Substituent Effects on Carborane Reactivity with Cyclic (Alkyl)(Amino)Carbene

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1. General Experimental Considerations:

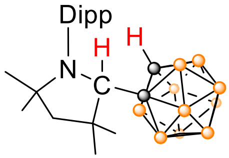
All preparations were carried out under an anhydrous N_2 atmosphere using standard Schlenk and glove box techniques. All glassware was oven-dried and cooled under vacuum before use. Commercial reagents were purchased from Sigma Aldrich, Yuanli Tech., Strem or Apollo Scientific and used without further purification unless indicated otherwise. NMR spectra were recorded at room temperature using a Bruker AvanceIII-400 MHz spectrometer. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sep = septet, m = multiplet, br = broad), coupling constant (Hz), assignment.

2. X-ray Crystallography:

The crystals for all the reported compounds herein were mounted on a cryoloop with Paratone oil, and all data were collected at 110(2) K. Single crystal X-ray diffraction data for $\mathbf{5^{nido}}$, $\mathbf{2^{clscls}}$, and $\mathbf{3^{nido}}$ were collected on a Bruker KAPPA APEXDuo diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a MoKα X-ray source (α = 0.71073 Å). Unit cell determination, refinement, and data collection were done using the Bruker APEX-III suite[1] data reduction and integration were performed using SAINT v8.34A (Bruker)[2] and absorption corrections and scaling were done using SADABS-2014/5 (Bruker)[3]. The crystal structures of $\mathbf{5^{nido}}$, $\mathbf{2^{clscls}}$, and $\mathbf{3^{nido}}$ were solved through the OLEX2[4] package using SHELXT[5] and the structures were refined using SHELXL[6]. All non-hydrogen atoms were refined anisotropically.

Single crystal X-ray diffraction data for $\mathbf{4^{nido}}$, $\mathbf{6^{nido}}$, $\mathbf{7^{nido}}$, $\mathbf{10^{nido}}$, **11**, $\mathbf{6^{cls}}$, and $\mathbf{7^{cls}}$ were collected on a Bruker D8 VENTURE FIXED CHI diffractometer with a microfocus sealed tube using a multilayer mirror as monochromator and a Bruker PHOTON III CPAD detector. The diffractometer was equipped with an Oxford Cryostream 1000 low-temperature device and used MoKα radiation (λ = 0.71073 Å). All data were integrated with SAINT V8.40B[7]. Multi-Scan absorption correction using SADABS 2016/2 was applied.[8] The structure was solved by Intrinsic Phasing methods with SHELXT 2018/2 and refined by full-matrix least-squares methods against F^2 using SHELXL-2019/2.[5,6] All non-hydrogen atoms were refined with anisotropic displacement parameters. Single crystal X-ray diffraction data for $\mathbf{8^{cls}}$ and $\mathbf{9^{cls}}$ were collected on a Rigaku Oxford Diffraction - XtaLAB Synergy-S diffractometer operated with a monochromated MoKα X-ray source (α = 0.71073 Å), and the data collection, cell refinement, data reduction, and analytical method absorption correction were performed using CrysAlisPro. CCDC numbers for the compounds $\mathbf{2^{clscls}}$, $\mathbf{3^{nido}}$, $\mathbf{4^{nido}}$, $\mathbf{5^{nido}}$, $\mathbf{6^{nido}}$, $\mathbf{6^{cls}}$, $\mathbf{7^{nido}}$, $\mathbf{7^{cls}}$, $\mathbf{8^{cls}}$, **11**, $\mathbf{9^{cls}}$, $\mathbf{10^{nido}}$ and, **1** 2503802, 2503803, 2503804, 2503805, 2503806, 2503807, 2503808, 2503809, 2503810, 2503811, 2503812, 2503813, and 2504008, respectively.

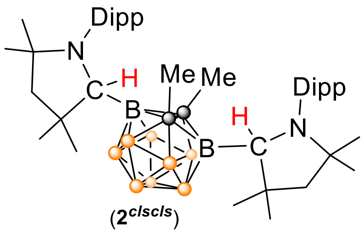
3. Synthetic Procedures:



(**1**)

3.1 Synthesis of 1: *o*-carborane (***o*****Cb**) (50 mg, 116.36 μmol), was dissolved in 2 mL of benzene, affording a transparent, clear solution. Simultaneously, $^{\mathbf{Me2}}$**CAAC**[9,10] (66.44 mg, 232.72 μmol) was dissolved in 5 mL of benzene and added to the first and combined. The reaction was stirred for 12 hours, and a yellowish-clear solution was observed. All volatiles were evaporated, affording a yellowish precipitate that was washed with cold pentane (3 x 2 mL). Evaporation of pentane afforded a white solid of **1**. Isolated yield:119 mg (80%).

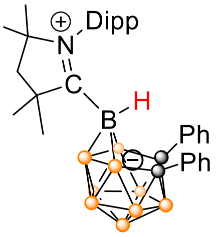
^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.23 (1H, t, *J* = 7.54 Hz, *p*-Ar-*H*), 7.12 (2H, d, *J* = 7.91 Hz, *m*-Ar-*H*), 4.53 (1H, s, pyrrolidine-C*H*), 3.91 (1H, s, carborane-C*H*), 3.52 (1H, sep, *J* = 6.69 Hz, $C\mathit{H}(CH_3)_2$), 2.96 (1H, sep, *J* = 6.68 Hz, $C\mathit{H}(CH_3)_2$), 2.30 (2H, d, *J* = 12.88 Hz, pyrrolidine-$C\mathit{H_2}$), 1.95 (2H, d, *J* = 12.86 Hz, pyrrolidine-$C\mathit{H_2}$), 1.72 (3H, s, pyrrolidine-$C\mathit{H_3}$), 1.55 (3H, s, pyrrolidine-$C\mathit{H_3}$), 1.40 (3H, d, *J* = 6.70 Hz, $CH(C\mathit{H}_3)_2$), 1.35 (3H, s, pyrrolidine-$C\mathit{H_3}$), 1.25 (3H, d, *J* = 6.82 Hz, $CH(C\mathit{H}_3)_2$), 1.23 (3H, d, *J* = 6.69 Hz, $CH(C\mathit{H}_3)_2$), 1.18 (3H, d, *J* = 6.6 Hz, $CH(C\mathit{H}_3)_2$), 0.85 (3H, s, pyrrolidine-$C\mathit{H_3}$) ppm. ^{13}**C{1H} NMR** (JMOD, 101 MHz, $CDCl_3$): δ 148.15, 147.23, 143.23, 127.32 (*p*-Ar-*C*), 126.64 (*m*-Ar-H), 125.11 (*m*-Ar-H), 78.85, 78.16 (pyrrolidine-*C*H), 63.35, 61.99, 60.15 (carborane-*C*H), 44.51, 33.08 (pyrrolidine-$\mathit{C}H_3$), 31.62 (pyrrolidine-$\mathit{C}H_3$), 29.41 ($\mathit{C}H(CH_3)_2$), 28.71 (pyrrolidine-$\mathit{C}H_3$), 27.95 ($\mathit{C}H(CH_3)_2$), 27.50 (pyrrolidine-$\mathit{CH_3}$ and $CH(C\mathit{H}_3)_2$), 25.74 ($CH(\mathit{C}H_3)_2$), 23.72 ($CH(\mathit{C}H_3)_2$), 23.60 ($CH(\mathit{C}H_3)_2$) ppm. ^{11}**B NMR** (128 MHz, $CDCl_3$) δ -4.16 (t, *J* = 132 Hz), -8.77, -9.95, -11.59, -14.05 (t, *J* = 156 Hz) ppm. ^{11}**B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ -4.22 (d, *J* = 123 Hz), -9.32 (s), -11.02 (s), -14.08 (d, *J* = 140 Hz) ppm. ^{1}**H{^{11}B} NMR** (400 MHz, $CDCl_3$) δ 7.23 (1H, t, *J* = 7.54 Hz, *p*-Ar-*H*), 7.12 (2H, d, *J* = 7.91 Hz, *m*-Ar-*H*), 4.53 (1H, s, pyrrolidine-C*H*), 3.91 (1H, s, carborane-C*H*), 3.52 (1H, sep, *J* = 6.69 Hz, $C\mathit{H}(CH_3)_2$), 2.96 (1H, sep, *J* = 6.68 Hz, $C\mathit{H}(CH_3)_2$), 2.70 (2H, br s, B-*H*), 2.30 (2H, d, *J* = 12.88 Hz, pyrrolidine-$C\mathit{H_2}$), 2.20-2.04 (7H, br s, B-*H*), 1.95 (2H, d, *J* = 12.86 Hz, pyrrolidine-$C\mathit{H_2}$), 1.72 (3H, s, pyrrolidine-$C\mathit{H_3}$), 1.67(1H, br s, B-*H*), 1.55 (3H, s, pyrrolidine-$C\mathit{H_3}$), 1.40 (3H, d, *J* = 6.70 Hz, $CH(C\mathit{H}_3)_2$), 1.35 (3H, s, pyrrolidine-$C\mathit{H_3}$), 1.25 (3H, d, *J* = 6.82 Hz, $CH(C\mathit{H}_3)_2$), 1.23 (3H, d, *J* = 6.69 Hz, $CH(C\mathit{H}_3)_2$), 1.18 (3H, d, *J* = 6.6 Hz, $CH(C\mathit{H}_3)_2$), 0.85 (3H, s, pyrrolidine-$C\mathit{H_3}$) ppm.



($\mathbf{2}^{clscls}$)

3.2 Synthesis of $\mathbf{2}^{\mathbf{clscls}}$: **$^{\mathbf{Me2}}$*o*Cb** (300 mg, 1.74 mmol) was synthesized[11] and dissolved in benzene (5 mL), affording a clear solution. Simultaneously, **$^{\mathbf{Me2}}$CAAC** (497.14 mg, 1.74 mmol) was also dissolved in benzene (3 mL) and added to the first solution mentioned. This afforded a yellowish solution. The reaction mixture was stirred overnight, and a clear orange solution was observed. Evaporation of all volatiles afforded an orange solid. Benzene was added to the solid again, and the solution was concentrated to allow crystallization. The product was afforded as transparent crystals $\mathbf{2}^{\mathbf{clscls}}$. Isolated yield: 168 mg (59% from CAAC).

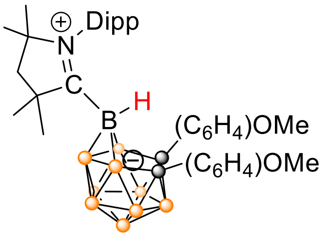
^{1}H NMR (400 MHz, C$_6$D$_6$) δ 6.89 (3H, m, Ar-*H*), 4.00 (2H, sep, *J* = 6.6 Hz, C*H*(CH$_3$)$_2$), 3.16 (2H, sep, *J* = 6.7 Hz, C*H*(CH$_3$)$_2$), 3.07 (2H, s, pyrrolidine-C*H*), 2.18 (2H, d, *J* = 12.4 Hz, pyrrolidine-C*H*$_2$), 1.88 (6H, s, pyrrolidine-C*H*$_3$), 1.74 (2H, d, *J* = 12.4 Hz, pyrrolidine-C*H*$_2$), 1.63 (6H, s, pyrrolidine-C*H*$_3$), 1.49 (3H, s, carborane-C*H*$_3$), 1.28 (6H, d, *J* = 6.4 Hz, CH(C*H*$_3$)$_2$), 1.26 (6H, s, pyrrolidine-C*H*$_3$), 1.17 (6H, d, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.10 (6H, d, *J* = 2.0 Hz, CH(C*H*$_3$)$_2$), 1.09 (6H, d, *J* = 2.4 Hz, CH(C*H*$_3$)$_2$), 0.89 (6H, s, pyrrolidine-C*H*$_3$), -0.29 (3H, s, carborane-C*H*$_3$) ppm. **^{13}C{1H} NMR** (JMOD, 101 MHz, C$_6$D$_6$) δ 150.89 (Ar-*C*), 147.06 (Ar-*C*), 146.38 (Ar-*C*), 126.10 (Ar-*C*H), 124.95 (Ar-*C*H), 124.84 (Ar-*C*H), 63.17 (pyrrolidine-*C*H), 62.34 (pyrrolidine-*C*H$_2$), 43.64, 32.52 (pyrrolidine-*C*H$_3$), 32.07 (pyrrolidine-*C*H$_3$), 30.40 (pyrrolidine-*C*H$_3$), 28.39 (pyrrolidine-*C*H$_3$), 27.94 (*C*H(CH$_3$)$_2$), 27.45 (*C*H(CH$_3$)$_2$), 27.15 (CH(*C*H$_3$)$_2$), 25.91 (CH(*C*H$_3$)$_2$), 25.17 (CH(*C*H$_3$)$_2$), 23.28 (CH(*C*H$_3$)$_2$), 19.49 (carborane-*C*H$_3$), 16.15 (carborane-*C*H$_3$) ppm. **^{11}B NMR** (128 MHz, C6D6) δ 1.89 (br s), -5.18 (br s), -10.48 (br s) ppm**.** **^{11}B{^{1}H} NMR** (128 MHz, C$_6$D$_6$) δ 2.54 (br s), -5.41 (br s), -11.03 (br s) ppm. **^{1}H{^{11}B} NMR** (400 MHz, C$_6$D$_6$) δ 6.89 (3H, m, Ar-*H*), 4.00 (2H, sep, *J* = 6.6 Hz, C*H*(CH$_3$)$_2$), 3.16 (3H, m, C*H*(CH$_3$)$_2$, B-*H*), 3.07 (2H, s, pyrrolidine-C*H*), 2.94-2.44 (9H, br s, B-*H*), 2.18 (2H, d, *J* = 12.4 Hz, pyrrolidine-C*H*$_2$), 1.88 (6H, s, pyrrolidine-C*H*$_3$), 1.74 (2H, d, *J* = 12.4 Hz, pyrrolidine-C*H*$_2$), 1.63 (6H, s, pyrrolidine-C*H*$_3$), 1.49 (3H, s, carborane-C*H*$_3$), 1.28 (6H, d, *J* = 6.4 Hz, CH(C*H*$_3$)$_2$), 1.26 (6H, s, pyrrolidine-C*H*$_3$), 1.17 (6H, d, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.10 (6H, d, *J* = 2.0 Hz, CH(C*H*$_3$)$_2$), 1.09 (6H, d, *J* = 2.4 Hz, CH(C*H*$_3$)$_2$), 0.89 (6H, s, pyrrolidine-C*H*$_3$), -0.29 (3H, s, carborane-C*H*$_3$) ppm.



(3^{nido})

3.3 Synthesis of 3^{nido}: **^{Ph2}*o*Cb** (70 mg, 236.16 µmol) was synthesized[12] and dissolved in 3 mL of benzene, and an equimolar amount of **^{Me2}CAAC** (67.42 mg, 236.16 µmol), also dissolved in 3 mL of benzene, was added to it. After 30 min, the solution changed color from colorless to light yellow and went darker with time. After 12 h, a white precipitate was formed. The removal of the solution and washing of the formed precipitate with benzene, followed by evaporation, afforded white powder. Crystallization from dichloromethane (DCM) afforded colorless crystals that were measured using X-ray crystallography. The molecular structure was determined as **3^{nido}** in a 71% yield (98.15 mg).

^{1}H-NMR (400 MHz, $CDCl_3$), δ 7.60 (1H, t, *J* = 7.7 Hz, Ar-*H*), 7.46 (2H, d, *J* = 7.7 Hz, Ar-*H*), 6.92 (10H, m, Ar-*H*), 2.84 (2H, br sep, *J* = 6.0 Hz, C*H*(CH$_3$)$_2$), 2.22 (2H, s, pyrrolidine-C*H*$_2$), 1.63 (12H, s, pyrrolidine-C*H*$_3$), 1.41 (6H, d, *J* = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.29 (6H, d, *J* = 6.4 Hz, CH(C*H*$_3$)$_2$) ppm. **^{13}C{1H} NMR** (JMOD, 101 MHz, $CDCl_3$), δ 145.56, 133.43, 130.67 (*Ar*-H), 130.53 (*Ar*-H), 126.86 (*Ar*-H), 126.19 (*Ar*-H), 126.01 (*Ar*-H), 79.08, 54.11(pyrrolidine-*C*H$_2$), 53.77, 29.54 (*C*H(CH$_3$)$_2$), 27.81(pyrrolidine-*C*H$_3$), 27.72 (pyrrolidine-*C*H$_3$), 25.81 (CH(*C*H$_3$)$_2$), 23.94 (CH(*C*H$_3$)$_2$) ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.54 (br s), -1.84 (br s), -7.99 (br s), -10.66 (d, *J* = 118 Hz), -15.78 (d, *J* = 115 Hz), -18.535 (d, *J* = 137 Hz) ppm. **^{11}B{^{1}H} NMR** (128 MHz, CDCl3) δ 28.12 (br s), -1.96 (br s), -8.20 (br s), -10.47 (s), -12.80 (s), -15.65 (s), -18.39 (s) ppm. **^{1}H{^{11}B} NMR** (400 MHz, $CDCl_3$) δ 7.60 (1H, t, *J* = 7.7 Hz, Ar-*H*), 7.46 (2H, d, *J* = 7.7 Hz, Ar-*H*), 6.92 (10H, m, Ar-*H*), 2.84 (2H, br sep, *J* = 6.0 Hz, C*H*(CH$_3$)$_2$), 2.49 (7H, br s, B-*H*), 2.22 (2H, s, pyrrolidine-C*H*$_2$), 2.05 (1H,br s, B-*H*), 1.63 (12H, s, pyrrolidine-C*H*$_3$), 1.41 (6H, d, *J* = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.29 (6H, d, *J* = 6.4 Hz, CH(C*H*$_3$)$_2$) ppm.

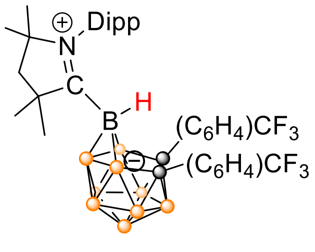


(7^{nido})

3.4 Synthesis of 7^{nido}: **^{Anis2}*o*Cb** (100 mg, 280.53 µmol) was synthesized,[13] dissolved in 3 mL of benzene, and an equimolar amount of **^{Me2}CAAC** (67.42 mg, 236.16 µmol), also dissolved in 3 mL of benzene, was added to it. After 3 h, the solution changed from colorless to a light yellow and darkened over time. After 12 h, a white precipitate was formed. The removal of the solution and washing of the formed precipitate with benzene, followed by evaporation, afforded a white powder. Crystallization from chloroform afforded colorless crystals that were measured using X-ray crystallography. The molecular structure was determined as **7^{nido}** in a 65% yield (117.71 mg).

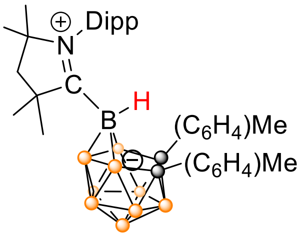
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (1H, t, *J* = 7.7 Hz , Ar-*H*), 7.45 (2H, d, *J* = 7.7 Hz , Ar-*H*), 7.26 (CDCl3), 6.87 (4H, br s, Ar-*H*), 6.43 (4H, Br d, *J* = 6.6 Hz, Ar-*H*), 3.69 (6H, s, OC*H*$_3$), 2.83 (2H, br sep, *J* = 6.3 Hz, C*H*(CH$_3$)$_2$), 2.21 (2H, s, pyrrolidine-C*H*$_2$) 1.64 (12H, br s, pyrrolidine-C*H*$_3$), 1.41 (6H, d, *J* =

6.6 Hz, CH(C*H*$_3$)$_2$), 1.29 (6H, d, *J* = 6.3 Hz, CH(C*H*$_3$)$_2$). **^{13}C{1H} NMR** (JMOD, 101 MHz, CDCl$_3$) δ 157.85, 145.57, 133.46, 131.58 (*Ar*-H), 130.64(*Ar*-H), 128.33, 125.96 (*Ar*-H), 112.02 (*Ar*-H), 79.02, 77.00, 55.05 (O*C*H$_3$), 54.11 (pyrrolidine-*C*H$_2$), 53.76, 29.53 (*C*H(CH$_3$)$_2$), 27.80 (pyrrolidine-*C*H3), 27.41(pyrrolidine-*C*H3), 25.50 (CH(*C*H$_3$)$_2$), 24.98 (CH(*C*H$_3$)$_2$). **^{1}H{^{11}B} NMR** (400 MHz, CDCl$_3$) δ 7.60 (1H, t, *J* = 7.7 Hz , Ar-*H*), 7.45 (2H, d, *J* = 7.7 Hz , Ar-*H*), 6.87 (4H, br s, Ar-*H*), 6.43 (4H, Br d, *J* = 6.6 Hz, Ar-*H*), 3.69 (6H, s, OCH$_3$), 2.83 (2H, br sep, *J* = 6.3 Hz, C*H*(CH$_3$)$_2$), 2.45 (br s, 8H, B-*H*), 2.22 (2H, s, pyrrolidine-C*H*$_2$), 2.02 (br s, 1H, B-*H*), 1.64 (12H, broad s, pyrrolidine-C*H*$_3$), 1.41 (6H, d, *J* = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.29 (6H, d, *J* = 6.4 Hz, CH(C*H*$_3$)$_2$). **^{11}B NMR** (128 MHz, CDCl$_3$) δ 27.90 (br s), -1.83 (br s), -10.86 (d, *J* = 124 Hz), -15.76 (d, *J* = 110 Hz), -18.77 (d, *J* = 143 Hz). **^{11}B{^{1}H} NMR** (128 MHz, CDCl$_3$) δ 27.95 (br s), -1.61 (br s), -10.75 (s), -15.67 (s), -18.55 (s).



(**4**^{nido})

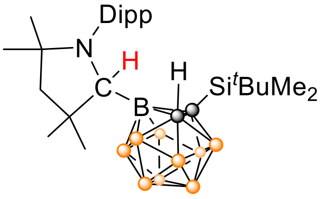
3.5 Synthesis of 4^{nido}: **^{pCF3Ph2}*o*Cb** (100 mg, 300.85 µmol) was synthesized,[2] dissolved in 3 mL of benzene, and an equimolar amount of **^{Me2}CAAC** (85.88 mg, 300.85 µmol), also dissolved in 3 mL of benzene, was added to it. After 5 h, the solution changed from colorless to a light purple and darkened over time. After 12 h, a white precipitate was formed. The removal of the solution and washing of the formed precipitate with benzene, followed by evaporation, afforded a white powder. Crystallization from chloroform afforded colorless crystals that were measured using X-ray crystallography. The molecular structure was determined as **4^{nido}** in a 79% yield (67.8 mg). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.65 (1H, t, *J* = 7.79 Hz, Ar-*H*), 7.48 (2H, d, *J* = 7.77 Hz, Ar-*H*), 7.05 (8H, br s, Ar-*H*), 2.83 (2H, br sep, *J* = 5.76 Hz, C*H*(CH$_3$)$_2$), 2.24 (2H, s, pyrrolidine-C*H*$_2$), 1.62 (12H, s, pyrrolidine-C*H*$_3$), 1.37 (6H, d, *J* = 6.55 Hz, CH(C*H*$_3$)$_2$), 1.31 (6H, d, *J* = 6.44 Hz, CH(C*H*$_3$)$_2$) ppm. **^{13}C{1H} NMR** (JMOD, 101 MHz, CDCl$_3$) δ 145.57, 133.33, 130.84 (*Ar*-H), 130.62 (*Ar*-H), 128.33, 126.09 (*Ar*-H), 123.84 (*Ar*-H), 79.45, 54.00 (pyrrolidine-*C*H$_2$), 53.78, 29.55 (*C*H(CH$_3$)$_2$), 28.46 (pyrrolidine-*C*H$_3$), 26.95 (pyrrolidine-*C*H$_3$), 24.46 (CH(*C*H$_3$)$_2$), 22.16 (CH(*C*H$_3$)$_2$) ppm. **^{1}H{^{11}B} NMR** (400 MHz, CDCl$_3$) δ 7.65 (1H, t, *J* = 7.78 Hz, Ar-*H*), 7.48 (2H, d, *J* = 7.75 Hz, Ar-*H*), 7.05 (8H, br s, Ar-*H*), 2.83 (2H, br sep, *J* = 5.76 Hz, C*H*(CH$_3$)$_2$), 2.48 (6H, br s, B-H), 2.24 (2H, s, pyrrolidine-C*H*$_2$), 2.08 (1H, br s, B-H), 1.62 (12H, s, pyrrolidine-C*H*$_3$), 1.37 (6H, d, *J* = 6.51 Hz, CH(C*H*$_3$)$_2$), 1.31 (6H, d, *J* = 6.42 Hz, CH(C*H*$_3$)$_2$). **^{11}B NMR** (128 MHz, CDCl$_3$) δ 29.92 (br s), 0.33 (br s), -7.12 (br s), -10.26 (d, *J* = 123 Hz), -15.21(br s), -18.23 (d, *J* = 143 Hz). **^{11}B{^{1}H} NMR** (128 MHz, CDCl$_3$) δ 29.90 (br s), 0.31 (br s), -7.34 (s), -10.19 (s), -15.24 (s), -18.21 (s). **^{19}F NMR** (377 MHz, CDCl$_3$) δ -62.51 (s).



(**6**^{nido})

3.6 Synthesis of 6^{nido}: **^{pTol2}*o*Cb** (90 mg, 277.38 µmol) was synthesized[2], dissolved in 3 mL of benzene, and an equimolar amount of **^{Me2}CAAC** (79.18 mg, 277.38 µmol), also dissolved in 3 mL of benzene, was added to it. After 5 h, the solution changed from colorless to a light yellow and darkened over time. After 12 h, a white precipitate was formed. The removal of the solution and washing of the formed precipitate with benzene, followed by evaporation, afforded a white powder. Crystallization from chloroform afforded colorless crystals that were measured using X-ray crystallography. The molecular structure was determined as **6^{nido}** in a 65% yield (109.97 mg).

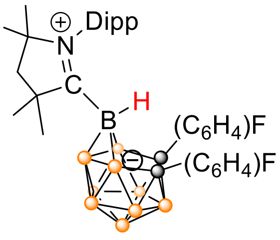
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (1H, t , *J* = 7.78 Hz, Ar-*H*), 7.46 (2H, d, *J* = 7.73 Hz, Ar-*H*), 6.70 (8H, Br s, Ar-*H*), 2.83 (2H, br sep, *J* = 6.16 Hz, C*H*$(CH_3)_2$), 2.21 (2H, s, pyrrolidine-C*H*$_2$), 2.17 (6H, s, tolyl-C*H*$_3$), 1.64 (12H, broad s, pyrrolidine-C*H*$_3$), 1.41 (6H, d, *J* = 6.61 Hz, CH(C*H*$_3$)$_2$), 1.31 (6H, d, *J* = 6.37 Hz, CH(C*H*$_3$)$_2$) ppm. **^{13}C{1H} NMR** (JMOD, 101 MHz, CDCl3) δ 145.62, 135.54, 130.37 (*Ar*-H), 127.45 (*Ar*-H), 126.00 (*Ar*-H), 78.98, 77.00, 65.85, 54.14 (pyrrolidine-*C*H$_2$), 53.75, 29.54 (*C*H$(CH_3)_2$), 28.66 (pyrrolidine-*C*H$_3$), 27.79 (pyrrolidine-*C*H$_3$), 25.83 (CH(*C*H$_3$)$_2$), 25.10 (CH(*C*H$_3$)$_2$), 20.82 (tolyl-*C*H$_3$) ppm. **^{1}H{^{11}B} NMR** (400 MHz, $CDCl_3$) δ 7.61 (1H, t , *J* = 7.78 Hz, Ar-*H*), 7.46 (2H, d, *J* = 7.73 Hz, Ar-*H*), 6.70 (8H, Br s, Ar-H), 2.83 (2H, br sep, *J* = 6.16 Hz, C*H*$(CH_3)_2$), 2.21 (2H, s, pyrrolidine-C*H*$_2$), 2.17 (6H, s, tolyl-C*H*$_3$), 2.02 (1H, s, B-*H*), 1.64 (12H, broad s, pyrrolidine-C*H*$_3$), 1.41 (6H, doublet, *J* = 6.61 Hz, CH(C*H*$_3$)$_2$), 1.31 (6H, doublet, *J* = 6.37 Hz, CH(C*H*$_3$)$_2$). **^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.38 (br s), -2.65 (d, *J* = 150 Hz, -9.97 (d, *J* = 119 Hz), -15.32 (br s), -18.32 (d, *J* = 135 Hz). **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ 27.25 (br s), -0.33 (br s), -10.68 (s), -15.75 (s), -18.67 (s).



(**8**^{cls})

3.7 Synthesis of 8^{cls}: **^{Si}*o*Cb** (145 mg, 560.97 µmol) was synthesized,[14] and dissolved in benzene (4 mL), **^{Me2}CAAC** (160.14 mg, 560.97 µmol) in benzene (3 mL) solution was added to it. The combined solution was heated to 80 °C for 6 h. All volatiles were evaporated, then a minimum amount of DCM was added (2 mL). After 12 h, crystals were observed. These crystals were determined by X-ray crystallography and gave product **8^{cls}** in 62% yield (189.4 mg).

^{1}H NMR (400 MHz, C_6D_6) δ 7.06 (3H, m, Ar-*H*), 4.19 (1H, sep, *J* = 6.72 Hz, $CH(CH_3)_2$), 3.50 (1H, s, pyrrolidine-C*H*), 3.36 (1H, sep, *J* = 6.68 Hz, $CH(CH_3)_2$) , 3.11 (1H, s, carborane-C*H*), 2.19 (2H, d, *J* = 12.64 Hz, pyrrolidine-CH_2), 1.92 (3H, s, pyrrolidine-CH_3), 1.71 (2H, d, *J* = 12.62 Hz, pyrrolidine-CH_2), 1.66 (3H, s, pyrrolidine-CH_3), 1.50 (3H, s, pyrrolidine-CH_3), 1.23 (3H, d, *J* = 6.74 Hz, $CH(CH_3)_2$), 1.17 (3H, d, *J* = 6.75 Hz, $CH(CH_3)_2$), 1.14 (3H, d, *J* = 2.66 Hz, $CH(CH_3)_2$), 1.13 (3H, d, *J* = 2.55 Hz, $CH(CH_3)_2$) , 0.88 (3H, s, Si-CH_3), 0.76 (9H, s, Si-$C(CH_3)_3$), 0.31 (3H, s, Si-CH_3). **^{13}C{1H} NMR** (JMOD, 101 MHz, C_6D_6) δ 151.74 (Ar-*C*), 148.59 (Ar-*C*), 146.76 (Ar-*C*), 126.88 (Ar-*C*H), 126.31 (Ar-*C*H), 125.42 (Ar-*C*H), 68.77, 64.55 (pyrrolidine-*C*H), 60.67 (carborane-*C*H), 60.55 (pyrrolidine-CH_2), 45.06, 35.75 (pyrrolidine-CH_3), 34.66 (pyrrolidine-CH_3), 31.56 (pyrrolidine-CH_3), 28.25 (Si-$C(CH_3)_3$), 27.87, 27.33 (Si-CH_3), 26.97 ($CH(CH_3)_2$) 26.58, 26.03, 24.70, 21.76, -3.16, -6.94. **^{11}B NMR** (128 MHz, C_6D_6) δ 0.02 (br s), -3.48 (d, *J* = 141 Hz), -4.58 (s), -8.12, -9.49, -11.33, -12.52. **^{11}B{^{1}H} NMR** (128 MHz, C_6D_6) δ 0.03, -4.05 (s), -8.67 (s), -10.69 (s), -11.95, -13.51. **^{1}H{^{11}B} NMR** (400 MHz, C_6D_6) δ 7.06 (3H, m, Ar-*H*), 4.19 (1H, sep, *J* = 6.72 Hz, $CH(CH_3)_2$), 3.50 (1H, s, pyrrolidine-C*H*), 3.36 (1H, sep, *J* = 6.68 Hz, $CH(CH_3)_2$) ,3.27-2.27 (10H, br s, B-*H*) 3.11 (1H, s, carborane-C*H*), 2.19 (2H, d, *J* = 12.64 Hz, pyrrolidine-CH_2), 1.92 (3H, s, pyrrolidine-CH_3), 1.71, 1.66 (3H, s, pyrrolidine-CH_3), 1.50 (3H, s, pyrrolidine-CH_3), 1.23 (3H, d, *J* = 6.74 Hz, $CH(CH_3)_2$), 1.17 (3H, d, *J* = 6.75 Hz, $CH(CH_3)_2$), 1.14 (3H, d, *J* = 2.66 Hz, $CH(CH_3)_2$), 1.13 (3H, d, *J* = 2.55 Hz, $CH(CH_3)_2$) , 0.88 (3H, s, Si-CH_3), 0.76 (9H, s, Si-$C(CH_3)_3$), 0.31 (3H, s, Si-CH_3), -0.87 (3H, s, Si-CH_3).

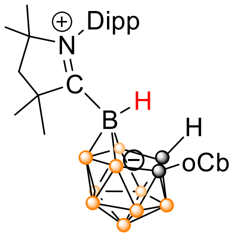


($\mathbf{10}^{nido}$)

3.8 Synthesis of 10^{nido}: **^{FPh2}*o*Cb** (90 mg, 270.76 μmol) was synthesized,[2] dissolved in 3 mL of benzene, and an equimolar amount of **^{Me2}CAAC** (77.30 mg, 270.76 μmol), also dissolved in 3 mL of benzene, was added to it. After 5 h, the solution changed from colorless to light purple and darkened over time. After 12 h, a white precipitate was formed. The removal of the solution and washing of the formed precipitate with benzene, followed by evaporation, afforded a white powder. Crystallization from chloroform afforded colorless crystals that were measured using X-ray crystallography. The molecular structure was determined as **10^{nido}** in a 60% yield (100.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (1H, t, *J* = 7.78 Hz, Ar-*H*), 7.45 (2H, d, *J* = 7.77 Hz, Ar-*H*), 6.74 (8H, br s, Ar-*H*), 2.82 (2H, br sep, *J* = 6.48 Hz, $CH(CH_3)_2$), 2.23 (2H, s, pyrrolidine-CH_2), 1.63 (12H, s, pyrrolidine-CH_3), 1.40 (6H, d, *J* = 6.62 Hz, $CH(CH_3)_2$), 1.30 (6H, d, *J* = 6.51 Hz, $CH(CH_3)_2$) ppm. **^{13}C{1H} NMR** (JMOD, 101 MHz, $CDCl_3$) δ 162.75, 160.31, 145.60, 132.05, 130.73 (*Ar*-H), 125.99 (*Ar*-H), 113.63 (*Ar*-H), 113.42 (*Ar*-H), 79.24, 54.06 (pyrrolidine-CH_2), 53.79, 29.54 ($CH(CH_3)_2$) ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 28.35 (br s), -0.72 (br s), -10.56 (d, *J* = 151 Hz), -15.66 (d, *J* = 131 Hz), -

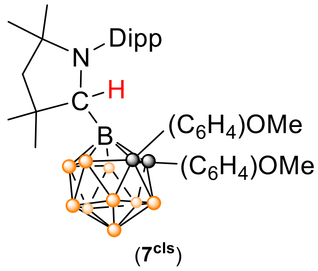
18.50 (d, *J* = 143 Hz) ppm. **^{11}B{^{1}H} NMR** (128 MHz, CDCl$_3$) δ 28.09 (br s), -0.72 (br s), -10.64 (s), -15.56 (s), -18.50 (s) ppm. **^{1}H{^{11}B} NMR** (400 MHz, CDCl$_3$) δ 7.61(1H, t, *J* = 7.78 Hz, Ar-H), 7.45 (2H, d, *J* = 7.77 Hz, Ar-*H*), 6.74 (8H, br s, Ar-*H*), 2.82 (2H, br sep, *J* = 6.48 Hz, C*H*(CH$_3$)$_2$), 2.44 (7H, br s, B-*H*), 2.23 (2H, s, pyrrolidine-C*H*$_2$), 2.04 (1H, s, B-*H*), 1.63(12H, s, pyrrolidine-C*H*$_3$), 1.40 (6H, d, *J* = 6.62 Hz, CH(C*H*$_3$)$_2$), 1.30 (6H, d, *J* = 6.51 Hz, CH(C*H*$_3$)$_2$). **^{19}F NMR** (376 MHz, CDCl$_3$) δ -110.75 (s).



(5^{nido})

3.9 Synthesis of 5^{nido}: **^{oCb}*o*Cb** (50 mg, 174.57 µmol) was synthesized,[15] then dissolved in 3 mL of benzene, mixed with **^{Me2}CAAC** (49.84 mg, 174.57 µmol) in 5 mL of benzene at rt for 12 h. The solution's colour turned yellow. Benzene was evaporated and replaced by 1 mL of DCM. Slow evaporation resulted in the formation of crystalline material. The molecular structure of these crystals was determined by X-ray as **5^{nido}** in a 72% yield (71.88 mg).

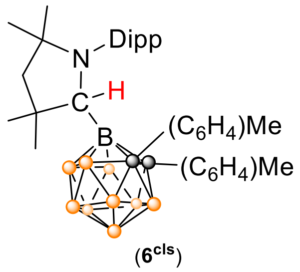
^{1}H NMR (400 MHz, C$_6$D$_6$) δ 7.03 (1H, t, *J* = 7.80 Hz, Ar-*H*), 6.87(2H, t, *J* = 7.82 Hz, Ar-*H*), 3.21 (2H, br s, Bis-Cb C*H*), 2.46 (1H, sep, *J* = 6.65 Hz, C*H*(CH$_3$)$_2$), 2.34 (1H, sep, *J* = 6.60 Hz, C*H*(CH$_3$)$_2$), 1.41 (3H, d, *J* = 6.58 Hz, CH(C*H*$_3$)$_2$), 1.38 (3H, s, pyrrolidine-C*H*$_3$), 1.36 (3H, d, *J* = 6.60 Hz, CH(C*H*$_3$)$_2$), 1.25 (2H, d, *J* = 7.96 Hz, pyrrolidine-C*H*$_2$), 1.25 (3H, s, pyrrolidine-C*H*$_3$) 0.92 (6H, d, *J* = 6.53 Hz, CH(C*H*$_3$)$_2$) 0.72 (3H, s, pyrrolidine-C*H*$_3$) ppm. **^{13}C{1H} NMR** (JMOD, 101 MHz, C6D6) δ 145.26, 130.90, 128.00, 126.12, 125.71, 71.03, 65.10, 52.17, 29.61, 29.23, 28.67, 25.88, 25.72 ppm. **^{11}B NMR** (128 MHz, C$_6$D$_6$) δ 36.06, -2.15, -8.82, -9.61, -19.03. **^{11}B{^{1}H} NMR** (128 MHz, C$_6$D$_6$) δ 36.32, -2.29, -9.09, -18.18, -20.09 ppm. **^{1}H{^{11}B} NMR** (400 MHz, C$_6$D$_6$) δ 7.03 (1H, t, *J* = 7.80 Hz, Ar-*H*), 6.87(2H, t, *J* = 7.82 Hz, Ar-*H*), 3.21 (2H, br s, Bis Cb C-*H*), 2.98-2.32 (22H, m, B-H, C*H*(CH$_3$)$_2$) 1.41 (3H, d, *J* = 6.58 Hz, CH(C*H*$_3$)$_2$), 1.38 (3H, s, pyrrolidine-C*H*$_3$), 1.36 (3H, d, *J* = 6.60 Hz, CH(C*H*$_3$)$_2$), 1.25 (2H, d, *J* = 7.96 Hz, pyrrolidine-C*H*$_2$) 1.25 (3H, s, pyrrolidine-C*H*$_3$) 0.92 (6H, d, *J* = 6.53 Hz, CH(C*H*$_3$)$_2$) 0.72 (3H, s, pyrrolidine-C*H*$_3$) ppm.



(**7**$^{\mathbf{cls}}$)

3.10 Synthesis of (7$^{\mathbf{cls}}$): **7**$^{\mathbf{nido}}$ (50 mg, 77.89 µmol) was synthesized,[2] then dissolved in 3 mL of chloroform (solution was colorless), and then heated up to 50 °C for 10 days. No visible change detected. chloroform was evaporated. Extraction with hexane resulted in the isolation of product **7**$^{\mathbf{cls}}$ from the starting material **7**$^{\mathbf{nido}}$. **7**$^{\mathbf{cls}}$ was crystallized from the slow evaporation of hexane. The molecular structure of these crystals was determined by X-ray as **7**$^{\mathbf{cls}}$ in a 30% yield (15 mg).

