Supporting Information for

Synthesis of Base-free Boriranes and their Conversion to Borirenes Using Strong Reductant

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1. Experimental details

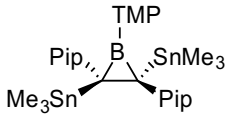
1.1. Methods and materials

All manipulations were performed 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. NMR spectra of isolated compounds were acquired on a Bruker Avance 500 (^{1}H: 500.1 MHz, ^{11}B: 160.5 MHz, ^{13}C: 125.8 MHz, ^{29}Si: 99.4 MHz) or 600 (^{1}H: 600.2 MHz, ^{11}B: 150.9 MHz, ^{13}C: 160.5 MHz, ^{119}Sn: 223.8 MHz) spectrometer. Routine NMR measurements were performed on a Brucker Avance 400 NMR 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: $BF_3{\cdot}OEt_2$, ^{119}Sn: $SnMe_4$). Resonances are identified as singlet (s), doublet (d), triplet (t), septet (sept), multiplet (m) or broad (br). Coupling constants (J) 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. Photochemical experiments were performed using a LOT-Quantum Design GmbH mercury-xenon vapor lamp (I = 19 A, U = 26 V).

Solvents and reagents were purchased from Sigma-Aldrich, abcr or Alfa Aesar. Compounds **1a**,[37] **1b**,[38] **2**,[39] **6**,[44] and **8**[45] were synthesised according to literature methods.

1.2. Synthetic procedures

Synthesis of 3a



To a solution of **1a** (170 mg, 877 µmol) in benzene (30 mL), a solution of [TMPB(SnMe$_3$)$_2$] (**2**, 400 mg, 833 µmol) in benzene (30 mL) was added and the mixture was stirred at room temperature for five days, resulting in a deep-yellow solution. All volatiles were removed *in vacuo,* and the residue was washed with cold hexane (10 mL) and recrystallised from Et_2O, yielding **3a** as a colourless solid (530 mg, 790 µmol, 95%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated hexane solution at room temperature.

*Note: In addition to borirane **3a**, the NMR spectra indicate traces of unidentified side products that could not be separated from the mixture. However, the overall purity is estimated to exceed 95%.*

^{1}H{^{11}B} NMR (600.2 MHz, C_6D_6): δ = 0.42 ($^3J_{H,Sn}$ = 47.1 Hz, 18H, SnC*H*$_3$), 1.04 (s, br, 2H, 3,4,5- NC$_5$*H*$_{10}$), 1.32–1.74 (m, 25H, TMP-C*H*$_2$, TMP-C*H*$_3$, 3,4,5- NC$_5$*H*$_{10}$), 1.79 (m, 2H, TMP-C*H*$_2$), 2.49 (m, br, 2H, 2,6-NC$_5$*H*$_{10}$), 2.71(m, br, 2H, 2,6-NC$_5$*H*$_{10}$), 3.39–3.48 (m, br, 4H, 2,6-NC$_5$*H*$_{10}$) ppm.

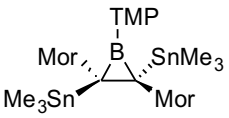
^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6): δ = −2.7 (br, Sn*C*H$_3$), 23.9 (TMP-*C*H$_2$), 26.9 (br, 3,4,5-N*C*$_5$H$_{10}$) 31.2 (TMP-*C*H$_3$), 35.2 (TMP-*C*H$_2$), 36.7 (TMP-*C*H$_2$), 56.4 (TMP-*C*$_q$), 56.6 (br, 2,6-N*C*$_5$H$_{10}$), 59.4 (br, 2,6-N*C*$_5$H$_{10}$), 71.2 (*C*$_q$–B–*C*$_q$) ppm.

^{11}B NMR (160.5 MHz, C_6D_6): δ = 35.2 ppm.

^{119}Sn NMR (223.8 MHz, C_6D_6): δ = −58.6 ppm.

HRMS LIFDI for [$C_{24}H_{47}BN_3Sn$]$^+$ = [M]$^+$: *m*/*z*: calcd. 508.2880; found 508.2864.

Synthesis of 3b



To a solution of **1b** (74.0 mg, 386 µmol) in benzene (30 mL), a solution of [TMPB(SnMe$_3$)$_2$] (**2**, 185 mg, 386 µmol) in benzene (30 mL) was added and the mixture was stirred at room temperature for five days, resulting in a deep-yellow solution. All volatiles were removed *in vacuo,* and the residue was washed with cold hexane (10 mL) and recrystallised from THF, yielding **3b** as a colourless solid (253 mg, 374 µmol, 97%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated Et_2O solution at room temperature.

^{1}H{^{11}B} NMR (600.2 MHz, C_6D_6): δ = 0.31 ($^{3}J_{H,Sn}$ = 47.1 Hz, 18H, SnCH_3), 1.19–1.23 (m, 2H, TMP-CH_2), 1.25 (s, 6H, TMP-CH_3), 1.41–1.54 (m, 8H, TMP-CH_3, TMP-CH_2), 1.72–1.76 (m, 2H, TMP-CH_2), 2.54–3.23 (br, 8H, NC$_4H_8$O), 3.31–3.95 (br, 8H, 2H, NC$_4H_8$O) ppm.

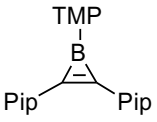
^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6): δ = −2.3 (s, br, SnCH_3), 31.7 (TMP-CH_2), 35.2 (TMP-CH_3), 35.9 (TMP-CH_2), 56.0 (br, NC_4H_8O), 56.7 (TMP-C_q), 58.9 (NC_4H_8O), 70.4 (C_q–B–C_q) ppm.

^{11}B NMR (160.5 MHz, C_6D_6): δ = 34.9 ppm.

^{119}Sn NMR (223.8 MHz, C_6D_6): δ = −57.9 ppm.

HRMS LIFDI for $[C_{22}H_{43}BN_3O_2Sn]^+ = [M]^+$: *m*/*z*: calcd. 512.2465; found 512.2459.

Synthesis of 4a



To a dispersion of KC_8 (161 mg, 1.19 mmol) in benzene (5 mL), a solution of **3a** (200 mg, 298 µmol) in benzene (5 mL) was added and the mixture was stirred at room temperature for 16 h. The solution was filtered over Celite, and all volatiles were removed *in vacuo*. The residue was extracted with hexane (2 x 2 mL) yielding **4a** as a solid (13 mg, 38.7 µmol, 13%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated hexane solution at room temperature.

Note: Instead of KC_8, lithium naphthalenide in THF can be used as a reducing reagent, reducing the reaction time to 1 h. The NMR spectrum shows residual naphthalene from the reaction and unidentified organotin species as side products.

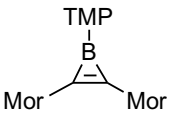
^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6): δ = 1.31–1.36 (m, 4H, TMP-CH_2), 1.46–1.53 (m, 24H, TMP-CH_3, 3,4,5-NC$_5H_{10}$), 1.58–1.63 (m, 2H, TMP-CH_2), 3.27 (m, 8H, 2,6-NC$_5H_{10}$) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 17.6 (TMP-CH_2), 24.8 (3,4,5-NC_5H_{10}), 26.8 (3,4,5-NC_5H_{10}), 33.0 (TMP-CH_3), 40.0 (TMP-CH_2), 52.2 (TMP-C_q), 52.9 (2,6-NC_5H_{10}), 134.9 (C_q–B–C_q) ppm.

^{11}B NMR (160.5 MHz, C_6D_6): δ = 11.9 ppm.

HRMS LIFDI for $[C_{21}H_{38}BN_3]^+ = [M]^+$: *m*/*z*: calcd. 343.3153; found 343.3146.

Synthesis of 4b



To a dispersion of KC_8 (161 mg, 1.19 mmol) in benzene (30 mL), a solution of **3b** (200 mg, 298 µmol) in benzene (30 mL) was added and the mixture was stirred at room temperature for 16 h. The solution was filtered over Celite, and all volatiles were removed *in vacuo*. The residue was extracted with hexane (10 mL) yielding

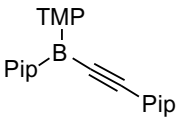
4b as a colourless solid (18.0 mg, 51.8 µmol, 17%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated hexane solution at room temperature.

^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6): δ = 1.41 (s, 12H, TMP-CH_3), 1.47–1.50 (m, 4H, TMP-CH_2), 1.55 – 1.60 (m, 2H, TMP-CH_2), 3.13 (m, 8H, NC$_4H_8$O), 3.51 (m, 8H, NC$_4H_8$O) ppm.
^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 17.0 (TMP-CH$_2$), 32.6 (TMP-CH$_3$), 39.4 (TMP-CH$_2$), 51.9 (TMP-C_q), 51.9 (NC_4H$_8$O), 66.9 (NC_4H$_8$O), 134.2 (C_q–B–C_q) ppm.
^{11}B NMR (160.5 MHz, C_6D_6): δ = 12.4 ppm.
HRMS LIFDI for $[C_{19}H_{34}BN_3O_2]^+$ = $[M]^+$: *m*/*z*: calcd. 347.2739; found 347.2730.

Reactivity towards Lewis Bases

To a solution of borirane (**3a** or **3b**) (50.0 µmol) or borirene (**4a** or **4b**) (50.0 µmol) in benzene, an excess amount of Lewis base (DMAP, PMe_3 or IMe) in benzene was added. These reactions were stirred at room temperature and studied via NMR spectroscopy. In all cases, no reaction was observed.

Synthesis of 5a

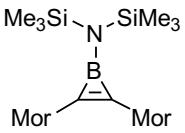


A solution of **4a** (10.0 mg, 34.2 µmol) in benzene (1 mL) was irradiated with UV light for 24 h at room temperature. All volatiles were removed *in vacuo* and the residue was extracted with hexane (2 mL) yielding **5a** as a colourless solid (10 mg, 34.2 µmol, 95%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated hexane solution at room temperature.
*Note: In addition to alkyne **5a**, the NMR spectra indicate traces of unidentified side products that could not be separated from the mixture. However, the overall purity is estimated to exceed 90%.*
^{1}H{^{11}B} NMR (600.2 MHz, C_6D_6): δ = 1.04–1.07 (m, 2H, 3,4,5-NC$_5H_{10}$), 1.21–1.25 (m, 4H, 3,4,5-NC$_5H_{10}$), 1.27–1.71 (m, 23H, TMP-CH_3, TMP-CH_2, 3,4,5-NC$_5H_{10}$), 1.96 (br, 1H, TMP-CH_2), 2.89 (m, 4H, 2,6-NC$_5H_{10}$), 3.37–3.81 (br, 4H, 2,6-NC$_5H_{10}$) ppm.
^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6): δ = 19.4 (TMP-CH$_2$), 23.8 (3,4,5-NC_5H$_{10}$), 25.3 (3,4,5-NC_5H$_{10}$), 26.2 (br, 3,4,5-NC_5H$_{10}$), 27.3 (br, 3,4,5-NC_5H$_{10}$), 28.2 (br, 3,4,5-NC_5H$_{10}$), 34.5 (br, TMP-CH$_3$), 41.7 (TMP-CH$_2$), 46.7 (br, 2,6-NC_5H$_{10}$), 49.2 (br, 2,6-NC_5H$_{10}$), 51.6 (TMP-C_q), 52.9 (2,6-NC_5H$_{10}$), 71.4 (B–CC), 115.2 (N–CC) ppm.

^{11}B NMR (192.6 MHz, C_6D_6): δ = 28.4 ppm.

HRMS ESI for $[C_{21}H_{38}BN_3] + H^+ = [M+H]^+$: *m*/*z*: calcd. 344.3232; found 344.3222.

Synthesis of 7



To a solution of **1b** (4.6 mg, 250 µmol) in benzene (1 mL), a solution of $[(OC)_5CrBN(SiMe_3)_2]$ (**6**, 36.2 mg, 100 µmol) in benzene (1 mL) was added and the mixture was stirred at room temperature for 2 h. The solution was filtered over Celite, and all volatiles were removed *in vacuo*. The residue was extracted with Et_2O (5 mL) yielding a yellow solid. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated hexane solution at room temperature.

*Note: In addition to borirene **7**, the NMR spectra indicate the presence of unidentified side products that could not be separated from the mixture.*

^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6): δ = 0.31 (s, 18H, Si(CH_3)$_3$), 3.05–3.07 (m, 8H, NC$_4H_8$O), 3.49–3.51 (m, 8H, NC$_4H_8$O) ppm.

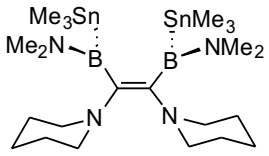
^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6): δ = 3.4 (CH_3, Si(*C*H$_3$)$_3$), 52.5 (CH_2, N*C*$_4H_8$O), 67.0 (CH_2, N*C*$_4H_8$O), 135.1 (C_q–B–C_q) ppm.

^{11}B NMR (160.5 MHz, C_6D_6): δ = 14.6 ppm.

^{29}Si{^{1}H}-NMR (99.4 MHz, C_6D_6): δ = 4.43 (s) ppm.

HRMS ESI for $[C_{19}H_{34}BN_3O_2] + H^+ = [M+H]^+$: *m*/*z*: calcd. 367.2277; found 367.2269.

Synthesis of 9



To a solution of **1a** (35.2 mg, 183 µmol) in benzene (5 mL), a solution of $[B(NMe_2)(SnMe_3)]_2$ (**8**, 80 mg, 183 µmol) in benzene (5 mL) was added and the mixture was stirred at room temperature for two days, resulting in a deep-yellow solution. All volatiles were removed *in vacuo,* and the oily residue was washed with cold pentane (1 mL) and recrystallised from benzene, yielding **9** as a light yellow solid (63.3 mg, 101 µmol, 55%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated benzene solution at room temperature.

*Note: NMR resonances of **9** were assigned based on its HSQC spectrum. The signals for the Cq atoms could not be identified.*

^{1}H{^{11}B} NMR (600.2 MHz, C_6D_6): δ = 0.31 (s, $^{3}J_{H,Sn}$ = 41.3 Hz, 18H, SnC*H*$_3$), 1.42–1.46 (m, 4H, 3,4,5-NC$_5$*H*$_{10}$), 1.54–1.58 (m, 8H, 3,4,5-NC$_5$*H*$_{10}$), 2.73 (s, 12H, NC*H*$_3$), 3.17 (s, br, 8H, 3,4,5-NC$_5$*H*$_{10}$).

^{13}C{^{1}H ^{11}B} NMR (150.9 MHz, C_6D_6): δ = −8.9 (Sn*C*H$_3$), 25.6 (3,4,5-N*C*$_5$H$_{10}$), 27.6 (3,4,5-N*C*$_5$H$_{10}$), 43.2 (N*C*H$_3$) 50.7 (3,4,5-N*C*$_5$H$_{10}$) ppm.

^{11}B NMR (160.5 MHz, C_6D_6): δ = 51.6 ppm.

^{119}Sn NMR (223.8 MHz, C_6D_6): δ = −103.6 ppm.

HRMS LIFDI for $[C_{19}H_{41}B_2N_4Sn]^+$ = $[M–SnMe_3]^+$: *m*/*z*: calcd. 467.2539; found 467.2537.

1.3. NMR spectra of isolated compounds

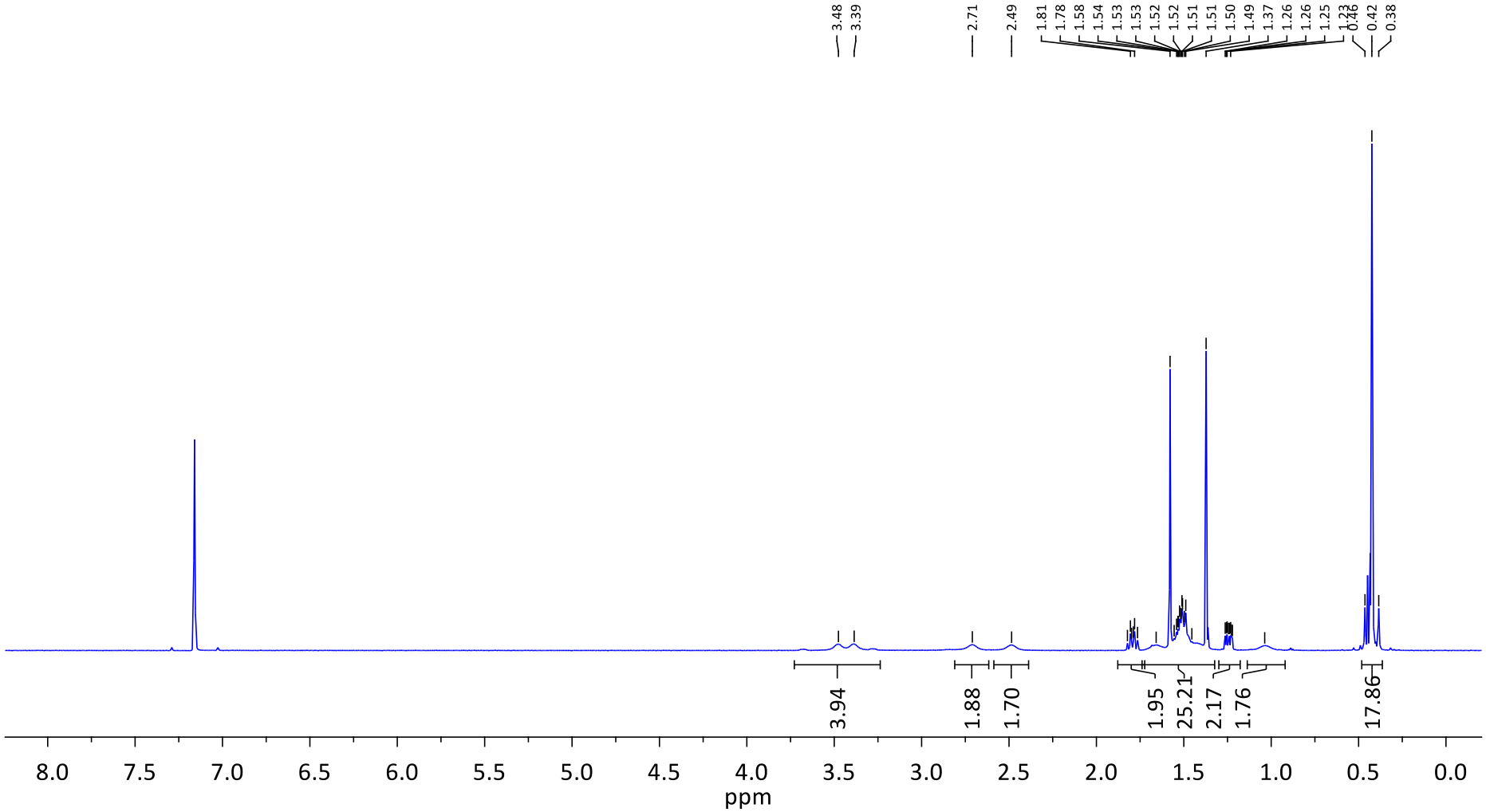


Fig. S1 $^{1}H\{^{11}B\}$ NMR spectrum of **3a** in C_6D_6.

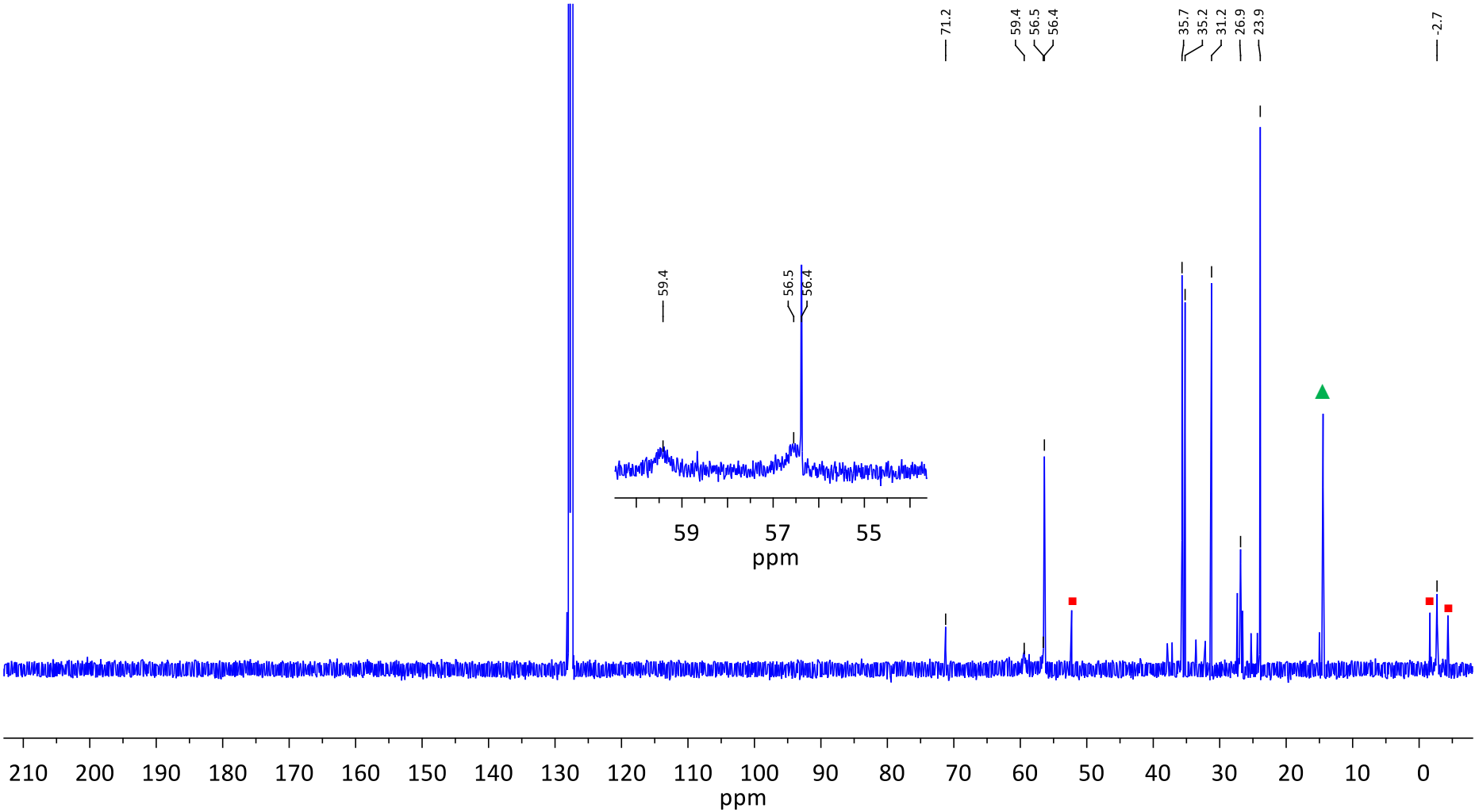


Fig. S2 $^{13}C\{^{1}H, ^{11}B\}$ NMR spectrum of **3a** in C_6D_6. ▲ = hexane, ■ = unknown side product.

