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Supporting Information for

Reactivity of cyano- and isothiocyanatoborylenes: metal coordination, one-electron oxidation and boron-centred Brønsted basicity

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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. NMR spectra were acquired either on a Bruker Avance 500 or a Bruker Avance 400 NMR spectrometer. Chemical shifts (δ) are listed in ppm and internally referenced to the carbon nuclei ($^{13}C\{^{1}H\}$) or residual protons (^{1}H) of the solvent. Heteronuclei NMR spectra are referenced to external standards (^{11}B: $BF_3{\cdot}OEt_2$). Solid-state IR spectra were recorded on a Bruker FT-IR spectrometer ALPHA II inside a glovebox. UV-vis spectra were measured on a METTLER TOLEDO UV-vis-Excellence UV5 spectrophotometer inside a glovebox. Microanalyses (C, H, N, S) were performed on an Elementar vario MICRO cube elemental analyzer. High-resolution mass spectrometry (HRMS) data were obtained from a Thermo Scientific Exactive Plus spectrometer. Photoreactions were performed using a LOT-Quantum Design GmbH mercury-xenon vapor lamp (I = 19 A, U = 26 V). *Note: both elemental analyses and HRMS were carried out for all new compounds but in some cases these decomposed too rapidly and only one type of analysis was possible.*

$M(CO)_6$ (M = Cr, Mo, W), PhSH, MeOTf (Tf = triflate, $O_3SCF_3^-$) and AgOTf were purchased from various chemicals companies, transferred into a glovebox and used as received. KC_8,[1] I*i*Pr (= 1,3-di*iso*propylimidazol-2-ylidene),[2] CAAC (= 1-(2,6-di*iso*propylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene),[3] (CAAC)BBr_2(CN) (**1**$^{\mathbf{CN}}$)[4] and (CAAC)(I*i*Pr)B(NCS) (**2**$^{\mathbf{NCS}}$)[5] were synthesised following literature procedures.

Synthetic procedures

(CAAC)(I*i*Pr)B(CN), 2^{CN}

To a suspension of I*i*Pr (174 mg, 1.14 mmol, 2.20 equiv.) and KC_8 (154 mg, 1.41 mmol, 2.20 equiv.) in 5 mL of benzene a dilute solution of (CAAC)BBr_2(CN) (250 mg, 0.52 mmol) in 10 mL of benzene was added dropwise under vigorous stirring. The resulting dark yellow suspension was stirred for 2 h at room temperature prior to filtration. After concentration of the filtrate to 5 mL *in vacuo*, slow evaporation of the solvent afforded $\mathbf{2^{CN}}$ (200 mg, 0.42 mmol, 81% yield) as yellow crystals suitable for X-ray diffraction analysis. ^{1}H NMR (500 MHz, C_6D_6, 297 K): δ = 7.47–7.44 (m, 1H, *p*-Ar*H*), 7.40–7.38 (m, 2H, *m*-Ar*H*), 6.22 (s, 2H, I*i*Pr-C*H*), 5.32 (sept, ^3J = 6.8 Hz, 2H, I*i*Pr-C*H*(CH$_3$)$_2$), 3.63 (sept, ^3J = 6.8 Hz, 2H, *i*Pr-C*H*), 1.91 (s, 2H, C*H*$_2$), 1.80 (d, ^3J = 6.7 Hz, 6H, *i*Pr-C*H*$_3$), 1.48 (d, ^3J = 6.7 Hz, 6H, *i*Pr-C*H*$_3$), 1.32 (s, 6H, NC(C*H*$_3$)$_2$), 1.13 (d, ^3J = 6.7 Hz, 6H, I*i*Pr-CH(C*H*$_3$)$_2$), 1.09 (s, 6H, C(C*H*$_3$)$_2$), 0.98 (d, ^3J = 6.9 Hz, 6H, I*i*Pr-CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): δ = 151.4 (*o*-Ar*C*), 138.1 (*i*-Ar*C*), 128.6 (*p*-Ar*C*), 124.8 (*m*-Ar*C*), 116.3 (I*i*Pr-*C*H), 63.8 (N*C*(CH$_3$)$_2$), 57.8 (*C*H$_2$), 51.0 (I*i*Pr-*C*H(CH$_3$)$_2$), 43.7 (*C*(CH$_3$)$_2$), 33.0 (C(*C*H$_3$)$_2$), 30.3 (NC(*C*H$_3$)$_2$), 28.8 (*i*Pr-*C*H), 26.7 (*i*Pr-*C*H$_3$), 25.4 (*i*Pr-*C*H$_3$), 24.1 (I*i*Pr-CH(*C*H$_3$)$_2$), 20.8 (I*i*Pr-CH(*C*H$_3$)$_2$) ppm. *Note: the* $C_{carbene}$ *and* C_{CN} *resonances were not detected, even by HMBC.* ^{11}B NMR (160 MHz, C_6D_6, 297 K): δ = –12.1 (s) ppm. Solid-state IR: ν(CN) = 2119 cm^{-1}. Elemental analysis for [$C_{30}H_{47}BN_4$] (M_w = 474.54): calcd. C 75.93, H 9.98, N 11.81 %; found C 76.34, H 9.88, N 11.27 %.

(CAAC)(I*i*Pr)B(NCS)(Cr(CO)$_5$), 2^{NCS}-Cr

A solution of Cr(CO)$_6$ (10.4 mg, 47.4 µmol, 1.20 equiv.) in 0.4 mL of THF was irradiated for 3 h and subsequently added to $\mathbf{2^{NCS}}$ (20.0 mg, 39.5 µmol) dissolved in 0.4 mL of THF. The colour changed instantly from orange to red. After evaporation of the solvent the residue was washed with hexane and dried *in vacuo* to afford $\mathbf{2^{NCS}}$**-Cr** (23.7 mg, 34.0 µmol, 86% yield) as a brown solid. *Note: all attempts to crystallise* $\mathbf{2^{NCS}}$***-Cr*** *resulted in the recovery of* $\mathbf{2^{NCS}}$. ^{1}H NMR (500 MHz, C_6D_6, 297 K): δ = 7.35–7.28 (m, 3H, *p*-Ar*H*, *m*-Ar*H*), 6.10 (s, 2H, I*i*Pr-C*H*), 5.06 (sept, ^3J = 6.8 Hz, 2H, I*i*Pr-C*H*(CH$_3$)$_2$), 3.50 (sept, ^3J = 6.7 Hz, 2H, *i*Pr-C*H*), 1.79 (s, 2H, C*H*$_2$), 1.54 (d, ^3J = 6.7 Hz, 6H, *i*Pr-C*H*$_3$), 1.39 (d, ^3J = 6.8 Hz, 6H, *i*Pr-C*H*$_3$), 1.19 (s, 6H, NC(C*H*$_3$)$_2$), 1.15 (d, ^3J = 6.6 Hz, 6H, I*i*Pr-CH(C*H*$_3$)$_2$), 0.93 (s, 6H, C(C*H*$_3$)$_2$), 0.90 (d, ^3J = 6.8 Hz, 6H, I*i*Pr-CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): δ = 223.8 (*C*O), 216.6 (*C*O), 149.4 (*o*-Ar*C*), 136.9 (*i*-Ar*C*), 129.2 (*p*-Ar*C*), 125.0 (*m*-Ar*C*), 116.9 (I*i*Pr-*C*H), 64.6 (N*C*(CH$_3$)$_2$), 57.3 (*C*H$_2$), 51.2 (I*i*Pr-*C*H(CH$_3$)$_2$), 43.1 (*C*(CH$_3$)$_2$), 32.8 (C(*C*H$_3$)$_2$), 29.9

(NC(*C*H$_3$)$_2$), 28.8 (*i*Pr-*C*H), 26.1 (I*i*Pr-CH(*C*H$_3$)$_2$), 24.9 (*i*Pr-*C*H$_3$), 24.8 (I*i*Pr-CH(*C*H$_3$)$_2$), 20.9 (*i*Pr-*C*H$_3$) ppm. *Note: the C$_{carbene}$ and C$_{NCS}$ resonances were not detected, even by HMBC.* ^{11}B NMR (160 MHz, C$_6$D$_6$, 297 K): δ = –3.8 (s) ppm. Solid-state IR: ν(NCS) = 2057 cm^{-1}; ν(CO) = 2057, 1968, 1932, 1903 cm^{-1}. Elemental analysis for [$C_{35}H_{47}BCrN_4O_5S$] (M$_w$ = 698.65): calcd. C 60.17, H 6.78, N 8.02, S 4.59 %; found C 60.67, H 7.14, N 8.17, S 4.77 %. *Note: HMRS only provided a peak for the* ***2^{NCS}*** *borylene.*

(CAAC)(I*i*Pr)B(NCS)(W(CO)$_5$), 2^{NCS}-W

W(CO)$_6$ (16.7 mg, 47.4 µmol, 1.20 equiv.) dissolved in 0.4 mL of THF was irradiated for 3 h and added to a solution of **2^{NCS}** (20.0 mg, 39.5 µmol) in 0.4 mL of THF. After a colour change from orange to red the solvent was removed *in vacuo*. The residue was washed with hexane and dried *in vacuo*, yielding **2^{NCS}-W** (26.9 mg, 32.4 µmol, 82% yield) as a brown solid. *Note: all attempts to crystallise* ***2^{NCS}-W*** *resulted in the recovery of* ***2^{NCS}***. ^{1}H NMR (500 MHz, C$_6$D$_6$, 297 K): δ = 7.35–7.28 (m, 3H, *p*-Ar*H*, *m*-Ar*H*), 6.13 (s, 2H, I*i*Pr-C*H*), 5.05 (sept, ^3J = 6.8 Hz, 2H, I*i*Pr-C*H*(CH$_3$)$_2$), 3.49 (sept, ^3J = 6.8 Hz, 2H, *i*Pr-C*H*), 1.78 (s, 2H, C*H*$_2$), 1.53 (d, ^3J = 6.8 Hz, 6H, *i*Pr-C*H*$_3$), 1.38 (d, ^3J = 6.8 Hz, 6H, *i*Pr-C*H*$_3$), 1.18 (s, 6H, NC(C*H*$_3$)$_2$), 1.13 (d, ^3J = 6.7 Hz, 6H, I*i*Pr-CH(C*H*$_3$)$_2$), 0.92 (s, 6H, C(C*H*$_3$)$_2$), 0.91 (d, ^3J = 6.9 Hz, 6H, I*i*Pr-CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 297 K): δ = 201.5 (*C*O), 198.8 (*C*O), 149.4 (*o*-Ar*C*), 136.9 (*i*-Ar*C*), 129.3 (*p*-Ar*C*), 125.0 (*m*-Ar*C*), 117.0 (I*i*Pr-*C*H), 64.7 (N*C*(CH$_3$)$_2$), 57.2 (*C*H$_2$), 51.2 (I*i*Pr-*C*H(CH$_3$)$_2$), 43.2 (*C*(CH$_3$)$_2$), 32.8 (C(*C*H$_3$)$_2$), 29.9 (NC(*C*H$_3$)$_2$), 28.8 (*i*Pr-*C*H), 26.1 (I*i*Pr-CH(*C*H$_3$)$_2$), 25.0 (*i*Pr-*C*H$_3$), 24.9 (I*i*Pr-CH(*C*H$_3$)$_2$), 20.8 (*i*Pr-*C*H$_3$) ppm. *Note: the C$_{carbene}$ and C$_{NCS}$ resonances were not detected, even by HMBC.* ^{11}B NMR (160 MHz, C$_6$D$_6$, 297 K): δ = –3.9 (s) ppm. Solid-state IR: ν(NCS) = 2106 cm^{-1}; ν(CO) = 2066, 1972, 1911, 1880 cm^{-1}. Elemental analysis for [$C_{35}H_{47}BN_4O_5SW$] (M$_w$ = 830.49): calcd. C 50.62, H 5.70, N 6.75, S 3.86 %; found C 50.98, H 6.14, N 6.92, S 4.11 %. *Note: HMRS only provided a peak for the* ***2^{NCS}*** *borylene.*

(CAAC)(I*i*Pr)B(CN)(Cr(CO)$_5$), 2^{CN}-Cr

A solution of Cr(CO)$_6$ (11.1 mg, 50.5 µmol, 1.20 equiv.) in 0.4 mL of THF was irradiated for 3 h and added to **2^{CN}** (20.0 mg, 42.1 µmol) dissolved in 0.4 mL of THF, whereupon the yellow colour intensified. After evaporation of the solvent the solid residue was washed with a 9:1 mixture of hexane/benzene. Drying *in vacuo* afforded **2^{CN}-Cr** (25.5 mg, 38.3 µmol, 91% yield) as a yellow solid and as the (*Z*)-isomer only. Single crystals of **(*Z*)-2^{CN}-Cr** were obtained by vapour diffusion of hexane into a saturated benzene solution. ^{1}H NMR (500 MHz, C$_6$D$_6$, 297 K): δ = 7.57 (t, ^3J = 7.7 Hz, 1H, *p*-Ar*H*), 7.40 (d, ^3J = 7.7 Hz, 1H, *p*-Ar*H*), 6.09 (s, 2H, I*i*Pr-C*H*), 5.07 (sept, ^3J = 6.8 Hz, 2H, I*i*Pr-C*H*(CH_3)$_2$), 3.34 (sept, ^3J = 6.7 Hz, 2H, *i*Pr-C*H*), 1.76 (s, 2H, CH_2), 1.61 (d, ^3J = 6.7 Hz, 6H, *i*Pr-CH_3), 1.39 (d, ^3J = 6.8 Hz, 6H, *i*Pr-CH_3), 1.17 (s, 6H, NC(CH_3)$_2$), 1.14 (d, ^3J = 6.7 Hz, 6H, I*i*Pr-CH(CH_3)$_2$), 0.92 (s, 6H, C(CH_3)$_2$), 0.90 (d, ^3J = 6.9 Hz, 6H, I*i*Pr-CH(CH_3)$_2$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 297 K): δ = 220.4 (*C*O), 215.4 (*C*O), 150.0 (*o*-Ar*C*), 136.4 (*i*-Ar*C*), 129.2 (*p*-Ar*C*), 125.6 (*m*-Ar*C*), 116.4 (I*i*Pr-*C*H), 64.6 (N*C*(CH_3)$_2$), 56.9 (*C*H_2), 51.0 (I*i*Pr-*C*H(CH_3)$_2$), 43.9 (*C*(CH_3)$_2$), 32.4 (C(*C*H_3)$_2$), 30.1 (NC(*C*H_3)$_2$), 28.8 (*i*Pr-*C*H), 26.6 (I*i*Pr-CH(*C*H_3)$_2$), 25.0 (*i*Pr-*C*H_3), 24.4 (I*i*Pr-CH(*C*H_3)$_2$), 20.6 (*i*Pr-*C*H_3) ppm. *Note: the* $C_{carbene}$ *and* C_{CN} *resonances were not detected, even by HMBC.* ^{11}B NMR (160 MHz, C_6D_6, 297 K): δ = –13.2 (s) ppm. Solid-state IR: ν(CN) = 2134 cm^{-1}; ν(CO) = 2064, 1975, 1928, 1884, 1862 cm^{-1}. Elemental analysis for [$C_{35}H_{47}BCrN_4O_5$] (M_w = 666.59): calcd. C 63.06, H 7.11, N 8.41 %; found C 62.59, H 7.16, N 7.92 %. HRMS LIFDI for [$C_{35}H_{47}BCrN_4O_5$] = [M]: calcd. 666.3039; found 666.3031.

(CAAC)(I*i*Pr)B(CN)(Mo(CO)$_5$), 2^{CN}-Mo

Mo(CO)$_6$ (13.3 mg, 50.5 µmol, 1.20 equiv.) dissolved in 0.4 mL of THF was irradiated for 3 h and added to a solution of **2^{CN}** (20.0 mg, 42.1 µmol) in 0.4 mL of THF. The yellow color intensified immediately and subsequently the solvent was evaporated. The residue was washed with a 9:1 mixture of hexane/benzene and dried *in vacuo*, yielding **2^{CN}-Mo** (26.7 mg, 37.5 µmol, 89% yield) as a yellow solid, in a 95:5 (*Z*)/(*E*) ratio. Single crystals of **(*Z*)-2^{CN}-Mo** were obtained by vapor diffusion of hexane into a saturated benzene solution. NMR data for **(*Z*)-2^{CN}-Mo**: ^1H NMR (500 MHz, C_6D_6, 297 K): δ = 7.56 (t, ^3J = 7.7 Hz, 1H, *p*-Ar*H*), 7.39 (d, ^3J = 7.7 Hz, 1H, *p*-Ar*H*), 6.10 (s, 2H, I*i*Pr-C*H*), 5.06 (sept, ^3J = 6.8 Hz, 2H, I*i*Pr-C*H*(CH_3)$_2$), 3.34 (sept, ^3J = 6.8 Hz, 2H, *i*Pr-C*H*), 1.76 (s, 2H, CH_2), 1.60 (d, ^3J = 6.7 Hz, 6H, *i*Pr-CH_3), 1.38 (d, ^3J = 6.7 Hz, 6H, *i*Pr-CH_3), 1.17 (s, 6H, NC(CH_3)$_2$), 1.12 (d, ^3J = 6.7 Hz, 6H, I*i*Pr-CH(CH_3)$_2$), 0.92 (s, 6H, C(CH_3)$_2$), 0.90 (d, ^3J = 6.9 Hz, 6H, I*i*Pr-CH(CH_3)$_2$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 297 K): δ = 212.9 (*C*O), 204.9 (*C*O), 150.1 (*o*-Ar*C*), 136.5 (*i*-Ar*C*), 129.2 (*p*-Ar*C*), 125.6 (*m*-Ar*C*), 116.5 (I*i*Pr-*C*H), 64.8 (N*C*(CH_3)$_2$), 56.8 (*C*H_2), 51.1 (I*i*Pr-*C*H(CH_3)$_2$), 44.0 (*C*(CH_3)$_2$), 32.4 (C(*C*H_3)$_2$), 30.1 (NC(*C*H_3)$_2$), 28.8 (*i*Pr-*C*H), 26.6 (I*i*Pr-CH(*C*H_3)$_2$), 25.0 (*i*Pr-*C*H_3), 24.3 (I*i*Pr-CH(*C*H_3)$_2$), 20.6 (*i*Pr-*C*H_3) ppm. *Note: the* $C_{carbene}$ *and* C_{CN} *resonances were not detected, even by HMBC.* ^{11}B NMR (160 MHz, C_6D_6, 297 K): δ = –13.6 (s) ppm. Solid-state IR: ν(CN) = 2126 cm^{-1}; ν(CO) = 2067, 1976, 1926, 1858 cm^{-1}. HRMS LIFDI for [$C_{35}H_{47}BMoN_4O_5$] = [M]: calcd. 712.2688; found 712.2682.

(CAAC)(I*i*Pr)B(CN)(W(CO)$_5$), 2$^{\text{CN}}$-W

A solution of W(CO)$_6$ (17.8 mg, 50.5 µmol, 1.20 equiv.) in 0.4 mL of THF was irradiated for 3 h and added to **2**$^{\text{CN}}$ (20.0 mg, 42.1 µmol) dissolved in 0.4 mL of THF, whereupon the yellow colour intensified. After evaporation of the solvent the residue was washed with a 9:1 mixture of hexane/benzene and dried *in vacuo*. **2**$^{\text{CN}}$**-W** was isolated as a 9:1 (*Z*)/(*E*) mixture, which isomerised to a 2:3 (*Z*)/(*E*) equilibrium ratio after heating for 10 days at 60 °C in C_6D_6, as determined by NMR-spectroscopic analysis. Single crystals of **(*E*)-2**$^{\text{CN}}$**-W** were obtained by slow evaporation of this solution. NMR data for **(*Z*)-2**$^{\text{CN}}$**-W**: ^{1}H NMR (500 MHz, C_6D_6, 297 K): δ = 7.58 (t, ^3J = 7.6 Hz, 1H, *p*-Ar*H*), 7.40 (d, ^3J = 7.7 Hz, 2H, *m*-Ar*H*), 6.08 (s, 2H, I*i*Pr-C*H*), 5.04 (sept, ^3J = 6.8 Hz, 2H, I*i*Pr-C*H*(CH$_3$)$_2$), 3.31 (sept, ^3J = 6.8 Hz, 2H, *i*Pr-C*H*), 1.74 (s, 2H, C*H*$_2$), 1.60 (d, ^3J = 6.7 Hz, 6H, *i*Pr-C*H*$_3$), 1.37 (d, ^3J = 6.8 Hz, 6H, *i*Pr-C*H*$_3$), 1.15 (s, 6H, NC(C*H*$_3$)$_2$), 1.11 (d, ^3J = 6.7 Hz, 6H, *i*Pr-C*H*$_3$), 0.91 (s, 6H, C(C*H*$_3$)$_2$), 0.89 (d, ^3J = 6.8 Hz, 6H, *i*Pr-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): δ = 201.9 (*C*O), 197.9 (*C*O), 150.0 (*o*-Ar*C*), 136.3 (*i*-Ar*C*), 129.4 (*p*-Ar*C*), 125.8 (*m*-Ar*C*), 116.6 (I*i*Pr-*C*H), 64.3 (N*C*(CH$_3$)$_2$), 56.7 (*C*H$_2$), 51.1 (I*i*Pr-*C*H(CH$_3$)$_2$), 44.1 (*C*(CH$_3$)$_2$), 32.3 (C(*C*H$_3$)$_2$), 30.1 (NC(*C*H$_3$)$_2$), 28.8 (*i*Pr-*C*H), 26.6 (I*i*Pr-CH(*C*H$_3$)$_2$), 25.0 (*i*Pr-*C*H$_3$), 24.4 (I*i*Pr-CH(*C*H$_3$)$_2$), 20.6 (*i*Pr-*C*H$_3$) ppm. *Note: the* $C_{carbene}$ *and* C_{CN} *resonances were not detected, even by HMBC.* ^{11}B NMR (160 MHz, C_6D_6, 297 K): δ = –13.9 (s) ppm. *Note: due to the very broad and partially overlapping resonances of* ***(E)-2***$^{\text{CN}}$***-W*** *its* ^{1}*H and* ^{13}*C{*^{1}*H} NMR spectra were not assigned.* ^{11}B NMR for **(*E*)-2**$^{\text{CN}}$**-W** (160 MHz, C_6D_6, 297 K): δ = –8.4 (s) ppm. Solid-state IR: ν(CN) = 2143 (**(*E*)-2**$^{\text{CN}}$**-W**), 2121 (**(*Z*)-2**$^{\text{CN}}$**-W**) cm^{-1}; ν(CO) = 2066, 1978, 1914, 1856 cm^{-1}. *Note: generous washing of the original 9:1 (Z)/(E) mixture of* ***2***$^{\text{CN}}$***-W*** *with a 3:2 mixture of hexane/THF and subsequent drying in vacuo afforded a few milligrams of pure* ***(Z)-2***$^{\text{CN}}$***-W****, enabling the assignment of* ν*(CN) in the solid-state IR spectrum.* HRMS LIFDI for [$C_{35}H_{47}BN_4O_5W$] = [M]: calcd. 798.3143; found 798.3136.

[(CAAC)(I*i*Pr)B(NCS)]$^{\bullet+}$[OTf]$^-$, [(*Z*)-2$^{\text{NCS}\bullet+}$][OTf$^-$]

2$^{\text{NCS}}$ (50.0 mg, 98.7 µmol) and AgOTf (25.4 mg, 98.7 µmol) were suspended in 2 mL of benzene for five minutes at room temperature. Filtration and evaporation of the solvent under atmospheric pressure afforded **[(*Z*)-2**$^{\text{NCS}\bullet+}$**][OTf**$^-$**]** (52.4 mg, 79.9 µmol, 81% yield) as yellow crystals suitable for X-ray diffraction analysis. Solid-state IR: ν(NCS) = 2056 cm^{-1}. HRMS LIFDI for [$C_{30}H_{47}BN_4S$]$^{\bullet+}$ = [M]$^{\bullet+}$: calcd. 506.3609; found 506.3606.

[(CAAC)(I*i*Pr)B(CN)]$^{•+}$[OTf]$^{–}$, [(*Z*)-2$^{CN•+}$][OTf$^{–}$]

2^{CN} (100 mg, 0.211 mmol) and AgOTf (54.2 mg, 0.211 μmol) were suspended in 5 mL of benzene for five minutes at room temperature, whereupon a black precipitate was formed. Filtration and evaporation of the solvent under atmospheric pressure afforded a large crop of yellow crystals of **[(*Z*)-2$^{CN•+}$][OTf$^{–}$]** (111 mg, 0.178 mmol, 85% yield) suitable for X-ray diffraction analysis. Solid-state IR: ν(CN) = 2145 cm^{-1}. HRMS LIFDI for [$C_{30}H_{48}BN_4$] = [M + H]$^{+}$: calcd. 475.3967; found 475.3959.

[(CAAC)(I*i*Pr)BH(NCS)][SPh], 3^{NCS}, and (CAACH)(I*i*Pr)B(NCS)(SPh), 4^{NCS}

A solution of **2^{NCS}** (100 mg, 197 μmol) and thiophenol (26.1 mg, 237 μmol, 1.20 equiv.) in 5 mL of benzene was stirred overnight at rt resulting in a colourless solution, the ^{1}H and ^{11}B NMR spectra of which showed the formation of a 2:3 mixture of **3^{NCS}** and **4^{NCS}**, respectively. Further stirring for 3 days at rt led to the formation of a colourless precipitate. The solvent was removed *in vacuo* and the solid residue was washed with hexane. Drying *in vacuo* afforded a 85:15 mixture of diastereomers of **4^{NCS}** (99.6 mg, 162 μmol, 82% yield). Colourless single crystals of the (*R*,*R*)/(*S*,*S*) diastereomer of **4^{NCS}** were obtained by vapour diffusion of hexane in a saturated benzene solution. *Note: due to its continuous conversion to* ***4^{NCS}*** *at rt in solution,* ***3^{NCS}*** *could not be isolated and only its ^{1}H and ^{11}B NMR data recorded in situ could be obtained.* NMR data for NMR **3^{NCS}**: ^{1}H{^{11}B} NMR (400 MHz, C_6D_6, 297 K): δ = 8.47–8.23 (m, 1H, *p*-Ar*H*), 8.06–7.76 (m, 2H, *m*-Ar*H*), 7.36–6.76 (m, 5H, SC_6H_5, overlapping with residual thiophenol), 4.73 (br s, 1H, I*i*Pr-C*H*(CH$_3$)$_2$), 4.29 (br s, 1H, I*i*Pr-C*H*(CH$_3$)$_2$), 3.76 (s, 1H, B*H*), 2.90 (sept, ^{3}J = 6.7 Hz, 1H, *i*Pr-C*H*), 2.63 (sept, ^{3}J = 6.6 Hz, 1H, *i*Pr-C*H*), 2.33 (d, ^{2}J = 13.5 Hz, 1H, C*H*$_2$), 2.00 (d, ^{2}J = 13.5 Hz, 1H, C*H*$_2$),1.70–0.95 (m, 37H, B*H*$_2$, NC(C*H*$_3$)$_2$, C(C*H*$_3$)$_2$, I*i*Pr-CH(C*H*$_3$)$_2$, *i*Pr-C*H*$_3$) ppm. ^{11}B NMR (128 MHz, C_6D_6, 297 K): δ = –18.9 (br s) ppm. *Note: for the minor diastereomer of* ***4^{NCS}*** *only the ^{1}H NMR data are provided.* NMR data for the minor diastereomer of **4^{NCS}** (15%): ^{1}H NMR (500 MHz, C_6D_6, 297 K): δ = 7.48–7.40 (m, Ar*H*), 7.01–6.92 (m, Ar*H*), 6.20 (s, I*i*Pr-C*H*), 6.14 (s, I*i*Pr-C*H*), 5.44 (br s, *i*Pr-C*H*), 5.20 (br s, *i*Pr-C*H*), 4.14 (sept, ^{3}J = 6.7 Hz, *i*Pr-C*H*), 3.79 (s, 1H, BC*H*), 1.95 (br s, NC(C*H*$_3$)$_2$), 1.76–1.74 (m), 1.57–1.54 (m), 1.44–1.42 (m), 1.32 (d, ^{3}J = 6.7 Hz, *i*Pr-C*H*$_3$), 1.29–1.15 (m), 0.88–0.86 (m), 0.79 (s), 0.51 (d, ^{3}J = 6.5 Hz, *i*Pr-C*H*$_3$) ppm. NMR data for the major diastereomer of **4^{NCS}** (85%): ^{1}H NMR (500 MHz, C_6D_6, 297 K): δ = 7.37 (dd, ^{3}J = 7.6 Hz, ^{2}J = 1.8 Hz, 1H, Ar*H*), 7.28 (t, ^{3}J = 7.6 Hz, 1H, Ar*H*), 7.18–7.17 (m, 1H, Ar*H*), 7.10–7.09 (m, 1H, Ar*H*), 7.08–7.07 (m, 1H, Ar*H*), 6.89 (t, ^{3}J = 7.7 Hz, 2H, Ar*H*), 6.80–6.76 (m, 1H, Ar*H*), 6.06 (d, ^{3}J = 2.2 Hz, 1H, I*i*Pr-C*H*), 6.05 (d, ^{3}J = 2.2 Hz, 1H, I*i*Pr-C*H*), 5.57 (sept, ^{3}J = 6.6 Hz, 1H, *i*Pr-C*H*), 5.49

(sept, ^3J = 6.6 Hz, 1H, *i*Pr-C*H*), 4.82 (sept, ^3J = 6.8 Hz, 1H, *i*Pr-C*H*), 3.70 (s, 1H, BC*H*), 3.45 (sept, ^3J = 6.8 Hz, 1H, *i*Pr-C*H*), 2.22 (d, ^2J = 12.2 Hz, 1H, CH_2), 2.02 (d, ^3J = 6.7 Hz, 3H, *i*Pr-CH_3), 2.01 (s, 3H, NC(CH_3)$_2$), 1.80 (d, ^2J = 12.2 Hz, 1H, CH_2), 1.61 (d, ^3J = 6.8 Hz, 3H, *i*Pr-CH_3), 1.48 (d, ^3J = 6.7 Hz, 3H, *i*Pr-CH_3), 1.41 (s, 3H, NC(CH_3)$_2$), 1.39 (d, ^3J = 6.6 Hz, 3H, *i*Pr-CH_3), 1.10 (s, 3H, NC(CH_3)$_2$), 1.08 (d, ^3J = 6.5 Hz, 3H, *i*Pr-CH_3), 1.00 (d, ^3J = 6.8 Hz, 3H, *i*Pr-CH_3), 0.91 (d, ^3J = 6.7 Hz, 3H, *i*Pr-CH_3), 0.90 (d, ^3J = 6.6 Hz, 3H, *i*Pr-CH_3), 0.89 (s, 3H, C(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): δ = 153.8 (Ar*C*), 147.8 (Ar*C*), 145.9 (Ar*C*), 140.8 (Ar*C*), 132.7 (Ar*C*), 126.3 (Ar*C*), 125.0 (Ar*C*), 124.6 (Ar*C*), 124.5 (Ar*C*), 117.5 (I*i*Pr-*C*H), 117.4 (I*i*Pr-*C*H), 72.1 (B*C*H), 63.2 (N*C*(CH$_3$)$_2$), 61.4 (*C*H$_2$), 51.5 (*i*Pr-*C*H), 50.8 (*i*Pr-*C*H), 41.9 (*C*(CH$_3$)$_2$), 35.4 (*C*(CH$_3$)$_2$), 33.4 (NC(*C*H$_3$)$_2$), 29.5 (C(*C*H$_3$)$_2$), 28.9 (NC(*C*H$_3$)$_2$), 28.6 (C(*C*H$_3$)$_2$), 28.0 (C(*C*H$_3$)$_2$), 27.5 (*i*Pr-*C*H$_3$), 25.7 (*i*Pr-*C*H$_3$), 25.6 (*i*Pr-*C*H$_3$), 25.5 (*i*Pr-*C*H$_3$), 24.1 (*i*Pr-*C*H$_3$), 23.8 (*i*Pr-*C*H$_3$), 23.1 (*i*Pr-*C*H$_3$), 22.8 (*i*Pr-*C*H$_3$) ppm. *Note: the* $C_{carbene}$ *and* C_{NCS} *resonances were not detected, even by HMBC.* ^{11}B NMR (160 MHz, C_6D_6, 297 K): δ = –6.0 (s) ppm. Solid-state IR: ν(NCS) = 2137 cm^{-1}. HRMS LIFDI for [$C_{36}H_{52}BN_4S_2$] = [M – H]$^-$: calcd. 615.3721; found 615.3715.

[(CAAC)(I*i*Pr)BH(CN)][SPh], 3^{CN}

Treatment of a solution of **2^{CN}** (20.0 mg, 42.1 μmol) in 0.5 mL of C_6D_6 with thiophenol (10.2 mg, 92.7 μmol, 2.20 equiv.) led to partial fading of the yellow colour of the solution. The reaction mixture was monitored *in situ* by ^{11}B, ^{11}B{^{1}H}, ^{1}H and ^{1}H{^{11}B} NMR spectroscopy. After 15 min at room temperature the NMR spectra showed ca. 85% conversion of **2^{CN}** to **3^{CN}**. The ratio of the mixture did not change over a course of 1 day, whereupon various attempts to isolate **3^{CN}** were made.

Attempt A. Prolonged heating of the reaction mixture at 80 °C afforded a 65:35 ratio of **2^{CN}** and **3^{CN}**, suggesting an equilibrium between **2^{CN}** and **3^{CN}**. Upon cooling a few colourless single crystals of **3^{CN}** suitable for X-ray diffraction analysis were obtained. *Note: due to the very weak diffraction the X-ray crystallographic data was of insufficient quality for structural discussion but provided proof of connectivity.*

Attempt B. After removal of the solvent *in vacuo* the residual yellow solid was dried *in vacuo* at 60 °C for 4 h. Redissolving this solid in 0.5 mL of C_6D_6 resulted in almost quantitative recovery of **2^{CN}** (see Figures S37 and S38).

Attempt C. The reaction mixture was left undisturbed overnight, yielding colourless crystals of **3^{CN}**, the supernatant of which was decanted. Subsequently, the crystals of **3^{CN}** were washed with small amounts of hexane (2 × 0.3 mL) and dried under atmospheric pressure for 1 h.

Redissolving these crystals in 0.5 mL of C_6D_6 afforded $\mathbf{2}^{\mathbf{CN}}$ and residual thiophenol. *Note: due to its continuous partial conversion to* $\mathbf{2}^{\mathbf{CN}}$ *at rt in solution, only the* ^1H *and* ^{11}B *NMR data of* $\mathbf{3}^{CN}$ *recorded in situ could be obtained. Further conversion of* $\mathbf{3}^{CN}$ *to the* $\mathbf{4}^{CN}$ *analogue of* $\mathbf{4}^{NCS}$ *was not observed, even in the presence of a vast excess of thiophenol.* NMR data for NMR $\mathbf{3}^{\mathbf{CN}}$: $^1H\{^{11}B\}$ NMR (400 MHz, C_6D_6, 297 K): δ = 8.53–7.79 (m, 3H, Ar*H*), 4.77 (br s, 1H, I*i*Pr-C*H*(CH_3)$_2$), 4.34 (br s, 1H, I*i*Pr-C*H*(CH_3)$_2$), 3.02 (s, 1H, B*H*), 2.93 (sept, ^3J = 6.7 Hz, 1H, *i*Pr-C*H*), 2.62 (sept, ^3J = 6.6 Hz, 1H, *i*Pr-C*H*), 2.40 (d, ^2J = 13.5 Hz, 1H, CH_2), 2.03 (d, ^2J = 13.5 Hz, 1H, CH_2) ppm. ^{11}B NMR (128 MHz, C_6D_6, 297 K): δ = –29.3 (br s) ppm. HRMS LIFDI for [$C_{30}H_{48}BN_4$] = [M – C_6H_5S]$^+$: calcd. 475.3967; found 475.3959.

