Supporting Information for

Cyclic Alkyl(amino)iminates (CAAIs) as Strong 2σ,4π-Electron Donor Ligands for the Stabilisation of Boranes and Diboranes(4): A Synthetic and Computational Study

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Contents

Methods and materials

All manipulations were performed either under an atmosphere of dry argon (Argon 5.0) or *in vacuo* using standard Schlenk line or glovebox techniques. The solvents used were dried over suitable drying agents, distilled under an argon atmosphere, and stored under argon over activated molecular sieves (4 Å). Deuterated solvents were dried over molecular sieves (4 Å or 3 Å) and degassed by three freeze-pump-thaw cycles prior to use. NMR spectra were acquired either on a Bruker Avance 400 (^{11}B:128.5 MHz) or a Bruker Avance 500 (^{1}H: 500.1 MHz, ^{11}B: 160.5 MHz, ^{13}C: 125.8 MHz) spectrometer. Chemical shifts (δ) are listed in ppm, and internally referenced to the carbon nuclei (^{13}C{^{1}H}) or residual protons (^{1}H) of the solvent. Heteronuclei NMR spectra are referenced to external standards (^{11}B: $BF_3{\cdot}OEt_2$). Resonances are given as singlet (s), doublet (d), triplet (t), septet (sept) or multiplet (m). The signals were assigned using standard 2D NMR experiments. High-resolution mass spectrometry (HRMS) data were determined from a Thermo Scientific Exactive Plus spectrometer. FT-IR spectra (solid-state) were recorded on a Bruker FT-IR spectrometer ALPHA II inside a glovebox.

Solvents and reagents were purchased from Sigma-Aldrich, ABCR or Alfa Aesar. (CAAC)NSiMe$_3$ (**1**, CAAC = 1-(2,6-di*iso*propylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene),[1] ClB(NMe$_2$)$_2$,[2] BrB(NMe$_2$)$_2$,[2] DurBCl$_2$ (Dur = 2,3,5,6-tetramethylphenyl),[3] MesBBr$_2$ (Mes = 2,4,6-trimethylphenyl), [4] PhBBr$_2$ [5] BCl$_3$(SMe$_2$),[6] BBr$_3$(SMe$_2$),[6] B$_2$Cl$_2$(NMe$_2$)$_2$,[7] B$_2$Br$_2$(NMe$_2$)$_2$,[7] B$_2$Mes$_2$Cl$_2$,[8,9] were synthesized using known literature procedures.

Synthetic Procedures

Synthesis of 2^{Cl}-NMe_2

To a solution of **1** (500 mg, 1.34 mmol) in benzene (7 mL) $ClB(NMe_2)_2$ (271 mg, 2.01 mmol) was added dropwise. After stirring at room temperature overnight, all volatiles were removed *in vacuo*. Extraction with hexane (7 × 5 mL), removal of the solvent and drying *in vacuo* afforded **2^{Cl}-NMe_2** (418 mg, 80%). Colourless crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated hexane solution at room temperature. $^1H\{^{11}B\}$ NMR (500.1 MHz, C_6D_6, 297 K): δ = 7.21 (t, 1H, ^3J = 7.8, 8.4 Hz, *p*-C*H*^{Dip}), 7.16-7.09 (m, 2H, *m*-C*H*^{Dip}), 3.12 (sept, 2H, ^3J = 6.7 Hz, C*H*$(CH_3)_2^{Dip}$), 2.79 (br s, 3H, N(C*H*$_3)_2$), 2.50 (br s, 3H, N(C*H*$_3)_2$), 1.72 (s, 2H, C*H*$_2^{CAAC}$), 1.34 (d, 6H, ^3J = 6.6 Hz, CH(C*H*$_3)_2^{Dip}$), 1.30 (s, 6H, C*H*$_3^{CAAC}$), 1.25 (d, 6H, ^3J = 6.9 Hz, CH(C*H*$_3)_2^{Dip}$), 1.00 (s, 6H, C*H*$_3^{CAAC}$) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 297 K): δ = 163.6 (*C*=N^{CAAC}), 149.2 (*o*-C_q^{Dip}), 132.2 (*i*- C_q^{Dip}), 128.2 (*p*-*C*H^{Dip}), 123.9 (*m*-*C*H^{Dip}), 60.8 (C_q^{CAAC}), 51.6 (*C*H$_2^{CAAC}$), 42.1 (C_q^{CAAC}), 29.4 (*C*H$_3^{CAAC}$), 28.8 (*C*H$(CH_3)_2^{Dip}$), 28.2 (*C*H$_3^{CAAC}$), 27.1 (CH(*C*H$_3)_2^{Dip}$), 23.1 (CH(*C*H$_3)_2^{Dip}$) ppm. ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 26.7 (s) ppm. Elemental analysis for [$C_{22}H_{37}BClN_3$] (M_w = 389.82 g mol^{-1}): calcd. C 67.79, H 9.57, N 10.78%; found C 67.37, H 9.66, N 10.52%. HRMS LIFDI for [$C_{22}H_{37}BClN_3$] (m/z): calcd. 389.2764, found 389.2757.

Synthesis of 2^{Br}-NMe_2

1 (300 mg, 810 μmol) was dissolved in benzene (4 mL) and $BrB(NMe_2)_2$ (217 mg, 1.22 mmol) was added dropwise at room temperature. The reaction mixture was stirred overnight. After removing all volatiles *in vacuo*, the product was extracted with hexane (7 × 5 mL) and dried *in vacuo* to yield **2^{Br}-NMe_2** (310 mg, 89%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated hexane solution at room temperature. $^1H\{^{11}B\}$ NMR (500.1 MHz, C_6D_6, 297 K): δ = 7.20 (t, 1H, ^3J = 7.6 Hz, *p*-C*H*^{Dip}), 7.15-7.10 (m, 2H, *m*-C*H*^{Dip}), 3.18 (sept, 2H, ^3J = 6.6 Hz, C*H*$(CH_3)_2^{Dip}$), 2.27 (s, 6H, N(C*H*$_3)_2$), 1.70 (s, 2H, C*H*$_2^{CAAC}$), 1.34 (d, 6H, ^3J = 6.7 Hz, CH(C*H*$_3)_2^{Dip}$), 1.32 (s, 6H, C*H*$_3^{CAAC}$), 1.25 (d, 6H, ^3J = 6.7 Hz, CH(C*H*$_3)_2^{Dip}$), 0.98 (s, 6H, C*H*$_3^{CAAC}$) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 297 K): δ = 163.8 (*C*=N^{CAAC}), 149.6 (*o*-C_q^{Dip}), 132.3 (*i*-C_q^{Dip}), 128.6 (*p*-*C*H^{Dip}), 124.3 (*m*-*C*H$_l^{Dip}$), 61.4 (C_q^{CAAC}), 51.9 (*C*H$_2^{CAAC}$), 42.6 (C_q^{CAAC}), 40.5-39.3 (N(C*H*$_3)_2$), 29.7 (*C*H$_3^{CAAC}$), 29.1 (*C*H$(CH_3)_2^{Dip}$), 28.4 (*C*H$_3^{CAAC}$), 27.8 (CH(*C*H$_3)_2^{Dip}$), 23.5 (CH(*C*H$_3)_2^{Dip}$) ppm.^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 24. (s) ppm. Elemental analysis for [$C_{22}H_{37}BBrN_3$] (M_w = 434.27 g

mol^{-1}): calcd. C 60.85, H 8.59, N 9.68%, found C 60.72, H 8.76, N 9.35%. HRMS LIFDI for [$C_{22}H_{37}BBrN_3$] (m/z): calcd. 434.2337, found 434.2254.

Synthesis of 2^{Cl}-Cl

2^{Cl}-NMe$_2$ (30.0 mg, 77.0 μmol) and $BCl_3(SMe_2)$ were combined in toluene (0.6 mL). After 1 d at room temperature, the reaction mixture was filtered and dried *in vacuo*. Single crystals of **2^{Cl}-Cl** (15 mg, 51%) suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated toluene solution at room temperature. $^1H\{^{11}B\}$ NMR (500.1 MHz, C_6D_6, 297 K): δ = 7.14 (t, 1H, ^3J = 7.7 Hz, *p*-C*H*^{Dip}, overlaps with the peak of the solvent), 7.06-7.03 (m, 2H, *m*-C*H*^{Dip}), 2.93 (sept, 2H, ^3J = 6.8 Hz, C*H*$(CH_3)_2^{Dip}$), 1.58 (s, 2H, CH_2^{CAAC}), 1.33 (d, 6H, ^3J = 6.7 Hz, CH(CH_3)$_2^{Dip}$), 1.20-1.14 (m, 12H, CH_3^{CAAC} + CH(CH_3)$_2^{Dip}$), 0.89 (s, 6H, CH_3^{CAAC}) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 297 K): δ = 163.2 (*C*=N^{CAAC}), 148.8 (*o*-C_q^{Dip}), 130.6 (*i*- C_q^{Dip}), 129.5 (*p*-*C*H$_{Aryl}^{Dip}$), 124.6 (*m*-*C*H$_{Aryl}^{Dip}$), 63.9 (C_q^{CAAC}), 50.4 (*C*H$_2^{CAAC}$), 43.7 (C_q^{CAAC}), 29.4 (*C*H$(CH_3)_2^{Dip}$), 29.2 (*C*H$_3^{CAAC}$), 28.3 (*C*H$_3^{CAAC}$), 26.8 (CH(*C*H$_3$)$_2^{Dip}$), 23.2 (CH(*C*H$_3$)$_2^{Dip}$) ppm. ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 24.8 (s) ppm. Elemental analysis for [$C_{20}H_{31}BCl_2N_2$] (M_w = 381.19 g mol^{-1}): calcd. C 63.02, H 8.20, N 7.35%; found C 62.09, H 8.63, N 6.78%. HRMS LIFDI for [$C_{20}H_{31}BCl_2N_2$] (m/z): calcd. 381.2030, found 381.2027.

Synthesis of 2^{Cl}-Dur

1 (20.0 mg, 50.0 mmol) and $DurBCl_2$ (11.5 mg, 50.0 μmol) were combined in benzene (0.6 mL). After 1 d at room temperature, all volatiles were removed *in vacuo*, the residue was redissolved in pentane and dried again *in vacuo* for 50 min. Single crystals of **2^{Cl}-Dur** (16.0 mg, 62%) suitable for X-ray diffraction analysis were obtained by vapour diffusion of pentane in a saturated benzene solution. $^1H\{^{11}B\}$ NMR (500.1 MHz, C_6D_6, 297 K): δ = 7.18 (t, 1H, ^3J = 7.6 Hz, *p*-C*H*^{Dip}, overlaps with the peak of the solvent), 7.12-7.07 (m, 2H, *m*-C*H*^{Dip}), 6.83 (s, 1H, C*H*^{Dur}), 3.00 (br, 2H, C*H*$(CH_3)_2^{Dip}$), 2.27-1.93 (m, 12H, CH_3^{Dur}), 1.70 (s, 2H, CH_2^{CAAC}), 1.38 (s, 6H, CH_3^{CAAC}), 1.29-1.01 (m, 12H, CH(CH_3)$_2^{Dip}$), 0.98 (s, 6H, CH_3^{CAAC}) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 297 K): δ = 161.3 (*C*=N^{CAAC}), 148.8 (*o*-C_q^{Dip}), 134.1 (C_q^{Dur}), 132.8 (*i*-C_q^{Dur}), 132.3 (*i*-C_q^{Dip}), 131.0 (*C*H$_{Aryl}^{Dur}$), 129.1 (*p*-*C*H$_{Aryl}^{Dip}$), 124.9 (*m*-*C*H$_{Aryl}^{Dip}$), 63.3 (C_q^{CAAC}), 51.2 (*C*H$_2^{CAAC}$), 43.0 (C_q^{CAAC}), 29.4 (*C*H$_3^{CAAC}$), 29.1 (*C*H$(CH_3)_2^{Dip}$), 28.9 (*C*H$_3^{CAAC}$), 24.2 (CH(*C*H$_3$)$_2^{Dip}$), 19.9 (*C*H$_3^{Dur}$) ppm. ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 30.4 (s) ppm. Elemental analysis for [$C_{30}H_{44}BClN_2$] (M_w = 478.96 g mol^{-1}): calcd. C 75.23, H 9.26,

N 5.85%, found C 75.14, H 9.25, N 5.75%. HRMS LIFDI for [$C_{30}H_{44}BClN_2$] (m/z): calcd. 478.3281, found 478.3276

Synthesis of 2^{Br}-Mes

To a solution of **1** (225 mg, 604 μmol) in 4 mL benzene $MesBBr_2$ (175 mg, 604 mmol) dissolved in 2 mL benzene was added dropwise. After heating at 60 °C for 1 d all volatiles were removed *in vacuo*, the residue was extracted with benzene (2 × 10 mL) and dried *in vacuo.* Colourless single crystals of **2^{Br}-Mes** (231 mg, 75%) suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated benzene solution at room temperature. $^1H\{^{11}B\}$ NMR (500.1 MHz, C_6D_6, 297 K): δ = 7.19-7.16 (m, 1H, *p*-C*H*^{Dip}, overlaps with the peak of the solvent), 7.14-7.05 (m, 2H, *m*-C*H*^{Dip}), 6.70 (s, 2H, C*H*$_{Aryl}^{Mes}$), 2.98 (br, 2H, C*H*$(CH_3)_2^{Dip}$), 2.54-1.99 (m, 9 H, C*H*$_3^{Mes}$), 1.67 (s, 2H, C*H*$_2^{CAAC}$), 1.50-1.27 (m, 9 H, CH(C*H*$_3)_2^{Dip}$ + C*H*$_3^{CAAC}$), 1.32-1.01 (m, 9 H, CH(C*H*$_3)_2^{Dip}$ + C*H*$_3^{CAAC}$), 0.96 (br s, 6H, C*H*$_3^{CAAC}$) ppm.$^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 297 K): δ = 162.0 (*C*=N^{CAAC}), 149.1 (*o*-C_q^{Dip}), 138.0 (*i*-C_q^{Mes}), 136.7 (C_q^{Mes}), 132.1 (*i*-C_q^{Dip}), 129.2 (*p*-*C*H^{Dip}), 127.5 (*C*H^{Mes}), 125.0 (*m*-*C*H^{Dip}), 63.7 (C_q^{CAAC}), 51.5 (*C*H$_2^{CAAC}$), 43.0 (*C*$_q^{CAAC}$), 29.1 (*C*H$(CH_3)_2^{Dip}$ + *C*H$_3^{CAAC}$), 28.6 (*C*H$_3^{CAAC}$), 24.1 (CH(*C*H$_3)_2^{Dip}$), 21.4 (*C*H$_3^{Mes}$) ppm. ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 26.2 (br s) ppm. Elemental analysis for [$C_{29}H_{42}BBrN_2$] (M_w = 509.38 g mol^{-1}): calcd. C 68.38, H 8.31, N 5.50%; found C 68.31, H 8.14, N 5.18%. HRMS LIFDI for [$C_{29}H_{42}BBrN_2$] (m/z): calcd. 509.2697; found 509.2695.

Synthesis of 2^{Br}-Ph

1 (100 mg, 270 μmol) and $PhBBr_2$ (66.5 mg, 270 μmol) were combined in benzene (2 mL) and was stirred at room temperature overnight. All volatiles were removed *in vacuo.* Colourless single crystals of **2^{Br}-Ph** (101 mg, 81%) were obtained by vapour diffusion of pentane in a saturated benzene solution. $^1H\{^{11}B\}$ NMR (500.1 MHz, C_6D_6, 297 K): δ = 8.12-8.05 (m, 2H, C*H*^{Ph}), 7.27-7.17 (m, 3H, C*H*^{Ph}, overlaps with the peak of the solvent), 7.10 (dd, 1H, ^3J = 7.8 Hz, *p*-C*H*^{Dip}), 7.03-6.99 (m, 2H, *m*-C*H*^{Dip}), 3.11 (sept, 2H, C*H*$(CH_3)_2^{Dip}$), 1.68 (s, 2H, C*H*$_2^{CAAC}$), 1.31 (d, 6H, ^3J = 6.5 Hz, CH(C*H*$_3)_2^{Dip}$), 1.26 (s, 6H, C*H*$_3^{CAAC}$), 1.22 (d, 6H, ^3J = 7.0 Hz, CH(C*H*$_3)_2^{Dip}$), 0.96 (s, 6H, C*H*$_3^{CAAC}$) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 297 K): δ = 162.2 (*C*=N^{CAAC}), 149.1 (*o*-C_q^{Dip}), 136.3 (*o*-*C*H$_{Aryl}^{Ph}$), 131. 0 (*i*-C_q^{Dip}), 130.6 (*p*-*C*H^{Ph}), 129.2 (*p*-*C*H^{Dip}), 127.5 (*m*-*C*H^{Ph}), 124.6 (*m*-*C*H^{Dip}), 63.5 (*C*$_q^{CAAC}$), 50.8 (*C*H$_2^{CAAC}$), 44.0 (*C*$_q^{CAAC}$), 29.5 (*C*H$_3^{CAAC}$), 29.3 (*C*H$(CH_3)_2^{Dip}$), 28.6 (*C*H$_3^{CAAC}$), 27.8 (CH(*C*H$_3)_2^{Dip}$), 23.6 (CH(*C*H$_3)_2^{Dip}$) ppm. ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 29.8 (s) ppm. Elemental analysis for

[$C_{26}H_{36}BBrN_2$] (M_w = 467.30 g mol^{-1}): calcd. C 66.89, H 7.77, N 5.99%; found C 66.72, H 8.03, N 5.93%. HRMS LIFDI for [$C_{26}H_{36}BBrN_2$] (m/z): calcd. 467.2228, found 467.2224.

Synthesis of 3-NMe$_2$

1 (143 mg, 390 μmol) and **2^{Cl}-NMe$_2$** (150 mg, 390 μmol) were combined in benzene (4 mL) and the reaction mixture was heated to 80 °C for 2 d. After removal of all volatiles *in vacuo*, the product was recrystallised from benzene (1.5 mL) leading to the formation of a large crop of colourless crystals, which were washed with benzene (3 × 0.5 mL) and dried *in vacuo* affording **3-NMe$_2$** (164 mg, 65%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated benzene solution at room temperature. ^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6, 297 K): δ = 7.23 (t, 2H, ^3J = 7.3 Hz, *p*-C*H*^{Dip}), 7.20-7,17 (m, 4H, *m*-C*H*^{Dip}, overlaps with the solvent peak), 3.27 (sept, 4H, ^3J = 6.8 Hz, C*H*(CH$_3$)$_2$^{Dip}), 2.73 (s, 6H, N(C*H*$_3$)$_2$), 1.72 (s, 4H, C*H*$_2$^{CAAC}), 1.36 (d, 12H, ^3J = 6.7 Hz, CH(C*H*$_3$)$_2$^{Dip}), 1.30 (d, 12H, ^3J = 6.7 Hz, CH(C*H*$_3$)$_2$^{Dip}), 1.19 (br s, 12H, C*H*$_3$^{CAAC}), 1.04 (s, 12H, C*H*$_3$^{CAAC}) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 297 K): δ = 160.9 (*C*=N^{CAAC}), 150.2 (*o*-*C*$_q$^{Dip}), 134.6 (*i*-*C*$_q$^{Dip}), 127.8 (*p*-*C*H^{Dip}, detected by HSQC, overlaps with the solvent peak), 124.1 (*m*-*C*H^{Dip}), 59.7 (*C*$_q$^{CAAC}), 53.6 (*C*H$_2$^{CAAC}), 41.8 (*C*$_q$^{CAAC}), 40.0 (N(C*H*$_3$)$_2$), 30.2 (*C*H$_3$^{CAAC}), 29.0 (*C*H(CH$_3$)$_2$^{Dip}), 28.3 (CH(*C*H$_3$)$_2$^{Dip}), 24.0 (*C*H$_3$^{CAAC}) ppm. *Note: the ^{13}C resonance for one CH$_3$^{CAAC} could not be detected, presumably due to broadening.* ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 27.3 (s) ppm. Elemental analysis for [$C_{42}H_{68}BN_5$] (M_w = 653.85 g mol^{-1}): calcd. C 77.15, H 10.48, N 10.71%, found C 76.89, H 10.70, N 10.42% HRMS LIFDI for [$C_{42}H_{68}BN_5$] (m/z): calcd. 653.5562, found 653.5554.

Synthesis of 3-Ph

A solution of $PhBBr_2$ (59.0 mg, 240 μmol) in 1 mL benzene was treated with **1** (177 mg, 480 μmol) dissolved in 1 mL benzene. After stirring for 1 d at room temperature, the reaction mixture turned orange. All volatiles were removed *in vacuo*. Colourless single crystals of **3-Ph** (105 mg, 64%) were obtained by slow evaporation of a saturated benzene solution at room temperature. ^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6, 297 K): δ = 7.92 (d, 2H, ^3J = 7.2 Hz, *o*-C*H*^{Ph}), 7.25 (t, 2H, ^3J = 7.4 Hz, *m*-C*H*^{Ph}), 7.28 (t, 1H, ^3J = 7.4 Hz, *p*-C*H*$_{Aryl}$^{Ph}), 7.22 (t, 2H, ^3J = 7.6 Hz, *p*-C*H*^{Dip}), 7.19-7.14 (m, 4H, *m*- C*H*^{Dip}, overlaps with the solvent peak), 3.37 (br s, 4H, C*H*(CH$_3$)$_2$^{Dip}), 1.72 (s, 4H, C*H*$_2$^{CAAC}), 1.46-1.35 (m, 12H, CH(C*H*$_3$)$_2$^{Dip}), 1.33 (d, 12H, ^3J = 6.7 Hz), 1.12-1.01 (m, 24H, C*H*$_3$^{CAAC}) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 297 K): δ = 159.7 (*C*=N^{CAAC}), 150.3 (*o*-*C*$_q$^{Dip}), 141.7 (*C*$_q$^{Ph}), 135.9 (*o*-*C*H^{Ph}), 134.3 (*i*- *C*$_q$^{Dip}), 128.7 (*p*-*C*H^{Ph}),

128.1 (*p*-*C*H^{Dip}), 126.6 (*m*-*C*H^{Ph}), 124.4 (*m*-*C*H^{Dip}), 60.4 (C_q^{CAAC}), 52.9 (CH_2^{CAAC}), 43.0 (C_q^{CAAC}), 30.1 (CH_3^{CAAC}), 29.1 (*C*H(CH$_3$)$_2^{Dip}$), 28.3 (CH(*C*H$_3$)$_2^{Dip}$), 24.0 (CH(*C*H$_3$)$_2^{Dip}$) ppm. ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 29.7 (br s) ppm. Elemental analysis for [$C_{46}H_{67}BN_4$] (M_w = 686.88 g mol^{-1}): calcd. C 80.44, H 9.83, N 8.16%; found C 81.12, H 9.79, N 7.72%. HRMS LIFDI for [$C_{46}H_{67}BN_4$] (m/z): calcd. 686.5453; found 686.5445.

Synthesis of 3-Cl

1 (200 mg, 537 μmol) and $BCl_3 \cdot SMe_2$ (48.0 mg, 268 μmol) were combined in benzene (4 mL) and the reaction mixture was heated at 60 °C for 2 d. After filtration, all volatiles were removed *in vacuo*. The product was collected by recrystallisation from hexane (2 mL), yielding **3-Cl** (105 mg, 61%) as a colourless solid. Colourless crystals of **3-Cl** suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated toluene solution at room temperature. ^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6, 297 K): δ = 7.21 (t, 2H, ^3J = 6.5 Hz, *p*-C*H*^{Dip}), 7.16-7.13 (m, 4H, *m*-C*H*^{Dip}), 3.17 (sept, 4H, ^3J = 6.7 Hz, C*H*(CH$_3$)$_2^{Dip}$), 1.67 (s, 4H, CH_2^{CAAC}), 1.43 (d, 12H, ^3J = 6.8 Hz, CH(C*H*$_3$)$_2^{Dip}$), 1.27 (d, 12H, ^3J = 6.8 Hz, CH(C*H*$_3$)$_2^{Dip}$), 1.20 (br s, 12H, CH_3^{CAAC}), 0.99 (s, 12H, CH_3^{CAAC}) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 297 K): δ = 162.1 (*C*=N^{CAAC}), 149.7 (*o*-C_q^{Dip}), 133.3 (*i*-C_q^{Dip}), 128.0 (*p*-*C*H^{Dip}), 124.1 (*m*-*C*H^{Dip}), 61.0 (C_q^{CAAC}), 52.5 (CH_2^{CAAC}), 43.3 (C_q^{CAAC}), 29.6 (CH_3^{CAAC}), 29.2 (*C*H(CH$_3$)$_2^{Dip}$), 29.1 (CH_3^{CAAC}), 27.2 (CH(*C*H$_3$)$_2^{Dip}$), 23.5 (CH(*C*H$_3$)$_2^{Dip}$) ppm. ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 23.9 (s) ppm. Elemental analysis for [$C_{40}H_{62}BClN_4$] (M_w = 645.22 g mol^{-1}): calcd. C 76.38, H 9.48, N 7.75%, found C 75.37, H 9.69, N 7.82%. HRMS LIFDI for [$C_{40}H_{62}BClN_4$] (m/z): calcd. 644.4751, found 644.4743.

Synthesis of 3-Br

1 (1.00 g, 2.68 mmol) was dissolved in benzene (3 mL) and $BBr_3(SMe_2)$ (420 mg, 1.34 mmol) in benzene (3 mL) was added, and the reaction mixture was heated to 60 °C overnight, whereupon the colour changed from colourless to pink. All volatiles were removed *in vacuo*, and the reaction mixture was filtrated and extracted with benzene (4 × 5 mL) and dried again *in vacuo* to afford **3-Br** as a colourless solid (800 mg, 86%). Colourless crystals were obtained by slow evaporation of a saturated benzene solution at room temperature. ^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6, 297 K): δ = 7.23-7.18 (m, 2H, *p*-C*H*^{Dip}), 7.16-7.13 (m, 4H, *m*-C*H*^{Dip}, overlaps with the solvent peak), 3.14 (sept, 4H, ^3J = 6.8 Hz, C*H*(CH$_3$)$_2^{Dip}$), 1.65 (s, 4H, CH_2^{CAAC}), 1.44 (d, 12H, ^3J = 6.8 Hz, CH(C*H*$_3$)$_2^{Dip}$), 1.26 (d, 12H, ^3J = 6.8 Hz, CH(C*H*$_3$)$_2^{Dip}$), 1.22 (br s, 12H, CH_3^{CAAC}), 0.98 (s, 12H, CH_3^{CAAC}) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 297 K): δ = 162.1

(*C*=N^{CAAC}), 149.6 (*o*-*C*$_q^{Dip}$), 133.1 (*i*-*C*$_q^{Dip}$), 128.5 (*p*-*C*H^{Dip}), 124.2 (*m*-*C*H^{Dip}), 61.3 (*C*$_q^{CAAC}$), 52.4 (*C*H$_2^{CAAC}$), 43.4 (*C*$_q^{CAAC}$), 29.6 (*C*H$_3^{CAAC}$), 29.2 (*C*H(CH$_3$)$_2^{Dip}$), 29.0 (*C*H$_3^{CAAC}$), 27.9 (CH(*C*H$_3$)$_2^{Dip}$), 23.5 (CH(*C*H$_3$)$_2^{Dip}$) ppm. ^{11}B NMR (160.5 MHz, C$_6$D$_6$, 297 K): δ = 21.0 (s) ppm. Elemental analysis for [C$_{40}$H$_{62}$BBrN$_4$] (M_w = 689.68 g mol^{-1}): calcd. C 69.66, H 9.06, N 8.12%, found C 69.40, H 9.27, N 8.05%. HRMS LIFDI for [C$_{40}$H$_{62}$BBrN$_4$] (m/z): calcd. 689.4324, found 689.4310.

Synthesis of 3-N$_3$

3-Br (200 mg, 290 μmol) was dissolved in dichloromethane (3.5 mL) and TMSN$_3$ (50.0 mg, 435 μmol) was added. After 1 d at room temperature, all volatiles were removed *in vacuo*. Colourless crystals of **3-N$_3$** (153 mg, 81%) suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated benzene solution at room temperature. ^{1}H{^{11}B} NMR (500.1 MHz, C$_6$D$_6$, 297 K): δ = 7.20 (t, 2H, ^3J = 6.4 Hz, *p*-C*H*^{Dip}), 7.16-7.13 (m, 4H, *m*-C*H*^{Dip}), 3.18 (sept, 4H, ^3J = 6.8 Hz, C*H*(CH$_3$)$_2^{Dip}$), 1.66 (s, 4H, C*H*$_2^{CAAC}$), 1.40 (d, 12H, ^3J = 6.6Hz, CH(C*H*$_3$)$_2^{Dip}$), 1.27 (d, 12H, ^3J = 6.8 Hz, CH(C*H*$_3$)$_2^{Dip}$), 1.14 (s, 12H, C*H*$_3^{CAAC}$), 0.99 (s, 12H, C*H*$_3^{CAAC}$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C$_6$D$_6$, 297 K): δ = 163.1 (*C*=N^{CAAC}), 149.8 (*o*-*C*$_q^{Dip}$), 133.5 (*i*- *C*$_q^{Dip}$), 128.3 (*p*-*C*H^{Dip}), 124.1 (*m*-*C*H^{Dip}), 60.7 (*C*$_q^{CAAC}$), 52.4 (*C*H$_2^{CAAC}$), 42.3 (*C*$_q^{CAAC}$), 29.6 (*C*H$_3^{CAAC}$), 29.2 (*C*H(CH$_3$)$_2^{Dip}$), 29.0 (*C*H$_3^{CAAC}$), 27.6 (CH(*C*H$_3$)$_2^{Dip}$), 23.5 (CH(*C*H$_3$)$_2^{Dip}$) ppm. ^{11}B NMR (160.5 MHz, C$_6$D$_6$, 297 K): δ = 24.3 ppm. FT-IR (solid-state): $\tilde{\nu}$ = 2139, 2109 2036, 2027 (N=N=N), 1670, 1614, 1591, 1577 (N=C$_{CAAI}$) cm^{-1}. Elemental analysis for [C$_{40}$H$_{62}$BN$_7$] (M_w = 651,80 g/mol): calcd. C 73.71, H 9.59, N 15.04%, found C 73.69, H 9.81, N 15.04%. HRMS LIFDI for [C$_{40}$H$_{62}$BN$_7$] (m/z): calcd. 651.5154, found 651.5140.

Synthesis of 3-NCS

To a solution of **3-Br** (20.0 mg, 30.0 μmol) dissolved in benzene (0.6 mL) TMSNCS (4.00 mg, 30.0 μmol) was added. After 1 d at room temperature, all volatiles were removed *in vacuo*. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated benzene solution, yielding **3-NCS** (18 mg, 93%). ^{1}H{^{11}B} NMR (500.1 MHz, C$_6$D$_6$, 297 K): δ = 7.18 (t, 2H, ^3J = 6.7 Hz, *p*-C*H*^{Dip}, overlaps with the solvent peak), 7.13-7.10 13 (m, 4H, *m*-C*H*^{Dip}), 3.09 (sept, 4H, ^3J = 6.8 Hz, C*H*(CH$_3$)$_2^{Dip}$), 1.61 (s, 4H, C*H*$_2^{CAAC}$), 1.39 44 (d, 12H, ^3J = 6.7 Hz, CH(C*H*$_3$)$_2^{Dip}$), 1.24 (d, 12H, ^3J = 6.8 Hz, CH(C*H*$_3$)$_2^{Dip}$), 1.07 (s, 12H, C*H*$_3^{CAAC}$), 0.95 (s, 12H, C*H*$_3^{CAAC}$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C$_6$D$_6$, 297 K): δ = 163.7 (*C*=N^{CAAC}), 149.5 (*o*-*C*$_q^{Dip}$), 133.1 (*i*-*C*$_q^{Dip}$), 128.5 (*p*-*C*H^{Dip}), 124.1 (*m*-*C*H^{Dip}), 61.2 (*C*$_q^{CAAC}$),

52.1 (CH_2^{CAAC}), 42.8 (C_q^{CAAC}), 29.5 (CH_3^{CAAC}), 29.2 ($CH(CH_3)_2^{Dip}$), 28.8 (CH_3^{CAAC}), 27.0 ($CH(CH_3)_2^{Dip}$), 23.3 ($CH(CH_3)_2^{Dip}$) ppm. ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 17.5 (s) ppm. FT-IR (solid-state): $\tilde{\nu}$ = 2105 (br, N=C_{NCS}), 1744, 1688 (N=C_{CAAI}) cm^{-1}. Elemental analysis for [$C_{41}H_{62}BN_5S$] (M_w = 667.85 g mol^{-1}): calcd. C 73.74, H 9.36, N 10.49, S 4.80%; found C 72.28, H 9.27, N 10.10, S 4.35%. HRMS LIFDI for [$C_{41}H_{62}BN_5S$] (m/z): calcd. 667.4813, found 667.4802.

Synthesis of 4

To a solution of **1** (159 mg, 430 μmol) dissolved in benzene (1.5 mL) $B_2Cl_2(NMe_2)_2$ (100 mg, 550 μmol) dissolved in benzene (1 mL) was added dropwise and stirred at room temperature overnight. All volatiles were removed *in vacuo* and the product was washed with hexane (4 × 4 mL). The product was dried again *in vacuo*, yielding **4** (146 mg, 77%) as a colourless solid. 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, 297 K): δ = 7.18 (t, 1H, ^3J = 6.6 Hz, *p*-C*H*^{Dip}), 7.12 (m, 2H, *m*-C*H*^{Dip}), 3.22 (sept, 2H, ^3J = 6.6 Hz, C*H*$(CH_3)_2^{Dip}$), 2.75 (s, 3H, N(C*H*$_3)_2$), 2.66 (s, 3H, N(C*H*$_3)_2$), 2.59 (s, 3H, N(C*H*$_3)_2$), 2.35 (s, 3H, N(C*H*$_3)_2$), 1.78 (s, 2H, C*H*$_2^{CAAC}$), 1.38 (br s, 6H, C*H*$_3^{CAAC}$), 1.27 (d, 6H, ^3J = 6.9 Hz, CH(C*H*$_3)_2^{Dip}$), 1.18 (br s, 6H, CH(C*H*$_3)_2^{Dip}$), 1.06 (s, 6H, C*H*$_3^{CAAC}$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 297 K): δ = 157.3 (*C*=N^{CAAC}), 150.2 (*o*-C_q^{Dip}), 134.1 (*i*-C_q^{Dip}), 128.1 (*p*-*C*H^{Dip}), 123.8 (*m*-*C*H^{Dip}), 59.8 (C_q^{CAAC}), 52.3 (CH_2^{CAAC}), 41.8 (N(C*H*$_3)_2$), 41.2 (N(C*H*$_3)_2$), 40.7 (C_q^{CAAC}), 37.9 (N(C*H*$_3)_2$), 37.4 (N(C*H*$_3)_2$, 29.0 ($CH(CH_3)_2^{Dip}$), 29.0 (CH_3^{CAAC}), 26.3 ($CH(CH_3)_2^{Dip}$), 23.5 (CH_3^{CAAC}) ppm. ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 40.8, 30.0 ppm. Elemental analysis for [$C_{24}H_{43}B_2ClN_4$] (M_w = 444.71 g mol^{-1}): calcd. C 64.82, H 9.75, N 12.60%, found C 64.74, H 9.92, N 12.47%. HRMS LIFDI for [$C_{22}H_{37}BBrN_3$] (m/z): calcd. 444.3355, found 444.3357.