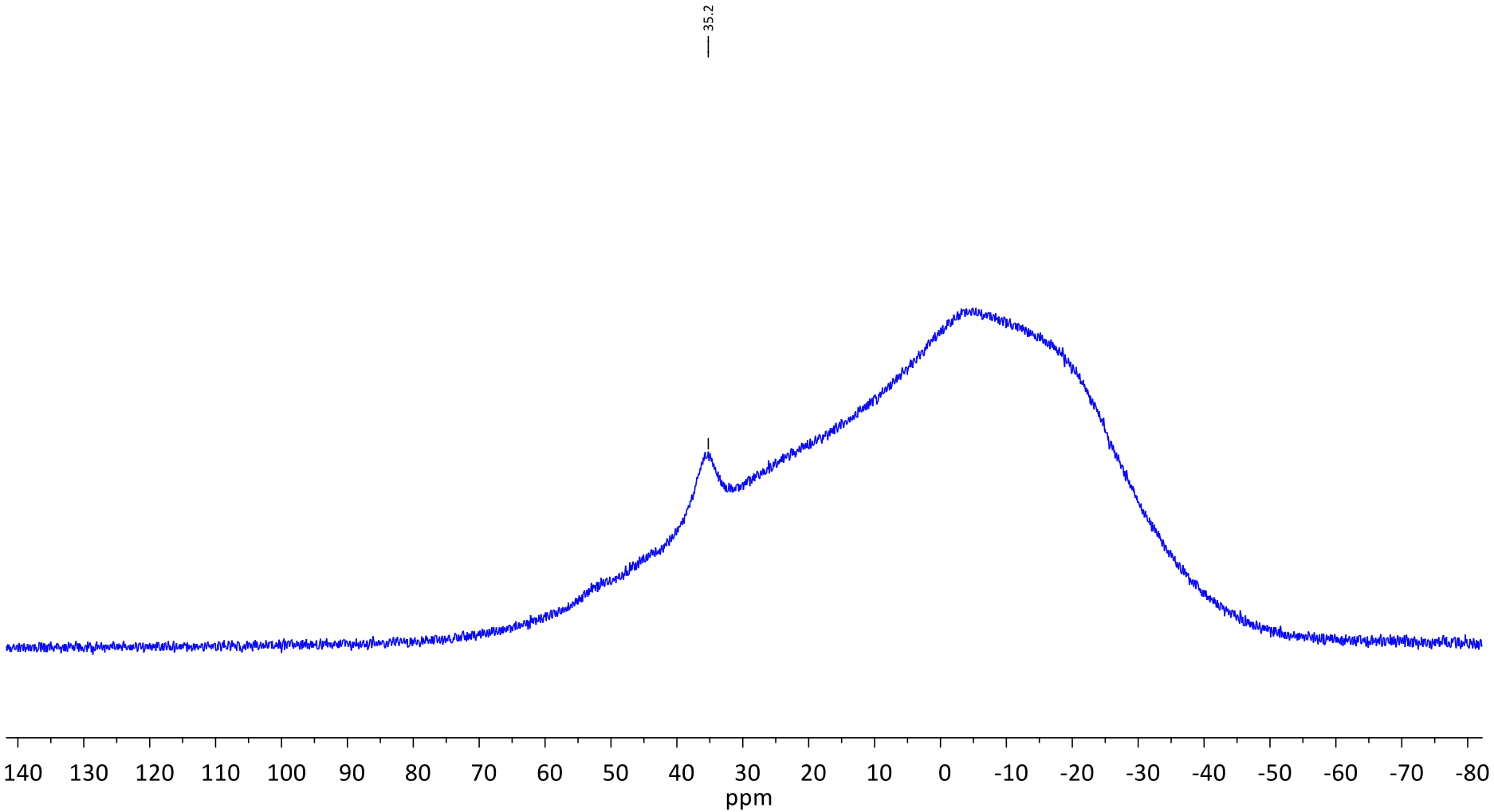


Fig. S3 ^{11}B NMR spectrum of **3a** in C_6D_6.

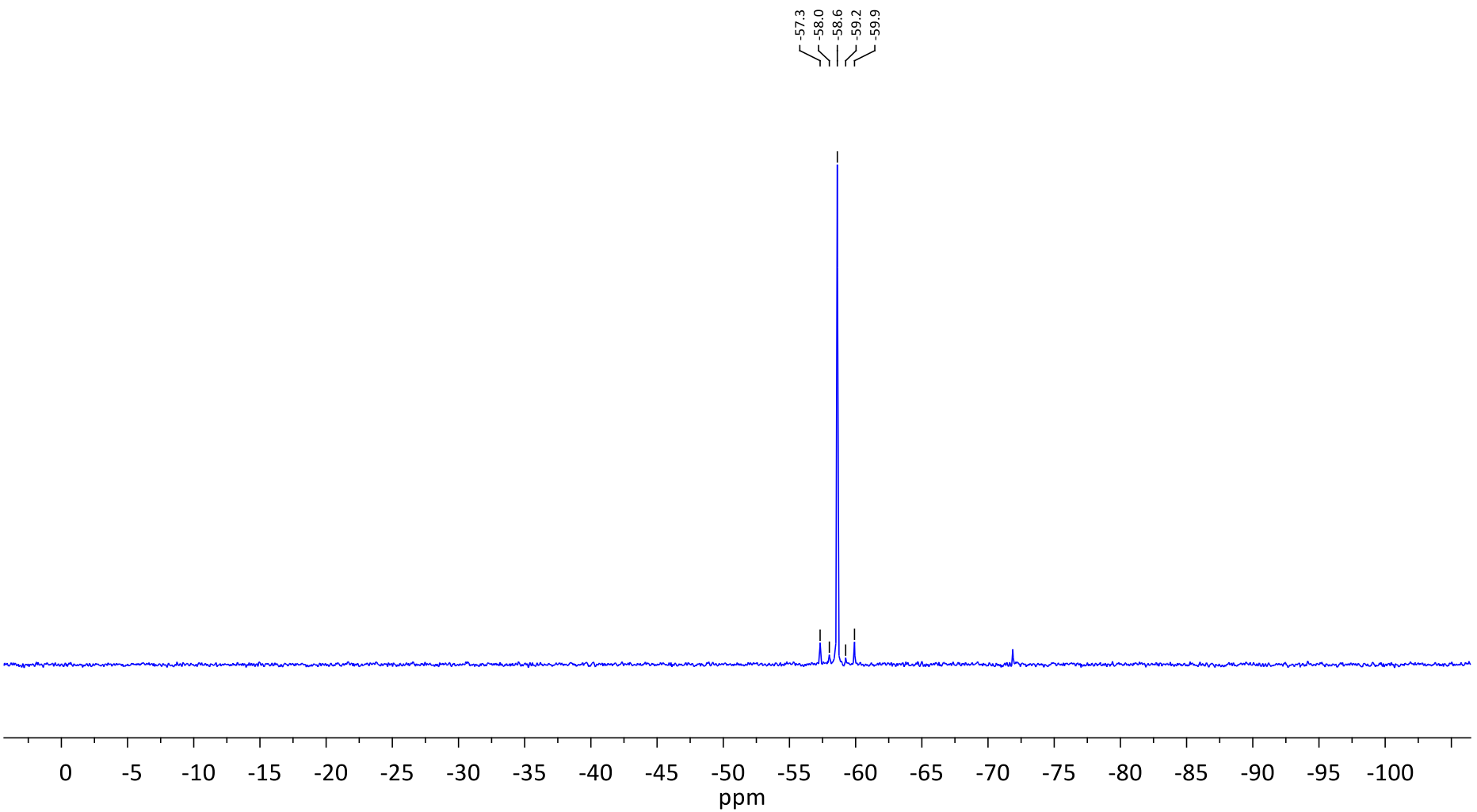


Fig. S4 ^{119}Sn NMR spectrum of **3a** in C_6D_6.

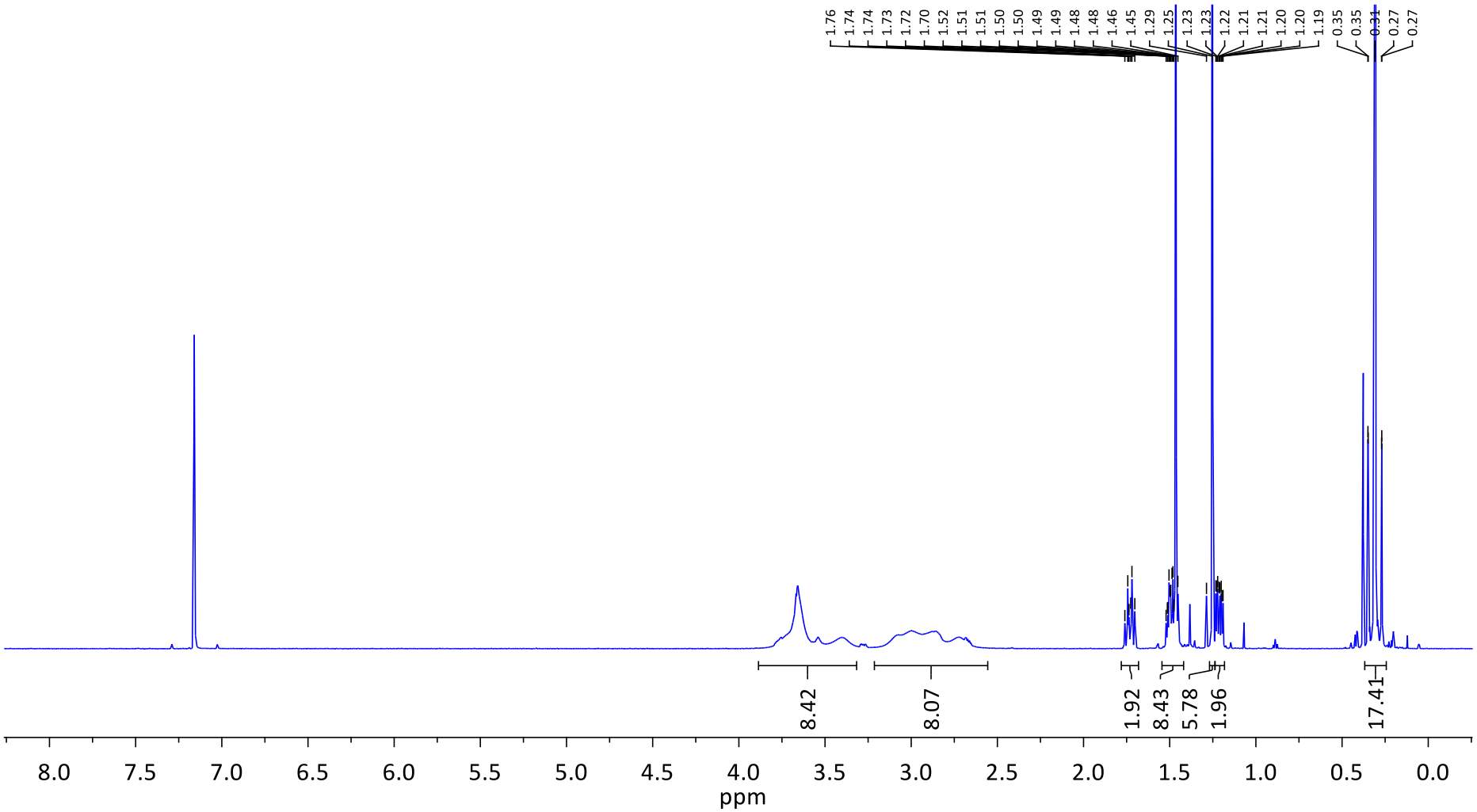


Fig. S5 $^{1}H\{^{11}B\}$ NMR spectrum of **3b** in C_6D_6.

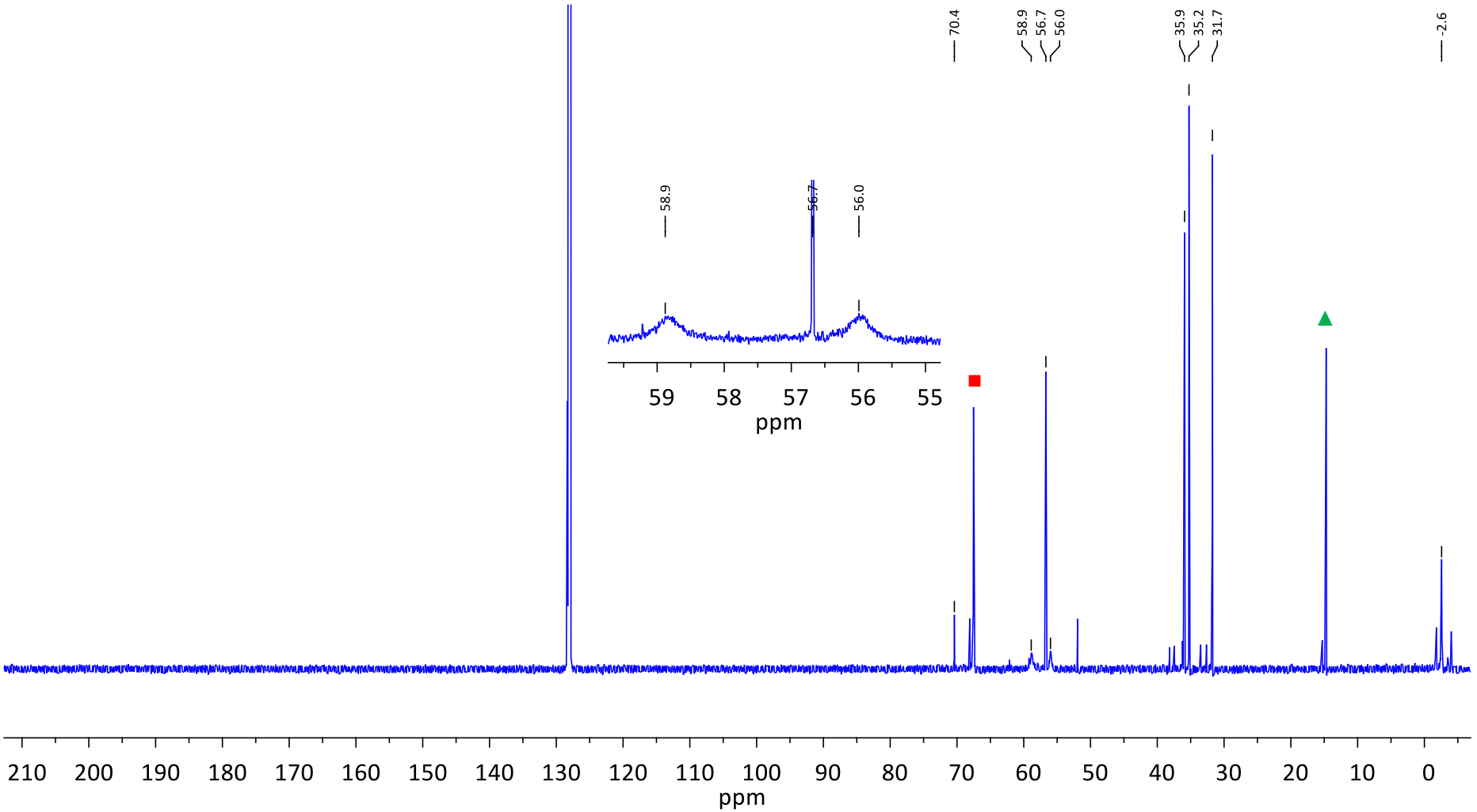


Fig. S6 $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in C_6D_6. ▲ = hexane, ■ = thf.

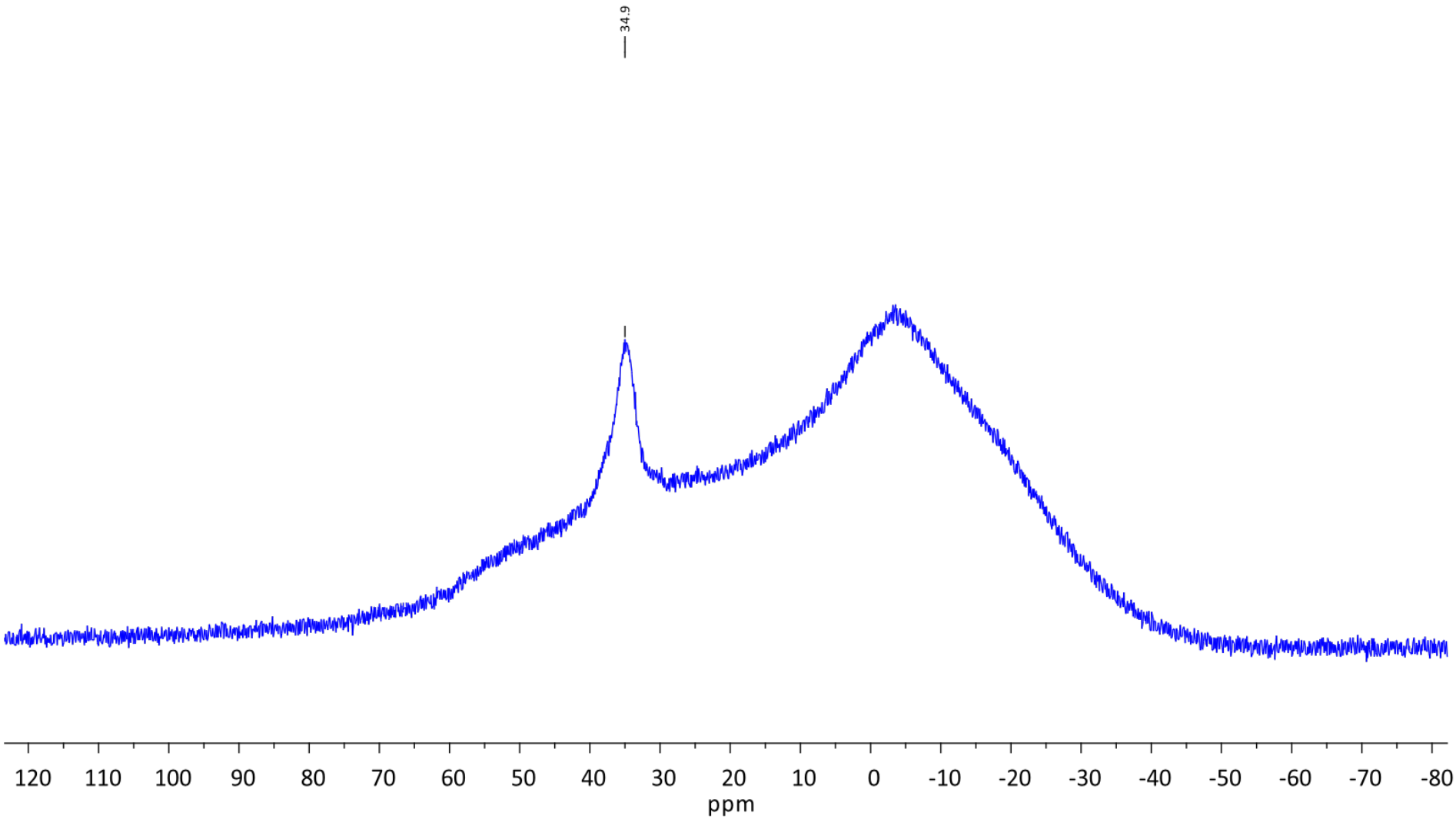


Fig. S7 ^{11}B NMR spectrum of **3b** in C_6D_6.

