/m$	$P2_1/c$	$P2_1/c$
a (Å)	9.7087(3)	9.8098(2)	10.4196(2)	10.3863(2)
b (Å)	12.5412(3)	17.0515(2)	7.59630(10)	15.2158(2)
c (Å)	15.1640(3)	10.0380(2)	22.2930(5)	14.1625(3)
α (°)	77.201(2)	90	90	90
β (°)	77.009(2)	110.109(2)	99.888(2)	105.698(2)
γ (°)	73.293(2)	90	90	90
V ($Å^3$)	1698.62(8)	1576.72(5)	1738.29(6)	2154.70(7)
Z	2	2	4	4
ρ_{calc} (g cm^{-3})	1.447	1.803	1.800	1.530
μ (mm^{-1})	5.846	9.257	8.240	5.721
F (000)	748.0	836.0	928.0	1000.0
Crystal dimensions (mm^3)	0.155 × 0.087 × 0.05	0.183 × 0.1 × 0.072	0.392 × 0.157 × 0.078	0.226 × 0.157 × 0.067
2θ max (°)	147.708	147.818	147.606	147.63
Reflections collected	38991	15522	16939	20876
Independent reflections	6767	3261	3462	4284
Parameters refined	344	176	181	241
Final R indexes [$I_0>2\sigma(I_0)$]	R_1 = 0.0288, wR_2 = 0.0678	R_1 = 0.0320, wR_2 = 0.0747	R_1 = 0.0464, wR_2 = 0.1131	R_1 = 0.0269, wR_2 = 0.0653
R indexes (all data)	R_1 = 0.0344, wR_2 = 0.0706	R_1 = 0.0353, wR_2 = 0.0764	R_1 = 0.0474, wR_2 = 0.1137	R_1 = 0.0322, wR_2 = 0.0679
Goodness-of-fit on F^2	1.044	1.102	1.153	1.080

	[(Br_2)·S(SIMes)}]	**[S(Br)·(IPr^{Me})]Br_3**	**[S(Br)·(ICy)]Br**
CCDC no.	2121850	2121851	2121852
Empirical formula	$C_{43}H_{54}Br_4Cl_2N_4S_2$	$C_{29}H_{40}Br_4N_2S$	$C_{15}H_{24}Br_2N_2S$
Formula weight (g mol^{-1})	1081.52	768.29	424.22
T (K)	100	100	100
λ (Å)	1.54184	1.54184	1.54184
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2/c	$P2_1/m$	$P2_1/c$
a (Å)	20.8862(5)	9.7651(2)	10.4976(9)
b (Å)	8.13980(10)	16.9691(3)	7.4915(5)
c (Å)	13.9252(2)	10.1288(2)	22.3272(17)
α (°)	90	90	90
β (°)	100.044(2)	110.132(2)	101.384(8)
γ (°)	90	90	90
V (Å3)	2331.13(7)	1575.85(6)	1721.3(2)
Z	2	2	4
ρ_{calc} (g cm^{-3})	1.541	1.619	1.637
μ (mm^{-1})	6.367	6.999	7.037
F (000)	1092.0	768.0	856.0
Crystal dimensions (mm^3)	0.251 × 0.139 × 0.071	0.116 × 0.081 × 0.062	0.221 × 0.134 × 0.079
2θ max (°)	147.832	147.572	148.522
Reflections collected	22608	15068	13193
Independent reflections	4645	3254	3409
Parameters refined	255	177	181
Final R indexes [$I_0>2\sigma(I_0)$]	R_1 = 0.0364, wR_2 = 0.0931	R_1 = 0.0355, wR_2 = 0.0880	R_1 = 0.0609, wR_2 = 0.1548
R indexes (all data)	R_1 = 0.0451, wR_2 = 0.1002	R_1 = 0.0420, wR_2 = 0.0915	R_1 = 0.0800, wR_2 = 0.1775
Goodness-of-fit on F^2	1.025	1.059	1.020

	[$SeCl_2$(IPr)]	**[$SeCl_2$(SIPr)]**	**[$SeCl_2$(SIMes)]**	**[$SeCl_2$(IPr*)]**	**[SIMes-Cl]HSO4**
CCDC no.	2121853	2121854	2121855	2121856	2121857
Empirical formula	$C_{27}H_{36}Cl_2N_2Se$	$C_{27}H_{38}Cl_2N_2Se$	$C_{21}H_{26}Cl_2N_2Se$	$C_{69}H_{56}Cl_2N_2Se$	$C_{21}H_{27}ClN_2O_4S$