VT-NMR experiment: $\mathbf{2}^{\mathbf{CN}}$ (9.30 mg, 0.20 mmol) in 0.5 mL of Toluene-d_8 was treated with an excess of thiophenol (ca. 2–5 eq.) whereupon the yellow colour vanished and a colourless solid precipitated. The mixture was monitored *in situ* by ^{11}B and ^1H NMR spectroscopy while heating stepweise from rt to 100 °C (see Figures S39 and S40). Upon cooling colourless single crystals of $\mathbf{3}^{\mathbf{CN}}$ suitable for X-ray diffraction analysis were obtained.

(CAACH)B(SPh)$_2$, 5

Route A. A solution of $\mathbf{2}^{\mathbf{NCS}}$ (100 mg, 197 µmol) and thiophenol (47.8 mg, 434 µmol, 2.20 equiv.) in 5 mL of benzene was stirred for 6 days at 60 °C until the orange colour disappeared. After evaporation of the solvent the residue was extracted with hexane. Removal of the solvent and drying *in vacuo* yielded **5** (75.0 mg, 146 µmol, 74% yield) as a colourless solid.

Route B. $\mathbf{4}^{\mathbf{NCS}}$ (10 mg, 16 µmol) and thiophenol (2.1 mg, 19 µmol, 1.2 equiv.) were combined in 0.6 mL of benzene and heated at 60 °C. After 6 days the ^{11}B NMR spectrum showed full conversion to **5**. ^1H NMR (500 MHz, C_6D_6, 297 K): δ = 7.49–7.47 (m, 2H, Ar*H*), 7.26–7.18 (m, 3H, Ar*H*), 6.94–6.81 (m, 6H, Ar*H*), 6.71–6.69 (m, 2H, Ar*H*), 3.64 (sept, ^3J = 6.7 Hz, 1H, *i*Pr-C*H*), 3.44 (sept, ^3J = 6.7 Hz, 1H, *i*Pr-C*H*), 2.91 (d, ^3J = 2.8 Hz, 1H, BC*H*), 2.55 (d, ^2J = 14.3 Hz, 1H, CH_2), 1.72 (d, ^3J = 6.7 Hz, 3H, *i*Pr-CH_3), 1.63 (d, ^3J = 6.7 Hz, 3H, *i*Pr-CH_3), 1.37 (d, ^3J = 6.7 Hz, 6H, *i*Pr-CH_3), 1.32 (s, 3H, NC(CH_3)$_2$), 1.30 (d, ^2J = 11.5 Hz, 1H, CH_2), 1.15 (s, 3H, NC(CH_3)$_2$), 1.09 (s, 3H, C(CH_3)$_2$), 0.89 (s, 3H, C(CH_3)$_2$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 297 K): δ = 149.4 (Ar*C*), 147.8 (Ar*C*), 140.1 (Ar*C*), 137.2 (Ar*C*), 136.2 (Ar*C*), 134.2 (Ar*C*), 129.0 (Ar*C*), 128.6 (Ar*C*), 127.0 (Ar*C*), 125.1 (Ar*C*), 125.1 (Ar*C*), 125.0 (Ar*C*), 59.3 (N*C*(CH_3)$_2$), 49.6 (*C*H_2), 43.6 (B*C*H), 35.3 (*C*(CH_3)$_2$), 33.0 (C(*C*H_3)$_2$), 30.4 (NC(*C*H_3)$_2$), 30.0 (C(*C*H_3)$_2$), 29.5 (NC(*C*H_3)$_2$), 29.4 (*i*Pr-*C*H), 29.1 (*i*Pr-*C*H), 27.1 (*i*Pr-*C*H_3), 27.0 (*i*Pr-*C*H_3), 24.5 (*i*Pr-*C*H_3), 24.1 (*i*Pr-*C*H_3) ppm. ^{11}B NMR (160 MHz, C_6D_6, 297 K): δ = 42.6 (broad s) ppm. HRMS LIFDI for [$C_{32}H_{42}BNS2$] = [M]: calcd. 515.2846; found 515.2843.

NMR spectra of isolated compounds

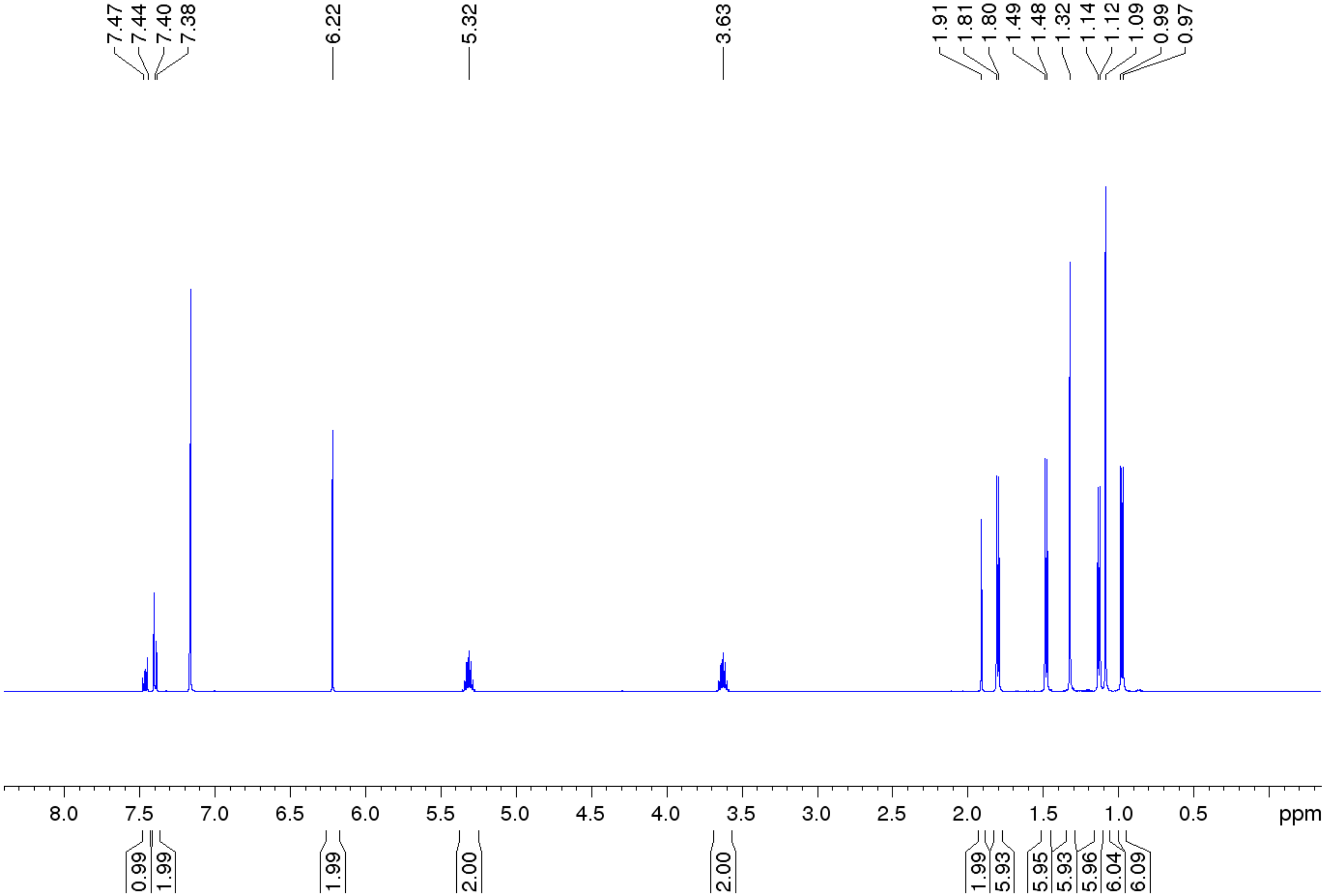

Figure S1. ^{1}H NMR spectrum of **2^{CN}** in C_6D_6.

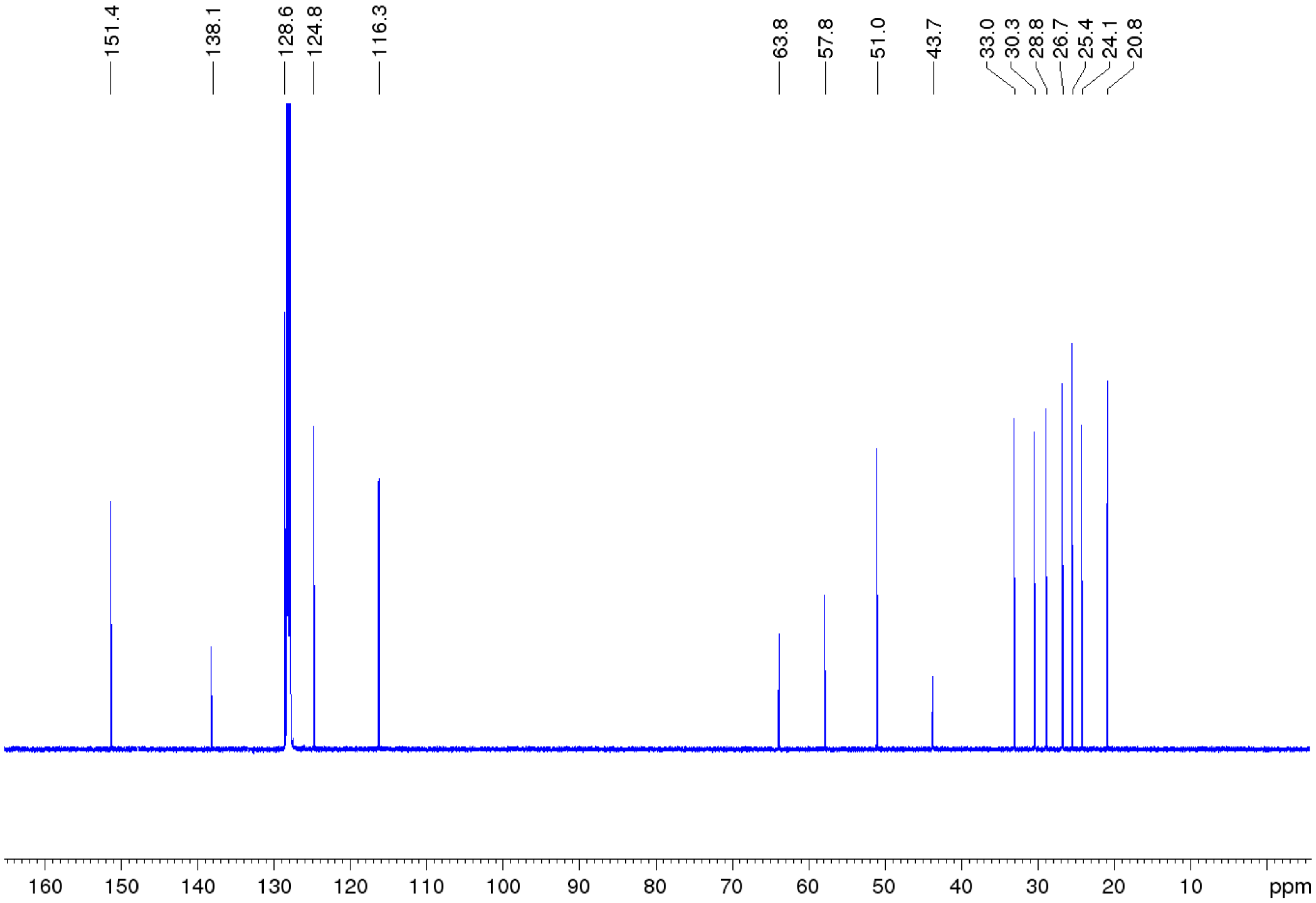

Figure S2. $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{2^{CN}}$ in C_6D_6.

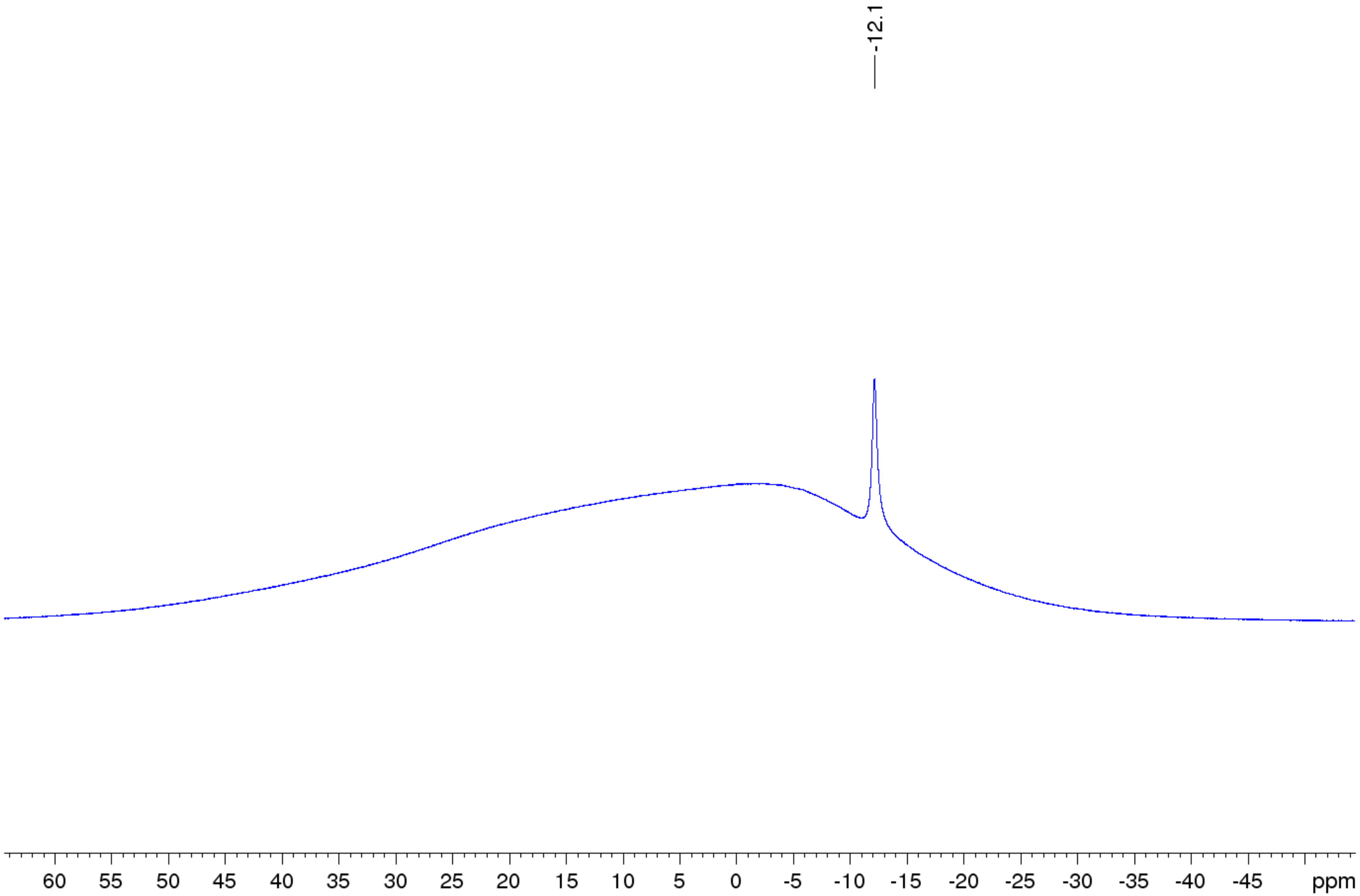

Figure S3. ^{11}B NMR spectrum of **2$^{\mathbf{CN}}$** in C_6D_6.

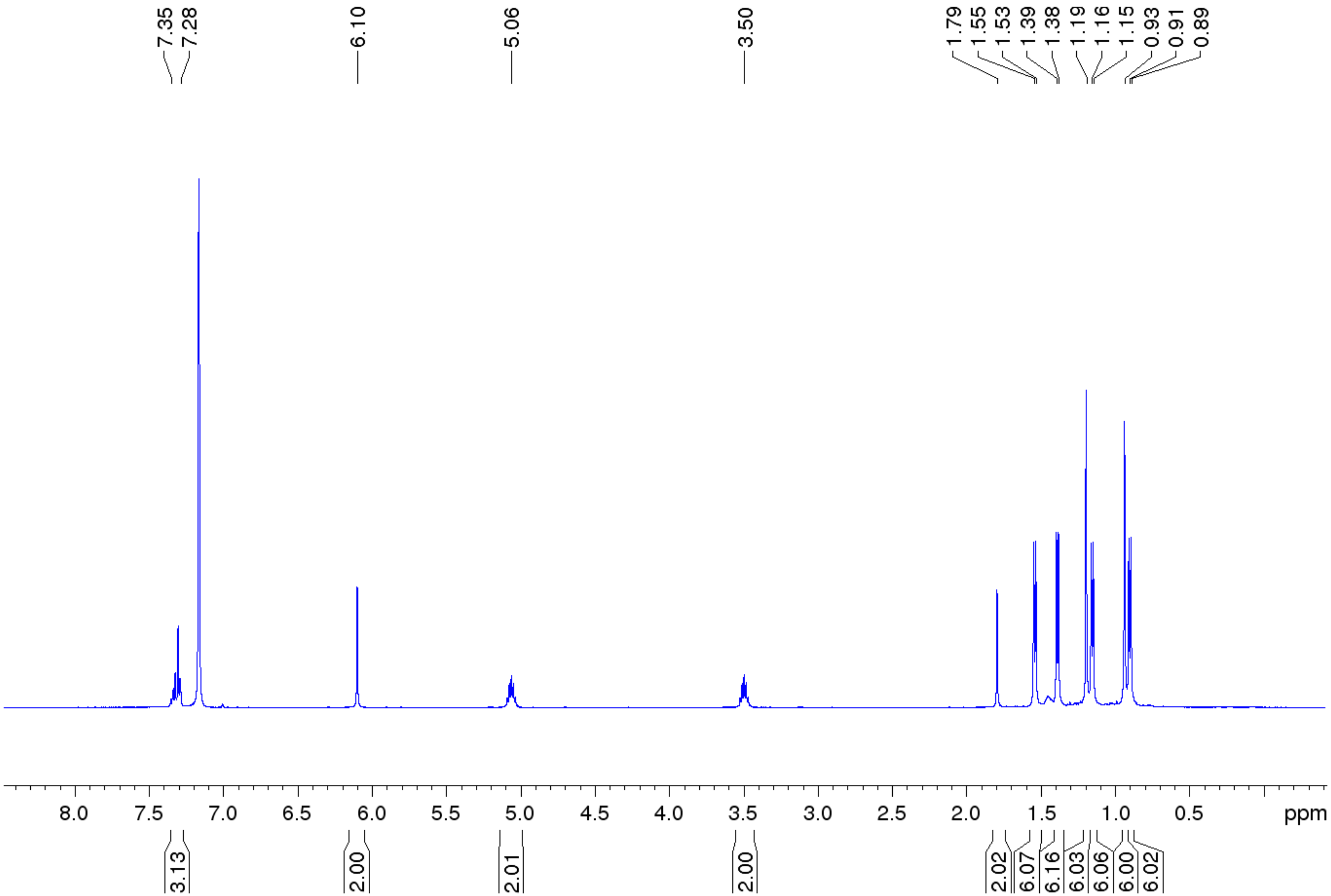

Figure S4. ^{1}H NMR spectrum of **2^{NCS}-Cr** in C_6D_6.

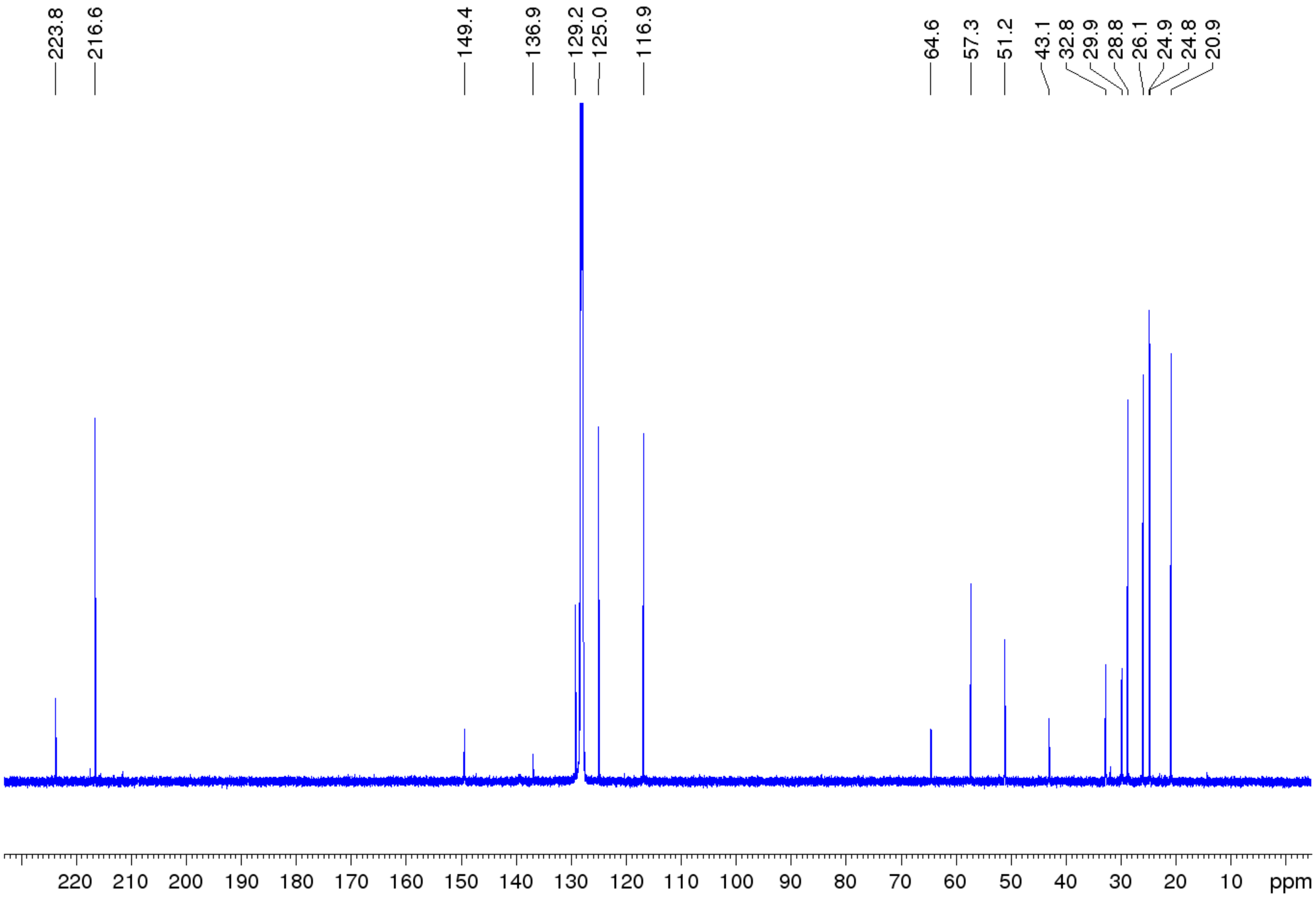

Figure S5. $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{2^{NCS}}$**-Cr** in C_6D_6.

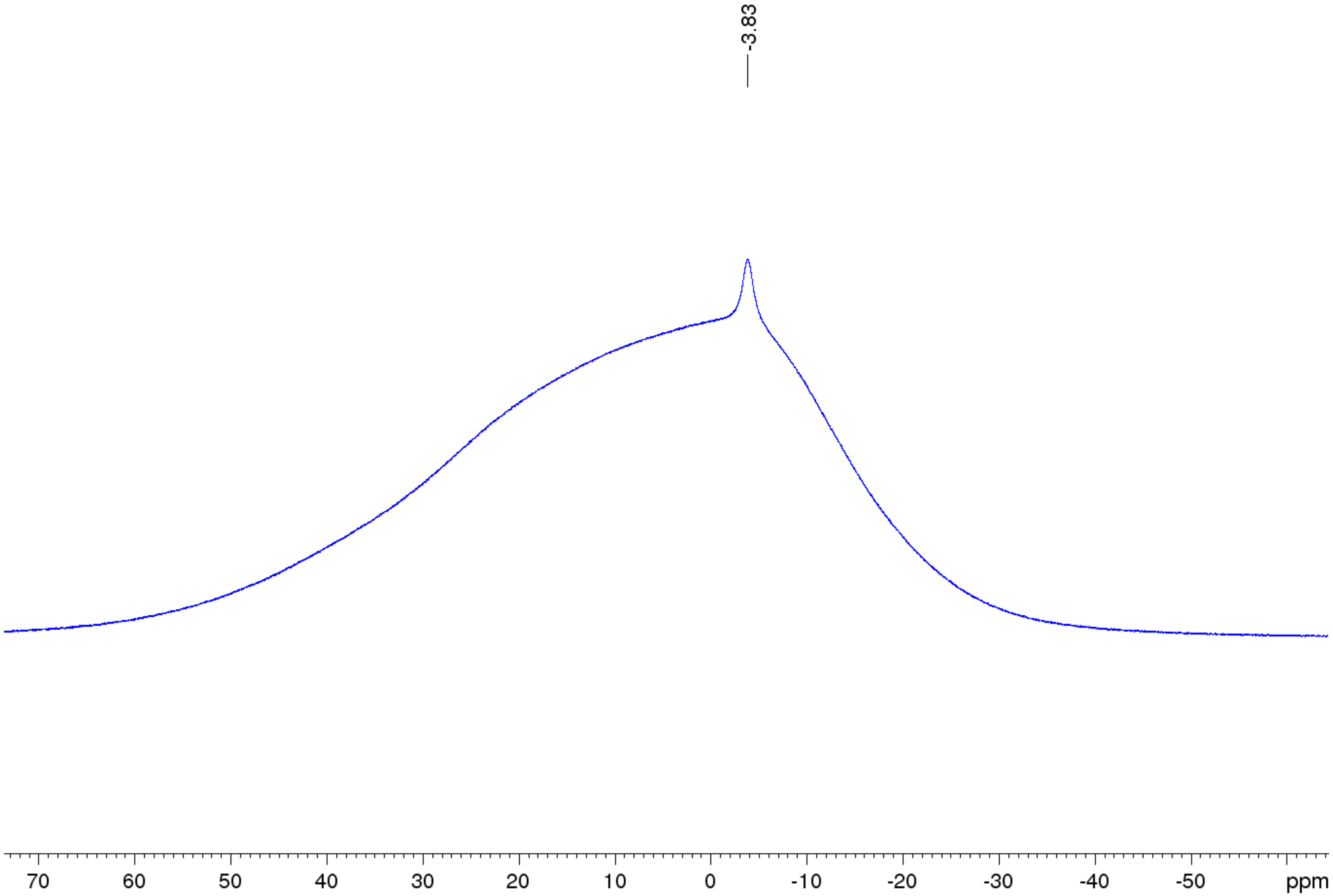

Figure S6. ^{11}B NMR spectrum of **2^{NCS}-Cr** in C_6D_6.

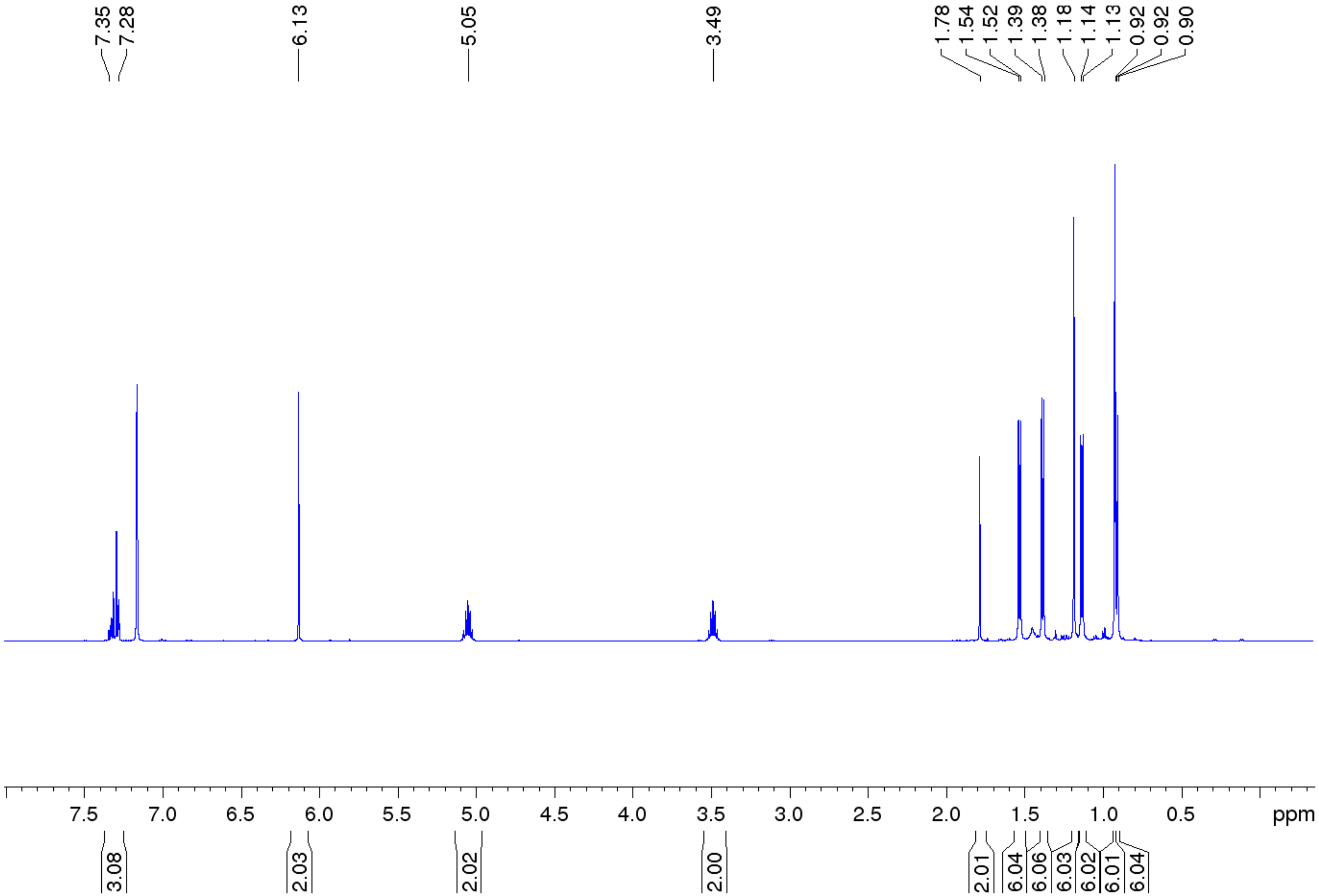

Figure S7. ^{1}H NMR spectrum of $\mathbf{2^{NCS}}$**-W** in C_6D_6.

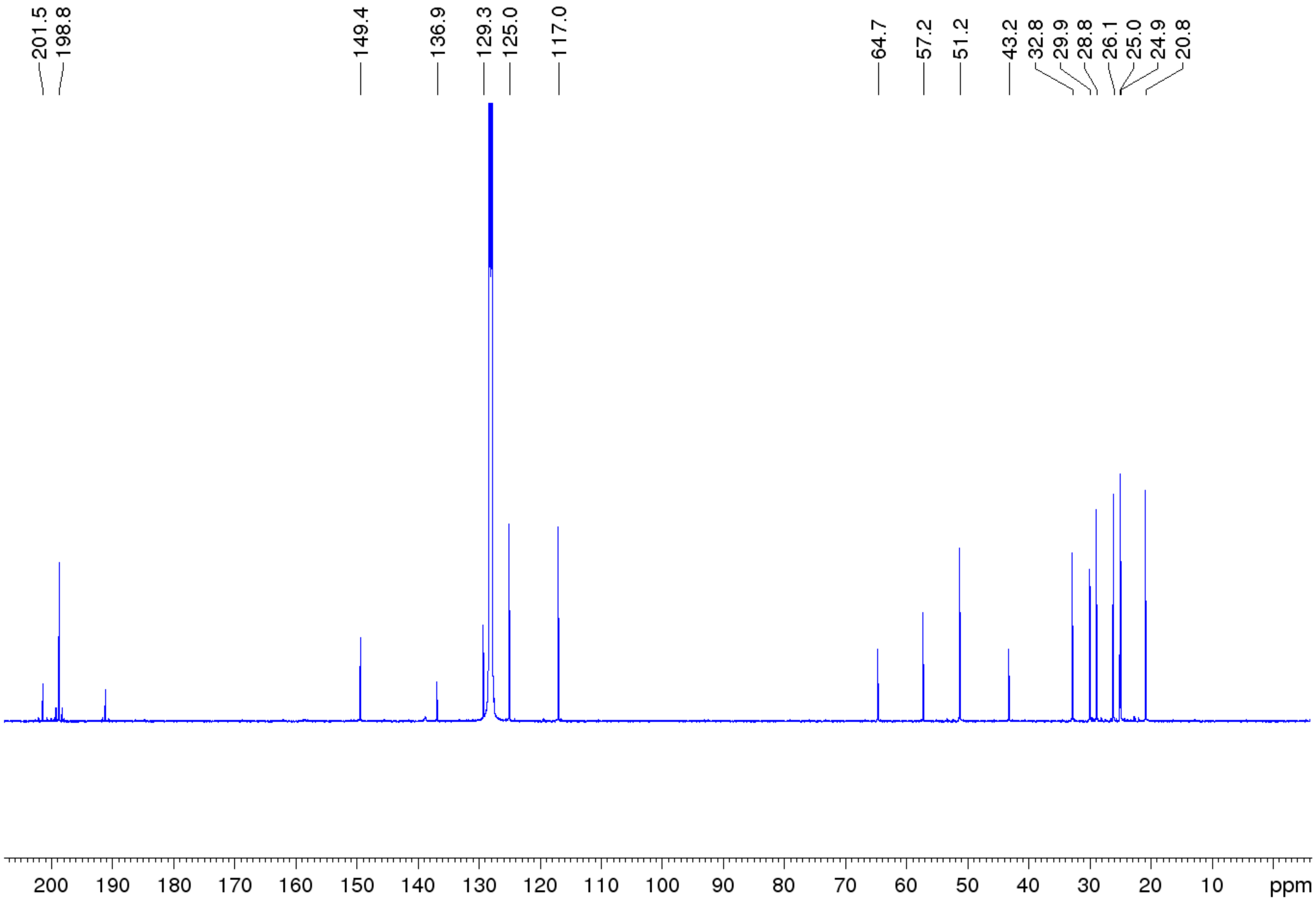

Figure S8. $^{13}C\{^1H\}$ NMR spectrum of **2^{NCS}-W** in C_6D_6.