Synthesis of 5-NMe$_2$

1 (100 mg, 270 μmol) and $B_2Br_2(NMe_2)_2$ (36 mg, 130 μmol) were combined in benzene (2.5 mL) and stirred at room temperature for 3 days. All volatiles were removed *in vacuo* and **5-NMe$_2$** was recrystallised from benzene (2 mL) leading to the formation colourless single crystals (58 mg, 61%), which were suitable for X-ray diffraction analysis. ^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6, 297 K): δ = 7.19-7.12 (m, 6H, *p*-C*H*^{Dip} + *m*-C*H*^{Dip}), 3.28 (sept, 4H, ^3J = 6.8 Hz, C*H*$(CH_3)_2^{Dip}$), 2.47 (s, 6H, N(C*H*$_3)_2$), 2.16 (s, 6H, N(C*H*$_3)_2$, 1.88 (br s, 4H, C*H*$_2^{CAAC}$), 1.30-1.28 (m, 36H, CH(C*H*$_3)_2^{Dip}$ + C*H*$_3^{CAAC}$), 1.20-1.01 (m, 12H, C*H*$_3^{CAAC}$) ppm. ^{13}C{^{1}H} NMR (125.8

MHz, C_6D_6, 297 K): δ = 153.4 (*C*=N^{CAAC}), 150.6 (*o*-C_q^{Dip}), 149.8 (*o*-C_q^{Dip}), 135.0 (*i*- C_q^{Dip}), 127.9 (*p*-*C*H^{Dip}), 124.1 (*m*-*C*H^{Dip}), 59.0 (C_q^{CAAC}), 52.8 (*C*H$_2^{CAAC}$), 40.5 (N(C*H*$_3$)$_2$), 39.8 (C_q^{CAAC}), 38.4 (N(C*H*$_3$)$_2$), 31.8 (*C*H$_3^{CAAC}$), 31.1 (*C*H$_3^{CAAC}$), 29.1 (*C*H(CH$_3$)$_2^{Dip}$), 28.3 (*C*H$_3^{CAAC}$), 26.3 (CH(*C*H$_3$)$_2^{Dip}$), 24.8 (CH(*C*H$_3$)$_2^{Dip}$), 23.3 (CH(*C*H$_3$)$_2^{Dip}$) ppm. ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 30.8 (br s) ppm. Elemental analysis for [$C_{24}H_{43}B_2ClN_4$] (M_w = 708.74 g mol^{-1}): calcd. C 74.57, H 10.52, N 11.86%, found C 74.91, H 10.78, N 11.92%. HRMS LIFDI for [$C_{24}H_{43}B_2ClN_4$] (m/z): calcd. 708.6144, found 708.6156.

Synthesis of 5-Mes

1 (20 mg, 54 μmol) and $B_2Mes_2Cl_2$ (9.0 mg, 27 μmol) were dissolved in benzene and the reaction mixture was heated to 80 °C for 3 days. All volatiles were removed *in vacuo* and small amount of yellow single crystals of **5-Mes** suitable for X-ray diffraction analysis could be obtained by slow evaporation of a saturated benzene solution (5.0 mg, 21%). ^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6, 297 K): δ = 7.08 (t, 2H, ^3J = 7.8 Hz, *p*-C*H*^{Dip}), 6.98-6.94 (m, 2H, *m*-C*H*^{Dip}), 6.94-6.89 (m, 2H, *m*-C*H*^{Dip}), 6.78 (s, 2H, *m*-C*H*^{Mes}), 6.53 (s, 2H, *m*-C*H*^{Mes}), 3.34 (sept, 2H, ^3J = 6.9 Hz, C*H*(CH$_3$)$_2^{Dip}$), 2.76 (sept, 2H, ^3J = 6.9 Hz, C*H*(CH$_3$)$_2^{Dip}$), 2.70 (s, 6H, C*H*$_3^{Mes}$), 2.26 (s, 6H, C*H*$_3^{Mes}$), 1.88 (d, 2H, ^2J = 12.7 Hz, C*H*$_2^{CAAC}$), 1.76 (d, 2H, ^2J = 12.6 Hz, C*H*$_2^{CAAC}$), 1.72 (s, 6H, C*H*$_3^{CAAC}$), 1.46 (s, 6H, C*H*$_3^{CAAC}$), 1.44 (s, 6H, C*H*$_3^{CAAC}$), 1.27 (s, 6H, C*H*$_3^{Mes}$), 1.17 (d, 6H, ^3J = 6.7 Hz, CH(C*H*$_3$)$_2^{Dip}$), 0.93 (d, 6H, ^3J = 6.9 Hz, CH(C*H*$_3$)$_2^{Dip}$), 0.75 (s, 6H, C*H*$_3^{CAAC}$), 0.72 (d, 6H, ^3J = 6.7 Hz, CH(C*H*$_3$)$_2^{Dip}$), 0.38 (d, 6H, ^3J = 6.9 Hz, CH(C*H*$_3$)$_2^{Dip}$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 297 K): δ = 152.8 (*C*=N^{CAAC}), 150.7 2 (*o*-C_q^{Dip}), 149.2 2 (*o*-C_q^{Dip}), 144.4 (C_q^{Mes}), 139.0 (C_q^{Mes}), 136.8 (C_q^{Mes}), 136.3 (*i*-C_q^{Dip}), 133.6 (*i*-C_q^{Mes}), 127.2 (*C*H^{Mes}) 125.3 (*p*-*C*H^{Dip}), 124.8 (*m*-*C*H^{Dip}), 124.4 (*m*-*C*H^{Dip}), 60.8 (C_q^{CAAC}), 53.0 (*C*H$_2^{CAAC}$), 42.1 (C_q^{CAAC}), 32.5 (*C*H$_3^{CAAC}$), 30.5 (*C*H$_3^{CAAC}$), 29.1 (*C*H$_3^{CAAC}$), 29.0 (*C*H(CH$_3$)$_2^{Dip}$), 28.6 (*C*H(CH$_3$)$_2^{Dip}$), 26.9 (*C*H$_3^{CAAC}$), 26.5 (CH(*C*H$_3$)$_2^{Dip}$), 25.4 (CH(*C*H$_3$)$_2^{Dip}$), 24.8 (*C*H$_3^{Mes}$), 24.5 (CH(*C*H$_3$)$_2^{Dip}$), 23.6 (CH(*C*H$_3$)$_2^{Dip}$), 21.6 (*C*H$_3^{Mes}$) ppm. ^{11}B NMR (160.5 MHz, C_6D_6, 297 K): δ = 35.8 ppm. Elemental analysis for [$C_{18}H_{22}B_2Cl_2$] (M_w = 858.96 g mol^{-1}): calcd. C 81.10, H 9.86, N 6.52%, found C 79.34, H 9.86, N 6.32%). HRMS LIFDI for [$C_{18}H_{22}B_2Cl_2$] (m/z): calcd. 857.6798, found 857.6783.

NMR spectra of isolated compounds

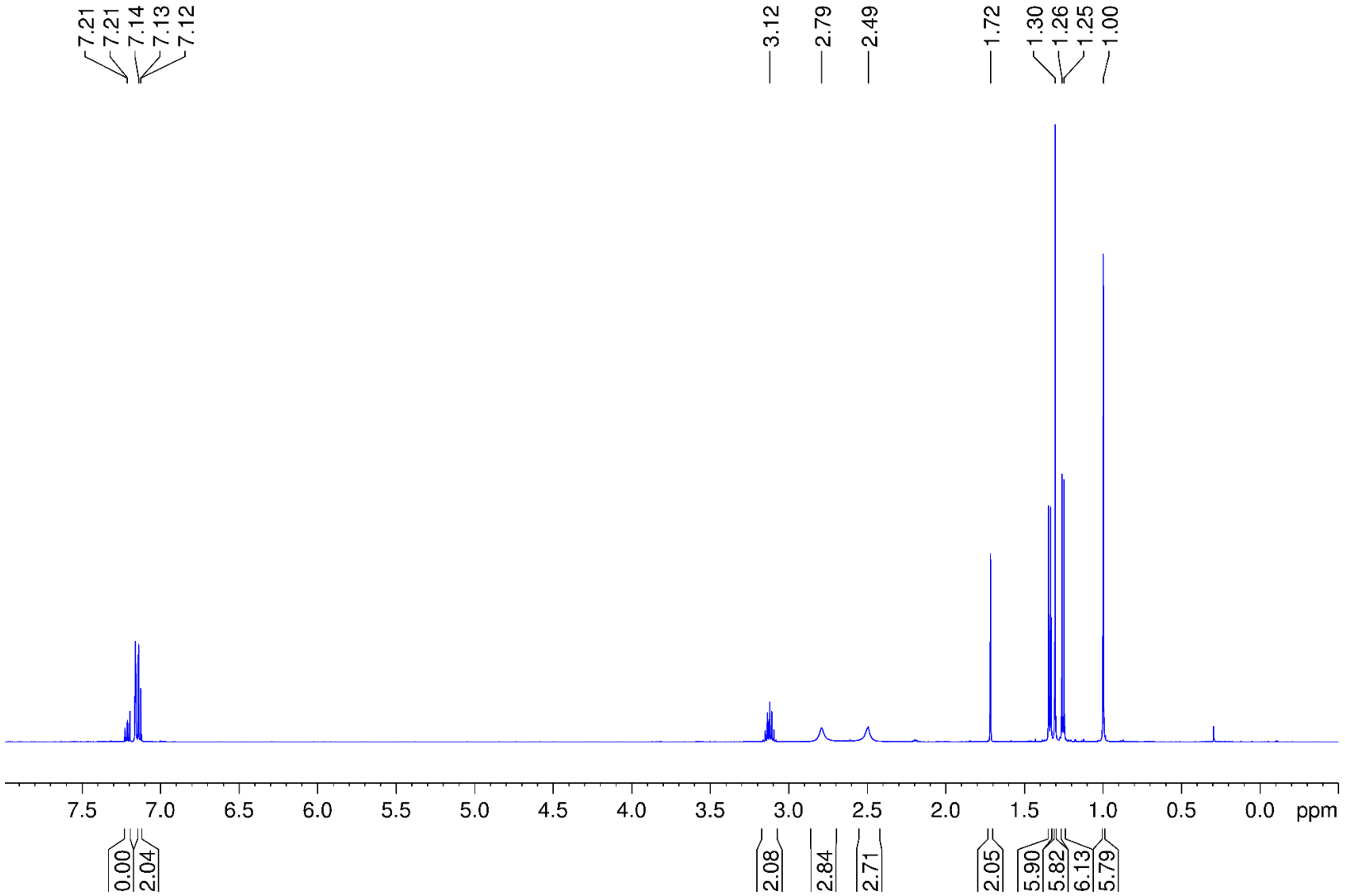


Figure S1. $^{1}H\{^{11}B\}$ NMR spectrum of **2^{Cl}-NMe_2** in C_6D_6.

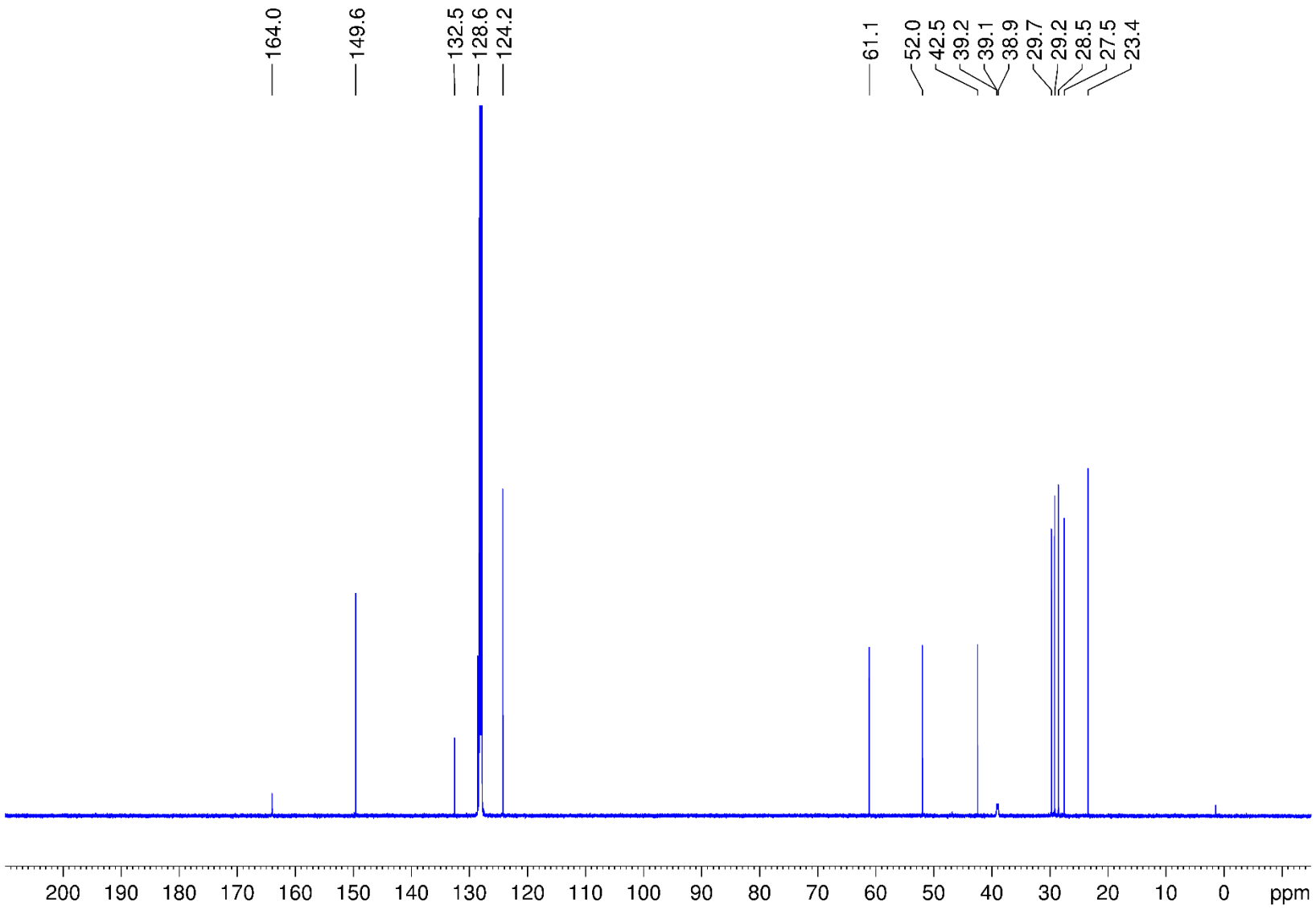


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **2^{Cl}-NMe$_2$** in C_6D_6.

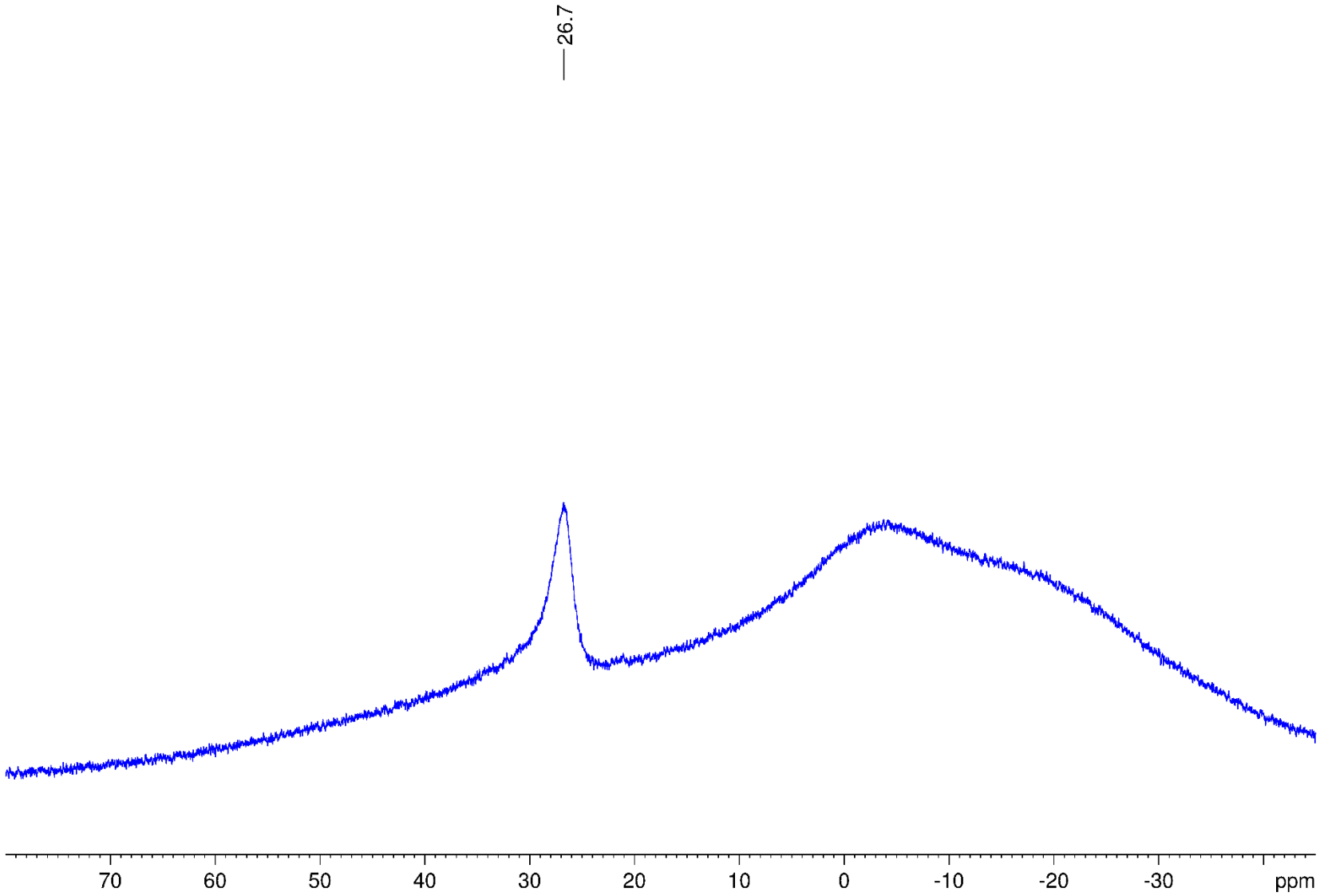


Figure S3. ^{11}B NMR spectrum of **2^{Cl}-NMe$_2$** in C_6D_6.

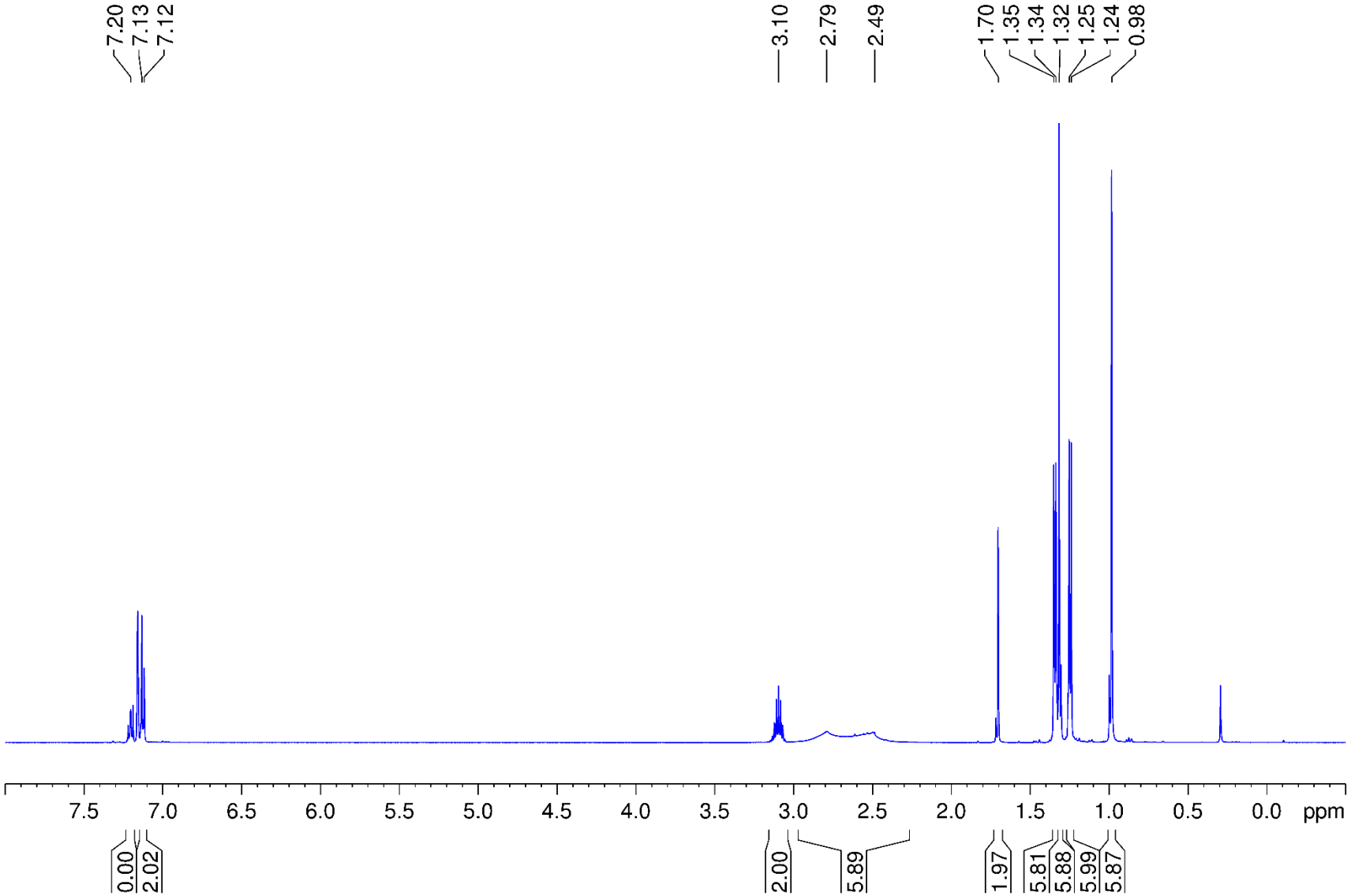


Figure S4. $^{1}H\{^{11}B\}$ NMR spectrum of **2^{Br}-NMe_2** in C_6D_6.

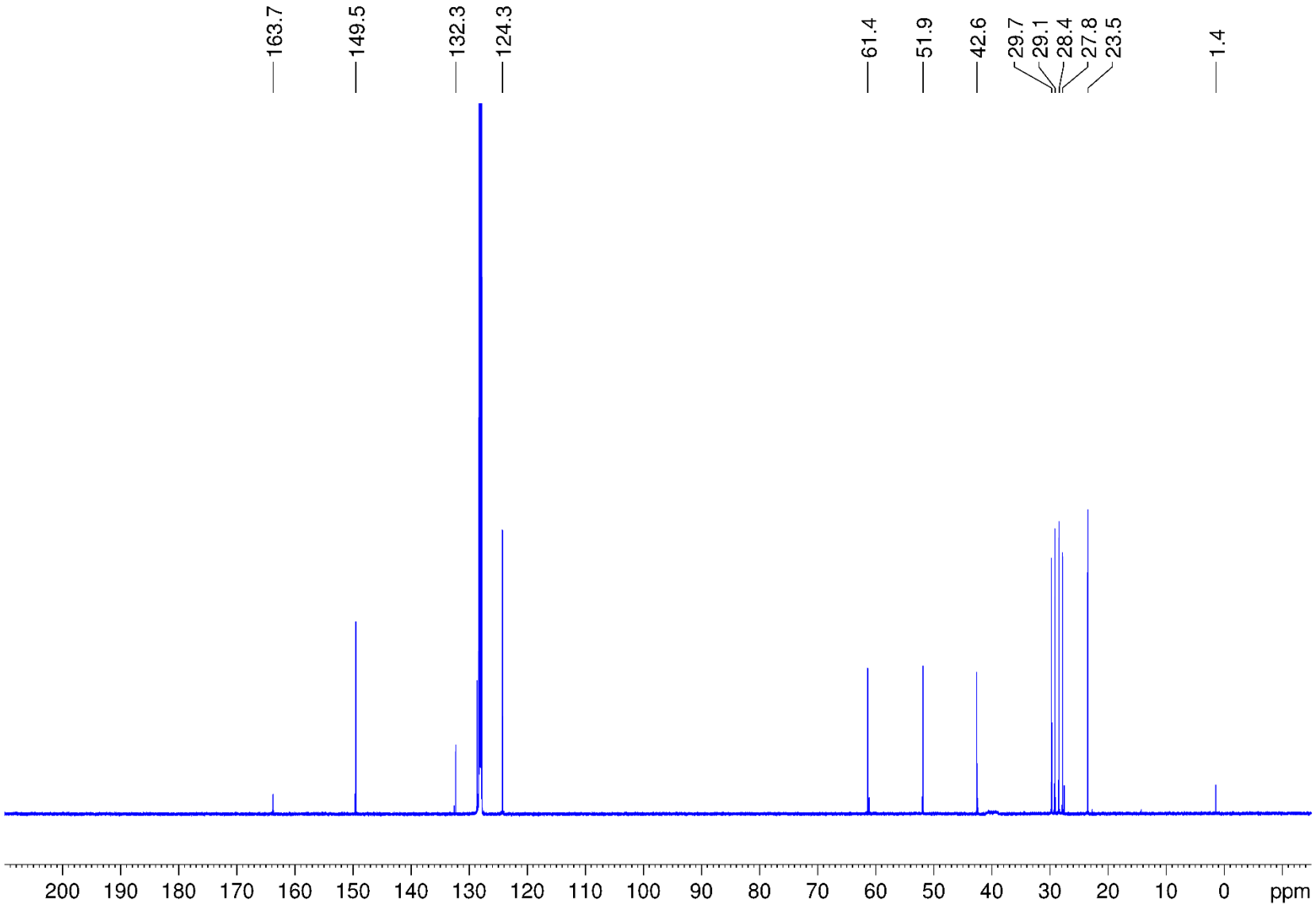


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **2^{Br}-NMe_2** in C_6D_6.

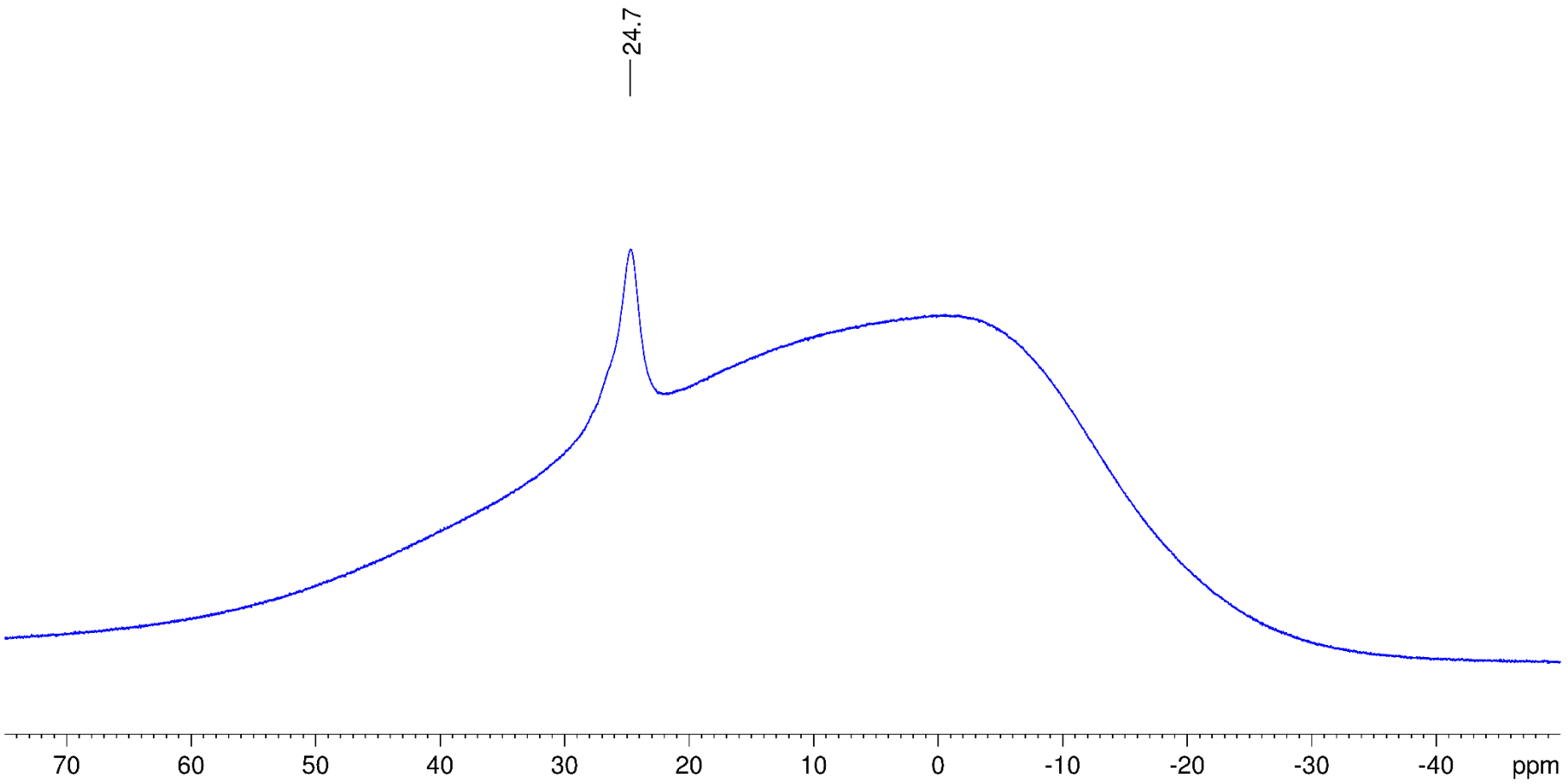


Figure S6. ^{11}B NMR spectrum of **2^{Br}-NMe$_2$** in C_6D_6.

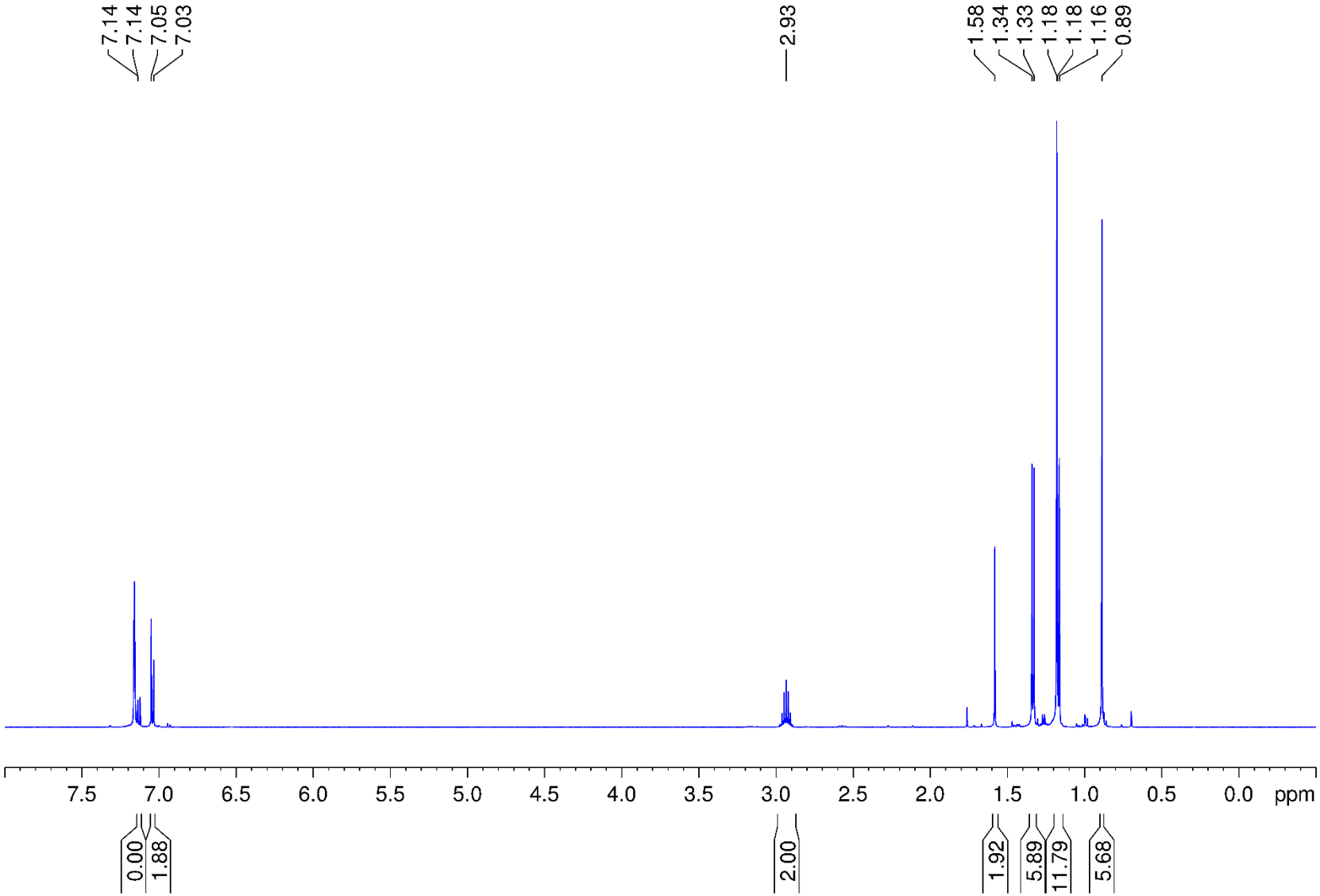


Figure S7. $^{1}H\{^{11}B\}$ NMR spectrum of **2^{Cl}-Cl** in C_6D_6.

