Supporting information for:

Pseudodiborenes: hydride-bridged diboranes(5) as two-electron reductants of chalcogens

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Experimental Details

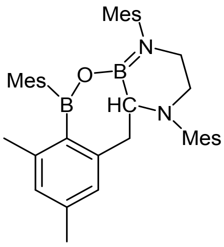
General information

All reactions were performed under an atmosphere of dry argon using standard Schlenk line or glovebox techniques. Deuterated solvents were degassed by three freeze-pump-thaw cycles and dried over molecular sieves. All other solvents were distilled and degassed from appropriate drying agents under an argon atmosphere. The solvents were then stored under argon over activated 4 Å molecular sieves. Diboranes(5) **1**[1] and **2**[2] were synthesised according to literature procedures. All other chemicals were purchased from either Sigma-Aldrich, Acros or TCI Chemical Co. and used as received unless otherwise specified.

NMR spectra were obtained from a Bruker Avance 500 NMR spectrometer (^{1}H and ^{1}H{^{11}B}: 500.1 MHz, ^{11}B: 160.5 MHz,^{13}C{^{1}H}: 125.8 MHz, ^{77}Se{^{1}H}: 95.4 MHz) or a Bruker Avance 400 (^{1}H and ^{1}H{^{11}B}: 400.1 MHz, ^{13}C{^{1}H}: 100.6 MHz; ^{11}B: 128.4 MHz) at 298 K. Chemical shifts (δ) are given in ppm and internally referenced to the carbon nuclei (^{13}C{^{1}H}) or residual protons (^{1}H) of the solvent. ^{11}B and ^{77}Se{^{1}H} NMR spectra were referenced to external standard [$BF_3 \cdot OEt_2$] or Me_2Se, respectively. High-resolution mass spectrometry was obtained from a Thermo Scientific Exactive Plus spectrometer. Cyclic voltammetry experiments were performed using a Gamry Instruments Reference 600 potentiostat.

Synthetic procedures

Synthesis of **1-O**



Diborane(5) **1** (50.0 mg, 0.09 mmol) was dissolved in benzene (0.7 mL) and 10.3 mg (0.09 mmol) NMMO (*N*-methylmorpholine-*N*-oxide) were added. After stirring for one day at room temperature, all volatiles were removed *in vacuo* and the light yellow residue was extracted with hexane. Slow evaporation of solution at room temperature yielded **1-O** (40.6 mg, 0.07 mmol, 79%) as colourless crystals.

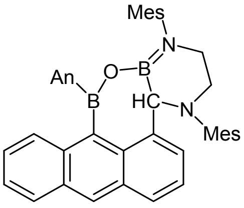
^{1}H NMR (500.1 MHz, C_6D_6): δ = 7.02 (s, 1 H, aryl-C*H*), 6.87 (s, 1 H, aryl-C*H*), 6.81 (s, 1 H, aryl-C*H*), 6.77 (s, 1 H, aryl-C*H*), 6.75 (s, 1 H, aryl-C*H*), 6.68 (s, 1 H, aryl-C*H*), 6.66 (s, 1 H, aryl-C*H*), 6.44 (s, 1 H, aryl-C*H*), 3.87–3.85 (m, 1 H, B-C*H*), 3.43 (m, 2 H, CH_2), 2.96 (dd, $^{3}J_{\mathrm{HH}}$ = 5.2 Hz, $^{2}J_{\mathrm{HH}}$ = 14 Hz, 1 H, CH_2), 2.86–2.81 (m, 1 H, CH_2), 2.62 (dd, $^{3}J_{\mathrm{HH}}$ = 3.2 Hz, $^{2}J_{\mathrm{HH}}$ = 14 Hz, 1 H, CH_2), 2.50–2.47 (m, 1 H, CH_2), 2.32 (s, 3 H, CH_3), 2.29 (s, 6 H, CH_3), 2.25 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 2.12 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 2.06 (s, 6 H, CH_3), 1.86 (s, 3 H, CH_3), 1.83 (s, 3 H, CH_3) ppm.

^{11}B NMR (160.5 MHz, C_6D_6): δ = 48.3 (br s), 32.8 (br s) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 144.63 (s, C_{q}), 144.55 (s, C_{q}), 141.9 (s, C_{q}), 141.7 (s, C_{q}), 141.4 (s, C_{q}), 141.3 (s, C_{q}), 138.8 (s, C_{q}), 138.6 (s, C_{q}), 138.4 (s, C_{q}), 136.8 (s, C_{q}), 135.7 (s, C_{q}), 135.3 (s, C_{q}), 135.0 (s, C_{q}), 134.6 (s, C_{q}), 130.7 (s, aryl-*C*H), 129.7 (s, aryl-*C*H), 129.5 (s, aryl-*C*H), 129.4 (s, aryl-*C*H), 129.1 (s, aryl-*C*H), 128.8 (s, aryl-*C*H), 128.7 (s, aryl-*C*H), 128.3 (s, aryl-*C*H), 56.4 (br s, B-*C*H), 52.2 (s, CH_2), 49.3 (s, CH_2), 35.8 (s, CH_2), 22.3 (s, CH_3), 22.0 (s, CH_3), 21.5 (s, CH_3), 21.4 (s, CH_3), 21.3 (s, CH_3), 20.98 (s, CH_3), 20.97 (s, CH_3), 20.3 (s, CH_3), 19.8 (s, CH_3), 18.2 (s, CH_3), 17.0 (s, CH_3) ppm.

LIFDI-MS for [$C_{39}H_{48}B_2N_2O$] calcd: 582.3947; found: 582.3939.

Synthesis of **2-O**



Diborane(5) **2** (30.0 mg, 0.04 mmol) was dissolved in benzene (0.7 mL) and NMMO (5.14 mg, 0.04 mmol) was added. After stirring for 3 h at room temperature a color change to yellow was observed. All volatiles were removed *in vacuo* and the yellow residue was extracted with hexane. Storage at room temperature of a saturated hexane solution yielded **2-O** as a yellow solid (19.0 mg, 0.03 mmol, 62%).

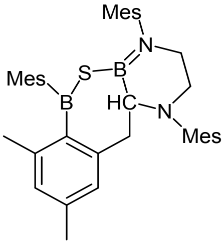
^{1}H NMR (500.1 MHz, C_6D_6): δ = 8.99–8.98 (m, 1 H, aryl-C*H*), 8.45–8.35 (m, 4 H, aryl-C*H*), 8.30 (s, 1 H, aryl-C*H*), 7.88–7.85 (m, 2 H, aryl-C*H*), 7.76–7.74 (m, 1 H, aryl-C*H*), 7.64–7.59 (m, 2 H, aryl-C*H*), 7.30–7.27 (m, 1 H, aryl-C*H*), 7.15–7.12 (m, 1 H, aryl-C*H*), 7.00–7.6.97 (m, 1 H, aryl-C*H*), 6.84–6.81 (m, 3 H, aryl-C*H*), 6.63 (s, 1 H, aryl-C*H*), 6.49 (s, 1 H, aryl-C*H*), 6.45–6.42 (m, 1 H, aryl-C*H*), 6.36–6.32 (m, 1 H, aryl-C*H*), 5.13 (s, 1 H, B-C*H*), 3.71–3.66 (m, 1 H, CH_2), 3.47–3.42 (m, 1 H, CH_2), 3.22–3.19 (m, 1 H, CH_2), 2.69–2.65 (m, 4 H, CH_2 + CH_3), 3.17 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3), 2.01 (s, 3 H, CH_3), 1.87 (s, 3 H, CH_3), 1.80 (s, 3 H, CH_3) ppm.

^{11}B NMR (160.5 MHz, C_6D_6): δ = 53.1 (br s), 27.4 (br s) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 147.4 (s, aryl-C_q), 141.2 (s, aryl-C_q), 141.0 (s, aryl-C_q), 140.8 (br s, aryl-C_q), 137.6 (s, aryl-C_q), 136.6 (br s, aryl-C_q), 135.9 (br s, aryl-C_q), (s, aryl-C_q), 135.7 (s, aryl-C_q), 135.4 (s, aryl-C_q), 135.3 (s, aryl-C_q), 135.3 (s, aryl-C_q), 135.3 (s, aryl-C_q), 134.9 (br s, aryl-C_q), 134.4 (s, aryl-C_q), 134.4 (s, aryl-C_q), 134.1 (s, aryl-*C*H), 132.9 (s, aryl-C_q), 132.5 (s, aryl-C_q), 131.8 (s, aryl-C_q), 131.5 (br s, aryl-*C*H), 131.4 (s, aryl-C_q), 130.5 (s, aryl-*C*H), 130.5 (s, aryl-*C*H), 130.0 (br s, aryl-*C*H), 129.4 (s, aryl-*C*H), 129.4 (s, aryl-*C*H), 129.3 (s, aryl-*C*H), 129.2 (s, aryl-*C*H), 129.1 (s, aryl-*C*H), 129.0 (s, aryl-*C*H), 128.6 (s, aryl-*C*H), 128.6 (s, aryl-*C*H), 126.6 (s, aryl-*C*H), 126.1 (s, aryl-*C*H), 125.8 (s, aryl-*C*H), 125.6 (s, aryl-*C*H), 125.5 (s, aryl-*C*H), 125.2 (s, aryl-*C*H), 125.1 (s, aryl-*C*H), 125.1 (s, aryl-*C*H), 59.9 (br s, *C*H), 53.9 (s, CH_2), 49.3 (s, CH_2), 21.0 (s, CH_3), 20.7 (s, CH_3), 20.6 (br s, CH_3), 19.8 (br s, CH_3), 18.8 (s, CH_3), 17.8 (s, CH_3) ppm.

LIFDI-MS for [$C_{49}H_{44}B_2N_2O$] calcd: 698.3634; found: 698.3626.

Synthesis of **1-S**



Diborane(5) **1** (30.0 mg, 0.05 mmol) was dissolved in benzene (0.7 mL) and an excess of elemental sulfur (21.3 mg, 0.67 mmol) was added. Heating at 60 °C for three days afforded a yellow solution. All volatiles were removed *in vacuo* and hexane (0.9 mL) was added. A colorless solid precipitated, which was separated and washed with cold hexane (–30 °C) to yield **1-S** as a colourless solid (15.3 mg, 0.03 mmol, 48%). Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated hexane solution at –30 °C.

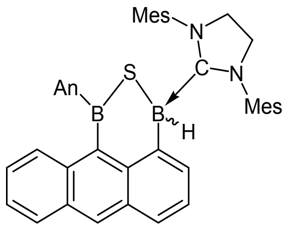
^{1}H NMR (500.1 MHz, C_6D_6): δ = 7.02 (s, 1 H, aryl-C*H*), 6.82 (s, 1 H, aryl-C*H*), 6.81 (s, 1 H, aryl-C*H*), 6.78 (s, 1 H, aryl-C*H*), 6.75 (s, 1 H, aryl-C*H*), 6.71 (s, 1 H, aryl-C*H*), 6.61 (s, 1 H, aryl-C*H*), 6.31 (s, 1 H, aryl-C*H*), 4.00 (t, $^{3}J_{HH}$ = 3.9 Hz, 1 H, B-C*H*), 3.54 (dd, $^{3}J_{HH}$ = 4.4 Hz, $^{2}J_{HH}$ = 13.6 Hz, 1 H, C*H*$_2$), 3.39–3.31 (m, 2 H, C*H*$_2$), 3.03–2.97 (m, 1 H, C*H*$_2$), 2.83–2.77 (m, 2 H, C*H*$_2$), 2.31 (s, 3 H, C*H*$_3$), 2.27 (s, 6 H, C*H*$_3$), 2.20 (s, 3 H, C*H*$_3$), 2.19 (s, 6 H, C*H*$_3$), 2.17 (s, 3 H, C*H*$_3$), 2.12 (s, 3 H, C*H*$_3$), 2.09 (s, 3 H, C*H*$_3$), 2.00 (s, 3 H, C*H*$_3$), 1.90 (s, 3 H, C*H*$_3$) ppm.

^{11}B NMR (160.5 MHz, C_6D_6): δ = 70.4 (br s), 42.0 (br s) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 145.0 (s, C_q), 144.9 (s, C_q), 143.1 (s, C_q), 141.4 (s, C_q), 139.5 (s, C_q), 138.8 (s, C_q), 138.2 (s, C_q), 138.1 (s, C_q), 137.5 (s, C_q), 136.3 (s, C_q), 135.8 (s, C_q), 134.1 (s, C_q), 134.2 (s, C_q), 134.1 (s, C_q), 130.8 (s, aryl-*C*H), 129.9 (s, aryl-*C*H), 129.8 (s, aryl-*C*H), 129.7 (s, aryl-*C*H), 129.5 (s, aryl-*C*H), 129.3 (s, aryl-*C*H), 129.0 (s, aryl-*C*H), 60.1 (br s, B-*C*H), 52.1 (s, *C*H$_2$), 50.5 (s, *C*H$_2$), 36.9 (s, *C*H$_2$), 23.8 (s, *C*H$_3$), 22.9 (s, *C*H$_3$), 22.2 (s, *C*H$_3$), 21.24 (s, *C*H$_3$), 21.19 (s, *C*H$_3$), 20.99 (s, *C*H$_3$), 20.97 (s, *C*H$_3$), 20.6 (s, *C*H$_3$), 19.7 (s, *C*H$_3$), 18.3 (s, *C*H$_3$), 17.2 (s, *C*H$_3$) ppm.

LIFDI-MS for [$C_{39}H_{48}B_2N_2S$] calcd: 598.3719; found: 598.3705.

Synthesis of **Int_2-S**



Diborane(5) **2** (30.0 mg, 0.04 mmol) was suspended in benzene (0.7 mL) and an excess of elemental sulfur (5 mg, 0.16 mmol) was added. Heating at 60 °C for 24 h afforded a yellow suspension. After removal of the solvent, the resulting residue was dissolved in hexane and upon storage at –30 °C for 24 h a yellow precipitate was formed, which was dried *in vacuo* to yield **Int_2-S** as a yellow solid (10.3 mg, 0.01 mmol, 36%).

