Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Tuneable reduction of cymantrenylboranes to diborenes or borylenes

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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. Solvents were stored under argon over activated 4 Å molecular sieves. NMR spectra were acquired on a Bruker Avance 400 or 500 NMR spectrometer. Chemical shifts (δ) are provided in ppm and internally referenced to the carbon nuclei ($^{13}C\{^1H\}$) or residual protons (^1H) 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 Jasco FT/IR-6200 spectrometer inside a glovebox. High-resolution mass spectrometry data were obtained from a Thermo Scientific Exactive Plus spectrometer in LIFDI mode. UV-vis spectra were acquired on a JASCO-V660 UV-vis spectrometer. 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.

Reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received. I*i*Pr (1,3-di*iso*propylimidazol-2-ylidene),[1] IMe (1,3-dimethylimidazol-2-ylidene),[2] BBr_2Cym (Cym = cymantrenyl = $(C_5H_5)Mn(CO)_3$)[3] and KC_8[4] were prepared according to literature procedures.

Synthetic procedures

Synthesis of (IMe)BBr_2Cym, $\mathbf{1^{IMe}}$

A solution of IMe (200 mg, 2.08 mmol) in hexane/toluene (15 mL:1 mL) was added dropwise to a solution of BBr_2Cym (777 mg, 2.08 mmol) in hexane (30 mL) at –78 °C. The precipitate was collected by filtration, washed with hexane (3 x 15 mL) and dried under reduced pressure to afford $\mathbf{1^{IMe}}$ as an off-white solid (750 g, 1.60 mmol, 77%). ^{1}H NMR (500 MHz, C_6D_6, 297 K): $\delta = 5.19$ (s, 2H, CH_{IMe}), 5.09 (m, 2H, CH_{Cp}), 4.23 (m, 2H, CH_{Cp}), 2.95 (s, 6H, $CH_{3\text{-IMe}}$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): $\delta = 226.2$ (*C*O), 121.5 (*C*H_{IMe}), 93.4, 82.7 (*C*H_{Cp}), 38.5 (*C*$H_{3\text{-IMe}}$) ppm. *Note: the resonances for C9 and C1 could not be detected due to broadening caused by quadrupolar coupling with boron.* ^{11}B NMR (160 MHz, C_6D_6, 297 K): $\delta = –8.1$ ppm. Solid-state IR: $\nu(CO) = 2007, 1925\ cm^{-1}$. HRMS-LIFDI calcd. for [$C_{13}H_{12}BBr_2MnN_2O_3$]: 469.8662; found: 469.8658.

Synthesis of (I*i*Pr)BBr_2Cym, $\mathbf{1^{I\mathit{i}Pr}}$

A solution of I*i*Pr (815 mg, 5.35 mmol) in hexane (15 mL) was added dropwise to a solution of BBr_2Cym (2.00 g, 5.35 mmol) in hexane (60 mL) at –78 °C. The precipitate was collected by filtration, washed with hexane (3 x 15 mL) and dried under reduced pressure to afford $\mathbf{1^{I\mathit{i}Pr}}$ as an off-white solid (2.67 g, 5.08 mmol, 95%). ^{1}H NMR (500 MHz, C_6D_6, 297 K): $\delta = 6.04$ (br, 2H, NC*H*), 5.22 (m, 2H, CH_{iPr}), 5.18 (m, 2H, CH_{Cp}), 4.27 (m, 2H, CH_{Cp}), 0.83 (d, $^{3}J = 6.5$ Hz, 12H, $CH_{3\text{-iPr}}$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): $\delta = 226.2$ (*C*O), 155.5 (br., BC_{IiPr}), 117.37 (N*C*H), 108.4 (br, BC_{Cp}), 92.9, 82.8 (*C*H_{Cp}), 50.5 (*C*H_{iPr}), 22.7 (*C*$H_{3\text{-}iPr}$) ppm. *Note: the resonances for C9 and C1 could not be detected due to broadening caused by quadrupolar coupling with boron.* ^{11}B NMR (160 MHz, C_6D_6, 297 K): $\delta = –7.7$ ppm. Solid-state IR: $\nu(CO) = 2010, 1906\ cm^{-1}$. HRMS-LIFDI calcd. for [$C_{17}H_{20}BBr_2MnN_2O_3$]: 525.9288; found: 525.9287.

Synthesis of $(IMe)_2B_2Cym_2$, $\mathbf{2^{IMe}}$

A suspension of $\mathbf{1^{IMe}}$ (140 mg, 298 μmol) and KC_8 (150 mg, 1.11 mmol, 3.7 equiv.) in 5 mL benzene was stirred for 16 h at 60 °C. The suspension was filtered, the solvent was removed under reduced pressure and the crude product was recrystallised from a saturated benzene solution to afford $\mathbf{2^{IMe}}$ as a purple solid (35 mg, 56 μmol, 38%). *Notes: ^{1}H NMR spectra of the crude product show the formation of cis- and trans-$\mathbf{2^{IMe}}$ in a 1:1 ratio. In solution at rt cis-$\mathbf{2^{IMe}}$*

*slowly isomerises to trans-***2**^{IMe}*. The isomerisation can be accelerated by heating.* ^{1}H NMR (500 MHz, C_6D_6, 297 K) for *trans*-**2**^{IMe}: δ = 6.04 (s, 4H, NCH_{IMe}), 4.31 (m, 4H, CH_{Cp}), 3.49 (m, 4, CH_{Cp}), 3.42 (s, 12H, C$H_{3\text{-IMe}}$) ppm; for *cis*-**2**^{IMe}: δ = 5.74 (s, 4H, NCH_{IMe}), 4.83 (m, 4H, CH_{Cp}), 4.31 (m, 4, CH_{Cp}), 2.84 (s, 12H, C$H_{3\text{-IMe}}$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K) for *trans*-**2**^{IMe}: δ = 229.3 (*C*O), 173.4 (C_{carbene}, HMBC), 119.7 (N*C*H), 83.8, 81.7 ($C\text{H}_{\text{Cp}}$) 35.7 ($\text{CH}_{3\text{-IMe}}$) ppm; for *cis*-**2**^{IMe}: δ = 229.3 (*C*O), 118.9 (N*C*H), 87.4, 82.5 ($C\text{H}_{\text{Cp}}$) 32.0 ($\text{CH}_{3\text{-IMe}}$) ppm. *Note: the resonance for C1 could not be detected due to broadening caused by quadrupolar coupling with boron.* ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): δ = *Note: the resonance for C1and C9 could not be detected due to broadening caused by quadrupolar coupling with boron.* ^{11}B NMR (160 MHz, C_6D_6, 297 K) for *cis/trans*-**2**^{IMe}: δ = 18.5 ppm. Solid-state IR: υ(*CO*) = 2002, 1976, 1891 cm^{-1}. HRMS-LIFDI calcd. for [$C_{26}H_{24}B_2Mn_2N_4O_6$ + H^+]: 621.0716; found: 621.0710.

Synthesis of (I*i*Pr)$_2$B$_2$Cym$_2$, 2^{IiPr}

A suspension of **1**^{IiPr} (150 mg, 285 µmol) and KC_8 (125 mg, 925 µmol, 3.2 equiv.) in 5 mL benzene was stirred for 6 h at 60 °C. The suspension was filtered, the solvent was removed under reduced pressure and the crude product was recrystallised from a saturated benzene solution to afford **2**^{IiPr} as a purple solid (53 mg, 72 µmol, 51%). *Notes: ^{1}H NMR spectra of the crude product show the formation of cis- and trans-***2**^{IiPr} *in a 1:2 ratio besides ca. 12% of the borylene* **3**^{IiPr}*. The reduction of* **1**^{IiPr} *with 3.9 equiv. KC_8 at rt yields the same ratio of* cis/trans-*diborene but a higher proportion of* **3**^{IiPr} *(ca. 32%). Heating isolated crystals of cis-***2**^{IiPr} *in C_6D_6 at 80 °C did not result in isomerisation to trans-***2**^{IiPr}*.* ^{1}H NMR (500 MHz, C_6D_6, 297 K) for *cis/trans*-**2**^{IiPr}: δ = 6.39 (s, 4H, NC*H*), 5.23 (m, 4H, CH_{iPr}), 4.28 (m, 4H, CH_{Cp}), 3.31 (m, 4H, CH_{Cp}), 1.26 (d, ^{3}J = 6.7 Hz, 12H, C$H_{3\text{-iPr}}$), 1.23 (d, ^{3}J = 6.7 Hz, 12H, C$H_{3\text{-iPr}}$) ppm; for *cis/trans*-**2**^{IiPr}: δ = 6.07 (s, 4H, NC*H*), 4.88 (m, 4H, CH_{iPr}), 4.78 (m, 4H, CH_{Cp}), 4.56 (m, 4H, CH_{Cp}), 0.96 (d, ^{3}J = 6.8 Hz, 12H, C$H_{3\text{-iPr}}$), 0.61 (d, ^{3}J = 6.8 Hz, 12H, C$H_{3\text{-iPr}}$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K) for *cis/trans*-**2**^{IiPr}: δ = 228.2 (*C*O), 170.7 ($C_{\text{Carbene,}}$ HMBC), 115.7 (N*C*H), 82.7, 79.9 ($C\text{H}_{\text{Cp}}$), 49.9 ($C\text{H}_{i\text{Pr}}$), 24.3 ($C\text{H}_{3\text{-}i\text{Pr}}$), 23.3 ($C\text{H}_{3\text{-}i\text{Pr}}$) ppm; for *cis/trans*-**2**^{IiPr}: 228.2 (*C*O), 114.9 (N*C*H), 84.0, 83.5 ($C\text{H}_{\text{Cp}}$), 49.5 ($C\text{H}_{i\text{Pr}}$), 23.7 ($C\text{H}_{3\text{-}i\text{Pr}}$), 21.8 ($C\text{H}_{3\text{-}i\text{Pr}}$) ppm. *Note: the resonance for C1 in cis/trans-***2**^{IiPr} *and those of C1 and C9 in cis/trans-***2**^{IiPr} *could not be detected due to broadening caused by quadrupolar coupling with boron.* ^{11}B NMR (160 MHz, C_6D_6, 297 K) *for* ***cis****/trans-***2**^{IiPr}: δ = 19.2 ppm. Solid-state IR: υ(*CO*) = 1990, 1980, 1900, 1878 cm^{-1}. HRMS-LIFDI calcd. for [$C_{34}H_{40}B_2Mn_2N_4O_6$]: 732.1889; found: 732.1876.

Synthesis of $(\mathrm{I}i\mathrm{Pr})_2$BCym, $3^{\mathrm{I}i\mathrm{Pr}}$

A suspension of $\mathbf{1}^{\mathbf{I}i\mathbf{Pr}}$ (200 mg, 380 µmol) and KC_8 (460 mg, 3.40 mmol, 8.9 equiv.) in 5 mL THF was stirred for 10 min at room temperature. The solvent was removed under reduced pressure. The solid was redissolved in 10 mL benzene and insoluble residues removed by filtration. The solvent was removed again under reduced pressure and the crude product was crystallised from a saturated benzene solution to afford $\mathbf{3}^{\mathbf{I}i\mathbf{Pr}}$ as a deep-blue solid (22 mg, 42 µmol, 22%). *Note: A ^1H NMR spectrum of the crude product showed quantitative conversion to the borylene. The poor isolated yield is owed to the very high solubility of the compound in hydrocarbon solvents.* ^{1}H NMR (500 MHz, C_6D_6, 297 K): δ = 6.16 (s, 4H, NCH), 5.00 (m, 2H, CH_{Cp}), 4.60 (m, 4H, CH_{iPr}), 4.19 (m, 2H, CH_{Cp}), 1.00 (d, ^3J = 6.7 Hz, 12H, C$H_{3\text{-iPr}}$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): δ = 229.3 (CO), 165.8 (B$C_{\mathrm{I}i\mathrm{Pr}}$, detected by HMBC), 143.6 (BC_{Cp}, detected by HMBC), 115.27 (NCH), 81.6, 75.3 (CH$_{\mathrm{Cp}}$), 50.3 (CH$_{\mathrm{iPr}}$), 22.5 (CH$_{3\text{-iPr}}$) ppm. ^{11}B NMR (160 MHz, C_6D_6, 297 K): δ = –12.6 ppm. Solid-state IR: $\upsilon(CO)$ = 2012, 1922, 1815 cm^{-1}. HRMS-LIFDI calcd. for $[C_{26}H_{36}BMnN_4O_3 + H]^+$: 519.2334; found: 519.2330.

NMR spectra of isolated compounds

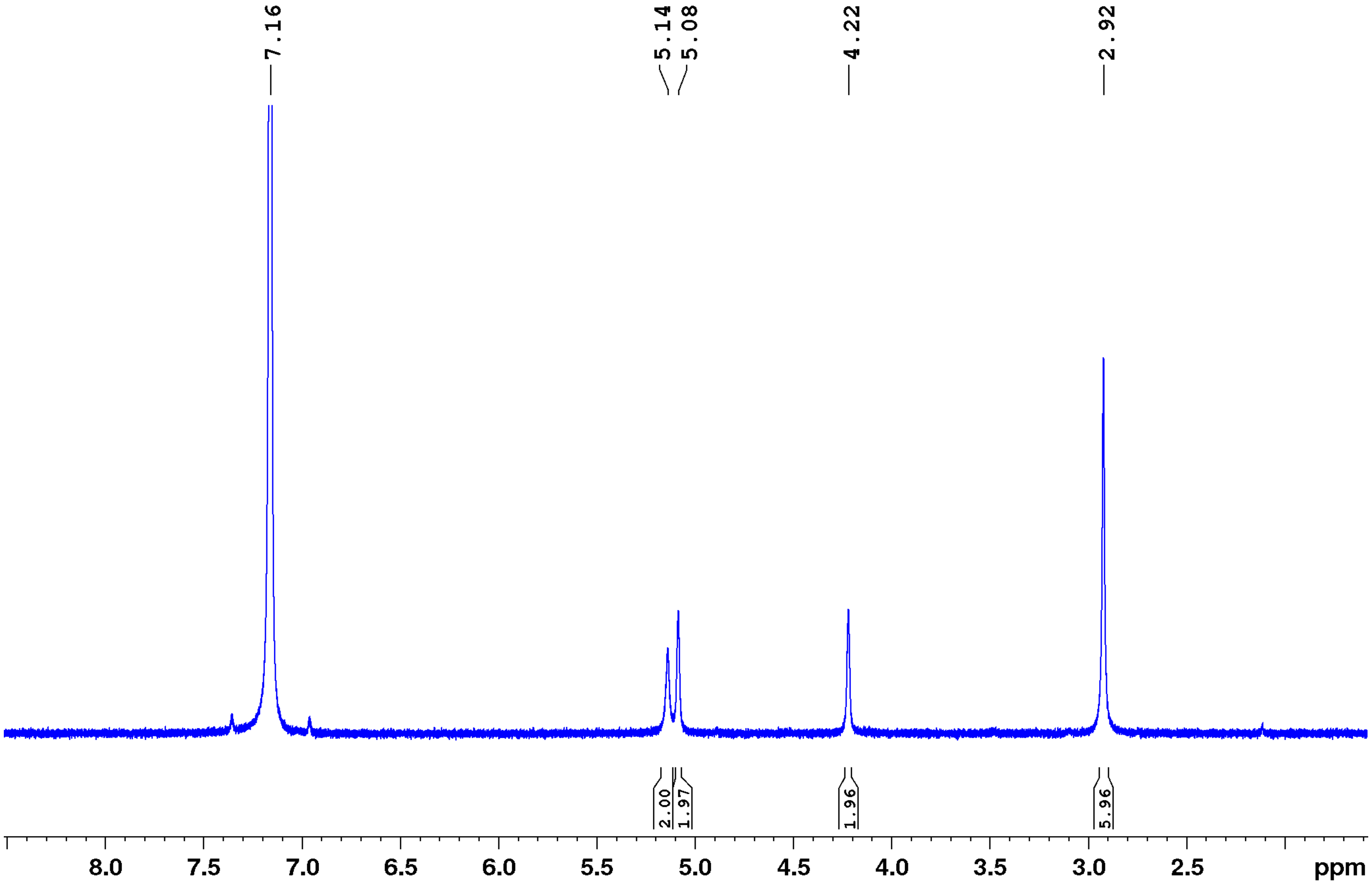


Figure S1. ^{1}H NMR spectrum of $\mathbf{1^{IMe}}$ in C_6D_6.

