Supplementary Information (SI) for Chemical Science.

Supporting Information for

Harnessing transient CAAC-stabilized mesitylborylenes for chalcogen activation

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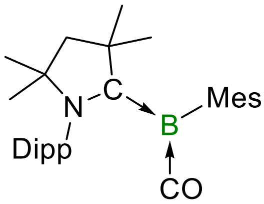
Contents

Methods and materials

All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Both deuterated and non-deuterated solvents were stored under argon over activated 4 Å molecular sieves. Liquid-phase NMR spectra were acquired on a Bruker Avance 500 (^{1}H: 500 MHz, ^{11}B: 160 MHz, ^{13}C: 125 MHz) or 600 (^{1}H: 600 MHz, ^{11}B: 193 MHz, ^{13}C: 151 MHz) spectrometer. Chemical shifts (δ) are reported in ppm and internally referenced to the carbon nuclei (^{13}C{^{1}H}) or residual protons (^{1}H) of the solvent. Heteronuclei NMR spectra are referenced to external standards (^{11}B: $BF_3{\cdot}OEt_2$). Resonances are identified as singlet (s), doublet (d), triplet (t), septet (sept), multiplet (m) or broad (br). Coupling constants are ^{1}H-^{1}H coupling constants unless specified otherwise. High-resolution mass spectrometry (HRMS) data were obtained from a Thermo Scientific Exactive Plus spectrometer. Solid-state IR spectra were recorded on a Bruker FT-IR spectrometer ALPHA II inside a glovebox. UV-vis spectra were acquired on a METTLER TOLEDO UV-vis-Excellence UV5 spectrophotometer.

Solvents and reagents were purchased from Sigma-Aldrich, abcr or Alfa Aesar. [(CAAC)B(Mes)Br_2] (**1-Br$_2$**, CAAC = 1-(2,6-di*iso*propylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene),[1] PMe_3Se,[2] P*n*Bu_3Te,[3] Na_2S_2,[4] and Na_2Se_2[4] were synthesized using literature procedures.

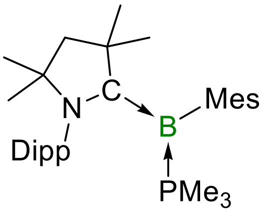
Synthetic procedures



Synthesis of [(CAAC)B(Mes)CO] (1-CO)

A mixture of (CAAC)B(Mes)Br_2 (400 mg, 0.67 mmol) and lithium sand (24 mg, 3.45 mmol) was cooled to − 78 °C and Et_2O (6 mL) was added slowly. The reaction mixture was stirred for 5 min and then frozen with liquid nitrogen. The atmosphere was removed and refilled with 1 atm of CO. The solution was allowed to warm to room temperature, stirred for another 4 h and subsequently dried *in vacuo*. The corresponding residue was extracted with 5 mL of a 1:1 benzene/pentane mixture. Slow evaporation of this solution at room temperature yielded **1-CO** as orange crystals (262 mg, 0.59 mmol, 88%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated hexane solution at −30 °C.

^{11}B NMR (193 MHz, C_6D_6): $\delta = -14.3$ ppm.
^{1}H NMR (600 MHz, C_6D_6): $\delta = 7.27$ (dd, $^3J = 7.7$ Hz, 1H, *para*-Dipp-C*H*), 7.17 (d, $^3J = 7.7$ Hz, 2H, *meta*-Dipp-C*H*), 6.97 (s, 2H, Mes-C*H*), 3.08 (sept, $^3J = 6.7$ Hz, 2H, *i*Pr-C*H*), 2.57 (s, 6H, *ortho*-Mes-CH_3), 2.24 (s, 3H, *para*-Mes-CH_3), 1.67 (s, 2H, C(CH_2)C), 1.52 (d, $^3J = 6.7$ Hz, 6H, *i*Pr-CH_3), 1.22 (s, 6H, CC(CH_3)$_2$C), 1.22 (d, $^3J = 6.7$ Hz, 6H, *i*Pr-CH_3), 1.06 (s, 6H, CC(CH_3)$_2$C).
$^{13}C\{^1H,^{11}B\}$ NMR (151 MHz, C_6D_6): $\delta = 221.3$ (CO-*C*q), 205.0 (Carben-*C*q), 149.6 (2 x Dipp-*C*q), 143.9 (Mes-*C*q), 136.5 (2x Mes-*C*q), 134.8 (Dipp-*C*q), 134.2 (Mes-*C*q), 130.3 (Dipp-*C*H), 128.4 (2x Mes-*C*H), 128.1 (Mes-*C*q), 128.0 (Mes-*C*H), 126.0 (2x Dipp-*C*H), 68.5 (C*C*(CH_3)$_2$C-Cq), 55.3 (C(*C*H_2)C), 48.5 (C*C*(CH_3)$_2$C-Cq), 30.1 (2x CC(*C*H_3)$_2$C), 30.0 (2x CC(*C*H_3)$_2$C), 28.6 (*i*Pr-*C*H), 27.0 (2 x *i*Pr–*C*H_3), 25.8 (2x Mes-*C*H_3), 25.2 (2x *i*Pr–*C*H_3), 21.3 (Mes-*C*H_3).
FT-IR (solid-state): $\tilde{\nu}$(CO) = 1947 cm^{-1}.
HRMS ASAP for $[C_{30}H_{42}BNO]^+ = [M]^+$: *m*/*z*: calcd. 443.3354; found 443.3352.



Synthesis of [(CAAC)B(Mes)PMe$_3$] (1-PMe$_3$)

A mixture of (CAAC)B(Mes)Br$_2$ (400 mg, 0.67 mmol) and potassium graphite (233 mg, 1.67 mmol) was cooled to −78 °C and toluene (4 mL) was added slowly. The reaction mixture was stirred for 10 min, after which PMe$_3$ (0.4 mL, 295 mg, 3.77 mmol) was added. The solution was allowed to warm to room temperature, stirred for another 4 h and subsequently dried *in vacuo*. The corresponding residue was extracted with 5 mL of benzene. Slow evaporation of this solution at room temperature yielded **1-PMe$_3$** as yellow crystals (148 mg, 0.30 mmol, 44%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated hexane solution at −30 °C.

*Note: **1-PMe$_3$** exist in solution as a mixture of two conformers (**A**) and (**B**), in an approximately 5:1 (**A**:**B**) ratio. Separation of the two conformers proved unsuccessful; therefore, they were characterized as a mixture.*

^{11}B NMR (160 MHz, tol-d$_8$): δ = 5.0 (br, **A**), 2.8 (br, **B**) ppm.

^{31}P{^{1}H} NMR (202 MHz, tol-d$_8$): δ = −27.33 (br, **A**), −29.62 (br, **B**).

^{1}H NMR (500 MHz, tol-d$_8$): **Conformer A (major)** δ = 7.10 – 7.06 (m, 2H, Dipp-C*H*), 6.89 – 6.85 (m, 2H, Dipp-C*H*), 6.84 (s, 1H, Mes-C*H*), 6.51 (s, 1H, Mes-C*H*), 3.42 (sept, ^3J = 6.7 Hz, 1H, *i*Pr-C*H*), 3.19 (sept, ^3J = 6.7 Hz, 1H, *i*Pr-C*H*), 2.58 (s, 3H, Mes-CH_3), 2.17 (d, J = 2.5 Hz, 3H, Mes-CH_3), 2.05 (d, ^2J = 12.1 Hz, 1H, C(CH_2)C), 1.88 (d, ^2J = 12.1 Hz, 1H, C(CH_2)C), 1.71 (s, 3H, CC(CH_3)$_2$C), 1.66 (s, 3H, CC(CH_3)$_2$C), 1.55 (s, 3H, CC(CH_3)$_2$C), 1.51 (d, ^3J = 6.7 Hz, 3H, *i*Pr-CH_3), 1.49 (s, 3H, Mes-CH_3), 1.30 (d, ^3J = 6.6 Hz, 3H, *i*Pr-CH_3), 1.17 (d, ^3J = 6.7 Hz, 3H, *i*Pr-CH_3), 0.93 (s, 3H, CC(CH_3)$_2$C), 0.70 (d, $^3J_{\text{P–H}}$ = 9.8 Hz, P(CH_3)$_3$, 9H), 0.24 (d, J = 6.6 Hz, *i*Pr-CH_3, 3H).

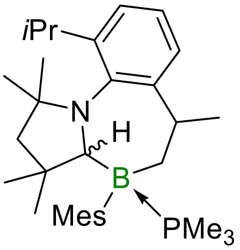
^{1}H NMR (500 MHz, tol-d$_8$): **Conformer B (minor)** δ = 7.02 – 7.01 (m, 1H, Dipp-CH), 6.98 – 6.97 (m, 2H, Dipp-CH), 6.94 (s, 2H, Mes-CH), 3.80 (sept, ^3J = 6.7 Hz, 2H, *i*Pr-C*H*), 2.57 (s, 6H, Mes-CH_3), 2.25 (d, 3H, Mes-CH_3), 1.81 (s, 2H, C(CH_2)C), 1.41 (s, 6H, CC(CH_3)$_2$C), 1.32 (d, ^3J = 6.7 Hz, 6H, *i*Pr-CH_3), 1.29 (d, ^3J = 6.7 Hz, 6H, *i*Pr-CH_3), 1.22 (s, 6H, CC(CH_3)$_2$C), 0.39 (d, $^3J_{\text{P–H}}$ = 9.8 Hz, 9H, P(CH_3)$_3$).

Integrals are reported for each conformer, but do not reflect relative abundance.

^{13}C{^{1}H} NMR (126 MHz, tol-d$_8$): δ = 150.5, 150.0, 148.5, 145.4, 145.0, 145.0, 144.0, 143.9 143.28, 143.2, 143.0, 142.9, 134.0, 134.0, 129.2, 128.2, 127.6, 127.6, 126.8, 126.8, 125.7, 125.4, 125.4, 123.6, 62.9, 62.9, 60.3, 45.2, 45.2, 36.5, 33.2, 33.2, 32.5, 32.5, 32.0, 31.8, 29.0, 28.2, 27.8, 27.7, 27.5, 27.4, 26.7, 26.7, 26.6, 26.2, 25.5, 25.4, 25.0, 24.7, 23.5, 23.1, 21.3, 21.3, 21.1, 21.1, 17.1, 16.8, 16.4, 16.3, 14.3, 14.2, 13.9.

Note: The complex conformer mixture hinders accurate assignment of ^{13}C NMR signals.

HRMS LIFDI for $[C_{32}H_{51}BNP]^+$ = $[M]^+$: *m*/*z*: calcd. 491.3847; found 491.3836.



Synthesis of [(CAACH)B(Mes)PMe$_3$] (1^{CH}-PMe$_3$)

A solution of **1-PMe$_3$** (30 mg, 61 µmol) was heated to 60 °C for 4 h, resulting in gradual decolorization. The corresponding colorless solution was freeze-dried in vacuo, yielding **(1^{CH}-PMe$_3$)** as an off-white solid (26 mg, 53 µmol, 87 %).

^{11}B {^{1}H} NMR (193 MHz, C$_6$D$_6$) δ = –28.3 (d, $^2J_{B\text{–}P}$ = 50.8 Hz) ppm.

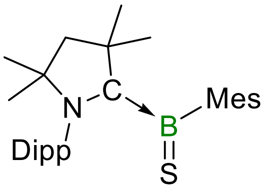
^{31}P {^{1}H} NMR (243 MHz, C$_6$D$_6$) δ = –6.54 – –7.67 (m) ppm.

^{1}H NMR (600 MHz, C$_6$D$_6$) δ = 7.15 – 7.13 (m, 1H, Dipp-C*H*), 7.07 – 7.04 (m, 1H, Dipp-C*H*), 7.05 (s, 2H, Mes-C*H*), 6.97 – 6.94 (m, 1H, Dipp-C*H*), 4.72 (d, ^5J = 3.5 Hz, 1H, CAAC-C*H*), 3.77 (sept, ^3J = 6.9 Hz, 1H, *i*Pr-C*H*), 3.58 (qd, ^3J = 7.1 Hz, ^5J = 3.5 Hz, 1H, CH$_3$C*H*CH$_2$), 2.77–2.20 (m, 2H, CH$_3$CHC*H*$_2$), 2.60 (d, 6H, *ortho*-Mes-C*H*$_3$), 2.33 (d, 3H, *para*-Mes-C*H*$_3$), 1.56 (d, ^2J = 12.2 Hz, 1H, C(C*H*$_2$)C), 1.48 (d, ^2J = 12.2 Hz, 1H, C(C*H*$_2$)C), 1.37 (d, ^3J = 6.9 Hz, 3H, C*H*$_3$CHCH$_2$), 1.28 (s, 3H, CC(C*H*$_3$)$_2$C), 1.22 (s, 3H, CC(C*H*$_3$)$_2$C), 1.21 (d, ^3J = 6.9 Hz, 3H, *i*Pr-C*H*$_3$), 1.16 (s, 3H, CC(C*H*$_3$)$_2$C), 1.08 (d, ^3J = 6.9 Hz, 3H, *i*Pr-C*H*$_3$), 1.02 (s, 3H, CC(C*H*$_3$)$_2$C), 0.54 (d, $^3J_{P\text{–}H}$ = 10.0 Hz, 9H).

^{13}C {^{1}H, ^{11}B} NMR (151 MHz, C$_6$D$_6$) δ = 154.2 (*C*q), 144.1 (Dipp-*C*q), 142.8 (d, *ortho*-Mes-*C*q) 140.01 (d, *ipso*-Mes-*C*q), 138.33 (Dipp-*C*q), 138.15 (Dipp-*C*q), 133.8 (d, *para*-Mes-*C*q), 125.8 (Dipp-*C*H), 124.6 (Mes-*C*H), 124.0 (Dipp-*C*H), 102.0 (CAAC-*C*H), 63.7(C*C*(CH$_3$)$_2$C),

53.7 (C*C*H_2C), 37.0 (C*C*(CH_3)$_2$C), 34.0 (CH_3*C*HCH_2), 30.0 (CC(*C*H_3)$_2$C), 29.5 (*i*Pr-*C*H), 28.71 (*i*Pr-*C*H_3), 28.1 (CC(*C*H_3)$_2$C), 27.0 (CC(*C*H_3)$_2$C), 25.7 (*C*H_3CHCH_2), 25.4 (*i*Pr-*C*H_3), 25.1 (d, *ortho*-Mes-*C*H_3), 23.7 (CC(*C*H_3)$_2$C), 21.3 (d, *para*-Mes-*C*H_3), 11.2 (d, $^2J_{\mathrm{P-C}}$ = 34.2 Hz) ppm.

Note: Due to the quadrupole of the boron-bound CH_2 moiety, the corresponding carbon signal could not be accurately assigned.



Synthesis of [(CAAC)B(Mes)S] (1-S)

Starting from 1-PMe$_3$

A mixture of **1-PMe$_3$** (30 mg, 61 µmol) and sulfur (5.8 mg, 0.18 mmol) was dissolved in benzene (0.5 mL) and stirred for 2 h, resulting in a color change of the reaction mixture from yellow to orange. All volatiles were removed *in vacuo* and the corresponding residue was washed with hexamethyldisiloxane (HMDSO, 2 x 0.5 mL) and extracted with benzene (0.5 mL). Slow evaporation of this solution at room temperature yielded **1-S** as orange crystals (12 mg, 26.8 µmol, 44%).

Starting from 1-CO

A mixture of **1-CO (**25 mg, 56 µmol) and sulfur (2.2 mg, 68 µmol, 1.2 eq.) was dissolved in benzene (0.5 mL) and irradiated at a wavelength of 390 nm for 16 h. All volatiles were removed *in vacuo* and the corresponding residue was washed with HMDSO (2 x 0.5 mL) and extracted with benzene (0.5 mL). Slow evaporation of this solution at room temperature yielded **1-S** as orange crystals (16 mg, 34 µmol, 64%).

Alternatively:

A mixture of **1-CO (**30 mg, 68 µmol) and PMe_3S (8 mg, 74 µmol, 1.1 eq.) was dissolved in benzene (0.5 mL) and irradiated at a wavelength of 390 nm for 16 h. All volatiles were removed *in vacuo* and the corresponding residue was washed with HMDSO (2 x 0.5 mL) and extracted with benzene (0.5 mL). Slow evaporation of this solution at room temperature yielded **1-S** as orange crystals (20 mg, 45 µmol, 66%).

Starting from 1-Br$_2$

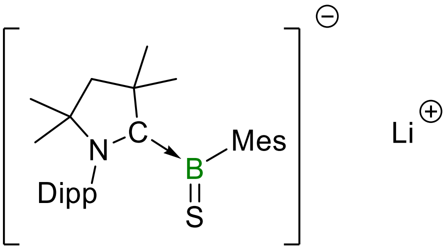
A mixture of **1-Br$_2$** (200 mg, 0.35 mmol) and sodium disulfide (84.5 mg, 0.77 mmol) was suspended in a 1:1 mixture of THF and Et$_2$O (8 mL). The reaction mixture was stirred for 4 h at room temperature and subsequently dried *in vacuo*. The corresponding residue was washed with 2 x 4 mL HMDSO and 2 mL pentane and then extracted with 2 x 3ml benzene. The resulting solution was freeze dried in vacuo yielding **1-S** as yellow solid (94 mg, 0.21 mmol, 60%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated hexane solution at –30 °C.

^{11}B NMR (160 MHz, tol-d$_8$, −40 °C): δ = 63.2 ppm.

^{1}H NMR (600 MHz, tol-d$_8$, −40 °C): δ 7.06 – 7.04 (m, 1H, Dipp-C*H*), 7.03 – 7.00 (m, 1H, Dipp-C*H*), 6.84 – 6.81 (m, 1H, Dipp-C*H*), 6.77 (s, 1H, Mes-C*H*), 6.61 (s, 1H, Mes-C*H*), 3.70 – 3.62 (m, 1H, *i*Pr-C*H*), 2.72 (s, 3H, Mes-CH_3), 2.57 – 2.49 (m, 1H, *i*Pr-C*H*), 2.18 (s, 3H, Mes-CH_3), 1.87 (s, 3H, CC(CH_3)$_2$C), 1.49 (s, 2H, C(CH_2)C), 1.50 (s, 3H, *i*Pr-CH_3), 1.40 (s, 3H, CC(CH_3)$_2$C), 1.24 (s, 3H, Mes-CH_3), 1.22 (s, 3H, CC(CH_3)$_2$C), 1.13 (s, 3H, *i*Pr-CH_3), 0.95 (s, 3H, iPr-CH_3, 3H), 0.72 (s, 3H, *i*Pr-CH_3), 0.69 (s, 3H, CC(CH_3)$_2$C) ppm.

^{13}C{^{1}H,^{11}B} NMR (126 MHz, tol-d$_8$, −40 °C): δ = 201.8 (Carben-*C*q), 147.4 (Dipp-*C*q), 144.11 (Mes-*C*q), 139.6 (Mes-*C*q), 135.8 (Mes-*C*q), 135.2 (Dipp-*C*q), 130.8 (Dipp-*C*H), 129.6 (Mes-*C*q), 128.7 (Mes-*C*H), 128.6 (Dipp-*C*q), 128.0 (Mes-*C*H), 127.1 (Dipp-*C*H), 125.2 (Dipp-*C*H), 76.0 (C*C*(CH$_3$)$_2$C-*C*q), 53.0 (C*C*(CH$_3$)$_2$C-*C*q), 51.5 (C(*C*H$_2$)C-CH$_2$), 33.2 (CC(*C*H$_3$)$_2$C-*C*H$_3$), 30.6 (*i*Pr-*C*H), 30.0 (*i*Pr-*C*H), 29.4 (CC(*C*H$_3$)$_2$C-*C*H$_3$), 28.0 (CC(*C*H$_3$)$_2$C-*C*H$_3$), 27.0 (*i*Pr-*C*H$_3$), 26.4 (CC(*C*H$_3$)$_2$C-*C*H$_3$), 25.7 (*i*Pr-*C*H$_3$), 25.5 (*i*Pr-*C*H$_3$), 25.1 (Mes-*C*H$_3$), 23.9 (*i*Pr-*C*H$_3$), 21.6 (Mes-*C*H$_3$) 21.5 (Mes-*C*H$_3$) ppm.

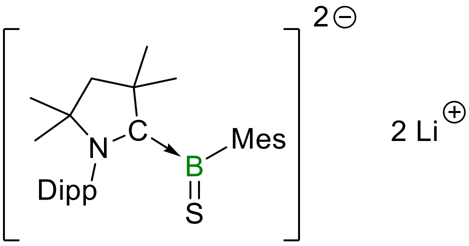
HRMS LIFDI for $[C_{29}H_{42}BNS]^+$ = $[M]^+$: *m*/*z*: calcd. 447.3126; found 447.3117.



Synthesis of [(CAAC)B(Mes)S]Li (Li[1-S])

A mixture of **1-S** (30 mg, 67 µmol) and lithium sand (2.3 mg, 0.33 mmol, 5 eq.) was dissolved in THF (0.2 mL) and stirred for 10 min, resulting in a color change from orange to red. The reaction mixture was filtered, and the resulting red solution was layered with pentane and stored at −30 °C. After 2 d **Li[1-S]** could be obtained as red crystals (9 mg, 20 µmol, 30%).

HRMS LIFDI for $[C_{29}H_{43}BNS]^+$ = $[M - Li + H]^+$: *m*/*z*: calcd. 448.3204; found 448.3198.



Synthesis of [(CAAC)B(Mes)S]Li₂ (Li₂[1-S])

A mixture of **1-S** (30 mg, 67 µmol) and lithium sand (5 mg, 0.72 mmol, 11 eq.) was dissolved in THF (0.2 mL) and stirred for 16 min, resulting in a color change of the reaction mixture from orange to yellow. The reaction mixture was filtered, and the resulting yellow solution was layered with pentane and stored at −30 °C. After 2 d **Li₂[1-S]** could be obtained as yellow crystals (16 mg, 35 µmol, 52%).

^{11}B NMR (160 MHz, THF-d$_8$, −40 °C): δ = 28.0 ppm.

^{1}H NMR (600 MHz, THF-d$_8$, −40 °C): δ = 6.95 (dd, ^3J = 7.5, ^4J = 1.9 Hz, 1H, *meta*-Dipp-C*H*), 6.90 (dd, ^3J = 7.5, ^4J = 1.9 Hz, 1H, *meta*-Dipp-C*H*), 6.79 (t, ^3J = 7.5 Hz, 1H, *para*-Dipp-C*H*), 6.50 (s, 1H, Mes-C*H*), 6.48 (s, 1H, Mes-C*H*), 4.89 (sept, ^3J = 6.6 Hz, 1H, *i*Pr-C*H*), 3.63 – 3.60

(m, 1H, *i*Pr-*C*H), 2.52 (s, 3H, Mes-CH_3), 2.41 (s, 3H, Mes-CH_3), 2.13 (s, 3H, Mes-CH_3), 1.96 (d, *J* = 12.1 Hz, 1H, CCH_2C), 1.55 – 1.52 (m, 6H, *i*Pr-CH_3, CC(CH_3)$_2$C), 1.48 (d, *J* = 12.1 Hz, 1H, CCH_2C), 1.34 (d, *J* = 6.6 Hz, 3H, *i*Pr-CH_3), 1.18 (d, ^3J = 6.6 Hz, 3H, *i*Pr-CH_3), 1.16 (d, ^3J = 6.6 Hz, 3H, *i*Pr-CH_3), 1.12 (s, 6H, CC(CH_3)$_2$C), 0.66 (s, 3H, CC(CH_3)$_2$C) ppm.

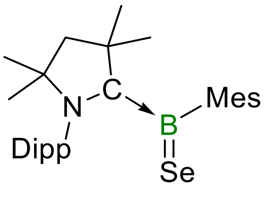
Note: A COSY experiment was necessary to identify one iPr-CH resonance due to overlap with the residual THF signal. Consequently, the corresponding coupling constant could not be determined.

^{7}Li NMR (233 MHz, THF-d$_8$, −40 °C): δ = 1.01 (s), 0.07(s) ppm.

^{13}C{^{1}H, ^{11}B} NMR (126 MHz, THF-d$_8$, −40 °C): δ = 155.9 (Mes-*C*q), 148.9 (Dipp-*C*q), 147.3 (Dipp-*C*q), 147.0 (Dipp-*C*q), 140.2 (Mes-*C*q), 140.1 (Mes-*C*q), 130.7 (Mes-*C*q), 126.8 (Mes-H), 126.2 (Mes-*C*H), 125.5 (Carben-*C*q), 124.0 (Dipp-*C*H), 123.7 (Dipp-*C*H), 123.1 (Dipp-*C*H), 62.4 (C*C*(CH$_3$)$_2$C), 61.6 (CCH$_2$C), 43.4 (C*C*(CH$_3$)$_2$C), 35.4 (CC(*C*H$_3$)$_2$C), 31.8 (CC(*C*H$_3$)$_2$C), 31.7 (CC(*C*H$_3$)$_2$C), 29.4 (*i*Pr-*C*H$_3$), 28.6 (CC(*C*H$_3$)$_2$C), 26.9 (Pr-CH$_3$), 26.9 (Mes-*C*H$_3$), 25.9 (*i*Pr-*C*H$_3$), 25.7 (*i*Pr-*C*H$_3$), 25.6 (*i*Pr-*C*H), 24.8 (Mes-*C*H$_3$), 23.6 (iPr-*C*H), 21.5 (Mes-CH_3)ppm.

Attempted Oxidation of 1-S

A mixture of **1-S** (30 mg, 67 µmol) and ferrocenium hexafluorophosphate (8.8 mg, 26 µmol, 0.4 eq) was dissolved in 1,2-difluorobenzene, resulting in an immediate color change to red. Both **1-F$_2$** (identified using X-ray diffraction) and remaining **1-S** were obtained.



Synthesis of [(CAAC)B(Mes)Se] (1-Se)

Starting from 1-PMe$_3$

A mixture of **1-PMe$_3$** (30 mg, 61 µmol) and selenium (14 mg, 0.18 mmol) was suspended in benzene (0.5 mL) and stirred for 2 d, resulting in a color change of the reaction mixture from yellow to red. All volatiles were removed *in vacuo* and the corresponding residue was washed with HMDSO (2 x 0.5 mL) and extracted with benzene (0.5 mL). Slow evaporation of this solution at room temperature yielded **1-Se** as red crystals (17 mg, 34.4 µmol, 44%).

Starting from 1-CO

A mixture of **1-CO** (30 mg, 67 µmol) and PMe_3Se (10 mg, 67 µmol) was dissolved in benzene (0.5 mL) and irradiated at a wavelength of 390 nm for 16 h, resulting in a color change of the reaction mixture from orange to red. All volatiles were removed *in vacuo*, the corresponding residue washed with HMDSO (2x 0.5 mL) and extracted with benzene (0.5 ml). Slow evaporation of this solution at room temperature yielded **1-Se** as red crystals (24 mg, 48 µmol, 72%).

Starting from 1-Br$_2$

A mixture of **1-Br$_2$** (200 mg, 0.35 mmol) and sodium diselenide (63.5 mg, 0.57 mmol) was suspended in a 1:1 mixture of THF and Et_2O (8 mL). The reaction mixture was stirred for 4 h at room temperature and subsequently dried *in vacuo*. The corresponding residue was washed with pentane (4 mL) and extracted with 4 mL of benzene. Fractional crystallization of this solution yielded **1-Se** as red crystals (43 mg, 8.7 µmol, 25%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated hexane solution at −30 °C.

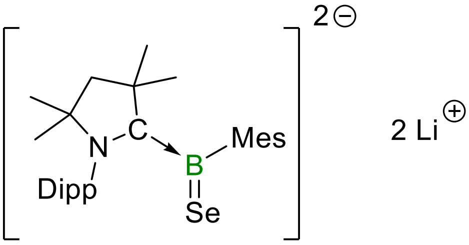
^{11}B NMR (160 MHz, tol-d$_8$): δ = 70.7 ppm.

^{77}Se{^{1}H,^{11}B} (114 MHz, tol-d$_8$, −40 °C): δ = 716.1 ppm.

^{1}H NMR (600 MHz, tol-d$_8$, −40 °C): δ = 7.08 – 7.03 (m, 2H, Dipp-C*H*), 6.82 (d, ^3J = 7.4 Hz, 1H, Dipp-C*H*), 6.75 (s, 1H, Mes-C*H*), 6.59 (s, 1H, Mes-C*H*), 3.67 (sept, ^3J = 6.6 Hz, 1H, *i*Pr-C*H*), 2.72 (s, 3H, Mes-CH_3), 2.55 (sept, ^3J = 6.6 Hz, 1H, *i*Pr-C*H*), 2.18 (s, 3H, Mes-CH_3), 2.12 (s, 1H, C(CH_2)C), 1.94 (s, 3H, CC(CH_3)$_2$C), 1.55 – 1.43 (m, 7H, CC(CH_3)$_2$C, *i*Pr-CH_3, C(CH_2)C), 1.24 (s, 3H, Mes-CH$_3$), 1.20 (s, 3H, CC(CH_3)$_2$C), 1.12 (d, ^3J = 6.6 Hz, 3H, *i*Pr-CH_3), 0.95 (d, ^3J = 6.6 Hz, 3H, *i*Pr-CH_3), 0.74 (d, ^3J = 6.6 Hz, 3H, iPr-CH_3), 0.68 (s, 3H, CC(CH_3)$_2$C) ppm.

^{13}C{^{1}H,^{11}B} NMR (126 MHz, tol-d$_8$, −40 °C): δ = 201.6 (Carben-Cq), 147.1 (Dipp-*C*q), 146.75 (Dipp-*C*q), 145.7 (Mes-*C*q), 135.3 (Mes-Cq), 134.9 (Dipp-*C*q), 130.3 (Dipp-*C*H), 129.2 (Dipp-*C*H), 128.9 (Mes-*C*H), 128.4 (Mes-*C*q), 128.2 (Mes-*C*q), 127.9 (Mes-*C*H), 125.3 (Dipp-*C*H), 75.1 (C*C*(CH$_3$)$_2$C), 52.8 (C(*C*H$_2$)C), 49.8 (C*C*(CH$_3$)$_2$C), 34.3 (CC(*C*H$_3$)$_2$C), 30.1 (*i*Pr-*C*H), 29.4 (CC(*C*H$_3$)$_2$C), 28.7 (*i*Pr-*C*H), 26.6 (*i*Pr-*C*H$_3$), 26.3 (CC(*C*H$_3$)$_2$C), 26.2 (*i*Pr-*C*H$_3$), 25.1 (Mes-

CH_3), 25.0 (*i*Pr-CH_3), 24.6 (Mes-CH_3), 23.4 (*i*Pr-CH_3), 21.3 (C(CH_2)C), 21.0 (Mes-CH_3), 20.6 (CC(CH_3)$_2$C) ppm.
HRMS LIFDI for $[C_{29}H_{42}BNSe]^+ = [M]^+$: *m*/*z*: calcd. 495.2570; found 495.2559.



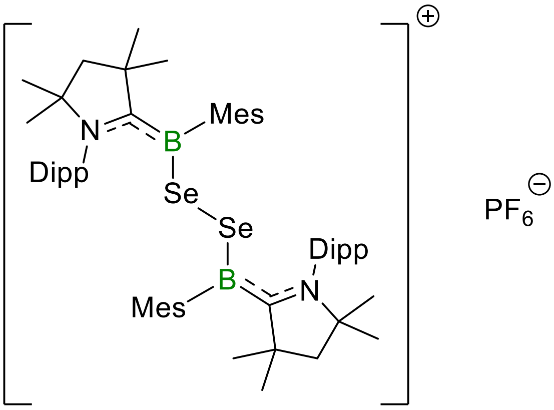
Synthesis of [(CAAC)B(Mes)Se]Li$_2$ (Li$_2$[1-Se])

A mixture of **1-Se** (30 mg, 61 µmol) and lithium sand (5 mg, 0.72 mmol, 12 eq.) was dissolved in THF (0.2 mL) and stirred for 16 min, resulting in a color change of the reaction mixture from orange to yellow. The reaction mixture was filtered, and the resulting yellow solution was layered with pentane and stored at –30 °C. After 2 d **Li$_2$[1-Se]** could be obtained as yellow crystals (23 mg, 45 µmol, 74%).

^{11}B NMR (160 MHz, THF-d$_8$, −40 °C): δ = 24.8 ppm.
^{1}H NMR (600 MHz, THF-d$_8$, −40 °C): δ = 6.94 (d, ^3J = 7.5 Hz, 1H, *meta*-Dipp-C*H*) 6.89 (d, ^3J = 7.5 Hz, 1H, *meta*-Dipp-C*H*), 6.80 (t, ^3J = 7.5 Hz, 1H, *para*-Dipp-C*H*), 6.50 (s, 1H, Mes-C*H*), 6.49 (s, 1H, Mes-C*H*), 4.91 (sept, ^3J = 6.6 Hz, 1H, *i*Pr-C*H*), 3.59 – 3.57 (m, 1H, *i*Pr-C*H*), 2.52 (s, 3H, Mes-CH_3), 2.40 (s, 3H, Mes-CH_3), 2.13 (s, 3H, Mes-CH_3), 1.95 (d, ^2J = 12.1 Hz, 1H, CCH_2C), 1.58 (d, ^3J = 6.6 Hz, 3H, *i*Pr-CH_3), 1.53 (s, 3H, CC(CH_3)$_2$C), 1.50 (d, ^2J = 12.1 Hz, 1H, CCH_2C), 1.35 (d, ^3J = 6.6 Hz, 3H, *i*Pr-CH_3), 1.20 (d, ^3J = 6.6 Hz, 3H, *i*Pr-CH_3), 1.15 (d, ^3J = 6.6 Hz, 3H, *i*Pr-CH_3), 1.13 (s, 3H, CC(CH_3)$_2$C), 1.11 (s, 3H, CC(CH_3)$_2$C), 0.65 (s, 3H, CC(CH_3)$_2$C) ppm.
Note: A COSY experiment was necessary to identify one iPr-CH resonance due to overlap with the residual THF signal. Consequently, the corresponding coupling constant could not be determined.
^{7}Li NMR (233 MHz, THF-d$_8$, −40 °C): δ = 1.4 (s), 0.3 (s) ppm.
^{77}Se {^{1}H,^{11}B} NMR (114 MHz, THF-d$_8$, −40 °C) δ = –428.8 ppm.
^{13}C{^{1}H,^{11}B} NMR (126 MHz, THF-d$_8$, −40 °C): δ = 155.8 (Mes-*C*q), 148.4 (Dipp-*C*q), 147.2 (Dipp-*C*q), 146.8 (Dipp-*C*q), 140.1 (Mes-*C*q), 139.8 (Mes-*C*q), 130.8 (Mes-*C*q), 127.5

(carbene-*C*q), 127.1 (Mes-*C*H), 126.5 (Mes-*C*H), 124.0 (*meta*-Dipp-*C*H), 123.9 (*meta*-Dipp-*C*H), 123.3 (*para*-Dipp-*C*H), 62.8 (C*C*(CH_3)$_2$C), 62.1 (C*C*H_2C), 44.1 (C*C*(CH_3)$_2$C), 34.9 (CC(*C*H_3)$_2$C), 31.8 (CC(*C*H_3)$_2$C), 31.7 (CC(*C*H_3)$_2$C), 29.6 (*i*Pr-*C*H), 28.8 (CC(*C*H_3)$_2$C), 27.4 (*i*Pr-*C*H_3), 26.6 (Mes-*C*H_3), 26.5 (*i*Pr-*C*H_3), 26.2 (*i*Pr-*C*H_3), 25.9 (*i*Pr-*C*H_3), 25.3 (Mes-*C*H_3), 25.0 (*i*Pr-*C*H), 21.6 (Mes-*C*H_3) ppm.