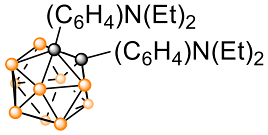
^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.34 (4H, m, Ar-*H*), 7.15(1H, dd, J_1 = 7.09, J_2 = 2.35 Hz, Ar-*H*), 6.67 (2H, d, *J* = 9.05 Hz, Ar-*H*), 6.37 (4H, q, *J* = 9.29 Hz, Ar-*H*), 4.05 (1H, sep, *J* = 6.84 Hz, C*H*(CH$_3$)$_2$), 3.81 (3H, s, OC*H*$_3$), 3.76 (3H, s, OC*H*$_3$), 3.61 (1H, s, $^{\mathbf{Me2}}$CAAC -C*H*), 3.17 (1H, sep, *J* = 6.67 Hz, C*H*(CH$_3$)$_2$), 2.22 (1H, d, *J* = 12.72 Hz, pyrrolidine-C*H*$_2$), 1.82 (1H, d, *J* = 12.70 Hz, pyrrolidine-C*H*$_2$), 1.66 (3H, s, pyrrolidine-C*H*$_3$), 1.44 (3H, d, *J* = 6.56 Hz, CH(C*H*$_3$)$_2$), 1.40 (3H, s, pyrrolidine-C*H*$_3$), 1.27 (3H, d, *J* = 6.64 Hz, CH(C*H*$_3$)$_2$), 1.16 (3H, d, *J* = 6.68 Hz, CH(C*H*$_3$)$_2$), 0.91 (3H, s, pyrrolidine-C*H*$_3$), 0.79 (3H, s, pyrrolidine-C*H*$_3$), 0.74 (3H, d, *J* = 6.72 Hz, CH(C*H*$_3$)$_2$). ^{13}**C{1H} NMR** (JMOD, 101 MHz, CDCl$_3$) δ 152.02, 132.71 (*Ar*-H), 132.58 (*Ar*-H), 132.10, 125.70 (*Ar*-H), 125.44 (*Ar*-H), 124.91 (*Ar*-H), 113.48, 113.35 (*Ar*-H), 112.81 (*Ar*-H), 80.76, 77.00, 64.32, 63.34 (pyrrolidine-*C*H$_2$), 55.35, 55.21, 35.13, 34.24 (pyrrolidine-*CH3*), 31.21 (pyrrolidine-*CH3*), 28.64 (pyrrolidine-*CH3*), 27.81, 27.71 (pyrrolidine-*CH3*), 27.47 (CH(*C*H$_3$)$_2$), 25.81 (CH(*C*H$_3$)$_2$), 25.08 (CH(*C*H$_3$)$_2$), 24.11 (CH(*C*H$_3$)$_2$). ^{11}**B NMR** (128 MHz, CDCl$_3$) δ 6.14, -2.13, -3.31, -5.45, -8.06, -10.08, -11.21. ^{11}**B {^{1}H} NMR** (128 MHz, CDCl$_3$) δ 5.50, -2.70, -4.76, -6.58, -8.90, -10.86. ^{1}**H {^{11}B} NMR** (400 MHz, CDCl$_3$) δ 7.34 (4H, m, Ar-*H*), 7.15(1H, dd, J_1 = 7.09, J_2 = 2.35 Hz, Ar-*H*), 6.67 (2H, d, *J* = 9.05 Hz, Ar-*H*), 6.37 (4H, q, *J* = 9.29 Hz, Ar-*H*), 4.05 (1H, sep, *J* = 6.84 Hz, C*H*(CH$_3$)$_2$), 3.81 (3H, s, OC*H*$_3$), 3.76 (3H, s, OC*H*$_3$), 3.61 (1H, s, $^{\mathbf{Me2}}$CAAC -C*H*), 3.17 (2H, m, C*H*(CH$_3$)$_2$, B-*H*), 2.91-2.40 (9H, br s, B-*H*), 2.22 (1H, d, *J* = 12.72 Hz, pyrrolidine-C*H*$_2$), 1.82 (1H, d, *J* = 12.70 Hz, pyrrolidine-C*H*$_2$), 1.66 (3H, s, pyrrolidine-C*H*$_3$), 1.44 (3H, d, *J* = 6.56 Hz, CH(C*H*$_3$)$_2$), 1.40 (3H, s, pyrrolidine-C*H*$_3$), 1.27 (3H, d, *J* = 6.64 Hz, CH(C*H*$_3$)$_2$), 1.16 (3H, d, *J* = 6.68 Hz, CH(C*H*$_3$)$_2$), 0.91 (3H, s, pyrrolidine-CH$_3$), 0.79 (3H, s, pyrrolidine-CH$_3$), 0.74 (3H, d, *J* = 6.72 Hz, CH(C*H*$_3$)$_2$).



(**6**$^{\mathbf{cls}}$)

3.11 Synthesis of 6$^{\mathbf{cls}}$: **6**$^{\mathbf{nido}}$ (60 mg, 98.37 µmol) was synthesized,[2] then dissolved in 3 mL of chloroform (solution was colorless), and then heated up to 70 °C for 3 days. No visible change detected. chloroform was evaporated. Extraction with hexane resulted in the isolation of product **6**$^{\mathbf{cls}}$ from the starting material **6**$^{\mathbf{nido}}$. **6**$^{\mathbf{cls}}$ was crystallized by slow evaporation of hexane. The molecular structure of these crystals was determined by X-ray as **6**$^{\mathbf{cls}}$ in a 30% yield (18 mg).

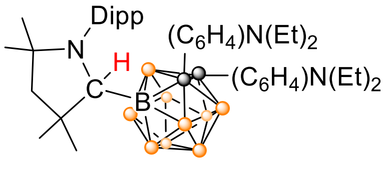
^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.27 (4H, m, Ar-*H*), 7.14 (1H, dd, J_1 = 7.31, J_2 = 2.11 Hz, Ar-*H*) , 6.95 (2H, d, *J* = 8.10 Hz, Ar-*H*), 6.64 (2H, d, *J* = 8.09 Hz, Ar-*H*), 6.29 (2H, d, *J* = 8.49 Hz, Ar-*H*), 4.03 (1H, sept, *J* = 6.68 Hz, C*H*(CH$_3$)$_2$), 3.59 (1H, s, $^{\mathrm{Me2}}$CAAC -C*H*), 3.13 (1H, sept, *J* = 6.56 Hz, C*H*(CH$_3$)$_2$), 2.31 (3H, s, tolyl-C*H*$_3$), 2.22 (4H, m, tolyl-C*H*$_3$, pyrrolidine-C*H*$_2$), 1.78 (1H, d, *J* = 12.72 Hz, pyrroldidne-C*H*$_2$), 1.63 (3H, s, pyrrolidine-C*H*$_3$), 1.42 (3H, d, *J* = 6.54 Hz, CH(C*H*$_3$)$_2$), 1.35 (3H, s, pyrrolidine-C*H*$_3$), 1.24 (3H, m, CH(C*H*$_3$)$_2$), 1.13 (3H, d, *J* = 6.69 Hz, CH(C*H*$_3$)$_2$), 0.88 (3H, s, pyrrolidine-C*H*$_3$), 0.71 (3H, s, pyrrolidine-C*H*$_3$), 0.66 (3H, d, *J* = 6.74 Hz, CH(C*H*$_3$)$_2$). ^{13}**C{1H} NMR** (JMOD, 101 MHz, CDCl$_3$) δ 131.22 (*Ar*-H), 130.98 (*Ar*-H), 128.74 (*Ar*-H), 128.25 (*Ar*-H), 125.68 (*Ar*-H), 125.53 (*Ar*-H), 124.83 (*Ar*-H), 64.36, 35.13, 34.18, 31.19, 28.64, 27.78, 27.70, 25.82, 25.10, 23.89, 22.54. ^{11}**B NMR** (128 MHz, CDCl$_3$) δ 5.66 (br s), -2.59 (d, *J* = 140 Hz), -5.55 (s), -8.52 (s), -10.89 (d, *J* = 157 Hz). ^{11}**B {**^{1}**H} NMR** (128 MHz, CDCl$_3$) δ 5.59 (br s), -2.65 (s), -4.78 (s), -6.96 (s), -9.06 (s), -10.67 (s). ^{1}**H {**^{11}**B} NMR** (400 MHz, CDCl$_3$) δ 7.27 (4H, m, Ar-*H*), 7.14 (1H, dd, J_1 = 7.31, J_2 = 2.11 Hz, Ar-*H*) , 6.95 (2H, d, *J* = 8.10 Hz, Ar-*H*), 6.64 (2H, d, *J* = 8.09 Hz, Ar-*H*), 6.29 (2H, d, *J* = 8.49 Hz, Ar-*H*), 4.03 (1H, sept, *J* = 6.68 Hz, C*H*(CH$_3$)$_2$), 3.59 (1H, s, $^{\mathrm{Me2}}$CAAC-C*H*), 3.13 (3H, m, B-*H*, C*H*(CH$_3$)$_2$), 2.88-2.39 (8H, br s, B-*H*), 2.31 (3H, s, tolyl-C*H*$_3$), 2.22 (4H, m, tolyl-C*H*$_3$, pyrrolidine-C*H*$_2$), 1.78 (1H, d, *J* = 12.72 Hz, pyrroldidne-C*H*$_2$), 1.63 (3H, s, pyrrolidine-C*H*$_3$), 1.42 (3H, d, *J* = 6.54 Hz, CH(C*H*$_3$)$_2$), 1.35 (3H, s, pyrrolidine-C*H*$_3$), 1.24 (3H, m, CH(C*H*$_3$)$_2$), 1.13 (3H, d, *J* = 6.69 Hz, CH(C*H*$_3$)$_2$), 0.88 (3H, s, pyrrolidine-C*H*$_3$), 0.71 (3H, s, pyrrolidine-C*H*$_3$), 0.66 (3H, d, *J* = 6.74 Hz, CH(C*H*$_3$)$_2$).



(**11**)

3.12 Synthesis of $^{\mathbf{anil2}}$***o*****Cb (11)**: A solution of 1.81 mL butyl lithium (1.6 M in n-hexane) was added slowly via syringe to a solution of diethyl amine (105.62 mg, 1.44 mmol) in 5 mL of THF, then stirred for 12 h at 25 °C. The reaction mixture turned dark yellow with time. $^{\mathbf{FPh2}}$***o*****Cb** dissolved in 3 mL of THF (320 mg, 962.71 µmol) was added to the reaction mixture, and the color of the solution turned dark-brown. After stirring for 8 h, the reaction mixture was quenched with 5 mL saturated aqueous solution of NaCl and extracted with H$_2$O (15 mL) and ethyl acetate (3 x 20 mL). The organic layer was separated and dried with anhydrous Na$_2$SO$_4$, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica using hexane/ethyl acetate mixture as eluent to afford the pure compound $^{\mathbf{anil2}}$***o*****Cb (11)** 78% (329.39 mg).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.23 (4H, d, *J* = 9.12 Hz, Ar-*H*), 6.36 (4H, d, *J* = 9.10 Hz, Ar-*H*), 3.26 (8H, q, *J* = 7.07, C*H*$_2$CH$_3$), 2.43 (10H, br s, B-*H*), 1.08 (12H, t, *J* = 7.07 Hz, CH$_2$C*H*$_3$). **^{1}H {^{11}B} NMR** (400 MHz, CDCl$_3$) δ 7.23 (4H, d, *J* = 9.12 Hz, Ar-*H*), 6.36 (4H, d, *J* = 9.10 Hz, Ar-*H*), 3.26 (8H, q, *J* = 7.07, C*H*$_2$CH$_3$), 3.13 (2H, br s, B-*H*), 2.45 (6H, br s, B-*H*), 2.19 (2H, br s, B-*H*), 1.08 (12H, t, *J* = 7.07 Hz, CH$_2$C*H*$_3$). **^{11}B NMR** (128 MHz, CDCl$_3$) δ -3.53 (d, *J* = 135 Hz), -11.50 (d, *J* = 146 Hz). **^{11}B {^{1}H} NMR** (128 MHz, CDCl$_3$) δ -3.49 (s), -9.31 (s), -11.43 (s). **^{13}C{1H} NMR** (JMOD, 101 MHz, CDCl$_3$) δ 148.49, 132.20 (*Ar*-H), 117.80, 110.37 (*Ar*-H), 88.54, 44.20 (*C*H$_2$CH$_3$), 12.41 (CH$_2$*C*H$_3$).



($\mathbf{9^{cls}}$)

3.13 Synthesis of $\mathbf{9^{cls}}$: $^{\mathbf{anil2}}$*o*Cb (11) (100 mg, 227.97 µmol) was synthesized,[16] then dissolved in 3 mL of benzene, mixed with **$^{\mathbf{Me2}}$CAAC** (65.08 mg, 227.97µmol) in 5 mL of benzene at 60 °C for 10 days. The solution's colour turned to dark yellow. Benzene was evaporated, and extraction with hexane and slow evaporation resulted in the formation of crystalline material. The molecular structure of these crystals was determined by X-ray as **$\mathbf{9^{cls}}$** in a 65% yield (107.30 mg).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.15 (3H,), 6.82 (4H, d, *J* = 8.57 Hz, Ar-*H*), 6.24 (4H, d, *J* = 9.08 Hz, Ar-*H*), 5.98 (4H, br s, Ar-*H*), 4.31 (1H, sep, *J* = 6.68 Hz, C*H*(CH$_3$)$_2$), 3.92 (1H, sep, *J* = 6.54 Hz, C*H*(CH$_3$)$_2$), 3.34 (1H, s, $^{\mathrm{Me2}}$CAAC-C*H*), 3.32-3.09 (8H, m, (C$_6$H$_4$)NC*H*$_2$CH$_3$), 2.91 (2H, m, C*H*(CH$_3$)$_2$), 2.83 (1H, s, $^{\mathrm{Me2}}$CAAC-C*H*), 2.10 (1H, d, *J* = 12.63 Hz, pyrrolidine-CH$_2$), 2.03 (1H, d, *J* = 12.57 Hz, pyrrolidine-CH$_2$), 1.76 (1H, d, *J* = 12.51 Hz, pyrrolidine-CH$_2$), 1.65 (1H, d, *J* = 12.43 Hz, pyrrolidine-CH$_2$), 1.60 (3H, s, pyrrolidine-CH$_3$), 1.53 (3H, d, *J* = 6.67 Hz, CH(C*H*$_3$)$_2$), 1.53 (3H, s, pyrrolidine-CH$_3$), 1.48 (3H, d, *J* = 6.47 Hz, CH(C*H*$_3$)$_2$), 1.27 (3H, s, pyrrolidine-CH$_3$), 1.23 (3H, d, CH(C*H*$_3$)$_2$), 1.21 (3H, d, *J* = 6.67 Hz, CH(C*H*$_3$)$_2$), 1.16, 1.14, 1.13, 1.04 (12H, m, (C$_6$H$_4$)NCH$_2$CH$_3$), 0.93 (3H, d, *J* = 6.68 Hz, CH(C*H*$_3$)$_2$), 0.88 (3H, s, pyrrolidine-CH$_3$), 0.73 (3H, s, pyrrolidine-CH$_3$), 0.58 (3H, s, pyrrolidine-CH$_3$), 0.35 (3H, d, *J* = 6.67 Hz, CH(CH$_3$)$_2$), 0.20 (3H, d, *J* = 6.70 Hz, CH(CH$_3$)$_2$). **^{13}C{1H} NMR** (JMOD, 101 MHz, CDCl$_3$) δ 152.17, 151.50, 148.51, 148.17, 148.05, 147.90, 147.62, 147.05, 146.92, 131.97 (*Ar*-H), 125.62 (*Ar*-H), 124.98 (*Ar*-H), 124.73 (*Ar*-H), 124.38 (*Ar*-H), 123.19 (*Ar*-H), 118.02, 117.80, 115.75, 110.59 (*Ar*-H), 110.32 (*Ar*-H), 88.11, 87.04, 77.01, 64.82, 63.30, 62.75, 61.30, 44.19, 34.28, 34.12, 33.89, 32.44, 31.68, 31.17, 28.93, 27.93, 27.68, 27.53, 27.18, 27.05, 26.42, 25.26, 24.94, 22.92, 22.58, 12.78, 12.40, 12.31. **^{1}H{^{11}B} NMR** (400 MHz, CDCl$_3$) δ 7.15 (3H,), 6.82 (4H, d, *J* = 8.57 Hz, Ar-*H*), 6.24 (4H, d, *J* = 9.08 Hz, Ar-*H*), 5.98 (4H, br s, Ar-*H*), 4.31 (1H, sep, *J* = 6.68 Hz, C*H*(CH$_3$)$_2$), 3.92 (1H, sep, *J* = 6.54 Hz, C*H*(CH$_3$)$_2$), 3.34 (1H, s, **$^{\mathbf{Me2}}$**CAAC-C*H*), 3.32-3.09 (8H, m, (C$_6$H$_4$)NC*H*$_2$CH$_3$), 2.91 (2H, m, C*H*(CH$_3$)$_2$), 2.83 (1H, s, **$^{\mathbf{Me2}}$**CAAC-C*H*), 2.76-2.20 (10H, br s, B-*H*), 2.10 (1H, d, *J* = 12.63 Hz, pyrrolidine-CH$_2$), 2.03 (1H, d, *J* = 12.57 Hz, pyrrolidine-CH_2), 1.76 (1H, d, *J* = 12.51 Hz, pyrrolidine-CH_2), 1.65 (1H, d, *J* = 12.43 Hz, pyrrolidine-CH_2), 1.60 (3H, s, pyrrolidine-CH_3), 1.53 (3H, d, *J* = 6.67 Hz, $CH(C\mathit{H}_3)_2$), 1.53 (3H, s, pyrrolidine-CH_3), 1.48 (3H, d, *J* = 6.47 Hz, $CH(C\mathit{H}_3)_2$), 1.27 (3H, s, pyrrolidine-CH_3), 1.23 (3H, d, $CH(C\mathit{H}_3)_2$), 1.21 (3H, d, *J* = 6.67 Hz, $CH(C\mathit{H}_3)_2$), 1.16, 1.14, 1.13, 1.04 (12H, m, $(C_6H_4)NCH_2CH_3$), 0.93 (3H, d, *J* = 6.68 Hz, $CH(C\mathit{H}_3)_2$), 0.88 (3H, s, pyrrolidine-CH_3), 0.73 (3H, s, pyrrolidine-CH_3), 0.58 (3H, s, pyrrolidine-CH_3), 0.35 (3H, d, *J* = 6.67 Hz, $CH(CH_3)_2$), 0.20 (3H, d, *J* = 6.70 Hz, $CH(CH_3)_2$). **^{11}B NMR** (128 MHz, $CDCl_3$) δ 3.64 (s), -3.41 (s), -10.72, -11.54. **^{11}B{^{1}H}** NMR (128 MHz, $CDCl_3$) δ 3.40, -2.52, -3.70, -11.23, -12.81.

4. NMR Spectra of Isolated Compounds

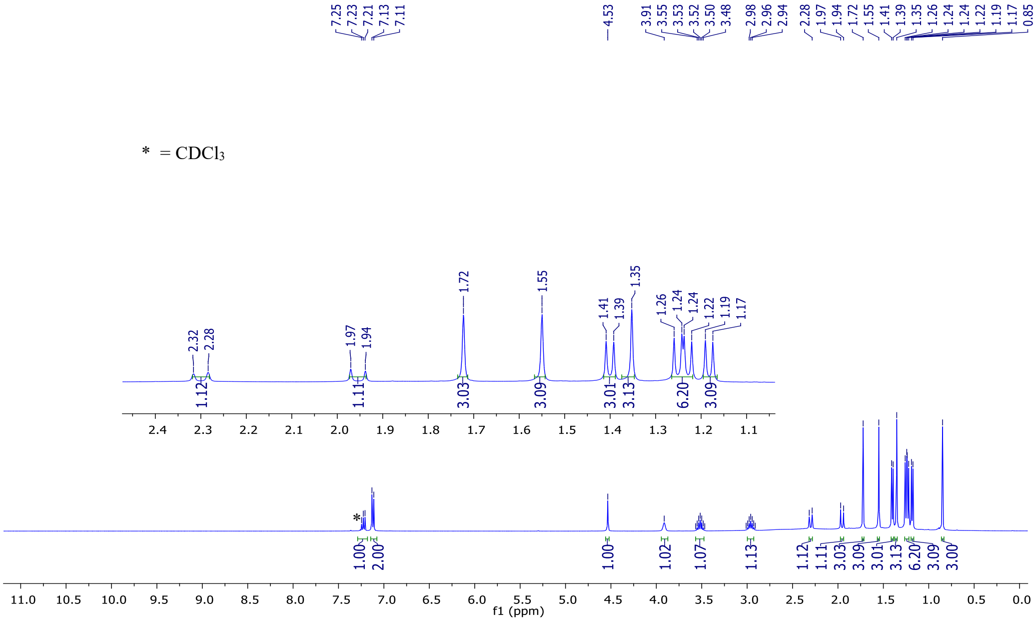


Figure S1. ^{1}H NMR spectrum (400 MHz, in $CDCl_3$) of **1**.

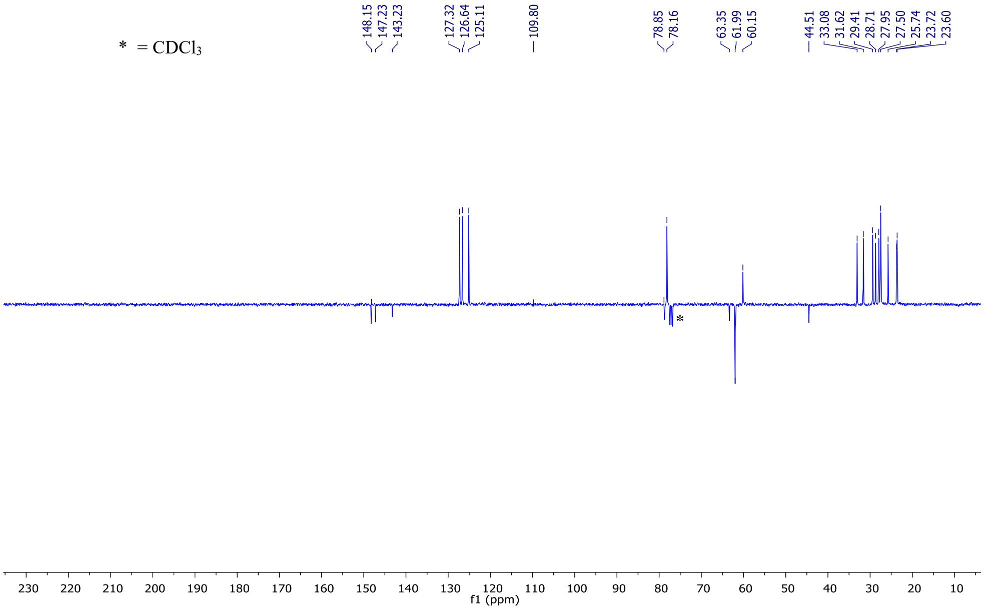


Figure S2. ^{13}C{1H} NMR spectrum (JMOD, 101 MHz, in $CDCl_3$) of **1**.

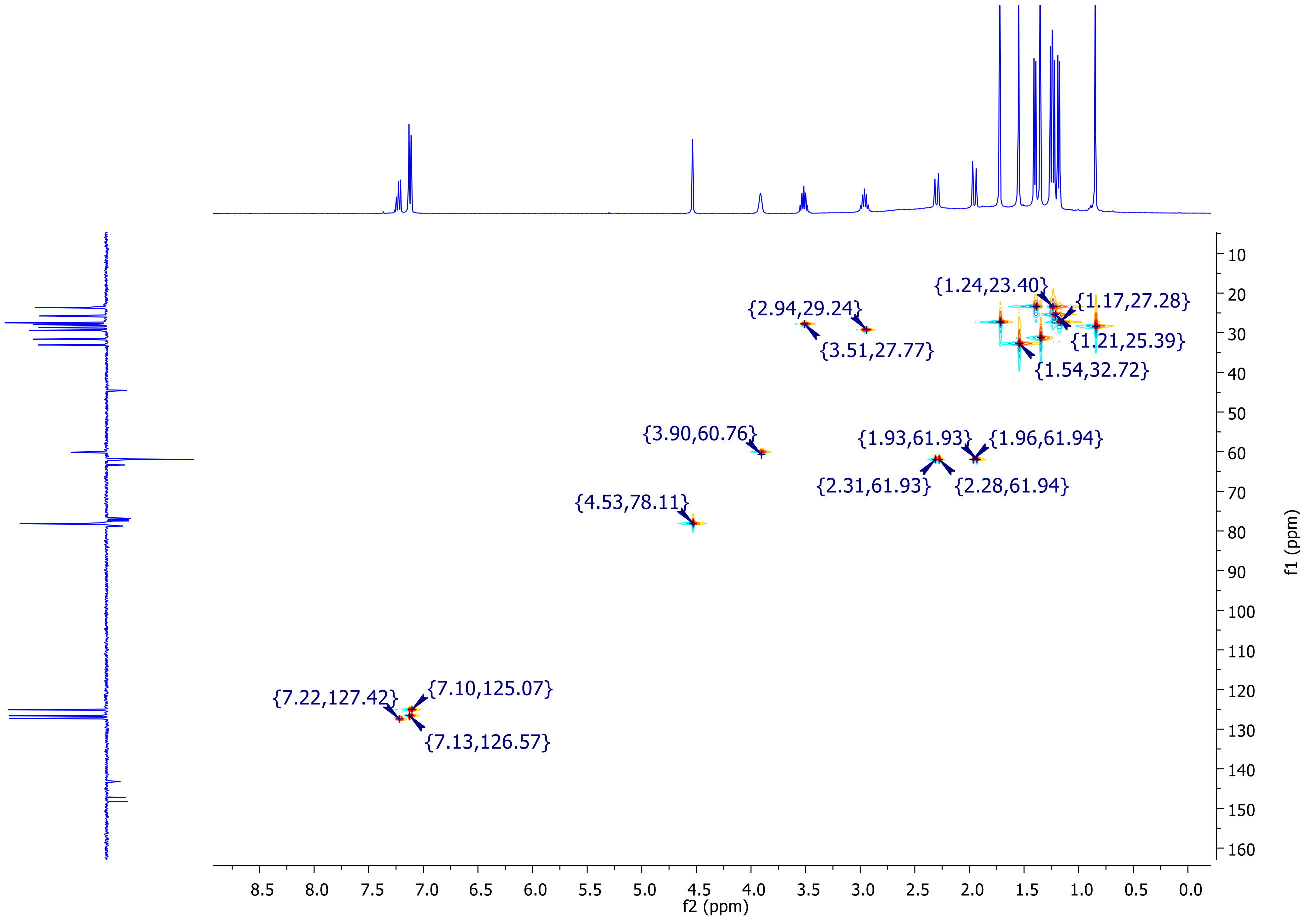


Figure S3. ^{1}H-^{13}C HSQC spectrum ($CDCl_3$) of **1**.

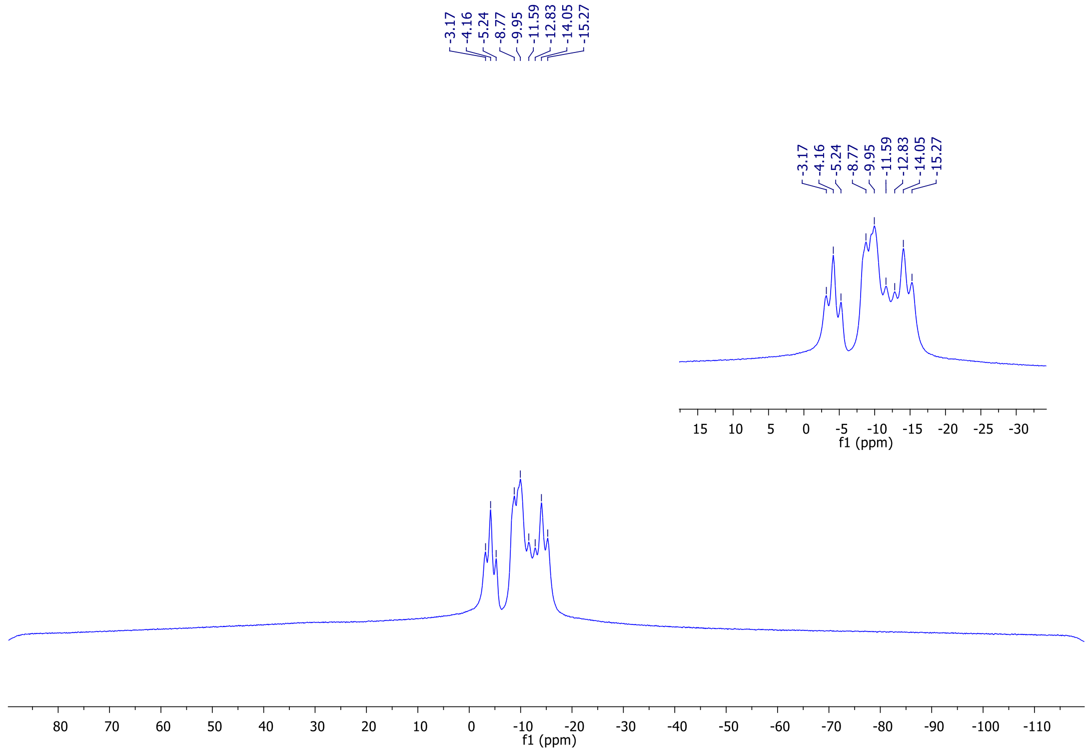


Figure S4. ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **1**.

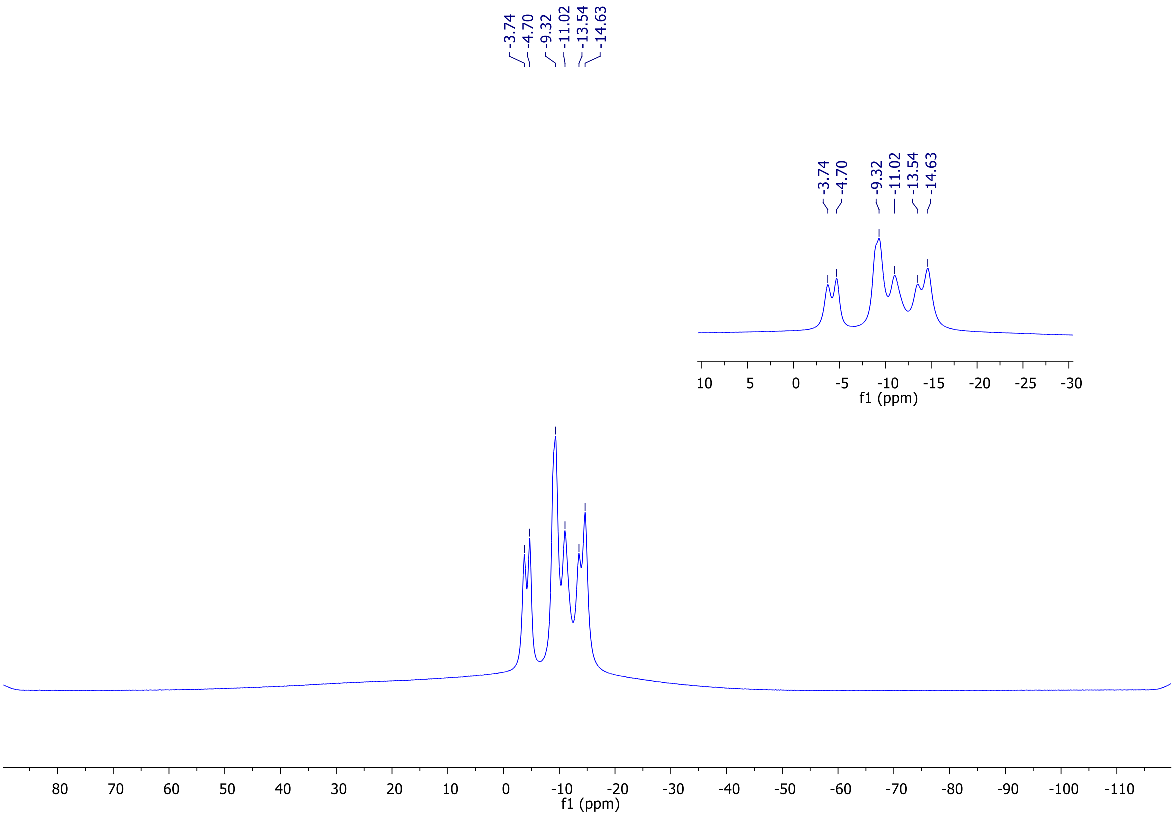


Figure S5. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, CDCl$_3$) of **1**.

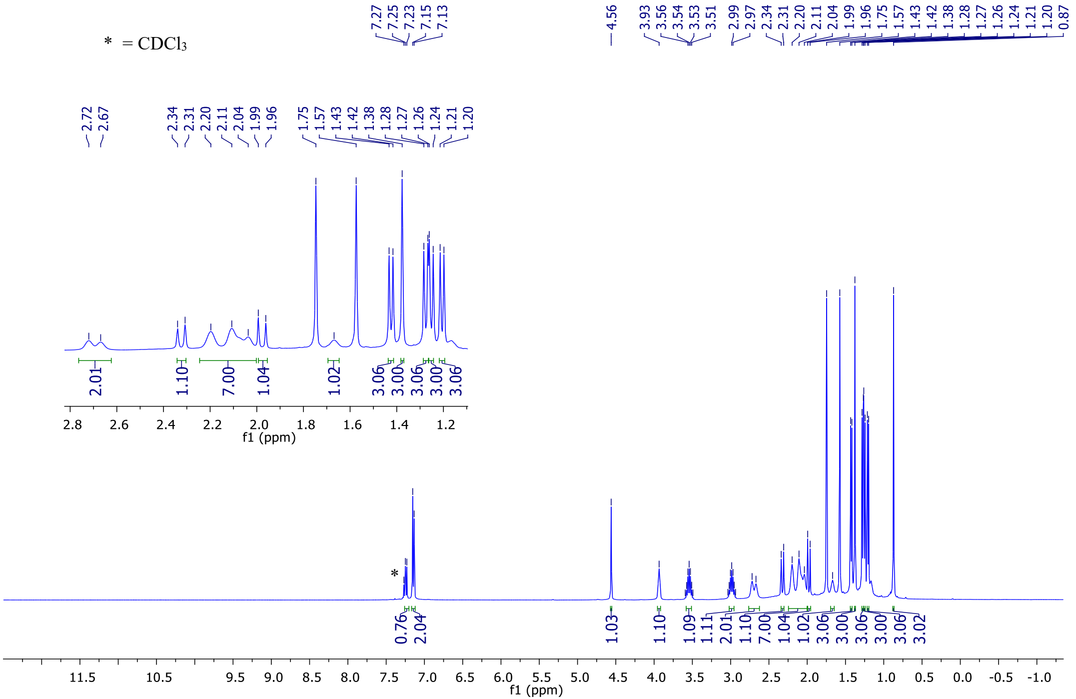


Figure S6. $^{1}H\{^{11}B\}$ NMR spectrum (400 MHz, CDCl$_3$) of **1**.

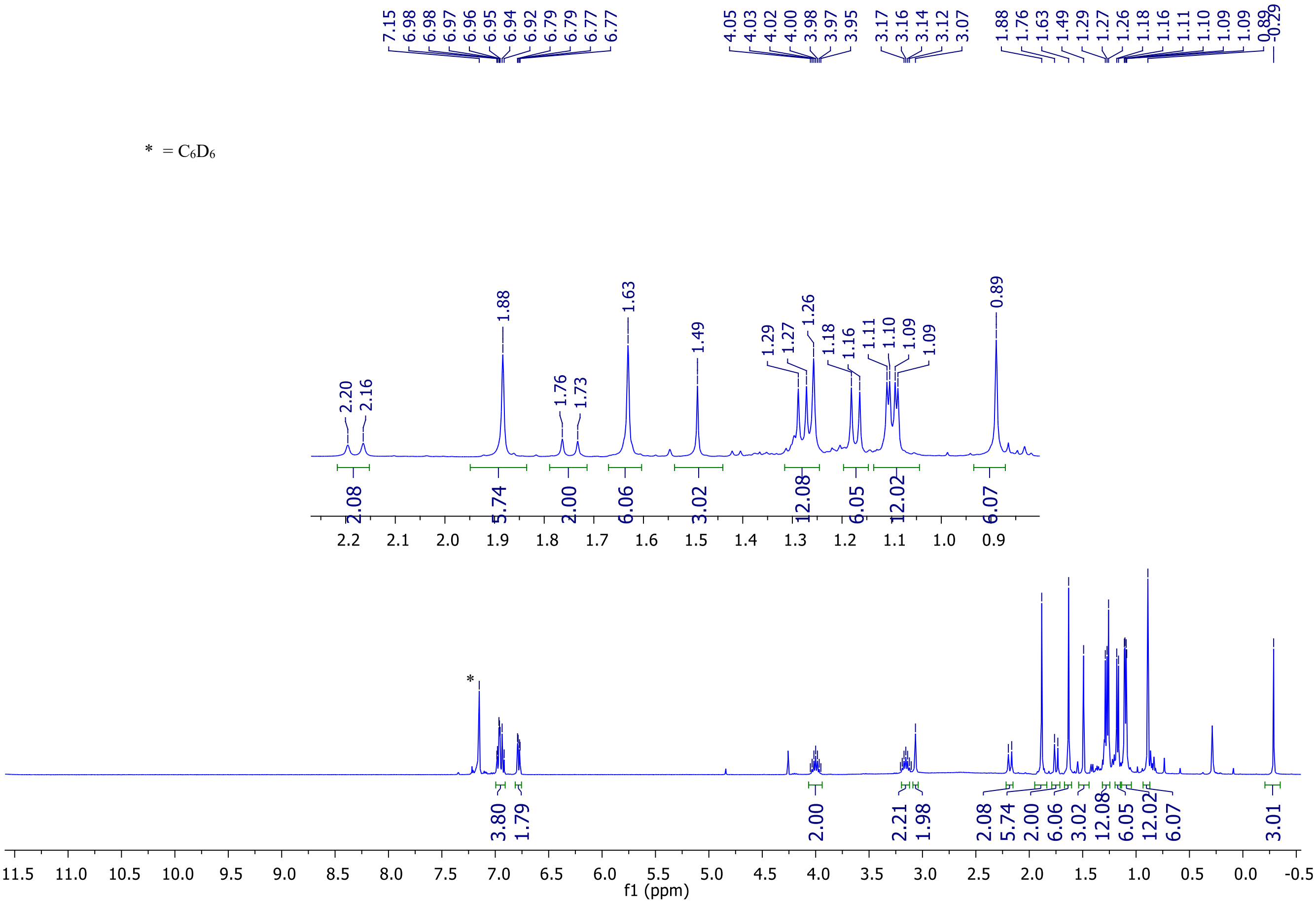


Figure S7. ${}^{1}H$ NMR spectrum (400 MHz, in C_6D_6) of $\mathbf{2^{clscls}}$.

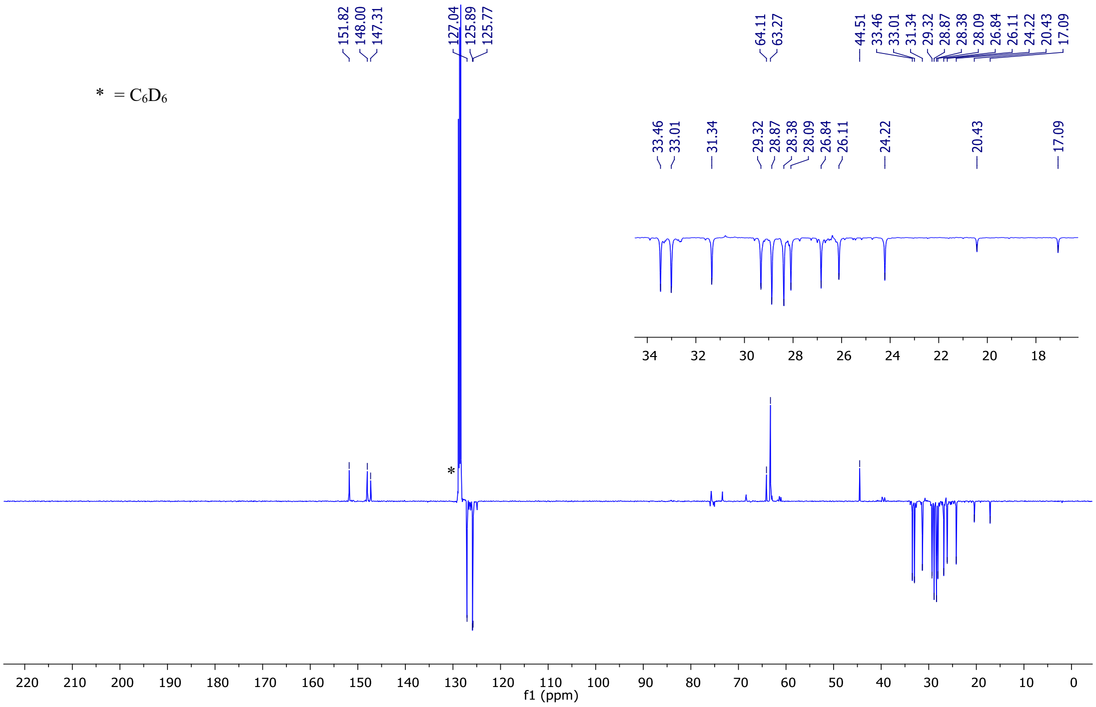


Figure S8. ${}^{13}C\{1H\}$ NMR spectrum (JMOD, 101 MHz, in C_6D_6) of $\mathbf{2^{clscls}}$.

