Electronic Supplementary Information

Convenient C-Alkylation of the $[HCB_{11}Cl_{11}]^-$ Carborane Anion

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Experimental

General Considerations. *Tert*-butyl alcohol was purchased from Acros Organics, iodo alkyls were purchased from Aldrich or Acros and used without further purification. Potassium *tert*-butoxide was purchased from Strem Chemicals and was used as received. $Me_3NH[HCB_{11}Cl_{11}]$ was prepared from $Cs[HCB_{11}H_{11}]$ using the previously published $SbCl_5$ chlorination procedure.[1] All operations were carried out open to air in Schlenk flasks in a fume hood unless otherwise indicated. NMR spectra were collected on Varian Inova 400 (^{11}B NMR, 128.190 MHz) and Varian Inova 500 (^{1}H NMR, 499.428 MHz; ^{13}C NMR, 125.581 MHz) spectrometers using deuterated solvents as indicated. In the case of ^{1}H and ^{13}C NMR, spectra were referenced to residual solvent peaks. For ^{11}B NMR, spectra were referenced externally to $\delta = 0$ ppm using $BF_3 \bullet Et_2O$. ^{19}F NMR spectra were referenced externally using 1.0 M CF_3CO_2H in $CDCl_3$ to $\delta = -78.5$ ppm. MALDI mass spectrometric analyses of the carborane anions were carried out by the Texas A&M University Laboratory for Biological Mass Spectrometry (LBMS). Elemental analyses were performed by CALI Labs, Inc. (Parsippany, NJ, USA).

General Synthesis of $Me_3NH[RCB_{11}Cl_{11}]$ (150 mg scale) using *tert*-butanol and K^tOBu. $Me_3NH[HCB_{11}Cl_{11}]$ (0.15 g, 0.25 mmol) was dissolved in *ca.* 40 mL of *tert*-butyl alcohol in a Schlenk flask and placed in a water bath at 35 °C to prevent crystallization of the solvent. The resulting solution was then treated with 3.5 equivalents of potassium *tert*-butoxide (0.098 g, 0.875 mmol) and the resulting mixture was stirred for 30 minutes. Once this time was completed, volatiles were removed in vacuo. To help remove volatiles, the flask can be placed in a water bath at 35 °C. The resulting residue was suspended in ca. 40 mL of *tert*-butyl alcohol and 7 equivalents of the alkyl iodide (1.7 mmol) were added in a single portion using a Hamilton microliter syringe and the mixture is stirred for one hour. At the end of this time an aliquot of reaction mixture was taken and analyzed by MALDI mass spectrometry (negative ion detection), showing complete conversion (Figures S2, S6, S10 and S14). The residue is dissolved in *ca.* 10 mL of water and the solution is then acidified with 3 drops of concentrated HCl. This solution is treated with 2 equivalents of solid Me_3NHCl (0.50 mmol) to immediately obtain a white precipitate. The solid was the recovered by filtration through a fine fritted funnel, washed with two portions of 10 mL of water, dissolved in HPLC grade acetone or dichloromethane and filtered through the same fritted glass funnel into a pre-weighed flask and dried overnight at 80 °C under vacuum to obtain white powders.

If additional purification is desired, after the final wash with water, the solid should be dissolved in the minimum possible amount of acetone and filtered through a fritted funnel. This mother liquor is then carefully layered on top of *ca.* 20 mL of water and let to slowly diffuse overnight to obtain white crystals.

R = Methyl

Yield: 119.0 mg (81%). ^1H (500 MHz, acetonitrile-d_3) (Figure S3) δ = 2.80 (s, 9H Me_3N), 1.57 (s, 3H). $^{13}C\{^1H\}$ (125.6 MHz, acetonitrile-d3) (Figure S4) δ = 12.72 (s, C-CH_3), 46.03 (s, HN-$(CH_3)_3^+$), 51.11 (s br, *ipso*-C). $^{11}B\{^1H\}$ (128 MHz, acetonitrile-d_3) (Figure S5) δ = −3.0 (s br, 1B), −9.9 (s br, 5B), −11.3 (s br, 5B).

Boron elemental analysis: Calculated (Found) 19.87% (19.84%).

R = Ethyl

Yield: 148.0 mg (94%). ^1H (500 MHz, acetonitrile-d_3) (Figure S7) δ = 1.31 (t, 3H), 2.40 (s, 2H), 2.80 (d, 9H Me_3N). $^{13}C\{^1H\}$ (125.6 MHz, acetonitrile-d_3) (Figure S8) δ = 10.68 (-CH_3), 25.99 (-

CH_2-), 46.06 (s, HN-*(CH₃)₃*$^+$), 51.69 (s br, *ipso*-C). $^{11}B\{^1H\}$ (128 MHz, acetonitrile-*d₃*) (Figure S9) δ = −2.6 (s, 1B), −9.5 (s, 5B), − 11.1 (s 5B).

Boron elemental analysis: Calculated (Found) 19.49% (19.32%).

R = Butyl

Yield: 154.0 mg (84%). ^1H (500 MHz, acetonitrile-d_3) (Figure S11) δ = 0.88 (t, 3H), 1.23 (sextet, 2H), 1.82 (m, 2 H), 2.25 (t, 2H), 2.80 (s, 9H Me_3N). $^{13}C\{^1H\}$ (125.6 MHz, acetonitrile-d_3) (Figure S12) δ = 13.75 (s, -CH_3), 23.86 (s, -CH_2-), 27.29 (s, -CH_2-), 31.73 (s, -CH_2-), 46.02 (s, HN-$(CH_3)_3^+$), 51.51 (s br, *ipso*-C). $^{11}B\{^1H\}$ (128 MHz, acetonitrile-d_3) (Figure S13) δ = −2.5 (s br, 1B), −9.5 (s br, 5B), −11.1 (s br, 5B).

Elemental analysis: Calculated (Found) C, 15.06% (15.00%); H, 3.00% (2.96%); B, 18.64% (18.53%); Cl, 61.11% (60.97%); N, 2.19% (2.10%).

R = Hexyl

Yield: 176.5 mg (93%). ^1H (500 MHz, acetonitrile-d_3) (Figure S15) δ = 0.87 (t, 3H), 1.25 (m, 6H), 1.84 (m, 2H), 2.25 (t, 2H), 2.80 (s, 9H Me_3N). $^{13}C\{^1H\}$ (125.6 MHz, acetonitrile-d_3) (Figure S16) δ = 14.22 (s, -CH_3), 23.08 (s, -CH_2-), 25.15 (s, -CH_2-), 30.32 (s, -CH_2-), 31.72 (s, -CH_2-), 32.02 (s, -CH_2-), 45.97 (s, HN-$(CH_3)_3^+$), 51.62 (s br, *ipso*-C). $^{11}B\{^1H\}$ (128 MHz, acetonitrile-d_3) (Figure S17) δ = −2.5 (s br, 1B), −9.5 (s br, 5B), −11.1 (s br, 5B).

Boron elemental analysis: Calculated (Found) 17.85% (17.69%).

General Synthesis of Na[$RCB_{11}Cl_{11}$] (100 mg scale). All procedures were carried out inside an argon-filled glovebox. $Me_3NH[HCB_{11}Cl_{11}]$ (0.10 g, 0.17 mmol) was dissolved in *ca.* 50 mL of dry THF and NaH (0.015 g, 0.44 mmol) was added in a single portion. The mixture was stirred vigorously for one hour and volatiles were then removed in vacuo. The resulting residue was resuspended in *ca*. 50 mL of dry THF and the corresponding alkyl iodide (0.87 mmol) was added in a single portion using a Hamilton microliter syringe. The resulting mixture was stirred for one hour. Volatiles were removed to dryness under vacuum, the residue was then suspended in ca. 20 mL of THF. This suspension was filtered through a fine frit and dried under vacuum to obtain a white powder.

R= Butyl

Yield: 95.0 mg (84.4%) MALDI (Figure S18), ^{1}H NMR (Figure S19).

R = Propyl

Yield: 71.0 mg (69%) MALDI (Figure S20), ^{1}H NMR (Figure S21).

R = Hexyl

Yield: 107.0 mg (95%) MALDI (Figure S22), ^{1}H NMR (Figure S23).

General Synthesis of donor-free Na[RCB$_{11}$Cl$_{11}$] (100 mg scale). All procedures were performed in an argon-filled, base-free glovebox. Me$_3$NH[RCB$_{11}$Cl$_{11}$] (0.100 g) was dissolved in enough dry fluorobenzene to effect dissolution. To this solution, 5 equivalents of sodium hydride were added in a single portion and the suspension was stirred for 2 hours. Volatiles were removed to obtain a tan powder that was resuspended in *ca.* 20 mL of dry fluorobenzene. This suspension was filtered through a fine-fritted funnel, the mother liquor collected and dried under vacuum to obtain white powders.

R =Methyl

Yield 0.095g (98%). 1H (Figure S30) Boron elemental analysis: Calculated (Found) 21.28% (20.95%).

R = Butyl

Yield 0.137g (90.5%). 1H (Figure S29) Boron elemental analysis: Calculated (Found) 19.79% (19.69%).

Synthesis of K[EtCB$_{11}$Cl$_{11}$] using methyl bromide. 0.113 g (0.194 mmol) of $Me_3NH[HCB_{11}Cl_{11}]$ were charged in a Schlenk flask, dissolved in *ca.* 40 mL of *tert*-butyl alcohol and placed in a water bath at 35 °C to prevent crystallization of the solvent. The resulting solution was then treated with 0.044 g (0.679 mmol) of potassium *tert*-butoxide and the resulting mixture was stirred for 30 minutes. Once this time was completed, volatiles were removed in vacuo. The resulting residue was suspended in ca. 40 mL of *tert*-butyl alcohol and 7 equivalents of the ethyl bromide (1.358 mmol) were added in a single portion using a Hamilton microliter syringe and the mixture is stirred for one hour. At the end of this time an aliquot of reaction mixture was taken and analyzed by MALDI mass spectrometry (negative ion detection) and $^{11}B\{^1H\}$ NMR showing *ca.* 50% conversion (figures S24 and S25).

Observation of dechlorination of HCB$_{11}$Cl$_{11}$$^-$. 0.072 g (0.124 mmol) of $Me_3NH[HCB_{11}Cl_{11}]$ were charged in a round bottom flask equipped with a Teflon valve and were dissolved in *ca.* 40 mL of *tert*-butyl alcohol. 0.071 g (0.633 mmol) of potassium *tert*-butoxide were charged and the flask was closed, placed in a silicon oil bath set at 70 °C for two days. The resulting solution had the appearance of egg yolk. An aliquot of the reaction mixture was analyzed by MALDI mass spectrometry (figure S27).

Observation of dechlorination of EtCB$_{11}$Cl$_{11}$$^-$. 0.060 g (0.098 mmol) of $Me_3NH[EtCB_{11}Cl_{11}]$, purified by crystallization as explained above, were charged in a round bottom flask equipped with a Teflon valve and were dissolved in *ca.* 40 mL of *tert*-butyl alcohol. 0.055 g (0.492 mmol) of potassium *tert*-butoxide were charged, the flask was closed and then was placed in a silicon oil bath set at 70 °C for two days, after which the solution had turned dark yellow. An aliquot of the reaction mixture was analyzed by MALDI mass spectrometry (figure S28).

Synthesis of Ag[BuCB$_{11}$Cl$_{11}$]. Me$_3$NH[BuCB$_{11}$Cl$_{11}$] was crystallized from acetone/water as described above to eliminate any traces of halides that may be present from previous synthetic steps. Me$_3$NH[BuCB$_{11}$Cl$_{11}$] (0.224 g, 0.35 mmol) was charged in a Schlenk flask and suspended in deionized water, then was treated with 0.52 mL of a 2.03 N NaOH aqueous solution (1.05 mmol). Once complete dissolution was effected, Me$_3$N was removed with under vacuum by reducing the original volume of solution by a half. The resulting solution is acidified with enough HOTf to achieve red color on litmus paper. To this solution, solid AgNO$_3$ (0.119 g, 0.70 mmol) is added and stirred until it is completely dissolved. Formation of a white colloidal suspension is observed shortly thereafter. Ag[BuCB$_{11}$Cl$_{11}$] is extracted from this suspension with 3 × 25 mL portions of toluene. The organic extracts were collected and the solvent removed in vacuo to obtain a tan solid. This solid was used directly to grow crystals for x-ray diffraction studies by diffusion of hexanes into a solution of Ag[BuCB$_{11}$Cl$_{11}$] at room temperature avoiding contact with light.

Yield: 132 mg (56 %). ^{1}H (500 MHz, acetonitrile-*d$_3$*) (Figure S29) δ = 0.88 (t, 3H), 1.25 (sextet, 2H), 1.83 (m, 2 H), 2.26 (t, 2H), 2.80. ^{11}B{^{1}H} (128 MHz, acetonitrile-*d$_3$*) (Figure S30) δ = −3.4 (s br, 1B), −10.3 (s br, 5B), −12.0 (s br, 5B). ^{13}C{^{1}H} (125.6 MHz, acetonitrile-*d$_3$*) (Figure S31) δ = 13.78 (s, -CH$_3$), 23.90 (s, -CH$_2$-), 27.38 (s, -CH$_2$-), 31.79 (s, -CH$_2$-), 51.44 (s br, *ipso*-C).

X-Ray data collection, solution, and refinement for $[Ag(\eta^2\text{-}C_6H_5F)(H_2O)][BuCB_{11}Cl_{11}]$ (Ag(CBu)). Crystals of this compound were grown by diffusion of hexanes into a saturated fluorobenzene solution of $Ag[BuCB_{11}Cl_{11}]$. A colorless, multi-faceted crystal suitable size and quality (0.46 x 0.15 x 0.13 mm) was selected using an optical microscope and mounted onto a nylon loop. Low temperature (150 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[2] An absorption correction was applied using SADABS.[3] The structure was solved in the monoclinic Cc space group using XS (incorporated in SHELXTL).[4] The solution was refined by full-matrix least squares on F^2. No additional symmetry was found using ADDSYMM incorporated into the PLATON program.[5] All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in idealized positions and refined using a riding model. The structure was refined (weighted least squares refinement on F^2) and the final least-squares refinement converged to $R_1 = 0.0225$ ($I > 2\sigma(I)$, 6241 data) and $wR_2 = 0.0561$ (F^2, 14456 data, 335 parameters). Disorder around the alkyl carbon atoms was modeled by dividing the disordered sites into two components, restraining the carbon atom distances to be 1.54 Å and by constraining their anisotropic displacement parameters to be identical. Crystallographic information is summarized in Table S1.

Table S1

Empirical formula	C11 H16 Ag B11 Cl11 F O	
Formula weight	799.97	
T [K]	150(2)	
└$_{\text{Mo⊇⟨}}$ [Å]	0.71073	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions		
	a = 8.931(5) Å	⟨= 90°
	b = 16.763(9) Å	®= 91.830(5)°
	c = 18.452(10) Å	© = 90°
V[Å^3]	2761(2)	
Z	4	
⟩$_{\text{calc.}}$ [g cm^{-3}]	1.924	
/ [mm^{-1}]	1.813	
F(000)	1552	
Crystal size (mm)	0.46 x 0.15 x 0.13	
Theta range for data collection	2.21 to 27.50°	
Index ranges	$-11 \leq h \leq 11, -21 \leq k \leq 21, -23 \leq l \leq 23$	
Reflections collected	14456	
Independent reflections	6241 [$R_{\text{int.}}$ = 0.0272]	
Completeness to theta = 27.50°	99.60%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8395 and 0.6124	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6241 / 8 / 335	
GooF	1.03	
Final R indices [*I* > 2 /(*I*)]	R_1 = 0.0225, wR_2 = 0.0561	
R indices (all data)	R_1 = 0.0233, wR_2 = 0.0566	
Absolute structure parameter	-0.001(15)	
Largest diff. peak and hole	0.546 and -0.343 e.Å^{-3}	

Observation of equilibration between $[CB_{11}Cl_{11}]^{2-}$ and $[HCB_{11}Cl_{11}]^{-}$ in solution. In a dry box, 50.6 mg (0.087 mmol) of $Me_3NH[HCB_{11}Cl_{11}]$ were charged in a J. Young NMR tube and 510 µL of dry THF were added to effect dissolution. To this solution, 34.0 mg of $KOBu^t$ (0.304 mmol, 3.5 equivalents) were added and a $^{11}B\{^1H\}$ NMR spectrum was collected, showing complete conversion to $K_2[CB_{11}Cl_{11}]$ (spectrum 5, figure S32).

Dilution 1: To the previous solution, 290 µL of $HOBu^t$ (3.04 mmol, 10 × $|KOBu^t|$) were added and a $^{11}B\{^1H\}$ NMR spectrum was collected (spectrum 4 in figure S32).

Dilution 2: An aliquot of 100 µL of dilution 1 and 290 µL of $HOBu^t$ (3.04 mmol, 90 × $|KOBu^t|$) were charged in an NMR tube and a $^{11}B\{^1H\}$ NMR spectrum was collected (spectrum 3, figure S32).

Dilution 3: An aliquot of 10 µL of dilution 1 and 290 µL of $HOBu^t$ (3.04 mmol, 810 × $|KOBu^t|$) were charged in an NMR tube and a $^{11}B\{^1H\}$ NMR spectrum was collected (spectrum 2, figure S32).

Typical reaction mixture: An aliquot of 500 µL was taken from a mixture of $Me_3NH[HCB_{11}Cl_{11}]$ (81.0 mg, 0.14mmol), $KOBu^t$ (56.0 mg, 0.50 mmol) and 30 mL (0.50 mol) of $HOBu^t$ (spectrum 1, figure S32).

Preparation of $Na_2[CB_{11}Cl_{11}]$. In a dry box, 51.2mg (0.088 mmol) of $Me_3NH[HCB_{11}Cl_{11}]$ and 6.2 mg (0.258 mmol) of NaH were charged in a J. Young NMR tube, and 700 µL of dry THF were added. $^{11}B\{^1H\}$ NMR of this reaction mixture was collected (figure S33).

