Supporting Information for

Zerovalent transition-metal inverse-sandwich complexes of a diborataanthracene dianion

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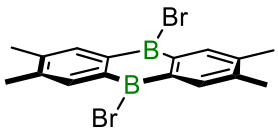
Contents

General methods

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 400 spectrometer (^{11}B: 128.5 MHz), on a Bruker Avance 500 spectrometer (^{1}H: 500.1 MHz, ^{11}B: 160.5 MHz, ^{13}C: 125.8 MHz, ^{7}Li: 194.4 MHz) or a Bruker Avance Neo I 600 spectrometer (^{1}H: 600.2 MHz, ^{13}C: 150.9 MHz, ^{7}Li: 233.3 MHz). Chemical shifts (δ) are provided 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: $BF_3{\cdot}OEt_2$, ^{7}Li: LiCl). NMR splitting patterns are given as singlet (s) or multiplet (m). High-resolution mass spectrometry (HRMS) data were obtained from a Thermo Scientific Exactive Plus spectrometer. UV-vis spectra were acquired on a METTLER TOLEDO UV-vis-Excellence UV5 spectrophotometer. Solid-state IR spectra were recorded on a Bruker FT-IR spectrometer ALPHA II inside a glovebox. Cyclic voltammetry experiments were performed using a Gamry Instruments Reference 600 potentiostat. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a Vycor tip, serving as the reference electrode. Formal redox potentials are referenced to the ferrocene/ferrocenium ($[Cp_2Fe]^{+/0}$) redox couple. Tetra(*n*-butyl)ammonium hexafluorophosphate ($[nBu_4N][PF_6]$) was employed as the supporting electrolyte. Compensation for resistive losses (*iR* drop) was employed for all measurements. Solvents and reagents were purchased from Sigma-Aldrich. 4,5-bis(trimethylsilyl)-1,2-dimethylbenzene[1] and $[(MeCN)_3M(CO)_3]$ (M = Cr, Mo, W)[2] were synthesized using literature procedures.

Synthetic procedures

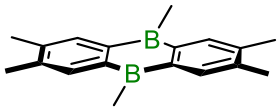
Compound 1



1

To a solution of 4,5-bis(trimethylsilyl)-1,2-dimethylbenzene (5.89 g, 23.5 mmol, 1.00 equiv.) in hexane (15 mL) in a thick-walled flask fitted with a Young valve, BBr_3 (13.0 g, 51.7 mmol, 4.91 mL, 2.20 equiv.) was slowly added via syringe while stirring. The reaction mixture was heated to 120 °C for 72 h. After cooling to rt, all volatiles were removed *in vacuo*. The crude product was washed with hexane (6 x 10 mL) and dried, yielding compound **1** as a yellow solid (2.33 g, 5.98 mmol, 51%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **1** in benzene at rt. ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 8.10 (s, 4H, Ar-C*H*), 2.39 (s, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2): δ = 144.2 (Ar-*C*Me), 140.7 (Ar-*C*B), 140.3 (Ar-*C*H), 20.3 (*C*H_3) ppm. ^{11}B NMR (160.5 MHz, CD_2Cl_2): δ = 62.5 (s, br) ppm. HRMS LIFDI (*m*/*z*) for $[C_{16}H_{16}B_2Br_2]^+ = [M]^+$: calc. 389.9779; found 389.9777.

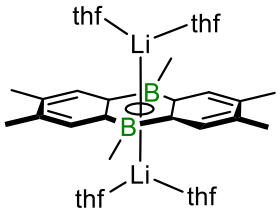
Compound 2



2

To a suspension of **1** (500 mg, 1.28 mmol, 1.00 equiv.) in toluene (25 mL) at –78 °C was slowly added a solution of MeMgBr in Et_2O (3.00 M, 2.69 mmol, 0.87 mL, 2.05 equiv.) via syringe while stirring. The reaction mixture was allowed to warm to rt and stirred for 16 h, generating a colourless precipitate. After filtration through celite the filtrate was dried *in vacuo*, yielding **2** as a colourless solid (323 mg, 1.24 mmol, 97%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **2** in benzene at rt. NMR data was collected in two different solvents (C_6D_6, d_8-THF) for comparative purposes with subsequent metal complexes. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 7.95 (s, 4H, Ar-C*H*), 2.11 (s, 12H, CCH_3), 1.47 (s, 6H, BCH_3) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 144.1 (Ar-*C*B), 141.0 (Ar-*C*Me), 137.8 (Ar-*C*H), 20.0 (C*C*H_3), 5.8 (B*C*H_3) ppm. ^{11}B{^{1}H} NMR (160.5 MHz, C_6D_6): δ = 67.2 (s, br) ppm. ^{1}H NMR (500.1 MHz, d_8-THF): δ = 7.78 (s, 4H, Ar-C*H*), 2.33 (s, 12H, CCH_3), 1.17 (s, 6H, BCH_3) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, d_8-THF): δ = 145.7 (Ar-*C*B), 139.8 (Ar-*C*Me), 136.9 (Ar-*C*H), 19.9 (C*C*H_3), 5.5 (B*C*H_3) ppm. ^{11}B{^{1}H} NMR (128.5 MHz, d_8-THF): δ = 58.3 (s, br) ppm. HRMS LIFDI (*m*/*z*) for $[C_{16}H_{16}B_2Br_2]^+ = [M]^+$: calc. 260.1902; found 260.1901.

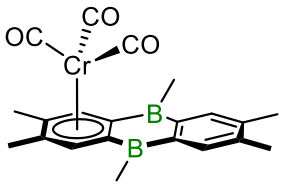
Complex 3



3

To a solution of **2** (10.0 mg, 38.5 µmol, 1.00 equiv.) in d_8-THF (0.5 mL) was added lithium sand (5.34 mg, 770 µmol, 20.0 equiv.). Upon stirring the mixture instantly turned pink, and after one minute, red. After stirring for 1 h at rt, and subsequent filtration, NMR-spectroscopic analysis revealed quantitative conversion to the dianion **3**. Single crystals suitable for X-ray diffraction were obtained by diffusion of hexane into a saturated solution of **3** in THF at –30 °C. ^{1}H NMR (500.1 MHz, d_8-THF): δ = 7.95 (s, 4H, Ar-C*H*), 2.29 (s, 12H, CH_3), 1.23 (s, 6H, BCH_3) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, d_8-THF): δ = 134.9 (Ar-*C*H), 133.7 (Ar-*C*B), 124.6 (Ar-*C*Me), 20.6 (C*C*H$_3$), –0.9 (B*C*H$_3$) ppm. ^{11}B NMR (160.5 MHz, d_8-THF): δ = 22.0 (s, br) ppm. ^{7}Li{^{1}H} NMR (194.4 MHz, d_8-THF): δ = –8.99 (s, br) ppm. UV-vis (THF): λ_{max} = 287, λ_2 = 333, λ_3 = 423, λ_4 = 481 (broad shoulder) nm. *Note: due to the instability of the isolated complex no further analytical data was collected.*

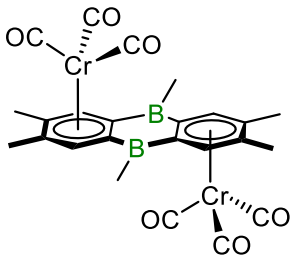
Complex 2-Cr



2-Cr

To a solution of **2** (40.0 mg, 154 µmol, 1.00 equiv.) in THF (4 mL) was added [(MeCN)$_3$Cr(CO)$_3$] (39.9 mg, 154 µmol, 1.00 equiv.) while stirring, upon which the mixture instantly turned red. After stirring for 16 h at rt all volatiles were removed *in vacuo*. The residue was extracted with toluene (8 mL, then 3 x 3 mL) and the combined extracts dried. The crude product was recrystallized from hexane (7 mL) at 4 °C and dried *in vacuo*, yielding **2-Cr** as a red solid (44.0 mg, 111 µmol, 72%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **2-Cr** in DME at rt. ^{1}H NMR (500.1 MHz, d_8-THF): δ = 7.69 (s, 2H, Ar-C*H*), 5.83 (s, 2H, Cr···Ar-C*H*), 2.31 (s, 6H, CCH_3), 2.28 (s, 6H, CCH_3), 0.91 (s, 6H, BCH_3) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, d_8-THF): δ = 234.5 (*C*O), 144.9 (Ar-*C*B), 138.9 (Ar-*C*Me), 136.6 (Ar-*C*H), 109.9 (Cr···Ar-*C*Me), 107.3 (Cr···Ar-*C*B), 103.0 (Cr···Ar-*C*H), 19.9 (C*C*H$_3$), 18.9 (Cr···C*C*H$_3$), 3.8 (B*C*H$_3$) ppm. ^{11}B{^{1}H} NMR (128.5 MHz, d_8-THF): δ = 46.3 (s, br) ppm. ^{11}B NMR (128.5 MHz, C_6D_6): δ = 64.9 (s, br) ppm. FT-IR (solid): $\tilde{\nu}$(CO) = 1955, 1895, 1859 cm^{-1}. UV-vis (THF): λ_{max} = 349 (broad), λ_2 = 287 (shoulder), λ_3 = 431 (broad), λ_4 = 497 (very broad) nm. HRMS ASAP (*m*/*z*) for $[C_{21}H_{23}B_2CrO_3]^+ = [M + H]^+$: calc. 397.1233; found 397.1231.

Complex 2-Cr$_2$

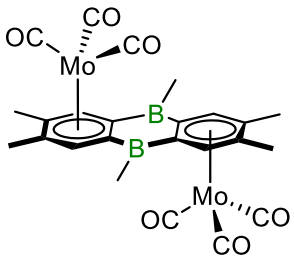


2-Cr$_2$

Route A) To a mixture of **2** (30.0 mg, 115 µmol, 1.00 equiv.) and [(MeCN)$_3$Cr(CO)$_3$] (62.6 mg, 242 µmol, 2.10 equiv.) in a thick-walled flask equipped with a Young valve was added hexane (4 mL), and the reaction mixture was stirred for 16 h at 100 °C. After cooling to rt all volatiles were removed *in vacuo*. The residue was extracted with toluene (10 mL, then 3 x 5 mL) and the combined extracts dried. The crude product was recrystallized from hexane (6 mL) at 4 °C and dried *in vacuo*, yielding **2-Cr$_2$** as a red solid (43.4 mg, 81.7 µmol, 71%). Single crystals suitable for X-ray diffraction were obtained by diffusion of hexane into a saturated solution of **2-Cr$_2$** in THF at –30 °C.

Route B) To a mixture of **2-Cr** (25.0 mg, 63.1 µmol, 1.00 equiv.) and [(MeCN)$_3$Cr(CO)$_3$] (18.0 mg, 69.4 µmol, 1.10 equiv.) was added THF (4 mL), and the reaction mixture was stirred for 16 h at rt. After cooling to rt all volatiles were removed *in vacuo*. The residue was extracted with toluene (8 mL, then 3 x 4 mL) and the combined extracts dried. The crude product was recrystallized from hexane (6 mL) at 4 °C and dried *in vacuo*, yielding **2-Cr$_2$** as a red solid (26.5 mg, 49.8 µmol, 79%). ^{1}H NMR (500.1 MHz, d$_8$-THF): δ = 5.86 (s, 4H, Ar-C*H*), 2.31 (s, 12H, CC*H*$_3$), 0.86 (s, 6H, BC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, d$_8$-THF): δ = 234.6 (*C*O), 111.4 (Ar-*C*Me), 104.9 (Ar-*C*B), 103.7 (Ar-*C*H), 18.8 (C*C*H$_3$), 3.9 (B*C*H$_3$) ppm. ^{11}B NMR (160.5 MHz, d$_8$-THF): δ = 49.1 (s, br) ppm. FT-IR (solid): $\tilde{\nu}$(CO) = 1938, 1859 cm^{-1}. UV-vis (THF): λ_{max} = 349 (broad), λ_2 = 287 (shoulder), λ_3 = 431 (broad), λ_4 = 497 (very broad) nm. HRMS ASAP (*m*/*z*) for [C$_{24}$H$_{23}$B$_2$Cr$_2$O$_6$]$^+$ = [M + H]$^+$: calc. 533.0485; found 533.0484.

Complex 2-Mo$_2$

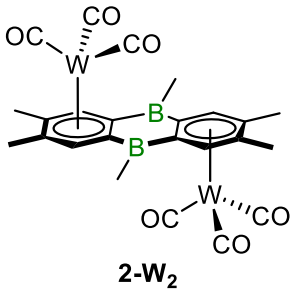


2-Mo$_2$

To a mixture of **2** (30.0 mg, 115 µmol, 1.00 equiv.) and [(MeCN)$_3$Mo(CO)$_3$] (73.4 mg, 242 µmol, 2.10 equiv.) in a thick-walled flask equipped with a Young valve was added hexane (4 mL), and the reaction mixture was stirred for 5 d at 100 °C. After cooling to rt, all volatiles were removed *in vacuo*. The residue was extracted with toluene (20 mL, then 3 x 7 mL) and the combined extracts dried. The crude product was washed with hexane (4 x 4 mL) and dried *in vacuo*, yielding **2-Mo$_2$** as a red solid (31.4 mg, 50.6 µmol, 44%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **2-Mo$_2$** in THF at rt. ^{1}H NMR (500.1 MHz, CD$_2$Cl$_2$): δ = 6.06 (s, 4H, Ar-C*H*), 2.36 (s, 12H, CC*H*$_3$), 0.91 (s, 6H, BC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, CD$_2$Cl$_2$): δ = 221.8 (*C*O), 113.9 (Ar-*C*Me), 104.7 (Ar-*C*H),

101.0 (Ar-*C*B), 19.6 (C*C*H$_3$), 1.5 (B*C*H$_3$) ppm. ^{11}B NMR (160.5 MHz, CD_2Cl_2): δ = 59.1 (s, br) ppm. ^{11}B NMR (128.5 MHz, d$_8$-THF): δ = 45.0 (s, br) ppm. FT-IR (solid): $\tilde{\nu}$(CO) = 1944, 1874 cm^{-1}. UV-vis (THF): λ_{max} = 336, λ_2 = 287 (shoulder), λ_3 = 417, λ_4 = 464 (broad shoulder) nm. HRMS ASAP (*m*/*z*) for $[C_{24}H_{23}B_2Mo_2O_6]^+ = [M + H]^+$: calc. 620.9797; found 620.9780.

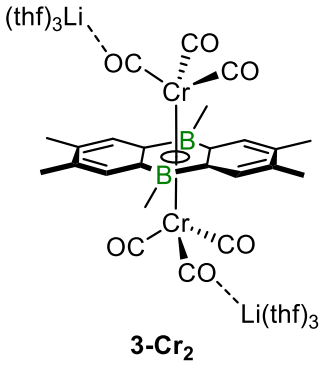
Complex 2-W$_2$



2-W$_2$

To a mixture of **2** (20.0 mg, 76.9 µmol, 1.00 equiv.) and [(MeCN)$_3$W(CO)$_3$] (63.0 mg, 161 µmol, 2.10 equiv.) in a thick-walled flask equipped with a Young valve was added hexane (5 mL), and the reaction mixture was stirred for 5 d at 100 °C. After cooling to rt, all volatiles were removed *in vacuo*. The residue was extracted with THF (15 mL, then 3 x 5 mL) and the combined extracts dried. The crude product was recrystallized from hexane (7 mL) at 4 °C and dried *in vacuo*, yielding **2-W$_2$** as a red solid (39.0 mg, 49.0 µmol, 64%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **2-W$_2$** in THF at rt. ^{1}H NMR (500.1 MHz, d$_8$-THF): δ = 5.99 (s, 4H, Ar-C*H*), 2.45 (s, 12H, CC*H*$_3$), 0.74 (s, 6H, BC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, d$_8$-THF): δ = 212.4 (*C*O), 110.5 (Ar-*C*Me), 103.8 (Ar-*C*B), 101.3 (Ar-*C*H), 18.7 (C*C*H$_3$), 3.2 (B*C*H$_3$) ppm. ^{11}B{^{1}H} NMR (160.5 MHz, d$_8$-THF): δ = 44.4 (s, br) ppm. FT-IR (solid): $\tilde{\nu}$(CO) = 1936, 1859 cm^{-1}. UV-vis (THF): λ_{max} = 334, λ_2 = 280, λ_3 = 358 (shoulder), λ_4 = 422 (shoulder), λ_5 = 469 (very broad) nm. HRMS ASAP (*m*/*z*) for $[C_{24}H_{23}B_2W_2O_6]^+ = [M + H]^+$: calc. 797.0686; found 797.0701.

Complex 3-Cr$_2$

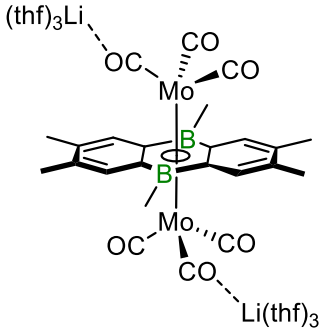


3-Cr$_2$

To a freshly prepared solution of **3** (31.5 mg, 115 µmol, 1.00 equiv.) in THF (3 mL) was added [(MeCN)$_3$Cr(CO)$_3$] (59.6 mg, 230 µmol, 2.00 equiv.) while stirring, upon which a dark suspension immediately formed. After filtration through celite and extraction of the solid residue with THF (3 x 2 mL), the combined filtrates were dried *in vacuo*. The crude product was washed with Et$_2$O (4 x 2 mL), benzene (6 x 2 mL), hexane (3 x 2 mL), and again with Et$_2$O (4 x 2 mL). Drying *in vacuo* yielded **3-Cr$_2$** as an orange solid (13.0 mg, 15.6 µmol, 14%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **3-Cr$_2$** in THF at rt. ^{1}H NMR (500.1 MHz, d$_8$-THF): δ = 7.44 (s, 4H, Ar-C*H*), 3.63-3.60 (m, 16H, thf-C*H*$_2$), 2.06 (s, 12H, CC*H*$_3$), 1.79-1.76 (m, 16H, thf-C*H*$_2$), 1.62 (s, 6H, BC*H*$_3$)

ppm. $^{13}C\{^{1}H, ^{11}B\}$ NMR (150.9 MHz, d_8-THF): δ = 242.0 (*C*O), 136.1 (Ar-*C*H), 128.7 (Ar-*C*Me), 101.2 (Ar-*C*B), 68.0 (thf-*C*H_2), 26.2 (thf-*C*H_2), 20.1 (C*C*H_3), 0.0 (B*C*H_3) ppm. $^{11}B\{^{1}H\}$ NMR (160.5 MHz, d_8-THF): δ = 11.9 (s, br) ppm. $^{7}Li\{^{1}H\}$ NMR (233.3 MHz, d_8-THF): δ = –0.98 (s) ppm. FT-IR (solid): $\tilde{\nu}$(CO) = 1935, 1881, 1792, 1773, 1713 cm^{-1}. UV-vis (THF): λ_{max} = 308, λ_2 = 290 (shoulder), λ_3 = 349 (shoulder), λ_4 = 418 (very broad) nm. HRMS ASAP (*m*/*z*) for $[C_{24}H_{22}B_2Cr_2O_6]^-$ = $[M]^-$: calc. 532.0418; found 532.0422.

Complex 3-Mo$_2$



3-Mo$_2$

To a freshly prepared solution of **3** (31.5 mg, 115 µmol, 1.00 equiv.) in THF (3 mL) was added $[(MeCN)_3Mo(CO)_3]$ (69.7 mg, 230 µmol, 2.00 equiv.) while stirring, upon which a dark suspension immediately formed. After filtration through celite and extraction of the solid residue with THF (3 x 2 mL), the combined filtrates were dried *in vacuo*. The crude product was washed with Et_2O (4 x 2 mL), benzene (8 x 3 mL), pentane (3 x 2 mL), and cold THF (4 x 2 mL, –30 °C). Drying *in vacuo* yielded **3-Mo$_2$** as a yellow solid (36.1 mg, 33.9 µmol, 29%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **3-Mo$_2$** in THF at rt. ^{1}H NMR (600.2 MHz, d_8-THF): δ = 7.45 (s, 4H, Ar-C*H*), 3.63-3.61 (m, 24H, thf-CH_2), 2.09 (s, 12H, CCH_3), 1.79-1.76 (m, 24H, thf-CH_2), 1.51 (s, 6H, BCH_3) ppm. $^{13}C\{^{1}H, ^{11}B\}$ NMR (150.9 MHz, d_8-THF): δ = 234.6 (*C*O), 135.4 (Ar-*C*H), 128.0 (Ar-*C*Me), 105.0 (Ar-*C*B), 68.0 (thf-*C*H_2), 26.2 (thf-*C*H_2), 20.1 (C*C*H_3), –0.2 (B*C*H_3) ppm. $^{11}B\{^{1}H\}$ NMR (160.5 MHz, d_8-THF): δ = 12.0 (s, br) ppm. $^{7}Li\{^{1}H\}$ NMR (194.4 MHz, d_8-THF): δ = –0.86 (s) ppm. FT-IR (solid): $\tilde{\nu}$(CO) = 1928, 1888, 1796, 1779, 1725, 1711 cm^{-1}. UV-vis (THF): λ_{max} = 296, λ_2 = 344 (broad tailing) nm. HRMS ASAP (*m*/*z*) for $[C_{24}H_{22}B_2Mo_2O_6]^-$ = $[M]^-$: calc. 619.9713; found 619.9746.

NMR spectra of isolated compounds

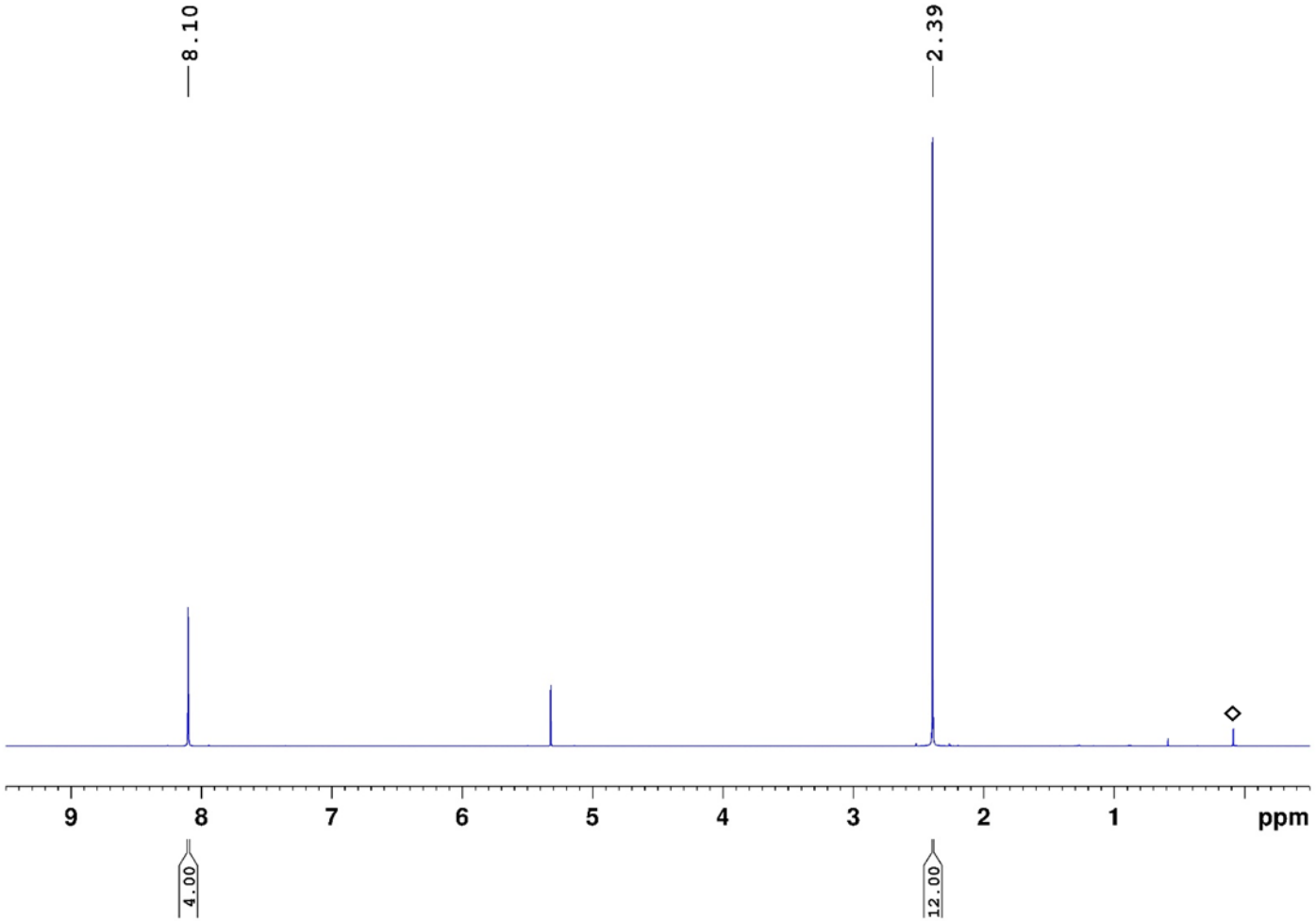


Figure S1. ^{1}H NMR spectrum of **1** in CD_2Cl_2. The resonance marked ◇ belongs to silicon grease.

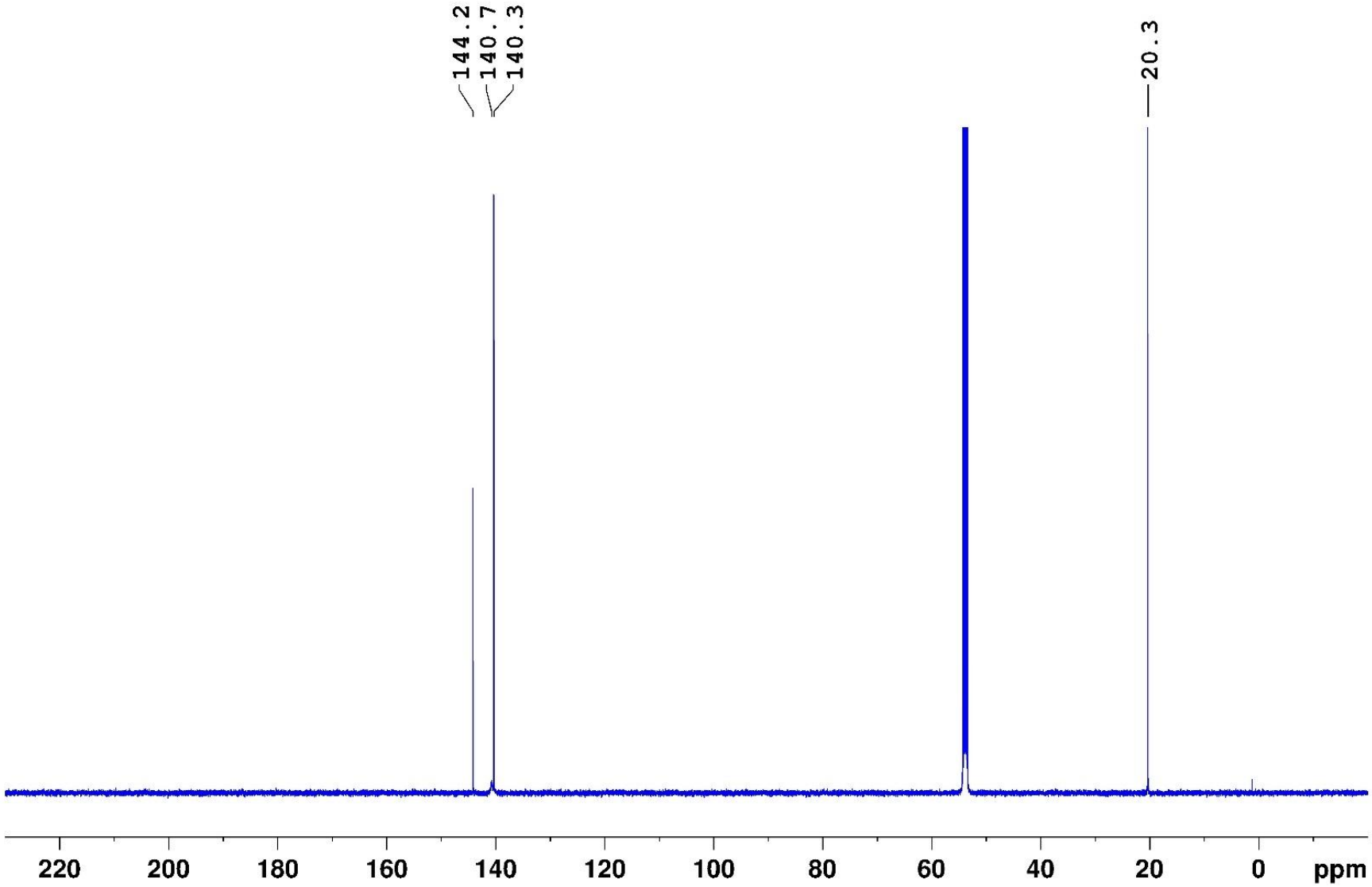


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in CD_2Cl_2.

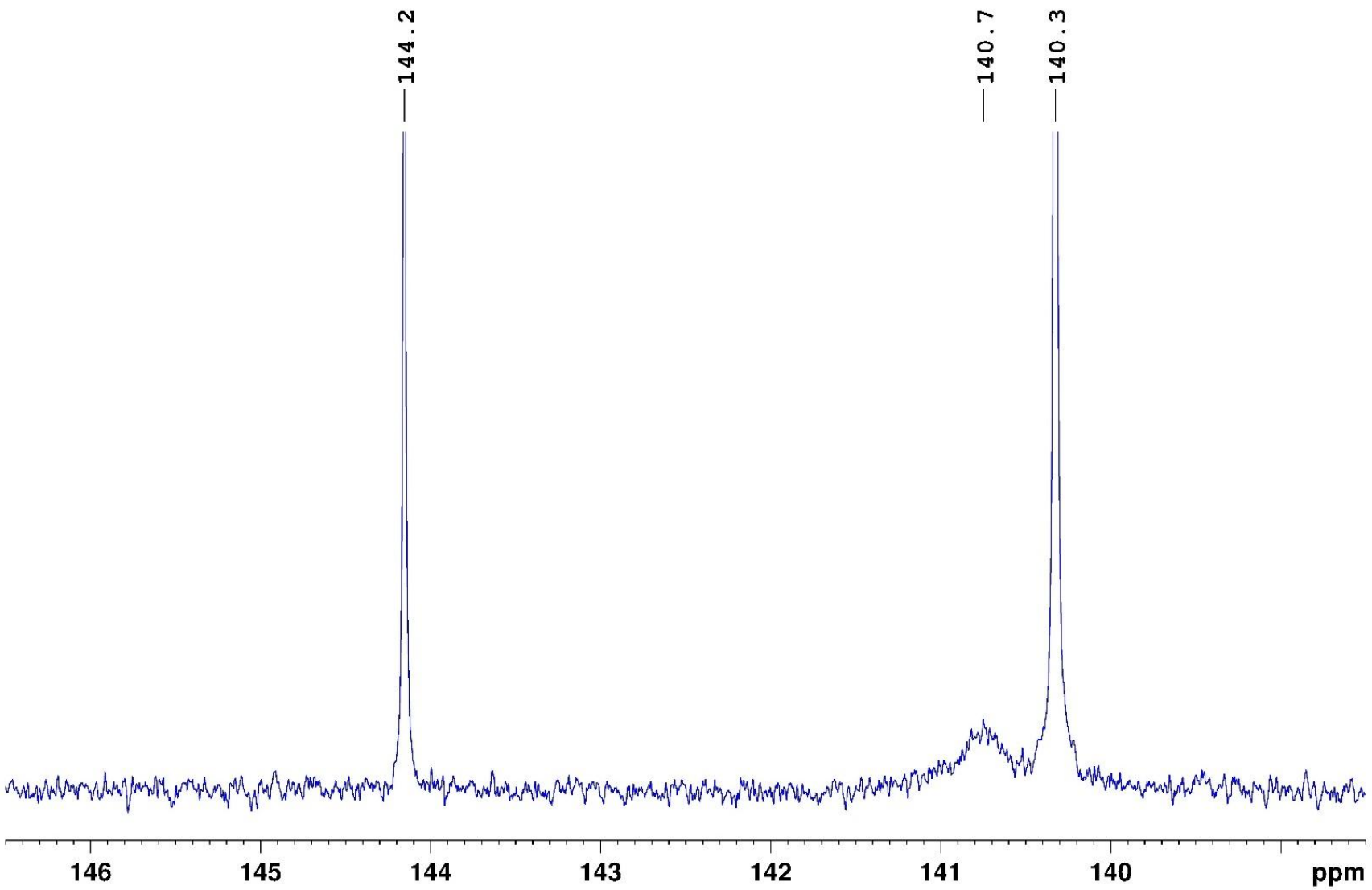


Figure S3. Aromatic region of the $^{13}C\{^{1}H\}$ NMR spectrum of **1** in CD_2Cl_2.

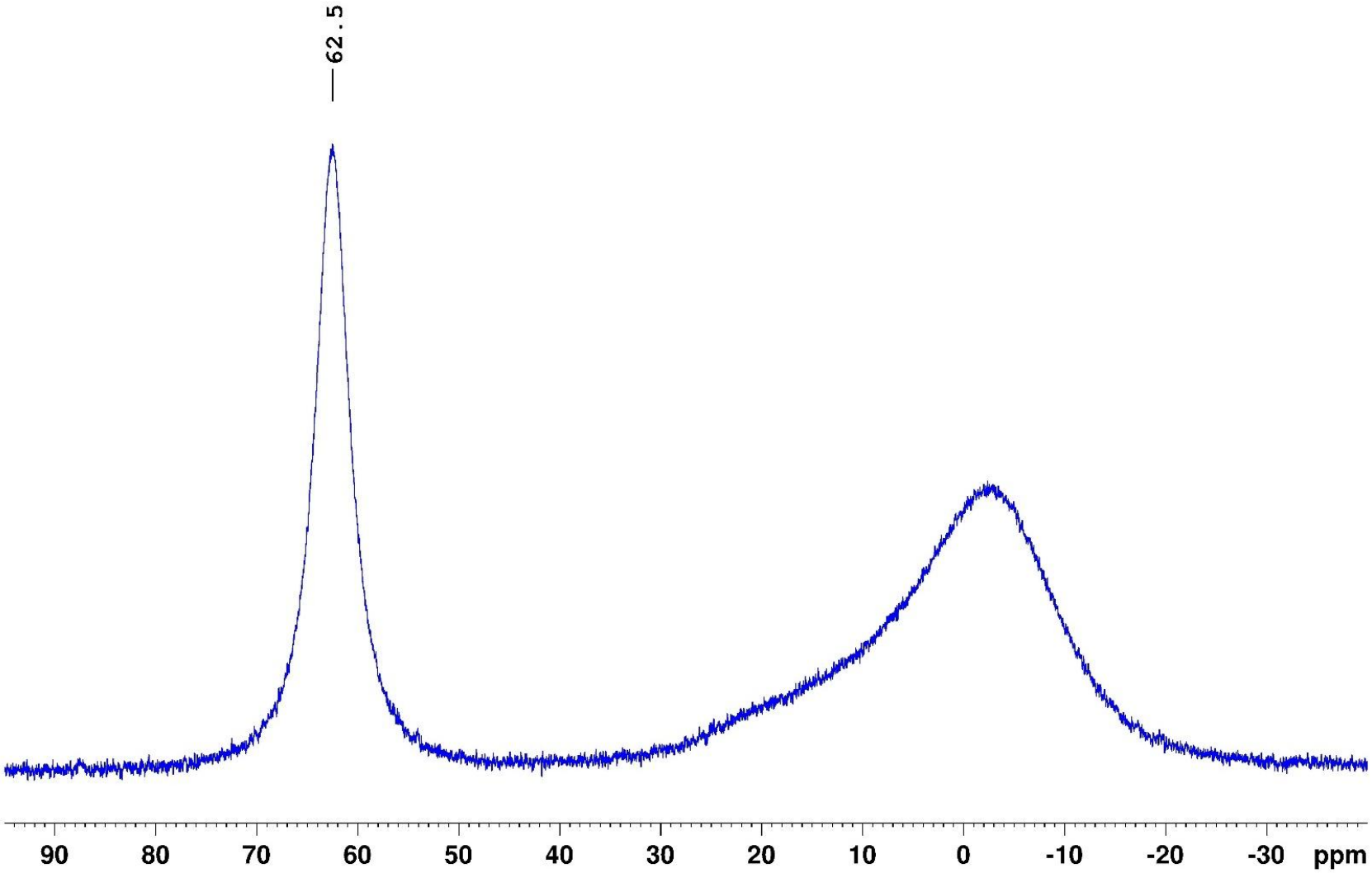


Figure S4. ^{11}B NMR spectrum of **1** in CD_2Cl_2.

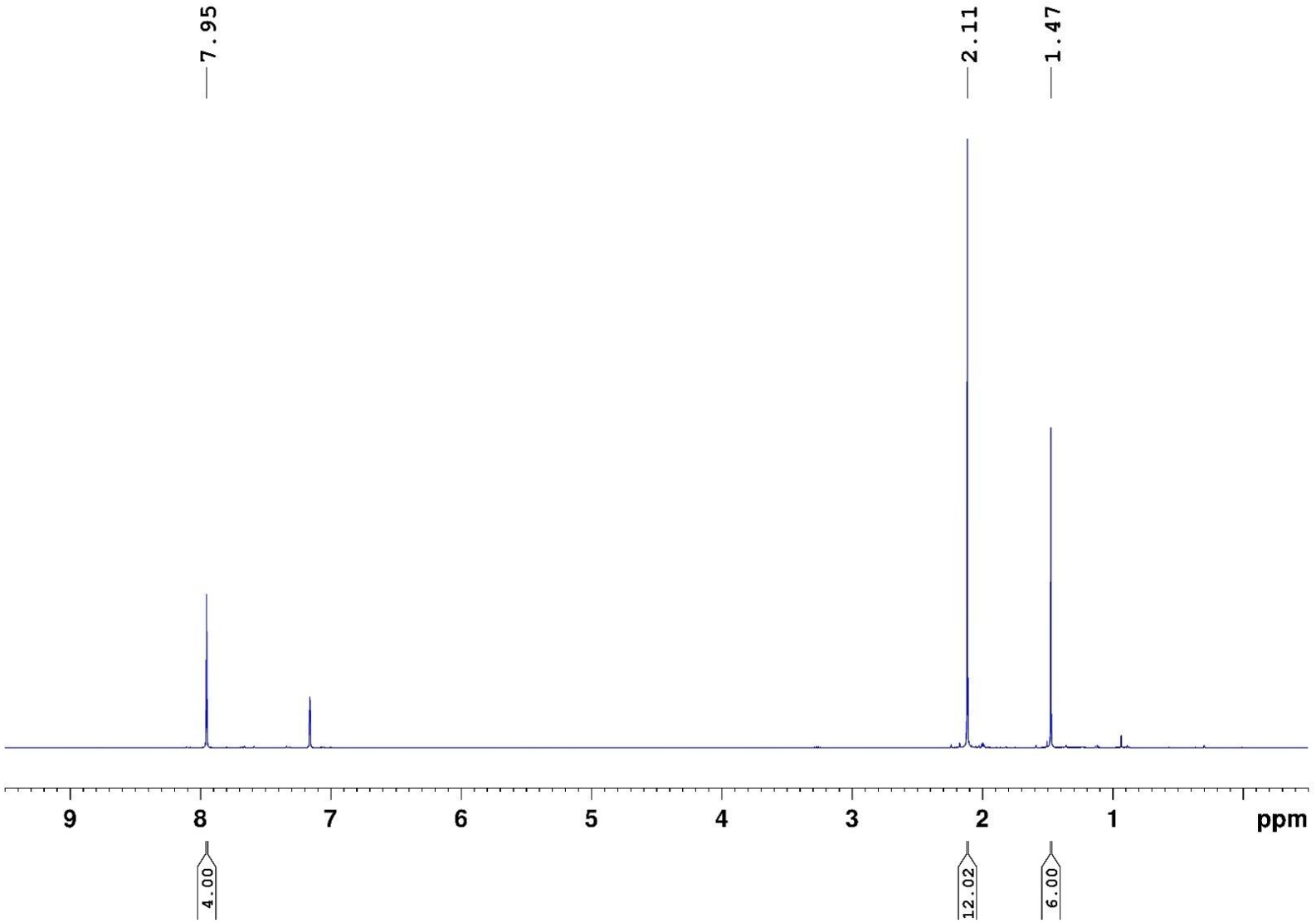


Figure S5. ^{1}H NMR spectrum of **2** in C_6D_6.

