Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Improved Methods for the Halogenation of the $[HCB_{11}H_{11}]^-$ Anion

Weixing Gu, Billy J. McCulloch, Joseph H. Reibenspies, and Oleg V. Ozerov*

Department of Chemistry, Texas A&M University,

College Station, TX 77842, USA

ozerov@chem.tamu.edu

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General considerations

Materials and methods. Cs[$HCB_{11}H_{11}$] was purchased from Katchem spol. s r.o. and used as received. $SbCl_5$ was purchased from Aldrich and fractionally distilled before use. All other chemicals were purchased from either Aldrich, Alfa Aesar or Acros and used as received unless otherwise noted. NMR spectra were recorded on a Varian Inova 300 spectrometer (^{1}H NMR, 299.951 MHz), Varian Mercury 300 spectrometer (^{13}C NMR, 75.426 MHz), or a Varian Inova 400 spectrometer (^{11}B NMR, 128.191 MHz) in noted solvents. Chemical shifts are given in δ (ppm). ^{11}B NMR spectra were referenced externally with BF_3 etherate at δ 0. ^{1}H and ^{13}C NMR spectra were referenced using the solvent signals. MS characterization of carborane anions were performed by Texas A&M University Laboratory for Biological Mass Spectrometry (LBMS) and by the Brandeis University Mass-Spectrometry lab (BUMS). Elemental analyses were performed by Complete Analysis Laboratories Inc., Parsippany, NJ, USA.

All reactions were performed in Schlenk or simple round-bottom flasks with a reflux condenser attached where appropriate. These systems were either open to air in the fume hood (via a glass Pasteur pipette connected to a glass adapter via Tygon tubing to minimize evaporation) or connected to a Schlenk line through which a continuous slow flow of ~1 atm of argon was maintained (oil bubbler at the exit).

Safety notes. The procedures detailed in this paper utilize very aggressive reagents, such as Br_2, SO_2Cl_2, and $SbCl_5$. These must be handled with extreme care and only in a functioning fume hood. Note that all of three of these compounds generate vapors of high density that may escape from the fume hood if released close to the sash. It is strongly recommended that they be handled well inside the fume hood. The reactions ensuing upon addition of neat bromine,

SO_2Cl_2, or $SbCl_5$ to $Cs[HCB_{11}H_{11}]$ are quite violent, and proceed with rapid evolution of gaseous by-products. In our hands, these additions were performed safely and without incident, but we urge nonetheless urge caution. We suggest that they be practiced on a small scale first.

Notes on the labeling in the mass spectra. In all spectra, $[HCB_{11}Cl_{11}]^-$ is labelled as Cl11; $[HCB_{11}HCl_{10}]^-$ as Cl10; $[HCB_{11}H_2Cl_9]^-$ as Cl9; $[HCB_{11}H_3Cl_8]^-$ as Cl8; $[HCB_{11}H_4Cl_7]^-$ as Cl7; $[HCB_{11}H_5Cl_6]^-$ as Cl6; $[HCB_{11}H_6Cl_5]^-$ as Cl5; $[HCB_{11}H_7Cl_4]^-$ as Cl4; $[HCB_{11}H_8Cl_3]^-$ as Cl3; $[HCB_{11}H_9Cl_2]^-$ as Cl2; $[HCB_{11}Cl_{10}OH]^-$ as Cl10OH; $[HCB_{11}Cl_{10}OSiMe_3]^-$ as Cl10OSiMe$_3$; $[HCB_{11}H_8Br_3]^-$ as Br3; $[HCB_{11}H_7Br_4]^-$ as Br4; $[HCB_{11}H_6Br_5]^-$ as Br5; $[HCB_{11}H_5Br_6]^-$ as Br6; $[HCB_{11}H_4Br_7]^-$ as Br7; $[HCB_{11}Br_{10}]^-$ as Br10; $[HCB_{11}Br_{11}]^-$ as Br11; $[HCB_{11}Br_{10}Cl]^-$ as Br10Cl.

Synthesis of $Me_3NH[HCB_{11}Cl_{11}]$ with $SbCl_5$ (1 g scale). A solution of $Cs[HCB_{11}H_{11}]$ (1.05 g, 3.8 mmol) in $SbCl_5$ (10 mL, 79 mmol) in a Schlenk flask was heated to reflux at 140 ^{o}C for 3 d. After removal of most of the volatiles, the residue was dissolved in 10% aq. NaOH, passed through Celite and then neutralized by dilute HCl solution. Treatment of the resultant solution with 0.5 g of Me_3NHCl (5.2 mmol) caused formation of a white precipitate. This solid was filtered off, washed with distilled water and dried under vacuum to give $Me_3NH[HCB_{11}Cl_{11}]$. Yield: 1.8 g (81%). ^{11}B NMR (128 MHz, aceotne): δ -1.7 (s, 1B), -9.1 (s, 5B), -12.2 (s, 5B). ^{1}H NMR (300 MHz, acetonitrile-d_3): δ 2.71 (s, 9H, Me_3N), 4.07 (s, 1H, cage C-H). $Me_3NH[HCB_{11}Cl_{11}]$ was recrystallized from acetone before it was sent for elemntal analyses. Less than 0.0167% of Sb was detected by elemental analysis. (Fig. S1 & S2)

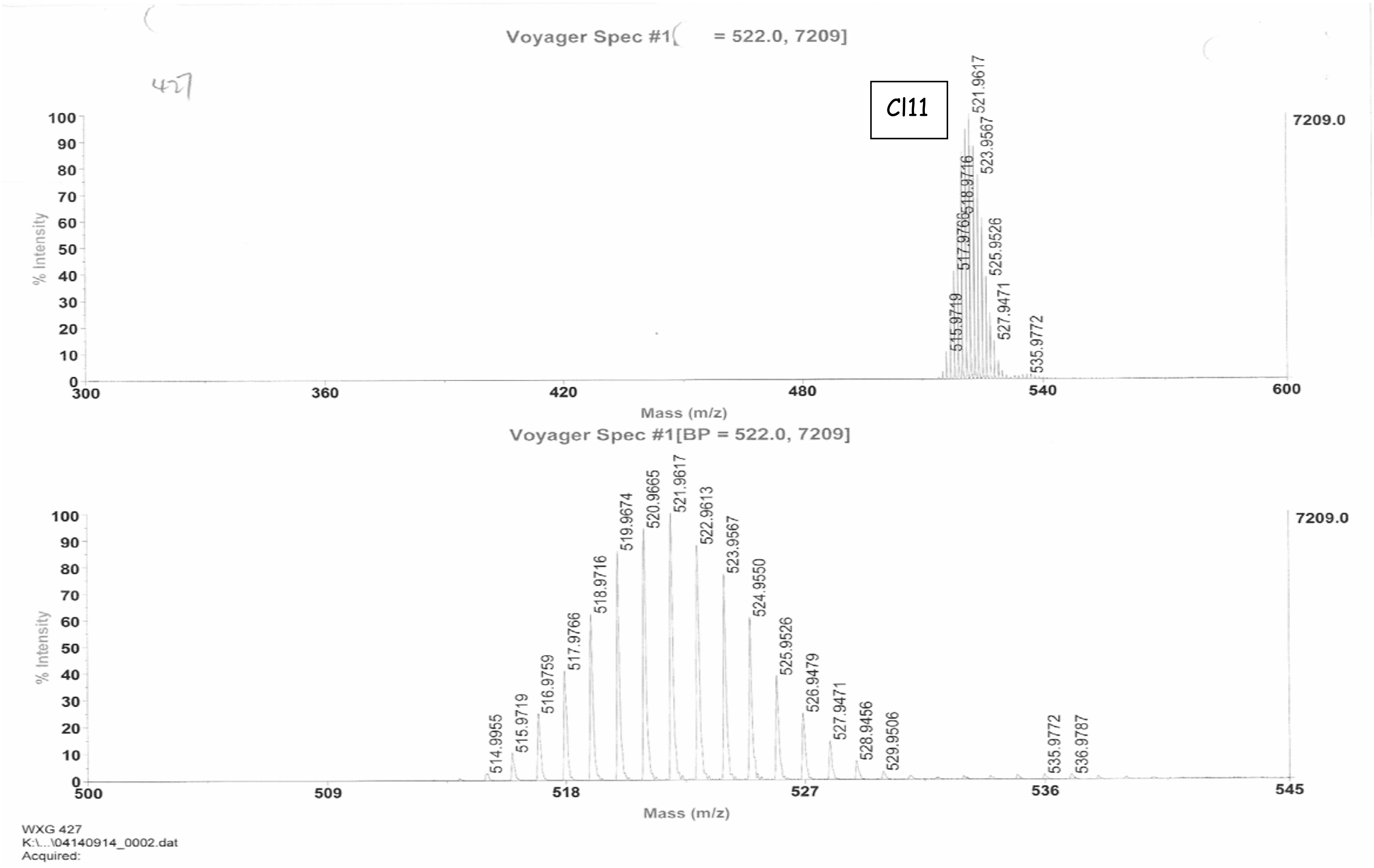


Figure S1. MALDI MS spectrum for the reaction with $SbCl_5$ at 1 g scale.

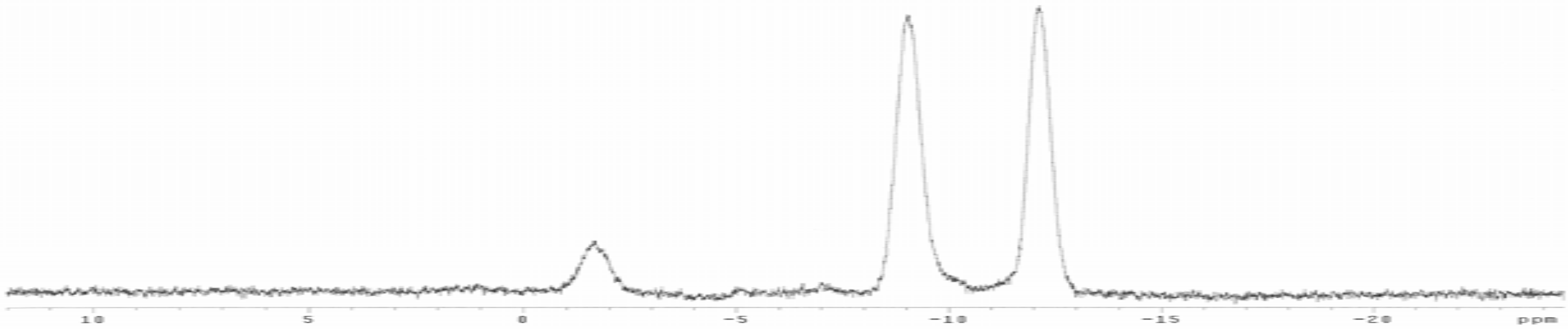


Figure S2. ^{11}B NMR spectrum of the $Me_3NH[HCB_{11}Cl_{11}]$ product from the reaction with $SbCl_5$ at 1 g scale.

Reaction of mixtures of partially chlorinated carborane anions with $SbCl_5$. A solution of $CsHCB_{11}H_xCl_{11-x}$ (130 mg, 0.23 mmol, x= 0~6, avg. ≈ 2.5 by MS; this material was obtained from a reaction of parent carborane with SO_2Cl_2 without Ar protection) in $SbCl_5$ (0.8 mL, 6.3 mmol) in a Schlenk flask was heated to reflux at 140 ^{o}C for 1 d. After removal of most of the volatiles, the residue was dissolved in 10% aq. NaOH, passed through Celite and then neutralized by dilute HCl solution. Treatment of the resultant solution with 0.1 g of Me_3NHCl (1.1 mmol) caused formation of a white precipitate. This solid was filtered off, washed with distilled water and dried under vacuum to give 125 mg (86%) of $Me_3NH[HCB_{11}Cl_{11}]$. (Fig. S3)

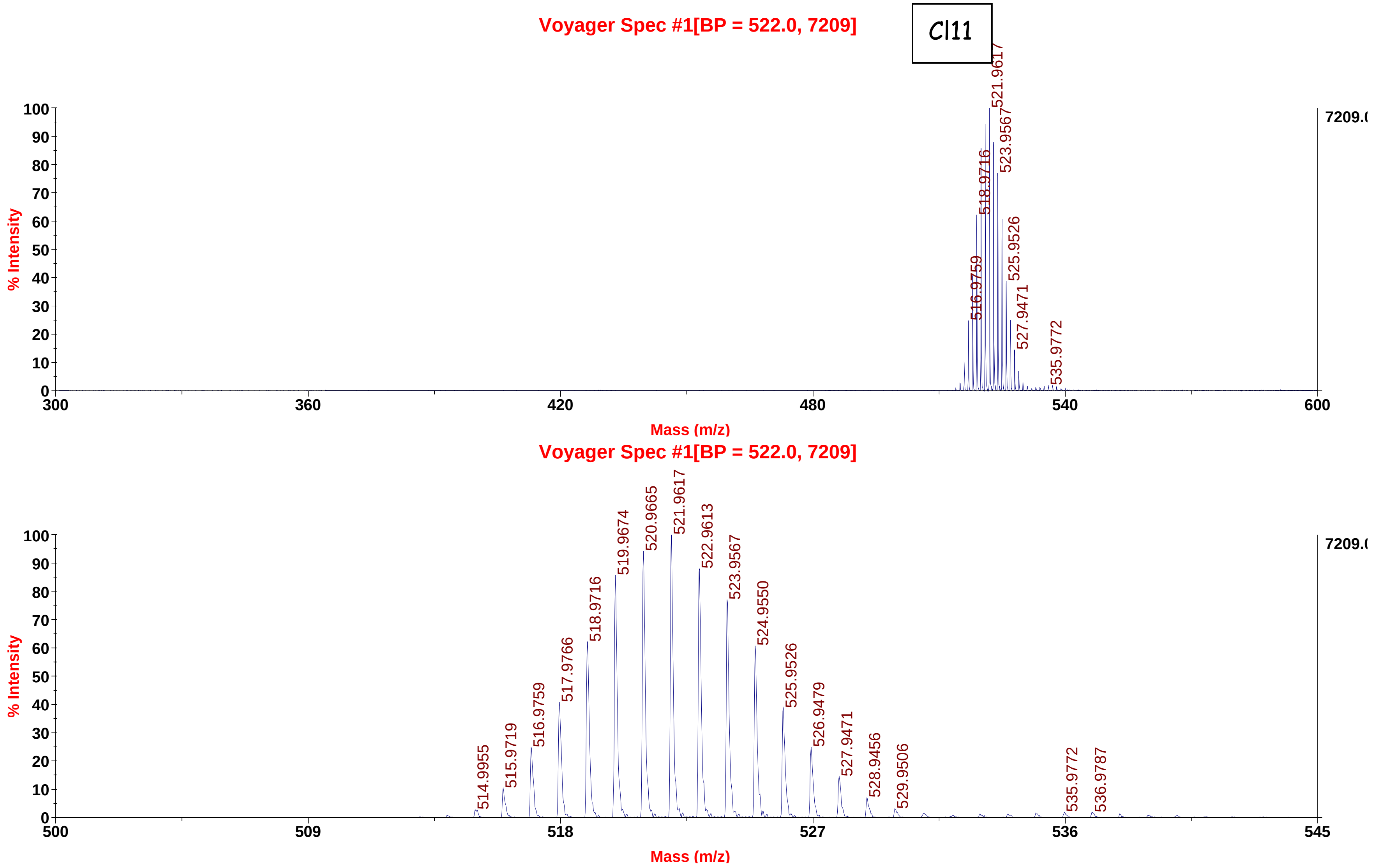


Figure S3. MALDI mass-spectrum for the reaction of mixtures of partially chlorinated carborane with $SbCl_5$.

Reaction of Cs[$HCB_{11}H_{11}$] with $SbCl_5$ (5 g scale). A solution of Cs[$HCB_{11}H_{11}$] (5.09 g, 18.4 mmol) in $SbCl_5$ (50 mL, 395 mmol) in a Schlenk flask was heated to reflux at 140 ^oC for 1 d. After removal of most of the volatiles, the residue was dissolved in 10% aq. NaOH, passed through Celite and then neutralized by dilute HCl solution. Treatment of the resultant solution with 3 g of Me_3NHCl (31 mmol) caused formation of a white precipitate. This solid was filtered off, washed with distilled water and dried under vacuum to give 8.9 g (82%) of Me_3NH[$HCB_{11}Cl_{11}$]. MALDI MS analysis showed two sets of carborane isotopic patterns. One set around 522 corresponds to the $HCB_{11}Cl_{11}$ anion (**Cl11**); another set around 503 corresponds to the $HCB_{11}Cl_{10}OH$ anion (**Cl10OH**). (Fig. S4)

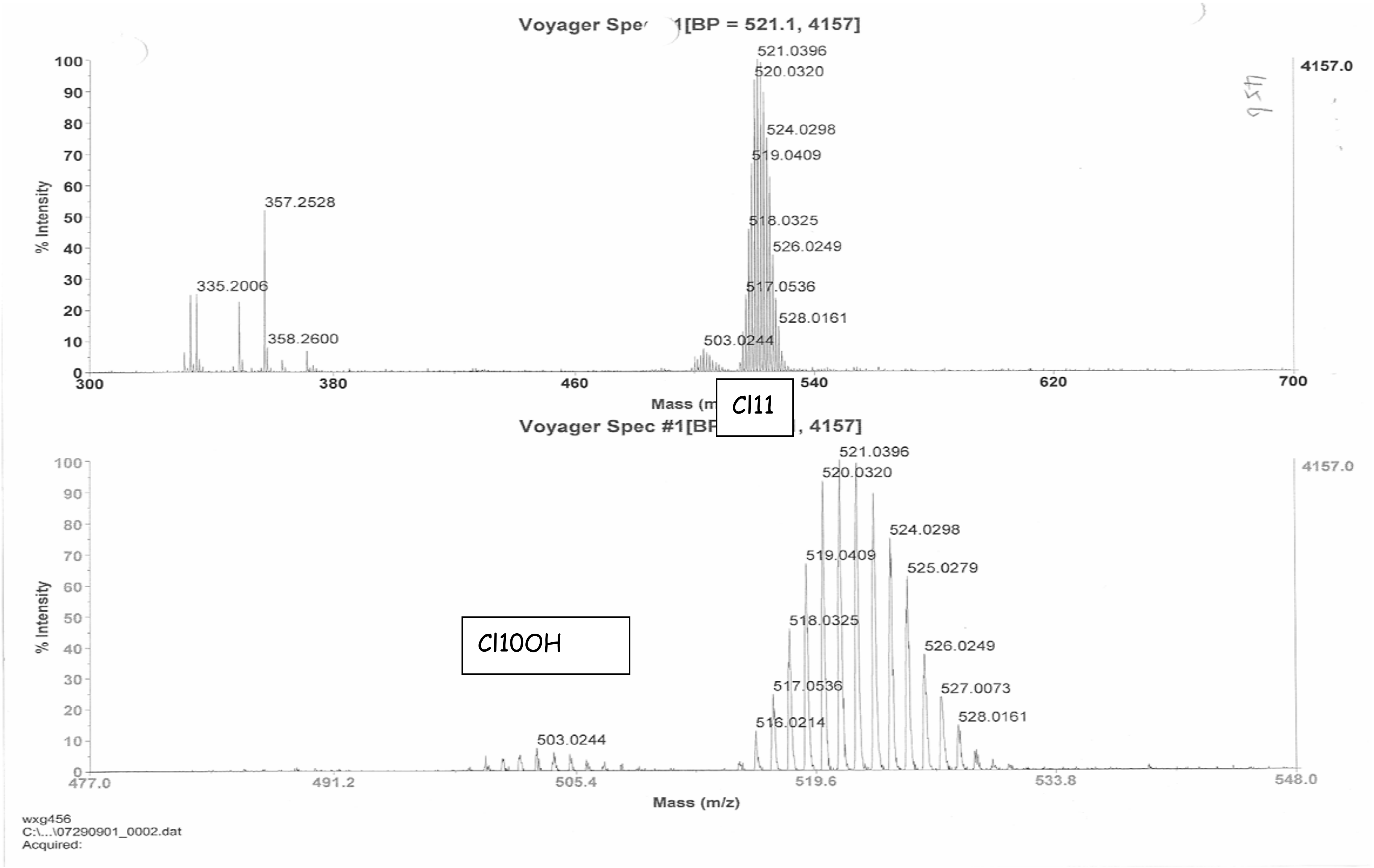


Figure S4. MALDI mass-spectrum for the reaction with $SbCl_5$ at 5 g scale.

Reaction of a mixture of $Me_3NH[HCB_{11}Cl_{11}]$ and $Me_3NH[HCB_{11}Cl_{10}OH]$ with hexamethyldisilazane. A CH_2Cl_2 solution of a mixture of $Me_3NH[HCB_{11}Cl_{11}]$ and $Me_3NH[HCB_{11}Cl_{10}OH]$ (110 mg, est. 0.22 mmol; obtained from a reaction of $Cs[HCB_{11}H_{11}]$ with $SbCl_5$ as described above) was treated with hexamethyldisilazane (500 μL, 2.4 mmol) and heated to reflux in a Schlenk flask for 24 h. Removal of the volatiles gave a white solid which was analyzed by MALDI MS. MS spectra showed three sets of signals with the carborane isotopic pattern. The set around 522 corresponds to the $HCB_{11}Cl_{11}$ anion (**Cl11**); the set around 487 corresponds to the $HCB_{11}Cl_{10}OH$ anion (**Cl10**); and a new set around 575 corresponds to the $HCB_{11}Cl_{10}OSiMe_3$ anion (**Cl10OSiMe$_3$**). (Fig. S5)

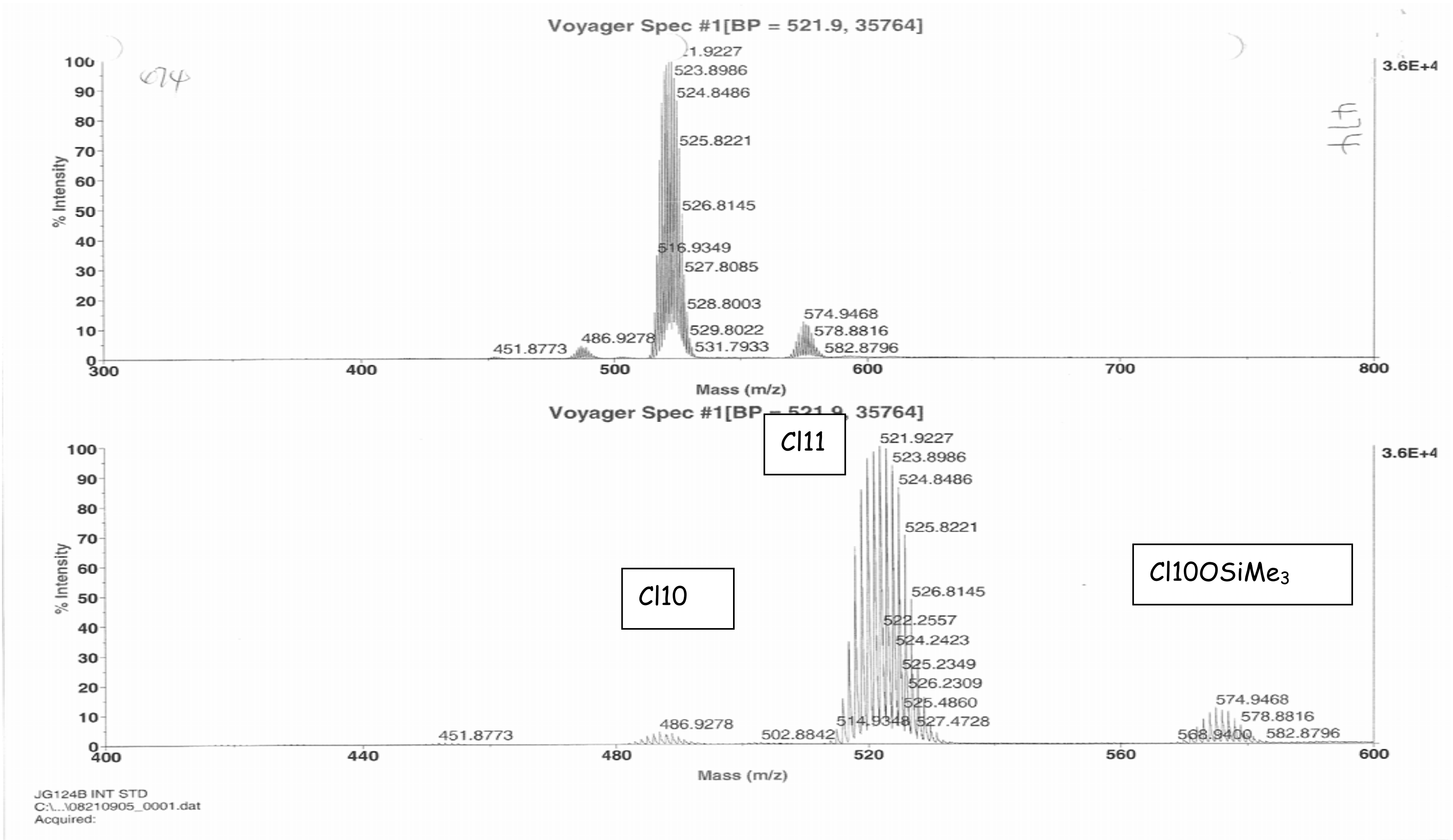


Figure S5. MALDI mass-spectrum for the reaction mixture of $Me_3NH[HCB_{11}Cl_{11}]$ and $Me_3NH[HCB_{11}Cl_{10}OH]$ with hexamethyldisilazane.

