

Supporting Information

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Reduction of Borazines Mediated by Low-Valent Chromium Species**

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Supporting Information

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Experimental Details

General: All experiments were conducted using standard Schlenk techniques or in a nitrogen filled glovebox. NMR spectra were recorded on Varian MR400, vnmrs 500, Inova 500, or vnmrs 700 MHz spectrometers. ^1H NMR, and solvent suppression ^1H NMR spectra were referenced relative to the protio solvent resonance, and ^{11}B , ^{13}C , and ^{19}F spectra are referenced indirectly based on the ^1H spectrum.^[1] As previously reported,^[2] the carbon atoms directly bound to boron were difficult to observe and/or unambiguously assign by ^{13}C NMR due to quadrupolar coupling. IR Spectra were recorded on a Nicolet iS-10 spectrometer from Thermo Scientific as either KBr pellets or on a diamond attenuated total reflectance (ATR) accessory. Cyclic voltammetry experiments were collected on a Pine Research Instrumentation WaveNow potentiostat. Experiments were conducted in a 0.05 M solution of tetrabutylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TBABAr⁺) in either diethyl ether or 1,2-dimethoxyethane solvent. A glassy carbon working electrode and a platinum disk counter electrode were used and voltammograms referenced relative to ferrocene ($\text{Fc}^{0/+}$) using a silver wire pseudo reference electrode. Potentials are reported as $E_{1/2}$ values where a return wave is present and as E_{pa} or E_{pc} values where a return wave is absent or very weak. Scan rate was 0.1 V/s unless otherwise specified. TBABAr⁺ was synthesized using a modified version of the procedure reported by Kobayashi and coworkers^[3] for the synthesis of tetraethylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. Tetrabutylammonium chloride was used in place of tetraethylammonium iodide, and extraction with ether followed by drying over MgSO_4 was used in-lieu of column chromatography. Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, hexamethylborazine ($\text{Me}_6\text{B}_3\text{N}_3$), and $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ were synthesized by previously reported routes.^[4] Diethyl ether, pentane, tetrahydrofuran, and 1,2-dimethoxyethane were ordered from Fisher Scientific and passed through an S.G. Waters solvent purification system. 1,4-dioxane was distilled from sodium and degassed prior to use. Deuterated NMR solvents were either obtained as sealed ampoules and used as received, or degassed and dried by standard methods.^[5] All other chemicals were purchased from commercial vendors and used as received.

Synthesis of 1 ($\eta^6\text{-(Me}_6\text{B}_3\text{N}_3\text{)Cr}(\text{CO})_3$): A simplified version of the procedure reported by Werner and co-workers^[6] was used. A solution of $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ (1.5 g, 5.8 mmol) and hexamethylborazine ($\text{Me}_6\text{B}_3\text{N}_3$; 4.8 g, 29.0 mmol) was prepared in 1,4-dioxane (50 mL). The orange solution was stirred at 25 °C under dynamic vacuum until the solvent evaporated. Reaction progress was monitored by IR spectroscopy and solvent addition and removal was repeated 5 times. Complete conversion to $\eta^6\text{-(Me}_6\text{B}_3\text{N}_3\text{)Cr}(\text{CO})_3$ was confirmed by the disappearance of $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ in the IR spectrum (bands at 1912 and 1772 cm^{-1}). The resulting yellow solid was then dissolved in Et_2O (200 mL), filtered through a medium porosity sintered glass frit, and the solvent was removed *in vacuo*. Solid was then washed 5 times with cold pentane (10 mL) and dried under vacuum. Yield: 1.2 g, (69%). The product obtained is spectroscopically identical to that previously reported in C_6D_6 , however, because borazine is slowly displaced by this solvent, we report characterization in substitutionally-inert solvent (CD_2Cl_2). ^1H NMR (399.54 MHz, CD_2Cl_2): δ 2.94 (s, 9H; N- CH_3), 0.79 (s, 9H; B- CH_3); ^{11}B NMR (128.19 MHz, CD_2Cl_2): δ 27.20 (s); Cyclic voltammetry (0.05 M TBABAr⁺ in Et_2O): E_{pa} (V vs. $\text{Fc}^{0/+}$) -1.38, -2.92, -3.57, $E_{1/2}$ (V vs. $\text{Fc}^{0/+}$) -0.59, 0.29, E_{pc} (V vs. $\text{Fc}^{0/+}$) 0.69, 0.05. Crystals suitable for X-ray diffraction were obtained from diethyl ether/pentane (1:1) at -35 °C.

Synthesis of 2 ($\eta^3\text{-(Me}_6\text{B}_3\text{N}_3\text{)(}\mu\text{-H)Cr}(\text{CO})_3\text{Li}(\text{Et}_2\text{O})_2$): To a frozen solution of **1** (21.0 mg, 0.070 mmol) in 10 mL Et_2O was added a solution (obtained by reducing a 1.0 M solution from Sigma Aldrich under vacuum to 1:1.5 mol/mol as determined by ^1H NMR integration) of LiEt_3BH in THF (44.3 mg, 0.210 mmol). The mixture was allowed to thaw in a -35 °C freezer and further react for 18 h. **2** is thermally sensitive and decomposes readily at room temperature, however, it can be observed in solutions of the reaction mixture by low temperature (-20 °C) ^{11}B and ^1H NMR spectroscopy. Solvent Suppression ^1H NMR (500.10 MHz, Et_2O): δ 2.57 (s, 3H; N- CH_3), 2.24 (s, 6H; N- CH_3), 0.33 (s, 6H; B- CH_3), 0.17 (s, 3H; B- CH_3), -2.92 (br, 1H; B-H-Cr); ^{11}B NMR (160.45 MHz, Et_2O): δ -0.82 (s). Note: while two ^{11}B resonances are expected, only one could be conclusively identified. Enhanced quadrupolar relaxation, introduced through asymmetry of the electric field gradient surrounding the B=N bonding scaffold, likely broadens the resulting ^{11}B resonance into the baseline.^[7] Similar observations have been reported previously.^[8] Crystals suitable for X-ray diffraction were obtained by performing the reaction in Et_2O /pentane (5:1) at -35 °C.

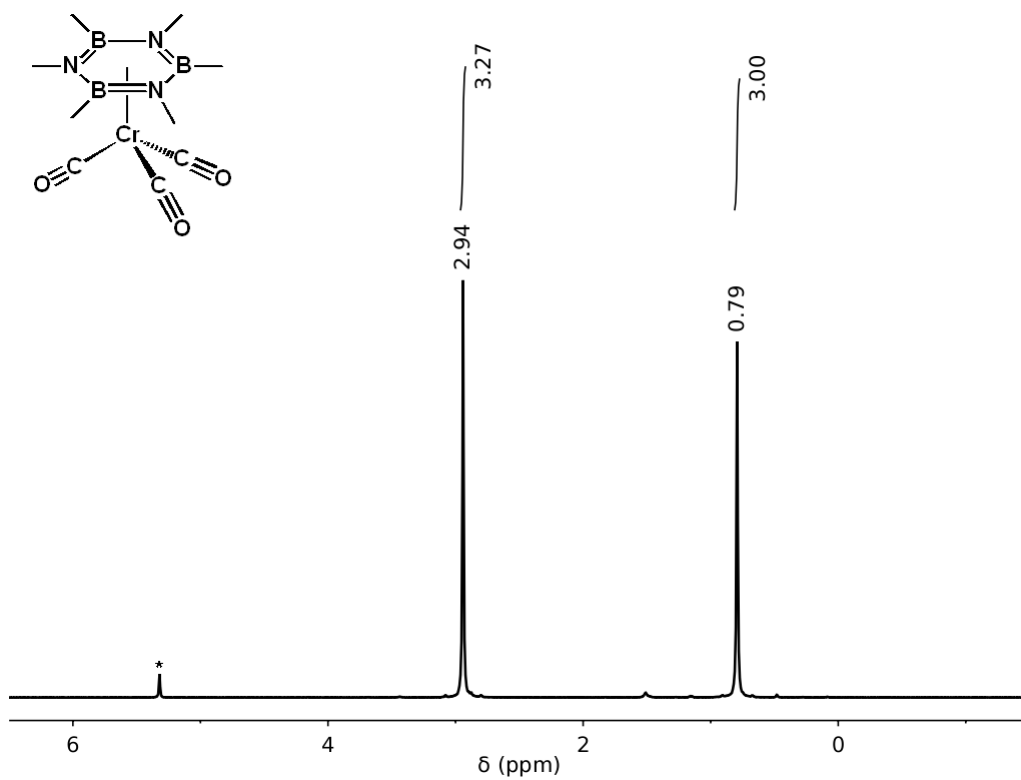
Synthesis of 3 ($\eta^5\text{-(Me}_6\text{B}_3\text{N}_3\text{)Cr}(\text{CO})_3\text{Mg}(\text{THF})_4\text{Br}$): To a frozen solution of **1** (60.0 mg, 0.2 mmol) in 5 mL Et_2O , was added a solution of MeMgBr (3.0 M in Et_2O from Sigma Aldrich; 66.0 μL , 0.22 mmol). The solution was allowed to thaw and the resulting yellow precipitate was collected on a glass microfiber filter pad, washed with pentane (3 x 1 mL), and passed through the filter with THF. The solvent was removed under vacuum to afford a yellow powder (77.4 mg; 95%). ^1H NMR (500.10 MHz, $[\text{D}_8]\text{THF}$): δ 2.85 (s, 3H; N- CH_3), 2.42 (s, 6H; N- CH_3), 0.55 (s, 6H; B- CH_3), -0.07 (s, 3H; B- CH_3), -0.83 (s, 3H; B- CH_3); ^{11}B NMR (128.19 MHz, $[\text{D}_8]\text{THF}$): δ 30.98 (s), 3.90 (s); ^{13}C NMR (125.71 MHz, $[\text{D}_8]\text{THF}$): δ 251.69 (s), 203.90 (s), 39.13(s), 38.04 (s); IR (KBr): ν_{CO} 1925, 1763, 1694 cm^{-1} , ν_{BN} 1468, 1456, 1400, 1384, 1350 cm^{-1} . Cyclic voltammetry (0.05 M TBABAr⁺ in 1,2-dimethoxyethane): $E_{1/2}$ (V vs. $\text{Fc}^{0/+}$) -0.77, E_{pa} (V vs. $\text{Fc}^{0/+}$) -0.13, 0.22. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a THF solution of **3** at -35 °C.

Synthesis of 4 ($\text{OAc}^{\text{F}}\text{Me}_6\text{B}_3\text{N}_3\text{Me}_3\text{D}_3$): To a frozen solution of **3** (20.9 mg, 0.030 mmol) in 2 mL DME was added DOAc^{F} (11.4 μL , 0.149 mmol). The solution was allowed to thaw and warm to room temperature over 10 minutes. The solvent was removed. Solid was washed with pentane (1 x 3 mL) and the pentane solution was decanted and retained. The solvent was removed to afford 4.5 mg (40.2% yield) of a white solid. **4** is obtained as a mixture of isomers. The most abundant isomer (ca. 75% of the mixture) is consistent with the solid-state structure and can be obtained in good purity by recrystallization from a saturated pentane solution stored at -35 °C. **4** decomposes slowly at room temperature, but is stable over periods of at least 2 weeks when stored at -35 °C. ^1H NMR (399.54 MHz, C_6D_6): δ 1.80 (s, 6H; N- CH_3), 1.73 (s, 3H; N- CH_3), -0.10 (s, 6H; B- CH_3), -0.28 (s, 3H; B- CH_3), -0.31 (s, 3H; B- CH_3); ^2H NMR (61.33 MHz, C_6H_6): δ 4.79 (s; N-D), 2.99 (s; N-D); ^{11}B NMR (128.19 MHz, C_6D_6): δ 6.31 (s), 0.94 (s); ^{19}F NMR (375.91 MHz,

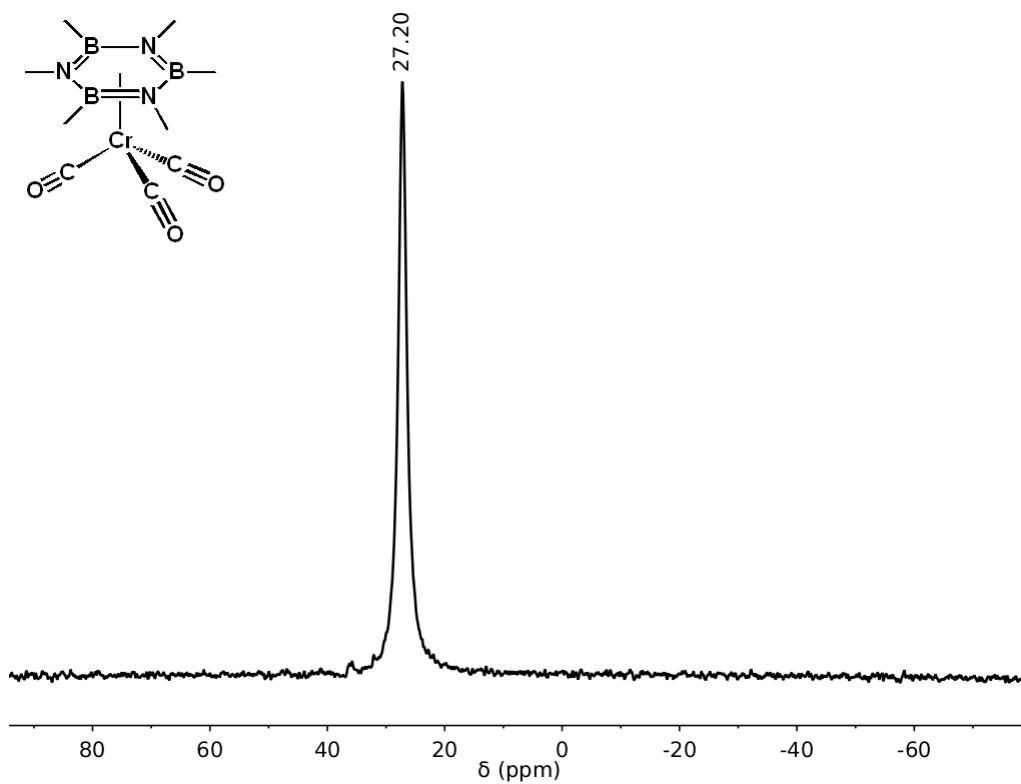
C_6D_6): δ -76.14 (s); IR (KBr): ν_{N-D} 2386, ν_{CO-OAc^F} 1716, ν_{BN} 1426, 1335, 1318 cm^{-1} . Crystals suitable for X-ray diffraction were obtained from a cooling a saturated pentane solution of **5** to -35 °C.