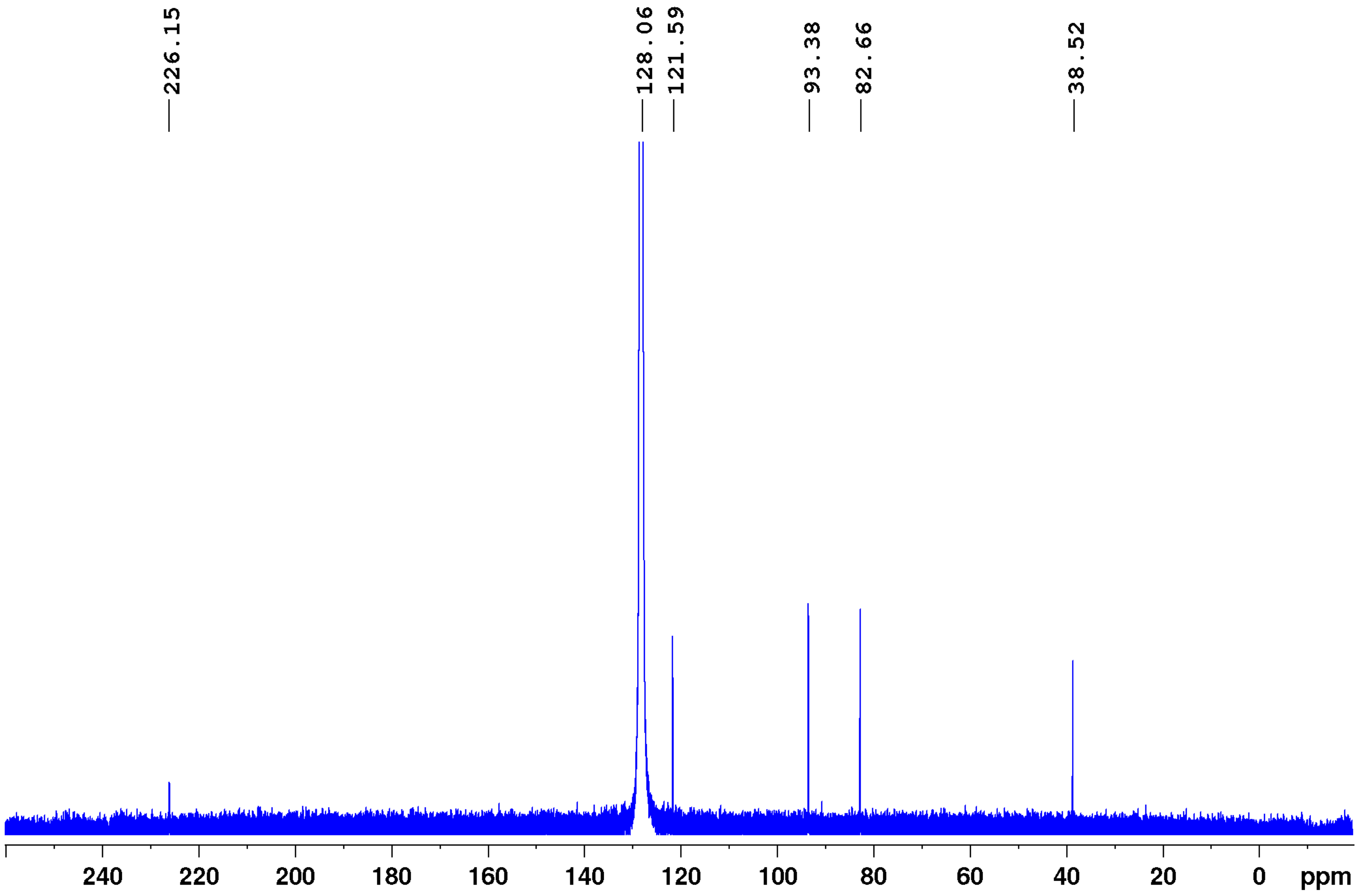


Figure S2. $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{1^{IMe}}$ in C_6D_6.

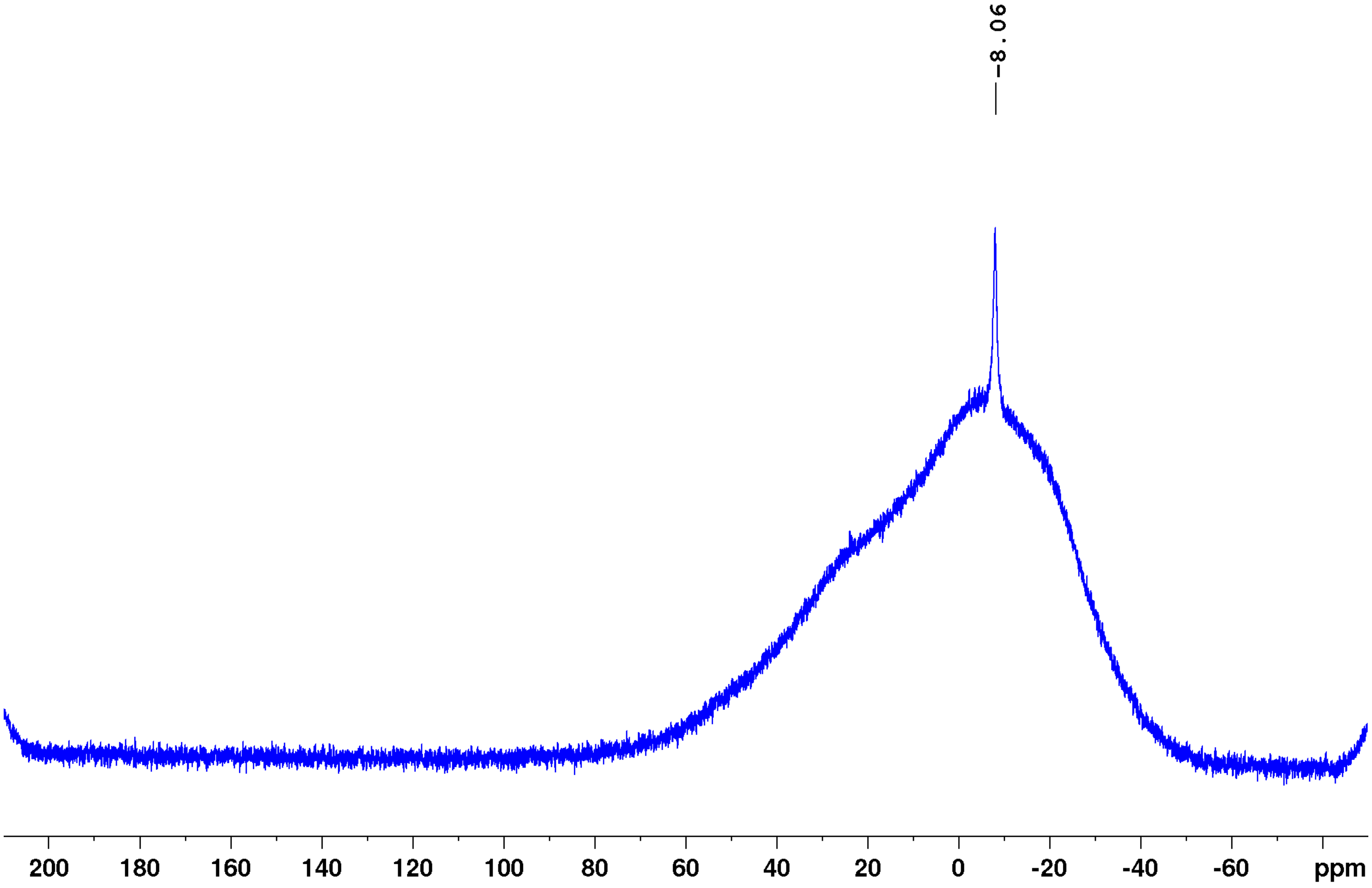


Figure S3. ^{11}B NMR spectrum of **1^{IMe}** in C_6D_6.

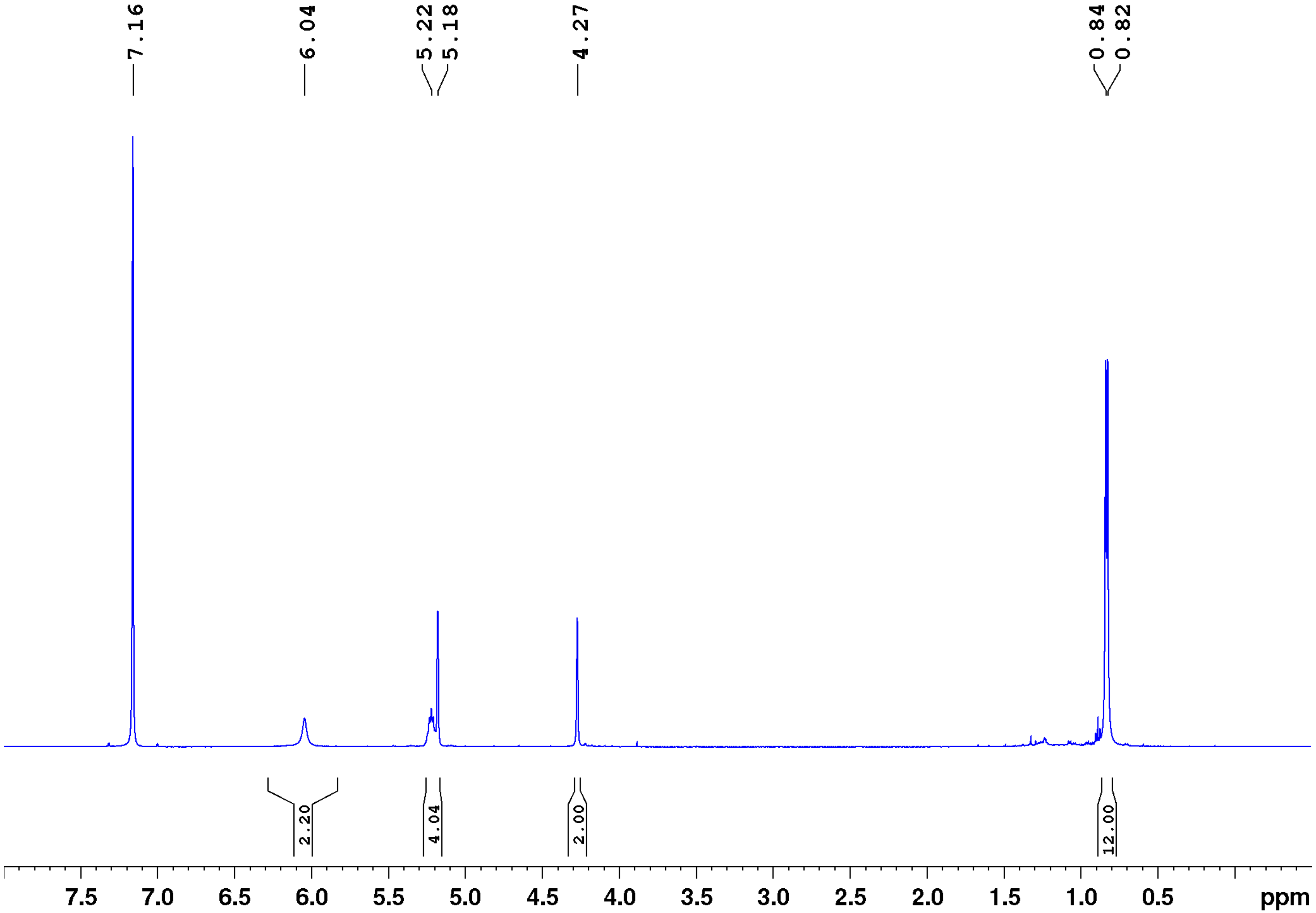


Figure S4. ^{1}H NMR spectrum of $\mathbf{1}^{\mathbf{I}i\mathbf{Pr}}$ in C_6D_6.

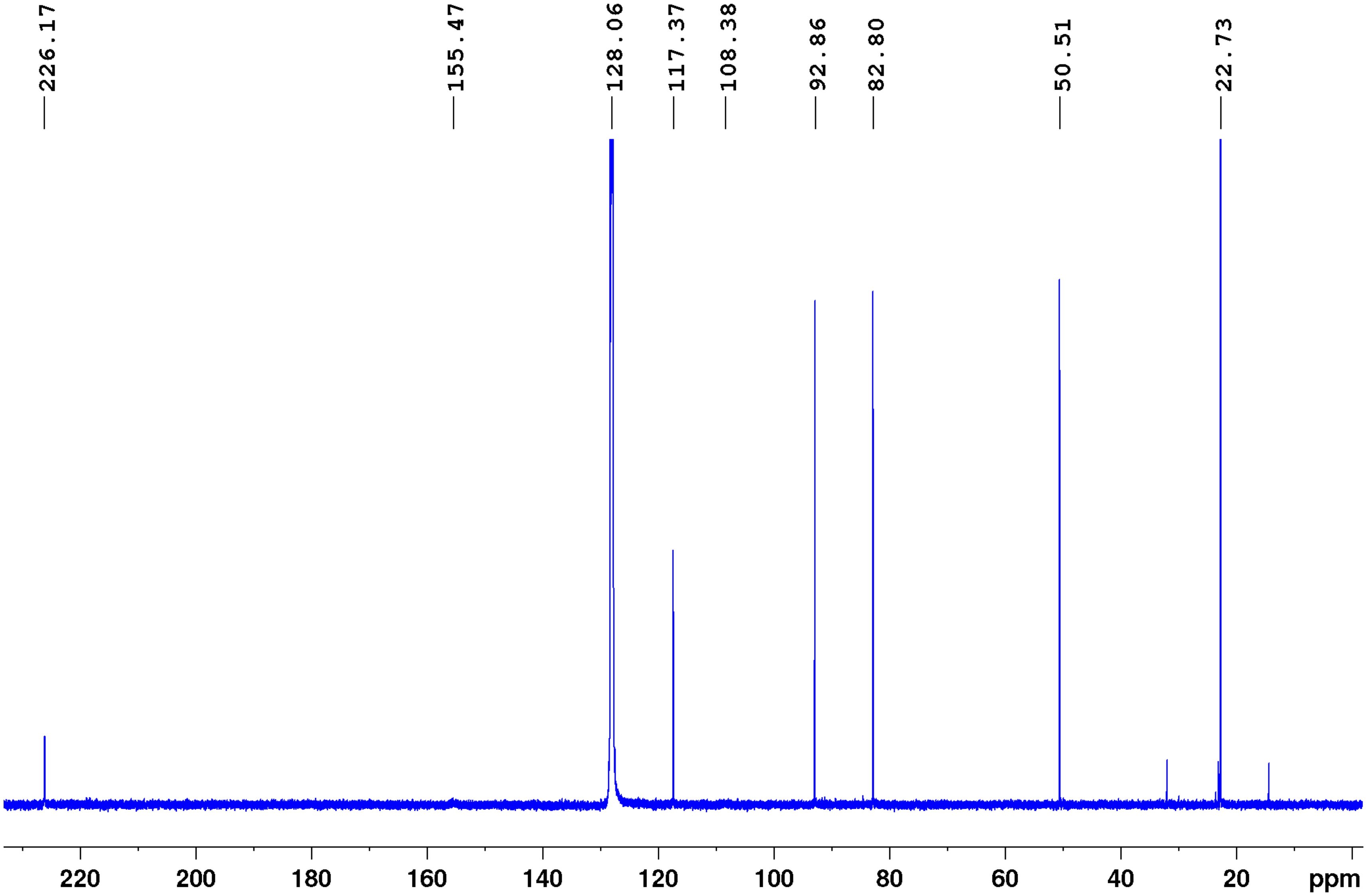


Figure S5. $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{1}^{\mathbf{IiPr}}$ in C_6D_6.