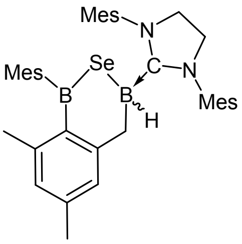
^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6): δ = 9.49 (dd, $^{4}J_{HH}$ = 0.7 Hz, $^{3}J_{HH}$ = 8.7 Hz, 1 H, aryl-C*H*), 8.42 (dd, $^{4}J_{HH}$ = 0.7 Hz, $^{3}J_{HH}$ = 8.7 Hz, 1 H, aryl-C*H*), 8.14 (s, 1 H, aryl-C*H*), 8.05–8.03 (m, 2 H, aryl-C*H*), 7.83 (dd, $^{4}J_{HH}$ = 1.3 Hz, $^{3}J_{HH}$ = 6.4 Hz, 1 H, aryl-C*H*), 7.82–7.78 (m, 1 H, aryl-C*H*), 7.58–7.53 (m, 3 H, aryl-C*H*), 7.50 (d, $^{3}J_{HH}$ = 8.5 Hz, 1 H, aryl-C*H*), 7.28–7.25 (m, 1 H, aryl-C*H*), 6.86–6.83 (m, 1 H, aryl-C*H*), 6.79–6.78 (m, 1 H, aryl-C*H*), 6.68–6.65 (m, 1 H, aryl-C*H*), 6.50–6.47 (m, 1 H, aryl-C*H*), 6.25 (s, 2 H, aryl-C*H*), 6.04–6.01 (m, 1 H, aryl-C*H*), 5.92 (s, 1 H, aryl-C*H*), 3.72 (br s, 1 H, B*H*), 3.02–2.92 (m, 4 H, CH_2), 2.39 (s, 6 H, CH_3), 2.08 (s, 6 H, CH_3), 1.85 (s, 6 H, CH_3) ppm.

^{11}B NMR (128.4 MHz, C_6D_6): δ = 69.8 (br s), –16.0 (s, *B*H) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 150.5 (s, C_q), 141.0 (s, C_q), 137.8 (s, C_q), 136.7 (s, C_q), 135.9 (s, C_q), 134.8 (s, C_q), 134.7 (s, C_q), 133.8 (s, C_q), 133.7 (s, C_q), 132.9 (s, aryl-*C*H), 132.4 (s, C_q), 132.1 (s, C_q), 132.0 (s, aryl-*C*H), 131.2 (s, C_q), 130.0 (s, aryl-*C*H), 129.8 (s, aryl-*C*H), 129.3 (s, aryl-*C*H), 129.1 (s, aryl-*C*H), 127.5 (s, aryl-*C*H), 126.5 (s, aryl-*C*H), 124.9 (s, aryl-*C*H), 124.5 (s, aryl-*C*H), 124.5 (s, aryl-*C*H), 124.4 (s, aryl-*C*H), 124.2 (s, aryl-*C*H), 124.1 (s, aryl-*C*H), 123.8 (s, aryl-*C*H), 49.8 (s, CH_2), 20.8 (s, CH_3), 18.8 (s, CH_3), 18.6 (s, CH_3) ppm.

LIFDI-MS for [$C_{49}H_{44}B_2N_2S$] calcd: 714.3406; found: 714.3393.

Synthesis of **Int_1-Se**



Diborane(5) **1** (50.0 mg, 0.09 mmol) was dissolved in benzene (0.7 mL) and elemental selenium (28.0 mg, 0.36 mmol) was added. Heating at 60 °C for 5 days afforded a yellow solution, which was filtered prior to removal of all volatiles *in vacuo*. The yellow residue was dissolved in a mixture of hexane and toluene (1:1) and stored at –30 °C. The formed solid was separated and dried *in vacuo* to yield **Int_1-Se** (43.8 mg, 0.07 mmol, 77%) as a colorless solid.

^{1}H{^{11}B} NMR (400 MHz, C_6D_6): δ = 6.97 (s, 1 H, aryl-C*H*), 6.78 (s, 1 H, aryl-C*H*), 6.76 (s, 1 H, aryl-C*H*), 6.72 (s, 2 H, aryl-C*H*), 6.65 (s, 2 H, aryl-C*H*), 6.61 (s, 1 H, aryl-C*H*), 3.09–3.00 (m, 4 H, CH_2), 2.61 (br s, 1 H, B*H*), 2.50 (s, 3 H, CH_3), 2.31 (s, 6 H, CH_3), 2.27 (s, 6 H, CH_3), 2.21 (d, $^2J_{HH}$ = 13 Hz, 1 H, CH_2), 2.18 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3), 2.05 (s, 6 H, CH_3), 2.04 (s, 3 H, CH_3), 1.87–1.81 (m, 1 H, CH_2) ppm.

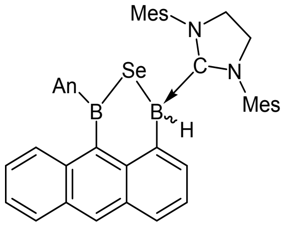
^{11}B NMR (128.4 MHz, C_6D_6): δ = 76.5 (br s), –19.7 (s, *B*H) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 193.6 (br s, C_{Carbene}), 153.7 (s, C_q), 148.8 (br s, C_q), 140.9 (s, C_q), 138.9 (s, C_q), 138.7 (s, C_q), 137.6 (br s, C_q), 137.4 (s, C_q), 135.9 (s, C_q), 135.6 (s, C_q), 135.3 (s, C_q), 135.2 (s, C_q), 134.9 (s, C_q), 129.9 (s, aryl-*C*H), 129.6 (s, aryl-*C*H), 128.7 (s, aryl-*C*H), 128.5 (s, aryl-*C*H), 128.4 (s, aryl-*C*H), 127.4 (s, aryl-*C*H), 50.1 (s, CH_2), 31.0 (br s, CH_2), 24.2 (s, CH_3), 23.5 (s, CH_3), 21.7 (s, CH_3), 21.5 (s, CH_3), 21.3 (s, CH_3), 21.0 (s, CH_3), 19.0 (s, CH_3), 18.5 (s, CH_3) ppm.

^{77}Se{^{1}H} NMR (95.4 MHz, C_6D_6): δ = 178.5 ppm.

LIFDI-MS for [$C_{39}H_{48}B_2N_2Se$ – H+] calcd: 645.3085; found: 645.3081.

Synthesis of **Int_2-Se**



Diborane(5) **2** (30.0 mg, 0.04 mmol) was dissolved in toluene (0.6 mL) and an excess of selenium (20.0 mg, 0.25 mmol) was added. Heating at 100 °C for three days afforded an orange solution. After removal of all volatiles *in vacuo* the residue was extracted with hexane. Upon storage of this solution at –30 °C a yellow solid formed, which was isolated and dried *in vacuo* to yield **Int_2-Se** (19.3 mg, 0.03 mmol, 58%) as a yellow solid.

^{1}H{^{11}B} NMR (400 MHz, C_6D_6): δ = 9.64 (d, $^3J_{HH}$ = 8.6 Hz, 1 H, aryl-C*H*), 8.47 (d, $^3J_{HH}$ = 8.8 Hz, 1 H, aryl-C*H*), 8.13 (s, 1 H, aryl-C*H*), 8.07 (s, 1 H, aryl-C*H*), 8.02 (d, $^3J_{HH}$ = 8.8 Hz, 1 H, aryl-C*H*), 7.92 (d, $^3J_{HH}$ = 5.7 Hz, 1 H, aryl-C*H*), 7.82 – 7.79 (m, 1 H, aryl-C*H*), 7.59 – 7.51 (m, 3 H, aryl-C*H*), 7.46 (d, $^3J_{HH}$ = 8.6 Hz, 1 H, aryl-C*H*), 7.27 – 7.23 (m, 1 H, aryl-C*H*), 6.85 – 6.79 (m, 1 H, aryl-C*H*), 6.67 – 6.62 (m, 2 H, aryl-C*H*), 6.52 – 6.48 (m, 1 H, aryl-C*H*), 6.29 (s, 2 H, aryl^{Mes}-C*H*), 6.07 – 6.03 (m, 1 H, aryl-C*H*), 5.92 (s, 2 H, aryl^{Mes}-C*H*), 3.85 (br s, 1 H, B*H*), 3.05 – 2.91 (m, 4 H, CH_2CH_2), 2.43 (s, 6 H, CH_3), 2.09 (s, 6 H, CH_3), 1.85 (s, 6 H, CH_3) ppm.

^{11}B NMR (128.4 MHz, C_6D_6): δ = 76.4 (br s), –18.6 (s, *B*H) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 141.5 (br s, C_q), 141.3 (s, C_q), 137.8 (s, C_q), 137.5 (s, aryl-*C*H), 136.7 (s, C_q), 134.8 (s, C_q), 134.7 (s, C_q), 133.9 (s, C_q), 133.5 (s, aryl-*C*H), 133.4 (s, C_q), 132.5 (s, C_q), 132.4 (s, C_q), 132.0 (s, aryl-*C*H), 131.9 (s, C_q), 131.2 (s, C_q), 130.6 (s, C_q), 130.2 (s, aryl-*C*H), 129.9 (s, aryl-*C*H), 129.4 (s, aryl^{Mes}-*C*H), 129.2 (s, aryl^{Mes}-*C*H), 128.9 (s, aryl-*C*H), 128.6 (s, aryl-*C*H), 126.5 (s, aryl-*C*H), 124.9 (s, aryl-*C*H), 124.5 (s, aryl-*C*H), 124.4 (s, aryl-*C*H), 124.2 (s, aryl-*C*H), 124.2 (s, aryl-*C*H), 124.0 (s, aryl-*C*H), 123.6 (s, aryl-*C*H), 49.8 (s, CH_2), 20.8 (s, CH_3), 18.8 (s, CH_3), 18.8 (s, CH_3) ppm.

Note: The ^{77}Se NMR resonance could not be detected presumably due to the strong coupling to the two quadrupolar boron nuclei.

LIFDI-MS for [$C_{49}H_{44}B_2N_2Se$] calcd: 762.2850; found: 762.2833.

NMR spectra of isolated compounds

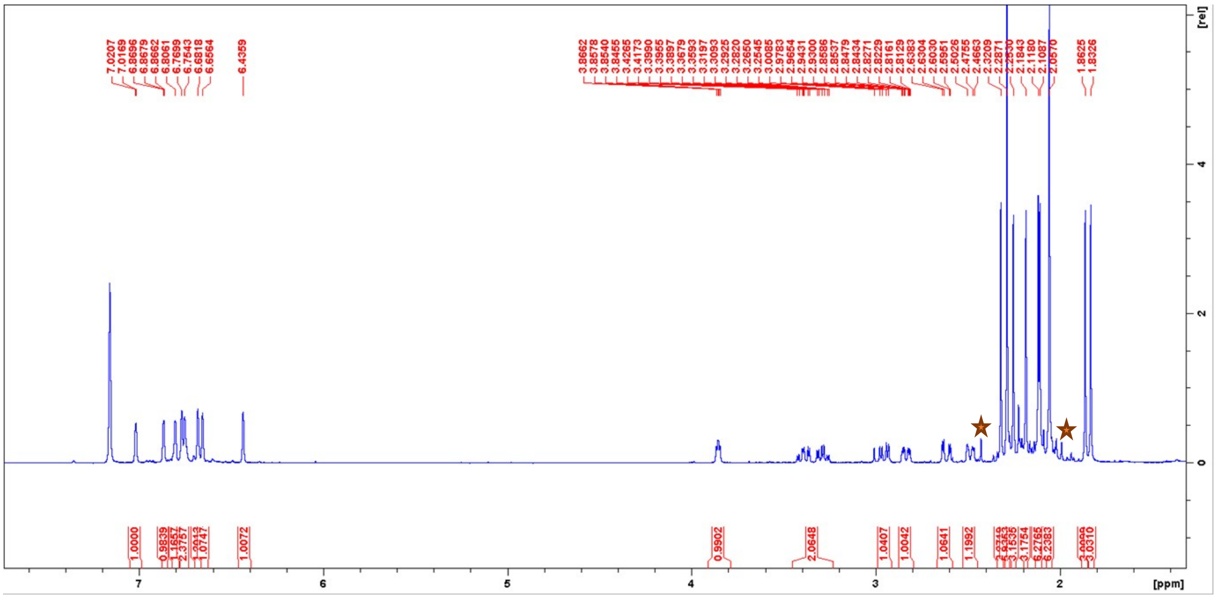


Figure S1. ^{1}H NMR spectrum of **1-O** in C_6D_6. The resonances marked with ★ belong to unknown impurities.

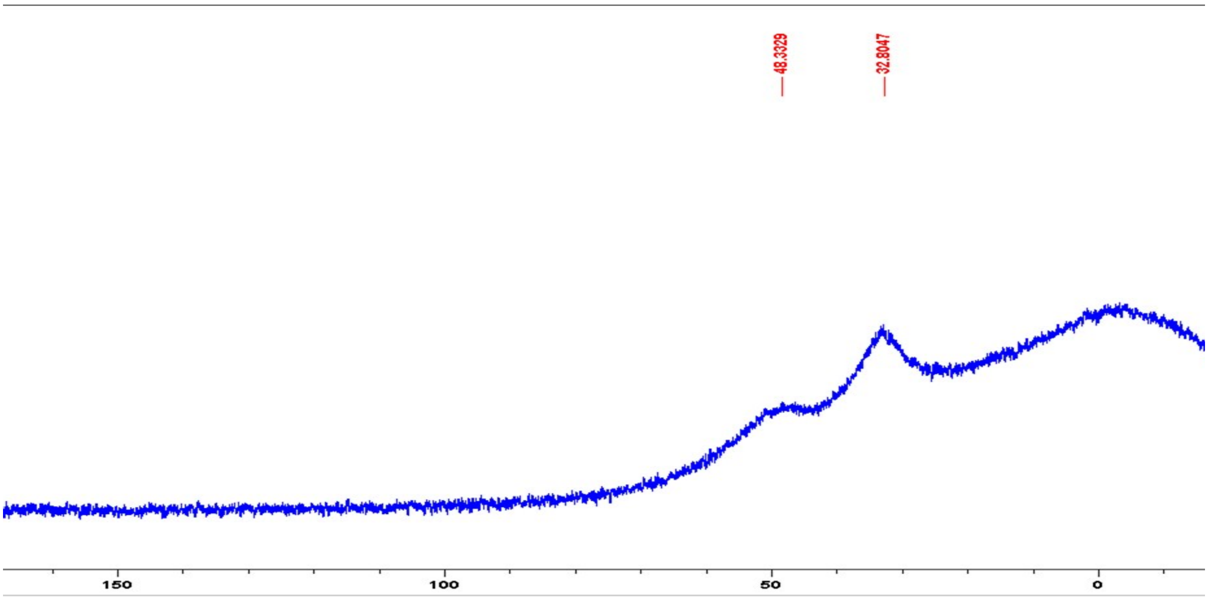


Figure S2. ^{11}B NMR spectrum of **1-O** in C_6D_6.