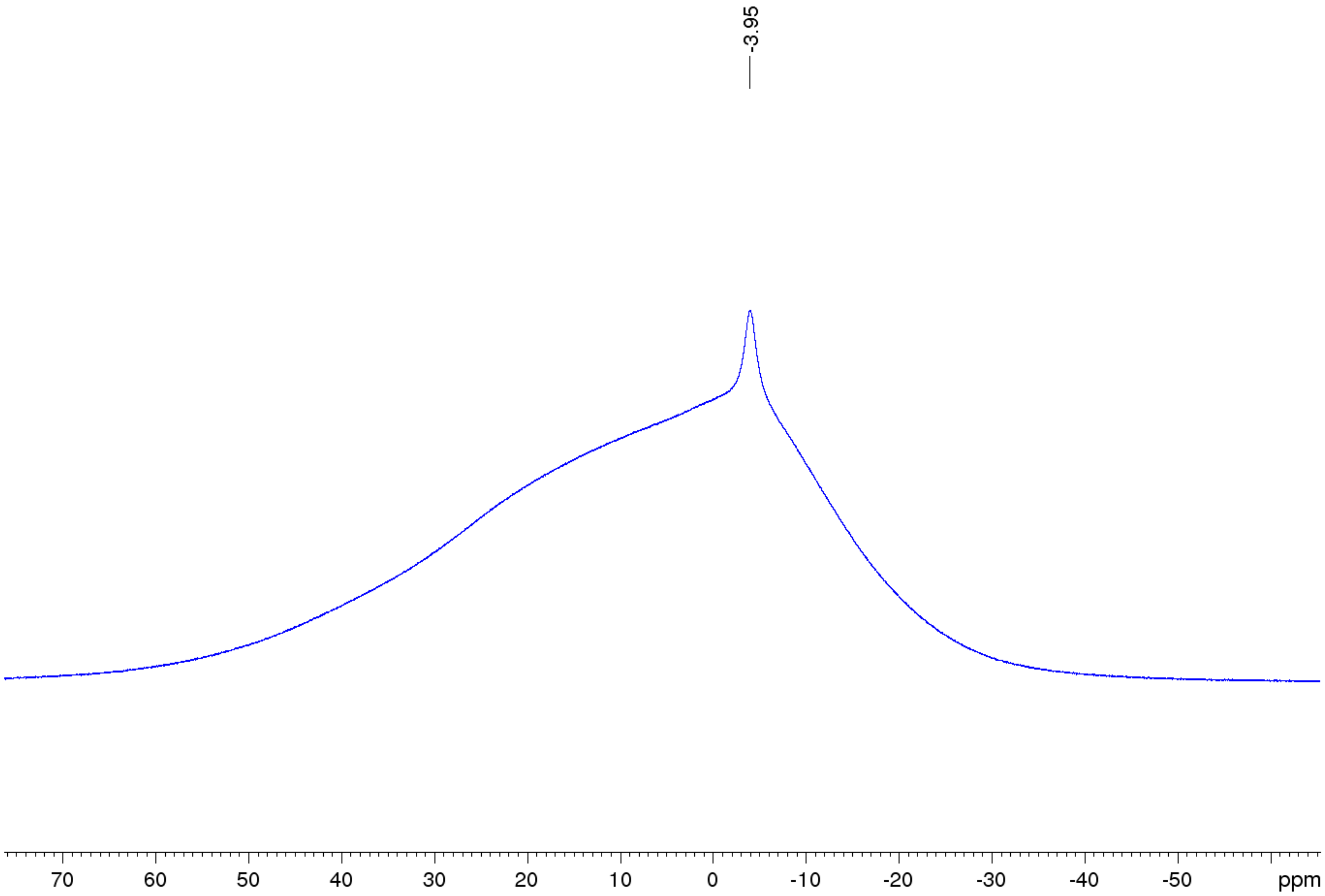

Figure S9. ^{11}B NMR spectrum of **2^{NCS}-W** in C_6D_6.

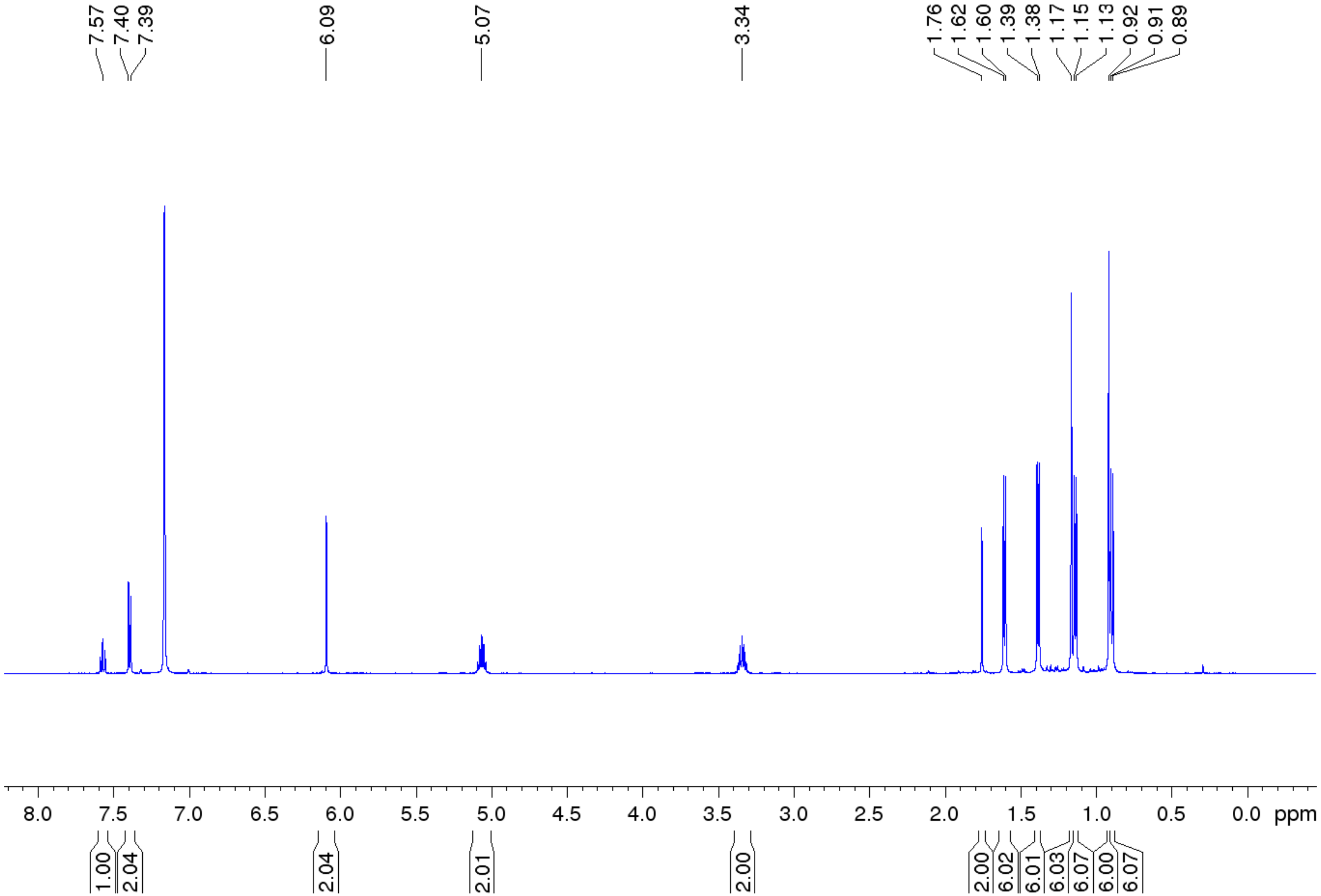

Figure S10. ^{1}H NMR spectrum of **2^{CN}-Cr** in C_6D_6.

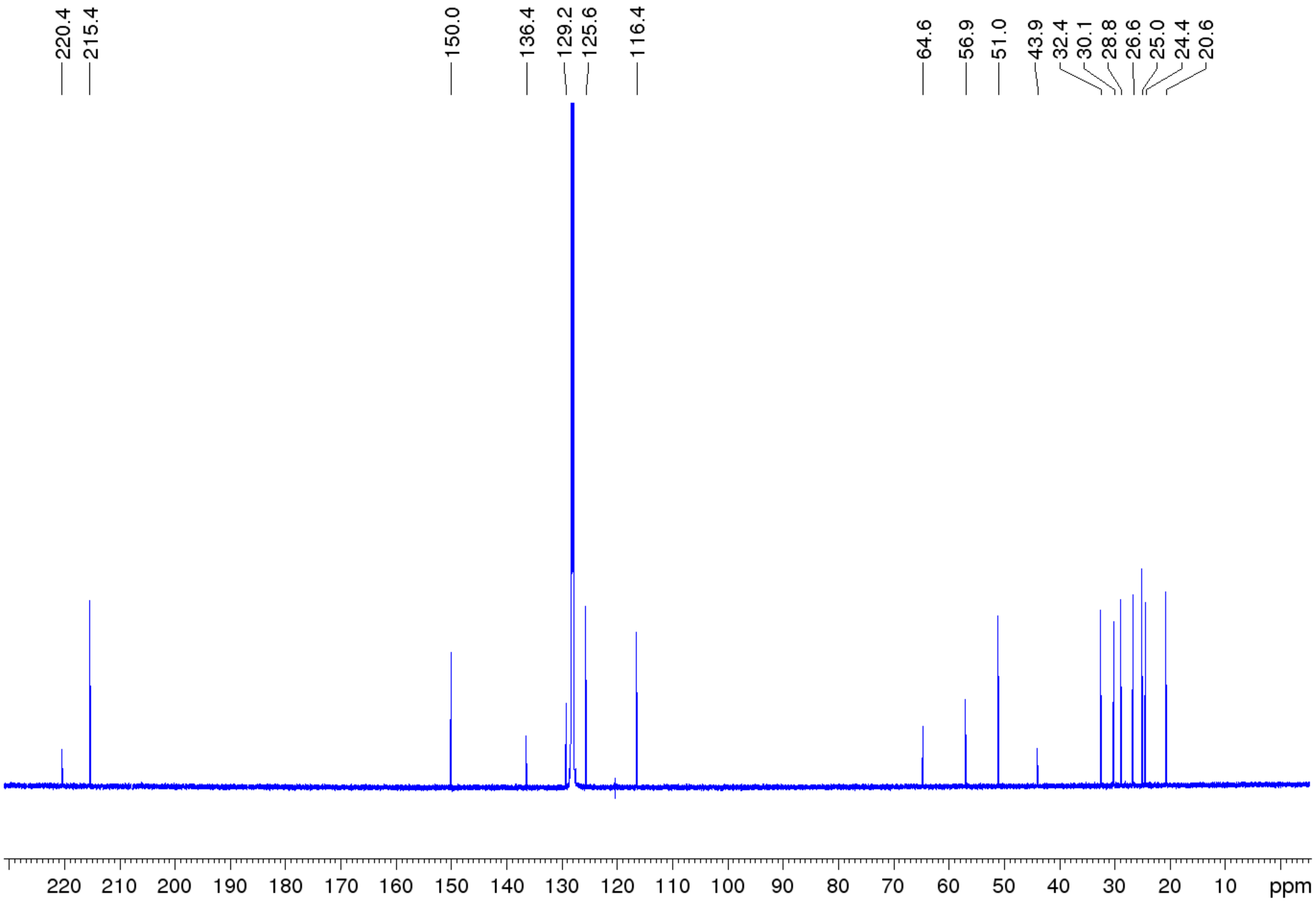

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **2^{CN}-Cr** in C_6D_6.

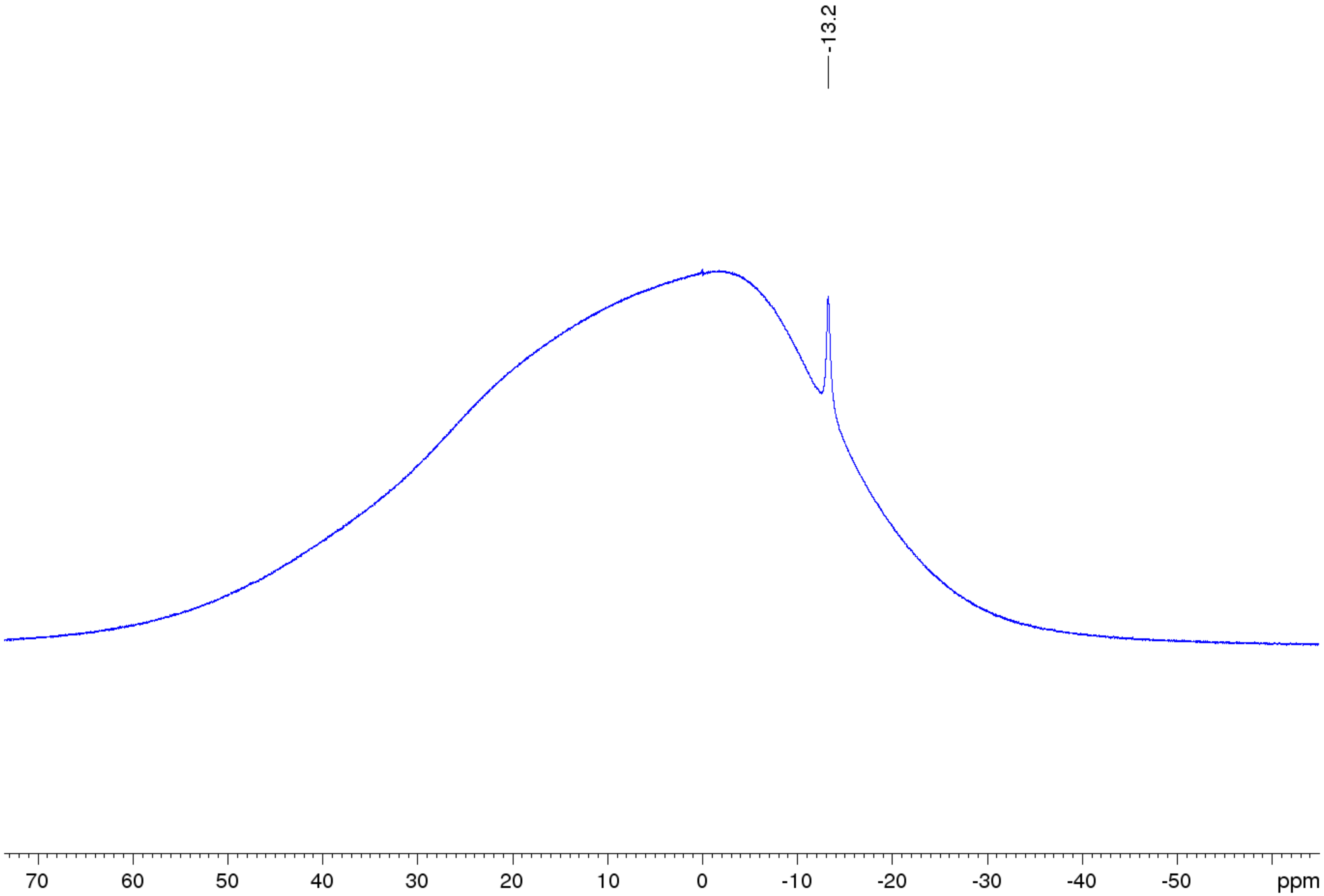

Figure S12. ^{11}B NMR spectrum of **2^{CN}-Cr** in C_6D_6.

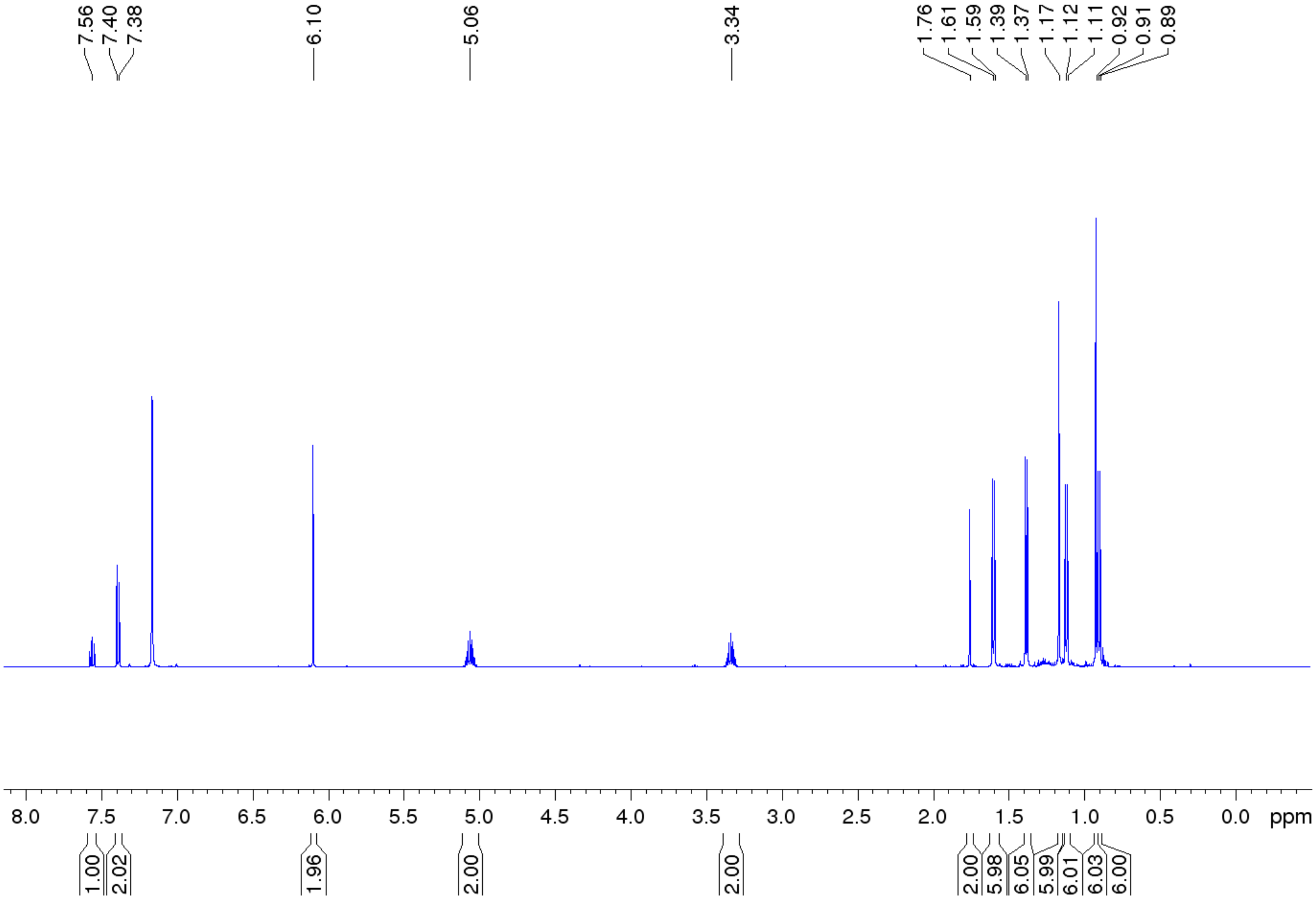

Figure S13. ^{1}H NMR spectrum of **(*Z*)-2$^{\mathbf{CN}}$-Mo** in C_6D_6.

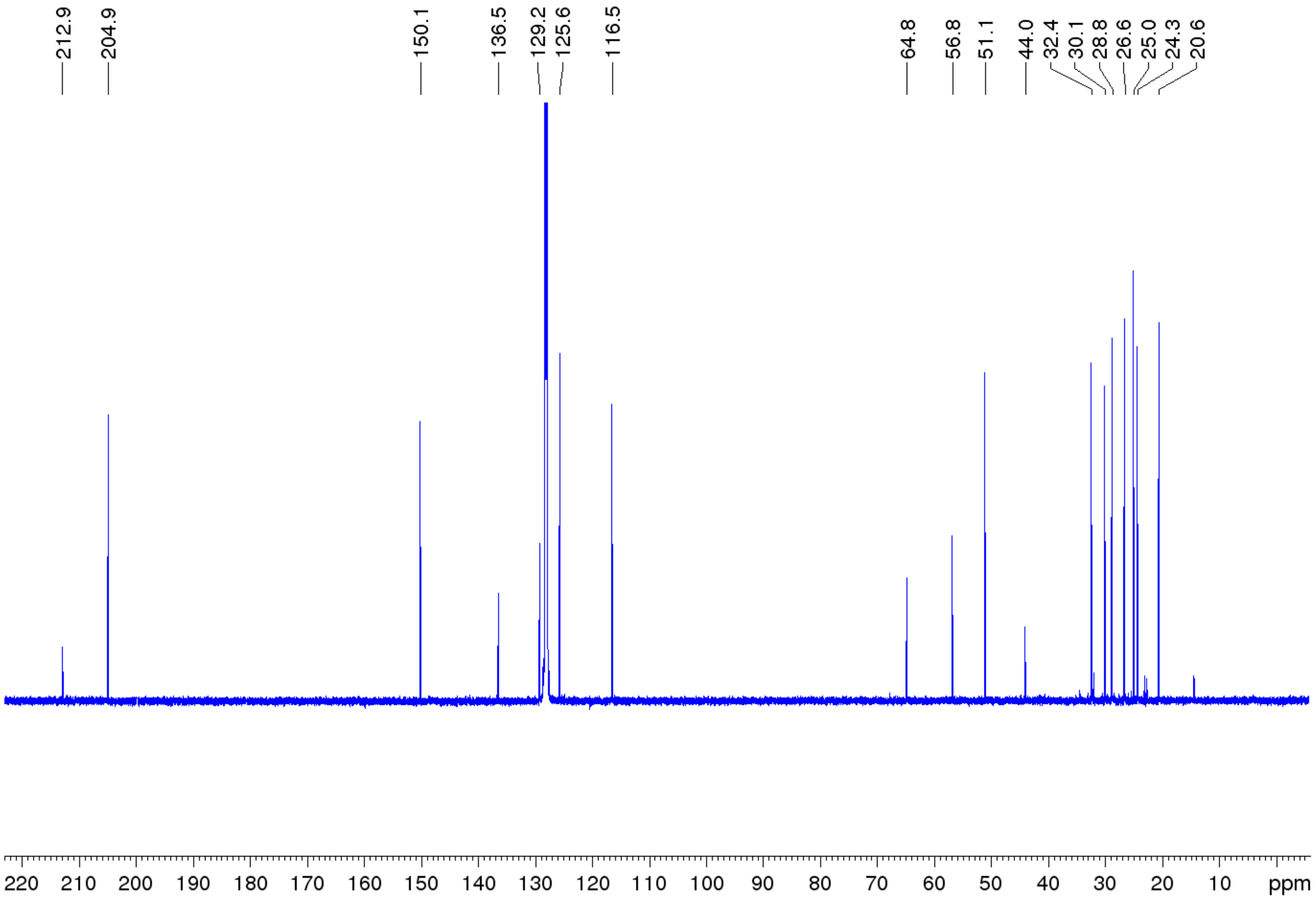

Figure S14. $^{13}C\{^1H\}$ NMR spectrum of **(*Z*)-2$^{\mathbf{CN}}$-Mo** in C_6D_6.

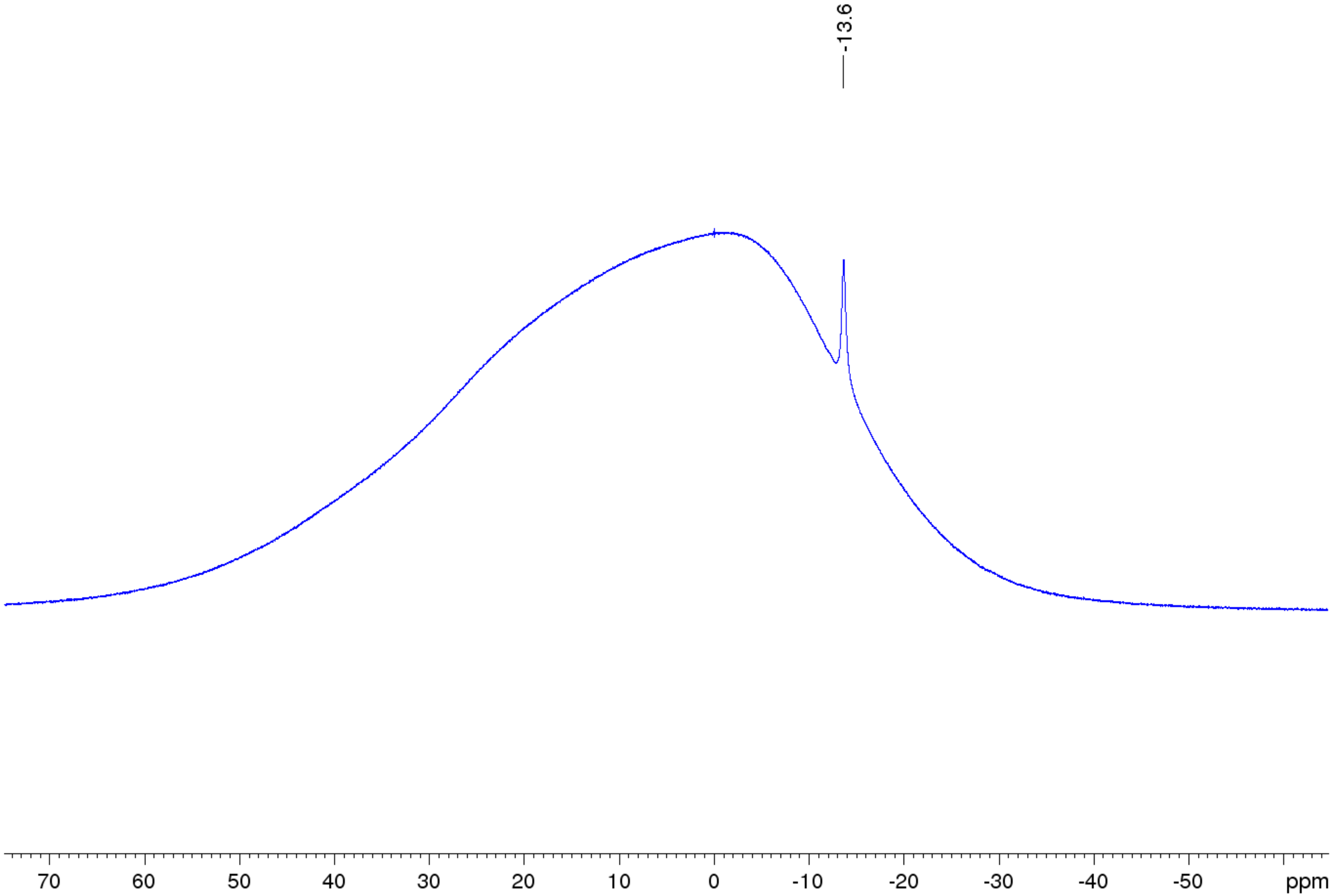

Figure S15. ^{11}B NMR spectrum of **(*Z*)-2$^{\mathbf{CN}}$-Mo** in C_6D_6.

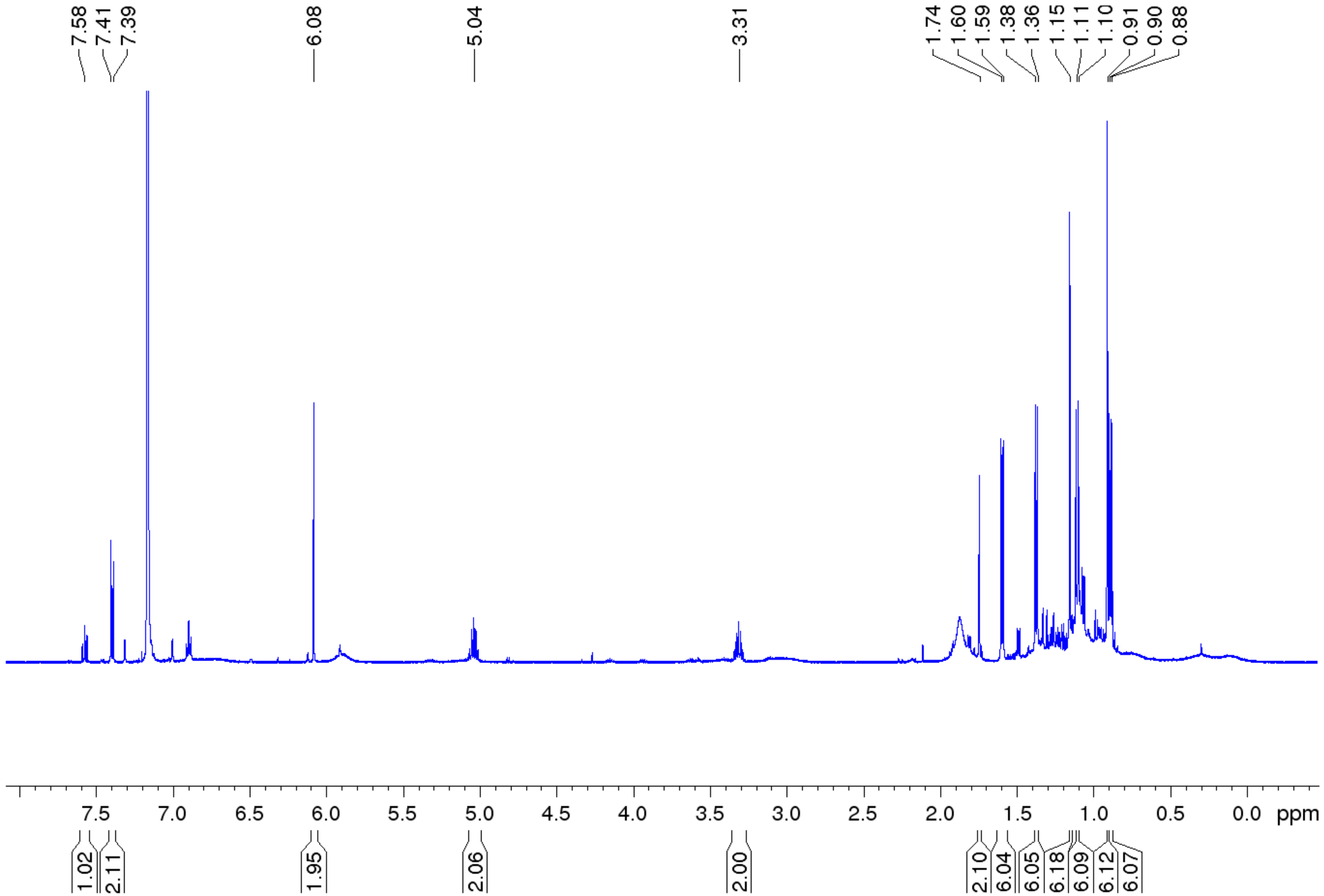

Figure S16. ^{1}H NMR spectrum of the 3:2 isomer mixture **(*E*)/(*Z*)-2$^{\mathbf{CN}}$-W** in C_6D_6. Only chemical shifts and integrals of the (*Z*)-isomer have been picked. The resonances of the (*E*)-isomer are strongly broadened by hindered rotation.

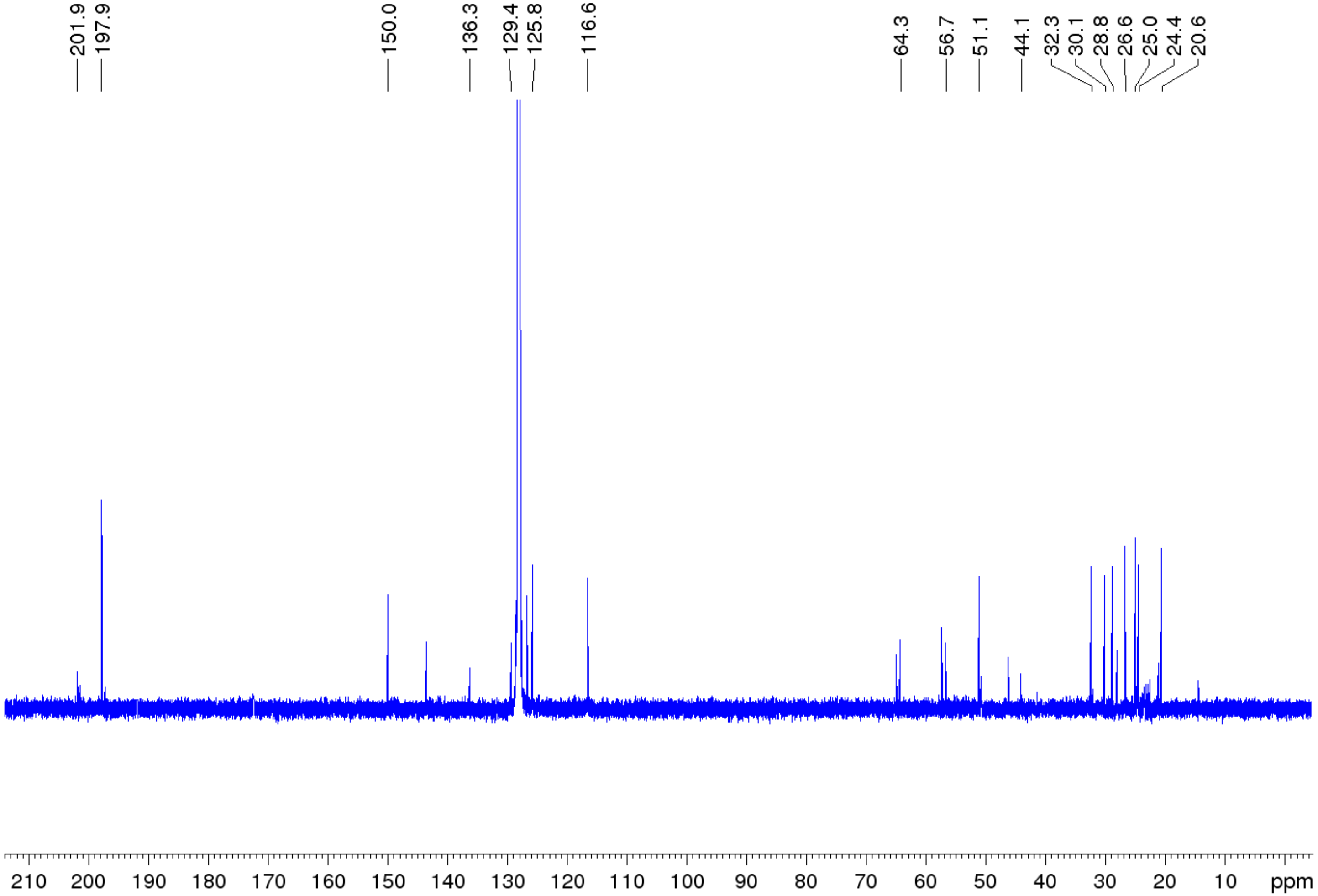

Figure S17. $^{13}C\{^1H\}$ NMR spectrum of the 3:2 isomer mixture ***(E)*/*(Z)*-2^{CN}-W** in C_6D_6. in C_6D_6. Only chemical shifts of the (*Z*)-isomer have been picked.