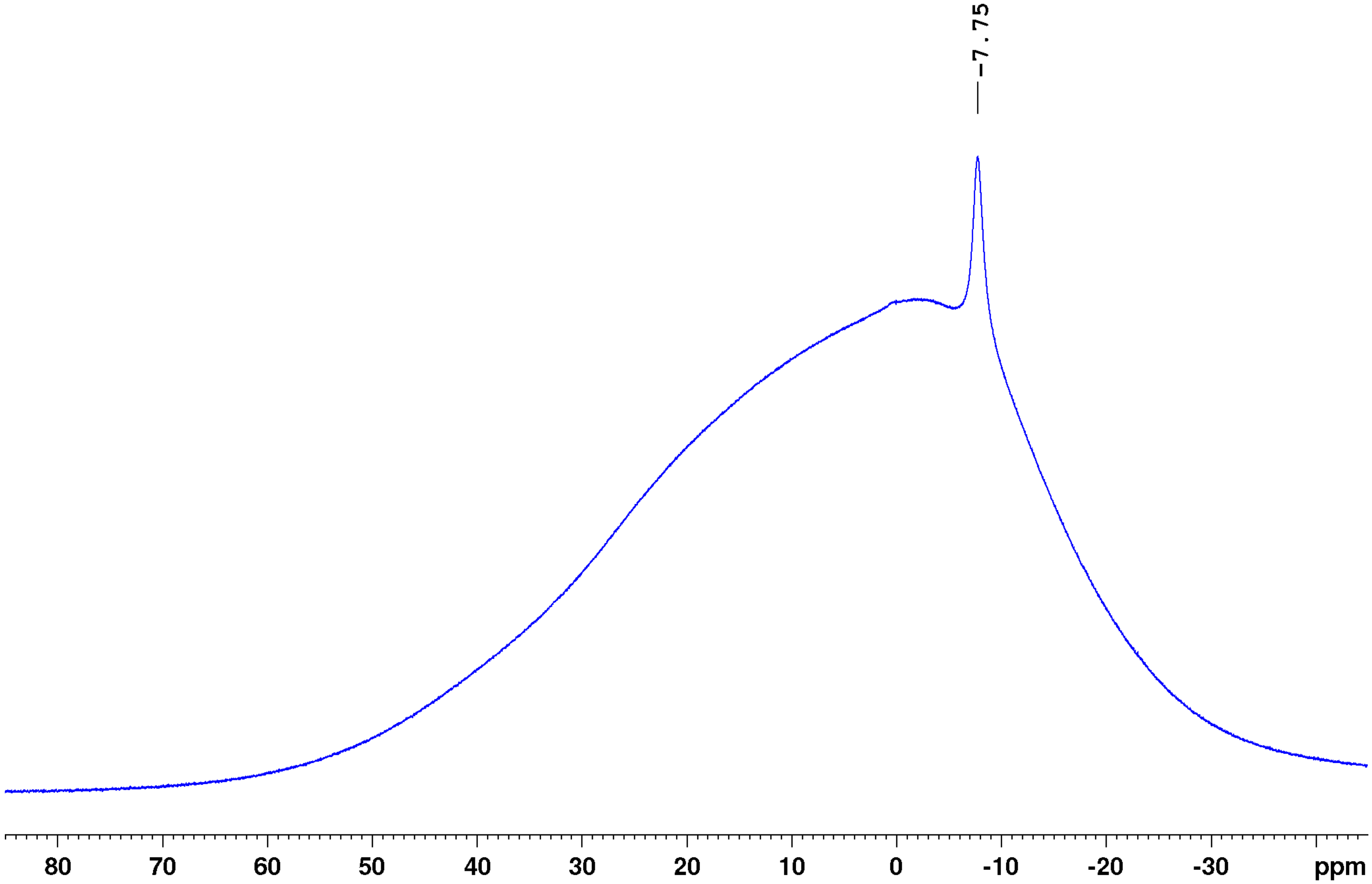


Figure S6. ^{11}B NMR spectrum of $\mathbf{1^{IiPr}}$ in C_6D_6.

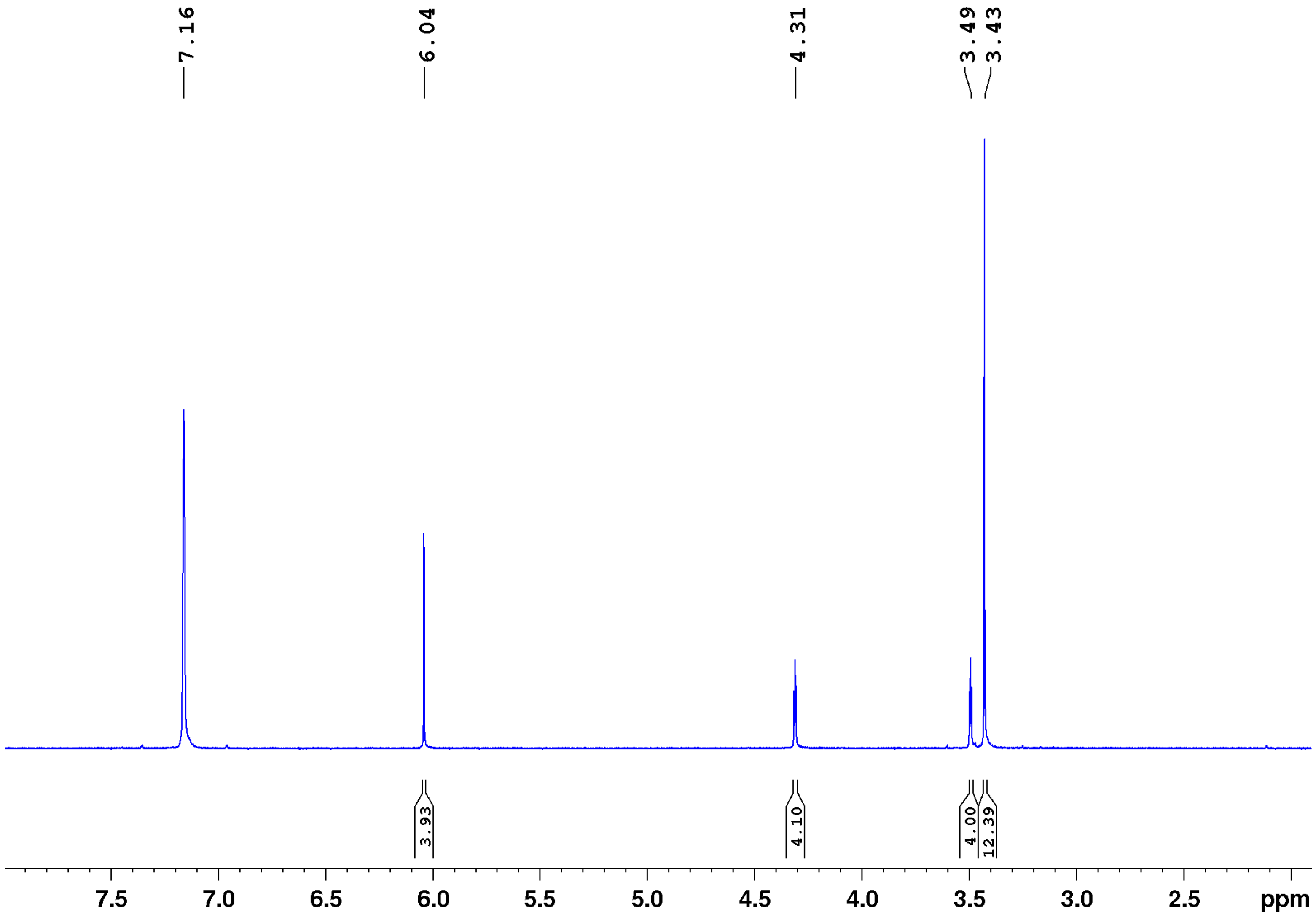


Figure S7. ^{1}H NMR spectrum of *trans*-$\mathbf{2^{IMe}}$ in C_6D_6.

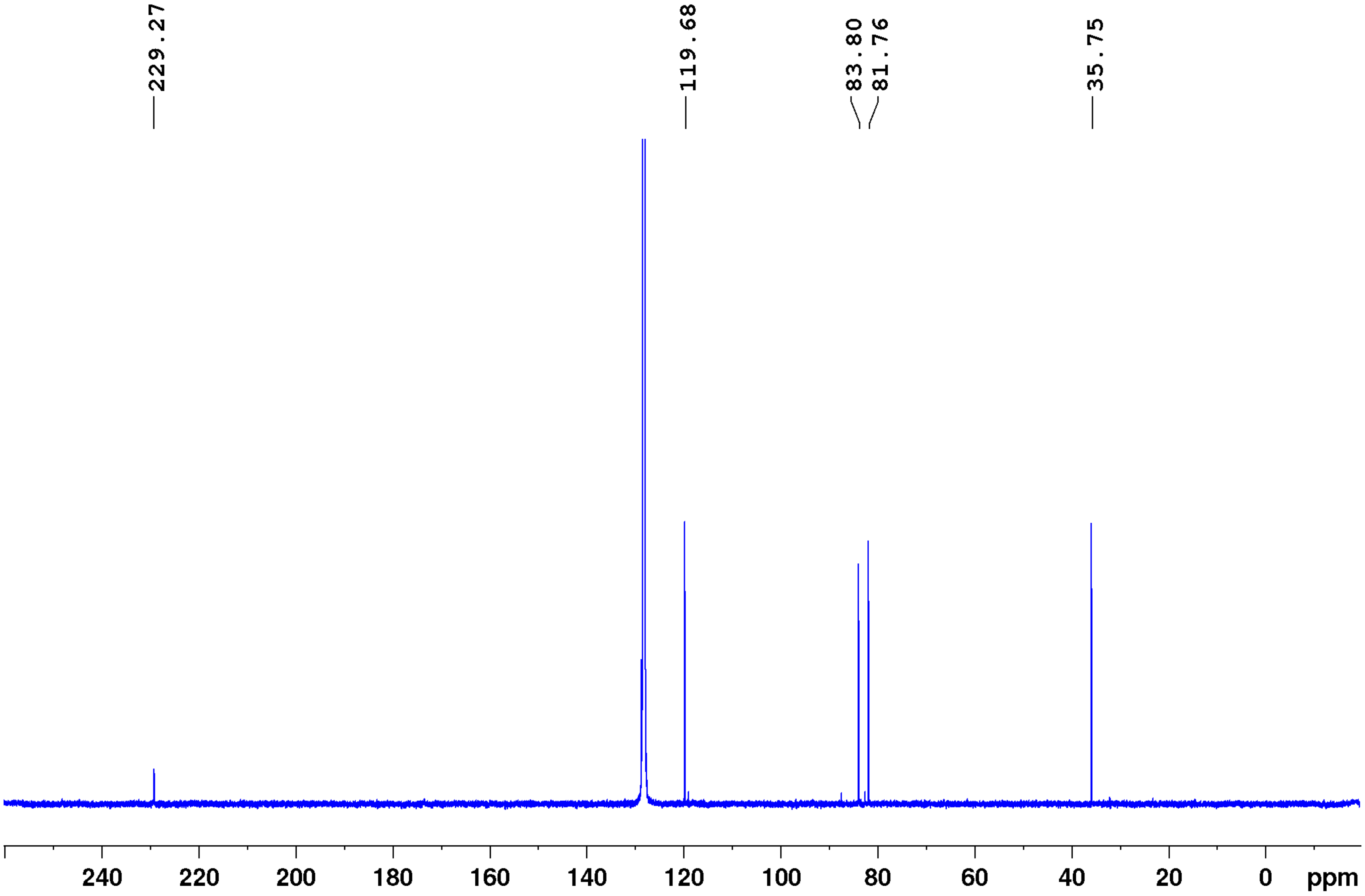


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of *trans*-$\mathbf{2^{IMe}}$ in C_6D_6.

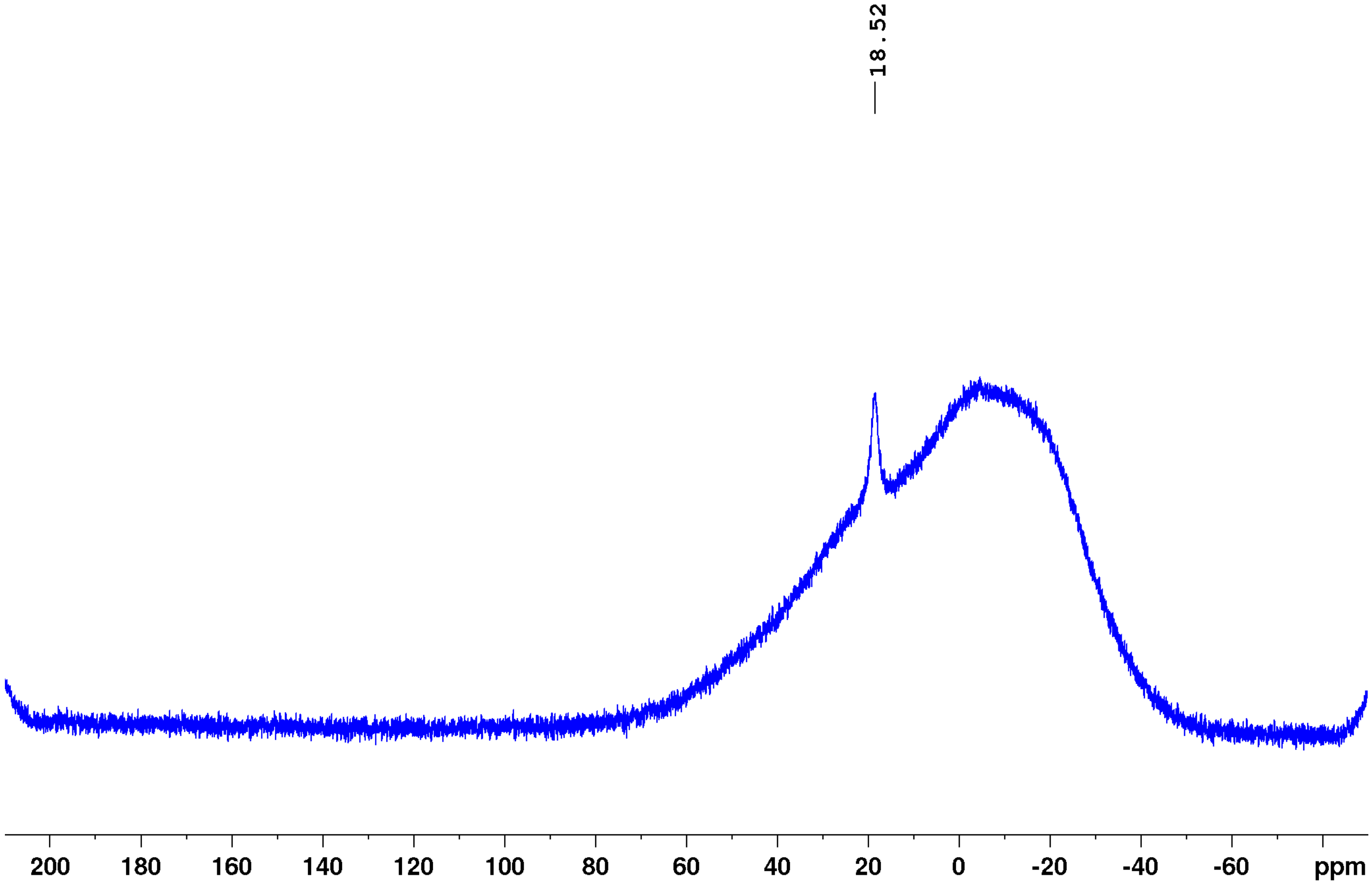


Figure S9. ^{11}B NMR spectrum of *trans*-$\mathbf{2^{IMe}}$ in C_6D_6.

