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Original Scientific Article

12-(*N*-Methylnitrilium)monocarba-*closo*-dodecaborate Ylide[†]

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Abstract. The syntheses, spectral characterization, and crystal structures of 12-(*N*-methylnitrilium)-monocarba-*closo*-dodecaborate and 12-(*N*-methylamidinium)-monocarba-*closo*-dodecaborate ylides are reported. The carborate anion behaves as an inert and non-conjugating negative charge.

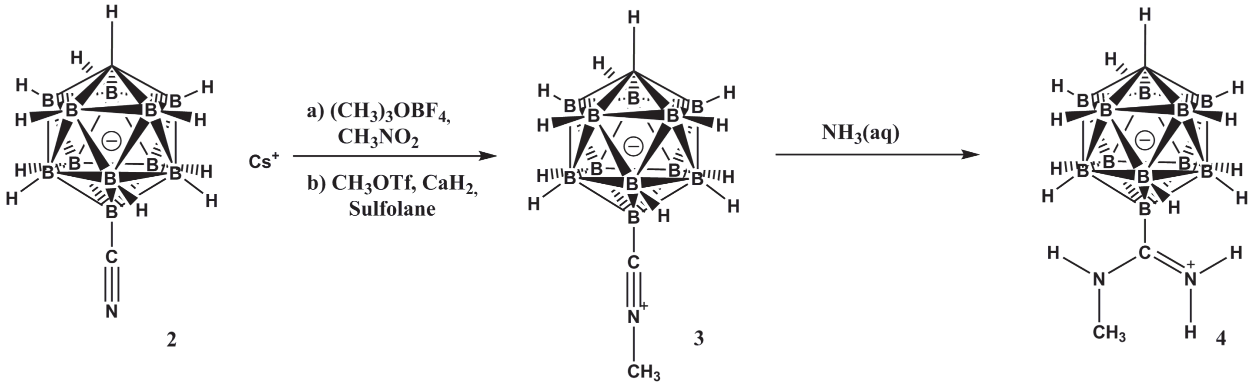
Keywords: ylide, carborane, monocarba-*closo*-dodecaborate, nitrilium

INTRODUCTION

Knowledge of the chemistry of the weakly coordinating, weakly nucleophilic, and highly stable icosahedral monocarba-*closo*-dodecaborate anion $CB_{11}H_{12}^{-}$(**1**) and its derivatives has been expanding rapidly for several decades.[1] Although several electroneutral ylides in which the negatively charged CB_{11}^{-} moiety carries a positively charged substituent are known,[2–5] their chemistry has been little explored. We now report the conversion of the 12-cyanomonocarba-closo-dodecaborate anion (**2**)[6,7] into a new member of this class, 12-(*N*-methylnitrilium)-monocarba-*closo*-dodecaborate ylide (**3**), in which the positively charged substituent is the highly reactive -$CN^{+}CH_3$ (*N*-methylnitrilium) group. Nitrilium cations and ylides are generally valued as versatile 3+2 cycloaddition partners in heterocyclic synthesis[8–11] but only a few nitrilium ylides with a negatively charged boron center attached to the carbon are known.[12–16]

RESULTS

The ylide **3** has been prepared from the 12-cyanomonocarba-*closo*-dodecaborate anion 12-$CNCB_{11}H_{11}^{-}$ (**2**)[6,7] by reaction with trimethyloxonium tetrafluoroborate in nitromethane or by treatment with methyl triflate in sulfolane under conditions ordinarily used for methylation of the BH vertices of **1**[17] (Scheme 1). The



Scheme 1. Preparation of 12-(*N*-methylnitrilium)-monocarba-*closo*-dodecaborate ylide (**3**) and its subsequent reaction with ammonia.

[†] Dedicated to Dr. Mirjana Eckert-Maksić on the occasion of her 70th birthday.
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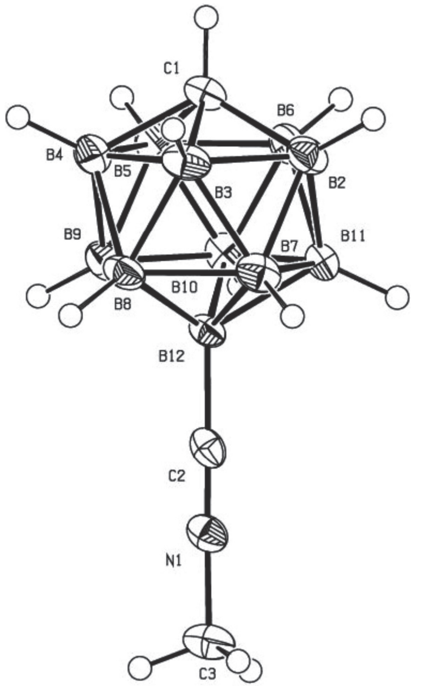

Figure 1. ORTEP representation of **3**. Thermal ellipsoids of non-hydrogen atoms are drawn at 50 % probability.

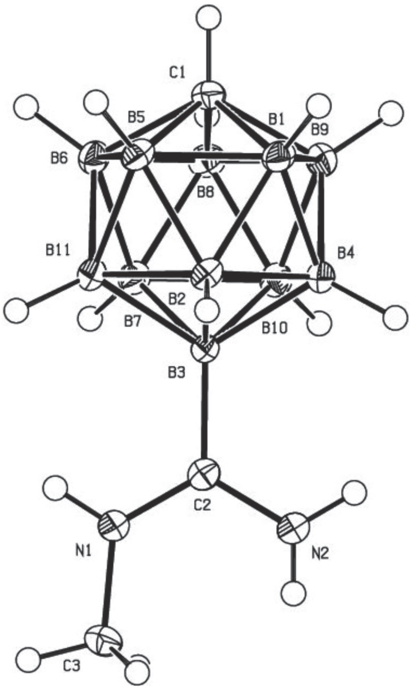

Figure 2. ORTEP representation of **4**. Thermal ellipsoids of non-hydrogen atoms are drawn at 50 % probability.

methylation reactions are clean and no substitution at the BH vertices in **2** occurs, illustrating the deactivating effect of the cyano group. Although the resulting *N*-methylnitrilium ylide (**3**) reacts readily with nucleophiles, it can be easily isolated. Reaction of **3** with aqueous NH_3 can be performed in situ or after isolation and affords the *N*-methylamidinium ylide **4**. Single crystals of **3** and **4** suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-pentane into a concentrated solution in CH_2Cl_2 (Figures 1 and 2). The quality of the single crystal of **3** and consequently the precision of structure determination were markedly affected by severe cracking of the crystal as it was cooled. An attempt to determine the structure at room temperature was unsuccessful due to overall disorder of the carborane cage. In spite of this drawback, the reported low-temperature structural parameters of **3**, like those of **4**, lie within the common range. For example, they compare well with parameters reported for cesium 12-(2-phenylethynyl)-closo-1-carbadodecaborate.[18]

Table 1 lists the most important bond lengths and stretching frequencies of the new ylide **3** and several related compounds and compares them with the results of DFT calculations (BP86/SV(P)). Natural atomic charges calculated by the NBO method[19] are also shown.

Table 1. Selected Observed and DFT (BP86/SV(P)) Calculated Characteristics of Nitriles, Nitrilium Cations, and Nitrilium Ylides

cmpd.	$[CB_{11}H_{11}CN]^-$	$CB_{11}H_{11}CNMe$ (**3**)	$[(CF_3)_3BCN]^-$	$(CF_3)_3BCNMe$	PhCN	$[PhCNMe]^+$	$[CpCN]^-$	CpCNMe
q(**R**–C≡N–CH$_3$)[a]	–0.10	–0.21	–0.06	–0.07	–0.22	–0.23	–0.30	–0.25
q(R–**C**≡N–CH$_3$)[a]	0.16	0.55	0.12	0.49	0.29	0.62	0.31	0.51
q(R–C≡**N**–CH$_3$)[a]	–0.38	–0.30	–0.40	–0.30	–0.31	–0.24	–0.49	–0.40
q(R–C≡N–**C**H$_3$)[a]	n/a	–0.44	n/a	–0.43	n/a	–0.43	n/a	–0.42
$\tilde{\nu}$ (C≡N) calcd.[b]	2238	2315	2240	2330	2265	2363	2192	2147
$\tilde{\nu}$ (C≡N) obsd.[b]	2215[7]	2357	2244[16]	n/a	2229[20]	2360[21]	n/a	n/a
r(C≡N) calcd.[c]	117.5	117.1	117.4	116.8	117.4	116.9	118.6	121.4
r(C≡N) obsd.[c]	113.3(4)[7]	113.2(4)	116.9[16]	n/a	n/a	n/a	n/a	n/a

[a] NBO atomic partial charge on the bold italicized atom (|e⁻|). The value for ***R*** refers to the first atom of the substituent R.