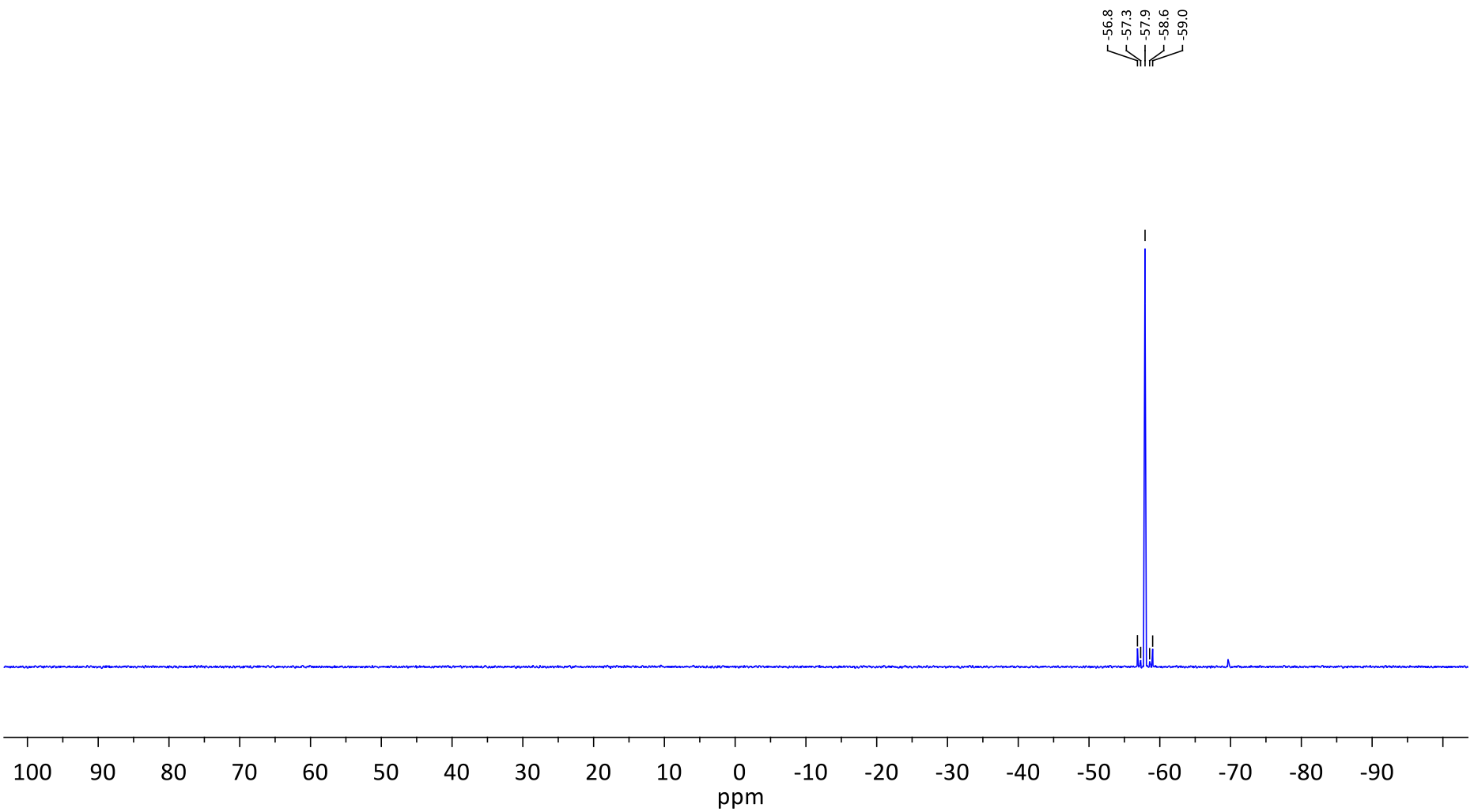


Fig. S8 ^{119}Sn NMR spectrum of **3b** in C_6D_6.

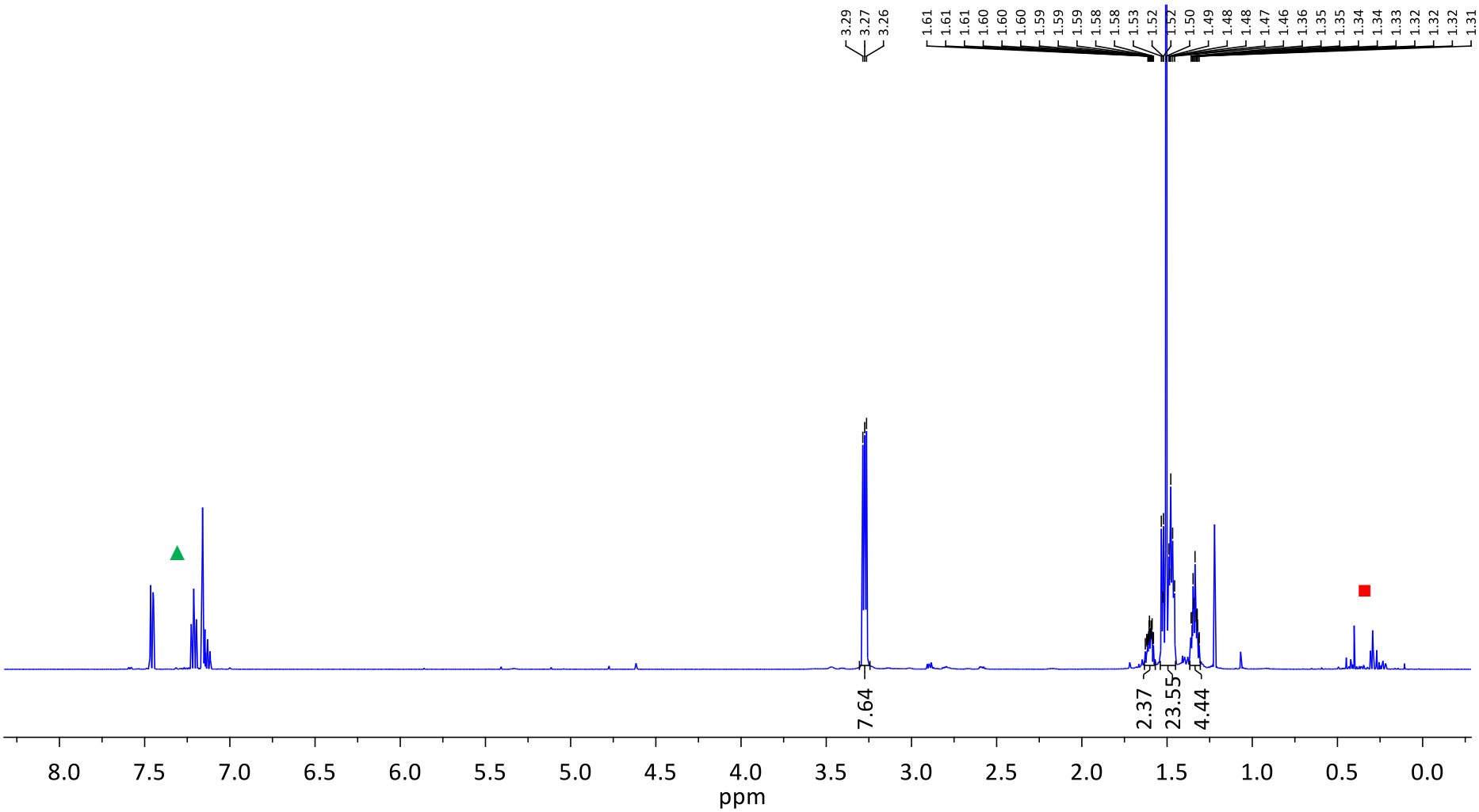


Fig. S9 $^{1}H\{^{11}B\}$ NMR spectrum of **4a** in C_6D_6. ▲ = naphthalene, ■ = Sn_xMe_y.

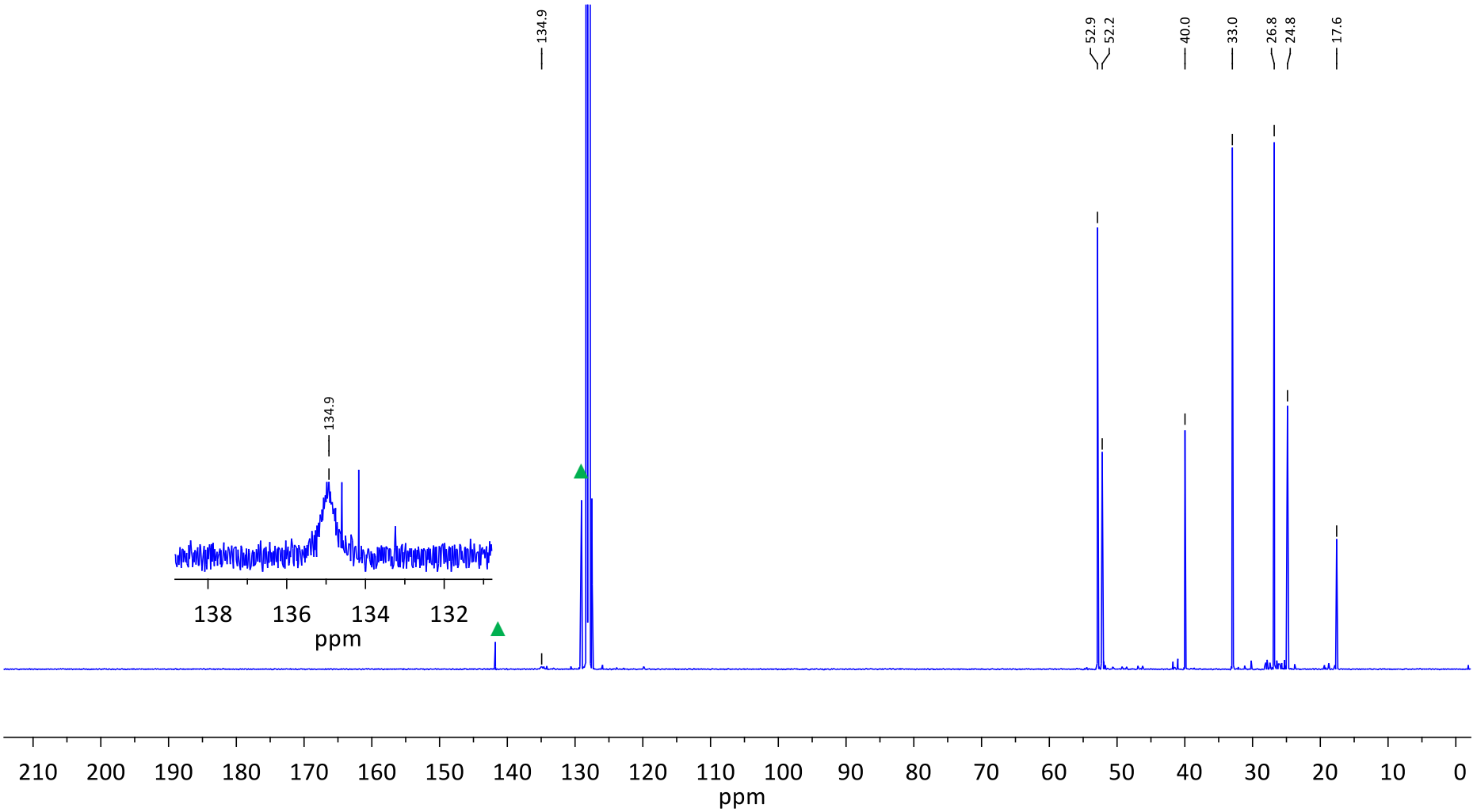


Fig. S10 $^{13}C\{^{1}H, ^{11}B\}$ NMR spectrum of **4a** in C_6D_6. ▲ = naphthalene.

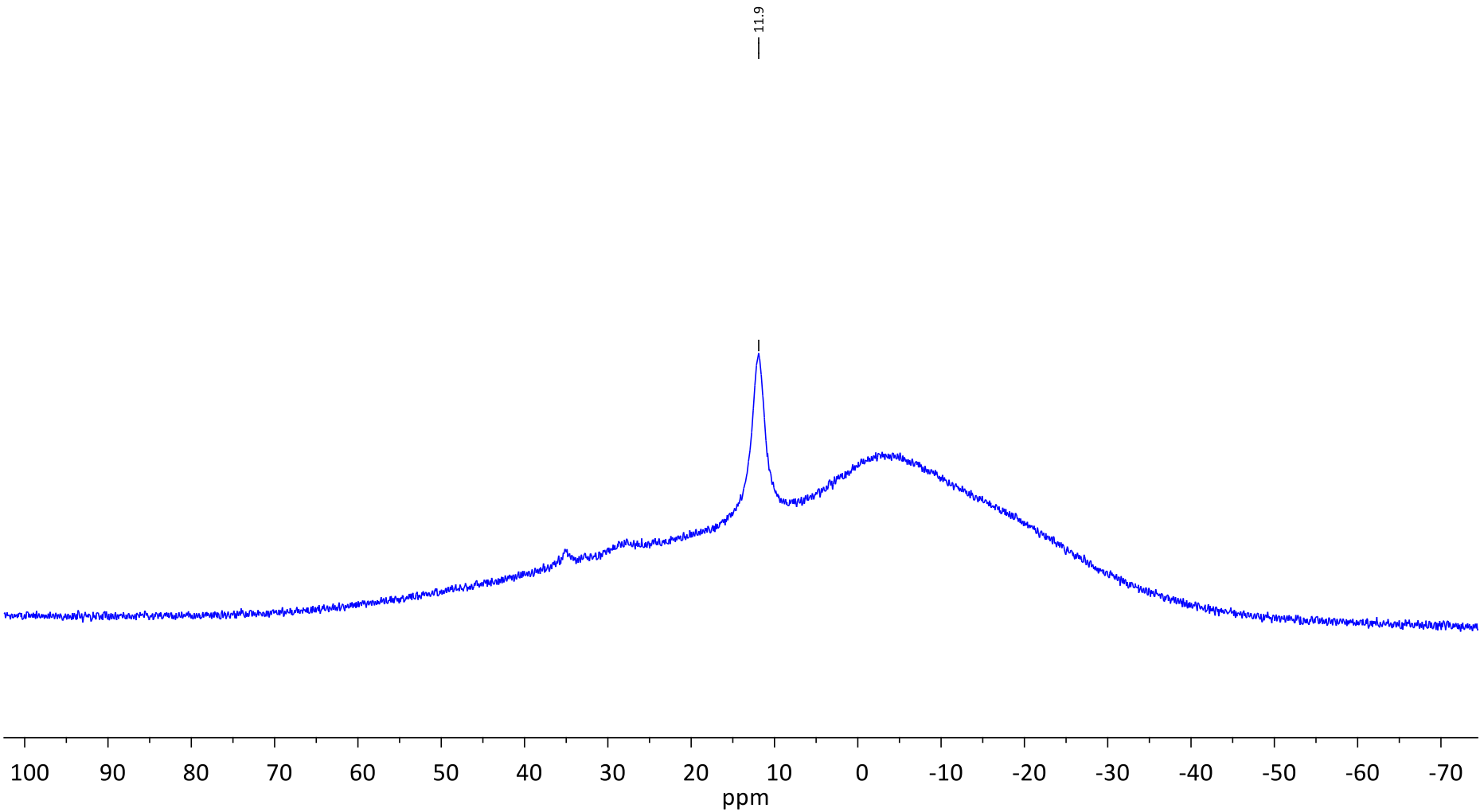


Fig. S11 ^{11}B NMR spectrum of **4a** in C_6D_6.

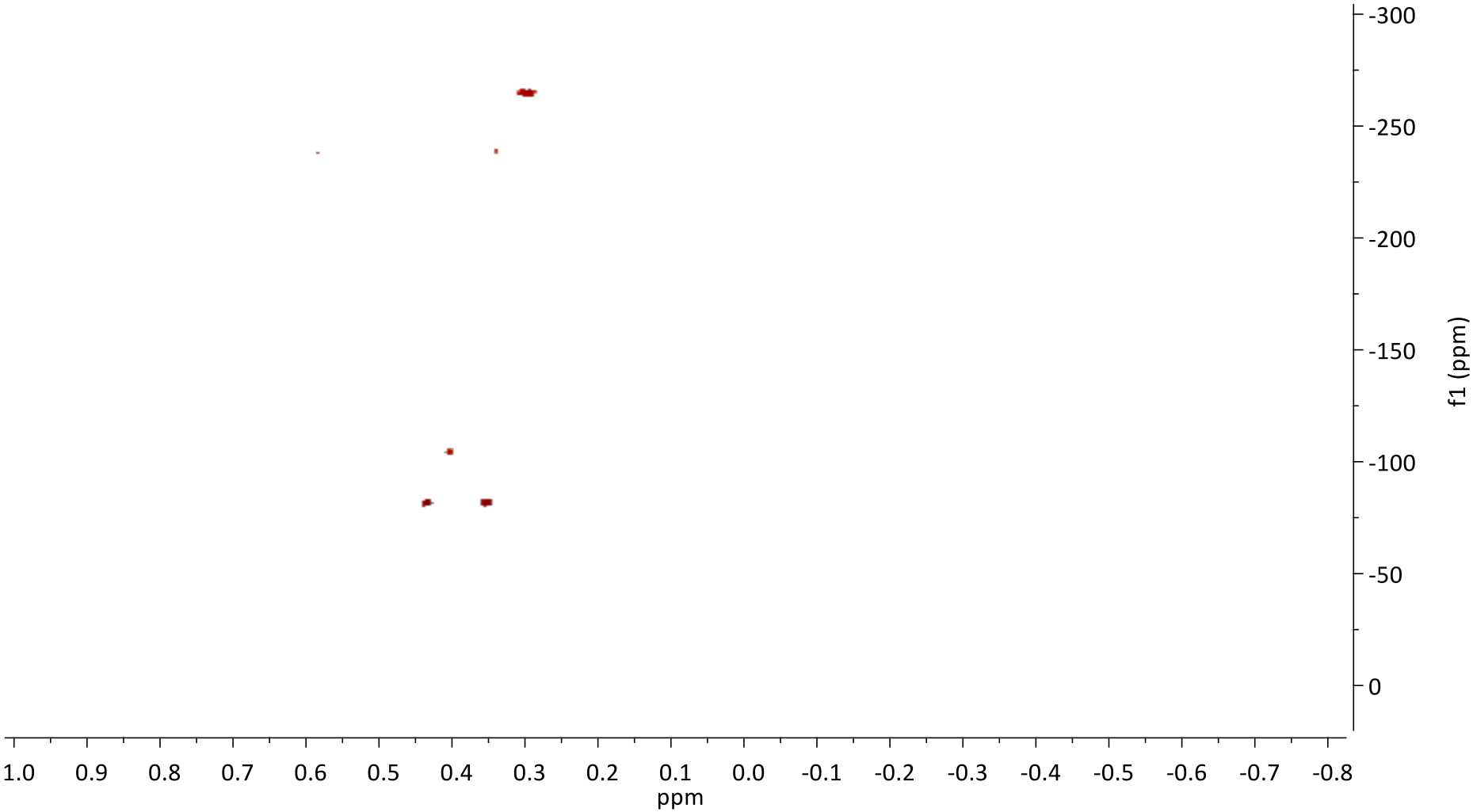


Fig. S12 $^{119}Sn^{1}H$ HMQC NMR spectrum of **4a** in C_6D_6.

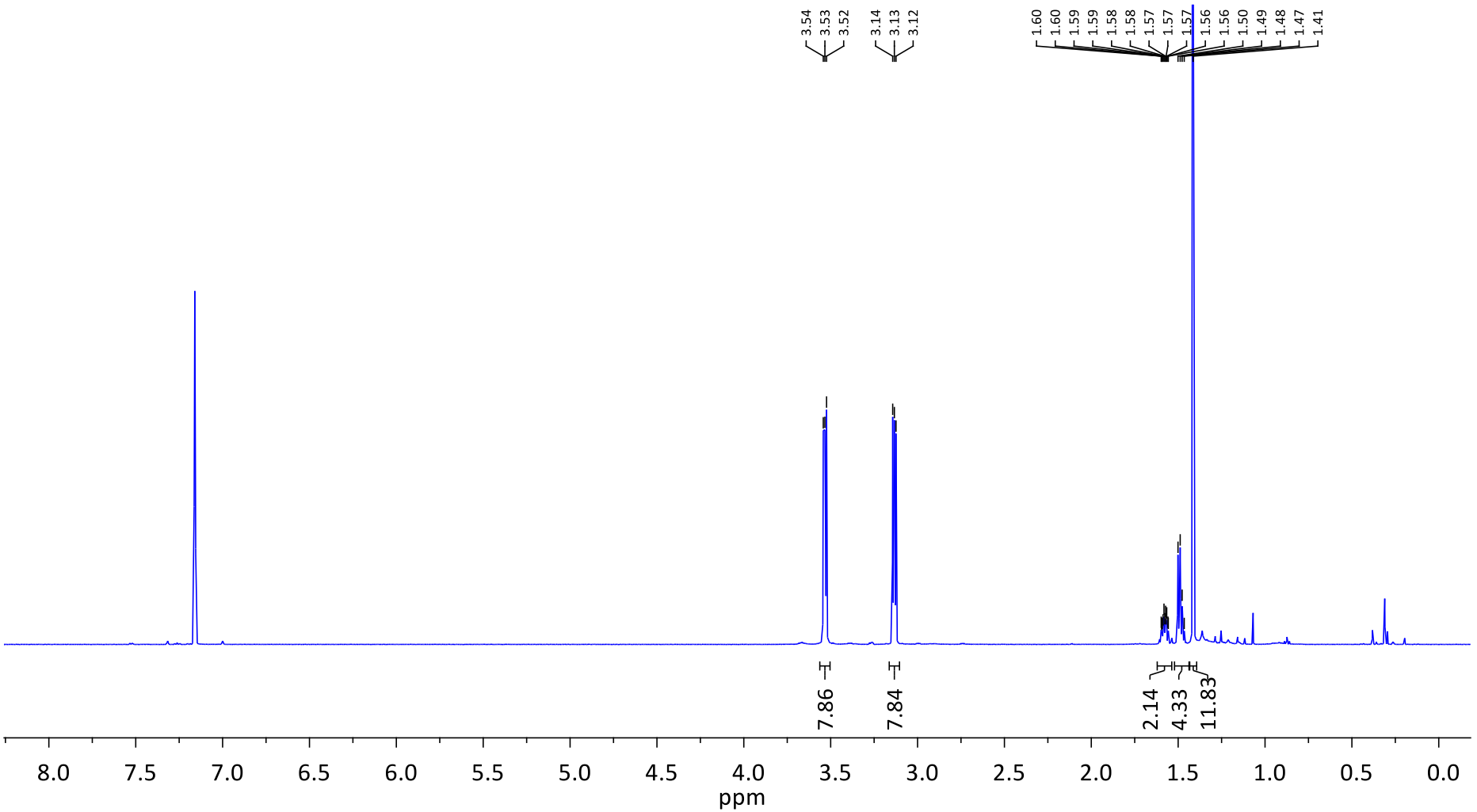


Fig. S13 $^{1}H\{^{11}B\}$ NMR spectrum of **4b** in C_6D_6.