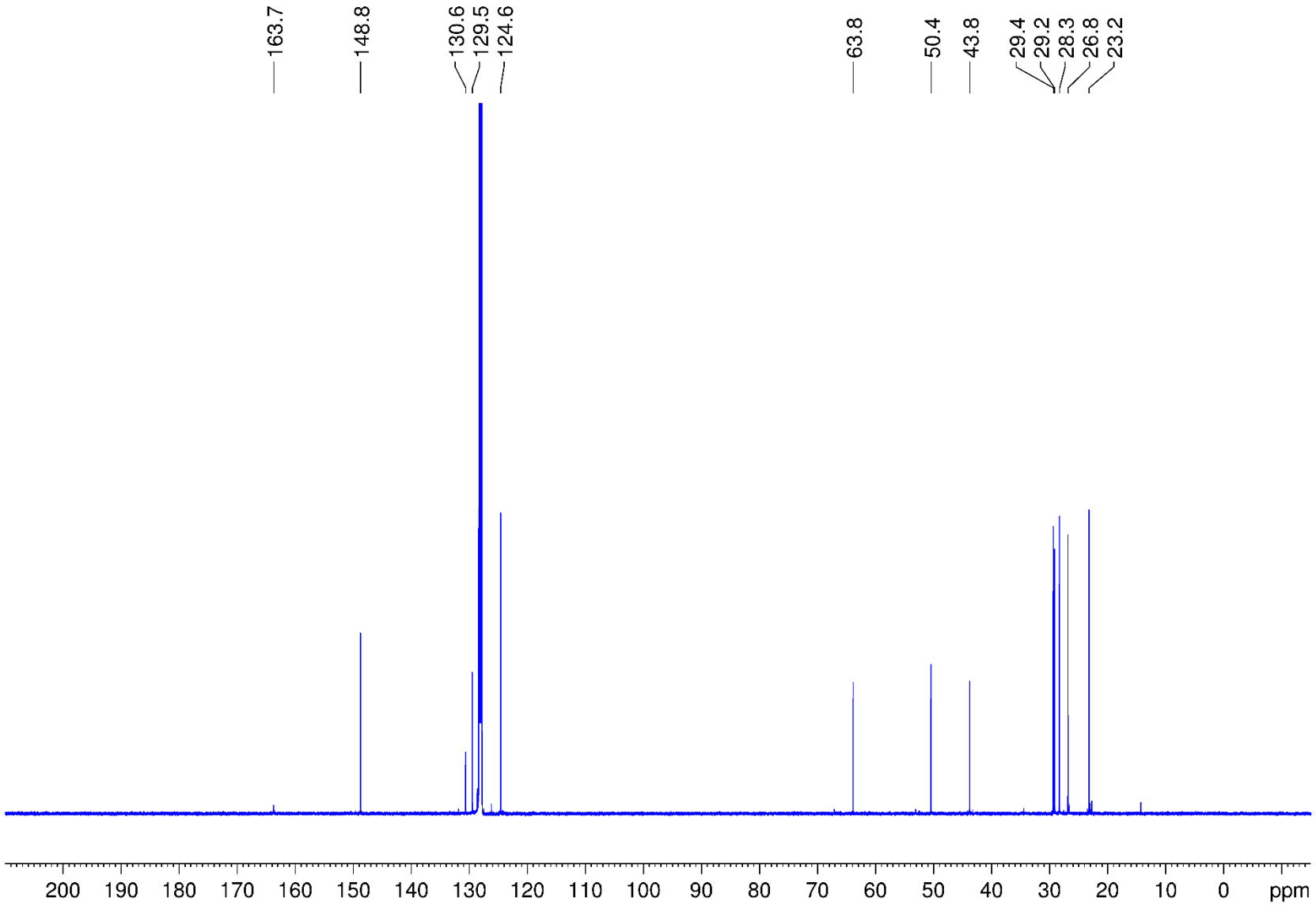


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **2^{Cl}-Cl** in C_6D_6.

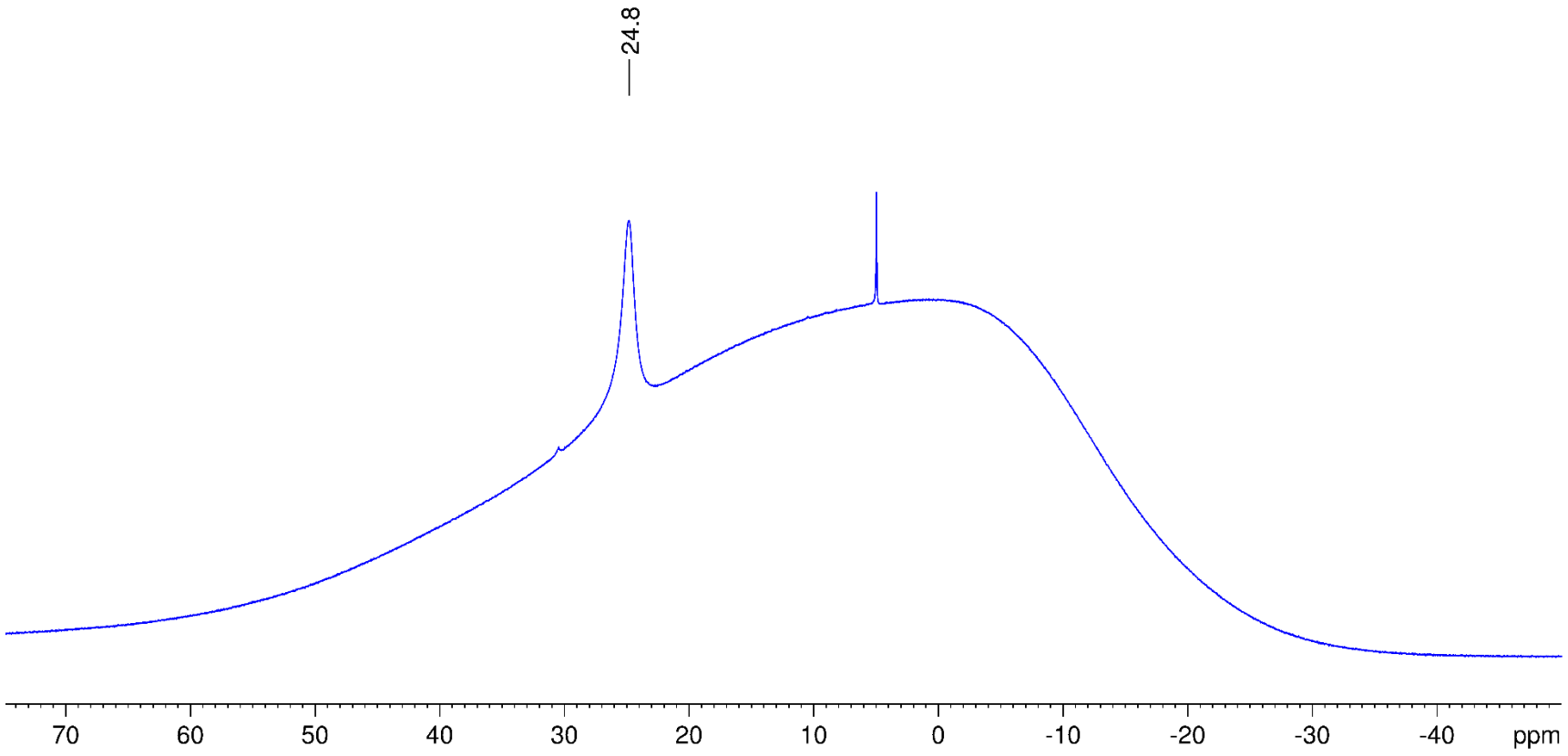


Figure S9. ^{11}B NMR spectrum of **2^{Cl}-Cl** in C_6D_6.

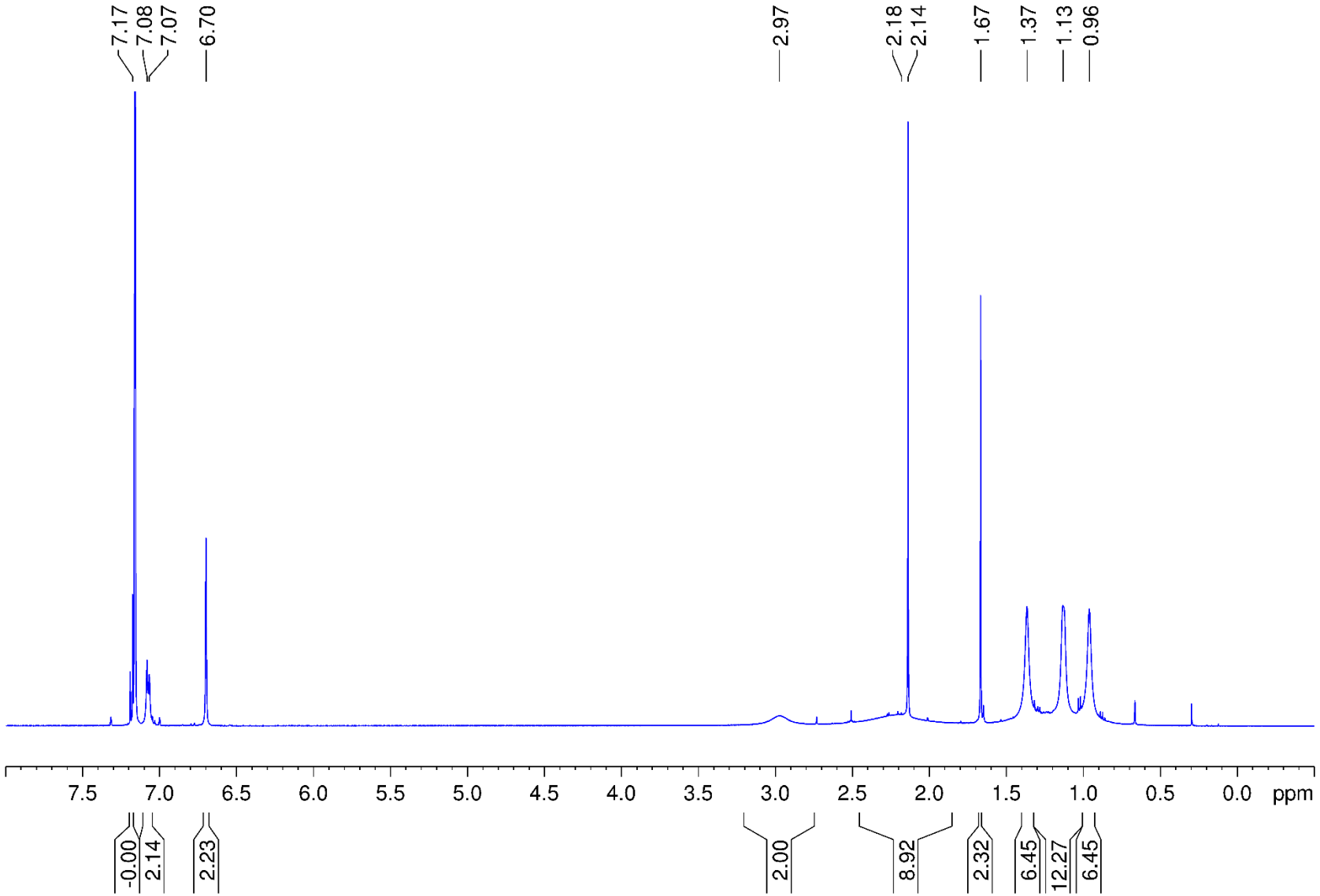


Figure S10. $^{1}H\{^{11}B\}$ NMR spectrum of **2^{Cl}-Dur** in C_6D_6.

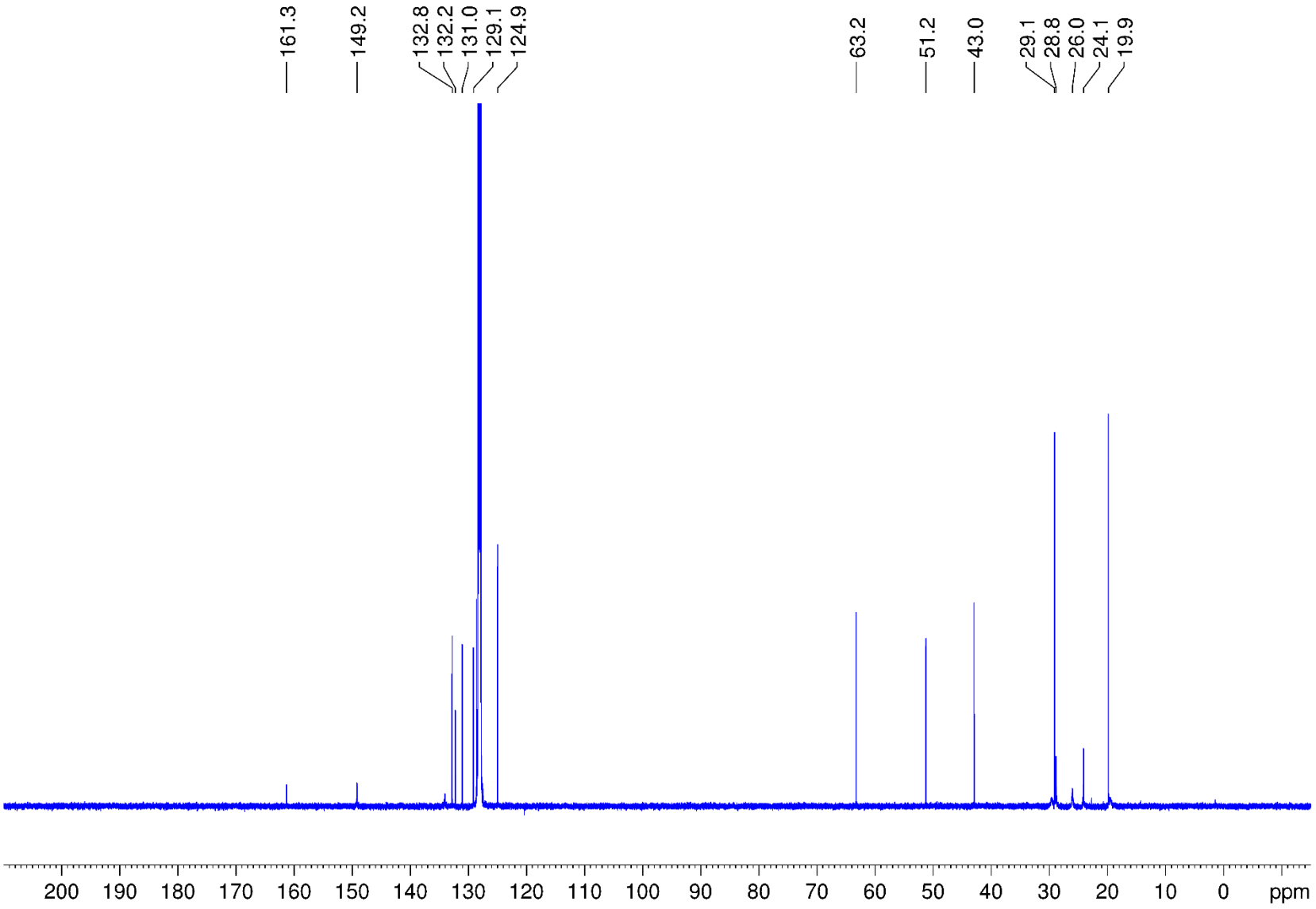


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **2^{Cl}-Dur** in C_6D_6.

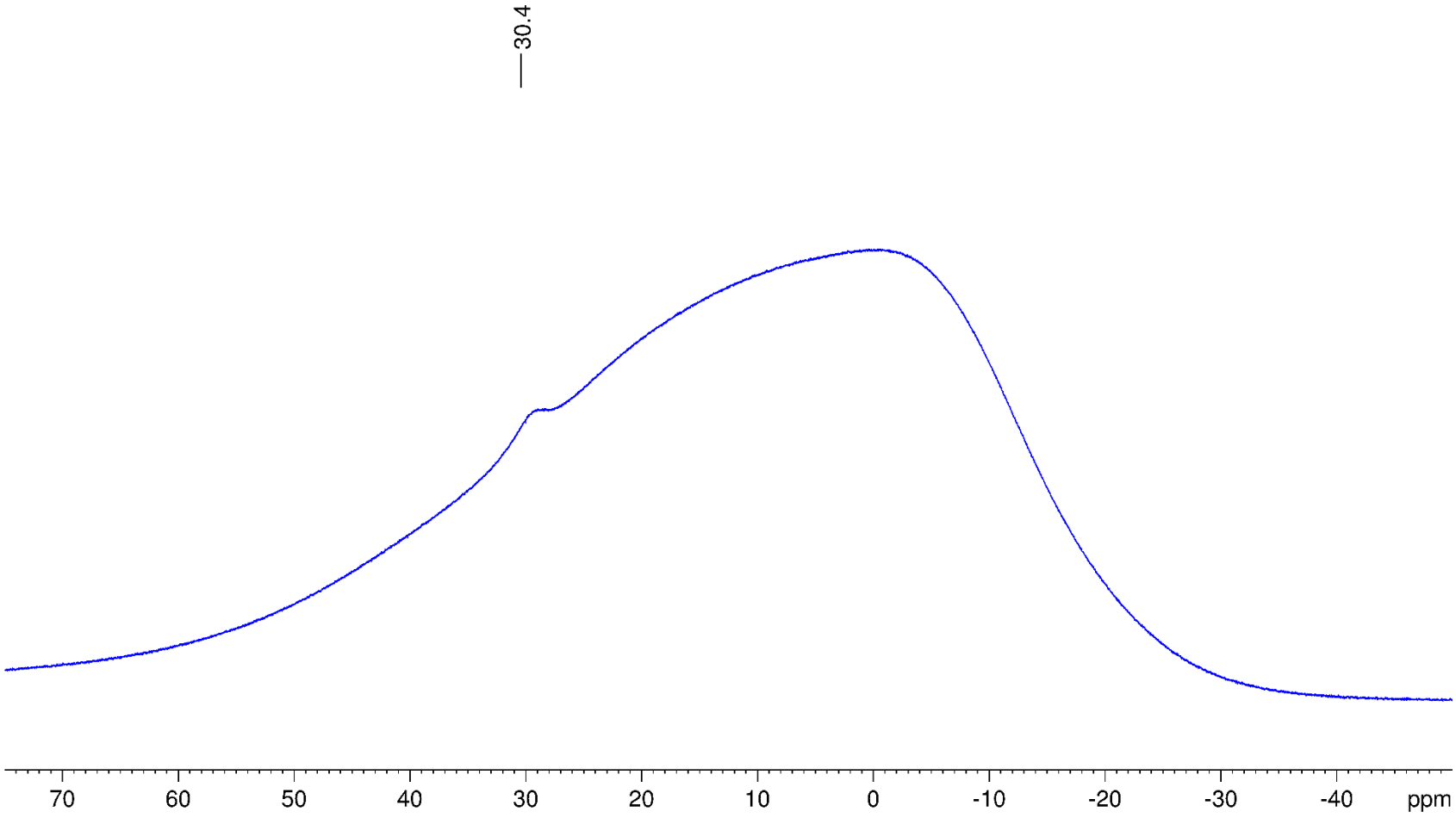


Figure S12. ^{11}B NMR spectrum of **2^{Cl}-Dur** in C_6D_6.

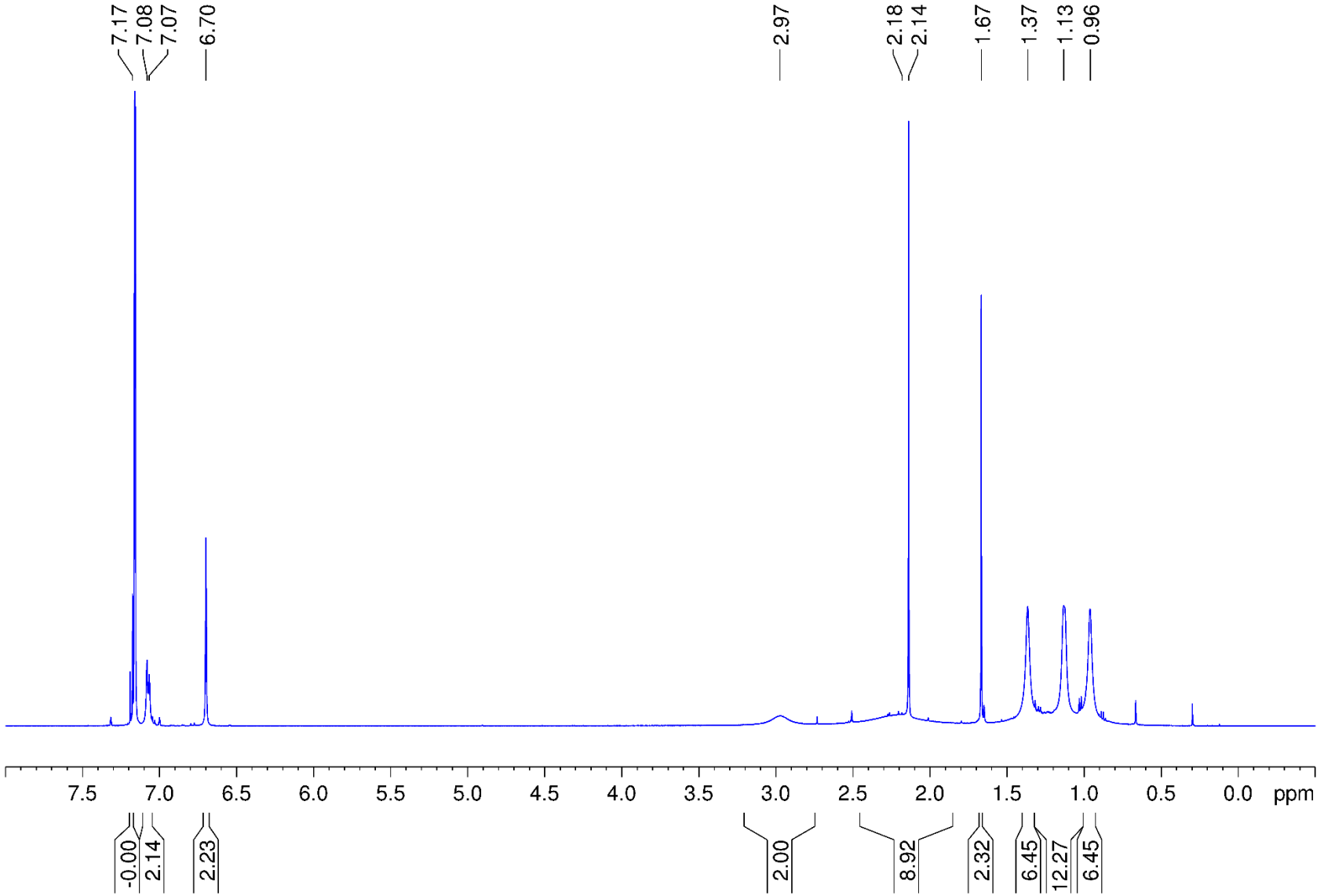


Figure S13. $^{1}H\{^{11}B\}$ NMR spectrum of **2^{Br}-Mes** in C_6D_6.

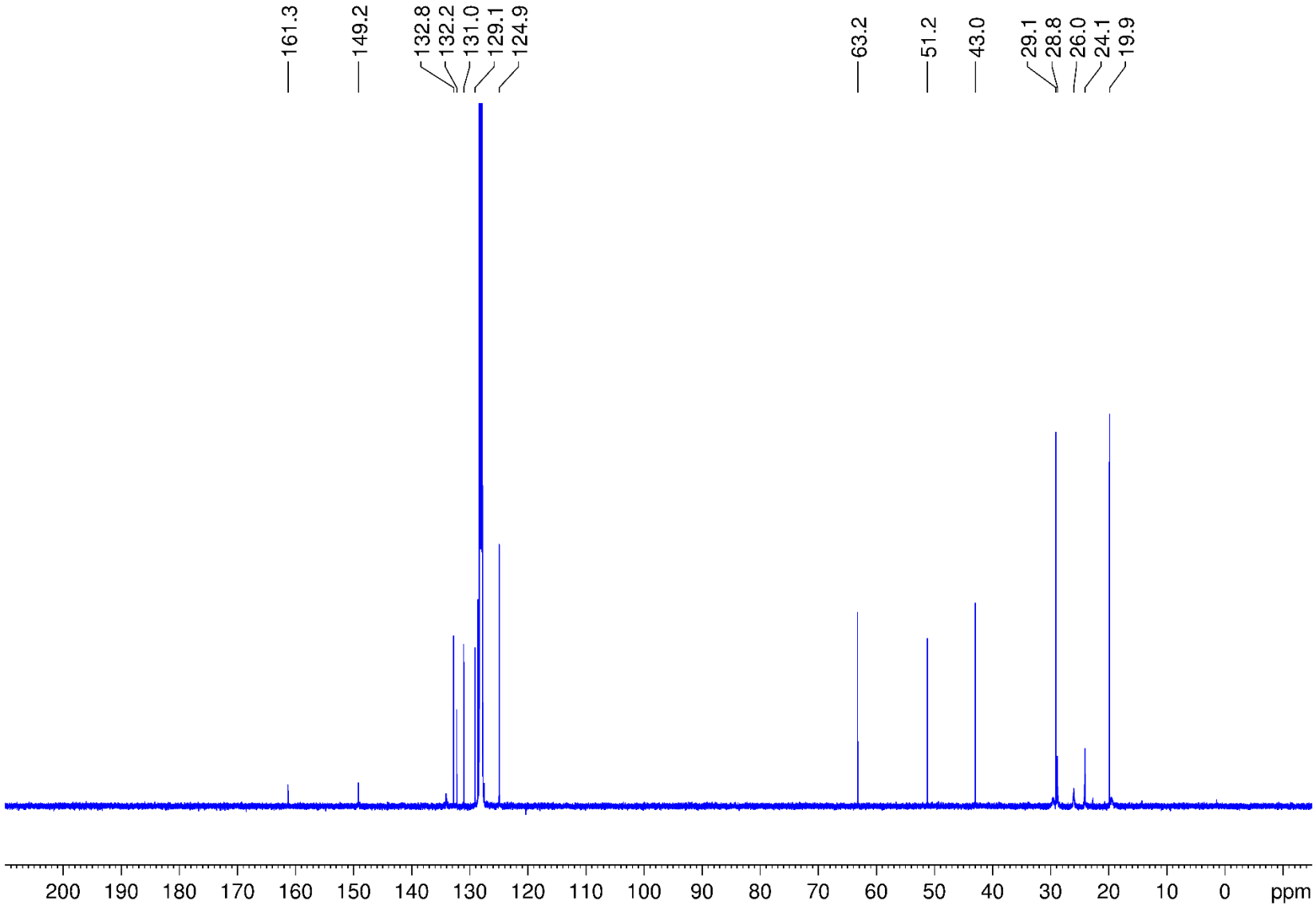


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **2^{Br}-Mes** in C_6D_6.

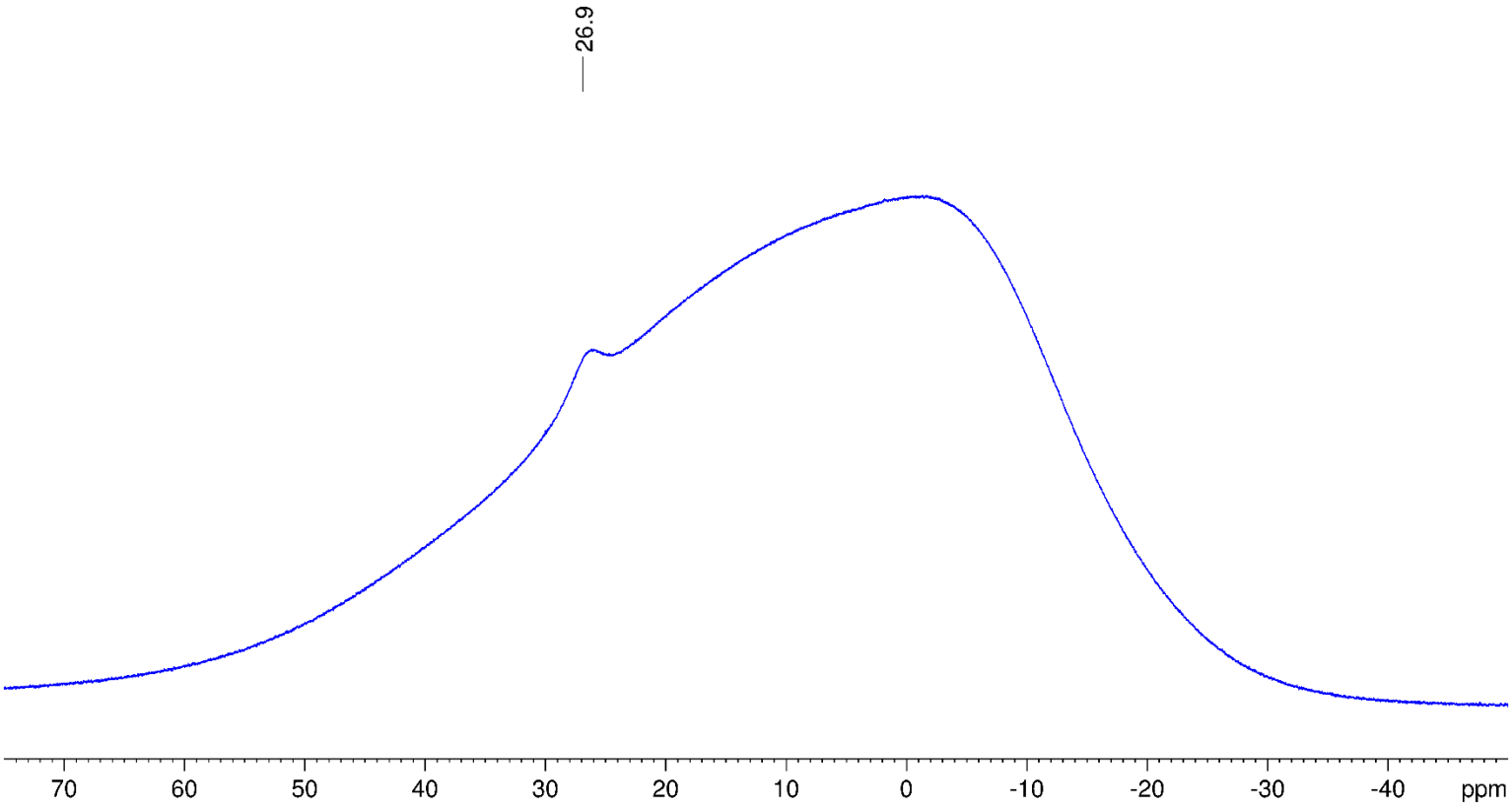


Figure S15. ^{11}B NMR spectrum of **2^{Br}-Mes** in C_6D_6.

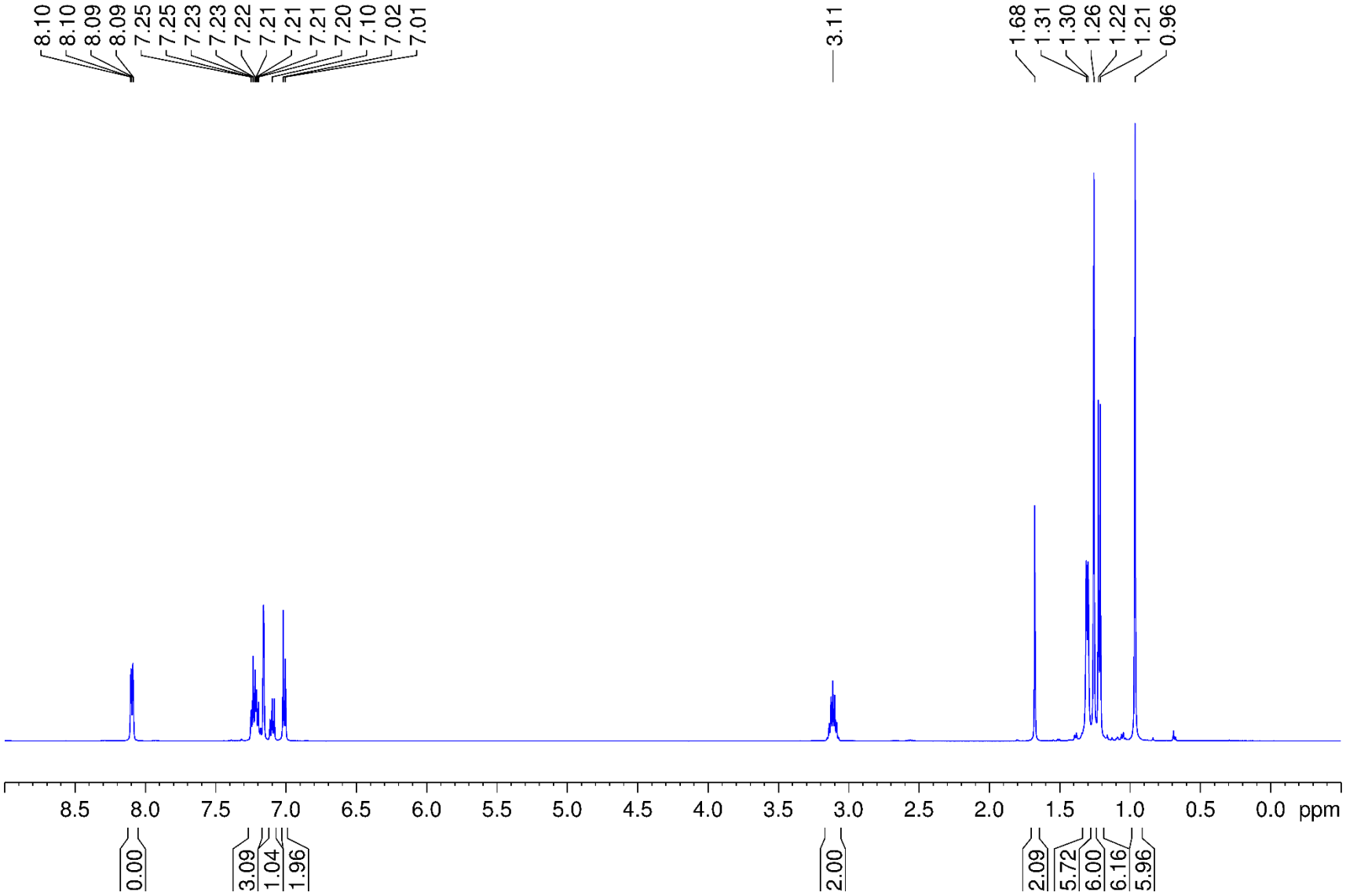


Figure S16. $^{1}H\{^{11}B\}$ NMR spectrum of **2^{Br}-Ph** in C_6D_6.

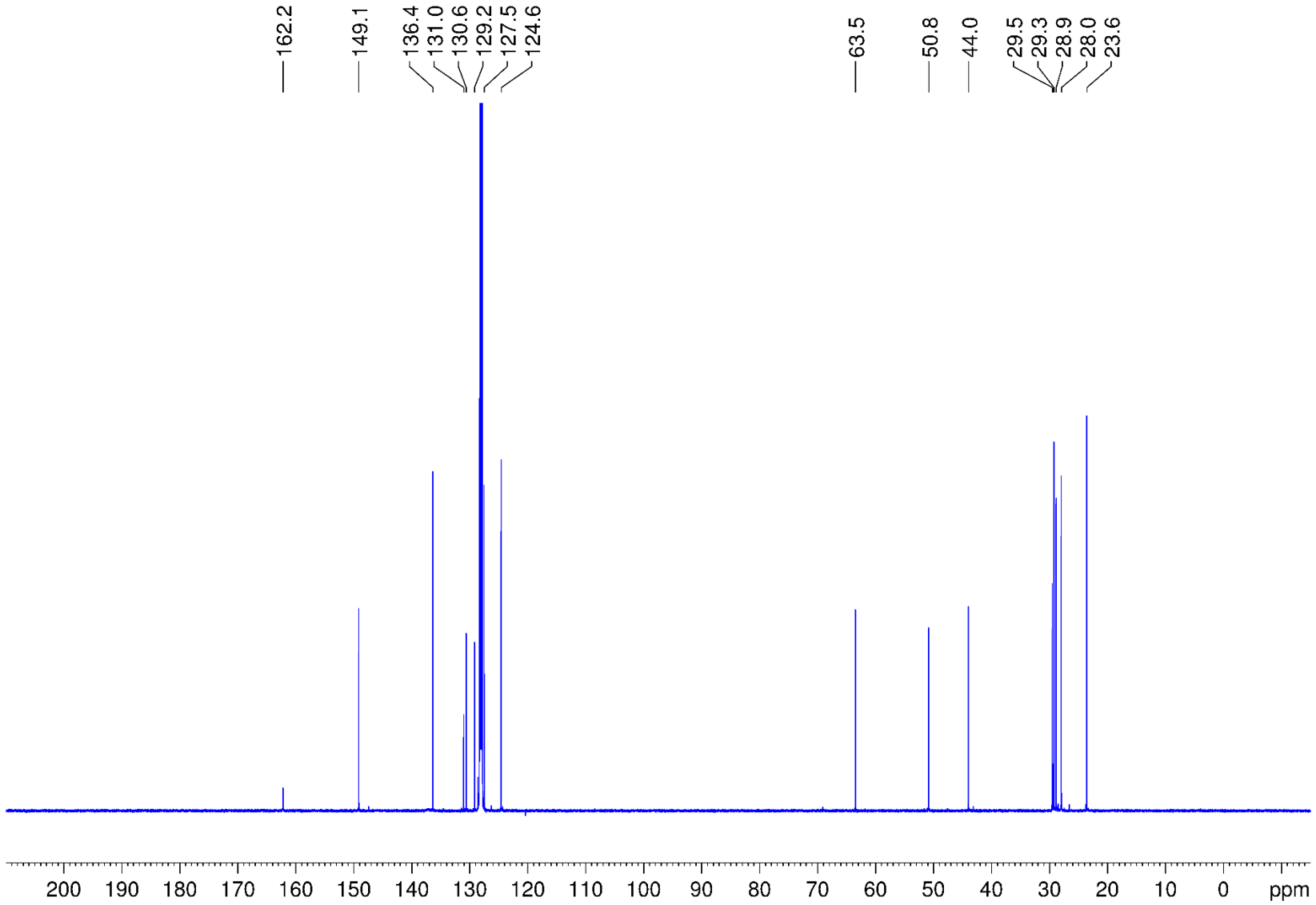


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **2^{Br}-Ph** in C_6D_6.

