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Cesium Carbonate Mediated C-H Functionalization of Perhalogenated 12-vertex Carborane Anions

Sergio O. Lovera,[a] Alex L. Bagdasarian [b] , Juchen Guo,[c] Hosea M. Nelson,*[b] Vincent Lavallo*[a]

a. Departments of Chemistry, University of California Riverside, Riverside, CA 92521, USA. E-mail: vincent.lavallo@ucr.edu; http://faculty.ucr.edu/~vincentl

b. Department of Chemistry and Chemical Engineering, Pasadena, CA 91125, USA. Email: hosea@caltech.edu; http://www.thenelsonlab.com

c. Department of Chemical and Environmental Engineering, University of California Riverside, Riverside, CA 92521, USA. Email: jguo@engr.ucr.edu; http://www.cee.ucr.edu/jguo

Supplementary Information

Contents

1. General Considerations

Cs($HCB_{11}Cl_{11}$), Cs($HCB_{11}Br_{11}$), Cs($HCB_{11}I_{11}$)[1], mixture of endo and exo (1S,4S)-bicyclo[2.2.1]hept-5-en-2-ylmethyl 4-methylbenzenesulfonate[2] were synthesized according to literature procedures. Epichlorohydrin was distilled *in vacuo* and stored over 3Å molecular sieves. Cesium carbonate was stored in an MBraun glovebox and as used as needed. All other reagents were purchased from commercial vendors and used without further purification. Dry acetonitrile and CD_3CN was obtained via distillation from CaH_2 under Argon. Acetone was dried over $MgSO_4$. Nuclear magnetic resonance (NMR) spectroscopy was carried out using a Bruker Avance 600 MHz, and Bruker NEO 400 MHz (Prodigy LN_2 cryoprobe). NMR chemical shifts are reported in parts per million (ppm) with ^1H and ^{13}C chemical shifts referenced to the residual non-deutero solvent. ^1H NMR Spectra taken in d6-Acetone contain signals indicative of HDO and H_2O at 2.81 and 2.84 respectively. Data for ^1H NMR spectra are as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), integration. Multiplicities are as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, td = triplet of doublet, h= heptet, and m = multiplet. High resolution mass spectra (HR-MS) were recorded utilizing an Agilent Technologies 1260 II HPLC system combined with an Agilent Technologies 6545 QTOF LC/MS.

2. Synthesis and Characterization of Dianionic Species **$2Cl_{11}$**, **$2Br_{11}$**, and **$2I_{11}$**

A large excess of Cs_2CO_3 (10-12 eq) was added to ~50 mg of $HNMe_3$(**$2X_{11}$**) and stirred overnight. The volatiles were removed *in vacuo* and dried for several hours at room temperature before dissolving in CD_3CN for characterization.

Spectral Data for Dianionic Species **$2Cl_{11}$**

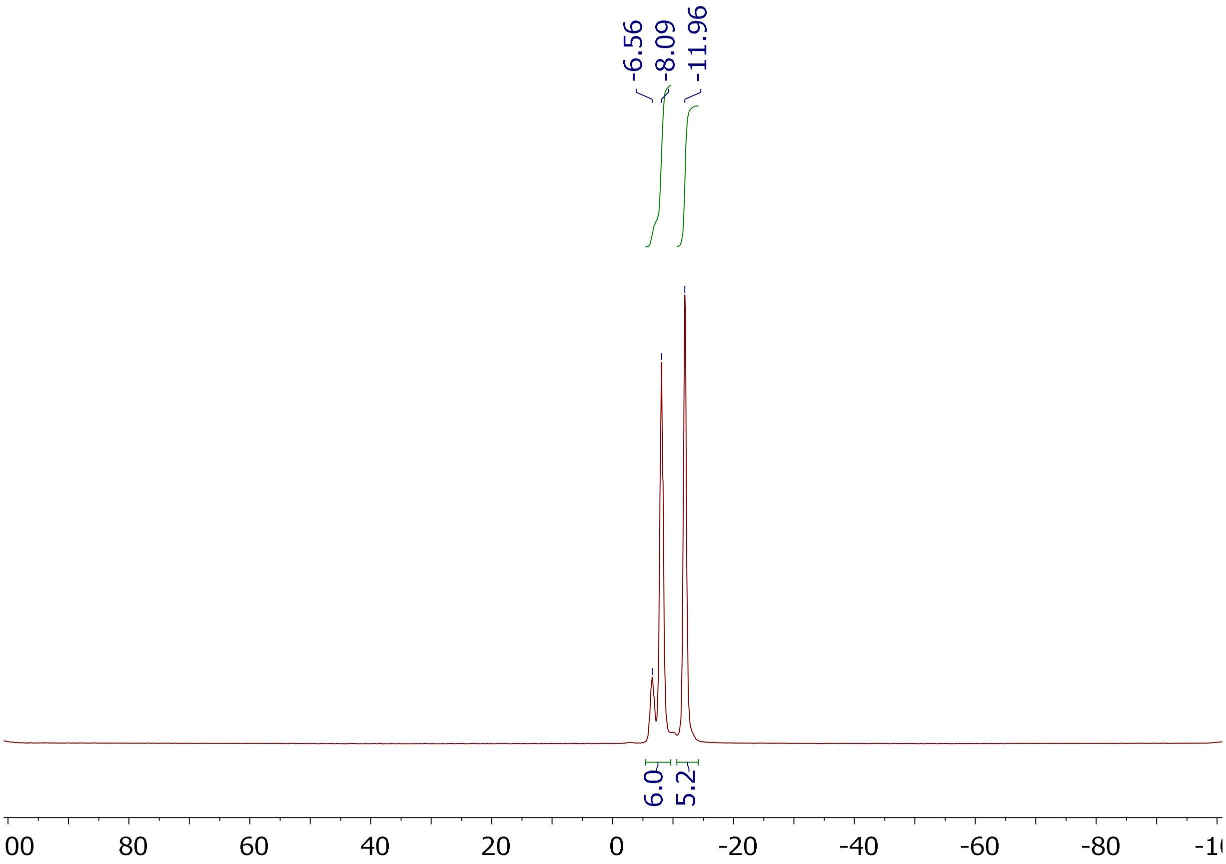


Figure 1: ^{11}B NMR spectra of **$Cs_2(2Cl_{11})$** in CD_3CN

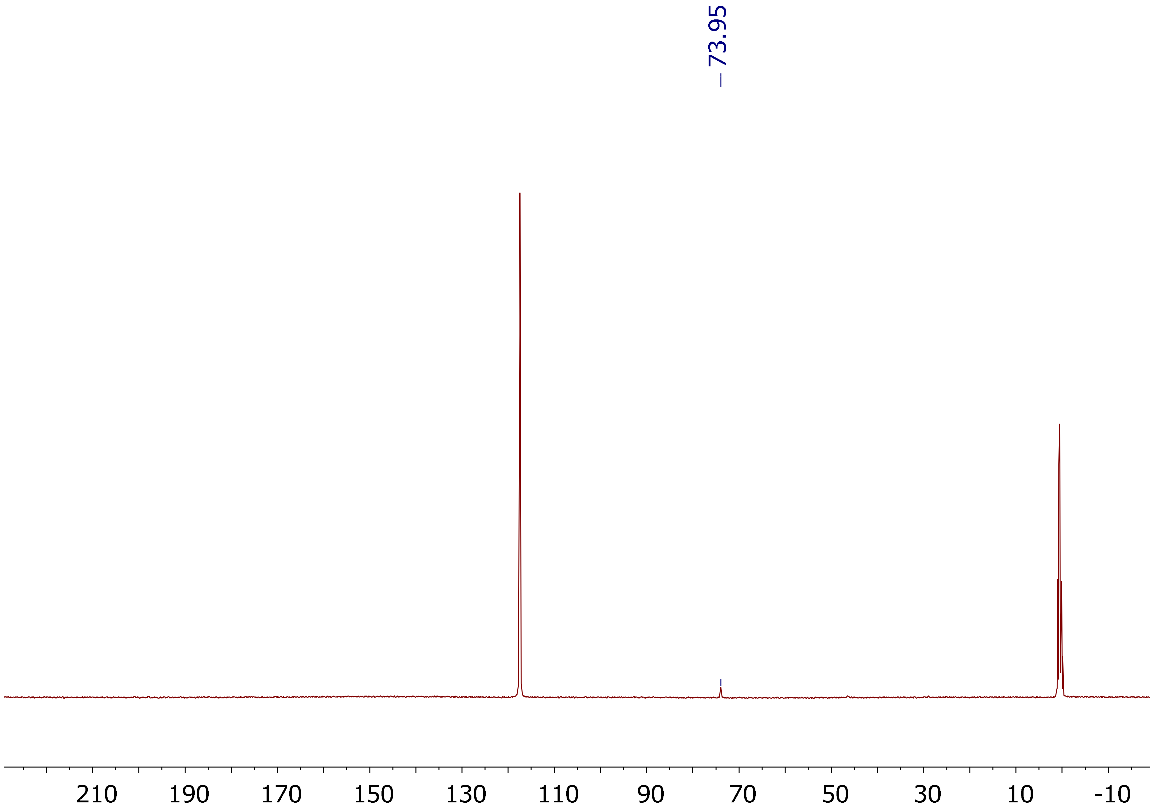


Figure 2: ^{13}C NMR spectra of **$Cs_2(2Cl_{11})$** in CD_3CN

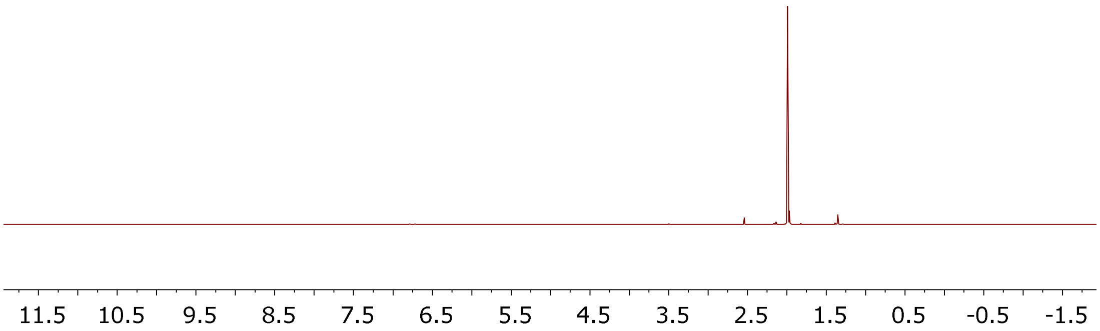


Figure 3: ^{1}H NMR spectra of **$Cs_2(2Cl_{11})$** in CD_3CN showing the absence of the carborane proton

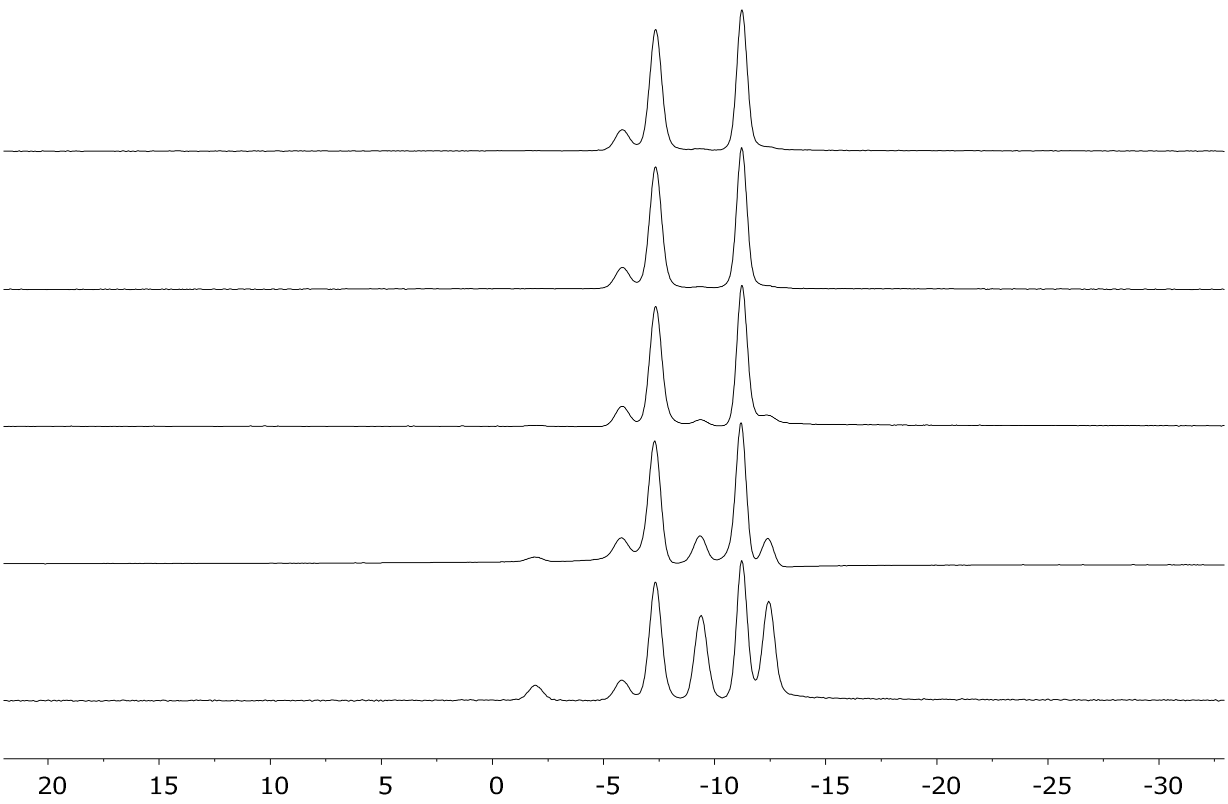


Figure 4: ^{11}B NMR spectra of mixtures of **Cs(1Cl$_{11}$)** and **Cs$_2$(2Cl$_{11}$)** with 1(bottom), 2, 3, 4 and 5(top) equivalents of Cs_2CO_3

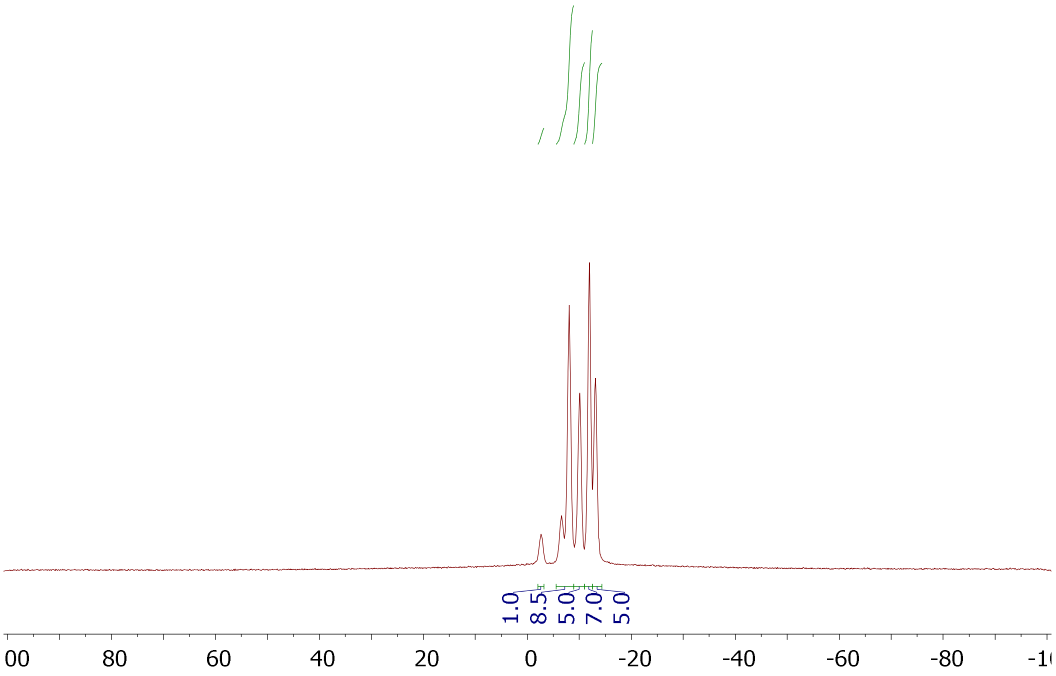


Figure 5: ^{11}B NMR spectra of the mixture of **Cs(1Cl$_{11}$)** and **Cs$_2$(2Cl$_{11}$)** with 1 equivalent of Cs_2CO_3

Spectral Data for Dianionic Species **$2Br_{11}$**

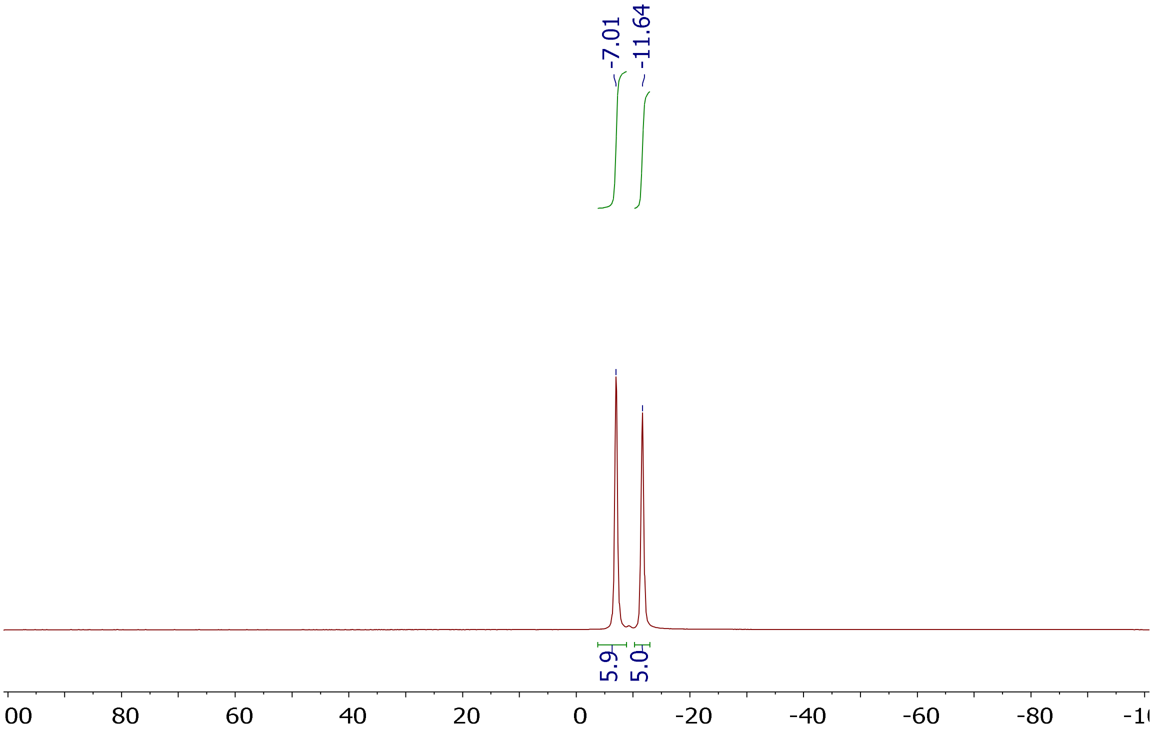


Figure 6: ^{11}B NMR spectra of **$Cs_2(2Br_{11})$**

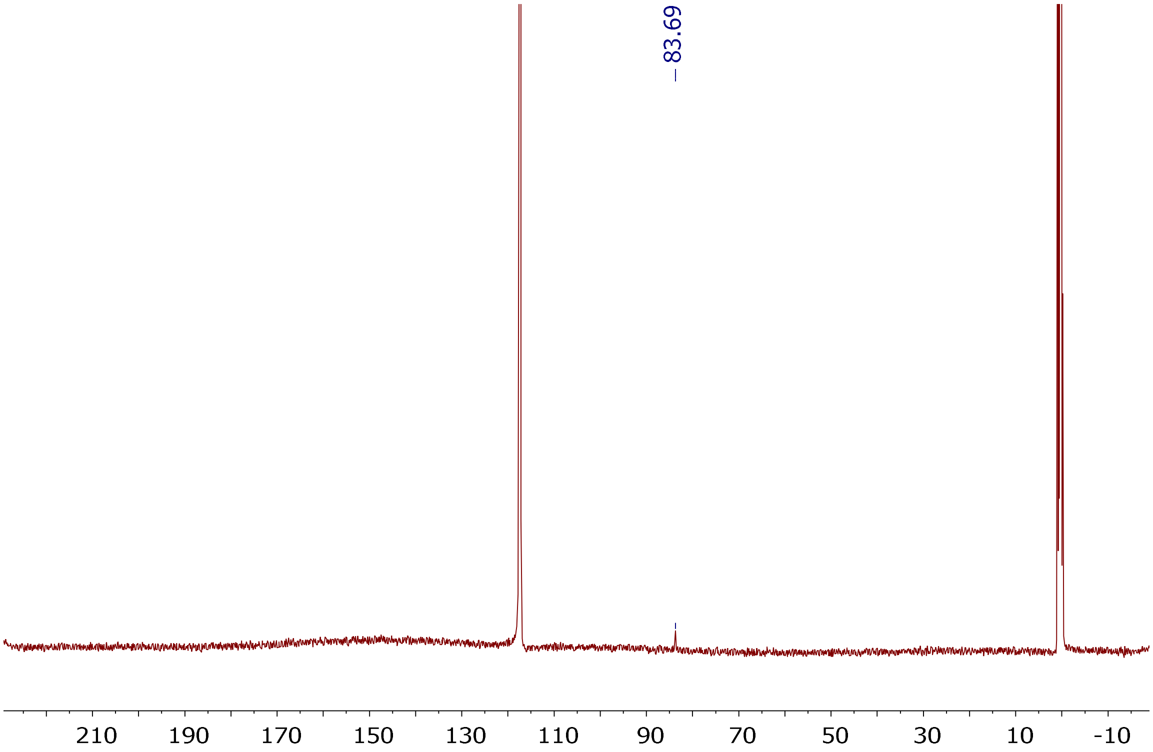


Figure 7: ^{13}C NMR spectra of **$Cs_2(2Br_{11})$**

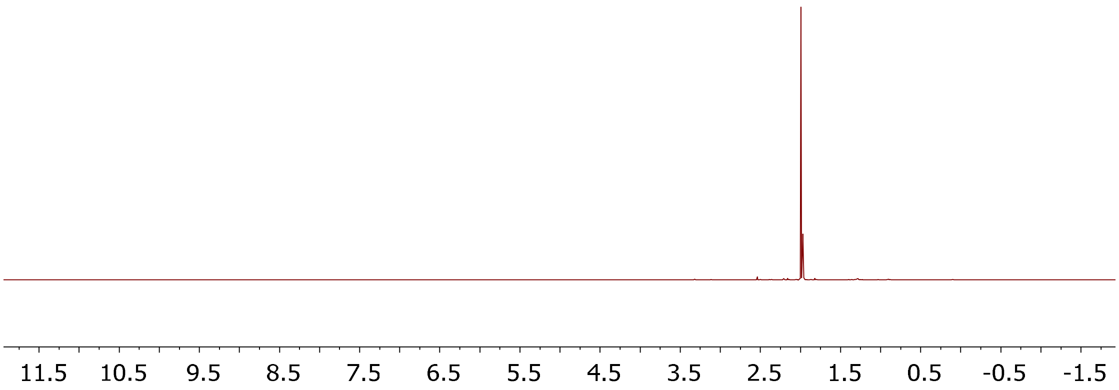


Figure 8: ^1H NMR spectra of **$Cs_2(2Br_{11})$** in CD_3CN showing the absence of the carborane proton

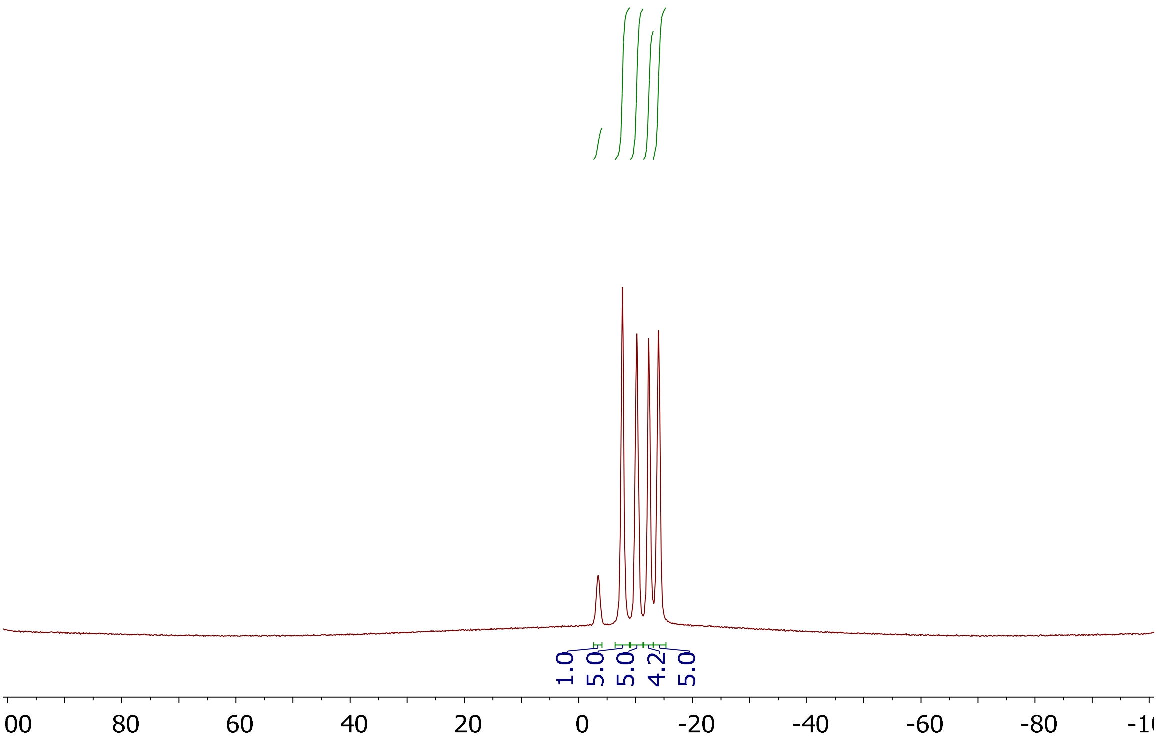


Figure 9: ^{11}B NMR spectra of the mixture of **$Cs(1Br_{11})$** and **$Cs_2(2Br_{11})$** with 1 equivalent of Cs_2CO_3

Spectral Data for Dianionic Species **$2I_{11}$**

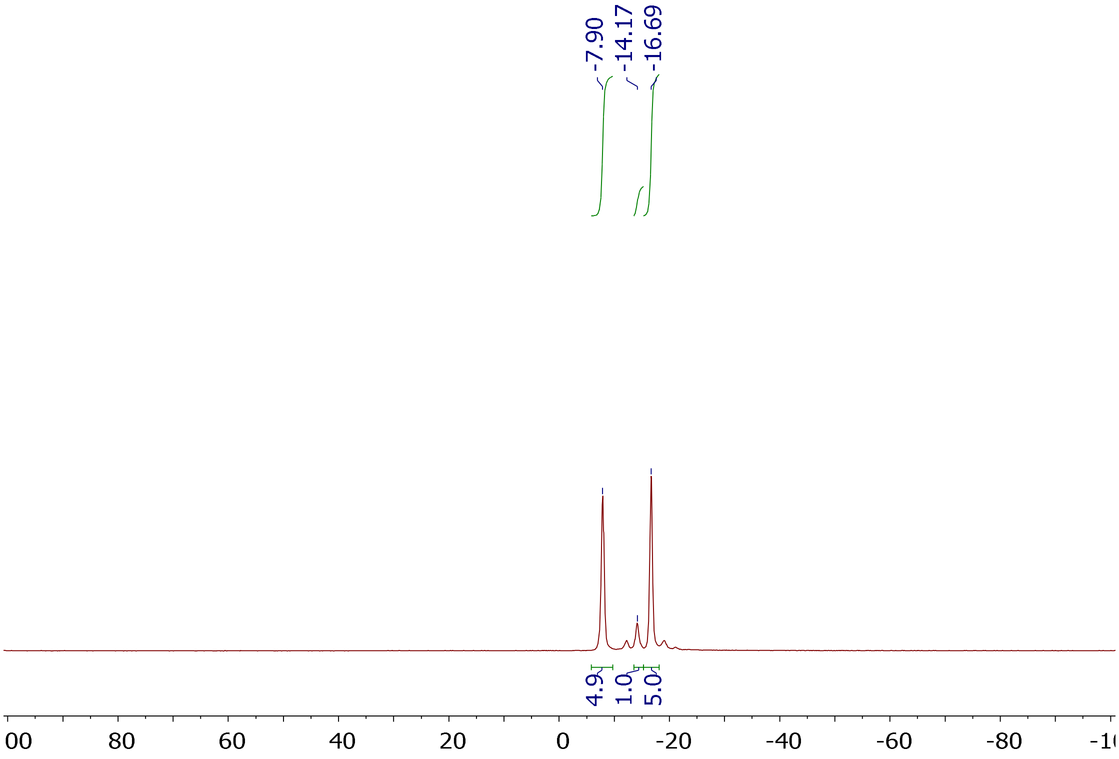


Figure 10: ^{11}B NMR spectra of **$Cs_2(2I_{11})$**. Integrated peaks belong to **$Cs_2(2I_{11})$** with the others belonging to residual **$Cs(1I_{11})$**

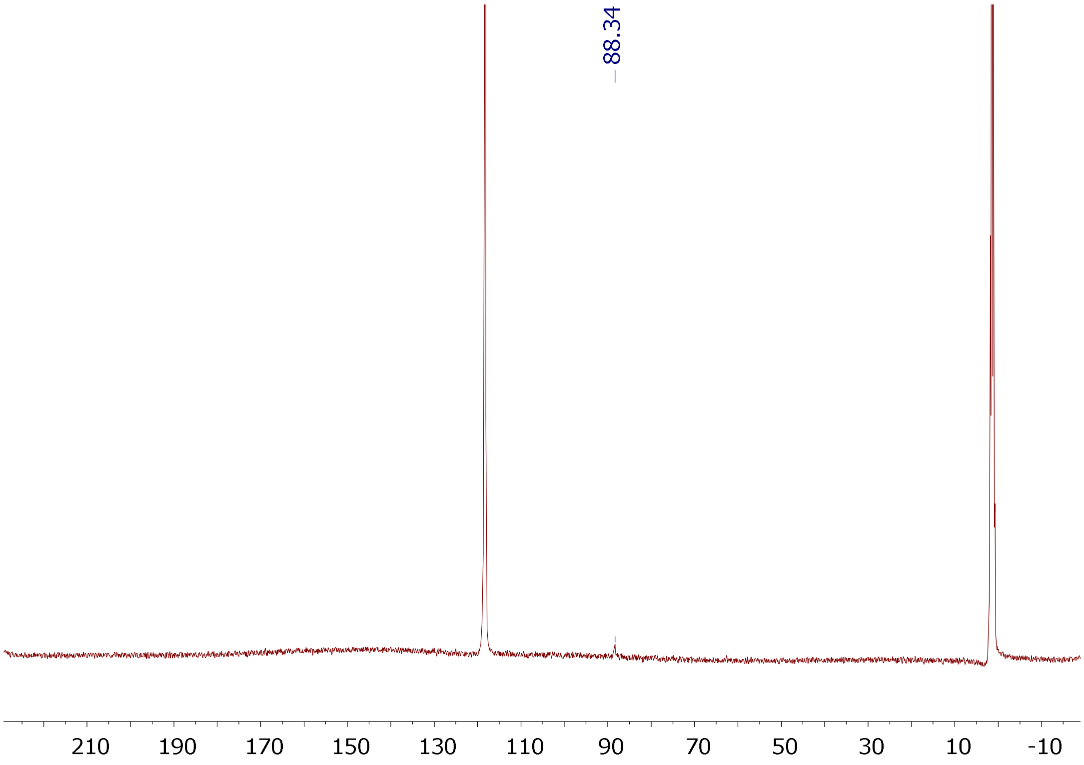


Figure 11: ^{13}C NMR spectra of **$Cs_2(2I_{11})$**.