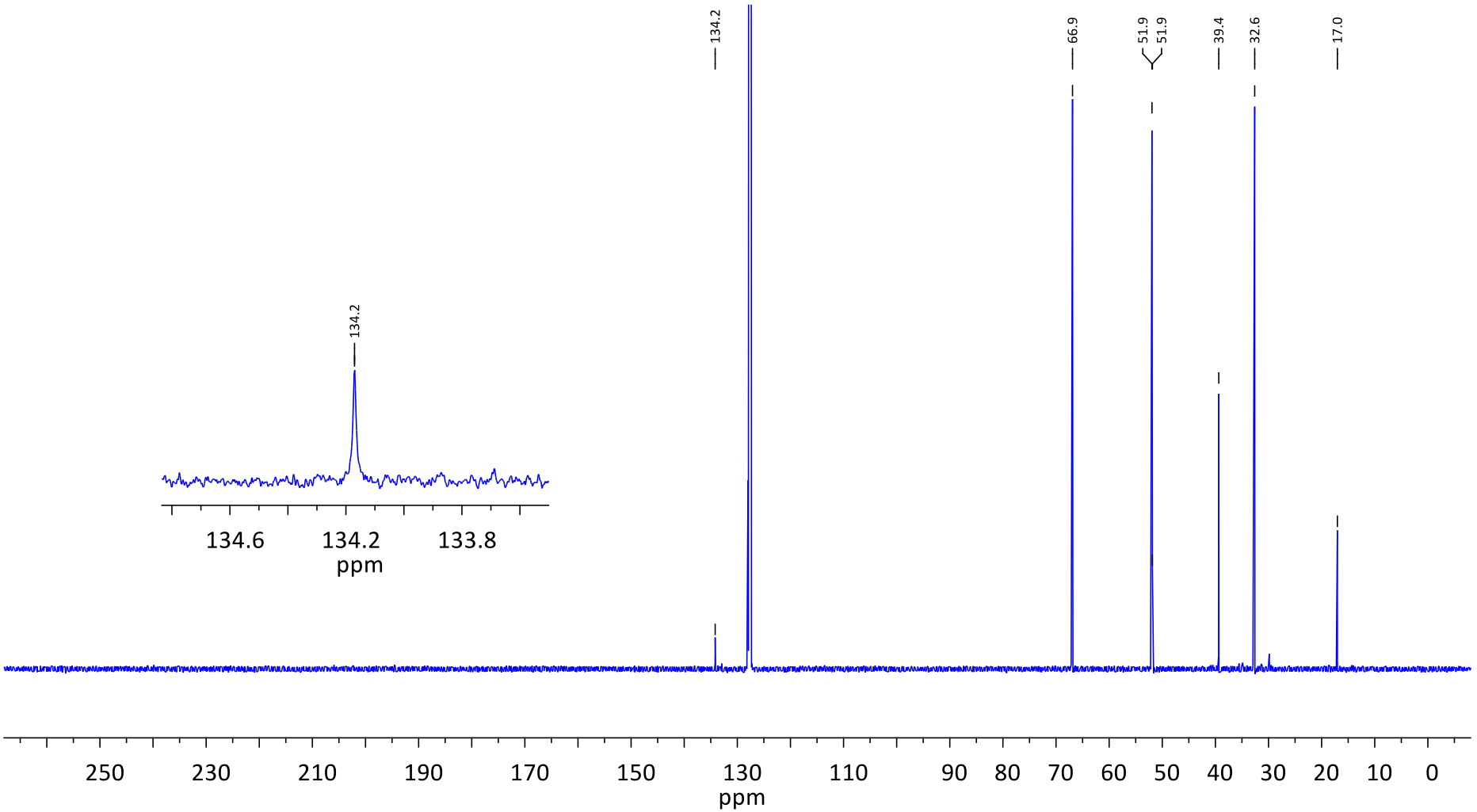


Fig. S14 $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **4b** in C_6D_6.

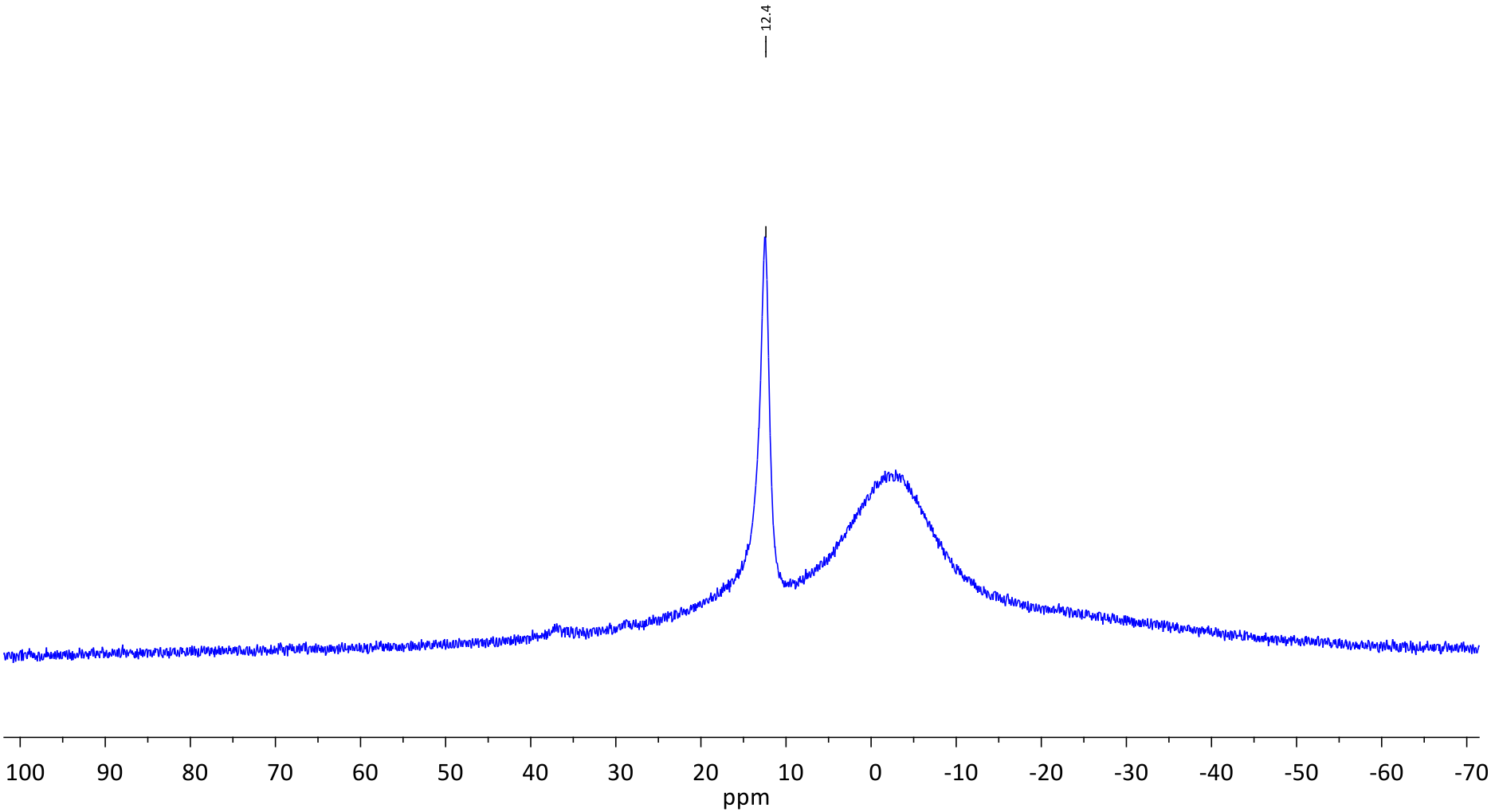


Fig. S15 ^{11}B NMR spectrum of **4b** in C_6D_6.

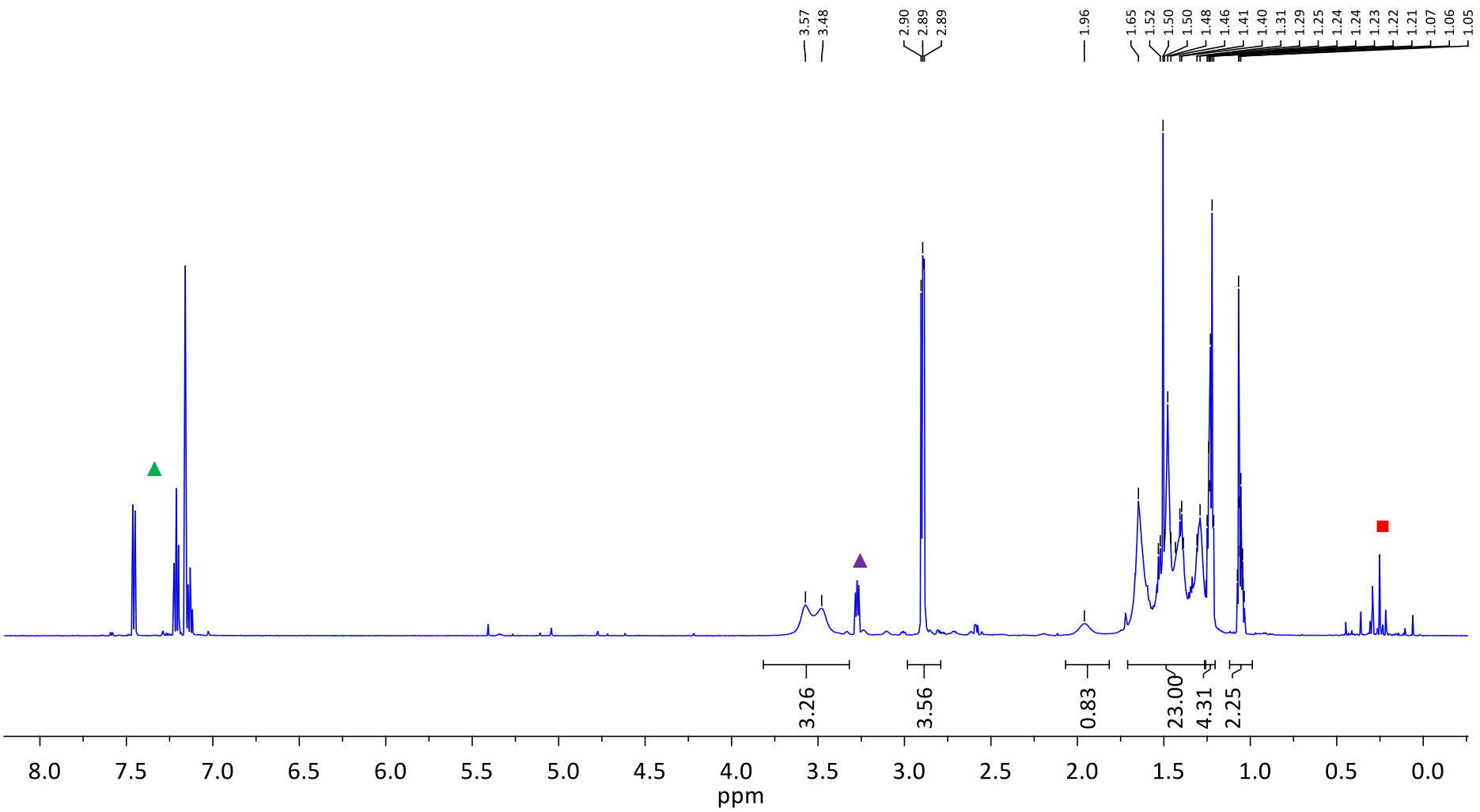


Fig. S16 $^{1}H\{^{11}B\}$ NMR spectrum of **5a** in C_6D_6. ▲ = naphthalene, ▲ = **4a**, ■ = Sn_xMe_y.

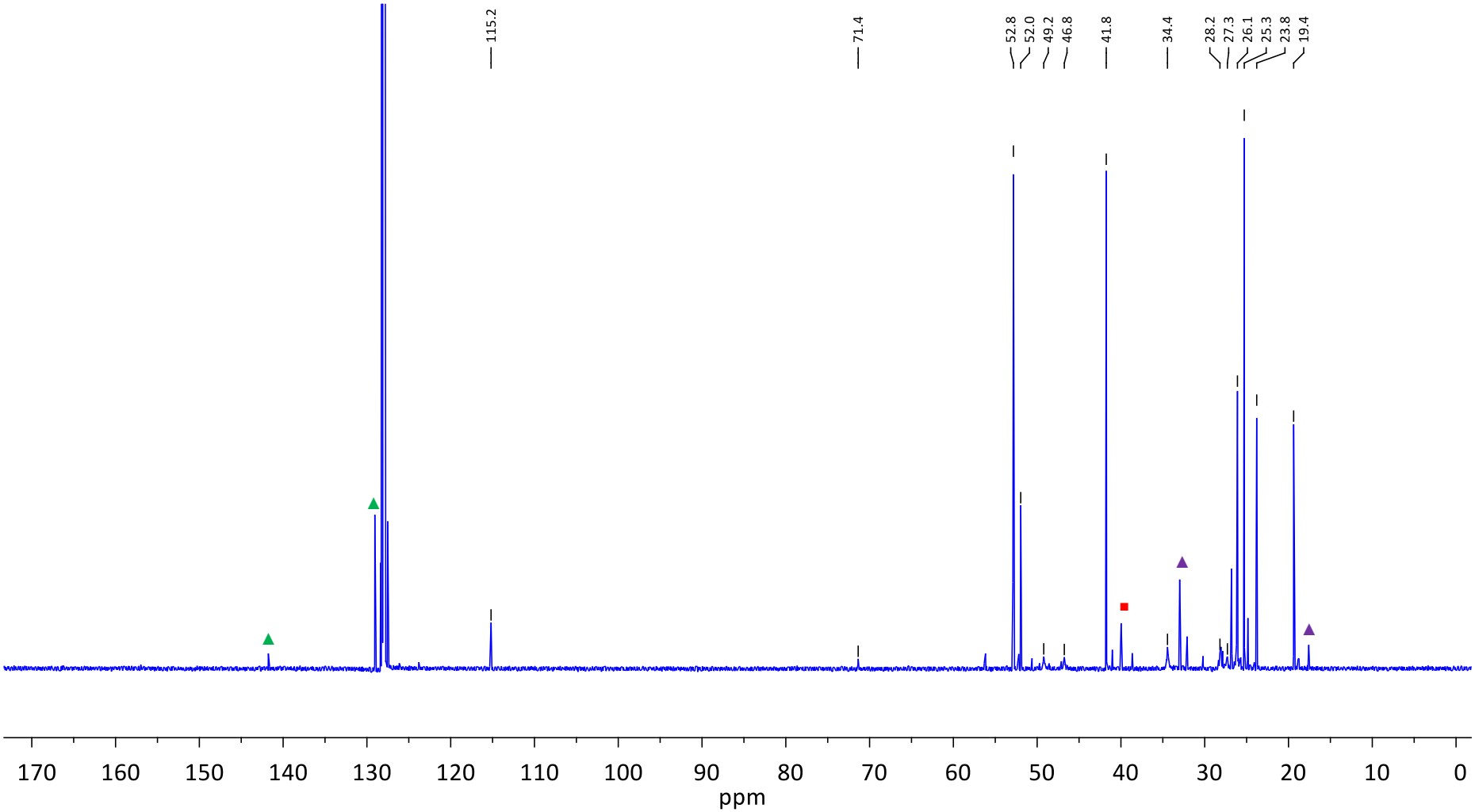


Fig. S17 $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **5a** in C_6D_6. ▲ = naphthalene, ▲ = **4a**, ■ = unknown side products.

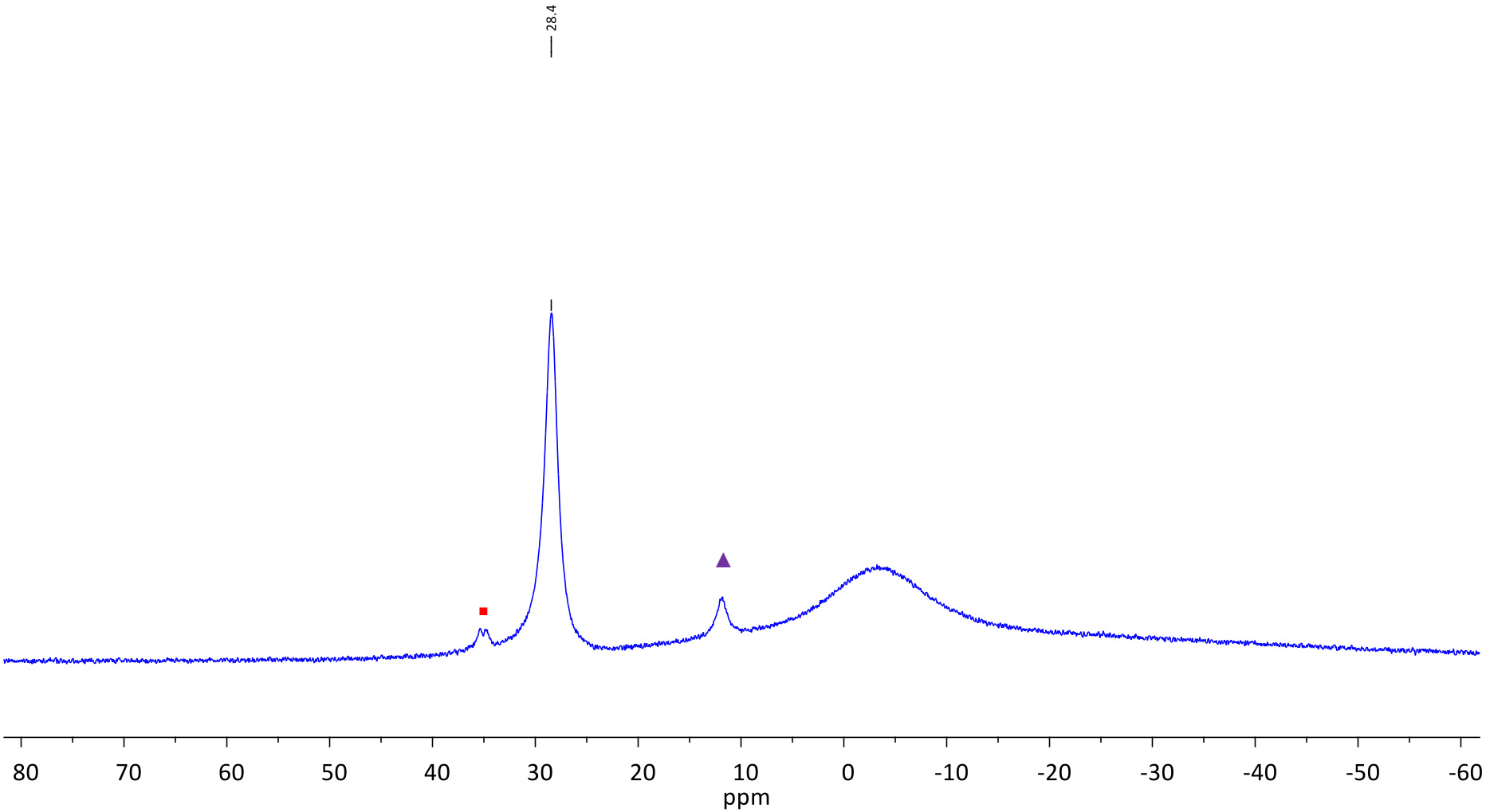


Fig. S18 ^{11}B NMR spectrum of **5a** in C_6D_6. ▲ = 4a, ■ = unknown side products.

