Supporting Information for

Harnessing the Electronic Differences between CAAC-Stabilised 1,4-Diborabenzene and 9,10-Diboraanthracene for Synthesis

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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 spectrometer (^{1}H: 500.1 MHz, ^{11}B: 129.9 or 160.5 MHz, ^{77}Se: 95.4 MHz). 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: $BF_3{\cdot}OEt_2$, ^{77}Se: Me_2Se). Resonances are given as singlet (s), doublet (d), triplet (t), septet (sept) or multiplet (m). The solid-state ^{13}C, ^{15}N, ^{77}Se CP/MAS (CP = cross-polarization, MAS = magic angle spinning) and ^{11}B RSHE/MAS (RSHE = rotor synchronized Hahn-Echo) NMR spectra of **1-S$_{4/5}$** and **1-Se$_4$** were recorded using a Bruker Avance Neo 400 spectrometer operating at 100.6 MHz for ^{13}C, 40.6 MHz for ^{15}N, 76.3 MHz for ^{77}Se and 128.4 MHz for ^{11}B, using a 4 mm (o. d.) ZrO_2 rotor. Chemical shifts were calibrated for all nuclei externally by adjusting the field manually, so that the low-field ^{13}C NMR shift of adamantane appears at 38.48 ppm to comply with IUPAC recommendations for reference. The solid-state ^{11}B magic-angle spinning (MAS) spectra were acquired by a rotor-synchronized Hahn-Echo (RSHE) at a spinning speed of 14.8 kHz and the ^{13}C, ^{15}N and ^{77}Se solid-state NMR spectra were obtained using a CP/MAS (CP = cross-polarization) sequence at spinning speeds of 13.0 kHz, 8.00 MHz and 11.0 kHz, respectively. The ^{11}B second-order quadrupolar powder pattern of **1-S$_{4/5}$** and **1-Se$_4$** (Figure S3 and S6) as well as the ^{77}Se spectrum (Figure S8) were simulated with the software package SOLA[1] within Topspin™ by Bruker. High-resolution mass spectrometry (HRMS) data were obtained from a Thermo Scientific Exactive Plus spectrometer. UV-vis spectra were acquired on a METTLER TOLEDO UV-vis-Excellence UV5 spectrophotometer inside a glovebox.

Solvents and reagents were purchased from Sigma-Aldrich or Alfa Aesar. $[(CAAC)_2(C_4H_4B_2)]$ (**V**)[2] and $[(CAAC)_2(C_{12}H_8B_2)]$ (**VI**)[3] were synthesized using literature procedures.

Synthetic procedures

Synthesis of 1-S$_{4/5}$.

To a solution of **V** (200 mg, 310 μmol) in benzene (2 mL) a suspension of elemental sulfur (49.7 mg, 1.55 mmol) in benzene (1 mL) was added dropwise, resulting in an immediate color change to orange-brown. The solution was filtered and storage at room temperature led to the formation of large crops of yellow crystals, which were washed with benzene (5 mL) and hexane (4 × 5 mL) and dried *in vacuo*, yielding **1-S$_{4/5}$** as yellow crystals suitable for X-ray diffraction analysis (**1-S$_4$**/**1-S$_5$** = 78:22, 198 mg, 253 μmol, 82% overall). *Note: the two products could not be separated further due to co-crystallization and were thus characterized together.* **1-S$_4$:** ^{1}H{^{11}B} NMR (500.1 MHz, C_6D_5Br, 297 K): δ = 7.21 (t, ^3J = 7.7 Hz, 2H, *p*-Dip-*H*), 7.10 (d, ^3J = 7.7 Hz, 4H, *m*-Dip-*H*), 6.38 (br s, 4H, BC*H*), 2.97–2.80 (m, 4H, CH_{iPr}), 1.67 (s, 4H, CH_2), 1.58 (s, 12H, C(CH_3)$_2$), 1.44 (d, ^3J = 6.5 Hz, 12H, CH(CH_3)$_2$), 1.14 (d, ^3J = 6.5 Hz, 12H, CH(CH_3)$_2$), 1.04 (s, 6H, NC(CH_3)$_2$). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_5Br, 297 K): δ = 230.5 ($C_{carbene}$, identified by HMBC), 146.6 (BC*H*), 145.3 (*o*-Dip-*C*), 135.1 (*i*-Dip-*C*), 129.7 (*p*-Dip-*C*, overlapping with C_6D_5Br, identified by DEPT135 and HSQC), 125.0 (*m*-Dip-*C*), 77.3 (N*C*(CH$_3$)$_2$), 54.4 (*C*(CH$_3$)$_2$), 53.4 (*C*H$_2$), 31.0 (C(*C*H$_3$)$_2$), 29.0 (NC(*C*H$_3$)$_2$), 26.5 (*C*H(CH$_3$)$_2$), 24.9 (*C*H(CH$_3$)$_2$) ppm. HRMS LIFDI for [$C_{44}H_{66}B_2N_2S_4$] = [M]: calcd. 772.4289; found 772.4271. **1-S$_5$:** ^{1}H{^{11}B} NMR (500.1 MHz, C_6D_5Br, 297 K): δ = 7.17 (t, ^3J = 7.7 Hz, 2H, *p*-Dip-*H*), 7.07 (d, ^3J = 7.7 Hz, 4H, *m*-Dip-*H*), 6.03 (br s, 4H, BC*H*), 2.97–2.80 (m, 4H, CH_{iPr}), 1.68 (s, 4H, CH_2), 1.52 (s, 12H, C(CH_3)$_2$), 1.30 (d, ^3J = 6.4 Hz, 12H, CH(CH_3)$_2$), 1.12 (d, ^3J = 6.6 Hz, 12H, CH(CH_3)$_2$), 1.06 (s, 6H, NC(CH_3)$_2$). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_5Br, 297 K): δ = 225.0 ($C_{carbene}$, identified by HMBC), 145.2 (*o*-Dip-*C*), 135.1 (*i*-Dip-*C*), 129.7 (*p*-Dip-*C*, overlapping with C_6D_5Br, identified by DEPT135 and HSQC), 125.0 (*m*-Dip-*C*), 77.1 (N*C*(CH$_3$)$_2$), 54.1 (*C*(CH$_3$)$_2$), 53.7 (*C*H$_2$), 30.6 (C(*C*H$_3$)$_2$), 28.8 (NC(*C*H$_3$)$_2$), 26.8 (*C*H(CH$_3$)$_2$), 25.0 (*C*H(CH$_3$)$_2$) ppm. *Note*: *The BCH resonances could not be detected due to quadrupolar broadening caused by coupling with the $^{10/11}$B nuclei.* **1-S$_{4/5}$:** ^{11}B NMR (RSHE/MAS, 14.8 kHz): δ_{iso} = –7.2 (C_Q = 2.05 MHz, η_Q = 0.709) ppm. ^{15}N NMR (CP/MAS, 8.00 kHz): δ = –151.2 (**1-S$_4$**), –155.6 (**1-S$_5$**) ppm. HRMS LIFDI for [$C_{44}H_{66}B_2N_2S_5$] = [M]: calcd. 804.4010; found 804.3992.

Synthesis of 1-Se_4.

To a solution of **V** (200 mg, 310 μmol) in benzene (5 mL) grey selenium (97.9 mg, 1.24 mmol) was added and the mixture was stirred at 60 °C for 2 h, whereupon the color changed to green and an orange solid precipitated. The solid was collected by filtration, washed with benzene (5 mL) and hexane (4 × 5 mL) and dried *in vacuo* to yield **1-Se_4** as a dark orange microcrystalline solid (232 mg, 242 μmol, 78%). Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of pentane in a saturated 1,2-difluorobenzene solution at –30 °C. *Note: due to the extremely low solubility of the target compound only solid-state NMR spectra could be obtained. Solvation of the product in different polar solvents led to decomposition and formation of elemental selenium.* ^{13}C NMR (CP/MAS, 13.0 kHz): δ = 228.7–225.9 (m, $C_{carbene}$), 154.4–151.5 (m, B*C*H), 146.5 ($C_{q,Ar}$), 145.3–142.2 (m, B*C*H), 144.2 ($C_{q,Ar}$), 137.5 ($C_{q,Ar}$), 130.4 (CH$_{Ar}$), 129.6 (CH$_{Ar}$), 123.5 (CH$_{Ar}$), 79.8 (N*C*(CH$_3$)$_2$), 54.4 (*C*(CH$_3$)$_2$), 53.5 (*C*H$_2$), 31.8 (*C*H$_3$), 30.4 (*C*H$_3$), 28.9 (*C*H$_3$), 28.6 (*C*H(CH$_3$)$_2$) , 27.5 (*C*H$_3$), 27.0 (*C*H$_3$), 25.7 (*C*H$_3$) ppm. ^{11}B NMR (RSHE/MAS, 14.8 kHz): δ_{iso} = –5.6 (C_Q = 2.37 MHz, η_Q = 0.596) ppm. ^{15}N NMR (CP/MAS, 8.00 kHz): δ = –157.2 ppm. ^{77}Se NMR (CP/MAS, 11.0 kHz): δ_{iso} = 915 (δ_{CSA} = 750 ppm, η_{CSA} = 0.420, (B–*Se*–Se)$_2$), 671 (δ_{CSA} = –523 ppm, η_{CSA} = 0.494, (B–Se–*Se*)$_2$) ppm. *Note: the CP/MAS ^{77}Se NMR spectrum showed a complex 22-line spinning side band pattern, spanning a 1700 ppm range. The shifts provided here are those of the isotropic peaks, δ_{iso}.* HRMS LIFDI for $[C_{44}H_{67}B_2N_2Se_2]^+$ = [(M – 2 Se) + H]$^+$: calcd. 805.3804; found 805.3839.

Synthesis of 2-O_2

Air was bubbled through a solution of **VI** (40.0 mg, 53.7 μmol) in benzene (1 mL), resulting in a color change to bright orange after 5 min. All volatiles were removed *in vacuo* and the remaining orange solid was washed with hexane (4 × 1 mL) and dried again, yielding **2-O_2** as a pale orange solid (31.0 mg, 39.9 μmol, 74%). Single crystals suitable for X-ray diffraction analysis of **2-O_2** were obtained by layering a saturated toluene solution with pentane at –30 °C. NMR spectra showed the formation of a 71:21:6:2 mixture of *mix*-**2-O_2** (unsymmetrical atropisomer, in which one Dip group displays an edge-to-face CH/π interaction with one of the diboraanthracene aryl groups, while the other points towards the O_2 bridge), *syn*-**2-O_2** (C_2-symmetric atropisomer, in which both Dip groups point towards the O_2 bridge), *rac*-**2-O_2** (C_2-symmetric atropisomer, in which each Dip group displays an edge-to-face CH/π interaction with one of the diboraanthracene aryl groups) and *meso*-**2-O_2** (C_2-symmetric atropisomer, in

which both Dip groups displays an edge-to-face CH/π interaction with the same diboraanthracene aryl group), respectively. The NMR resonances of the four atropisomers were assigned on the basis of COSY, HSQC, HMBC and NOESY spectra. Due to the low concentration of *rac*-**2-O₂** and *meso*-**2-O₂** only a few of their ^{1}H NMR resonances could be assigned. ^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6, 297 K) for *mix*-**2-O₂** (71%): δ = 8.12 (d, ^{3}J = 7.3 Hz, 1H, *o*-DBA-*H*), 7.43 (ddd, ^{3}J = 7.3 Hz, ^{3}J = 4.8 Hz, ^{4}J = 4.0 Hz, 1H, *m*-DBA-*H*), 7.29–7.24 (m, 3H, DBA-*H* + *p*-Dip-*H*), 7.17 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.6 Hz, 1H, *m*-Dip-*H*, overlapping with C_6D_6), 7.11–6.98 (m, 6H, DBA-*H* + Dip-*H*), 6.70 (dt, ^{3}J = 7.4 Hz, ^{4}J = 1.6 Hz, 1H, *m*-DBA-*H*), 4.66 (d, ^{3}J = 7.4 Hz, 1H, *o*-DBA-*H*···Dip), 3.57 (sept, ^{3}J = 6.6 Hz, 1H, C*H*$_{iPr}$), 3.05 (sept, ^{3}J = 6.5 Hz, 1H, C*H*$_{iPr}$), 3.02–2.93 (m, 2H, C*H*$_{iPr}$), 1.94 (d, ^{2}J = 12.8 Hz, 1H, C*H*$_2$), 1.86 (s, 3H, C(C*H*$_3$)$_2$), 1.79 (d, ^{2}J = 12.9 Hz, 1H, C*H*$_2$), 1.70 (s, 3H, C(C*H*$_3$)$_2$), 1.64 (d, ^{3}J = 6.7 Hz, 3H, CH(C*H*$_3$)$_2$), 1.62 (s, 3H, C(C*H*$_3$)$_2$), 1.52 (d, ^{2}J = 12.8 Hz, 1H, C*H*$_2$), 1.46 (s, 3H, C(C*H*$_3$)$_2$), 1.42 (d, ^{2}J = 12.9 Hz, 1H, C*H*$_2$), 1.24 (d, ^{3}J = 6.5 Hz, 3H, CH(C*H*$_3$)$_2$), 1.19–1.15 (m, 6H, CH(C*H*$_3$)$_2$), 1.12 (d, ^{3}J = 6.6 Hz, 3H, CH(C*H*$_3$)$_2$), 1.10 (d, ^{3}J = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.07 (s, 3H, NC(C*H*$_3$)$_2$), 1.05 (s, 3H, NC(C*H*$_3$)$_2$), 0.88 (s, 3H, NC(C*H*$_3$)$_2$), 0.86 (s, 3H, NC(C*H*$_3$)$_2$), 0.74 (d, ^{3}J = 6.5 Hz, 3H, CH(C*H*$_3$)$_2$), 0.71 (d, ^{3}J = 6.6 Hz, 3H, CH(C*H*$_3$)$_2$) ppm; for *syn*-**2-O₂** (21%): δ = 7.58 (dd, ^{3}J = 5.3 Hz, ^{4}J = 3.3 Hz, 4H, DBA-*H*), 7.33 (dd, ^{3}J = 5.3 Hz, ^{4}J = 3.3 Hz, 4H, DBA-*H*), 6.95 (dd, 2H, ^{3}J = 8.4 Hz, ^{3}J = 6.9 Hz, *p*-Dip-*H*), 6.89–6.86 (m, 4H, *m*-Dip-*H*), 2.82 (sept, ^{3}J = 6.6 Hz, 4H, C*H*$_{iPr}$), 1.82 (s, 12H, C(C*H*$_3$)$_2$), 1.76 (s, 4H, C*H*$_2$), 1.19–1.15 (m, 12H, CH(C*H*$_3$)$_2$), 0.95 (s, 12H, NC(C*H*$_3$)$_2$), 0.80 (d, ^{3}J = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$) ppm; for *rac*-**2-O₂** (6%): δ = 6.65 (dt, ^{3}J = 7.4 Hz, ^{4}J = 1.2 Hz, 2H, *m*-DBA-*H*), 4.64 (d, ^{3}J = 7.4 Hz, 2H, *o*-DBA-*H*···Dip), 3.53 (sept, ^{3}J = 6.6 Hz, 2H, C*H*$_{iPr}$), 3.13 (sept, ^{3}J = 6.6 Hz, 2H, C*H*$_{iPr}$), 1.39, 1.08, 0.70, 0.50 (four d, ^{3}J = 6.6 Hz, 6H each, CH(C*H*$_3$)$_2$, detected by COSY) ppm; for *meso*-**2-O₂** (2%): 6.44 (dd, ^{3}J = 5.4 Hz, ^{4}J = 3.4 Hz, 2H, *m*-DBA-*H*), 4.76 (dd, ^{3}J = 5.4 Hz, ^{4}J = 3.4 Hz, 2H, *o*-DBA-*H*) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 297 K) for *mix*-**2-O₂** (71%): δ = 238.9 ($C_{carbene}$, identified by HMBC), 238.2 ($C_{carbene}$, identified by HMBC), 161.4 (BAr-*C*, identified by HMBC), 160.7 (BAr-*C*, identified by HMBC), 147.7 (*o*-Dip-*C*), 147.5 (*o*-Dip-*C*), 146.5 (*o*-Dip-*C*), 145.0 (*o*-Dip-*C*), 135.7 (*i*-Dip-*C*), 135.5 (*i*-Dip-*C*), 130.3 (*p*-Dip-*C*), 129.1 (DBA-*C*), 128.8 (DBA-*C*), 128.5 (*p*-Dip-*C*), 128.2 (DBA-*C*, overlapping with C_6D_6, identified by DEPT135 and HSQC), 128.1 (DBA-*C*, overlapping with C_6D_6, identified by DEPT135 and HSQC), 126.4 (*m*-Dip-*C*), 125.1 (*m*-Dip-*C*), 124.1 (*m*-Dip-*C*), 123.2 (*m*-Dip-*C*), 122.5 (DBA-*C*), 121.5 (DBA-*C*), 121.1 (DBA-*C*), 120.8 (DBA-*C*), 79.0 (N*C*(CH$_3$)$_2$), 78.3 (N*C*(CH$_3$)$_2$), 57.8 (*C*(CH$_3$)$_2$), 53.0 (*C*(CH$_3$)$_2$), 51.5 (*C*H$_2$), 50.4 (*C*H$_2$), 32.4 (NC(*C*H$_3$)$_2$), 32.2 (NC(*C*H$_3$)$_2$), 31.6 (C(*C*H$_3$)$_2$), 31.3 (C(*C*H$_3$)$_2$), 31.2

(C(*C*H$_3$)$_2$), 31.0 (*C*H(CH$_3$)$_2$), 30.0 (*C*H(CH$_3$)$_2$), 29.0 (*C*H(CH$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 28.4 (C(*C*H$_3$)$_2$), 28.3 (CH(*C*H$_3$)$_2$), 26.9 (CH(*C*H$_3$)$_2$), 26.8 (NC(*C*H$_3$)$_2$), 26.4 (CH(*C*H$_3$)$_2$), 26.2 (NC(*C*H$_3$)$_2$), 25.9 (CH(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$), 23.2 (CH(*C*H$_3$)$_2$), 23.0 (CH(*C*H$_3$)$_2$) ppm; for *syn*-**2-O$_2$** (21%): δ = 237.5 ($C_{carbene}$, identified by HMBC), 145.7 (*o*-Dip-*C*), 134.7 (*i*-Dip-*C*), 129.2 (DBA-*C*), 128.3 (*p*-Dip-*C*), 123.6 (*m*-Dip-*C*), 122.4 (DBA-*C*), 78.4 (N*C*(CH$_3$)$_2$), 53.1 (*C*(CH$_3$)$_2$), 51.8 (*C*H$_2$), 30.1 (*C*H(CH$_3$)$_2$), 30.0 (C(*C*H$_3$)$_2$), 29.2 (NC(*C*H$_3$)$_2$), 26.6 (*C*H(CH$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$) ppm. *Note*: *Some of the* DBA-*C resonances of the atrospisomers could not be detected due to quadrupolar broadening caused by coupling with the $^{10/11}$B nuclei.* ^{11}B NMR (129.9 MHz, C$_6$D$_6$, 297 K): δ = 1.8 (br s), 0.9 (br s) ppm. HRMS LIFDI for [C$_{52}$H$_{70}$B$_2$N$_2$O$_2$] = [M]: calcd. 776.5618; found 776.5601.

Synthesis of 2-S.