Preparation of $Li_2[CB_{11}Cl_{11}]$. In a dry box, 48.7 mg (0.084 mmol) of $Me_3NH[HCB_{11}Cl_{11}]$ were charged in a J. Young NMR tube and 700 µL of dry THF were added to effect complete dissolution. To this solution, 84 μL (0.210 mmol) of a 2.5M Butyllithium solution in hexanes were added. $^{11}B\{^1H\}$ NMR of this reaction mixture was collected (figure S34).

ESI References

1 Gu, W. X.; McCulloch, B. J.; Reibenspies, J. H.; Ozerov, O. V. *Chem. Comm.* **2010**, *46*, 9263.

2 APEX2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, June 2006.

3 Sheldrick, G.M. "SADABS (version 2008/1): Program for Absorption Correction for Data from Area Detector Frames", University of Göttingen, 2008.

4 Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

5 Spek, A. L. (2006) PLATON – A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. Spek, A. L. (1990) Acta Cryst. A46, C34.

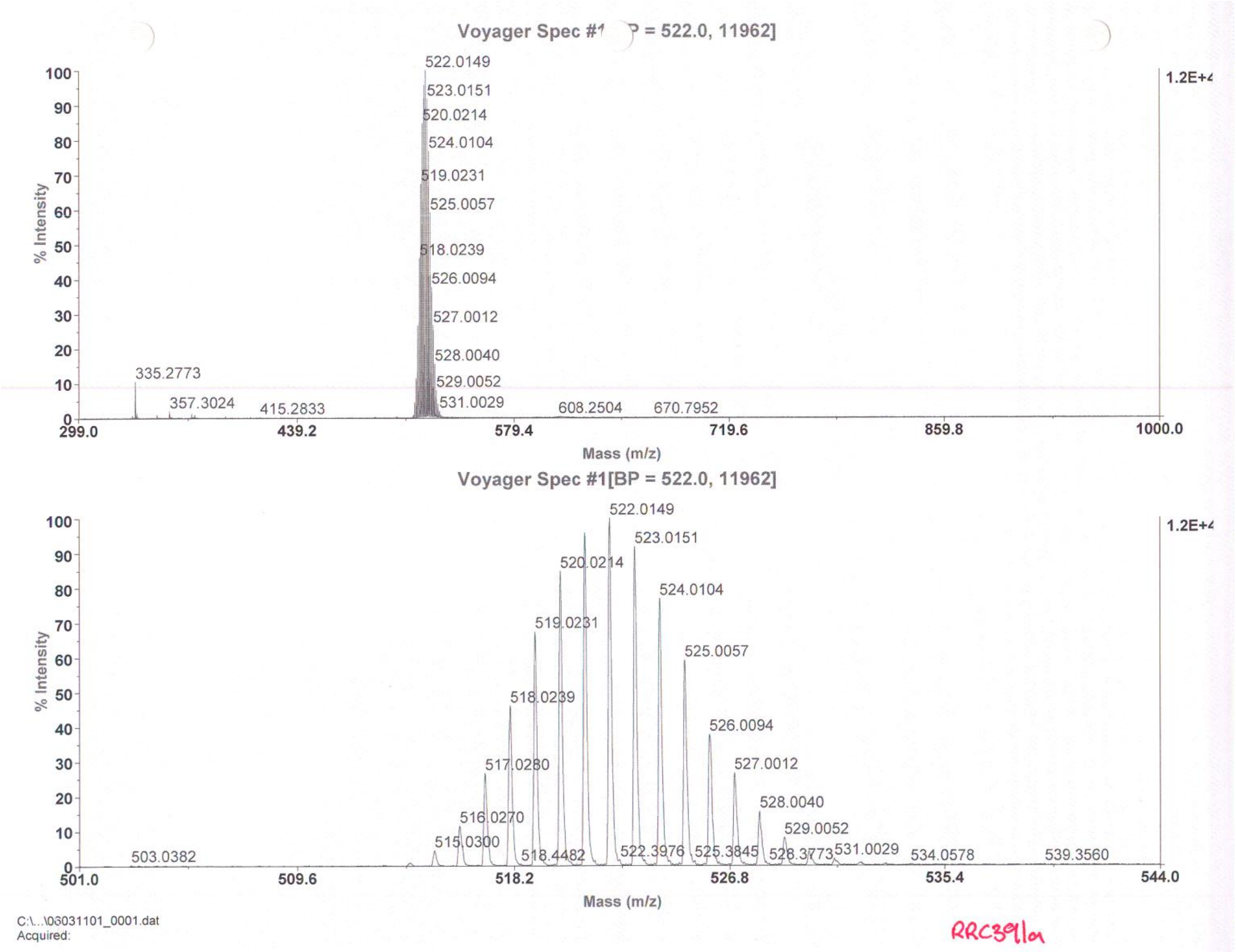

Figure S1. MALDI MS analysis of $Me_3NH[HCB_{11}Cl_{11}]$ used as the starting material for the reactions described herein.

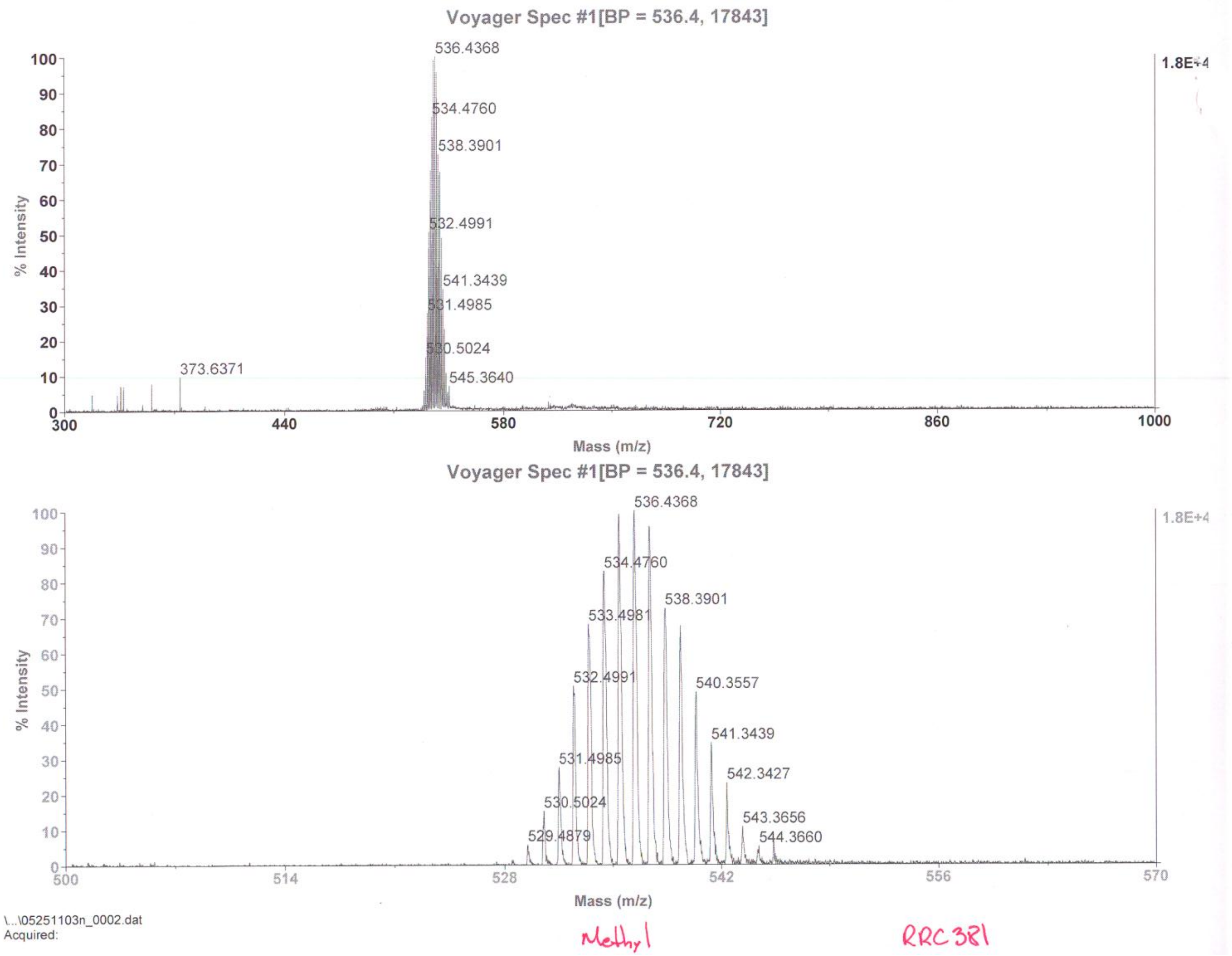

Figure S2. MALDI MS analysis of crude K[$MeCB_{11}Cl_{11}$] in *tert*-butanol solution.

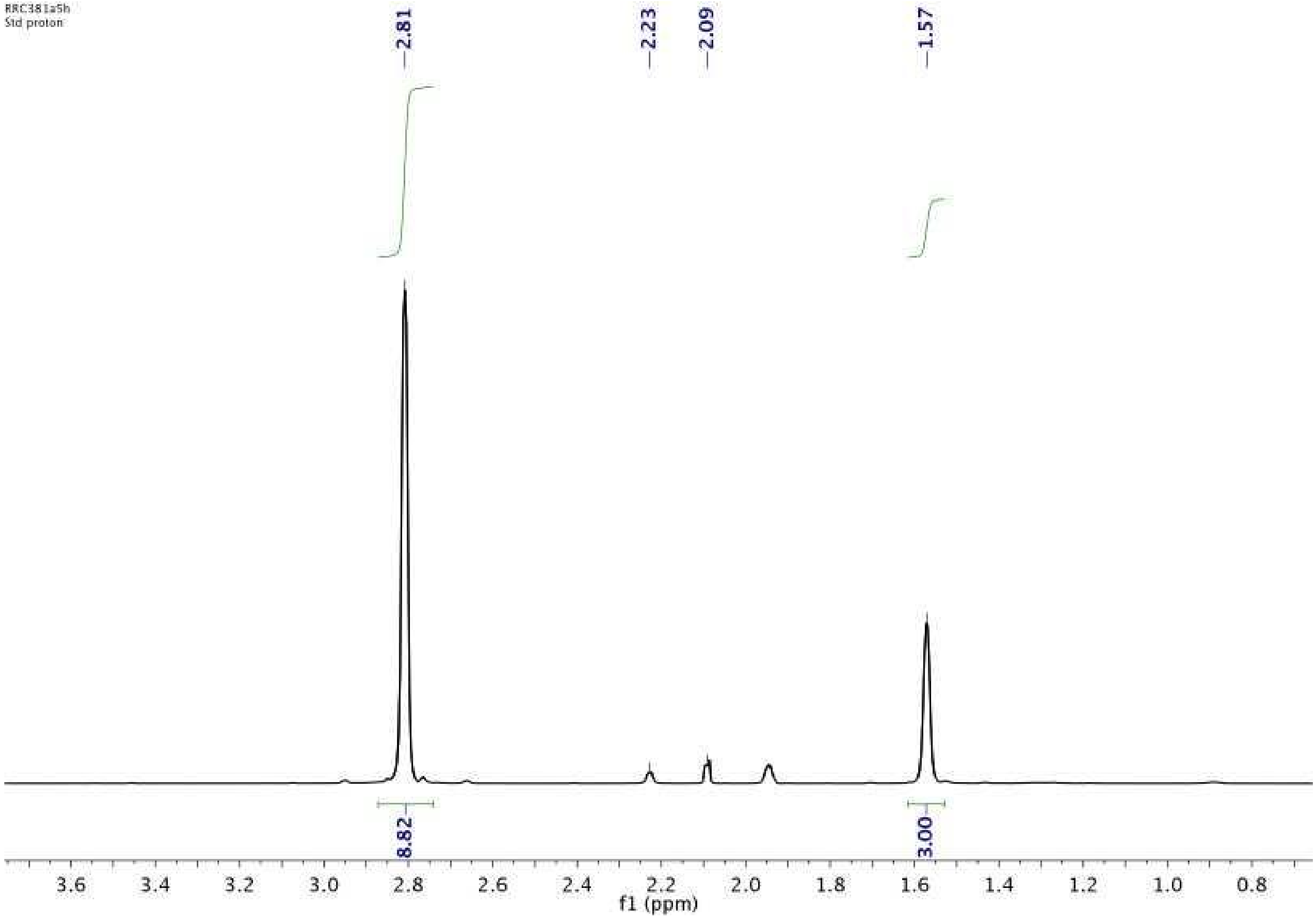

Figure S3. ^{1}H NMR spectrum in acetonitrile-d_3 of $Me_3NH[MeCB_{11}Cl_{11}]$. Signals at $\delta = 2.23$ and $\delta = 2.09$ correspond to residual water and acetone.

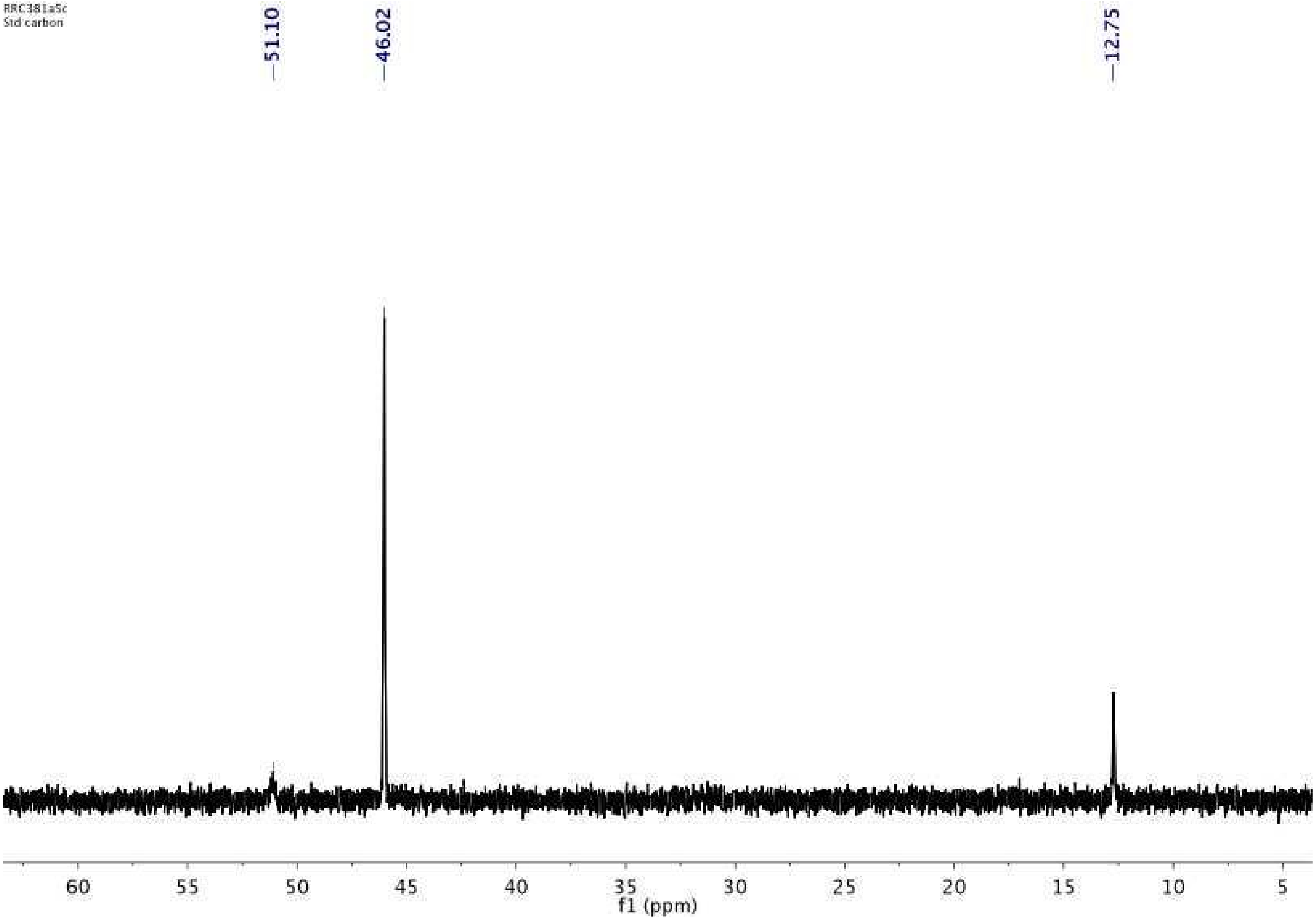

Figure S4. $^{13}C\{^1H\}$ NMR spectrum of $Me_3NH[MeCB_{11}Cl_{11}]$ in acetonitrile-d_3.