[b] Nitrile stretching vibration (cm^{-1}).

[c] C≡N bond length (pm).

DISCUSSION

Numerous nitrilium ylides are known, such as nitrile oxides,[22] sulfides,[23] and ylides carrying carbocyclic[24] or heterocyclic[25,26] anionic groups at the cyano nitrogen, as well as nitriliumphosphane ylides, which are usually used as reactive intermediates generated in situ.[27–29] However, only a limited number of stable nitrilium ylides have been isolated and thoroughly characterized.[25,26,30]

Most nitrilium ylides carry their negatively charged group at the nitrogen atom and allow this group to conjugate with the CN group. They display a characteristic IR stretch band at 2150–2200 cm^{-1}, strongly red-shifted from an ordinary cyano group of nitriles, suggesting a description of bonding in terms of cumulated double bonds. Only a few known nitrilium ylides carry a non-conjugating negatively charged group on the CN carbon[12–16] and in these, the IR stretch occurs near 2300 cm^{-1} and is thus similar to that in free nitrilium cations[31] and the related ylides of the type $R_3BC{=}NMe$, which are best described as Lewis acid-base adducts of RB_3 with an isonitrile.[32,33]

The new ylide **3** carries a negative charge adjacent to the CN carbon atom and thus belongs to the rarer category. Its CN stretch occurs at 2347 cm^{-1}, in a region characteristic of free nitrilium cations.[31] Among the known nitrilium ylides of this type, $(CF_3)_3B{-}CN{-}Me$ offers the closest analogy, in that it has also been prepared from the anionic nitrile by methylation on nitrogen. Both compounds carry the negative charge delocalized at a weakly coordinating anionic moiety adjacent to the nitrilium carbon, and the similarity is reflected in the calculated charge distribution (Table 1). The CB_{11} anion thus clearly acts as a non-conjugating substituent, and its negative charge is not available for donation of electron density to stabilize a cumulene resonance structure, which would weaken the CN bond and red-shift of the CN stretching band. These unconventional nitrilium ylides resemble their cationic analogs much more closely than the more usual ylide systems and are thus best described as carborane-nitrilium zwitterions.

The differences in the frequencies of the CN stretching vibration in **3** and in a series of more conventional nitrilium ylides have been reproduced by DFT calculations. While these did not reproduce the absolute magnitude of the experimentally observed frequencies very well, the tendency towards significantly higher wave numbers for the boron based nitrilium ylides after methylation is clearly reflected. These calculations also revealed that the charge distribution in **3** closely resembles that in free nitrilium cations[31] and differs strongly from that in the more ordinary nitrilium ylides.

EXPERIMENTAL PART

Materials

Unless otherwise noted, all reactions were carried out under argon atmosphere with dry solvents, freshly distilled under anhydrous conditions. Standard Schlenk and vacuum line techniques were employed for all manipulations of air- or moisture-sensitive compounds. Yields refer to isolated, spectroscopically homogenous materials. $NHMe_3^+CB_{11}H_{12}^{-1}$ (**1**) was purchased from Katchem Ltd. (Elišky Krásnohorské 6, Prague 110 00, Czech Republic). Sulfolane, CH_3NO_2, Me_3OBF_4, and MeOTf were purchased from Sigma Aldrich.

Equipment and Measurements

NMR spectra were measured in acetone-d_6 and chloroform-d. ^1H NMR chemical shifts were referenced with respect to the chemical shift of the residual protons present in the deuterated solvents: acetone-d_6 (2.05 ppm) and methylene chloride-d_2 (5.32 ppm). For ^{11}B NMR signal $BF_3.Et_2O$ in a coaxial capillary was used as an external standard. For ^{13}C NMR, the signal of the acetone-d_6 trideuteriomethyl group (δ = 29.80 ppm) and methylene chloride-d_2 (54.00 ppm) were used. ^1H and ^{13}C spectra were recorded with Bruker Avance 400 and 500 spectrometers working at 400.1 and 499.8 MHz for ^1H NMR, and at 100.6 MHz and 125.7 MHz for ^{13}C NMR. $^1H\{^{11}B\}$, ^{11}B and ^{11}B $\{^1H\}$ NMR spectra were accumulated with Bruker Avance 400 and 500 spectrometers working at 400.1 MHz and 499.8 MHz for ^1H NMR and 128.3 MHz and 160.4 MHz for ^{11}B NMR. The carbon signal of the C-1 carborane vertex is usually not easily detectable directly because of ^{13}C-^{11}B coupling, and therefore HSQC and HMBC were used for the assignment of ^{13}C NMR resonances. Assignments of boron signals were done by ^{11}B and ^{11}B COSY NMR. Electrospray ionization mass spectrometry (ESI-) spectra were recorded with a Waters Micromass ZQ spectrometer. IR spectra were recorded in KBr pellets with a Bruker EQUINOX 55 (IFS 55) spectrometer. Elemental analyses were obtained using a Perkin-Elmer PE 2400 Series II analyzer. Single-crystal X-ray diffraction data were obtained from Nonius KappaCCD difractometer equipped with Bruker ApexII-CCD detector using monochromatized MoKα radiation (λ = 0.71073 Å) at 150(2) K. The structures were solved by direct methods and refined by full-matrix least squares based on F^2 (SHELXS; SHELXL97).[34] The hydrogen atoms were found on difference Fourier map and recalculated into idealized positions (riding model) with assigned temperature factors, either $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or 1.5 U_{eq} for methyl moiety.

*12-(*N*-Methylnitrilium)-monocarba-*closo*-dodecacarborate ylide (3)*

Under argon atmosphere, the cesium salt of the cyanocarborate **2**[6,7] (100 mg, 0.32 mmol), prepared from its trimethylammonium salt using a standard procedure,[35] was placed into an oven-dried Schlenk flask and dissolved in CH_3NO_2 (5 mL). Me_3OBF_4 (147 mg, 9.96 mmol, 3 equiv.) was added and the mixture was stirred for 4 h. The completion of the reaction was indicated by a loss of the MS ESI(−) carborate signal. At that point the reaction mixture was evaporated to dryness. Most of the solid residue was dissolved in a minimal amount of anhydrous CH_2Cl_2 and the remainder was removed by filtration through a 200 nm syringe filter. The pure product was crystallized by slow diffusion of *n*-pentane into the CH_2Cl_2 solution, giving colorless crystals (54 mg, 89 %). IR (KBr pellet): ν/cm^{-1} = 3067 (w, ν(C_{carb}-H)), 2856 (w, ν(C-H, NCH_3)), 2572 (s, ν(B-H)), 2351 (w, ν(C≡N)), 1412 δ(C-H, NCH_3), 1080−700 δ(B-H); $^1H\{^{11}B\}$ NMR (400.1 MHz, methylene chloride-d_2): δ/ppm = 3.64−3.61 (m, 3H, N-CH_3), 2.61 (s, 1H, C_{carb}-H), 1.88 (s, 5H, B-H-2-6), 1.86 (s, 5H, B-H-7-11); ^{11}B NMR (128.3 MHz, methylene chloride-d_2): δ/ppm = −12.91 (d, 5B, J_{B-H} = 148.0 Hz, B-7-11), −15.07 (d, 5B, J_{B-H} = 160.2 Hz, B-2-6), −17.40 (s, 1B, B-12); ^{13}C NMR (125.7 MHz, methylene chloride-d_2): δ/ppm = 120.85 (HMBC, C≡N), 58.73(s, C_{carb}), 31.15 (t, NCH_3). Anal. Calcd for $C_3H_{14}B_{11}N$: C, 19.68; H, 7.71; N, 7.65. Found: C, 19.75; H, 7.75; N, 7.60.

Crystal data for **3**: $C_3H_{14}B_{11}N$, M_r = 183.06, Monoclinic, $P2_1/c$ (No 14), a = 11.2868 (12) Å, b = 7.7193 (8) Å, c = 13.8340 (14) Å, β = 106.606 (4)°, V = 1155.0 (2)Å^3, Z = 4, D_x = 1.053 Mg m^{-3}, colorless prism of dimensions 0.82 × 0.52 × 0.36 mm, multi-scan absorption correction (μ = 0.05 mm^{-1}) T_{min} = 0.963, T_{max} = 0.984; a total of 7000 measured reflections (θ_{max}= 26°), from which 2253 were unique (R_{int} = 0.030) and 1713 observed according to the $I > 2\sigma(I)$ criterion. The refinement converged ($\Delta/\sigma_{max} \leq 0.001$) to R = 0.088 for observed reflections and $wR(F^2)$ = 0.229, GOF = 1.09 for 137 parameters and all 2253 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.41, $\Delta\rho_{min}$ −0.27 e Å^{-3}).