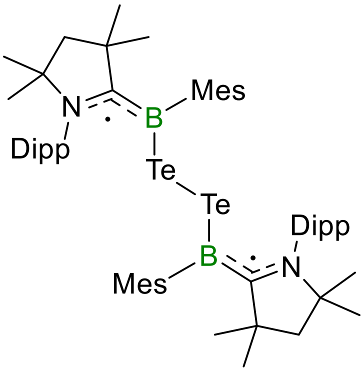
Due to the high sensitivity of ***Li_2[1-Se]*** *towards air, neither HRMS nor EA data could be obtained.*



Synthesis of [{(CAAC)B(Mes)Se}$_2$][PF_6] ([(1-Se)$_2$]PF_6)

A mixture of **1-Se** (20 mg, 40 µmol) and ferrocenium hexafluorophosphate (5 mg, 15 µmol, 0.4 eq) was dissolved in 1,2-difluorobenzene, resulting in an immediate color change to purple. The mixture was stirred for 5 min and then filtrated. Slow diffusion of pentane into this solution at −30 °C yielded **[(1-Se)$_2$]PF_6** as deep purple crystals (16 mg, 14 µmol, 70% (relative to **1-Se**)).

HRMS LIFDI for [$C_{58}H_{84}B_2N_2Se_2$]$^+$ = [M]$^+$: *m*/*z*: calcd. 990.5167; found 990.5167.



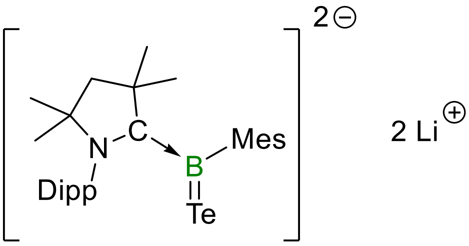
Synthesis of [{(CAAC)B(Mes)Te}$_2$] ((1-Te)$_2$)

Starting from 1-PMe$_3$

A mixture of **1-PMe$_3$** (30 mg, 61.0 µmol) and tellurium (23.3 mg, 183.0 µmol) was suspended in benzene (0.5 mL) and stirred for 7 d, resulting in a color change of the reaction mixture from yellow to blue-green. All volatiles were removed *in vacuo* and the corresponding residue was washed with HMDSO (2 x 0.5 mL) and extracted with benzene (0.5 mL). Slow evaporation of this solution at room temperature yielded **(1-Te)$_2$** as deep blue-green crystals (19 mg, 17.5 µmol, 57% (relative to two eq. of **1-PMe$_3$**)).

Starting from 1-CO

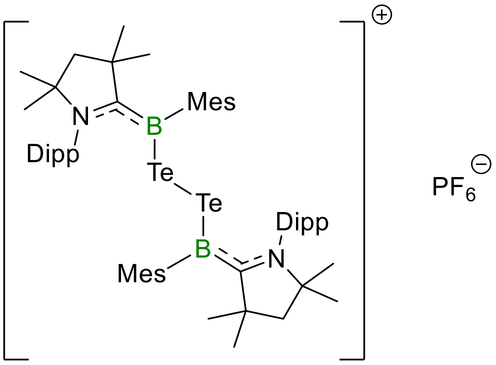
A mixture of **1-CO** (30.0 mg, 67.7 µmol) and P*n*Bu$_3$Te (22.3 mg, 67.7 µmol) was dissolved in benzene (0.5 mL) and irradiated at a wavelength of 390 nm for 16 h, resulting in a color change of the reaction mixture from orange to deep blue-green. All volatiles were removed *in vacuo* and the corresponding residue was washed with HMDSO (2x 0.5 mL) and extracted with benzene (0.5 mL). Slow evaporation of this solution at room temperature yielded **(1-Te)$_2$** as deep blue-green crystals (22 mg, 20.2 µmol, 60% (relative to two eq. of **1-CO**)).
HRMS LIFDI for $[C_{58}H_{84}B_2N_2Te_2]^+ = [M]^+$: *m*/*z*: calcd. 1086.4936; found 1086.4883.



Synthesis of [(CAAC)B(Mes)Te]Li₂ (Li₂[1-Te])

A mixture of **(1-Te)₂** (20 mg, 18 µmol) and lithium sand (5 mg, 0.72 mmol, 40 eq.) was dissolved in THF (0.2 mL) and stirred for 16 h, resulting in a color change of the reaction mixture from deep blue-green to yellow. The reaction mixture was filtered, and the resulting yellow solution was layered with pentane and stored at −30 °C. After 2 d **Li₂[1-Te]** could be obtained as yellow crystals (12 mg, 21 µmol, 58% (relative to 0.5 eq. of **(1-Te)₂**).

^{11}B NMR (193 MHz, THF-d_8, −40 °C) δ = 17.1 ppm.
^{125}Te NMR (189 MHz, THF-d_8, −40 °C) δ = −1183.1 ppm.
^{1}H NMR (600 MHz, THF-d_8, −40 °C) δ = 6.93 (d, ^3J = 7.5 Hz, 1H, *meta*-Dipp-C*H*), 6.90 (d, ^3J = 7.5 Hz, 1H, *meta*-Dipp-C*H*), (t, ^3J = 7.5 Hz, 1H, *para*-Dipp-C*H*), 6.48 (s, 2H, Mes-C*H*), 4.96 – 4.84 (m, 1H, *i*Pr-C*H*), 3.54 – 3.48 (m, 1H, *i*Pr-C*H*), 2.50 (s, 3H, Mes-CH_3), 2.40 (s, 3H, Mes-CH_3), 2.14 (s, 3H, Mes-CH_3), 1.92 (d, ^2J = 12.2 Hz, 1H, CCH_2C), 1.65 (d, ^3J = 6.5 Hz, 3H, *i*Pr-CH_3), 1.53 (s, 3H, CC(CH_3)$_2$C), 1.51 (d, ^2J = 12.2 Hz, 1H, CCH_2C), 1.36 (d, ^3J = 6.5 Hz, 3H, *i*Pr-CH_3), 1.26 (d, ^3J = 6.5 Hz, 3H, *i*Pr-CH_3), 1.16 – 1.14 (m, 6H, CC(CH_3)$_2$C + *i*Pr-CH_3), 1.09 (s, 3H, CC(CH_3)$_2$C), 0.62 (s, 3H, CC(CH_3)$_2$C).
^{7}Li NMR (233 MHz, THF-d_8, −40 °C): δ = 1.3 (s), 0.3 (s) ppm
^{13}C NMR (151 MHz, THF-d_8, −40 °C) δ = 155.8 (Mes-*C*q), 147.5 (Dipp-*C*q), 147.0 (Dipp-*C*q), 146.4 (Dipp-*C*q), 140.1 (Mes-*C*q), 139.0 (Mes-*C*q), 130.7 (Mes-*C*q), 127.3 (Mes-*C*H), 126.8 (Mes-*C*H), 124.1 (*meta*-Dipp-*C*H), 124.0 (*meta*-Dipp-*C*H), 123.6 (*para*-Dipp-*C*H), 63.3 (C*C*(CH$_3$)$_2$C), 62.9 (C*C*H$_2$C), 45.3 (C*C*(CH$_3$)$_2$C), 34.0 (CC(*C*H$_3$)$_2$C), 31.7 (CC(*C*H$_3$)$_2$C), 31.6 (CC(*C*H$_3$)$_2$C), 29.6 (*i*Pr-*C*H), 29.1 (CC(*C*H$_3$)$_2$C), 27.3 (*i*Pr-*C*H$_3$), 26.7 (*i*Pr-*C*H$_3$), 26.6 (Mes-*C*H$_3$), 25.9 (*i*Pr-*C*H$_3$), 25.8 (*i*Pr-*C*H$_3$), 25.7 (Mes-*C*H$_3$), 25.1 (*i*Pr-*C*H), 21.6 (Mes-*C*H$_3$). *Quadropole broadening prevented the identification of the resonance signal from the quaternary carbene carbon. Due to the high sensitivity of* **Li₂[1-Te]** *to air, neither HRMS nor EA data could be obtained.*



Synthesis of [{(CAAC)B(Mes)Te}$_2$][PF$_6$] ([(1-Te)$_2$]PF$_6$)

A mixture of **(1-Te)$_2$** (10 mg, 9.2 µmol) and ferrocenium hexafluorophosphate (3 mg, 9.2 µmol) was dissolved in 1,2-difluorobenzene, stirred for 5 min and then filtrated. Slow diffusion of pentane into this solution at −30 °C yielded **[(1-Te)$_2$](PF$_6$)** as deep blue-green crystals (7 mg, 5.6 µmol, 62%).

HRMS LIFDI for $[C_{58}H_{84}B_2N_2Te_2]^+ = [M]^+$: *m*/*z*: calcd. 1086.4910; found 1086.4893.

Attempted synthesis of [(CAAC)B(Mes)O] (1-O)

1-PMe$_3$ was treated with several oxygen sources such as iodosobenzene, pyridine-N-oxide, oxygen, and nitrous oxide to generate **1-O**. However, in every instance, only the formation of the corresponding boroxine (MesBO)$_3$ was observed, consistent with literature reports showing an ^{11}B NMR resonance at approximately 31 ppm. This was further confirmed by single-crystal X-ray diffraction analysis.[5]

NMR spectra of isolated compounds

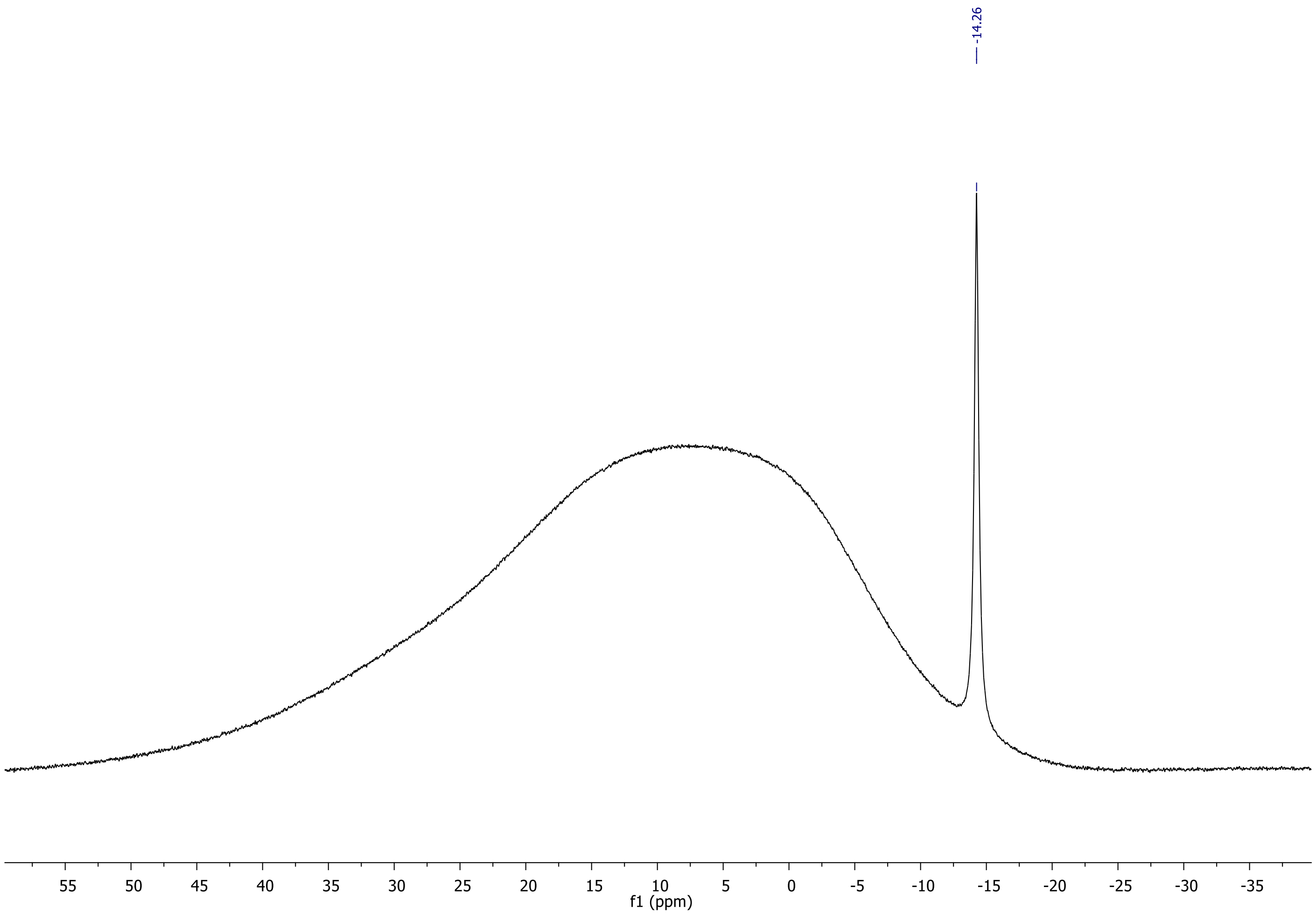


Figure S1. ^{11}B NMR spectrum of **1-CO** in C_6D_6.

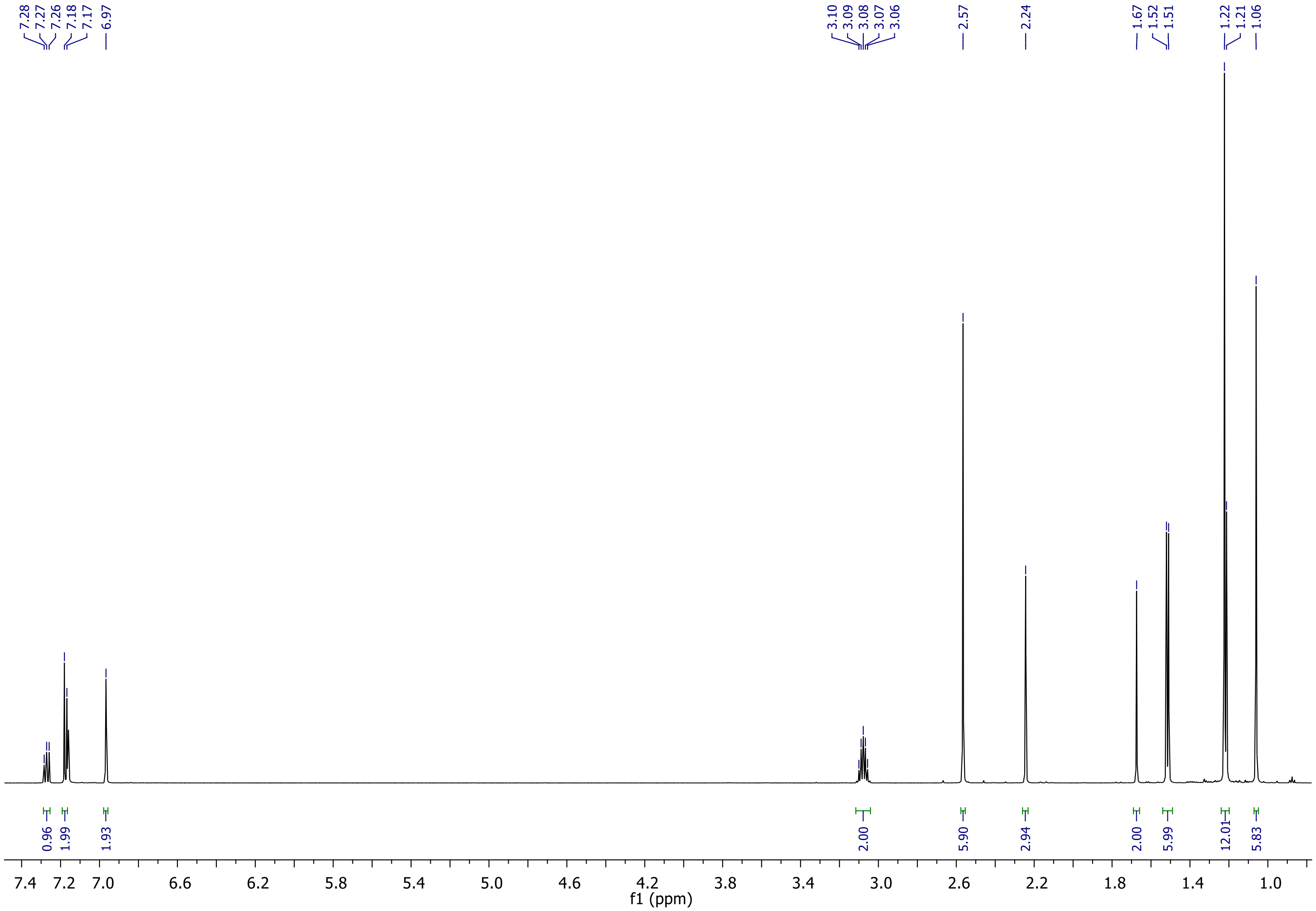


Figure S2. ^{1}H NMR spectrum of **1-CO** in C_6D_6.

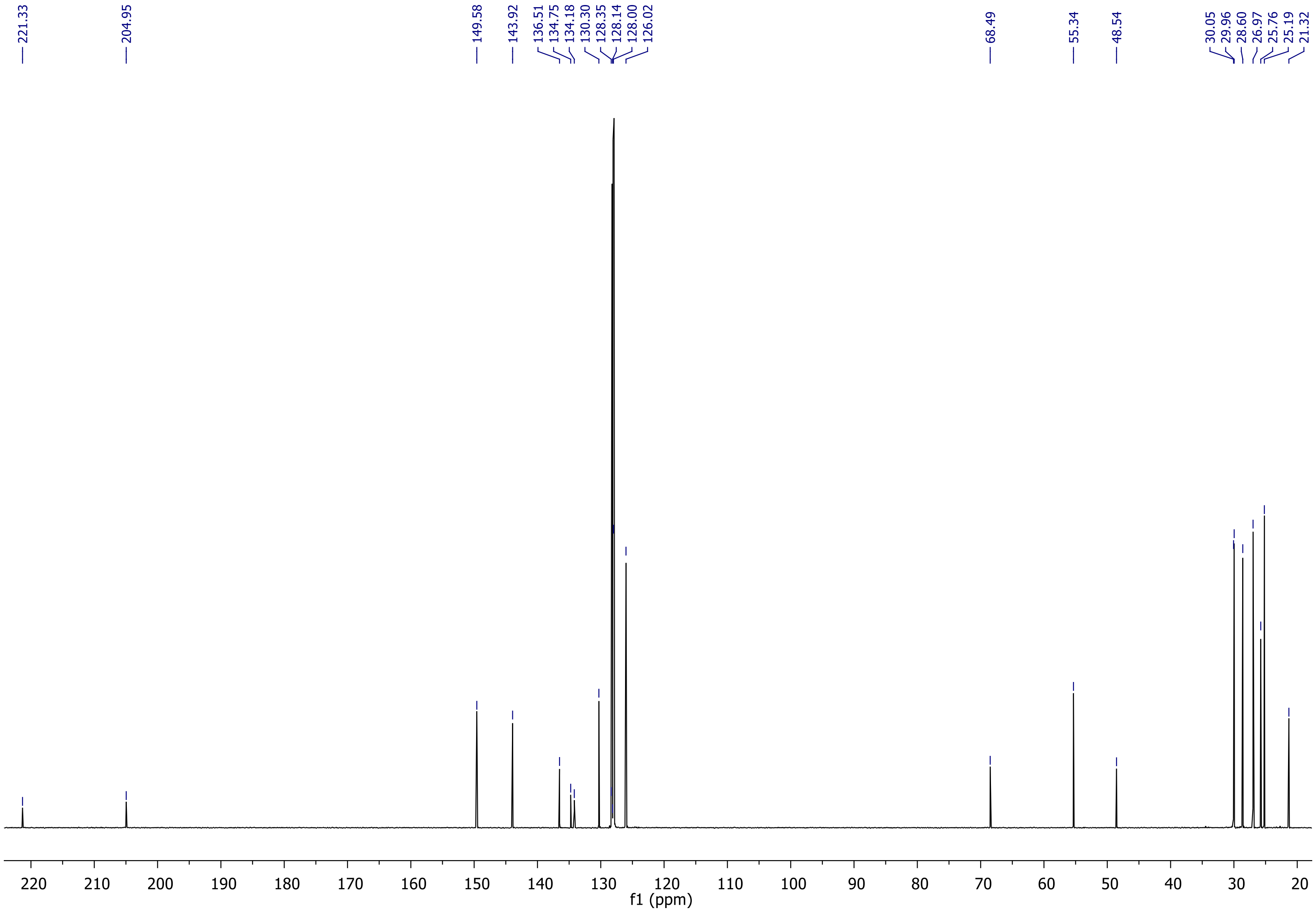


Figure S3. $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **1-CO** in C_6D_6.

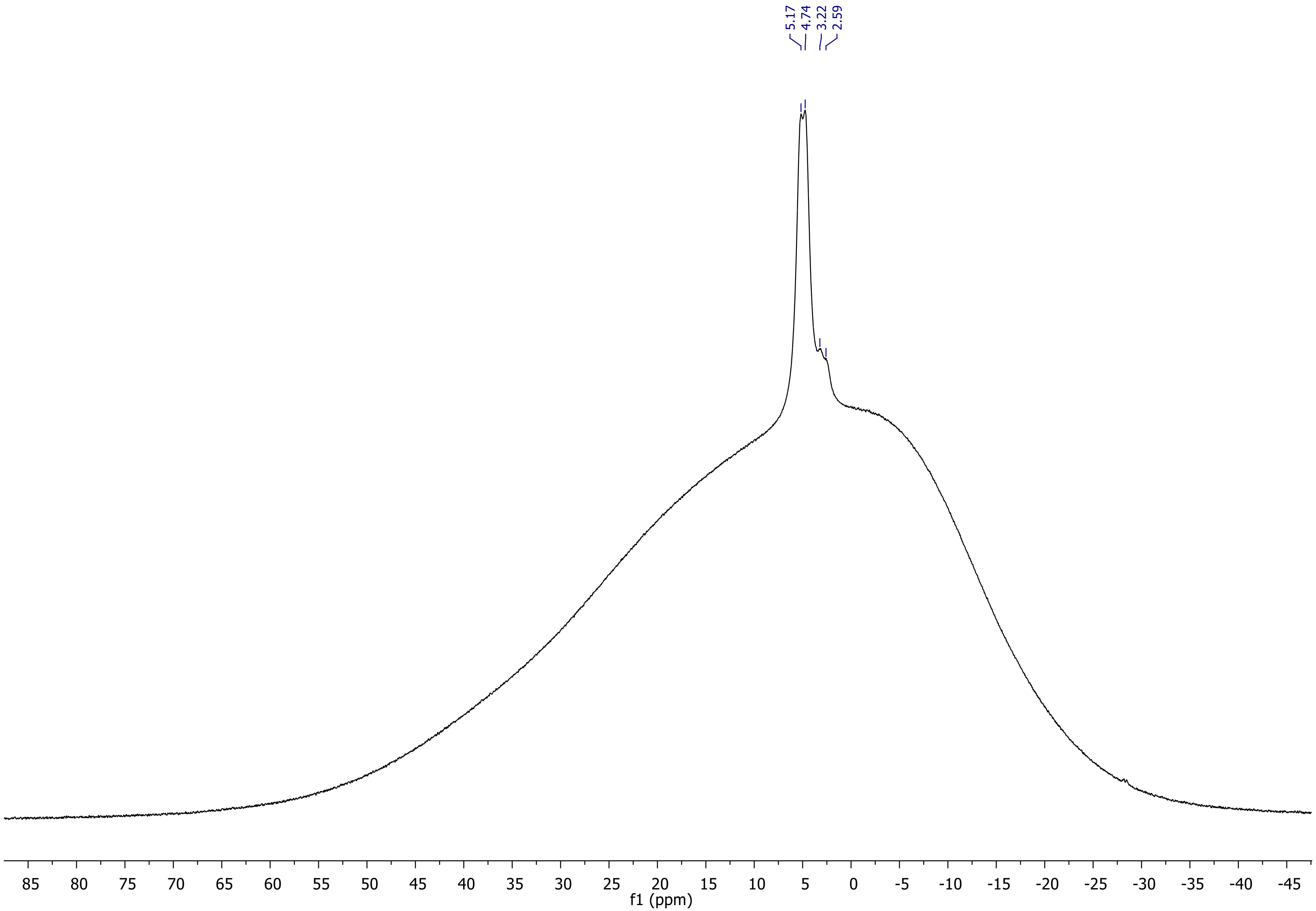


Figure S4. ^{11}B NMR spectrum of **1-PMe$_3$** in toluene-d_8.

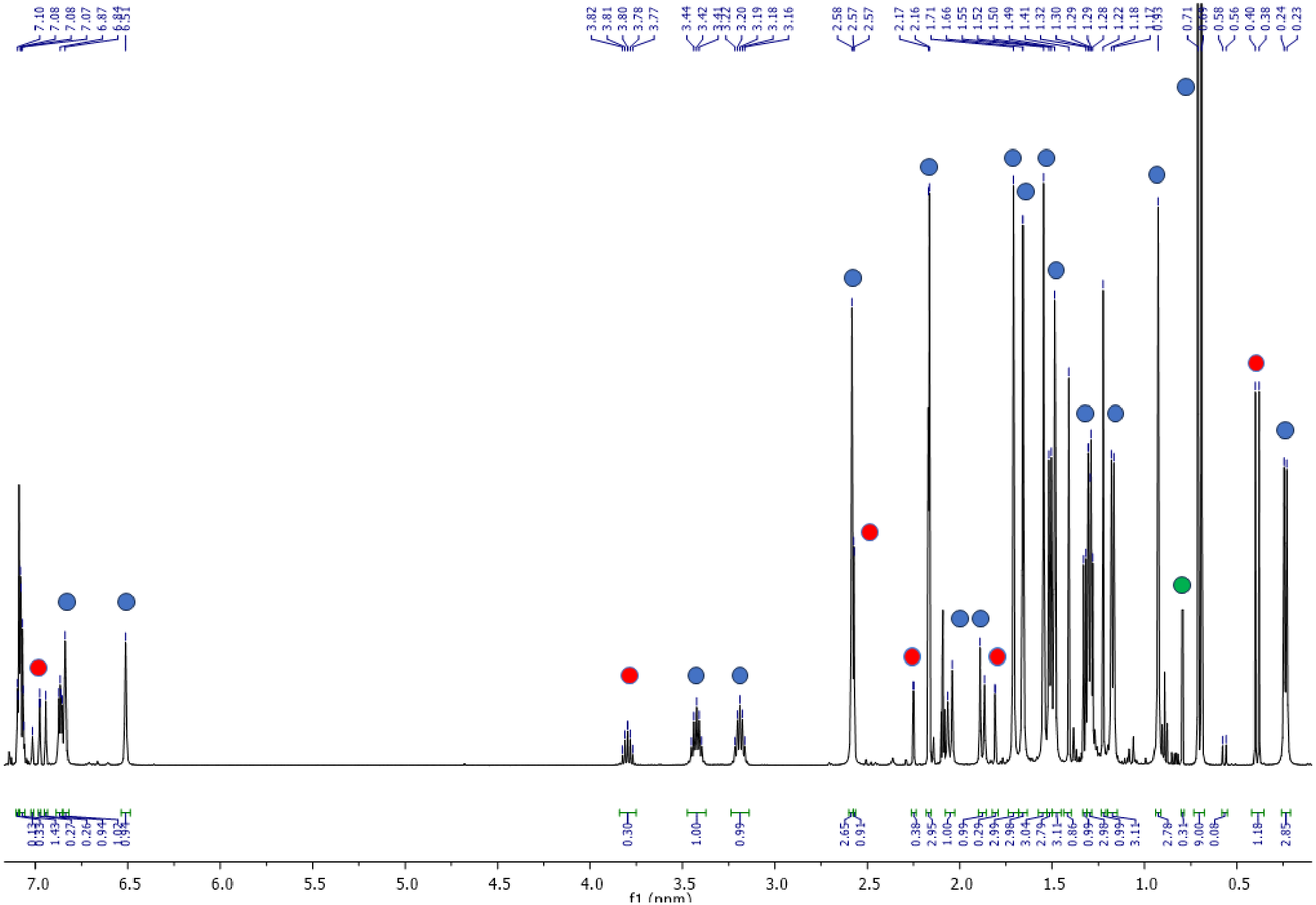


Figure S5. ^{1}H NMR spectrum of **1-PMe$_3$** in toluene-d_8, showing resonances from conformer **A** (blue dot), conformer **B** (red dot), and free **PMe$_3$** (green dot).

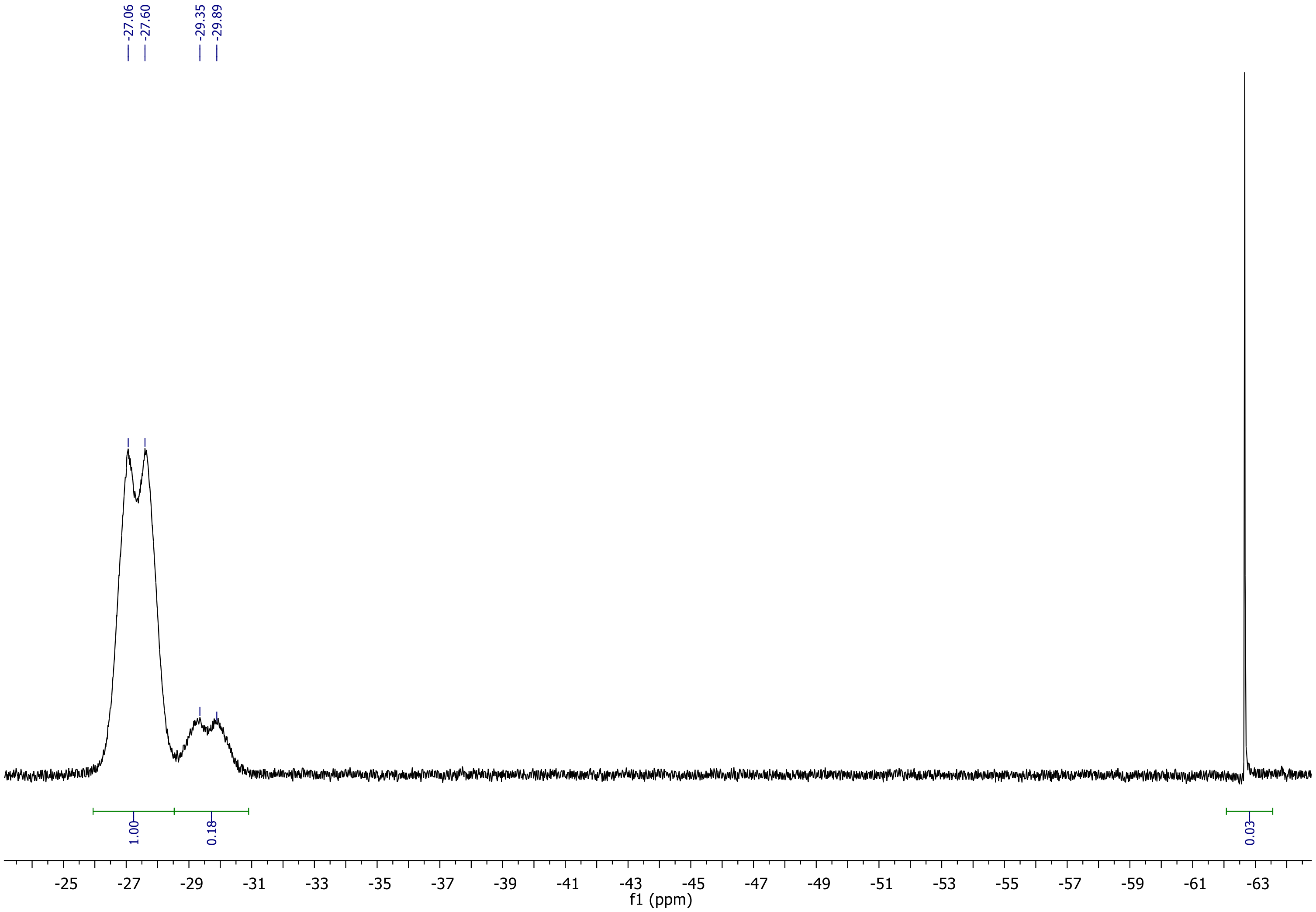


Figure S6. $^{31}P\{^1H\}$ NMR spectrum of **1-PMe$_3$** in toluene-*d*$_8$.