Synthesis of 5 (OAc^F₃Me₃B₃N₃Me₃D₃): To a frozen solution of hexamethylborazine (76.4 mg, 0.46 mmol) in 10 mL pentane was added DOAc^F (180 μ L, 2.30 mmol). The solution was allowed to thaw and warm to room temperature over 10 minutes with stirring. Following the formation of a white precipitate, the solution was decanted and the solid was rinsed with Et₂O (2 x 2 mL). The solid was dried in-vacuo to give 178.9 mg (76.3 % yield) of the title compound. **4** is obtained as a mixture of isomers with distinct ¹H and ¹⁹F resonances but with an identical ¹¹B resonance. This, in combination with elemental analysis is taken as evidence that all species present share the same empirical formula. NMR data is presented for the most abundant isomer. **4** decomposes slowly at room temperature, but is stable over periods of at least 2 weeks when stored at -35 °C. ¹H NMR (500.09 MHz, CDCl₃): δ 2.37 (s, 9H; N-CH₃), 0.11 (s, 9H; B-CH₃); ²H NMR (61.33 MHz, CHCl₃): δ 4.89 (s; N-D); ¹¹B NMR (160.45 MHz, CDCl₃): δ 5.87.; ¹⁹F NMR (470.52 MHz, CDCl₃): δ -75.90 (s); ¹³C NMR (125.71 MHz, CDCl₃): δ 160.16 (s, OAc^F-CO), δ 114.40 (q, CF₃, ²J(C,F)=287.43 Hz), δ 29.97 (s, N-CH₃); IR (KBr): ν_{N-D} 2407, 2380 cm^{-1} , ν_{CO-OAc^F} 1767, 1721 cm^{-1} , ν_{BN} 1421, 1396, 1334 cm^{-1} . Elemental analysis calculated (corrected for deuterium) for C₁₂H₁₈B₃D₃F₉N₃O₆: C 28.27, H 4.18, N 8.24; found: C 28.40, H 4.11, N 8.11. Note that when HOAc^F is used a product which is identical to the deuterate is obtained with the exception of the N-H bonds as visualized by IR spectroscopy: ν_{N-H} 3233, 3207 cm^{-1} (See Figures SI-18 and SI-19).

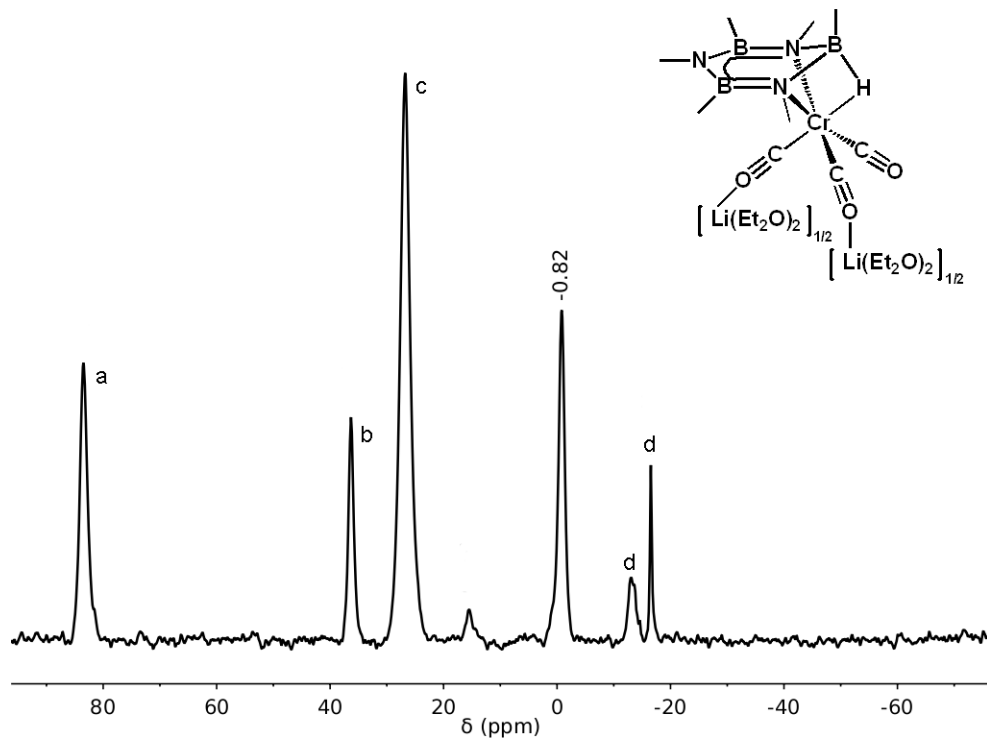
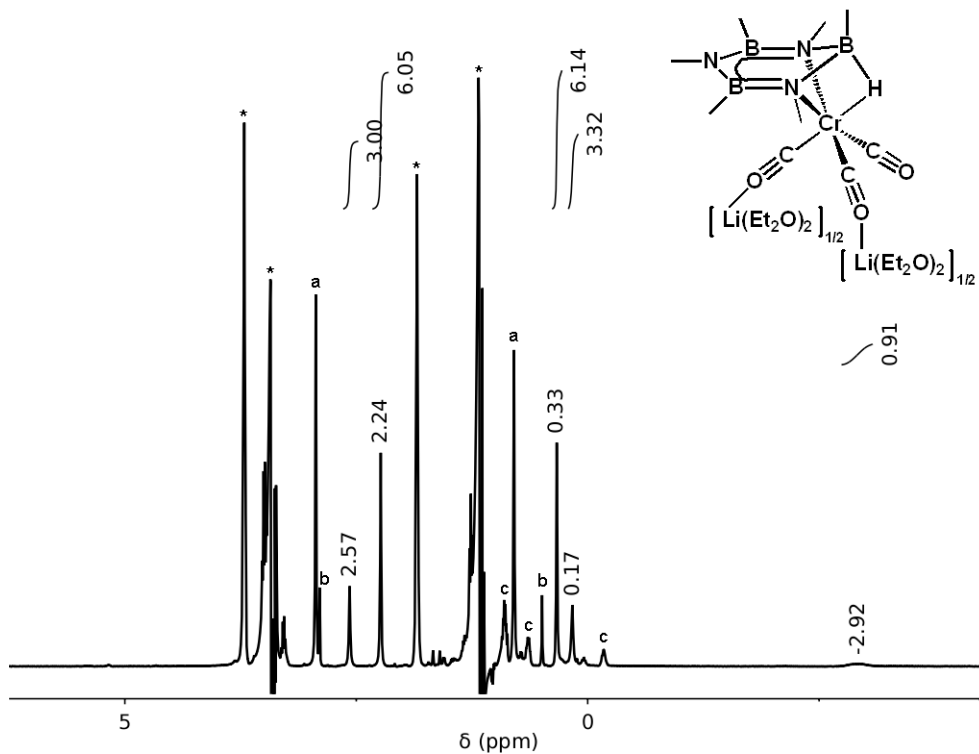
NMR Spectra

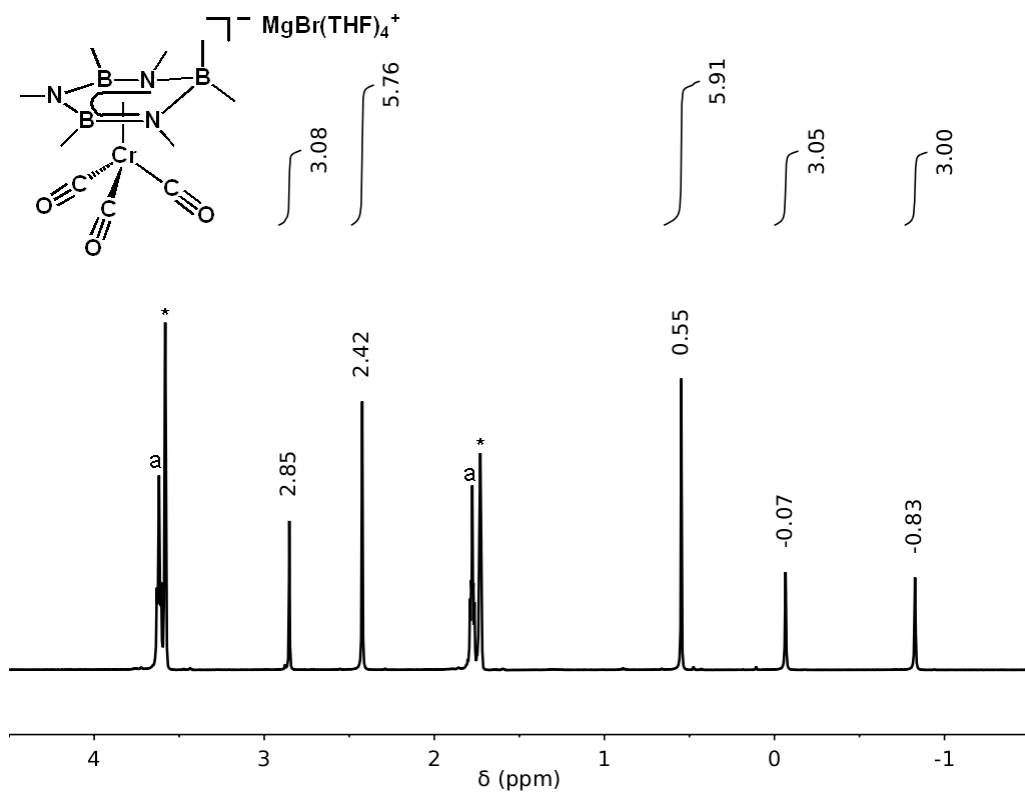


SI Figure 1: ¹H NMR spectrum of **1**, 399.54 MHz, CD₂Cl₂.

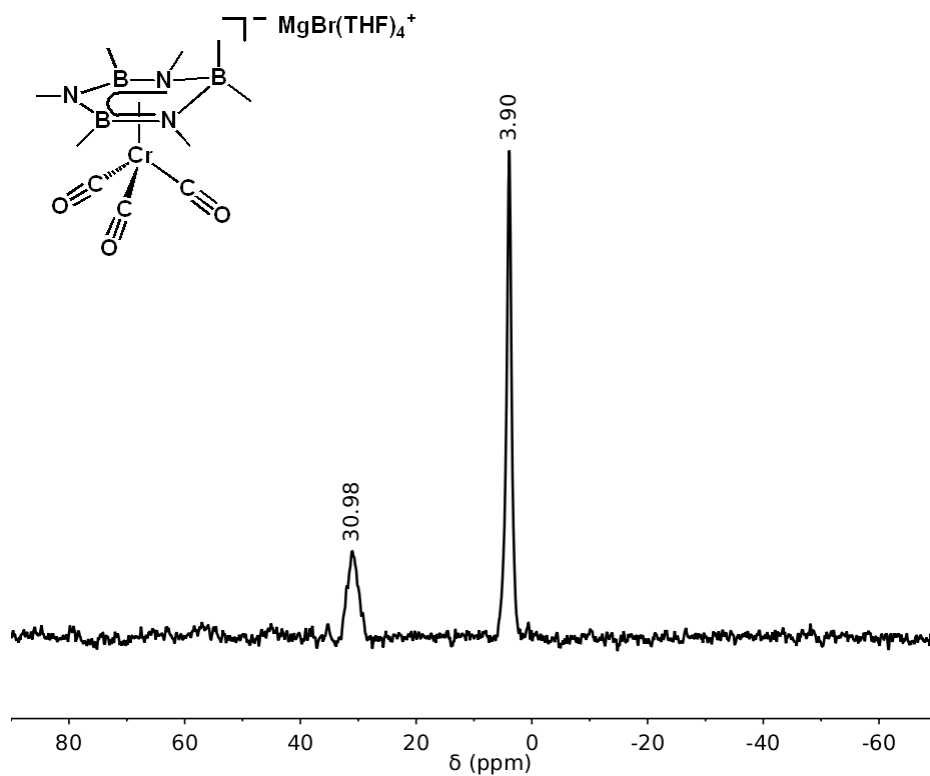


SI Figure 2: ¹¹B NMR spectrum of **1**, 128.19 MHz, CD₂Cl₂.

