

## Supporting Information for

# CAAC-stabilised 9,10-diboraanthracene: an electronically and structurally flexible platform for small-molecule activation and metal complexation

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## **Methods and materials**

All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Both deuterated and non-deuterated solvents were stored under argon over activated 4 Å molecular sieves. Liquid-phase NMR spectra were acquired on a Bruker Avance 500 ( $^1\text{H}$ : 500.1 MHz,  $^{11}\text{B}$ : 160.5 MHz,  $^{13}\text{C}$ : 125.8 MHz) spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm and internally referenced to the carbon nuclei ( $^{13}\text{C}\{^1\text{H}\}$ ) or residual protons ( $^1\text{H}$ ) of the solvent. Heteronuclei NMR spectra are referenced to external standards ( $^{11}\text{B}$ :  $\text{BF}_3\cdot\text{OEt}_2$ ). Resonances are identified as singlet (s), doublet (d), triplet (t), septet (sept), multiplet (m) or broad (br). Coupling constants are  $^1\text{H}$ - $^1\text{H}$  coupling constants unless specified otherwise. High-resolution mass spectrometry (HRMS) data were obtained from a Thermo Scientific Exactive Plus spectrometer. Solid-state IR spectra were recorded on a Bruker FT-IR spectrometer ALPHA II inside a glovebox. UV-vis spectra were acquired on a METTLER TOLEDO UV-vis-Excellence UV5 spectrophotometer inside a glovebox.

Solvents and reagents were purchased from Sigma-Aldrich, abcr or Alfa Aesar.  $[(\text{CAAC})_2(\text{C}_{12}\text{H}_8\text{B}_2)] = \text{II}$  (CAAC = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene)<sup>1</sup> and  $[(\text{MeCN})_3\text{M}(\text{CO})_3]$  (M = Cr, Mo, W)<sup>2</sup> were synthesised using literature procedures.

## Synthetic procedures

### Synthesis of **1**

A solution of **II** (60.0 mg, 80.6  $\mu\text{mol}$ ) in benzene (4 mL) was placed under an atmosphere of dihydrogen (1 atm) *via* three freeze-pump-thaw cycles. The solution was stirred at room temperature for 30 min, resulting in a colourless solution. All volatiles were removed *in vacuo* and the residue was washed with hexane ( $3 \times 1$  mL) and dried, yielding **1** as a colourless solid (48.0 mg, 64.3  $\mu\text{mol}$ , 80%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated benzene/pentane (2:1) solution at room temperature.  $^1\text{H}\{^{11}\text{B}\}$  NMR (500.1 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 8.20–8.12 (m, 1H, DBA-*H*), 7.60–7.53 (m, 1H, DBA-*H*), 7.42–7.34 (m, 2H, DBA-*H*), 7.31–7.22 (m, 3H, *m*-Ar-*H* + *p*-Ar-*H*), 7.18–6.96 (m, 6H, *m*-Ar-*H* + *p*-Ar-*H* + DBA-*H*), 6.83–6.74 (m, 1H, DBA-*H*), 5.25 (s, 1H, NCH), 4.23 (sept,  $^3J$  = 6.6 Hz, 1H, *i*Pr-CH), 4.05 (sept,  $^3J$  = 6.6 Hz, 1H, *i*Pr-CH), 3.22 (br s, 1H, BH), 3.18 (sept,  $^3J$  = 6.6 Hz, 1H, *i*Pr-CH), 3.05 (sept,  $^3J$  = 6.6 Hz, 1H, *i*Pr-CH), 1.84 (d,  $^2J$  = 12.3 Hz, 1H,  $\text{CH}_2$ ), 1.78 (d,  $^2J$  = 12.3 Hz, 1H,  $\text{CH}_2$ ), 1.58 (d,  $^2J$  = 12.9 Hz, 1H,  $\text{CH}_2$ ), 1.45 (d,  $^3J$  = 6.6 Hz, 3H, *i*Pr- $\text{CH}_3$ ), 1.40 (d,  $^3J$  = 6.6 Hz, 3H, *i*Pr- $\text{CH}_3$ ), 1.37 (d,  $^2J$  = 12.9 Hz, 1H,  $\text{CH}_2$ ), 1.33 (d,  $^3J$  = 6.6 Hz, 3H, *i*Pr- $\text{CH}_3$ ), 1.32 (s, 6H,  $\text{NC}(\text{CH}_3)_2$ ), 1.23 (s, 3H,  $\text{C}(\text{CH}_3)_2$ ), 1.22 (d,  $^3J$  = 6.6 Hz, 3H, *i*Pr- $\text{CH}_3$ ), 1.18 (d,  $^3J$  = 6.6 Hz, 3H, *i*Pr- $\text{CH}_3$ ), 1.16 (d,  $^3J$  = 6.6 Hz, 3H, *i*Pr- $\text{CH}_3$ ), 0.95 (s, 6H,  $\text{NC}(\text{CH}_3)_2$  +  $\text{C}(\text{CH}_3)_2$ ), 0.91 (d,  $^3J$  = 6.6 Hz, 3H, *i*Pr- $\text{CH}_3$ ), 0.91 (s, 3H,  $\text{C}(\text{CH}_3)_2$ ), 0.89 (s, 3H,  $\text{NC}(\text{CH}_3)_2$ ), 0.85 (s, 3H,  $\text{C}(\text{CH}_3)_2$ ), 0.74 (d,  $^3J$  = 6.6 Hz, 3H, *i*Pr- $\text{CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 243.5 ( $\text{C}_{\text{carbene}}$ , identified by HMBC), 153.0 (*o*-Ar-C), 151.0 (DBA- $\text{C}_\text{B}$ ), 150.5 (*o*-Ar-C), 146.8 (DBA- $\text{C}_\text{B}$ ), 146.5 (*o*-Ar-C), 145.3 (*o*-Ar-C), 143.9 (*i*-Ar-C), 135.1 (DBA-C), 134.3 (DBA-C), 134.1 (DBA-C + *i*-Ar-C), 133.3 (DBA-C), 129.4 (*p*-Ar-C), 127.1 (DBA-C), 126.4 (*p*-Ar-C), 126.1 (DBA-C), 125.3 (*m*-Ar-C), 125.3 (*m*-Ar-C), 124.9 (*m*-Ar-C), 124.9 (*m*-Ar-C), 123.5 (DBA-C), 123.3 (DBA-C), 77.7 ( $\text{NC}(\text{CH}_3)_2$ ), 73.7 (NCH), 63.5 ( $\text{NC}(\text{CH}_3)_2$ ), 60.1 ( $\text{CH}_2$ ), 54.5 ( $\text{C}(\text{CH}_3)_2$ ), 52.7 ( $\text{CH}_2$ ), 44.2 ( $\text{C}(\text{CH}_3)_2$ ), 33.2 ( $\text{C}(\text{CH}_3)_2$ ), 31.4 ( $\text{C}(\text{CH}_3)_2$ ), 31.2 ( $\text{C}(\text{CH}_3)_2$ ), 30.5 ( $\text{C}(\text{CH}_3)_2$ ), 30.3 ( $\text{NC}(\text{CH}_3)_2$ ), 29.6 (*i*Pr-CH), 29.6 (*i*Pr-CH), 29.3 (*i*Pr-CH), 29.1 ( $\text{NC}(\text{CH}_3)_2$ ), 28.3 (*i*Pr-CH), 28.1 ( $\text{NC}(\text{CH}_3)_2$ ), 27.5 (*i*Pr- $\text{CH}_3$ ), 27.4 (*i*Pr- $\text{CH}_3$ ), 27.0 (*i*Pr- $\text{CH}_3$ ), 26.2 (*i*Pr- $\text{CH}_3$ ), 25.8 ( $\text{NC}(\text{CH}_3)_2$ ), 25.1 (*i*Pr- $\text{CH}_3$ ), 24.8 (*i*Pr- $\text{CH}_3$ ), 23.9 (*i*Pr- $\text{CH}_3$ ), 23.7 (*i*Pr- $\text{CH}_3$ ) ppm.  $^{11}\text{B}$  NMR (160.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = -14.4 (d,  $^1J_{\text{B-H}}$  = 71.1 Hz) ppm. Note: The second  $^{11}\text{B}$  resonance could not be detected. FT-IR (solid-state):  $\tilde{\nu}(\text{B-H})$  = 2353  $\text{cm}^{-1}$ . HRMS LIFDI for  $[\text{C}_{52}\text{H}_{72}\text{B}_2\text{N}_2]^+ = [\text{M}]^+$ :  $m/z$ : calcd. 746.5876; found 746.5845.

## Synthesis of 2

To a solution of **II** (50.0 mg, 67.1  $\mu\text{mol}$ ) in benzene (2 mL) was added phenyl azide (9.58 mg, 80.5  $\mu\text{mol}$ ) and the mixture stirred at room temperature for 5 min, resulting in a greenish yellow solution. All volatiles were removed *in vacuo* and the residue was washed with hexane ( $3 \times 2$  mL) and dried, yielding *anti*-**2** as a pale yellow solid (42.3 mg, 49.0  $\mu\text{mol}$ , 73%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated benzene solution at room temperature. *Note: Heating a solution of anti-2 at 60 °C for 4 d led to quantitative isomerisation to syn-2.*

Analytical data for *anti*-**2**:  $^1\text{H}\{^{11}\text{B}\}$  NMR (500.1 MHz, THF- $d_8$ ):  $\delta$  = 7.61 (t,  $^3J$  = 7.8 Hz, 1H, *p*-Ar-H), 7.51 (t,  $^3J$  = 7.7 Hz, 1H, *p*-Ar-H), 7.47 (dd,  $^3J$  = 7.8 Hz,  $^4J$  = 1.5 Hz, 1H, *m*-Ar-H), 7.46 (dd,  $^3J$  = 7.7 Hz,  $^4J$  = 1.7 Hz, 1H, *m*-Ar-H), 7.45 (dd,  $^3J$  = 7.8 Hz,  $^4J$  = 1.5 Hz, 1H, *m*-Ar-H), 7.28 (dd,  $^3J$  = 7.7 Hz,  $^4J$  = 1.7 Hz, 1H, *m*-Ar-H), 7.10–7.02 (m, 4H, *o*-Ph-H + *m*-Ph-H), 6.91 (d,  $^3J$  = 7.1 Hz, 1H, DBA-H), 6.76 (d,  $^3J$  = 7.1 Hz, 1H, DBA-H), 6.67 (tt,  $^3J$  = 6.9 Hz,  $^4J$  = 1.5 Hz, 1H, *p*-Ph-H), 6.19 (dt,  $^3J$  = 7.1 Hz,  $^4J$  = 1.0 Hz, 1H, DBA-H), 6.17 (dt,  $^3J$  = 7.1 Hz,  $^4J$  = 1.0 Hz, 1H, DBA-H), 5.87 (t,  $^3J$  = 7.3 Hz, 2H, DBA-H), 4.69 (d,  $^3J$  = 7.3 Hz, 1H, DBA-H), 4.39 (sept,  $^3J$  = 6.5 Hz, 1H, *iPr*-CH), 4.21 (d,  $^3J$  = 7.3 Hz, 1H, DBA-H), 3.52 (sept,  $^3J$  = 6.6 Hz, 1H, *iPr*-CH), 3.42 (sept,  $^3J$  = 6.6 Hz, 1H, *iPr*-CH), 3.34 (sept,  $^3J$  = 6.7 Hz, 1H, *iPr*-CH), 2.27 (d,  $^2J$  = 11.7 Hz, 1H, CH<sub>2</sub>), 2.21 (d,  $^2J$  = 12.6 Hz, 1H, CH<sub>2</sub>), 2.14 (d,  $^2J$  = 12.6 Hz, 1H, CH<sub>2</sub>), 1.85 (s, 3H, NC(CH<sub>3</sub>)<sub>2</sub>), 1.76 (s, 3H, NC(CH<sub>3</sub>)<sub>2</sub>), 1.73 (d,  $^2J$  = 11.7 Hz, 1H, CH<sub>2</sub>, overlapping with THF- $d_8$ ), 1.57 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 1.52 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 1.50 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 1.48 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 1.45 (d,  $^3J$  = 6.6 Hz, 3H, *iPr*-CH<sub>3</sub>), 1.38 (d,  $^3J$  = 6.7 Hz, 3H, *iPr*-CH<sub>3</sub>), 1.36 (d,  $^3J$  = 6.6 Hz, 3H, *iPr*-CH<sub>3</sub>), 1.31 (d,  $^3J$  = 6.5 Hz, 3H, *iPr*-CH<sub>3</sub>), 1.28 (d,  $^3J$  = 6.6 Hz, 3H, *iPr*-CH<sub>3</sub>), 1.14 (d,  $^3J$  = 6.7 Hz, 3H, *iPr*-CH<sub>3</sub>), 1.07 (s, 3H, NC(CH<sub>3</sub>)<sub>2</sub>), 0.95 (s, 3H, NC(CH<sub>3</sub>)<sub>2</sub>), 0.57 (d,  $^3J$  = 6.6 Hz, 3H, *iPr*-CH<sub>3</sub>), 0.47 (d,  $^3J$  = 6.5 Hz, 3H, *iPr*-CH<sub>3</sub>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, THF- $d_8$ ):  $\delta$  = 235.7 (*C*<sub>carbene</sub>, identified by HMBC), 230.5 (*C*<sub>carbene</sub>, identified by HMBC), 168.4 (DBA-C<sub>B</sub>, identified by HMBC), 164.4 (DBA-C<sub>B</sub>, identified by HMBC), 161.3 (DBA-C<sub>B</sub>, identified by HMBC), 158.7 (DBA-C<sub>B</sub>, identified by HMBC), 156.1 (*i*-Ph-C), 150.5 (*o*-Ar-C), 148.1 (*o*-Ar-C), 147.6 (*o*-Ar-C), 147.4 (*o*-Ar-C), 136.2 (*i*-Ar-C), 136.2 (*i*-Ar-C), 130.8 (*p*-Ar-C), 130.2 (*p*-Ar-C), 129.7 (DBA-C), 129.2 (DBA-C), 128.8 (DBA-C), 128.6 (*o*-Ph-C), 127.2 (*m*-Ar-C), 126.8 (DBA-C), 126.5 (*m*-Ar-C), 126.2 (*m*-Ar-C), 125.6 (*m*-Ar-C), 122.0 (DBA-C), 120.9 (DBA-C), 119.9 (*m*-Ph-C), 119.8 (DBA-C), 119.7 (DBA-C), 119.6 (*p*-Ph-C), 80.1 (NC(CH<sub>3</sub>)<sub>2</sub>), 78.3 (NC(CH<sub>3</sub>)<sub>2</sub>), 56.6 (C(CH<sub>3</sub>)<sub>2</sub>), 56.2 (C(CH<sub>3</sub>)<sub>2</sub>), 53.3 (CH<sub>2</sub>), 52.7 (CH<sub>2</sub>), 36.4 (C(CH<sub>3</sub>)<sub>2</sub>), 32.9 (C(CH<sub>3</sub>)<sub>2</sub>), 31.7 (NC(CH<sub>3</sub>)<sub>2</sub>), 31.5 (C(CH<sub>3</sub>)<sub>2</sub>), 30.8 (*iPr*-CH), 30.7 (NC(CH<sub>3</sub>)<sub>2</sub>), 29.6 (*iPr*-CH), 29.5 (*iPr*-CH), 29.2 (*iPr*-CH), 28.8 (*iPr*-CH<sub>3</sub>), 28.5 (*iPr*-CH<sub>3</sub>), 27.5

(*i*Pr-CH<sub>3</sub>), 27.3 (NC(CH<sub>3</sub>)<sub>2</sub>), 27.2 (NC(CH<sub>3</sub>)<sub>2</sub>), 26.5 (*i*Pr-CH<sub>3</sub>), 25.3 (C(CH<sub>3</sub>)<sub>2</sub>), overlapping with THF-*d*<sub>8</sub>, identified by HSQC), 24.7 (*i*Pr-CH<sub>3</sub>), 23.9 (*i*Pr-CH<sub>3</sub>), 23.9 (*i*Pr-CH<sub>3</sub>), 23.8 (*i*Pr-CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160.5 MHz, THF-*d*<sub>8</sub>): δ = -1.3 (br s), -4.4 (br s) ppm. FT-IR (solid-state):  $\tilde{\nu}(\text{N}=\text{N}=\text{N}) = 1423, 1251 \text{ cm}^{-1}$ . UV-vis (THF):  $\lambda_{\text{max}} = 348 \text{ nm}$ ,  $\lambda_2 = 296 \text{ nm}$ . HRMS LIFDI for [C<sub>58</sub>H<sub>75</sub>B<sub>2</sub>N<sub>5</sub>]<sup>+</sup> = [M]<sup>+</sup>: *m/z*: calcd. 863.6203; found 863.6186.