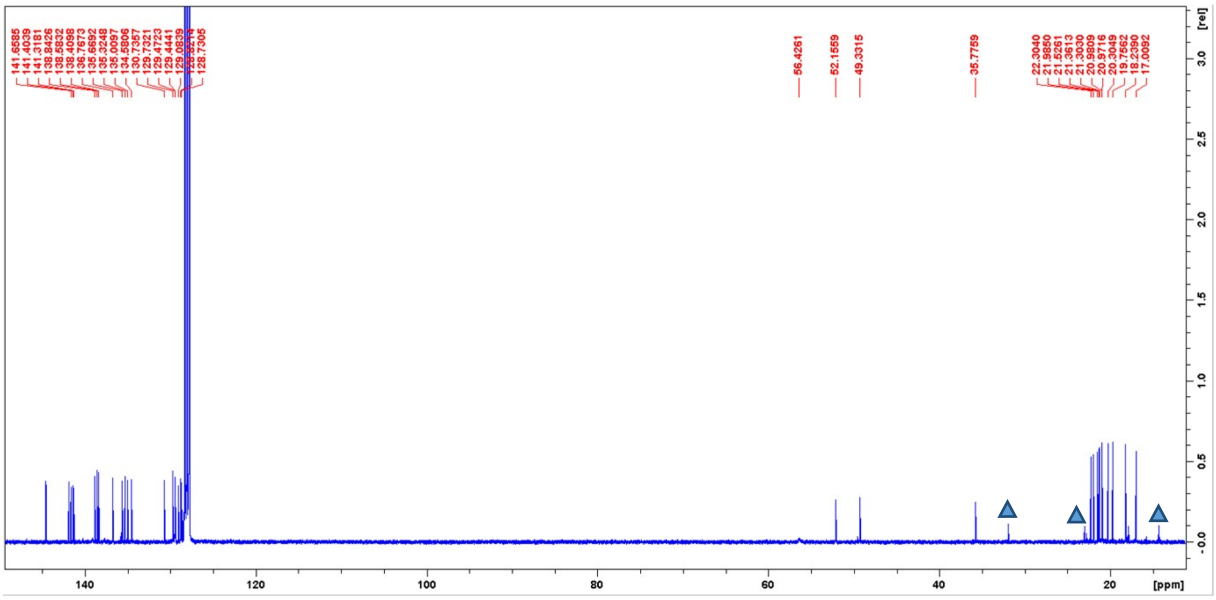


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **1-O** in C_6D_6. The resonances marked with ▲ belong to residual hexane.

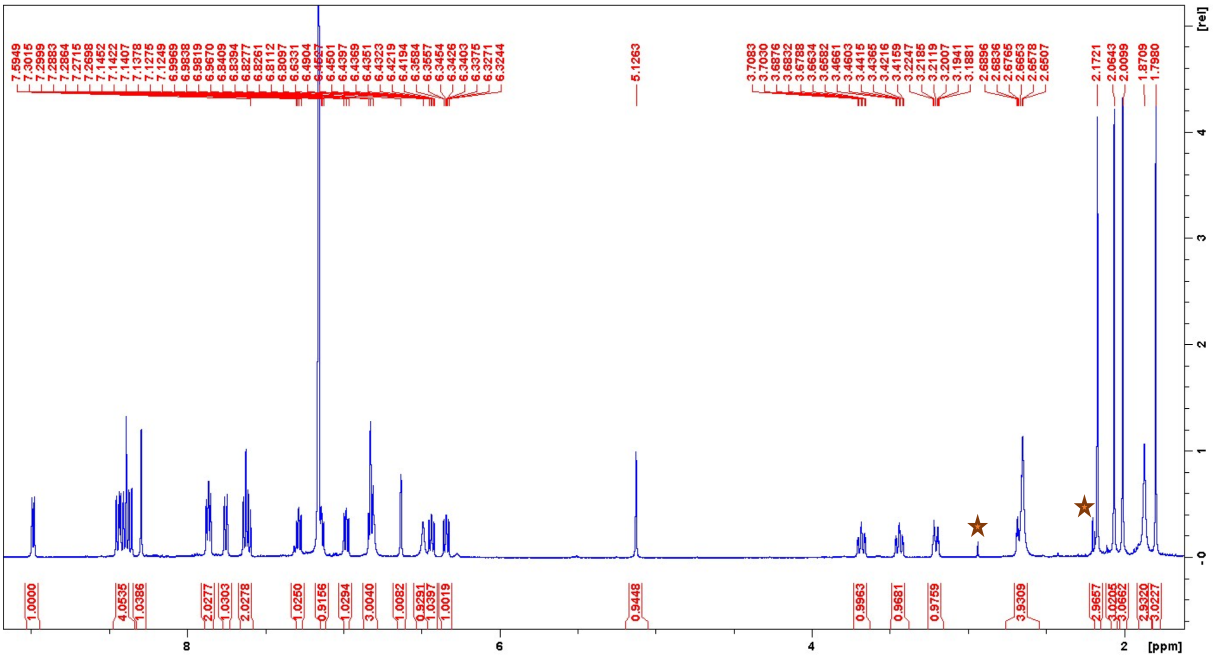


Figure S4. ^{1}H NMR spectrum of **2-O** in C_6D_6. The resonances marked with ★ belong to unknown impurities.

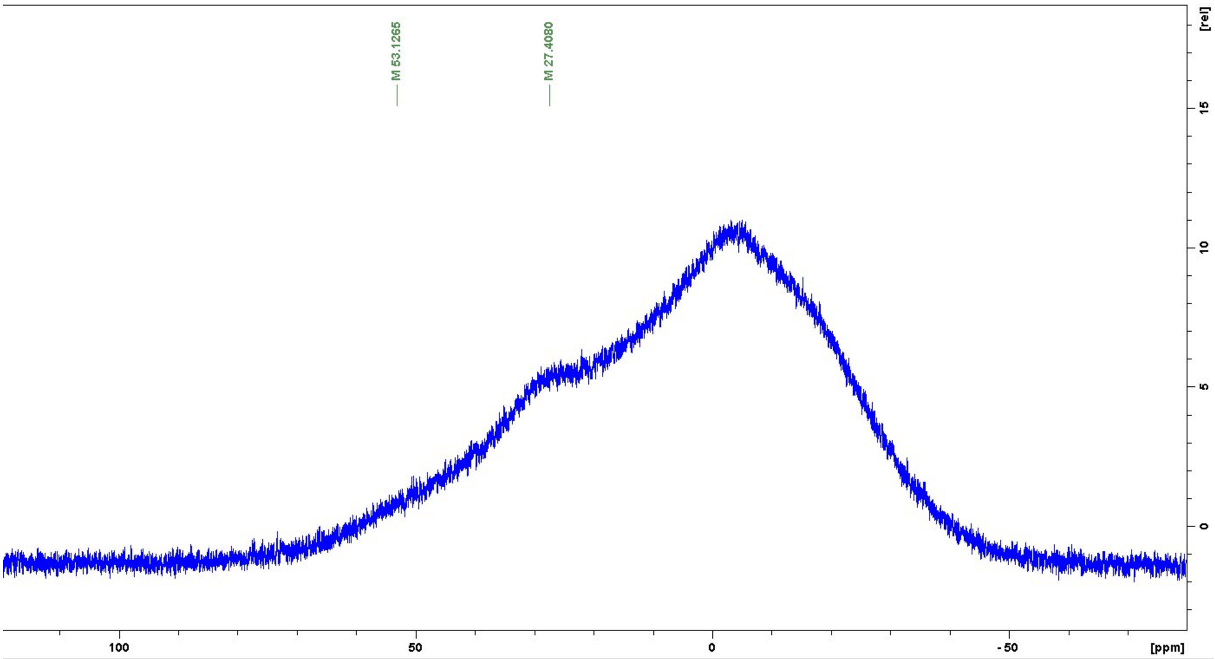


Figure S5. ^{11}B NMR spectrum of **2-O** in C_6D_6.

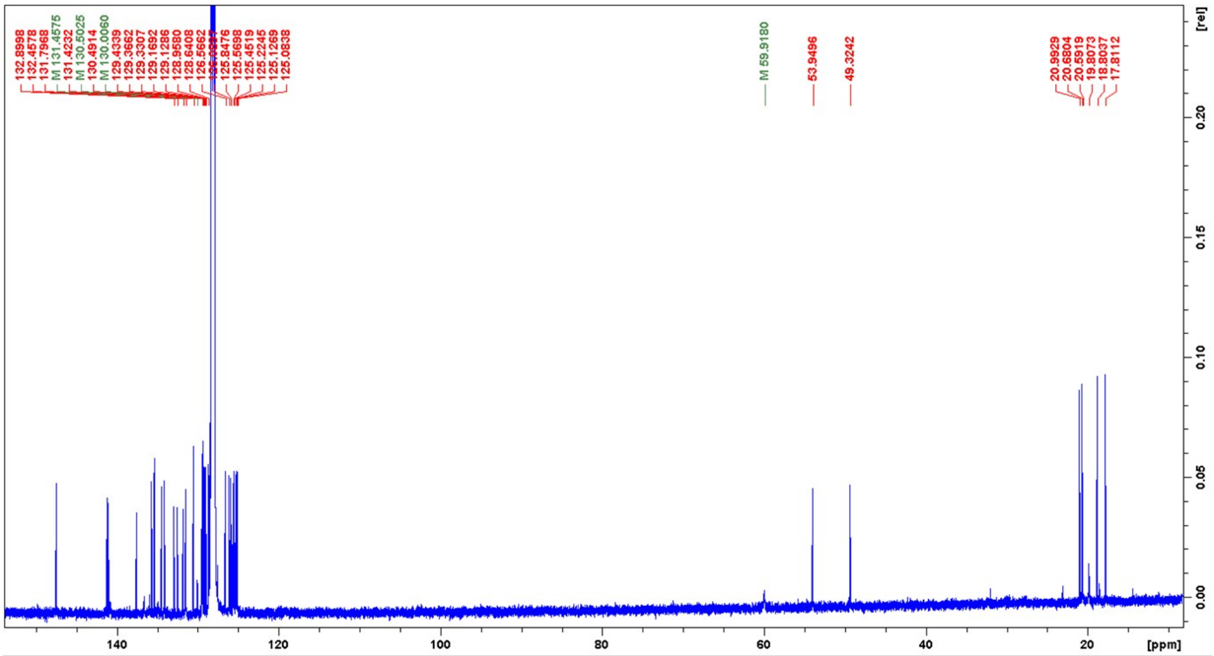


Figure S6. $^{13}C\{^1H\}$ NMR spectrum of **2-O** in C_6D_6.

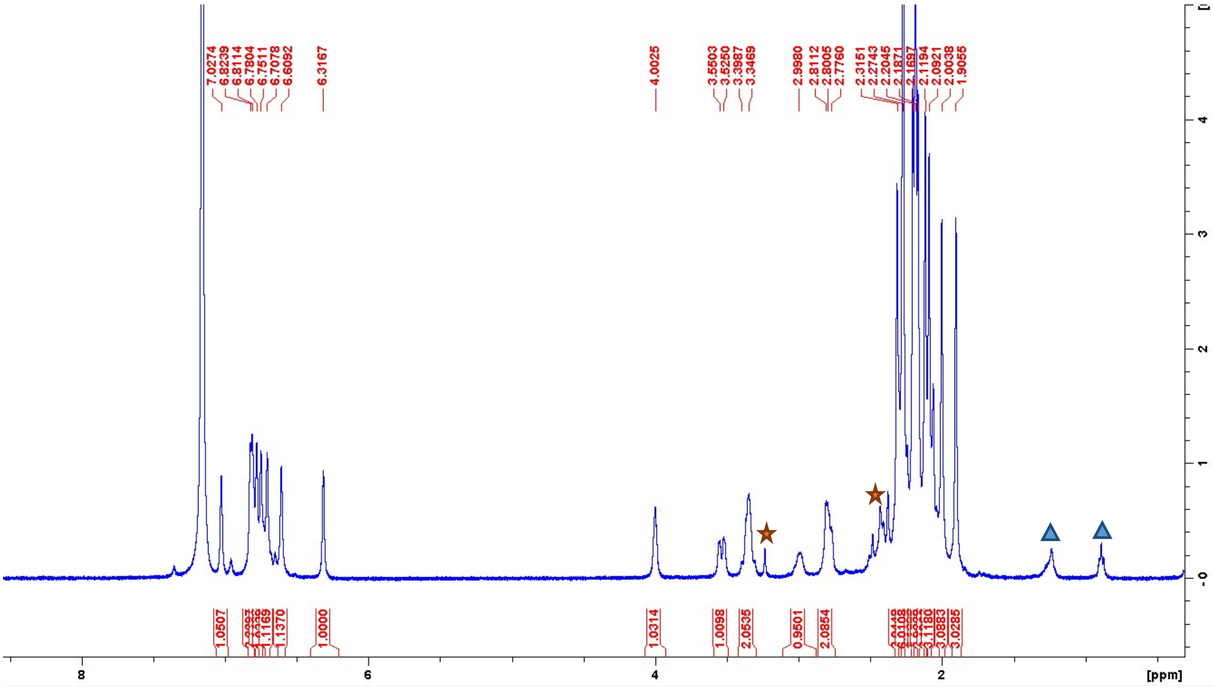


Figure S7. ^{1}H NMR spectrum of **1-S** in C_6D_6. The resonances marked with ★ belong to unknown impurities. The resonances marked with ▲ belong to residual hexane.

