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Supporting Information

Thermal Dehydrogenation of Base-Stabilized $B_2H_5^+$ Complexes and Its Role in C–H Borylation

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General Remarks

All reactions were performed at room temperature (unless otherwise stated), under an atmosphere of dry nitrogen, either in a glovebox, or using standard Schlenk techniques. Every possible effort was made to protect the reaction mixtures from exposure to air and moisture. Where possible, disposable glassware flame-dried at the glass softening temperature was used. J. Young NMR tubes were dried in a heating oven at ca. 200 °C overnight, and the fitted Teflon valves were dried in a dessicator over Drierite.

Dichloromethane was dried by passing through a column of activated alumina, and further dried by storing over activated 3Å molecular sieves in the glovebox. Commercially available NMR grade deuterated solvents (Cambridge Isotope Laboratories), as well as fluorobenzene were not distilled; instead they were simply dried with freshly activated 3Å molecular sieves in the glovebox. Commercial grade Ph_3C^+ $B(C_6F_5)_4^-$ (Strem) and $B(C_6F_5)_3$ (Aldrich) were used without further purification. $Me_3P–BH_3$ and $Me_3N–BH_3$ were crystallized from hexanes and dried under reduced pressure before use. All other reagents were used as received from commercial suppliers.

Nuclear magnetic resonance experiments were performed on Varian Inova 700, Varian Inova 500 and Inova 400 spectrometers at the following frequencies: ^{1}H 700 MHz, 500 MHz or 400 MHz; ^{11}B and ^{11}B{^{1}H} 225 MHz, 160 MHz or 128 MHz; ^{13}C{^{1}H} 176 MHz or 101 MHz; ^{19}F 377 MHz; ^{31}P 162 MHz. All spectra were recorded in $CDCl_3$, CD_2Cl_2, or d_5-PhBr and referenced to the ^{1}H signal of internal Me_4Si according to IUPAC recommendations,[S1] using a Ξ of 32.083974 for $BF_3{\cdot}OEt_2$ (^{11}B), a Ξ of 25.145020 for Me_4Si (^{13}C), a Ξ of 94.094011 for CCl_3F (^{19}F), and a Ξ of 40.480742 for H_3PO_4 (^{31}P). When the internal Me_4Si reference could not be used, residual solvent peaks in ^{1}H NMR spectra were referenced instead.

Experimental Procedures

Reaction of $Me_3P–BH_3$ with $Ph_3C[B(C_6F_5)_4]$. *In Situ* NMR Study

The reaction was set up in a dry J. Young NMR tube under N_2 atmosphere in a glovebox. The reaction tube was charged with a mixture of solid Ph_3C^+ $B(C_6F_5)_4^-$ (49.7 mg, 53.9 μmol) and $Me_3P–BH_3$ (9.7 mg, 0.108 mmol). To the solid mixture was added 0.6 mL d_5-PhBr, the tube was sealed with the fitted Teflon valve, and then shaken vigorously for ca. 1 min. The NMR assay performed within the first 30 minutes following mixing the reagents indicated clean formation of cation **18a** (δ ^{11}B −25.5 ppm), although a minor trace of unreacted $Me_3P–BH_3$ (δ ^{11}B −36.2 ppm) was still observed. The sealed reaction tube was then heated at 90 °C for 18 h. As evidenced by ^{11}B NMR, at this point the reaction mixture contained triboron cation **20a** (δ ^{11}B −9.8, −38.9 ppm) and boronium cation **19a** (δ ^{11}B −33.5 ppm) in ca. 1:1 ratio. Stability of the counterion ($B(C_6F_5)_4^-$) and Ph_3CH byproduct during heating was confirmed by ^{19}F and ^{1}H NMR spectroscopy, respectively.

20a: ^{11}B NMR (225 MHz, d_5-PhBr): δ −9.8 (br s), −16.2 (s), −38.9 ppm (m, $J_{B–P}$ = 110 Hz). MS (ESI+): m/z 191 $[M]^+$, 177 $[M−BH_3]^+$.