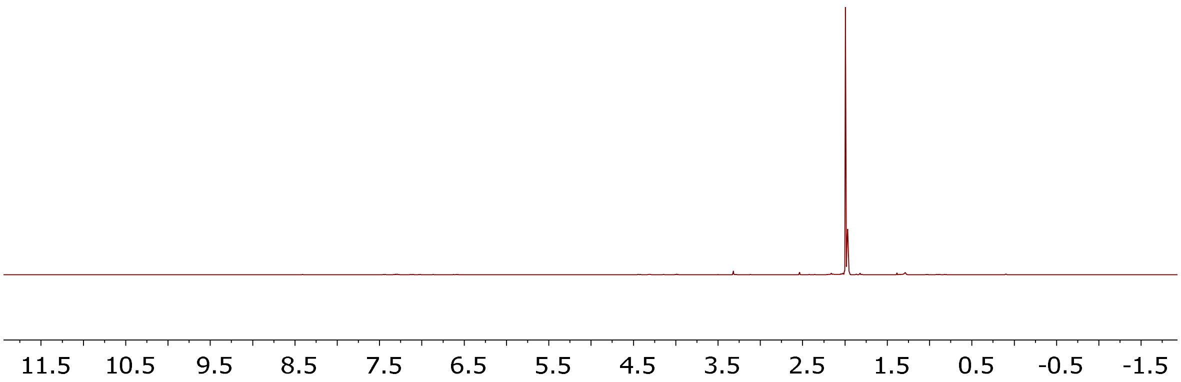


Figure 12: ^{1}H NMR spectra of **Cs$_2$(2I$_{11}$)** in CD$_3$CN showing the absence of the carborane proton

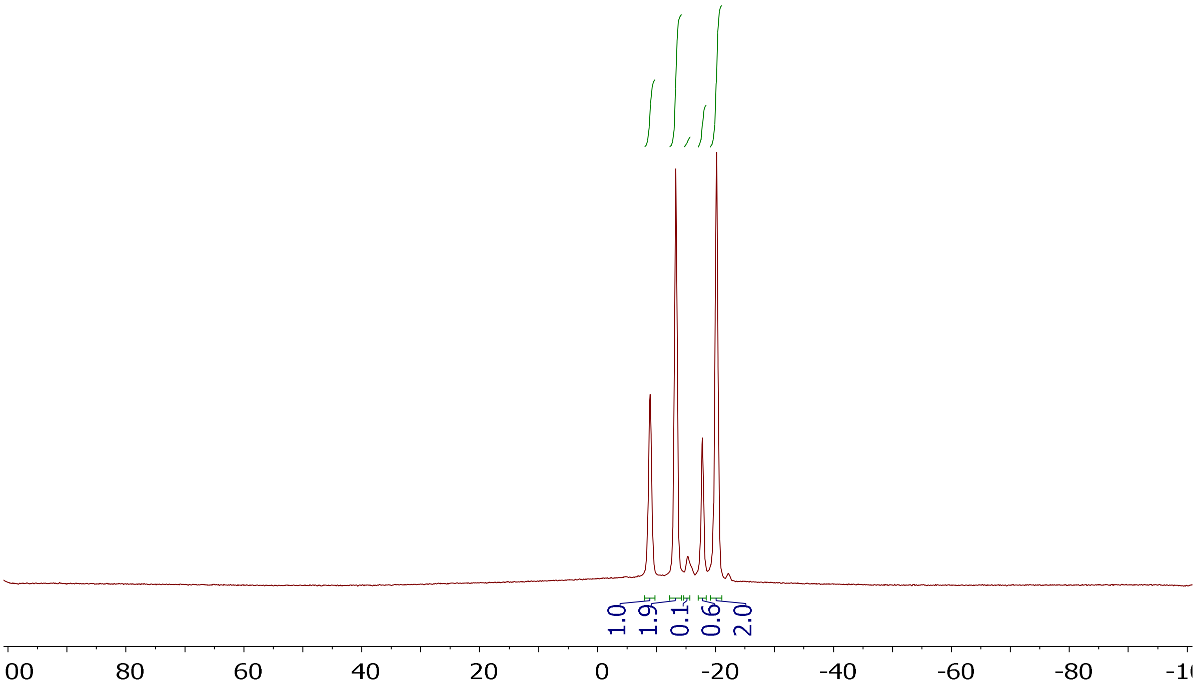


Figure 13: ^{11}B NMR spectra of the mixture of **Cs(1I$_{11}$)** and **Cs$_2$(2I$_{11}$)** with 1 equivalent of Cs$_2$CO$_3$

3. General Alkylation Procedures

50 mg (0.076 mmol) of $CsHCB_{11}X_{11}$ and 124 mg Cs_2CO_3 (0.38 mmol) were added to an oven-dried round-bottom flask. The desired electrophile (0.23 mmol) was then weighed and subsequently diluted with 3 mL of acetonitrile and added to the contents of the round bottom flask. An extra 2-3 mL of acetonitrile was used to transfer remaining electrophile. Reactions were stirred for 4 hours before being checked by HRMS for the absence of $[HCB_{11}X_{11}^{-}]$ starting materials. Once the starting material was completely consumed, the reaction contents were filtered and solvent was removed *in vacuo*. Electrophiles used, further purification, and spectral data for each compound is reported below.

Attempted alkylation in aqueous media

30 mg (0.045 mmol) of $CsHCB_{11}Cl_{11}$ was dissolved in 5mL of DI H_2O and was subsequently charged with 73 mg (0.223 mmol) Cs_2CO_3. After stirring for 15 min, an ^{11}B NMR was taken and demonstrated no change associated with conversion to the nucleophilic $Cs_2CB_{11}Cl_{11}$. 34 mg (0.134 mmol) of ethyl 4-bromocrotonate (75% tech grade) was then added and stirred overnight. Evidence of product formation was not observed by ^{11}B NMR.

4. Purification and Characterization of compounds **a**-**n**

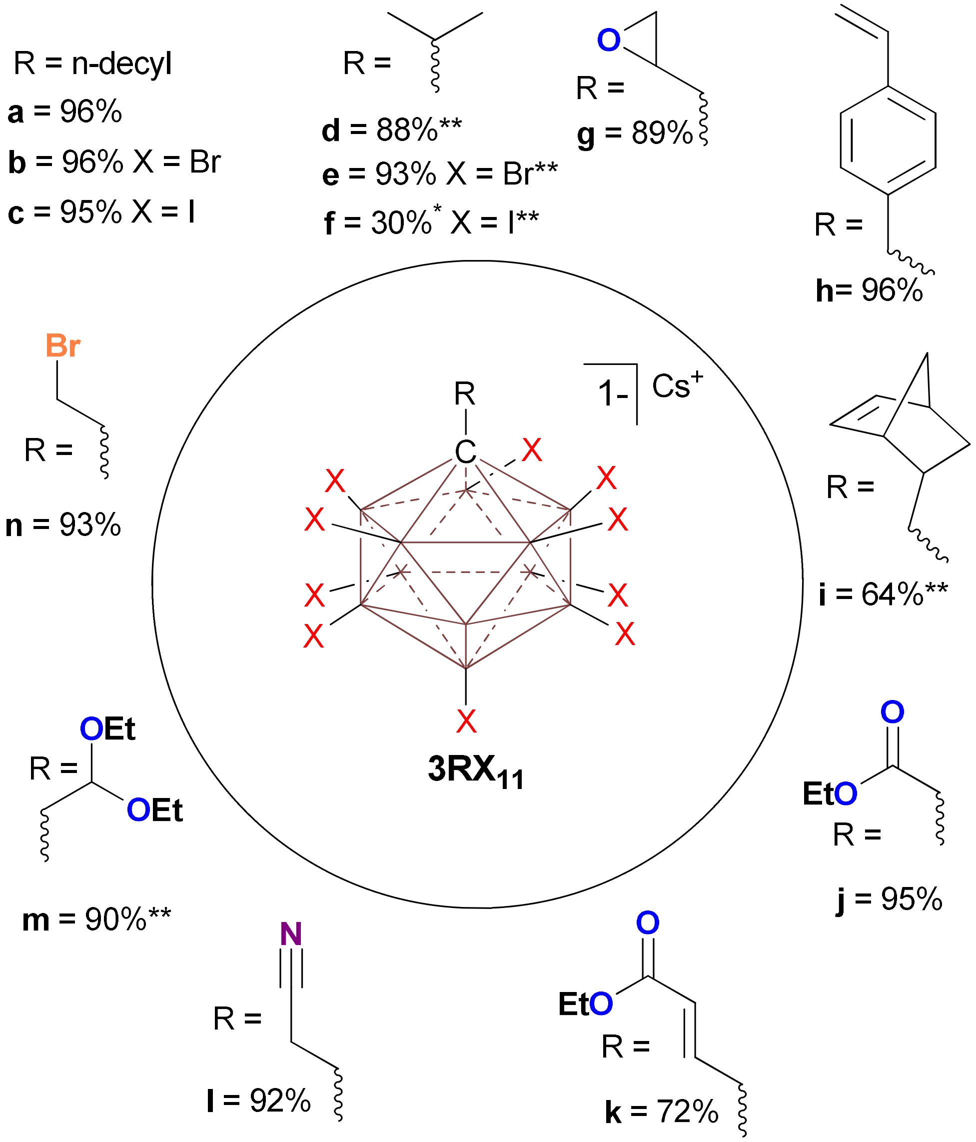
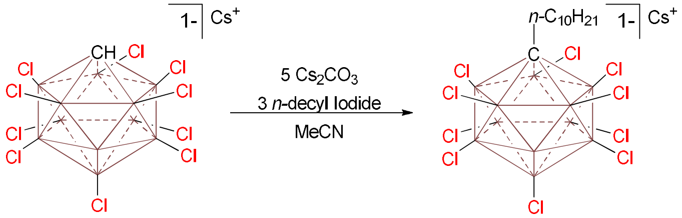


Figure 14: Synthesized compounds **a-n**

Purification and Characterization of **a**



Electrophile used: *n*-Decyl Iodide. The recovered oily solid was triturated with hexanes and filtered. The filtered solid was then washed through the filter with acetone and pumped dry yielding $Cs[C_{10}H_{21}CB_{11}Cl_{11}]$ in 96% yield.

^1H NMR (400 MHz, Acetonitrile-d_3) δ 2.31 – 2.24 (m, 2H), 1.92 – 1.78 (m, 2H), 1.29 (s, 14H), 0.88 (t, 3H).

^{11}B NMR (128 MHz, Acetonitrile) δ -2.28 (s, 1B), -9.28 (s, 5B), -10.90 (s, 5B).

^{13}C NMR (101 MHz, CD$_3$CN) δ 32.57, 32.00, 30.55, 30.11, 29.96, 29.42, 25.12, 23.36, 14.38.

m/z calcd for $C_{10}H_{21}CB_{11}Cl_{11}^-$: 660.9259 Found: 660.9275

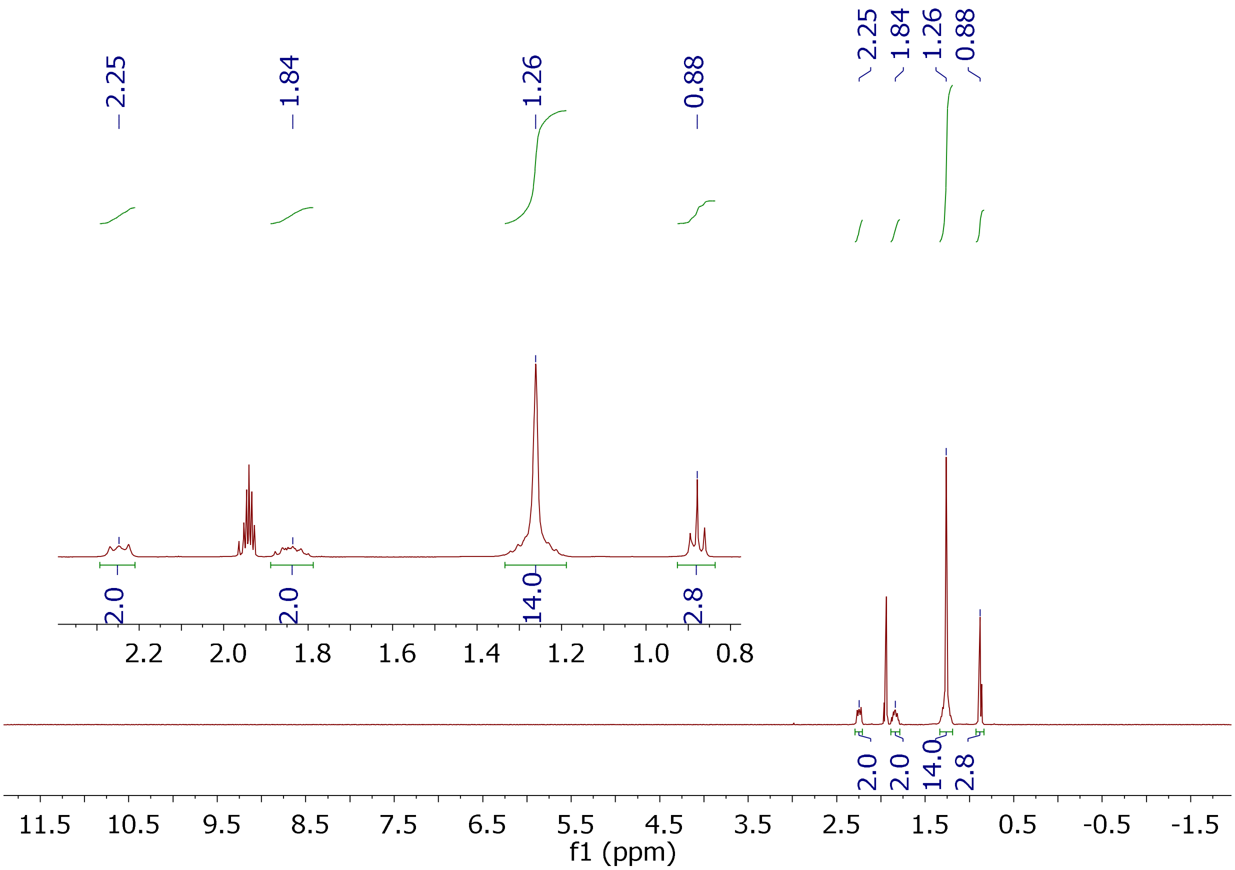


Figure 15: ^{1}H NMR spectra of compound **a** in CD$_3$CN

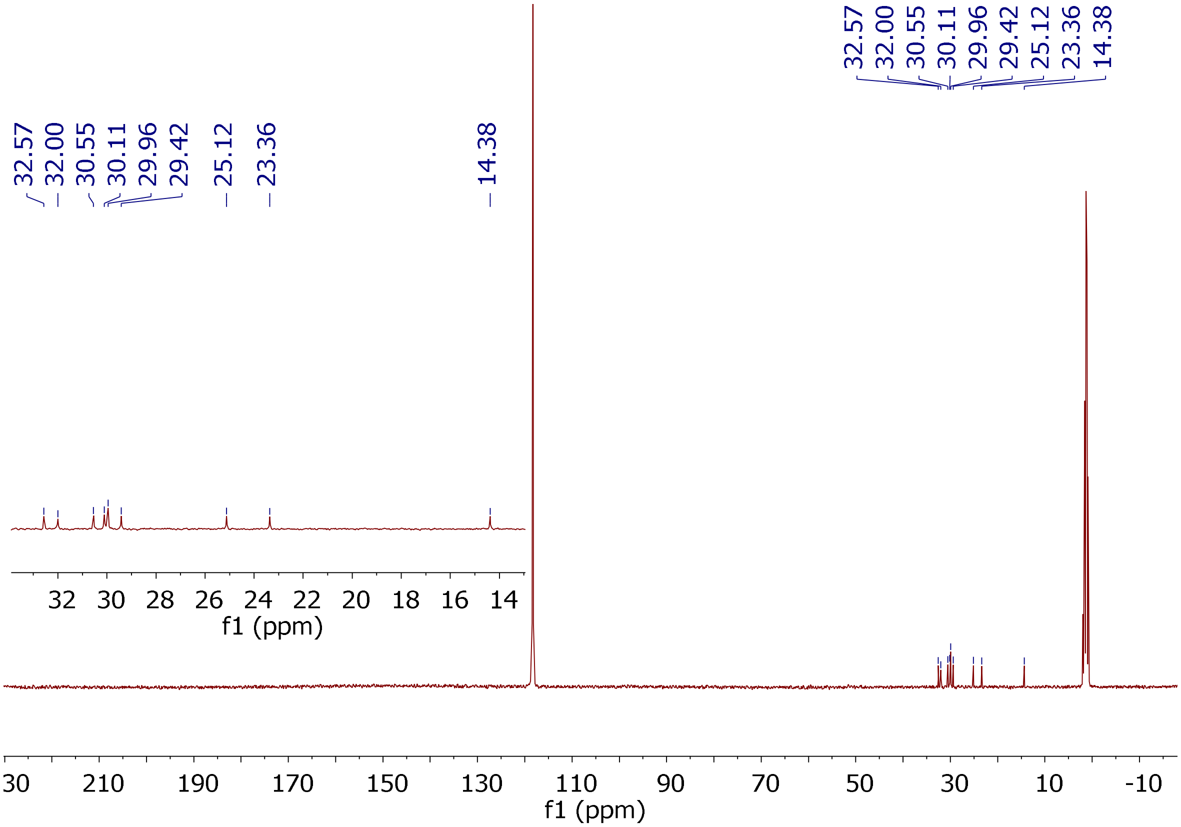


Figure 16: ^{13}C NMR spectra of compound **a** in CD3CN

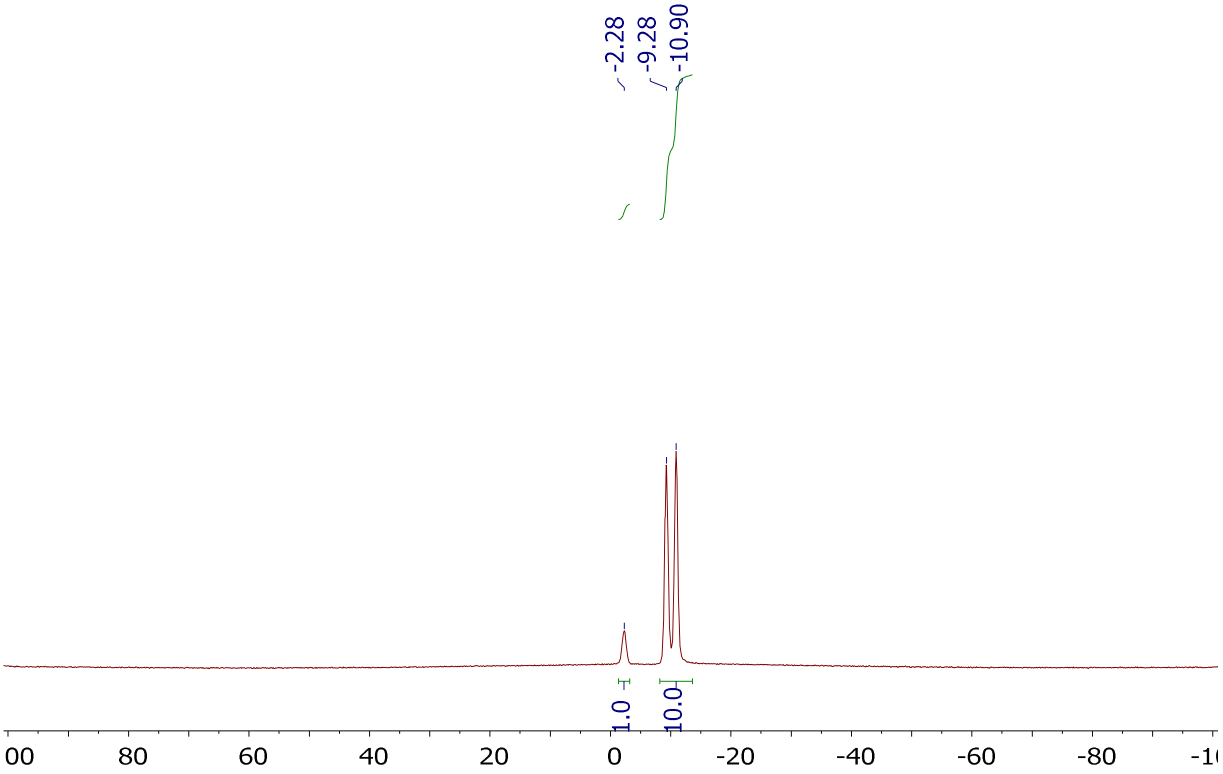


Figure 17: ^{11}B NMR of **a** in acetonitrile

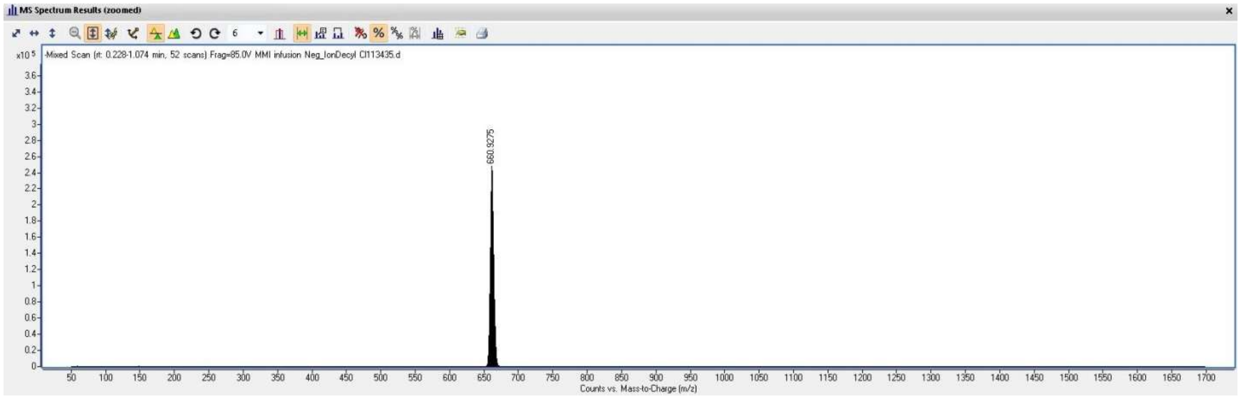


Figure 18: HRMS spectrum of compound **a**

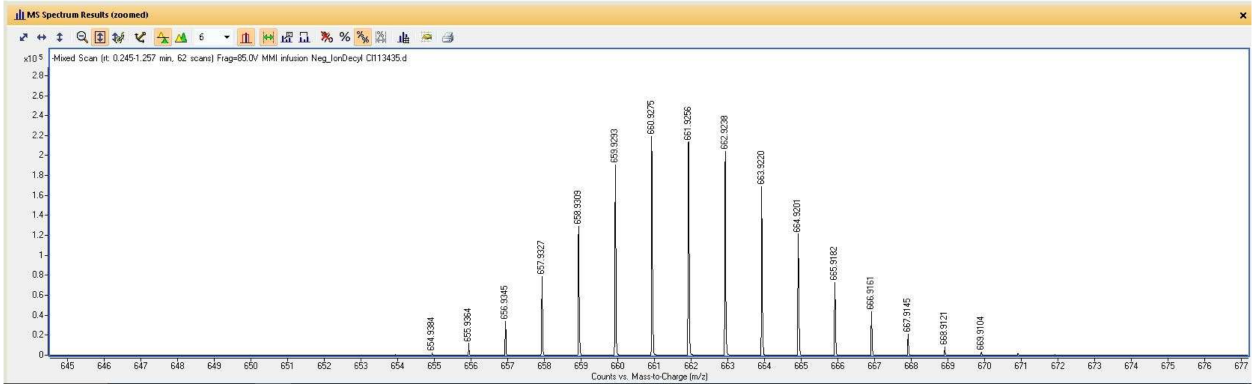
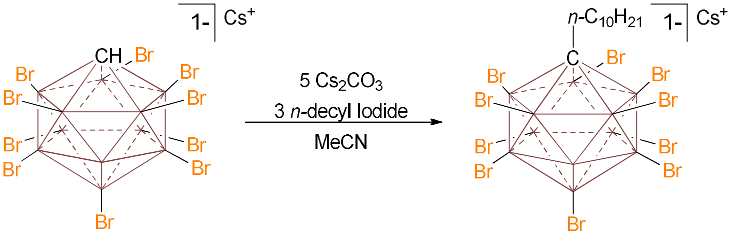


Figure 19: Zoomed in HRMS spectrum of compound **a**

Purification and Characterization of **b**



Electrophile used: *n*-Decyl Iodide. The recovered oily solid was triturated with hexanes and filtered. The filtered solid was then washed through the filter with acetone and pumped dry yielding Cs[$C_{10}H_{21}CB_{11}Br_{11}$] in 96% yield.

^{1}H NMR (400 MHz, Acetone-d_6) δ 2.44 – 2.36 (m, 1H), 2.02 (m, 1H), 1.31 (m, 14H), 0.88 (t, J = 7.0 Hz, 3H).