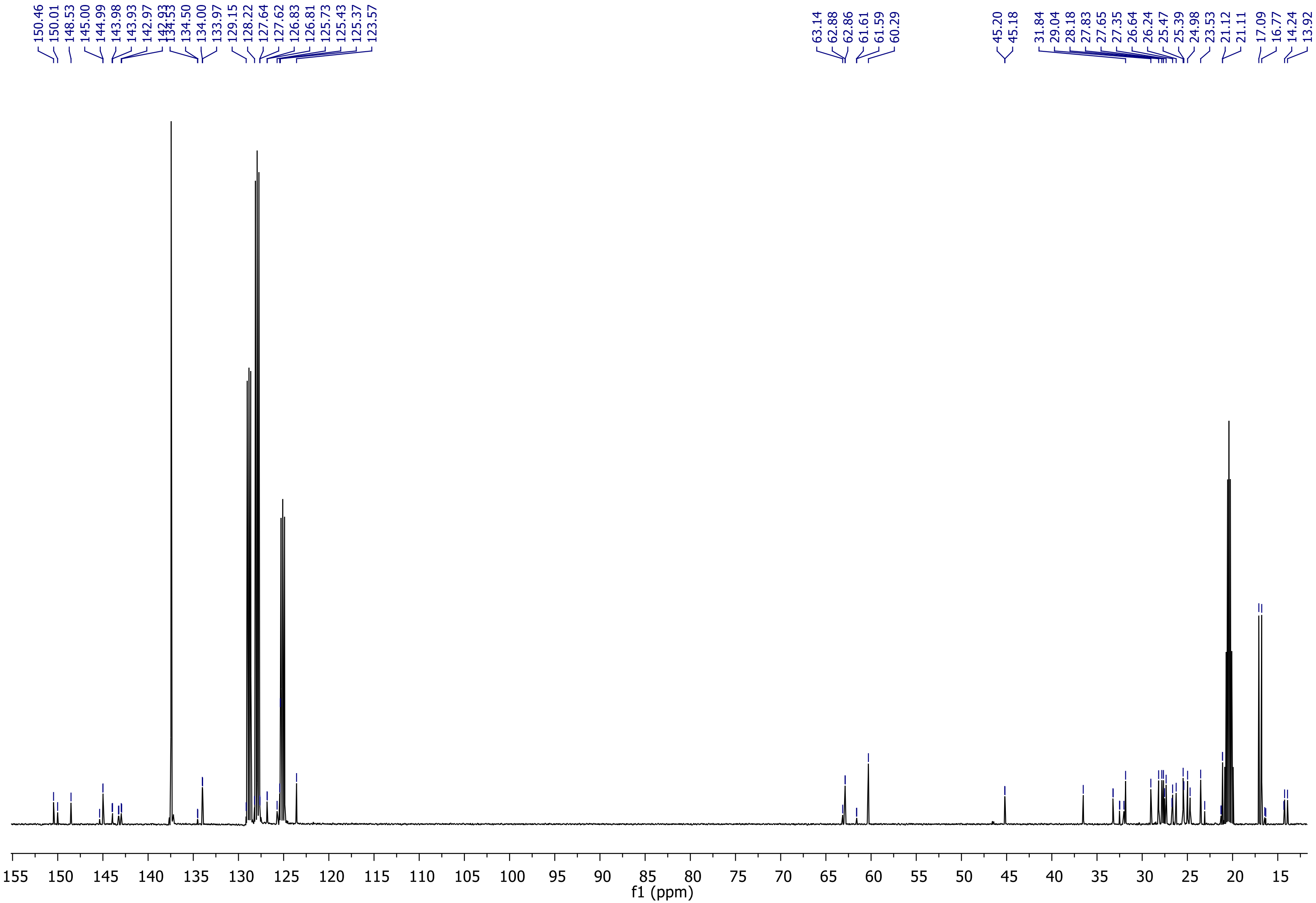


Figure S7. $^{13}C\{^1H\}$ NMR spectrum of **1-PMe$_3$** in toluene-*d*$_8$.

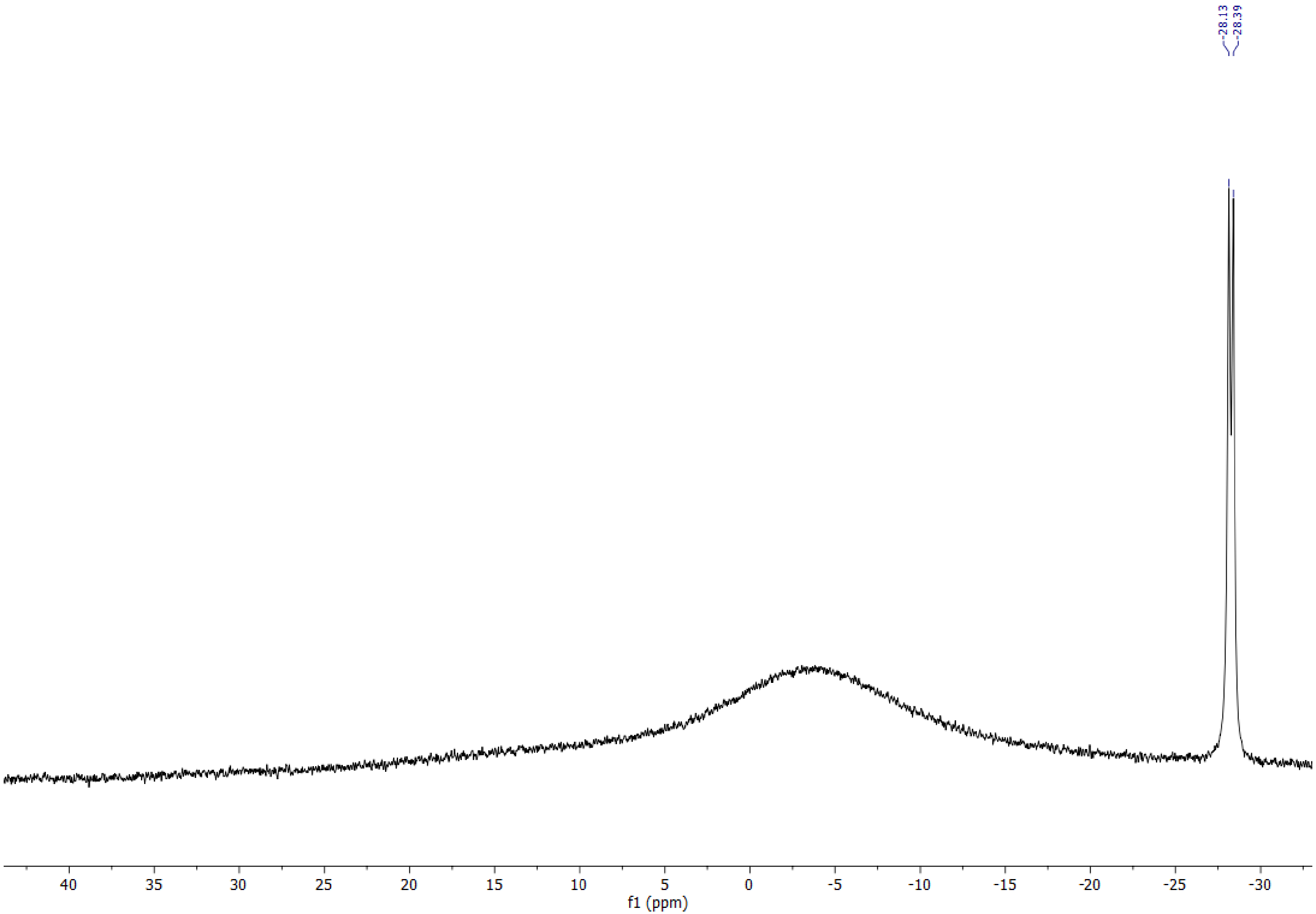


Figure S8. ^{11}B NMR spectrum of **1^{CH}-PMe$_3$** in C_6D_6.

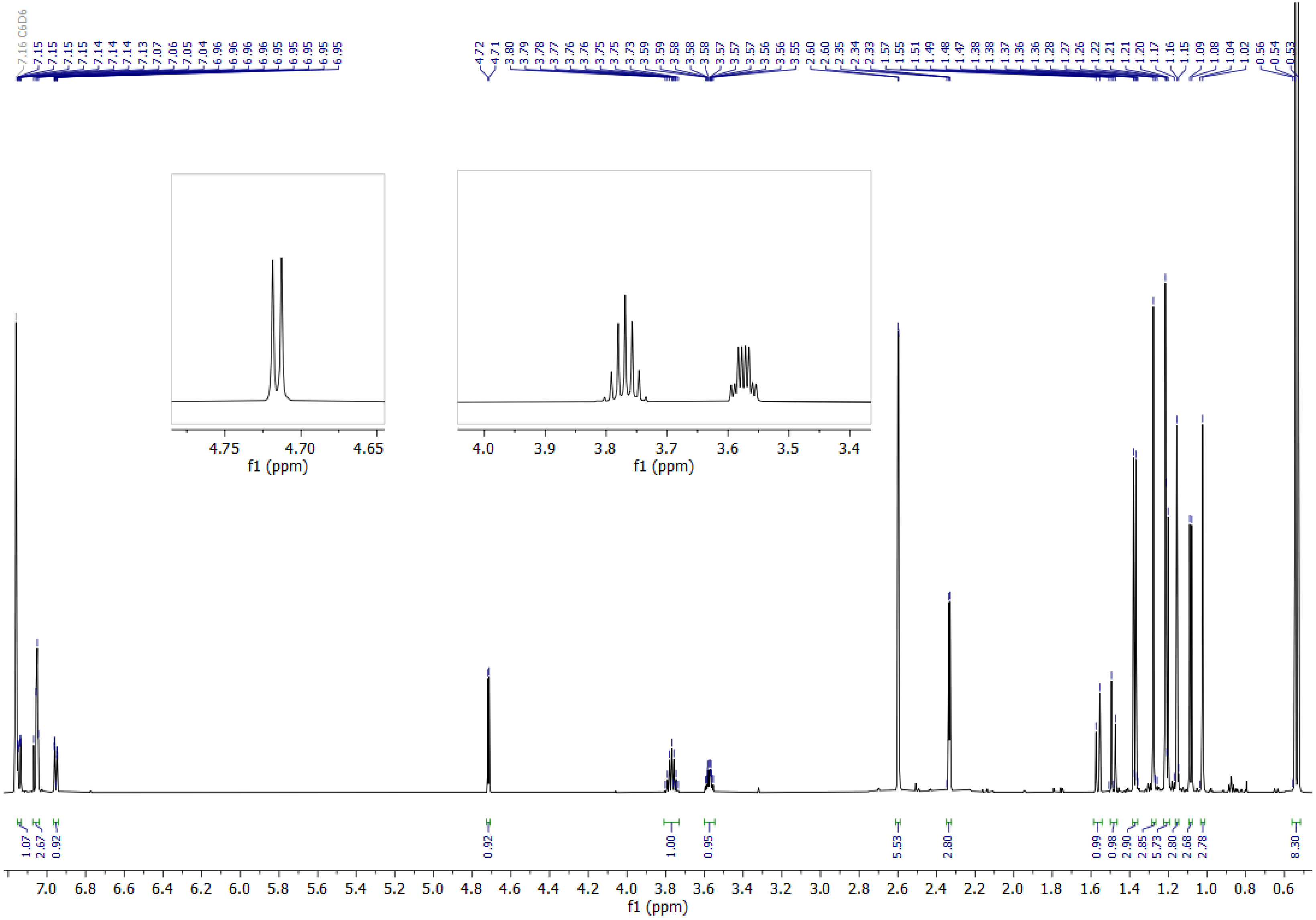


Figure S9. ^{1}H NMR spectrum of $\mathbf{1^{CH}\text{-}PMe_3}$ in C_6D_6.

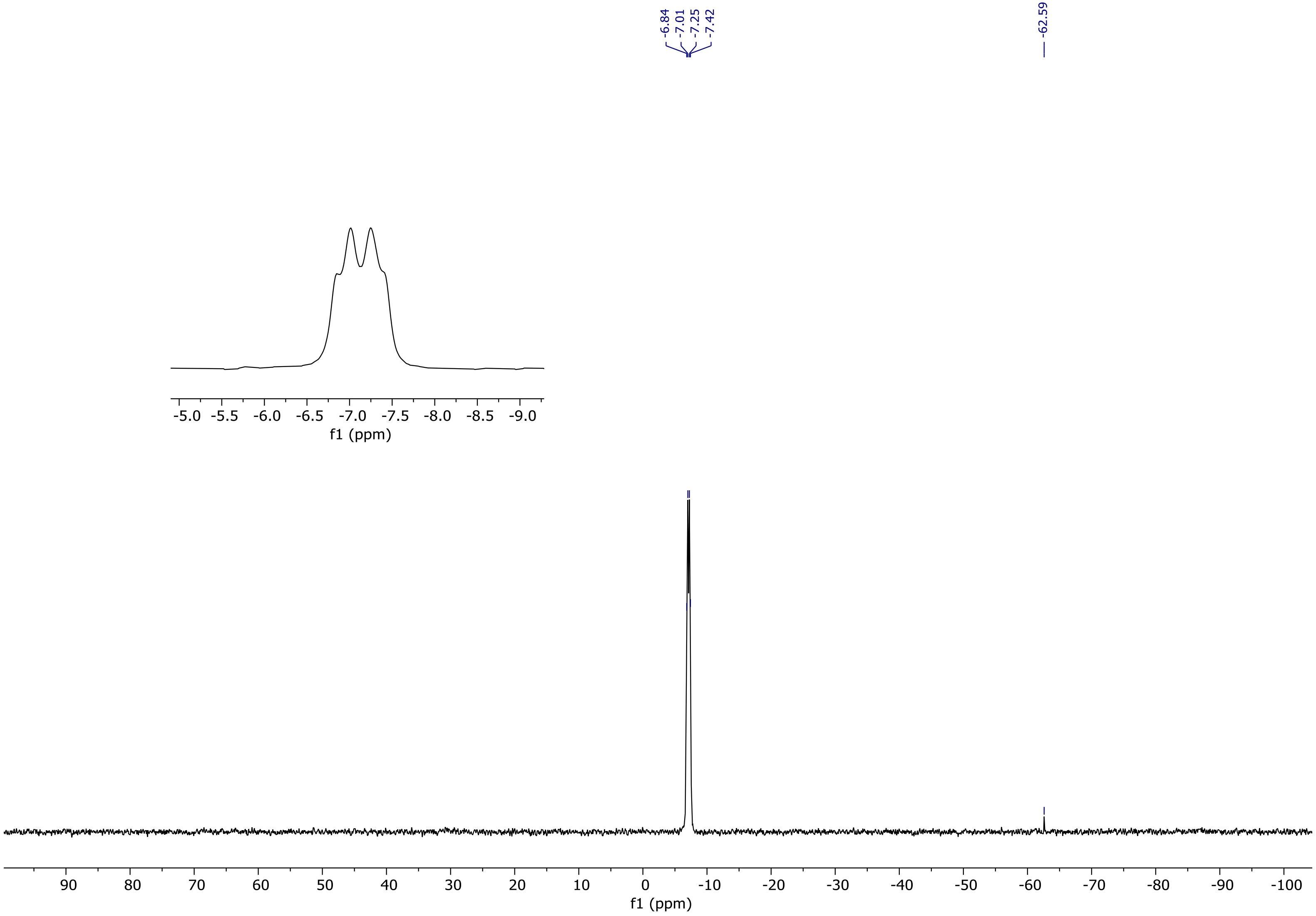


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **1^{CH}-PMe$_3$** in C_6D_6.

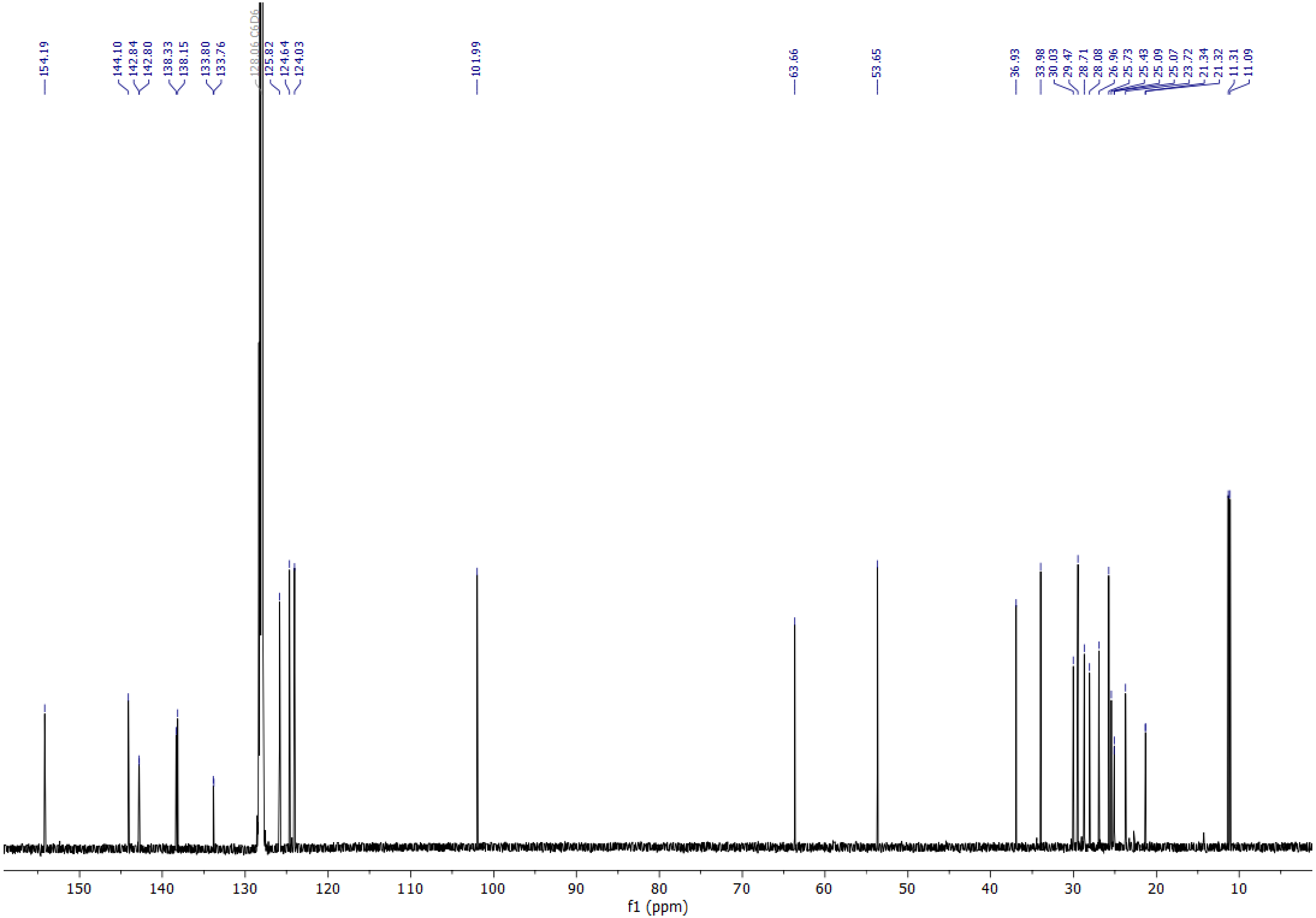


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{1^{CH}\text{-}PMe_3}$ in C_6D_6.

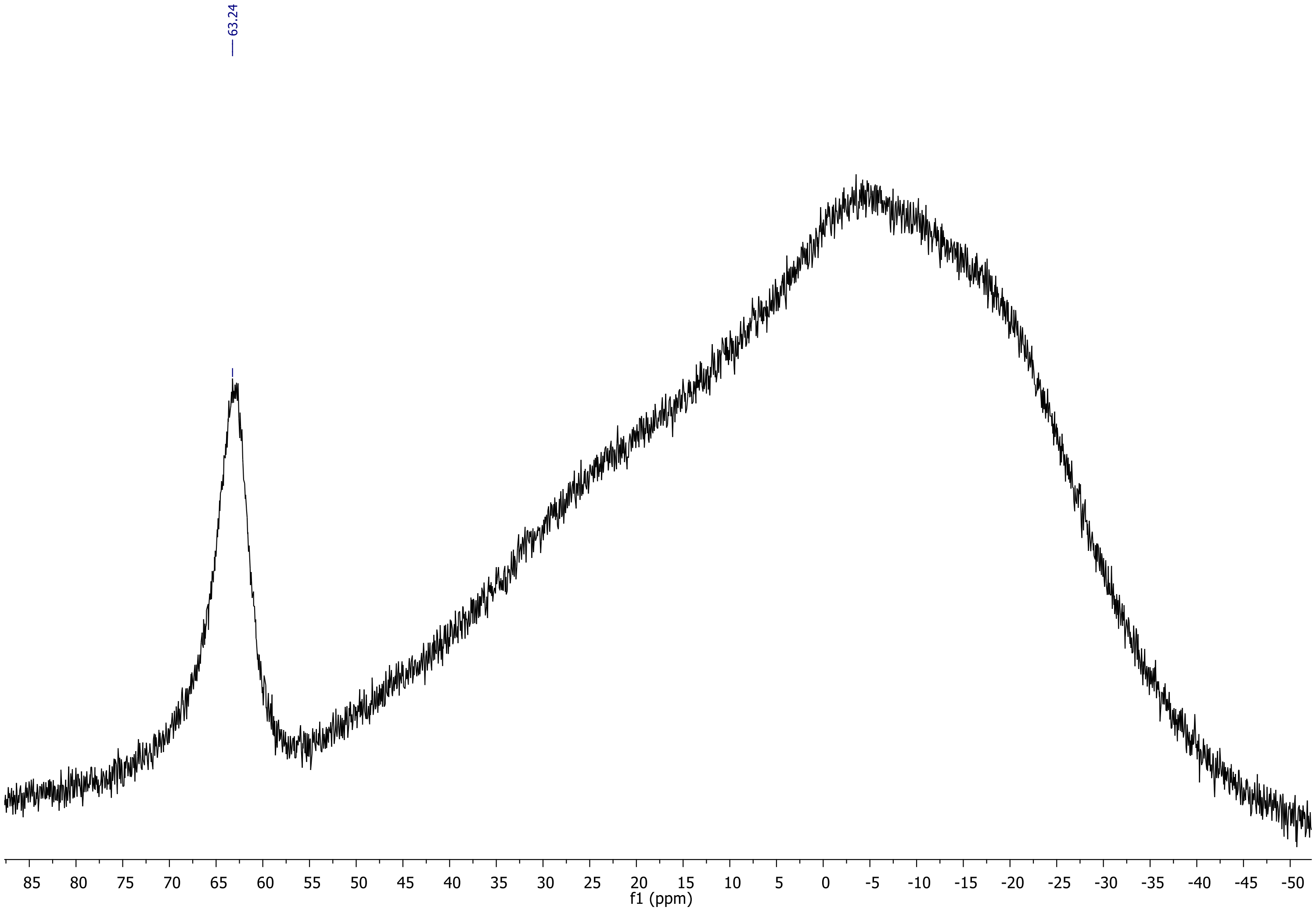


Figure S12. ^{11}B NMR spectrum of **1-S** in toluene-d_8.

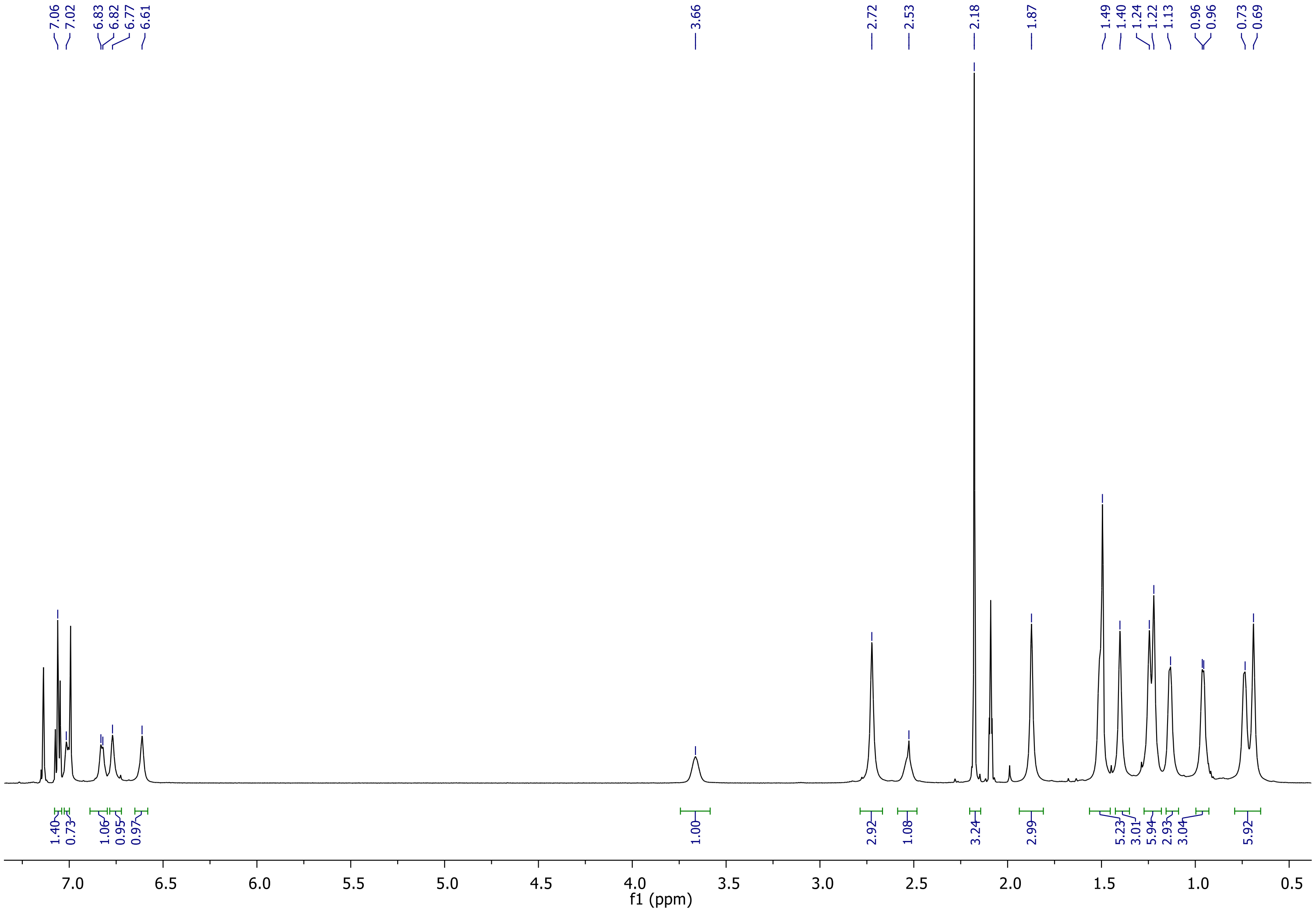


Figure S13. ^{1}H NMR spectrum of **1-S** in toluene-d_8 at −40 °C.

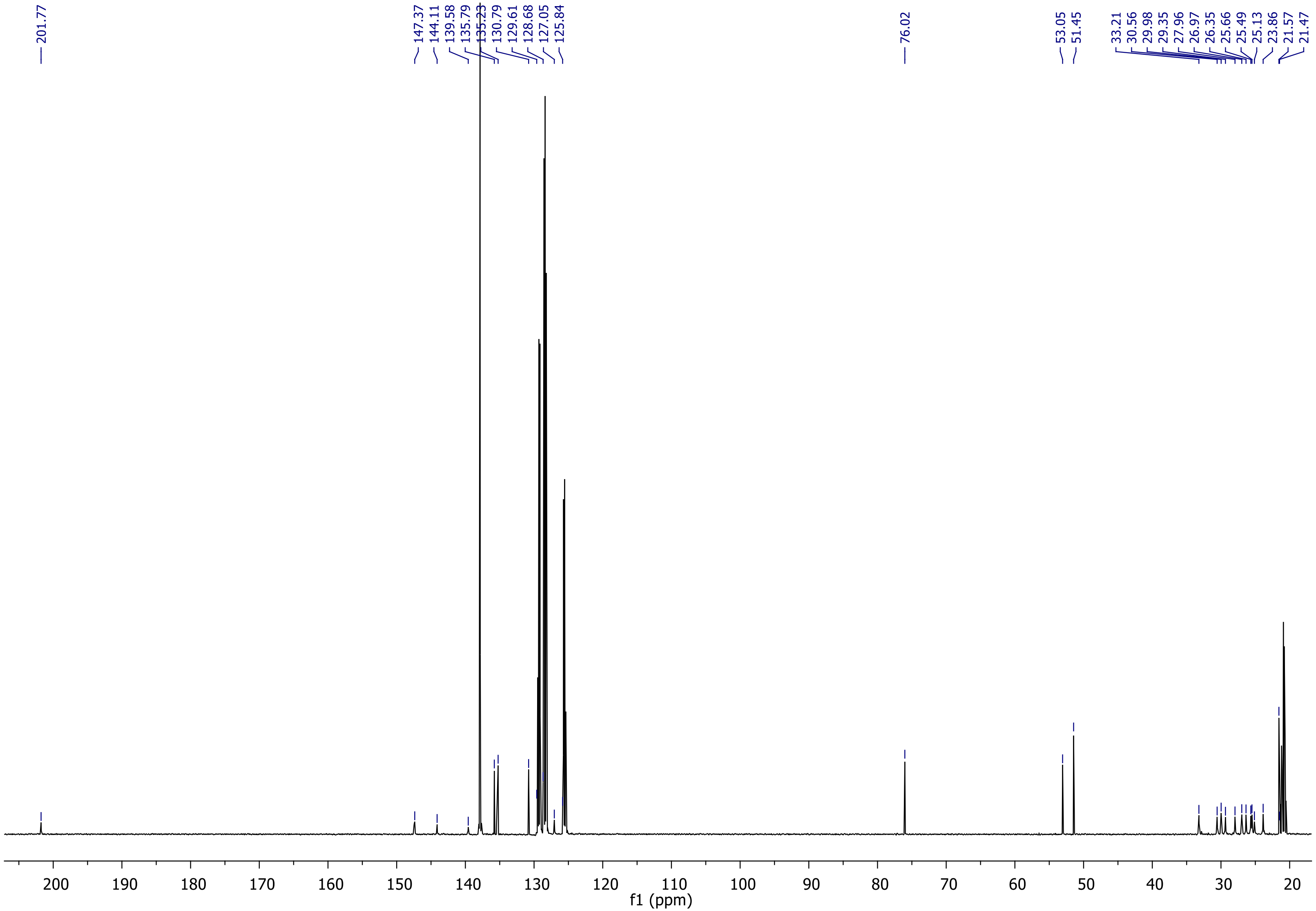


Figure S14. $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **1-S** in toluene-d_8 at −40 °C.

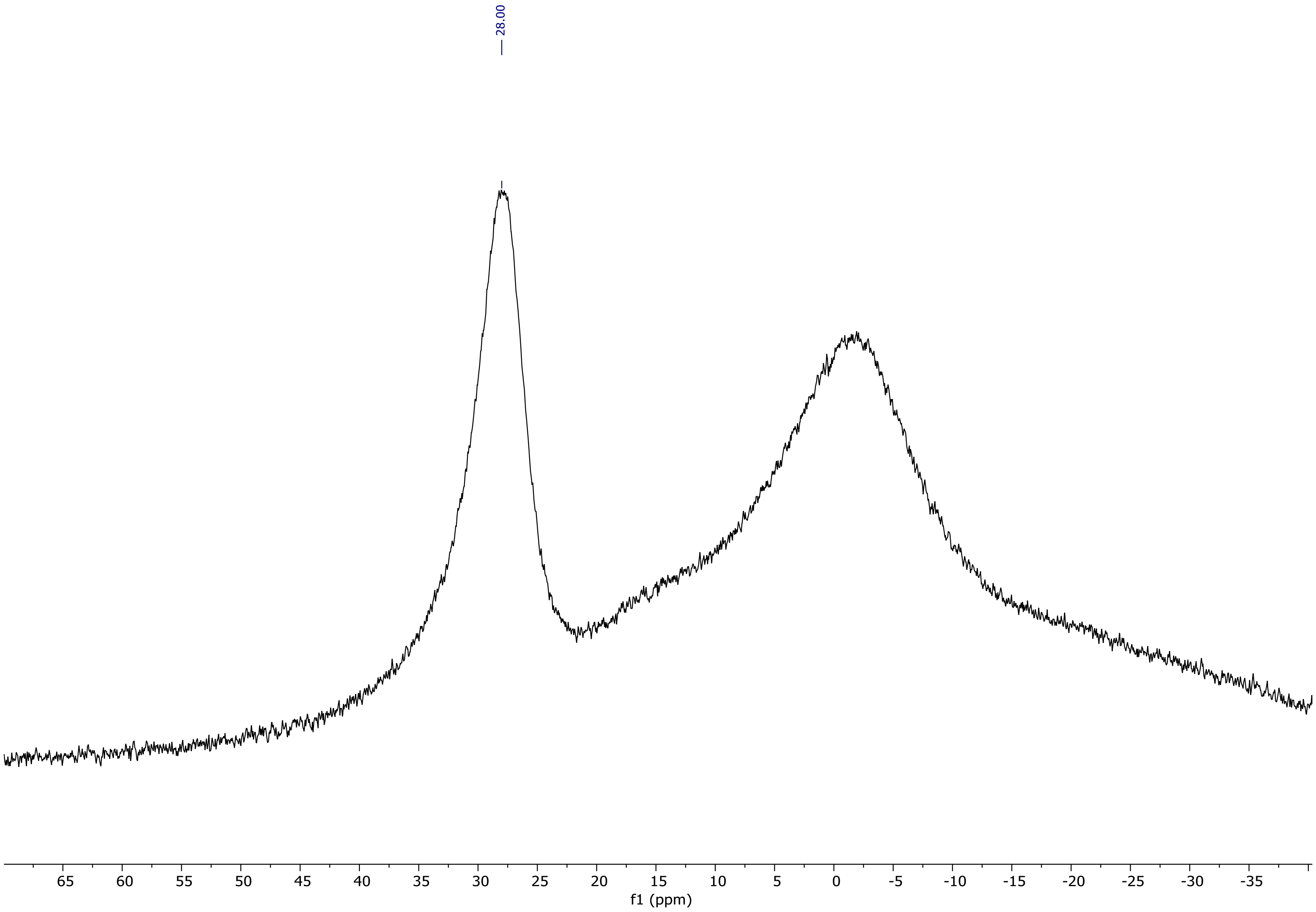


Figure S15. ^{11}B NMR spectrum of **Li$_2$[1-S]** in THF-d_8 at −40 °C.