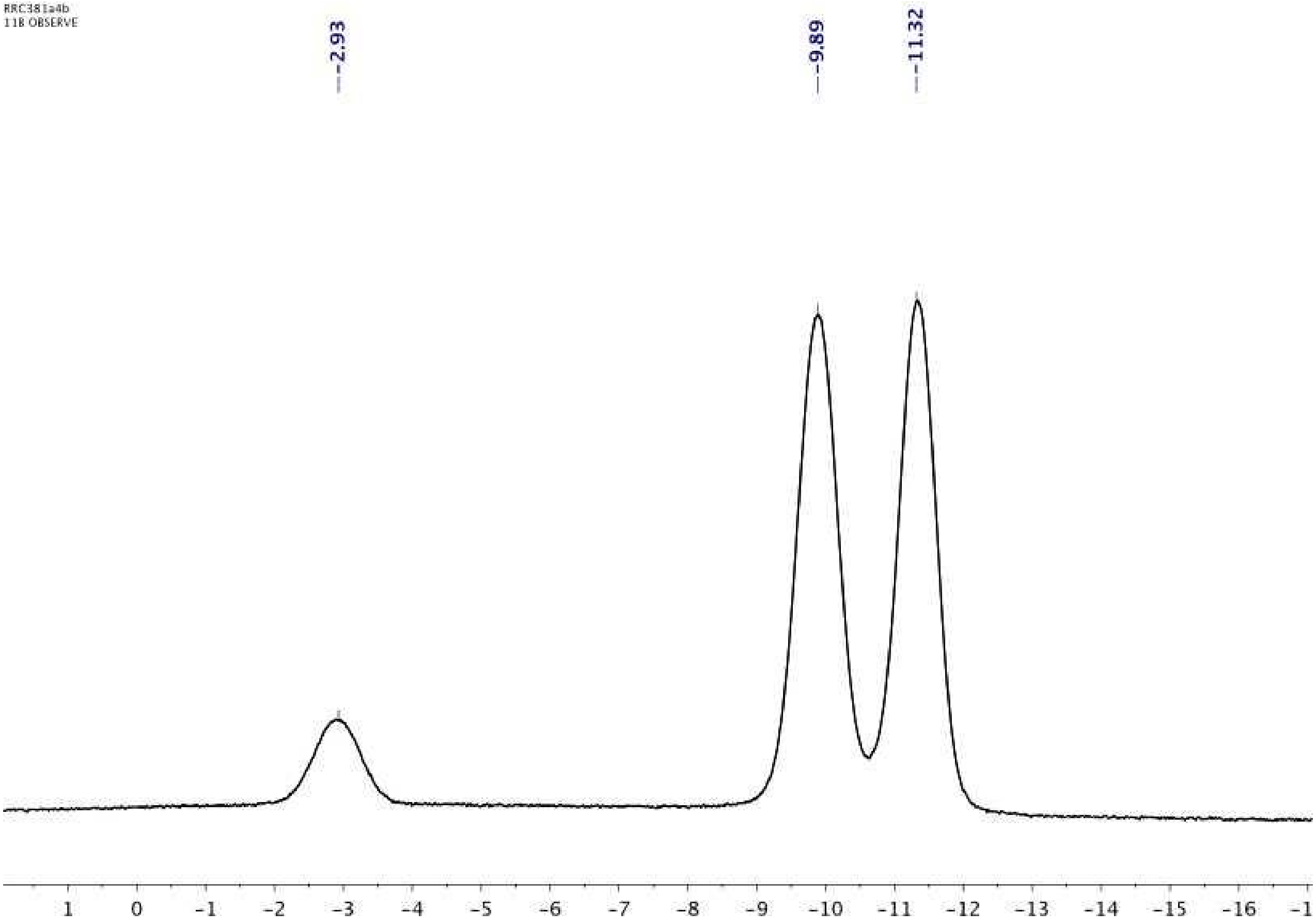

Figure S5. $^{11}B\{^{1}H\}$ NMR spectrum of $Me_3NH[MeCB_{11}Cl_{11}]$ in acetonitrile-d_3.

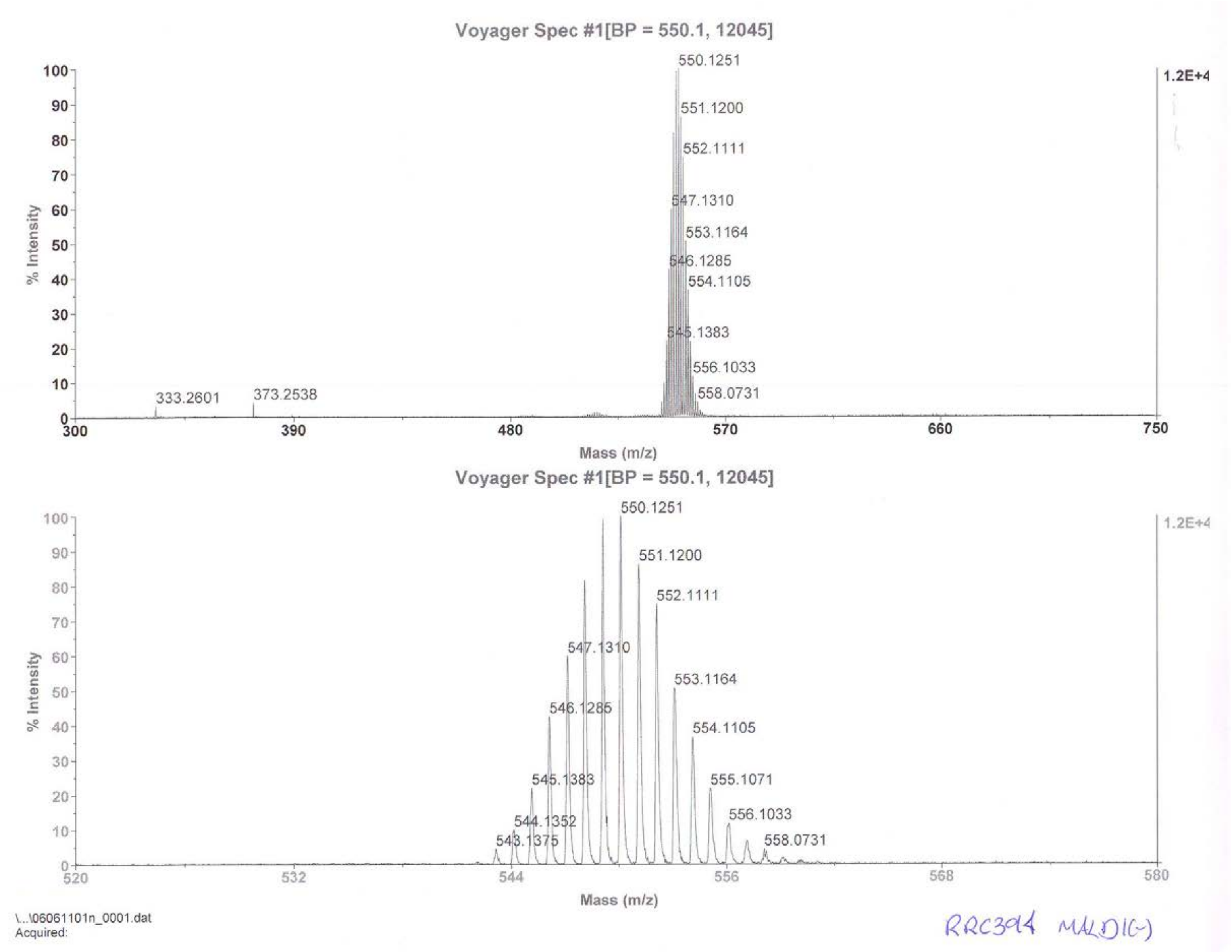

Figure S6. MALDI MS analysis of crude K[$EtCB_{11}Cl_{11}$] in *tert*-butanol solution.

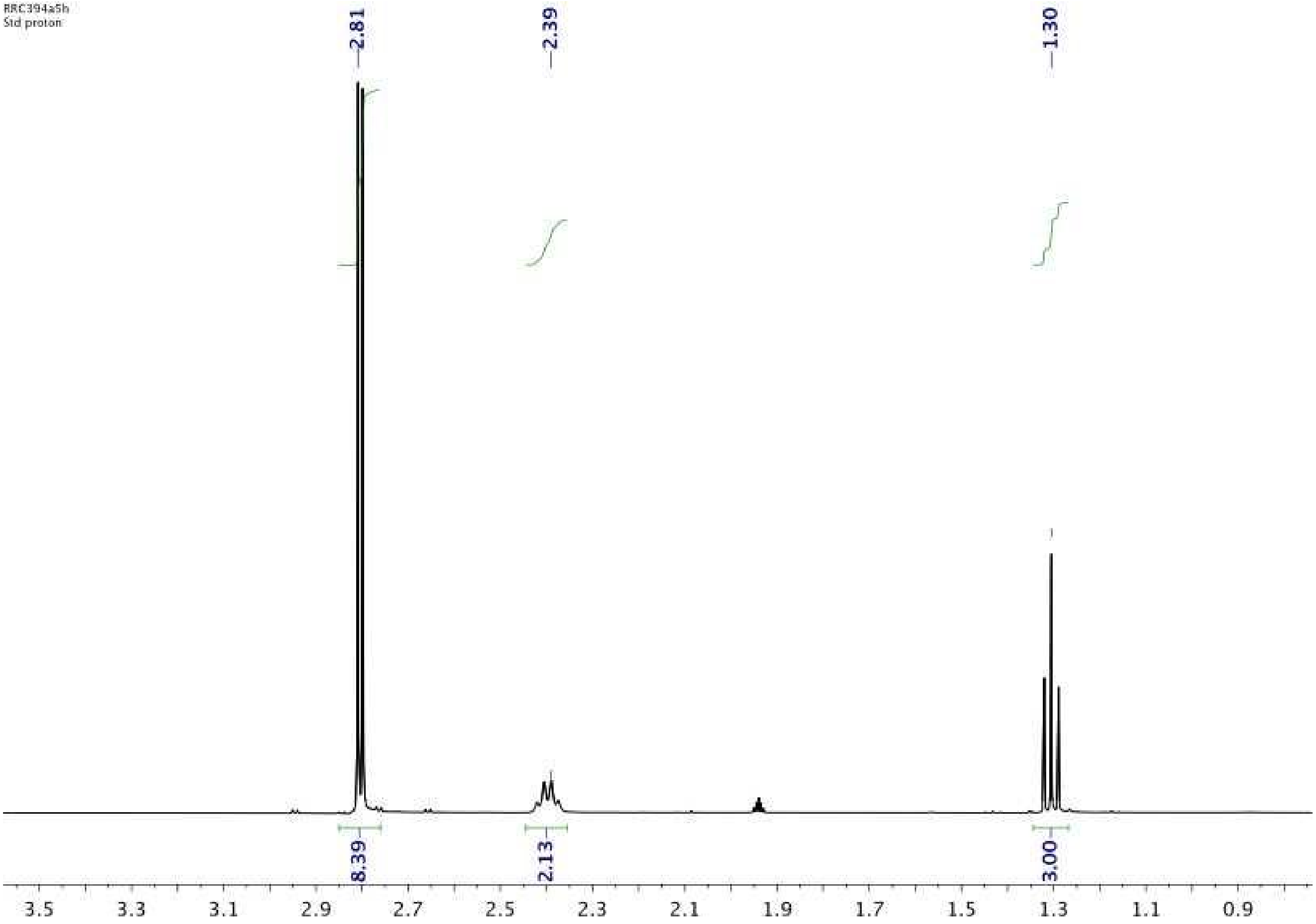

Figure S7. ^{1}H NMR spectrum of $Me_3NH[EtCB_{11}Cl_{11}]$ in acetonitrile-d_3.

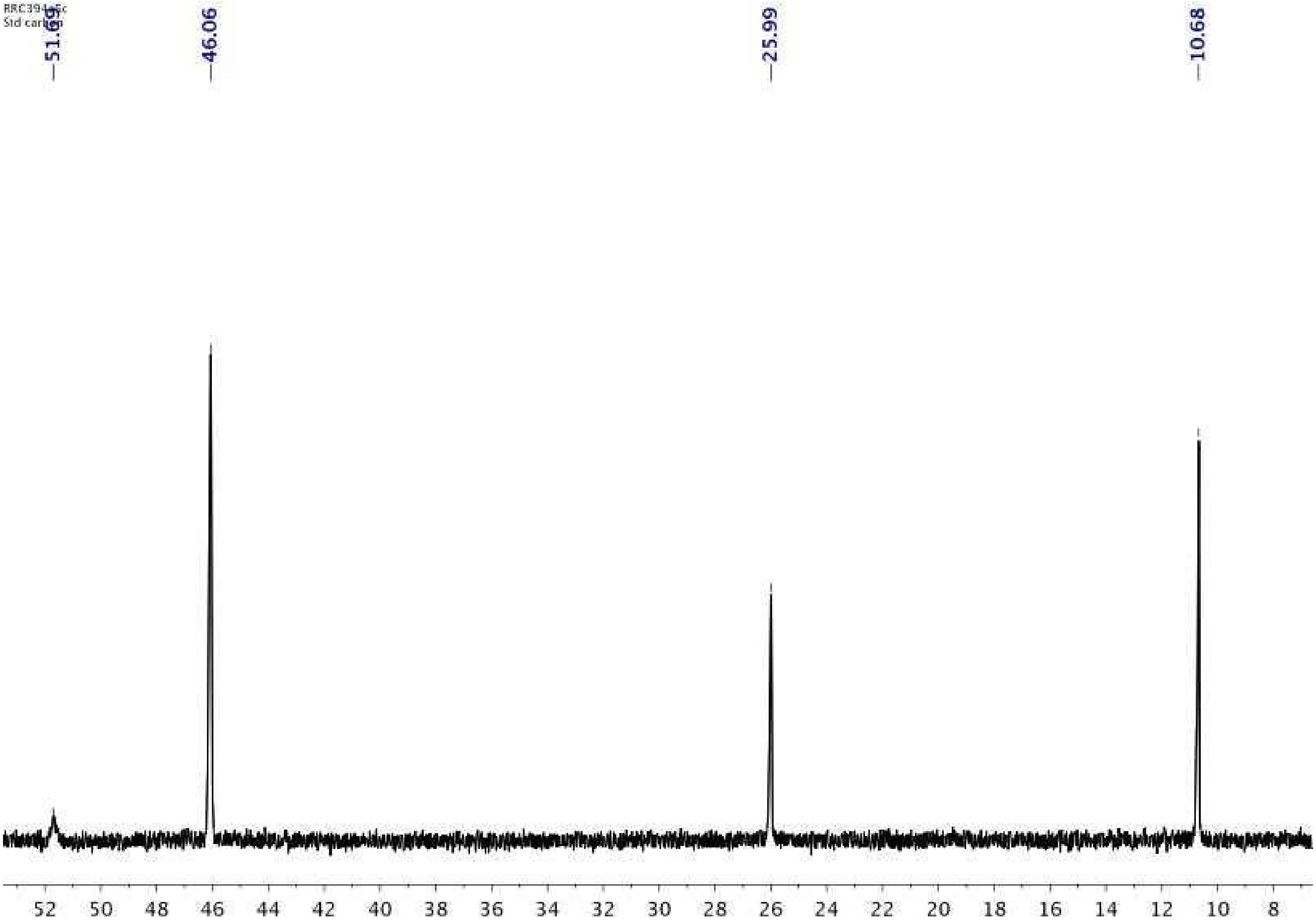

Figure S8. $^{13}C\{^1H\}$ NMR spectrum of $Me_3NH[EtCB_{11}Cl_{11}]$ in acetonitrile-d_3.

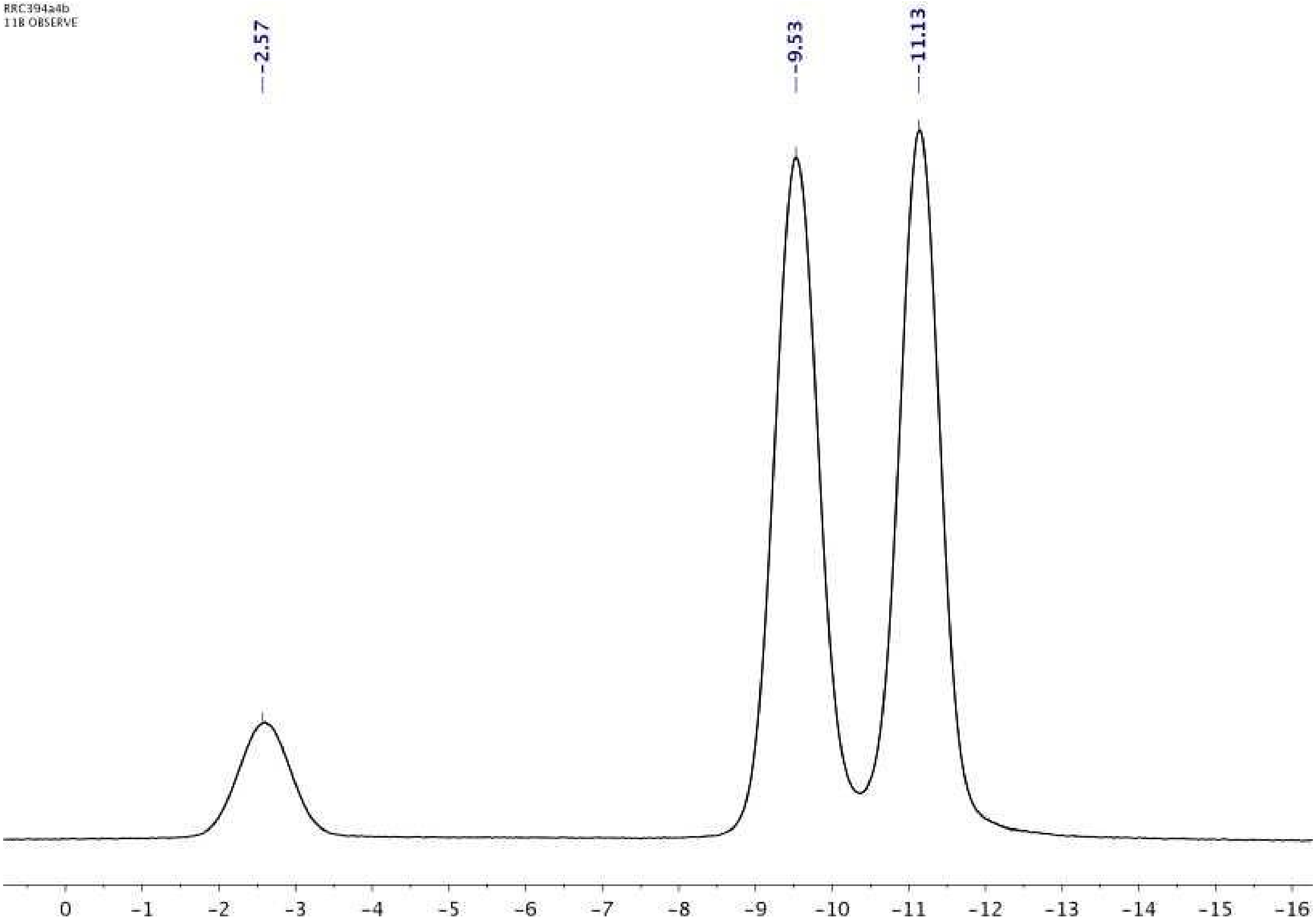

Figure S9. $^{11}B\{^1H\}$ NMR spectrum of $Me_3NH[EtCB_{11}Cl_{11}]$ in acetonitrile-d_3.