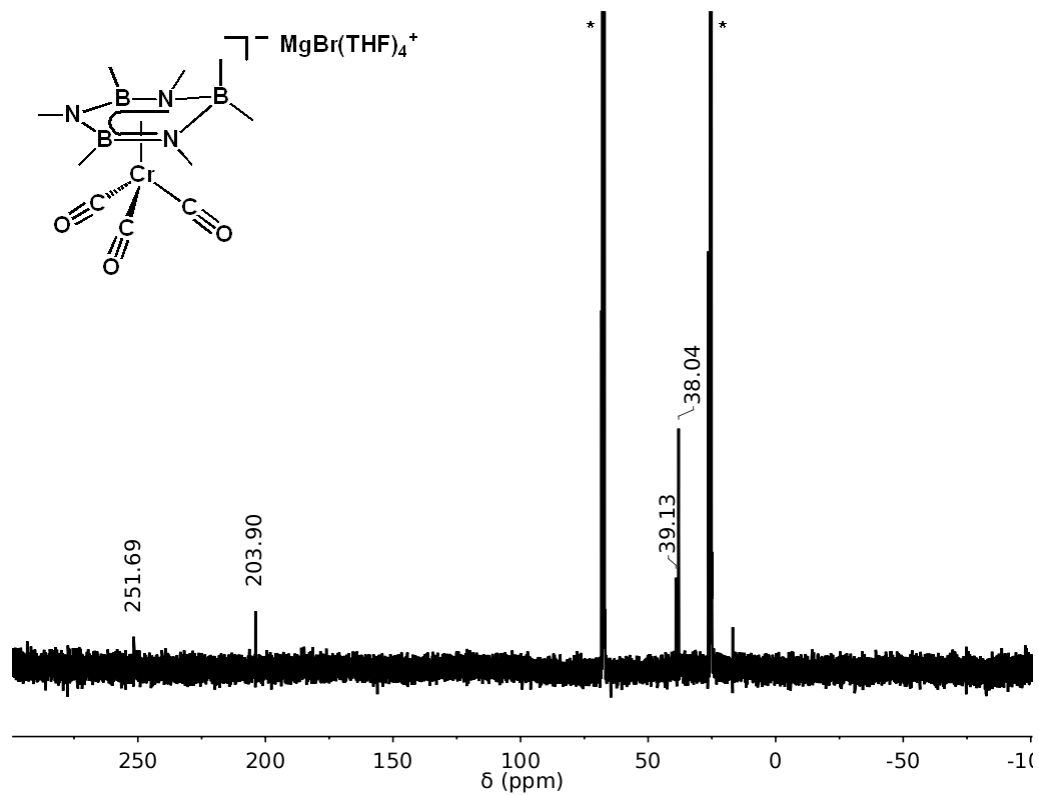




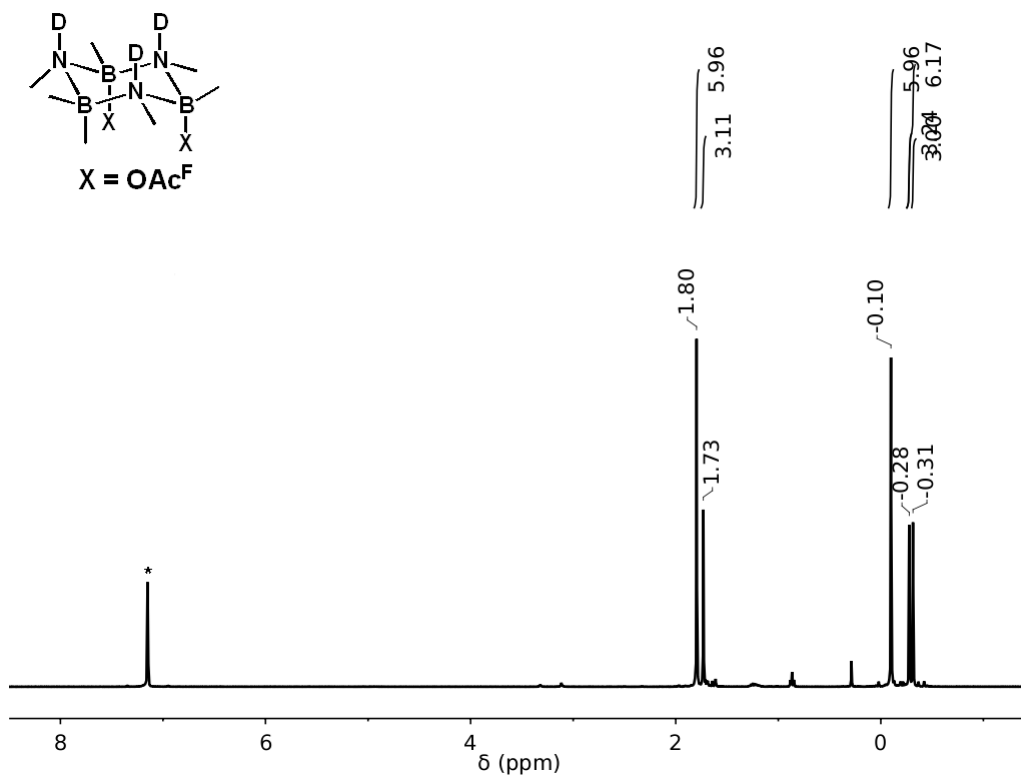
SI Figure 5: ^1H NMR spectrum of **3**, 500.10 MHz, $[\text{D}_8]\text{THF}$.
 a) Protic THF associated with Mg^{2+} cation.



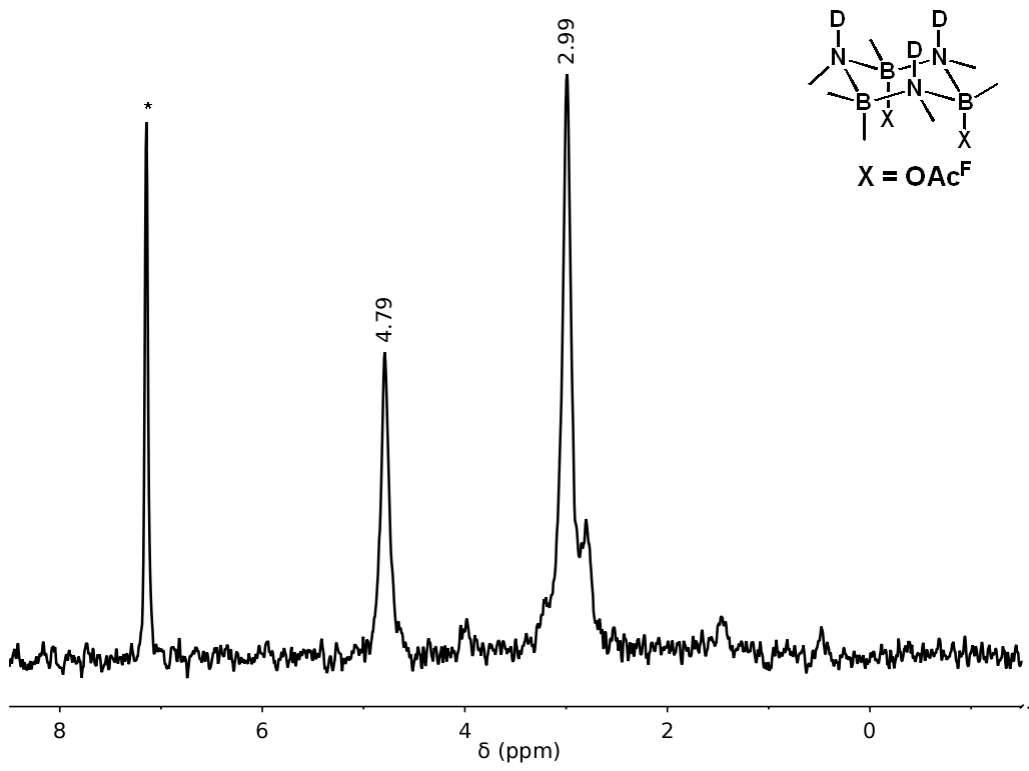
SI Figure 6: ^{11}B NMR of **3**, 128.19 MHz, $[\text{D}_8]\text{THF}$.



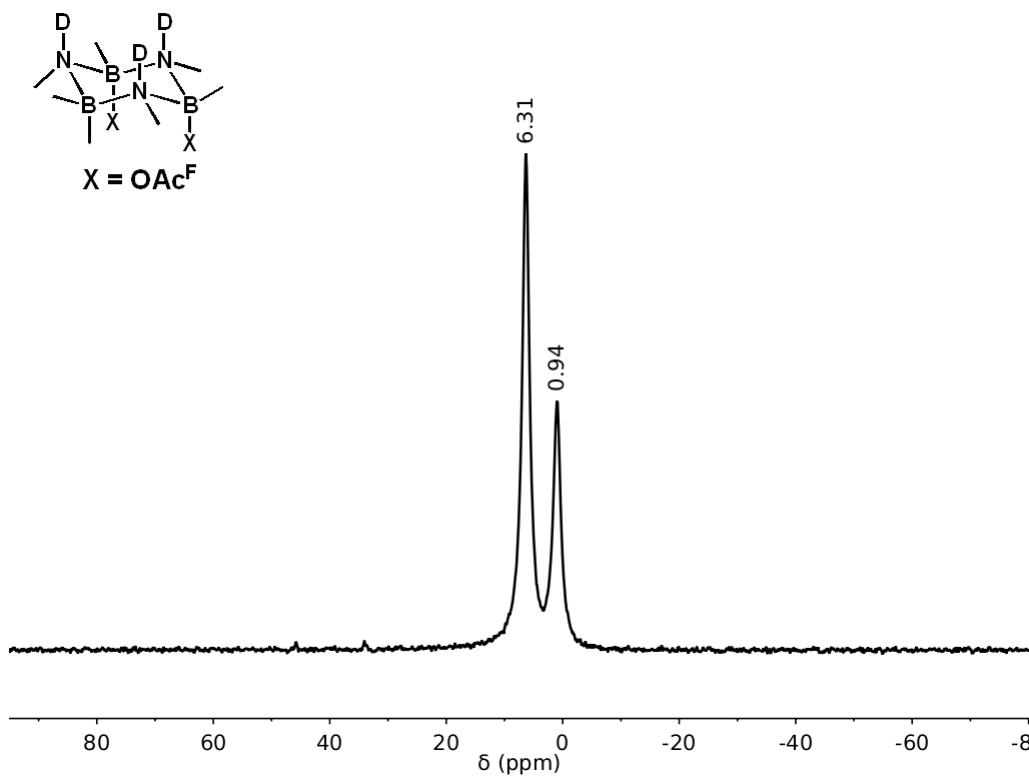
SI Figure 7: ^{13}C NMR spectrum of **3**, 125.71 MHz, $[\text{D}_8]\text{THF}$.



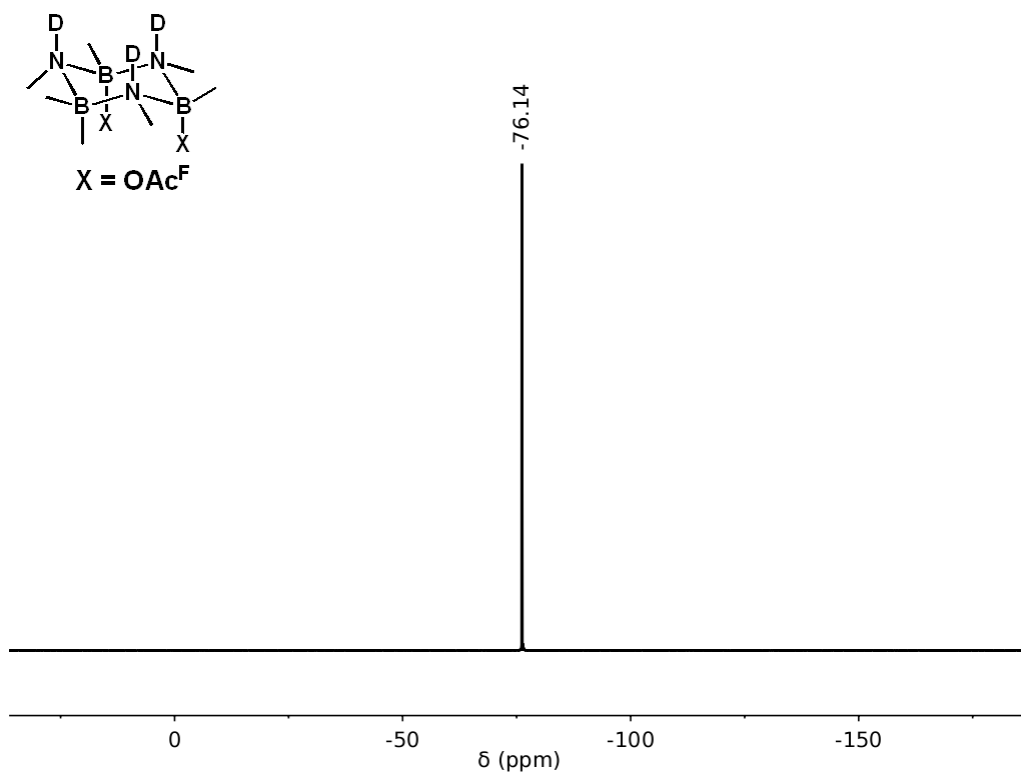
SI Figure 8: ^1H NMR spectrum of **4**, 399.54 MHz, C_6D_6 .