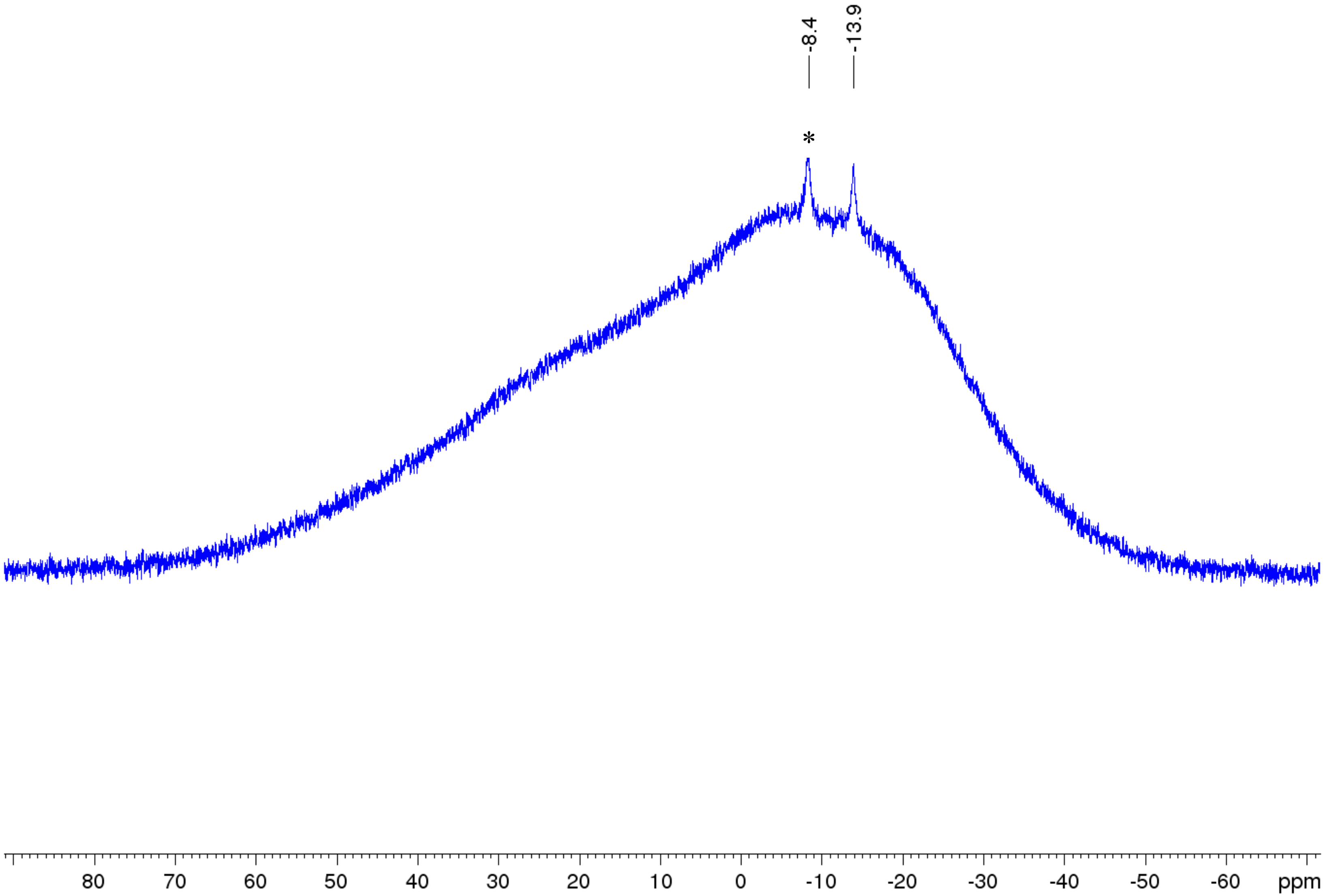

Figure S18. ^{11}B NMR spectrum of the 3:2 isomer mixture of **(*E*)-2$^{\mathbf{CN}}$-W** (*) and **(*Z*)-2$^{\mathbf{CN}}$-W** in C_6D_6.

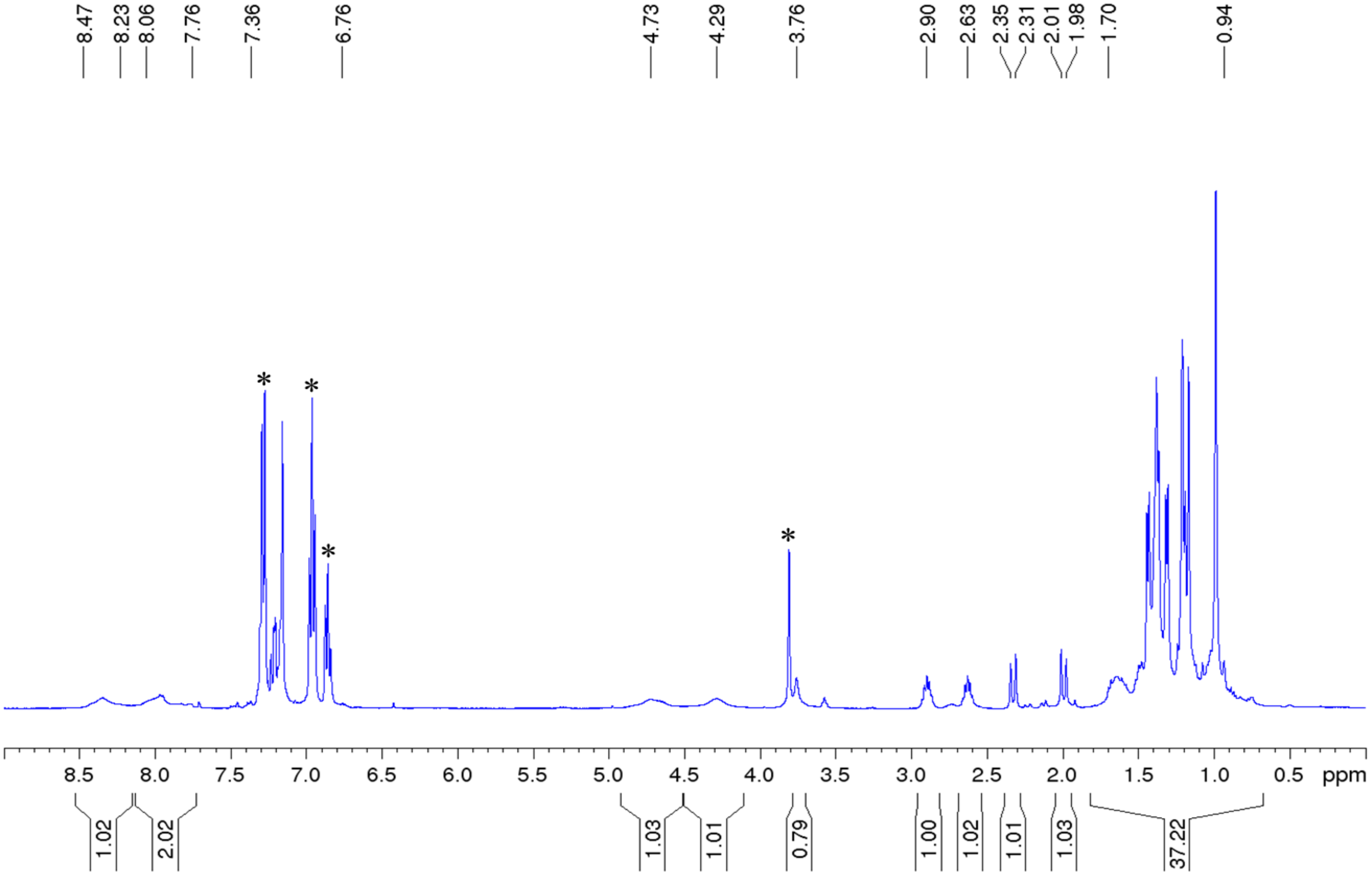

Figure S19. $^{1}H\{^{11}B\}$ NMR spectrum of $\mathbf{3^{NCS}}$ recorded *in situ* from the reaction mixture in C_6D_6 with excess thiophenol. The additional resonances belong to residual thiophenol (*).

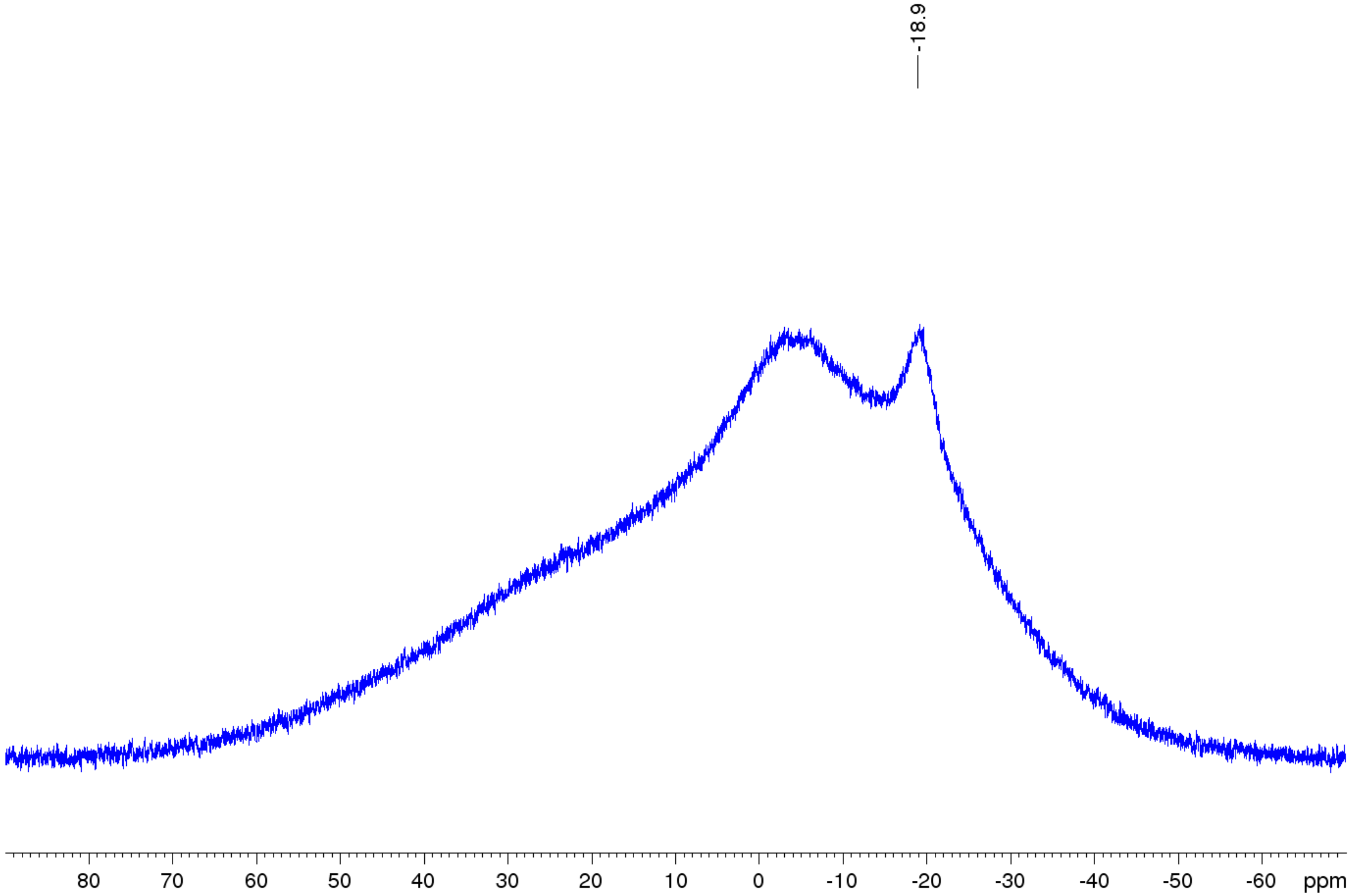

Figure S20. ^{11}B NMR spectrum of **3**$^{\mathbf{NCS}}$ recorded *in situ* from the reaction mixture in C_6D_6 with excess thiophenol.

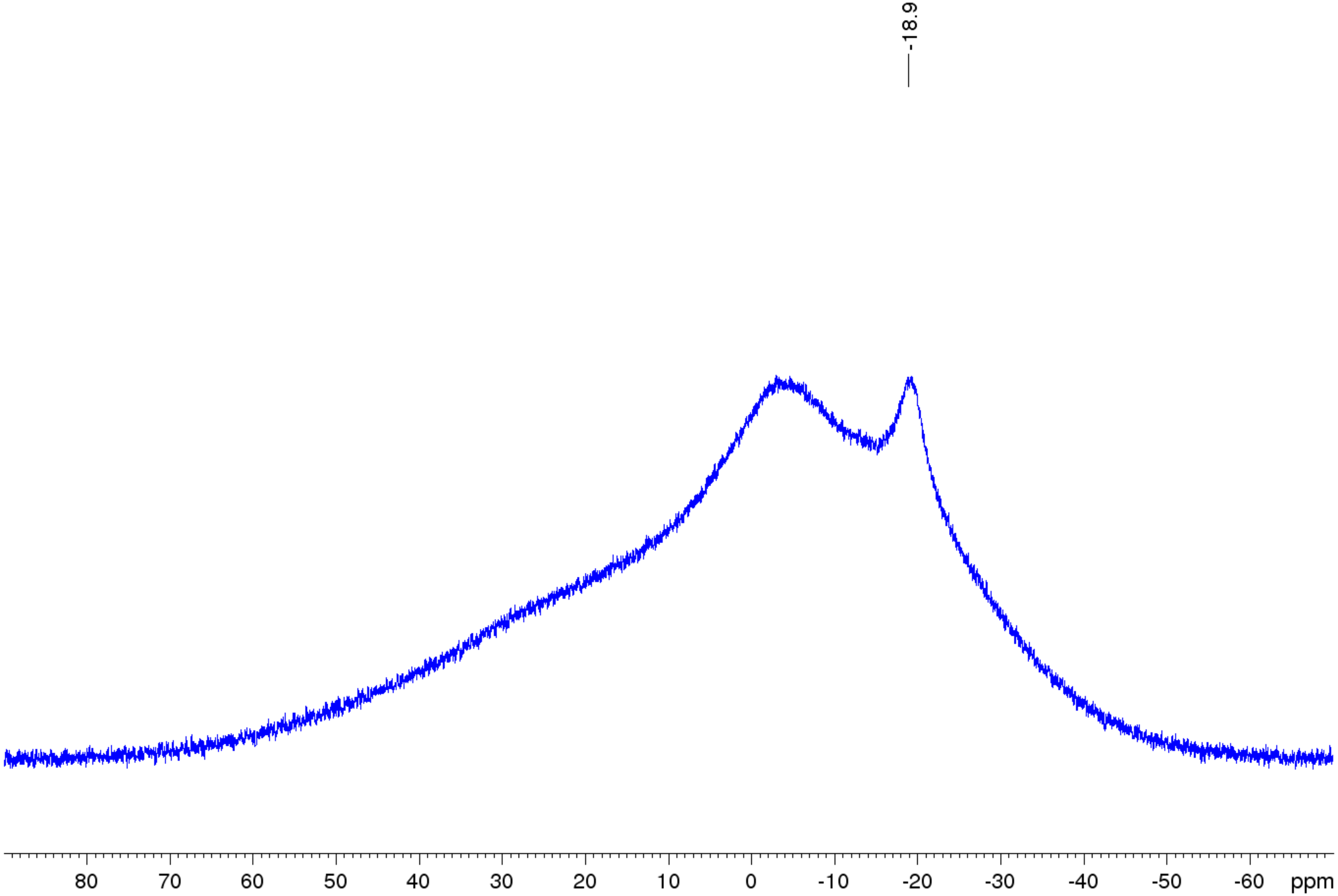

Figure S21. $^{11}B\{^1H\}$ NMR spectrum of $\mathbf{3}^{\mathbf{NCS}}$ recorded *in situ* from the reaction mixture in C_6D_6 with excess thiophenol.

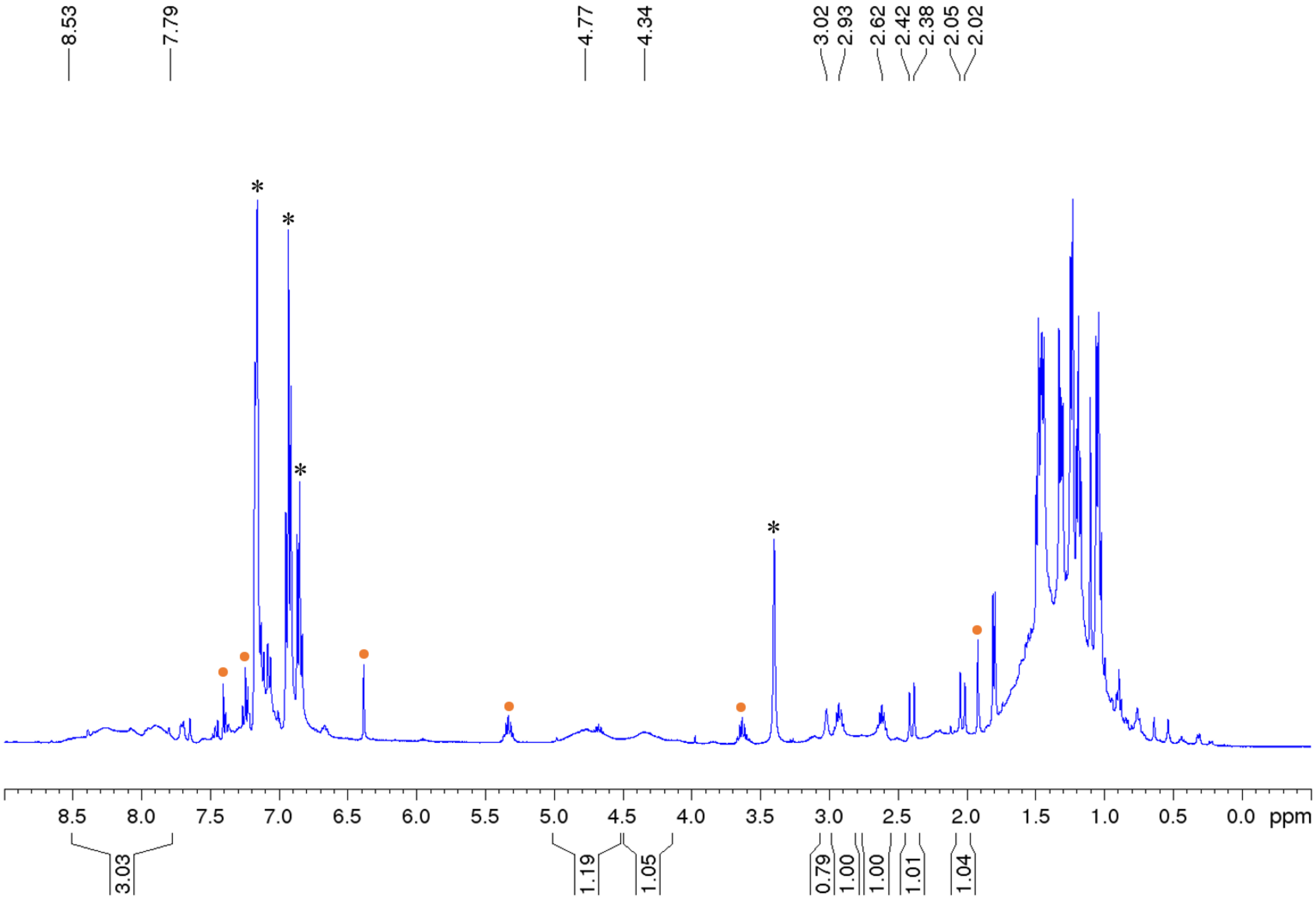

Figure S22. $^1H\{^{11}B\}$ NMR spectrum of $\mathbf{3^{CN}}$ recorded *in situ* from the reaction mixture in C_6D_6 with excess thiophenol. Additional resonances belong to residual thiophenol (*) and **(*Z*)-2**$^{\mathbf{CN}}$ (●). Only characteristic resonances in the region between ca. 2–9 ppm were assigned.

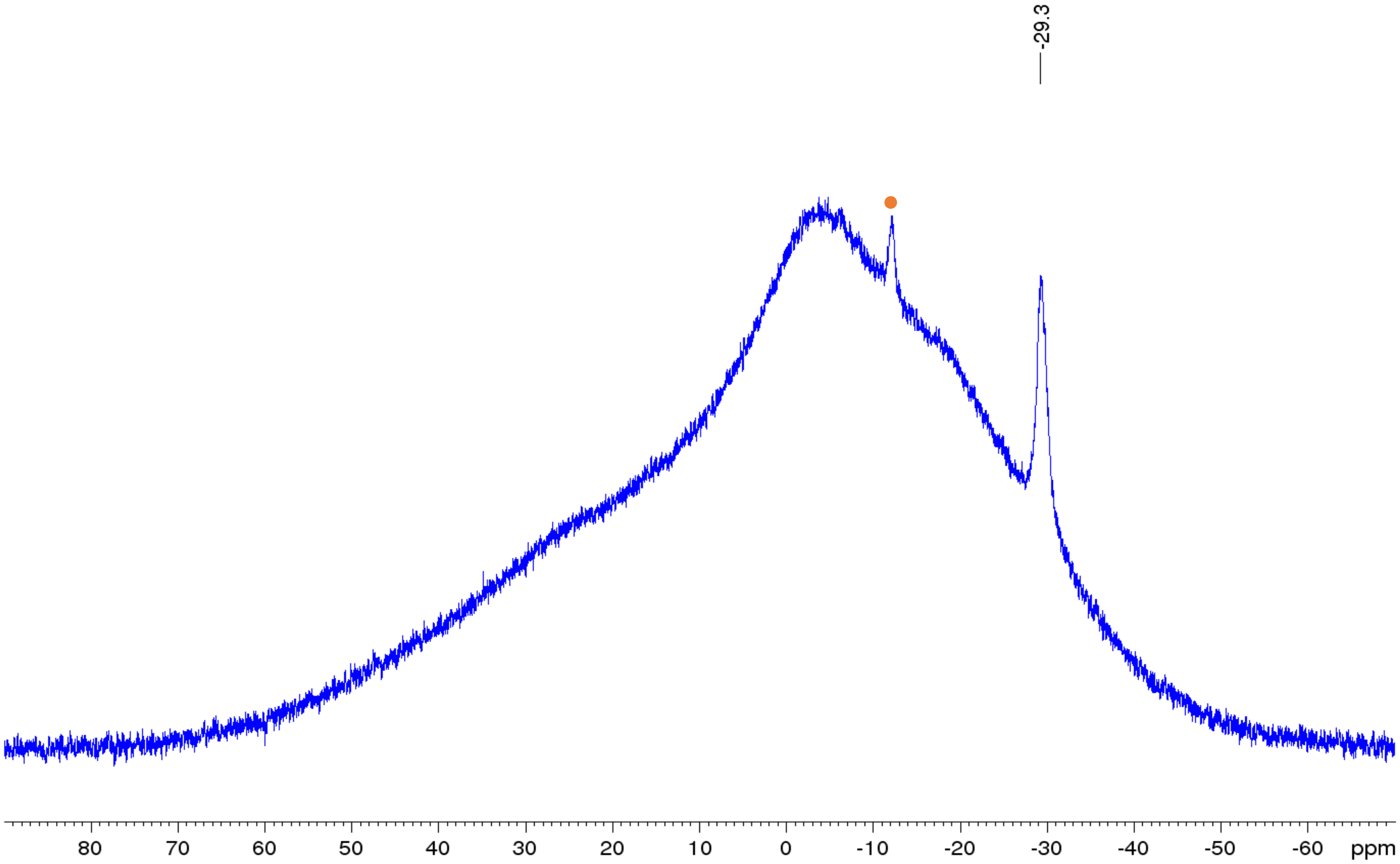

Figure S23. *In situ* recorded ^{11}B NMR spectrum of **3**$^{\text{CN}}$ recorded *in situ* from the reaction mixture in C_6D_6 with excess thiophenol. The additional resonance belongs to residual **(*Z*)-2**$^{\text{CN}}$ (●).

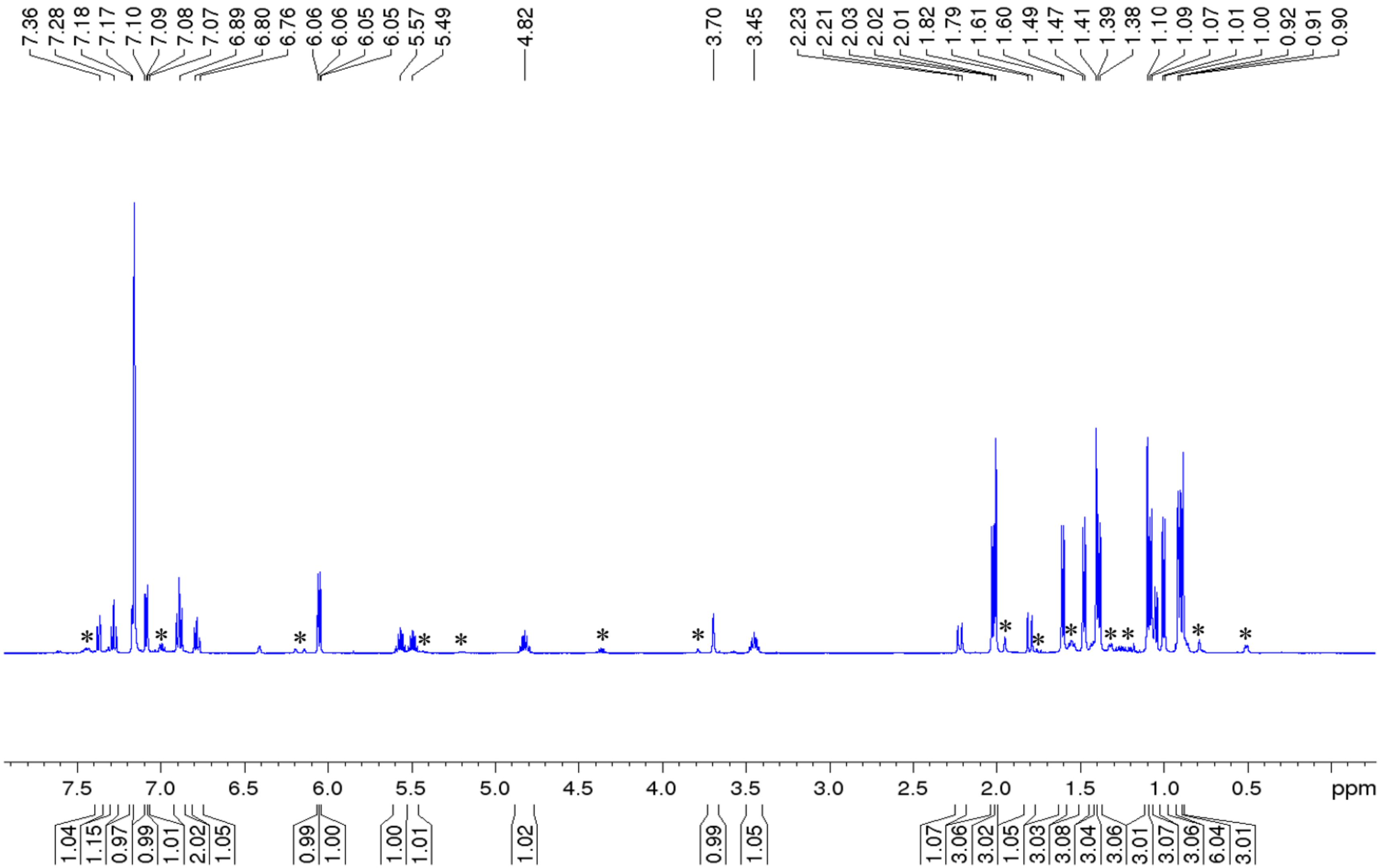

Figure S24. ^{1}H NMR spectrum of $\mathbf{4}^{\mathbf{NCS}}$ in C_6D_6. Only chemical shifts and integrals of the major diastereomer (85%) have been picked. The additional resonances belong to the minor diastereomer (*).

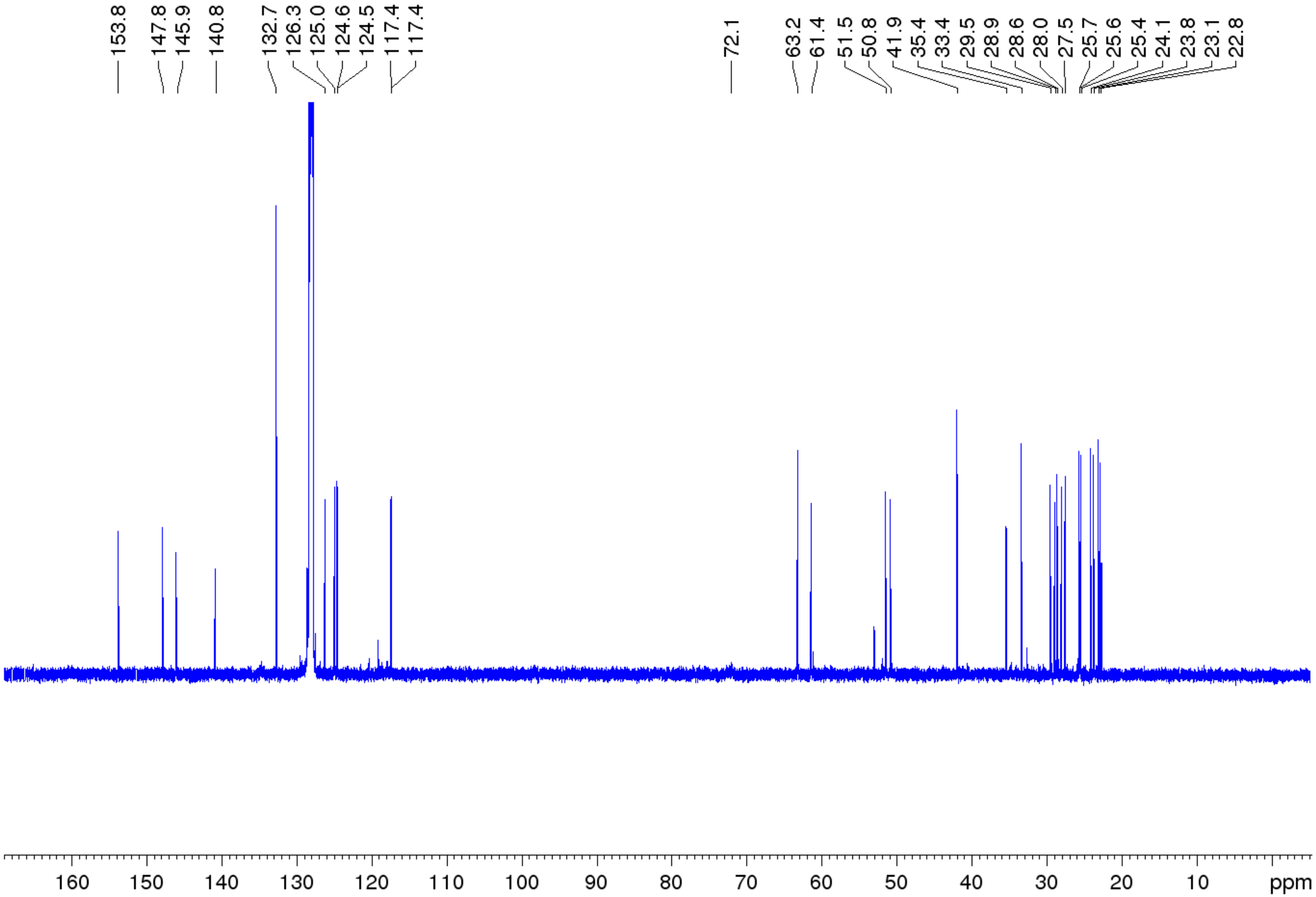

Figure S25. $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{4}^{\mathbf{NCS}}$ in C_6D_6.

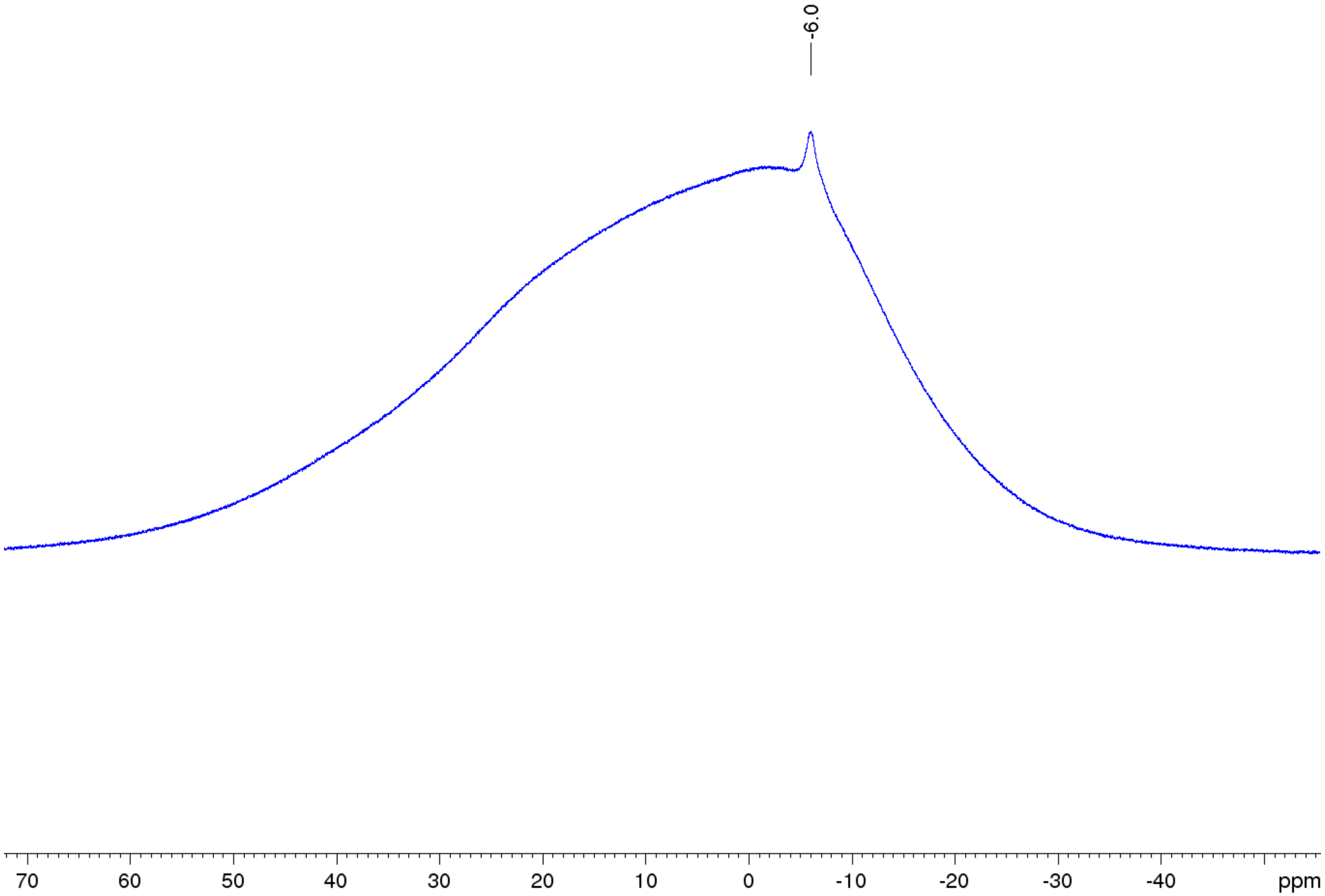

Figure S26. ^{11}B NMR spectrum of $\mathbf{4}^{\mathbf{NCS}}$ in C_6D_6.