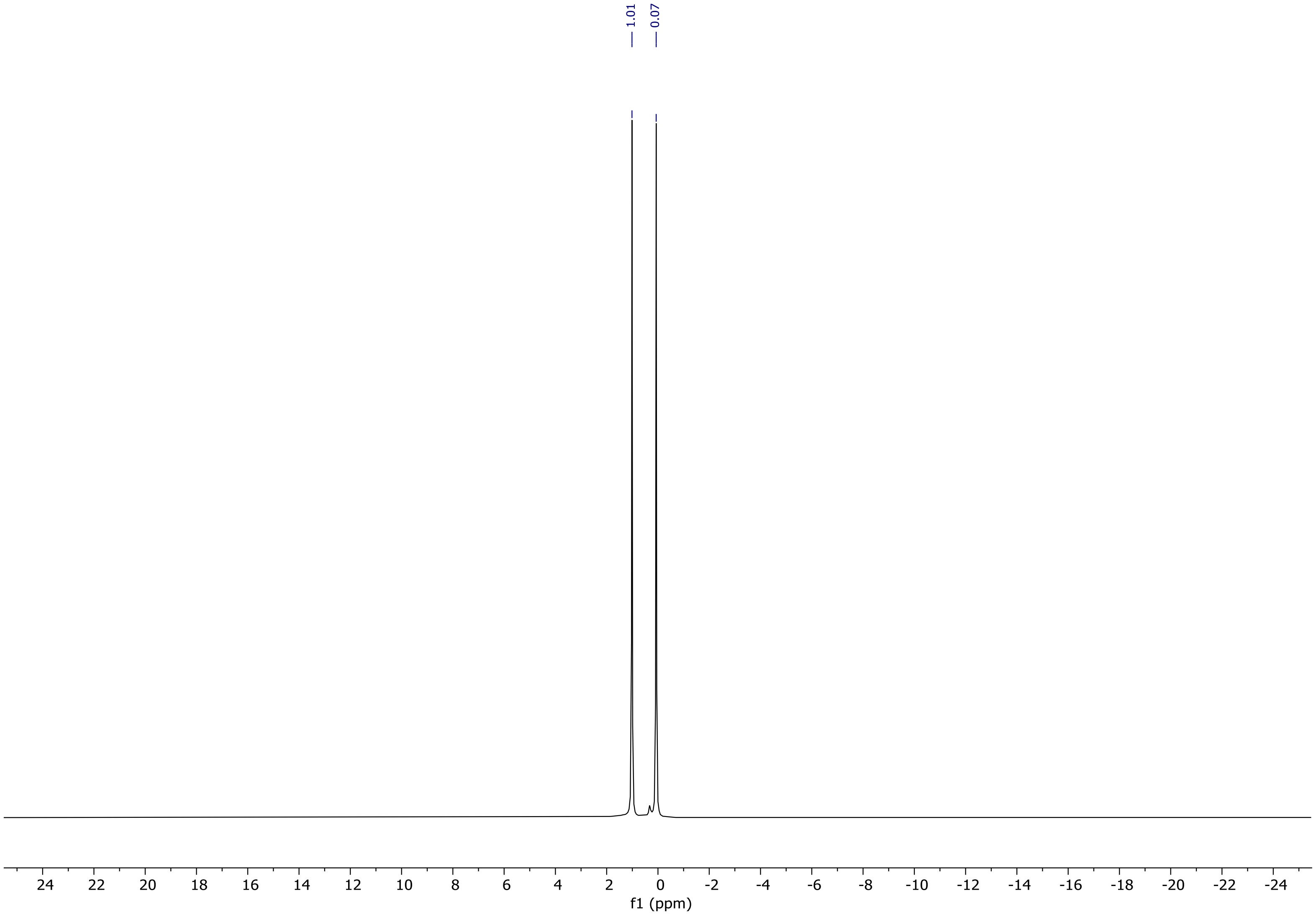


Figure S16. ^{7}Li NMR spectrum of **Li$_2$[1-S]** in THF-d_8 at −40 °C.

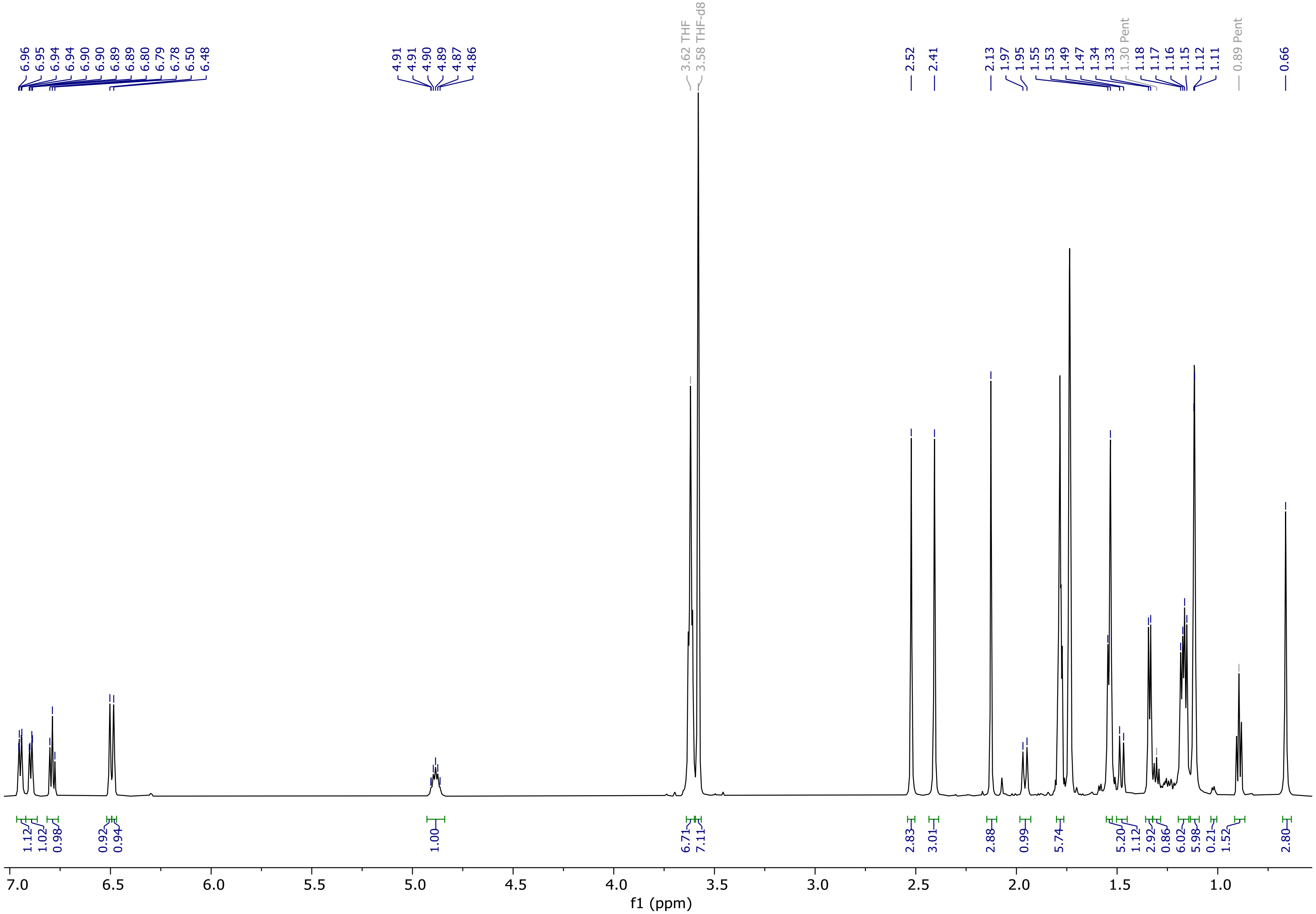


Figure S17. ^{1}H NMR spectrum of **Li$_2$[1-S]** in THF-d_8 at −40 °C.

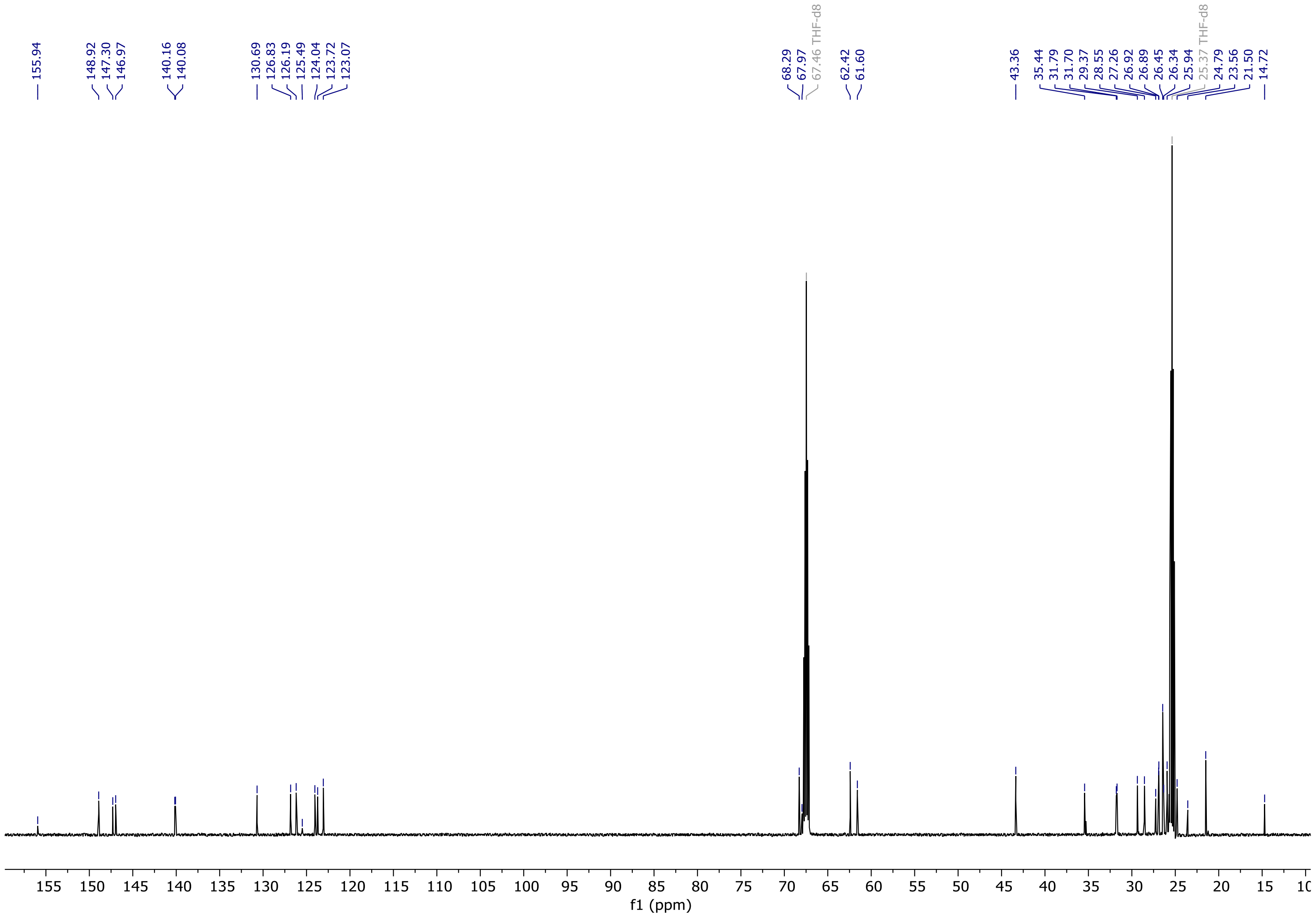


Figure S18. ^{13}C NMR spectrum of **Li$_2$[1-S]** in THF-d_8 at −40 °C.

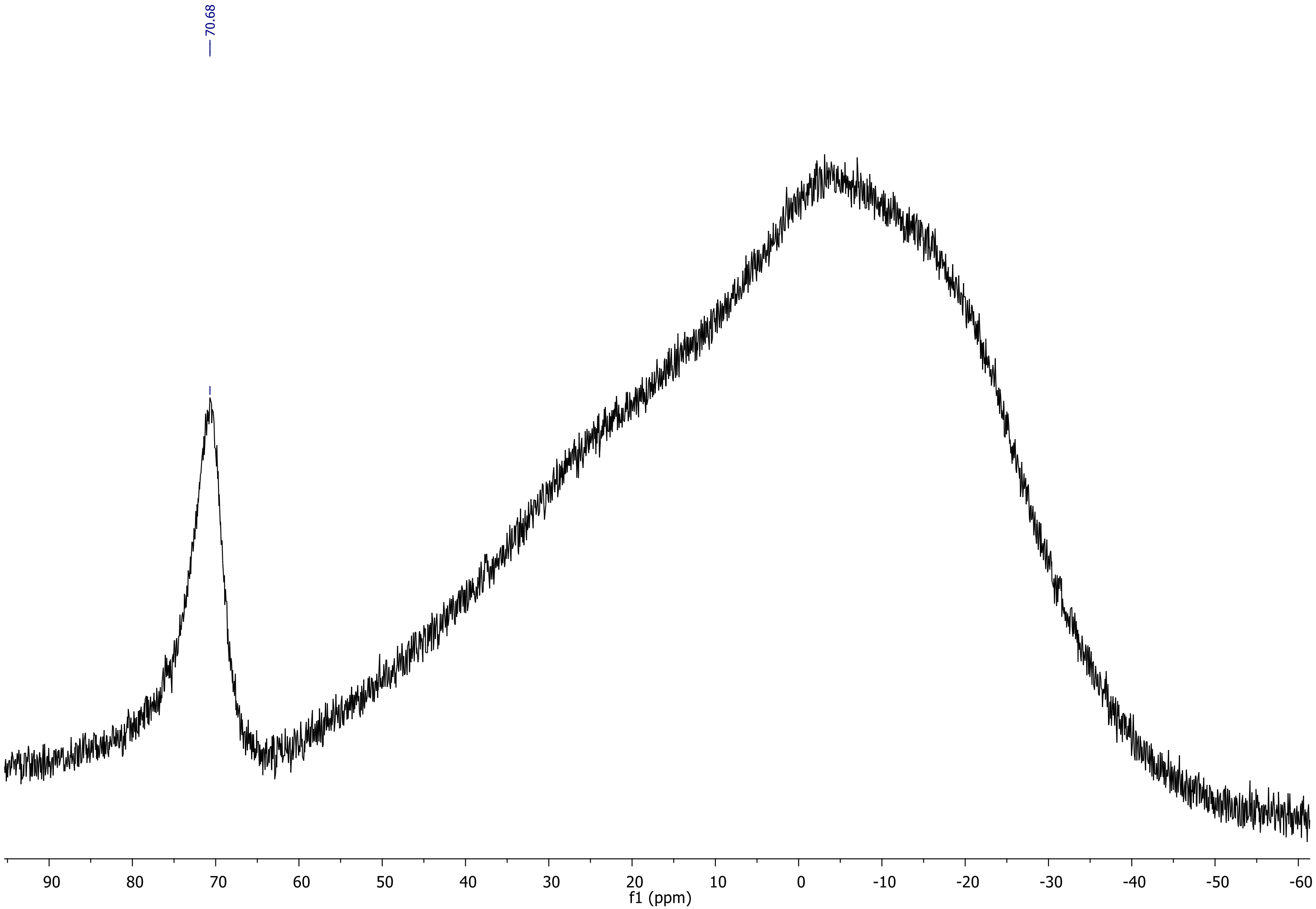


Figure S19. ^{11}B NMR spectrum of **1-Se** in toluene-d_8.

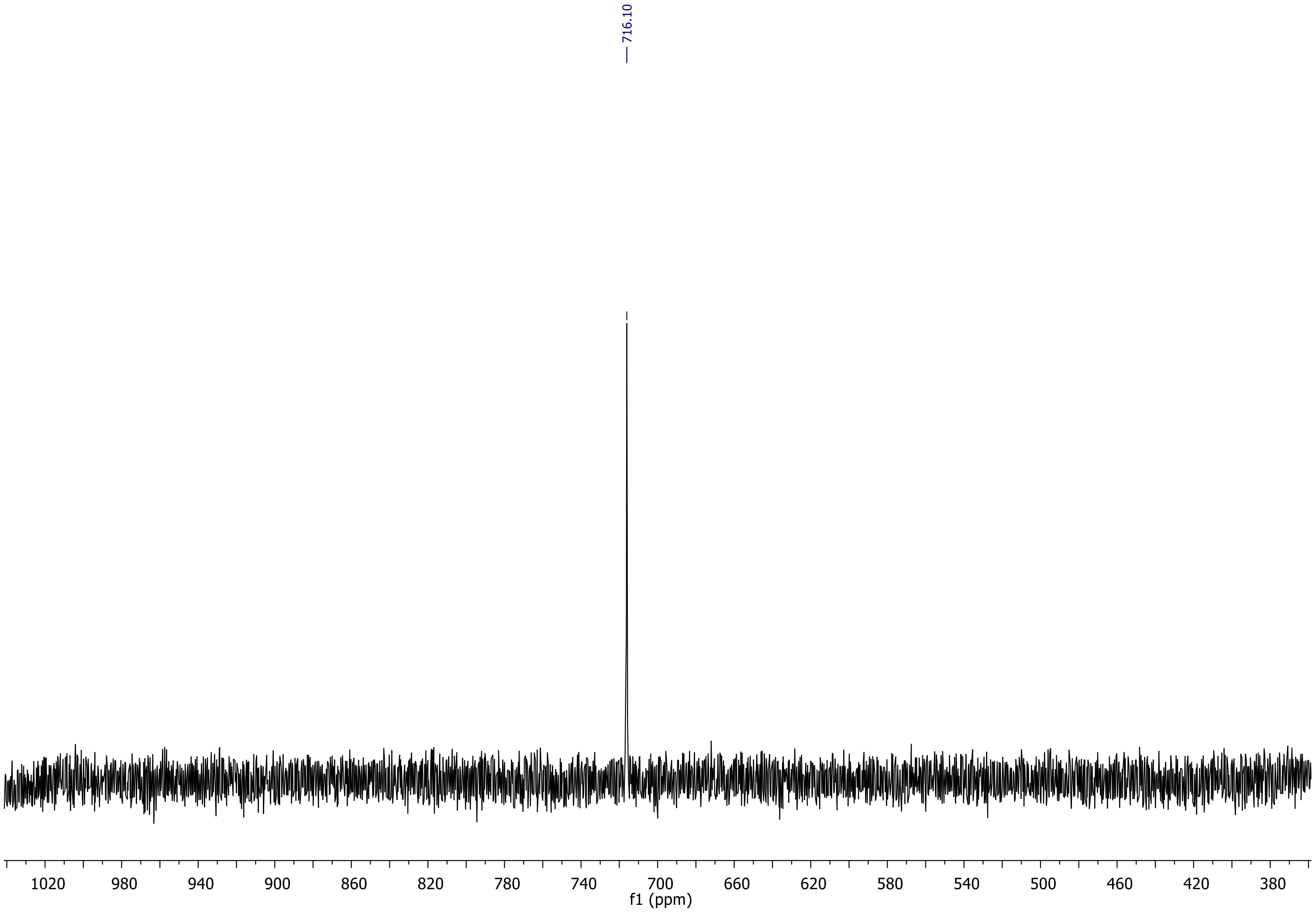


Figure S20. ^{77}Se{^{1}H,^{11}B} NMR spectrum of **1-Se** in toluene-d_8 at −40 °C.

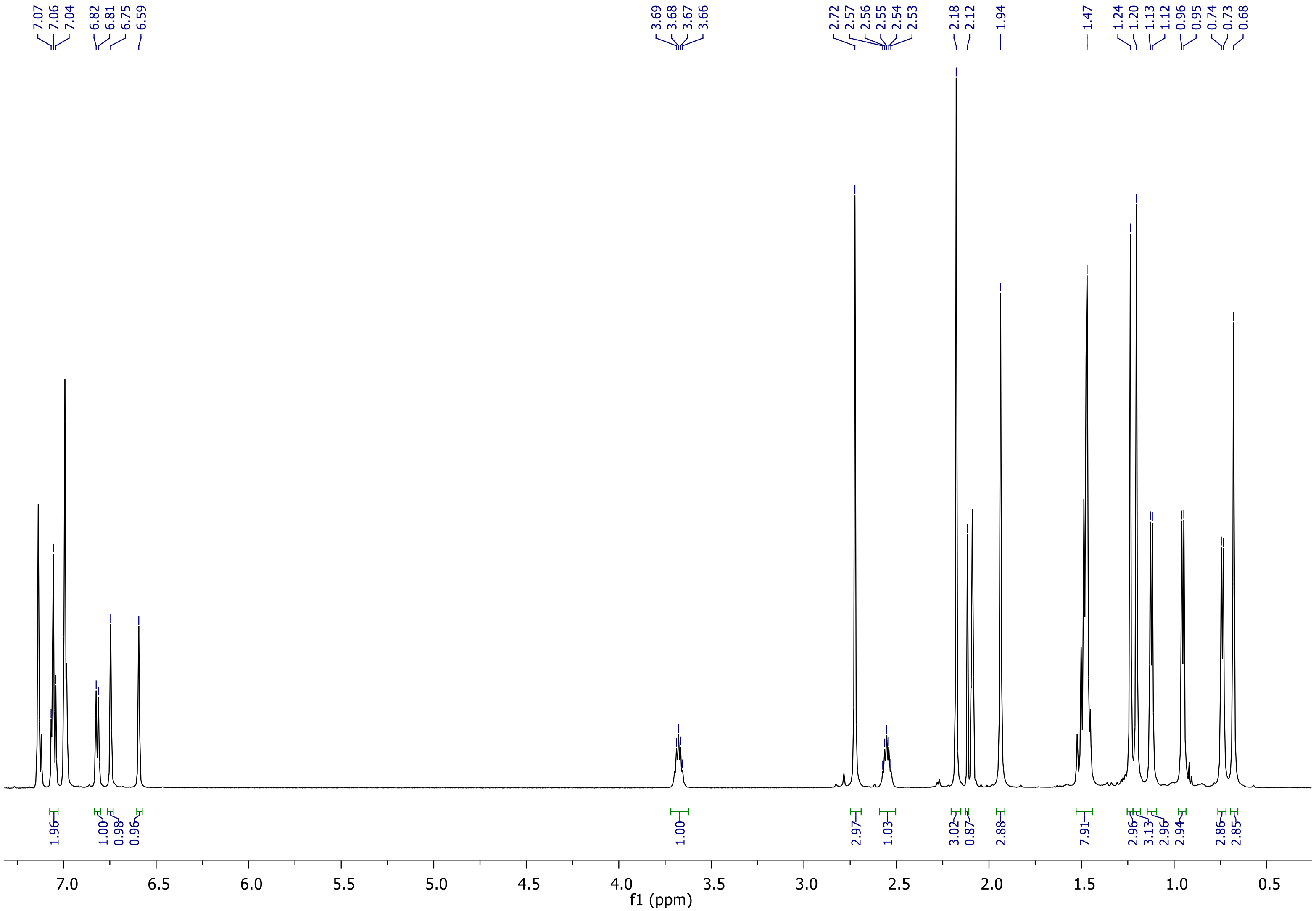


Figure S21. ^{1}H NMR spectrum of **1-Se** in toluene-d_8 at −40 °C.

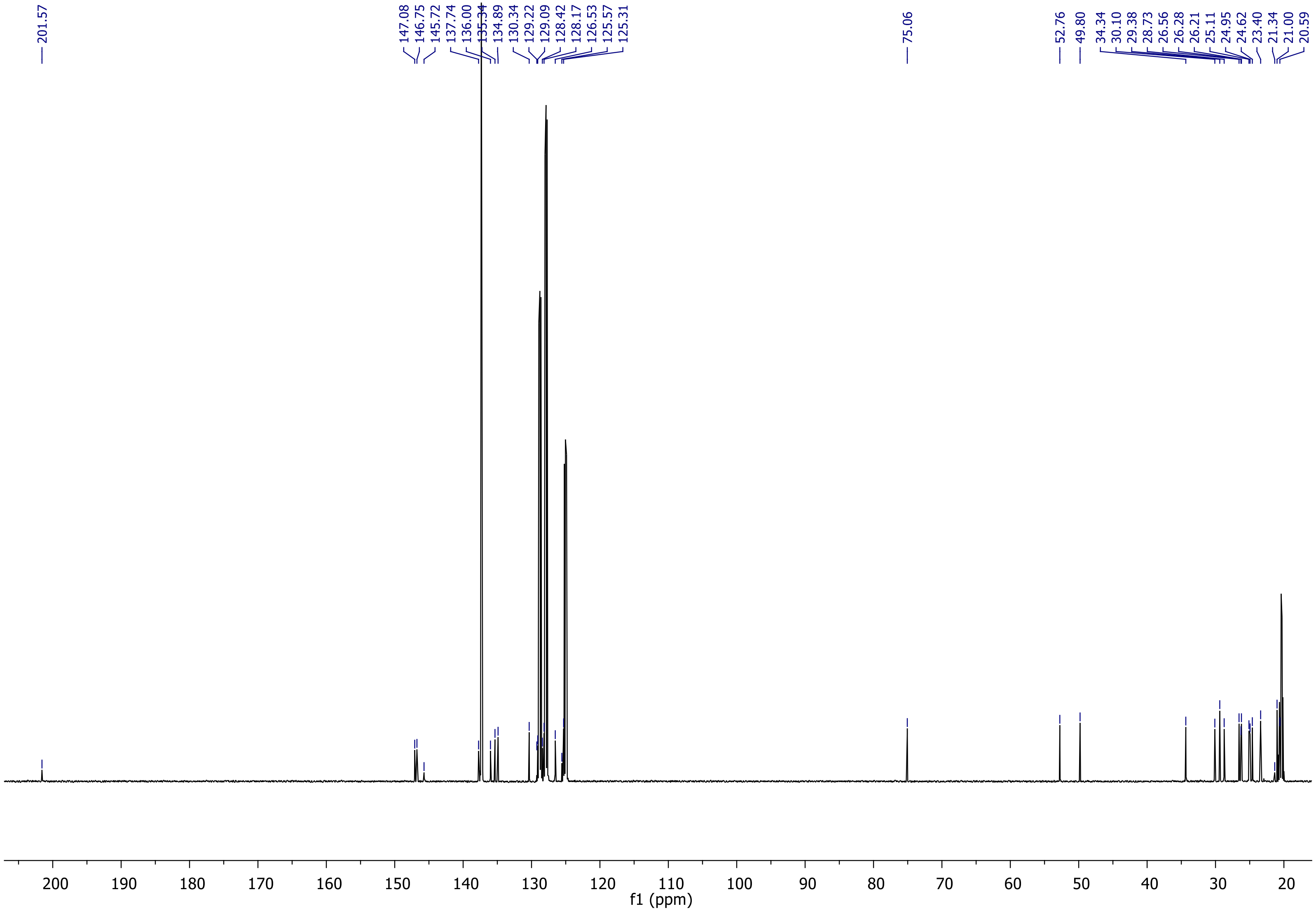


Figure S22. $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **1-Se** in toluene-d_8 at −40 °C.

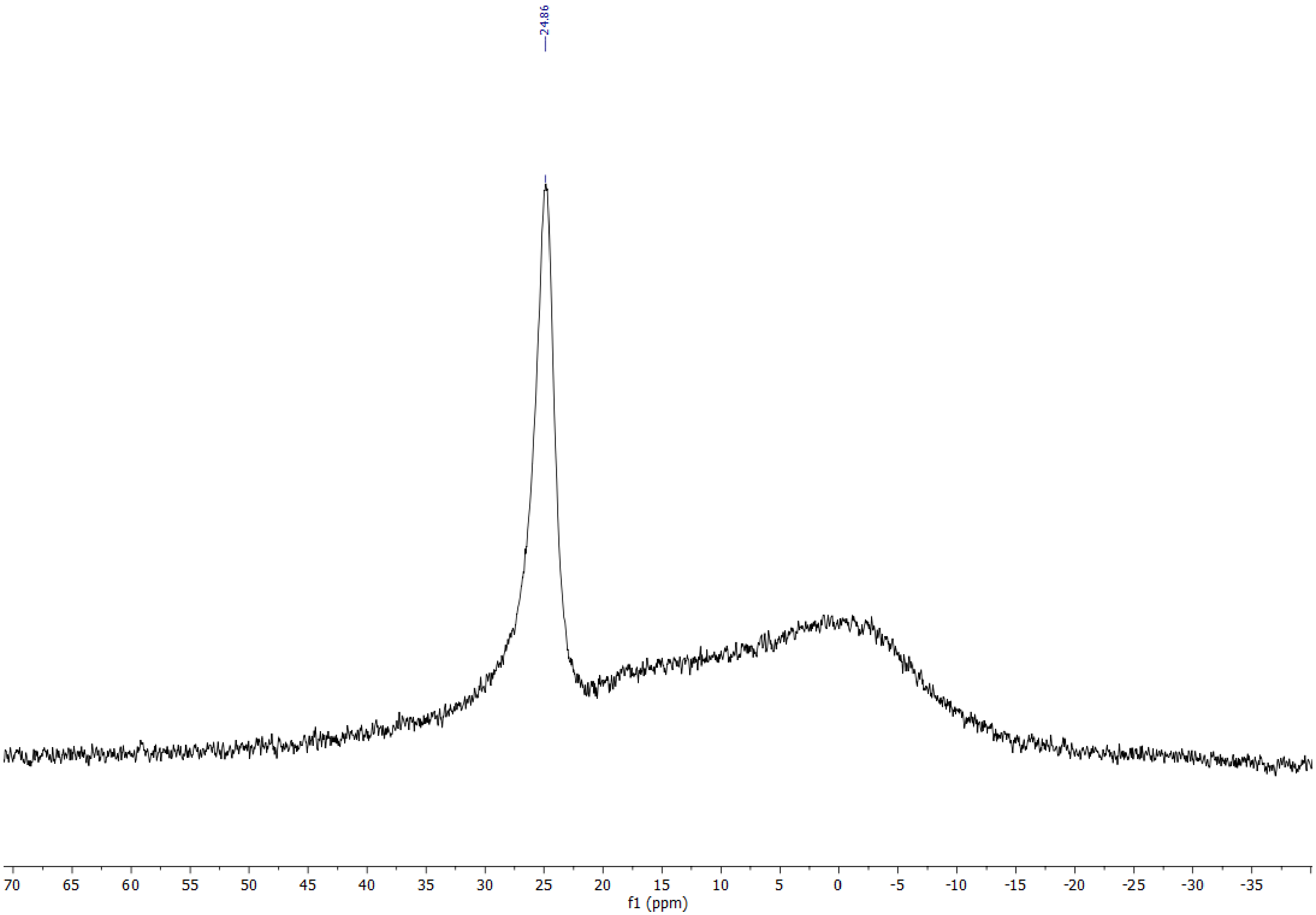


Figure S23. ^{11}B NMR spectrum of **Li_2[1-Se]** in THF-d_8 at −40 °C.

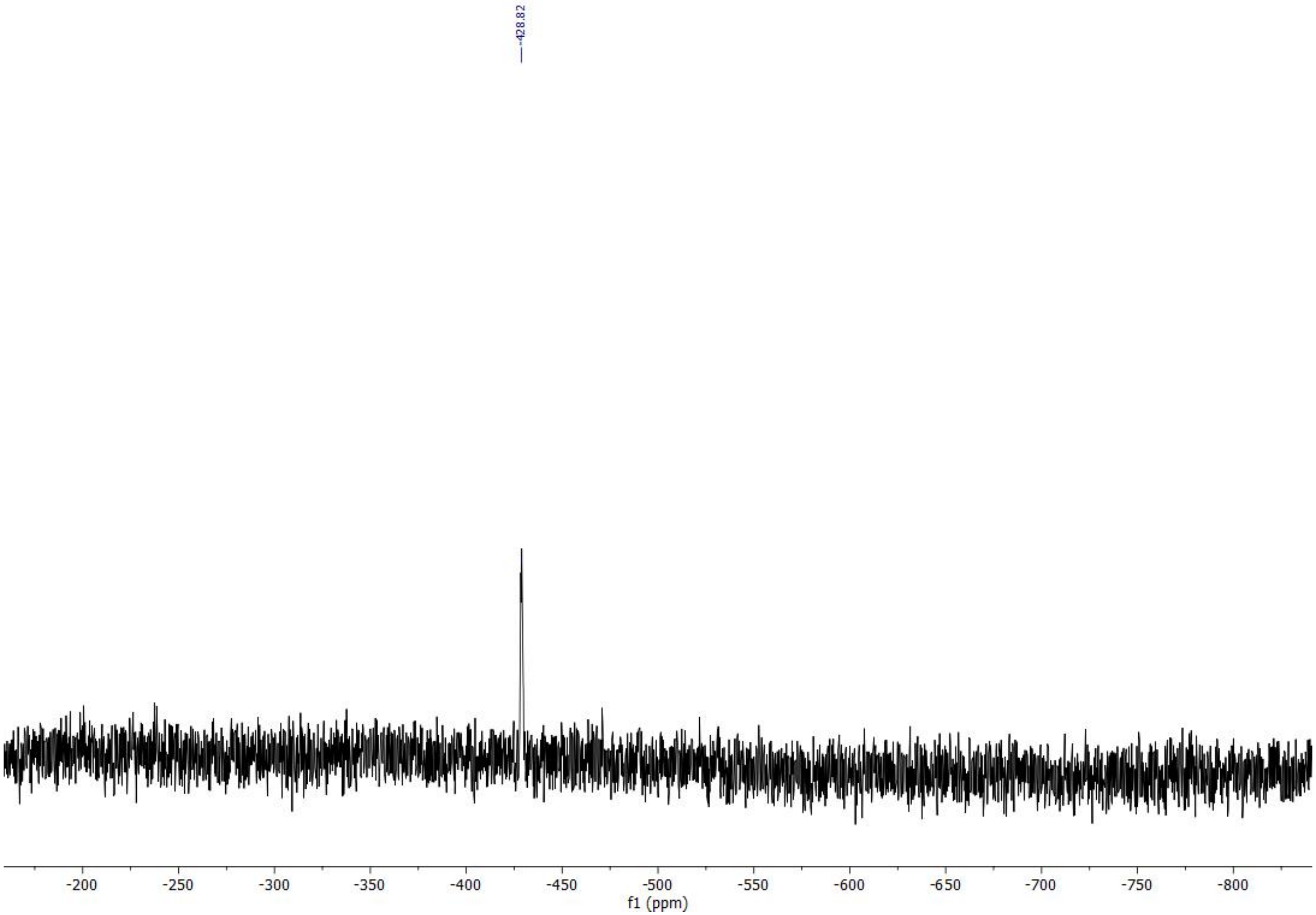


Figure S24. ^{77}Se{^{1}H,^{11}B} NMR spectrum of **Li$_2$[1-Se]** in THF-d_8 at −40 °C.

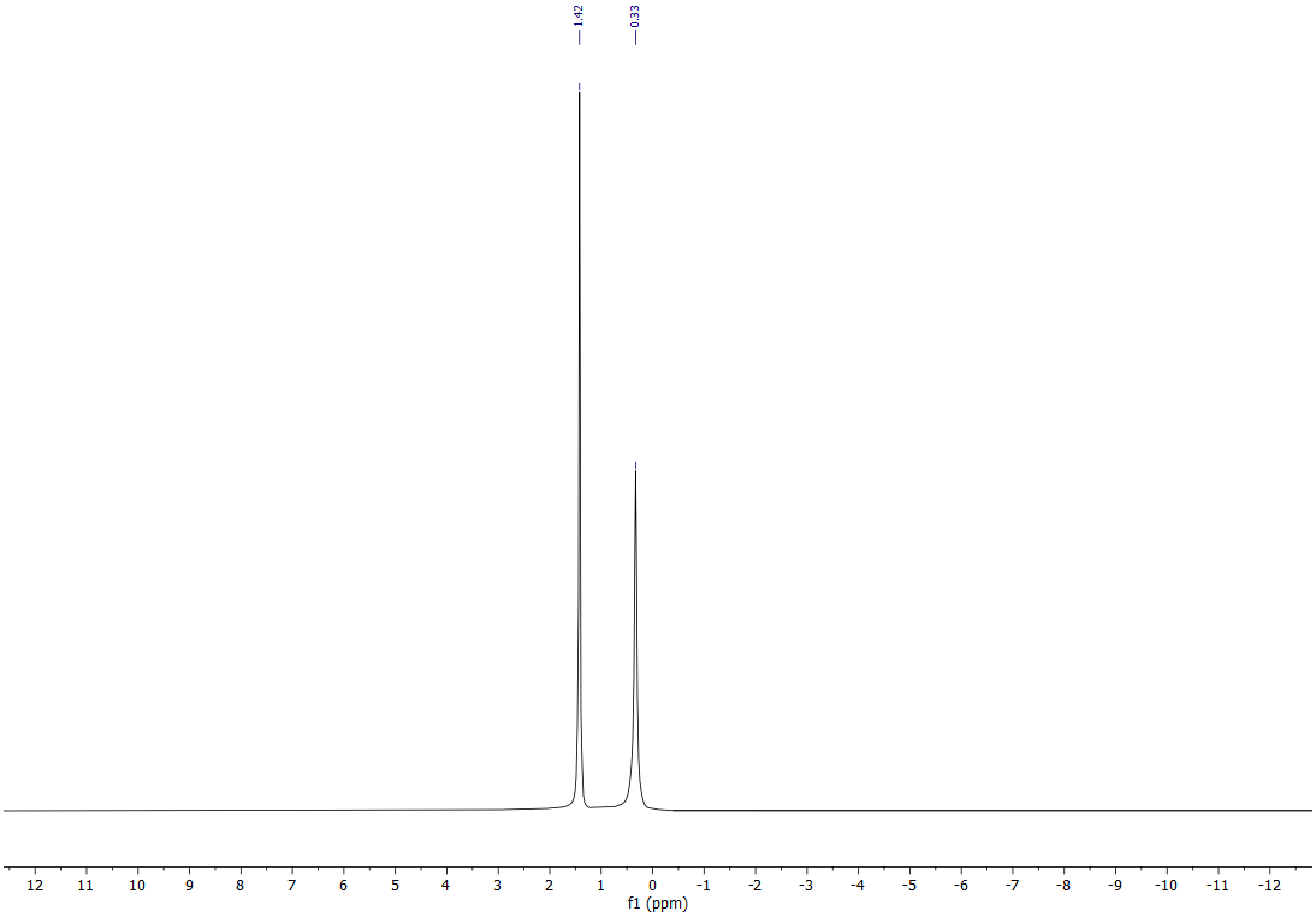


Figure S25. ^{7}Li NMR spectrum of **Li$_2$[1-Se]** in THF-d_8 at −40 °C.