^{11}B NMR (128 MHz, Acetone) δ -2.67, -8.89, -11.08.

^{13}C NMR (101 MHz, CD_3CN) δ 37.24, 31.61, 29.24, 29.13, 29.01, 28.95, 28.40, 24.99, 22.41, 13.44

m/z calcd for $C_{10}H_{21}CB_{11}Br_{11}^-$: 1151.3623 Found: 1151.3499

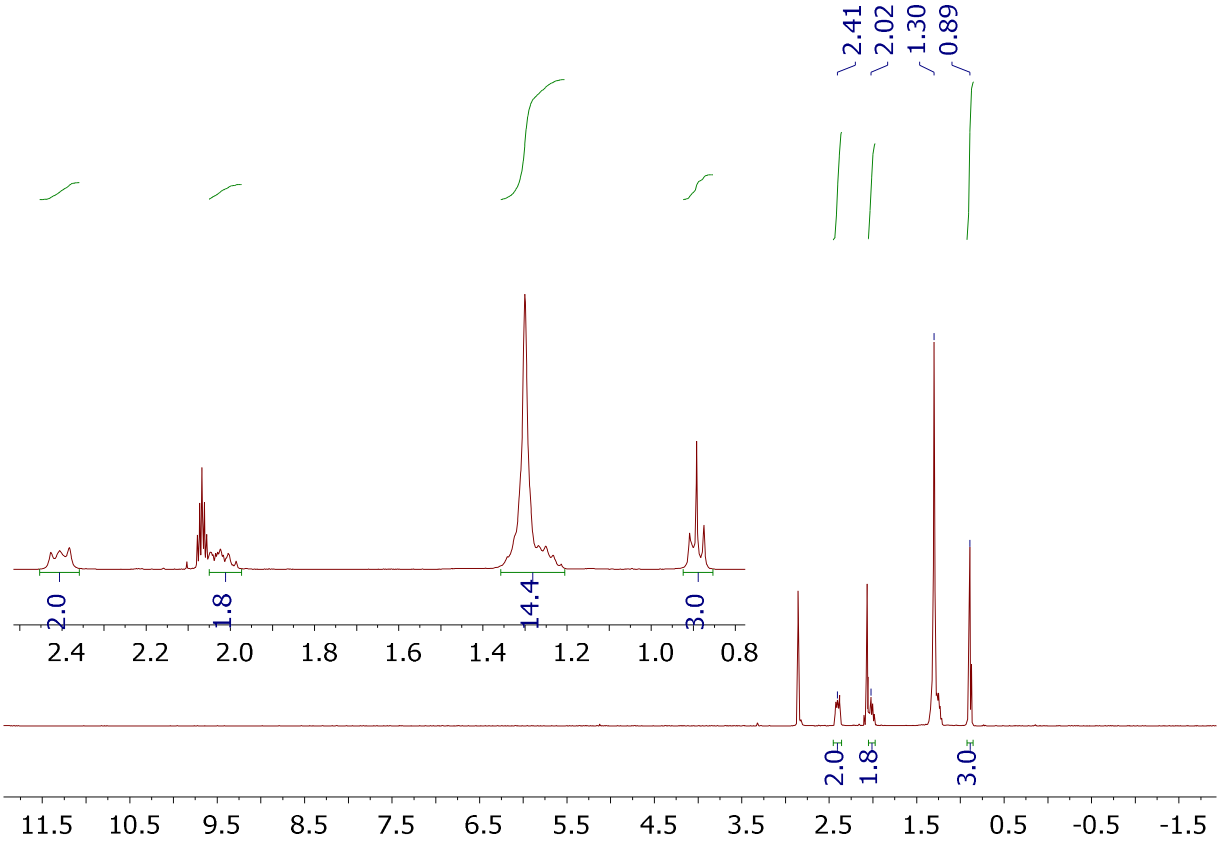


Figure 20: ^{1}H NMR spectra of compound **b** in acetone-d_6

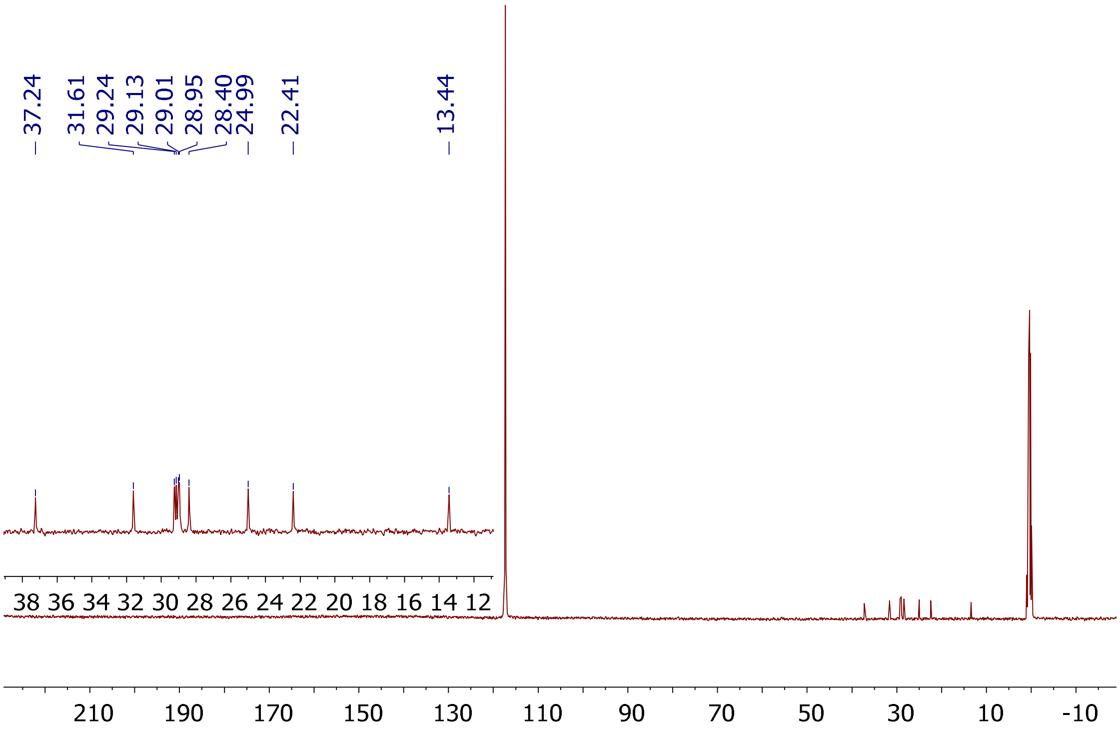


Figure 21: ^{13}C NMR spectra of compound **b** in CD_3CN

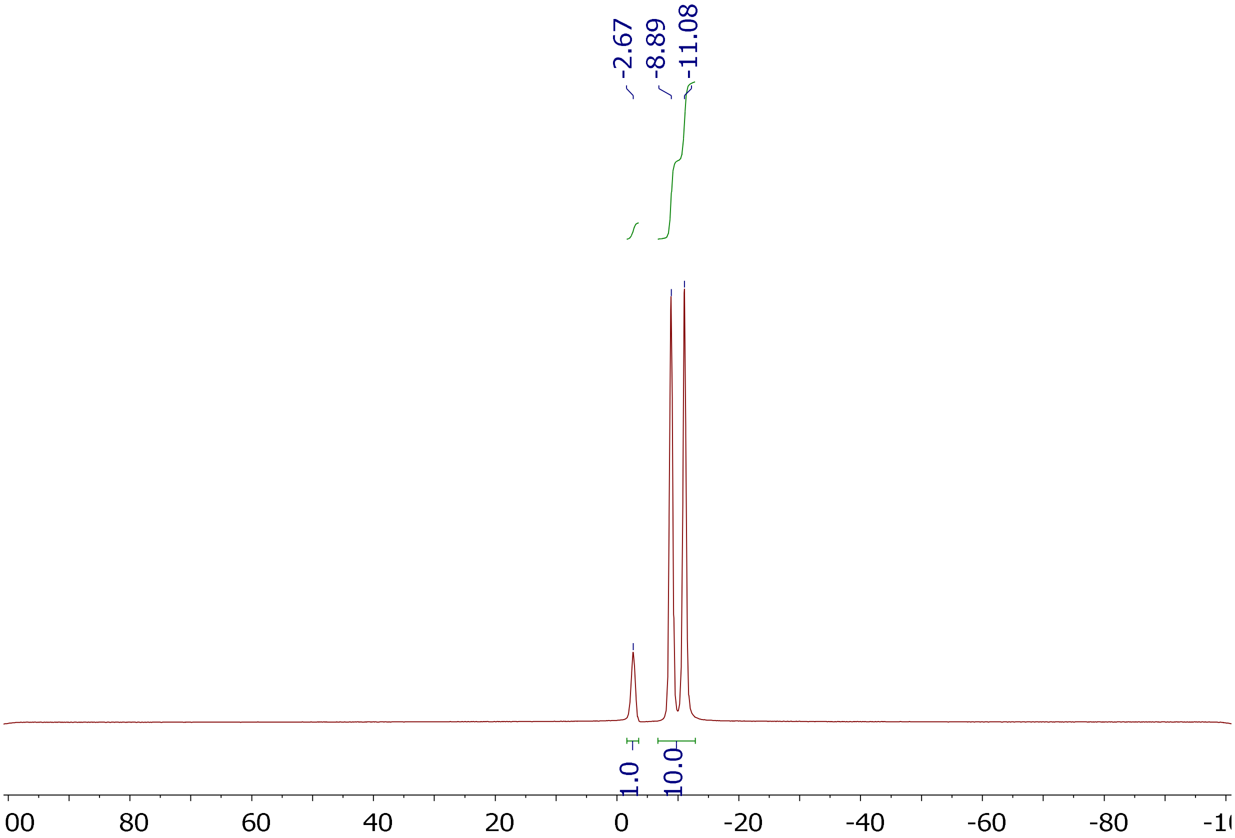


Figure 22: ^{11}B NMR spectra of compound **b** in acetone-d_6

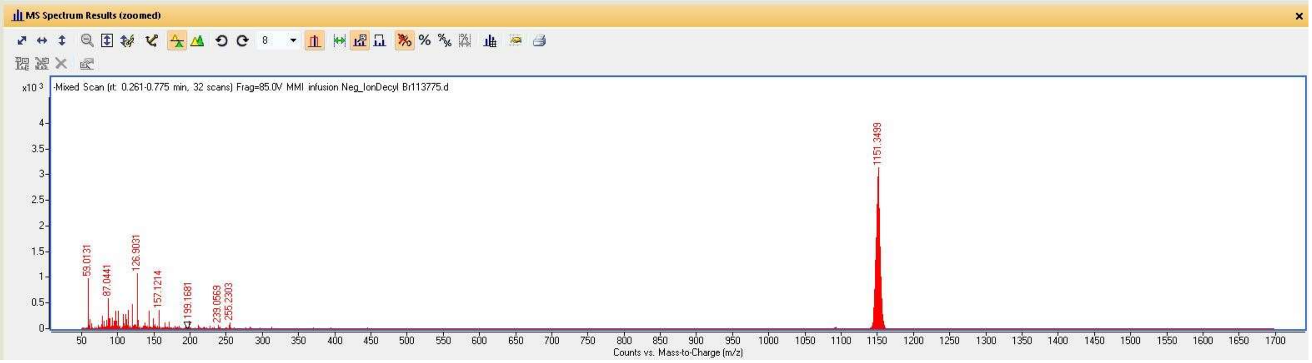


Figure 23: HRMS spectrum of compound **b**

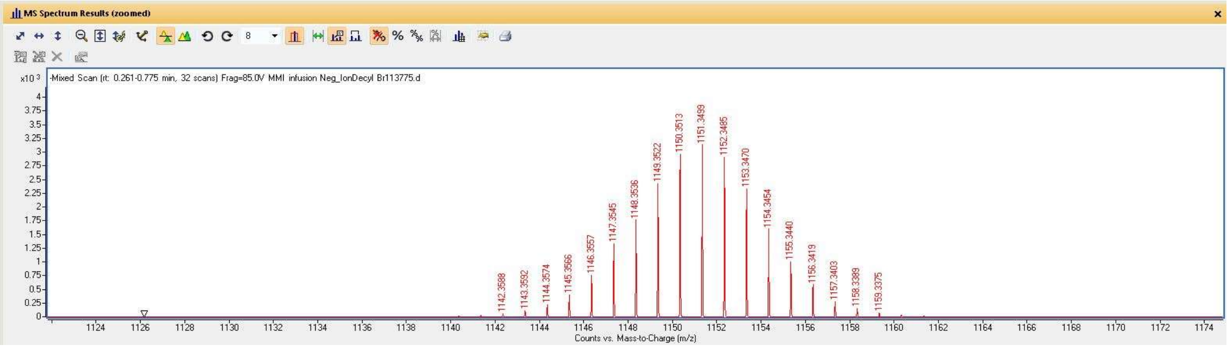
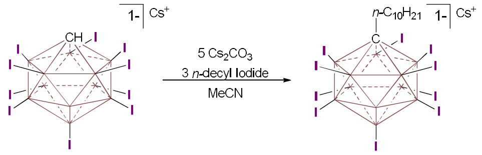


Figure 24: Zoomed in HRMS spectrum of compound **b**

Purification and Characterization of **c**



Electrophile used: *n*-Decyl Iodide. The recovered oily solid was triturated with hexanes and filtered. The filtered solid was then washed through the filter with acetone and pumped dry yielding $Cs[C_{10}H_{21}CB_{11}I_{11}]$ in 95% yield.

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 2.54 (m, 2H), 2.19 (m, 2H), 1.29 (m, 14H), 0.88 (t, 3H).

^{11}B NMR (128 MHz, Acetone) δ -8.64, -12.01, -17.11, -19.57.

^{13}C NMR (101 MHz, CD_3CN) δ 47.63, 31.65, 29.15, 29.06, 28.97, 28.47, 28.39, 27.10, 22.44, 13.50.

m/z calcd for $C_{10}H_{21}CB_{11}I_{11}^-$: 1668.2236 Found: 1668.2023

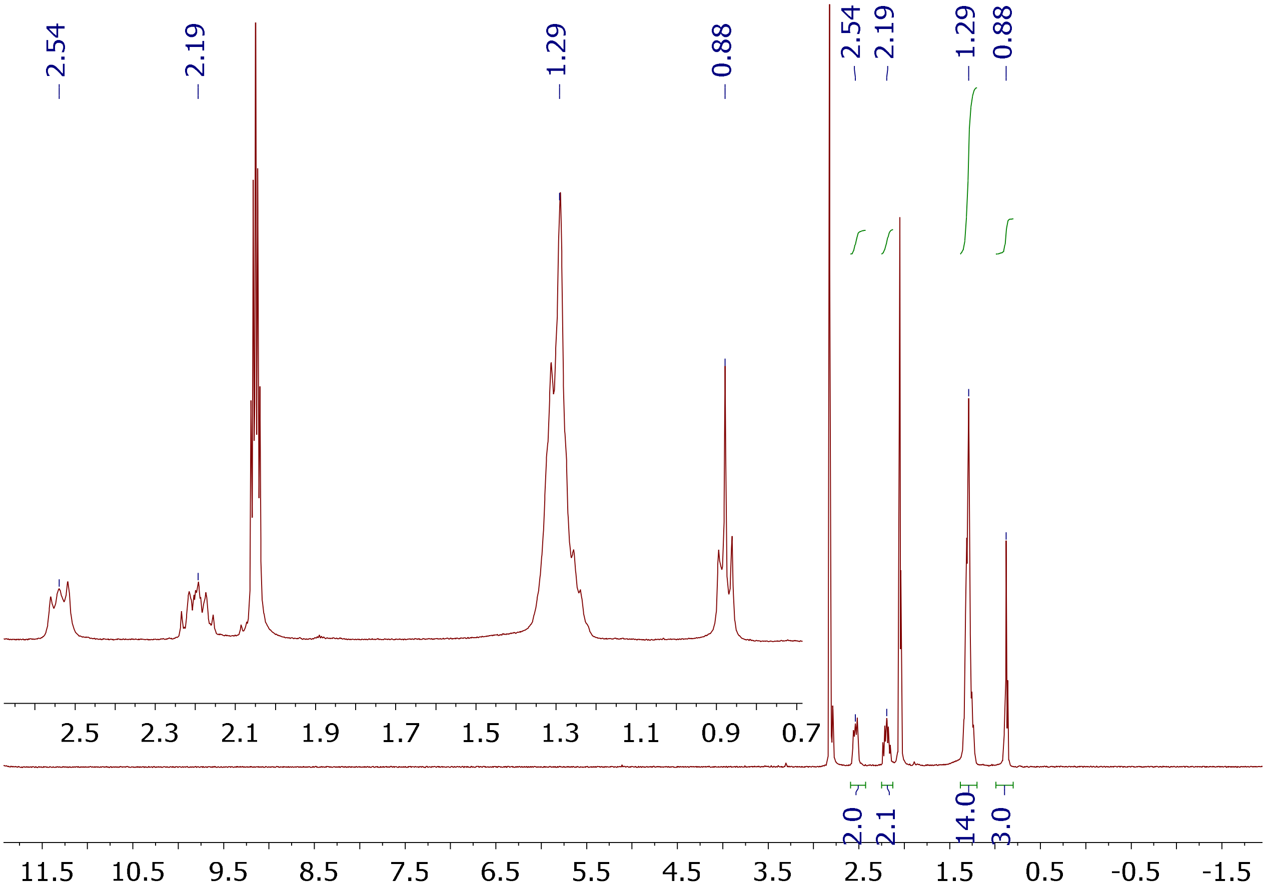


Figure 25: ^{1}H NMR spectra of compound **c** in acetone-d$_6$

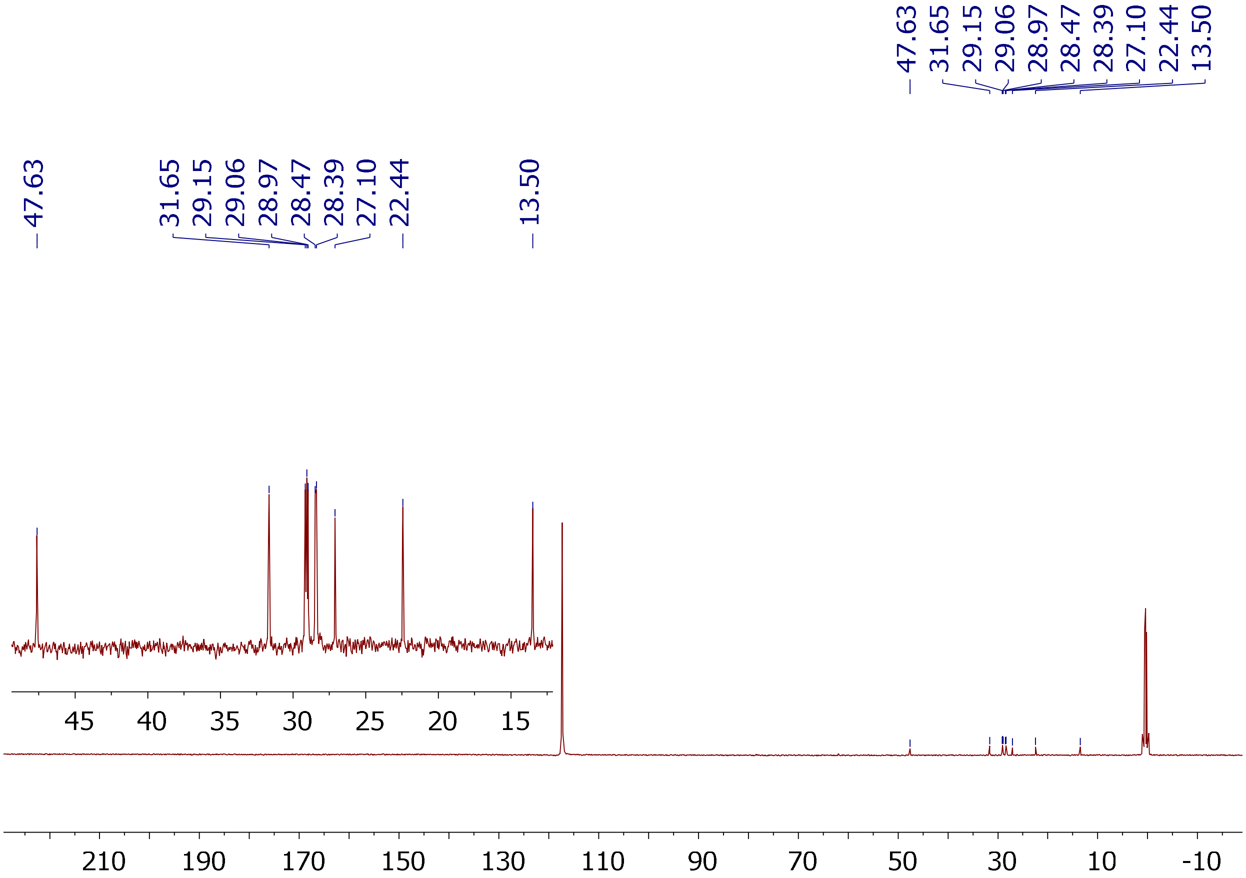


Figure 26: ^{13}C NMR spectra of compound **c** in CD_3CN

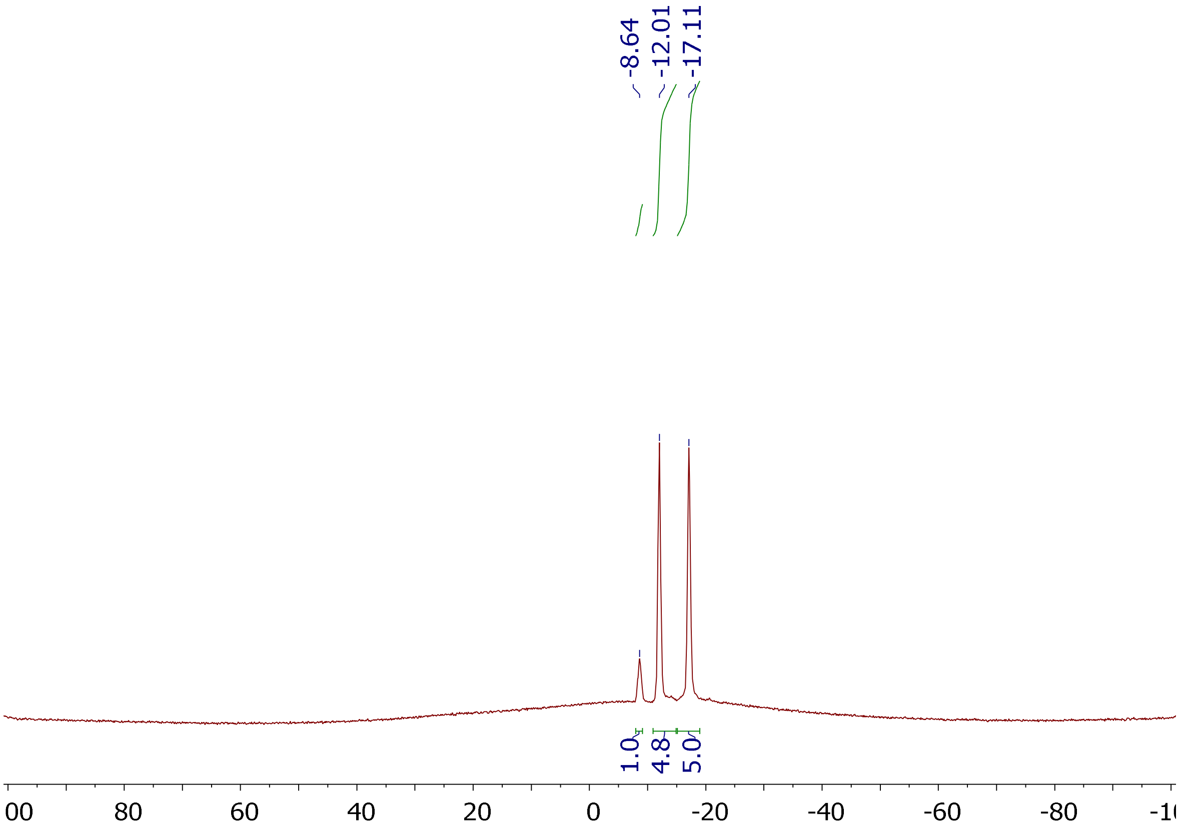


Figure 27: ^{11}B NMR spectra of compound **c** in acetone-d_6

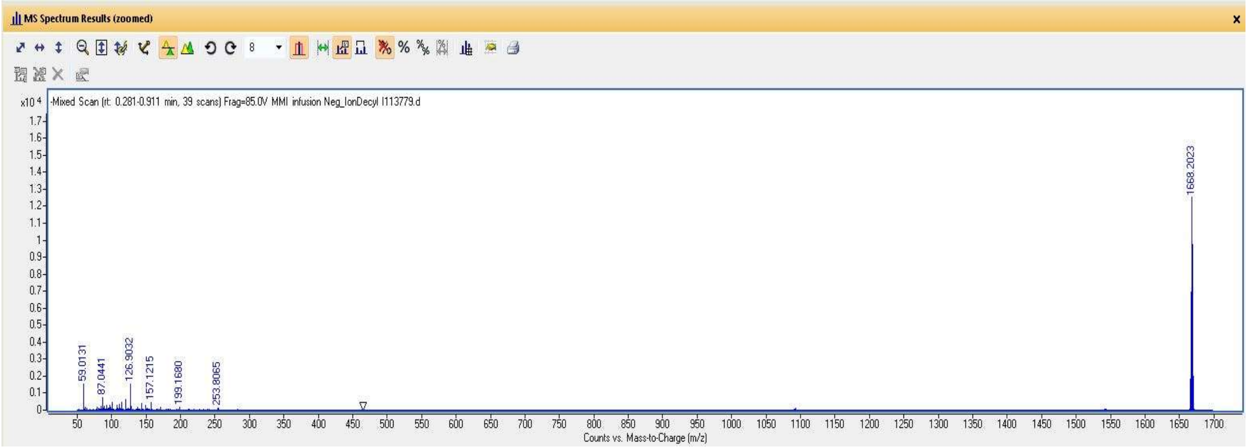


Figure 28: HRMS spectrum of **c**

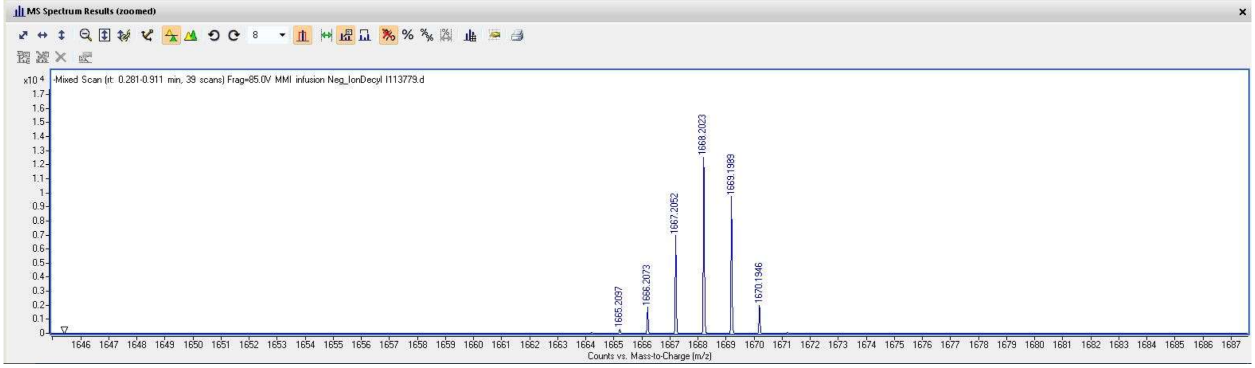
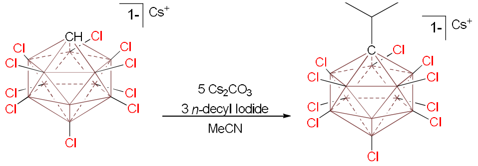


Figure 29: Zoomed in HRMS spectrum of **c**

Purification and Characterization of **d**



Electrophile: isopropyl iodide. The recovered oily solid was triturated with hexanes and filtered. The filtered solid was then washed through the filter with acetone and pumped dry yielding compound **d** in 89% yield.