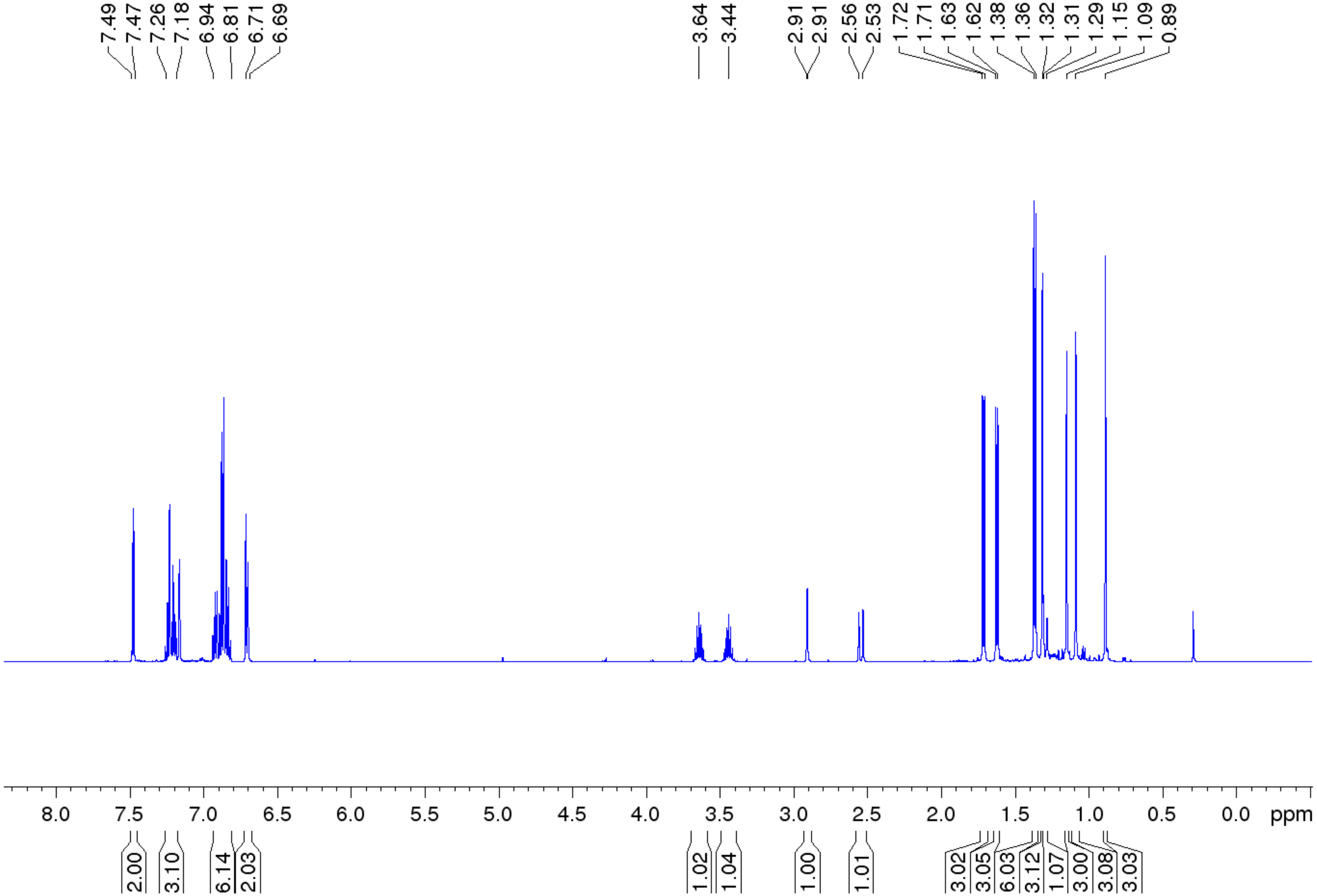

Figure S27. ^{1}H NMR spectrum of **5** in C_6D_6.

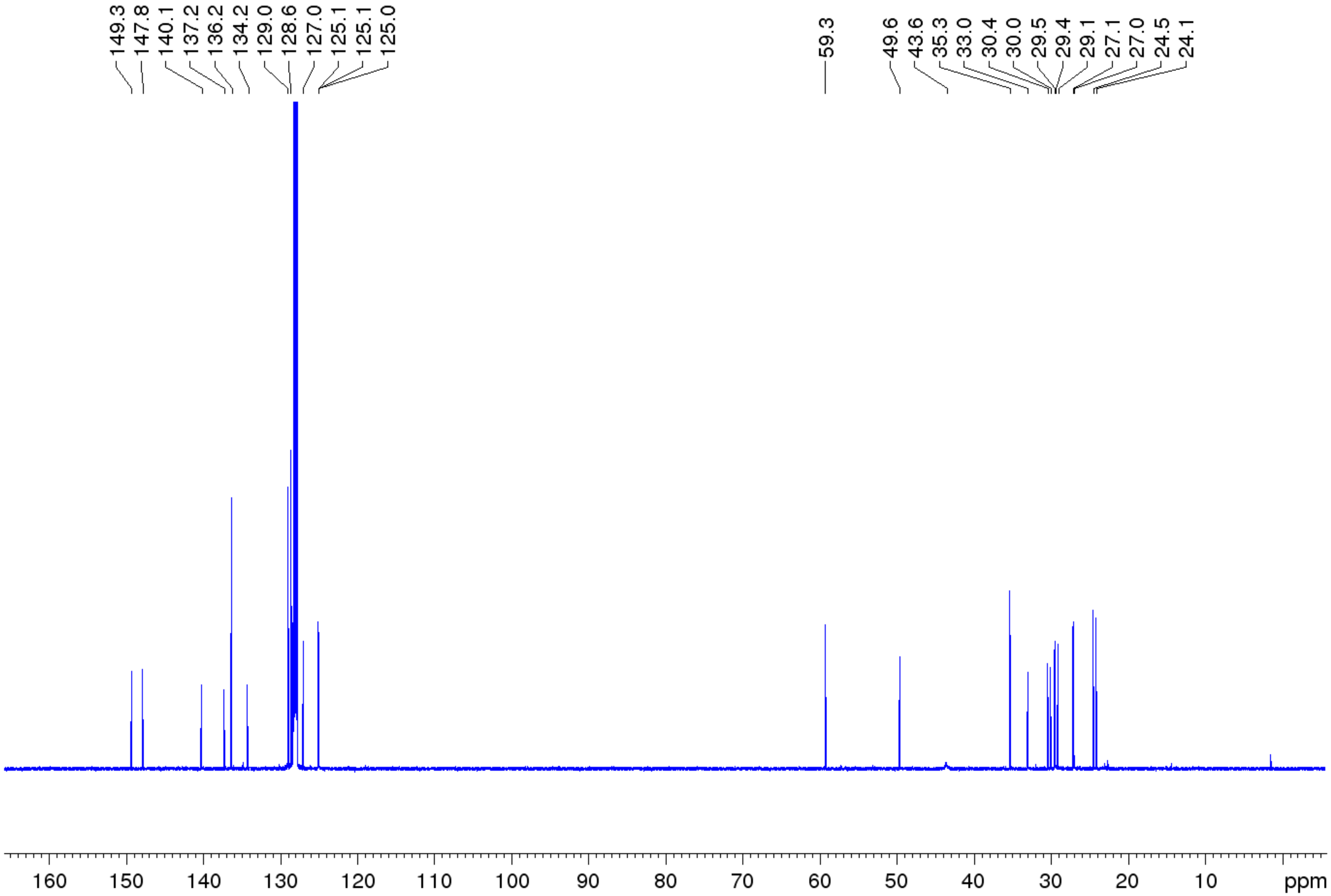

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in C_6D_6.

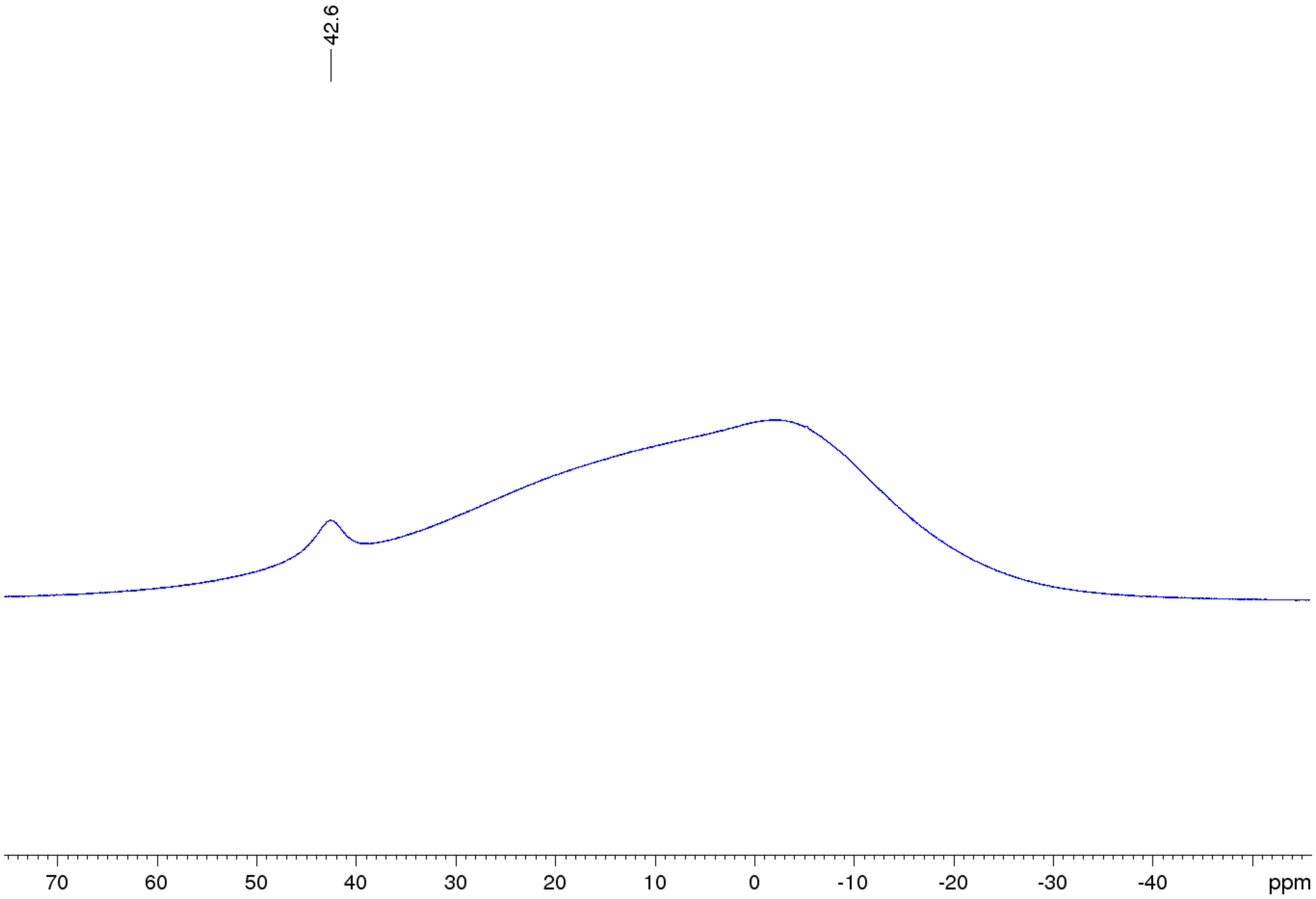

Figure S29. ^{11}B NMR spectrum of **5** in C_6D_6.

Stack-plot of ^{1}H NMR spectra of 2^{NCS}, 2^{NCS}-Cr and 2^{NCS}-W

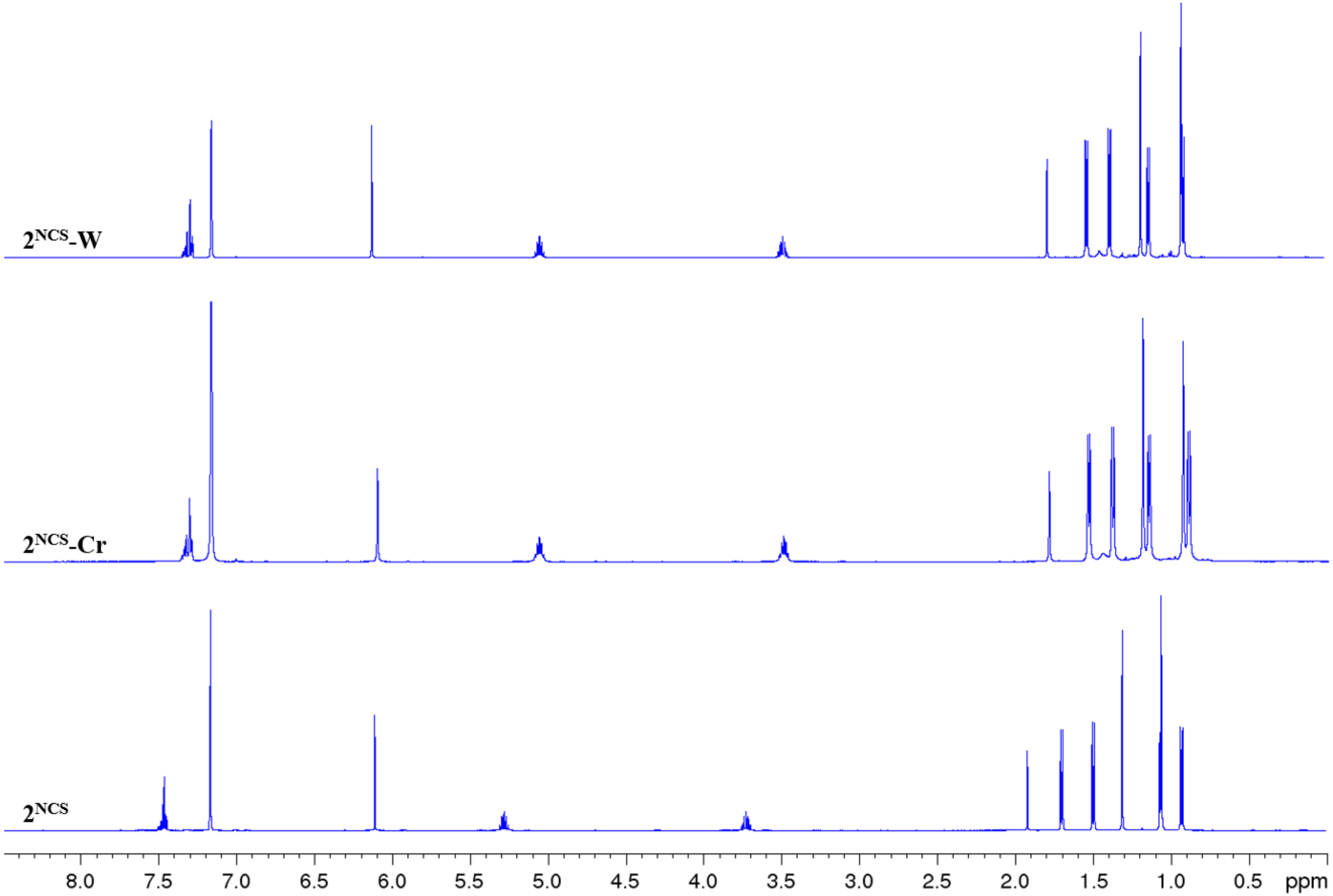

Figure S30. Stack-plot of ^{1}H NMR spectra of **2^{NCS}**, **2^{NCS}-Cr** and **2^{NCS}-W** in C_6D_6.

NMR studies of the *E*/*Z* isomerisation of 2^{CN}-W

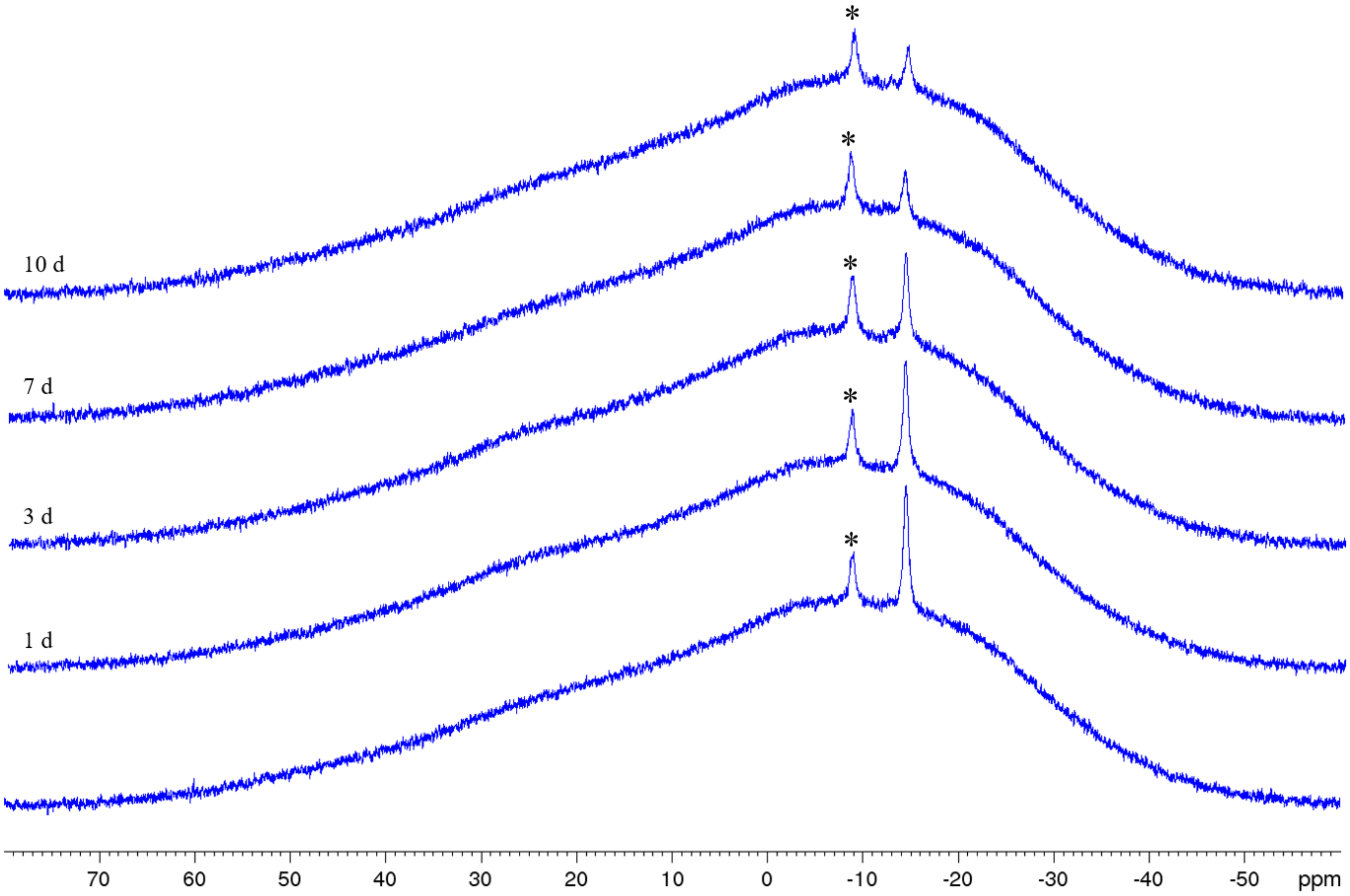

Figure S31. Stack-plot of ^{11}B NMR spectra for the thermal conversion of **(*Z*)-2^{CN}-W** to **(*E*)-2^{CN}-W** (*) in C_6D_6 at 60 °C.

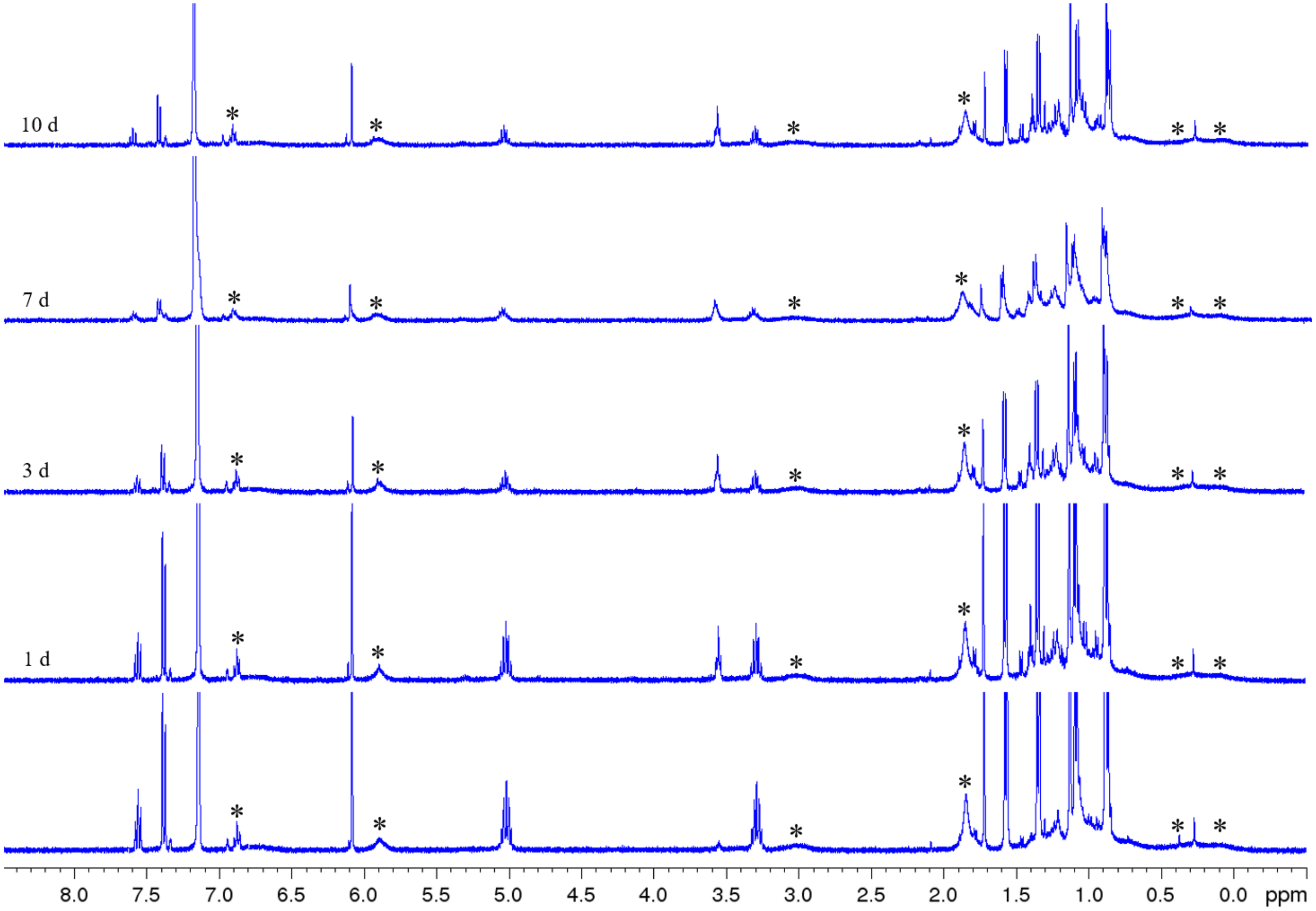

Figure S32. Stack-plot of ^{1}H NMR spectra for the thermal conversion of **(*Z*)-2$^{\mathbf{CN}}$-W** to **(*E*)-2$^{\mathbf{CN}}$-W** (*) in C_6D_6 at 60 °C.

NMR studies of the irreversible protonation of (*Z*)-2^{NCS} by PhSH

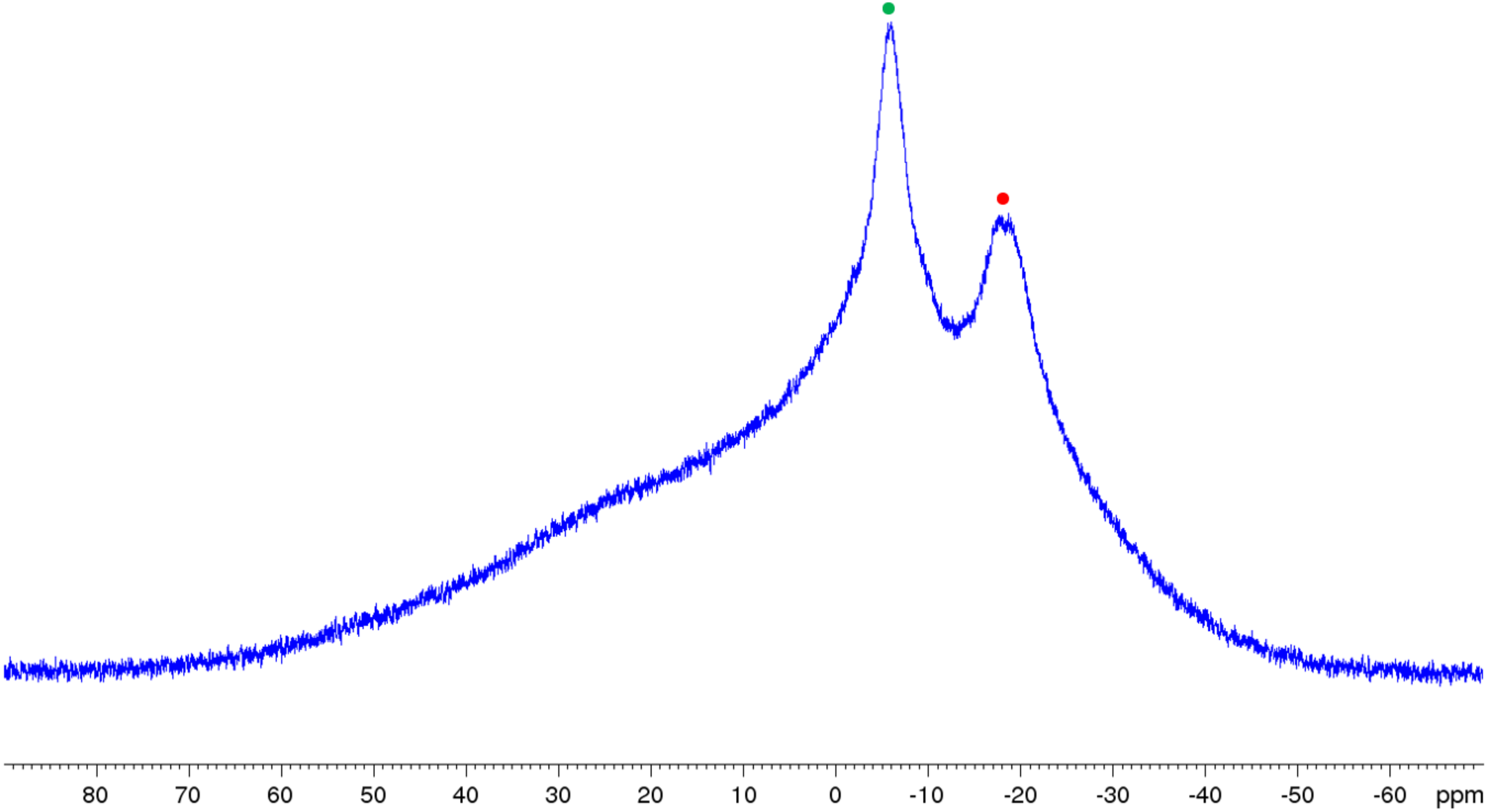

Figure S33. ^{11}B NMR spectrum of the conversion of **(*Z*)-2^{NCS}** to **3^{NCS}** (●) and **4^{NCS}** (●) recorded *in situ* in C_6D_6 after 12 h at room temperature.

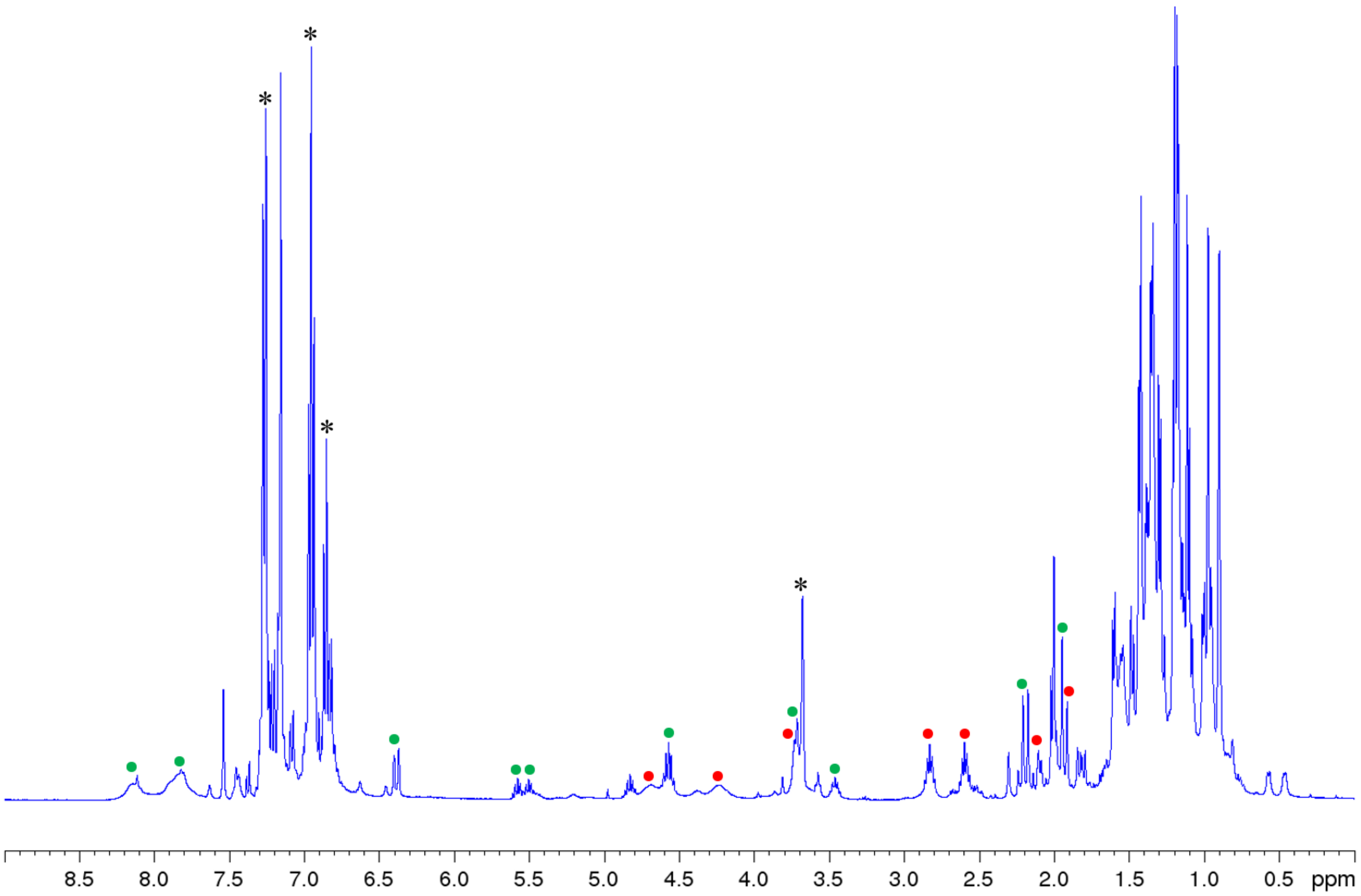

Figure S34. ^{1}H{^{11}B} NMR spectrum of the conversion of **(*Z*)-$\mathbf{2}^{\mathbf{NCS}}$** to $\mathbf{3}^{\mathbf{NCS}}$ (●) and $\mathbf{4}^{\mathbf{NCS}}$ (●) recorded *in situ* in C_6D_6 after 12 h at room temperature. The additional resonances belong to residual thiophenol (*). Only characteristic resonances in the region between ca. 2–9 ppm were assigned. See ^{1}H NMR spectra of $\mathbf{3}^{\mathbf{NCS}}$ and $\mathbf{4}^{\mathbf{NCS}}$, respectively, for full assignment.

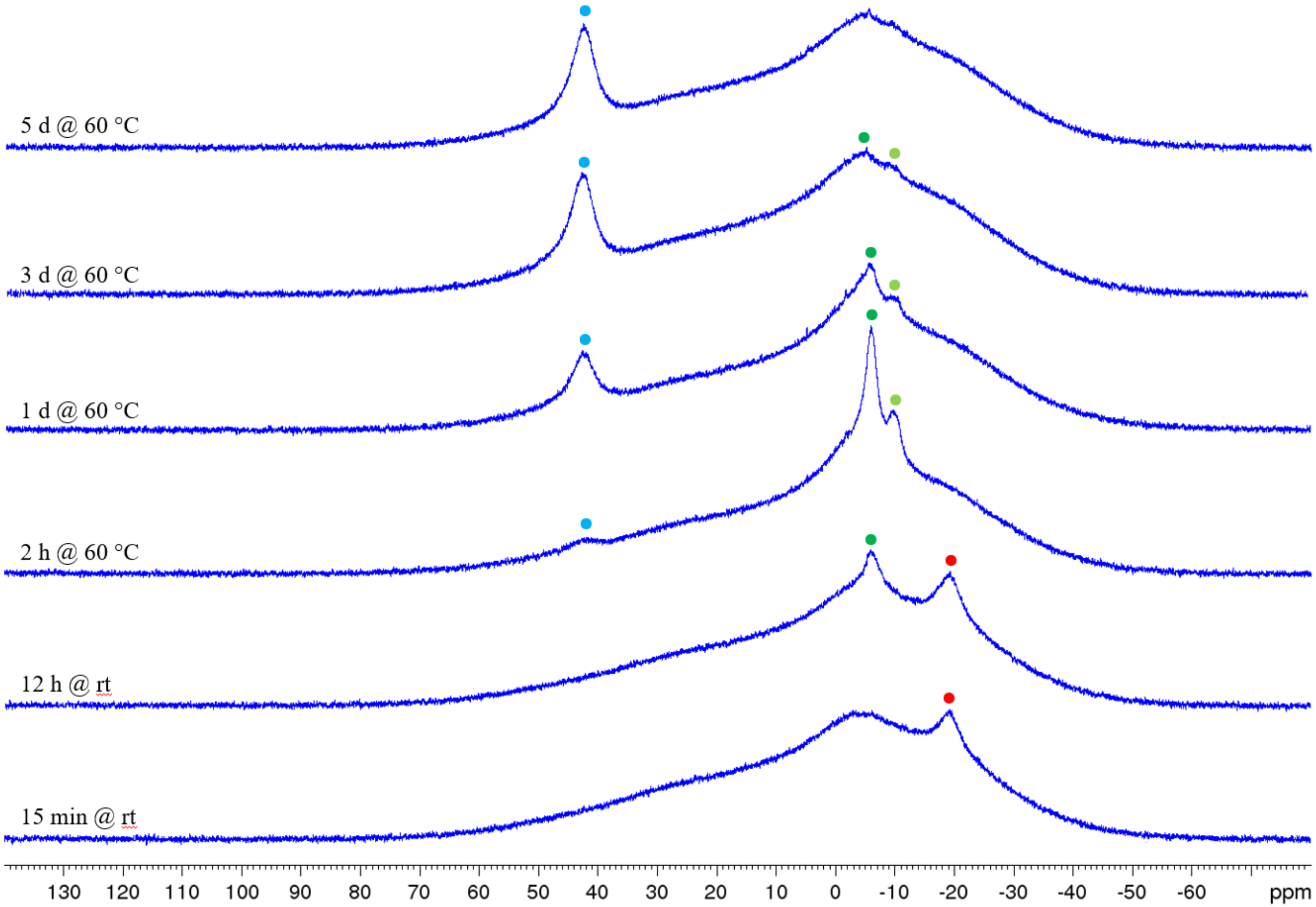

Figure S35. Stack-plot of ^{11}B NMR spectra of the conversion of ***(Z)*-2**$^{\mathbf{NCS}}$ to **5** (●) via **3**$^{\mathbf{NCS}}$ (●) and **4**$^{\mathbf{NCS}}$ (major diastereomer●, minor diastereomer●) in C_6D_6.

