Supplementary Information to

Simple and scalable synthesis of the carborane anion $CB_{11}H_{12}^-$

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General details

NMR spectra for purified products were measured in acetone-d_6, and the following referencing was used: ^{1}H and ^{13}C – internal TMS (δ=0.00 ppm); ^{10}B and ^{11}B, signal of $BF_3 \cdot Et_2O$ as an external standard (δ=0.00 ppm). Crude reaction mixtures were analyzed in nondeuterated solvents without deuterium lock. ^{1}H, ^{10}B, $^{10}B\{^{1}H\}$, ^{11}B, $^{11}B\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 700 spectrometer working at 700.1 MHz, 75.2 MHz, 224.6 MHz, 176.0 MHz for ^{1}H, ^{10}B, ^{11}B, ^{13}C, respectively. All the NMR measurements were carried out at 25.0 °C, except for the reaction monitoring experiments that were carried out 60.0 °C. For a reaction monitoring experiment a 5 mm heavy wall NMR sample tube with a gas-tight quick pressure valve was used. Before addition of CF_3SiMe_3 to the substrate and NaH mixture in THF, the NMR tube was cooled to -10 °C.

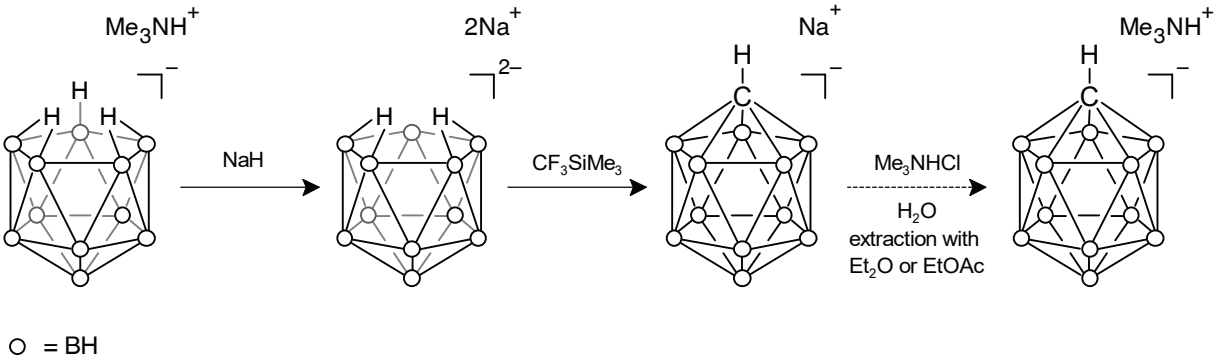
Melting points were determined with capillary melting point apparatus Büchi B-540 (with a range between ambient and 410 °C) and are uncorrected.

ATR-IR spectra were recorded on a Thermo Electron Nicolet 6700 FT-IR device with Smart Orbit micro-ATR and diamond crystal. Spectrometer had a DTGS CsI detector and CsI beamsplitter. 128 scans were recorded over the range of 400–4000 cm^{-1}. Spectrum is not ATR-corrected.

HRMS spectra were measured on Thermo Electron LTQ Orbitrap XL spectrometer with ESI method, and $[M]^-$ ions were detected.

For reactions conducted with CF_3SiMe_3, Ace pressure tubes, round-bottomed flasks or bottles with total capacities ranging from 8–950 mL and pressure ratings of 60–150 psig were used. The reaction vessels were plugged hand tightly with “front seal” type Teflon screw caps. Howeve, the FETFE (fluoroelastomer compound with TFE additives) O-rings supplied with the PTFE plugs for sealing the pressure vessels were not stable under the reaction conditions and therefore these were replaced with wrapping PTFE-tape (plumber's tape) around the lower part of the screw cap’s thread. Closed reaction vessels were immersed in an oil bath preheated at 60 °C.

Tested conditions



○ = BH

Table S1. Tested conditions.