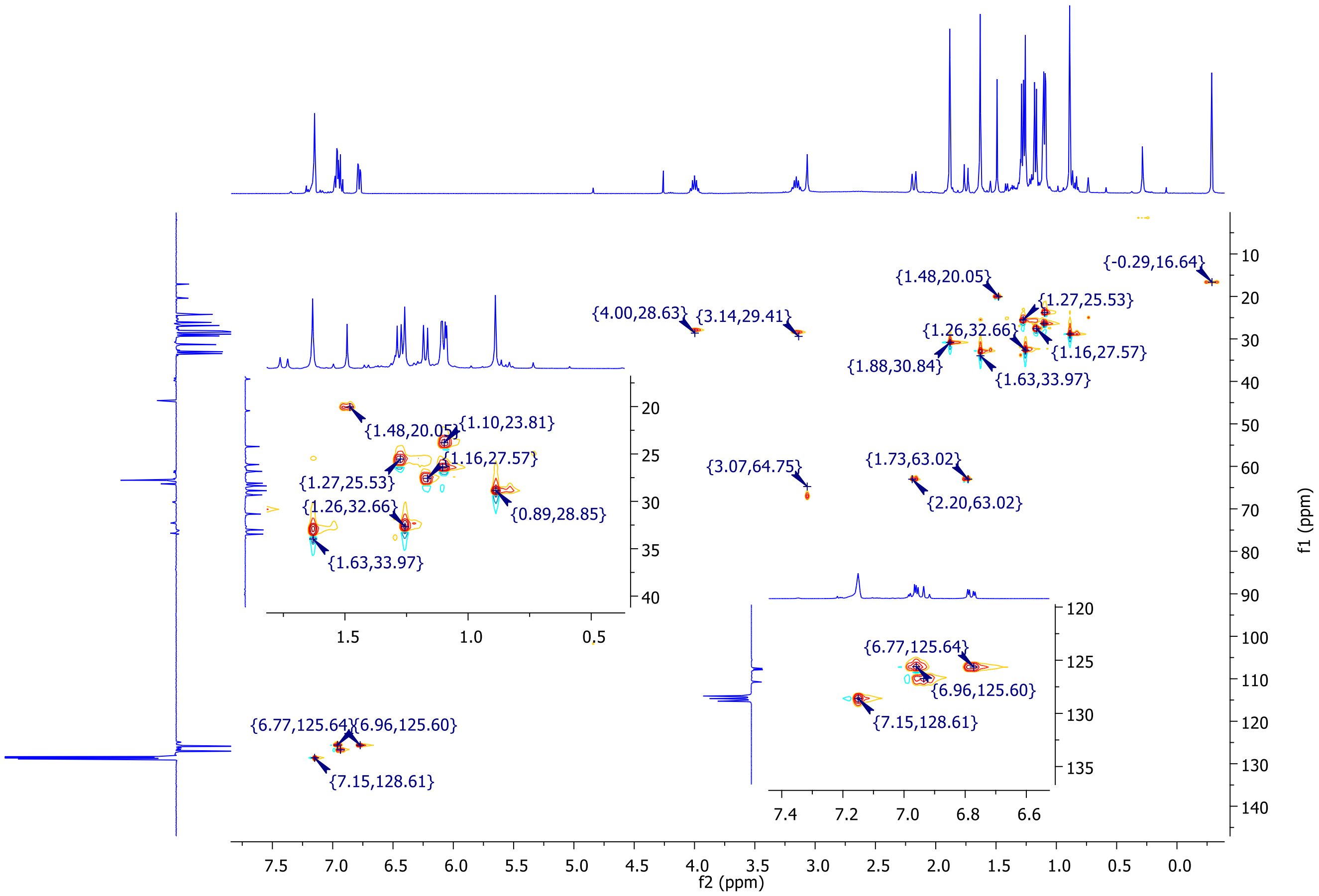


Figure S9. ^{1}H-^{13}C HSQC spectrum (CDCl$_3$) of **2$^{\mathbf{clscls}}$**.

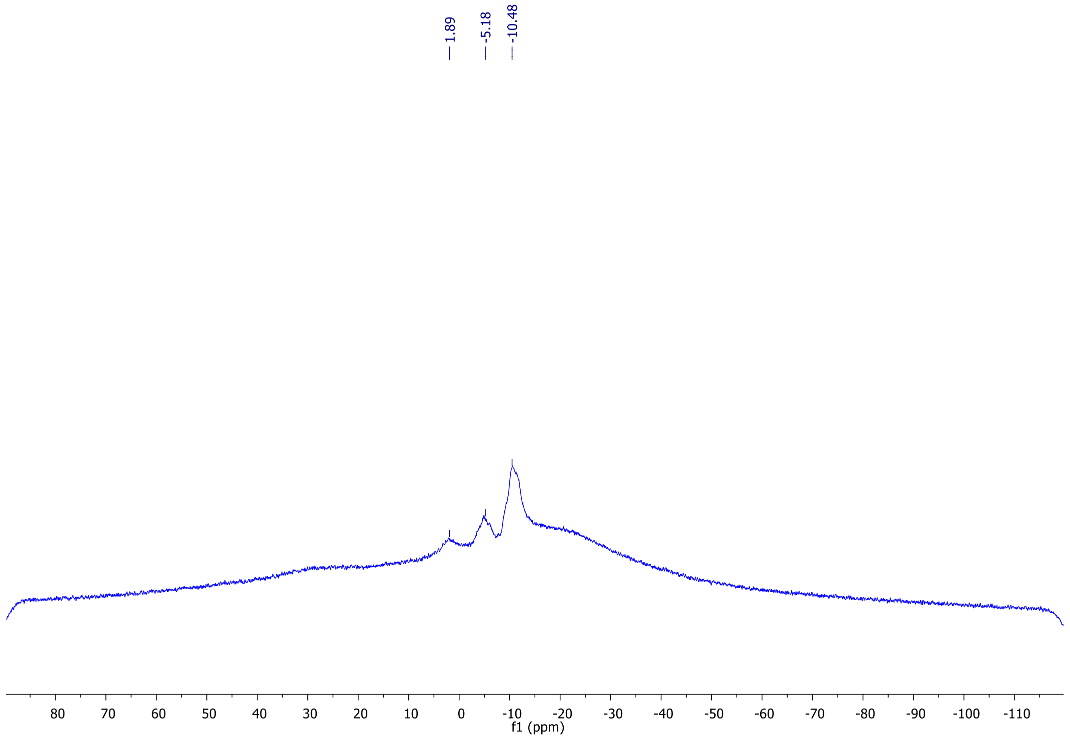


Figure S10. ^{11}B NMR spectrum (128 MHz, CDCl$_3$) of **2$^{\mathbf{clscls}}$**.

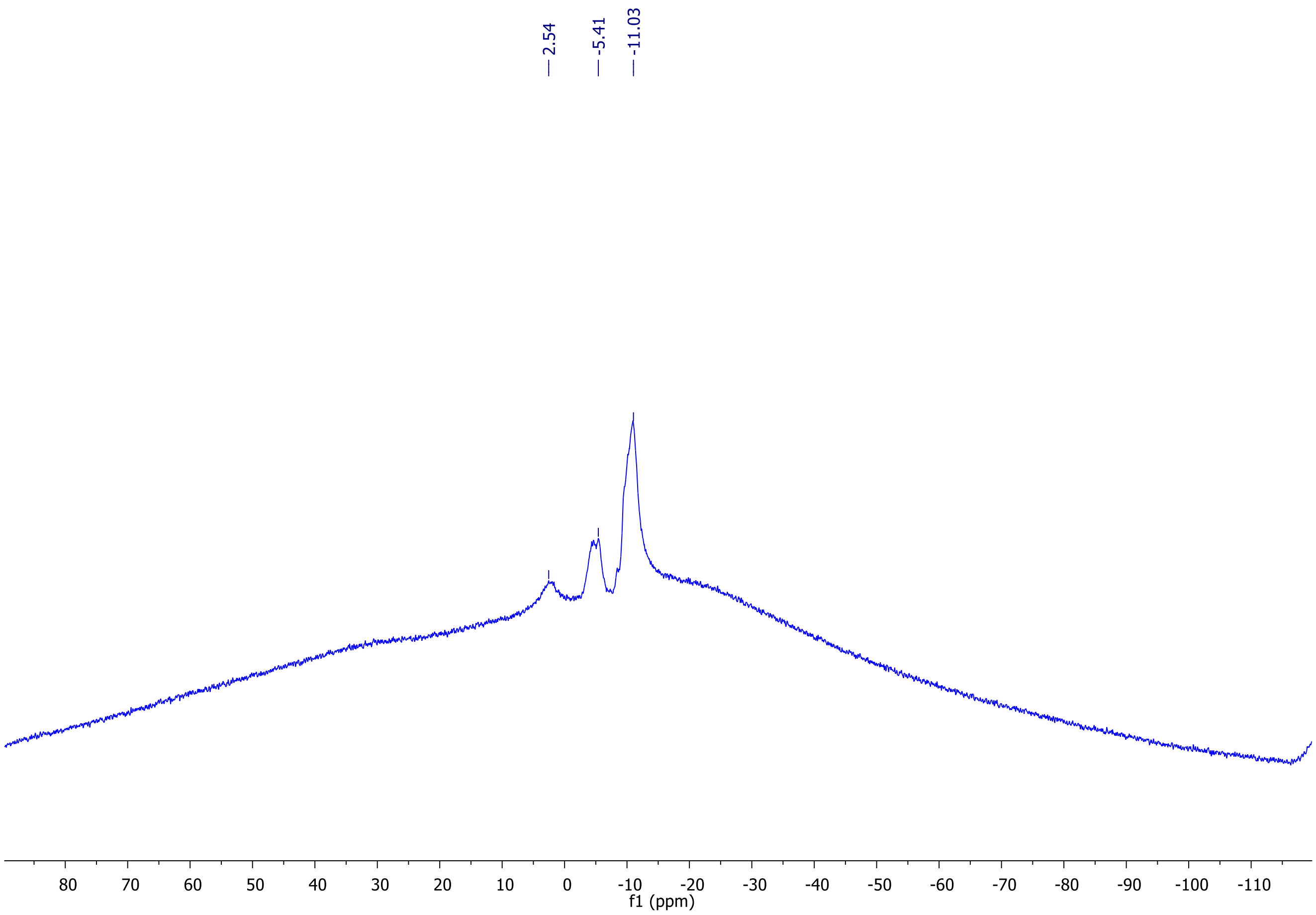


Figure S11. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, $CDCl_3$) of $\mathbf{2^{clscls}}$.

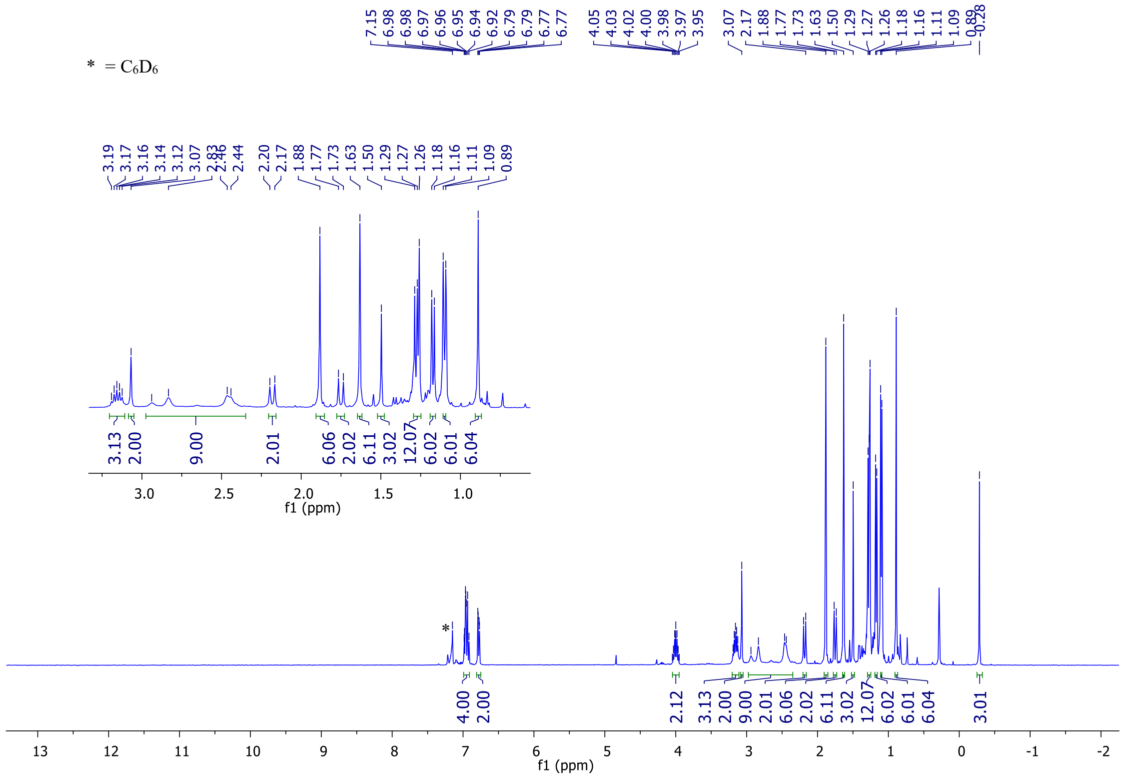


Figure S12. $^{1}H\{^{11}B\}$ NMR spectrum (128 MHz, $CDCl_3$) of $\mathbf{2^{clscls}}$.

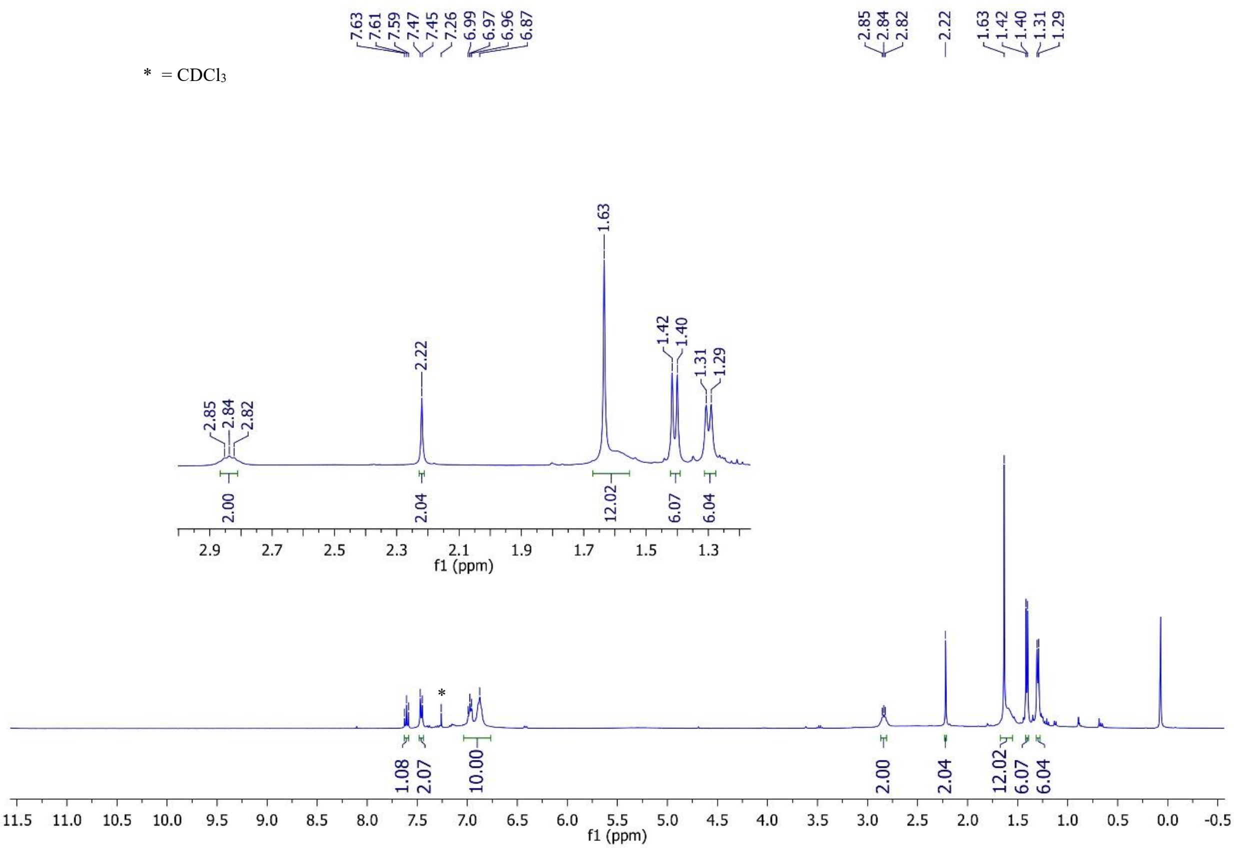


Figure S13. ^{1}H NMR spectrum (400 MHz, in CDCl$_3$) of $\mathbf{3^{nido}}$.

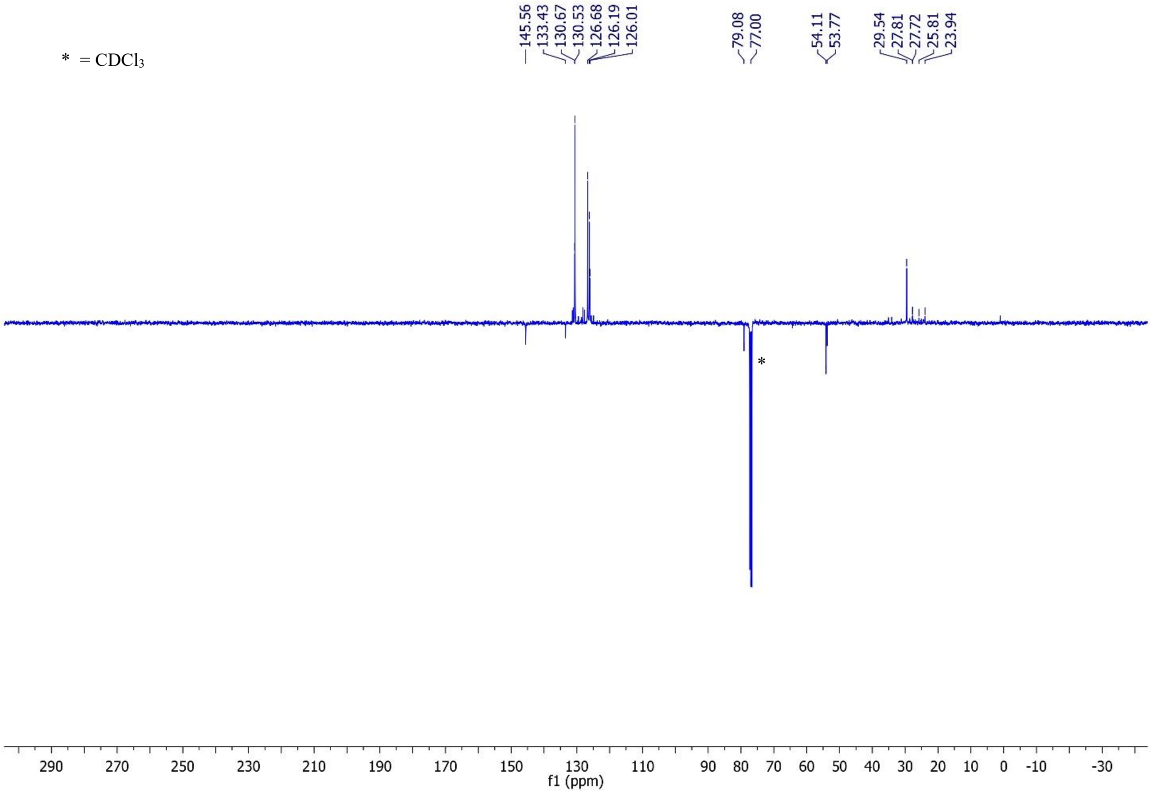


Figure S14. ^{13}C{1H} NMR spectrum (JMOD, 101 MHz, in CDCl$_3$) of $\mathbf{3^{nido}}$.

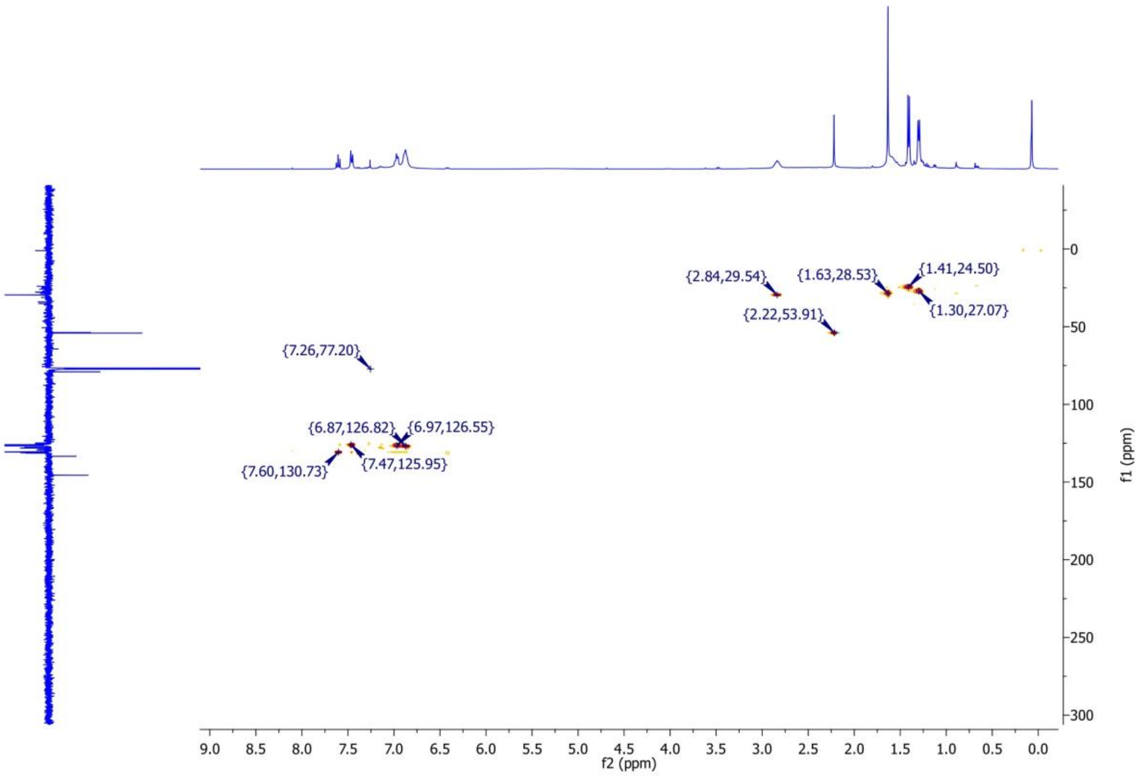


Figure S15. ^{1}H-^{13}C HSQC NMR spectrum (CDCl$_3$) of **3$^{\mathbf{nido}}$**.

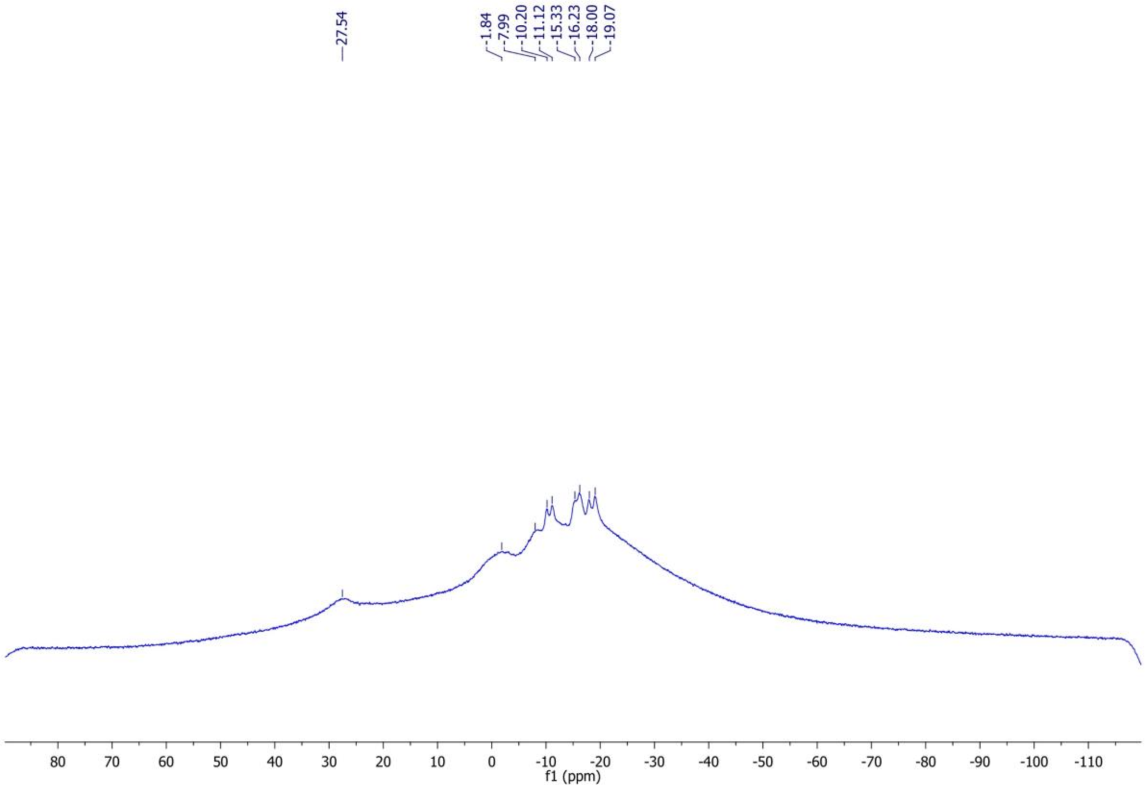


Figure S16. ^{11}B NMR spectrum (128 MHz, in CDCl$_3$) of **3$^{\mathbf{nido}}$**.

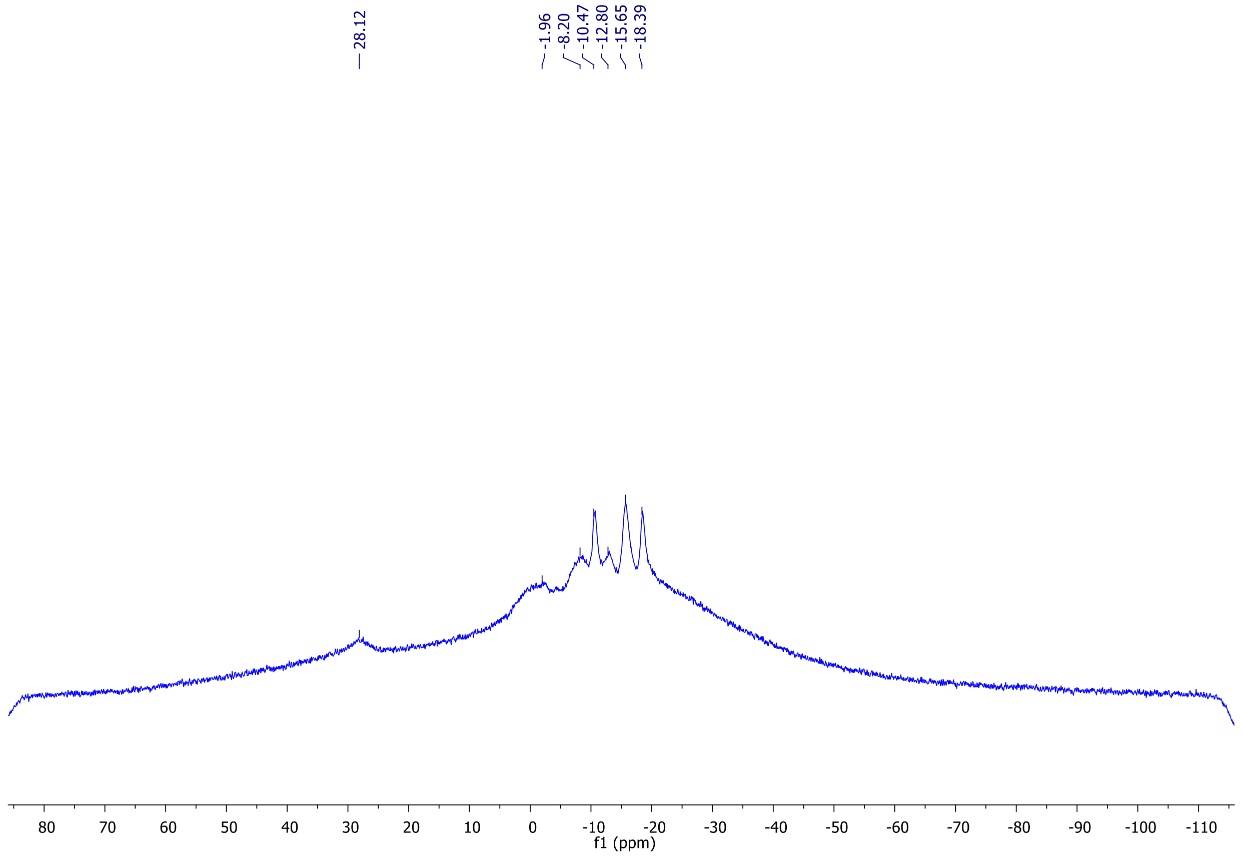


Figure S17. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, in $CDCl_3$) of $\mathbf{3^{nido}}$.

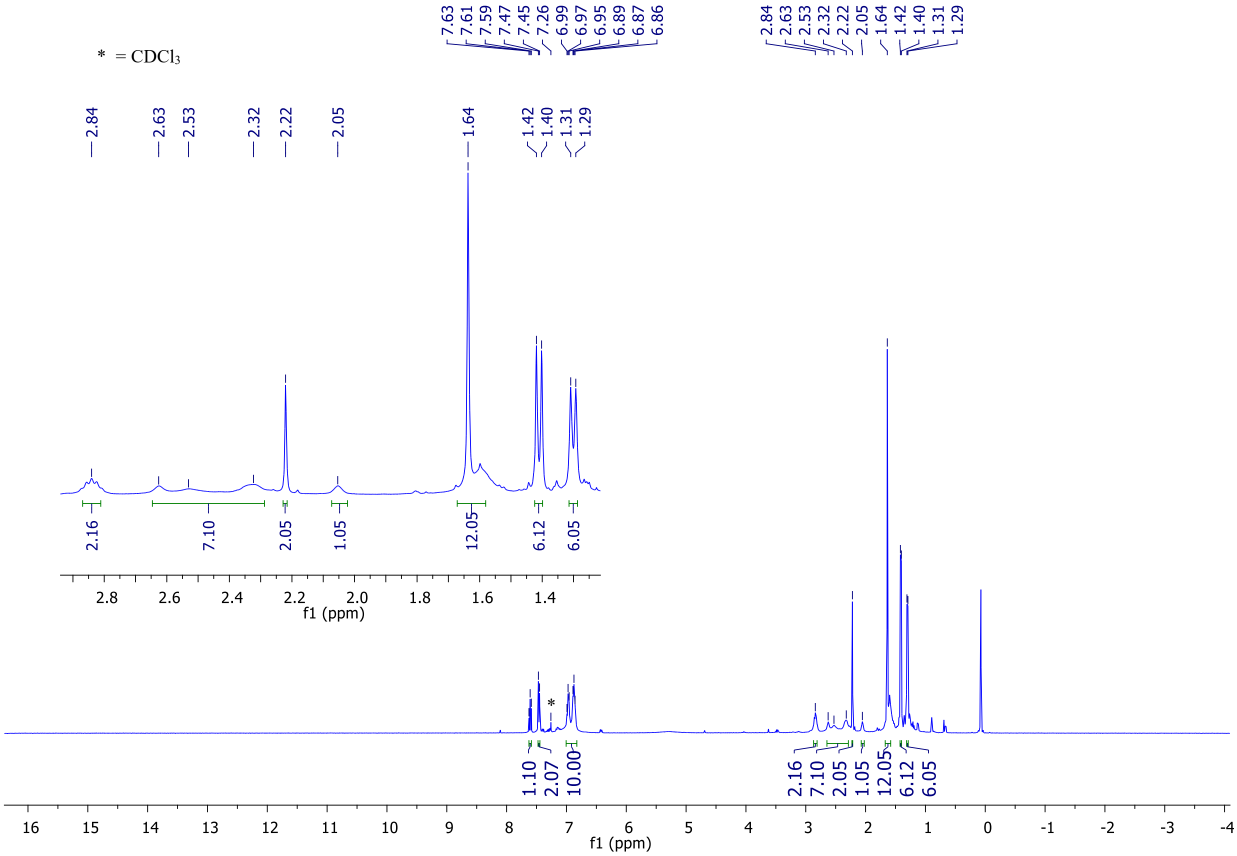


Figure S18. $^{1}H\{^{11}B\}$ NMR spectrum (400 MHz, in $CDCl_3$) of $\mathbf{3^{nido}}$.

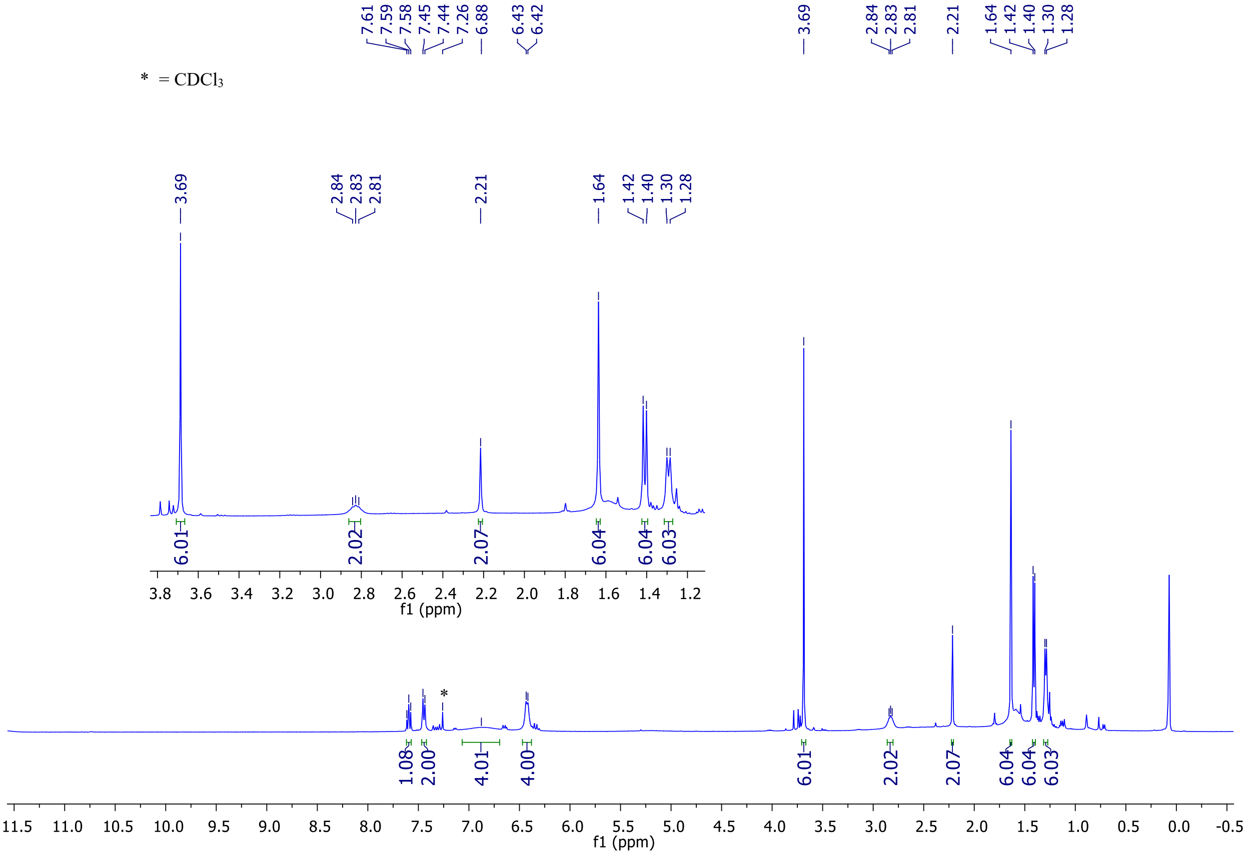


Figure S19. ^{1}H NMR spectrum (400 MHz, in $CDCl_3$) of $\mathbf{7^{nido}}$.

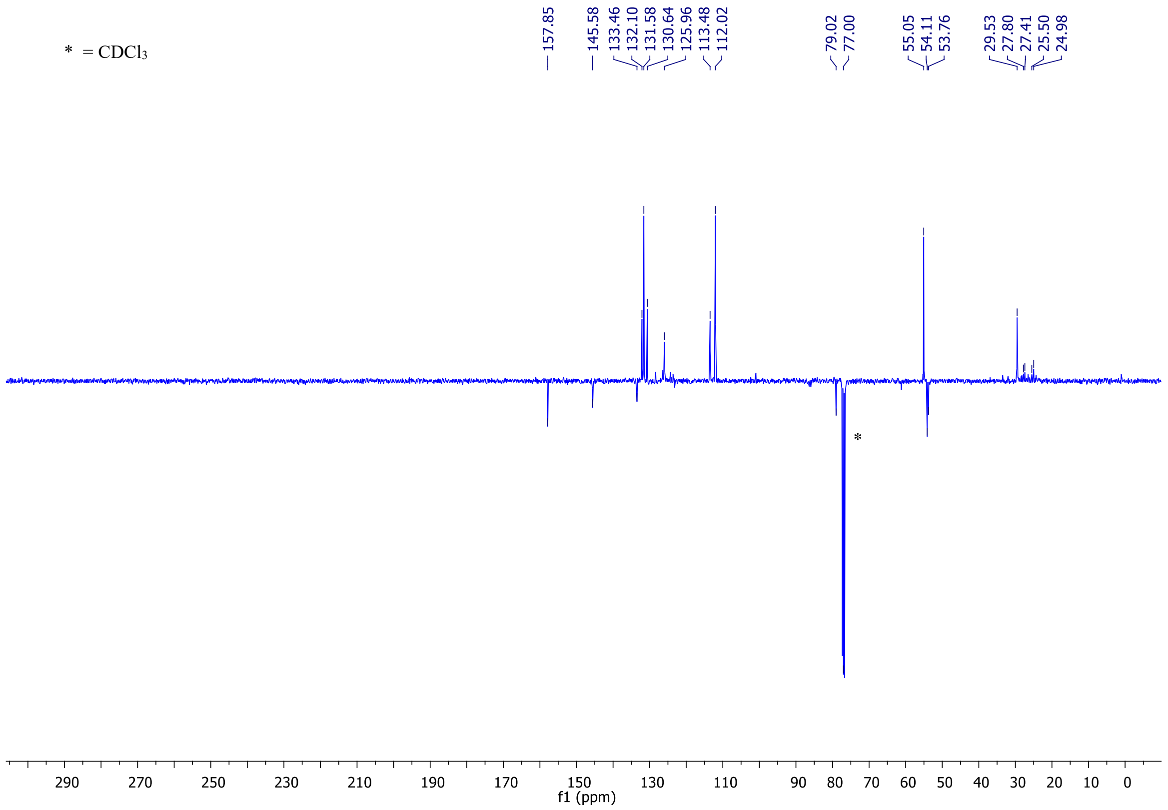


Figure S20. ^{13}C{1H} NMR spectrum (JMOD, 101 MHz, in $CDCl_3$) of $\mathbf{7^{nido}}$.