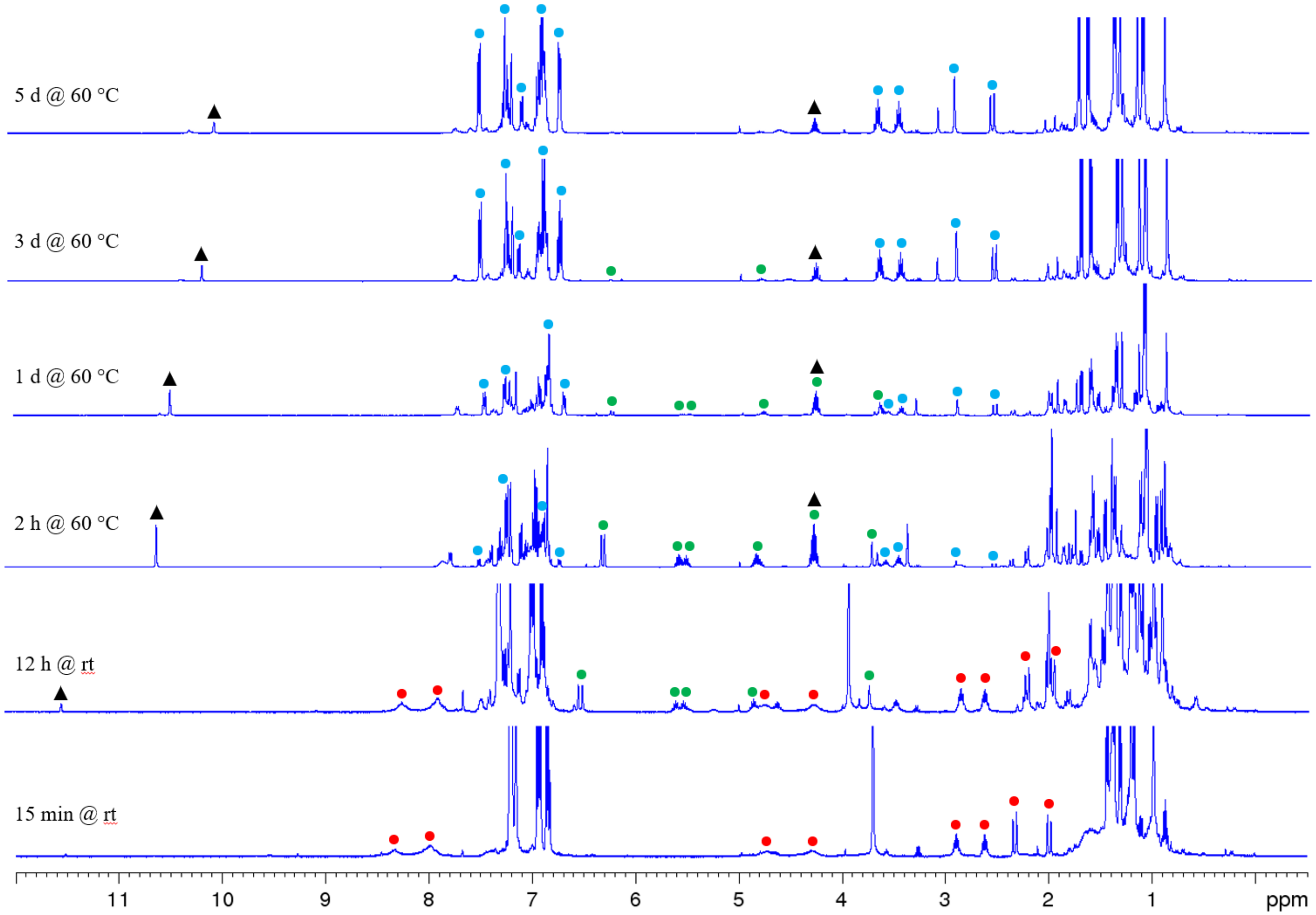

Figure S36. Stack-plot of ^{1}H NMR spectra of the conversion of **(*Z*)-$\mathbf{2}^{\mathbf{NCS}}$** to **5** (●) via **$\mathbf{3}^{\mathbf{NCS}}$** (●) and **$\mathbf{4}^{\mathbf{NCS}}$** (major diastereomer only●) and the formation of [I*i*Pr-H][NCS] (▲ in C_6D_6. Only characteristic resonances in the region between ca. 2–11 ppm were assigned. See ^{1}H NMR spectra of **$\mathbf{3}^{\mathbf{NCS}}$**, **$\mathbf{4}^{\mathbf{NCS}}$** and **5**, respectively, for full assignment.

NMR studies of the reversible protonation of (*Z*)-2^{CN} by PhSH

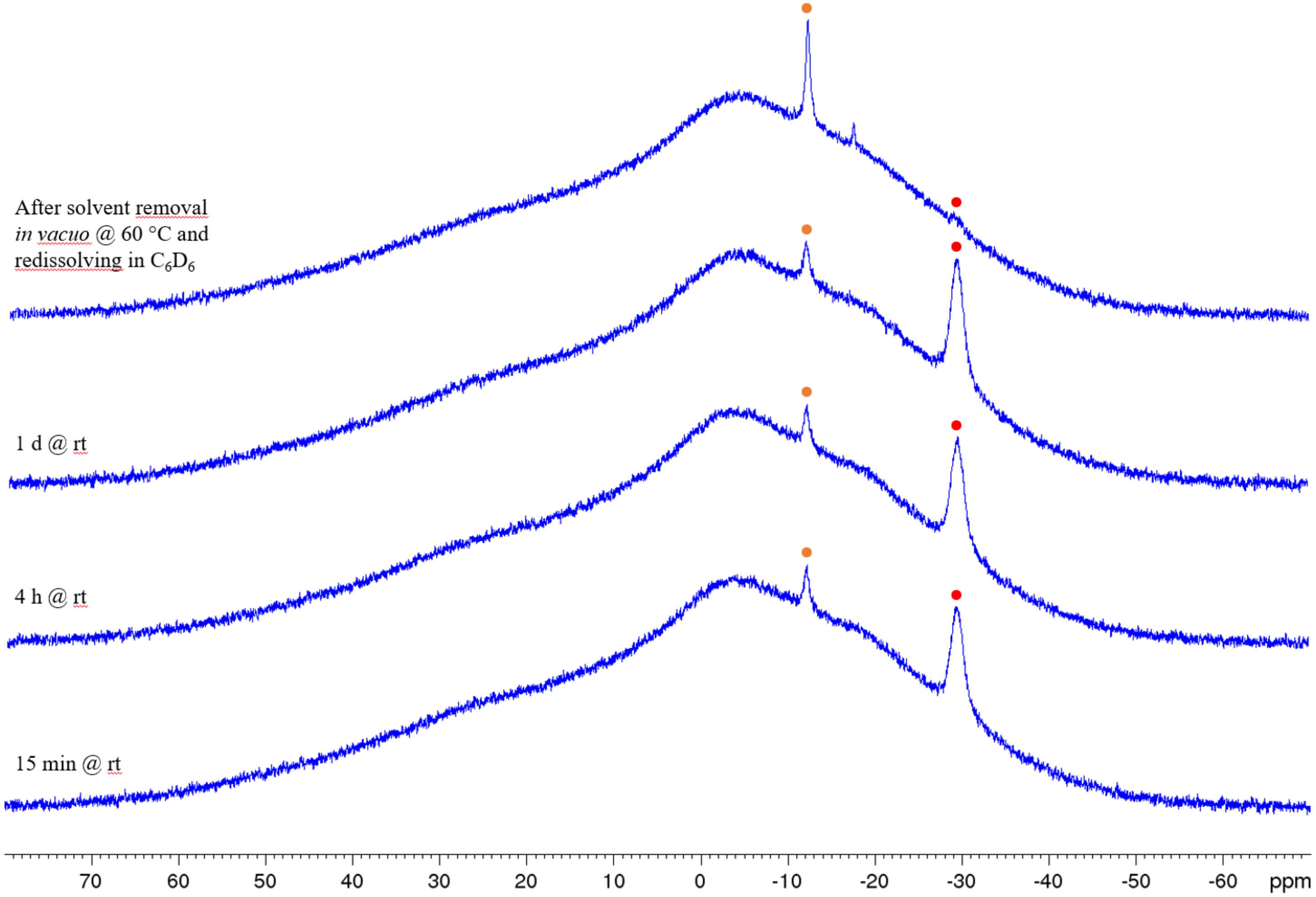

Figure S37. Stack-plot of ^{11}B NMR spectra of the reversible reaction of **(*Z*)-2^{CN}** (●) and thiophenol to **3^{CN}** (●) in C_6D_6. The additional resonance at –17 ppm belongs to an unidentified decomposition product.

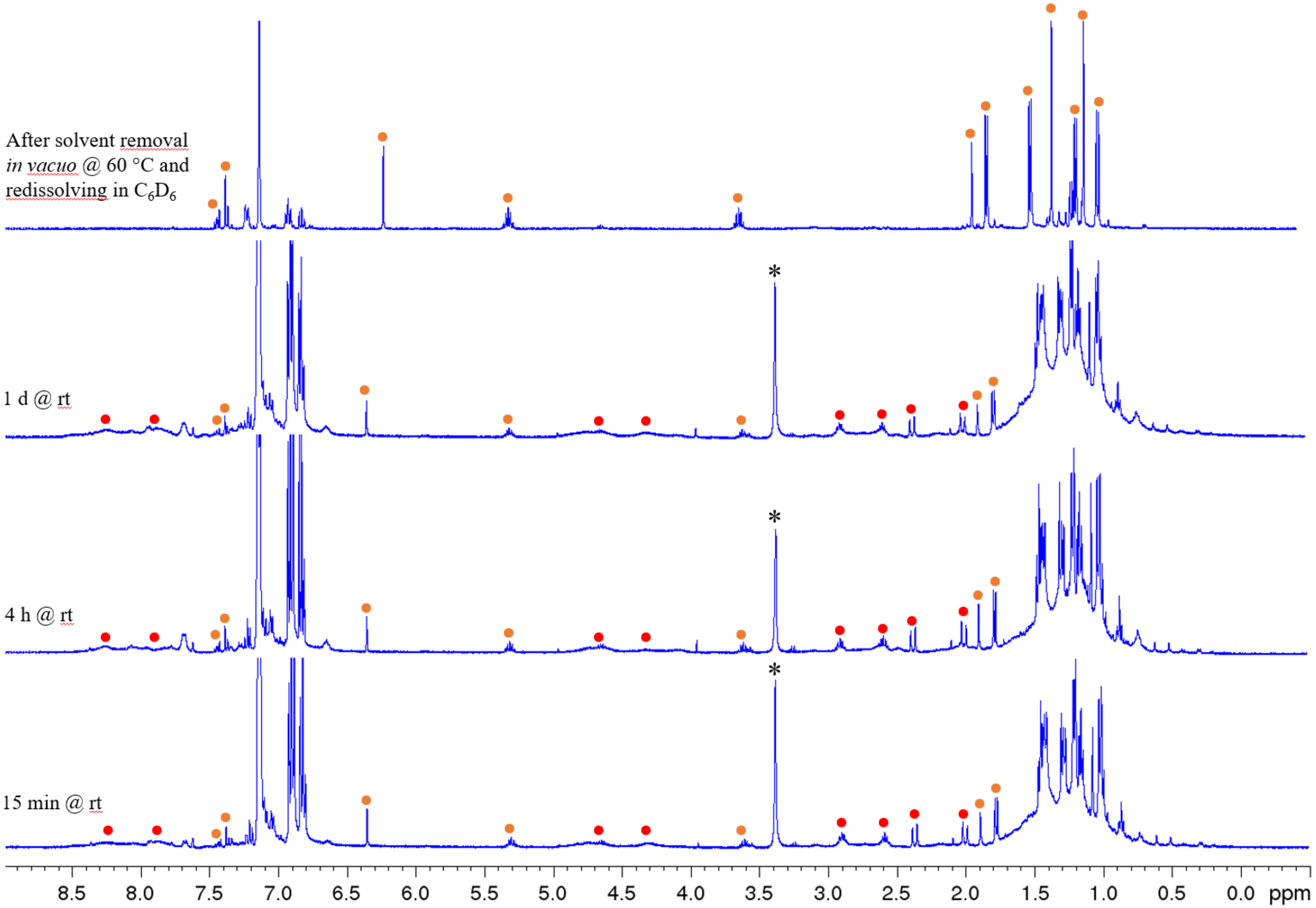

Figure S38. Stack-plot of ^{1}H NMR spectra of the reversible reaction of ***(Z)*-2$^{\mathbf{CN}}$** (●) and thiophenol (*) to **3$^{\mathbf{CN}}$** (●) in C_6D_6. Only characteristic resonances in the region between ca. 2–9 ppm were assigned.

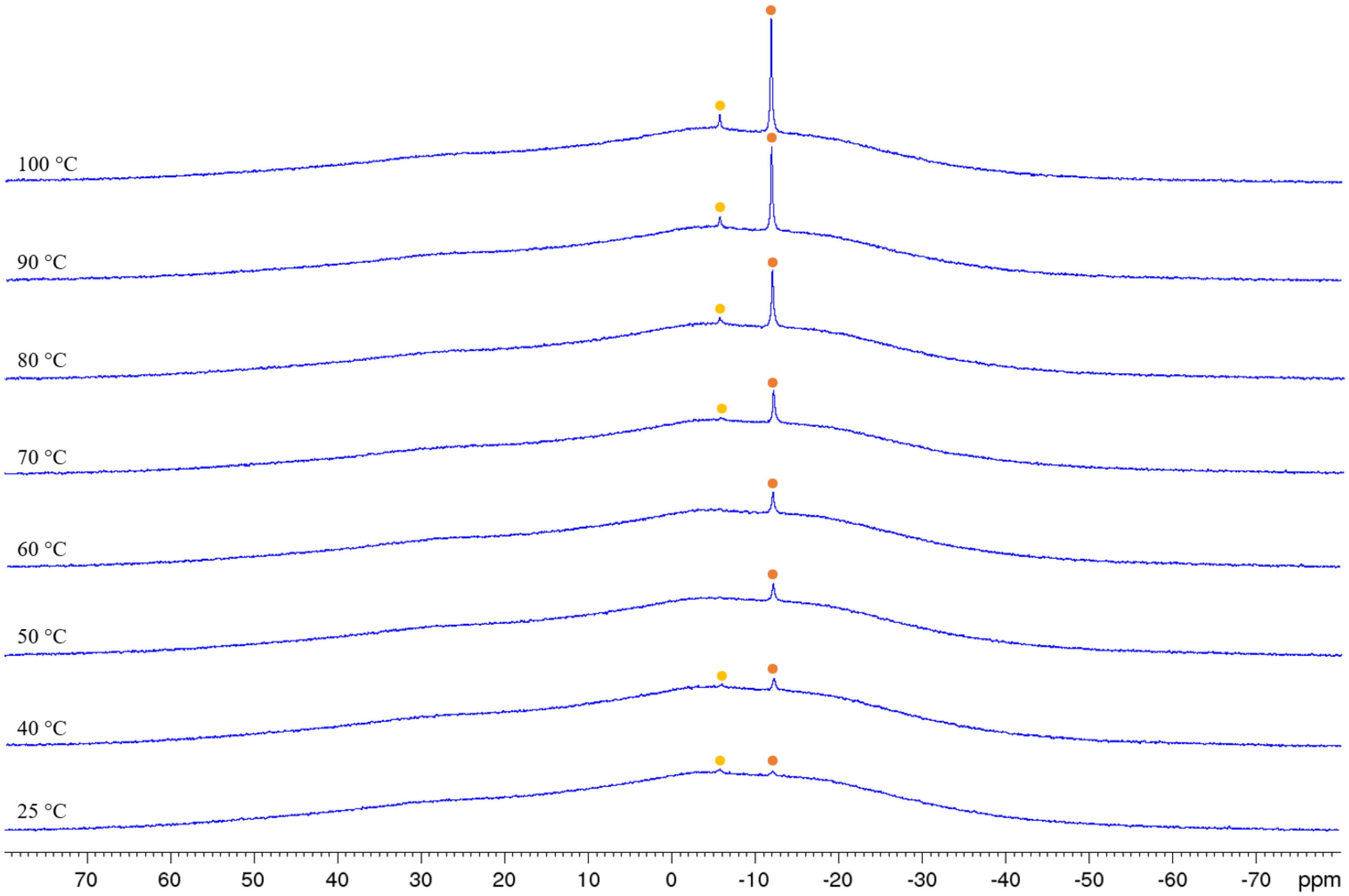

Figure S39. Stack-plot of ^{11}B NMR spectra of the reversible protonation of ***(Z)*-2$^{\mathbf{CN}}$** (●) with thiophenol in toluene-d$_8$ from 25 to 100 °C. The resonance of **3$^{\mathbf{CN}}$** was not observed due to quantitative precipitation. The additional resonance at –5.4 ppm was assigned to the isomer ***(E)*-2$^{\mathbf{CN}}$** (●).

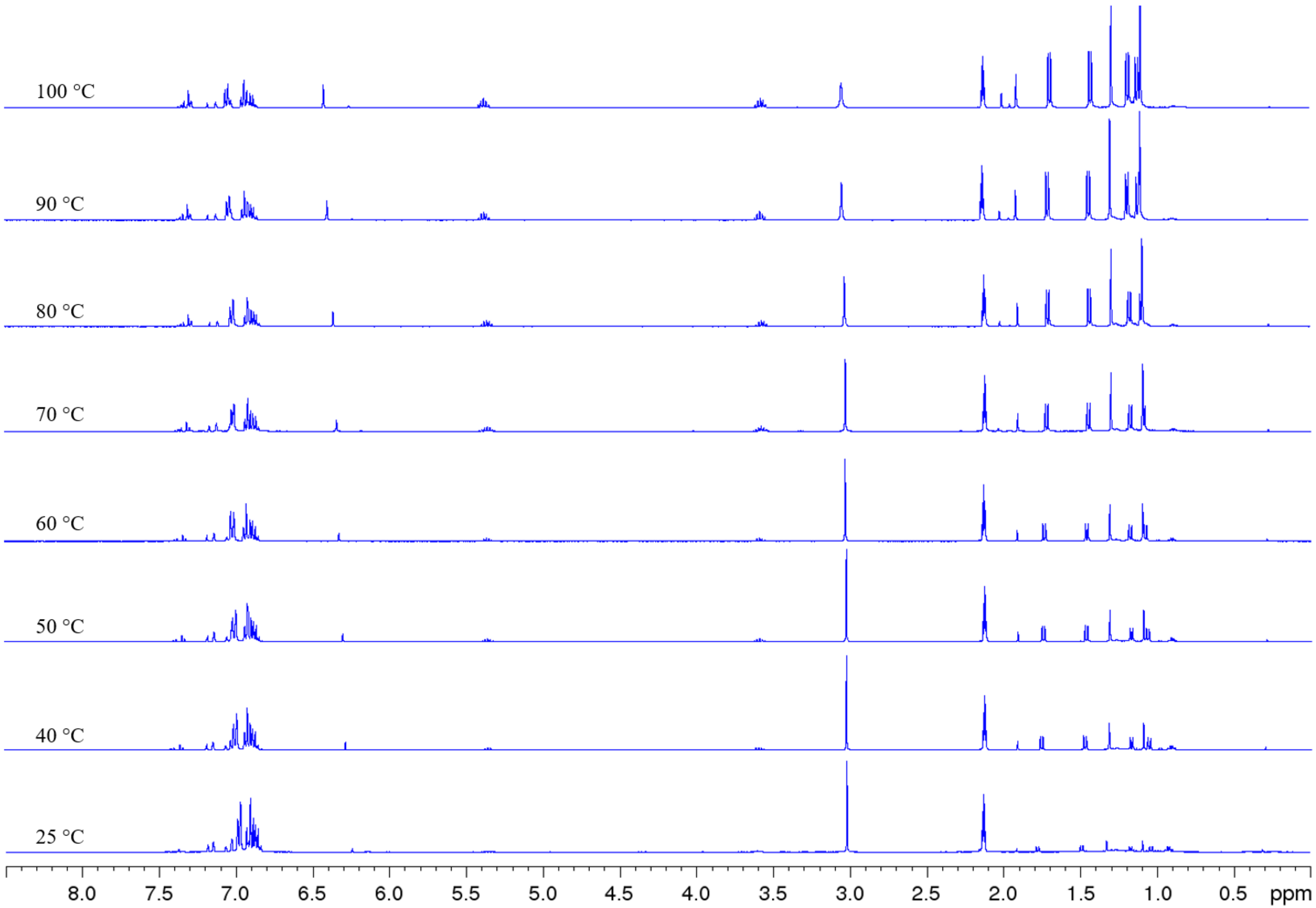

Figure S40. Stack-plot of ^{1}H NMR spectra of the reversible protonation of **(*Z*)-2$^{\mathbf{CN}}$** with thiophenol in toluene-d_8 from 25 to 100 °C. The resonances of **3$^{\mathbf{CN}}$** were not observed due to quantitative precipitation.

IR spectra

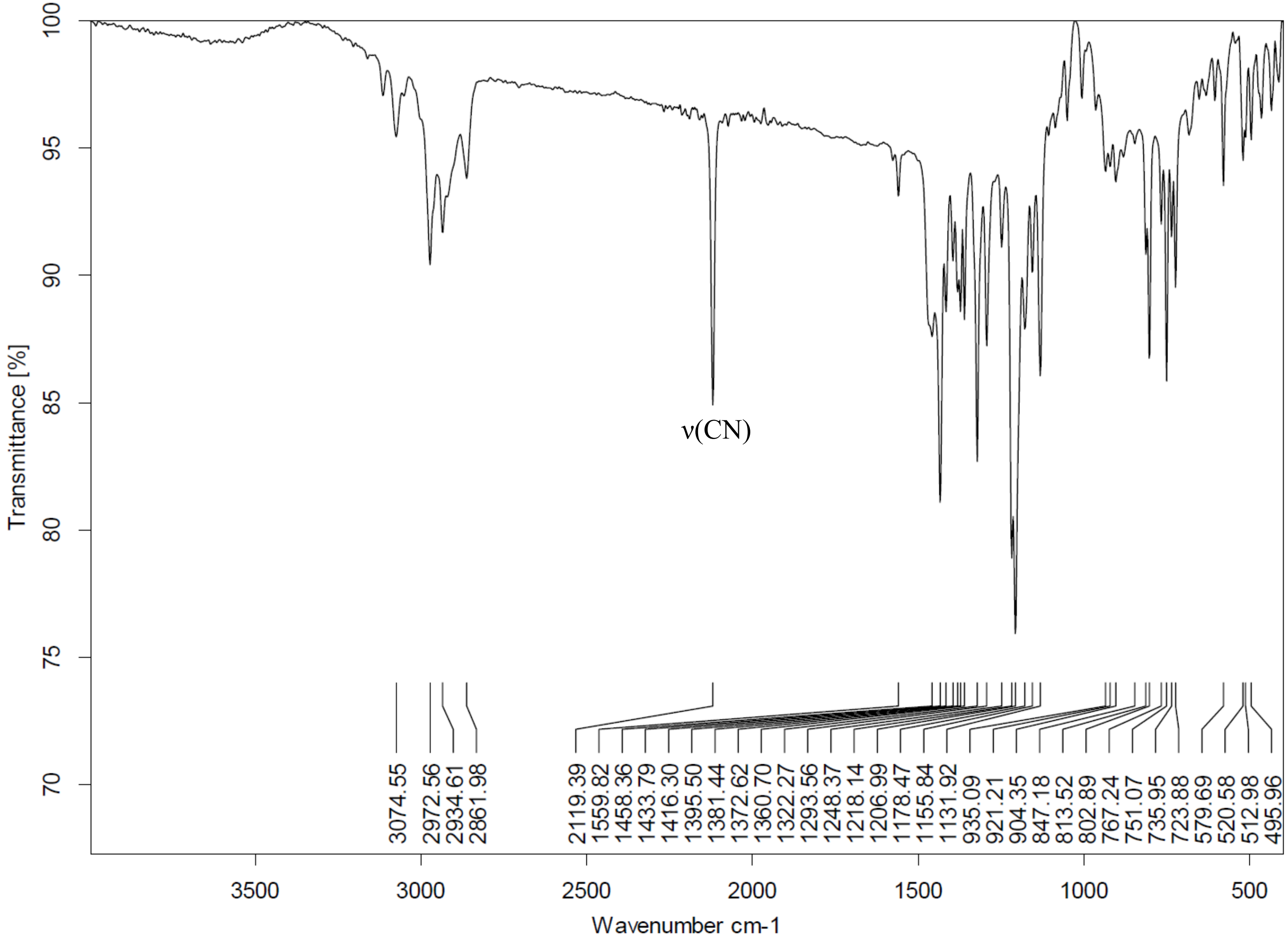

Figure S41. Solid-state IR spectrum of **(*Z*)-2$^{\mathbf{CN}}$**.

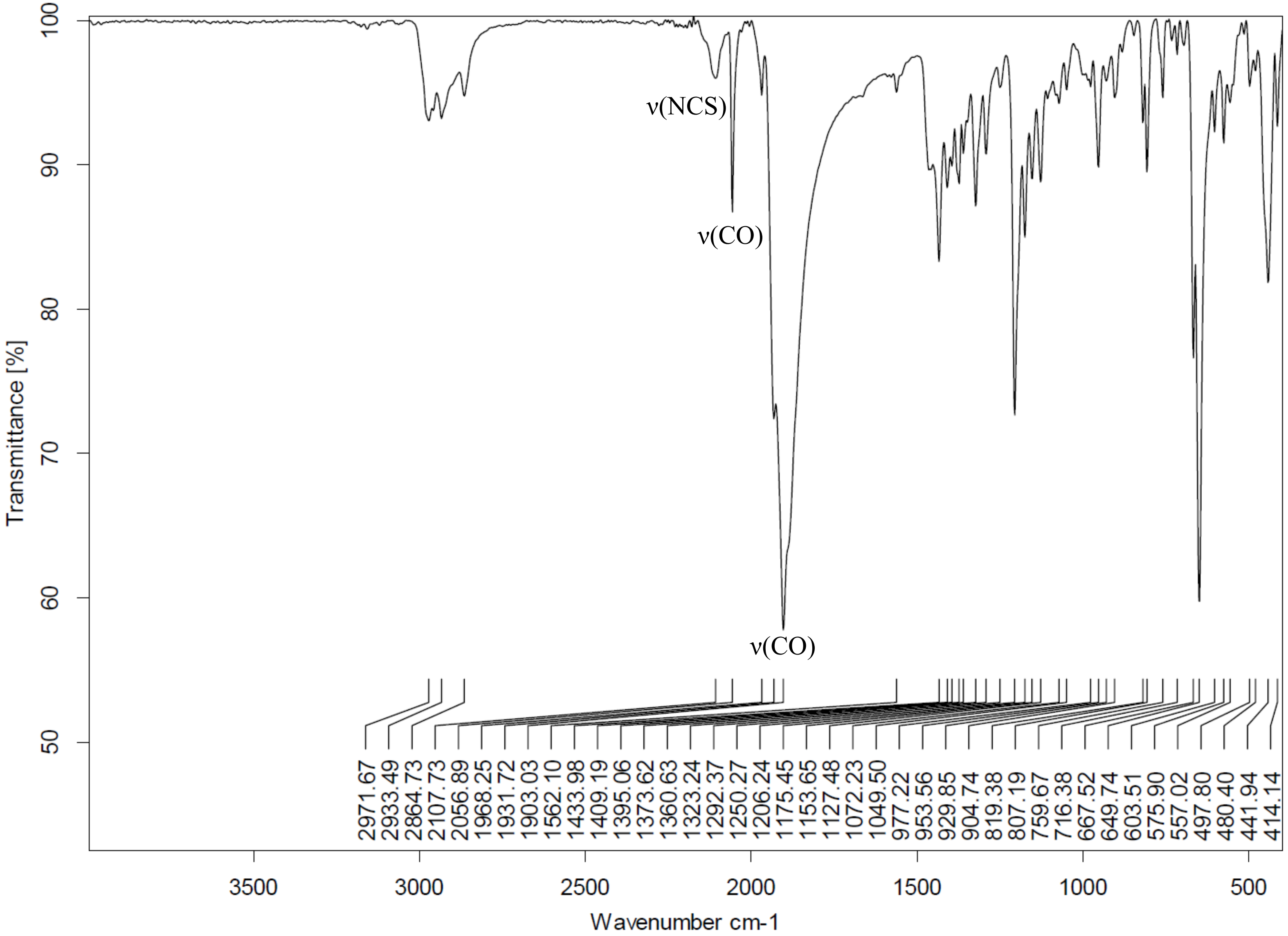

Figure S42. Solid-state IR spectrum of **(*Z*)-2$^{\mathbf{NCS}}$-Cr**.

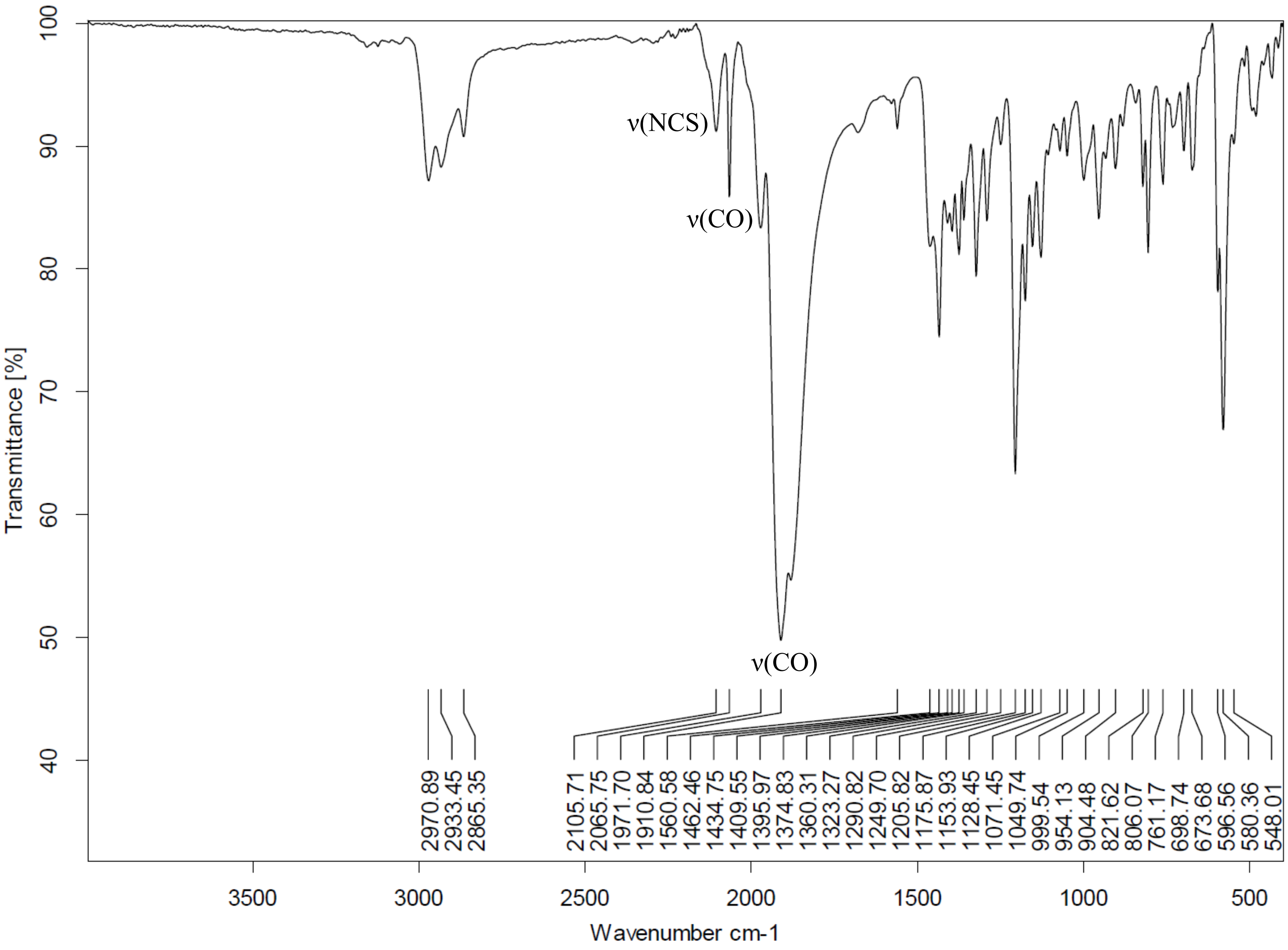

Figure S43. Solid-state IR spectrum of ***(Z)*-2^{NCS}-W**.

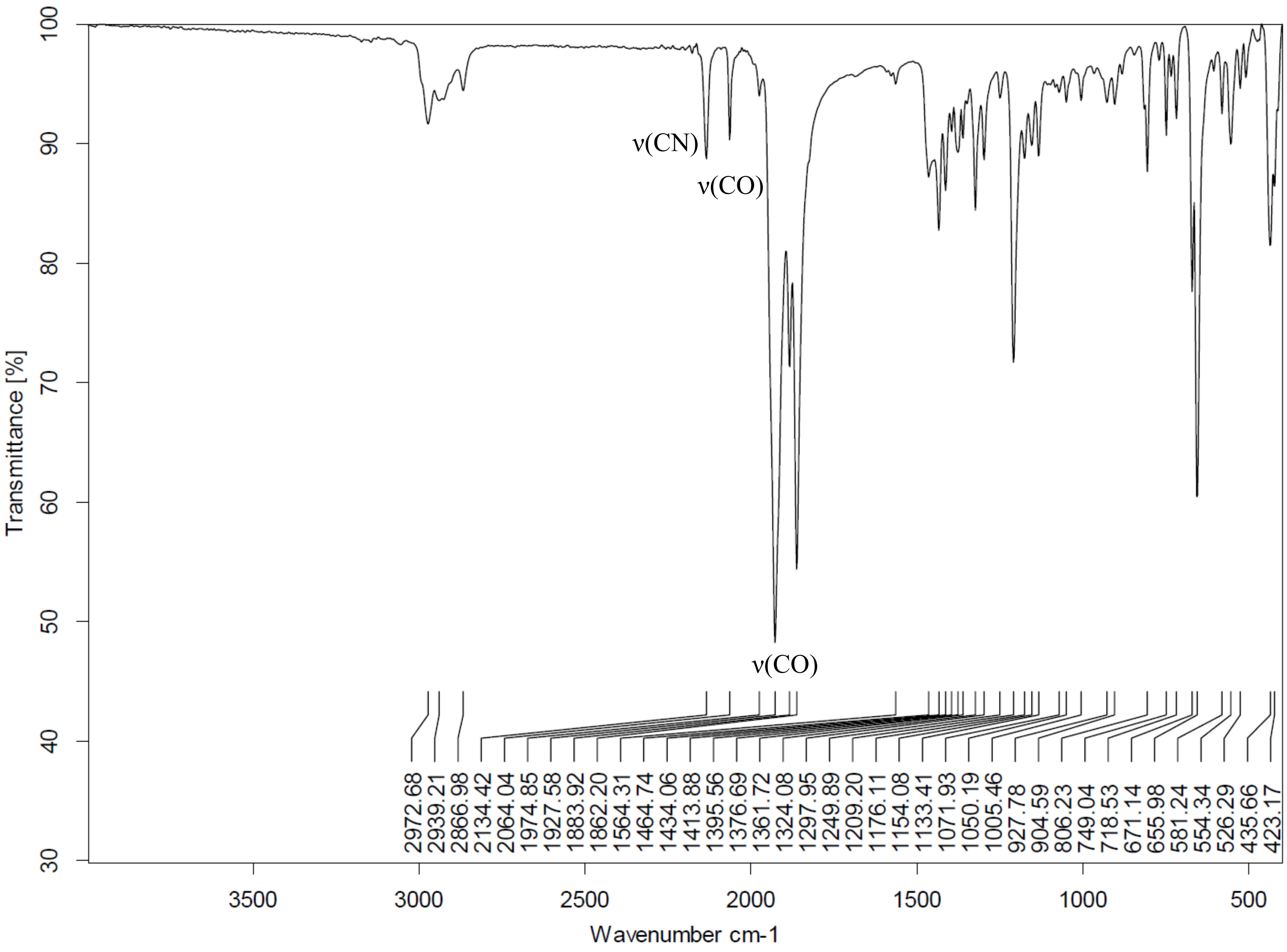

Figure S44. Solid-state IR spectrum of ***(Z)*-2$^{\mathbf{CN}}$-Cr**.