^{1}H NMR (400 MHz, Acetone-d_6) δ 3.10 (hept, J = 7.1 Hz, 1H), 1.52 (d, J = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, Acetone) δ 37.21, 21.99.
^{11}B NMR (128 MHz, Acetone) δ -1.68, -8.90, -10.94.
m/z calcd for $C_3H_7CB_{11}Cl_{11}^-$: 563.8127 Found: 563.8183

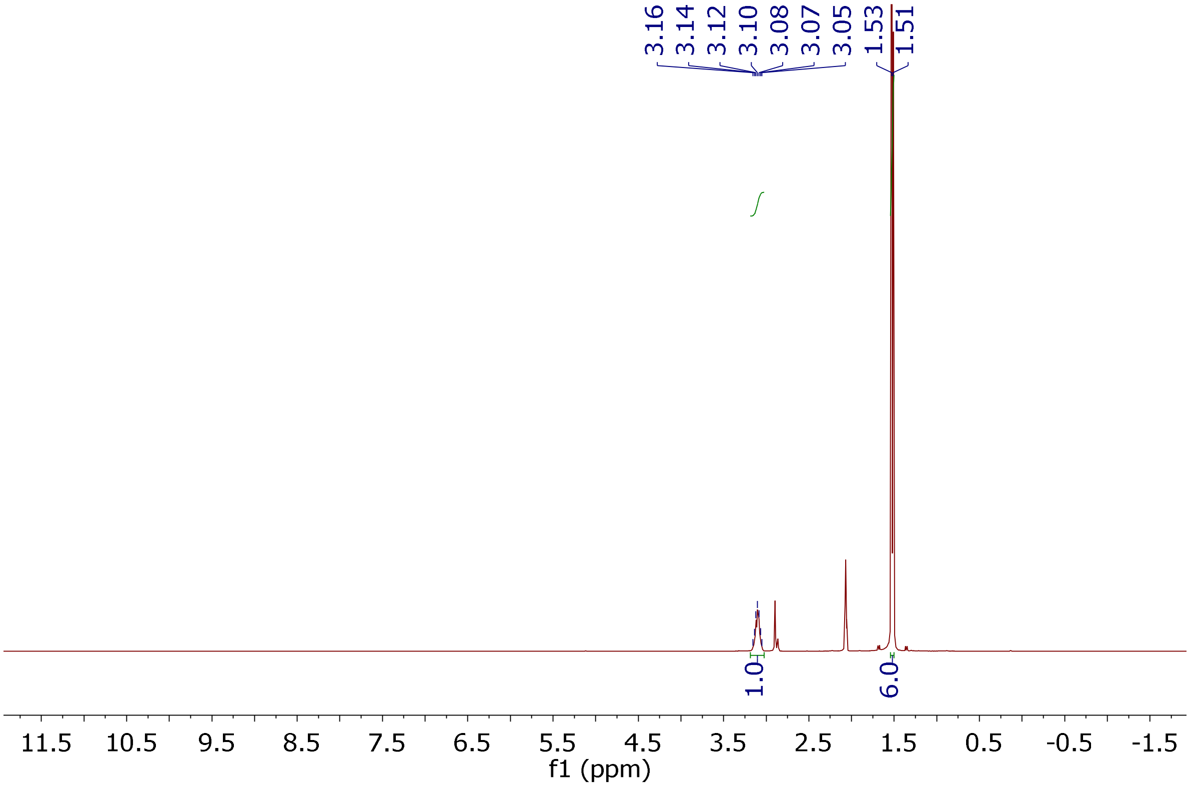


Figure 30: ^{1}H NMR spectrum of compound **d** in d_6-Acetone

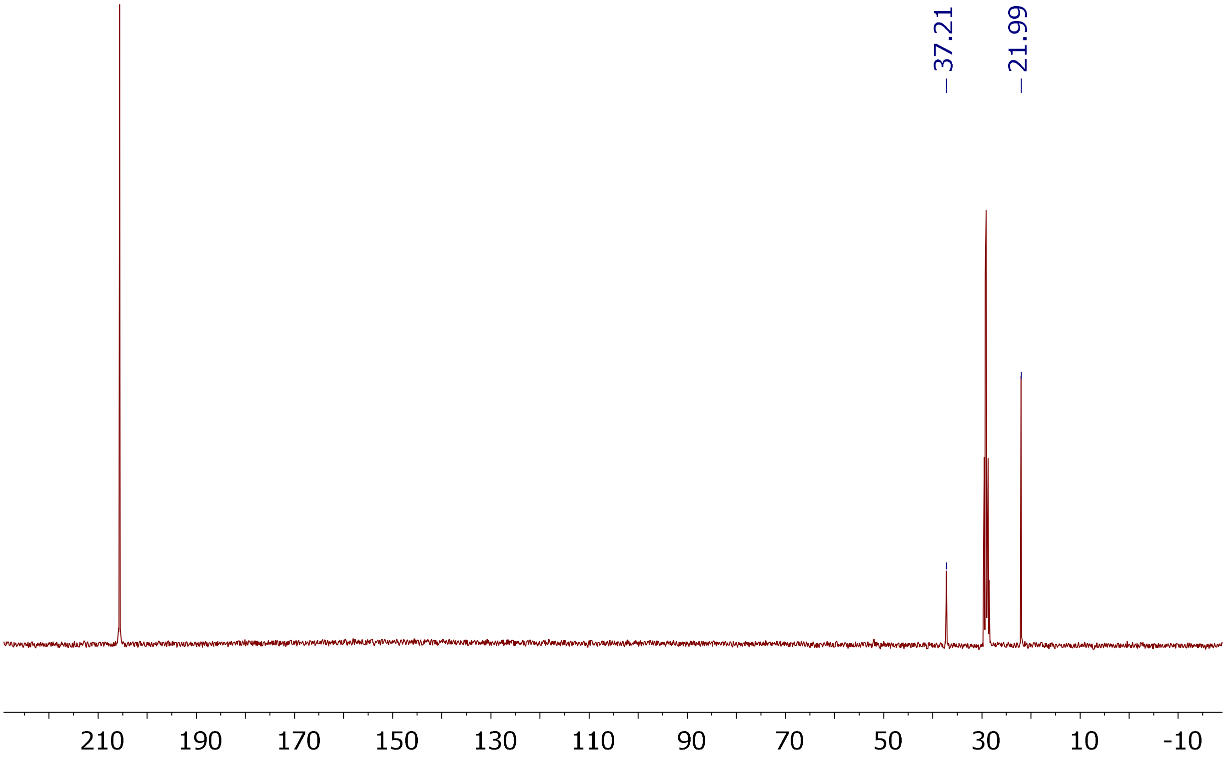


Figure 31: ^{13}C NMR spectrum of compound **d** in d_6-Acetone

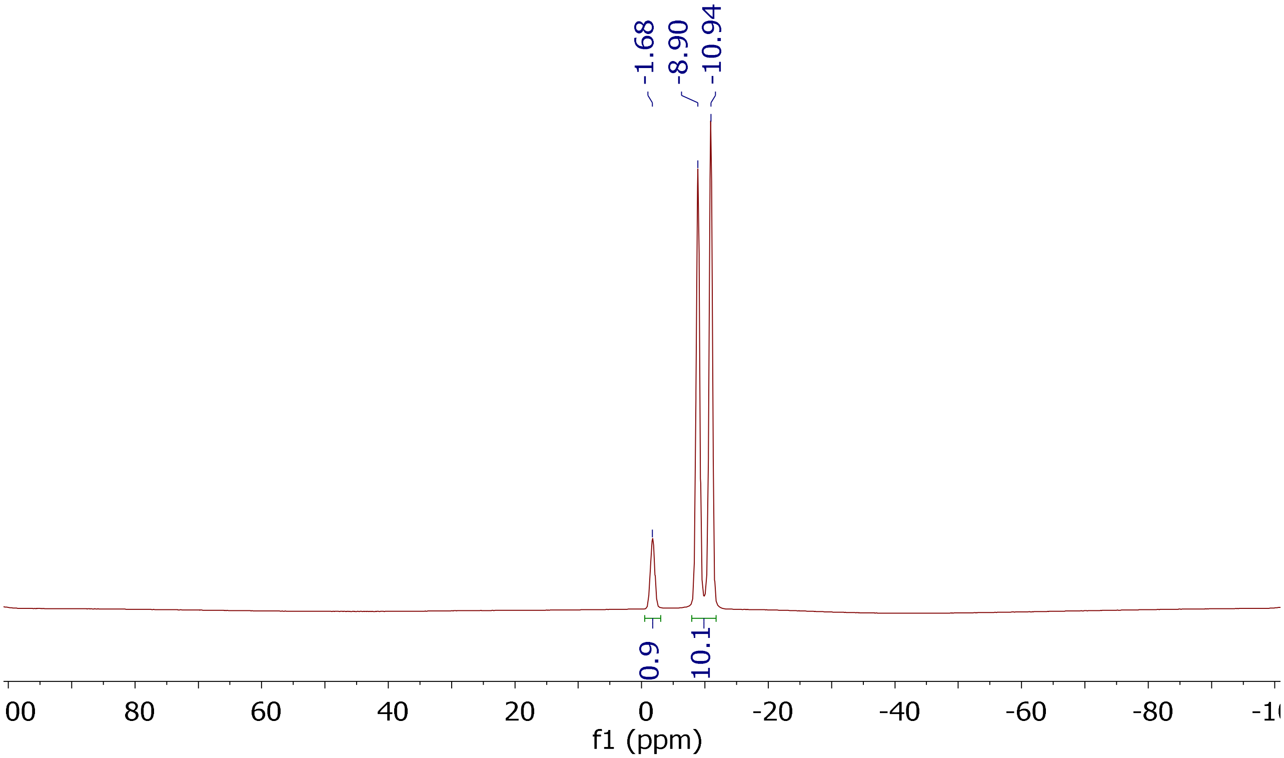


Figure 32: ^{11}B NMR spectrum of compound **d** in d_6-Acetone

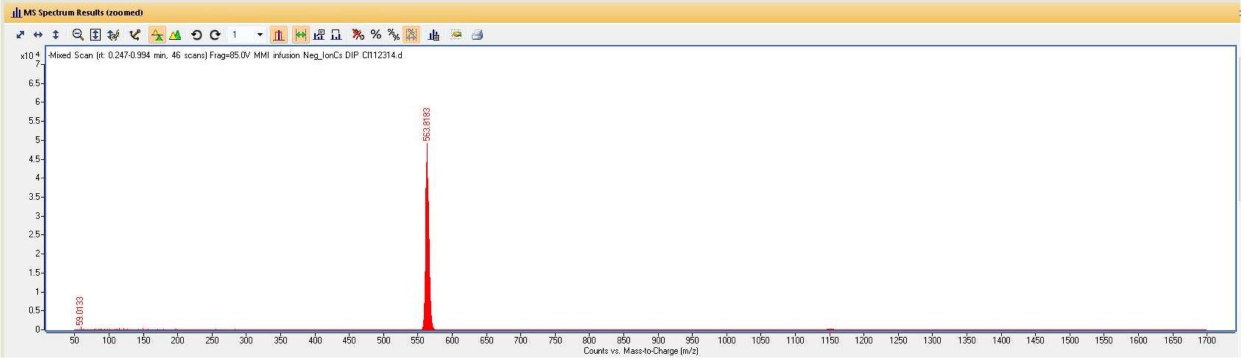


Figure 33: HRMS spectrum of compound **d**

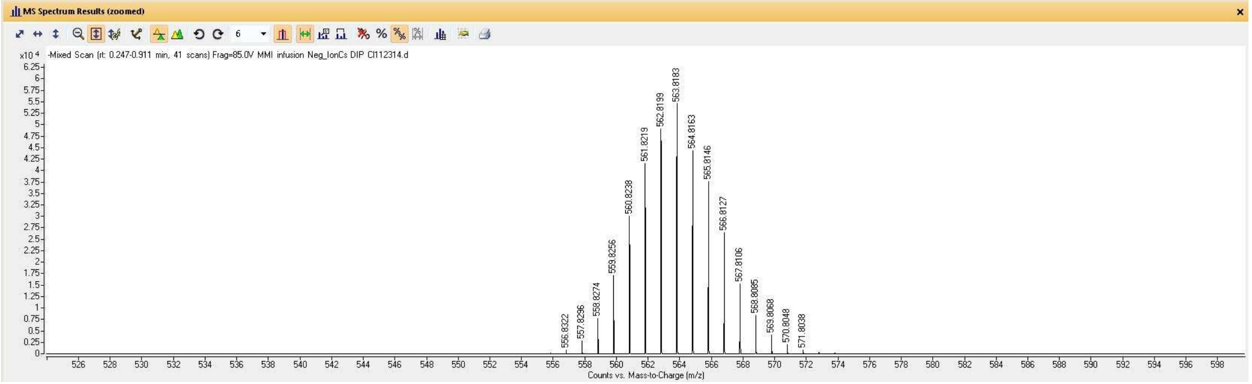
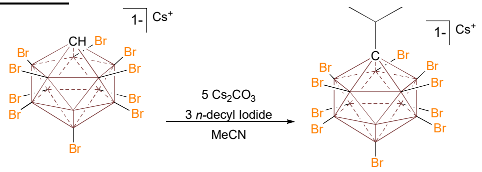


Figure 34: Zoomed in HRMS spectrum of compound **d**

Purification and Characterization of **e**



Electrophile: isopropyl iodide. The recovered oily solid was triturated with hexanes and filtered. The filtered solid was then washed through the filter with acetone and pumped dry yielding Cs[$C_3H_5CB_{11}Br_{11}$] in 89% yield.

^{1}H NMR (600 MHz, Acetone-d_6) δ 3.12 (hept, J = 7.3 Hz, 1H), 1.61 (d, J = 7.2 Hz, 6H)

^{13}C NMR (151 MHz, Acetone) δ 42.03, 23.86.

^{11}B NMR (128 MHz, Acetone) δ -2.52, -8.87, -12.14.

m/z calcd for $C_3H_7CB_{11}Br_{11}^-$:1052.2564 Found: 1052.2403

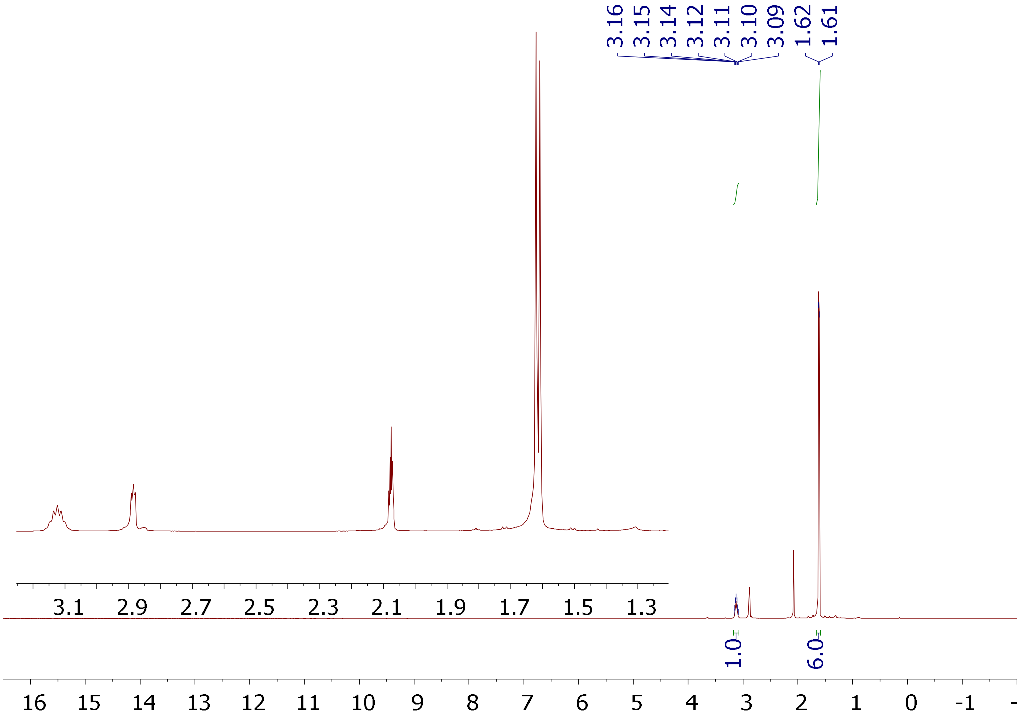


Figure 35: ^{1}H NMR spectrum of compound **e** in d_6-Acetone

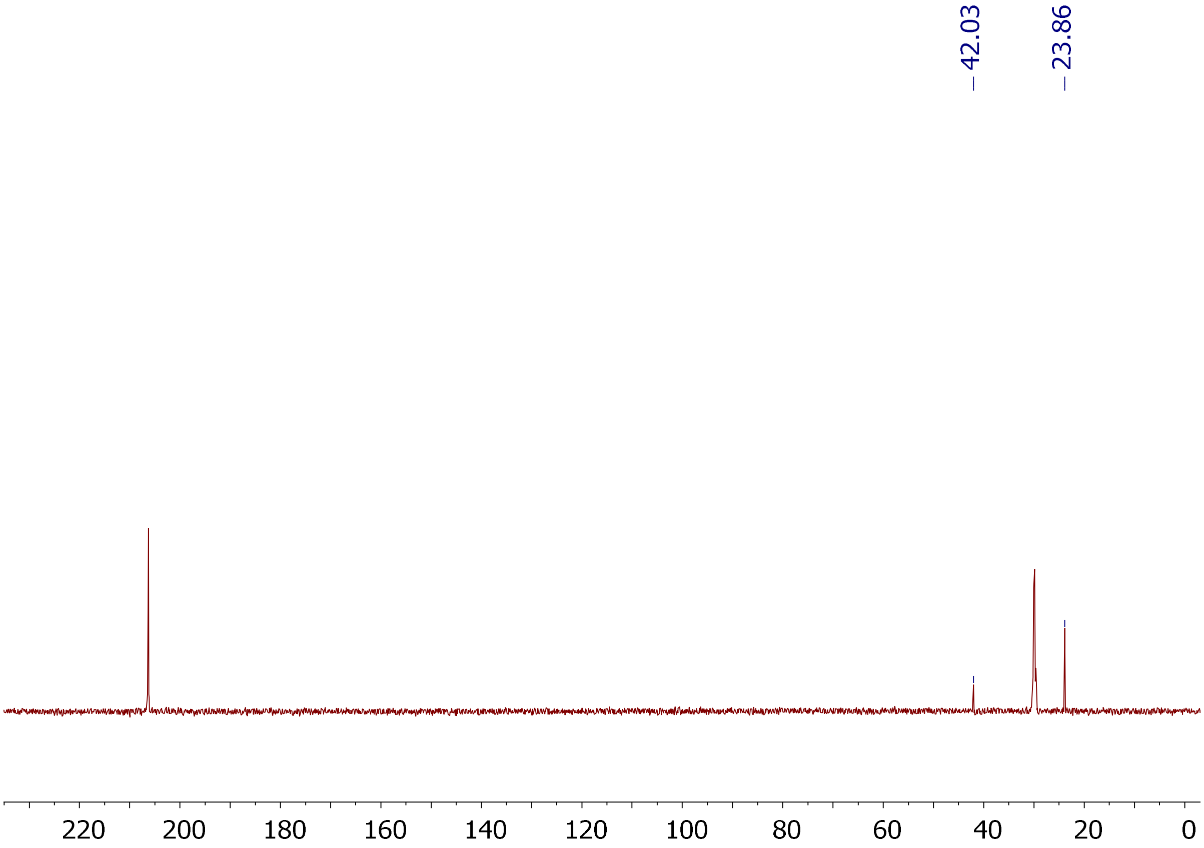


Figure 36: ^{13}C NMR spectrum of compound **e** in d_6-Acetone

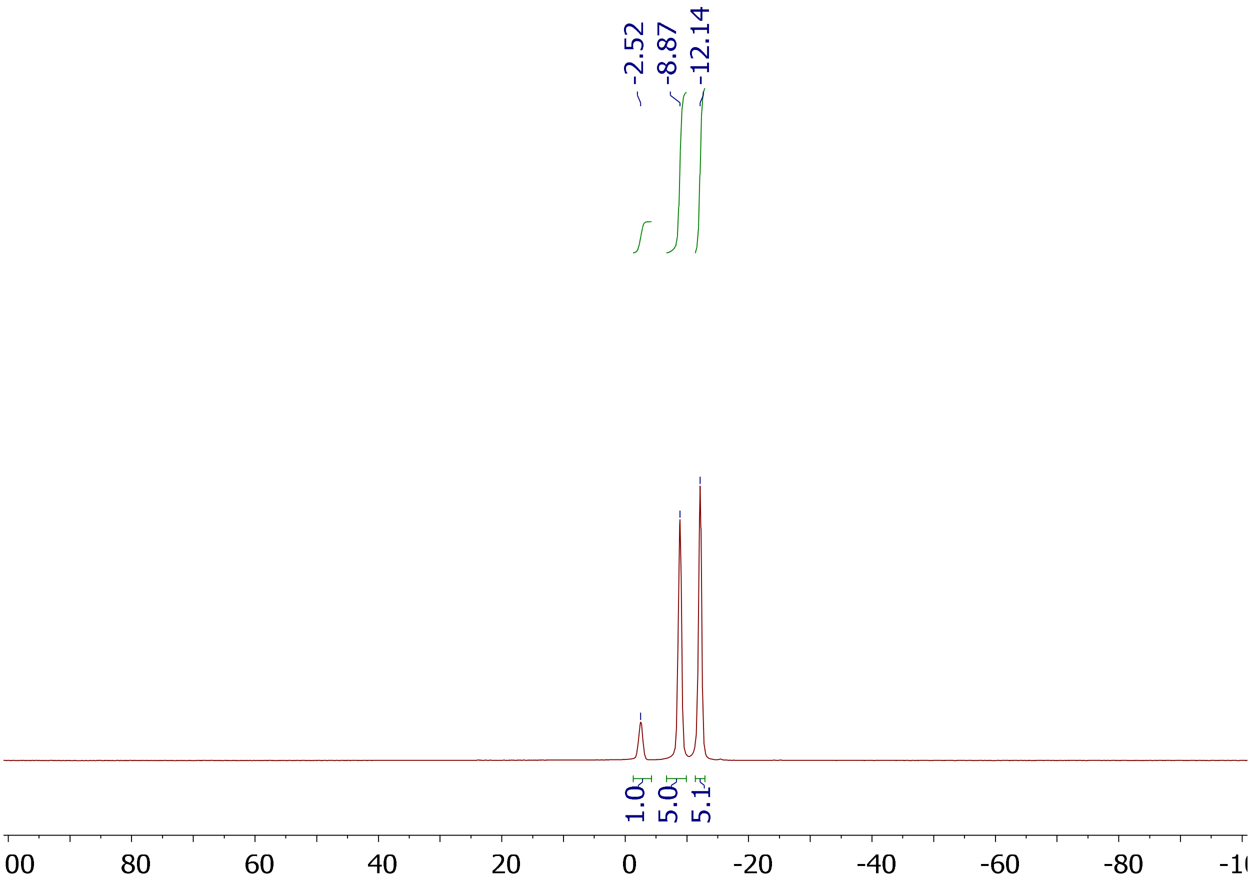
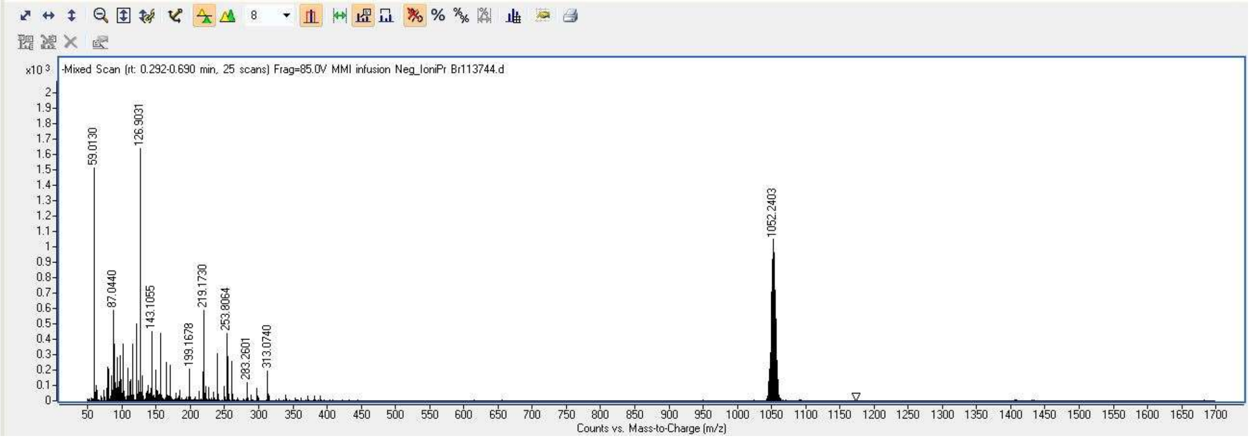


Figure 37: ^{11}B NMR spectrum of compound **e** in d$_6$-Acetone



-Mixed Scan (rt: 0.292-0.690 min, 25 scans) Frag=85.0V MMI infusion Neg_IoniPr Br113744.d

Figure 38: HRMS spectrum of **e**

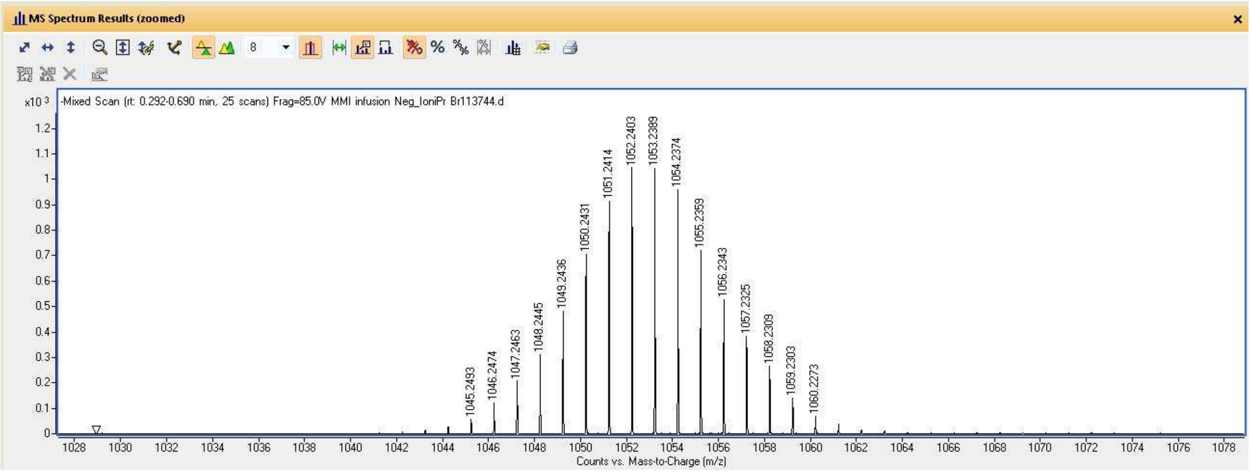
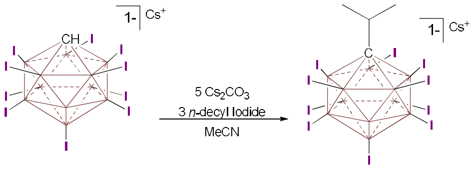


Figure 39: Zoomed in HRMS spectrum of **e**

Characterization of **f**



Electrophile: isopropyl iodide. Conversion to **f** is estimated from ^{11}B NMR and presence of product is confirmed by HRMS.