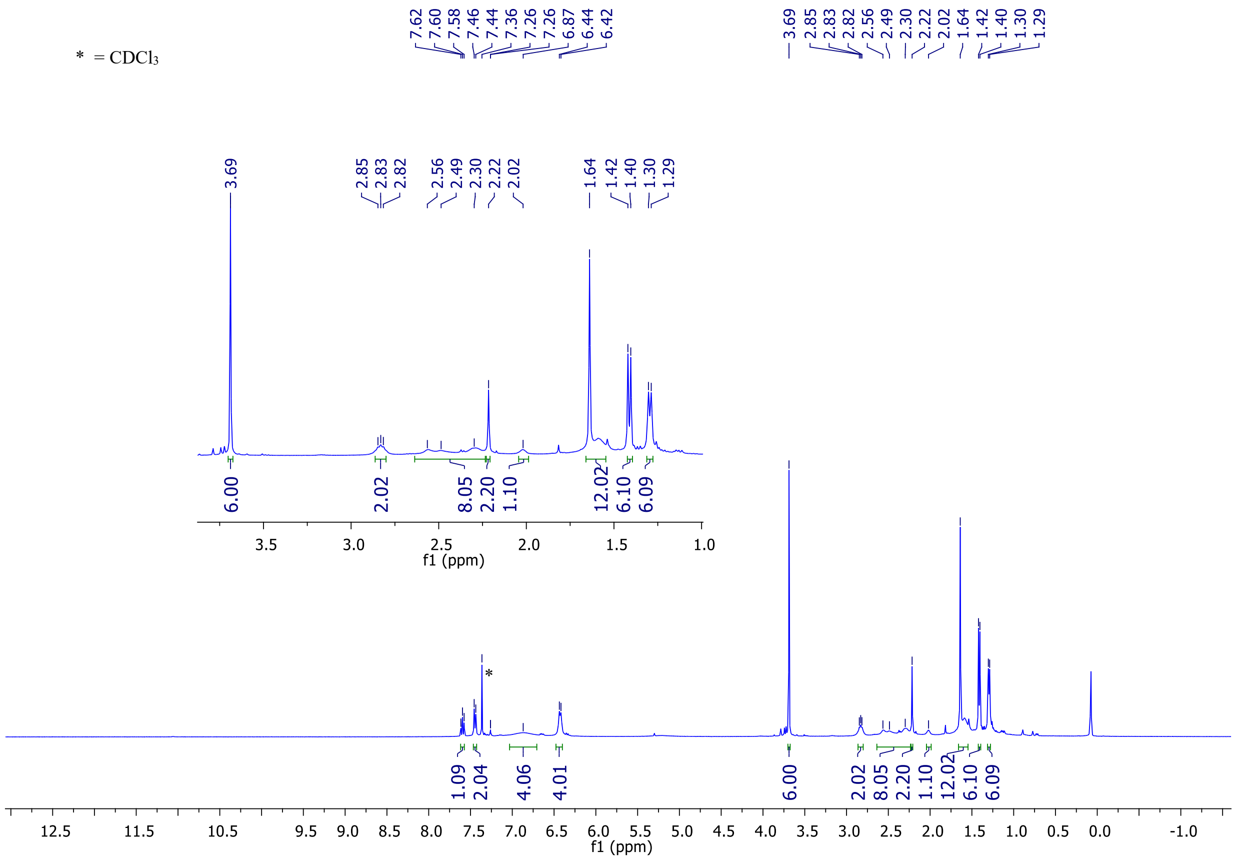


Figure S21. $^1H\{^{11}B\}$ NMR spectrum (400 MHz, in $CDCl_3$) of **7**$^{\mathbf{nido}}$.

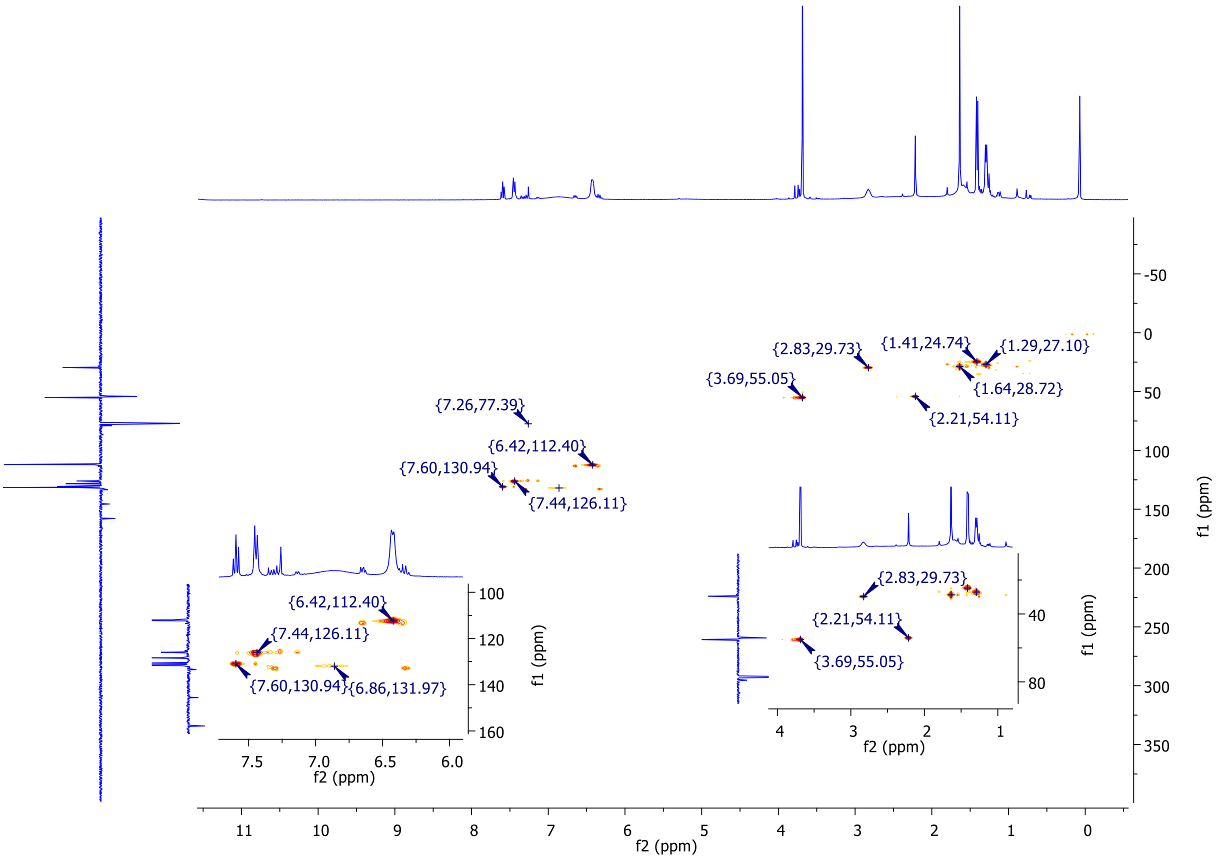


Figure S22. ^1H-^{13}C HSQC spectrum ($CDCl_3$) of **7**$^{\mathbf{nido}}$.

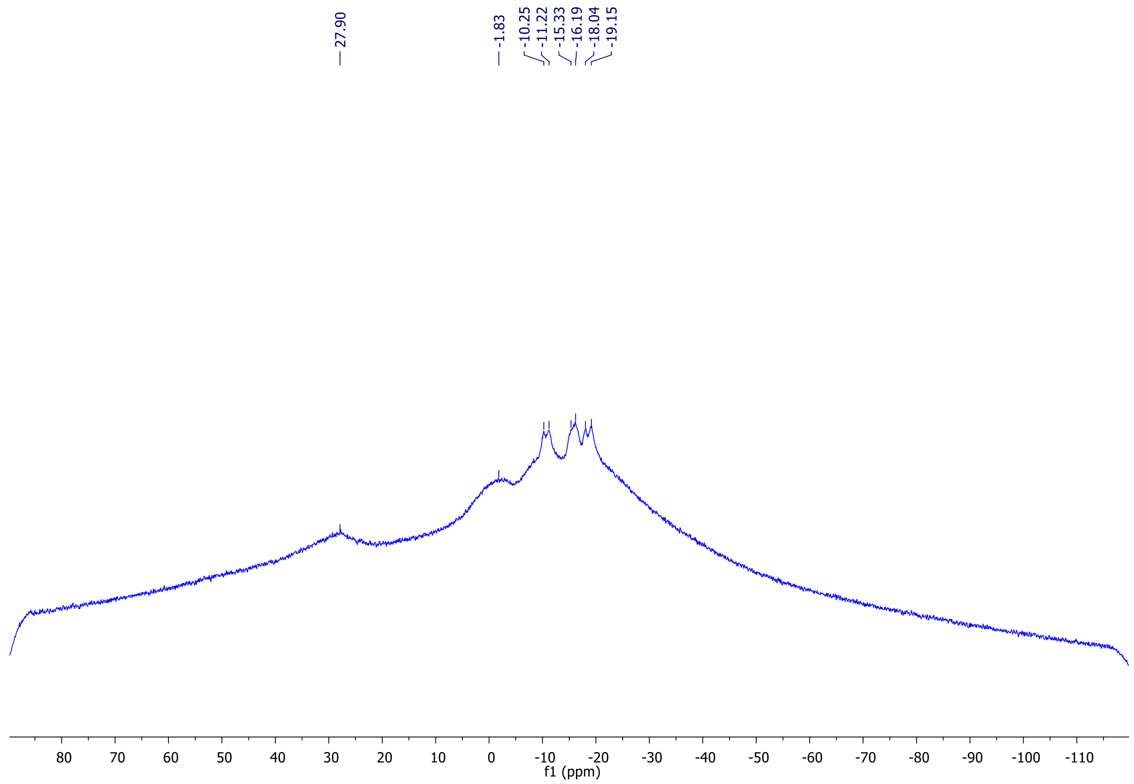


Figure S23. ^{11}B NMR spectrum(128 MHz, $CDCl_3$) of **7^{nido}**.

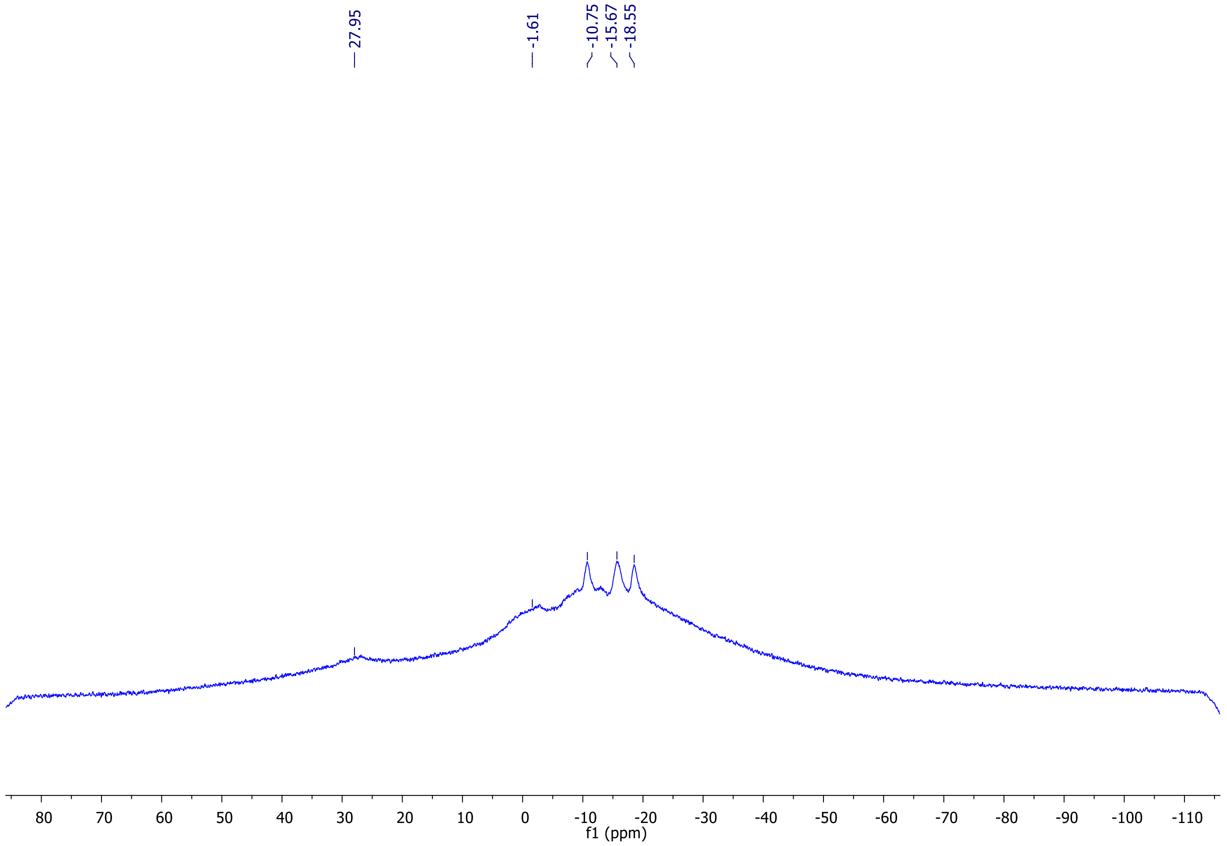


Figure S24. $^{11}B\{^{1}H\}$ NMR spectrum(128 MHz, $CDCl_3$)of **7^{nido}**.

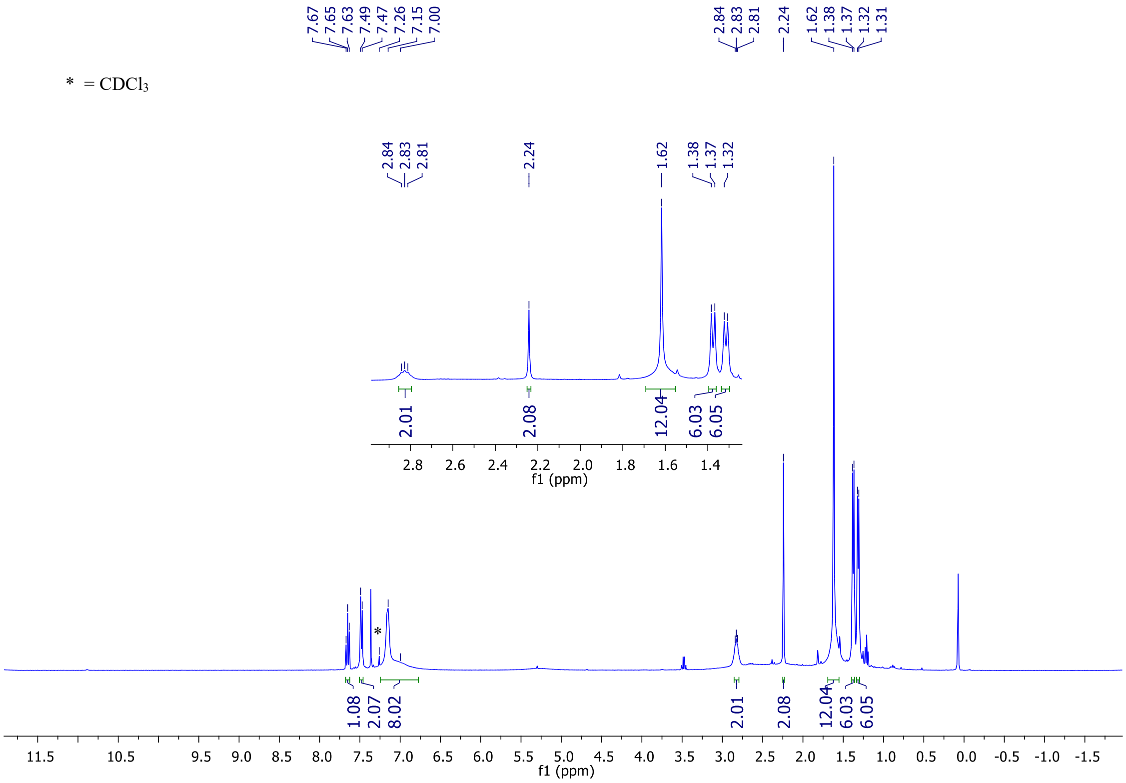


Figure S25. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **4$^{\text{nido}}$**.

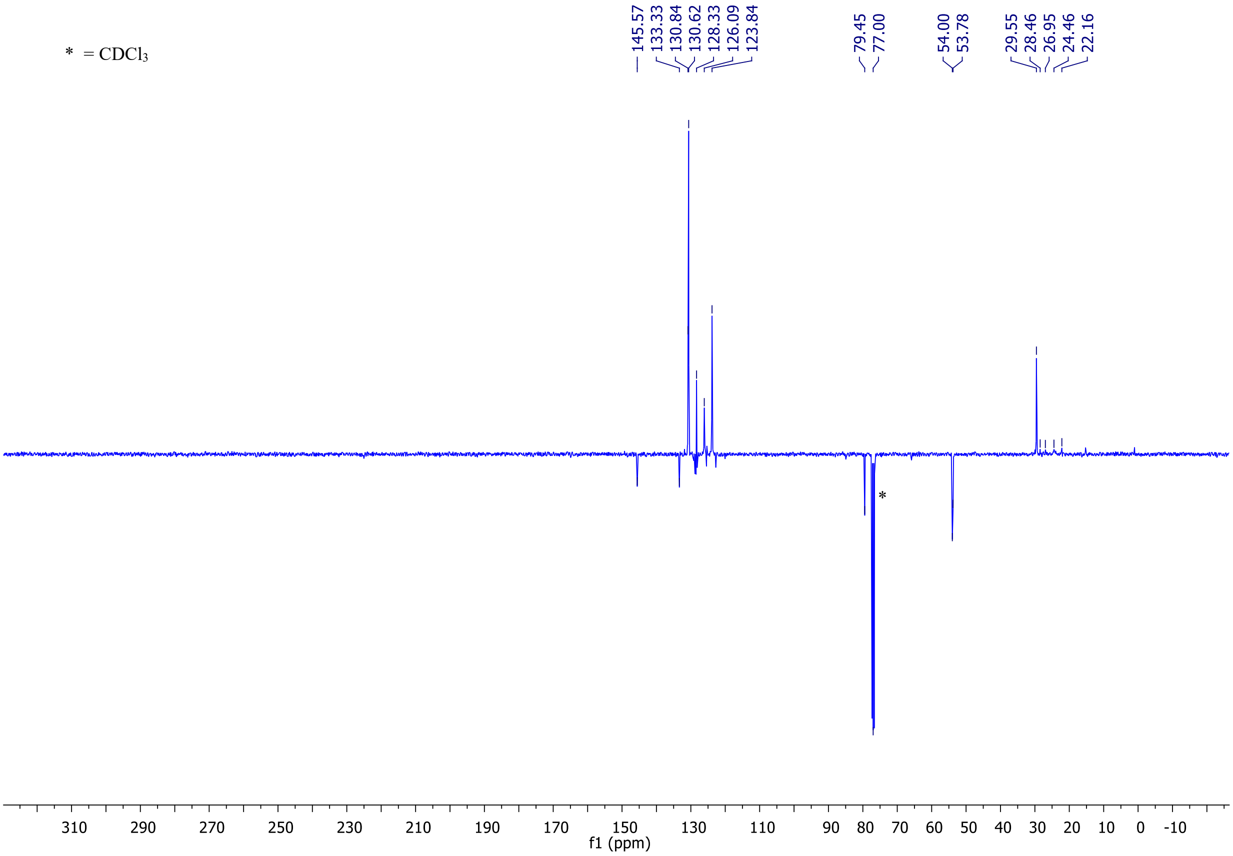


Figure S26. ^{13}C{1H} NMR spectrum (JMOD, 101 MHz, CDCl$_3$) of **4$^{\text{nido}}$**.

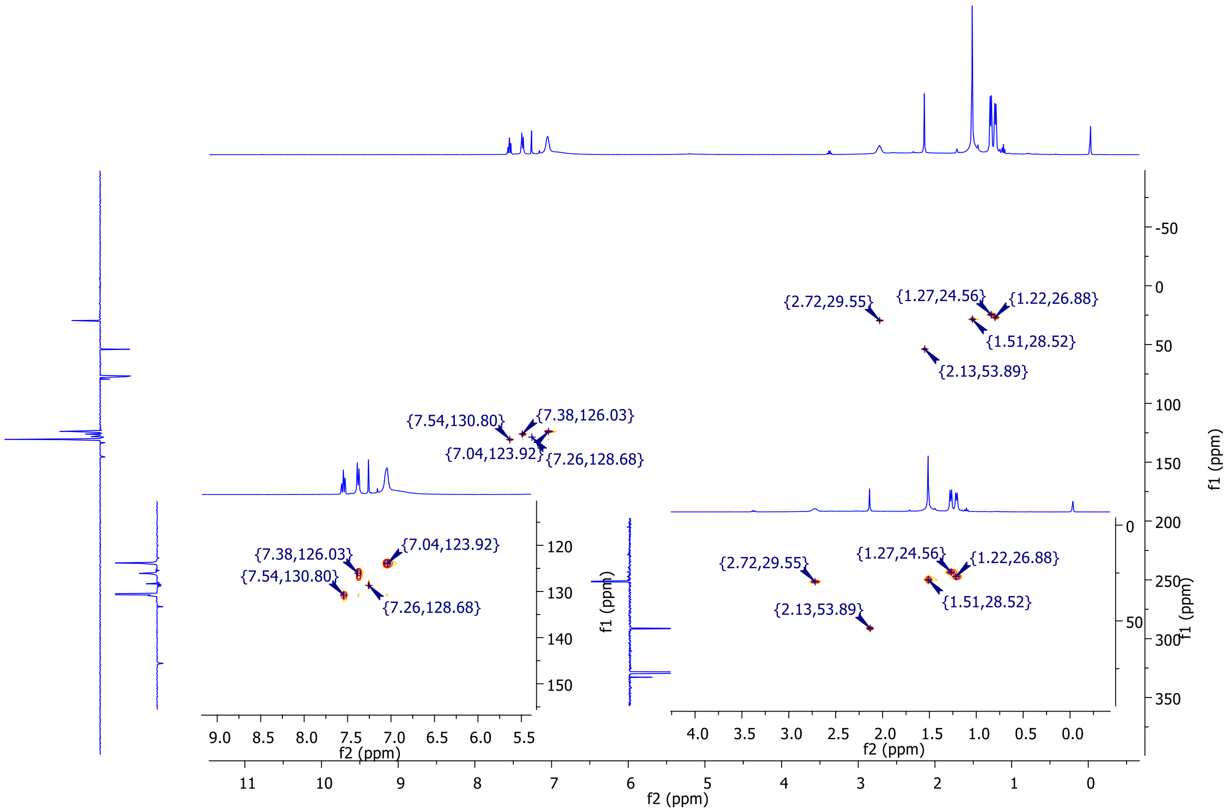


Figure S27. ^1H-^{13}C HSQC NMR spectrum ($CDCl_3$) of $\mathbf{4^{nido}}$.

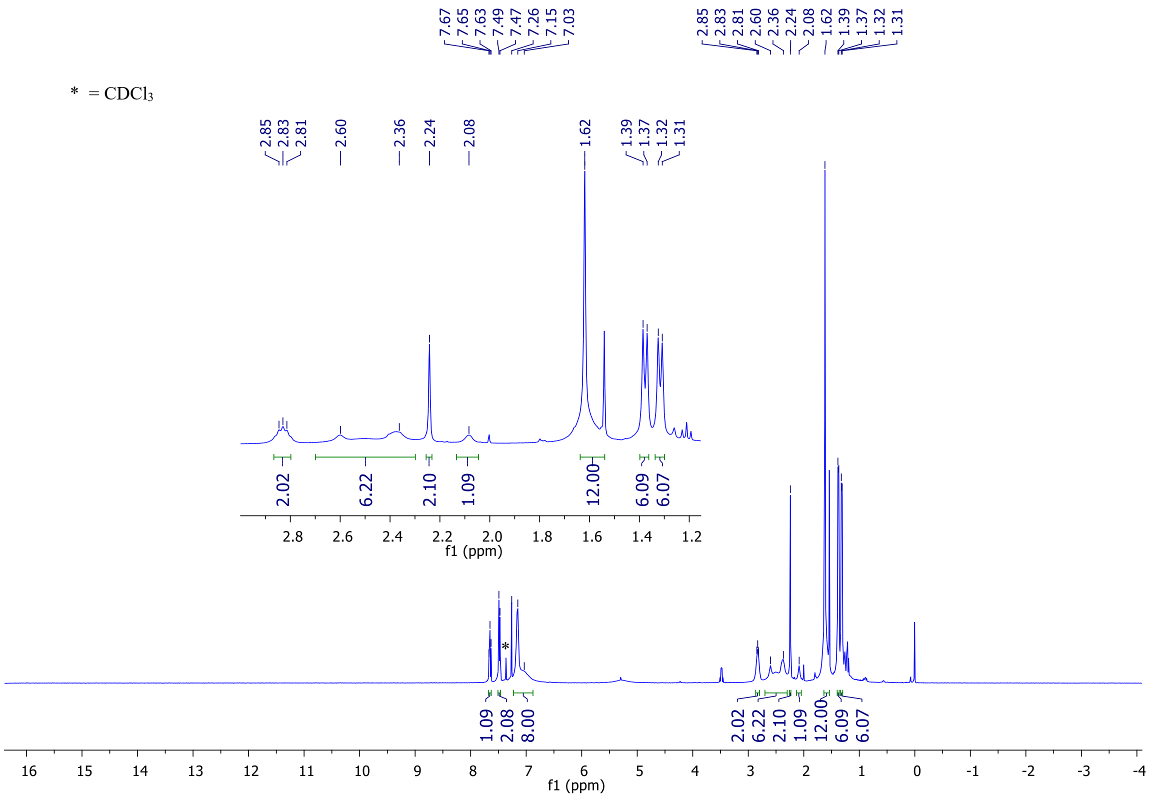


Figure S28. $^1H\{^{11}B\}$ NMR spectrum (400 MHz, $CDCl_3$) of $\mathbf{4^{nido}}$.

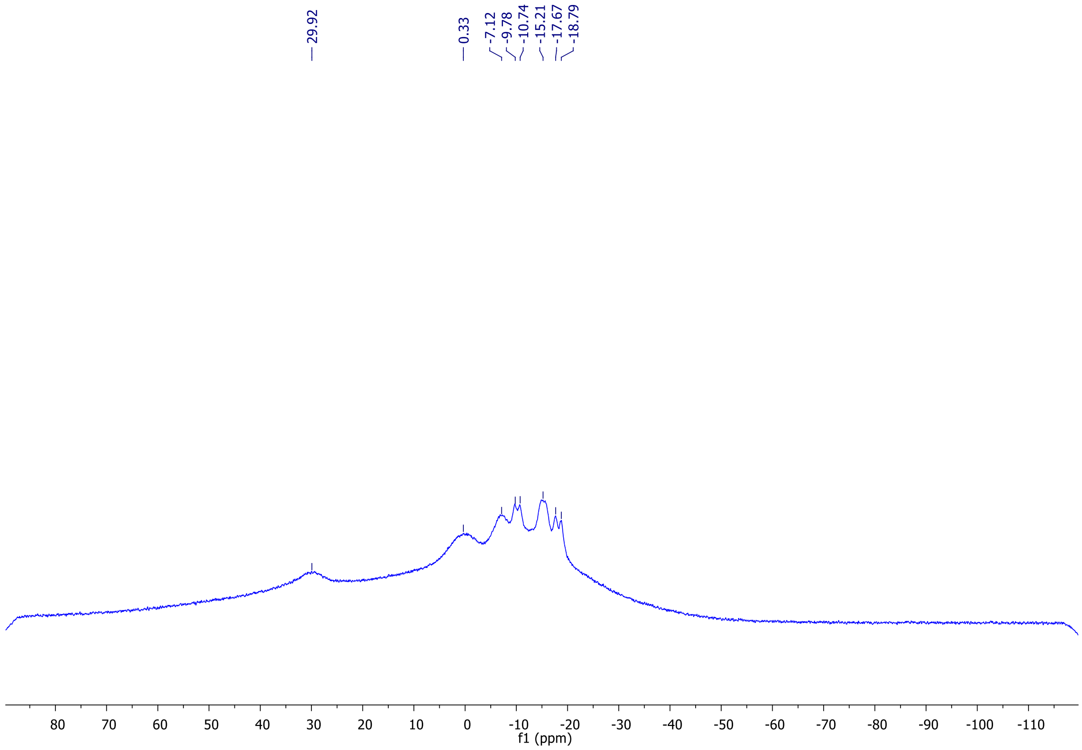


Figure S29. ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **4^{nido}**.

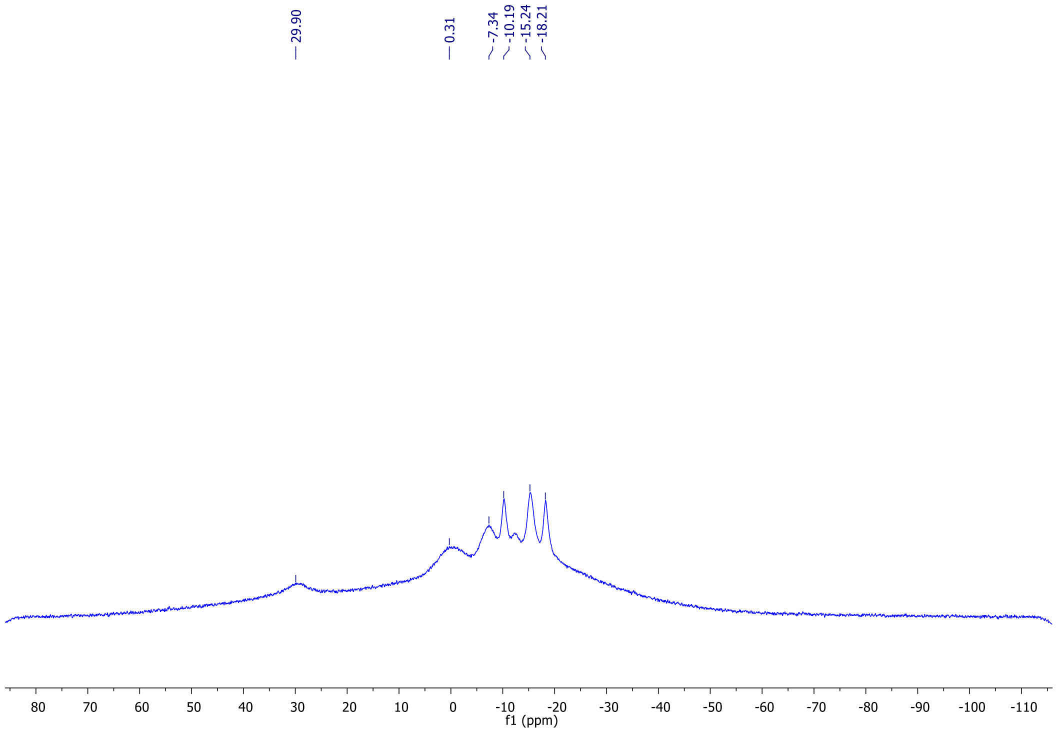


Figure S30. ^{11}B{^{1}H} NMR spectrum (128 MHz, $CDCl_3$) of **4^{nido}**.

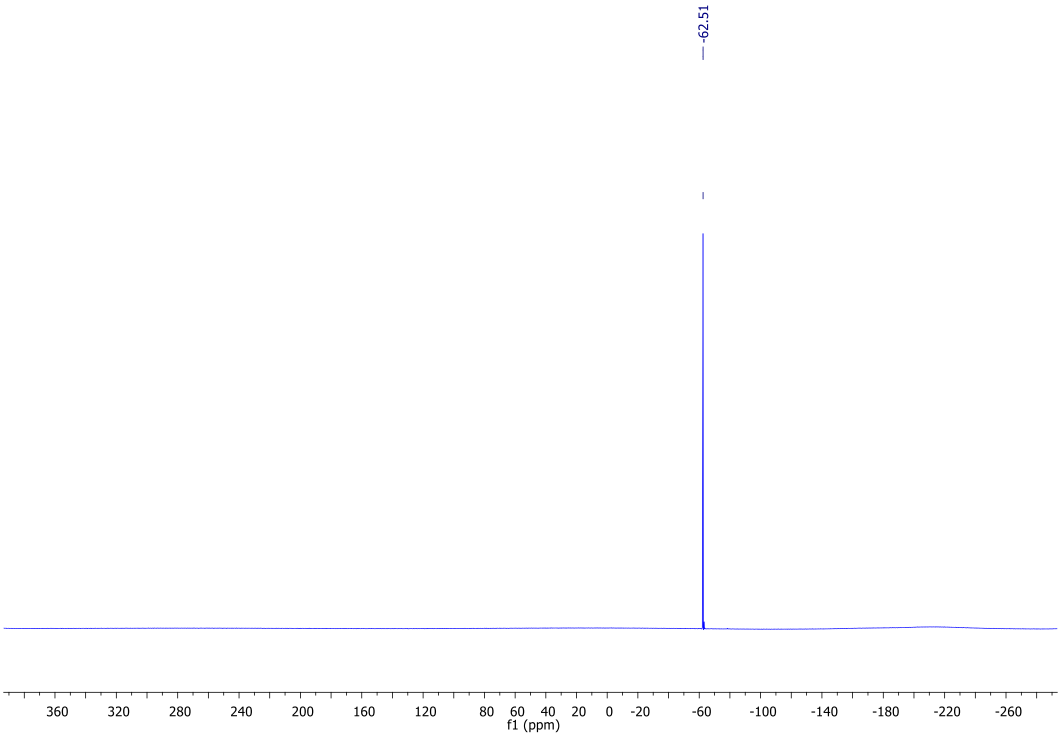


Figure S31. ^{19}F NMR spectrum (377 MHz, CDCl$_3$) of **4^{nido}**.

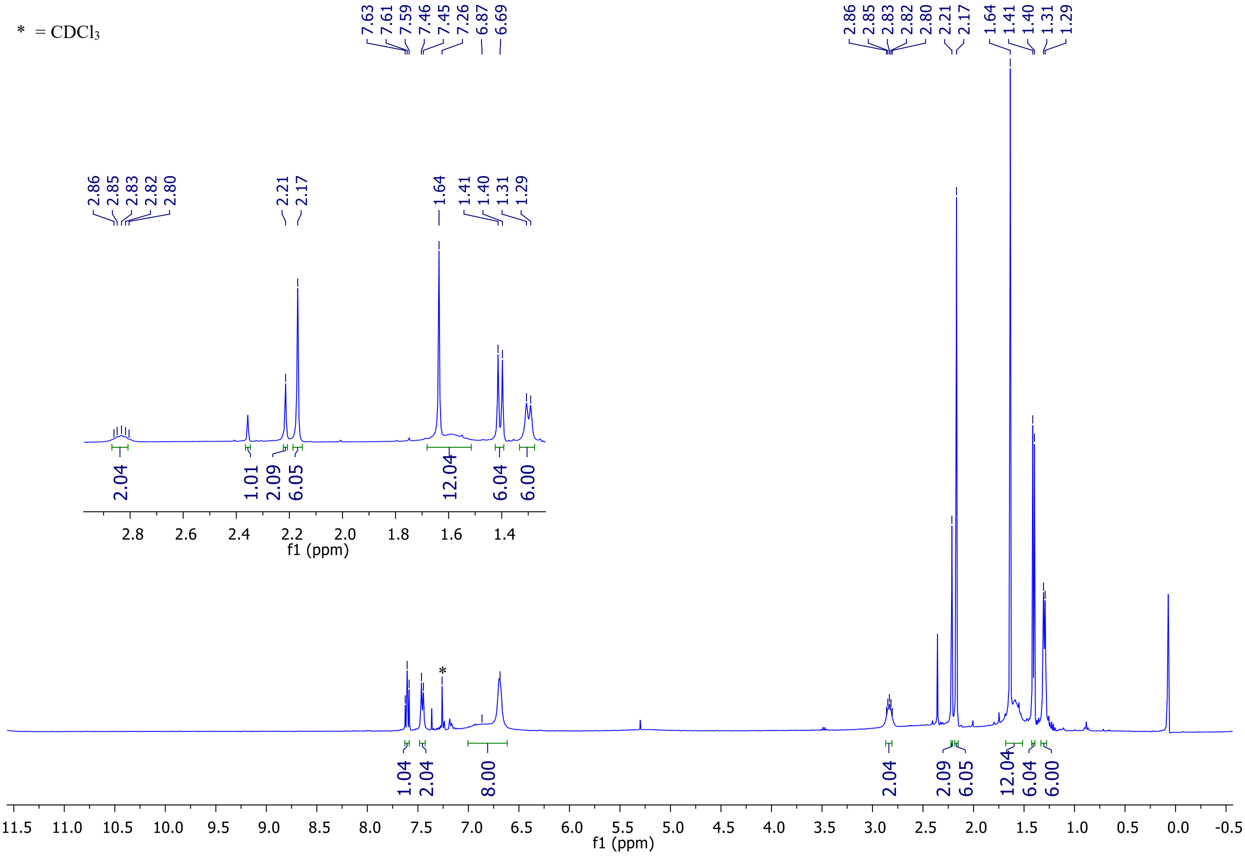


Figure S32. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **6^{nido}**.

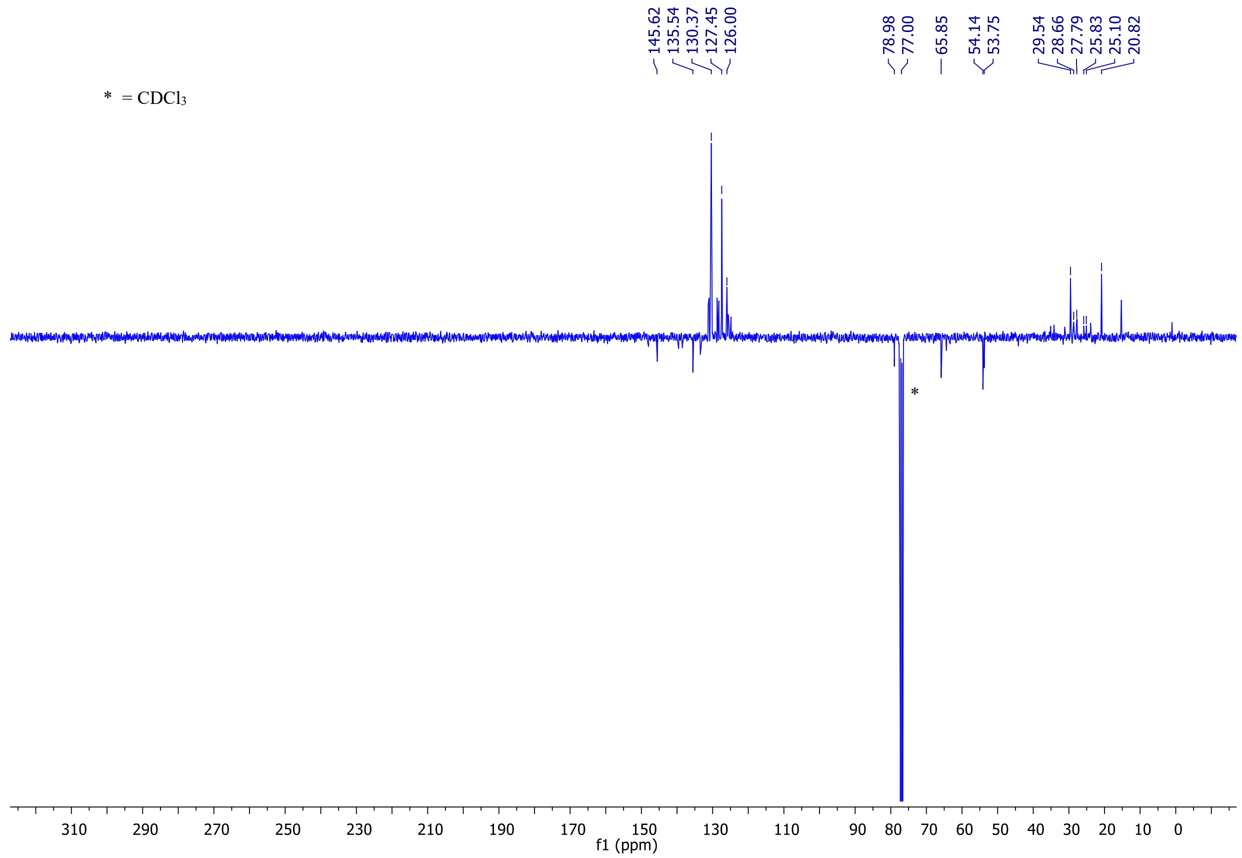


Figure S33. ${}^{13}C\{1H\}$ NMR spectrum (JMOD, 101 MHz, CDCl$_3$) of **6** $^{\mathbf{nido}}$.