NMR data for *syn*-**2**: <sup>1</sup>H{<sup>11</sup>B} NMR (500.1 MHz, THF-*d*<sub>8</sub>): δ = 7.50 (t, <sup>3</sup>*J* = 7.8 Hz, 1H, *p*-Ar-*H*), 7.43 (dd, <sup>3</sup>*J* = 7.8 Hz, <sup>4</sup>*J* = 1.5 Hz, 1H, *m*-Ar-*H*), 7.39 (t, <sup>3</sup>*J* = 7.7 Hz, 1H, *p*-Ar-*H*), 7.37 (dd, <sup>3</sup>*J* = 7.8 Hz, <sup>4</sup>*J* = 2.3 Hz, 1H, *m*-Ar-*H*), 7.30 (dd, <sup>3</sup>*J* = 7.8 Hz, <sup>4</sup>*J* = 1.5 Hz, 1H, *m*-Ar-*H*), 7.27 (dd, <sup>3</sup>*J* = 8.5 Hz, <sup>4</sup>*J* = 1.0 Hz, 2H, *o*-Ph-*H*), 7.15–7.11 (m, 1H, DBA-*H*), 7.08–7.03 (m, 3H, *m*-Ar-*H* + *m*-Ph-*H*), 7.03–7.01 (m, 1H, DBA-*H*), 6.67 (tt, <sup>3</sup>*J* = 7.2 Hz, <sup>4</sup>*J* = 1.0 Hz, 1H, *p*-Ph-*H*), 6.47–6.42 (m, 2H, DBA-*H*), 5.44 (dt, <sup>3</sup>*J* = 7.3 Hz, <sup>4</sup>*J* = 1.4 Hz, 1H, DBA-*H*), 5.39 (dt, <sup>3</sup>*J* = 7.3 Hz, <sup>4</sup>*J* = 1.4 Hz, 1H, DBA-*H*), 4.39 (dd, <sup>3</sup>*J* = 7.3 Hz, <sup>4</sup>*J* = 0.8 Hz, 1H, DBA-*H*), 4.17 (dd, <sup>3</sup>*J* = 7.3 Hz, <sup>4</sup>*J* = 0.8 Hz, 1H, DBA-*H*), 3.61 (sept, <sup>3</sup>*J* = 6.6 Hz, 1H, *i*Pr-*CH*, overlapping with THF-*d*<sub>8</sub>), 3.47 (sept, <sup>3</sup>*J* = 6.6 Hz, 1H, *i*Pr-*CH*), 3.42 (sept, <sup>3</sup>*J* = 6.6 Hz, 1H, *i*Pr-*CH*), 2.72 (d, <sup>2</sup>*J* = 12.1 Hz, 1H, CH<sub>2</sub>), 2.40 (d, <sup>2</sup>*J* = 12.7 Hz, 1H, CH<sub>2</sub>), 2.22 (d, <sup>2</sup>*J* = 12.7 Hz, 1H, CH<sub>2</sub>), 2.11 (d, <sup>2</sup>*J* = 12.1 Hz, 1H, CH<sub>2</sub>), 1.98 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 1.77 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 1.63 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 1.60 (s, 3H, NC(CH<sub>3</sub>)<sub>2</sub>), 1.56 (s, 3H, NC(CH<sub>3</sub>)<sub>2</sub>), 1.55 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 1.55 (s, 3H, NC(CH<sub>3</sub>)<sub>2</sub>), 1.53 (s, 3H, NC(CH<sub>3</sub>)<sub>2</sub>), 1.46 (d, <sup>3</sup>*J* = 6.6 Hz, 3H, *i*Pr-*CH*<sub>3</sub>), 1.45 (d, <sup>3</sup>*J* = 6.6 Hz, 3H, *i*Pr-*CH*<sub>3</sub>), 1.32 (d, <sup>3</sup>*J* = 6.6 Hz, 3H, *i*Pr-*CH*<sub>3</sub>), 1.18 (d, <sup>3</sup>*J* = 6.6 Hz, 3H, *i*Pr-*CH*<sub>3</sub>), 0.90 (d, <sup>3</sup>*J* = 6.6 Hz, 6H, *i*Pr-*CH*<sub>3</sub>), 0.57 (d, <sup>3</sup>*J* = 6.6 Hz, 3H, *i*Pr-*CH*<sub>3</sub>), -0.11 (d, <sup>3</sup>*J* = 6.6 Hz, 3H, *i*Pr-*CH*<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, THF-*d*<sub>8</sub>): δ = 233.8 (C<sub>Carbene</sub>, identified by HMBC), 230.6 (C<sub>Carbene</sub>, identified by HMBC), 164.2 (DBA-C<sub>B</sub>, identified by HMBC), 163.8 (DBA-C<sub>B</sub>, identified by HMBC), 163.6 (DBA-C<sub>B</sub>, identified by HMBC), 162.8 (DBA-C<sub>B</sub>, identified by HMBC), 155.3 (*i*-Ph-C), 150.7 (*o*-Ar-C), 147.9 (*o*-Ar-C), 146.9 (*o*-Ar-C), 146.8 (*o*-Ar-C), 136.6 (*i*-Ar-C), 136.0 (*i*-Ar-C), 131.3 (DBA-C), 130.7 (*p*-Ar-C), 130.2 (*p*-Ar-C), 128.7 (DBA-C), 128.6 (*m*-Ph-C), 128.4 (DBA-C), 128.3 (DBA-C), 127.3 (*m*-Ar-C), 126.9 (*m*-Ar-C), 126.0 (*m*-Ar-C), 125.6 (*m*-Ar-C), 121.2 (DBA-C), 121.0 (DBA-C), 120.3 (*p*-Ph-C), 120.1 (DBA-C), 119.9 (DBA-C), 119.3 (*o*-Ph-C), 80.3 (NC(CH<sub>3</sub>)<sub>2</sub>), 78.5 (NC(CH<sub>3</sub>)<sub>2</sub>), 56.7 (C(CH<sub>3</sub>)<sub>2</sub>), 56.7 (C(CH<sub>3</sub>)<sub>2</sub>), 54.1 (CH<sub>2</sub>), 53.2 (CH<sub>2</sub>), 35.1 (C(CH<sub>3</sub>)<sub>2</sub>), 34.2 (C(CH<sub>3</sub>)<sub>2</sub>), 34.1 (C(CH<sub>3</sub>)<sub>2</sub>), 31.0 (*i*Pr-*CH*), 30.8 (NC(CH<sub>3</sub>)<sub>2</sub>), 30.7 (NC(CH<sub>3</sub>)<sub>2</sub>), 29.6 (*i*Pr-*CH*), 29.6 (*i*Pr-*CH*), 29.5 (*i*Pr-*CH*<sub>3</sub>), 29.4 (*i*Pr-*CH* + *i*Pr-*CH*<sub>3</sub>), 28.5 (NC(CH<sub>3</sub>)<sub>2</sub>), 27.9 (NC(CH<sub>3</sub>)<sub>2</sub>), 27.2 (C(CH<sub>3</sub>)<sub>2</sub>), 27.1 (*i*Pr-*CH*<sub>3</sub>), 26.1 (*i*Pr-*CH*<sub>3</sub>), 24.9 (*i*Pr-*CH*<sub>3</sub>), 24.7 (*i*Pr-*CH*<sub>3</sub>), 24.2 (*i*Pr-*CH*<sub>3</sub>), 24.1 (*i*Pr-*CH*<sub>3</sub>) ppm. <sup>11</sup>B NMR (160.5 MHz, THF-*d*<sub>8</sub>): δ = -1.2 (br s), -4.1 (br s) ppm.

### Synthesis of **3**

**II** (30.0 mg, 40.3  $\mu\text{mol}$ ) and TEMPO (18.9 mg, 80.6  $\mu\text{mol}$ ) were combined in benzene (1 mL) and the suspension was stirred at room temperature for 30 min, resulting in a colourless reaction mixture. All volatiles were removed *in vacuo* and the residue was washed with hexane ( $2 \times 0.5$  mL) and dried, yielding **3** as a colourless solid (16.6 mg, 34.1  $\mu\text{mol}$ , 85%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated benzene solution at room temperature. *Note: The NMR spectra showed the formation of a 77:23 mixture of anti-3 and syn-3. The NMR resonances of the two atropisomers were assigned on the basis of COSY, HSQC and HMBC spectra.*  $^1\text{H}\{^{11}\text{B}\}$  NMR (500.1 MHz,  $\text{CD}_2\text{Cl}_2$ ) for *anti-3* (77%):  $\delta = 9.41\text{--}9.36$  (m, 2H, DBA-*H*), 8.26–8.22 (m, 2H, DBA-*H*), 7.51–7.44 (m, 4H, DBA-*H*), 1.85–1.64 (m, 12H,  $\text{CH}_2$ ), 1.34 (s, 12H,  $\text{CH}_3$ ), 1.09 (s, 12H,  $\text{CH}_3$ ) ppm; for *syn-3* (23%):  $\delta = 9.49\text{--}9.44$  (m, 2H, DBA-*H*), 8.17–8.13 (m, 2H, DBA-*H*), 7.51–7.44 (m, 4H, DBA-*H*), 1.85–1.64 (m, 6H,  $\text{CH}_2$ ), 1.55–1.47 (m, 6H,  $\text{CH}_2$ ), 1.33 (s, 12H,  $\text{CH}_3$ ), 1.09 (s, 12H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{CD}_2\text{Cl}_2$ ) for *anti-3*:  $\delta = 138.2$  (Ar-C), 132.9 (Ar-C), 130.9 (Ar-C), 129.9 (Ar-C), 60.6 ( $\text{NC}(\text{CH}_3)_2$ ), 40.0 ( $\text{CH}_2$ ), 32.2 ( $\text{CH}_3$ ), 20.4 ( $\text{CH}_3$ ), 17.7 ( $\text{CH}_2$ ) ppm; for *syn-3*:  $\delta = 138.1$  (Ar-C), 132.3 (Ar-C), 130.6 (Ar-C), 129.9 (Ar-C), 60.6 ( $\text{NC}(\text{CH}_3)_2$ ), 40.0 ( $\text{CH}_2$ ), 32.2 ( $\text{CH}_3$ ), 20.4 ( $\text{CH}_3$ ), 17.7 ( $\text{CH}_2$ ) ppm.  $^{11}\text{B}$  NMR (160.5 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 41.1$  (br s) ppm. HRMS LIFDI for  $[\text{C}_{30}\text{H}_{44}\text{B}_2\text{N}_2\text{O}_2]^+ = [\text{M}]^+$ :  $m/z$ : calcd. 486.3583; found 486.3578.

### Synthesis of **4-Cr**

To a mixture of **II** (30.0 mg, 40.3  $\mu\text{mol}$ ) and  $[(\text{MeCN})_3\text{Cr}(\text{CO})_3]$  (10.4 mg, 40.3  $\mu\text{mol}$ ) was added THF (1 mL) and the reaction mixture was stirred at 60  $^\circ\text{C}$  for 5 d, resulting in a colour change to dark green. The reaction mixture was filtered and layered with hexane, resulting in crystallisation of the product. The crystals were collected by filtration, washed with benzene ( $2 \times 1$  mL) and hexane ( $3 \times 1$  mL) and dried *in vacuo*, yielding **4-Cr** as black crystals (24.1 mg, 27.4  $\mu\text{mol}$ , 68%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated THF solution at room temperature.  $^1\text{H}\{^{11}\text{B}\}$  NMR (500.1 MHz, THF- $d_8$ ):  $\delta = 7.25\text{--}7.20$  (m, 2H, DBA-*H*), 7.13 (t,  $^3J = 7.8$  Hz, 2H, *p*-Ar-*H*), 6.84 (d,  $^3J = 7.8$  Hz, 4H, *m*-Ar-*H*), 6.29–6.24 (m, 4H, DBA-*H*), 2.79 (sept,  $^3J = 6.4$  Hz, 4H, *iPr-CH*), 2.52 (s, 4H,  $\text{CH}_2$ ), 2.41 (s, 12H,  $\text{C}(\text{CH}_3)_2$ ), 1.51 (s, 12H,  $\text{NC}(\text{CH}_3)_2$ ), 1.14 (d,  $^3J = 6.4$  Hz, 12H, *iPr-CH}\_3), 0.18 (d,  $^3J = 64$  Hz, 12H, *iPr-CH}\_3) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, THF- $d_8$ ):  $\delta = 241.5$  (CO), 235.2 ( $\text{C}_{\text{carbene}}$ , identified by HMBC), 146.8 (*o*-Ar-C), 137.8 (DBA-C), 134.0**

(*i*-Ar-C), 129.5 (*p*-Ar-C), 126.3 (*m*-Ar-C), 119.2 (DBA-C), 108.8 (DBA-C<sub>B</sub>), 82.1 (NC(CH<sub>3</sub>)<sub>2</sub>), 58.4 (C(CH<sub>3</sub>)<sub>2</sub>), 52.4 (CH<sub>2</sub>), 31.4 (C(CH<sub>3</sub>)<sub>2</sub>), 30.8 (NC(CH<sub>3</sub>)<sub>2</sub>), 29.3 (*i*Pr-CH), 28.0 (*i*Pr-CH<sub>3</sub>), 26.1 (*i*Pr-CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160.5 MHz, THF-*d*<sub>8</sub>): δ = 14.6 (br s) ppm. FT-IR (solid-state):  $\tilde{\nu}(\text{C}=\text{O}) = 1882, 1777 \text{ cm}^{-1}$ . UV-vis (THF):  $\lambda_{\text{max}} = 340 \text{ nm}$ ,  $\lambda_2 = 392 \text{ nm}$  (shoulder),  $\lambda_3 = 602 \text{ nm}$  (broad). HRMS LIFDI for [C<sub>55</sub>H<sub>70</sub>B<sub>2</sub>CrN<sub>2</sub>O<sub>3</sub>]<sup>+</sup> = [M]<sup>+</sup>: *m/z*: calcd. 880.4972; found 880.4968.

### Synthesis of 4-Mo

To a mixture of **II** (30.0 mg, 40.3 μmol) and [(MeCN)<sub>3</sub>Mo(CO)<sub>3</sub>] (12.2 mg, 40.3 μmol) was added THF (1 mL) and the reaction mixture was stirred at 60 °C for 5 d, resulting in a colour change to dark green. The reaction mixture was filtered and layered with hexane, resulting in crystallisation of the product. The crystals were collected by filtration, washed with benzene (2 × 1 mL) and hexane (3 × 1 mL) and dried *in vacuo*, yielding **4-Mo** as black crystals. (21.3 mg, 23.0 μmol, 57%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated THF solution at room temperature. <sup>1</sup>H{<sup>11</sup>B} NMR (500.1 MHz, THF-*d*<sub>8</sub>): δ = 7.31–7.26 (m, 2H, DBA-*H*), 7.15 (t, <sup>3</sup>*J* = 7.8 Hz, 2H, *p*-Ar-*H*), 6.86 (d, <sup>3</sup>*J* = 7.8 Hz, 4H, *m*-Ar-*H*), 6.29–6.24 (m, 4H, DBA-*H*), 2.80 (sept, <sup>3</sup>*J* = 6.4 Hz, 4H, *i*Pr-CH), 2.50 (s, 4H, CH<sub>2</sub>), 2.36 (s, 12H, C(CH<sub>3</sub>)<sub>2</sub>), 1.52 (s, 12H, NC(CH<sub>3</sub>)<sub>2</sub>), 1.14 (d, <sup>3</sup>*J* = 6.4 Hz, 12H, *i*Pr-CH<sub>3</sub>), 0.18 (d, <sup>3</sup>*J* = 64 Hz, 12H, *i*Pr-CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, THF-*d*<sub>8</sub>): δ = 234.5 (C<sub>Carbene</sub>, identified by HMBC), 232.8 (CO), 146.8 (*o*-Ar-C), 137.1 (DBA-C), 134.1 (*i*-Ar-C), 129.5 (*p*-Ar-C), 126.3 (*m*-Ar-C), 118.9 (DBA-C), 112.6 (DBA-C<sub>B</sub>), 82.2 (NC(CH<sub>3</sub>)<sub>2</sub>), 58.2 (C(CH<sub>3</sub>)<sub>2</sub>), 51.8 (CH<sub>2</sub>), 31.9 (C(CH<sub>3</sub>)<sub>2</sub>), 30.7 (NC(CH<sub>3</sub>)<sub>2</sub>), 29.3 (*i*Pr-CH), 27.8 (*i*Pr-CH<sub>3</sub>), 26.1 (*i*Pr-CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160.5 MHz, THF-*d*<sub>8</sub>): δ = 14.8 (br s) ppm. FT-IR (solid-state):  $\tilde{\nu}(\text{C}=\text{O}) = 1892, 1784 \text{ cm}^{-1}$ . UV-vis (THF):  $\lambda_{\text{max}} = 347 \text{ nm}$ ,  $\lambda_2 = 393 \text{ nm}$  (shoulder),  $\lambda_3 = 490 \text{ nm}$  (shoulder),  $\lambda_4 = 593 \text{ nm}$  (broad). HRMS LIFDI for [C<sub>55</sub>H<sub>70</sub>B<sub>2</sub>MoN<sub>2</sub>O<sub>3</sub>]<sup>+</sup> = [M]<sup>+</sup>: *m/z*: calcd. 924.4651; found 924.4639.

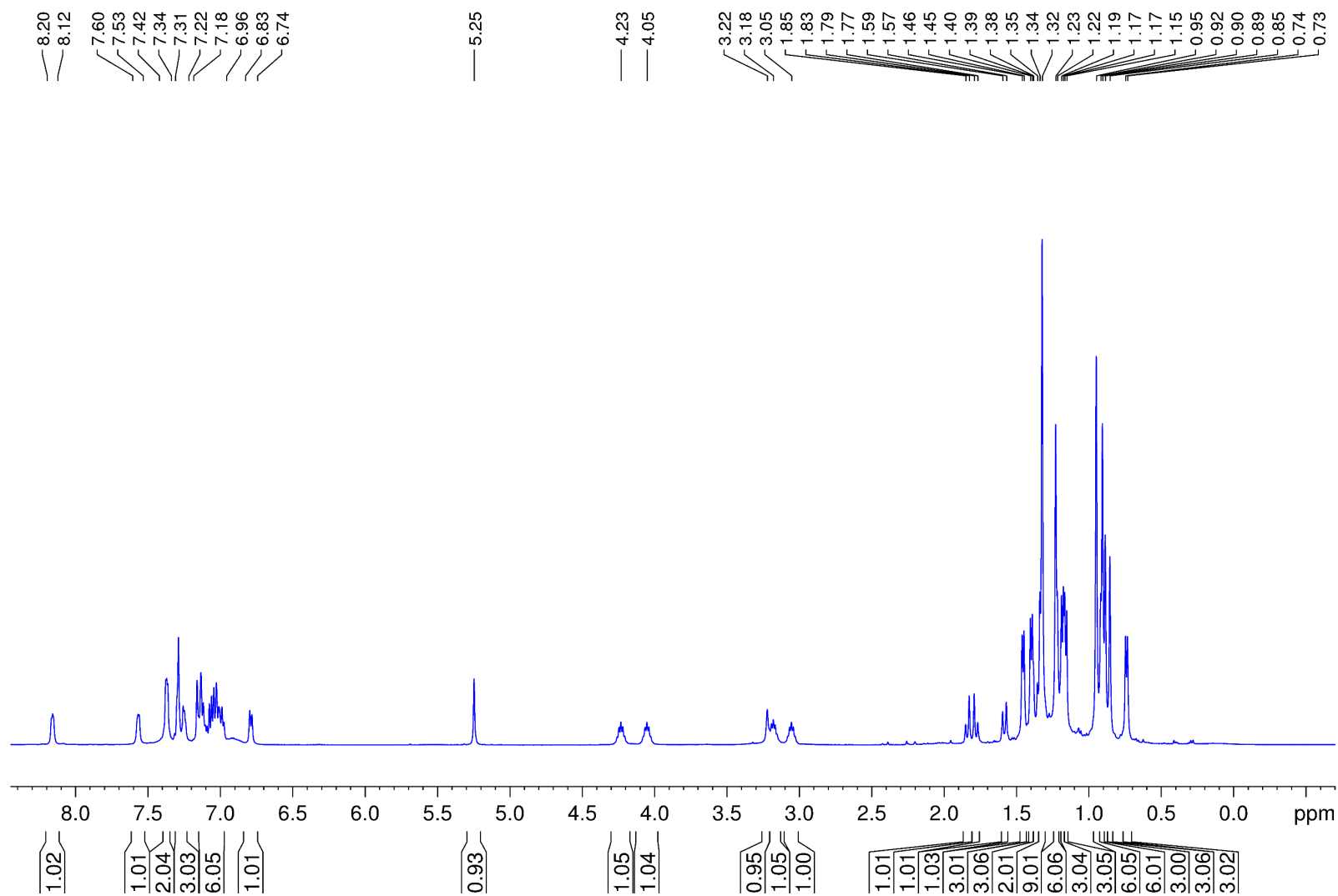
### Synthesis of 4-W

To a mixture of **II** (30.0 mg, 40.3 μmol) and [(MeCN)<sub>3</sub>W(CO)<sub>3</sub>] (15.8 mg, 40.3 μmol) was added THF (1 mL) and the reaction mixture was stirred at 60 °C for 5 d, resulting in a colour change to dark green. The reaction mixture was filtered and layered with hexane, resulting in