To a solution of **VI** (50.0 mg, 67.1 μmol) in benzene (1 mL) elemental sulfur (2.15 mg, 67.1 μmol) was added, resulting in an immediate color change to dark-yellow. All volatiles were removed *in vacuo* and the resulting pale yellow solid was washed with hexane (4 × 1 mL) and recrystallized from benzene. After drying *in vacuo* **2-S** was obtained as yellow crystals (36.0 mg, 46.3 μmol, 69%) suitable for X-ray diffraction analysis. NMR spectra showed the formation of an 87:13 mixture of *rac*-**2-S** and *meso*-**2-S**. The NMR resonances of two atropisomers were assigned on the basis of COSY, HSQC and HMBC spectra. ^{1}H{^{11}B} NMR (500.1 MHz, C$_6$D$_6$, 297 K) for *rac*-**2-S** (87%): δ = 7.28 (t, ^3J = 7.8 Hz, 2H, *p*-Dip-*H*), 7.17 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 2H, *m*-Dip-*H*, overlapping with C$_6$D$_6$), 7.09 (dd, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 2H, *m*-Dip-*H*), 6.98 (dd, ^3J = 6.9 Hz, ^4J = 1.0 Hz, 2H, *o*-DBA-*H*), 6.82 (ddd, ^3J = 7.4 Hz, ^3J = 6.9 Hz, ^4J = 1.0 Hz, 2H, *m*-DBA-*H*), 6.51 (ddd, ^3J = 7.4 Hz, ^3J = 6.9 Hz, ^4J = 1.3 Hz, 2H, *m*-DBA-*H*), 4.45 (dd, ^3J = 7.4 Hz, ^4J = 1.3 Hz, 2H, *o*-DBA-*H*···Dip), 3.30–3.14 (two overlapping sept, ^3J = 6.6 Hz, 4H, C*H*$_{iPr}$), 2.13 (s, 6H, C(C*H*$_3$)$_2$), 1.94 (s, 6H, C(C*H*$_3$)$_2$), 1.80 (d, ^2J = 12.7 Hz, 2H, C*H*$_2$), 1.50 (d, ^3J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.49 (d, ^2J = 12.7 Hz, 2H, C*H*$_2$), 1.16 (d, ^3J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.11 (d, ^3J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.96 (s, 6H, NC(C*H*$_3$)$_2$), 0.90 (s, 6H, NC(C*H*$_3$)$_2$), 0.83 (d, ^3J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$) ppm; for *meso*-**2-S** (13%): δ = 7.31–7.28 (m, 2H, *o*-DBA-*H*), 7.22 (t, ^3J = 7.8 Hz, 2H, *p*-Dip-*H*), 7.11–7.08 (m, 2H, *m*-Dip-*H*), 7.06–7.03 (m, 4H, *m*-Dip-*H* + *m*-DBA-*H*), 6.11 (dd, ^3J = 5.5 Hz, ^4J = 3.2 Hz, 2H, *m*-DBA-*H*), 4.53 (dd, ^3J = 5.5 Hz, ^4J = 3.2 Hz, 2H, *o*-DBA-*H*···Dip), 3.30–3.14 (m, 4H, C*H*$_{iPr}$), 2.11 (s, 6H, C(C*H*$_3$)$_2$), 2.09 (s, 6H, C(C*H*$_3$)$_2$), 1.77 (d, ^2J = 12.7 Hz, 2H, C*H*$_2$), 1.62 (d, ^2J = 12.7 Hz, 2H, C*H*$_2$), 3.30–3.14 (m, 16 H, CH(C*H*$_3$)$_2$ + CH(C*H*$_3$)$_2$ + CH(C*H*$_3$)$_2$), 1.00 (s, 6H, NC(C*H*$_3$)$_2$), 0.95–0.93 (m, 12H, NC(C*H*$_3$)$_2$ + CH(C*H*$_3$)$_2$)

ppm. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6, 297 K) for *rac*-**2-S**: δ = 237.5 ($C_{carbene}$, identified by HMBC), 169.2 (BAr-*C*, identified by HMBC), 163.5 (BAr-*C*, identified by HMBC), 148.1 (*o*-Dip-*C*), 147.0 (*o*-Dip-*C*), 135.4 (*i*-Dip-*C*), 130.1 (*p*-Dip-*C*), 128.4 (DBA-*C*), 127.5 (DBA-*C*), 125.9 (*m*-Dip-*C*), 125.5 (*m*-Dip-*C*), 120.4 (DBA-*C*), 119.0 (DBA-*C*), 77.6 (N*C*(CH_3)$_2$), 56.7 (*C*(CH_3)$_2$), 52.4 (*C*H_2), 32.9 (C(*C*H_3)$_2$), 31.2 (NC(*C*H_3)$_2$), 31.1 (*C*(CH_3)$_2$), 30.5 (*C*H(CH_3)$_2$), 29.1 (*C*H(CH_3)$_2$), 29.1 (CH(*C*H_3)$_2$), 26.9 (CH(*C*H_3)$_2$), 26.6 (NC(*C*H_3)$_2$), 24.3 (CH(*C*H_3)$_2$), 23.4 (CH(*C*H_3)$_2$) ppm; for *meso*-**2-S**: δ = 233.5 ($C_{carbene}$, identified by HMBC), 148.2 (*o*-Dip-*C*), 146.6 (*o*-Dip-*C*), 135.7 (*i*-Dip-*C*), 130.0 (*p*-Dip-*C*), 128.2 (DBA-*C*, overlapping with C_6D_6, identified by DEPT135 and HSQC), 126.5 (DBA-*C*), 125.9 (*m*-Dip-*C*), 125.3 (*m*-Dip-*C*), 120.6 (DBA-*C*), 119.1 (DBA-*C*), 77.2 (N*C*(CH_3)$_2$), 56.7 (*C*(CH_3)$_2$), 52.5 (*C*H_2), 33.4 (C(*C*H_3)$_2$), 32.1 (C(*C*H_3)$_2$), 30.0 (CH(*C*H_3)$_2$), 30.0 (*C*H(CH_3)$_2$), 29.2 (*C*H(CH_3)$_2$), 28.2 (NC(*C*H_3)$_2$), 28.0 (NC(*C*H_3)$_2$), 26.8 (CH(*C*H_3)$_2$), 24.6 (CH(*C*H_3)$_2$), 23.4 (CH(*C*H_3)$_2$) ppm. *Note*: *The BAr-C resonances of the minor atropisomer B could not be detected due to quadrupolar broadening caused by coupling with the $^{10/11}$B nuclei.* ^{11}B NMR (129.9 MHz, C_6D_6, 297 K): δ = –2.1 (br s, *meso*-**2-S**), –3.1 (br s, *rac*-**2-S**) ppm. HRMS LIFDI for [$C_{52}H_{70}B_2N_2S$] = [M]: calcd. 776.5446; found 776.5440.

Synthesis of 2-Se

To a solution of **VI** (30.0 mg, 40.3 μmol) in benzene (1 mL) grey selenium (3.18 mg, 40.3 μmol) was added and the mixture was heated at 80 °C for 1 h, leading to a dark red solution. All volatiles were removed *in vacuo* and the resulting pale red solid was washed with hexane (4 × 1 mL) and recrystallized from benzene. After drying *in vacuo* **2-Se** was obtained as red crystals (26.0 mg, 31.6 μmol, 78%) suitable for X-ray diffraction analysis. NMR spectra showed the formation of a 42:58 mixture of *rac*-**2-Se** and *meso*-**2-Se**. The NMR resonances of two atropisomers were assigned on the basis of COSY, HSQC and HMBC spectra. $^{1}H\{^{11}B\}$ NMR (500.1 MHz, C_6D_6, 297 K) for *meso*-**2-Se** (58%): δ = 7.37 (dd, ^{3}J = 5.2 Hz, ^{4}J = 3.2 Hz, 2H, *o*-DBA-*H*), 7.21 (t, ^{3}J = 7.8 Hz, 2H, *p*-Dip-*H*), 7.08 (d, ^{3}J = 7.8 Hz, 2H, *m*-Dip-*H*), 7.04 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1,6 Hz, 2H, *m*-Dip-*H*), 7.02 (dd, ^{3}J = 5.2 Hz, ^{4}J = 3.2 Hz, 2H, *m*-DBA-*H*), 6.04 (dd, ^{3}J = 5.5 Hz, ^{4}J = 3.3 Hz, 2H, *m*-DBA-*H*), 4.70 (dd, ^{3}J = 5.5 Hz, ^{4}J = 3.3 Hz, 2H, *o*-DBA-*H*···Dip), 3.36 (sept, ^{3}J = 6.6 Hz, 2H, C*H*$_{iPr}$), 3.29 (sept, ^{3}J = 6.6 Hz, 2H, C*H*$_{iPr}$), 2.15 (s, 6H, C(C*H*$_3$)$_2$), 2.08 (s, 6H, C(C*H*$_3$)$_2$), 1.78 (d, ^{2}J = 12.7 Hz, 2H, C*H*$_2$), 1.71 (d, ^{2}J = 12.7 Hz, 2H, C*H*$_2$), 1.17 (d, ^{3}J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, ^{3}J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.09–1.06 (overlapping d + s, 12H, CH(C*H*$_3$)$_2$ + NC(C*H*$_3$)$_2$), 0.97 (d, ^{3}J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.93 (s, 6H, NC(C*H*$_3$)$_2$) ppm; for *rac*-**2-Se** (42%): δ = 7.21 (t, ^{3}J = 7.8 Hz, 2H, *p*-Dip-*H*), 7.18–7.15

(m, 2H, *m*-Dip-*H*, overlapping with C_6D_6), 7.08 (d, ^3J = 7.8 Hz, 2H, *m*-Dip-*H*), 6.96 (dd, ^3J = 6.8 Hz, ^4J = 1.1 Hz, 2H, DBA-*H*), 6.79 (dd, ^3J = 7.4 Hz, ^3J = 6.8 Hz, 2H, DBA-*H*), 6.46 (dd, ^3J = 7.5 Hz, ^3J = 7.4 Hz, 2H, DBA-*H*), 4.48 (d, ^3J = 7.5 Hz, 2H, *o*-DBA-*H*···Dip), 3.26 (sept, ^3J = 6.6 Hz, 2H, C*H*$_{iPr}$), 3.18 (sept, ^3J = 6.6 Hz, 2H, C*H*$_{iPr}$), 2.09 (s, 6H, C(C*H*$_3$)$_2$), 1.97 (s, 6H, C(C*H*$_3$)$_2$), 1.78 (d, ^2J = 12.7 Hz, 2H, C*H*$_2$), 1.54 (d, ^3J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.51 (d, ^2J = 12.7 Hz, 2H, C*H*$_2$), 1.18 (d, ^3J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.10 (d, ^3J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.98 (s, 6H, NC(C*H*$_3$)$_2$), 0.88 (s, 6H, NC(C*H*$_3$)$_2$), 0.84 (d, ^3J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 297 K) for *meso*-**2-Se**: δ = 228.8 ($C_{carbene}$, identified by HMBC), 166.2 (BAr-*C*, identified by HMBC), 163.1 (BAr-*C*, identified by HMBC), 148.7 (*o*-Dip-*C*), 146.8 (*o*-Dip-*C*), 136.2 (*i*-Dip-*C*), 129.9 (*p*-Dip-*C*), 128.7 (DBA-*C*), 126.3 (DBA-*C*), 126.0 (*m*-Dip-*C*), 125.4 (*m*-Dip-*C*), 121.1 (DBA-*C*), 119.3 (DBA-*C*), 76.2 (N*C*(CH$_3$)$_2$), 56.2 (*C*(CH$_3$)$_2$), 52.7 (*C*H$_2$), 35.3 (C(*C*H$_3$)$_2$), 32.1 (C(*C*H$_3$)$_2$), 29.5 (*C*H(CH$_3$)$_2$), 29.2 (*C*H(CH$_3$)$_2$), 29.1 (NC(*C*H$_3$)$_2$), 28.6 (NC(*C*H$_3$)$_2$), 27.4 (CH(*C*H$_3$)$_2$), 27.2 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$) ppm. for *rac*-**2-Se**: δ = 235.3 ($C_{carbene}$, identified by HMBC), 167.1 (BAr-*C*, identified by HMBC), 163.5 (BAr-*C*, identified by HMBC), 148.2 (*o*-Dip-*C*), 147.1 (*o*-Dip-*C*), 135.7 (*i*-Dip-*C*), 130.1 (*p*-Dip-*C*), 128.5 (DBA-*C*), 128.3 (DBA-*C*, overlapping with C_6D_6, identified by DEPT135 and HSQC), 126.0 (*m*-Dip-*C*), 125.2 (*m*-Dip-*C*), 120.4 (DBA-*C*), 119.1 (DBA-*C*), 77.1 (N*C*(CH$_3$)$_2$), 56.5 (*C*(CH$_3$)$_2$), 52.8 (*C*H$_2$), 34.9 (C(*C*H$_3$)$_2$), 30.9 (C(*C*H$_3$)$_2$), 30.7 (NC(*C*H$_3$)$_2$), 30.3 (*C*H(CH$_3$)$_2$), 29.4 (*C*H(CH$_3$)$_2$), 28.6 (CH(*C*H$_3$)$_2$), 27.2 (CH(*C*H$_3$)$_2$), 26.7 (NC(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$) ppm. ^{11}B NMR (129.9 MHz, C_6D_6, 297 K): δ = –0.9 (br s, *meso*-**2-Se**), –4.1 (br s, *rac*-**2-Se**) ppm. ^{77}Se NMR (95.4 MHz, C_6D_6, 297 K): δ = 658 (*meso*-**2-Se**, identified by ^1H-^{77}Se-HMQC), 472 (*rac*-**2-Se**, identified by ^1H-^{77}Se-HMQC) ppm. HRMS LIFDI for [$C_{52}H_{70}B_2N_2Se$] = [M]: calcd. 824.4890; found 824.4885.

.

NMR spectra of isolated compounds

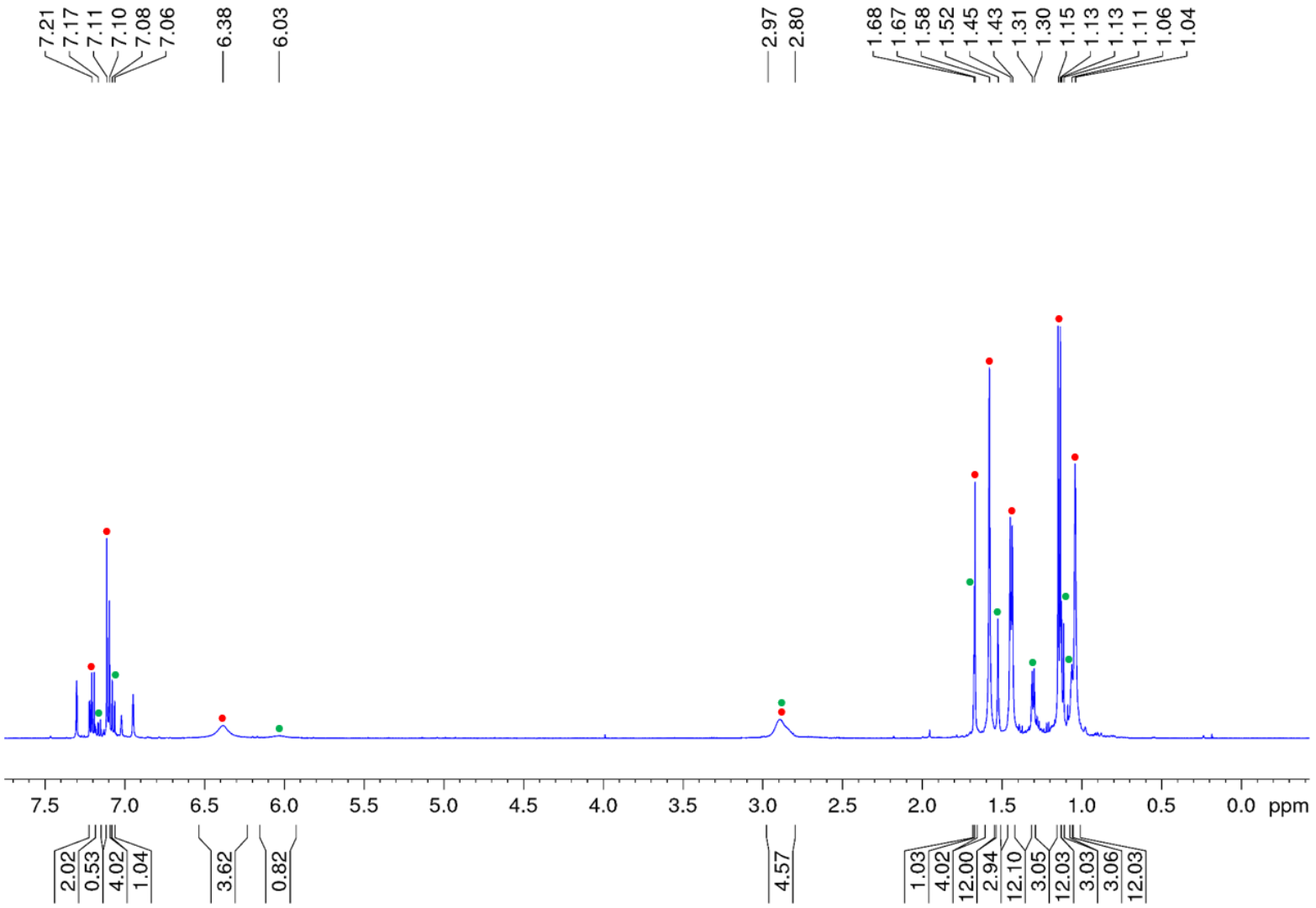

Figure S1. Annotated $^{1}H\{^{11}B\}$ NMR spectrum of **1-S4/5** in C_6D_5Br (● **1-S4**, ● **1-S5**).