*12-(*N*-Methylamidinium)-monocarba-*closo*-dodecacarborate ylide (4)*

Under argon atmosphere, the cyanocarborate **2**[6,7] (100 mg, 0.32 mmol) was placed into an oven-dried flask and dissolved in sulfolane (8 mL). CaH_2 (67 mg, 1.66 mmol, 5 equiv.) was added and the mixture was stirred for 20 min before MeOTf (0.1 mL, 0.96 mmol, 3 equiv.) was added. The resulting mixture was stirred for 12 h at rt. The completion of the reaction was indicated by loss of the MS ESI(–) signal of **2**. The reaction mixture was diluted with CH_2Cl_2 (30 mL) and solids were removed by filtration through a pad of diatomaceous earth under reduced pressure and washed by CH_2Cl_2 (4 × 20 mL). Saturated aqueous NH_3 (30 mL) was added and all volatiles were removed under reduced pressure. Ice-cold water (30 mL) was added and the thick residue was extracted with Et_2O (3 × 20 mL). Combined organic phases were dried over Cs_2CO_3, filtered and all volatiles were removed under reduced pressure. Residual sulfolane was removed on a Kugelrohr apparatus at 150 °C and 10^{-2} mbar. The solid was triturated with anhydrous CH_2Cl_2 (3 × 3 mL). The volume was reduced to approx 2 mL and slow diffusion of *n*-pentane into the CH_2Cl_2 solution afforded the pure product as colorless crystals (57 mg, 88 %). IR (KBr pellet): ν/cm^{-1} = 3478 (s, ν(NH_2)), 3402 (m, ν(NH)), 3381 (s, ν(NH_2)), 3068 (C_{carb}-H)), 2884 (w, ν(C-H, NCH_3)), 2588 (s), 2598 (s), 2537 (s), 2519 (s) and 2496 (s, ν(B-H)), 1641 (s, δ(NH_2)), 1601 (s, ν(C=$N^{\delta+}$)), 1454 (m, δ_A(CH_3)), 1413(m, δ_S(CH_3)), 1090−700 (δ(B-H)); $^1H\{^{11}B\}$ NMR (400.1 MHz, acetone-d_6): δ/ppm = 7.54 (bs, 1H, N-H *cis*), 7.45 (bs, 1H, CH_3N-H), 7.12 (bs, 1H, N-H *trans*), 2.98 (d, 3H, J = 5.1 Hz, N-CH_3), 2.52 (s, 1H, C_{carb}-H), 1.77 (s, 5H, B-H-2-5), 1.72 (s, 5H, B-H-7-11); ^{11}B NMR (128.3 MHz, acetone-d_6): δ/ppm –5.17 (s, 1B, B-12) , –13.59 (d, J_{B-H} = 140.3 Hz, B-7-11), –16.03 (d, J_{B-H} = 155.4 Hz, B-2-5); ^{13}C NMR (125.7 MHz, acetone-d_6): δ/ppm 178.24 (dd, J = 154.1, 76.1 Hz, $C_{amidinium}$), 51.53 (s, C_{carb}), 29.30 (HMBC, CH_3). MS ESI(–): 199.4 (M – H^+) center of the isotope cluster. Anal. Calcd for $C_3H_{17}B_{11}N_2$: C, 18.01; H, 8.56; N, 14.00. Found: C, 18.15; H, 8.60; N, 13.82.

Crystal data for **4**: $C_3H_{17}B_{11}N_2$, M_r = 200.10, triclinic, $P\,{-1}$ (No 2), a = 7.3056 (2) Å, b = 7.5839 (2) Å, c = 10.4886 (3) Å, α = 80.606 (1)°, β = 88.175 (1) °, γ = 89.057 (1); Z = 2, D_x = 1.160 Mg m^{-3}, colorless crystal of dimensions 0.31 × 0.29 × 0.22 mm, absorption was neglected (μ = 0.06 mm^{-1}); 7518 diffraction collected (θ_{max}= 27.5°), 2628 independent (R_{int} = 0.021) and 2242 observed ($I > 2\sigma(I)$)). 188 refined parameters, goodness of fit 1.05, final R indices $R[F^2 > 2\sigma(F^2)]$ = 0.038, $wR(F^2)$ = 0.110, maximal/mi-nimal residual electron density ($\Delta\rho_{max}$ = 0.32, $\Delta\rho_{min}$ −0.22 e Å^{-3}).

Supplementary Materials. – Supporting informations to the paper are enclosed to the electronic version of the article. These data can be found on the website of *Croatica Chemica Acta* (http://public.carnet.hr/ccacaa).