Amount of substrate $B_{11}H_{14}^-$ Me_3NH^+	Solvent	Reagents*	Heating time, temperature, setup†	Result, yield*
50 mg, 0.26 mmol	THF 3 mL	CF_3SiMe_3 (400 µL, 385 mg, 2.7 mmol, 10 eq)	48 h, 50 °C, 15 mL Ace tube	No reaction, just unreacted $B_{11}H_{14}^-$
100 mg, 0.52 mmol	THF 4 mL	NaH (60% dispersion in oil, 52 mg, 1.3 mmol, 2.5 eq), CF_3SiMe_3 (150 µL, 144 mg, 1.0 mmol, 2 eq), NaI (150 mg, 1.0 mmol, 2 eq)	20 h, 25 °C, reflux setup	Mostly unreacted $B_{11}H_{14}^-$, some borate, <5% $CB_{11}H_{12}^-$ detected
100 mg, 0.52 mmol	THF 4 mL	NaH (60% dispersion in oil, 52 mg, 1.3 mmol, 2.5 eq), CF_3SiMe_3 (150 µL, 144 mg, 1.0 mmol, 2 eq), NaI (150 mg, 1.0 mmol, 2 eq)	22 h, 65 °C, reflux setup	Mostly unreacted $B_{11}H_{14}^-$, a lot of borate, <5% $CB_{11}H_{12}^-$ detected
100 mg, 0.52 mmol	THF 5 mL	NaH (60% dispersion in oil, 100 mg, 2.5 mmol, 5 eq), CF_3SiMe_3 (400 µL, 385 mg, 2.7 mmol, 5 eq), NaI (390 mg, 2.6 mmol, 5 eq)	60 h, 25 °C, 15 mL Ace tube	Ca 6:3:1 ratio of $CB_{11}H_{12}^-$/$B_{11}H_{14}^-$/borate
100 mg, 0.52 mmol	THF 4 mL	NaH (60% dispersion in oil, 400 mg, 10 mmol, 19 eq), CF_3SiMe_3 (800 µL, 770 mg, 5.4 mmol, 10 eq), NaI (780 mg, 5.2 mmol, 10 eq)	23 h, 25 °C, 15 mL Ace tube	Ca 1:1:5 ratio of $CB_{11}H_{12}^-$/$B_{11}H_{14}^-$/borate
100 mg, 0.52 mmol	THF 5 mL	NaH (60% dispersion in oil, 400 mg, 10 mmol, 19 eq), CF_3SiMe_3 (800 µL, 770 mg, 5.4 mmol, 10 eq), NaI (780 mg, 5.2 mmol, 10 eq)	100 h, 25 °C, 9 mL Ace tube	Ca 50% conversion
100 mg, 0.52 mmol	THF 5 mL	NaH (60% dispersion in oil, 400 mg, 10 mmol, 19 eq), CF_3SiMe_3 (2×800 µL, 2×10 eq), NaI (780 mg, 5.2 mmol, 10 eq)	71 h + 48 h, 50 °C, 15 mL Ace tube	Mostly $CB_{11}H_{12}^-$, just some residue of $B_{11}H_{14}^-$
100 mg, 0.52 mmol	THF 6 mL	NaH (60% dispersion in oil, 108 mg, 2.7 mmol, 5.2 eq), CF_3SiMe_3 (188 mg, 1.32 mmol, 2.5 eq), TBAT (15 mg, 28 µmol, 5 mol%)	20 h, 25 °C, 15 mL Ace tube	Less than 50% conversion
100 mg, 0.52 mmol	THF 6 mL	NaH (60% dispersion in oil, 108 mg, 2.7 mmol, 5.2 eq), CF_3SiMe_3 (408 mg, 2.9 mmol, 5.5 eq), TBAT (18 mg, 33 µmol, 6 mol%)	20 h, 25 °C, 15 mL Ace tube	Less than 50% conversion

100 mg, 0.52 mmol	THF 5 mL	NaH (60% dispersion in oil, 400 mg, 10 mmol, 19 eq), CF_3SiMe_3 (800 µL, 770 mg, 5.4 mmol, 10 eq)	93 h, 50 °C, 15 mL Ace tube	Mostly $CB_{11}H_{12}^-$, almost no $B_{11}H_{14}^-$ left, no borate
100 mg, 0.52 mmol	THF 5 mL	NaH (60% dispersion in oil, 400 mg, 10 mmol, 19 eq), CF_3SiMe_3 (800 µL, 770 mg, 5.4 mmol, 10 eq), NaI (780 mg, 5.2 mmol, 10 eq)	93 h, 0 °C, 10 mL screw-cap vial	No $B_{11}H_{14}^-$, correct product, but strong borate signal
100 mg, 0.52 mmol	THF 5 mL	NaH (60% dispersion in oil, 400 mg, 10 mmol, 19 eq), CF_3SiMe_3 (800 µL, 770 mg, 5.4 mmol, 10 eq)	22 h, 50 °C, 15 mL Ace tube	Ca 80% conversion, unknown impurities visible
100 mg, 0.52 mmol	THF 5 mL	NaH (60% dispersion in oil, 400 mg, 10 mmol, 19 eq), CF_3SiMe_3 (750 µL, 722 mg, 5.1 mmol, 10 eq)	20 h, 100 °C, 15 mL Ace tube	>80% conversion
93 mg, 0.48 mmol	THF 4 mL	NaH (95% purity, 295 mg, 11.7 mmol, 24 eq), CF_3SiMe_3 (600 µL, 580 mg, 4.1 mmol, 8.5 eq)	94 h, 60 °C, glove-box, 15 mL Ace tube	Correct product, no $B_{11}H_{14}^-$
100 mg, 0.52 mmol	THF 4 mL	NaH (95% purity, 64 mg, 2.5 mmol, 4.8 eq), CF_3SiMe_3 (368 mg, 2.59 mmol, 5 eq)	69 h, 60 °C, glove-box, 15 mL Ace tube	Correct product, no $B_{11}H_{14}^-$, no borate
100 mg, 0.52 mmol	THF 4 mL	NaH (95% purity, 62 mg, 2.45 mmol, 4.7 eq), CF_3SiMe_3 (176 mg, 1.24 mmol, 2.4 eq)	91 h, 60 °C, glove-box, 8 mL Ace tube	Correct product, just minor $B_{11}H_{14}^-$ signals
500 mg, 2.59 mmol	THF 8 mL	NaH (60% dispersion in oil, 2.00 g, 50 mmol, 19 eq), CF_3SiMe_3 (1.5 mL, 1.44 g, 10.2 mmol, 3.9 eq)	90 h, 50 °C, 15 mL Ace tube	440 mg, 2.17 mmol, 84%
1.50 g, 7.77 mmol	THF 25 mL	NaH (95% purity, 973 mg, 38.5 mmol, 5 eq), CF_3SiMe_3 (3.0 mL, 2.89 g, 20.3 mmol, 2.6 eq)	68 h, 60 °C, glove-box, 100 mL Ace tube	1.48 g, 7.29 mmol, 94%
1.436 g, 7.43 mmol	THF 25 mL	NaH (95% purity, 1037 mg, 41.0 mmol, 5.5 eq), CF_3SiMe_3 (3.0 mL, 2.89 g, 20.3 mmol, 2.7 eq)	68 h, 60 °C, glove-box, 100 mL Ace flask	1.44 g, 7.09 mmol, 95%
1.51 g, 7.82 mmol	THF 25 mL	NaH (60% dispersion in oil, 1.73 g, 43.3 mmol, 5.5 eq), CF_3SiMe_3 (3.0 mL, 20.3 mmol, 2.6 eq)	72 h, 60-70 °C, 100 mL Ace flask	1.509 g, 7.43 mmol, 95%
15.01 g, 77.7 mmol	THF 300 mL	NaH (60% dispersion in oil, 17.5 g, 438 mmol, 5.6 eq), CF_3SiMe_3 (31.0 mL, 210 mmol, 2.7 eq)	63 h, 60 °C, 950 mL Ace bottle	13.76 g, 67.7 mmol, 87%