Reaction of $Me_3N–BH_3$ with $Ph_3C[B(C_6F_5)_4]$. *In Situ* NMR Study

The reaction was set up in a dry J. Young NMR tube under N_2 atmosphere in a glovebox. The reaction tube was charged with a mixture of solid Ph_3C^+ $B(C_6F_5)_4^-$ (74.6 mg, 80.9 μmol) and $Me_3N–BH_3$ (11.8 mg, 0.162 mmol). To the solid mixture was added 0.8 mL d_5-PhBr, the tube was sealed with the fitted Teflon valve, and then shaken vigorously for ca. 1 min. The NMR assay performed within the first 30 minutes following mixing the reagents indicated clean formation of cation **18b** (δ ^{11}B −0.3 ppm), although a minor trace of unreacted $Me_3N–BH_3$ (δ ^{11}B −7.7 ppm) was still observed. The sealed reaction tube was then heated at 90 °C for 21 h. As evidenced by ^{11}B NMR, at this point the reaction mixture contained triboron cation **20b** (δ ^{11}B −10.2, −15.8 ppm) and boronium cation **19b** (δ ^{11}B +3.6 ppm). In this case NMR assay of the product mixture was performed at 90 °C to prevent precipitation of products from the reaction

mixture. Stability of the counterion ($B(C_6F_5)_4^-$) and Ph_3CH byproduct during heating was confirmed by ^{19}F and ^1H NMR spectroscopy, respectively.

20b: ^{11}B NMR (160 MHz, d_5-PhBr, 90 °C): δ −10.2 (br s), −15.8 (m), −16.1 ppm (s). MS (ESI+): m/z 157 $[M]^+$, 143 $[M-BH_3]^+$.

Reaction of $Et_3N–BH_3$ with $B(C_6F_5)_3$. *In Situ* NMR Study

The reaction was set up in a dry J. Young NMR tube under N_2 atmosphere in a glovebox. The reaction tube was charged with a solution of $B(C_6F_5)_3$ (27.0 mg, 52.7 μmol) in 0.6 mL CD_2Cl_2. To this solution neat $Et_3N–BH_3$ (14.7 μL, 0.100 mmol) was added via a microsyringe in one portion. No substantial exotherm was observed, potentially due to the small scale of the reaction. The tube was immediately sealed with the fitted Teflon valve, and then shaken vigorously for ca. 1 min. The NMR assay performed within the first 30 minutes following mixing the reagents indicated clean formation of salt **21**. The sealed reaction tube was then heated at 40 °C for 1 h. Formation of disproportionation product **22** was observed according to ^{11}B NMR assay.

21: ^1H NMR (400 MHz, CD_2Cl_2): δ 4.1-1.9 (br m, 5H), 2.93 (q, J = 7.3 Hz, 12H), 1.23 (t, J = 7.3 Hz, 17H), −2.0–−3.3 ppm (br s, 1H). ^{11}B NMR (128 MHz, CD_2Cl_2): δ −3.0 (unres t), −25.4 ppm (d, J = 80 Hz). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 150.3-146.9 (m), 140.2-136.6 (m), 138.6-135.2 (m), 127.1-123.7 (br m), 52.4, 8.3 ppm. ^{19}F NMR (377 MHz, CD_2Cl_2): δ −134.0 (s), −164.7 (s), −167.6 ppm (s).

Preparation of Amine and Phosphine $C_6F_5BH_2$ Complexes

General Procedure. In the glovebox, a dry 4 mL scintillation vial was charged with a mixture of solid amine borane or phosphine borane and $B(C_6F_5)_3$. The solid mixture was then dissolved by adding the specified solvent to the vial in one portion at rt, the vial was sealed and then heated as indicated below. No special precautions were necessary when isolating the products, since they were found to be reasonably stable to both air and moisture. Passing the

reaction mixture through a short (3-4 cm) plug of silica while flushing with $CHCl_3$ afforded pure products in all cases except when $Ph_3P–BH_3$ was used as the starting material. In that case the product was purified as indicated below.