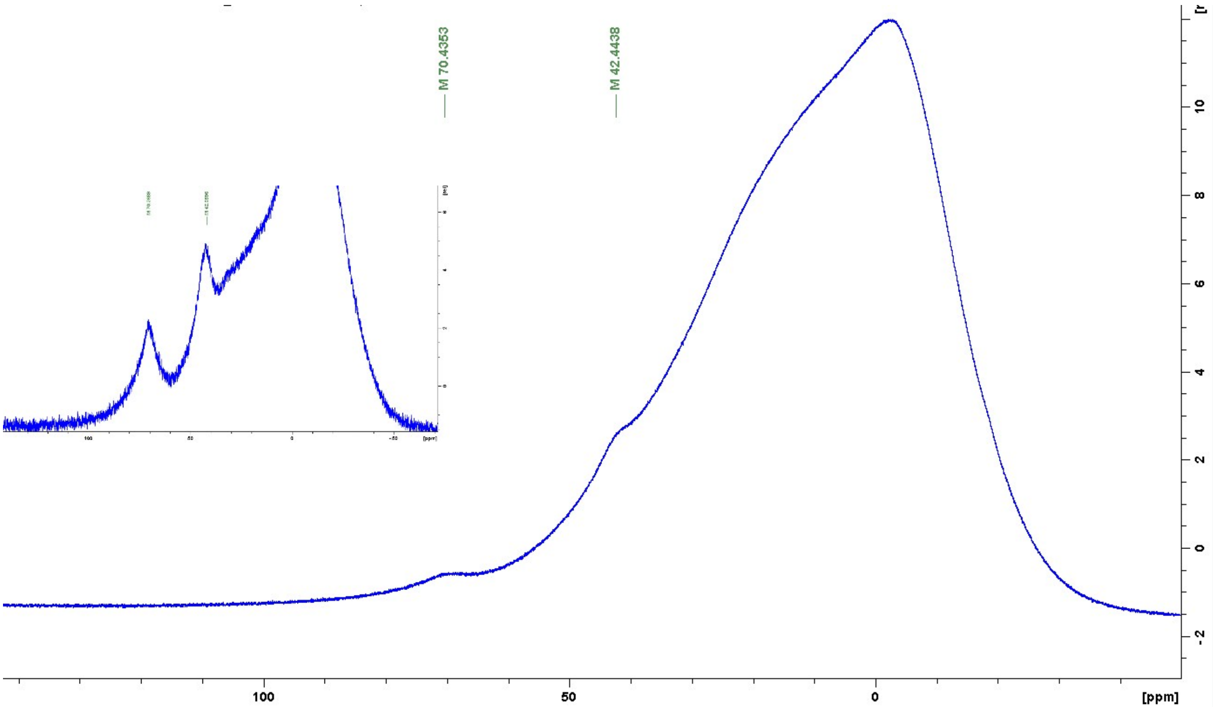


Figure S8. ^{11}B NMR spectrum of **1-S** in C_6D_6 including an excerpt of the two broad boron resonances for a better illustration.

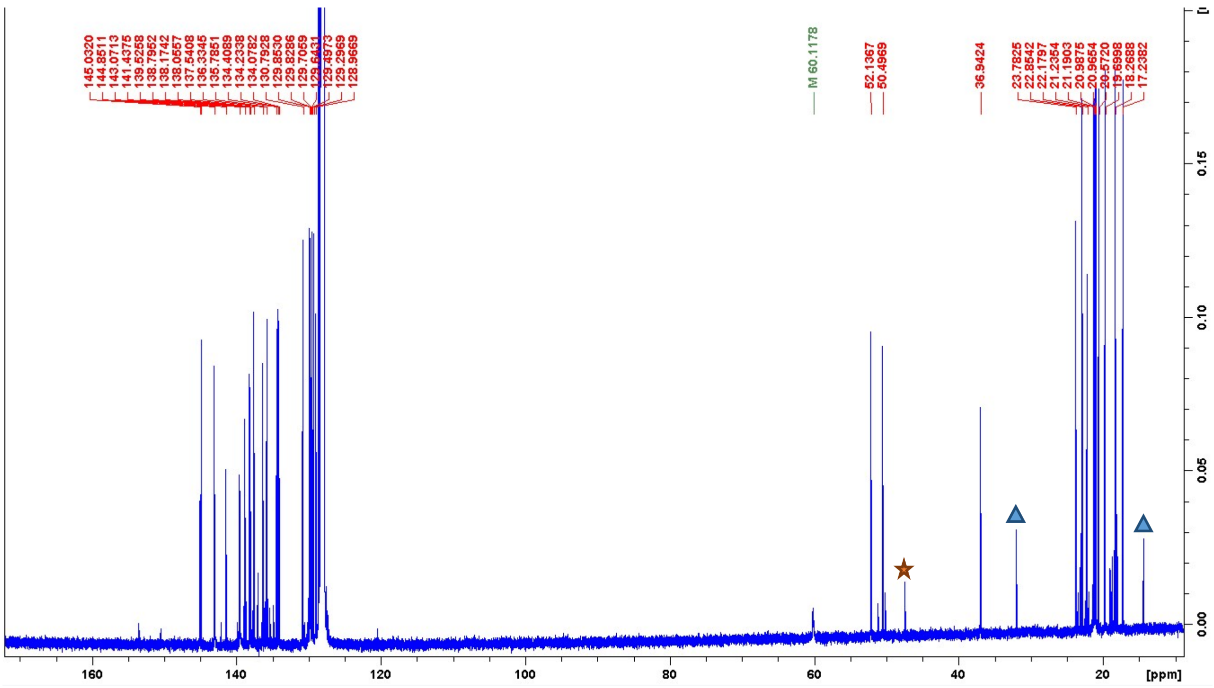


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **1-S** in C_6D_6. The resonance marked with ★ belongs to unknown impurities. The resonances marked with ▲ belong to residual hexane.

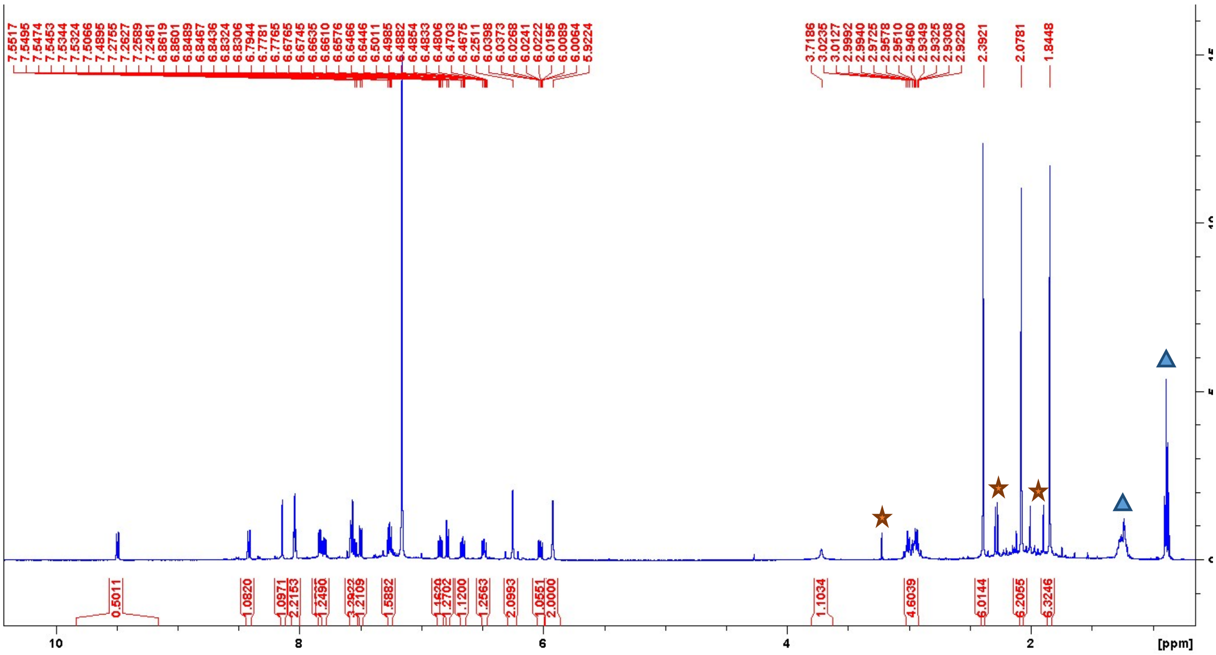


Figure S10. $^{1}H\{^{11}B\}$ NMR spectrum of **Int_2-S** in C_6D_6. The resonances marked with ★ belong to unknown impurities. The resonances marked with ▲ belong to residual hexane.

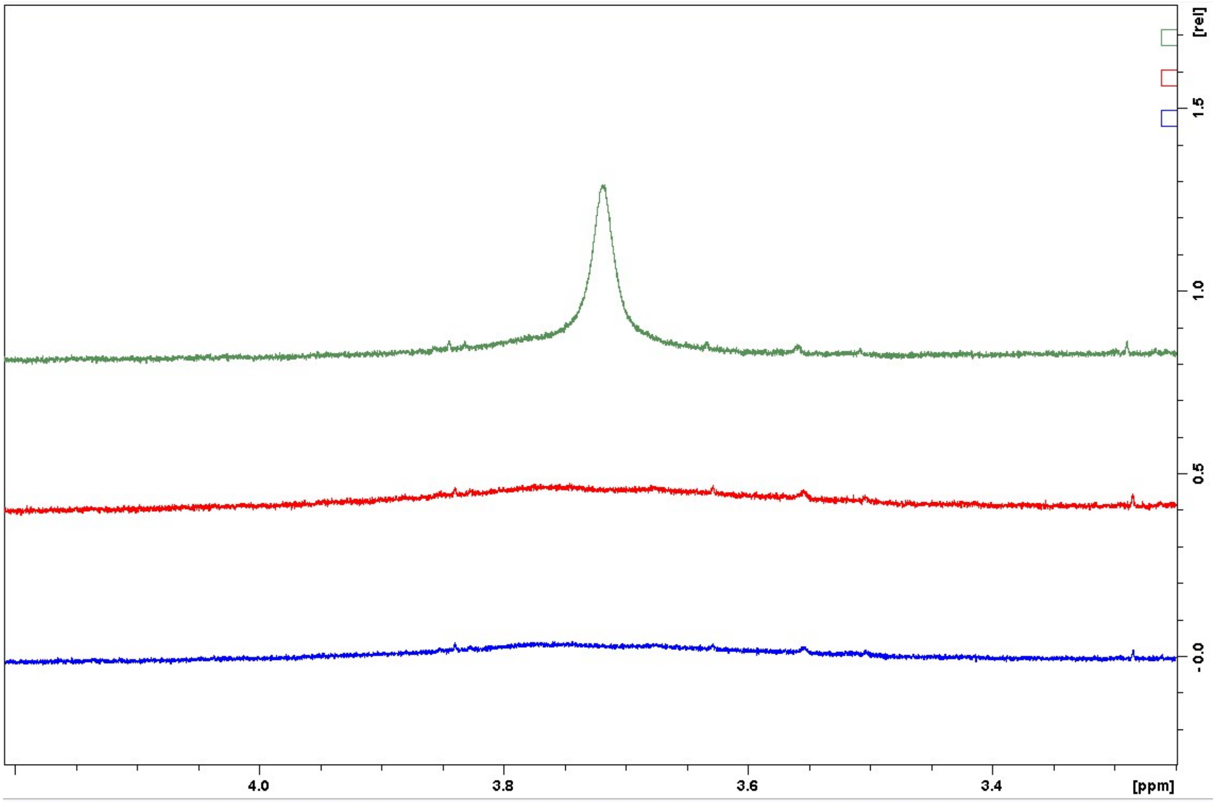


Figure S11. Width changes of the B-H resonance (δ = 3.72 ppm) in the ^{1}H NMR spectrum of **Int_2-S** in C_6D_6 at RT. Bottom (blue): non-decoupled ^{1}H NMR spectrum; middle (red): decoupler offset of 71.0 ppm; top (green): decoupler offset of −16.0 ppm.

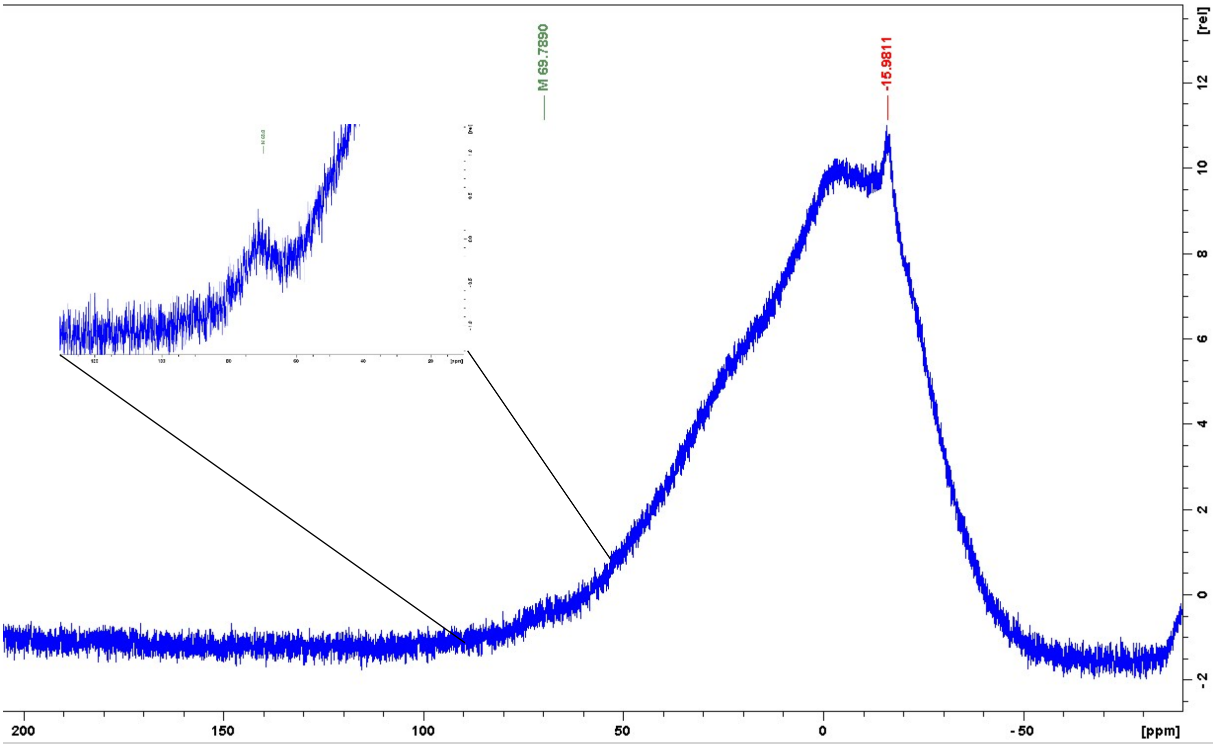


Figure S12. ^{11}B NMR spectrum of **Int_2-S** in C_6D_6 including an excerpt of the broad boron resonance at 67.8 ppm.