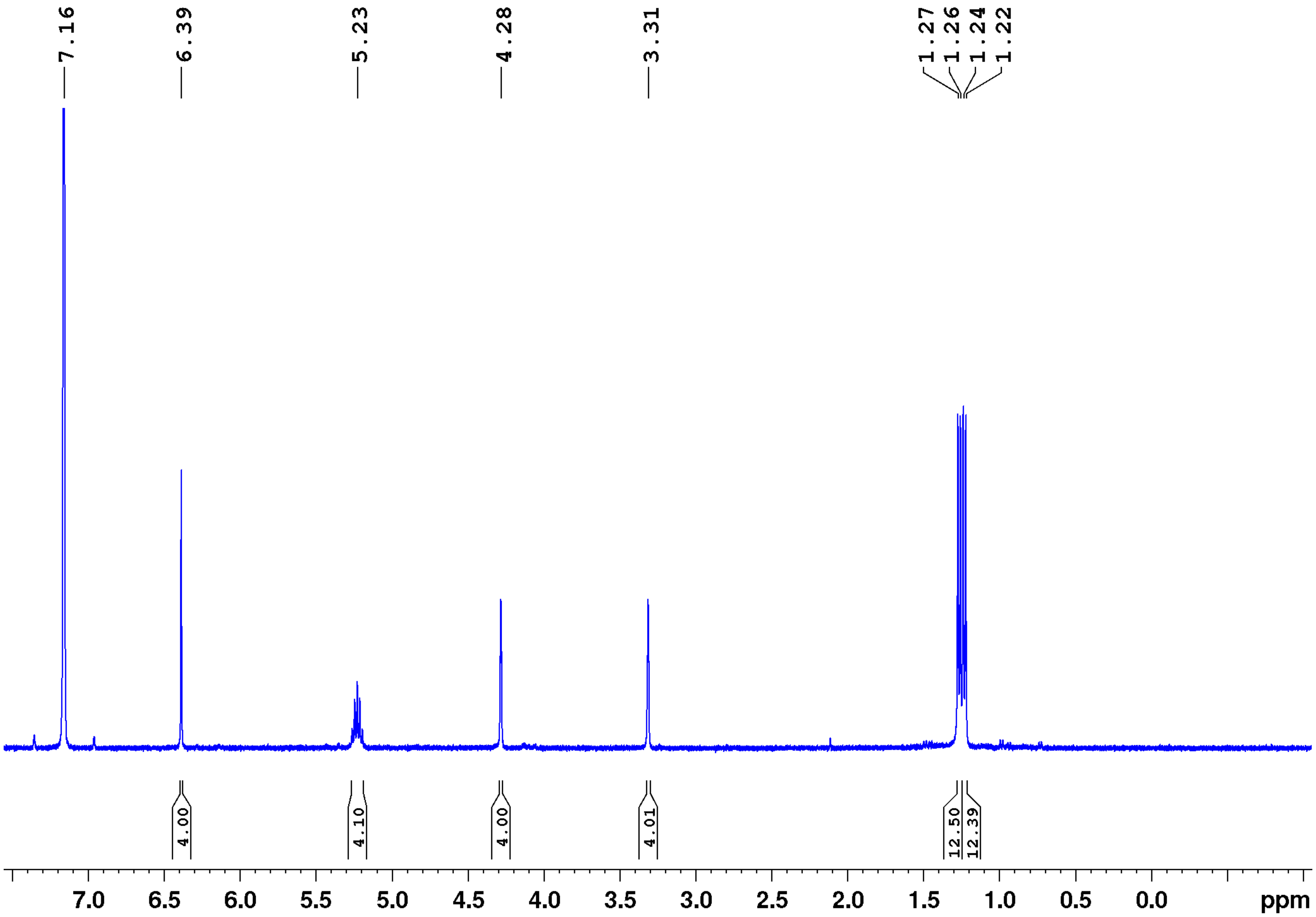


Figure S10. ^{1}H NMR spectrum of *cis*-**2**$^{\mathbf{IiPr}}$ in C_6D_6.

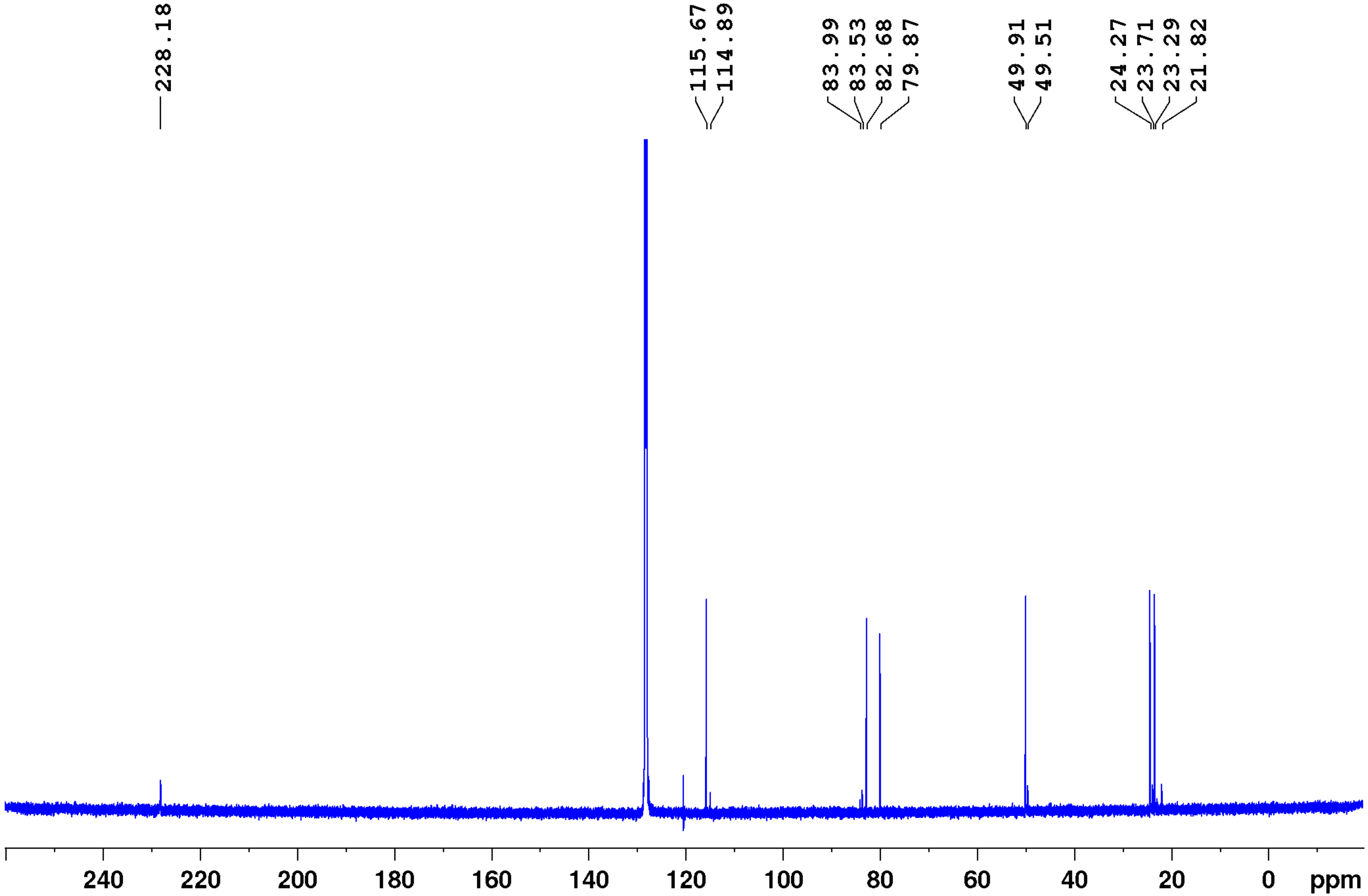


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of *cis*-**2**$^{\mathbf{I}i\mathbf{Pr}}$ in C_6D_6.

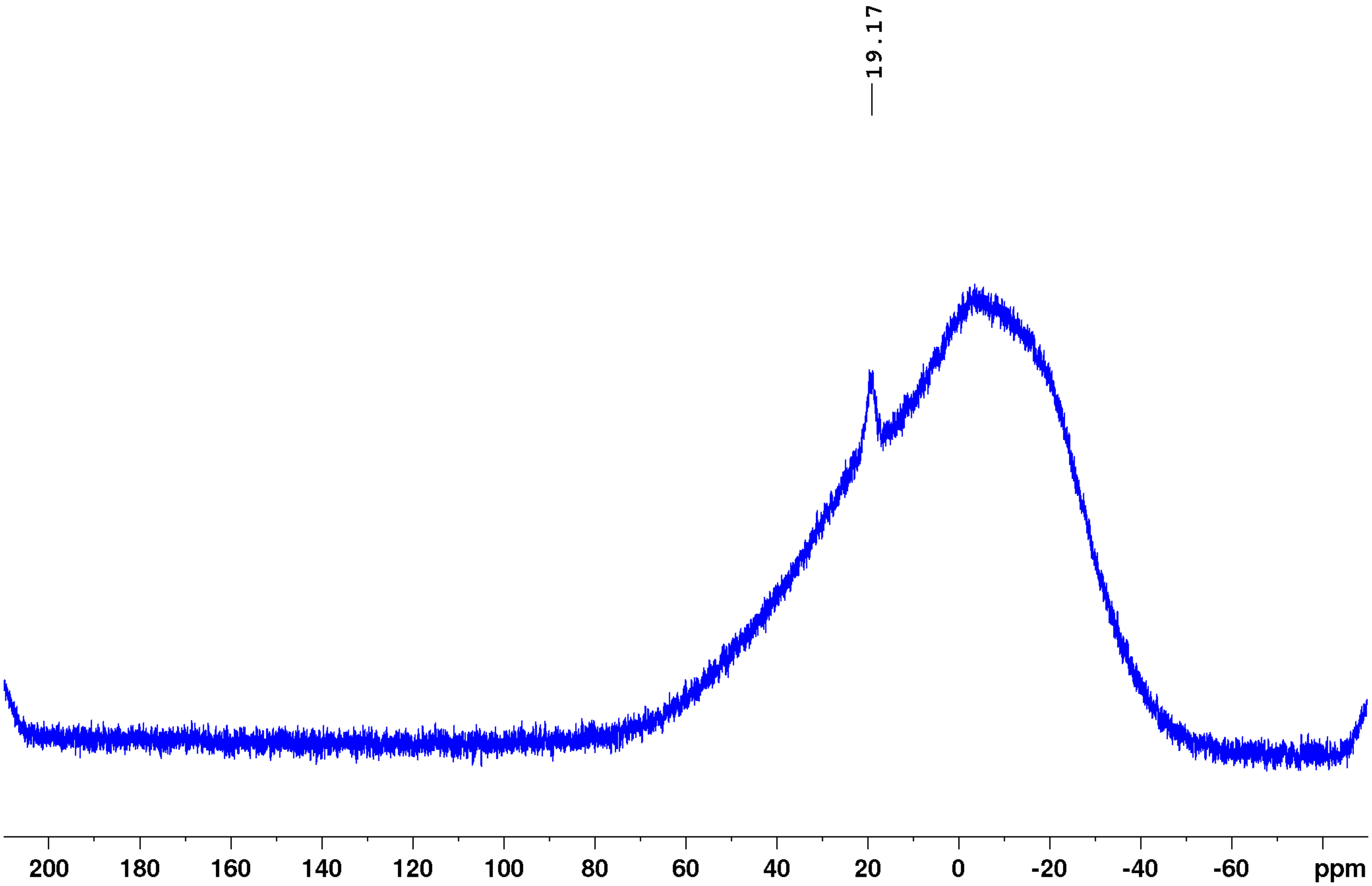


Figure S12. ^{11}B NMR spectrum of *cis*-$\mathbf{2}^{\mathbf{IiPr}}$ in C_6D_6.

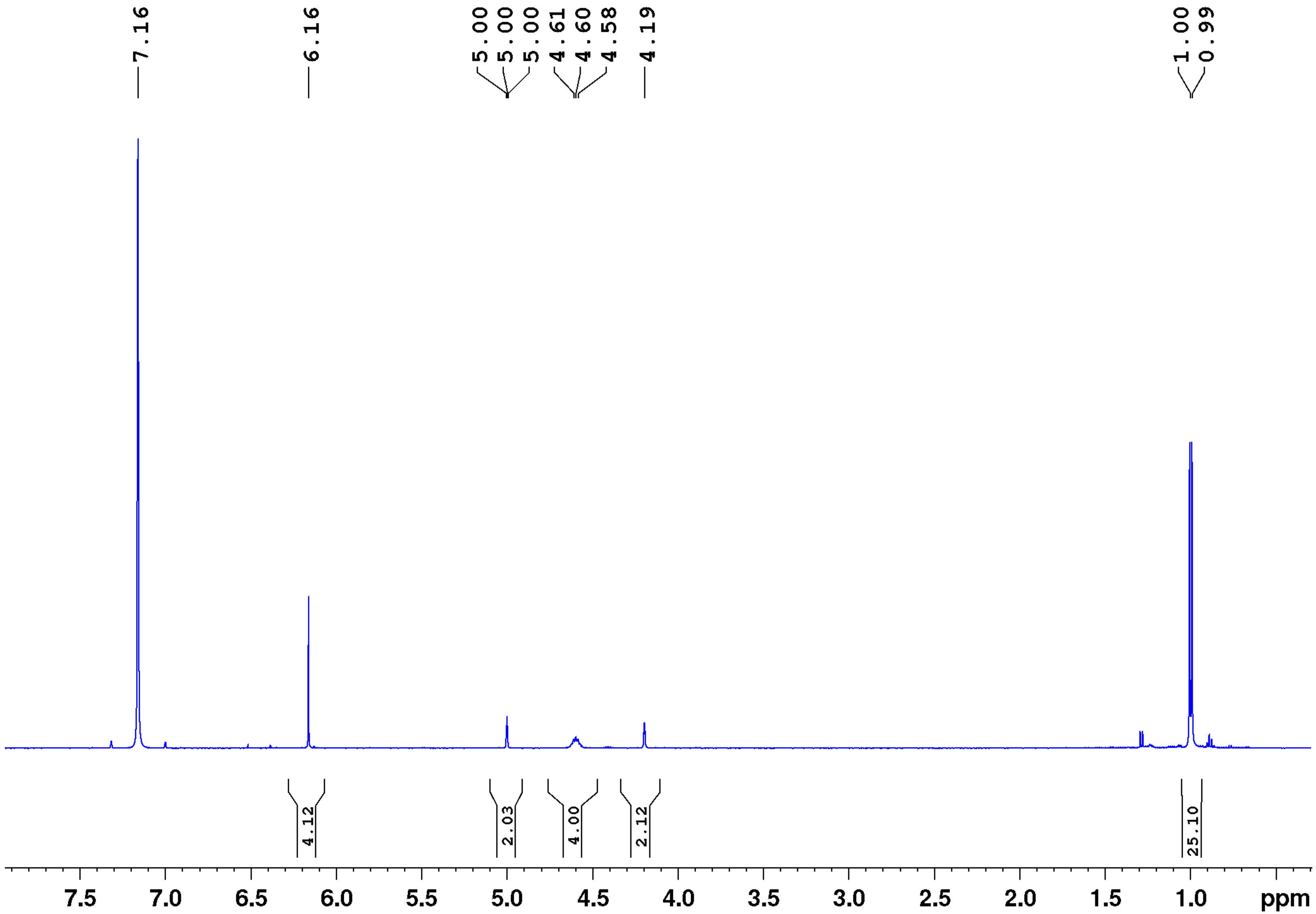


Figure S13. ^{1}H NMR spectrum of $\mathbf{3}^{\mathit{IiPr}}$ in C_6D_6.

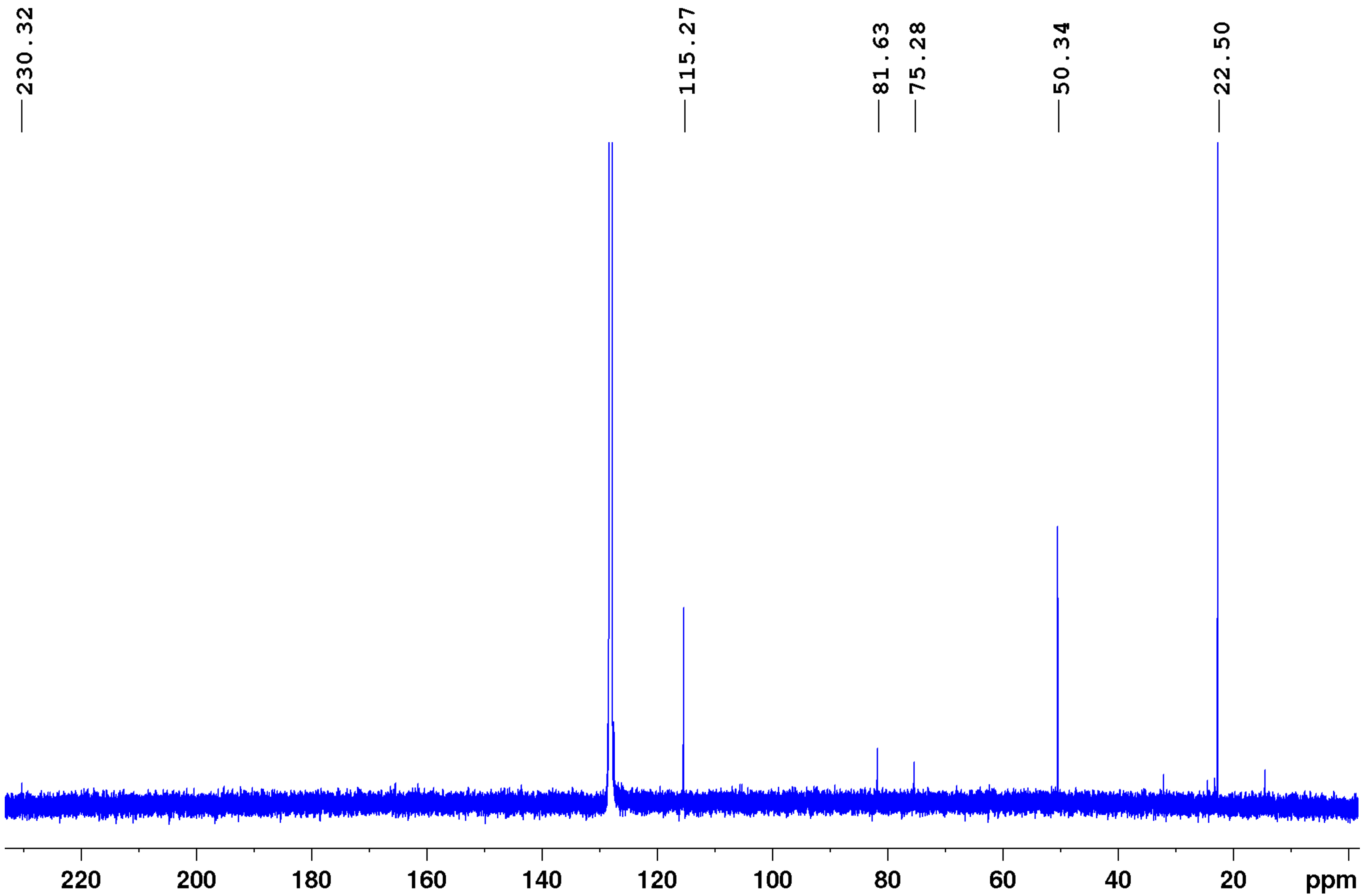


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{3^{IiPr}}$ in C_6D_6.