Reaction of Cs[$HCB_{11}H_{11}$] with $SbCl_5$ with added H_2O. A solution of Cs[$HCB_{11}H_{11}$] (100 g, 0.36 mmol) in $SbCl_5$ (1 mL, 8 mmol) with added H_2O (30 μL, 1.7 mmol) in a Schlenk flask was heated to reflux at 140 ^{o}C for 1 d. After removal of the volatiles, the residue was dissolved in 10% aq. NaOH, passed through Celite and then neutralized by dilute HCl solution. Treatment of the resultant solution with 0.1 g of Me_3NHCl (1.1 mmol) caused formation of a white precipitate. This solid was filtered off, washed with distilled water and dried under vacuum to give 150 mg of a solid. MALDI MS analysis showed two sets of carborane isotopic patterns. One set around 522 corresponds to the $HCB_{11}Cl_{11}$ anion (**Cl11**); another set around 503 corresponds to the $HCB_{11}Cl_{10}OH$ anion (**Cl10OH**). (Fig. S6)

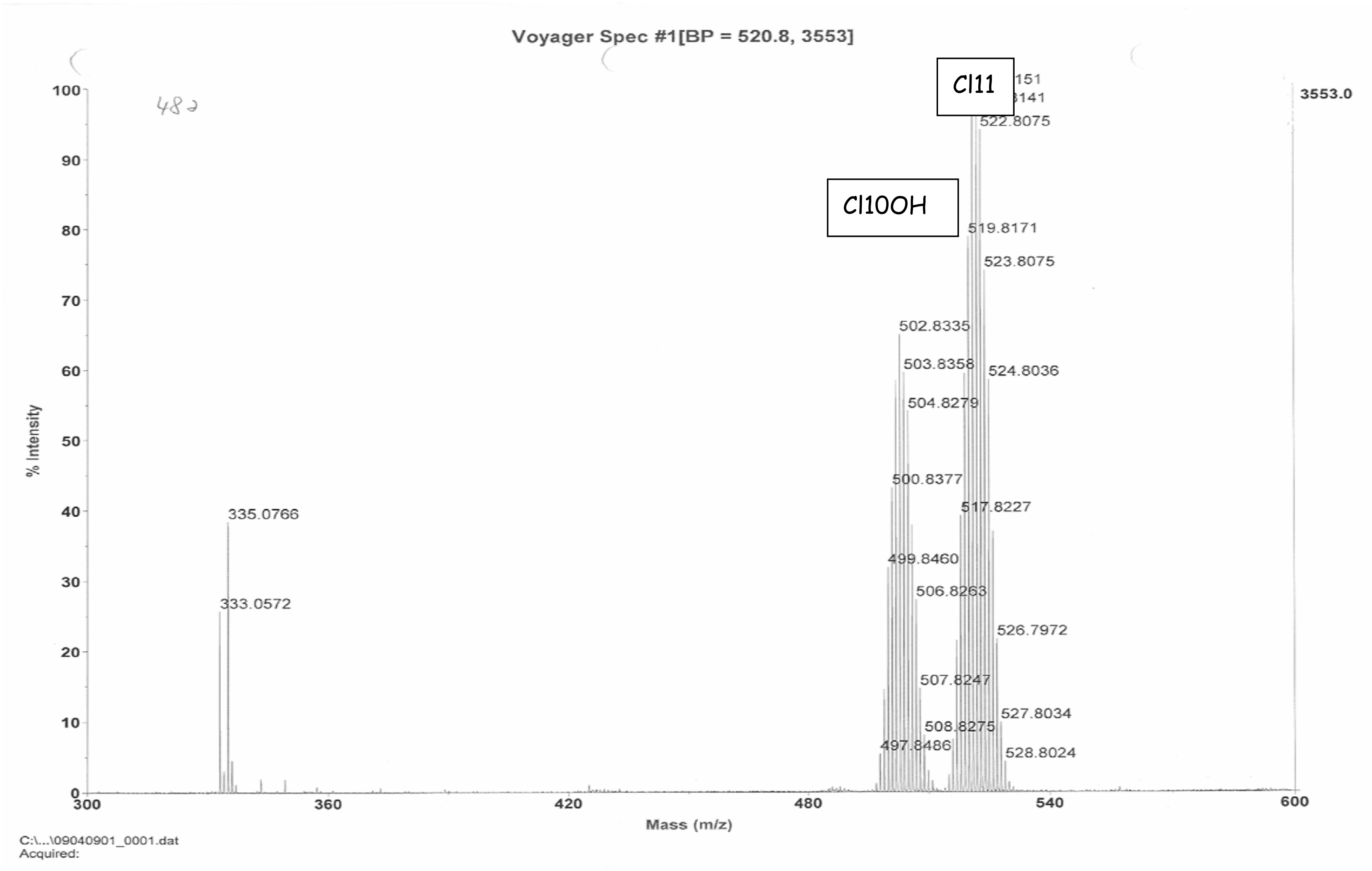


Figure S6. MALDI mass-spectrum for the reaction with $SbCl_5$ and H_2O.

Reaction of mixture of $Me_3NH[HCB_{11}Cl_{11}]$ and $Me_3NH[HCB_{11}Cl_{10}OH]$ with SO_2Cl_2. A solution of a mixture of $Me_3NH[HCB_{11}Cl_{11}]$ and $Me_3NH[HCB_{11}Cl_{10}OH]$ (220 mg, est. 0.44 mmol; obtained from a reaction of $Cs[HCB_{11}H_{11}]$ with $SbCl_5$ as described above) in SO_2Cl_2 (1.0 mL, 12.4 mmol) was heated to reflux at 80 °C in a Schlenk flask for 24 h. Removal of the volatiles gave a white solid (220 mg) which was analyzed by MALDI MS. MS spectra showed only one set of signals with a carborane pattern around 522 which corresponds to the $HCB_{11}Cl_{11}$ anion (**Cl11**). (Fig. S7)

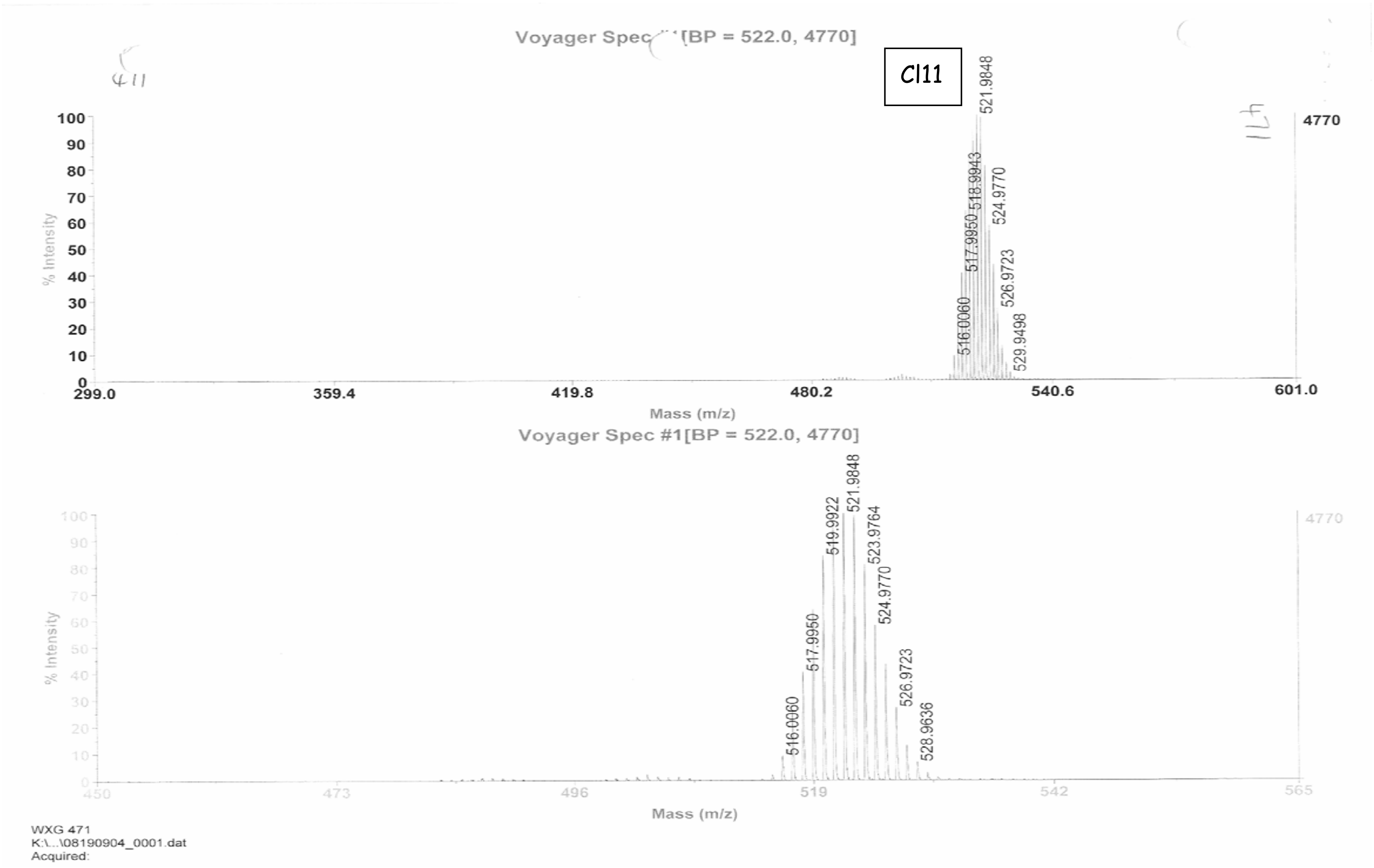


Figure S7. MALDI mass-spectrum for the reaction mixture of $Me_3NH[HCB_{11}Cl_{11}]$ and $Me_3NH[HCB_{11}Cl_{10}OH]$ with SO_2Cl_2.

Reaction of mixture of $Me_3NH[HCB_{11}Cl_{11}]$ and $Me_3NH[HCB_{11}Cl_{10}OH]$ with $SbCl_5$. A solution of a mixture of $Me_3NH[HCB_{11}Cl_{11}]$ and $Me_3NH[HCB_{11}Cl_{10}OH]$ (207 mg, est. 0.41 mmol; obtained from a reaction of $Cs[HCB_{11}H_{11}]$ with $SbCl_5$ as described above) in $SbCl_5$ (0.5 mL, 4 mmol) was heated to reflux at 140 ^{o}C in a Schlenk flask for 24 h. After removal of the volatiles, the residue was dissolved in 10% aq. NaOH, passed through Celite and then neutralized by dilute HCl solution. Treatment of the resultant solution with 0.1 g of Me_3NHCl (1.1 mmol) caused formation of a white precipitate. This solid was filtered off, washed with distilled water and dried under vacuum to give 175 mg of a solid. MALDI MS analysis showed only one set of signals with a carborane pattern around 522 which corresponds to the $HCB_{11}Cl_{11}$ anion (**Cl11**). (Fig. S8)

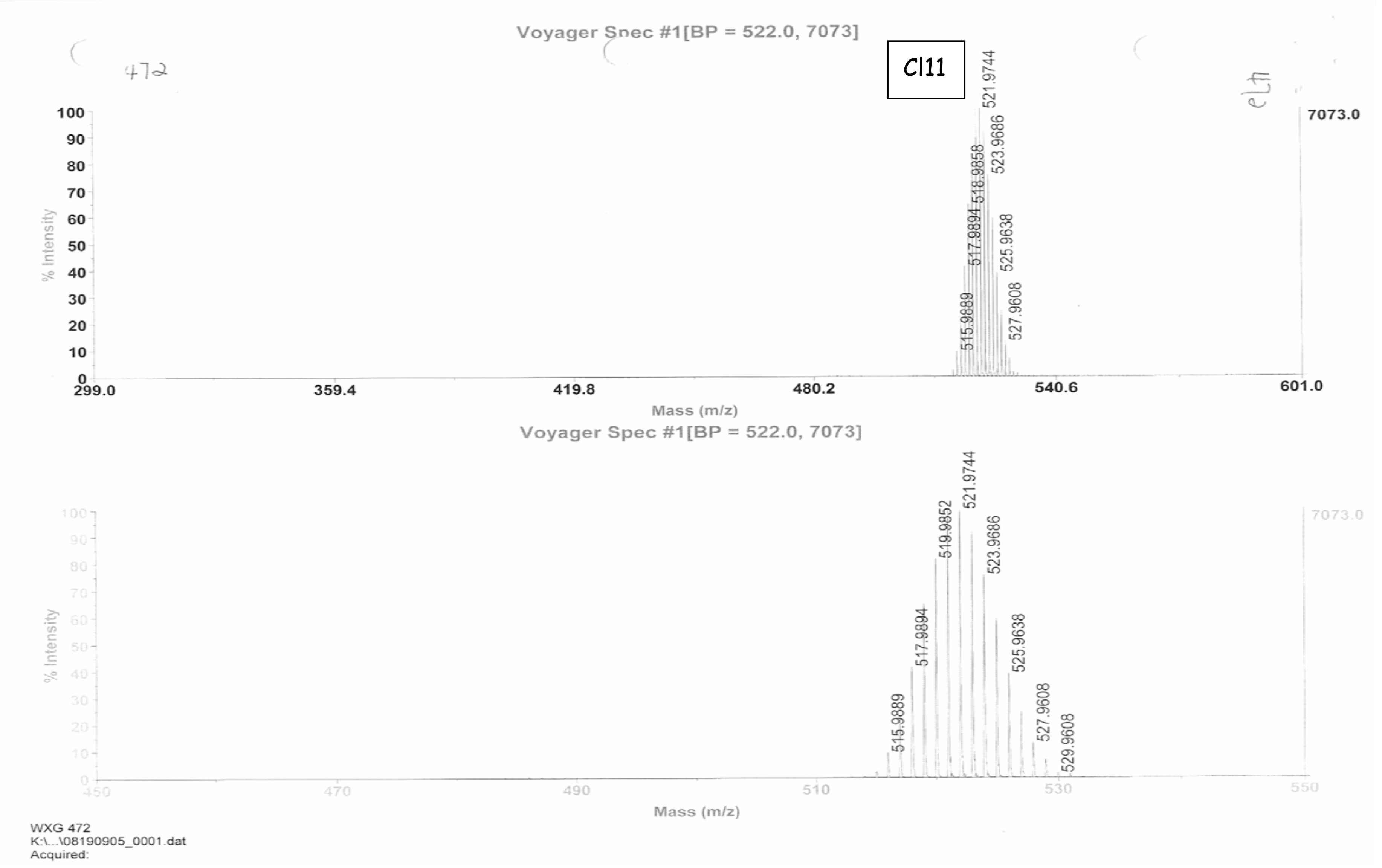


Figure S8. MALDI mass-spectrum for the reaction mixture of $Me_3NH[HCB_{11}Cl_{11}]$ and $Me_3NH[HCB_{11}Cl_{10}OH]$ with $SbCl_5$.

Reaction of Cs[$HCB_{11}H_{11}$] with SO_2Cl_2 at ambient temperature without Ar protection. A solution of Cs[$HCB_{11}H_{11}$] (120 mg, 0.43 mmol) in SO_2Cl_2 (8.0 mL, 100 mmol) in a Schlenk flask was stirred at room temperature for 24 h. Aliquot were taken after 1, 2, 3, 4, 5, 6, 8, and 24 h and analyzed by MALDI MS which indicated mixtures of partially chlorinated carboranes. (Fig. S9-S16))

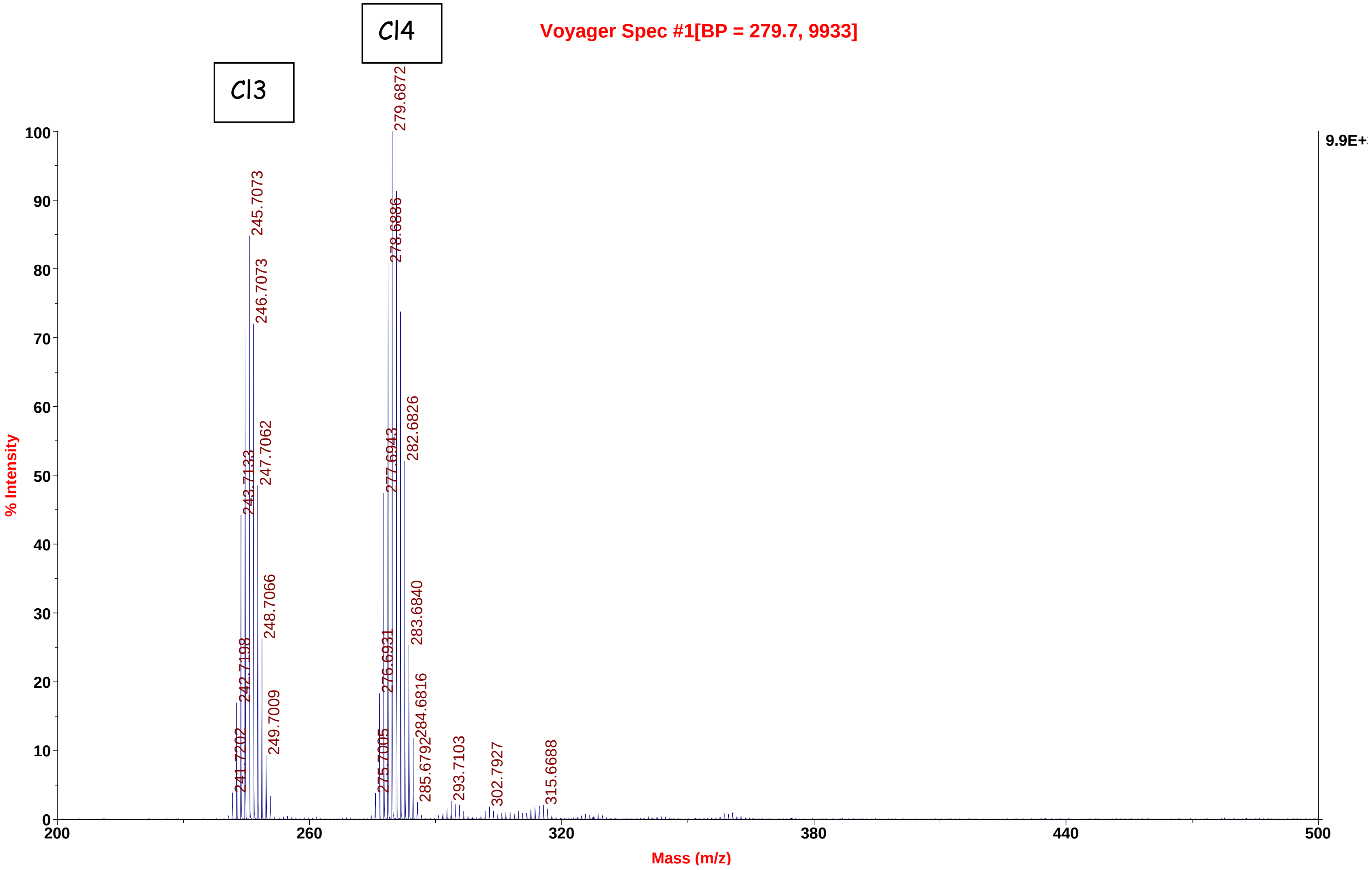


Figure S9. MALDI mass-spectrum for the reaction with SO_2Cl_2 at ambient temperature without Ar protection for 1 h.

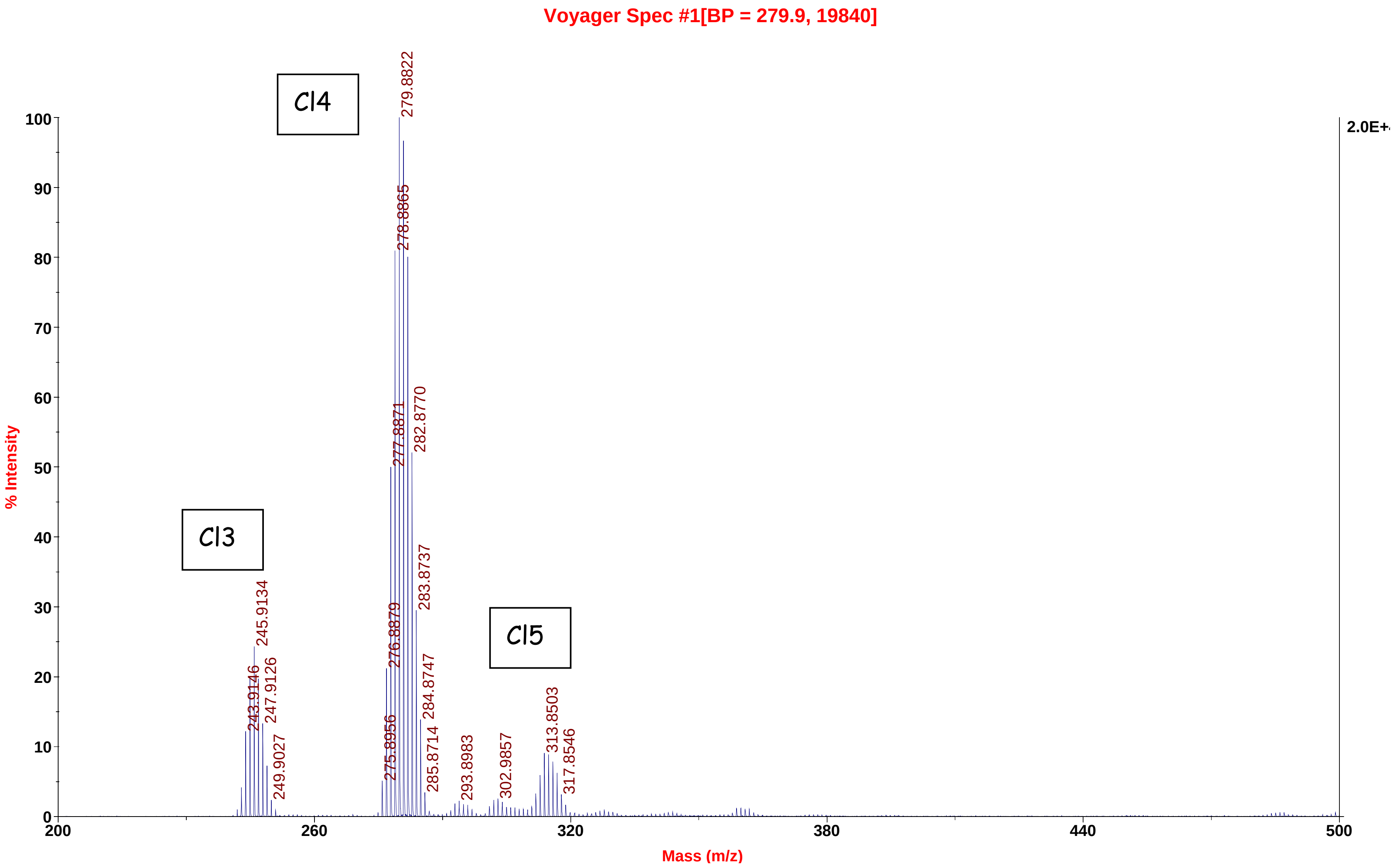


Figure S10. MALDI mass-spectrum for the reaction with SO_2Cl_2 at ambient temperature without Ar protection for 2 h.