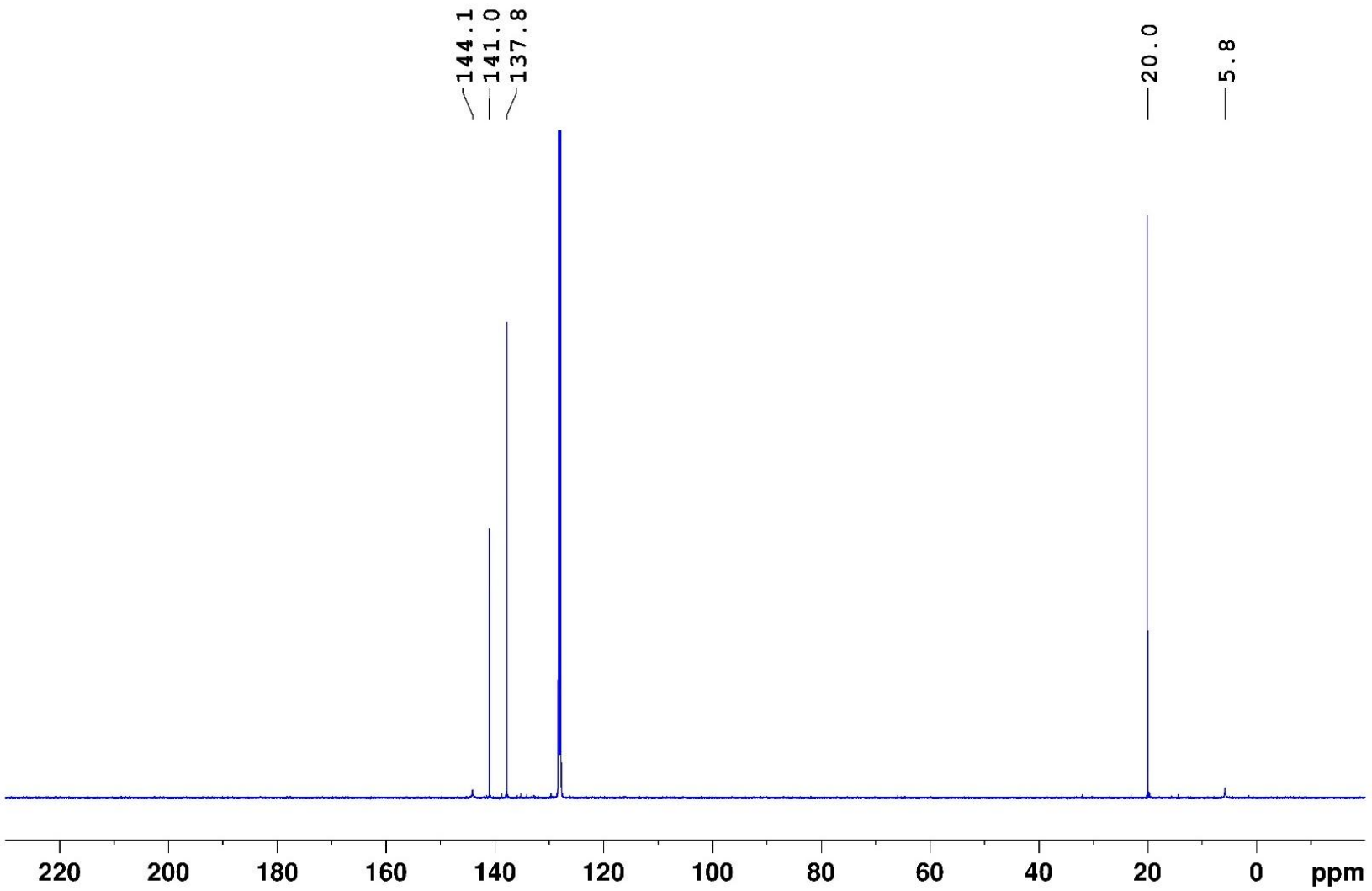


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6.

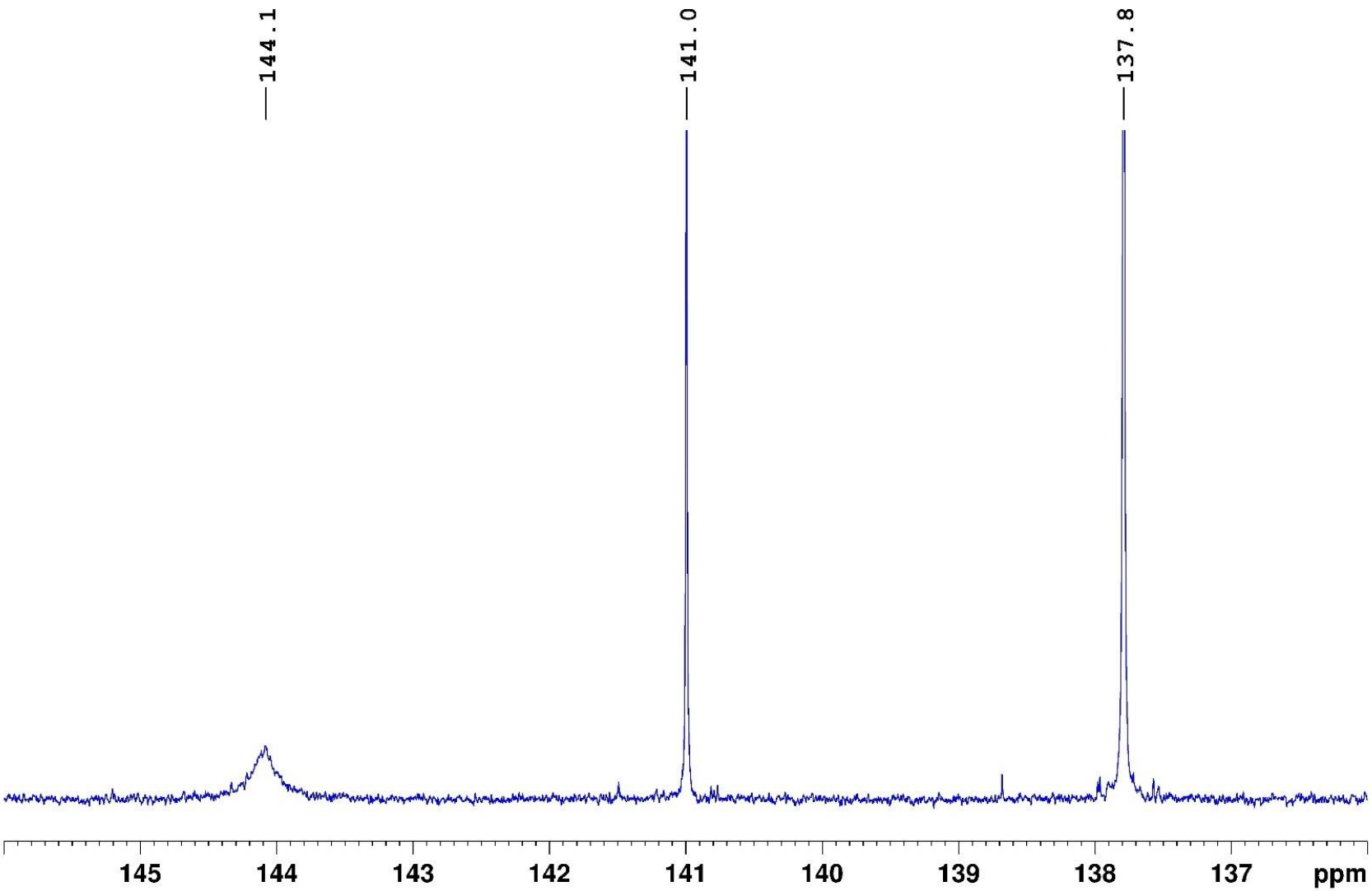


Figure S7. Aromatic region of the $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6.

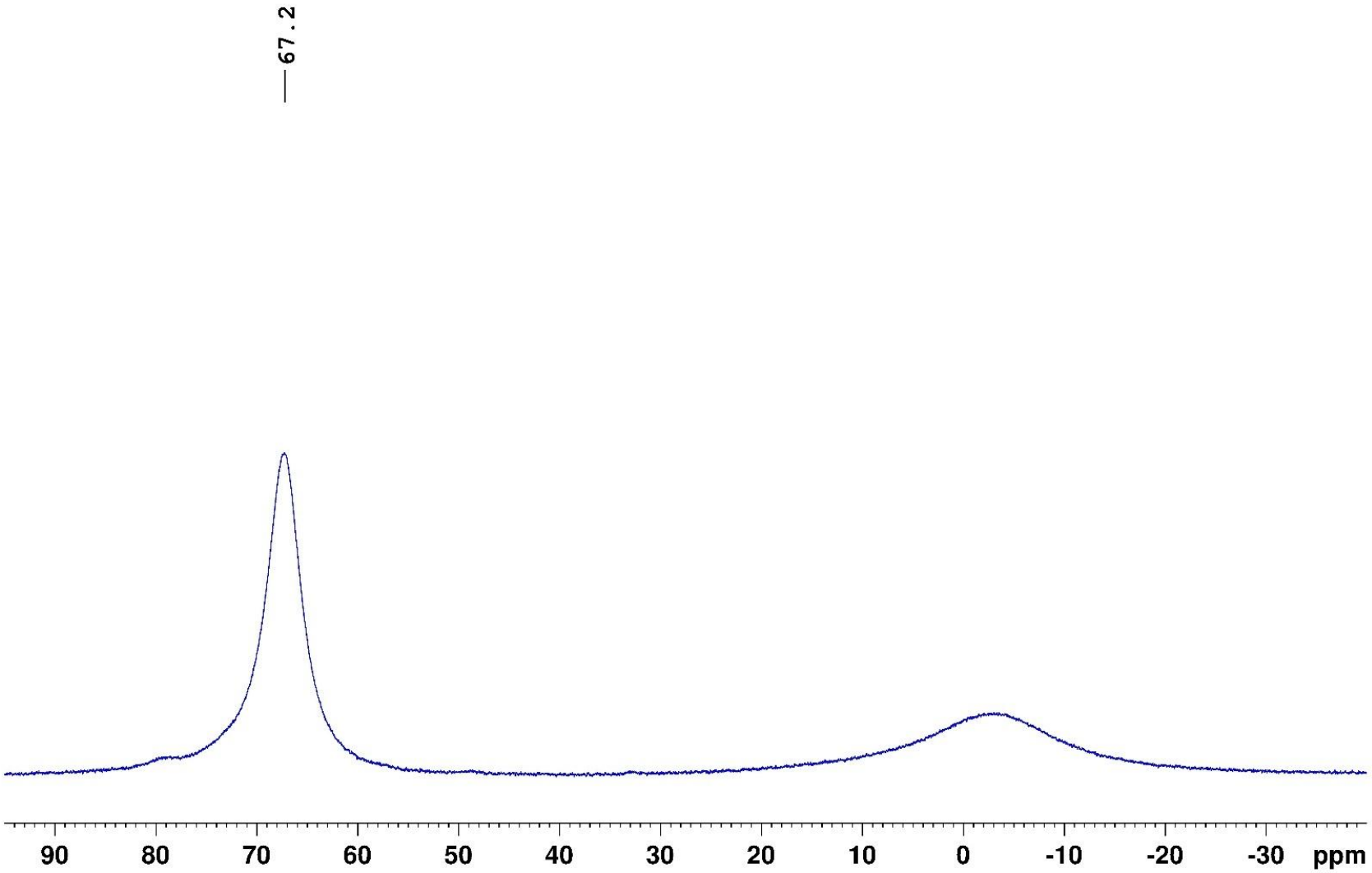


Figure S8. $^{11}B\{^{1}H\}$ NMR spectrum of **2** in C_6D_6.

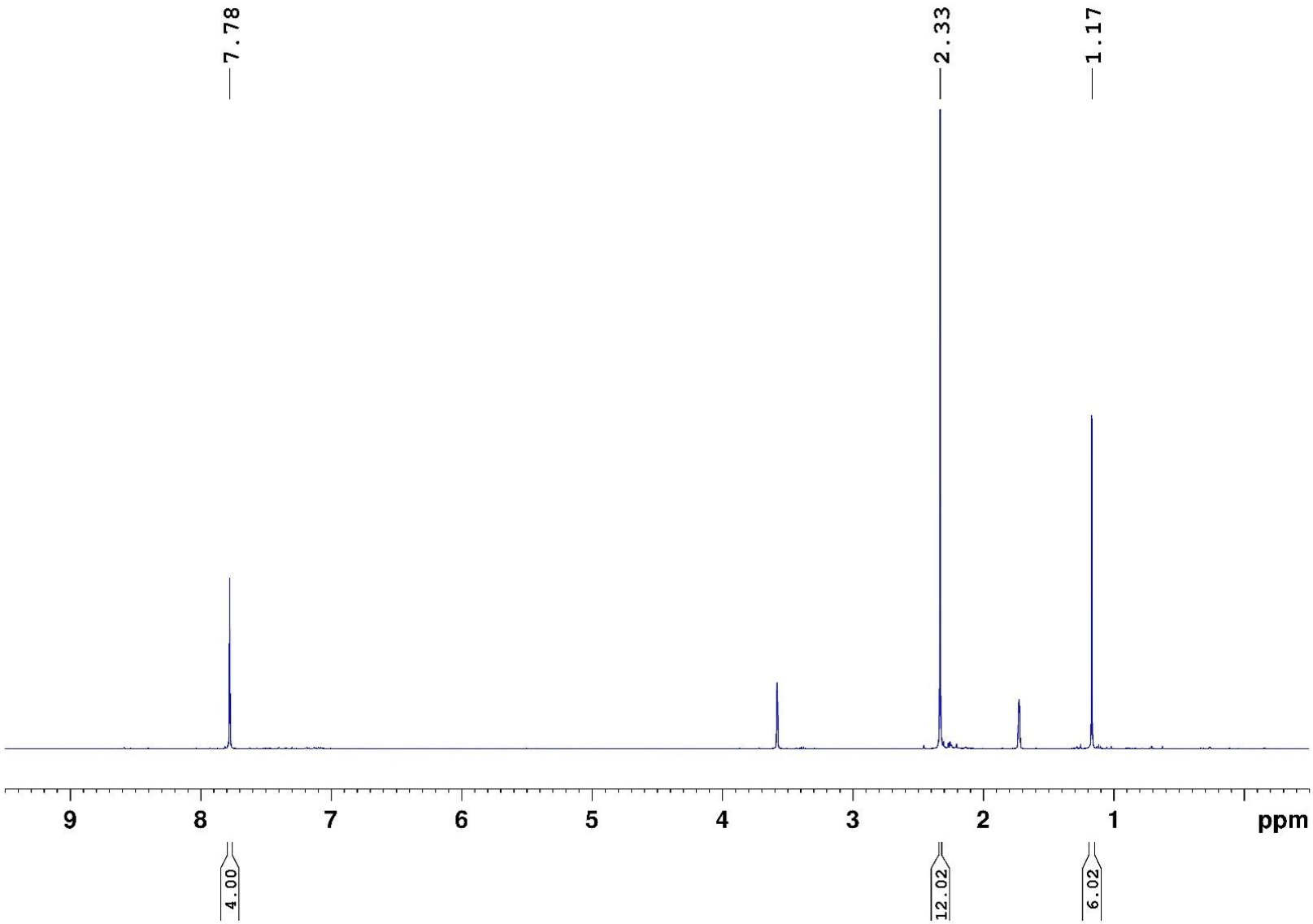


Figure S9. ^{1}H NMR spectrum of **2** in d_8-THF.

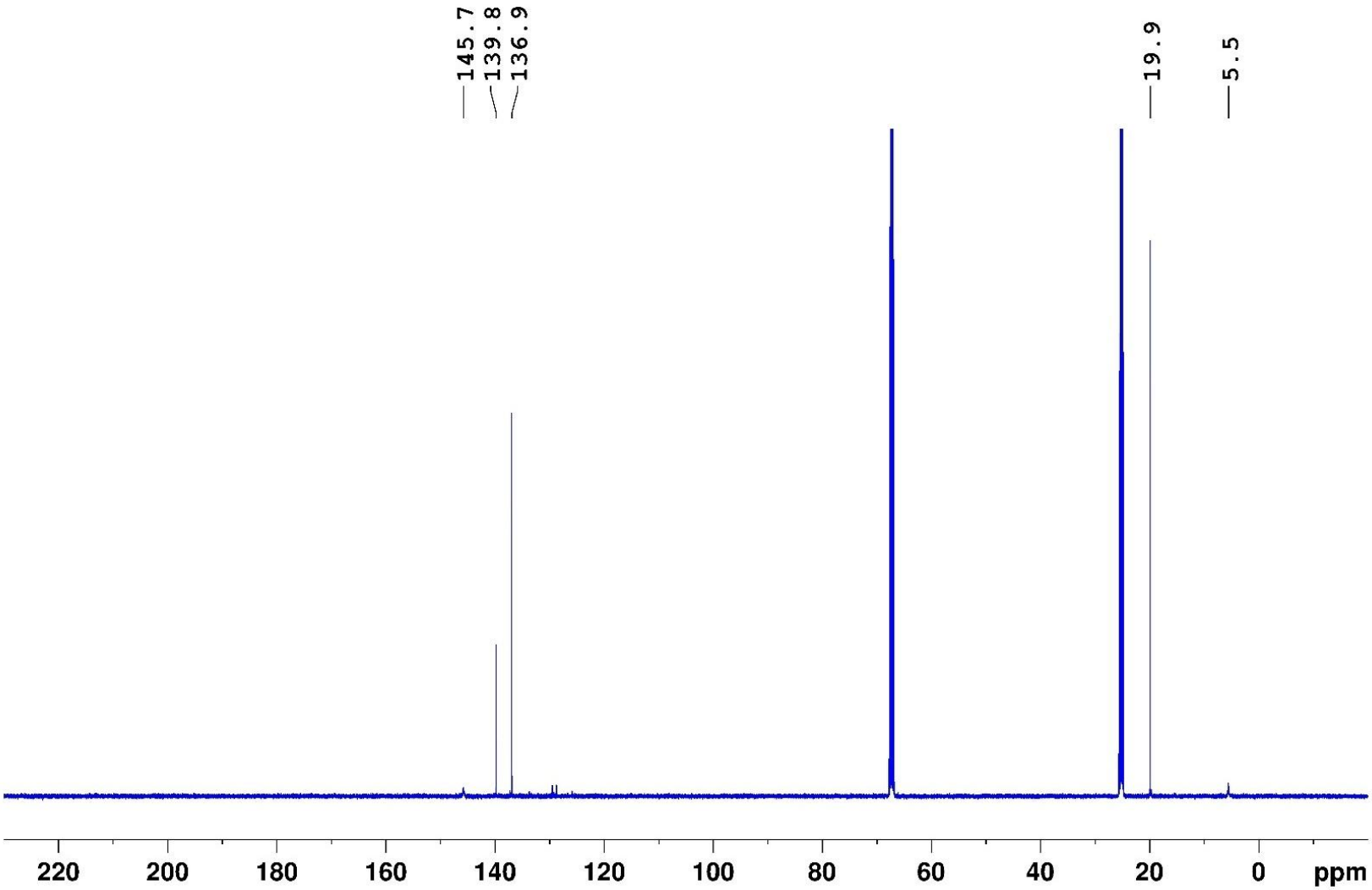


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in d_8-THF.

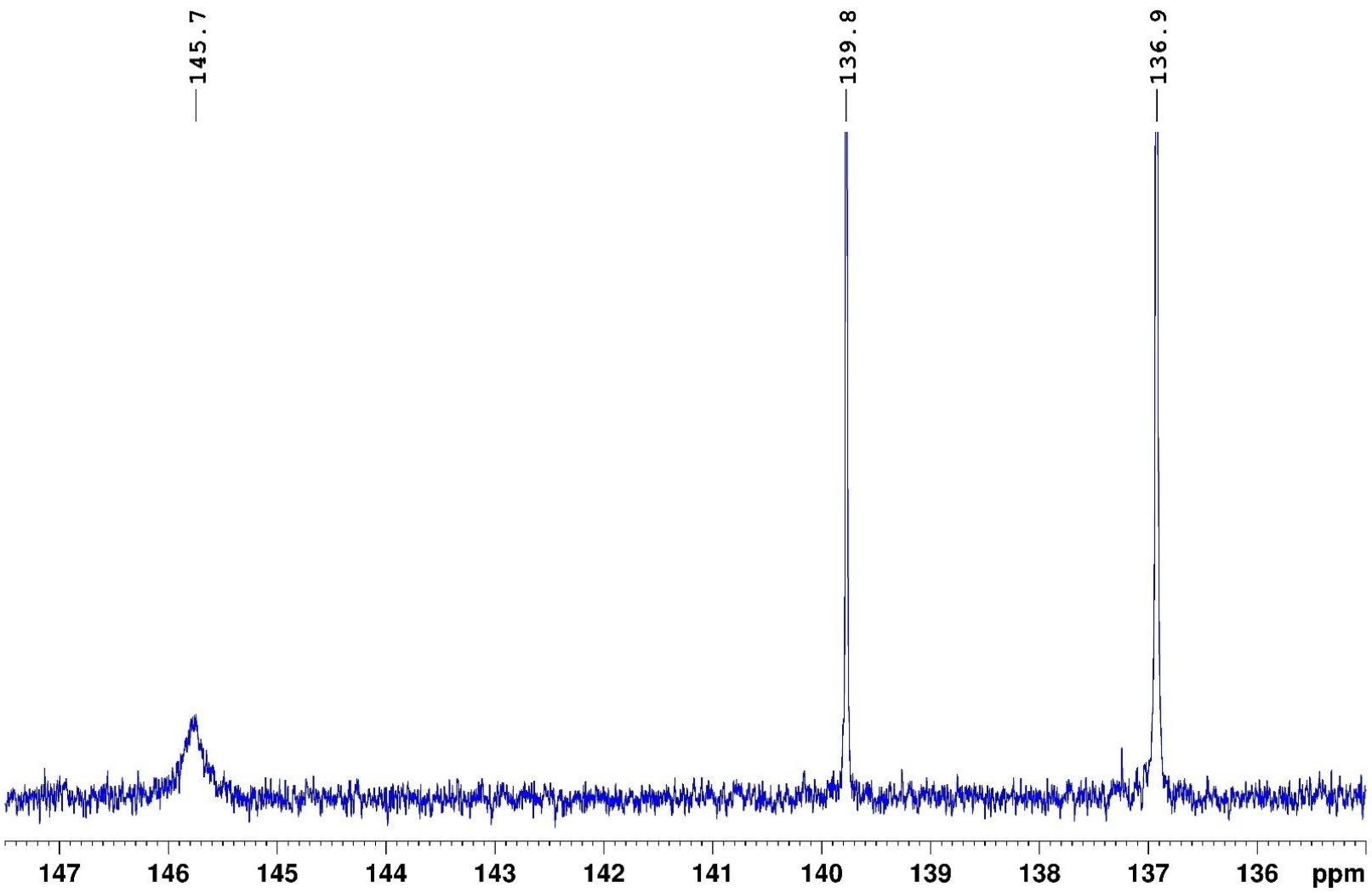


Figure S11. Aromatic region of the $^{13}C\{^{1}H\}$ NMR spectrum of **2** in d_8-THF.

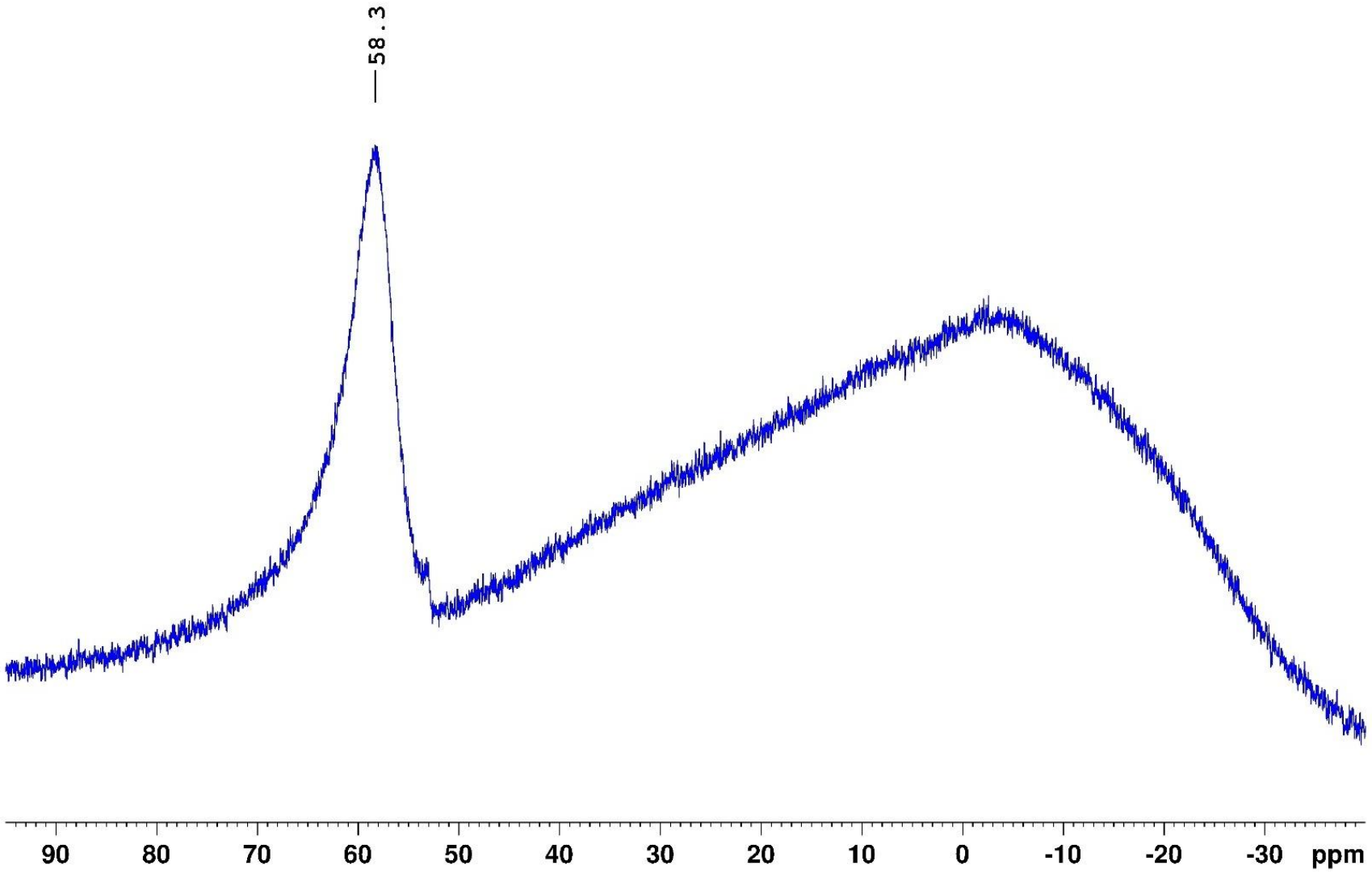


Figure S12. $^{11}B\{^{1}H\}$ NMR spectrum of **2** in d_8-THF.

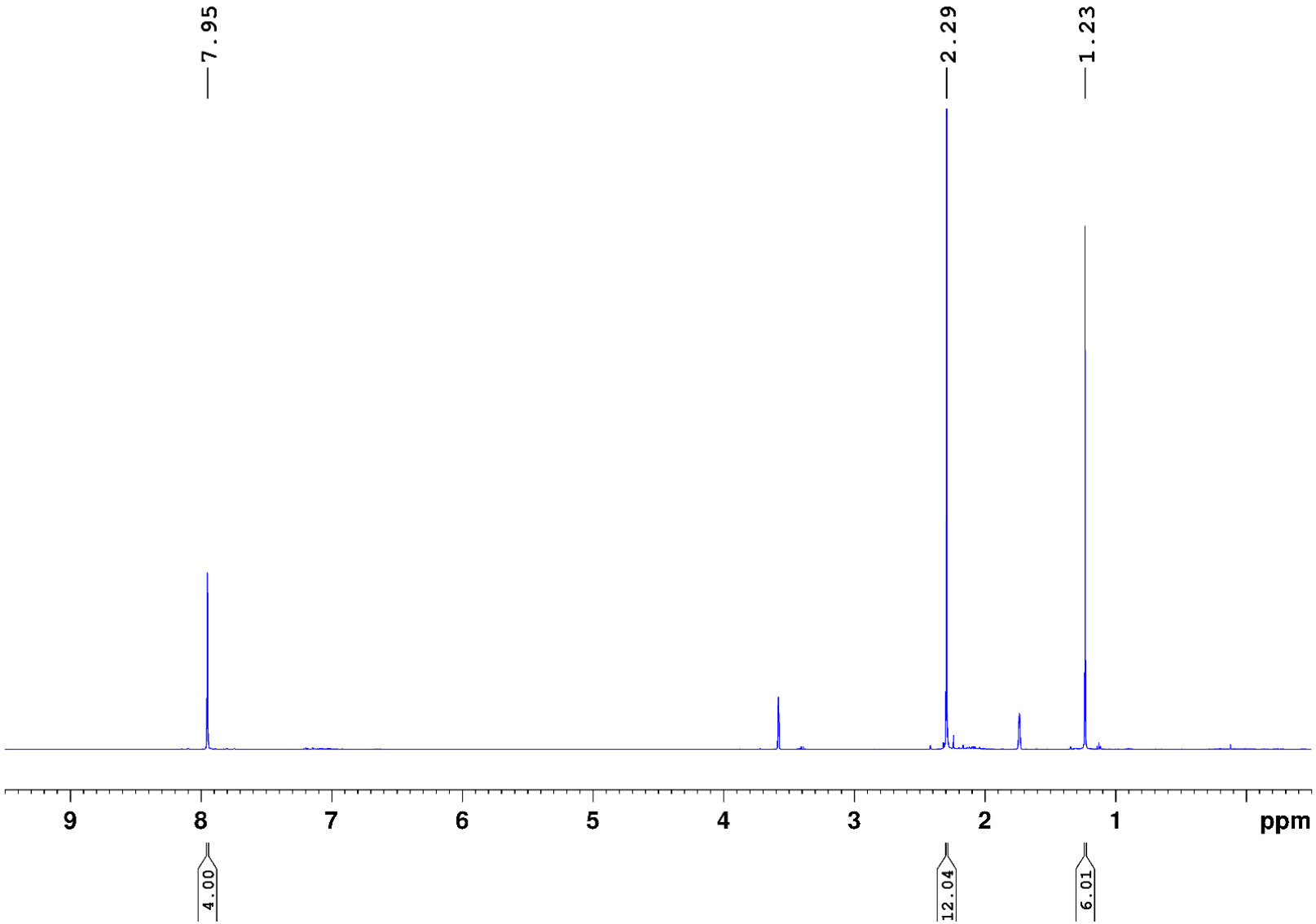


Figure S13. ^{1}H NMR spectrum of **3** in d_8-THF.

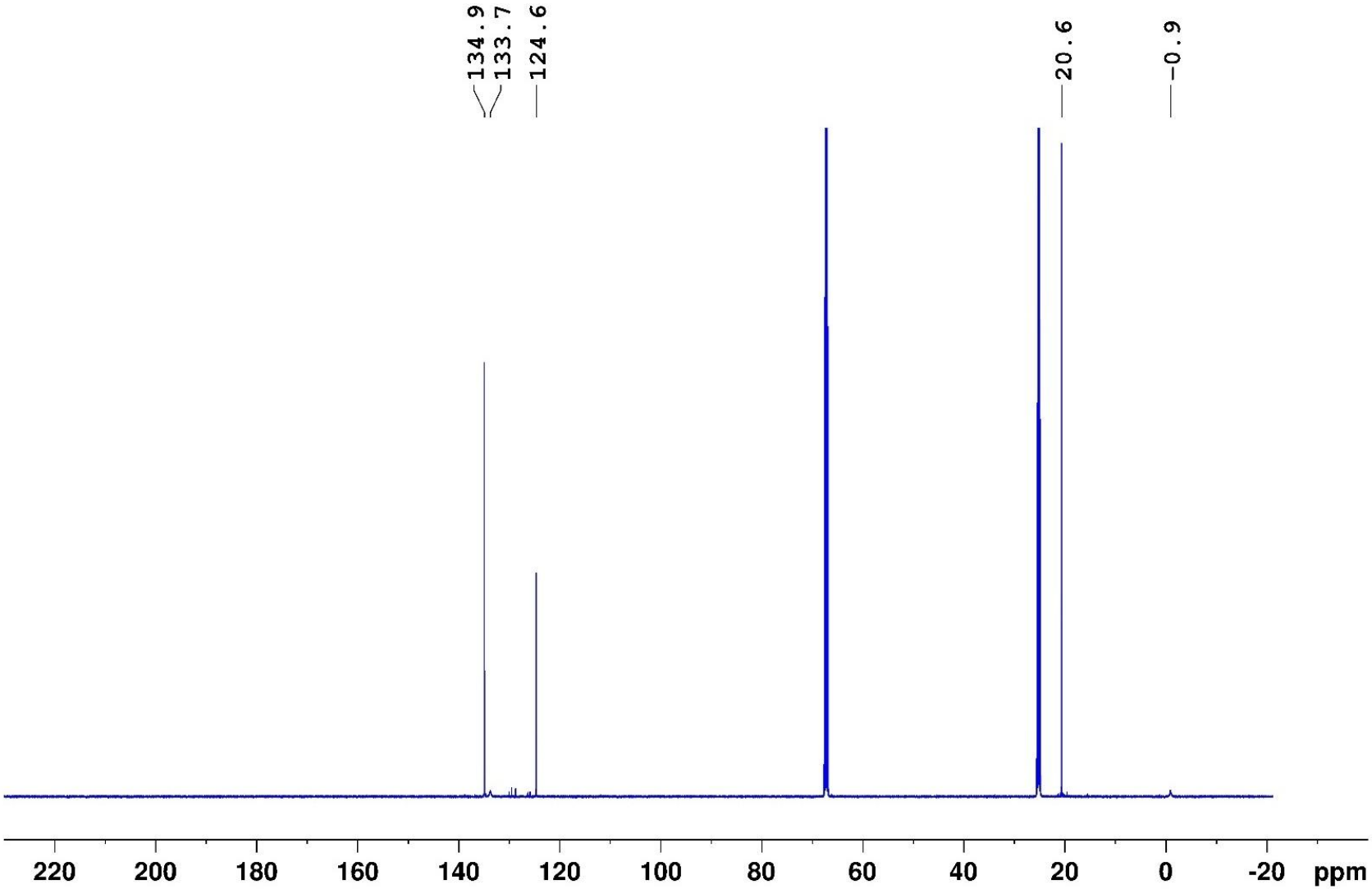


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in d_8-THF.

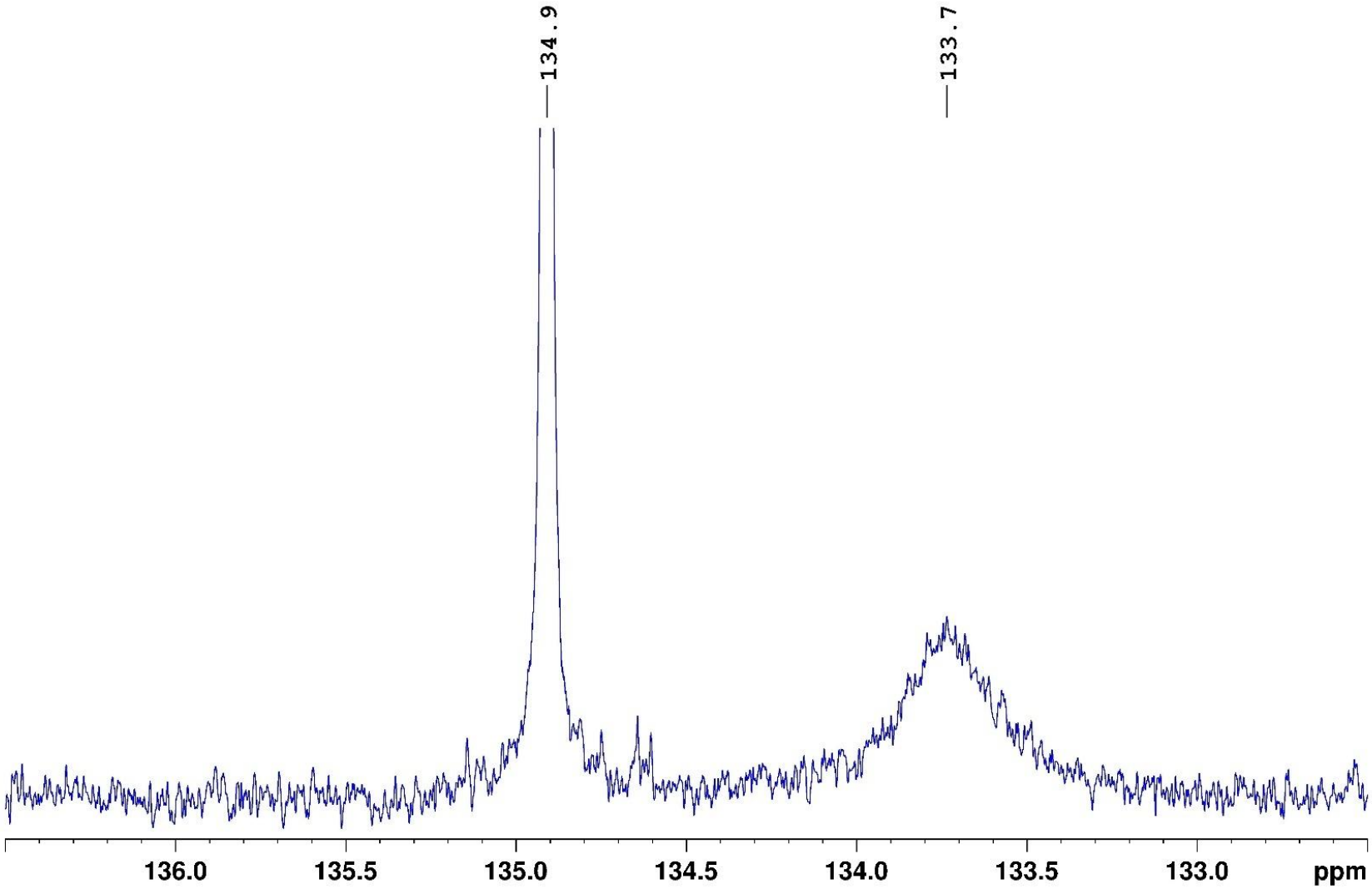


Figure S15. Aromatic region of the $^{13}C\{^{1}H\}$ NMR spectrum of **3** in d_8-THF.

