Supporting Information

Boron-Vertex Modification of Carba-*closo*-dodecaborate for High-Performance Magnesium-Ion Battery Electrolyte

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Table of Contents

1. General Information

Instrumentation

NMR spectra were obtained on a BRUKER AVANCE III HD 500 spectrometer. Chemical shifts are expressed in δ (ppm) values and coupling constants are expressed in hertz (Hz). Chemical shifts were reported in ppm on the δ scale relative to residual undeuterated solvent (Acetone: δ = 2.05 for ^{1}H NMR) as internal references. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet (denotes complex pattern), dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, and br = broad signal. We determined the position of the halogen introduction from results of 1) a signal derived from a proton on 1-C position was seen around 2.0 ppm in the ^{1}H NMR data, and 2) a signal derived from 12-B vertex was seen as a broad singlet without ^{1}H coupling in the $^{11}B\{^1H\}$ NMR data. ESI and mass spectra were measured on a Bruker micrOTOF-II spectrometer.

Materials

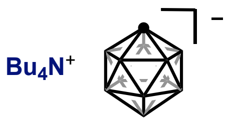
Unless otherwise noted, materials were purchased from Aldrich Inc., Wako Pure Chemical Industries, Ltd., Tokyo Kasei Co., and other commercial suppliers and were used after appropriate purification. $[Me_3NH]^+[HCB_{11}H_{11}]^-$ and $Cs^+[HCB_{11}H_{11}]^-$ were purchased from KATCHEM spol. s.r.o. $Cs^+[HCB_{11}H_5Br_6]^-$, $[Me_3NH]^+[HCB_{11}H_5Br_6]^-$, $Cs^+[HCB_{11}H_{10}Br]^-$, $Cs^+[HCB_{11}H_{10}Cl]^-$, $[Me_3NH]^+[ClCB_{11}H_{11}]^-$, $[Et_3NH]^+[FCB_{11}H_{11}]^-$, and $[Mg(DME)_3]^{2+}[HCB_{11}H_{11}]_2^{2-}$ were prepared as described previously.[1–5] Di-n-butylmagnesium in ether and hexane was obtained from Aldrich Inc. The concentration of di-n-butylmagnesium was determined by titration prior to use.[6] n-BuLi in n-hexane was obtained from Kanto Chemical Co. Ltd. The concentration of n-BuLi was determined by titration prior to use.[7] Air- and moisture-sensitive manipulations were performed with standard Schlenk techniques or in a glove box under argon atmosphere (O_2, H_2O < 0.1 ppm). Normal-phase column chromatography was performed with silica gel 60 (230–400 mesh) from Merck. Reverse-phase column chromatography was performed with COSMOSIL® C18-OPN purchased from Nacalai Tesque, Inc.

2. Experimental Section

General Procedure of Synthesis of Tetraethylammonium Salt from Cesium Salt

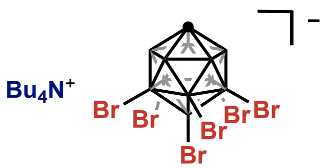
$Cs^+[HCB_{11}H_{11}]^-$ (Cs^+[CCA]) (100 mg 0.36 mmol) was dissolved in an aqueous solution of HCl (10%, 200 ml) and extracted with Et_2O five times. 10 ml of deionized water was added to the combined organic layer and Et_2O was removed in vacuo. The aqueous solution was filtrated and tetrabutylammonium bromide (467 mg 1.45 mmol) dissolved in small amount of deionized water was added. The mixture was stirred for 1 h and then filtrated. The solid was washed with small amount of deionized water and dried under reduced pressure at 120 ℃ for 1 h to obtain pure $[Bu_4N]^+[HCB_{11}H_{11}]^-$ (136.7 mg, 97.8% based on Cs^+[CCA]) as a white powder.

$[Bu_4N]^+[HCB_{11}H_{11}]^-$ ($[Bu_4N]^+$[CCA])



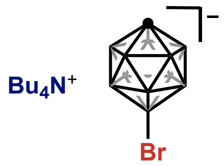
^{1}H NMR (500.13 MHz, acetone-d_6): δ 0.97 (t, J = 7.3 Hz, 12H), 1.43 (td, J = 14.9, 7.3 Hz, 8H), 1.79–1.86 (m, 8H), 2.22 (s, 1H), 3.43–3.46 (m, 8H); **^{1}H{^{11}B} NMR (500.13 MHz, acetone-d_6)**: δ 0.98 (t, J = 7.3 Hz, 12H), 1.43 (td, J = 14.9, 7.3 Hz, 8H), 1.57 (bs, 5H), 1.66 (bs, 5H), 1.73 (bs, 1H), 1.79–1.86 (m, 8H), 2.21 (s, 1H), 3.43–3.46 (m, 8H); **^{11}B NMR (160.46 MHz, acetone-d_6)**: δ –16.21 (d, J = 148.5 Hz, 5B), –13.13 (d, J = 135.0 Hz, 5B), –6.71 (d, J = 139.1 Hz, 1B); **^{11}B{^{1}H} NMR (160.46 MHz, acetone-d_6)**: δ –16.22 (bs, 5B), –13.12 (bs, 5B), –6.65 (bs, 1B); **MS (ESI (–))**: m/z calcd for $HCB_{11}H_{11}$ $[M–Bu_4N]^-$ 143.2041, found 143.2024.

$[Bu_4N]^+[HCB_{11}H_5Br_6]^-$ ($[Bu_4N]^+$[7–12-Br_6-CCA])



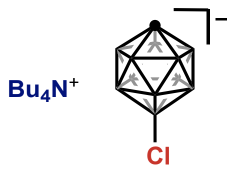
Using the General Procedure, the titled compound was obtained as a white powder in 81.3% yield (139.8 mg). **^{1}H NMR (500.13 MHz, acetone-d_6)**: δ 0.97 (t, J = 7.3 Hz, 12H), 1.40–1.47 (m, 8H), 1.80–1.86 (m, 8H), 3.04 (s, 1H), 3.43–3.47 (m, 8H); **^{1}H{^{11}B} NMR (500.13 MHz, acetone-d_6)**: δ 1.00 (t, J = 7.3 Hz, 12H), 1.42–1.50 (m, 8H), 1.83–1.89 (m, 8H), 2.35 (bs, 5H), 3.06 (bs, 1H), 3.46–3.50 (m, 8H); **^{11}B NMR (160.46 MHz, acetone-d_6)**: δ –20.17 (d, J = 234.1 Hz, 5B), –9.78 (bs, 5B), –1.76 (bs, 1B); **^{11}B{^{1}H} NMR (160.46 MHz, acetone-d_6)**: δ –20.14 (bs, 5B), –9.73 (bs, 5B), –1.86 (bs, 1B); **MS (ESI (–))**: m/z calcd for $HCB_{11}H_5Br_6$ $[M–Bu_4N]^-$ 616.6613, found 616.6622.

$[Bu_4N]^+[HCB_{11}H_{10}Br]^-$ ($[Bu_4N]^+$[12-Br-CCA])



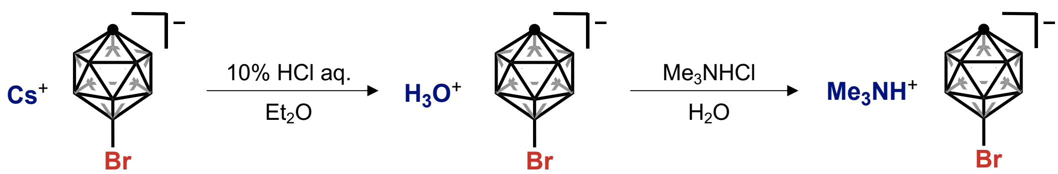
Using the General Procedure, the titled compound was obtained as a white powder in 97.4% yield (191.3 mg). **^{1}H NMR (500.13 MHz, acetone-*d*$_6$)**: δ 1.00 (t, *J* = 7.5 Hz, 12H), 1.46 (td, *J* = 14.8, 7.3 Hz, 8H), 1.82–1.89 (m, 8H), 2.10 (bs, 1H), 3.46–3.49 (m, 8H); **^{1}H{^{11}B} NMR (500.13 MHz, acetone-*d*$_6$)**: δ 0.98 (t, *J* = 7.5 Hz, 12H), 1.43 (td, *J* = 14.9, 7.5 Hz, 8H), 1.64 (bs, 5H), 1.80–1.86 (m, 8H), 1.90 (bs, 5H), 2.26 (bs, 1H), 3.43–3.47 (m, 8H); **^{11}B NMR (160.46 MHz, acetone-*d*$_6$)**: δ –17.01 (d, *J* = 152.6 Hz, 5B), –12.41 (d, *J* = 132.6 Hz, 5B), –2.83 (bs, 1B); **^{11}B{^{1}H} NMR (160.46 MHz, acetone-*d*$_6$)**: δ –17.01 (bs, 5B), –12.42 (bs, 5B), –2.88 (bs, 1B); **MS (ESI (–))**: *m/z* calcd for $HCB_{11}H_{10}Br$ $[M–Bu_4N]^-$ 222.1115, found 222.1128.

$[Bu_4N]^+[HCB_{11}H_{10}Cl]^-$ ($[Bu_4N]^+$[12-Cl-CCA])



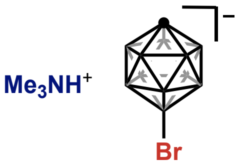
Using the General Procedure, the titled compound was obtained as a white powder in 90.9% yield (24.6 mg). **^{1}H NMR (500.13 MHz, acetone-*d*$_6$)**: δ 0.97 (t, *J* = 7.3 Hz, 12H), 1.43 (td, *J* = 15.0, 7.3 Hz, 8H); 1.80–1.86 (m, 8H), 2.10 (bs, 1H), 3.43–3.46 (m, 8H); **^{1}H{^{11}B} NMR (500.13 MHz, acetone-*d*$_6$)**: δ 0.98 (t, *J* = 7.5 Hz, 12H), 1.43 (td, *J* = 14.9, 7.5 Hz, 8H), 1.60 (bs, 5H), 1.80–1.86 (m, 8H), 1.81 (bs, 5H), 2.10 (bs, 1H), 3.45 (t, *J* = 8.6 Hz, 8H); **^{11}B NMR (160.46 MHz, acetone-*d*$_6$)**: δ –17.56 (d, *J* = 153.8 Hz, 5B), –12.72 (d, *J* =143.8 Hz, 5B), 3.87 (bs, 1B); **^{11}B{^{1}H} NMR (160.46 MHz, acetone-*d*$_6$)**: δ –17.56 (bs, 5B), –12.71 (bs, 5B), 3.79 (bs, 1B); **MS (ESI (–))**: *m/z* calcd for $HCB_{11}H_{10}Cl$ $[M–Bu_4N]^-$ 177.1646, found 177.1640.

General Procedure of Synthesis of Trimethylammonium Salt from Cesium Salt



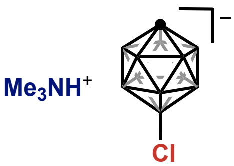
$Cs^+[HCB_{11}H_{10}Br]^-$ (Cs^+[12-Br-CCA]) (2.13 g 6.00 mmol) was dissolved in an aqueous solution of HCl (10%, 200 ml) and extracted with Et_2O five times. 10 ml of deionized water was added to the combined organic layer and Et_2O was removed in vacuo. The aqueous solution was filtrated and trimethylammonium chloride (1.72 g 18.0 mmol) dissolved in small amount of deionized water was added. The mixture was stirred for 1 h and then filtrated. The solid was washed with small amount of deionized water and dried under reduced pressure at 120 ºC for 1 h to obtain pure $[Me_3NH]^+[HCB_{11}H_{10}Br]^-$ (1.55 g, 91.6% based on Cs^+[12-Br-CCA]) as a white powder.

$[Me_3NH]^+[HCB_{11}H_{10}Br]^-$ ($[Me_3NH]^+$[12-Br-CCA])



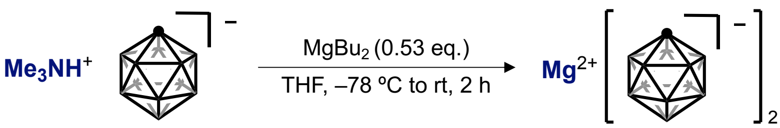
^{1}H NMR (500.13 MHz, acetone-*d*$_6$): δ 2.27 (bs, 1H), 2.81 (bs, 1H), 3.23 (s, 9H); **^{1}H{^{11}B} NMR (500.13 MHz, acetone-*d*$_6$)**: δ 1.65 (bs, 5H), 1.90 (bs, 5H), 2.26 (bs, 1H), 2.78 (bs, 1H), 3.23 (s, 9H); **^{11}B NMR (160.46 MHz, acetone-*d*$_6$)**: δ –17.03 (d, J = 152.6 Hz, 5B), –12.40 (d, J = 141.4 Hz, 5B), –2.84 (bs, 1B); **^{11}B{^{1}H} NMR (160.46 MHz, acetone-*d*$_6$)**: δ –17.03 (bs, 5B), –12.41 (bs, 5B), –2.85 (bs, 1B); **MS (ESI (–))**: *m/z* calcd for $HCB_{11}H_{10}Br$ [M–$HNMe_3$]$^-$ 222.1115, found 222.1136.

$[Me_3NH]^+[HCB_{11}H_{10}Cl]^-$ ($[Me_3NH]^+$[12-Cl-CCA])



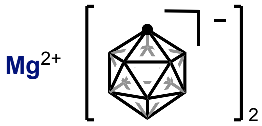
Using the General Procedure, the titled compound was obtained as a white powder in 98.1% yield (1.63 g). **^{1}H NMR (500.13 MHz, acetone-*d*$_6$)**: δ 2.10 (bs, 1H), 2.81 (bs, 1H), 3.23 (s, 9H); **^{1}H{^{11}B} NMR (500.13 MHz, acetone-*d*$_6$)**: δ 1.60 (bs, 5H), 1.82 (bs, 5H), 2.10 (bs, 1H), 2.79 (bs, 1H), 3.23 (s, 9H); **^{11}B NMR (160.46 MHz, acetone-*d*$_6$)**: δ –17.57 (d, J = 153.2 Hz, 5B), –12.70 (d, J = 140.3 Hz, 5B), –3.84 (bs 1B); **^{11}B{^{1}H} NMR (160.46 MHz, acetone-*d*$_6$)**: δ –17.55 (bs, 5B), –12.71 (bs, 5B), 3.83 (bs, 1B); **MS (ESI (–))**: *m/z* calcd for $HCB_{11}H_{10}Cl$ [M–$HNMe_3$]$^-$ 177.1646, found 177.1649.

General Procedure of Synthesis of Magnesium Salt from Trimethylammonium Salt



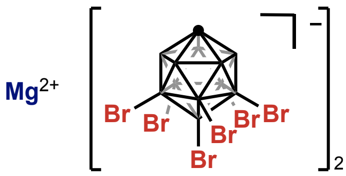
$[Me_3NH]^+[HCB_{11}H_{11}]^-$ ($[Me_3NH]^+$[CCA]) (1.50 g 7.38 mmol) was charged in a Schlenk flask and dried under reduced pressure at 120 ºC for 1 h. The flask was charged with argon, and 30 mL of anhydrous THF was added at room temperature. The solution was cooled to –78 ºC and di-n-butylmagnesium (0.970 M in ether and n-hexane, 3.91 mmol) was added. The mixture was stirred at the same temperature for 30 min and then at rt for 1.5 h. The reaction mixture was pumped up and dried under reducer pressure at rt for 1.5 h. The flask was charged with argon and 15 mL of anhydrous THF was added at room temperature. The suspension was stirred at rt for 2 h and then filtrated under argon atmosphere. The solid was washed with THF and dried on the funnel for 45 min to obtain pure $[Mg(THF)_6]^{2+}[HCB_{11}H_{11}]_2^{2-}$ (2.27 g, 82.8% based on $[Me_3NH]^+[CCA]$) as a white powder.

$[Mg(THF)_6]^{2+}[HCB_{11}H_{11}]_2^{2-}$ ($Mg^{2+}[CCA]_2$)



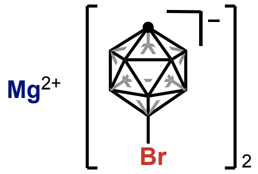
^{1}H NMR (500.13 MHz, acetone-*d*$_6$): δ 1.77–1.80 (m, 24H), 2.23 (bs, 2H), 3.61–3.64 (m, 24H); **^{1}H{^{11}B} NMR (500.13 MHz, acetone-*d*$_6$)**: δ 1.56 (bs, 10H), 1.66 (bs, 10H), 1.71 (bs, 2H), 1.78–1.80 (m, 24H), 2.23 (bs, 2H), 3.61–3.64 (m, 24H); **^{11}B NMR (160.46 MHz, acetone-*d*$_6$)**: δ –16.21 (d, J = 150.8 Hz, 10B), –13.14 (d, J = 135.6 Hz, 10B), –6.77 (d, J = 131.5 Hz, 2B); **^{11}B{^{1}H} NMR (160.46 MHz, acetone-*d*$_6$)**: δ –16.22 (bs, 10B), –13.15 (bs, 10B), –6.71 (bs, 2B); **MS (ESI (–))**: *m/z* calcd for $HCB_{11}H_{11}$ $[(M–Mg(THF)_6)_{0.5}]^-$ 143.2041, found 143.2037.

$[Mg(THF)_6]^{2+}[HCB_{11}H_5Br_6]_2^{2-}$ ($Mg^{2+}[7–12\text{-}Br_6\text{-}CCA]_2$)



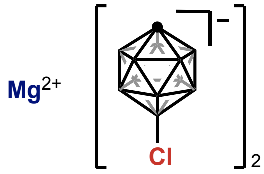
Using the General Procedure, the titled compound was obtained as a white powder in 74.9% yield (2.88 g). **^{1}H NMR (500.13 MHz, acetone-*d*$_6$)**: δ 1.77–1.79 (m, 24H), 3.05 (bs, 2H), 3.61–3.64 (m, 24H); **^{1}H{^{11}B} NMR (500.13 MHz, acetone-*d*$_6$)**: δ 1.78–1.80 (m, 24H), 2.33 (bs, 10H), 3.04 (bs, 2H), 3.61–3.64 (m, 24H); **^{11}B NMR (160.46 MHz, acetone-*d*$_6$)**: δ –20.19 (d, J = 167.8 Hz, 10B), –9.72 (bs, 10B), –1.65 (bs, 2B); **^{11}B{^{1}H} NMR (160.46 MHz, acetone-*d*$_6$)**: δ –20.24 (bs, 10B), –9.73 (bs, 10B), –1.66 (bs, 2B); **MS (ESI (–))**: *m/z* calcd for $HCB_{11}H_5Br_6$ $[(M–Mg(THF)_6)_{0.5}]^-$ 616.6613, found 616.6608.

[Mg(THF)$_6$]$^{2+}$[HCB$_{11}$H$_{10}$Br]$_2^{2-}$ (Mg^{2+}[12-Br-CCA]$_2$)



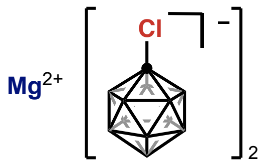
Using the General Procedure, the titled compound was obtained as a white powder in 97.1% yield (2.75 g). **^{1}H NMR (500.13 MHz, acetone-*d*$_6$)**: δ 1.77–1.80 (m, 24H), 2.27 (bs, 2H), 3.61–3.64 (m, 24H); **^{1}H{^{11}B} NMR (500.13 MHz, acetone-*d*$_6$)**: δ 1.64 (bs, 10H), 1.78–1.80 (m, 24H), 1.89 (bs, 10H), 2.27 (bs, 2H), 3.61–3.64 (m, 24H); **^{11}B NMR (160.46 MHz, acetone-*d*$_6$)**: δ –17.03 (d, *J* = 153.2 Hz, 10B), –12.41 (d, *J* = 144.9 Hz, 10B), –2.86 (bs, 2B); **^{11}B{^{1}H} NMR (160.46 MHz, acetone-*d*$_6$)**: δ –17.03 (bs, 10B), –12.41 (bs, 10B), –2.86 (bs, 2B); **MS (ESI (–))**: *m/z* calcd for HCB$_{11}$H$_{10}$Br [(M–Mg(THF)$_6$)$_{0.5}$]$^-$ 222.1115, found 222.1132.

[Mg(THF)$_6$]$^{2+}$[HCB$_{11}$H$_{10}$Cl]$_2^{2-}$ (Mg^{2+}[12-Cl-CCA]$_2$)



Using the General Procedure, the titled compound was obtained as a white powder in 96.6% yield (2.48 g). **^{1}H NMR (500.13 MHz, acetone-*d*$_6$)**: δ 1.77–1.80 (m, 24H), 2.10 (bs, 2H), 3.61–3.64 (m, 24H); **^{1}H{^{11}B} NMR (500.13 MHz, acetone-*d*$_6$)**: δ 1.60 (bs, 10H), 1.78–1.80 (m, 24H), 1.81 (bs, 10H), 2.10 (bs, 2H), 3.61–3.64 (m, 24H); **^{11}B NMR (160.46 MHz, acetone-*d*$_6$)**: δ –17.56 (d, *J* = 155.5 Hz, 10B), –12.70 (d, *J* = 139.1 Hz, 10B), 3.78 (bs, 1B); **^{11}B{^{1}H} NMR (160.46 MHz, acetone-*d*$_6$)**: δ –17.56 (bs, 10B), –12.73 (bs, 10B), 3.80 (bs, 2B); **MS (ESI (–))**: *m/z* calcd for HCB$_{11}$H$_{10}$Cl [(M–Mg(THF)$_6$)$_{0.5}$]$^-$ 177.1646, found 177.1655.

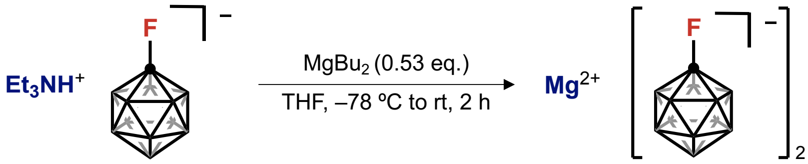
[Mg(THF)$_6$]$^{2+}$[ClCB$_{11}$H$_{11}$]$_2^{2-}$ (Mg^{2+}[1-Cl-CCA]$_2$)



Using the General Procedure, the titled compound was obtained as an off-white powder in 51.2% yield (104.1 mg). **^{1}H NMR (500.13 MHz, acetone-*d*$_6$)**: δ 1.76–1.79 (m, 24H), 3.60–3.63 (m, 24H); **^{1}H{^{11}B} NMR (500.13 MHz, acetone-*d*$_6$)**: δ 1.56 (bs, 2H), 1.76–1.79 (bs, 20H), 1.76–1.79 (m, 24H), 3.60–3.62 (m, 24H); **^{11}B NMR (160.46 MHz, acetone-*d*$_6$)**: δ –13.51 (d, *J* = 150.4 Hz, 10B), –12.53 (d, *J* = 164.8 Hz, 10B), –11.45 (d, *J* = 181.3 Hz, 2B); **^{11}B{^{1}H} NMR (160.46 MHz, acetone-*d*$_6$)**: δ –13.53

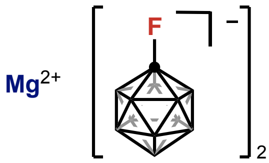
(bs, 10B), –12.50 (bs, 10B), –11.36 (bs, 2B); **MS (ESI (–))**: *m/z* calcd for $ClCB_{11}H_{11}$ [(M–Mg(THF)$_6$)$_{0.5}$]$^-$ 177.1646, found 177.1661.