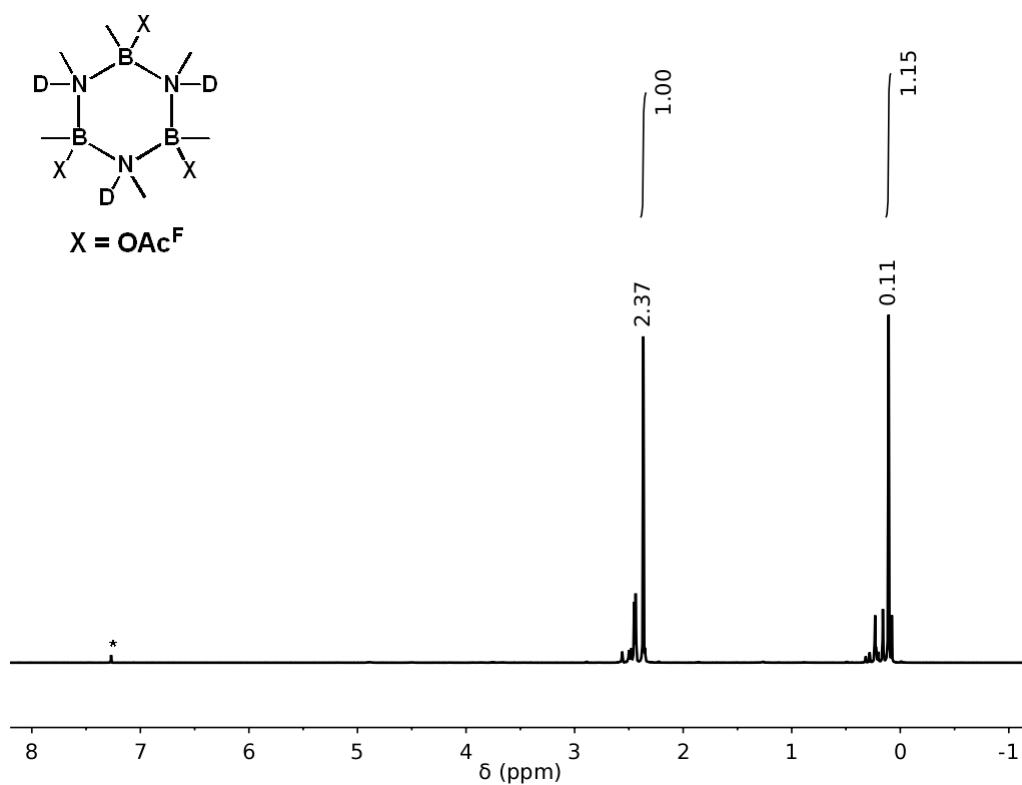
SI Figure 9: ^2H NMR spectrum of 4, 61.33 MHz, C_6D_6 .



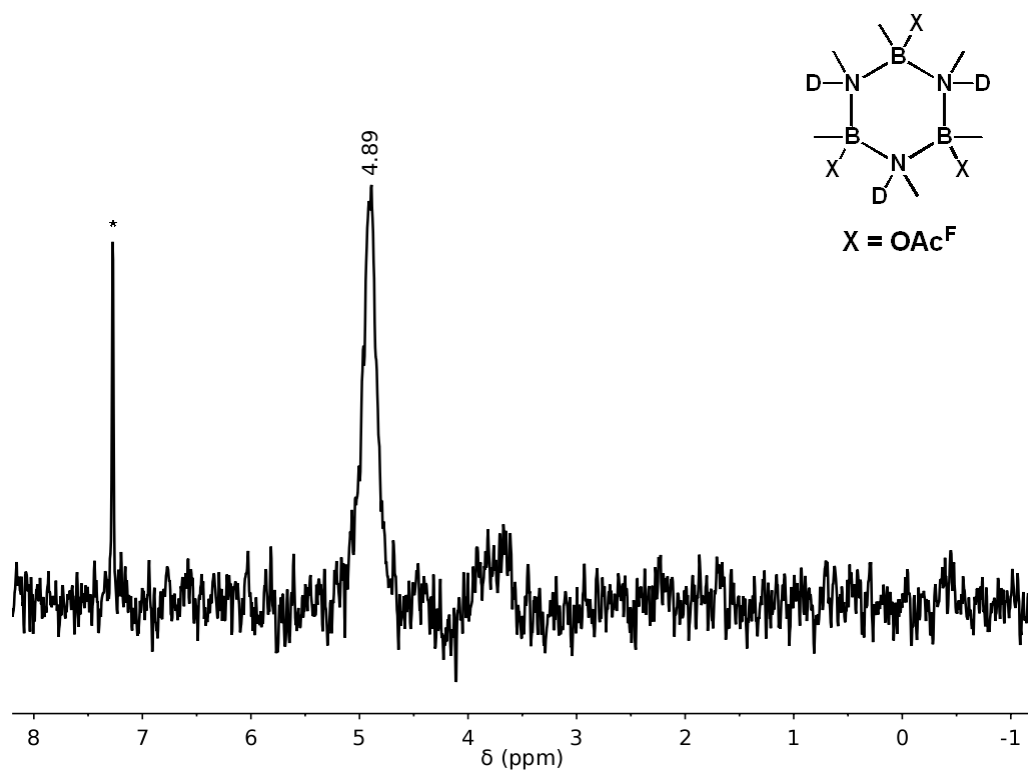
SI Figure 10: ^{11}B NMR spectrum of 4, 128.19 MHz, C_6D_6 .



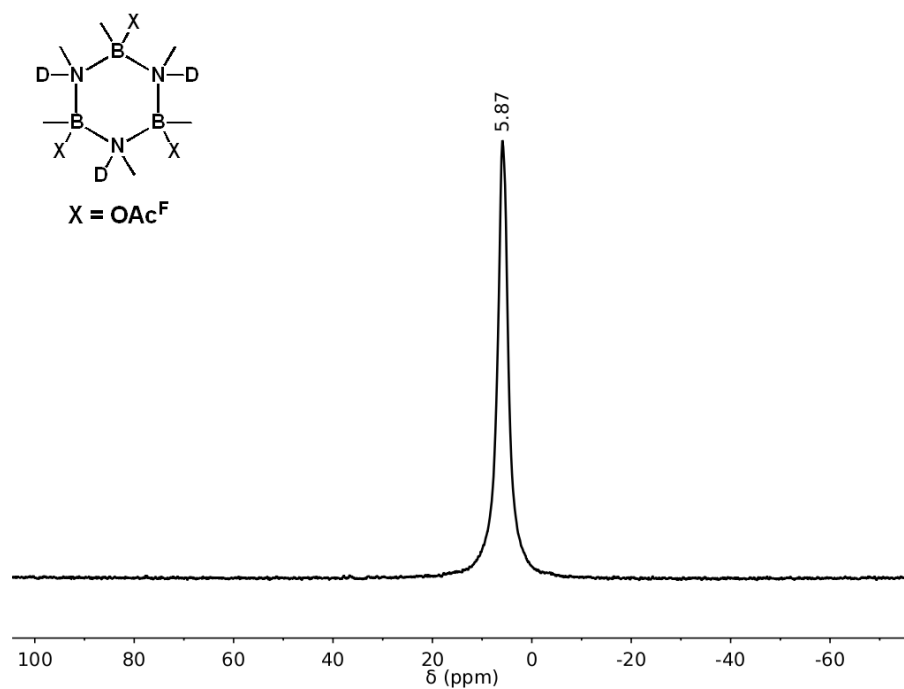
SI Figure 11: ^{19}F NMR spectrum of **4**, 375.91 MHz, C_6D_6 .



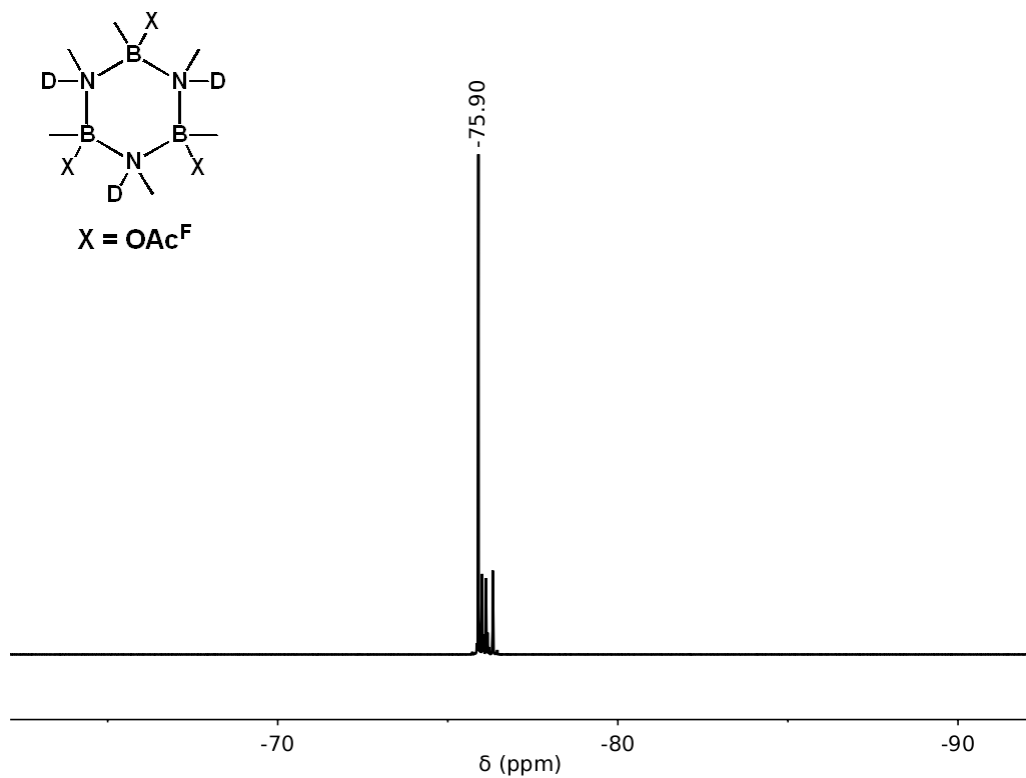
SI Figure 12: ^1H NMR spectrum of **5** with major isomer labeled, 500.09 MHz, CDCl_3 .



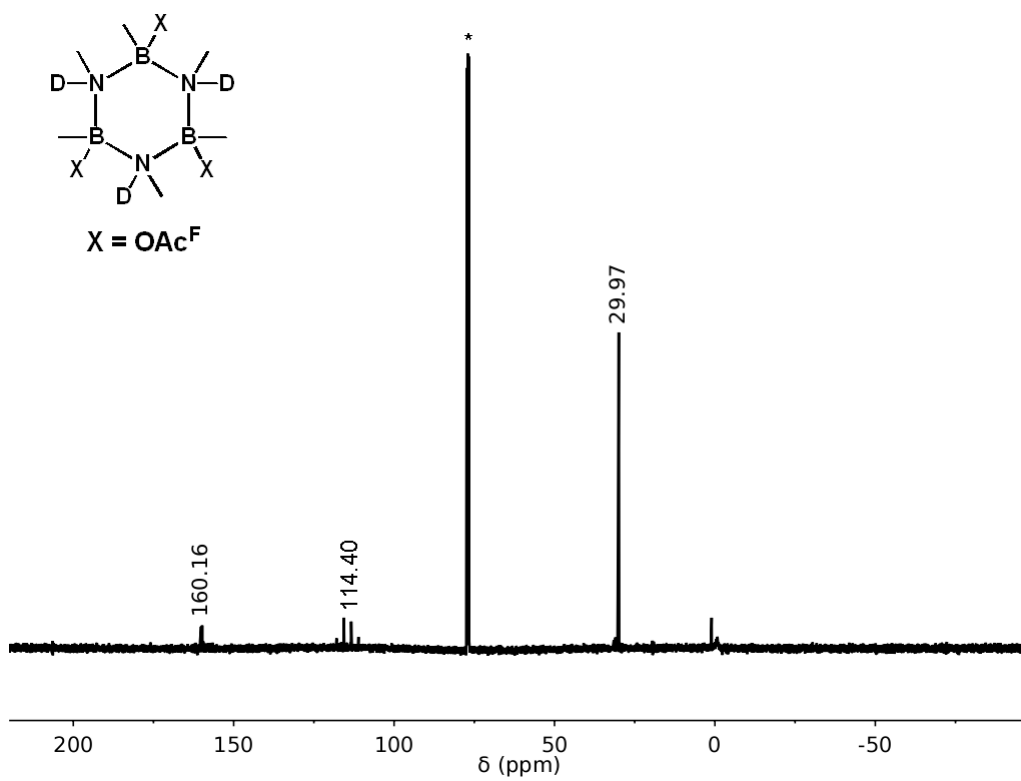
SI Figure 13: ²H NMR spectrum of **5**, 61.33 MHz, CDCl₃.



SI Figure 14: ¹¹B NMR spectrum of **5**, 160.45 MHz, CDCl₃.

