# Electronic Supplementary Information

## Enhanced Methods for the Undecachlorination of $[HCB_{11}H_{11}]^-$ and Syntheses of $[XCB_{11}Cl_{11}]^-$ from $[HCB_{11}Cl_{11}]^-$ (X = Cl, Br, I, $NH_2$)

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## I. General Considerations

Unless specified otherwise, all manipulations were performed on the benchtop exposed to air. $CD_3CN$ was dried over $CaH_2$ then vacuum transferred and then stored over molecular sieves in an Ar-filled glovebox. Ottawa sand was purchased from Fisher Scientific and was washed with water and ethanol, then dried in a 160 °C oven overnight before use. All other chemicals were used as received from commercial vendors. Chlorination reactions involving $SbCl_5$ used ground glass joints wrapped with a single layer of PTFE tape rather than using silicone grease.

All NMR spectra were recorded on a Bruker Avance 400 spectrometer ($^1$H NMR, 400.200 MHz; $^{13}$C NMR, 100.630 MHz; $^{11}$B NMR, 128.400 MHz); Bruker Avance 500 spectrometer ($^1$H NMR, 500.13 MHz; $^{13}$C NMR, 125.77 MHz; $^{11}$B NMR, 160.462 MHz); and Varian Inova 500 spectrometer ($^1$H NMR, 499.703 MHz; $^{13}$C NMR, 125.580 MHz; $^{11}$B NMR, 160.462 MHz). Chemical shifts are reported in δ (ppm). For $^1$H and $^{13}$C NMR spectra, the residual solvent peak was used as an internal reference ($CHD_2CN$, $CHDCl_2$). $^{11}B\{^1H\}$ NMR spectra were referenced externally to δ = 0 ppm by using $BF_3 \cdot Et_2O$. Negative-ion electrospray ionization mass spectrometry (referred to as "ESI-MS") experiments were performed on a Thermo Scientific Q Exactive Focus in the Texas A&M Chemistry Mass Spectrometry facility. The peak seen at approximately m/z = 485 in various mass spectra is an impurity leached from Eppendorf tubes during sample preparation, and does not represent the analyte. IR spectra were taken on an Agilent Cary 630 FTIR spectrometer located in an argon-filled glovebox.

## II. Undecachlorination of the carba-*closo*-dodecaborate anion

### II.1 Chlorination using $SbCl_3/SbCl_5$

**Synthesis of $[Me_3NH][HCB_{11}Cl_{11}]$ (500 mg scale)** – In a glovebox, a 100 mL Schlenk flask equipped with a magnetic stir bar was charged with $SbCl_3$ (30 g, 144 mmol). The flask was removed from the glovebox and placed in a sand bath under argon on a Schlenk line. To the flask was then added $[Cs][HCB_{11}H_{11}]$ (500 mg, 1.81 mmol), and the flask was warmed until the solid mixture became a homogenous solution. To this solution, $SbCl_5$ (3.7 mL, 28.9 mmol) was slowly added over 5 min. The flask was equipped with a reflux condenser, and the solution was heated to reflux under Ar overnight. The next morning, an aliquot was taken, dissolved in 2 mL of $CH_2Cl_2$, and filtered prior to analyzing the conversion to the desired product by ESI-MS. The volatiles were then removed via vacuum distillation, and 20 mL of a 3M aqueous NaOH solution were added to the residue. The resulting mixture was left to stir overnight before being filtered through a pad of Celite. The filter cake was washed with an additional 50 mL of the 3M NaOH solution. The solution was neutralized by dilute HCl solution until pH = 6 and then treated with $Me_3NHCl$ (300 mg, 3.14 mmol), causing the formation of a white precipitate. This solid was filtered off, washed with distilled water, and left to air dry overnight to give the product as a beige solid (917 mg, 1.57 mmol, 87%).

**Aliquot quench procedure** – A small amount of the solution (~ 5 drops) was transferred to an 8 mL vial, where the sample was quenched with 3 mL of deionized water, resulting in the precipitation of a white solid. To this cloudy mixture, 3 mL of $CH_2Cl_2$ were added, and the vial was shaken vigorously. After allowing the mixture to sit for 5 min, the organic layer was extracted and filtered through a pad of celite before being submitted for analysis.

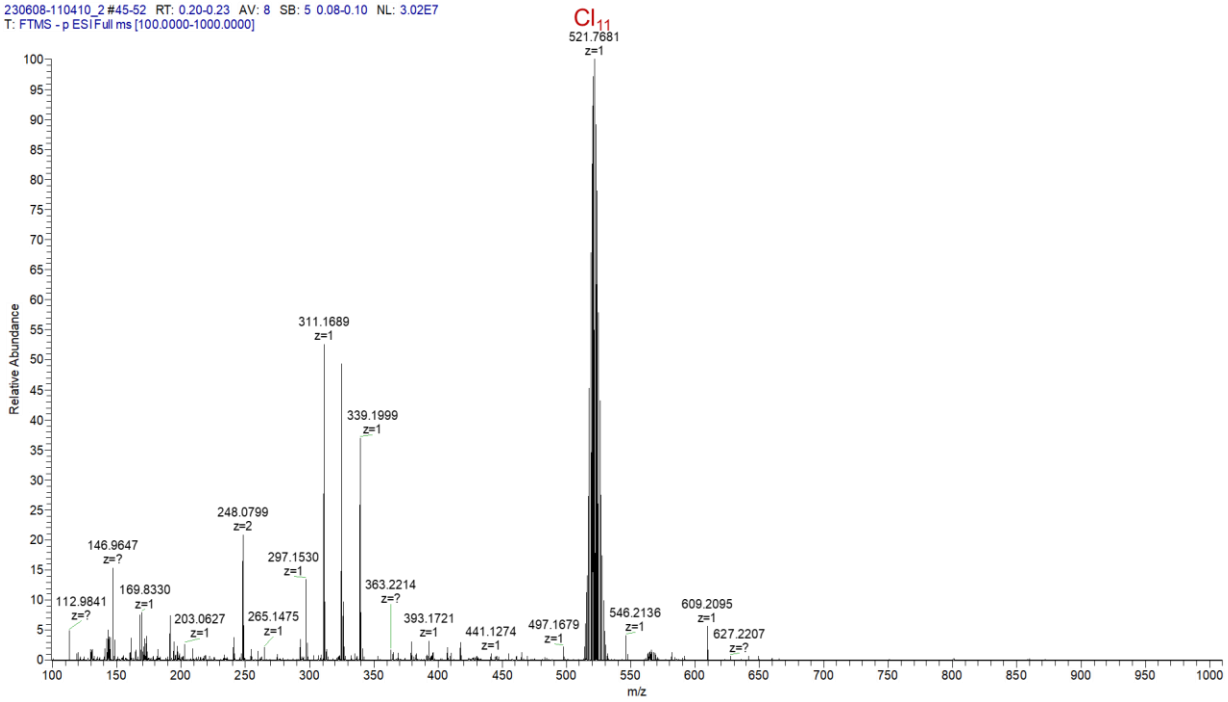


**Figure S1.** ESI-MS of quenched aliquot for the chlorination (500 mg scale) of [Cs][$HCB_{11}H_{11}$] after refluxing overnight.

**Synthesis of [$Me_3NH$][$HCB_{11}Cl_{11}$] (6 g scale)** – In a glovebox, a 500 mL 3-neck round bottom flask equipped with a magnetic stir bar was charged with $SbCl_3$ (500 g, 2.19 mol). The flask was removed from the glovebox and placed in a sand bath under argon on a Schlenk line. To the flask was then added [Cs][$HCB_{11}H_{11}$] (6.05 g, 21.9 mmol), and the flask was warmed until the solid mixture became a homogenous solution. To this solution, $SbCl_5$ (56 mL, 438 mmol) was slowly added over 15 min. The flask was equipped with a reflux condenser, and the solution was heated to reflux under Ar overnight. The next morning, an aliquot was taken, quenched, and the conversion to the desired product was confirmed by ESI-MS. The volatiles were then removed via vacuum distillation, and 200 mL of a 3M aqueous NaOH solution were added to the residue. The resulting mixture was left to stir overnight before being filtered through a pad of Celite. The filter cake was washed with an additional 100 mL of the 3M NaOH solution. The solution was acidified with 6M HCl until pH = 6 and then treated with $Me_3NHCl$ (4.19 g, 43.8 mmol), causing the formation of a white precipitate. Solids were filtered off, washed with distilled water, and left to air dry overnight to give the product as a beige solid (11.3 g, 19.5 mmol, 89%).

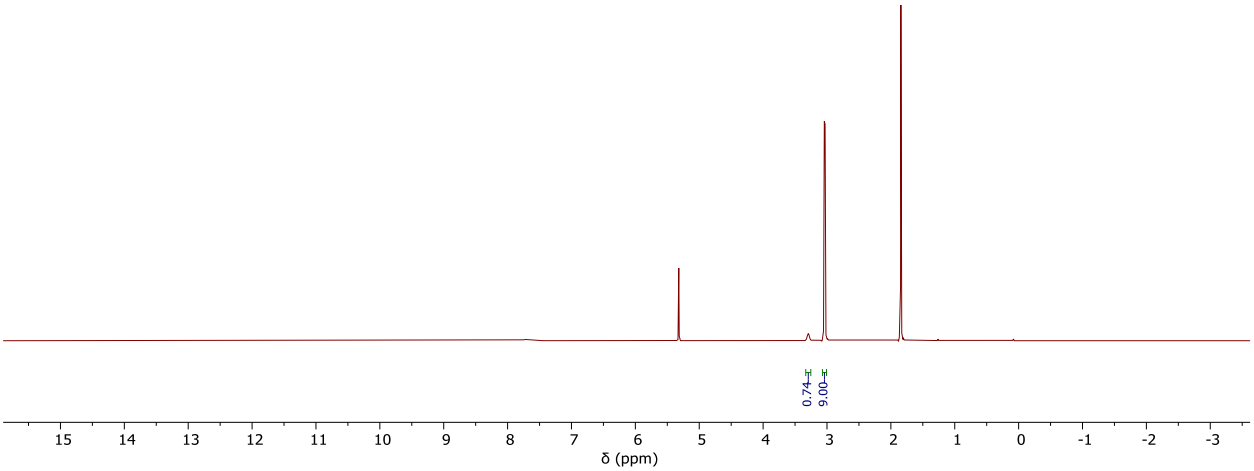


**Figure S2.** $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) NMR Spectrum of $[HNMe_3][HCB_{11}Cl_{11}]$. Sample contains residual water from solvent and product (δ 1.84).

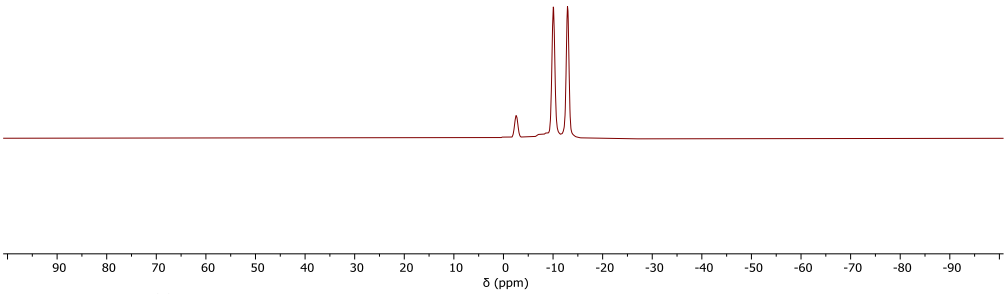


**Figure S3.** $^{11}B$ NMR (128 MHz, $CD_2Cl_2$) NMR Spectrum of $[HNMe_3][HCB_{11}Cl_{11}]$.

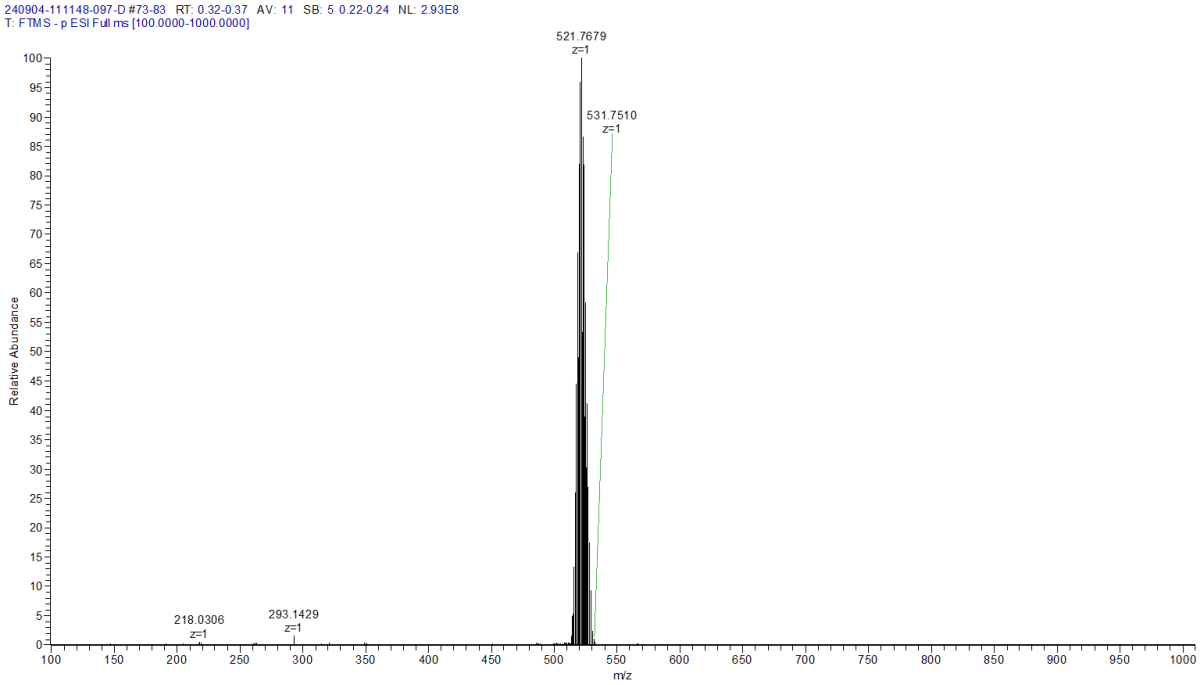


**Figure S4.** ESI-MS of $[HNMe_3][HCB_{11}Cl_{11}]$.

**Control experiment – Analysis of reaction aliquot without quenching** – In a glovebox, a 100 mL Schlenk flask equipped with a magnetic stir bar was charged with $SbCl_3$ (19 g, 83 mmol). The flask was removed from the glovebox and placed in a sand bath under argon on a Schlenk line. To the flask was then added [Cs][$HCB_{11}H_{11}$] (251 mg, 0.906 mmol), and the flask was warmed until the solid mixture became a homogenous solution. To this solution, $SbCl_5$ (1.9 mL, 15 mmol) was slowly added over 5 min. The flask was equipped with a reflux condenser, and the solution was heated to reflux under Ar overnight. The next morning, an aliquot was taken, dissolved in 2 mL of $CH_2Cl_2$, and the conversion to the desired product was confirmed by ESI-MS.

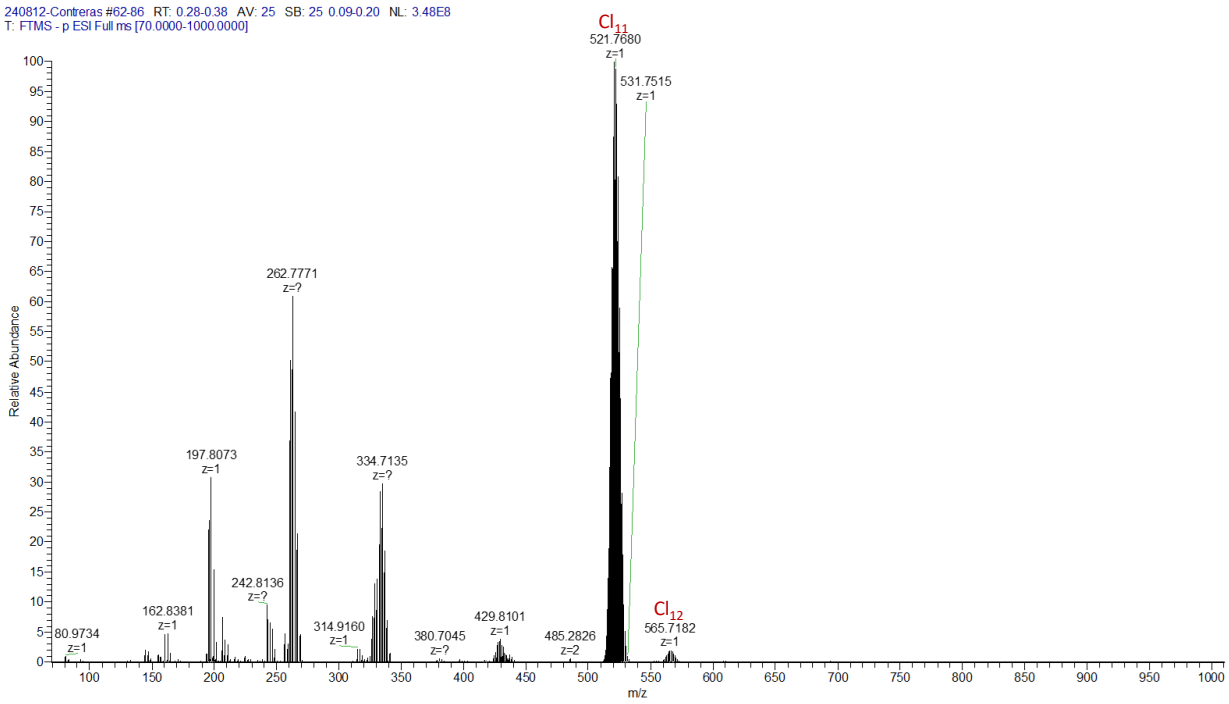


**Figure S5.** ESI-MS of the aliquot for the chlorination (250 mg scale) of [Cs][$HCB_{11}H_{11}$] after refluxing overnight.

**Control experiment – Chlorination of [Cs][$HCB_{11}H_{11}$] with only $SbCl_3$ then $SbCl_5$** – In a glovebox, a 25 mL Schlenk flask equipped with a magnetic stir bar was charged with $SbCl_3$ (7.6 g, 33.3 mmol). The flask was removed from the glovebox and placed in a sand bath under argon on a Schlenk line. To the flask was then added [Cs][$HCB_{11}H_{11}$] (132 mg, 0.478 mmol), and the flask was heated to reflux. Aliquots were taken at multiple time intervals, and the progress of chlorination was tracked via ESI-MS. After 3 d, the mixture appeared to consist of the anions $[HCB_{11}Cl_2H_9]^-$ and $[HCB_{11}Cl_3H_8]^-$, and it was left to cool to room temperature before adding $SbCl_5$ (1.2 mL, 9.4 mmol) and allowing to reflux for an additional 16 h. After 16 h, a fourth aliquot was taken, and ESI-MS analysis showed full conversion to the $[HCB_{11}Cl_{11}]^-$ anion (**Figure S9**).

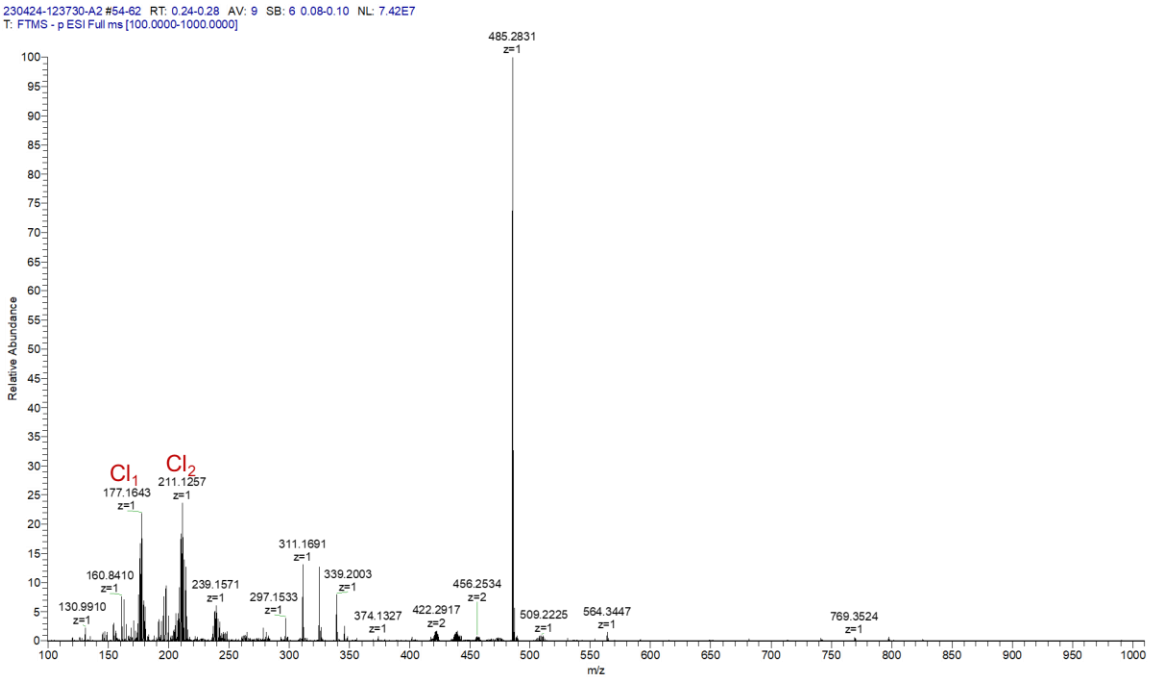


**Figure S6.** ESI-MS of quenched aliquot for the chlorination of [Cs][$HCB_{11}H_{11}$] with $SbCl_3$ after refluxing for 24 h.

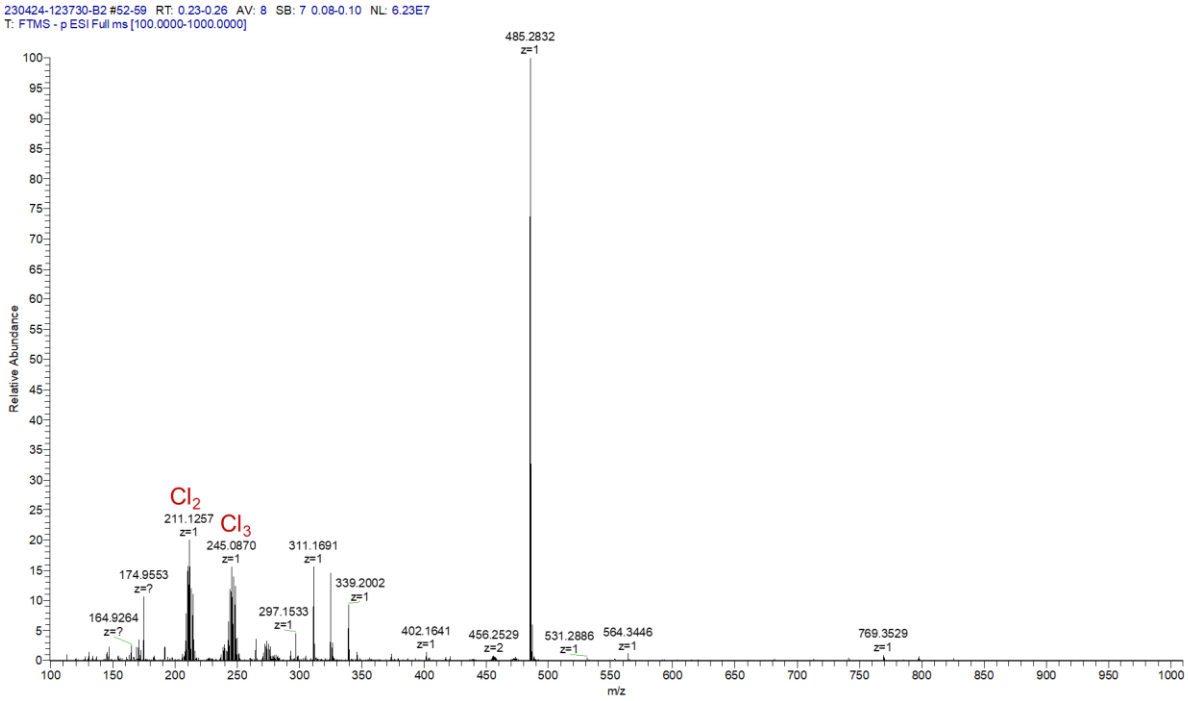


**Figure S7.** ESI-MS of quenched aliquot for the chlorination of $[Cs][HCB_{11}H_{11}]$ with $SbCl_3$ after refluxing for 42 h.