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Supporting information

12-(*N*-Methylnitrilium)monocarba-*closo*-dodecaborate Ylide

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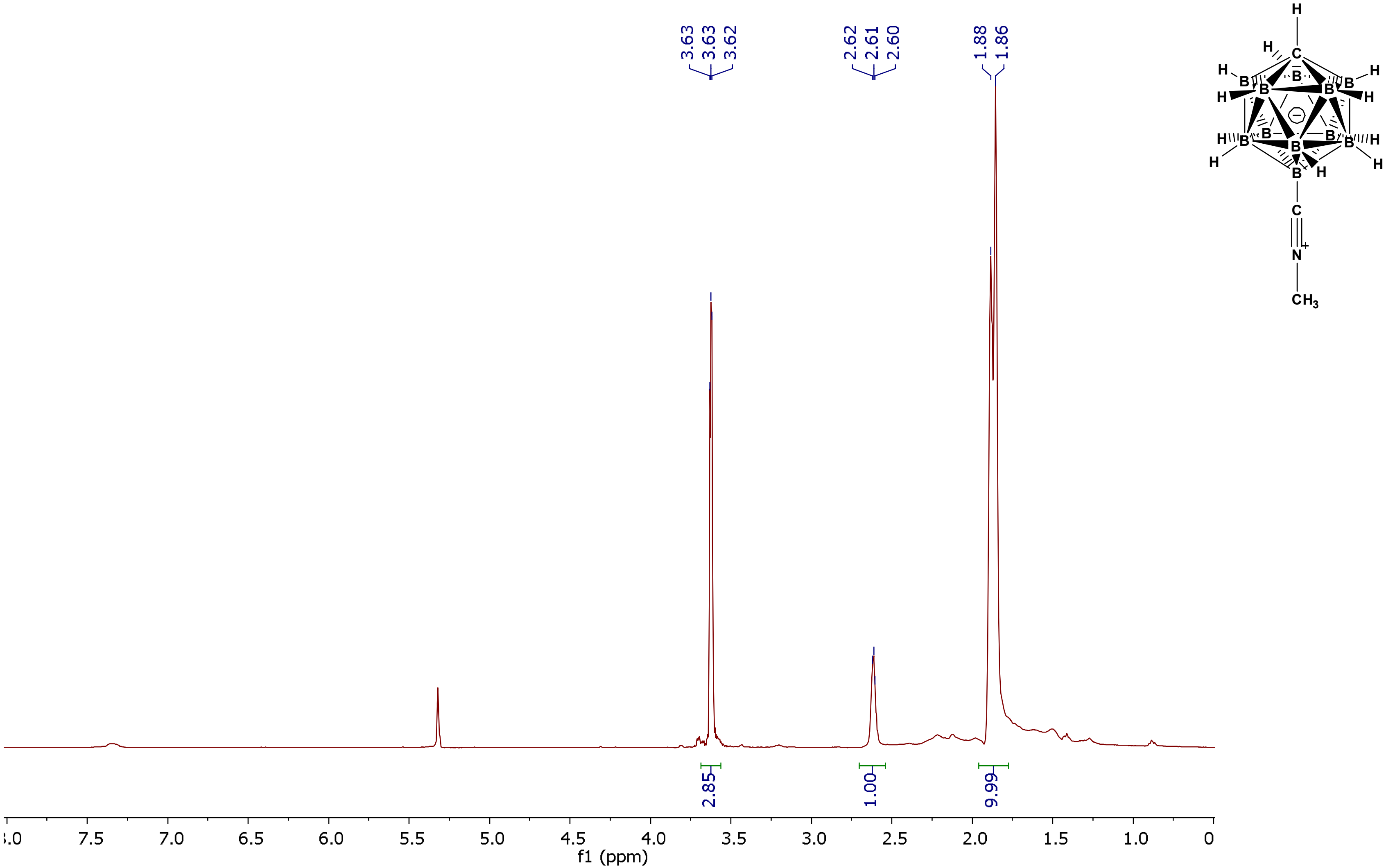
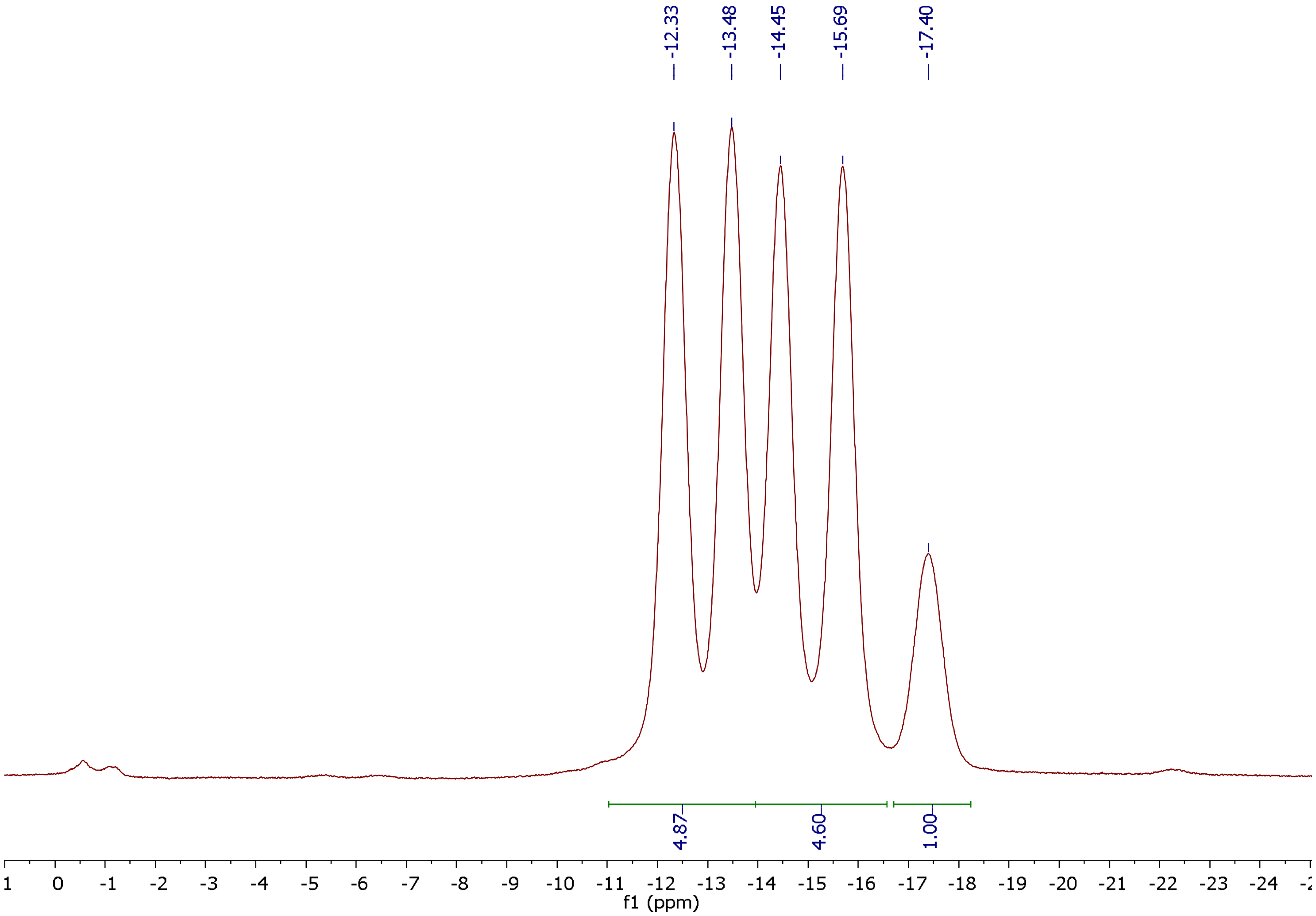
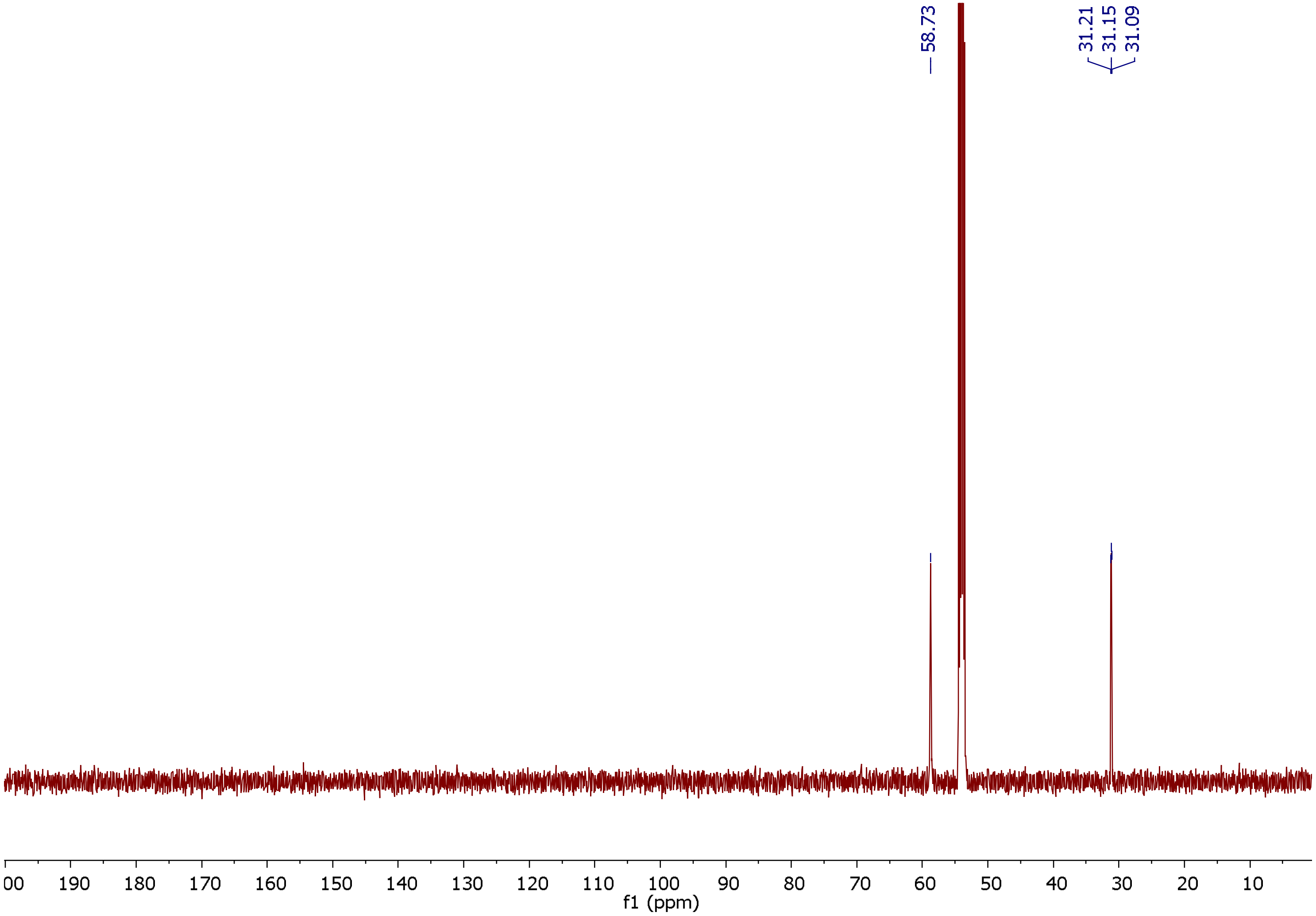
^{1}H{^{11}B} NMR (400 MHz, methylene chloride-d_2): **12-(*N*-methylnitrilium)-CB$_{11}$H$_{11}^{-}$ (3)**