* TBAT = Tetrabutylammonium difluorotriphenylsilicate

† *Reflux setup* – a reaction was carried out in a round-bottomed flask with a Liebig condenser and an Ar balloon; *glove-box* – reagent transfers and mixing were carried out inside a glove-box, the Ace tubes were tightly closed with a screw-cap and then removed from the glove-box for the heating procedure; if setup is not noted, then reagent transfers and mixing were carried out in a fumehood under Ar gas flow.

* Isolated yield (the product $CB_{11}H_{12}^-$ Me_3NH^+ was isolated only in larger scale (*i.e.* >500 mg of substrate) reactions having a full conversion in the 2nd step). Conversion of the reaction was evaluated from $^{10}B\{^1H\}$ NMR spectra of the crude reaction mixture.

Photos of the 15 g scale reaction

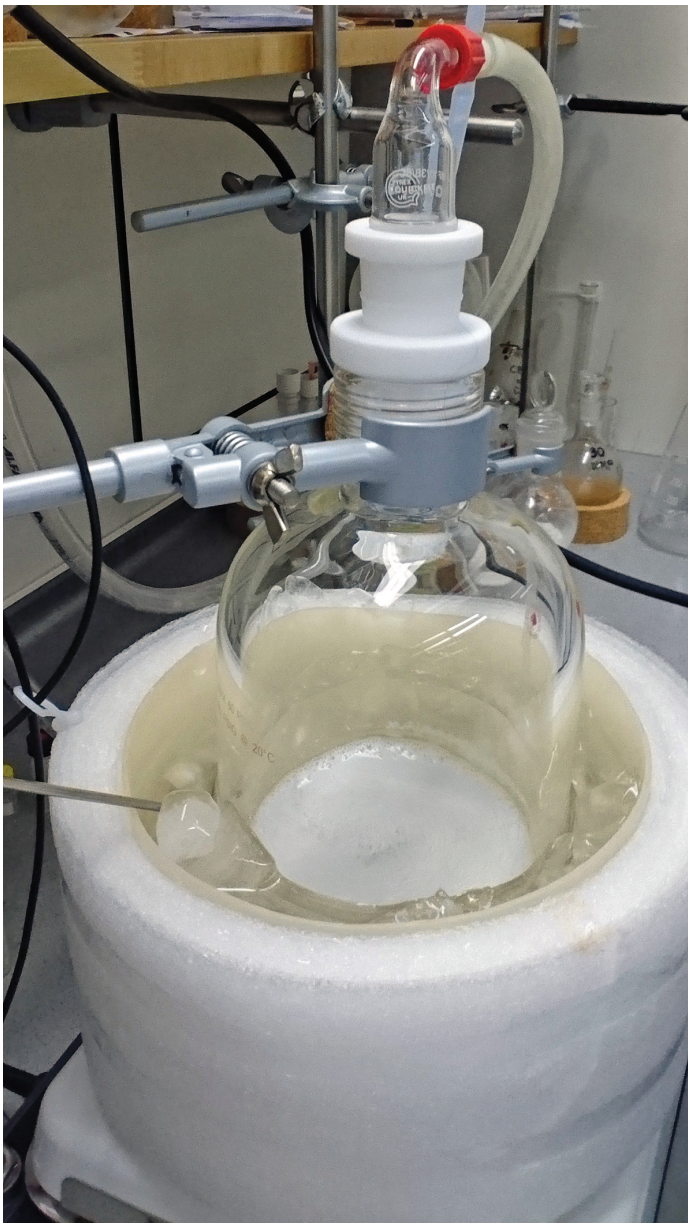
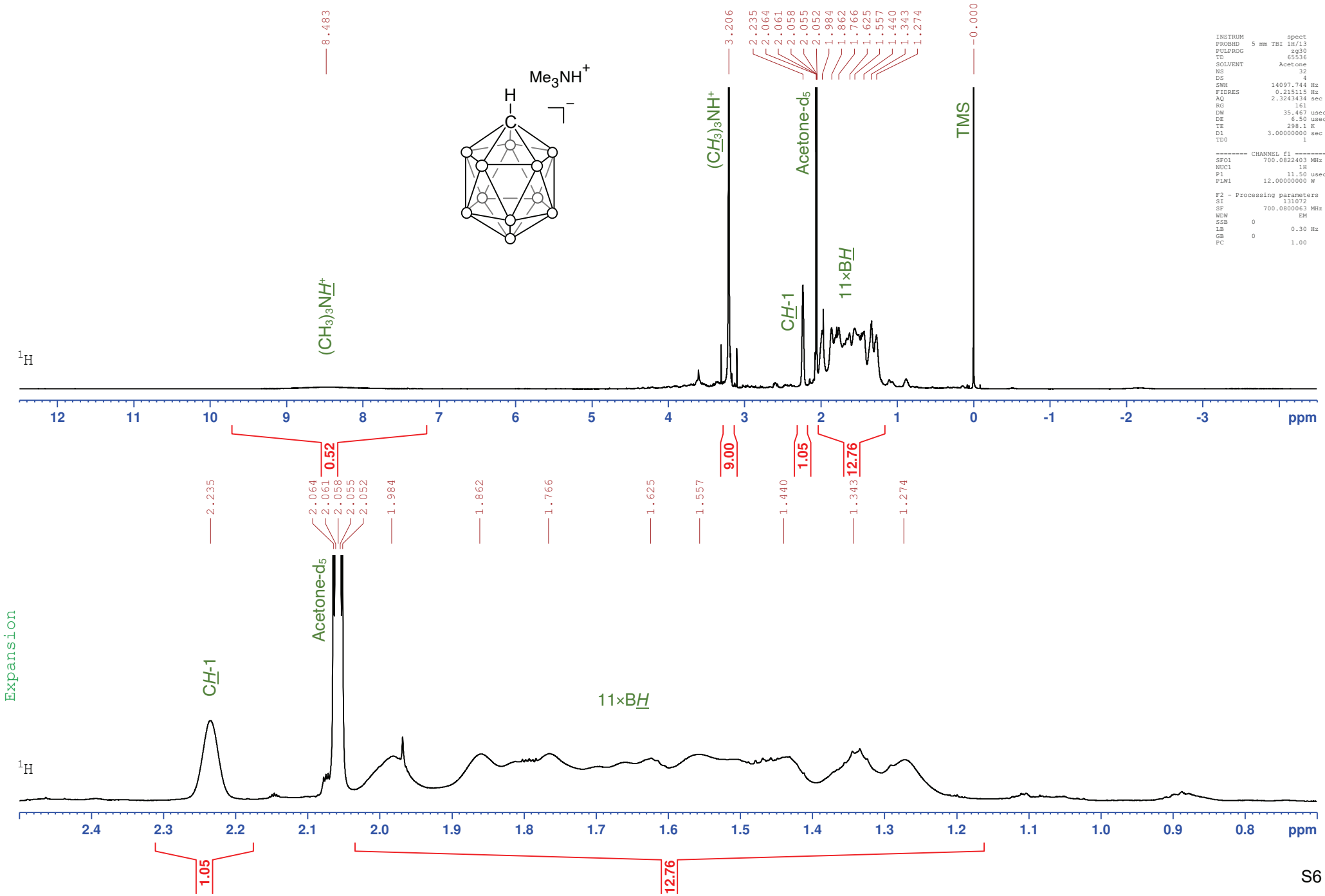


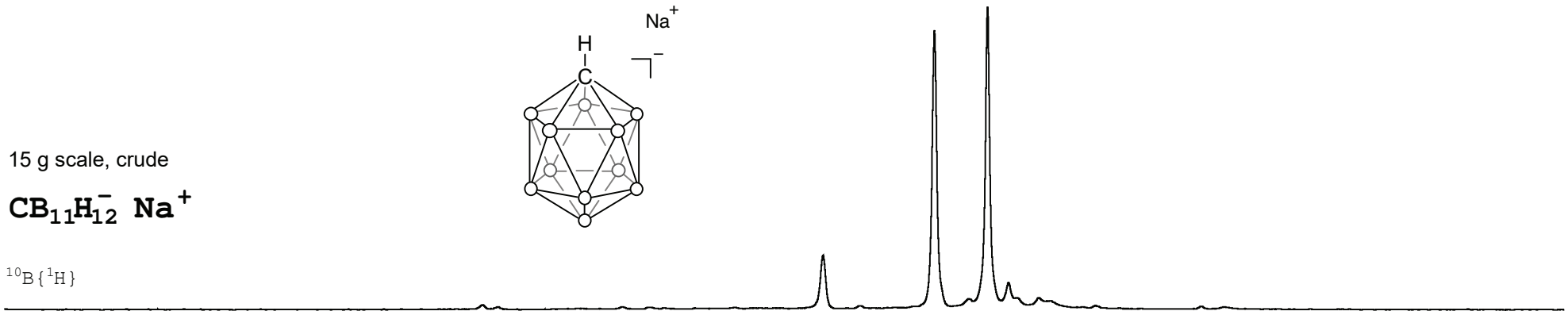
Photo 1. Evacuation of the reaction mixture under vacuum (300 mbar) after addition of NaH. 950 mL heavy walled glass vessel (from Ace Glass Inc.) attached to a vacuum line and placed in a ice-water cooling bath.