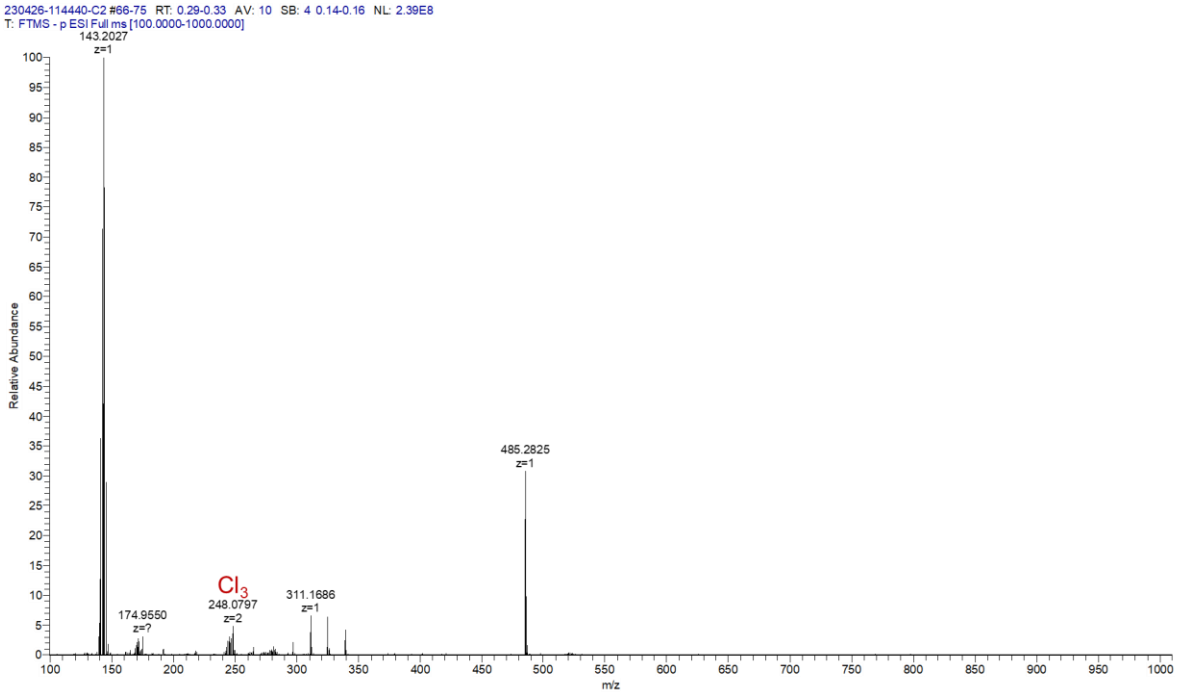


**Figure S8.** ESI-MS of quenched aliquot for the chlorination of $[Cs][HCB_{11}H_{11}]$ with $SbCl_3$ after refluxing for 72 h.

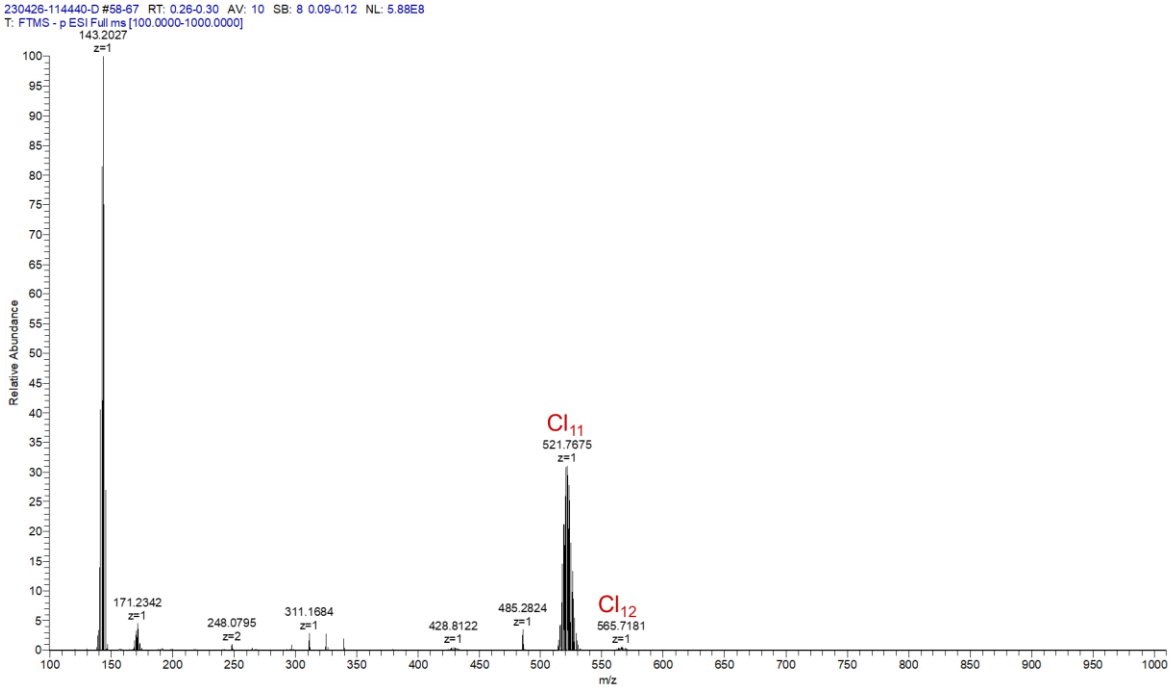


**Figure S9.** ESI-MS of quenched aliquot for the control experiment for the chlorination of [Cs][$HCB_{11}H_{11}$].

**Tracking experiment for the improved chlorination of [Cs][$HCB_{11}H_{11}$] –** In a glovebox, a 100 mL Schlenk flask equipped with a magnetic stir bar was charged with $SbCl_3$ (79 g, 346 mmol). The flask was removed from the glovebox and placed in a sand bath under argon on a Schlenk line. To the flask was then added [Cs][$HCB_{11}H_{11}$] (1.01 g, 3.62 mmol), and the flask was warmed until the solid mixture became a homogenous solution. To this solution, $SbCl_5$ (8.5 mL, 72.5 mmol) was slowly added over 5 min. The flask was equipped with a reflux condenser, and the solution was heated to reflux under Ar. Aliquots were taken at multiple time intervals, and the progress of chlorination was tracked via ESI-MS. The chlorination appeared complete within 4 h of refluxing.

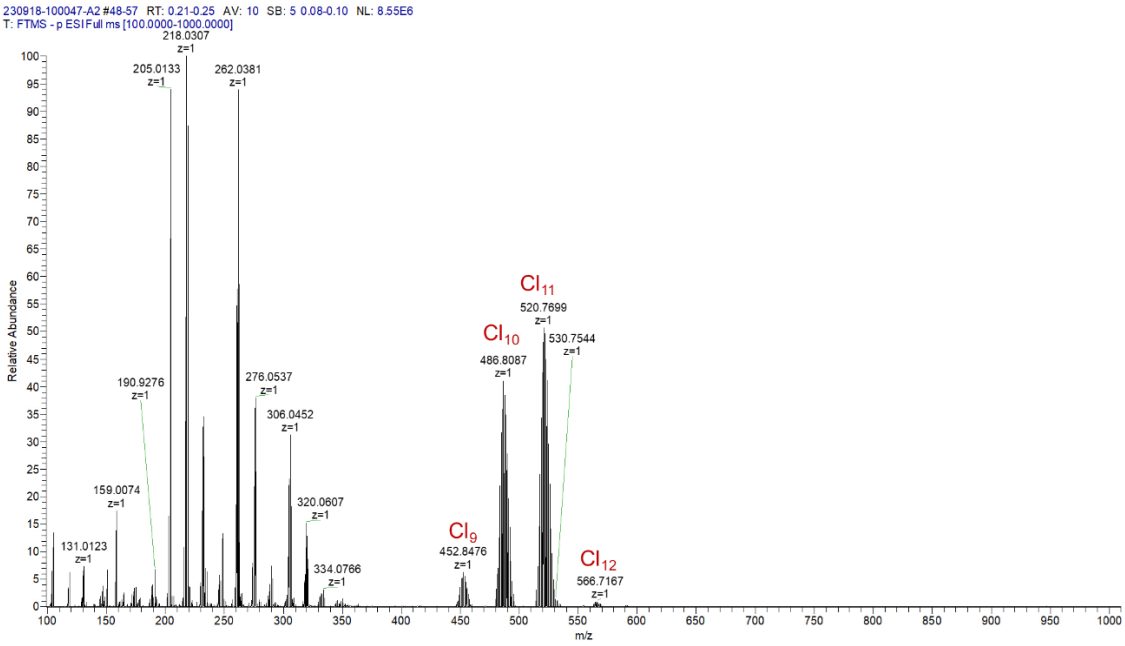


**Figure S10.** ESI-MS of quenched aliquot for the tracked chlorination of [Cs][$HCB_{11}H_{11}$] with $SbCl_3$/$SbCl_5$ after 1 h.

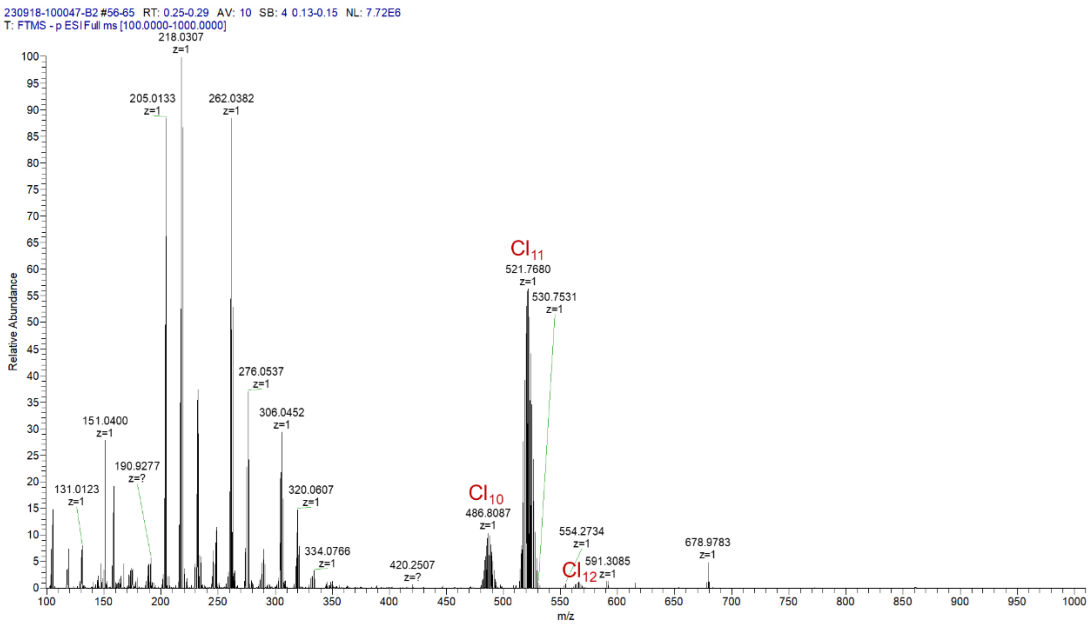


**Figure S11.** ESI-MS of quenched aliquot for the tracked chlorination of $[Cs][HCB_{11}H_{11}]$ with $SbCl_3/SbCl_5$ after 2 h.

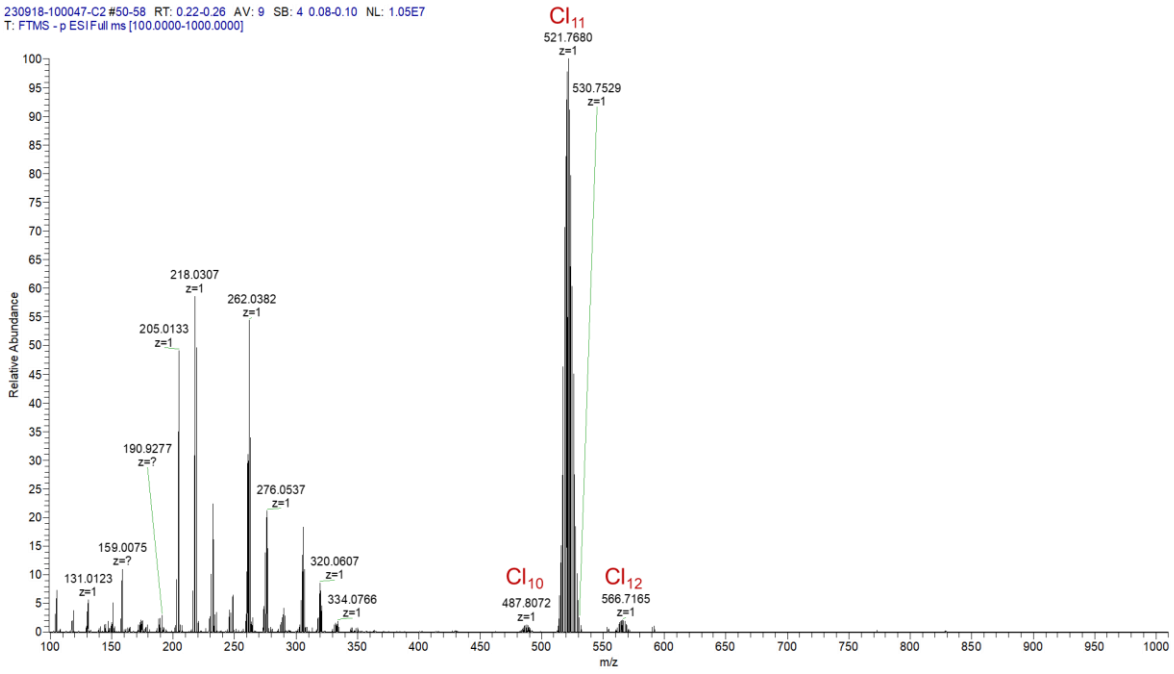


**Figure S12.** ESI-MS of quenched aliquot for the tracked chlorination of $[Cs][HCB_{11}H_{11}]$ with $SbCl_3/SbCl_5$ after 3 h.

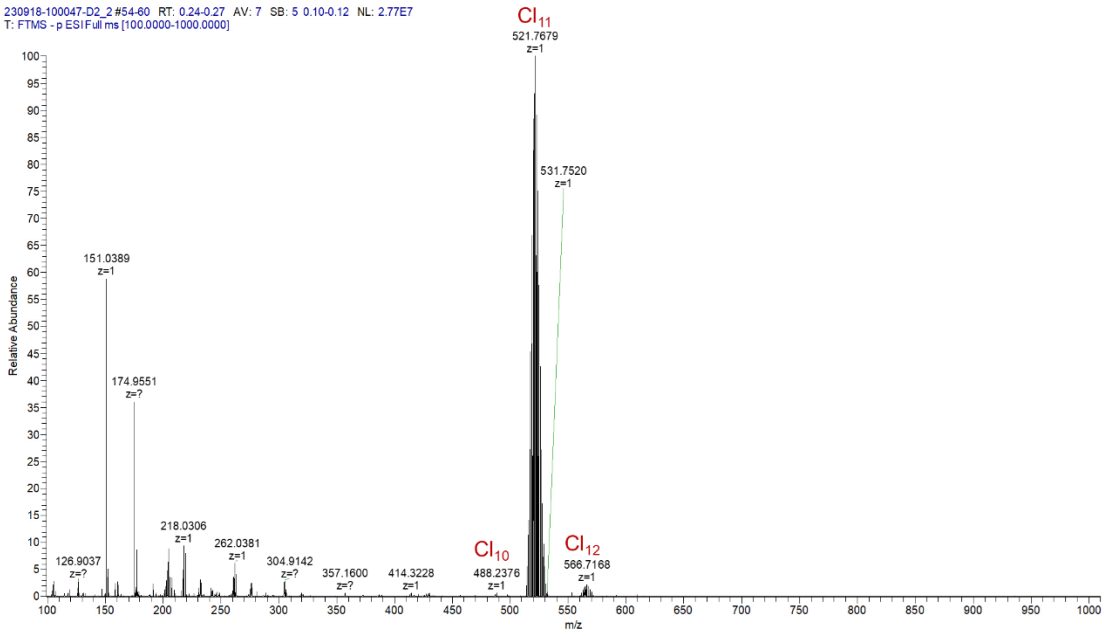


**Figure S13.** ESI-MS of quenched aliquot for the tracked chlorination of $[Cs][HCB_{11}H_{11}]$ with $SbCl_3/SbCl_5$ after 4 h.

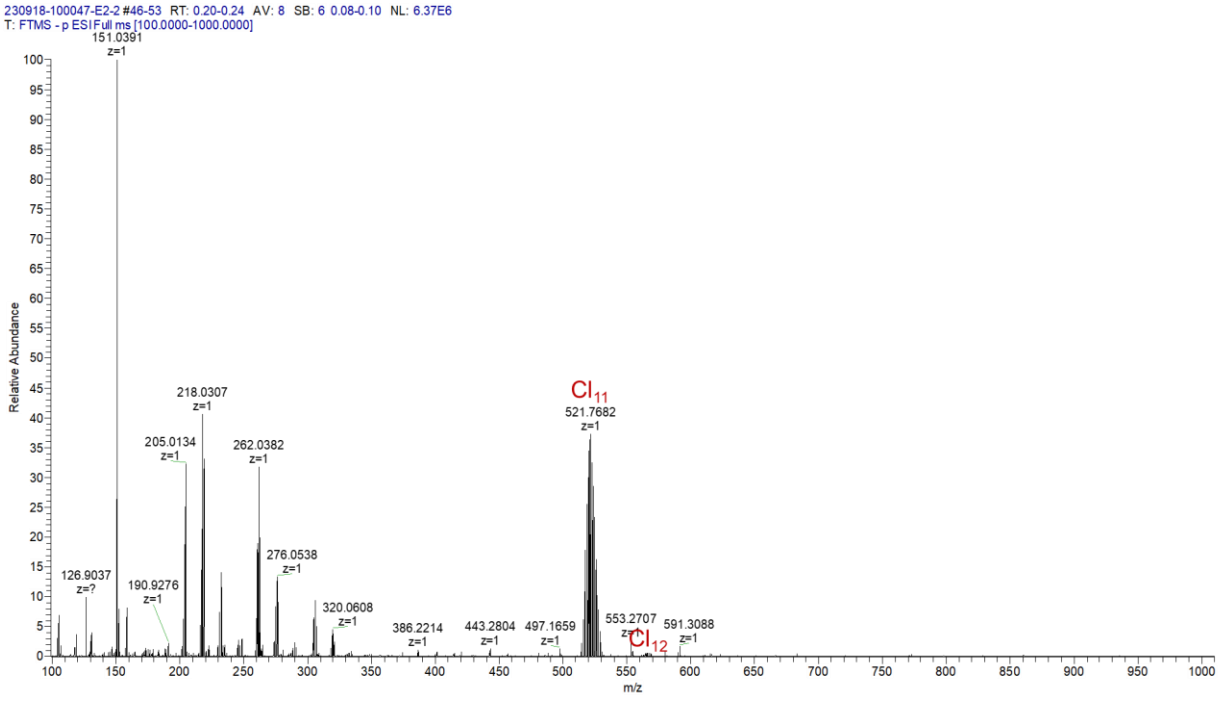


**Figure S14.** ESI-MS of quenched aliquot for the tracked chlorination of $[Cs][HCB_{11}H_{11}]$ with $SbCl_3/SbCl_5$ after 6 h.

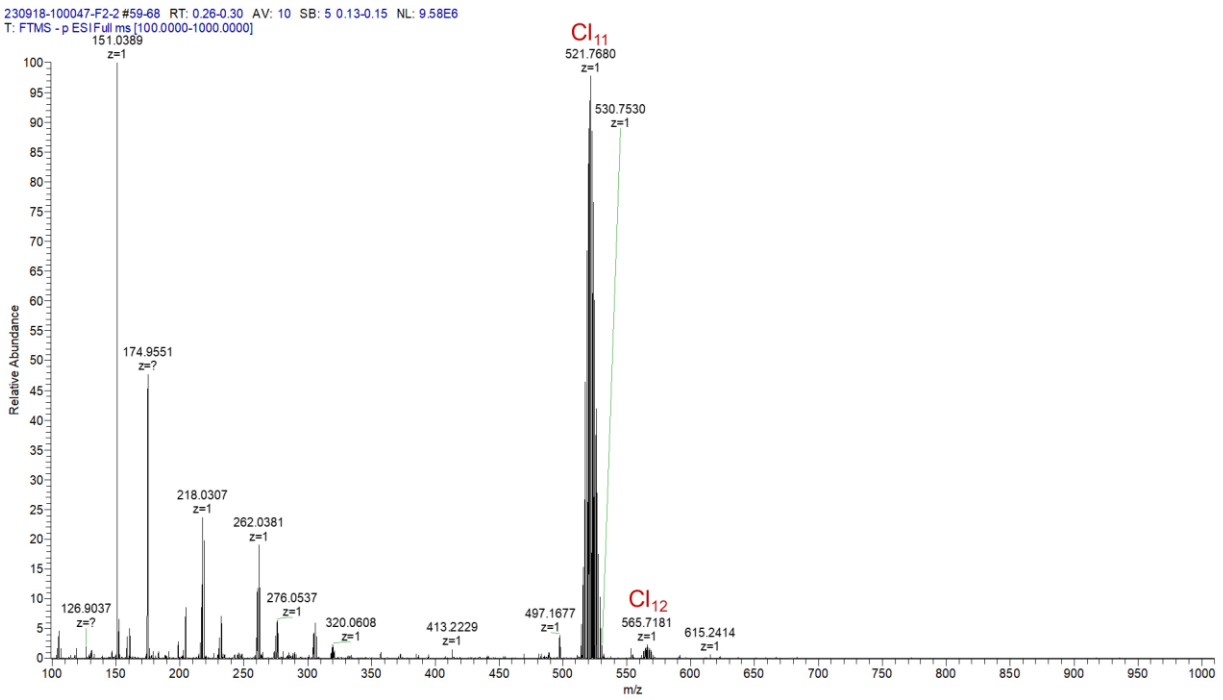


**Figure S15.** ESI-MS of quenched aliquot for the tracked chlorination of $[Cs][HCB_{11}H_{11}]$ with $SbCl_3/SbCl_5$ after 2 d.

## II.2 Chlorination using $VCl_4$

**Attempted Synthesis of $[HNMe_3][HCB_{11}Cl_{11}]$ with $VCl_4$ –** $[Cs][HCB_{11}H_{11}]$ (100 mg, 0.362 mmol) was added to a 25 mL Schlenk flask equipped with a stir bar. $VCl_4$ (~10 mL, ~5.5 g, 29 mmol) was added to the flask . The flask was equipped with a reflux condenser, and the solution was heated to reflux for 48 h. After 48 h, the mixture was allowed to cool and an aliquot was taken up in $CH_2Cl_2$ that indicated conversion to a mixture of cages ranging from $[HCB_{11}Cl_5H_6]^-$ to $[HCB_{11}Cl_{11}]^-$ by MALDI$^-$ mass spectrometry.