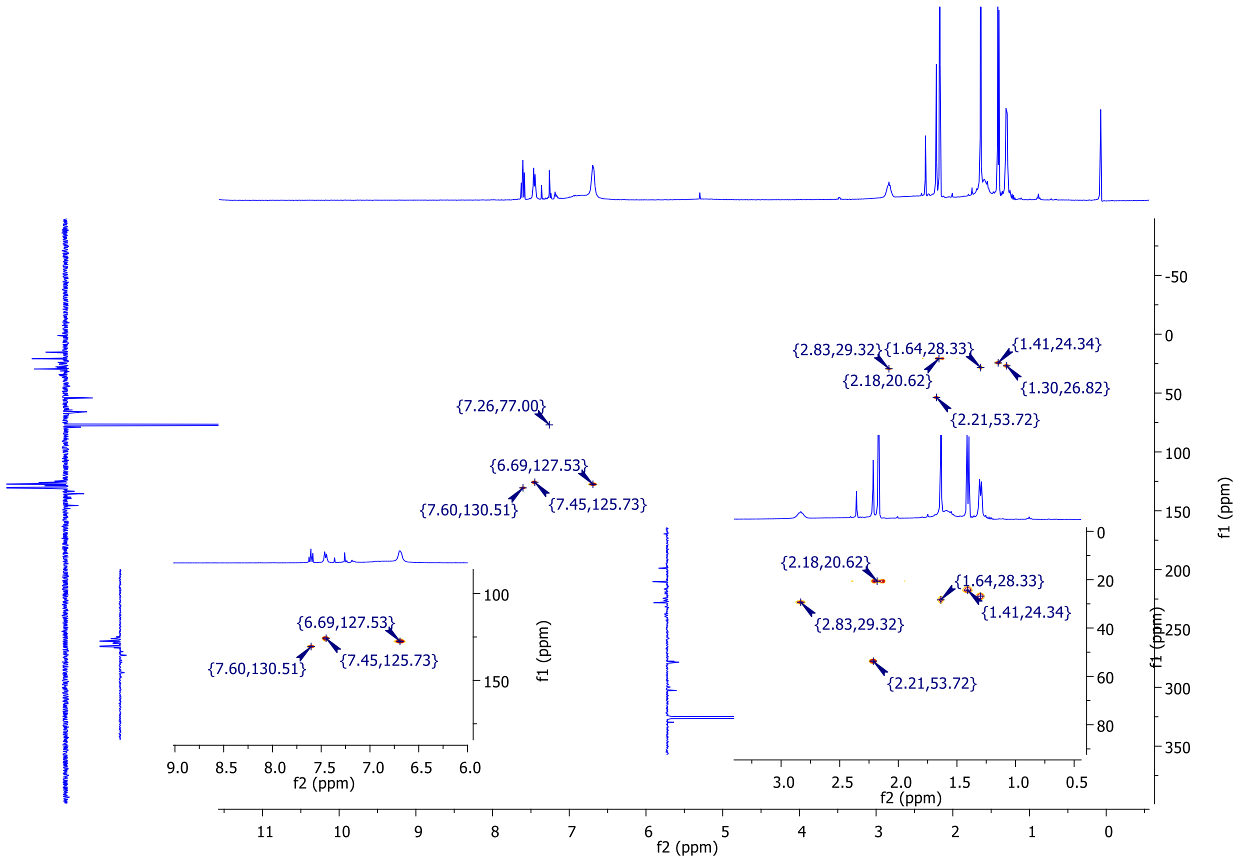


Figure S34. ${}^{1}H$-${}^{13}C$ HSQC NMR spectrum (CDCl$_3$) of $\mathbf{6}^{\mathbf{nido}}$.

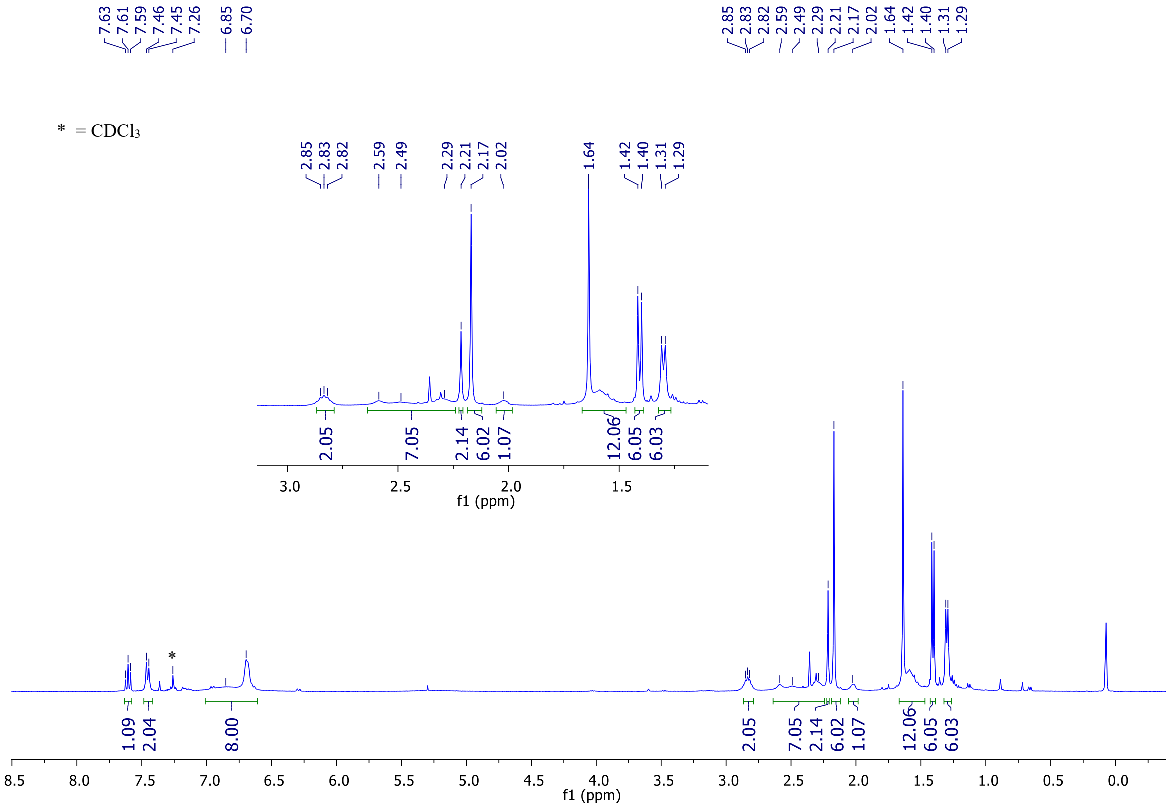


Figure S35. $^{1}H\{^{11}B\}$ NMR spectrum (400 MHz, $CDCl_3$) of **6^{nido}**.

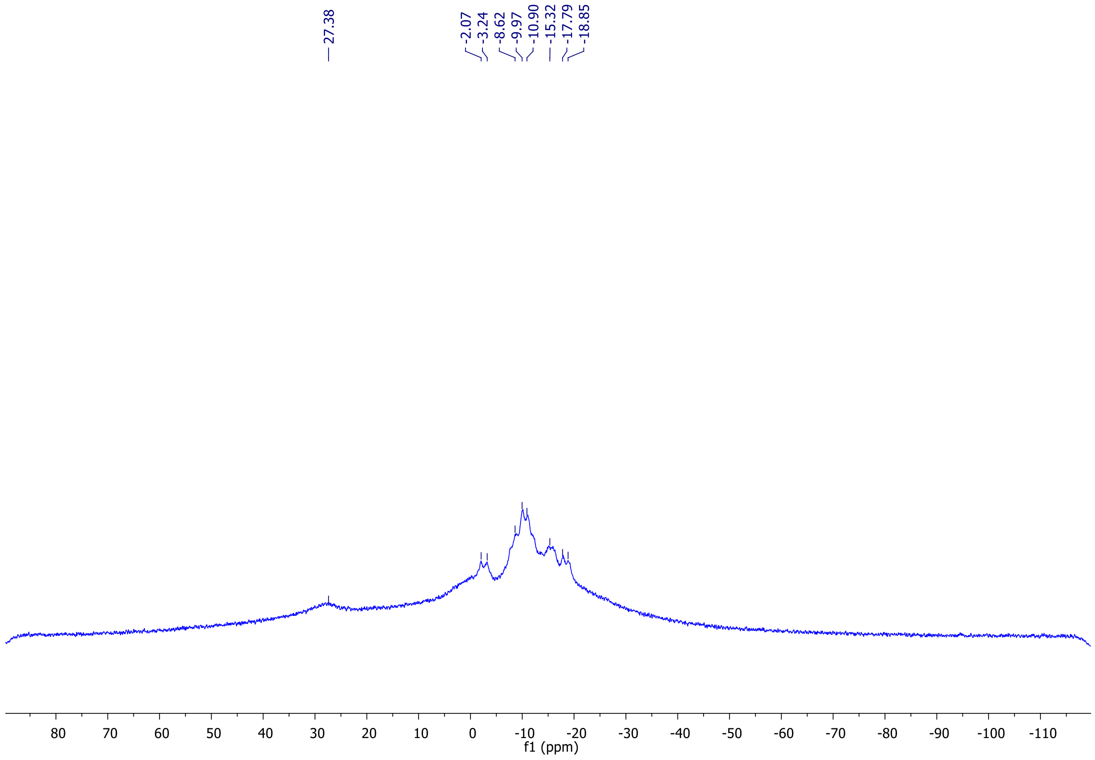


Figure S36. ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **6^{nido}.**

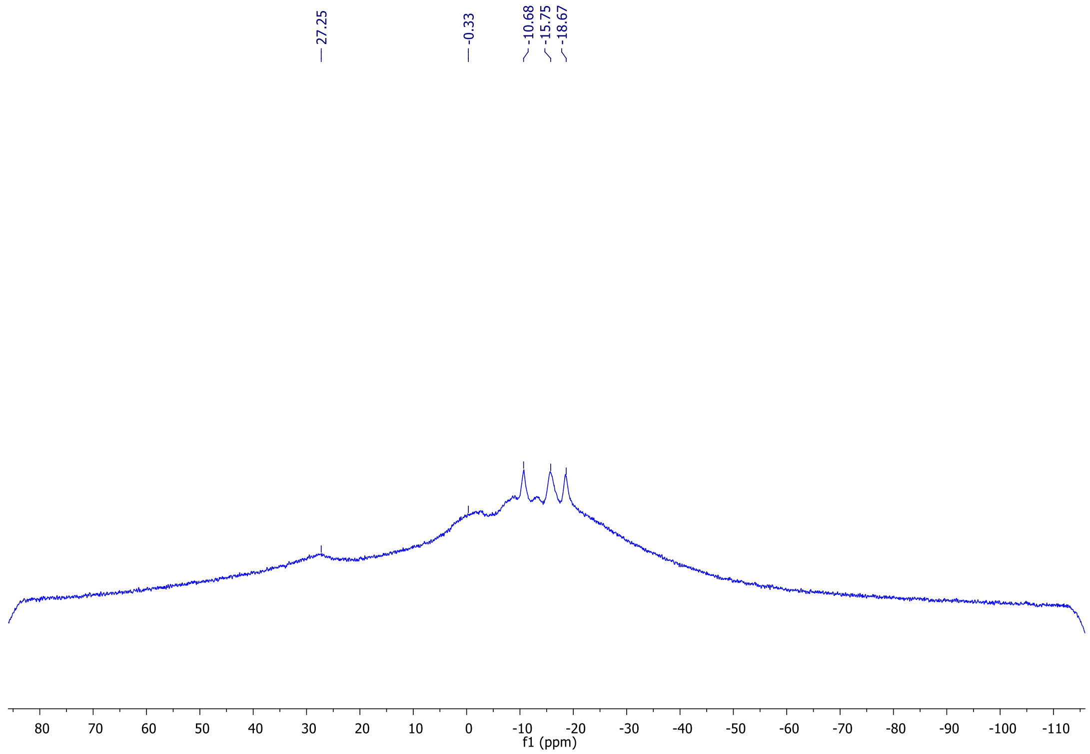


Figure S37. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, $CDCl_3$) of $\mathbf{6^{nido}}$.

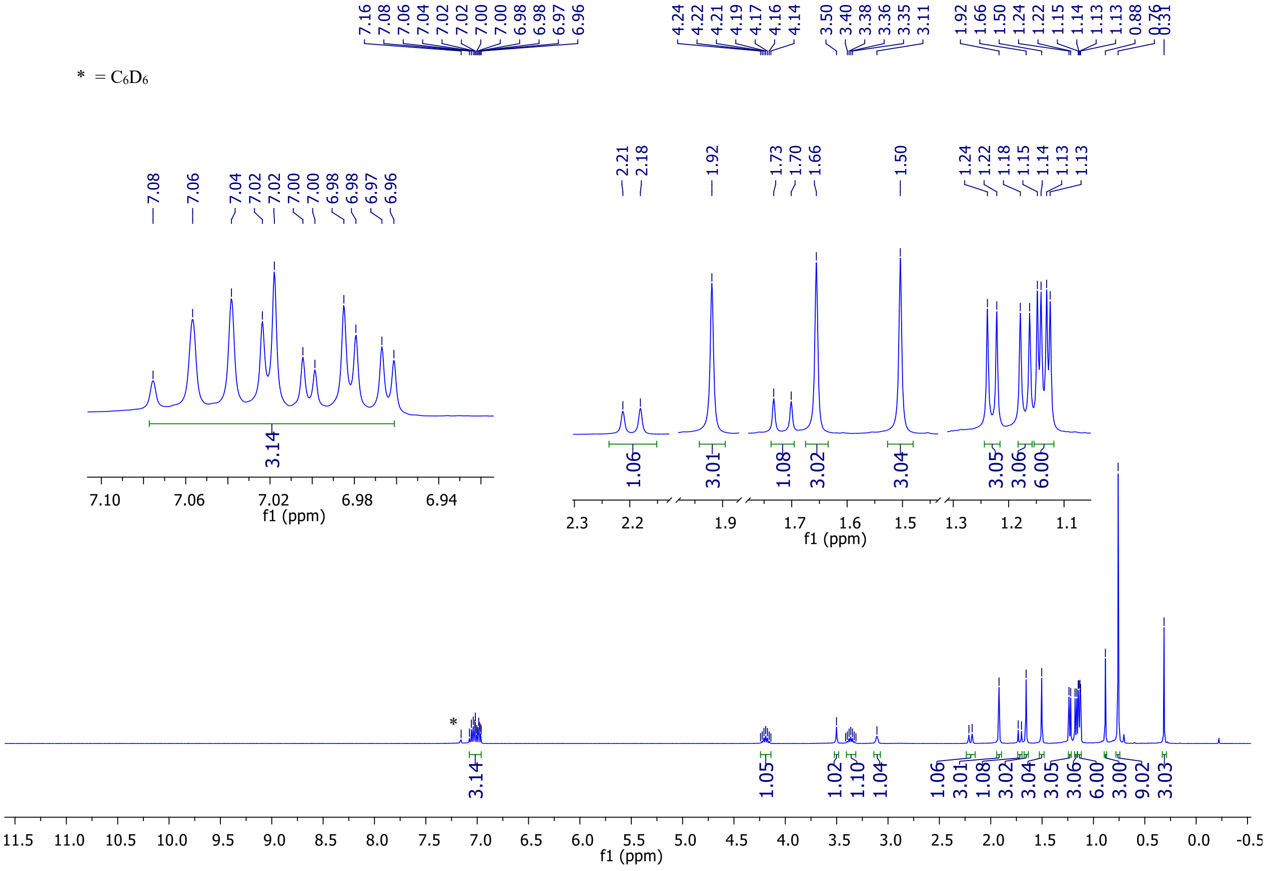


Figure S38. ^{1}H NMR spectrum (400 MHz, C_6D_6) of $\mathbf{8^{cls}}$.

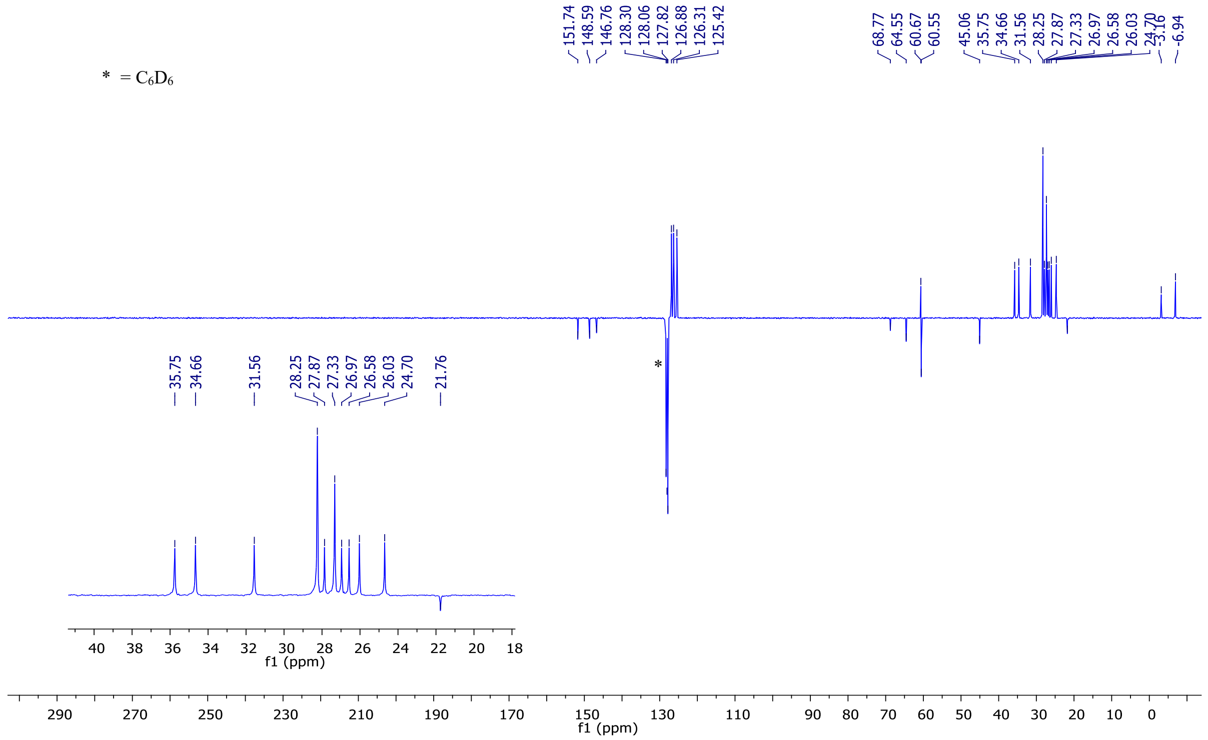


Figure S39. $^{13}C\{1H\}$ NMR spectrum (JMOD, 101 MHz, C_6D_6) of $\mathbf{8^{cls}}$.

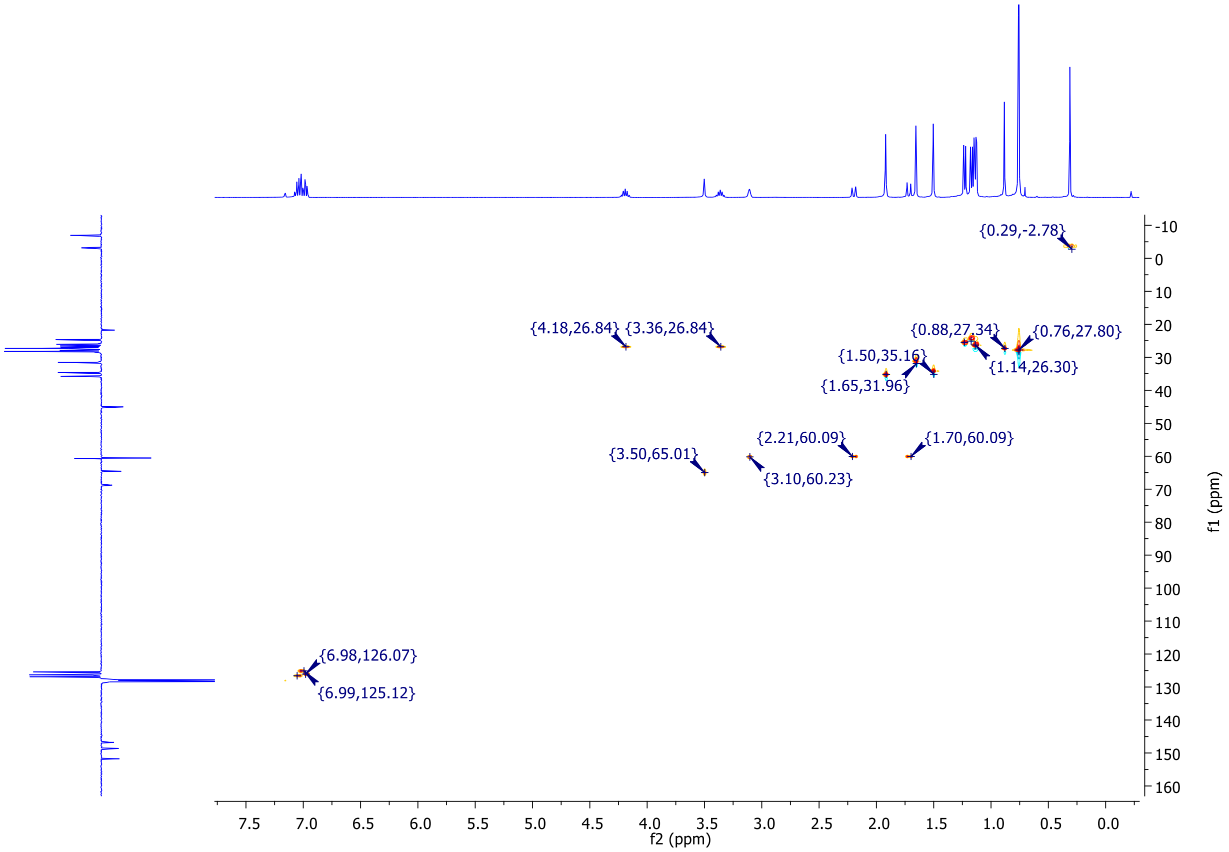


Figure S40. ^1H-^{13}C HSQC NMR spectrum (C_6D_6) of $\mathbf{8^{cls}}$.

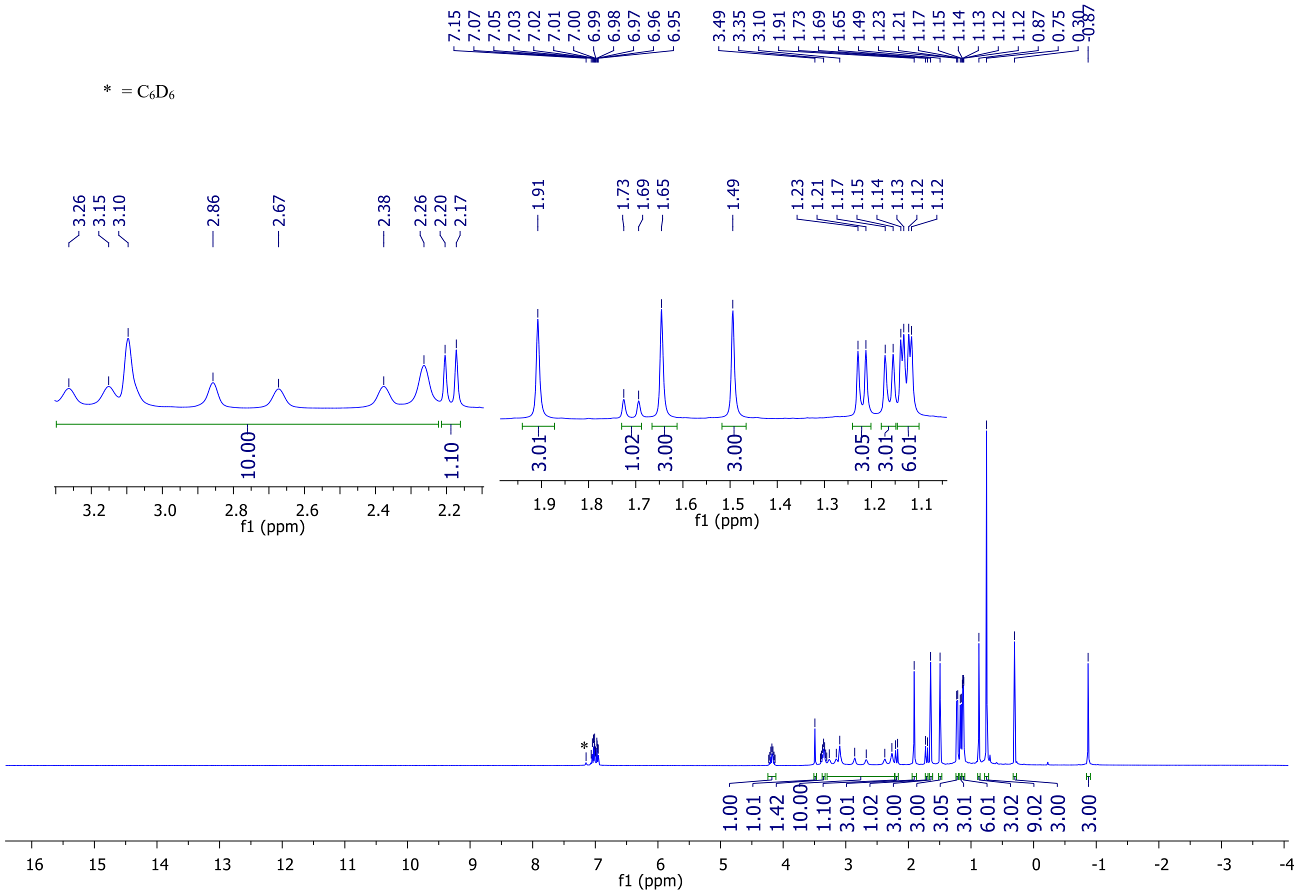


Figure S41. $^1H\{^{11}B\}$ NMR spectrum (400 MHz, C_6D_6) of **8^{cls}**.

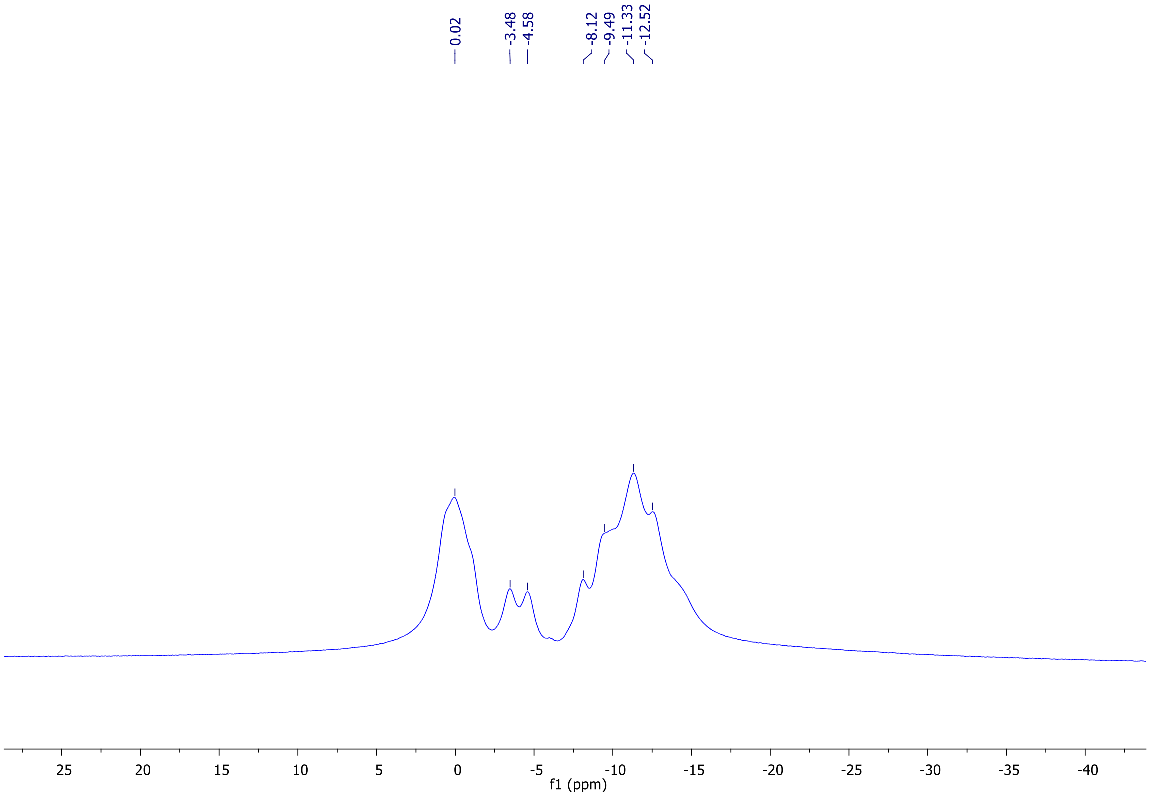


Figure S42. ^{11}B NMR spectrum (128 MHz, C_6D_6) of **8^{cls}.**

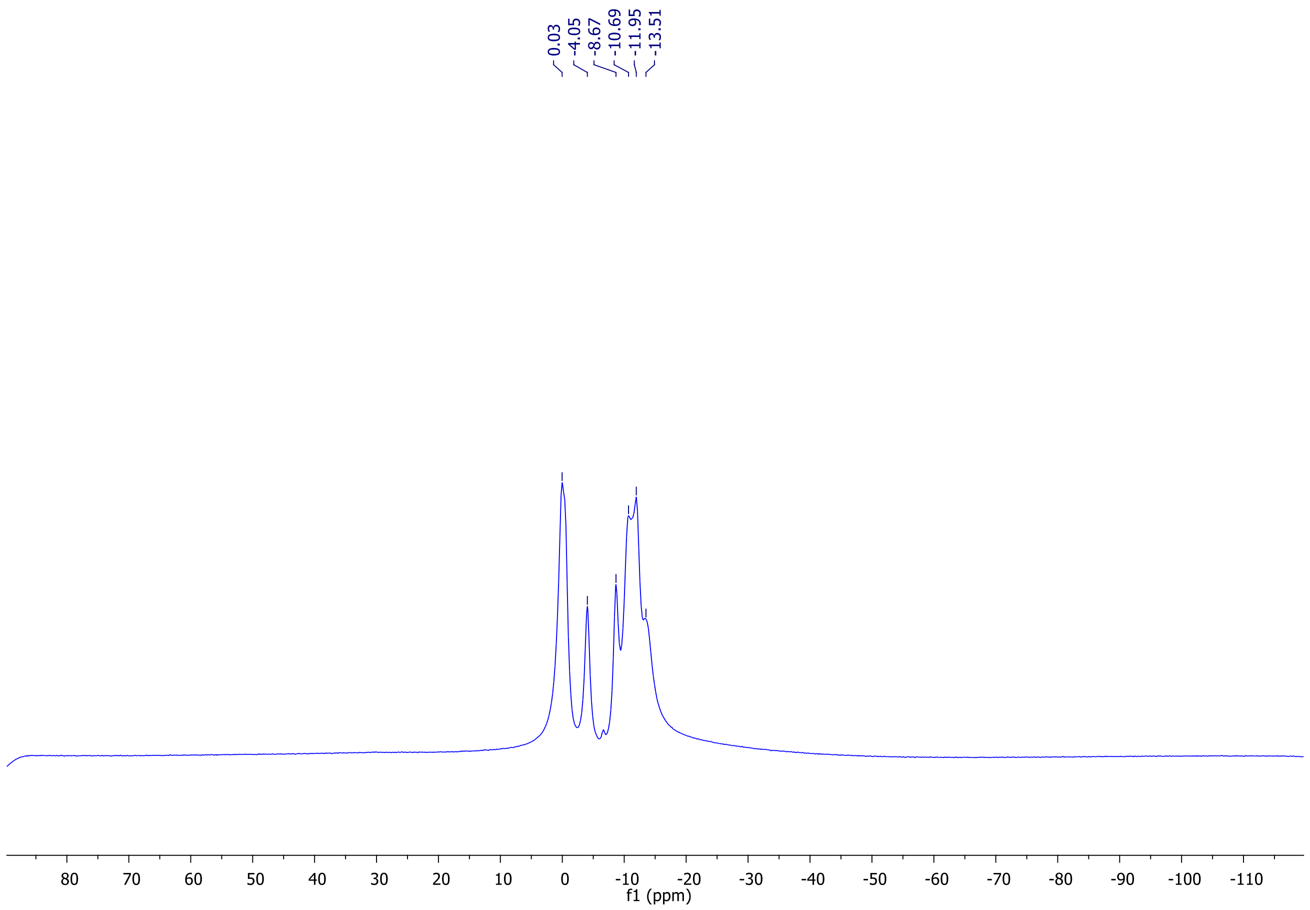


Figure S43. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, C_6D_6) of **8^{cls}**.

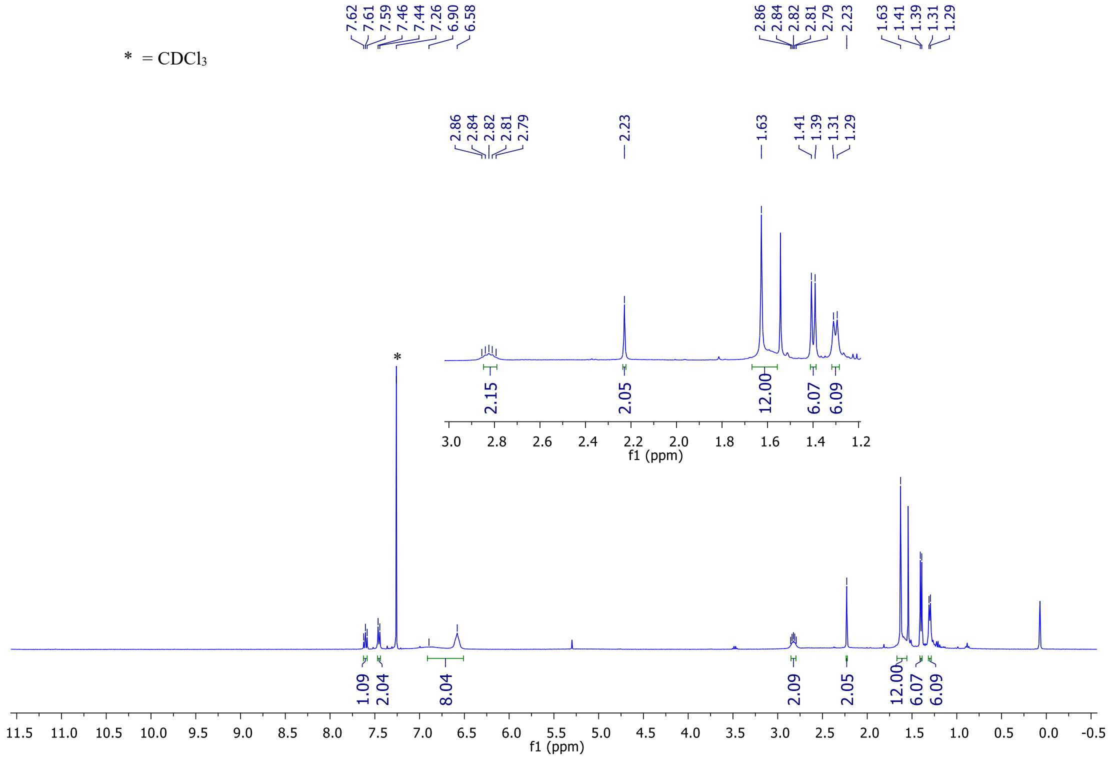


Figure S44. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **10^{nido}**.

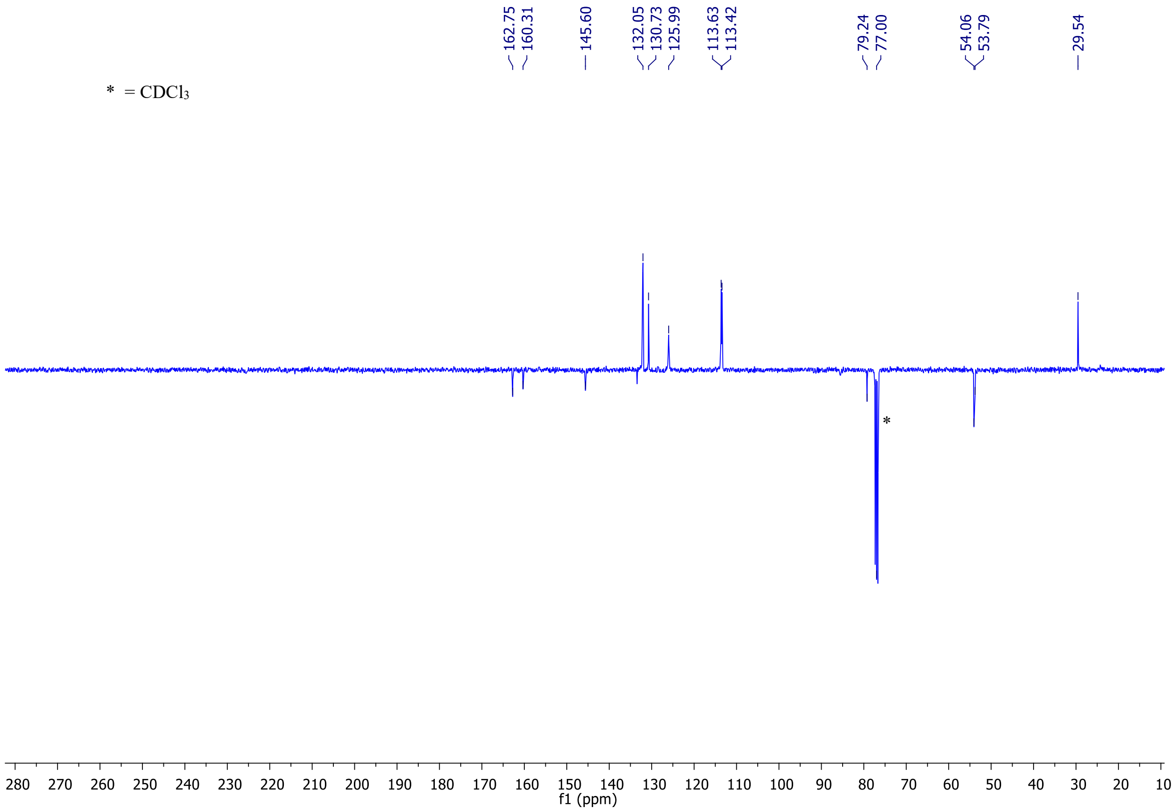


Figure S45. $^{13}C\{1H\}$ NMR spectrum (JMOD, 101 MHz, $CDCl_3$) of $\mathbf{10^{nido}}$.

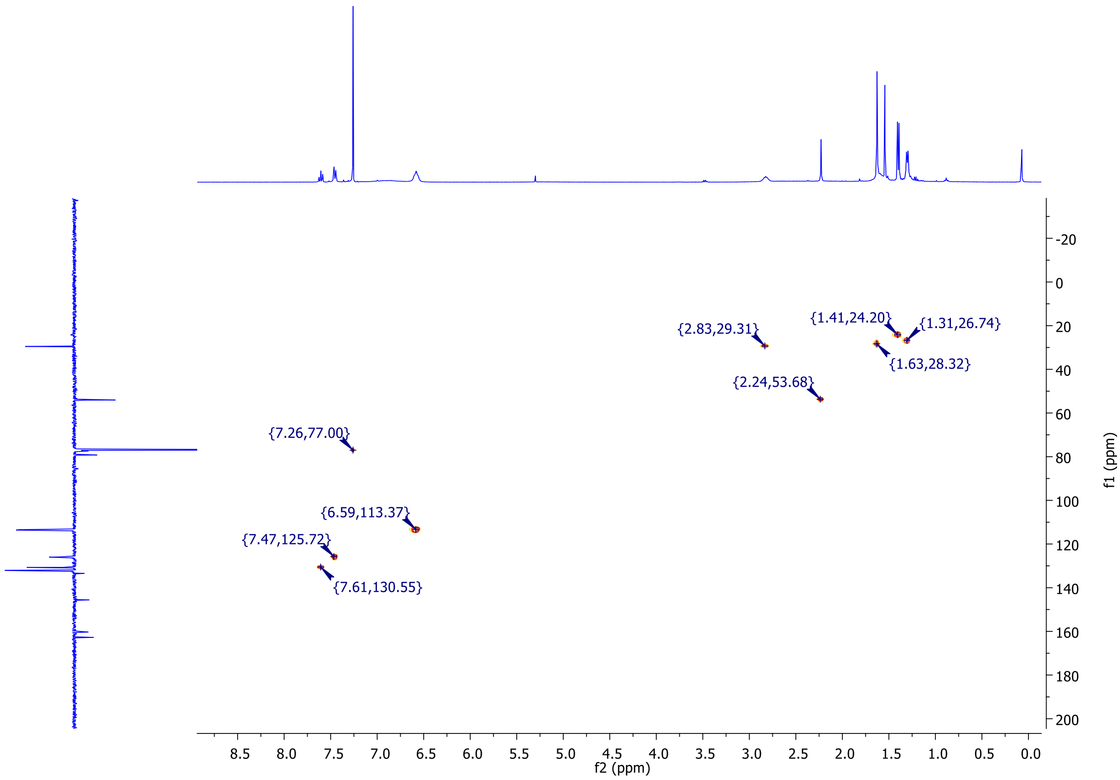


Figure S46. ^{1}H-^{13}C HSQC NMR spectrum ($CDCl_3$) of $\mathbf{10^{nido}}$.