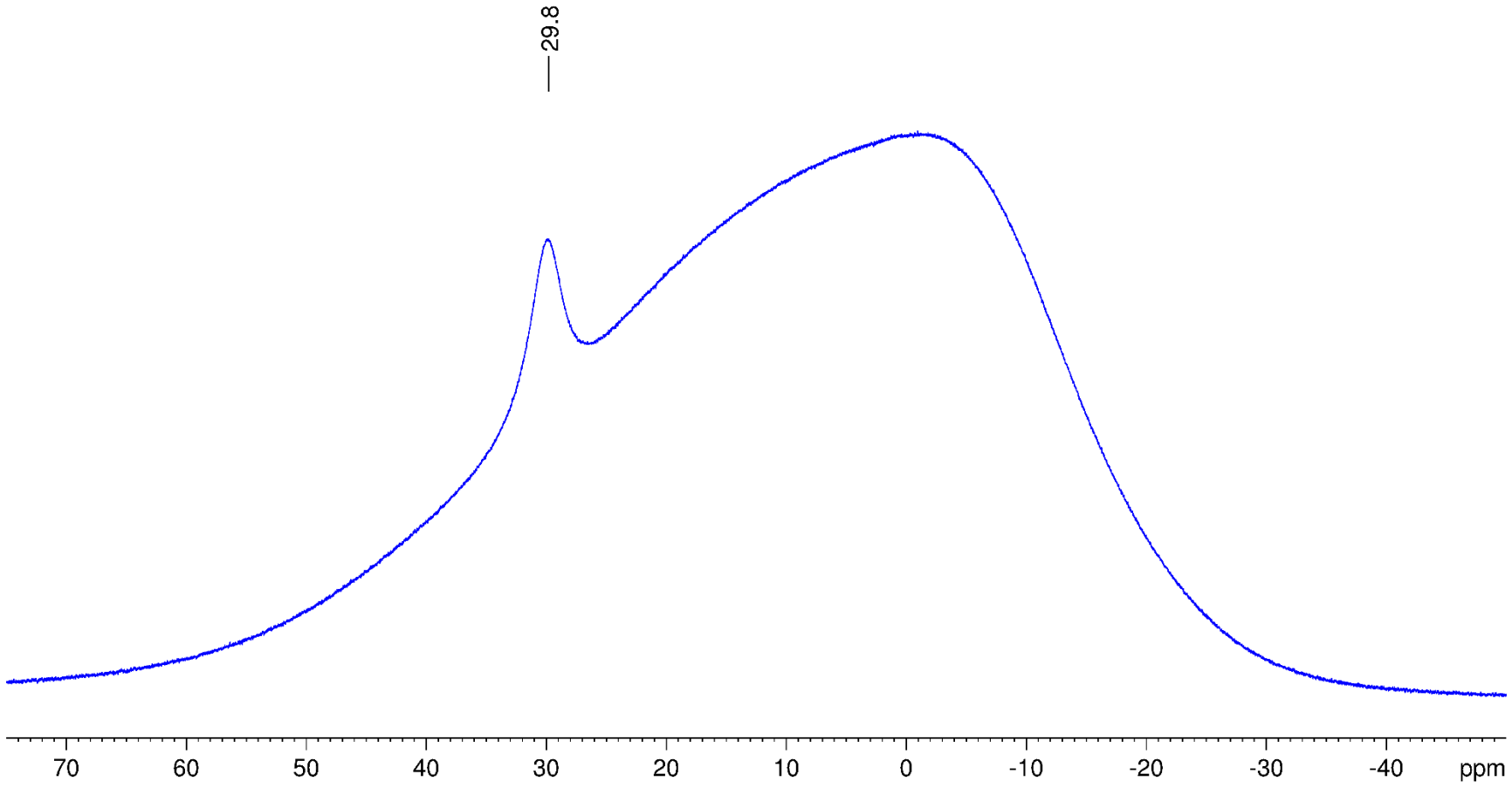


Figure S18. ^{11}B NMR spectrum of **2^{Br}-Ph** in C_6D_6.

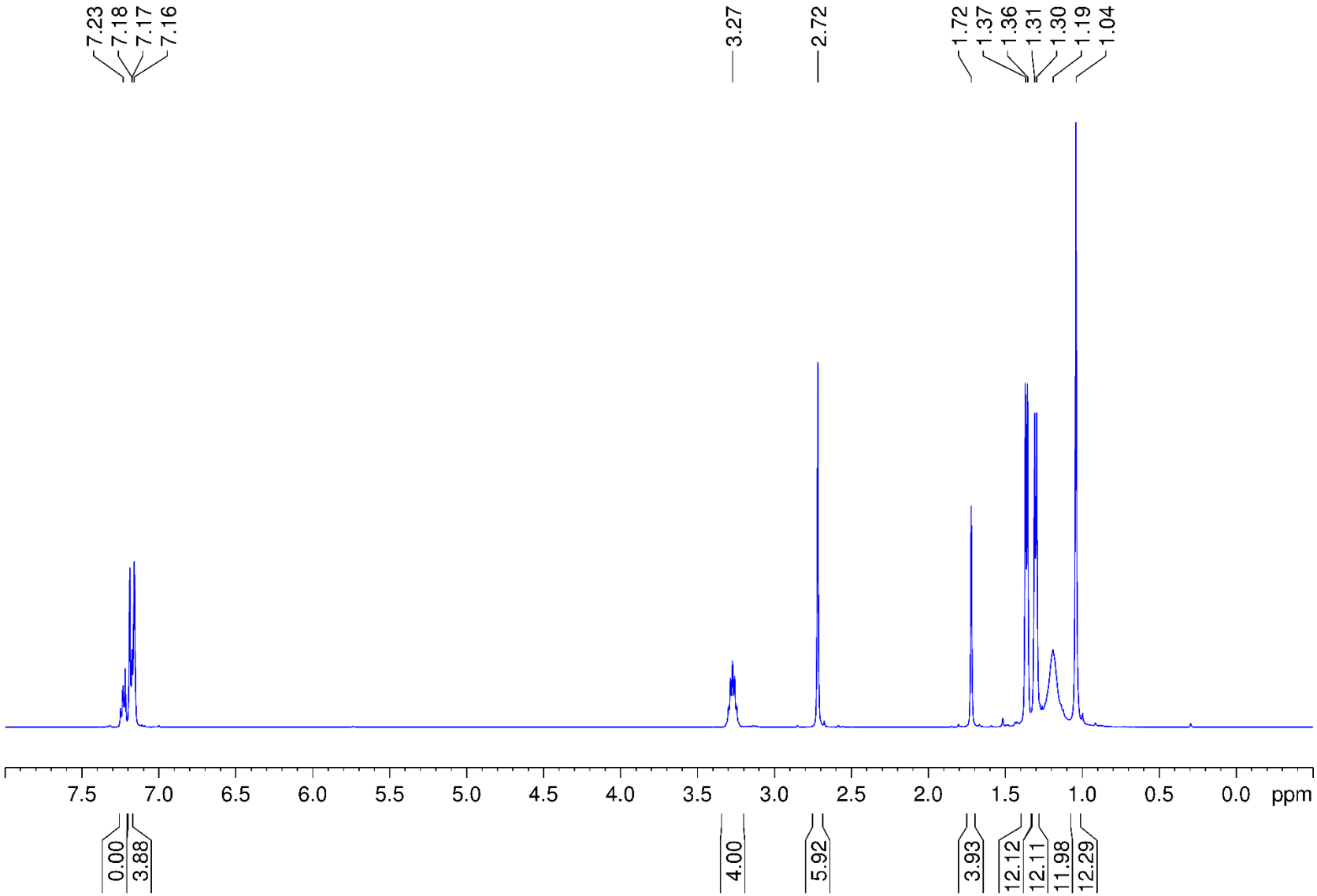


Figure S19. $^{1}H\{^{11}B\}$ NMR spectrum of **3-NMe$_2$** in C_6D_6.

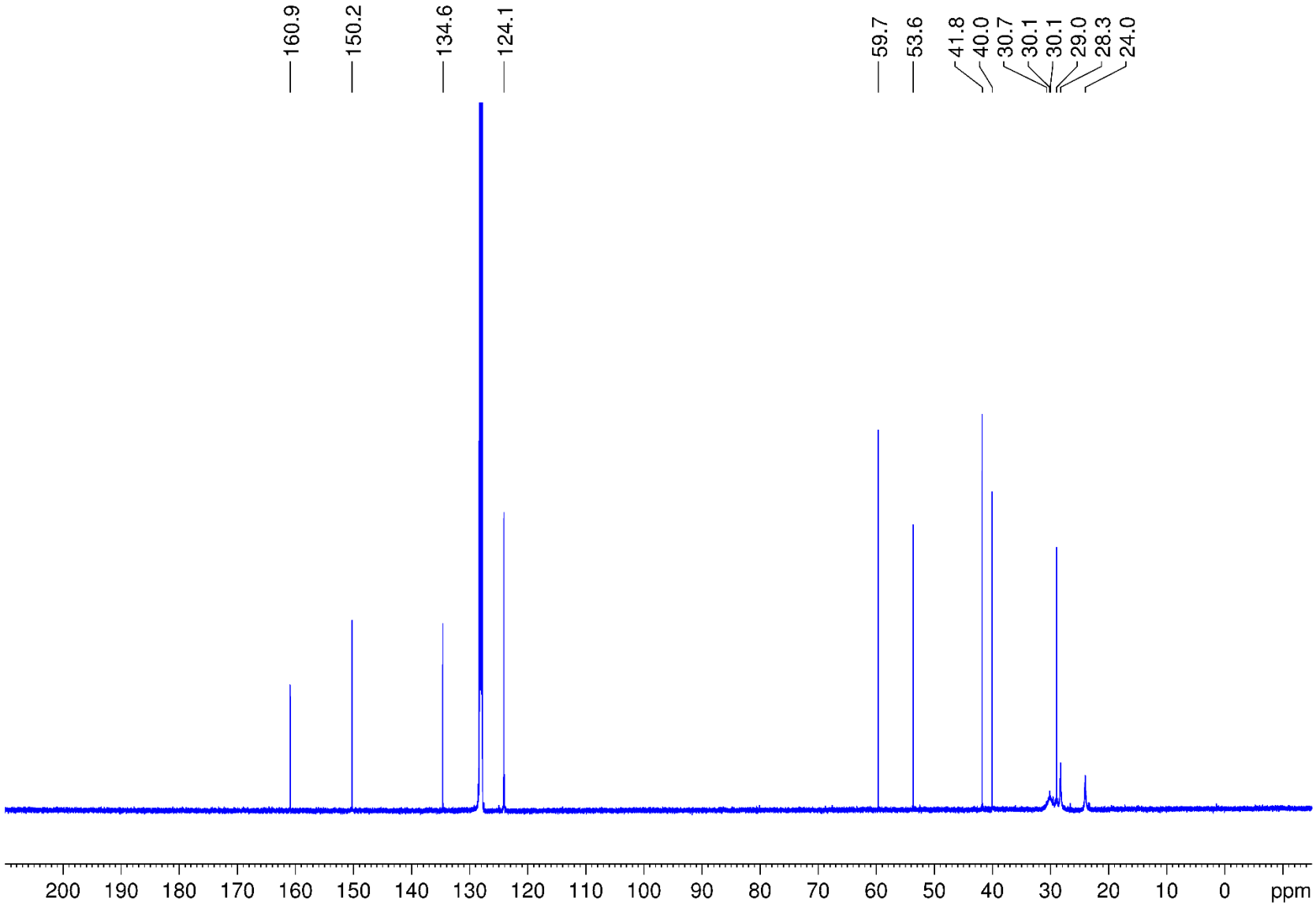


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **3-NMe$_2$** in C_6D_6.

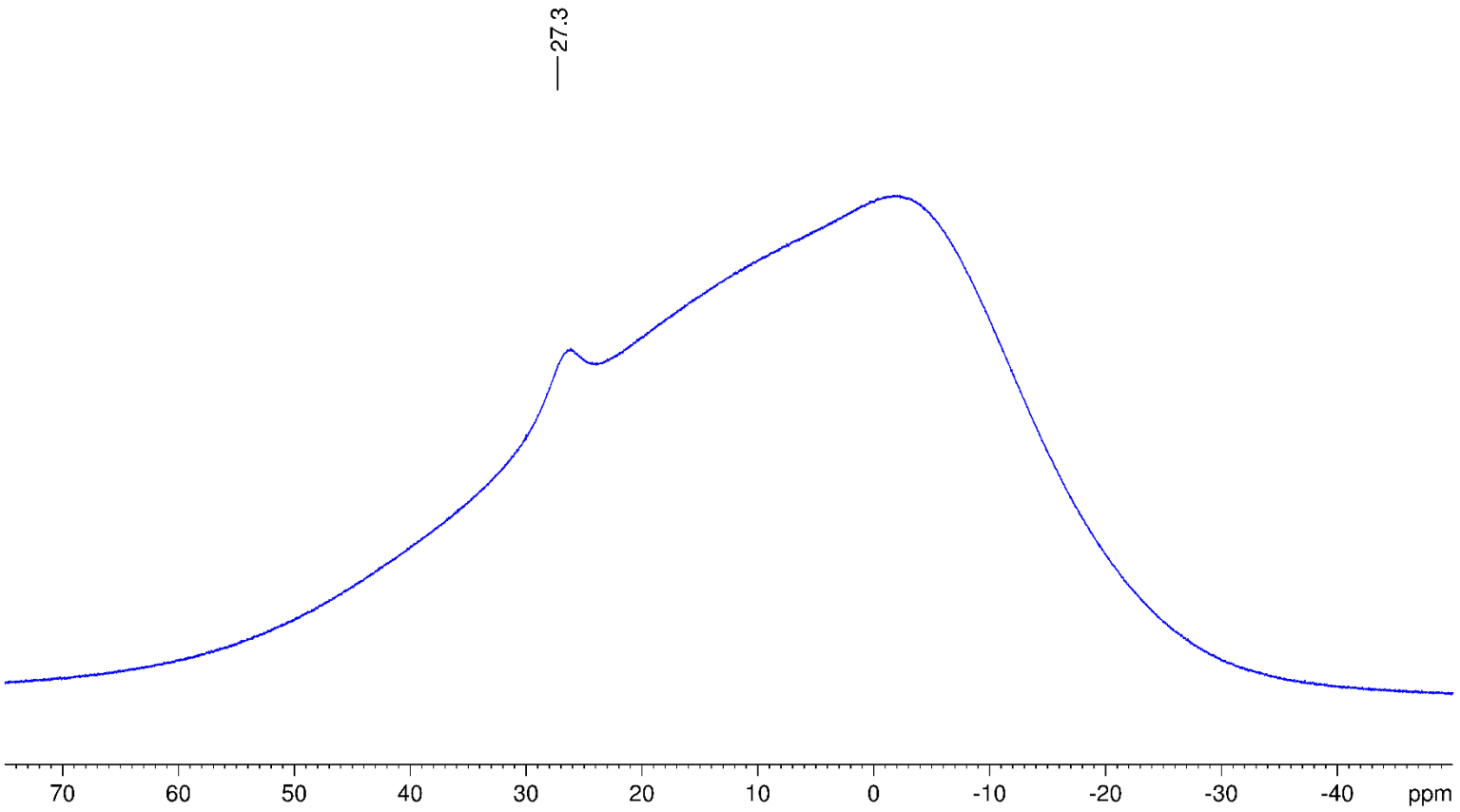


Figure S21. ^{11}B NMR spectrum of **3-NMe$_2$** in C_6D_6.

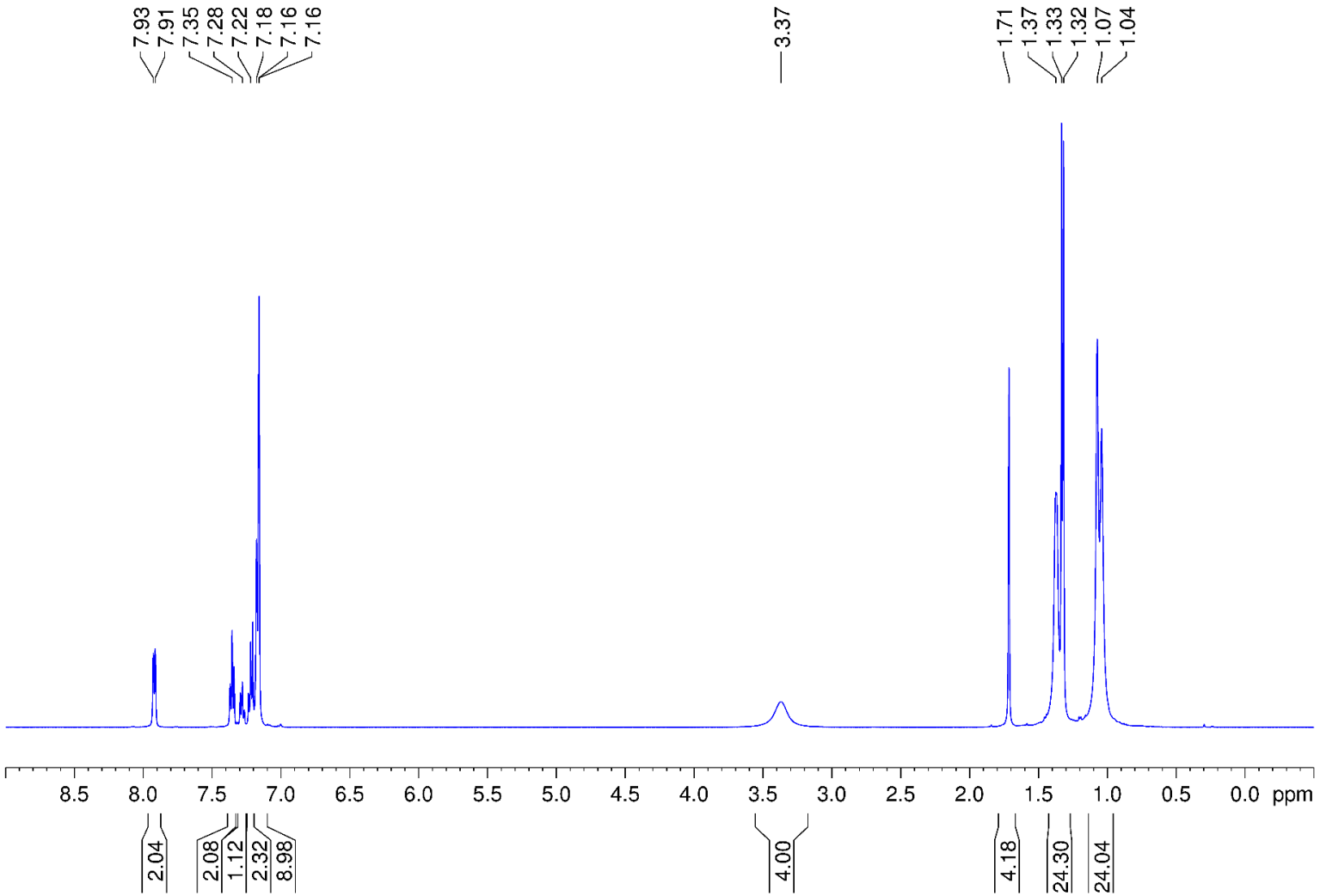


Figure S22. $^{1}H\{^{11}B\}$ NMR spectrum of **3-Ph** in C_6D_6.

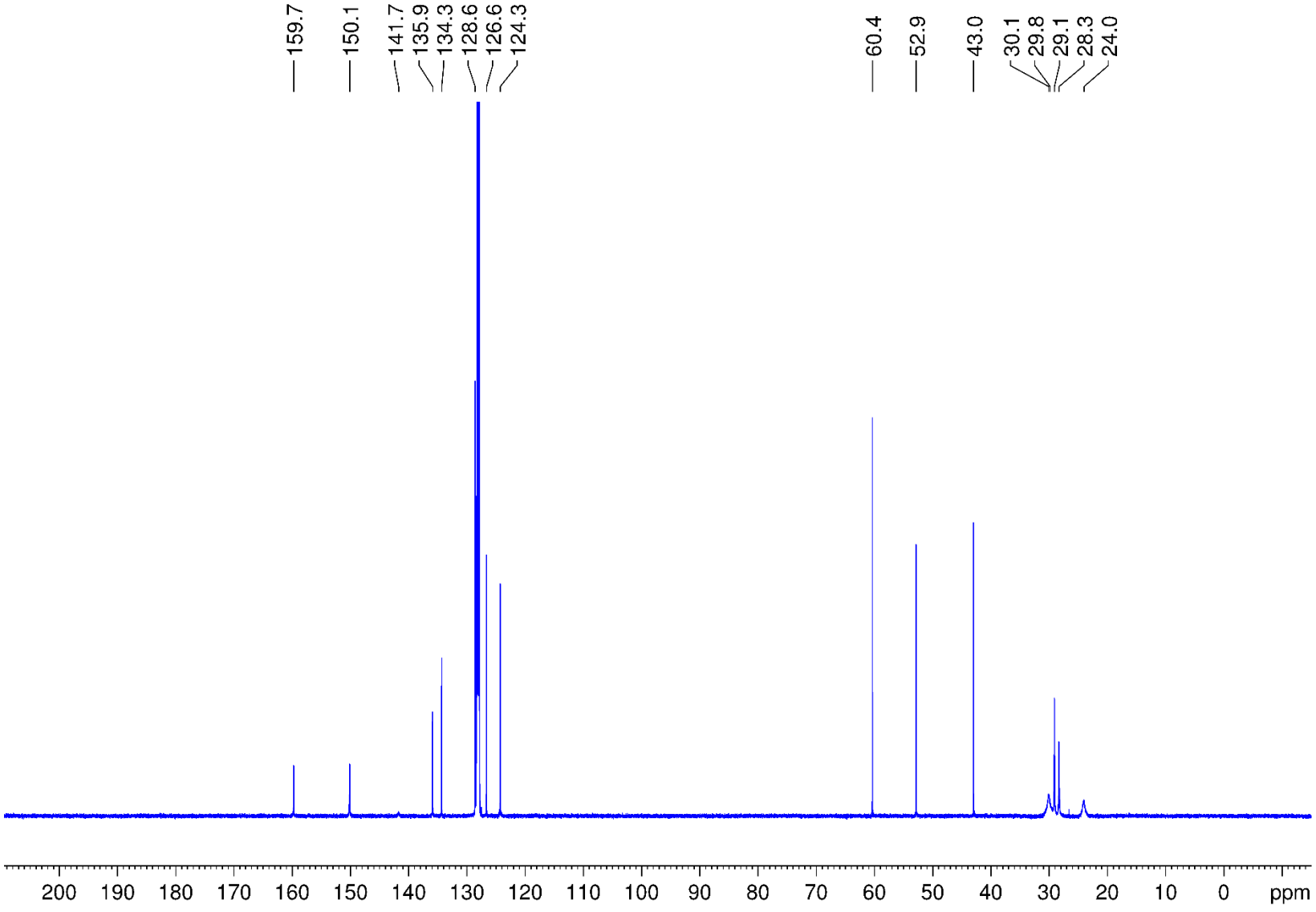


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **3-Ph** in C_6D_6.

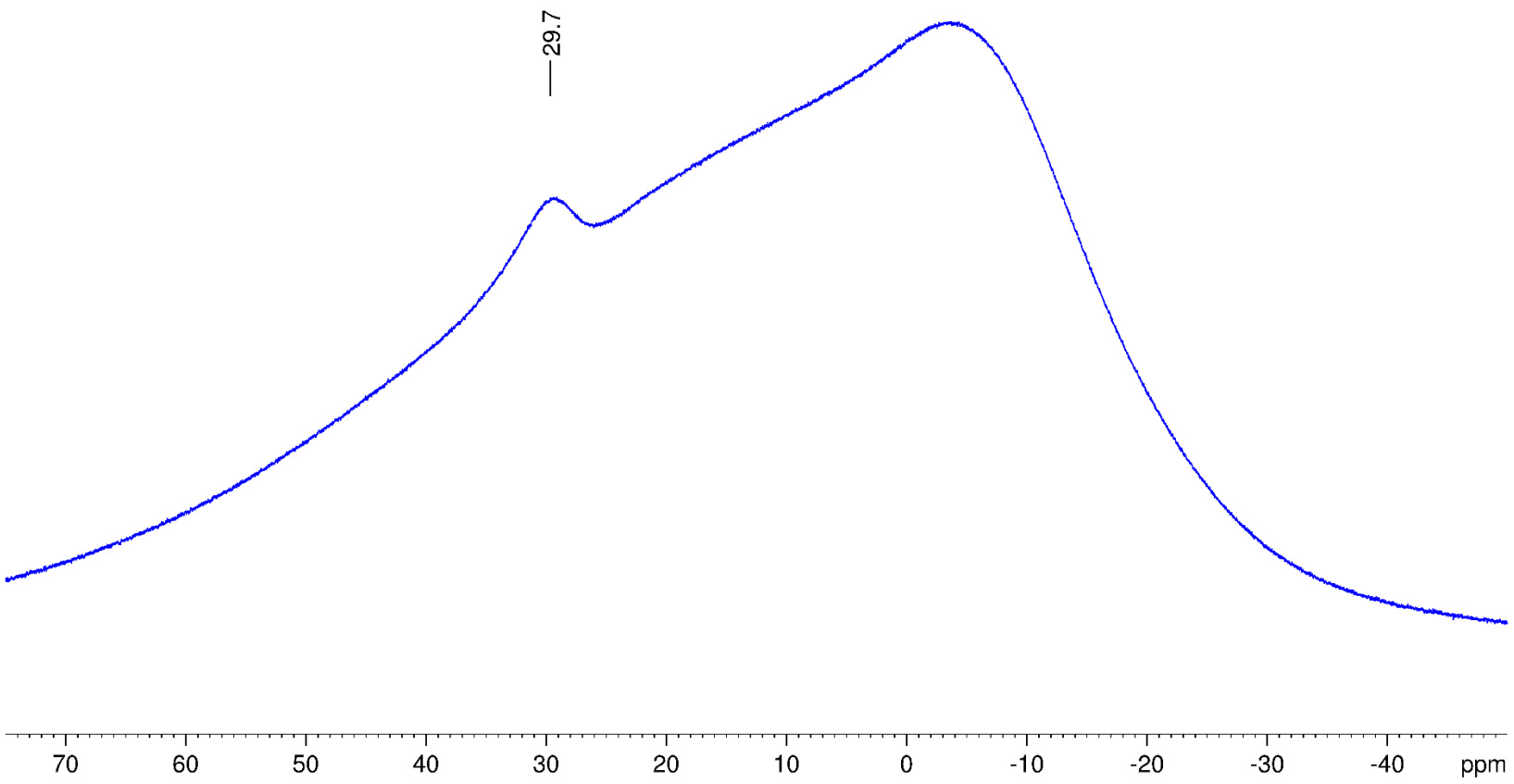


Figure S24. ^{11}B NMR spectrum of **3-Ph** in C_6D_6.

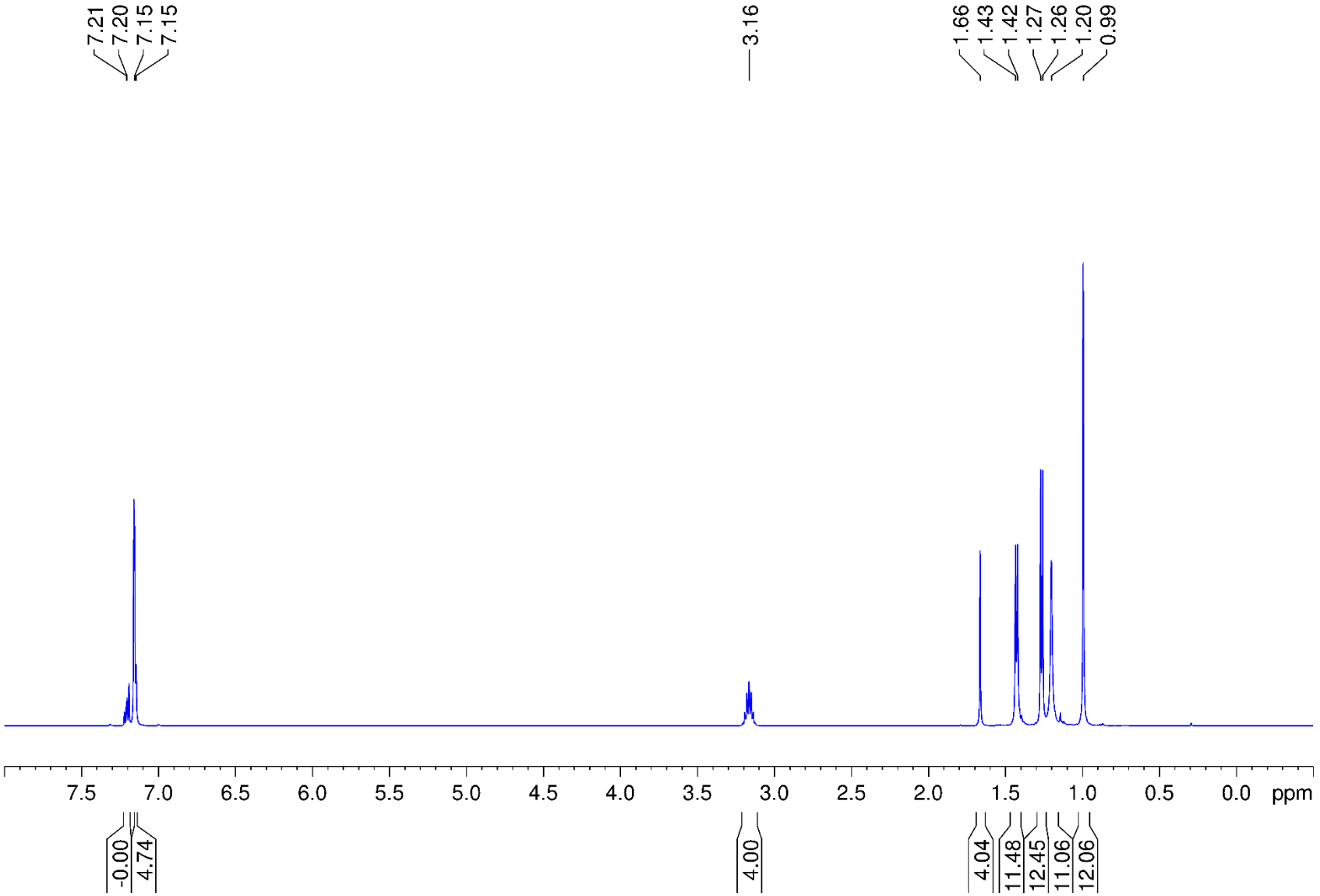


Figure S25. $^{1}H\{^{11}B\}$ NMR spectrum of **3-Cl** in C_6D_6.

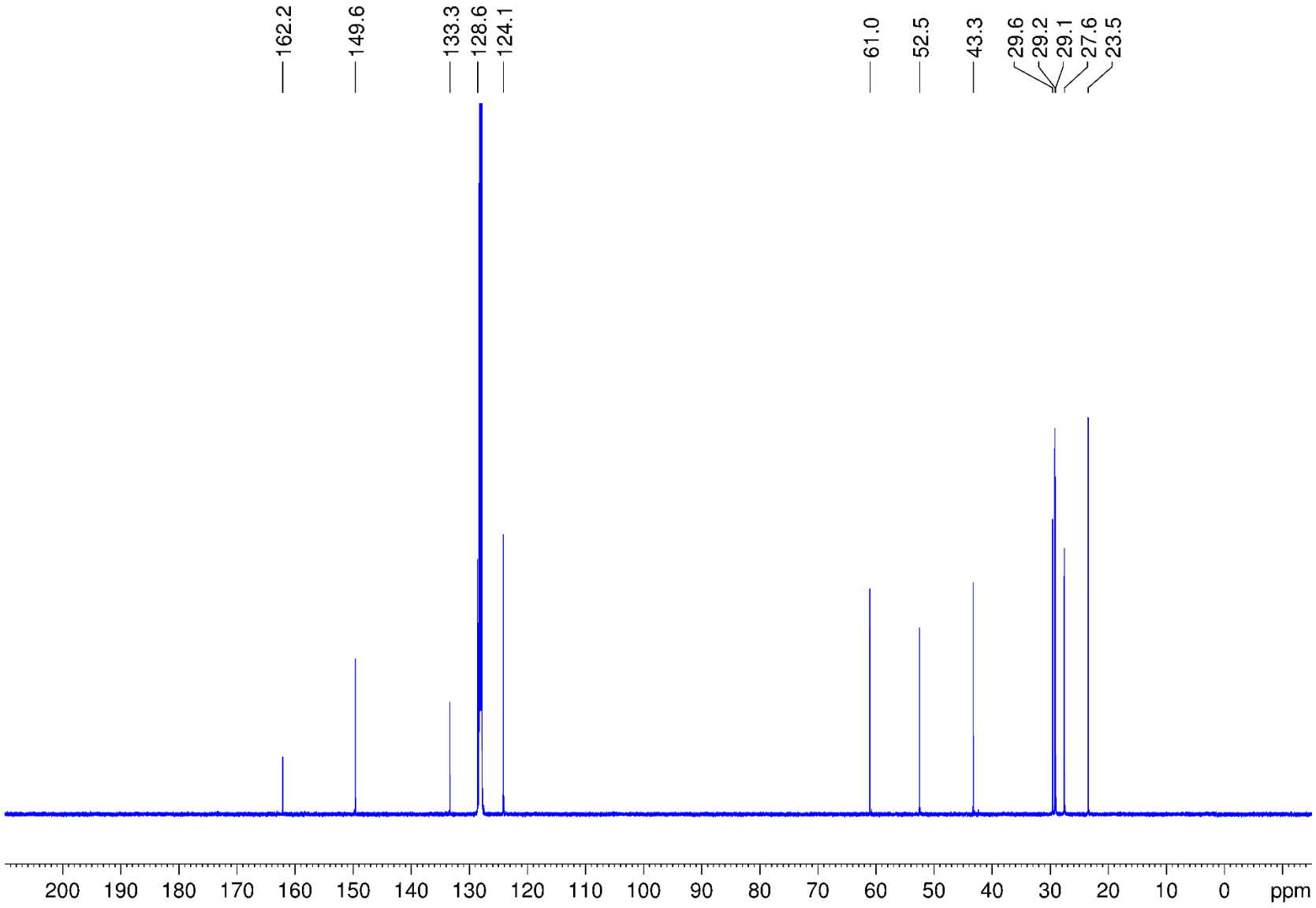


Figure S26. {^{1}H} NMR spectrum of **3-Cl** in C_6D_6.