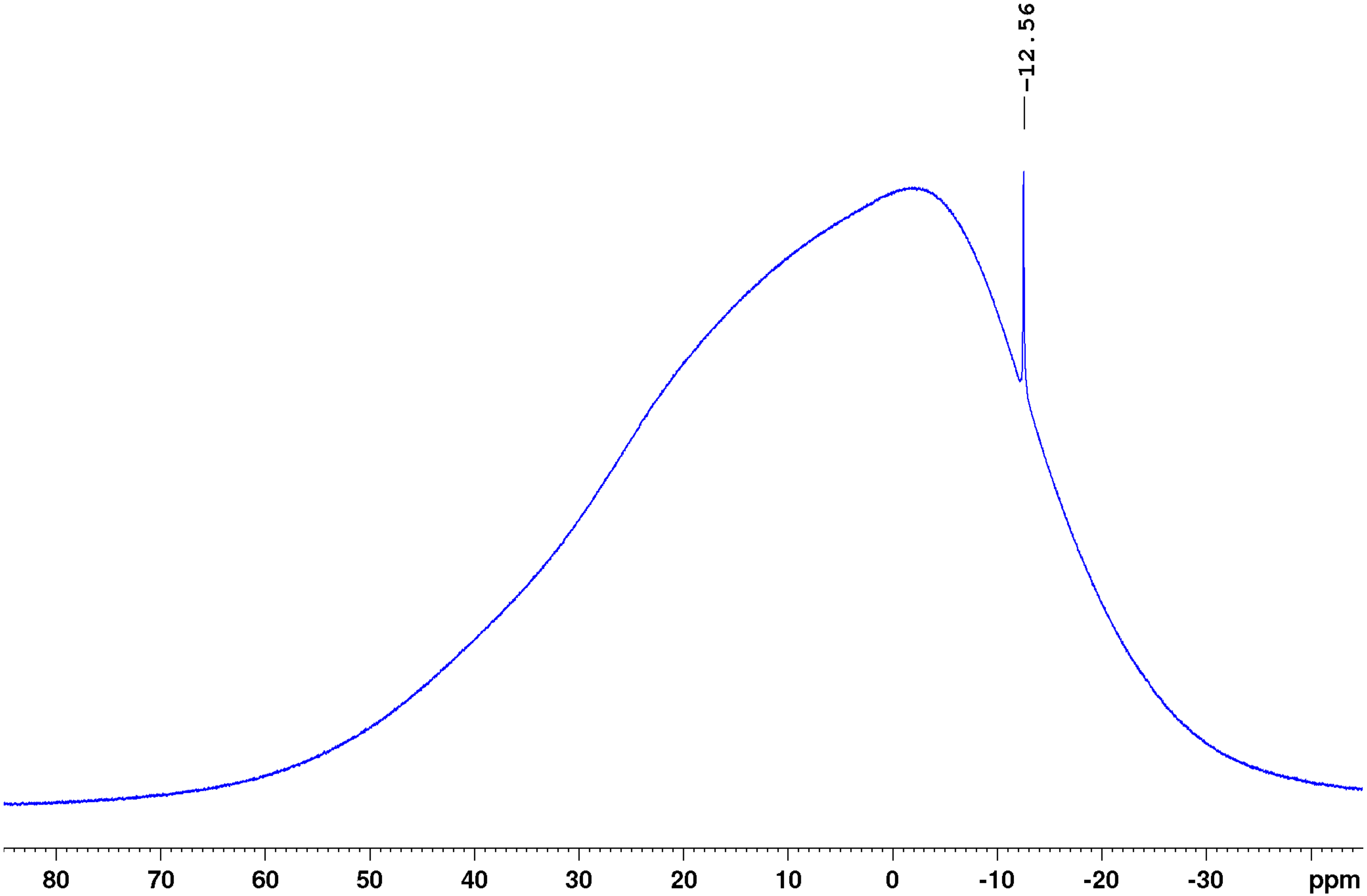


Figure S15. ^{11}B NMR spectrum of **3$^{\mathbf{I}\boldsymbol{i}\mathbf{Pr}}$** in C_6D_6.

^{1}H NMR spectra of *cis/trans*-diborene mixtures

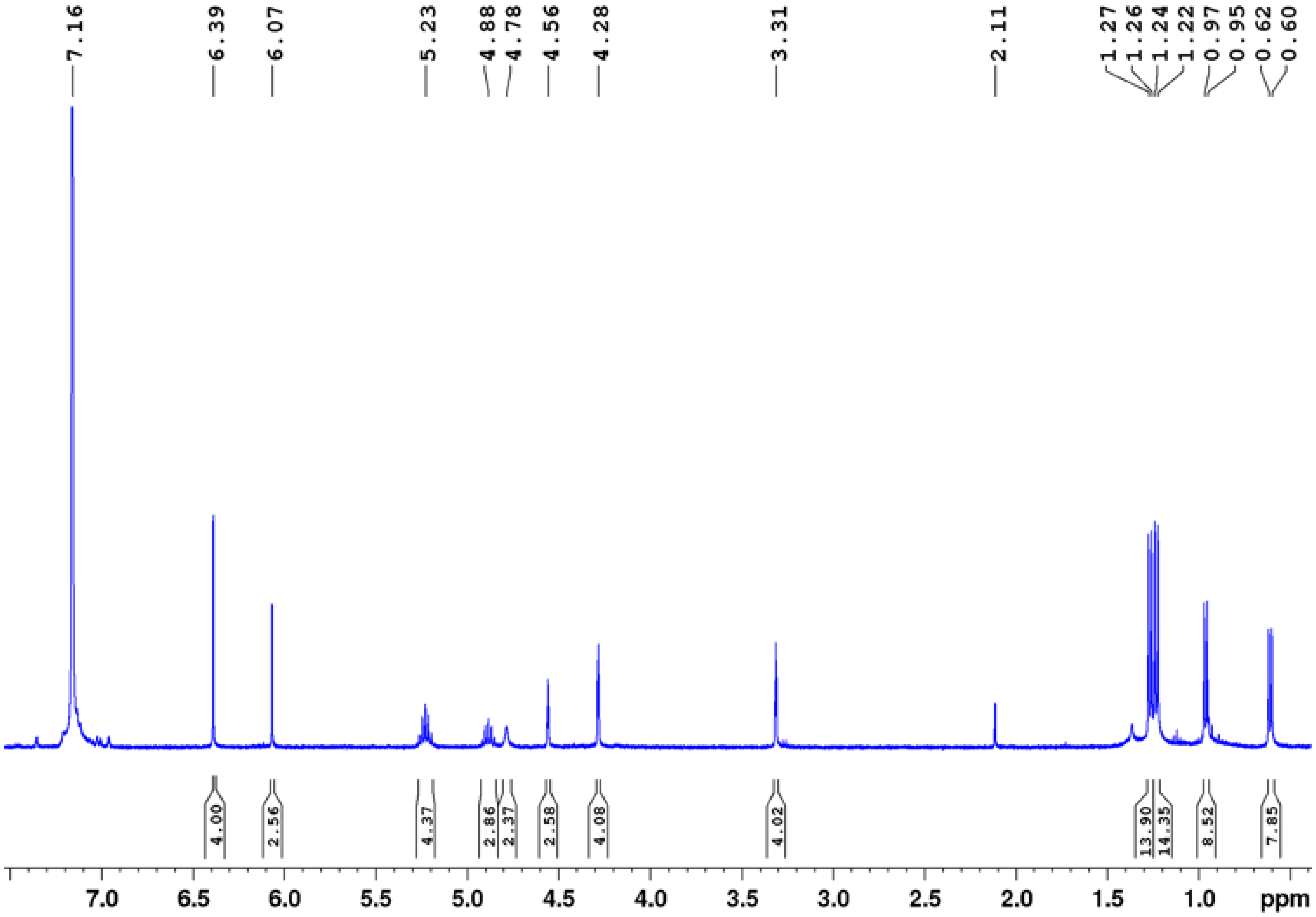


Figure S16. ^{1}H NMR spectrum showing the slow conversion of *cis*-$\mathbf{2^{IiPr}}$ to *trans*-$\mathbf{2^{IiPr}}$ in C_6D_6 at rt.

UV-vis spectra

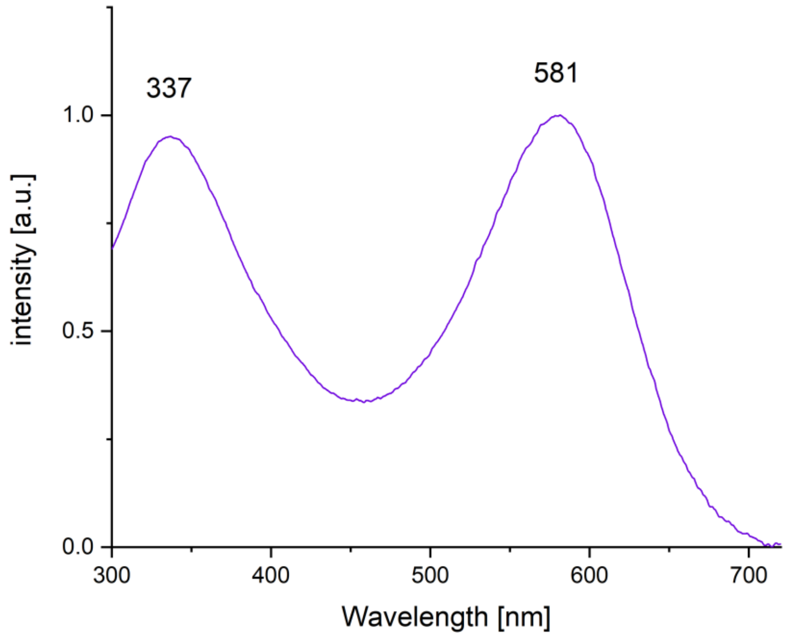


Figure S17. UV-vis spectrum of $\mathbf{2}^{\mathbf{IMe}}$ in benzene.

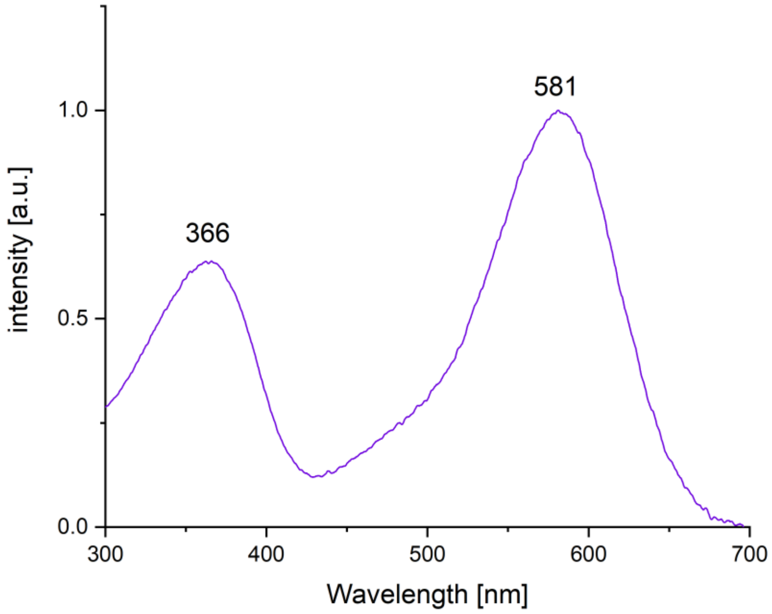


Figure S18. UV-vis spectrum of $\mathbf{2}^{\mathbf{I}\boldsymbol{i}\mathbf{Pr}}$ in benzene.

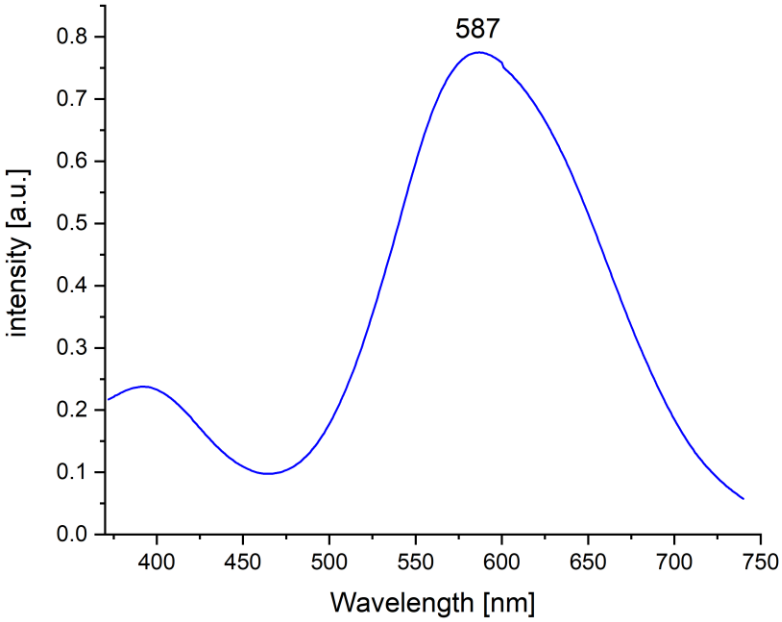


Figure S19. UV-vis spectrum of $\mathbf{3}^{\mathbf{I}i\mathbf{Pr}}$ in benzene.

IR spectra

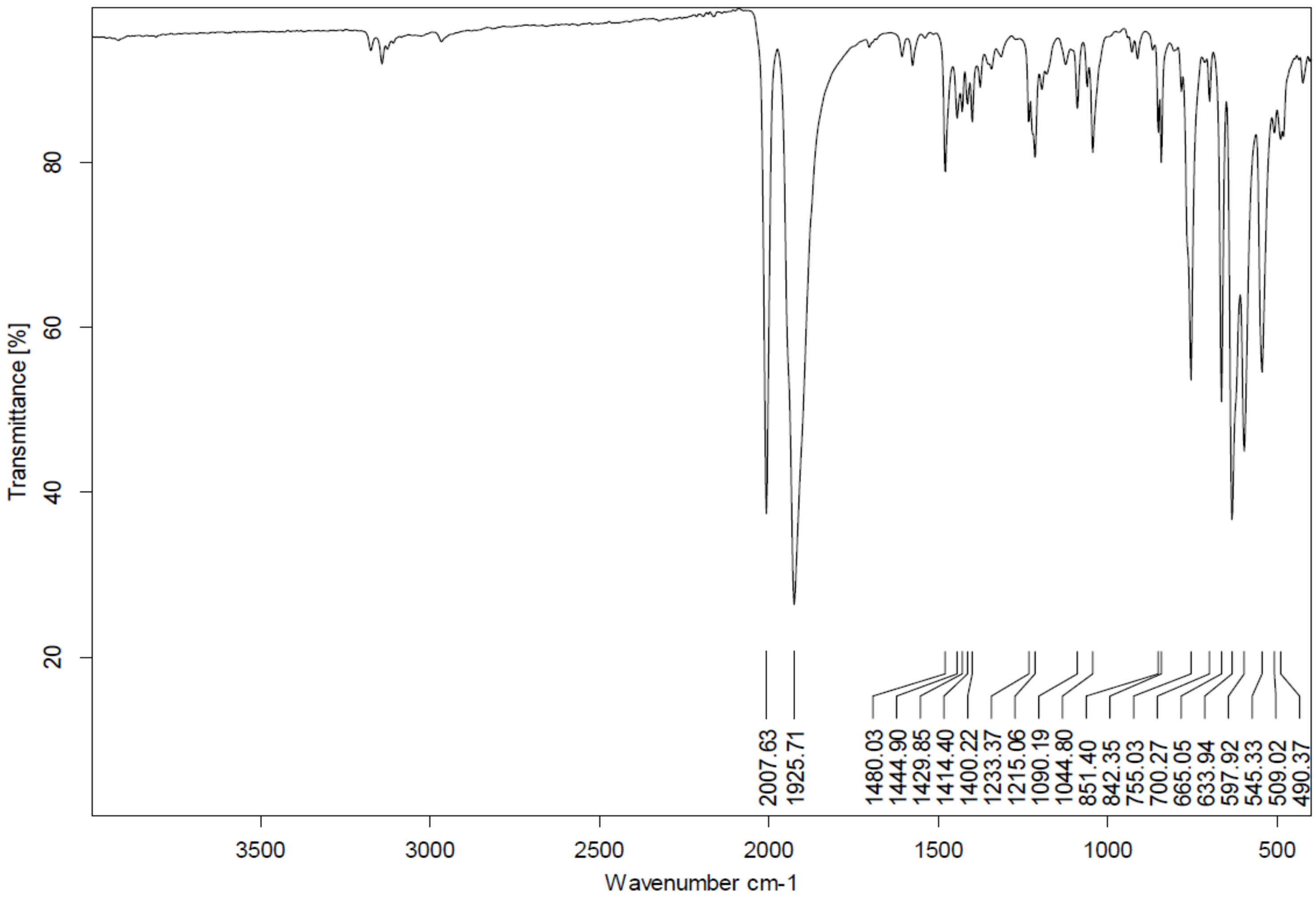


Figure S20. Solid-state IR spectrum of $\mathbf{1}^{\mathbf{IMe}}$.