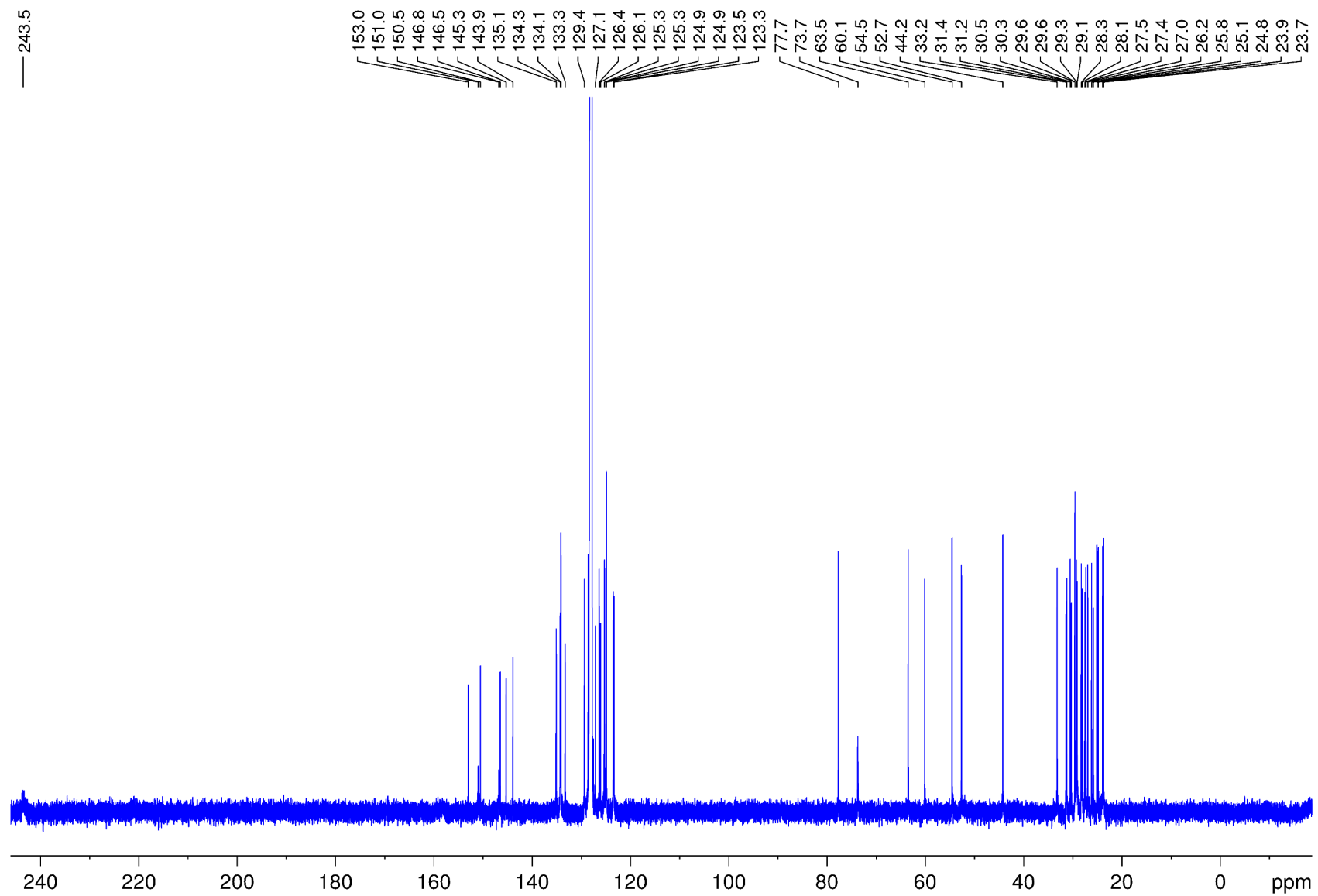
crystallisation of the product. The crystals were collected by filtration, washed with benzene ( $2 \times 1$  mL) and hexane ( $3 \times 1$  mL) and dried *in vacuo*, yielding **4-W** as black crystals (28.6 mg, 28.2  $\mu\text{mol}$ , 70%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated THF solution at room temperature.  $^1\text{H}\{^{11}\text{B}\}$  NMR (500.1 MHz, THF- $d_8$ ):  $\delta = 7.20\text{--}7.15$  (m, 6H, DBA-*H* + *p*-Ar-*H*), 6.89 (d,  $^3J = 7.8$  Hz, 4H, *m*-Ar-*H*), 6.21–6.16 (m, 4H, DBA-*H*), 2.79 (sept,  $^3J = 6.4$  Hz, 4H, *i*Pr-*CH*), 2.49 (s, 4H, *CH*<sub>2</sub>), 2.30 (s, 12H, C(*CH*<sub>3</sub>)<sub>2</sub>), 1.52 (s, 12H, NC(*CH*<sub>3</sub>)<sub>2</sub>), 1.15 (d,  $^3J = 6.4$  Hz, 12H, *i*Pr-*CH*<sub>3</sub>), 0.23 (d,  $^3J = 6.4$  Hz, 12H, *i*Pr-*CH*<sub>3</sub>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, THF- $d_8$ ):  $\delta = 233.8$  (*C*<sub>carbene</sub>, identified by HMBC), 222.3 (s + satellites,  $^1J_{\text{W-C}} = 191.2$  Hz, CO), 146.8 (*o*-Ar-C), 137.1 (DBA-C), 134.1 (*i*-Ar-C), 129.6 (*p*-Ar-C), 126.4 (*m*-Ar-C), 119.2 (DBA-C), 108.8 (DBA-C<sub>B</sub>), 82.4 (NC(*CH*<sub>3</sub>)<sub>2</sub>), 58.4 (C(*CH*<sub>3</sub>)<sub>2</sub>), 51.8 (*CH*<sub>2</sub>), 32.0 (C(*CH*<sub>3</sub>)<sub>2</sub>), 30.7 (NC(*CH*<sub>3</sub>)<sub>2</sub>), 29.3 (*i*Pr-*CH*), 27.9 (*i*Pr-*CH*<sub>3</sub>), 26.1 (*i*Pr-*CH*<sub>3</sub>) ppm.  $^{11}\text{B}$  NMR (160.5 MHz, THF- $d_8$ ):  $\delta = 13.5$  (br s) ppm. FT-IR (solid-state):  $\tilde{\nu}(\text{C}=\text{O}) = 1886, 1771$   $\text{cm}^{-1}$ . UV-vis (THF):  $\lambda_{\text{max}} = 342$  nm,  $\lambda_2 = 387$  nm (shoulder),  $\lambda_3 = 595$  nm (broad). HRMS LIFDI for  $[\text{C}_{55}\text{H}_{70}\text{B}_2\text{N}_2\text{O}_3\text{W}]^+ = [\text{M}]^+$ ; *m/z*: calcd. 1012.5102; found 1012.5090.



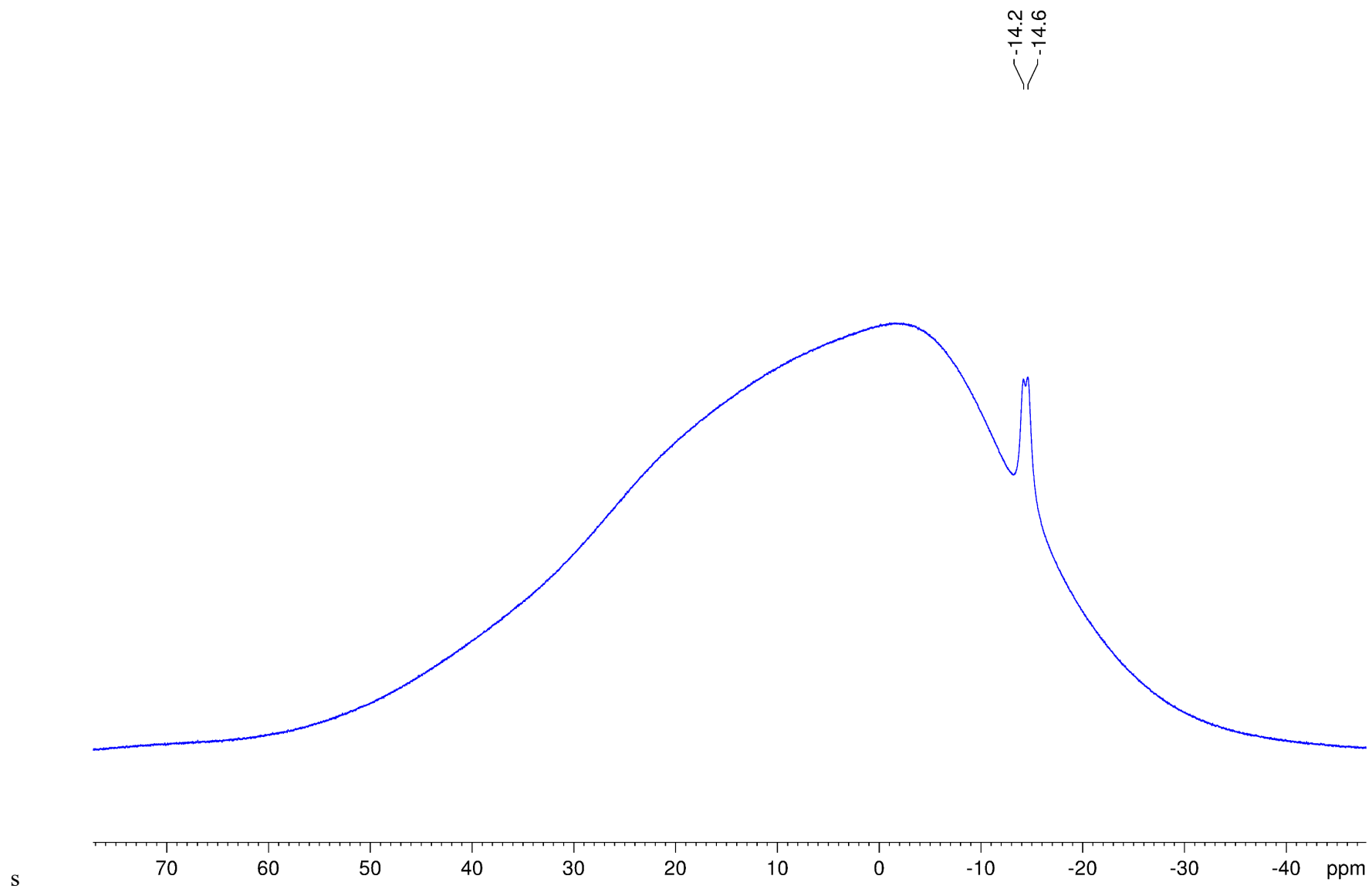
## NMR spectra of isolated compounds



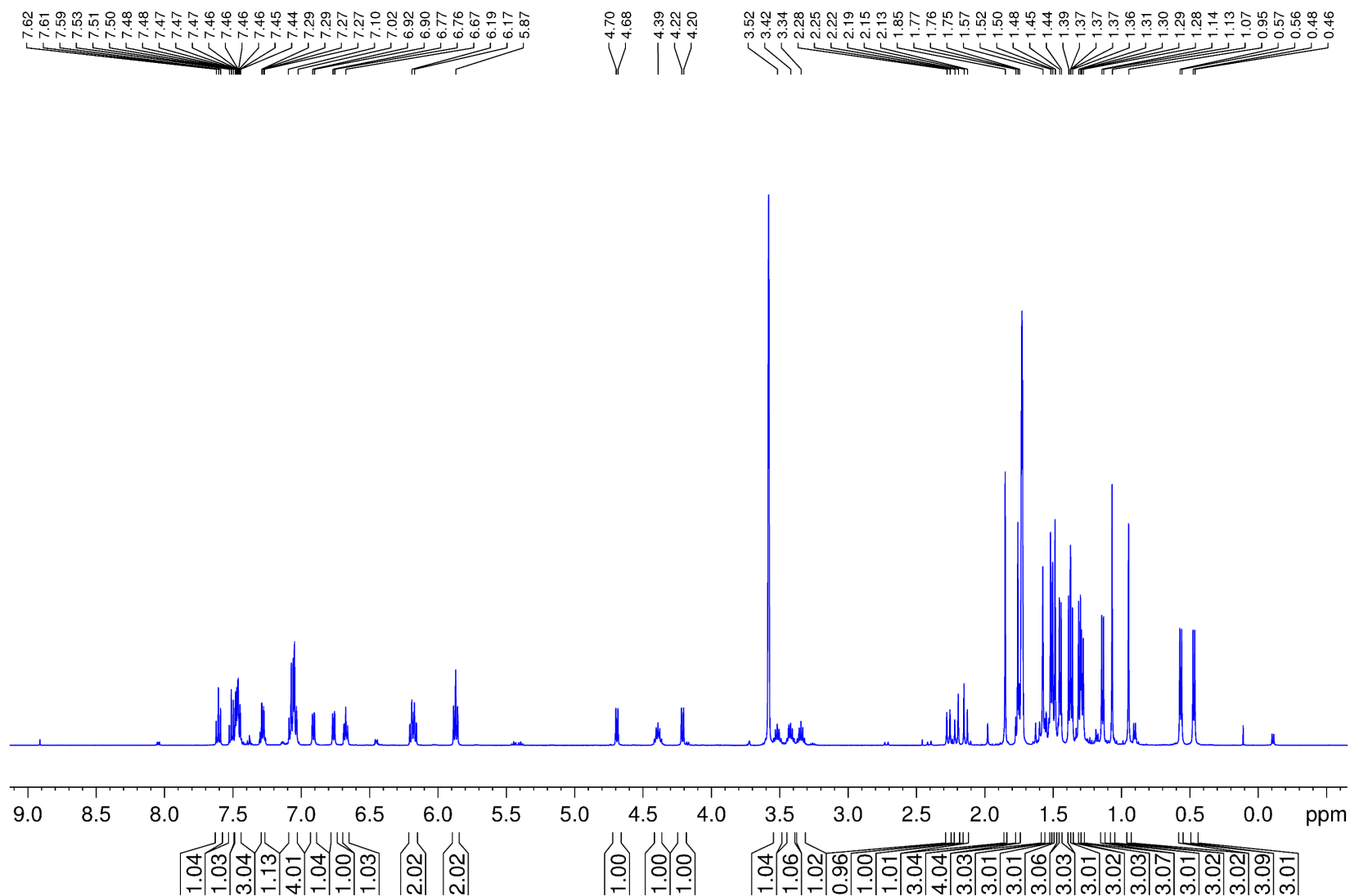
**Figure S1.**  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ .



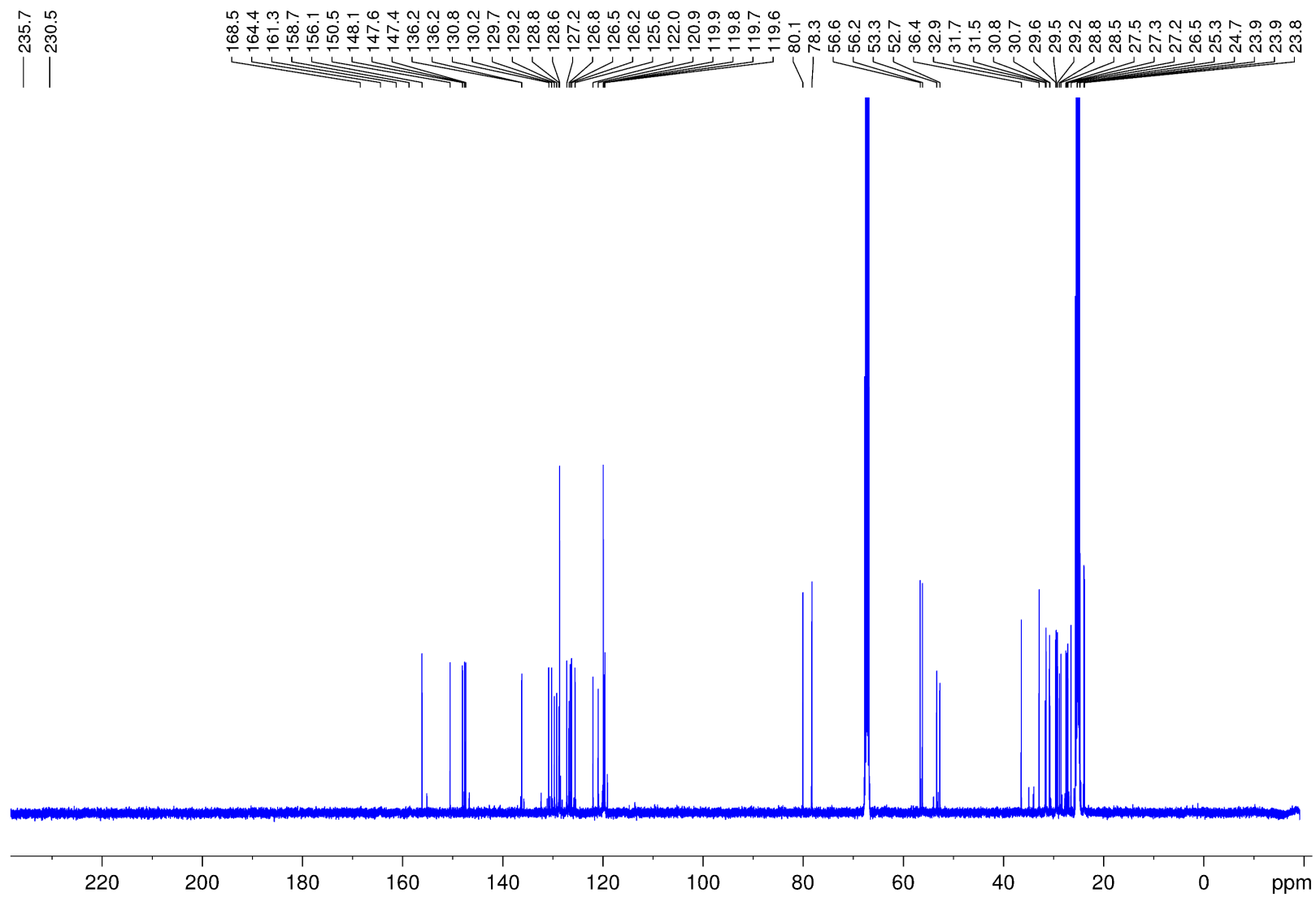
**Figure S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ .



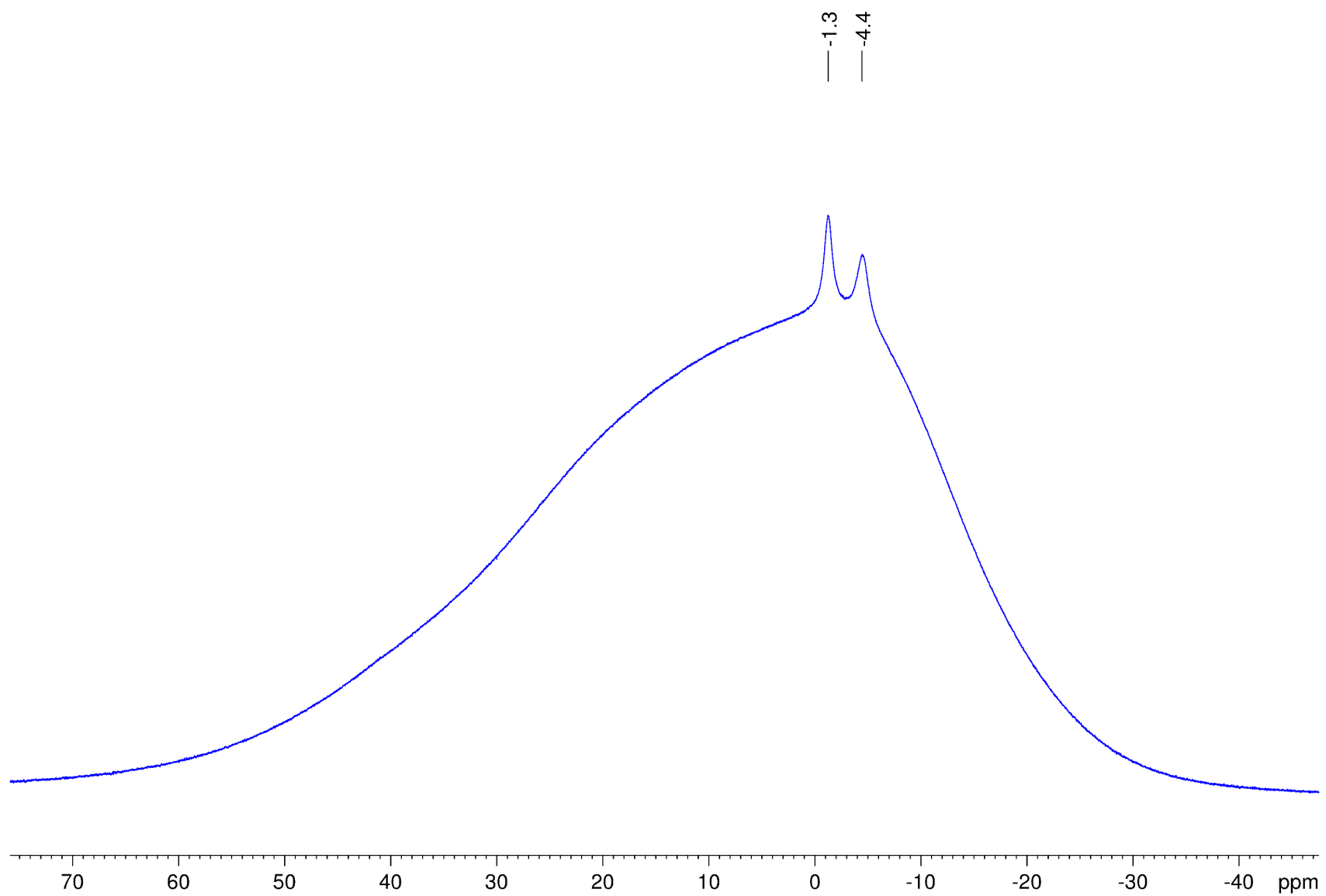
**Figure S3.**  $^{11}\text{B}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ .