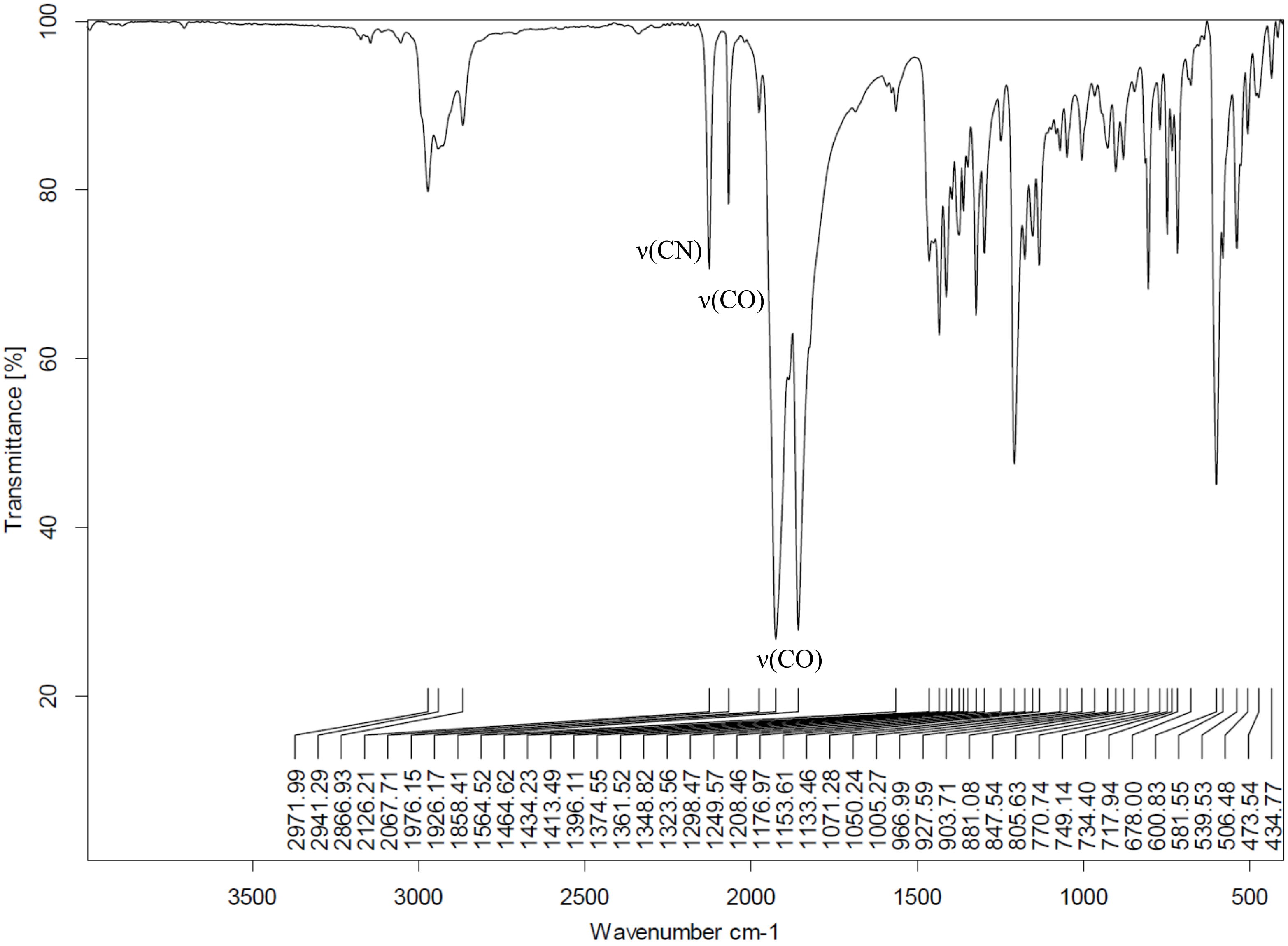

Figure S45. Solid-state IR spectrum of ***(Z)*-2$^{\mathbf{CN}}$-Mo**.

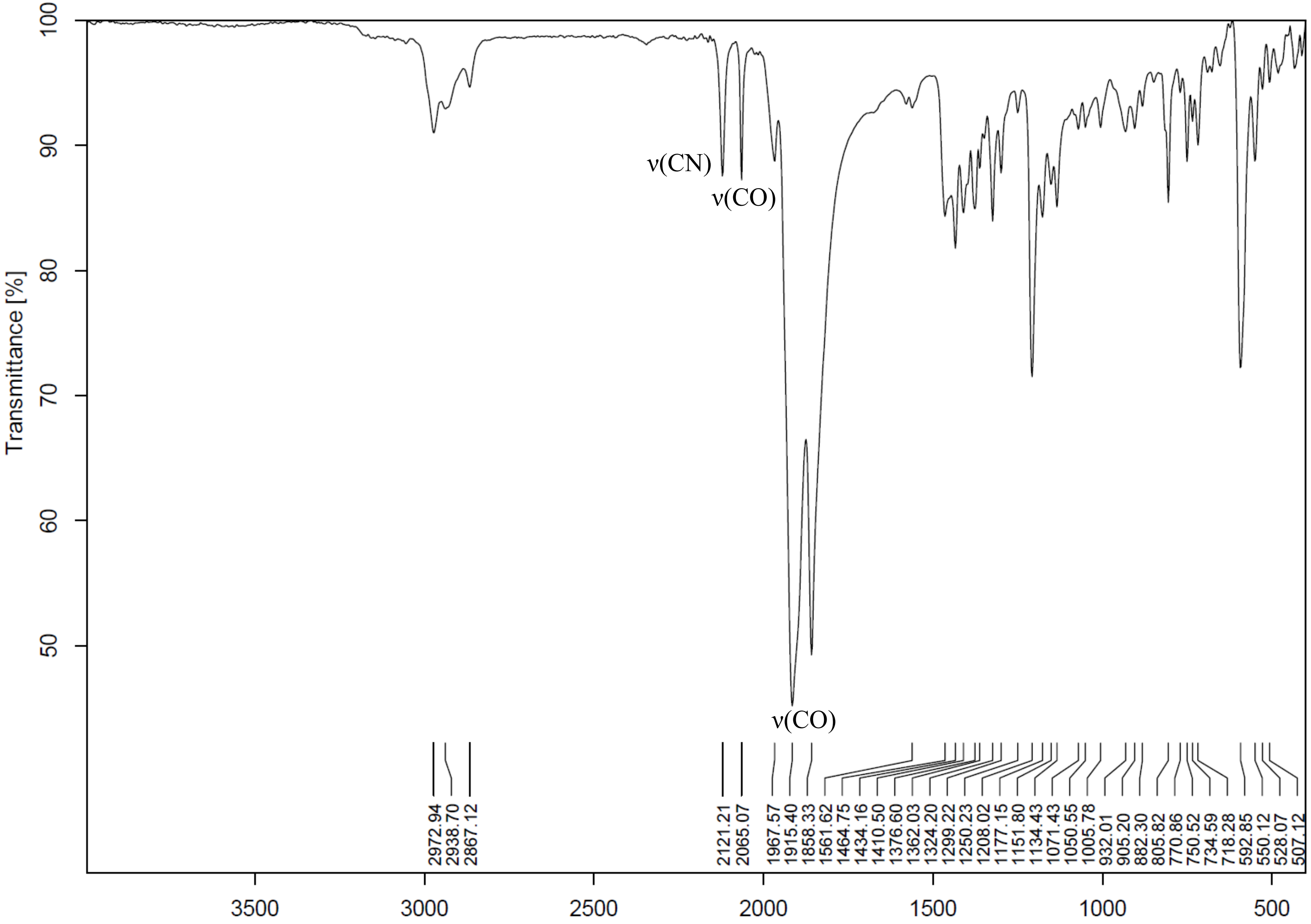

Figure S46. Solid-state IR spectrum of **(*Z*)-2$^{\mathbf{CN}}$-W** directly after workup.

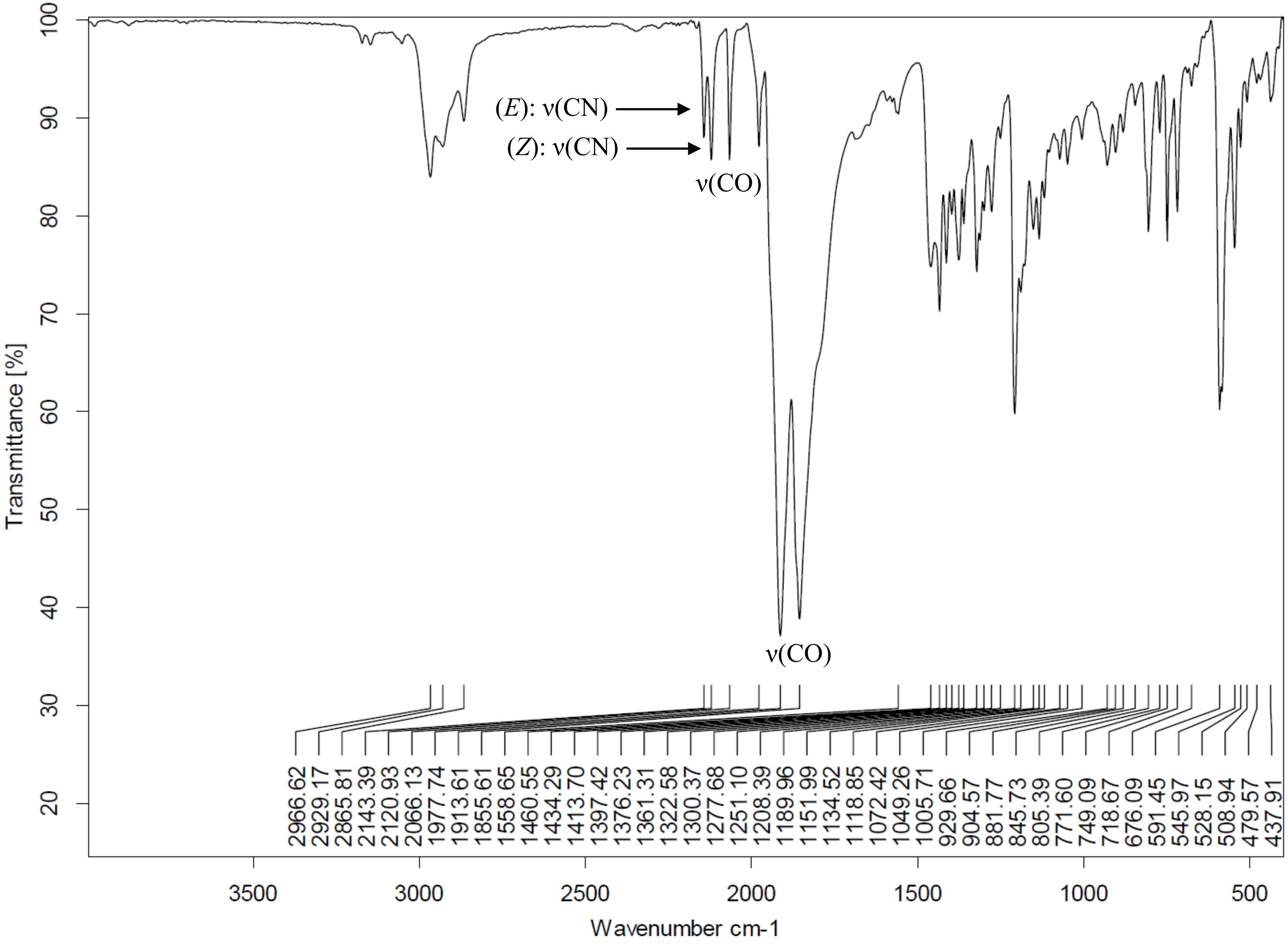

Figure S47. Solid-state IR spectrum of a mixture of both isomers of **(*E*)/(*Z*)-2$^{\mathrm{CN}}$-W**.

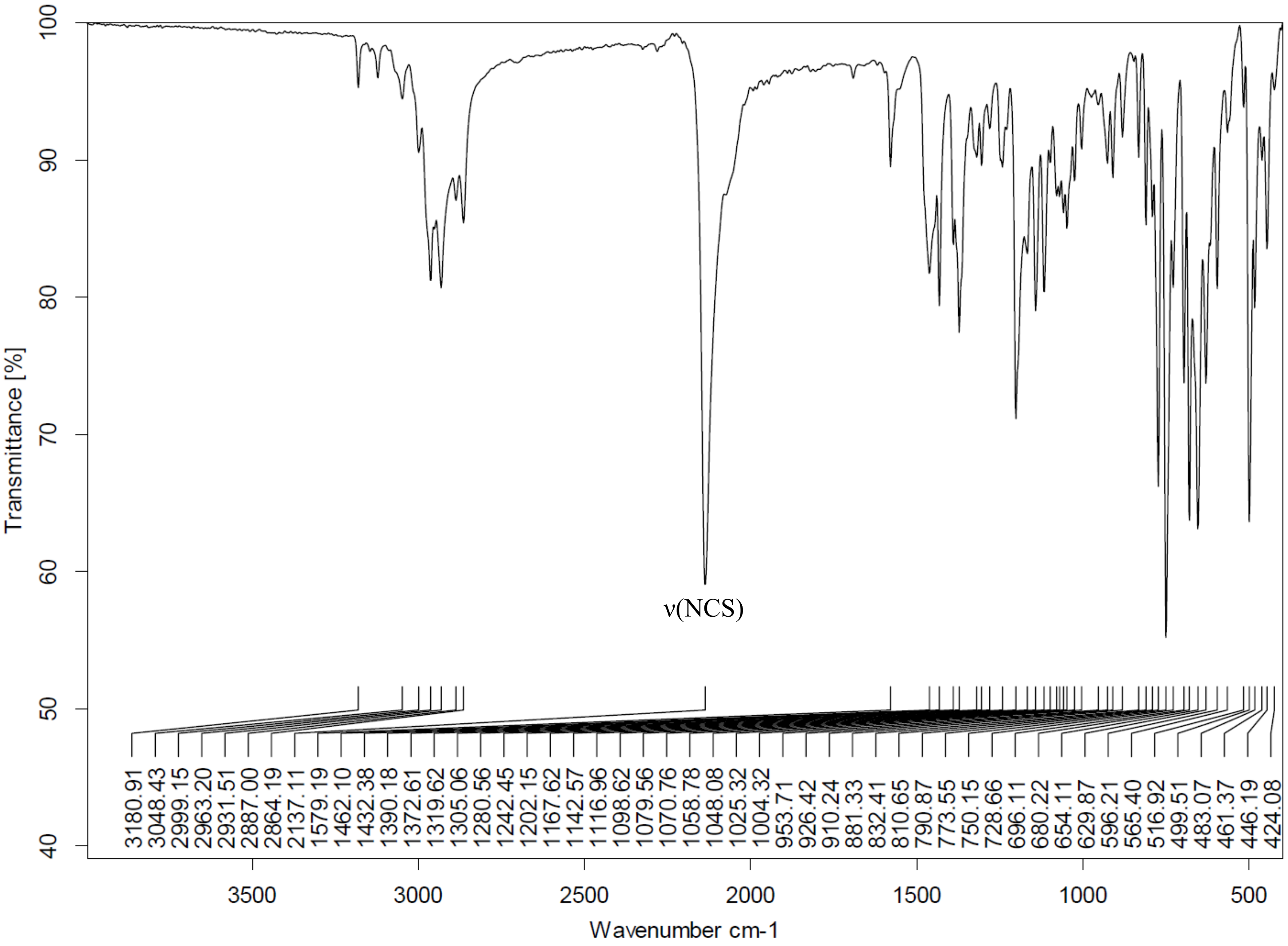

Figure S48. Solid-state IR spectrum of $\mathbf{4}^{\mathbf{NCS}}$.

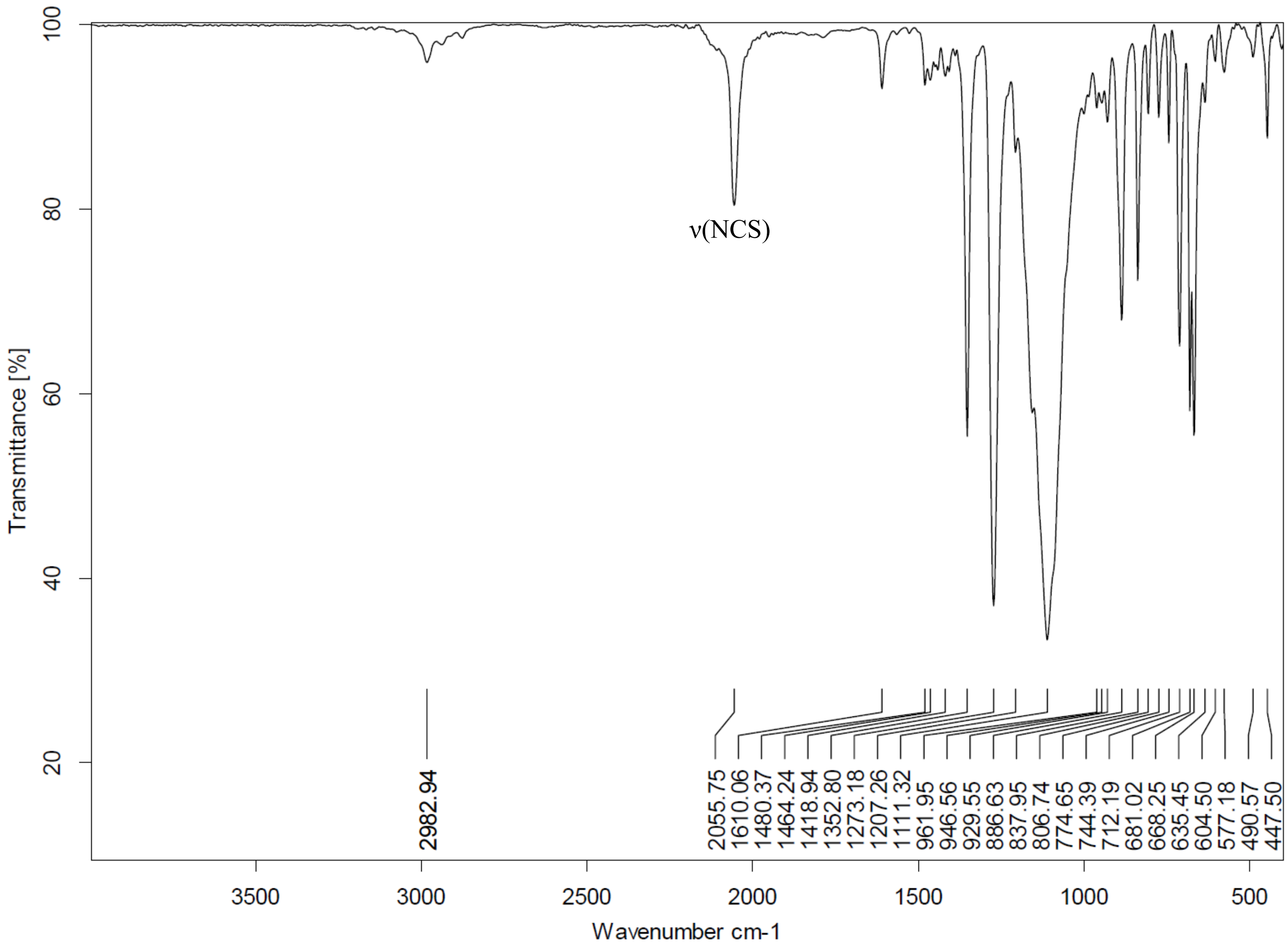

Figure S49. Solid-state IR spectrum of **[(*Z*)-2$^{\mathrm{NCS}\bullet+}$][OTf$^-$]**.

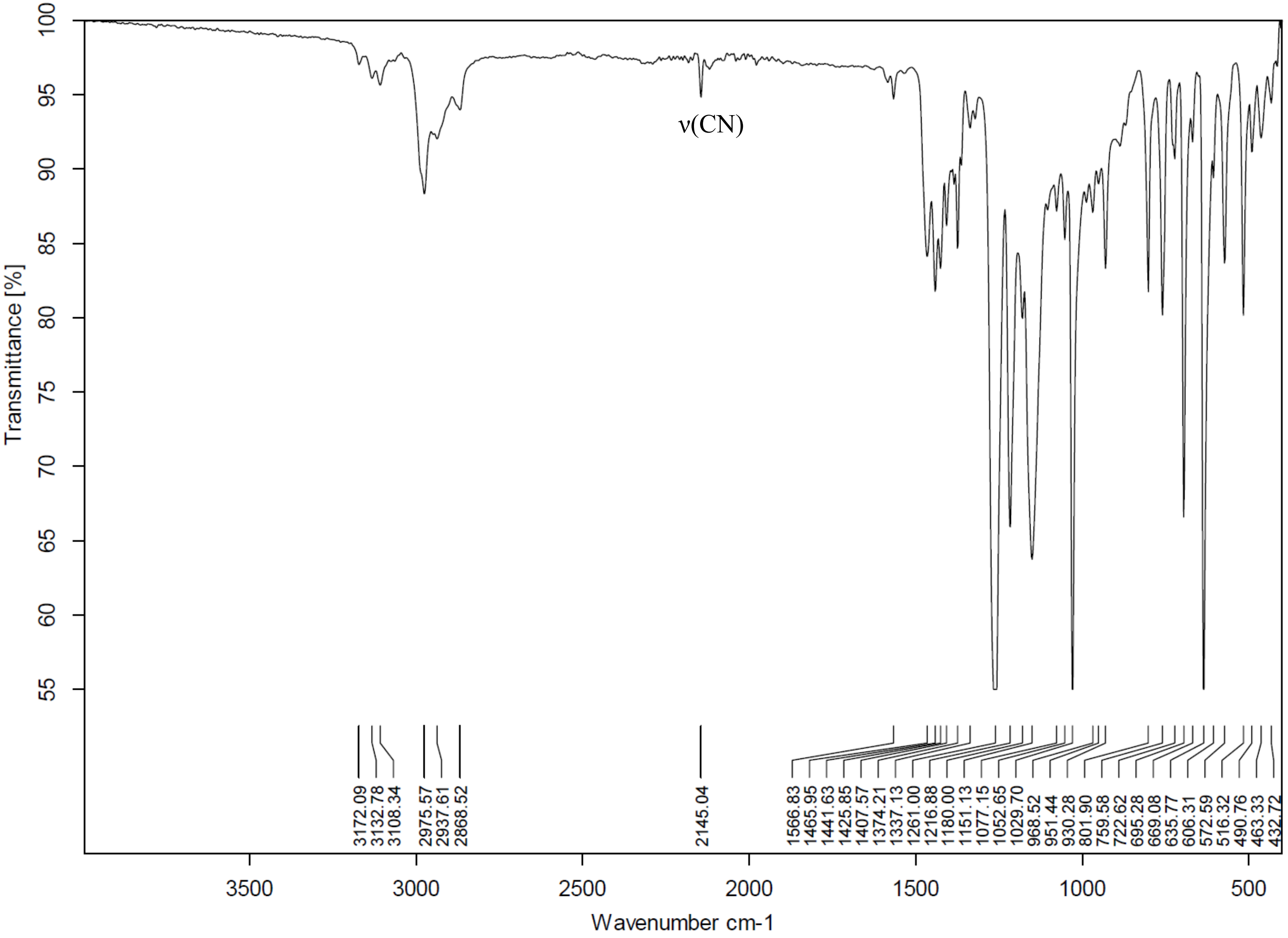

Figure S50. Solid-state IR spectrum of **[(*Z*)-2$^{\mathbf{CN\bullet+}}$][OTf^{-}]**.

Cyclic voltammetry

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 by using decamethylferrocene ($[Cp^*{}_2Fe]$; $E_{1/2} = -0.427$ V in THF) as an internal standard. Tetra-*n*-butylammonium hexafluorophosphate ($[n\text{-}Bu_4N][PF_6]$) was employed as the supporting electrolyte. Compensation for resistive losses (*iR* drop) was employed for all measurements.

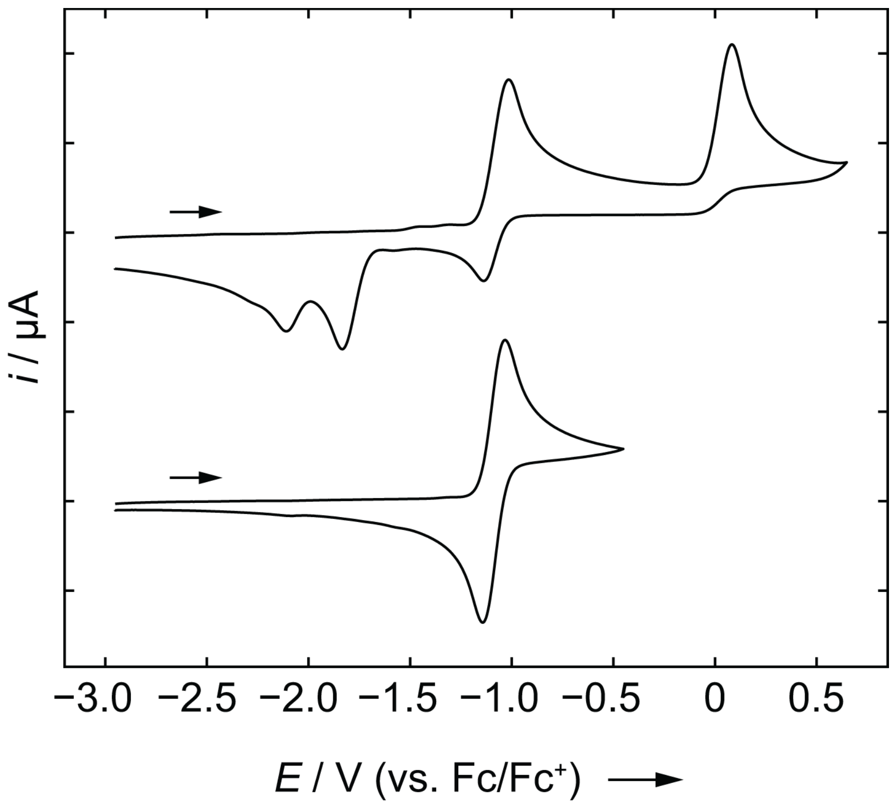

Figure S51. Cyclic voltammograms of **(*Z*)-2$^{\mathbf{NCS}}$** in THF with $[n\text{-}Bu_4N][PF_6]$ (0.1 M) as supporting electrolyte (scan rate, $\nu = 250$ mV s^{-1}, 20 ºC). The voltammogram at the bottom shows the reversibility of the first oxidation wave. Formal potentials: $E_{1/2} = -1.06$ V, E_{pa} = ca. +0.08 V (corresponding reduction peaks at −1.83 V and −2.10 V; relative to the $[Cp_2Fe]^{+/0}$ couple).

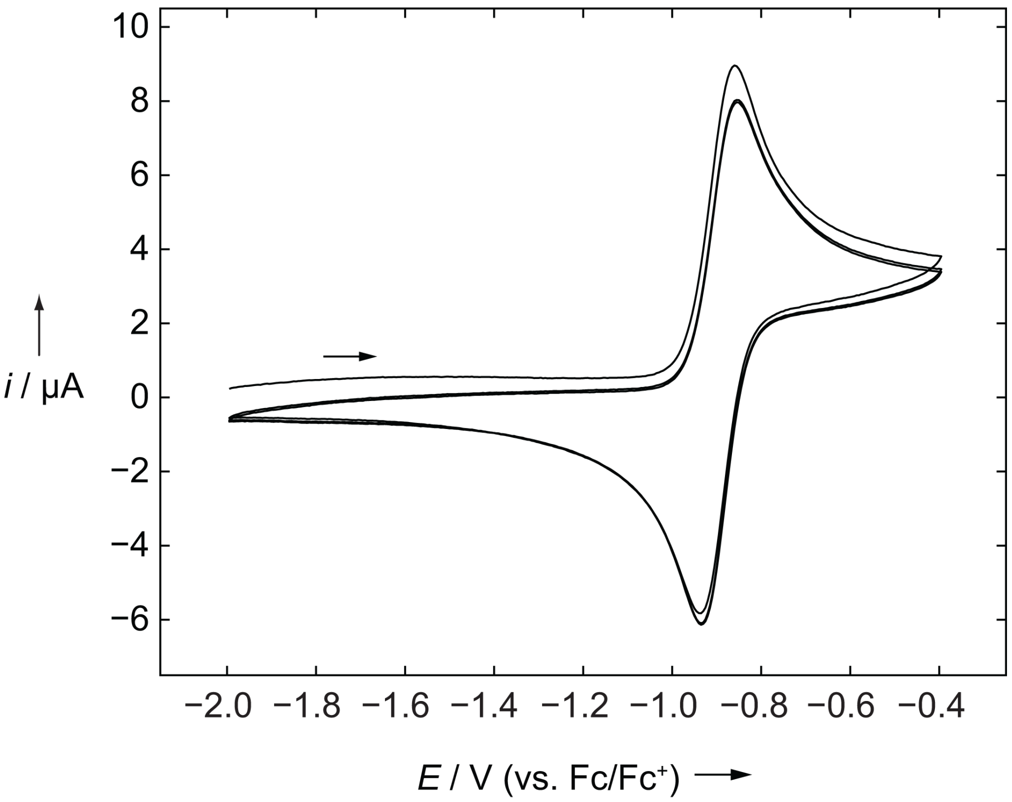

Figure S52. Cyclic voltammogram of **(*Z*)-2^{CN}** in THF with [*n*-Bu_4N][PF_6] (0.1 M) as supporting electrolyte (scan rate, ν = 250 mV s^{-1}, 20 ºC). Formal potential: $E_{1/2} = -0.89$ V relative to the [Cp_2Fe]$^{+/0}$ couple.

EPR spectra

EPR measurements at X-band (9.85 GHz) were carried out at room temperature using a Bruker ELEXSYS E580 CW EPR spectrometer. CW EPR spectra were measured using 1 mW microwave power and 0.5 G field modulation at 100 kHz, with a conversion time of 20 ms. The spectral simulations were performed using MATLAB 8.6 and the EasySpin 5.2.25 toolbox.[6]

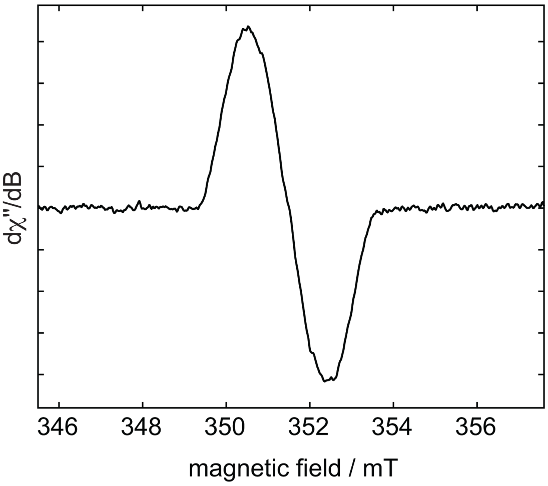

Figure S53. Experimental continuous-wave X-band EPR spectrum of **[(*Z*)-2$^{\mathrm{NCS}\bullet+}$][OTf^{-}]** in benzene solution at room temperature. The isotropic *g* value is 2.003 and the peak-to-peak linewidth is 1.9 mT.

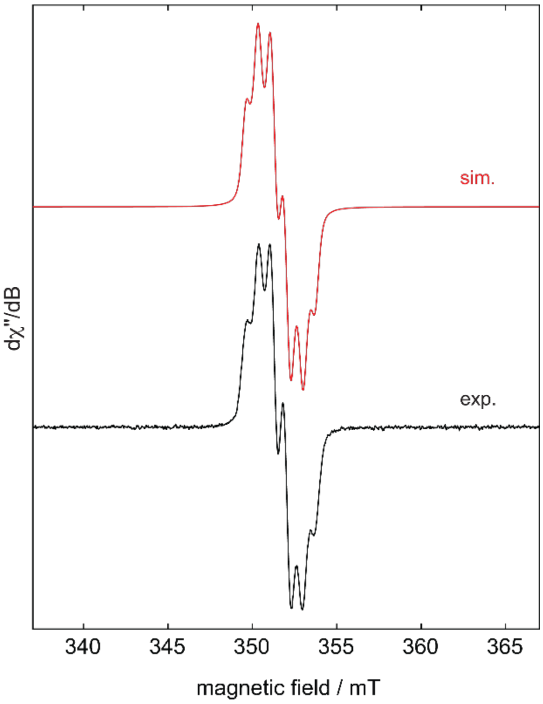

Figure S54. Experimental (black line) and simulated (red line) continuous-wave X-band EPR spectra of **[(*Z*)-2$^{\mathrm{CN}\bullet+}$][OTf^{-}]** in benzene solution at room temperature. Best-fit simulation parameters: g_{iso} = 2.0025, a(^{10,11}B) = 9.0 MHz, a(^{14}N) = 21.7 MHz, and a(^{14}N) = 18.0 MHz.

UV-vis spectra

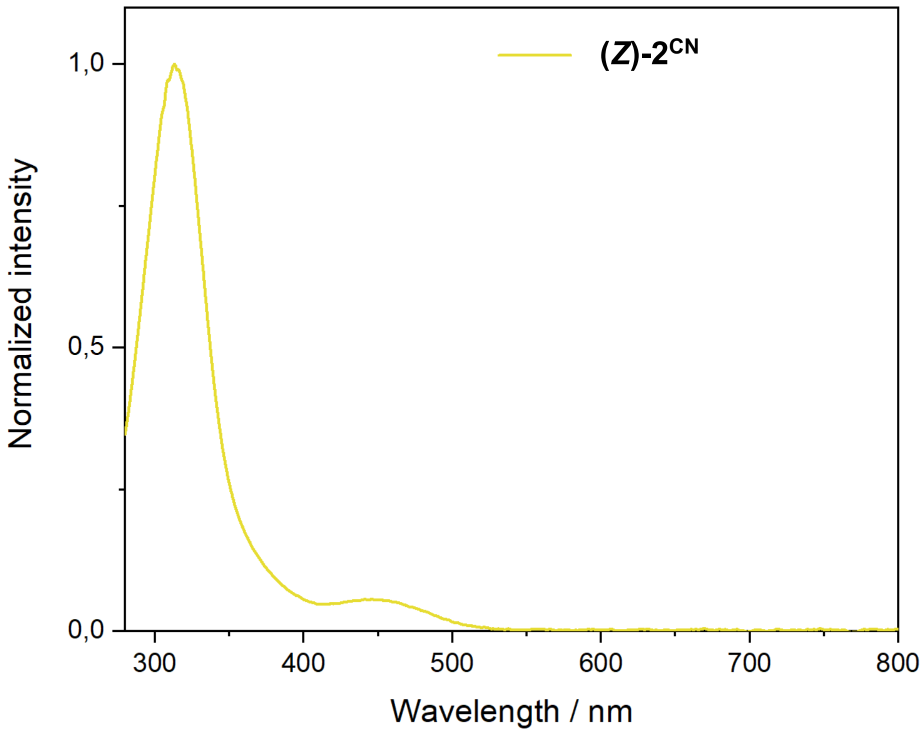

Figure S55. UV-vis absorption spectrum of **(*Z*)-2$^{\mathrm{CN}}$** in benzene at 25 °C.