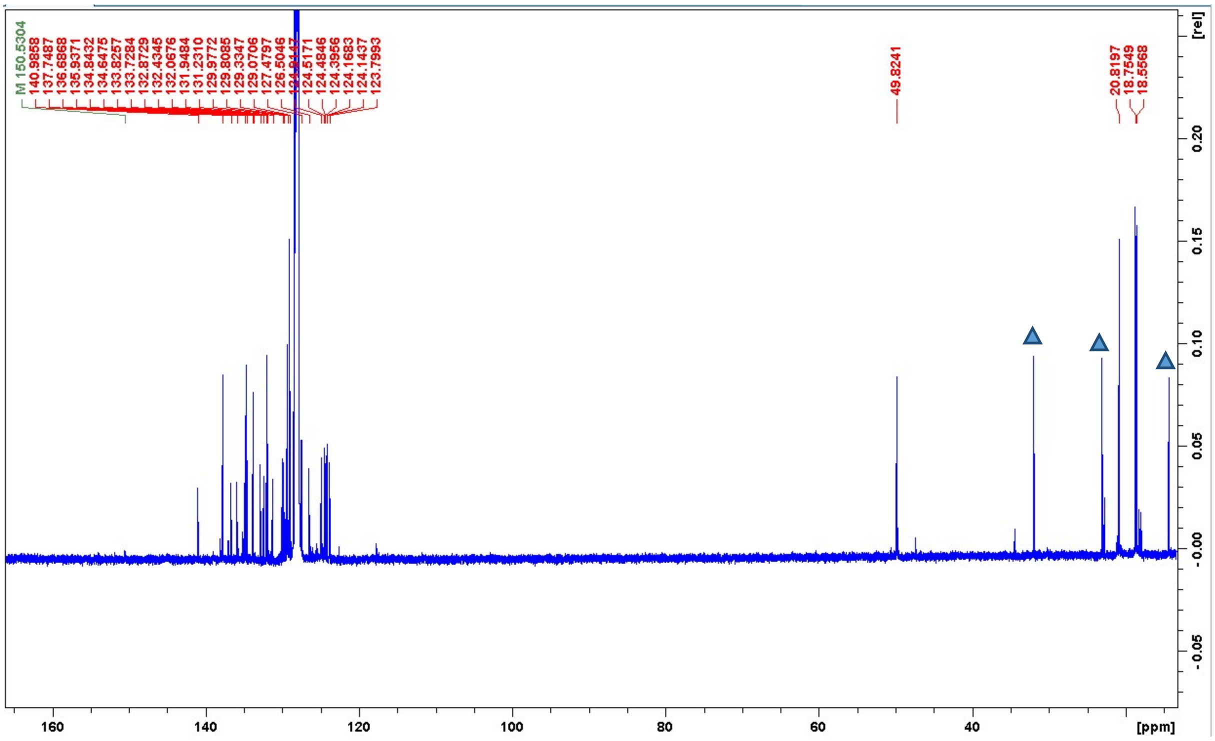


Figure S13. ^{13}C{^{1}H} NMR spectrum of **Int_2-S** in C_6D_6. The resonances marked with ▲ belong to residual hexane.

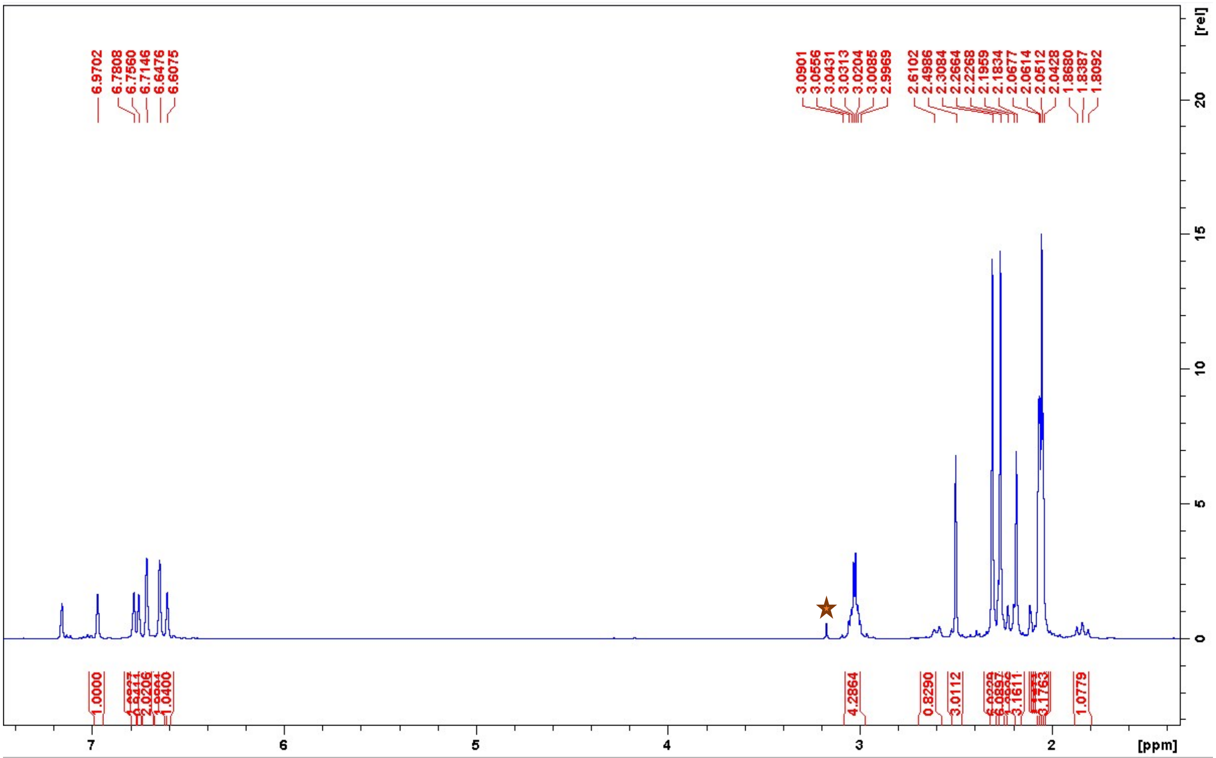


Figure S14. $^{1}H\{^{11}B\}$ NMR spectrum of **Int_1-Se** in C_6D_6. The resonance marked with ★ belongs to unknown impurities.

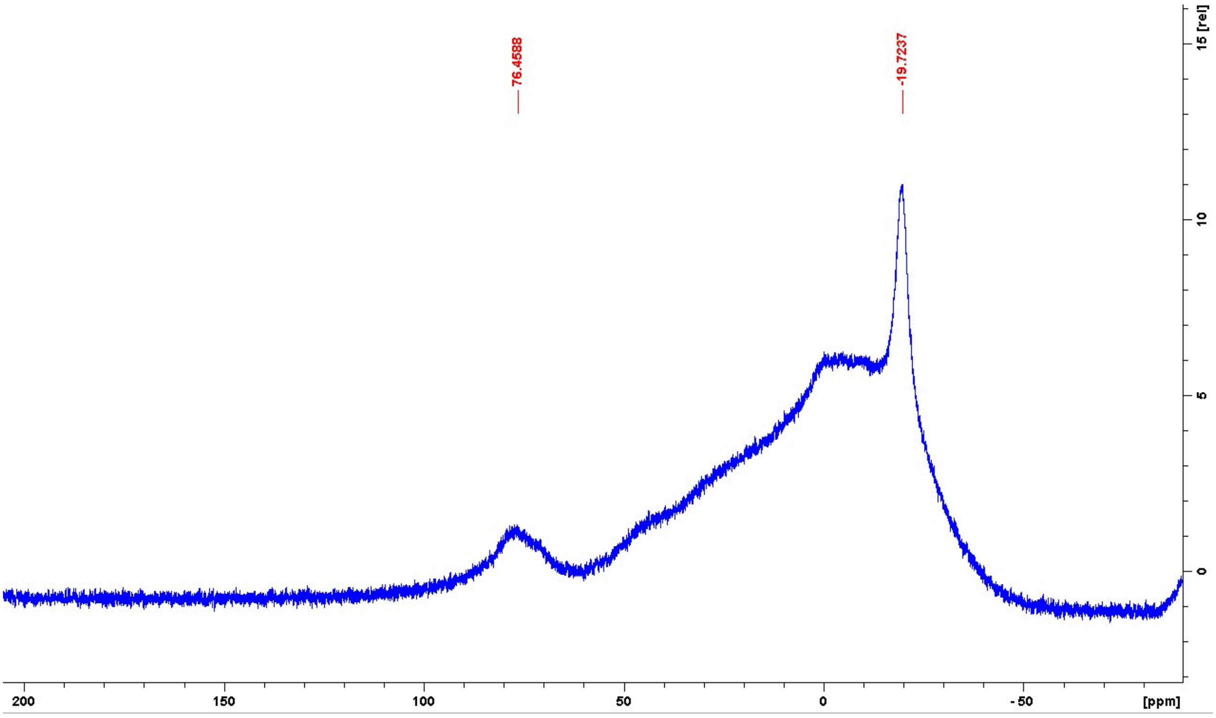


Figure S15. ^{11}B NMR spectrum of **Int_1-Se** in C_6D_6.

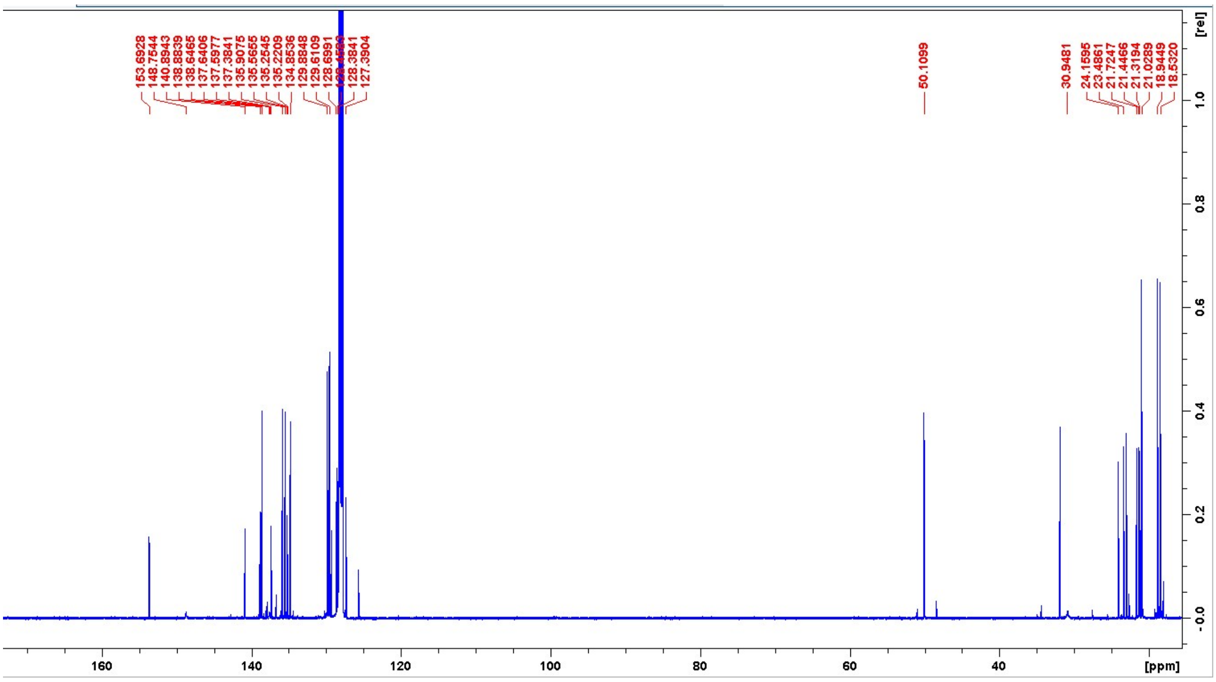


Figure S16. $^{13}C\{^1H\}$ NMR spectrum of **Int_1-Se** in C_6D_6.

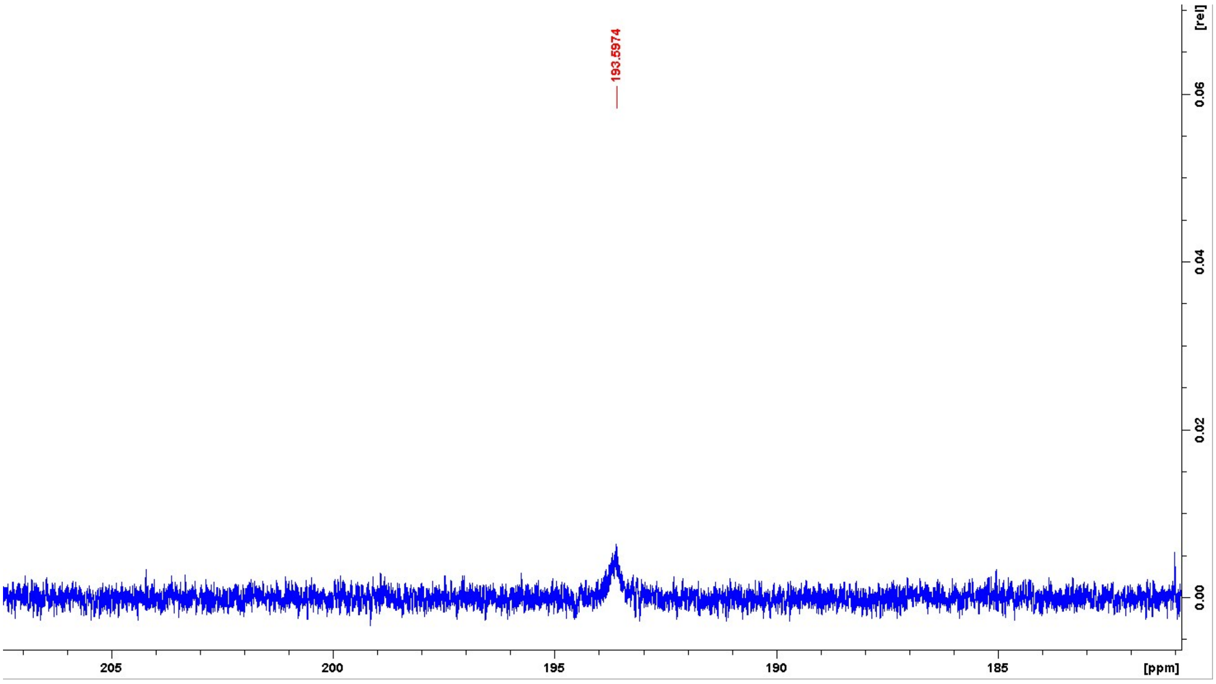


Figure S17. $^{13}C\{^1H\}$ NMR spectrum of **Int_1-Se** in C_6D_6 (low field excerpt for illustration of the resonance of the carbene carbon atom).