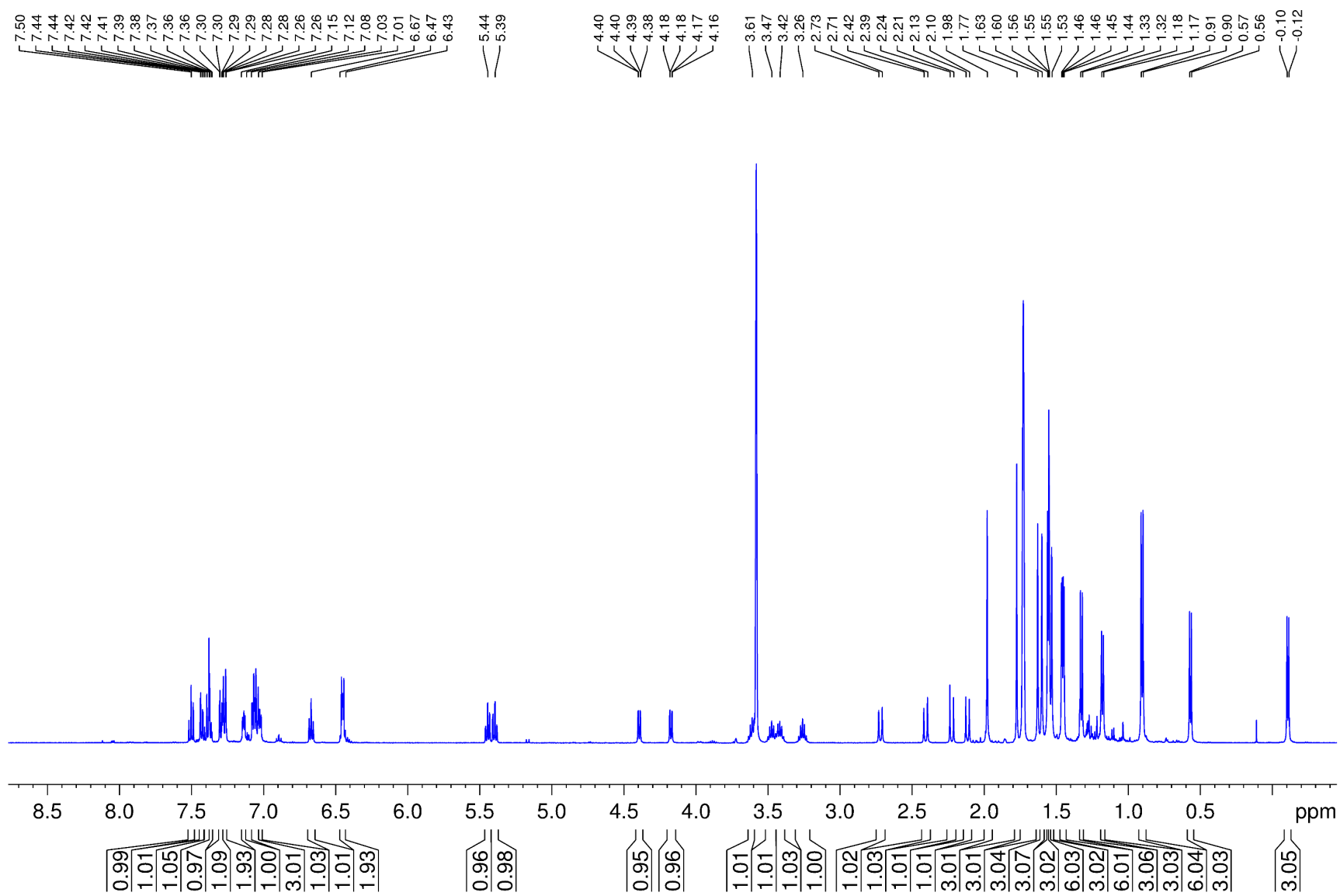
**Figure S4.**  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of *anti*-**2** in  $\text{THF-d}_8$ . The additional smaller resonances are those of the *syn* isomer, which is formed very slowly at rt.



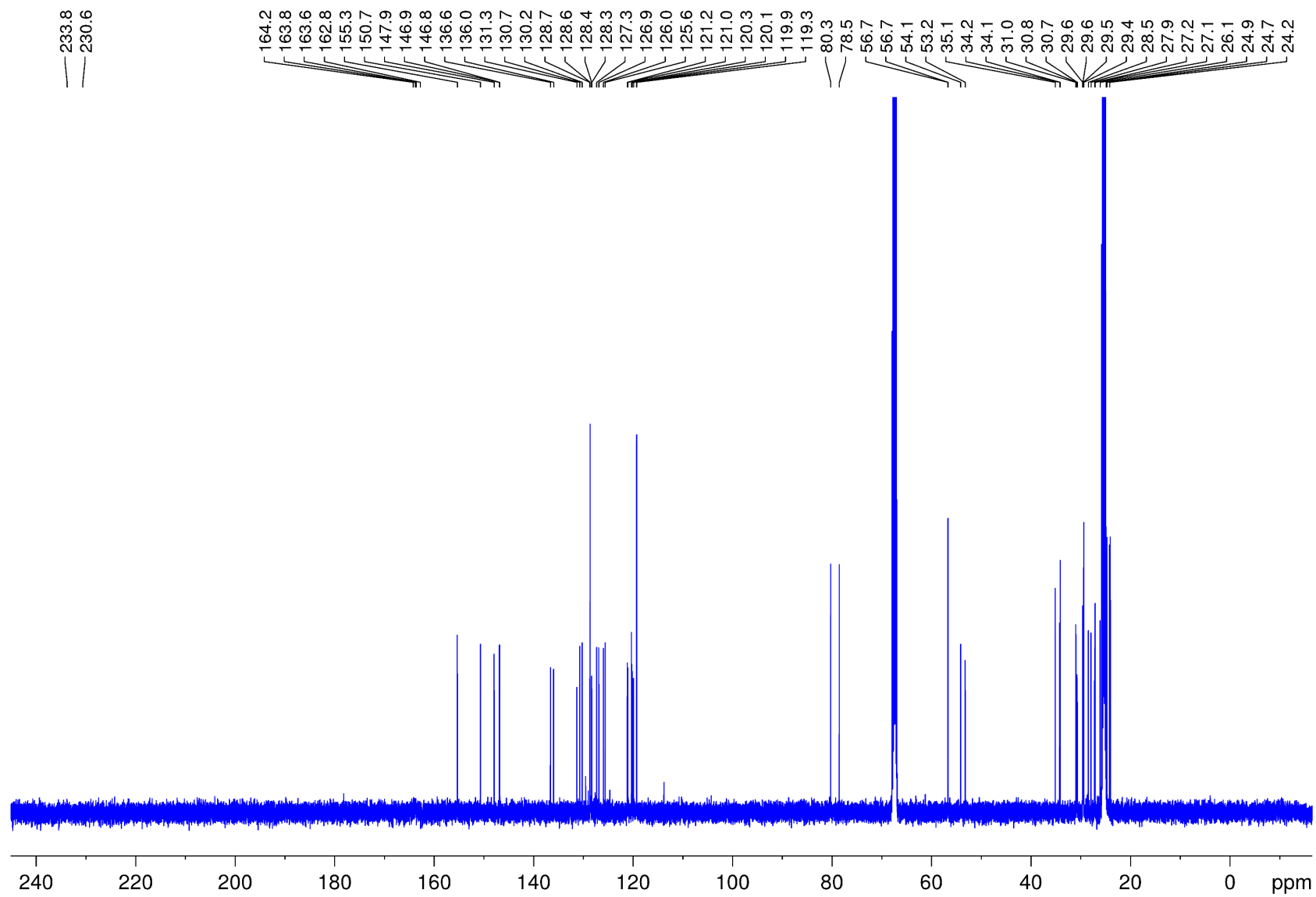
**Figure S5.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of *anti*-**2** in THF- $d_8$ . The additional smaller resonances are those of the *syn* isomer, which is formed very slowly at rt.