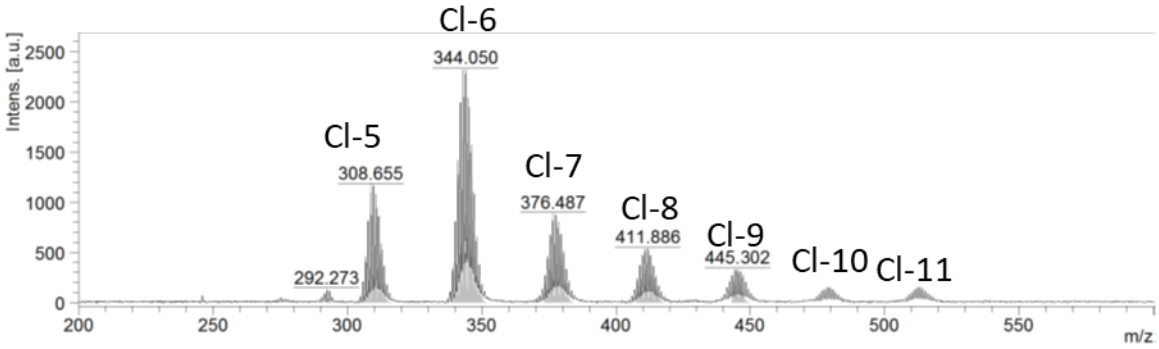


**Figure S16.** MALDI(-) mass spectrum of the chlorination mixture after refluxing in $VCl_4$ for 48 h.

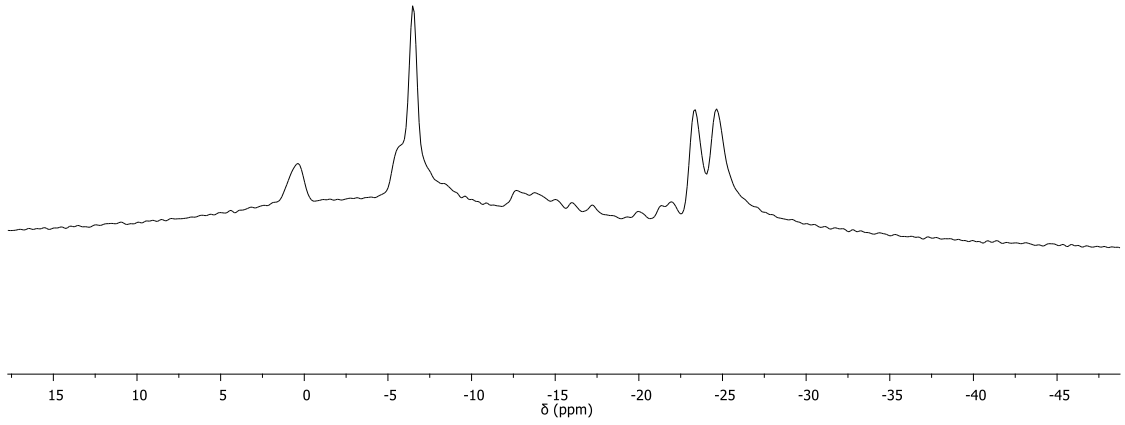


**Figure S17.** $^{11}B$ NMR (128 MHz, $CH_2Cl_2$) spectrum of the chlorination mixture after refluxing in $VCl_4$ for 48 h.

### II.3 Chlorination using TCCA

**Synthesis of $[Me_3NH][HCB_{11}Cl_{11}]$ (100 mg scale)** – Using a mortar and pestle, $[Cs][HCB_{11}H_{11}]$ (100 mg, 0.362 mmol) and trichloroisocyanuric acid (TCCA) (1.35 g, 5.80 mmol) were each ground separately for 10 min. The solids were then stirred together in a 25 mL Schlenk flask and heated to 200 °C for 16 h in a sand bath. [*Caution! Initial contact between $[Cs][HCB_{11}H_{11}]$ and TCCA solids may lead to a highly exothermic reaction with potential for material ejection and gas evolution, the severity of which depends on the amounts involved, the particle size, and degree of contact. Although this procedure on the 100 mg scale of $Cs[HCB_{11}H_{11}]$ has been performed in our laboratory without adverse consequences multiple times using proper personal protective equipment (goggles, flame-resistant lab coat, and a blast shield), performing this reaction on a scale larger than >100 mg of $[Cs][HCB_{11}H_{11}]$, or grinding these two solids together on any scale is not advisable. Performing this reaction in a tightly closed container on any scale should not be done.*] After 16 h, the mixture was allowed to cool and an aliquot was taken that indicated nearly full conversion to $[ClCB_{11}Cl_{11}]^-$ by ESI-MS. In a separate flask, $Na_2SO_3$ (2.24 g, 17.7 mmol) was dissolved in 20 mL water. Once dissolved, the $Na_2SO_3$ solution was immediately added to the flask containing the chlorination mixture and was allowed to stir for 5 min. The solution was acidified with 6 M HCl until pH = 6 and then filtered through a pad of Celite, which was washed with water (5 × 5 mL). The filtrate was treated with $Me_3NHCl$ (69 mg, 0.724 mmol), causing the formation of a white precipitate. Solids were filtered off, washed with distilled water, and left to air dry overnight to give the product as a white solid (191 mg, 0.328 mmol, 91%).

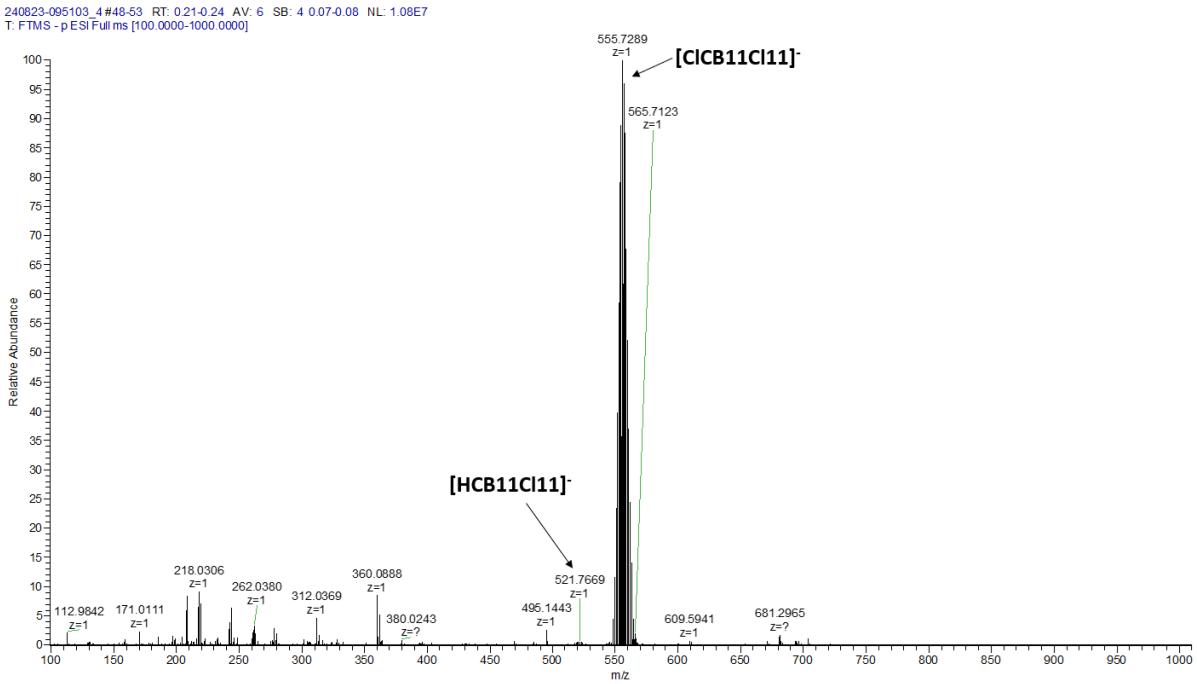


**Figure S18.** ESI-MS of the chlorination mixture after heating at 200 °C for 16 h.

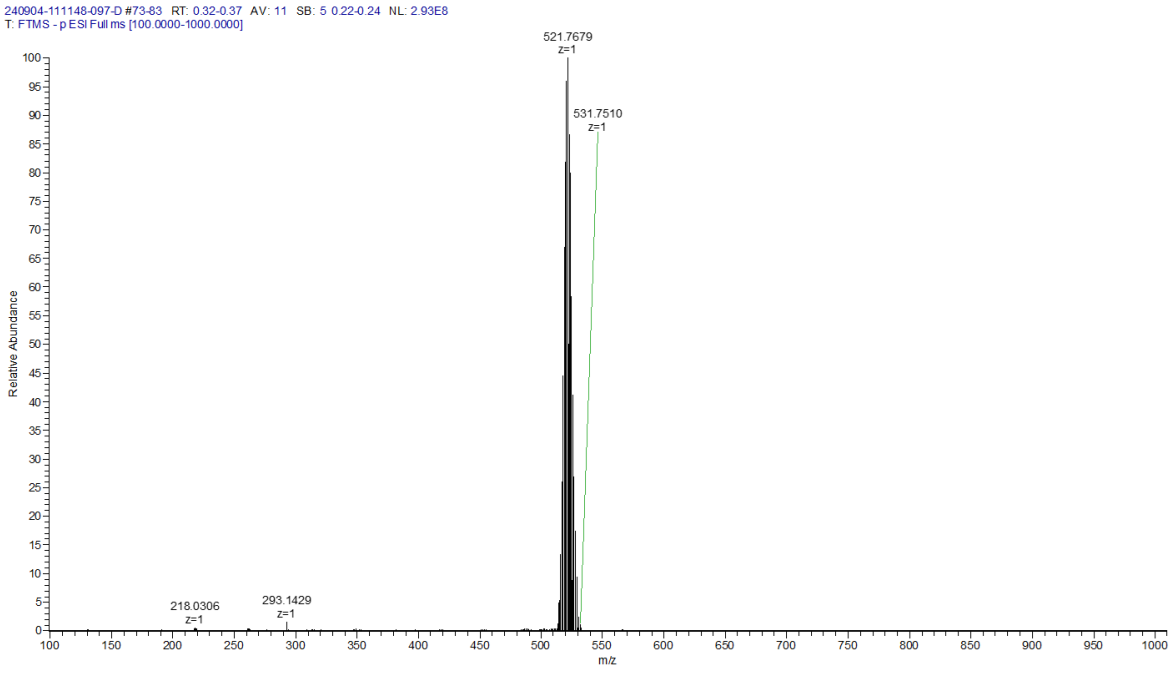


**Figure S19.** ESI-MS of the final product **[HNMe$_3$][HCB$_{11}$Cl$_{11}$]** after workup.

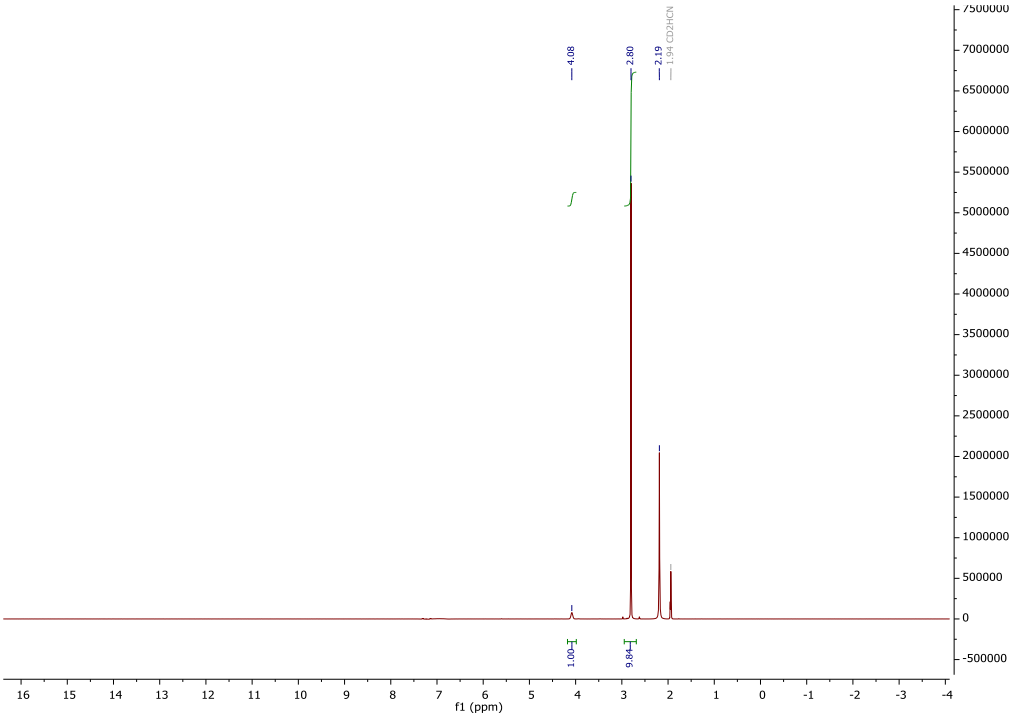


**Figure S20.** $^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][HCB$_{11}$Cl$_{11}$]** product. Residual water from the deuterated solvent is seen at 2.19 ppm.

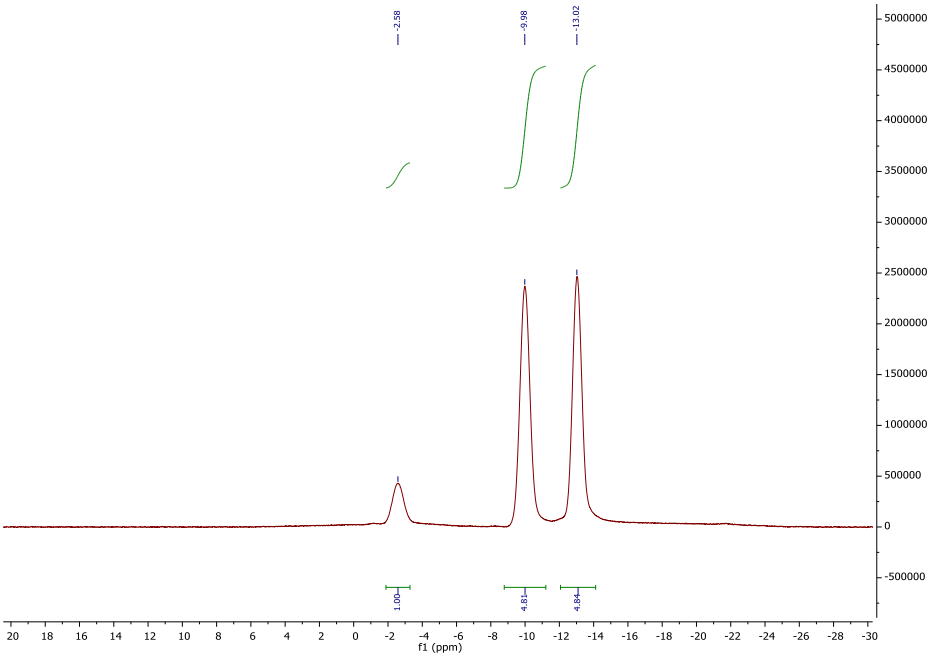


**Figure S21.** $^{11}$B{$^{1}$H} NMR (128 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][HCB$_{11}$Cl$_{11}$]** product.

**Synthesis of [HNMe$_3$][HCB$_{11}$Cl$_{11}$] with NaCl (1 g scale) –** Using a mortar and pestle, [Cs][HCB$_{11}$H$_{11}$] (1.00 g, 3.62 mmol) and TCCA (13.5 g, 58.0 mmol) were each ground separately for 10 min. The ground TCCA was manually mixed with NaCl (200 g) in a 500 mL round bottom flask using a spatula. To the flask, [Cs][HCB$_{11}$H$_{11}$] was added slowly in five approximately equal portions over the course of 2 h to avoid a runaway reaction, and the mixture was agitated with a spatula upon each addition. The flask was then placed in a sand bath and heated to 200 °C for 16 h. After 16 h in total, the mixture was allowed to cool and an aliquot was taken that indicated nearly full conversion to [ClCB$_{11}$Cl$_{11}$]$^-$ by ESI-MS. The mixture of solids was mixed with 250 mL water and Na$_2$SO$_3$ (23.2 g, 181 mmol) and allowed to stir for 15 min. The solution was acidified with 6 M HCl until pH = 6 and then filtered through a pad of Celite, which was washed with water (5 × 10 mL). The filtrate was treated with Me$_3$NHCl (693 mg, 7.25 mmol), causing the formation of a white precipitate. Solids were filtered off, washed with distilled water, and left to air dry overnight to give the product as a white solid (1.17 g, 2.01 mmol, 55%). Upon ESI-MS analysis, it appeared that the chlorination was not complete, and there remained ca. 10% [HNMe$_3$][HCB$_{11}$Cl$_{10}$H] in the mixture.

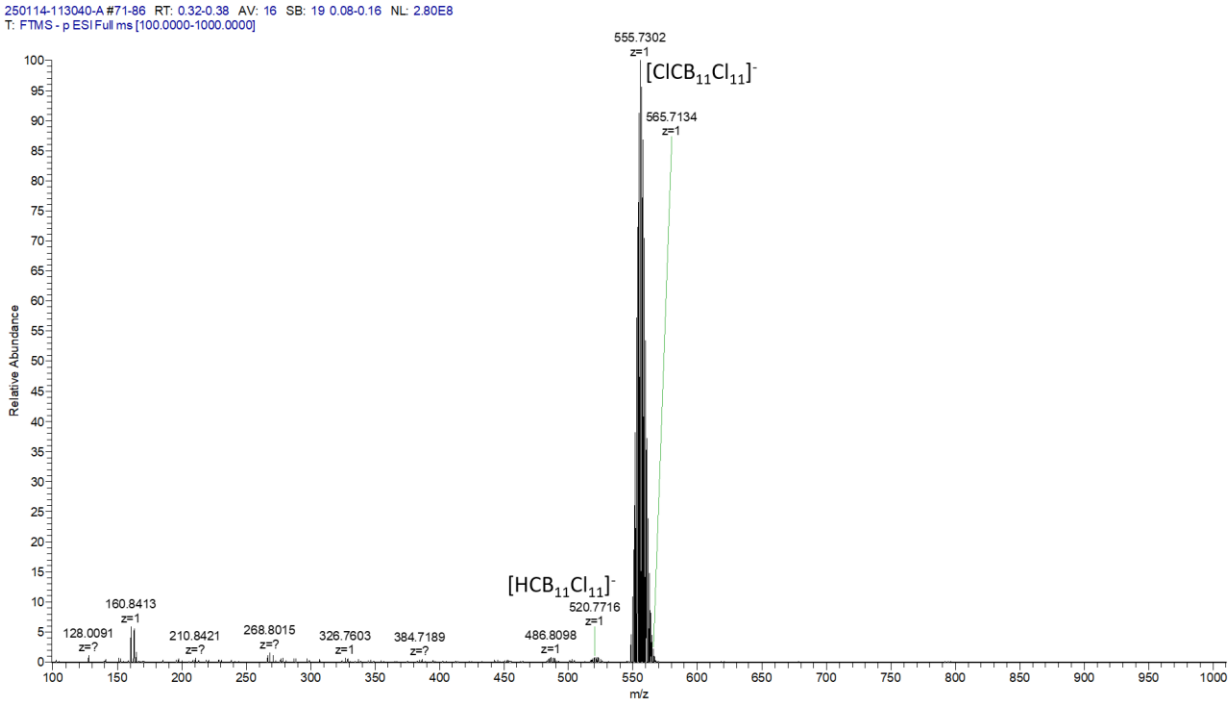


**Figure S22.** ESI-MS of the chlorination mixture after heating at 200 °C for 16 h.

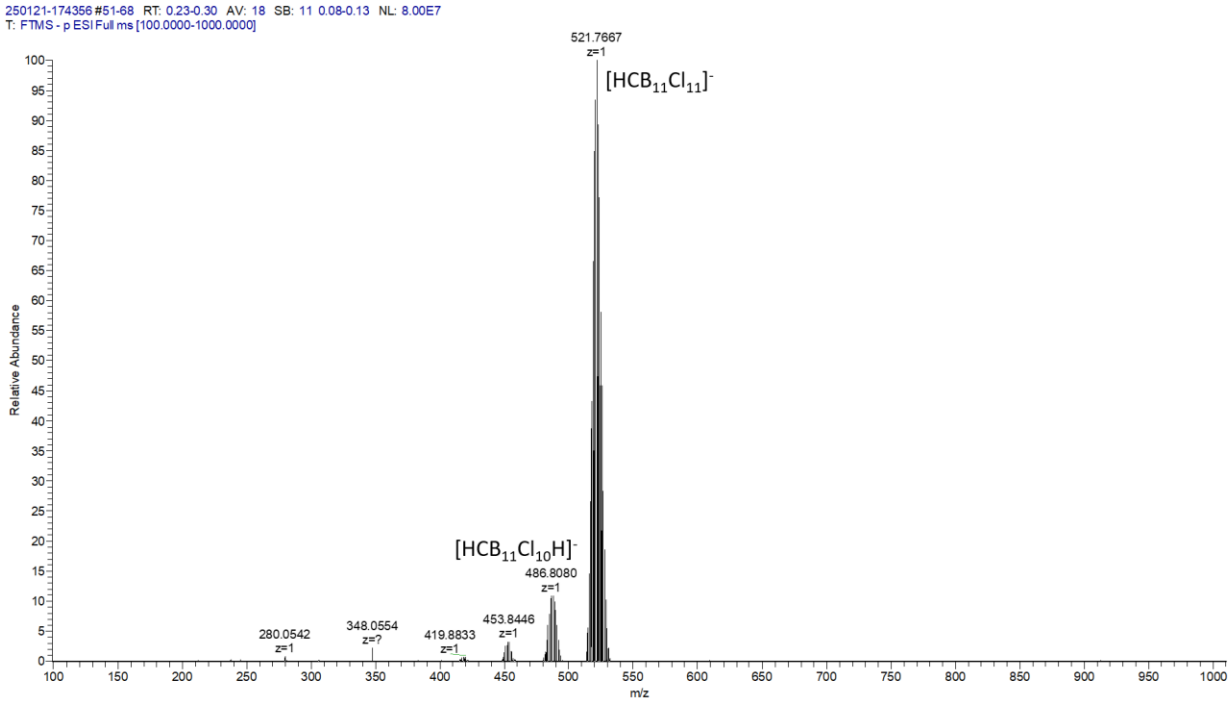


**Figure S23.** ESI-MS of the mixture of cages after workup.

**Synthesis of $[HNMe_3][HCB_{11}Cl_{11}]$ with sand (1 g scale) –** Using a mortar and pestle, $[Cs][HCB_{11}H_{11}]$ (1.00 g, 3.62 mmol) and TCCA (13.5 g, 58.0 mmol) were each ground separately for 10 min. The ground TCCA was manually mixed with Ottawa sand (275 g) in a 500 mL round bottom flask using a spatula. To the flask, $[Cs][HCB_{11}H_{11}]$ was added slowly in five approximately equal portions over the course of 2 h to avoid a runaway reaction, and the mixture was agitated with a spatula upon each addition. The flask was then placed in a sand bath and heated to 200 °C, and the contents were mixed using a spatula three times in two hour intervals. After 4 h of heating and stirring twice, an aliquot was taken, dissolved in 2 mL of $CH_2Cl_2$, and the conversion to the desired product was measured by ESI-MS. The mixture was then left in the 200 °C sand bath for 12 h. After 18 h in total, the mixture was allowed to cool and an aliquot was taken that indicated nearly full conversion to $[ClCB_{11}Cl_{11}]^-$ by ESI-MS. The mixture of solids was washed with 250 mL methanol twice over a 600 mL coarse frit, and filtrate volatiles were removed *in vacuo*. In a separate flask, $Na_2SO_3$ (4.59 g, 36.4 mmol) was dissolved in 40 mL water. Once dissolved, the $Na_2SO_3$ solution was immediately added to the flask containing the chlorination mixture and was allowed to stir for 5 min. The solution was acidified with 6M HCl until pH = 6 and then filtered through a pad of Celite, which was washed with water (5 × 10 mL). The filtrate was treated with $Me_3NHCl$ (693 mg, 7.25 mmol), causing the formation of a white precipitate. Solids were filtered off, washed with distilled water, and left to air dry overnight to give the product as a white solid. Upon NMR and ESI-MS analysis, there appeared to be approximately 5% of a $[ClCB_{11}Cl_{11}]^-$ impurity remaining in the final product. All solids were placed into a 100 mL round bottom flask, along with $Na_2SO_3$ (4.59 g, 36.4 mmol) and distilled water (50 mL). The mixture was heated to 60 °C and allowed to stir for 4 h before cooling. Additional $Me_3NHCl$ (346 mg, 3.62 mmol) was

added to the mixture, and solids were filtered of on a fine frit, washed with distilled water, and left to air dry overnight to give the product as a white solid (1.64 g, 2.82 mmol, 77%).