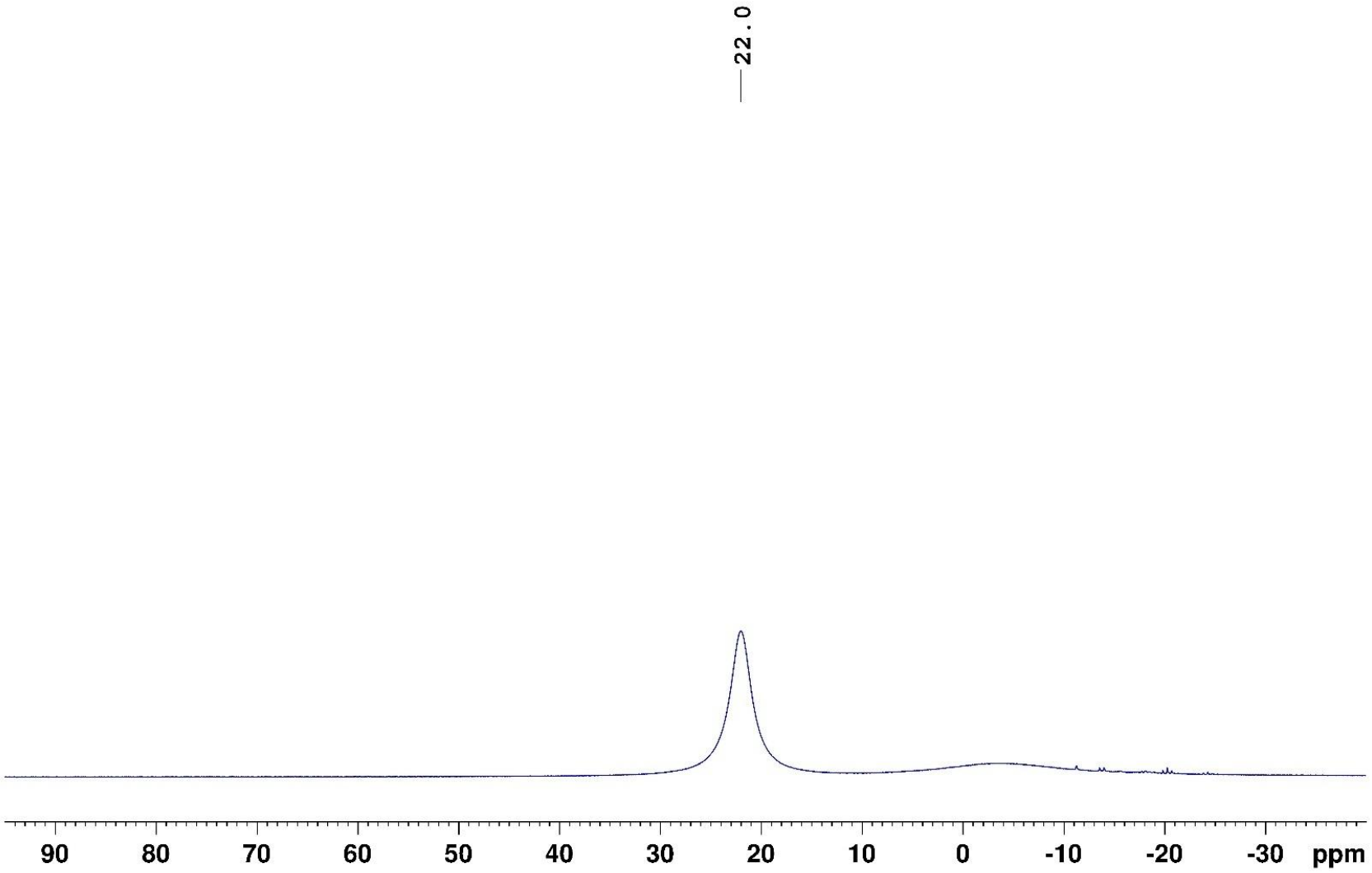


Figure S16. ^{11}B NMR spectrum of **3** in d_8-THF.

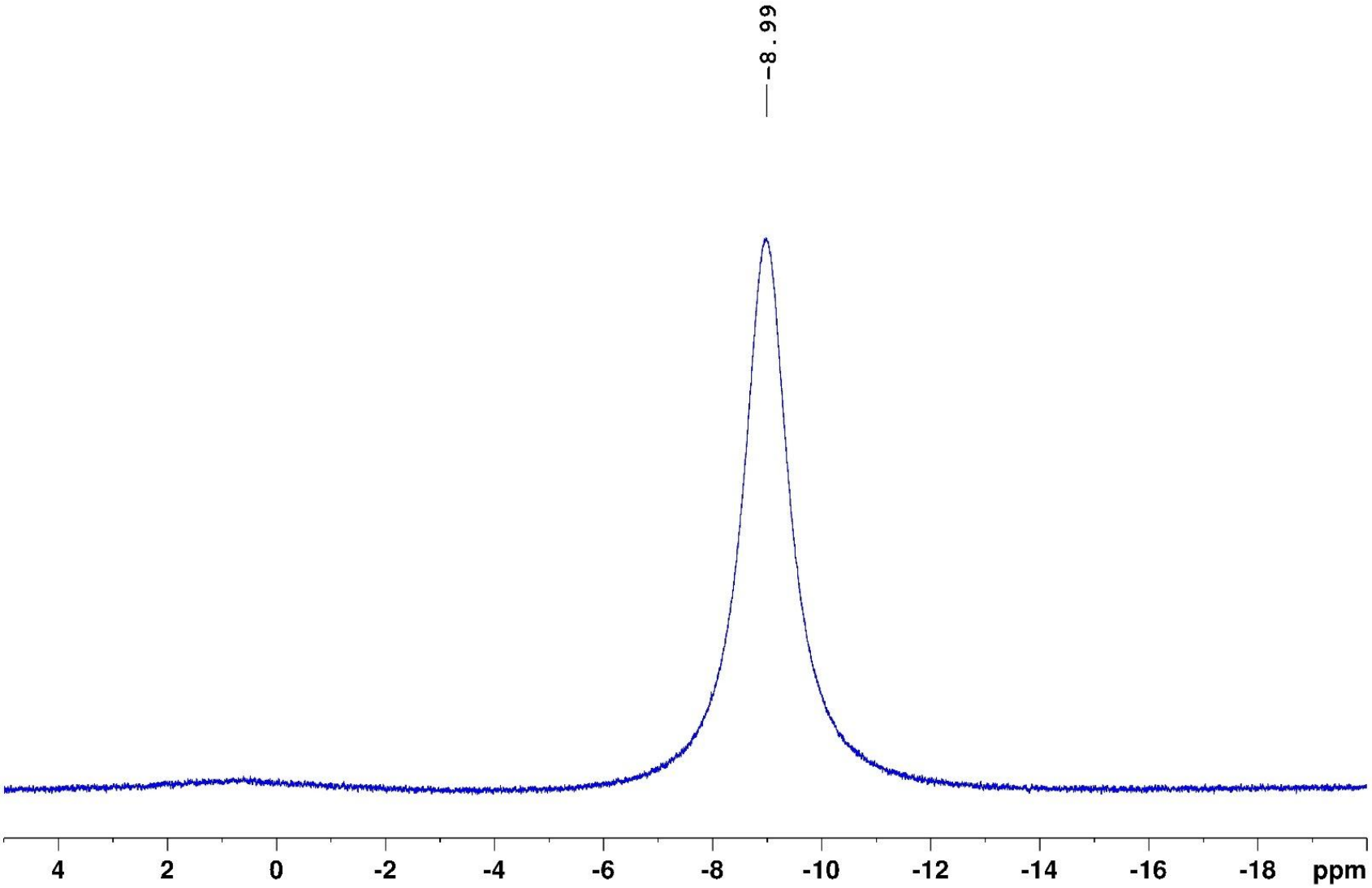


Figure S17. $^{7}Li\{^{1}H\}$ NMR spectrum of **3** in d_8-THF.

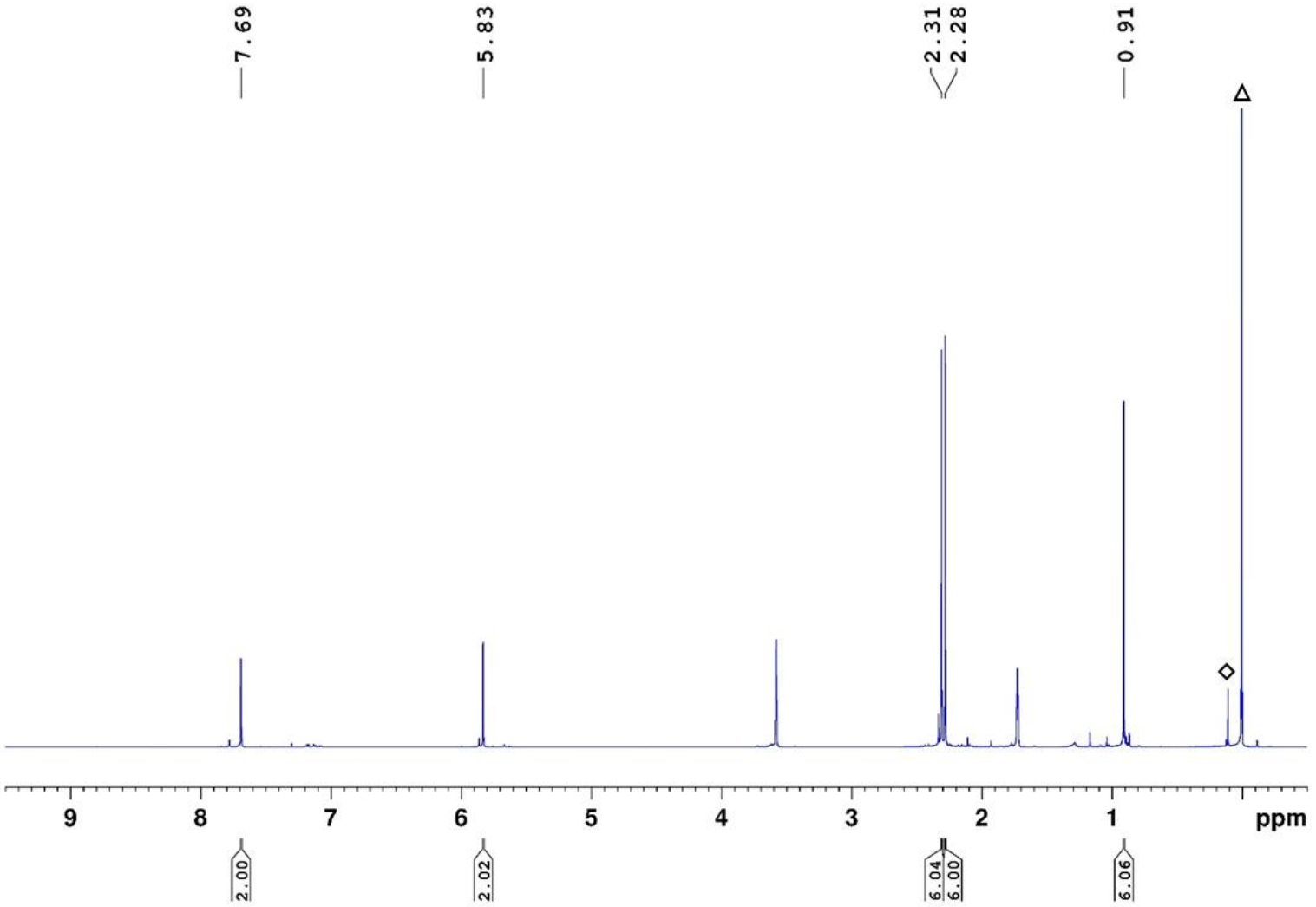


Figure S18. ^{1}H NMR spectrum of **2-Cr** in d_8-THF. The resonance marked ◇ belongs to silicon grease, that marked Δ to the internal standard tetramethylsilane (TMS).

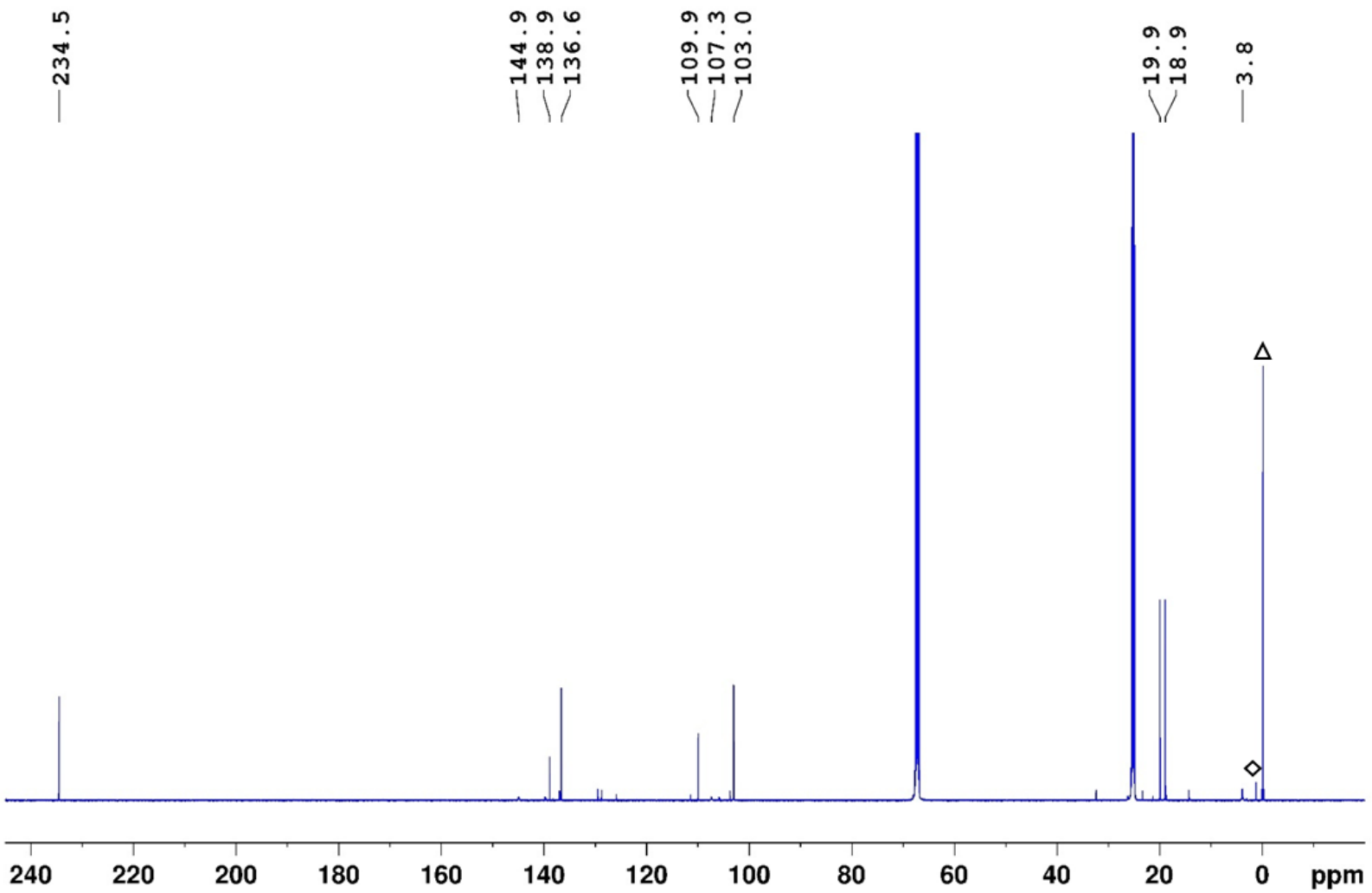


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **2-Cr** in d_8-THF. The resonance marked ◇ belongs to silicon grease, that marked △ to the internal standard TMS.

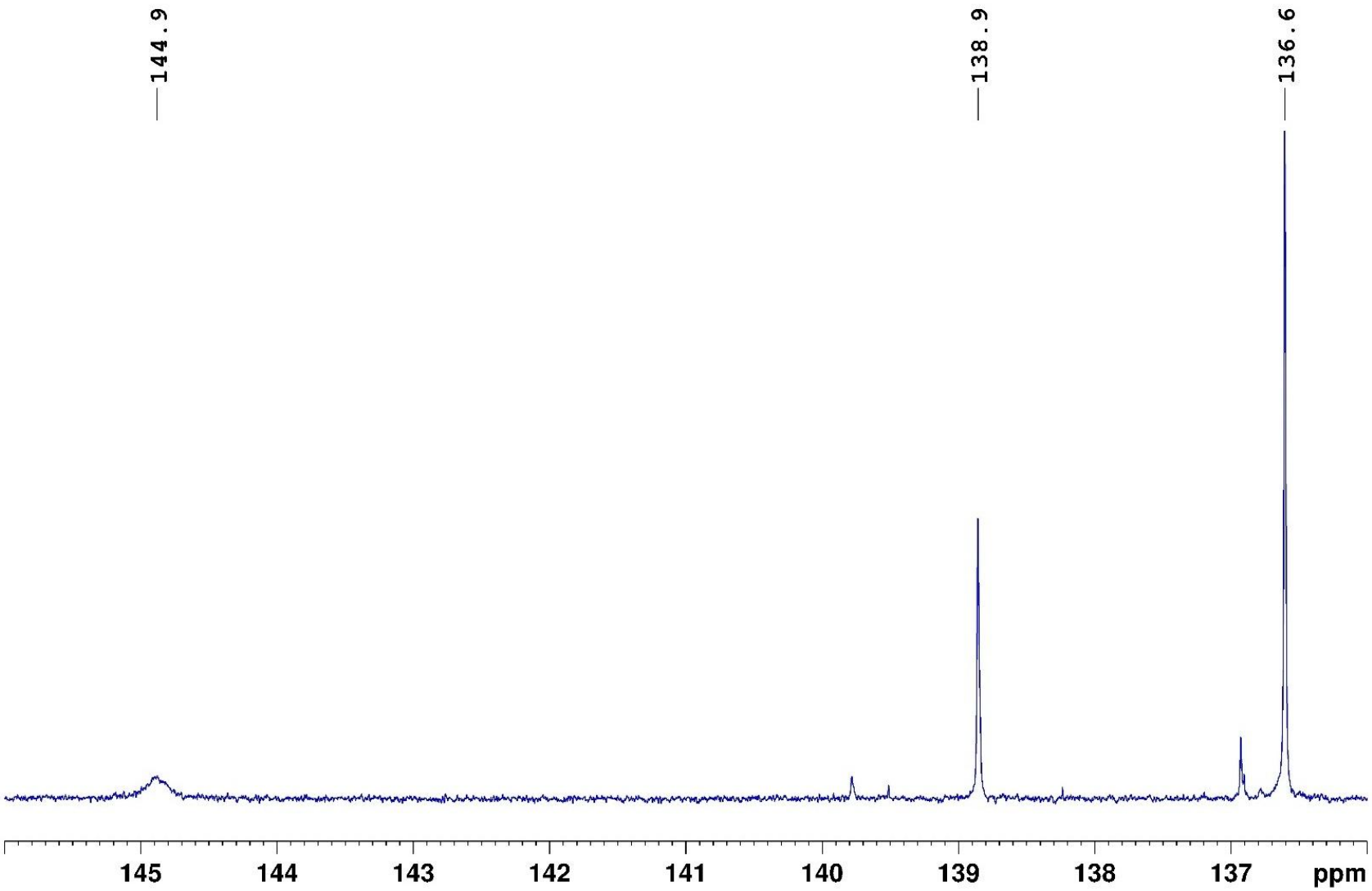


Figure S20. Aromatic region of the $^{13}C\{^{1}H\}$ NMR spectrum of **2-Cr** in d_8-THF.

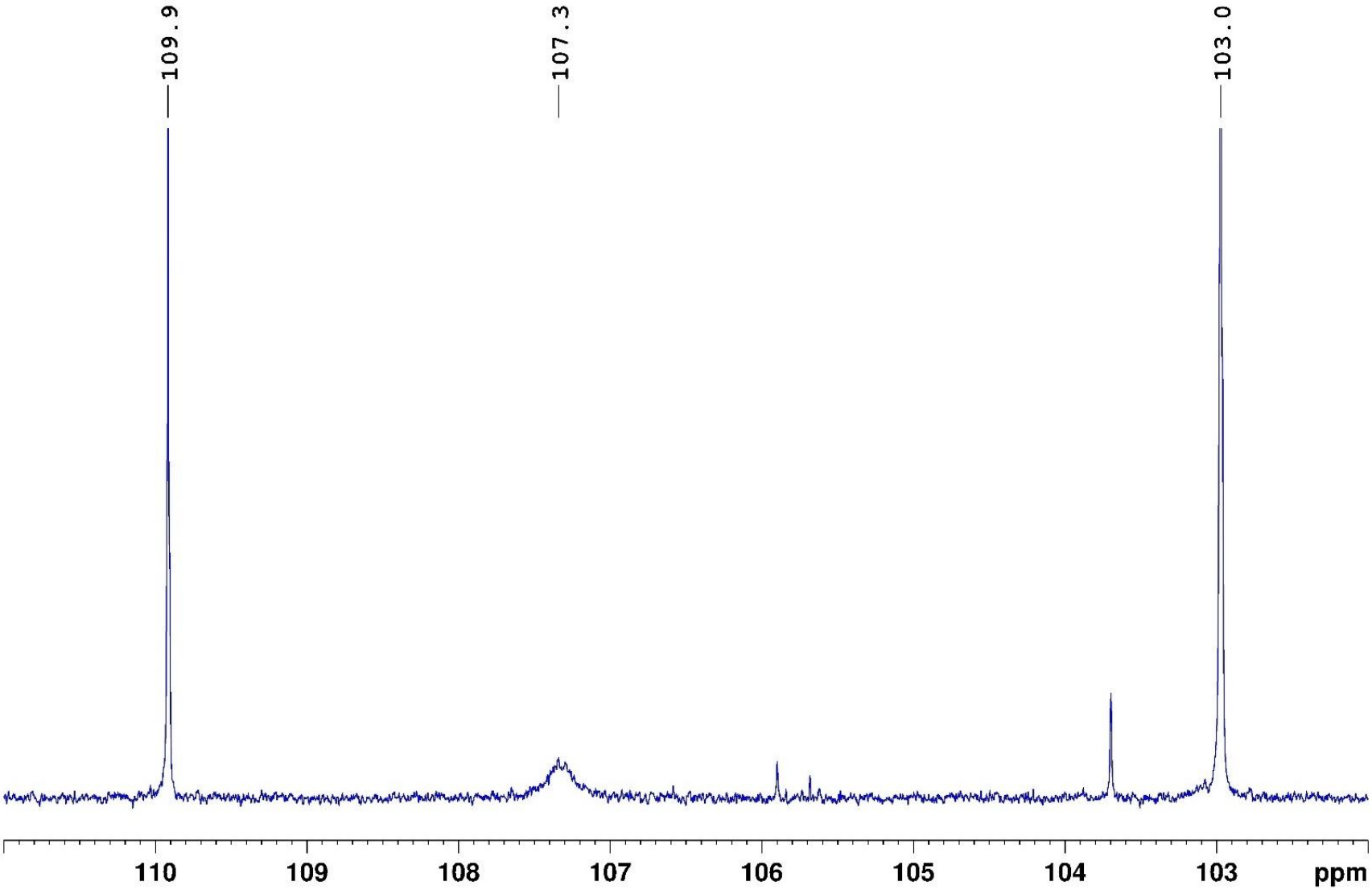


Figure S21. Aromatic region of the $^{13}C\{^{1}H\}$ NMR spectrum of **2-Cr** in d_8-THF.

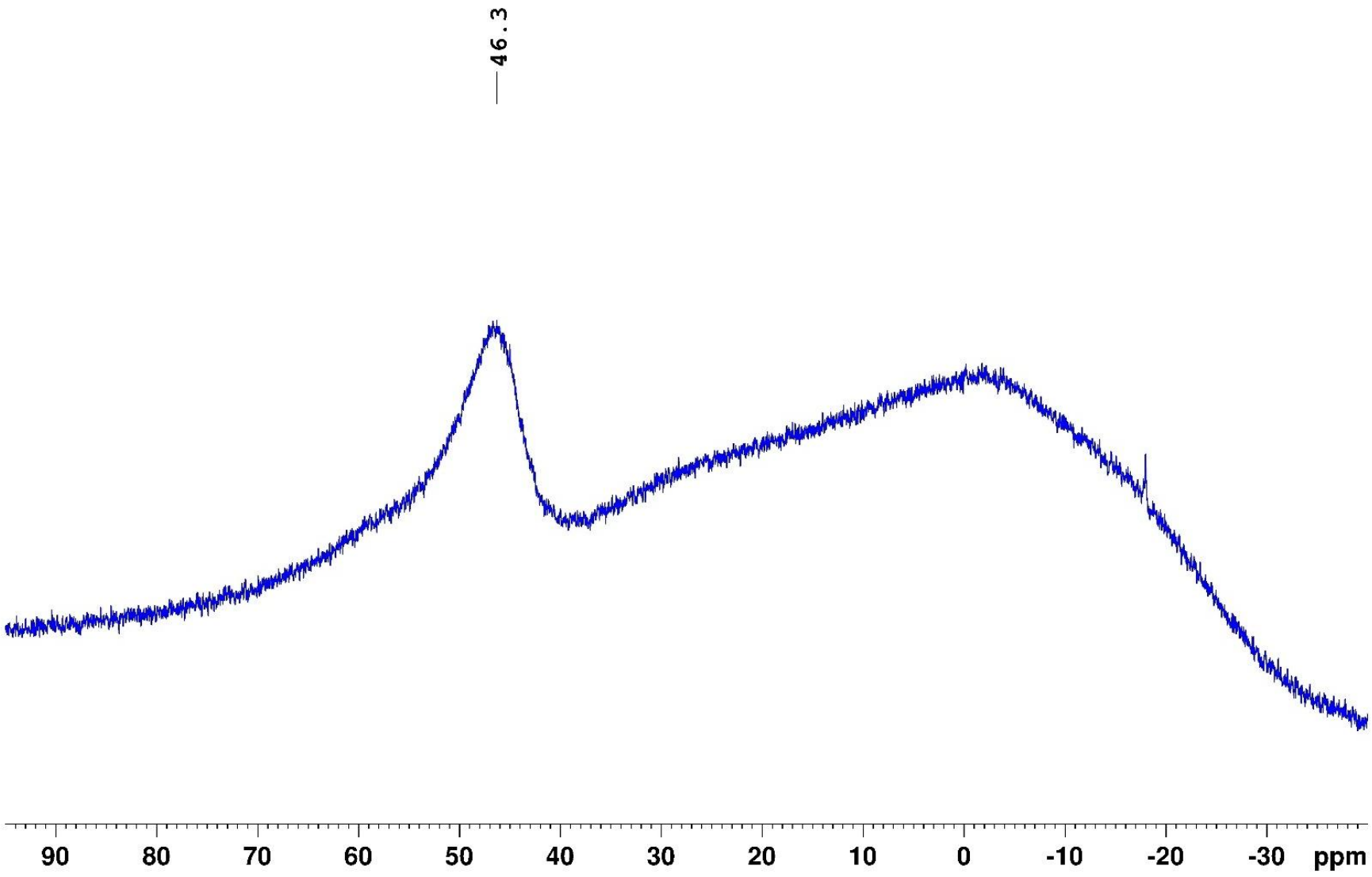


Figure S22. $^{11}B\{^{1}H\}$ NMR spectrum of **2-Cr** in d_8-THF.

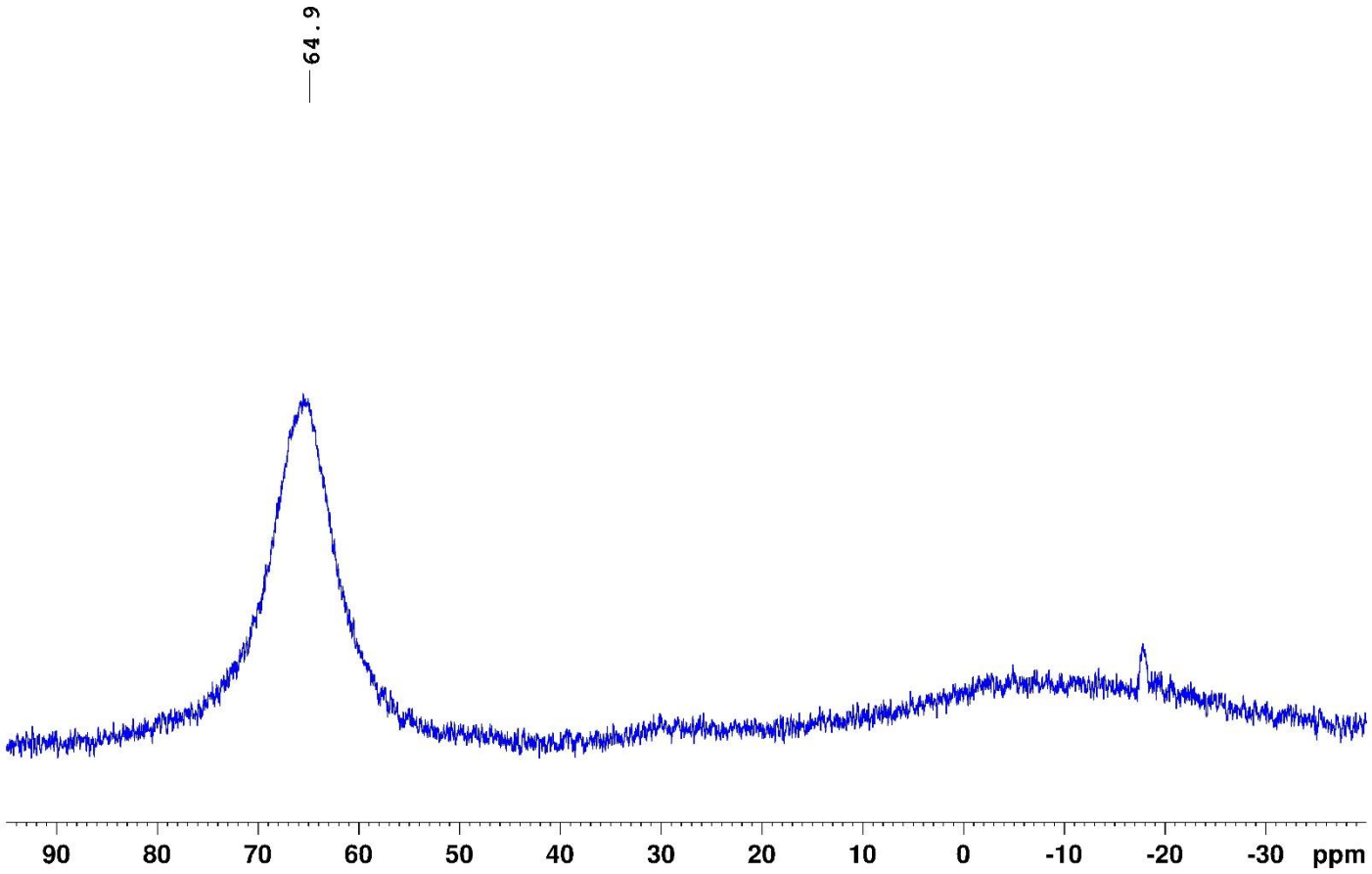


Figure S23. ^{11}B NMR spectrum of **2-Cr** in C_6D_6.

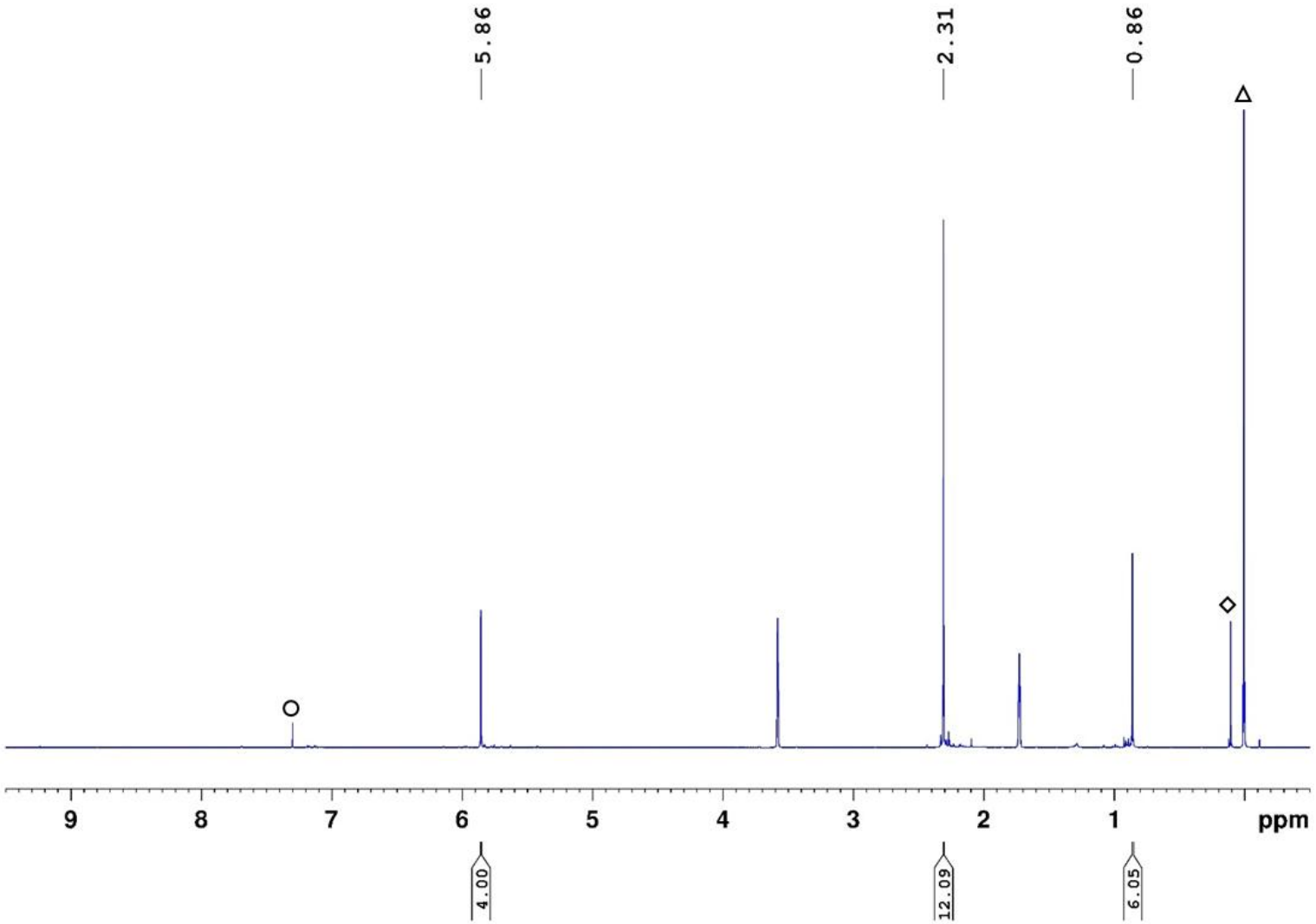


Figure S24. ^{1}H NMR spectrum of **2-Cr$_2$** in d$_8$-THF. The resonance marked ○ belongs to residual benzene solvent, that marked ◇ to silicon grease, and that marked △ to the internal standard TMS.

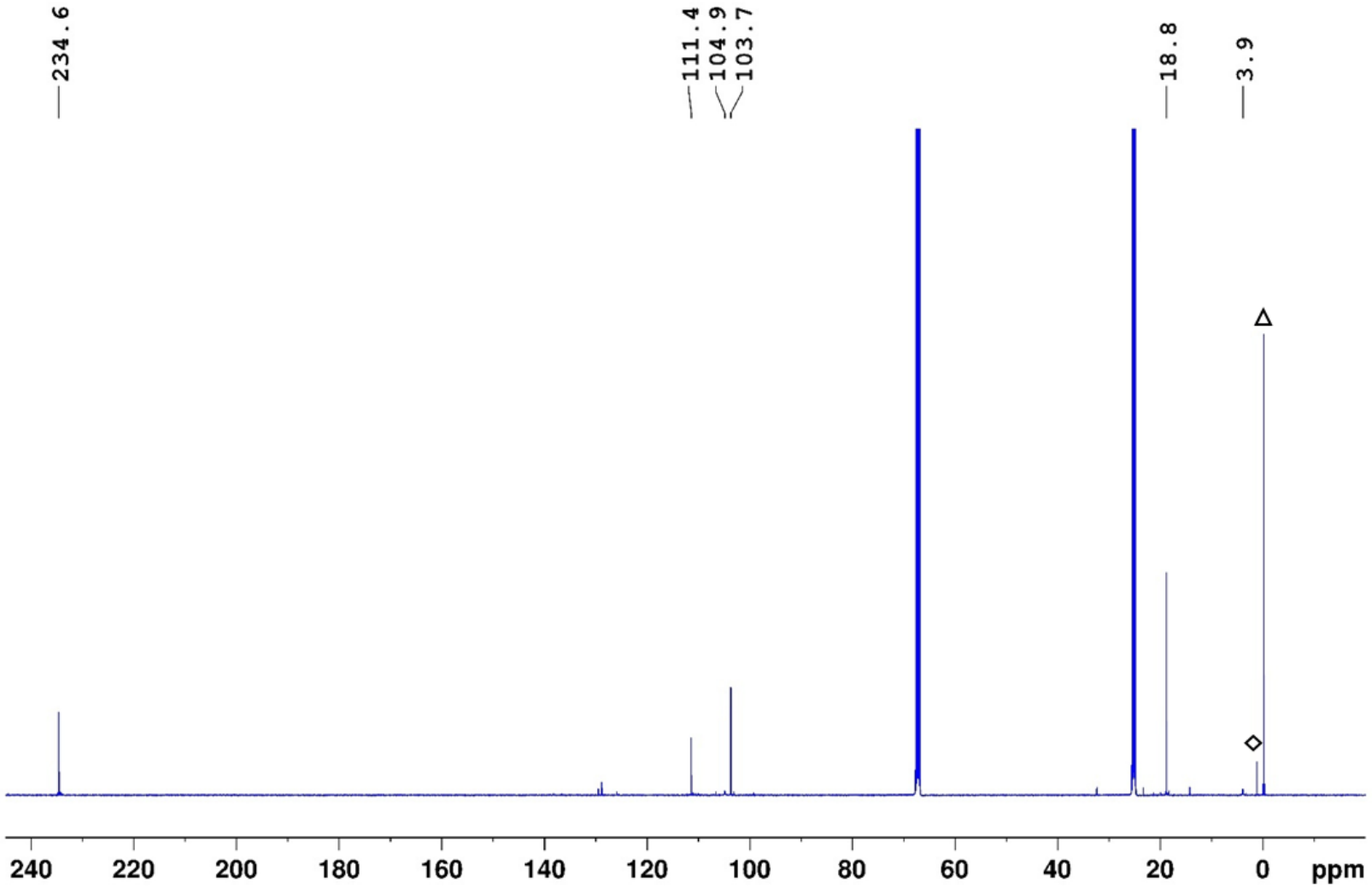


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **2-Cr$_2$** in d_8-THF. The resonance marked ◇ belongs to silicon grease, and that marked Δ to the internal standard TMS.