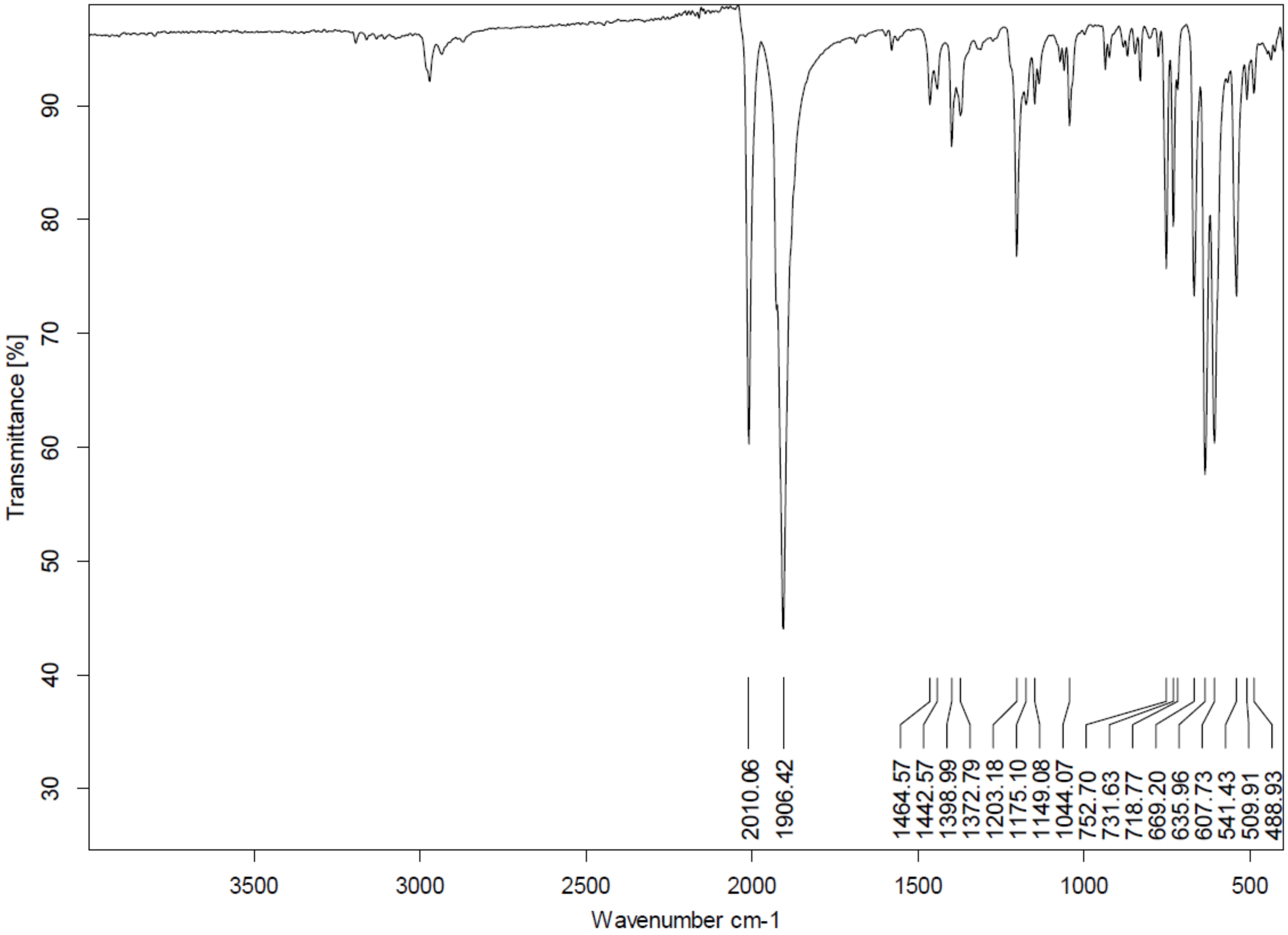


Figure S21. Solid-state IR spectrum of $\mathbf{1}^{\mathbf{I}i\mathbf{Pr}}$.

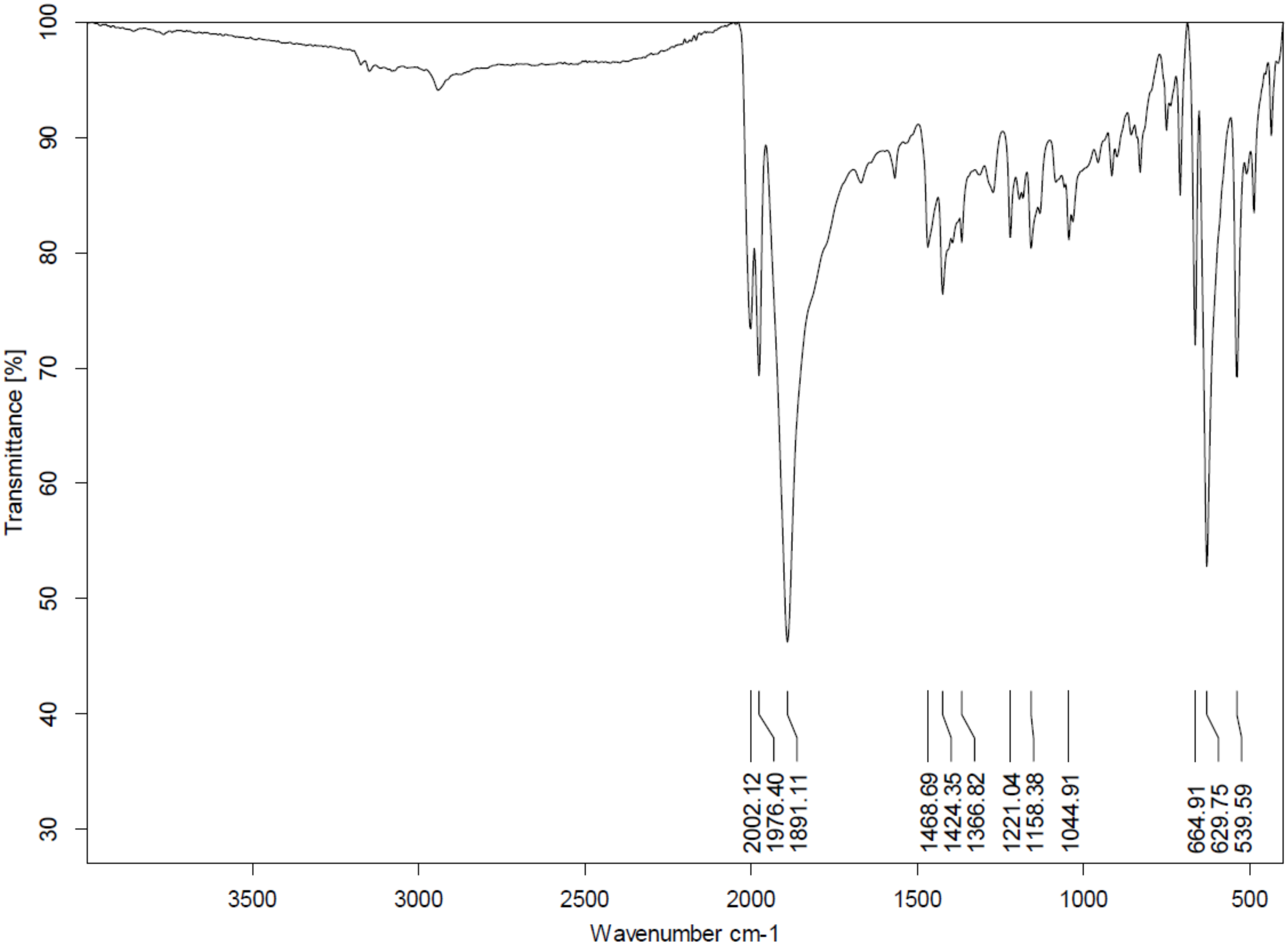


Figure S22. Solid-state IR spectrum of $\mathbf{2^{IMe}}$.

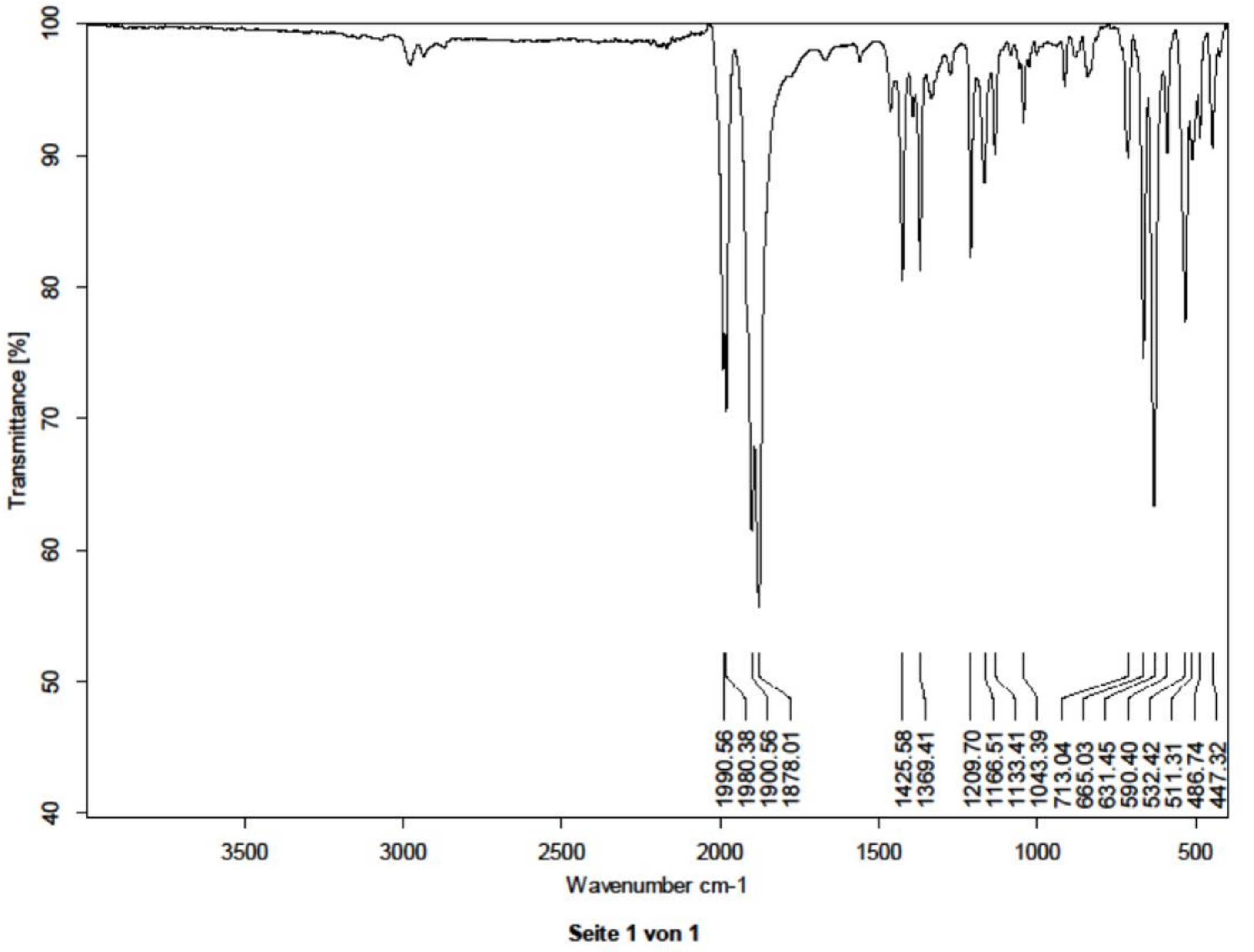


Figure S23. Solid-state IR spectrum of $\mathbf{2}^{\mathbf{I}\boldsymbol{i}\mathbf{Pr}}$.

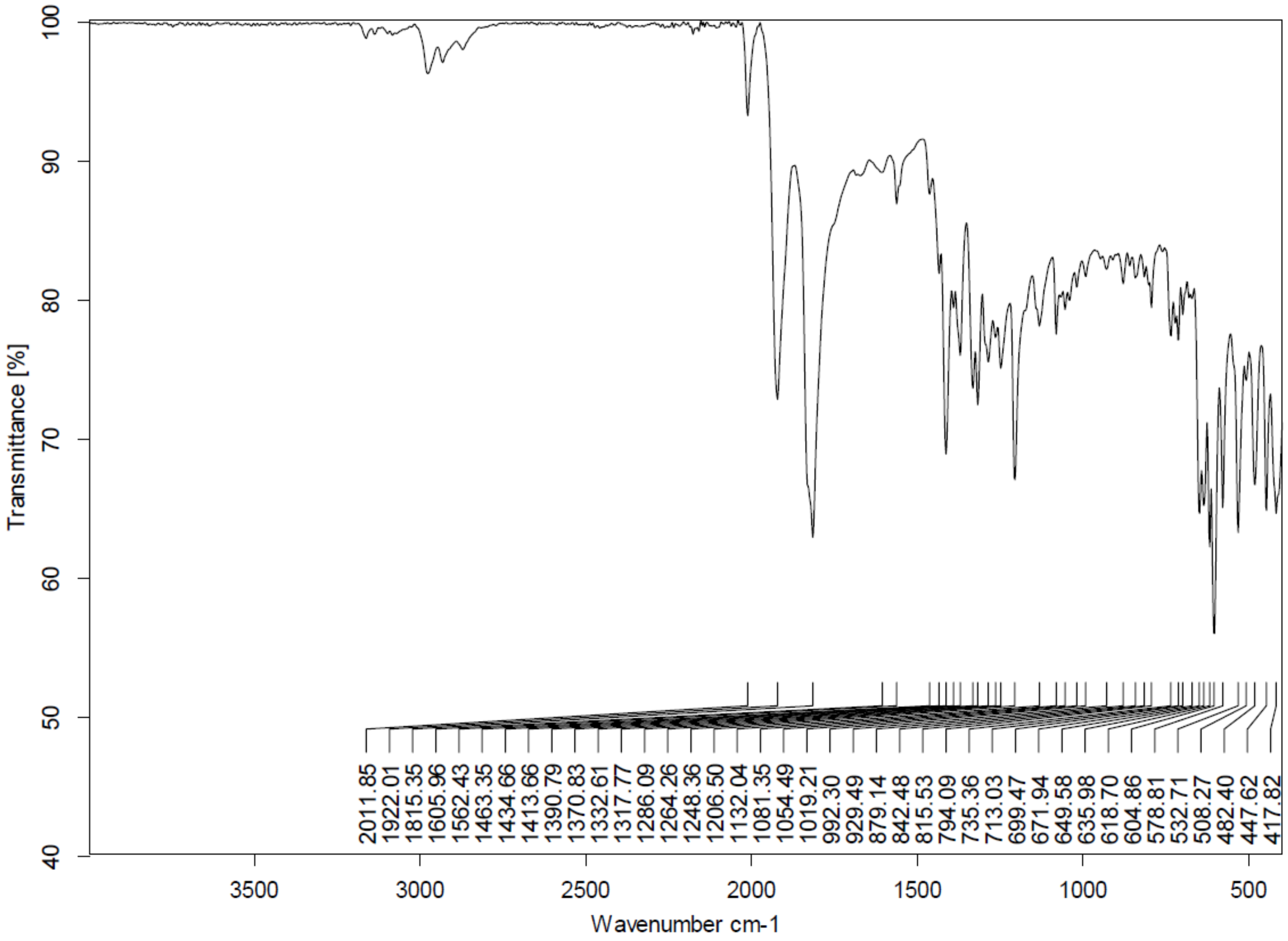


Figure S24. Solid-state IR spectrum of $\mathbf{3}^{\mathbf{I}\boldsymbol{i}\mathbf{Pr}}$.