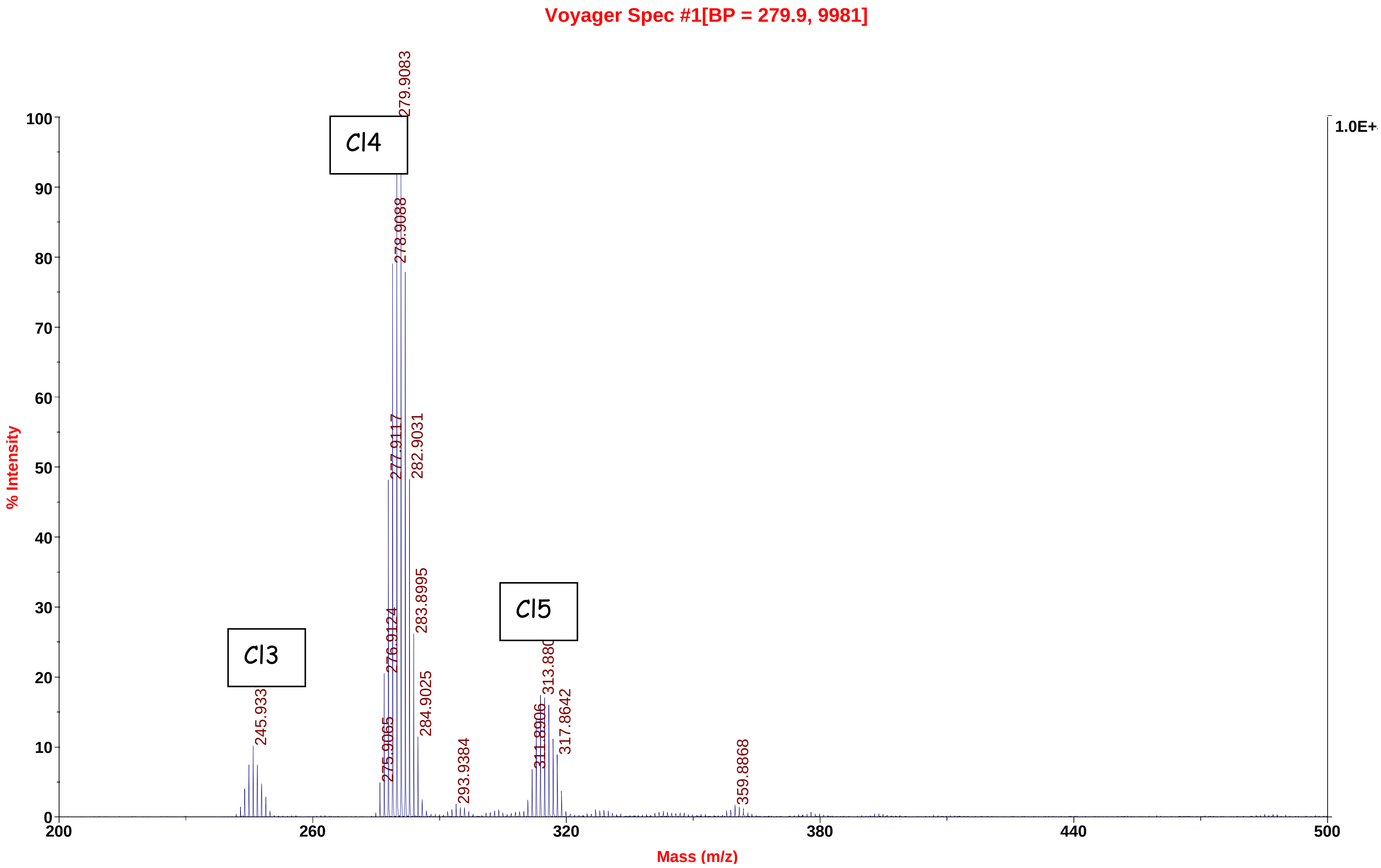


Figure S11. MALDI mass-spectrum for the reaction with SO_2Cl_2 at ambient temperature without Ar protection for 3 h.

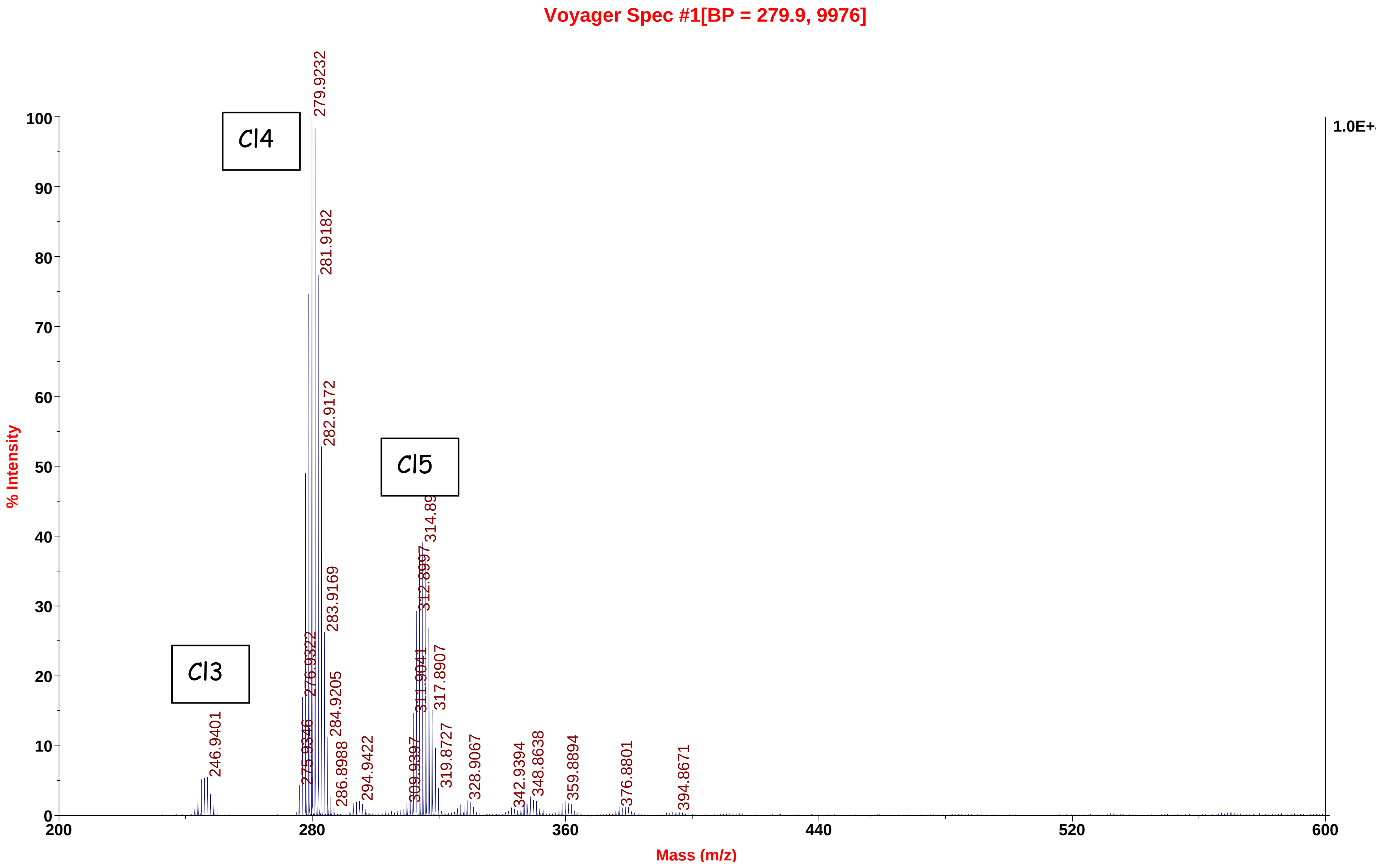


Figure S12. MALDI mass-spectrum for the reaction with SO_2Cl_2 at ambient temperature without Ar protection for 4 h.

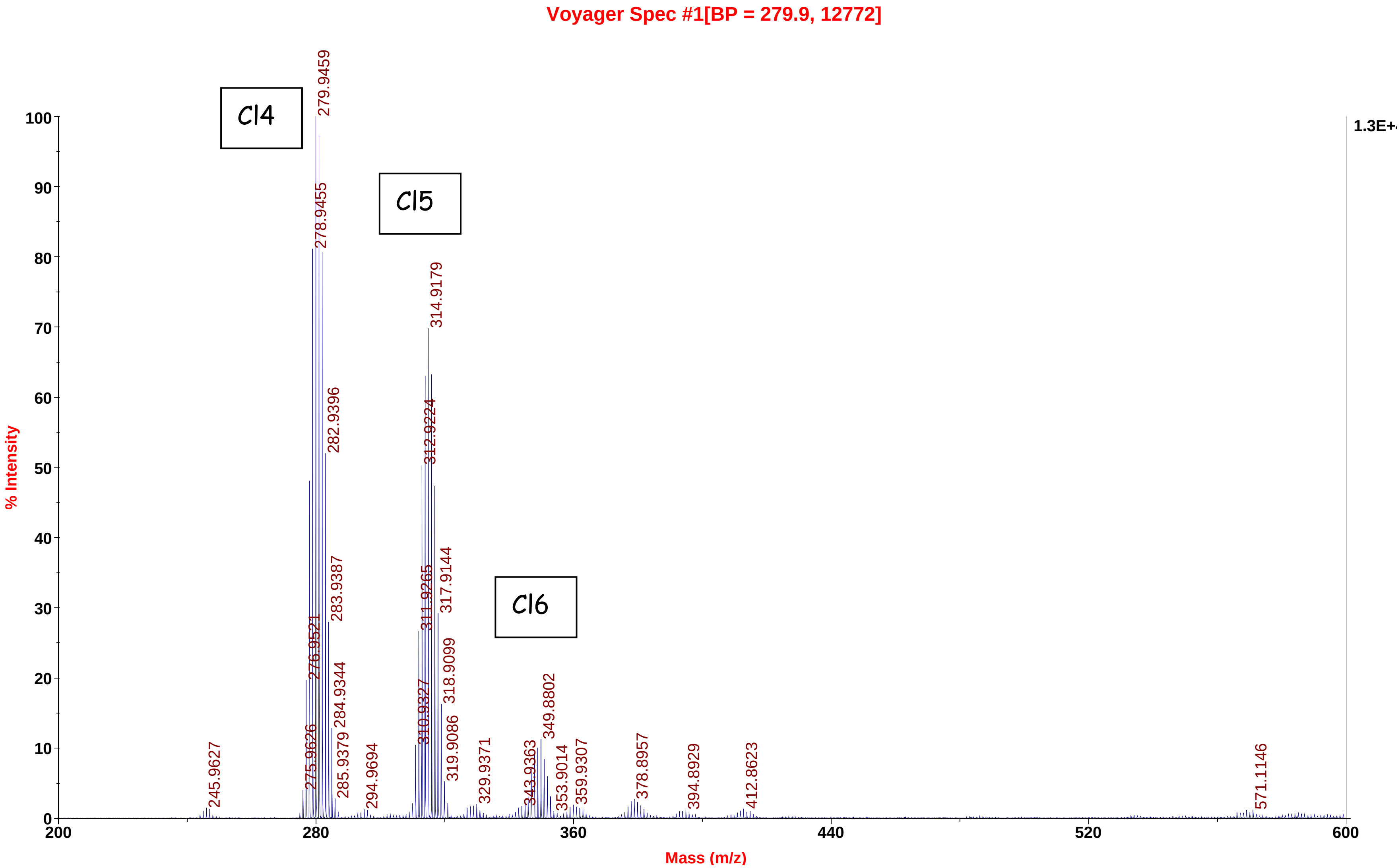


Figure S13. MALDI mass-spectrum for the reaction with SO_2Cl_2 at ambient temperature without Ar protection for 5 h.

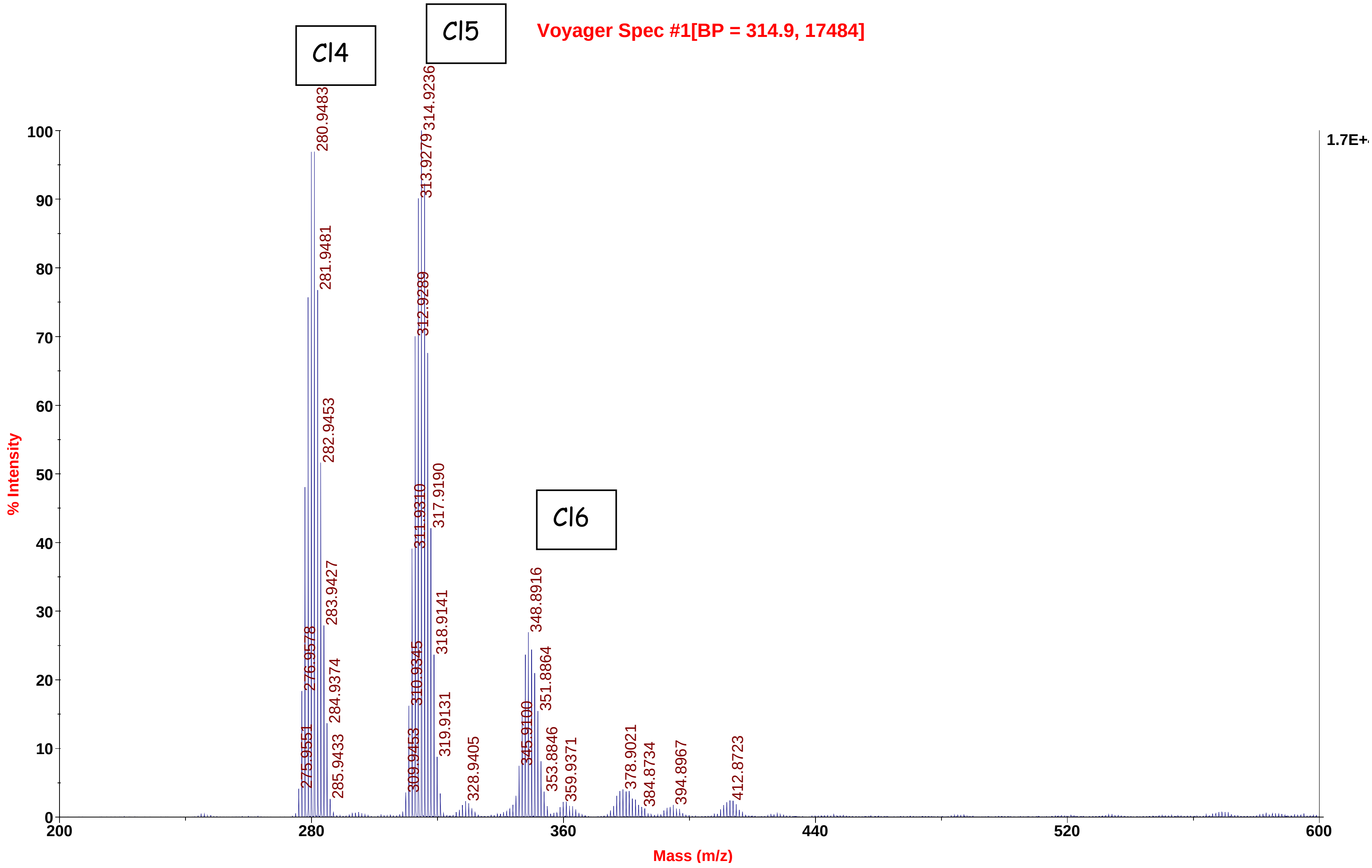


Figure S14. MALDI mass-spectrum for the reaction with SO_2Cl_2 at ambient temperature without Ar protection for 6 h.

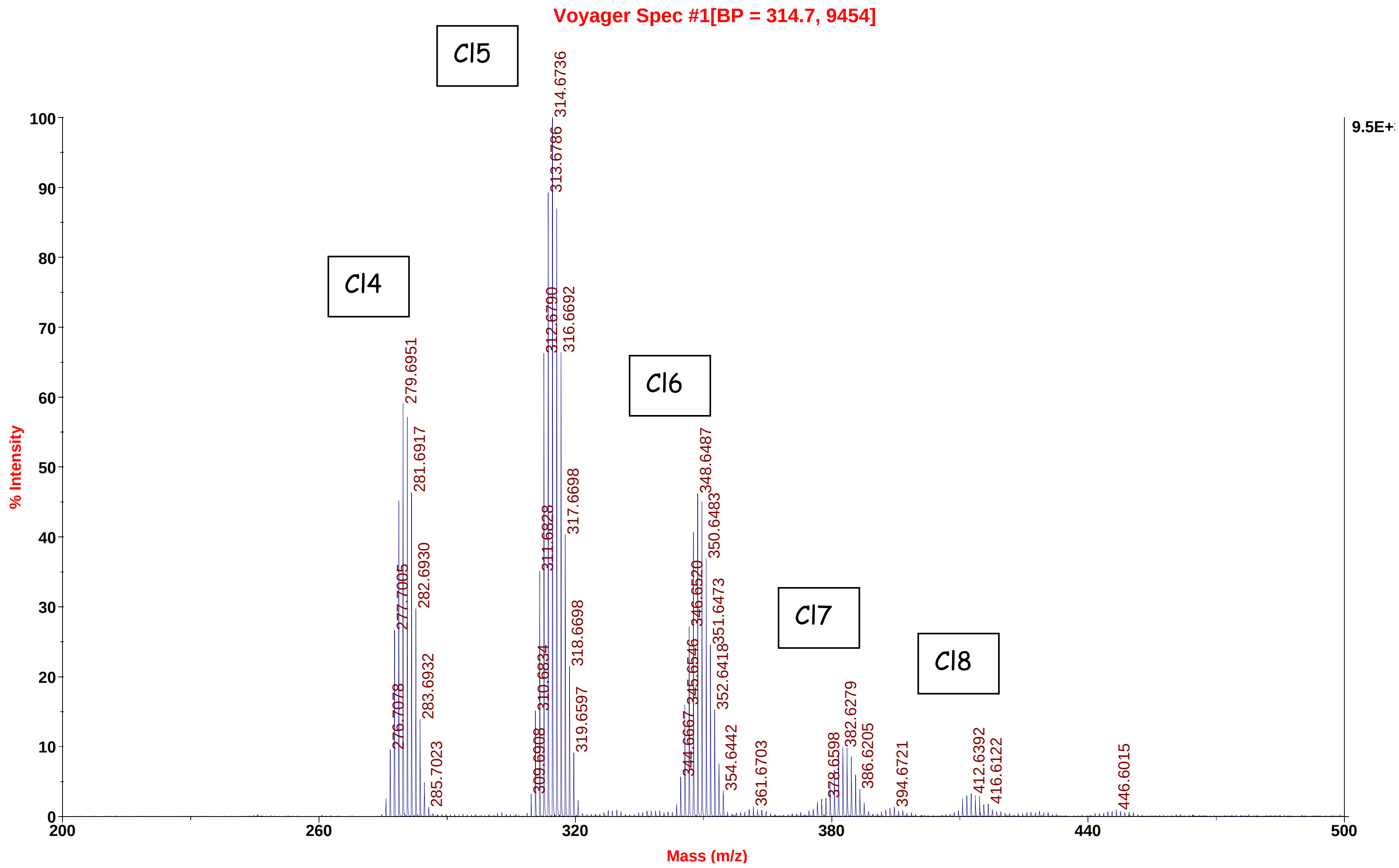


Figure S15. MALDI mass-spectrum for the reaction with SO_2Cl_2 at ambient temperature without Ar protection for 8 h.

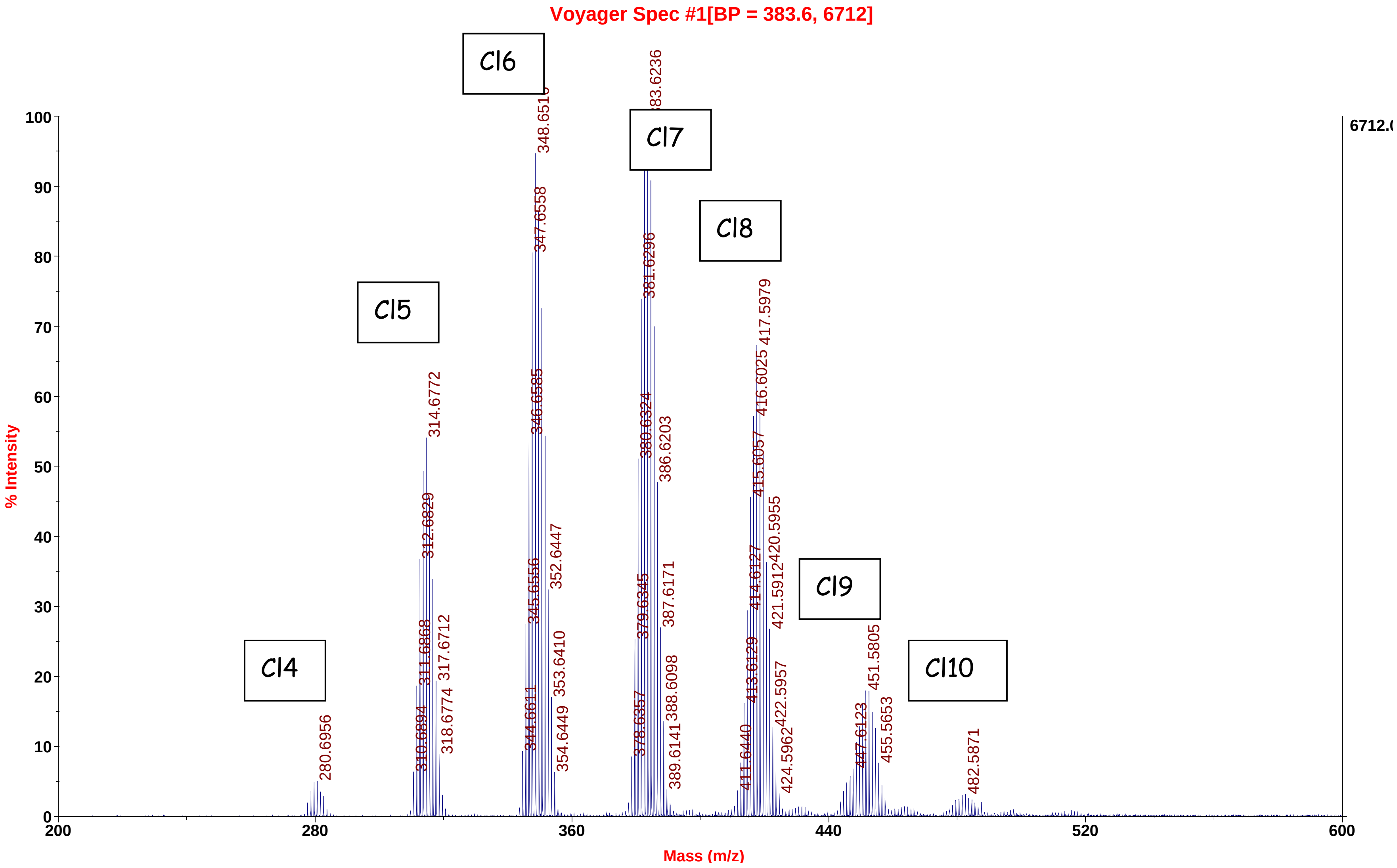


Figure S16. MALDI mass-spectrum for the reaction with SO_2Cl_2 at ambient temperature without Ar protection for 24 h.