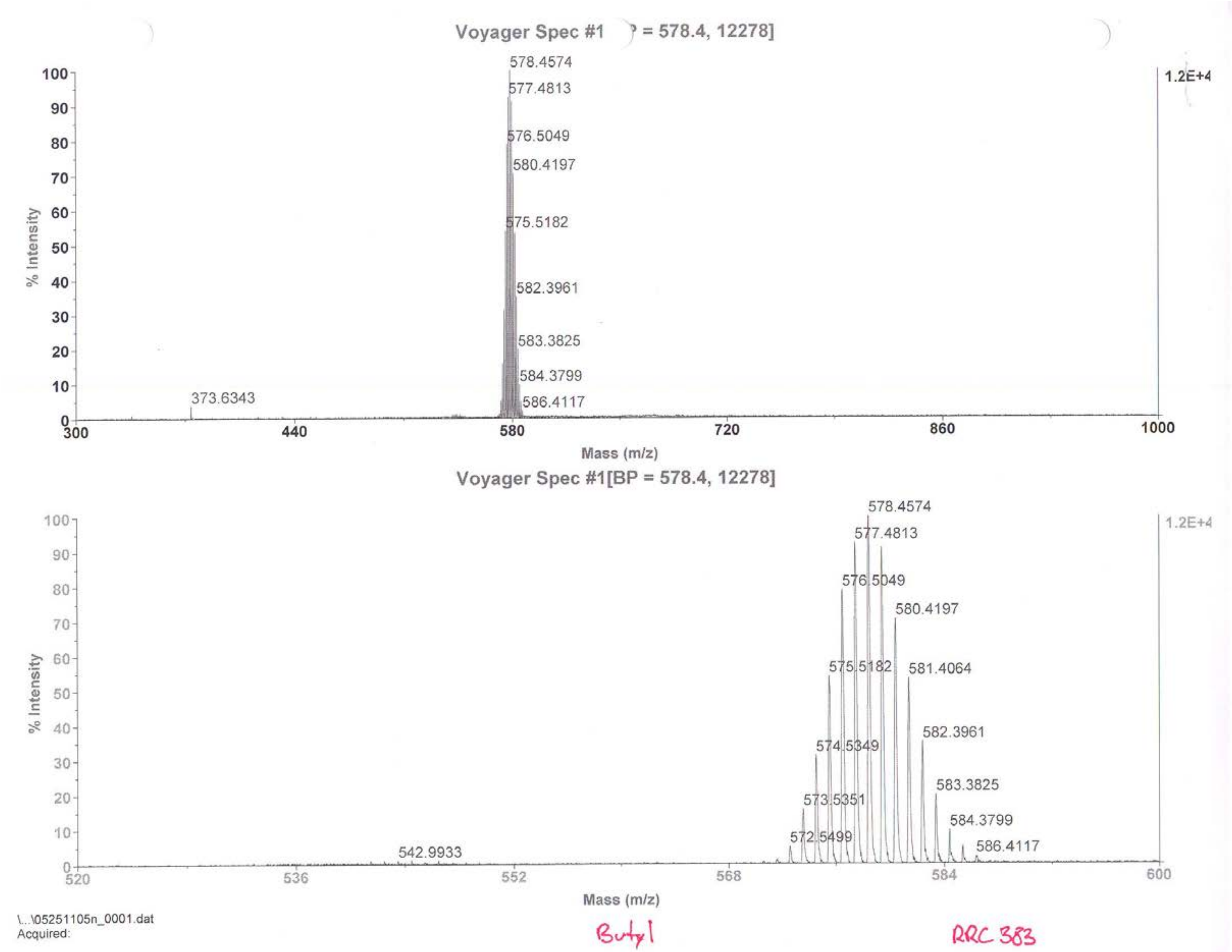

Figure S10. MALDI MS analysis of crude K[$BuCB_{11}Cl_{11}$] in *tert*-butanol solution.

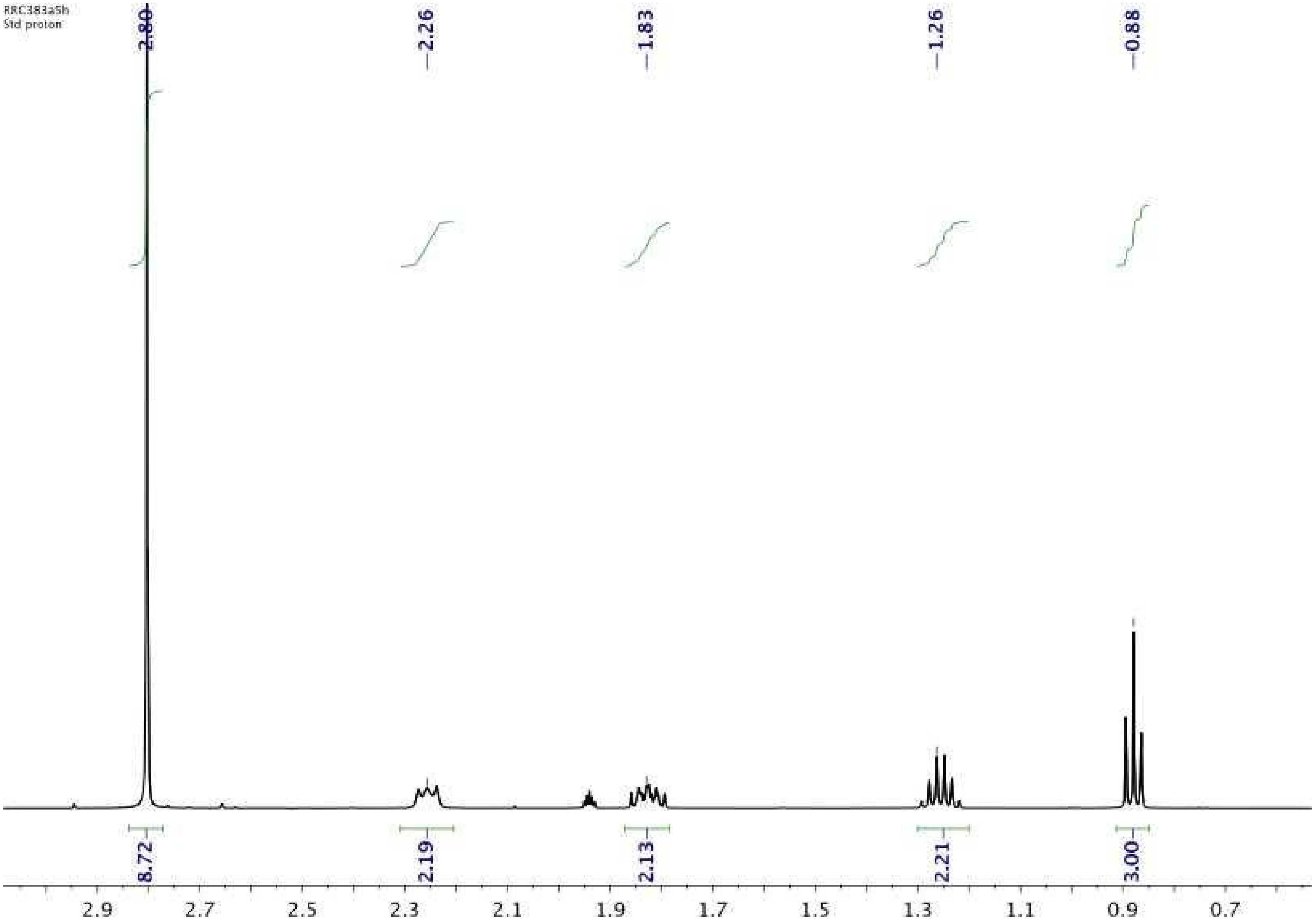

Figure S11. ^{1}H NMR spectrum of $Me_3NH[BuCB_{11}Cl_{11}]$ in acetonitrile-d$_3$.

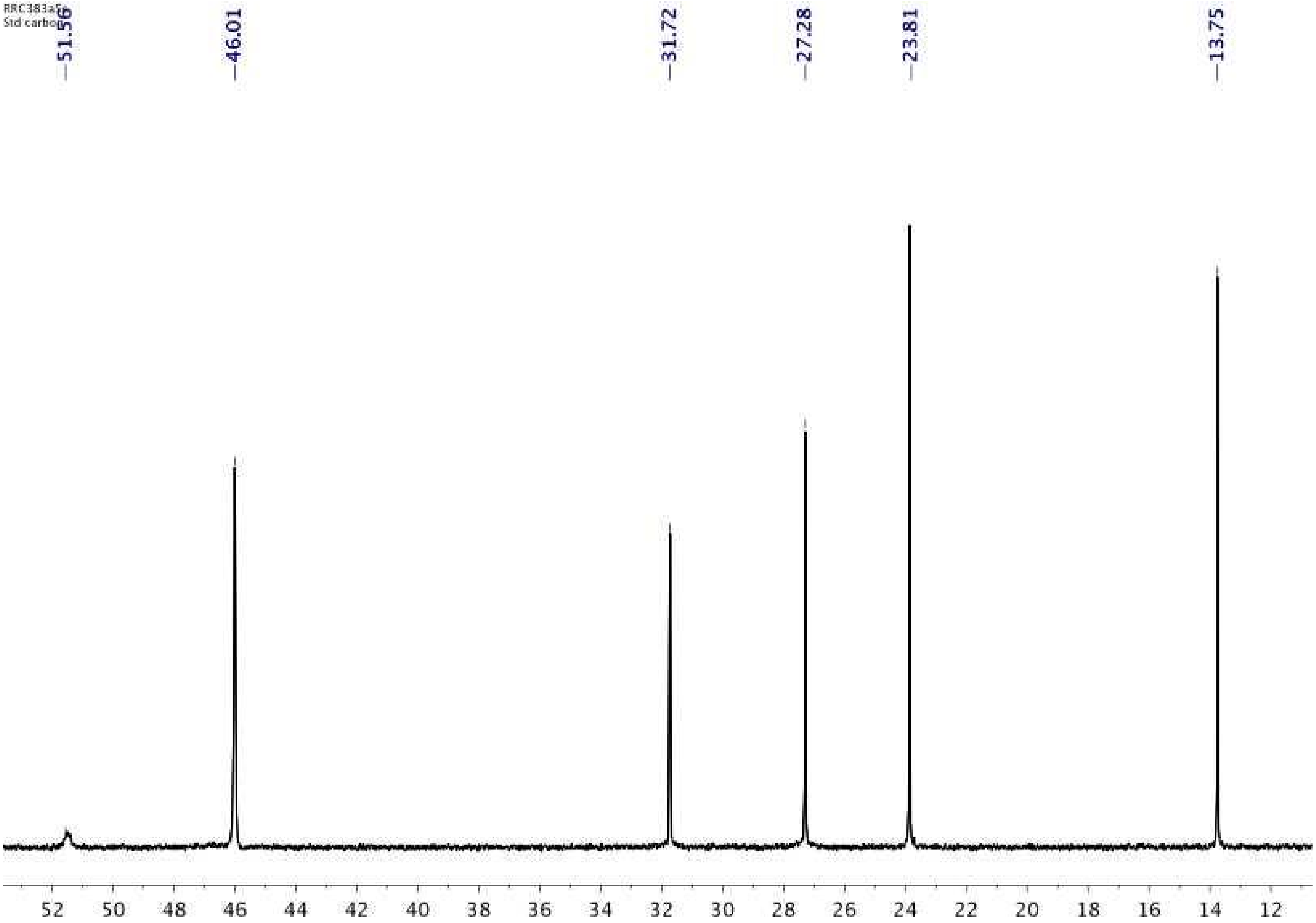

Figure S12. $^{13}C\{^1H\}$ NMR spectrum of $Me_3NH[BuCB_{11}Cl_{11}]$ in acetonitrile-d_3.

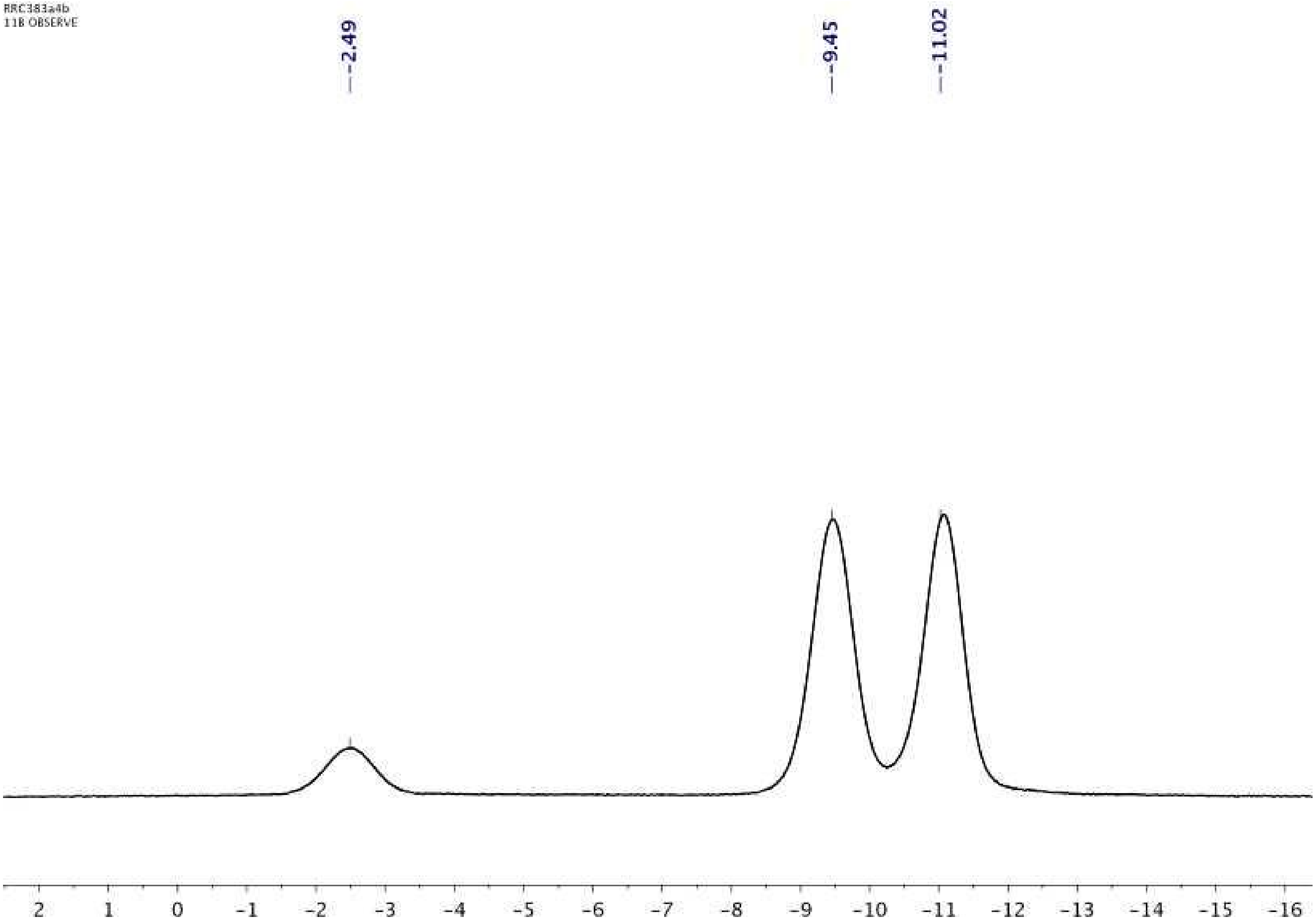

Figure S13. $^{11}B\{^1H\}$ NMR spectrum of $Me_3NH[BuCB_{11}Cl_{11}]$ in acetonitrile-d_3.

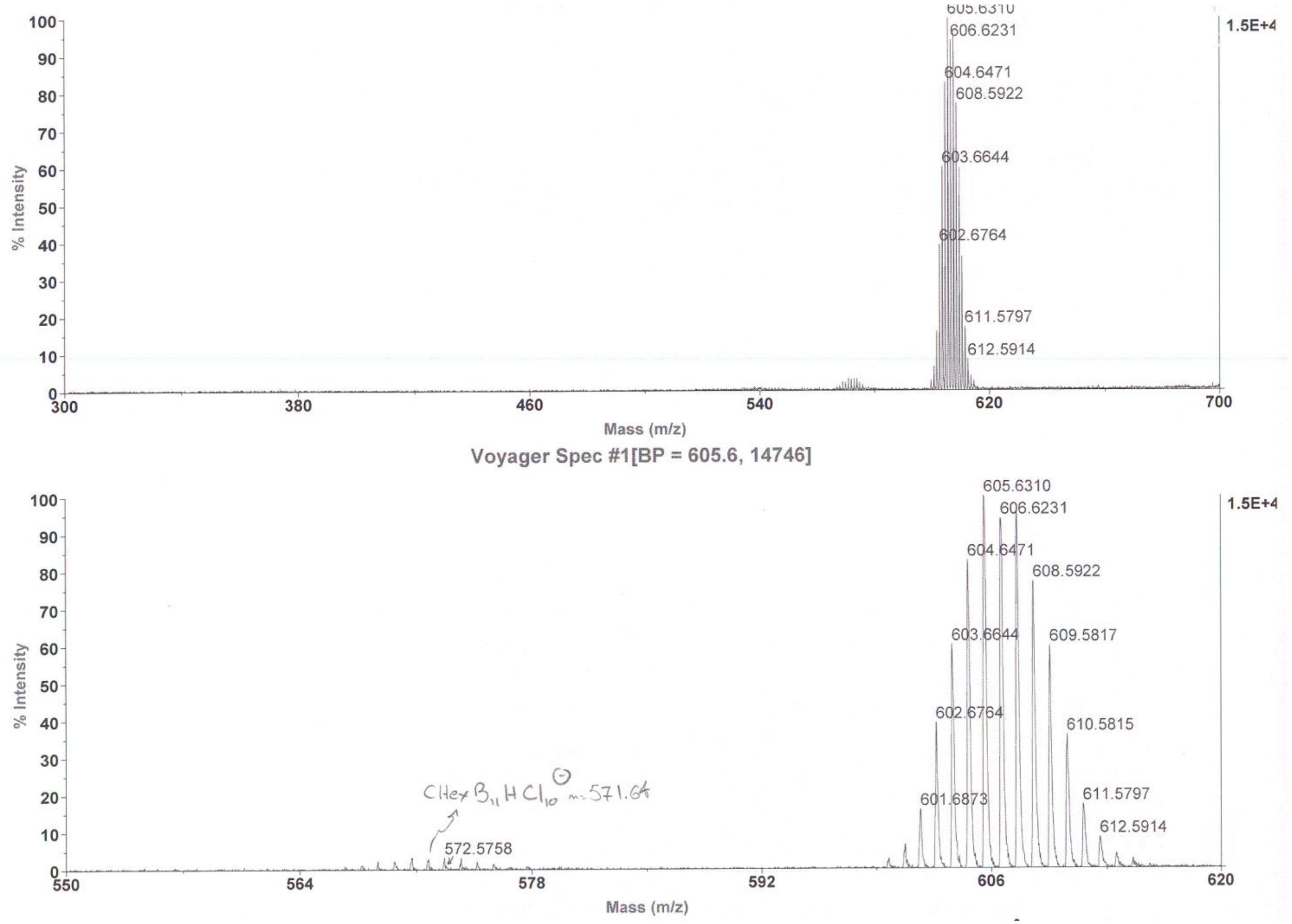

Figure S14. MALDI MS analysis of crude K[$HexCB_{11}Cl_{11}$] in *tert*-butanol solution. Signal at m/z 572.56 is consistent with an anion of formula $[HexCB_{11}Cl_{10}H]^{-}$ not observable by ^{1}H or ^{11}B NMR.