22: Prepared following the general procedure using $B(C_6F_5)_3$ (43.0 mg, 84.0 μmol) and $Et_3N–BH_3$ (34.4 μL, 0.233 mmol) in 0.5 mL of anhydrous PhF. Since $Et_3N–BH_3$ is a liquid at rt, it was added via a microsyringe to the solution of $B(C_6F_5)_3$. Heated in a sealed vial at 50 °C for 3 h. Isolated as described above providing a colorless oil in nearly quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.9-1.7 (br m, 2H), 2.76 (q, *J* = 7.2 Hz, 6H), 1.26 ppm (t, *J* = 7.2 Hz, 9H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −14.2 ppm (t, *J* = 100 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.7-147.8 (m), 141.3-137.8 (m), 138.8-135.4 (m), 118.5-115.7 (br m), 50.5, 8.4 ppm. ^{19}F NMR (377 MHz, $CDCl_3$): δ −128.4 (m), −158.0 (t, *J* = 20 Hz), −164.2 ppm (m). HRMS (EI+): m/z calculated for $C_{12}H_{16}BF_5N$ $[M−H]^+$ 280.1296, found 280.1295 (0 ppm). IR($CDCl_3$, NaCl): 2990, 2431, 2383, 1641, 1512, 1394, 1281, 1131, 1085 cm^{-1}.

23: Prepared following the general procedure using $B(C_6F_5)_3$ (0.211 g, 0.412 mmol) and $Me_3N–BH_3$ (83.2 mg, 1.14 mmol) in 1 mL of anhydrous CH_2Cl_2. Heated in a sealed vial at 50 °C for 1 h. Isolated as described above providing 0.264 g (97%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.0-1.8 (br m, 2H), 2.62 ppm (s, 9H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −9.6 ppm (t, *J* = 100 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.3-147.0 (m), 141.7-138.5 (m), 138.5-135.2 (m), 117.8-115.3 (br m), 52.4 ppm. ^{19}F NMR (377 MHz, $CDCl_3$): δ −129.6 (m), −157.5 (m), −164.0 ppm (m). HRMS (EI+): m/z calculated for $C_9H_{10}BF_5N$ $[M−H]^+$ 238.0826, found 238.0829 (+1 ppm). IR($CDCl_3$, NaCl): 2418, 2358, 1641, 1483, 1466, 1283, 1150, 1101, 1085 cm^{-1}. m.p. 99 °C (from CH_2Cl_2).

24: Prepared following the general procedure using $B(C_6F_5)_3$ (43.0 mg, 84.0 μmol) and $BnMe_2N–BH_3$ (34.7 mg, 0.233 mmol) in 0.5 mL of anhydrous PhF. Heated in a sealed vial at 50 °C for 1 h. Isolated as described above providing a white solid in nearly quantitative yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45-7.38 (m, 3H), 7.30-7.24 (m, 2H), 4.00 (s, 2H), 3.0-2.0 (br m, 2H), 2.45 ppm (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −8.8 ppm (unres t). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.4-147.2 (m), 141.7-138.6 (m), 138.6-135.4 (m), 132.4, 130.1, 129.4, 128.7, 117.7-115.3 (br m), 65.9, 47.4 ppm. ^{19}F NMR (377 MHz, $CDCl_3$): δ −129.0 (m), −157.2 (t, *J* = 20 Hz),

−163.8 ppm (m). HRMS (EI+): dissociates to $BnNMe_2$ and $C_6F_5BH_2$ under EI-MS conditions. m/z calculated for $C_6F_5BH_2$ $[M]^+$ 180.0170, found 180.0163 (−4 ppm); m/z calculated for $C_9H_{13}N$ $[M]^+$ 135.1048, found 135.1042 (−4 ppm). IR($CDCl_3$, NaCl): 3010, 2957, 2418, 2358, 1641, 1513, 1466, 1283, 1155, 1086, 1036 cm^{-1}. m.p. 79 °C (from CH_2Cl_2).

25: Prepared following the general procedure using $B(C_6F_5)_3$ (43.0 mg, 84.0 μmol) and $Ph_3P–BH_3$ (64.3 mg, 0.233 mmol) in 0.5 mL of anhydrous CH_2Cl_2. Heated in a sealed vial at 40 °C for 1 h. The reaction mixture was passed through a short plug of silica gel while eluting with $CHCl_3$. Concentration of the solution provided the crude product as a white solid. Double crystallization from cyclohexane provided 73 mg (71%) of a white crystalline solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65-7.48 (m, 9H), 7.46-7.41 (m, 6H), 3.2-2.2 ppm (br m, 2H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −31.3 ppm (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.0-146.6 (m), 140.6-137.4 (m), 138.4-135.1 (m), 133.4 (d, *J* = 9 Hz), 131.7, 128.9 (d, *J* = 10 Hz), 127.0 (d, *J* = 59 Hz), 116.5-114.2 ppm (br m). ^{19}F NMR (377 MHz, $CDCl_3$): δ −128.1 (m), −159.5 (dt, *J* = 6.8, 20 Hz), −164.7 ppm (m). ^{31}P NMR (162 MHz, $CDCl_3$): δ 12.8 ppm. HRMS (EI+): m/z calculated for $C_{24}H_{16}BF_5P$ $[M−H]^+$ 441.1003, found 441.1001 (0 ppm). IR($CDCl_3$, NaCl): 2420, 2394, 2253, 1511, 1470 cm^{-1}.