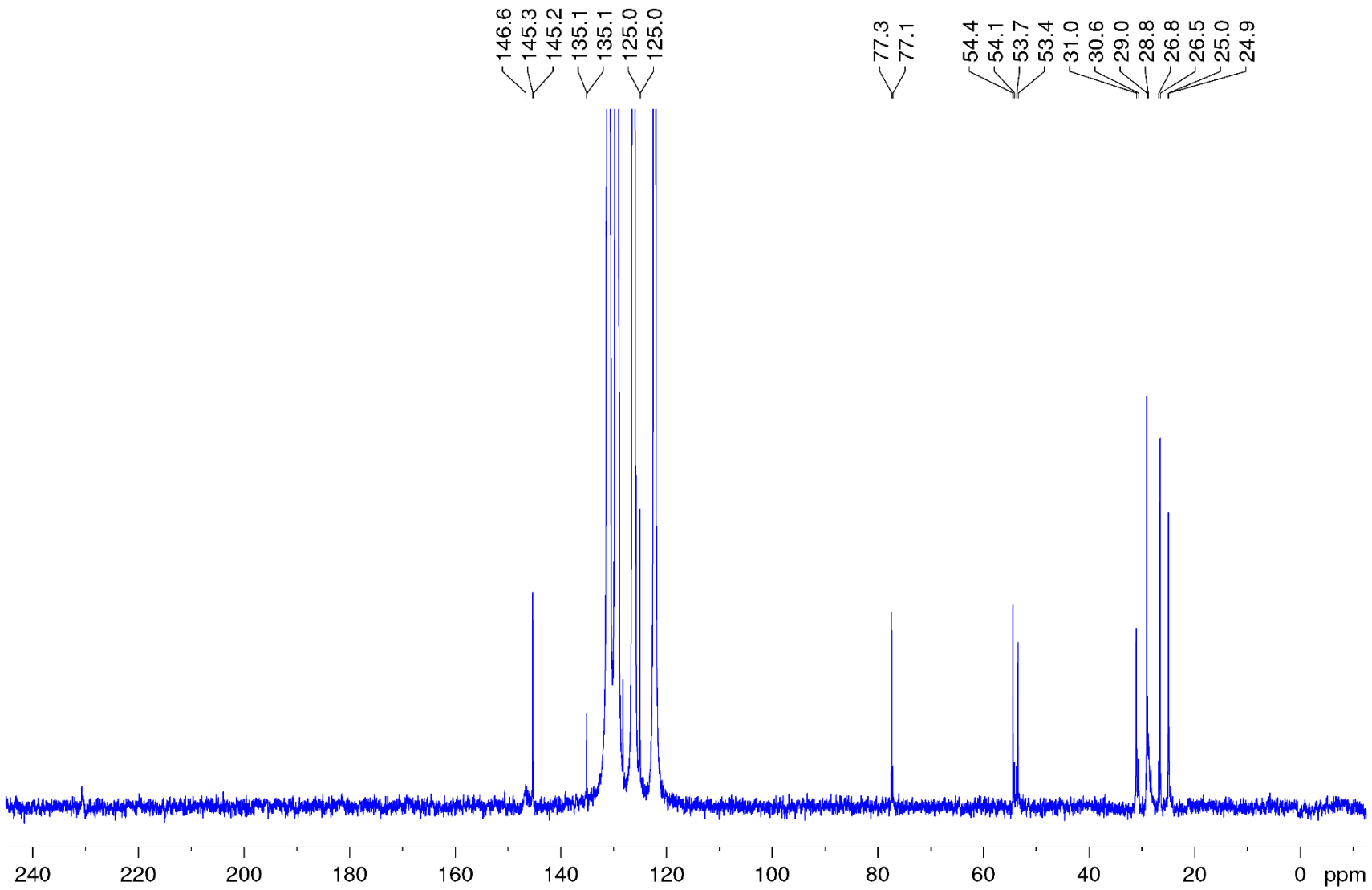

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1-S$_{4/5}$** in C_6D_5Br.

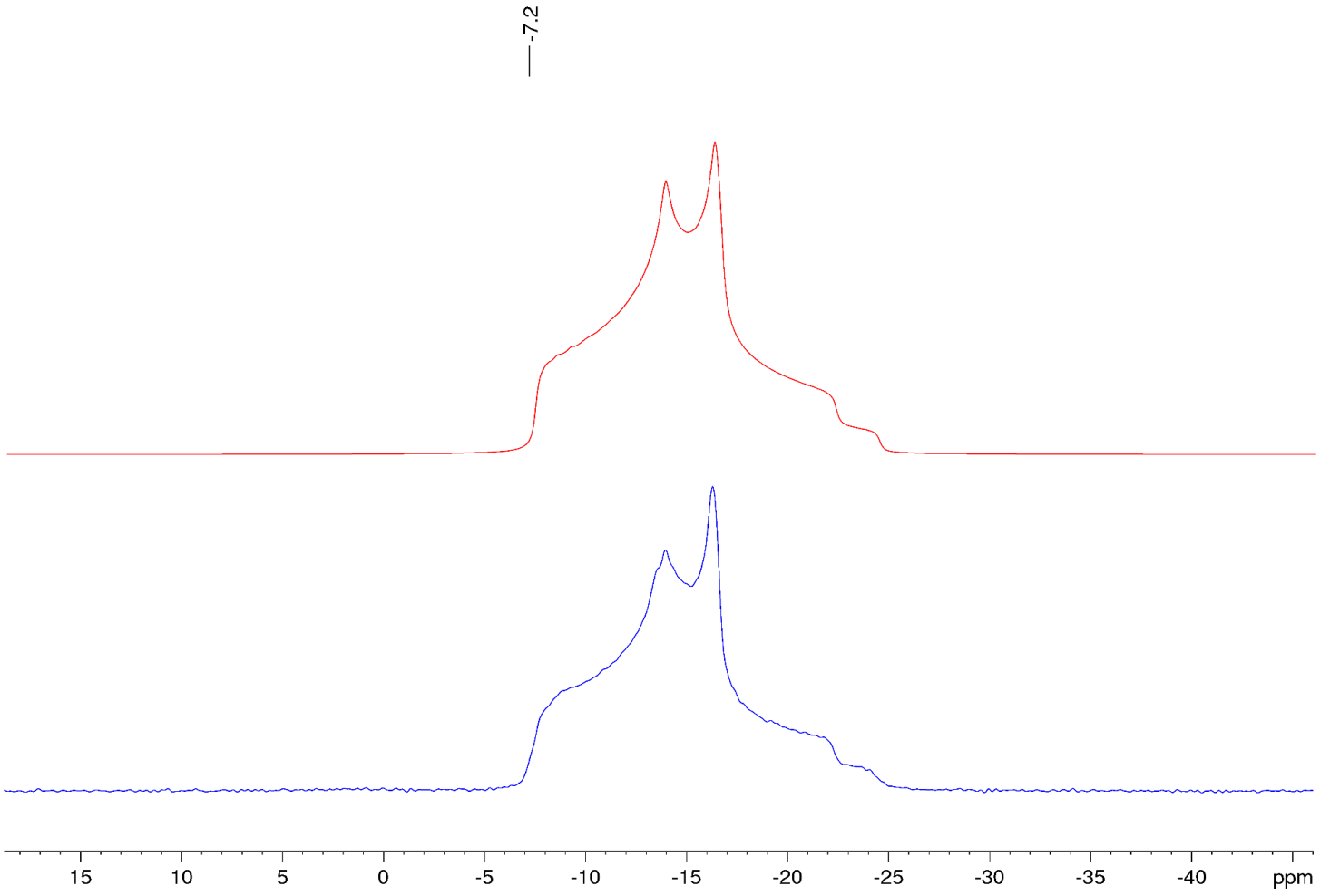

Figure S3. Solid-state ^{11}B RSHE/MAS NMR spectrum of **1-S$_{4/5}$** at 14.8 kHz (top: Simulation). Isotropic chemical shift δ_{iso} = –7.2 ppm, quadrupolar coupling constant C_Q = 2.05 MHz, quadrupolar asymmetry parameter η_Q = 0.709.

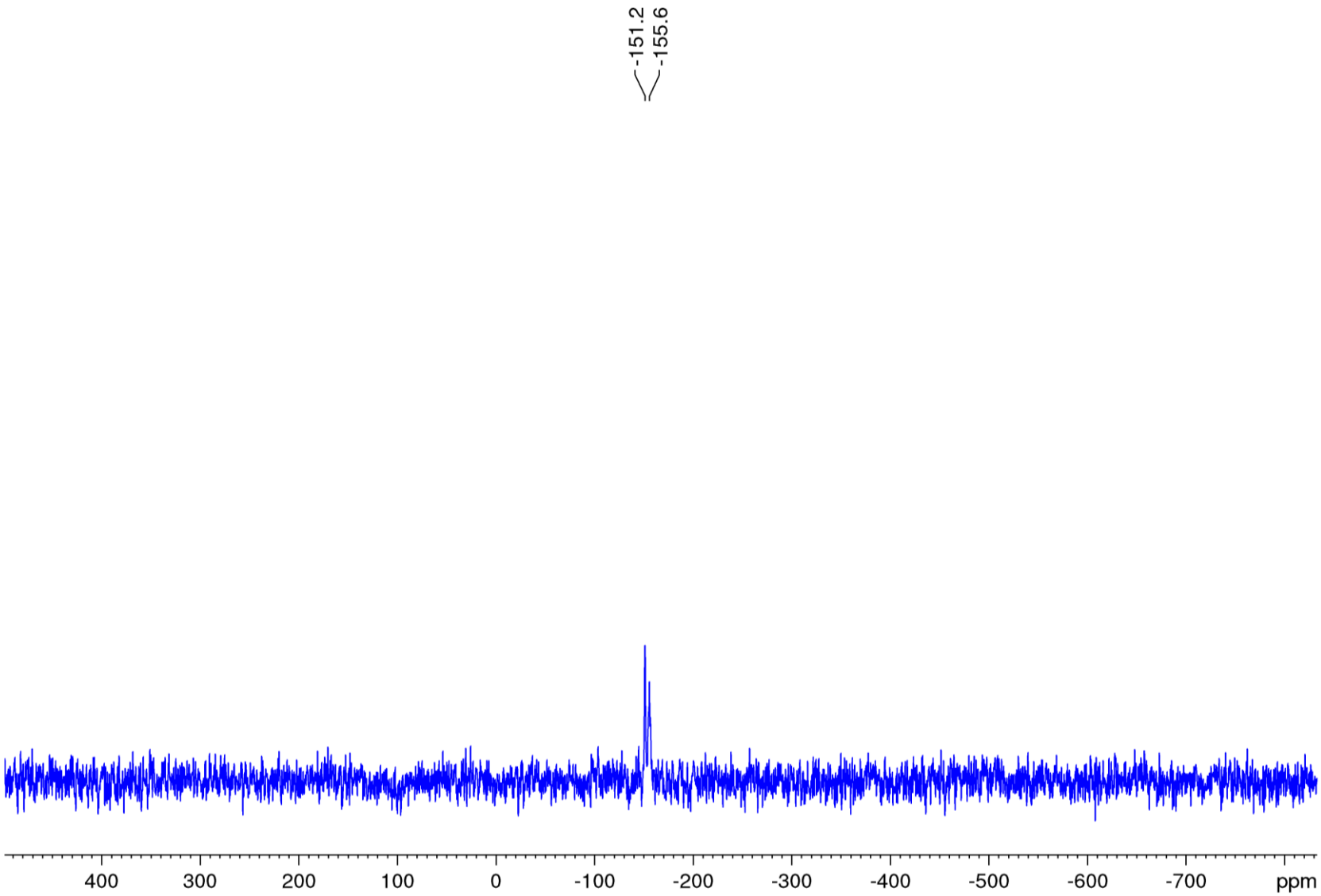

Figure S4. Solid-state ^{15}N CP/MAS NMR spectrum of **1-S$_{4/5}$** at 8.0 kHz.

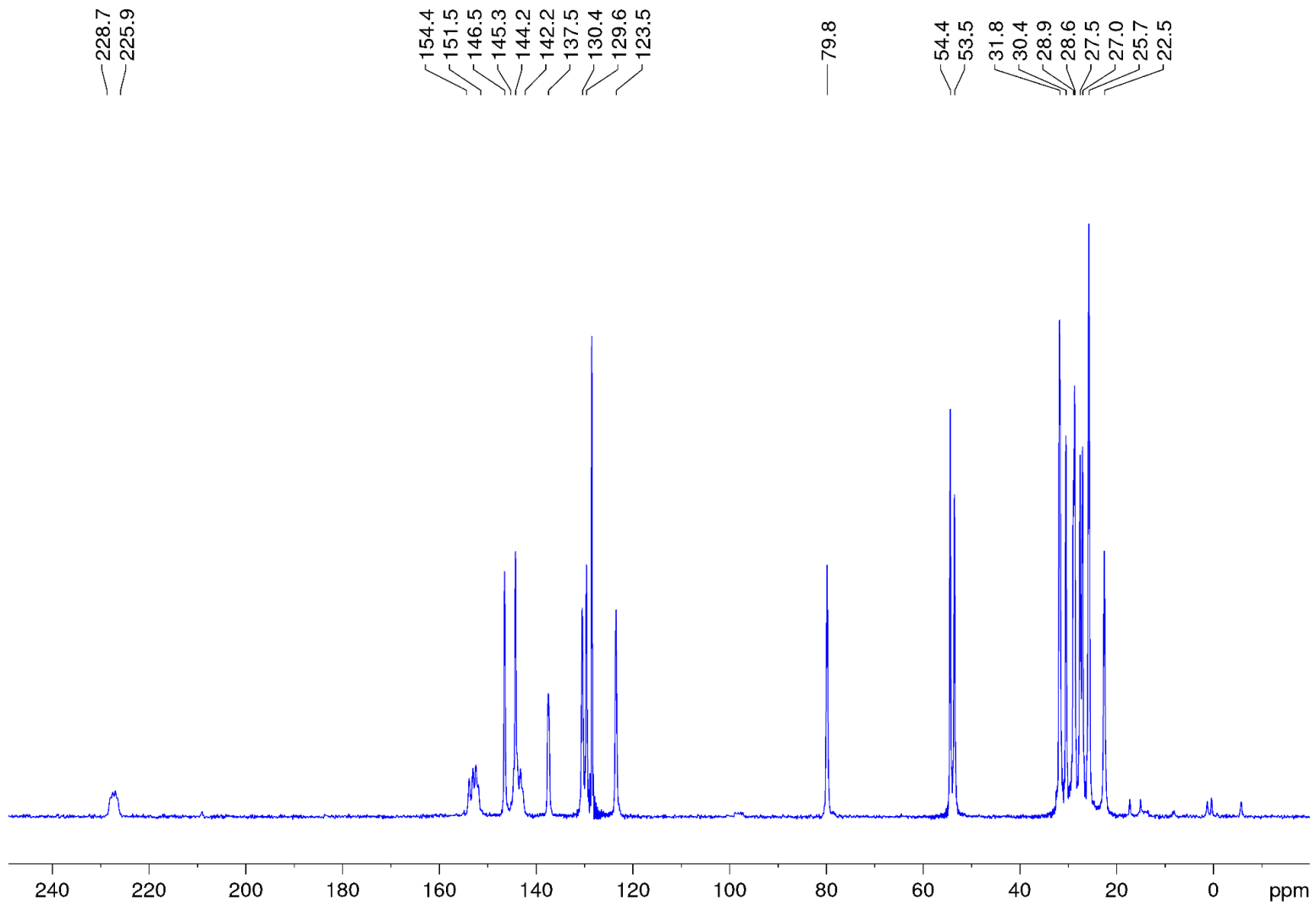

Figure S5. Solid-state ^{13}C CP/MAS NMR spectrum of **1-Se$_4$** at 13.0 kHz.

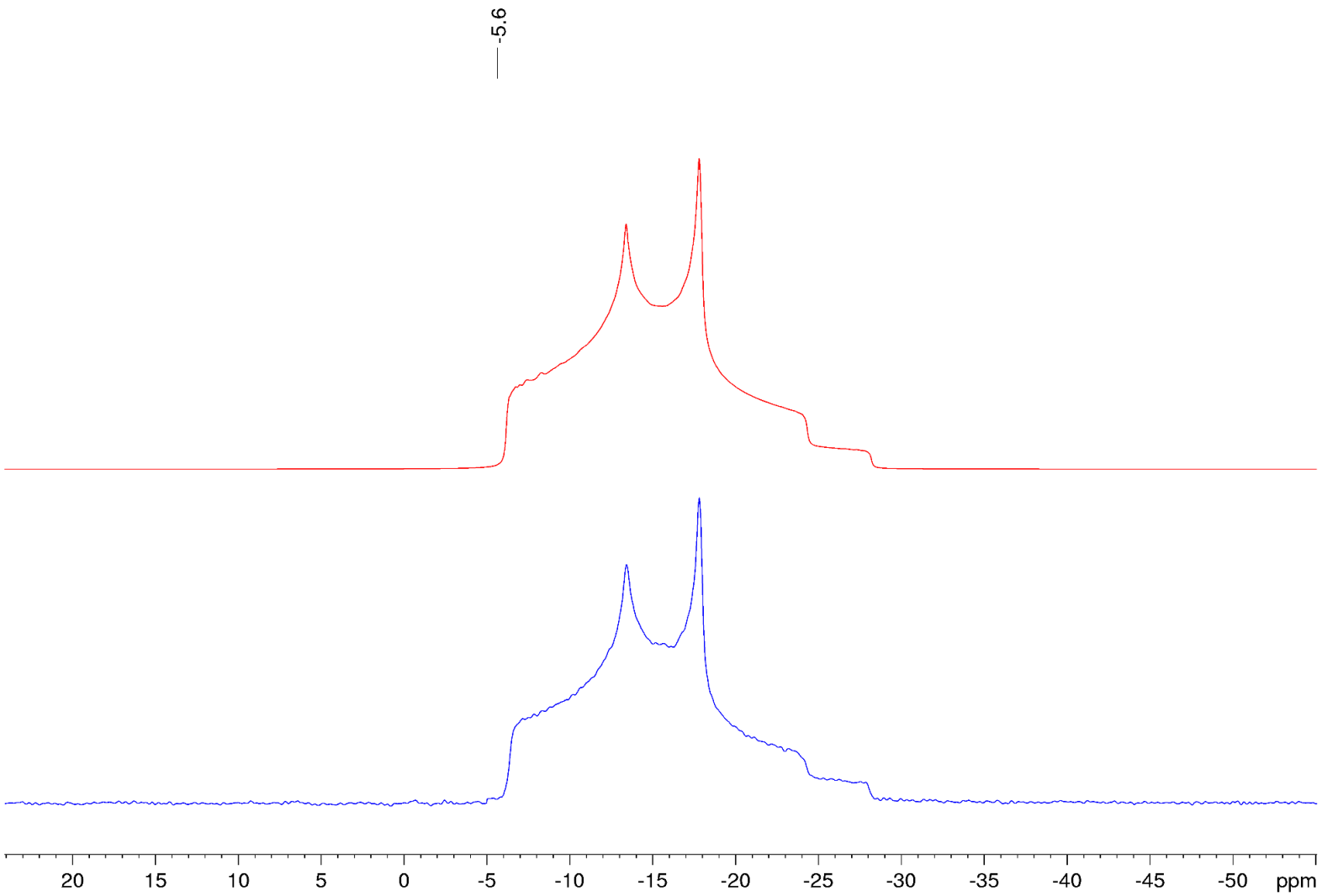

Figure S6. Solid-state ^{11}B RSHE/MAS NMR spectrum of **1-Se$_4$** at 14.8 kHz (top: Simulation). Isotropic chemical shift δ_{iso} = –5.6 ppm, quadrupolar coupling constant C_Q = 2.37 MHz, quadrupolar asymmetry parameter η_Q = 0.596.