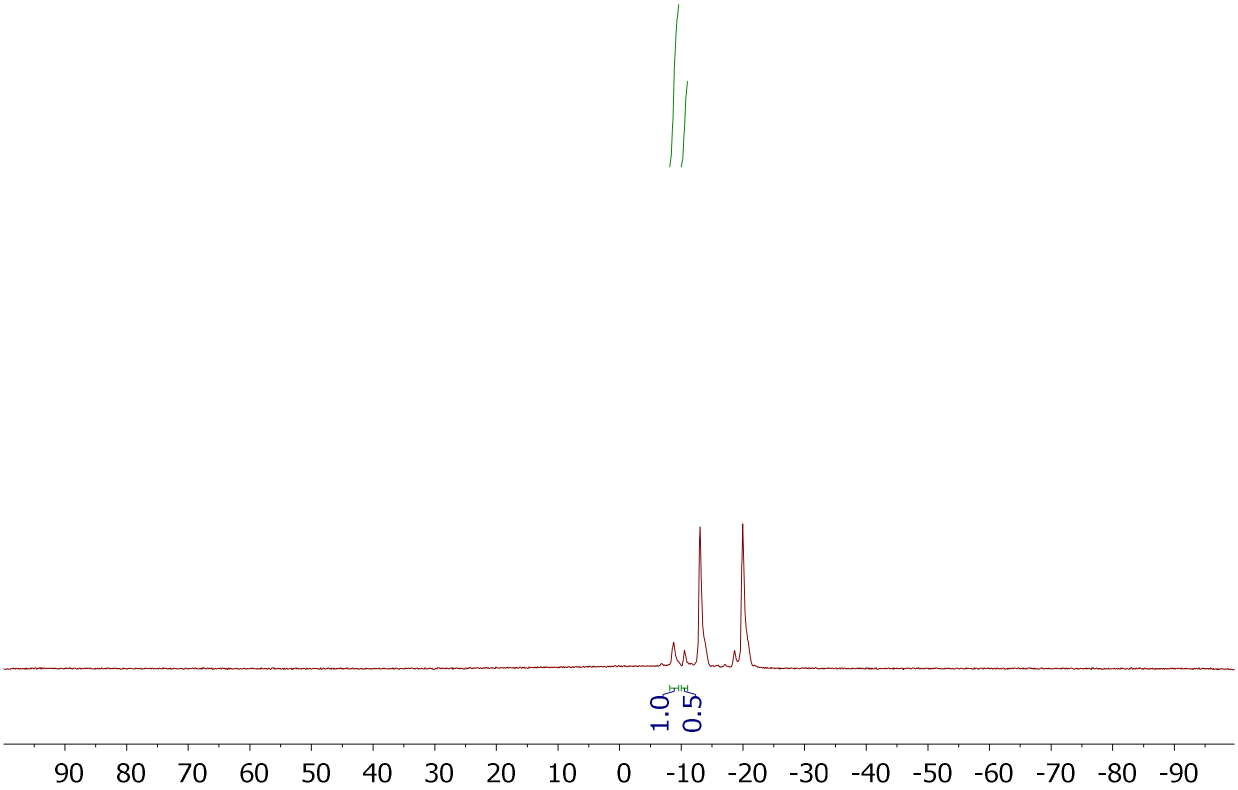
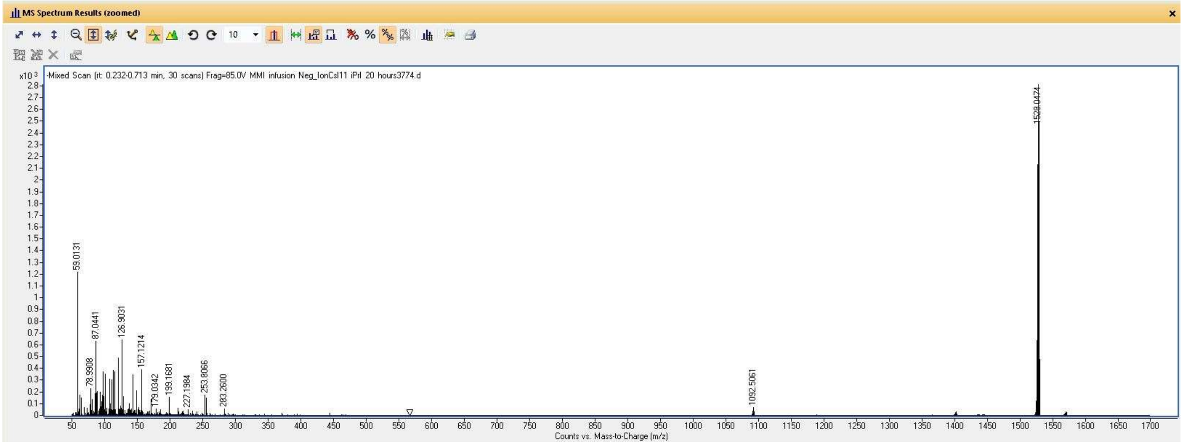


Figure 40: ^{11}B NMR spectrum of a crude mixture of compound **f** and starting materials after reacting 1 week at 85°C



-Mixed Scan (rt: 0.232-0.713 min, 30 scans) Frag=85.0V MMI infusion Neg_IonCsI11 iPrI 20 hours3774.d

Figure 41: HRMS spectrum of crude reaction mixture

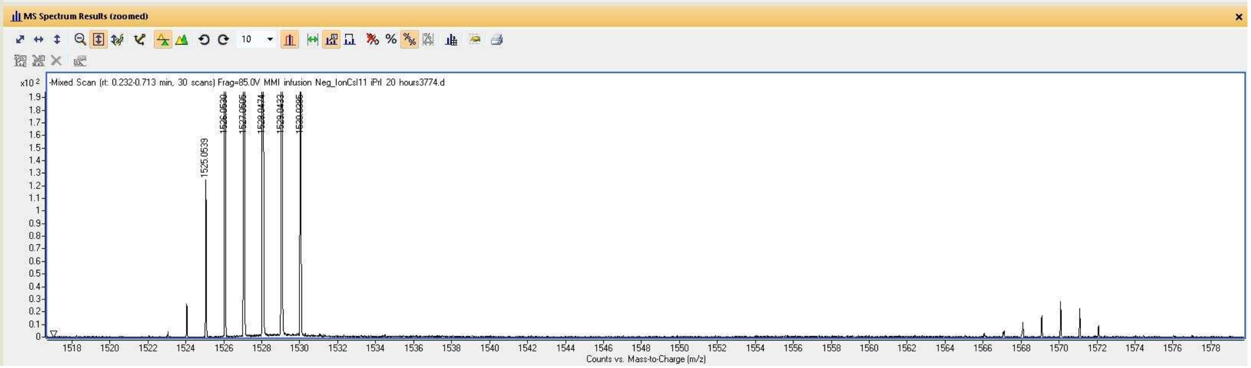
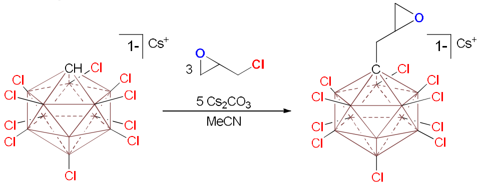


Figure 42: zoomed in HRMS spectrum of crude reaction mixture

Purification and Characterization of **g**



Electrophile: epichlorohydrin. The recovered oily solid was triturated with hexanes and filtered. The filtered solid was then washed through the filter with acetone and pumped dry yielding Cs[$C_3H_5OCB_{11}Cl_{11}^-$] in 89% yield.

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 3.46 (dtd, *J* = 7.9, 3.9, 2.5 Hz, 1H), 2.77 (ddd, *J* = 4.9, 3.8, 1.1 Hz, 1H), 2.72 (dd, *J* = 15.6, 3.9 Hz, 1H), 2.57 (dd, *J* = 4.9, 2.5 Hz, 1H), 2.01 (dd, *J* = 15.6, 8.0 Hz, 1H).

^{13}C NMR (151 MHz, Acetone) δ 50.39, 47.42, 34.71.

^{11}B NMR (192 MHz, Acetone-*d*$_6$) δ -2.28, -9.78, -11.65.

m/z calcd for : 577.7920   Found: 577.7945

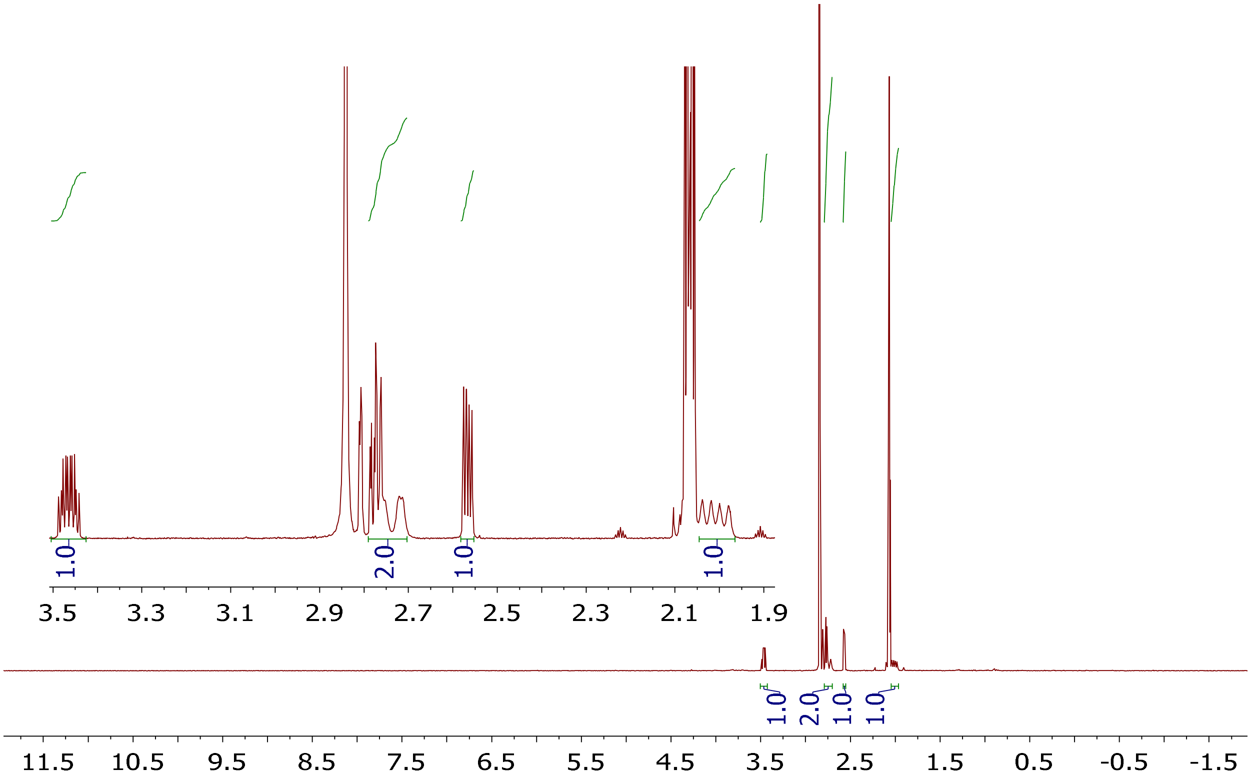


Figure 43: ^{1}H NMR spectrum of compound **g** in d_6-Acetone

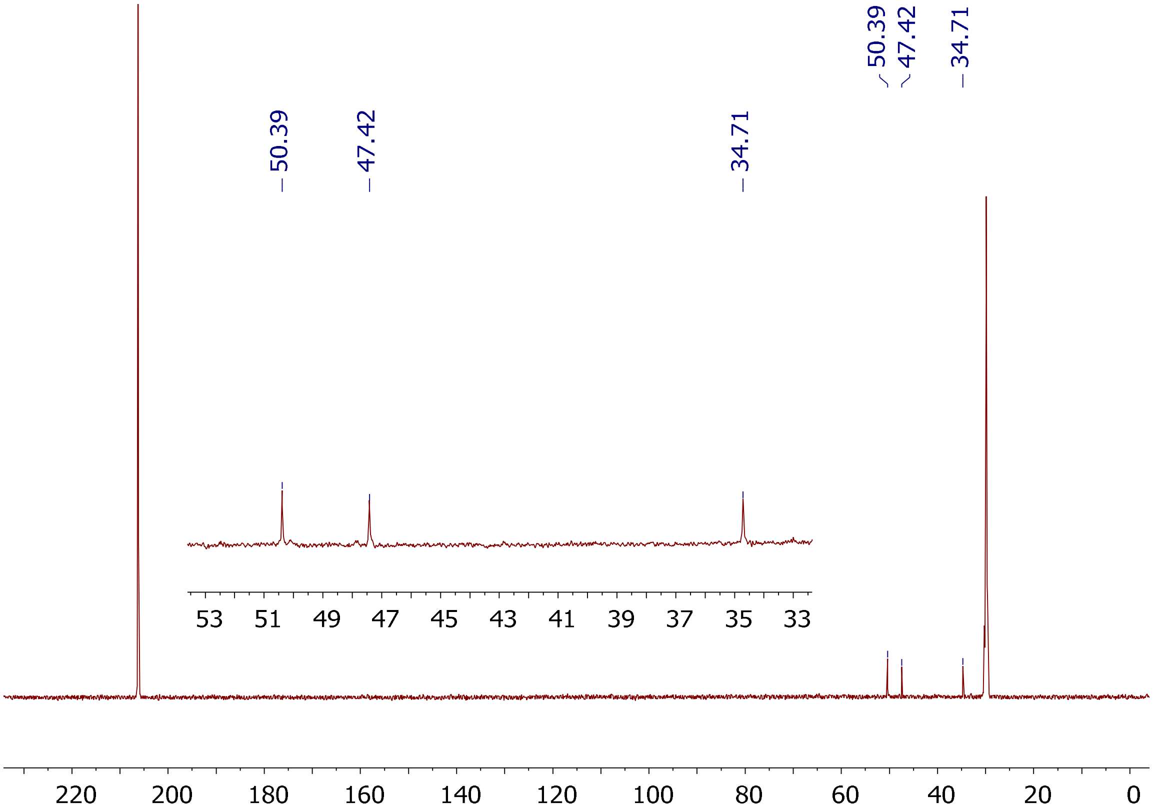


Figure 44: ^{13}C NMR of **3** in d_6-Acetone

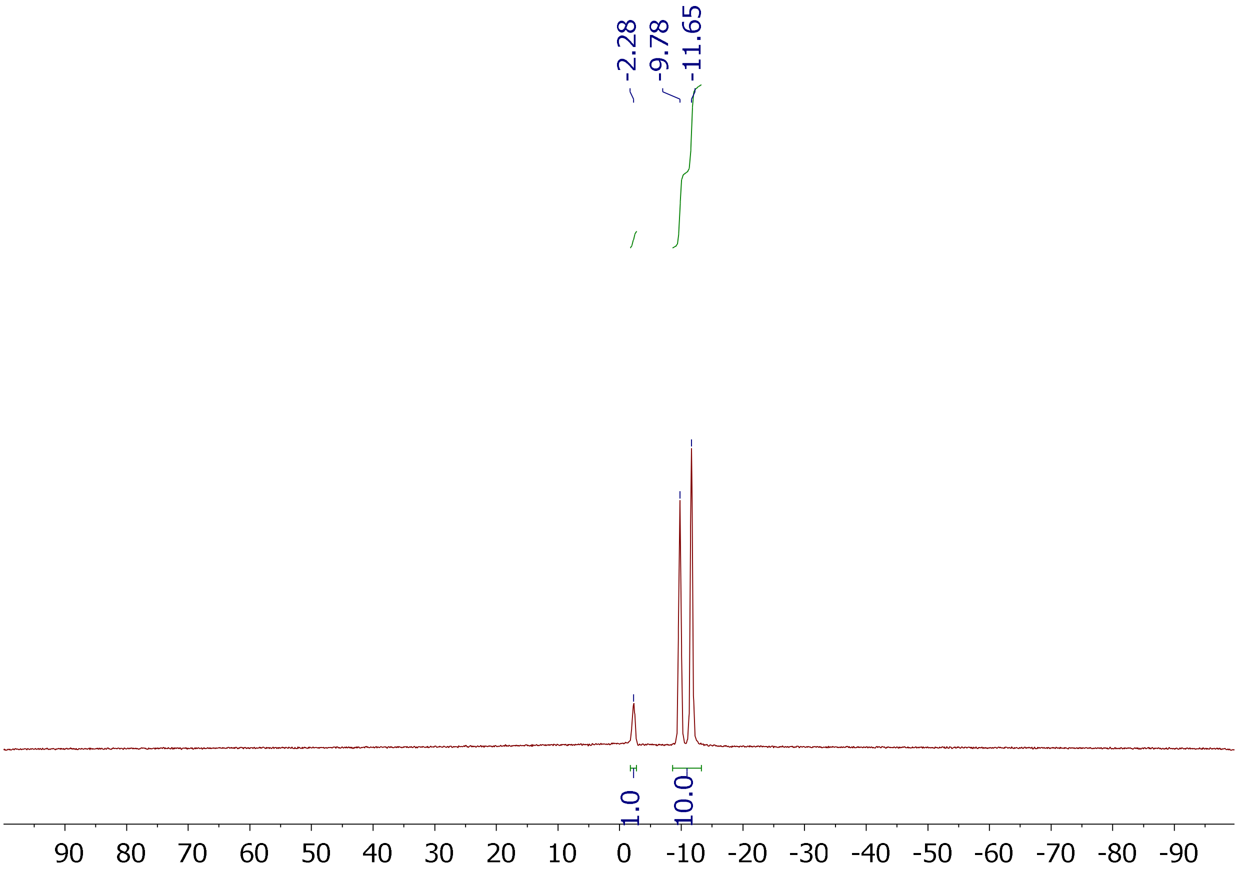
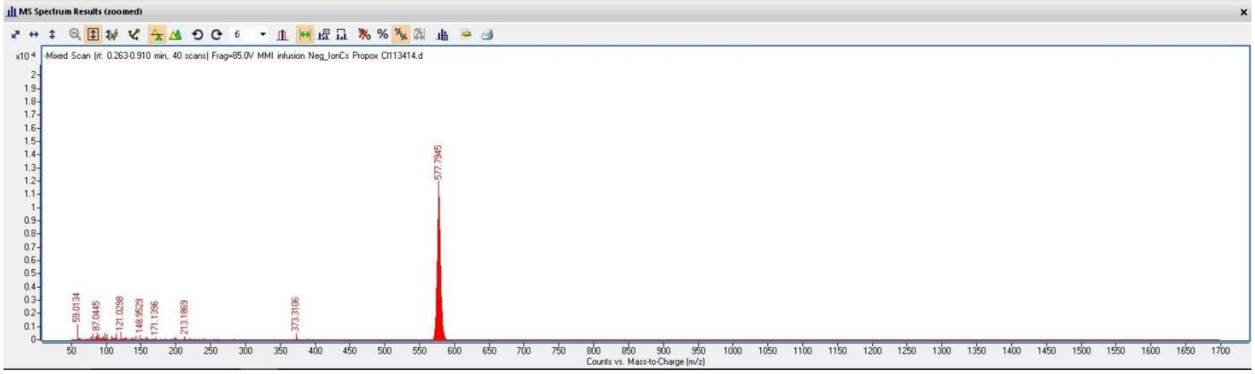


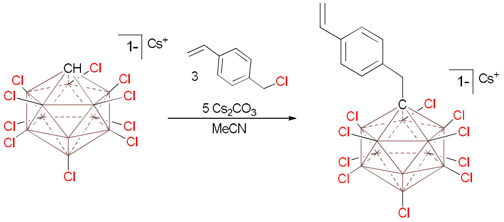
Figure 45: ^{11}B NMR spectrum of compound **g** in d_6-Acetone



-Mixed Scan (rt: 0.263-0.910 min, 40 scans) Frag=85.0V MMI infusion Neg_IonCs Propox CI113414.d

Figure 46: HRMS spectrum of **g**

Purification and Characterization of **h**



Electrophile used: 90% Vinylbenzyl chloride. The recovered oily solid was triturated with hexanes and filtered. The filtered solid was then washed through the filter with acetone and pumped dry yielding Cs[$C_9H_9CB_{11}Cl_{11}$] in 96% yield.

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.74 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.82 (dd, *J* = 17.6, 1.1 Hz, 1H), 5.23 (dd, *J* = 10.9, 1.0 Hz, 1H), 3.66 (s, 2H).

^{13}C NMR (101 MHz, Acetone) δ 137.67, 137.49, 134.88, 131.50, 125.59, 114.18, 36.28.

^{11}B NMR (192 MHz, Acetone) δ -2.38, -9.84, -11.53.

m/z calcd for $C_9H_9CB_{11}Cl_{11}^-$: 637.8284 Found: 637.8326

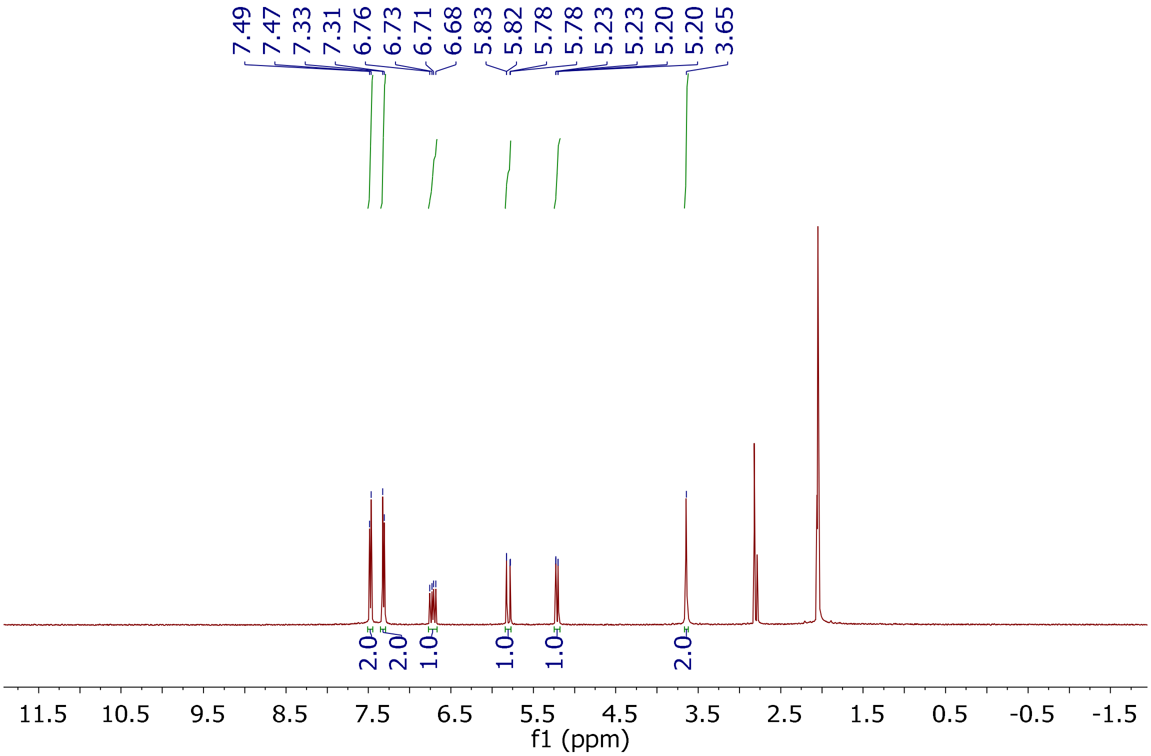


Figure 47: ^{1}H NMR of **h** in d$_6$-Acetone

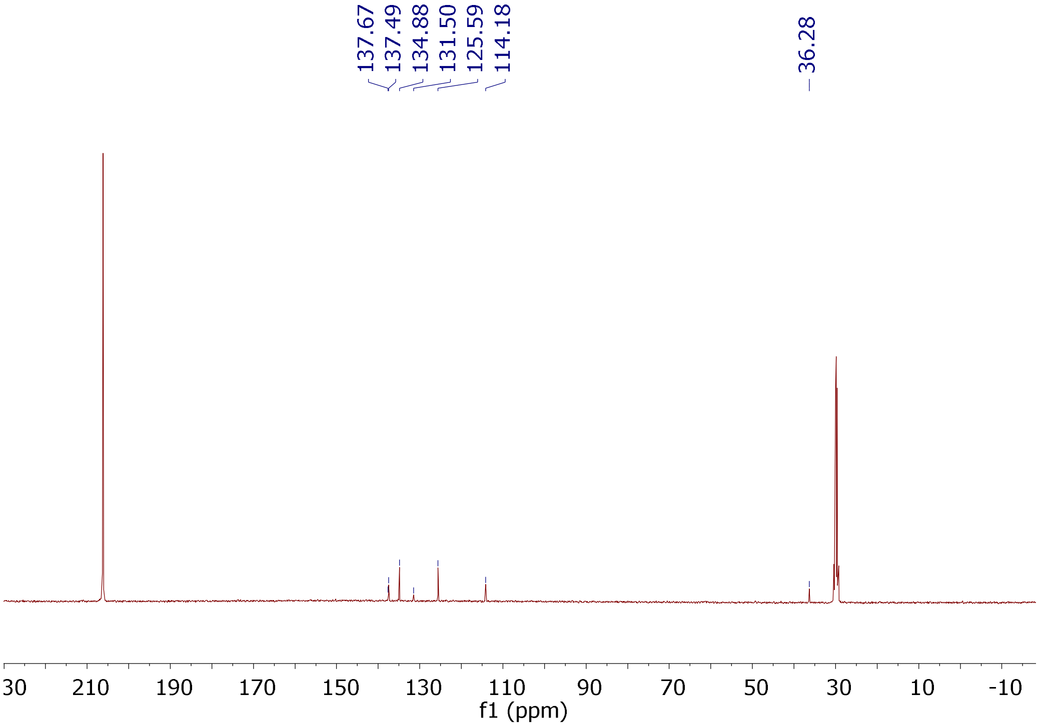


Figure 48: ^{13}C NMR of **h** in d_6-Acetone

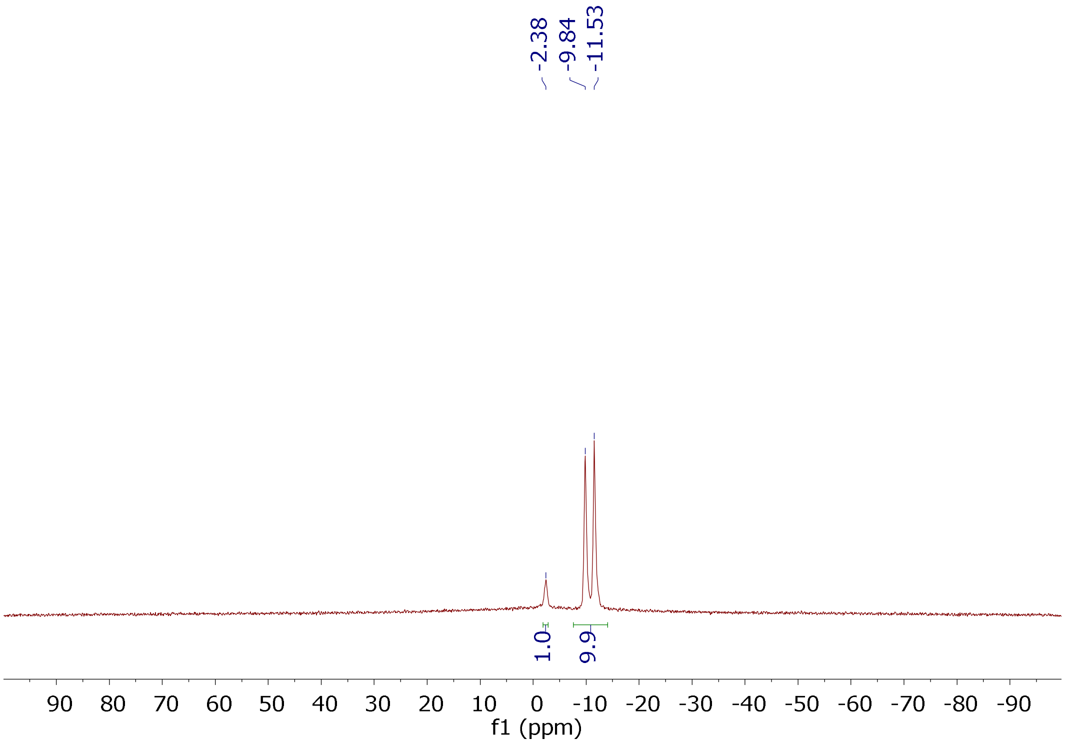


Figure 49: ^{11}B NMR of **h** in acetone

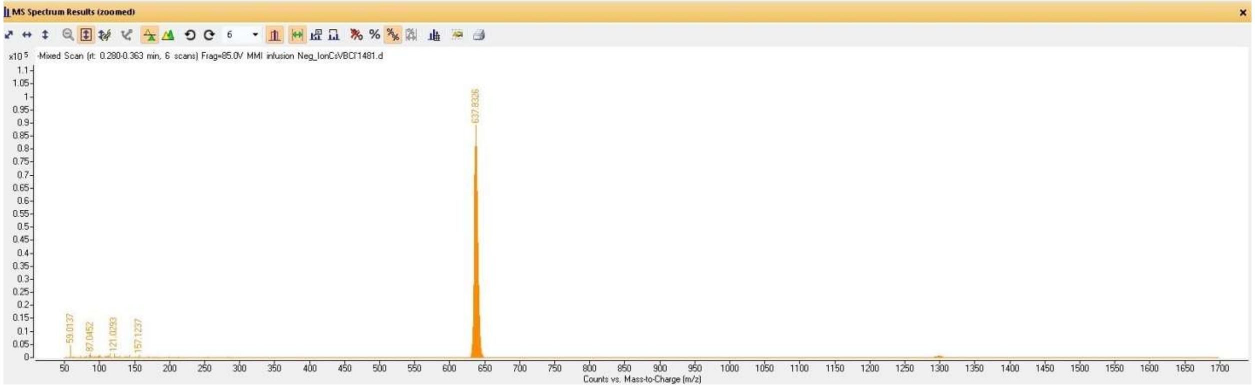


Figure 50: HRMS spectrum of compound **h**

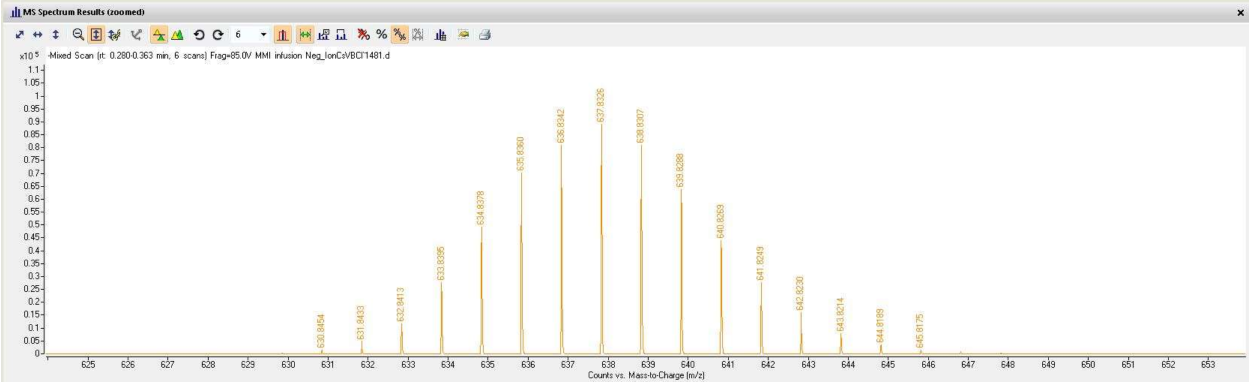
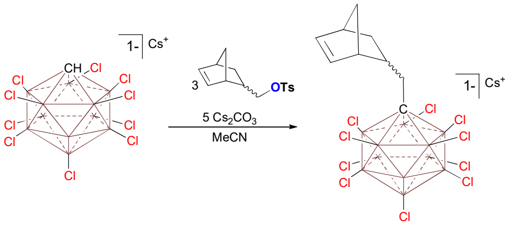


Figure 51: Zoomed in HRMS spectrum of compound **h**

Purification and Characterization of **i**



Electrophile: (1S,4S)-bicyclo[2.2.1]hept-5-en-2-ylmethyl 4-methylbenzenesulfonate. Diethyl ether was added to the recovered oily solid until a suspension formed consisting of mostly CsOTs. Absence of CsOTs was confirmed by ^{1}H NMR before filtering. The filtrate had its solvent removed *in vacuo* before being washed with a mixture of dichloromethane and hexanes.