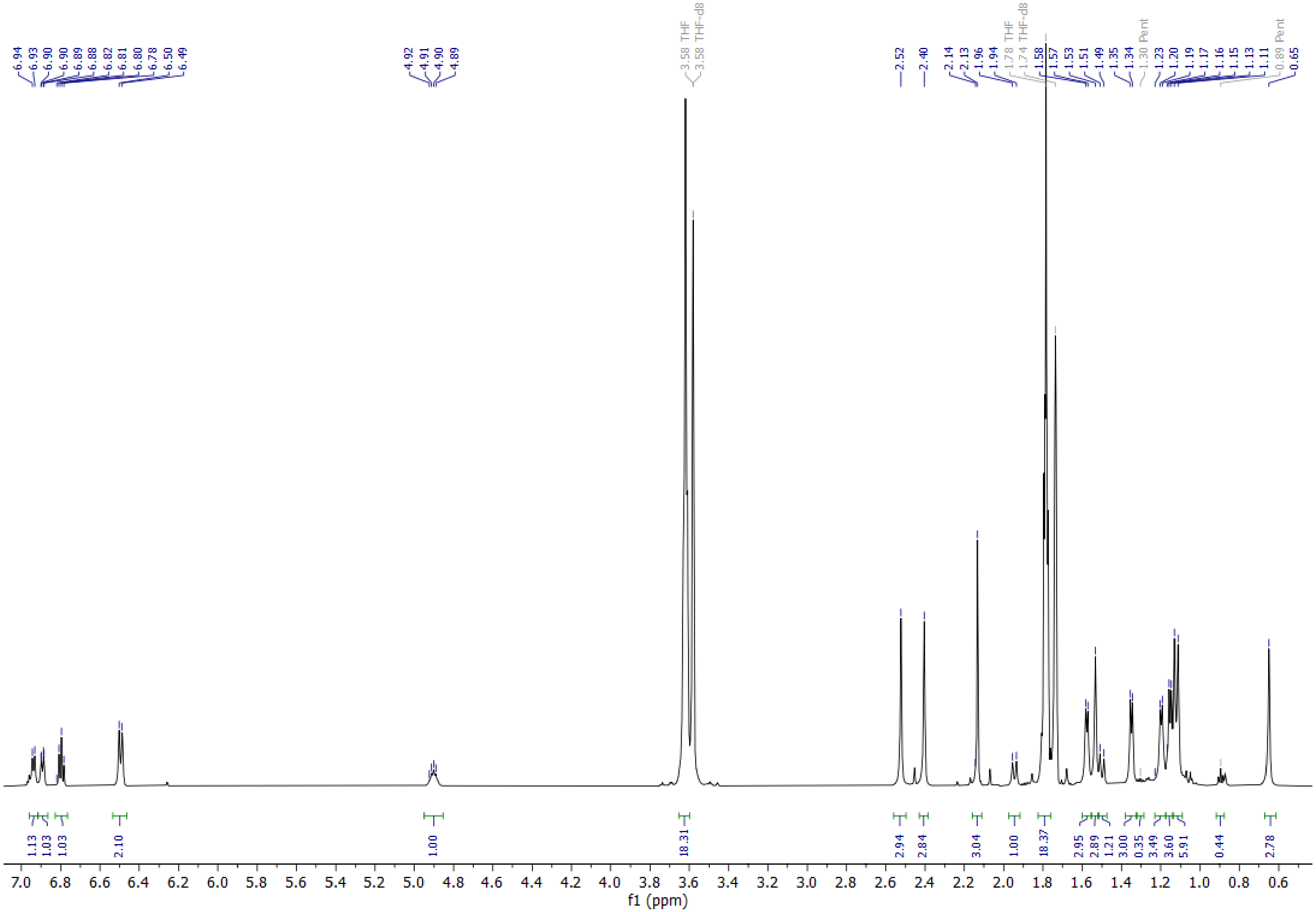


Figure S26. ^{1}H NMR spectrum of **Li$_2$[1-Se]** in THF-d_8 at −40 °C.

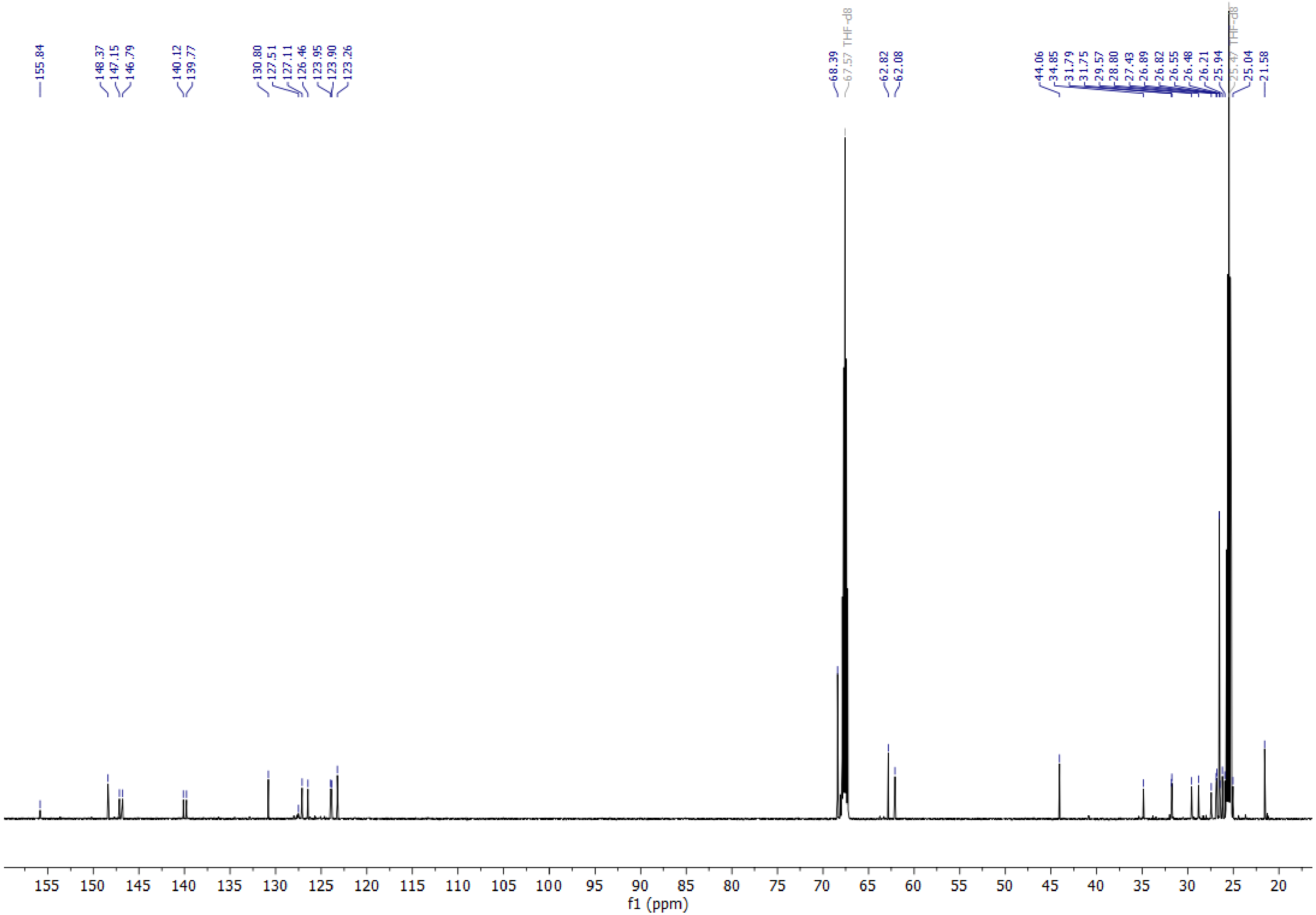


Figure S27. $^{13}C\{^1H\}$ NMR spectrum of **Li$_2$[1-Se]** in THF-d_8 at −40 °C.

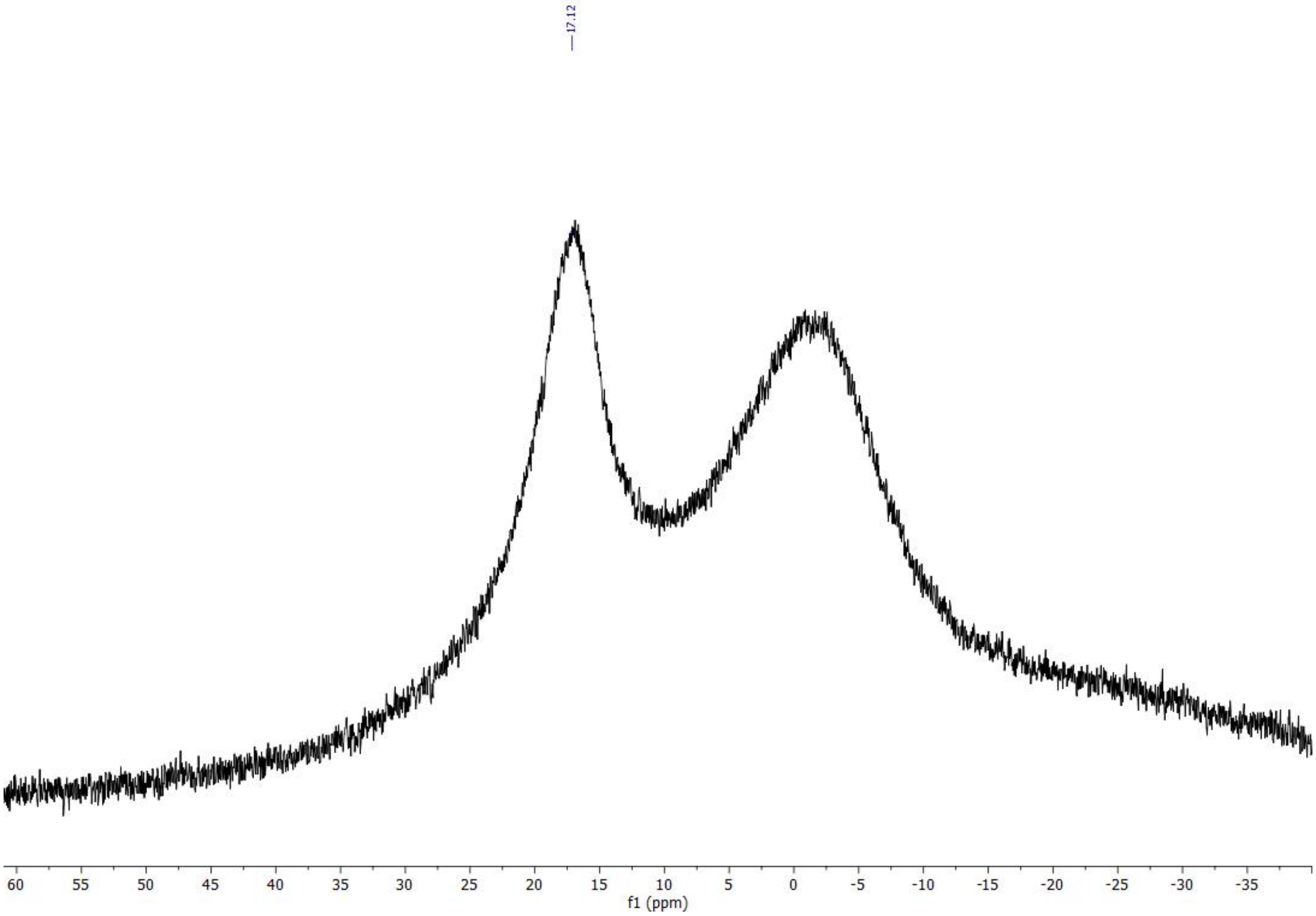


Figure S28. ^{11}B NMR spectrum of **Li$_2$[1-Te]** in THF-d_8 at −40 °C.

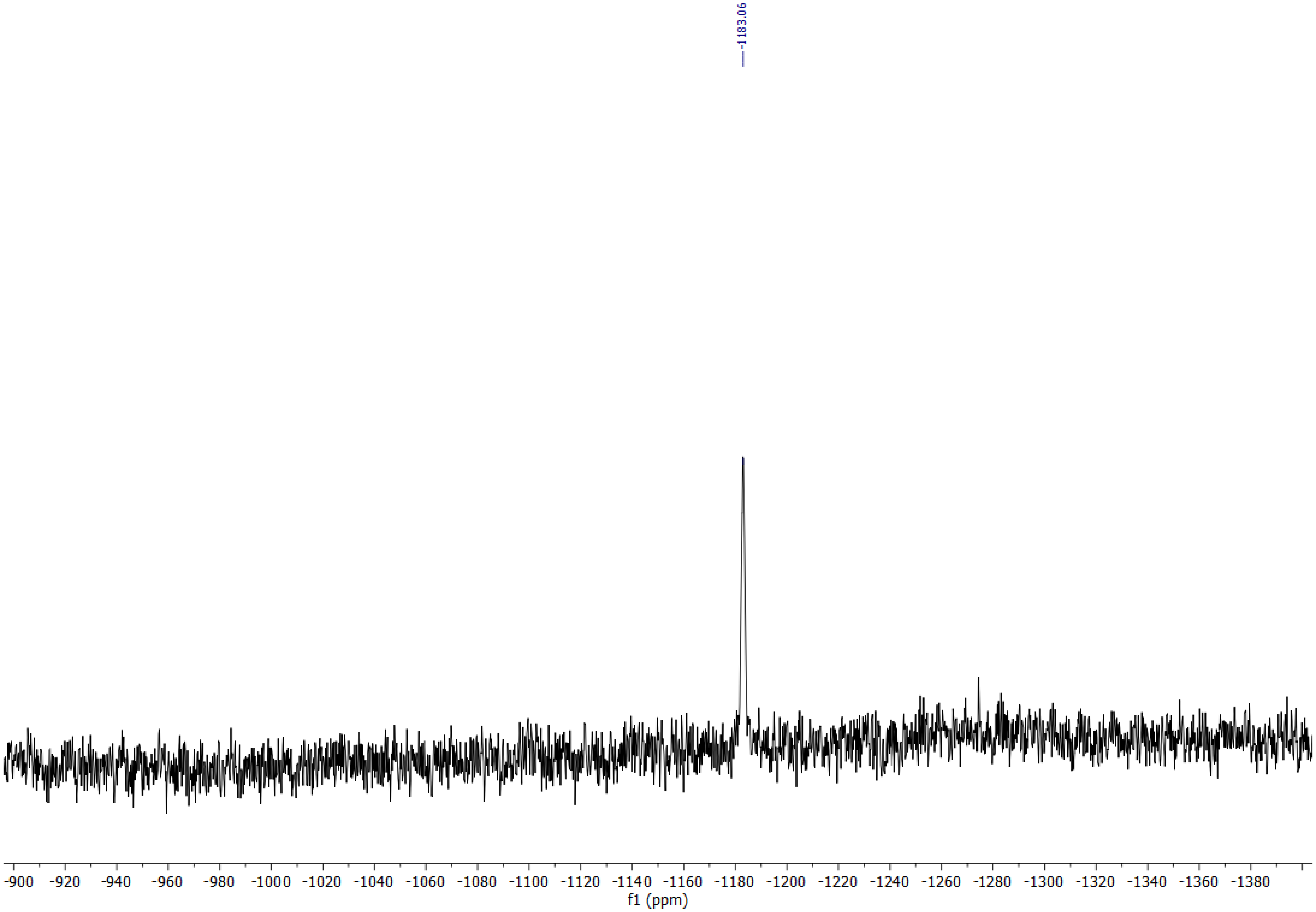


Figure S29. ^{125}Te{^{1}H} NMR spectrum of **Li$_2$[1-Te]** in THF-d_8 at −40 °C.

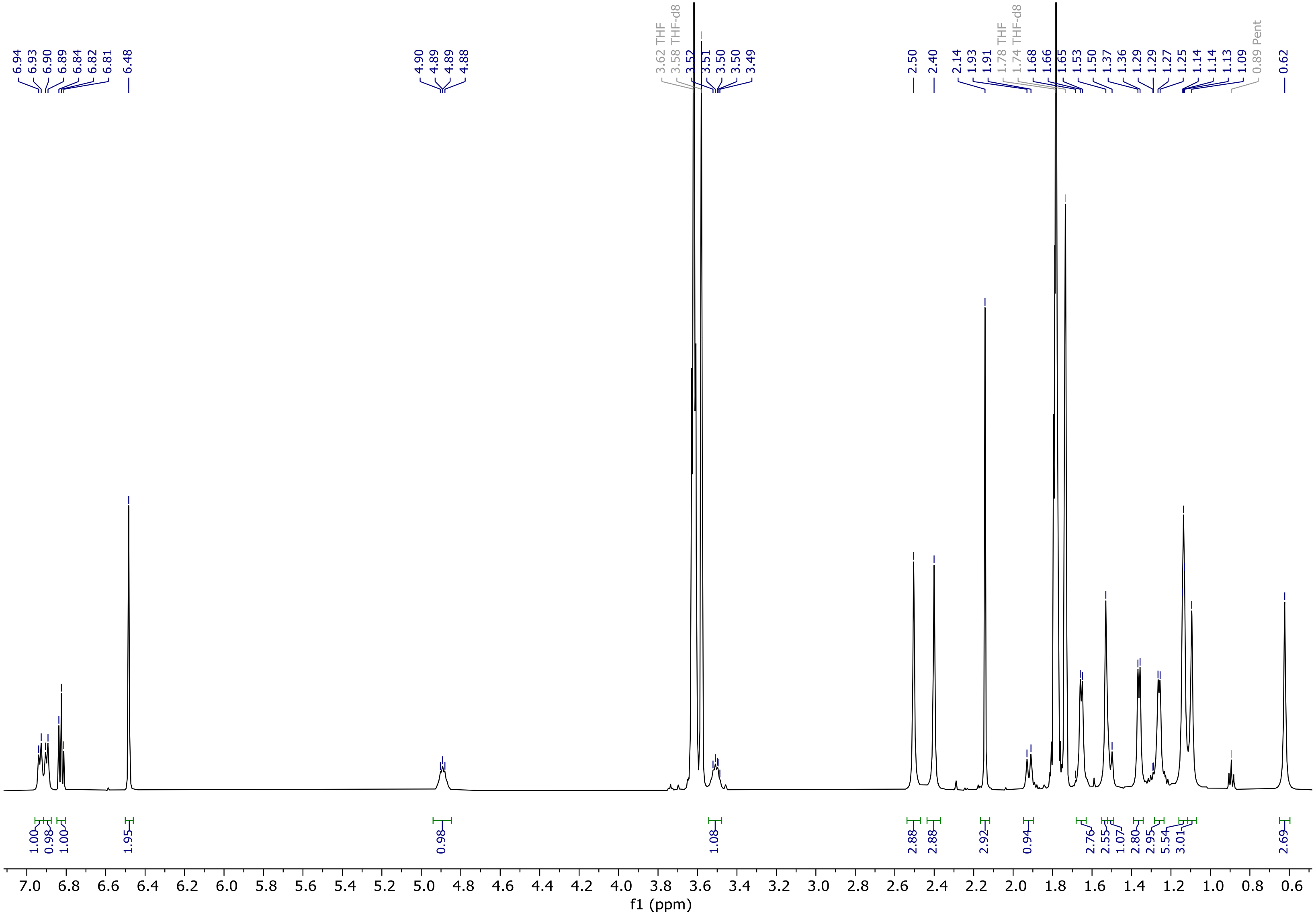


Figure S30. ^{1}H NMR spectrum of **Li$_2$[1-Te]** in THF-d_8 at −40 °C.

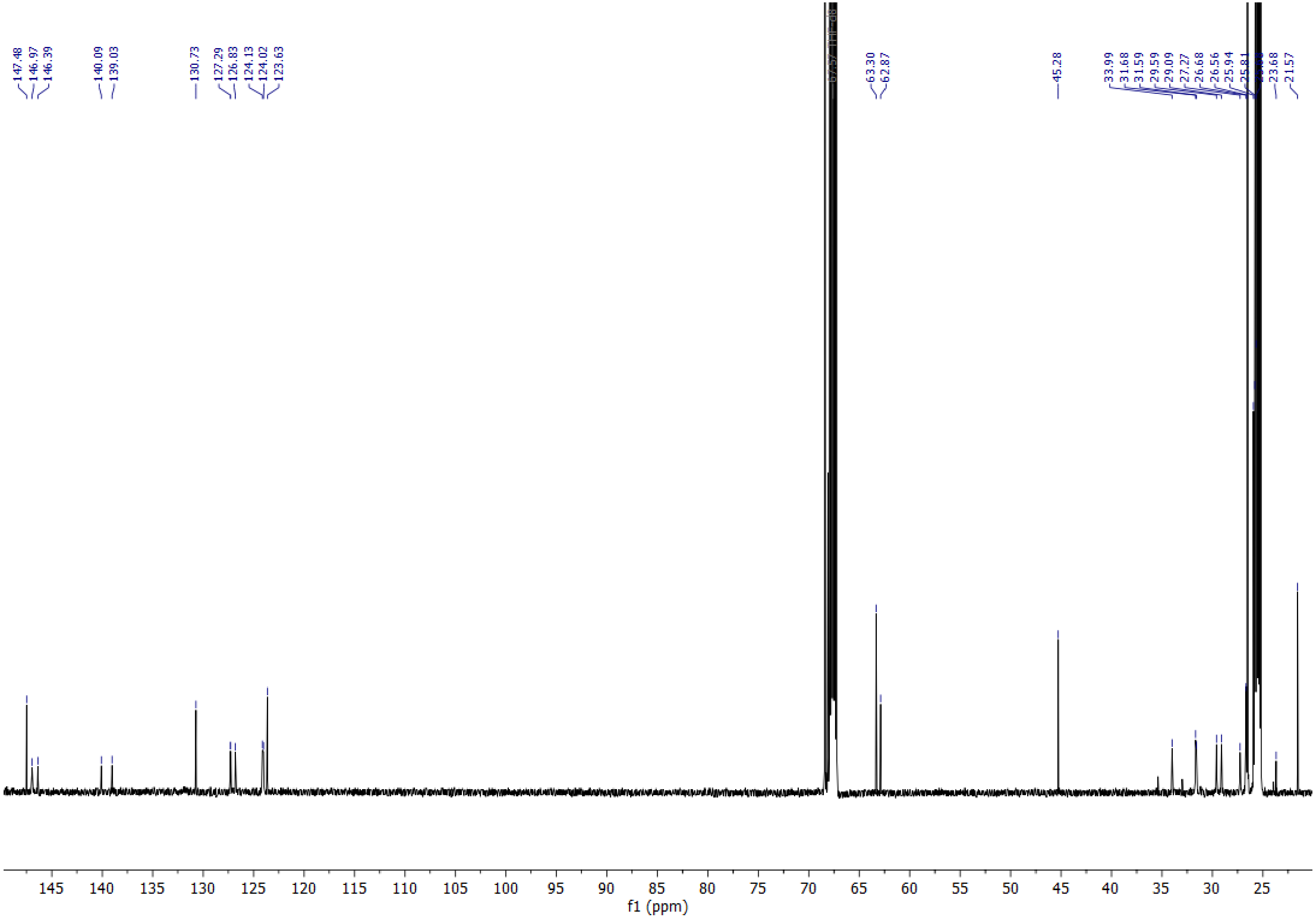


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **Li₂[1-Te]** in THF-d_8 at −40 °C

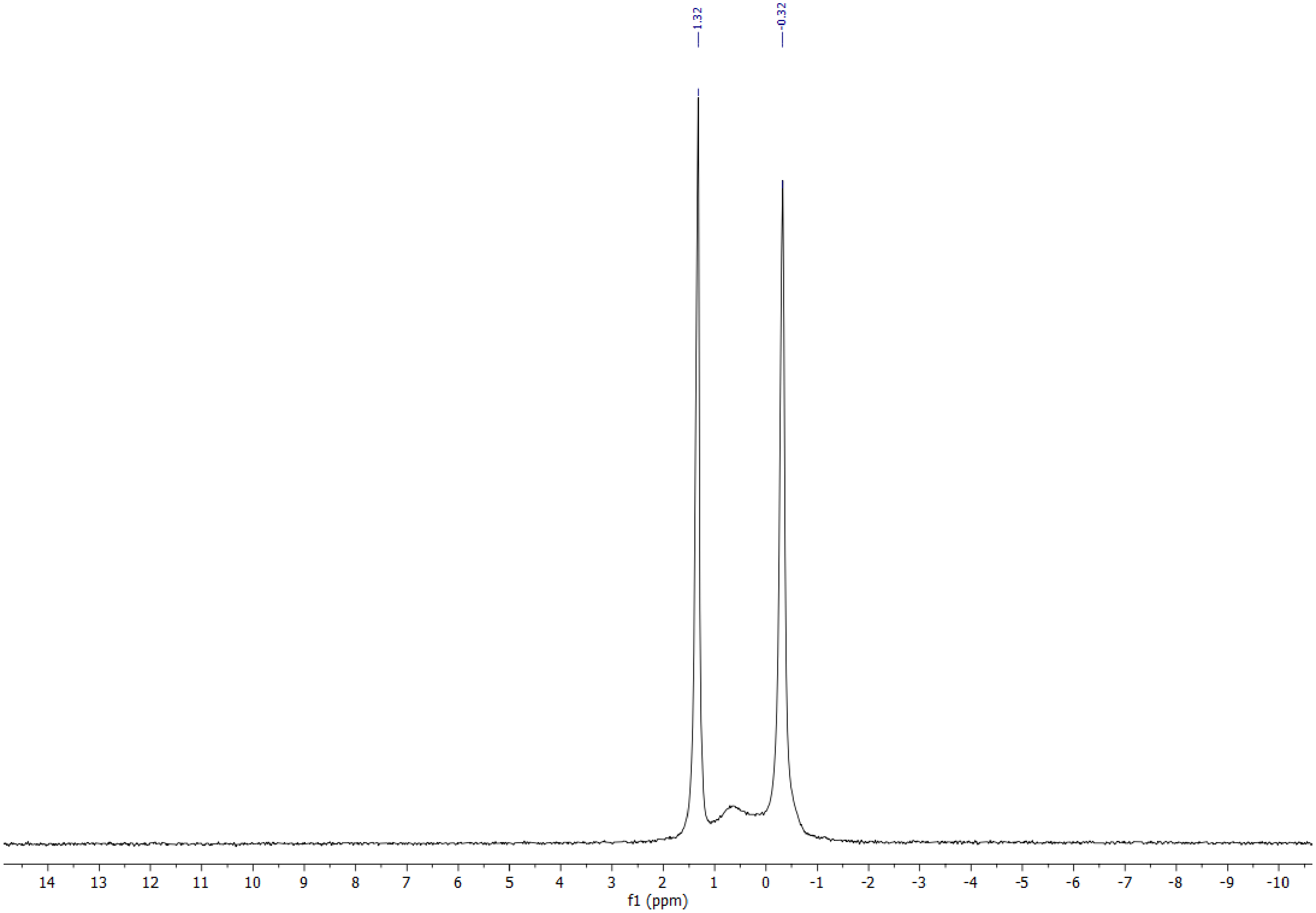


Figure S32. ^{7}Li NMR spectrum of **Li$_2$[1-Te]** in THF-d_8 at −40 °C

EPR spectroscopy

EPR measurements at X-band were carried out using a Bruker ELEXSYS E580 CW EPR spectrometer. The spectral simulations were performed using MATLAB (24.1.0.2578822) and the EasySpin 5.2.36 toolbox.[7]

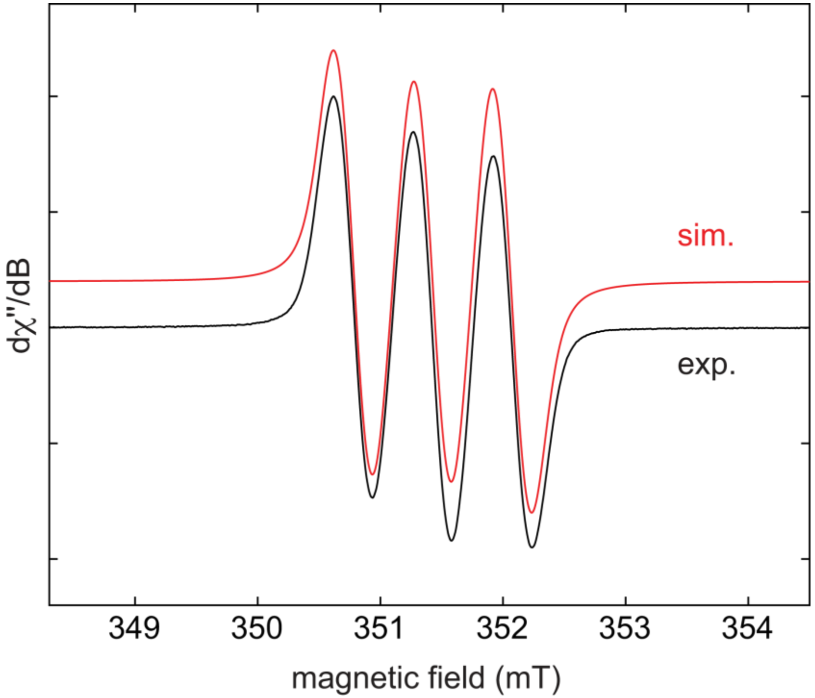


Figure S33. Experimental (black) and simulated (red) continuous-wave (CW) X-band EPR spectra of **[Li(1-S)]** in toluene at room temperature. The best-fit simulation parameters are g_{iso} = 2.0039, $a(^{11}B)$ = 2.0 MHz and $a(^{14}N)$ = 18.1 MHz. Experimental parameters: microwave frequency = 9.86 GHz; microwave power = 0.2 mW; modulation amplitude = 0.5 G; conversion time = 40 ms; modulation frequency = 100 kHz.

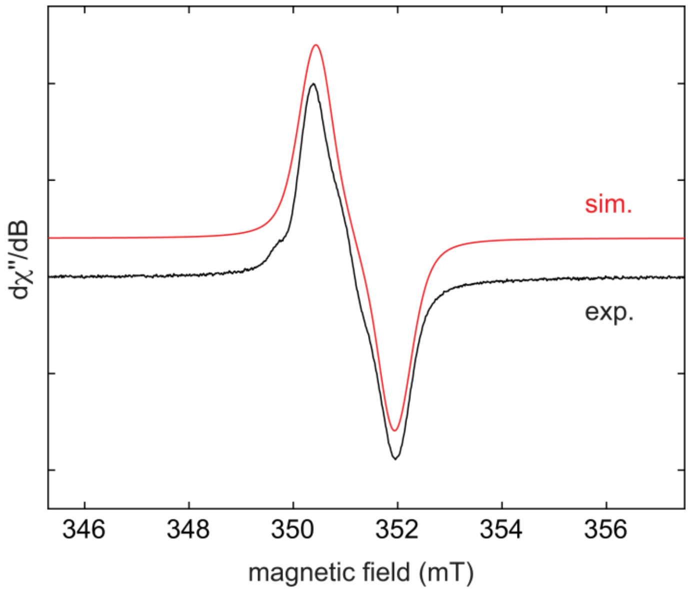


Figure S34. Experimental (black) and simulated (red) continuous-wave (CW) X-band EPR spectra of **[(1-Se)$_2$]PF$_6$** in a toluene 1,2-difluorobenzene mixture at room temperature. The signal is centered at a *g*-value of 2.0053. The simulated spectrum (red) includes coupling constants of $a(^{14}N)$ = 14.0 MHz and $a(^{11}B)$ = 2.0 MHz. Experimental parameters: microwave frequency = 9.85 GHz; microwave power = 1 mW; modulation amplitude = 0.5 G; conversion time = 40 ms; modulation frequency = 100 kHz.

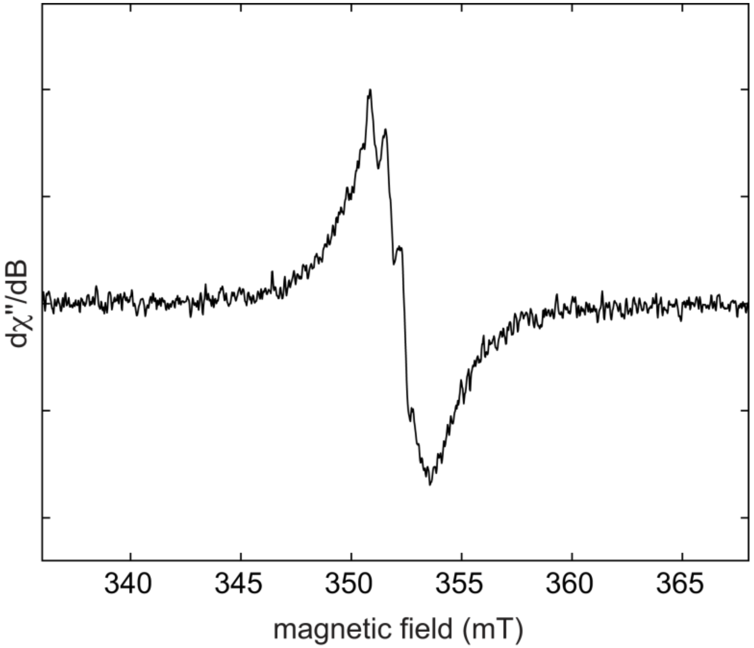


Figure S35. Experimental continuous-wave (CW) X-band EPR spectrum of **[(1-Te)$_2$]PF$_6$** at room temperature in a mixture of toluene and 1,2-difluorobenzene. The *g*-value of the signal is approximately 1.9997.