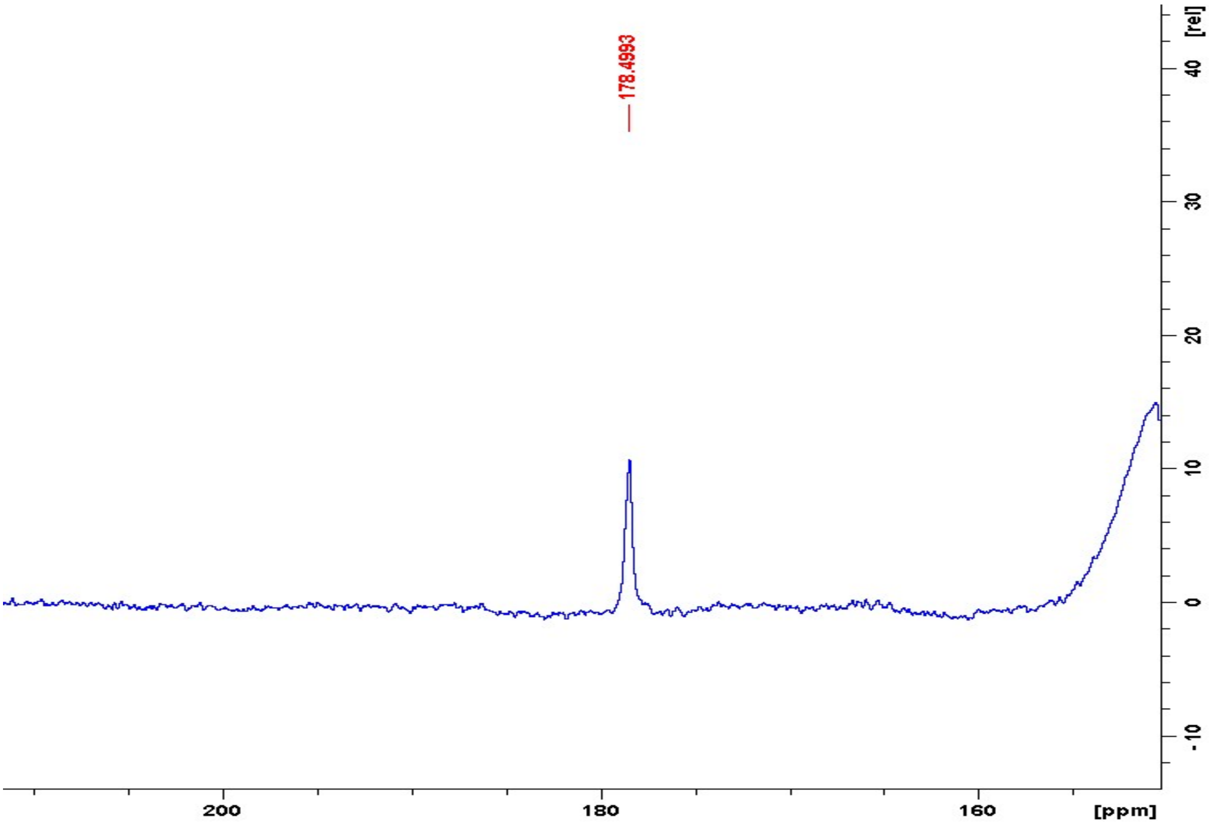


Figure S18. ^{77}Se{^{1}H} NMR spectrum of **Int_1-Se** in C_6D_6.

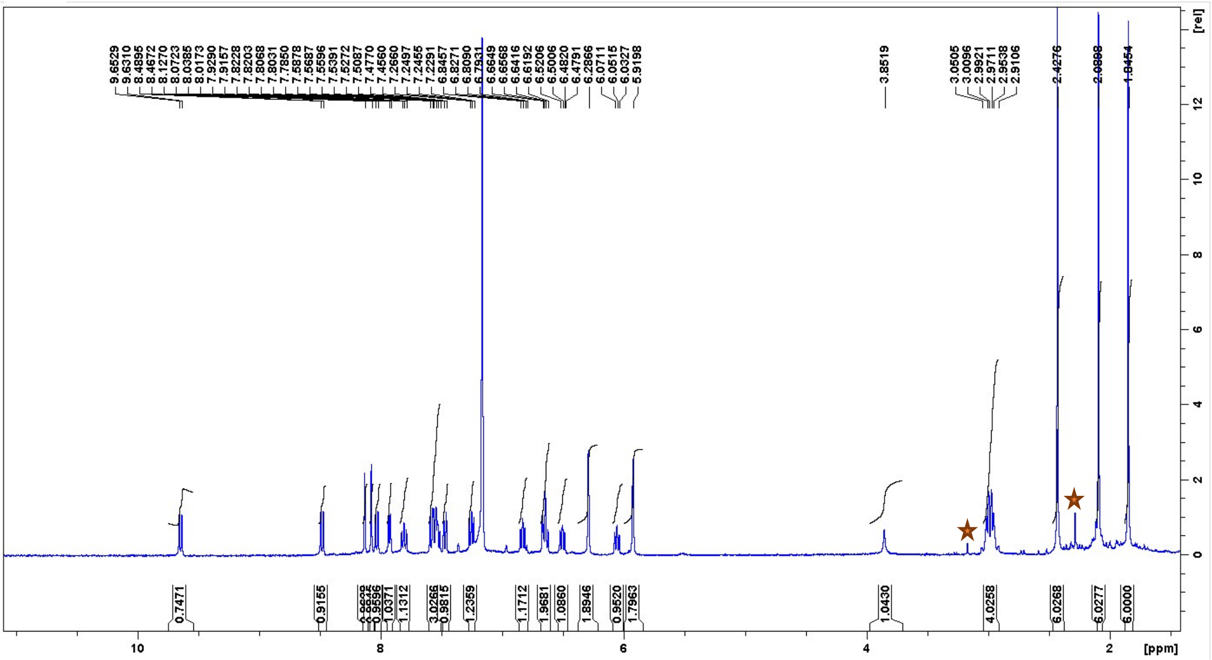


Figure S19. ^{1}H{^{11}B} NMR spectrum of **Int_2-Se** in C_6D_6. The resonances marked with ★ belong to unknown impurities.

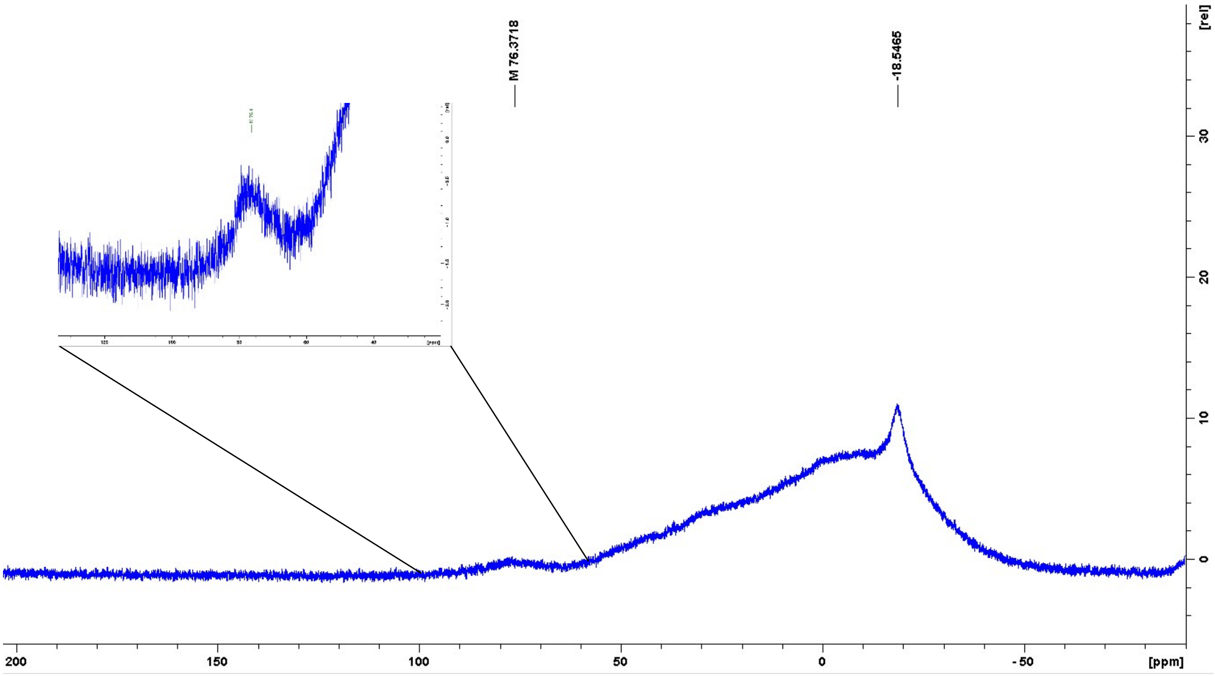


Figure S20. ^{11}B NMR spectrum of **Int_2-Se** in C_6D_6 including an excerpt of the broad boron resonance at 76.4 ppm.

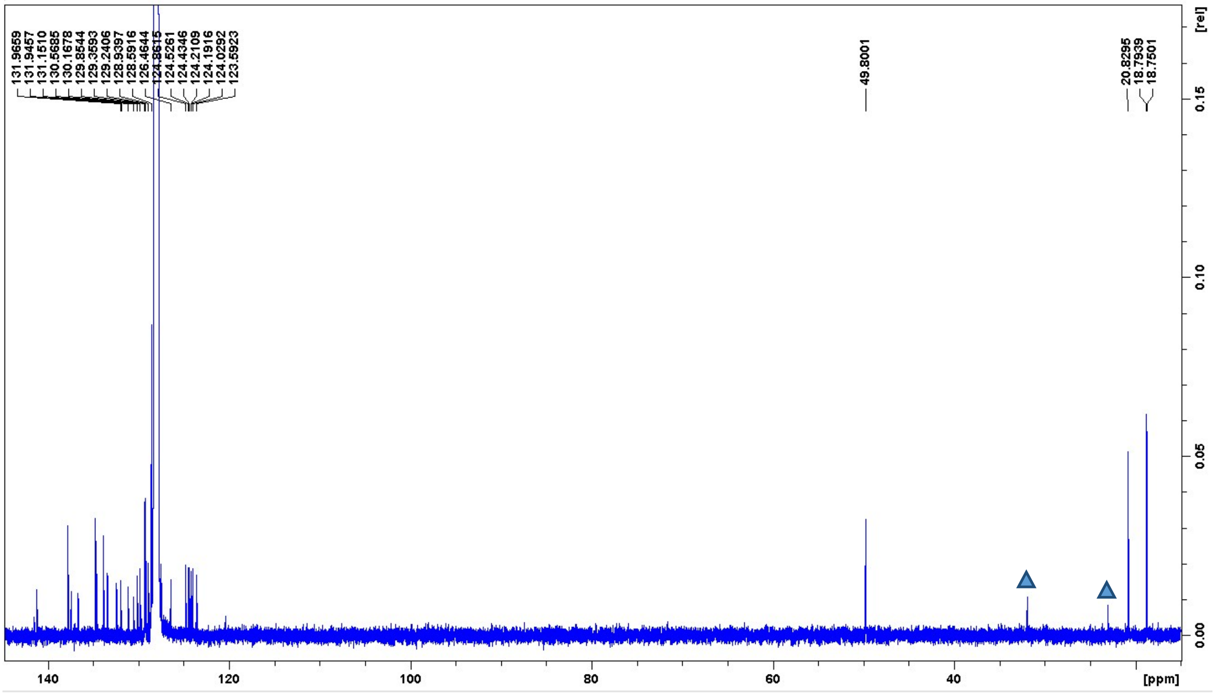


Figure S21. $^{13}C\{^1H\}$ NMR spectrum of **Int_2-Se** in C_6D_6. The resonances marked with ▲ belong to residual hexane.

HRMS spectra of isolated compounds

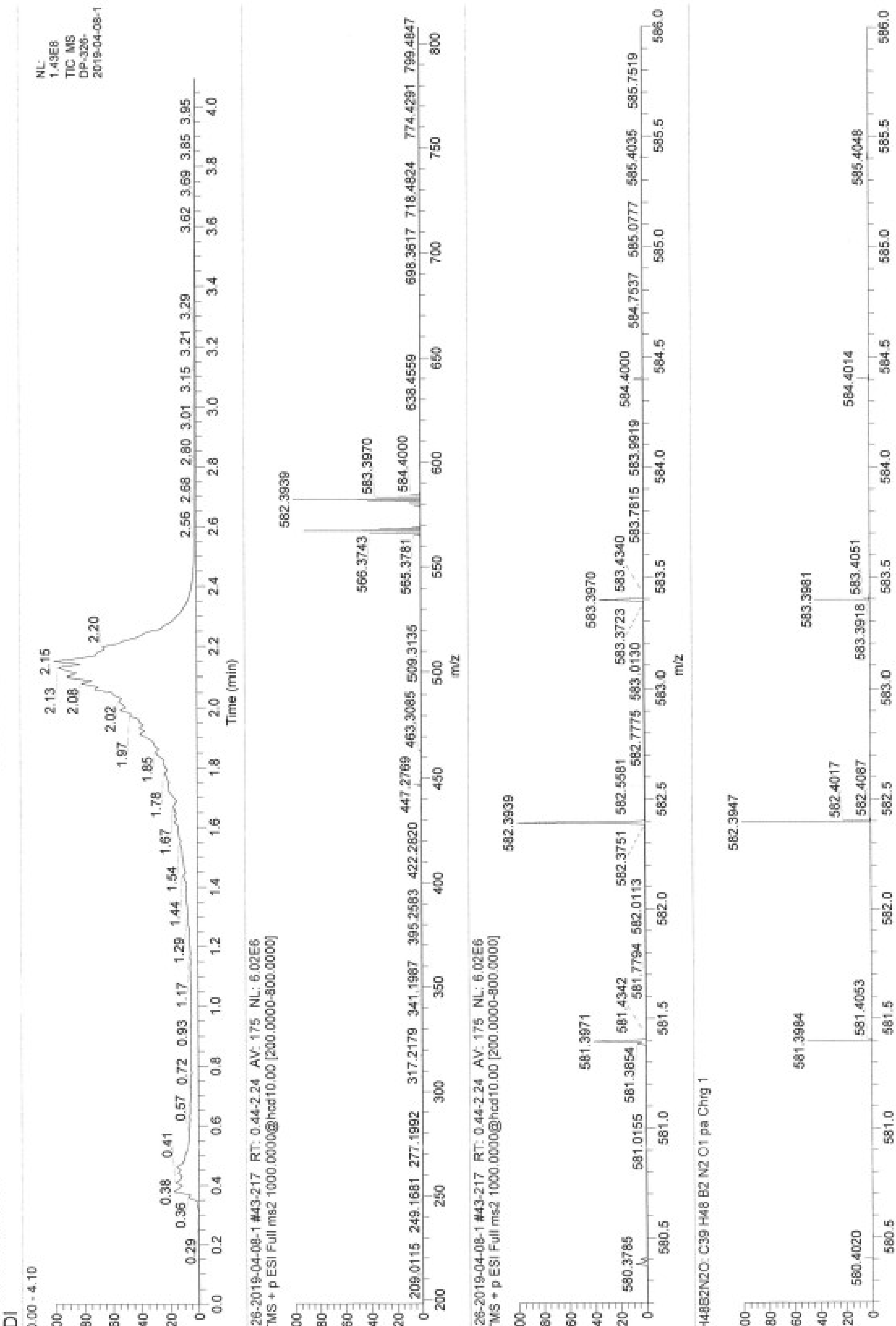


Figure S22. HRMS spectrum of **1-O**.