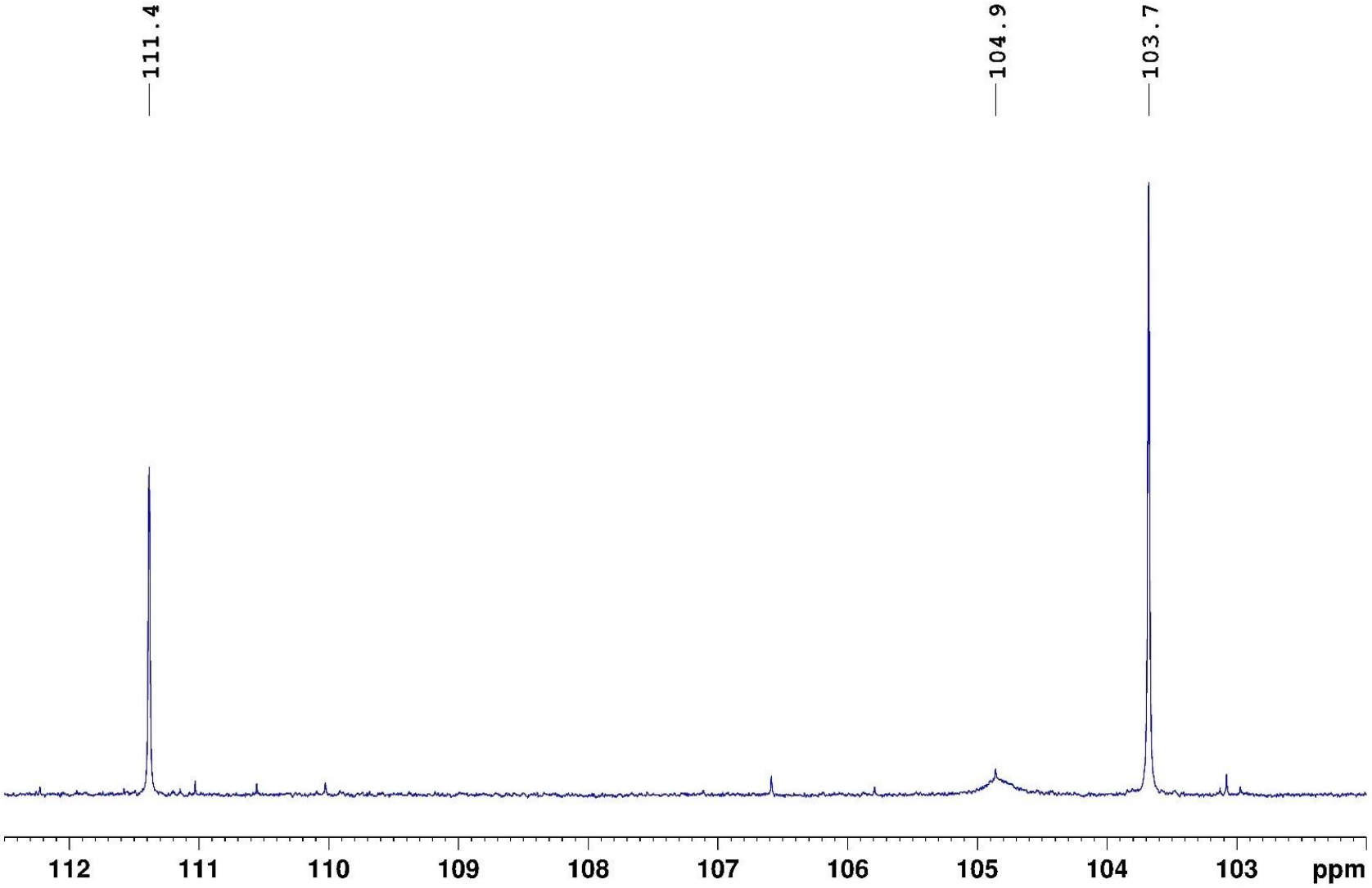


Figure S26. Aromatic region of the $^{13}C\{^{1}H\}$ NMR spectrum of **2-Cr$_2$** in d_8-THF.

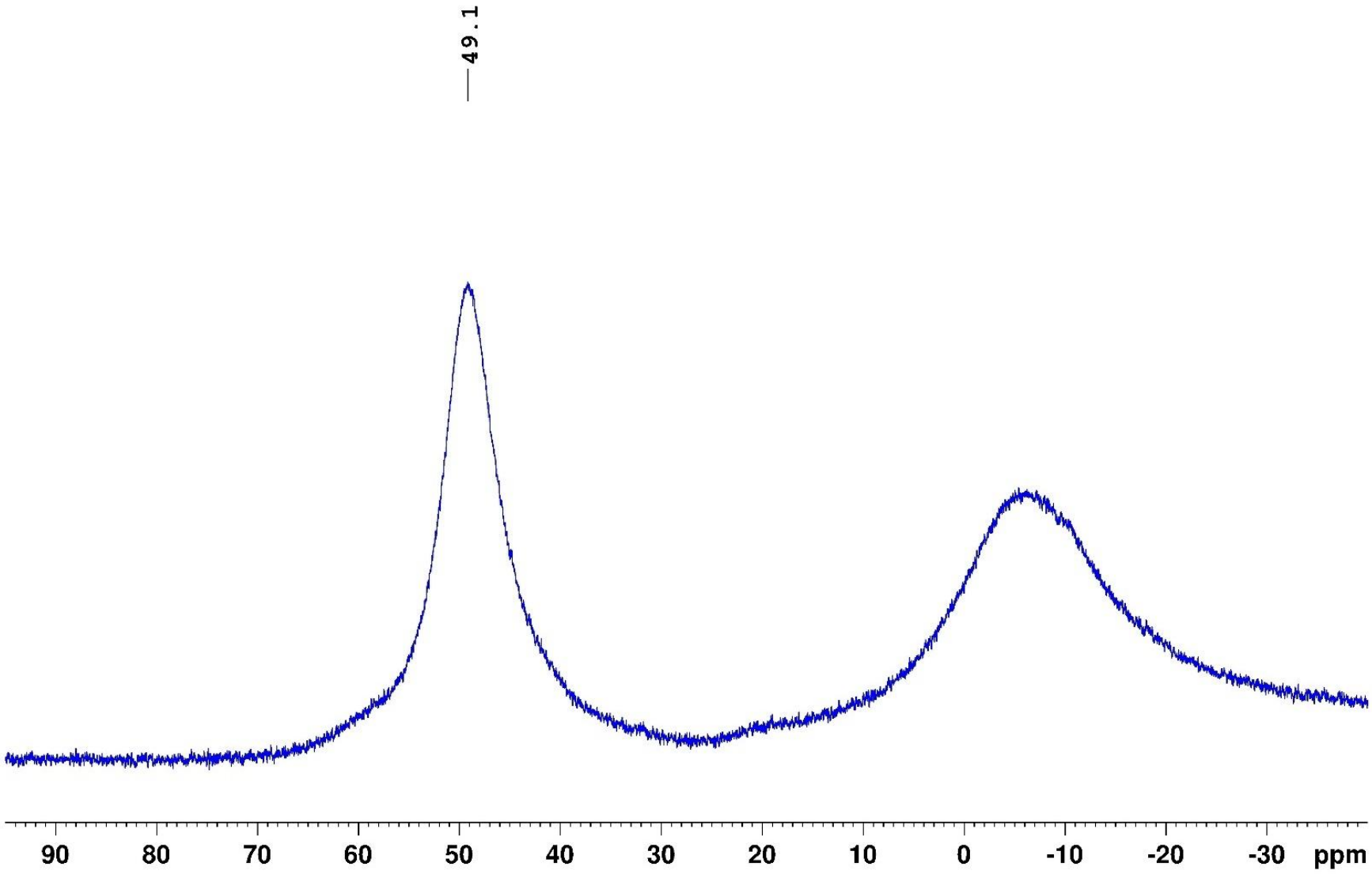


Figure S27. ^{11}B NMR spectrum of **2-Cr$_2$** in d$_8$-THF.

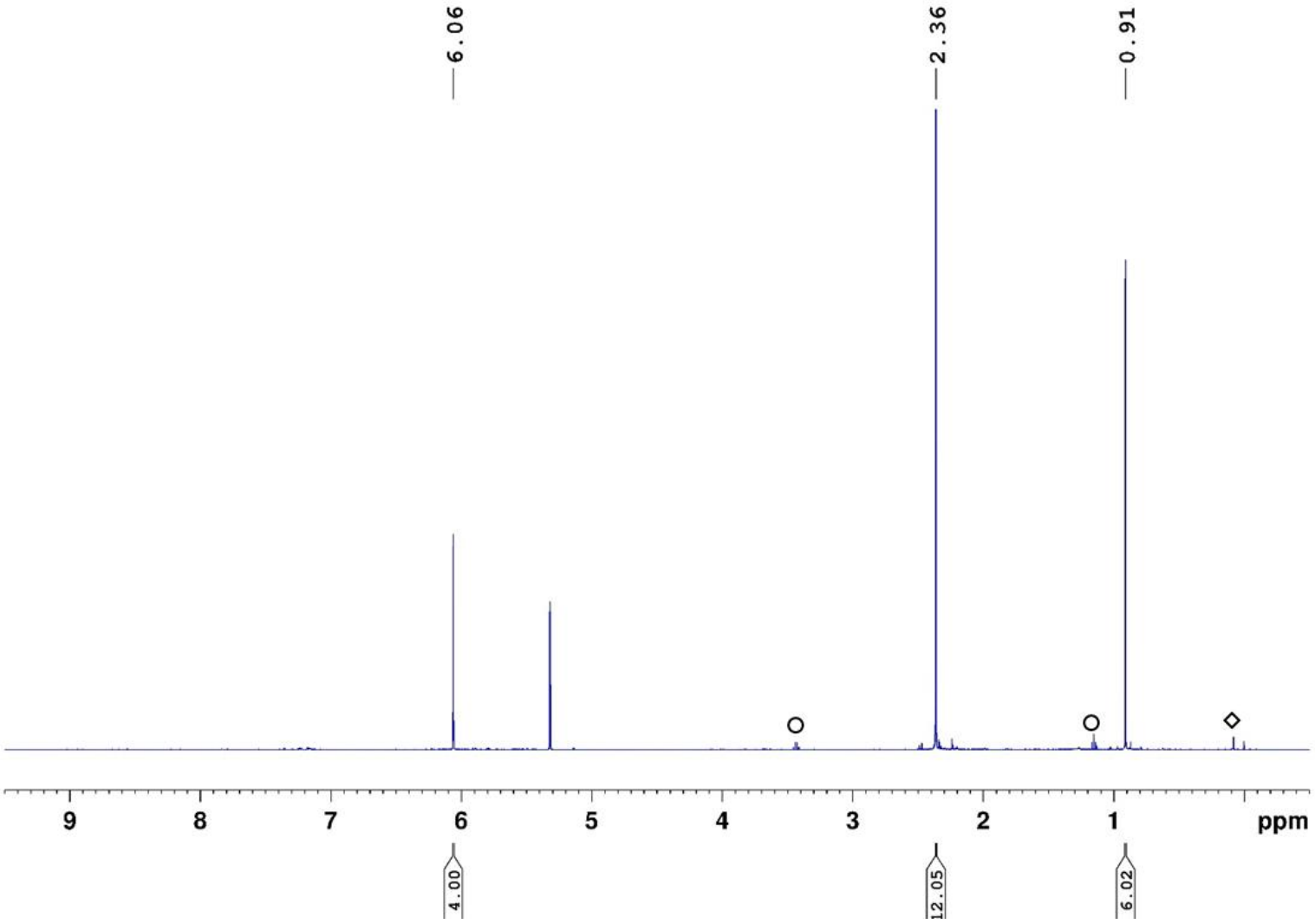


Figure S28. ^{1}H NMR spectrum of **2-Mo$_2$** in CD_2Cl_2. The resonances marked ○ belong to residual Et_2O solvent, and that marked ◇ to silicon grease.

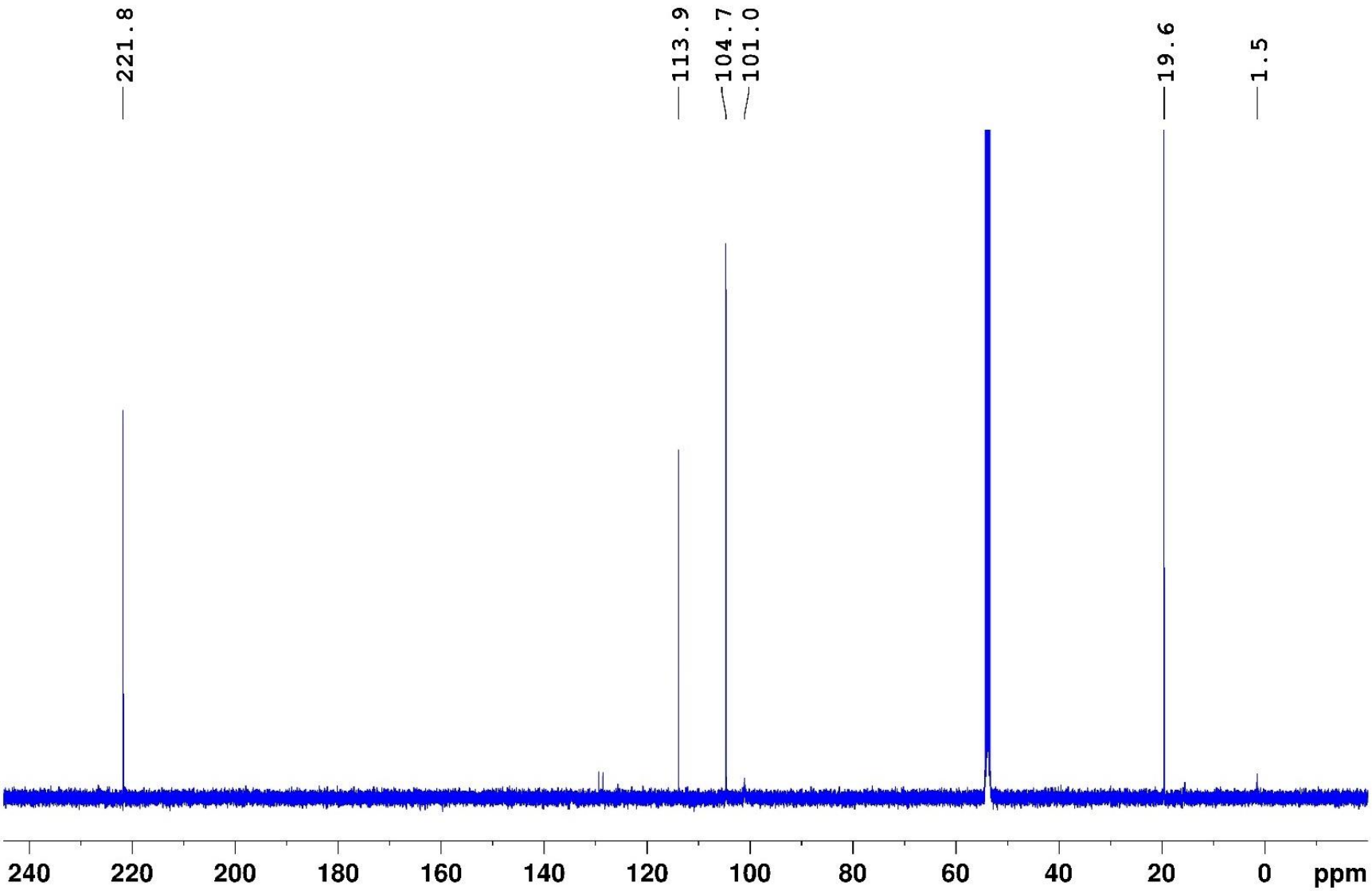


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **2-Mo$_2$** in CD_2Cl_2.

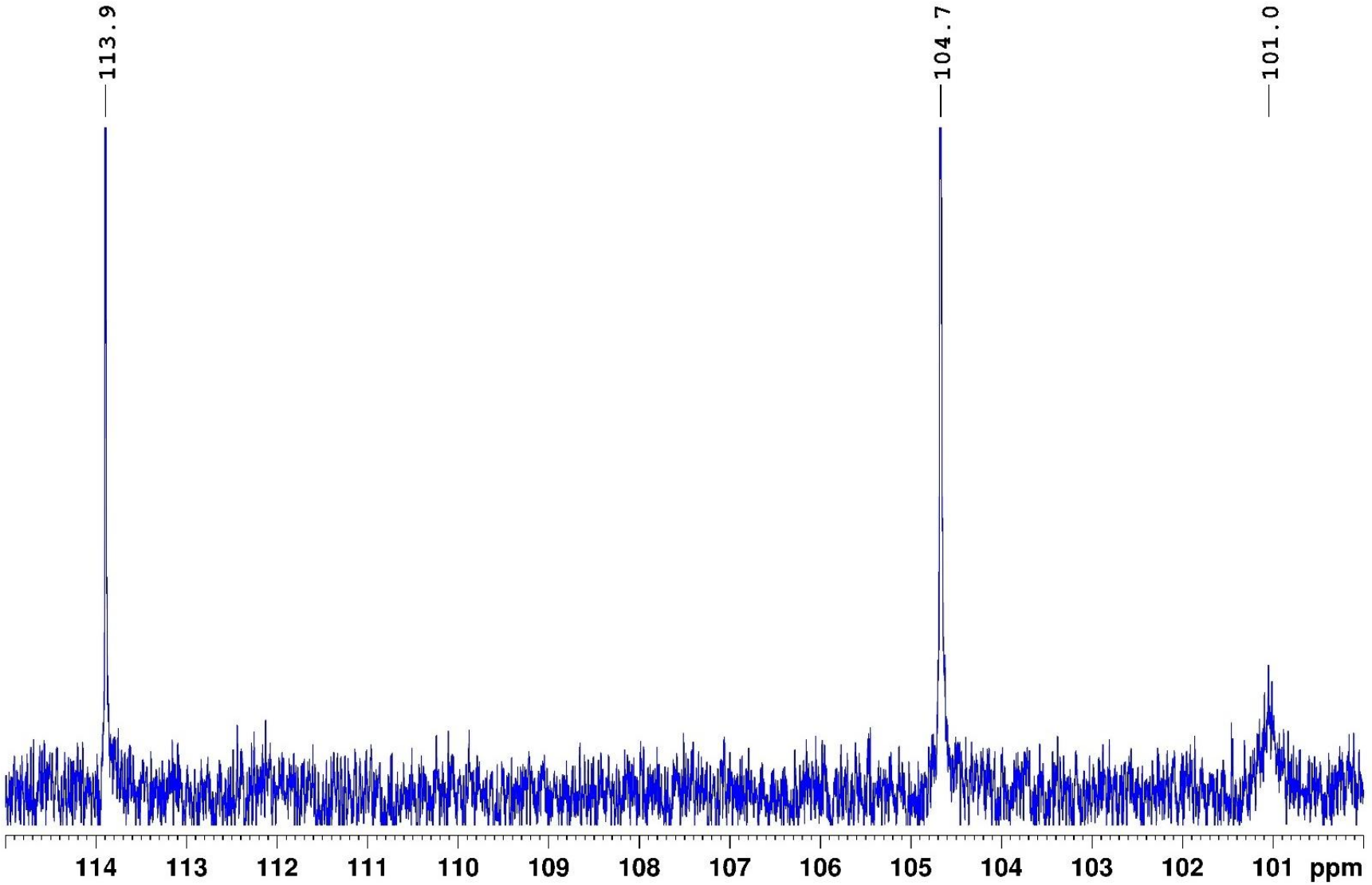


Figure S30. Aromatic region of the $^{13}C\{^{1}H\}$ NMR spectrum of **2-Mo2** in CD_2Cl_2.

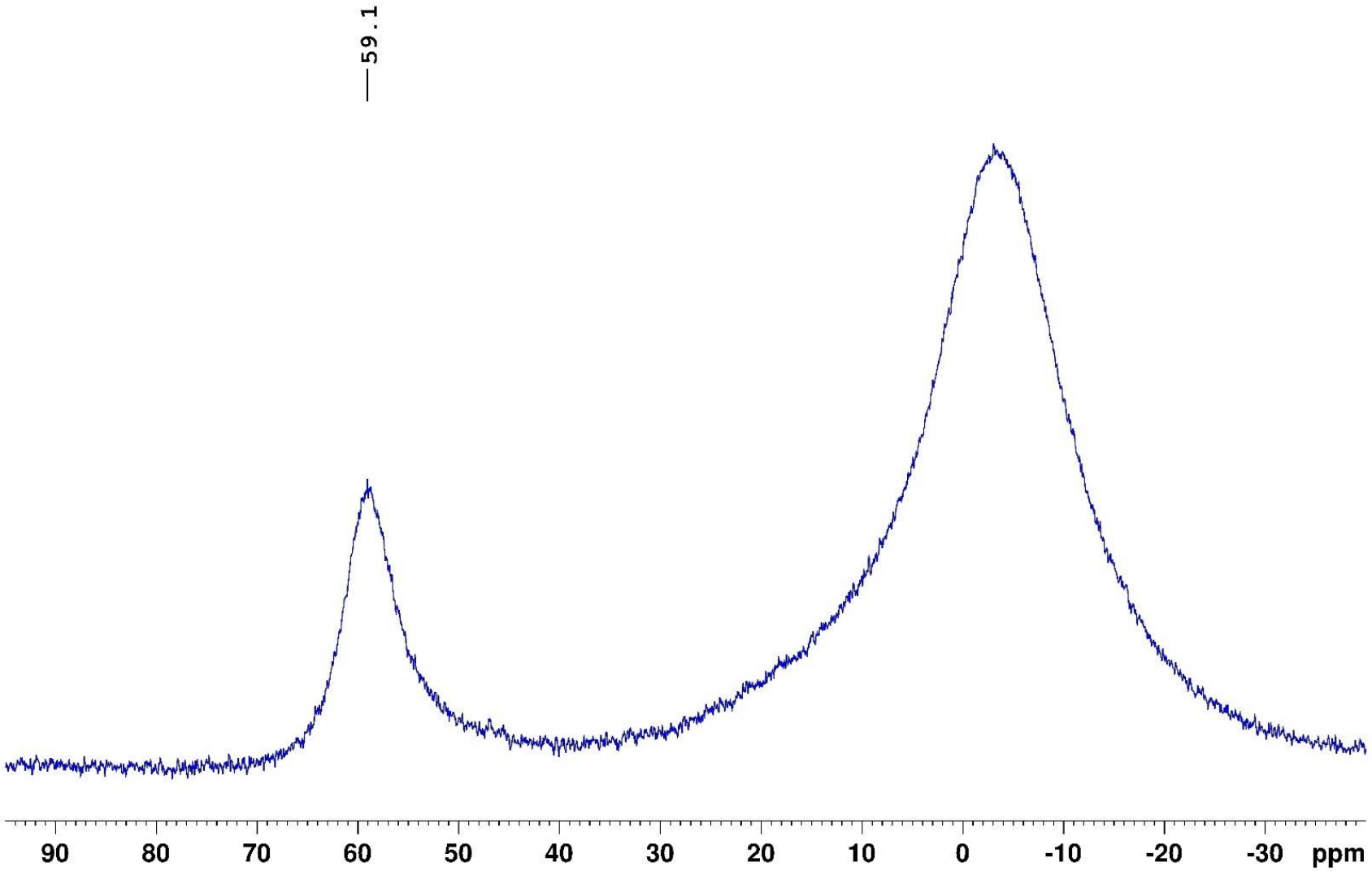


Figure S31. ^{11}B NMR spectrum of **2-Mo$_2$** in CD_2Cl_2.

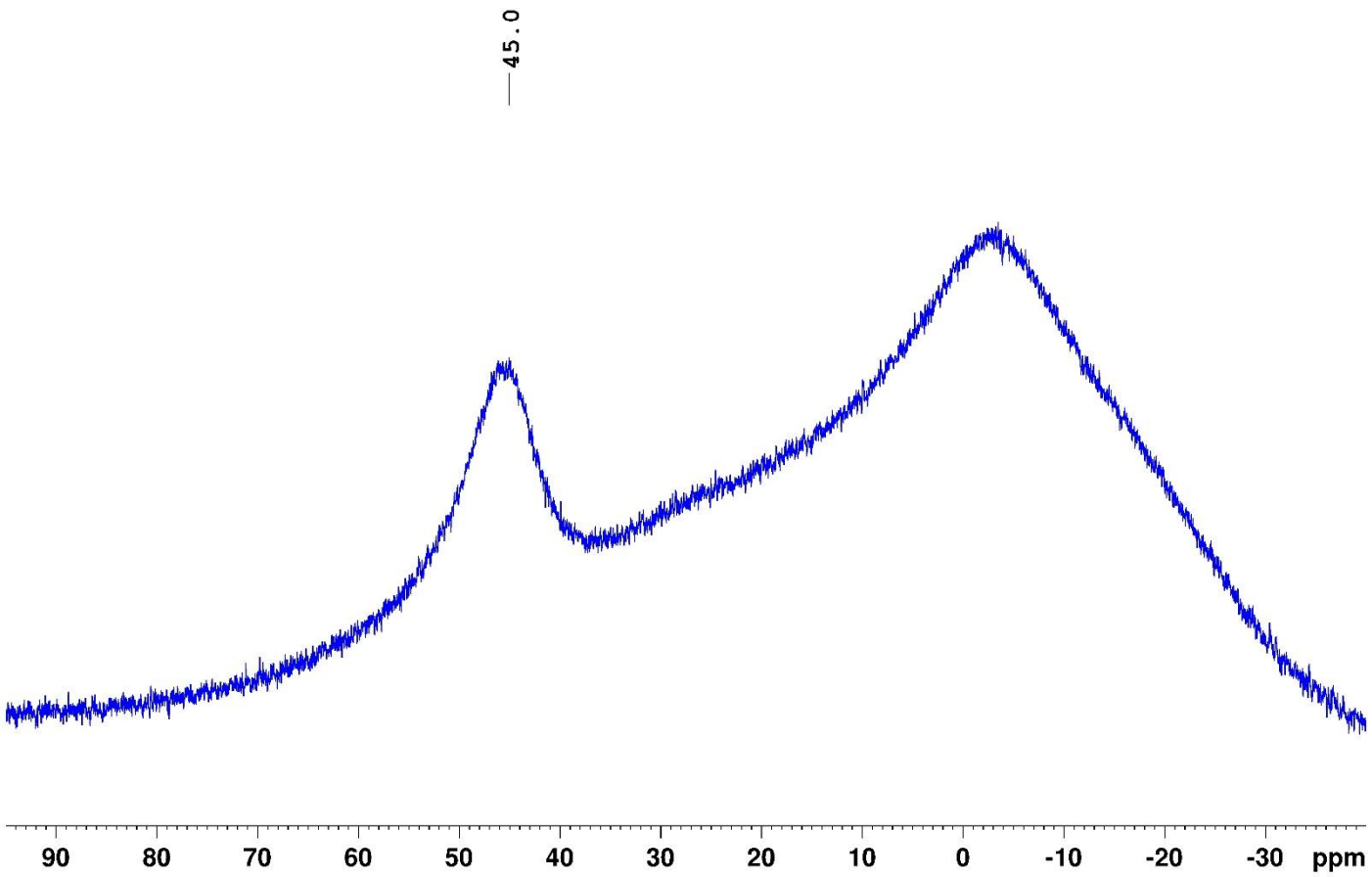


Figure S32. ^{11}B NMR spectrum of **2-Mo$_2$** in d$_8$-THF.

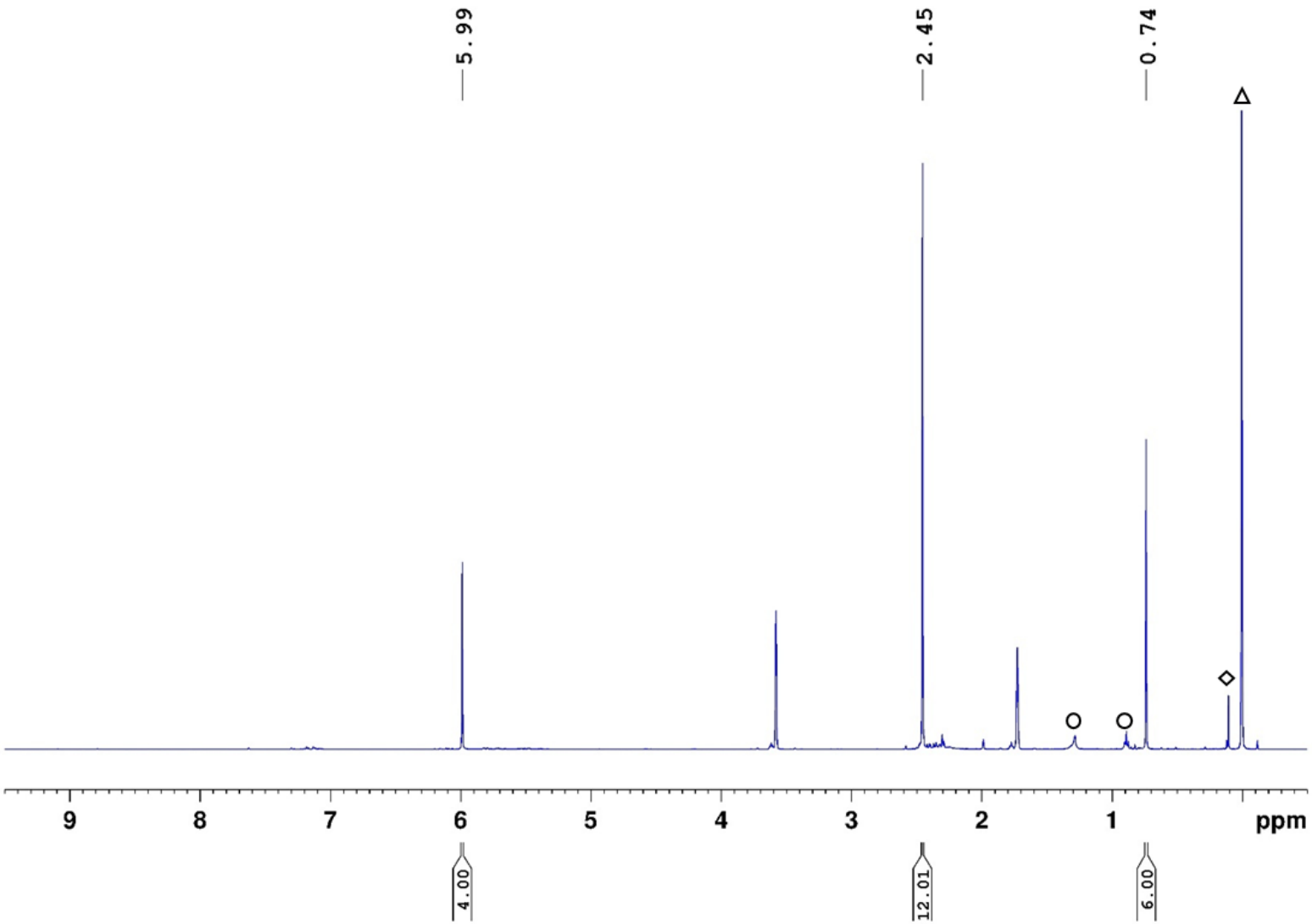


Figure S33. ^{1}H NMR spectrum of **2-W$_2$** in d$_8$-THF. The resonances marked ○ belong to residual hexane solvent, that marked ◇ to silicon grease, and that marked △ to the internal standard TMS.

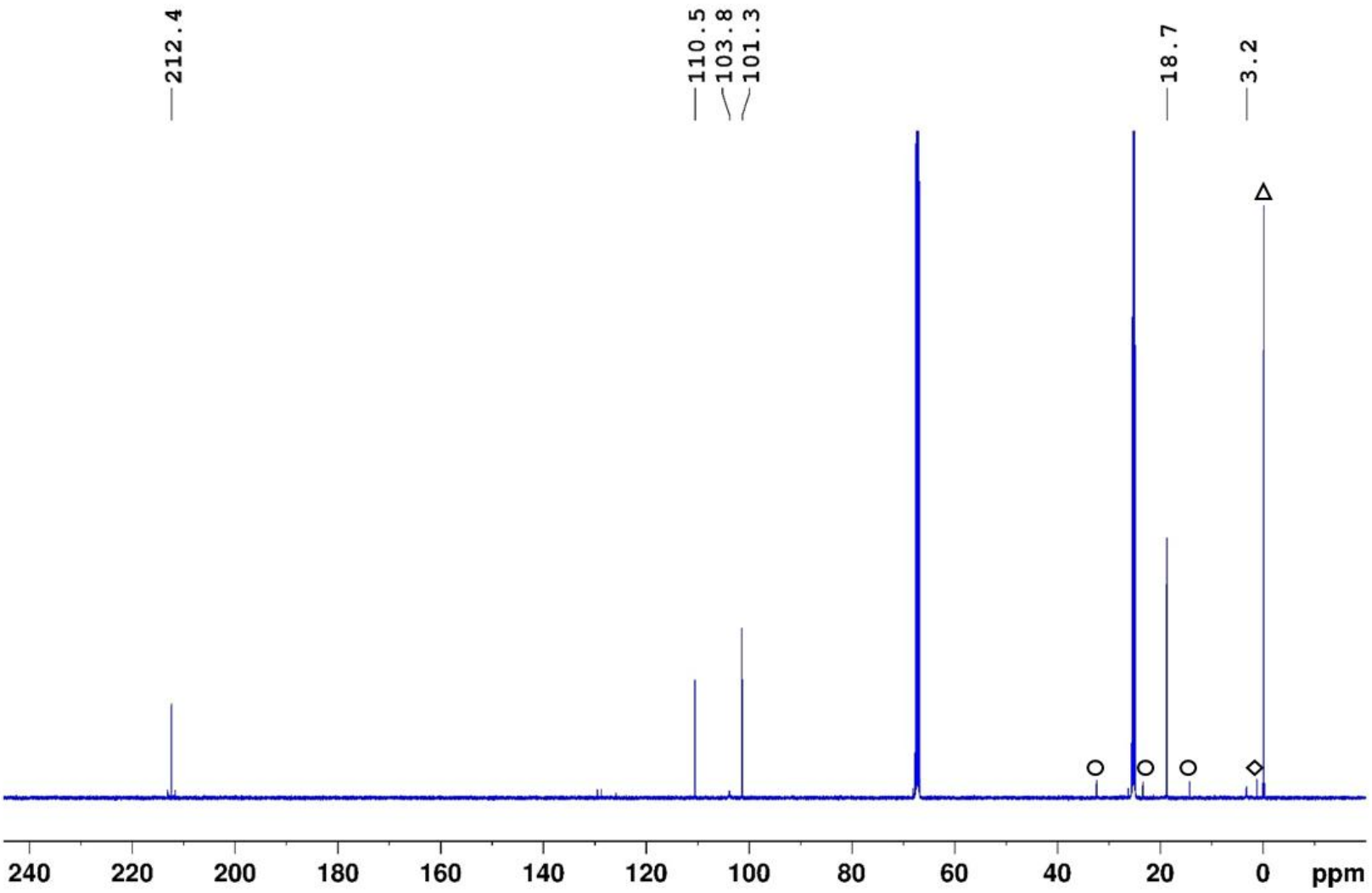


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of **2-W$_2$** in d_8-THF. The resonances marked ○ belong to residual hexane solvent, that marked ◇ to silicon grease, and that marked △ to the internal standard TMS.

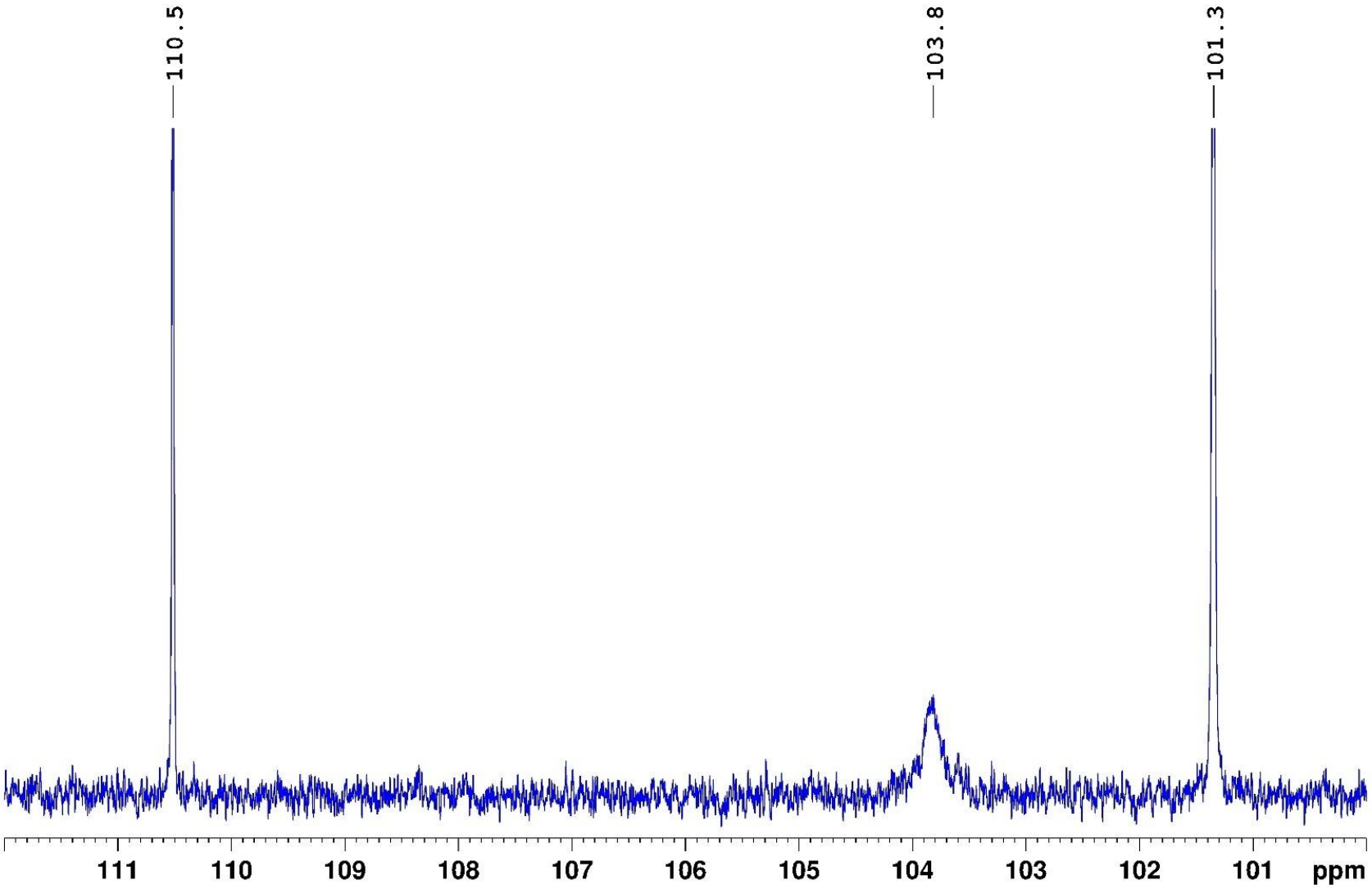


Figure S35. Aromatic region of the $^{13}C\{^{1}H\}$ NMR spectrum of **2-W$_2$** in d_8-THF.