^{1}H NMR (400 MHz, Acetone-d_6) δ 6.26 – 6.22 (dd, *J* = 5.7, 3.0 Hz), 6.10 (dd, *J* = 5.7, 3.0 Hz), 6.04 (dd, *J* = 5.8, 2.9 Hz), 2.98 – 2.90 (m), 2.78 (m), 2.57 – 2.22 (m), 1.51 (ddd, *J* = 11.2, 8.2, 2.4 Hz), 1.38 – 1.20 (m), 0.79 – 0.67 (m).

^{13}C NMR (101 MHz, Acetone-d_6) δ 139.49, 137.72, 137.21, 132.68, 52.11, 50.51, 49.92, 48.77, 45.87, 44.08, 42.55, 38.24, 37.94, 36.47, 33.88, 33.73.

^{11}B NMR (128 MHz, Acetone) δ 0.03, -7.17, -8.97.

$C_8H_{11}CB_{11}Cl_{11}^-$: 627.8440 Found: 627.8473

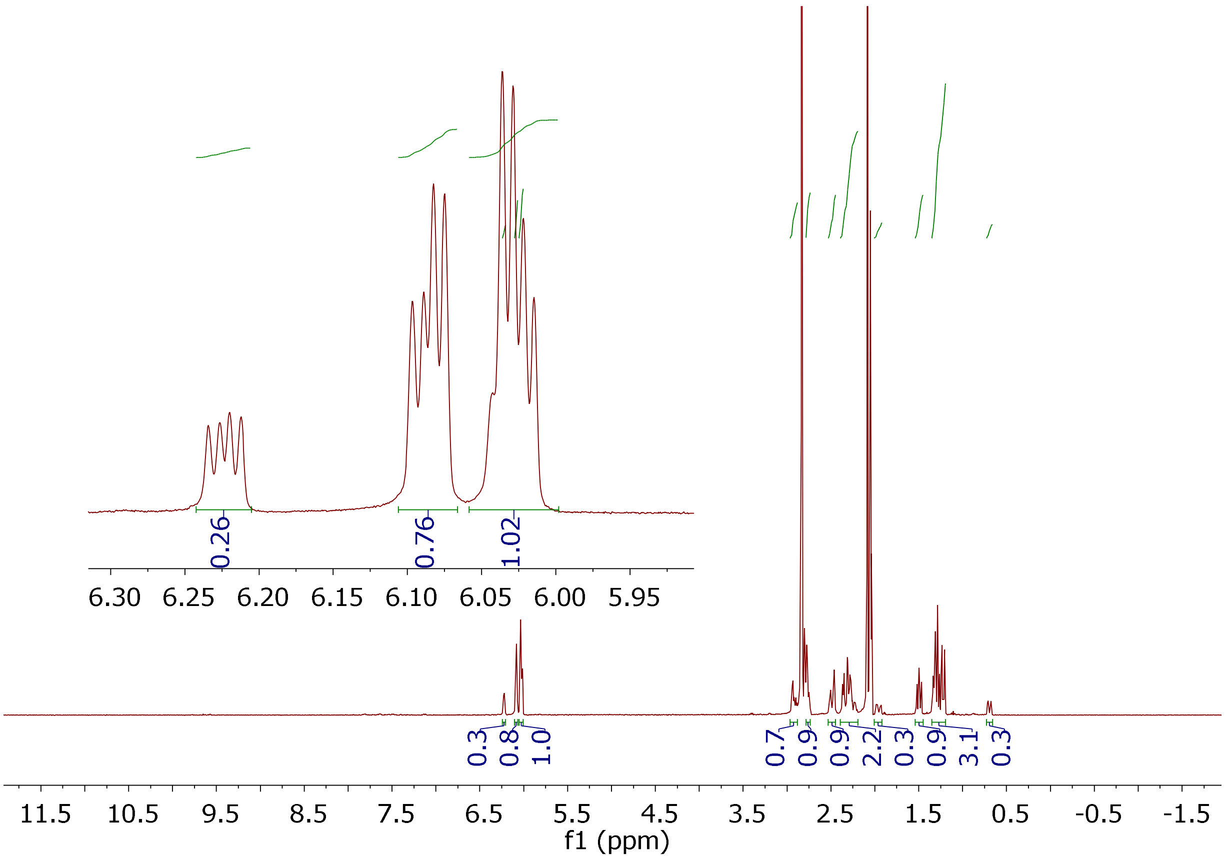


Figure 52: ^{1}H NMR spectrum of **i** in d_6-Acetone

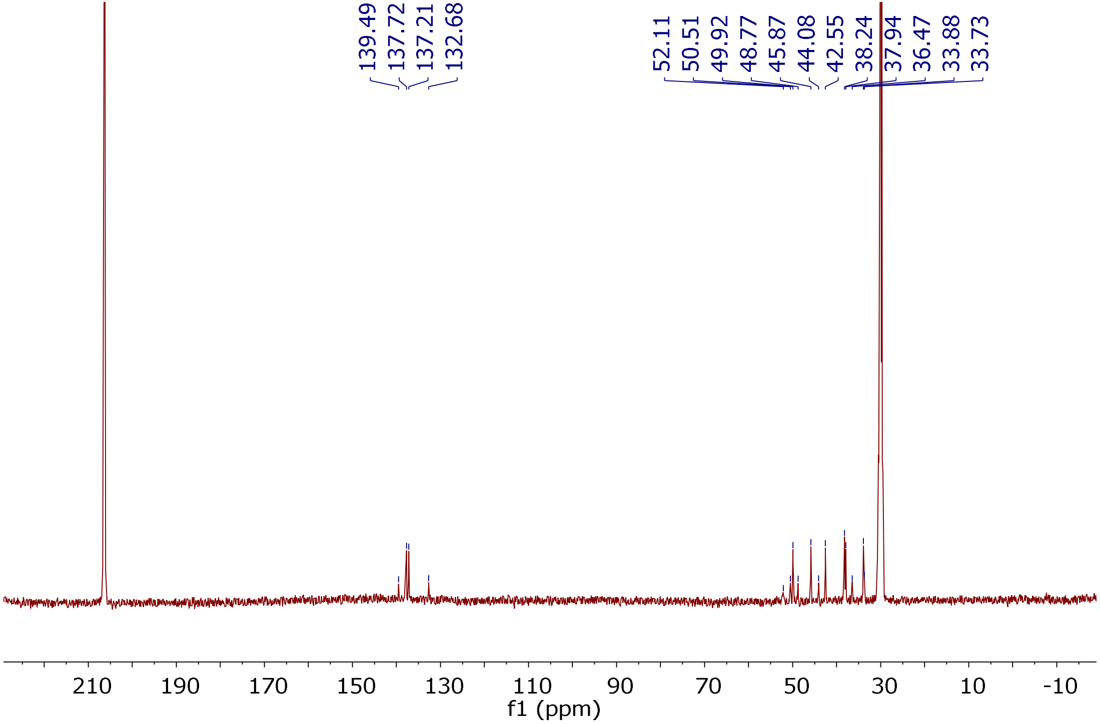


Figure 53: ^{13}C NMR of **i** in d_6-Acetone

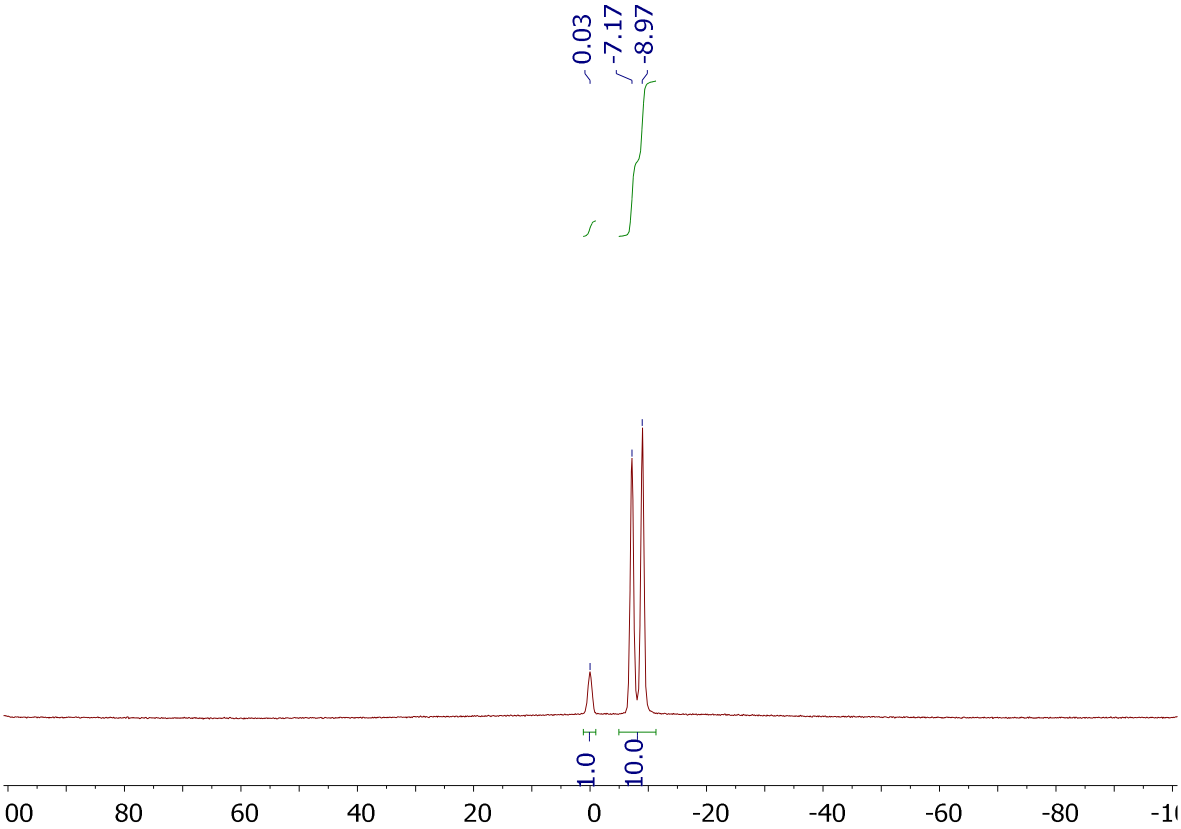
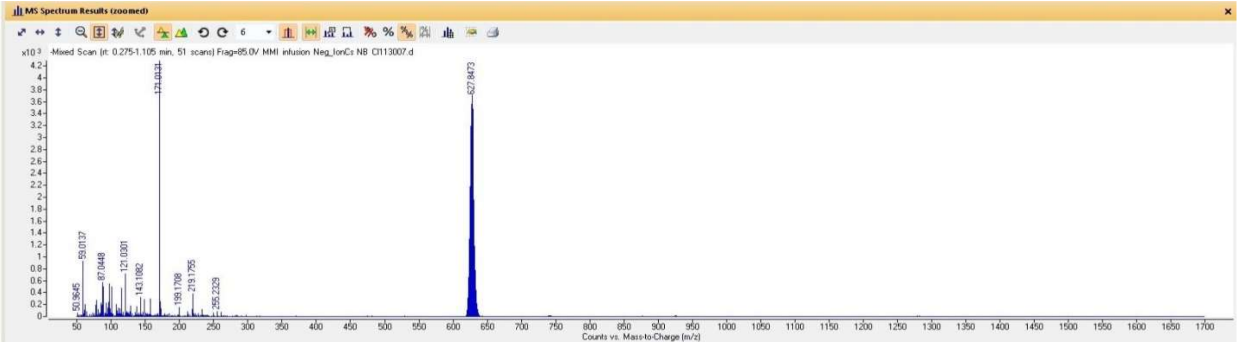


Figure 54: ^{11}B NMR of **i** in d_6-Acetone



-Mixed Scan (rt: 0.275-1.105 min, 51 scans) Frag=85.0V MMI infusion Neg_IonCs NB CI113007.d

Figure 55: HRMS spectrum of **i**

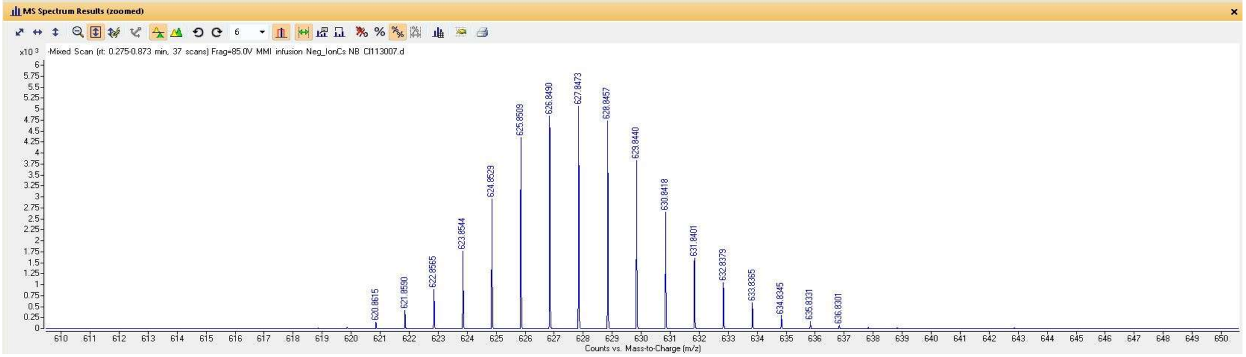
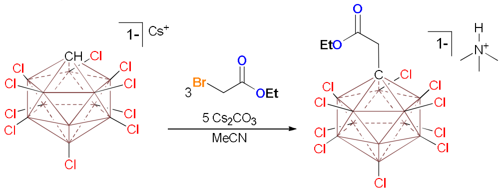


Figure 56: Zoomed in HRMS spectrum of **i**

Purification and Characterization of **j**



Electrophile: ethyl bromoacetate. The recovered solid was triturated with hexanes and filtered. The solid was collected and dissolved in warm water. 15 equivalents of trimethylammonium hydrochloride was added and allowed to cool while stirring. The white solid was filtered and compound **j** was collected in 95% yield.

^{1}H NMR (600 MHz, Acetone-*d*$_6$) δ 4.07 (q, *J* = 7.2 Hz, 2H), 3.22 (s, 9H), 3.08 (s, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 165.57, 61.96, 46.39, 35.08, 14.32.

^{11}B NMR (192 MHz, Acetone) δ -2.73, -9.76, -11.79.

m/z calculated $C_4H_7O_2CB_{11}Cl_{11}^-$: 607.8026 Found: 607.7981

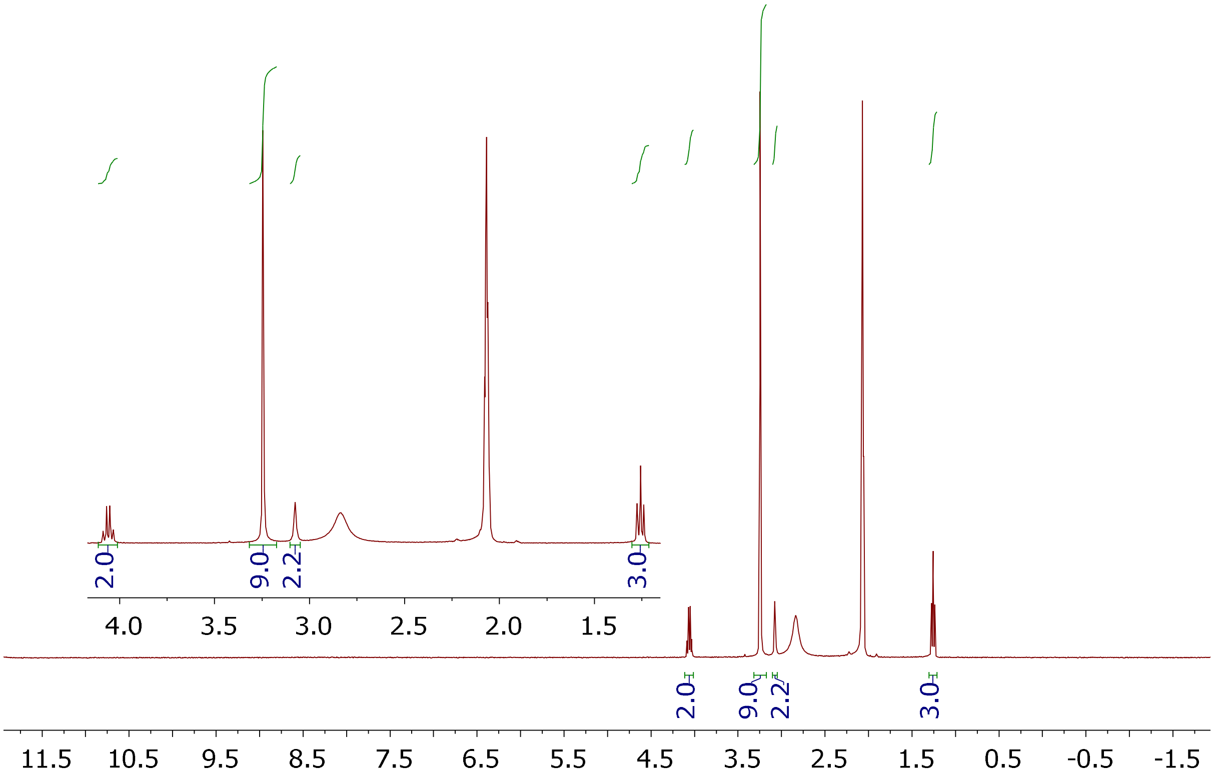


Figure 57: ^{1}H NMR of **j** in d_6-Acetone. Water signals appear at ~2.8 ppm and are broadened due to exchange with $HNMe_3^+$ cation

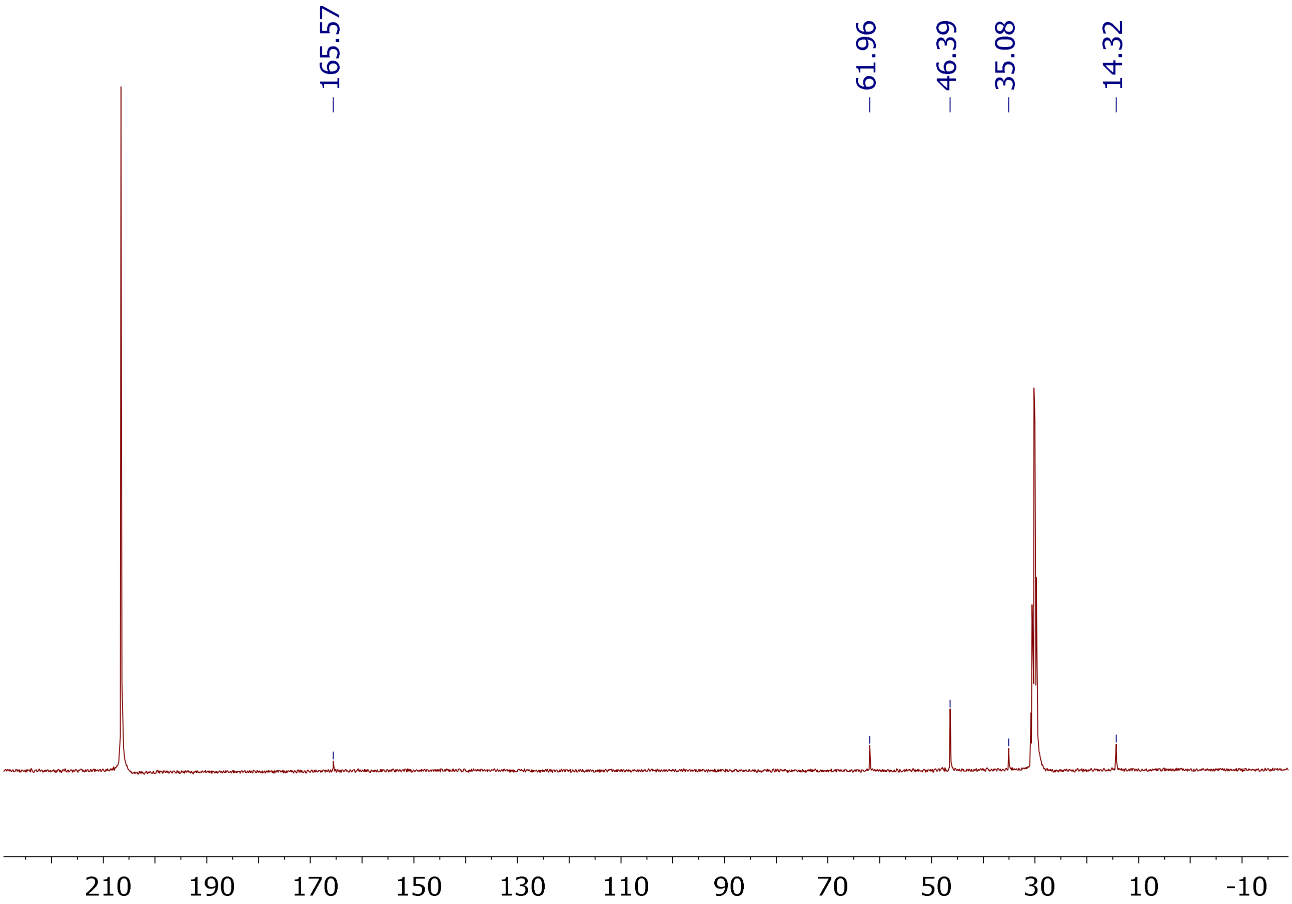


Figure 58: ^{13}C NMR of **j** in d$_6$-Acetone

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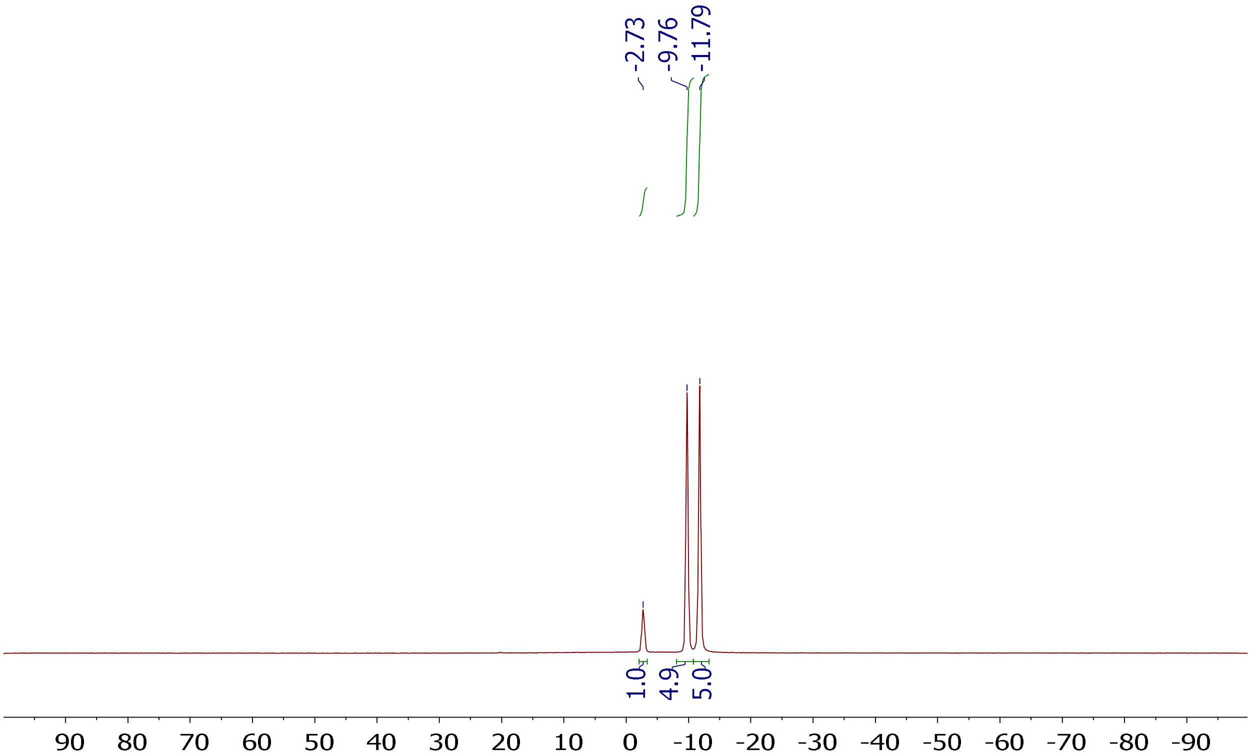
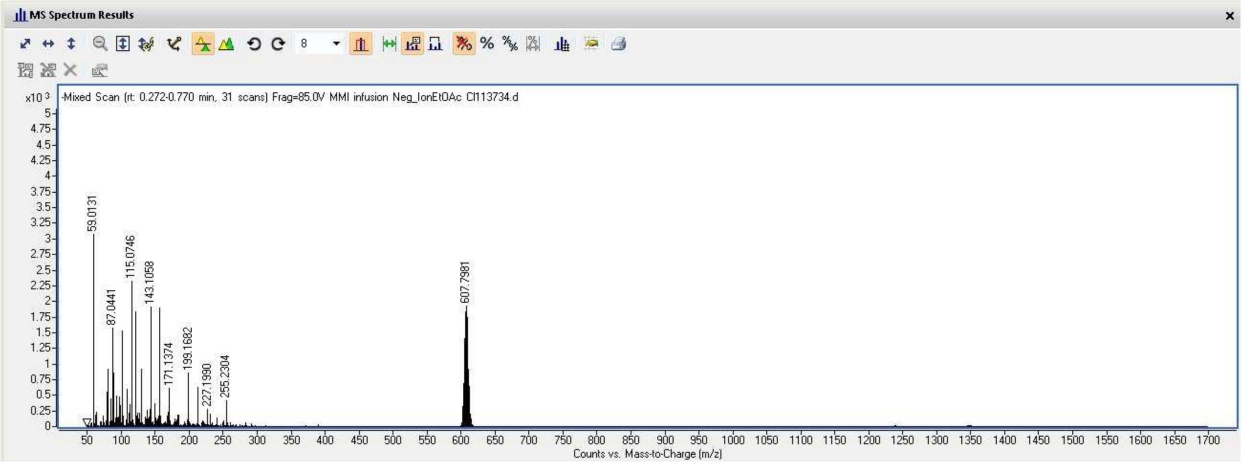


Figure 59: ^{11}B NMR of **j** in acetonitrile



-Mixed Scan (rt: 0.272-0.770 min, 31 scans) Frag=85.0V MMI infusion Neg_IonEtOAc CI113734.d

Figure 60: HRMS spectrum of **j**

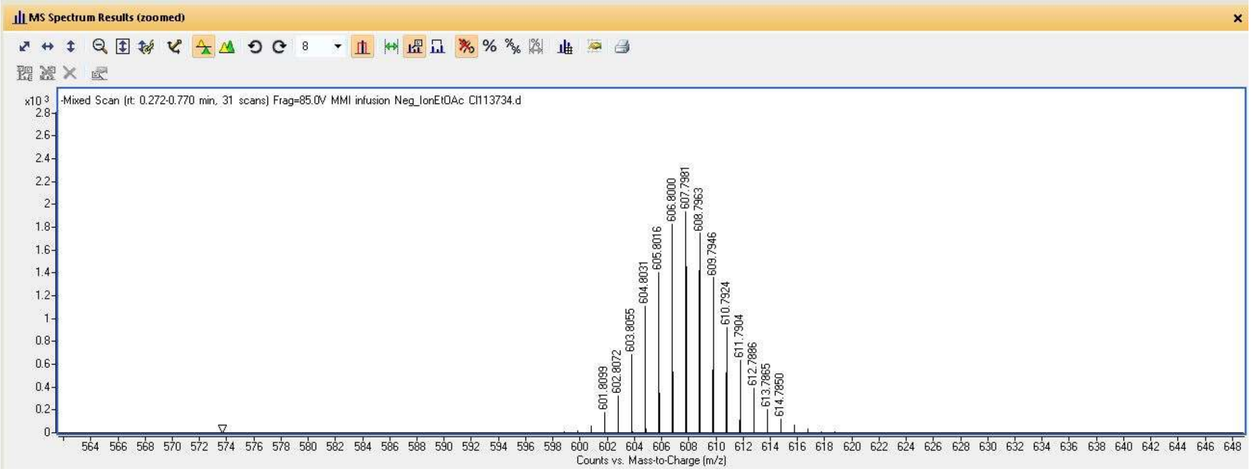
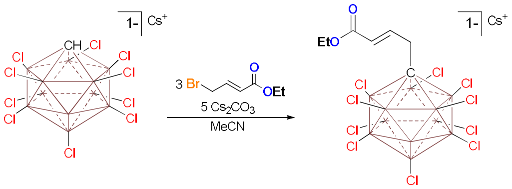


Figure 61: Zoomed in HRMS spectrum of **j**

Purification and Characterization of **k**



Electrophile: 75% tech. grade Ethyl 4-bromocrotonate. The recovered solid was triturated with hexanes and filtered. The solid was collected and dissolved in warm deionized water and filtered while hot. 5 equivalents of CsCl were added and **k** was recrystallized in 72% yield in two combined crops of crystals.