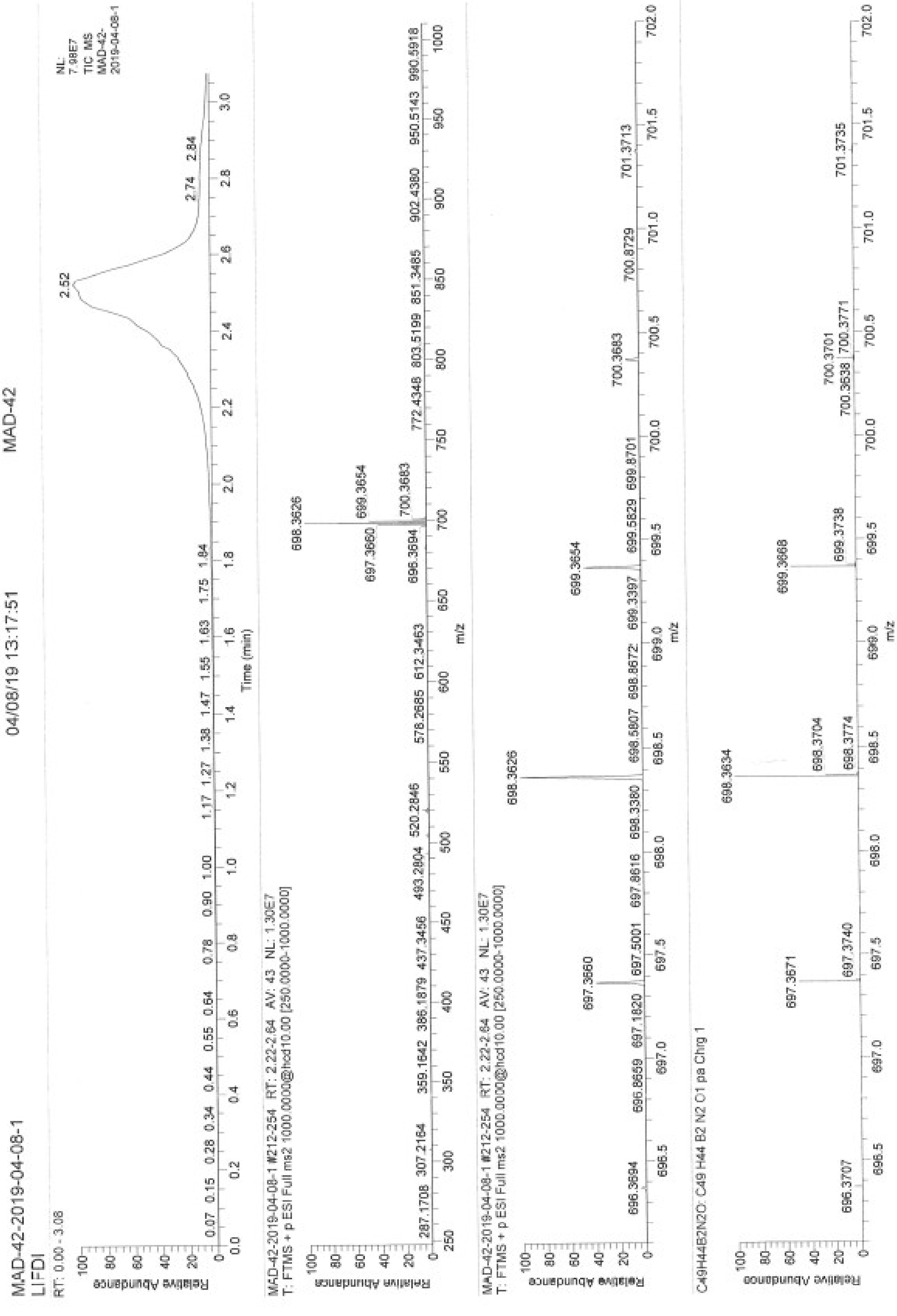


Figure S23. HRMS spectrum of **2-O**.

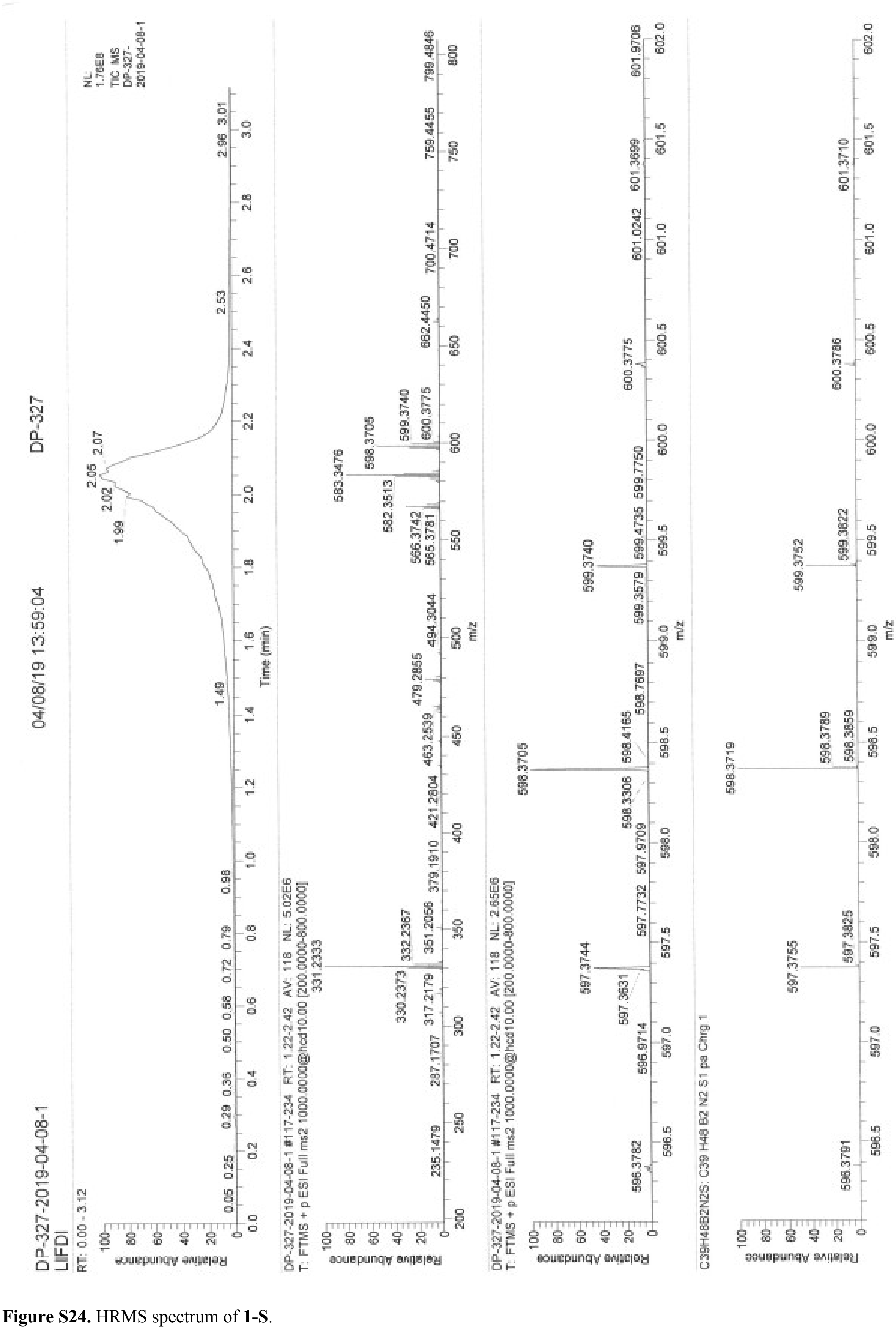


Figure S24. HRMS spectrum of **1-S**.

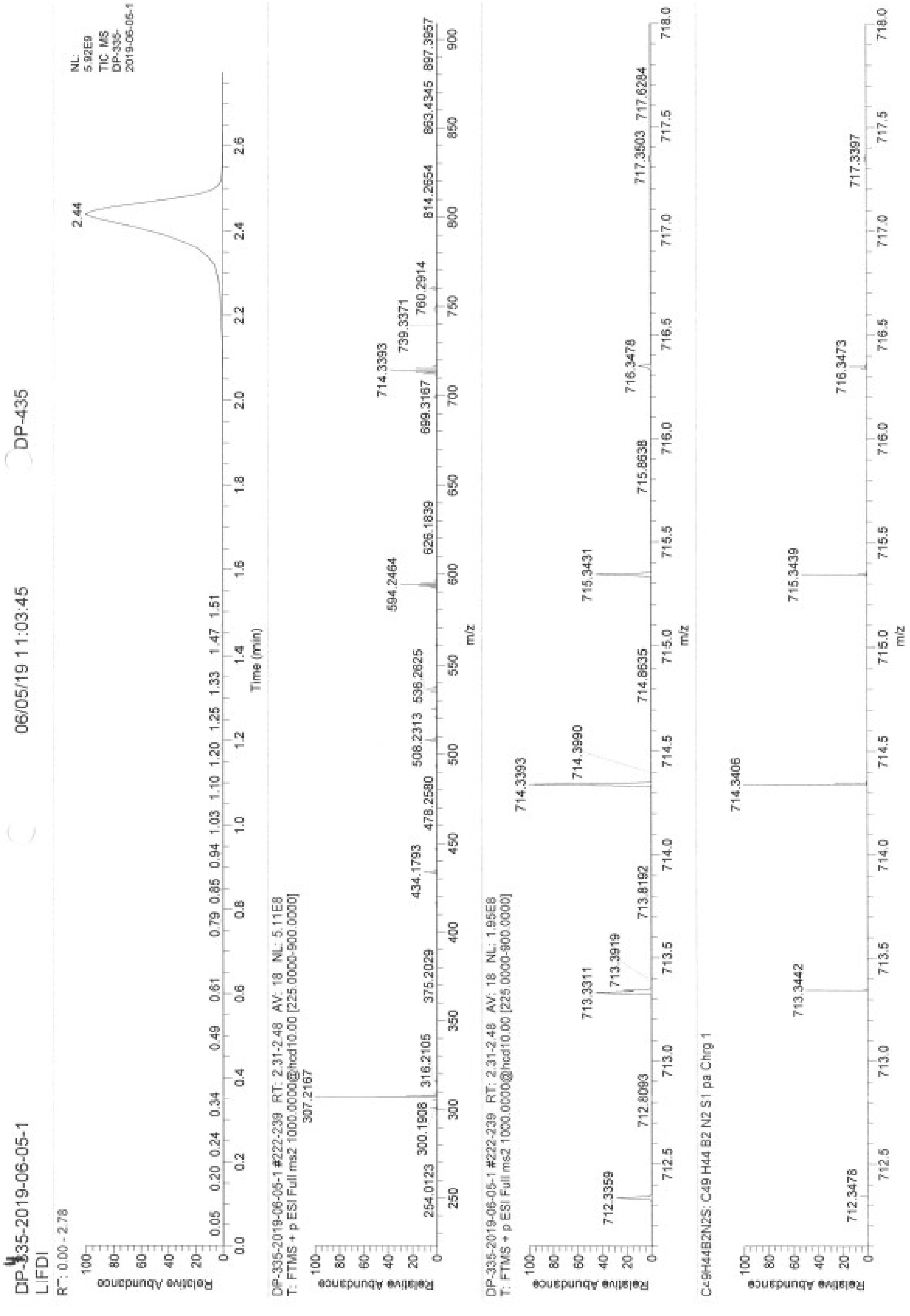


Figure S25. HRMS spectrum of **Int_2-S**.