Synthesis of Magnesium Salt from Triethylammonium Salt



$[Et_3NH]^+[FCB_{11}H_{11}]^-$ ($[Et_3NH]^+$[1-F-CCA]) (950 mg 3.61 mmol) was charged in a Schlenk flask and dried under reduced pressure at 120 ºC for 1 h. The flask was charged with argon, and 30 mL of anhydrous THF was added at room temperature. The solution was cooled to –78 ºC and di-n-butylmagnesium (0.970 M in ether and n-hexane, 2.17 mmol) was added. The mixture was stirred at the same temperature for 30 min and then at rt for 1.5 h. N-hexane (30 ml) was added to the reaction mixture and then filtrated under argon atmosphere. The solid was washed with THF and dried on the funnel for 45 min to obtain pure $[Mg(THF)_6]^{2+}[FCB_{11}H_{11}]_2^{2-}$ (1.17 g, 83.1% based on $[Et_3NH]^+$[1-F-CCA]$^-$) as a white powder.

$[Mg(THF)_6]^{2+}[FCB_{11}H_{11}]_2^{2-}$ (Mg^{2+}[1-F-CCA]$_2$)



^1H NMR (500.13 MHz, acetone-*d*$_6$): δ 1.77–1.80 (m, 24H), 3.61–3.64 (m, 24H); **$^1H\{^{11}B\}$ NMR (500.13 MHz, acetone-*d*$_6$)**: δ1.34–1.37 (m, 2H), 1.44 (bs, 10H), 1.77–1.80 (m, 24H), 2.02 (bd, 10H), 3.61–3.64 (m, 24H); **^{11}B NMR (160.46 MHz, acetone-*d*$_6$)**: δ –15.85 (d, J = 154.9 Hz, 22B); **$^{11}B\{^1H\}$ NMR (160.46 MHz, acetone-*d*$_6$)**: δ –15.90 (bs, 22B); **^{19}F NMR (470.55 MHz, acetone-*d*$_6$)**: δ –159.08 (s, 2F); **MS (ESI (–))**: *m/z* calcd for $FCB_{11}H_{11}$ [(M–Mg(THF)$_6$)$_{0.5}$]$^-$ 161.1947, found 161.1944.

Electrochemical Analysis of $[TBA]^+$[CCAs]

Cyclic voltammetry measurements were carried out with a Hokuto Denko HZ-3000 voltammetric analyzer. The cell contained inlets for a glassy carbon disk working electrode of 3.0 mm diameter and a platinum-wire counter electrode. The reference electrode was Ag/AgCl. Ferrocene was used as an external standard. The scan rates were 100 mV/s for CV. To measure oxidation potentials of $[TBA]^+$[CCAs], voltammograms of 0.1 M / 2.0 mM solution of $[Bu_4N]^+[PF_6]^-$ / $[TBA]^+$[CCAs] were recorded at room temperature in HFIP (1.5 mL) which was dried over 4 A molecular sieves. To measure reduction potentials of $[TBA]^+$[CCAs], voltammograms of 0.1 M / 2.0 mM solution of $[Bu_4N]^+[AsF_6]^-$ / $[TBA]^+$[CCAs] were recorded at ambient temperature in anhydrous MeCN (1.5 mL).

General procedure for the preparation of the electrolyte solutions

Battery grade dimethoxyethane (DME) and triglyme (G3) were purchased from KISHIDA CHEMICAL Co., Ltd. and used without purification unless indicated otherwise. $[Mg]^{2+}$[12-Br-CCA]$_2$•THF electrolyte solutions and $[Mg]^{2+}$[12-Cl-CCA]$_2$•THF electrolyte solutions for Cyclic voltammetry were prepared by dissolving the corresponding salts in DME respectively, and these mixtures were stirred for 30 minutes to obtain the clear solutions in Argon-filled grove box. $[Mg]^{2+}$[12-Br-CCA]$_2$•DME electrolyte solution and $[Mg]^{2+}$[CCA]$_2$•DME electrolyte solution for Linear sweep voltammetry were prepared by dissolving the corresponding salts in DME and G3 respectively, and these mixtures were stirred for 30 minutes to obtain the clear solutions in Argon-filled grove box.

Electrochemical Analysis of $[Mg]^{2+}$[CCAs]$_2$

All electrochemical experiments were conducted by using an electrochemical system (Biologic VSP-300) in Argon-filled grove box. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV/s in a standard three-electrode cell. The cell was composed of a Pt disk working electrode (3 mm dia), a fresh polished Mg ribbon quasi-reference electrode, and fresh polished Mg ribbon counter electrode. Mg ribbon used as the electrodes was purchased from The Nilaco Corporation. The Coulombic efficiency (CE) was calculated by the ratio of the total amount of charge for Mg stripping to that for Mg plating in the range of –1.0 V to 2.0 V (vs. Mg/Mg^{2+}). The ion conductivity of the electrolyte solutions was measured using a conductivity meter (METTLER TOLEDO Seven2GO™ RoutineS3). Linear sweep voltammetry was carried out at room temperature with an electrochemical system (Biologic VSP-300) in Argon-filled grove box. The cell was composed of aluminium working electrode (2.9 mm dia), a fresh polished Mg ribbon quasi-reference electrode, and fresh polished Mg ribbon counter electrode. The scan rate was 0.1 mV/s. To measure oxidation potentials of $[Mg]^{2+}$[12-Br-CCA]$_2$•DME or $[Mg]^{2+}$[CCA]$_2$•DME electrolyte, the voltammogram of 0.3 M $[Mg]^{2+}$[12-Br-

CCA]$_2$•DME or [Mg]$^{2+}$[CCA]$_2$•DME electrolyte were recorded in the range of 2.0 V to 4.5 V (vs. Mg/Mg^{2+}).

Solubility of the Mg^{2+}[12-Br-CCA]$_2$ and Mg^{2+}[12-Cl-CCA]$_2$ in DME

The solubility of Mg^{2+}[CCAs]$_2$ for DME was investigated by diluting the mixtures containing 0.3 mmol salts and 0.3 mL of DME. To obtain 1.0 M DME solutions of Mg^{2+}[CCAs]$_2$, 0.3 mL of DME was added to Mg^{2+}[CCA]$_2$ salt (coordinating solvent: DME) (174.2 mg, 0.3 mmol), Mg^{2+}[CCA]$_2$ (coordinating solvent: THF) (222.9 mg, 0.3 mmol), Mg^{2+}[1-F-CCA]$_2$ (233.7 mg, 0.3 mmol), Mg^{2+}[1-Cl-CCA]$_2$ (243.6 mg, 0.3 mmol), Mg^{2+}[12-Cl-CCA]$_2$ (243.6 mg, 0.3 mmol) and Mg^{2+}[12-Br-CCA]$_2$ (270.2 mg, 0.3 mmol) respectively. After these mixtures were stirred for 30 min, the solubility of Mg^{2+}[CCAs]$_2$ in DME was examined. If insoluble, DME was more added to the mixtures. For example, 0.8 M DME solution of Mg^{2+}[12-Cl-CCA]$_2$ was prepared by adding 75 μ L of DME to 0.3 mL of 1.0 M DME solution of Mg^{2+}[12-Cl-CCA]$_2$. The ion conductivity of these solutions was measured at each concentration.

Galvanostatic Deposition

Galvanostatic deposition of magnesium was performed in a standard three-electrode cell using 0.25 M Mg^{2+}[12-Br-CCA]$_2$ electrolyte solution. The cell was composed of a Pt disk working electrode (3 mm dia), a fresh polished Mg ribbon quasi-reference electrode, and fresh polished Mg ribbon counter electrode. A constant current corresponding to a potential of –0.5 V (vs. Mg) was applied for 96 hours. The dismantled Pt disk from the cell was rinsed in DME and dried under vacuum for 5 hours. The deposit on the Pt disk was analyzed by SEM and EDS to confirm the deposition of magnesium.

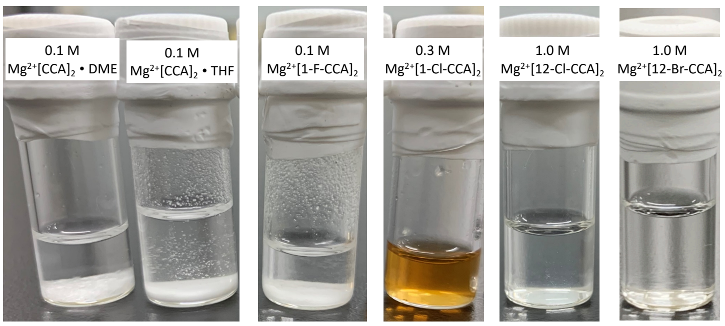


Figure S1. Snapshots of solubility testing.

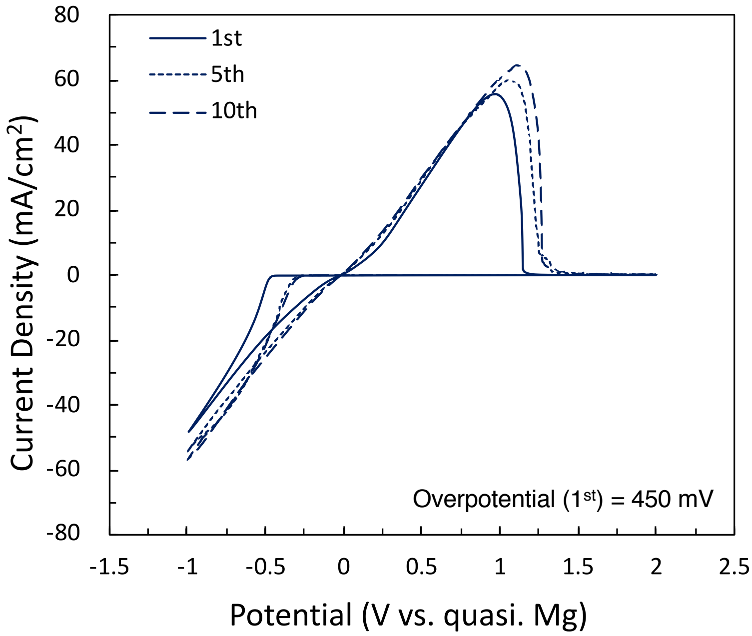


Figure S2. Cyclic voltammograms (1st, 5th, and 10th cycles) of 1.0 M Mg^{2+}[12-Cl-CCA]$_2$ in DME.

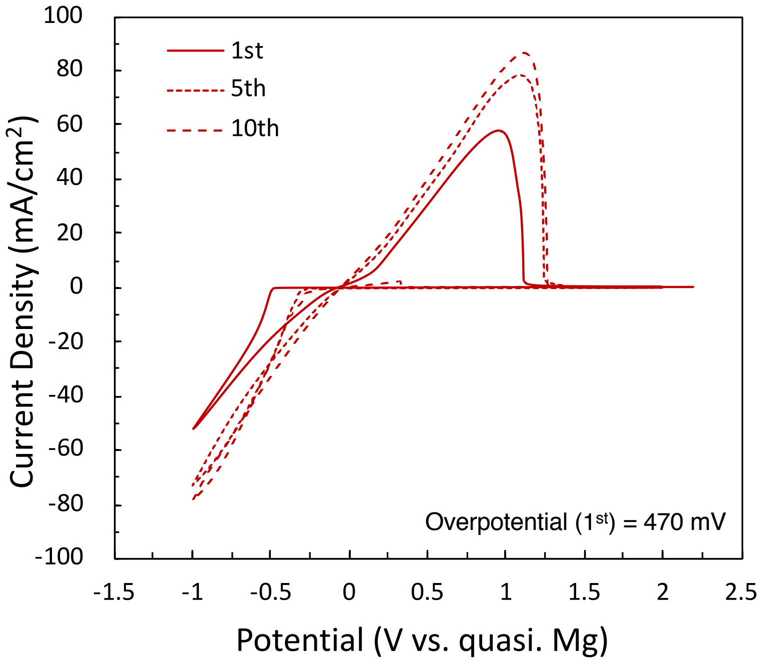


Figure S3. Cyclic voltammograms (1st, 5th, and 10th cycles) of 0.8 M Mg^{2+}[12-Br-CCA]$_2$ in DME.

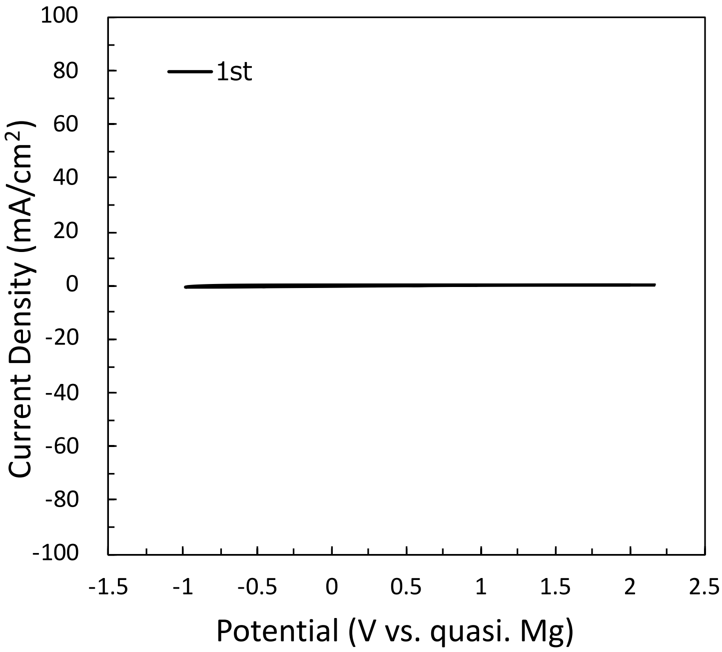


Figure S4. Cyclic voltammograms (1st cycle) of 0.5 M $Mg^{2+}[7–12-Br_6-CCA]_2$ in G3.

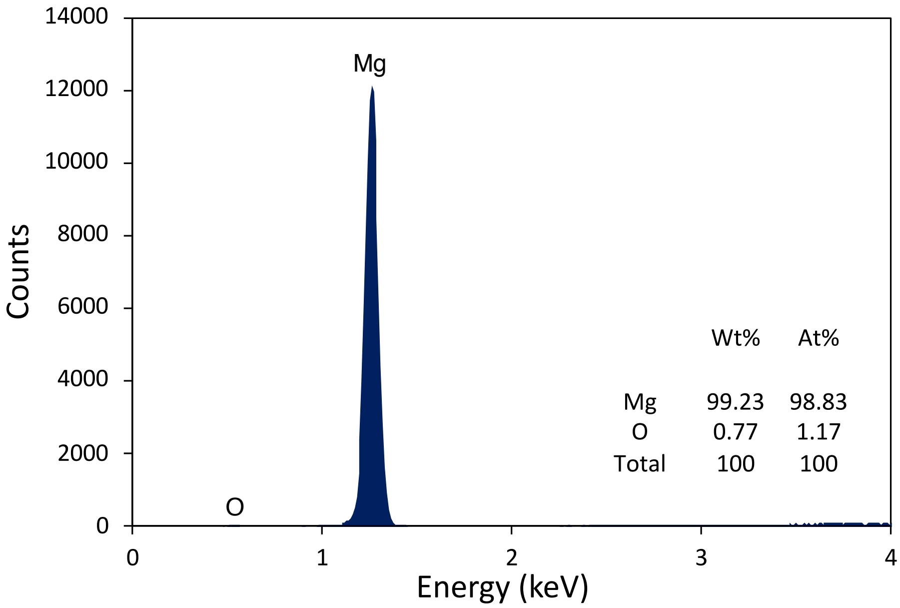


Figure S5. Energy dispersive X-ray spectroscopy (EDS) spectrum.

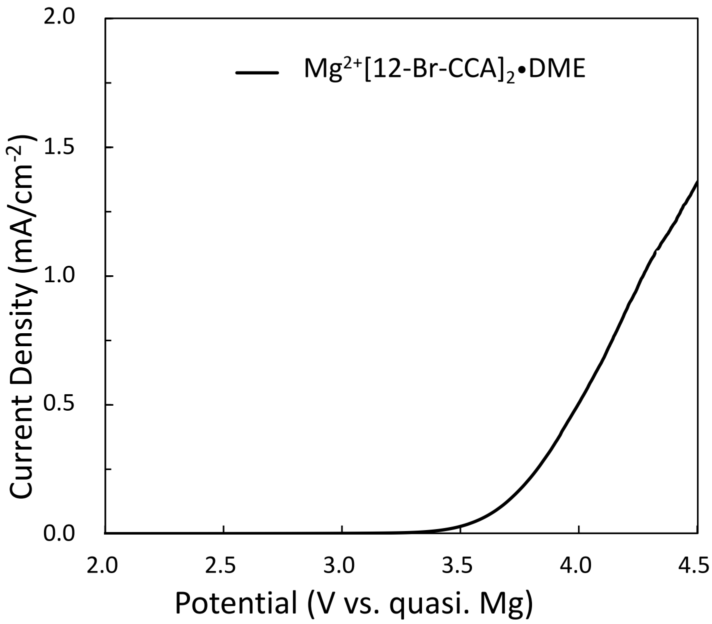


Figure S6. Linear sweep voltammogram of 0.3 M Mg^{2+}[12-Br-CCA]$_2$•DME electrolyte on aluminium electrode at scan rate of 0.1 mV/s.

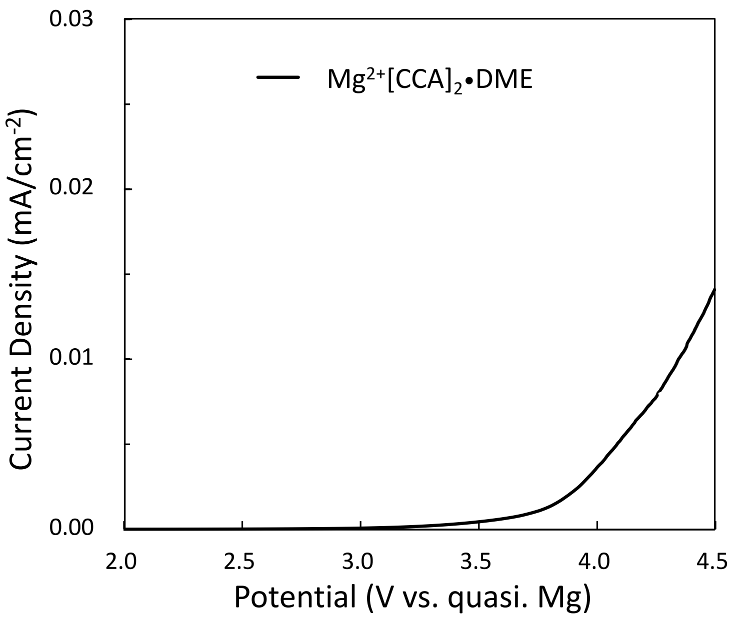


Figure S7. Linear sweep voltammogram of 0.3 M Mg^{2+}[CCA]$_2$•DME electrolyte on aluminium electrode at scan rate of 0.1 mV/s.

3. Computational Section

All calculations were carried with the Gaussian 16 program package.[8] Structure optimizations were carried out at the B3LYP-D3(BJ) level using the 6-311++G(d,p) basis set.[9–12] Solvent effects were accounted for with the PCM method[13,14] using 1,1,2-trichloroethane as an alternative solvent to DME, since the dielectric constant of 1,1,2-trichloroethane (ε = 7.1937 Fm^{-1}) is very similar to that for DME.[15] To model anodic and cathodic stabilities, ionization potentials (IPs) and electron affinities (EAs) were computed under the adiabatic approximation,[16,17] which accounts for orbital and geometric relaxation between charge states. The EA is the energy gained for a reduced anion, while IP represents the energy penalty to oxidize an anion. These computed values are converted to oxidation and reduction potentials, respectively, referenced to Mg by assuming the $Mg^{0/2+}$ standard reduction potential at −2.37 V vs SHE corresponds to an absolute electrode potential of 2.06 eV relative to the vacuum level. The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum (no imaginary frequency) and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. The Gibbs free energy used for discussion in this study was calculated by adding the Gibbs free energy correction.

```
CCA_monoanion
Sum of electronic and thermal Free
Energies= -319.039875 A.U.
------------------------------------------
B   -0.63170300    1.36923600   -0.73913000
B   -1.50017000   -0.17962300   -0.73326500
B   -0.29539800   -1.48410400   -0.72815000
B    1.31755800   -0.74151300   -0.73105300
B    1.10979900    1.02197800   -0.73766700
B    0.29680200    1.49107300    0.76292500
B   -1.32363900    0.74501000    0.76557000
H   -1.04585400    2.26624300   -1.39220700
B   -1.11482200   -1.02645100    0.77242000
H   -2.48345600   -0.29807000   -1.38257900
B    0.63464300   -1.37544400    0.77370800
H   -0.48900200   -2.45758300   -1.37415700
B    1.50701800    0.18044600    0.76785500
H    2.18113900   -1.22814900   -1.37917600
H    1.83737500    1.69125700   -1.38977900
B   -0.00005000    0.00650400    1.70035300
H    0.50675000    2.54611100    1.26779400
H   -2.26043500    1.27196200    1.27222800
H   -1.90374500   -1.75299500    1.28421300
H    1.08351400   -2.34903100    1.28619400
H    2.57350700    0.30812100    1.27607000
H   -0.00013700    0.01110800    2.88946000
C    0.00002400   -0.00576900   -1.52084800
H    0.00000500   -0.00992500   -2.60080000
------------------------------------------
```

```
CCA_dianion_radical
Sum of electronic and thermal Free
Energies= -319.049862 A.U.
------------------------------------------
B   -0.72153200    0.25734500   -1.48916300
B   -0.72023300    1.49520100   -0.22465500
B   -0.73787800    0.67513400    1.34323200
B   -0.75030800   -1.06941400    1.04784100
B   -0.74020200   -1.32771200   -0.70279200
B    0.77227200   -0.68012200   -1.35276400
B    0.78469400    1.07711900   -1.05513300
H   -1.37237600    0.42741900   -2.46970300
B    0.77455900    1.33694500    0.70802900
H   -1.36968500    2.47988200   -0.37388900
B    0.75571500   -0.25964100    1.50001900
H   -1.39912100    1.12074200    2.22531200
B    0.75430000   -1.50625000    0.22644200
H   -1.41967700   -1.77113000    1.73596300
H   -1.40288200   -2.19946500   -1.16650000
B    1.70278400   -0.01417200    0.01193000
H    1.28797300   -1.16264500   -2.31294800
H    1.30928600    1.84185500   -1.80406700
H    1.29185000    2.28612500    1.21025700
H    1.26002400   -0.44301900    2.56439900
H    1.25666000   -2.57505800    0.38679700
H    2.89469200   -0.02370700    0.02055800
C   -1.51502500    0.01255500   -0.01050700
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```
H   -2.61744600    0.02151000   -0.01807700
-------------------------------------------
```

CCA_neutral_radical
Sum of electronic and thermal Free
Energies= -318.793844 A.U.

```
-------------------------------------------
B    0.02360100   -0.45088600    1.58003400
B    1.39294700   -0.83960000    0.51813000
B    0.73578500   -1.02985000   -1.10990600
B   -1.06677200   -0.82067000   -1.02658600
B   -1.49627300   -0.49794800    0.65627000
B   -0.75844100    1.04995800    1.09300500
B    1.09573400    0.82465000    1.01541900
H    0.01668600   -0.82243600    2.70370600
B    1.53699300    0.46839200   -0.65717900
H    2.25507800   -1.54279900    0.90447100
B   -0.02279400    0.46474800   -1.59041300
H    1.14511100   -1.82925500   -1.87561700
B   -1.44587300    0.81877500   -0.51685600
H   -1.72291200   -1.50541500   -1.72769300
H   -2.45783200   -0.97554400    1.13995200
B    0.20789600    1.72453700   -0.26324000
H   -1.21961400    1.86812300    1.81469800
H    1.79418900    1.47743500    1.71226800
H    2.54787500    0.81035500   -1.15923900
H   -0.01916400    1.17846400   -2.54870600
H   -2.38472600    1.40707100   -0.91885100
C   -0.16837200   -1.49117500    0.25439100
H    0.32619300    2.86883500   -0.50477500
H   -0.28466300   -2.54831500    0.44005300
-------------------------------------------
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7–12-Br_6-CCA_monoanion
Sum of electronic and thermal Free
Energies= -15760.668634 A.U.