**Figure S6.**  $^{11}\text{B}$  NMR spectrum of *anti*-2 in THF- $d_8$ .

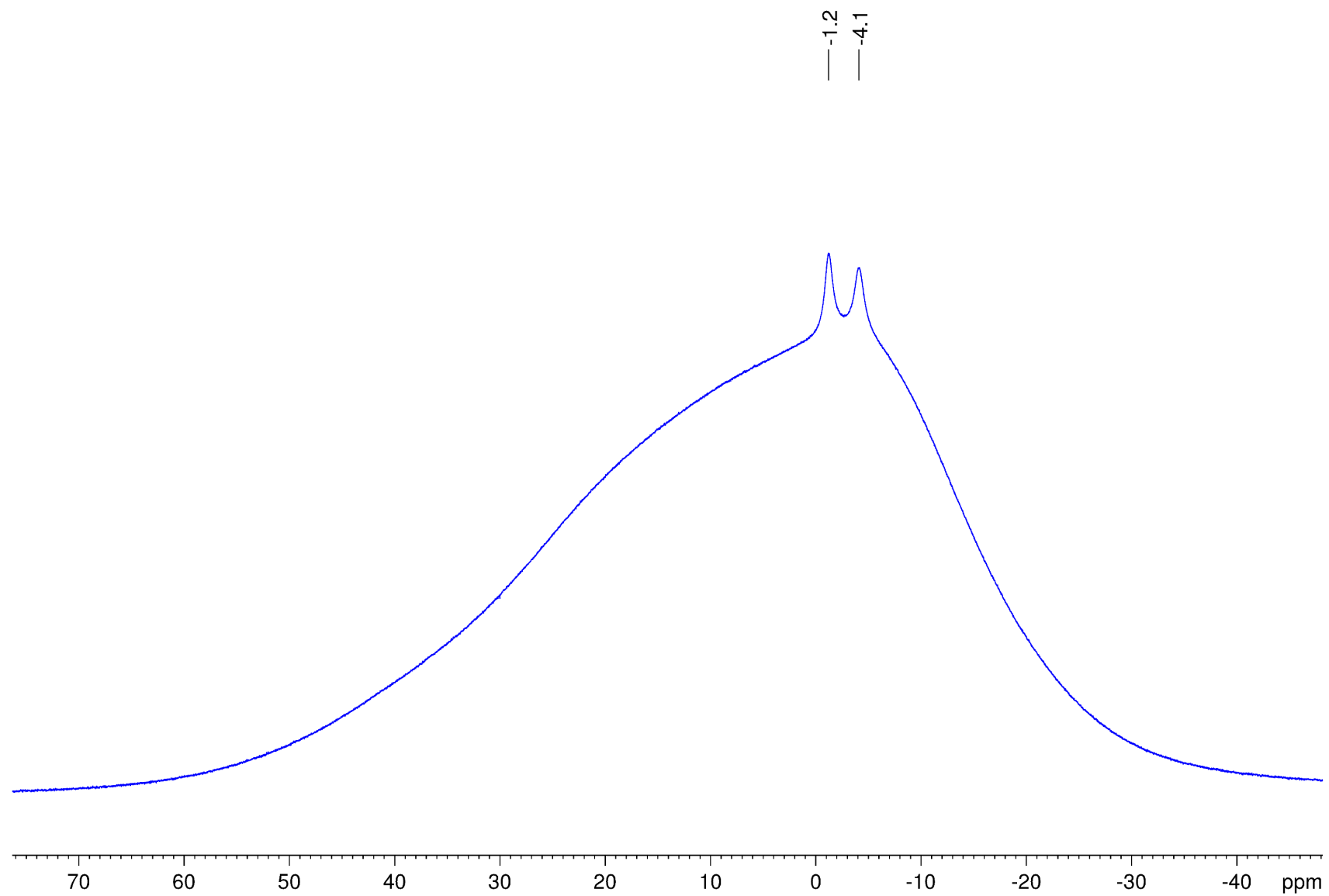


**Figure S7.**  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of *syn-2* in  $\text{THF-d}_8$ .

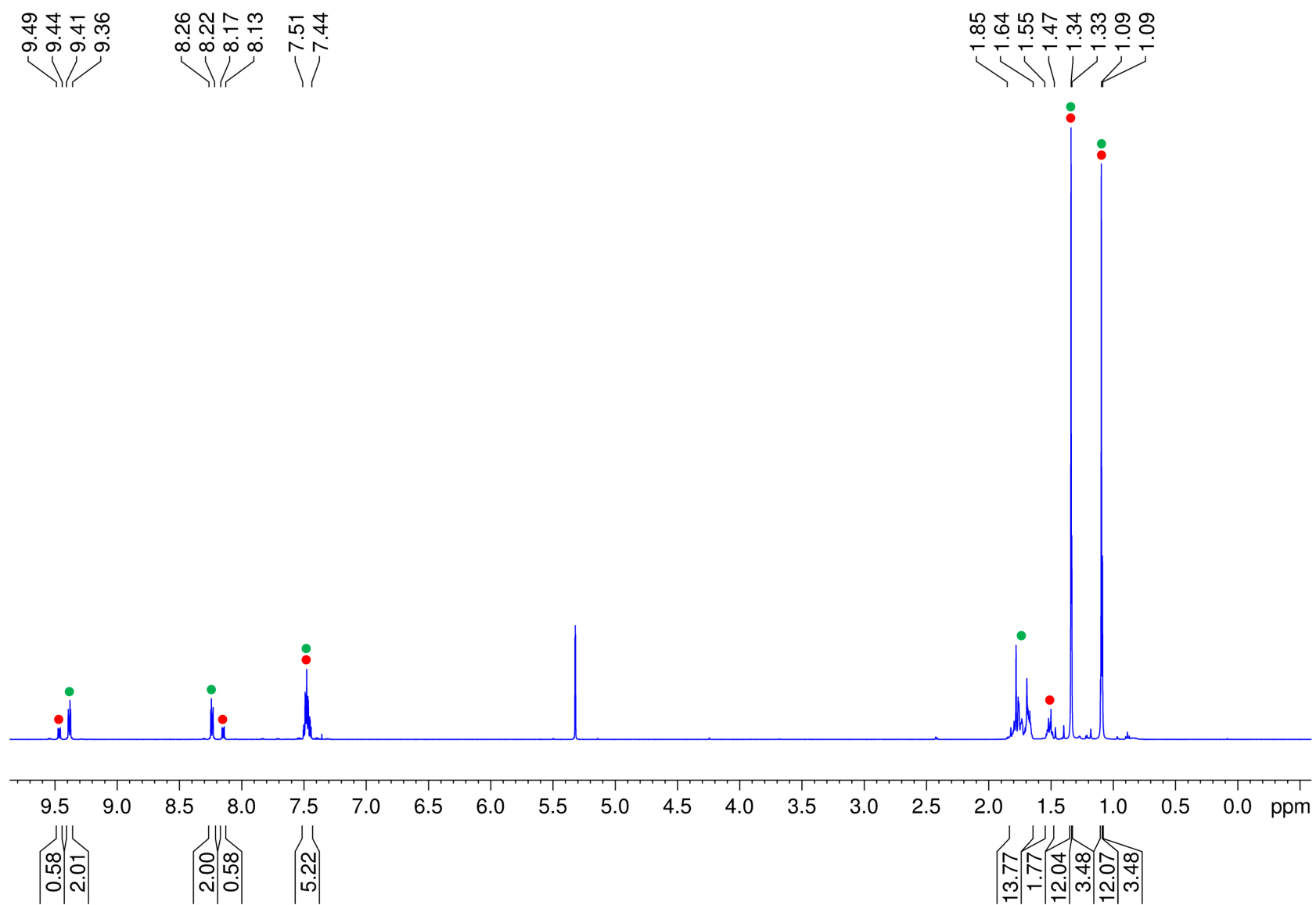


**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of *syn-2* in  $\text{THF-d}_8$ .

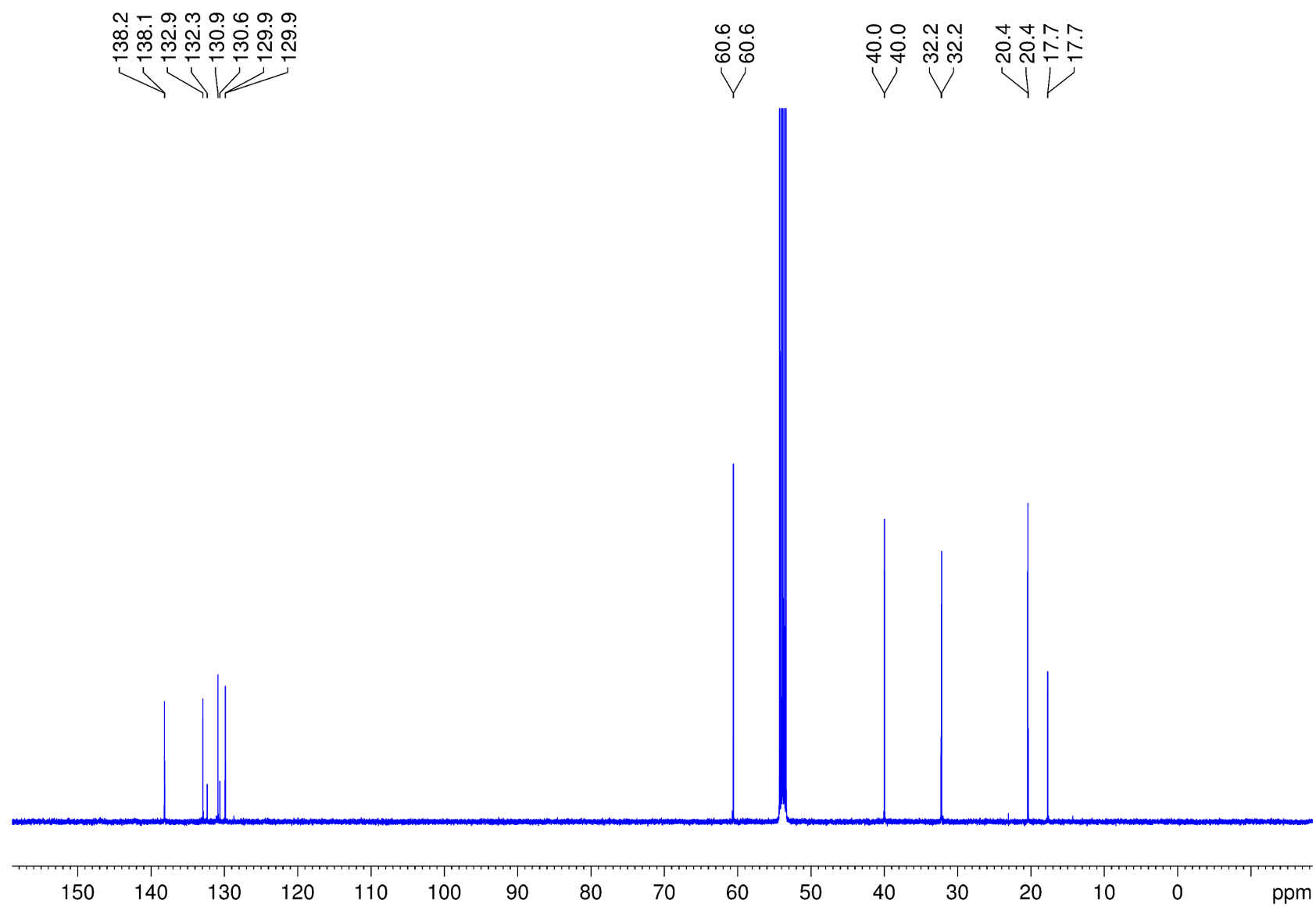




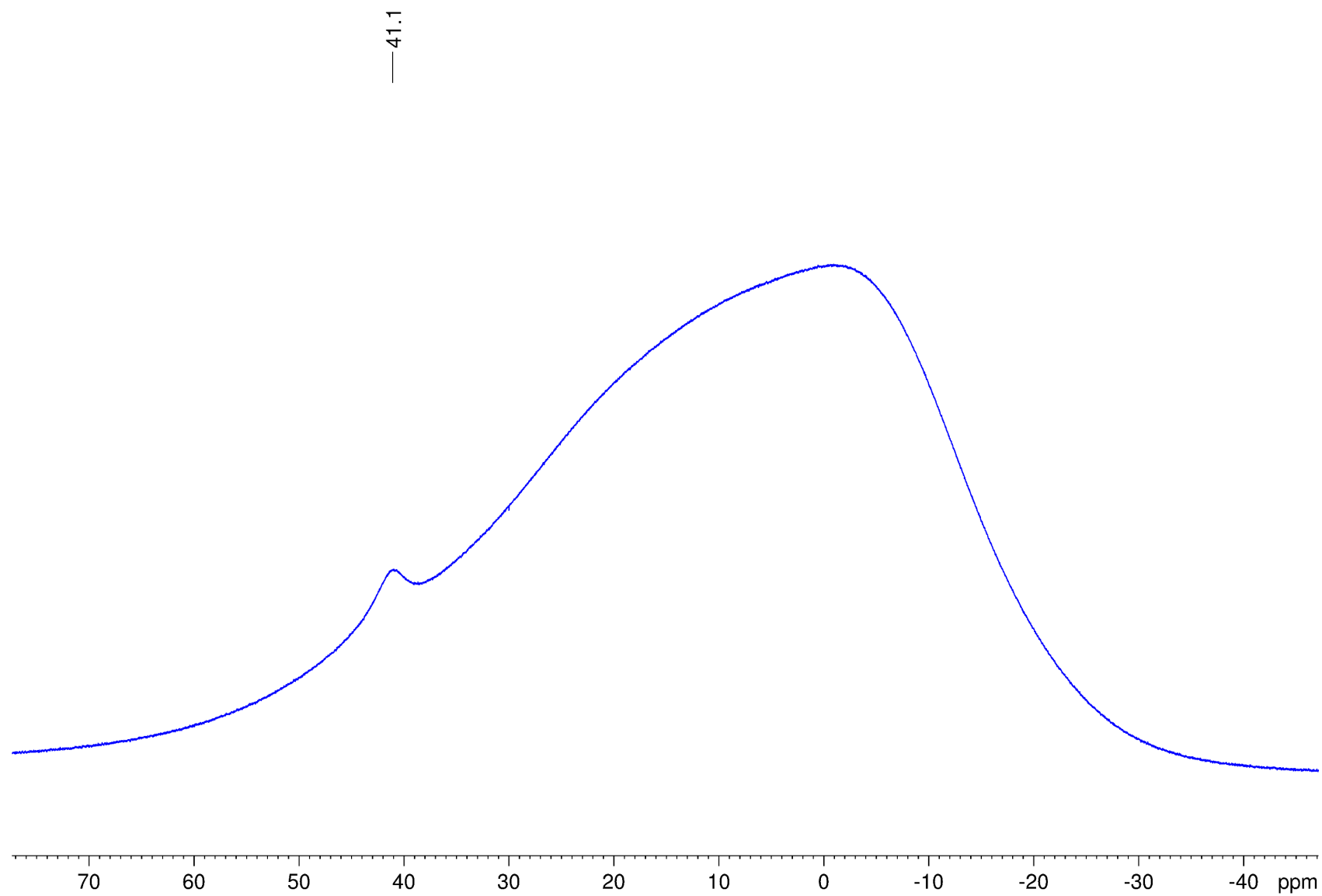
**Figure S9.**  $^{11}\text{B}$  NMR spectrum of *syn-2* in  $\text{THF-d}_8$ .



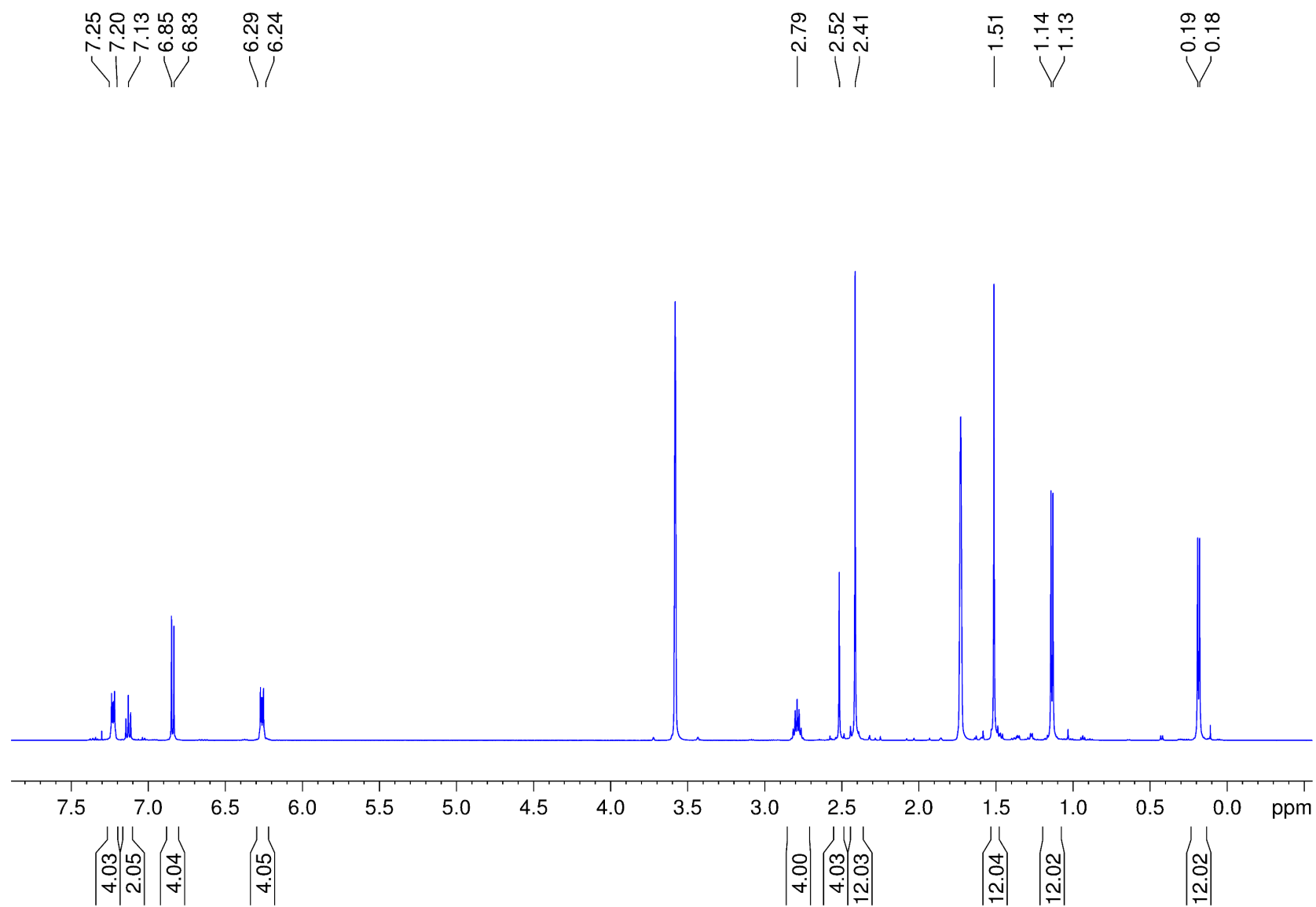
**Figure S12.**  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of **3** in  $\text{CD}_2\text{Cl}_2$  (● *anti*-**3**, ● *syn*-**3**).



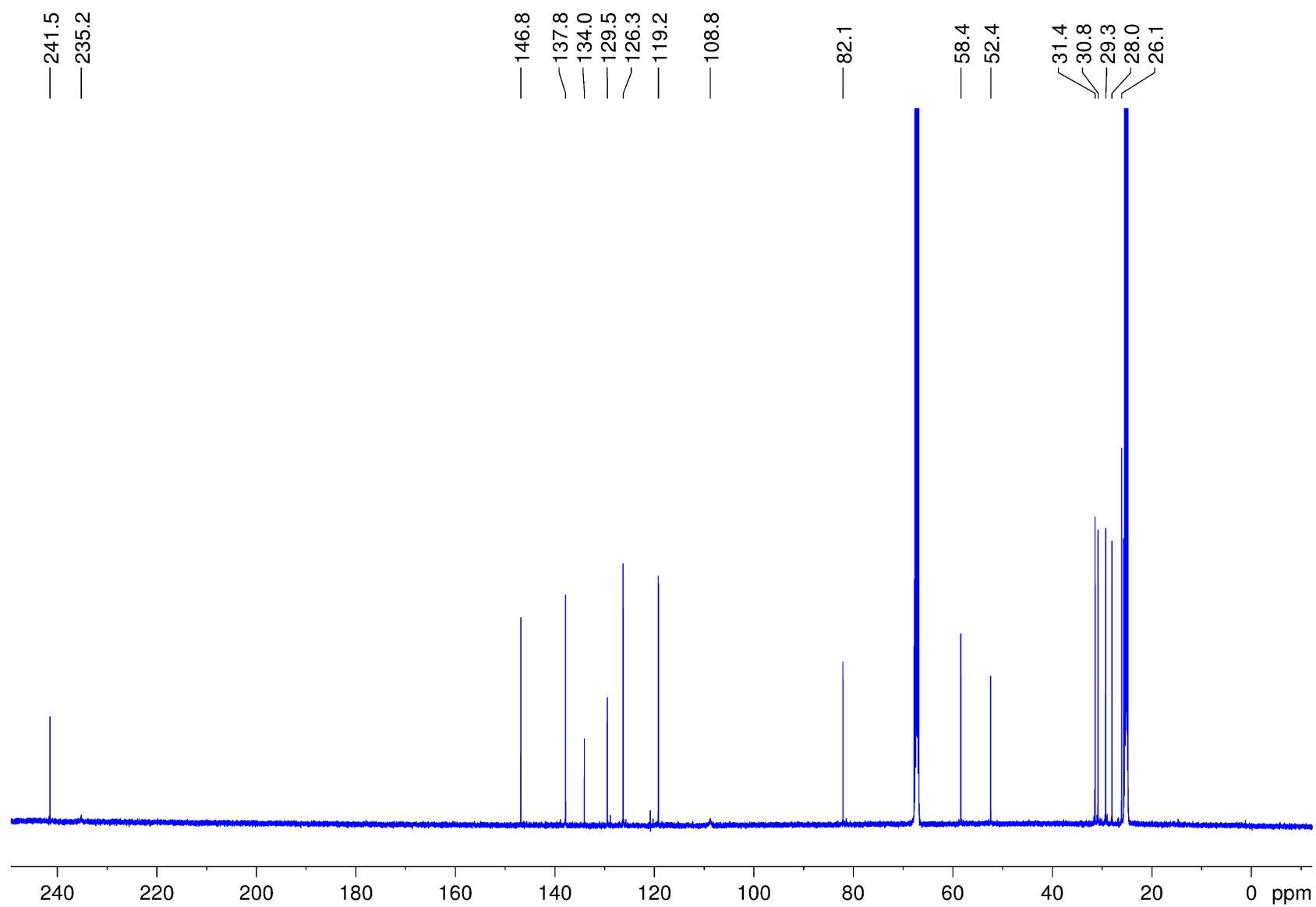
**Figure S13.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{CD}_2\text{Cl}_2$ .



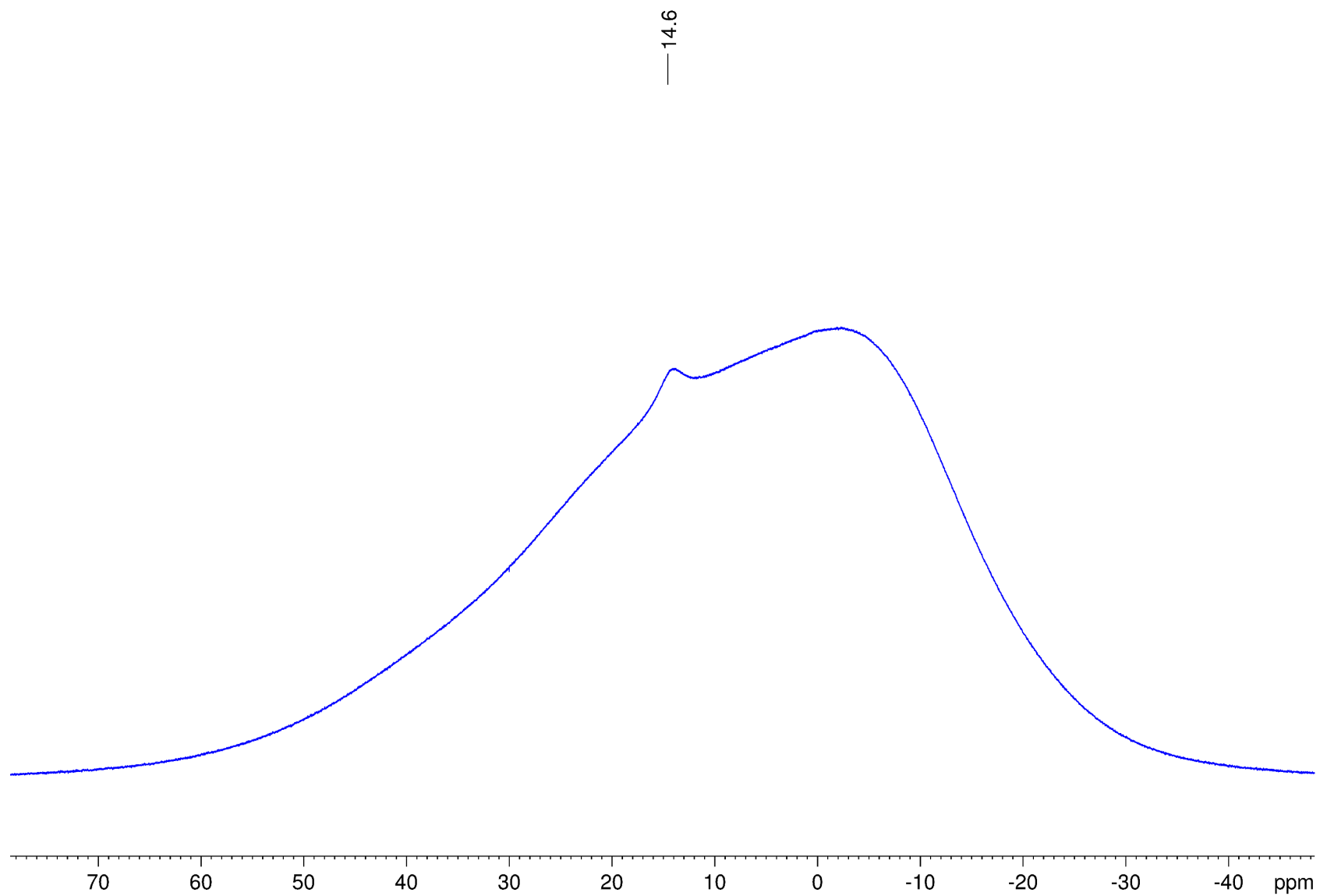
**Figure S14.**  $^{11}\text{B}$  NMR spectrum of **3** in  $\text{CD}_2\text{Cl}_2$ .



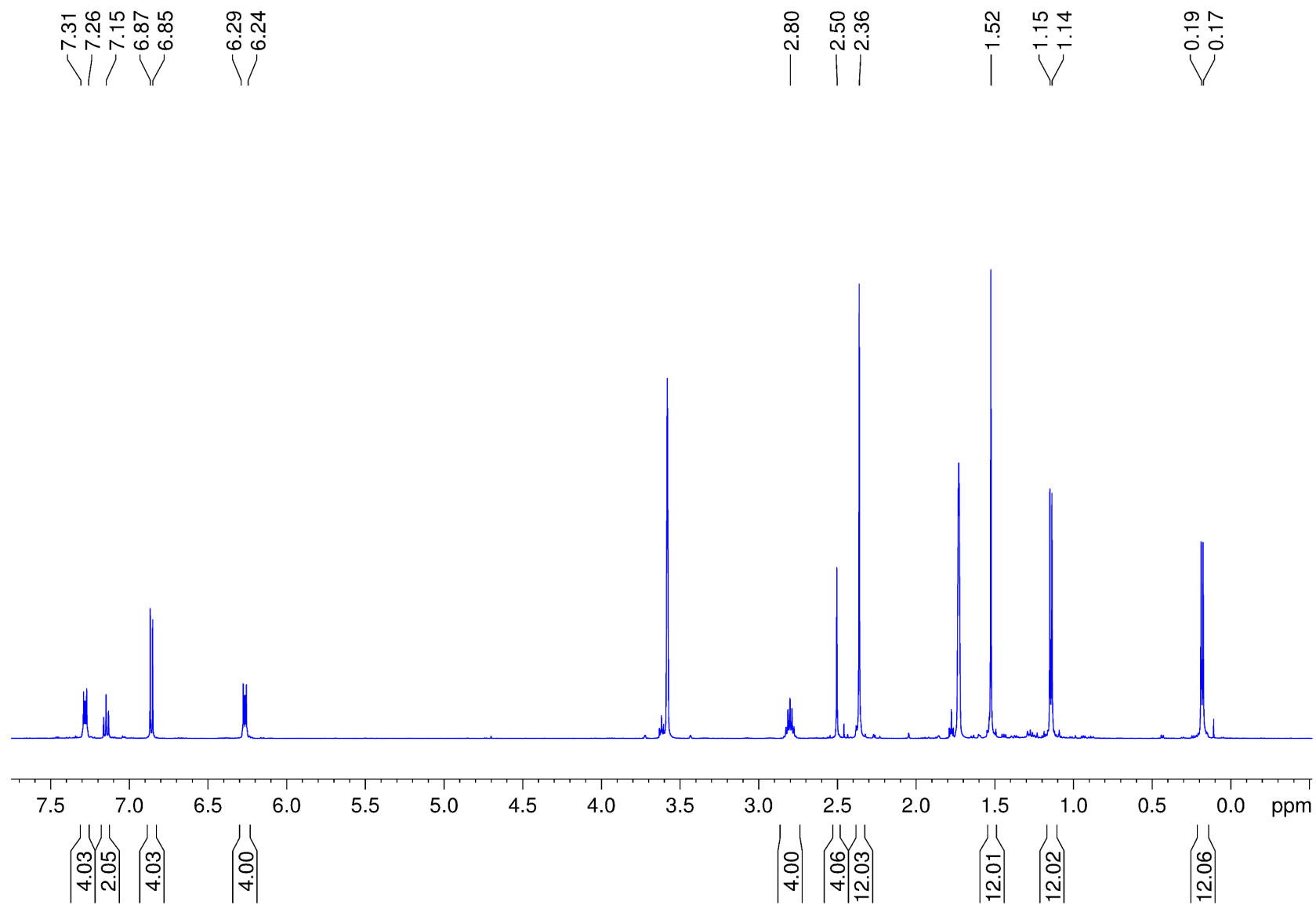
**Figure S15.**  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of **4-Cr** in  $\text{THF-d}_8$ .