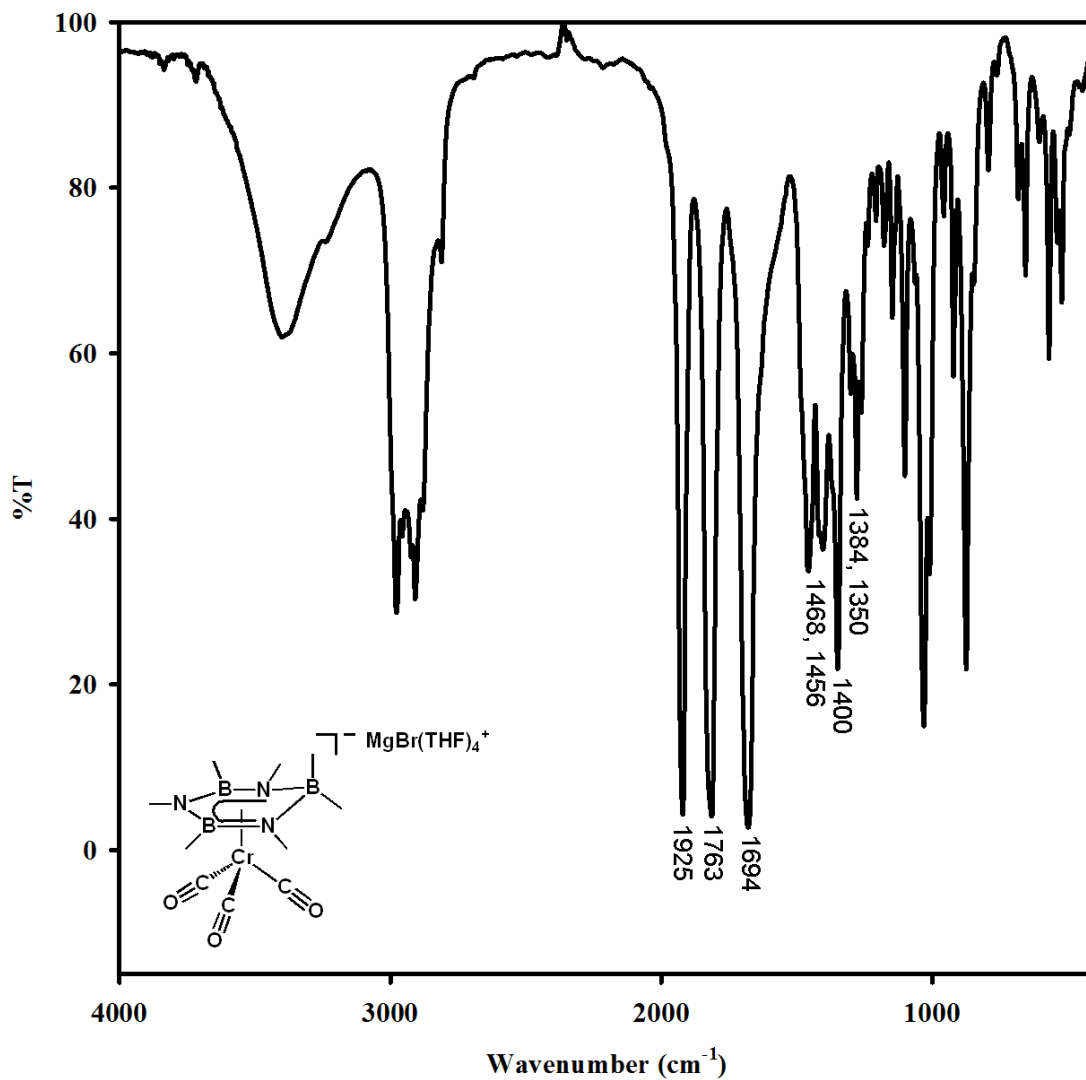


SI Figure 15: ^{19}F NMR spectrum of **5** with major isomer labeled, 470.52 MHz, CDCl_3 .

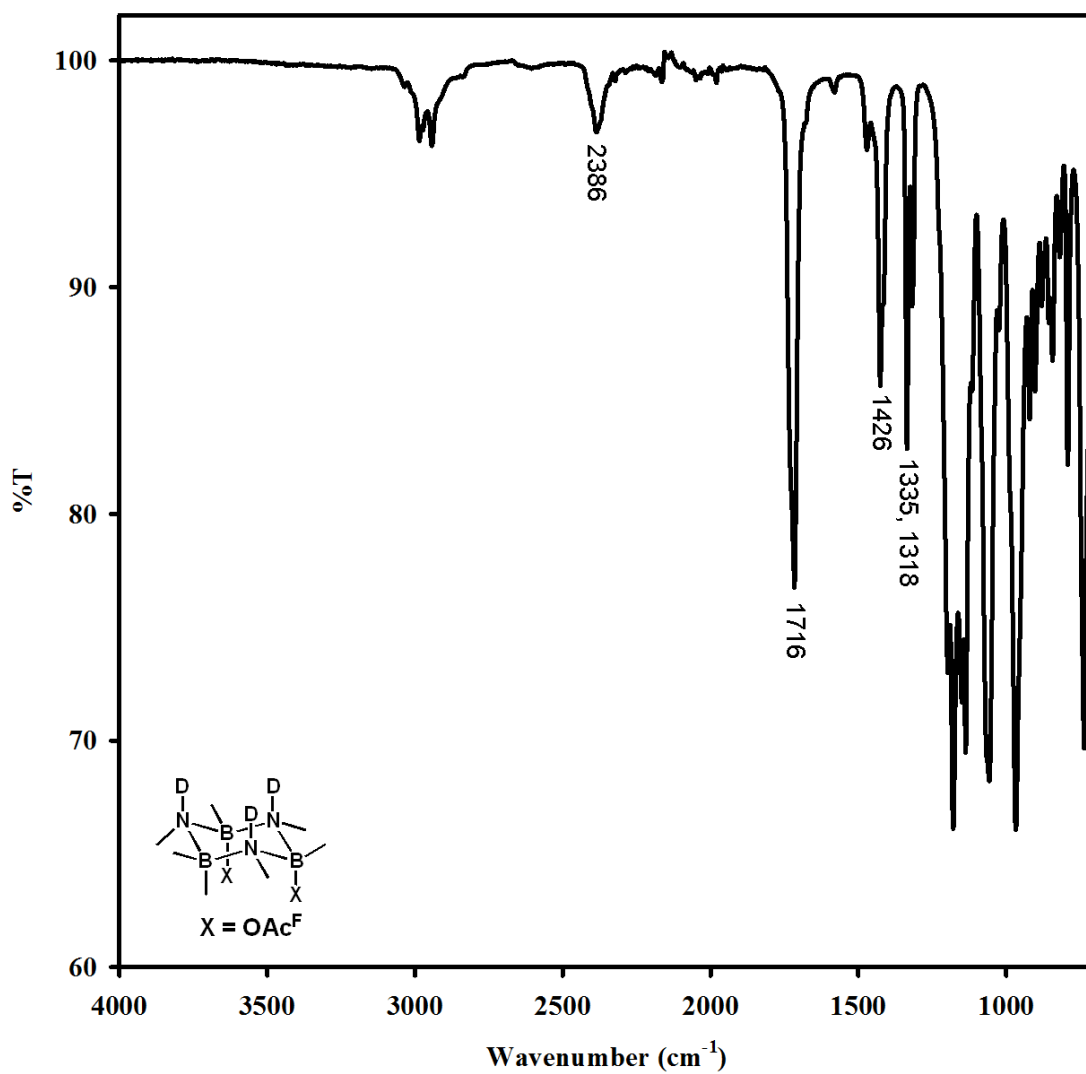


SI Figure 16: ^{13}C NMR spectrum of **5**, 125.71 MHz, CDCl_3 .

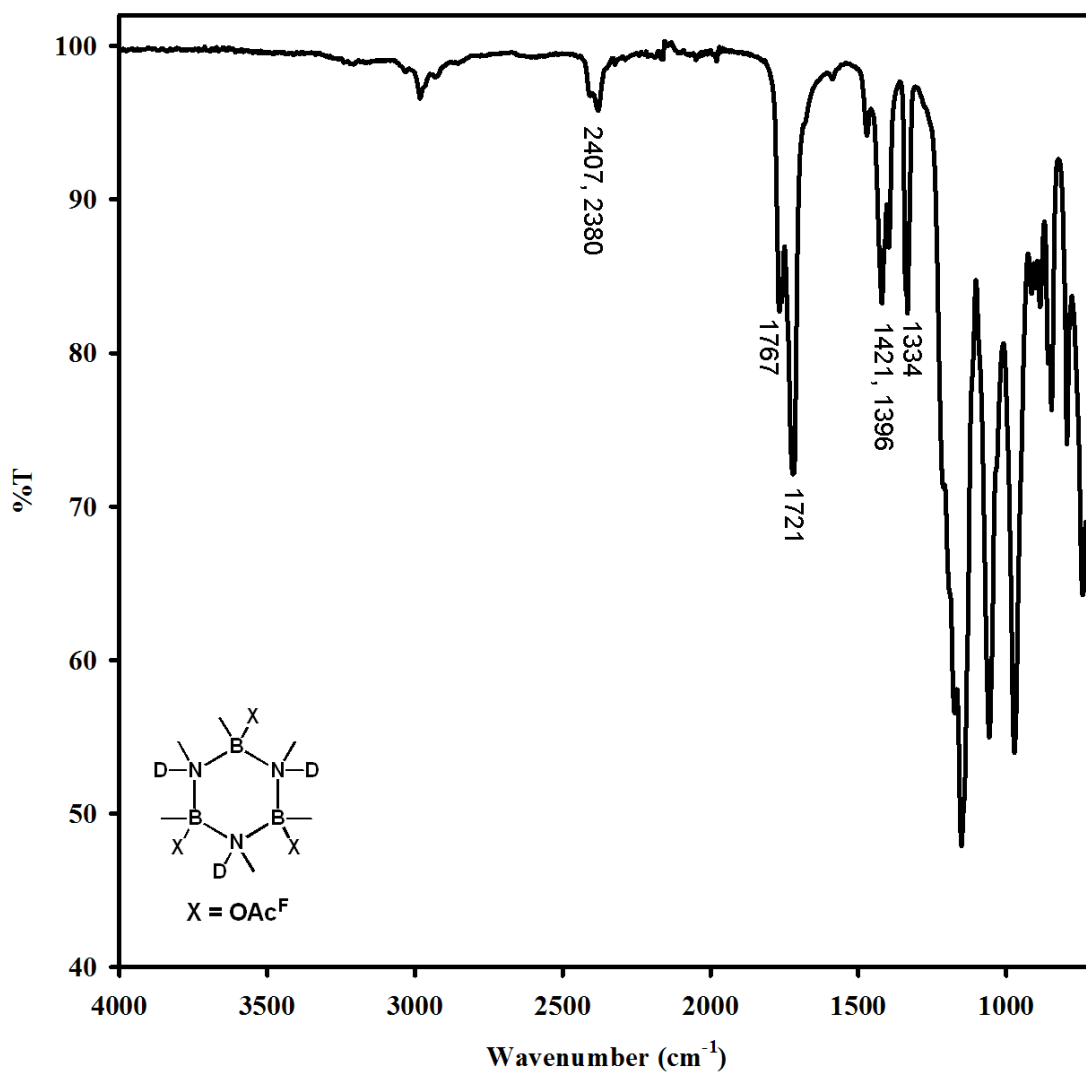
IR Spectra



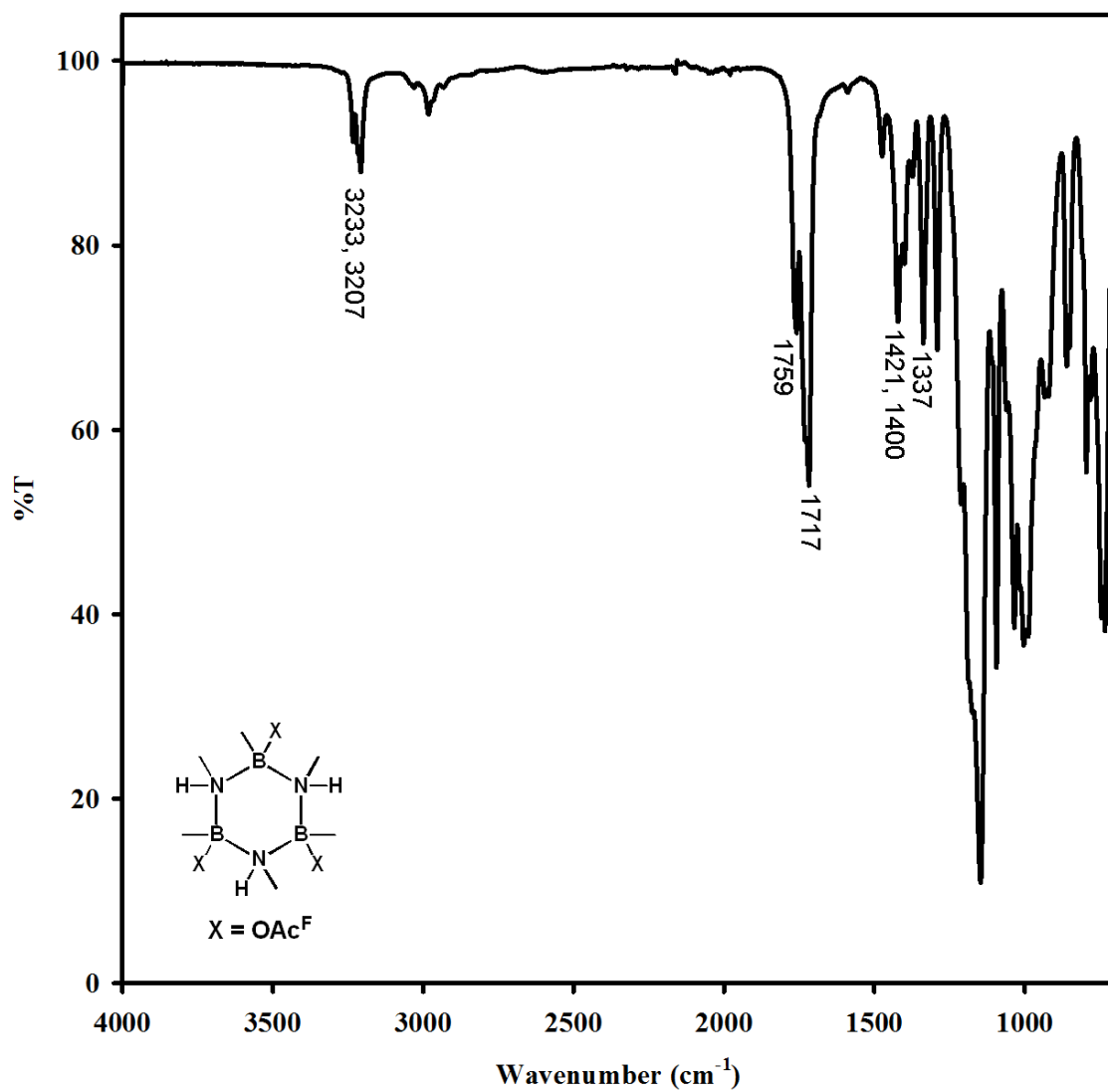
SI Figure 17: IR spectrum of 3, KBr pellet.