```
-------------------------------------------
B   -0.88650600   -1.22161600    2.18532300
B   -1.43600800    0.46602700    2.18506200
B   -0.00073500    1.51014900    2.18469500
B    1.43569000    0.46782700    2.18465900
B    0.88828300   -1.22045700    2.18510400
B    0.00093900   -1.51691200    0.68407800
B   -1.44268300   -0.46965600    0.68416300
H   -1.47626100   -2.03440100    2.79880500
B   -0.89260500    1.22700800    0.68393200
H   -2.39136200    0.77592500    2.79827800
B    0.89107100    1.22786700    0.68346500
H   -0.00124800    2.51476600    2.79761000
B    1.44304400   -0.46770900    0.68372300
H    2.39080300    0.77901000    2.79762200
H    1.47922000   -2.03257000    2.79834900
B   -0.00051900   -0.00000800   -0.26463100
C    0.00023500    0.00060200    2.96369600
H    0.00037000    0.00084200    4.04300900
Br  -0.00232400   -0.00065900   -2.22787100
Br   3.13784100   -1.01584600   -0.16135000
Br   0.00305000   -3.29800600   -0.16130300
Br  -3.13670800   -1.02070800   -0.16082600
Br  -1.94112100    2.66705000   -0.16080700
Br   1.93918200    2.66760400   -0.16252100
-------------------------------------------
```

7–12-Br_6-CCA_dianion_radical
Sum of electronic and thermal Free
Energies= -15760.726832 A.U.

```
-------------------------------------------
B   -0.01902400   -1.50200000    2.19087500
B   -1.43798800   -0.43935900    2.18958400
B   -0.86579700    1.23815300    2.18489400
B    0.90703300    1.21284800    2.18307800
B    1.42989900   -0.48116500    2.18717000
B    0.86095000   -1.21803100    0.68897600
B   -0.89340400   -1.19172900    0.69024300
H   -0.03289200   -2.50104100    2.82344500
B   -1.41107700    0.48344700    0.68691300
H   -2.39335900   -0.73261400    2.82112200
B    0.02273600    1.49448300    0.68304700
H   -1.44214700    2.05774600    2.81235800
B    1.42745600    0.44268300    0.68406300
H    1.50716800    2.01488800    2.81060200
H    2.37739400   -0.80269600    2.81703600
B    0.00096000    0.00015900   -0.22739600
C    0.00353900    0.00782000    2.97523400
H    0.00455200    0.01105300    4.05870000
Br  -0.00351500   -0.01198600   -2.32311600
Br   0.04788600    3.37514300   -0.14956900
Br   3.22539400    0.99598500   -0.14945300
Br   1.94623000   -2.75839600   -0.14056100
Br  -2.02618000   -2.69292200   -0.14166400
Br  -3.19412000    1.08384100   -0.14426300
-------------------------------------------
```

7–12-Br_6-CCA_neutral_radical
Sum of electronic and thermal Free
Energies= -15760.415068 A.U.