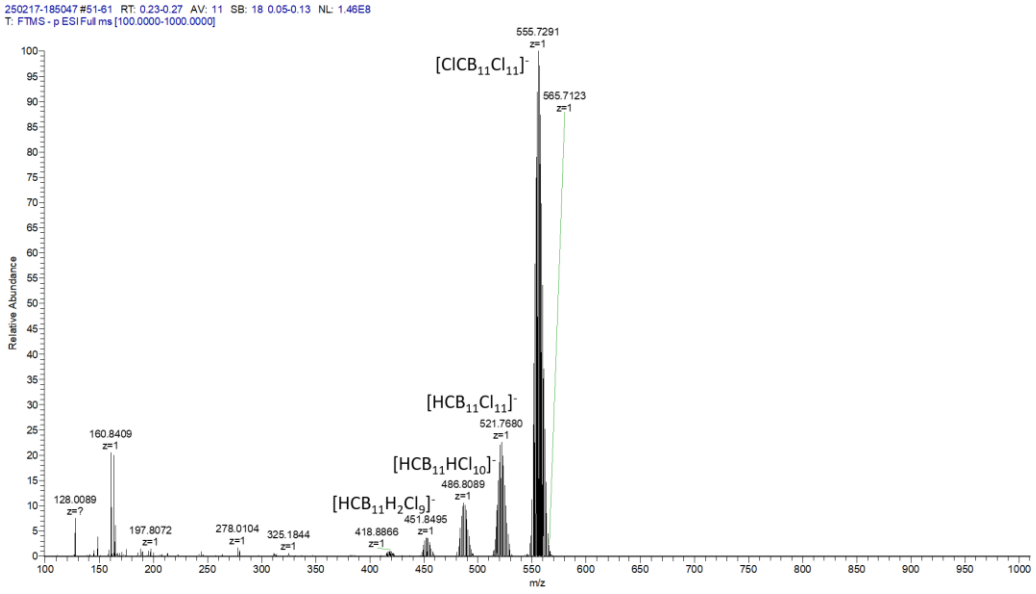


**Figure S24.** ESI-MS of the reaction between **[Cs][HCB$_{11}$H$_{11}$]** and TCCA in sand after 4 h.

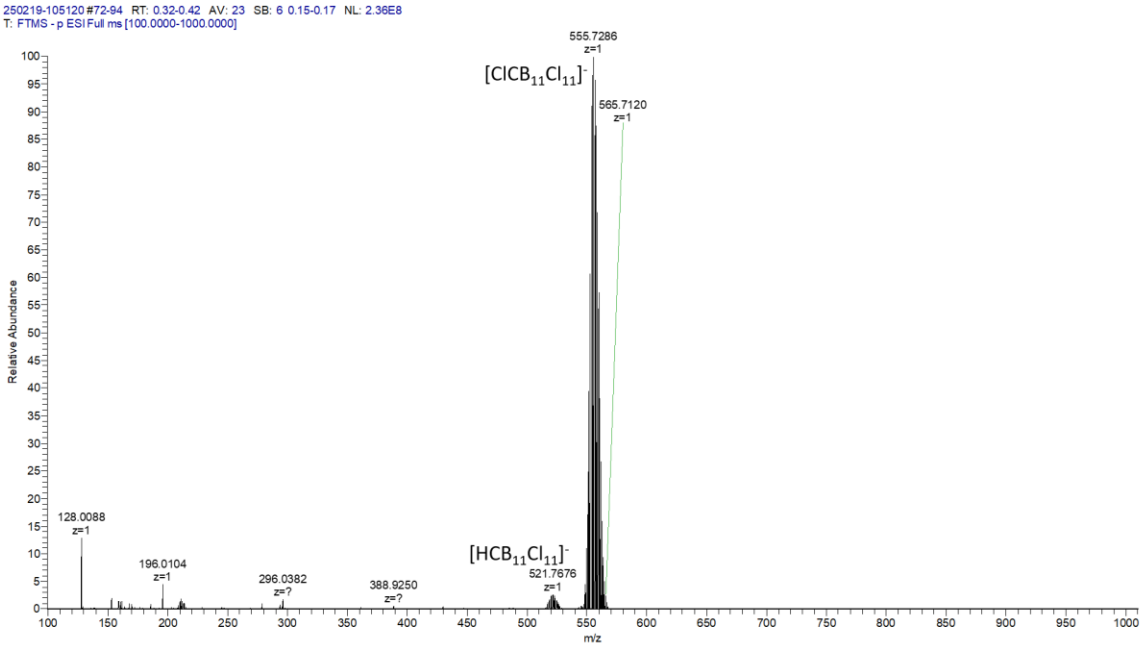


**Figure S25.** ESI-MS of the chlorination mixture after heating at 200 °C for 18 h.

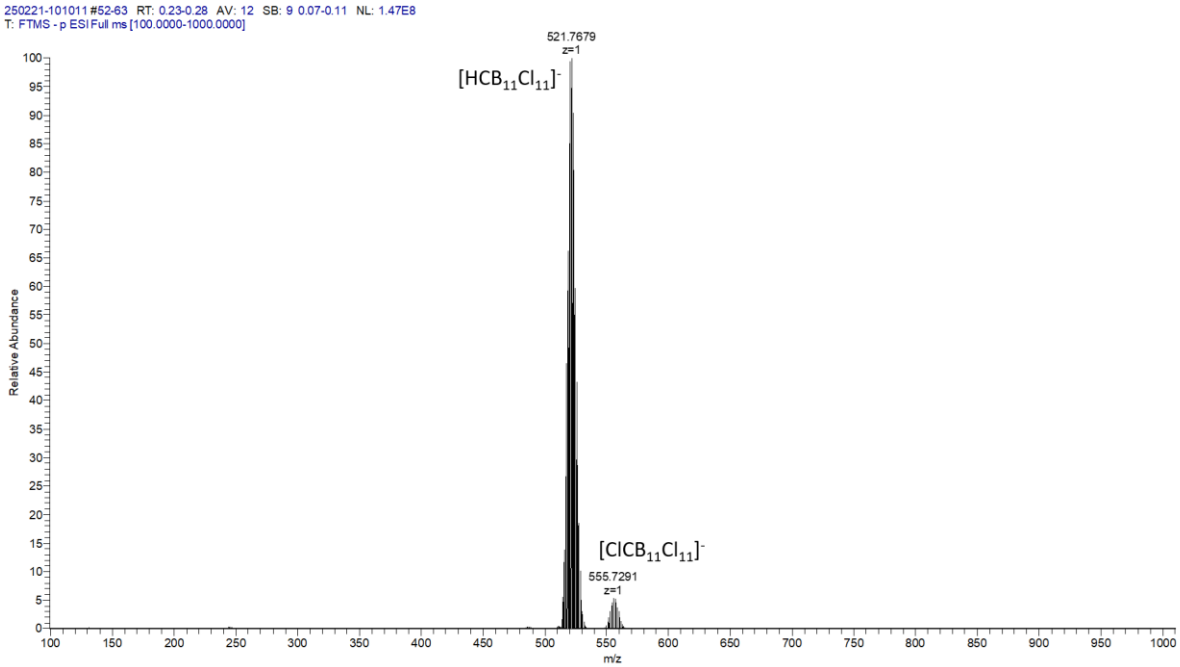


**Figure S26.** ESI-MS of the impure mixture of carborane cages.

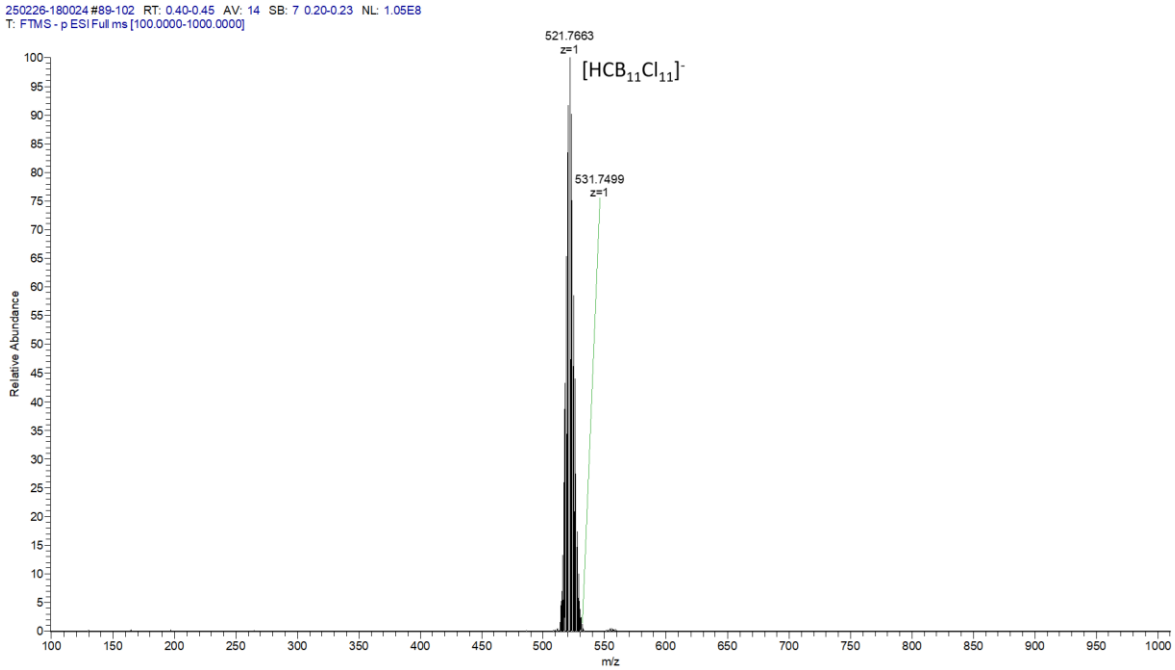


**Figure S27.** ESI-MS of the final product **[HNMe$_3$][HCB$_{11}$Cl$_{11}$]** after workup.

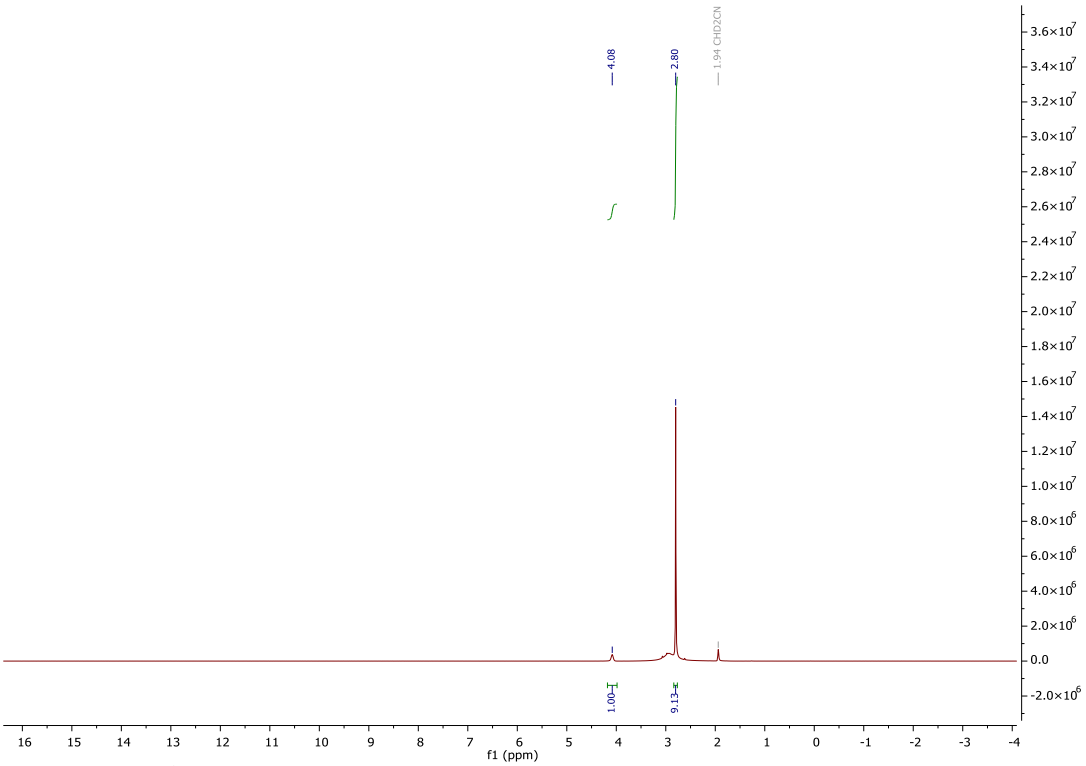


**Figure S28.** $^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][HCB$_{11}$Cl$_{11}$]** product.

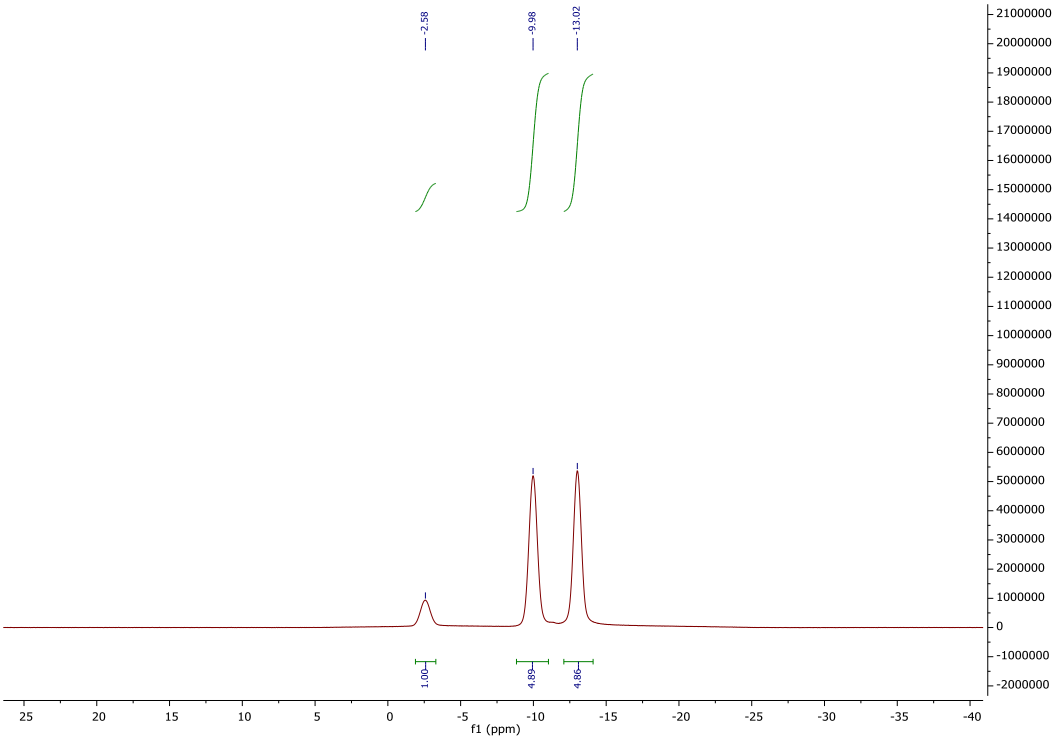


**Figure S29.** $^{11}$B{$^{1}$H} NMR (128 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][HCB$_{11}$Cl$_{11}$]** product.

**Chlorination of Cs[$HCB_{11}H_{11}$] with TCCA in Water –** Using a mortar and pestle, [Cs][$HCB_{11}H_{11}$] (100 mg, 0.362 mmol) and trichloroisocyanuric acid (TCCA) (1.35 g, 5.80 mmol) were each ground separately for 10 min. In a 25 mL Schlenk flask, the crushed [Cs][$HCB_{11}H_{11}$] was dissolved in 15 mL water, then the crushed TCCA was added to the mixture. The flask was equipped with a reflux condenser, and the solution was heated to reflux overnight. After 16 h, the mixture was allowed to cool and an aliquot was taken that indicated conversion to a mixture of cages ranging from $[ClCB_{11}Cl_6H_5]^-$ to $[HCB_{11}Cl_{11}]^-$ by ESI-MS. [*Caution! On at least one occasion, the scaled-up version of this reaction (1.00 g [Cs][$HCB_{11}H_{11}$] and 13.5 g TCCA, both crushed, in 100 mL of water in a 200 mL round bottom flask equipped with a reflux condenser) resulted in an explosion ca. 1 h after the mixture was brought to reflux. We advise against performing any reaction with TCCA in boiling water.*]

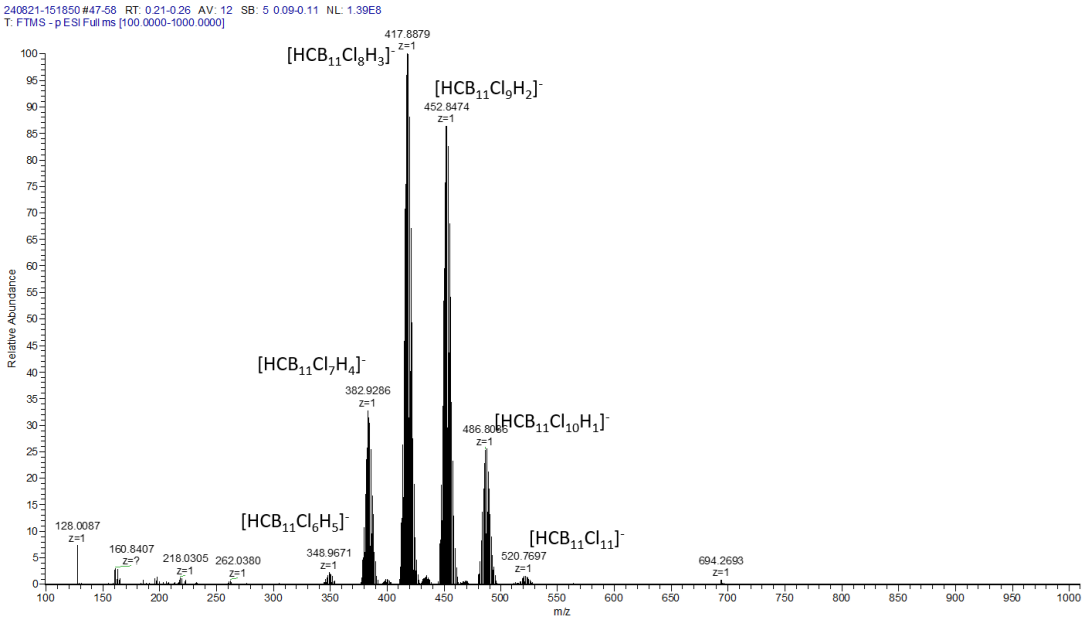


**Figure S30.** ESI-MS of the chlorination mixture after refluxing in water for 16 h.

## II.4. Chlorination using NCS.

**Attempted Synthesis of $[HNMe_3][HCB_{11}Cl_{11}]$ with NCS –** Using a mortar and pestle, $[Cs][HCB_{11}H_{11}]$ (101 mg, 0.380 mmol) and NCS (N-Chlorosuccinimide) (2.04 g, 15.3 mmol) were each ground separately for 10 min. In a 50 mL Schlenk flask, both ground solids were added along with a stir bar. The flask was heated in a 150 °C oil bath for 3 h. After 3 h, an aliquot of the black liquid was taken up in $CH_2Cl_2$ that indicated conversion to a mixture of cages ranging from $[HCB_{11}Cl_4H_7]^-$ to $[HCB_{11}Cl_7H_4]^-$ by ESI-MS. Upon heating to 200 °C for an additional 16 h, there was only a slight increase in the amount of $[HCB_{11}Cl_7H_4]^-$ observed.