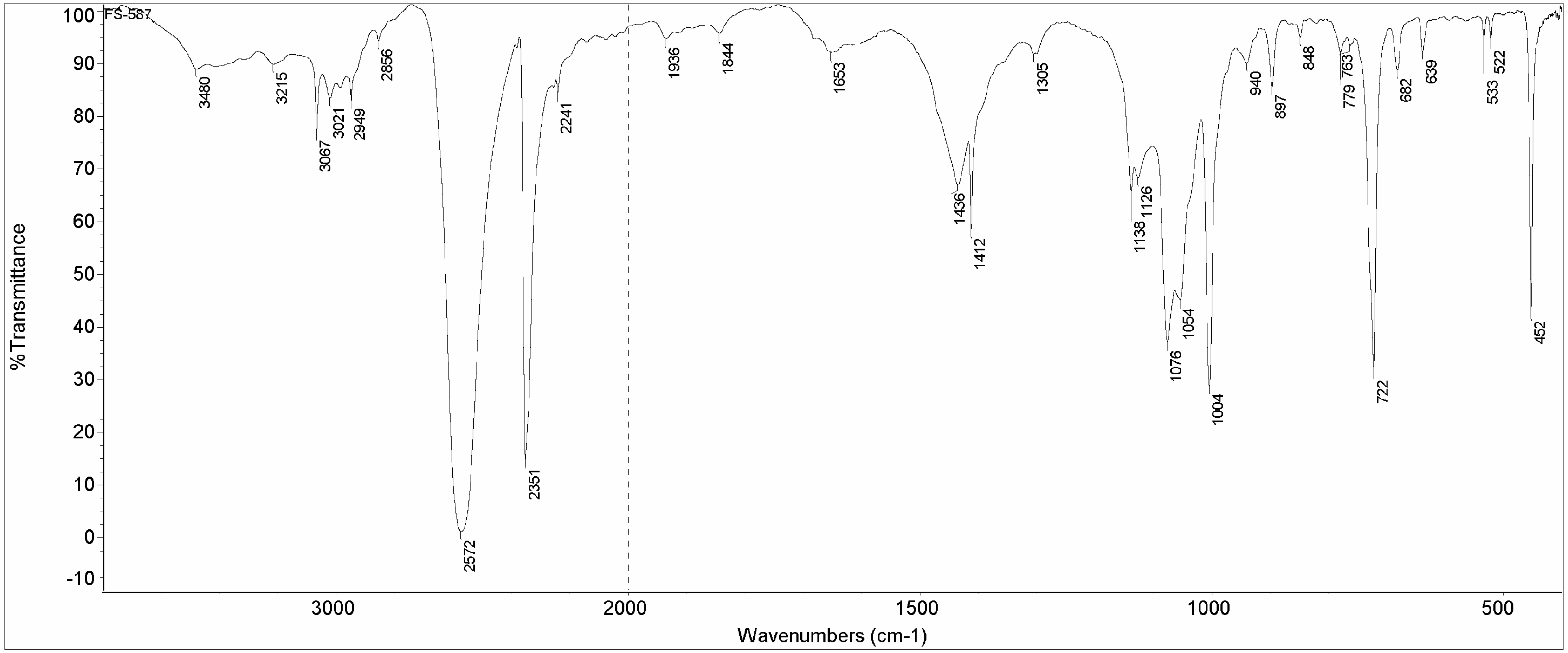
^{11}B NMR (128 MHz, methylene chloride-*d$_2$*): **12-(*N*-methylnitrilium)-CB$_{11}$H$_{11}$$^-$** (**3**)



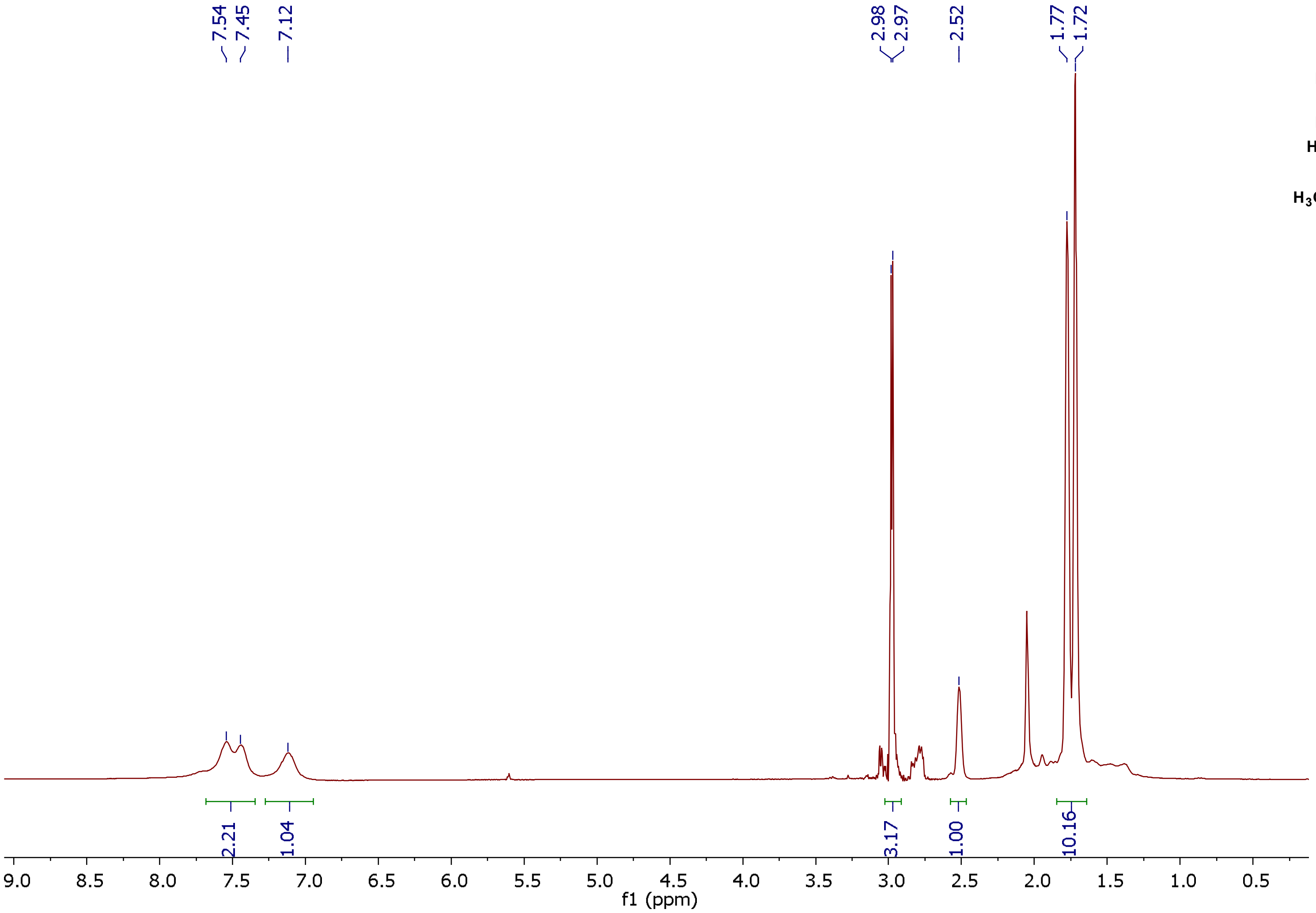
^{13}C NMR (126 MHz, methylene chloride-d_2): **12-(*N*-methylnitrilium)-$CB_{11}H_{11}^-$ (3)**