```
-------------------------------------------
B    1.11214500    1.04632400    2.18289600
B    1.36405800   -0.68855500    2.18640300
B   -0.20439500   -1.49660700    2.17315400
B   -1.47326200   -0.22409400    2.17375000
B   -0.62823700    1.36907300    2.17126600
B    0.24876600    1.51171100    0.65529700
B    1.51912200    0.22616700    0.63844100
```

H	1.83693900	1.75364700	2.77666400
B	0.67628500	-1.37685500	0.65181200
H	2.26467000	-1.15638500	2.77640000
B	-1.08434200	-1.05288200	0.66171900
H	-0.38302300	-2.48445000	2.78178300
B	-1.33705100	0.69486800	0.66089100
H	-2.46279700	-0.36641500	2.78842800
H	-1.08647100	2.26082100	2.78183100
B	0.01550600	0.00027700	-0.30150700
C	0.02274500	0.00121200	2.95297100
H	0.01809900	0.00172700	4.03262100
Br	0.02408500	-0.00118400	-2.25121400
Br	-2.92049600	1.50057600	-0.14666300
Br	0.51875900	3.25922100	-0.14996500
Br	3.26549400	0.48374800	-0.15403700
Br	1.44414400	-2.96770200	-0.15034300
Br	-2.37103900	-2.27646900	-0.14566900

12-Br-CCA_monoanion
Sum of electronic and thermal Free
Energies= -2892.649055 A.U.

B	-1.91144200	-1.40482600	-0.55716500
B	-1.91138700	0.09550700	-1.50832200
B	-1.91198500	1.46367200	-0.37540700
B	-1.91262600	0.80888800	1.27593200
B	-1.91202100	-0.96401700	1.16359200
B	-0.41199100	-1.47384300	0.37791600
B	-0.41174100	-0.81448000	-1.28483400
H	-2.55610100	-2.32682200	-0.92294400
B	-0.41186500	0.97067800	-1.17165300
H	-2.55605200	0.15809700	-2.49832400
B	-0.41273300	1.41462600	0.56118700
H	-2.55703100	2.42429600	-0.62167100
B	-0.41276700	-0.09610000	1.51883300
H	-2.55817100	1.33978300	2.11317400
H	-2.55715500	-1.59672200	1.92710200
B	0.49255500	0.00028000	0.00049200
H	0.11654500	-2.50186700	0.64144000
H	0.11679900	-1.38296300	-2.18089500
H	0.11666700	1.64772800	-1.98882800
H	0.11483800	2.40137800	0.95281200
H	0.11491400	-0.16296000	2.57831900
C	-2.69725600	-0.00031500	-0.00053300
H	-3.77690500	-0.00055100	-0.00090800
Br	2.50872000	0.00001600	0.00003100

12-Br-CCA_dianion_radical
Sum of electronic and thermal Free
Energies= -2892.661598 A.U.

B	-1.91476600	-1.32096000	-0.72486800
B	-1.91633000	0.28018800	-1.47973300
B	-1.91854800	1.49283700	-0.19019300
B	-1.91839300	0.64119400	1.36168800
B	-1.91573800	-1.09807300	1.03104600
B	-0.41611300	-1.50808900	0.19188300
B	-0.41652300	-0.64757200	-1.37569500
H	-2.57071900	-2.19059600	-1.20117300
B	-0.41852200	1.10937900	-1.04160900
H	-2.57383500	0.46437500	-2.45313000
B	-0.41986100	1.33457700	0.73234400
H	-2.57691800	2.47478100	-0.31596000
B	-0.41842700	-0.28283000	1.49503600
H	-2.57687300	1.06290800	2.25702300
H	-2.57178800	-1.82062900	1.70977500
B	0.48323800	0.00162900	0.00072600
H	0.11820600	-2.56267600	0.32639900
H	0.11754600	-1.10020500	-2.33761800
H	0.11377200	1.88523800	-1.77003300
H	0.11073400	2.26830300	1.24456700
H	0.11368300	-0.48014500	2.54071500
C	-2.69543300	-0.00194700	-0.00070300
H	-3.79601300	-0.00349000	-0.00130600
Br	2.52042100	0.00006900	0.00005200

12-Br-CCA_neutral_radical
Sum of electronic and thermal Free
Energies= -2892.406666 A.U.

B	-1.88655300	-0.98093400	1.15276500
B	-1.90247000	-1.41767400	-0.55464000
B	-1.85923600	0.10115700	-1.50618900
B	-1.90472500	1.47859900	-0.36803700
B	-1.88007600	0.81960300	1.27028100
B	-0.41096100	-0.10724200	1.54635400
B	-0.40256500	-1.50722100	0.36570200
H	-2.51020400	-1.60058300	1.93903400
B	-0.39944100	-0.85836200	-1.28986400
H	-2.54997300	-2.32276700	-0.94167300
B	-0.39748800	1.02210600	-1.16497500
H	-2.45467000	0.16507100	-2.52381600
B	-0.40114600	1.44925000	0.55224900
H	-2.55653700	2.42534500	-0.62614000
H	-2.49619900	1.33698400	2.13325100
B	0.52698900	-0.00002500	0.00310100
H	0.20293600	-0.16759400	2.55097900
H	0.14988800	-2.51284300	0.64271500
H	0.19492800	-1.36943800	-2.17072300
H	0.18796900	1.64469600	-1.97764200
H	0.15505500	2.40445500	0.96588200
C	-2.66196700	0.00109900	-0.00525400

H	-3.74176800	0.00182000	-0.00918400
Br	2.45653500	-0.00022900	0.00043200

12-Cl_CCA_monoanion

Sum of electronic and thermal Free Energies= -778.729086 A.U.

B	-1.37427600	-0.75256900	1.31021300
B	-1.37384800	-1.47891900	-0.31082000
B	-1.37412000	-0.16149200	-1.50227800
B	-1.37422500	1.37889800	-0.61786200
B	-1.37454100	1.01358400	1.12038200