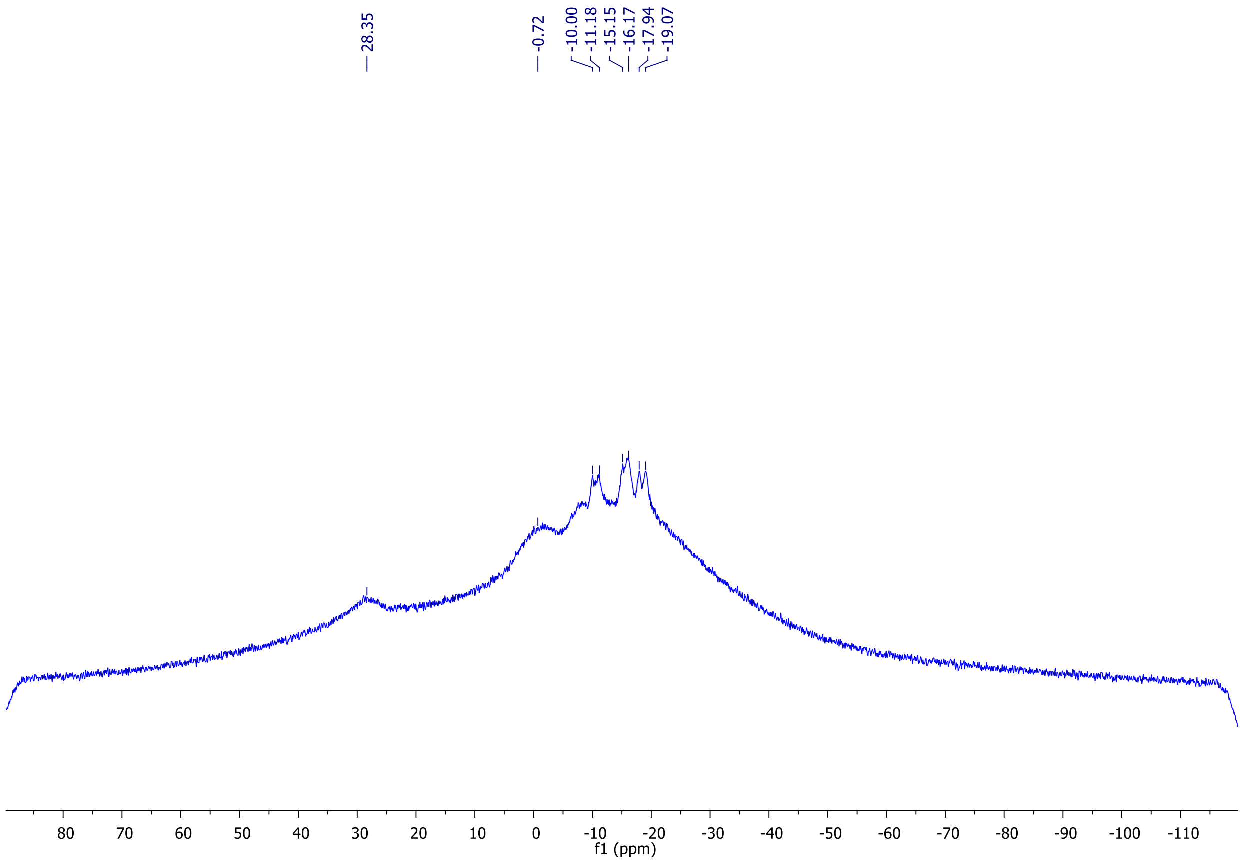


Figure S47. ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **10^{nido}**.

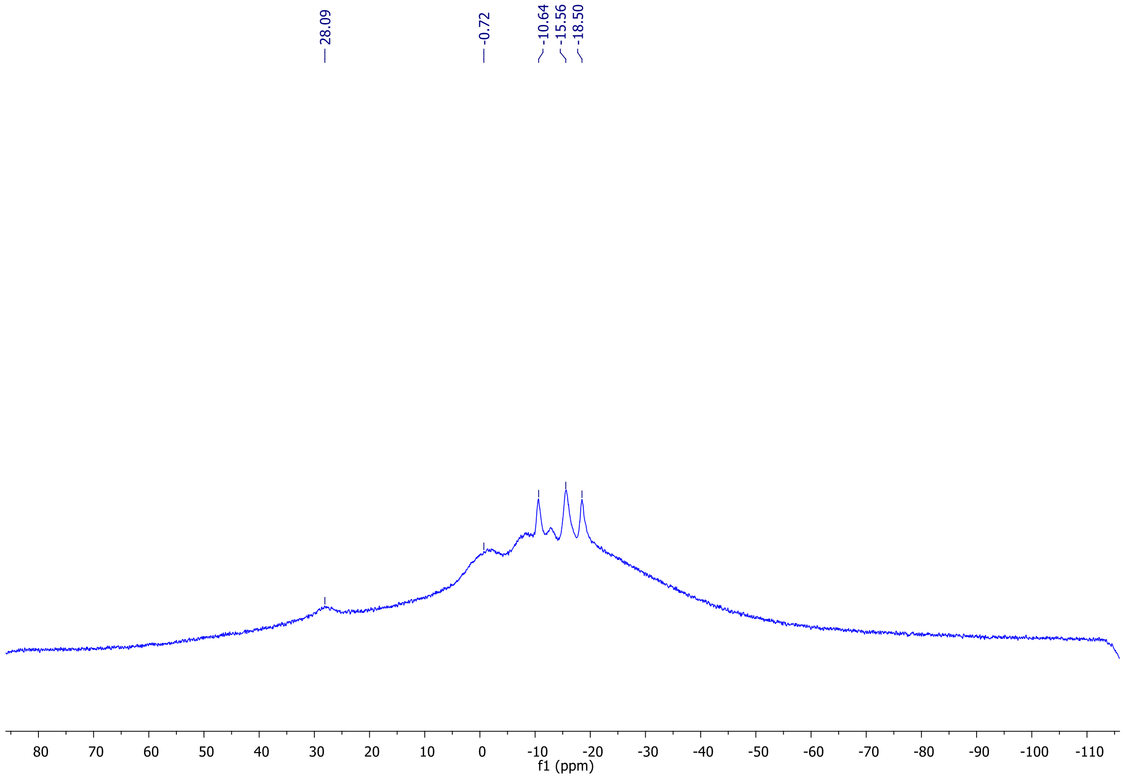


Figure S48. ^{11}B{^{1}H} NMR spectrum (128 MHz, $CDCl_3$) of **10^{nido}**.

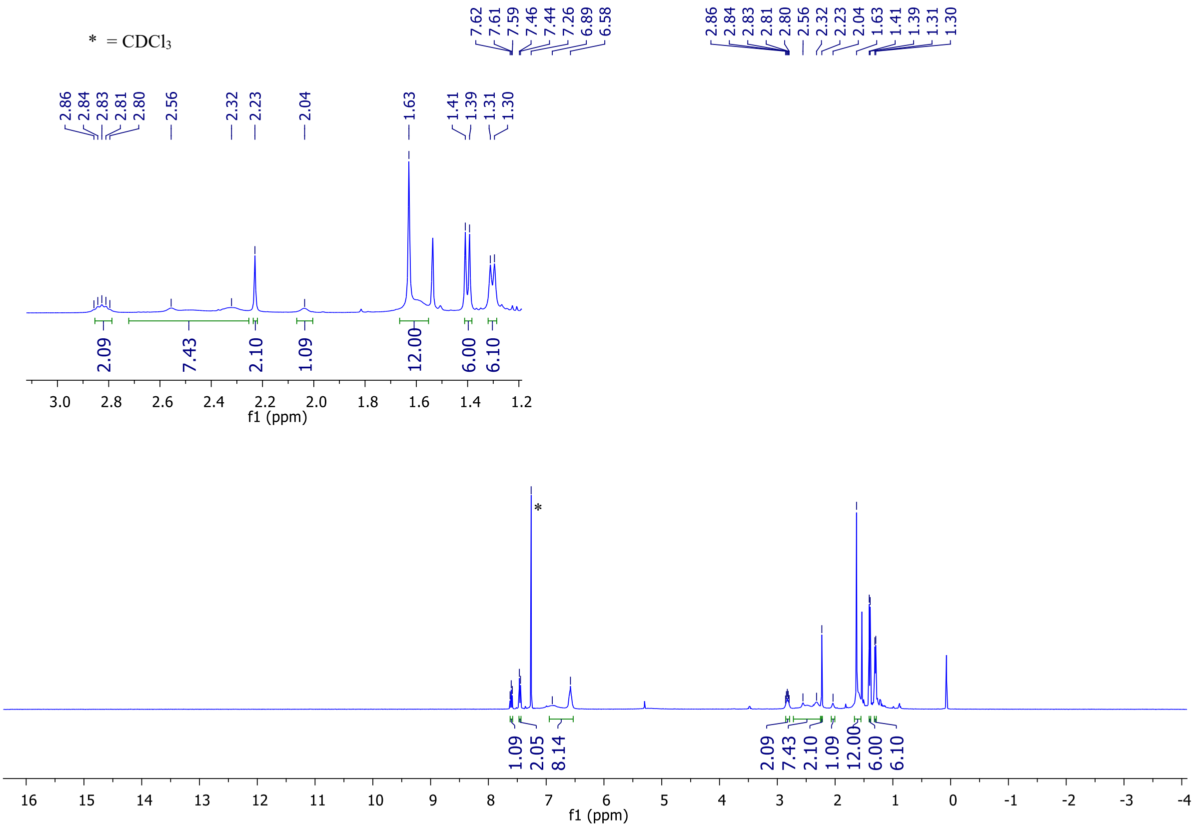


Figure S49. ^{1}H{^{11}B} NMR spectrum (400 MHz, CDCl3) of **10**$^{\mathbf{nido}}$.

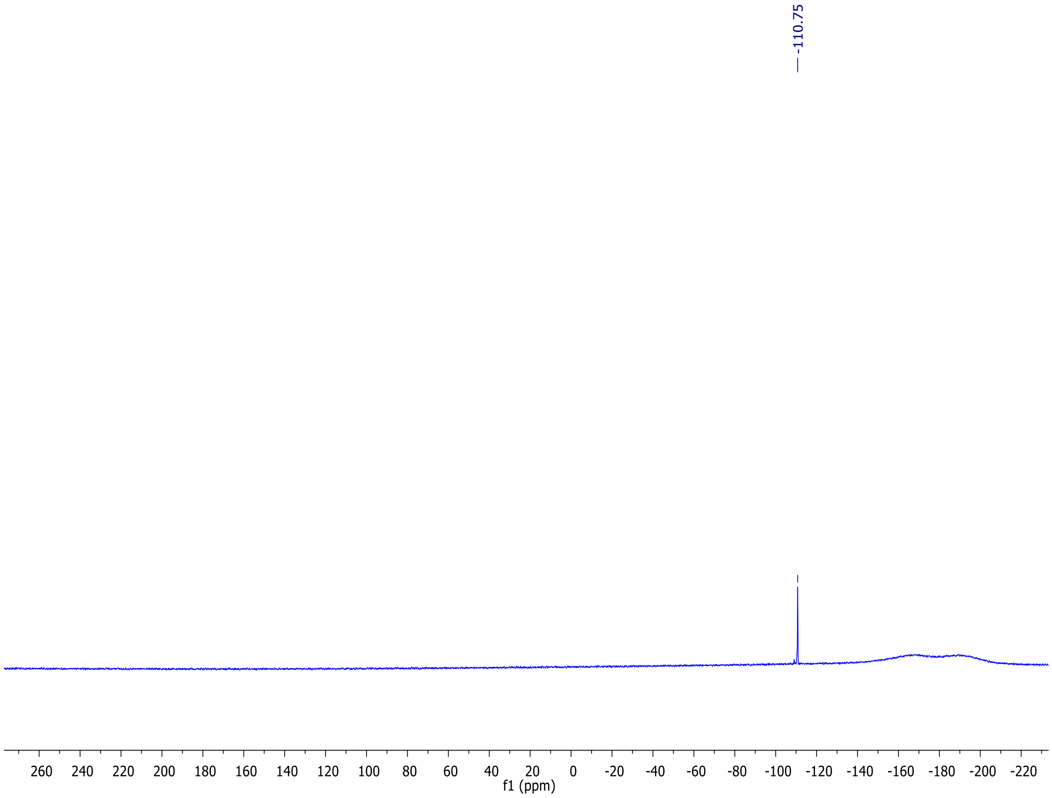


Figure S50. ^{19}F NMR spectrum (376 MHz, CDCl$_3$) of **10**.

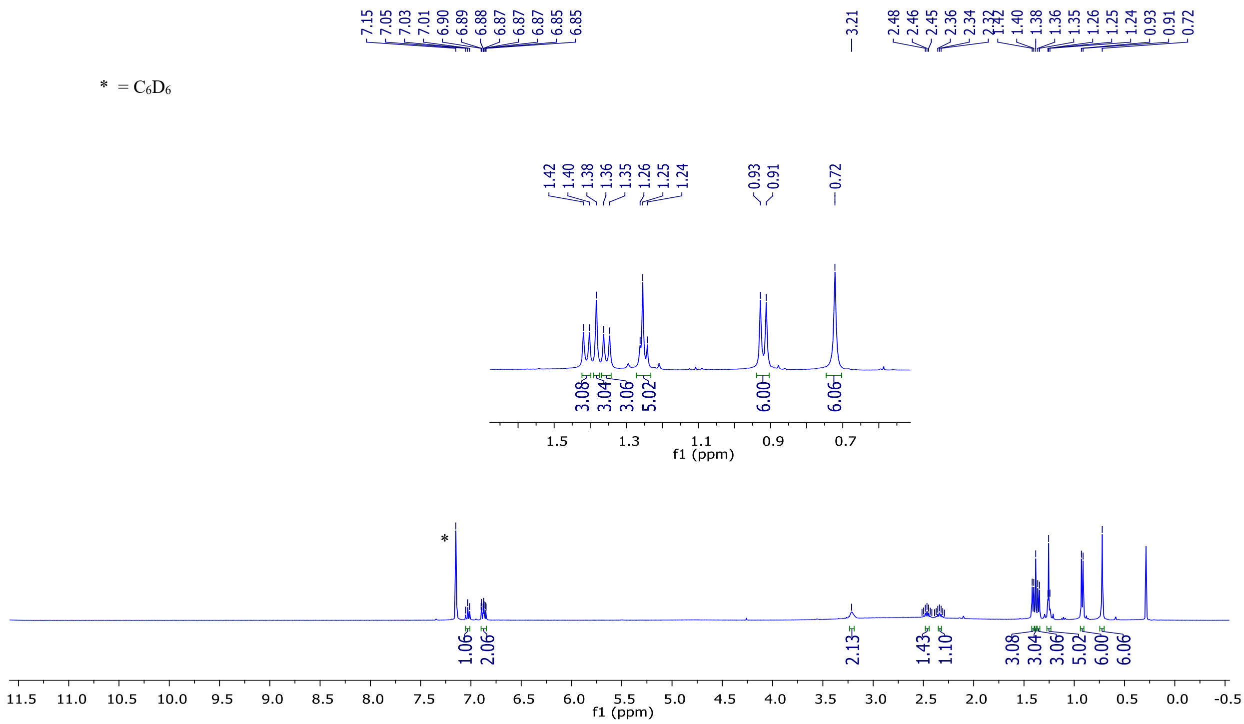


Figure S51. ^{1}H NMR Spectrum (400 MHz, C_6D_6) of **5$^{\textbf{nido}}$**.

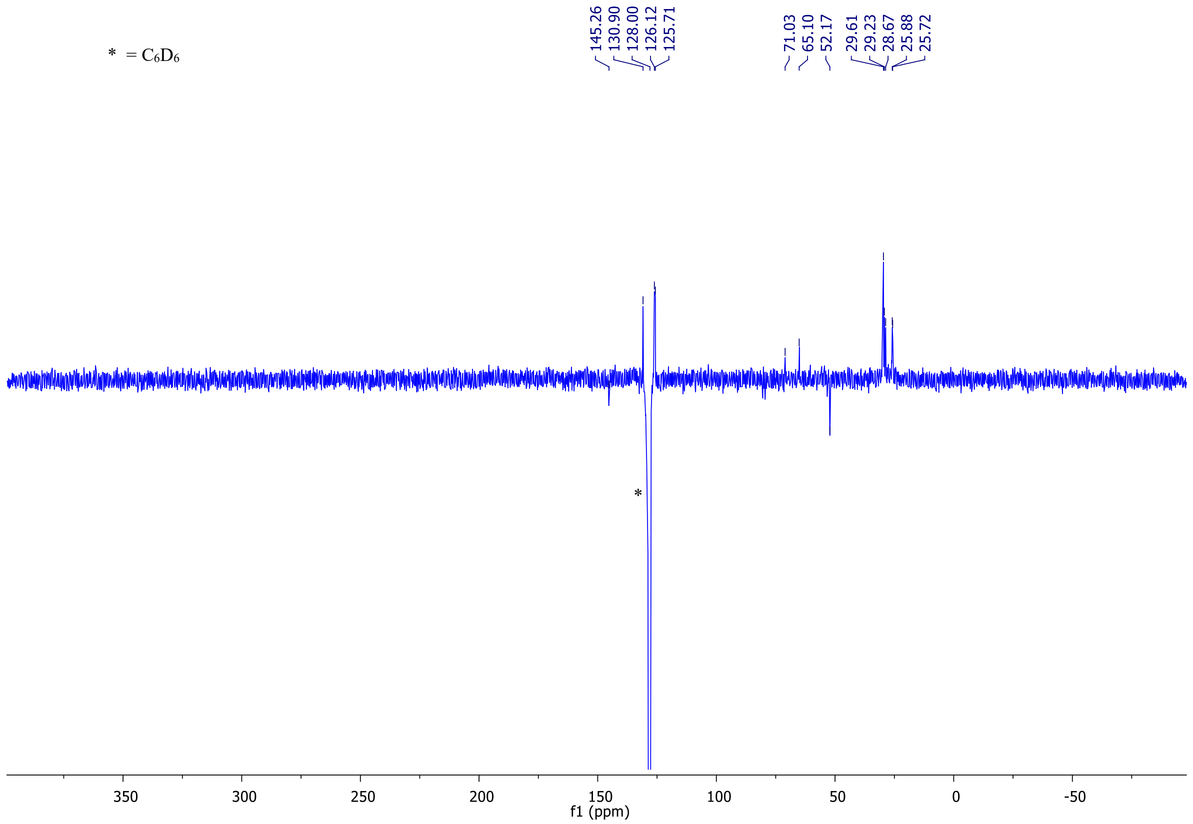


Figure S52. ^{13}C{1H} NMR spectrum (JMOD, 101 MHz, C_6D_6) of **5$^{\textbf{nido}}$**.

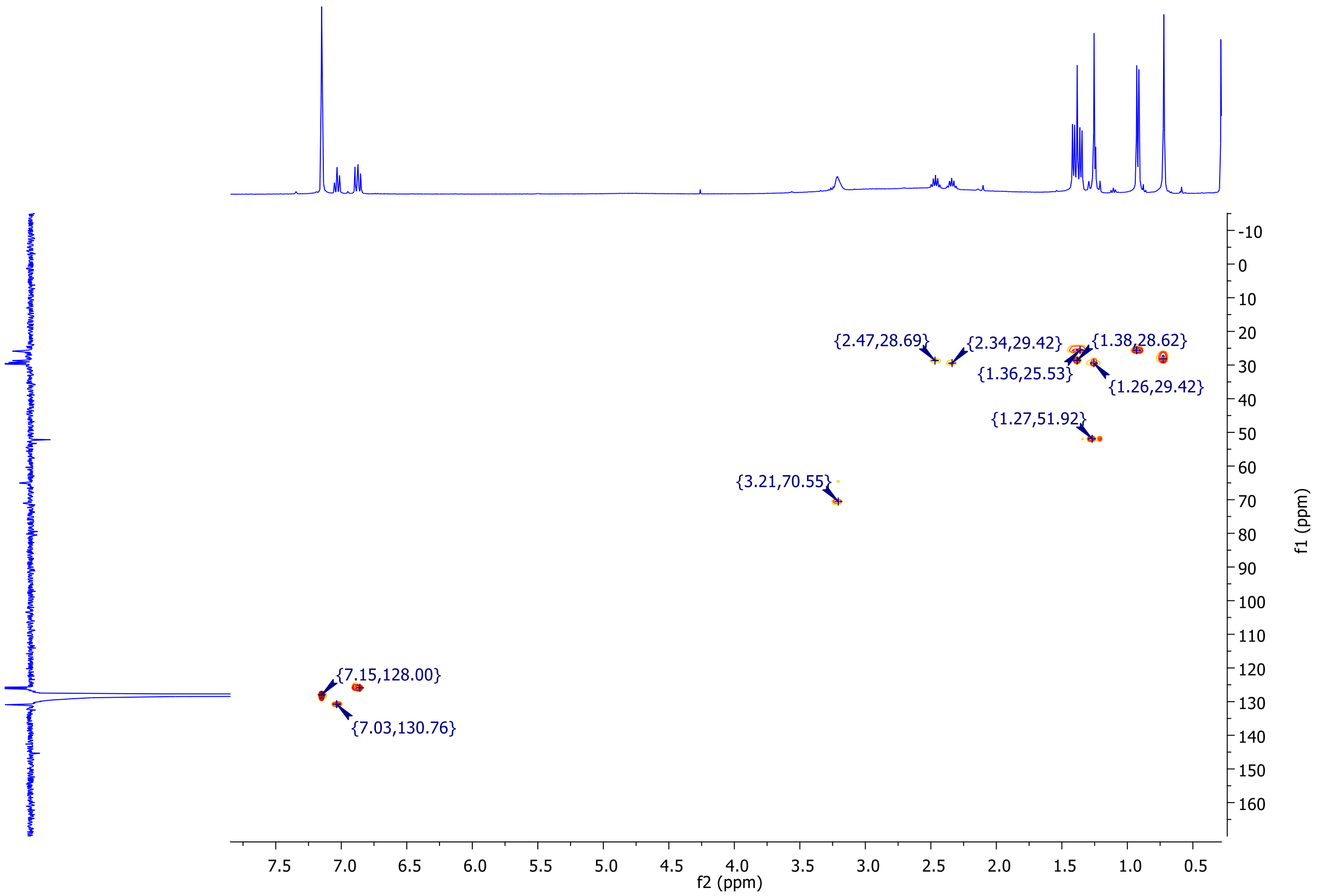


Figure S53. ^{1}H-^{13}C HSQC NMR spectrum (C_6D_6) of **5$^{\mathbf{nido}}$**.

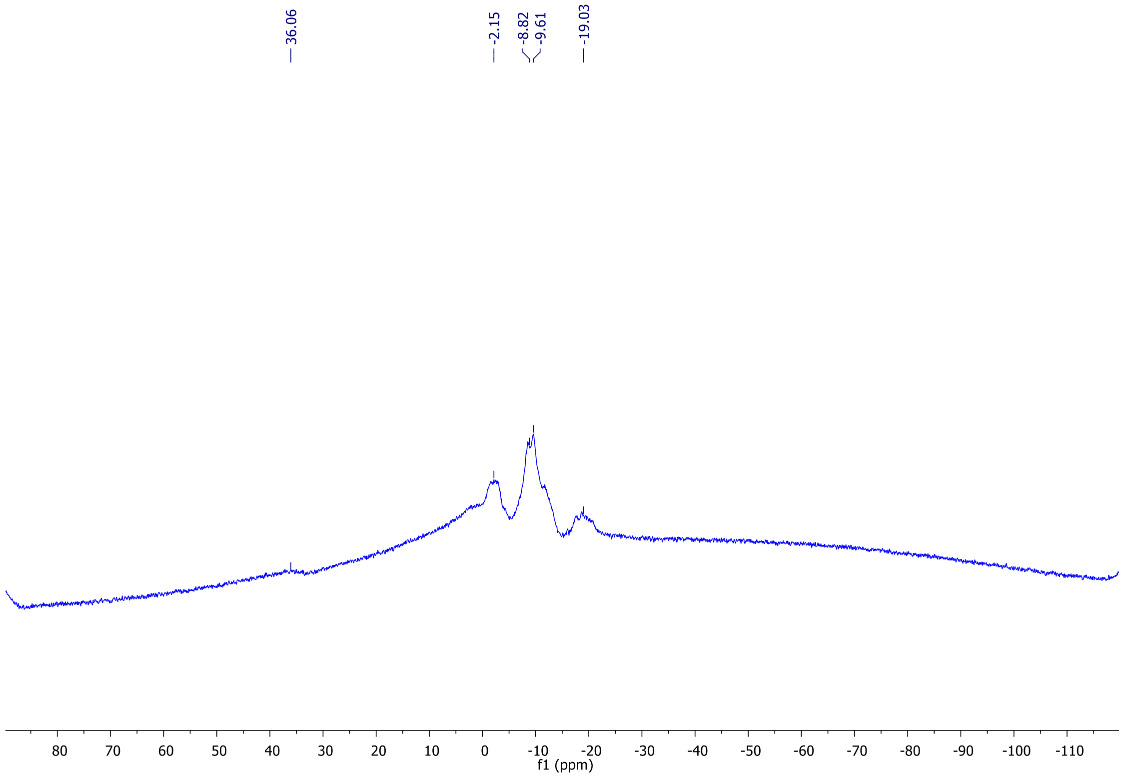


Figure S54. ^{11}B NMR spectrum (128 MHz, C_6D_6) of **5$^{\mathbf{nido}}$**.

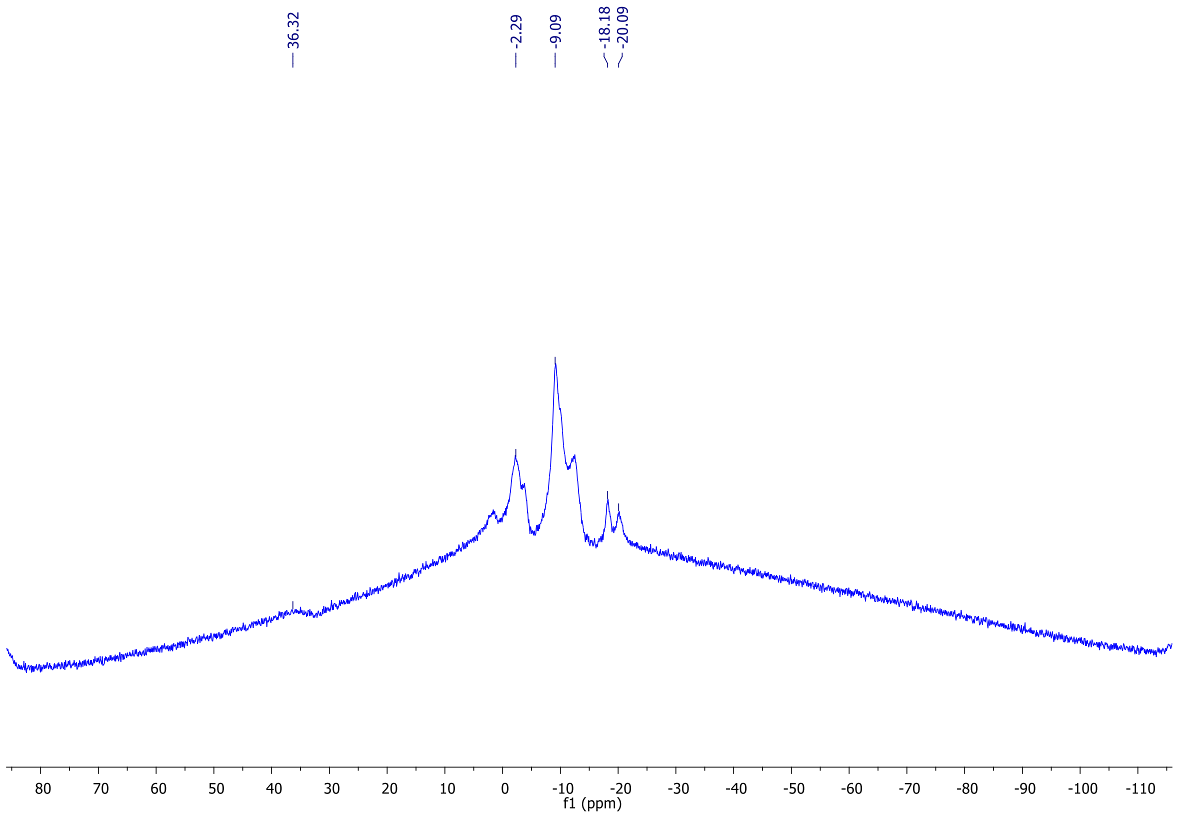


Figure S55. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, C_6D_6) of **5^{nido}**.

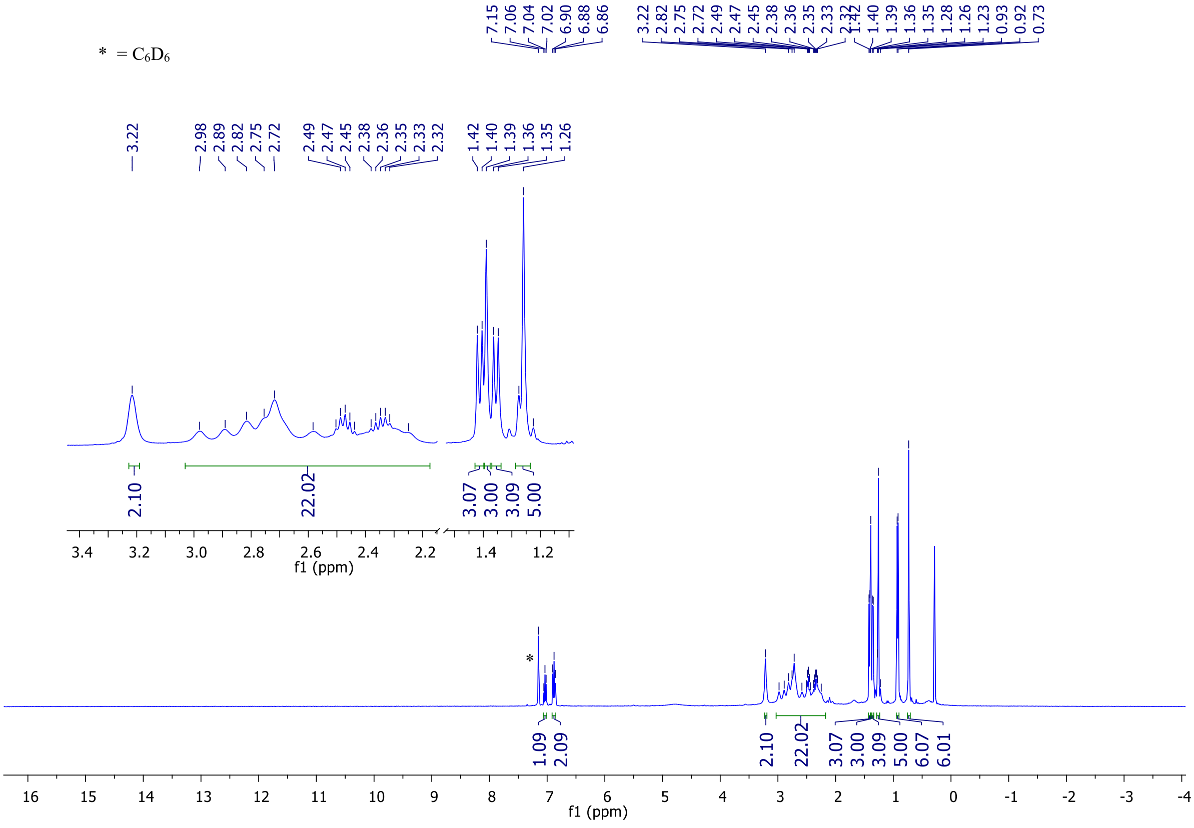


Figure S56. $^{1}H\{^{11}B\}$ NMR spectrum (400 MHz, C_6D_6) of **5^{nido}**.

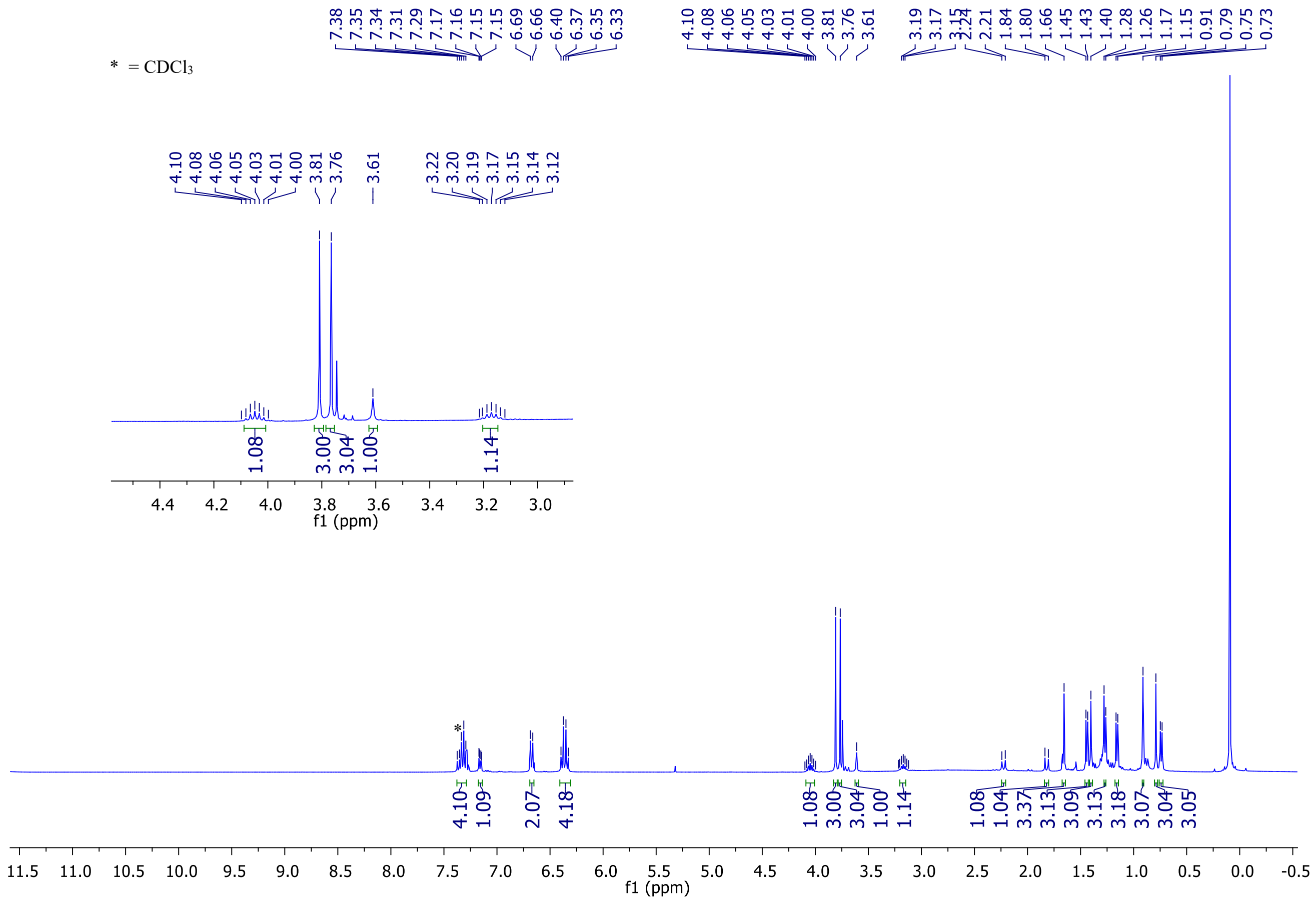


Figure S57. ^{1}H NMR Spectrum (400 MHz, CDCl$_3$) of **7$^{\mathbf{cls}}$**.

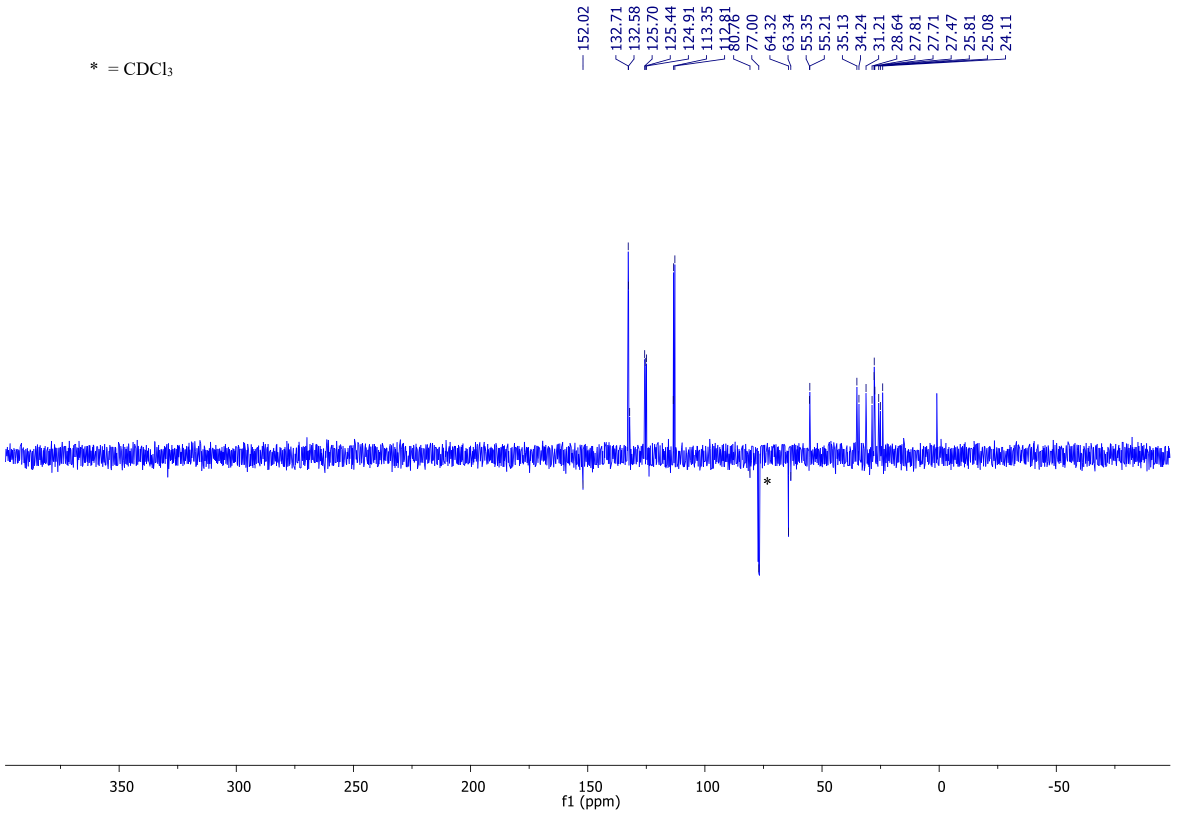


Figure S58. ^{13}C{1H} NMR spectrum (JMOD, 101 MHz, CDCl$_3$) of **7$^{\mathbf{cls}}$**.

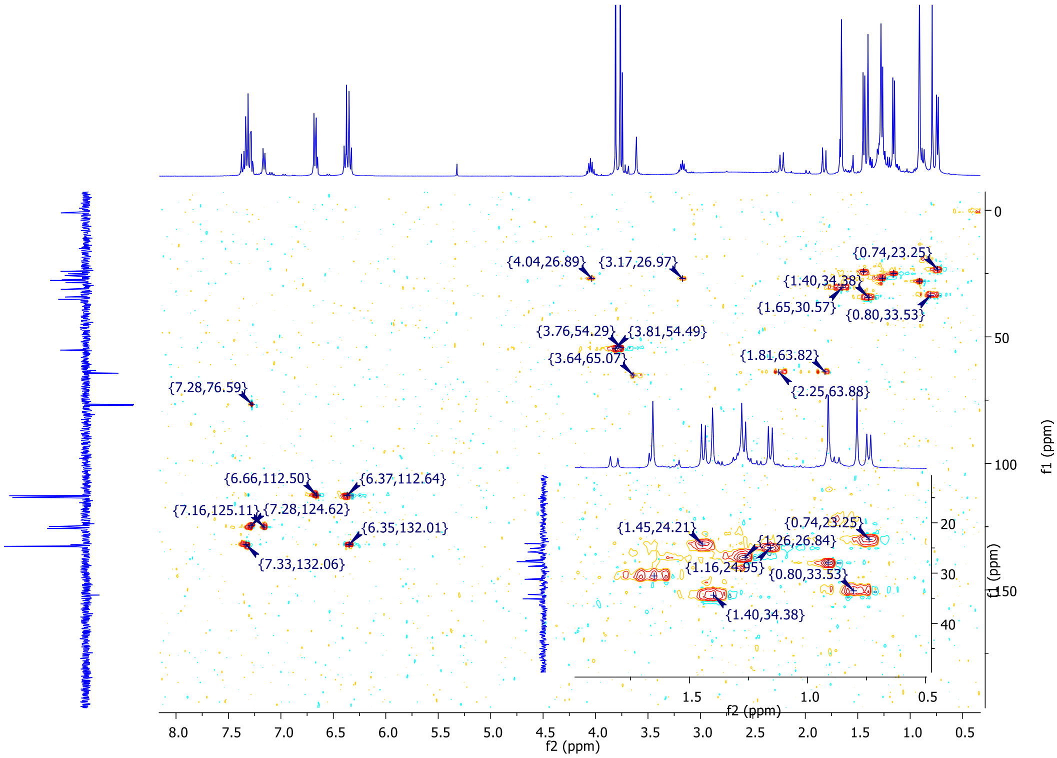


Figure S59. ^{1}H-^{13}C HSQC NMR spectrum (CDCl$_3$) of **7$^{\text{cls}}$**.