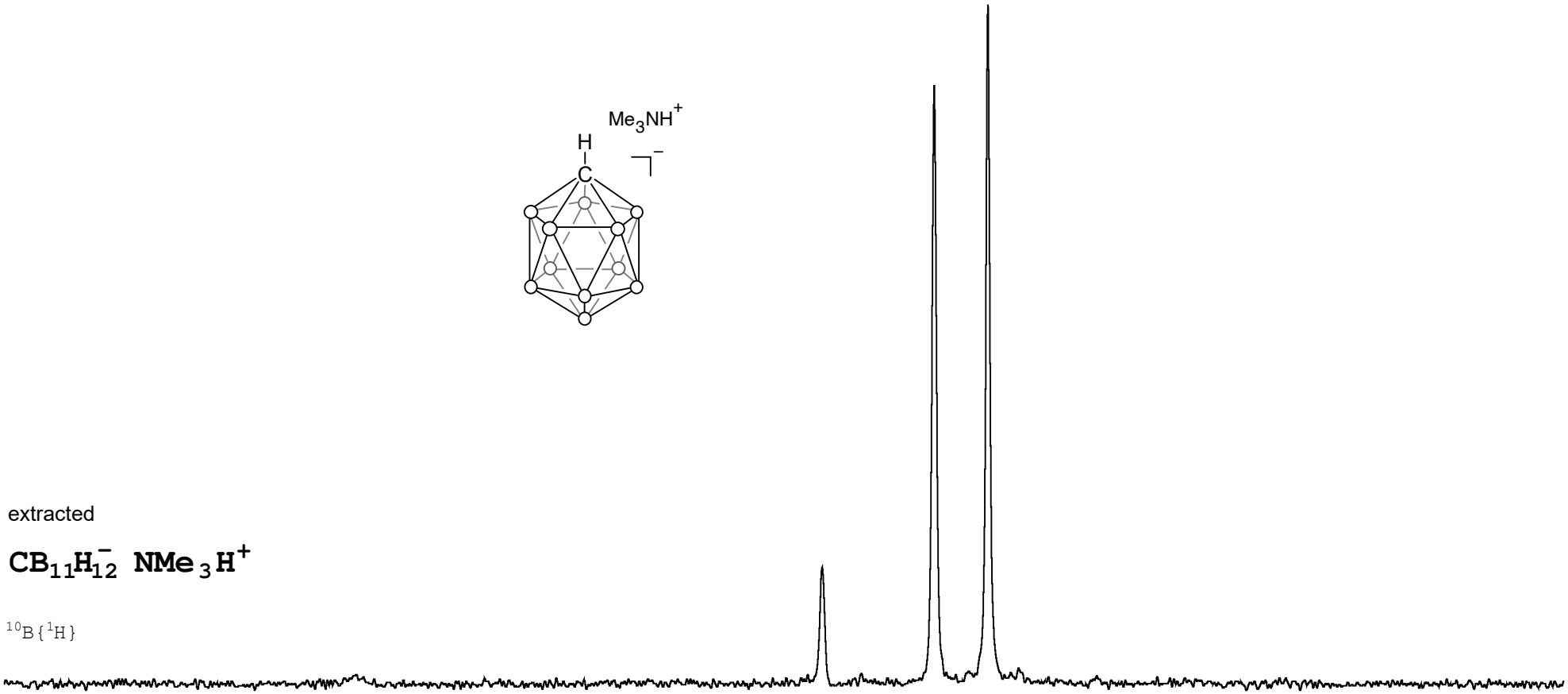
Photo 2. Heating of the reaction mixture at 60 °C after addition of CF_3SiMe_3 in a tightly closed reaction vessel immersed in an oil bath preheated at 60 °C.