**Figure S16.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4-Cr** in THF- $d_8$ .

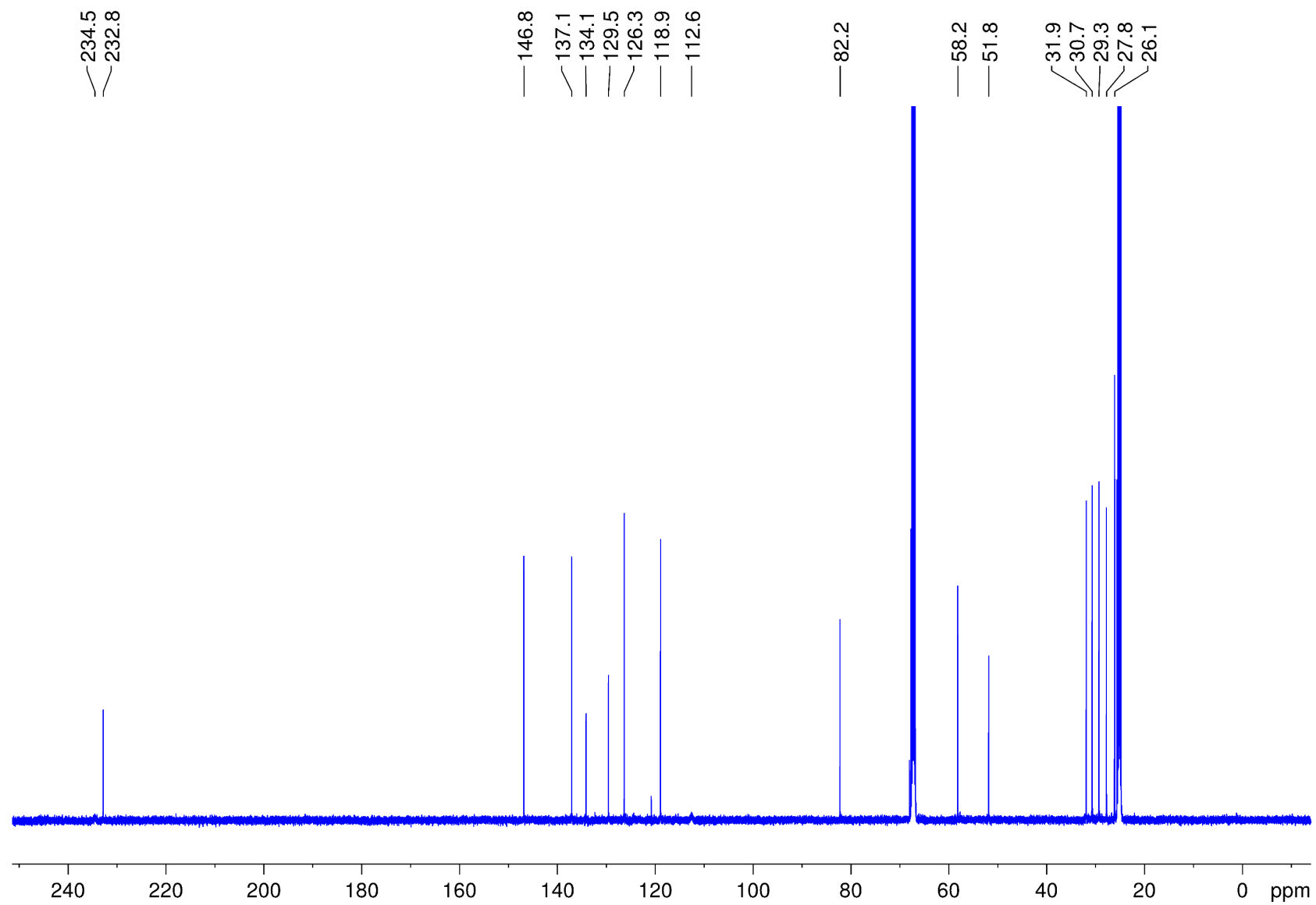


**Figure S17.**  $^{11}\text{B}$  NMR spectrum of **4-Cr** in THF- $d_8$ .

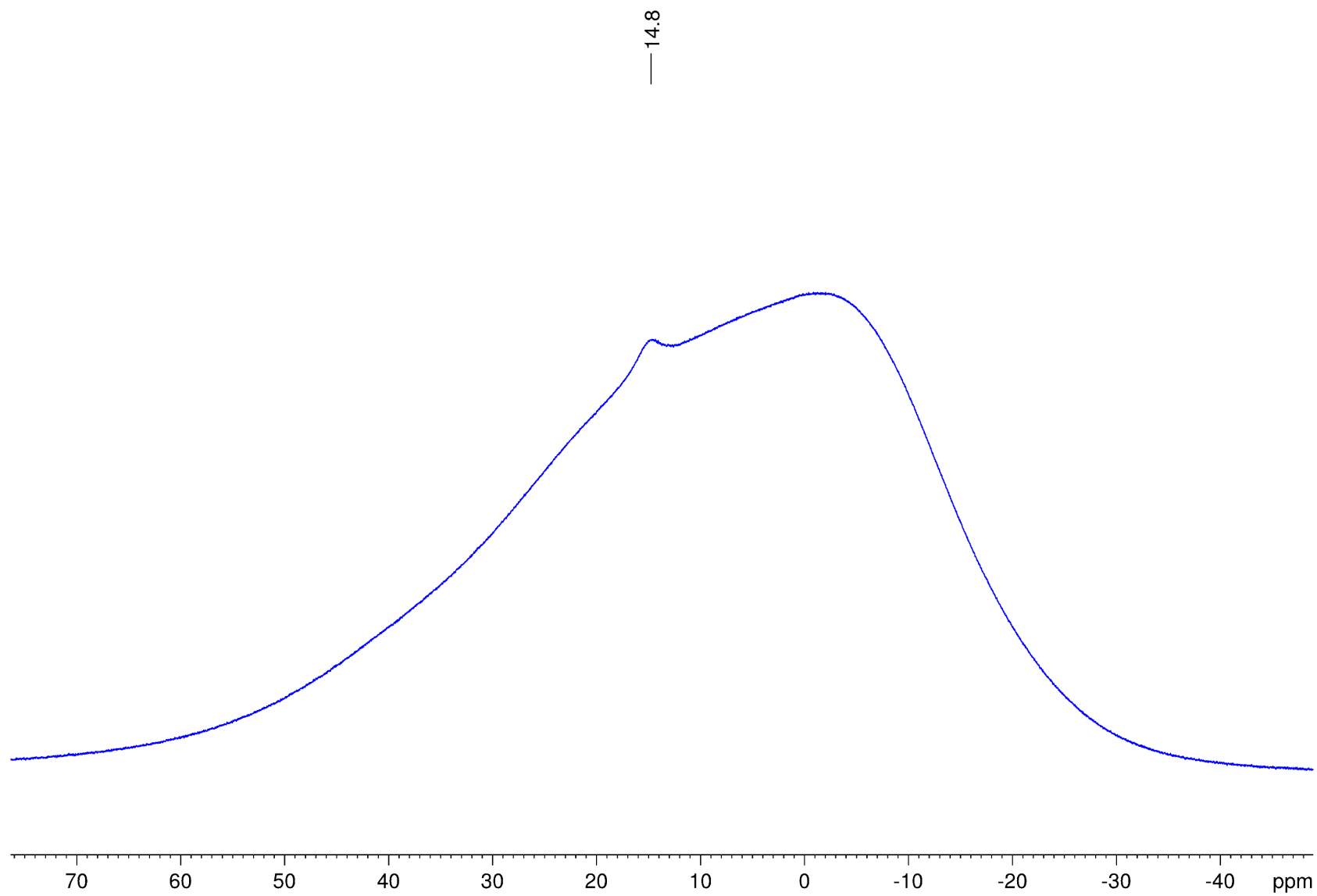


**Figure S18.**  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of **4-Mo** in  $\text{THF-d}_8$ .

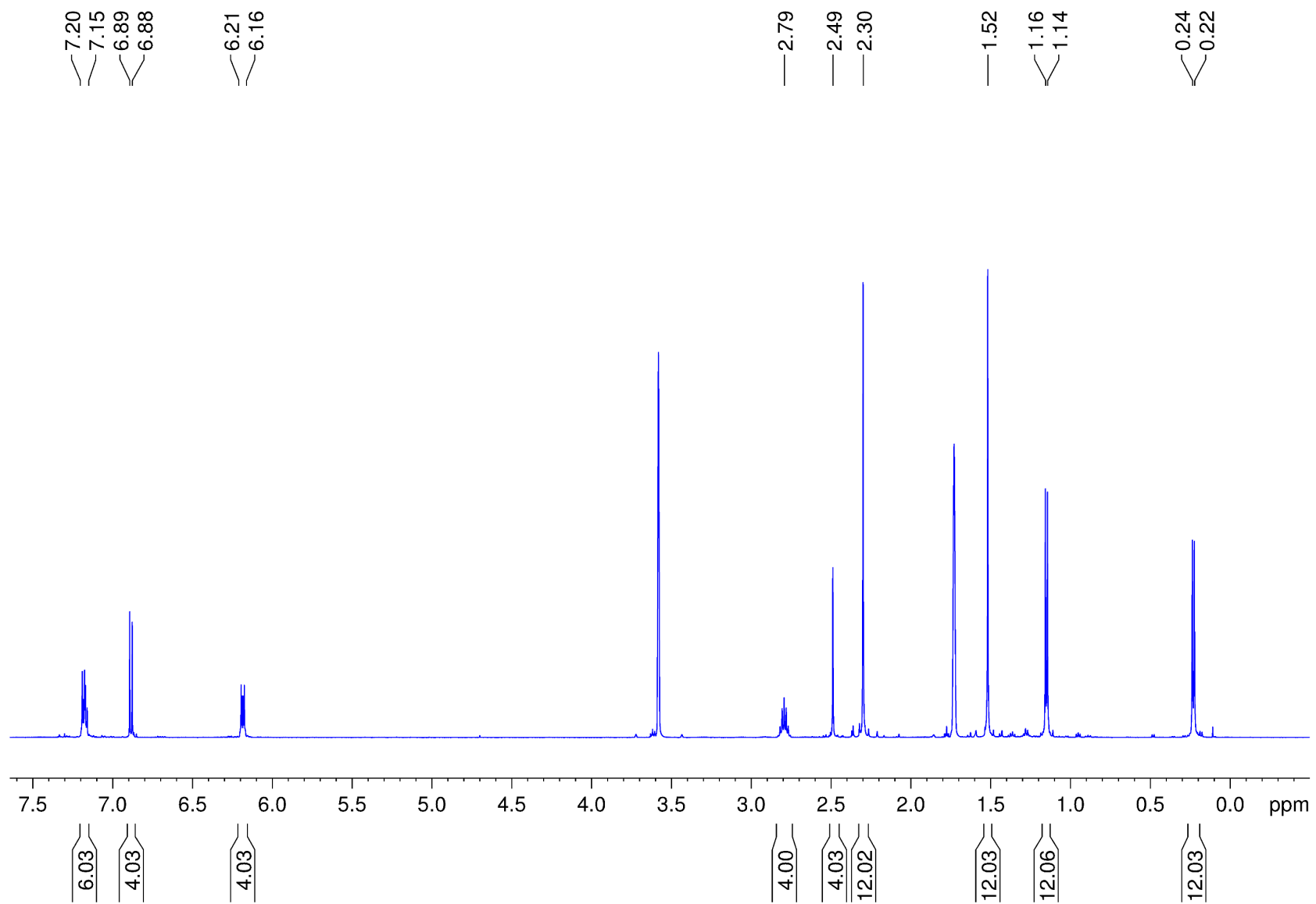




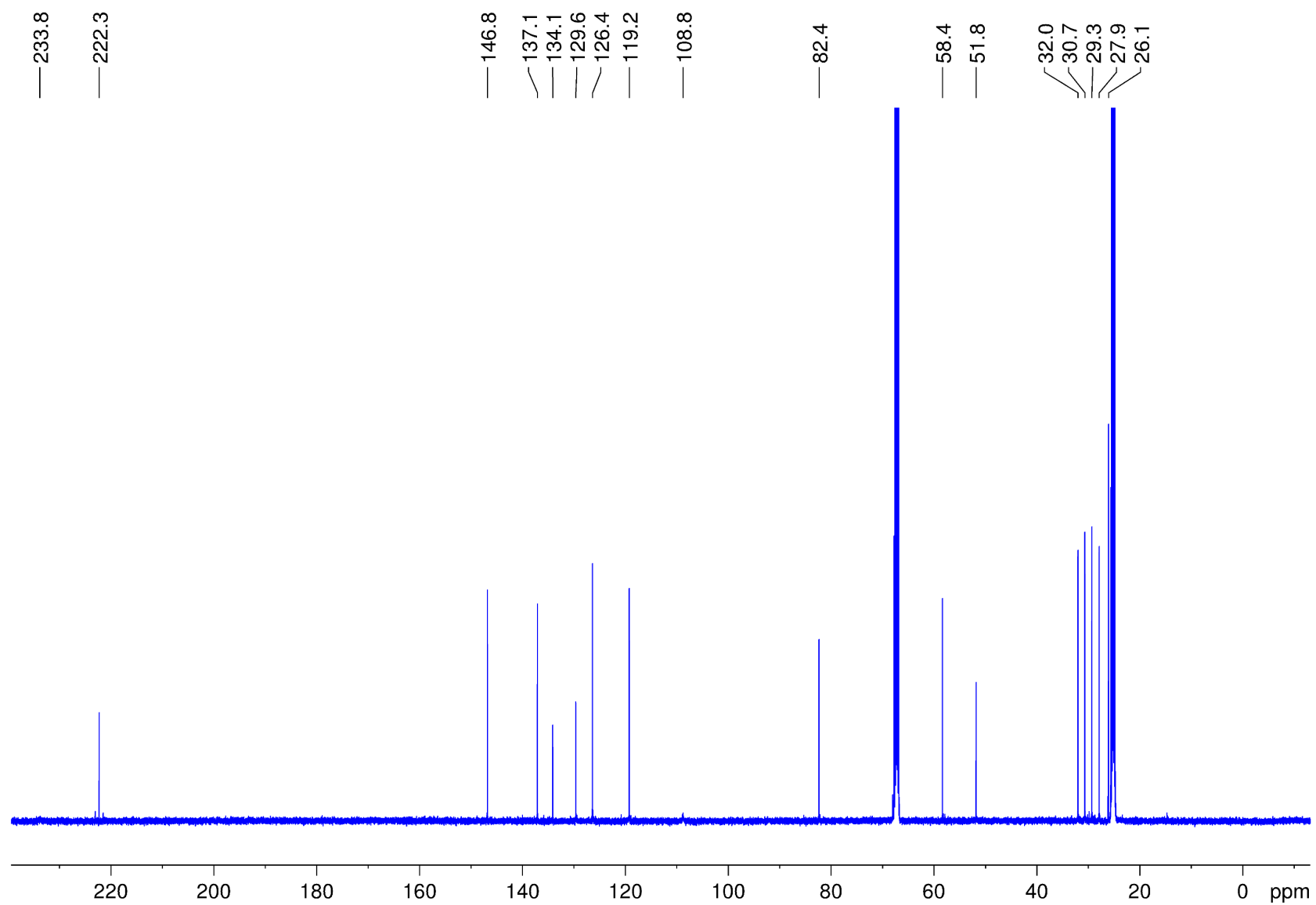
**Figure S19.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4-Mo** in THF- $d_8$ .



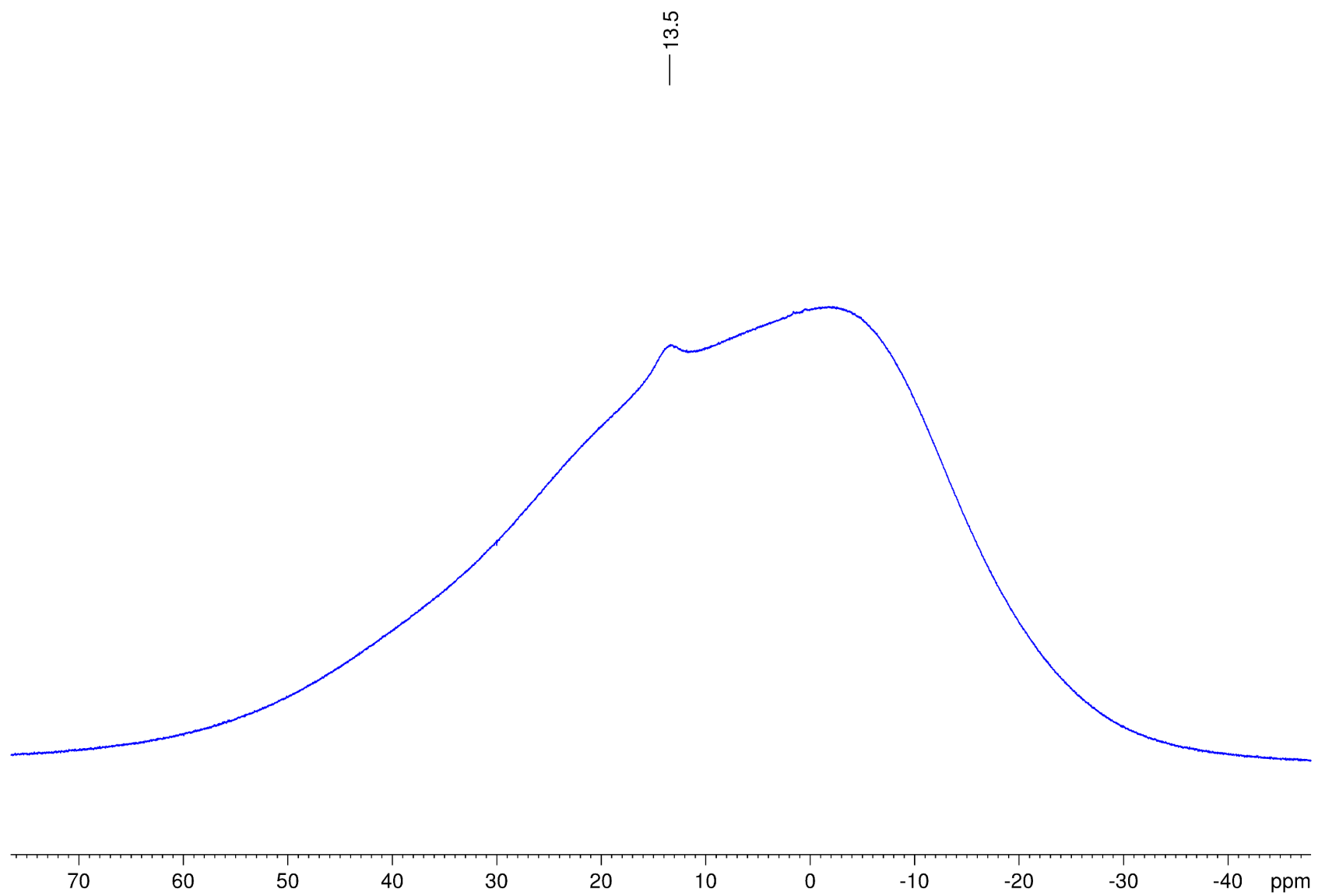
**Figure S20.**  $^{11}\text{B}$  NMR spectrum of **4-Mo** in THF- $d_8$ .