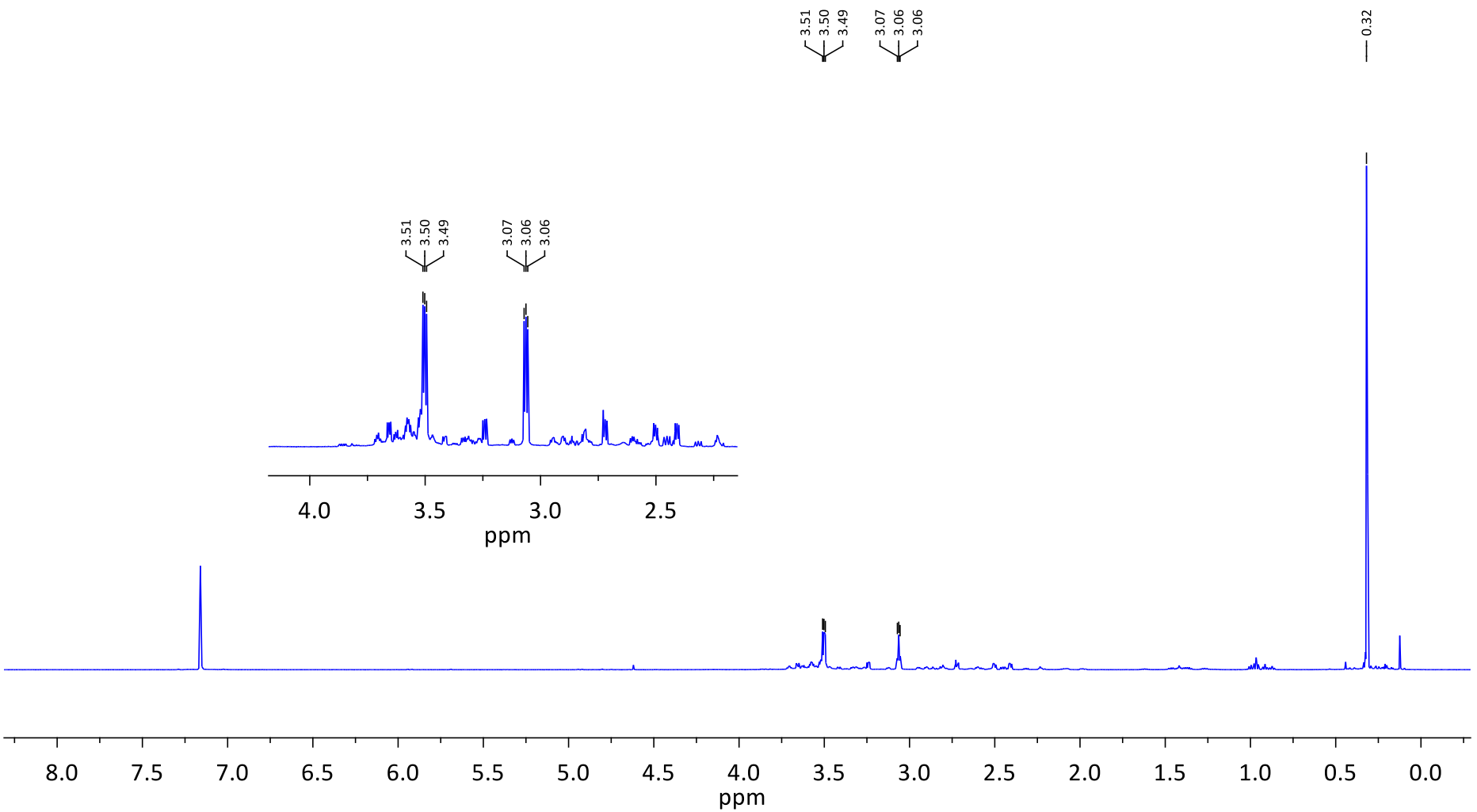


Fig. S19 $^{1}H\{^{11}B\}$ NMR spectrum of **7** in C_6D_6.

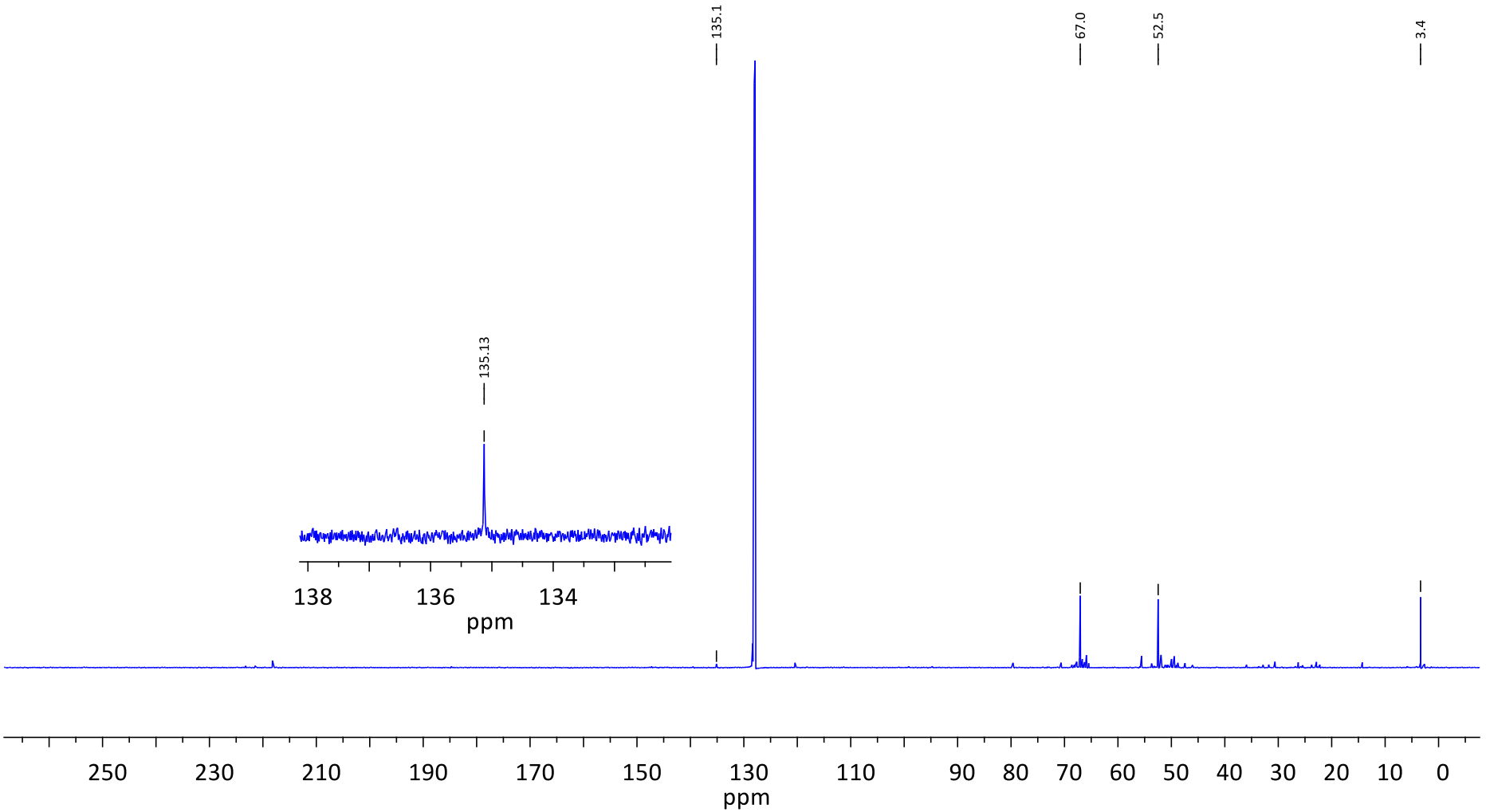


Fig. S20 $^{13}C\{^{1}H, ^{11}B\}$ NMR spectrum of **7** in C_6D_6.

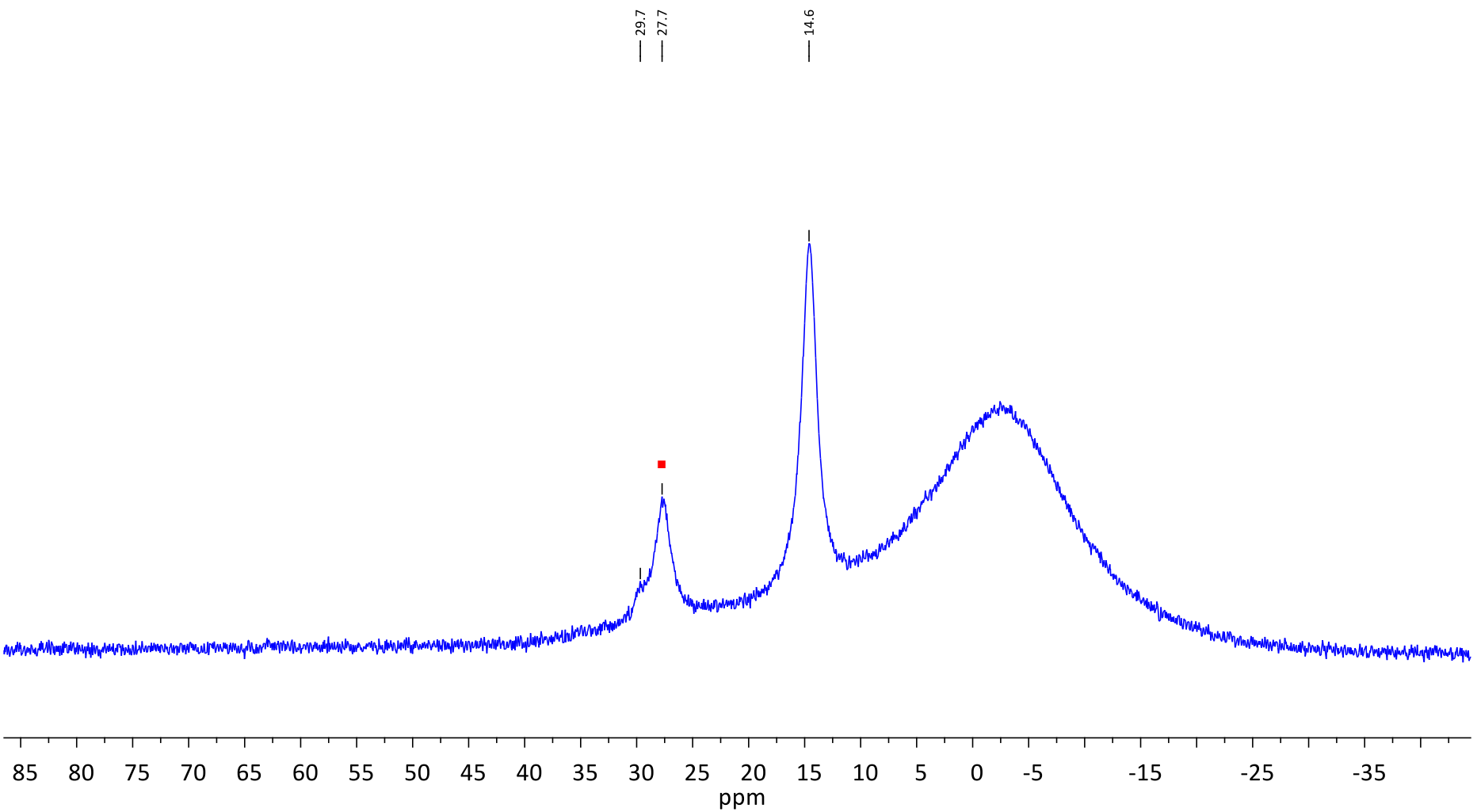


Fig. S21 ^{11}B NMR spectrum of **7** in C_6D_6. ■ = unknown side products.

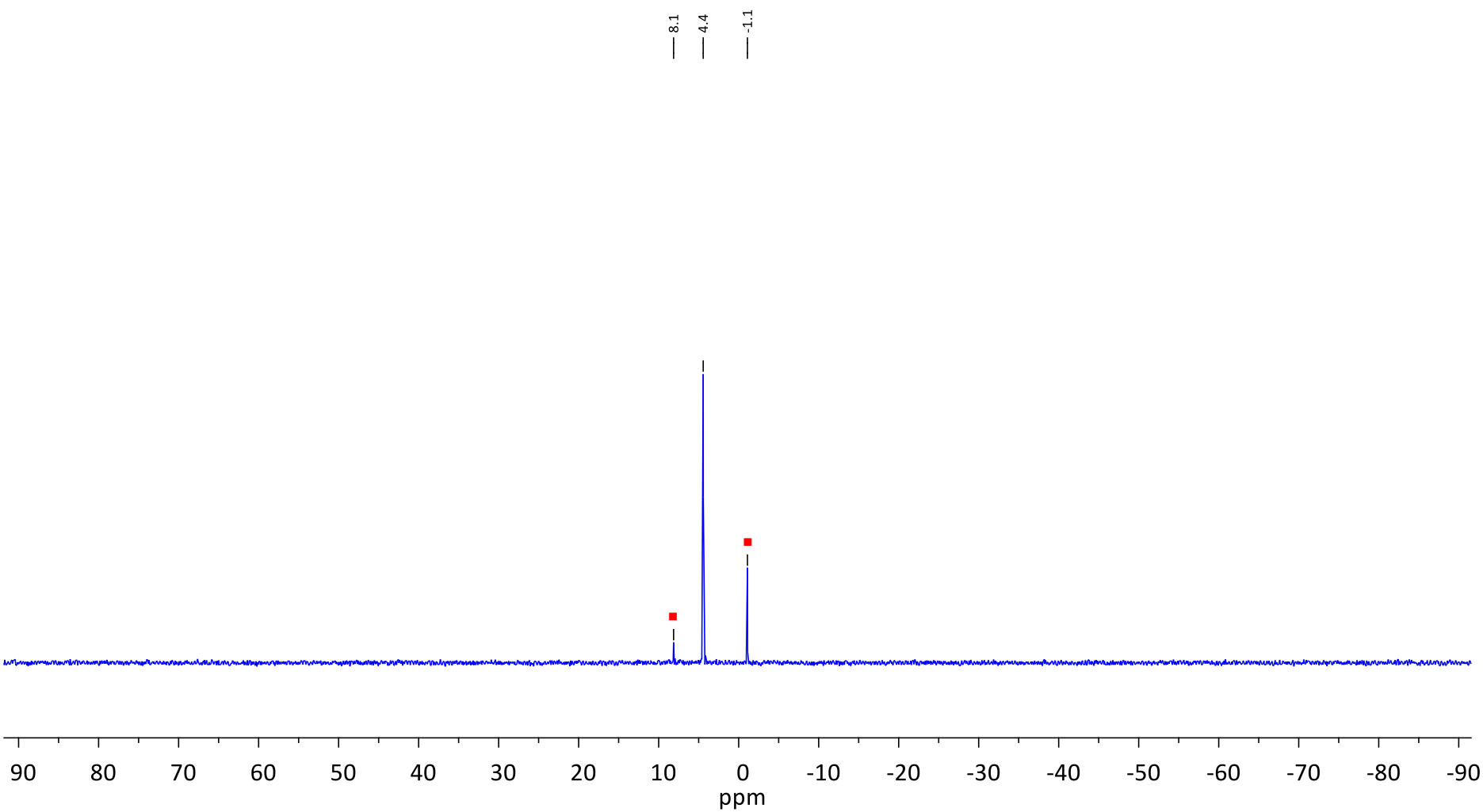


Fig. S22 ^{29}Si NMR spectrum of **7** in C_6D_6. ■ = unknown side products.

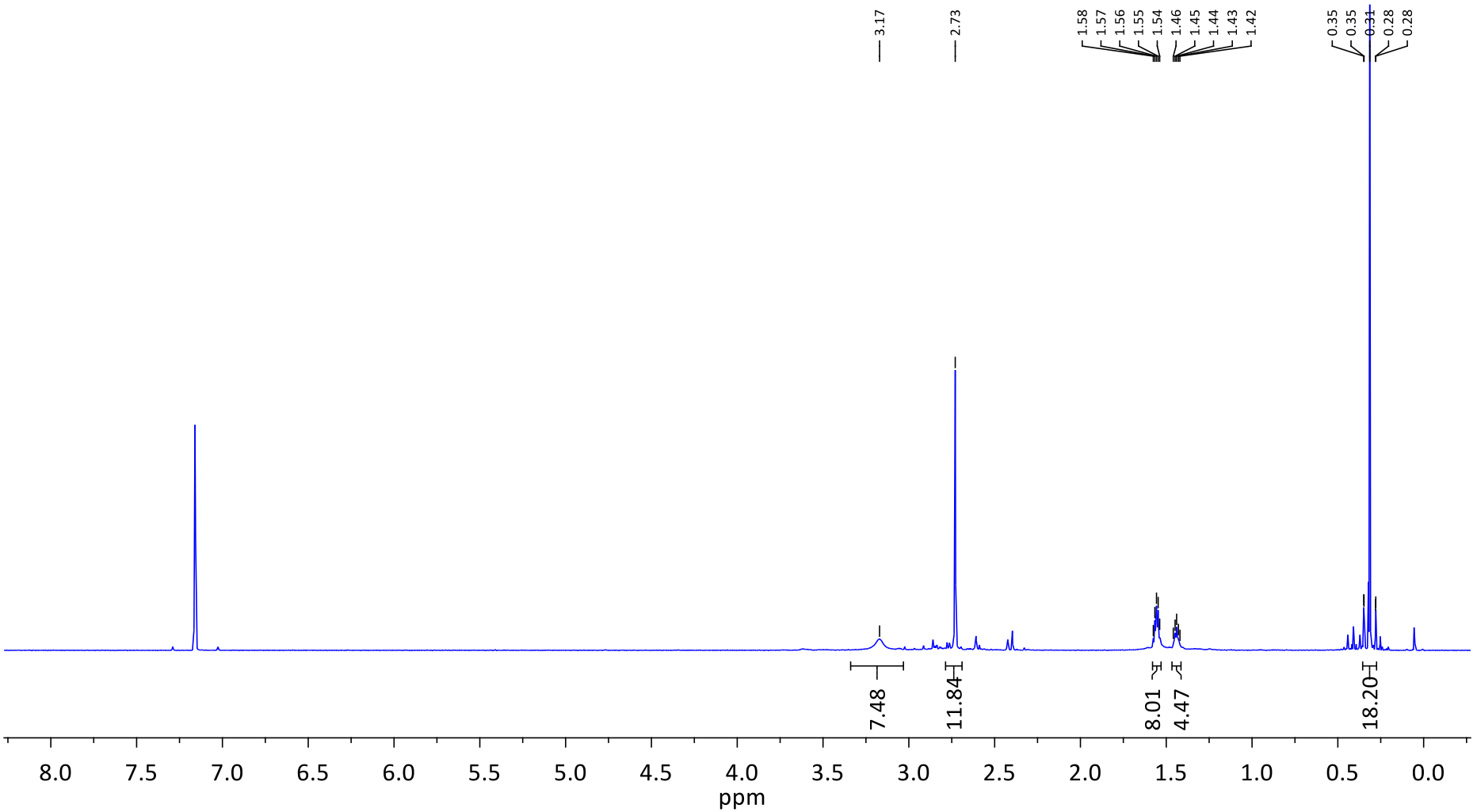


Fig. S23 $^{1}H\{^{11}B\}$ NMR spectrum of **9** in C_6D_6.

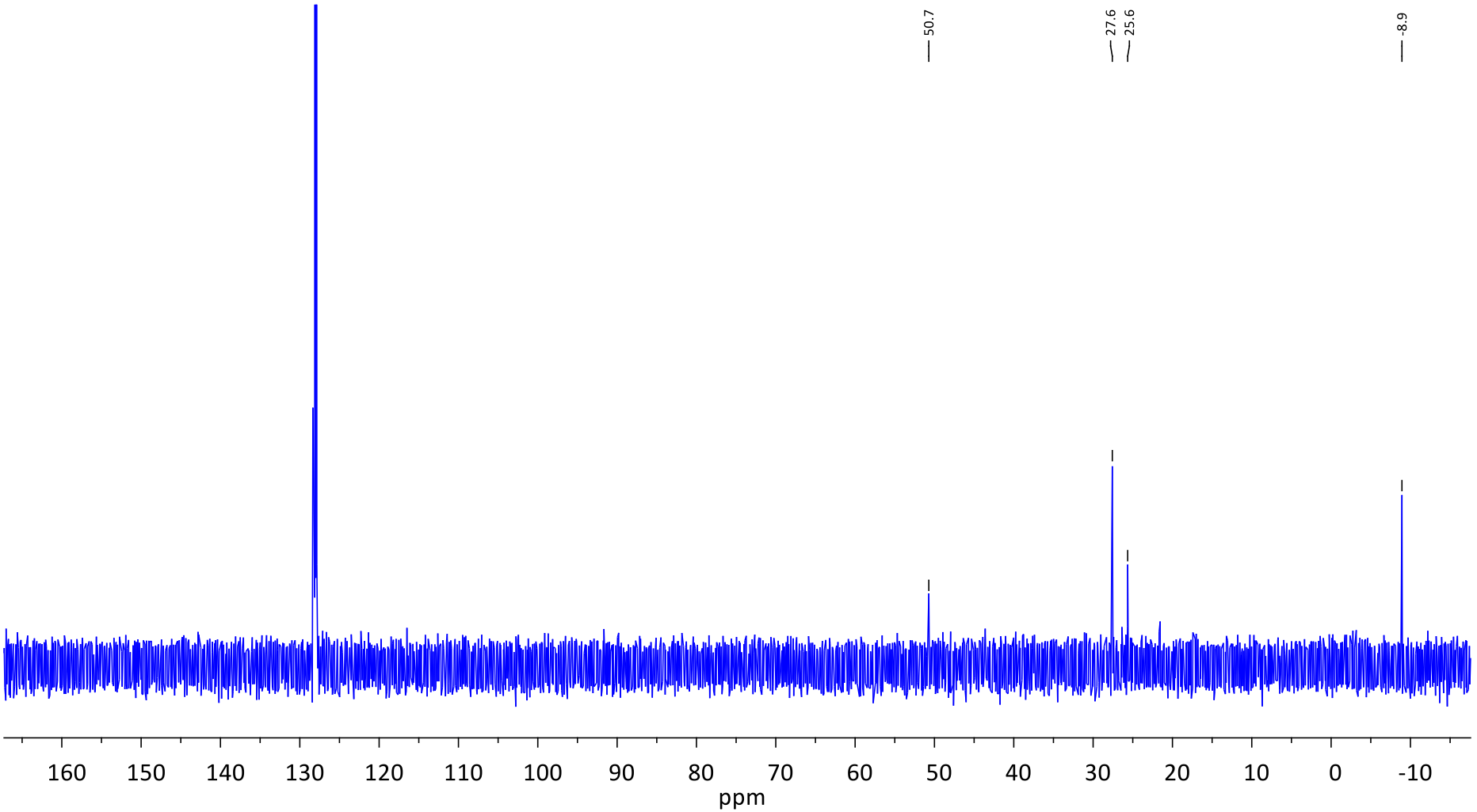


Fig. S24 $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **9** in C_6D_6.