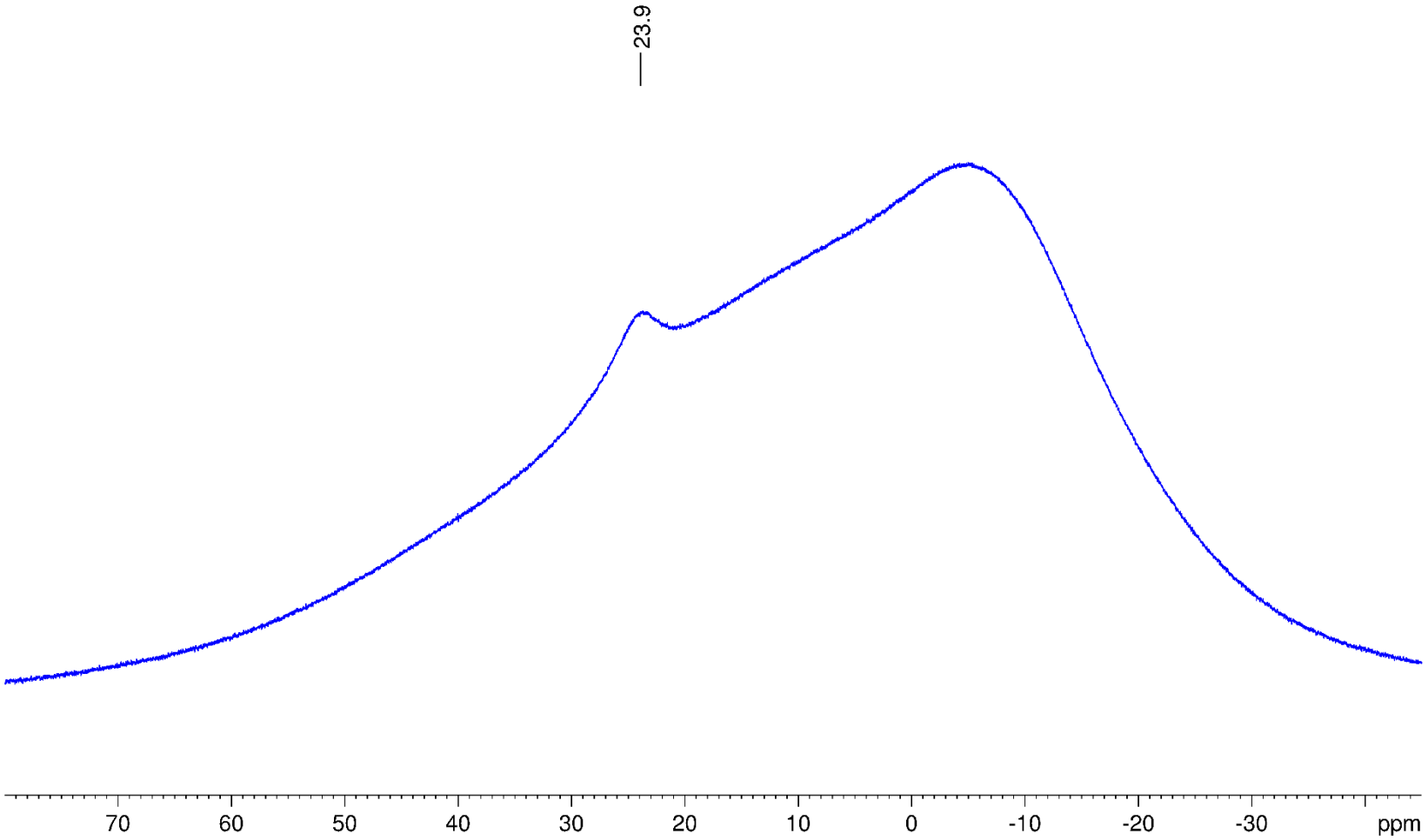


Figure S27. ^{11}B NMR spectrum of **3-Cl** in C_6D_6.

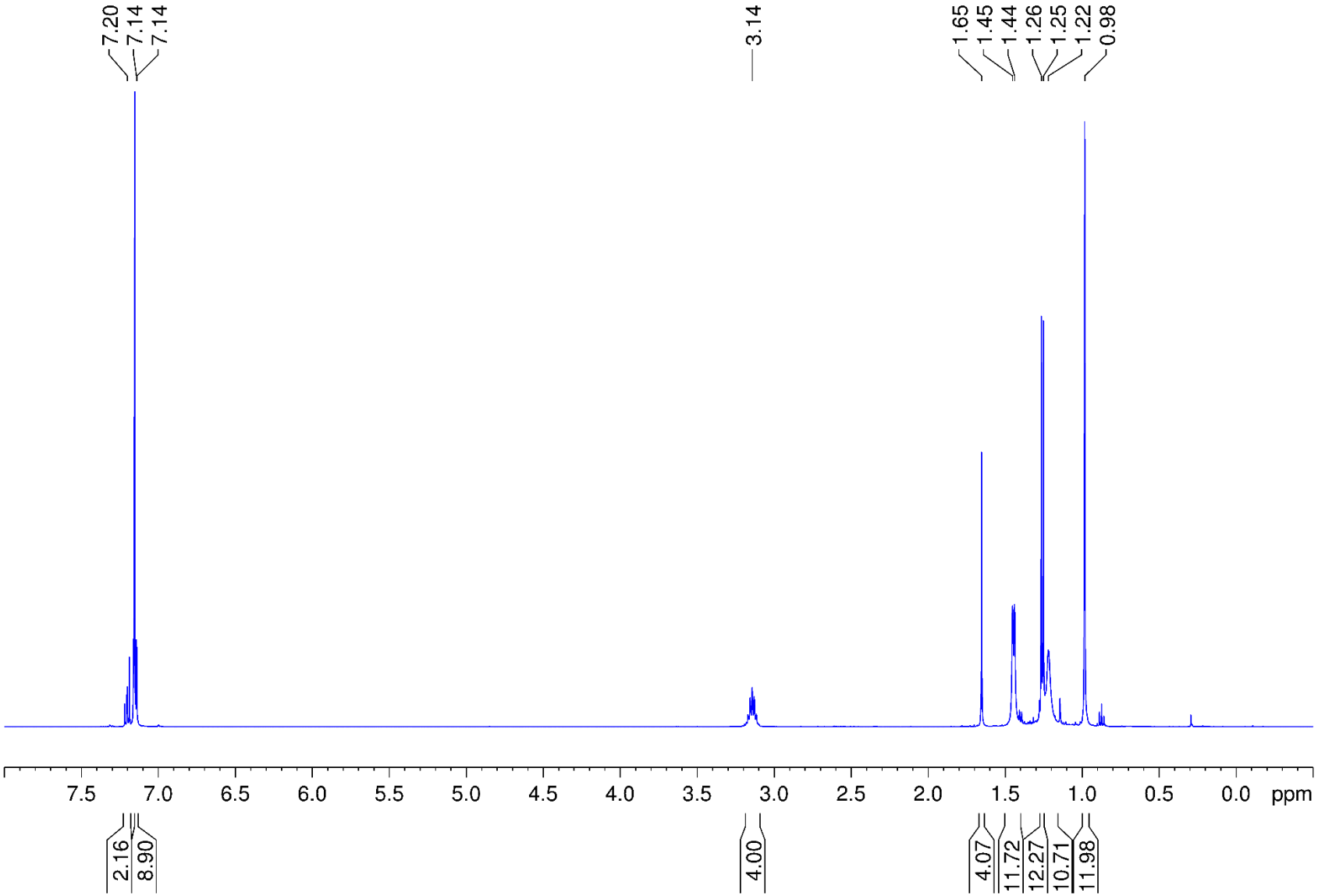


Figure S28. $^{1}H\{^{11}B\}$ NMR spectrum of **3-Br** in C_6D_6.

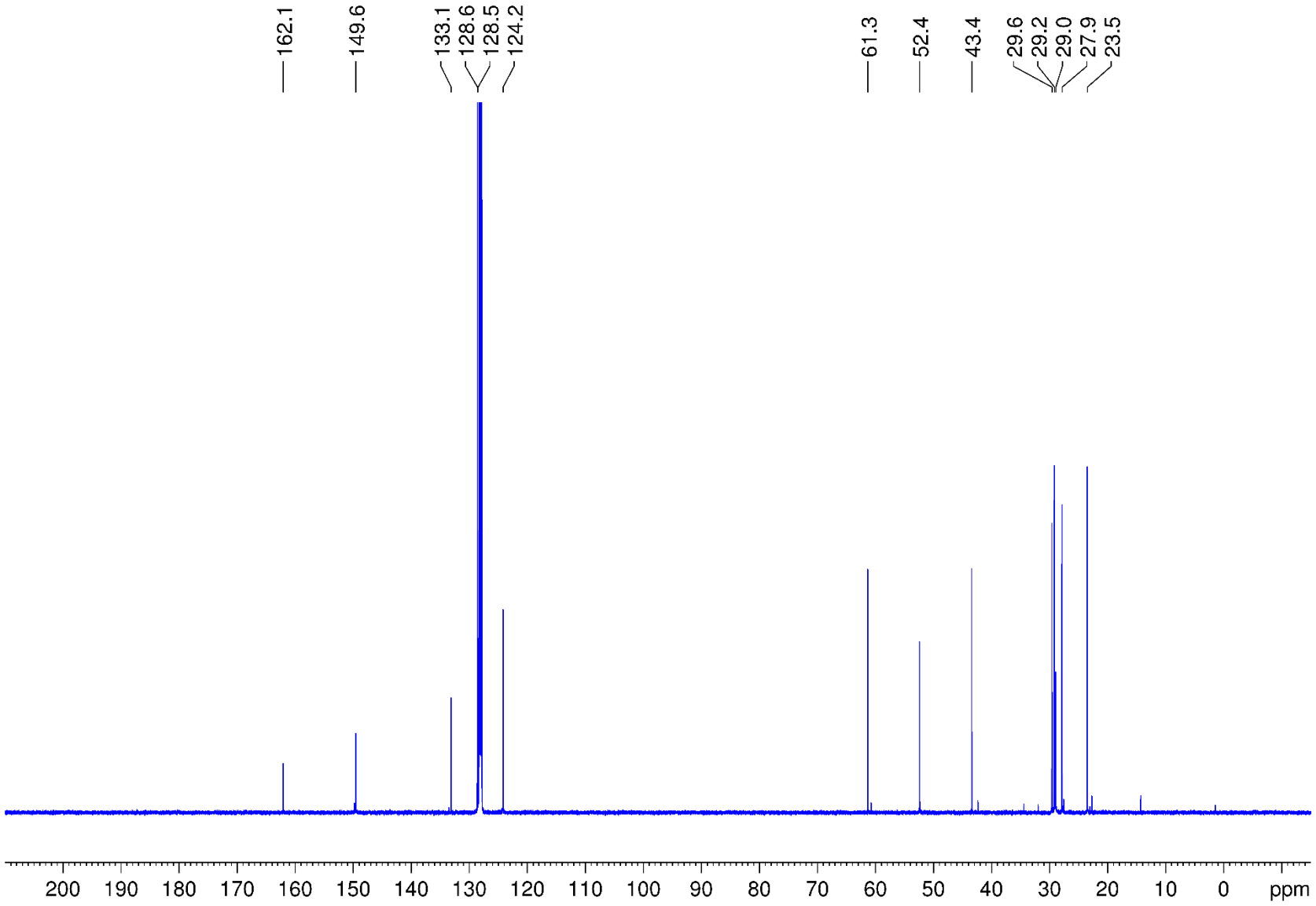


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **3-Br** in C_6D_6.

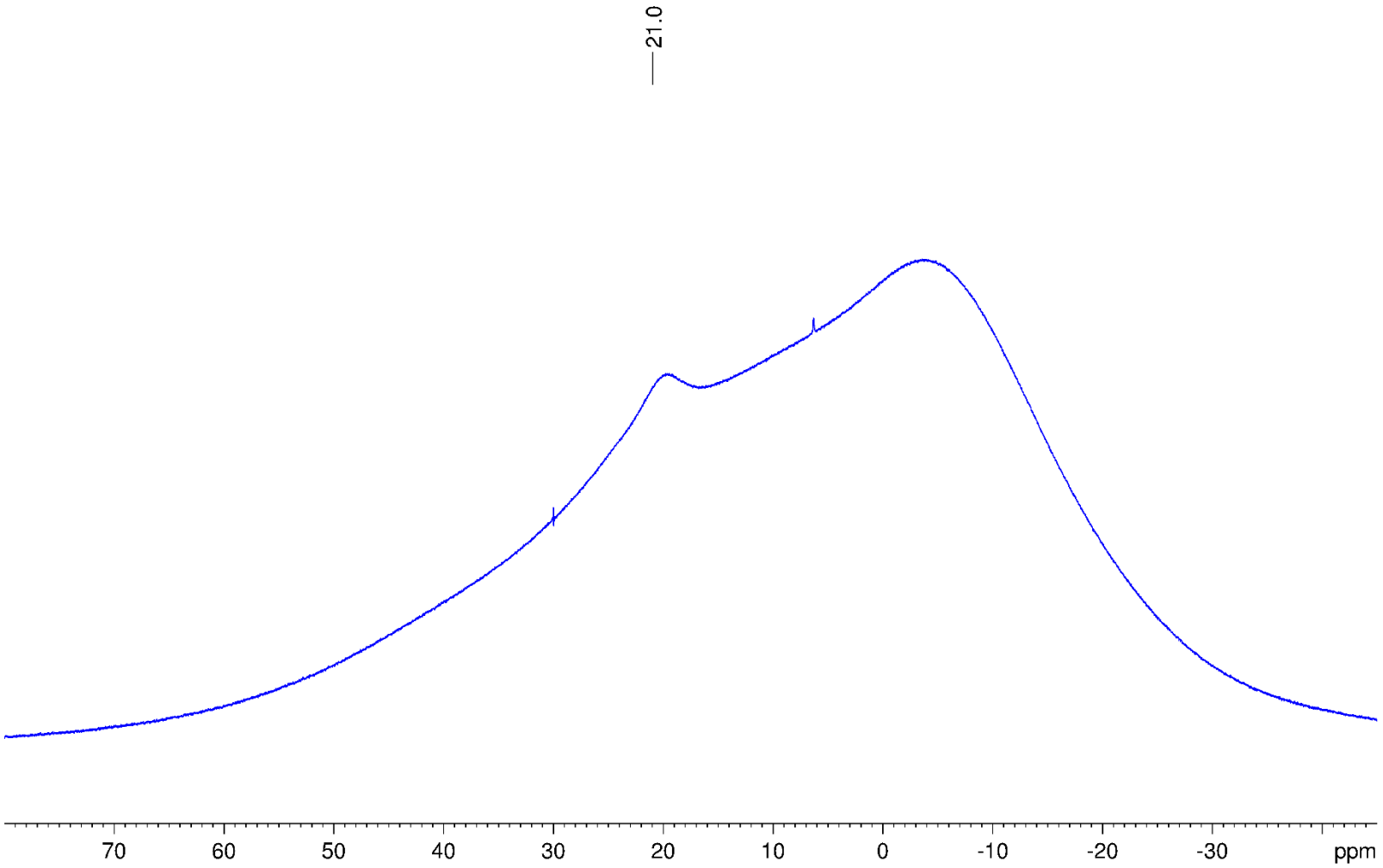


Figure S30. ^{11}B NMR spectrum of **3-Br** in C_6D_6.

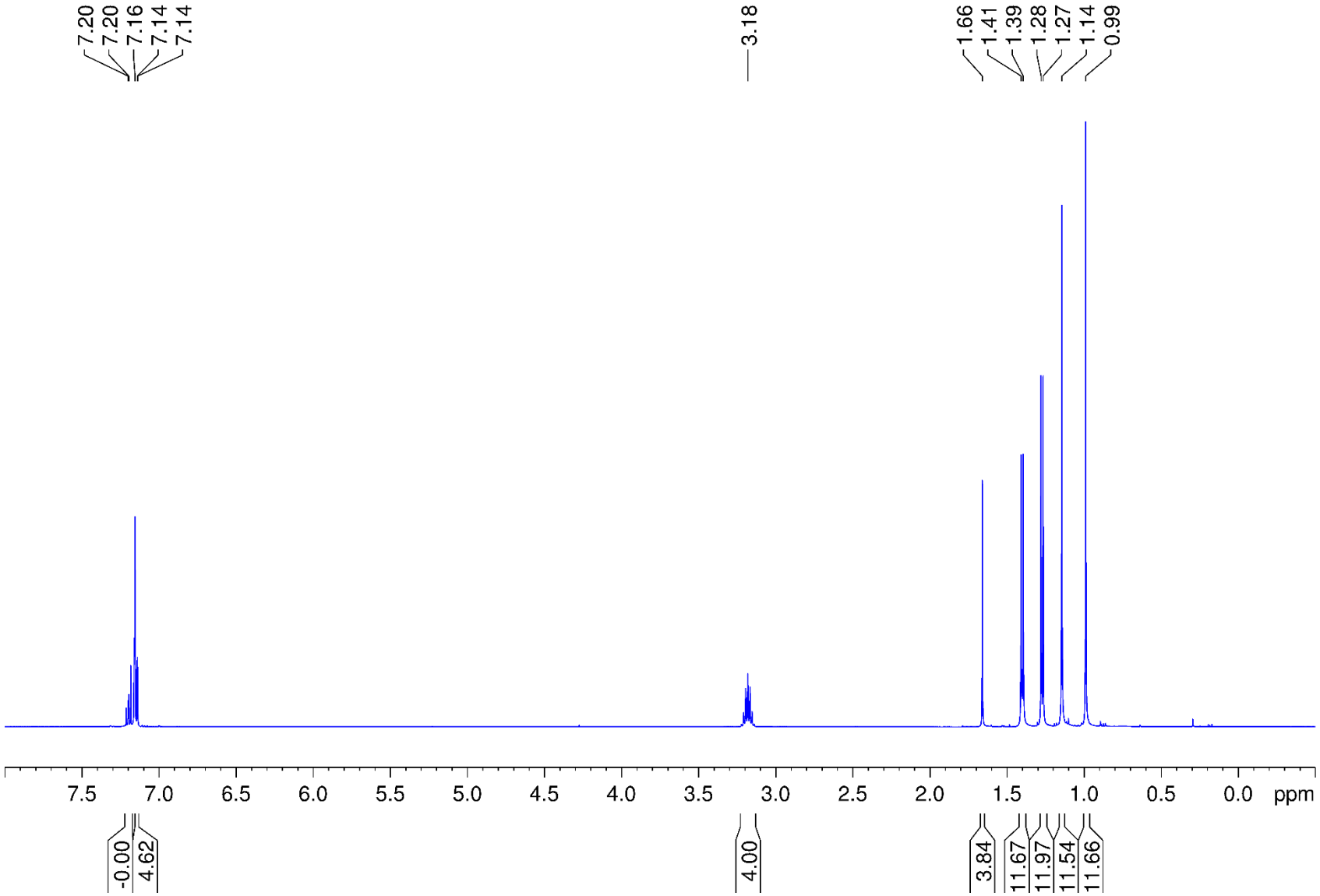


Figure S31. $^{1}H\{^{11}B\}$ NMR spectrum of **3-N$_3$** in C_6D_6.

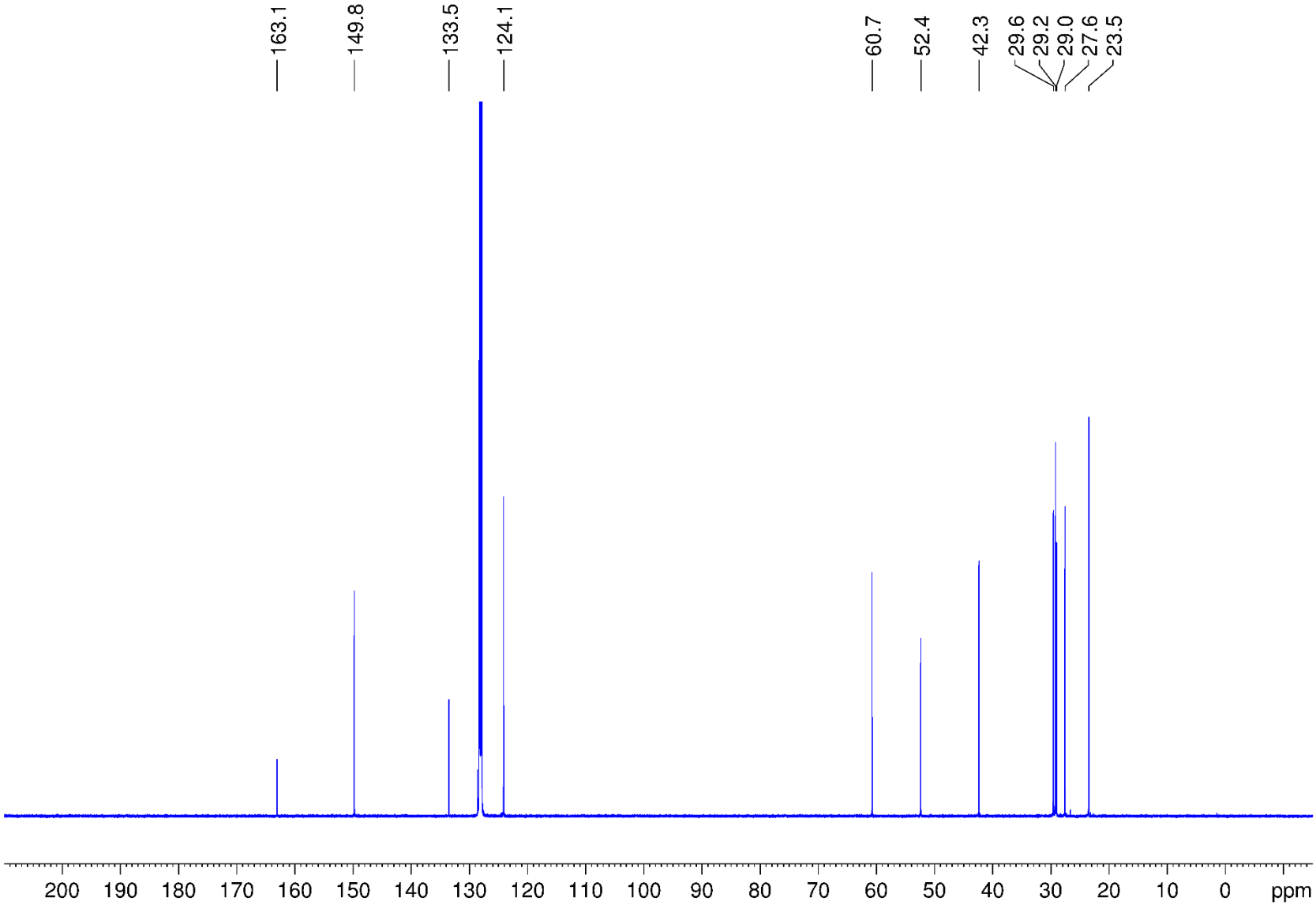


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of **3-N$_3$** in C_6D_6.

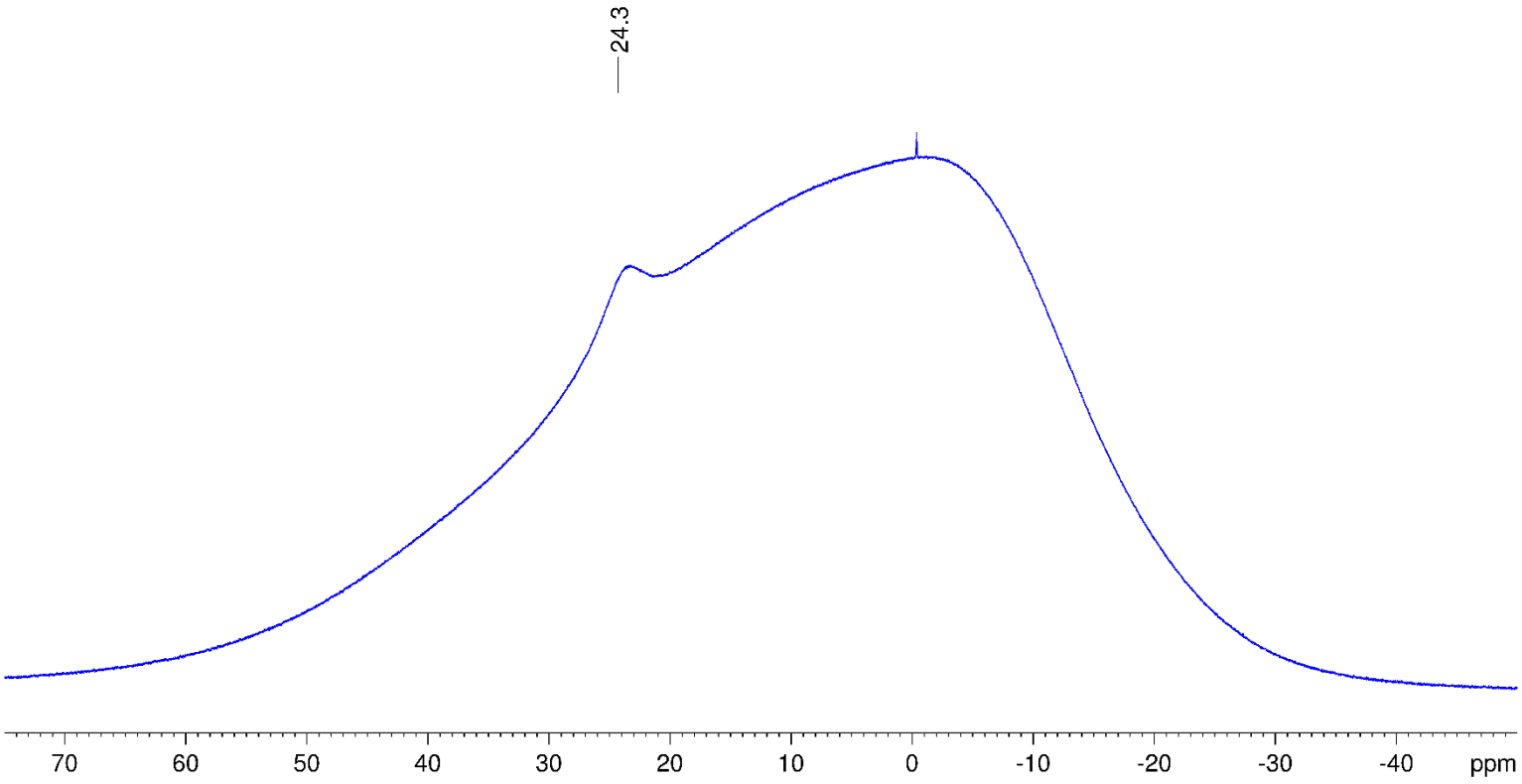


Figure S33. ^{11}B NMR spectrum of **3-N$_3$** in C_6D_6.

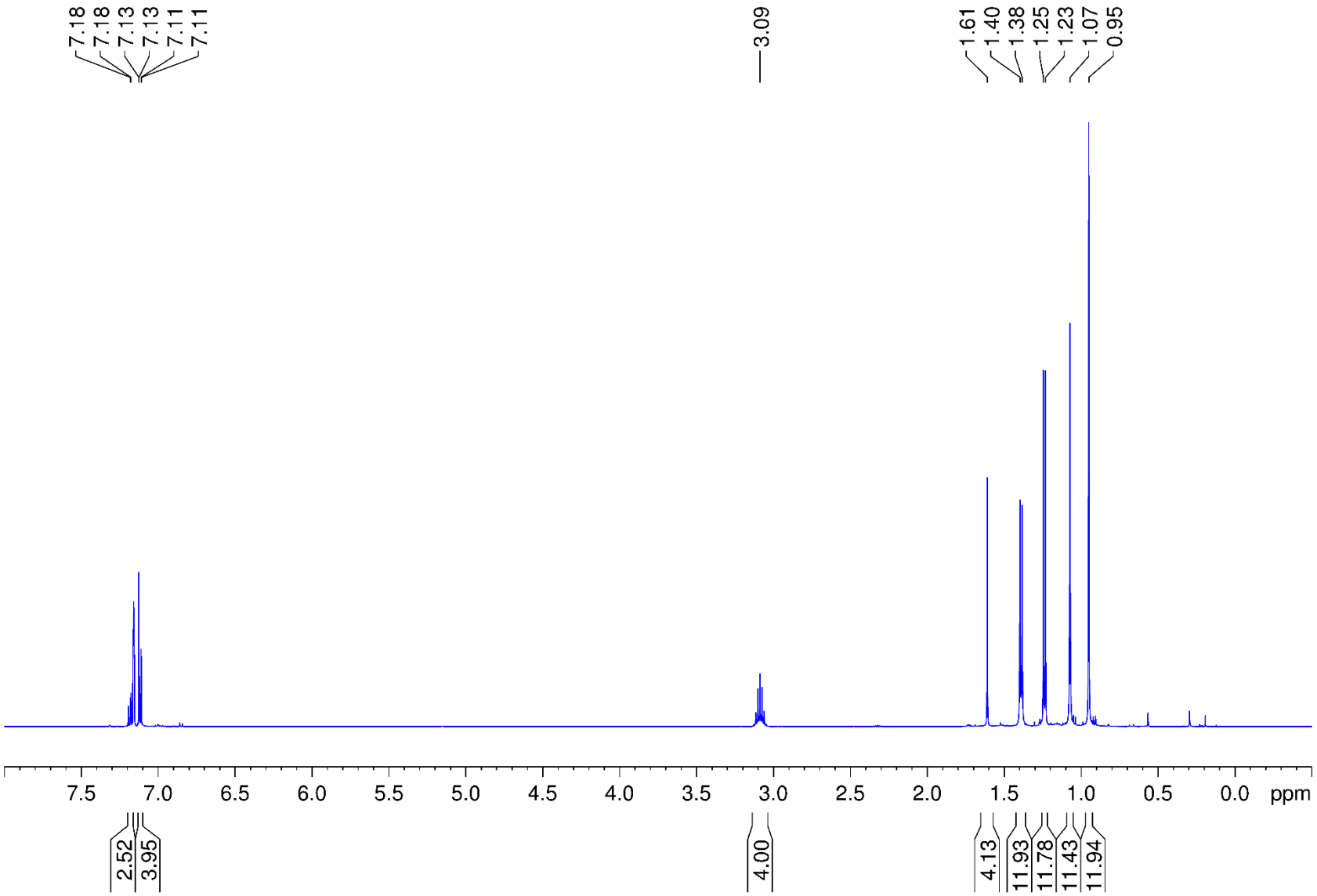


Figure S34. $^{1}H\{^{11}B\}$ NMR spectrum of **3-NCS** in C_6D_6.

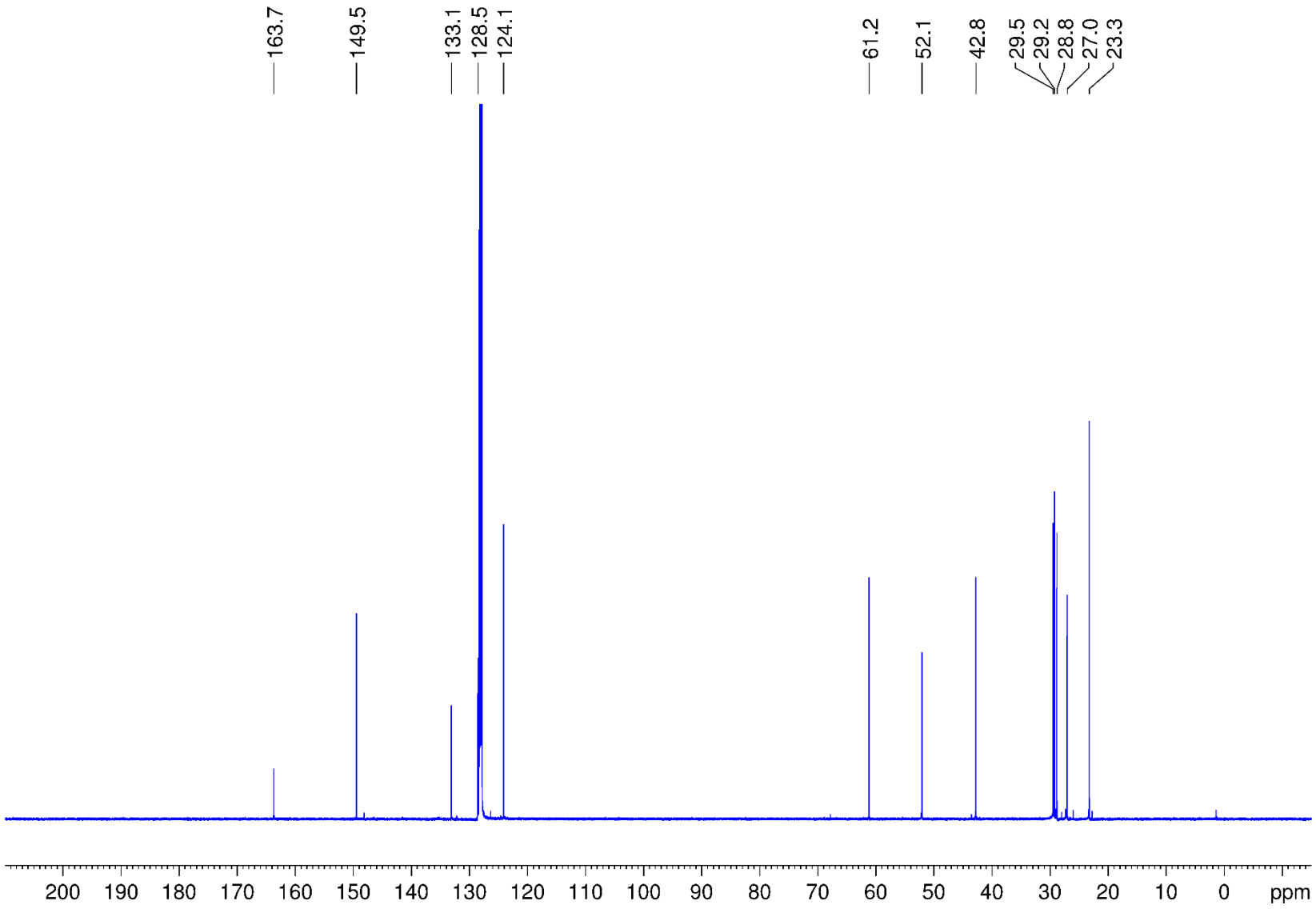


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **3-NCS** in C_6D_6.