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 7.26 (dt, *J* = 15.5, 7.8 Hz, 1H), 5.96 (dt, *J* = 15.4, 1.5 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 3H), 3.20 (d, *J* = 7.7 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 4H).

^{13}C NMR (101 MHz, Acetone) δ 164.90, 139.68, 125.02, 59.90, 32.65, 13.69.

^{11}B NMR (128 MHz, Acetone) δ -2.50, -10.02, -11.84.

$C_4H_7O_2CB_{11}Cl_{11}^-$: 633.8182 Found: 633. 8247

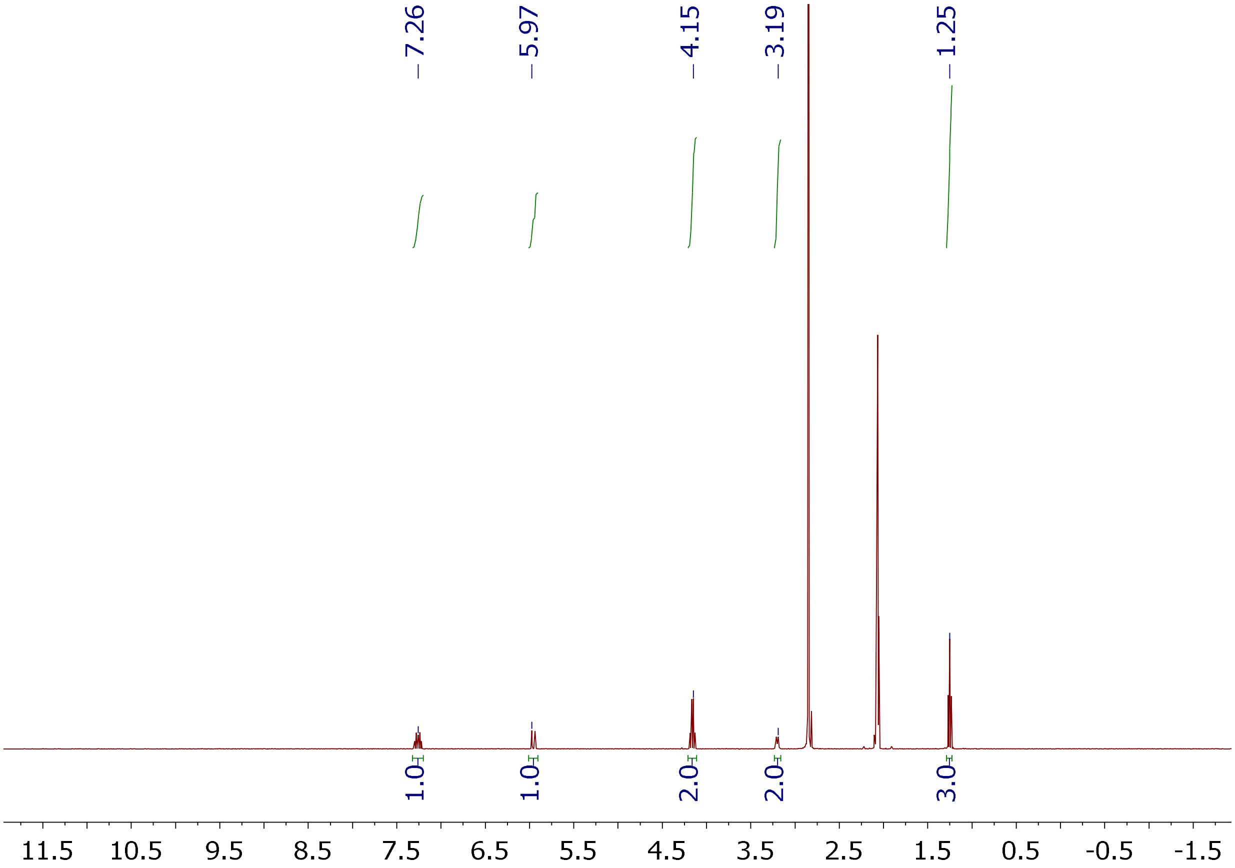


Figure 62: ^{1}H NMR of **k** in d_6-Acetone

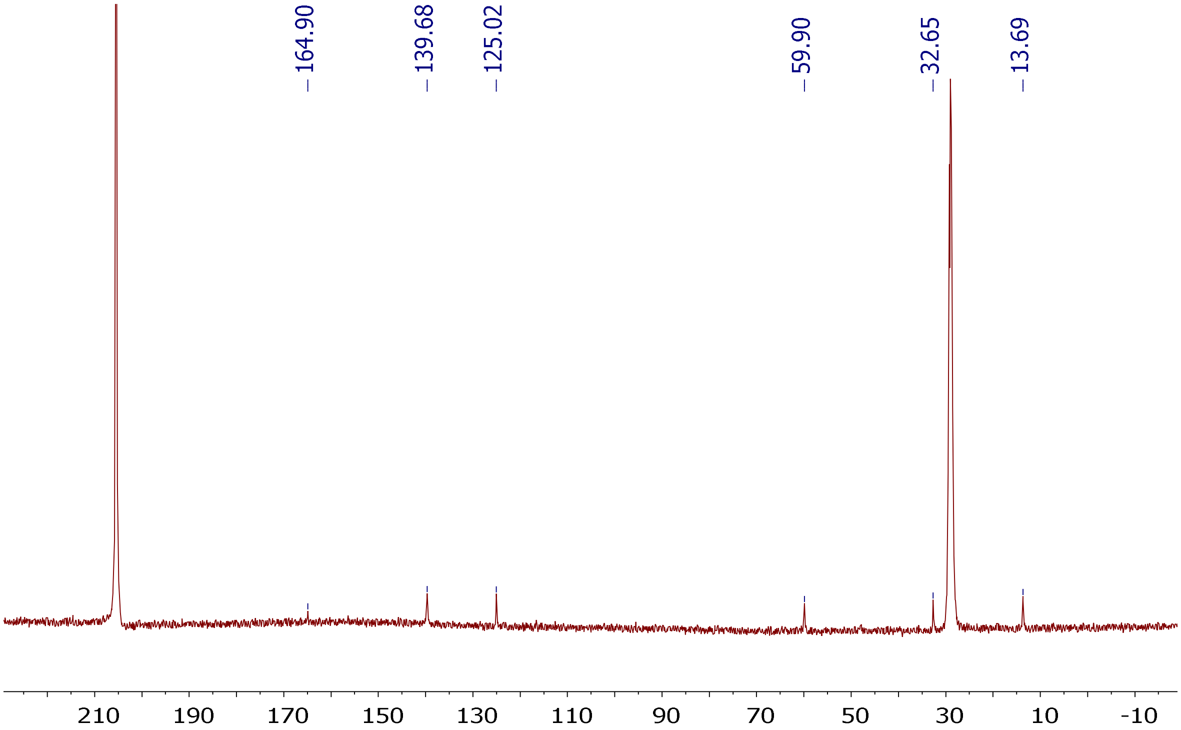


Figure 63: ^{13}C NMR of **k** in d_6-Acetone

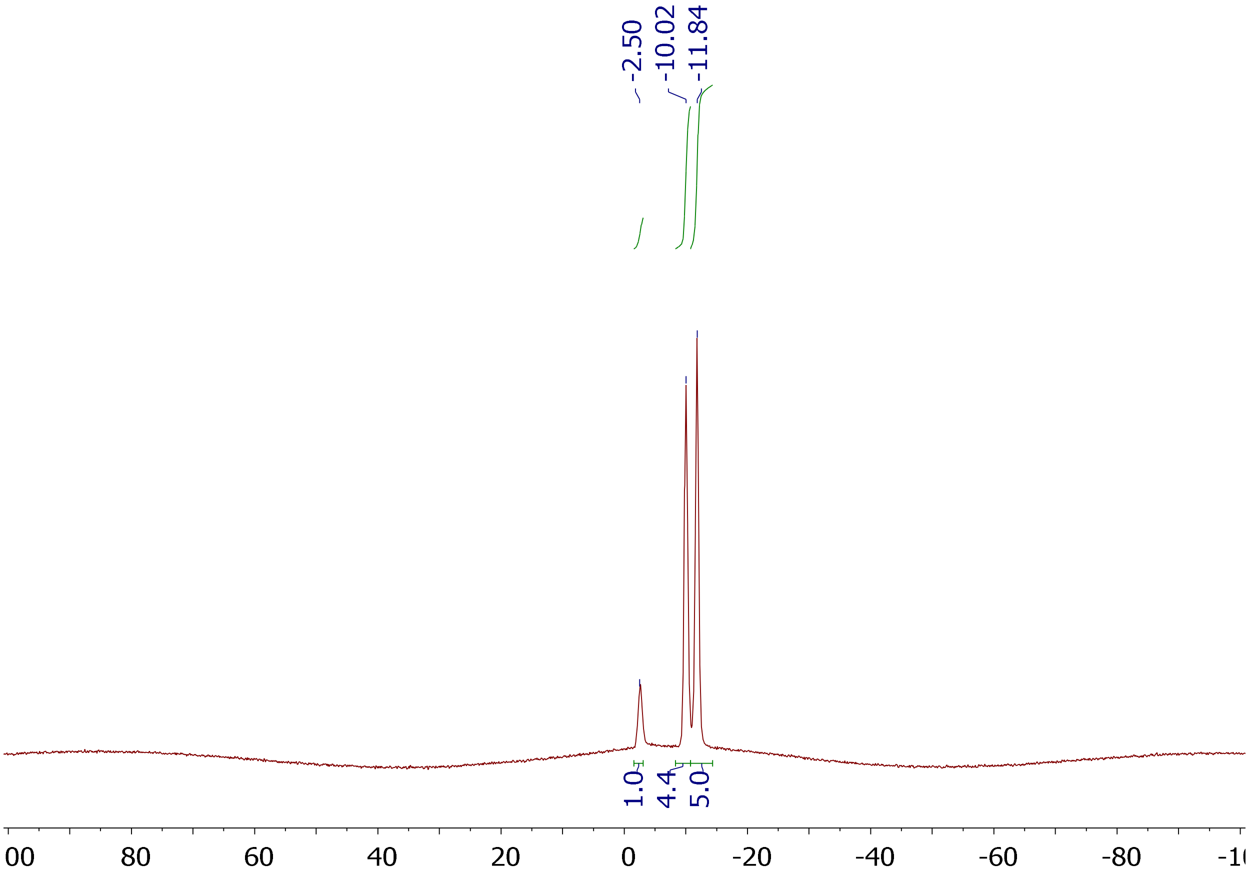
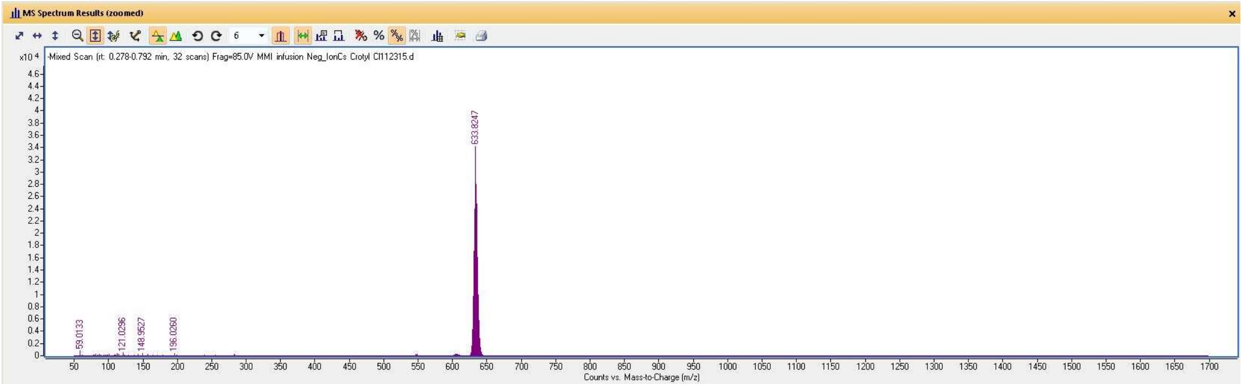


Figure 64: ^{11}B NMR of **k** in Acetone



-Mixed Scan (rt: 0.278-0.792 min, 32 scans) Frag=85.0V MMI infusion Neg_IonCs Crotyl CI112315.d

Figure 65: HRMS spectrum of **k**

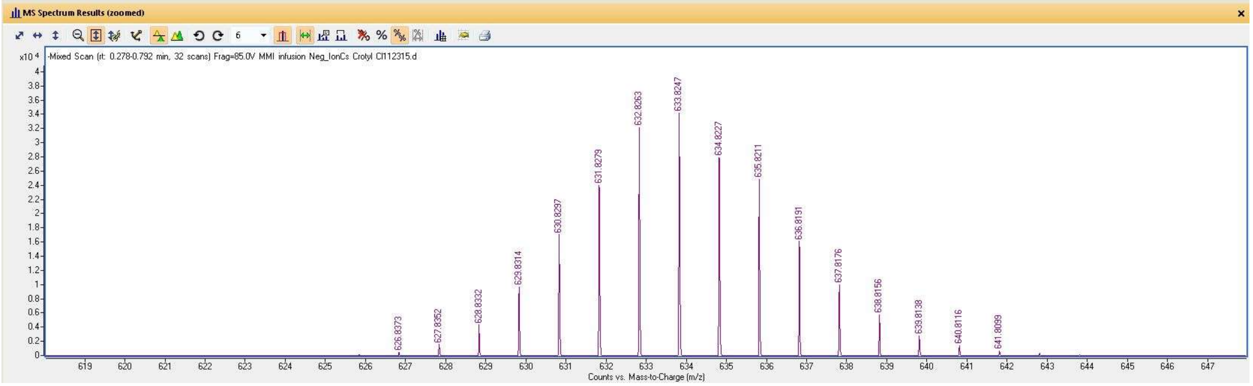
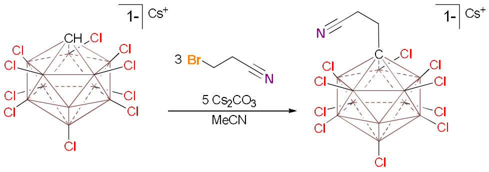


Figure 66: Zoomed in HRMS spectrum of **k**

Purification and Characterization of **l**



Electrophile used: 3-bromopropionitrile. The recovered oily solid was triturated with hexanes and filtered. The filtered solid was then washed through the filter with acetone and pumped dry yielding compound **l** in 92% yield.

^{1}H NMR (600 MHz, Acetone-*d*$_6$) δ 3.13 – 3.07 (m, 2H), 2.70 (m, 2H).

^{13}C NMR (151 MHz, Acetone) δ 118.85, 27.79, 14.07.

^{11}B NMR (192 MHz, Acetone) δ -1.25, -8.84, -10.77.

m/z calcd for: 574.7923 Found: 574.7952

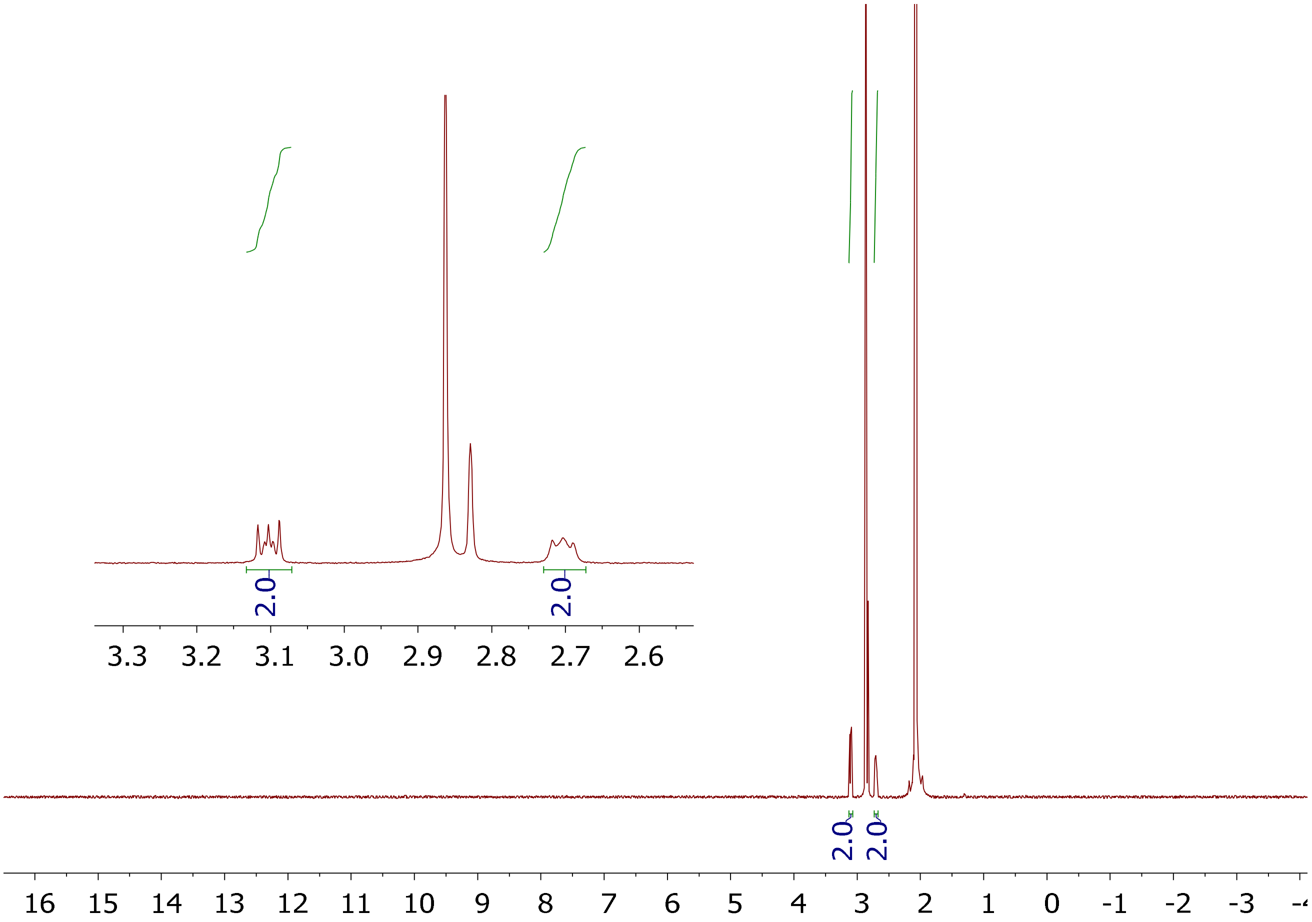


Figure 67: ^{1}H NMR of **I** in d_6-Acetone

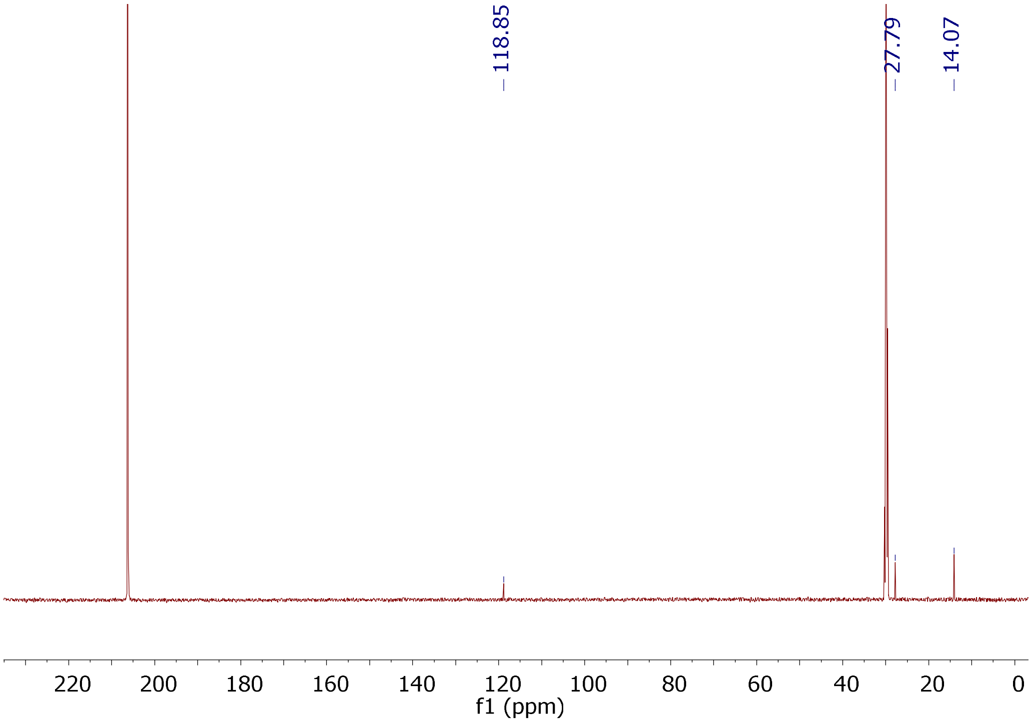


Figure 68: ^{13}C NMR of **I** in d_6-Acetone

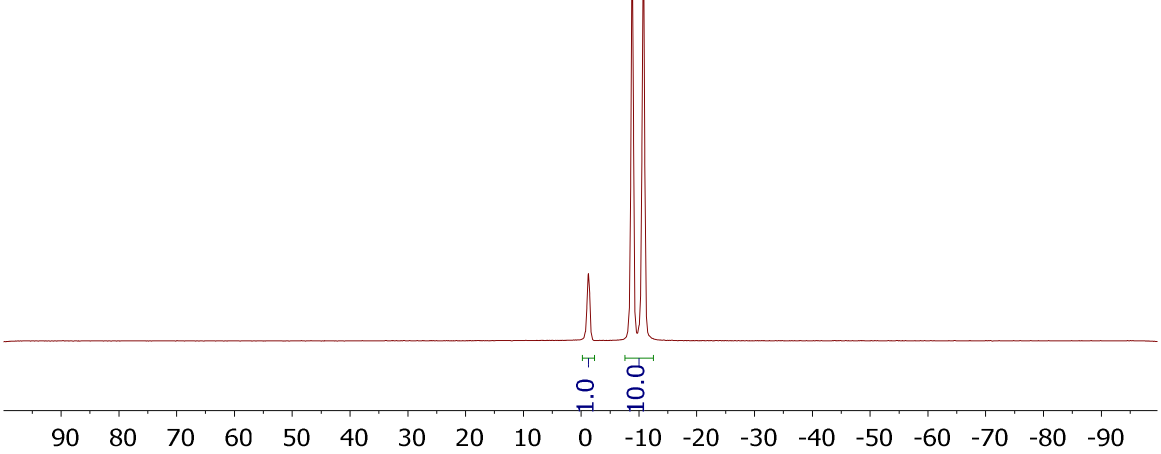


Figure 69: ^{11}B NMR of **I** in acetone

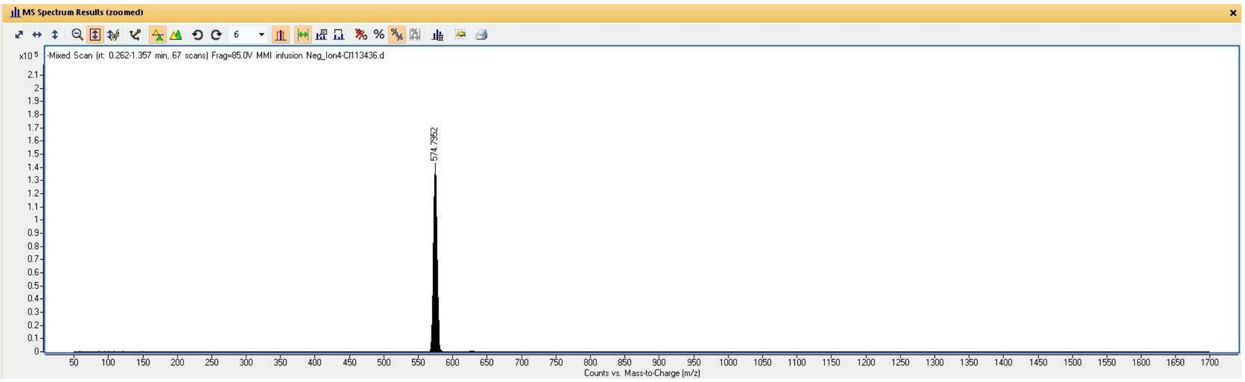


Figure 70: HRMS spectrum of **l**

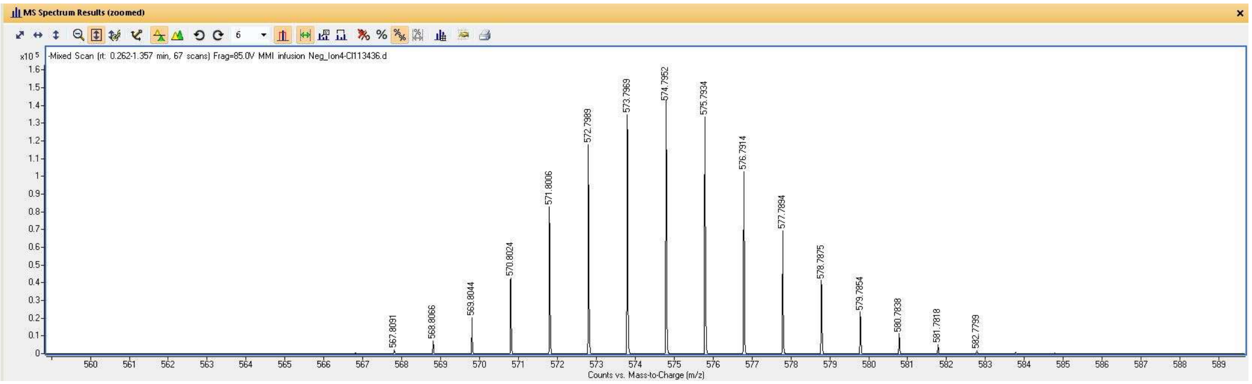
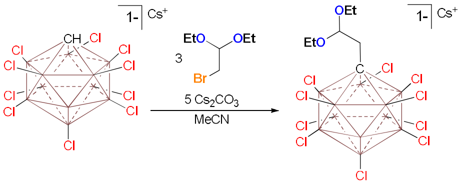


Figure 71: Zoomed in HRMS spectrum of **l**

Purification and Characterization of **m**



Electrophile: bromoacetaldehyde diethyl acetal.