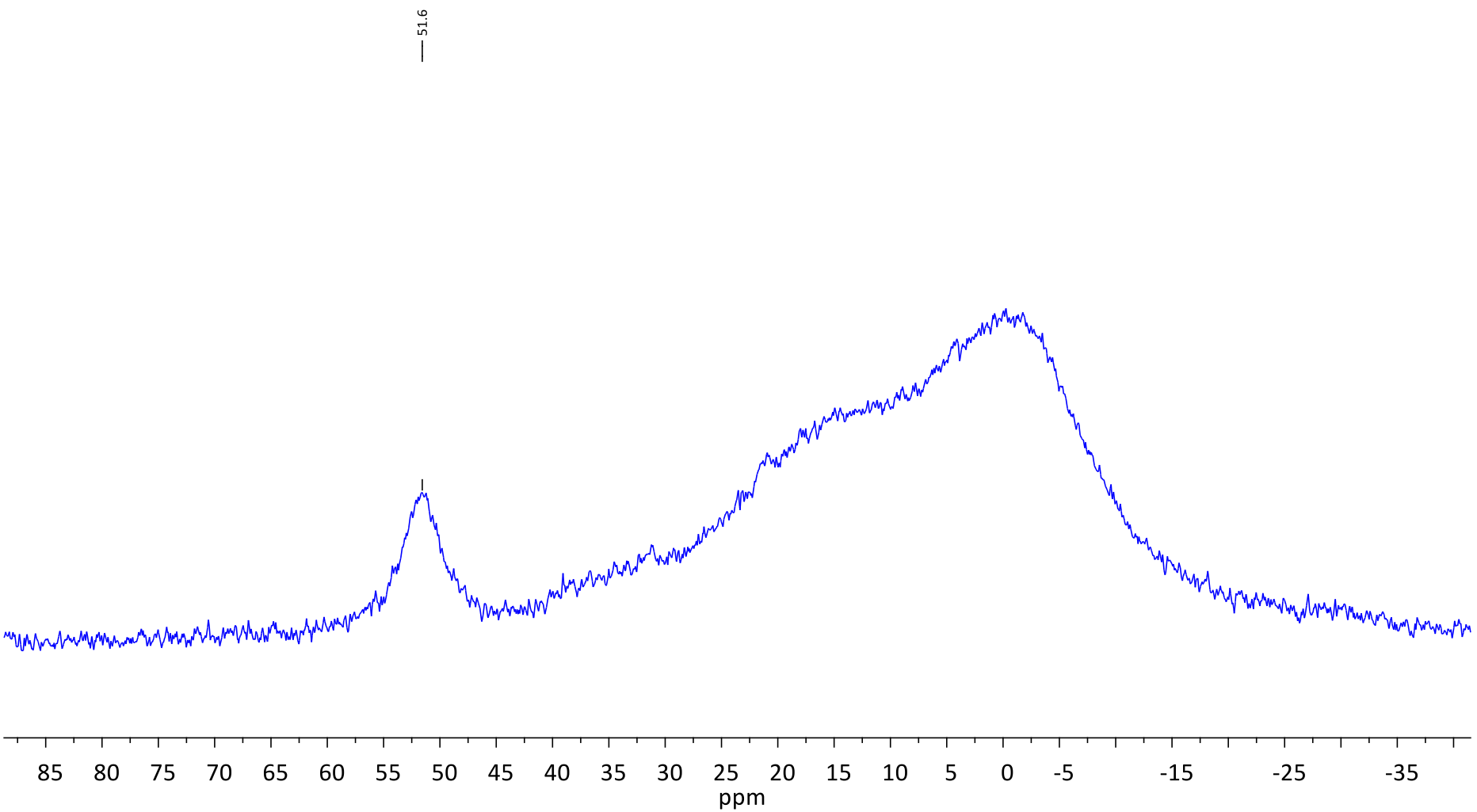


Fig. S25 ^{11}B NMR spectrum of **9** in C_6D_6.

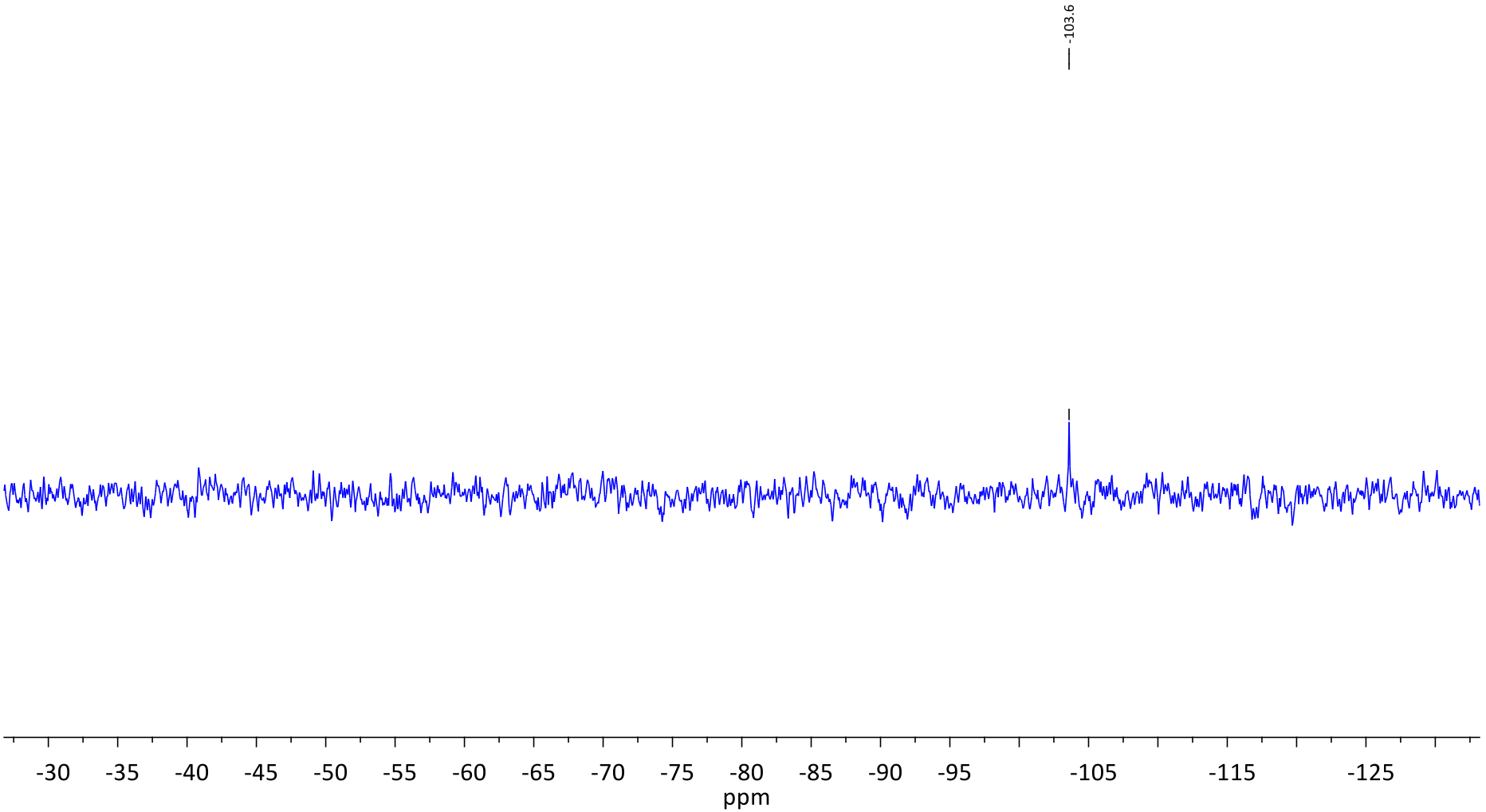


Fig. S26 $^{119}Sn\{^{1}H,^{11}B\}$ NMR spectrum of **9** in C_6D_6.

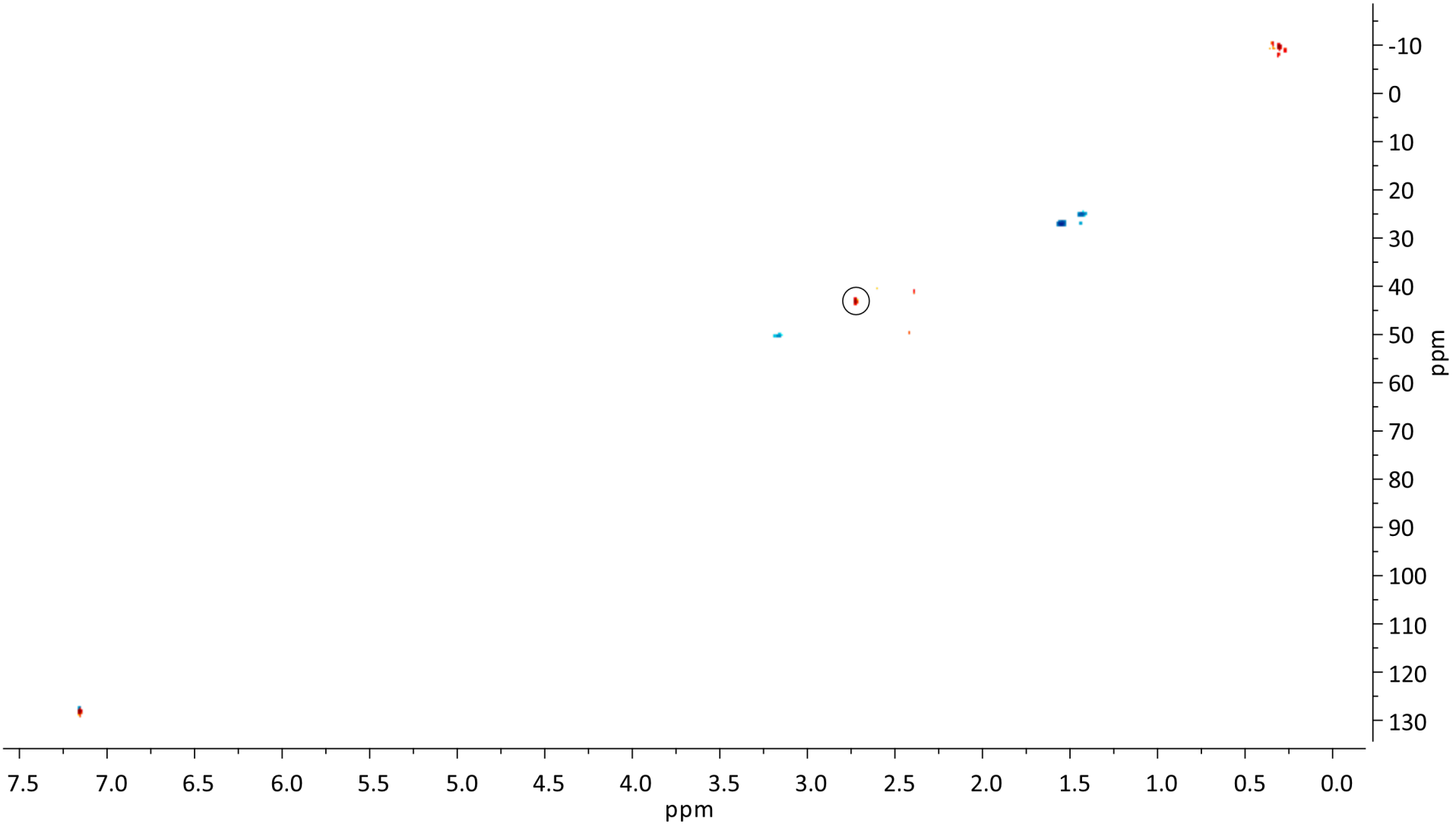


Fig. S27 HSQC spectrum of **9** in C_6D_6 exhibiting the ^{13}C NMR signal at 43.2 ppm for the NMe_3 carbons.

1.4. X-ray crystallographic data

The crystal data were collected on an *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,[50] refined with the ShelXL program[51] 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, and the related CCDC numbers are as follows: 2394530 (**3a**), 2394531 (**3b**), 2394532 (**4a**), 2394533 (**4b**), 2394534 (**5a**), 2394494 (**7**), and 2394535 (**9**). 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 3a: $C_{27}H_{56}BN_3Sn_2$, $M_r = 670.93$, colourless block, 0.370×0.210×0.120 mm^3, tetragonal space group $I4_1cd$, $a = 16.74320(10)$ Å, $b = 16.74320(10)$ Å, $c = 21.92770(10)$ Å, $V = 6147.10(8)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.450$ g·cm^{-3}, $\mu = 13.043$ mm^{-1}, $F(000) = 2752$, $T = 100(2)$ K, $R_1 = 0.0338$, $wR_2 = 0.0989$, Flack parameter = –0.006(10), 2928 independent reflections [$2\theta \leq 150.598°$] and 156 parameters. Some reflections were removed from refinement as outliers.

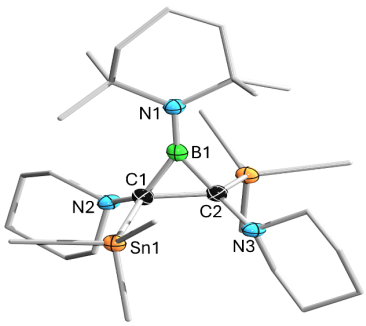


Fig. S28 Crystallographically-derived solid-state structure of **3a**; atomic displacement ellipsoids drawn at 50% probability level. Ellipsoids of TMP, $SnMe_3$ and piperidyl carbon atoms and hydrogen atoms omitted for clarity.

Crystal data for 3b: $C_{25}H_{52}BN_3O_2Sn_2$, M_r = 674.88, colourless block, 0.170×0.160×0.120 mm^3, monoclinic space group $P2_1/n$, a = 10.04570(10) Å, b = 16.51580(10) Å, c = 18.33080(10) Å, β = 98.1740(10)°, V = 3010.42(4) Å^3, Z = 4, ρ_{calcd} = 1.489 g·cm^{-3}, μ = 13.374 mm^{-1}, F(000) = 1376, T = 100(2) K, R_1 = 0.0231, wR_2 = 0.0553, 5902 independent reflections [2θ≤149.506°] and 308 parameters.

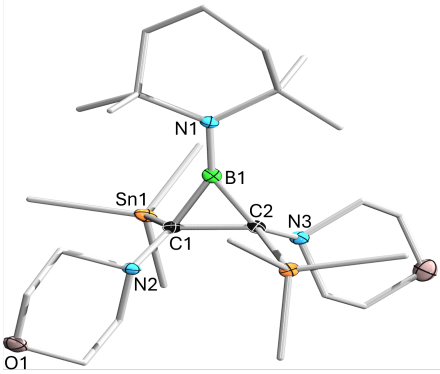


Fig. S29 Crystallographically-derived solid-state structure of **3b**; atomic displacement ellipsoids drawn at 50% probability level. Ellipsoids of TMP, $SnMe_3$ and morpholinyl carbon atoms and hydrogen atoms omitted for clarity.

Crystal data for 4a;: $C_{21}H_{38}BN_3$, M_r = 343.35, colourless plate, 0.130×0.110×0.050 mm^3, monoclinic space group $P2_1/n$, a = 12.2086(3) Å, b = 11.1581(2) Å, c = 16.0725(3) Å, β = 105.649(2)°, V = 2108.31(8) Å^3, Z = 4, ρ_{calcd} = 1.082 g·cm^{-3}, μ = 0.469 mm^{-1}, F(000) = 760, T = 100(2) K, R_1 = 0.0494, wR_2 = 0.1107, 4080 independent reflections [2θ≤146.57°] and 230 parameters

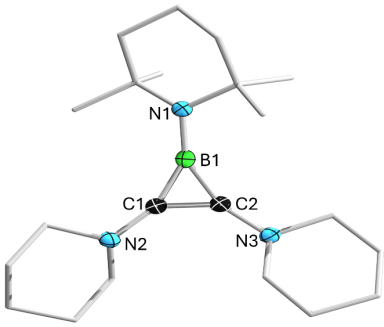


Fig. S30 Crystallographically-derived solid-state structure of **4a**; atomic displacement ellipsoids drawn at 50% probability level. Ellipsoids of TMP and piperidyl carbon atoms and hydrogen atoms omitted for clarity.

Crystal data for 4b: $C_{19}H_{34}BN_3O_2$, $M_r = 347.30$, colourless plate, 0.190×0.070×0.020 mm^3, orthorhombic space group $P2_12_12_1$, $a = 6.38220(10)$ Å, $b = 8.04120(10)$ Å, $c = 39.2727(6)$ Å, $V = 2015.50(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.145$ g·cm^{-3}, $\mu = 0.575$ mm^{-1}, $F(000) = 760$, $T = 100(2)$ K, $R_1 = 0.0435$, $wR_2 = 0.0931$, Flack parameter = 0.2(3), 3934 independent reflections [$2\theta \leq 149.782°$] and 231 parameters. Refined as a two-component inversion twin. The BASF parameter was refined to 23.3%.

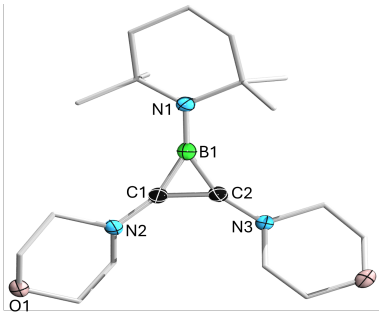


Fig. S31 Crystallographically-derived solid-state structure of **4b**; atomic displacement ellipsoids drawn at 50% probability level. Ellipsoids of TMP and morpholinyl carbon atoms and hydrogen atoms omitted for clarity.

Crystal data for 5a: $C_{21}H_{38}BN_3$, $M_r = 343.35$, colourless plate, 0.210×0.080×0.050 mm^3, orthorhombic space group $Pna2_1$, $a = 18.5782(5)$ Å, $b = 13.3262(4)$ Å, $c = 8.4378(2)$ Å, $V = 2089.00(10)$ Å^3, $Z = 4$, $r_{calcd} = 1.092$ g·cm^{-3}, $m = 0.474$ mm^{-1}, $F(000) = 760$, $T = 100(2)$ K, $R_1 = 0.0399$, $wR_2 = 0.0817$, Flack parameter = 0.1(2), 3968 independent reflections [$2q \leq 146.526°$] and 230 parameters.

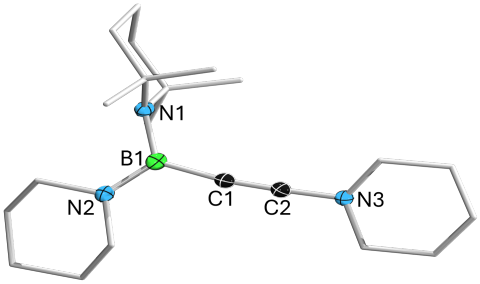


Fig. S32 Crystallographically-derived solid-state structure of **5a**; atomic displacement ellipsoids drawn at 50% probability level. Ellipsoids of TMP and piperidyl carbon atoms and hydrogen atoms omitted for clarity.

Crystal data for 7: $C_{16}H_{34}BN_3O_2Si_2$, $M_r = 367.45$, clear pale colourless plate, 0.140×0.090×0.060 mm^3, triclinic space group $P\bar{1}$, $a = 6.2636(2)$ Å, $b = 9.1707(3)$ Å,

c = 18.6096(6) Å, α = 91.745(3)°, β = 91.755(2)°, γ = 94.665(3)°, V = 1064.34(6) Å^3, Z = 2, ρ_{calcd} = 1.147 g·cm^{-3}, μ = 1.610 mm^{-1}, F(000) = 400, T = 100(2) K, R_1 = 0.0647, wR_2 = 0.1407, 4103 independent reflections [2$\theta \leq$148.854°] and 278 parameters. One disordered morpholinyl substituent was restrained using keyword ISOR (0.012), SIMU (0.006), RIGU (0.003) and DELU (0.006).

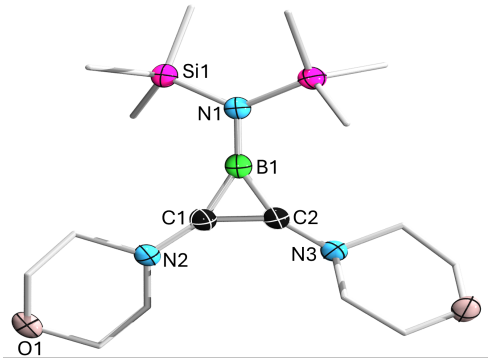


Fig. S33 Crystallographically-derived solid-state structure of **7**; atomic displacement ellipsoids drawn at 50% probability level. Ellipsoids of $SiMe_3$ and morpholinyl carbon atoms and hydrogen atoms omitted for clarity.

Crystal data for 9: $C_{22}H_{50}B_2N_4Sn_2$, M_r = 629.66, yellow block, 0.300×0.230×0.090 mm^3, monoclinic space group $C2/c$, a = 13.8317(2) Å, b = 11.31540(10) Å, c = 19.0710(2) Å, β = 97.6470(10)°, V = 2958.28(6) Å^3, Z = 4, ρ_{calcd} = 1.414 g·cm^{-3}, μ = 13.519 mm^{-1}, F(000) = 1280, T = 100(2) K, R_1 = 0.0381, wR_2 = 0.1066, 2965 independent reflections [2$\theta \leq$149.66°] and 141 parameters.