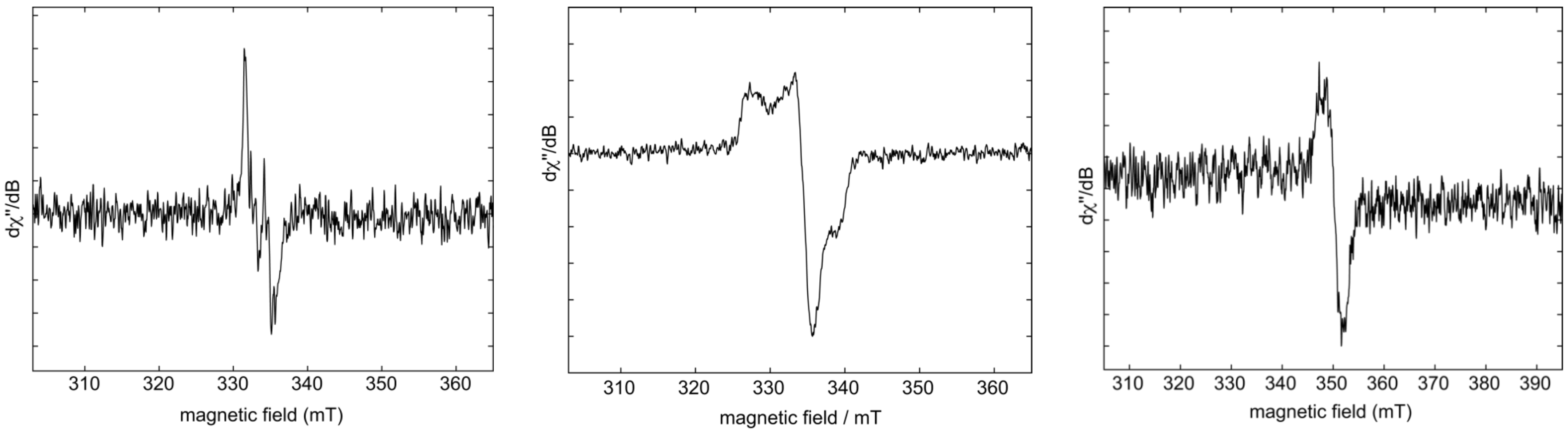


Figure S36. Experimental continuous-wave (CW) X-band EPR spectra of **(1-Te)$_2$**: a) in toluene solution at room temperature (*left*), b) in frozen toluene solution at 120 K (*center*), and c) in solid form (*right*). The diradical exhibits only extremely weak signals at room temperature, lacking any characteristic features of a triplet state, even at low temperatures or the solid state. The signal in frozen solution (*center*) seems to reveal rhombic *g* values ranging from 2.05 to 1.98, but these cannot be unambiguously assigned to the diradical.

IR spectra

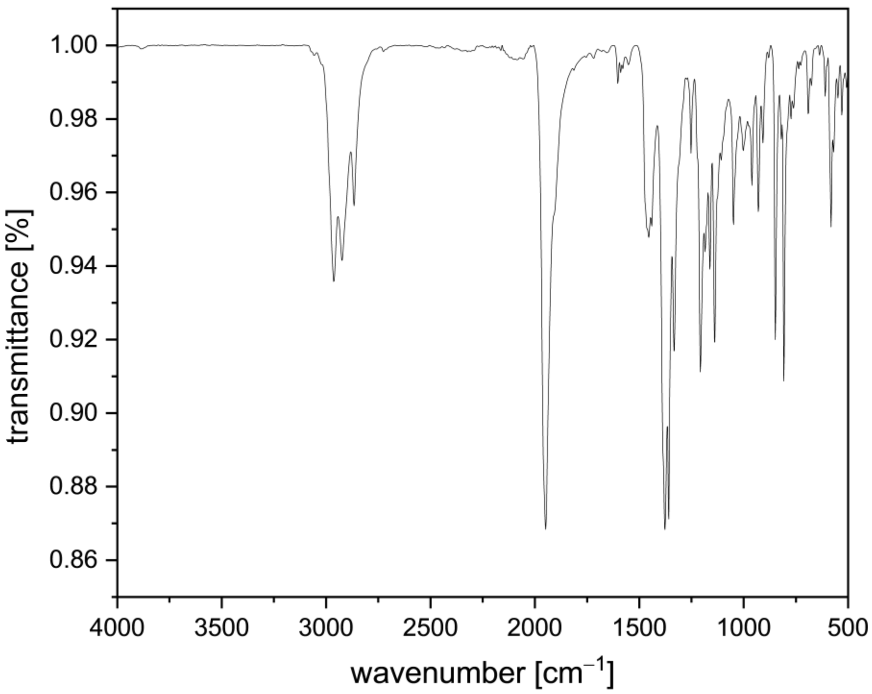


Figure S37. Solid-state IR spectrum of **1-CO**.

UV-vis spectra

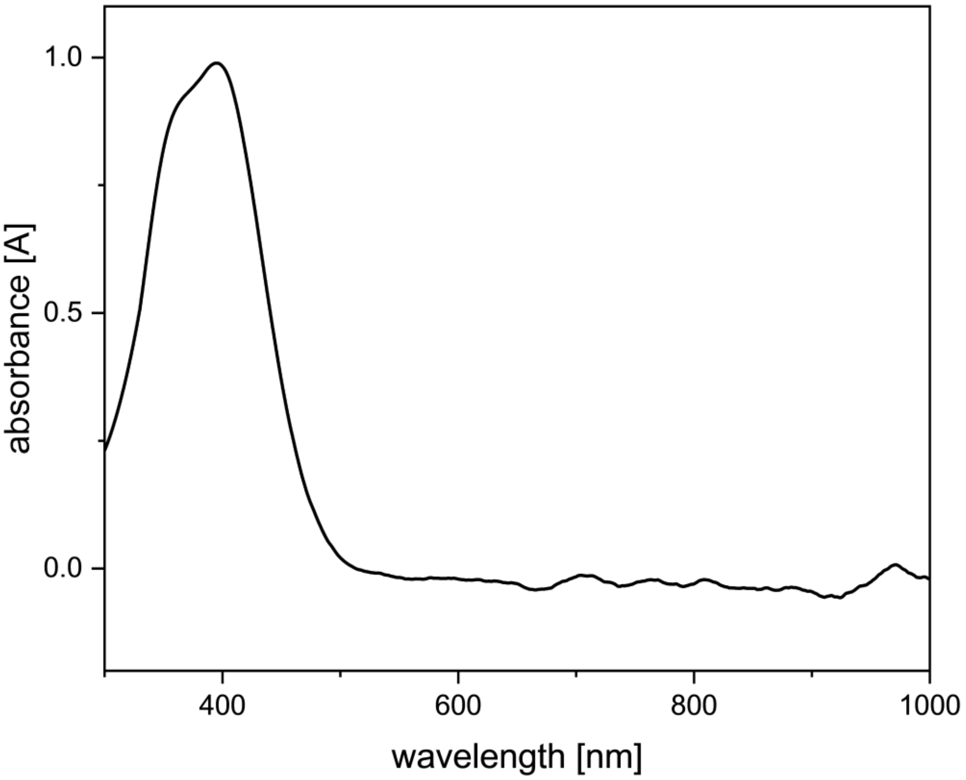


Figure S38. UV-vis absorption spectrum of **1-S** in hexane at 25 °C. λ_{max} = 394 nm.

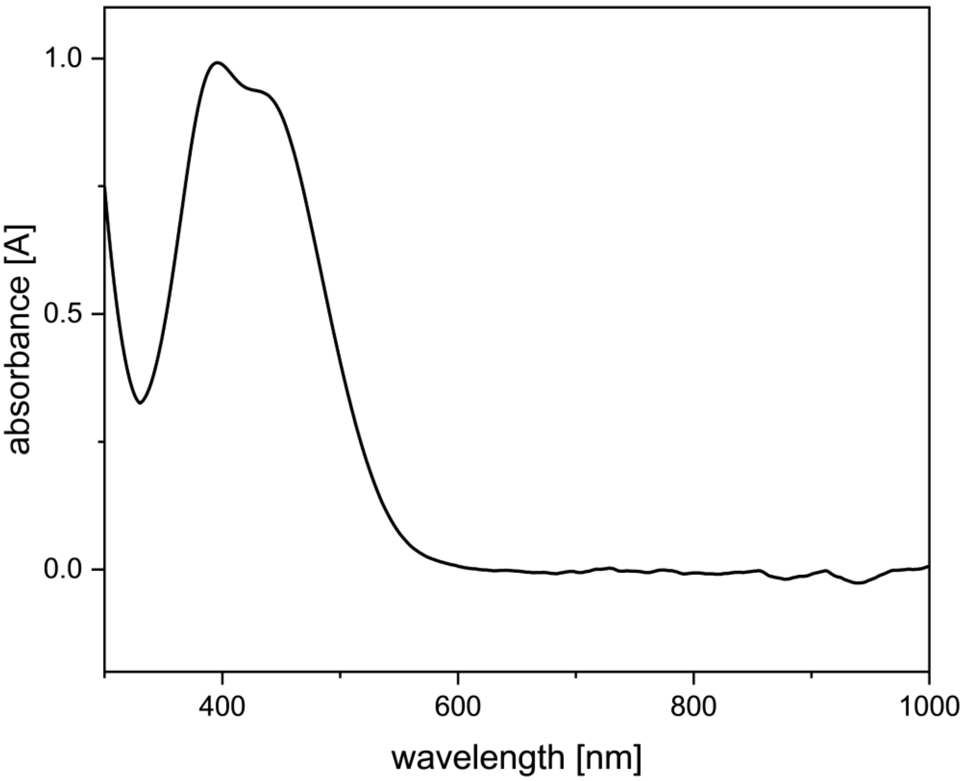


Figure S39. UV-vis absorption spectrum of **1-Se** in hexane at 23 °C. λ_{max} = 396 nm.

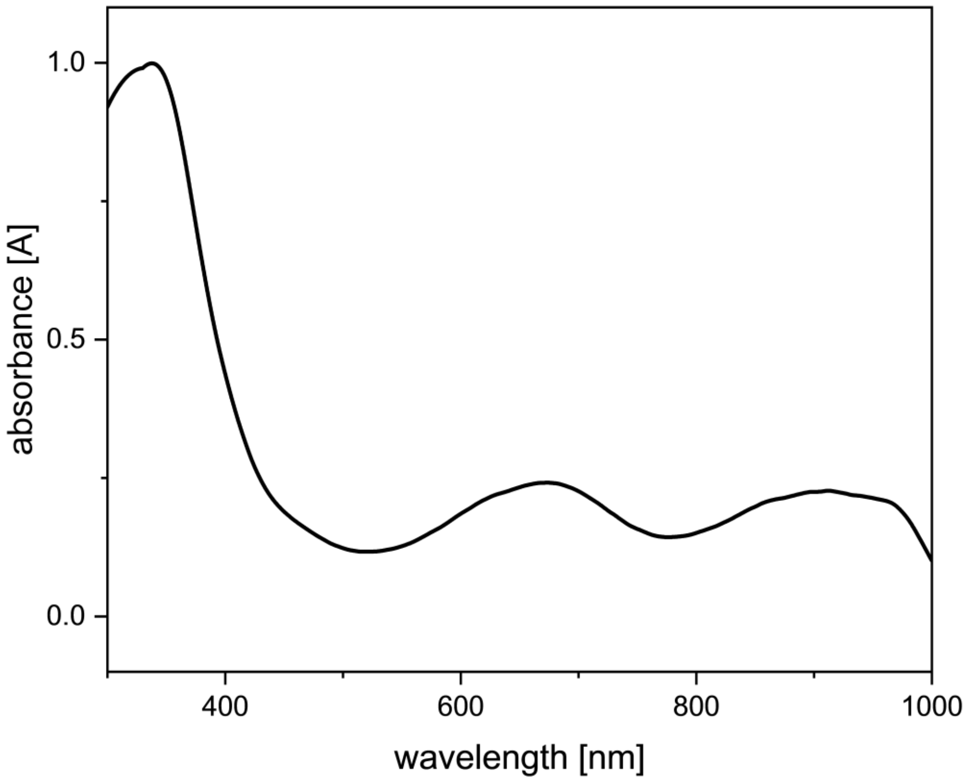


Figure S40. UV-vis absorption spectrum of (**1-Te**)$_2$ in hexane at 23 °C. λ_{max} = 338 nm, λ_1 = 674 nm, λ_2 = 913 nm.

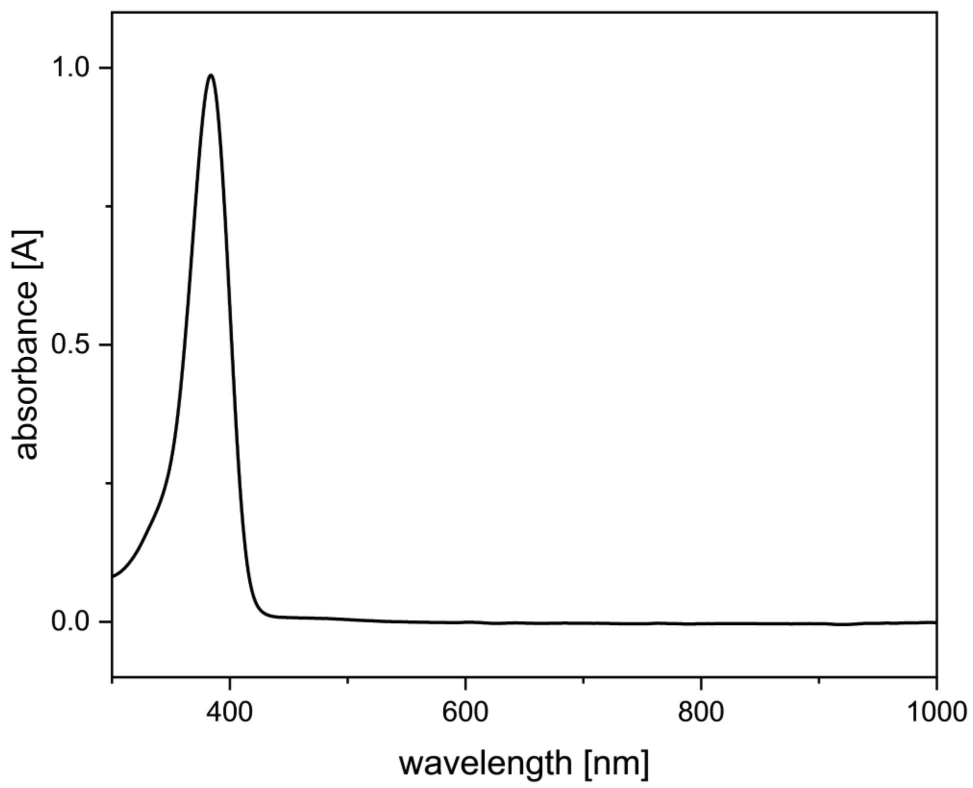


Figure S41. UV-vis absorption spectrum of **1-CO** in hexane at 23 °C. λ_{max} = 384 nm.

Cyclic voltammetric studies

All cyclic voltammetry experiments were conducted in an argon-filled glovebox, 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 reported versus the ferrocene/ferrocenium (Fc/Fc+) redox couple obtained by using ferrocene (Fc) as an internal standard. Compensation for resistive losses (*iR* drop) was employed for all measurements.

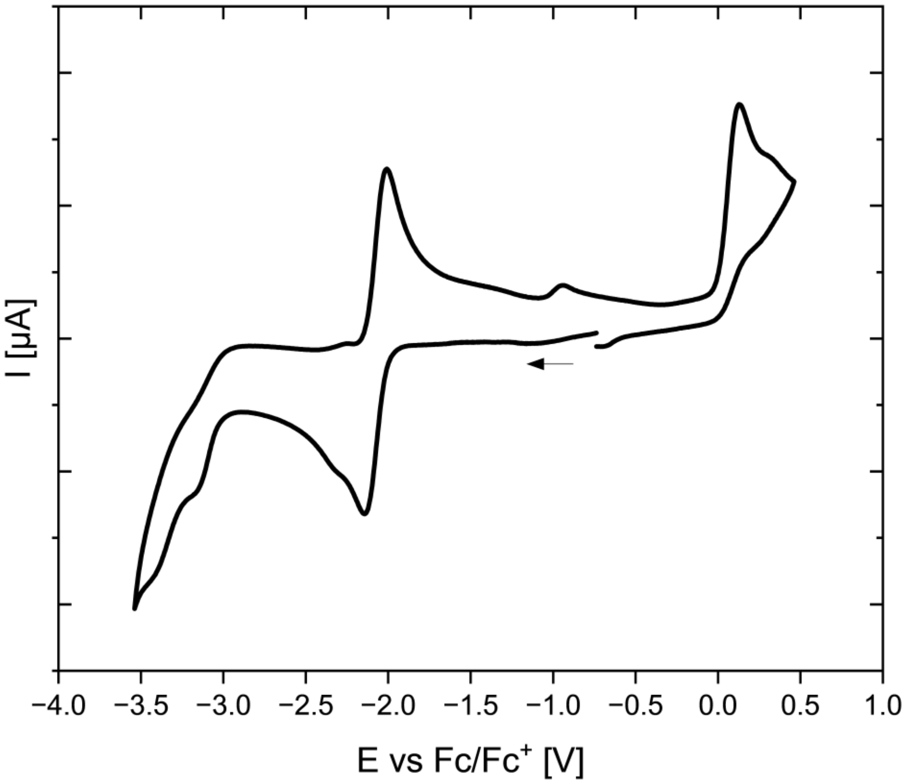


Figure S42. Cyclic voltammogram of **1-S** in THF/0.1 M [nBu$_4$N][PF$_6$] measured at 250 mV s^{-1}. Formal potentials: $E_{\text{pa,ox1}}$ = 0.13 V, $E_{1/2,\text{red1}}$ = −2.08 V, $E_{\text{pc,red2}}$ = −3.13 V.

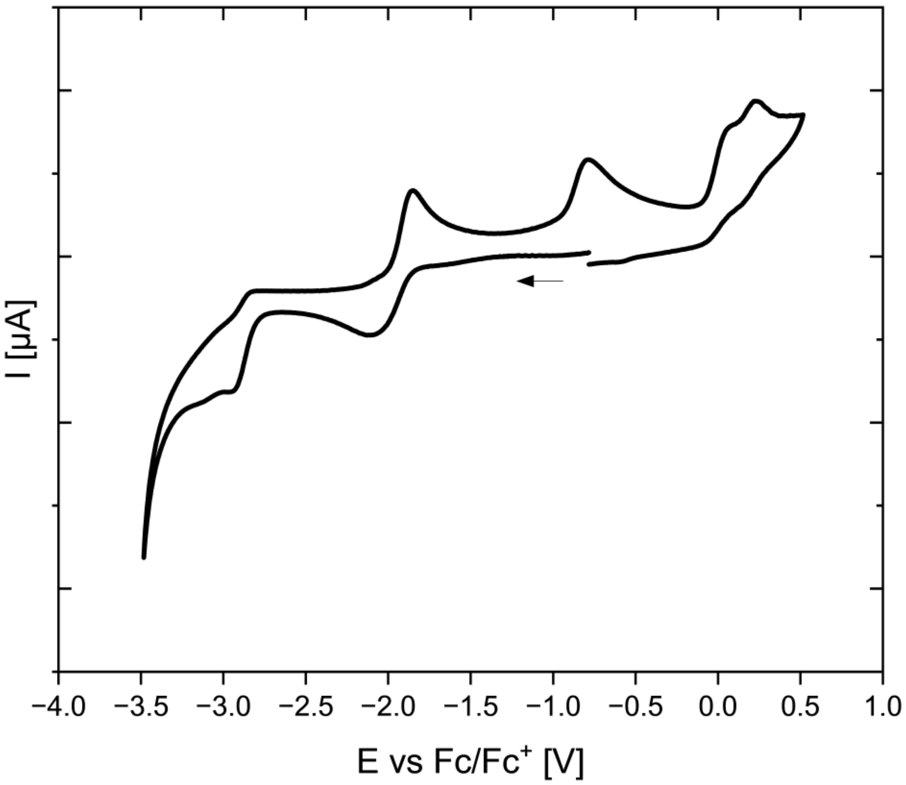


Figure S43. Cyclic voltammogram of **1-Se** in THF/0.1 M [nBu$_4$N][PF$_6$] measured at 250 mV s^{-1}. Formal potentials: $E_{pa,ox1}$ = 0.22 V, $E_{1/2,red1}$ = −1.96 V, and $E_{pc,red2}$ = −2.94 V.

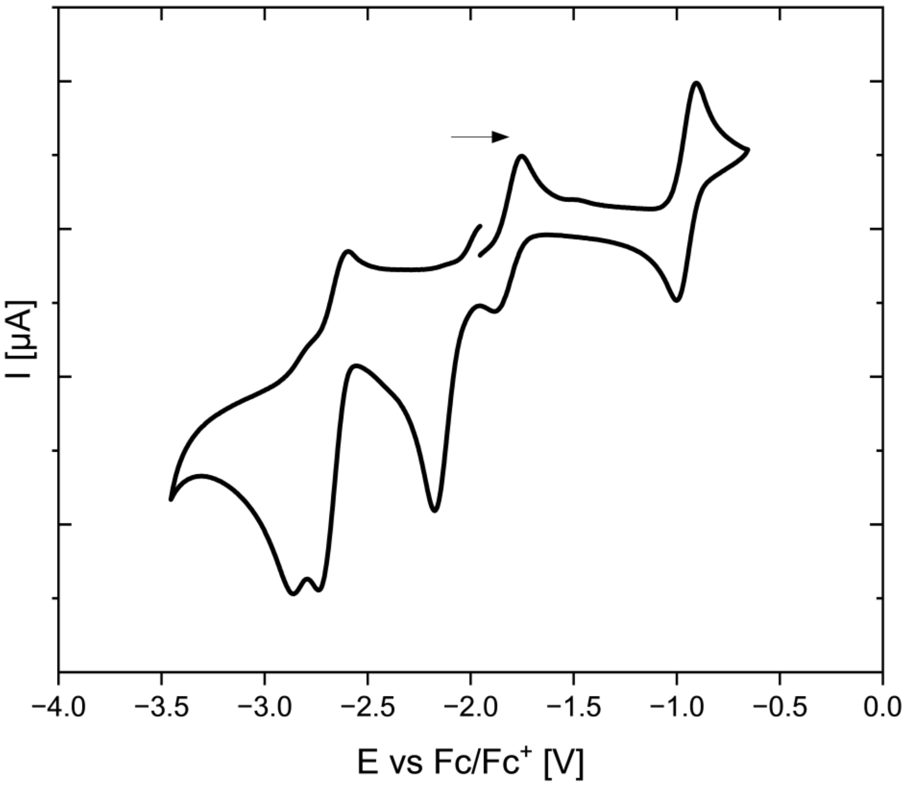


Figure S44. Cyclic voltammogram of **(1-Te)$_2$** in THF/0.1 M [*n*Bu$_4$N][PF$_6$] measured at 250 mV s^{-1}. Formal potentials: $E_{1/2,\text{ox1}} = -0.95$ V, $E_{\text{pc,red1}} = -2.17$ V, $E_{\text{pc,red2}} = -2.73$ V.

X-ray crystallographic data

The crystal data were collected on a *XtaLAB Synergy Dualflex HyPix* diffractometer with a Hybrid Pixel array detector and multi-layer mirror monochromated $Cu_{K\alpha}$ radiation. The structures were solved using the intrinsic phasing method,[8] refined with the ShelXL program[9] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-2392197 (**1-CO**), CCDC-2392198 (**1-PMe$_3$**), CCDC-2392199 (**1-S**), CCDC-2392200 (**1-Se**), CCDC-2392201 (**1-Te**), CCDC-2392202 (**Li[1-S]**), CCDC-2392203 (**Li$_2$[1-S]**), CCDC-2392204 (**Li$_2$[1-Se]**), CCDC-2392205 (**Li$_2$[1-Te]**), CCDC-2392206 (**[(1-Te)$_2$]PF$_6$**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **1-CO**: $C_{30}H_{42}BNO$, M_r = 443.45, orange block, 0.460×0.220×0.130 mm^3, monoclinic space group $P2_1/c$, a = 9.15680(10) Å, b = 11.11500(10) Å, c = 26.1678(3) Å, α = 90°, β = 95.7630(10)°, γ = 90°, V = 2649.84(5) Å^3, Z = 4, ρ_{calcd} = 1.112 g·cm^{-3}, μ = 0.490 mm^{-1}, $F(000)$ = 968, T = 100(2) K, R_1 = 0.0555, wR_2 = 0.1388, 5435 independent reflections [$2\theta \leq 150.986°$] and 309 parameters.

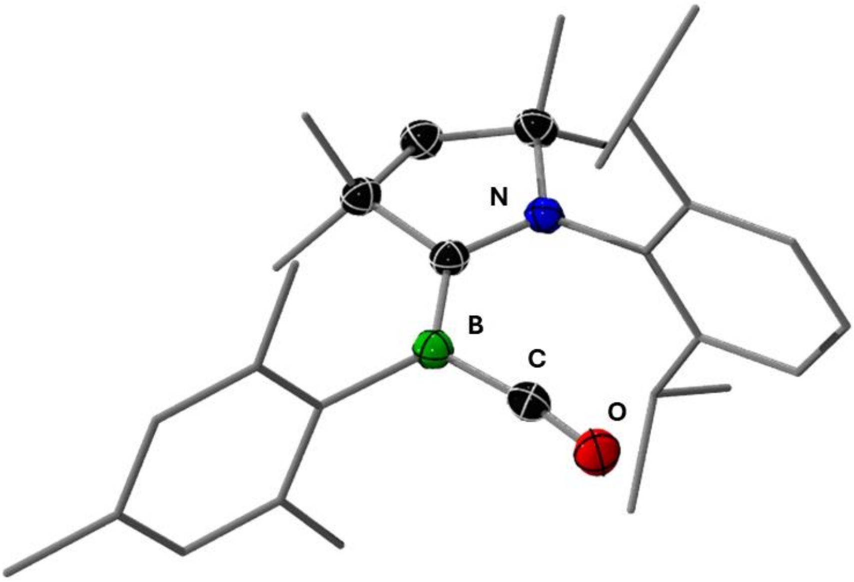


Figure S45. Solid-state structure of **1-CO**. Atomic displacement ellipsoids represented at 50%. For clarity, ellipsoids of the carbon atoms of the aryl and alkyl groups, as well as the hydrogen atoms, are omitted.

Crystal data for **1-PMe$_3$**: $C_{32}H_{51}BNP$, M_r = 491.51, yellow block, 0.265×0.206×0.160 mm^3, space group $P\bar{1}$, a = 9.69840(10) Å, b = 11.0467(2) Å, c = 14.5864(2) Å, α = 96.8190(10)°, β = 105.4270(10)°, γ = 92.3820(10)°, V = 1491.38(4) Å^3, Z = 2, ρ_{calcd} = 1.095 g·cm^{-3}, μ = 0.939 mm^{-1}, F(000) = 540, T = 100.01(10) K, R_1 = 0.0380, wR_2 = 0.1001, 5994 independent reflections [$2\theta \leq 149.966°$] and 330 parameters.

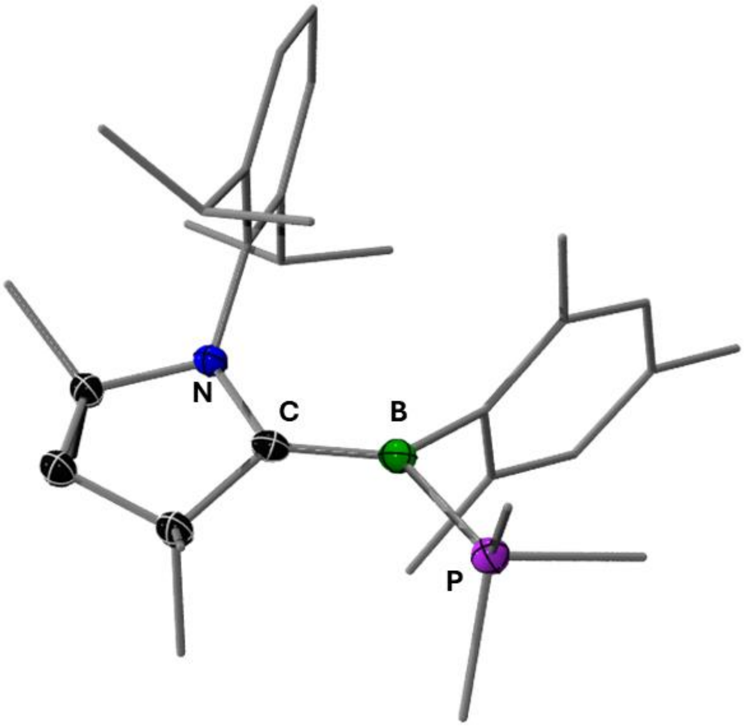


Figure S46. Solid-state structure of **1-PMe$_3$**. Atomic displacement ellipsoids represented at 50%. For clarity, ellipsoids of the carbon atoms of the aryl and alkyl groups, as well as the hydrogen atoms, are omitted.

Crystal data for **1-S**: $C_{29}H_{42}BNS$, M_r = 447.50, orange block, 0.100×0.080×0.080 mm^3, monoclinic space group $P2_1/c$, a = 18.00600(10) Å, b = 8.46370(10) Å, c = 17.39900(10) Å, α = 90°, β = 93.3370(10)°, γ = 90°, V = 2647.07(4) $Å^3$, Z = 4, ρ_{calcd} = 1.123 $g\cdot cm^{-3}$, μ = 1.182 mm^{-1}, $F(000)$ = 976, T = 100(2) K, R_1 = 0.0406, wR_2 = 0.1016, 5457 independent reflections [$2\theta \leq 150.738°$] and 300 parameters.

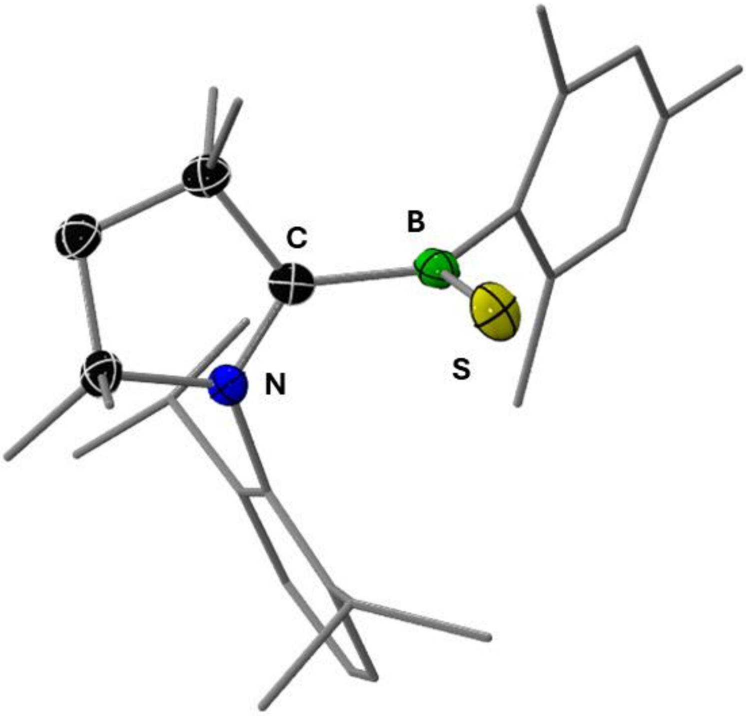


Figure S47. Solid-state structure of **1-S**. Atomic displacement ellipsoids represented at 50%. For clarity, ellipsoids of the carbon atoms of the aryl and alkyl groups, as well as the hydrogen atoms, are omitted.

Refinement details for Li[1-S]: In the unit cell, one highly disordered pentane molecule has been treated as a diffuse contribution to the overall scattering, without specific atom positions, by SQUEEZE/PLATON.[10]

Crystal data for **Li[1-S]**: $C_{74}H_{116}B_2Li_2N_2O_4S_2$, $M_r = 1197.30$, red block, $0.170\times0.120\times0.090$ mm^3, triclinic space group $P\bar{1}$, $a = 10.5609(3)$ Å, $b = 13.0367(4)$ Å, $c = 14.8835(4)$ Å, $\alpha = 82.383(2)°$, $\beta = 79.577(2)°$, $\gamma = 68.461(2)°$, $V = 1869.70(10)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.063$ g·cm^{-3}, $\mu = 0.980$ mm^{-1}, $F(000) = 654$, $T = 100(2)$ K, $R_1 = 0.0635$, $wR_2 = 0.1664$, 7406 independent reflections [$2\theta \leq 149.568°$] and 491 parameters.

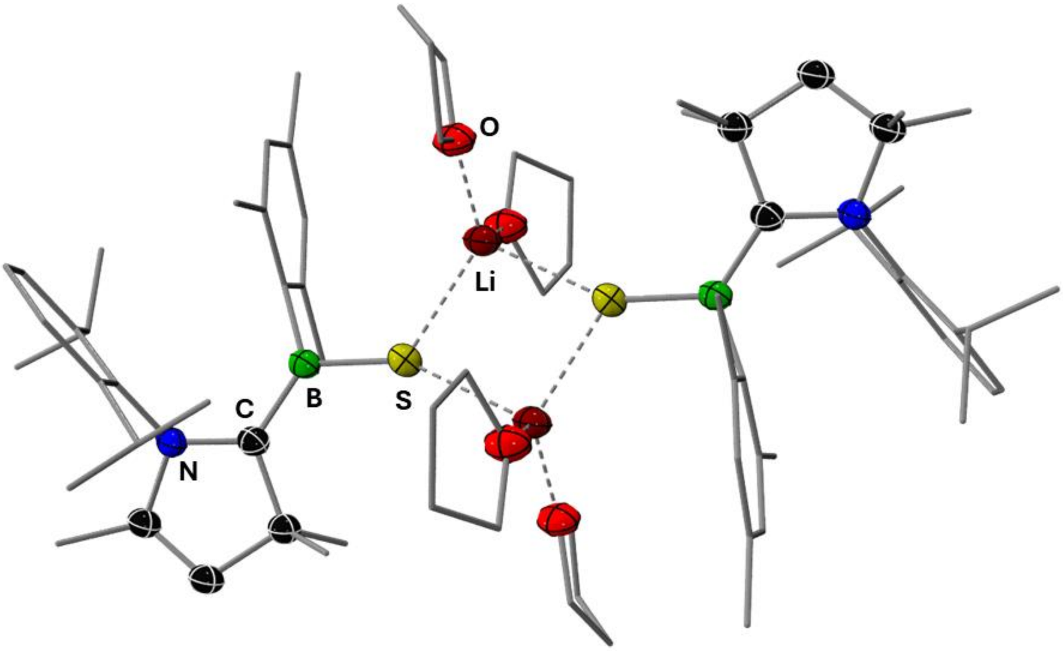


Figure S48. Solid-state structure of **Li[1-S]**. Atomic displacement ellipsoids represented at 50%. For clarity, ellipsoids of the carbon atoms of the aryl and alkyl groups, as well as THF molecules and the hydrogen atoms, are omitted.