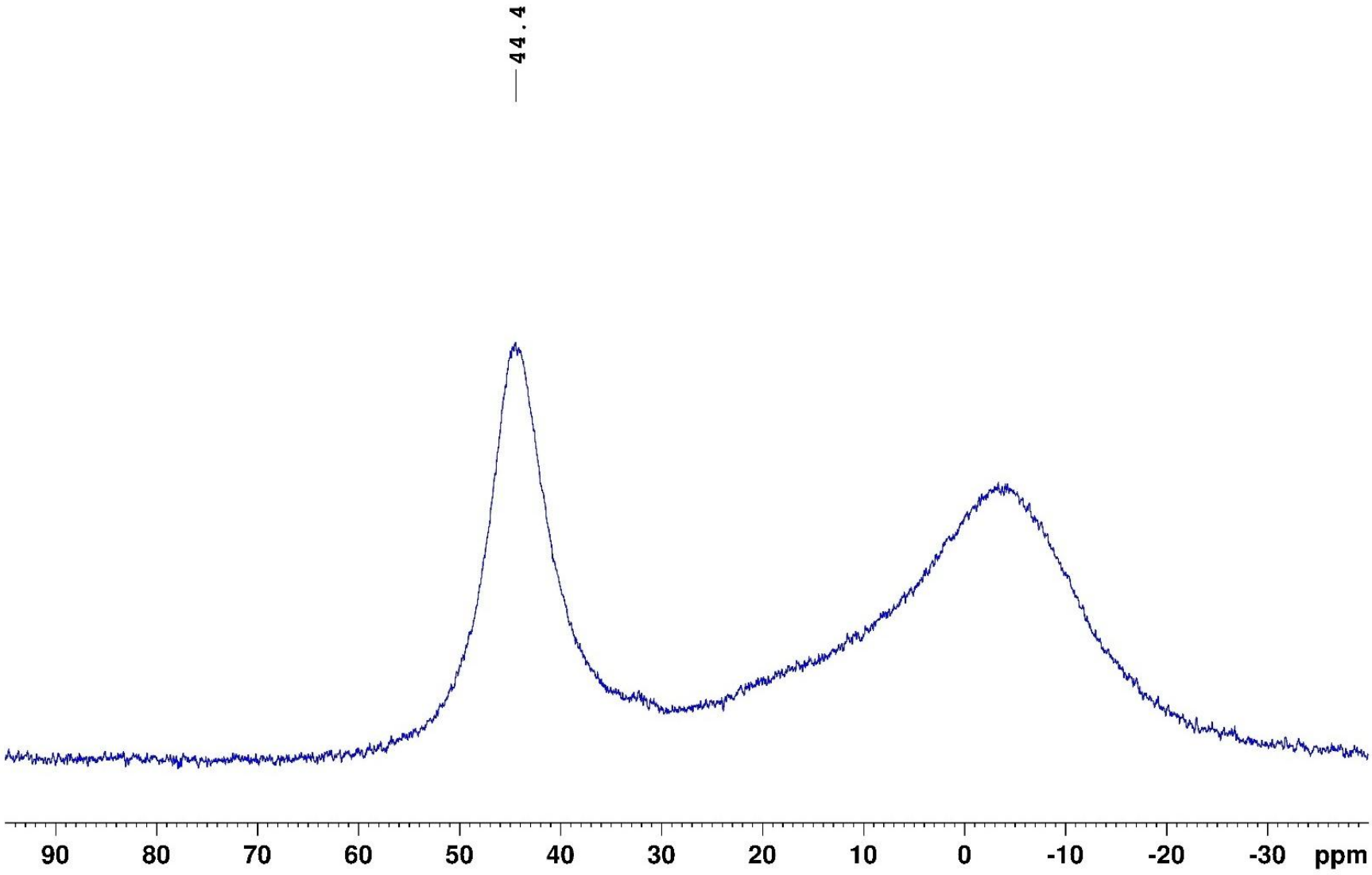


Figure S36. $^{11}B\{^{1}H\}$ NMR spectrum of **2-W$_2$** in d_8-THF.

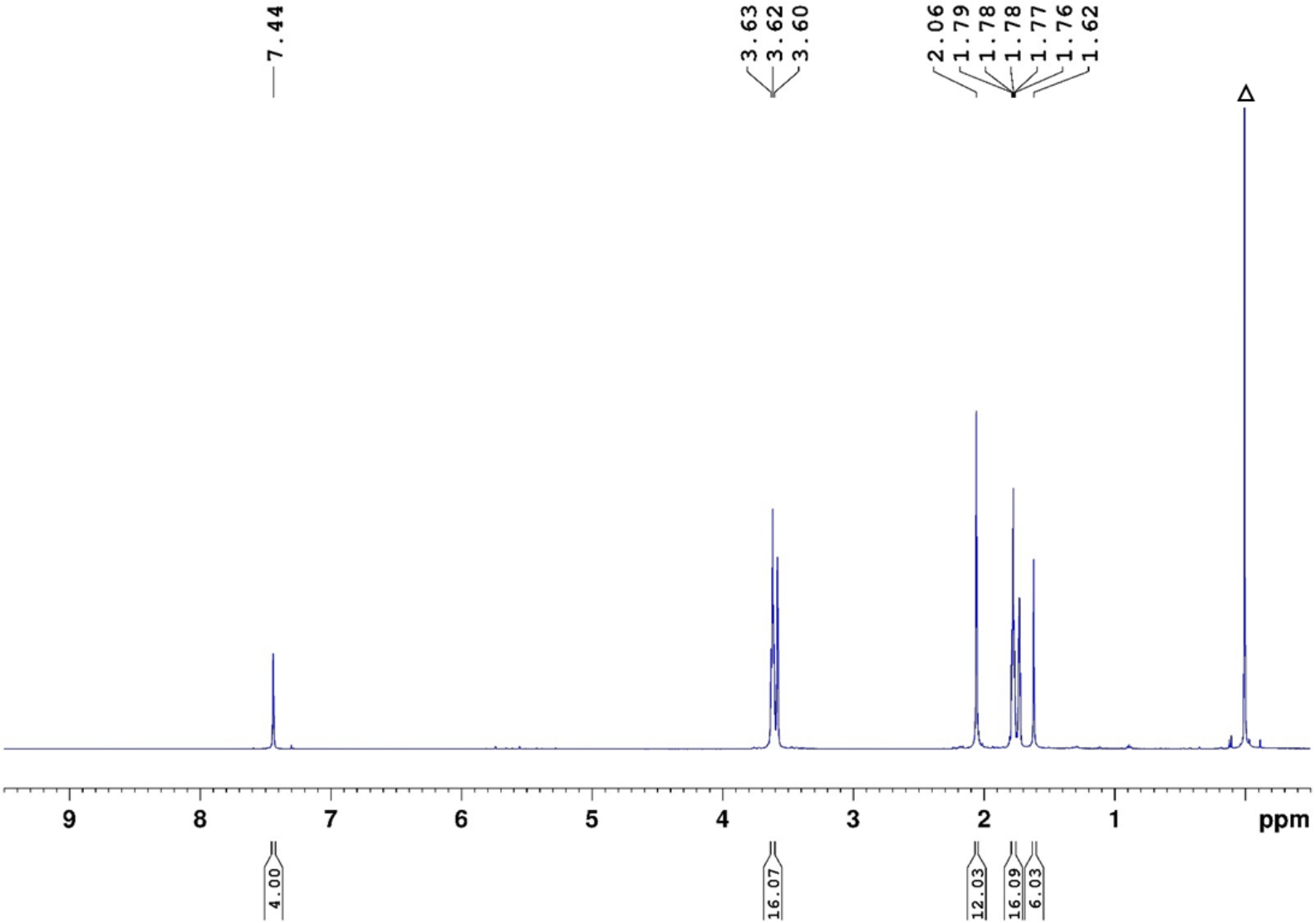


Figure S37. ^{1}H NMR spectrum of **3-Cr$_2$** in d_8-THF. The resonance marked Δ belongs to the internal standard TMS.

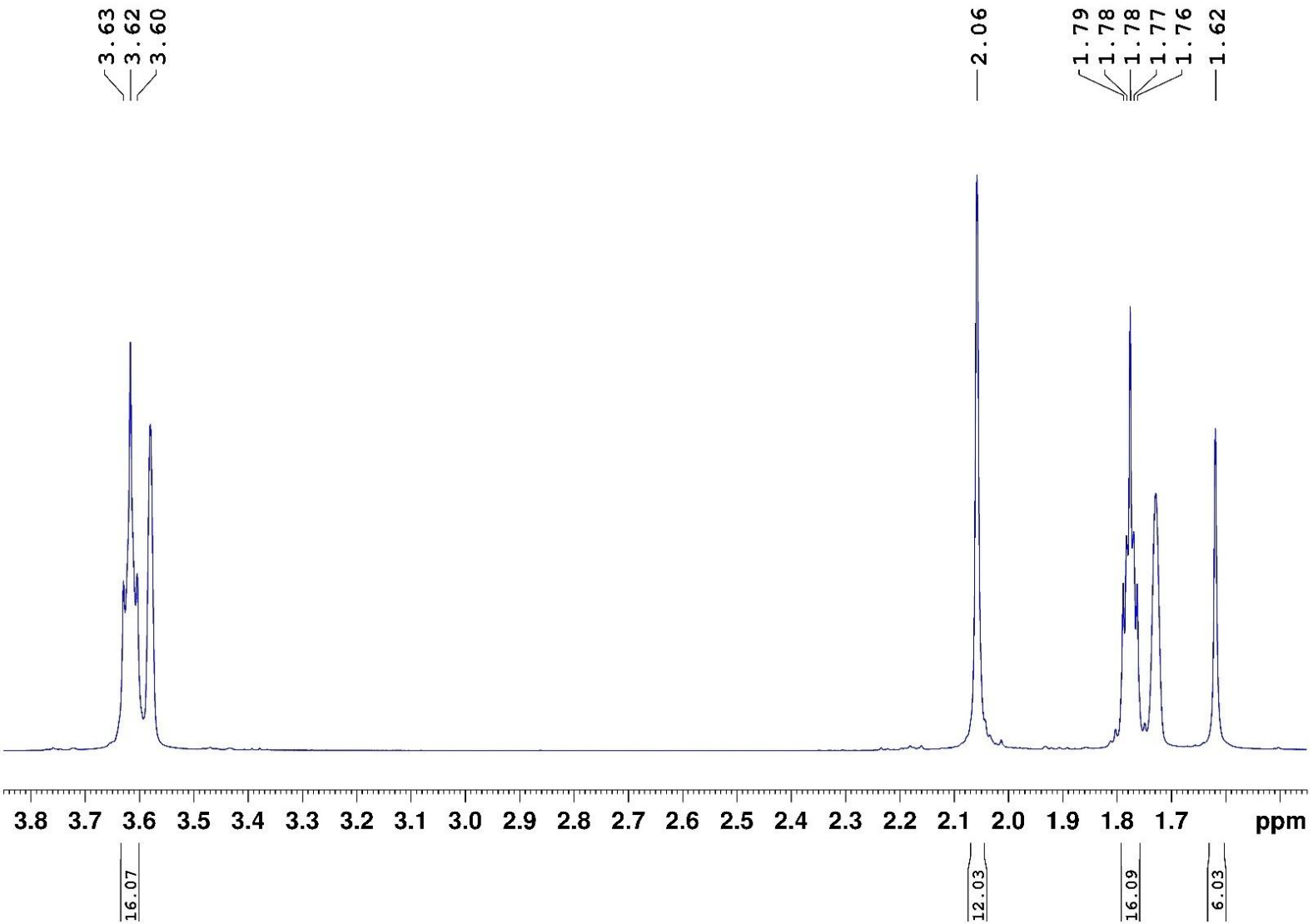


Figure S38. Aliphatic region of the ^{1}H NMR spectrum of **3-Cr$_2$** in d$_8$-THF.

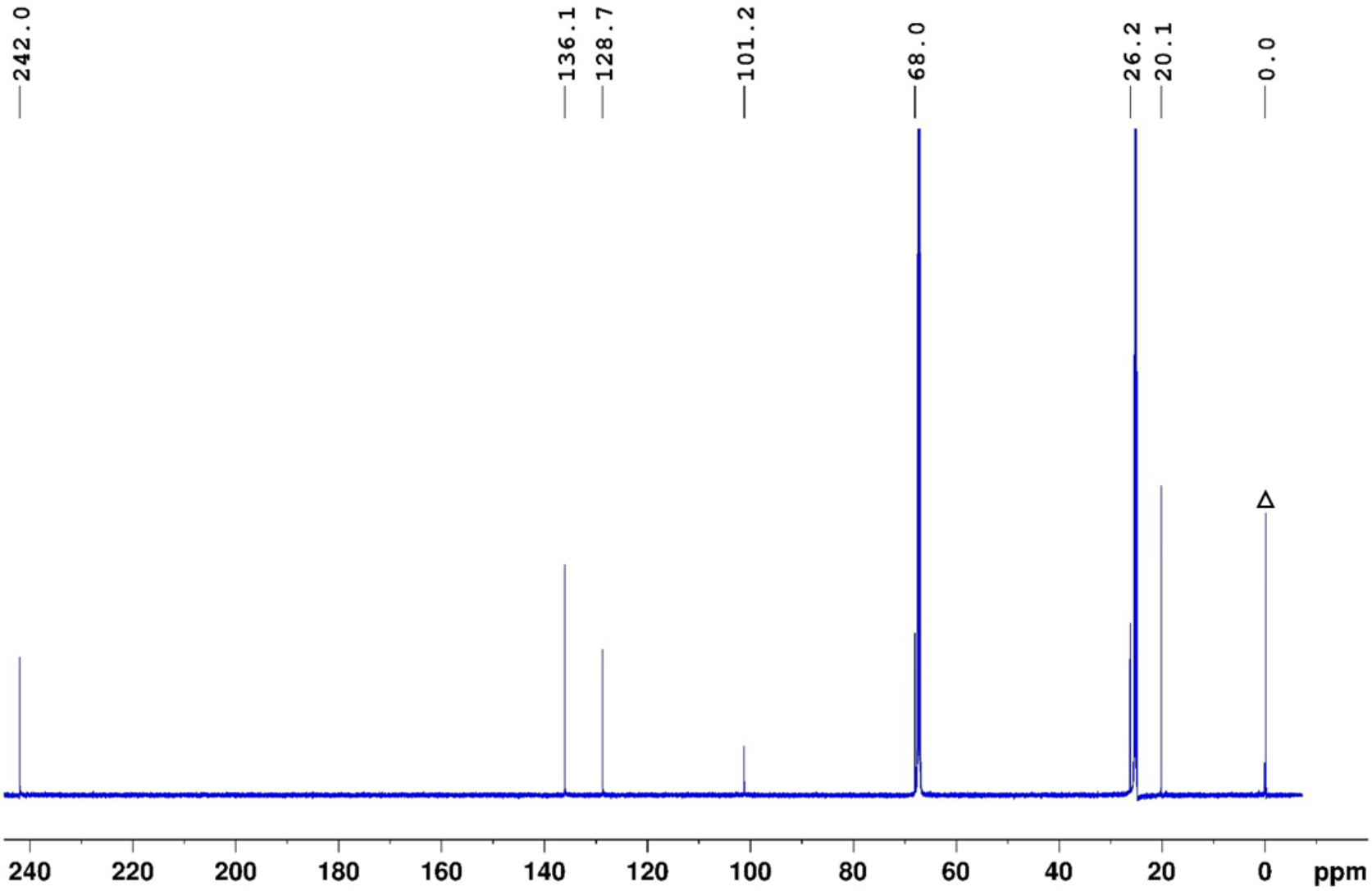


Figure S39. $^{13}C\{^{1}H, ^{11}B\}$ NMR spectrum of **3-Cr2** in d_8-THF. The resonance marked Δ belongs to the internal standard TMS.

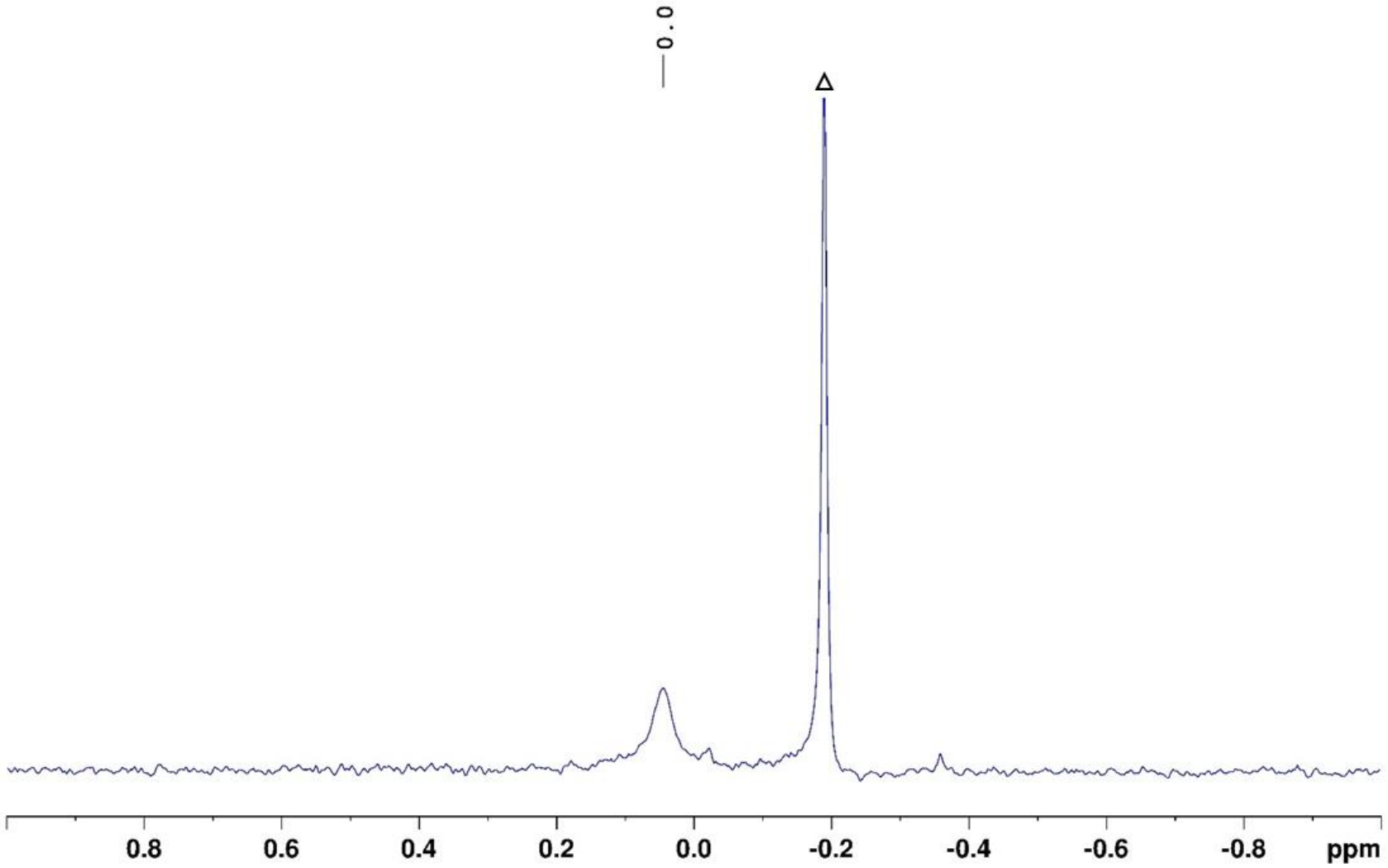


Figure S40. Part of the aliphatic region of the $^{13}C\{^{1}H, ^{11}B\}$ NMR spectrum of **3-Cr$_2$** in d_8-THF. The resonance marked Δ belongs to the internal standard TMS.

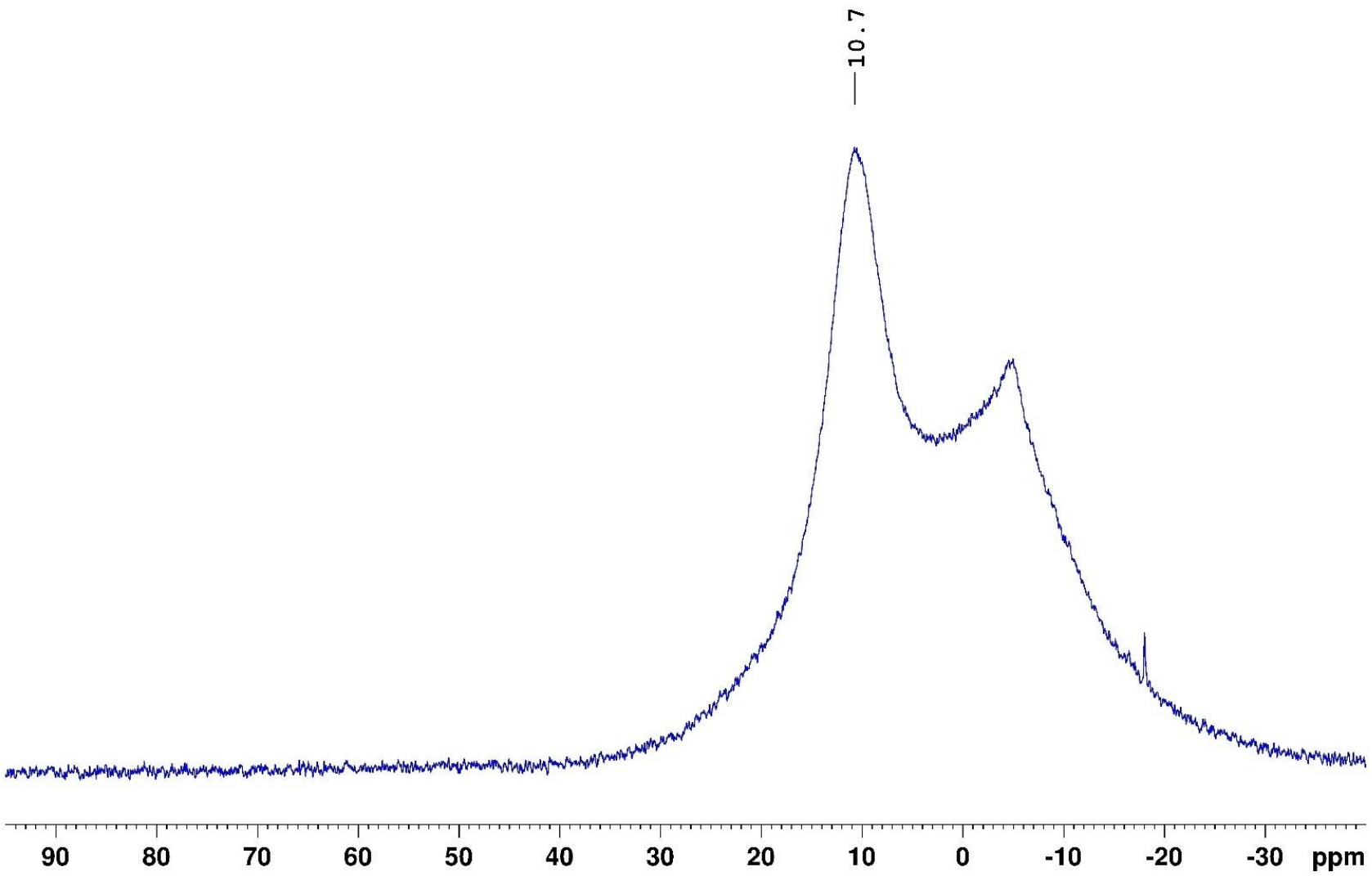


Figure S41. $^{11}B\{^{1}H\}$ NMR spectrum of **3-Cr$_2$** in d_8-THF.

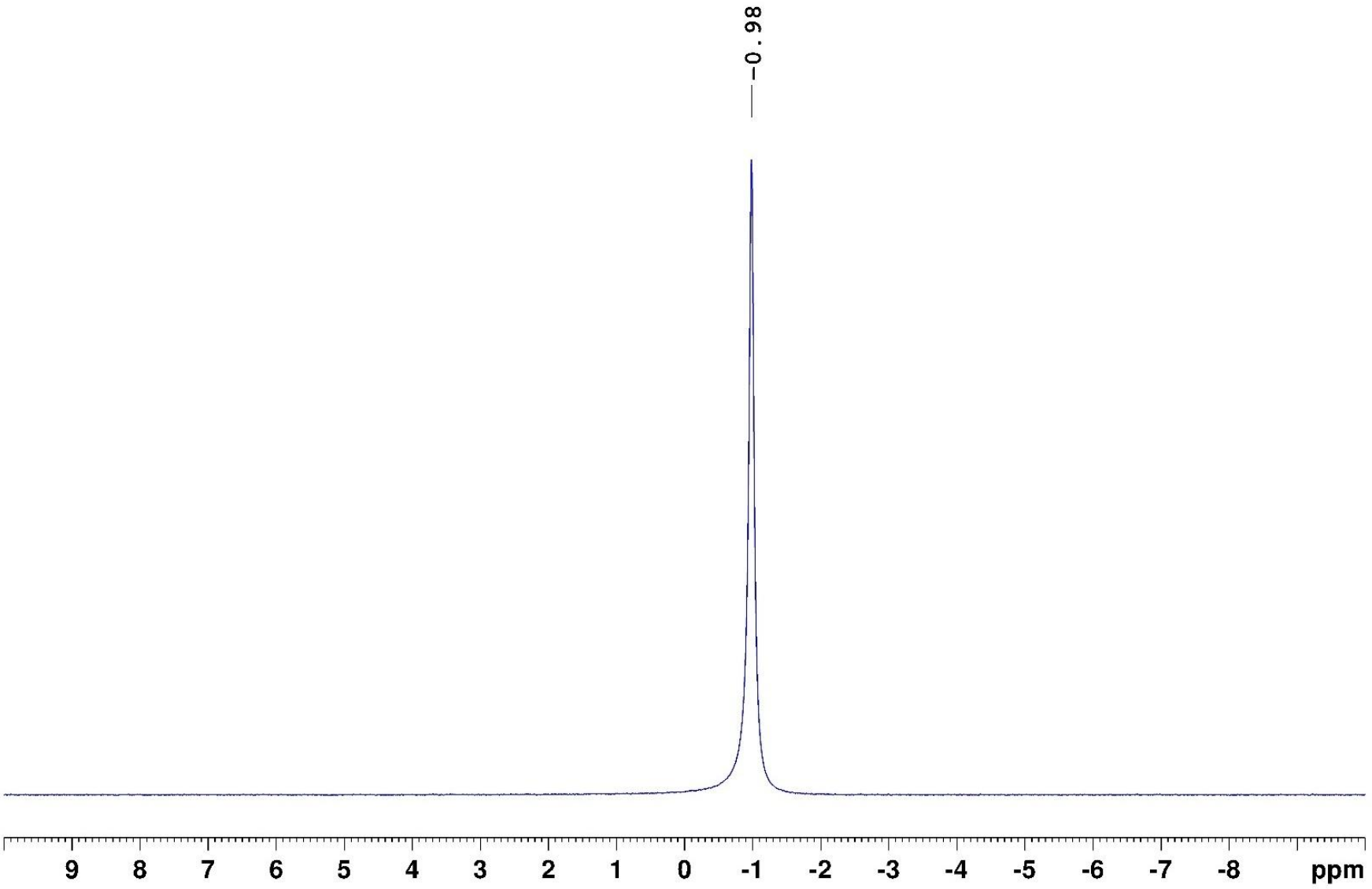


Figure S42. $^{7}Li\{^{1}H\}$ NMR spectrum of **3-Cr$_2$** in d_8-THF.

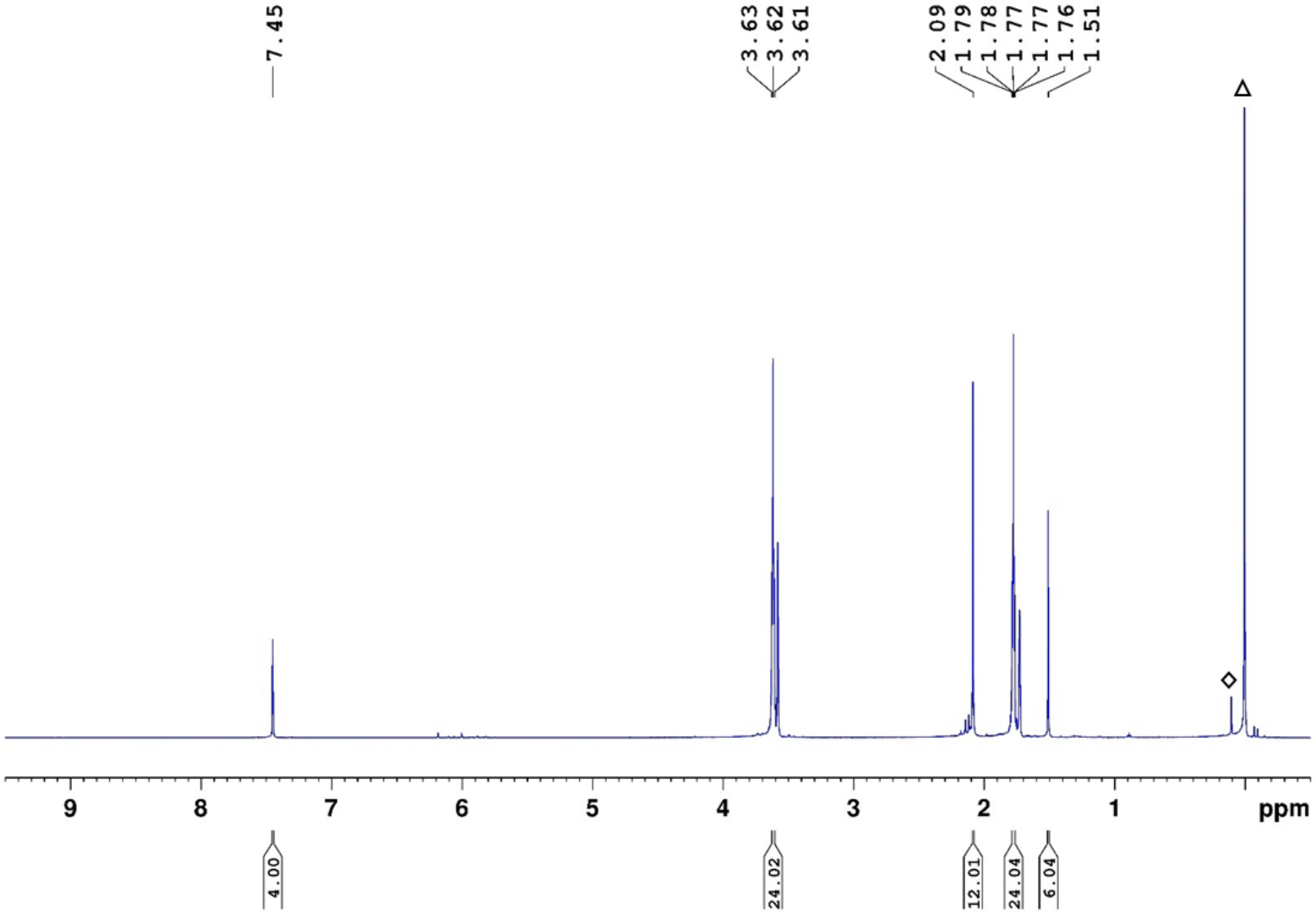


Figure S43. ^{1}H NMR spectrum of **3-Mo$_2$** in d$_8$-THF. The resonance marked ◇ belongs to silicon grease, and that marked Δ to the internal standard TMS.

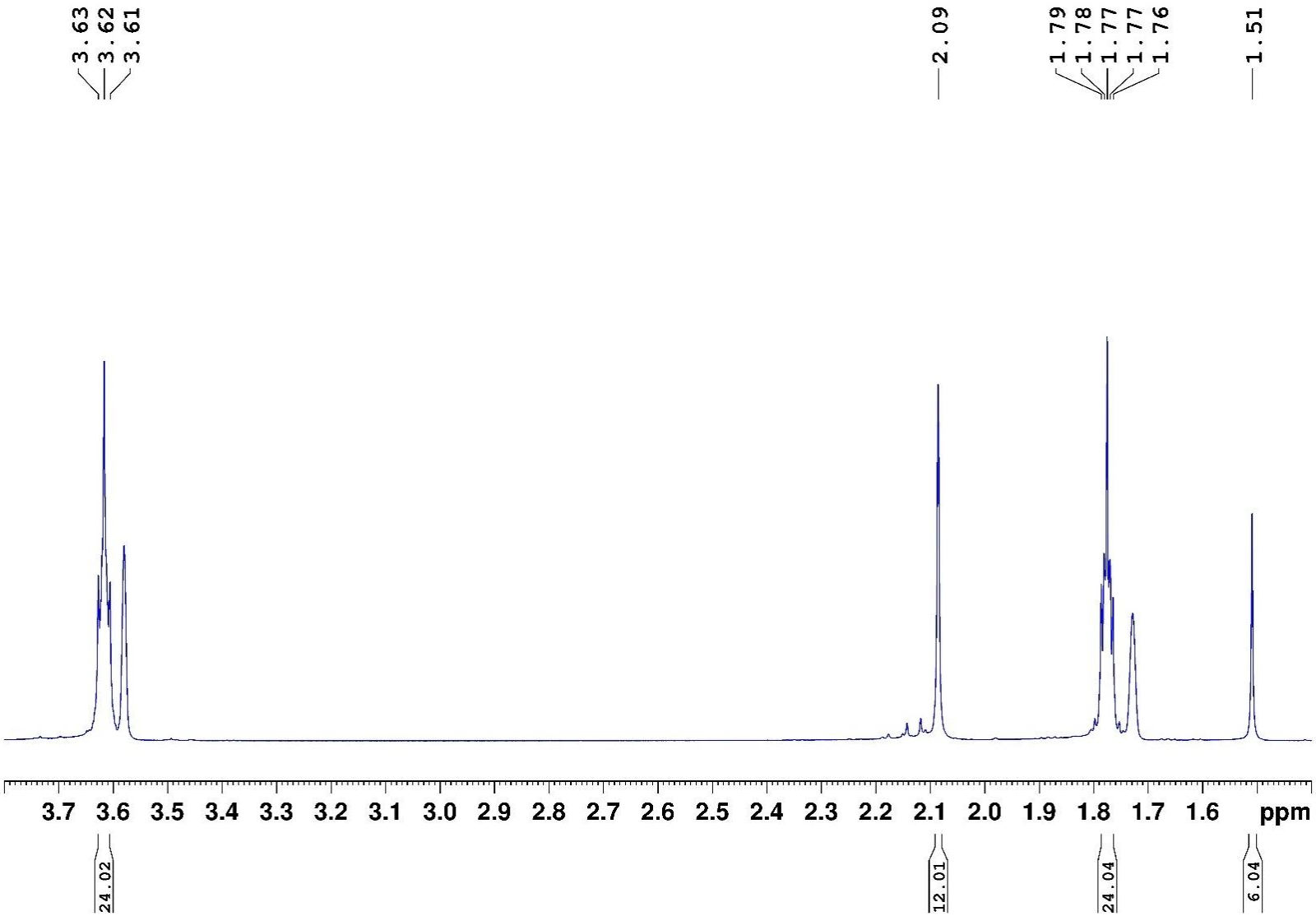


Figure S44. Part of the aliphatic region of the ^{1}H NMR spectrum of **3-Mo2** in d_8-THF.

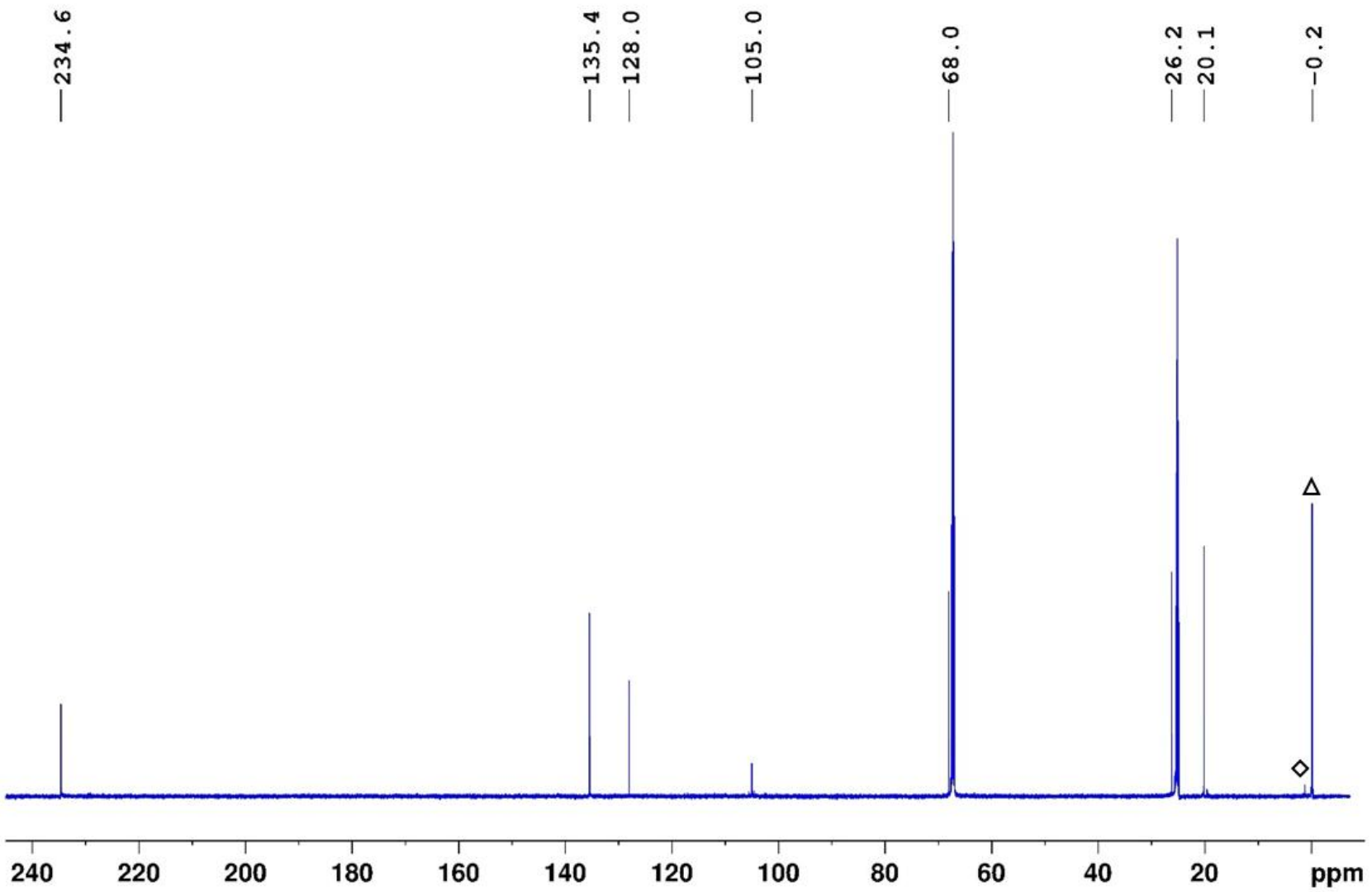


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of **3-Mo$_2$** in d_8-THF. The resonance marked ◇ belongs to silicon grease, and that marked Δ to the internal standard TMS.