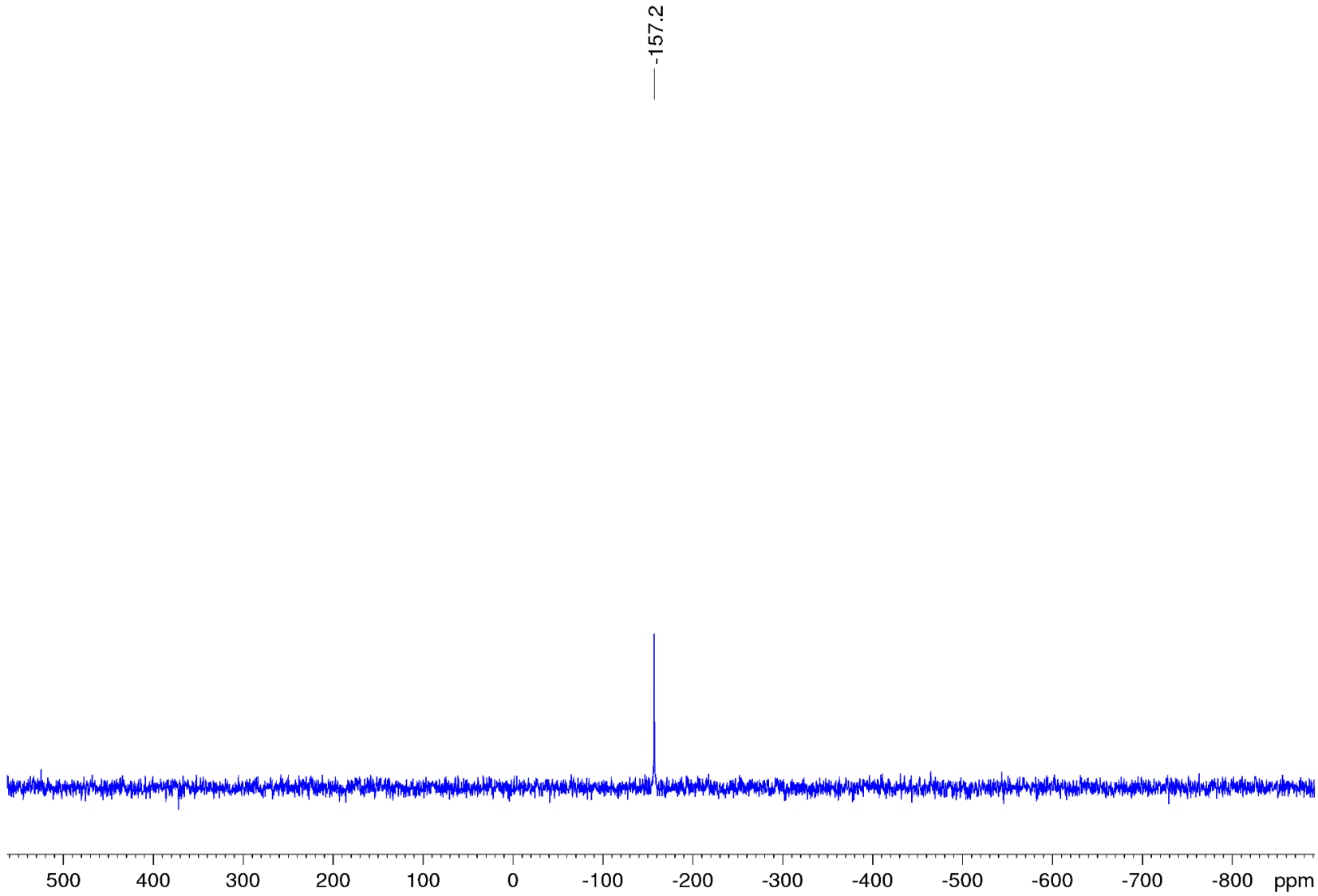

Figure S7. Solid-state ^{15}N CP/MAS NMR spectrum of **1-Se$_4$** at 8.0 kHz.

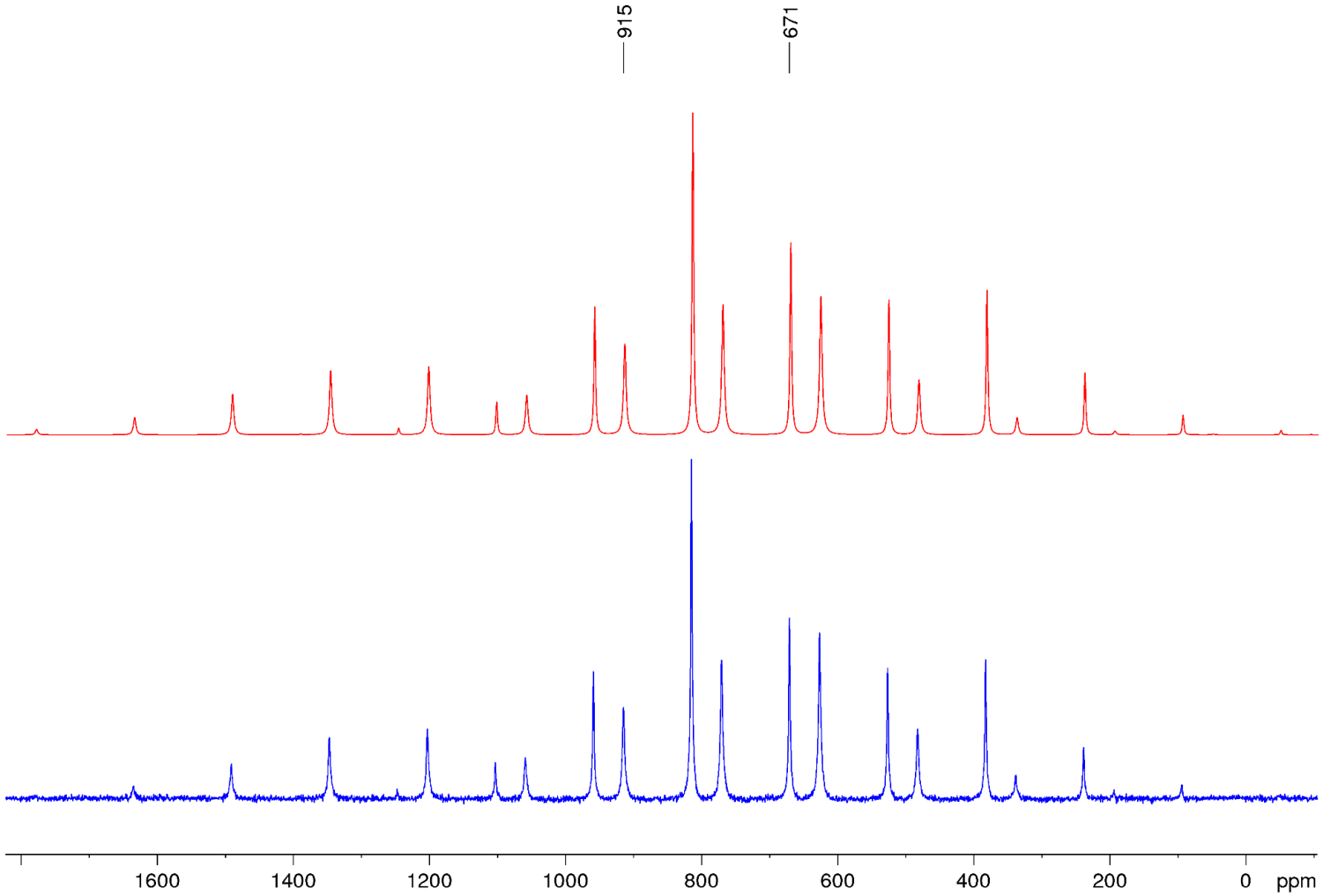

Figure S8. Solid-state ^{77}Se CP/MAS NMR spectrum of **1-Se$_4$** at 11.0 kHz (top: Simulation). (B–*Se*–Se)$_2$: Isotropic chemical shift δ_{iso} = 915 ppm, chemical shift anisotropy width δ_{CSA} = 750 ppm, chemical shift anisotropy η_{CSA} = 0.420; (B–Se–*Se*)$_2$: Isotropic chemical shift δ_{iso} = 671 ppm, chemical shift anisotropy width δ_{CSA} = –523 ppm, chemical shift anisotropy η_{CSA} = 0.494.

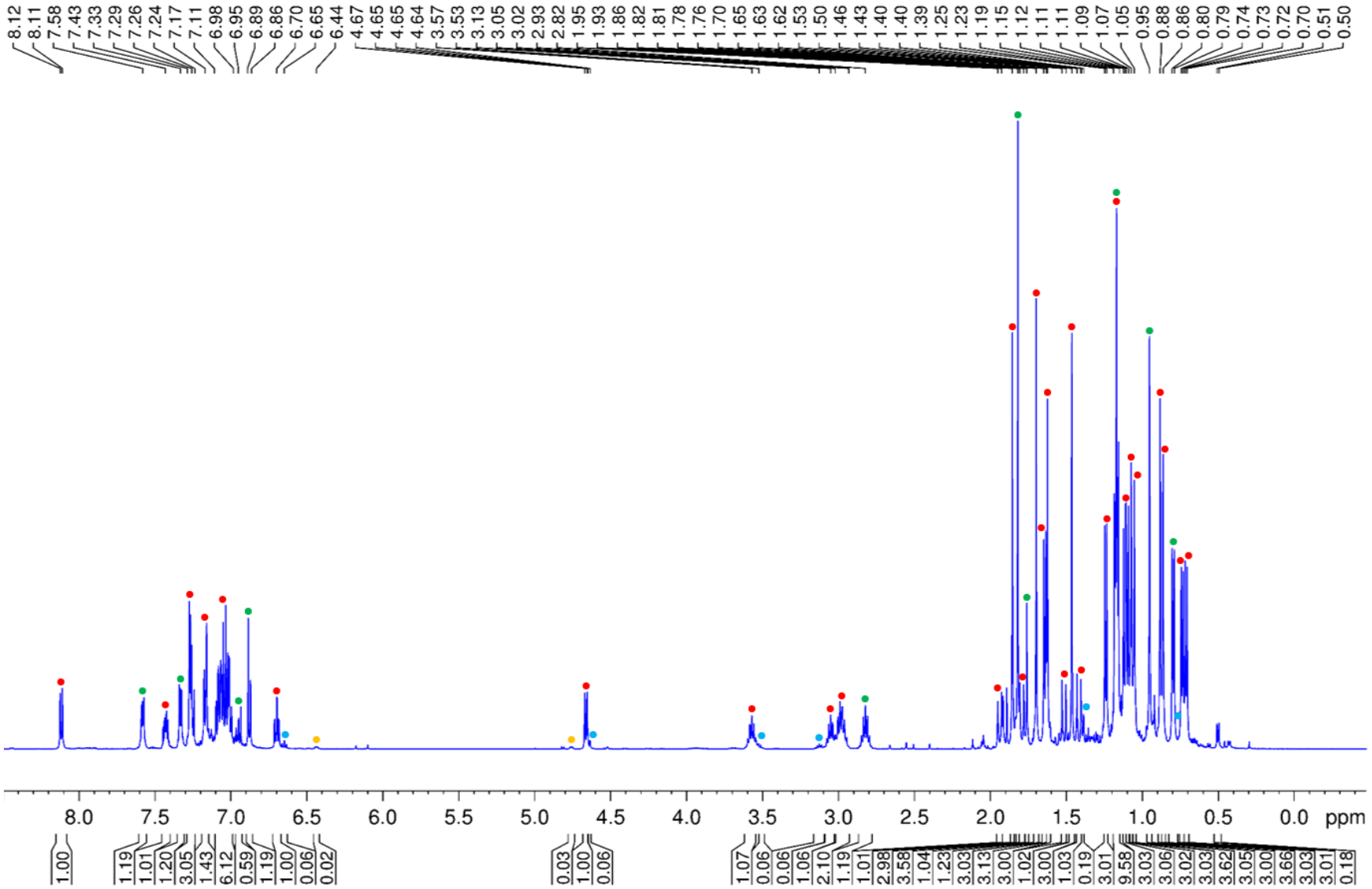

Figure S9. $^{1}H\{^{11}B\}$ NMR spectrum of **2-O₂** in C_6D_6 (71:21:6:2 *mix*/*syn*/*rac*/*meso* mixture, ● ***mix*-2-O₂,** ● ***syn*-2-O₂,** ● ***rac*-2-O₂,** ● ***meso*-2-O₂**).

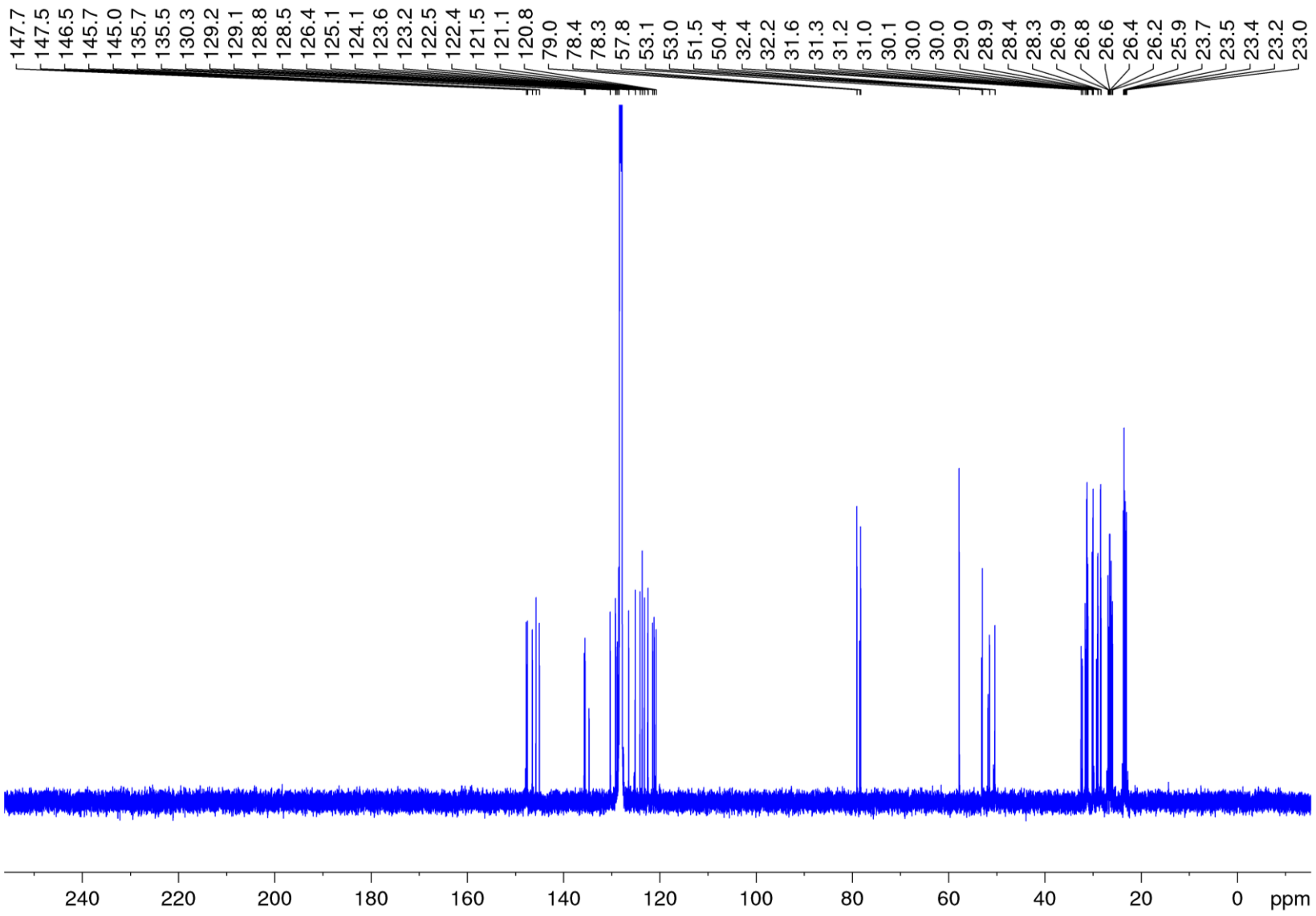

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **2-O₂** in C_6D_6.

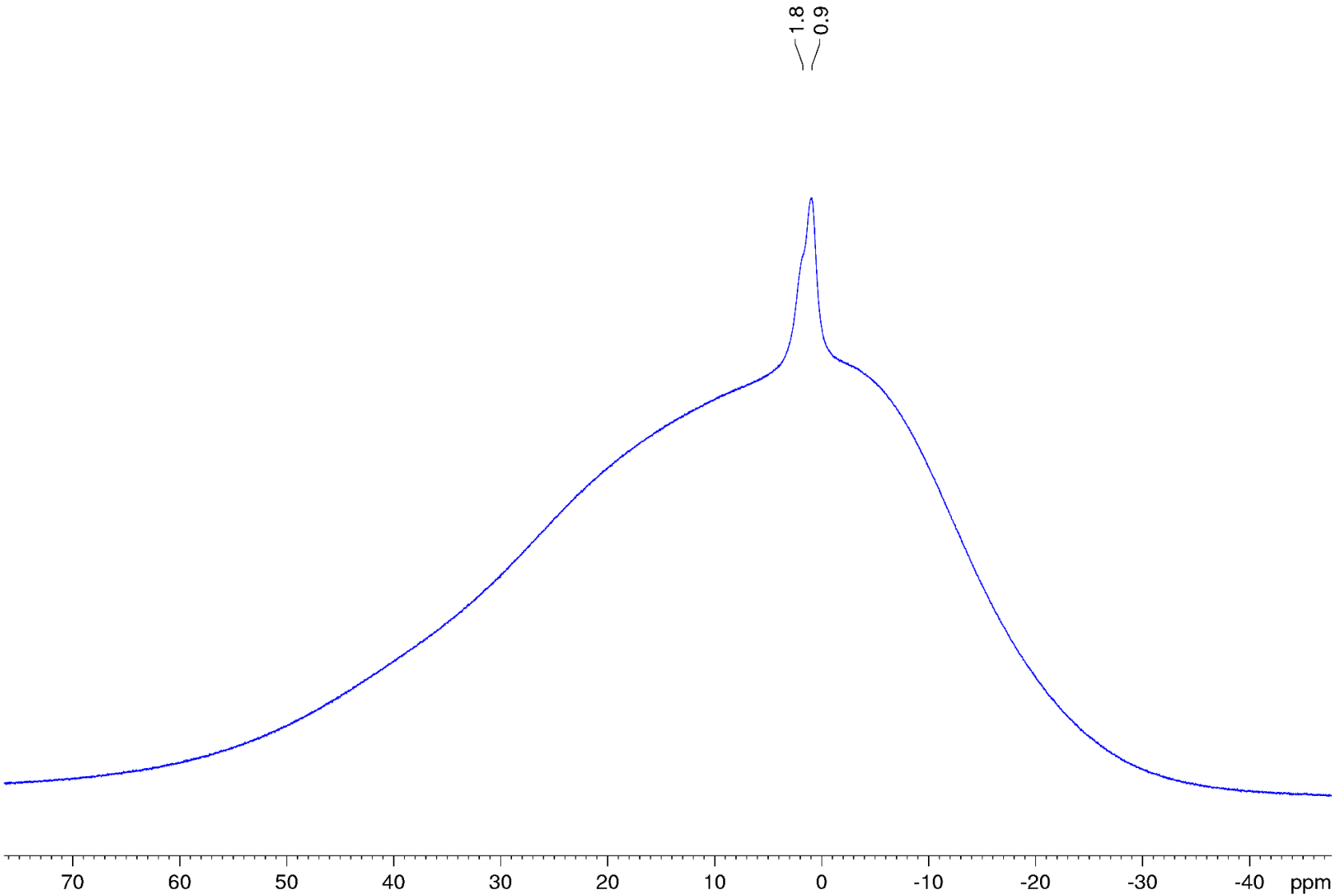

Figure S11. ^{11}B NMR spectrum of **2-O$_2$** in C_6D_6.