**Figure S21.**  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of **4-W** in  $\text{THF-d}_8$ .

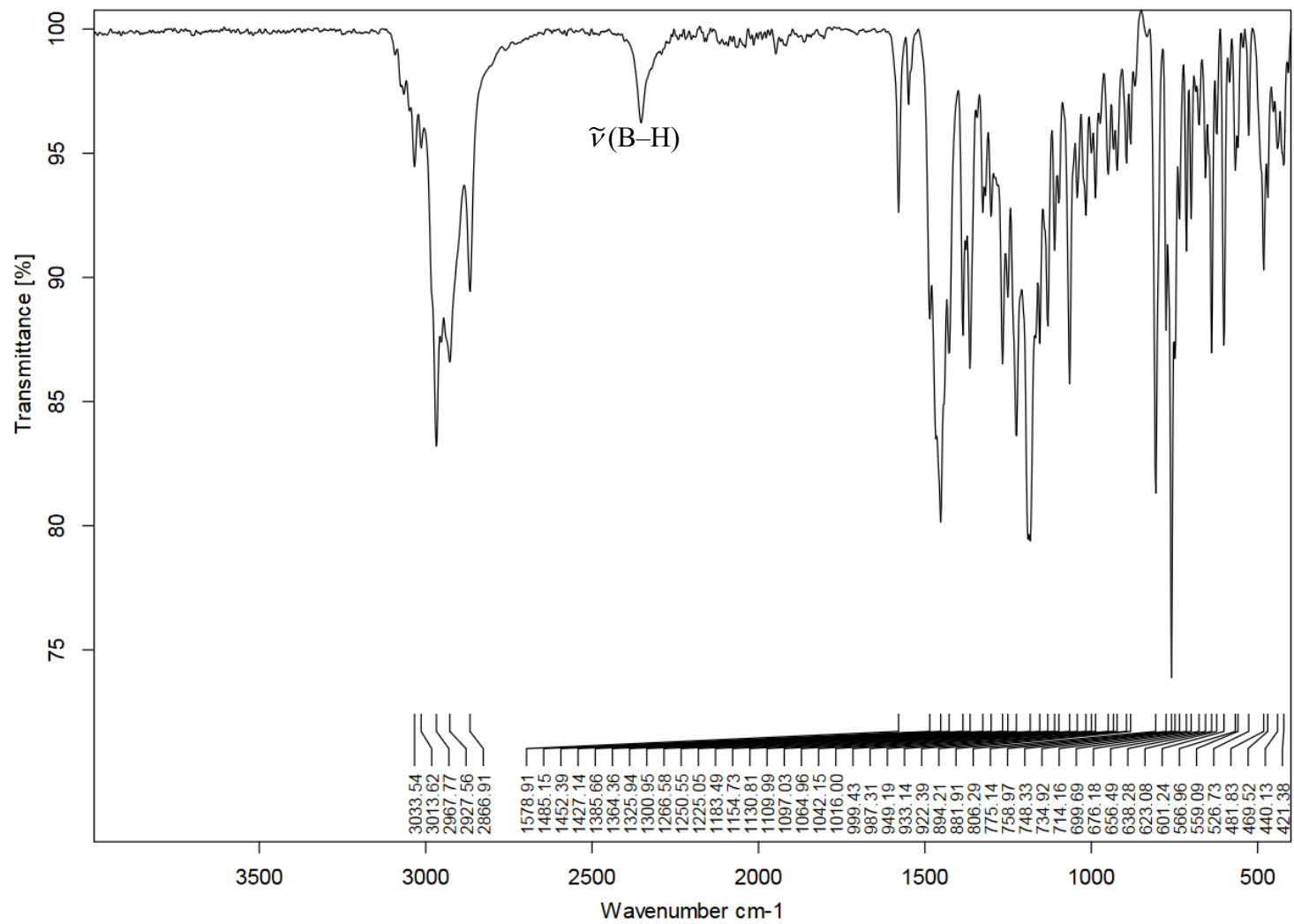


**Figure S22.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4-W** in  $\text{THF-d}_8$ .



**Figure S23.**  $^{11}\text{B}$  NMR spectrum of 4-W in THF- $d_8$ .

## IR spectra



**Figure S24.** Solid-state IR spectrum of **1**.

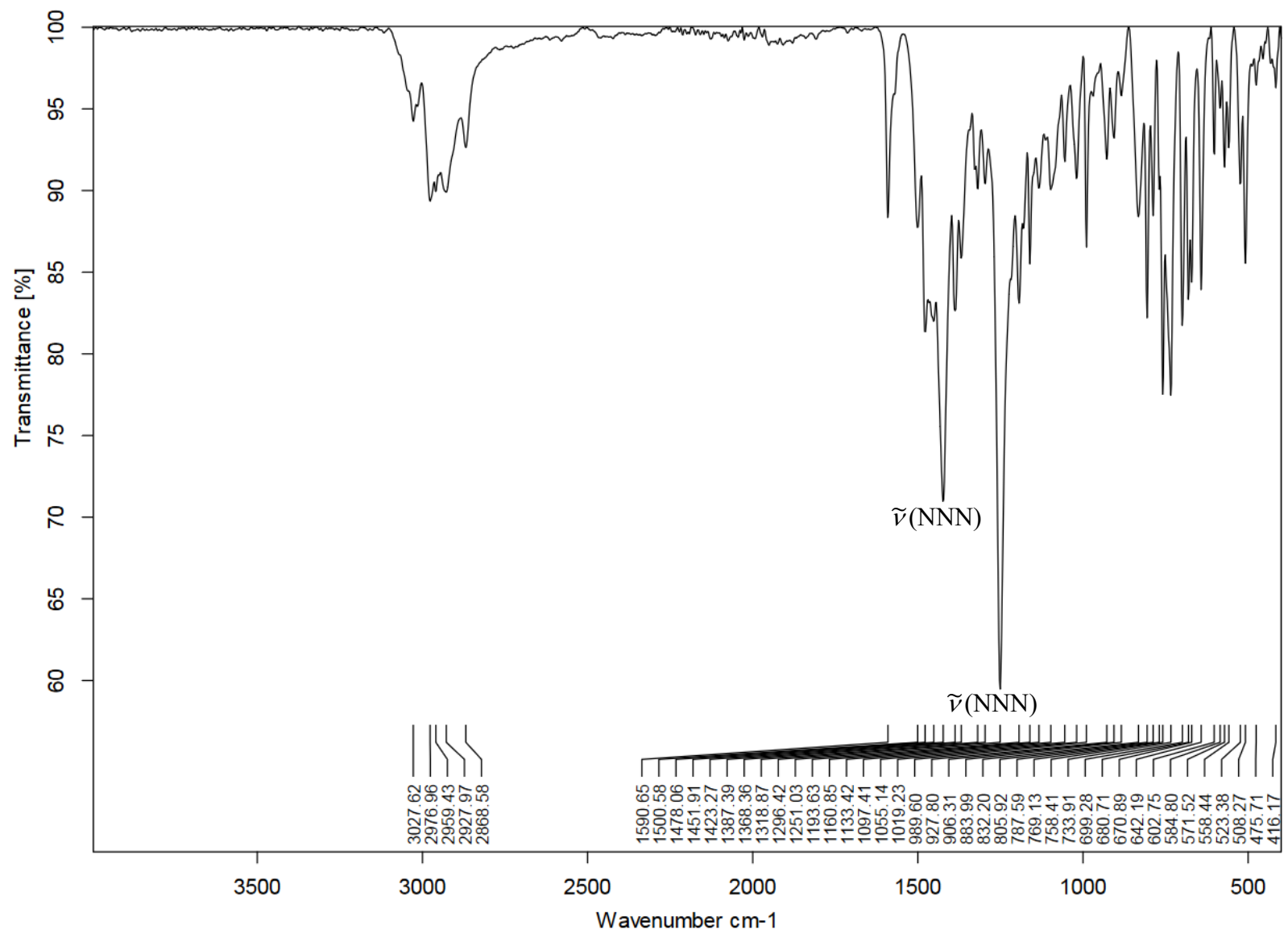


Figure S25. Solid-state IR spectrum of *anti*-2.

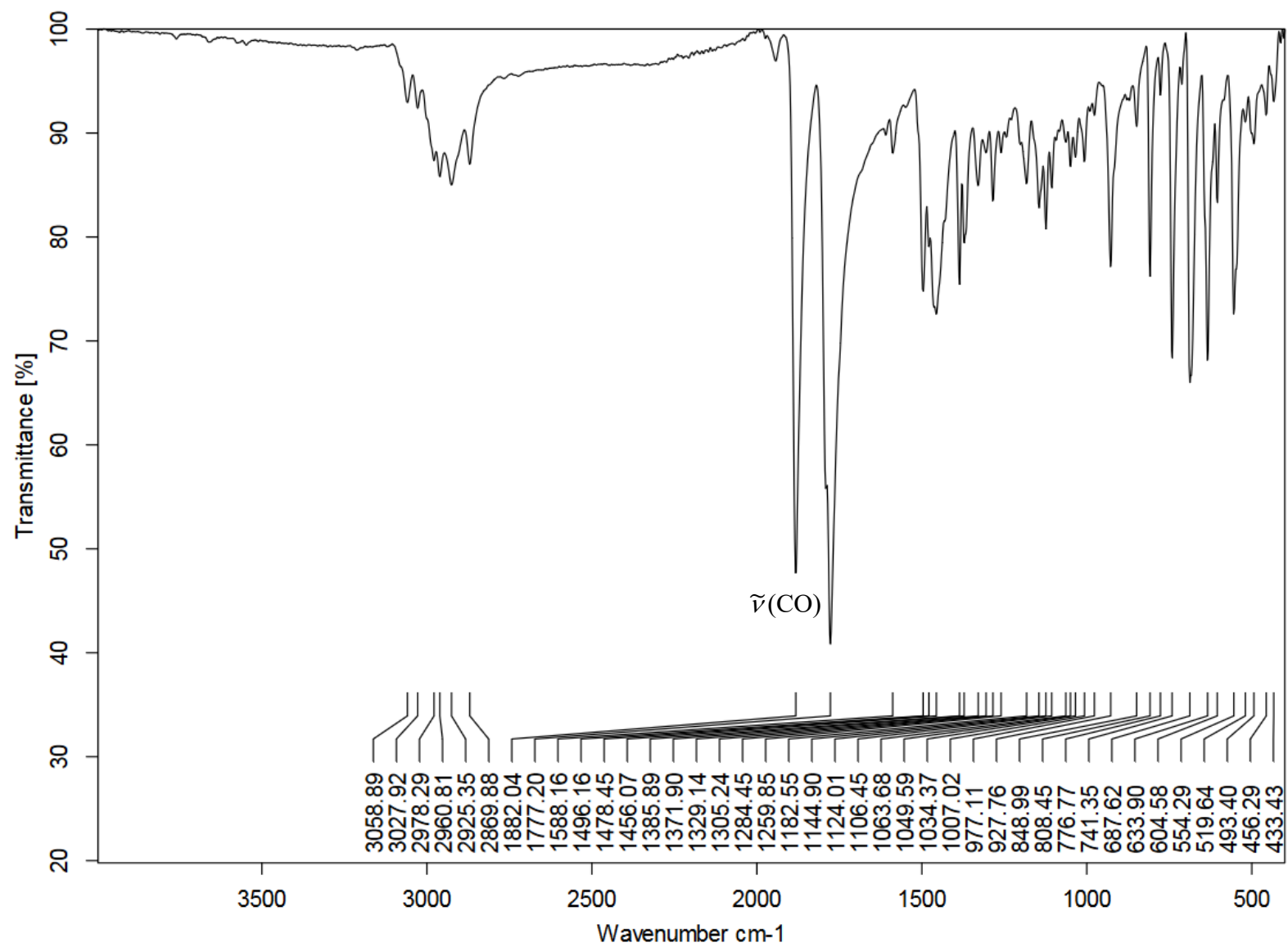


Figure S26. Solid-state IR spectrum of 4-Cr.



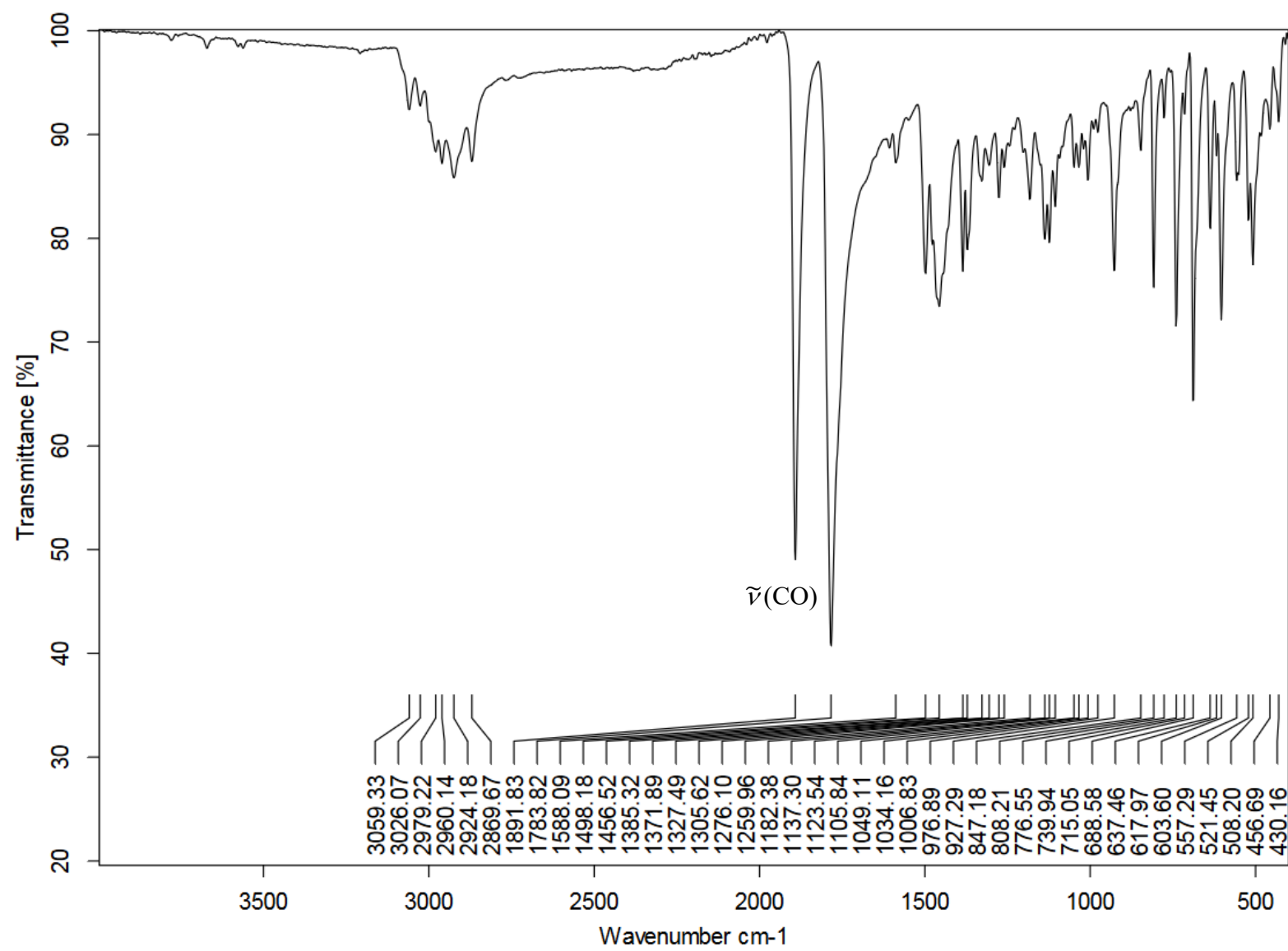


Figure S27. Solid-state IR spectrum of 4-Mo.

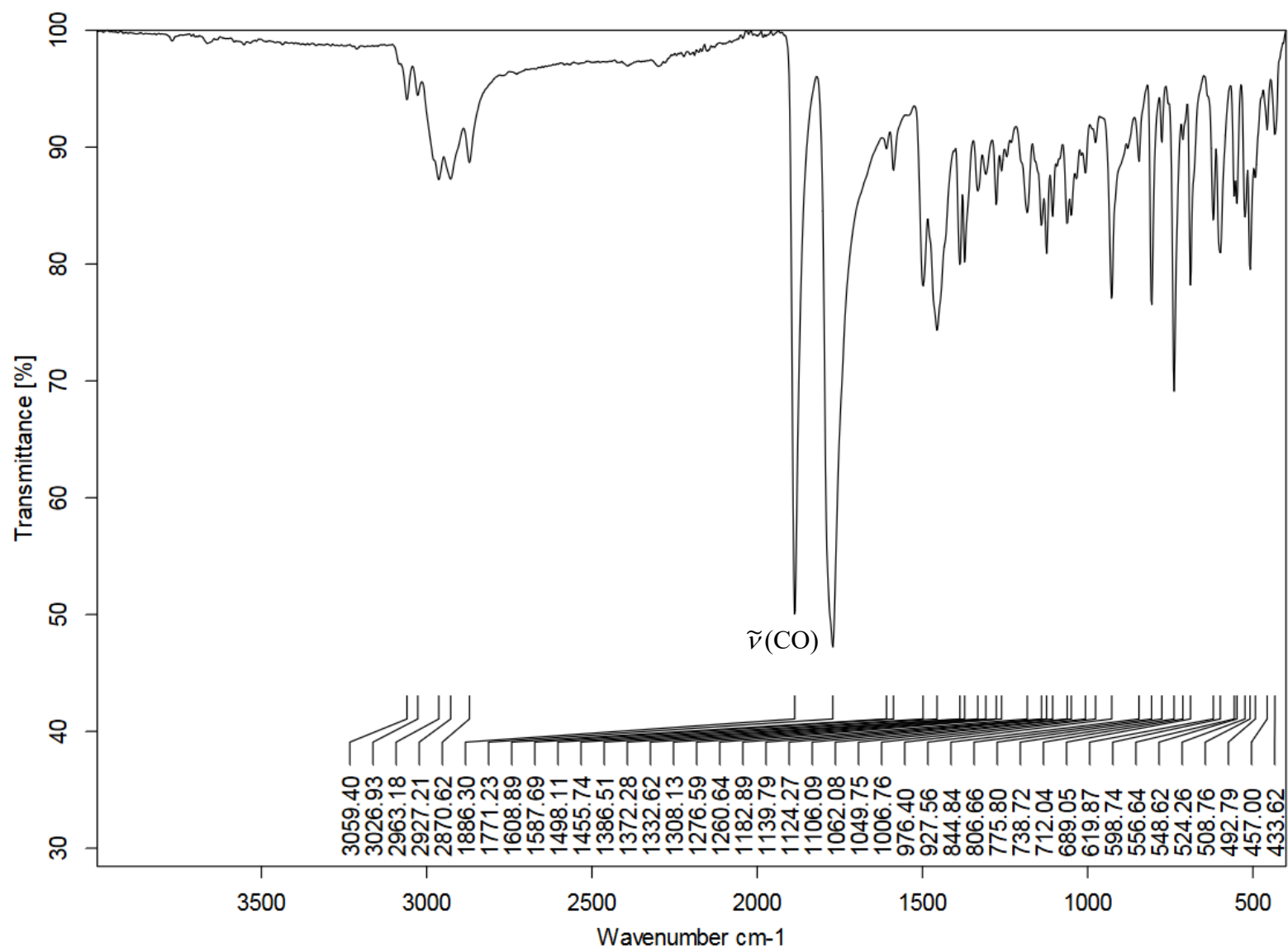
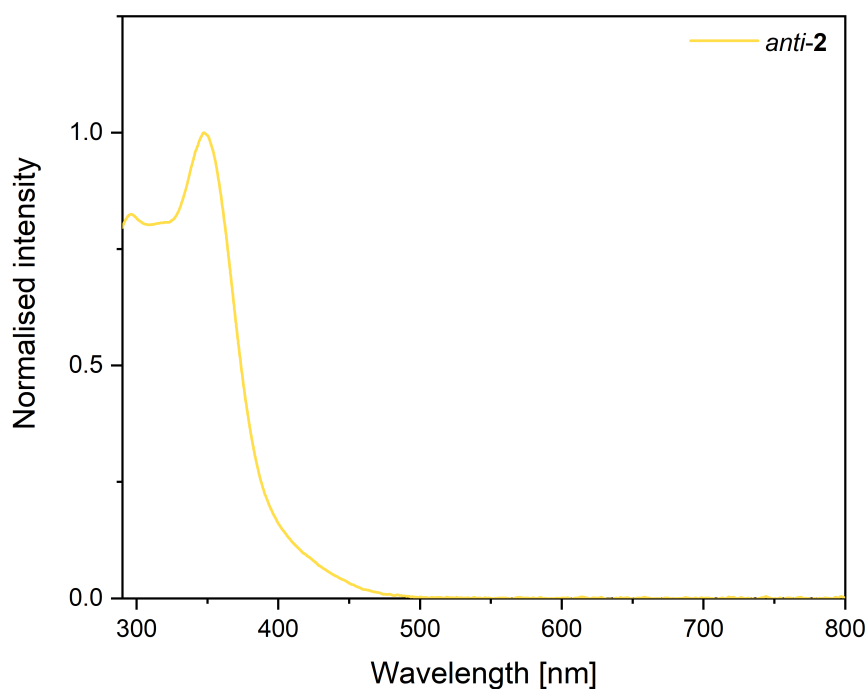
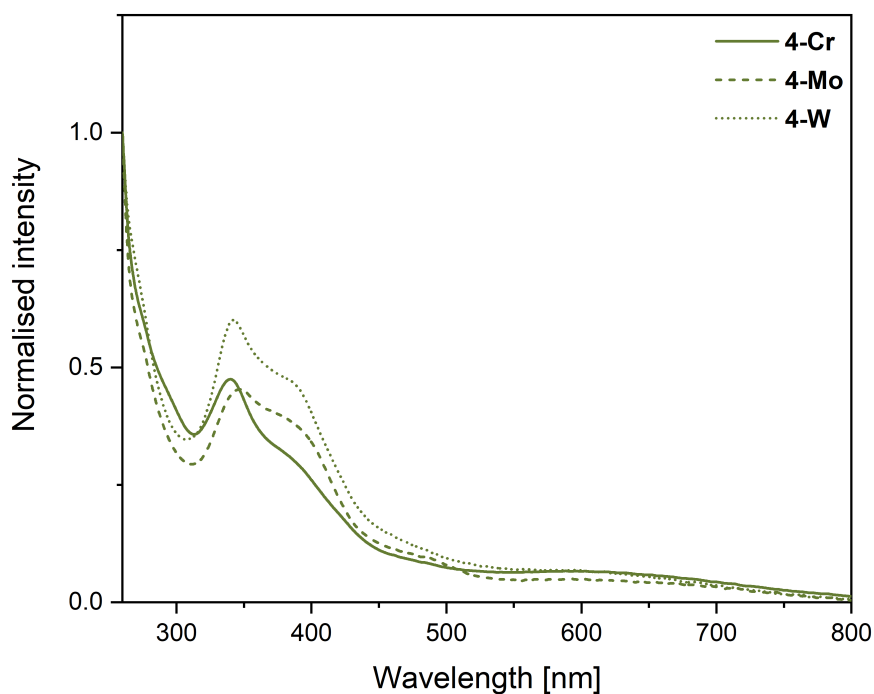


Figure S28. Solid-state IR spectrum of 4-W.