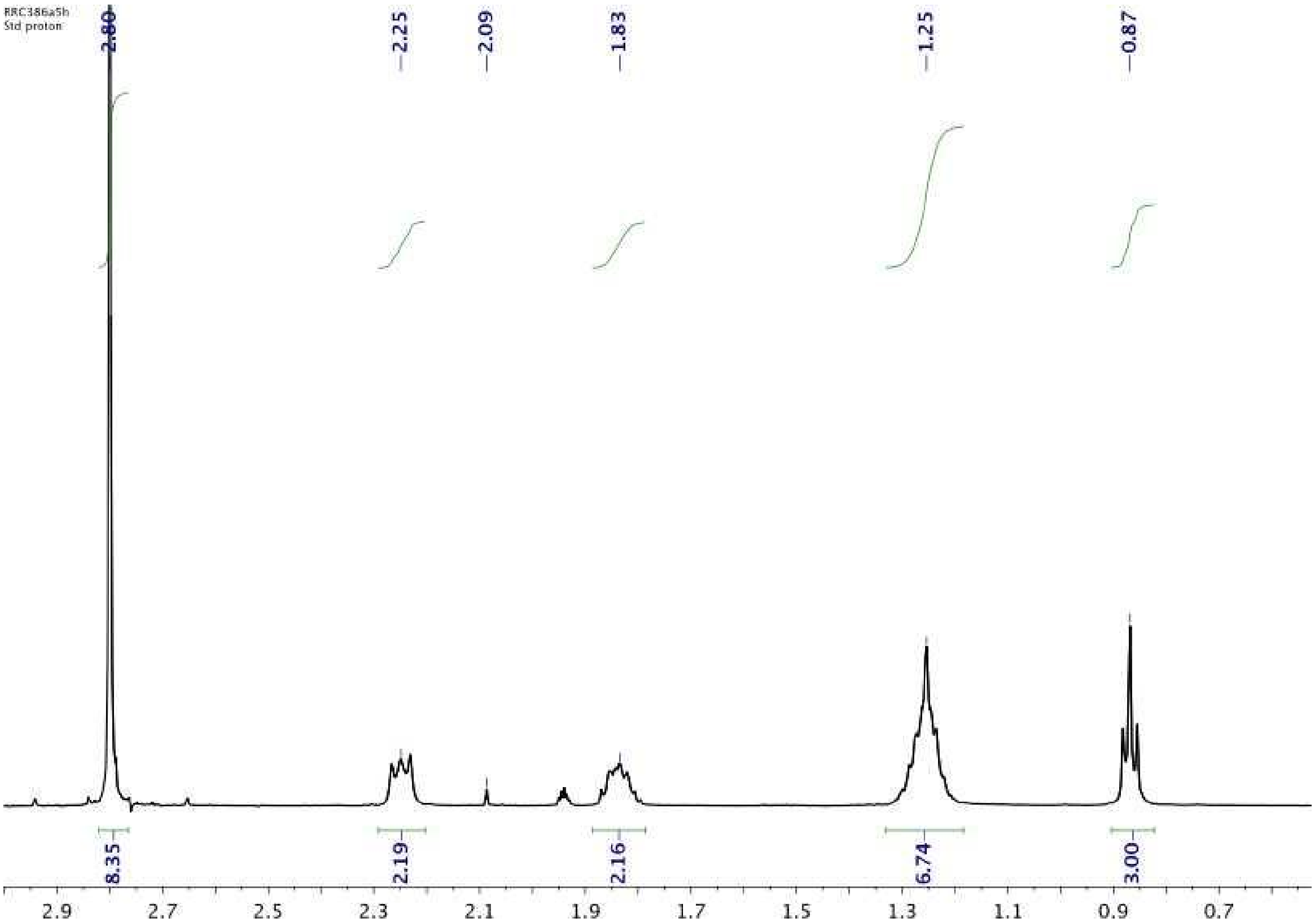

Figure S15. ^{1}H NMR spectrum of $Me_3NH[HexCB_{11}Cl_{11}]$ in acetonitrile-d_3. Residual acetone signal at $\delta = 2.09$ ppm.

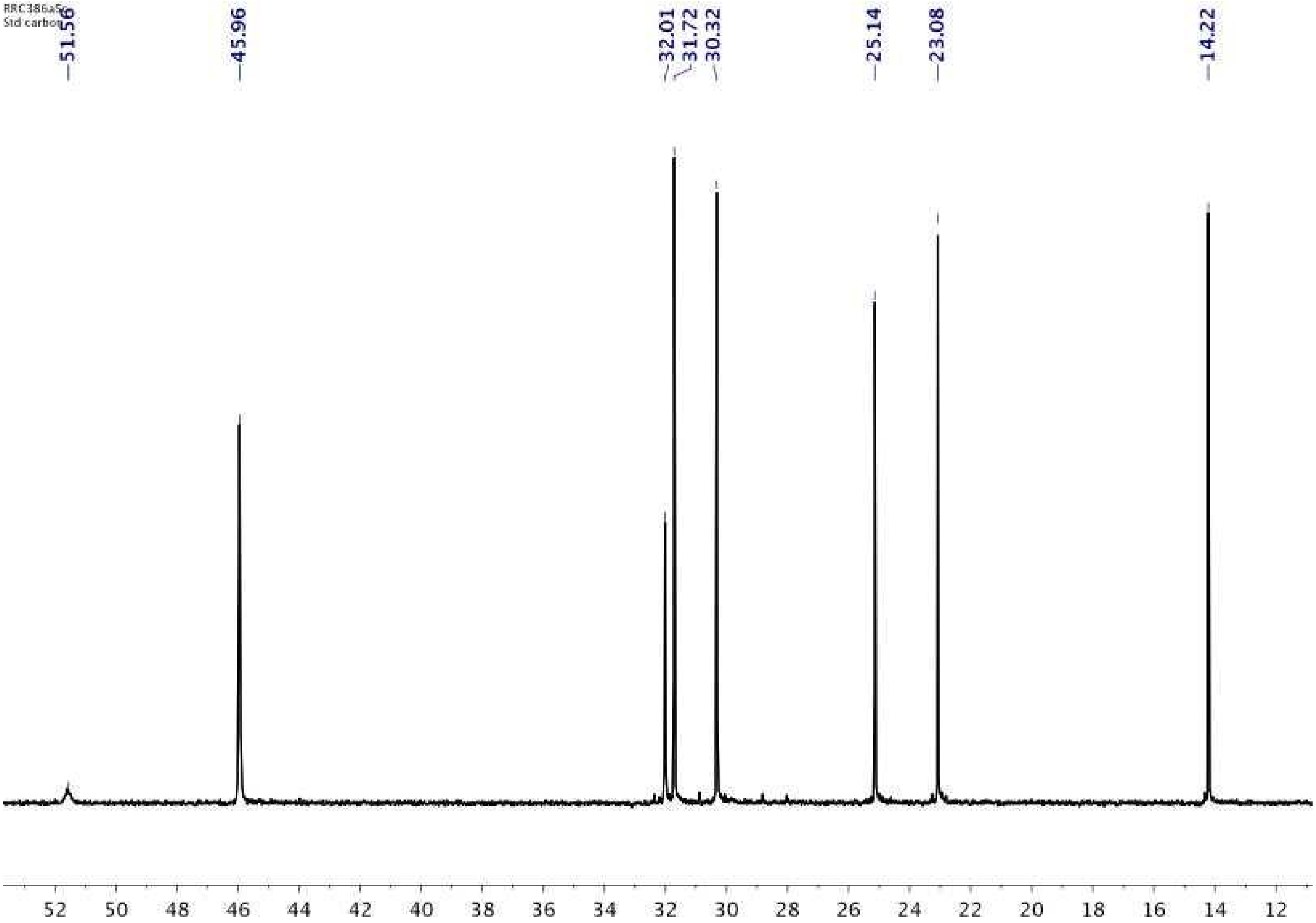

Figure S16. $^{13}C\{^1H\}$ NMR spectrum of $Me_3NH[HexCB_{11}Cl_{11}]$ in acetonitrile-d_3.

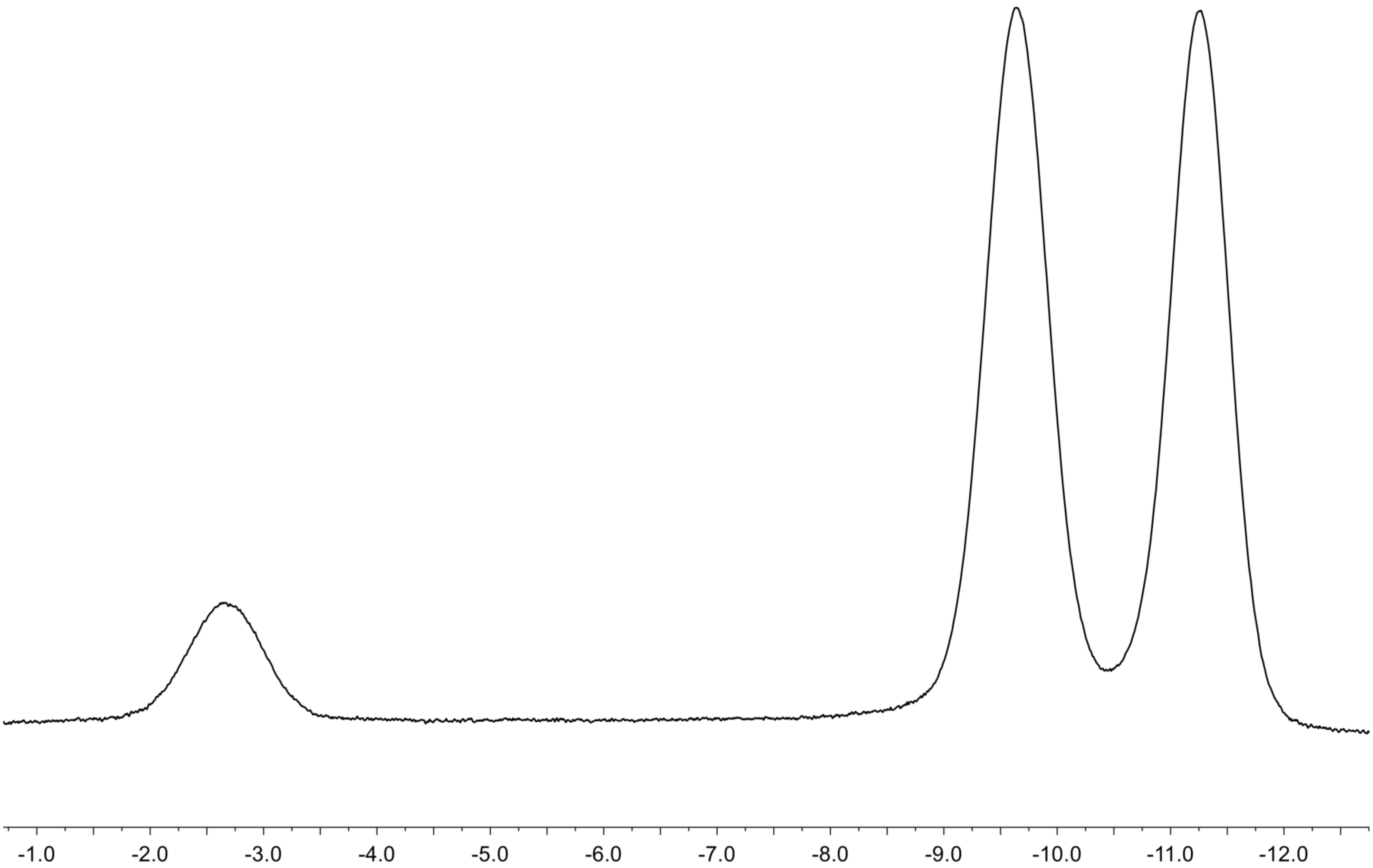

Figure S17. $^{11}B\{^1H\}$ NMR spectrum of $Me_3NH[HexCB_{11}Cl_{11}]$ in acetonitrile-d_3.

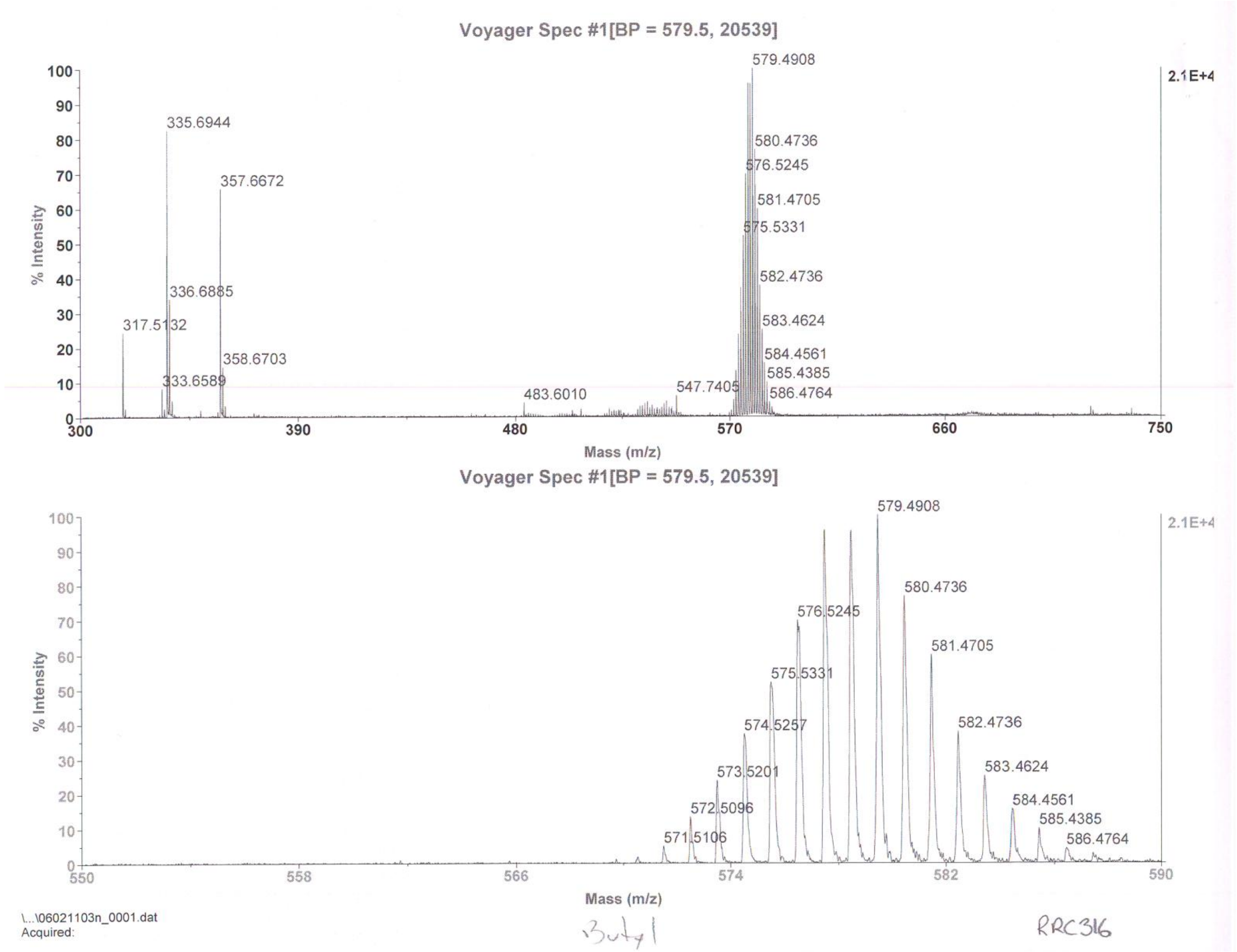

Figure S18. MALDI mass spectrum of Na[$BuCB_{11}Cl_{11}$] made by treatment of Me_3NH[$HCB_{11}Cl_{11}$] with sodium hydride and butyl iodide in THF.