Reaction of Cs[$HCB_{11}H_{11}$] with SO_2Cl_2 at refluxing temperature without Ar protection. A solution of Cs[$HCB_{11}H_{11}$] (1.03 g, 3.71 mmol) in SO_2Cl_2 (50 mL, 620 mmol) in a Schlenk flask was heated to reflux. After 1 h, formation of white precipitate was observed and an additional 50 mL (620 mmol) of SO_2Cl_2 was added. The mixture was allowed to stir at refluxing temperature for 5 d. An aliquot was taken every day and analyzed by MALDI MS. After 5 days, removal of the volatiles gave a white solid. MALDI MS analysis indicated that this solid is a mixture of octa-, nona-, deca-, and undecachlorocarborane anions. (Fig. S17-S21)

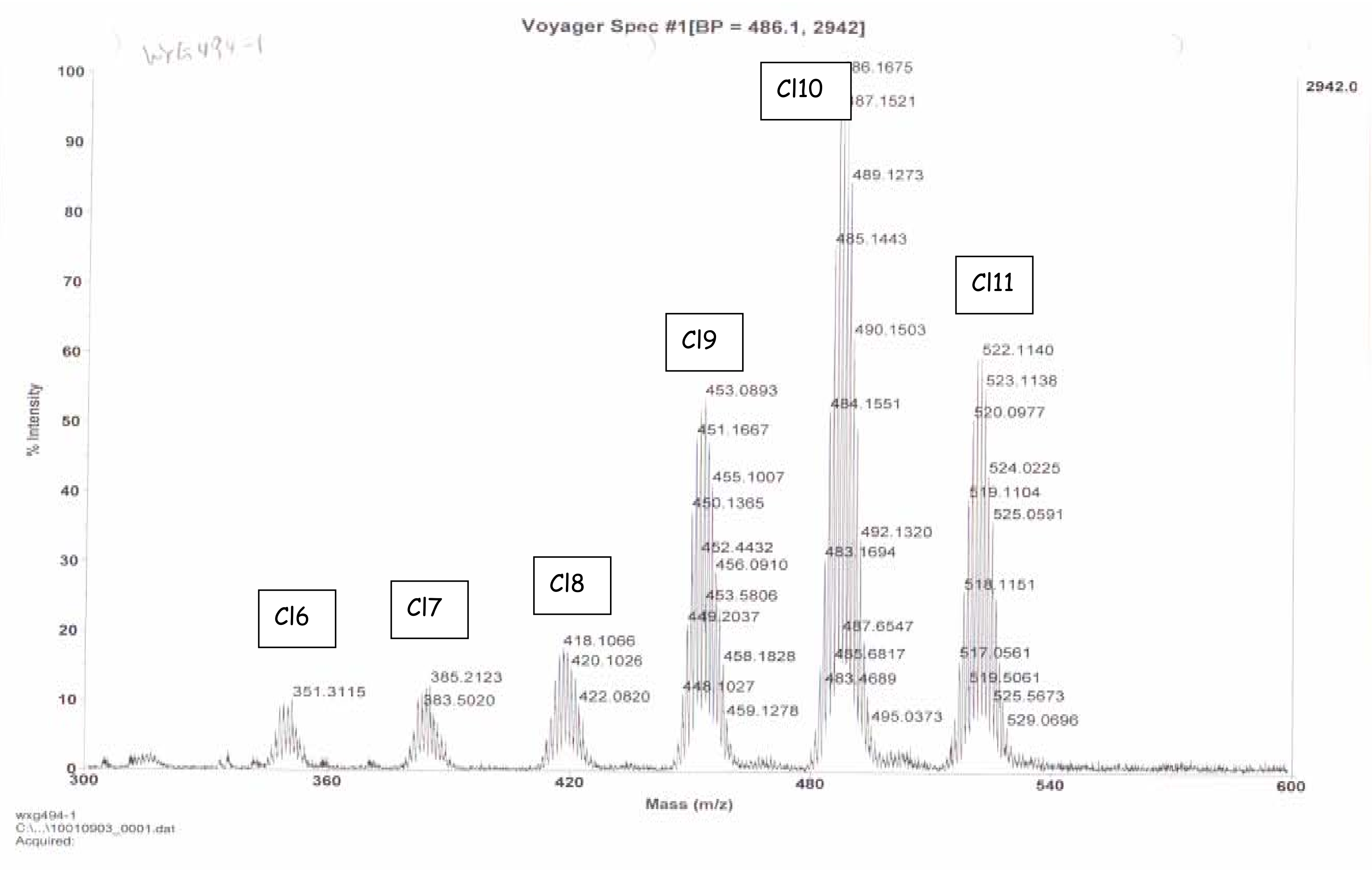


Figure S17. MALDI mass-spectrum for the reaction with SO_2Cl_2 at refluxing temperature without Ar protection for 1 d.

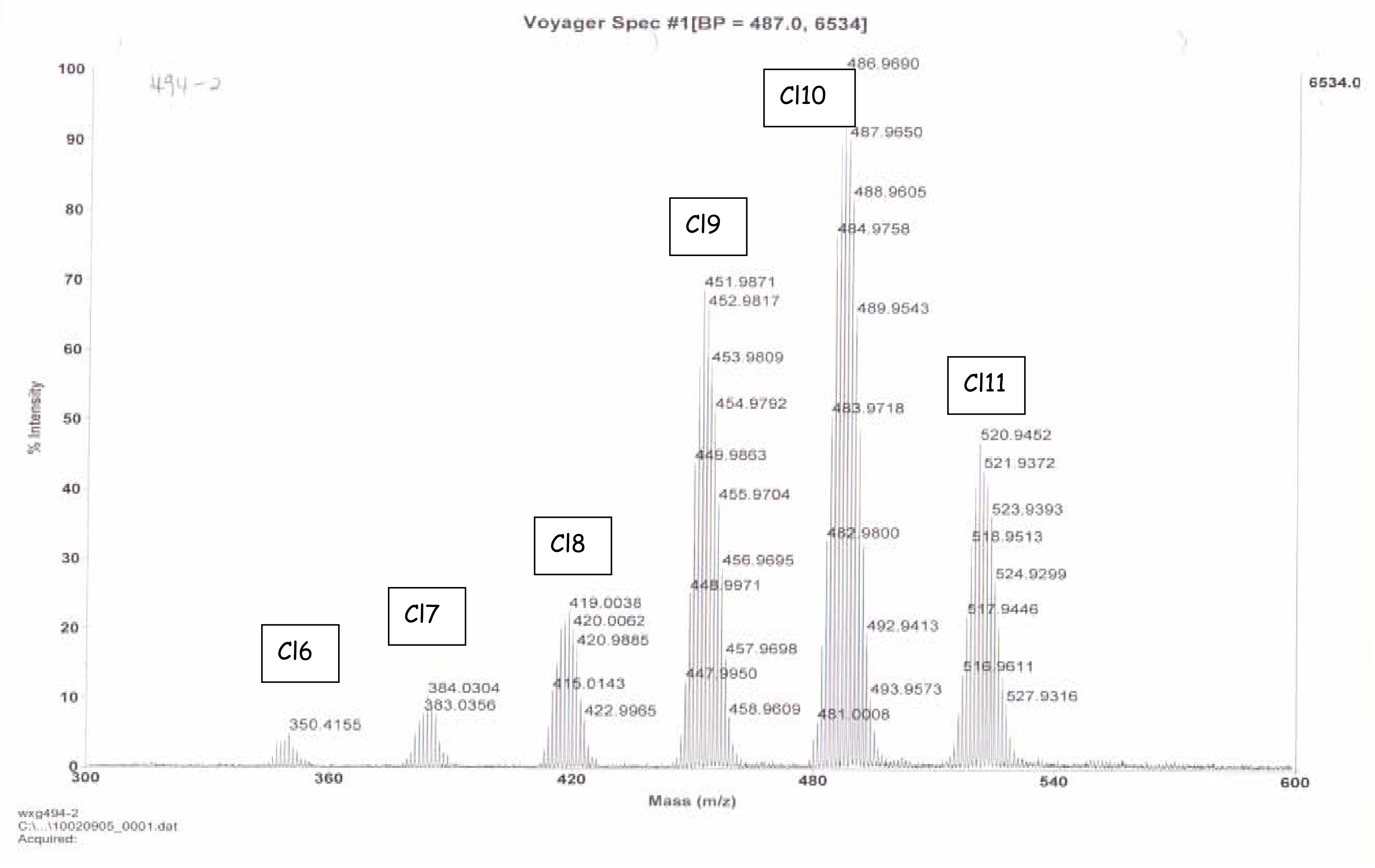


Figure S18. MALDI mass-spectrum for the reaction with SO_2Cl_2 at refluxing temperature without Ar protection for 2 d.

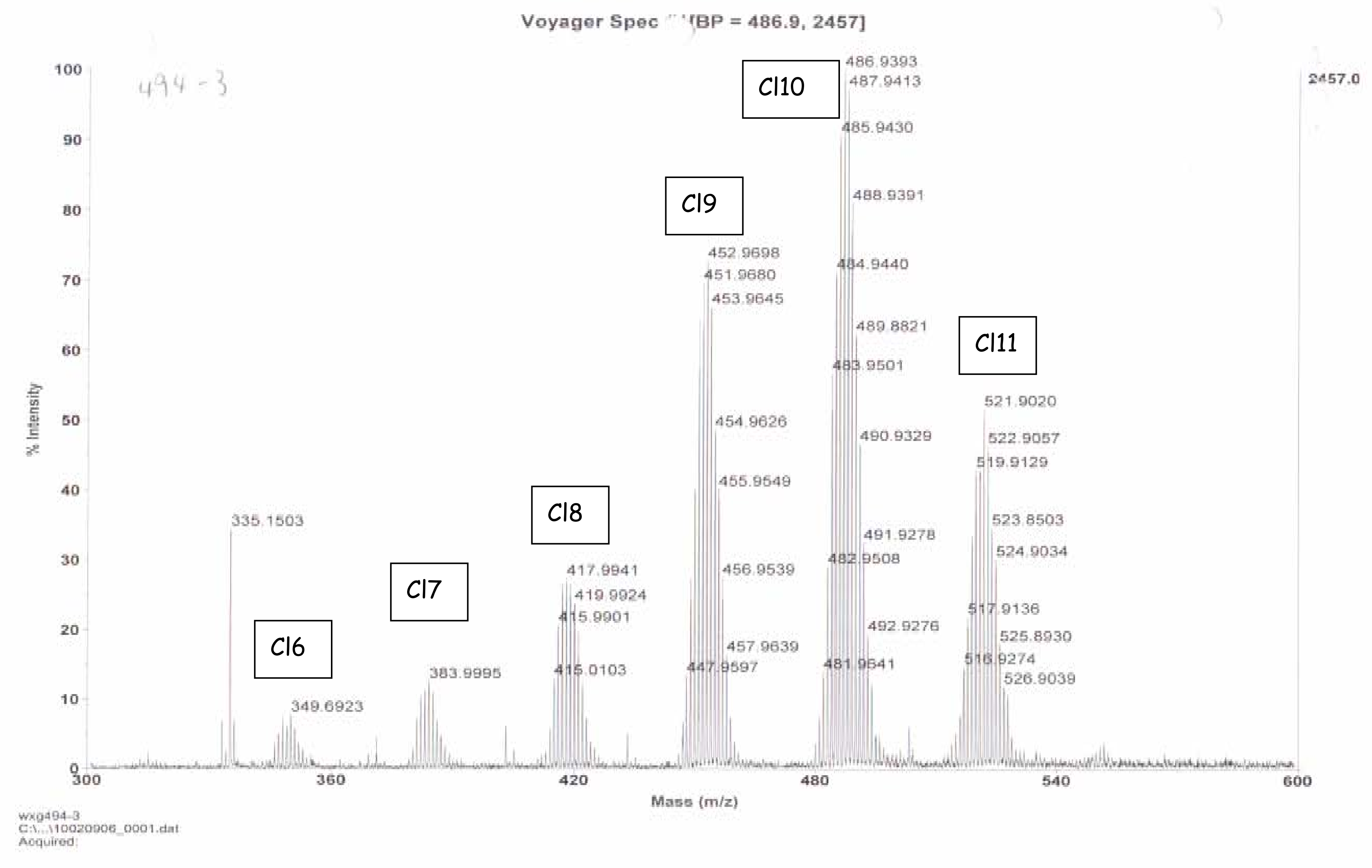


Figure S19. MALDI mass-spectrum for the reaction with SO_2Cl_2 at refluxing temperature without Ar protection for 3 d.

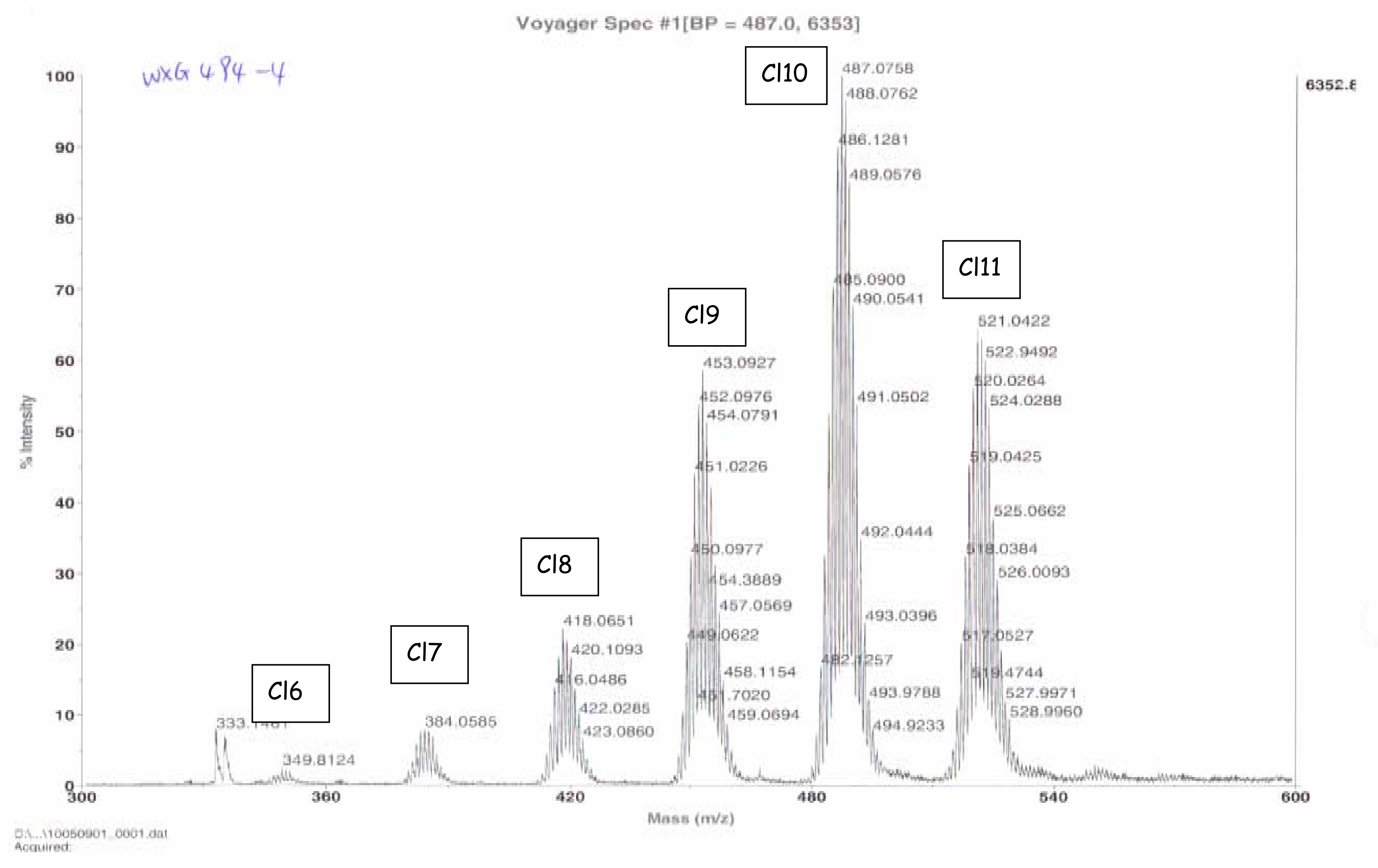


Figure S20. MALDI mass-spectrum for the reaction with SO_2Cl_2 at refluxing temperature without Ar protection for 4 d.

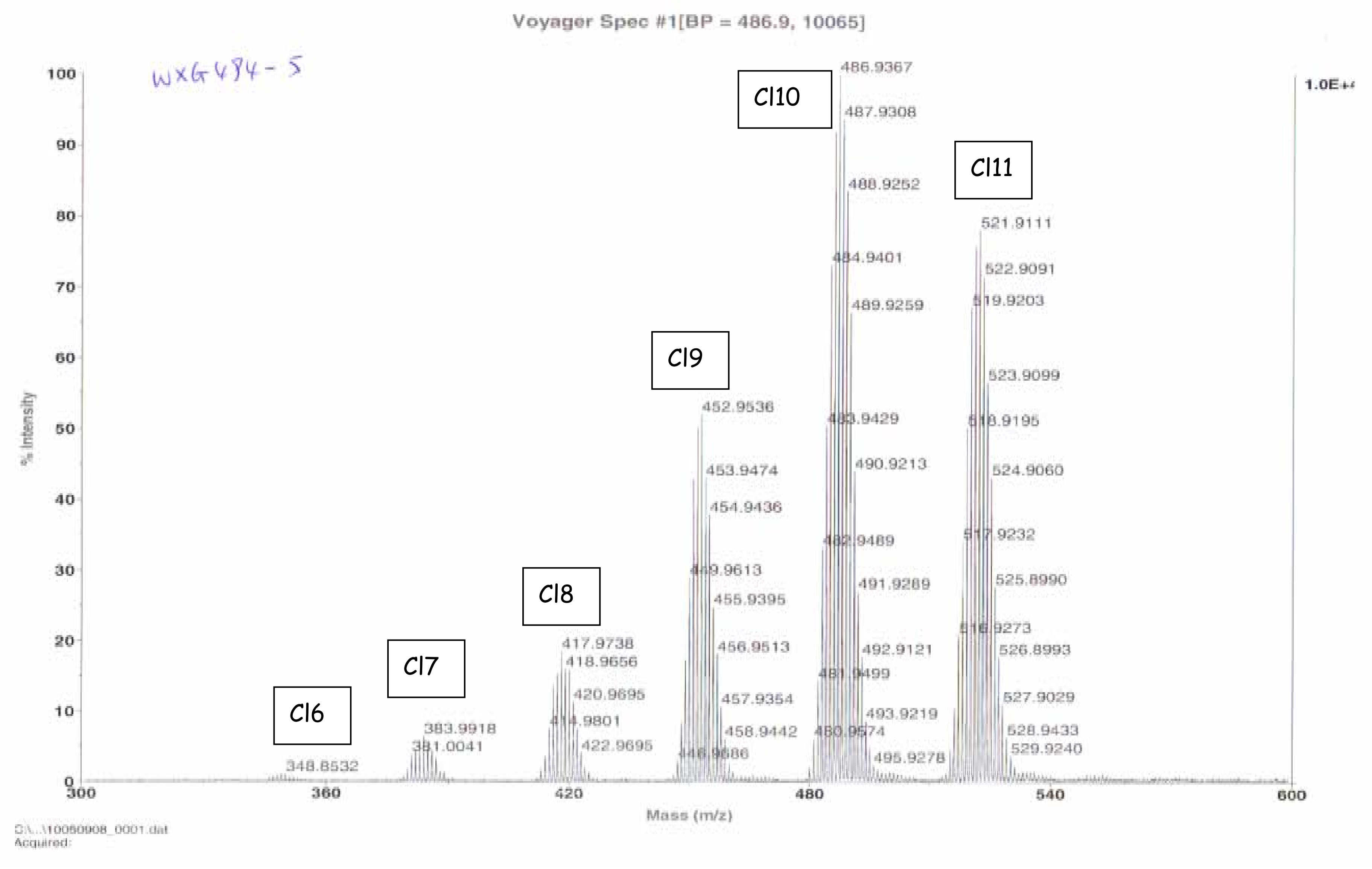


Figure S21. MALDI mass-spectrum for the reaction with SO_2Cl_2 at refluxing temperature without Ar protection for 5 d.

Reactions of Cs[$HCB_{11}H_{11}$] with SO_2Cl_2 and $AlCl_3$ without Ar protection. A solution of Cs[$HCB_{11}H_{11}$] (90 mg, 0.32 mmol) in SO_2Cl_2 (5.0 mL, 62 mmol) with added $AlCl_3$ (0.60 g, 4.5 mmol) in a Schlenk flask was heated to reflux for 3 d. Removal of the volatiles gave a white solid. MS spectra showed the product is a mixture of predominantly nona- and decachlorocarborane anions. (Fig. S22)

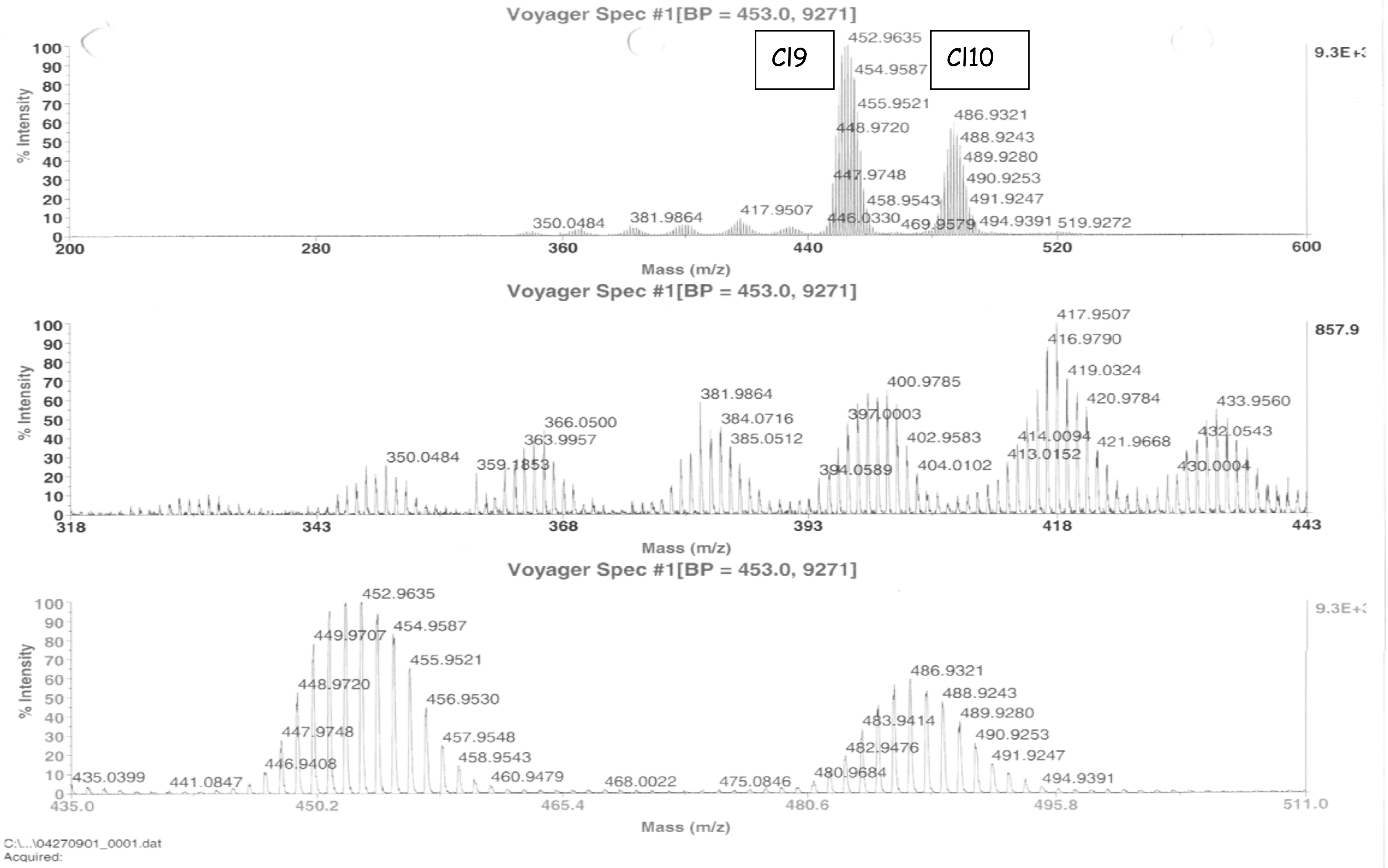


Figure S22. MALDI mass-spectrum for the reaction with SO_2Cl_2 and $AlCl_3$ without Ar protection.