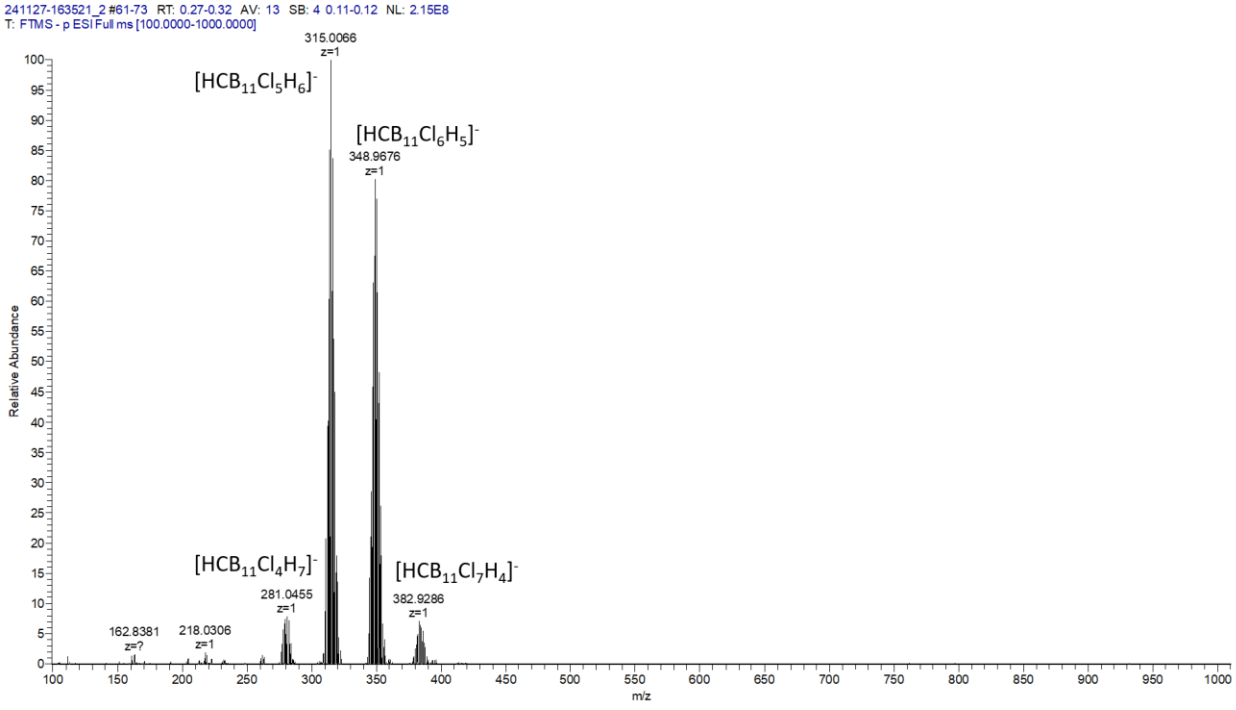


**Figure S31.** ESI-MS of the chlorination mixture after heating in NCS at 150 °C for 3 h.

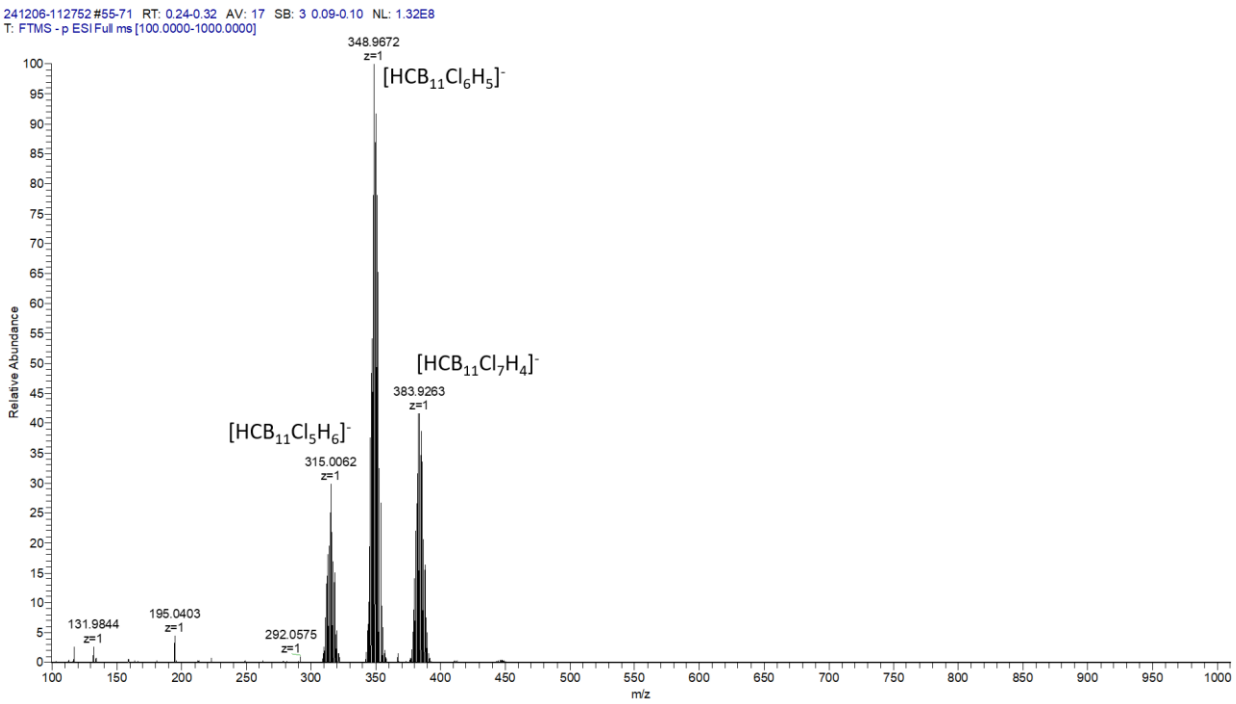


**Figure S32.** ESI-MS of chlorination mixture after additional heating in NCS at 200 °C for 16 h.

## II.5. Chlorination using DCDMH

**Attempted Synthesis of [HNMe$_3$][HCB$_{11}$Cl$_{11}$] with DCDMH –** Using a mortar and pestle, [Cs][HCB$_{11}$H$_{11}$] (101 mg, 0.380 mmol) and DCDMH (1,3-dichloro-5,5-dimethlhydantoin) (3.49 g, 17.7 mmol) were each ground separately for 10 min. In a 25 mL Schlenk flask, both ground solids were added along with a stir bar. The flask was equipped with a reflux condenser under Ar flow and flushed with Ar for 15 min, then was heated in a 250 °C sand bath for 16 h. After 16 h, an aliquot of the black solids was taken up in $CH_2Cl_2$ that indicated conversion to a mixture of primarily $[HCB_{11}Cl_{10}H]^-$ and $[HCB_{11}Cl_{11}]^-$ by ESI-MS. After another 2 d of heating at 250 °C, no additional chlorination was observed.

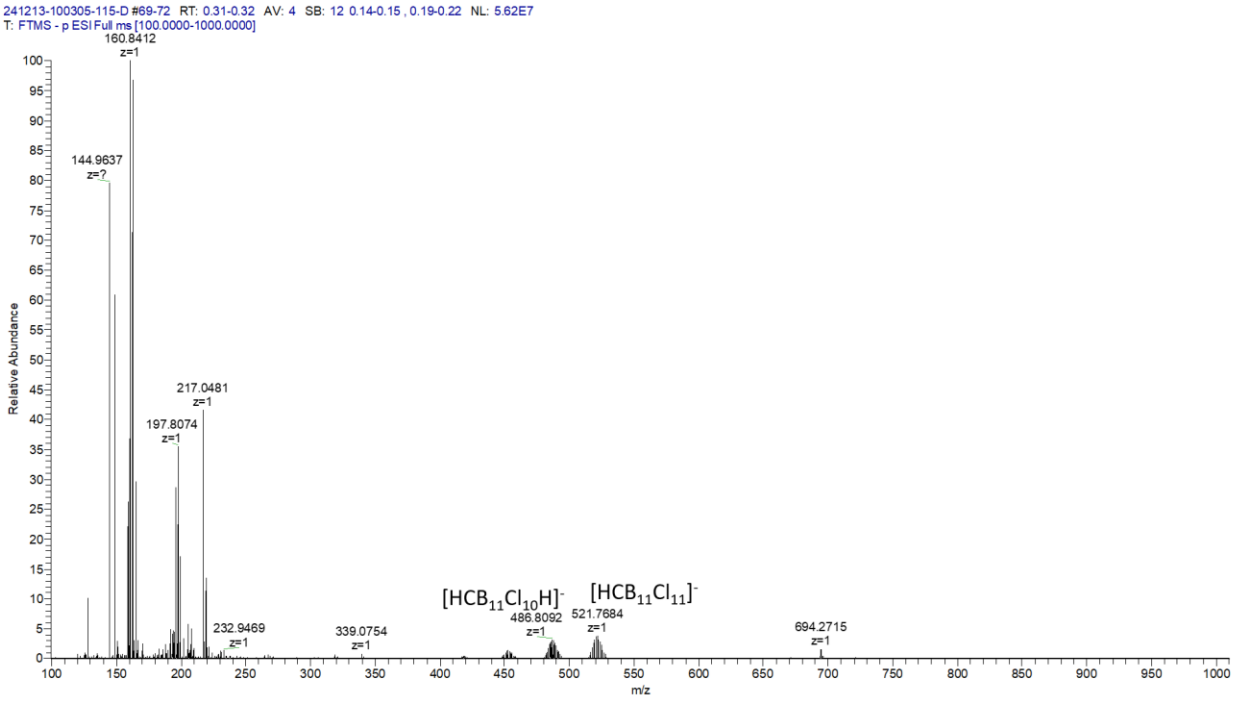


**Figure S33.** ESI-MS of the chlorination mixture after heating in DCDMH for 3 h.

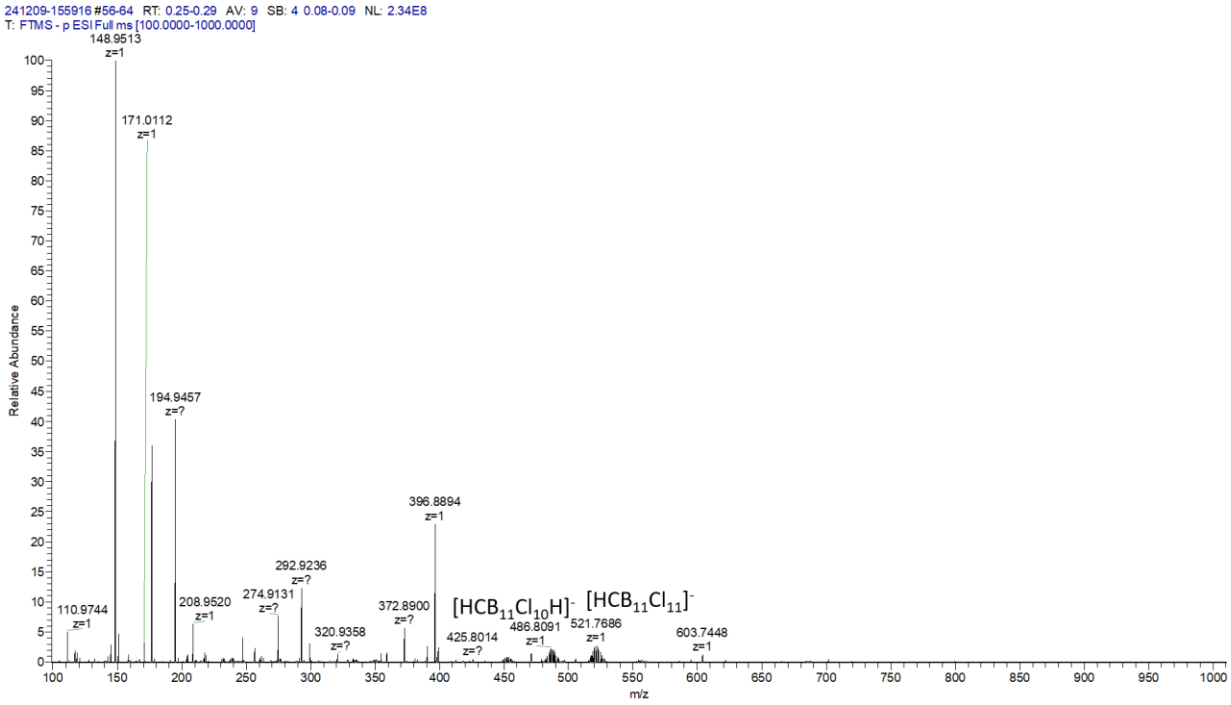


**Figure S34.** ESI-MS of the chlorination mixture after heating in DCDMH for an additional 2 d.

## III. Carbon vertex functionalization

### Synthesis of $[HNMe_3][ClCB_{11}Cl_{11}]$:

**Method 1 (TCCA) –** A 20 mL glass vial was loaded with **$Na[HCB_{11}Cl_{11}]$** (50 mg, 0.092 mmol) and a PTFE coated stir bar in 5 mL of water. NaOH (5 mg, 0.125 mmol) was added to the mixture. Solids were allowed to dissolve and trichloroisocyanuric acid (TCCA) (21.4 mg, 0.092 mmol) was added, and the mixture was allowed to stir for 15 min. In situ $^{11}B\{^1H\}$ NMR analysis at 15 min showed that **$[ClCB_{11}Cl_{11}]^-$** was the only species observed. Once complete, 6M HCl was added to acidify the solution until pH = 6 was measured. $Me_3NHCl$ (18 mg, 0.184 mmol) was added to the mixture which precipitated white solids, which were then filtered off with a fine frit and washed with water. Solids were dried under vacuum at 150 °C for 24 h and were characterized via $^1H$, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. IR spectroscopy was used to confirm the absence of TCCA or its cyanuric acid derivatives in the final product (Figure S41). Yield of **$[HNMe_3][ClCB_{11}Cl_{11}]$:** 46 mg (81%).

**Method 2 (NaOCl) –** A 20 mL glass vial was loaded with **$Na[HCB_{11}Cl_{11}]$** (50 mg, 0.092 mmol) and a PTFE coated stir bar in 5 mL of water. NaOH (5 mg, 0.125 mmol) was added to the mixture. After the solids had dissolved, a 12.5% NaOCl solution (66 mg, 0.110 mmol) measured by weight was added, and the mixture was allowed to stir for 15 min. In situ $^{11}B\{^1H\}$ NMR analysis at 15 min showed that **$[ClCB_{11}Cl_{11}]^-$** was the only species observed. Once complete, 6M HCl was added to acidify the solution until pH = 6 was measured. $Me_3NHCl$ (18 mg, 0.184 mmol) was added to the mixture which precipitated white solids, which were then filtered off with a fine frit and washed with water. Solids were then dried under vacuum at 150 °C for 24 h. Yield of **$[HNMe_3][ClCB_{11}Cl_{11}]$:** 33 mg (58%). $^1H$ NMR (400 MHz, 25 °C, $CD_3CN$): δ 6.85 (t, $^1J_{H\text{-}N}$ = 55.4 Hz, 1H, N*H*$Me_3$), 2.81 (d, $^3J_{H\text{-}H}$ = 3.3 Hz, 9H, NH$Me_3$). $^{11}B\{^1H\}$ NMR (128 MHz, 25 °C, $CD_3CN$):

δ -3.3 (br s, 1B), –11.4 (br s, 10B). $^{13}C\{^{1}H\}$ NMR (126 MHz, 25 °C, $CD_3CN$): δ 59.6 (s, Cl*C*$B_{11}Cl_{11}$), 46.0 (s, HN*Me*$_3$). HRMS ($ESI^-$) m/z $[M]^-$: calc'd for $ClCB_{11}Cl_{11}$: 555.7258, found 555.7289.

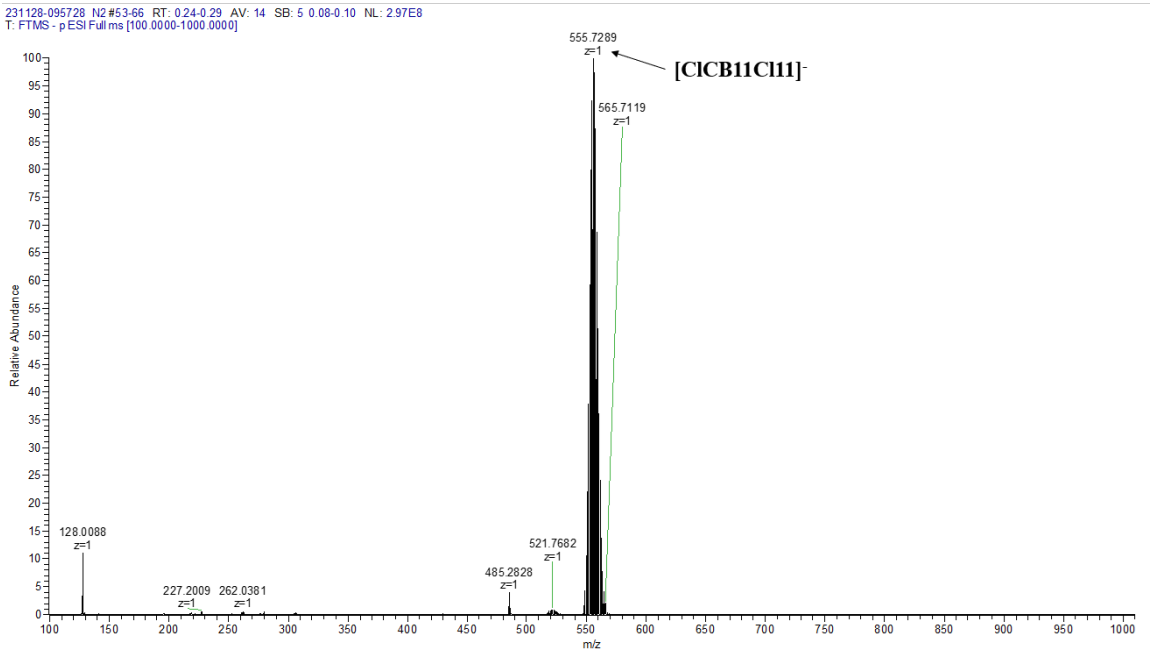


**Figure S35.** ESI-MS of **[HNMe$_3$][ClCB$_{11}$Cl$_{11}$]**.

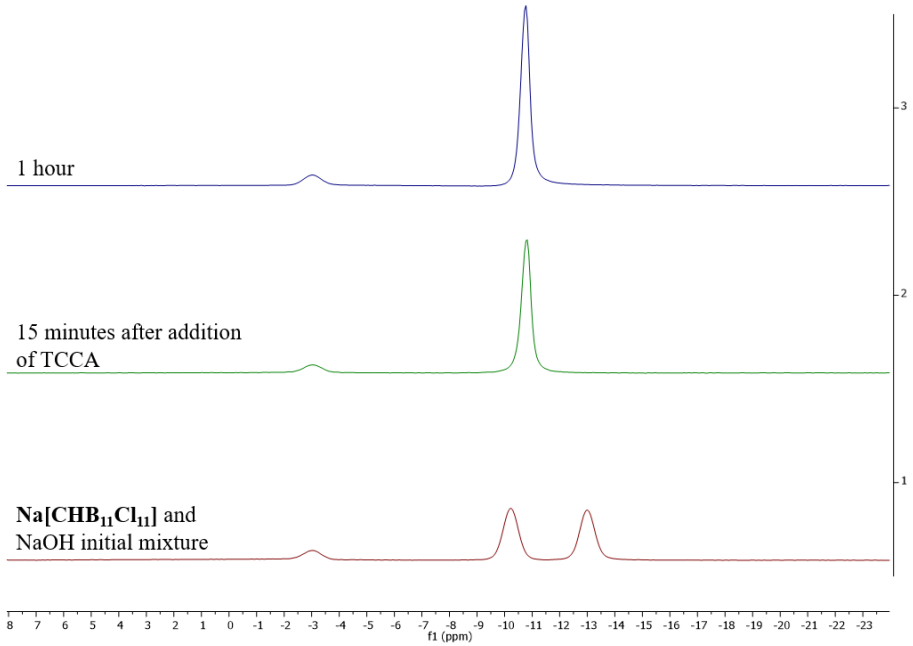


**Figure S36.** $^{11}B\{^{1}H\}$ NMR (400 MHz, $H_2O$ unlocked/unshimmed) in situ spectra of the conversion of **Na[HCB$_{11}$Cl$_{11}$]** to **Na[ClCB$_{11}$Cl$_{11}$]**.

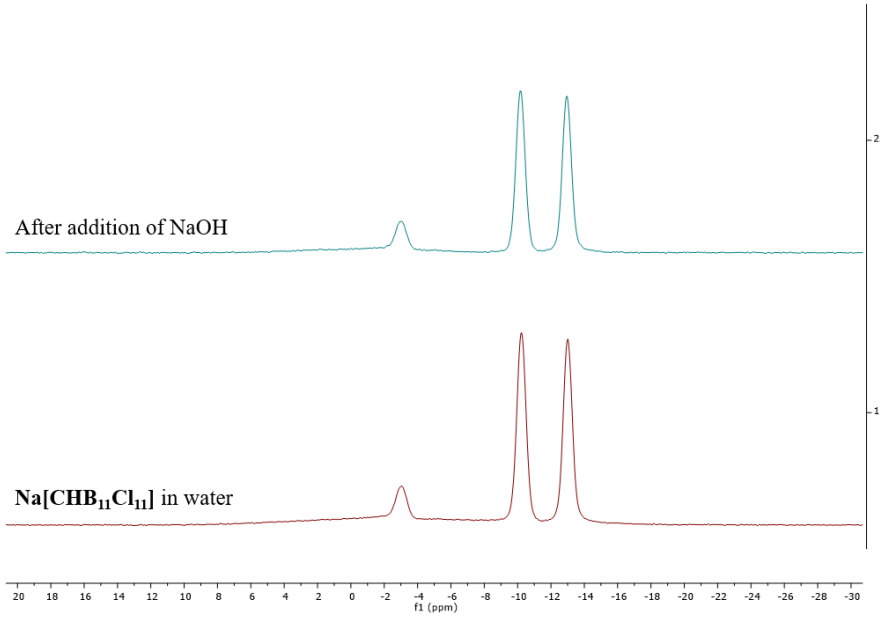


**Figure S37.** $^{11}B\{^{1}H\}$ NMR (128 MHz, $H_2O$ unlocked/unshimmed) spectrum of 50 mg **[Na][ClCB$_{11}$Cl$_{11}$]** in 5 mL aqueous solution before and after addition of 5 mg NaOH (1.4 eq).

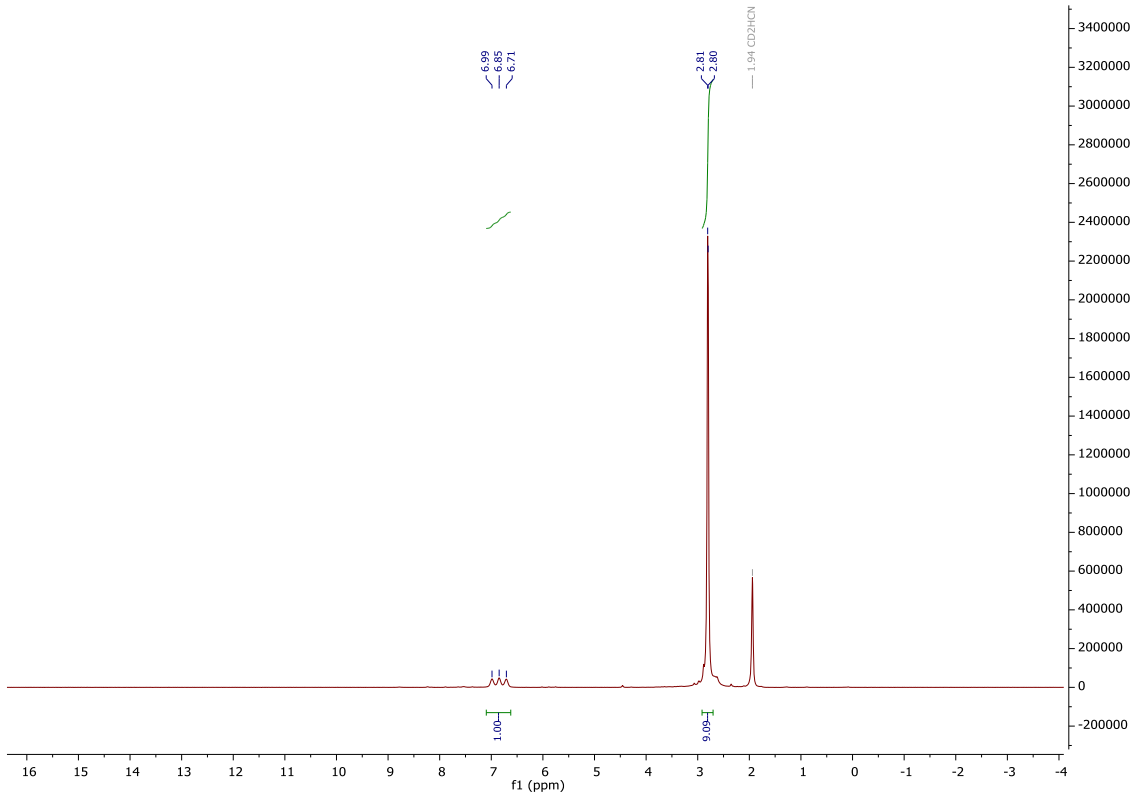


**Figure S38.** $^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][ClCB$_{11}$Cl$_{11}$]**.

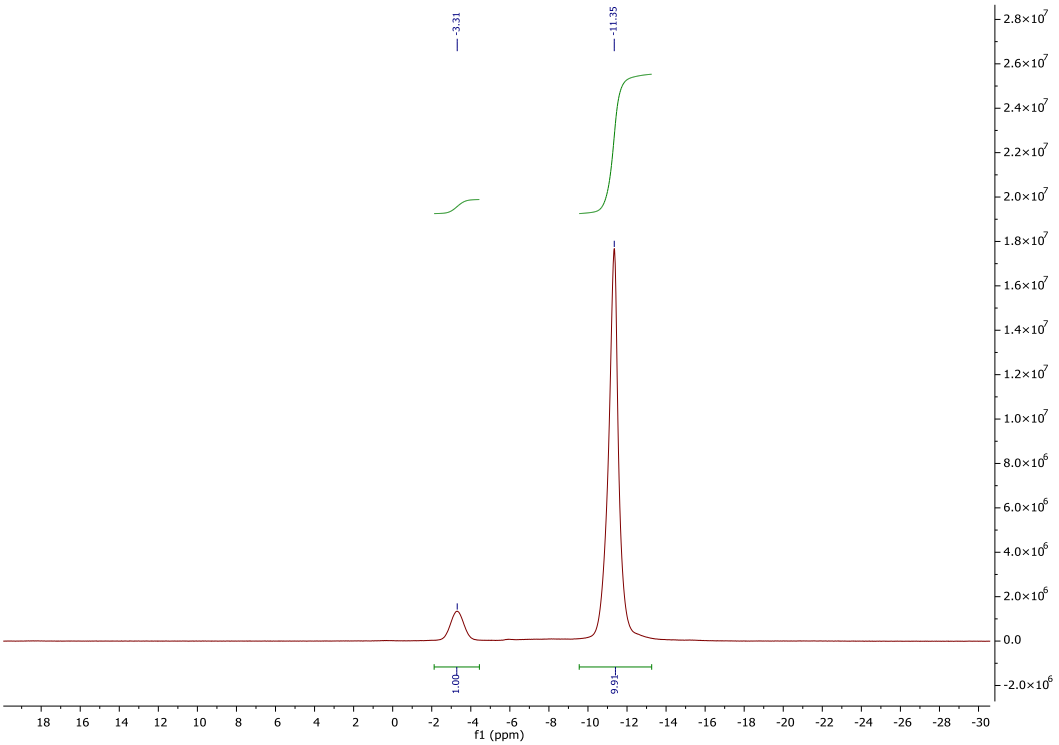


**Figure S39.** $^{11}$B{$^{1}$H} NMR (128 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][ClCB$_{11}$Cl$_{11}$]**.