B	0.12474500	0.16250600	1.51156100
B	0.12541300	-1.38739500	0.62161900
H	-2.01967600	-1.24626000	2.17006000
B	0.12535600	-1.01962700	-1.12735700
H	-2.01911000	-2.44920100	-0.51494300
B	0.12509600	0.75716600	-1.31823800
H	-2.01954800	-0.26750500	-2.48807000
B	0.12497100	1.48784100	0.31269600
H	-2.01982900	2.28347100	-1.02327600
H	-2.02013100	1.67849800	1.85560700
B	1.03787500	0.00016000	0.00012200
H	0.65320100	0.27633000	2.56700800
H	0.65456400	-2.35578200	1.05570200
H	0.65430000	-1.73146500	-1.91447100
H	0.65387200	1.28556800	-2.23869600
H	0.65387000	2.52648300	0.53117500
C	-2.16023900	-0.00024100	-0.00014100
H	-3.23977000	-0.00034400	-0.00023700
Cl	2.88632100	0.00005200	0.00004700

12-Cl-CCA_dianion_radical

Sum of electronic and thermal Free Energies= -778.740923 A.U.

B	1.37596000	-1.31675400	0.73040600
B	1.37550900	0.28779500	1.47830500
B	1.37538600	1.49484700	0.18330500
B	1.37586400	0.63618400	-1.36481200
B	1.37605200	-1.10140300	-1.02659500
B	-0.12312500	-1.50954300	-0.18516900
B	-0.12337700	-0.64248800	1.37798200
H	2.03297000	-2.18266500	1.21119800
B	-0.12369100	1.11201600	1.03662400
H	2.03140100	0.47763800	2.45102000
B	-0.12335100	1.32954500	-0.73760300
H	2.03092700	2.47858700	0.30378300
B	-0.12306900	-0.29060700	-1.49260500
H	2.03242700	1.05459200	-2.26258300
H	2.03324900	-1.82613800	-1.70142600
B	-1.03267800	-0.00019700	-0.00028800
H	-0.65698800	-2.56469700	-0.31455700
H	-0.65744900	-1.09173800	2.34129100
H	-0.65777400	1.88959300	1.76131000
H	-0.65734100	2.25904200	-1.25345200
H	-0.65689700	-0.49332200	-2.53619800
C	2.15533900	0.00035700	0.00023600
H	3.25706700	0.00043000	0.00014700
Cl	-2.89476600	-0.00002600	0.00001800

12-Cl-CCA_neutral_radical

Sum of electronic and thermal Free Energies= -778.484673 A.U.

B	-1.36587100	-0.98303600	1.15015400
B	-1.38473600	-1.42083200	-0.55412900
B	-1.33170200	0.10123200	-1.50206200
B	-1.38652700	1.48207100	-0.36819700
B	-1.35740800	0.82175300	1.26698200
B	0.10118700	-0.10840600	1.54246700
B	0.11526000	-1.51476400	0.36332400
H	-1.98657900	-1.59686300	1.94326100
B	0.11784600	-0.86637800	-1.28428900
H	-2.03577800	-2.32071700	-0.94596400
B	0.12154700	1.03028100	-1.15953300
H	-1.91612000	0.16479500	-2.52677600
B	0.11772800	1.45737200	0.54849900
H	-2.04227300	2.42447000	-0.62997300
H	-1.96817300	1.33464600	2.13663600
B	1.07982600	0.00033800	0.00077200
H	0.77036500	-0.16434200	2.51271900
H	0.67000200	-2.51623300	0.64818600
H	0.74439200	-1.35481100	-2.15618900
H	0.73114300	1.63094200	-1.97114500
H	0.67836400	2.40487600	0.97218100
C	-2.14096800	0.00156600	-0.00599400
H	-3.22064300	0.00284700	-0.01077900
Cl	2.84031500	-0.00100900	0.00258000

12-F-CCA_monoanion

Sum of electronic and thermal Free Energies= -418.378292 A.U.

B	1.04177700	0.21906300	-1.49445200
B	1.04041400	-1.35448600	-0.67018500
B	1.04043000	-1.05615500	1.08102400
B	1.04081800	0.70175100	1.33797400
B	1.04253700	1.48927600	-0.25336400
B	-0.45706300	1.06289900	-1.08665200

B	-0.45721800	-0.70514700	-1.34612800
H	1.68898600	0.36203700	-2.47533900
B	-0.45789300	-1.49857900	0.25460400
H	1.68715200	-2.24327400	-1.10974400
B	-0.45821800	-0.22086600	1.50328900
H	1.68720400	-1.74881200	1.79044300
B	-0.45823600	1.36233500	0.67453500
H	1.68783900	1.16189800	2.21610300
H	1.68967800	2.46640600	-0.41982800
B	-1.38425100	0.00022900	-0.00041800
H	-0.98372300	1.80661100	-1.84805200
H	-0.98440700	-1.19897900	-2.28869500
H	-0.98608700	-2.54719300	0.43290600
H	-0.98600200	-0.37525300	2.55578300
H	-0.98540900	2.31577800	1.14675900
C	1.82843000	-0.00054400	0.00043500
H	2.90798800	-0.00131300	0.00085200
F	-2.78436400	0.00041800	-0.00055000

12-F-CCA_dianion_radical
Sum of electronic and thermal Free Energies= -418.388924 A.U.

B	1.04115600	-1.37051800	0.62315400
B	1.04163700	0.16881400	1.49581200
B	1.04230200	1.47473300	0.30152800
B	1.04148000	0.74252300	-1.30949600
B	1.04163200	-1.01621300	-1.11084200
B	-0.45698100	-1.48884500	-0.30424700
B	-0.45733900	-0.74900900	1.32147300
H	1.69850800	-2.27225000	1.03303700
B	-0.45660100	1.02579600	1.12090300
H	1.69920900	0.27925300	2.47997800
B	-0.45759200	1.38359600	-0.62906700
H	1.70025000	2.44457000	0.50033100
B	-0.45769500	-0.17080400	-1.50974000
H	1.69893600	1.23118800	-2.17096100