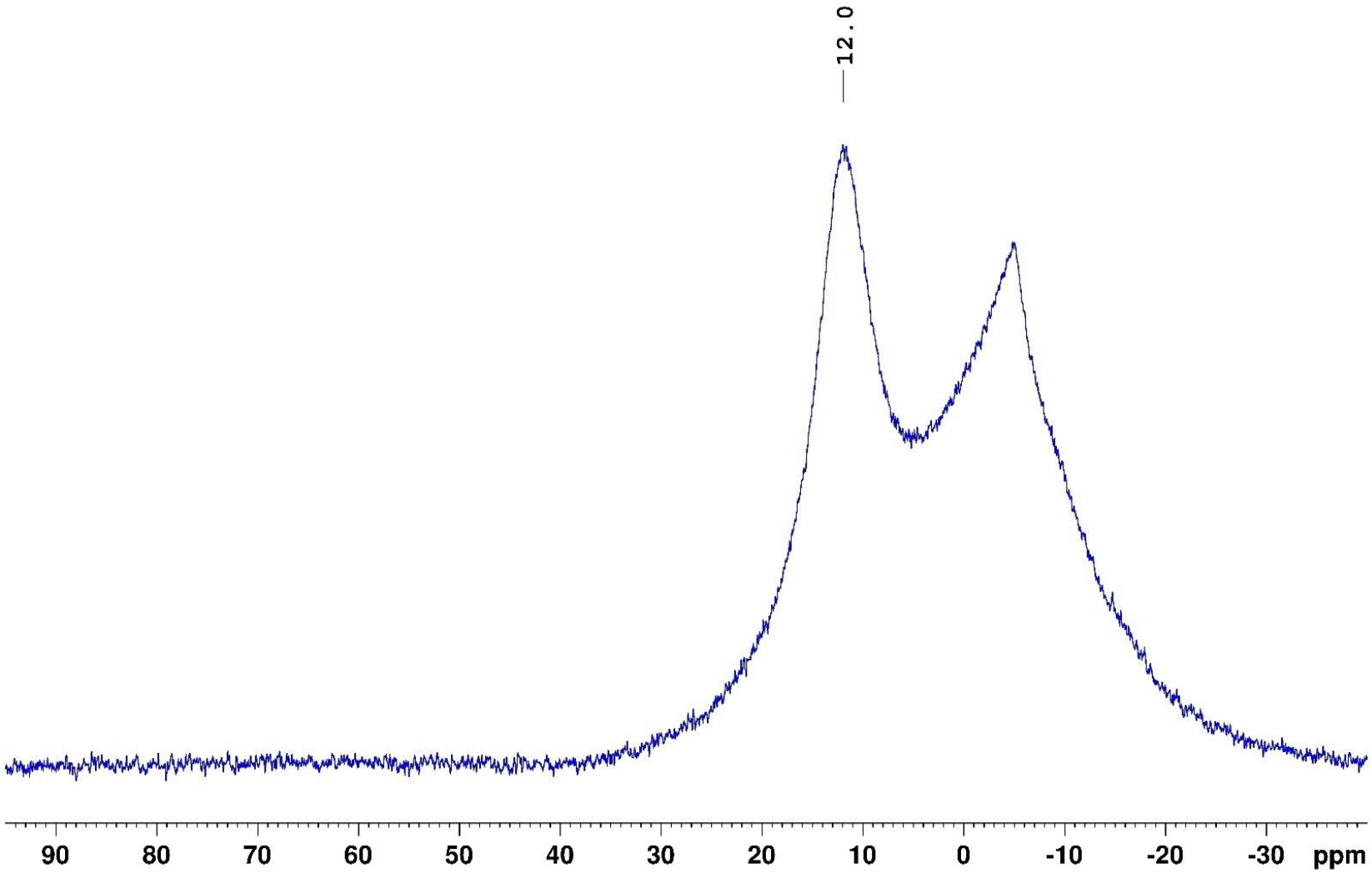


Figure S46. $^{11}B\{^{1}H\}$ NMR spectrum of **3-Mo2** in d_8-THF.

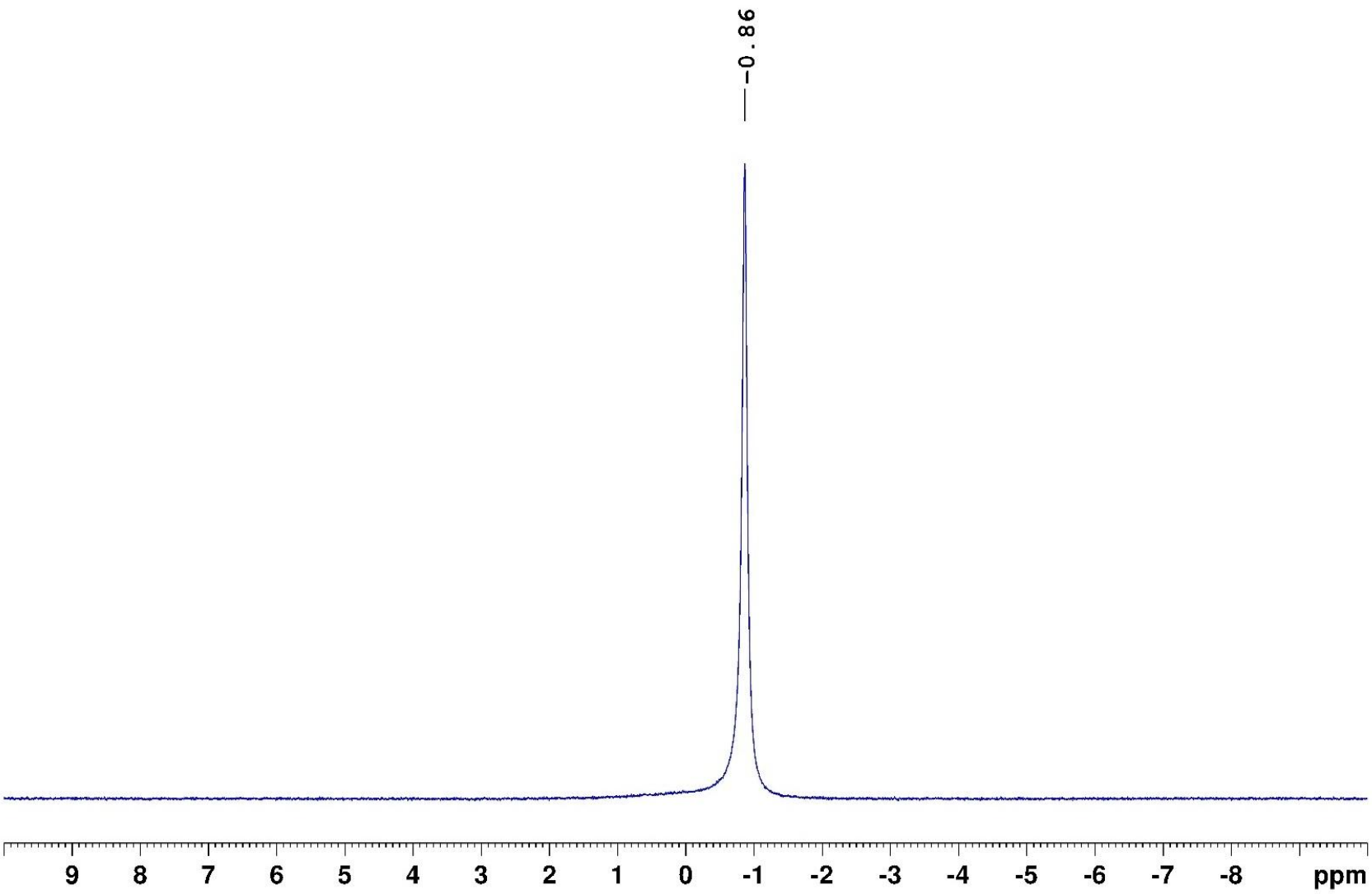


Figure S47. $^{7}Li\{^{1}H\}$ NMR spectrum of **3-Mo$_2$** in d_8-THF.

IR spectra

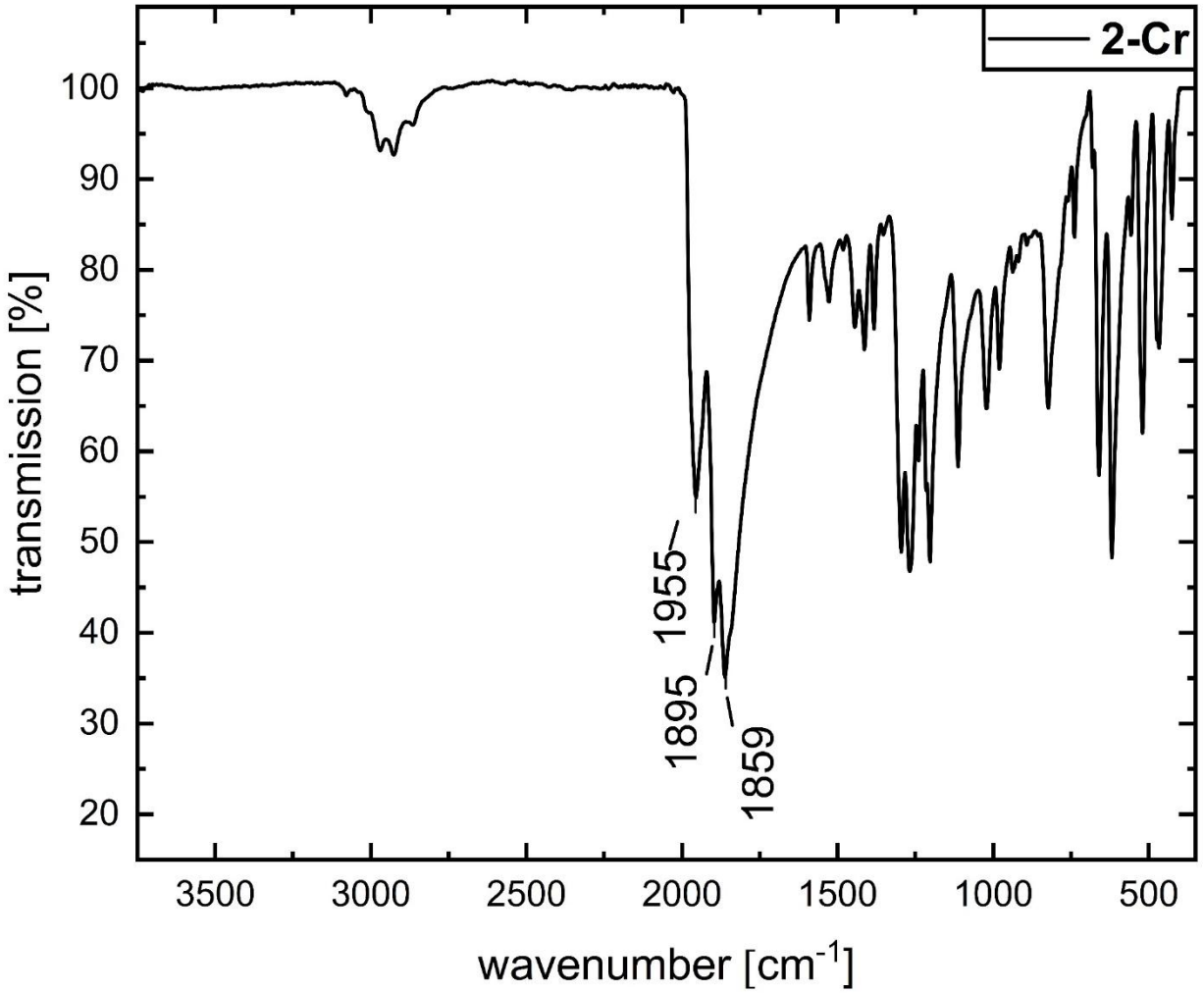


Figure S48. Solid-state IR spectrum of **2-Cr**.

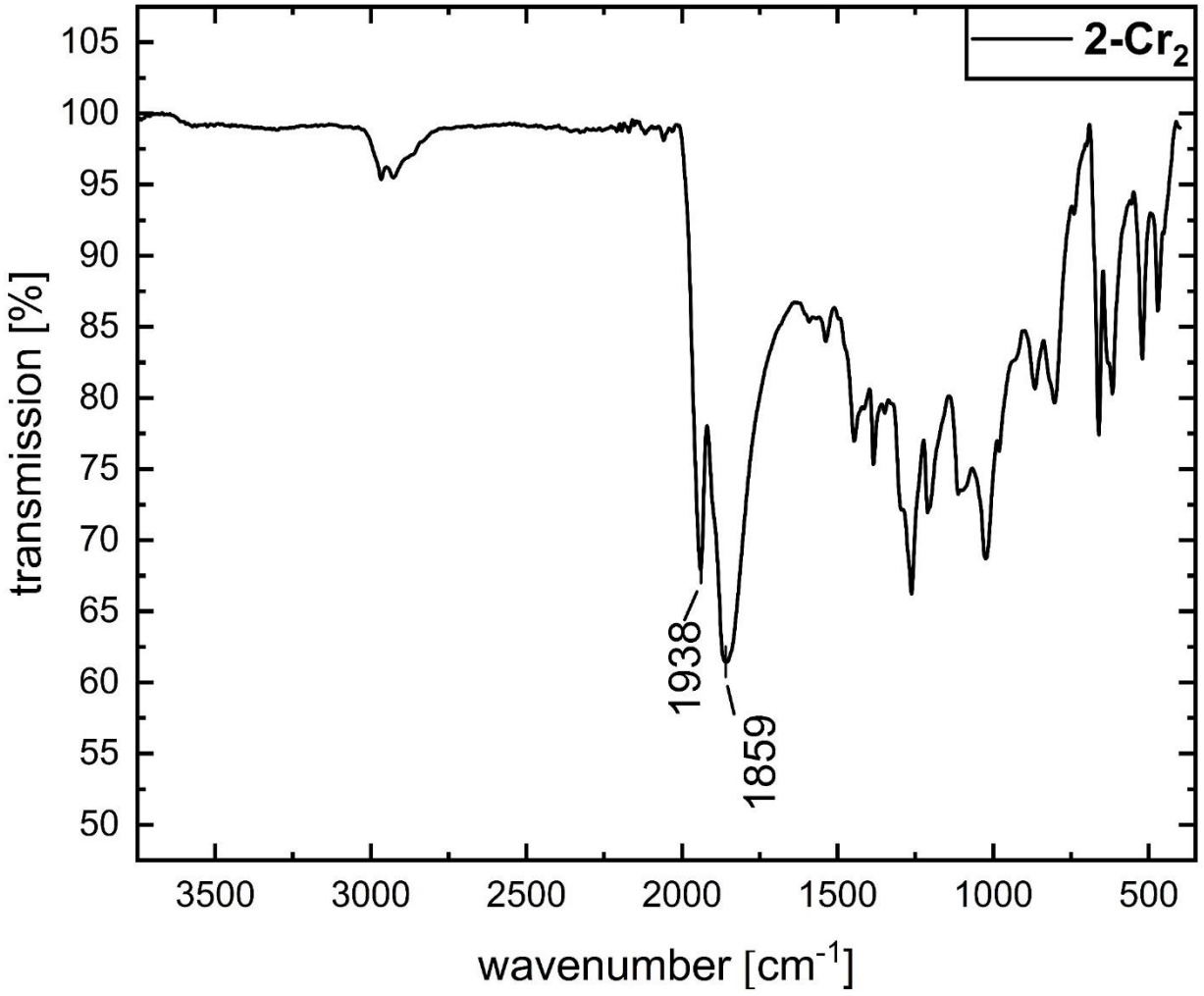


Figure S49. Solid-state IR spectrum of **2-Cr2**.

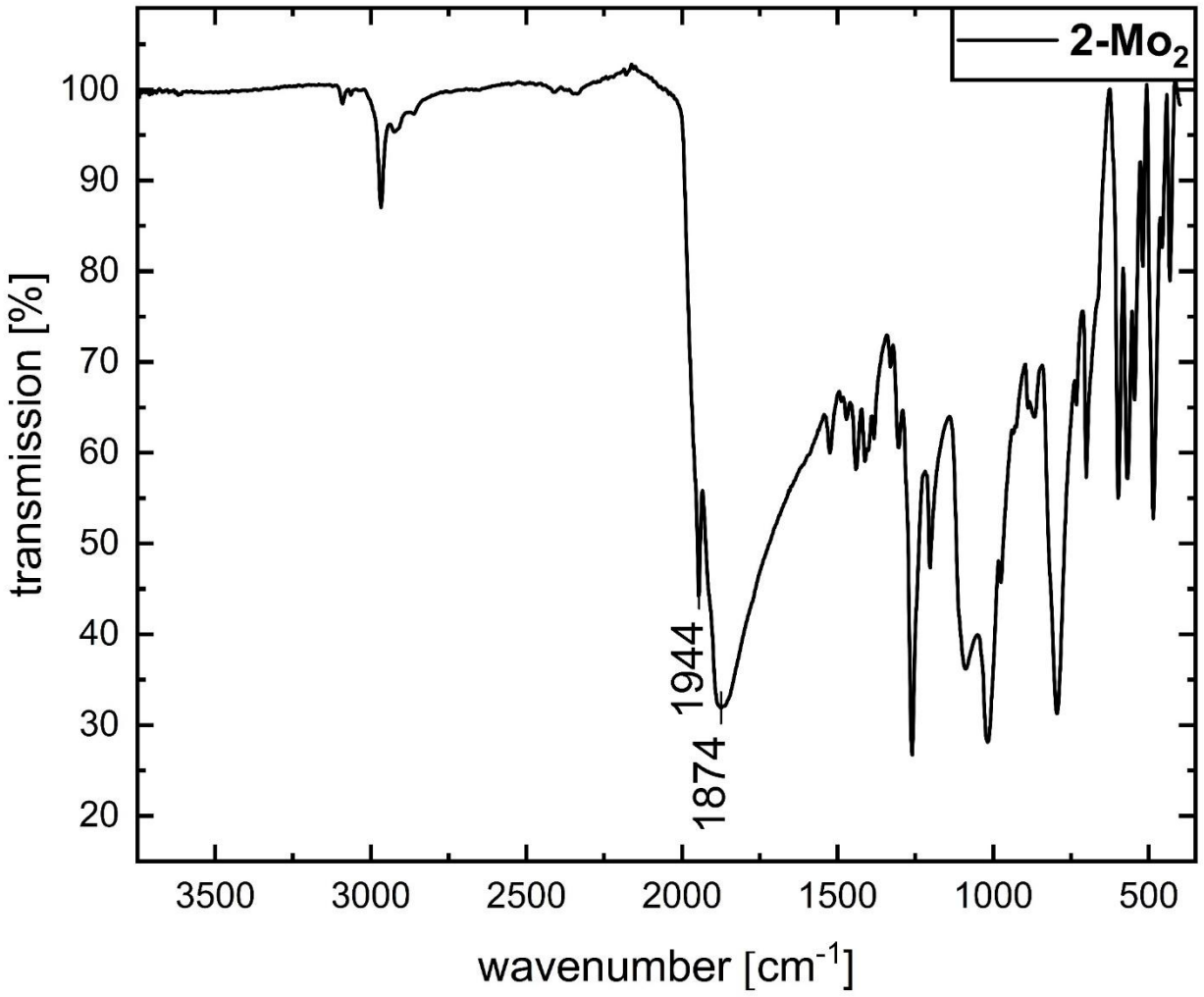


Figure S50. Solid-state IR spectrum of **2-Mo2**.

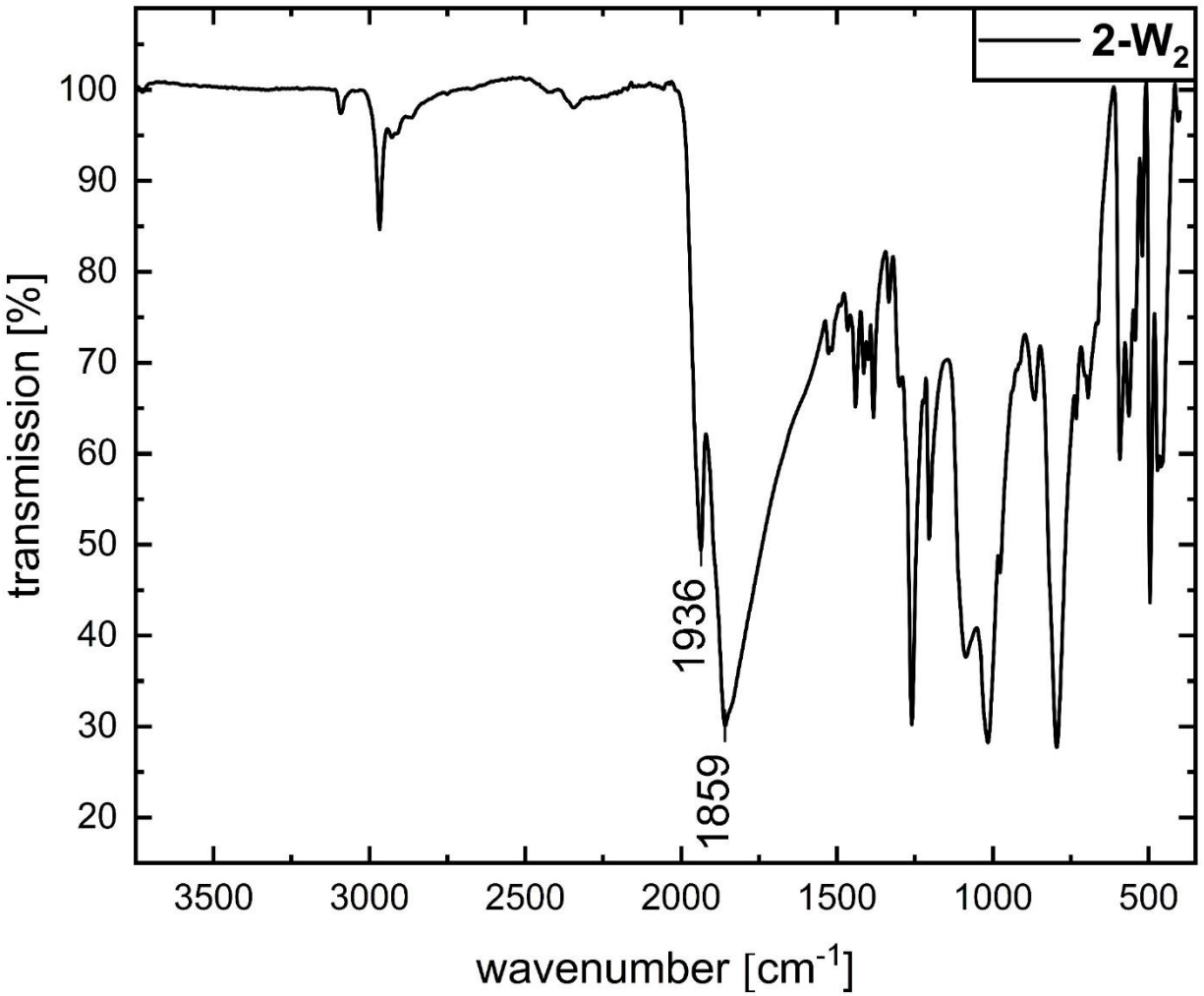


Figure S51. Solid-state IR spectrum of **2-W₂**.

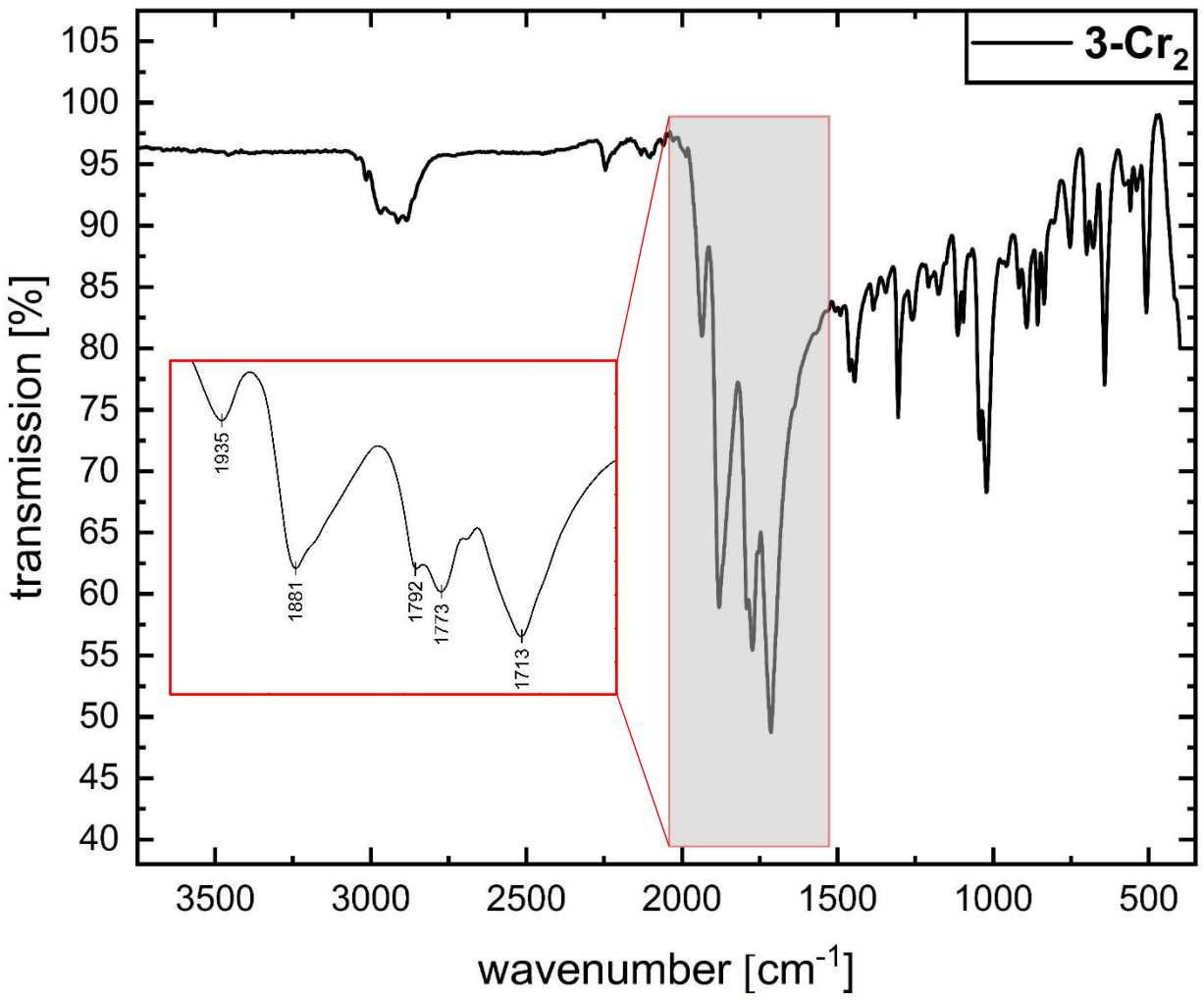


Figure S52. Full solid-state IR spectrum and zoomed-in C=O stretching region (insert) of **3-Cr2**.

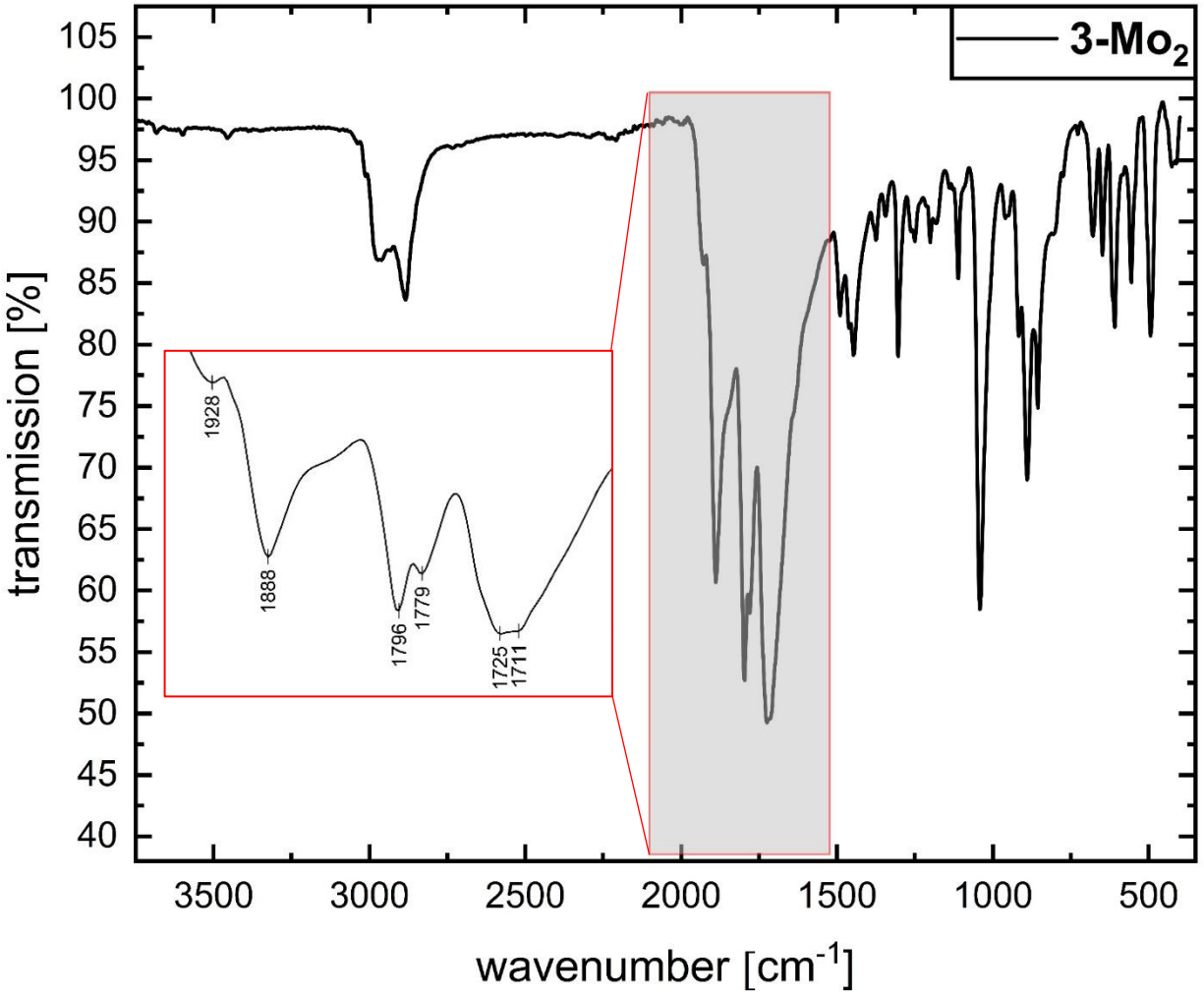


Figure S53. Full solid-state IR spectrum and zoomed-in C=O stretching region (insert) of **3-Mo$_2$**.

UV-vis spectra

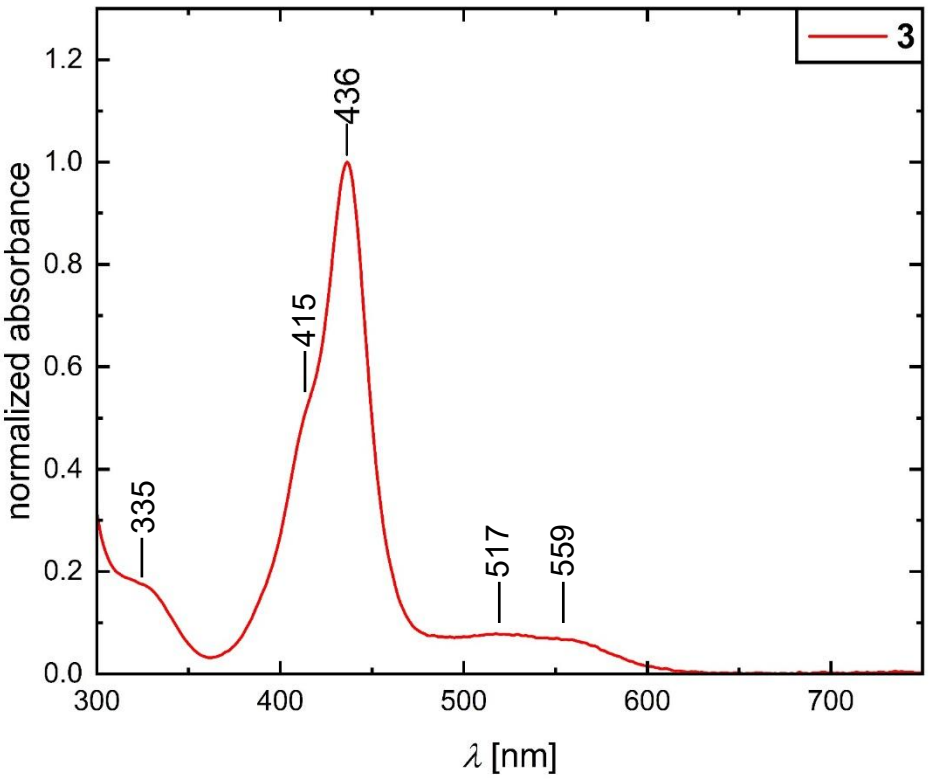


Figure S54. UV-vis absorption spectrum of **3** in THF. λ_{max} = 436, λ_2 = 335, λ_3 = 415 (shoulder), λ_4 = 517 (broad), λ_4 = 559 (broad) nm.

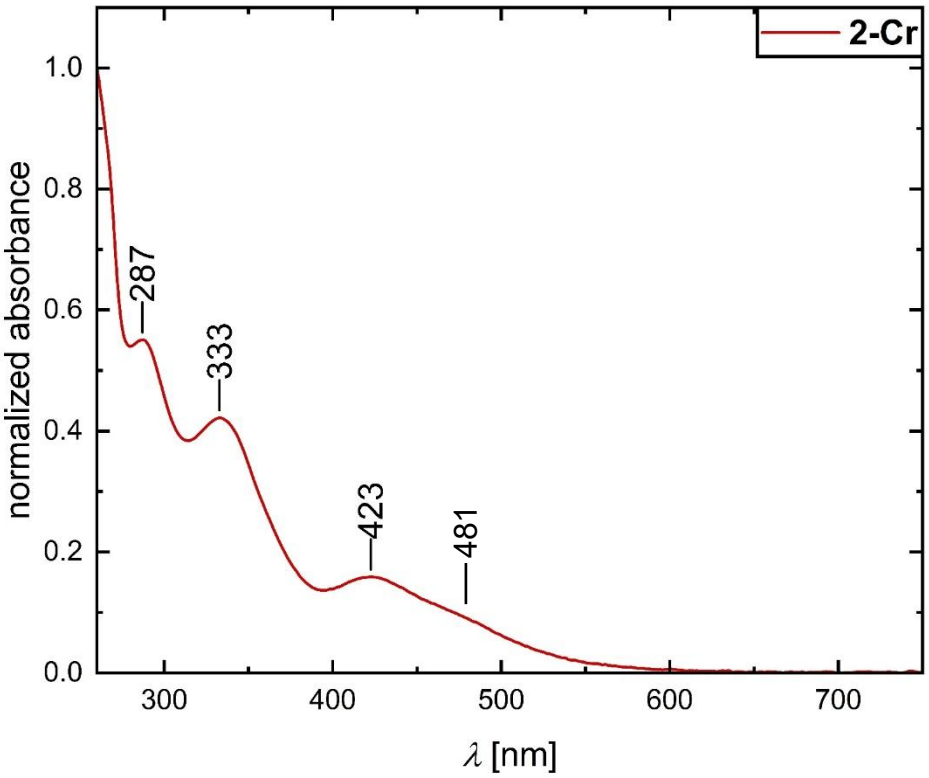


Figure S55. UV-vis absorption spectrum of **2-Cr** in THF. λ_{max} = 287, λ_2 = 333, λ_3 = 423, λ_4 = 481 (broad shoulder) nm.

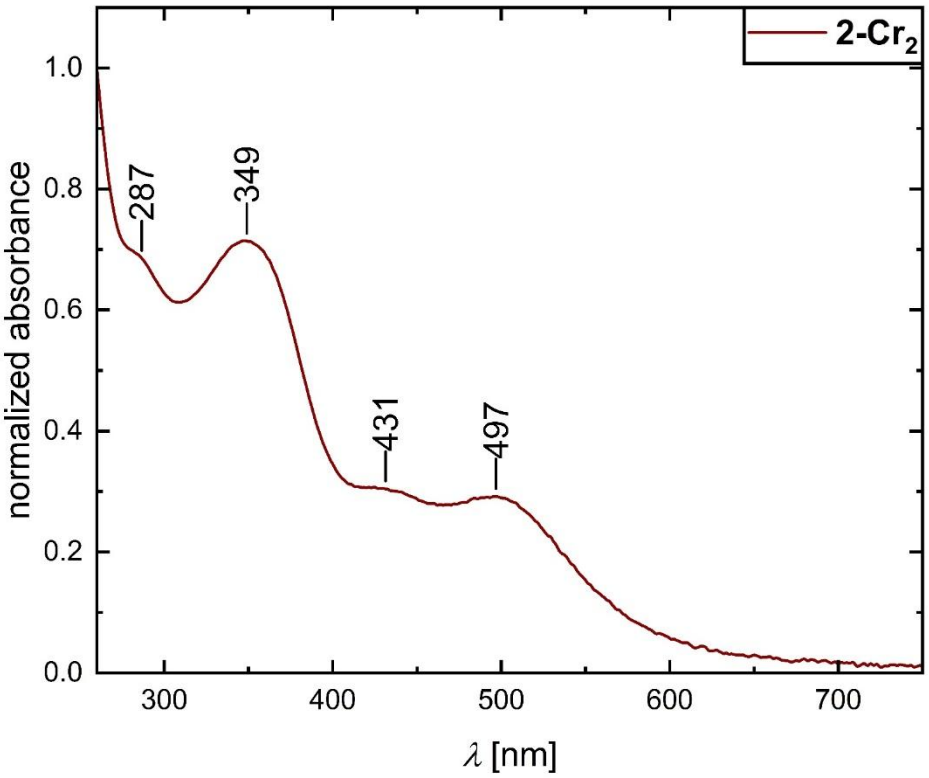


Figure S56. UV-vis absorption spectrum of **2-Cr$_2$** in THF. λ_{max} = 349 (broad), λ_2 = 287 (shoulder), λ_3 = 431 (broad), λ_4 = 497 (very broad) nm.