SI Figure 18: IR spectrum of 4, Diamond ATR accessory.

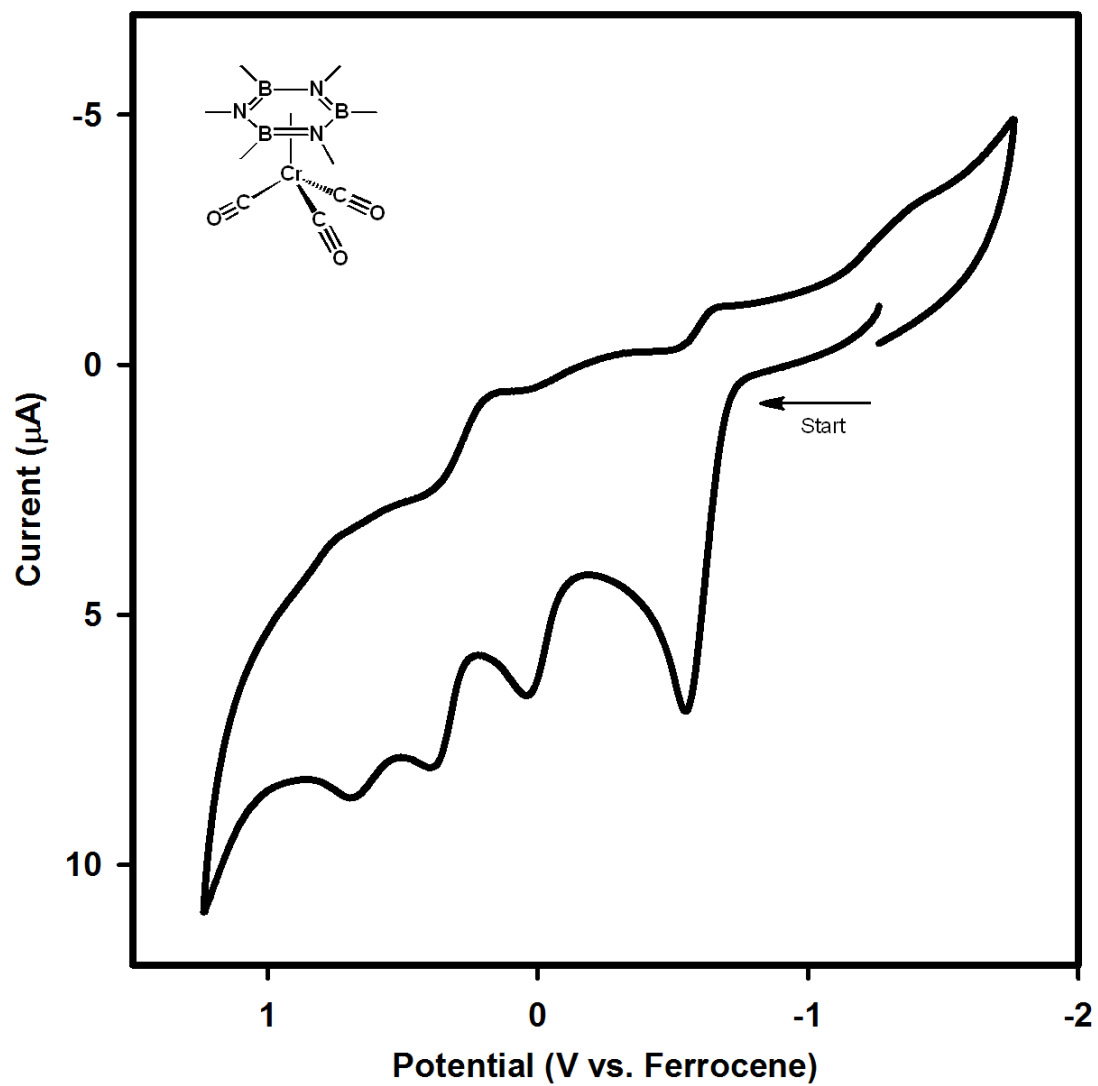


SI Figure 19: IR spectrum of 5, Diamond ATR accessory.

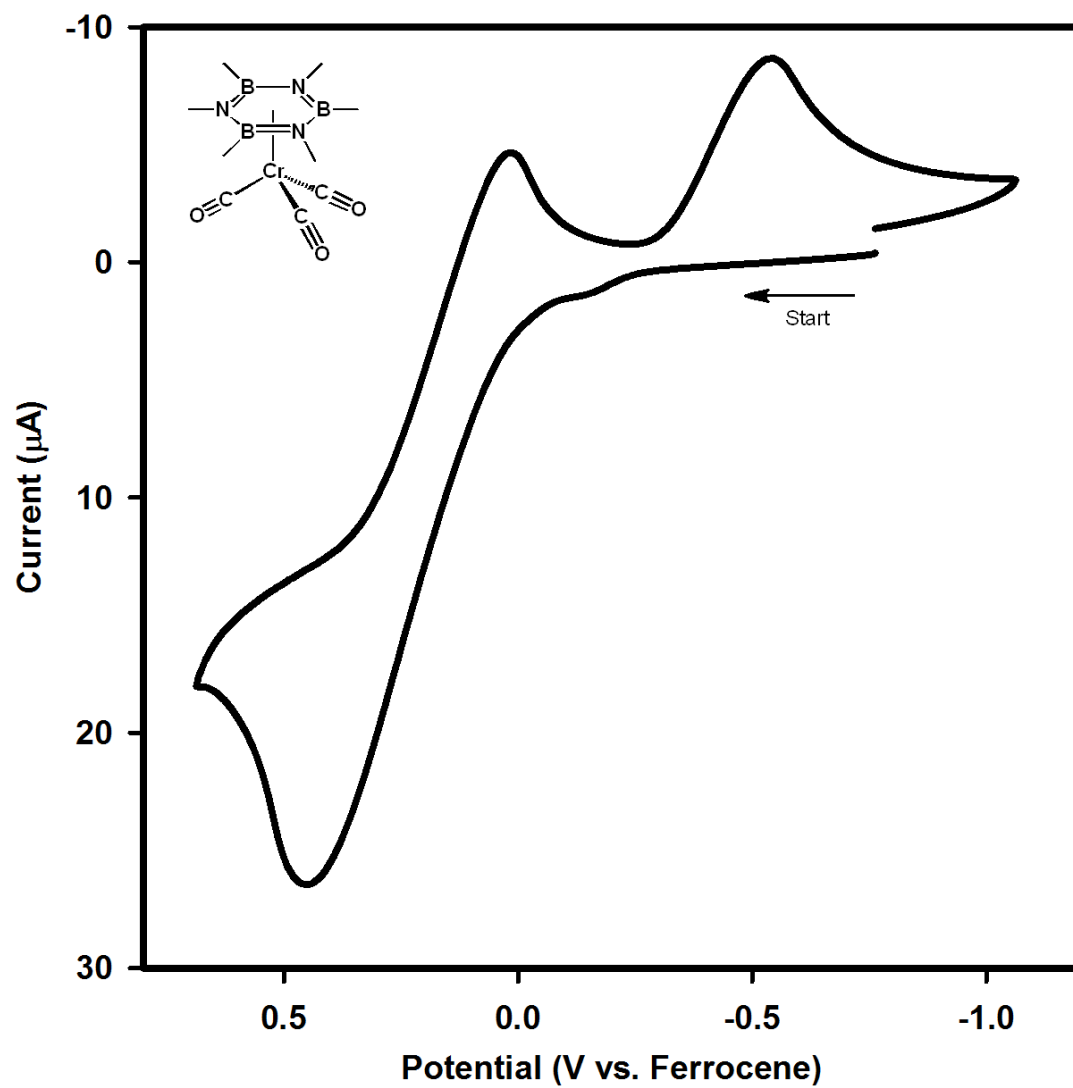


SI Figure 20: IR spectrum of protic isotopologue of 5, Diamond ATR accessory.