Reactions of Cs[$HCB_{11}H_{11}$] with SO_2Cl_2 and $TiCl_4$ without Ar protection. A solution of Cs[$HCB_{11}H_{11}$] (100 mg, 0.36 mmol) in SO_2Cl_2 (5.0 mL, 62 mmol) with added $TiCl_4$ (3.0 mL, 27 mmol) in a Schlenk flask was heated to reflux for 3 d. Removal of the volatiles gave a white solid which was analyzed by MALDI MS. (Fig. S23)

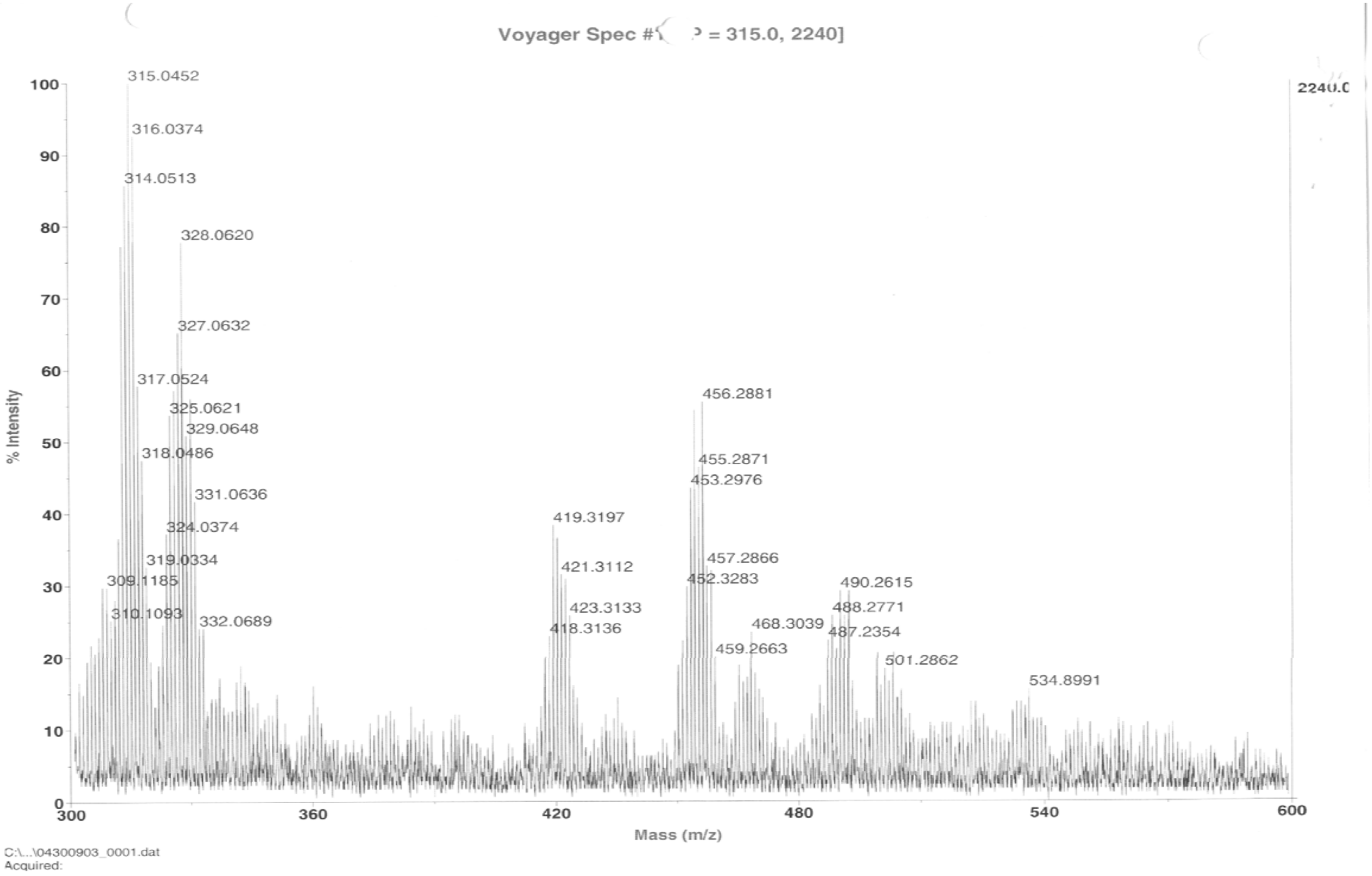


Figure S23. MALDI mass-spectrum for the reaction with SO_2Cl_2 and $TiCl_4$ without Ar protection.

Synthesis of Cs[$HCB_{11}Cl_{11}$] with SO_2Cl_2 under Ar (1 g scale). A solution of Cs[$HCB_{11}H_{11}$] (1.03 g, 3.71 mmol) in SO_2Cl_2 (50 mL, 620 mmol) in a Schlenk flask was heated to reflux at 80 ^{o}C under Ar protection. After 1 h, formation of white precipitate was observed and an additional 50 mL (620 mmol) of SO_2Cl_2 was added. The mixture was allowed to stir at refluxing temperature for another 24 h. Removal of the volatiles gave a white solid which was recrystallized from water to give pure Cs[$HCB_{11}Cl_{11}$]. Yield: 2.05 g (85%). ^{11}B NMR (128 MHz, aceotne): δ -1.7 (s, 1B), -9.0 (s, 5B), -12.1 (s, 5B). ^{1}H NMR (300 MHz, acetonitrile-d_3): δ 4.07 (s). Elemental Analysis Calculated (Found) for $CsHCB_{11}Cl_{11}$: H, 0.15% (0.30%); C, 1.83% (1.87%); B, 18.16% (17.97%); Cl, 59.55% (59.39%). Negative-ion MALDI MS, *m/z* (isotopic abundance): calculated for $HCB_{11}Cl_{11}$ 520 (84.7), 521 (96.7), 522 (100), 523 (93.8), 524 (80.3); found 519.7 (80.6), 520.7 (93.2), 521.7 (100), 522.7 (88.2), 523.7 (77.3). (Fig. S24 & S25)

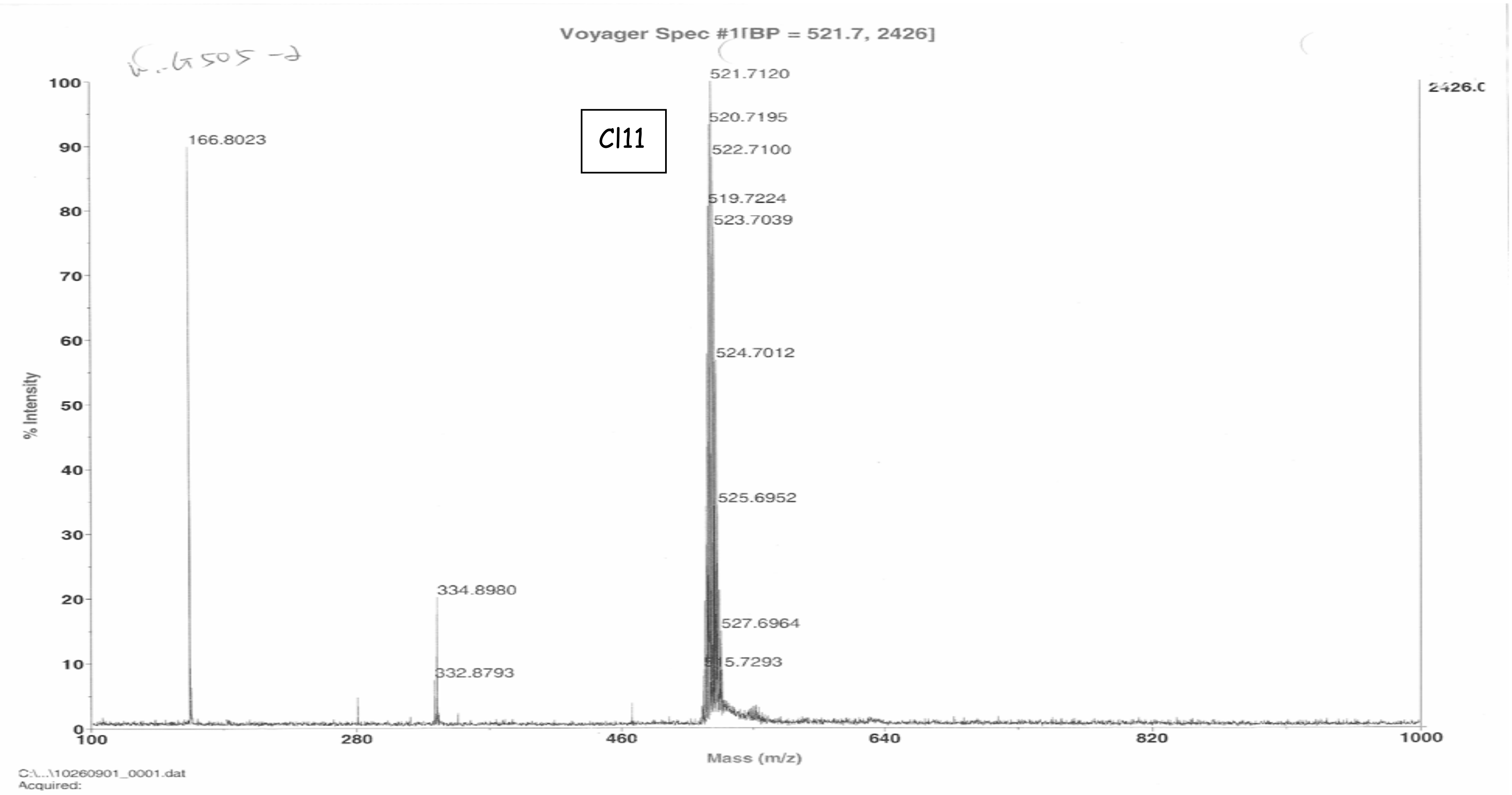


Figure S24. MALDI mass-spectrum for the reaction with SO_2Cl_2 under Ar protection at 1 g scale.

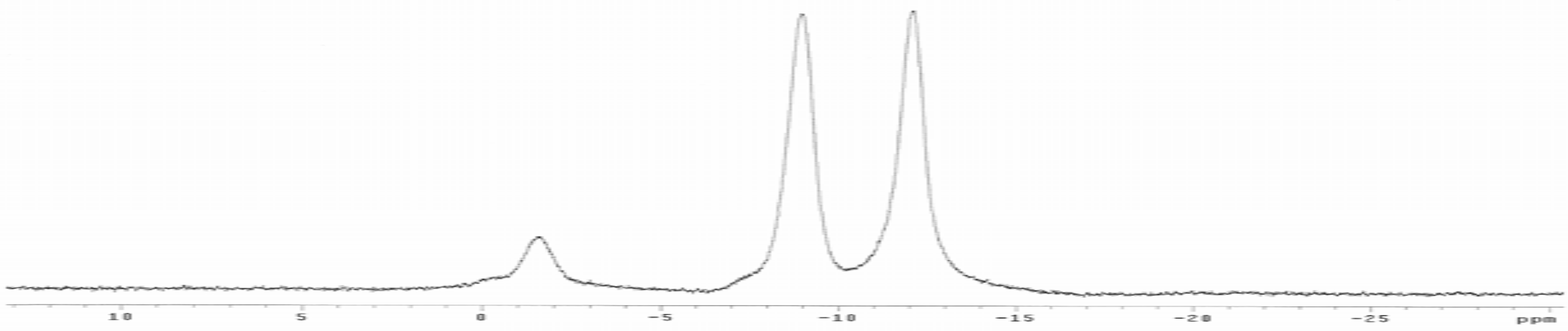


Figure S25. ^{11}B NMR spectrum of the Cs[HCB$_{11}$Cl$_{11}$] product from the reaction with SO$_2$Cl$_2$ under Ar protection at 1 g scale.

Synthesis of Cs[$HCB_{11}Cl_{11}$] with SO_2Cl_2 under Ar (100 mg scale). A solution of Cs[$HCB_{11}H_{11}$] (110 mg, 0.40 mmol) in SO_2Cl_2 (5.0 mL, 62 mmol) in a Schlenk flask was heated to reflux under Ar protection. After 1 h, formation of white precipitate was observed and an additional 5.0 mL (62 mmol) of SO_2Cl_2 was added. The mixture was allowed to stir at refluxing temperature for another 24 h. Removal of the volatiles gave a white solid which was recrystallized from water to give pure Cs[$HCB_{11}Cl_{11}$]. Yield: 220 mg (84%). (Fig. S26 & S27)

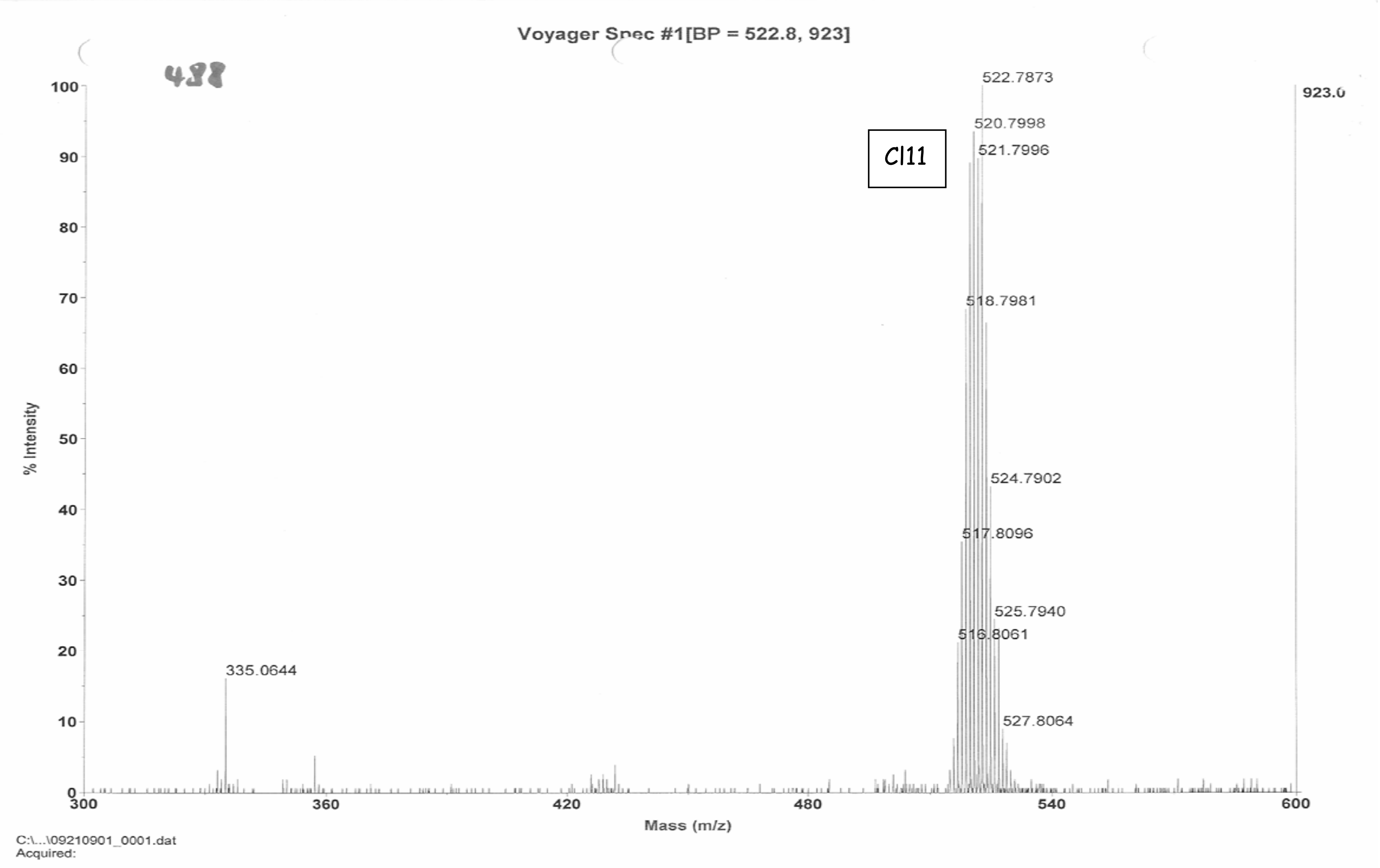


Figure S26. MALDI mass-spectrum for the reaction with SO_2Cl_2 under Ar protection at 100 mg scale.

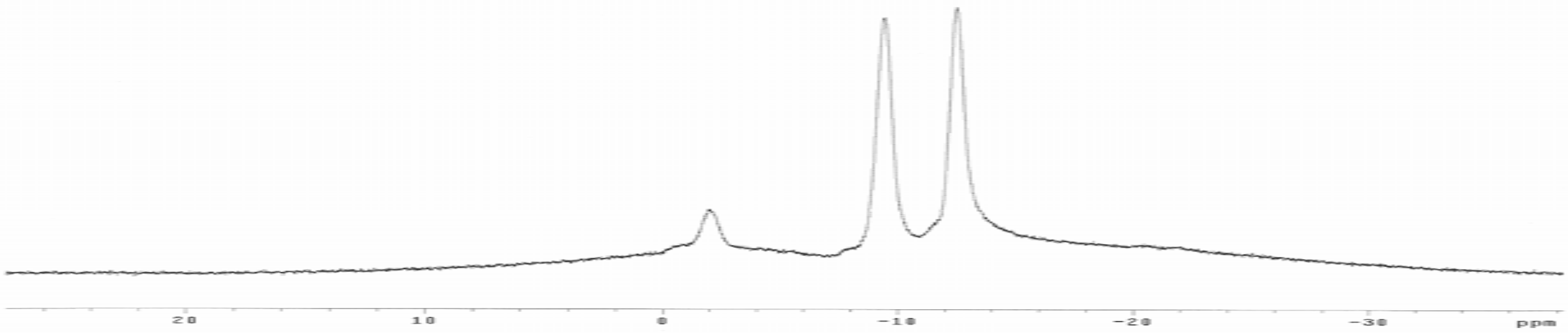


Figure S27. ^{11}B NMR spectrum of the Cs[$HCB_{11}Cl_{11}$] product from the reaction with SO_2Cl_2 under Ar protection at 100 mg scale.

Synthesis of Cs[$HCB_{11}Cl_{11}$] with SO_2Cl_2 under Ar (5 g scale). A solution of Cs[$HCB_{11}H_{11}$] (5.01 g, 18.02 mmol) in SO_2Cl_2 (250 mL, 3.09 mol) in a Schlenk flask was heated to reflux under Ar protection. After 1 h, formation of white precipitate was observed and an additional 250 mL (3.09 mol) of SO_2Cl_2 was added. The mixture was allowed to stir at refluxing temperature for another 24 h. Removal of the volatiles gave a white solid which was recrystallized from water to give pure Cs[$HCB_{11}Cl_{11}$]. Yield: 10.4 g (87%). (Fig. S28 & S29)

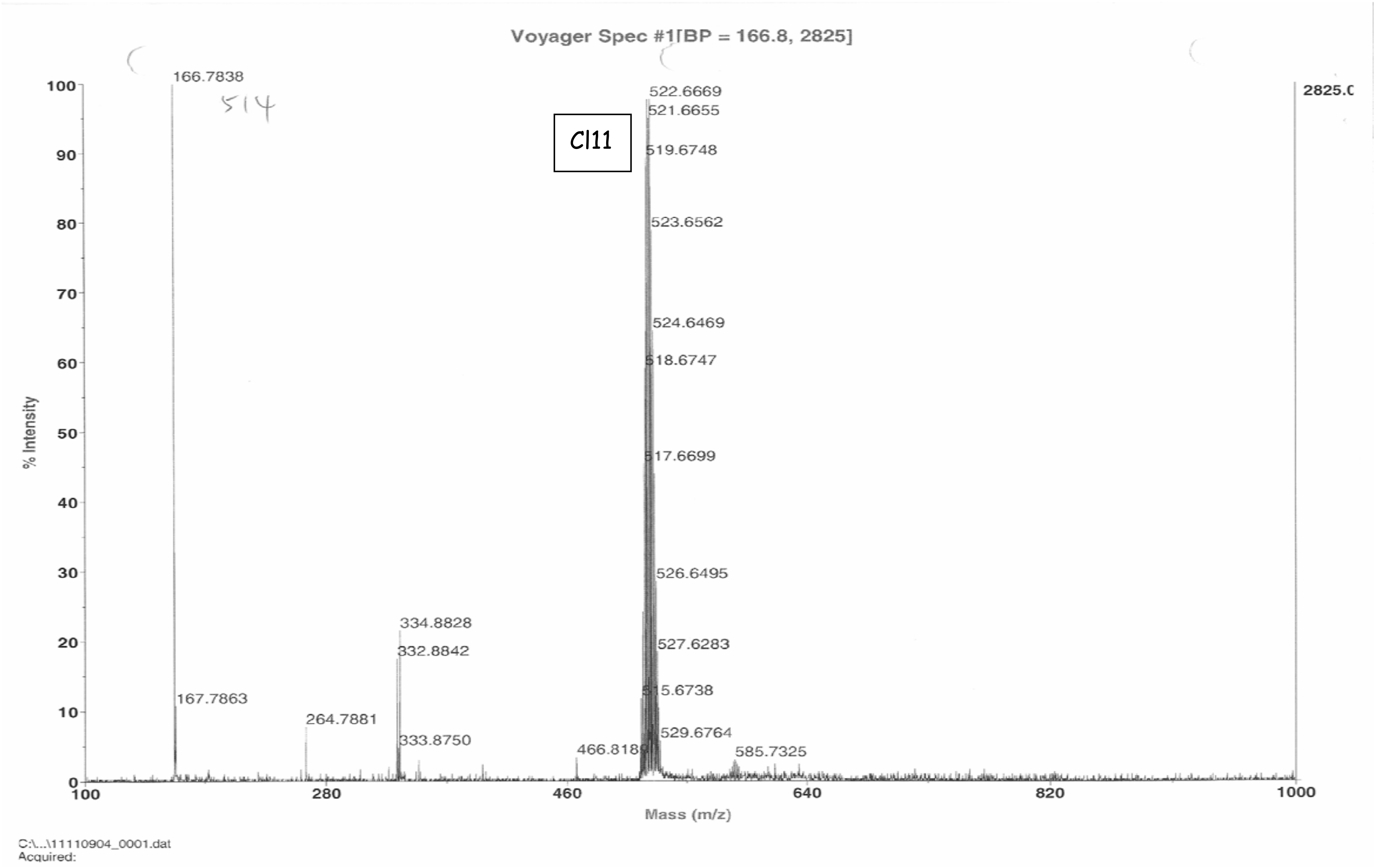


Figure S28. MALDI mass-spectrum for the reaction with SO_2Cl_2 under Ar protection at 5 g scale.