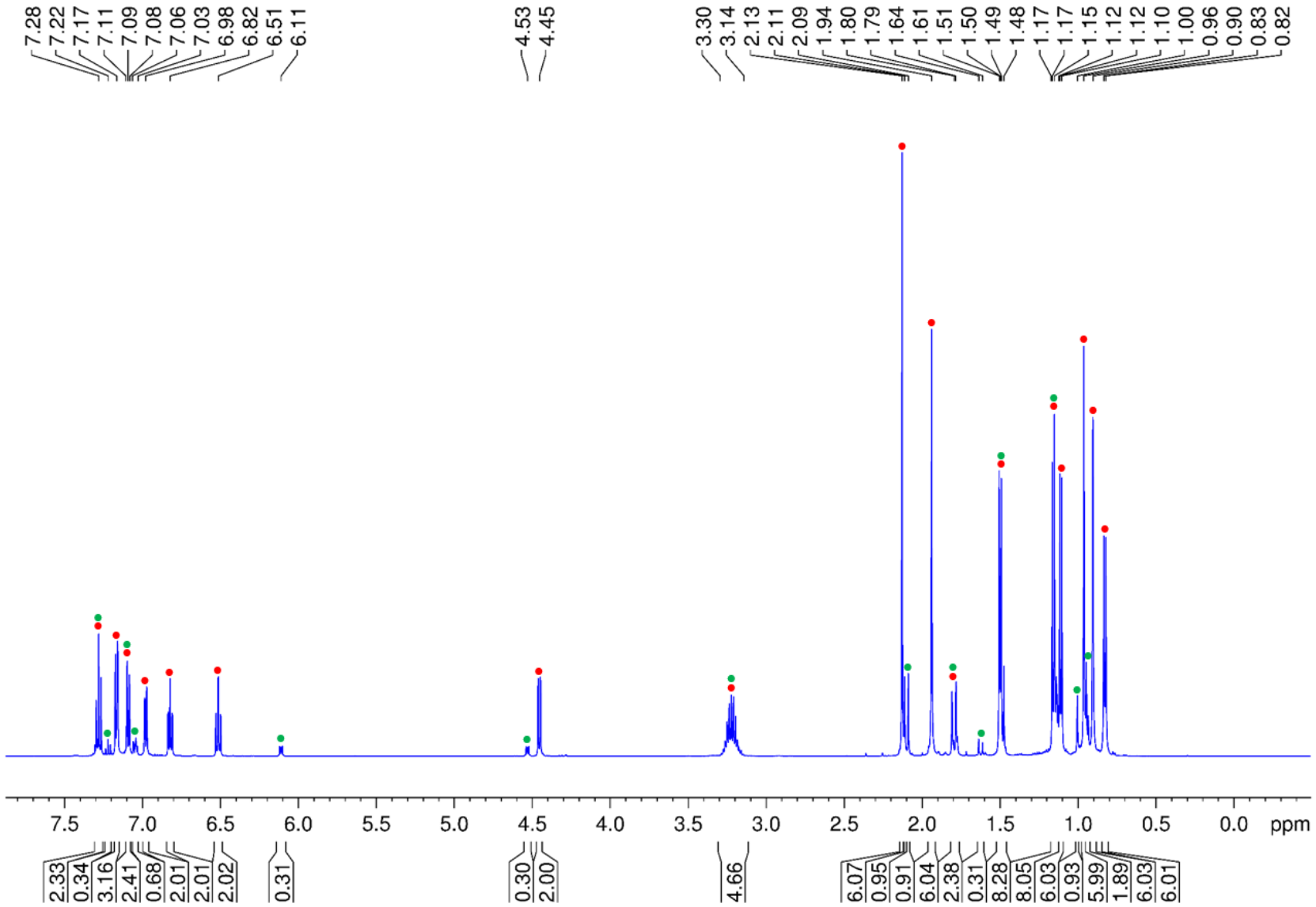

Figure S12. $^{1}H\{^{11}B\}$ NMR spectrum of **2-S** in C_6D_6 (87:13 *rac*/*meso* mixture, ● *rac*-**2-S**, ● *meso*-**2-S**).

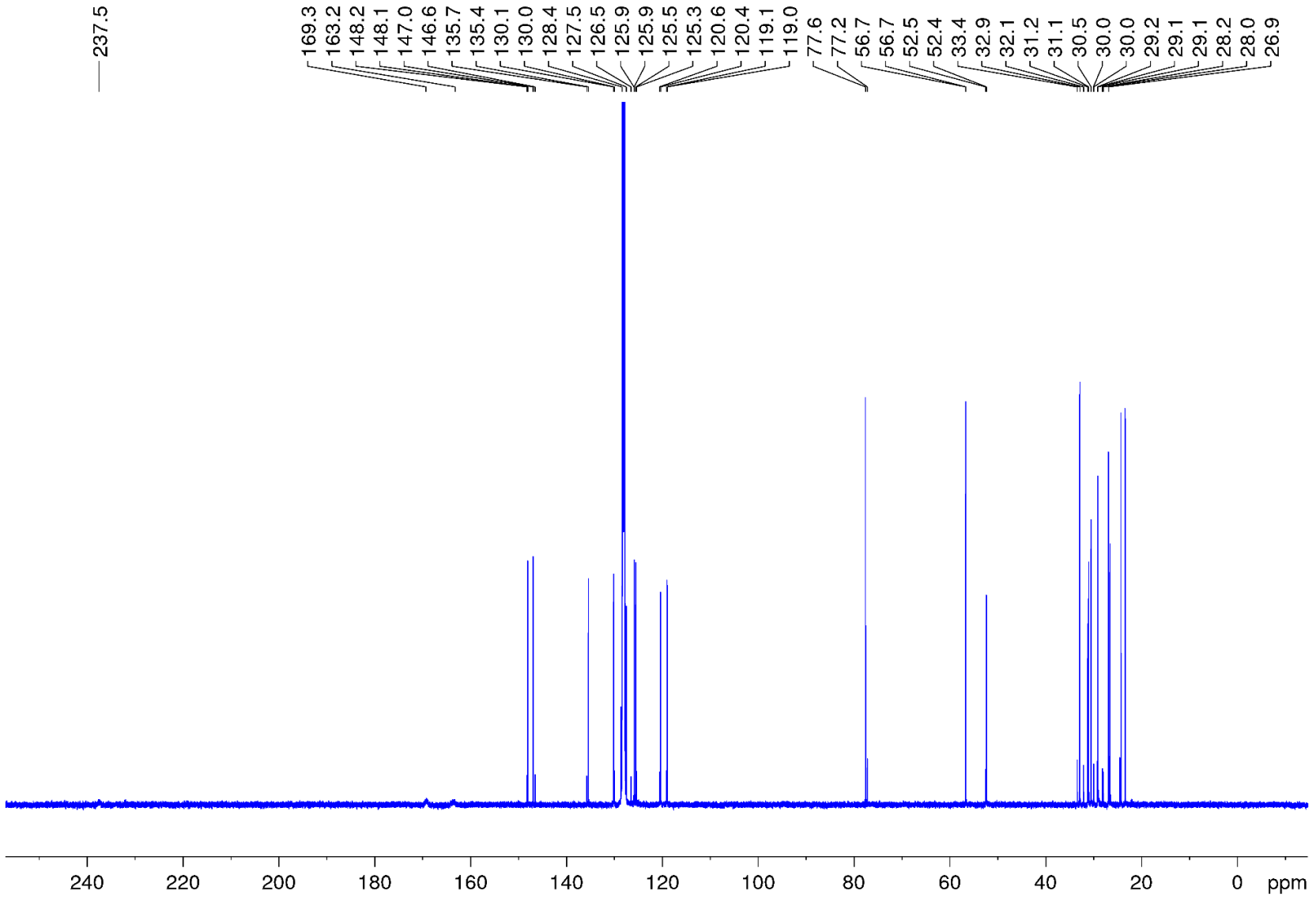

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of **2-S** in C_6D_6.

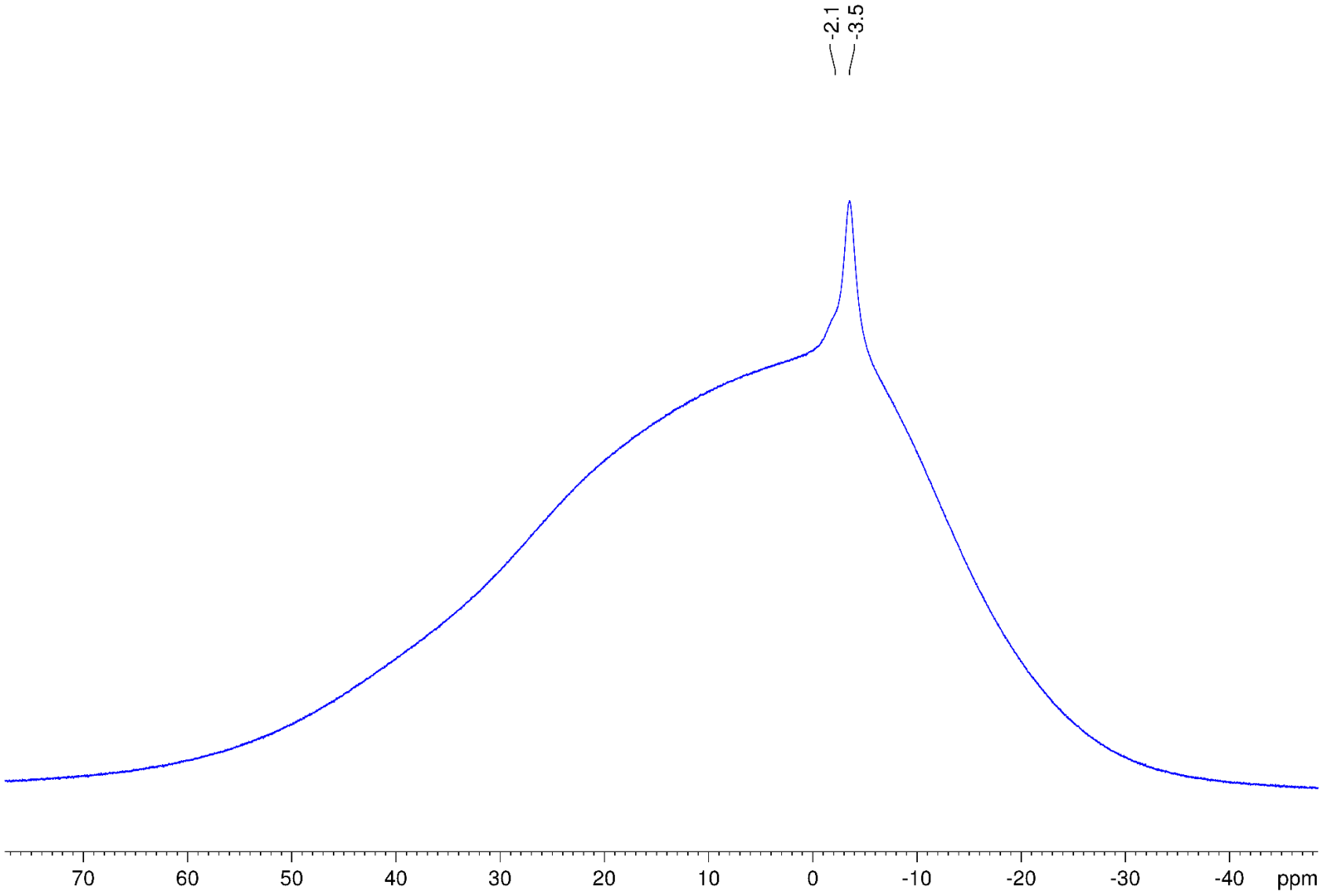

Figure S14. ^{11}B NMR spectrum of **2-S** in C_6D_6.

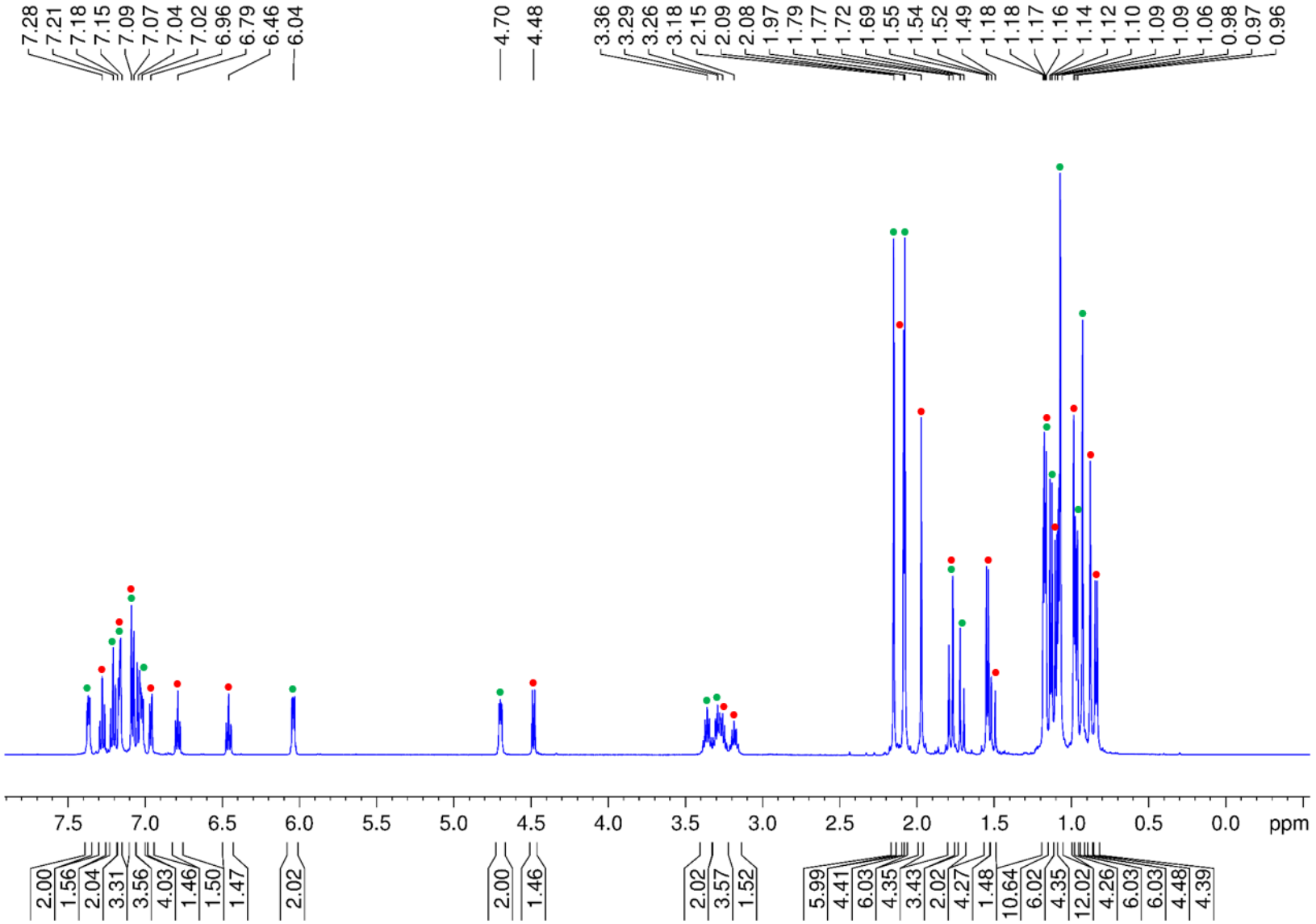

Figure S15. $^{1}H\{^{11}B\}$ NMR spectrum of **2-Se** in C_6D_6 (42:58 *rac*/*meso* mixture, ● *rac*-**2-Se**, ● *meso*-**2-Se**).

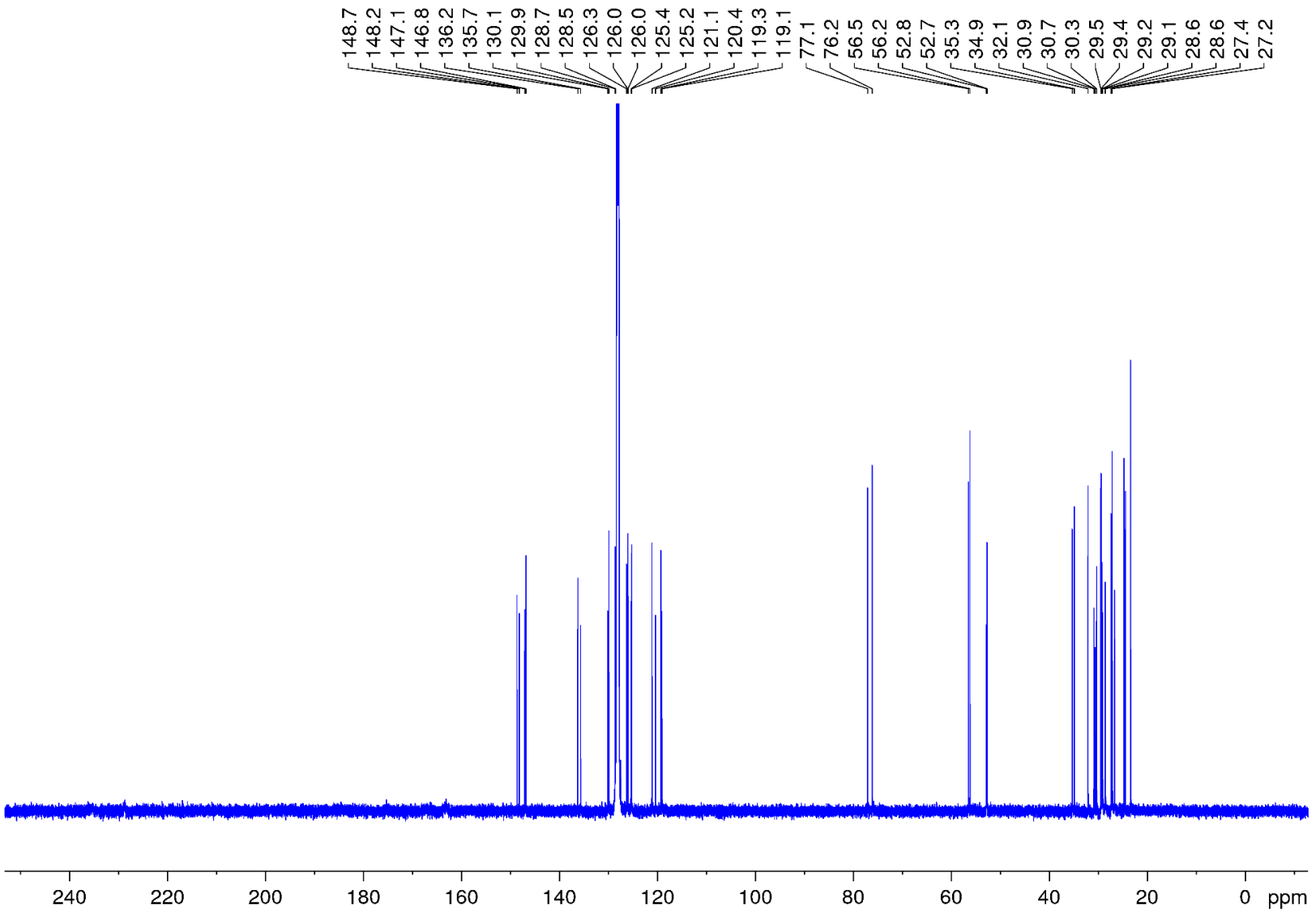

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **2-Se** in C_6D_6.