^{1}H NMR spectrum (700.1 MHz) of $CB_{11}H_{12}^-$ NMe_3H^+ in acetone-d_6

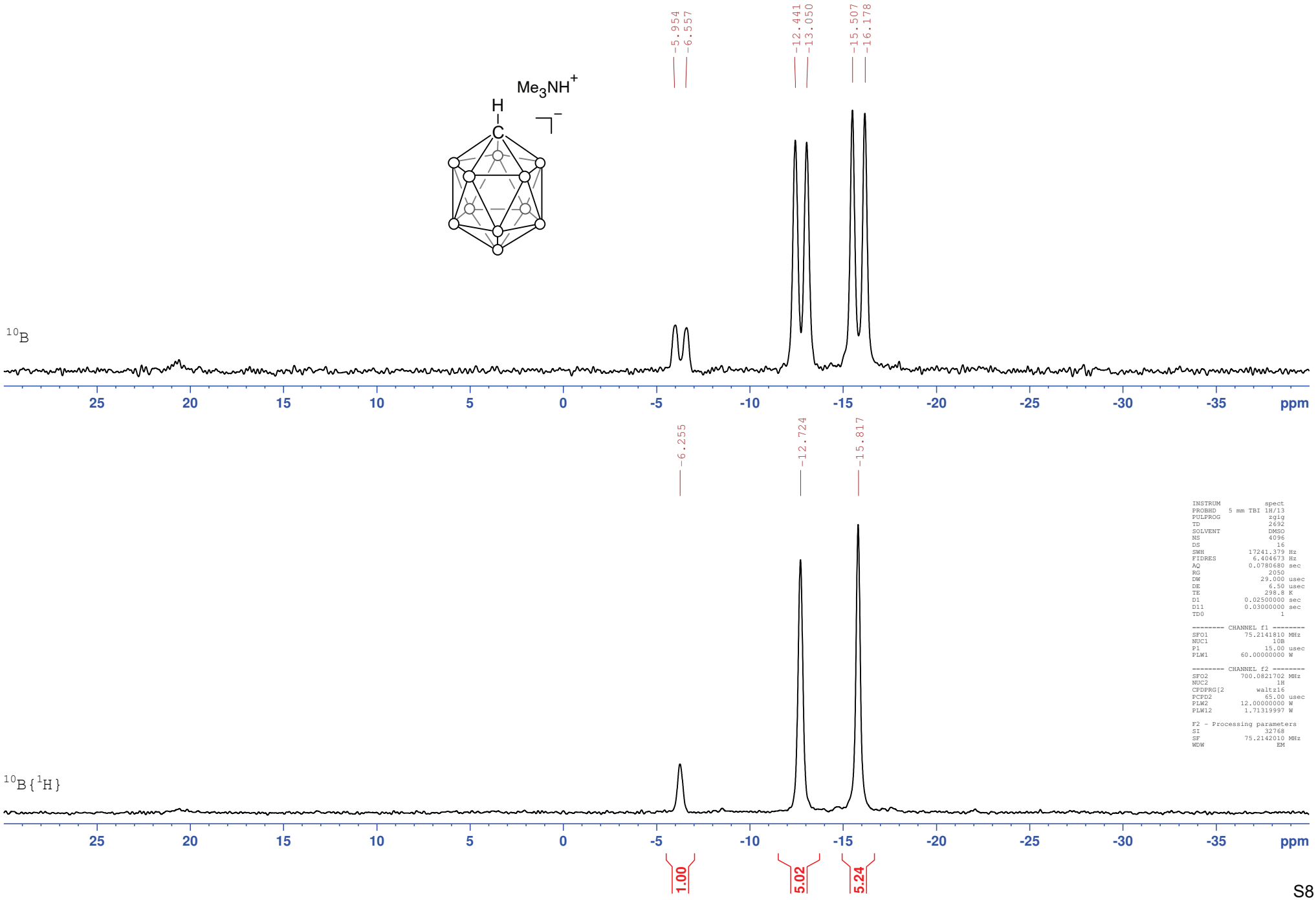


$^{10}B\{^{1}H\}$ NMR spectra (75.2 MHz) of $CB_{11}H_{12}^-$





^{10}B and $^{10}B\{^1H\}$ NMR spectra (75.2 MHz) of $CB_{11}H_{12}^-$ NMe_3H^+ in acetone-d_6

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RG                 2050
DW               29.000 usec
DE                6.50 usec
TE                298.8 K
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D11          0.03000000 sec
TD0                   1