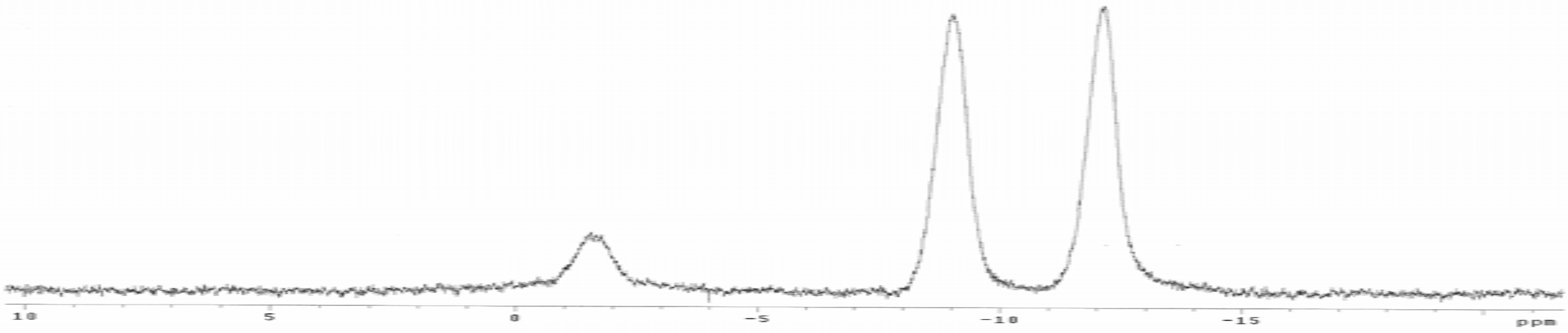


Figure S29. ^{11}B NMR spectrum of the Cs[HCB$_{11}$Cl$_{11}$] product from the reaction with SO$_2$Cl$_2$ under Ar protection at 5 g scale.

Reactions of Cs[$HCB_{11}H_{11}$] with SO_2Cl_2 with added H_2O versus a control without added H_2O. A pair of reactions were set up in the following way: RX1: 100 mg (0.36 mmol) of Cs[$HCB_{11}H_{11}$] was mixed with 22 μL (1.22 mmol) of H_2O and 5.0 mL (62 mmol) of SO_2Cl_2 in a Schlenk flask and heated to reflux; RX2: 100 mg (0.36 mmol) of Cs[$HCB_{11}H_{11}$] was mixed with 5.0 mL (62 mmol) SO_2Cl_2 in a Schlenk flask and heated to reflux. After 1 h, an additional 5.0 mL (62 mmol) of SO_2Cl_2 was added to each reaction. The mixture was allowed to stir at refluxing temperature for 24 h. Removal of the volatiles gave in each case a white solid which were analyzed by MALDI MS (Fig. S30 & S31) which revealed a lower chlorination level in the reaction with added water.

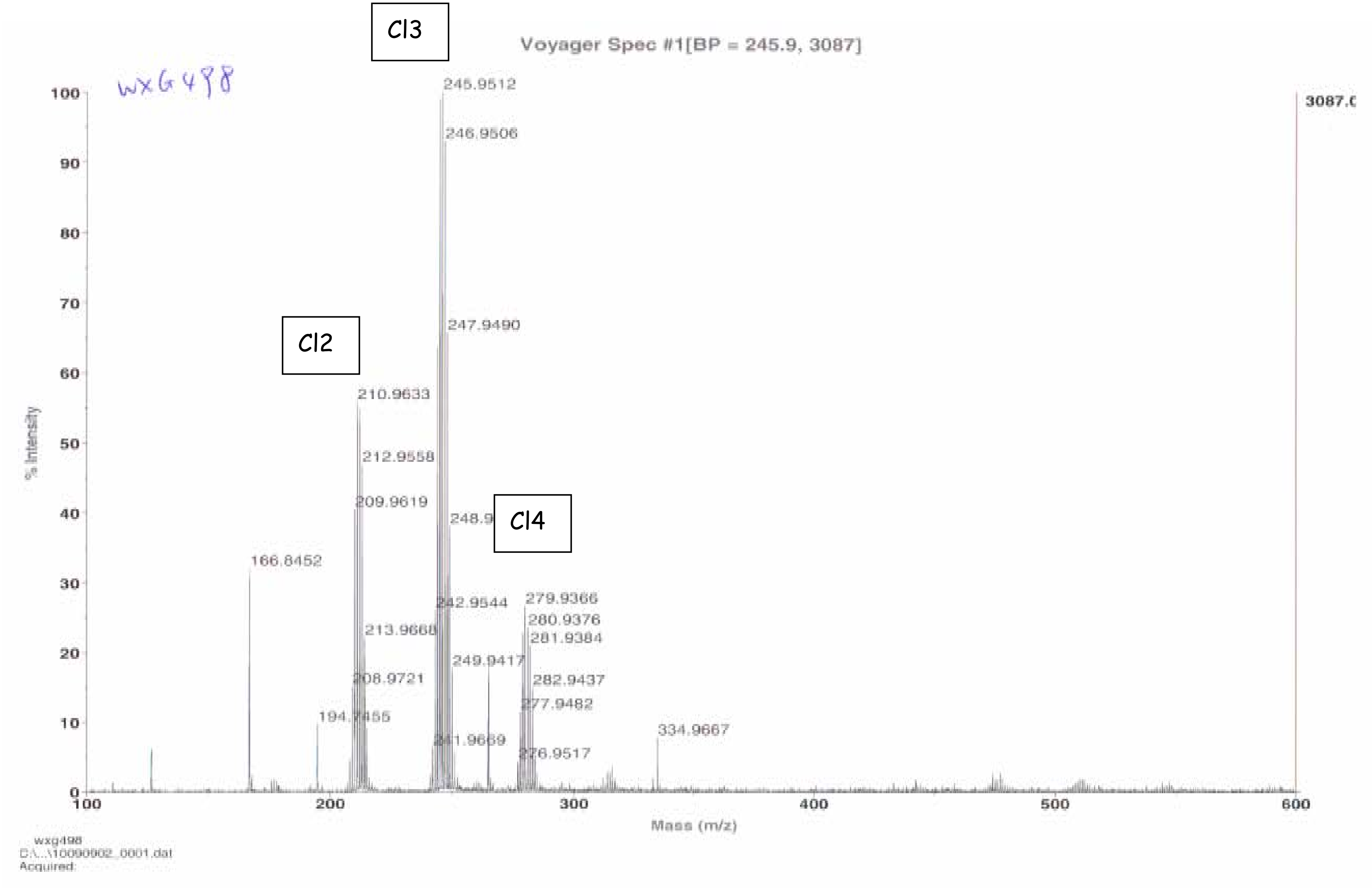


Figure S30. MALDI mass-spectrum for the reaction with SO_2Cl_2 with 2% H_2O.

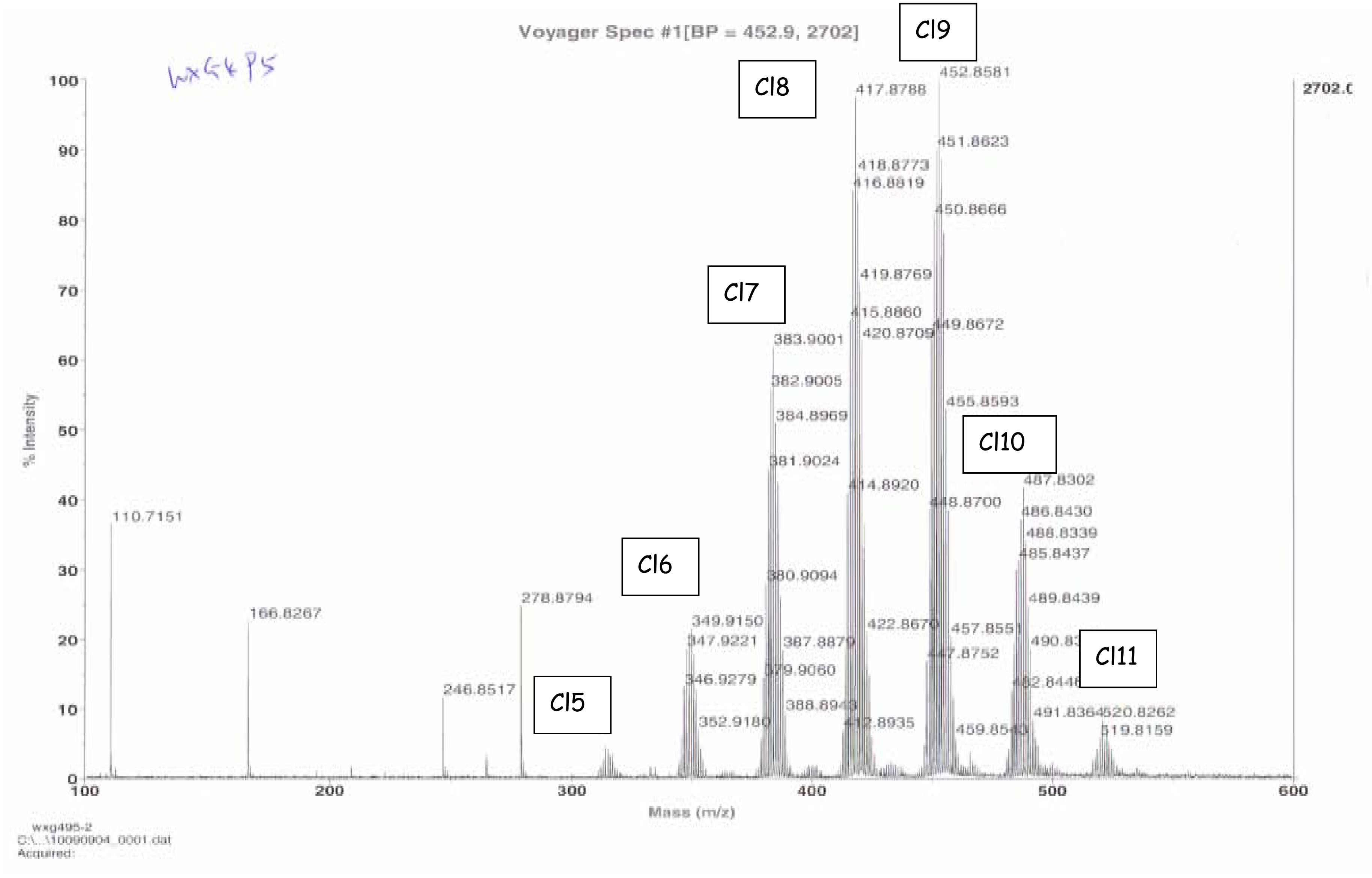
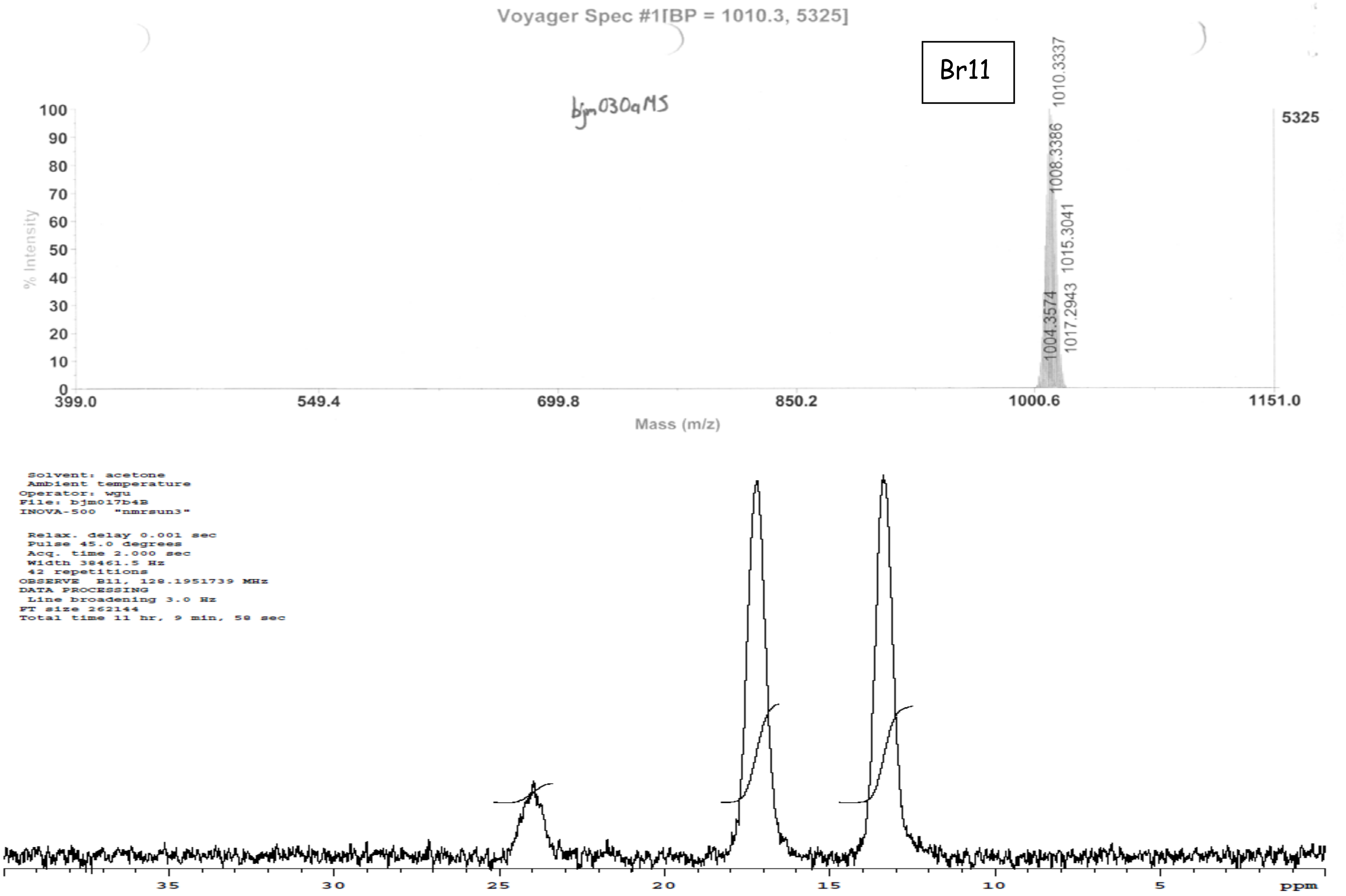


Figure S31. MALDI mass-spectrum for the reaction with SO_2Cl_2 without H_2O.

Synthesis of $Me_3NH[HCB_{11}Br_{11}]$. A round bottom flask charged with $Cs[HCB_{11}H_{11}]$ (101 mg, 0.365 mmol) was equipped with a stir bar and condenser. In this order, Br_2 (0.4 mL, 8 mmol) and $SbCl_5$ (1.0 mL, 8 mmol) were added through the condenser. The solution was blanketed with argon and stirred for 1 h in an oil bath which was brought to 150 °C. The flask was then removed from heat and cooled to room temperature; the volatiles were removed *in vacuo* as much as possible, first at room temperature, and then with the help of a warm water bath. Aqueous 10% NaOH was added to the residue until basic to litmus, forming a thick white, creamy precipitate. This was filtered through Celite over a medium fritted filter funnel, washing with 100 mL of 70 °C water. The filtrate was made acidic to litmus with aqueous 10% HCl, and an excess (87 mg, 0.91 mmol) of Me_3NHCl was added, immediately precipitating a white solid. The precipitate was allowed to settle for 1 h, and the suspension was filtered through Celite over a fine fritted filter funnel, washing with cool water. The receiving flask was changed, and the $Me_3NH[HCB_{11}Br_{11}]$ product washed through with 15 mL of acetone. The volatiles were removed *in vacuo*, leaving $Me_3NH[HCB_{11}Br_{11}]$ as a fine white powder. Yield: 302 mg (0.282 mmol, 77%). ^1H NMR (acetone-d_6, 25°C): δ 4.67 (br s, 1H, $\mathit{H}N(CH_3)_3^+$), 3.20 (s, 9H, $HN(C\mathit{H}_3)_3^+$) $^{13}C\{^1H\}$ NMR (acetone-d_6, 25°C): δ 54.3 (br s, 1C, $H\mathit{C}B_{11}Br_{11}^-$), 46.0 (s, 3C, $HN(\mathit{C}H_3)_3^+$) *Unreferenced* ^{11}B NMR (acetone-d_6, 25°C): δ 24.0 (br s, 1B, $HCB_{11}Br_{11}^-$), 17.2 (br s, 5B, $HCB_{11}Br_{11}^-$), 13.4 (br s, 5B, $HCB_{11}Br_{11}^-$). Negative-ion MALDI MS, m/z (isotopic abundance): Calculated for [HCB11Br11]- 1001.2 (2.5), 1002.2 (4.5), 1003.2 (10.2), 1004.2 (18.0), 1005.2 (29.5), 1006.2 (44.2), 1007.2 (60.4), 1008.2 (76.9), 1009.2 (90.5), 1010.2 (98.7), 1011.2 (100.0), 1012.2 (93.8), 1013.2 (82.1), 1014.2 (67.2), 1015.2 (49.8), 1016.2 (35.3), 1017.2 (21.1), 1018.2 (12.6), 1019.2 (6.3), 1020.2 (3.2), 1021.2 (1.1); Found 1003.4 (3.8), 1004.4 (10.3), 1005.4 (20.7), 1006.3 (36.8), 1007.3 (54.6), 1008.3 (73.3), 1009.3 (89.9), 1010.3 (100.0), 1011.3