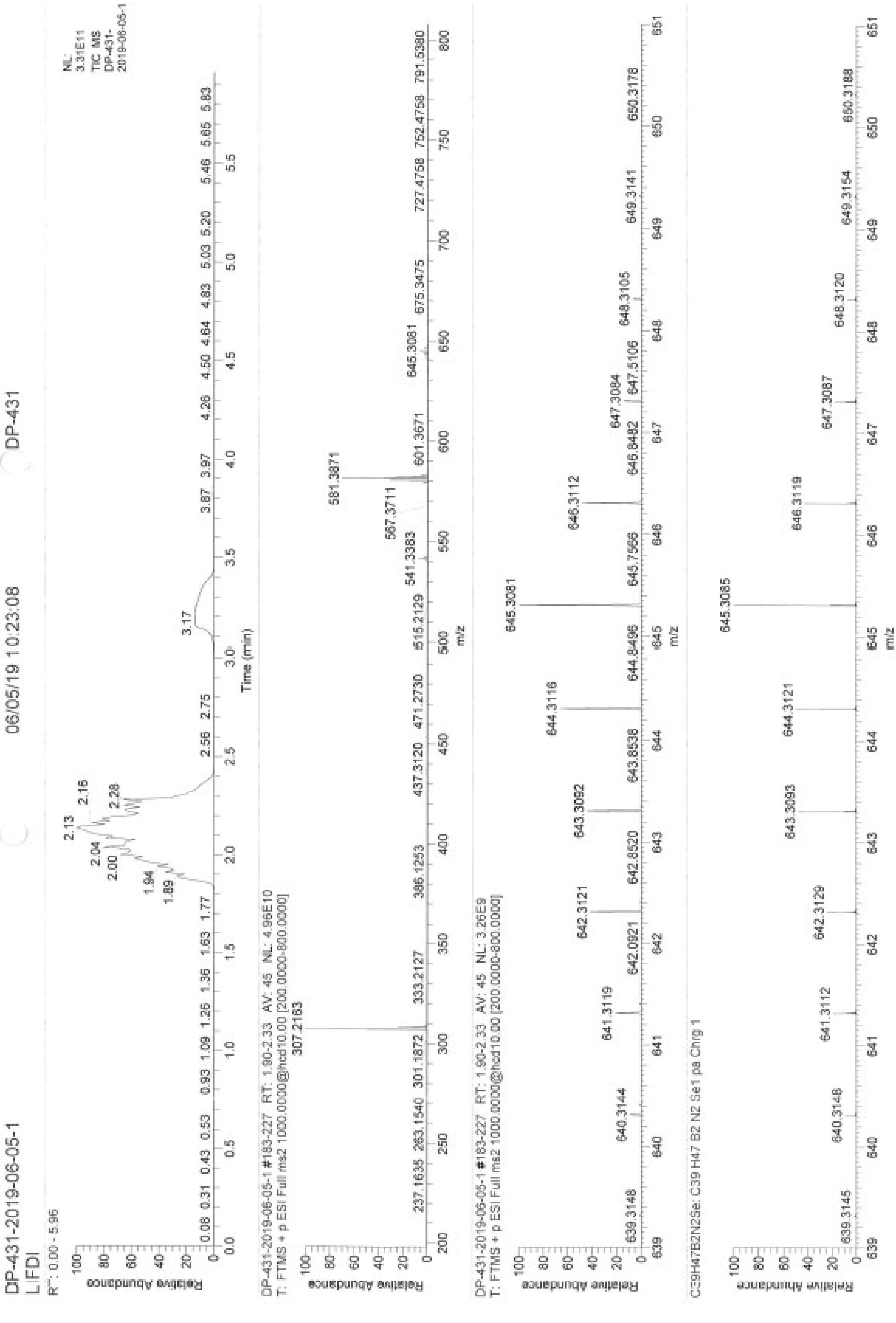


Figure S26. HRMS spectrum of **Int_1-Se**.

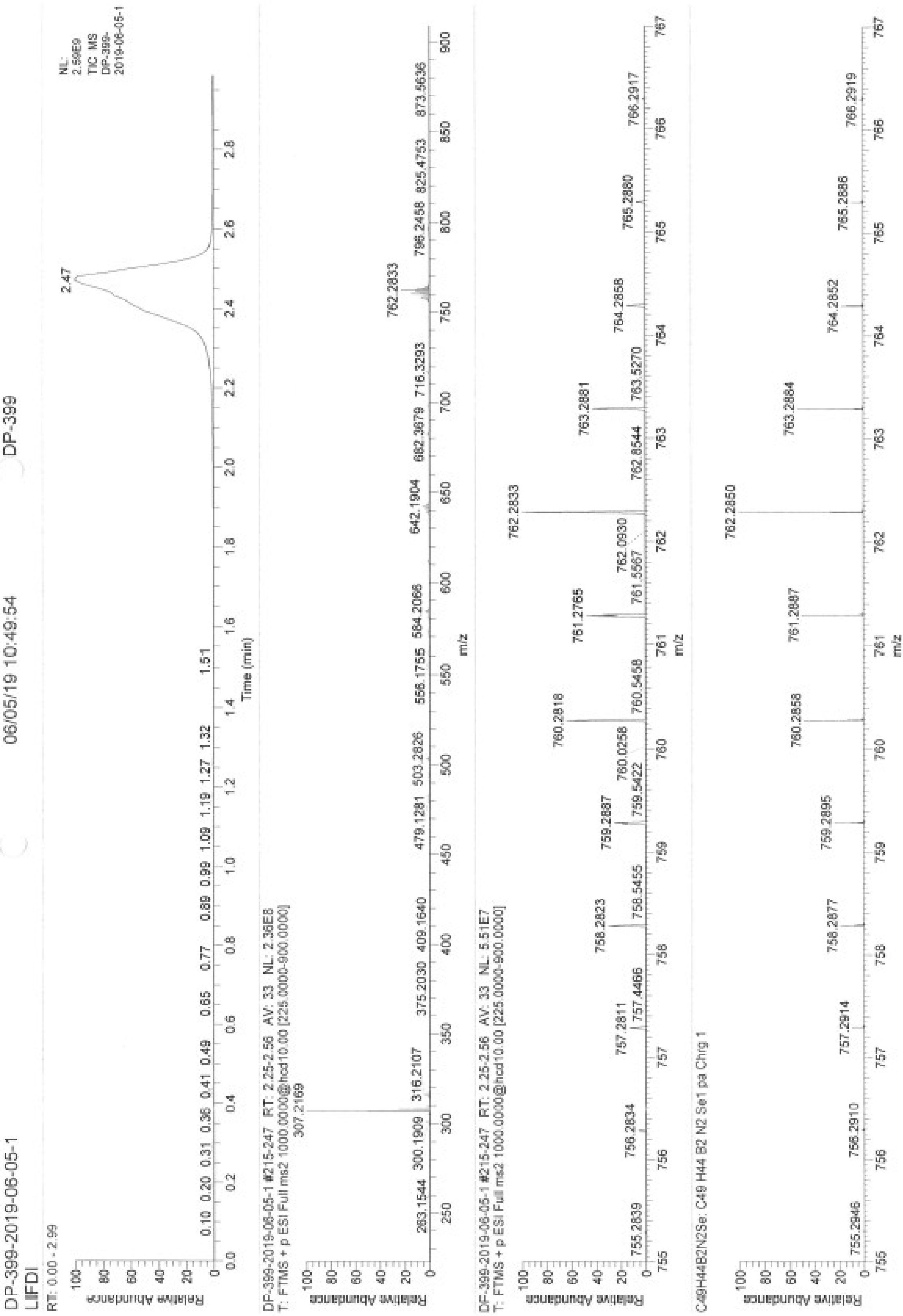


Figure S27. HRMS spectrum of **Int_2-Se**.

Cyclic voltammetry

Cyclic voltammetry experiments were performed using a Gamry Instruments Reference 600 potentiostat. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a *Vycor* tip, serving as the reference electrode. Formal redox potentials are referenced to the ferrocene/ferrocenium (Fc/Fc^+) redox couple. Tetra-*n*-butylammonium hexafluorophosphate ($[n\mathrm{Bu}_4\mathrm{N}][\mathrm{PF}_6]$) was employed as the supporting electrolyte. Compensation for resistive losses (*iR* drop) was employed for all measurements. For all measured cyclic voltammograms, the scan rate was 250 mV/s.

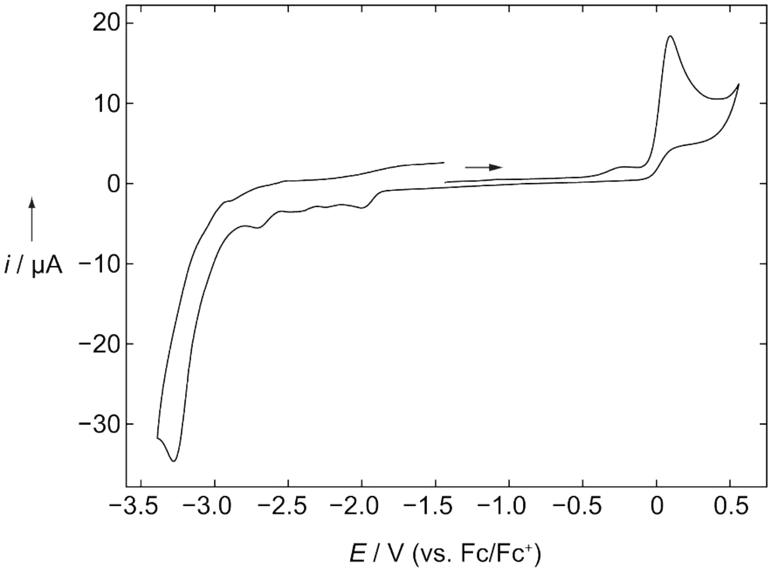


Figure S28. Cyclic voltammogram of **1** in THF. Formal potentials for oxidation: E_{pa} = +0.10 V (irreversible); for reduction: E_{pc} = –3.25 V (irreversible).

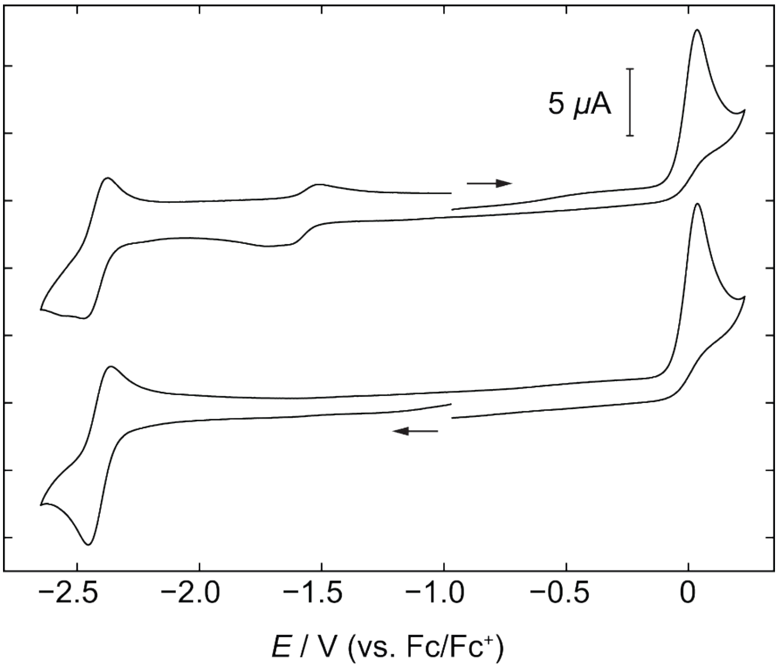


Figure S29. Cyclic voltammograms of **2** with different scan directions in THF. Formal potentials for oxidation: E_{pa} = +0.05 V (irreversible); for reduction: $E_{1/2}$ = –2.41 V (reversible).

X-ray crystallographic details

The crystal data of **1-O** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The crystal data of **1-S** and **Int_1-Se** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structures were solved using intrinsic phasing method,[3] refined with the SHELXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms, expecpt H1, were assigned to idealised geometric positions. All hydrogen atoms were assigned to idealised positions with exception of the boron-bound hydride in **Int_1-Se**, which was located in the difference Fourier map and refined freely.

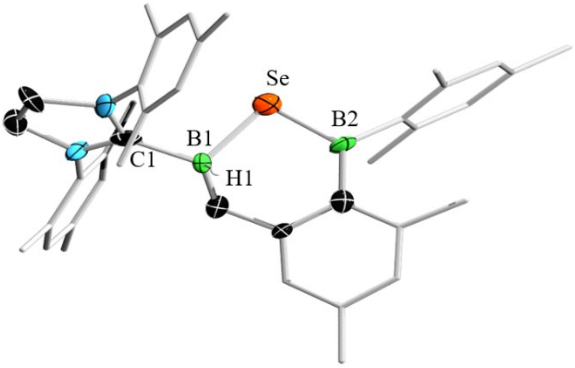


Figure S30. Crystallographically-determined solid-state structure of **Int_1-Se**. Atomic displacement ellipsoids are depicted at the 50% probability level and omitted for the ligand periphery. Hydrogen atoms except H1 are omitted for clarity. The structure is depicted for proof of connectivity only; the data are not sufficient for discussion of bond lengths and angles.

Crystal data for **1-O**: $C_{39}H_{48}B_2N_2O$, $M_r = 582.41$, colourless block, 0.201×0.189×0.121 mm^3, monoclinic space group $P2_1/c$, $a = 12.017(5)$ Å, $b = 8.345(4)$ Å, $c = 33.497(13)$ Å, $\beta = 94.968(14)°$, $V = 3346(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.156$ g·cm^{-3}, $\mu = 0.067$ mm^{-1}, $F(000) = 1256$, $T = -173$ K, $R_1 = 0.0920$, $wR^2 = 0.1295$, 6849 independent reflections [$2\theta \leq 52.744°$] and 408 parameters.

Crystal data for **1-S**: $C_{39}H_{48}B_2N_2S$, $M_r = 598.47$, yellow block, 0.377×0.328×0.172 mm^3, monoclinic space group $P2_1/c$, $a = 12.3083(17)$ Å, $b = 8.2219(11)$ Å, $c = 34.364(5)$ Å, $\beta = 93.549(8)°$, $V = 3470.9(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.145$ g·cm^{-3}, $\mu = 0.122$ mm^{-1}, $F(000) = 1288$, $T = -173$ K, $R_1 = 0.0526$, $wR^2 = 0.1195$, 6825 independent reflections [$2\theta \leq 52.044°$] and 412 parameters.

Crystal data for **Int_1-Se**: $C_{156}H_{192}B_8N_8Se_4$, M_r = 2581.48, yellow block, 0.083×0.021×0.002 mm^3, triclinic space group P1, a = 11.422(4) Å, b = 13.831(4) Å, c = 21.994(7) Å, α = 90.009(10)°, β = 90.034(8)°, γ = 90.047(13)°, V = 3474.5(19) $Å^3$, Z = 1, ρ_{calcd} = 1.234 g·cm^{-3}, μ = 1.110 mm^{-1}, F(000) = 1360, T = 139(2) K, R1 = 0.1991, wR^2 = 0.2380, 22026 independent reflections [2θ≤49.426°] and 1646 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC: 1922537 (**1-O**), 1922538 (**1-S**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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2 S. R. Wang, D. Prieschl, J. D. Mattock, M. Arrowsmith, C. Pranckevicius, T. E. Stennett, R. D. Dewhurst, A. Vargas and H. Braunschweig, *Angew. Chem. Int. Ed.* 2018, **57**, 6347-6351.

3 G. Sheldrick, *Acta Cryst.* 2015, **A71**, 3–8.

4 G. Sheldrick, *Acta Cryst.* 2008, **A64**, 112–122.