X-ray crystallographic data

The crystal data of *trans*-**2**$^{\mathbf{IMe}}$, *cis*-**2**$^{\mathbf{IiPr}}$, and **3**$^{\mathbf{IiPr}}$ were collected on a Bruker D8 Quest diffractometer with a CMOS area detector and multi-layer mirror monochromated $\mathrm{Mo}_{\mathrm{K}\alpha}$ radiation. The crystal data of **1**$^{\mathbf{IiPr}}$ were collected on a XtaLAB Synergy, Dualflex, HyPix diffractometer with a Hybrid Pixel Array Detector and multi-layer mirror monochromated $\mathrm{Cu}_{\mathrm{K}\alpha}$ radiation. The structures were solved using the intrinsic phasing method,[5] refined with the ShelXL program[6] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-2033095 (*trans*-**2**$^{\mathbf{IMe}}$), 2033096 (**1**$^{\mathbf{IiPr}}$), 2033097 (**3**$^{\mathbf{IiPr}}$) and 2033098 (*cis*-**2**$^{\mathbf{IiPr}}$). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for 1$^{\mathbf{IiPr}}$**:** $C_{17}H_{20}BBr_2MnN_2O_3$, $M_r = 525.92$, yellow block, 0.398×0.296×0.148 mm^3, orthorombic space group *Pna*2$_1$, $a = 21.3022(6)$ Å, $b = 6.6071(2)$ Å, $c = 14.2946(5)$ Å, $V = 2011.92(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.736$ g·cm^{-3}, $\mu = 4.647$ mm^{-1}, $F(000) = 1040.000$, $T = 100.0(5)$ K, $R_1 = 0.0208$, $wR^2 = 0.0409$, 3923 independent reflections [$2\theta \leq 52.03°$] and 239 parameters.

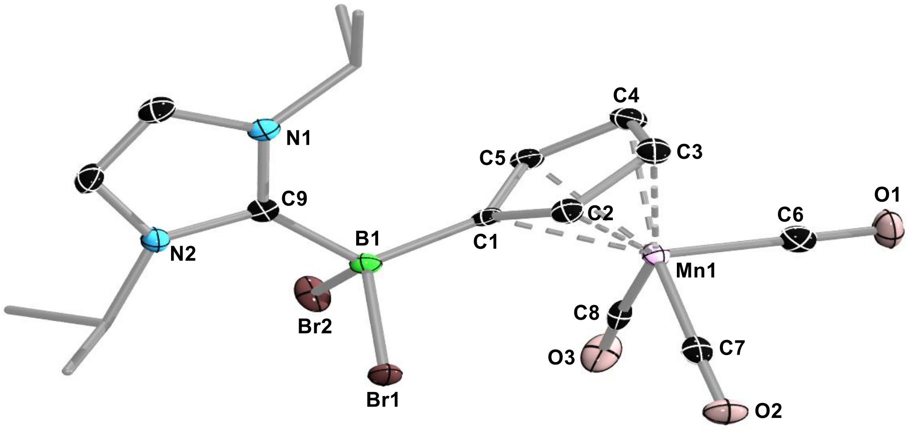


Figure S25. Crystallographically-derived molecular structure of **1**$^{\mathbf{IiPr}}$. Atomic displacement ellipsoids drawn at 50% probability level. Ellipsoids on the ligand periphery and hydrogen atoms omitted for clarity.

Crystal data for *trans*-2$^{\mathbf{IMe}}$: $C_{26}H_{24}B_2Mn_2N_4O_6$, M_r = 619.99, purple plate, 0.522×0.169×0.032 mm^3, triclinic space group $P\bar{1}$, a = 7.40010(10) Å, b = 9.77170(10) Å, c = 10.0587(2) Å, α = 90.5381(5)°, β = 107.5042(6)°, γ = 100.9048(5)°, V = 679.445(18) Å^3, Z = 1, ρ_{calcd} = 1.515 g·cm^{-3}, μ = 0.977 mm^{-1}, F(000) = 316, T = 100(2) K, R_1 = 0.0254, wR^2 = 0.0594, 2662 independent reflections [$2\theta \leq 52.032°$] and 183 parameters.

Refinement details for *cis*-2$^{\mathbf{IiPr}}$: The asymmetric unit contains a benzene molecule with half occupation on an inversion center, which was modelled as fourfold disordered in a 18:25:23:34 ratio using SUMP for the four FVAR. The benzene rings were idealised with AFIX 66 and ADPs restrained with SIMU 0.01 and ISOR 0.01.

Crystal data for *cis*-2$^{\mathbf{IiPr}}$: $C_{40}H_{46}B_2Mn_2N_4O_6$, M_r = 911.59, purple block, 0.256×0.16×0.096 mm^3, hexagonal space group $R\bar{3}c{:}H$, a = 21.3966(4) Å, b = 21.3966(4) Å, c = 47.4878(19) Å, V = 18827.9(10) Å^3, Z = 18, ρ_{calcd} = 1.286 g·cm^{-3}, μ = 0.652 mm^{-1}, F(000) = 7596, T = 100(2) K, R_1 = 0.0753, wR^2 = 0.1314, 4295 independent reflections [$2\theta \leq 52.774°$] and 393 parameters.

Refinement details for 3$^{\mathbf{IiPr}}$: The asymmetric unit contains two distinct molecules of the borylene, one of which presents a twofold rotational disorder in the *i*Pr group C21 > C23, modelled with FVAR in a 78:22 ratio and ADPs restrained with ISOR.

Crystal data for 3$^{\mathbf{IiPr}}$: $C_{26}H_{36}BMnN_4O_3$, M_r = 518.34, purple plate, 0.407×0.229×0.085 mm^3, triclinic space group $P\bar{1}$, a = 12.207(7) Å, b = 12.655(7) Å, c = 18.576(9) Å, α = 88.111(8)°, β = 71.902(8)°, γ = 78.154(7)°, V = 2668(2) Å^3, Z = 4, ρ_{calcd} = 1.290 g·cm^{-3}, μ = 0.528 mm^{-1}, F(000) = 1096, T = 108(2) K, R_1 = 0.0870, wR^2 = 0.1709, 10497 independent reflections [$2\theta \leq 52.044°$] and 671 parameters.

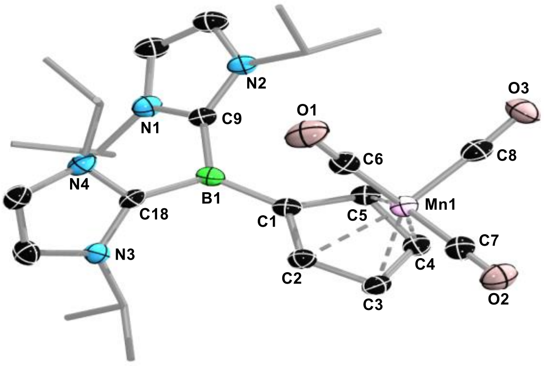
Computational details

We started our computational investigation by performing geometry optimisation and Hessian calculations at the density functional theory (DFT) level for compounds **2^{IMe}** and **2^{IiPr}** in their *cis* and *trans* configurations. For that, the PBE[7] functional was used in conjunction with Ahlrich's def2-SVP[8] basis set for all elements except for Mn, which was treated with def2-TZVP. Dispersion corrections were taken into account by using Grimme's D3[9] method together with the Becke-Johnson damping function.[10] All structures were characterised as minimum energy geometries as only real frequencies were observed in their vibrational analyses. Furthermore, we tested the stability[11] of the single-determinant wavefunction at the optimised geometries, and no restricted/unrestricted Hartree-Fock instability was observed for any of the closed-shell wavefunctions.

Aiming at investigating the bonding situation in **3^{IiPr}**, additional DFT calculations with dispersion corrections were performed in conjunction with the energy decomposition analysis with natural orbitals of chemical valence (EDA-NOCV)[12] calculations. Charge and population analyses were carried out using Mayer bond order (MBO),[13] and Mulliken,[14] Löwdin[15] and Atomic dipole-corrected Hirshfeld (ADCH)[16] approaches. The geometrical parameters of **3^{IiPr}** were found to be very sensitive with respect to the functional. The calculations were employed using the following functionals: B3LYP,[17] PBE,[7] BLYP,[17b,18] PBE0,[19] BP86,[18a,20] CAM-B3LYP,[21] B3PW91,[17c,22] M06,[23] M06L,[24] and wB97XD.[25] The best agreement between the X-ray structure and calculations was obtained using BLYP, with solvent effects (SMD,[26] solvent=THF, ε=7.4257) being taken into consideration during the geometry optimisation procedure. The EDA-NOCV calculations were performed using B3LYP-D3(BJ)/TZ2P from single-point calculations at the optimised geometry at BLYP-D3(BJ)/def2-SVP,def2-TZVP(Mn)+SMD(THF).

All DFT calculations were performed using Gaussian 16, revision B.01.[27] The population analyses were carried out using Multiwfn 3.7.[28] The EDA-NOCV calculations were done using ADF 2018.[29] The frontier Kohn-Sham (KS) orbitals, molecular structures and deformation densities were visualised and plotted with ADFview and Gaussview.

Table S1. Comparison of calculated structural properties of $\mathbf{3^{IiPr}}$ using distinct functionals. In all cases, the def2-SVP,def2-TZVP(Mn) basis set (bs1) was used.



$\mathbf{3^{IiPr}}$	B1–C9 (Å)	B1–C18 (Å)	B1–C1 (Å)	Error B1–C1 (pm)
X-ray structure	1.572	1.567	1.490	-
BLYP-D3(BJ)/bs1+SMD(THF)	1.555	1.566	1.517	0.27
PBE-D3(BJ)/bs1+SMD(THF)	1.556	1.566	1.521	0.31
M06L-D3/bs1	1.535	1.545	1.535	0.46
BLYP-D3(BJ)/bs1	1.544	1.553	1.539	0.49
BP86-D3(BJ)/bs1	1.542	1.550	1.539	0.50
BLYP-D3/bs1	1.548	1.560	1.541	0.51
PBE-D3(BJ)/bs1	1.545	1.554	1.543	0.53
B3PW91-D3/bs1	1.534	1.549	1.543	0.54
M06-D3/bs1	1.532	1.549	1.546	0.56
B3LYP/bs1	1.535	1.553	1.550	0.60
PBE0-D3(BJ)/bs1	1.528	1.546	1.553	0.64
BLYP/bs1	1.558	1.566	1.556	0.66
ωB97XD/bs1	1.527	1.552	1.558	0.68
CAM-B3LYP-D3(BJ)/bs1	1.512	1.551	1.562	0.72

Table S2. EDA-NOCV results of $\mathbf{3^{IiPr}}$ from isolated “2 NHC” and BCym fragments. Energy values are given in kcal mol^{-1}.

Energy Terms	$\mathbf{3^{IiPr}}$
ΔE_{int}	–276.9
ΔE_{Pauli}	529.7
ΔE_{disp}[*]	–22.8 (2.8%)
ΔE_{elstat}[*]	–312.2 (38.7%)
ΔE_{orb}[*]	–471.7 (58.5%)
$\Delta E_{orb(1)}$[†]	–197.8 (41.9%)
$\Delta E_{orb(2)}$[†]	–83.4 (17.7%)
$\Delta E_{orb(3)}$[†]	–103.2 (21.9%)
$\Delta E_{orb(rest)}$[†]	–87.2 (18.5%)

[*] The values in parentheses show the weight of each contribution with respect to the total attractive interaction. [†] The values in parentheses show the weight of each contribution with respect to the total orbital interaction, ΔE_{orb}.

Cartesian coordinates

***cis*-2$^{\mathrm{IMe}}$**

PBE-D3(BJ)/def2-SVP,def2TZVP(Mn)

E+ZPE = –4023.454298 E$_h$

B	0.655863000	0.234719000	-0.477294000
Mn	3.529242000	-1.260571000	0.188223000
O	4.785653000	1.390105000	-0.138922000
N	1.607422000	2.715337000	-0.425161000
C	2.694699000	-1.034875000	-1.764117000
H	2.986146000	-0.219858000	-2.438967000
O	6.005540000	-2.592206000	1.099944000
N	1.121613000	1.959179000	-2.408175000
C	3.375333000	-2.291419000	-1.678477000
H	4.233190000	-2.612015000	-2.281088000
O	2.540263000	-0.549525000	2.873601000
C	2.721583000	-3.056508000	-0.651395000
H	2.998313000	-4.065175000	-0.321907000
C	1.658270000	-2.257722000	-0.129745000
H	0.995224000	-2.549703000	0.693084000
C	4.315793000	0.324378000	0.000158000
C	5.027960000	-2.058794000	0.746581000
C	2.973159000	-0.847289000	1.825465000
C	1.135554000	1.601394000	-1.077458000
C	1.866298000	3.741667000	-1.323063000
H	2.256610000	4.712316000	-1.004278000
C	1.565456000	3.263709000	-2.572508000
H	1.626484000	3.741390000	-3.554734000
C	1.905805000	2.768076000	0.996227000
H	1.230941000	3.478425000	1.514556000
H	2.961283000	3.068871000	1.144821000

H	1.745400000	1.751192000	1.401800000
C	0.586788000	1.111218000	-3.460841000
H	1.374938000	0.480554000	-3.917330000
H	0.124835000	1.740576000	-4.244131000
H	-0.180569000	0.445602000	-3.014519000
C	1.581251000	-0.987616000	-0.832020000
B	-0.655845000	0.234743000	0.477346000
N	-1.121401000	1.959354000	2.408084000
C	-1.658724000	-2.257894000	0.130563000
H	-0.995736000	-2.550468000	-0.692094000
N	-1.607543000	2.715350000	0.425051000
C	-2.722286000	-3.056150000	0.652519000
H	-2.999372000	-4.064849000	0.323421000
C	-3.375868000	-2.290479000	1.679263000
H	-4.233810000	-2.610546000	2.282025000
C	-2.694898000	-1.034035000	1.764328000
H	-2.986201000	-0.218606000	2.438784000
C	-1.135493000	1.601455000	1.077352000
C	-1.565341000	3.263845000	2.572360000
H	-1.625989000	3.741700000	3.554527000
C	-1.866355000	3.741708000	1.322924000
H	-2.256555000	4.712404000	1.004129000
C	-0.586312000	1.111507000	3.460687000
H	-0.125040000	1.740977000	4.244258000
H	-1.374137000	0.480125000	3.916740000
H	0.181596000	0.446420000	3.014403000
C	-1.906334000	2.767797000	-0.996248000
H	-2.962066000	3.067746000	-1.144655000
H	-1.232092000	3.478596000	-1.514794000
H	-1.745139000	1.751020000	-1.401848000
C	-1.581372000	-0.987483000	0.832349000
Mn	-3.529528000	-1.260498000	-0.187903000

O	-2.537929000	-0.549182000	-2.872216000
O	-6.004138000	-2.593477000	-1.102245000
O	-4.787427000	1.389722000	0.137347000
C	-2.971861000	-0.846993000	-1.824513000
C	-5.027284000	-2.059483000	-0.747751000
C	-4.317076000	0.324100000	-0.000830000

***trans*-2$^{\mathrm{IMe}}$**

PBE-D3(BJ)/def2-SVP,def2TZVP(Mn)