H	1.69929100	-1.68429600	-1.84165300
B	-1.38353400	0.00011900	0.00009500
H	-0.98897700	-2.53305700	-0.51748700
H	-0.98946900	-1.27436600	2.24848400
H	-0.98791700	1.74463000	1.90806000
H	-0.98879700	2.35407500	-1.06992800
H	-0.98952500	-0.29052700	-2.56866600
C	1.82322500	-0.00015500	-0.00021800
H	2.92464300	-0.00016400	-0.00066600
F	-2.78975800	0.00010200	0.00032500

12-F-CCA_neutral_radical
Sum of electronic and thermal Free Energies= -418.134611 A.U.

B	1.05068300	-0.97365600	-1.15542900
B	1.06509200	-1.42893400	0.54532900
B	0.99681100	0.08703100	1.49865600
B	1.06258100	1.48328800	0.38745400
B	1.03950000	0.83790300	-1.25356100
B	-0.41171000	-0.09335200	-1.52905800
B	-0.42641000	-1.52504200	-0.38077700
H	1.67392500	-1.56746600	-1.96155700
B	-0.44444700	-0.88304000	1.26271000
H	1.72220900	-2.32533600	0.93377200
B	-0.45048200	1.02223100	1.15911700
H	1.56125300	0.14031900	2.53600400
B	-0.43349100	1.47425200	-0.53757700
H	1.72149300	2.41884900	0.66391500
H	1.64964200	1.34803700	-2.12534200
B	-1.42923900	0.00066300	0.00434000
H	-1.17409600	-0.13745300	-2.43462900
H	-0.98112100	-2.51963400	-0.68785100
H	-1.10708200	-1.36708300	2.11299600
H	-1.08630300	1.60033100	1.96920200
H	-0.99394000	2.41933400	-0.96641000
C	1.81934600	0.00321500	0.01077600
H	2.89877300	0.00626300	0.02049400
F	-2.76614100	-0.00468600	-0.01458600

12-Me-CCA_monoanion
Sum of electronic and thermal Free Energies= -358.355808 A.U.

B	1.08411300	-1.36380900	-0.64809000
B	1.08504100	-1.03756400	1.09656600
B	1.08422100	0.72261100	1.32536400
B	1.08423600	1.48447600	-0.27790300
B	1.08332300	0.19488800	-1.49751300
B	-0.41922800	-0.72439700	-1.32827500
B	-0.41685700	-1.48800600	0.27877800
H	1.73212000	-2.25914500	-1.07475200
B	-0.41783700	-0.19587000	1.50077900
H	1.73366900	-1.71818100	1.81734100
B	-0.41799100	1.36722900	0.64911100
H	1.73195900	1.19726400	2.19636900
B	-0.41816100	1.04030600	-1.09865900
H	1.73256600	2.45914700	-0.46006700
H	1.73030900	0.32210000	-2.48175200
B	-1.37357600	-0.00023300	0.00086800
H	-0.93263100	-1.23758900	-2.27052000
H	-0.93285400	-2.54123000	0.47518800
H	-0.93138600	-0.33270000	2.56485500
H	-0.93267100	2.33487800	1.11099800
H	-0.93497000	1.77552000	-1.87772800

C	1.87301700	0.00028400	-0.00064800
H	2.95288500	0.00060400	-0.00098500
C	-2.97275400	-0.00006300	0.00013800
H	-3.38064700	0.55571400	0.85153700
H	-3.37753100	0.46003100	-0.90785600
H	-3.37882500	-1.01590200	0.05530200

12-Me-CCA_dianion_radical

Sum of electronic and thermal Free Energies= -358.364258 A.U.

B	-1.08511600	-0.18241700	-1.49262100
B	-1.08435200	1.36422400	-0.63527400
B	-1.08354900	1.02613400	1.10062500
B	-1.08487700	-0.72914000	1.31566600
B	-1.08598700	-1.47634400	-0.28702500
B	0.41717800	-1.03217200	-1.10624300
B	0.41748500	0.73358700	-1.32273700
H	-1.74184600	-0.30316400	-2.47683800
B	0.41835800	1.48448500	0.28815300
H	-1.74084800	2.26339300	-1.05362800
B	0.41919300	0.18311000	1.50079000
H	-1.73876800	1.70259500	1.82696900
B	0.41614400	-1.37201200	0.63872700
H	-1.74135200	-1.20879100	2.18370400
H	-1.74388300	-2.44865100	-0.47728000
B	1.37507600	-0.00099200	-0.00058700
H	0.93322200	-1.76463700	-1.89359000
H	0.93702800	1.25249600	-2.26262700
H	0.93872600	2.53773200	0.49468900
H	0.93725600	0.31427500	2.56733000
H	0.93641200	-2.34482200	1.09228800
C	-1.86957700	0.00110200	0.00049100
H	-2.97185700	0.00168800	0.00055800
C	2.97707200	-0.00029700	-0.00032000
H	3.38512700	0.04591900	-1.01631600
H	3.38316700	0.85744500	0.54762000
H	3.38488300	-0.90262600	0.46872300

12-Me-CCA_neutral_radical

Sum of electronic and thermal Free Energies= -358.116615 A.U.

B	-1.04494100	-0.00606800	1.49785800
B	-1.11071300	-1.45824300	0.46279600
B	-1.09415200	-0.90101400	-1.20938100
B	-1.09533000	0.91079000	-1.20220500
B	-1.11033100	1.45458900	0.47378600
B	0.40460400	0.93908000	1.20586500
B	0.40569500	-0.94891700	1.19801300
H	-1.61008300	-0.01078000	2.53690300
B	0.38429100	-1.49586000	-0.46481200
H	-1.76827300	-2.37856600	0.79212200
B	0.36364000	0.00708400	-1.51327800
H	-1.71164000	-1.45086300	-2.05176200
B	0.38426700	1.49873900	-0.45445100
H	-1.71333700	1.46629600	-2.04040300
H	-1.76752600	2.37234200	0.81102400
B	1.43134400	0.00089000	0.00400300
H	1.03994300	1.47690700	2.04634500