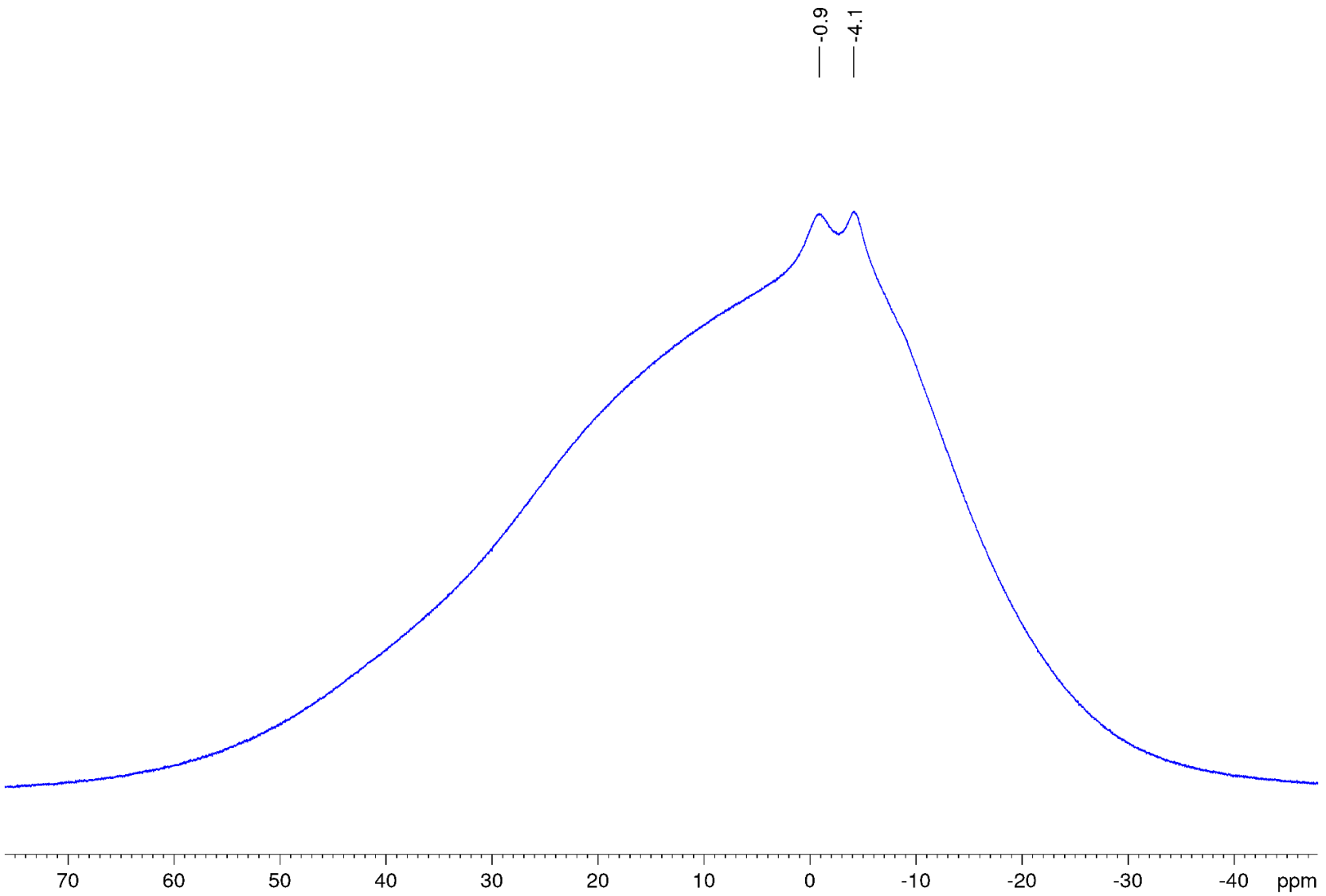

Figure S17. ^{11}B NMR spectrum of **2-Se** in C_6D_6.

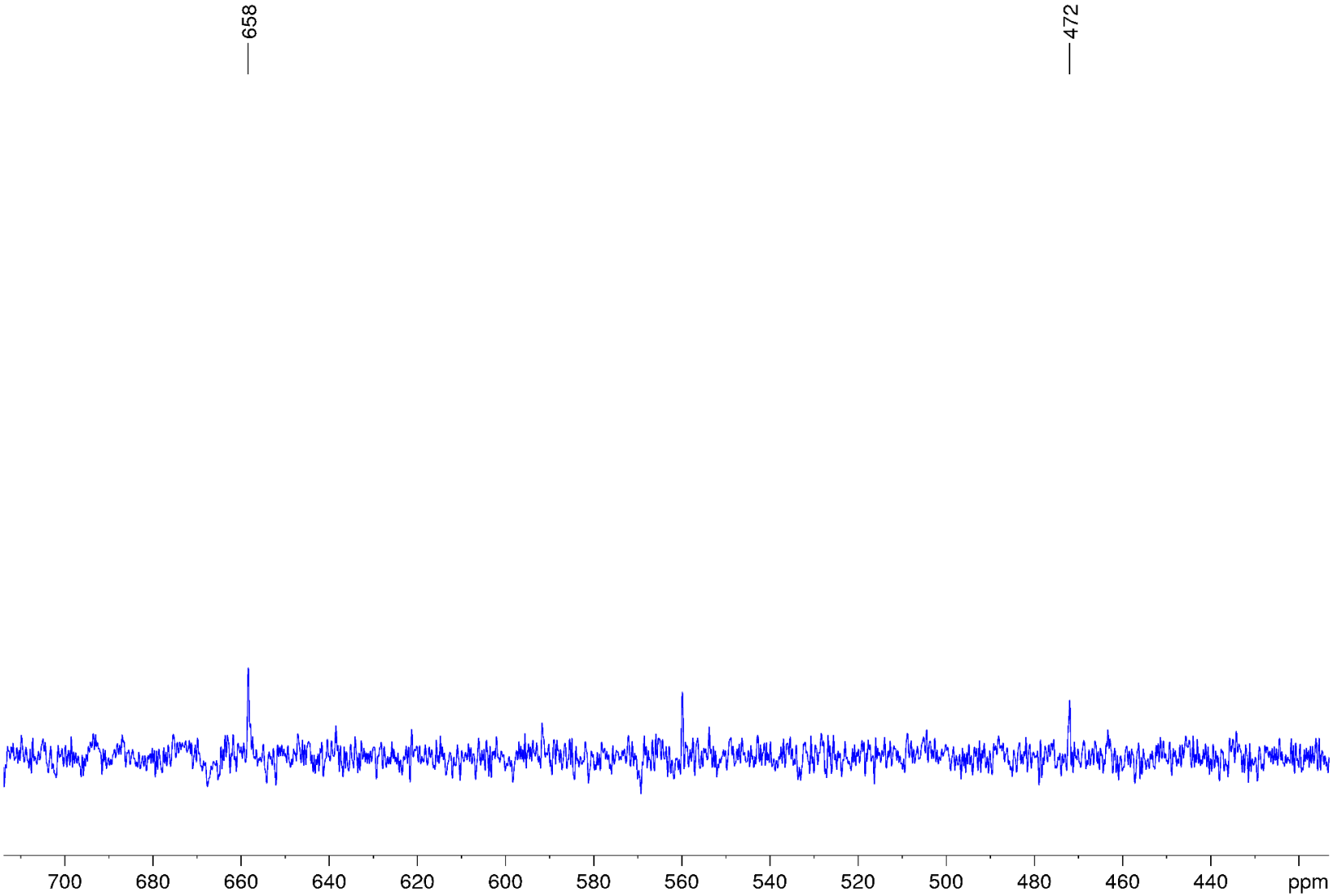

Figure S18. ^{77}Se NMR spectrum of **2-Se** in C_6D_6. Offset at 560 ppm.

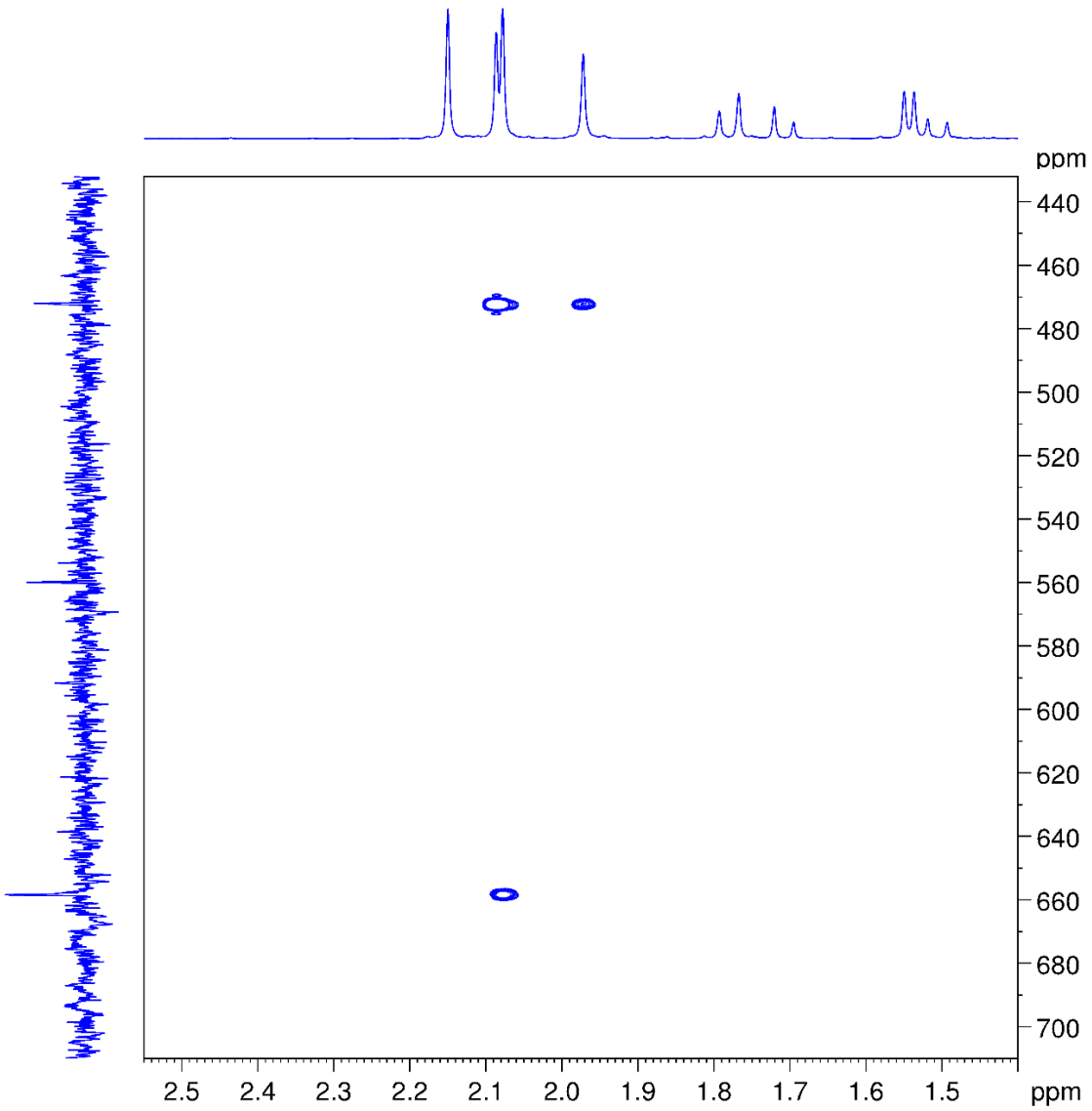

Figure S19. ^{1}H-^{77}Se-HMQC plot of **2-Se** in C_6D_6 (*meso*: δ_{77Se} = 658 ppm; *rac*: δ_{77Se} = 472 ppm).

Variable temperature NMR experiment on rac/meso-2-Se

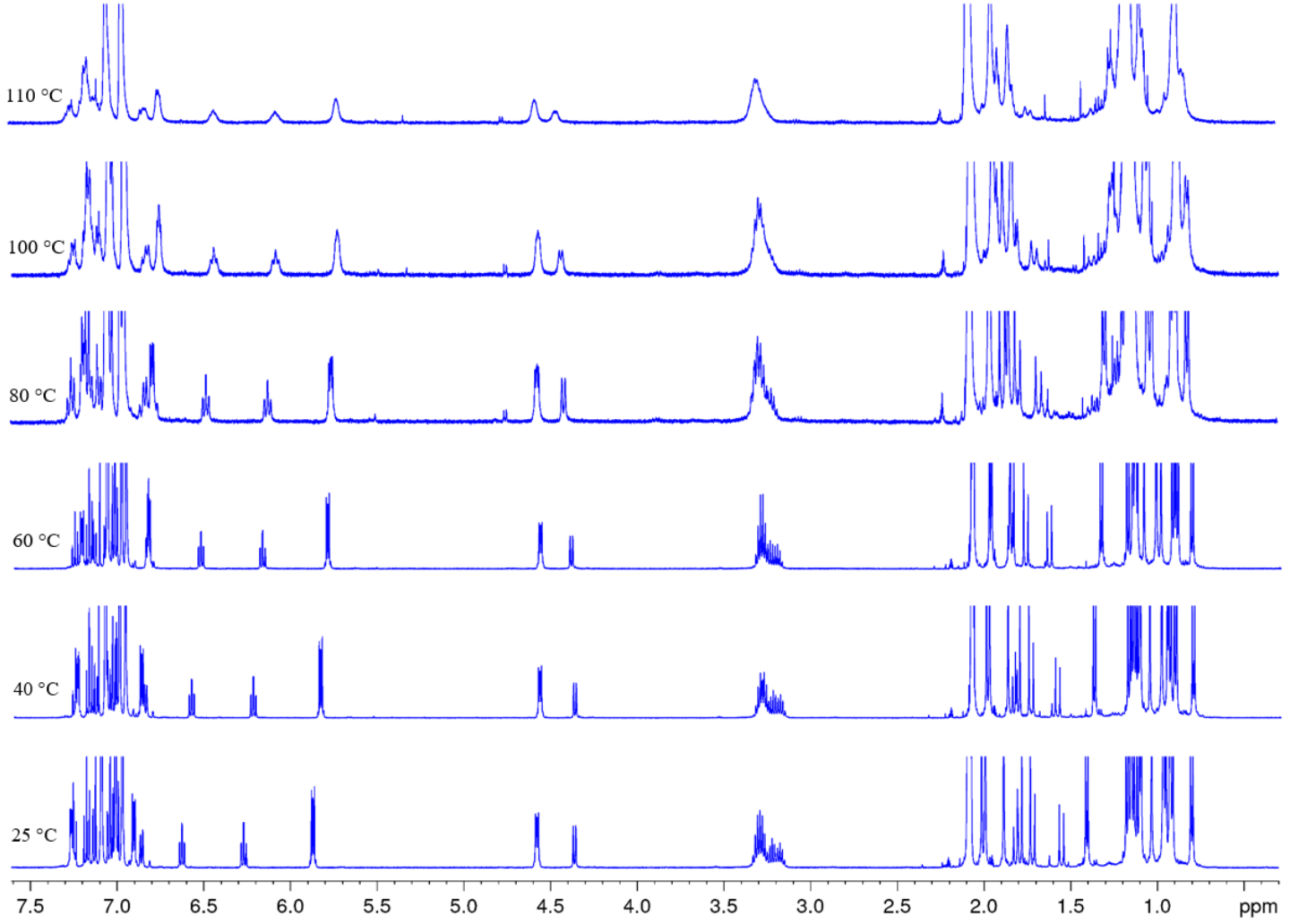

Figure S20. Stack-plot of ^{1}H NMR spectra of *rac/meso*-**2-Se** in toluene-d_8 from 25 to 110 °C.

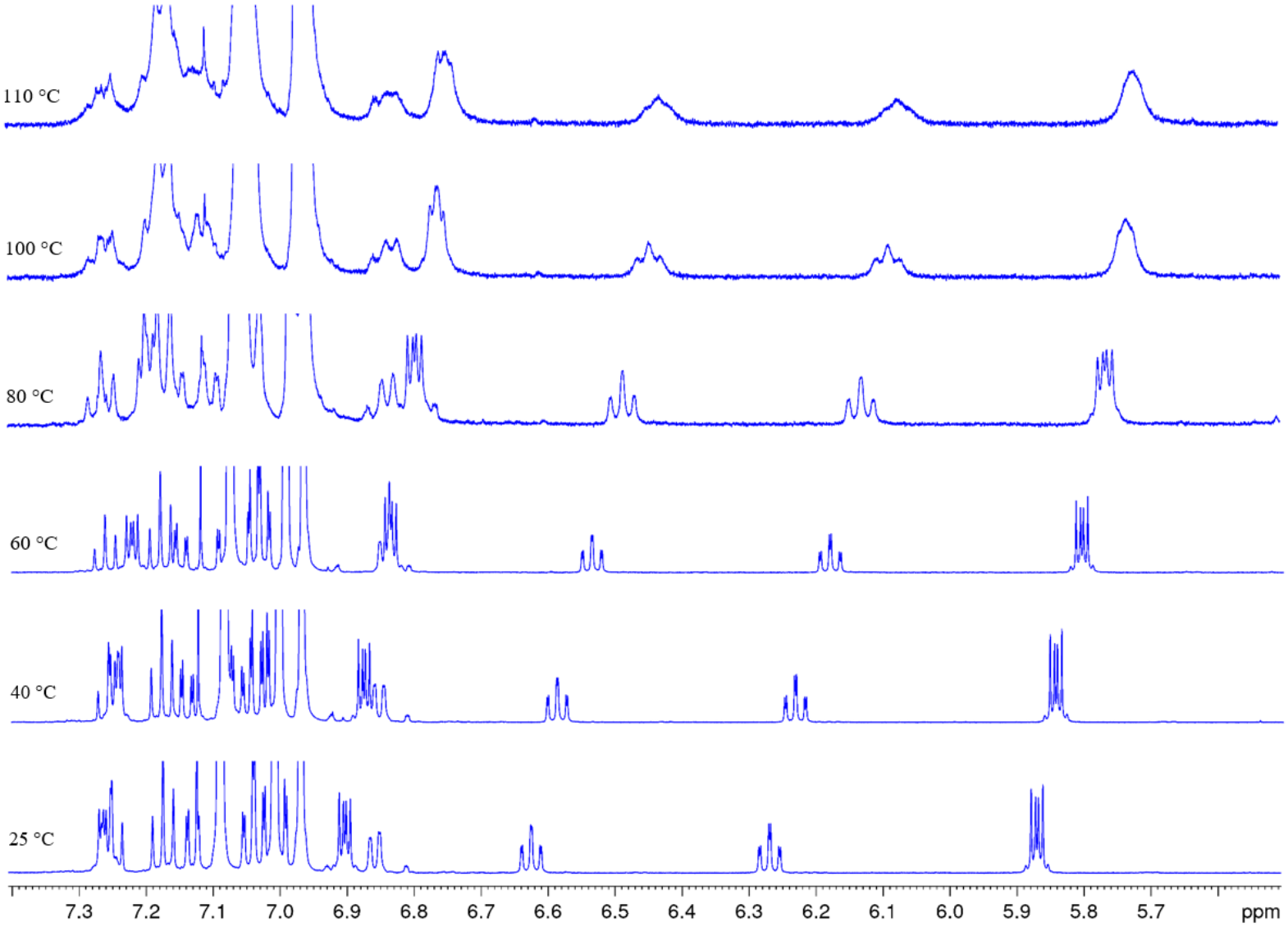

Figure S21. Stack-plot of ^{1}H NMR spectra of *rac/meso*-**2-Se** in toluene-d_8 from 25 to 110 °C with close-up of the aromatic region.