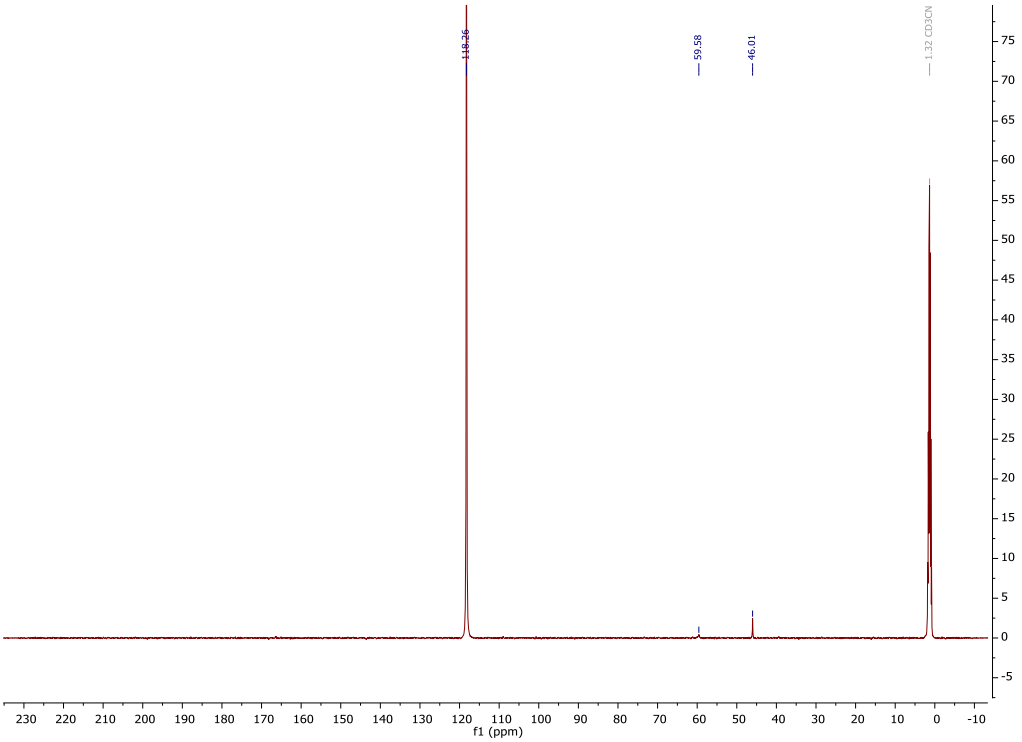


**Figure S40.** $^{13}C\{^{1}H\}$ NMR (126 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][ClCB$_{11}$Cl$_{11}$]**.

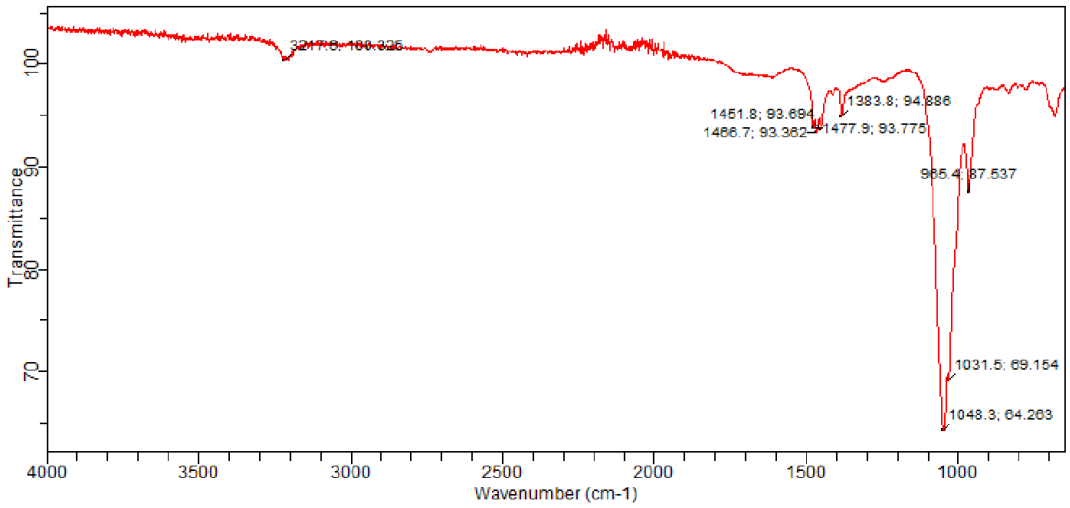


**Figure S41.** IR spectrum of **[HNMe$_3$][ClCB$_{11}$Cl$_{11}$]** final product. The lack of a carbonyl stretching peak indicates that there is no TCCA or an of its cyanuric acid derivatives in the final product.

**Synthesis of [HNMe$_3$][ICB$_{11}$Cl$_{11}$] –** A 20 mL glass vial was loaded with **Na[HCB$_{11}$Cl$_{11}$]** (100 mg, 0.184 mmol) and a PTFE coated stir bar in 10 mL of water. NaOH (9 mg, 0.225 mmol) was added to the mixture. In a separate vial, $I_2$ crystals (56 mg, 0.221 mmol) were dissolved in 2 mL ethanol. The iodine solution was added to the carborane reaction mixture and was allowed to stir for 15 min. In situ $^{11}B\{^1H\}$ NMR analysis at 15 min showed that **[ICB$_{11}$Cl$_{11}$]$^-$** was the only species observed. Once complete, 6M HCl was added to acidify the solution until pH = 6 was measured. $Me_3NHCl$ (35 mg, 0.368 mmol) was added to the mixture which precipitated white solids, which were then filtered off with a fine frit and washed with water. Solids were then dried under vacuum at 150 °C for 24 h. Yield of **[HNMe$_3$][ICB$_{11}$Cl$_{11}$]:** 112 mg (86%). $^1H$ NMR (400 MHz, 25 °C, $CD_3CN$): δ 6.81 (t, $^1J_{N\text{-}H}$ = 55.3 Hz, 1H, N*H*Me$_3$), 2.81 (d, $^3J_{H\text{-}H}$ = 5.3 Hz, 9H, NH*Me$_3$*). $^{11}B\{^1H\}$ NMR (128 MHz, 25 °C, $CD_3CN$): δ -2.2 (br s, 1B), –10.7 (br s, 10B). $^{13}C\{^1H\}$ NMR (126 MHz, 25 °C, $CD_3CN$): δ 46.0 (s, HN*Me$_3$*), 27.9 (s, I*C*B$_{11}$Cl$_{11}$). HRMS (ESI$^-$) m/z [M]$^-$: calc'd for ICB$_{11}$Cl$_{11}$: 647.6614, found 647.6644.

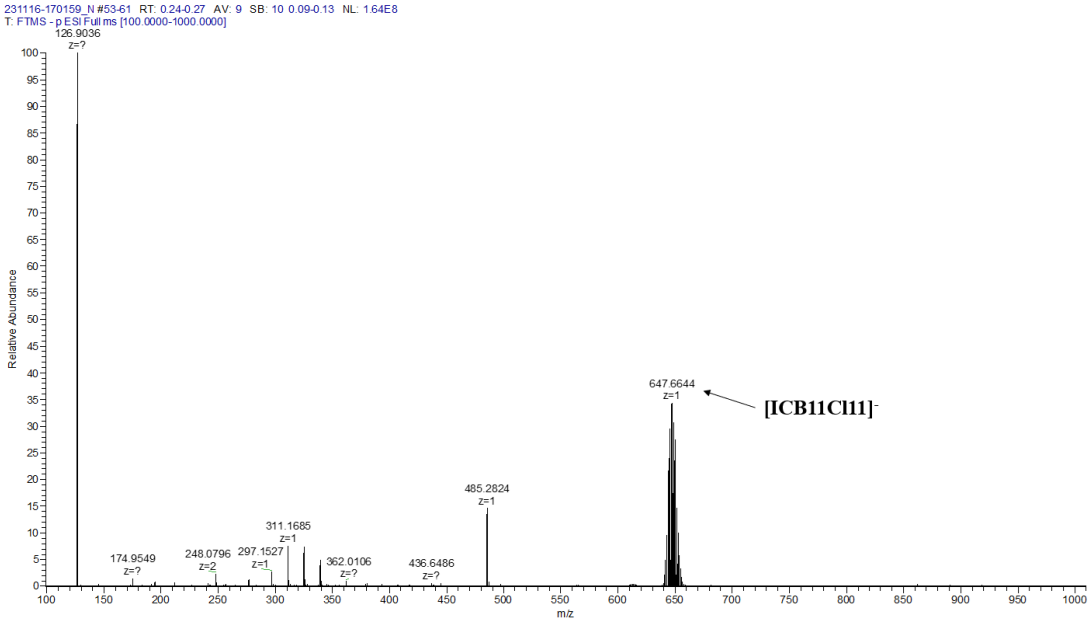


**Figure S42.** ESI-MS of **[HNMe$_3$][ICB$_{11}$Cl$_{11}$]**.

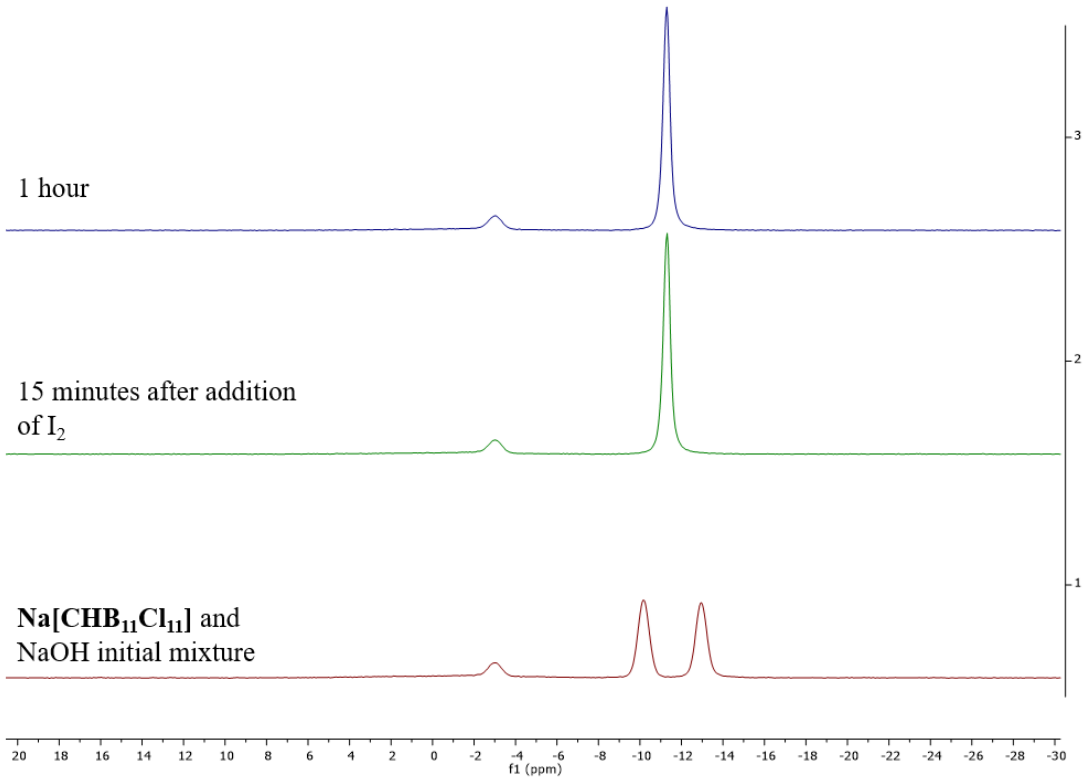


**Figure S43.** $^{11}B\{^{1}H\}$ NMR (400 MHz, $H_2O$ unlocked/unshimmed) in situ spectra of the conversion of **Na[HCB$_{11}$Cl$_{11}$]** to **Na[ICB$_{11}$Cl$_{11}$]**.

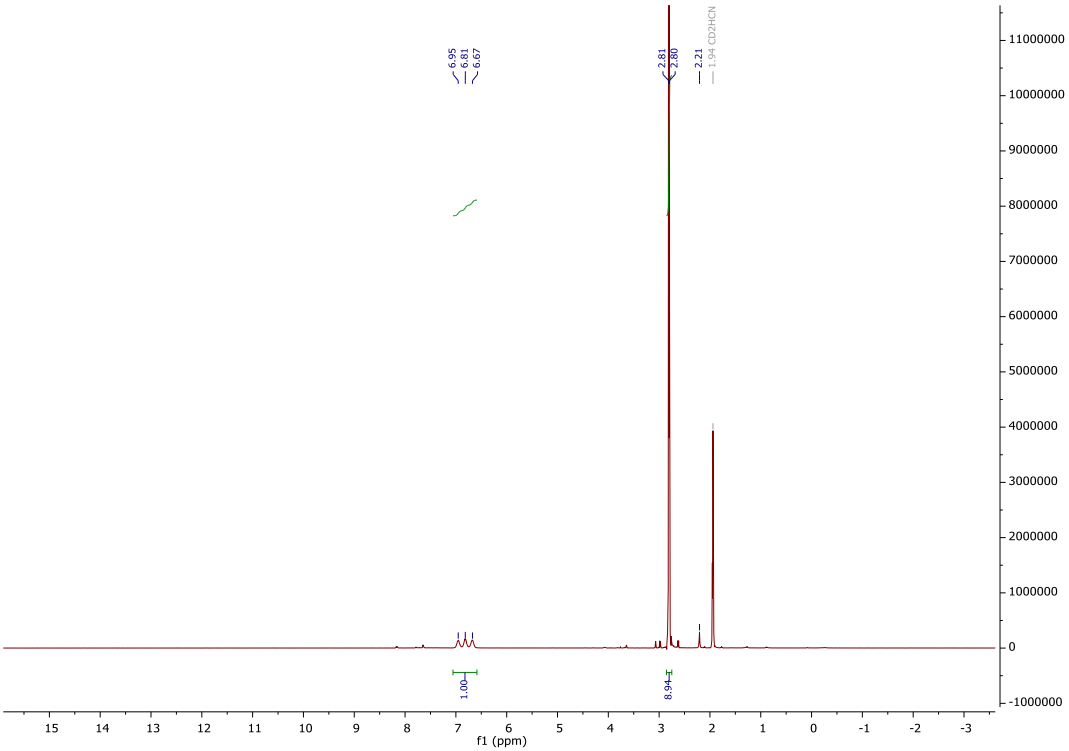


**Figure S44.** $^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][ICB$_{11}$Cl$_{11}$]**. A small amount of residual water impurity is seen at 2.21 ppm.

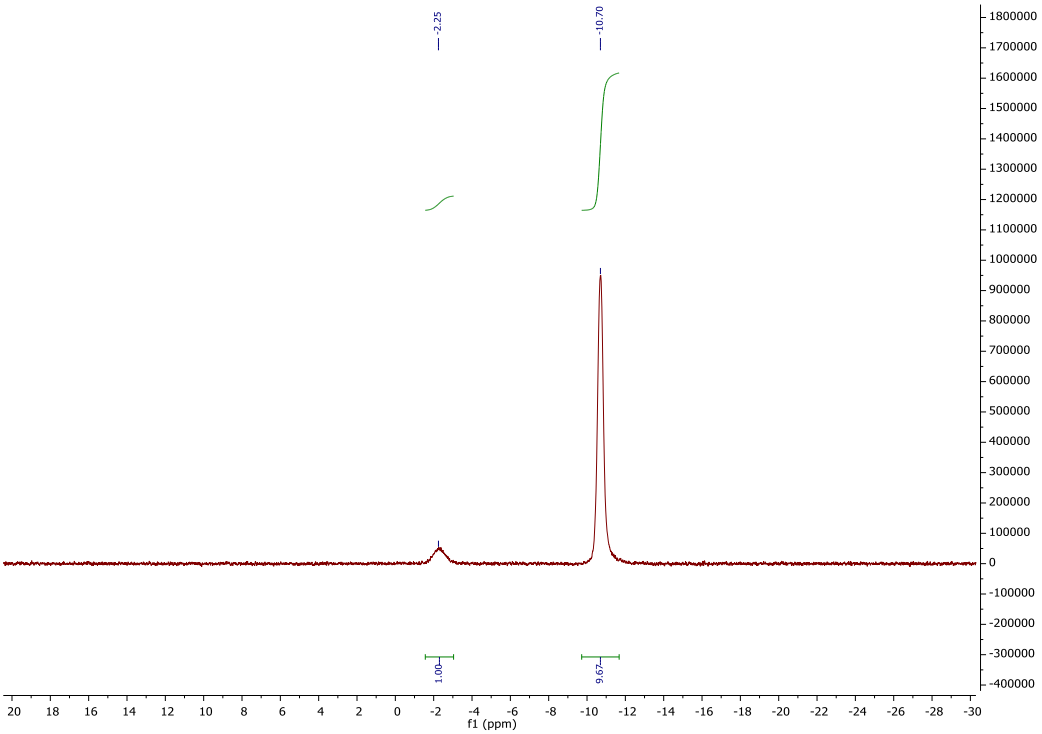


**Figure S45.** $^{11}$B{$^{1}$H} NMR (128 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][ICB$_{11}$Cl$_{11}$]**.

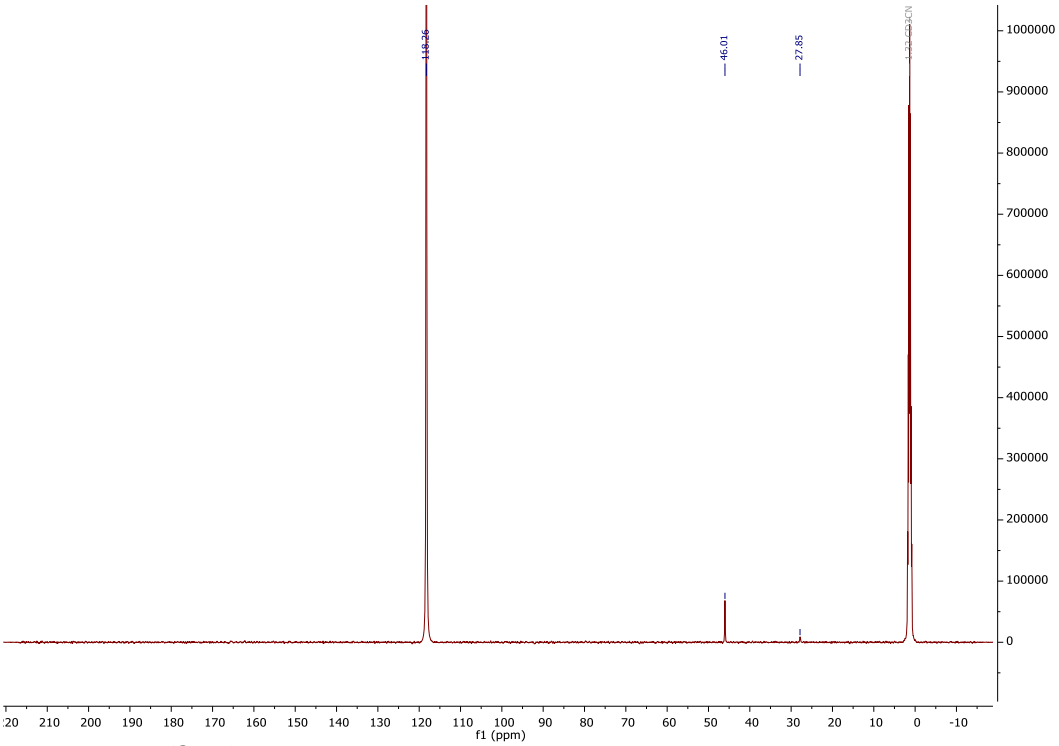


**Figure S46.** $^{13}C\{^{1}H\}$ NMR (126 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][ICB$_{11}$Cl$_{11}$]**.

**Synthesis of [HNMe$_3$][H$_2$NCB$_{11}$Cl$_{11}$] –** A 20 mL glass vial was loaded with **Na[HCB$_{11}$Cl$_{11}$]** (50 mg, 0.092 mmol) and a PTFE coated stir bar in 5 mL of water. NaOH (25 mg, 0.625 mmol) was added to the mixture. Solids were allowed to dissolve and hydroxylamine-*o*-sulfonic acid (23 mg, 0.202 mmol) was added, and the mixture was allowed to stir for 1 h. In situ $^{11}B\{^1H\}$ NMR analysis at 1 h showed that **[H$_2$NCB$_{11}$Cl$_{11}$]$^-$** was the only species observed. Once complete, 6M HCl was added to acidify the solution until pH = 6 was measured. Me$_3$NHCl (18 mg, 0.184 mmol) was added to the mixture which precipitated white solids, which were then filtered off with a fine frit and washed with water. Solids were then dried under vacuum at 150 °C for 24 h. Yield of **[HNMe$_3$][H$_2$NCB$_{11}$Cl$_{11}$]:** 44 mg (82%). $^1H$ NMR (400 MHz, 25 °C, CD$_3$CN): δ 6.82 (t, $^1J_{N\text{-}H}$ = 54.7 Hz, 1H, N*H*Me$_3$), 2.81 (d, $^3J_{H\text{-}H}$ = 4.5 Hz, 9H, NH*Me$_3$*), 2.58 (s, 2H, N*H$_2$*). $^{11}B\{^1H\}$ NMR (128 MHz, 25 °C, CD$_3$CN): δ -5.8 (br s, 1B), -12.0 (br s, 10B). $^{13}C\{^1H\}$ NMR (126 MHz, 25 °C, CD$_3$CN): δ 67.4 (s, (NH$_2$)*C*B$_{11}$Cl$_{11}$), 46.0 (s, HN*Me$_3$*). HRMS (ESI$^-$) m/z [M]$^-$: calc'd for (NH$_2$)CB$_{11}$Cl$_{11}$: 536.7756, found 536.7795.