Refinement details for Li2[1-S]: The crystal exhibited non-merohedral and racemic twinning. However, non-merohedral twinning was discounted due to a high R*int* in the second domain. Therefore, the crystal structure was refined as a two-component inversion twin. The BASF parameter was refined to 43.5%.

Crystal data for **Li2[1-S]**: $C_{70}H_{108}B_2Li_4N_2O_3S_2$, M_r = 1139.08, yellow block, 0.241×0.141×0.089 mm^3, monoclinic space group $P2_1$, a = 10.65140(10) Å, b = 21.0348(2) Å, c = 16.8392(2) Å, β = 106.0250(10)°, V = 3626.22(7) Å^3, Z = 2, ρ_{calcd} = 1.043 g·cm^{-3}, μ = 0.974 mm^{-1}, F(000) = 1240, T = 100(2) K, R_1 = 0.0294, wR_2 = 0.0763, Flack parameter = 0.435(10), 12842 independent reflections [$2\theta \leq 149.62°$] and 909 parameters.

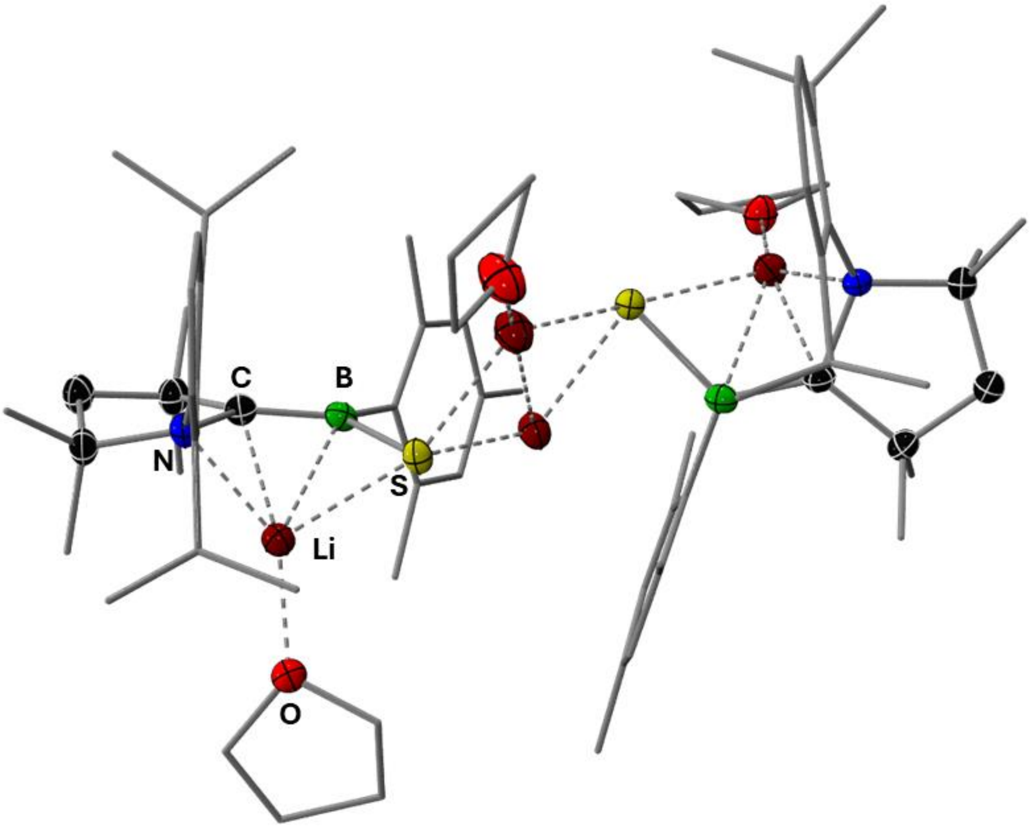


Figure S49. Solid-state structure of **Li2[1-S]**. Atomic displacement ellipsoids represented at 50%. For clarity, ellipsoids of the carbon atoms of the aryl and alkyl groups, as well as THF molecules and the hydrogen atoms, are omitted.

Refinement details for 1-Se: The disordered THF moiety was treated with SIMU and RIGU.

Crystal data for **1-Se**: $C_{33}H_{50}BNOSe$, $M_r = 566.51$, red needle, 0.600×0.070×0.040 mm^3, orthorhombic space group *Pna*2$_1$, $a = 14.23860(10)$ Å, $b = 14.04470(10)$ Å, $c = 15.38680(10)$ Å, $V = 3077.00(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.223$ g·cm^{-3}, $\mu = 1.822$ mm^{-1}, $F(000) = 1208$, $T = 100(2)$ K, $R_1 = 0.0373$, $wR_2 = 0.0972$, Flack parameter = 0.002(13), 6209 independent reflections [$2\theta \leq 149.702°$] and 391 parameters.

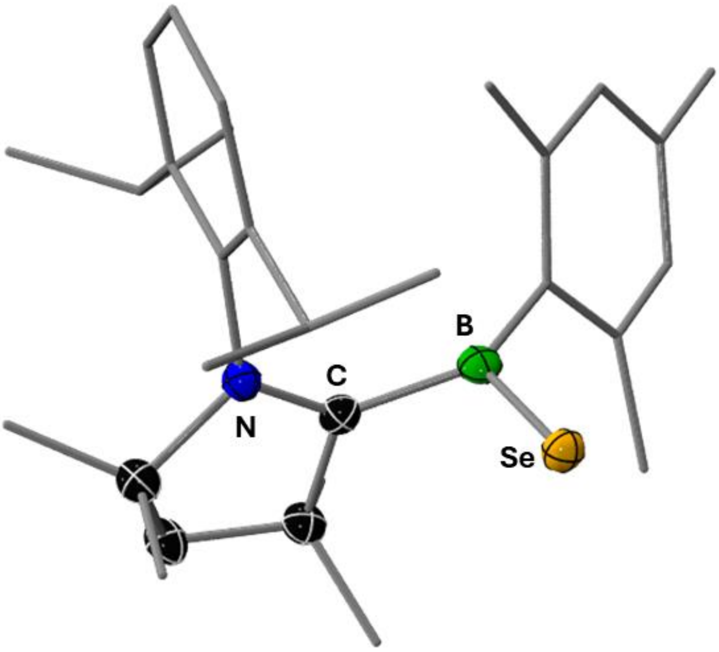


Figure S50. Solid-state structure of **1-Se**. Atomic displacement ellipsoids represented at 50%. For clarity, ellipsoids of the carbon atoms of the aryl and alkyl groups, as well as the hydrogen atoms, are omitted.

Refinement details for Li_2[1-Se]: Refined as a two-component twin. Component 2 rotated by –179.9122° around [0.99 0.03 0.15] (reciprocal) or [1.00 –0.00 0.00] (direct). The BASF parameter was refined to 43%. The disordered THF molecules were treated with RIGU, SIMU and SAME.

Crystal data for **Li_2[1-Se]**: $C_{45}H_{74}BLi_2NO_4Se$, $M_r = 796.70$, yellow plate, $0.627\times0.091\times0.038$ mm^3, triclinic space group $P\bar{1}$, $a = 10.7762(2)$ Å, $b = 16.8779(3)$ Å, $c = 24.5726(3)$ Å, $\alpha = 81.4390(10)°$, $\beta = 86.2260(10)°$, $\gamma = 88.7940(10)°$, $V = 4409.59(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.200$ g·cm^{-3}, $\mu = 1.455$ mm^{-1}, $F(000) = 1712$, $T = 100(2)$ K, $R_1 = 0.0703$, $wR_2 = 0.1619$, 36914 independent reflections [$2\theta\leq150.034°$] and 1272 parameters.

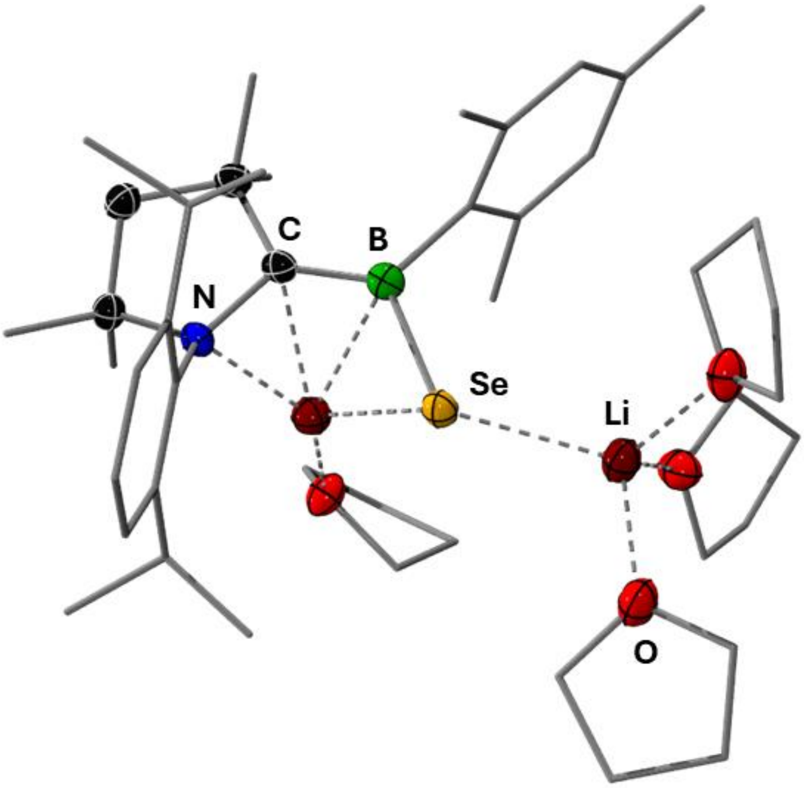


Figure S51. Solid-state structure of **Li_2[1-Se]**. Atomic displacement ellipsoids represented at 50%. For clarity, ellipsoids of the carbon atoms of the aryl and alkyl groups, as well as THF molecules and the hydrogen atoms, are omitted.

Refinement details for [(1-Se)$_2$]PF$_6$: Both disordered PF_6 moieties were treated with SIMU and RIGU to ensure stable refinement. Additionally, the P atoms were restrained with EXYZ and EADP.

Crystal data for **[(1-Se)$_2$]PF$_6$**: $C_{82}H_{100}B_2F_{14}N_2PSe_2$, $M_r = 1590.14$, black block, $0.310\times0.250\times0.160$ mm^3, monoclinic space group $P2_1/n$, $a = 15.90140(10)$ Å, $b = 46.7100(2)$ Å, $c = 21.05150(10)$ Å, $\beta = 90.61°$, $V = 15635.20(14)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.351$ g·cm^{-3}, $\mu = 2.032$ mm^{-1}, $F(000) = 6600$, $T = 100(2)$ K, $R_1 = 0.1417$, $wR_2 = 0.3132$, 31779 independent reflections [$2\theta \leq 150.018°$] and 1524 parameters.

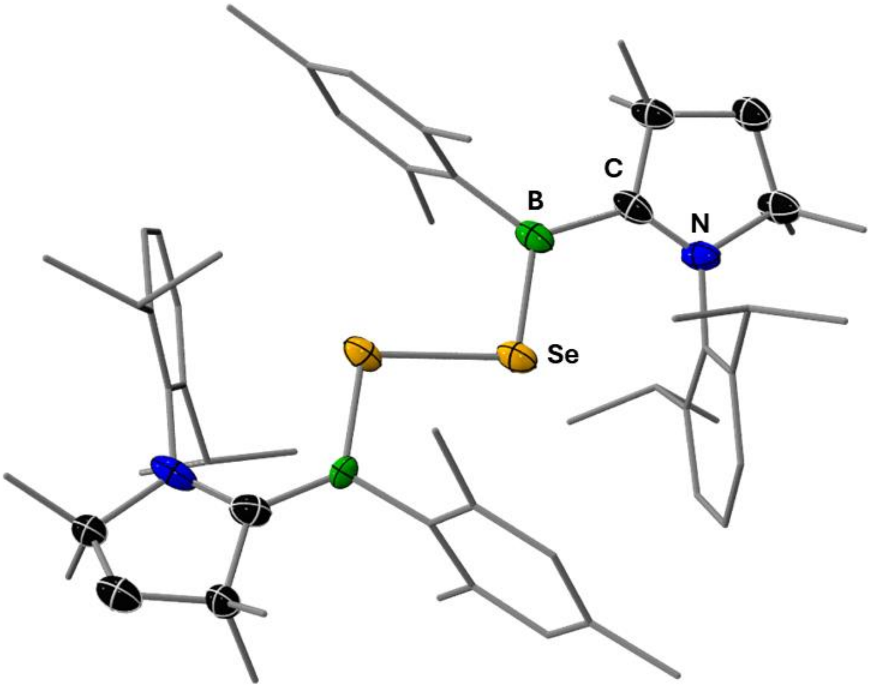


Figure S52. Solid-state structure of **[(1-Se)$_2$]PF$_6$**. Atomic displacement ellipsoids represented at 50%. For clarity, ellipsoids of the carbon atoms of the aryl and alkyl groups, as well as THF molecules, the hydrogen atoms and the counteranion, are omitted.

Refinement details for (1-Te)₂: Some reflections were removed from the refinement as outliers.

Crystal data for **(1-Te)₂**: $C_{58}H_{84}B_2N_2Te_2$, M_r = 1086.09, black plate, 0.150×0.070×0.040 mm^3, triclinic space group $P\bar{1}$, a = 10.15650(10) Å, b = 10.34690(10) Å, c = 14.22450(10) Å, α = 69.7800(10)°, β = 80.9350(10)°, γ = 81.8990(10)°, V = 1379.14(2) $Å^3$, Z = 1, ρ_{calcd} = 1.308 g·cm^{-3}, μ = 8.607 mm^{-1}, $F(000)$ = 560, T = 100(2) K, R_1 = 0.0345, wR_2 = 0.0965, 5447 independent reflections [$2\theta \leq 149.688°$] and 300 parameters.

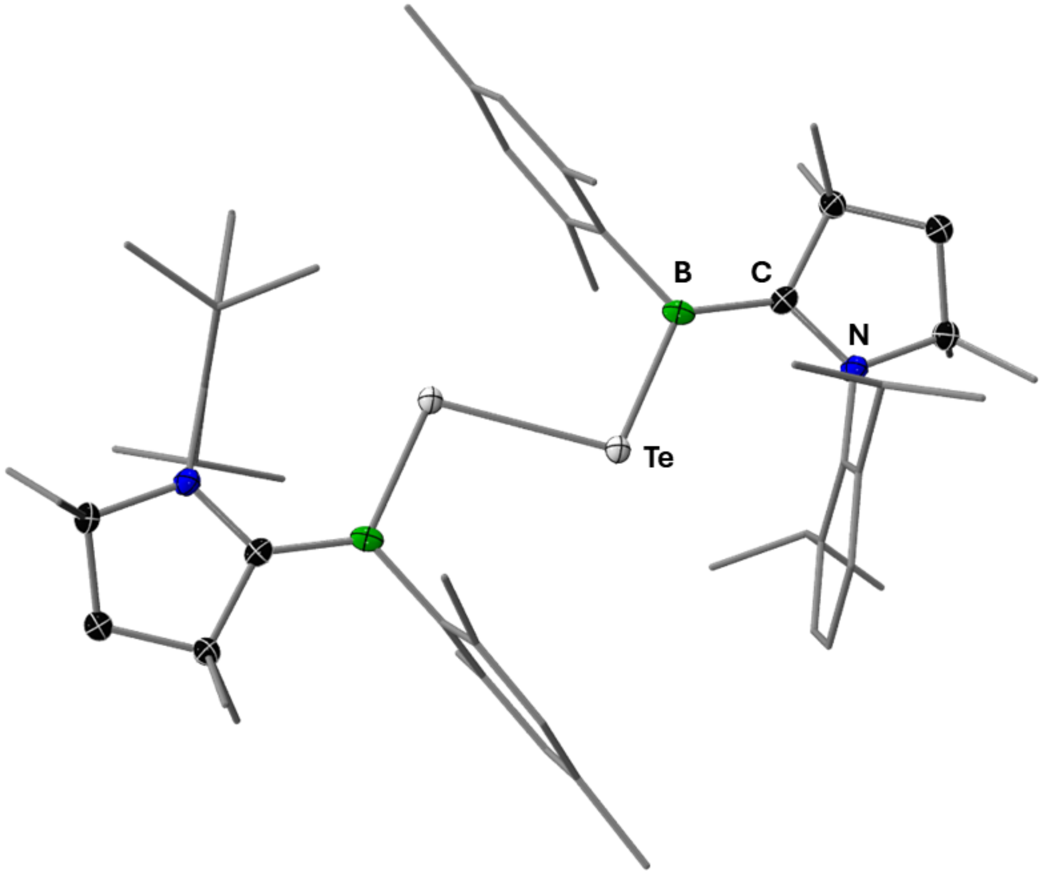


Figure S53. Solid-state structure of **(1-Te)₂**. Atomic displacement ellipsoids represented at 50%. For clarity, ellipsoids of the carbon atoms of the aryl and alkyl groups, as well as the hydrogen atoms, are omitted.

Refinement details for Li_2[1-Te]: Some reflections were removed from the refinement as outliers. To ensure stable refinement due to disordered THF moieties, the structure was treated with SIMU, RIGU and SAME restraints.

Crystal data for **Li_2[1-Te]**: $C_{45}H_{74}BLi_2NO_4Te$, $M_r = 845.34$, yellow block, $0.250 \times 0.050 \times 0.050$ mm^3, triclinic space group $P\bar{1}$, $a = 10.77840(10)$ Å, $b = 16.91210(10)$ Å, $c = 24.81310(10)$ Å, $\alpha = 82.1330(10)°$, $\beta = 86.65°$, $\gamma = 88.61°$, $V = 4472.26(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.255$ g·cm^{-3}, $\mu = 5.549$ mm^{-1}, $F(000) = 1784$, $T = 100(2)$ K, $R_1 = 0.0285$, $wR_2 = 0.0711$, 17771 independent reflections [$2\theta \leq 149.496°$] and 1225 parameters.

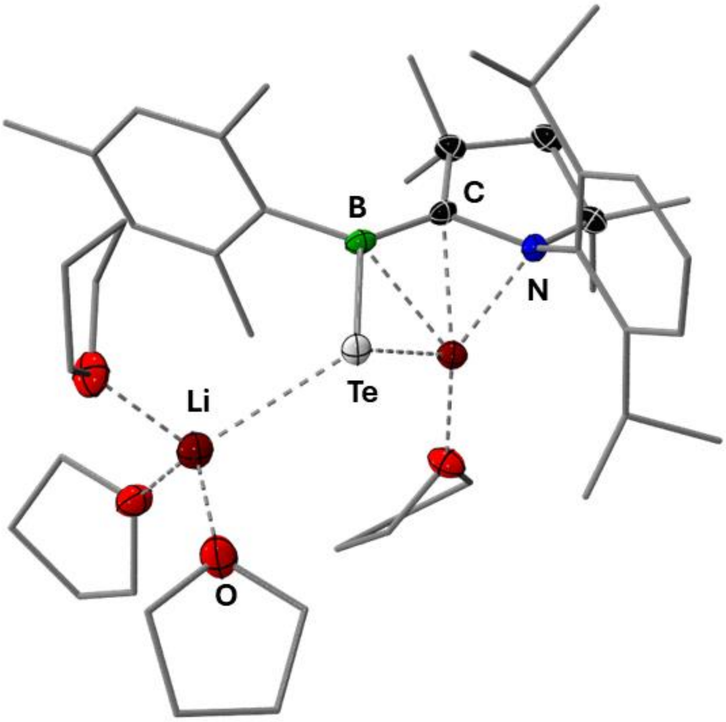


Figure S54. Solid-state structure of **Li_2[1-Te]**. Atomic displacement ellipsoids represented at 50%. For clarity, ellipsoids of the carbon atoms of the aryl and alkyl groups, as well as THF molecules and the hydrogen atoms, are omitted.

Refinement details for [(1-Te)$_2$]PF$_6$: The unit cell contained one highly disordered 1,2-difluorobenzene molecule, which has been treated as a diffuse contribution to the overall scattering, without specific atom positions, by SQUEEZE/PLATON.[10] The highly disordered PF$_6$ moiety was treated with SIMU, RIGU, DELU and ISOR restraints, to ensure stable refinement. In addition, the P atoms were restrained with EXYZ and EADP, and the 1,2 and 1,3 distances were restrained with SAME.

Crystal data for **[(1-Te)$_2$]PF$_6$**: $C_{64}H_{88}B_2F_{7.79}N_2P_{0.96}Te_2$, $M_r = 1340.06$, orange plate, $0.170\times0.114\times0.035$ mm^3, triclinic space group $P\bar{1}$, $a = 12.79920(10)$ Å, $b = 16.27830(10)$ Å, $c = 17.37610(10)$ Å, $\alpha = 106.6370(10)°$, $\beta = 94.0290(10)°$, $\gamma = 96.3900(10)°$, $V = 3427.31(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.299$ g·cm^{-3}, $\mu = 7.403$ mm^{-1}, $F(000) = 1369$, $T = 100(2)$ K, $R_1 = 0.0349$, $wR_2 = 0.0884$, 13696 independent reflections [$2\theta \leq 149.658°$] and 923 parameters.

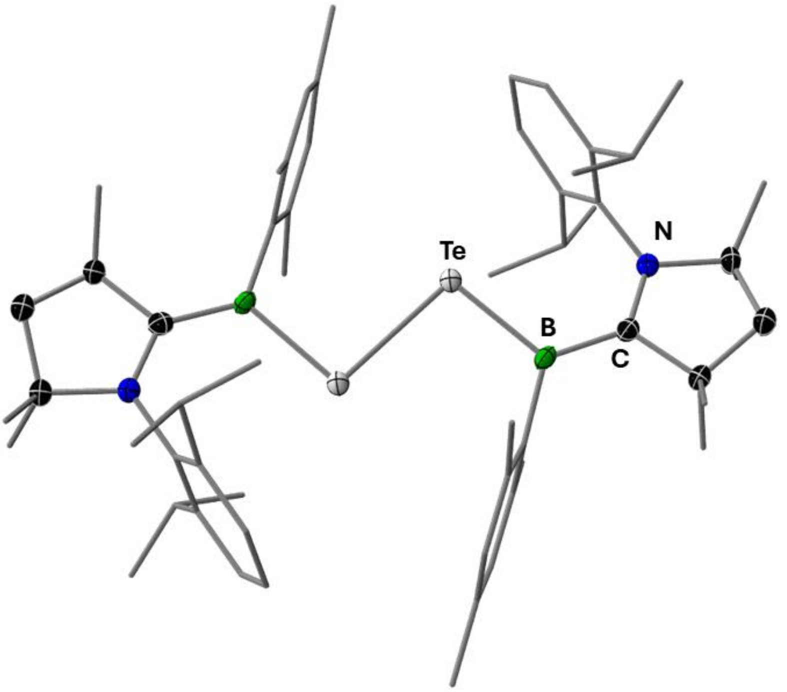
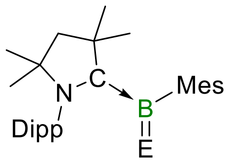
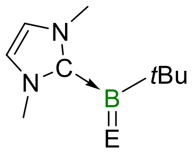


Figure S55. Solid-state structure of **[(1-Te)$_2$]PF$_6$**. Atomic displacement ellipsoids represented at 50%. For clarity, ellipsoids of the carbon atoms of the aryl and alkyl groups, as well as THF molecules, the hydrogen atoms and the counteranion, are omitted.

Comparison of Significant Spectroscopic and Bonding Parameters Across Redox States of 1-E



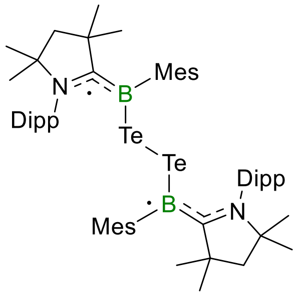
1-S
1-Se



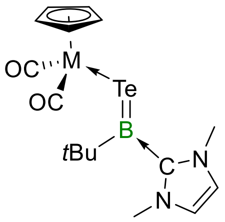
I-S
I-Se

	1-E	**I-E**
NMR resonances [ppm]		
^{11}B (E = S)	δ = 63.2	δ = 66.4
^{11}B (E = Se)	δ = 70.7	δ = 73.5
Bond lengths [Å]		
B−S	1.735(1)	1.739(2)
B−Se	1.882(4)	1.876(4)

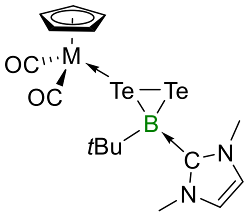
Figure S56. Comparison of analytical parameters of **1-S** and **1-Se** with literature-known NHC compounds.



(1-Te)$_2$



II-Te



II-Te$_2$

	(1-Te)$_2$		**II-Te**	**II-Te$_2$**	
Bond	B−Te	Te −Te	B−Te	B−Te	Te −Te
Bond length [Å]	2.191(3)	2.7251(3)	2.100(4)	2.333(2) 2.296(3)	2.7541(4)
WBI	1.31	1.08	1.69	0.8942 0.9957	0.8722

Figure S57. Comparison of calculated and experimentally determined bonding parameters of **(1-Te)$_2$** with other literature-known boron-tellurium compounds.

Table S1. Comparison of Significant Bonding Parameters of **$1^{Mes}S$** with Increasing Charge.

	$1^{Mes}S$	**$Li[1^{Mes}S]$**	**$Li_2[1^{Mes}S]$**
Bonding parameters [Å]/[°]			
N1−C1	1.314(1)	1.394(3)	1.503(5)
C1−B1	1.613(2)	1.535(3)	1.468(6)
B1−S1	1.735(1)	1.808(2)	1.899(6)
N1−C1−B1−S1	75.4(1)	15.1(2)	1.2(6)

Table S2. Comparison of Significant Bonding Parameters of Dianionic Compounds.

	$Li_2[1^{Mes}S]$	**$Li_2[1^{Mes}Se]$**	**$Li_2[1^{Mes}Te]$**
Bonding parameters [Å]/[°]			
N1−C1	1.503(5)	1.503(4), 1.511(4)	1.509(2), 1.510(2)
C1−B1	1.468(6)	1.467(4), 1.466(4)	1.461(3), 1.461(3)
B1−E1	1.899(6)	2.039(3), 2.030(3)	2.260(2), 2.259(2)
N1−C1−B1−E1	1.2(6)	3.7(4), 1.1(4)	2.7(3), 5.2(3)
NMR resonances [ppm]			
^{11}B	28.0	24.8	17.1
^{13}C(C1)	125.5	127.5	130.7
$^{77}Se/^{125}Te$	-	−428.8	−1183.1
Natural charge densities (NBO)			
N1	−0.50	−0.50	−0.51
C1	−0.46	−0.47	−0.48
B1	+0.35	+0.33	+0.31
E1	−0.86	−0.84	−0.82

Computational Details

All calculations were done using the Gaussian 16, Revision C.01[11] and the ORCA 5.0.4[12] quantum chemistry program packages. Geometry optimizations of **1-E**, **[1-E]$^{2-}$** (E = S, Se, Te) and **(1-Te)$_2$** were performed at the (U) ωB97X-D[13]/Def2-SVP[14] level of theory. All optimized geometries were characterized as minima on the corresponding potential energy surface by vibrational frequency calculations, which revealed that all eigenvalues of the Hessian matrices are positive.

To analyze the diradical character as well as the ground state multiplicity[15] of **(1-Te)$_2$**, single-point calculations using the *complete-active-space self-consistent field* (CASSCF)[16] and the *domain-based local pair natural orbital* (DLPNO)[17] approximation of the *N-electron valence state 2nd order perturbation theory* (NEVPT2)[18] were performed. An active space of two electrons in two molecular orbitals was constructed. The Def2-TZVP[14] basis set was chosen for these calculations, which were done in combination with the *resolution of identity* approximation for coulomb integrals (RI-J)[19] and the numerical *chain-of-spheres* integration for the Hartree-Fock exchange integrals (COSX).[20] The biradical character y_0[21] was obtained using the *natural orbital occupation numbers* (NOON)[22] of the CASSCF(2,2) calculations:

$$y_0 = 1 - \frac{\mathrm{ON_{HONO}} - \mathrm{ON_{LUNO}}}{1 + \left(\frac{\mathrm{ON_{HONO}} - \mathrm{ON_{LUNO}}}{2}\right)^2} \tag{S1}$$

$\mathrm{ON_{HONO}}$ and $\mathrm{ON_{LUNO}}$ are the occupation numbers of the *highest occupied natural orbital* (HONO) and the *lowest unoccupied natural orbital* (LUNO).

To assess the bonding situations in the systems **1-E** and **[1-E]$^{2-}$** (E = S, Se, Te) Mayer bond orders (MBOs)[23] were calculated at the ωB97X-D/Def2-TZVP level of theory. For this the Multiwfn 3.8[24] tool was used.

For the thermodynamical properties of the dimerization the Gibbs free energies were considered with respect to the thermal correction obtained from frequency calculation and the concentration correction of 1.89 kcal mol^{-1} to account for the conversion from gas phase to solution at 298.15 K.

To quantify the atomic spin density populations in **(1-Te)$_2$** and the charge distributions in **[1-E]$^{2-}$** (E = S, Se, Te) the natural bond orbital (NBO) method 7.0[25] at the UωB97X-D/Def2-TZVP level of theory was used. For the charge distributions the dianionic systems without the lithium cations and their respective THF moieties were considered to lower the computational cost. The influence on the charge distributions, when compared to the complete systems, was negligible.