(98.1), 1012.3 (94.9), 1013.3 (82.2), 1014.3 (63.0), 1015.3 (40.6), 1016.3 (26.1), 1017.3 (12.1), 1018.3 (5.7), 1019.3 (1.6)



```
 Solvent: acetone
 Ambient temperature
Operator: wgu
File: bjm017b4B
INOVA-500  "nmrsun3"

 Relax. delay 0.001 sec
 Pulse 45.0 degrees
 Acq. time 2.000 sec
 Width 38461.5 Hz
 42 repetitions
OBSERVE  B11, 128.1951739 MHz
DATA PROCESSING
 Line broadening 3.0 Hz
FT size 262144
Total time 11 hr, 9 min, 58 sec
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Figure S32. MALDI MS (top) and ^{11}B NMR (bottom) spectra (acetone-d_6) of isolated $Me_3NH[HCB_{11}Br_{11}]$.

Reaction of Cs[HCB$_{11}$H$_{11}$] with pre-mixed Br$_2$ and SbCl$_5$. Cs[HCB$_{11}$H$_{11}$] (102 mg, 0.370 mmol) was added to a Schlenk flask equipped with a stirbar and condenser. An addition funnel was fitted above the condenser and the system was maintained under Ar. Br$_2$ (0.4 mL, 8 mmol) and SbCl$_5$ (1 mL, 8 mmol) were mixed in the addition funnel. The contents of the addition funnel were emptied into the flask through the condenser. The system was heated to 150°C for 1 day, and a sample for MALDI MS was taken, which indicated a mixture containing [HCB$_{11}$HBr$_{10}$]$^-$ and predominantly [HCB$_{11}$Br$_{11}$]$^-$ (Figure S33).

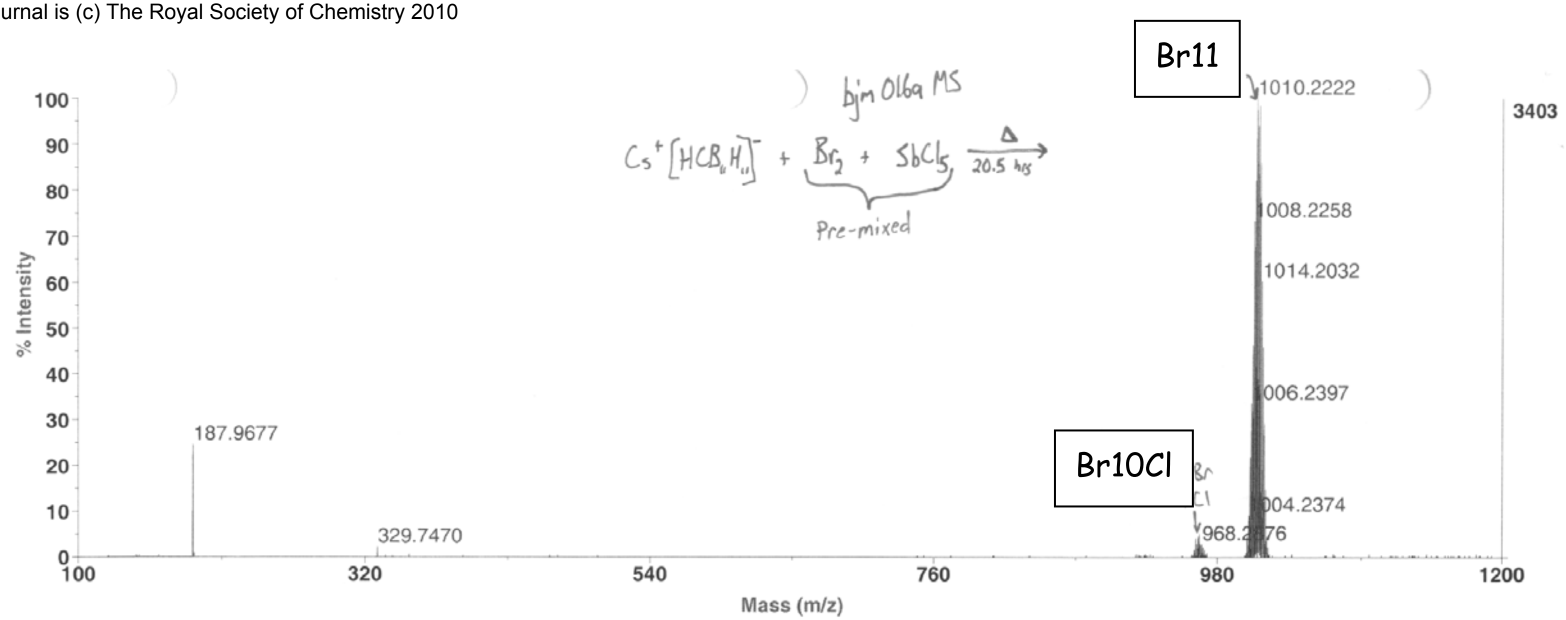

Figure S33. MALDI mass-spectrum for the reaction of Cs[$HCB_{11}H_{11}$] with pre-mixed Br_2 and $SbCl_5$ for 1 day at 150° C.

Reaction of partially brominated carborane with Br_2/$SbCl_5$. Cs[$HCB_{11}H_{11}$] (101 mg, 0.366 mmol) was added to a Schlenk flask equipped with a stirbar. CH_2Cl_2 (1 mL) was added to the flask, followed by Br_2 (239 mg, 1.50 mmol) dissolved in CH_2Cl_2 (4 mL). A condenser was attached, the system was blanketed with argon and stirred while being heated to reflux for 3.5 h, after which the solution appeared cloudy orange. A sample was collected for MALDI MS analysis, which indicated a mixture of $[HCB_{11}H_8Br_3]^-$ and $[HCB_{11}H_7Br_4]^-$ (Figure S34, top). A sample taken after refluxing for 1 day showed the formation of a small amount $[HCB_{11}H_6Br_5]^-$, but overall little change in the composition by MS (Figure S34, bottom).

All volatiles were removed *in vacuo*, and an addition funnel was equipped to the condenser. Br_2 (0.4 mL, 8 mmol) and $SbCl_5$ (1 mL, 8 mmol) were added to the addition funnel, which was then emptied through the condenser into the flask. The mixture was stirred and heated to 150°C for 1 day, after which a MALDI MS sample was obtained, which indicated complete conversion to $[HCB_{11}Br_{11}]^-$ (Figure S35).

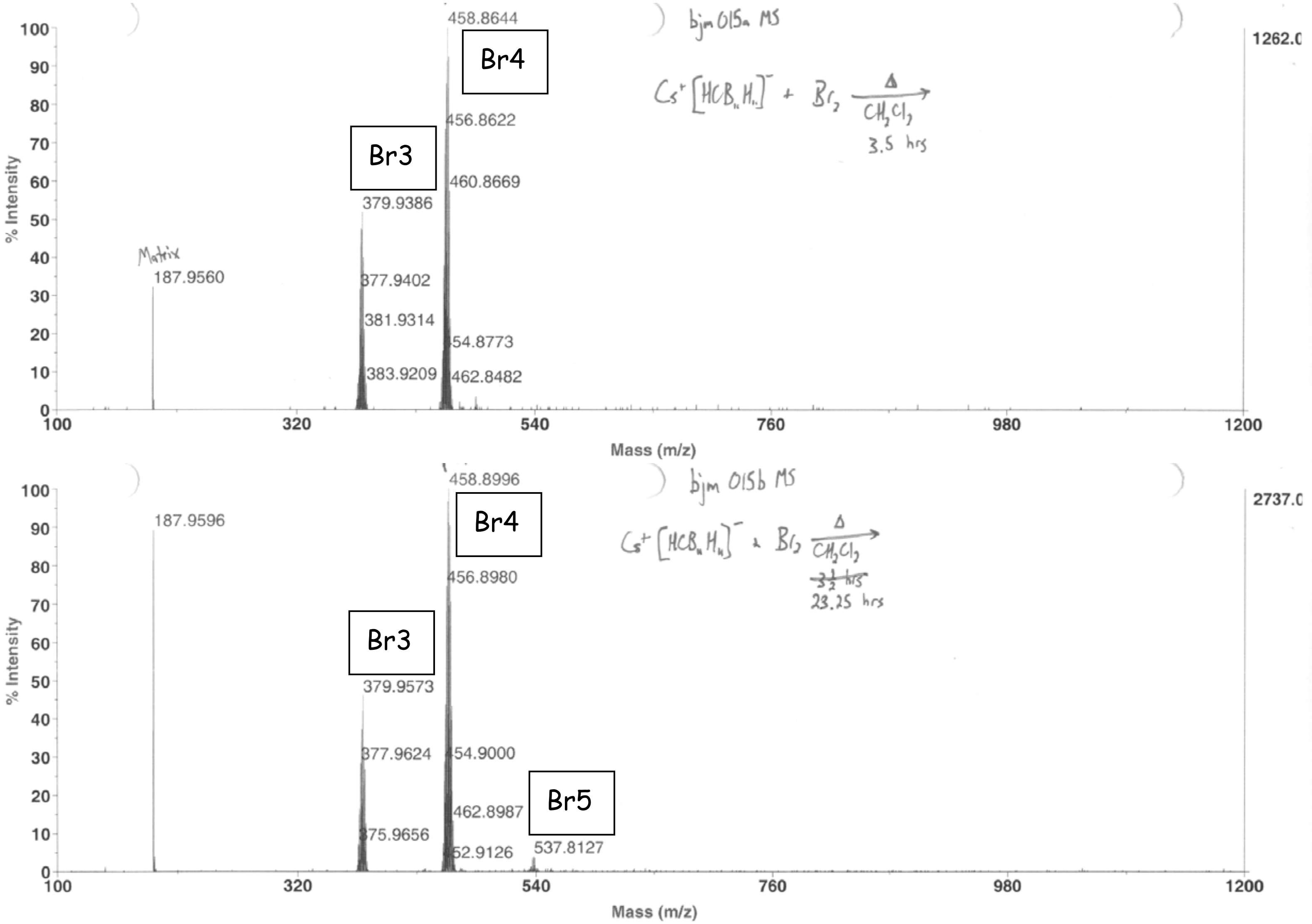

Figure S34. MALDI mass-spectra for the reaction of Cs[$HCB_{11}H_{11}$] with 4.1 equiv. Br_2 in CH_2Cl_2 at reflux after 3.5 h (top) and after 23 h (bottom).

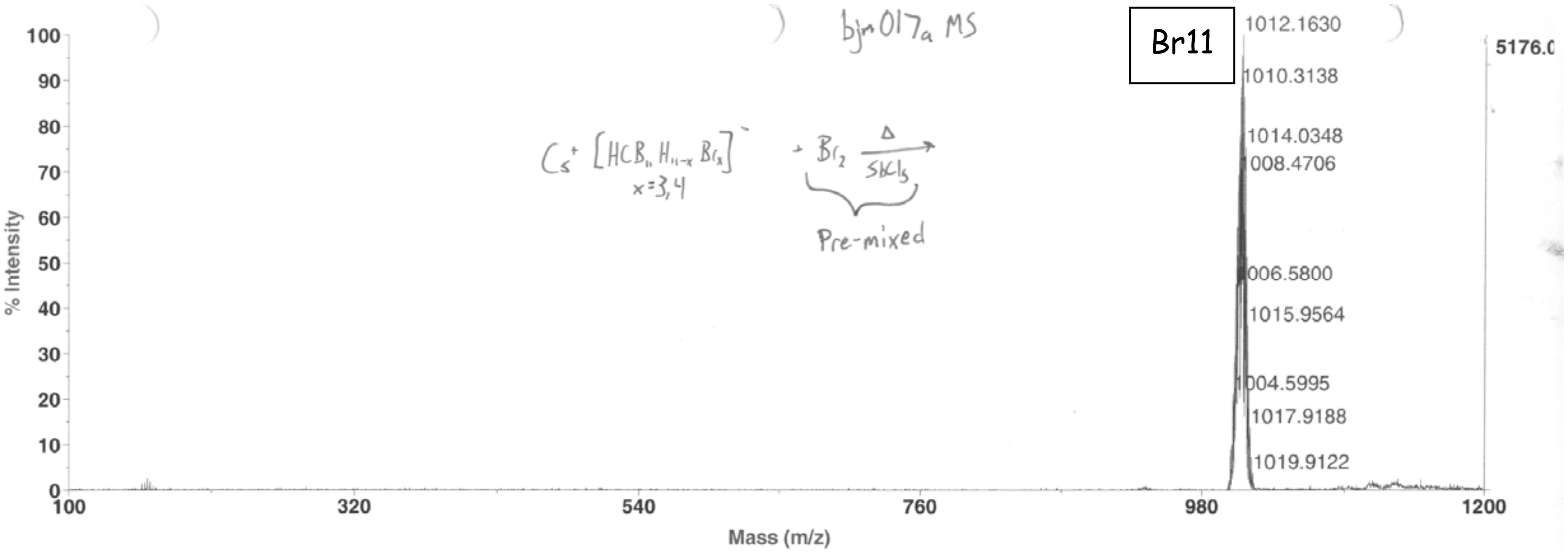

Figure S35. MALDI mass-spectrum for the reaction of partially brominated carborane (from Scheme S34) with pre-mixed Br_2 and $SbCl_5$ for 1 day at 150° C.

Reaction of partially brominated carborane with Br_2 and $SbCl_5$ at room temperature. A round bottom flask charged with $Cs[HCB_{11}H_{11}]$ (100 mg, 0.362 mmol) was equipped with a stir bar. Br_2 (177 mg, 1.11 mmol) dissolved in CH_2Cl_2 (4 mL) was added. A condenser was then affixed to the flask, stirring initiated under Ar, and the system was heated to reflux for 2 h. All volatiles were then removed *in vacuo*. Br_2 (0.4 mL, 8 mmol) followed by $SbCl_5$ (1 mL, 8 mmol) were added through the condenser, and the system placed under Ar. Stirring was again initiated and the system maintained at room temperature. After 75 minutes, a sample was taken for MALDI MS analysis, which indicated a mixture containing $[HCB_{11}HBr_{10}]^-$ and predominantly $[HCB_{11}Br_{11}]^-$ (Figure S36, top). A second sample was obtained after 4 days, showing the same mixture, but with a higher proportion of undecabrominated product (Figure S36, bottom).

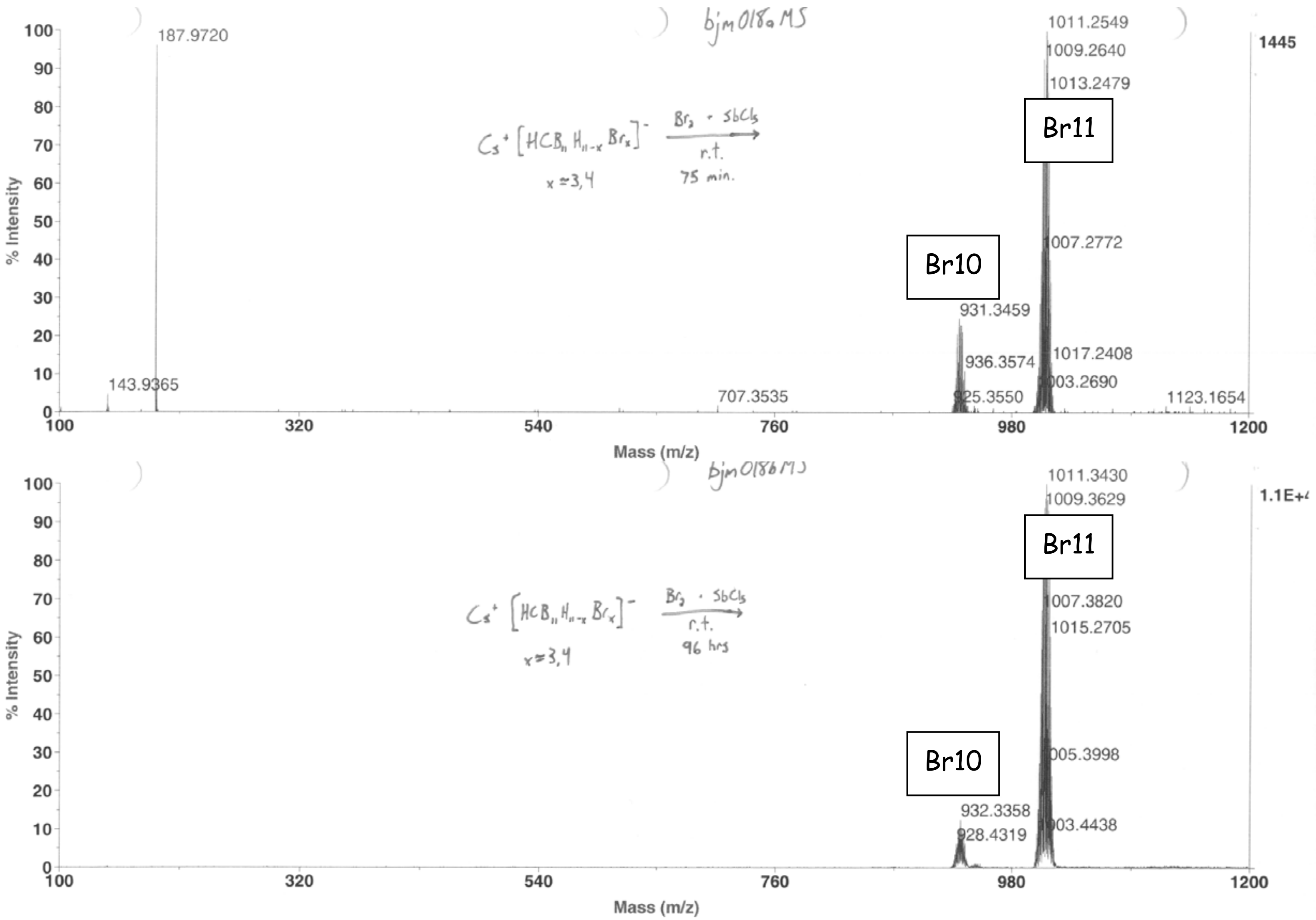

Figure S36. MALDI mass-spectra for the reaction in which Cs[$HCB_{11}H_{11}$] was first treated with Br_2 in CH_2Cl_2 and then with $Br_2/SbCl_5$ for 75 min (top) and 4 d (bottom) at room temperature.

Reaction of Cs[HCB$_{11}$Br$_{11}$] with Br$_2$ and SbCl$_5$ at 70°C. A round bottom flask charged with Cs[HCB$_{11}$H$_{11}$] (100 mg, 0.362 mmol) was equipped with a stir bar and condenser. Br$_2$ (0.4 mL, 8 mmol) followed by SbCl$_5$ (1 mL, 8 mmol) were added through the condenser, and the system placed under Ar. Stirring was initiated and the system maintained at 70°C for 2 d. A sample was taken for MALDI MS analysis, which indicated a mixture containing [HCB$_{11}$HBr$_{10}$]$^-$ and predominantly [HCB$_{11}$Br$_{11}$]$^-$ (Figure S37).

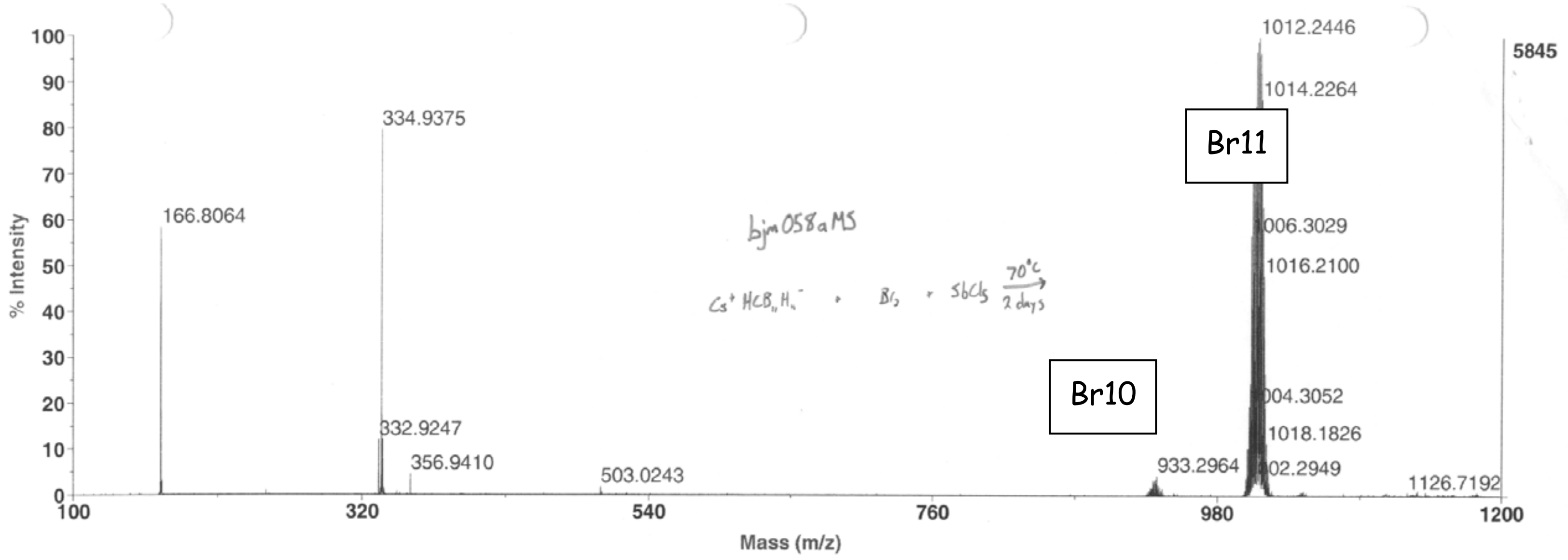

Figure S37. MALDI mass-spectrum for reaction of $Cs[HCB_{11}H_{11}]$ with Br_2 and $SbCl_5$ for 2 days at 70° C.

Reaction of Cs[$HCB_{11}H_{11}$] with neat Br_2. A Schlenk flask charged with Cs[$HCB_{11}H_{11}$] (100 mg, 0.362 mmol) was equipped with a stir bar and condenser. Br_2 was added through the condenser (1 mL, 20 mmol), and the system maintained under Ar. The system was then heated to reflux, and maintained for 2 d. MALDI MS samples were taken after 30 min at room temperature (Figure S38, top) and after 48 h (Figure S38, bottom) at reflux. The final product was predominantly $[HCB_{11}H_5Br_6]^-$, with some penta- and hepta-brominated product observed.

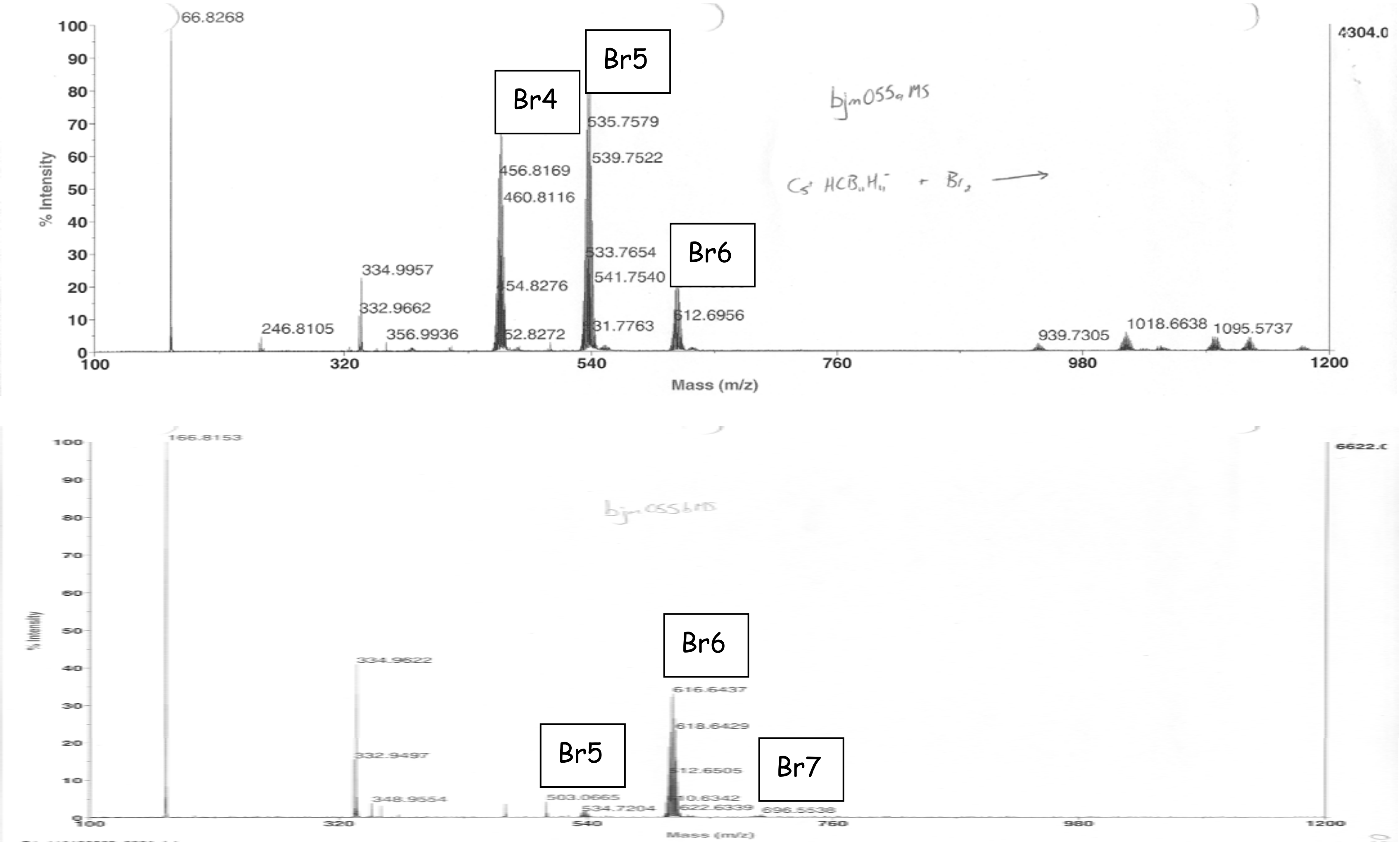

Figure S38. MALDI mass-spectrum for the reaction of $Cs[HCB_{11}H_{11}]$ with Br_2 for 30 min at room temperature (top) and 48 hours at reflux (bottom).

$Ph_3C[HCB_{11}Br_{11}]$ was synthesized from $HNMe_3[HCB_{11}Br_{11}]$ analogously to literature procedures[1] for synthesis of trityl salts of halogenated carboranes (via the Ag salt). Recrystallization from toluene at –35 ˚C yielded a small quantity of X-ray quality single crystals, one of which was used for the X-ray diffraction study.

1. (a) C.-W. Tsang, Q. Yang, E. T.-P. Sze, T. C. W. Mak, D. T. W. Chan, and Z. Xie, *Inorg. Chem*. 2000, **39**, 5851. (b) Z. Xie, T. Jelinek, R. Bau, and C. A. Reed, *J. Am. Chem. Soc*. 1994, **116**, 1907.

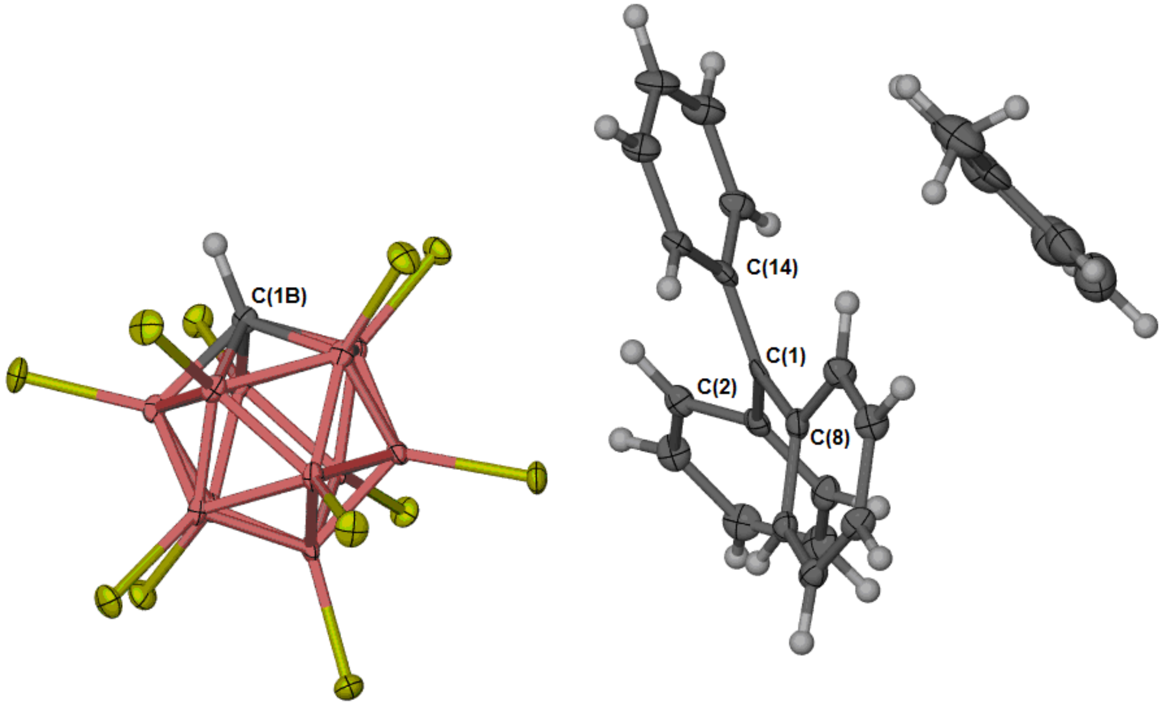

Figure S39. ORTEP view of the full asymmetric unit (including the toluene solvent molecule, top right) of the solid-state structure of $Ph_3C[HCB_{11}Br_{11}]$.

Table S1. Crystal data and structure refinement for $Ph_3C[HCB_{11}Br_{11}]$.

Empirical formula	C27 H24 B11 Br11	
Formula weight	1346.38	
Temperature	70(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.968(5) Å	α= 90.000(5)°.
	b = 21.852(5) Å	β= 96.936(5)°.
	c = 13.127(5) Å	γ = 90.000(5)°.
Volume	3977(2) $Å^3$	
Z	4	
Density (calculated)	2.248 Mg/m^3	
Absorption coefficient	11.103 mm^{-1}	
F(000)	2504	
Crystal size	0.30 x 0.10 x 0.10 mm^3	
Theta range for data collection	2.74 to 25.00°.	
Index ranges	-6<=h<=16, -25<=k<=15, -14<=l<=13	
Reflections collected	23031	
Independent reflections	6468 [R(int) = 0.0457]	
Completeness to theta = 25.00°	92.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4031 and 0.1355	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6468 / 447 / 442	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0767	
R indices (all data)	R1 = 0.0544, wR2 = 0.0859	
Largest diff. peak and hole	0.995 and -0.834 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $Ph_3C[HCB_{11}Br_{11}]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	8643(1)	470(1)	6183(1)	21(1)
Br(2)	8499(1)	-591(1)	3991(1)	20(1)
Br(3)	6136(1)	221(1)	4538(1)	21(1)
Br(4)	6838(1)	1832(1)	5438(1)	19(1)
Br(5)	6678(1)	45(1)	1785(1)	17(1)
Br(6)	9603(1)	1971(1)	5433(1)	19(1)
Br(7)	9480(1)	216(1)	1833(1)	16(1)
Br(8)	5731(1)	1594(1)	2652(1)	19(1)
Br(9)	10184(1)	1796(1)	2728(1)	18(1)
Br(10)	7840(1)	2675(1)	3216(1)	17(1)
Br(11)	7821(1)	1573(1)	955(1)	16(1)
C(1B)	9153(4)	800(2)	3979(5)	14(1)
B(1)	8303(4)	785(3)	4831(6)	14(1)
B(2)	8240(4)	261(3)	3734(6)	14(1)
B(3)	7187(4)	653(3)	4011(6)	14(1)
B(4)	7518(4)	1408(3)	4460(5)	13(1)
B(5)	7451(4)	576(3)	2739(6)	13(1)
B(6)	8788(4)	1493(3)	4438(6)	14(1)
B(7)	8719(4)	652(3)	2727(5)	13(1)
B(8)	7011(4)	1286(3)	3158(5)	12(1)
B(9)	9054(4)	1411(3)	3153(5)	14(1)
B(10)	7998(4)	1809(3)	3433(5)	13(1)
B(11)	7946(4)	1283(3)	2350(5)	12(1)
C(1)	7033(4)	-922(2)	-248(5)	15(1)
C(2)	6989(4)	-417(3)	-973(5)	17(1)
C(3)	7695(4)	55(3)	-827(5)	18(1)
C(4)	7616(4)	553(3)	-1470(5)	22(1)

C(5)	6882(4)	595(3)	-2260(5)	25(1)
C(6)	6195(4)	134(3)	-2431(5)	26(1)
C(7)	6254(4)	-365(3)	-1774(5)	21(1)
C(8)	6153(4)	-1201(3)	-11(5)	18(1)
C(9)	5311(4)	-849(3)	-8(5)	18(1)
C(10)	4501(4)	-1102(3)	306(5)	20(1)
C(11)	4473(4)	-1710(3)	578(5)	21(1)
C(12)	5289(4)	-2068(3)	577(5)	23(1)
C(13)	6130(4)	-1817(3)	305(5)	21(1)
C(14)	7948(4)	-1144(2)	232(5)	17(1)
C(15)	8769(4)	-1145(3)	-310(5)	21(1)
C(16)	9636(4)	-1364(3)	165(6)	28(1)
C(17)	9706(4)	-1571(3)	1150(6)	28(1)
C(18)	8930(4)	-1563(3)	1716(5)	24(1)
C(19)	8044(4)	-1359(3)	1241(5)	19(1)
C(1T)	6935(5)	-3364(3)	51(6)	32(1)
C(2T)	7709(5)	-3021(3)	-195(6)	34(1)
C(3T)	7665(5)	-2710(3)	-1128(6)	39(1)
C(4T)	6844(6)	-2745(3)	-1806(7)	46(2)
C(5T)	6070(6)	-3086(3)	-1575(7)	46(2)
C(6T)	6107(5)	-3389(3)	-661(6)	39(1)
C(7T)	6969(5)	-3705(3)	1048(6)	45(2)

Table S3. Bond lengths [Å] and angles [°] for $Ph_3C[HCB_{11}Br_{11}]$.

Br(1)-B(1)	1.910(7)
Br(2)-B(2)	1.920(6)
Br(3)-B(3)	1.941(6)
Br(4)-B(4)	1.925(7)