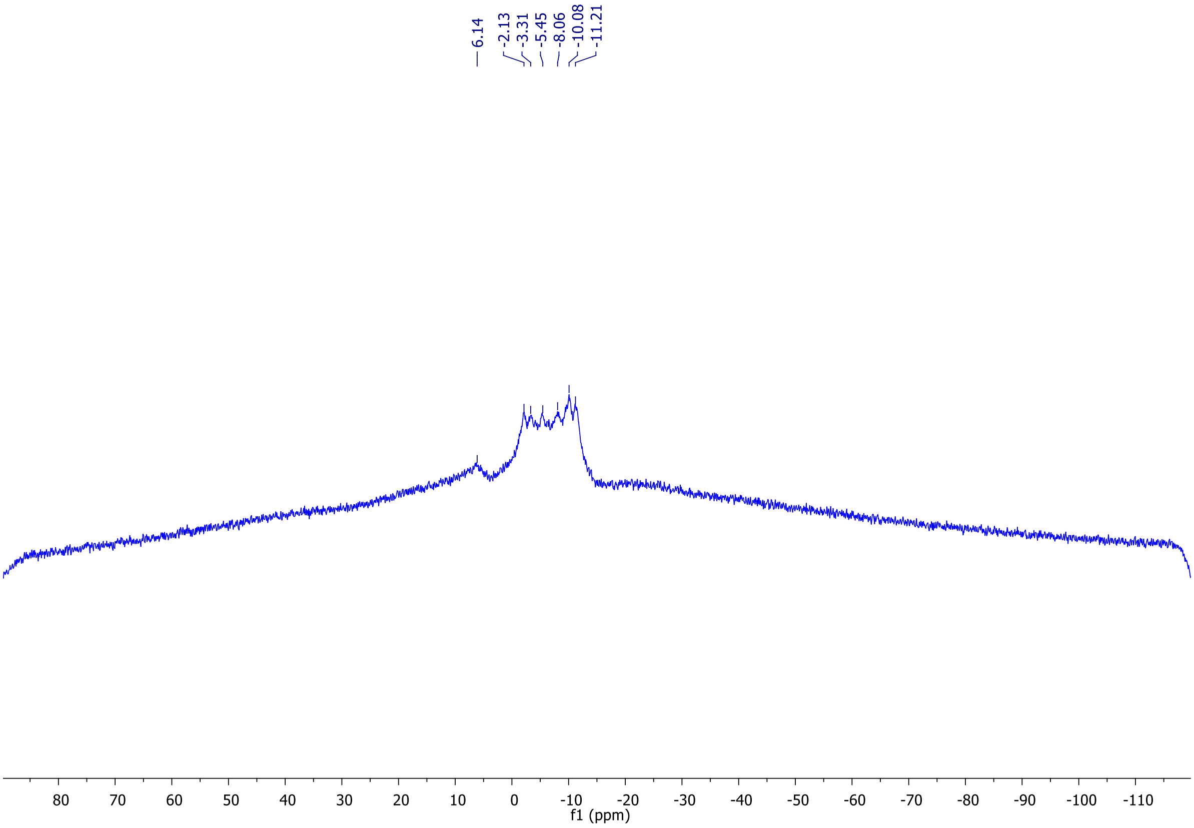


Figure S60. ^{11}B NMR spectrum (128 MHz, CDCl$_3$) of **7$^{\text{cls}}$**.

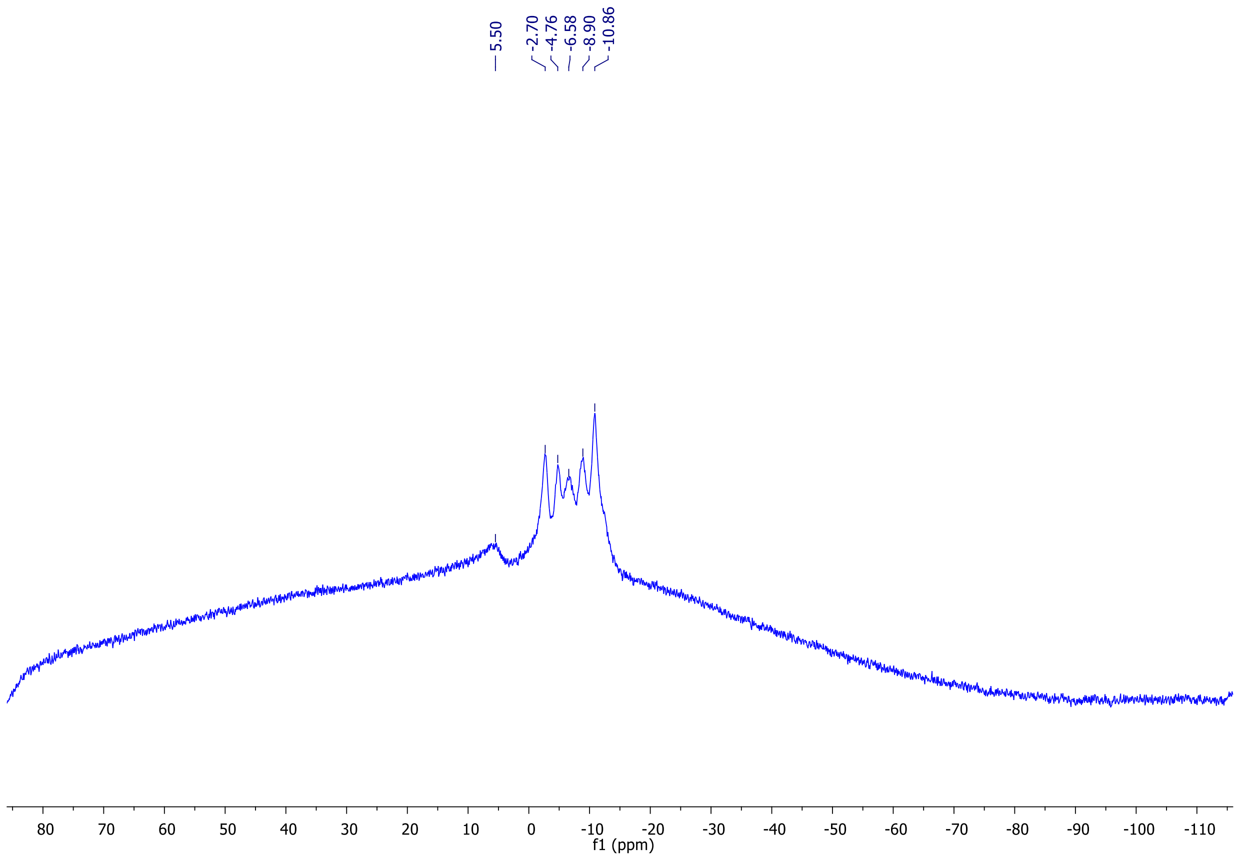


Figure S61. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, $CDCl_3$) of $\mathbf{7^{cls}}$.

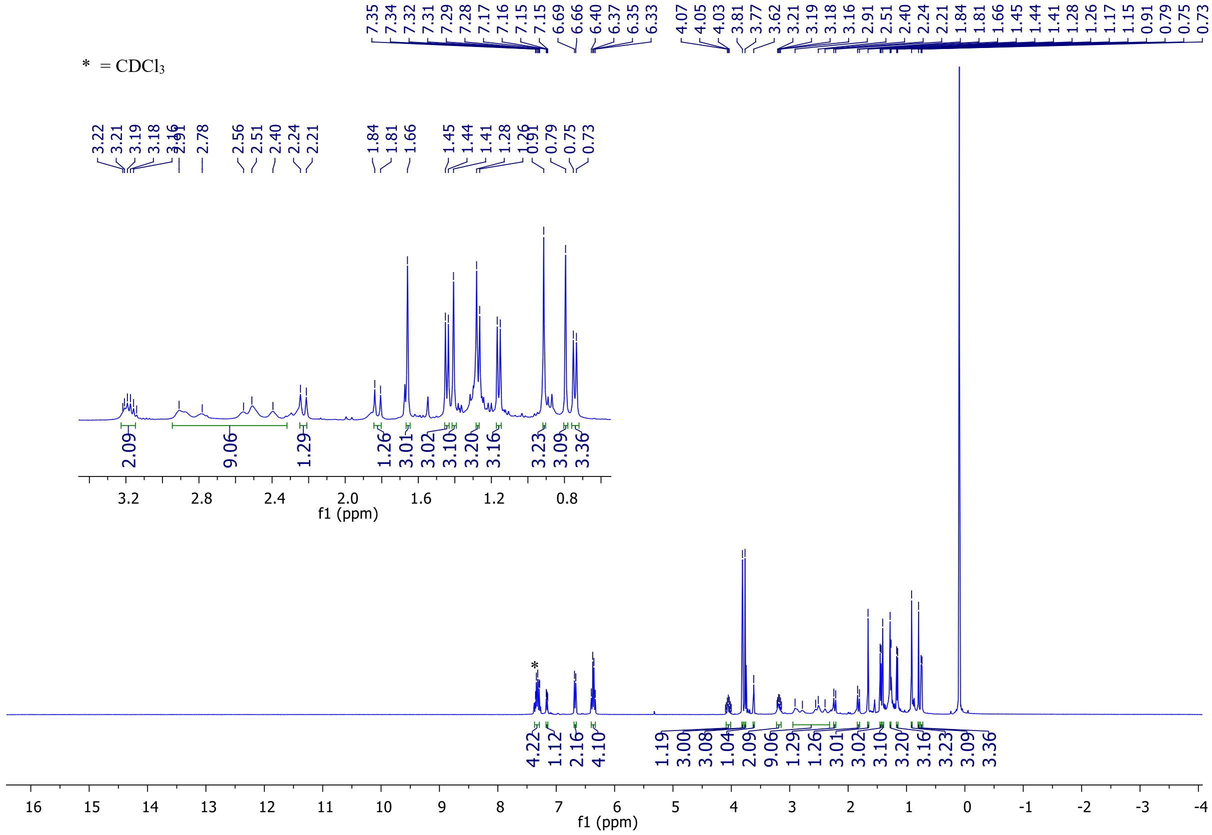


Figure S62. $^{1}H\{^{11}B\}$ NMR spectrum (400 MHz, $CDCl_3$) of $\mathbf{7^{cls}}$.

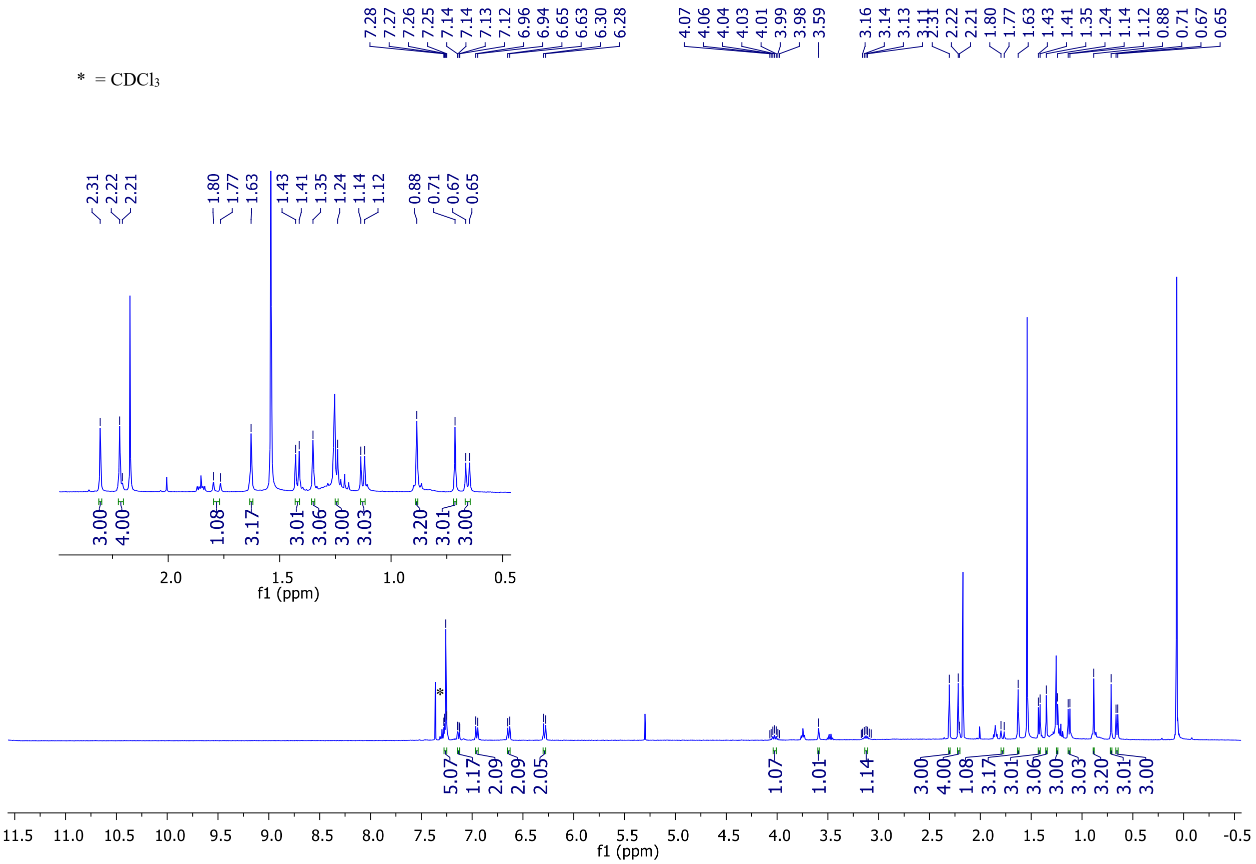


Figure S63. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **6^{cls}**.

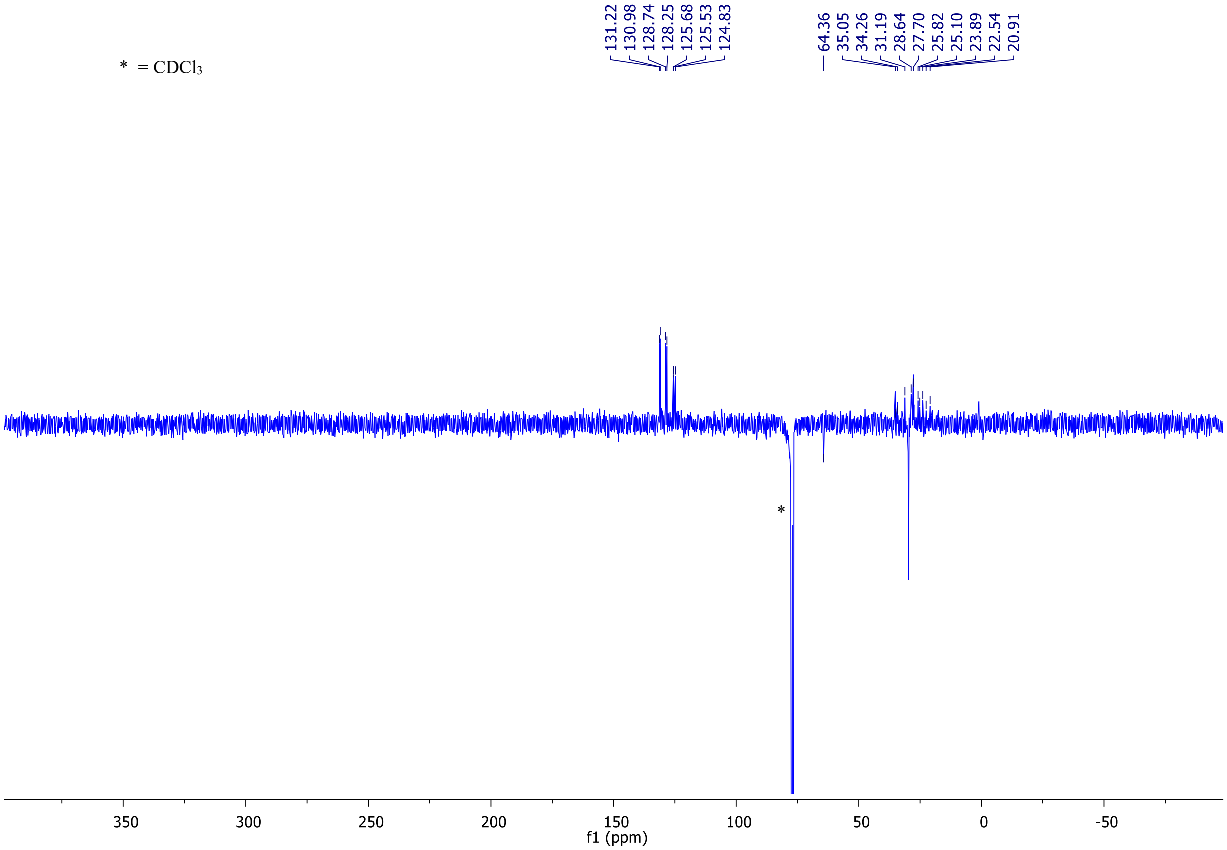


Figure S64. ^{13}C{1H} NMR spectrum (JMOD, 101 MHz, CDCl$_3$) of **6^{cls}**.

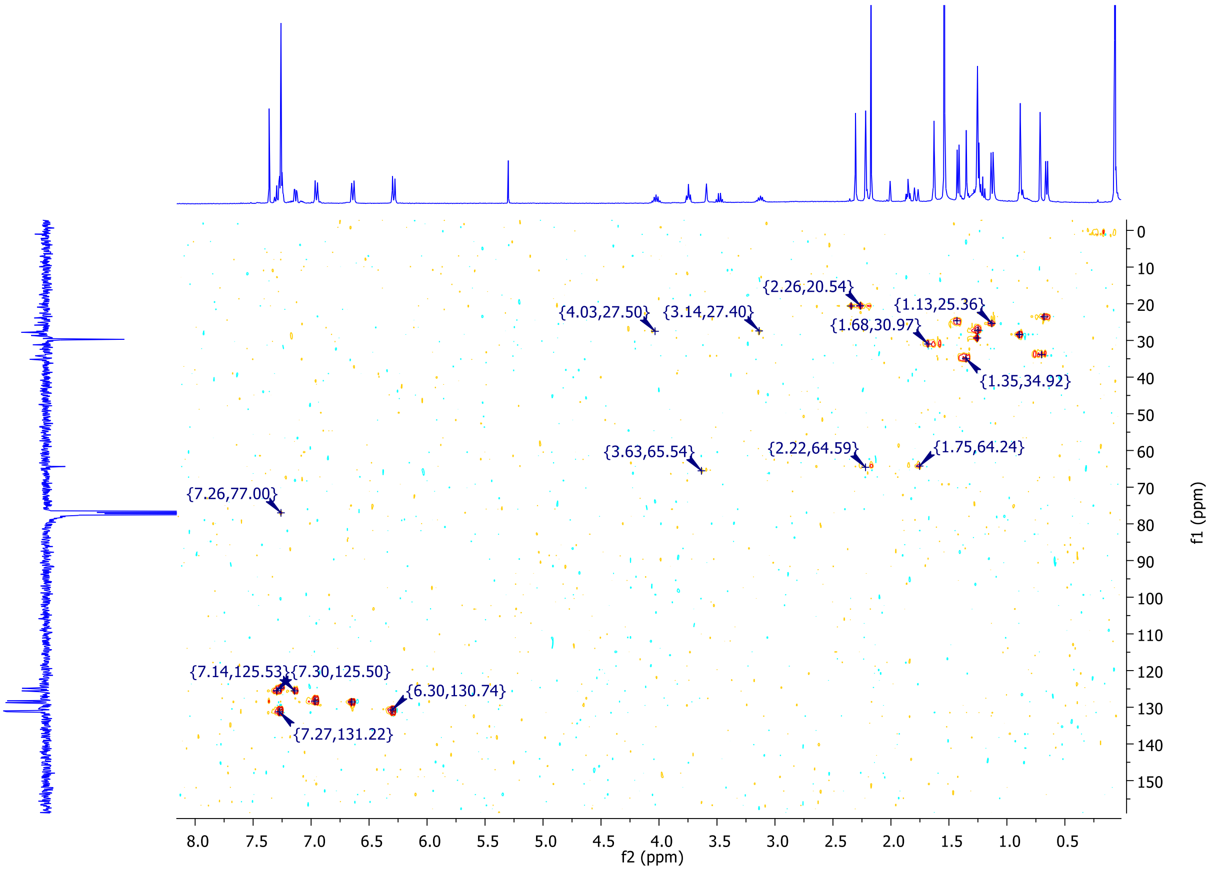


Figure S65. ^{1}H-^{13}C HSQC spectrum (CDCl$_3$) of **6$^{\mathbf{cls}}$**.

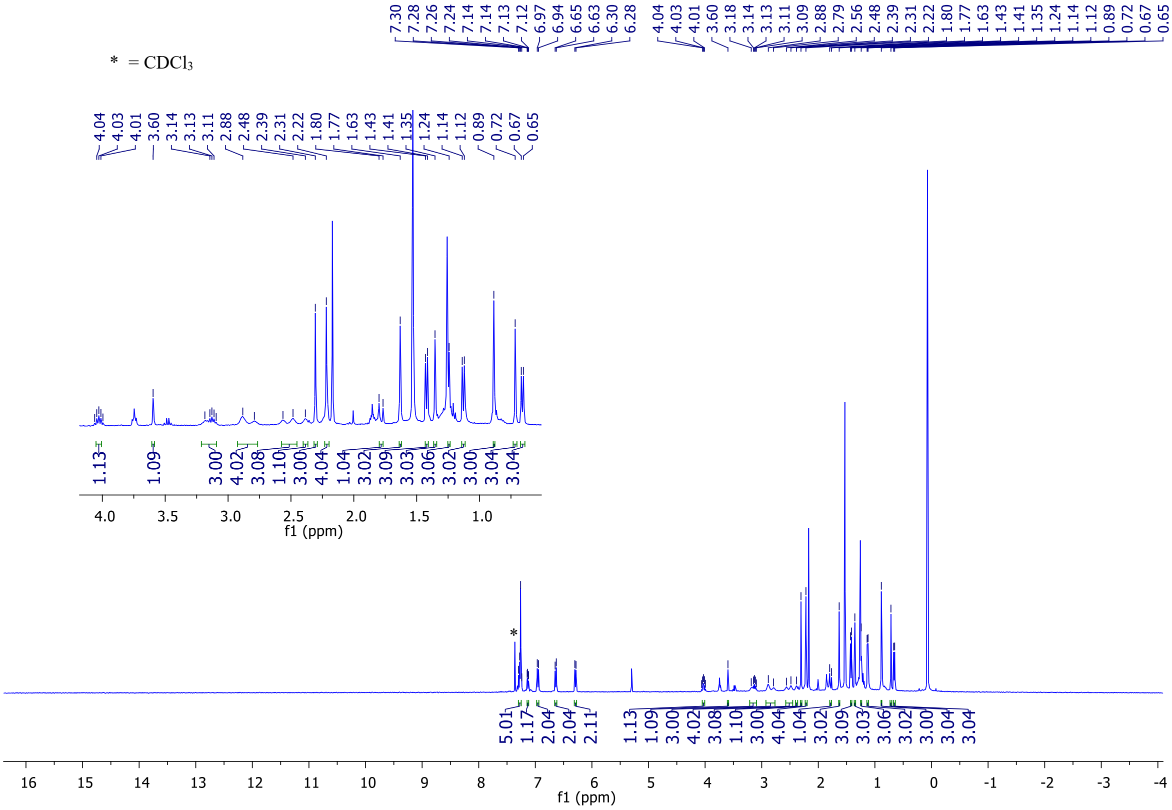


Figure S66. ^{1}H{^{11}B} NMR spectrum (400 MHz, CDCl$_3$) of **6$^{\mathbf{cls}}$**.

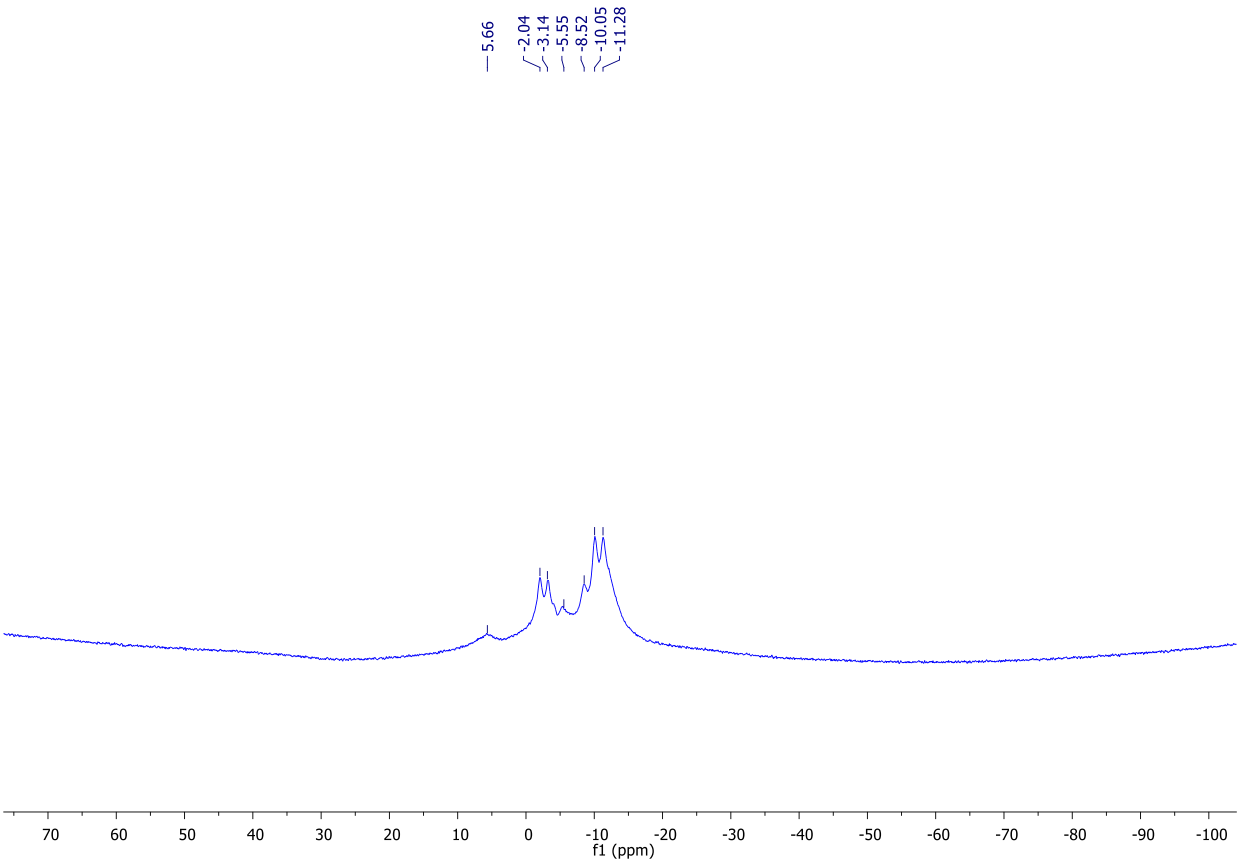


Figure S67. ^{11}B NMR spectrum (128 MHz, CDCl$_3$) of **6$^{\mathbf{cls}}$**.

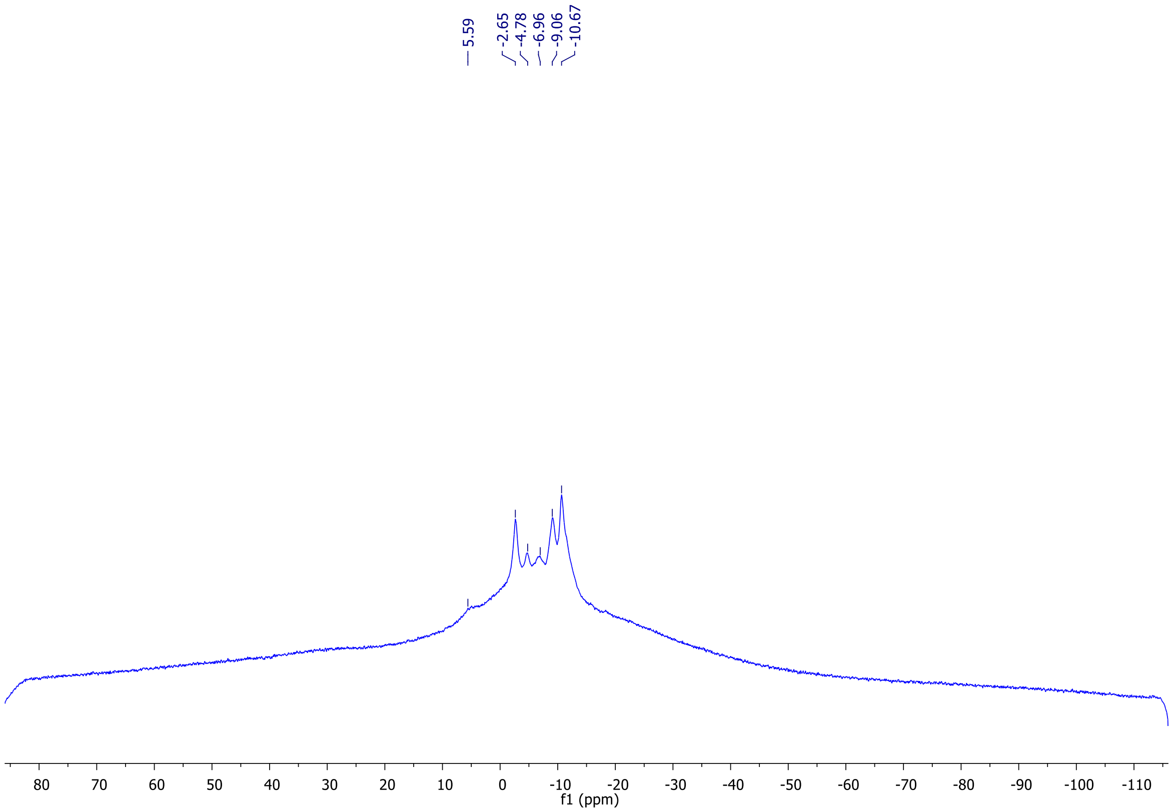


Figure S68. ^{11}B{^{1}H} NMR spectrum (128 MHz, CDCl3) of **6$^{\mathbf{cls}}$**.

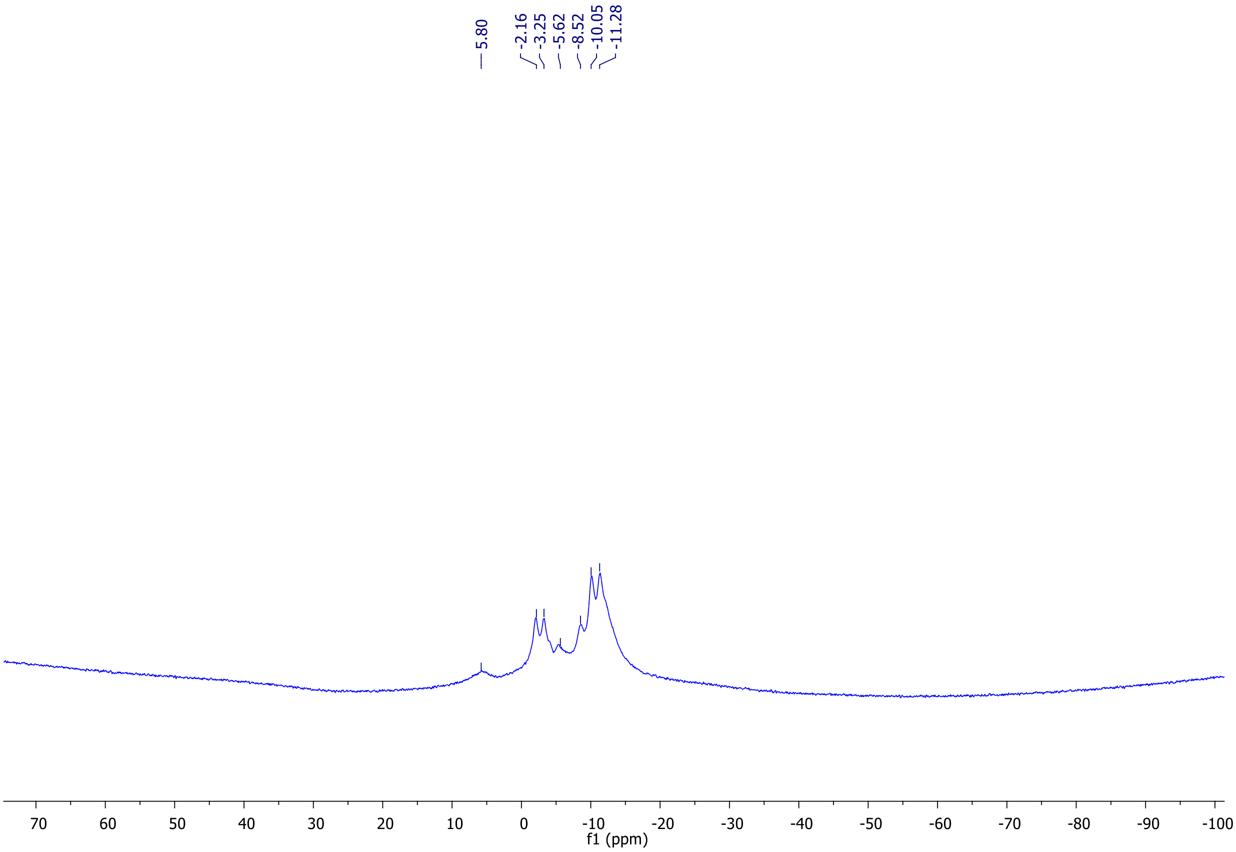


Figure S69. ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **6^{cls}**.

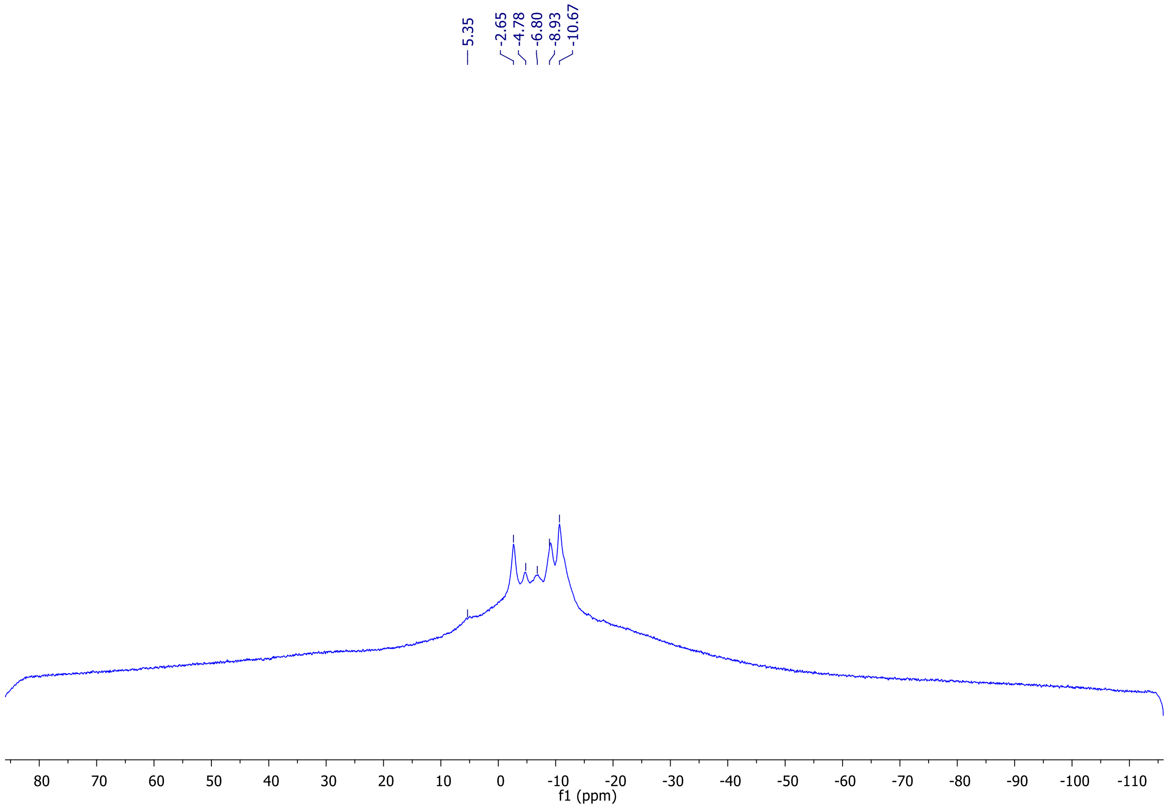


Figure S70. ^{11}B {^{1}H} NMR spectrum (128 MHz, CDCl3) of **6^{cls}**.

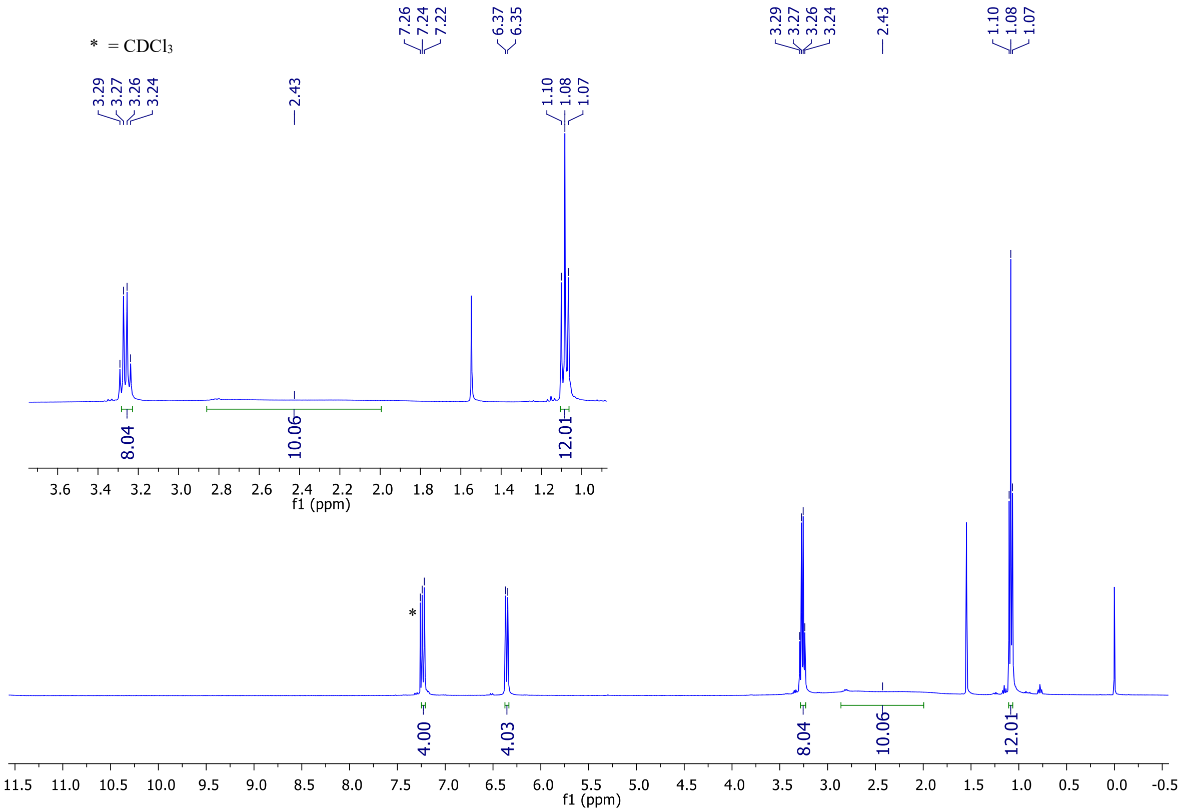


Figure S71. ^{1}H NMR spectrum (400 MHz, CDCl3) of **11**.