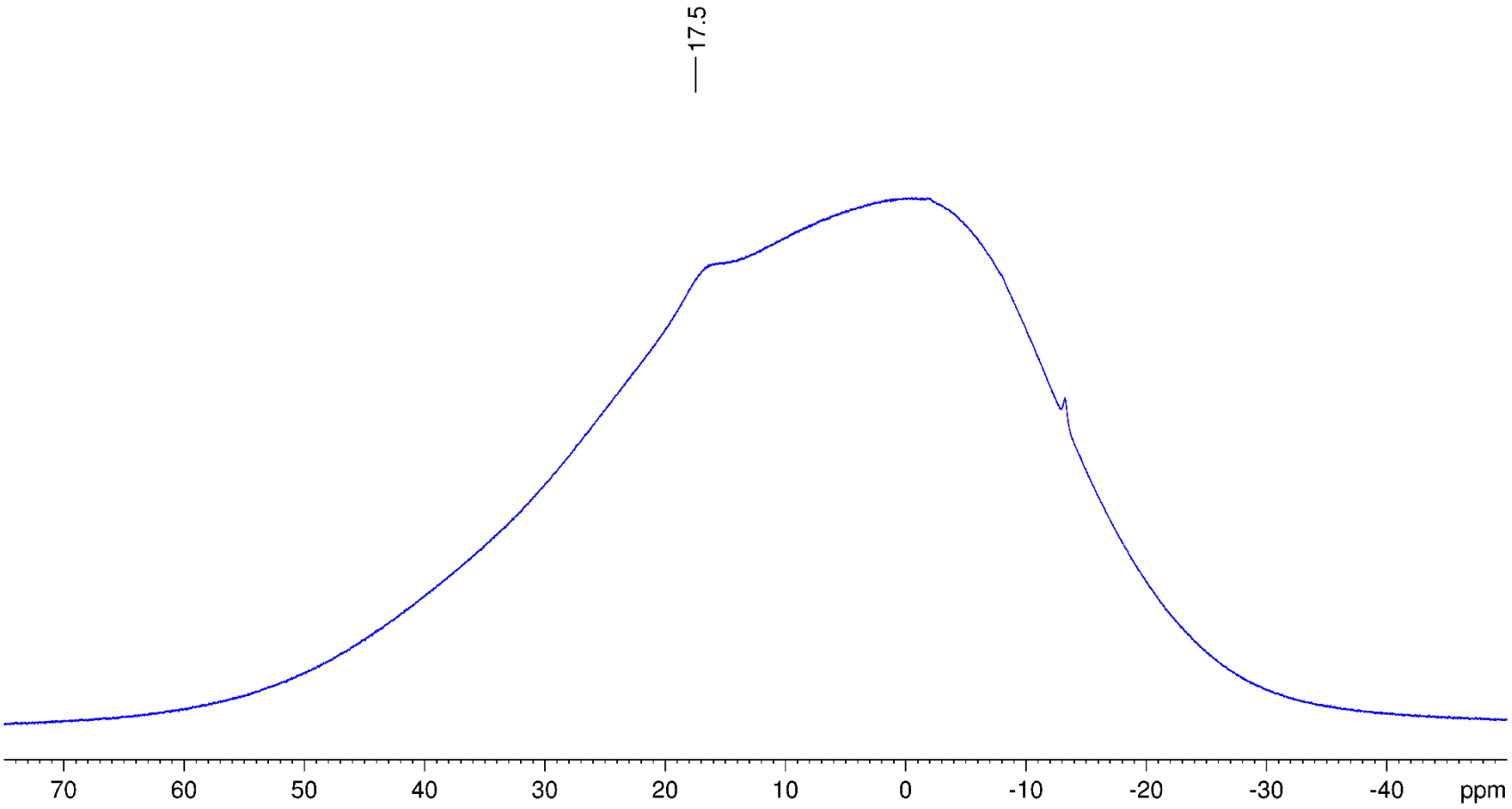


Figure S36. ^{11}B NMR spectrum of **3-NCS** in C_6D_6.

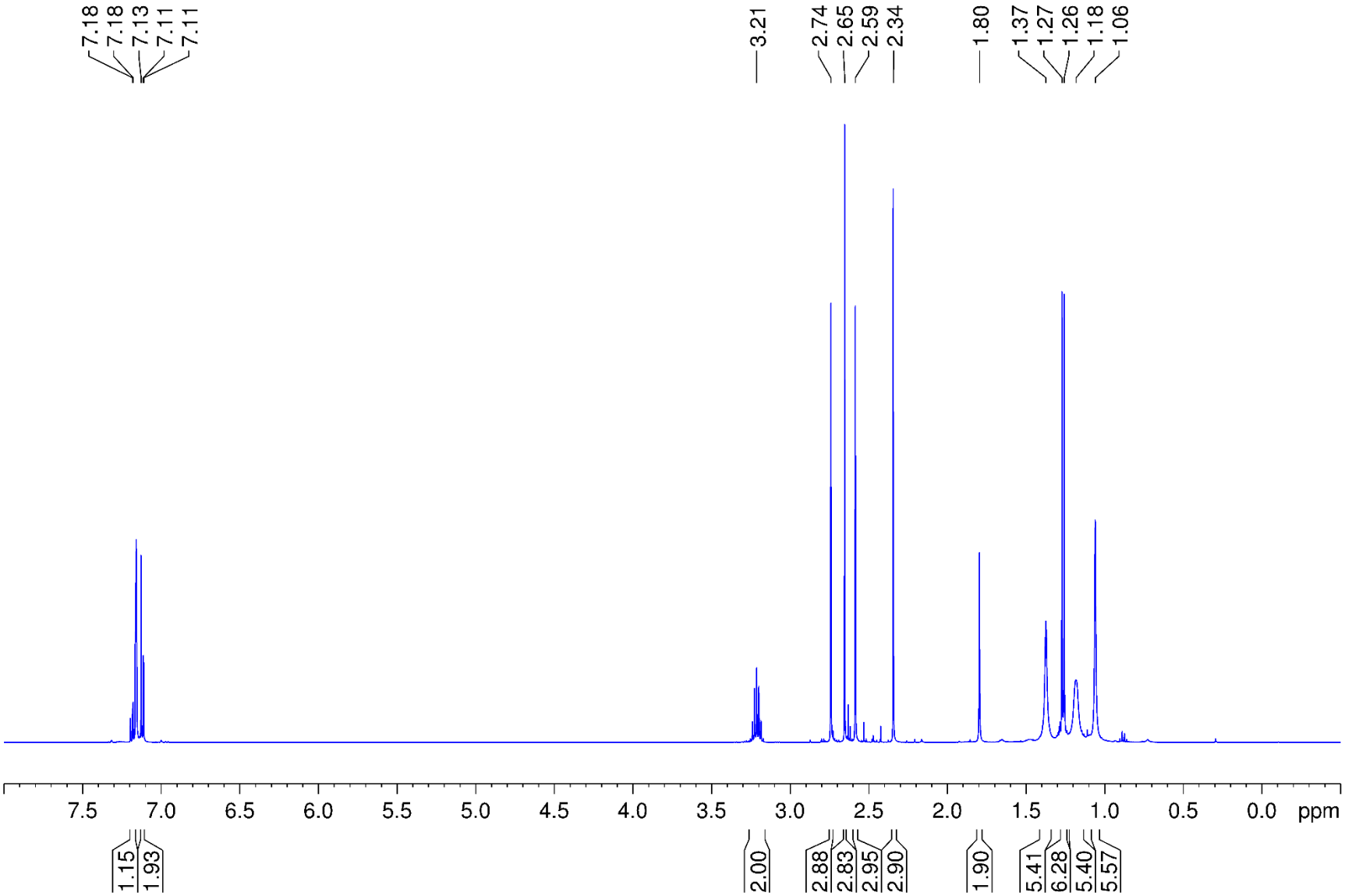


Figure S37. $^{1}H\{^{11}B\}$ NMR spectrum of **4** in C_6D_6.

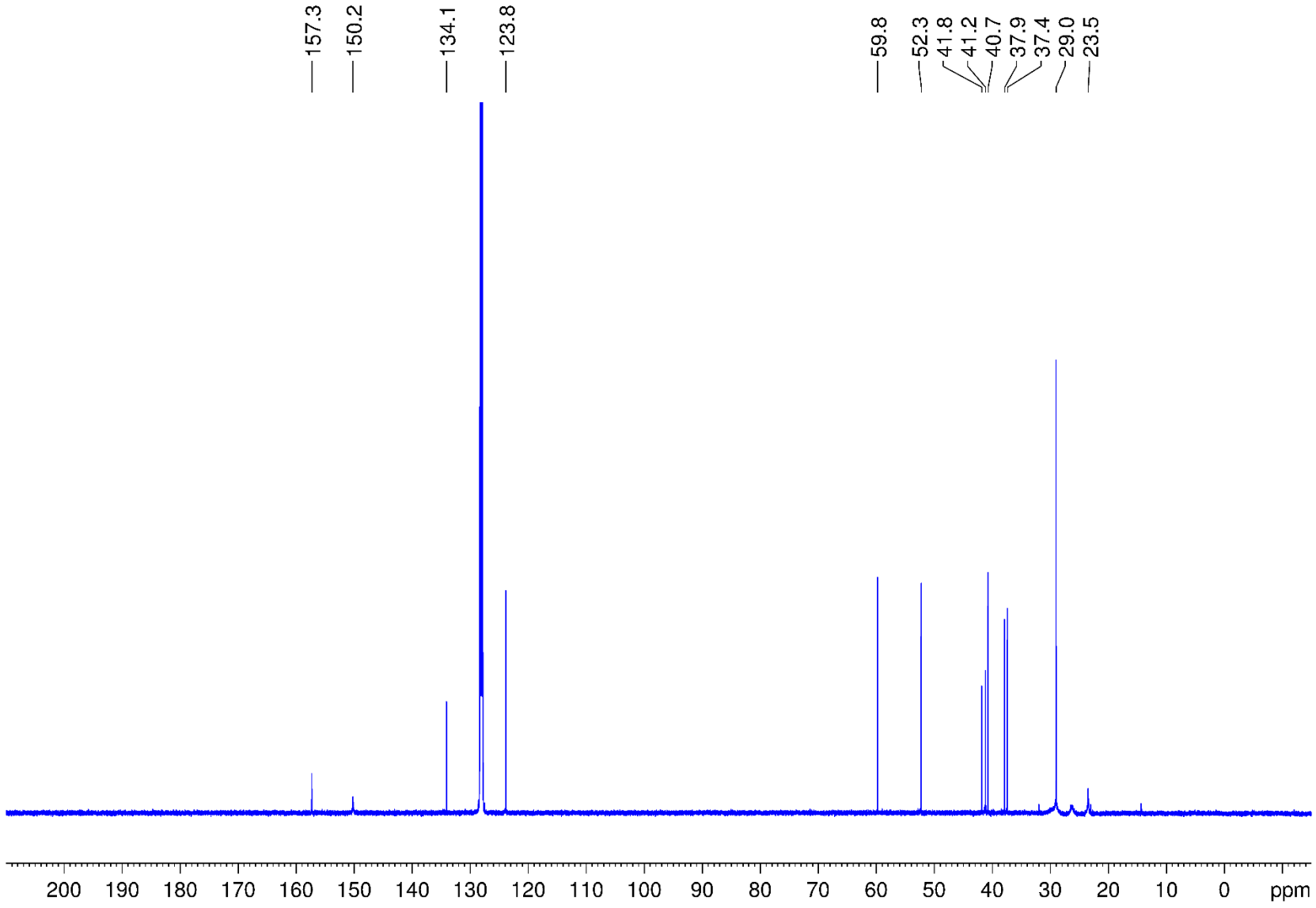


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

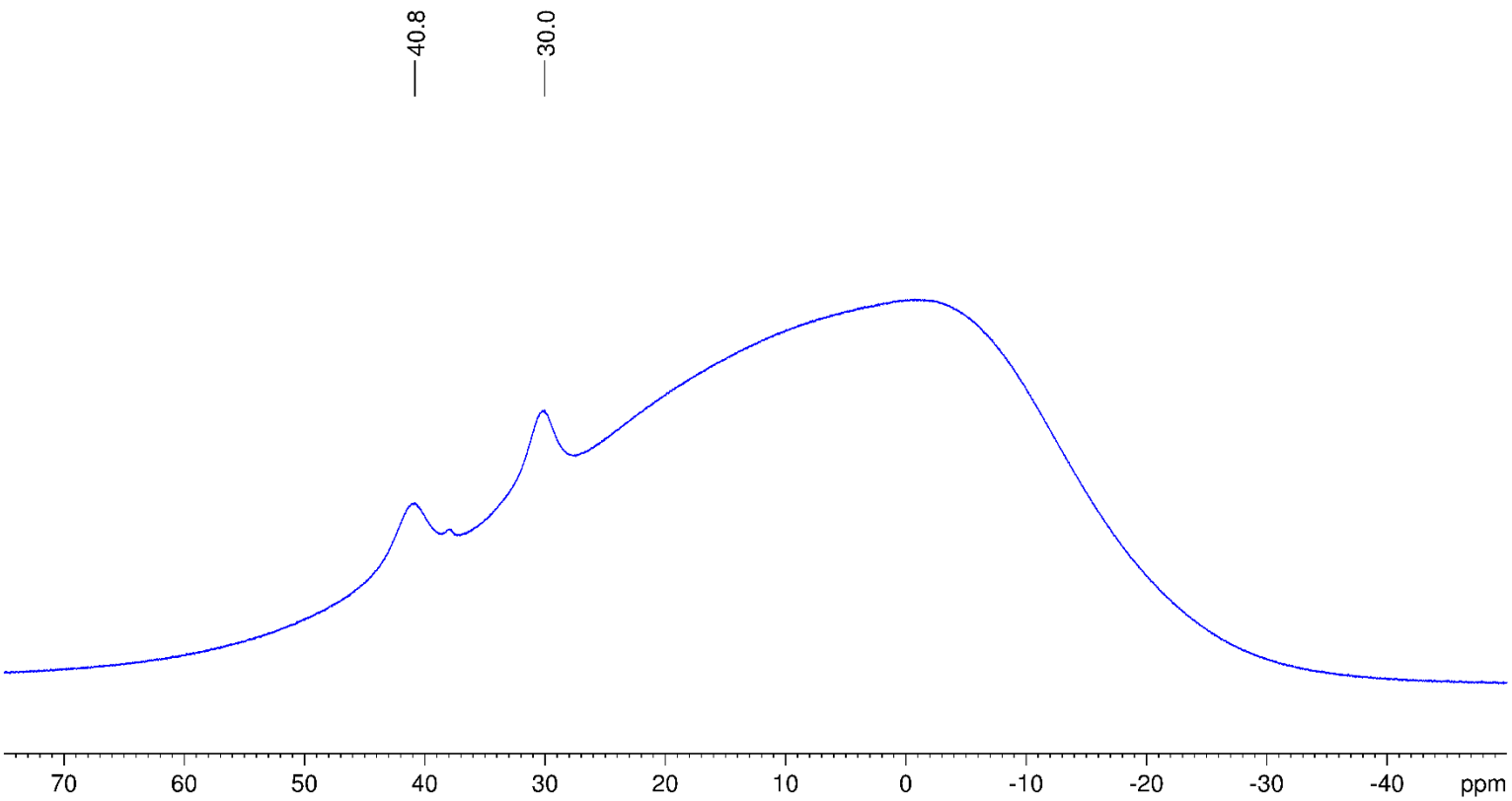


Figure S39. ^{11}B NMR spectrum of **4** in C_6D_6.

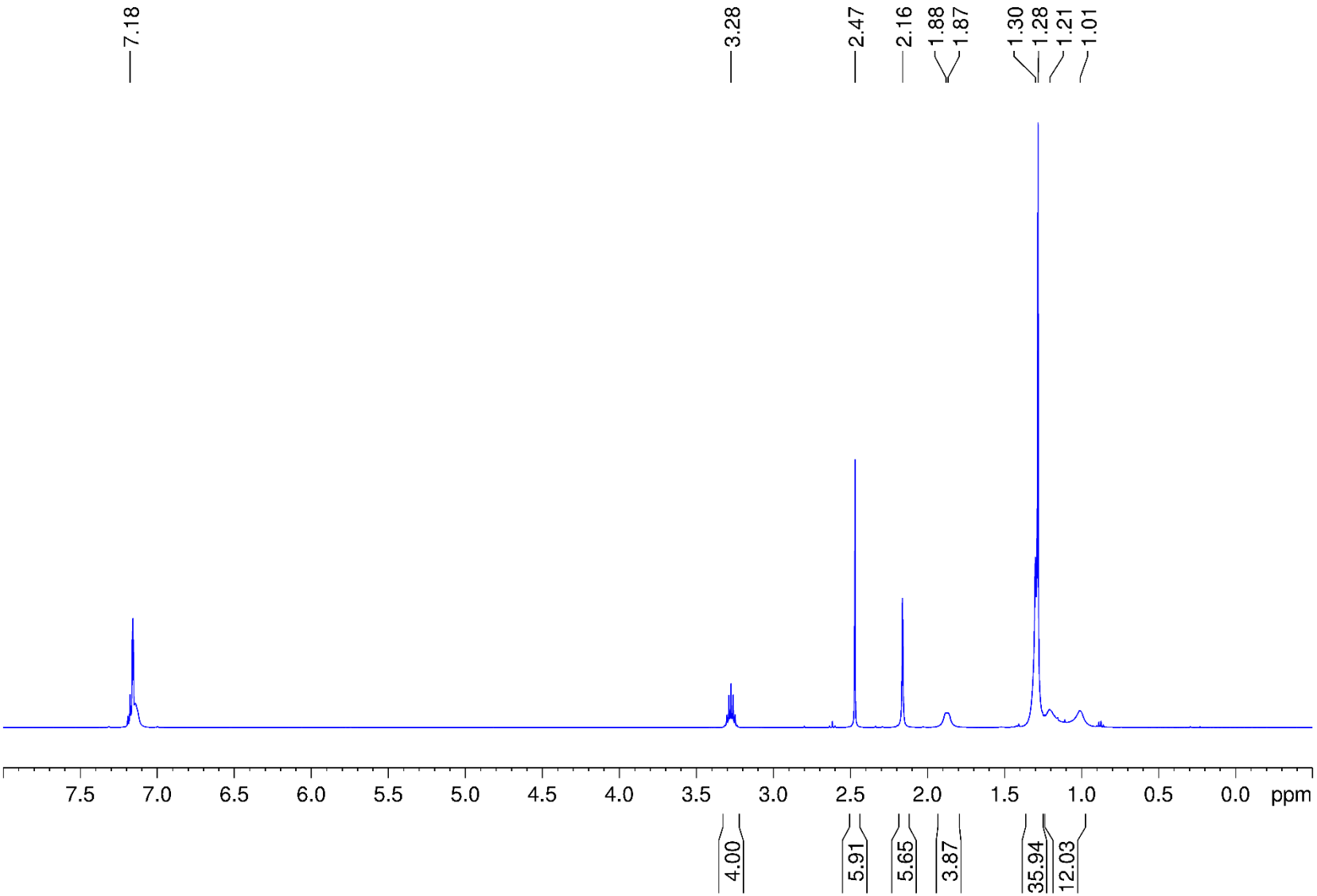


Figure S40. $^{1}H\{^{11}B\}$ NMR spectrum of **5-NMe$_2$** in C_6D_6.

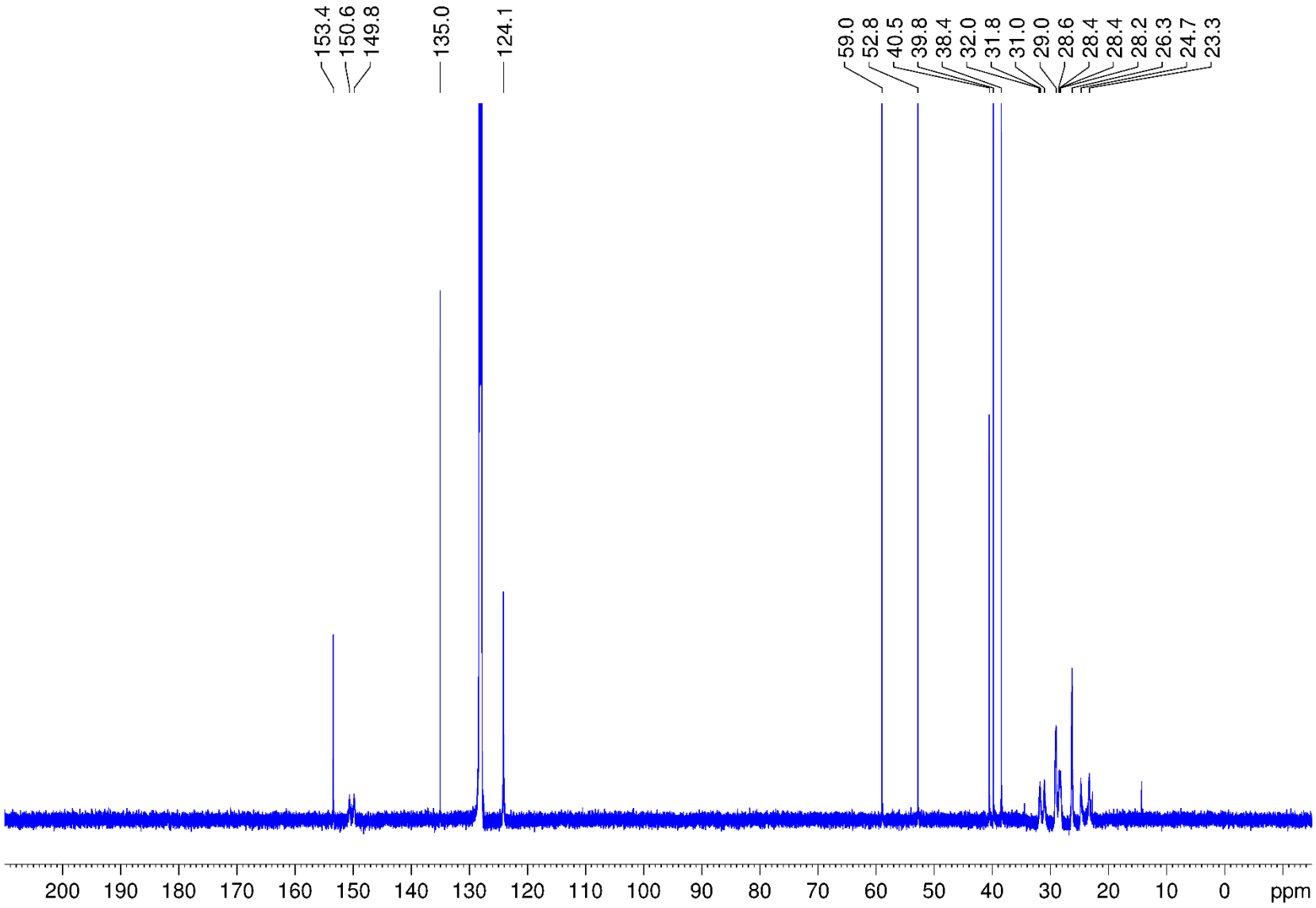


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of **5-NMe$_2$** in C_6D_6.

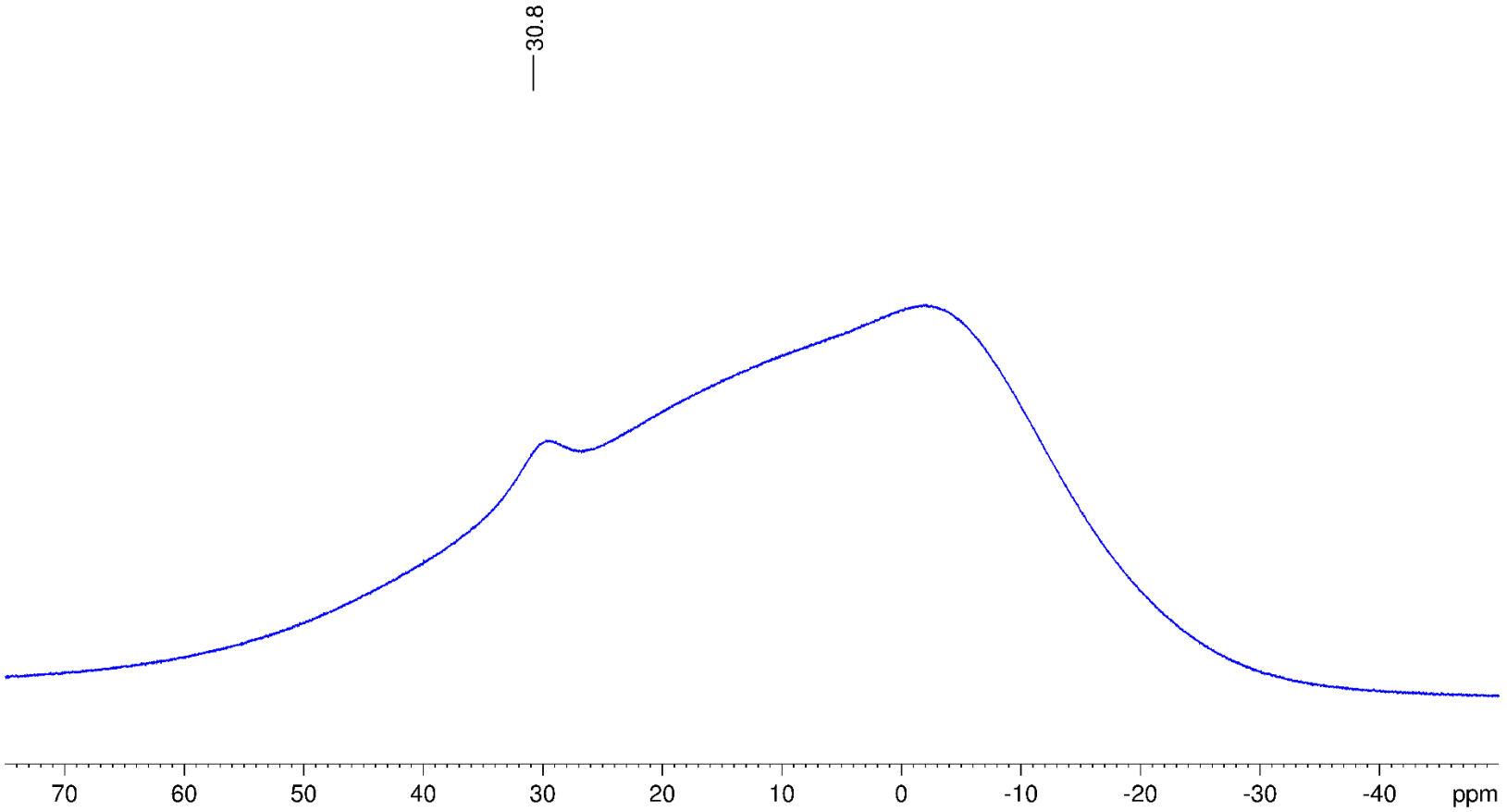


Figure S42. ^{11}B NMR spectrum of **5-NMe$_2$** in C_6D_6.

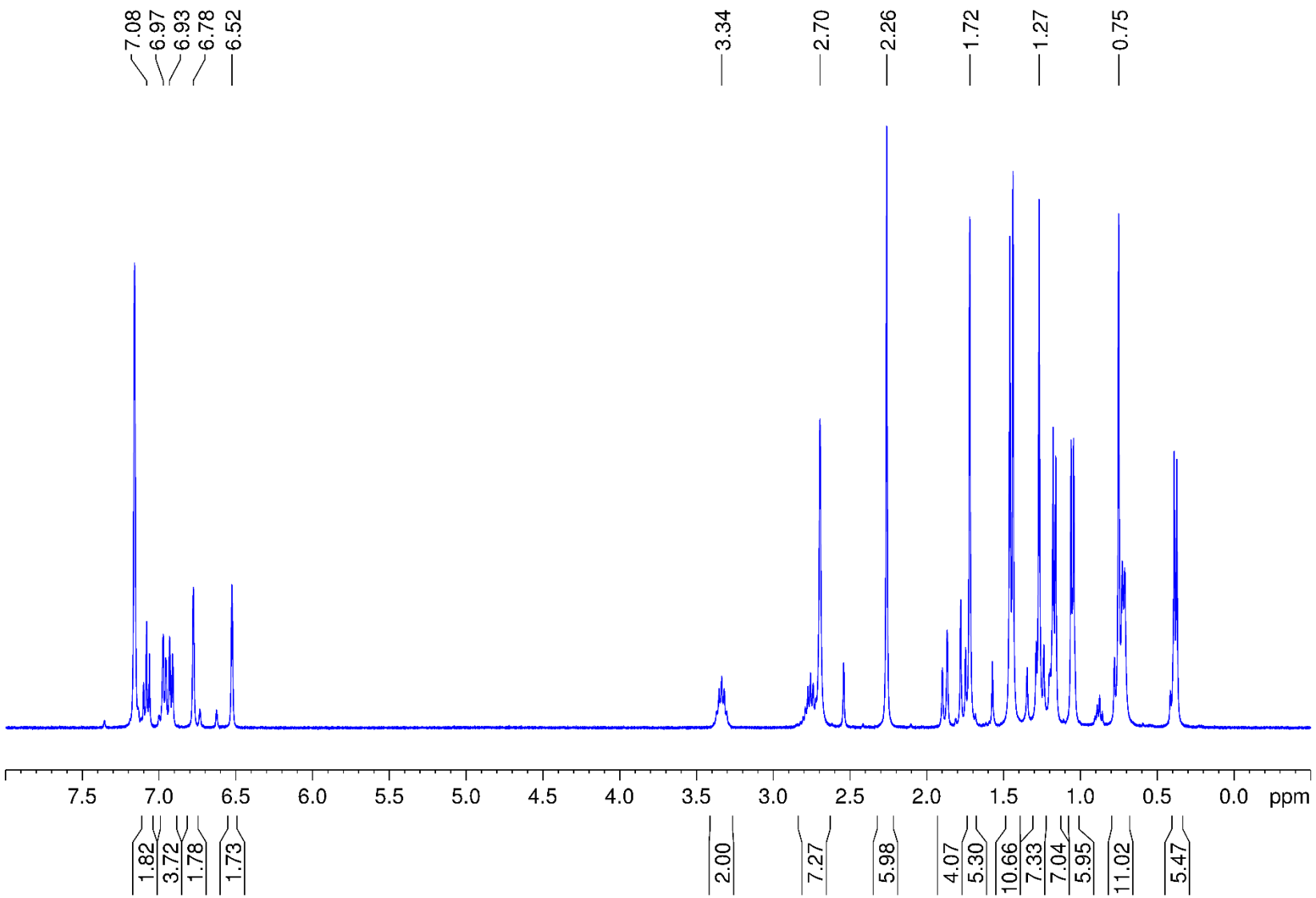


Figure S43. $^{1}H\{^{11}B\}$ NMR spectrum of **5-Mes** in C_6D_6.

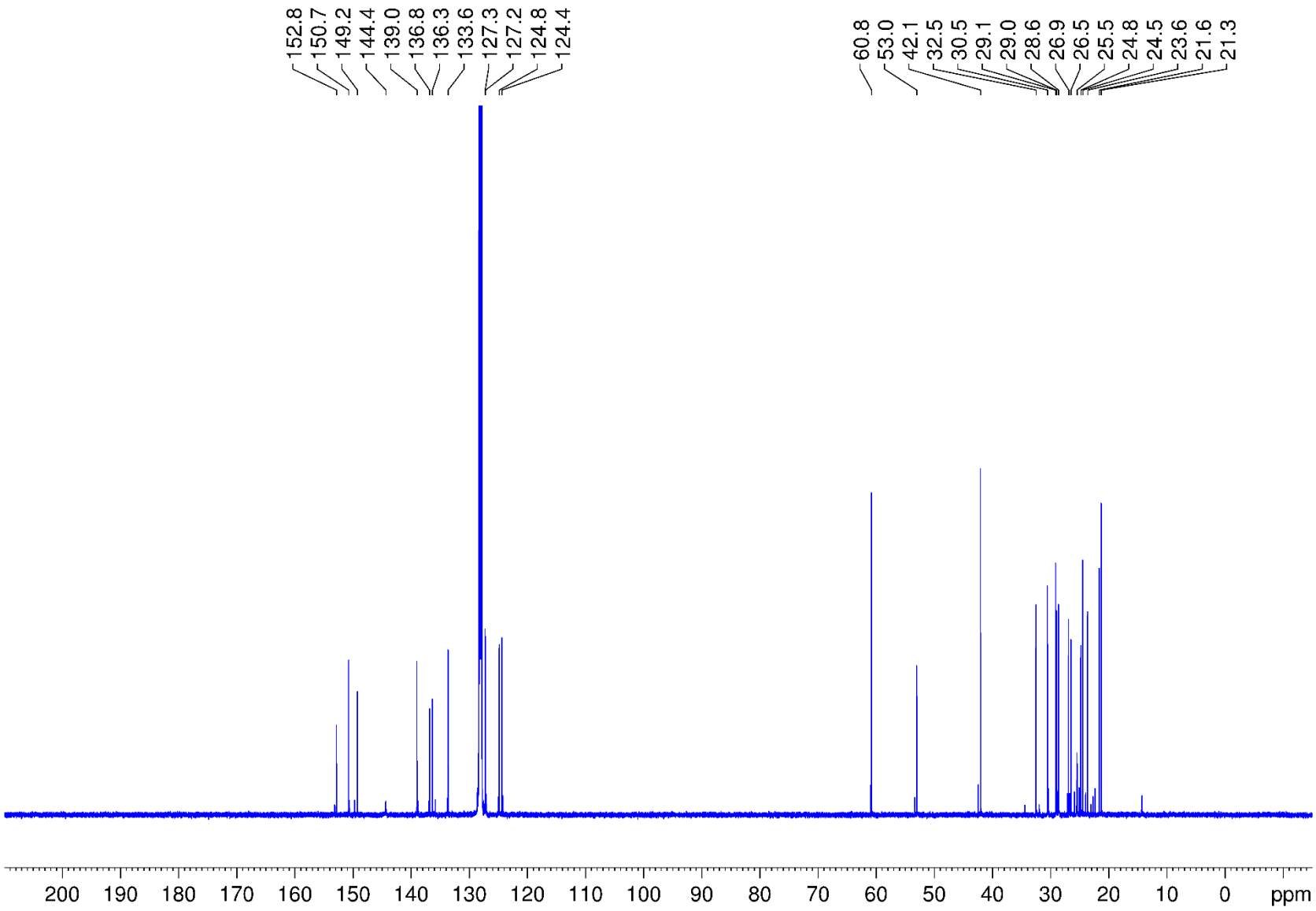


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of **5-Mes** in C_6D_6.