Br(5)-B(5)	1.938(6)
Br(6)-B(6)	1.933(7)
Br(7)-B(7)	1.928(7)
Br(8)-B(8)	1.950(6)
Br(9)-B(9)	1.930(6)
Br(10)-B(10)	1.922(6)
Br(11)-B(11)	1.926(7)
C(1B)-B(7)	1.712(9)
C(1B)-B(9)	1.714(9)
C(1B)-B(1)	1.727(8)
C(1B)-B(6)	1.729(8)
C(1B)-B(2)	1.738(8)
B(1)-B(4)	1.778(9)
B(1)-B(6)	1.788(9)
B(1)-B(3)	1.807(9)
B(1)-B(2)	1.834(10)
B(2)-B(5)	1.745(9)
B(2)-B(7)	1.771(9)
B(2)-B(3)	1.777(8)
B(3)-B(5)	1.761(10)
B(3)-B(8)	1.778(9)
B(3)-B(4)	1.794(9)
B(4)-B(6)	1.786(8)
B(4)-B(8)	1.789(10)
B(4)-B(10)	1.804(9)
B(5)-B(7)	1.780(8)
B(5)-B(8)	1.781(8)
B(5)-B(11)	1.792(9)
B(6)-B(10)	1.756(9)

B(6)-B(9)	1.780(10)
B(7)-B(11)	1.784(9)
B(7)-B(9)	1.794(9)
B(8)-B(11)	1.780(9)
B(8)-B(10)	1.794(8)
B(9)-B(11)	1.786(9)
B(9)-B(10)	1.788(9)
B(10)-B(11)	1.823(9)
C(1)-C(14)	1.438(8)
C(1)-C(8)	1.439(7)
C(1)-C(2)	1.455(8)
C(2)-C(7)	1.383(8)
C(2)-C(3)	1.423(8)
C(3)-C(4)	1.374(8)
C(4)-C(5)	1.370(9)
C(5)-C(6)	1.390(8)
C(6)-C(7)	1.387(9)
C(8)-C(9)	1.404(7)
C(8)-C(13)	1.412(8)
C(9)-C(10)	1.367(8)
C(10)-C(11)	1.377(8)
C(11)-C(12)	1.383(8)
C(12)-C(13)	1.382(8)
C(14)-C(19)	1.395(9)
C(14)-C(15)	1.421(8)
C(15)-C(16)	1.379(8)
C(16)-C(17)	1.362(10)
C(17)-C(18)	1.385(8)
C(18)-C(19)	1.390(8)
C(1T)-C(2T)	1.385(9)
C(1T)-C(6T)	1.397(10)
C(1T)-C(7T)	1.501(10)
C(2T)-C(3T)	1.395(10)
C(3T)-C(4T)	1.367(10)
C(4T)-C(5T)	1.377(10)
C(5T)-C(6T)	1.366(11)

B(7)-C(1B)-B(9)	63.2(4)
B(7)-C(1B)-B(1)	115.2(4)
B(9)-C(1B)-B(1)	114.5(4)
B(7)-C(1B)-B(6)	114.5(4)
B(9)-C(1B)-B(6)	62.3(4)
B(1)-C(1B)-B(6)	62.3(3)
B(7)-C(1B)-B(2)	61.8(4)
B(9)-C(1B)-B(2)	114.2(4)
B(1)-C(1B)-B(2)	63.9(4)
B(6)-C(1B)-B(2)	114.6(4)
C(1B)-B(1)-B(4)	105.0(4)
C(1B)-B(1)-B(6)	58.9(3)
B(4)-B(1)-B(6)	60.1(3)
C(1B)-B(1)-B(3)	103.2(5)
B(4)-B(1)-B(3)	60.0(3)
B(6)-B(1)-B(3)	107.2(4)
C(1B)-B(1)-B(2)	58.3(3)
B(4)-B(1)-B(2)	107.1(5)
B(6)-B(1)-B(2)	107.4(5)
B(3)-B(1)-B(2)	58.4(3)
C(1B)-B(1)-Br(1)	119.7(4)
B(4)-B(1)-Br(1)	127.3(4)
B(6)-B(1)-Br(1)	121.3(4)
B(3)-B(1)-Br(1)	126.5(4)
B(2)-B(1)-Br(1)	119.1(4)
C(1B)-B(2)-B(5)	104.7(4)
C(1B)-B(2)-B(7)	58.4(3)
B(5)-B(2)-B(7)	60.8(4)
C(1B)-B(2)-B(3)	104.0(4)
B(5)-B(2)-B(3)	60.0(4)
B(7)-B(2)-B(3)	108.5(4)
C(1B)-B(2)-B(1)	57.8(3)
B(5)-B(2)-B(1)	107.9(4)
B(7)-B(2)-B(1)	107.3(4)
B(3)-B(2)-B(1)	60.1(4)

C(1B)-B(2)-Br(2)	120.5(4)
B(5)-B(2)-Br(2)	127.1(4)
B(7)-B(2)-Br(2)	121.3(4)
B(3)-B(2)-Br(2)	125.1(4)
B(1)-B(2)-Br(2)	118.6(4)
B(5)-B(3)-B(2)	59.1(4)
B(5)-B(3)-B(8)	60.4(4)
B(2)-B(3)-B(8)	107.5(4)
B(5)-B(3)-B(4)	108.9(4)
B(2)-B(3)-B(4)	108.9(4)
B(8)-B(3)-B(4)	60.1(4)
B(5)-B(3)-B(1)	108.4(4)
B(2)-B(3)-B(1)	61.5(4)
B(8)-B(3)-B(1)	107.1(4)
B(4)-B(3)-B(1)	59.2(3)
B(5)-B(3)-Br(3)	123.0(4)
B(2)-B(3)-Br(3)	121.3(4)
B(8)-B(3)-Br(3)	123.3(4)
B(4)-B(3)-Br(3)	120.4(4)
B(1)-B(3)-Br(3)	120.1(4)
B(1)-B(4)-B(6)	60.2(3)
B(1)-B(4)-B(8)	107.9(4)
B(6)-B(4)-B(8)	106.2(5)
B(1)-B(4)-B(3)	60.8(4)
B(6)-B(4)-B(3)	107.9(4)
B(8)-B(4)-B(3)	59.5(4)
B(1)-B(4)-B(10)	107.7(4)
B(6)-B(4)-B(10)	58.6(3)
B(8)-B(4)-B(10)	59.9(4)
B(3)-B(4)-B(10)	107.8(5)
B(1)-B(4)-Br(4)	121.6(4)
B(6)-B(4)-Br(4)	122.1(4)
B(8)-B(4)-Br(4)	122.6(4)
B(3)-B(4)-Br(4)	122.3(4)
B(10)-B(4)-Br(4)	121.5(4)
B(2)-B(5)-B(3)	60.9(4)

B(2)-B(5)-B(7)	60.3(4)
B(3)-B(5)-B(7)	108.8(5)
B(2)-B(5)-B(8)	108.8(5)
B(3)-B(5)-B(8)	60.2(4)
B(7)-B(5)-B(8)	107.6(4)
B(2)-B(5)-B(11)	108.8(4)
B(3)-B(5)-B(11)	108.7(4)
B(7)-B(5)-B(11)	59.9(3)
B(8)-B(5)-B(11)	59.7(3)
B(2)-B(5)-Br(5)	120.0(4)
B(3)-B(5)-Br(5)	120.4(4)
B(7)-B(5)-Br(5)	121.8(4)
B(8)-B(5)-Br(5)	122.3(4)
B(11)-B(5)-Br(5)	122.4(4)
C(1B)-B(6)-B(10)	105.5(5)
C(1B)-B(6)-B(9)	58.5(4)
B(10)-B(6)-B(9)	60.8(4)
C(1B)-B(6)-B(4)	104.5(4)
B(10)-B(6)-B(4)	61.2(4)
B(9)-B(6)-B(4)	109.0(5)
C(1B)-B(6)-B(1)	58.8(3)
B(10)-B(6)-B(1)	109.4(4)
B(9)-B(6)-B(1)	108.4(5)
B(4)-B(6)-B(1)	59.7(3)
C(1B)-B(6)-Br(6)	122.3(4)
B(10)-B(6)-Br(6)	124.1(4)
B(9)-B(6)-Br(6)	121.4(4)
B(4)-B(6)-Br(6)	123.4(4)
B(1)-B(6)-Br(6)	119.1(4)
C(1B)-B(7)-B(2)	59.8(4)
C(1B)-B(7)-B(5)	104.3(5)
B(2)-B(7)-B(5)	58.8(3)
C(1B)-B(7)-B(11)	104.6(4)
B(2)-B(7)-B(11)	108.0(4)
B(5)-B(7)-B(11)	60.4(3)
C(1B)-B(7)-B(9)	58.5(4)

B(2)-B(7)-B(9)	108.7(5)
B(5)-B(7)-B(9)	107.8(4)
B(11)-B(7)-B(9)	59.9(3)
C(1B)-B(7)-Br(7)	121.3(4)
B(2)-B(7)-Br(7)	120.1(4)
B(5)-B(7)-Br(7)	125.5(4)
B(11)-B(7)-Br(7)	125.0(4)
B(9)-B(7)-Br(7)	120.3(4)
B(3)-B(8)-B(11)	108.5(4)
B(3)-B(8)-B(5)	59.3(4)
B(11)-B(8)-B(5)	60.4(3)
B(3)-B(8)-B(4)	60.4(4)
B(11)-B(8)-B(4)	109.6(4)
B(5)-B(8)-B(4)	108.3(4)
B(3)-B(8)-B(10)	108.9(4)
B(11)-B(8)-B(10)	61.3(4)
B(5)-B(8)-B(10)	109.4(4)
B(4)-B(8)-B(10)	60.4(4)
B(3)-B(8)-Br(8)	122.4(4)
B(11)-B(8)-Br(8)	120.4(4)
B(5)-B(8)-Br(8)	122.2(4)
B(4)-B(8)-Br(8)	121.0(4)
B(10)-B(8)-Br(8)	119.9(4)
C(1B)-B(9)-B(6)	59.3(4)
C(1B)-B(9)-B(11)	104.5(4)
B(6)-B(9)-B(11)	108.1(4)
C(1B)-B(9)-B(10)	104.8(4)
B(6)-B(9)-B(10)	59.0(4)
B(11)-B(9)-B(10)	61.3(3)
C(1B)-B(9)-B(7)	58.4(4)
B(6)-B(9)-B(7)	108.2(4)
B(11)-B(9)-B(7)	59.8(3)
B(10)-B(9)-B(7)	108.9(4)
C(1B)-B(9)-Br(9)	121.0(4)
B(6)-B(9)-Br(9)	120.1(4)
B(11)-B(9)-Br(9)	125.3(4)

B(10)-B(9)-Br(9)	124.8(4)
B(7)-B(9)-Br(9)	120.3(4)
B(6)-B(10)-B(9)	60.3(4)
B(6)-B(10)-B(8)	107.3(4)
B(9)-B(10)-B(8)	106.3(4)
B(6)-B(10)-B(4)	60.2(4)
B(9)-B(10)-B(4)	107.9(4)
B(8)-B(10)-B(4)	59.6(4)
B(6)-B(10)-B(11)	107.4(4)
B(9)-B(10)-B(11)	59.3(3)
B(8)-B(10)-B(11)	58.9(3)
B(4)-B(10)-B(11)	107.0(4)
B(6)-B(10)-Br(10)	123.3(4)
B(9)-B(10)-Br(10)	122.1(4)
B(8)-B(10)-Br(10)	121.7(4)
B(4)-B(10)-Br(10)	122.8(4)
B(11)-B(10)-Br(10)	120.8(4)
B(8)-B(11)-B(7)	107.5(4)
B(8)-B(11)-B(9)	107.1(5)
B(7)-B(11)-B(9)	60.3(3)
B(8)-B(11)-B(5)	59.8(3)
B(7)-B(11)-B(5)	59.7(3)
B(9)-B(11)-B(5)	107.6(4)
B(8)-B(11)-B(10)	59.7(3)
B(7)-B(11)-B(10)	107.8(5)
B(9)-B(11)-B(10)	59.4(3)
B(5)-B(11)-B(10)	107.6(5)
B(8)-B(11)-Br(11)	125.2(4)
B(7)-B(11)-Br(11)	120.0(4)
B(9)-B(11)-Br(11)	118.8(4)
B(5)-B(11)-Br(11)	124.1(4)
B(10)-B(11)-Br(11)	121.6(4)
C(14)-C(1)-C(8)	120.0(5)
C(14)-C(1)-C(2)	120.6(5)
C(8)-C(1)-C(2)	119.4(5)
C(7)-C(2)-C(3)	118.8(6)

C(7)-C(2)-C(1)	121.9(5)
C(3)-C(2)-C(1)	119.2(5)
C(4)-C(3)-C(2)	119.2(6)
C(5)-C(4)-C(3)	121.0(6)
C(4)-C(5)-C(6)	120.8(6)
C(7)-C(6)-C(5)	118.8(6)
C(2)-C(7)-C(6)	121.3(6)
C(9)-C(8)-C(13)	118.2(5)
C(9)-C(8)-C(1)	120.5(5)
C(13)-C(8)-C(1)	121.1(5)
C(10)-C(9)-C(8)	120.2(6)
C(9)-C(10)-C(11)	121.3(5)
C(10)-C(11)-C(12)	119.8(5)
C(13)-C(12)-C(11)	120.1(6)
C(12)-C(13)-C(8)	120.3(5)
C(19)-C(14)-C(15)	118.9(5)
C(19)-C(14)-C(1)	120.5(5)
C(15)-C(14)-C(1)	120.6(6)
C(16)-C(15)-C(14)	119.4(6)
C(17)-C(16)-C(15)	120.2(6)
C(16)-C(17)-C(18)	122.2(6)
C(17)-C(18)-C(19)	118.4(6)
C(18)-C(19)-C(14)	120.8(5)
C(2T)-C(1T)-C(6T)	118.2(7)
C(2T)-C(1T)-C(7T)	121.8(7)
C(6T)-C(1T)-C(7T)	120.0(7)
C(1T)-C(2T)-C(3T)	121.0(7)
C(4T)-C(3T)-C(2T)	119.3(7)
C(3T)-C(4T)-C(5T)	120.4(8)
C(6T)-C(5T)-C(4T)	120.5(8)
C(5T)-C(6T)-C(1T)	120.6(7)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3) for $Ph_3C[HCB_{11}Br_{11}]$. The anisotropic displacement factor exponent takes the form:

$$-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	27(1)	28(1)	9(1)	5(1)	2(1)	2(1)
Br(2)	28(1)	12(1)	19(1)	4(1)	4(1)	2(1)
Br(3)	20(1)	23(1)	20(1)	2(1)	8(1)	-7(1)
Br(4)	23(1)	20(1)	14(1)	-4(1)	7(1)	1(1)
Br(5)	21(1)	15(1)	15(1)	-6(1)	-1(1)	-3(1)
Br(6)	21(1)	22(1)	14(1)	-5(1)	-4(1)	-5(1)
Br(7)	20(1)	18(1)	12(1)	-1(1)	5(1)	4(1)
Br(8)	14(1)	21(1)	21(1)	-3(1)	-1(1)	2(1)
Br(9)	16(1)	22(1)	17(1)	1(1)	4(1)	-6(1)
Br(10)	20(1)	10(1)	20(1)	0(1)	2(1)	0(1)
Br(11)	20(1)	19(1)	8(1)	4(1)	0(1)	1(1)
C(1B)	15(2)	16(2)	10(2)	1(2)	2(2)	-1(2)
B(1)	13(2)	16(2)	12(2)	1(2)	2(2)	-2(2)
B(2)	16(2)	13(2)	13(2)	2(2)	0(2)	-2(2)
B(3)	16(2)	13(2)	13(2)	-2(2)	2(2)	-3(2)
B(4)	15(2)	15(2)	9(2)	-2(2)	0(2)	-3(2)
B(5)	14(2)	9(2)	15(2)	-3(2)	2(2)	0(2)
B(6)	15(2)	14(2)	12(2)	0(2)	-1(2)	-2(2)
B(7)	15(2)	13(2)	12(2)	0(2)	1(2)	0(2)
B(8)	15(2)	14(2)	9(2)	-5(2)	2(2)	-1(2)
B(9)	15(2)	14(2)	12(2)	1(2)	0(2)	-3(2)
B(10)	18(2)	11(2)	9(2)	0(2)	0(2)	-3(2)
B(11)	16(2)	12(2)	9(2)	0(2)	2(2)	0(2)
C(1)	19(2)	13(2)	13(2)	-7(2)	6(2)	1(2)
C(2)	19(2)	19(2)	14(2)	-4(2)	5(2)	3(2)
C(3)	21(2)	19(2)	16(3)	-1(2)	7(2)	0(2)
C(4)	25(2)	24(2)	20(3)	1(2)	9(2)	-4(2)

C(5)	30(2)	30(3)	16(3)	6(2)	8(2)	3(2)
C(6)	30(2)	35(3)	14(3)	2(2)	0(2)	1(2)
C(7)	23(2)	26(2)	15(3)	-2(2)	3(2)	-2(2)
C(8)	19(2)	18(2)	15(3)	-5(2)	2(2)	-2(2)
C(9)	19(2)	19(2)	15(3)	-3(2)	1(2)	-1(2)
C(10)	16(2)	27(2)	16(3)	-4(2)	2(2)	0(2)
C(11)	16(2)	30(2)	18(3)	1(2)	6(2)	-2(2)
C(12)	25(2)	24(2)	22(3)	1(2)	6(2)	-2(2)
C(13)	19(2)	20(2)	23(3)	0(2)	6(2)	-1(2)
C(14)	20(2)	13(2)	20(2)	-5(2)	6(2)	3(2)
C(15)	20(2)	18(2)	28(3)	1(2)	8(2)	1(2)
C(16)	22(2)	25(3)	37(3)	5(2)	10(2)	5(2)
C(17)	22(2)	23(3)	39(3)	7(2)	5(2)	10(2)
C(18)	24(2)	22(3)	27(3)	4(2)	4(2)	6(2)
C(19)	19(2)	16(2)	22(3)	-2(2)	4(2)	4(2)
C(1T)	39(2)	20(3)	40(3)	-8(2)	11(2)	12(2)
C(2T)	38(2)	23(3)	43(3)	-9(2)	10(2)	12(2)
C(3T)	48(3)	30(3)	43(3)	-8(3)	18(3)	3(2)
C(4T)	60(3)	39(3)	39(3)	-4(3)	9(3)	4(3)
C(5T)	55(3)	42(3)	41(3)	-7(3)	1(3)	3(3)
C(6T)	43(3)	33(3)	42(3)	-11(3)	9(2)	3(2)
C(7T)	56(4)	34(4)	48(4)	0(3)	14(3)	13(3)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for $Ph_3C[HCB_{11}Br_{11}]$.

	x	y	z	U(eq)
H(1)	9871	659	4339	20
H(3A)	8214	25	-291	22
H(4A)	8077	873	-1366	27
H(5A)	6842	943	-2697	30
H(6A)	5695	161	-2987	31
H(7A)	5780	-678	-1877	26
H(9A)	5305	-434	-224	21
H(10A)	3947	-854	337	24
H(11A)	3895	-1883	765	25
H(12A)	5271	-2488	764	28
H(13A)	6695	-2061	331	25
H(15A)	8721	-996	-994	26
H(16A)	10186	-1371	-196	33
H(17A)	10307	-1726	1460	33
H(18A)	9001	-1695	2411	29
H(19A)	7498	-1365	1607	23
H(2TA)	8278	-2998	279	41
H(3TA)	8200	-2477	-1290	47
H(4TA)	6806	-2533	-2440	55
H(5TA)	5505	-3111	-2055	56
H(6TA)	5565	-3619	-507	47
H(7TA)	7596	-3638	1455	68
H(7TB)	6879	-4143	909	68
H(7TC)	6455	-3556	1430	68