UV-vis spectra

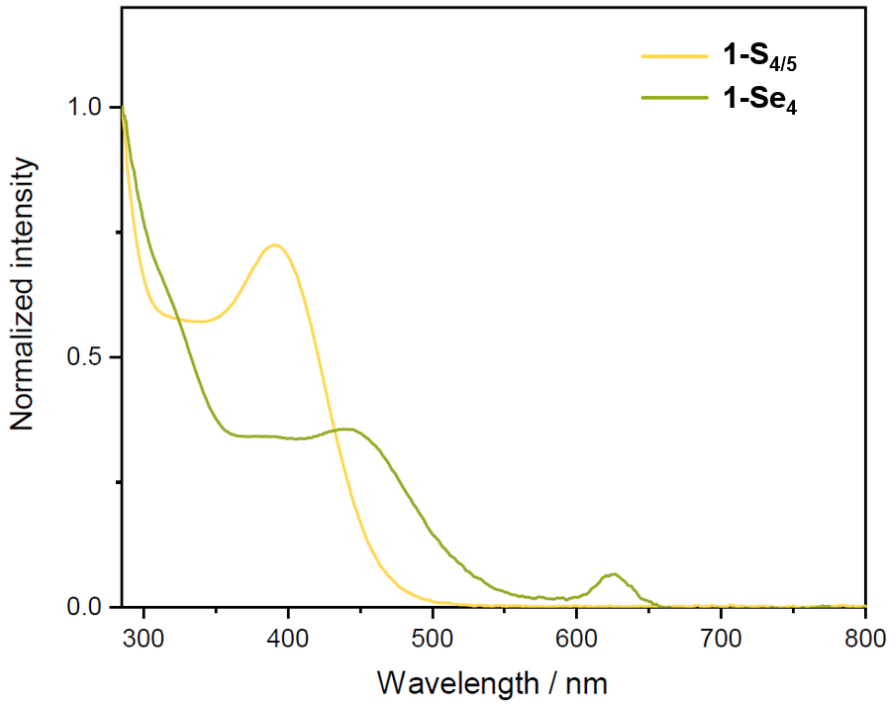

Figure S22. UV-vis absorption spectra of **1-S$_{4/5}$** (yellow) and **1-Se** (green) in 1,2-$F_2C_6H_4$ at 23 °C.

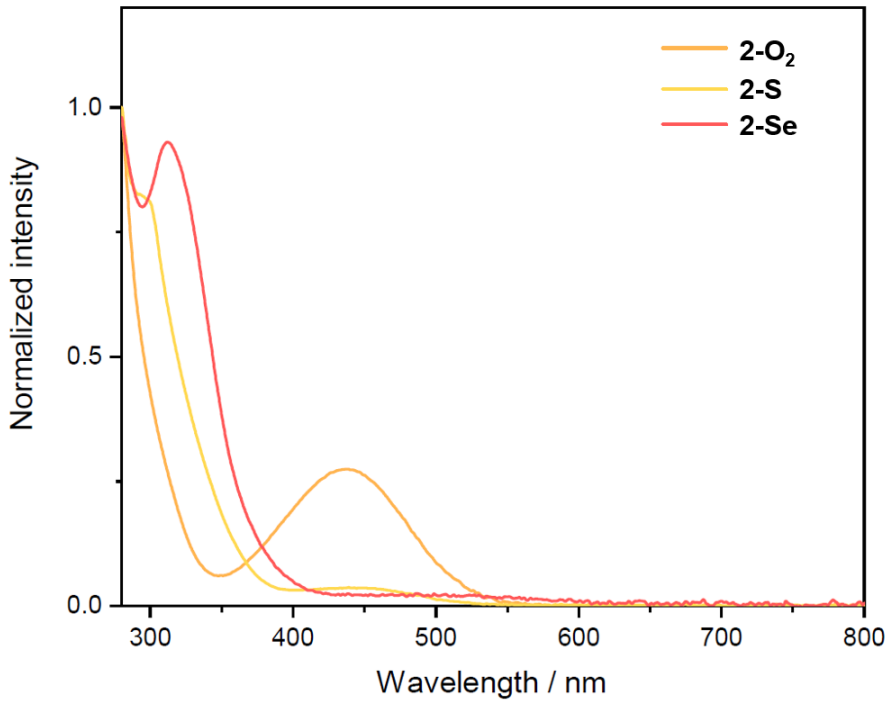

Figure S23. UV-vis absorption spectra of **2-O$_2$** (orange), **2-S** (yellow) and **2-Se** (red) in benzene at 23 °C.

X-ray crystallographic data

The crystal data of **1-Se$_4$**, *syn*-**2-O$_2$** and *rac*-**2-S** 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 crystal data of **1-S$_{4/5}$** and *rac*-**2-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 the intrinsic phasing method,[5] refined with the ShelXL program[6] 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 idealized geometric positions.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 2106400 (*syn*-**2-O$_2$**), 2106401 (**1-S$_{4/5}$**), 2106402 (*rac*-**2-S**), 2106403 (**1-Se$_4$**) and 2106404 (*rac*-**2-Se**). These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

Refinement details 1-S$_{4/5}$: The bridging S_4-chain (RESI 2 S4) showed an overlap with an S_5-chains (RESI 12 S5) in a ratio 92:8 ratio (this co-crystallization was also observed in the NMR spectra). The ADPs of overlapping atoms from these residues were restrained with SIMU 0.003. Correspondingly a 92:8 disorder was also modelled in the B_2C_4 core (RESI 1 and 11 MAIN), which otherwise showed elongated carbon ellipsoids. 1,2- and 1,3-distances within residues MAIN were restrained with SAME 0.005 and additionally the C2-C3 and C5-C6 bond lengths were restrained to similarity with SADI 0.005. ADPs within this disorder were restrained with SIMU 0.005. Both CAAC backbones showed a twofold flip-disorder in the C4, C6 and C7 atoms. These were modelled in a 89:11 ratio (RESI 31 and 32 DIS) and 85:15 ratio (RESI 41 and 42 DIS), respectively. ADPs within these disorders were restrained with SIMU 0.01 and 0.005, respectively.

Crystal data for 1-S$_{4/5}$: $(C_{44}H_{66}B_2N_2S_4)_{0.92}\cdot(C_{44}H_{66}B_2N_2S_5)_{0.08}$, M_r = 775.27, yellow block, 0.226×0.132×0.083 mm^3, monoclinic space group $P2_1/n$, a = 13.639(5) Å, b = 15.761(5) Å, c = 20.224(7) Å, β = 95.777(10)°, V = 4325(2) Å^3, Z = 4, ρ_{calcd} = 1.191 g·cm^{-3},

μ = 0.256 mm^{-1}, F(000) = 1677, T = 100(2) K, R_1 = 0.0800, wR_2 = 0.1344, 8521 independent reflections [$2\theta \leq$ 52.044°] and 531 parameters.

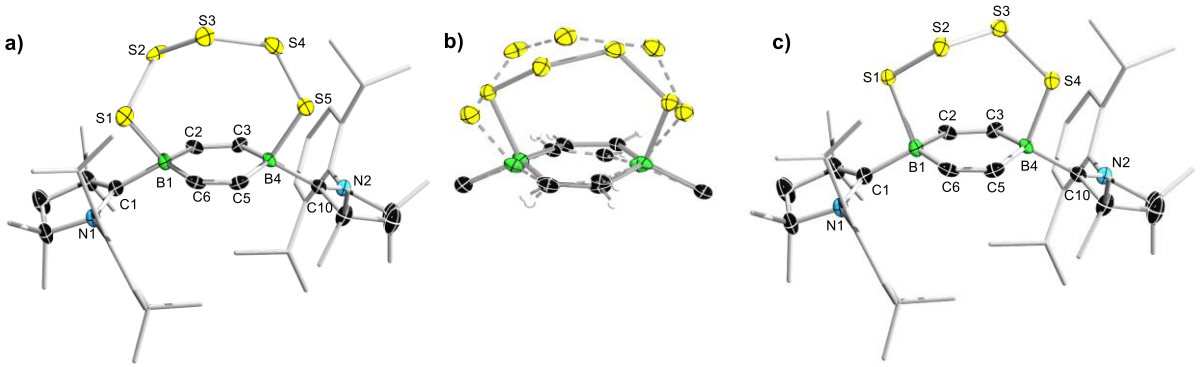

Figure S24. Crystallographically-derived solid-state structures of **1-S$_4$** (**a**) and **1-S$_5$** (**c**), which are overlayed in the asymmetric unit as shown in **c** (only the central, disordered part of the molecule is shown) Atomic displacement ellipsoids drawn at 50% probability level. Ellipsoids on the ligand periphery and hydrogen atoms, except for those of the diborabenzene ring, omitted for clarity.

Refinement details 1-Se$_4$: 9 solvent molecules per unit cell, composed of a mix of highly disordered benzene + difluorobenzene positioned on C_2 axes and on an inversion centers on C_3 axes have been treated as a diffuse contribution to the overall scattering without specific atom positions by Squeeze/Platon.[7] 433 electrons were thus squeezed from the unit cell, i.e. 72.2 per asymmetric unit, corresponding to ca. 0.93 benzene molecules (ca. 39 electrons) and 0.58 difluorobenzene molecules (ca. 33 electrons), i.e. 1.5 solvent molecules in total.

Crystal data for 1-Se$_4$: $C_{44}H_{66}B_2N_2Se_4$, M_r = 960.44, orange block, 0.281×0.080×0.061 mm^3, trigonal space group $P\bar{3}$ c1, a = b = 23.3247(2) Å, c = 16.22090(10) Å, γ = 120°, V = 7642.54(14) Å^3, Z = 6, ρ_{calcd} = 1.252 g·cm^{-3}, μ = 3.645 mm^{-1}, F(000) = 2940, T =100.0(1) K, R_1 = 0.0354, wR_2 = 0.0893, 5414 independent reflections [$2\theta \leq$ 144.670°] and 243 parameters.

Refinement details *syn*-**2-O$_2$**: The asymmetric unit contains 0.485 toluene molecules and 0.015 disordered pentane molecules overlapping on an inversion center, which were treated as a diffuse contribution to the overall scattering without specific atom positions by

Squeeze/Platon.[7] 200 Electrons were thus squeezed from the unit cell, which corresponds to 4×(0.485 toluene + 0.015 pentane) molecules.

Crystal data for *syn*-**2-O$_2$**: $C_{52}H_{70}B_2N_2O_2$, M_r = 776.72, orange block, 0.281×0.080×0.061 mm^3, monoclinic space group *C*2/*c*, *a* = 18.8333(4) Å, *b* = 15.3268(2) Å, *c* = 19.3381(4) Å, β = 116.438(2)°, *V* = 4998.24(19) Å^3, *Z* = 4, ρ_{calcd} = 1.032 g·cm^{-3}, μ = 0.461 mm^{-1}, *F*(000) = 1688, *T* = 99.9(7) K, R_1 = 0.0630, wR_2 = 0.1547, 4908 independent reflections [$2\theta \leq 144.254°$] and 270 parameters.

Refinement details *rac*-**2-S**: Refined as a 2-component twin. BASF refined to value of 0.34046. Five reflections affected strongly by the beamstop were omitted.

Crystal data for *rac*-**2-S**: $C_{52}H_{70}B_2N_2S$, M_r = 776.78, yellow plate, 0.262×0.176×0.104 mm^3, monoclinic space group $P2_1/c$, *a* = 14.76758(13) Å, *b* = 17.41451(14) Å, *c* = 18.25979(18) Å, β = 107.2385(10)°, *V* = 4484.92(7) Å^3, *Z* = 4, ρ_{calcd} = 1.150 g·cm^{-3}, μ = 0.903 mm^{-1}, *F*(000) = 1688, *T* = 99.9(6) K, R_1 = 0.0547, wR_2 = 0.1233, 15322 independent reflections [$2\theta \leq 144.216°$] and 531 parameters.

Refinement details *rac*-**2-Se**: The unit cell contains solvent molecules (mixture of benzene + THF) which have been treated as a diffuse contribution to the overall scattering without specific atom positions by Squeeze/Platon.[7] The four most disagreeable reflections (0 3 3, 1 3 0, 2 2 1, 0 3 5) were omitted.

Crystal data for *rac*-**2-Se**: $C_{52}H_{70}B_2N_2Se$, M_r = 823.68, red block, 0.431×0.301×0.178 mm^3, orthorhombic space group *Pnnm*, *a* = 14.749(2) Å, *b* = 17.494(7) Å, *c* = 24.885(9) Å, *V* = 6421(4) Å^3, *Z* = 4, ρ_{calcd} = 0.852 g·cm^{-3}, μ = 0.611 mm^{-1}, *F*(000) = 1760, *T* = 100(2) K, R_1 = 0.0720, wR_2 = 0.1635, 6482 independent reflections [$2\theta \leq 52.042°$] and 258 parameters.

Computational details

Geometry optimizations of *mix*-, *syn*-, *rac*- and *meso*-**2-O$_2$** were carried out starting from the crystallographically-derived structure of *syn*-**2-O$_2$** by rotation about the B–C$_{CAAC}$ bond, using the BP86 functional[8] with Grimme's D3(BJ) dispersion correction[9] and the def2-TZVP basis set,[10] as implemented in the software Turbomole[11] with the user interface TmoleX 2021.[12]

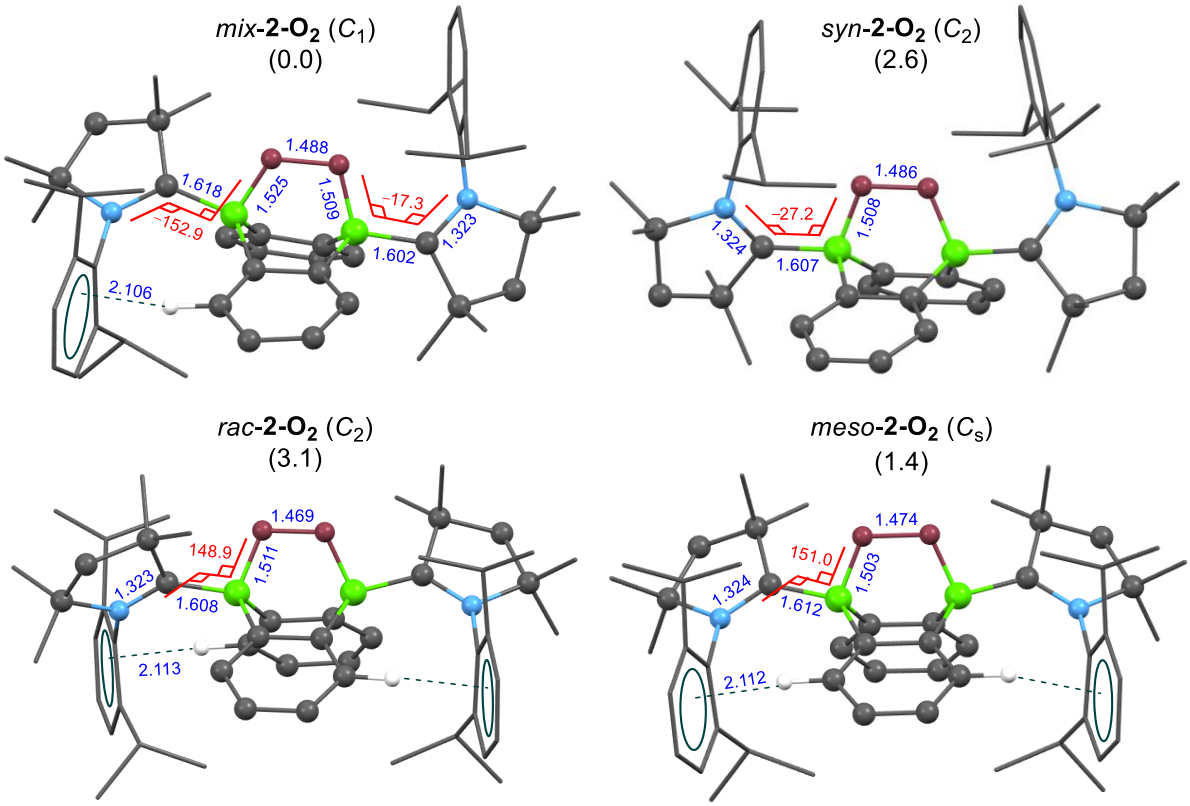

Figure S25. Optimized structures of *mix*-, *syn*-, *rac*- and *meso*-**2-O$_2$** at the BP86-D3(BJ)-Def2-TZVP level of theory. Relative energies (kcal mol^{-1}) in parentheses, distances (Å) in blue and (N–C–B–O) torsion angles (°) in red.

Table S1. Cartesian coordinates and energies (hartrees) of the optimized structures of *mix*-, *syn*, *rac*- and *meso*-**2-O$_2$** at the BP86-D3(BJ)-Def2-TZVP level of theory.

mix-**2-O$_2$**

E_h = –2334.52871731326

B	-1.226573	-0.745681	-0.738313
C	-1.589094	-2.179399	1.605574
H	-2.677128	-2.160815	1.512746
C	-1.045535	-2.756909	2.756296
H	-1.699952	-3.199074	3.510246
C	0.336863	-2.748422	2.936996
H	0.782402	-3.187172	3.831933
C	1.145129	-2.140237	1.972808
H	2.219204	-2.088353	2.166928
C	0.614564	-1.581077	0.803466
C	-2.824984	-0.851378	-0.753118
N	-3.638727	0.037590	-0.208322
C	-3.652157	-2.086465	-1.166335
C	-4.908982	-1.925970	-0.282087
H	-5.796237	-2.392184	-0.727908
H	-4.733738	-2.403664	0.693764
C	-5.091341	-0.419134	-0.072050
C	-5.684675	-0.103771	1.296858
H	-5.691105	0.975852	1.492644
H	-5.148759	-0.611170	2.105449
H	-6.726099	-0.454479	1.306612
C	-5.953193	0.277358	-1.132316
H	-5.607469	0.089192	-2.152309
H	-5.954946	1.362088	-0.961632
H	-6.987398	-0.081575	-1.047982
C	-4.064734	-2.012081	-2.668582
H	-3.319254	-2.509554	-3.294618

H	-4.194420	-0.991730	-3.047864
H	-5.019357	-2.542809	-2.790254
C	-2.961277	-3.443750	-0.981622
H	-3.598842	-4.227386	-1.417459
H	-2.781854	-3.688319	0.069410
H	-1.996483	-3.452135	-1.504116
C	-3.316314	1.429451	0.042726
C	-3.226432	2.307704	-1.059894
C	-3.069063	3.673096	-0.791041
H	-2.993701	4.369118	-1.627090
C	-2.983840	4.151466	0.511381
H	-2.867286	5.220406	0.695689
C	-3.000772	3.256209	1.576982
H	-2.862493	3.625338	2.593512
C	-3.149310	1.880721	1.369106
C	-2.943082	0.940150	2.544490
H	-3.201955	-0.075638	2.220514
C	-3.201791	1.853034	-2.509205
H	-3.387089	0.771755	-2.533540
C	0.986760	-1.417846	-1.817742
O	0.749692	0.655337	-0.449769
B	1.376794	-0.732926	-0.387277
C	1.751910	-1.912328	-2.883919
H	2.814517	-2.082927	-2.771372
C	1.198346	-2.185522	-4.138395
H	1.834454	-2.579351	-4.934181
C	-0.144112	-1.903919	-4.375009
H	-0.578290	-2.039399	-5.367993
C	-0.929686	-1.440574	-3.315958
H	-1.962638	-1.171512	-3.520334
C	-0.414469	-1.271355	-2.025551
C	2.833597	-0.440868	0.252702