Formula weight (g mol^{-1})	538.44	540.45	456.30	1063.02	438.95
T (K)	100	100	100	100	100
λ (Å)	1.54184	1.54184	1.54184	1.54184	1.54184
Crystal system	tetragonal	orthorhombic	monoclinic	triclinic	triclinic
Space group	$P4_32_12$	Pbca	$P2_1/n$	P-1	P-1
a (Å)	14.07600(10)	19.3439(3)	7.3535(2)	10.5501(4)	11.7200(7)
b (Å)	14.07600(10)	12.9998(2)	15.3563(4)	13.3094(5)	13.2714(8)
c (Å)	13.5004(2)	21.4322(4)	18.1591(4)	21.9568(9)	15.9571(8)
α (°)	90	90	90	104.727(3)	78.387(5)
β (°)	90	90	92.485(2)	92.152(3)	74.490(5)
γ (°)	90	90	90	96.504(3)	66.020(6)
V ($Å^3$)	2674.89(5)	5389.49(15)	2048.64(9)	2955.5(2)	2173.0(2)
Z	4	8	4	2	4
ρ_{calc} (g cm^{-3})	1.337	1.332	1.479	1.194	1.342
μ (mm^{-1})	3.855	3.826	4.926	2.001	2.702
F (000)	1120.0	2256.0	936.0	1104.0	928.0
Crystal dimensions (mm^3)	0.179 × 0.118 × 0.088	0.27 × 0.157 × 0.084	0.127 × 0.088 × 0.04	0.132 × 0.097 × 0.064	0.128 × 0.085 × 0.054
2θ max (°)	147.576	147.81	147.444	148.022	147.664
Reflections collected	13122	26447	19695	42669	32389
Independent reflections	2688	5362	4089	11737	8649
Parameters refined	150	297	241	669	537
Final R indexes [$I_0>2\sigma(I_0)$]	R_1 = 0.0295, wR_2 = 0.0654	R_1 = 0.0443, wR_2 = 0.1065	R_1 = 0.0471, wR_2 = 0.1113	R_1 = 0.0674, wR_2 = 0.1660	R_1 = 0.0514, wR_2 = 0.0976
R indexes (all data)	R_1 = 0.0353, wR_2 = 0.0680	R_1 = 0.0550, wR_2 = 0.1158	R_1 = 0.0631, wR_2 = 0.1187	R_1 = 0.0837, wR_2 = 0.1772	R_1 = 0.0912, wR_2 = 0.1141
Goodness-of-fit on F^2	1.043	1.040	1.109	1.044	0.992

	[I_2·Se(IPr)]	**[I_2·Se(IMes)]**	**[I_2·Se(SIMes)]**	**[I_2·Se(IPr^{Cl})]**	**[{Se(SIPr)}$_2$(μ-I)]I_5**
CCDC no.	2121858	2121859	2121860	2121861	2121862
Empirical formula	$C_{28}H_{38}Cl_2I_2N_2Se$	$C_{21}H_{24}I_2N_2Se$	$C_{21}H_{26}I_2N_2Se$	$C_{27}H_{34}Cl_2I_2N_2Se$	$C_{55}H_{78}Cl_2I_6N_4Se_2$
Formula weight (g mol^{-1})	806.26	637.18	639.20	790.22	1785.44
T (K)	100	100	100	100	100
λ (Å)	1.54184	1.54184	1.54184	1.54184	1.54184
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	C2/c	P-1	$P2_1/n$
a (Å)	10.7433(2)	7.4915(2)	30.1615(4)	8.6805(2)	10.67600(10)
b (Å)	18.7344(2)	15.8395(5)	44.2672(7)	10.5911(2)	32.7882(2)
c (Å)	16.2982(2)	19.5337(5)	18.8321(3)	18.1694(4)	18.84640(10)
α (°)	90	90	90	74.003(2)	90
β (°)	102.6540(10)	95.970(3)	97.730(2)	89.506(2)	90.7280(10)
γ (°)	90	90	90	73.080(2)	90
V ($Å^3$)	3200.65(8)	2305.33(11)	24915.5(7)	1531.57(6)	6596.59(8)
Z	4	4	40	2	4
ρ_{calc} (g cm^{-3})	1.673	1.836	1.704	1.714	1.798
μ (mm^{-1})	18.405	23.276	21.537	19.219	24.459