H	1.03811700	-1.49382800	2.03603800
H	0.92739700	-2.47340500	-0.84273800
H	1.14159300	0.00705500	-2.41071700
H	0.92588700	2.48097900	-0.82236900
C	-1.87062400	-0.00026000	0.01063700
H	-2.95016800	-0.00042800	0.02066800
C	2.98640800	0.00037300	-0.02019400
H	3.37506700	-0.01077700	1.00738900
H	3.39229200	-0.88543500	-0.51657500
H	3.39416200	0.89447700	-0.49955800

1-F-CCA_monoanion

Sum of electronic and thermal Free Energies= -418.308237 A.U.

B	0.44282400	-0.18780900	1.50404200
B	0.44263000	1.37254100	0.64345600
B	0.44286700	1.03593400	-1.10628500
B	0.44283300	-0.73212100	-1.32723800
B	0.44295100	-1.48846700	0.28611200
B	-1.05636000	-1.03819200	1.10861500
B	-1.05675400	0.73359100	1.32986700
H	1.11695700	-0.30820400	2.46762500
B	-1.05664500	1.49147600	-0.28680500
H	1.11674800	2.25181000	1.05563200
B	-1.05650400	0.18815400	-1.50713300
H	1.11686600	1.69981300	-1.81511400
B	-1.05640300	-1.37521100	-0.64473000
H	1.11713600	-1.20102300	-2.17749100
H	1.11707600	-2.44203900	0.46961200
B	-1.98693800	-0.00014800	-0.00001500
H	-1.56057900	-1.77258000	1.89274200
H	-1.56116700	1.25216100	2.27060800
H	-1.56099800	2.54634300	-0.48973100
H	-1.56091700	0.32146700	-2.57298100
H	-1.56058900	-2.34794700	-1.10068000
H	-3.17420800	-0.00025600	-0.00004000
C	1.21675800	0.00007400	0.00005500
F	2.59673600	0.00014100	0.00000600

1-F-CCA_dianion_radical
Sum of electronic and thermal Free
Energies= -418.313800 A.U.

B	0.44175900	-1.04873600	1.08905400
B	0.44168500	0.71178900	1.33394500
B	0.44162300	1.48871400	-0.26473000
B	0.44193400	0.20817300	-1.49746300
B	0.44169600	-1.36005400	-0.66086200
B	-1.05495100	-1.49137900	0.26511500
B	-1.05482800	-0.20858300	1.50027400
H	1.11255000	-1.73058000	1.79775400
B	-1.05506400	1.36251100	0.66197600
H	1.11232300	1.17439500	2.20190900
B	-1.05496800	1.05051200	-1.09132100
H	1.11250800	2.45677100	-0.43681800
B	-1.05479000	-0.71305800	-1.33652400
H	1.11331000	0.34364500	-2.47110000
H	1.11294200	-2.24421900	-1.09034600
B	-1.98411000	-0.00006600	0.00004700
H	-1.56080100	-2.55559300	0.45484400
H	-1.56113600	-0.35819000	2.57057500
H	-1.56097100	2.33475600	1.13444900
H	-1.56109000	1.80032500	-1.86975000
H	-1.56043600	-1.22188300	-2.29039100
H	-3.17647900	0.00005500	0.00014700
C	1.20458500	0.00003900	0.00006000
F	2.60442700	0.00013000	0.00009000

1-F-CCA_neutral_radical
Sum of electronic and thermal Free
Energies= -418.054905 A.U.

B	-0.40557200	-0.00107600	1.49507300
B	-0.46427900	-1.46385700	0.46779100
B	-0.46177500	-0.91158200	-1.21427500
B	-0.46187800	0.91330600	-1.21307500
B	-0.46446000	1.46315700	0.46982600
B	1.04931800	0.94152300	1.19675400
B	1.04927200	-0.94323500	1.19562600
H	-0.97634300	-0.00156300	2.53025700
B	1.01984000	-1.50154600	-0.47527700
H	-1.14809000	-2.36345500	0.79522300
B	0.99368900	0.00108900	-1.50995500
H	-1.10786400	-1.44474100	-2.04355100
B	1.01961600	1.50241700	-0.47320300
H	-1.10821100	1.44753400	-2.04146200
H	-1.14828700	2.36222700	0.79866200
B	2.03952600	-0.00014000	0.00629400
H	1.67713800	1.50691100	2.02368700
H	1.67683000	-1.50966000	2.02202500
H	1.55127400	-2.48438800	-0.84946400
H	1.83049700	0.00231900	-2.35990300
H	1.55119800	2.48568900	-0.84601300
C	-1.22132500	-0.00001500	0.00740100
F	-2.58333400	-0.00012400	0.02525000
H	3.21332300	0.00006100	-0.02900900

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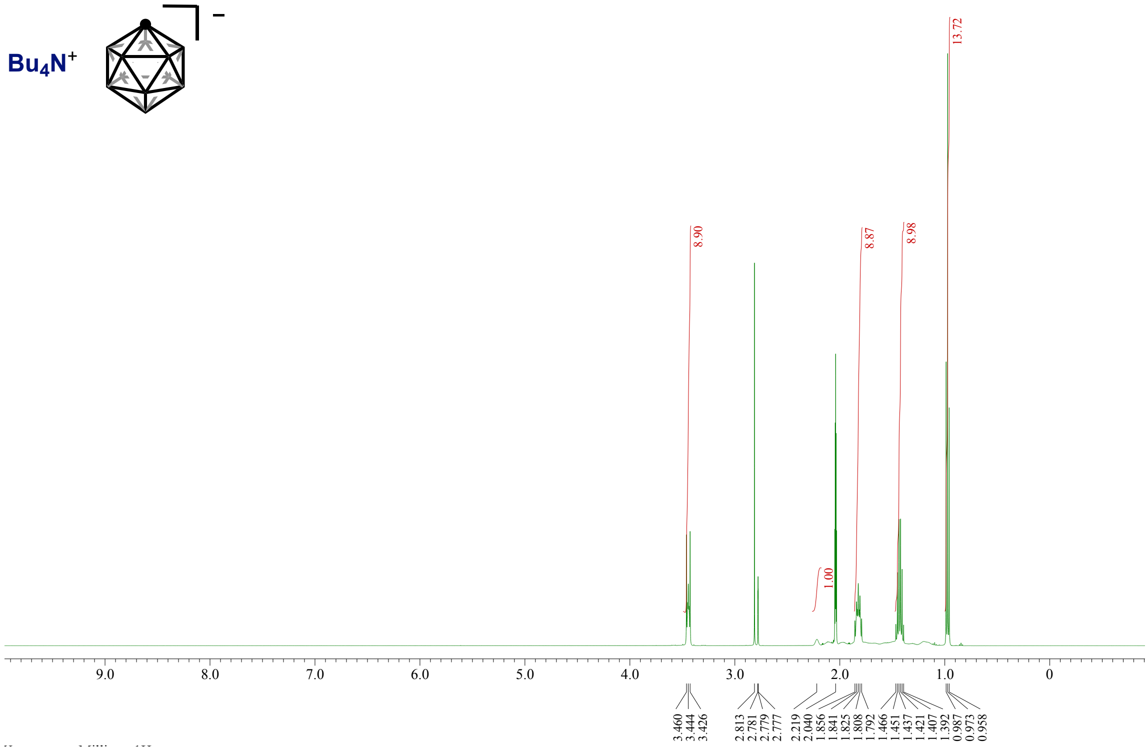
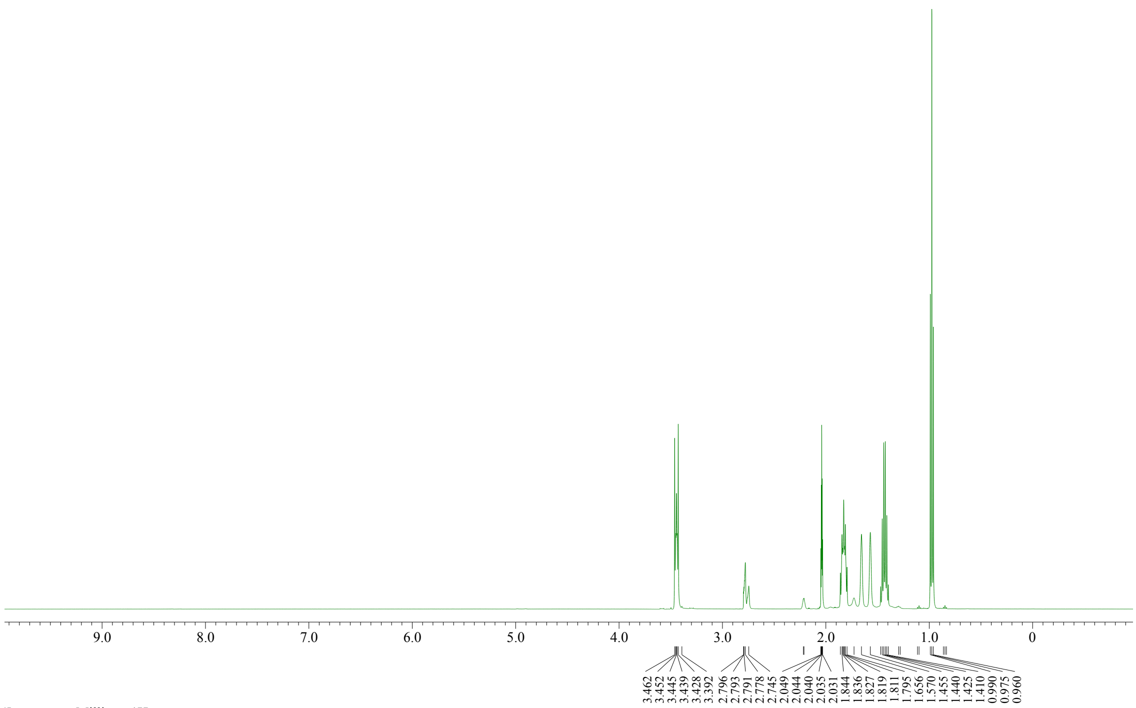
5. Copies of NMR Spectra

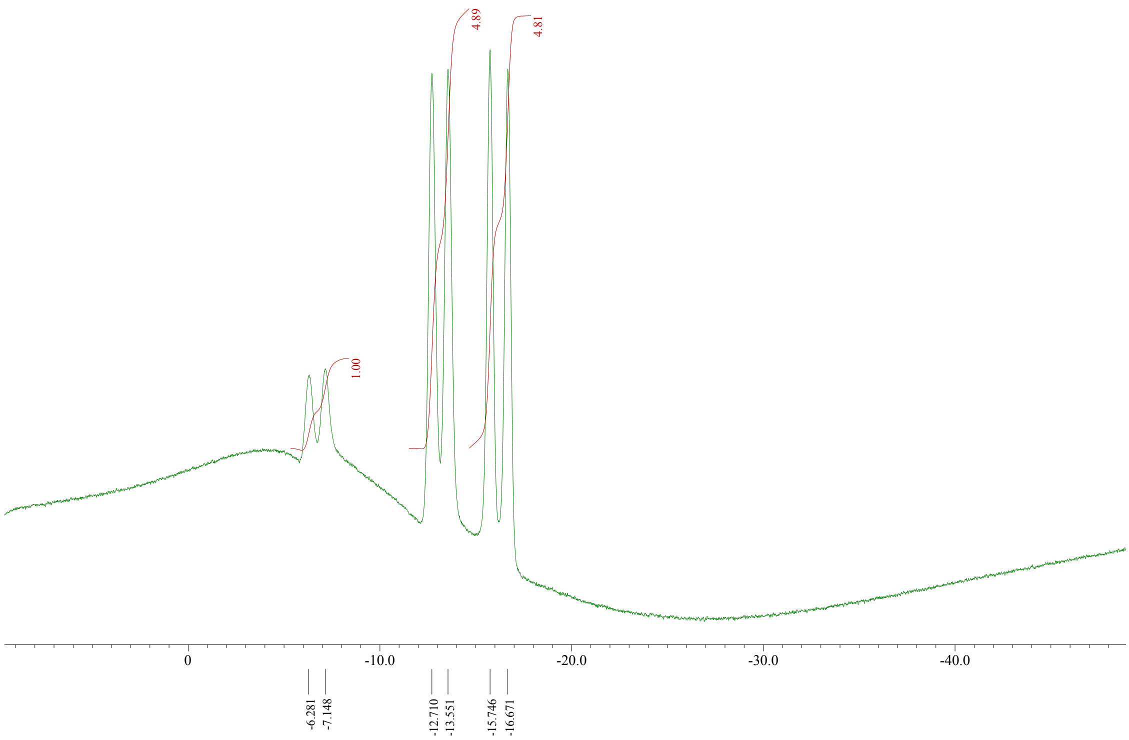
$[Bu_4N]^+[CCA]$: ^1H NMR (Acetone-d_6)



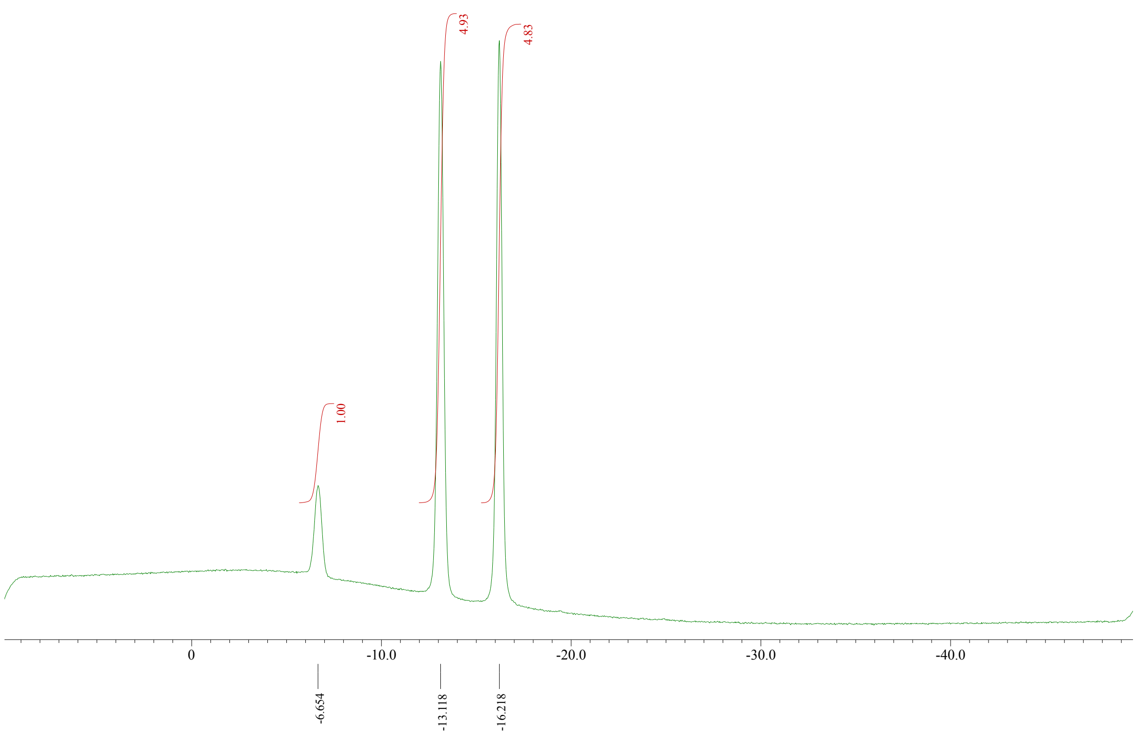
$[Bu_4N]^+[CCA]$: $^1H\{^{11}B\}$ NMR (Acetone-d_6)



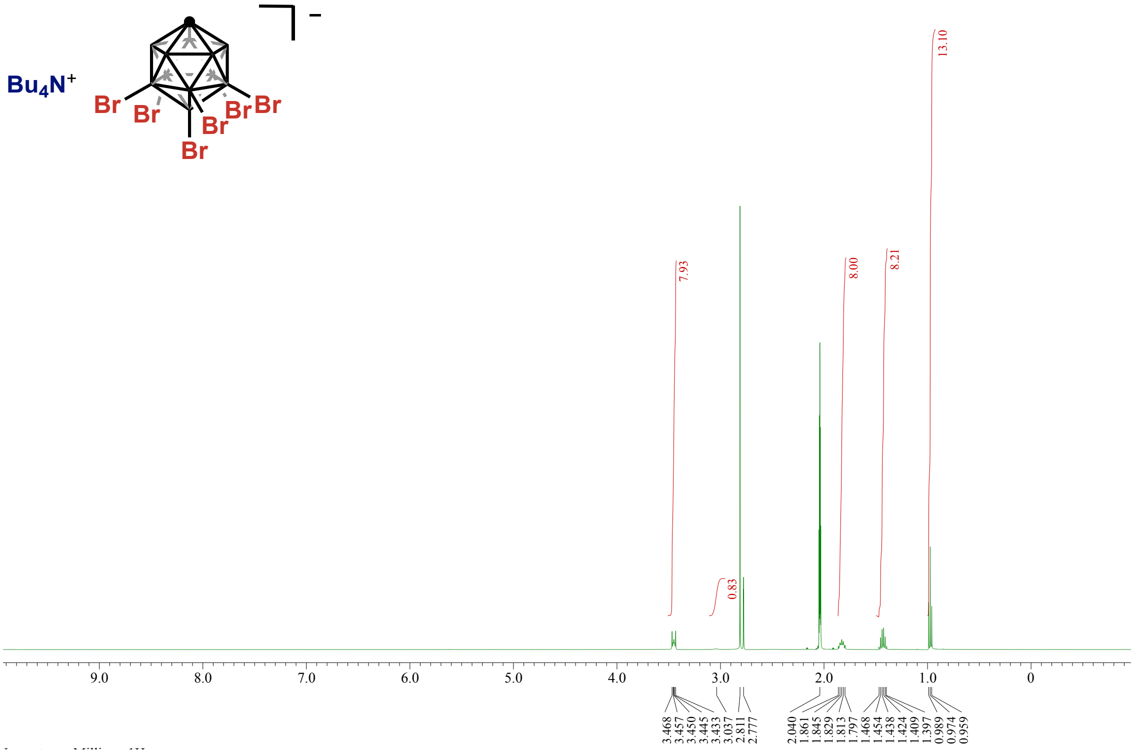
[Bu4N]+[CCA]: [11]B NMR (Acetone-d_6)



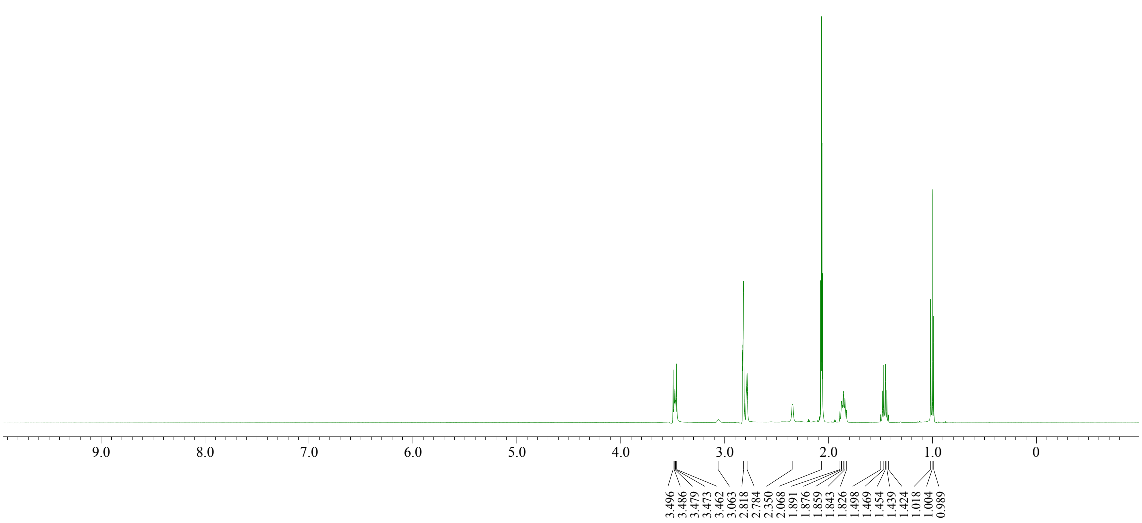
[Bu4N]+[CCA]: [11]B{[1]H} NMR (Acetone-d_6)



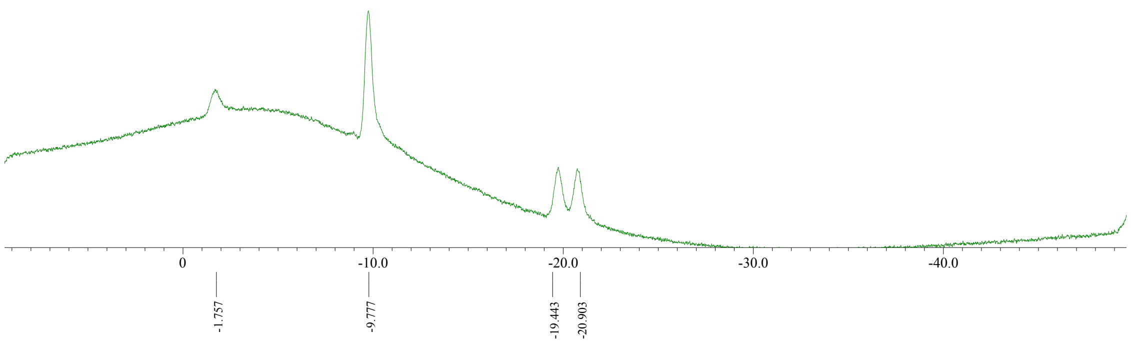
$[Bu_4N]^+[7\text{–}12\text{-}Br_6\text{-}CCA]$: ^{1}H NMR (Acetone-$d_6$)



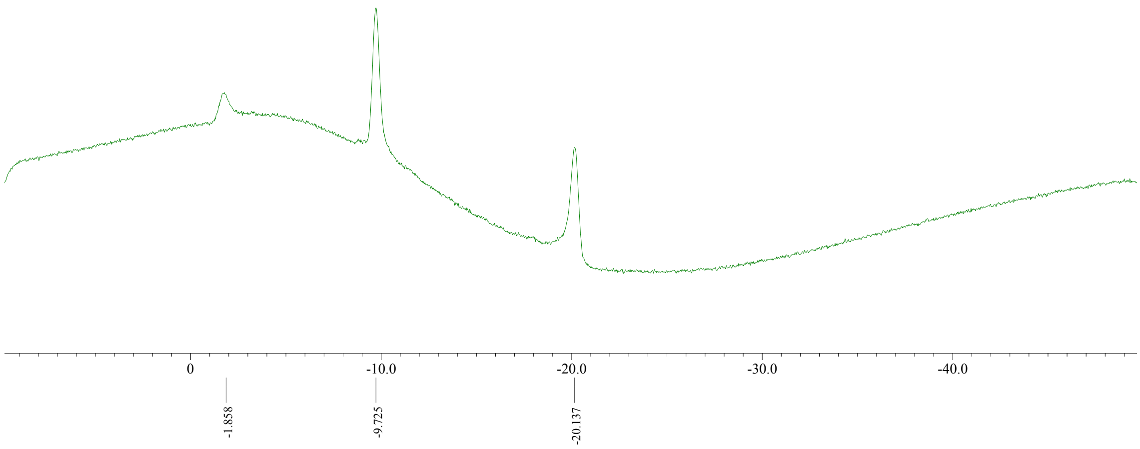
$[Bu_4N]^+[7\text{–}12\text{-}Br_6\text{-}CCA]$: ^{1}H{^{11}B} NMR (Acetone-d_6)



$[Bu_4N]^+[7–12-Br_6-CCA]$: ^{11}B NMR (Acetone-d_6)



$[Bu_4N]^+[7–12-Br_6-CCA]$: $^{11}B\{^1H\}$ NMR (Acetone-d_6)



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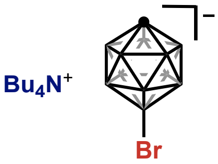