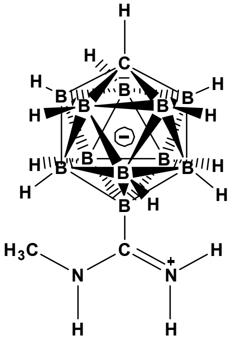


IR (KBr pellet): **12-(*N*-methylnitrilium)-$CB_{11}H_{11}^{-}$ (3)**

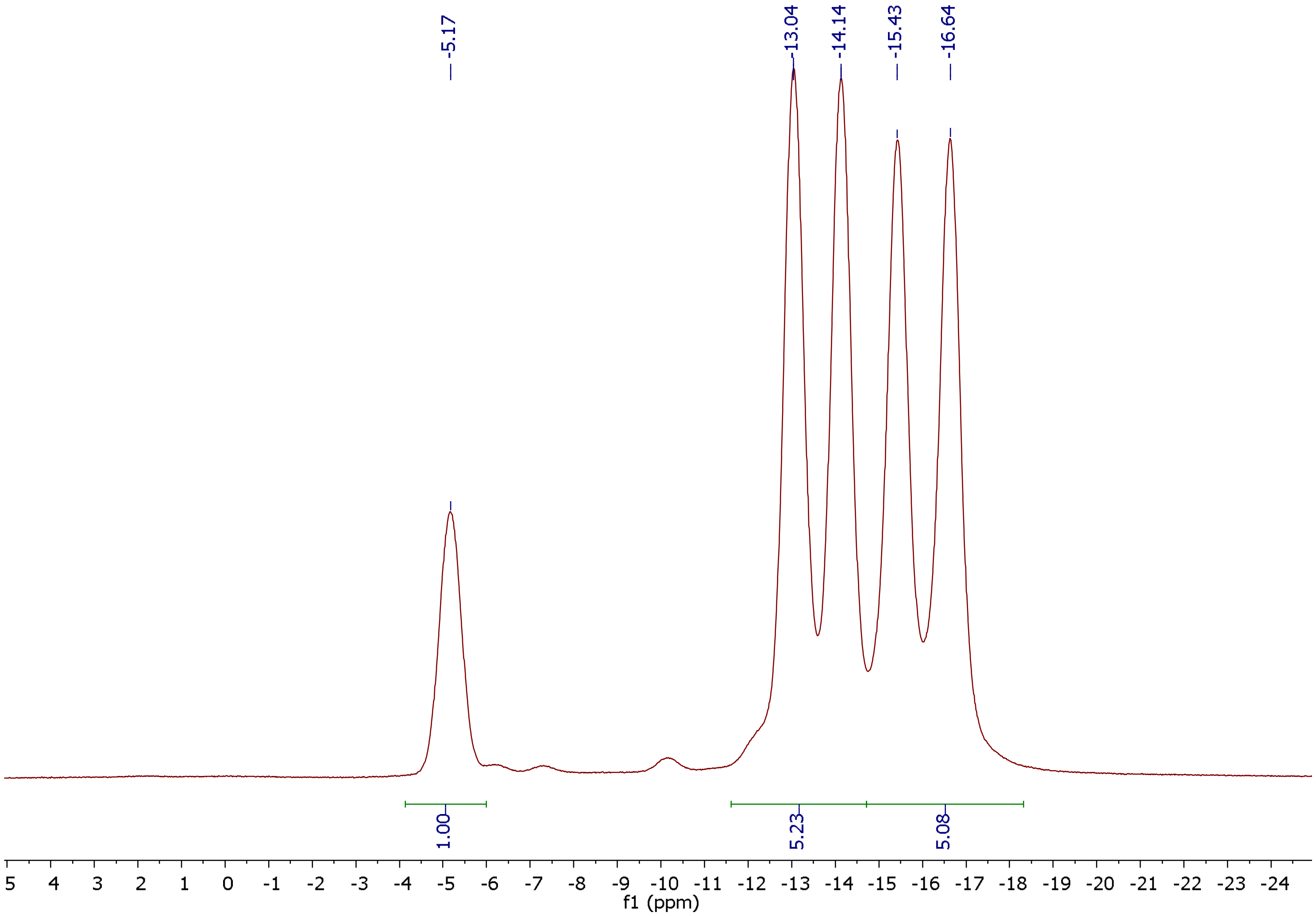


$^{1}H\{^{11}B\}$ NMR (400 MHz, acetone-d_6): **12-(*N*-methylamidinium)-$CB_{11}H_{11}^{-}$ (4)**