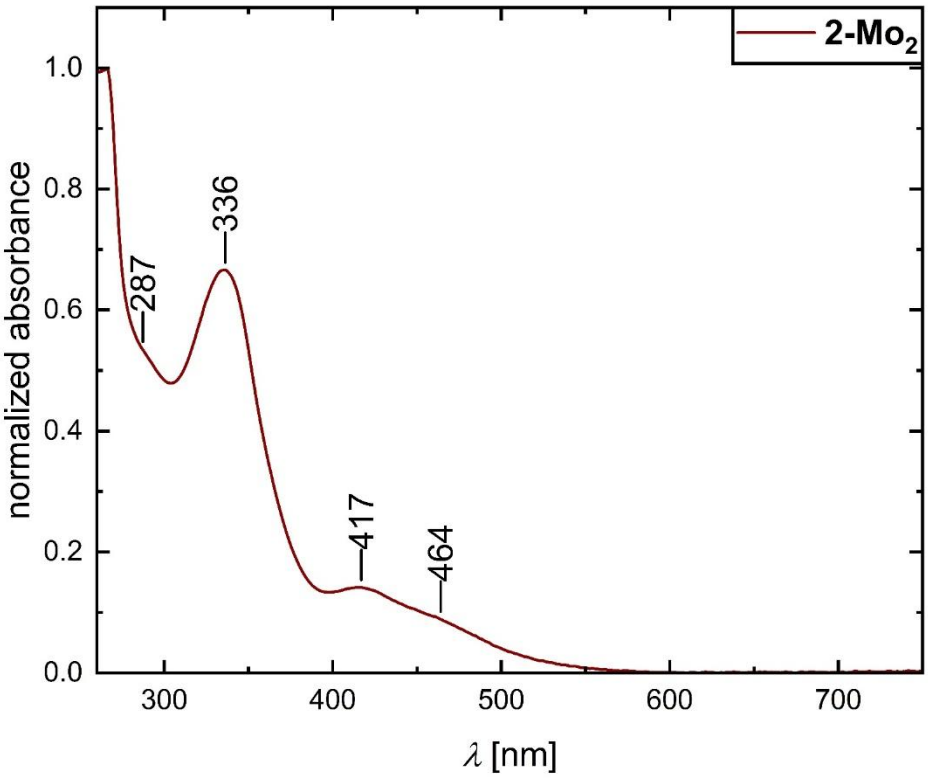


Figure S57. UV-vis absorption spectrum of **2-Mo₂** in THF. $\lambda_{max} = 336$, $\lambda_2 = 287$ (shoulder), $\lambda_3 = 417$, $\lambda_4 = 464$ (broad shoulder) nm.

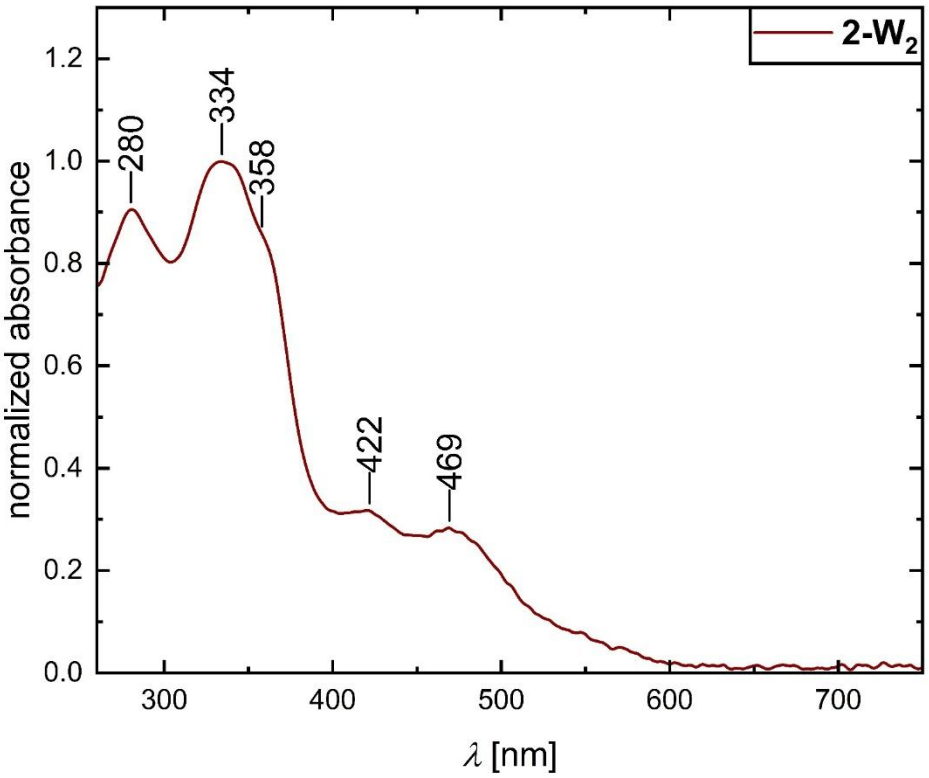


Figure S58. UV-vis absorption spectrum of **2-W₂** in THF. $\lambda_{max} = 334$, $\lambda_2 = 280$, $\lambda_3 = 358$ (shoulder), $\lambda_4 = 422$ (shoulder), $\lambda_5 = 469$ (very broad) nm.

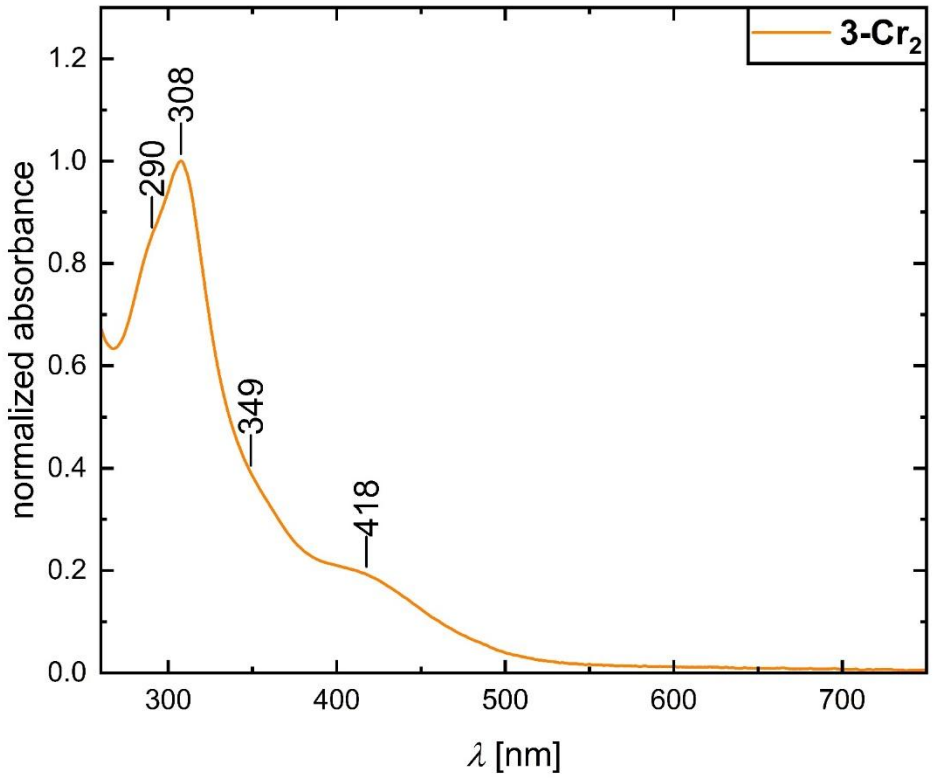


Figure S59. UV-vis absorption spectrum of **3-Cr$_2$** in THF. λ_{max} = 308, λ_2 = 290 (shoulder), λ_3 = 349 (shoulder), λ_4 = 418 (very broad) nm.

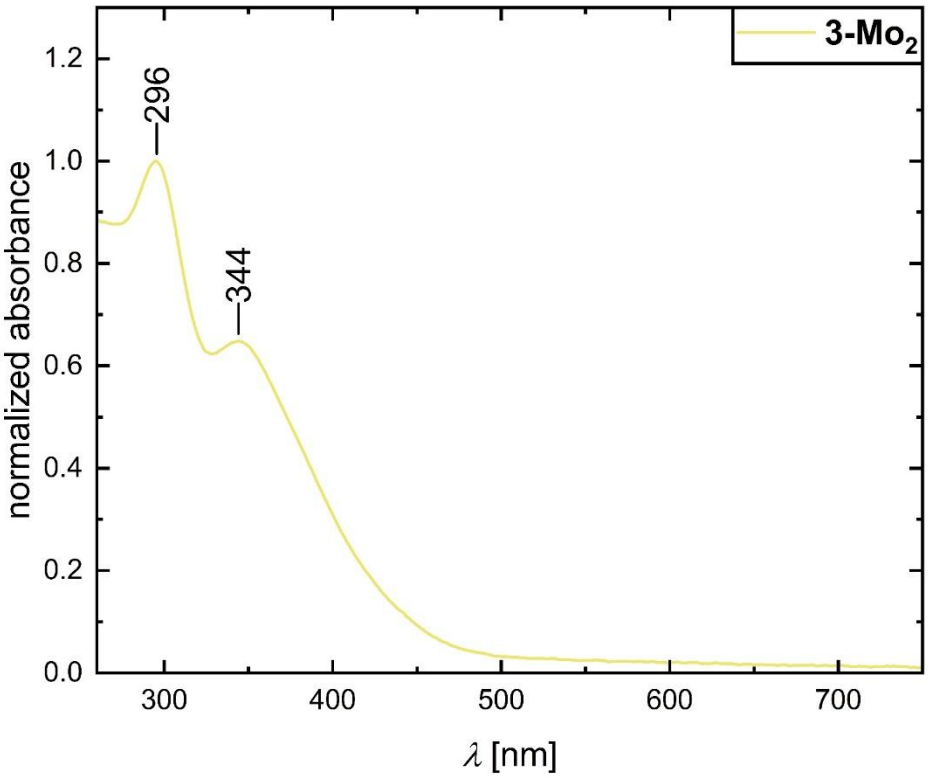


Figure S60. UV-vis absorption spectrum of **3-Mo2** in THF. λ_{max} = 296, λ_2 = 344 (broad tailing) nm.

Cyclic voltammetry

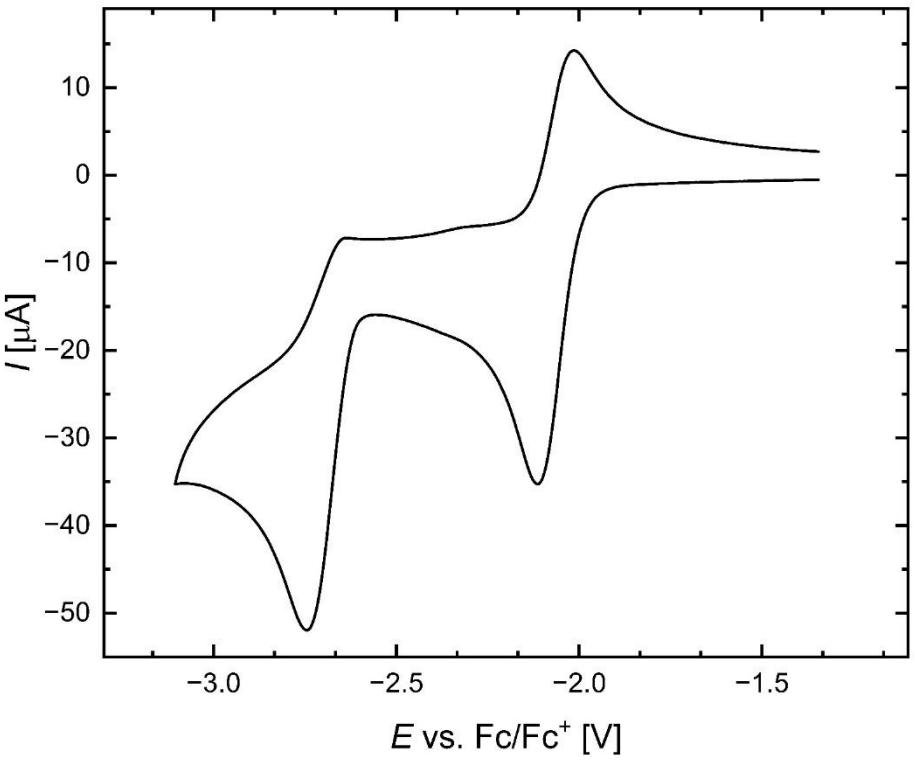


Figure S61. Cyclic voltammogram of **2** in THF/0.1 M [nBu$_4$N][PF$_6$] measured at 250 mV s^{-1} with voltammetric response. Formal potentials: $E_{1/2}$ = −2.06 V, E^{pc} = −2.71 V.

X-ray crystallographic data

All crystal data were collected on a Rigaku XtaLAB Synergy-R diffractometer with a Hybrid Pixel array detector and multi-layer mirror monochromated $Cu_{K\alpha}$ radiation. The structures were solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions unless otherwise stated.

Crystallographic data has been deposited at the Cambridge Crystallographic Data Center as supplementary publication with deposition numbers 2538786-2538794. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S1. CCDC numbers of crystallographically characterised compounds.

Compound	CCDC number
1	2538786
2	2538789
2-Cr	2538793
2-Cr_2	2538790
2-Mo_2	2538791
2-W_2	2538788
3	2538792
3-Cr_2	2538794
3-Mo_2	2538787

Crystal data for 1: $C_{16}H_{16}B_2Br_2$, M_r = 389.73, yellow plate, 0.150×0.100×0.020 mm^3, triclinic space group $P\bar{1}$, a = 9.6057(3) Å, b = 9.6622(4) Å, c = 10.3382(4) Å, α = 63.110(4)°, β = 88.157(3)°, γ = 66.225(4)°, V = 769.77(6) Å^3, Z = 2, ρ_{calcd} = 1.681 g·cm^{-3}, μ = 6.530 mm^{-1}, $F(000)$ = 384, T = 100(2) K, R_1 = 0.0484, wR_2 = 0.1301, 2886 independent reflections [$2\theta \leq 140.144°$] and 185 parameters.

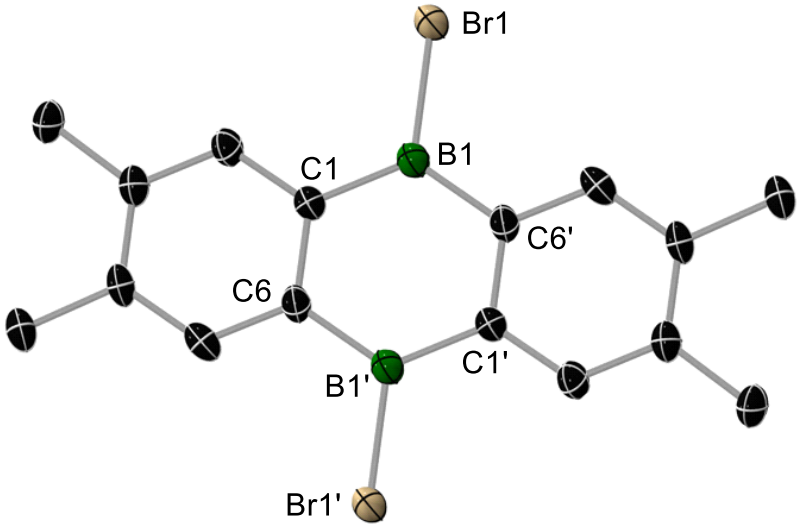


Figure S62. Crystallographically determined solid-state structure of one of the two centrosymmetric molecules of **1** present in the asymmetric unit. Hydrogen atoms are omitted for clarity.

Crystal data for 2: $C_{18}H_{22}B_2$, M_r = 259.97, colourless plate, 0.230×0.110×0.030 mm^3, triclinic space group $P\bar{1}$, a = 8.3196(3) Å, b = 9.7359(3) Å, c = 10.7962(3) Å, α = 69.942(3)°, β = 75.684(3)°, γ = 66.726(3)°, V = 748.24(5) Å^3, Z = 2, ρ_{calcd} = 1.154 g·cm^{-3}, μ = 0.459 mm^{-1}, F(000) = 280, T = 100(2) K, R_1 = 0.0708, wR_2 = 0.1852, 2988 independent reflections [2$\theta \leq$150.804°] and 187 parameters.

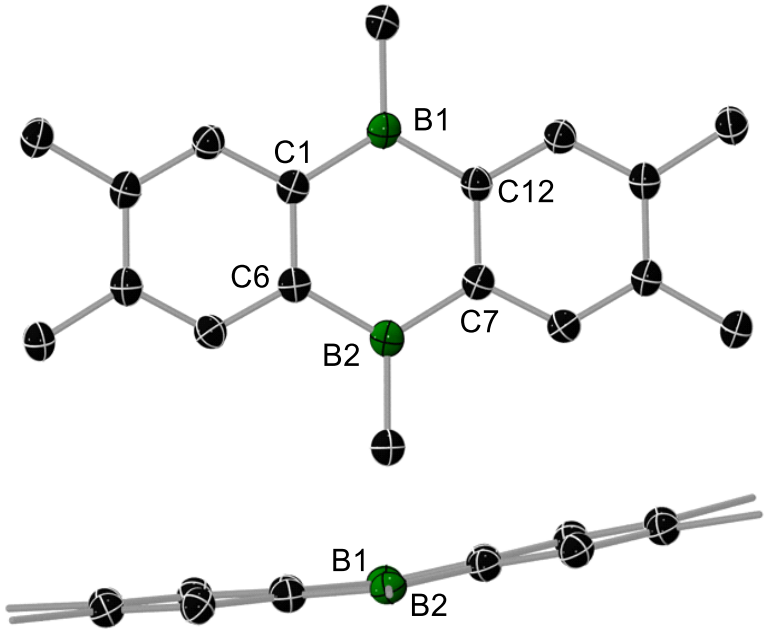


Figure S63. Top: crystallographically determined solid-state structure of **2**. Bottom: side view of **2** (methyl group ellipsoids omitted for clarity) showing the bend in the C_4B_2 ring. Atomic displacement ellipsoids are set at 50%. Hydrogen atoms are omitted for clarity.

Refinement details for 3: The data was twinned (ca. 10%) but could not by satisfactorily solved as such, and was therefore integrated as a single crystal, hence the high wR_2 value. Some reflections were removed from refinement as outliers: (1 4 10), (1 3 5), (0 1 1), (-4 0 8) and (-6 0 12). The two Li-bound THF molecules were both modelled as twofold disordered in a 39:61 ratio. ADPs within the $Li(THF)_2$ fragment were restrained to similarity using SIMU 0.01.

Crystal data for 3: $C_{34}H_{54}B_2Li_2O_4$, $M_r = 562.27$, red block, 0.180×0.140×0.120 mm^3, monoclinic space group $P2_1/c$, $a = 8.7241(2)$ Å, $b = 9.44190(10)$ Å, $c = 19.9924(4)$ Å, $\beta = 96.948(2)°$, $V = 1634.72(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.142$ g·cm^{-3}, $\mu = 0.539$ mm^{-1}, $F(000) = 612$, $T = 100(2)$ K, $R_1 = 0.0803$, $wR_2 = 0.2148$, 3100 independent reflections [$2\theta \leq 140.12°$] and 284 parameters.

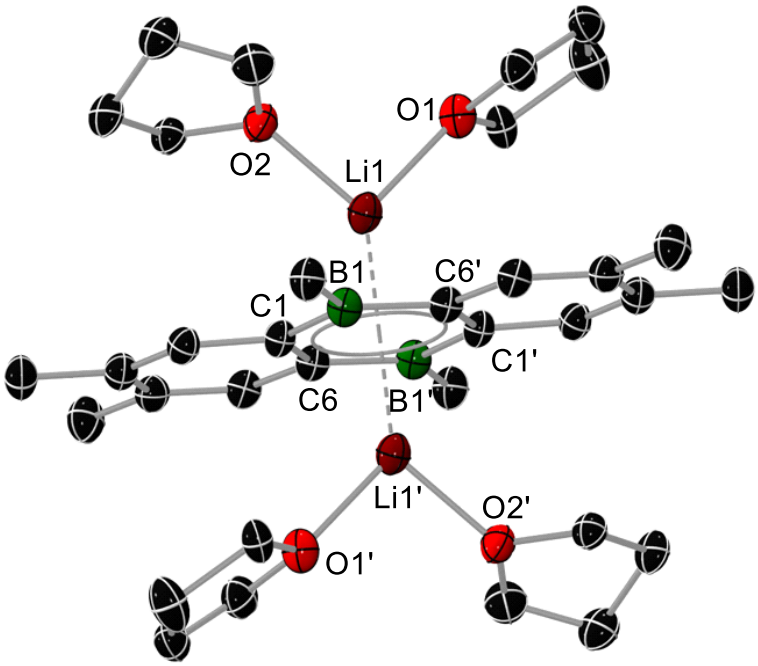


Figure S64. Crystallographically determined solid-state structure of **3**. Atomic displacement ellipsoids are set at 50%. Hydrogen atoms are omitted for clarity.

Crystal data for 2-Cr: $C_{21}H_{22}B_2CrO_3$, $M_r = 396.00$, red block, 0.300×0.140×0.070 mm^3, monoclinic space group $P2_1/n$, $a = 10.14580(10)$ Å, $b = 13.7582(2)$ Å, $c = 13.59200(10)$ Å, $\beta = 91.0970(10)°$, $V = 1896.93(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.387$ g·cm^{-3}, $\mu = 5.102$ mm^{-1}, $F(000) = 824$, $T = 100(2)$ K, $R_1 = 0.0708$, $wR_2 = 0.1844$, 3609 independent reflections [$2\theta \leq 140.06°$] and 250 parameters.

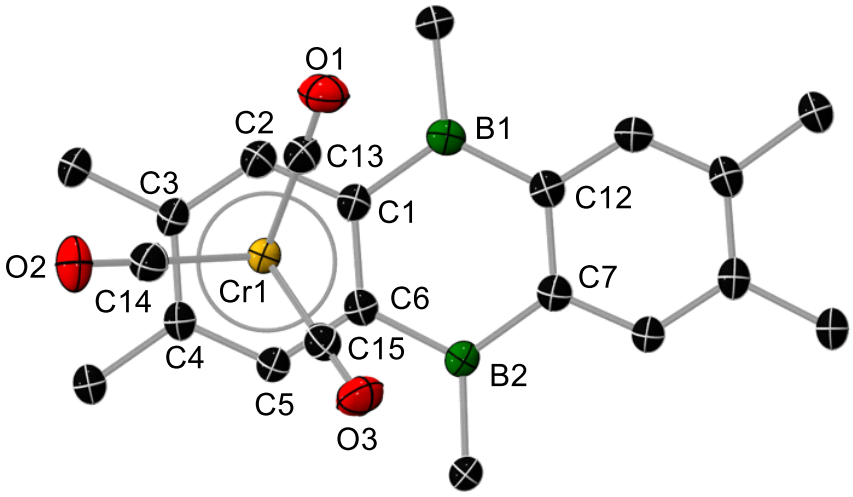


Figure S65. Crystallographically determined solid-state structure of **2-Cr**. Atomic displacement ellipsoids are set at 50%. Hydrogen atoms are omitted for clarity.

Refinement details for 2-Cr$_2$: The data showed multiple minor twinning components amounting to less than 20% overall, which could not be solved satisfactorily. As a result, only data from the major twin component was used for structure solution and refinement. One reflection was removed from refinement as an outlier: (1 16 5).

Crystal data for 2-Cr$_2$: $C_{24}H_{22}B_2Cr_2O_6$, $M_r = 532.03$, red block, 0.160×0.090×0.060 mm^3, monoclinic space group $I2/a$, $a = 12.6159(2)$ Å, $b = 13.9295(2)$ Å, $c = 14.9564(3)$ Å, $\beta = 114.150(2)°$, $V = 2398.30(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.473$ g·cm^{-3}, $\mu = 7.785$ mm^{-1}, $F(000) = 1088$, $T = 100(2)$ K, $R_1 = 0.0641$, $wR_2 = 0.1396$, 2271 independent reflections [$2\theta \leq 140.148°$] and 157 parameters.

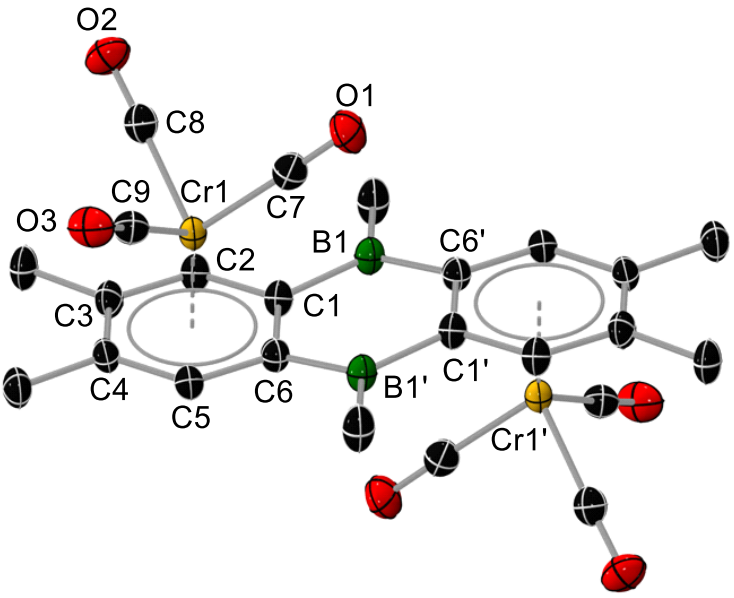


Figure S66. Crystallographically determined solid-state structure of **2-Cr$_2$**. Atomic displacement ellipsoids are set at 50%. Hydrogen atoms are omitted for clarity.

Refinement details for 2-Mo$_2$: Three reflections were omitted as outliers: (-2 4 13), (-2 6 13) and (-2 2 13).

Crystal data for 2-Mo$_2$: $C_{24}H_{22}B_2Mo_2O_6$, M_r = 619.91, red block, 0.090×0.050×0.020 mm^3, monoclinic space group $P2_1/n$, a = 8.49810(10) Å, b = 10.5870(2) Å, c = 13.5435(2) Å, β = 101.946(2)°, V = 1192.11(3) Å^3, Z = 2, ρ_{calcd} = 1.727 g·cm^{-3}, μ = 8.939 mm^{-1}, F(000) = 616, T = 100(2) K, R_1 = 0.0305, wR_2 = 0.0724, 2381 independent reflections [2θ≤147.542°] and 157

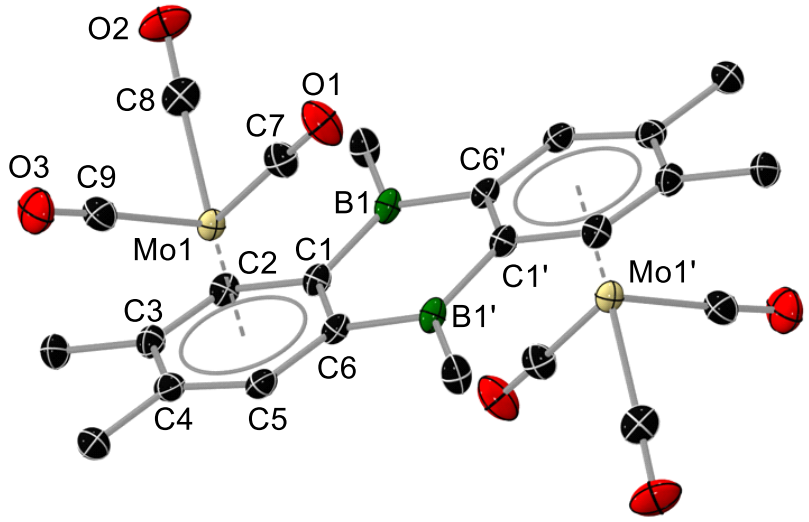


Figure S67. Crystallographically determined solid-state structure of **2-Mo$_2$**. Atomic displacement ellipsoids are set at 50%. Hydrogen atoms are omitted for clarity.

Crystal data for 2-W₂: $C_{24}H_{22}B_2O_6W_2$, $M_r = 795.73$, red block, 0.160×0.070×0.040 mm^3, monoclinic space group $P2_1/n$, $a = 7.10870(10)$ Å, $b = 10.15770(10)$ Å, $c = 16.8094(2)$ Å, $\beta = 93.3110(10)°$, $V = 1211.75(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.181$ g·cm^{-3}, $\mu = 17.607$ mm^{-1}, $F(000) = 744$, $T = 100(2)$ K, $R_1 = 0.0322$, $wR_2 = 0.0850$, 2426 independent reflections [$2\theta \leq 149.944°$] and 157 parameters.

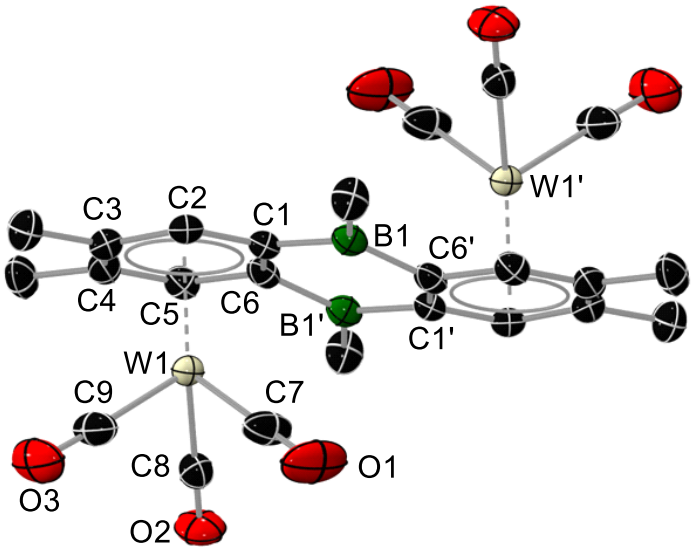


Figure S68. Crystallographically determined solid-state structure of **2-W₂**. Atomic displacement ellipsoids are set at 50%. Hydrogen atoms are omitted for clarity.

Refinement details for 3-Cr$_2$: The asymmetric unit contains two crystallographically distinct molecules of the complex. One CO ligand of the second molecule was modelled as twofold disordered (RESI 21/22 CO) in a 1:1 ratio without additional restraints. All twelve Li-bound THF molecules were modelled as disordered using a total of 13 FVAR in the following ratios: molecule 1 at Li1: (RESI 5/51 THF) 61:39, (RESI 6/61 THF) 50:50, (RESI 7/71 THF) 65:35; molecule 1 at Li2: (RESI 8/81 THF) 69:31, (RESI 9/91 THF) 58:42, (RESI 10/110 THF) 77:33; molecule 2 at Li1: (RESI 11/111 THF) 65:35, (RESI 12/112 THF) 63:33, (RESI 13/113/213 THF) 50:38:12; molecule 2 at Li2: (RESI 14/114 THF) 61:39, (RESI 15/115/215 THF) 44:36:20, (RESI 16/116 THF) 54:46. ADPs within the THF disorders were restrained to similarity with SIMU 0.01, 1,2- and 1,3-distances with SAME.

Crystal data for 3-Cr$_2$: $C_{48}H_{70}B_2Cr_2Li_2O_{12}$, $M_r = 978.54$, orange block, 0.310×0.220×0.160 mm^3, monoclinic space group $P2_1/c$, $a = 41.931(2)$ Å, $b = 10.3833(5)$ Å, $c = 23.8066(12)$ Å, $\beta = 104.726(4)°$, $V = 10024.4(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.297$ g·cm^{-3}, $\mu = 4.046$ mm^{-1}, $F(000) = 4144$, $T = 100(2)$ K, $R_1 = 0.0401$, $wR_2 = 0.1040$, 19053 independent reflections [$2\theta \leq 140.138°$] and 1863 parameters.

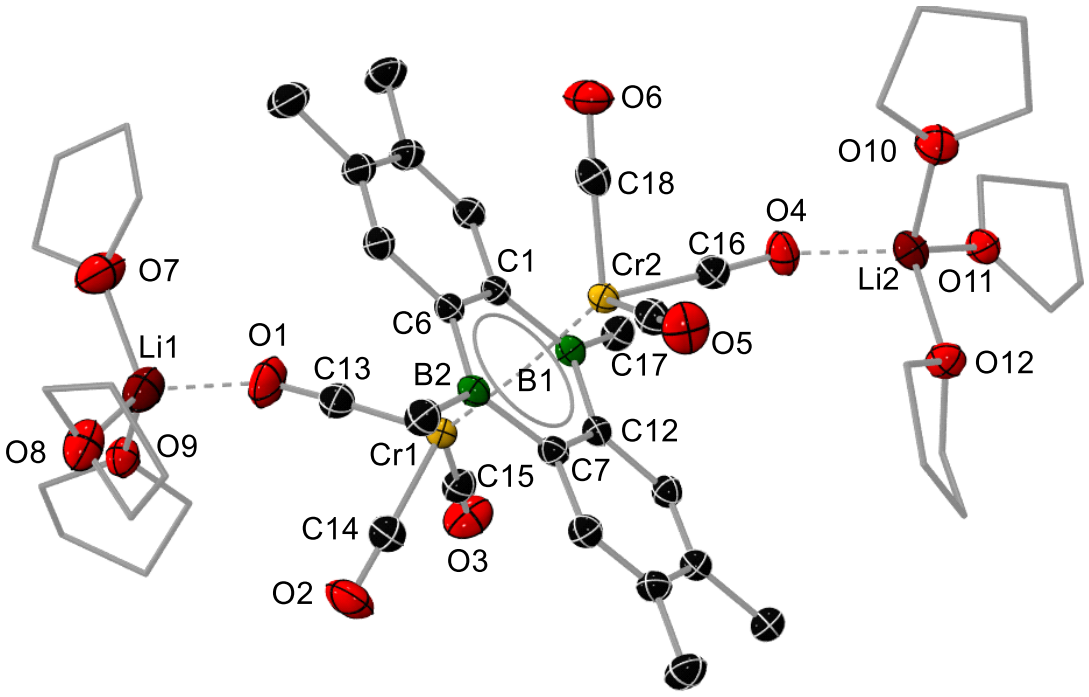


Figure S69. Crystallographically determined solid-state structure of one of the two crystallographically distinct molecules of **3-Cr$_2$** present in the asymmetric unit. Atomic displacement ellipsoids are set at 50%. Hydrogen atoms are omitted for clarity.

Refinement details for 3-Mo$_2$: The crystal was partially twinned (<10% non-overlapping reflections) but the twinning could not be resolved satisfactorily. Seven outlying reflections had to be omitted: (-5 1 25), (-10 0 20), (-10 1 1), (-11 2 25), (-6 0 24), (-14 0 26) and (-13 1 25). The asymmetric unit contains two crystallographically distinct molecules of the complex. One CO ligand of the second molecule was modelled as twofold disordered (RESI 44/444 CO) in a 60:40 ratio. ADPs within this disorder were restrained to similarity with Mo1_4 using SIMU 0.01. All twelve Li-bound THF molecules were modelled as disordered using a total of 9 FVAR in the following ratios: molecule 1 at Li1: (RESI 5/51 THF) 71:29, (RESI 6/61 THF) 70:30, (RESI 7/71 THF) 67:33; molecule 1 at Li2: (RESI 8/81 THF) 57:43, (RESI 9/91 THF) 60:40, (RESI 10/101 THF) 78:22; molecule 2 at Li1: (RESI 11/111 THF) 60:40, (RESI 12/121 THF) 61:41, (RESI 13/131 THF) 75:25; molecule 2 at Li2: (RESI 14/141 THF) 61:39, (RESI 15/151 THF) 60:40, (RESI 16/116 THF) 60:40. ADPs within the THF disorders were restrained to similarity with SIMU 0.008, 1,2- and 1,3-distances with SAME. The Li2–O8/81 and Li2–O15/151 distances were restrained to similarity using SADI 0.005.

Crystal data for 3-Mo$_2$: $C_{48}H_{70}B_2Li_2Mo_2O_{12}$, M_r = 1066.42, yellow plate, 0.350×0.290×0.150 mm^3, monoclinic space group $P2_1/c$, a = 42.0401(4) Å, b = 10.40700(10) Å, c = 24.2315(2) Å, β = 105.1540(10)°, V = 10232.90(17) Å^3, Z = 8, ρ_{calcd} = 1.384 g·cm^{-3}, μ = 4.480 mm^{-1}, F(000) = 4432, T = 100(2) K, R_1 = 0.0732, wR_2 = 0.1589, 19427 independent reflections [2θ≤140.148°] and 1768 parameters.

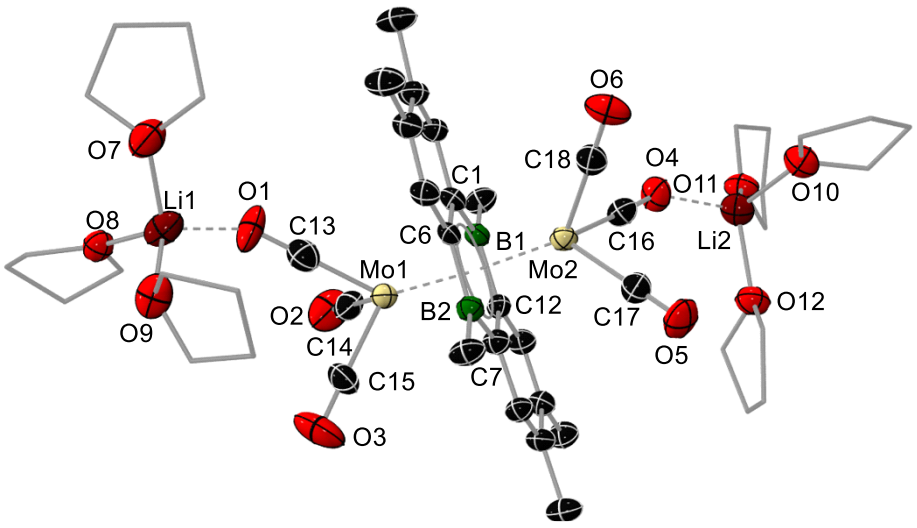


Figure S70. Crystallographically determined solid-state structure of one of the two crystallographically distinct molecules of **3-Mo$_2$** present in the asymmetric unit. Atomic displacement ellipsoids are set at 50%. Hydrogen atoms are omitted for clarity.

Computational details

Density functional theory (DFT) calculations were carried out with Turbomole version 7.9[5] as implemented in the user interface TmoleX2024.[6] Optimizations were carried out at the ωB97X[7]-D4[8]-def2-SVP[9,10] level of theory using the relevant crystallography-derived solid-state structures as starting points, where possible. True minima were confirmed by frequency calculations, which provided no imaginary frequencies. Wiberg bond indices (WBI)[11] and natural bond orbital (NBO)[12] charges were computed within the TmoleX2024 SCF Population Properties module. Bond critical points (BCPs) were calculated using the atoms in molecules (AIM)[13] module implemented in TmoleX2024. Intrinsic bond orbitals (IBOs)[14] were computed with the Turbomole program "proper". Plots of the frontier MOs and IBOs were generated with the TmoleX2024 3D-Visualizer module.

Table S2. Comparison of selected experimental and calculated [in square brackets] structural parameters for **2**, **2-Cr**, **2-Cr$_2$**, **3** and **3-Cr$_2$**. Optimisations carried out at the ωB97X-D4-def2-SVP level of theory.

	$\overline{a/a'}$	$\overline{e/e'}$	$\overline{M\cdots DBA}$	$\overline{M{-}C_{d/e}}$	$\lvert\omega_{max}\rvert$
2	1.565(2) [1.577]	1.419(2) [1.418]	–	–	10.6(2) [6.0]
3	1.531(3) [1.538]	1.472(3) [1.458]	1.87 [1.85]	2.385(4) [1.383][c]	1.1(3) [0.1]
2-Cr	1.573(4) [1.582][a]	1.433(4) [1.428][a]	1.72 [1.68]	2.193(3) [2.184][c]	8.4(4) [4.6]
	1.557(4) [1.572][b]	1.421(4) [1.419][b]		2.263(3) [2.229][d]	
2-Cr$_2$	1.559(3) [1.572]	1.451(3) [1.446]	1.71 [1.68]	2.201(2) [2.184][c]	2.5(3) [1.8]
				2.263(2) [2.230][d]	
3-Cr$_2$[e]	1.551(3) [1.555]	1.457(2) [1.446]	1.78 [1.77]	2.287(2) [2.275]	2.0(2) [0.6]
				2.369(2) [2.355][f]	

[a] Within the metal-containing complex moiety; [b] within the metal-free complex moiety; [c] $\overline{M{-}C_{e/e'}}$; [d] $\overline{M{-}C_{d/d'}}$; [e] values provided for both molecules present in the asymmetric unit; [f] different avg. values measured for the e and e' edges.