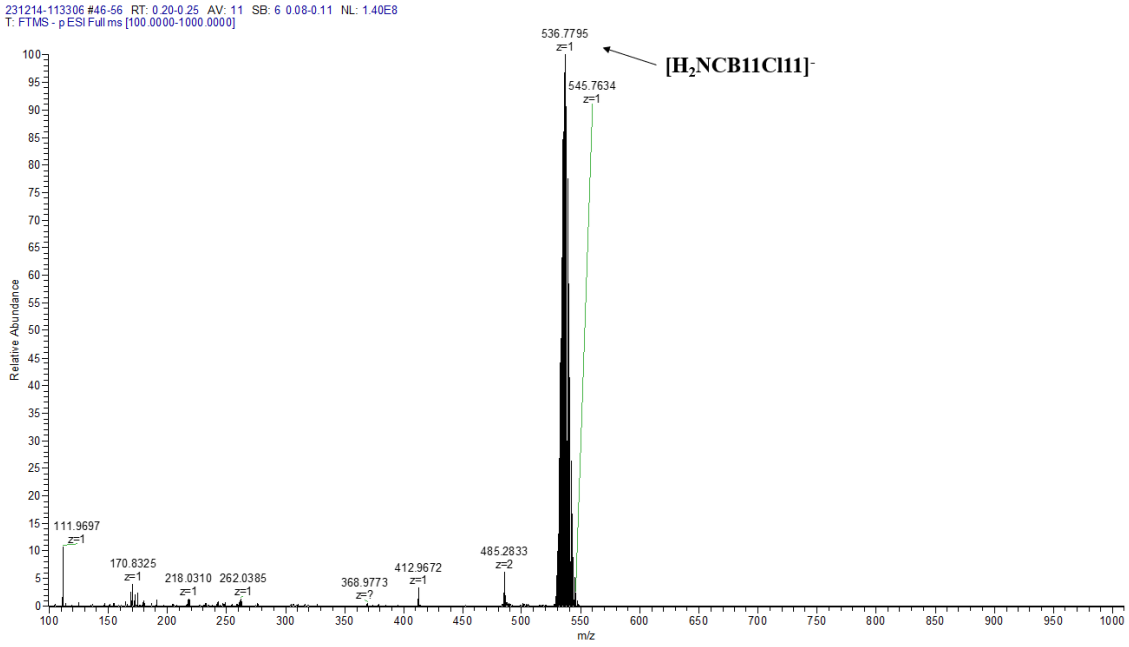


**Figure S47.** ESI-MS of **[HNMe$_3$][H$_2$NCB$_{11}$Cl$_{11}$]**.

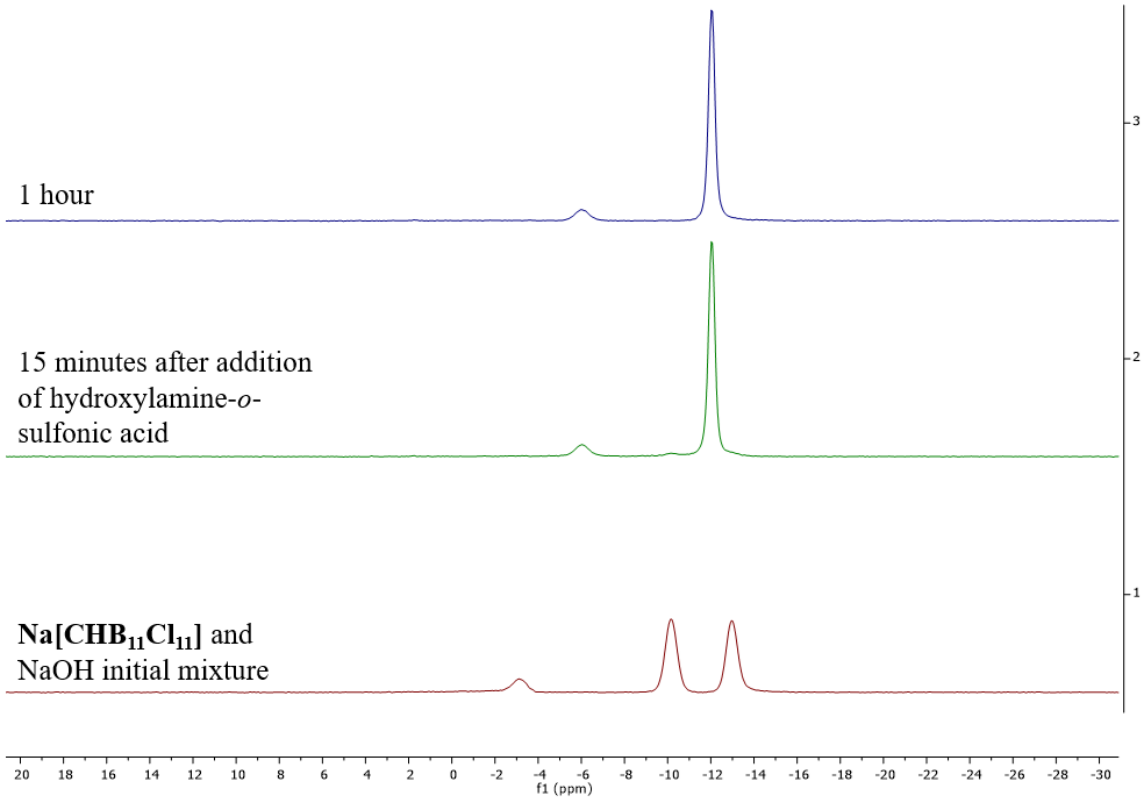


**Figure S48.** $^{11}B\{^{1}H\}$ NMR (400 MHz, $H_2O$ unlocked/unshimmed) in situ spectra of the conversion of **Na[HCB$_{11}$Cl$_{11}$]** to **Na[H$_2$NCB$_{11}$Cl$_{11}$]**.

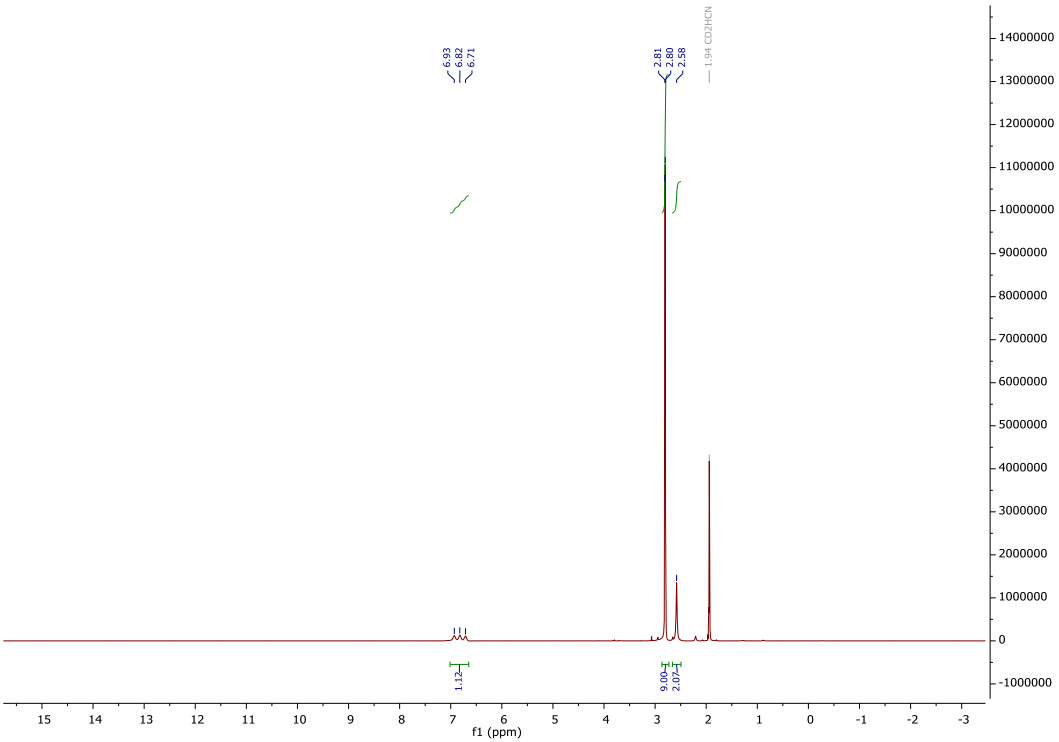


**Figure S49.** $^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][H$_2$NCB$_{11}$Cl$_{11}$]**.

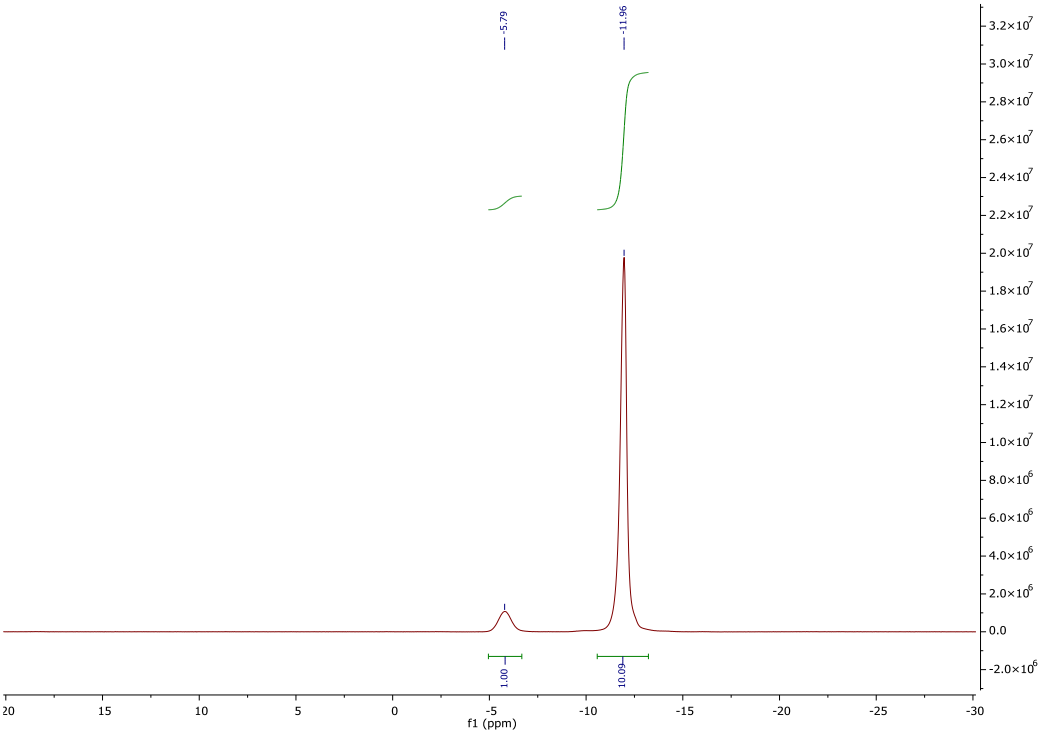


**Figure S50.** $^{11}$B{$^{1}$H} NMR (128 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][H$_2$NCB$_{11}$Cl$_{11}$]**.

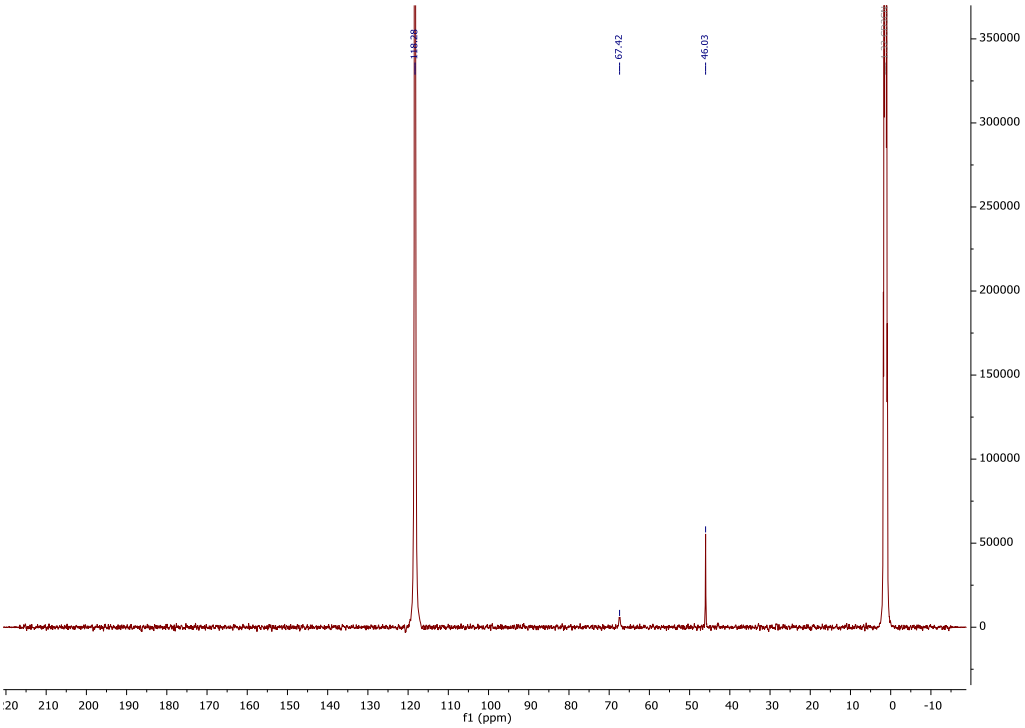


**Figure S51.** $^{13}C\{^{1}H\}$ NMR (126 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][H$_2$NCB$_{11}$Cl$_{11}$]**.

**Synthesis of [HNMe$_3$][BrCB$_{11}$Cl$_{11}$] –** A 20 mL glass vial was loaded with **Na[HCB$_{11}$Cl$_{11}$]** (80 mg, 0.147 mmol) and a PTFE coated stir bar in 5 mL of acetonitrile. N-Bromosuccinimide (29 mg, 0.161 mmol) was added and the solution was heated to 70 °C on a heating plate. The mixture was allowed to stir for 5 h, at which point in situ $^{11}$B{$^1$H} NMR analysis indicated 95% conversion to **[BrCB$_{11}$Cl$_{11}$]$^-$**. After 5 h, the solution was allowed to cool and all acetonitrile was pumped off. 2 mL of water was added to dissolve the solids, and 6 M HCl was added to acidify the solution until pH = 6 was measured. Me$_3$NHCl (29 mg, 0.30 mmol) was added to the mixture which precipitated white solids, which were then filtered off with a fine frit and washed with water. Solids were then dried under vacuum at 150 °C for 24 h. Yield of **[HNMe$_3$][BrCB$_{11}$Cl$_{11}$]:** 78 mg (80%). $^1$H NMR (400 MHz, 25 °C, CD$_3$CN): δ 6.85 (t, $^1J_{N\text{-}H}$ = 54.8 Hz, 1H, N*H*Me$_3$), 2.81 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 9H, NH*Me$_3$*). $^{11}$B{$^1$H} NMR (128 MHz, 25 °C, CD$_3$CN): δ -2.8 (br s, 1B), –11.1 (br s, 10B). $^{13}$C{$^1$H} NMR (126 MHz, 25 °C, CD$_3$CN): δ 48.6 (s, Br*C*B$_{11}$Cl$_{11}$), 46.0 (s, HN*Me$_3$*). HRMS (ESI$^-$) m/z [M]$^-$ : calc'd for BrCB$_{11}$Cl$_{11}$: 600.6768, found 600.6777.

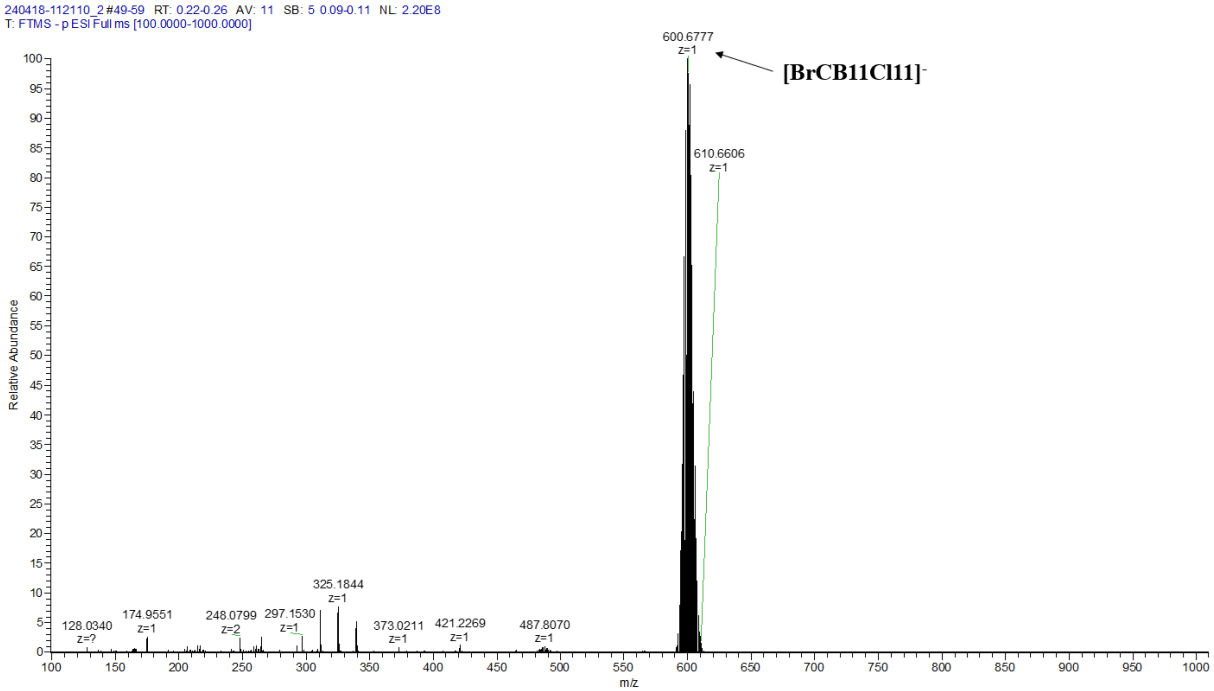


**Figure S52.** ESI-MS of **[HNMe$_3$][BrCB$_{11}$Cl$_{11}$]**.

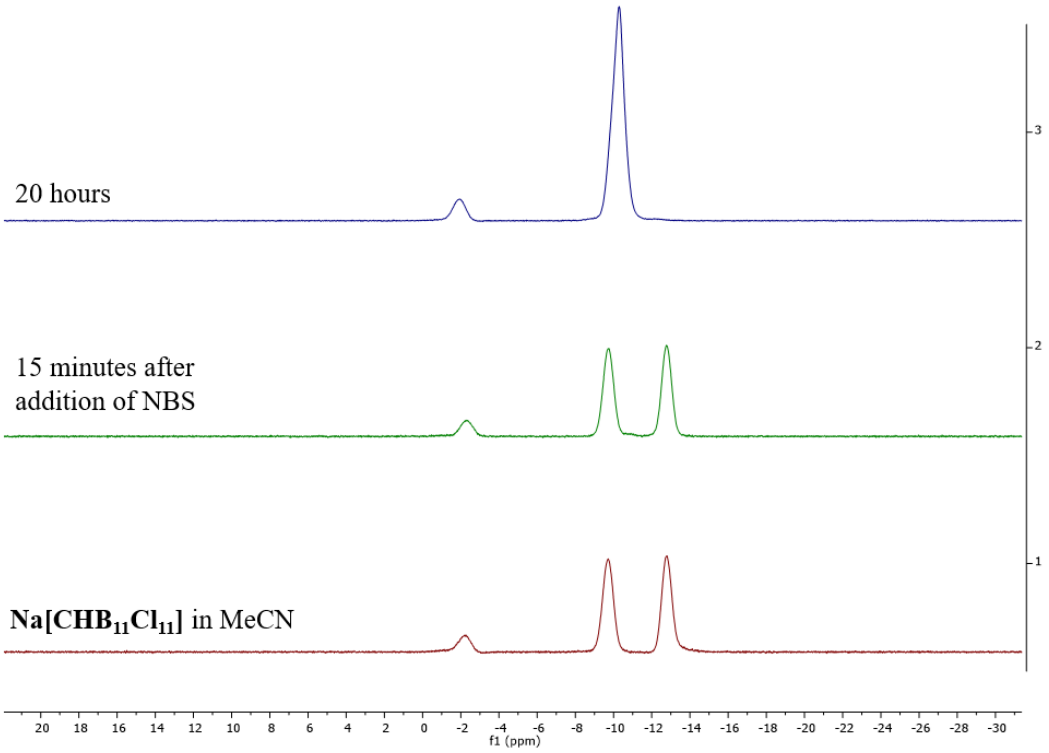


**Figure S53.** $^{11}B\{^{1}H\}$ NMR (400 MHz, $H_2O$ unlocked/unshimmed) in situ spectra of the conversion of **Na[HCB$_{11}$Cl$_{11}$]** to **Na[BrCB$_{11}$Cl$_{11}$]**.

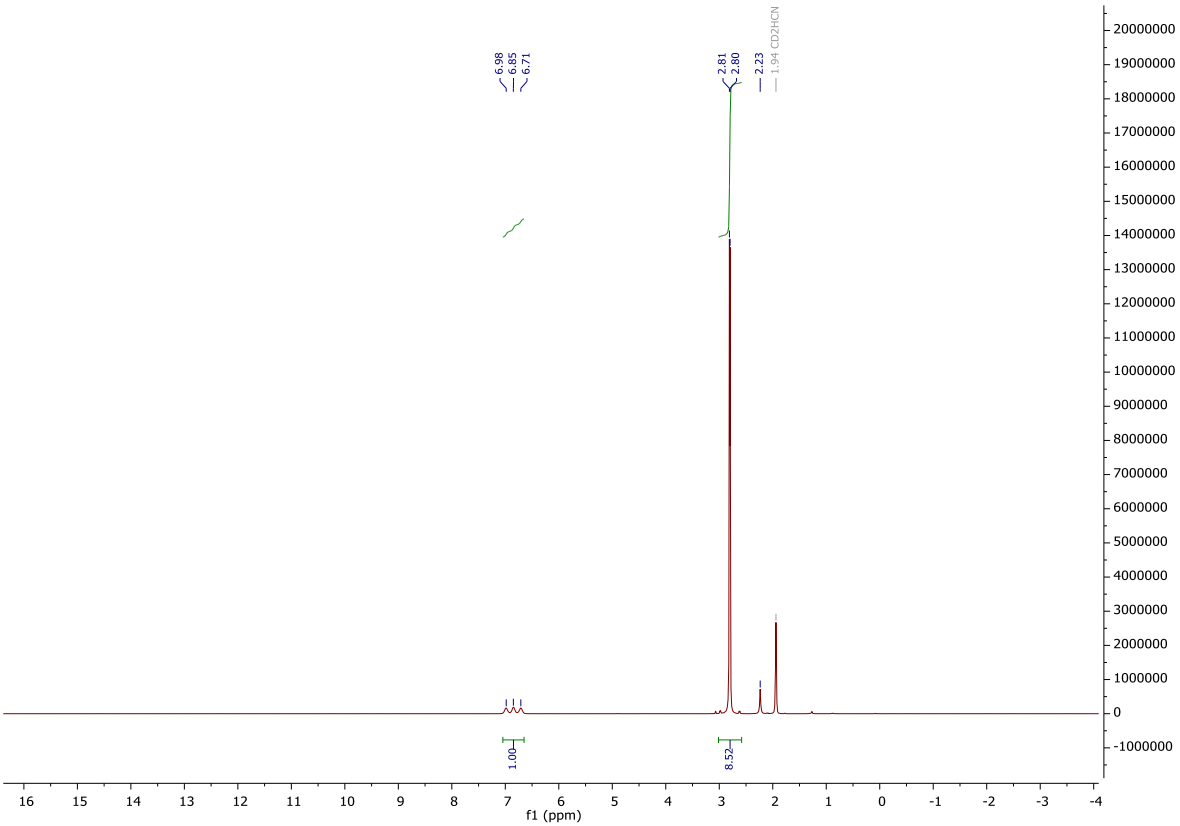


**Figure S54.** $^{1}$H NMR (400 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][BrCB$_{11}$Cl$_{11}$]**. A small amount of residual water impurity is seen at 2.23 ppm.