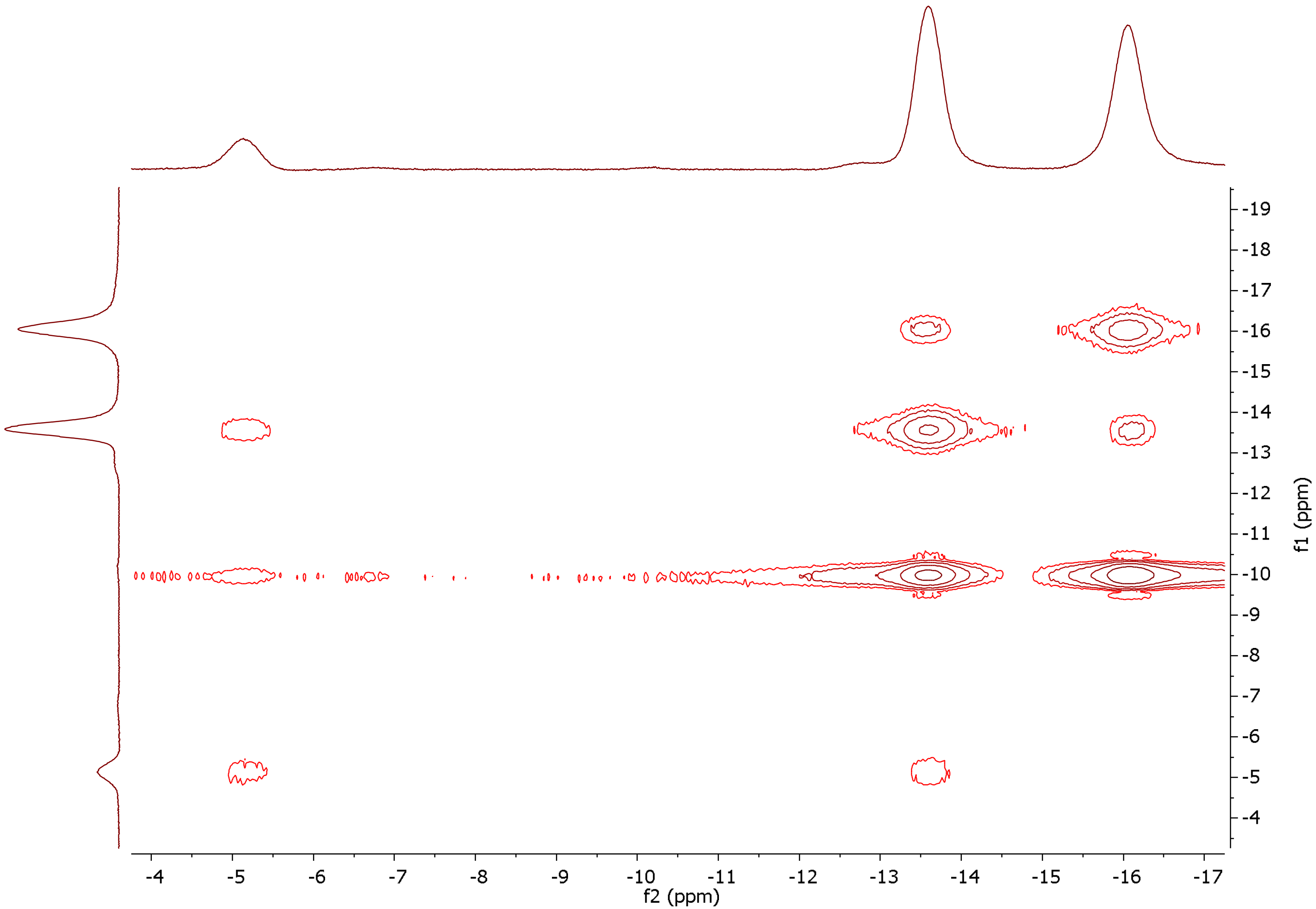




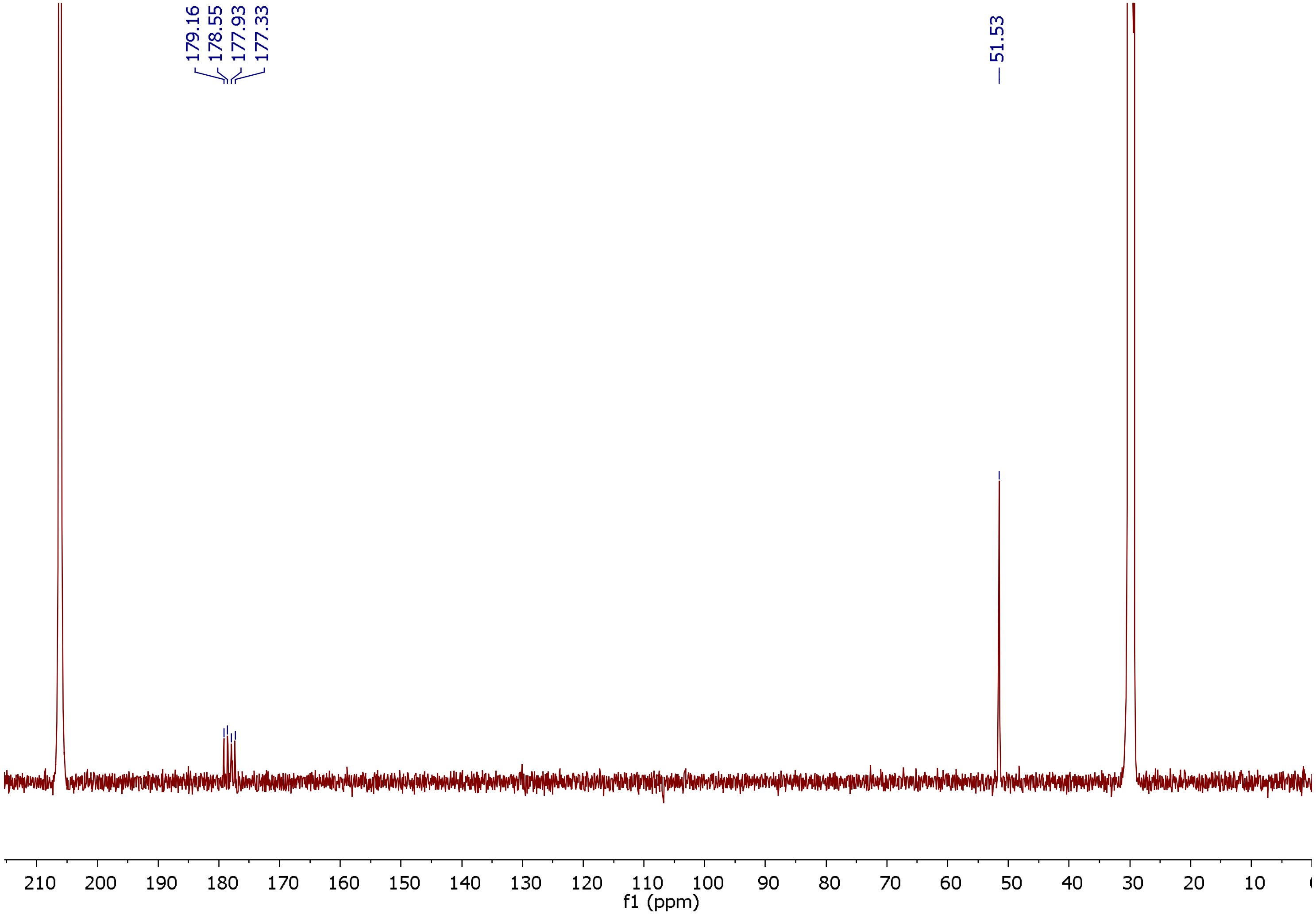
^{11}B NMR (128 MHz, acetone-d_6): **12-(*N*-methylamidinium)-$CB_{11}H_{11}^-$ (4)**



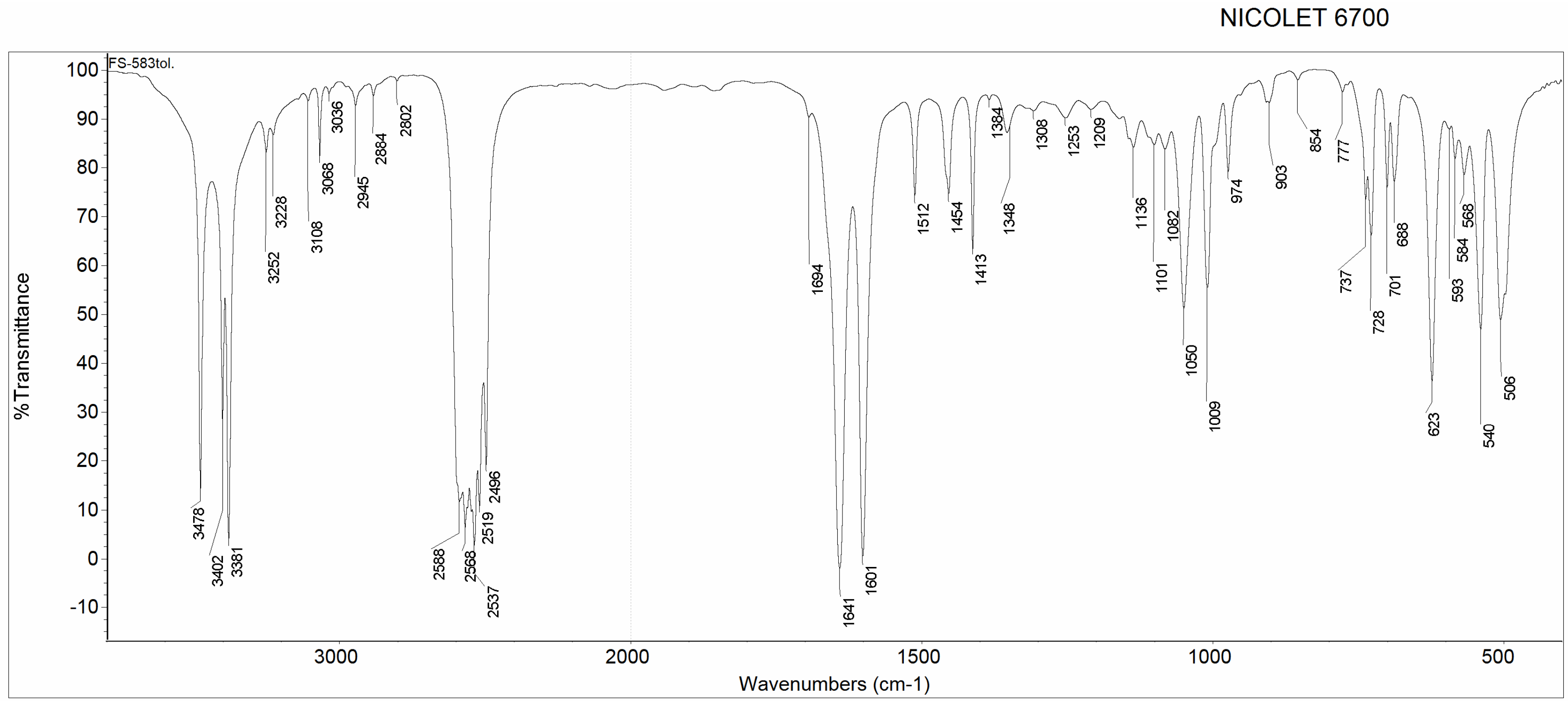
^{11}B ^{11}B COSY-NMR (128 MHz, acetone-d_6): **12-(*N*-methylamidinium)-$CB_{11}H_{11}^-$ (4)**



^{13}C NMR (126 MHz, acetone-d_6) NMR: **12-(*N*-methylamidinium)-$CB_{11}H_{11}^-$ (4)**



IR (KBr pellet): **12-(*N*-methylamidinium)-$CB_{11}H_{11}^{-}$ (4)**



Quantum chemical calculations

All quantum-chemical calculations were performed on RI-BP86/def2-SV(P) level using TURBOMOLE.[1,2,3,4,5] Molecular vibrations were calculated with the AOFORCE module and checked for imaginary frequencies to ensure true minima structures.

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Computed optimized geometry of $[CB_{11}H_{11}CN]^-$

```
    0.00000000000000      0.00000000000000     -3.25957774253562  c
    0.00000000000000      0.00000000000000     -5.33923174215398  h
    2.32619818442496     -1.69008190955360     -1.76764300394345  b
    3.88047834770949     -2.81933254861492     -3.03430331772313  h
    2.32619818442496      1.69008190955360     -1.76764300394345  b
    3.88047834770949      2.81933254861492     -3.03430331772313  h
   -0.88852864188204      2.73460997342903     -1.76764300394345  b
   -1.48221083621698      4.56177588924780     -3.03430331772313  h
   -2.87533908508586      0.00000000000000     -1.76764300394345  b
   -4.79653502298499      0.00000000000000     -3.03430331772313  h
   -0.88852864188204     -2.73460997342903     -1.76764300394345  b
   -1.48221083621698     -4.56177588924780     -3.03430331772313  h
    2.89913903648890      0.00000000000000      1.08915834441275  b
    4.97137811505057      0.00000000000000      2.09629816342677  h
    0.89588323133086      2.75724507229844      1.08915834441275  b
    1.53624032301433      4.72806155128596      2.09629816342677  h
   -2.34545274957531      1.70407116999358      1.08915834441275  b
   -4.02192938053962      2.92210273959626      2.09629816342677  h
   -2.34545274957531     -1.70407116999358      1.08915834441275  b
   -4.02192938053962     -2.92210273959626      2.09629816342677  h
    0.89588323133086     -2.75724507229844      1.08915834441275  b
    1.53624032301433     -4.72806155128596      2.09629816342677  h
    0.00000000000000      0.00000000000000      2.85573816257316  b
    0.00000000000000      0.00000000000000      5.80921808977368  c
    0.00000000000000      0.00000000000000      8.02994597776121  n
```