F (000)	1576.0	1216.0	12240.0	768.0	3424.0
Crystal dimensions (mm^3)	0.166 × 0.087 × 0.078	0.077 × 0.065 × 0.049	0.184 × 0.11 × 0.068	0.254 × 0.119 × 0.088	0.277 × 0.201 × 0.103
2θ max (°)	147.838	147.69	148.646	147.546	147.812
Reflections collected	36795	17618	119022	23063	41544
Independent reflections	6397	4617	24869	6085	12790
Parameters refined	324	241	1201	315	638
Final R indexes [$I_0>2\sigma(I_0)$]	R_1 = 0.0350, wR_2 = 0.0886	R_1 = 0.0495, wR_2 = 0.0989	R_1 = 0.0435, wR_2 = 0.0746	R_1 = 0.0257, wR_2 = 0.0621	R_1 = 0.0404, wR_2 = 0.1016
R indexes (all data)	R_1 = 0.0408, wR_2 = 0.0933	R_1 = 0.0801, wR_2 = 0.1196	R_1 = 0.0885, wR_2 = 0.0913	R_1 = 0.0287, wR_2 = 0.0640	R_1 = 0.0448, wR_2 = 0.1054
Goodness-of-fit on F^2	1.019	1.089	0.948	1.059	1.041

	[SeI_2(ICy)]	**[SeI(IPr^{Me})]I_3**	**[I_2·S(IPr*)]**	**[I_2·S(IMes)]**	**[I_2·S(ICy)]**
CCDC no.	2121863	2121864	2121865	2121866	2121867
Empirical formula	$C_{15}H_{24}I_2N_2Se$	$C_{29}H_{40}I_4N_2Se$	$C_{69}H_{56}I_2N_2S$	$C_{21}H_{24}I_2N_2S$	$C_{31}H_{50}Cl_2I_4N_4S_2$
Formula weight (g mol^{-1})	565.12	1003.19	1199.02	590.28	1121.37
T (K)	100	100	100	100	100
λ (Å)	1.54184	1.54184	1.54184	1.54184	1.54184
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/m$	$P2_1/c$	$P2_1/c$	P2/n
a (Å)	10.4570(4)	10.2704(2)	13.00810(10)	12.55015(17)	14.8192(6)
b (Å)	11.6249(5)	16.8187(3)	17.9100(2)	11.35537(12)	9.6293(3)
c (Å)	16.1590(7)	10.5634(2)	24.2237(2)	15.8885(2)	15.9429(6)
α (°)	107.039(4)	90	90	90	90
β (°)	101.991(3)	110.816(2)	93.0680(10)	96.6229(11)	117.447(5)
γ (°)	91.225(3)	90	90	90	90
V ($Å^3$)	1829.99(14)	1705.56(6)	5635.43(9)	2249.19(5)	2018.95(15)
Z	4	2	4	4	2
ρ_{calc} (g cm^{-3})	2.051	1.953	1.413	1.743	1.845
μ (mm^{-1})	29.205	30.052	9.437	22.874	26.621
F (000)	1072.0	948.0	2424.0	1144.0	1084.0
Crystal dimensions (mm^3)	0.123 × 0.082 × 0.049	0.09 × 0.068 × 0.039	0.14 × 0.119 × 0.08	0.1 × 0.087 × 0.067	0.14 × 0.111 × 0.054
2θ max (°)	148.124	147.504	147.826	147.816	147.894
Reflections collected	34175	14762	54281	21875	9337
Independent reflections	7269	3515	11204	4500	3769
Parameters refined	361	177	669	241	195
Final R indexes [$I_0>2\sigma(I_0)$]	R_1 = 0.0409, wR_2 = 0.0973	R_1 = 0.0451, wR_2 = 0.1197	R_1 = 0.0346, wR_2 = 0.0840	R_1 = 0.0234, wR_2 = 0.0487	R_1 = 0.0561, wR_2 = 0.1573
R indexes (all data)	R_1 = 0.0546, wR_2 = 0.1059	R_1 = 0.0542, wR_2 = 0.1263	R_1 = 0.0494, wR_2 = 0.0916	R_1 = 0.0313, wR_2 = 0.0518	R_1 = 0.0669, wR_2 = 0.1686
Goodness-of-fit on F^2	1.033	1.084	1.009	1.002	1.056