N	3.963433	-1.115989	0.115381
C	3.060285	0.659344	1.297011
C	4.288953	0.157453	2.084999
H	4.939740	0.985499	2.395131
H	3.944074	-0.353184	2.995285
C	5.030804	-0.836687	1.181734
C	5.370455	-2.136478	1.911009
H	5.843969	-2.861303	1.236219
H	4.480326	-2.595164	2.356231
H	6.079771	-1.909212	2.718338
C	6.324464	-0.264999	0.592363
H	6.196899	0.747452	0.194682
H	6.726674	-0.912337	-0.197658
H	7.070208	-0.212334	1.397124
C	3.368922	1.945090	0.484522
H	3.527719	2.771836	1.192061
H	2.515919	2.187266	-0.161272
H	4.268779	1.851432	-0.135100
C	1.911551	0.998720	2.249591
H	2.265741	1.769216	2.951420
H	1.581547	0.128678	2.826581
H	1.059497	1.387685	1.687166
C	4.319971	-1.986122	-0.988671
C	4.920263	-1.380933	-2.120677
C	5.360981	-2.215357	-3.153334
H	5.820079	-1.769955	-4.035303
C	5.189287	-3.595327	-3.090796
H	5.532093	-4.227047	-3.911174
C	4.548159	-4.160007	-1.995559
H	4.369768	-5.235204	-1.970836
C	4.096733	-3.376566	-0.924178
C	3.304363	-4.057421	0.176154

H	3.093919	-3.312781	0.948786
C	5.003056	0.125764	-2.306192
H	4.942885	0.584478	-1.316947
C	-0.786092	-1.617276	0.604379
O	-0.732838	0.643889	-0.416763
C	-1.446723	0.914857	2.891036
C	-3.780216	1.293846	3.779655
C	-1.802199	2.077337	-3.110366
C	-4.278741	2.536671	-3.365020
C	1.945200	-4.539979	-0.359389
C	4.065835	-5.222902	0.825423
C	6.324910	0.582138	-2.937065
C	3.801907	0.659101	-3.106213
H	-0.864965	0.687922	1.992477
H	-1.122814	1.890786	3.282340
H	-1.238164	0.144331	3.646306
H	-3.644036	0.527145	4.556068
H	-4.852880	1.368577	3.555786
H	-3.462331	2.252819	4.213214
H	-4.269951	2.123215	-4.383910
H	-5.286188	2.404772	-2.948335
H	-4.090864	3.616825	-3.448581
H	5.055367	-4.921042	1.193532
H	4.211207	-6.049292	0.115135
H	3.489454	-5.617751	1.674242
H	-1.583585	3.153240	-3.185967
H	-1.750570	1.647328	-4.120950
H	-1.034914	1.607652	-2.483286
H	1.341367	-4.940866	0.466743
H	1.386207	-3.720091	-0.824549
H	2.081910	-5.333272	-1.109307
H	6.395836	1.678387	-2.899264

H	6.394510	0.291867	-3.995025
H	7.195810	0.162590	-2.413850
H	3.740645	0.177634	-4.092535
H	2.850687	0.476041	-2.591638
H	3.909853	1.743225	-3.256835

syn-**2-O$_2$**

E_h = –2334.53280358204

B	-1.221755	-1.019104	-0.485176
C	-2.175158	-2.252012	1.795103
H	-3.207216	-2.232430	1.439851
C	-1.944346	-2.753603	3.078685
H	-2.773580	-3.128209	3.681932
C	-0.643451	-2.760126	3.574334
H	-0.433445	-3.140807	4.575898
C	0.397380	-2.263838	2.783477
H	1.393400	-2.269892	3.218873
C	0.193153	-1.772796	1.485323
C	-2.806011	-0.951472	-0.748695
N	-3.618489	-0.003429	-0.307286
C	-3.658245	-2.091306	-1.316011
C	-5.015462	-1.889931	-0.610880
H	-5.855946	-2.204804	-1.243394
H	-5.047647	-2.492643	0.307256
C	-5.098338	-0.396758	-0.249222
C	-5.655973	-0.198535	1.158435
H	-5.656716	0.861310	1.440226
H	-5.091041	-0.766840	1.904901
H	-6.696162	-0.552958	1.169742
C	-5.947759	0.451158	-1.204474
H	-5.685376	0.318114	-2.258076
H	-5.852168	1.516917	-0.958459

H	-7.000944	0.166909	-1.079779
C	-3.832635	-1.818965	-2.841642
H	-4.069595	-2.764063	-3.349725
H	-2.934630	-1.397829	-3.303498
H	-4.654089	-1.120919	-3.032761
C	-3.104572	-3.505541	-1.114530
H	-3.809848	-4.227121	-1.552301
H	-2.974176	-3.746077	-0.054306
H	-2.133098	-3.629236	-1.605619
C	-3.261363	1.384858	-0.054477
C	-3.169317	2.237701	-1.177981
C	-2.928282	3.597144	-0.953192
H	-2.839889	4.268108	-1.807733
C	-2.795474	4.103467	0.335348
H	-2.613581	5.167926	0.490071
C	-2.867837	3.240862	1.423115
H	-2.716735	3.630147	2.430419
C	-3.086902	1.867541	1.258172
C	-2.959162	0.970419	2.474200
H	-3.194534	-0.055438	2.170849
C	-3.251496	1.732143	-2.607887
H	-3.702728	0.736449	-2.586407
C	1.141086	-1.766664	-0.997809
O	0.687703	0.375462	0.282065
B	1.224436	-1.019744	0.478456
C	2.180197	-2.236979	-1.809189
H	3.212173	-2.217820	-1.453692
C	1.950389	-2.731023	-3.095866
H	2.780299	-3.100540	-3.701308
C	0.649568	-2.736625	-3.591723
H	0.440341	-3.111300	-4.595714
C	-0.392229	-2.247249	-2.797836

H	-1.388186	-2.252293	-3.233412
C	-0.189022	-1.764055	-1.496586
C	2.808537	-0.950672	0.742290
N	3.619343	0.001413	0.306609
C	3.662744	-2.092377	1.302843
C	5.019730	-1.884338	0.599253
H	5.860647	-2.201326	1.230133
H	5.053299	-2.481603	-0.322376
C	5.099910	-0.388936	0.246399
C	5.657128	-0.181354	-1.160055
H	5.655911	0.880151	-1.435479
H	5.093137	-0.746229	-1.909829
H	6.697962	-0.533832	-1.173593
C	5.947815	0.454692	1.206765
H	5.685402	0.315064	2.259516
H	5.850674	1.521748	0.967013
H	7.001462	0.172775	1.080634
C	3.836009	-1.828654	2.830170
H	4.072142	-2.776607	3.333270
H	2.937761	-1.409734	3.293608
H	4.657550	-1.131964	3.025808
C	3.111809	-3.506418	1.092695
H	3.818224	-4.229250	1.526547
H	2.982422	-3.740853	0.031015
H	2.140318	-3.634899	1.582535
C	3.260208	1.390664	0.061990
C	3.167544	2.236877	1.190443
C	2.925753	3.597466	0.973637
H	2.837026	4.263357	1.832091
C	2.792409	4.111188	-0.311918
H	2.609918	5.176426	-0.460443
C	2.865068	3.254957	-1.404684

H	2.713609	3.650017	-2.409689
C	3.085217	1.880852	-1.247779
C	2.958211	0.990717	-2.469021
H	3.195126	-0.036584	-2.171840
C	3.249538	1.722898	2.617352
H	3.701616	0.727701	2.590280
C	-1.136976	-1.774817	0.986564
O	-0.687623	0.375907	-0.280269
C	-1.493547	0.964171	2.933681
C	-3.876872	1.365652	3.638499
C	-1.842820	1.564541	-3.193887
C	-4.130869	2.608463	-3.509724
C	1.492361	0.985285	-2.927814
C	3.874857	1.394067	-3.631377
C	4.127635	2.594556	3.524911
C	1.840620	1.550642	3.201401
H	1.326821	2.520562	3.265398
H	1.889288	1.119052	4.212276
H	1.232131	0.901086	2.561174
H	-1.233443	0.911405	-2.558172
H	-1.329710	2.535175	-3.252204
H	-1.891906	1.139253	-4.207407
H	0.827234	0.796049	-2.080014
H	1.332356	0.201455	-3.681089
H	1.224244	1.956256	-3.370423
H	3.760306	0.678737	-4.458786
H	4.935682	1.422136	-3.348876
H	3.607771	2.387438	-4.020168
H	3.676910	3.581730	3.701141
H	5.127231	2.753829	3.096618
H	4.245277	2.113401	4.506704
H	-4.937603	1.394068	3.355684

H	-3.761771	0.645564	4.461695
H	-3.611275	2.357036	4.033381
H	-0.827781	0.780904	2.085081
H	-1.226956	1.932819	3.382287
H	-1.332836	0.176055	3.682291
H	-5.130363	2.764270	-3.079918
H	-3.681100	3.597074	-3.680225
H	-4.248649	2.133113	-4.494329

rac-**2-O$_2$**

E_h = –2334.53363635414

C	0.965337	1.342285	0.383802
B	1.365183	-0.026052	-0.414327
C	1.713758	2.272006	1.120192
H	2.776379	2.125808	1.269052
B	-1.215934	0.413077	-0.609037
C	1.143848	3.412233	1.695343
H	1.771185	4.096044	2.270943
C	-0.212978	3.669312	1.522675
H	-0.674700	4.560243	1.953446
C	-0.975544	2.767994	0.775338
H	-2.030696	3.001359	0.618047
C	-0.424733	1.606927	0.224998
C	0.459496	-1.201002	0.323787
C	0.922769	-2.346826	0.976776
H	1.989569	-2.579781	0.983627
C	0.057462	-3.233689	1.622616
H	0.450219	-4.111963	2.139149
C	-1.310239	-2.979570	1.581933
H	-2.016359	-3.652876	2.072282
C	-1.788430	-1.855550	0.901035
H	-2.861475	-1.711822	0.883687

C	-0.938634	-0.937423	0.267611
C	2.774056	-0.774409	-0.617417
N	3.868188	-0.754286	0.125274
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C	4.090923	-2.714477	-1.177869
H	3.650962	-3.586975	-0.674839
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C	4.874252	-1.873794	-0.159159
C	3.391478	-1.049408	-2.996178
H	3.528829	-1.774555	-3.811348
H	4.338247	-0.511522	-2.863135
H	2.611939	-0.332854	-3.278968
C	1.727089	-2.664732	-2.104131
H	2.012353	-3.328615	-2.934518
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H	1.382207	-3.282391	-1.268385
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H	6.906371	-2.159223	-0.793587
H	6.629992	-0.580606	-0.028553
H	6.088653	-0.879014	-1.702316
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H	5.852204	-3.479481	0.875960
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H	5.666302	-2.018532	1.869581
C	4.255785	0.309549	1.030435
C	4.885722	1.445643	0.465794
C	5.346644	2.440575	1.335132
H	5.827682	3.325436	0.919219
C	5.171937	2.335833	2.711734
H	5.534068	3.125482	3.371270
C	4.501706	1.238467	3.238196
H	4.318134	1.183564	4.311317

C	4.022995	0.207223	2.418288
C	4.985622	1.680684	-1.032176
H	4.846188	0.718815	-1.531623
C	3.851599	2.598133	-1.523285
H	3.962817	2.780587	-2.602135
H	3.879192	3.566973	-1.004132
H	2.863566	2.154382	-1.351533
C	6.355225	2.223321	-1.462518
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H	6.512235	3.255166	-1.117337
H	6.422230	2.236365	-2.559546
C	3.184636	-0.883750	3.059191
H	2.975403	-1.639213	2.297122
C	1.825568	-0.320974	3.510632
H	1.286557	0.139242	2.675186
H	1.959260	0.440635	4.293017
H	1.201424	-1.131365	3.912219
C	3.896765	-1.572349	4.232707
H	4.884913	-1.959204	3.949626
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C	-2.581493	1.151719	-1.029408
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C	-2.601560	2.174419	-2.173871
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H	-4.334887	3.427171	-2.710069
C	-4.726349	2.253151	-0.901563
C	-1.333583	3.010600	-2.394964
H	-0.469390	2.362848	-2.577059
H	-1.111542	3.650653	-1.534625
H	-1.497082	3.651903	-3.274565

C	-2.853399	1.367817	-3.476044
H	-2.872136	2.071922	-4.321014
H	-3.809028	0.829909	-3.465788
H	-2.041173	0.647475	-3.627093
C	-5.956757	1.692484	-1.623743
H	-6.647693	2.522593	-1.822182
H	-6.483449	0.957922	-1.000670
H	-5.707475	1.229927	-2.584331
C	-5.203451	3.055124	0.308697
H	-5.841101	3.876903	-0.045423
H	-4.364130	3.489582	0.863495
H	-5.798717	2.434360	0.990817
C	-4.283880	0.100079	0.415463
C	-4.240730	0.232422	1.819499
C	-4.830647	-0.780485	2.588363
H	-4.793586	-0.703105	3.675074
C	-5.427885	-1.888072	1.999334
H	-5.878376	-2.663400	2.620318
C	-5.415187	-2.022244	0.614077
H	-5.838344	-2.915723	0.155861
C	-4.836578	-1.046670	-0.205610
C	-4.728893	-1.315472	-1.697349
H	-4.521168	-0.364543	-2.194229
C	-3.495043	1.336813	2.546081
H	-3.174247	2.071670	1.802812
C	-2.217074	0.784286	3.201698
H	-1.565554	0.303596	2.463769
H	-2.463689	0.042749	3.975381
H	-1.653906	1.604518	3.668004
C	-4.363552	2.056263	3.588488
H	-5.298453	2.439862	3.158191
H	-3.808361	2.904243	4.013988

H	-4.627446	1.387118	4.420034
C	-3.537788	-2.240423	-2.005836
H	-3.501036	-2.449980	-3.084863
H	-3.635021	-3.196211	-1.471141
H	-2.582751	-1.789095	-1.711444
C	-6.026069	-1.871609	-2.300332
H	-5.942197	-1.907178	-3.395635
H	-6.895687	-1.251874	-2.041287
H	-6.227976	-2.896850	-1.958937
O	-0.556861	0.160497	-1.944547
O	0.907784	0.197035	-1.836960

meso-**2-O$_2$**

E_h = –2334.530877

C	-0.060761	-0.689281	1.131755
C	0.255837	-1.609889	2.139341
C	1.367154	-1.459662	2.973331
C	-0.645051	-0.592150	-1.402891
B	-1.333276	-0.638999	0.111813
C	-0.044680	-1.330751	-3.656859
C	-0.763089	-1.490598	-2.469273
O	-2.053071	0.647686	0.405953
H	-0.362572	-2.482931	2.297822
H	1.583258	-2.217900	3.729076
H	-0.148329	-2.058430	-4.464271
H	-1.443035	-2.341805	-2.395841
C	-2.547424	-1.665133	-0.157560
C	-3.812951	-1.218485	-0.904162
C	-4.336054	-2.531440	-1.527139
C	-3.753949	-3.686470	-0.700951
N	-2.614430	-2.973288	0.034266
C	-4.779794	-0.662598	0.174351
C	-3.657325	-0.132766	-1.976185

C	-3.190698	-4.799486	-1.583385
C	-4.764058	-4.307660	0.269072
C	-0.682156	-4.439890	0.609996
C	-0.030550	-5.209161	1.583668
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C	-1.612116	-4.533432	3.262664
C	-2.299209	-3.740495	2.336995
C	-1.839259	-3.732770	0.997154
C	-0.035518	-4.324705	-0.757631
C	1.267814	-3.511126	-0.672859
C	0.225738	-5.689909	-1.409845
C	-3.422835	-2.846811	2.835941
C	-4.386428	-3.571560	3.785163
C	-2.865729	-1.568170	3.486998
H	-5.688512	-0.298672	-0.327071
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H	-3.249549	0.780157	-1.531923
H	-2.997776	-0.450923	-2.790187
H	-4.652644	0.081561	-2.395149
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H	-4.019079	-5.258764	-2.139807
H	-5.491974	-4.885543	-0.315900
H	-4.272213	-4.994803	0.969909
H	-5.318376	-3.556430	0.840965
H	0.875707	-5.747826	1.306365
H	0.032083	-5.878941	3.630821
H	-1.945667	-4.544810	4.299825
H	-0.715589	-3.763217	-1.403541
H	1.680760	-3.364784	-1.680558
H	1.095100	-2.525182	-0.226755
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H	0.609377	-5.549531	-2.430650
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H	-4.002905	-2.522886	1.968296
H	-5.250115	-2.927291	4.002631
H	-4.757042	-4.511422	3.353235
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H	-3.695754	-0.953938	3.866200
H	-2.289874	-0.963784	2.775260
H	-2.204005	-1.813219	4.330063
H	-2.465193	-4.414248	-2.309547
H	-3.979591	-2.602357	-2.564646
H	-5.433086	-2.564740	-1.549834
H	-4.304936	0.172876	0.702994
C	0.778598	0.463104	0.979673
C	1.865968	0.608378	1.851056
C	2.178305	-0.339736	2.829211
C	0.191742	0.533009	-1.554023
B	0.210186	1.465227	-0.175579
C	0.786756	-0.221443	-3.804211
C	0.877741	0.704487	-2.761815
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H	2.508467	1.475836	1.784466
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H	1.346406	-0.065930	-4.728640
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C	0.765902	2.853861	-0.780916
C	-0.137399	3.774124	-1.616318
C	0.866195	4.529871	-2.515099
C	2.230601	4.474628	-1.813897
N	1.999684	3.331428	-0.820142
C	-0.843055	4.722857	-0.611470
C	-1.234944	3.115851	-2.461342
C	3.360423	4.113190	-2.777801
C	2.602919	5.782131	-1.106525
C	4.052388	2.045264	-0.230006
C	5.090508	1.830258	0.687042

C	5.151652	2.517709	1.892841
C	4.145213	3.420709	2.222275
C	3.080145	3.672813	1.350078
C	3.067240	2.998300	0.104014
C	3.993548	1.159801	-1.461372
C	3.639991	-0.285738	-1.071171
C	5.291009	1.193684	-2.281898
C	1.941487	4.559331	1.827262
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C	0.979460	3.779947	2.741516
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H	-0.139763	5.352326	-0.052468
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H	-1.799312	3.912054	-2.970693
H	4.316475	4.002853	-2.250159
H	3.468709	4.924782	-3.510395
H	2.856952	6.527256	-1.871950
H	3.481332	5.648670	-0.461781
H	1.780518	6.186306	-0.508079
H	5.850769	1.085336	0.452444
H	5.968413	2.329658	2.590657
H	4.165692	3.921580	3.189472
H	3.180612	1.522255	-2.096575
H	3.531274	-0.898656	-1.976825
H	2.699432	-0.329449	-0.511432
H	4.428788	-0.726316	-0.443576
H	5.164721	0.610320	-3.205150
H	5.580267	2.216357	-2.559489
H	6.128604	0.748231	-1.726153
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H	3.152121	6.389507	1.886885
H	2.908256	5.634885	3.477266

H	0.183011	4.449605	3.097638
H	0.509663	2.937563	2.218951
H	1.509001	3.377544	3.617322
H	3.146554	3.187612	-3.325511
H	0.929528	4.020721	-3.487132
H	0.549962	5.564602	-2.701084
H	-1.433599	4.134828	0.101148

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