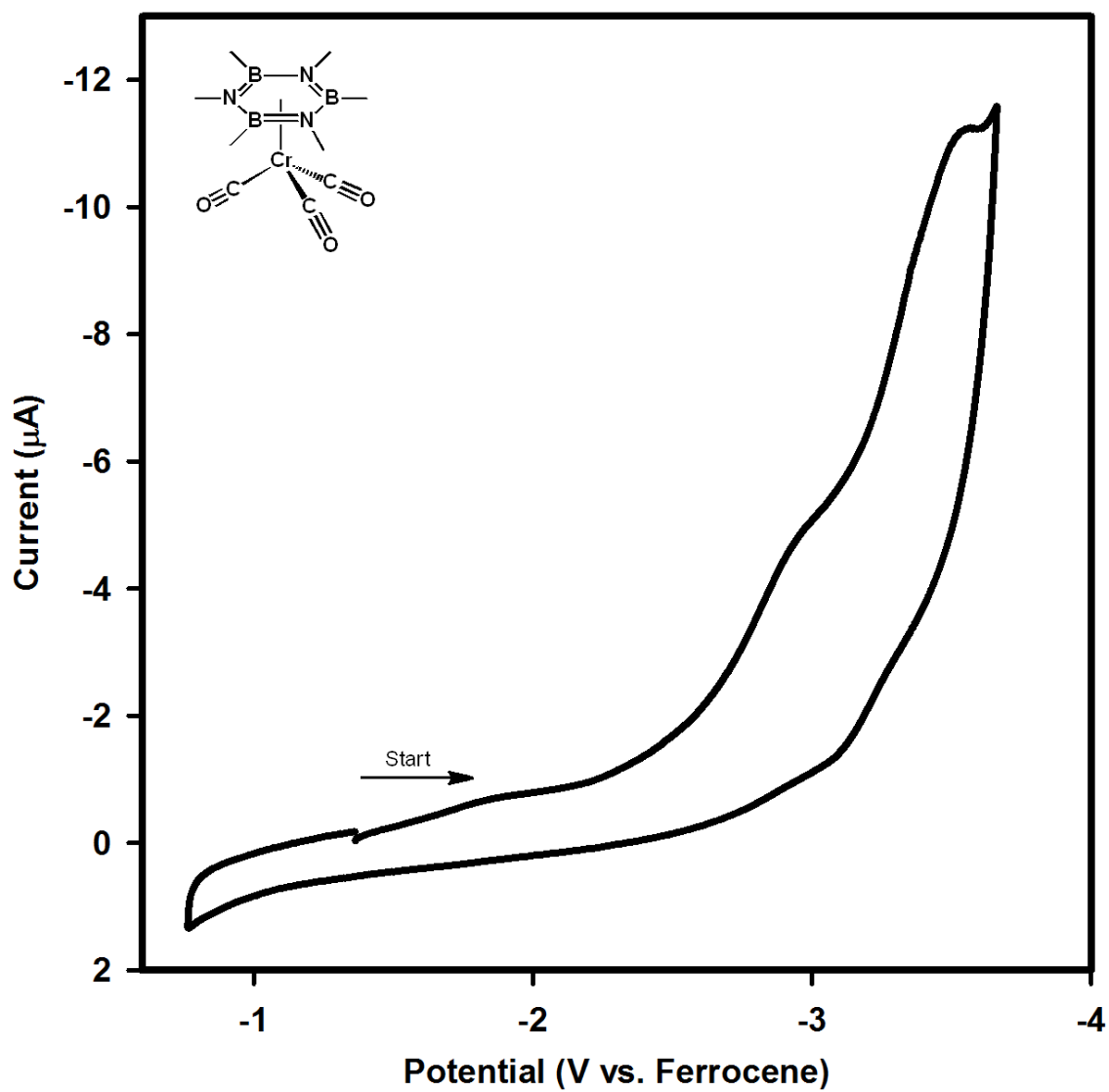
Cyclic Voltammetry



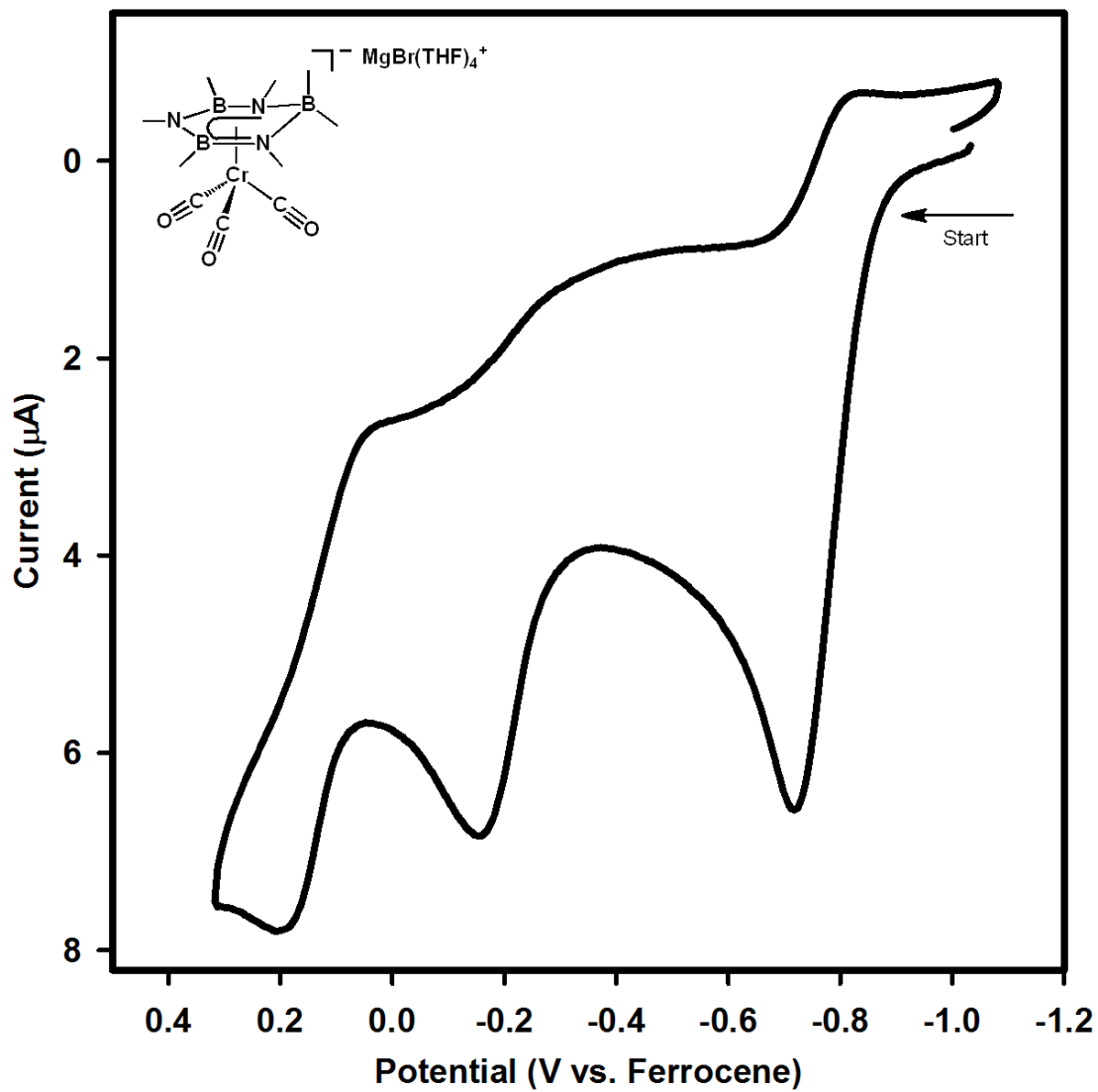
SI Figure 21: Cyclic voltammogram of **1**, oxidative portion, 0.05 M TBABAr⁺ solution in diethyl ether.



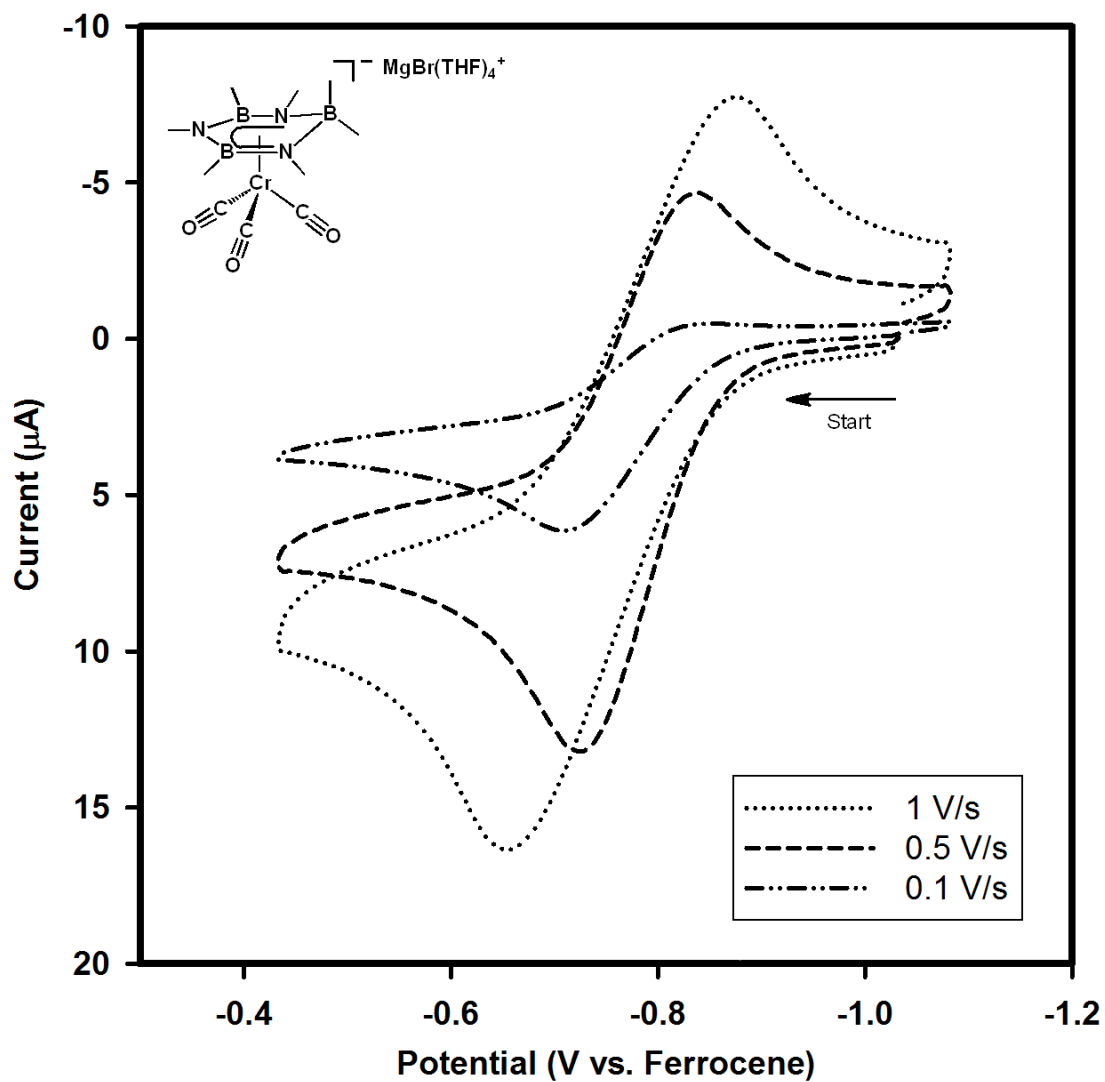
SI Figure 22: Cyclic voltammogram of first oxidation of **1**, 0.05 M TBABAr⁺ solution in diethyl ether.



SI Figure 23: Cyclic voltammogram of **1**, reductive portion, 0.05 V/s, 0.05 M TBABAr⁺ solution in diethyl ether.



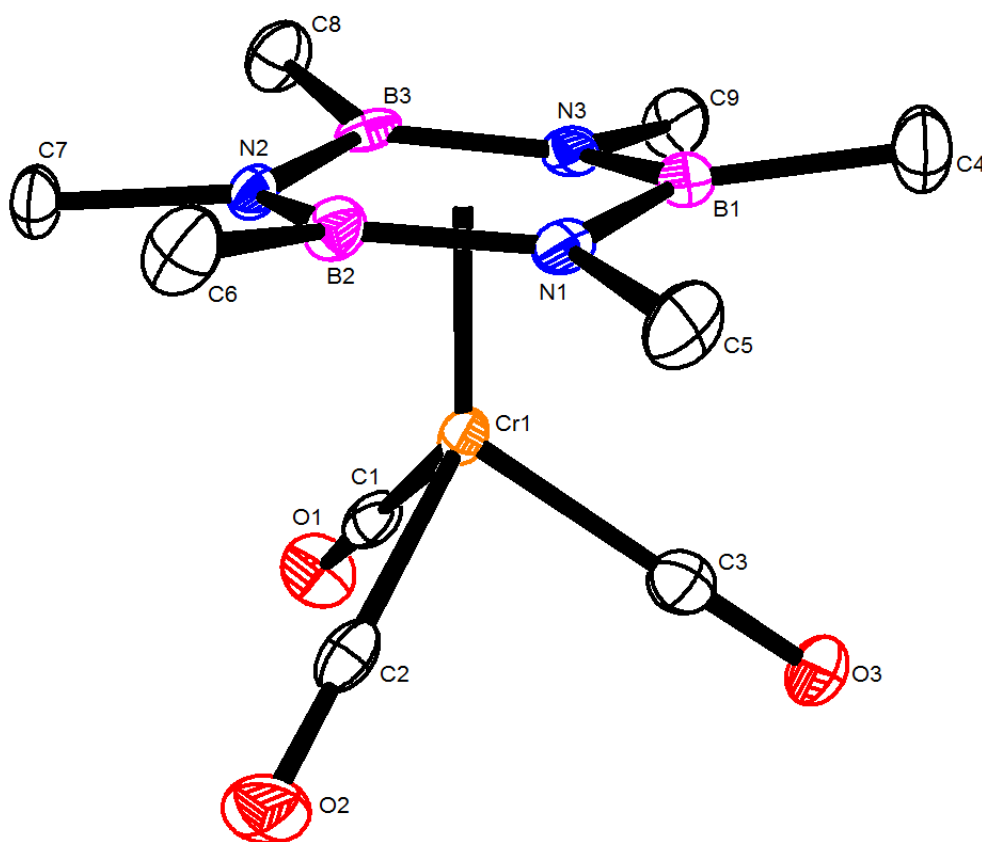
SI Figure 24: Cyclic voltammogram of **2**, 0.05 M TBABAr⁺ solution in 1,2-dimethoxyethane.



SI Figure 25: Quasi-reversible oxidation of **2** at several scan rates, 0.05 M TBABAr⁺ solution in 1,2-dimethoxyethane.