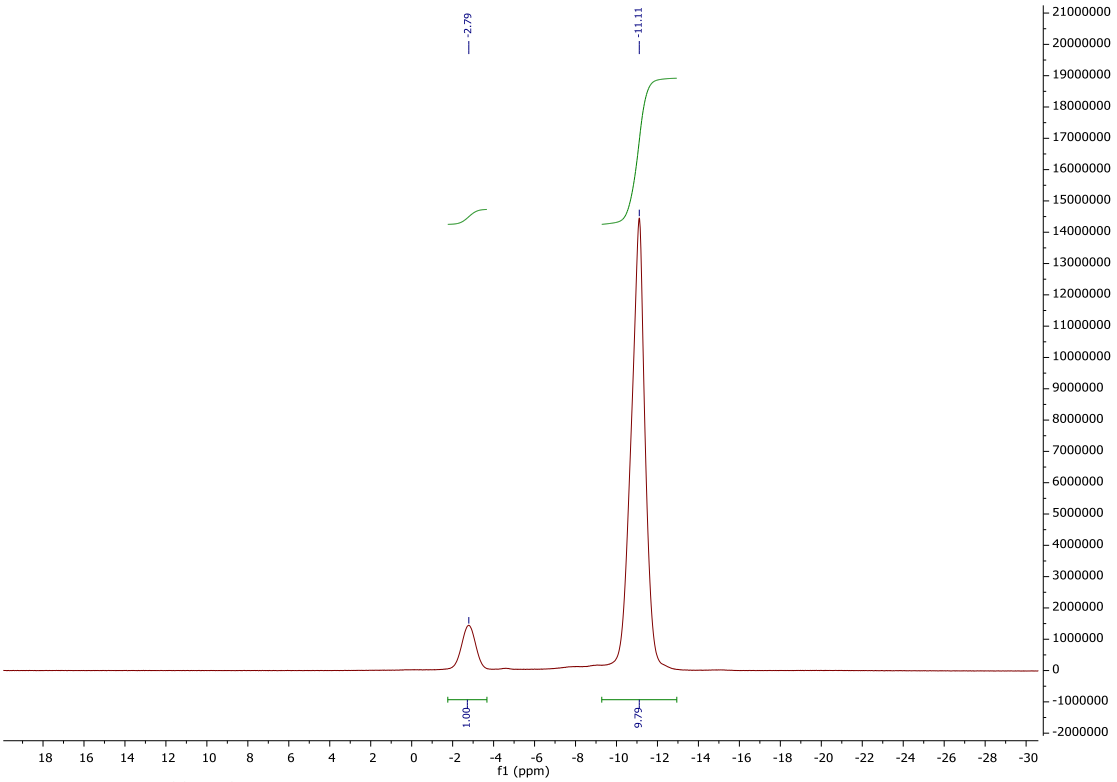


**Figure S55.** $^{11}B\{^{1}H\}$ NMR (128 MHz, $CD_2Cl_2$) spectrum of **[HNMe$_3$][BrCB$_{11}$Cl$_{11}$]**.

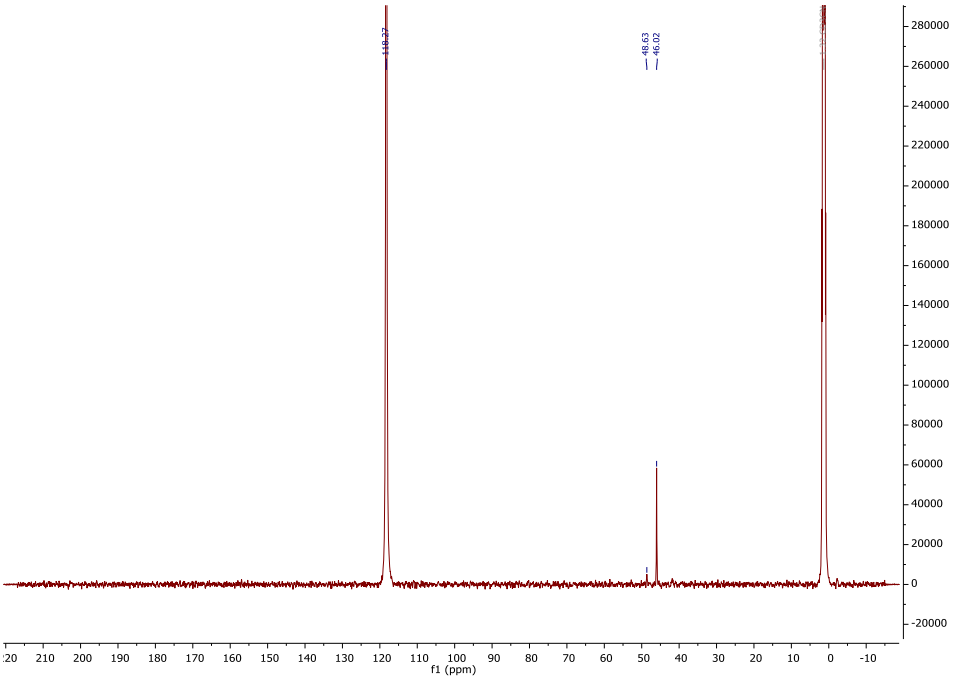


**Figure S56.** $^{13}C\{^{1}H\}$ NMR (126 MHz, $CD_3CN$) spectrum of **[HNMe$_3$][BrCB$_{11}$Cl$_{11}$]**.

**Attempted Synthesis of [Na][HOCB$_{11}$Cl$_{11}$]:**

**Method 1 (N-hydroxysuccinimide)** – A 20 mL glass vial was loaded with **Na[HCB$_{11}$Cl$_{11}$]** (50 mg, 0.092 mmol) and a PTFE coated stir bar in 5 mL of acetonitrile. N-hydroxysuccinimide (13 mg, 0.110 mmol) was added and the solution was heated to 70 °C on a heating plate. The mixture was allowed to stir for 24 h in total, and in situ $^{11}B\{^{1}H\}$ NMR analysis indicated that there was no change from the **Na[HCB$_{11}$Cl$_{11}$]** starting material at any point in the experiment.

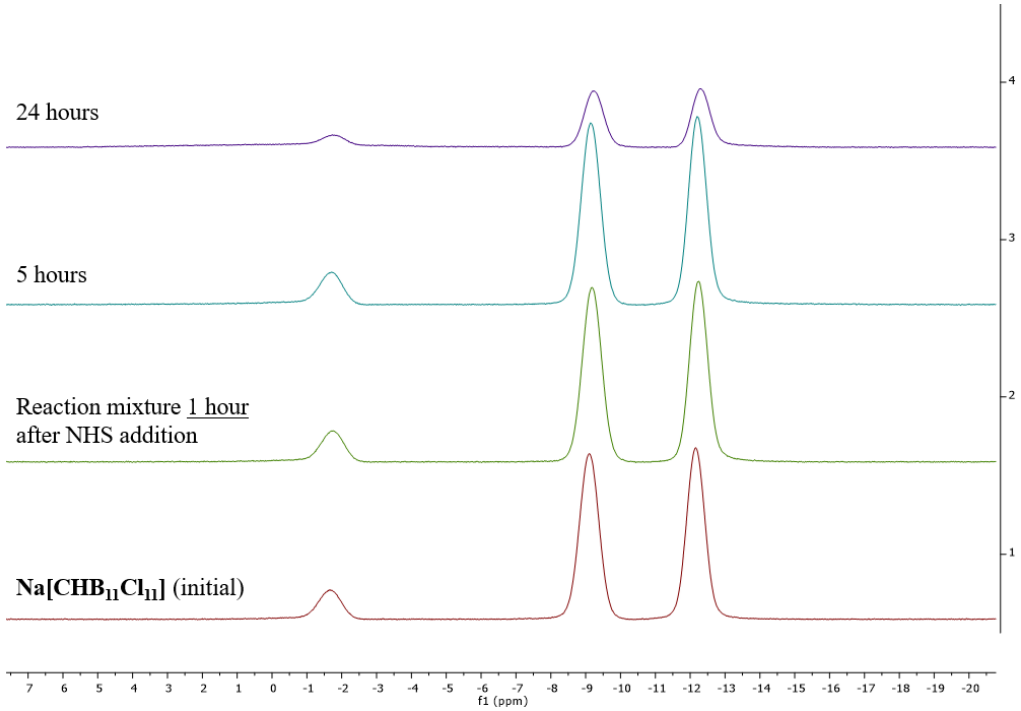


**Figure S57.** $^{11}B\{^{1}H\}$ NMR (128 MHz, $CH_3CN$ unlocked/unshimmed) spectra of the attempted synthesis of **[Na][HOCB$_{11}$Cl$_{11}$]** using N-hydroxysuccinimide (NHS).

**Method 2 (Hydrogen Peroxide)** – A 20 mL glass vial was loaded with **Na[HCB$_{11}$Cl$_{11}$]** (50 mg, 0.092 mmol) and a PTFE coated stir bar in 5 mL of water. NaOH (12 mg, 0.300 mmol) was then added to the mixture. After the solids had dissolved, a 35% $H_2O_2$ solution (11 mg, 0.110 mmol) measured by weight was added, and the mixture was allowed to stir for 2 h. In situ $^{11}B\{^1H\}$ NMR analysis indicated that there was no change from the **Na[HCB$_{11}$Cl$_{11}$]** starting material at any point in the experiment.

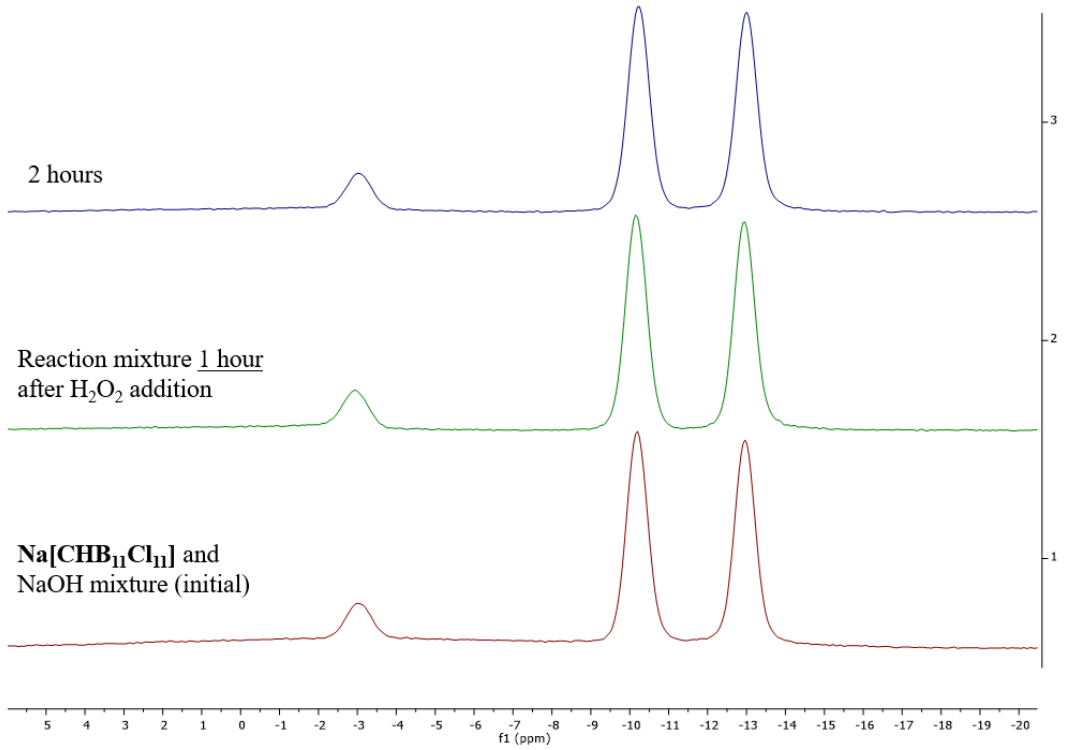


**Figure S58.** $^{11}B\{^1H\}$ NMR (128 MHz, $H_2O$ unlocked/unshimmed) spectra of the attempted synthesis of **[Na][HOCB$_{11}$Cl$_{11}$]** using hydrogen peroxide.

## IV. Dehalogenation of the carbon vertex

**Dehalogenation of [Na][ClCB$_{11}$Cl$_{11}$]** – A 20 mL glass vial was loaded with **Na[HCB$_{11}$Cl$_{11}$]** (20 mg, 0.037 mmol) and a PTFE coated stir bar in 2 mL of water. NaOH (2 mg, 0.050 mmol) was added to the mixture. After the solids had dissolved, a 12.5% NaOCl solution (6 mg, 0.081 mmol) measured by weight was added, and the mixture was allowed to stir for 15 min. In situ $^{11}B\{^{1}H\}$ NMR analysis at 15 min showed that **[ClCB$_{11}$Cl$_{11}$]$^-$** was the only species observed. At this point, $Na_2SO_3$ (9 mg, 0.071 mmol) was added to the mixture, and in situ $^{11}B\{^{1}H\}$ NMR indicated that **[Na][ClCB$_{11}$Cl$_{11}$]** had been fully reduced to **Na[HCB$_{11}$Cl$_{11}$]** after 10 min.

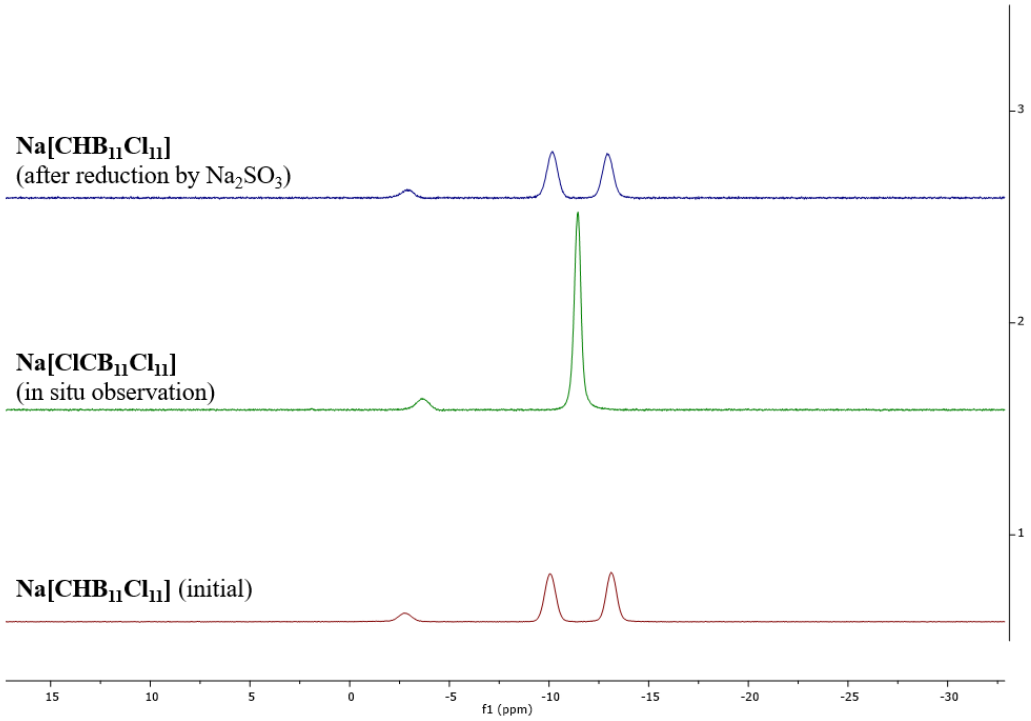


**Figure S59.** $^{11}B\{^{1}H\}$ NMR (128 MHz, $H_2O$ unlocked/unshimmed) spectrum of the in situ synthesis and subsequent dehalogenation of **[Na][ClCB$_{11}$Cl$_{11}$]**.

**Dehalogenation of [Na][BrCB$_{11}$Cl$_{11}$]** – A 20 mL glass vial was loaded with **Na[HCB$_{11}$Cl$_{11}$]** (50 mg, 0.092 mmol) and a PTFE coated stir bar in 5 mL of acetonitrile. N-Bromosuccinimide (20 mg, 0.112 mmol) was added and the solution was heated to 70 °C on a heating plate. The mixture was allowed to stir for 5 h, at which point in situ $^{11}B\{^{1}H\}$ NMR analysis indicated 95% conversion to **[BrCB$_{11}$Cl$_{11}$]$^-$**. At this point, a solution of $Na_2SO_3$ (46 mg, 0.365 mmol) in 5 mL of water was added to the mixture, and in situ $^{11}B\{^{1}H\}$ NMR indicated that **[Na][BrCB$_{11}$Cl$_{11}$]** had been fully reduced to **Na[HCB$_{11}$Cl$_{11}$]** after 10 min.

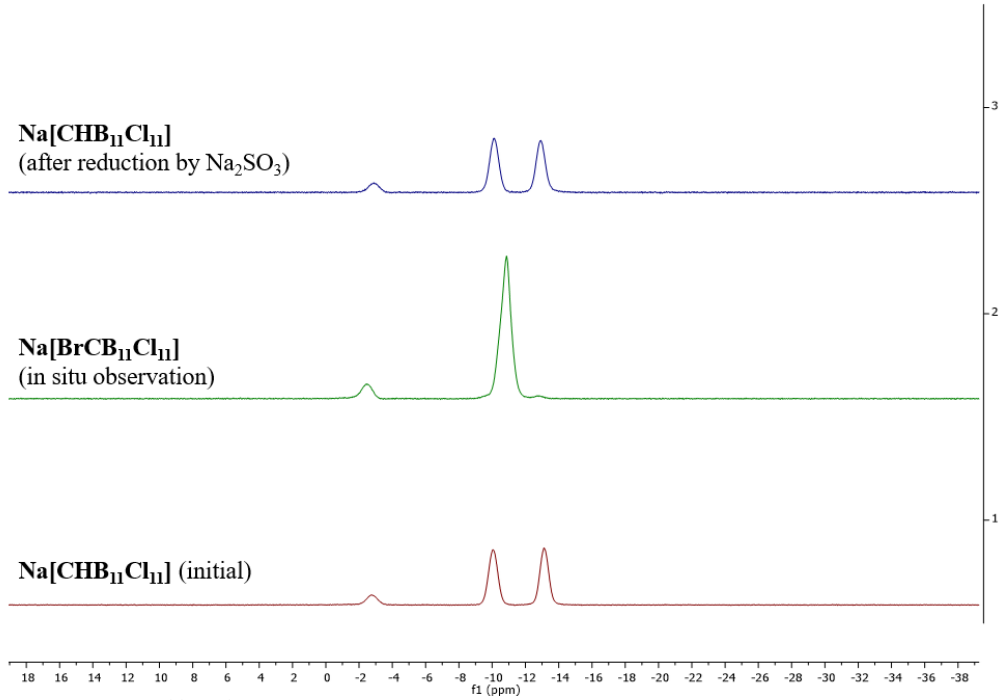


**Figure S60.** $^{11}B\{^{1}H\}$ NMR (128 MHz, $CH_3CN$ unlocked/unshimmed) spectrum of the in situ synthesis and subsequent dehalogenation of **[Na][BrCB$_{11}$Cl$_{11}$]**.

**Dehalogenation of [Na][ICB$_{11}$Cl$_{11}$]** – A 20 mL glass vial was loaded with **Na[HCB$_{11}$Cl$_{11}$]** (20 mg, 0.037 mmol) and a PTFE coated stir bar in 2 mL of water. NaOH (2 mg, 0.050 mmol) was added to the mixture. In a separate vial, $I_2$ crystals (11 mg, 0.044 mmol) were dissolved in 2 mL ethanol. The iodine solution was added to the carborane reaction mixture and was allowed to stir for 15 min. In situ $^{11}B\{^1H\}$ NMR analysis at 15 min showed that **[ICB$_{11}$Cl$_{11}$]$^-$** was the only species observed. At this point, $Na_2SO_3$ (11 mg, 0.087 mmol) was added to the mixture, and in situ $^{11}B\{^1H\}$ NMR indicated that **[Na][ICB$_{11}$Cl$_{11}$]** had been fully reduced to **Na[HCB$_{11}$Cl$_{11}$]** after 10 min.

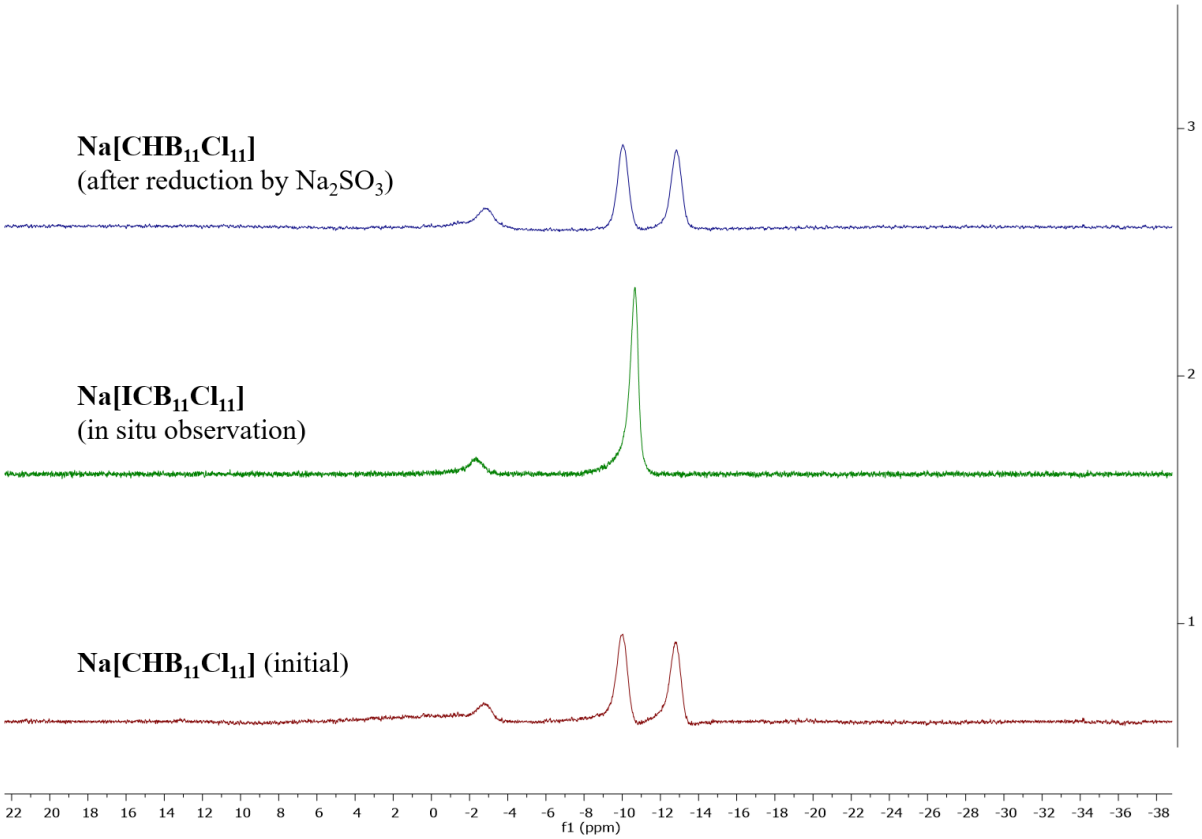


**Figure S61.** $^{11}B\{^1H\}$ NMR (128 MHz, $H_2O$ unlocked/unshimmed) spectra of the in situ synthesis.