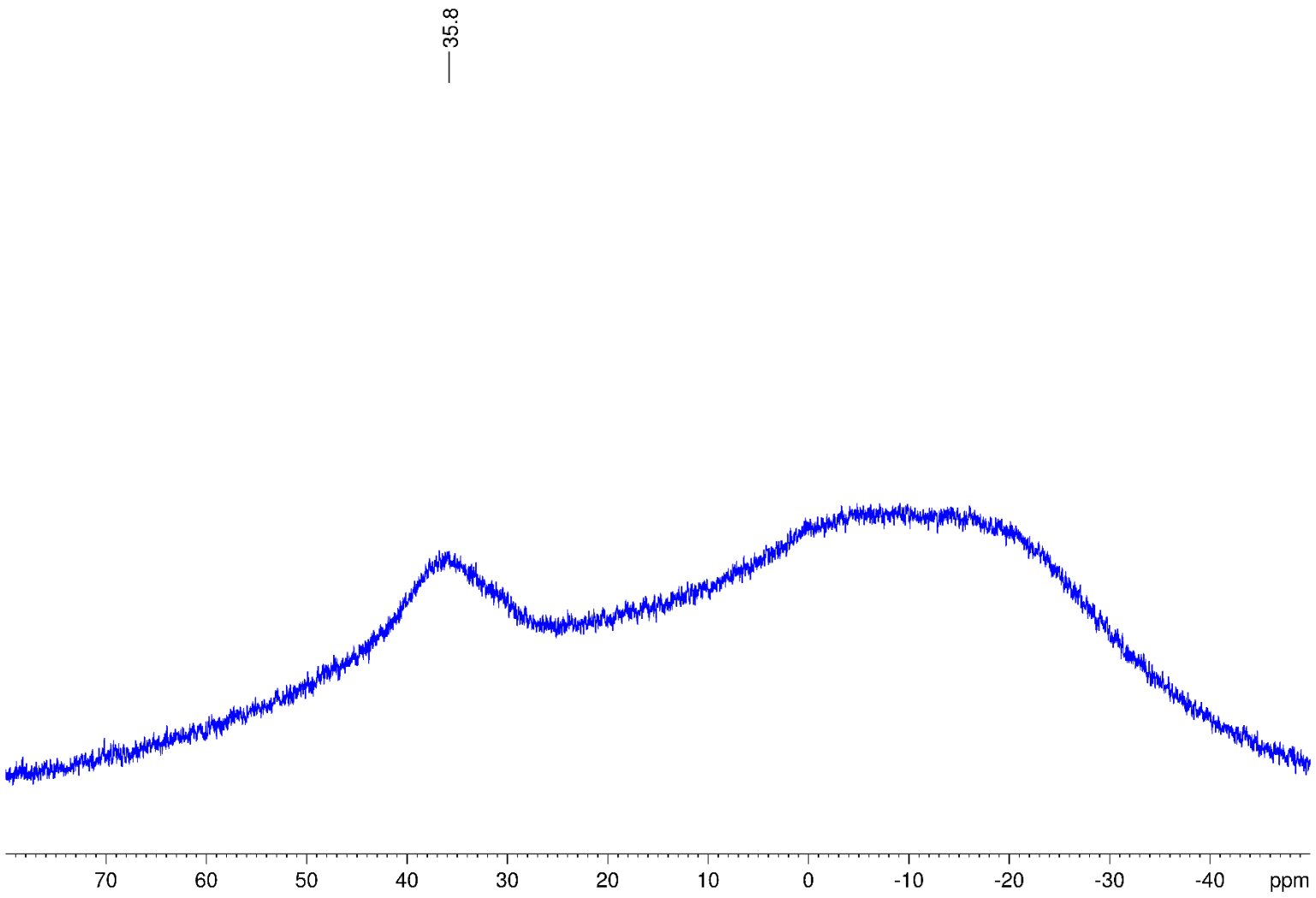


Figure S45. ^{11}B NMR spectrum of **5-Mes** in C_6D_6.

IR spectra

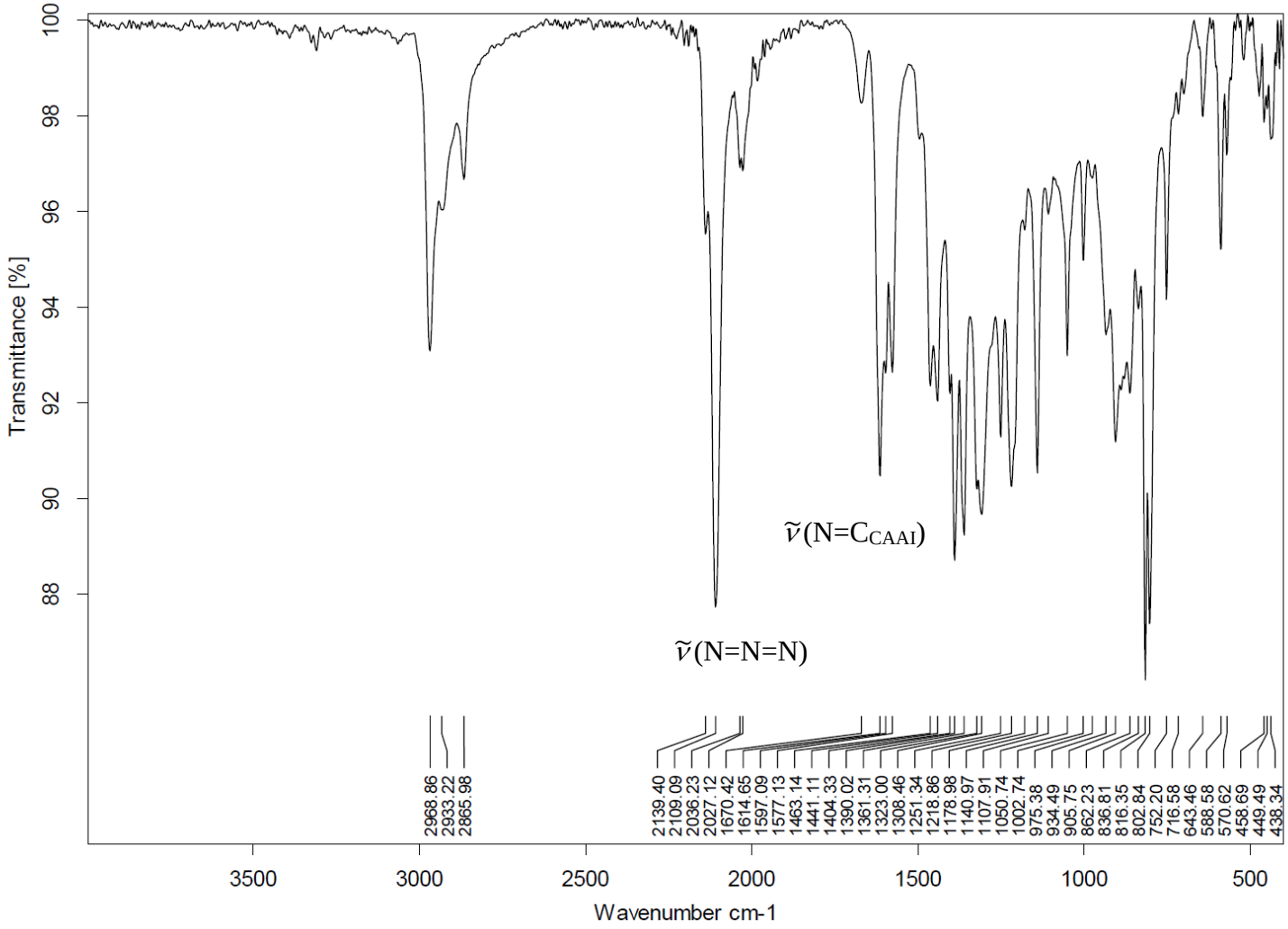


Figure S46. Solid-state IR spectrum of **3-N$_3$**.

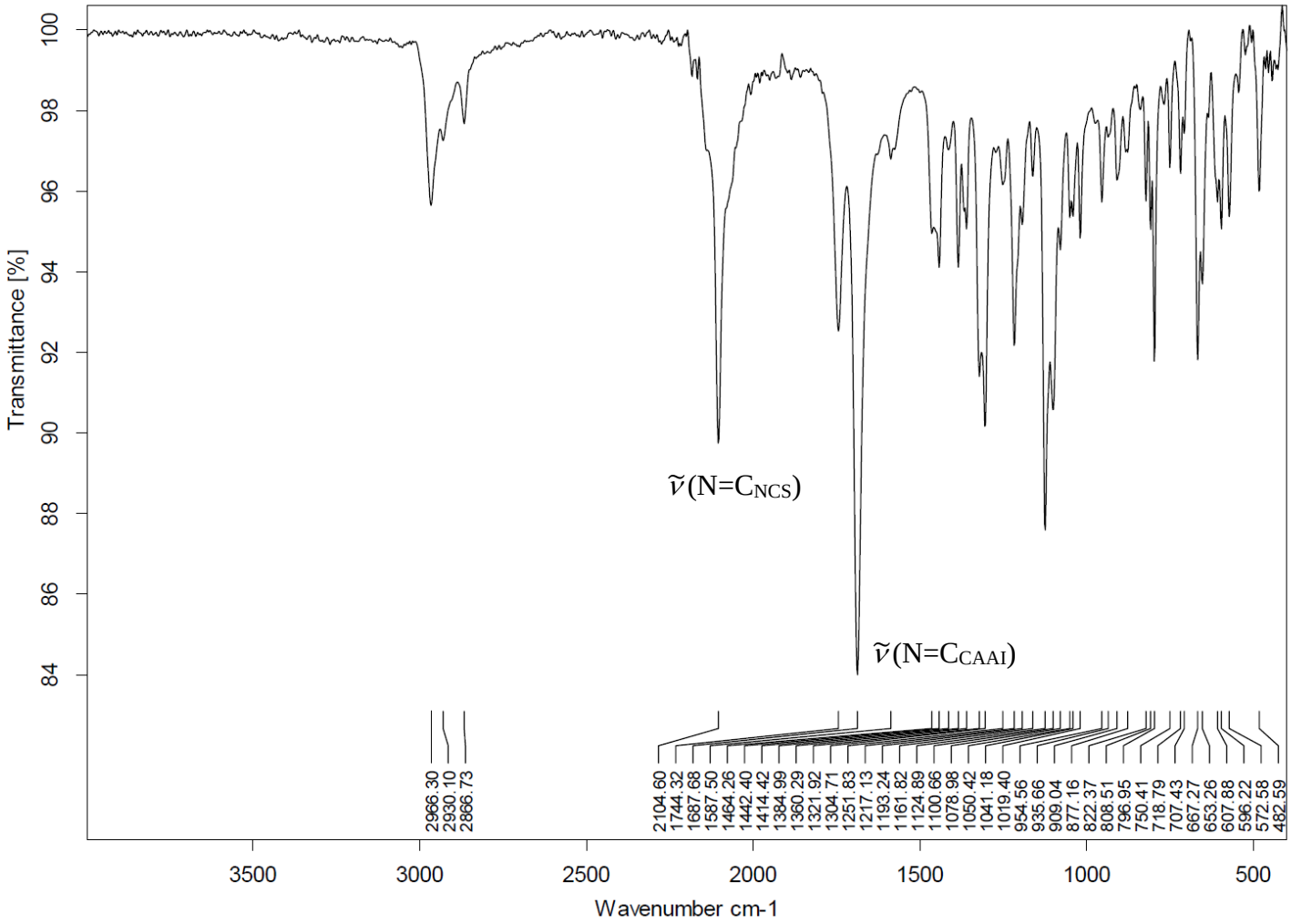


Figure S47. Solid-state IR spectrum of **3-NCS**.

X-ray crystallographic data

The crystal data of **2^{Br}-NMe_2**, **2^{Br}-Mes**, **2^{Br}-Ph**, **3-Br**, **3-N_3** and **5-NMe_2** were collected on a RIGAKU XTALAB SYNERGY-S diffractometer with a HPA area detector and multi-layer mirror monochromated $Cu_{K\alpha}$ radiation. The crystal data of **2^{Cl}-NMe_2** and **2^{Cl}-Cl** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated Mo_{Ka} radiation. The crystal data of **2^{Cl}-Dur**, **3-NMe_2**, **3-Ph**, **4** and **5-Mes** were collected on a Bruker D8 Quest diffractometer with a CMOS area detector and multi-layer mirror monochromated Mo_{Ka} radiation. The structure was solved using intrinsic phasing method,[7] refined with the SHELXL program, and expanded using Fourier techniques.[11] All non-hydrogen atoms were refined anisotropically.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-2237053-2237066. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S1. CCDC numbers of structurally characterised compounds.

	CCDC		CCDC
2^{Cl}-NMe_2	2237055	**3-Ph**	2237056
2^{Br}-NMe_2	2237066	**3-Br**	2237065
2^{Cl}-Cl	2237054	**3-N_3**	2237058
2^{Cl}-Dur	2237061	**3-NCS**	2237063
2^{Br}-Mes	2237053	**4**	2237057
2^{Br}-Ph	2237064	**5-NMe_2**	2237059
3-NMe_2	2237062	**5-Mes**	2237060

Crystal data for 2^{Cl}-NMe$_2$: $C_{22}H_{37}BClN_3$, M_r = 389.80, colourless block, 0.36×0.321×0.21 mm^3, monoclinic space group $P2_1/c$, a = 17.943(10) Å, b =9.057(4) Å, c = 14.529(8) Å, β = 105.28(3)°, V = 2278(2) Å^3, Z = 4, ρ_{calcd} = 1.137 g·cm^{-3}, μ = 0.179 mm^{-1}, F(000) = 848, T = 100(2) K, R_1 = 0.0587, wR_2 = 0.1038, 4476 independent reflections [2θ≤52.04°] and 254 parameters.

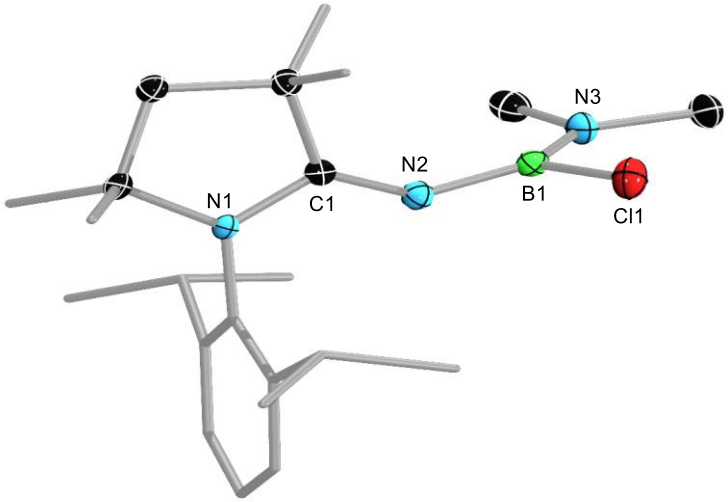


Figure S48. Solid-state structures of 2^{Cl}-NMe$_2$. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Refinement details for 2^{Br}-NMe_2: The $BBrNMe_2$ fragment (B1 > C6) was modelled as twofold flip-disordered in a 85:15 ratio. 1,2- and 1,3-distances were restrained to similarity with SAME, ADPs with SIMU 0.002.

Crystal data for 2^{Br}-NMe_2: $C_{22}H_{37}BBrN_3$, M_r = 434.26, colourless plate, 0.410×0.110×0.070 mm^3, monoclinic space group $P2_1/c$, a = 18.0177(2) Å, b =9.08810(10) Å, c = 14.5514(2) Å, β = 104.9120(10)°, V = 2302.50(5) $Å^3$, Z = 4, ρ_{calcd} = 1.253 $g \cdot cm^{-3}$, μ = 2.495 mm^{-1}, $F(000)$ = 920, T = 100(2) K, R_1 = 0.0475, wR_2 = 0.1250, 4836 independent reflections [$2\theta \leq 154.638°$] and 302 parameters.

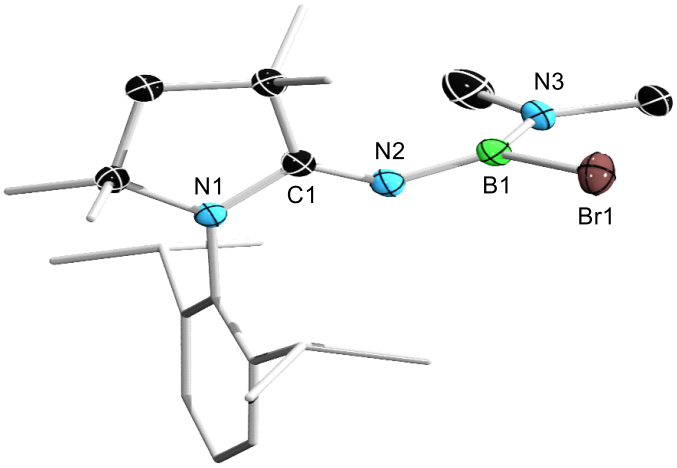


Figure S49. Solid-state structures of 2^{Br}-NMe_2. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Refinement details for 2^{Cl}-Cl: The BCl_2 unit was modelled as twofold rotationally disordered in a 94:6 ratio. ADPs within the disorder were restrained with SIMU 0.005.

Crystal data for 2^{Cl}-Cl: $C_{20}H_{31}BCl_2N_2$, M_r = 381.18, colourless block, 0.488×0.298×0.270 mm^3, monoclinic space group $P2_1/n$, a = 14.270(6) Å, b =10.149(4) Å, c = 14.806(6) Å, β = 97.11(2)°, V = 2127.9(15) $Å^3$, Z = 4, ρ_{calcd} = 1.190 $g \cdot cm^{-3}$, μ = 0.310 mm^{-1}, $F(000)$ = 816, T = 100(2) K, R_1 = 0.0436, wR_2 = 0.1004, 4202 independent reflections [$2\theta \leq 52.038°$] and 253 parameters.

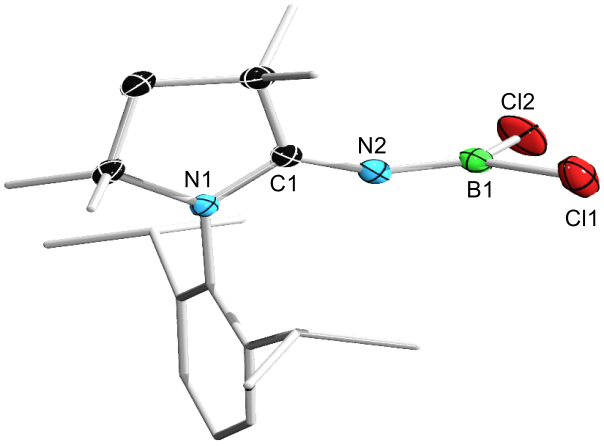


Figure S50. Solid-state structures of **2^{Cl}-Cl**. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Crystal data for 2^{Cl}-Dur: $C_{30}H_{44}BClN_2$, M_r = 478.93, colourless block, 0.405×0.275×0.199 mm^3, monoclinic space group $P2_1/n$, a = 10.300(2) Å, b =16.861(3) Å, c = 16.843(5) Å, β = 103.065(16)°, V = 2849.4(12) Å^3, Z = 4, ρ_{calcd} = 1.116 g·cm^{-3}, μ = 0.154 mm^{-1}, F(000) = 1040, T = 100(2) K, R_1 = 0.0534, wR_2 = 0.1182, 6076 independent reflections [$2\theta \leq 53.766°$] and 319 parameters.

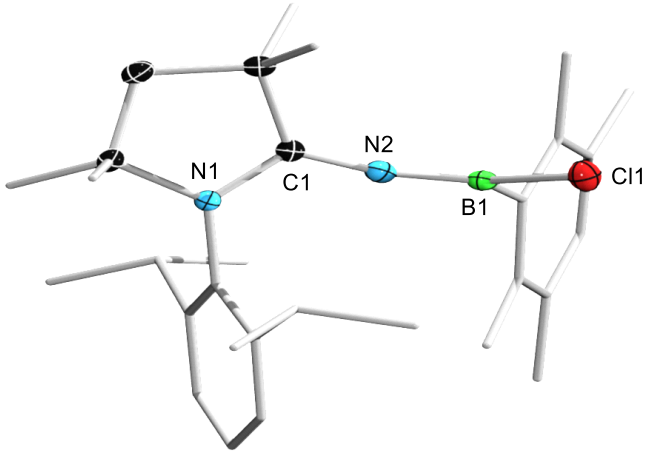


Figure S51. Solid-state structures of 2^{Cl}-**Dur**. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Crystal data for 2^{Br}-Mes: $C_{29}H_{42}BBrN_2$, M_r = 509.36, colourless block, 0.289×0.230×0.063 mm^3, monoclinic space group $P1_21/n1$, a = 10.0184(3) Å, b =16.7493(4) Å, c = 17.4941(5) Å, β = 106.480(3)°, V = 2814.92(15) Å^3, Z = 4, ρ_{calcd} = 1.202 g·cm^{-3}, μ = 1.479 mm^{-1}, F(000) = 1080, T = 99.98(12) K, R_1 = 0.0549, wR_2 = 0.0811, 7292 independent reflections [$2\theta \leq 62.2058°$] and 309 parameters.

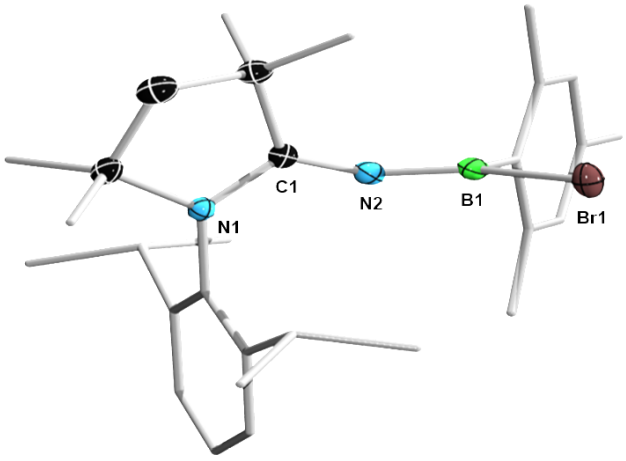


Figure S52. Solid-state structures of 2^{Br}-**Mes**. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Refinement details for 2^{Br}-Ph: Refined as a 2-component twin. Component 2 rotated by –179.9271° around [0.00 0.00 1.00] (reciprocal) or [–0.16 –0.06 0.98] (direct) The BASF parameter was refined to 30.6%. Some reflections were removed from refinement as outliers, these likely belong to a third twin component, which could not be modelled adequately.

Crystal data for 2^{Br}-Ph: $C_{26}H_{36}BBrN_2$, M_r = 467.29, colourless plate, 0.149×0.038×0.006 mm^3, triclinic space group $P\bar{1}$, a = 9.3778(3) Å, b = 13.0392(3) Å, c = 20.8478(6) Å, α = 86.673(2)°, β = 85.097(2)°, γ = 75.815(2)°, V = 2460.66(12) Å^3, Z = 4, ρ_{calcd} = 1.261 g·cm^{-3}, μ = 2.365 mm^{-1}, F(000) = 984, T = 100(2) K, R_1 = 0.0884, wR_2 = 0.2428, 14301 independent reflections [$2\theta \leq 140.15°$] and 558 parameters.

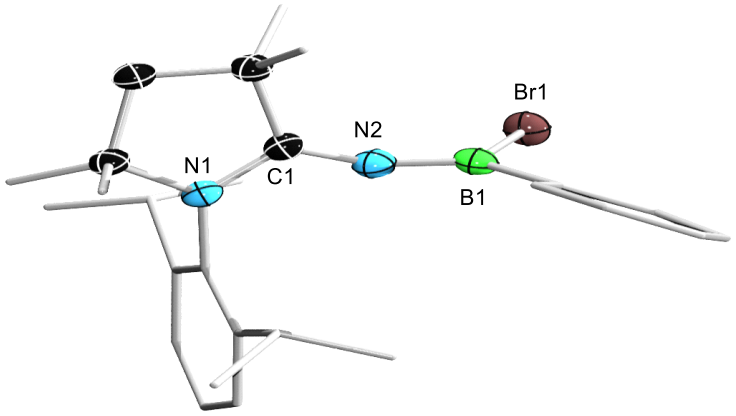


Figure S53. Solid-state structures of 2^{Br}-Ph. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Crystal data for 3-NMe2: $C_{42}H_{68}BN_5$, M_r = 653.82, colourless block, 0.604×0.285×0.212 mm^3, triclinic space group $P\bar{1}$, a = 9.654(3) Å, b =14.571(4) Å, c = 16.429(10) Å, α = 65.392(11)°, β = 79.27(2)°, γ = 70.736(12)°, V = 1980.4(15) Å^3, Z = 2, ρ_{calcd} = 1.096 g·cm^{-3}, μ = 0.064 mm^{-1}, F(000) = 720, T = 100 K, R_1 = 0.0609, wR^2 = 0.1018, 7781 independent reflections [$2\theta \leq 52.044°$] and 451 parameters.

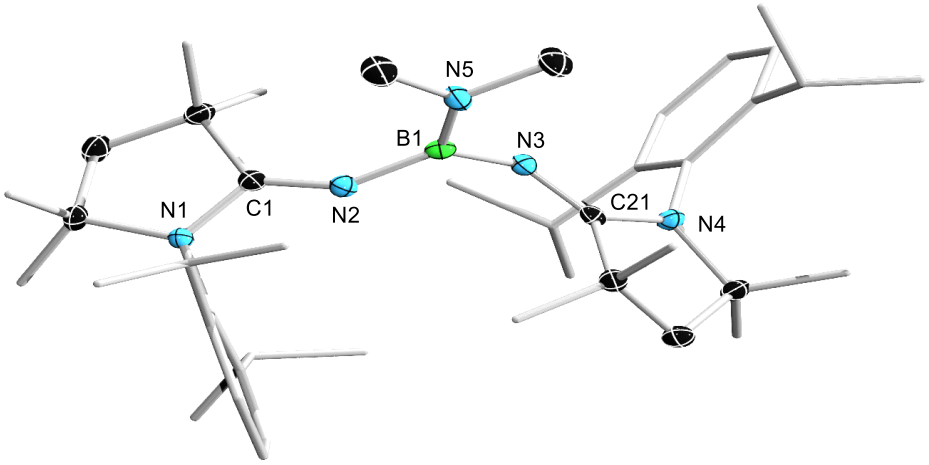


Figure S54. Solid-state structures of **3-NMe2**. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Refinement details for 3-Ph: The asymmetric unit contains half a toluene molecules positioned on an inversion centre and modelled as twofold rotational disordered in an 11:39 ratio with PARTs -1 and -2. The phenyl rings within this disorder were idealized with AFIX 66. 1,2- and 1,3-distances were restrained to similarity with SAME 0.005 and ADPs with SIMU 0.01 and ISOR 0.005.

Crystal data for 3-Ph: $C_{49.50}H_{71}BN_4$, M_r = 732.91, colourless block, 0.492×0.456×0.343 mm^3, triclinic space group $P\ \bar{1}$, a = 9.261(15) Å, b =11.923(19) Å, c = 20.48(3) Å, α = 91.46(3)°, β = 91.08(5)°, γ = 96.36(3)°, V = 2246(6) Å^3, Z = 2, ρ_{calcd} = 1.084 g·cm^{-3}, μ = 0.062 mm^{-1}, F(000) = 802, T = 100(2) K, R_1 = 0.0978, wR_2 = 0.1490, 8867 independent reflections [2θ≤52.044°] and 581 parameters.

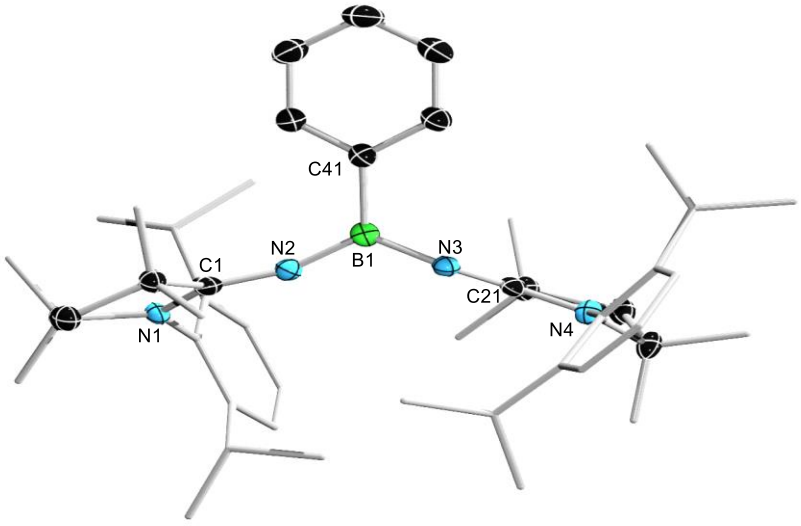


Figure S55. Solid-state structures of **3-Ph**. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Crystal data for 3-Br: $C_{40}H_{62}BBrN_4$, M_r = 689.65, colourless block, 0.289×0.169×0.164 mm^3, monoclinic space group $P2_1$, a = 9.55970(10) Å, b = 9.60350(10) Å, c = 21.56940(10) Å, β = 94.2800(10)°, V = 1974.69(3) Å^3, Z = 2, ρ_{calcd} = 1.160 g·cm^{-3}, μ = 1.638 mm^{-1}, F(000) = 740, T = 100.00(10) K, R_1 = 0.0229, wR_2 = 0.0614, Flack parameter = –0.019(6), 7493 independent reflections [2θ≤140.136°] and 431 parameters.

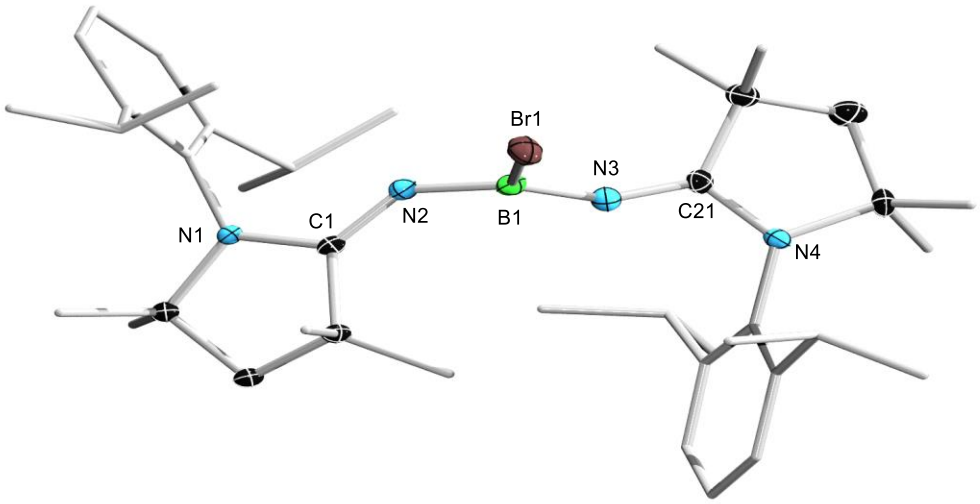


Figure S56. Solid-state structures of **3-Br**. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Refinement details for 3-N_3: The ADPs of the azide nitrogen atoms N5 > N7 were restrained with SIMU 0.001 to avoid a Hirshfeld test alert.

Crystal data for 3-N_3: $C_{40}H_{62}BN_7$, M_r = 651.77, colourless block, 0.271×0.194×0.115 mm^3, monoclinic space group $P2_1/c$, a = 9.52340(10) Å, b = 12.29820(10) Å, c = 33.6499(2) Å, β = 96.8590(10)°, V = 3912.89(6) $Å^3$, Z = 4, ρ_{calcd} = 1.106 $g \cdot cm^{-3}$, μ = 0.500 mm^{-1}, $F(000)$ = 1424, T = 99.99(10) K, R_1 = 0.0395, wR_2 = 0.0963, 8054 independent reflections [$2\theta \leq 150.644°$] and 449 parameters.

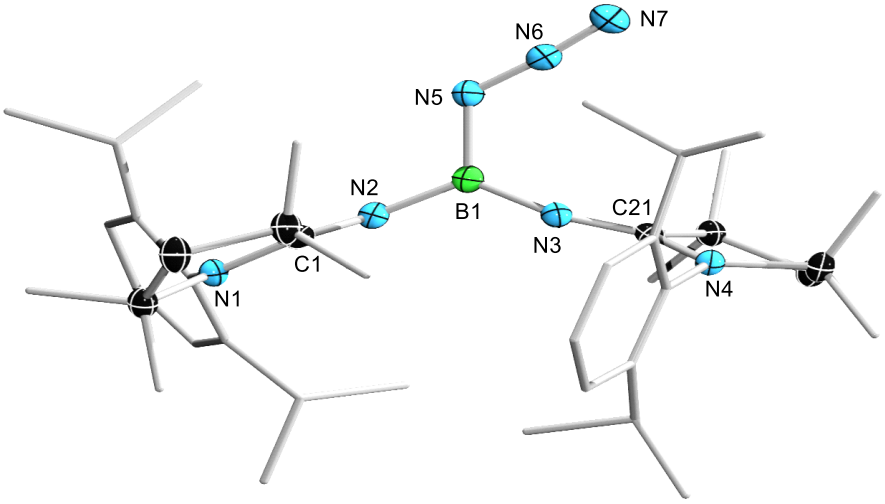


Figure S57. Solid-state structures of **3-N_3**. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Refinement details for 3-NCS: The CAAC backbone was modelled with a twofold flip-disorder in C3 > C9 in a 57:43 ratio. 1,2- and 1,3-distances within the disorder were restrained with SAME, ADPs with SIMU 0.002.

Crystal data for 3-NCS: $C_{41}H_{62}BN_5S$, M_r = 667.82, colourless plate, 0.383×0.181×0.047 mm^3, monoclinic space group $P2_1/c$, a = 9.53740(10) Å, b =19.8419(2) Å, c = 21.4198(2) Å, β = 97.1630(10)°, V = 4021.85(7) Å^3, Z = 4, ρ_{calcd} = 1.103 g·cm^{-3}, μ = 0.955 mm^{-1}, F(000) = 1456, T = 100.00(10) K, R_1 = 0.0472, wR_2 = 0.1059, 7646 independent reflections [$2\theta \leq 140.144°$] and 517 parameters.

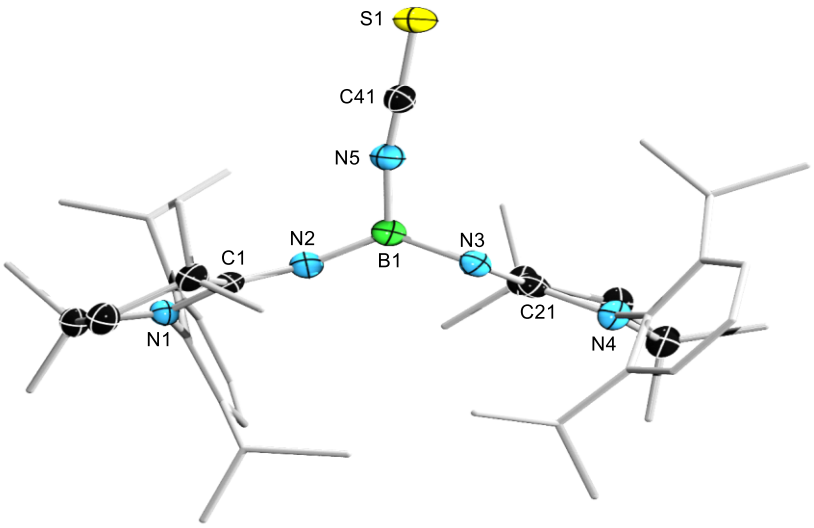


Figure S58. Solid-state structures of **3-NCS**. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Crystal data for 4: $C_{48}H_{86}B_4Cl_2N_8$, M_r = 889.38, colourless plate, 0.317×0.252×0.100 mm^3, triclinic space group $P\bar{1}$, a = 10.834(3) Å, b =16.640(5) Å, c = 16.947(6) Å, α = 65.006(8)°, β = 89.810(8)°, γ = 78.779(12)°, V = 2705.3(16) Å^3, Z = 2, ρ_{calcd} = 1.092 g·cm^{-3}, μ = 0.159 mm^{-1}, F(000) = 968, T = 100(2) K, R_1 = 0.0536, wR^2 = 0.0923, 10646 independent reflections [2θ≤52.04°] and 583 parameters.