Computed optimized geometry of $CB_{11}H_{11}CNMe$

```
    0.17816296608090      0.02623191375047     -4.76042302274017  c
    0.25826707672592      0.03704713323950     -6.83813073554559  h
    1.01282528223710     -2.72309293991966     -3.26688632616938  b
```

1.65513193815294	-4.54466918395507	-4.50128301838302	h
3.00270310348018	0.01896876858955	-3.17639676147776	b
4.97137270113768	0.02575060784499	-4.34931315098051	h
1.01083078277308	2.76044663066429	-3.23831689092737	b
1.65190605166558	4.59527699897720	-4.45361300534175	h
-2.20951459130359	1.71299419570085	-3.36746094922986	b
-3.71638664120080	2.84935740473322	-4.66780120978571	h
-2.20826524607221	-1.67671990675952	-3.38509722333247	b
-3.71429827119670	-2.80065141355784	-4.69719976969029	h
2.37786295734886	-1.71515042492230	-0.36203902615481	b
3.98771746754734	-2.91972098714474	0.75149625361932	h
2.37658896462357	1.72332025598218	-0.34405897061608	b
3.98563683862044	2.91756095198279	0.78166295483149	h
-0.89139447309248	2.78476656648232	-0.46397119352182	b
-1.56391434662962	4.72025734951725	0.57816869404573	h
-2.90964835681251	0.00322885040974	-0.55555143357208	b
-4.98918386285710	-0.00259490710774	0.42300530563190	h
-0.88937063888008	-2.77777562604811	-0.49292644102277	b
-1.56055261169962	-4.72454401351696	0.52880576163537	h
-0.05099775789710	-0.00503789198068	1.23104310145228	b
-0.15713673405817	-0.02177985305728	4.12888268699314	c
-0.32554761081957	-0.05331411146376	9.01227900846322	c
1.37764661040720	0.90454473057446	9.77978381021058	h
-0.37921966123407	-2.03587019402966	9.70075575882458	h
-2.04667118003462	0.95695862094362	9.66396636053988	h
-0.23455075701246	-0.03578952592916	6.34061943224391	n

Computed optimized geometry of $[(CF_3)_3BCN]^-$

-0.50596411861738	2.87165267630187	0.69925763257913	c
0.43064011037983	-0.02509877691970	0.06719228416019	b
-0.97842291590189	-2.05519995229484	1.95563307941375	c
-0.16499708237435	-0.72556770409552	-2.90334486100077	c
0.38074105022145	4.61886412219174	-1.00031903746468	f
-3.08229854330364	3.16209251945359	0.70596166017788	f
0.28719219909849	3.71360202435588	3.01719957358456	f
0.32884184108349	-3.20530666162333	-3.48136914267920	f
1.24755329271190	0.65893663267812	-4.57737222290608	f
-2.63172720992692	-0.33332470363739	-3.59583623699296	f
0.01449049766265	-4.44393831113652	1.79824388545938	f
-0.80609596965185	-1.40707426792568	4.46178286501833	f
-3.51309796905732	-2.33306753172526	1.49059654143458	f
3.40098395889598	-0.18942011233726	0.51643537113478	c
5.59216085877955	-0.30714995328570	0.84593860808097	n

Computed optimized geometry of $(CF_3)_3BCNMe$

-8.99663506034169	2.97743621367865	0.09322514311755	c
-8.15545188409826	0.05353773009279	-0.56223868762658	b
-9.46469754374854	-2.01442399005186	1.36207798097335	c

-8.65772422701418	-0.65578690441825	-3.55226810435076	c
-8.10384329392817	4.66645577933767	-1.64028202903322	f
-11.53529994510389	3.26326521611030	0.18218956212869	f
-8.07063503878338	3.76003564034272	2.38025016071001	f
-8.21593152431990	-3.14531817863994	-4.06217314233354	f
-7.09316676824960	0.67724870541992	-5.12842735595931	f
-11.05334348468524	-0.15214083427686	-4.28364506886897	f
-8.26770074997288	-4.31087492146031	1.24994298486964	f
-9.35074859870505	-1.28063168231678	3.83084370355958	f
-11.92634493419882	-2.43444364766498	0.81852192730921	f
-5.21707797240082	-0.12193017056385	-0.13168176909666	c
-3.03647772710986	-0.26528517961565	0.17729248517550	n
-0.39345699701384	-0.45482985650328	0.54202327113504	c
0.05708996856360	-2.31080098387282	1.41254448110841	h
0.57790901346667	-0.29424284707307	-1.31143333233219	h
0.24842209383971	1.09030793997950	1.80888535059413	h

Computed optimized geometry of PhCN

0.00000000000000	0.00000000000000	-3.27898639774264	c
-2.30250321224401	0.00000000000000	-1.95184141820057	c
0.00000000000000	0.00000000000000	-5.36212249038732	h
-4.10782320147565	0.00000000000000	-2.99066394763672	h
0.00000000000000	0.00000000000000	2.03985160620986	c
-4.11082113650457	0.00000000000000	1.74959272412310	h
-2.31566365613702	0.00000000000000	0.69691045119549	c
4.11082113650457	0.00000000000000	1.74959272412310	h
2.31566365613702	0.00000000000000	0.69691045119549	c
4.10782320147565	0.00000000000000	-2.99066394763672	h
2.30250321224401	0.00000000000000	-1.95184141820057	c
0.00000000000000	0.00000000000000	6.97543508916807	n
0.00000000000000	0.00000000000000	4.75603833246946	c

Computed optimized geometry of $[PhCNMe]^+$

-5.59260020825413	-0.66889067547004	0.00165654238588	c
-4.00283806029855	-2.80509475363799	-0.00768669671588	c
-7.65928449386226	-0.92722907313524	0.00091345435210	h
-4.82087554602464	-4.71879236502536	-0.01578702863340	h
-0.35781207287022	-0.01533440595853	0.00345514269688	c
-0.12016044578429	-4.16352006975557	-0.01506540709342	h
-1.37934949461682	-2.50800952529024	-0.00709827588798	c
-1.14578122356012	4.06342743831529	0.02058725652988	h
-1.96018537764635	2.14955699949198	0.01289769872339	c
-5.83990535821484	3.44605059109907	0.01870035737890	h
-4.57654624049774	1.79234202901626	0.01187010517491	c
4.48662811155437	0.54492316039084	0.00527065751082	n
2.29013015384356	0.30267194504031	0.00310490959111	c
7.83748726792632	0.95352887434816	-1.99350724906189	h
7.66874471080451	2.56958904794788	1.03746698766448	h

8.01693111597316	-0.83977334731154	0.93491609603857	h
7.15541716152753	0.82455412993423	-0.01169455065415	c

Computed optimized geometry of $[\mathrm{CpCN}]^-$

-1.35357165648341	0.00000000000000	-2.54896223938666	c
-2.19417720827562	0.00000000000000	-0.02529265327759	c
1.35357165648341	0.00000000000000	-2.54896223938666	c
2.19417720827562	0.00000000000000	-0.02529265327759	c
0.00000000000000	0.00000000000000	1.58524400463171	c
0.00000000000000	0.00000000000000	4.25848189576804	c
0.00000000000000	0.00000000000000	6.49939851183636	n
-4.16561207034175	0.00000000000000	0.64377365245895	h
-2.57447045189456	0.00000000000000	-4.24043079064748	h
2.57447045189456	0.00000000000000	-4.24043079064748	h
4.16561207034175	0.00000000000000	0.64377365245895	h

Computed optimized geometry of CpCNMe

1.30439452636522	-4.18331577185952	-2.60466553856622	c
2.22083198532888	-2.14990111584593	-1.25254728372898	c
-1.42625663482314	-4.31825742867176	-2.30408422017856	c
-2.22080047782946	-2.36929601571294	-0.76384839718738	c
0.04067524898353	-0.93696284352113	-0.04452715958610	c
0.09985948198510	1.14686642437235	1.42929003453987	c
0.17791886719070	2.89148336408557	2.91583682496718	n
0.02015903105967	5.60986827820351	2.69431556525089	c
-1.56940335577282	6.29701445372874	3.88221232794223	h
1.78285697880038	6.45583908991519	3.46075111257113	h
-0.26001530082718	6.25388224661780	0.71012653406101	h
4.18825664904511	-1.51563337389232	-1.06988322323315	h
2.45232471369384	-5.50135409535058	-3.73110226712268	h
-2.65702317600932	-5.75395363536848	-3.16899512612681	h
-4.15377853719046	-1.92627957670045	-0.15287918360245	h