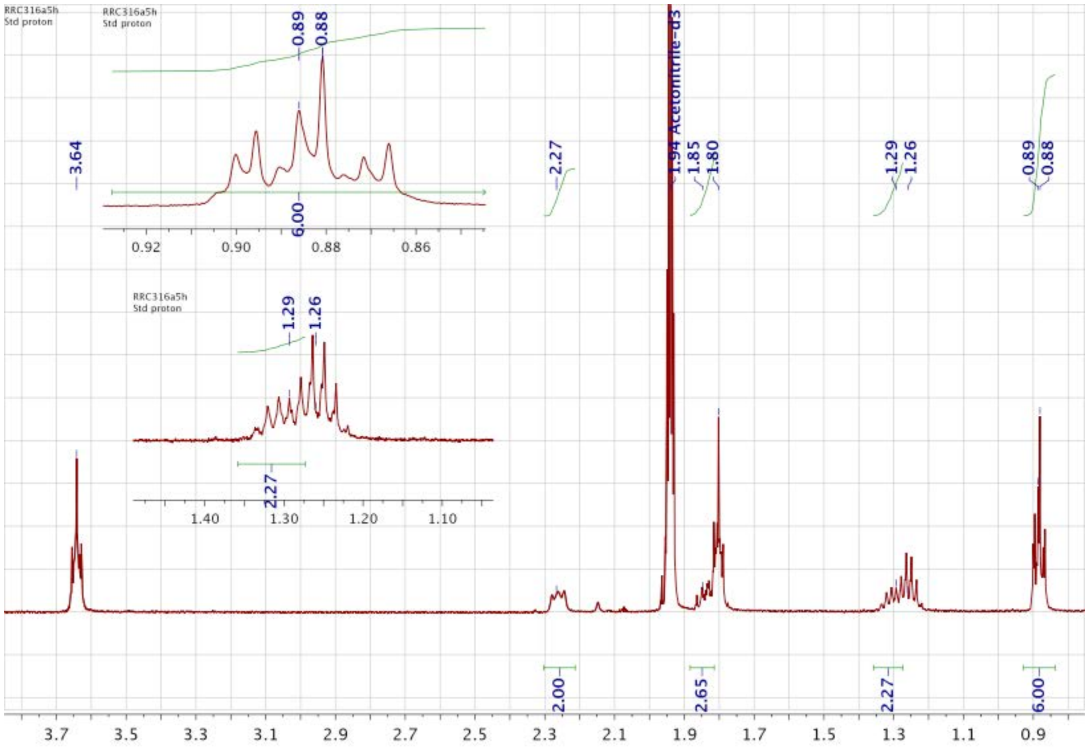

Figure S19. ^{1}H NMR spectrum in acetonitrile-d$_3$ of crude Na[BuCB$_{11}$Cl$_{11}$] made by treatment of Me$_3$NH[HCB$_{11}$Cl$_{11}$] with sodium hydride and butyl iodide in THF. Overlapping pentane resonances observed at $\delta = 0.88$ and 1.29 ppm (see inserts). THF resonantes observed at $\delta = 1.80$ and 1.29 ppm.

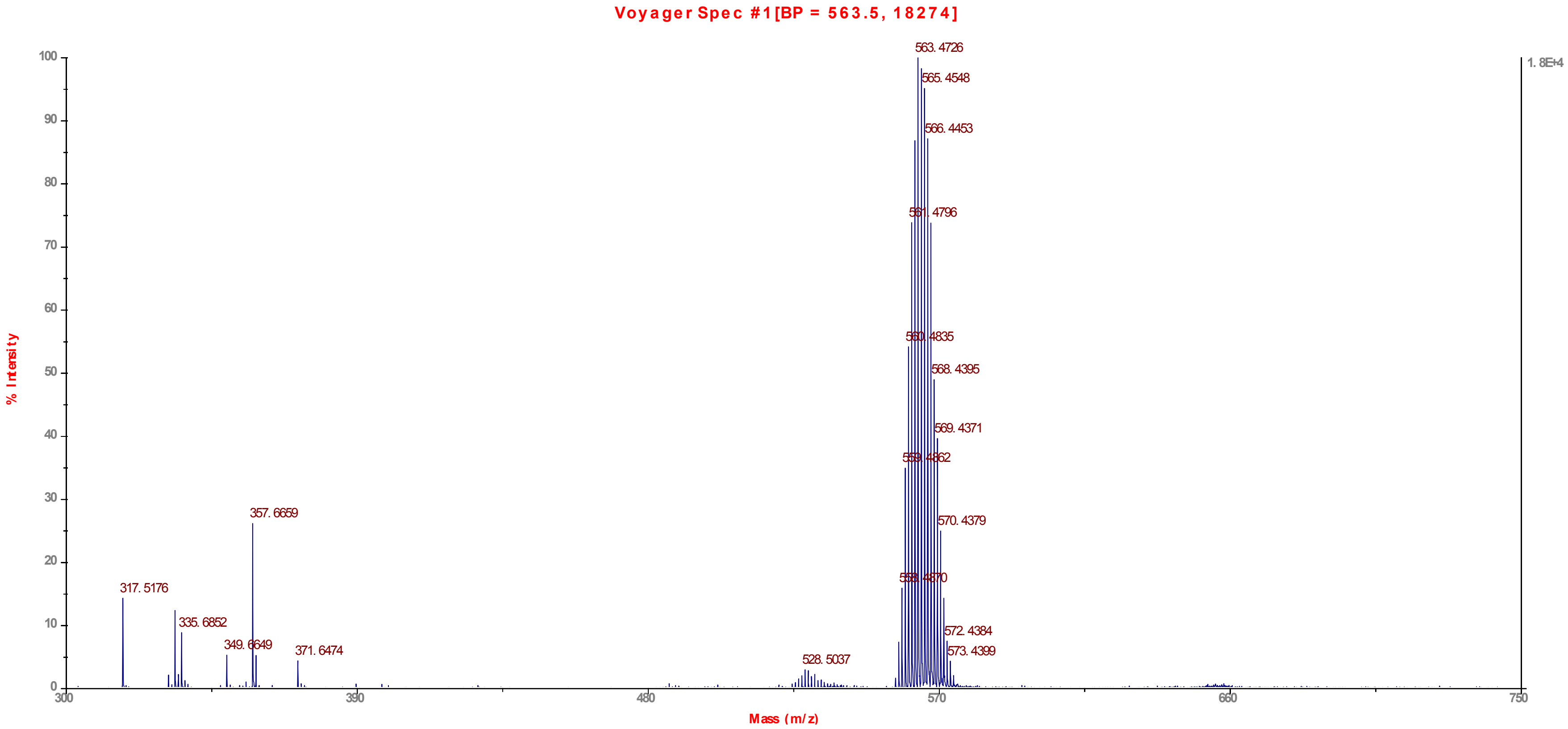

Figure S20. MALDI mass spectrum of crude solid Na[Propyl$CB_{11}Cl_{11}$] prepared in THF using propyl iodide and sodium hydride. Signals at m/z 528 and 550 correspond to [Propyl$CB_{11}Cl_{10}H$]$^-$ and [Propyl$CB_{11}Cl_{11}$]$^-$ anions respectively.

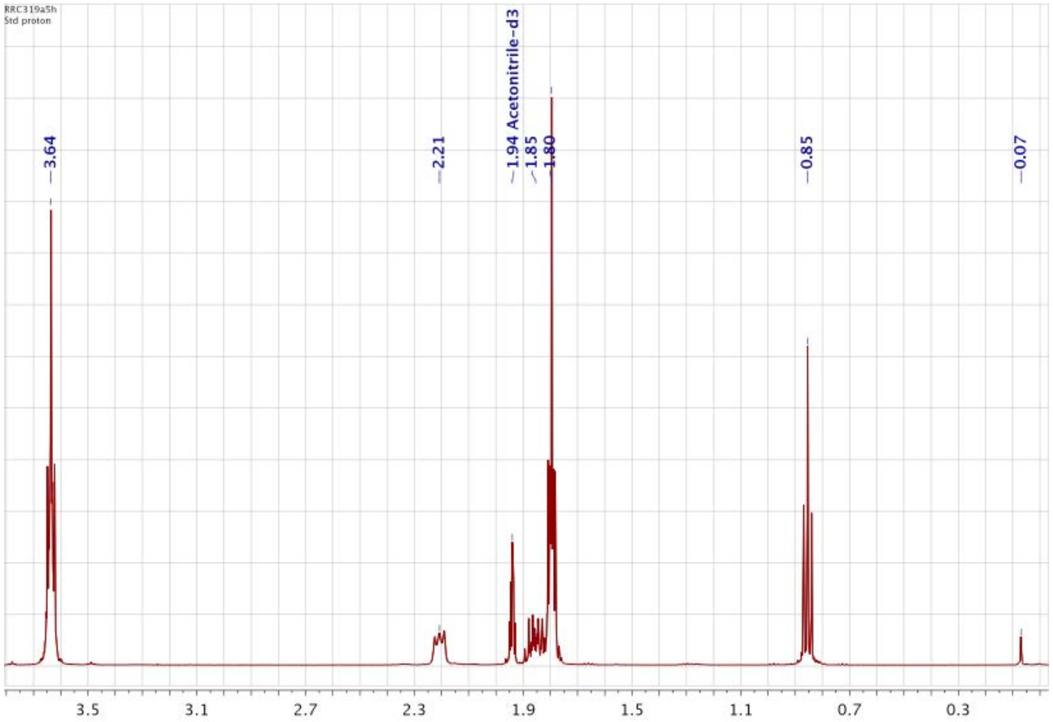

Figure S21. ^{1}H NMR spectrum in acetonitrile-d$_3$ of crude solid Na[PropylCB$_{11}$Cl$_{11}$] prepared in THF using propyl iodide and sodium hydride.

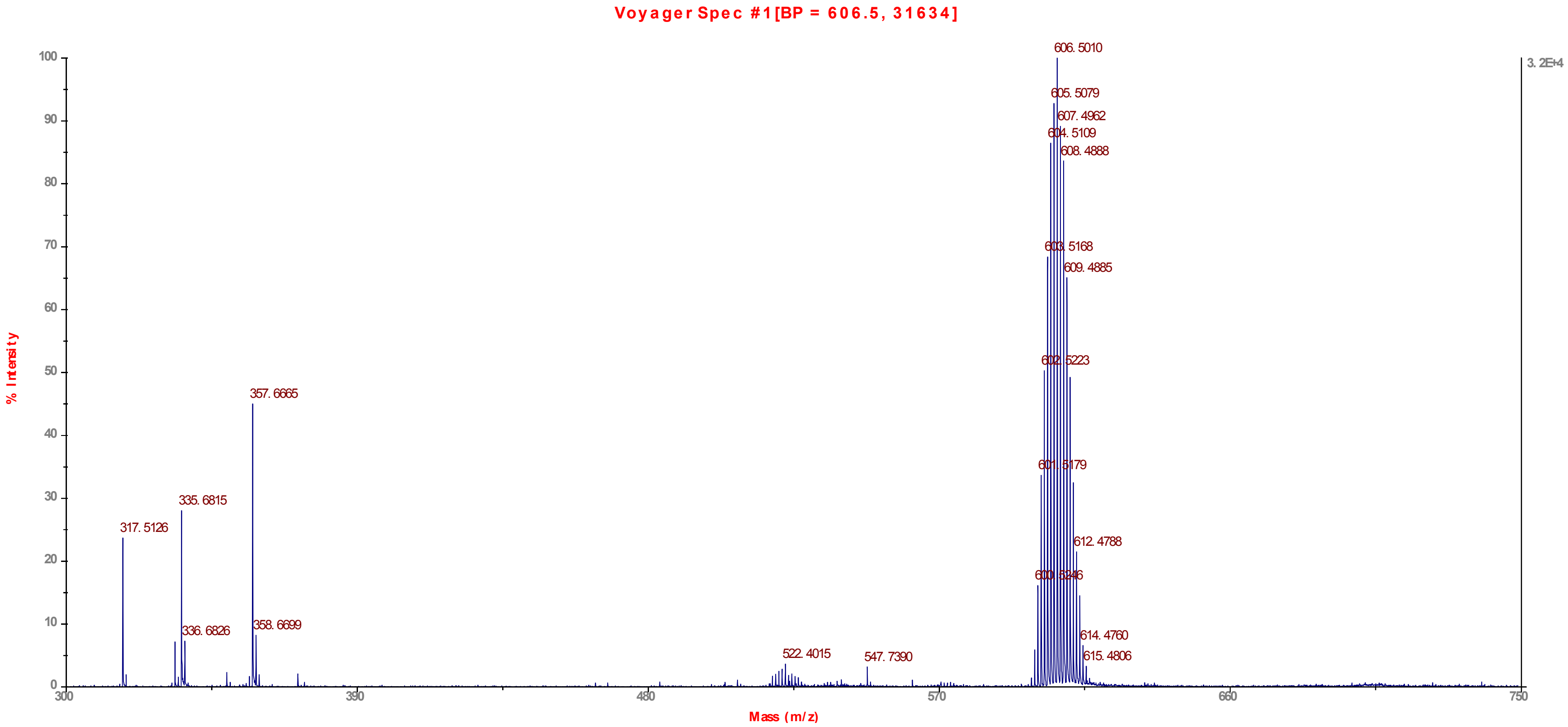

Figure S22. MALDI mass spectrum of crude solid Na[HexCB$_{11}$Cl$_{11}$] prepared in THF using hexyl iodide and sodium hydride. Signals at m/z 522 and 607 correspond to [HCB$_{11}$Cl$_{11}$]$^-$ and [HexCB$_{11}$Cl$_{11}$]$^-$ anions respectively.

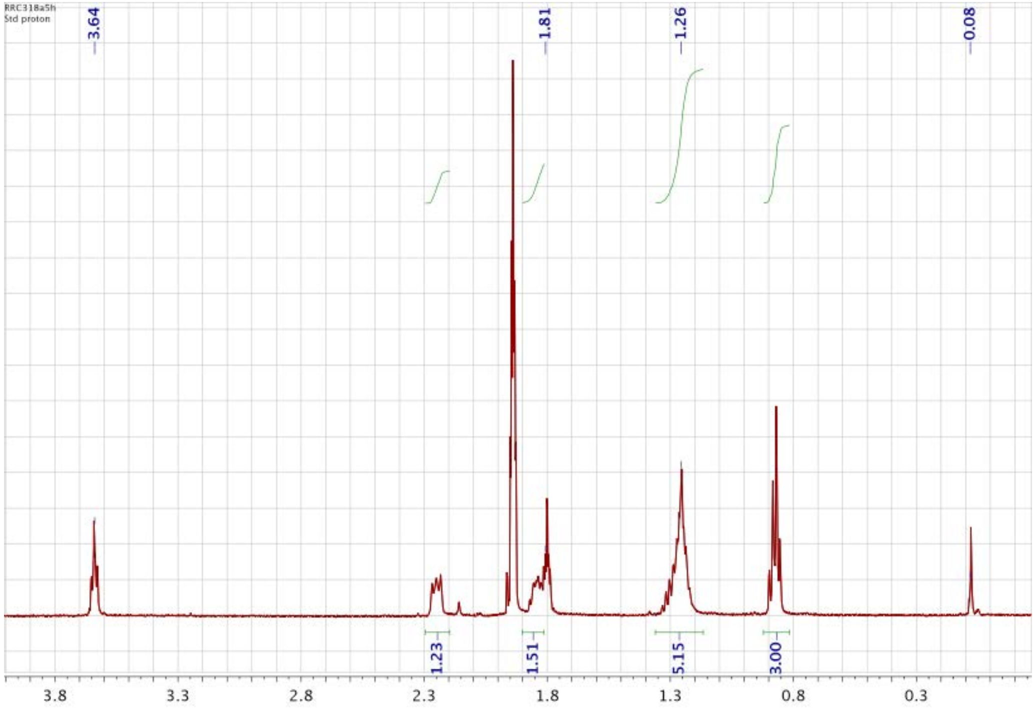

Figure S23. ^{1}H NMR spectrum in acetonitrile-d$_3$ of crude solid Na[HexCB$_{11}$Cl$_{11}$] prepared in THF using hexyl iodide and sodium hydride. THF signals can be observed at δ = 3.64 and 1.81, as well as silicon grease at δ = 0.08.

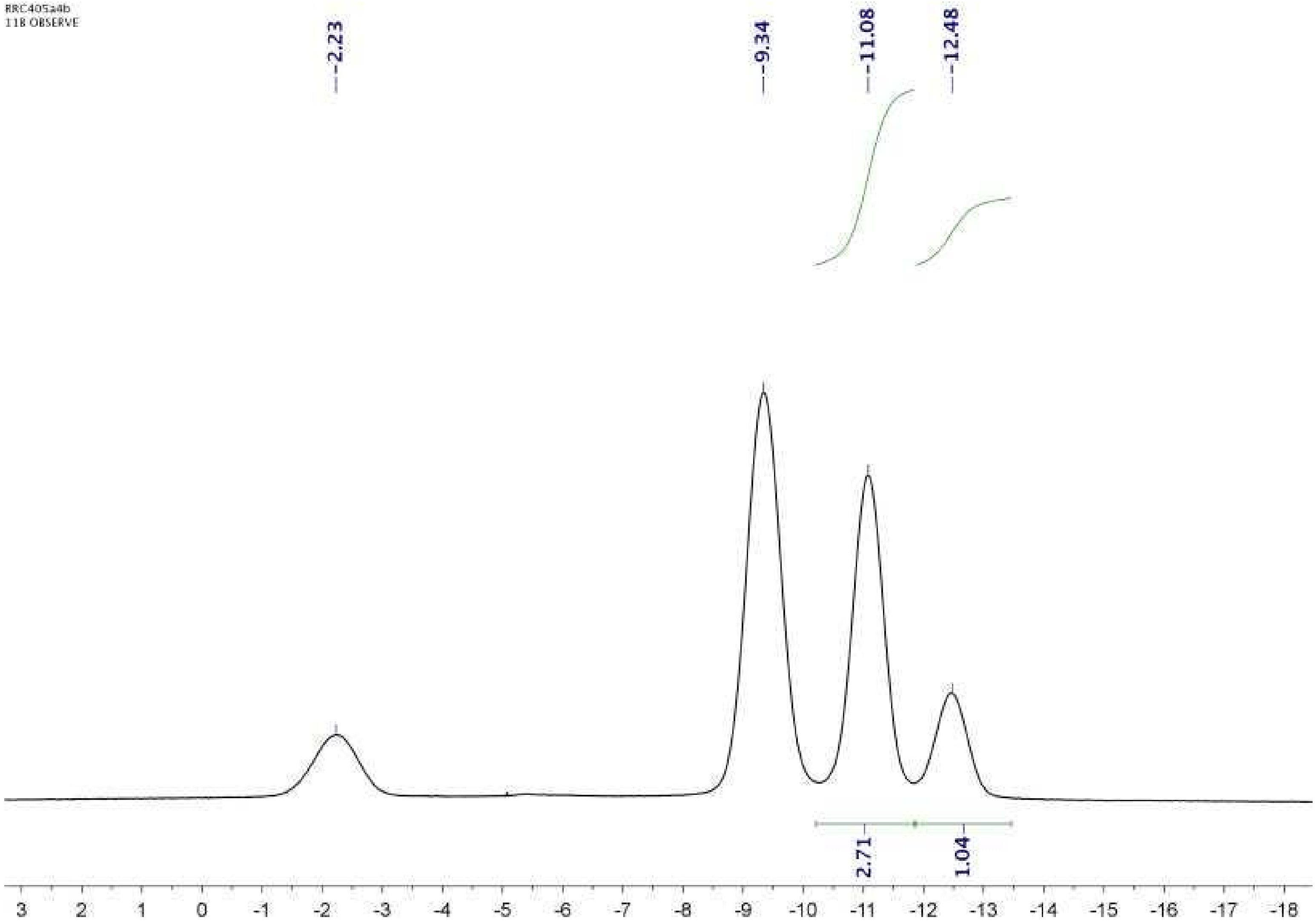

Figure S24. Attempted synthesis of $[EtCB_{11}Cl_{11}]^-$ using ethyl bromide as the electrophile. $^{11}B\{^1H\}$ NMR spectrum of an aliquot of the reaction mixture in *tert*-butanol solution after one hour of treatment with ethyl bromide.