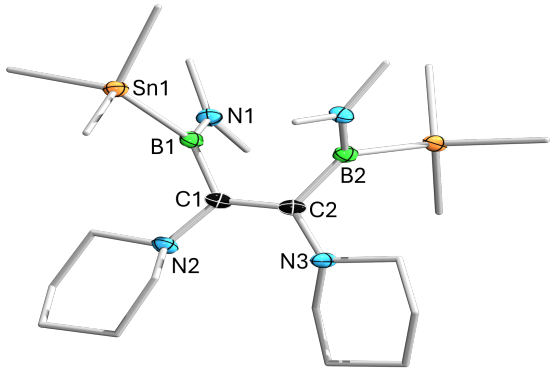


Fig. S34 Crystallographically-derived solid-state structure of **9**; atomic displacement ellipsoids drawn at 50% probability level. Ellipsoids of NMe_2, $SnMe_3$ and piperidyl carbon atoms and hydrogen atoms omitted for clarity.

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2. Computational details

All molecules were fully optimised using the Gaussian 16, Rev. C.01[52] quantum chemistry program package at the ωB97X-D[53]/Def2-SVP level of theory. The model compounds were fully optimised in gaseous state (no solvent effect) starting from the X-ray crystallographic coordinates. Frequency calculations were performed at the same level of theory to verify the nature of the stationary states and the absence of any imaginary frequency to confirm that all structures represent minima on the potential energy hypersurface. Natural bonding analyses were performed with the natural bond orbital (NBO 7.0) partitioning scheme as implemented in the Gaussian 16 suite of programs.[54-56] Natural charges were obtained from a natural bond orbital analysis. To analyse the bonding situation, the Wiberg bond indices (WBI)[57] were obtained from NBO analysis and using the Multiwfn V.3.8 package.[58] In order to understand the nature of bonding in the synthesised molecules in greater detail, the QTAIM analysis[59,60] was carried out utilising the Multiwfn V.3.8 package[58] whereas the wavefunctions were generated with Gaussian16 at the same level of theory as for geometry optimisation. The nucleus-independent chemical shift (NICS) values were calculated by computing NMR shielding (NMR = GIAO)[61,62] of a ghost atom placed at the center of the ring and then displaced above and below the plane of ring in intervals of 1 Å. Pictures of MOs, and NBOs were generated by means of the ChemCraft1.8 program.[63]

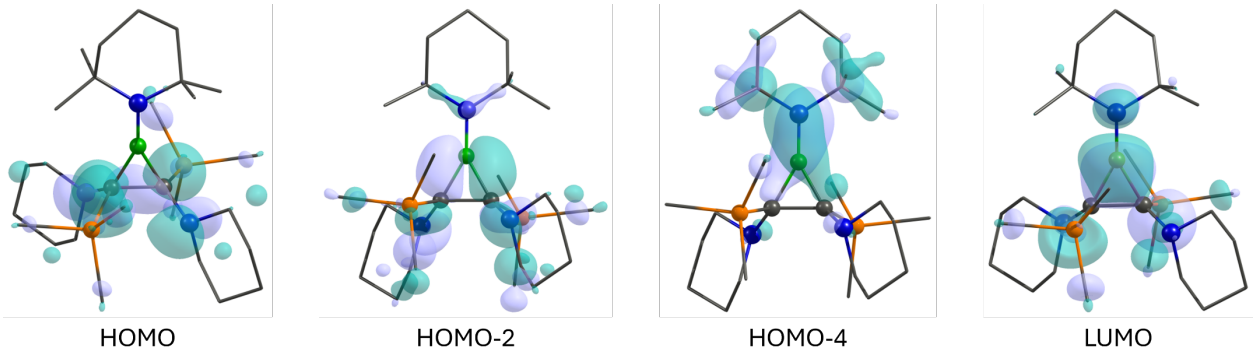


Fig. S35 Selected molecular orbitals of **3a** (isosurface plot at 0.04 a.u.).

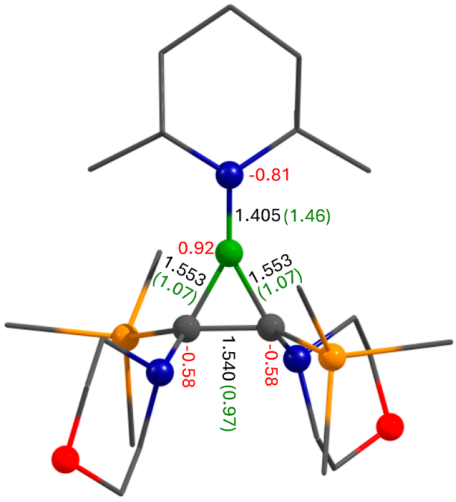


Fig. S36 Optimised geometry of **3b**. Interatomic distances (in Å), WBIs, and natural charges are given in black, green and red, respectively.

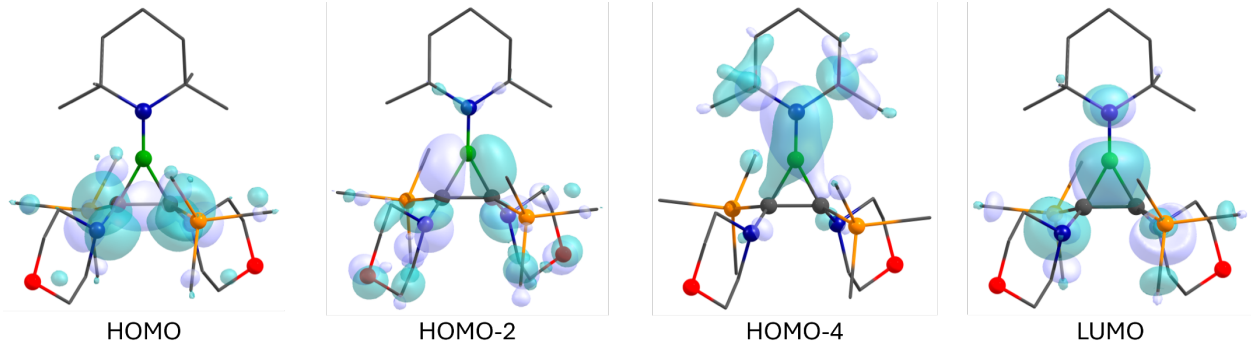


Fig. S37 Selected molecular orbitals of **3b** (isosurface plot at 0.04 a.u.).

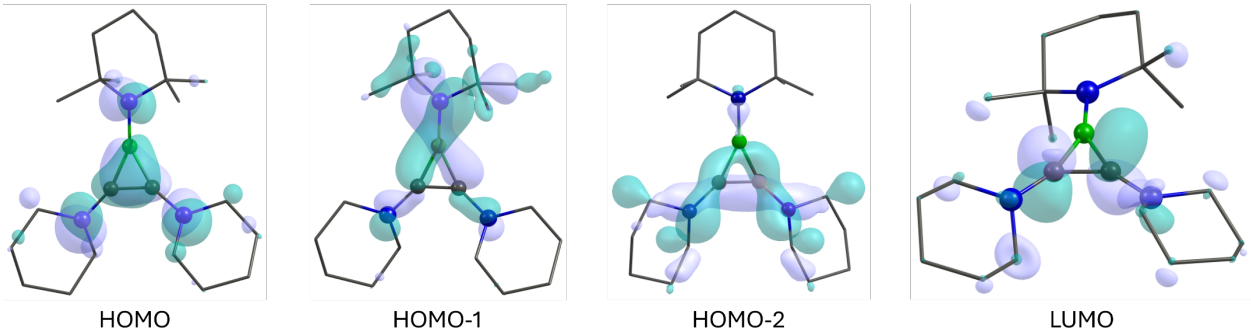


Fig. S38 Selected molecular orbitals of **4a** (isosurface plot at 0.04 a.u.).

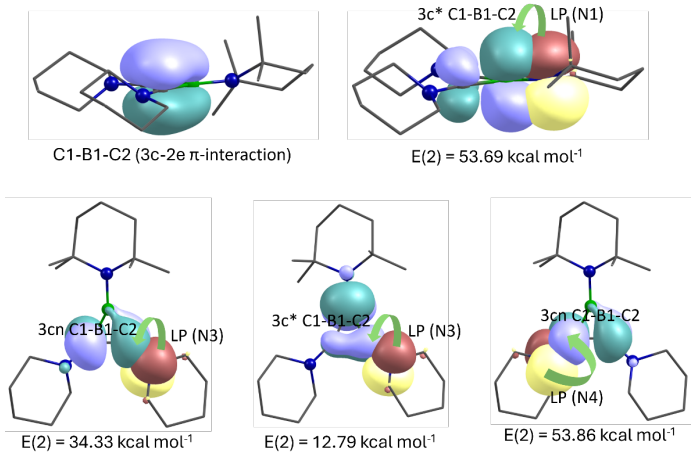


Fig. S39 Selected natural bonding orbitals (NBOs) of **4a** (isosurface plot at 0.04 a.u.).

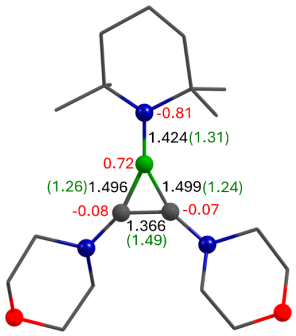


Fig. S40 Optimised geometry of **4b**. Interatomic distances (in Å), WBIs, and natural charges are given in black, green and red, respectively.

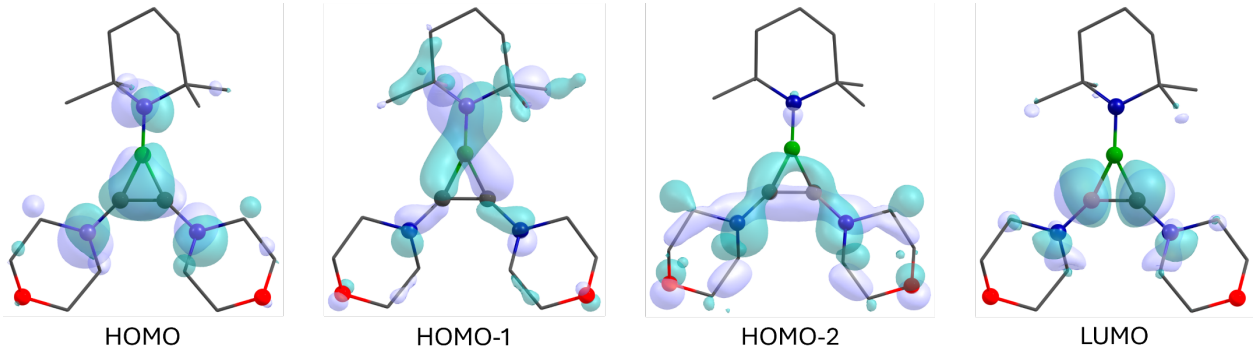


Fig. S41 Selected molecular orbitals of **4b** (isosurface plot at 0.04 a.u.).

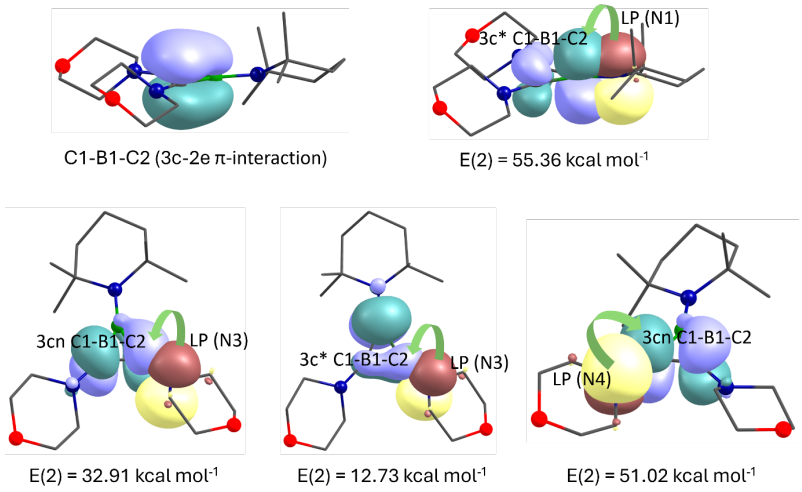


Fig. S42 Selected natural bonding orbitals (NBOs) of **4b** (isosurface plot at 0.04 a.u.).

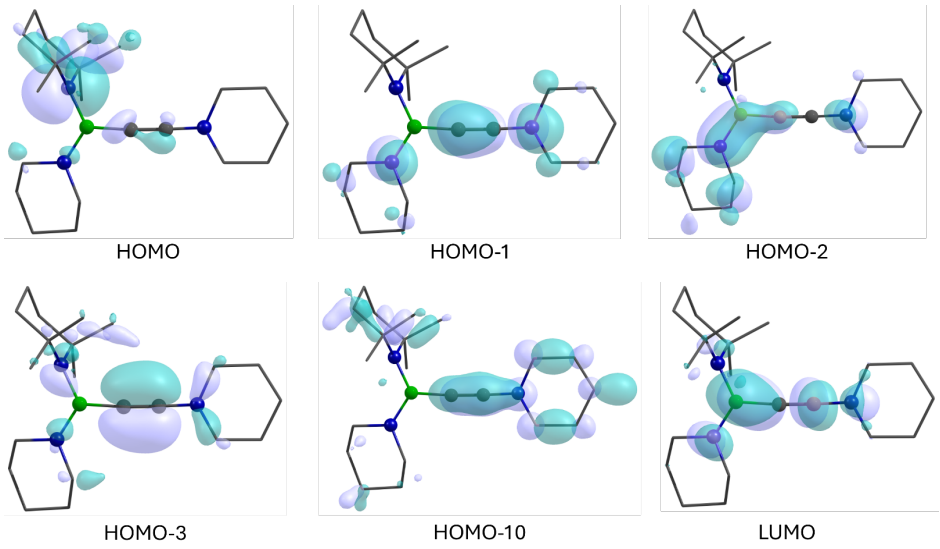


Fig. S43 Selected molecular orbitals of **5a** (isosurface plot at 0.04 a.u.).

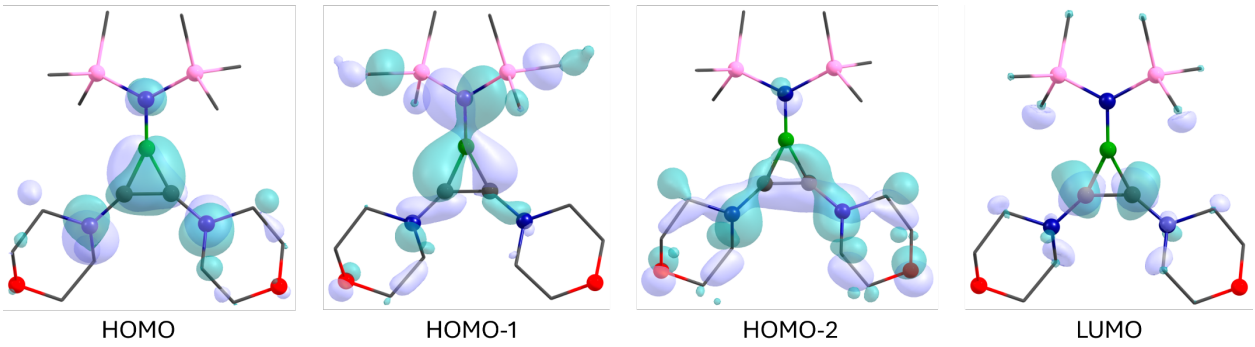
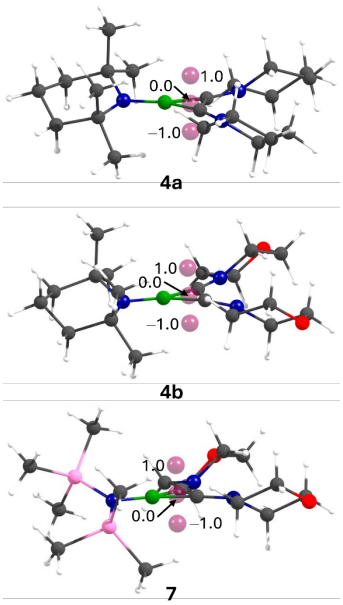


Fig. S44 Selected molecular orbitals of **7** (isosurface plot at 0.04 a.u.).

Table S1. NICS values of triaminoborirenes **4a**,**b** and **7**. NICS isotropic values are an average of the NICS value in the plane of the ring and out of the plane of the ring. $NICS_{zz}$ quantifies the out-of-plane aromaticity. NICS(1.0) and NICS (–1.0) are the NICS values at 1.0 Å above and below the perpendicular plane of the $\{BC_2\}$ triangular ring, respectively, as shown at right.

	4a	**4b**	**7**
NICS (0.0)	–29.7	–29.6	–29.8
$NICS_{zz}$(0.0)	–15.6	–15.9	–15.5
NICS (1.0)	–11.6	–11.7	–11.5
$NICS_{zz}$(1.0)	–12.2	–12.7	–12.6
NICS (–1.0)	–11.3	–11.4	–11.4
$NICS_{zz}$(–1.0)	–12.5	–12.8	–12.2



Coordinates of Optimised Geometries

Compound 3a, ωB97X-D/Def2-SVP
Energy = –1679.242535 Eh
Imaginary frequency = 0

C	-0.111589000000	0.762098000000	-0.353463000000
B	0.000000000000	0.000000000000	0.996004000000
N	0.000000000000	0.000000000000	2.403409000000
C	0.000000000000	1.280397000000	3.189898000000
C	-0.654263000000	1.076437000000	4.568822000000
H	-1.716938000000	0.842969000000	4.403670000000
H	-0.641339000000	2.045102000000	5.090585000000
C	0.000000000000	0.000000000000	5.432828000000
C	-0.841068000000	2.352722000000	2.494616000000
H	-1.871269000000	1.998730000000	2.348127000000
H	-0.435977000000	2.642491000000	1.523850000000
H	-0.880764000000	3.253652000000	3.124493000000
C	1.437229000000	1.798285000000	3.367790000000
H	1.432928000000	2.788067000000	3.849709000000
H	1.940116000000	1.890278000000	2.397022000000
H	2.049970000000	1.128007000000	3.984284000000
N	0.845773000000	1.614061000000	-1.031239000000
C	1.230888000000	2.825515000000	-0.328714000000
H	1.507458000000	2.551373000000	0.695139000000
H	0.379024000000	3.539791000000	-0.254619000000
C	2.400267000000	3.532296000000	-1.004729000000
H	2.649309000000	4.443442000000	-0.438377000000
H	3.285100000000	2.873985000000	-0.968913000000
C	2.069195000000	3.861075000000	-2.456203000000
H	2.929310000000	4.325622000000	-2.962861000000
H	1.246546000000	4.598037000000	-2.483983000000
C	1.638262000000	2.587748000000	-3.175587000000
H	1.301033000000	2.806450000000	-4.200910000000
H	2.497732000000	1.905182000000	-3.256279000000
C	0.514344000000	1.884480000000	-2.422947000000
H	-0.404058000000	2.513057000000	-2.494526000000
H	0.277092000000	0.931019000000	-2.914457000000
Sn	-2.263525000000	1.144704000000	-0.693407000000
C	-2.665930000000	3.265802000000	-0.445546000000
H	-3.737608000000	3.453122000000	-0.617257000000
H	-2.097408000000	3.847500000000	-1.187257000000
H	-2.407181000000	3.636600000000	0.555607000000
C	-2.968693000000	0.749001000000	-2.700105000000
H	-3.417844000000	1.664600000000	-3.113492000000
H	-3.733874000000	-0.040831000000	-2.687972000000

H	-2.153060000000	0.433459000000	-3.364827000000
C	-3.490744000000	0.062418000000	0.713911000000
H	-3.113554000000	0.175055000000	1.740262000000
H	-3.486504000000	-1.007102000000	0.459619000000
H	-4.527284000000	0.429787000000	0.679033000000
C	0.111589000000	-0.762098000000	-0.353463000000
C	0.000000000000	-1.280397000000	3.189898000000
C	0.654263000000	-1.076437000000	4.568822000000
H	1.716938000000	-0.842969000000	4.403670000000
H	0.641339000000	-2.045102000000	5.090585000000
C	0.841068000000	-2.352722000000	2.494616000000
H	1.871269000000	-1.998730000000	2.348127000000
H	0.435977000000	-2.642491000000	1.523850000000
H	0.880764000000	-3.253652000000	3.124493000000
C	-1.437229000000	-1.798285000000	3.367790000000
H	-1.432928000000	-2.788067000000	3.849709000000
H	-1.940116000000	-1.890278000000	2.397022000000
H	-2.049970000000	-1.128007000000	3.984284000000
N	-0.845773000000	-1.614061000000	-1.031239000000
C	-1.230888000000	-2.825515000000	-0.328714000000
H	-1.507458000000	-2.551373000000	0.695139000000
H	-0.379024000000	-3.539791000000	-0.254619000000
C	-2.400267000000	-3.532296000000	-1.004729000000
H	-2.649309000000	-4.443442000000	-0.438377000000
H	-3.285100000000	-2.873985000000	-0.968913000000
C	-2.069195000000	-3.861075000000	-2.456203000000
H	-2.929310000000	-4.325622000000	-2.962861000000
H	-1.246546000000	-4.598037000000	-2.483983000000
C	-1.638262000000	-2.587748000000	-3.175587000000
H	-1.301033000000	-2.806450000000	-4.200910000000
H	-2.497732000000	-1.905182000000	-3.256279000000
C	-0.514344000000	-1.884480000000	-2.422947000000
H	0.404058000000	-2.513057000000	-2.494526000000
H	-0.277092000000	-0.931019000000	-2.914457000000
Sn	2.263525000000	-1.144704000000	-0.693407000000
C	2.665930000000	-3.265802000000	-0.445546000000
H	3.737608000000	-3.453122000000	-0.617257000000
H	2.097408000000	-3.847500000000	-1.187257000000
H	2.407181000000	-3.636600000000	0.555607000000
C	2.968693000000	-0.749001000000	-2.700105000000
H	3.417844000000	-1.664600000000	-3.113492000000
H	3.733874000000	0.040831000000	-2.687972000000
H	2.153060000000	-0.433459000000	-3.364827000000
C	3.490744000000	-0.062418000000	0.713911000000
H	3.113554000000	-0.175055000000	1.740262000000
H	3.486504000000	1.007102000000	0.459619000000