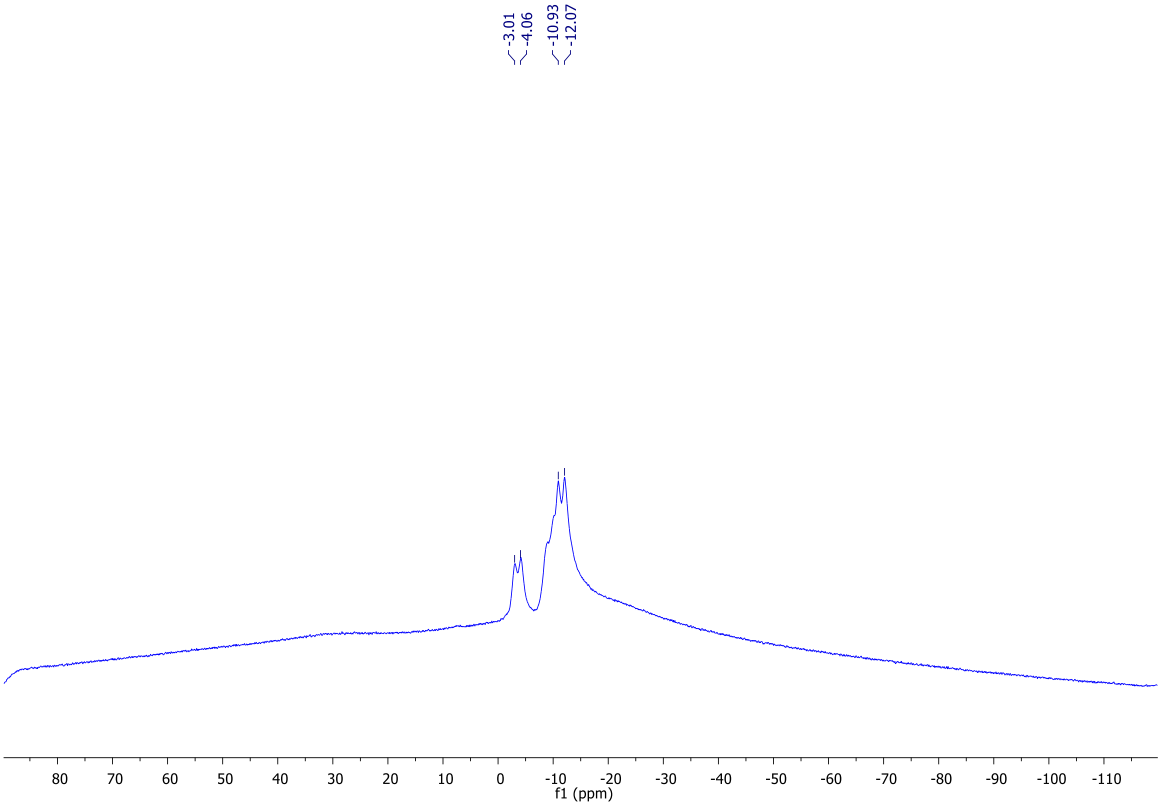


Figure S72. ^{11}B NMR spectrum (128 MHz, CDCl3) of **11**.

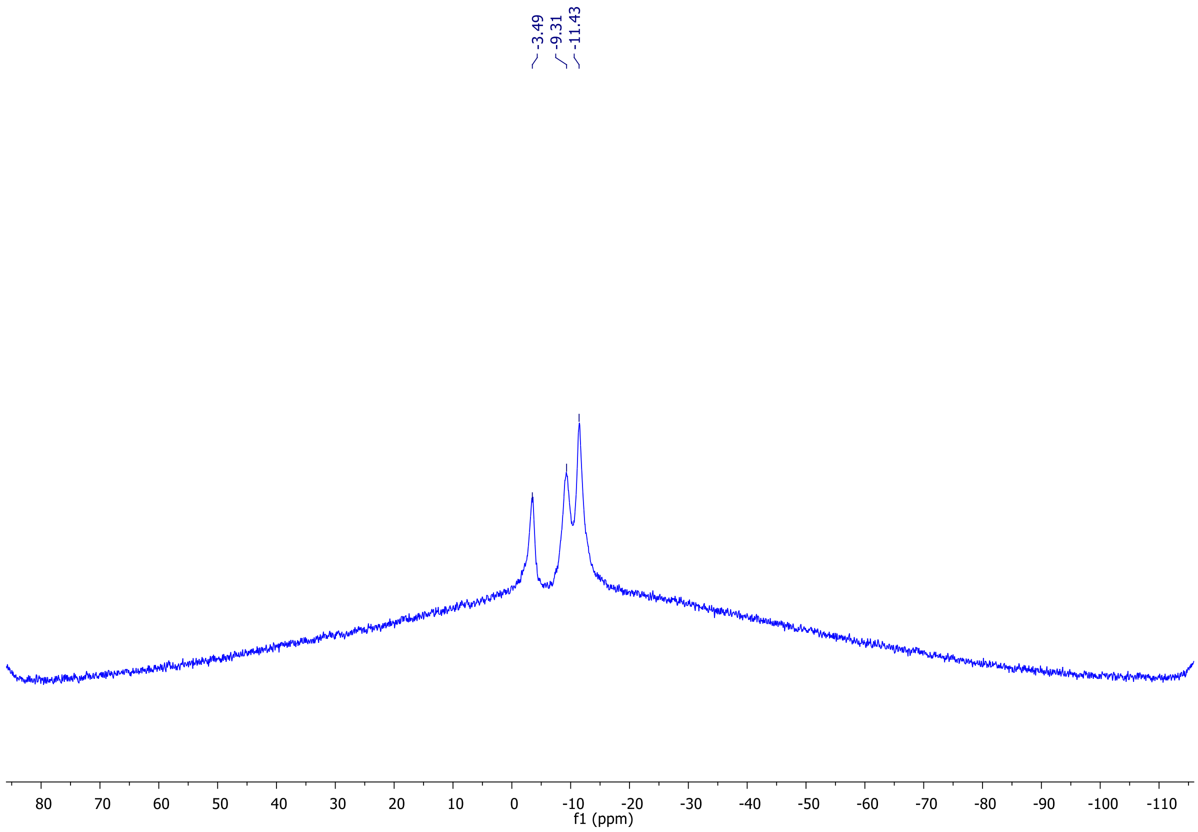


Figure S73. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, CDCl3) of **11**.

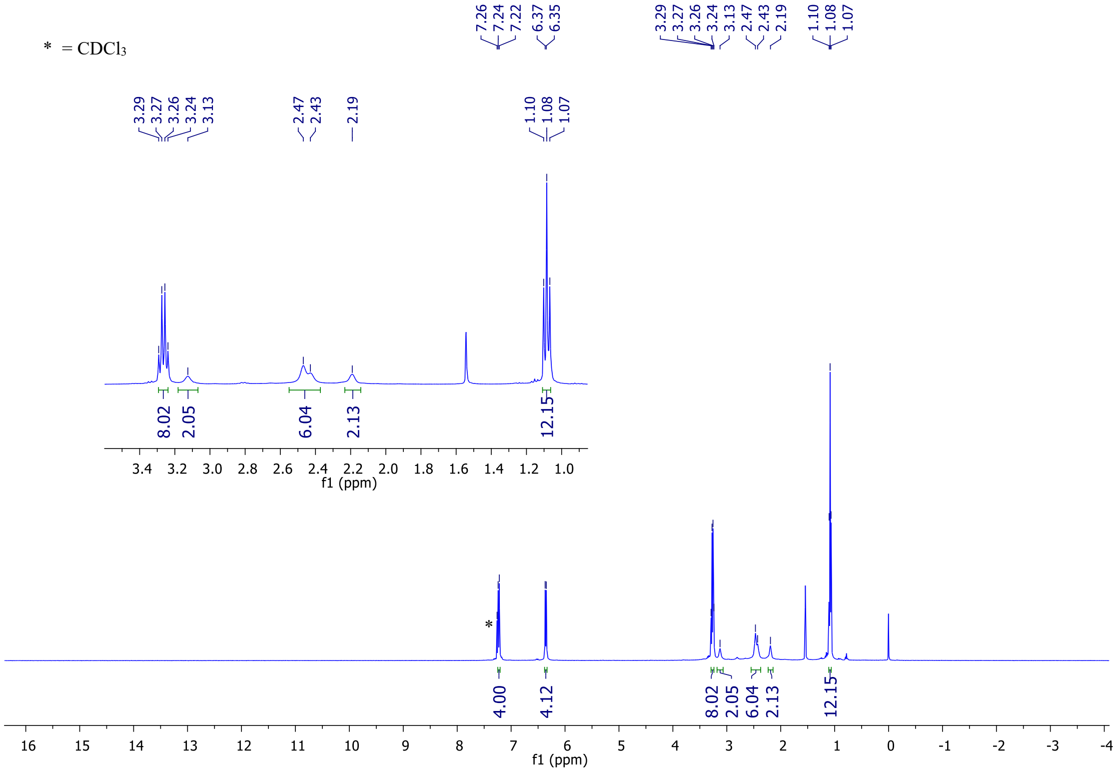


Figure S74. $^{1}H\{^{11}B\}$ NMR spectrum (400 MHz, CDCl3) of **11**.

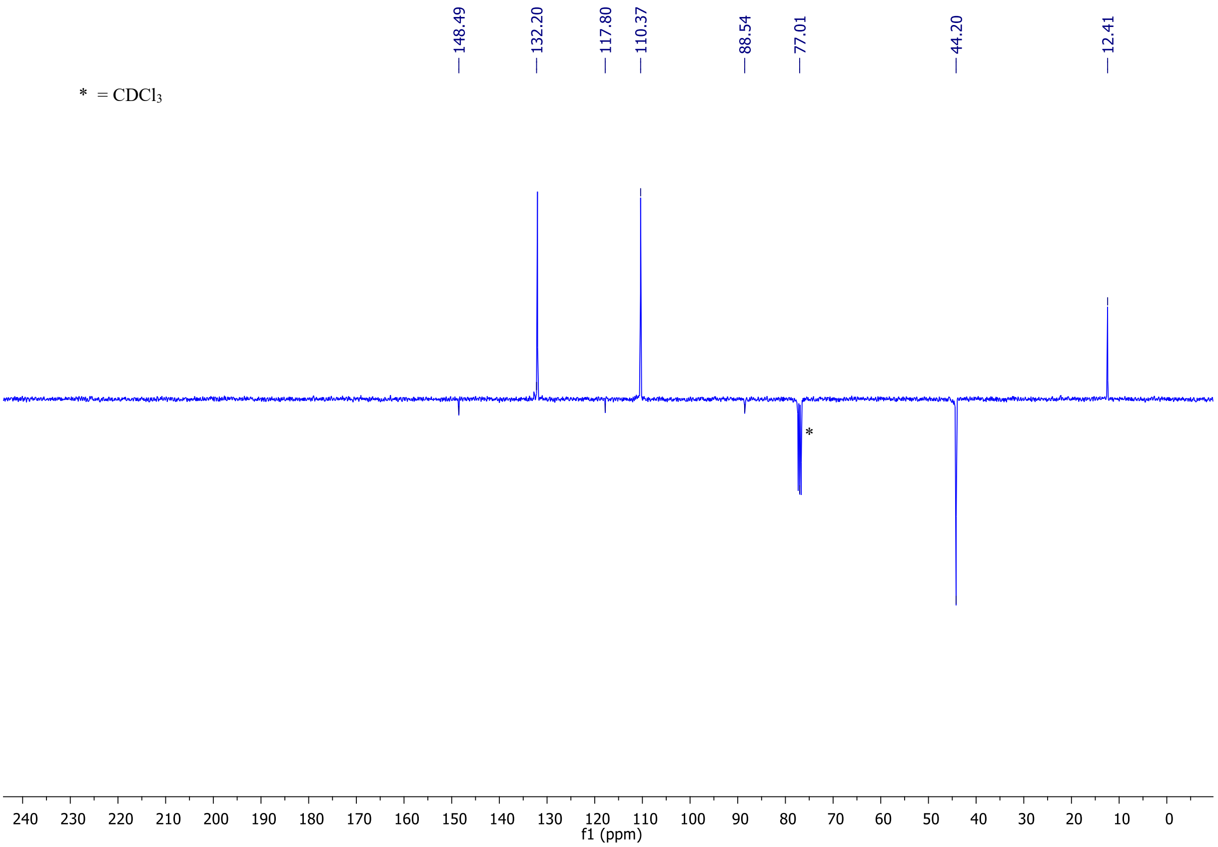


Figure S75. ^{13}C{1H} NMR spectrum (JMOD, 101 MHz, CDCl3) of **11**.

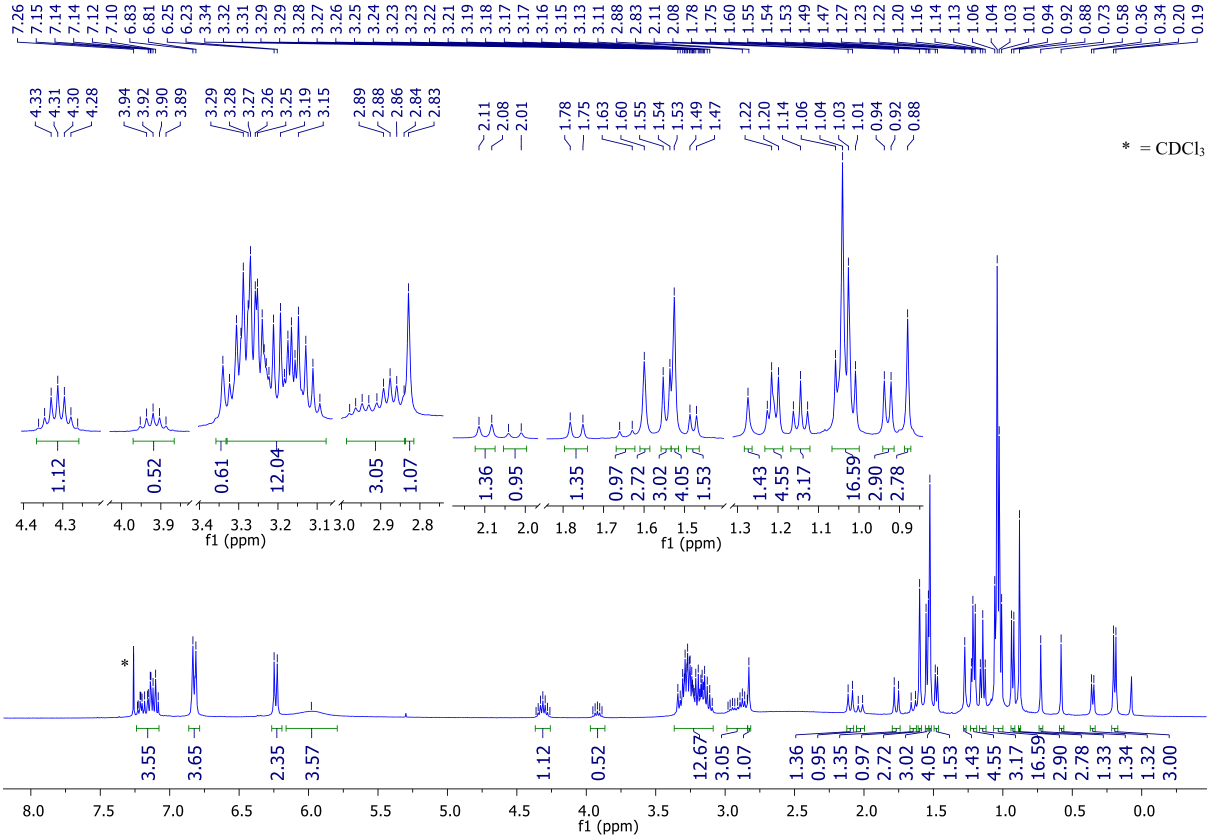


Figure S76. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **9^{cls}**.

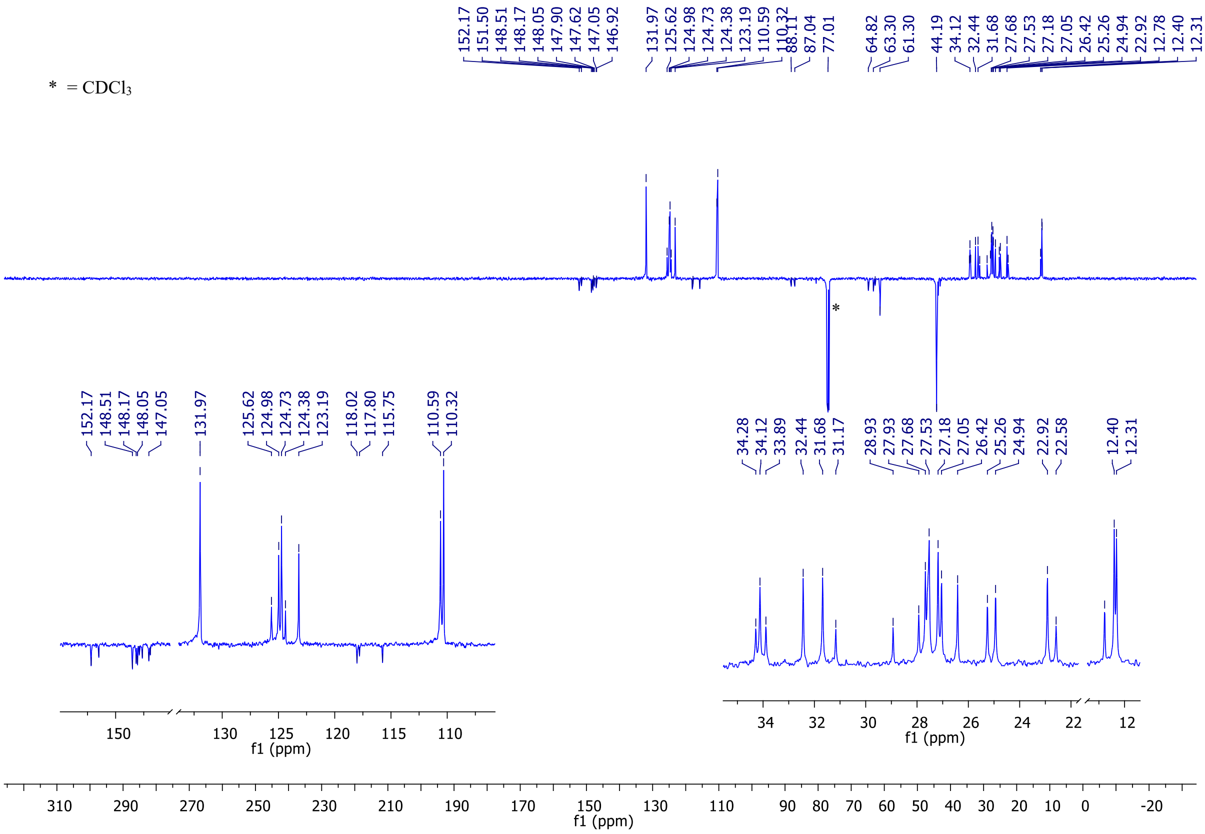


Figure S77. ^{13}C{1H} NMR spectrum (JMOD, 101 MHz, CDCl$_3$) of **9$^{\mathbf{cls}}$**.

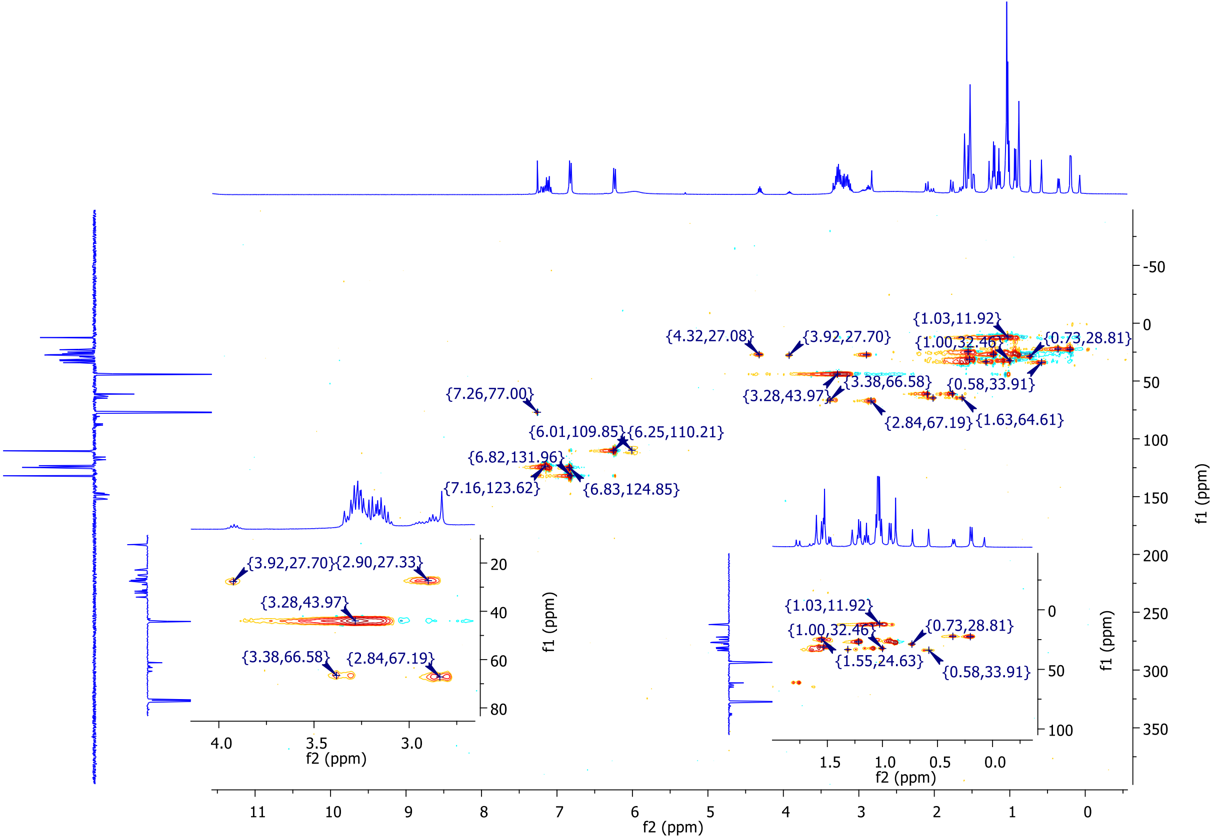


Figure S78. ^{1}H-^{13}C HSQC spectrum (CDCl$_3$) of **9$^{\mathbf{cls}}$**.

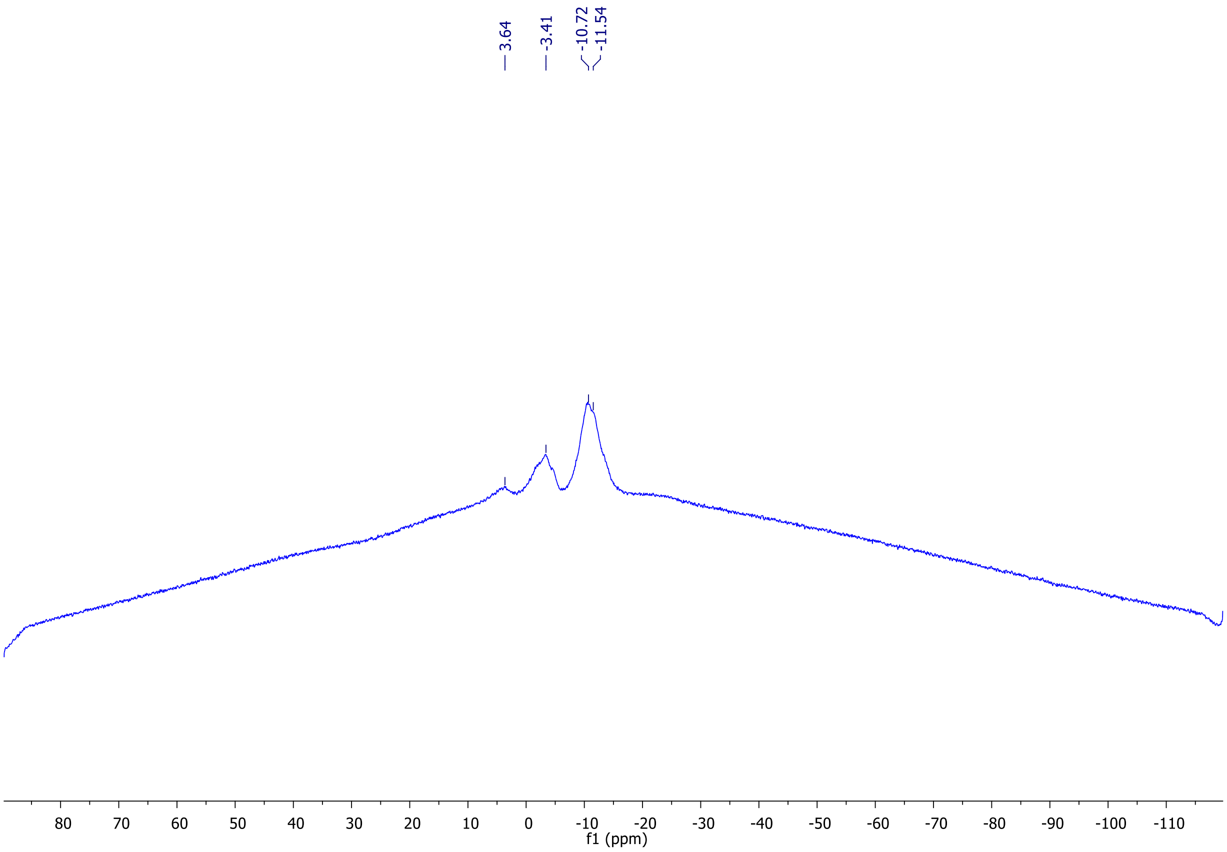


Figure S79. ^{11}B NMR spectrum (128 MHz, CDCl$_3$) of **9**$^{\text{cls}}$.

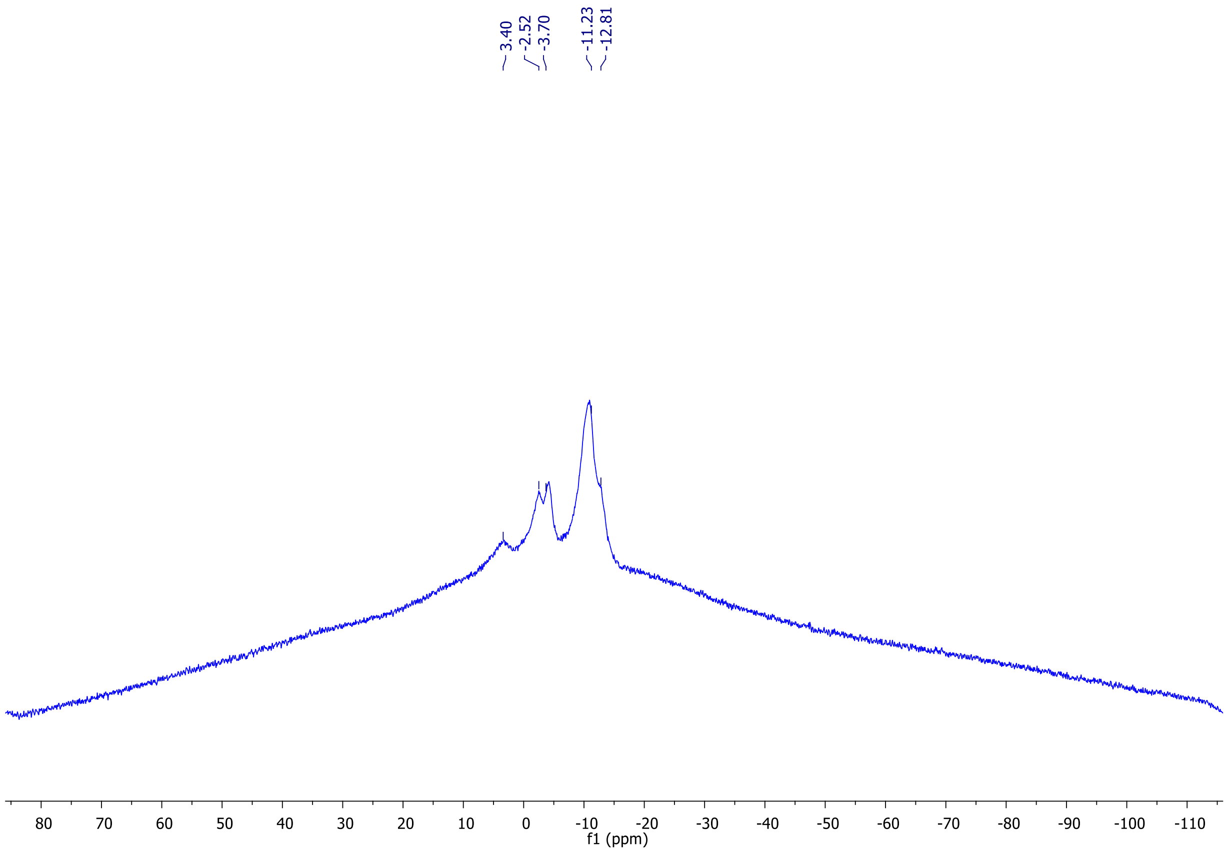


Figure S80. ^{11}B{^{1}H} NMR spectrum (128 MHz, CDCl$_3$) of **9**$^{\text{cls}}$.

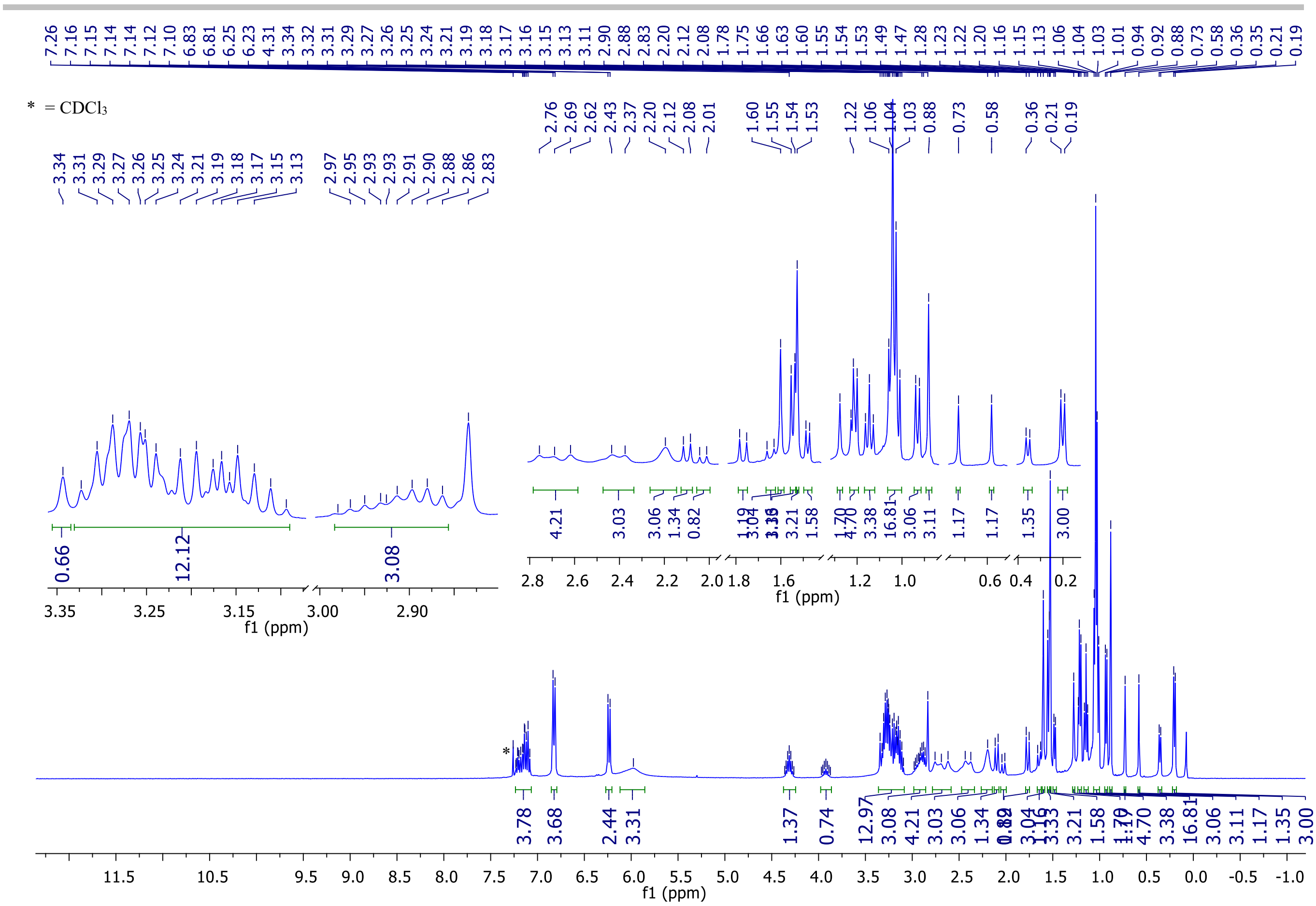


Figure S81. $^1H\{^{11}B\}$ NMR spectrum (400 MHz, $CDCl_3$) of **9^cls^**.

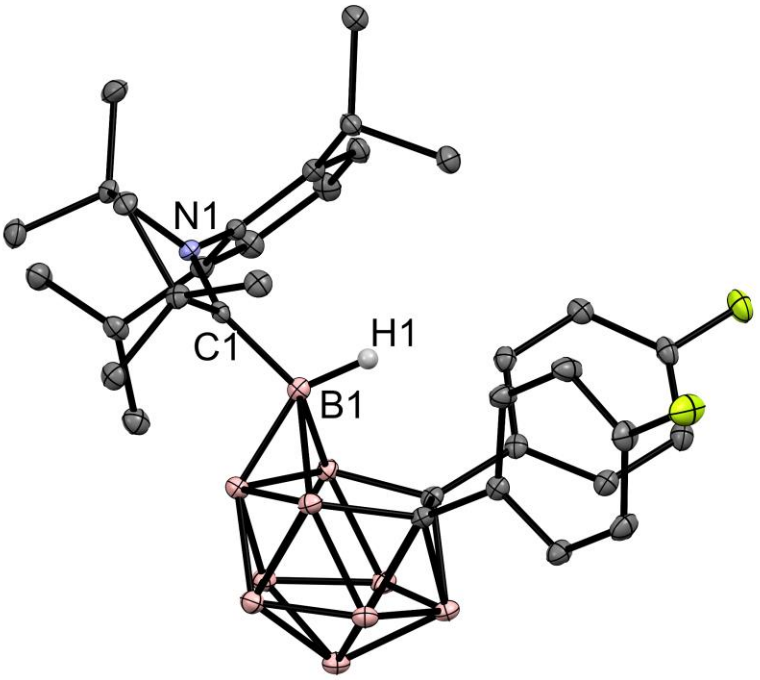


Figure S82. POV-ray depiction of **10*nido***. Thermal ellipsoids at 50% probability, non-relevant hydrogen atoms were omitted for clarity.

5. DFT Calculations

DFT calculations were performed using Gaussian 09.2.[17] Geometry optimization of all the molecules was carried out using the BP86-D3 method with Ahlrichs' def2-TZVP basis set (and def2-SVP where mentioned),[17,18,19] implemented in the Gaussian 09 software. Thermal energy corrections were extracted from the results of frequency analysis performed at the same level of theory. Frequency analysis of all the molecules and intermediates contained no imaginary frequency, showing that these are energy minima. The transition states geometries gave one imaginary frequency at the expected reaction coordinates, confirming that it is a first-order saddle point. IRC (Intrinsic Reaction Coordinate) calculations and subsequent geometry optimizations were also used to ensure the minima are related to the isolated transition states.

In the reaction of $^{\mathbf{Me2}}$**CAAC** with $^{\mathbf{Anil2}}$***o*****Cb**, no experimental evidence for the formation of a **9B3**$^{\mathbf{\textit{nido}}}$ intermediate was detected. Upon slow heating of the reaction mixture to 60 °C and monitoring by NMR spectroscopy, no formation of **9B3**$^{\mathbf{\textit{nido}}}$ was observed. Importantly, the reaction is performed in benzene, in which *nido* species are insoluble; however, at no point during the very slow reaction was precipitation detected.

These observations strongly suggest that any *nido* intermediate formed in the reaction (**9B4**$^{\mathbf{nido}}$ or **9B3**$^{\mathbf{nido}}$) must be unstable and possess a low barrier toward hydride migration and formation of the final product **9B4**$^{\mathbf{cls}}$ (or **9B3**$^{\mathbf{cls}}$ before vertex migration). In other words, the rate-determining step (RDS) must occur before formation of the *nido* intermediate; otherwise, the *nido* species would accumulate and be observed experimentally.

To clarify this point, we examined both competing mechanisms computationally. The calculated energy barriers for carbene attack at B3 and B4 are very similar ($\Delta G^{\ddagger} = 14.6$ and 17.1 kcal mol^{-1}, respectively; see Figure S83). Thus, kinetically, both **9B3**$^{\mathbf{nido}}$ and **9B4**$^{\mathbf{nido}}$ could form. Thermodynamically, however, **9B3**$^{\mathbf{nido}}$ is more stable than **9B4**$^{\mathbf{nido}}$ ($\Delta G = 12.2$ and $\Delta H = 14.2$ kcal mol^{-1} in favor of **9B3**$^{\mathbf{nido}}$; see Figure S83).

If **9B3**$^{\mathbf{nido}}$ is formed, the subsequent hydride migration to give **9B3**$^{\mathbf{cls}}$ is calculated to be exergonic and exothermic ($\Delta G = -8.1$ and $\Delta H = -11.1$ kcal mol^{-1}), but proceeds via a relatively high energy barrier of $\Delta G^{\ddagger} = 20.0$ kcal mol^{-1}. This would make the hydride migration step the RDS. Such a scenario contradicts the experimental observation that no *nido* intermediate is detected, since the *nido* species would be expected to accumulate (RDS after the formation of the nido species). Therefore, this pathway appears less feasible (see Figure S83).

In addition, **9B3**$^{\mathbf{cls}}$ would need to undergo vertex migration to give the experimentally observed product **9B4**$^{\mathbf{cls}}$, which is calculated to be thermodynamically more stable, likely due to reduced steric repulsion relative to **9B3**$^{\mathbf{cls}}$ (see Figure S83). Alternatively, vertex migration at the *nido* stage (between **9B3**$^{\mathbf{nido}}$ and **9B4**$^{\mathbf{nido}}$) was considered; however, this transformation is highly endergonic and endothermic, further reducing the plausibility of this pathway in light of the experimental observations (absence of observable *nido* intermediates).

In contrast, if **9B4**$^{\mathbf{nido}}$ is formed, the subsequent hydride migration to give **9B4**$^{\mathbf{cls}}$ is highly exergonic and exothermic ($\Delta G = -33.1$ and $\Delta H = -36.9$ kcal mol^{-1}) and proceeds via a very low barrier of only $\Delta G^{\ddagger} =$ 3.1 kcal mol^{-1}. In this case, the RDS would be the initial formation of **9B4**$^{\mathbf{nido}}$, fully consistent with the requirement that the RDS precedes *nido* formation, and therefore in agreement with the experimental observations (see Figure S83).

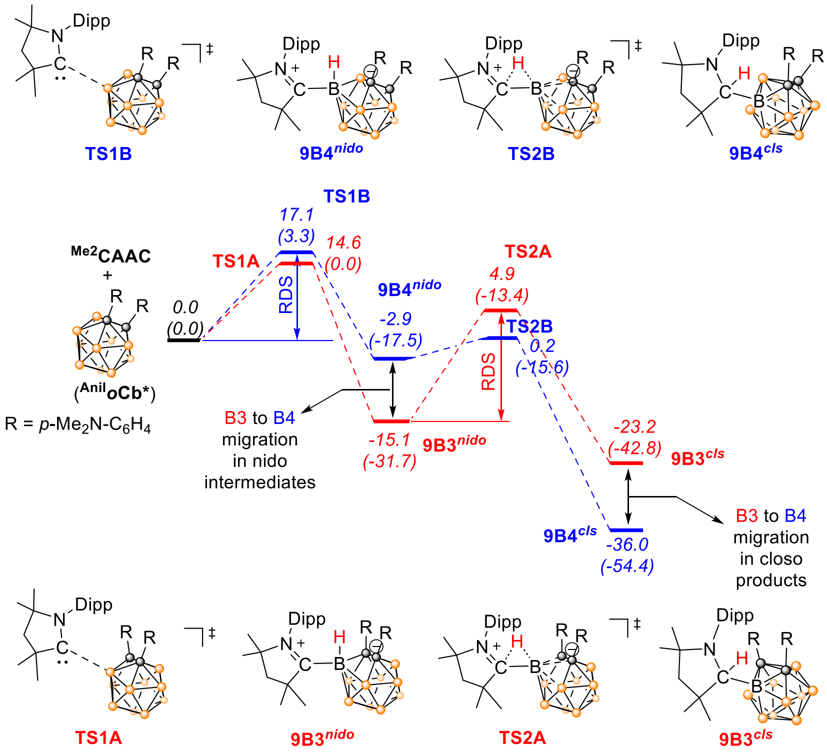


Figure S83. DFT computed mechanism for the reaction between **$^{\text{Anil}}$*o*Cb*** with **$^{\text{Me2}}$CAAC** leading to the formation of **9B3^{cls}** vs. **9B4^{cls}**.

6. References

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