Computational Studies

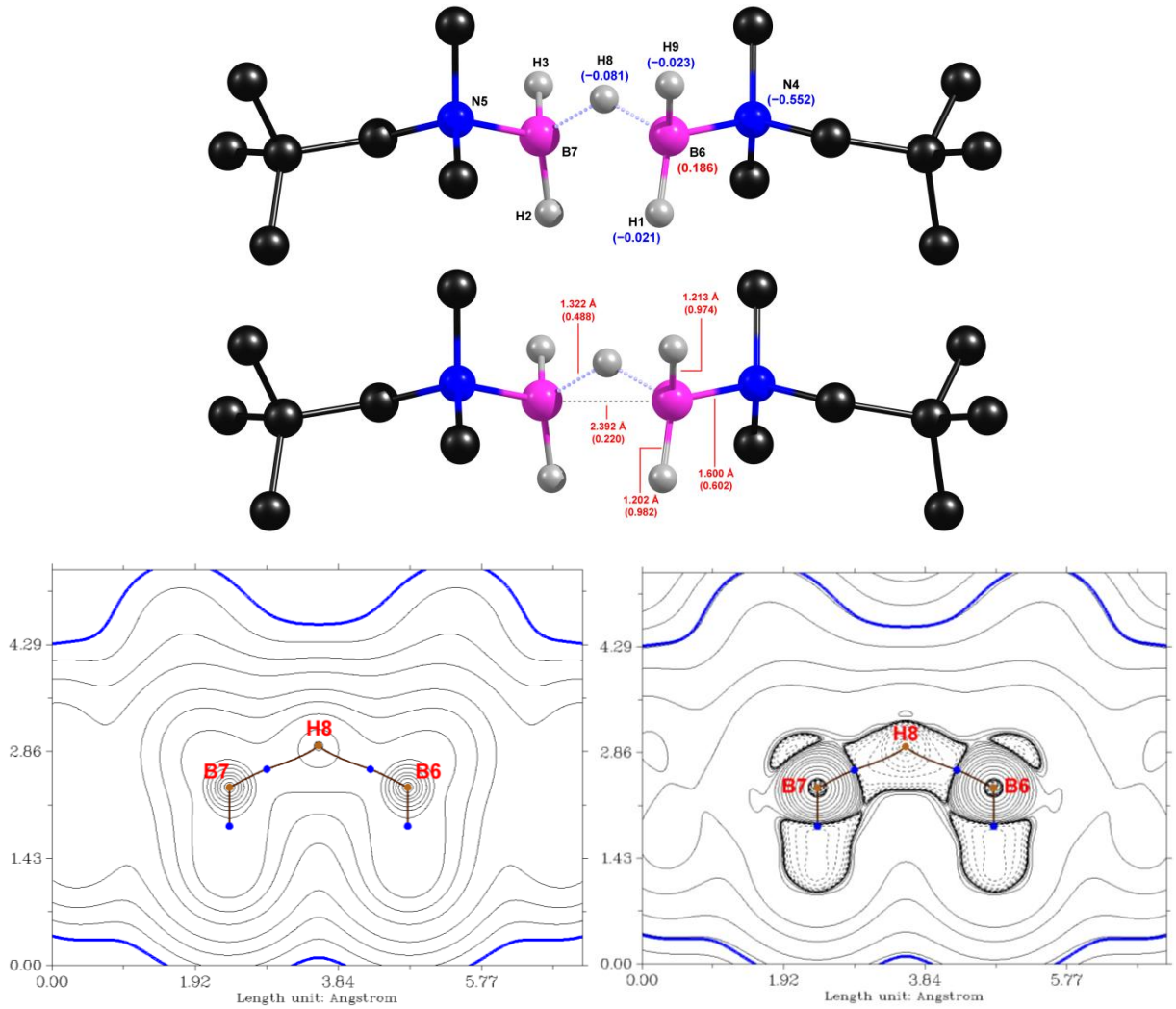
All calculations employing Møller-Plesset perturbation theory were performed using Firefly 8.1.0 software[S2] (which is partially based on GAMESS (US)[S3] source code), while DFT calculations were performed using Gaussian 09 Rev A.02 suite of computational programs.[S4] In both software packages spherical harmonics were used. In Firefly, extra tight convergence criteria for energies, geometries and gradients were used throughout the calculations. In Gaussian, ultrafine integration grids were used, along with increased precision in 2-electron integral calculation (`int=ultrafine` and `Acc2e=11` keywords). Gas phase geometry optimizations (counterions not included), as well as harmonic frequency and IRC calculations were performed at MP2(FC)/cc-pVDZ level of theory. The obtained geometries were then used in single point DFT calculations at M06-2X/6-311++G(3df,2p) level of theory,[S5] either in gas phase, or using SMD solvation model.[S6] Single point gas-phase energies were also calculated at MP4(SDTQ)/cc-pVDZ and (where feasible) MP4(SDTQ)/cc-pVTZ levels of theory, and were found to be consistent with DFT results. All stationary points were confirmed to be either true minima or transition states by performing frequency calculations, and the vibrational frequencies were scaled by 0.977 for the thermochemical analysis.[S7] The potential energy surfaces were explored by IRC calculations in both directions from all transition states. Solution free energies were corrected for concentration change relative to the gas phase. Where applicable, the highest possible symmetry groups were used in calculations. Natural Bond Orbital (NBO) analysis (M06-2X/6-311++G(3df,2p)) was performed using NBO Version 3.1,[S8] as implemented in Gaussian. The Quantum Theory of Atoms in Molecules (QTAIM) electron density topology analysis (M06-2X/6-311++G(3df,2p)) was performed using Multiwfn 3.3.7.[S9]