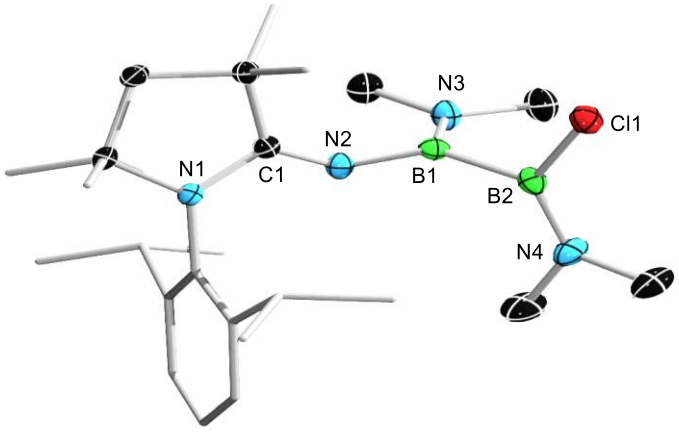


Figure S59. Solid-state structures of **4**. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Refinement details for 5-NMe$_2$: The CAAC backbone was modelled as twofold flip-disordered in C4 > C9 in a87:13 ratio. ADPs within the disorder were restrained with SIMU 0.005. One reflection affected by the beamstop was omitted (11 3 10).

Crystal data for 5-NMe$_2$: $C_{44}H_{74}B_2N_6$, M_r = 708.71, colourless block, 0.360×0.230×0.190 mm^3, monoclinic space group *C*2/*c*, a = 10.63470(10) Å, b =16.5638(3) Å, c = 25.4585(3) Å, β = 100.6440(10)°, V = 4407.38(10) Å^3, Z = 4, r_{calcd} = 1.068 g·cm^{-3}, μ = 0.465 mm^{-1}, F(000) = 1560, T = 100(2) K, R_1 = 0.0592, wR_2 = 0.1509, 4554 independent reflections [$2\theta \leq 154.926°$] and 304 parameters.

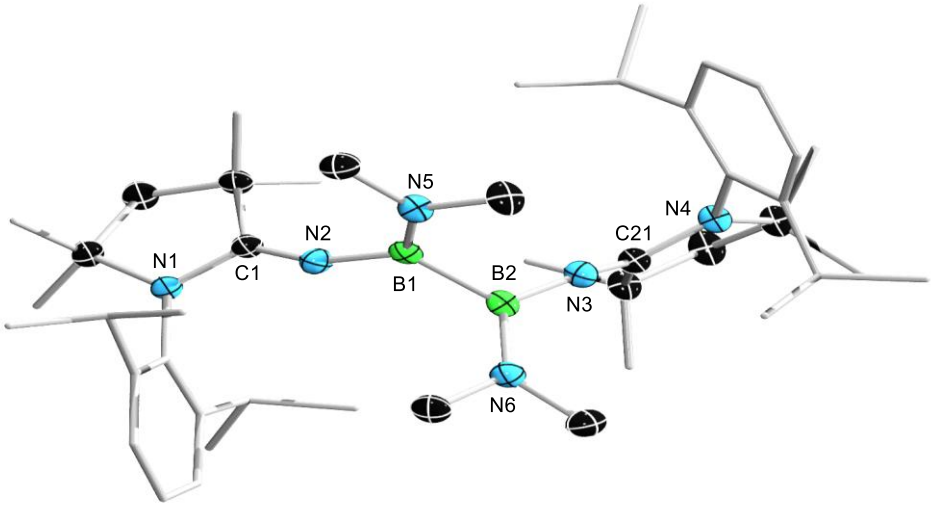


Figure S60. Solid-state structures of **5-NMe$_2$**. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Refinement details for 5-Mes: The benzene molecule was modelled as twofold rotationally disordered in a 7:3 ratio. The rings within this disorder were idealized with AFIX 6 and ADPs restrained with SIMU 0.005.

Crystal data for 5-Mes: $C_{64}H_{90}B_2N_4$, M_r = 937.01, colourless block, 0.327×0.262×0.253 mm^3, triclinic space group $P\ \bar{1}$, a = 10.897(2) Å, b = 13.450(3) Å, c = 20.469(4) Å, α = 88.759(12)°, β = 74.992(10)°, γ = 82.039(7)°, V = 2869.4(10) Å^3, Z = 2, ρ_{calcd} = 1.085 g·cm^{-3}, μ = 0.062 mm^{-1}, F(000) = 1024, T = 100(2) K, R_1 = 0.0483, wR_2 = 0.1067, 11289 independent reflections [$2\theta \leq 52.044°$] and 684 parameters.

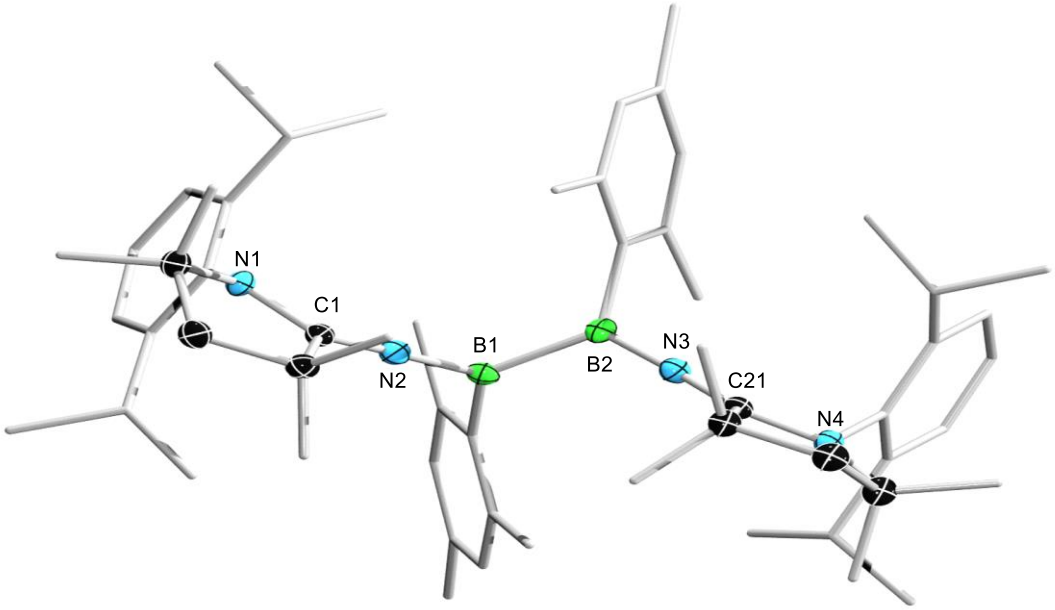


Figure S61. Solid-state structures of **5-Mes**. Atomic displacement ellipsoids shown at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Computational details

Density functional theory (DFT) calculations were carried out using the program Turbomole V7.2[12] implemented in the user interface TmoleX2022.[13] Geometry optimisations were carried out at the B3LYP[14]-D3(BJ)[15]/Def2-SVP[16] level of theory and minima were confirmed by the absence of negative frequencies. Wiberg bond indices (WBIs)[17] and partial charges, obtained by natural population analysis (NPA),[18] were calculated using TmoleX2022. Molecular orbital plots were generated within the TmoleX2022 orbital viewer.

NMR shielding calculations were performed on the structures of **2^{Cl}-Y** (Y = Cl, NMe_2, Dur) and **3-Y** (Y = Cl, NMe_2, Dur) optimised at the B3LYP-D3(BJ)/Def2-SVP level of theory (see structural data in Table S2), using $BF_3(OEt_2)$ (δ_{11B} = 0 ppm) as a reference and various levels of theory (functionals: B3LYP, ωB97X-D,[19] LC[20]-TPSS;[21] basis sets: Def2-SVP, pcSseg-1/2;[22] solvent model: PCM(benzene)).[23] These calculations were carried out using Gaussian 16.[24] The results are summarised in Table S3 and show that the calculated ^{11}B NMR shifts and their relative order are highly dependent upon the level of theory used. The experimentally observed chemical shift order of Y = Dur > NMe_2 > Cl could only be reproduced for the **3-Y** series when using the pcsseg-1 basis set (highlighted in green in Table S3), albeit with a large upfield-shift of ca. 4 ppm for **3-NMe_2** compared to the experimental value.

Table S2. Comparison of selected experimental and calculated (B3LYP-D3(BJ)/Def2-SVP) structural parameters for **2^{Cl}-Y** (Y = Cl, NMe_2, Dur) and **3-Y** (Y = NMe_2, Dur).

	C=N		$B–N_{CAAI}$		C-N-B	
	exp.	calcd.	exp.	calcd.	exp.	calcd.
2^{Cl}-Dur	1.270(2)	1.262	1.344(2)	1.357	168.51(15)	169.87
2^{Cl}-NMe_2	1.271(2)	1.271	1.406(3)	1.403	139.30(15)	138.33
2^{Cl}-Cl	1.276(2)	1.268	1.332(2)	1.356	155.78(15)	154.06
3-Ph	1.275(3)		1.444(3)		132.57(19)	
	1.266(3)		1.402(3)		154.0(2)	
3-NMe_2	1.2636(18)	1.259	1.427(2)	1.421	146.81(13)	150.85
	1.2694(19)	1.270	1.455(2)	1.446	131.18(12)	132.63

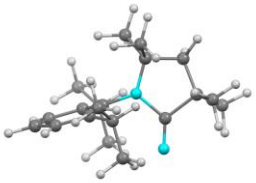
Table S3. Experimental and calculated ^{11}B NMR shifts (ppm) of **2^{Cl}-Y** (Y = Cl, NMe_2, Dur) and **3-Y** (Y = Cl, NMe_2, Dur) optimised at the B3LYP-D3(BJ)-Def2-SVP level of theory. Highlighted in green are the results which reflect the experimental order of the NMR shifts.

	2^{Cl}-Dur	**2^{Cl}-NMe_2**	**2^{Cl}-Cl**	**3-Ph**	**3-NMe_2**	**3-Cl**
exp.	30.4	26.7	24.8	29.7	27.3	23.9
B3LYP/Def2-SVP	30.99	26.24	28.67	27.86	23.14	24.40
ωB97X-D/Def2-SVP	30.25	26.21	28.28	30.95	23.66	25.08
ωB97X-D/Def2-SVP/PCM(benzene)	29.81	26.20	27.78	31.04	23.85	24.95
ωB97X-D/pcSseg-1	28.70	26.12	27.05	29.27	23.49	23.28
ωB97X-D/pcSseg-1/PCM(benzene)	28.24	26.11	26.50	29.39	23.71	23.16
ωB97X-D/pcSseg-2	29.73	26.42	28.27	29.78	23.15	23.78
ωB97X-D/pcSseg-2/PCM(benzene)	29.24	26.37	27.68	29.86	23.34	23.60
LC-TPSS/pcSseg-1	30.59	28.16	28.94	32.30	25.76	25.51
LC-TPSS/ pcSseg-1/PCM(benzene)	30.11	28.19	28.40	32.42	25.99	25.42

Cartesian coordinates

Table S4. Cartesian coordinates (Å) of compounds optimized at the B3LYP-D3(BJ)/Def2-SVP level of theory, with SCF energies and lowest calculated IR frequencies.

CAAI anion A



E_{SCF} = –889.1654531288 Ha

Lowest IR frequency = 48.07 cm^{-1}

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C 3.1010768 9.7510528 7.8599343
C 1.6609098 9.7848357 8.4591321
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H 1.7415949 9.9847375 9.5404515
C 1.0245110 8.4050888 8.2539237
C 3.1351287 10.3761551 6.4434742
H 2.9021152 11.4548027 6.4860669
H 2.4063166 9.9016926 5.7727996
H 4.1356315 10.2614392 5.9962381
C 4.0585645 10.5861253 8.7349419
H 3.7615344 11.6498159 8.7249946
H 5.0946023 10.5174209 8.3651156
H 4.0468062 10.2417260 9.7785476
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H -0.6773193 8.9531198 6.9660171
H -0.0942746 7.2590508 6.8043031
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C 5.6062764 7.5733673 8.6315948
C 6.9015444 7.1369745 8.3230050
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C 6.3298851 6.9940227 5.9874801
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C 5.0257551 7.4303594 6.2598816
C 5.1435498 7.6343548 10.0782310
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H 3.1026297 7.9325650 5.5411295
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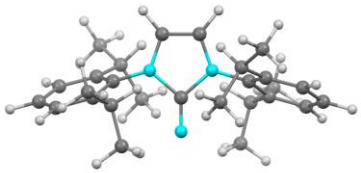
NHI anion B



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Lowest IR frequency = 37.93 cm^{-1}

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C 1.7761903 9.7238414 8.6215452
N 1.1459231 8.5049465 8.4320716
C 4.5686475 7.7674961 7.5649620
C 5.4565185 7.5055404 8.6335741
C 6.7289013 7.0076048 8.3467574
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C 7.1059143 6.7270185 7.0347779
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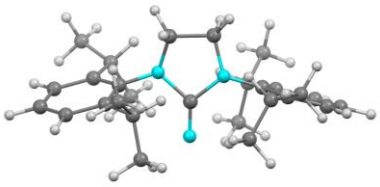
SNHI anion C



E_{SCF} = –1214.492310168 Ha

Lowest IR frequency = 38.78 cm^{-1}

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C 1.6914744 9.8130936 8.6146951
N 1.1012361 8.6384706 8.0278351
C 4.5801795 7.7126404 7.7474856
C 5.5029500 7.2747504 8.7298497
C 6.7571872 6.8007642 8.3295660

H 7.4790492 6.4666380 9.0785575
C 7.0910563 6.7297625 6.9744679
H 8.0736308 6.3551739 6.6706828
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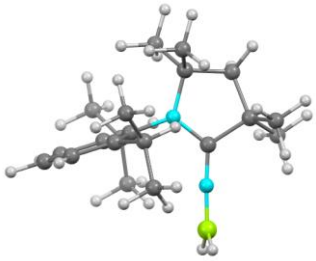
H 5.2490957 8.4688223 3.6597348
H 4.8065573 9.8404102 4.7052158
C -0.2635556 8.3650507 8.2701880
C -1.2021576 8.7077949 7.2655207
C -2.5657530 8.5021030 7.5024879
C -3.0014319 7.9375407 8.7043459
C -2.0705071 7.5546172 9.6675544
C -0.6953594 7.7565582 9.4702027
C -0.6772915 9.1814704 5.9196739
H -3.2989719 8.7681932 6.7374693
H -4.0701640 7.7784091 8.8794395
H -2.4158941 7.0795216 10.5903040
C 0.3008114 7.2558397 10.5053893
H 1.2918166 7.6318987 10.2210156
C -0.0032790 7.7682046 11.9200461
C 0.3829823 5.7220045 10.4458227
C -0.2004955 7.9578746 5.1141062
C -1.6651981 10.0327966 5.1175524
H 0.2144282 9.7923036 6.1272835
H -1.0657366 7.3397267 4.8155410
H 0.3282946 8.2721839 4.1971308
H 0.4706339 7.3271995 5.7204597
H -0.5894334 5.2629334 10.6995450
H 0.6813796 5.4293799 9.4258770
H 1.1362614 5.3454537 11.1586847
H -0.0525421 8.8697347 11.9475923
H -0.9636738 7.3810714 12.3013350
H 0.7826558 7.4434362 12.6231127
H -2.0325314 10.8945061 5.6998529
H -2.5432068 9.4483286 4.7926974
H -1.1815917 10.4181926 4.2043039
H 1.5810354 9.8486263 9.7237209
H 3.8355685 10.1526078 8.9732365
H 3.3680297 10.1640518 7.2509097
H 1.2571225 10.7510502 8.2185452

CAAI-BH_2, D



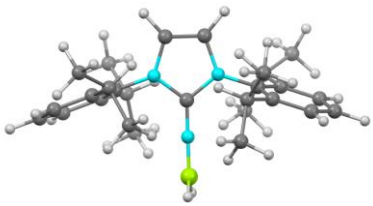
E_{SCF} = –915.2439858111 Ha

Lowest IR frequency = 41.48 cm^{-1}

N 2.235739 6.216919 8.151518
C 2.248779 7.474750 8.107594
N 3.348957 8.258322 7.844070
C 3.063836 9.720448 7.829457
C 1.659292 9.767454 8.480873
H 1.038605 10.566519 8.048965
H 1.772303 9.986306 9.553581
C 1.021276 8.371050 8.313113
C 3.060179 10.291613 6.402117
H 2.827460 11.367067 6.434371
H 2.314918 9.803470 5.760923
H 4.048100 10.174705 5.934141
C 4.088120 10.510960 8.651322

H 3.838879 11.582486 8.612904
H 5.104175 10.384023 8.248554
H 4.090619 10.202487 9.704254
C 0.119801 8.268530 7.069680
H -0.755517 8.929450 7.176070
H -0.237413 7.235374 6.943423
H 0.652341 8.553049 6.150467
C 0.238125 7.937212 9.556214
H -0.622929 8.605014 9.720289
H 0.873091 7.964137 10.455806
H -0.137200 6.909424 9.438882
C 4.635891 7.688451 7.581328
C 5.519832 7.456165 8.662145
C 6.798165 6.955285 8.383267
H 7.495455 6.775970 9.204775
C 7.187155 6.661316 7.078140
H 8.190540 6.275854 6.879173
C 6.281696 6.824771 6.032866
H 6.575012 6.543728 5.018934
C 4.990864 7.321056 6.262090
C 5.095165 7.638941 10.112623
H 4.124069 8.150840 10.110333
C 6.080380 8.495045 10.920995
H 5.685458 8.682873 11.932669
H 6.266814 9.467505 10.440232
H 7.052668 7.990377 11.039644
C 4.877206 6.269680 10.779219
H 4.514854 6.396601 11.812958
H 5.817779 5.696412 10.819597
H 4.139158 5.672715 10.225538
C 3.995485 7.346249 5.110943
H 3.087097 7.844573 5.468829
C 3.594612 5.912687 4.721904
H 2.827606 5.929137 3.929723
H 3.186606 5.367776 5.584317
H 4.460681 5.348478 4.338584
C 4.511554 8.120404 3.889663
H 3.727091 8.190198 3.118451
H 5.377924 7.618073 3.430352
H 4.822107 9.143222 4.152330
B 2.146784 4.861762 8.234118
H 2.341554 4.297942 9.293216
H 1.878083 4.203393 7.248272

NHI-BH_2, D



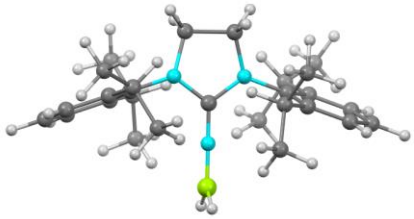
E_{SCF} = –1239.349164150 Ha

Lowest IR frequency = 35.37 cm^{-1}

N 1.886954 6.323435 7.599673
C 2.083358 7.531066 7.908955
N 3.298425 8.214783 7.951938
C 3.085471 9.543406 8.339015
C 1.758543 9.704703 8.547836
N 1.132918 8.479928 8.285430
C 4.551274 7.627419 7.604716
C 5.381386 7.138102 8.636556
C 6.602614 6.559760 8.270061
H 7.271198 6.172513 9.040667
C 6.975084 6.463033 6.927849
H 7.928610 5.999727 6.661340
C 6.136317 6.948854 5.926970
H 6.438533 6.864755 4.880551
C 4.906818 7.543075 6.244955
C 4.926661 7.188550 10.089191
H 4.248182 8.049821 10.191227
C 6.076324 7.397388 11.081253
H 5.676042 7.550832 12.095901
H 6.688091 8.274618 10.817540
H 6.743024 6.521177 11.128106
C 4.116880 5.926621 10.439023
H 3.728472 5.988102 11.468906
H 4.752292 5.028607 10.366877
H 3.267470 5.788365 9.756468
C 3.995343 8.066258 5.144942
H 3.114799 8.514627 5.626591
C 3.492930 6.924980 4.248136
H 2.783893 7.308881 3.496773
H 2.978744 6.155159 4.840747

H 4.325855 6.444053 3.709374
C 4.678023 9.172400 4.326679
H 3.981251 9.584698 3.578655
H 5.558532 8.790607 3.784287
H 5.014362 9.998391 4.973178
C -0.259753 8.199090 8.416424
C -1.121521 8.523420 7.346442
C -2.483107 8.234318 7.496703
C -2.964088 7.637936 8.664121
C -2.092268 7.318830 9.703067
C -0.721065 7.593875 9.601119
C -0.567852 9.105196 6.052442
H -3.178540 8.469340 6.689330
H -4.030431 7.417933 8.761278
H -2.480923 6.848291 10.609254
C 0.224145 7.233772 10.737312
H 1.233433 7.556838 10.445871
C -0.137135 7.983265 12.028508
C 0.277639 5.714498 10.958200
C -0.150183 7.972973 5.096068
C -1.526953 10.083067 5.363962
H 0.343022 9.668341 6.309032
H -1.028826 7.379156 4.794957
H 0.311654 8.386156 4.184324
H 0.567663 7.287766 5.568124
H -0.700464 5.321871 11.281933
H 0.568644 5.192789 10.035143
H 1.013997 5.465037 11.739019
H -0.147954 9.073212 11.869202
H -1.131690 7.689092 12.401770
H 0.594995 7.760149 12.821609
H -1.865603 10.873774 6.052194
H -2.420402 9.573629 4.967828
H -1.025772 10.563972 4.509110
H 1.185375 10.571707 8.860843
H 3.911643 10.242210 8.424150
B 1.680804 5.018089 7.268810
H 1.709388 4.146963 8.120853
H 1.462974 4.694489 6.114440

SNHI-BH$_2$, F



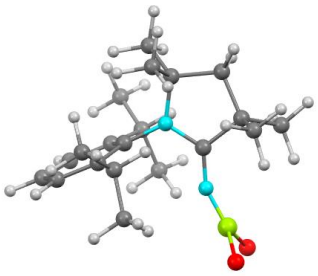
E_{SCF} = – 1240.559419284 Ha

Lowest IR frequency = 42.18 cm^{-1}

N 1.886639 6.373508 7.598561
C 2.084913 7.579523 7.895975
N 3.318933 8.195271 8.067634
C 3.166978 9.638717 8.202235
C 1.701428 9.771733 8.639355
N 1.110787 8.546492 8.114854
C 4.544480 7.595091 7.654103
C 5.414603 7.101399 8.651768
C 6.622910 6.522086 8.247327
H 7.314109 6.129467 8.994946
C 6.953971 6.432390 6.893915
H 7.900267 5.974236 6.594631
C 6.082024 6.921454 5.923744
H 6.351098 6.842034 4.867795
C 4.862417 7.513243 6.283046
C 5.002214 7.150972 10.116312
H 4.361144 8.038010 10.239539
C 6.181635 7.294607 11.083640
H 5.812700 7.451800 12.109695
H 6.826918 8.146537 10.816845
H 6.808416 6.388453 11.103096
C 4.143344 5.923131 10.468817
H 3.779611 5.986440 11.507752
H 4.734958 4.998062 10.370186
H 3.274670 5.835796 9.802457
C 3.926979 8.041512 5.204194
H 3.027039 8.434795 5.696502
C 3.462890 6.922335 4.260667
H 2.735959 7.312097 3.529865
H 2.980344 6.110201 4.822077
H 4.308911 6.496354 3.697350
C 4.567576 9.203241 4.428409
H 3.857046 9.618187 3.694755
H 5.461716 8.872473 3.875049

H 4.877329 10.015847 5.104633
C -0.266261 8.226677 8.301281
C -1.167518 8.527835 7.255778
C -2.521276 8.225495 7.442750
C -2.964650 7.638752 8.629664
C -2.060983 7.345305 9.648429
C -0.695971 7.634061 9.506291
C -0.651517 9.108025 5.946266
H -3.240629 8.444280 6.651953
H -4.025129 7.406623 8.758288
H -2.420306 6.882127 10.570533
C 0.272352 7.304651 10.633926
H 1.283635 7.581389 10.305670
C -0.038807 8.124950 11.895761
C 0.299332 5.798691 10.934132
C -0.178995 7.978794 5.013095
C -1.657312 10.022732 5.239473
H 0.234363 9.714637 6.191730
H -1.026907 7.335012 4.727119
H 0.261584 8.393205 4.091206
H 0.571961 7.342250 5.500290
H -0.675843 5.445342 11.307298
H 0.550692 5.223156 10.032013
H 1.053965 5.574111 11.704948
H -0.034092 9.206379 11.684893
H -1.030527 7.871658 12.304844
H 0.707175 7.924531 12.682130
H -2.035064 10.810079 5.911180
H -2.524552 9.461123 4.855682
H -1.181874 10.509829 4.373329
H 1.610168 9.822096 9.741395
H 3.870366 10.046400 8.944229
H 3.350571 10.153698 7.239792
H 1.211798 10.662925 8.217937
B 1.660952 5.068779 7.276272
H 1.598866 4.218609 8.144202
H 1.519510 4.734102 6.115576

2^{Cl}-Cl



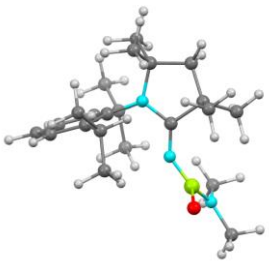
E_{SCF} = –1834.17565305554 Ha

Lowest IR frequency = 37.84 cm^{-1}

N 2.269053 6.231719 8.150483
B 1.686328 5.013097 8.270466
C 2.262328 7.499223 8.100691
N 3.349497 8.274135 7.838636
C 3.065102 9.739918 7.821368
C 1.653123 9.786693 8.458043
H 1.031793 10.574131 8.006800
H 1.752200 10.021901 9.528520
C 1.028301 8.382921 8.301564
C 3.078586 10.301321 6.391666
H 2.851554 11.377969 6.417124
H 2.336265 9.813737 5.746656
H 4.070160 10.176294 5.933691
C 4.083943 10.525557 8.652864
H 3.835694 11.597136 8.613397
H 5.102986 10.397797 8.258394
H 4.076782 10.215686 9.705339
C 0.131862 8.255561 7.055019
H -0.760162 8.892862 7.163596
H -0.196077 7.213825 6.921953
H 0.658035 8.558894 6.138141
C 0.248635 7.949821 9.547914
H -0.599285 8.631515 9.720914
H 0.889398 7.958340 10.443425
H -0.150352 6.931222 9.430704
C 4.640177 7.702722 7.580898
C 5.517243 7.474879 8.666978
C 6.798641 6.979939 8.391857
H 7.493310 6.802413 9.215778
C 7.193312 6.688461 7.087835
H 8.199320 6.308187 6.892488
C 6.290440 6.844994 6.039258
H 6.587610 6.562209 5.027086

C 4.996075 7.334304 6.263340
C 5.084030 7.648981 10.116055
H 4.112314 8.160076 10.114502
C 6.064045 8.501809 10.934286
H 5.663123 8.683270 11.944632
H 6.252982 9.477166 10.460218
H 7.035788 7.997009 11.056004
C 4.864728 6.274787 10.772558
H 4.502148 6.395457 11.806847
H 5.805572 5.701845 10.809442
H 4.123873 5.681225 10.219934
C 4.000192 7.341677 5.112370
H 3.086474 7.835771 5.463341
C 3.612216 5.900125 4.740353
H 2.840541 5.899627 3.952901
H 3.207967 5.361351 5.607331
H 4.482747 5.341013 4.359963
C 4.509460 8.107263 3.883008
H 3.724714 8.159800 3.110867
H 5.380769 7.608126 3.429837
H 4.809776 9.136243 4.133524
Cl 0.895909 4.205079 6.871646
Cl 1.715623 4.099082 9.813836

2^{Cl}-NMe_2



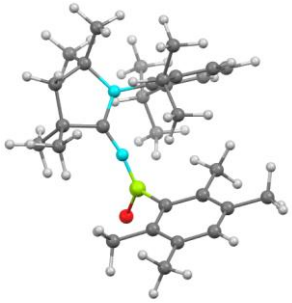
E_{SCF} = –1508.559911158 Ha

Lowest IR frequency = 39.31 cm^{-1}

B 14.987309 3.617760 2.696297
Cl 16.078369 2.168043 2.936988
N 15.506454 4.723735 1.978751
C 16.814434 4.795007 1.360730
H 16.729319 4.996076 0.275656
H 17.358023 3.853580 1.498585
H 17.417982 5.613857 1.798246
C 14.731775 5.939260 1.826936
H 14.590964 6.194623 0.759551
H 15.237298 6.799388 2.307542
H 13.743253 5.819095 2.283248
N 11.731891 3.340551 4.460301
C 13.054835 3.656198 4.280932
C 13.626907 4.156496 5.616989
C 12.352459 4.485322 6.420682
H 12.470907 4.289526 7.496672
H 12.119822 5.555373 6.307345
C 11.196272 3.652433 5.814268
C 14.451715 3.021972 6.256066
H 13.848206 2.117723 6.418491
H 14.844853 3.348278 7.232526
H 15.297400 2.744374 5.610838
C 14.516249 5.388350 5.423131
H 15.409000 5.145148 4.828441
H 14.853683 5.770532 6.400014
H 13.975302 6.195752 4.905942
C 10.902137 2.380441 6.623985
H 10.151475 1.760791 6.112774
H 10.499387 2.655453 7.611011
H 11.800251 1.770397 6.784883
C 9.904910 4.475253 5.736568
H 10.061433 5.423925 5.206116
H 9.557711 4.709107 6.754920
H 9.106910 3.917224 5.224392
N 13.673600 3.522892 3.178595
C 10.952332 2.677636 3.456655
C 10.179336 3.443368 2.553666
C 9.326521 2.773251 1.666316
H 8.715248 3.351516 0.969796
C 9.266101 1.381790 1.640517
H 8.589987 0.874411 0.947560
C 10.103177 0.638770 2.469773
H 10.097735 -0.451194 2.402073
C 10.970697 1.265094 3.375278
C 10.347640 4.949941 2.424641
H 10.970015 5.286147 3.264900
C 11.978992 0.418723 4.139217
H 12.472364 1.066683 4.872764
C 11.124393 5.260989 1.132643

H 10.532612 4.990784 0.242609
H 12.063904 4.692332 1.103942
H 11.360568 6.336158 1.066773
C 9.022038 5.721743 2.470214
H 9.209085 6.807495 2.442677
H 8.447956 5.496809 3.381436
H 8.383882 5.478873 1.605672
C 13.072140 -0.075507 3.175836
H 12.652755 -0.763206 2.422507
H 13.859753 -0.613949 3.727565
H 13.543511 0.767785 2.654637
C 11.341872 -0.752391 4.898587
H 10.901762 -1.490939 4.209484
H 10.546147 -0.416941 5.580865
H 12.103570 -1.279278 5.495875

2^{Cl}-Dur



E_{SCF} = –1762.55593278544 Ha

Lowest IR frequency = 35.52 cm^{-1}

N 5.474528 9.392200 3.440038
C 3.261972 10.640513 3.945431
B 4.118031 9.414028 3.449668
Cl 3.228476 7.913105 2.896830
N 7.674704 9.070790 4.155255
C 6.714078 9.324894 3.214370
C 9.044372 8.916577 3.584296
C 8.870152 9.577736 2.193963
H 9.186852 10.629938 2.258333
H 9.499367 9.092690 1.433489
C 7.366877 9.518083 1.841699
C 10.103631 9.628379 4.429425
H 10.135876 9.221511 5.451309
H 9.921984 10.708223 4.491930
H 11.093823 9.478537 3.972479
C 9.440524 7.435813 3.461381
H 9.532333 6.969906 4.451700
H 10.416460 7.354693 2.958273
H 8.708453 6.861606 2.877705
C 6.995018 8.326697 0.940608
H 5.902383 8.258258 0.829636
H 7.345690 7.371297 1.356897
H 7.443689 8.450254 -0.058016
C 6.869172 10.821823 1.205679
H 7.061916 11.684230 1.862739
H 5.787009 10.773787 1.020576
H 7.378457 10.996828 0.244150
C 7.352945 9.052022 5.552503
C 7.348818 10.280869 6.258490
C 7.058049 10.259696 7.628109
H 7.055231 11.196446 8.189249
C 6.752483 9.067380 8.282045
H 6.528232 9.070965 9.351703
C 6.702513 7.877187 7.562284
H 6.422314 6.952195 8.071241
C 6.986314 7.845453 6.189056
C 6.824939 6.532940 5.436255
H 7.101304 6.715022 4.390648
C 7.574951 11.622220 5.571910
H 7.936470 11.419501 4.555071
C 7.744231 5.433802 5.991628
H 7.446972 5.142963 7.012139
H 8.795051 5.758883 6.035839
H 7.690933 4.530491 5.362633
C 5.359678 6.067031 5.439377
H 5.003374 5.871438 6.463935
H 5.256210 5.132291 4.864724
H 4.696967 6.811644 4.979297
C 6.251402 12.391746 5.427851
H 5.816048 12.623055 6.413959
H 5.508326 11.814361 4.863746
H 6.415679 13.347210 4.902769
C 8.634482 12.477170 6.282360
H 9.576162 11.925636 6.428111
H 8.287262 12.810462 7.273180
H 8.853193 13.382591 5.693410

C 2.749513 11.574530 3.021191
C 2.051581 12.708723 3.483601
C 1.872780 12.873023 4.861101
H 1.332046 13.754041 5.221870
C 2.355283 11.949365 5.793850
C 3.058639 10.818815 5.330947
C 2.944158 11.379488 1.536021
H 3.399137 10.406414 1.306698
H 3.587253 12.165873 1.102837
H 1.985369 11.425709 0.993643
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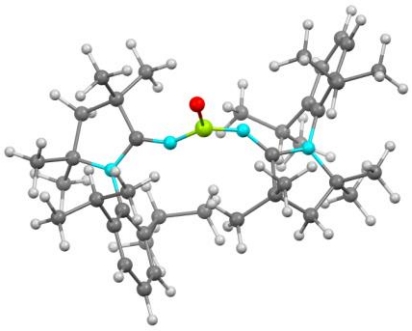
3-Cl



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H 11.200089 3.191709 2.891029
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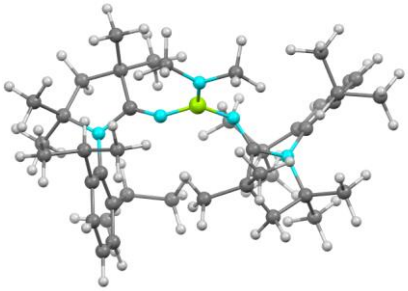
3-NMe$_2$



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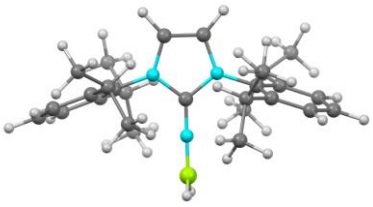
3-Ph



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Lowest IR frequency = 28.03 cm^{-1}

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