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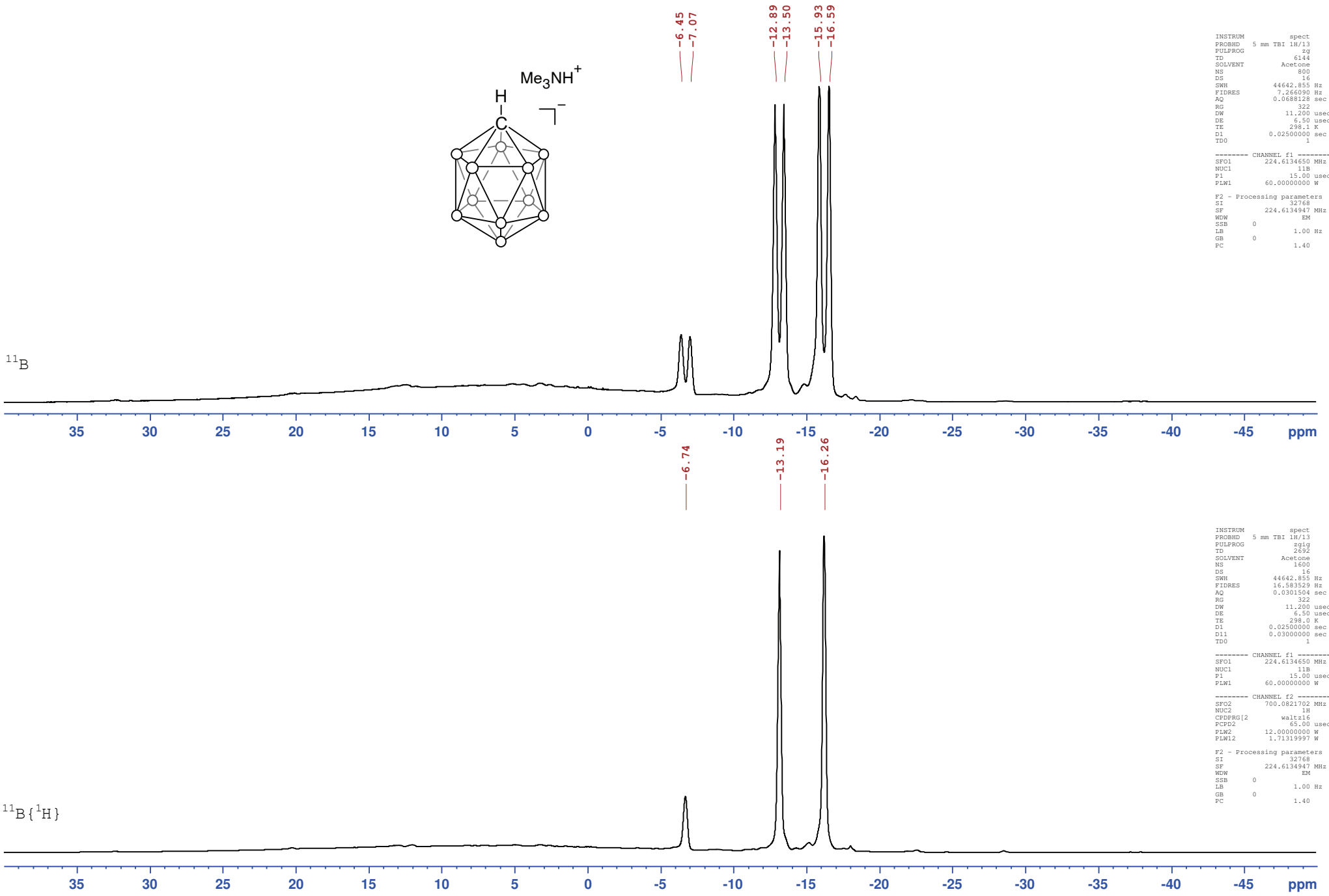
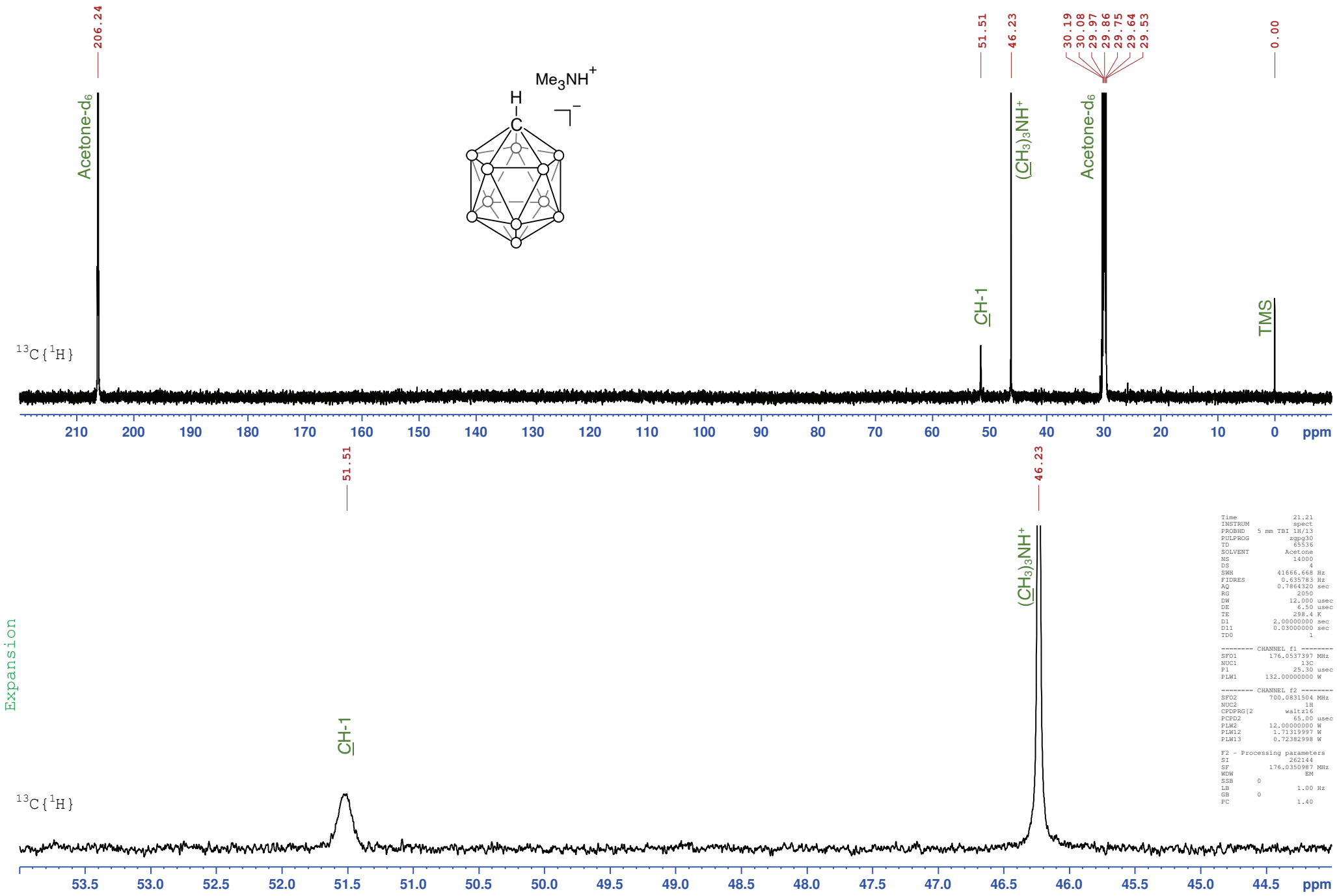
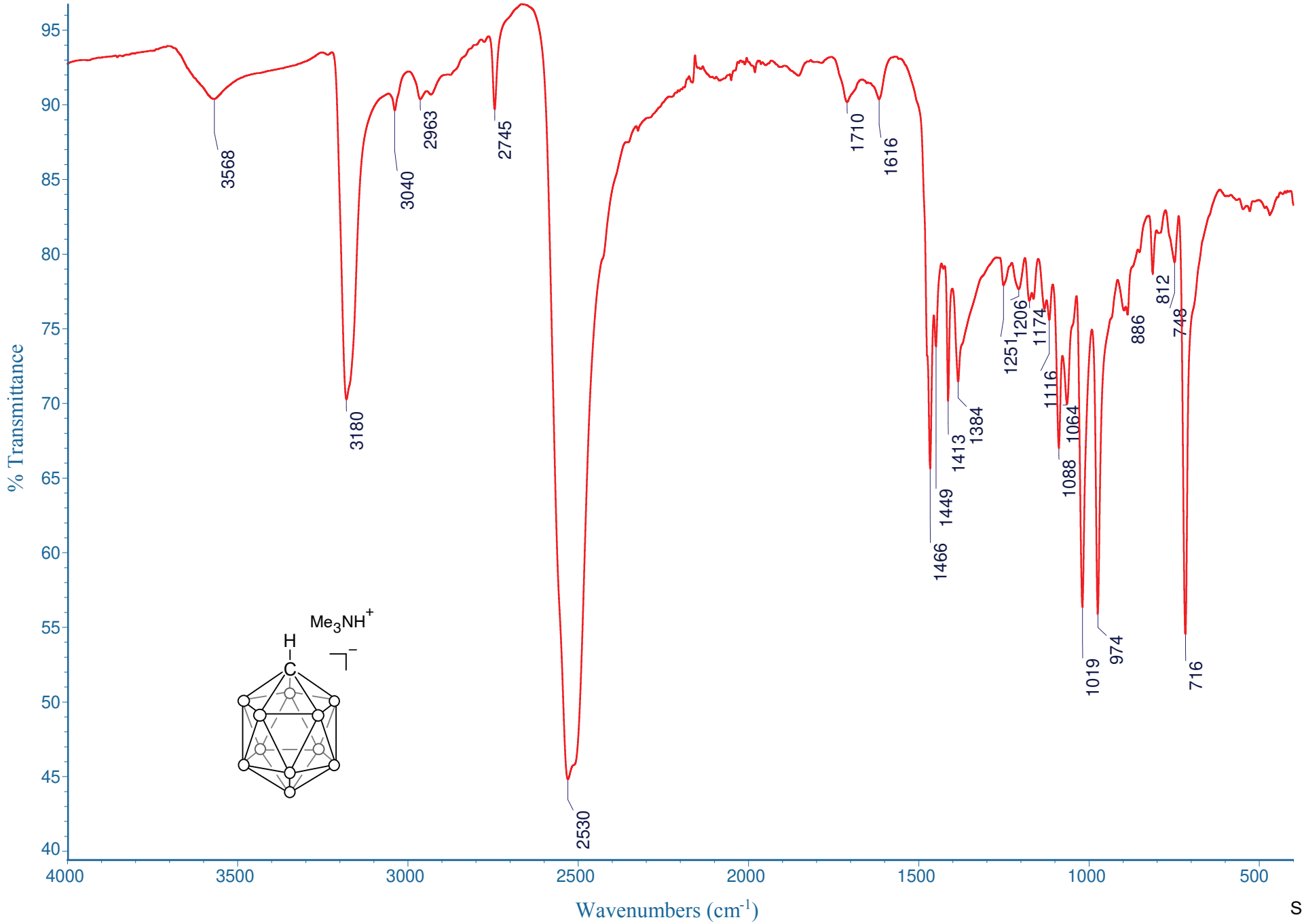
^{11}B and $^{11}B\{^1H\}$ NMR spectra (224.6 MHz) of $CB_{11}H_{12}^-$ NMe_3H^+ in acetone-d_6



$^{13}C\{^{1}H\}$ NMR spectrum (176.0 MHz) of $CB_{11}H_{12}^{-}$ NMe_3H^{+} in acetone-d_6



IR spectrum of $CB_{11}H_{12}^{-}$ NMe_3H^{+}



HRMS of 1-carba-*closo*-dodecaborate(–) anion $CB_{11}H_{12}^-$

A $CB_{11}H_{12}^-$ $(CH_3)_3NH^+$ sample.