NMR shielding calculations for the determination of nuclear-independent chemical shifts (NICS)[15] were carried out at the B3LYP[16]-D4-def2-SVP level of theory on the previously optimised structures. For NICS calculations a dummy atom Q1 was generated at the centre of one of the 9,10-(DH)DBA rings using the TmoleX option "add atom at centre" in the molecule viewer. The entire molecule was then translated so that this Q1 atom would be at the coordinates (0, 0, 0). The entire molecule was then rotated so that corresponding ring would be in the (x, y) plane, before adding two more dummy atoms Q2 and Q3 at the coordinates (0, 0, 1) and (0, 0, –1), respectively. This procedure was repeated for all three (DH)DBA rings, providing a total of nine dummy atoms (Figure S70), three at the ring centres for determining NICS(0) values, and three each at 1 Å above and below the rings, respectively, for determining NICS(1) and NICS(±1)$_{zz}$ values.

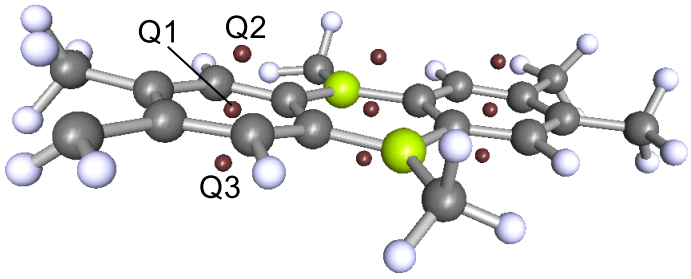


Figure S71. Dummy atoms for NICS calculations added to the optimised structure of compound **2** at the ωB97X-D4-def2-SVP level of theory. Atom colours: white = hydrogen, grey = carbon, green = boron, brown = dummy atoms.

Optimisation of the putative η^6-C_4B_2 isomer of **2-Cr** at the ωB97X-D4-def2-SVP level of theory converges to a minimum for the eclipsed conformation, **2′-Cr** (Figure S71).

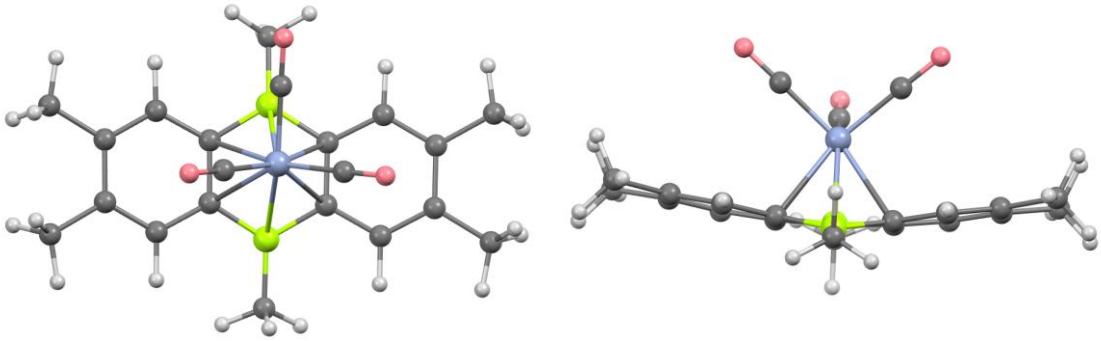


Figure S72. Two views of the optimised structure of **2′-Cr** at the ωB97X-D4-def2-SVP level of theory. Atom colours: white = hydrogen, grey = carbon, green = boron, salmon = oxygen, steel = chromium.

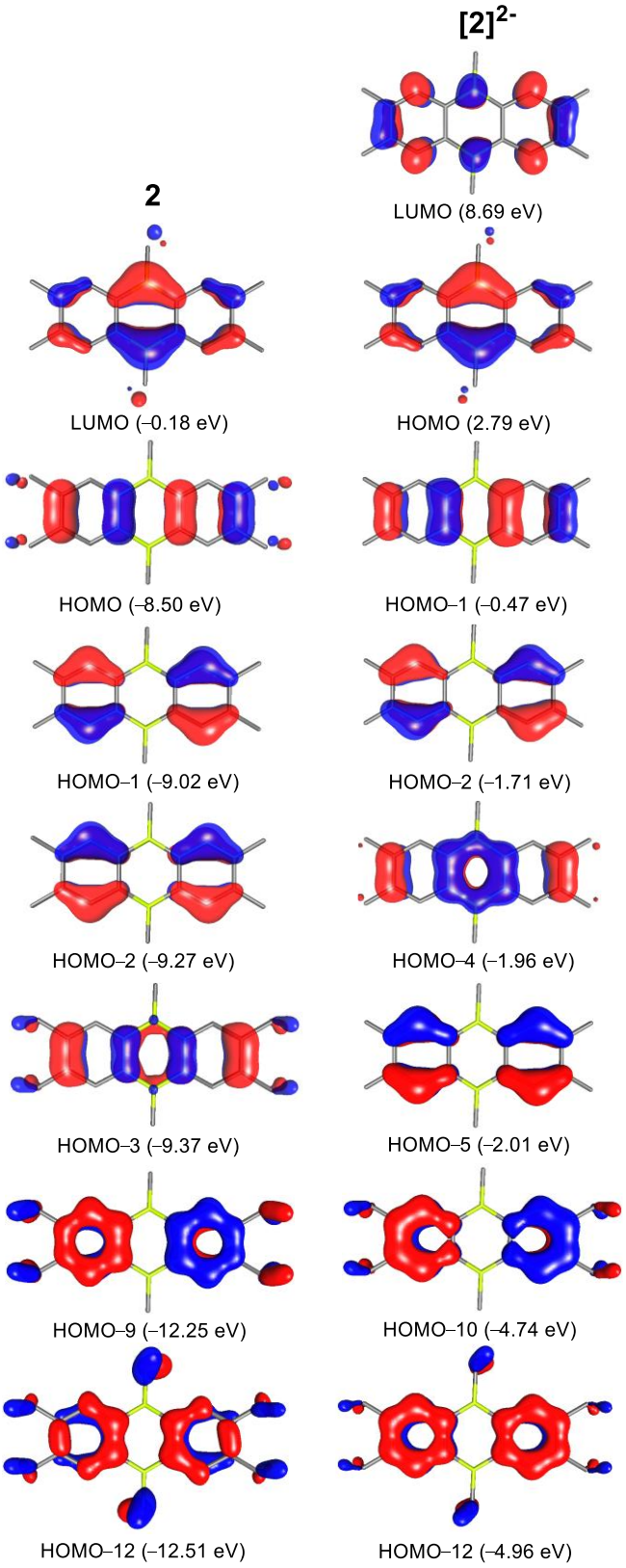


Figure S73. Plots of the frontier MOs of π symmetry of **2** (left) and **[2]**$^{2-}$ (right) with their energy levels in parentheses. Hydrogen atoms omitted for clarity. Isovalues: 0.04.

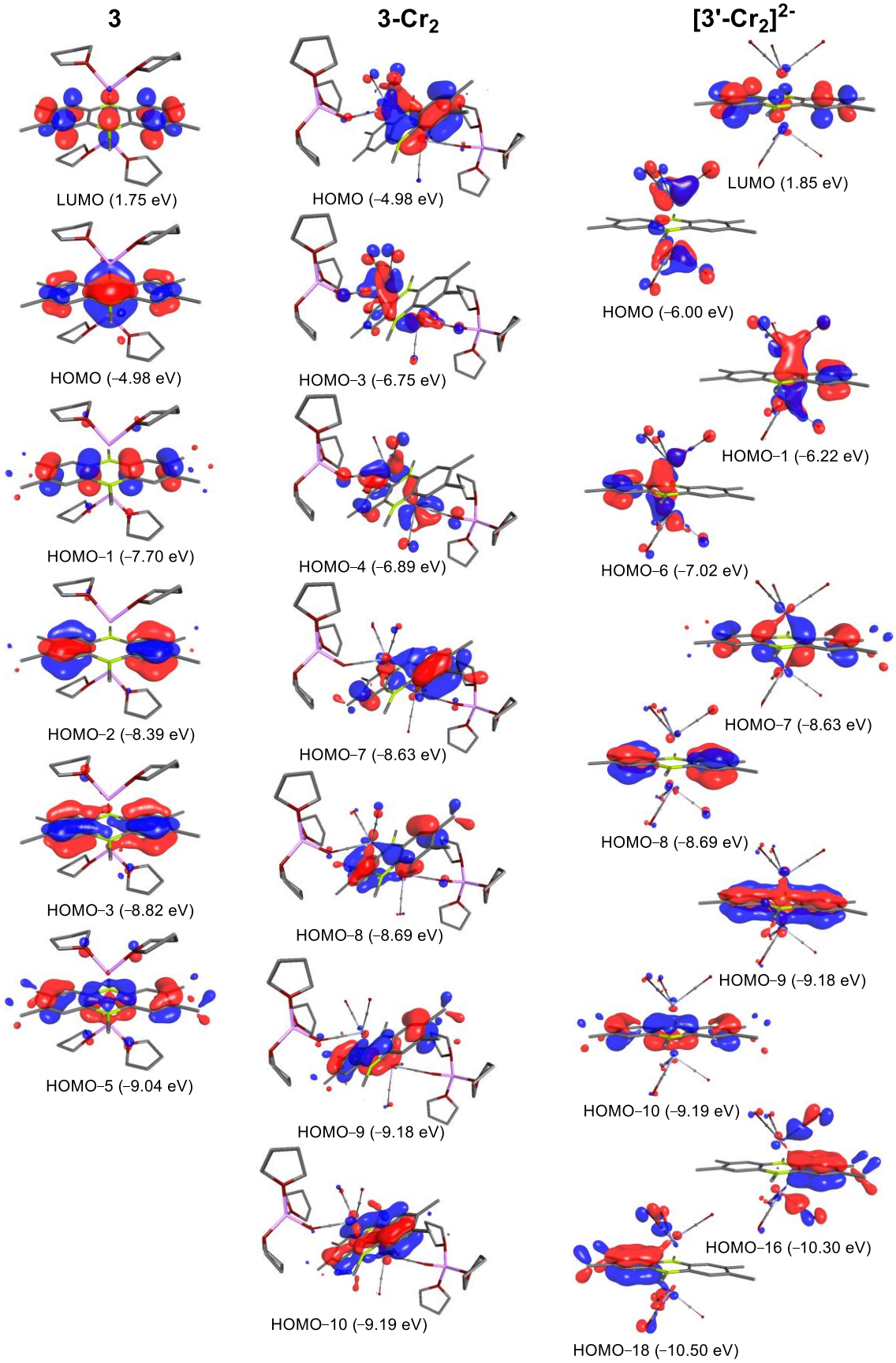


Figure S74. Plots of the frontier MOs of π symmetry of **3** (left), **3-Cr₂** (centre) and **[3′-Cr₂]²⁻** (right) with their energy levels in parentheses. Hydrogen atoms omitted for clarity. Isovalues: 0.04.

To determine the conformational minimum for **2-Cr**, a fixed dummy atom Q was added at the centre of the Cr-capped benzo ring and the C1–Q–Cr1–C5 torsion angle β was fixed to a value between –30° and +30° in 5° increments. At each value of β the geometry was optimised at the ωB97X-D4-def2-SVP level of theory and the final SCF energies plotted against β (Figure S72).

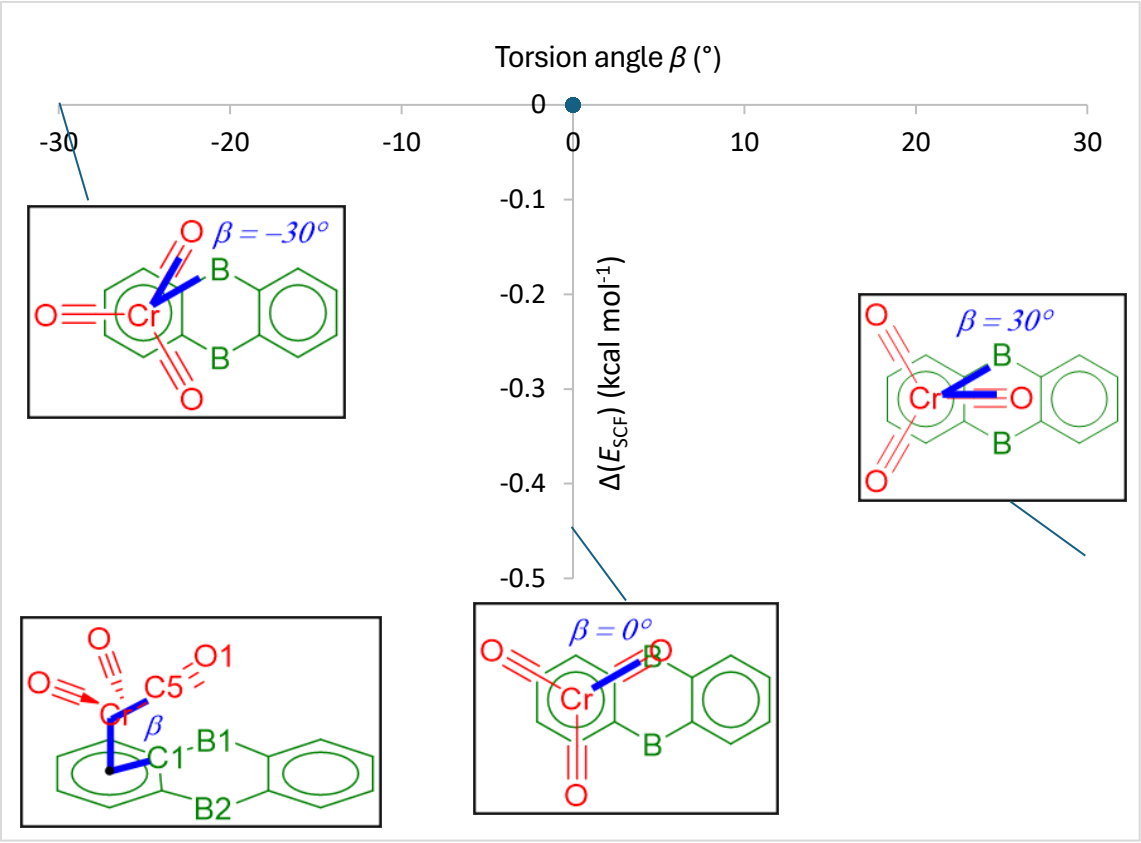


Figure S75. Evolution of the SCF energy of **2-Cr**, depending on the torsion angle β.

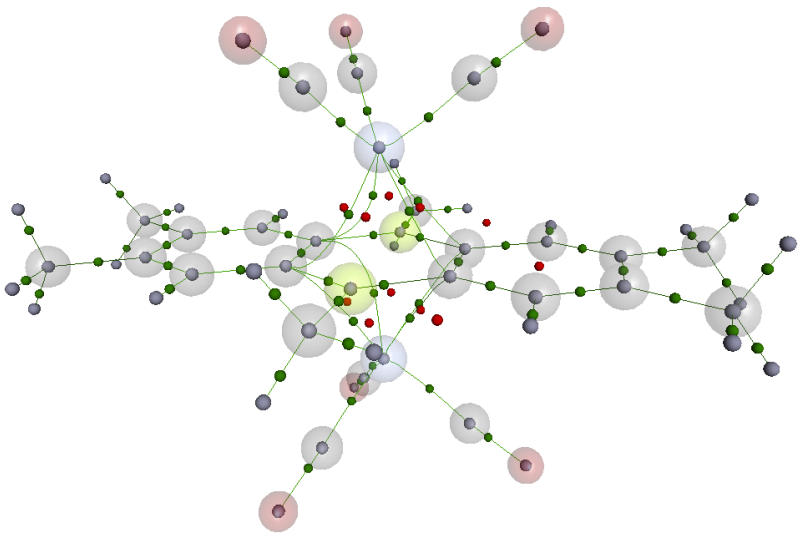
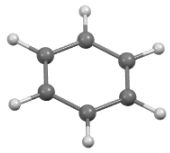


Figure S76. Bond critical points (dark green dots), bond paths (light green lines), and ring points (red dots) of **[3´-Cr$_2$]$^{2-}$**.

Cartesian coordinates of optimised compounds

Benzene *(including NICS dummy atoms)*



E_{SFC} = –232.0171050 Ha

ν_{min} = 420.56 cm^{-1}

C	-1.088171	-0.872226	0.000002
C	0.211279	-1.378477	-0.000002
C	1.299466	-0.506281	0.000000
C	1.088153	0.872210	0.000001
C	-0.211294	1.378461	-0.000001
C	-1.299483	0.506263	-0.000001
H	-1.941593	-1.556295	0.000008
H	0.376929	-2.459592	-0.000008
H	2.318527	-0.903455	0.000003
H	1.941579	1.556274	0.000001
H	-0.376951	2.459575	-0.000001
H	-2.318541	0.903444	-0.000003
Q	0.000000	0.000000	0.000000
Q	0.000000	0.000000	1.000000
Q	0.000000	0.000000	-1.000000

2 *(including NICS dummy atoms)*

E_{SFC} = –748.2261786 Ha

ν_{min} = 15.46 cm^{-1}

B	-1.513603	-0.016267	-0.172292
C	-0.718390	1.345743	-0.115790
C	-1.397248	2.569242	-0.060189
H	-2.492802	2.577187	-0.069333
C	-0.738781	3.800760	-0.060921
C	0.665524	3.816441	0.021977
C	1.350224	2.599696	-0.047580
H	2.444886	2.632415	-0.046598

C	0.699383	1.360984	-0.109568
B	1.513233	0.012834	-0.157701
C	0.717402	-1.347237	-0.071442
C	1.394932	-2.564947	0.142832
H	2.490793	-2.576817	0.029847
C	0.737253	-3.797853	0.128402
C	-0.668444	-3.813466	0.119176
C	-1.352147	-2.599131	0.008795
H	-2.446676	-2.632063	-0.001200
C	-0.700554	-1.362490	-0.079960
C	-1.520828	5.086338	0.084108
H	-1.301633	5.646687	0.992429
H	-2.603465	4.897461	0.063223
H	-1.276021	5.751331	-0.760341
C	1.416636	5.118915	0.098759
H	2.503332	4.953947	0.089948
H	1.165202	5.674567	1.017089
H	1.166800	5.777994	-0.748890
C	3.092743	-0.005276	-0.240928
H	3.464456	-0.794571	-0.913425
H	3.478938	-0.220994	0.807096
H	3.553971	0.945560	-0.542887
C	1.516498	-5.080739	0.242705
H	1.262413	-5.564346	1.411590
H	2.599389	-4.892410	0.231896
H	1.285437	-5.786363	-0.355925
C	-1.420406	-5.113508	0.223090
H	-2.506955	-4.949179	0.197999
H	-1.178909	-5.643986	1.158801
H	-1.161214	-5.795261	-0.603559
C	-3.092014	0.003484	-0.274806
H	-3.557999	-0.962676	-0.513750
H	-3.444367	0.743854	-1.010998
H	-3.499816	0.331120	0.699751
Q	0.000000	0.000000	0.000000
Q	0.000000	0.000000	1.000000
Q	0.000000	0.000000	-1.000000
Q	0.021475	-2.581537	0.020843
Q	0.021158	-2.493485	1.016957
Q	0.021792	-2.669589	-0.975271
Q	-0.023494	2.582247	-0.049325
Q	-0.013503	2.542259	0.949805
Q	-0.033486	2.622237	-1.048495

[2]$^{2-}$ *(including NICS dummy atoms)*

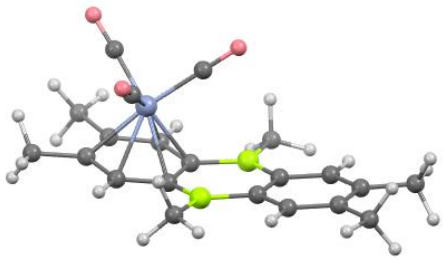
E_{SFC} = –748.1310879 Ha

ν_{min} = 36.45 cm^{-1}

B	-1.530875	-0.011378	0.003841
C	-0.737062	1.294798	0.008661
C	-1.397041	2.565712	0.021792
H	-2.498381	2.569450	0.026988
C	-0.763134	3.788649	0.029869
C	0.677215	3.807762	0.023234
C	1.346754	2.603803	0.010249
H	2.446778	2.645536	0.005633
C	0.726620	1.312766	0.003332
B	1.530880	0.011459	-0.006651
C	0.737076	-1.294740	-0.007087
C	1.397065	-2.565718	-0.009725
H	2.498401	-2.569473	-0.013611
C	0.763168	-3.788684	-0.006747
C	-0.677185	-3.807762	-0.001378
C	-1.346721	-2.603739	0.000062
H	-2.446752	-2.645512	0.004494
C	-0.726599	-1.312692	-0.002153
C	-1.542596	5.080695	0.045785
H	-1.321202	5.704881	0.934907
H	-2.626901	4.878601	0.048607
H	-1.329295	5.722387	-0.832826
C	1.421227	5.120878	0.030295
H	2.510752	4.948897	0.022557
H	1.191982	5.740142	0.920869
H	1.181893	5.755215	-0.846945
C	3.166975	-0.020586	-0.012618
H	3.574048	-0.571692	-0.885100
H	3.582412	-0.532149	0.880043
H	3.632791	0.982097	-0.037336
C	1.542660	-5.080806	-0.008604
H	1.333501	-5.672208	1.104514
H	2.626962	-4.878728	-0.013129
H	1.321702	-5.714655	-0.890972
C	-1.421251	-5.120857	0.003674
H	-2.510780	-4.948738	0.006182
H	-1.184687	-5.745436	0.888645
H	-1.189316	-5.749990	-0.879240

C	-3.166953	0.020508	0.008859
H	-3.632677	-0.982064	-0.021029
H	-3.579429	0.578707	-0.856588
H	-3.576984	0.524653	0.908183
Q	0.000000	0.000000	0.000000
Q	0.000000	0.000000	1.000000
Q	0.000000	0.000000	-1.000000
Q	0.024467	-2.562222	-0.004505
Q	0.024500	-2.552263	0.995493
Q	0.024500	-2.572263	-1.004407
Q	-0.024442	2.562248	0.016190
Q	-0.024400	2.562200	1.016200
Q	-0.024400	2.562200	-0.983800

2-Cr



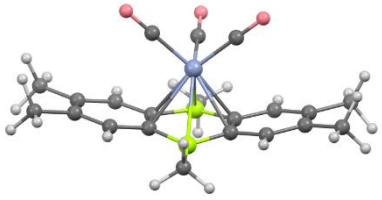
E_{SFC} = –2132.273890826 Ha

ν_{min} = 18.49 cm^{-1}

Cr	7.275331	4.127975	10.159101
B	6.176039	5.759843	7.494013
B	6.055911	2.724091	7.418532
C	6.255947	7.333729	7.571881
H	5.495796	7.778590	8.232733
H	6.201081	7.841259	6.598822
H	7.239871	7.590988	8.009533
C	6.013183	1.146795	7.415174
H	5.234891	0.725721	8.070170
H	6.983401	0.792423	7.814030
H	5.899557	0.698160	6.418391
C	6.538359	4.967216	6.186147
C	6.956224	5.644388	5.034349
H	7.009368	6.737774	5.042500
C	7.325829	4.987270	3.856704
C	7.270769	3.583541	3.821913
C	6.848464	2.899847	4.966264
H	6.815552	1.806585	4.920009
C	6.482653	3.549845	6.150951
C	5.725121	3.510466	8.750339
C	5.782474	4.936472	8.786417
C	5.630629	5.587854	10.048126

H	5.704580	6.677167	10.096394
C	5.492504	4.889770	11.258439
C	5.435973	3.455712	11.222707
C	5.520851	2.811021	9.978555
H	5.509169	1.718224	9.972192
C	7.777027	5.766311	2.650565
H	8.799945	5.484814	2.351648
H	7.767372	6.847664	2.846703
H	7.127576	5.572524	1.781165
C	7.662185	2.832439	2.577815
H	7.560859	1.747019	2.717510
H	8.706975	3.041982	2.295734
H	7.036748	3.124995	1.718574
C	5.387303	5.630124	12.564626
H	4.377287	5.520212	12.990966
H	5.583977	6.701733	12.422582
H	6.103067	5.250904	13.308751
C	5.271626	2.660625	12.490198
H	4.272050	2.825145	12.923595
H	6.012783	2.945513	13.251370
H	5.386532	1.585720	12.293776
C	8.499648	5.393421	9.606239
O	9.063744	1.927496	9.192087
O	9.248513	6.200310	9.270233
C	8.387741	2.783551	9.559450
O	8.577926	4.029503	12.845922
C	8.120769	4.066147	11.789281

2′-Cr



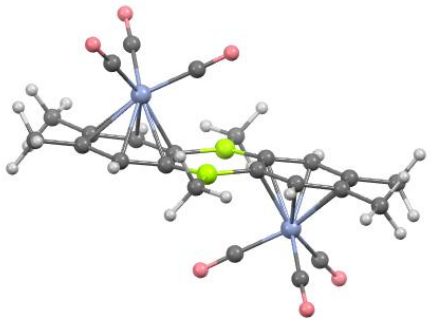
E_{SFC} = –2132.23820630756 Ha

ν_{min} = 27.55 cm^{-1}

Cr	19.748112	5.231579	24.490431
O	17.230019	5.643267	26.063746
C	18.195490	5.470871	25.466943
O	20.660397	7.670596	25.926035
C	20.326905	6.752916	25.309893
O	21.270462	3.801439	26.639675
C	20.674209	4.340448	25.819863
B	19.490438	3.977061	22.194689
B	20.650669	6.703897	22.909494

C	18.924581	2.594424	21.685769
H	18.075374	2.695198	20.993760
H	18.549180	2.035209	22.565378
H	19.686358	1.956870	21.212846
C	21.318410	8.146891	22.904177
H	20.654236	8.944714	23.268579
H	21.583644	8.398934	21.861621
H	22.243820	8.210658	23.495759
C	18.558222	5.220113	22.394012
C	17.144513	5.085858	22.321199
H	16.715066	4.091482	22.158966
C	16.282457	6.156846	22.454882
C	16.833509	7.455688	22.646102
C	18.207329	7.601061	22.718784
H	18.610876	8.606516	22.874261
C	19.110803	6.513883	22.612340
C	21.531822	5.393565	22.958616
C	22.880894	5.436700	23.391309
H	23.349151	6.412448	23.554705
C	23.637371	4.303315	23.631300
C	23.047695	3.021940	23.438374
C	21.743153	2.955144	22.988684
H	21.300178	1.966628	22.826772
C	20.953708	4.110939	22.738964
C	14.791206	5.966499	22.401946
H	14.317644	6.285832	23.344492
H	14.529978	4.912725	22.231815
H	14.336855	6.565616	21.596452
C	15.926196	8.647784	22.781543
H	16.502422	9.573026	22.919795
H	15.249818	8.535501	23.644320
H	15.289638	8.771014	21.890414
C	23.836836	1.773524	23.724051
H	23.245219	0.871539	23.514192
H	24.149208	1.736321	24.780260
H	24.755229	1.729105	23.116790
C	25.060278	4.415226	24.106109
H	25.755359	3.915847	23.411855
H	25.189426	3.933878	25.089017
H	25.367522	5.465976	24.199693

2-Cr_2



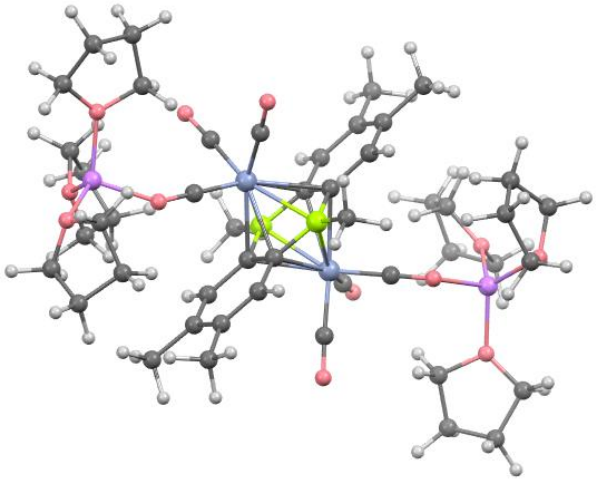
E_{SFC} = –3516.319955345 Ha

ν_{min} = 21.92 cm^{-1}

Cr	3.184941	8.002069	3.383542
C	4.343337	7.367622	4.670524
C	4.208724	7.179083	2.091088
C	4.244178	9.517062	3.211232
O	5.035268	6.947927	5.487475
O	4.814226	6.639514	1.275380
O	4.914170	10.444689	3.103089
B	1.734237	10.474393	4.947292
C	1.845551	10.556168	6.519123
H	0.967384	11.103162	6.906622
H	2.729836	11.137872	6.827142
H	1.880423	9.591005	7.041697
C	1.619123	6.636652	4.198233
C	1.547348	6.613969	2.786291
C	1.415164	7.848157	2.091947
H	1.402058	7.810844	0.999667
C	1.410716	9.102612	2.734693
C	1.494252	9.129733	4.178339
C	1.571625	7.894731	4.857211
H	1.684108	7.894229	5.943779
C	1.747555	5.369394	5.000000
H	0.797280	4.811539	4.998744
H	2.010197	5.591377	6.043743
H	2.523978	4.706964	4.592097
C	1.593769	5.320684	2.018126
H	0.637525	4.781385	2.113120
H	2.389285	4.657033	2.384874
H	1.776168	5.505139	0.950297
B	1.514717	10.420012	1.876346
C	1.403598	10.338181	0.304504
H	2.281294	9.790358	-0.082869
H	0.518818	9.757207	-0.003497
H	1.369597	11.303308	-0.218189
C	1.629082	14.257754	2.625453
C	1.700880	14.280433	4.037395
C	1.833348	13.046262	4.731719
H	1.846461	13.083560	5.824002

C	1.838039	11.791815	4.088958
C	1.754489	11.764699	2.645316
C	1.676854	12.999693	1.966459
H	1.564354	13.000180	0.879892
C	1.500357	15.524994	1.823703
H	2.450507	16.083061	1.824958
H	1.237754	15.302966	0.779959
H	0.723789	16.187244	2.231624
C	1.654193	15.573698	4.805579
H	2.610305	16.113224	4.710550
H	0.858503	16.237165	4.438872
H	1.471883	15.389187	5.873414
Cr	0.063561	12.892002	3.440160
C	-1.095006	13.526285	2.153229
C	-0.960358	13.714736	4.732687
C	-0.995445	11.376819	3.612420
O	-1.787045	13.945883	1.336322
O	-1.565941	14.254148	5.548436
O	-1.665337	10.449120	3.720528

3-Cr$_2$



E_{SFC} = –4925.001827430 Ha

ν_{min} = 15.04 cm^{-1}

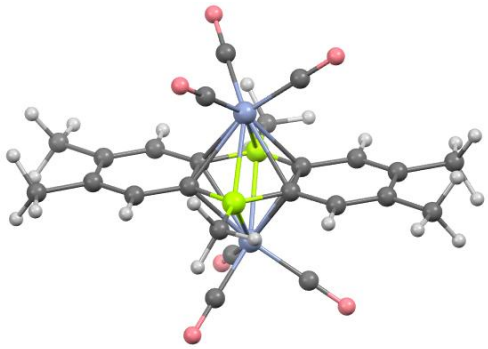
Li	16.375600	4.570160	27.321030
Li	23.912615	4.874898	18.407800
Cr	19.788295	5.210565	24.623910
Cr	20.368861	5.391521	21.140935
O	17.541559	3.873356	25.964544
C	18.455120	4.405526	25.409661
O	19.515078	7.499903	26.485016
C	19.631783	6.611738	25.735649
O	21.542466	3.923690	26.648801
C	20.883603	4.429997	25.839566

O	18.726766	4.126771	19.011826
C	19.337837	4.632599	19.860114
O	20.713777	7.819583	19.472844
C	20.540073	6.883047	20.148323
O	22.712663	4.277081	19.773802
C	21.759416	4.734443	20.324629
B	19.374780	3.923876	22.694027
B	20.661855	6.739788	23.054776
C	18.661977	2.504162	22.495772
H	18.197817	2.425196	21.497371
H	17.856438	2.353775	23.236521
H	19.343338	1.646020	22.597723
C	21.259407	8.211662	23.259103
H	20.727241	8.745468	24.065073
H	21.154216	8.825048	22.346428
H	22.325412	8.223195	23.533966
C	18.542841	5.242996	22.624377
C	17.119673	5.185448	22.365459
H	16.667053	4.199204	22.215762
C	16.326964	6.290265	22.275272
C	16.920587	7.598495	22.459861
C	18.257911	7.687696	22.707349
H	18.702882	8.679843	22.837597
C	19.132987	6.538487	22.795145
C	21.491105	5.435247	23.123777
C	22.930147	5.477443	23.355005
H	23.394824	6.461206	23.476011
C	23.715924	4.375614	23.432461
C	23.104818	3.054967	23.302244
C	21.773010	2.965440	23.068650
H	21.324071	1.972072	22.976307
C	20.886715	4.119066	22.960727
C	14.855314	6.173384	21.976276
H	14.236583	6.592942	22.789402
H	14.563794	5.122302	21.836222
H	14.585058	6.723556	21.060142
C	16.058658	8.830351	22.367232
H	16.650667	9.739905	22.544638
H	15.236991	8.811711	23.104250
H	15.588615	8.921763	21.374087
C	23.953516	1.822587	23.477428
H	23.365860	0.911102	23.294028
H	24.358078	1.760821	24.501744
H	24.819808	1.810362	22.794890
C	25.201905	4.486482	23.653515
H	25.771568	4.040984	22.817439
H	25.521481	3.958681	24.567135
H	25.509908	5.538558	23.748168
O	17.421499	4.554090	28.953844

C	17.133507	3.979137	30.229891
H	16.465000	3.115147	30.089951
H	16.606385	4.726469	30.850654
C	18.487924	3.614571	30.826280
H	18.799562	2.614122	30.485807
H	18.475343	3.611308	31.925696
C	19.396242	4.685139	30.223196
H	19.292732	5.634869	30.772935
H	20.459736	4.408804	30.215969
C	18.835244	4.813189	28.816108
H	18.967878	5.808594	28.365497
H	19.272114	4.063883	28.135869
O	15.895361	6.418753	26.976961
C	16.105088	7.069155	25.707156
H	15.225509	6.888887	25.064703
H	16.982747	6.611101	25.226521
C	16.310075	8.554372	26.017033
H	17.117954	8.979409	25.404473
H	15.389809	9.126572	25.815611
C	16.638945	8.566270	27.511816
H	16.367501	9.509302	28.008229
H	17.713750	8.385682	27.655780
C	15.833219	7.384391	28.025581
H	16.245772	6.917136	28.933181
H	14.778006	7.659416	28.215424
O	14.797366	3.449017	26.987352
C	15.081034	2.166224	26.424184
H	14.356074	1.434789	26.824091
H	16.092833	1.877324	26.740259
C	14.944174	2.328369	24.899690
H	15.925467	2.280624	24.407377
H	14.312702	1.533385	24.476332
C	14.311516	3.722783	24.728539
H	15.075224	4.448127	24.404979
H	13.494317	3.741329	23.992530
C	13.832940	4.062098	26.136639
H	13.818896	5.136471	26.368362
H	12.833992	3.633458	26.344579
O	24.563409	6.576632	19.031781
C	23.924718	7.753047	18.503625
H	22.900454	7.488437	18.194952
H	24.487251	8.092875	17.619451
C	23.907647	8.771629	19.639045
H	24.792961	9.426659	19.590259
H	23.004858	9.397281	19.604022
C	23.958269	7.883661	20.880911
H	22.957897	7.492270	21.119179
H	24.344901	8.398367	21.772640
C	24.854877	6.745443	20.425697

H	25.927780	6.987439	20.542849
H	24.636242	5.799255	20.946831
O	25.118921	3.340607	18.357930
C	26.191250	3.352219	19.310982
H	26.045184	4.212090	19.987192
H	27.146062	3.491724	18.779700
C	26.109447	2.022435	20.062136
H	26.388623	2.128277	21.121178
H	26.787094	1.280014	19.610729
C	24.651260	1.611184	19.857001
H	24.482007	0.530721	19.970260
H	23.985924	2.147645	20.553186
C	24.397522	2.105158	18.443640
H	24.786146	1.401751	17.684027
H	23.338055	2.314361	18.234782
O	22.779853	5.019710	16.855317
C	23.157054	4.746571	15.505959
H	23.960360	3.992715	15.512827
H	23.551021	5.669458	15.042491
C	21.878451	4.283643	14.820498
H	21.717710	3.207781	14.997499
H	21.897702	4.451404	13.734047
C	20.820046	5.107768	15.552450
H	20.786965	6.133363	15.150737
H	19.807590	4.685479	15.489189
C	21.345083	5.107491	16.980976
H	21.091102	6.016937	17.546787
H	20.983960	4.236967	17.552005

[3′-Cr$_2$]$^{2-}$



E_{SFC} = –3516.3577171 Ha

ν_{min} = 21.04 cm^{-1}

Cr	19.766523	5.220413	24.646980
Cr	20.379587	5.376438	21.128485
O	17.521828	3.748186	25.912380
C	18.404306	4.335592	25.418369

O	19.345959	7.576079	26.401518
C	19.503227	6.643760	25.712986
O	21.616894	4.087480	26.672737
C	20.888695	4.532436	25.875628
O	18.753527	3.997643	19.064482
C	19.392803	4.550455	19.873074
O	20.479570	7.882672	19.541708
C	20.434351	6.890877	20.159761
O	22.842892	4.435479	19.764454
C	21.874205	4.806861	20.300449
B	19.375048	3.920179	22.703850
B	20.672316	6.724820	23.057402
C	18.648163	2.500736	22.514330
H	18.182354	2.425685	21.515293
H	17.849337	2.363158	23.264997
H	19.329870	1.640613	22.614416
C	21.285431	8.199078	23.230152
H	20.810587	8.727866	24.076057
H	21.117233	8.805674	22.322138
H	22.370888	8.204083	23.420406
C	18.552206	5.241078	22.618542
C	17.129250	5.193454	22.363987
H	16.668310	4.207992	22.235264
C	16.341215	6.300308	22.275961
C	16.944023	7.604564	22.444115
C	18.281794	7.686614	22.683945
H	18.733932	8.676401	22.810602
C	19.150230	6.534230	22.782574
C	21.489386	5.420194	23.139849
C	22.924776	5.455636	23.390169
H	23.390814	6.438261	23.518337
C	23.708086	4.354247	23.471058
C	23.099709	3.037417	23.302071
C	21.768188	2.952924	23.071203
H	21.322180	1.960760	22.945320
C	20.881514	4.105643	22.974409
C	14.862300	6.187190	22.007021
H	14.262260	6.630848	22.821163
H	14.564993	5.132526	21.905897
H	14.573465	6.710094	21.078117
C	16.089373	8.842888	22.352673
H	16.698338	9.747216	22.501848
H	15.288655	8.845394	23.113298
H	15.593795	8.927464	21.369385
C	23.962049	1.804470	23.385487
H	23.357334	0.896459	23.238438
H	24.464262	1.719948	24.365614
H	24.756941	1.807529	22.618528
C	25.188829	4.460866	23.729710

H	25.781446	4.019979	22.908409
H	25.483105	3.933723	24.654694
H	25.490747	5.514411	23.833239

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