H	4.527284000000	-0.429787000000	0.679033000000
H	-0.757990000000	-0.443272000000	6.096477000000
H	0.757990000000	0.443272000000	6.096477000000

Compound 3b, ωB97X-D/Def2-SVP
Energy = –1750.935484 Eh
Imaginary frequency = 0

B	0.997695000000	-0.000071000000	-0.000047000000
C	-0.351073000000	0.591199000000	0.493687000000
C	-0.351183000000	-0.591181000000	-0.493687000000
N	2.403310000000	-0.000110000000	-0.000119000000
C	3.188458000000	0.848163000000	0.959611000000
C	4.567863000000	1.202683000000	0.374778000000
H	4.403273000000	1.845496000000	-0.503183000000
H	5.089821000000	1.833422000000	1.109864000000
C	5.431360000000	-0.000280000000	-0.000152000000
H	6.094881000000	-0.275958000000	0.833562000000
H	6.095006000000	0.275318000000	-0.833791000000
C	4.567731000000	-1.203138000000	-0.375135000000
H	4.403146000000	-1.846001000000	0.502792000000
H	5.089576000000	-1.833871000000	-1.110307000000
C	3.188322000000	-0.848474000000	-0.959870000000
C	3.360795000000	0.113769000000	2.299482000000
H	2.386598000000	-0.196434000000	2.698307000000
H	3.844816000000	0.769488000000	3.039443000000
H	3.971942000000	-0.793018000000	2.203985000000
C	2.491837000000	2.187752000000	1.205344000000
H	1.521205000000	2.074490000000	1.690855000000
H	2.344168000000	2.724980000000	0.257829000000
H	3.120575000000	2.815324000000	1.853915000000
C	2.491527000000	-2.187988000000	-1.205529000000
H	2.343831000000	-2.725162000000	-0.257986000000
H	3.120146000000	-2.815668000000	-1.854112000000
H	1.520890000000	-2.074599000000	-1.690996000000
C	3.360663000000	-0.114124000000	-2.299768000000
H	2.386484000000	0.196216000000	-2.698524000000
H	3.844531000000	-0.769928000000	-3.039754000000
H	3.971959000000	0.792568000000	-2.204328000000
N	-1.025526000000	0.435506000000	1.766292000000
C	-0.349367000000	0.969679000000	2.933953000000
H	-0.270559000000	2.077853000000	2.894802000000
H	0.668189000000	0.563032000000	2.976687000000
C	-1.092839000000	0.586521000000	4.204516000000
H	-1.060947000000	-0.515701000000	4.328789000000

H	-0.611615000000	1.045980000000	5.079597000000
O	-2.421624000000	1.032856000000	4.176264000000
C	-3.103698000000	0.492261000000	3.075998000000
H	-4.124839000000	0.898823000000	3.091550000000
H	-3.166848000000	-0.608410000000	3.169099000000
C	-2.419312000000	0.849759000000	1.764749000000
H	-2.944230000000	0.356893000000	0.934245000000
H	-2.513689000000	1.947855000000	1.610383000000
N	-1.025784000000	-0.435408000000	-1.766196000000
C	-0.349804000000	-0.969532000000	-2.933982000000
H	-0.271009000000	-2.077708000000	-2.894907000000
H	0.667752000000	-0.562895000000	-2.976839000000
C	-1.093454000000	-0.586274000000	-4.204410000000
H	-1.061531000000	0.515957000000	-4.328621000000
H	-0.612382000000	-1.045697000000	-5.079592000000
O	-2.422251000000	-1.032553000000	-4.175991000000
C	-3.104155000000	-0.492002000000	-3.075599000000
H	-4.125306000000	-0.898543000000	-3.091026000000
H	-3.167302000000	0.608672000000	-3.168630000000
C	-2.419593000000	-0.849580000000	-1.764466000000
H	-2.944358000000	-0.356715000000	-0.933866000000
H	-2.514014000000	-1.947672000000	-1.610118000000
Sn	-0.696633000000	2.459792000000	-0.638693000000
C	-0.446471000000	4.159274000000	0.688219000000
H	-1.182559000000	4.114748000000	1.505360000000
H	-0.624045000000	5.087251000000	0.122403000000
H	0.557780000000	4.211944000000	1.130302000000
C	-2.706864000000	2.720196000000	-1.396297000000
H	-3.373303000000	1.902816000000	-1.088786000000
H	-2.698439000000	2.769078000000	-2.494907000000
H	-3.118701000000	3.663983000000	-1.008392000000
C	0.702858000000	2.658328000000	-2.268543000000
H	0.430920000000	1.960602000000	-3.073498000000
H	1.727734000000	2.429787000000	-1.943480000000
H	0.681997000000	3.683188000000	-2.668068000000
Sn	-0.696866000000	-2.459746000000	0.638725000000
C	0.702775000000	-2.658523000000	2.268421000000
H	0.430907000000	-1.960925000000	3.073510000000
H	1.727631000000	-2.429952000000	1.943316000000
H	0.681924000000	-3.683449000000	2.667778000000
C	-0.447105000000	-4.159186000000	-0.688310000000
H	-0.624434000000	-5.087237000000	-0.122545000000
H	0.556994000000	-4.211761000000	-1.130748000000
H	-1.183476000000	-4.114601000000	-1.505194000000
C	-2.707051000000	-2.719869000000	1.396554000000
H	-2.698426000000	-2.769093000000	2.495152000000

H	-3.119193000000	-3.663436000000	1.008438000000
H	-3.373343000000	-1.902232000000	1.089431000000

Compound 4a, ωB97X-D/Def2-SVP
Energy = –1011.253156 Eh
Imaginary frequency = 0

B	0.692593000000	-0.112675000000	-0.157096000000
C	-0.678123000000	-0.706063000000	-0.122139000000
C	-0.590746000000	0.659321000000	-0.093245000000
N	2.118068000000	-0.168261000000	-0.203816000000
C	2.800377000000	-1.331106000000	0.419653000000
C	4.245913000000	-1.468612000000	-0.090710000000
H	4.746165000000	-2.257326000000	0.493520000000
H	4.211885000000	-1.820287000000	-1.136407000000
C	5.030258000000	-0.169970000000	-0.043703000000
H	5.151001000000	0.177515000000	0.995717000000
H	6.047525000000	-0.321893000000	-0.437022000000
C	4.292298000000	0.860557000000	-0.878470000000
H	4.268272000000	0.506874000000	-1.923506000000
H	4.824146000000	1.825443000000	-0.883503000000
C	2.843094000000	1.111960000000	-0.419718000000
C	2.790951000000	-1.221567000000	1.957689000000
H	3.398916000000	-0.383445000000	2.323502000000
H	3.182868000000	-2.143068000000	2.416441000000
H	1.761068000000	-1.070801000000	2.315842000000
C	2.071028000000	-2.624995000000	0.040831000000
H	1.097998000000	-2.700388000000	0.539387000000
H	2.674593000000	-3.493209000000	0.346146000000
H	1.910819000000	-2.674132000000	-1.046471000000
C	2.841157000000	1.988430000000	0.847762000000
H	3.196876000000	3.005617000000	0.620602000000
H	3.487047000000	1.580601000000	1.637193000000
H	1.822842000000	2.059892000000	1.256440000000
C	2.163914000000	1.889050000000	-1.557441000000
H	1.161827000000	2.235309000000	-1.281928000000
H	2.071484000000	1.251409000000	-2.449093000000
H	2.768478000000	2.770736000000	-1.820064000000
N	-1.688467000000	-1.638688000000	-0.107420000000
C	-1.397513000000	-3.028619000000	-0.400497000000
H	-1.050519000000	-3.566623000000	0.509572000000
H	-0.579919000000	-3.065642000000	-1.132158000000
C	-2.641572000000	-3.725307000000	-0.947162000000
H	-2.421085000000	-4.789309000000	-1.126937000000
H	-2.896987000000	-3.274514000000	-1.920921000000

C	-3.822270000000	-3.573551000000	0.012225000000
H	-3.604486000000	-4.126571000000	0.943738000000
H	-4.731105000000	-4.024758000000	-0.415542000000
C	-4.057822000000	-2.101415000000	0.351115000000
H	-4.404281000000	-1.564551000000	-0.548723000000
H	-4.844749000000	-1.997905000000	1.114893000000
C	-2.770435000000	-1.452131000000	0.847478000000
H	-2.908692000000	-0.377001000000	1.025581000000
H	-2.491176000000	-1.897351000000	1.827746000000
N	-1.450504000000	1.721085000000	-0.058165000000
C	-0.957759000000	3.072915000000	0.121786000000
H	-0.736890000000	3.548223000000	-0.858753000000
H	-0.014747000000	3.029879000000	0.681736000000
C	-1.990861000000	3.918316000000	0.864144000000
H	-1.626504000000	4.953572000000	0.956446000000
H	-2.103471000000	3.517949000000	1.885728000000
C	-3.341941000000	3.884043000000	0.148182000000
H	-4.098402000000	4.442914000000	0.720811000000
H	-3.246085000000	4.393717000000	-0.827534000000
C	-3.797704000000	2.443107000000	-0.086431000000
H	-4.024969000000	1.963469000000	0.881193000000
H	-4.721436000000	2.419709000000	-0.685969000000
C	-2.705834000000	1.642562000000	-0.789039000000
H	-2.987939000000	0.587645000000	-0.903319000000
H	-2.565474000000	2.041173000000	-1.816960000000

Compound 4b, ωB97X-D/Def2-SVP
Energy = –1082.943505 Eh
Imaginary frequency = 0

B	0.682085000000	-0.105863000000	-0.160787000000
C	-0.689169000000	-0.703568000000	-0.135363000000
C	-0.605222000000	0.658660000000	-0.072373000000
N	2.104969000000	-0.154731000000	-0.210137000000
C	2.790844000000	-1.345267000000	0.357267000000
C	4.242291000000	-1.446499000000	-0.144159000000
H	4.741584000000	-2.259986000000	0.405670000000
H	4.222469000000	-1.746148000000	-1.206271000000
C	5.016282000000	-0.146573000000	-0.024310000000
H	5.121156000000	0.152121000000	1.031774000000
H	6.039460000000	-0.272606000000	-0.411070000000
C	4.281075000000	0.915926000000	-0.820068000000
H	4.272517000000	0.609834000000	-1.880205000000
H	4.805660000000	1.883614000000	-0.775359000000
C	2.824959000000	1.138031000000	-0.368561000000

C	2.765410000000	-1.314732000000	1.898307000000
H	1.730644000000	-1.195143000000	2.254226000000
H	3.359278000000	-0.488448000000	2.311424000000
H	3.164793000000	-2.253340000000	2.313615000000
C	2.074562000000	-2.621811000000	-0.097771000000
H	1.099538000000	-2.732168000000	0.389404000000
H	2.682355000000	-3.501046000000	0.164159000000
H	1.922650000000	-2.612556000000	-1.187414000000
C	2.801137000000	1.961127000000	0.933469000000
H	3.167109000000	2.984513000000	0.756277000000
H	3.427759000000	1.516004000000	1.718319000000
H	1.774736000000	2.022237000000	1.323509000000
C	2.153568000000	1.954923000000	-1.482421000000
H	1.145853000000	2.282863000000	-1.205770000000
H	2.077068000000	1.353360000000	-2.400208000000
H	2.753865000000	2.851053000000	-1.701990000000
N	-1.701075000000	-1.635503000000	-0.137243000000
C	-1.413332000000	-3.026365000000	-0.427531000000
H	-1.007483000000	-3.553935000000	0.460989000000
H	-0.664175000000	-3.081921000000	-1.229031000000
C	-2.698918000000	-3.716884000000	-0.863503000000
H	-3.033178000000	-3.281919000000	-1.827306000000
H	-2.530442000000	-4.793436000000	-1.007625000000
O	-3.707537000000	-3.583969000000	0.105894000000
C	-4.002012000000	-2.238635000000	0.377620000000
H	-4.778360000000	-2.228039000000	1.155974000000
H	-4.410217000000	-1.744117000000	-0.528285000000
C	-2.764794000000	-1.485789000000	0.843778000000
H	-2.989892000000	-0.420073000000	0.990625000000
H	-2.444115000000	-1.889498000000	1.826857000000
N	-1.474540000000	1.713785000000	-0.005265000000
C	-0.991026000000	3.067357000000	0.185333000000
H	-0.693385000000	3.531685000000	-0.777362000000
H	-0.110647000000	3.050646000000	0.841812000000
C	-2.099684000000	3.904255000000	0.811080000000
H	-2.306650000000	3.523820000000	1.832009000000
H	-1.794811000000	4.957535000000	0.887304000000
O	-3.268607000000	3.869325000000	0.032017000000
C	-3.750382000000	2.561630000000	-0.141188000000
H	-4.646161000000	2.628678000000	-0.774958000000
H	-4.046938000000	2.128846000000	0.836810000000
C	-2.700806000000	1.668372000000	-0.785991000000
H	-3.057154000000	0.631855000000	-0.860384000000
H	-2.510332000000	2.022358000000	-1.820065000000

Compound 5a, ωB97X-D/Def2-SVP
Energy = –1011.274626 Eh
Imaginary frequency = 0

B	-0.770500000000	0.418024000000	-0.236634000000
C	0.767641000000	0.414821000000	-0.205001000000
C	1.990149000000	0.323444000000	-0.166849000000
N	-1.447579000000	1.640957000000	-0.455929000000
C	-0.767569000000	2.900017000000	-0.706814000000
H	-1.020427000000	3.252936000000	-1.726967000000
H	0.316747000000	2.731118000000	-0.682129000000
C	-1.173747000000	3.971506000000	0.304071000000
H	-0.668978000000	4.920776000000	0.063356000000
H	-0.825327000000	3.662173000000	1.304430000000
C	-2.691219000000	4.152260000000	0.319186000000
H	-3.013530000000	4.575385000000	-0.649518000000
H	-2.992222000000	4.875716000000	1.093192000000
C	-3.385028000000	2.807906000000	0.535615000000
H	-4.478400000000	2.913793000000	0.452346000000
H	-3.172228000000	2.447779000000	1.556238000000
C	-2.894689000000	1.764395000000	-0.468955000000
H	-3.320873000000	0.775285000000	-0.256483000000
H	-3.228142000000	2.061129000000	-1.484334000000
N	-1.528769000000	-0.842168000000	-0.054631000000
C	-1.590502000000	-1.409979000000	1.306158000000
C	-2.829957000000	-2.318530000000	1.411633000000
H	-2.830818000000	-2.817412000000	2.394816000000
H	-3.727422000000	-1.676997000000	1.375011000000
C	-2.917150000000	-3.340989000000	0.286493000000
H	-3.846102000000	-3.925910000000	0.377779000000
H	-2.092079000000	-4.068504000000	0.363814000000
C	-2.875067000000	-2.632686000000	-1.061094000000
H	-3.774160000000	-1.999393000000	-1.155465000000
H	-2.906645000000	-3.362026000000	-1.887317000000
C	-1.638042000000	-1.730764000000	-1.229054000000
C	-0.325573000000	-2.188949000000	1.736673000000
H	-0.367389000000	-2.414101000000	2.814004000000
H	0.574941000000	-1.588901000000	1.544369000000
H	-0.215696000000	-3.144940000000	1.210057000000
C	-1.768891000000	-0.255915000000	2.303615000000
H	-1.898412000000	-0.652944000000	3.321603000000
H	-2.654928000000	0.343975000000	2.053886000000
H	-0.890951000000	0.408838000000	2.313725000000
C	-0.381807000000	-2.595799000000	-1.487103000000
H	-0.252486000000	-3.390940000000	-0.742637000000
H	0.521083000000	-1.968522000000	-1.473252000000

H	-0.450757000000	-3.081554000000	-2.473246000000
C	-1.850006000000	-0.869640000000	-2.484050000000
H	-0.966886000000	-0.249533000000	-2.703010000000
H	-2.718903000000	-0.207022000000	-2.370648000000
H	-2.024687000000	-1.518182000000	-3.355599000000
N	3.311784000000	0.186340000000	-0.098295000000
C	4.176804000000	1.283574000000	-0.517656000000
H	3.640274000000	2.225954000000	-0.343116000000
H	4.375387000000	1.212464000000	-1.606990000000
C	5.495076000000	1.251807000000	0.248413000000
H	5.296025000000	1.480901000000	1.308652000000
H	6.158642000000	2.041440000000	-0.136744000000
C	6.161163000000	-0.119634000000	0.137804000000
H	7.087542000000	-0.146910000000	0.731609000000
H	6.454075000000	-0.299546000000	-0.912258000000
C	5.202179000000	-1.220621000000	0.590274000000
H	5.654042000000	-2.214953000000	0.451714000000
H	4.989160000000	-1.105975000000	1.666212000000
C	3.888969000000	-1.152267000000	-0.181359000000
H	4.063895000000	-1.421099000000	-1.243479000000
H	3.154697000000	-1.864062000000	0.219530000000

Compound 7, ωB97X-D/Def2-SVP
Energy = –1547.654786 Eh
Imaginary frequency = 0

B	0.533893000000	0.003521000000	-0.073946000000
N	1.965538000000	-0.024346000000	-0.033696000000
Si	2.787596000000	1.477181000000	-0.468547000000
C	1.849595000000	2.313751000000	-1.866783000000
H	2.340492000000	3.261080000000	-2.142041000000
H	0.806890000000	2.533535000000	-1.600039000000
H	1.837445000000	1.665919000000	-2.757730000000
Si	2.676901000000	-1.550921000000	0.503109000000
C	2.879301000000	2.612364000000	1.029262000000
H	3.340957000000	3.580742000000	0.778161000000
H	3.478058000000	2.147753000000	1.828764000000
H	1.876498000000	2.807970000000	1.439221000000
C	4.426858000000	-1.311713000000	1.155587000000
H	4.712195000000	-2.210204000000	1.726479000000
H	4.498623000000	-0.449981000000	1.838169000000
H	5.167500000000	-1.181099000000	0.353964000000
C	1.656661000000	-2.244107000000	1.923148000000
H	2.068356000000	-3.210295000000	2.256565000000
H	0.604675000000	-2.398112000000	1.644603000000
H	1.677376000000	-1.551847000000	2.779959000000

C	2.726564000000	-2.772551000000	-0.925093000000
H	3.132119000000	-3.747133000000	-0.609473000000
H	3.359748000000	-2.387347000000	-1.740047000000
H	1.719408000000	-2.939300000000	-1.335371000000
C	4.533283000000	1.159908000000	-1.099203000000
H	4.881404000000	2.057018000000	-1.636402000000
H	4.564432000000	0.316799000000	-1.807683000000
H	5.251351000000	0.959855000000	-0.291549000000
C	-0.781016000000	0.716978000000	-0.038951000000
N	-1.664321000000	1.752090000000	0.045931000000
O	-3.489808000000	3.867268000000	0.229436000000
C	-0.802551000000	-0.649232000000	-0.154273000000
C	-1.196258000000	3.103794000000	0.282394000000
H	-0.934831000000	3.612434000000	-0.667942000000
H	-0.295209000000	3.068726000000	0.909447000000
C	-2.298678000000	3.894412000000	0.975229000000
H	-2.468189000000	3.470441000000	1.985745000000
H	-2.010831000000	4.949532000000	1.084107000000
C	-3.956214000000	2.559145000000	0.021002000000
H	-4.874235000000	2.635305000000	-0.578937000000
H	-4.210790000000	2.082457000000	0.990226000000
C	-2.913952000000	1.711112000000	-0.694307000000
H	-3.252894000000	0.671295000000	-0.795830000000
H	-2.765663000000	2.108419000000	-1.719182000000
N	-1.737830000000	-1.654255000000	-0.244230000000
O	-3.501014000000	-3.833676000000	-0.073644000000
C	-2.841975000000	-1.644434000000	0.703536000000
H	-3.200520000000	-0.615686000000	0.848748000000
H	-2.506406000000	-2.016213000000	1.694201000000
C	-3.964025000000	-2.535520000000	0.192227000000
H	-4.761098000000	-2.623410000000	0.944174000000
H	-4.397121000000	-2.086021000000	-0.725173000000
C	-2.458292000000	-3.835969000000	-1.015564000000
H	-2.817569000000	-3.436715000000	-1.985700000000
H	-2.156302000000	-4.882660000000	-1.160806000000
C	-1.278722000000	-2.999261000000	-0.539887000000
H	-0.826842000000	-3.483082000000	0.350452000000
H	-0.512043000000	-2.950627000000	-1.325521000000

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