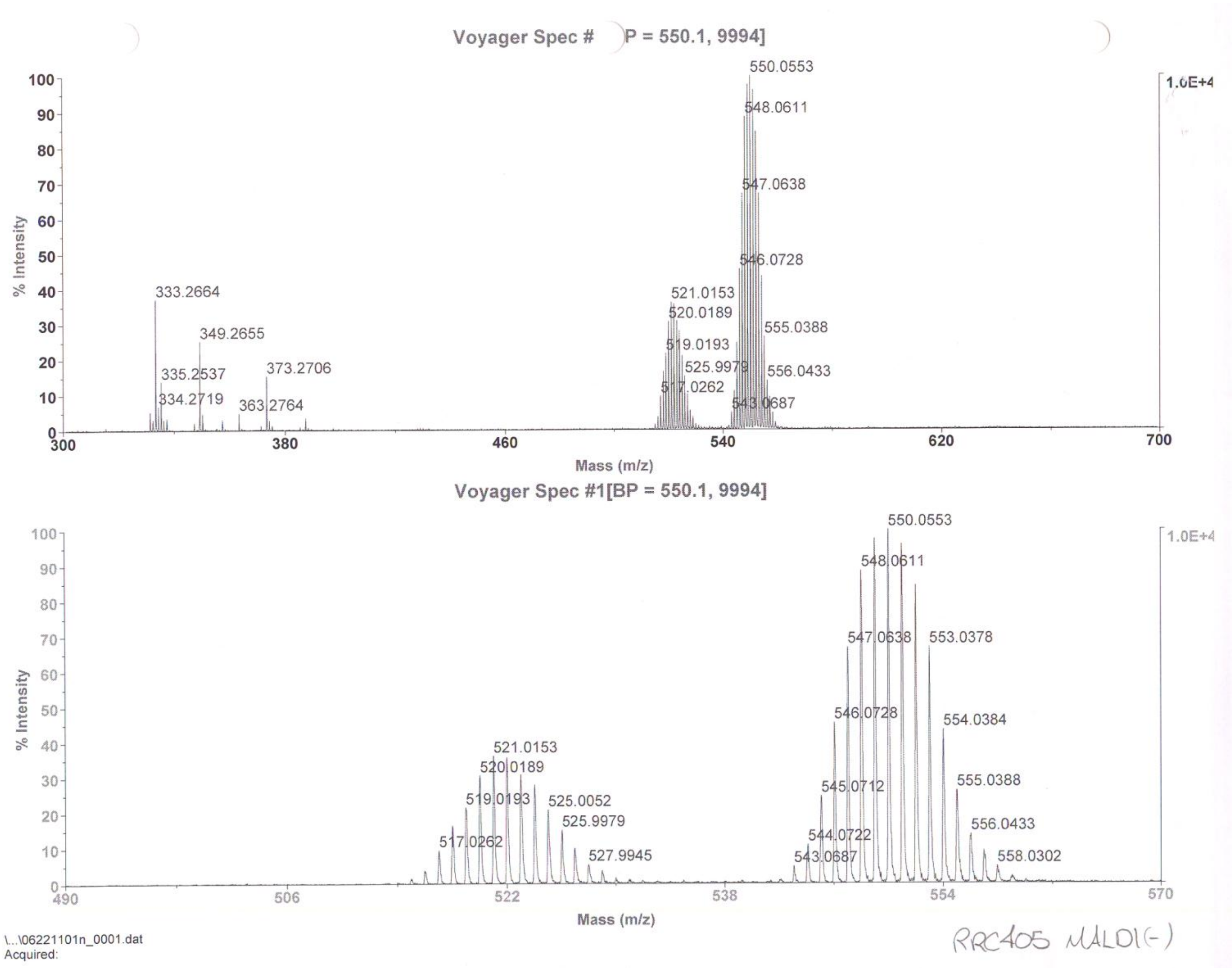

Figure S25. Attempted synthesis of $[EtCB_{11}Cl_{11}]^-$ using ethyl bromide as the electrophile. MALDI mass spectrum of an aliquot of the reaction mixture after one hour of treatment with ethyl bromide. Signals at m/z 521 and 550 correspond to $HCB_{11}Cl_{11}^-$ and $EtCB_{11}Cl_{11}^-$ anions respectively.

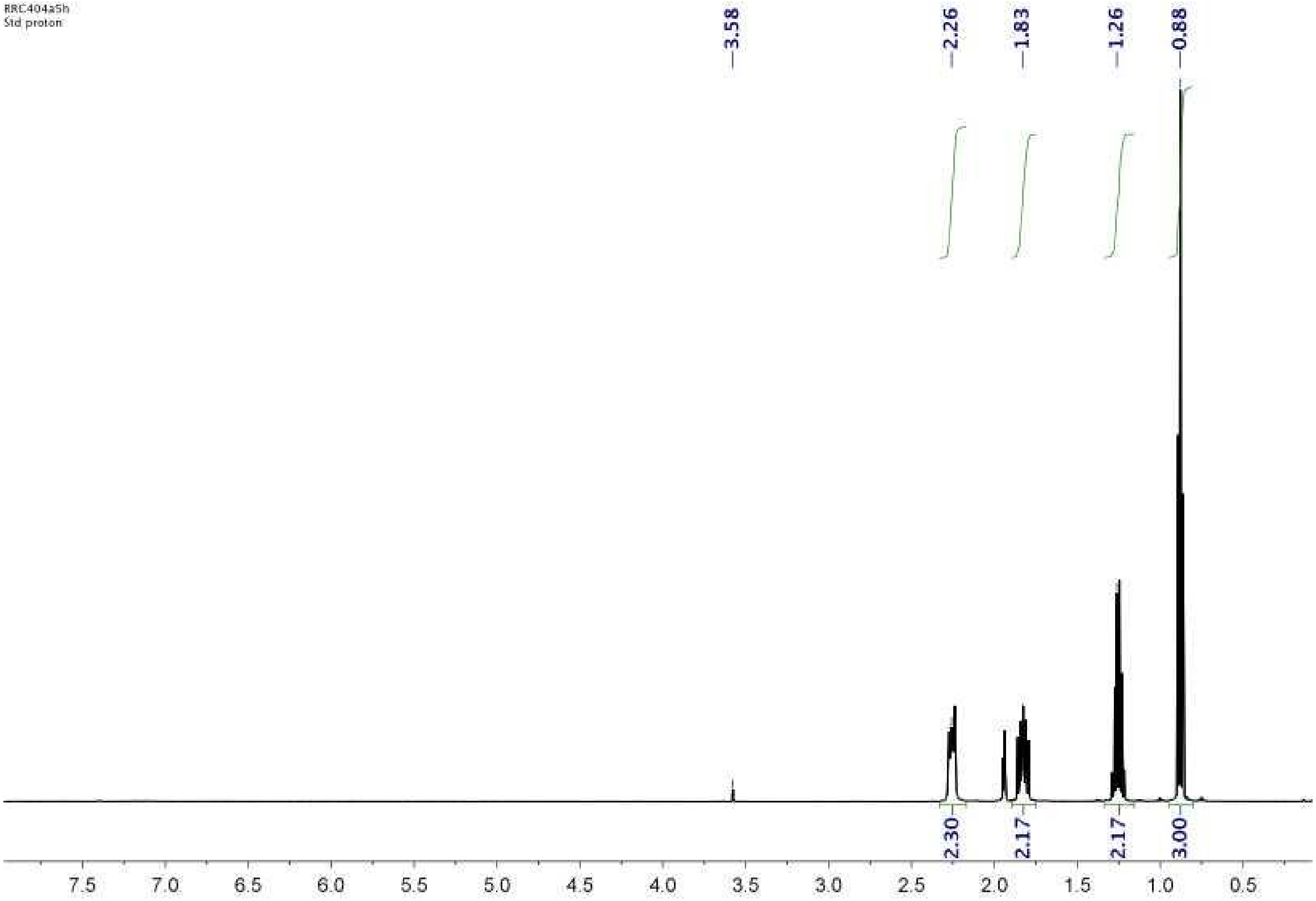

Figure S26. ^{1}H NMR spectrum of donor-free $Na[BuCB_{11}Cl_{11}]$ in acetonitrile-d_3.

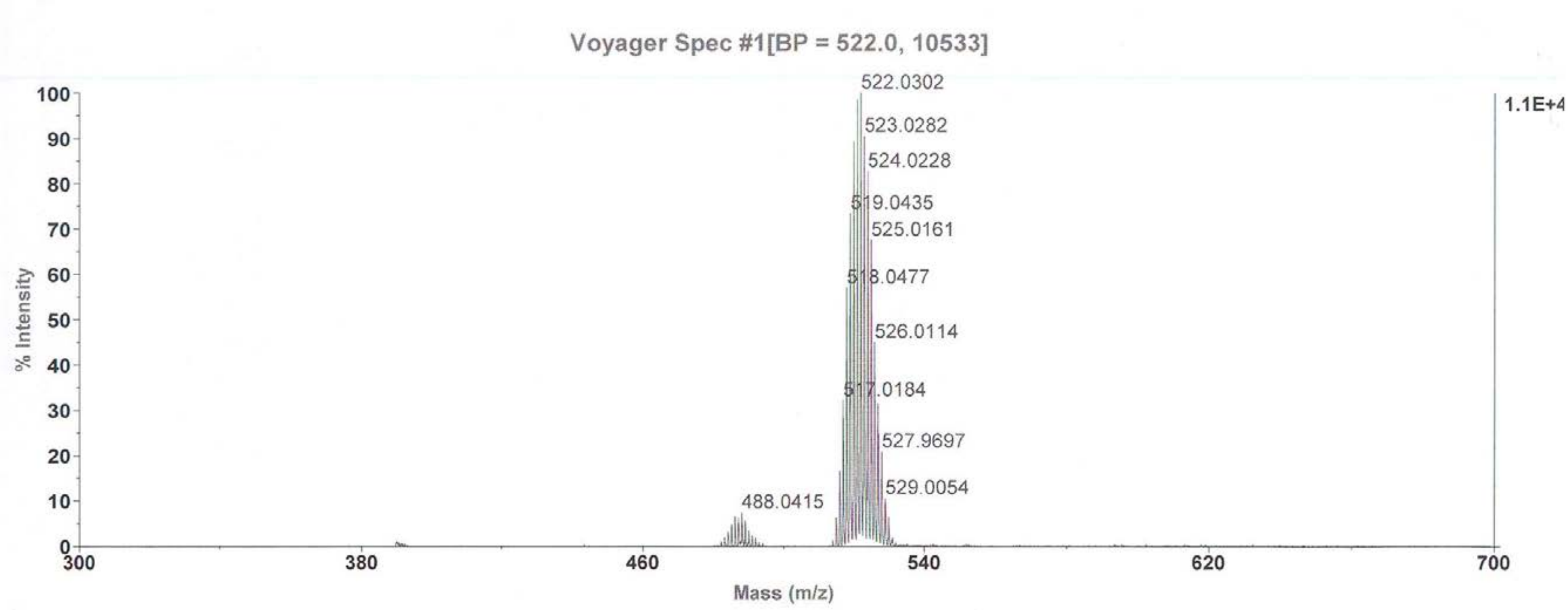

Figure S27. MALDI mass spectrum of the reaction mixture of $Me_3NH[HCB_{11}Cl_{11}]$ and potassium *tert*-butoxide in *tert*-butanol after heating at 70 °C for two days. Signal at m/z = 488 consistent with an anion of formulation $[HCB_{11}Cl_{10}H]^-$.

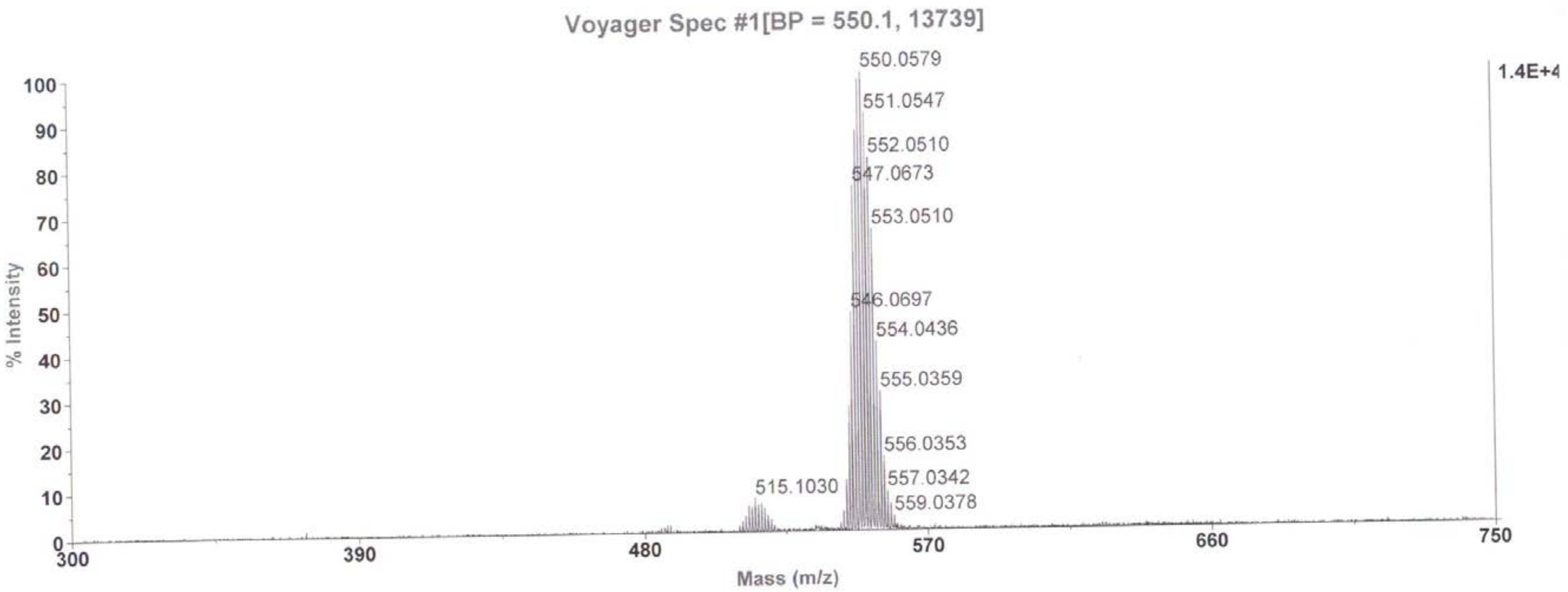

Figure S28. MALDI mass spectrum of the solution of $Me_3NH[EtCB_{11}Cl_{11}]$ and potassium *tert*-butoxide in *tert*-butanol after heating at 70 °C for two days. Signal at m/z = 515 consistent with an anion of formulation $[EtCB_{11}Cl_{10}H]^-$.