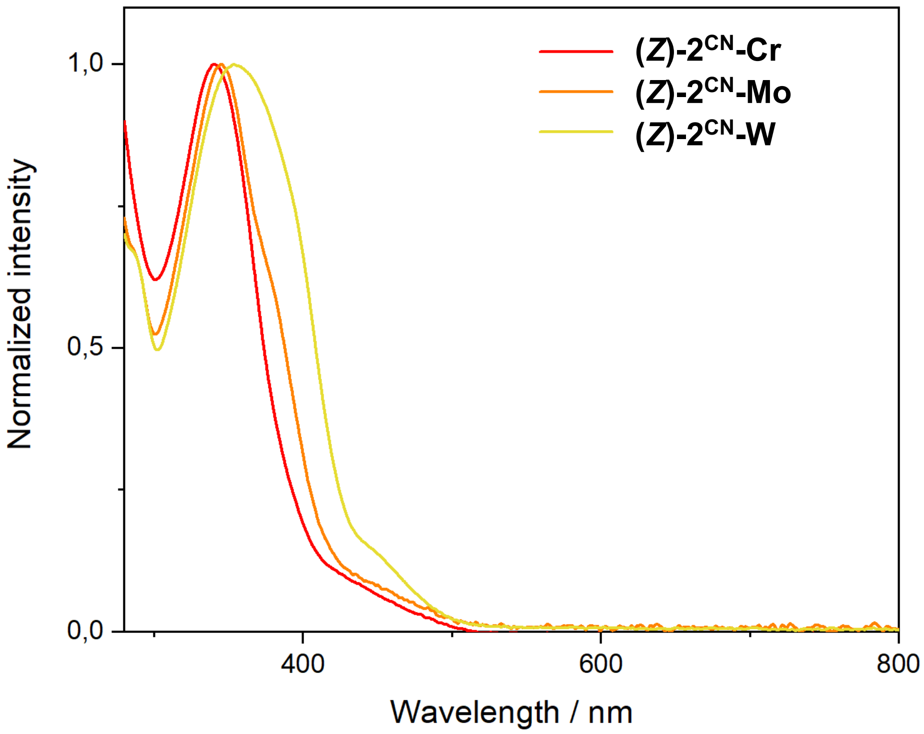

Figure S56. Overlay of UV-vis absorption spectra of **(*Z*)-2$^{\mathrm{CN}}$-Cr** (red), **(*Z*)-2$^{\mathrm{CN}}$-Mo** (orange) and **(*E*)/(*Z*)-2$^{\mathrm{CN}}$-W** (yellow) in benzene at 25 °C.

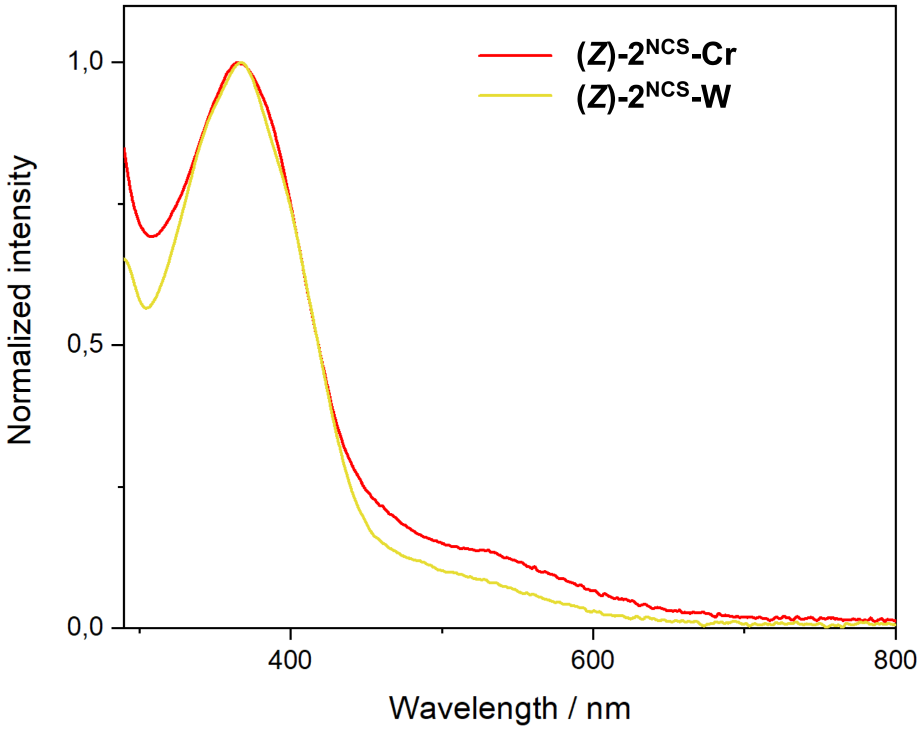

Figure S57. Overlay of UV-vis absorption spectra of **(*Z*)-2$^{\mathbf{NCS}}$-Cr** (red) and **(*Z*)-2$^{\mathbf{NCS}}$-W** (yellow) in benzene at 25 °C.

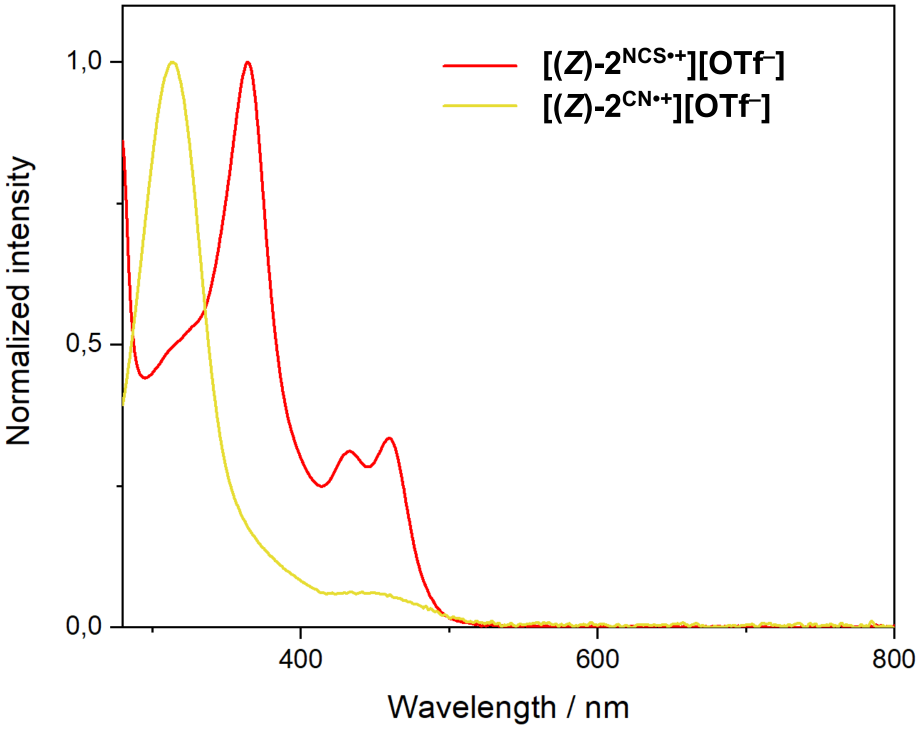

Figure S58. Overlay of UV-vis absorption spectra of boryl radical cations **[(*Z*)-2$^{\mathbf{NCS\bullet+}}$][OTf^{-}]** and **[(*Z*)-2$^{\mathbf{CN\bullet+}}$][OTf^{-}]** in benzene at 25 °C.

X-ray crystallographic details

The crystal data of **2^{CN}-Cr**, **2^{CN}-Mo**, **2^{CN}-W** and **3^{NCS}** were collected on a Bruker D8 Quest diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{κα}$ radiation. The crystal data of **[(*Z*)-$2^{CN•+}$][OTf^-]** was collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{κα}$ radiation. The crystal data of **2^{CN}**, **[(*Z*)-$2^{NCS•+}$][OTf^-]** and [**2^{CN}-H^+][SPh^-]** were collected on a XtaLAB Synergy, Dualflex diffractometer with a HyPix area detector and multi-layer mirror monochromated $Cu_{κα}$ radiation. The structures were solved using the intrinsic phasing method,[7] refined with the ShelXL program[8] 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, with the exception of those bound to boron, which were detected in the difference Fourier map and freely refined.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 2071470–2071477. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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Refinement details for 2^{CN}: The asymmetric unit contains two half benzene molecules positioned on inversion centers and two molecules of the compound, one of which presents a twofold disorder in the C2 > C8 CAAC backbone (RESI 51 and 52 CAAC) modelled with FVAR in a 95:5 ratio, with SIMU 0.01 and SAME restraints.

Crystal data for 2^{CN}: $C_{30}H_{47}BN_4{\cdot}(C_6H_6)_{0.5}$, $M_r = 513.58$, yellow plate, 0.110×0.094×0.047 mm^3, monoclinic space group $P2_1/c$, $a = 32.7131(2)$ Å, $b = 9.67986(7)$ Å, $c = 21.35114(15)$ Å, $\beta = 108.9322(8)°$, $V = 6395.27(8)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.067$ g·cm^{-3}, $\mu = 0.467$ mm^{-1}, $F(000) = 2248$, $T = 100(2)$ K, $R_1 = 0.0503$, $wR^2 = 0.1128$, 13395 independent reflections [$2\theta \leq 72.13°$] and 807 parameters.

Crystal data for 2^{CN}-Cr: $C_{35}H_{47}BCrN_4O_5$, $M_r = 666.57$, yellow block, 0.518×0.404×0.386 mm^3, monoclinic space group $P2_1/c$, $a = 19.185(7)$ Å, $b = 11.123(4)$ Å,

c = 19.623(6) Å, β = 118.54(2)°, V = 3679(2) Å^3, Z = 4, ρ_{calcd} = 1.204 g·cm^{-3}, μ = 0.354 mm^{-1}, F(000) = 1416, T = 100(2) K, R_1 = 0.0528, wR^2 = 0.1044, 7245 independent reflections [$2\theta \leq 52.044°$] and 427 parameters.

Crystal data for 2$^{\mathrm{CN}}$-Mo: $C_{35}H_{47}BMoN_4O_5{\cdot}C_6H_6$, M_r = 788.62, yellow block, 0.322×0.204×0.136 mm^3, orthorhombic space group $P2_12_12_1$, a = 13.190(6) Å, b = 14.868(5) Å, c = 21.174(7) Å, V = 4152(3) Å^3, Z = 4, ρ_{calcd} = 1.261 g·cm^{-3}, μ = 0.361 mm^{-1}, F(000) = 1656, T = 100(2) K, R_1 = 0.0463, wR^2 = 0.0746, 8028 independent reflections [$2\theta \leq 52.044°$] and 481 parameters.

Crystal data for 2$^{\mathrm{CN}}$-W: $C_{35}H_{47}BN_4O_5W$, M_r = 798.42, yellow block, 0.317×0.233×0.226 mm^3, triclinic space group $P\,\bar{1}$, a = 9.653(4) Å, b = 10.588(7) Å, c = 19.881(9) Å, α = 78.11(2)°, β = 83.576(15)°, γ = 67.077(16)°, V = 1830.2(17) Å^3, Z = 2, ρ_{calcd} = 1.449 g·cm^{-3}, μ = 3.200 mm^{-1}, F(000) = 808, T = 100(2) K, R_1 = 0.0411, wR^2 = 0.0786, 7190 independent reflections [$2\theta \leq 52.044°$] and 427 parameters.

Crystal data for [2$^{\mathrm{NCS}\bullet+}$][OTf$^-$]: [$C_{30}H_{47}BN_4S$][CF_3O_3S], M_r = 655.66, red block, 0.246×0.205×0.142 mm^3, orthorhombic space group P b c a. a = 12.31193(8) Å, b = 15.53996(11) Å, c = 36.3830(2) Å, V = 1611.98(7) Å^3, Z = 8, ρ_{calcd} = 1.251 g·cm^{-3}, μ = 1.827 mm^{-1}, F(000) = 2792, T = 100(2) K, R_1 = 0.0464, wR^2 = 0.1188, 6847 independent reflections [$2\theta \leq 72.118°$] and 409 parameters.

Refinement details for [(*Z*)-2$^{\mathrm{CN}\bullet+}$][OTf$^-$]: The structure was refined as a two-component twin. A number of reflections affected by the beamstop were omitted. The structure provides proof of connectivity, however the quality of the data is insufficient for structural discussions. The asymmetric unit contains a twofold disordered triflate counteranion refined to a 66:34 ratio (RESI 3 and RESI 31), the ADPs of which were restrained to the same value with similarity restraint SIMU 0.01. The half benzene solvent molecule, positioned on an inversion center, was also modelled as twofold disordered (RESI 2 and 21), refined to a 50:50 ratio and ADPs restrained using SIMU 0.01.

Crystal data for [(*Z*)-$2^{CN•+}$][OTf^-]: $[C_{30}H_{47}BN_4S][CF_3O_3S]\cdot(C_6H_6)_{0.5}$, $M_r = 663.92$, yellow block, $0.541\times0.493\times0.334$ mm^3, triclinic space group $P\bar{1}$, $a = 9.430(7)$ Å, $b = 9.763(7)$ Å, $c = 20.736(15)$ Å, $\alpha = 95.574(13)°$, $\beta = 96.19(3)°$, $\gamma = 101.684(14)°$, $V = 1845(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.195$ g·cm^{-3}, $\mu = 0.140$ mm^{-1}, $F(000) = 709$, $T = 99(2)$ K, $R_1 = 0.1103$, $wR^2 = 0.2519$, 7248 independent reflections [$2\theta\leq52.04°$] and 559 parameters.

Refinement details for [2^{CN}-H^+][PhS^-]: The asymmetric unit contains half a toluene molecule positioned on an inversion center, the benzene ring of which was modelled using AFIX 66. The PhS^- anion was modelled as twofold disordered, with parts refined to a 55:45 ratio. The benzene rings of both parts were idealised with AFIX 66 and ADPs restrained with SIMU 0.01. The ADPs of C2_15 were additionally restrained with ISOR 0.001.

Crystal data for [2^{CN}-H^+][PhS^-]: $[C_{30}H_{47}BN_4S][C_6H_5S]\cdot(C_7H_8)_{0.5}$, $M_r = 630.76$, yellow block, $0.329\times0.111\times0.087$ mm^3, triclinic space group $P\bar{1}$, $a = 9.78460(10)$ Å, $b = 11.33740(10)$ Å, $c = 17.2083(2)$ Å, $\alpha = 95.3960(10)°$, $\beta = 95.5070(10)°$, $\gamma = 99.3500(10)°$, $V = 1863.18(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.124$ g·cm^{-3}, $\mu = 0.997$ mm^{-1}, $F(000) = 686$, $T = 99.8(8)$ K, $R_1 = 0.0572$, $wR^2 = 0.1551$, 7909 independent reflections [$2\theta\leq156.014°$] and 487 parameters.

Refinement details for 3^{NCS}: The asymmetric unit contains one benzene molecule, which was modelled as twofold disordered in a 56:44 ratio. The benzene rings were idealised with AFIX 66. ADPs were restrained with SIMU 0.005.

Crystal data for 3^{NCS}: $C_{36}H_{53}BN_4S_2\cdot C_6H_6$, $M_r = 694.86$, colourless block, $0.308\times0.21\times0.191$ mm^3, monoclinic space group Pc, $a = 10.657(7)$ Å, $b = 16.337(11)$ Å, $c = 11.950(9)$ Å, $\beta = 106.86(2)°$, $V = 1991(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.159$ g·cm^{-3}, $\mu = 0.168$ mm^{-1}, $F(000) = 752$, $T = 100(2)$ K, $R_1 = 0.0369$, $wR^2 = 0.0740$, 7672 independent reflections [$2\theta\leq52.04°$] and 485 parameters.

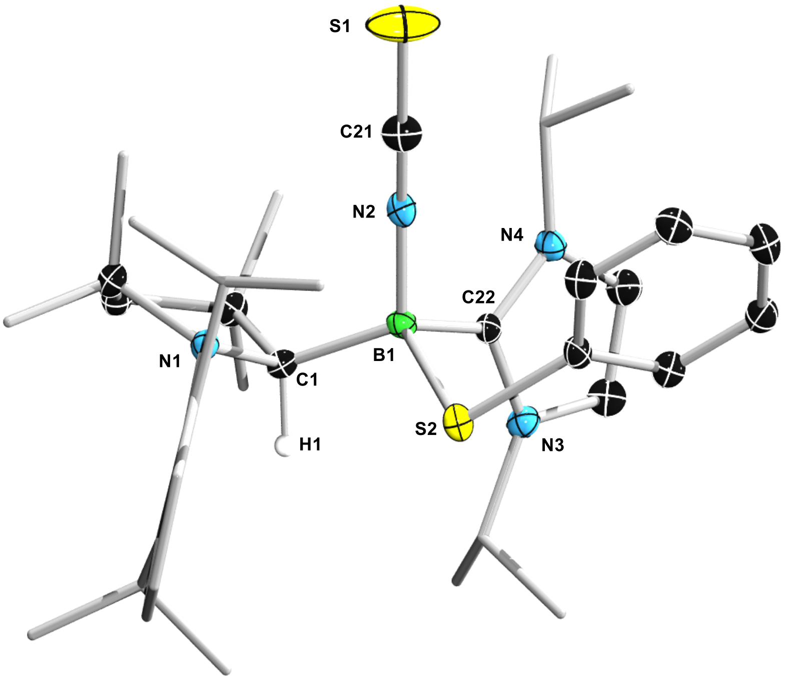

Figure S58. Crystallographically-derived solid-state structure of $\mathbf{3}^{\mathrm{NCS}}$. Atomic displacement ellipsoids drawn at 50% probability. Ellipsoids on ligand periphery and hydrogen atoms (except H bound to CAAC) omitted for clarity. Selected bond lengths (Å): N1–C1 1.507(3), C1–B1 1.643(4), B1–C22 1.661(4), B1–N2 1.515(3), N2–C21 1.156(3), C21–S1 1.603(3), B1–S2 1.968(3).

Computational details

Geometry optimisations and Hessian calculations were performed for **(*Z*)-2$^{\mathrm{CN}}$**, **(*Z*)-2$^{\mathrm{NCS}}$**, **[(*Z*)-2$^{\mathrm{CN}\bullet+}$]**, and **[(*Z*)-2$^{\mathrm{NCS}\bullet+}$]** at the OLYP[9]/TZ2P level of theory. All optimised structures were characterised as minimum energy geometries as only positive eigenvalues were obtained in the vibrational frequency calculations. Atomic charges were obtained using the Hirshfeld analysis.[10] Spin densities were obtained from the multipole derived charges up to quadrupole expansion (MDC-q).[11] All calculations were performed with ADF 2019.[12]

Cartesian coordinates

(*Z*)-2$^{\mathrm{CN}}$

C	19.371008000	3.731360000	4.840826000
N	20.481692000	4.155358000	4.074913000
C	21.533165000	3.098582000	3.885510000
C	21.221120000	2.175862000	5.069457000
H	21.799481000	2.510405000	5.936379000
H	21.508627000	1.138853000	4.873284000
C	19.715612000	2.316288000	5.383385000
C	21.433426000	2.330176000	2.542648000
H	22.105894000	1.466035000	2.572467000
H	21.746850000	2.952183000	1.705648000
H	20.429579000	1.960291000	2.337449000
C	22.971066000	3.635341000	3.975305000
H	23.670439000	2.807644000	3.818528000
H	23.184726000	4.065508000	4.951879000
H	23.174339000	4.387313000	3.208894000
C	19.531757000	2.162275000	6.907379000
H	19.962684000	1.209285000	7.240809000
H	18.479613000	2.154687000	7.194579000
H	20.035257000	2.965017000	7.451794000
C	18.892686000	1.191770000	4.709570000
H	19.294115000	0.207600000	4.981958000
H	18.889557000	1.262957000	3.621361000

H	17.856145000	1.222288000	5.046618000
C	20.641836000	5.489600000	3.544180000
C	21.226914000	6.504974000	4.359145000
C	21.449931000	7.771514000	3.807989000
H	21.897532000	8.548493000	4.421032000
C	21.106320000	8.068752000	2.497358000
H	21.291940000	9.060996000	2.090808000
C	20.501770000	7.093556000	1.719801000
H	20.205316000	7.342626000	0.705052000
C	20.245559000	5.807736000	2.212792000
C	19.508548000	4.844078000	1.280651000
H	19.420277000	3.892061000	1.802081000
C	18.072063000	5.316738000	0.971983000
H	17.547562000	4.552645000	0.384779000
H	18.068068000	6.240328000	0.383947000
H	17.507678000	5.506480000	1.883843000
C	20.260896000	4.598421000	-0.044564000
H	19.793767000	3.776670000	-0.600003000
H	21.312470000	4.344690000	0.109568000
H	20.232973000	5.481626000	-0.690790000
C	21.598092000	6.311318000	5.831555000
H	21.430299000	5.261117000	6.074403000
C	20.685239000	7.141721000	6.758396000
H	20.884937000	6.891229000	7.807708000
H	19.632728000	6.958499000	6.546673000
H	20.864176000	8.215387000	6.638202000
C	23.073816000	6.640978000	6.141690000
H	23.317846000	6.341430000	7.167940000
H	23.272684000	7.714645000	6.065079000
H	23.768293000	6.133257000	5.468902000
B	18.114522000	4.480365000	5.100906000
C	17.745318000	5.903952000	4.642704000
N	17.320473000	6.969074000	4.391244000
C	16.832368000	3.959800000	5.917234000

N	16.495239000	4.233231000	7.216447000
C	15.222273000	3.784370000	7.494570000
H	14.758288000	3.890487000	8.462015000
C	14.740266000	3.222298000	6.356036000
H	13.785395000	2.759273000	6.165686000
N	15.726242000	3.337273000	5.399448000
C	17.325109000	5.028973000	8.153777000
H	18.288830000	5.094773000	7.643043000
C	17.509529000	4.317473000	9.497393000
H	18.234347000	4.876851000	10.096506000
H	17.890038000	3.301589000	9.372485000
H	16.580091000	4.271830000	10.074561000
C	16.750967000	6.442352000	8.309901000
H	17.429807000	7.041594000	8.924193000
H	15.775099000	6.428604000	8.807187000
H	16.646383000	6.933898000	7.341074000
C	15.541666000	3.001777000	3.965626000
H	16.549194000	3.100405000	3.551960000
C	15.045418000	1.565882000	3.774493000
H	15.070109000	1.322394000	2.708009000
H	14.011819000	1.435205000	4.111686000
H	15.673364000	0.841521000	4.297537000
C	14.628676000	4.031583000	3.288618000
H	14.591147000	3.829403000	2.213847000
H	15.005631000	5.045817000	3.430481000
H	13.605050000	3.978758000	3.674670000

(*Z*)-2$^{\mathrm{NCS}}$

C	2.424022000	-0.272470000	14.954256000
C	1.964174000	-0.734665000	17.309141000
C	1.127888000	0.382982000	17.988592000
C	1.846543000	-1.979728000	18.203014000
C	3.428454000	-0.301332000	17.163080000
C	3.580216000	0.361186000	15.774971000

C	3.491857000	1.903723000	15.876178000
C	4.990315000	0.028642000	15.241512000
C	0.595292000	-1.945808000	15.498537000
C	0.965763000	-3.288126000	15.182521000
C	2.414140000	-3.776866000	15.114060000
C	2.826828000	-4.126325000	13.669021000
C	2.698697000	-4.983970000	16.032880000
C	-0.036689000	-4.219930000	14.890866000
C	-1.380291000	-3.873927000	14.895796000
C	-1.738004000	-2.563157000	15.170145000
C	-0.782149000	-1.580904000	15.460547000
C	-1.295730000	-0.157225000	15.681812000
C	-2.305180000	-0.061163000	16.845259000
C	-1.922308000	0.446609000	14.407749000
C	0.479443000	-1.179011000	11.807590000
C	3.081741000	0.755497000	12.464642000
C	3.598465000	2.418953000	11.023665000
C	4.437754000	1.382176000	10.768674000
C	1.621906000	2.820198000	12.553075000
C	2.044901000	4.225763000	12.989488000
C	0.496082000	2.849756000	11.512126000
C	4.699933000	-0.990165000	11.604106000
C	6.228476000	-0.954297000	11.696414000
C	4.211255000	-1.748981000	10.363903000
N	1.611511000	-0.992861000	15.874403000
N	1.160076000	-0.782368000	12.702829000
N	2.773395000	2.026793000	12.055459000
N	4.111477000	0.371448000	11.647269000
S	-0.448847000	-1.714627000	10.617075000
B	2.222967000	-0.143855000	13.491223000
H	1.597396000	0.659108000	18.939052000
H	0.118289000	0.044367000	18.216343000
H	1.056101000	1.284732000	17.381078000
H	2.120268000	-1.710672000	19.228475000

H	2.515252000	-2.776085000	17.881137000
H	0.826136000	-2.370416000	18.226286000
H	4.062048000	-1.192837000	17.204948000
H	3.749984000	0.358694000	17.974021000
H	4.221727000	2.284082000	16.602187000
H	2.504207000	2.251833000	16.180197000
H	3.724525000	2.363977000	14.914763000
H	5.751984000	0.345866000	15.965976000
H	5.203059000	0.549636000	14.307327000
H	5.111662000	-1.044844000	15.077046000
H	3.049625000	-2.952504000	15.439092000
H	3.896613000	-4.365574000	13.627573000
H	2.628351000	-3.298127000	12.989723000
H	2.281269000	-4.999189000	13.295413000
H	3.775102000	-5.191766000	16.057929000
H	2.204099000	-5.892388000	15.674482000
H	2.365079000	-4.816270000	17.059382000
H	0.238927000	-5.243434000	14.652728000
H	-2.141804000	-4.617467000	14.669232000
H	-2.789321000	-2.291094000	15.142606000
H	-0.434640000	0.461319000	15.928804000
H	-2.511788000	0.988587000	17.084358000
H	-1.942871000	-0.548529000	17.754076000
H	-3.261155000	-0.528267000	16.587418000
H	-2.213554000	1.487876000	14.593590000
H	-2.822001000	-0.095027000	14.098744000
H	-1.224059000	0.429394000	13.571949000
H	3.534263000	3.386637000	10.552559000
H	5.227206000	1.296579000	10.039348000
H	1.285497000	2.253287000	13.426520000
H	1.195890000	4.714661000	13.476718000
H	2.336256000	4.853366000	12.140841000
H	2.871443000	4.201531000	13.702320000
H	-0.383588000	3.334128000	11.946775000

H	0.209031000	1.843610000	11.203283000
H	0.783702000	3.418935000	10.621663000
H	4.294819000	-1.470452000	12.497988000
H	6.599646000	-1.978230000	11.800721000
H	6.573407000	-0.382937000	12.560205000
H	6.687578000	-0.534216000	10.795559000
H	4.568970000	-2.781956000	10.409410000
H	4.596636000	-1.303530000	9.440692000
H	3.121800000	-1.771349000	10.309888000

[(*Z*)-2$^{\mathrm{CN}\bullet+}$]

N	1.224811000	0.630843000	3.465545000
B	3.386326000	1.180212000	4.757309000
C	1.856077000	1.092157000	4.568227000
N	5.380208000	0.346696000	3.148397000
C	-0.309854000	0.770279000	3.528963000
N	4.710334000	1.149317000	7.072500000
C	-0.507178000	0.953468000	5.035578000
H	-0.705931000	-0.019884000	5.492667000
H	-1.365457000	1.591602000	5.255003000
N	4.618084000	3.103600000	6.124011000
C	0.803783000	1.529399000	5.614218000
C	-1.047444000	-0.464369000	3.002686000
H	-2.121531000	-0.271662000	3.077898000
H	-0.835139000	-1.355588000	3.588482000
H	-0.822535000	-0.662336000	1.953040000
C	-0.816502000	1.986992000	2.730348000
H	-1.883617000	2.102510000	2.939782000
H	-0.713097000	1.834065000	1.658506000
H	-0.325762000	2.920724000	3.000804000
C	0.744270000	3.067797000	5.771038000
H	-0.112832000	3.335987000	6.396787000
H	0.639514000	3.593231000	4.821013000
H	1.637011000	3.444009000	6.269937000

C	1.035056000	0.920619000	7.012354000
H	0.152621000	1.111416000	7.632288000
H	1.887134000	1.367967000	7.523502000
H	1.175679000	-0.162258000	6.966549000
C	1.877682000	-0.000236000	2.314169000
C	2.235093000	0.772930000	1.175485000
C	2.791815000	0.099171000	0.081579000
H	3.077255000	0.666599000	-0.798044000
C	3.003951000	-1.270068000	0.091432000
H	3.438679000	-1.763751000	-0.774314000
C	2.673689000	-2.002880000	1.220942000
H	2.863800000	-3.071080000	1.225644000
C	2.110088000	-1.405590000	2.353620000
C	2.107348000	2.294699000	1.056685000
H	1.621409000	2.667258000	1.958334000
C	3.483322000	2.990404000	0.976409000
H	3.347630000	4.077826000	0.972042000
H	4.016659000	2.725264000	0.059184000
H	4.127507000	2.723214000	1.813623000
C	1.248110000	2.727589000	-0.151538000
H	1.032399000	3.799750000	-0.094440000
H	0.296313000	2.194587000	-0.207396000
H	1.770531000	2.554024000	-1.096405000
C	1.827531000	-2.320838000	3.551221000
H	1.309827000	-1.738201000	4.315655000
C	3.130135000	-2.843615000	4.194981000
H	2.895045000	-3.415146000	5.099954000
H	3.810901000	-2.034731000	4.458969000
H	3.670035000	-3.511636000	3.517781000
C	0.923565000	-3.521807000	3.194866000
H	0.616521000	-4.040709000	4.109304000
H	1.450760000	-4.251733000	2.574618000
H	0.022109000	-3.226717000	2.654677000
C	4.446740000	0.679609000	3.769354000

C	4.172491000	1.819792000	6.014800000
C	5.463408000	2.011224000	7.839419000
H	5.975675000	1.702646000	8.736213000
C	5.406377000	3.231523000	7.247052000
H	5.862399000	4.163252000	7.539999000
C	4.634728000	-0.322664000	7.313039000
H	3.858102000	-0.668752000	6.628392000
C	4.203952000	-0.638528000	8.748306000
H	4.030883000	-1.715047000	8.832115000
H	3.280292000	-0.126713000	9.025732000
H	4.977327000	-0.380210000	9.477221000
C	5.962248000	-0.991234000	6.935978000
H	5.853573000	-2.075710000	7.025906000
H	6.770541000	-0.682246000	7.605366000
H	6.252518000	-0.763198000	5.908804000
C	4.449488000	4.184377000	5.107405000
H	3.678757000	3.805167000	4.432619000
C	5.750849000	4.373949000	4.318307000
H	5.580399000	5.095453000	3.514500000
H	6.091274000	3.438822000	3.869649000
H	6.549691000	4.767182000	4.953905000
C	3.955292000	5.486464000	5.744027000
H	3.707338000	6.193754000	4.947696000
H	4.721991000	5.957932000	6.365342000
H	3.060489000	5.337878000	6.352015000

[(*Z*)-2$^{\mathrm{NCS}\bullet+}$]

C	5.286052000	7.906272000	13.345873000
N	6.178848000	7.747722000	12.329897000
C	7.008378000	6.457327000	12.433787000
C	6.146238000	5.653256000	13.409963000
H	6.749951000	4.988402000	14.031123000
H	5.457109000	5.022358000	12.841323000
C	5.333204000	6.656605000	14.256552000

C	7.168064000	5.732170000	11.093308000
H	6.215394000	5.407780000	10.681100000
H	7.772024000	4.836107000	11.263356000
H	7.689873000	6.342509000	10.353822000
C	8.424656000	6.708573000	12.988738000
H	8.433201000	7.253670000	13.931301000
H	9.046853000	7.239420000	12.271170000
H	8.894397000	5.737020000	13.166525000
C	3.949503000	6.041005000	14.546573000
H	3.374801000	5.884812000	13.630167000
H	3.361647000	6.647551000	15.235391000
H	4.085074000	5.062342000	15.019622000
C	6.013223000	6.948741000	15.615995000
H	6.978111000	7.447004000	15.515169000
H	6.177195000	6.009438000	16.154075000
H	5.376035000	7.570871000	16.243978000
C	6.348727000	8.651916000	11.191486000
C	7.332084000	9.679119000	11.226660000
C	7.506735000	10.457539000	10.075219000
H	8.252062000	11.246255000	10.078579000
C	6.749528000	10.258538000	8.931701000
H	6.911178000	10.876733000	8.051880000
C	5.771346000	9.275910000	8.926164000
H	5.167399000	9.144115000	8.034281000
C	5.538951000	8.455028000	10.035811000
C	8.193455000	10.040937000	12.441045000
H	7.996447000	9.311418000	13.225856000
C	7.828319000	11.423483000	13.022583000
H	6.775352000	11.485719000	13.296920000
H	8.031527000	12.229098000	12.311251000
H	8.429345000	11.619701000	13.917683000
C	9.706228000	10.002966000	12.135057000
H	10.012443000	9.083243000	11.631854000
H	10.279646000	10.085858000	13.064444000

H	10.008813000	10.837186000	11.495813000
C	4.398891000	7.435995000	9.918020000
H	4.409576000	6.806677000	10.809713000
C	4.538583000	6.506800000	8.692609000
H	5.529895000	6.056383000	8.615804000
H	4.349550000	7.040455000	7.757069000
H	3.802813000	5.697610000	8.752986000
C	3.017215000	8.123319000	9.874728000
H	2.859339000	8.776939000	10.732474000
H	2.224034000	7.367252000	9.863756000
H	2.900207000	8.731905000	8.973249000
B	4.377122000	9.132356000	13.566835000
N	4.306829000	10.251602000	12.675845000
C	3.991374000	11.288888000	12.158386000
S	3.603260000	12.643358000	11.451885000
N	2.029632000	9.166063000	14.849831000
N	3.663701000	10.066848000	15.964156000
C	3.375516000	9.383404000	14.819261000
C	1.493533000	9.694641000	16.004006000
H	0.444857000	9.631221000	16.245225000
C	2.513690000	10.258327000	16.699647000
H	2.503216000	10.770521000	17.648025000
C	1.207008000	8.557069000	13.762940000
H	1.940349000	8.137021000	13.072055000
C	0.320309000	7.426168000	14.292678000
H	-0.150988000	6.923755000	13.443258000
H	-0.484927000	7.799317000	14.931843000
H	0.889308000	6.680424000	14.850557000
C	0.398211000	9.637387000	13.034893000
H	1.034575000	10.440980000	12.660650000
H	-0.365483000	10.074205000	13.685185000
H	-0.114155000	9.185561000	12.180877000
C	4.982484000	10.663913000	16.329658000
H	5.684988000	10.226452000	15.616961000

C	4.953573000	12.184330000	16.131529000
H	5.955722000	12.586912000	16.303145000
H	4.276539000	12.668701000	16.841305000
H	4.647665000	12.457996000	15.120435000
C	5.404596000	10.273543000	17.749187000
H	6.433338000	10.606275000	17.913515000
H	5.371250000	9.194459000	17.910721000
H	4.785138000	10.756873000	18.510021000

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