## UV-vis spectra



**Figure S29.** UV-vis absorption spectrum of *anti-2* in THF at 23 °C.  $\lambda_{\max} = 348$  nm,  $\lambda_2 = 296$  nm.



**Figure S30.** Overlay of UV-vis absorption spectra of **4-Cr** (normal), **4-Mo** (dashed) and **4-W** (dotted) in THF at 23 °C. **4-Cr**:  $\lambda_{\max} = 340$  nm,  $\lambda_2 = 392$  nm (shoulder),  $\lambda_3 = 602$  nm (broad); **4-Mo**:  $\lambda_{\max} = 347$  nm,  $\lambda_2 = 393$  nm (shoulder),  $\lambda_3 = 490$  nm (shoulder),  $\lambda_4 = 593$  nm (broad); **4-W**:  $\lambda_{\max} = 342$  nm,  $\lambda_2 = 387$  nm (shoulder),  $\lambda_3 = 595$  nm (broad).

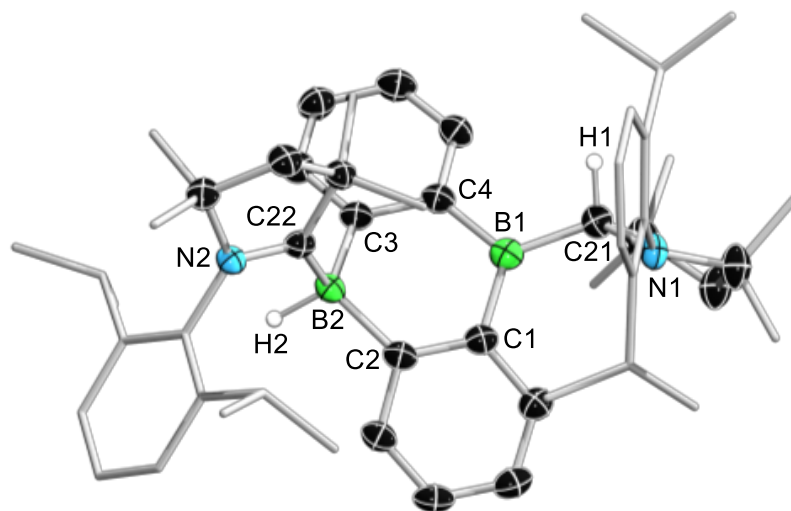
## **X-ray crystallographic data**

The crystal data of **1**, *anti-2* and **4-Cr** were collected on a *XtaLAB Synergy Dualflex HyPix* diffractometer with a Hybrid Pixel array detector and multi-layer mirror monochromated  $\text{Cu}_{\text{K}\alpha}$  radiation. The crystal data of *anti-3*, **4-Mo** and **4-W** were collected on a *Bruker D8 Quest* diffractometer with a CMOS area detector and multi-layer mirror monochromated  $\text{Mo}_{\text{K}\alpha}$  radiation. The structures were solved using the intrinsic phasing method,<sup>3</sup> refined with the ShelXL program<sup>4</sup> and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-2306744 (**1**), 2306745 (*anti-2*), 2306746 (*anti-3*), 2306747 (**4-Cr**), 2306748 (**4-Mo**), 2306749 (**4-W**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

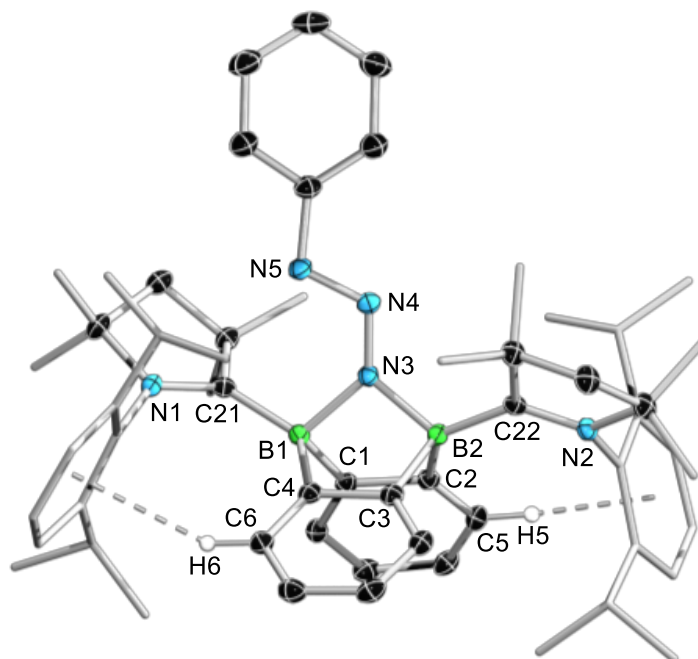
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**Crystal data for 1:**  $C_{52}H_{72}B_2N_2$ ,  $M_r = 746.73$ , clear colourless block,  $0.120 \times 0.100 \times 0.030$  mm<sup>3</sup>, orthorhombic space group *Pbca*,  $a = 13.89720(10)$  Å,  $b = 15.60870(10)$  Å,  $c = 41.3288(3)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 8964.93(11)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{calcd} = 1.107$  g·cm<sup>-3</sup>,  $\mu = 0.460$  mm<sup>-1</sup>,  $F(000) = 3264$ ,  $T = 100(2)$  K,  $R_1 = 0.0595$ ,  $wR_2 = 0.1287$ , 8508 independent reflections [ $2\theta \leq 140.15^\circ$ ] and 524 parameters.



**Figure S31.** Solid-state structure of **1**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms except B–H and CAAC–H omitted for clarity.

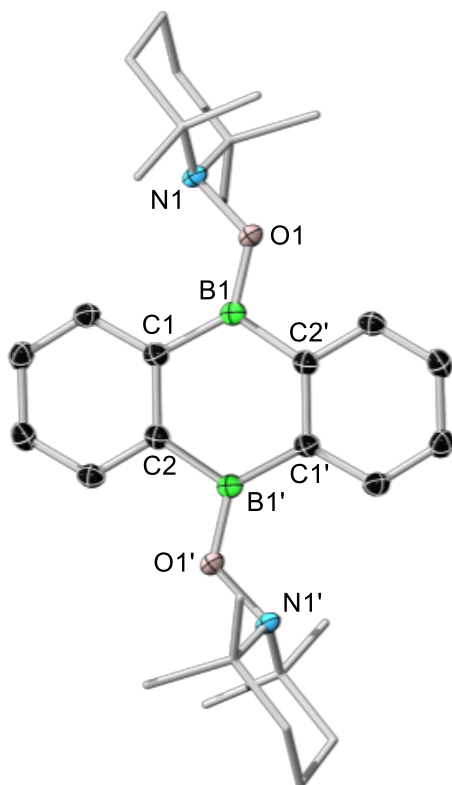
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**Crystal data for *anti*-2:** C<sub>79</sub>H<sub>96</sub>B<sub>2</sub>N<sub>5</sub>,  $M_r = 1137.22$ , yellow block, 0.220×0.200×0.080 mm<sup>3</sup>, triclinic space group  $\bar{P}1$ ,  $a = 11.47910(10)$  Å,  $b = 13.02450(10)$  Å,  $c = 22.38830(10)$  Å,  $\alpha = 79.3390(10)^\circ$ ,  $\beta = 86.6270(10)^\circ$ ,  $\gamma = 86.6760(10)^\circ$ ,  $V = 3280.00(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.151$  g·cm<sup>-3</sup>,  $\mu = 0.495$  mm<sup>-1</sup>,  $F(000) = 1230$ ,  $T = 100(2)$  K,  $R_I = 0.0383$ ,  $wR_2 = 0.0962$ , 12419 independent reflections [ $2\theta \leq 140.142^\circ$ ] and 791 parameters.



**Figure S32.** Solid-state structure of *anti*-2. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms except DBA–H···Dipp omitted for clarity.

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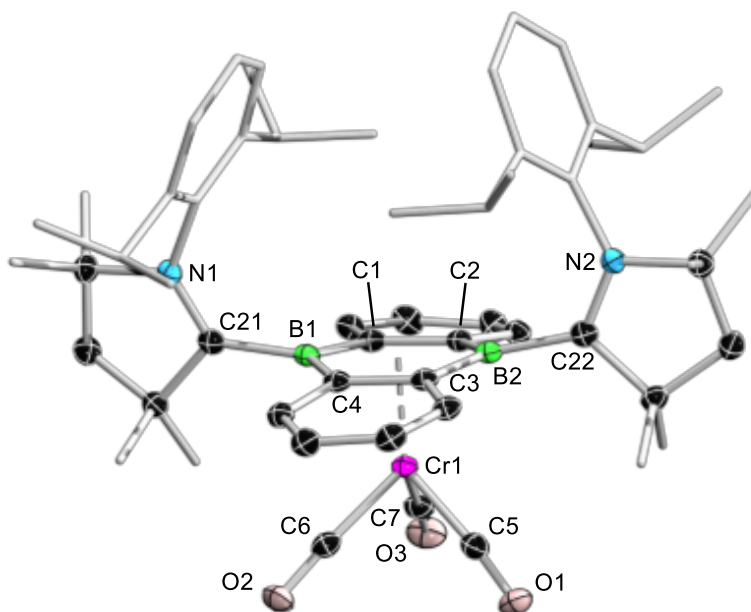
**Crystal data for *anti*-3:** C<sub>36</sub>H<sub>50</sub>B<sub>2</sub>N<sub>2</sub>O<sub>2</sub>,  $M_r = 564.40$ , colourless block, 0.513×0.226×0.215 mm<sup>3</sup>, triclinic space group  $P\bar{1}$ ,  $a = 7.7792(17)$  Å,  $b = 10.300(3)$  Å,  $c = 10.4076(19)$  Å,  $\alpha = 78.833(8)^\circ$ ,  $\beta = 82.411(11)^\circ$ ,  $\gamma = 78.433(9)^\circ$ ,  $V = 797.8(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $\rho_{\text{calcd}} = 1.175$  g·cm<sup>-3</sup>,  $\mu = 0.071$  mm<sup>-1</sup>,  $F(000) = 306$ ,  $T = 100(2)$  K,  $R_I = 0.0477$ ,  $wR_2 = 0.0986$ , 3138 independent reflections [ $2\theta \leq 52.042^\circ$ ] and 194 parameters.



**Figure S33.** Solid-state structure of *anti*-3. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

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**Crystal data for 4-Cr:**  $C_{59}H_{78}B_2CrN_2O_4$ ,  $M_r = 952.85$ , clear brown block,  $0.350 \times 0.130 \times 0.090 \text{ mm}^3$ , monoclinic space group  $P2_1/n$ ,  $a = 11.25260(10) \text{ \AA}$ ,  $b = 22.8684(2) \text{ \AA}$ ,  $c = 19.7806(2) \text{ \AA}$ ,  $\beta = 93.8830(10)^\circ$ ,  $V = 5078.44(8) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.246 \text{ g}\cdot\text{cm}^{-3}$ ,  $\mu = 2.229 \text{ mm}^{-1}$ ,  $F(000) = 2048$ ,  $T = 100(2) \text{ K}$ ,  $R_I = 0.0375$ ,  $wR_2 = 0.0981$ , 9635 independent reflections [ $2\theta \leq 140.148^\circ$ ] and 629 parameters.

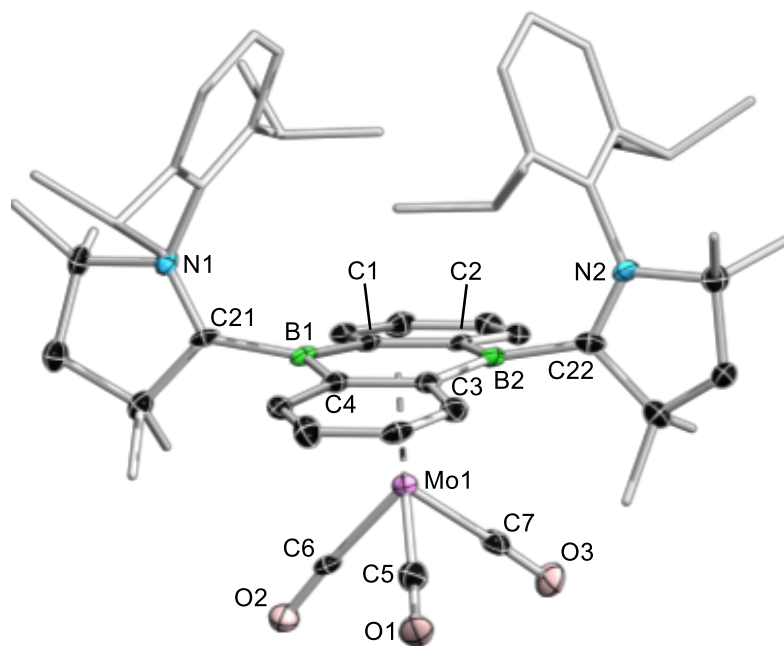


**Figure S34.** Solid-state structure of 4-Cr. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.



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**Refinement details for 4-Mo:** Refined as a two-component twin. The BASF parameter was refined to 11.8%. Two outlying reflections affected by the beamstop were omitted: 1 1 0 and - 8 0 12. The ADPs of the boron atoms, distorted by their coordination to the heavy Mo atom, were restricted to similarity with the neighbouring carbon atoms using SIMU.

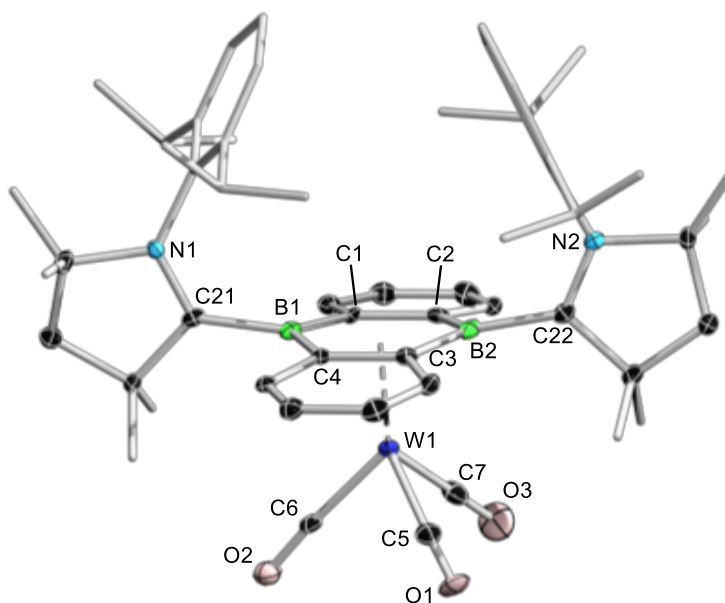
**Crystal data for 4-Mo:**  $C_{59}H_{78}B_2MoN_2O_4$ ,  $M_r = 996.79$ , black block,  $0.350 \times 0.130 \times 0.090 \text{ mm}^3$ , monoclinic space group  $Pc$ ,  $a = 19.1301(8) \text{ \AA}$ ,  $b = 10.9095(4) \text{ \AA}$ ,  $c = 24.8499(11) \text{ \AA}$ ,  $\beta = 93.027(2)^\circ$ ,  $V = 5178.9(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.278 \text{ g}\cdot\text{cm}^{-3}$ ,  $\mu = 0.302 \text{ mm}^{-1}$ ,  $F(000) = 2120$ ,  $T = 100(2) \text{ K}$ ,  $R_I = 0.0804$ ,  $wR_2 = 0.1433$ , Flack parameter =  $0.05(4)$ , 13327 independent reflections [ $2\theta \leq 54.264^\circ$ ] and 1258 parameters.



**Figure S35.** Solid-state structure of **4-Mo**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

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**Refinement details for 4-W:** Refined as a two-component inversion twin. The BASF parameter was refined to 43.2%. Ten low-resolution reflections that were affected by the beamstop were removed from refinement. The ADPs of the boron atoms, distorted by their coordination to the heavy W atom, were restrained to similarity with the neighbouring carbon atoms using SIMU. An ISOR restraint was additionally applied to B8\_10. In each of the two complexes the ADP of the carbonyl carbon atom C4, distorted by its coordination to the heavy W atom, was restrained to similarity with the neighbouring tungsten atom using SIMU.

**Crystal data for 4-W:**  $C_{59}H_{78}B_2N_2O_4W$ ,  $M_r = 1084.70$ , black block,  $0.462 \times 0.304 \times 0.210$  mm<sup>3</sup>, monoclinic space group  $Pc$ ,  $a = 19.1470(6)$  Å,  $b = 10.9198(4)$  Å,  $c = 24.8088(10)$  Å,  $\beta = 93.0270(10)^\circ$ ,  $V = 5179.8(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{calcd} = 1.391$  g·cm<sup>-3</sup>,  $\mu = 2.279$  mm<sup>-1</sup>,  $F(000) = 2248$ ,  $T = 100(2)$  K,  $R_1 = 0.0234$ ,  $wR_2 = 0.0482$ , Flack parameter = 0.432(5), 20179 independent reflections [ $2\theta \leq 52.044^\circ$ ] and 1258 parameters.



**Figure S36.** Solid-state structure of 4-W. Atomic displacement ellipsoids represented at 50%. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

## References

- 1 C. Saalfrank, F. Fantuzzi, T. Kupfer, B. Ritschel, K. Hammond, I. Krummenacher, R. Bertermann, R. Wirthensohn, M. Finze, P. Schmid, V. Engel, B. Engels and H. Braunschweig, *Angew. Chem. Int. Ed.*, 2020, **59**, 19338–19343.
- 2 D. P. Tate, W. R. Knipple and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433–34.
- 3 G. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3–8.
- 4 G. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112–122.