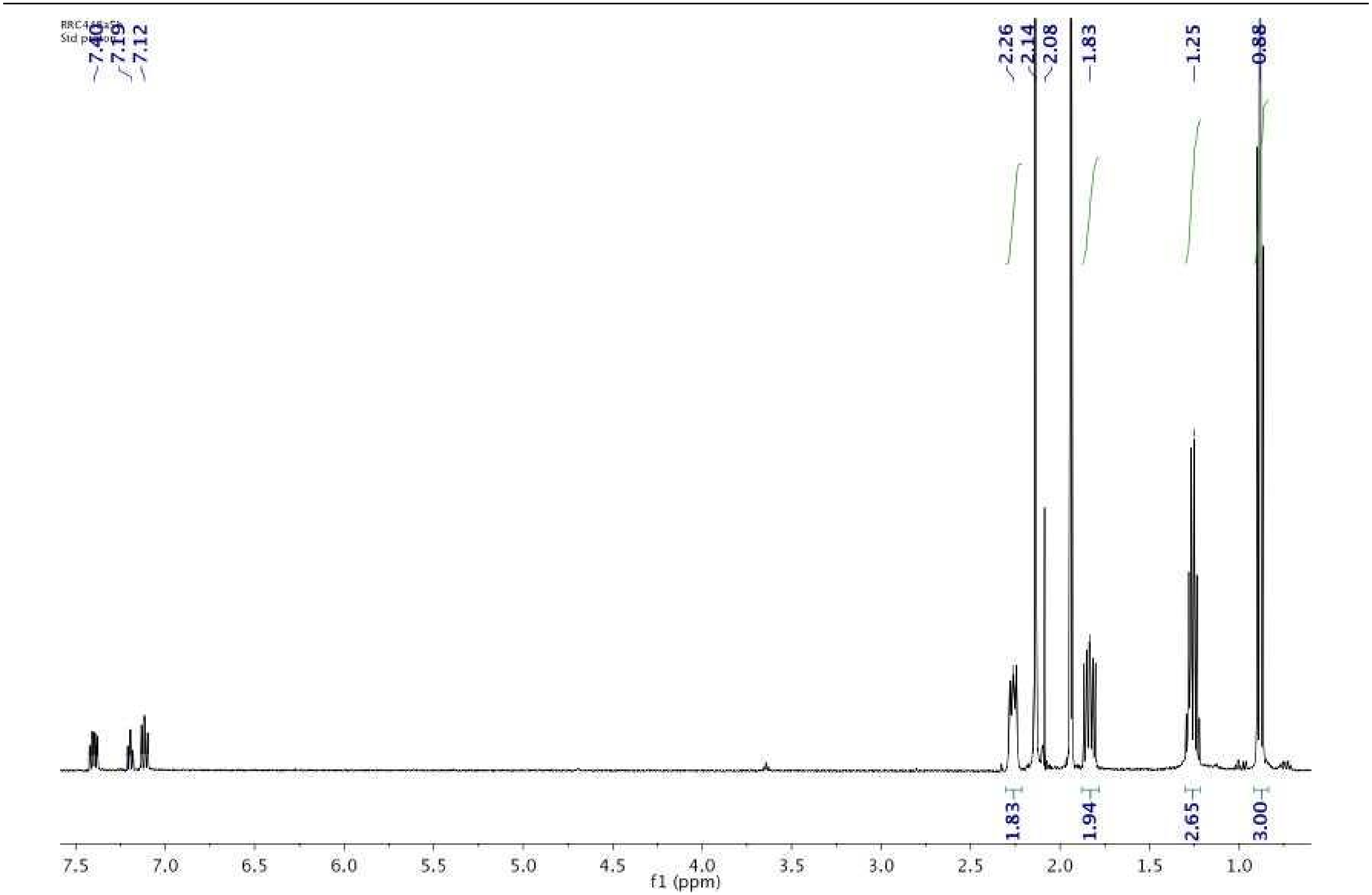

Figure S29. ^{1}H NMR spectrum of Ag[BuCB$_{11}$Cl$_{11}$] in acetonitrile-d$_3$. Peaks at δ = 2.08, 2.14 and 7.12-7.40 ppm correspond to residual acetone, water and fluorobenzene.

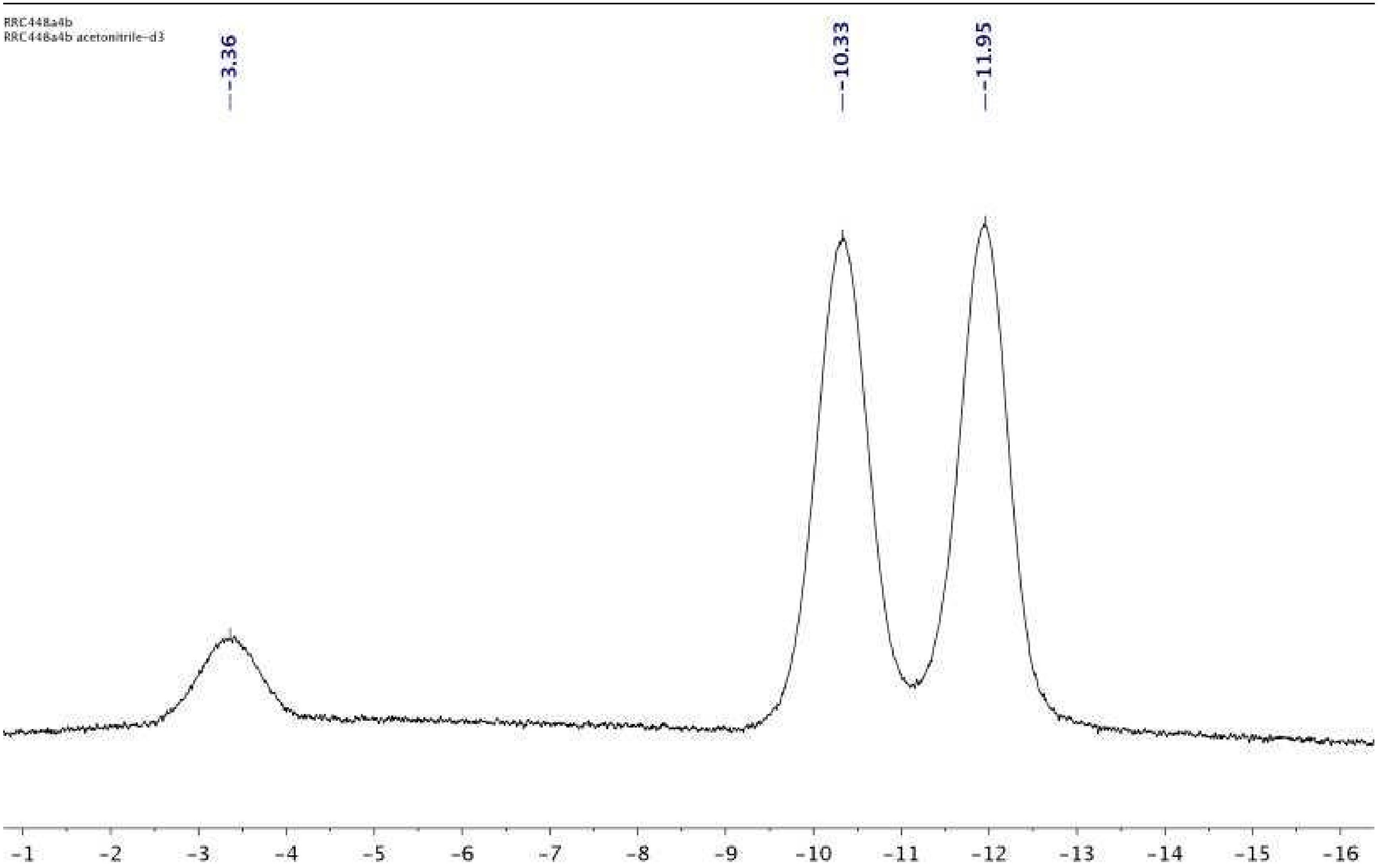

Figure S30. $^{11}B\{^{1}H\}$ NMR spectrum of $Ag[BuCB_{11}Cl_{11}]$ in acetonitrile-d_3.

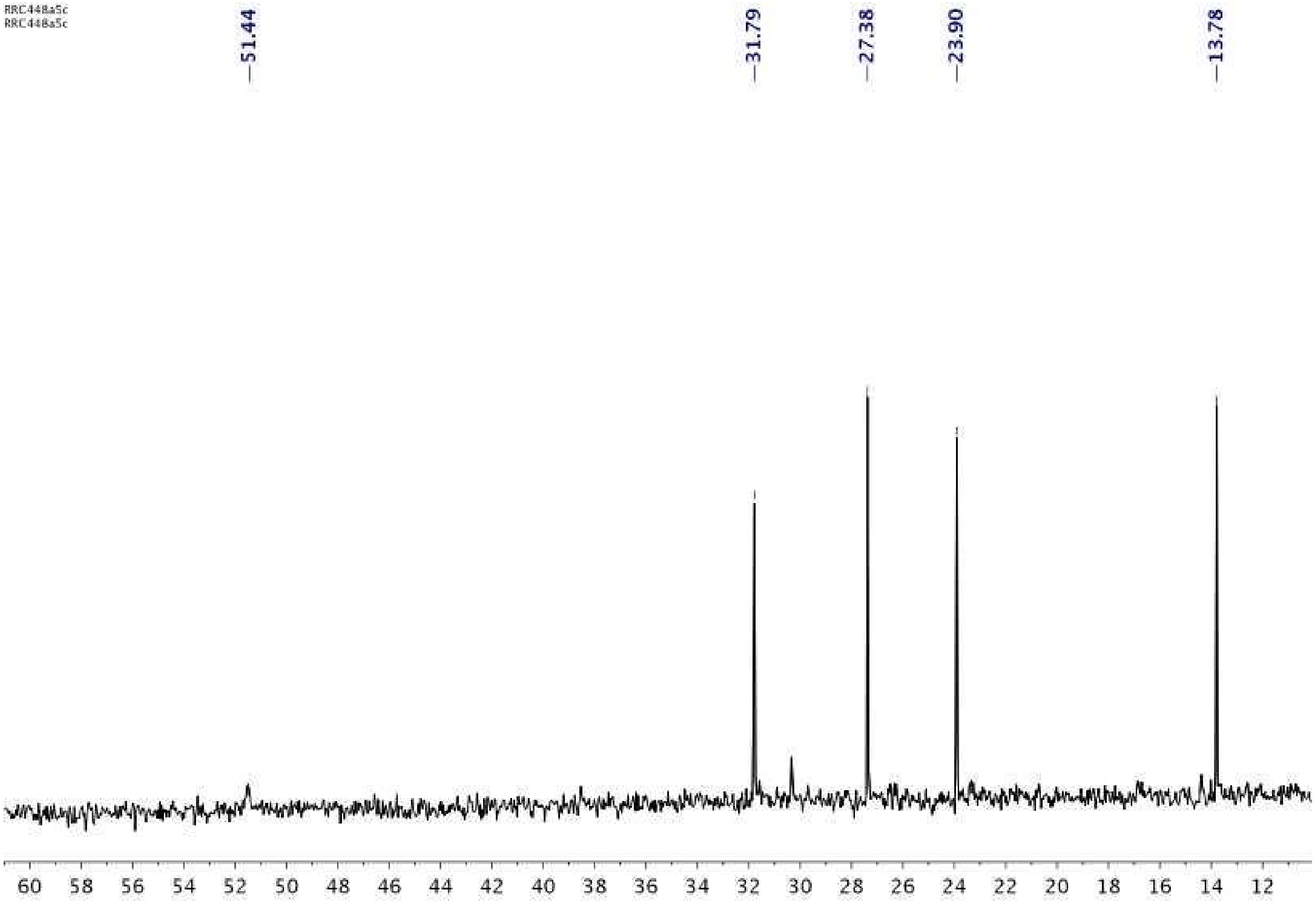

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of $Ag[BuCB_{11}Cl_{11}]$ in acetonitrile-d_3.

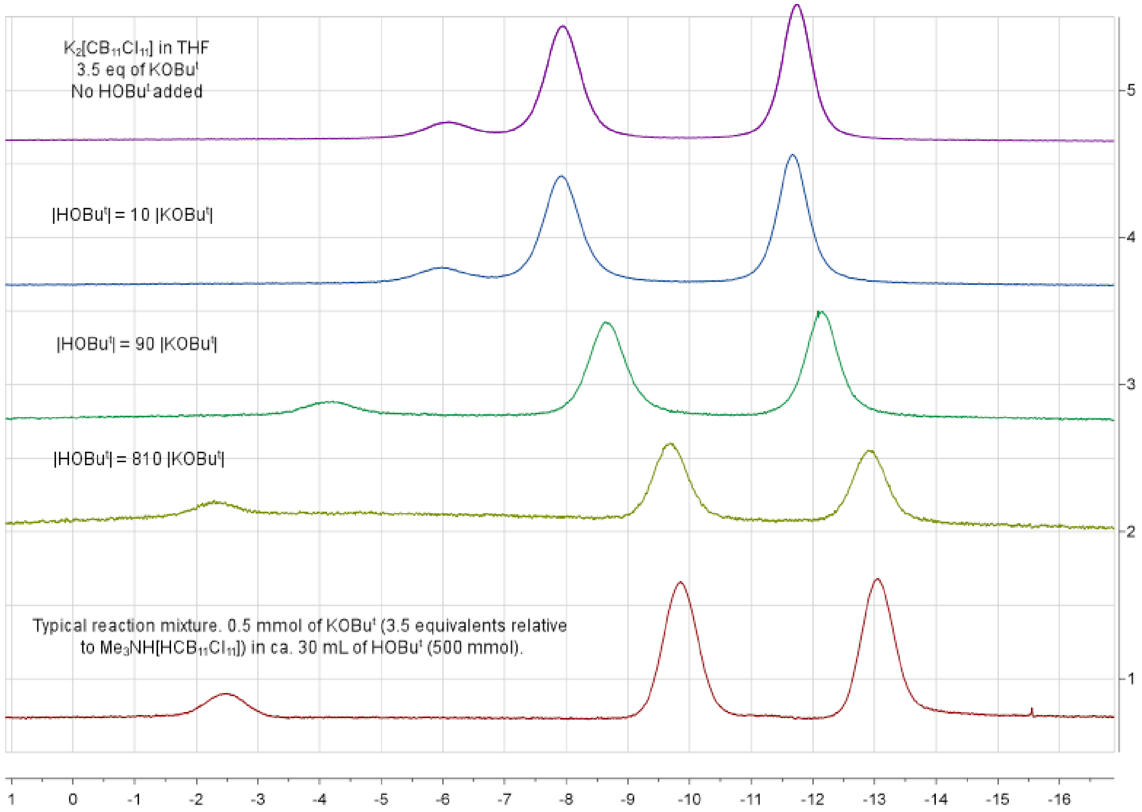

Figure S32. Observation of equilibration of $[HCB_{11}Cl_{11}]^-$ and $[CB_{11}Cl_{11}]^{2-}$ in solution by $^{11}B\{^1H\}$ NMR.

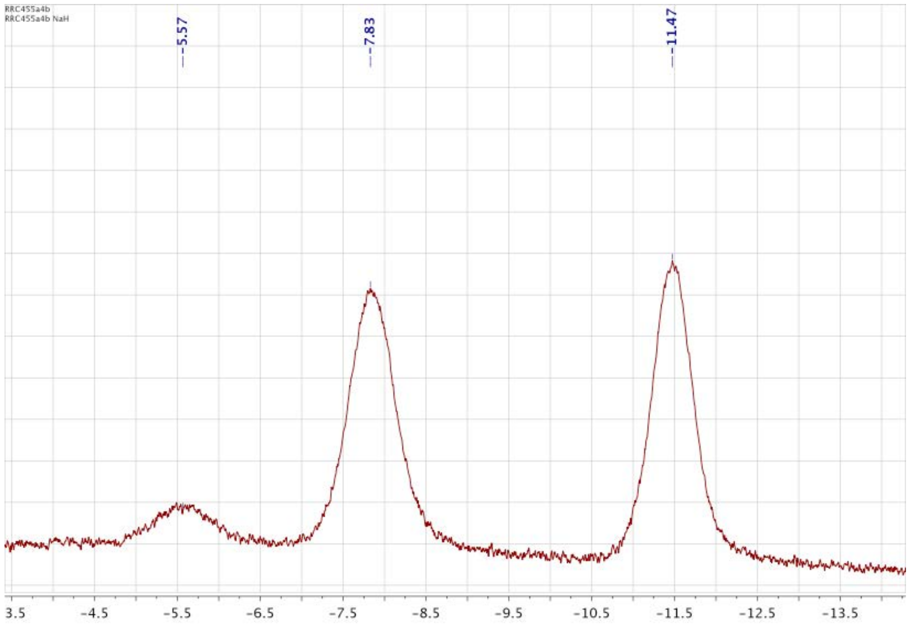

Figure S33. $^{11}B\{^1H\}$NMR of $Na_2[CB_{11}Cl_{11}]$ in THF solution. Salt prepared from $Me_3NH[HCB_{11}Cl_{11}]$ and NaH in dry THF.

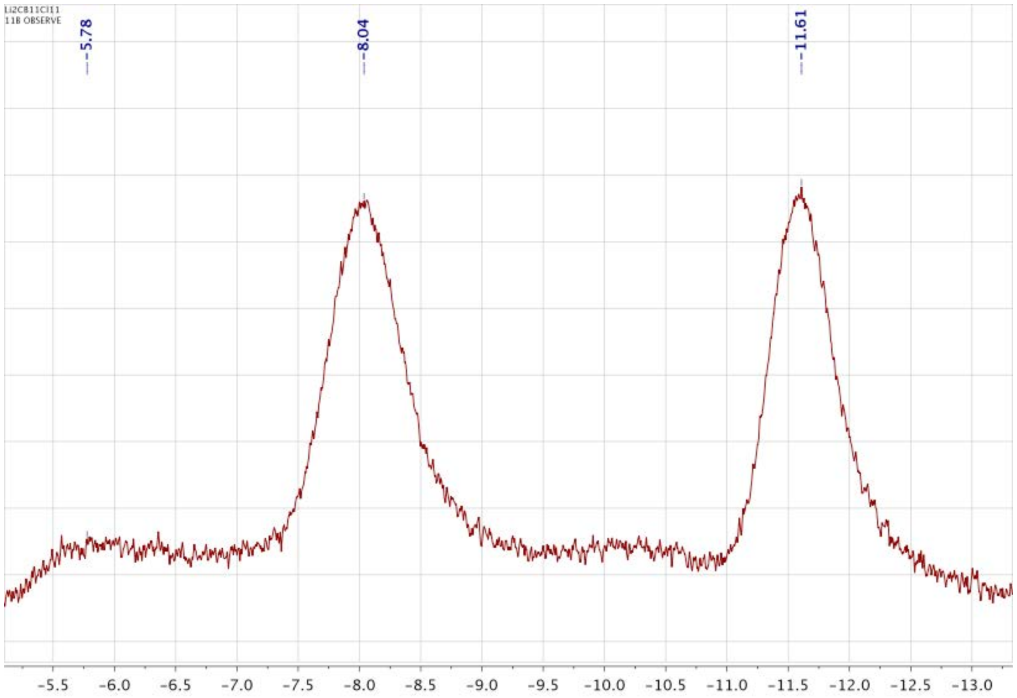

Figure S34. $^{11}B\{^1H\}$NMR of $Li_2[CB_{11}Cl_{11}]$ in THF solution. Salt prepared from $Me_3NH[HCB_{11}Cl_{11}]$ and butyllithium in dry THF.