Cartesian Coordinates

Compound 1-S, ωB97X-D/Def2-SVP

Geometry of the lowest singlet state

Energy = –1606.91787453 E_h

S	-0.2349890	1.7664140	-2.2367400
B	-0.8931320	0.9050510	-0.8812290
N	1.4012180	0.5849080	0.3731590
C	1.6139040	-0.8240830	0.1483200
C	0.2562170	1.2232710	0.1813870
C	1.2721000	-1.6956060	1.2083330
C	-2.4461930	-1.1868490	-0.7603220
C	2.1735720	-1.3097050	-1.0472250
C	1.4949710	-3.0628960	1.0395050
H	1.2276020	-3.7535380	1.8413630
C	-2.3069410	0.2148070	-0.6839220
C	0.6289060	-1.2122650	2.5006690
H	0.7992650	-0.1310250	2.5733040
C	-1.2902810	-2.0759930	-1.1432460
H	-0.5360040	-1.5326350	-1.7269700
H	-1.6369920	-2.9230750	-1.7526870
H	-0.7841830	-2.4947960	-0.2610730
C	2.4709880	1.4698860	0.9582030
C	-3.6862560	-1.7872320	-0.5167360
H	-3.7664790	-2.8772770	-0.5810710
C	1.2535450	-1.8429810	3.7490050
H	2.3500940	-1.7482320	3.7498220
H	1.0108220	-2.9130860	3.8355670
H	0.8658990	-1.3507120	4.6538080
C	0.2249060	2.4725740	1.0810560
C	2.5857260	-0.4220240	-2.2086960
H	2.2687730	0.6026560	-1.9776540
C	2.0384220	-3.5620860	-0.1380150
H	2.2016180	-4.6354890	-0.2548420
C	2.3704450	-2.6908270	-1.1643290
H	2.7961540	-3.0886000	-2.0879010
C	-4.8208560	-1.0372110	-0.2184990
C	1.6063350	2.4314440	1.7800900
H	2.0638930	3.4275390	1.8502170
H	1.5017550	2.0482030	2.8069860
C	-0.8958830	2.2491730	2.1153970
H	-0.9053670	3.0882710	2.8281800
H	-0.7439370	1.3230700	2.6859480
H	-1.8834560	2.1853030	1.6426670
C	-0.8886080	-1.4288300	2.4739640
H	-1.3470330	-1.0673000	3.4077910
H	-1.1310080	-2.4986010	2.3718930
H	-1.3643480	-0.9004230	1.6356860
C	3.4768380	0.6921490	1.7963750
H	4.0168630	-0.0482250	1.1886420
H	3.0030930	0.1696420	2.6375790
H	4.2138210	1.3973550	2.2072490

C	-3.4766600	0.9887640	-0.4788380
C	1.8757160	-0.8064600	-3.5105010
H	2.1655140	-0.1108380	-4.3124600
H	0.7849290	-0.7400840	-3.4012840
H	2.1399810	-1.8243570	-3.8386060
C	3.1954090	2.2195610	-0.1670400
H	2.4790240	2.6443150	-0.8853680
H	3.8798090	1.5613160	-0.7146290
H	3.7912370	3.0365680	0.2655770
C	-4.6960730	0.3535630	-0.2327280
H	-5.5877940	0.9678940	-0.0715510
C	-0.0075480	3.8029260	0.3592860
H	0.0024180	4.6173790	1.1003900
H	-0.9721370	3.8171040	-0.1615300
H	0.7694870	3.9965090	-0.3912890
C	-6.1414180	-1.6939530	0.0882000
H	-6.3199020	-1.7284720	1.1755170
H	-6.1742340	-2.7276280	-0.2849760
H	-6.9794620	-1.1412500	-0.3619690
C	4.1083280	-0.4493920	-2.3955810
H	4.4189790	0.3020050	-3.1376760
H	4.4477420	-1.4337400	-2.7555760
H	4.6447690	-0.2459250	-1.4561870
C	-3.4698480	2.4966080	-0.5842130
H	-2.8545550	2.8263760	-1.4329990
H	-3.0683180	2.9834820	0.3180120
H	-4.4899580	2.8800810	-0.7254350

Compound 1-Se, ωB97X-D/Def2-SVP

Geometry of the lowest singlet state

Energy = –3610.17090908 E_h

Se	-0.1126070	-2.3263620	-1.5883960
B	-0.8409670	-1.0289830	-0.4538660
N	1.4060950	-0.2454880	0.6544910
C	1.5399310	1.0448200	0.0232400
C	2.1443440	1.1928300	-1.2386640
C	0.3264610	-1.9127530	1.8876270
C	0.3085690	-0.9926450	0.6465850
C	2.6885420	0.0327030	-2.0540040
H	2.4060750	-0.8975830	-1.5442670
C	1.0884540	2.1663330	0.7576940
C	2.5011530	-0.8258720	1.5102770
C	-0.8629120	-1.5046770	2.7772100
H	-1.8205410	-1.7871810	2.3272090
H	-0.8837410	-0.4218780	2.9627290
H	-0.7776570	-2.0147920	3.7493300
C	1.6574560	-1.5272610	2.5771960
H	1.4651680	-0.8310720	3.4084490
H	2.1737940	-2.4011150	2.9972180
C	3.4236910	0.2432860	2.0800130
H	4.1799240	-0.2447360	2.7119130
H	2.8839290	0.9714210	2.6989390
H	3.9480090	0.7882330	1.2818390

C	0.4135960	2.0526740	2.1174510
H	0.6170320	1.0478330	2.5075790
C	-2.2569720	-0.3157510	-0.4900060
C	3.3168010	-1.8430340	0.7014500
H	2.6617930	-2.5115530	0.1240810
H	3.9246850	-2.4497550	1.3885100
H	3.9995420	-1.3472160	0.0021870
C	2.2711480	2.4863880	-1.7579700
H	2.7307460	2.6206250	-2.7393330
C	4.2182170	0.1130270	-2.1471490
H	4.6257110	-0.8019140	-2.6039860
H	4.6876280	0.2423120	-1.1601320
H	4.5334000	0.9657890	-2.7693390
C	1.8290890	3.5977620	-1.0562140
H	1.9390530	4.5965790	-1.4836450
C	1.2437040	3.4336820	0.1931850
H	0.8915610	4.3106520	0.7394940
C	0.2545360	-3.4182210	1.6151660
H	1.0945470	-3.7618240	0.9984300
H	-0.6677150	-3.6926990	1.0892230
H	0.2787090	-3.9535940	2.5772400
C	-3.4095960	-0.9355680	0.0411420
C	-1.2727590	1.6320830	-1.8139150
H	-0.5496290	0.9053170	-2.2055570
H	-0.7270730	2.3157150	-1.1475260
H	-1.6442550	2.2281100	-2.6598470
C	-1.1079510	2.1908060	1.9927250
H	-1.5374410	1.4213160	1.3367840
H	-1.3804060	3.1720790	1.5728500
H	-1.5854860	2.1023380	2.9811950
C	0.9718040	3.0477570	3.1403840
H	2.0703330	3.0088300	3.1946280
H	0.5708670	2.8241320	4.1406560
H	0.6867420	4.0840970	2.9032430
C	2.0707720	-0.0372370	-3.4538840
H	2.4537590	-0.9208530	-3.9864240
H	2.3184870	0.8501130	-4.0578260
H	0.9781940	-0.1359200	-3.4022660
C	-2.4114940	0.9536740	-1.0975230
C	-3.4279090	-2.3697020	0.5173830
H	-4.1431250	-2.9503490	-0.0854820
H	-3.7537780	-2.4503770	1.5667940
H	-2.4542900	-2.8606910	0.4068950
C	-3.6447670	1.6055430	-1.0604900
H	-3.7365490	2.5868110	-1.5374970
C	-4.6267480	-0.2446570	0.0733050
H	-5.5026250	-0.7437920	0.5009320
C	-4.7640550	1.0383660	-0.4488680
C	-6.0703430	1.7846880	-0.3738660
H	-6.2619980	2.3522110	-1.2966560
H	-6.0624760	2.5076030	0.4583820
H	-6.9166630	1.1021640	-0.2104770

Compound 1-Te, ωB97X-D/Def2-SVP

Geometry of the lowest singlet state

Energy = –1476.92796995 E_h

Te	-0.0834750	-2.7091060	-0.9017910
B	-0.8305530	-0.9388910	-0.0683490
N	1.3973940	0.1541330	0.7711720
C	1.5200610	1.2174160	-0.1989710
C	2.1659120	1.0250220	-1.4346620
C	0.3162620	-1.0797680	2.4409590
C	0.3100060	-0.5834760	0.9736510
C	2.7738800	-0.2953760	-1.8734360
H	2.4788400	-1.0610700	-1.1431780
C	1.0243810	2.4884320	0.1778180
C	2.4842080	-0.1219680	1.7782950
C	-0.8894330	-0.4360220	3.1526090
H	-1.8377490	-0.8630250	2.8116650
H	-0.9318020	0.6496630	2.9928890
H	-0.8029930	-0.6173530	4.2352270
C	1.6313180	-0.4815980	2.9958960
H	1.4174470	0.4291190	3.5765910
H	2.1511710	-1.1797840	3.6657540
C	3.3835040	1.0841830	2.0120560
H	4.1329760	0.8206450	2.7724020
H	2.8239620	1.9552440	2.3757810
H	3.9166630	1.3736830	1.0953040
C	0.3301660	2.7572350	1.5057060
H	0.5324590	1.9052600	2.1656380
C	-2.2378880	-0.2565590	-0.3171170
C	3.3247680	-1.3232930	1.3271420
H	2.6882560	-2.1475440	0.9732490
H	3.9281650	-1.6814170	2.1740530
H	4.0129690	-1.0542830	0.5181940
C	2.2797100	2.1226450	-2.2954330
H	2.7708110	1.9892930	-3.2613510
C	4.3051000	-0.1964910	-1.9078790
H	4.7517630	-1.1872970	-2.0829780
H	4.7172220	0.2044170	-0.9697200
H	4.6400530	0.4695990	-2.7188740
C	1.7865440	3.3717770	-1.9503690
H	1.8859370	4.2118630	-2.6408160
C	1.1663190	3.5481340	-0.7201280
H	0.7780220	4.5323440	-0.4515940
C	0.2641360	-2.5958130	2.6525120
H	1.1062550	-3.1054990	2.1671460
H	-0.6573130	-3.0330440	2.2488300
H	0.2989310	-2.8019390	3.7337010
C	-3.3956880	-0.6635520	0.3832520
C	-1.2419420	1.1665380	-2.1914540
H	-0.5291230	0.3446480	-2.3377830
H	-0.6855530	2.0203410	-1.7790090
H	-1.6175620	1.4681500	-3.1798140
C	-1.1899200	2.8496290	1.3330100
H	-1.6133590	1.9251720	0.9180800
H	-1.4584480	3.6710920	0.6500780

H	-1.6761780	3.0441400	2.3018610
C	0.8742670	4.0038950	2.2126870
H	1.9723140	3.9911830	2.2846060
H	0.4645740	4.0668650	3.2322610
H	0.5860710	4.9296040	1.6916970
C	2.2424000	-0.7592620	-3.2330960
H	2.6366570	-1.7598180	-3.4662670
H	2.5489110	-0.0821620	-4.0460910
H	1.1464380	-0.8310780	-3.2319000
C	-2.3801350	0.7622430	-1.2909480
C	-3.4393990	-1.8893190	1.2657610
H	-4.1135960	-2.6377560	0.8207960
H	-3.8303460	-1.6585200	2.2694110
H	-2.4624750	-2.3753790	1.3660880
C	-3.6036140	1.4138840	-1.4515130
H	-3.6852740	2.1993670	-2.2098480
C	-4.6006300	0.0261690	0.2065470
H	-5.4795320	-0.3008110	0.7719640
C	-4.7241210	1.0867690	-0.6866320
C	-6.0172770	1.8440620	-0.8380680
H	-6.2077780	2.1067220	-1.8892670
H	-5.9903380	2.7858970	-0.2657820
H	-6.8731240	1.2593080	-0.4714930

Compound (1-Te)$_2$, ωB97X-D/Def2-SVP

Geometry of the lowest singlet state

Energy = –2953.91408692 E_h

Te	-0.1913780	-0.6632930	1.1942300
B	-1.3258720	0.9325980	2.1802580
C	-1.6762760	0.8987770	3.6628890
N	-1.2209090	0.0090050	4.6143080
C	-1.5196000	0.4426920	6.0091340
C	-0.3778860	1.2871140	6.6015800
H	0.4775030	0.6657610	6.8894580
H	-0.7334740	1.8019010	7.5066680
H	-0.0249870	2.0470090	5.8925940
C	-1.7907100	-0.7357950	6.9388140
H	-2.6400540	-1.3385360	6.5947410
H	-2.0283430	-0.3545720	7.9428480
H	-0.9133670	-1.3938510	7.0222800
C	-2.7663420	1.3005240	5.7743410
H	-2.8925170	2.0741950	6.5455550
H	-3.6564480	0.6525520	5.8154920
C	-2.6274720	1.8969400	4.3571620
C	-2.0978280	3.3406150	4.3992460
H	-2.0171630	3.7575470	3.3868180
H	-1.1127890	3.4158770	4.8784700
H	-2.7965060	3.9730230	4.9699150
C	-4.0074730	1.9220350	3.6822030
H	-3.9654000	2.4129580	2.7009870
H	-4.7174780	2.4844740	4.3103970
H	-4.4049900	0.9038880	3.5489730
C	-0.7229470	-1.3004810	4.3134950

C	0.6619420	-1.5832920	4.3429490
C	1.7129620	-0.5442780	4.7001060
H	1.2001790	0.4230630	4.7804370
C	2.8005850	-0.3867100	3.6310240
H	2.3675510	-0.1197000	2.6579600
H	3.3807170	-1.3135110	3.4981120
H	3.5059770	0.4046280	3.9288590
C	2.3522220	-0.8807220	6.0547100
H	2.9766430	-1.7848060	5.9756660
H	1.5985140	-1.0756770	6.8320580
H	2.9981370	-0.0577510	6.3986590
C	1.0842970	-2.8803670	4.0362770
H	2.1523520	-3.1087110	4.0408760
C	0.1782470	-3.8737380	3.6945830
H	0.5323440	-4.8739970	3.4398710
C	-1.1801330	-3.5872580	3.6714900
H	-1.8884270	-4.3725540	3.3985790
C	-1.6582740	-2.3135140	3.9858050
C	-3.1622230	-2.0763640	3.9559290
H	-3.3481080	-1.0687390	4.3493640
C	-3.7136590	-2.1148400	2.5271420
H	-3.1958310	-1.3952500	1.8810650
H	-4.7895340	-1.8781180	2.5229380
H	-3.5864450	-3.1138910	2.0803190
C	-3.9192420	-3.0693760	4.8467640
H	-4.9819970	-2.7890440	4.9108990
H	-3.5120380	-3.1046510	5.8679950
H	-3.8753500	-4.0914910	4.4398340
C	-1.6734010	2.1575460	1.2309810
C	-0.7858770	3.2549250	1.1799300
C	0.4885980	3.2511400	1.9873780
H	1.2242560	2.5699610	1.5269520
H	0.3256780	2.8912730	3.0134580
H	0.9399620	4.2523750	2.0366670
C	-1.0453070	4.3283920	0.3218080
H	-0.3482990	5.1721230	0.3026360
C	-2.1599540	4.3465010	-0.5149920
C	-2.4615980	5.5291960	-1.3977790
H	-2.8181130	5.2104570	-2.3893970
H	-1.5750760	6.1646370	-1.5390510
H	-3.2513040	6.1596630	-0.9573040
C	-3.0040230	3.2345200	-0.4985250
H	-3.8679590	3.2106500	-1.1707000
C	-2.7742490	2.1448830	0.3438900
C	-3.6753470	0.9410080	0.2439340
H	-4.5374260	1.1363090	-0.4094040
H	-4.0539240	0.6259420	1.2262070
H	-3.1214400	0.0834760	-0.1725420
Te	0.1913780	0.6632930	-1.1942300
B	1.3258720	-0.9325980	-2.1802580
C	1.6762760	-0.8987770	-3.6628890
N	1.2209090	-0.0090050	-4.6143080
C	1.5196000	-0.4426920	-6.0091340
C	0.3778860	-1.2871140	-6.6015800
H	-0.4775030	-0.6657610	-6.8894580

H	0.7334740	-1.8019010	-7.5066680
H	0.0249870	-2.0470090	-5.8925940
C	1.7907100	0.7357950	-6.9388140
H	2.6400540	1.3385360	-6.5947410
H	2.0283430	0.3545720	-7.9428480
H	0.9133670	1.3938510	-7.0222800
C	2.7663420	-1.3005240	-5.7743410
H	2.8925170	-2.0741950	-6.5455550
H	3.6564480	-0.6525520	-5.8154920
C	2.6274720	-1.8969400	-4.3571620
C	2.0978280	-3.3406150	-4.3992460
H	2.0171630	-3.7575470	-3.3868180
H	1.1127890	-3.4158770	-4.8784700
H	2.7965060	-3.9730230	-4.9699150
C	4.0074730	-1.9220350	-3.6822030
H	3.9654000	-2.4129580	-2.7009870
H	4.7174780	-2.4844740	-4.3103970
H	4.4049900	-0.9038880	-3.5489730
C	0.7229470	1.3004810	-4.3134950
C	-0.6619420	1.5832920	-4.3429490
C	-1.7129620	0.5442780	-4.7001060
H	-1.2001790	-0.4230630	-4.7804370
C	-2.8005850	0.3867100	-3.6310240
H	-2.3675510	0.1197000	-2.6579600
H	-3.3807170	1.3135110	-3.4981120
H	-3.5059770	-0.4046280	-3.9288590
C	-2.3522220	0.8807220	-6.0547100
H	-2.9766430	1.7848060	-5.9756660
H	-1.5985140	1.0756770	-6.8320580
H	-2.9981370	0.0577510	-6.3986590
C	-1.0842970	2.8803670	-4.0362770
H	-2.1523520	3.1087110	-4.0408760
C	-0.1782470	3.8737380	-3.6945830
H	-0.5323440	4.8739970	-3.4398710
C	1.1801330	3.5872580	-3.6714900
H	1.8884270	4.3725540	-3.3985790
C	1.6582740	2.3135140	-3.9858050
C	3.1622230	2.0763640	-3.9559290
H	3.3481080	1.0687390	-4.3493640
C	3.7136590	2.1148400	-2.5271420
H	3.1958310	1.3952500	-1.8810650
H	4.7895340	1.8781180	-2.5229380
H	3.5864450	3.1138910	-2.0803190
C	3.9192420	3.0693760	-4.8467640
H	4.9819970	2.7890440	-4.9108990
H	3.5120380	3.1046510	-5.8679950
H	3.8753500	4.0914910	-4.4398340
C	1.6734010	-2.1575460	-1.2309810
C	0.7858770	-3.2549250	-1.1799300
C	-0.4885980	-3.2511400	-1.9873780
H	-1.2242560	-2.5699610	-1.5269520
H	-0.3256780	-2.8912730	-3.0134580
H	-0.9399620	-4.2523750	-2.0366670
C	1.0453070	-4.3283920	-0.3218080
H	0.3482990	-5.1721230	-0.3026360

C	2.1599540	-4.3465010	0.5149920
C	2.4615980	-5.5291960	1.3977790
H	2.8181130	-5.2104570	2.3893970
H	1.5750760	-6.1646370	1.5390510
H	3.2513040	-6.1596630	0.9573040
C	3.0040230	-3.2345200	0.4985250
H	3.8679590	-3.2106500	1.1707000
C	2.7742490	-2.1448830	-0.3438900
C	3.6753470	-0.9410080	-0.2439340
H	4.5374260	-1.1363090	0.4094040
H	4.0539240	-0.6259420	-1.2262070
H	3.1214400	-0.0834760	0.1725420

Compound (1-Te)$_2$, ωB97X-D/Def2-SVP

Geometry of the lowest triplet state

Energy = –2953.91376505 E_h

Te	-0.1886240	-0.6647710	1.1953380
B	-1.3252230	0.9317140	2.1807120
C	-1.6760860	0.8991970	3.6637000
N	-1.2191420	0.0106790	4.6154730
C	-1.5177460	0.4453350	6.0101300
C	-0.3765360	1.2913050	6.6013190
H	0.4793270	0.6709470	6.8898820
H	-0.7324000	1.8069860	7.5057800
H	-0.0242810	2.0505450	5.8913210
C	-1.7874980	-0.7325860	6.9409100
H	-2.6361600	-1.3366120	6.5974030
H	-2.0255540	-0.3506440	7.9445680
H	-0.9094340	-1.3895820	7.0249890
C	-2.7653720	1.3018370	5.7750730
H	-2.8920570	2.0758990	6.5458030
H	-3.6548520	0.6530500	5.8169080
C	-2.6274880	1.8973700	4.3574370
C	-2.0986960	3.3414300	4.3982810
H	-2.0186450	3.7576640	3.3855280
H	-1.1135130	3.4176450	4.8770390
H	-2.7975560	3.9738230	4.9687380
C	-4.0078220	1.9212150	3.6830170
H	-3.9664350	2.4115360	2.7014770
H	-4.7179140	2.4836050	4.3111530
H	-4.4048240	0.9027700	3.5505480
C	-0.7208290	-1.2991050	4.3158450
C	0.6641020	-1.5816340	4.3462950
C	1.7148400	-0.5420970	4.7027460
H	1.2018920	0.4252560	4.7818250
C	2.8027410	-0.3855000	3.6338050
H	2.3697470	-0.1199060	2.6603310
H	3.3831690	-1.3123030	3.5022040
H	3.5078170	0.4063920	3.9309160
C	2.3536650	-0.8769400	6.0579420
H	2.9781700	-1.7810690	5.9801600
H	1.5997350	-1.0710250	6.8352930
H	2.9994190	-0.0535260	6.4011270

C	1.0868000	-2.8788920	4.0410410
H	2.1549010	-3.1069950	4.0462690
C	0.1810850	-3.8727970	3.6998920
H	0.5355340	-4.8731790	3.4461180
C	-1.1773020	-3.5866020	3.6759960
H	-1.8853460	-4.3722040	3.4033410
C	-1.6558150	-2.3126210	3.9889410
C	-3.1597790	-2.0757790	3.9582040
H	-3.3460140	-1.0677020	4.3502800
C	-3.7104640	-2.1162170	2.5291970
H	-3.1912660	-1.3986590	1.8819420
H	-4.7860610	-1.8782590	2.5239120
H	-3.5841300	-3.1162400	2.0843130
C	-3.9170680	-3.0676810	4.8500210
H	-4.9799790	-2.7876670	4.9128850
H	-3.5106640	-3.1011290	5.8716350
H	-3.8724430	-4.0904300	4.4447840
C	-1.6738970	2.1561160	1.2312550
C	-0.7870830	3.2539830	1.1799680
C	0.4876200	3.2507420	1.9870040
H	1.2250110	2.5735050	1.5235500
H	0.3259540	2.8861040	3.0116590
H	0.9360320	4.2531020	2.0403430
C	-1.0472360	4.3270490	0.3215970
H	-0.3505880	5.1710590	0.3019340
C	-2.1620490	4.3442580	-0.5150210
C	-2.4641070	5.5263320	-1.3984980
H	-2.8209930	5.2068600	-2.3897330
H	-1.5776250	6.1616400	-1.5406050
H	-3.2536130	6.1571260	-0.9581360
C	-3.0057250	3.2319810	-0.4978330
H	-3.8697480	3.2074210	-1.1698590
C	-2.7751520	2.1426960	0.3448000
C	-3.6752580	0.9380700	0.2453160
H	-4.5405860	1.1342160	-0.4034610
H	-4.0488740	0.6195600	1.2283740
H	-3.1221260	0.0825290	-0.1762860
Te	0.1886240	0.6647710	-1.1953380
B	1.3252230	-0.9317140	-2.1807120
C	1.6760860	-0.8991970	-3.6637000
N	1.2191420	-0.0106790	-4.6154730
C	1.5177460	-0.4453350	-6.0101300
C	0.3765360	-1.2913050	-6.6013190
H	-0.4793270	-0.6709470	-6.8898820
H	0.7324000	-1.8069860	-7.5057800
H	0.0242810	-2.0505450	-5.8913210
C	1.7874980	0.7325860	-6.9409100
H	2.6361600	1.3366120	-6.5974030
H	2.0255540	0.3506440	-7.9445680
H	0.9094340	1.3895820	-7.0249890
C	2.7653720	-1.3018370	-5.7750730
H	2.8920570	-2.0758990	-6.5458030
H	3.6548520	-0.6530500	-5.8169080
C	2.6274880	-1.8973700	-4.3574370
C	2.0986960	-3.3414300	-4.3982810

H	2.0186450	-3.7576640	-3.3855280
H	1.1135130	-3.4176450	-4.8770390
H	2.7975560	-3.9738230	-4.9687380
C	4.0078220	-1.9212150	-3.6830170
H	3.9664350	-2.4115360	-2.7014770
H	4.7179140	-2.4836050	-4.3111530
H	4.4048240	-0.9027700	-3.5505480
C	0.7208290	1.2991050	-4.3158450
C	-0.6641020	1.5816340	-4.3462950
C	-1.7148400	0.5420970	-4.7027460
H	-1.2018920	-0.4252560	-4.7818250
C	-2.8027410	0.3855000	-3.6338050
H	-2.3697470	0.1199060	-2.6603310
H	-3.3831690	1.3123030	-3.5022040
H	-3.5078170	-0.4063920	-3.9309160
C	-2.3536650	0.8769400	-6.0579420
H	-2.9781700	1.7810690	-5.9801600
H	-1.5997350	1.0710250	-6.8352930
H	-2.9994190	0.0535260	-6.4011270
C	-1.0868000	2.8788920	-4.0410410
H	-2.1549010	3.1069950	-4.0462690
C	-0.1810850	3.8727970	-3.6998920
H	-0.5355340	4.8731790	-3.4461180
C	1.1773020	3.5866020	-3.6759960
H	1.8853460	4.3722040	-3.4033410
C	1.6558150	2.3126210	-3.9889410
C	3.1597790	2.0757790	-3.9582040
H	3.3460140	1.0677020	-4.3502800
C	3.7104640	2.1162170	-2.5291970
H	3.1912660	1.3986590	-1.8819420
H	4.7860610	1.8782590	-2.5239120
H	3.5841300	3.1162400	-2.0843130
C	3.9170680	3.0676810	-4.8500210
H	4.9799790	2.7876670	-4.9128850
H	3.5106640	3.1011290	-5.8716350
H	3.8724430	4.0904300	-4.4447840
C	1.6738970	-2.1561160	-1.2312550
C	0.7870830	-3.2539830	-1.1799680
C	-0.4876200	-3.2507420	-1.9870040
H	-1.2250110	-2.5735050	-1.5235500
H	-0.3259540	-2.8861040	-3.0116590
H	-0.9360320	-4.2531020	-2.0403430
C	1.0472360	-4.3270490	-0.3215970
H	0.3505880	-5.1710590	-0.3019340
C	2.1620490	-4.3442580	0.5150210
C	2.4641070	-5.5263320	1.3984980
H	2.8209930	-5.2068600	2.3897330
H	1.5776250	-6.1616400	1.5406050
H	3.2536130	-6.1571260	0.9581360
C	3.0057250	-3.2319810	0.4978330
H	3.8697480	-3.2074210	1.1698590
C	2.7751520	-2.1426960	-0.3448000
C	3.6752580	-0.9380700	-0.2453160
H	4.5405860	-1.1342160	0.4034610
H	4.0488740	-0.6195600	-1.2283740

H	3.1221260	-0.0825290	0.1762860

Compound [1-S]$^{2-}$, ωB97X-D/Def2-SVP

Geometry of the lowest singlet state

Energy = –1606.84690442 E_h

S	-0.3516000	0.0577580	-2.3464200
B	-0.9569350	-0.1164850	-0.6186740
C	-2.5798090	-0.1276860	-0.5578270
C	-3.2909540	-1.3460270	-0.6991390
C	-2.5141110	-2.6139940	-0.9418450
H	-3.1765970	-3.4831200	-1.0973570
H	-1.8282520	-2.8192210	-0.1057520
H	-1.8686240	-2.4604390	-1.8240980
C	-4.6890600	-1.3753920	-0.6724880
H	-5.2044320	-2.3400580	-0.7742660
C	-5.4482680	-0.2100590	-0.5295550
C	-6.9545270	-0.2613100	-0.4413310
H	-7.3693170	-1.0786490	-1.0550300
H	-7.4113750	0.6808010	-0.7872580
H	-7.3047670	-0.4283110	0.5944360
C	-4.7552640	1.0005180	-0.4607420
H	-5.3229780	1.9386330	-0.3963710
C	-3.3560450	1.0530340	-0.4889820
C	-2.6566850	2.3862860	-0.5378120
H	-1.9605400	2.5091570	0.3046170
H	-3.3682720	3.2298140	-0.5397430
H	-2.0346100	2.4154150	-1.4478350
C	-0.1746170	-0.2244790	0.6438790
N	1.2868470	-0.3442300	0.7000400
C	1.6797780	-1.0289680	1.9335960
C	3.0948070	-0.6880550	2.4038060
H	3.2656500	-1.1263540	3.4021720
H	3.2336040	0.4019800	2.4678570
H	3.8622620	-1.0744770	1.7181470
C	1.5158450	-2.5653370	1.8597980
H	1.3533830	-3.0013420	2.8608650
H	2.4031320	-3.0485270	1.4260770
H	0.6470390	-2.7994530	1.2271060
C	0.6447110	-0.4314970	2.9098470
H	1.0138580	0.5626310	3.2161550
H	0.5208280	-1.0337110	3.8291390
C	-0.6651970	-0.2653100	2.1097750
C	-1.3814470	1.0179410	2.5814530
H	-1.5975260	0.9929920	3.6694920
H	-2.3390570	1.1359700	2.0522320
H	-0.7655550	1.9075770	2.3794950
C	-1.6293600	-1.4312140	2.4145670
H	-1.9295460	-1.4361890	3.4820270
H	-1.1741340	-2.4051780	2.1870370
H	-2.5406770	-1.3388160	1.8063890
C	2.2147110	0.2925620	-0.1220850
C	2.2631870	1.7076910	-0.2810090
C	1.1716200	2.5991930	0.2795740

H	0.3340350	1.9234990	0.5137210
C	0.6540010	3.5830640	-0.7713390
H	-0.2181710	4.1385050	-0.3864670
H	0.3413820	3.0083120	-1.6579700
H	1.4166250	4.3271470	-1.0675170
C	1.6154970	3.2985210	1.5662920
H	0.7871900	3.8828230	2.0053410
H	2.4585280	3.9905190	1.3851390
H	1.9411800	2.5619280	2.3181650
C	3.3553010	2.2942180	-0.9179180
H	3.3965670	3.3865470	-0.9864360
C	4.4040690	1.5400660	-1.4447170
H	5.2650130	2.0265750	-1.9139960
C	4.2940770	0.1539460	-1.4109290
H	5.0501190	-0.4584670	-1.9164030
C	3.2044410	-0.4769560	-0.8075480
C	2.9781300	-1.9561210	-1.0825580
H	2.0858290	-2.2434240	-0.5159710
C	2.6160670	-2.1488400	-2.5604290
H	2.3584330	-3.2043180	-2.7635200
H	3.4588530	-1.8698590	-3.2185270
H	1.7376820	-1.5161790	-2.7928010
C	4.1444390	-2.8579700	-0.6683940
H	3.8931600	-3.9212060	-0.8278410
H	4.4106450	-2.7287860	0.3930750
H	5.0497540	-2.6437890	-1.2633630

Compound [1-Se]$^{2–}$, ωB97X-D/Def2-SVP

Geometry of the lowest singlet state

Energy = –3610.11128111 E$_h$

Se	0.3449470	0.0935090	-2.3328990
C	2.6326980	2.3822320	-0.2977370
H	1.9182890	2.4801130	0.5323320
H	2.0310090	2.4360240	-1.2208810
H	3.3411150	3.2274860	-0.2601920
N	-1.3128550	-0.3744330	0.8396210
C	0.1507190	-0.2651980	0.7866870
C	-1.7146850	-1.0710170	2.0639350
C	3.3374770	1.0517120	-0.2681620
C	2.5720370	-0.1344940	-0.3758160
C	-2.2389430	0.2951710	0.0350780
C	-1.5751710	-2.6084590	1.9624690
H	-1.4241460	-3.0650140	2.9560860
H	-0.7088800	-2.8471720	1.3284680
H	-2.4680080	-3.0691380	1.5167690
C	4.7359520	1.0090060	-0.2130120
H	5.2938180	1.9503690	-0.1192620
C	2.5429910	-2.6195400	-0.7995560
H	1.8208750	-2.8327440	0.0028640
H	3.2208290	-3.4817890	-0.9233770
H	1.9383390	-2.4763980	-1.7121390
C	-2.2764350	1.7147770	-0.0722050
C	3.2970120	-1.3453050	-0.5215950

C	4.6943260	-1.3624260	-0.4668130
H	5.2195660	-2.3210590	-0.5735040
C	1.3714120	0.9176970	2.7564280
H	0.7691830	1.8208020	2.5747420
H	2.3328760	1.0349840	2.2347920
H	1.5812010	0.8625640	3.8441330
C	0.6387200	-0.3440420	2.2559410
C	-0.6726320	-0.5086320	3.0515860
H	-1.0275040	0.4830470	3.3806080
H	-0.5566060	-1.1322550	3.9572420
C	-3.3521500	2.3328540	-0.7079390
H	-3.3826630	3.4267030	-0.7440510
C	-3.1236290	-0.7158670	2.5424000
H	-3.3019520	-1.1756960	3.5296090
H	-3.8987970	-1.0699990	1.8486970
H	-3.2429190	0.3742790	2.6344490
C	-3.2333360	-0.4438470	-0.6738710
C	-1.1923510	2.5790760	0.5437720
H	-0.3528700	1.8968720	0.7463740
C	-3.0519730	-1.9273130	-0.9610780
H	-2.1481190	-2.2375920	-0.4247780
C	1.5843020	-1.5298840	2.5381500
H	1.8705860	-1.5657330	3.6084780
H	2.5044410	-1.4329450	1.9446460
H	1.1200000	-2.4918540	2.2804290
C	5.4407660	-0.1939350	-0.2896700
C	-4.3073800	0.2180770	-1.2727460
H	-5.0678200	-0.3706620	-1.7987180
C	-0.6703070	3.6291790	-0.4386560
H	-1.4302720	4.3935710	-0.6849870
H	-0.3534990	3.1214360	-1.3637020
H	0.2004800	4.1557710	-0.0126800
C	6.9452830	-0.2346720	-0.1726900
H	7.2763690	-0.4279060	0.8647910
H	7.3998740	0.7207670	-0.4829130
H	7.3796620	-1.0306660	-0.8006710
C	-4.3980240	1.6051920	-1.2731270
H	-5.2452100	2.1141130	-1.7435270
C	-4.2287150	-2.7986440	-0.5095970
H	-4.4595140	-2.6664840	0.5592760
H	-4.0112820	-3.8677190	-0.6791020
H	-5.1452100	-2.5574080	-1.0762870
C	-2.7532000	-2.1352950	-2.4507240
H	-2.5278410	-3.1974650	-2.6557610
H	-1.8723550	-1.5255500	-2.7262380
H	-3.6146320	-1.8427530	-3.0778070
C	-1.6520510	3.2037260	1.8633710
H	-2.4954320	3.9016670	1.7097400
H	-0.8308570	3.7656850	2.3427090
H	-1.9838360	2.4272390	2.5705430
B	0.9554430	-0.1333080	-0.4509790

Compound [1-Te]$^{2–}$, ωB97X-D/Def2-SVP

Geometry of the lowest singlet state

Energy = –1476.88677548 E_h

Te	0.3510940	-2.4166230	0.0173210
N	-1.3376870	1.0071480	0.3546240
C	-2.2662670	0.1863760	-0.3025520
C	2.5807340	-0.4711410	2.6667390
H	1.8011010	0.2877800	2.8279060
H	3.2695360	-0.4800590	3.5289030
H	2.0462050	-1.4353610	2.6028900
C	3.3085980	-0.2340370	1.3697860
C	-3.1464010	2.7369890	0.5704960
H	-3.3280150	3.7441660	0.9829500
H	-3.9334390	2.0646500	0.9372190
H	-3.2439230	2.7827890	-0.5243050
C	-1.7464030	2.2707060	0.9752690
C	4.7036240	-0.1381100	1.3704810
H	5.2385070	-0.1835460	2.3283410
C	4.7197280	0.0071790	-1.0093530
H	5.2669140	0.0756370	-1.9588270
C	0.1276200	0.9486080	0.2543910
C	2.5698750	-0.1678720	0.1591070
C	3.3236080	-0.0888870	-1.0384170
C	-0.6956050	3.2281100	0.3830750
H	-1.0337000	3.5109240	-0.6281270
H	-0.5873180	4.1617720	0.9647870
C	5.4358530	0.0044140	0.1890190
C	-3.2689080	-0.4972520	0.4466950
C	-2.2947540	0.0522200	-1.7190840
C	1.3692040	2.8743830	-0.9900920
H	1.5730930	3.9637600	-0.9704340
H	0.7831800	2.6594720	-1.8964520
H	2.3340900	2.3534120	-1.0717180
C	-3.1427670	-0.7017490	1.9502810
H	-2.2204800	-0.1914340	2.2533640
C	0.6155710	2.4260700	0.2775330
C	-3.3569980	-0.6119420	-2.3315790
H	-3.3771080	-0.6776940	-3.4238770
C	-4.3297570	-1.1238940	-0.2116660
H	-5.0981600	-1.6309170	0.3824220
C	-1.6922450	1.9655120	-3.2464980
H	-0.8768000	2.4408530	-3.8196330
H	-2.0332160	2.6873720	-2.4882390
H	-2.5331960	1.7847430	-3.9404420
C	1.5380390	2.7616440	1.4668350
H	1.8035290	3.8373770	1.4686730
H	2.4704670	2.1838440	1.4033130
H	1.0649730	2.5292280	2.4307290
C	-0.6818720	-0.3255460	-3.6310010
H	0.1832100	0.1059340	-4.1621830
H	-1.4384710	-0.5877550	-4.3928990
H	-0.3534900	-1.2446200	-3.1197790
C	-1.2163180	0.6647660	-2.5942060
H	-0.3789720	0.8900210	-1.9187420

C	2.6160360	-0.1851590	-2.3635340
H	1.8652310	0.6091560	-2.4789740
H	2.0572130	-1.1364140	-2.3982180
H	3.3200250	-0.1355540	-3.2115790
C	6.9366570	0.1643660	0.2103160
H	7.3936850	-0.1939950	-0.7268350
H	7.3923570	-0.3995750	1.0412980
H	7.2398670	1.2207100	0.3342790
C	-4.4007750	-1.1695680	-1.5981360
H	-5.2358780	-1.6662780	-2.1016950
C	-1.6353960	2.2459710	2.5181680
H	-1.5008060	3.2622490	2.9273480
H	-0.7712110	1.6313210	2.8078040
H	-2.5330150	1.8160360	2.9832470
C	-4.3224550	-0.1392160	2.7523930
H	-4.1465010	-0.2537270	3.8361720
H	-5.2560130	-0.6779980	2.5131220
H	-4.4998450	0.9282340	2.5514840
C	-2.9421760	-2.1870800	2.2740950
H	-2.7494180	-2.3221890	3.3532890
H	-2.0736290	-2.5714530	1.7102260
H	-3.8368160	-2.7805850	2.0135960
B	0.9613690	-0.2646160	0.1750380

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