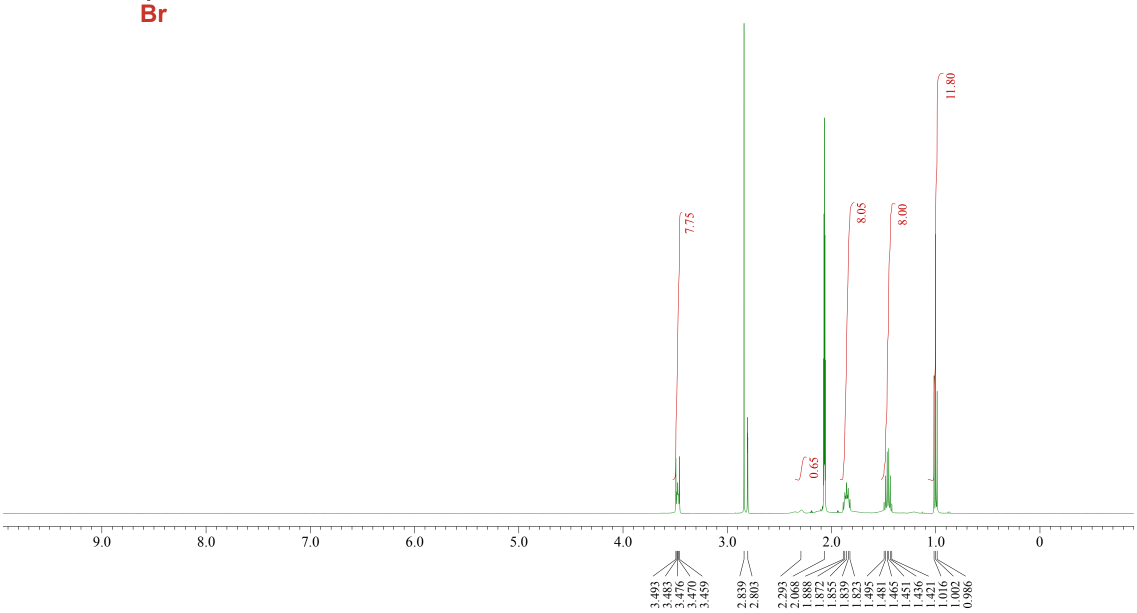

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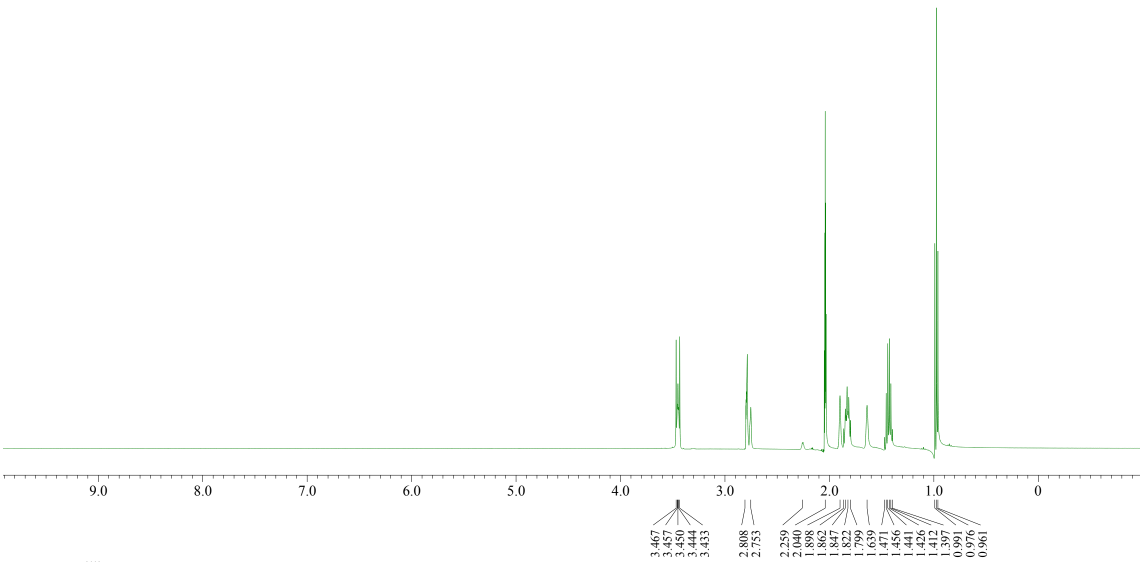
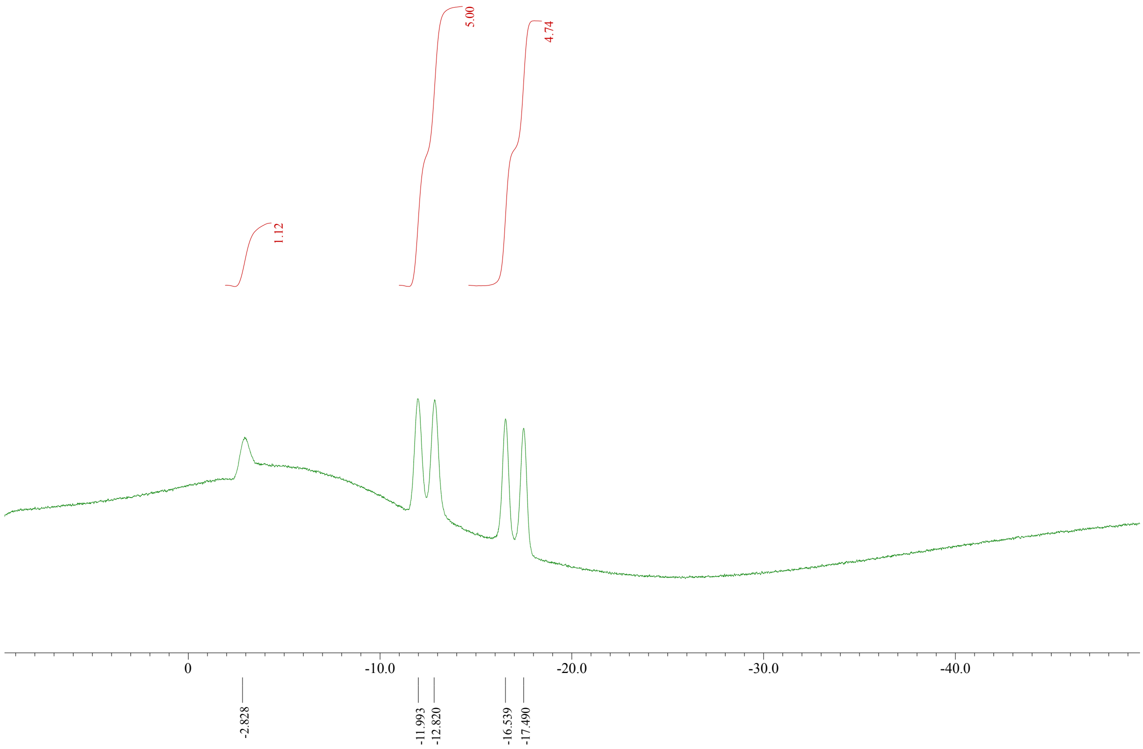


[$Bu_4N]^+[12\text{-}Br\text{-}CCA]$: ^{11}B NMR (Acetone-d_6)



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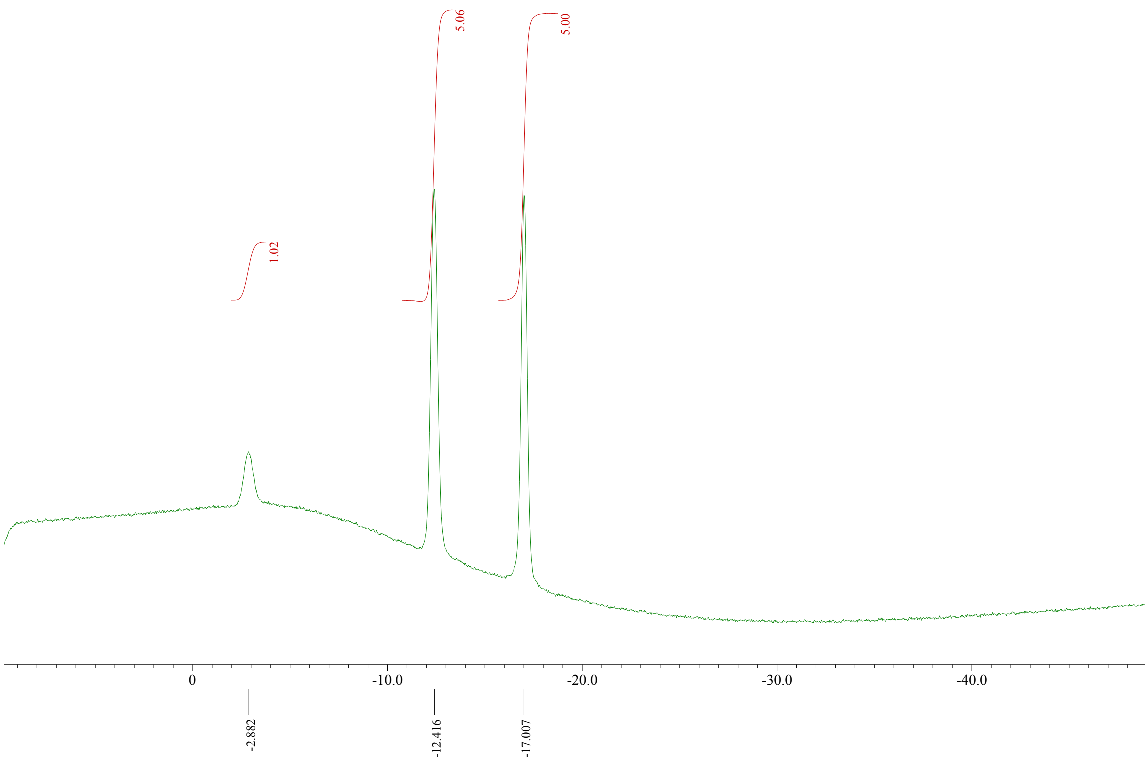

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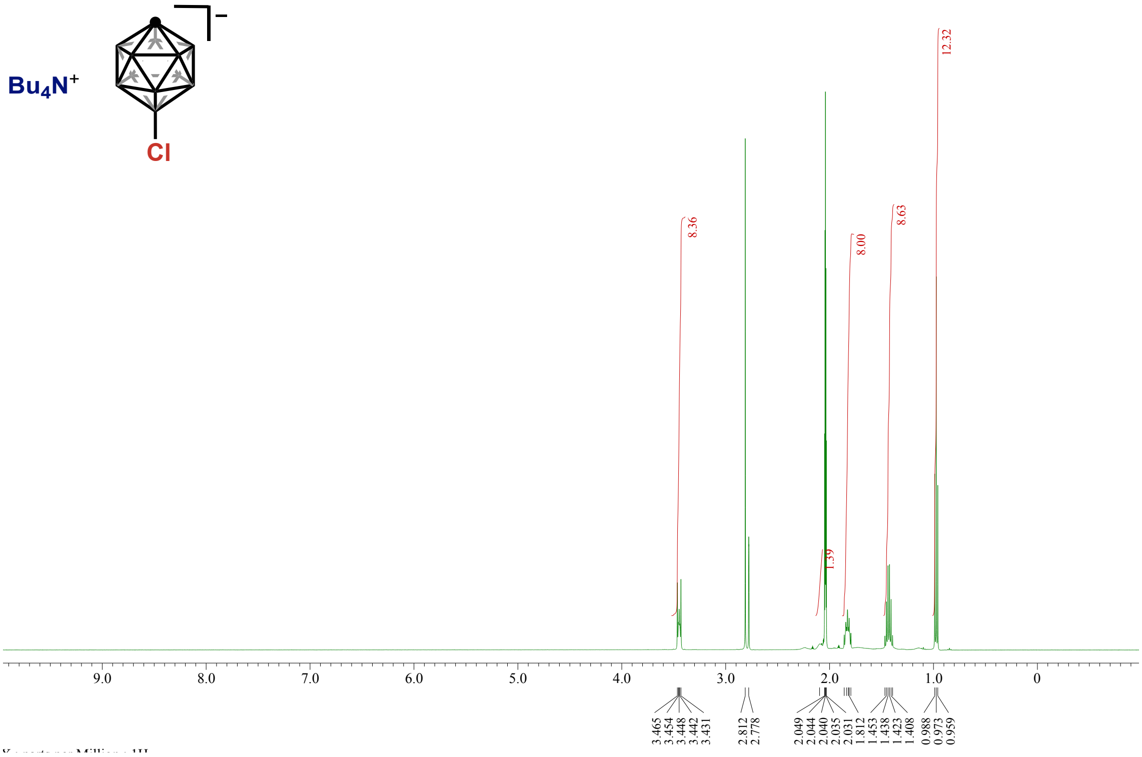

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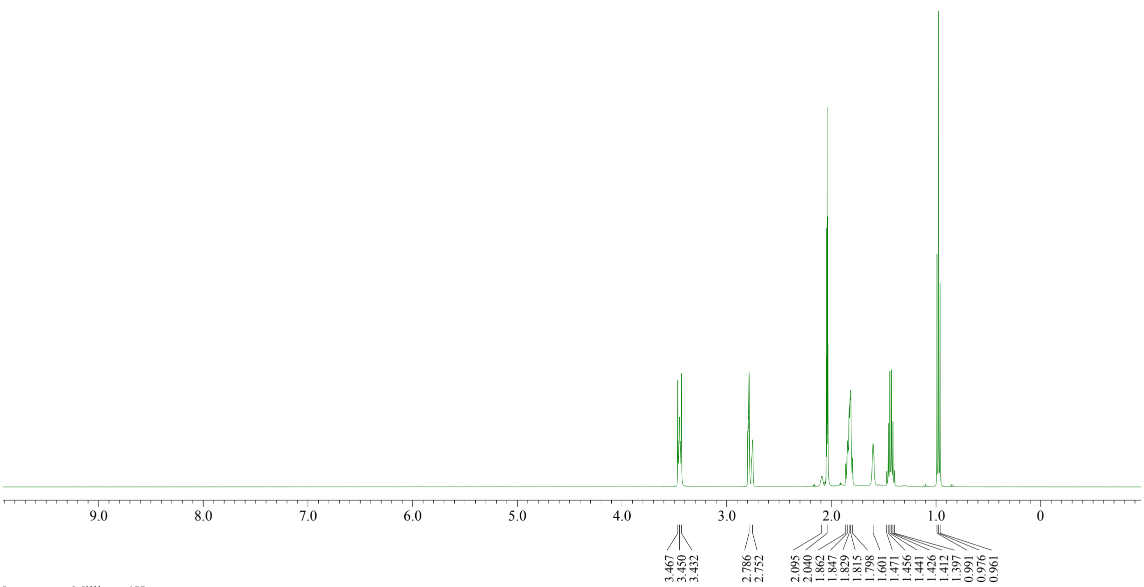

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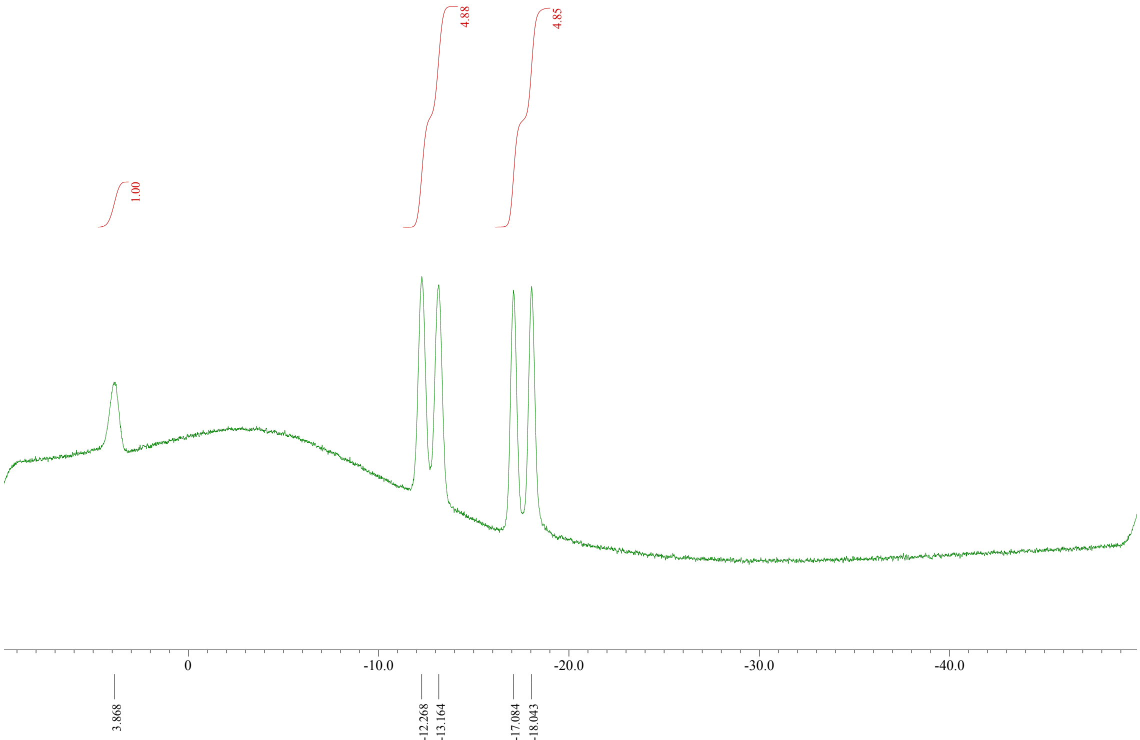

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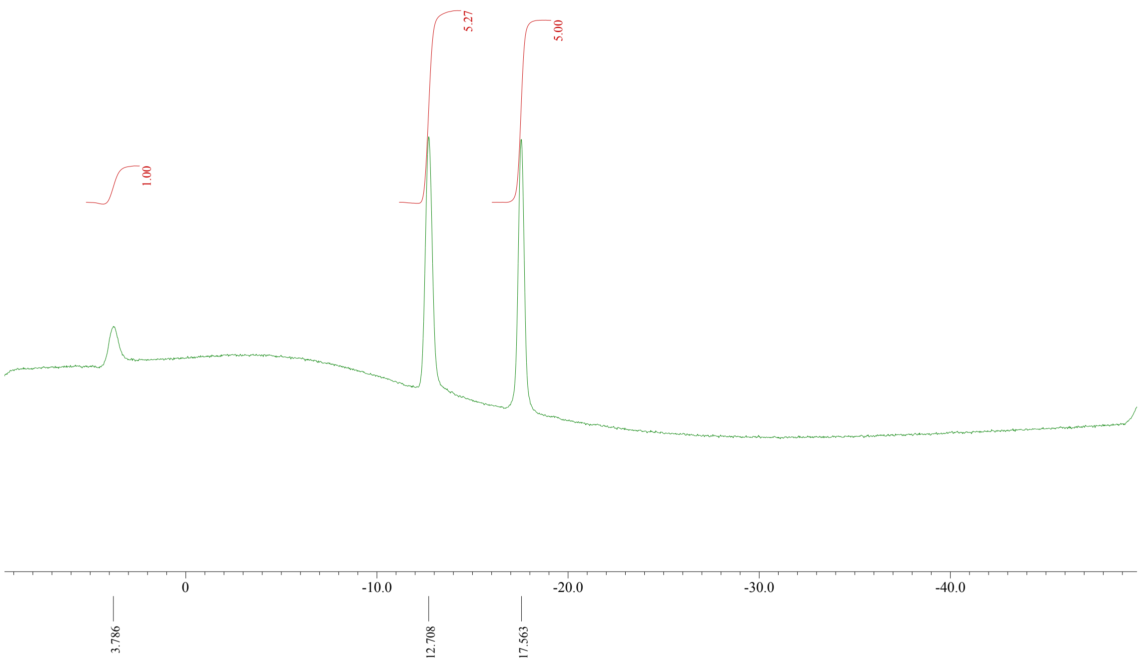
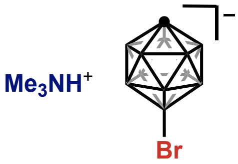
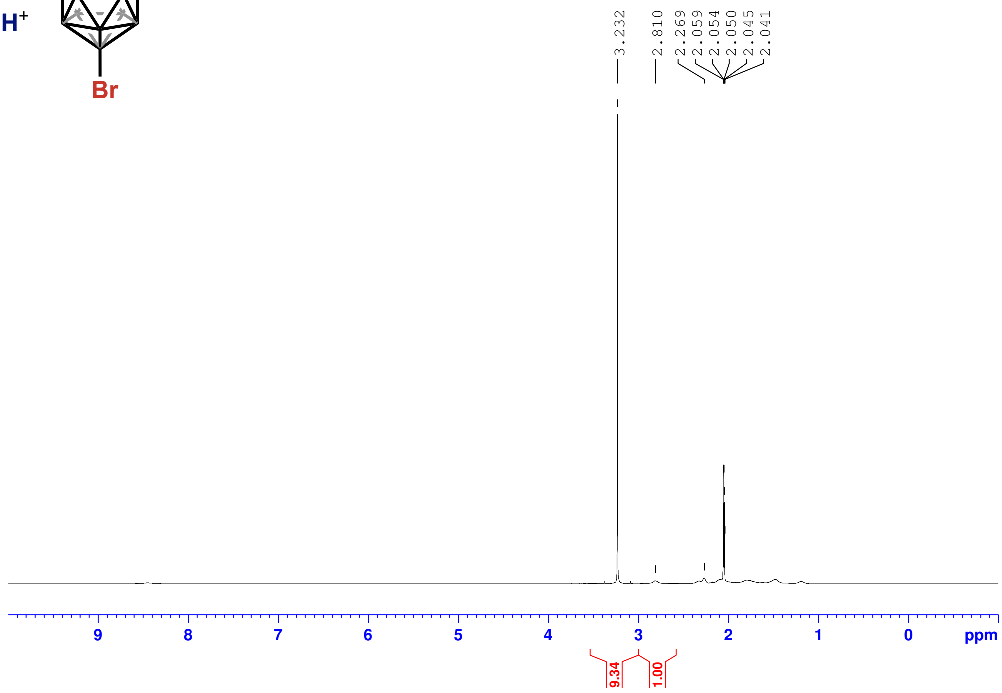


[Me3NH]+[12-Br-CCA]: ^{1}H NMR (Acetone-d_6)





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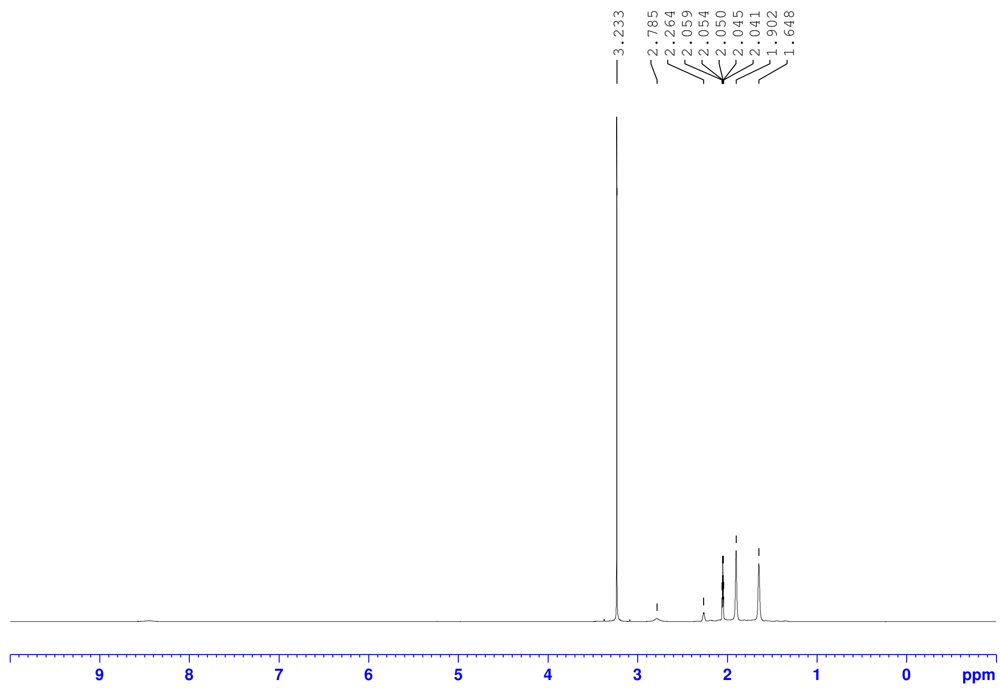

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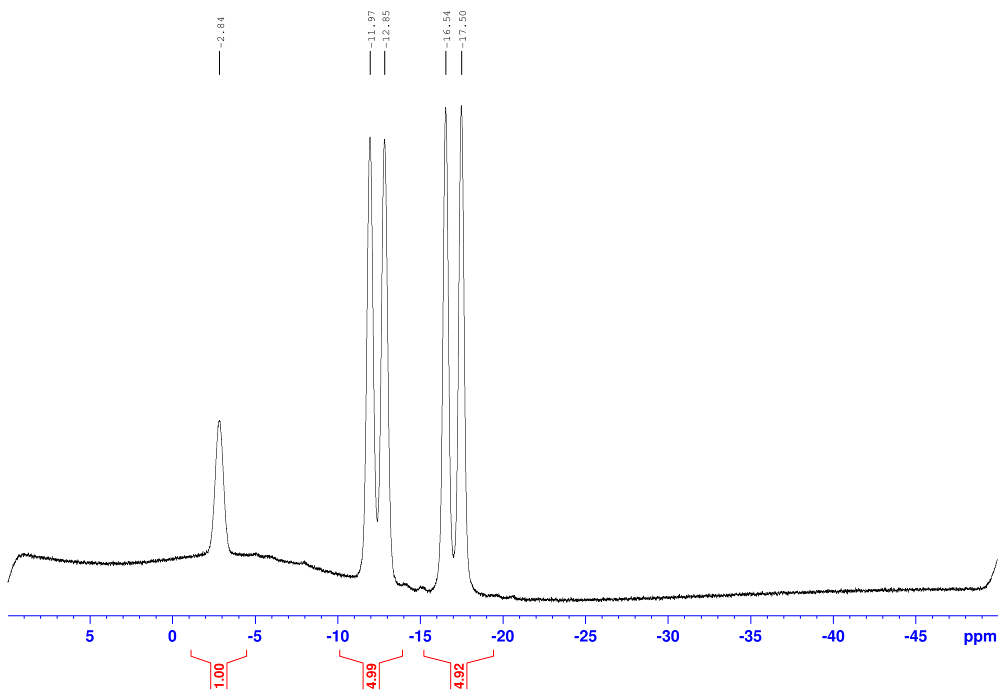

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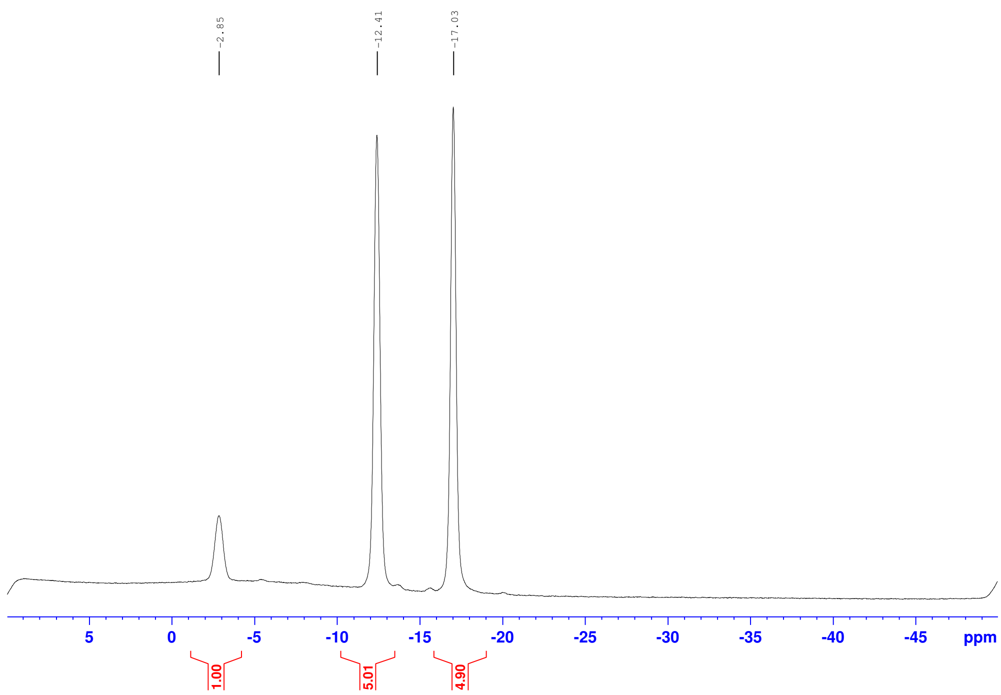

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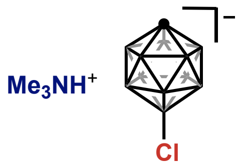

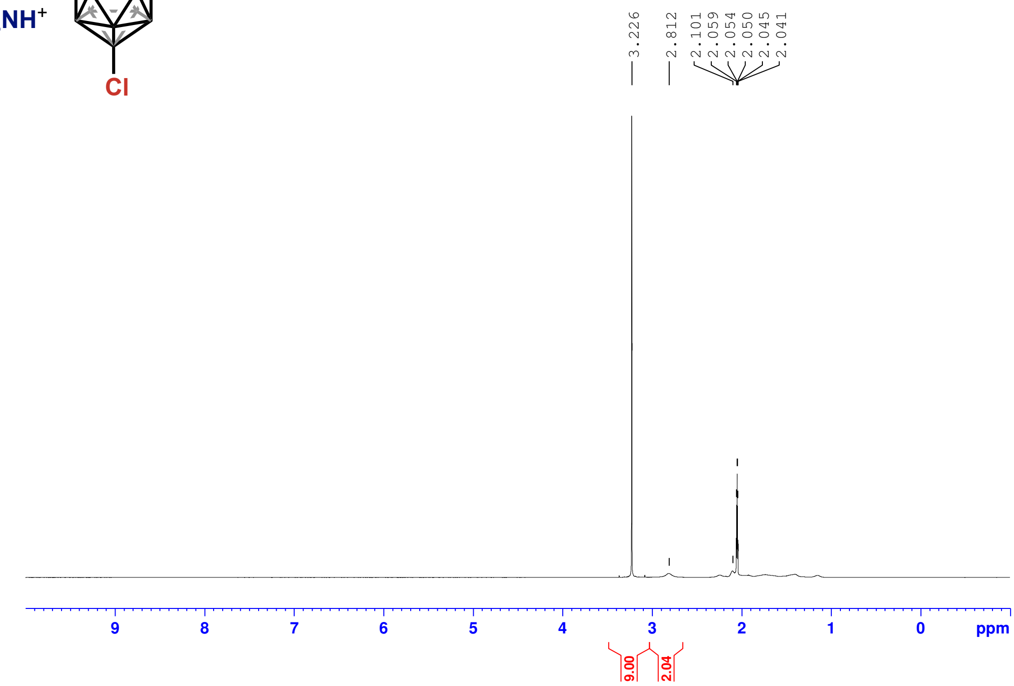

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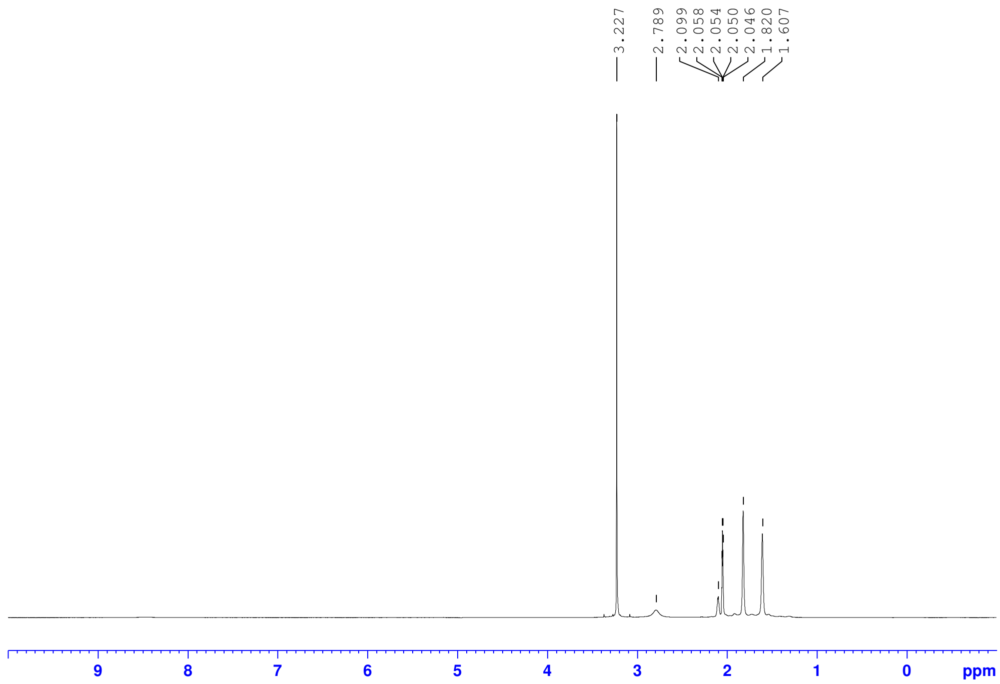

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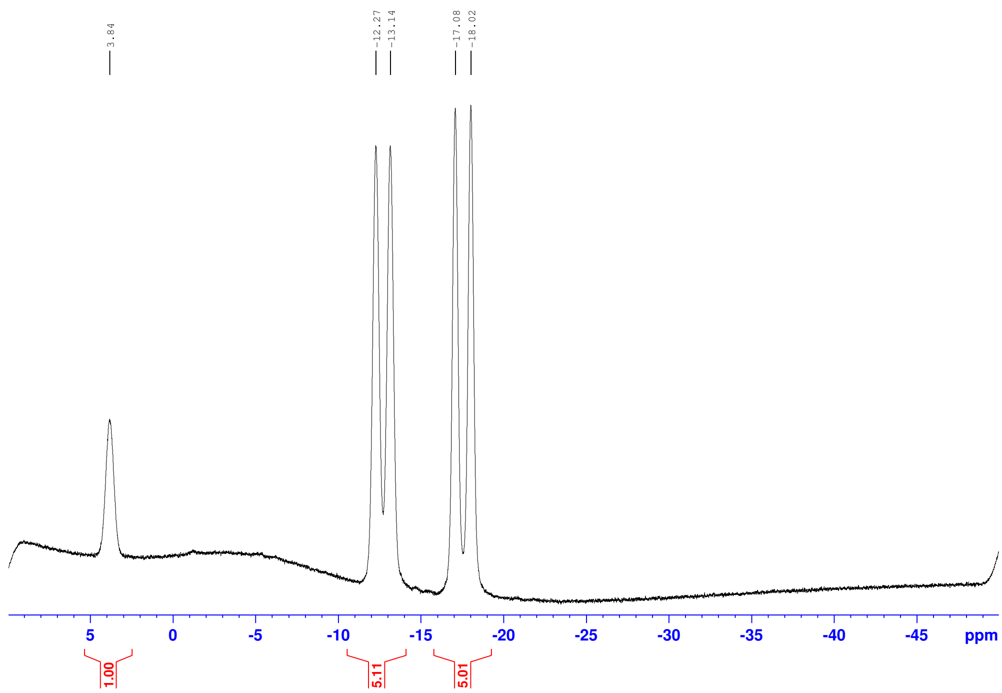

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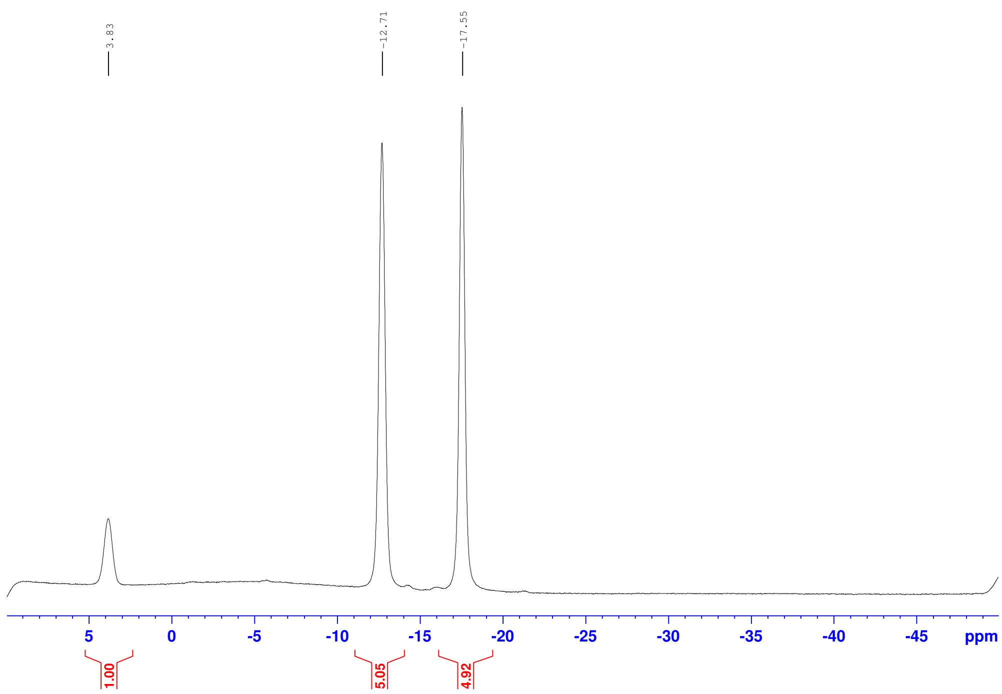
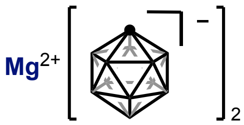
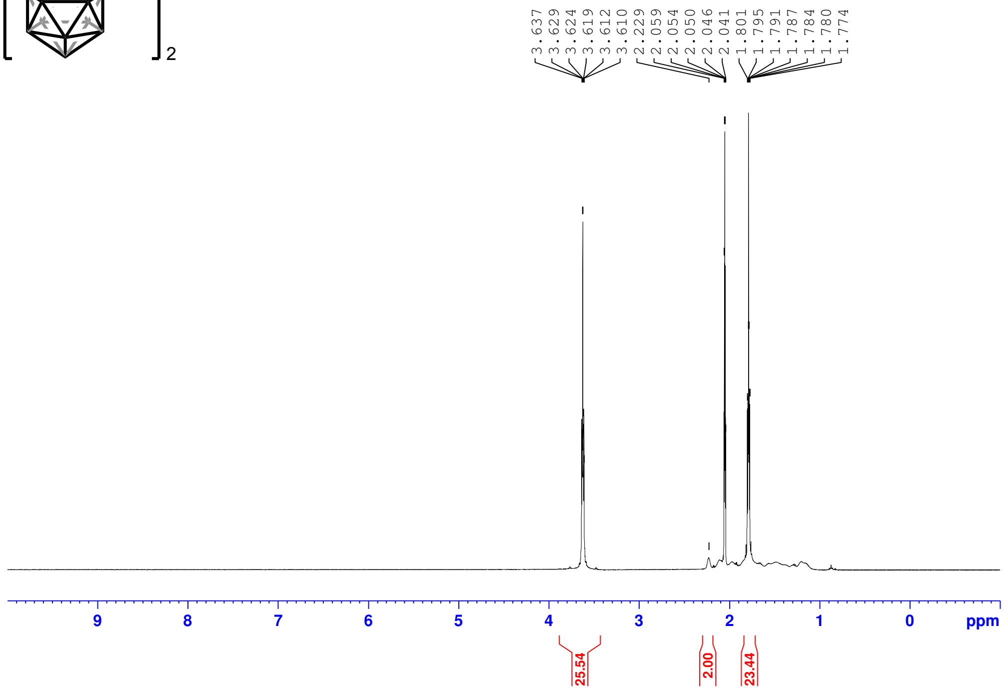
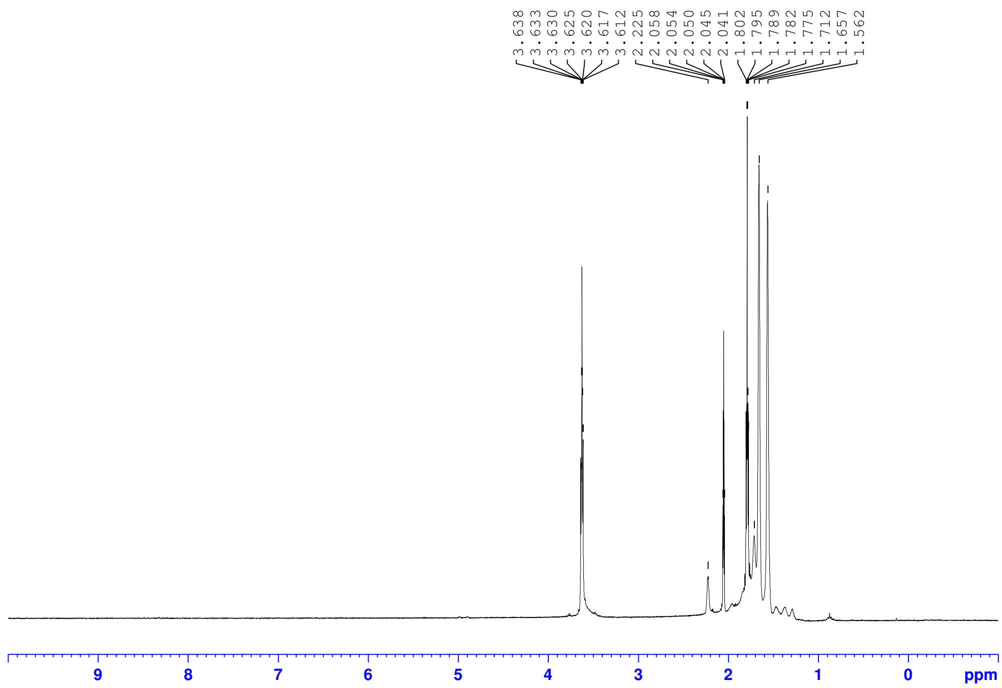


Mg^{2+}[CCA]$_2$: ^{1}H NMR (Acetone-d_6)





Mg^{2+}[CCA]$_2$: ^{1}H{^{11}B} NMR (Acetone-d_6)



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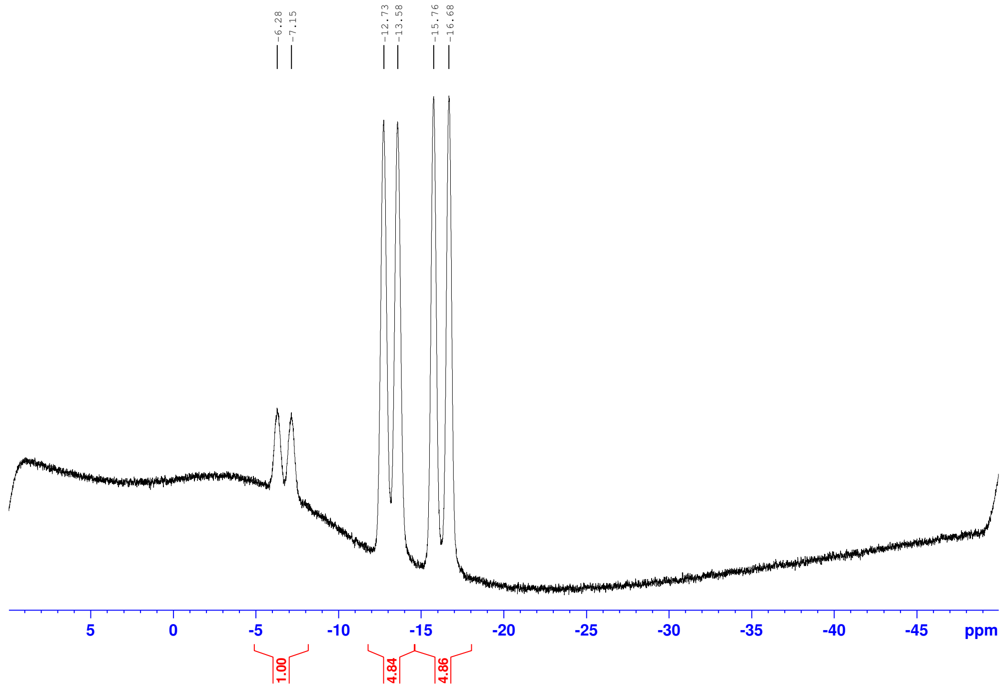

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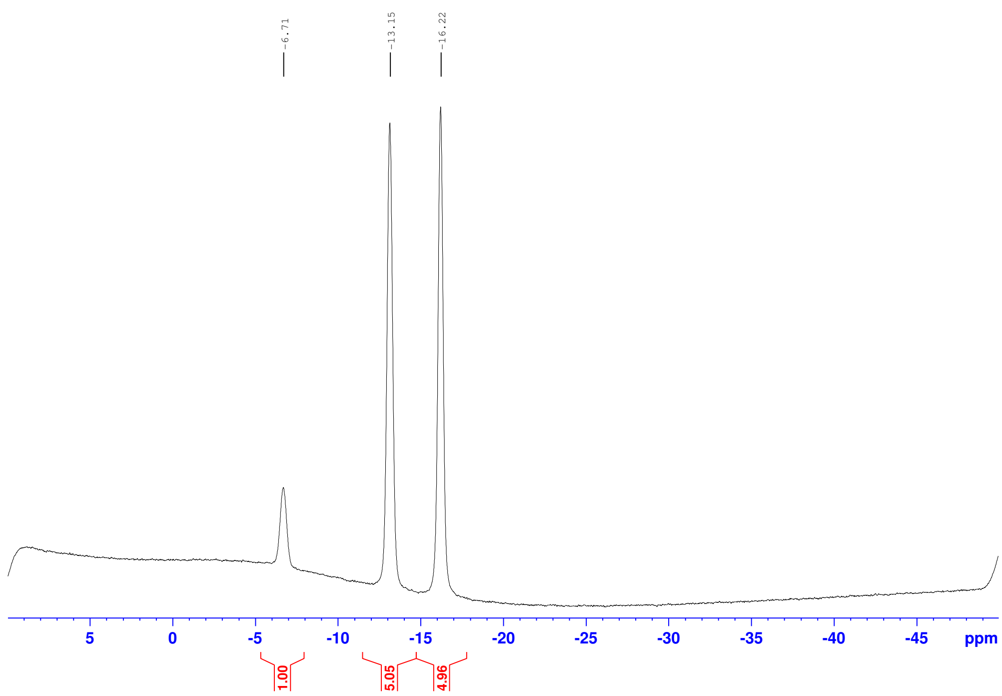

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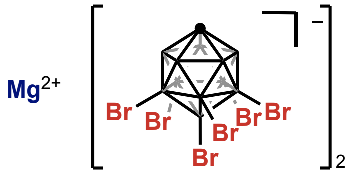

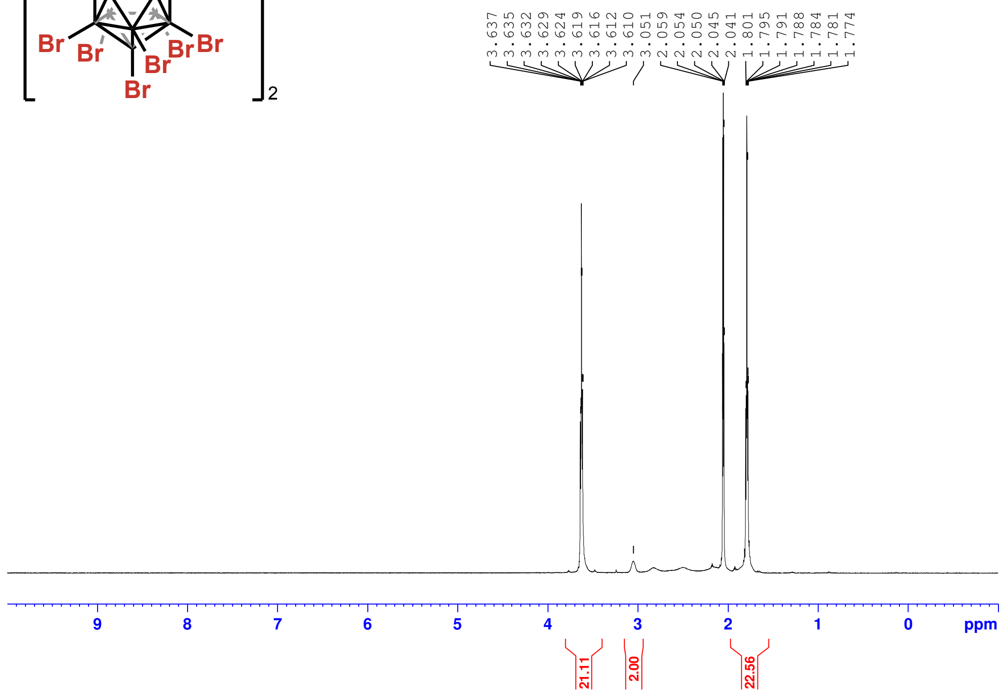

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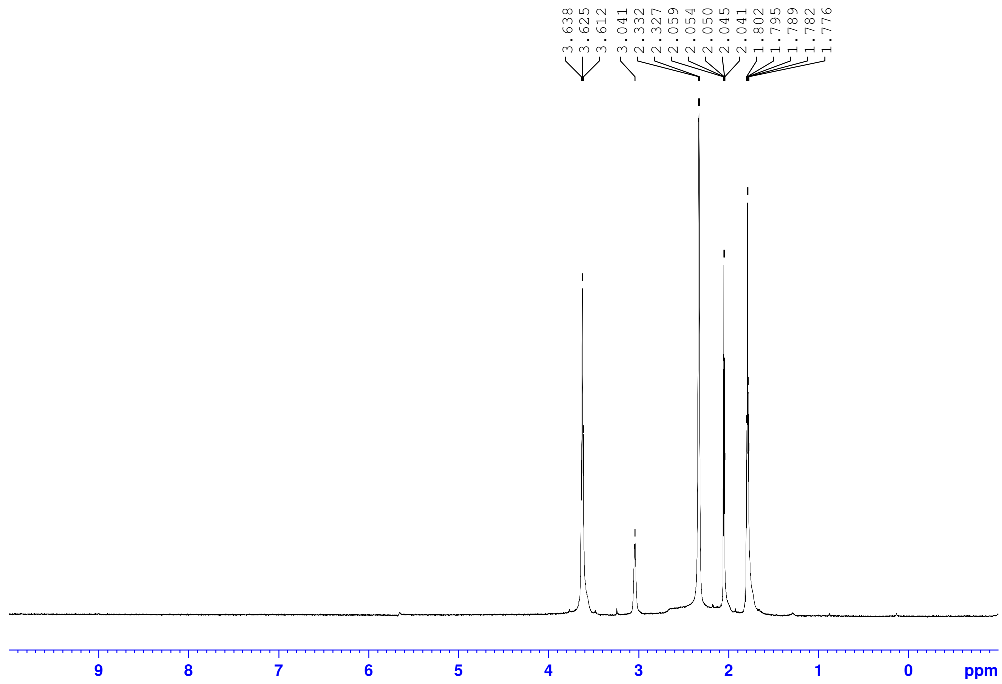

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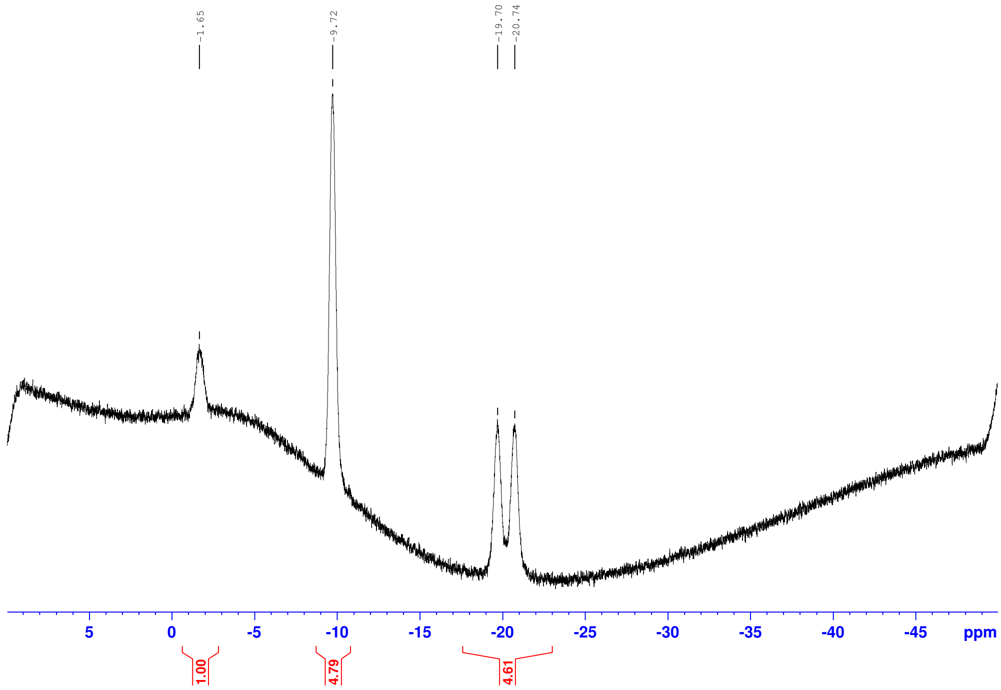

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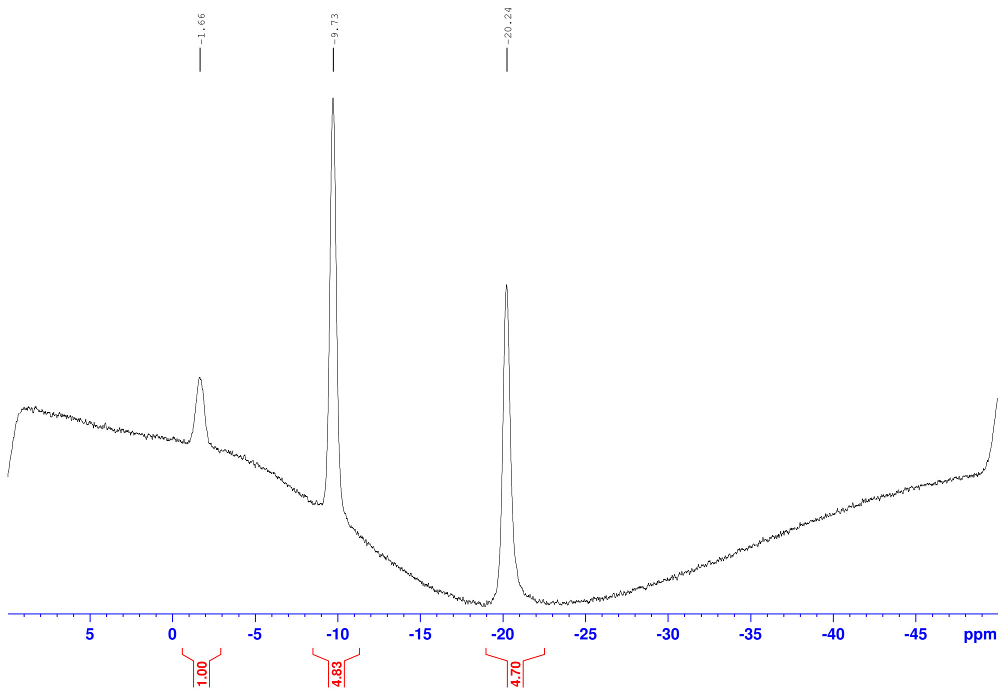

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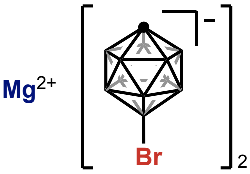

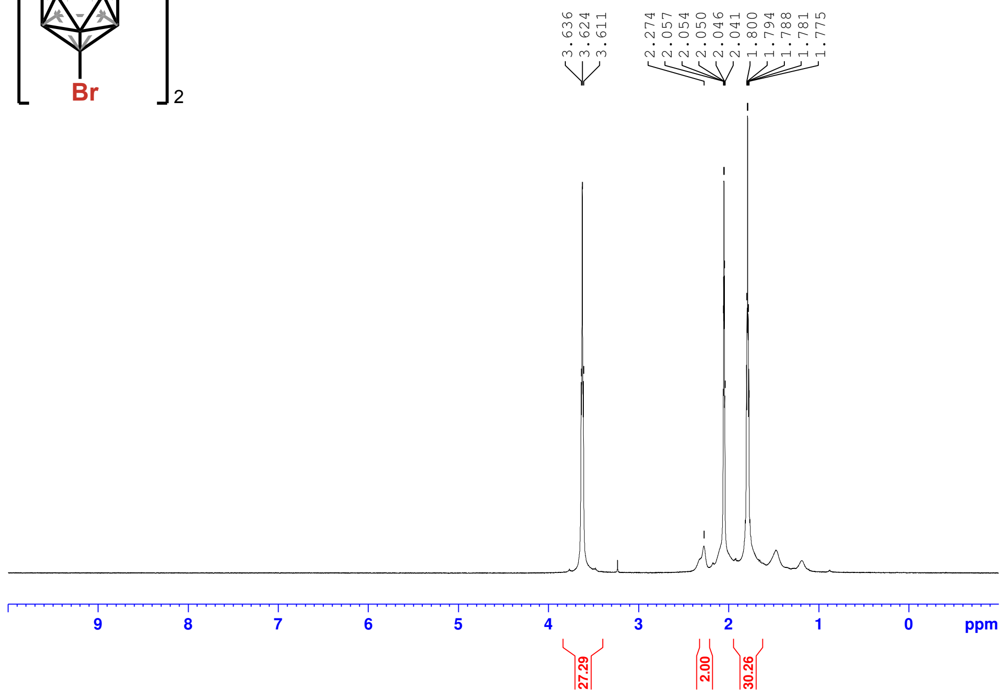

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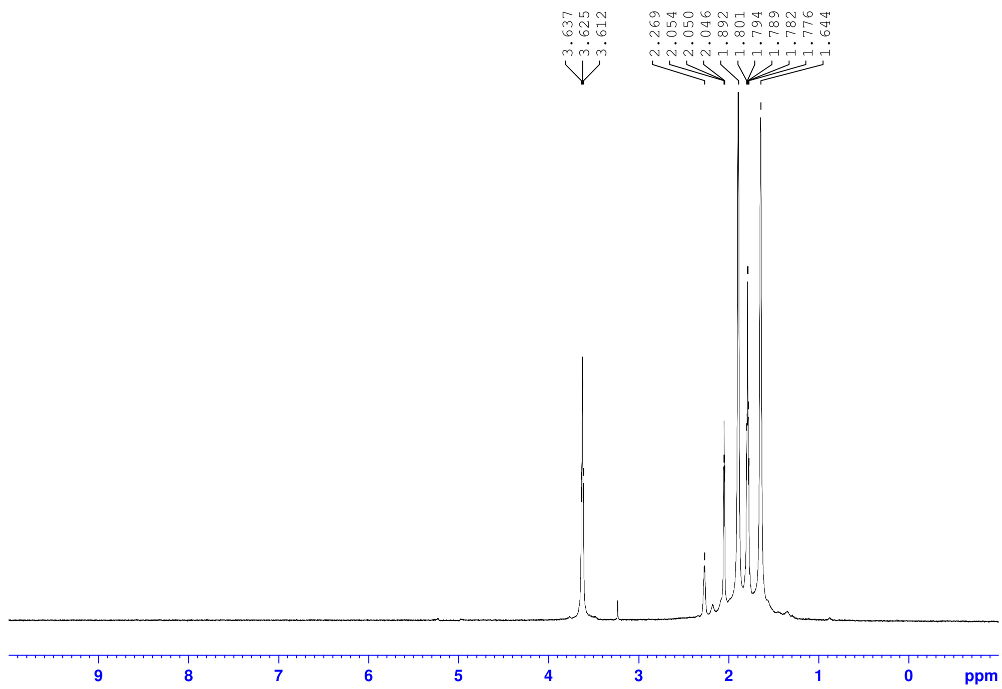

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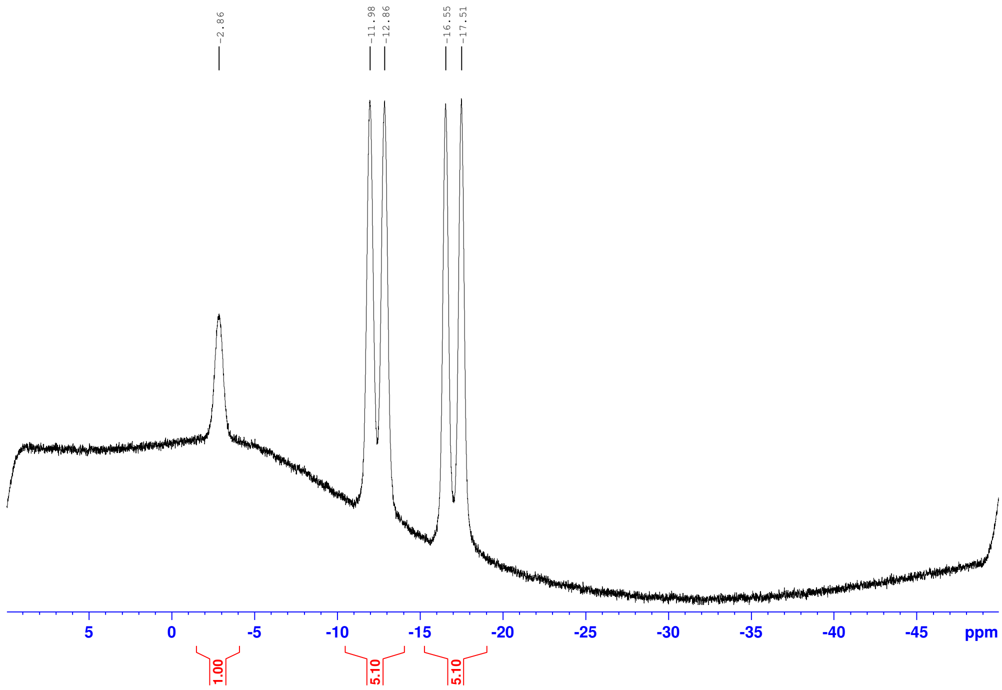

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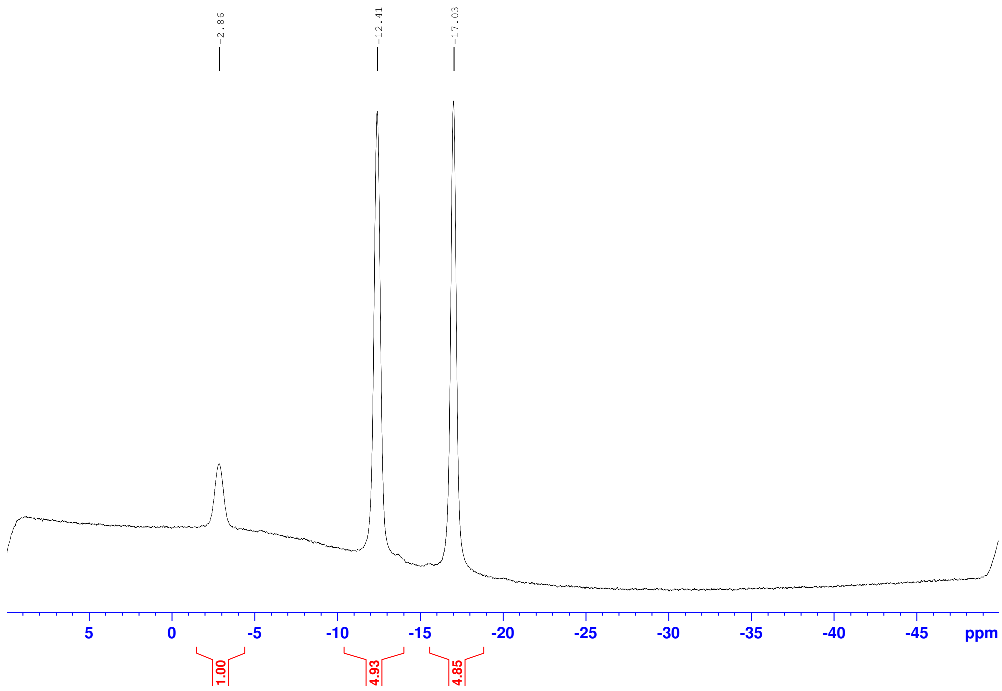

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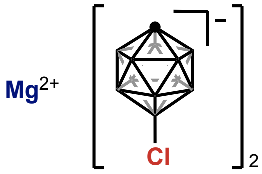

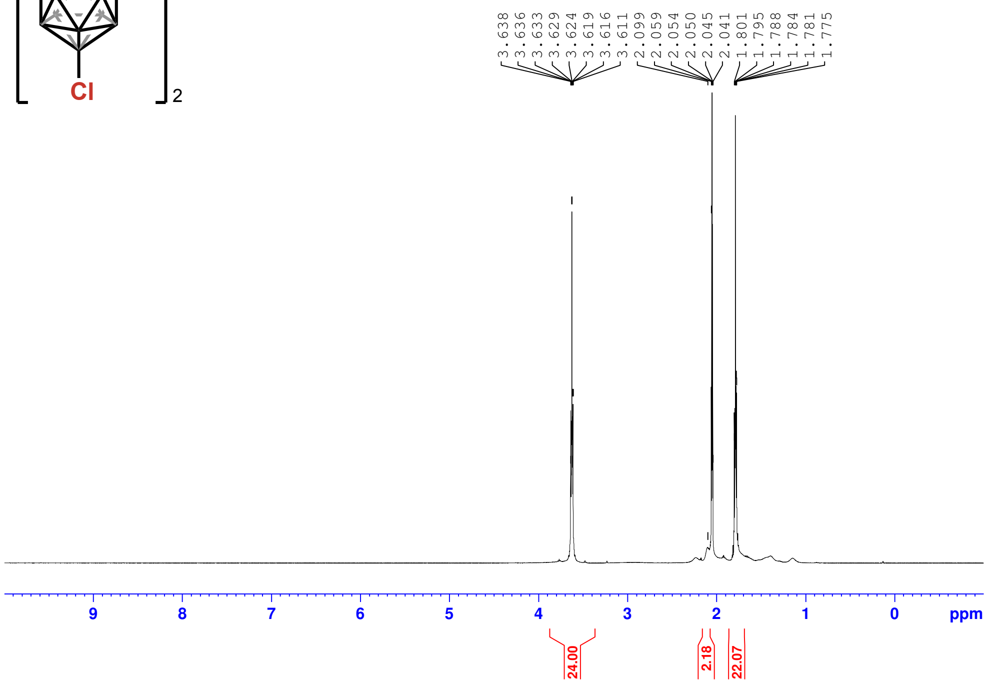

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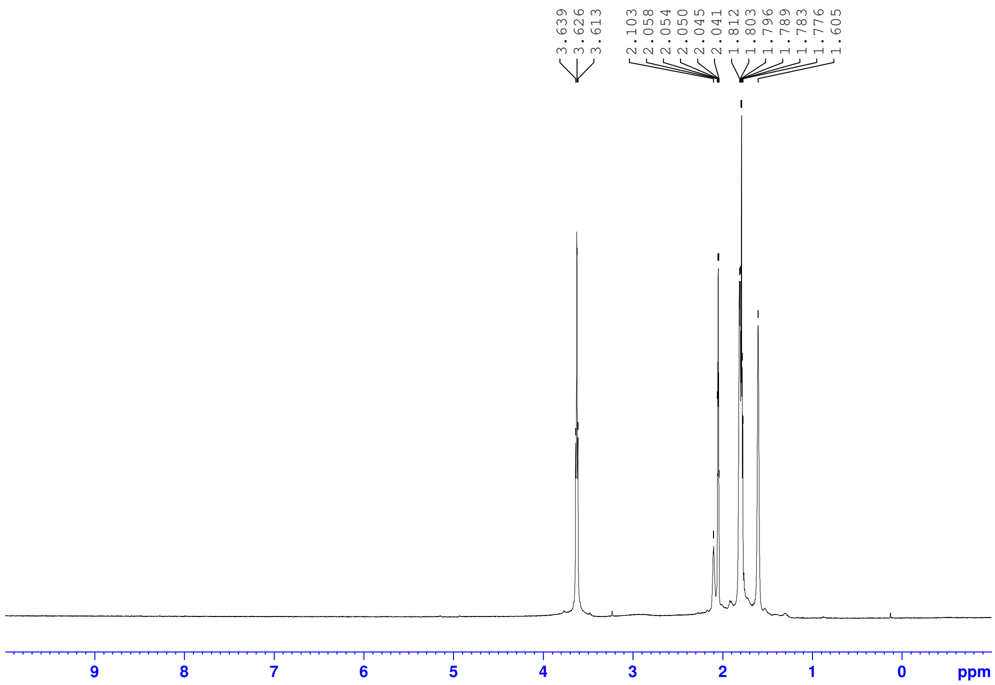

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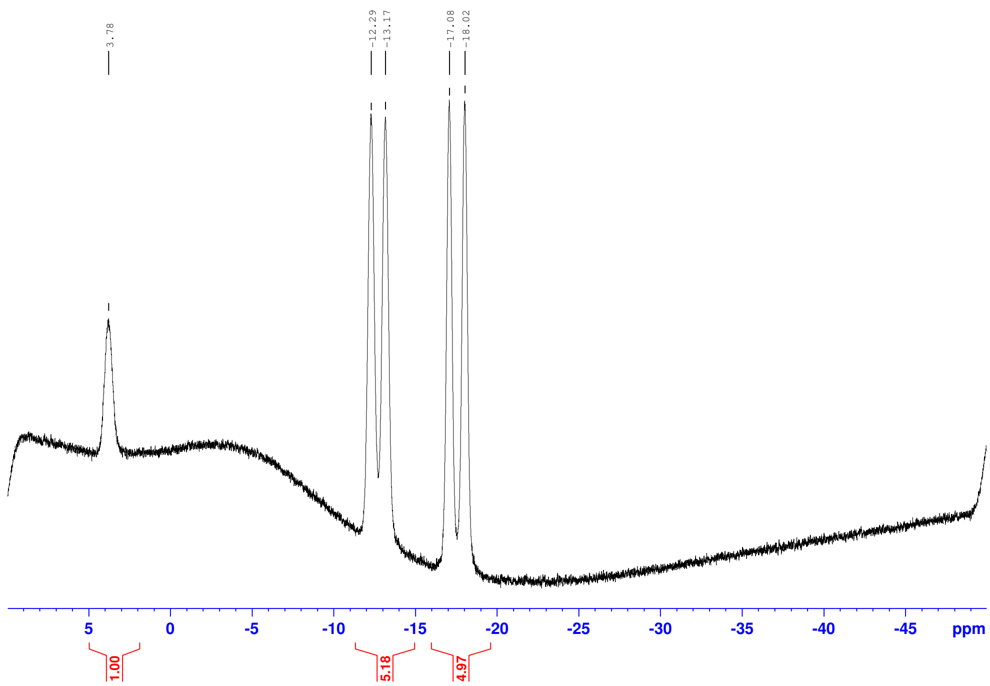

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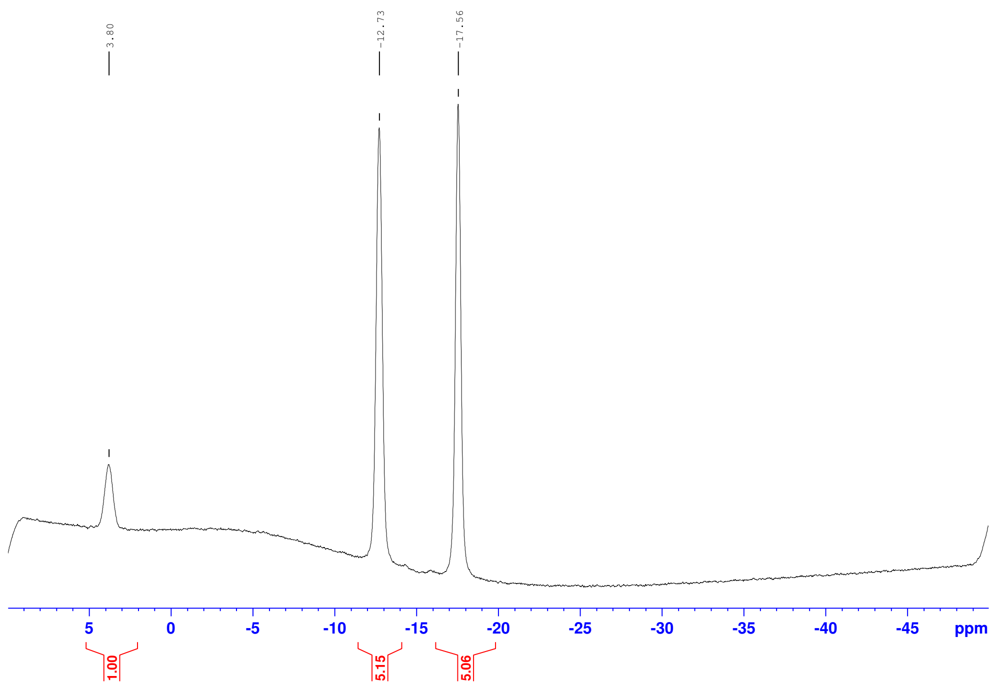

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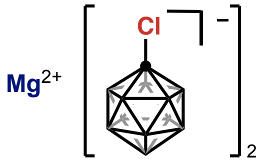

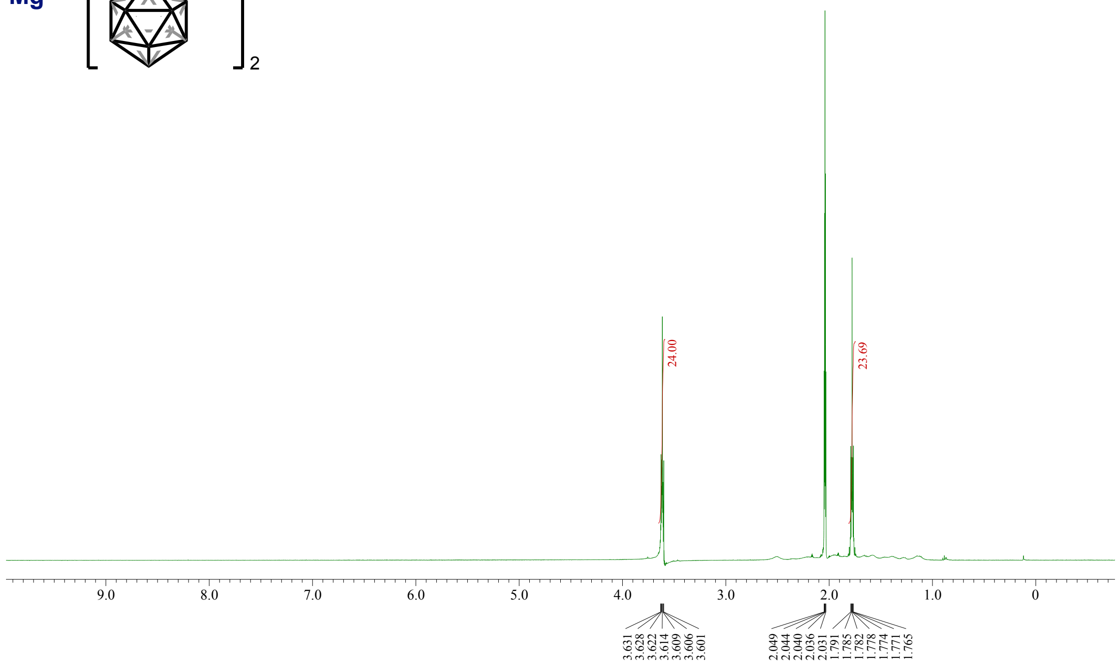

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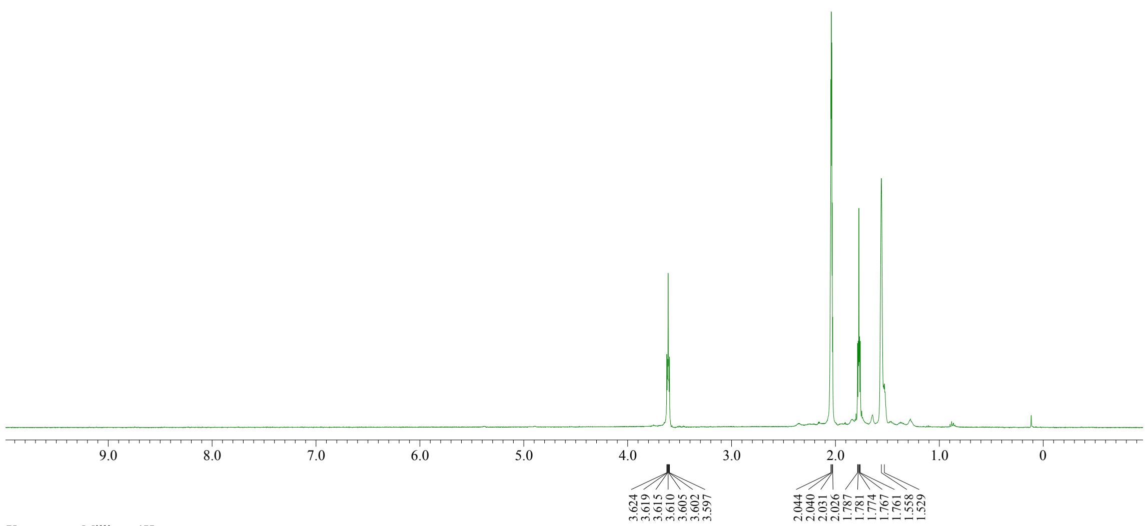

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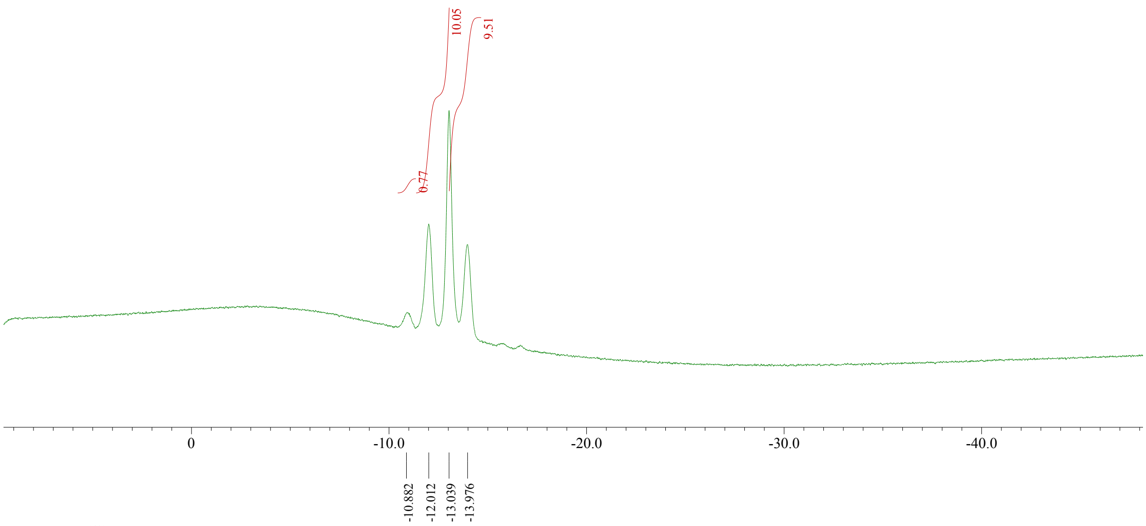

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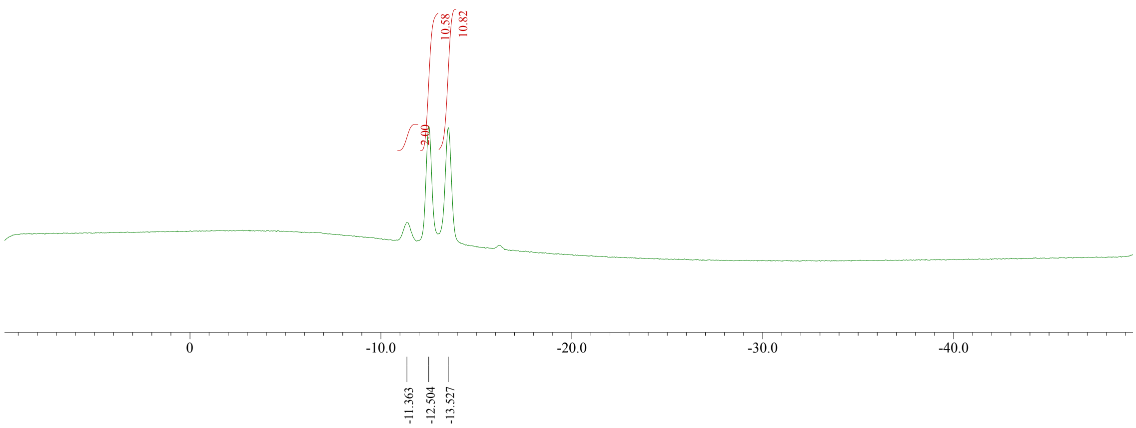

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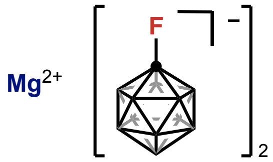
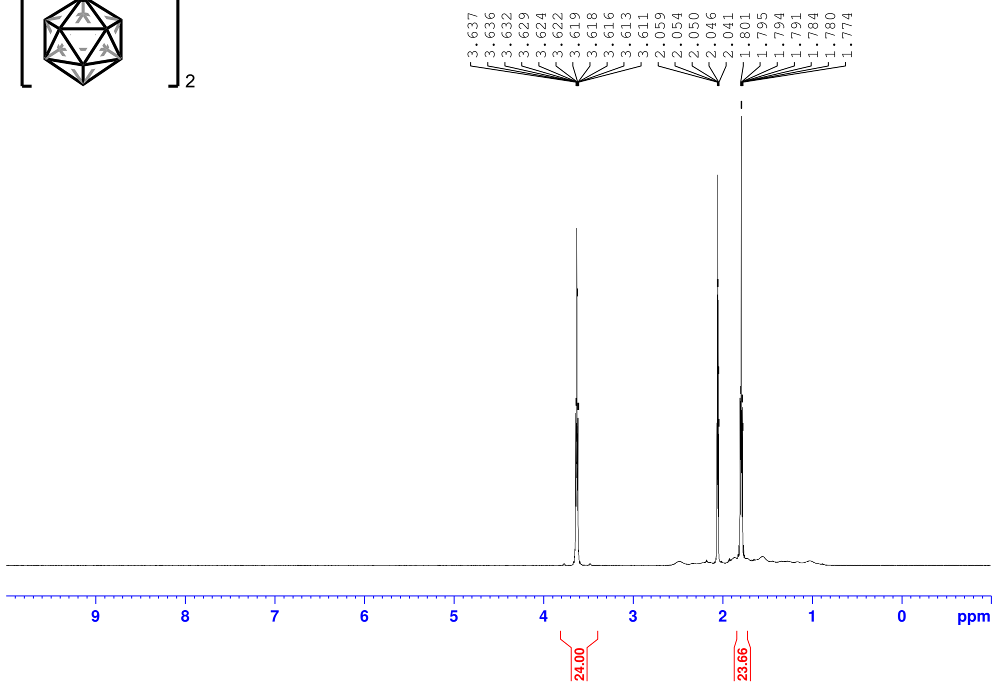
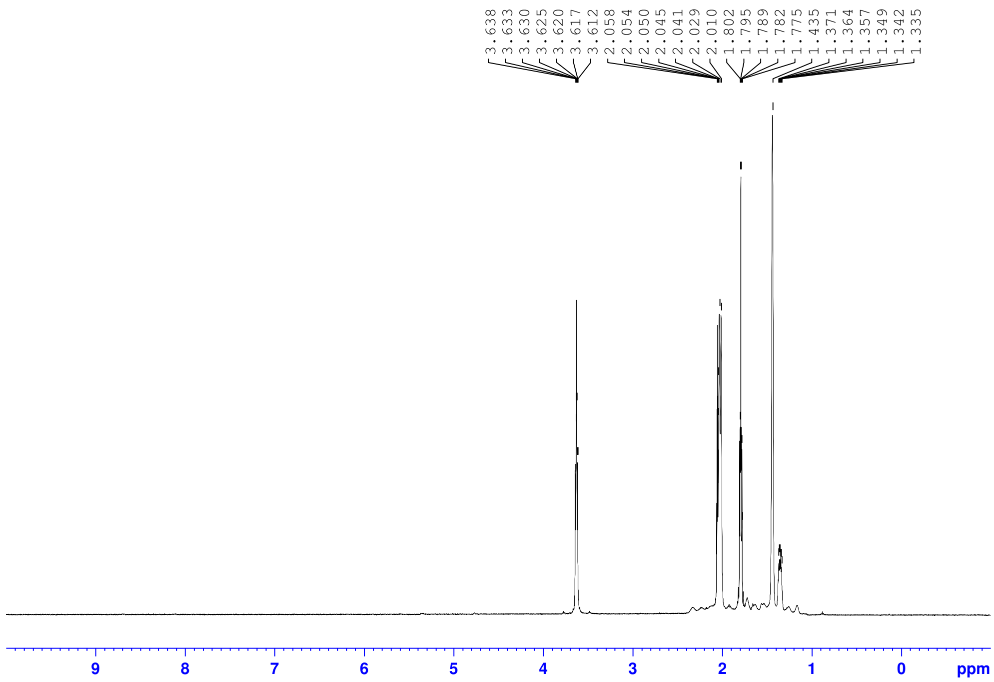
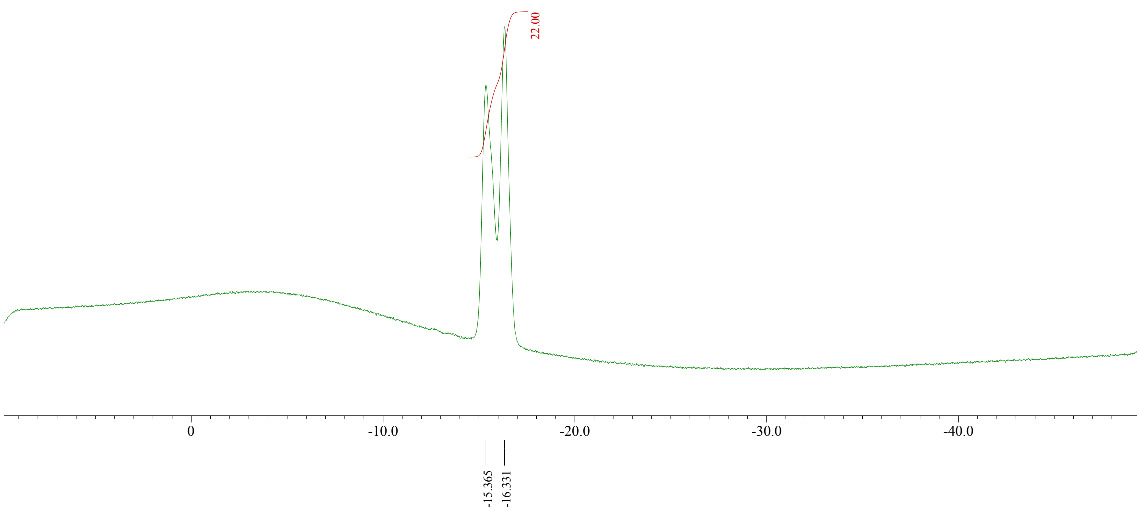




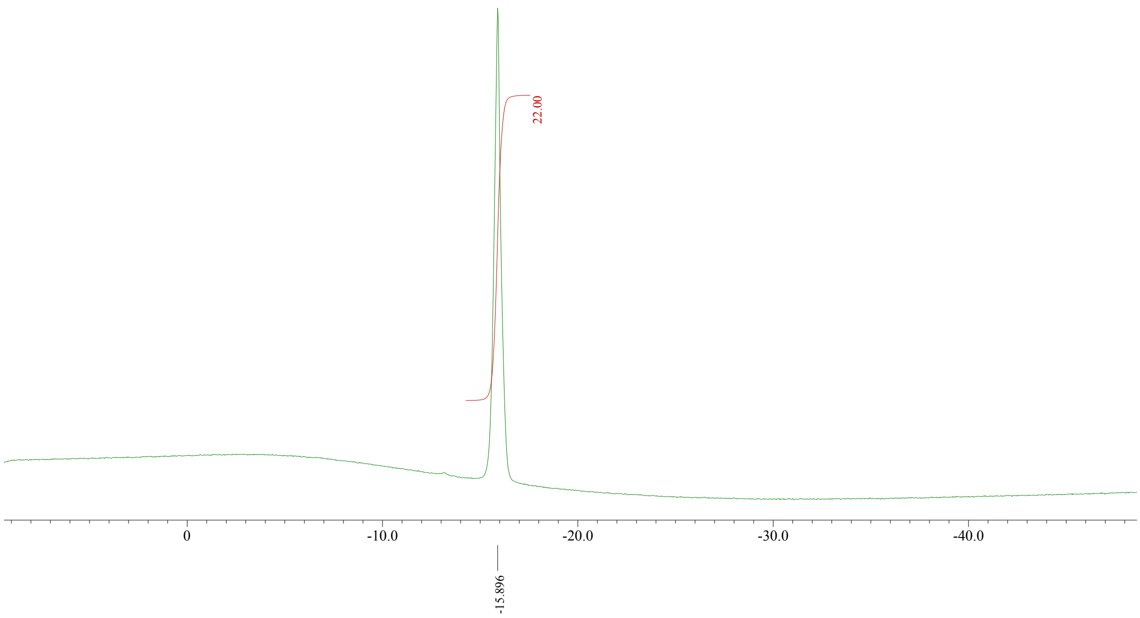
Mg^{2+}[1-F-CCA]$_2$: ^{1}H{^{11}B} NMR (Acetone-d_6)



Mg^{2+}[1-F-CCA]$_2$: ^{11}B NMR (Acetone-d_6)



Mg^{2+}[1-F-CCA]$_2$: ^{11}B{^{1}H} NMR (Acetone-d_6)



Mg^{2+}[1-F-CCA]$_2$: ^{19}F NMR (Acetone-d_6)