E+ZPE = –4023.459529 E_h

B	-0.163550000	0.785285000	-0.091520000
Mn	-0.372811000	3.093088000	2.373563000
O	1.558178000	1.262648000	3.644445000
N	0.024100000	2.032383000	-2.420223000
C	-1.663368000	1.399896000	2.105026000
H	-1.538492000	0.460947000	2.657265000
O	-0.478460000	5.001473000	4.627309000
N	1.900192000	1.857791000	-1.338015000
C	-2.421323000	2.515850000	2.578690000
H	-2.979668000	2.568878000	3.521016000
O	1.771996000	4.528631000	0.940596000
C	-2.308375000	3.562553000	1.599532000
H	-2.770065000	4.555428000	1.653458000
C	-1.481023000	3.062419000	0.544925000
H	-1.190811000	3.640851000	-0.341806000
C	0.799834000	2.017273000	3.164063000
C	-0.427228000	4.246164000	3.736929000
C	0.922701000	3.977325000	1.532200000
C	0.565978000	1.555232000	-1.252733000
C	1.002054000	2.604517000	-3.220500000

H	0.778552000	3.034755000	-4.200988000
C	2.186171000	2.492502000	-2.537007000
H	3.197663000	2.813824000	-2.801112000
C	-1.378743000	1.890435000	-2.773514000
H	-1.474337000	1.478110000	-3.794929000
H	-1.906424000	2.862101000	-2.703275000
H	-1.824336000	1.172885000	-2.057621000
C	2.872807000	1.568535000	-0.296216000
H	3.347359000	2.508037000	0.046697000
H	3.638617000	0.861936000	-0.671799000
H	2.318816000	1.090153000	0.535571000
C	-1.087358000	1.686038000	0.800670000
B	0.163550000	-0.785285000	0.091520000
N	-0.024100000	-2.032383000	2.420223000
C	1.663368000	-1.399896000	-2.105026000
H	1.538492000	-0.460947000	-2.657265000
N	-1.900192000	-1.857791000	1.338015000
C	2.421323000	-2.515850000	-2.578690000
H	2.979668000	-2.568878000	-3.521016000
C	2.308375000	-3.562553000	-1.599532000
H	2.770065000	-4.555428000	-1.653458000
C	1.481023000	-3.062419000	-0.544925000
H	1.190811000	-3.640851000	0.341806000
C	-0.565978000	-1.555232000	1.252733000
C	-1.002054000	-2.604517000	3.220500000
H	-0.778552000	-3.034755000	4.200988000
C	-2.186171000	-2.492502000	2.537007000
H	-3.197663000	-2.813824000	2.801112000
C	1.378743000	-1.890435000	2.773514000

H	1.474337000	-1.478110000	3.794929000
H	1.906424000	-2.862101000	2.703275000
H	1.824336000	-1.172885000	2.057621000
C	-2.872807000	-1.568535000	0.296216000
H	-3.347359000	-2.508037000	-0.046697000
H	-3.638617000	-0.861936000	0.671799000
H	-2.318816000	-1.090153000	-0.535571000
C	1.087358000	-1.686038000	-0.800670000
Mn	0.372811000	-3.093088000	-2.373563000
O	-1.558178000	-1.262648000	-3.644445000
O	0.478460000	-5.001473000	-4.627309000
O	-1.771996000	-4.528631000	-0.940596000
C	-0.799834000	-2.017273000	-3.164063000
C	0.427228000	-4.246164000	-3.736929000
C	-0.922701000	-3.977325000	-1.532200000

***cis*-2**$^{\mathbf{IiPr}}$

PBE-D3(BJ)/def2-SVP,def2TZVP(Mn)

E+ZPE = –4337.117141 E$_{h}$

Mn	-2.185809000	-2.689124000	0.474174000
N	2.900353000	-1.816423000	-0.268249000
O	-4.653269000	-1.612619000	1.689759000
C	-0.771138000	-1.583406000	-0.850427000
B	0.475903000	-0.699742000	-0.420955000
O	-0.497898000	-1.931211000	2.778860000
N	2.102280000	-1.587986000	-2.283896000
C	-0.720465000	-3.024395000	-1.051298000
H	0.173743000	-3.646372000	-0.917595000
O	-2.631440000	-5.406098000	1.536438000

C	-2.002926000	-3.506284000	-1.483658000
H	-2.259274000	-4.543878000	-1.730730000
C	-2.888061000	-2.387191000	-1.525372000
H	-3.945686000	-2.404856000	-1.814663000
C	-2.142333000	-1.225709000	-1.118081000
H	-2.541253000	-0.207535000	-1.070124000
C	1.805971000	-1.346449000	-0.956811000
C	-2.460491000	-4.324421000	1.125924000
C	-1.176637000	-2.229211000	1.871009000
C	-3.678259000	-2.055378000	1.219450000
C	3.844003000	-2.344350000	-1.140699000
H	4.787819000	-2.776944000	-0.797888000
C	3.341157000	-2.197905000	-2.407804000
H	3.773854000	-2.462965000	-3.376552000
C	2.929612000	-1.966693000	1.198064000
H	2.101071000	-1.310549000	1.536921000
C	2.588829000	-3.406400000	1.591979000
H	2.528721000	-3.491692000	2.694797000
H	3.354468000	-4.123513000	1.230089000
H	1.602370000	-3.697534000	1.180773000
C	4.258406000	-1.479438000	1.771498000
H	4.223959000	-1.512216000	2.877609000
H	4.469939000	-0.435711000	1.467850000
H	5.107623000	-2.119761000	1.453283000
C	1.227321000	-1.204391000	-3.411073000
H	0.359441000	-0.717684000	-2.921210000
C	1.904664000	-0.173122000	-4.315765000
H	1.206621000	0.121004000	-5.123073000
H	2.824278000	-0.574681000	-4.789888000

H	2.160990000	0.743402000	-3.753371000
C	0.755922000	-2.441230000	-4.177061000
H	0.030436000	-2.142823000	-4.958831000
H	0.253654000	-3.158359000	-3.500938000
H	1.600370000	-2.956833000	-4.680938000
N	2.952694000	1.727826000	0.265874000
C	-0.721445000	1.603611000	0.852610000
B	0.497532000	0.681831000	0.422899000
N	2.153238000	1.520271000	2.283214000
C	-0.626668000	3.041822000	1.057030000
H	0.286479000	3.636440000	0.926843000
C	-1.894777000	3.562139000	1.487619000
H	-2.119535000	4.606539000	1.736742000
C	-2.814077000	2.470836000	1.524470000
H	-3.871353000	2.520360000	1.811357000
C	-2.103733000	1.287906000	1.115952000
H	-2.533486000	0.282602000	1.064753000
C	1.847123000	1.288705000	0.956667000
C	3.913076000	2.227847000	1.136440000
H	4.868014000	2.633675000	0.791691000
C	3.409293000	2.094571000	2.404681000
H	3.851632000	2.346370000	3.372620000
C	2.982321000	1.877589000	-1.200541000
H	2.133879000	1.246021000	-1.536954000
C	2.682791000	3.326775000	-1.593169000
H	2.621614000	3.413976000	-2.695772000
H	3.470398000	4.020960000	-1.233709000
H	1.706634000	3.646761000	-1.178822000
C	4.294426000	1.351587000	-1.778106000

H	4.257327000	1.385806000	-2.884106000
H	4.476038000	0.301925000	-1.475522000
H	5.163183000	1.966443000	-1.462391000
C	1.270082000	1.160534000	3.411944000
H	0.388115000	0.698336000	2.923408000
C	1.920266000	0.110460000	4.314888000
H	1.215885000	-0.164464000	5.123453000
H	2.851573000	0.486187000	4.787361000
H	2.150140000	-0.812585000	3.751739000
C	0.834818000	2.409488000	4.179679000
H	0.103218000	2.130741000	4.963007000
H	0.350932000	3.140657000	3.505214000
H	1.694422000	2.901182000	4.681851000
Mn	-2.097910000	2.755913000	-0.472714000
O	-4.599410000	1.768143000	-1.694142000
O	-0.435285000	1.943343000	-2.777143000
O	-2.445186000	5.488402000	-1.531890000
C	-2.313506000	4.400812000	-1.122500000
C	-1.103929000	2.263160000	-1.869179000
C	-3.610392000	2.175788000	-1.221380000

***trans*-2$^{\mathrm{IiPr}}$**

PBE-D3(BJ)/def2-SVP,def2TZVP(Mn)

E+ZPE = –4337.125180 E_h

Mn	-4.090522000	0.048913000	-0.542391000
N	-0.856182000	-2.701733000	1.070577000
O	-6.724150000	1.382986000	-0.575221000
C	-1.860413000	-0.045499000	-1.058387000
B	-0.570274000	-0.456999000	-0.269256000

O	-3.738491000	0.573605000	2.341197000
N	0.320912000	-2.933699000	-0.739762000
C	-2.694303000	-0.909515000	-1.868401000
H	-2.572427000	-1.997783000	-1.943667000
O	-5.230612000	-2.618107000	-0.000754000
C	-3.654555000	-0.144996000	-2.616275000
H	-4.367825000	-0.529954000	-3.354100000
C	-3.495048000	1.222597000	-2.215919000
H	-4.076357000	2.075623000	-2.587097000
C	-2.451270000	1.274373000	-1.239069000
H	-2.114215000	2.192956000	-0.746643000
C	-0.387153000	-2.012562000	-0.014013000
C	-4.803088000	-1.547289000	-0.207538000
C	-3.869623000	0.375446000	1.189547000
C	-5.681487000	0.855040000	-0.554796000
C	-0.441234000	-4.022076000	1.033912000
H	-0.704011000	-4.745282000	1.810308000
C	0.297532000	-4.171464000	-0.113121000
H	0.801548000	-5.049758000	-0.523866000
C	-1.610086000	-2.055930000	2.163805000
H	-1.980445000	-1.123359000	1.697571000
C	-2.794478000	-2.910817000	2.606193000
H	-3.426410000	-2.317101000	3.294524000
H	-2.471124000	-3.821343000	3.152722000
H	-3.424190000	-3.212876000	1.747853000
C	-0.671092000	-1.674859000	3.309127000
H	-1.241238000	-1.129959000	4.087361000
H	0.137199000	-1.013794000	2.939994000
H	-0.216379000	-2.571974000	3.778457000

C	1.030310000	-2.624698000	-1.999263000
H	1.154527000	-1.521860000	-1.962045000
C	2.403065000	-3.294810000	-2.029650000
H	2.969654000	-2.916629000	-2.900779000
H	2.326516000	-4.397307000	-2.130472000
H	2.990799000	-3.053850000	-1.122839000
C	0.173010000	-2.988848000	-3.213294000
H	0.710176000	-2.716791000	-4.143023000
H	-0.788136000	-2.441268000	-3.203007000
H	-0.038205000	-4.078004000	-3.246273000
N	-0.277217000	2.959648000	0.959762000
C	1.899955000	0.172801000	1.025980000
B	0.582306000	0.545343000	0.264172000
N	0.715010000	2.884315000	-0.970882000
C	2.435371000	-1.134389000	1.374089000
H	2.006747000	-2.097696000	1.077685000
C	3.550744000	-0.990891000	2.266482000
H	4.108476000	-1.808829000	2.739065000
C	3.809885000	0.404615000	2.423808000
H	4.595955000	0.855505000	3.040953000
C	2.839607000	1.104316000	1.620703000
H	2.777677000	2.196567000	1.530283000
C	0.355774000	2.105354000	0.093302000
C	-0.306276000	4.246596000	0.441615000
H	-0.768083000	5.084972000	0.968388000
C	0.317184000	4.197148000	-0.779821000
H	0.503958000	4.984298000	-1.515473000
C	-0.900772000	2.525761000	2.229715000
H	-1.141976000	1.456714000	2.045093000

C	0.091805000	2.608955000	3.390599000
H	-0.393500000	2.251855000	4.320394000
H	0.427602000	3.653515000	3.558351000
H	0.979253000	1.975872000	3.202044000
C	-2.186026000	3.305966000	2.498335000
H	-2.727774000	2.832097000	3.337442000
H	-2.861669000	3.290387000	1.621159000
H	-1.982271000	4.360564000	2.778311000
C	1.386595000	2.355526000	-2.172576000
H	1.524468000	1.282316000	-1.932149000
C	0.467097000	2.457623000	-3.390040000
H	0.948691000	1.966039000	-4.257933000
H	0.264849000	3.512902000	-3.669230000
H	-0.498294000	1.950592000	-3.195285000
C	2.748182000	3.018390000	-2.372507000
H	3.280524000	2.520783000	-3.205476000
H	3.376910000	2.918358000	-1.466554000
H	2.651731000	4.095801000	-2.622157000
Mn	4.097578000	-0.149110000	0.394100000
O	6.019520000	2.034532000	-0.110366000
O	3.363153000	-0.267815000	-2.462578000
O	6.098345000	-2.292472000	0.045613000
C	5.313019000	-1.435574000	0.179853000
C	3.643983000	-0.219393000	-1.322190000
C	5.277276000	1.151326000	0.085095000

3^{liPr}

BLYP-D3(BJ)/def2-SVP,def2TZVP(Mn)+SMD(THF)

E = –2631.648012 E_h

B	0.623012000	0.093942000	-0.409975000
Mn	-3.124017000	0.545005000	-0.173506000
O	-1.959318000	-0.338850000	2.419938000
N	2.474201000	-1.689822000	-0.964530000
C	-1.381009000	1.870382000	-0.561416000
H	-0.997724000	2.582622000	0.176290000
N	0.495381000	-2.573147000	-0.575692000
O	-4.792654000	-1.864578000	-0.679761000
C	-2.481147000	2.139592000	-1.448579000
H	-3.050478000	3.072809000	-1.515784000
N	1.976647000	2.306090000	0.260131000
O	-5.331081000	2.192754000	0.950038000
C	-2.684031000	0.959350000	-2.235673000
H	-3.428173000	0.820148000	-3.026953000
N	2.000841000	0.695118000	1.751444000
C	-1.687278000	-0.001894000	-1.824713000
H	-1.579074000	-0.988312000	-2.287786000
C	-2.452555000	-0.005874000	1.400701000
C	-4.456267000	1.541519000	0.501748000
C	-4.168439000	-0.886529000	-0.464185000
C	1.155277000	-1.348613000	-0.641214000
C	2.609936000	-3.076260000	-1.073135000
H	3.559142000	-3.555435000	-1.319678000
C	1.376027000	-3.623719000	-0.841097000
H	1.058151000	-4.668004000	-0.828204000
C	3.496913000	-0.719708000	-1.418675000
H	2.927294000	0.222459000	-1.523307000
C	4.047535000	-1.106886000	-2.804078000
H	4.679021000	-0.283663000	-3.191554000

H	3.223427000	-1.280931000	-3.522772000
H	4.677010000	-2.017959000	-2.761861000
C	4.612658000	-0.518911000	-0.379259000
H	5.342873000	0.226689000	-0.750710000
H	5.159192000	-1.465617000	-0.192140000
H	4.208280000	-0.154051000	0.580771000
C	-0.883573000	-2.776602000	-0.069516000
H	-1.322520000	-1.769328000	-0.007158000
C	-0.862608000	-3.389760000	1.342343000
H	-1.894198000	-3.438655000	1.740710000
H	-0.262592000	-2.772288000	2.035035000
H	-0.444816000	-4.416703000	1.333446000
C	-1.713361000	-3.615321000	-1.056367000
H	-2.771749000	-3.626287000	-0.735790000
H	-1.356879000	-4.664242000	-1.104979000
H	-1.671664000	-3.188149000	-2.076600000
C	1.503279000	1.020972000	0.495203000
C	2.758492000	2.744750000	1.328588000
H	3.234322000	3.727362000	1.342517000
C	2.781697000	1.735617000	2.257555000
H	3.269023000	1.684384000	3.232947000
C	1.830368000	3.046650000	-1.018176000
H	1.167702000	2.404786000	-1.627829000
C	1.163137000	4.414054000	-0.793848000
H	0.974318000	4.900395000	-1.770547000
H	1.814009000	5.089597000	-0.202543000
H	0.196747000	4.310494000	-0.268140000
C	3.192975000	3.180268000	-1.725468000
H	3.055062000	3.660966000	-2.713328000

H	3.661478000	2.191649000	-1.886570000
H	3.894625000	3.805413000	-1.138134000
C	1.551440000	-0.480114000	2.540883000
H	0.699059000	-0.870222000	1.955495000
C	2.639767000	-1.561665000	2.633881000
H	2.258786000	-2.423948000	3.215203000
H	3.544604000	-1.177985000	3.147629000
H	2.932056000	-1.924773000	1.632908000
C	1.026285000	-0.041556000	3.918590000
H	0.557237000	-0.909570000	4.420436000
H	0.256415000	0.745048000	3.811601000
H	1.837104000	0.330955000	4.576086000
C	-0.706644000	0.607466000	-0.927824000

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