Selected NBO and QTAIM Results

A set of four diagrams is presented below for each structure. The first diagram (H atoms omitted except where relevant) shows selected atom labels and NBO charges (in parenthesis), while the second one shows interatomic distances and NBO Wiberg bond indices (in parenthesis). The bottom two images show contour maps of the electron density (left) and the Laplacian distribution (right). In the bottom images, (3, −3) critical points are shown in brown, while (3,

−1) critical points are shown in blue. The bond paths are also shown, as well as the van der Waals surfaces (blue line).

*H-Bridged Cation **7***

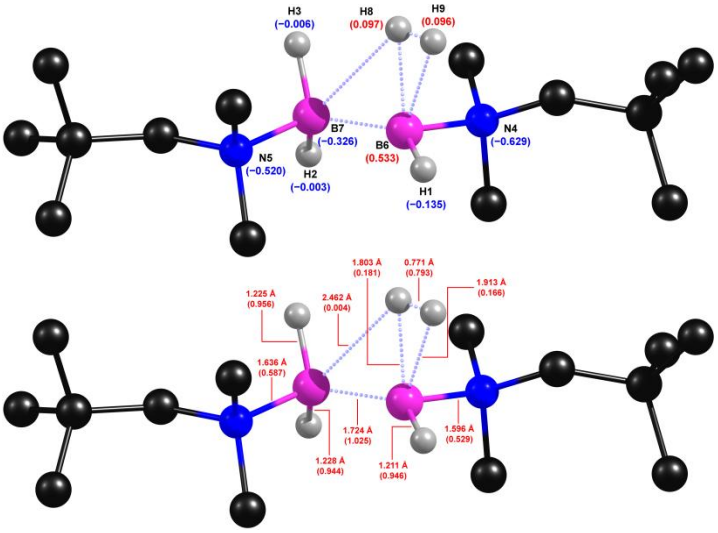


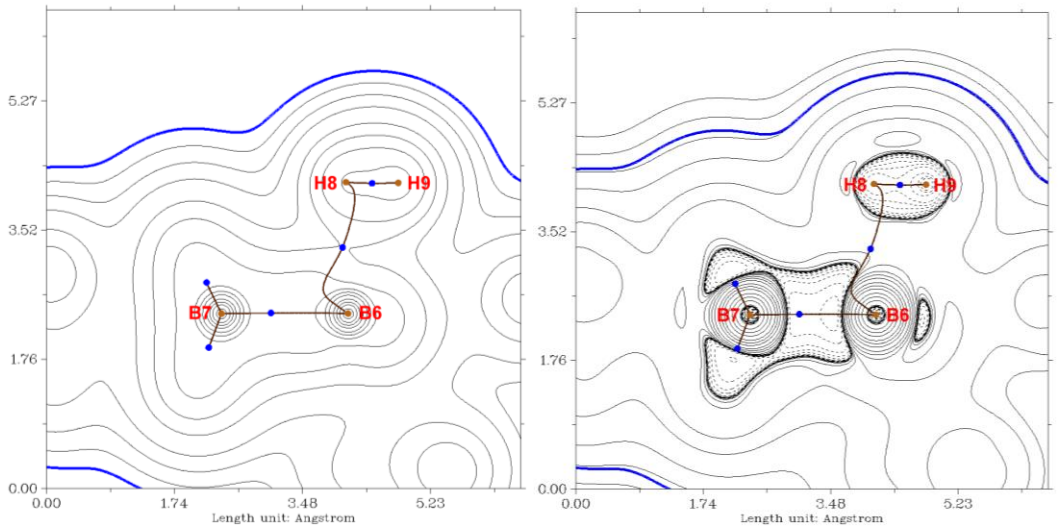
B6–H8: $\rho(\mathbf{r})$ = 0.1033; $\nabla^2\rho(\mathbf{r})$ = 0.0619; $G(\mathbf{r})$ = 0.1004; $V(\mathbf{r})$ = −0.1854; ε = 0.4203.

B6–H1: $\rho(\mathbf{r})$ = 0.1822; $\nabla^2\rho(\mathbf{r})$ = −0.3842; $G(\mathbf{r})$ = 0.1063; $V(\mathbf{r})$ = −0.3087; ε = 0.0694.

B6–H9: $\rho(\mathbf{r})$ = 0.1763; $\nabla^2\rho(\mathbf{r})$ = −0.3558; $G(\mathbf{r})$ = 0.1034; $V(\mathbf{r})$ = −0.2957; ε = 0.0666.