Note: Reaction was refluxed for at least 36 hours before work up. The recovered oily solid was triturated with hexanes and filtered. The filtered solid was then washed through the filter with acetone and pumped dry yielding compound **m** in 90% yield.

^{1}H NMR (600 MHz, Acetone-*d*$_6$) δ 5.13 (t, *J* = 4.4 Hz, 1H), 3.61 (dq, *J* = 9.3, 7.0 Hz, 2H), 3.46 (dq, *J* = 9.2, 7.1 Hz, 2H), 2.56 (d, *J* = 4.3 Hz, 2H), 1.17 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, Acetone) δ 98.25, 62.35, 36.27, 15.08.

^{11}B NMR (128 MHz, acetone) δ -2.38, -9.82, -11.46.

m/z calcd for $C_6H_{13}O_2CB_{11}Cl_{11}^-$: 637.8495 Found: 637.8527

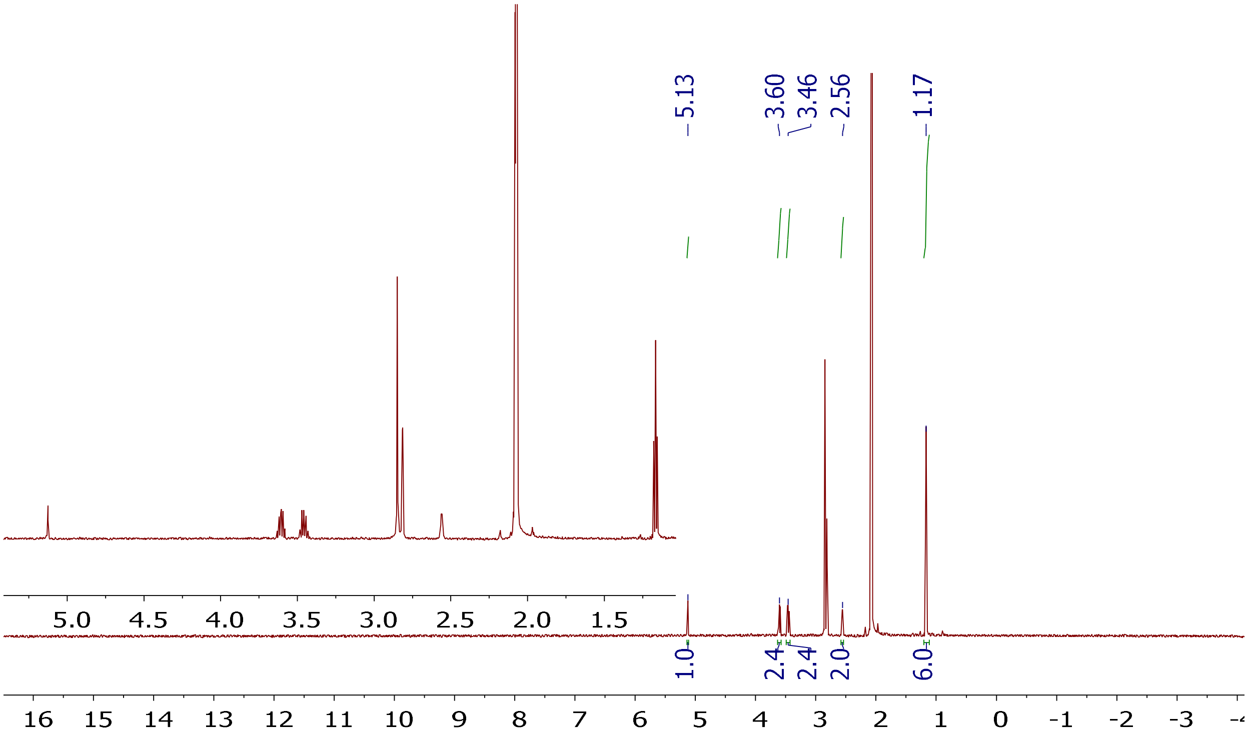


Figure 72: ^{1}H NMR of **m** in d_6-Acetone

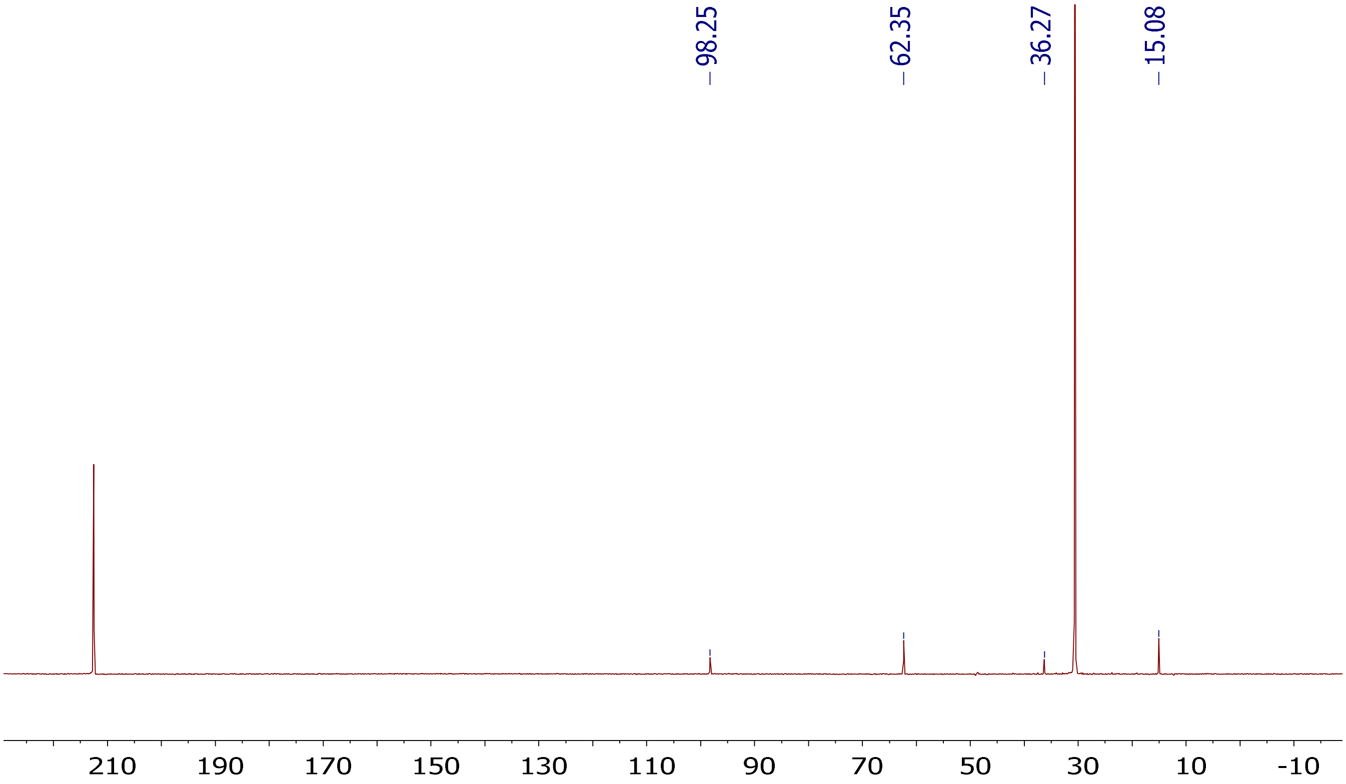


Figure 73: ^{13}C NMR of **m** in d_6-Acetone

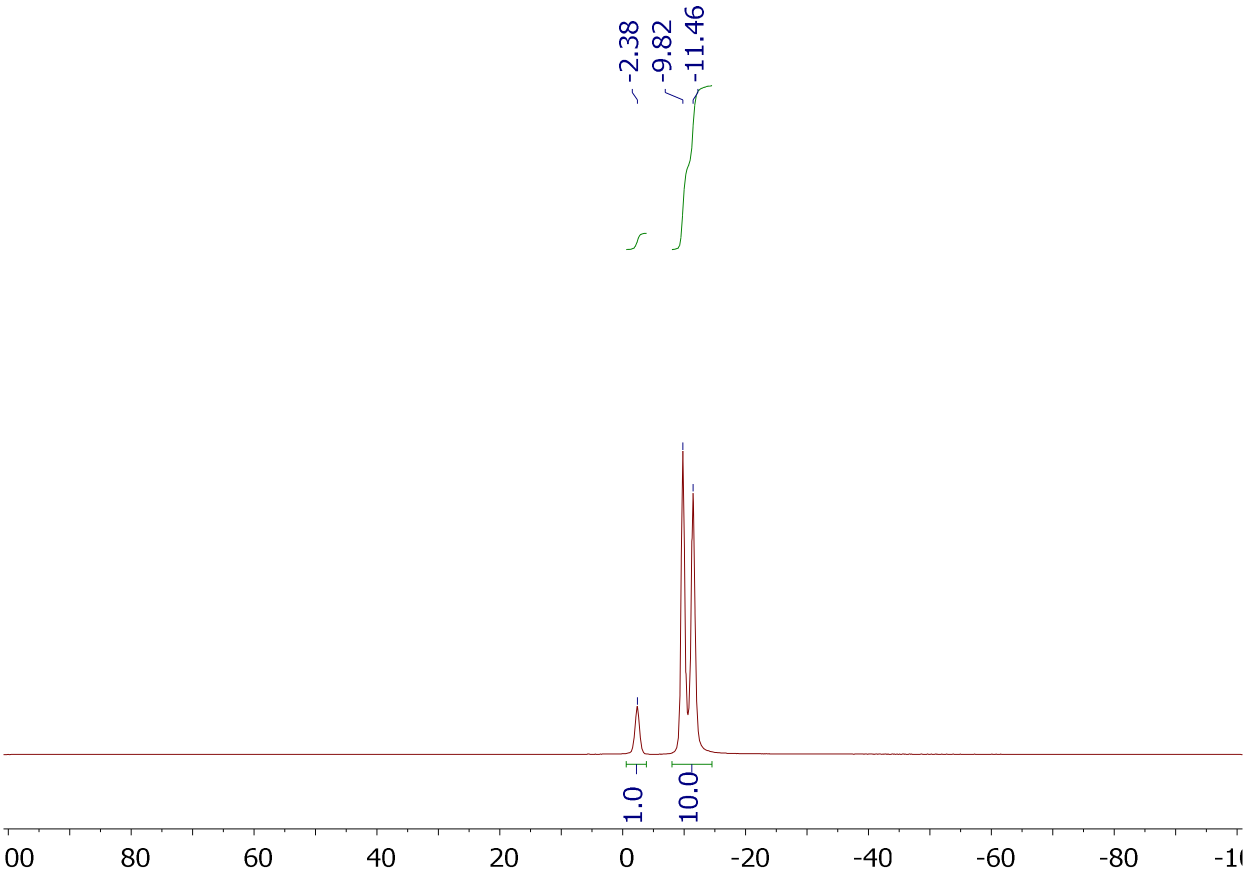
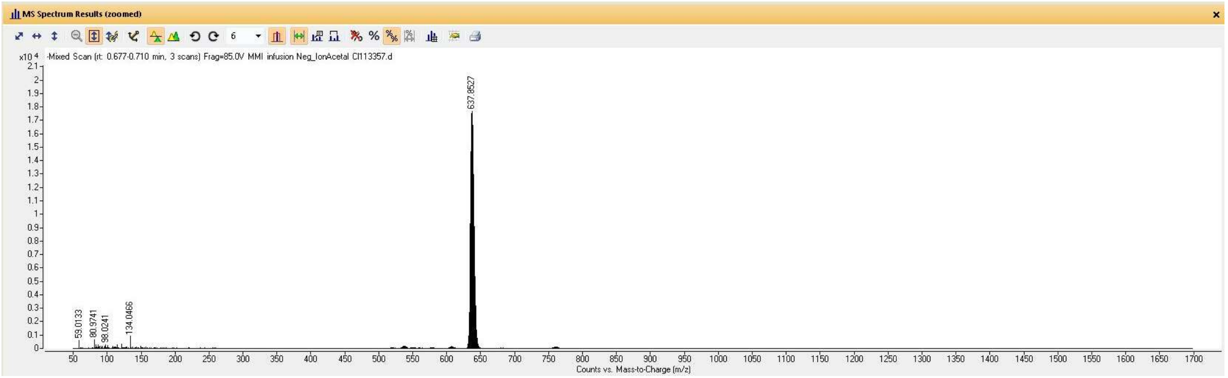


Figure 74: ^{11}B NMR of **m** in acetone



-Mixed Scan (rt: 0.677-0.710 min, 3 scans) Frag=85.0V MMI infusion Neg_IonAcetal CI113357.d

Figure 75: HRMS spectrum of **m**

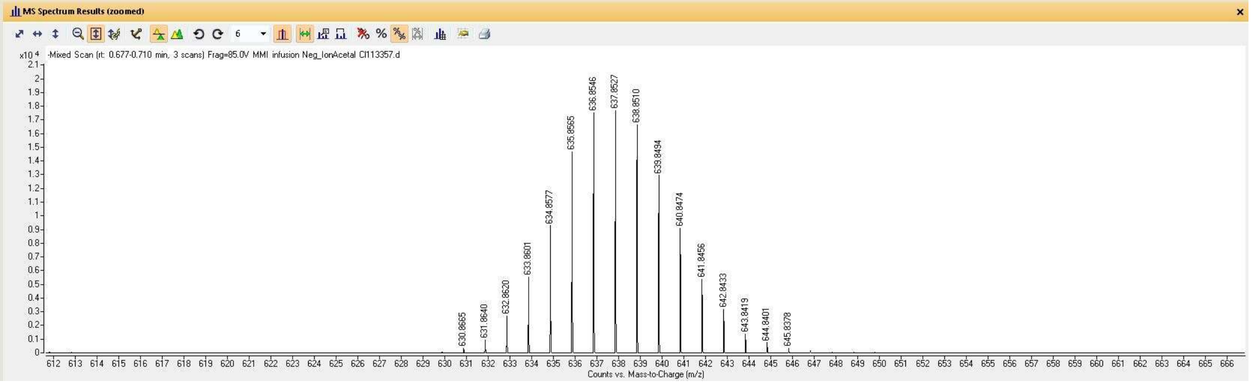
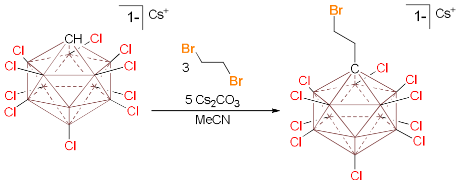


Figure 76: Zoomed in HRMS spectrum of **m**

Purification and Characterization of **n**



Electrophile: dibromoethane. The recovered oily solid was triturated with hexanes and filtered. The filtered solid was then washed through the filter with acetone and pumped dry yielding compound **n** in 92% yield ^{1}H NMR (400 MHz, Acetonitrile-*d*$_3$) δ 3.88 (ddd, *J* = 18.2 Hz, 2.9, 1.6 Hz, 2H), 2.84 – 2.76 (m, 2H).

^{13}C NMR (101 MHz, CD_3CN) δ 49.78, 33.87, 26.17.

^{11}B NMR (128 MHz, CD_3CN) δ -2.54, -10.04, -11.86.

m/z calcd for $BrC_2H_4CB_{11}Cl_{11}^-$: 628.7092 Found: 628.7096

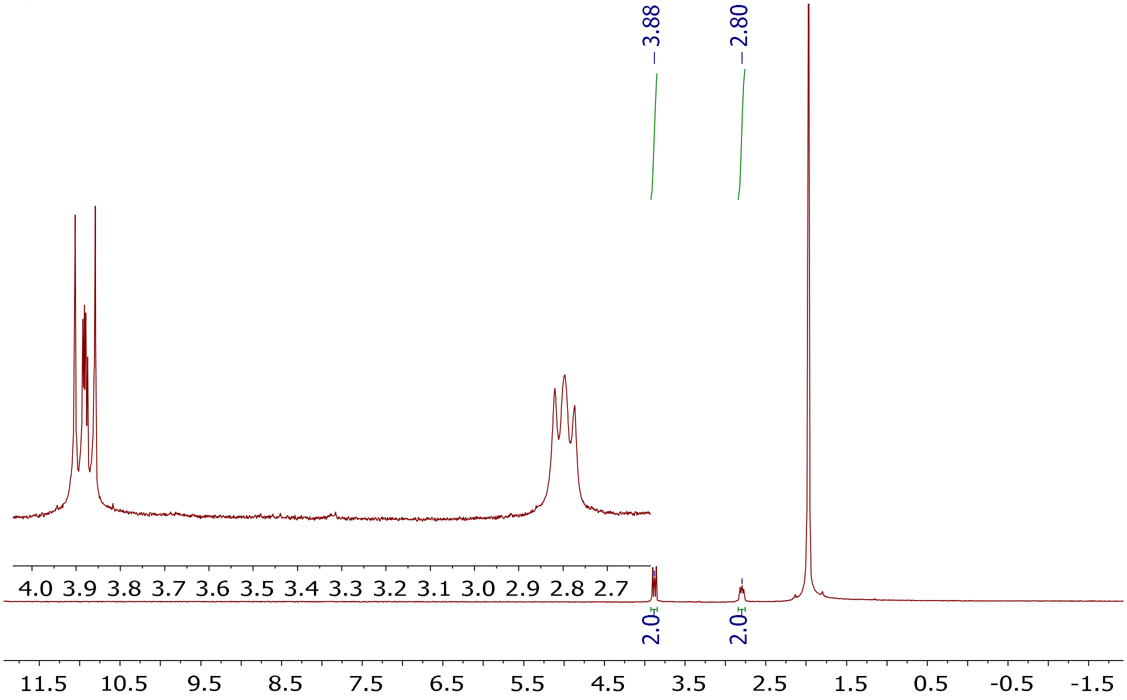


Figure 77: ^{1}H NMR of **n** in CD_3CN

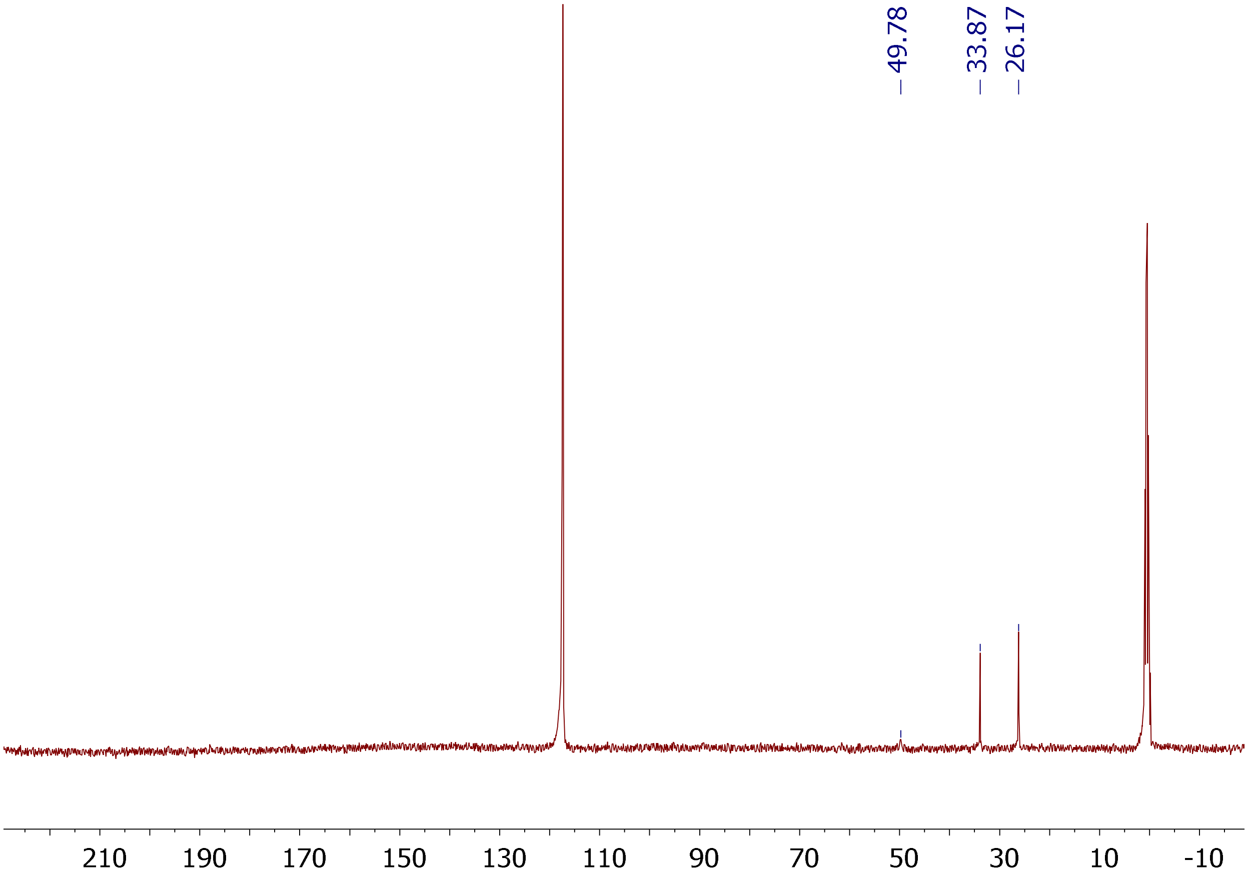


Figure 78: ^{13}C NMR of **n** in CD_3CN

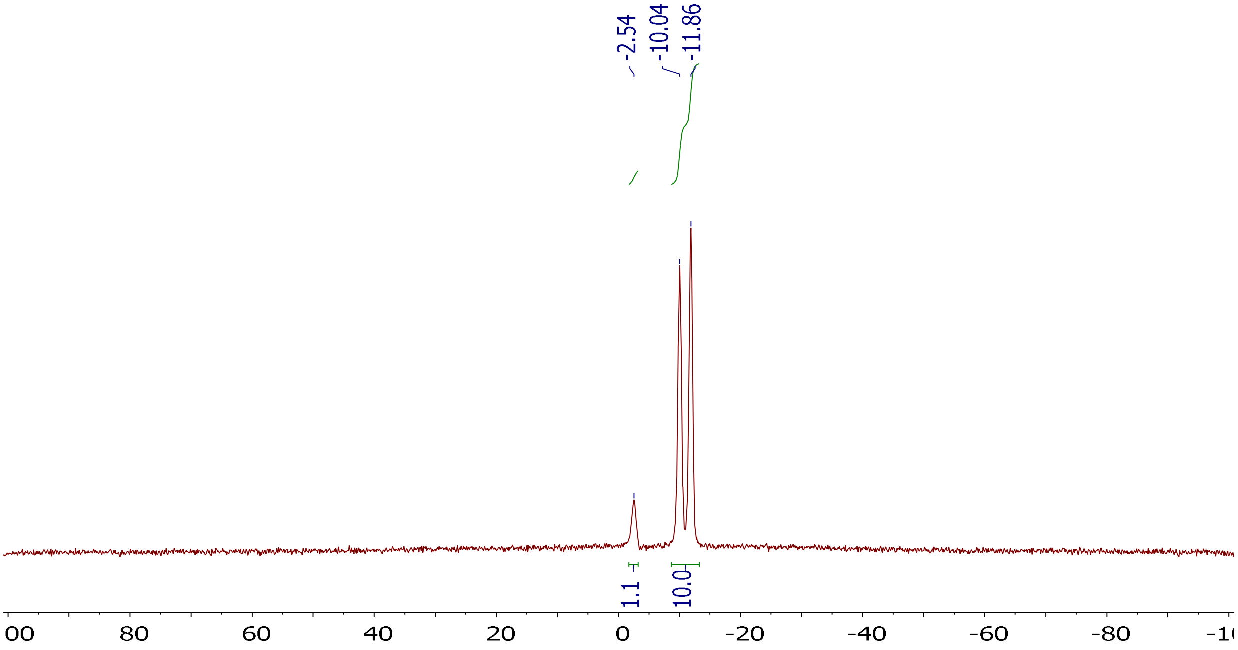
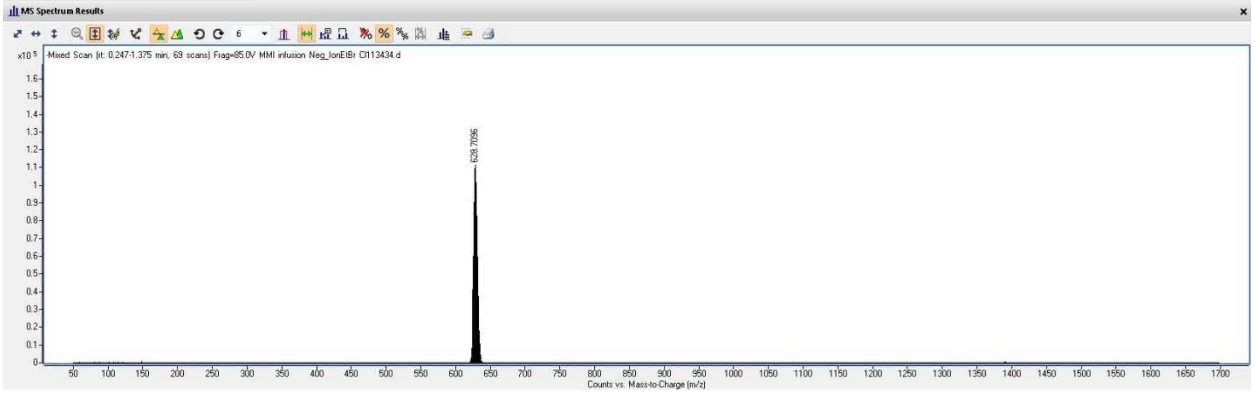
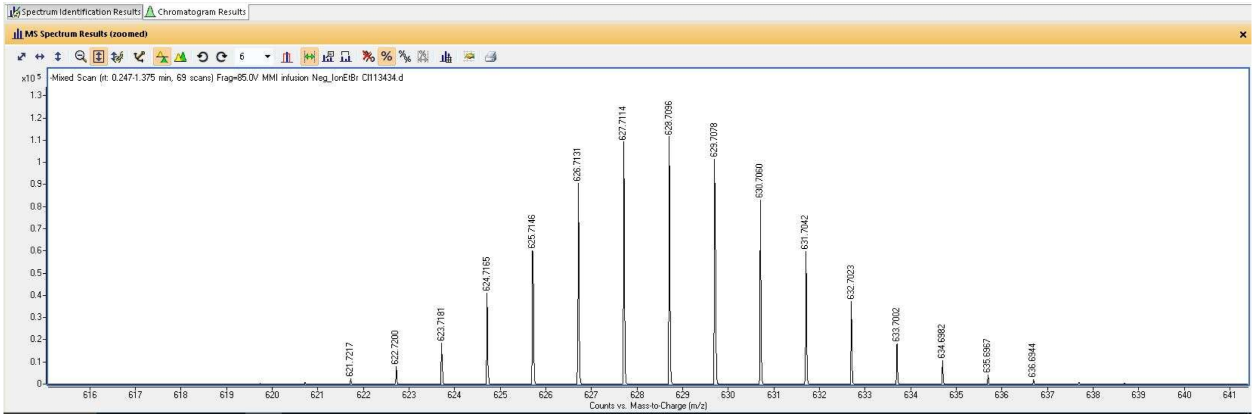


Figure 79: ^{11}B NMR of **n** in acetonitrile



-Mixed Scan (rt: 0.247-1.375 min, 69 scans) Frag=85.0V MMI infusion Neg_IonEtBr CI113434.d

Figure 80: HRMS spectrum of **n**



-Mixed Scan (rt: 0.247-1.375 min, 69 scans) Frag=85.0V MMI infusion Neg_IonEtBr CI113434.d

Figure 81: Zoomed in HRMS spectrum of **n**

References

1. *Inorg. Chem.,* **1998**, 37, 6444-6451

2. *RSC Advances*, **2012**, 2, 8672–8680