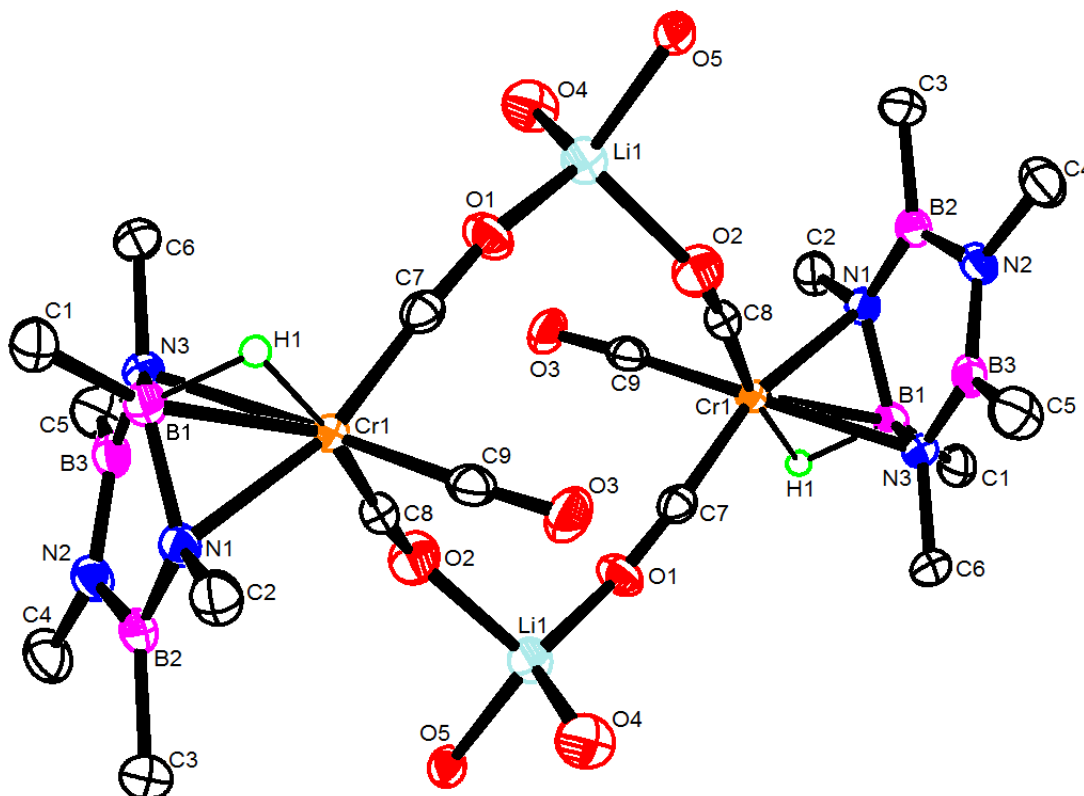
X-Ray Crystallographic Data

Structure Determination of 1: Orange needles of **1** were grown from a diethyl ether and pentane solution of the compound at -35 deg. C. A crystal of dimensions $0.13 \times 0.13 \times 0.09$ mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187$ Å) operated at 0.3 kW power (30 kV, 10 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 1014 images were collected with an oscillation width of 1.0° in ω . The exposure time was 15 sec. for the low angle images, 30 sec. for high angle. The integration of the data yielded a total of 21196 reflections to a maximum 2θ value of 136.48° of which 2654 were independent and 2477 were greater than $2\sigma(I)$. The final cell constants were based on the xyz centroids of 17109 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0^[10] and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package.^[11] Refined formula: $C_9H_{18}B_3CrN_3O_3$, $M_r = 300.69$, Monoclinic, space group $P2(1)/c$, $a = 8.6474(6)$, $b = 25.7574(5)$, $c = 7.1476(2)$ Å, $\alpha = 90$, $\beta = 114.412(8)$, $\gamma = 90^\circ$, $V = 1449.69(11)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.378$ Mg m⁻³, $\mu = 6.533$ mm⁻¹, reflections collected: 21196, independent reflections: 2654 (Rint = 0.0674), Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0401$, $wR2 = 0.1042$, R indices (all data): $R1 = 0.0424$, $wR2 = 0.1066$. The crystal was a pseudo-merohedral twin (1 0 1, 0 -1 0, 0 0 -1) and refined twin volume ratio 0.472(2). CIF file available under CCDC 895043.



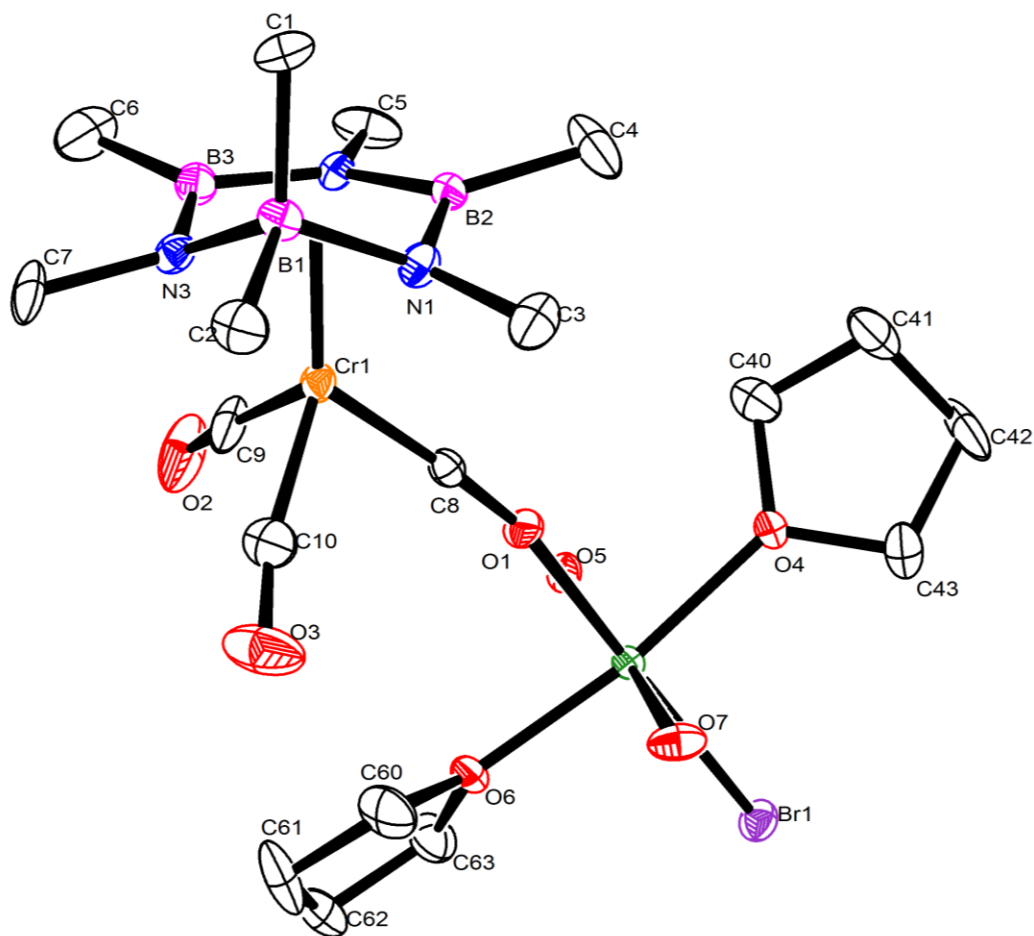
SI Figure 26: Thermal ellipsoid plot of **1** shown at 50% probability. Hydrogens omitted for clarity.

Structure Determination of 2: Orange plates of **2** were grown from a diethyl ether and pentane solution of a reaction mixture containing the compound at -35 deg. C. A crystal of dimensions $0.13 \times 0.10 \times 0.04$ mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187$ Å) operated at 0.3 kW power (30 kV, 10 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 1493 images were collected with an oscillation width of 2.0° in ω . The exposure time was 20 sec. for the low angle images, 35 sec. for high angle. The integration of the data yielded a total of 26770 reflections to a maximum 2θ value of 136.40° of which 4605 were independent and 4303 were greater than $2\sigma(I)$. The final cell constants were based on the xyz centroids 14740 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package. Refined Formula: $C_{34}H_{78}B_6Cr_2Li_3N_6O_{10}$, $M_r = 913.76$, Triclinic, space group P1bar, $a = 10.4686(2)$, $b = 10.6651(2)$, $c = 12.9445(9)$ Å, $\alpha = 70.204$, $\beta = 83.211$, $\gamma = 70.904^\circ$, $V = 1284.96(10)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.181$ Mgmm⁻³, $\mu = 3.895$ mm⁻¹, reflections collected: 26770, independent reflections: 4605 (Rint = 0.0605), Final R indices [$I > 2\sigma(I)$]: R1 = 0.0475, wR2 = 0.1172, R indices (all data): R1 = 0.0500, wR2 = 0.1192. CIF file available under CCDC 895042.



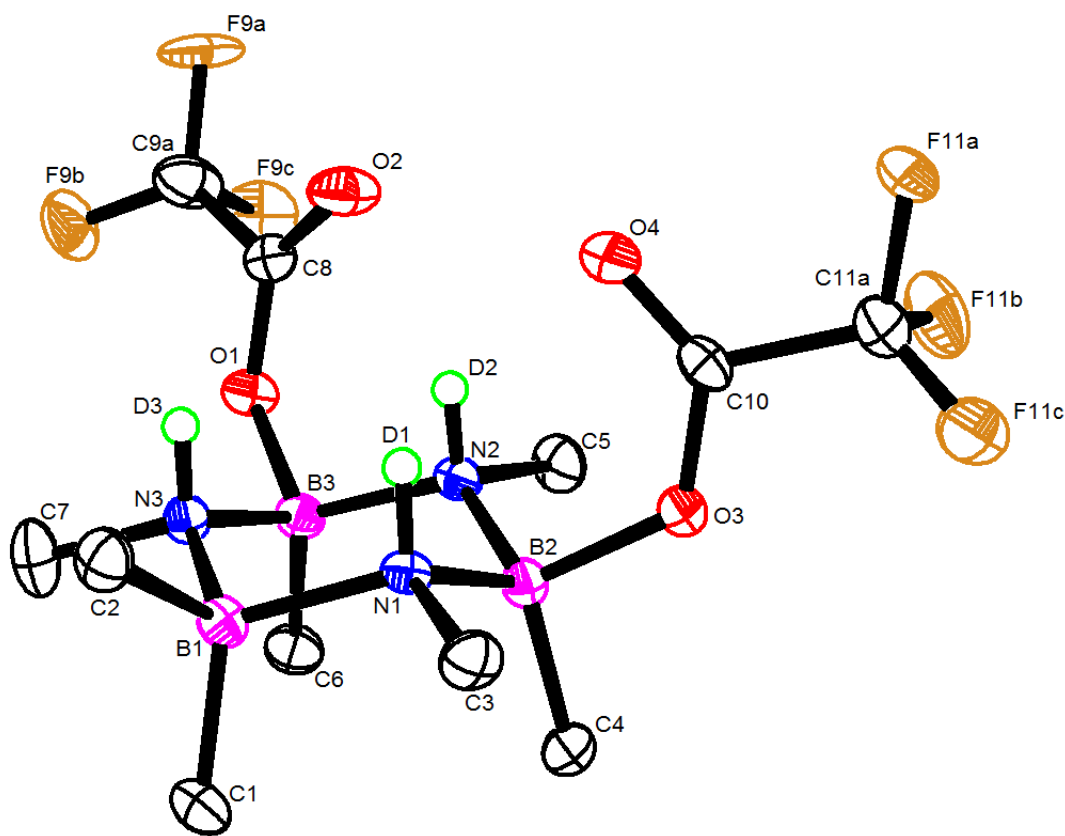
SI Figure 27: Thermal ellipsoid plot of **2** shown at 50% probability. Hydrogens and carbons attached to diethyl ether solvent molecules (O4 and O5) have been omitted for clarity

Structure Determination of 3: Yellow plates of **3** were grown from a tetrahydrofuran/pentane solution of the compound at 24 deg. C. A crystal of dimensions 0.14 x 0.13 x 0.12 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187 \text{ \AA}$) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 3753 images were collected with an oscillation width of 1.0° in ω . The exposure time was 1 sec. for the low angle images, 4 sec. for high angle. The integration of the data yielded a total of 91823 reflections to a maximum 2θ value of 136.46° of which 6464 were independent and 6153 were greater than $2\sigma(I)$. The final cell constants were based on the xyz centroids 61306 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package. Refined Formula: $C_{26}H_{53}B_3BrCrMgN_3O_7$, $M_r = 708.36$, Monoclinic, space group $C2/c$, $a = 17.1605(3)$, $b = 17.7737(3)$, $c = 23.9599(17) \text{ \AA}$, $\alpha = 90$, $\beta = 104.678(7)$, $\gamma = 90^\circ$, $V = 7096.4(5) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 1.331 \text{ Mg m}^{-3}$, $\mu = 4.510 \text{ mm}^{-1}$, reflections collected: 91823, independent reflections: 6464 (Rint = 0.0919), Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0558$, $wR2 = 0.1416$, R indices (all data): $R1 = 0.0572$, $wR2 = 0.1427$. The borazine and tetrahydrofuran ligands show conformational disorder. CIF file available under CCDC 895044.



SI Figure 28: Thermal ellipsoid plot of **3** shown at 50% probability. Two THF solvent molecules (containing O5 and O7) have been truncated for clarity. Also, hydrogens and alternative orientations of atoms exhibiting conformational disorder have been removed.

Structure Determination of 4: Colorless plates of **4** were grown from a pentane solution of the compound at -35 deg. C. A crystal of dimensions $0.14 \times 0.10 \times 0.10$ mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187$ Å) operated at 0.2 kW power (20 kV, 10 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 3897 images were collected with an oscillation width of 1.0° in ω . The exposure time was 4 sec. for the low angle images, 8 sec. for high angle. The integration of the data yielded a total of 22060 reflections to a maximum 2θ value of 136.44° of which 3372 were independent and 2904 were greater than $2\sigma(I)$. The final cell constants were based on the xyz centroids 12519 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package. Refined Formula: $C_{11}H_{21}B_3CrD_3F_6N_3O_4$, $M_r = 411.78$, Orthorhombic, space group Pbc a , $a = 16.7286(12)$, $b = 12.9871(2)$, $c = 16.9917(3)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 3691.5(3)$ Å 3 , $Z = 8$, $\rho_{\text{calcd}} = 1.482$ Mg m $^{-3}$, $\mu = 1.268$ mm $^{-1}$, reflections collected: 22060, independent reflections: 3372 (Rint = 0.0518), Final R indices [$I > 2\sigma(I)$]: R1 = 0.0479, wR2 = 0.1196, R indices (all data): R1 = 0.0536, wR2 = 0.1241. The CF $_3$ substituents show conformational disorder. CIF file available under CCDC 895045.



SI Figure 29: Thermal ellipsoid plot of **4** shown at 50% probability. Hydrogens and alternative orientations of fluorine atoms exhibiting conformational disorder removed for clarity.

Supporting References

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