Borenium B–H Insertion TS ***13***



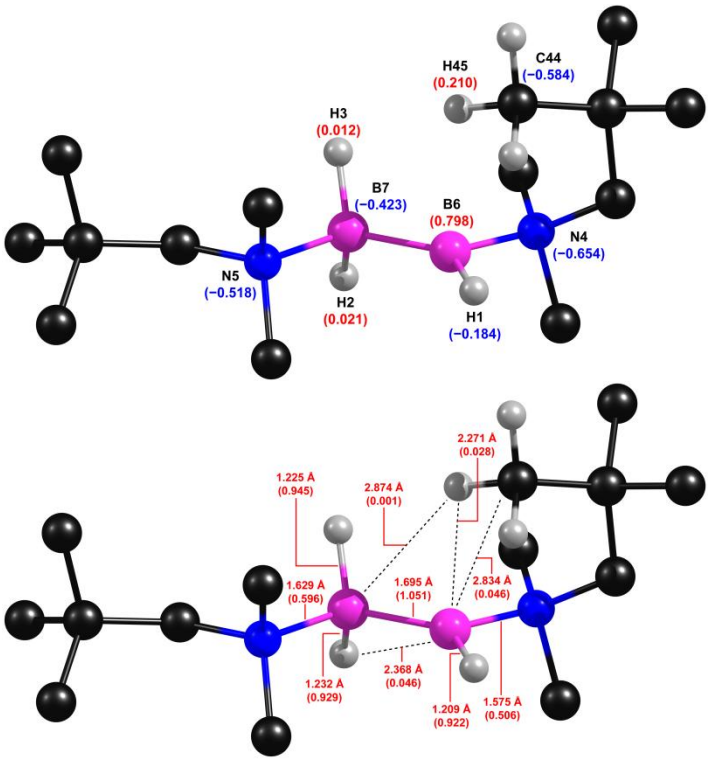


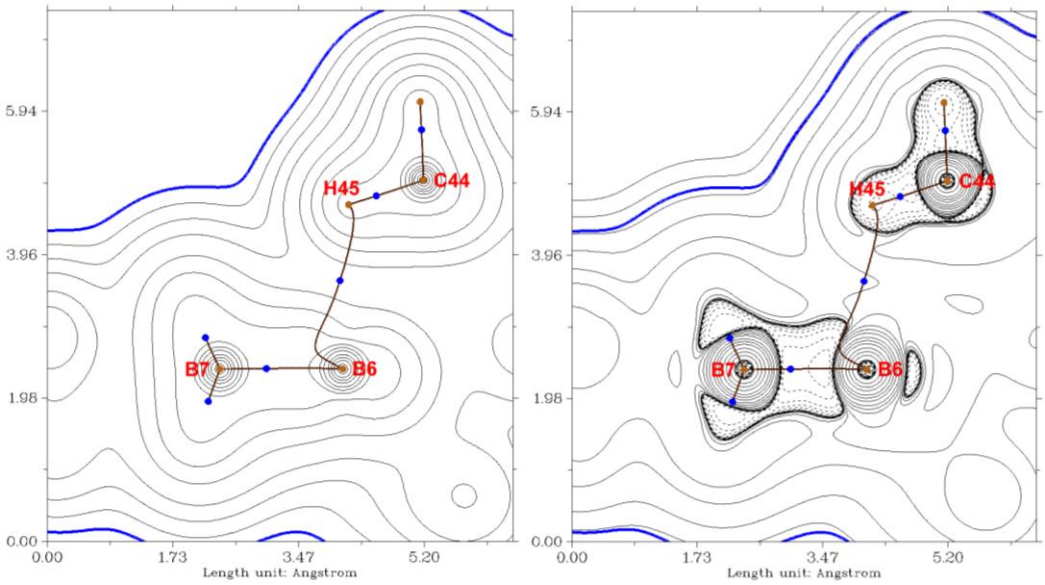
B6–B7: $\rho(\mathbf{r})$ = 0.1491; $\nabla^2\rho(\mathbf{r})$ = −0.3650; $G(\mathbf{r})$ = 0.0304; $V(\mathbf{r})$ = −0.1520; ε = 0.1215.

B6–H8: $\rho(\mathbf{r})$ = 0.0406; $\nabla^2\rho(\mathbf{r})$ = 0.0436; $G(\mathbf{r})$ = 0.0218; $V(\mathbf{r})$ = −0.0328; ε = 0.5914.

H8–H9: $\rho(\mathbf{r})$ = 0.2541; $\nabla^2\rho(\mathbf{r})$ = −1.0951; $G(\mathbf{r})$ = 0.0021; $V(\mathbf{r})$ = −0.2780; ε = 0.0210.

*Borenium B–H Insertion Product **14**, Conformation 2 (lowest energy structure, from IRC of **15**)*



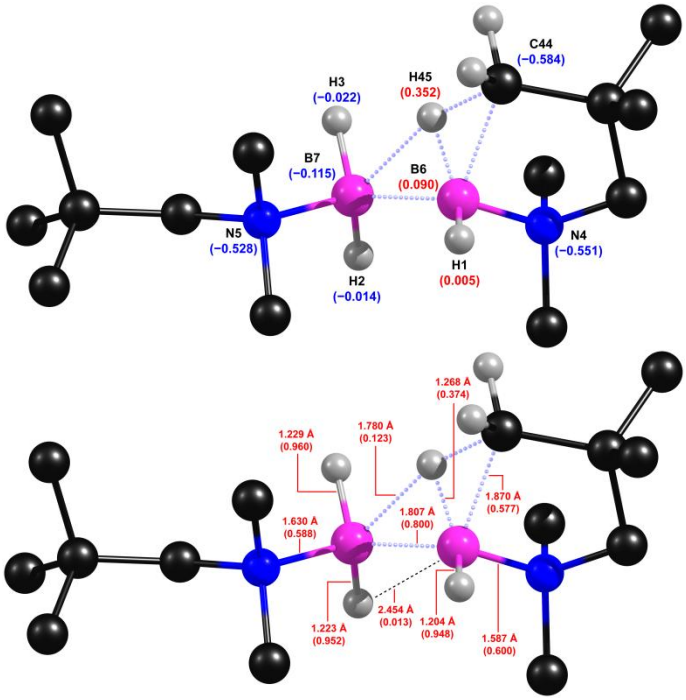


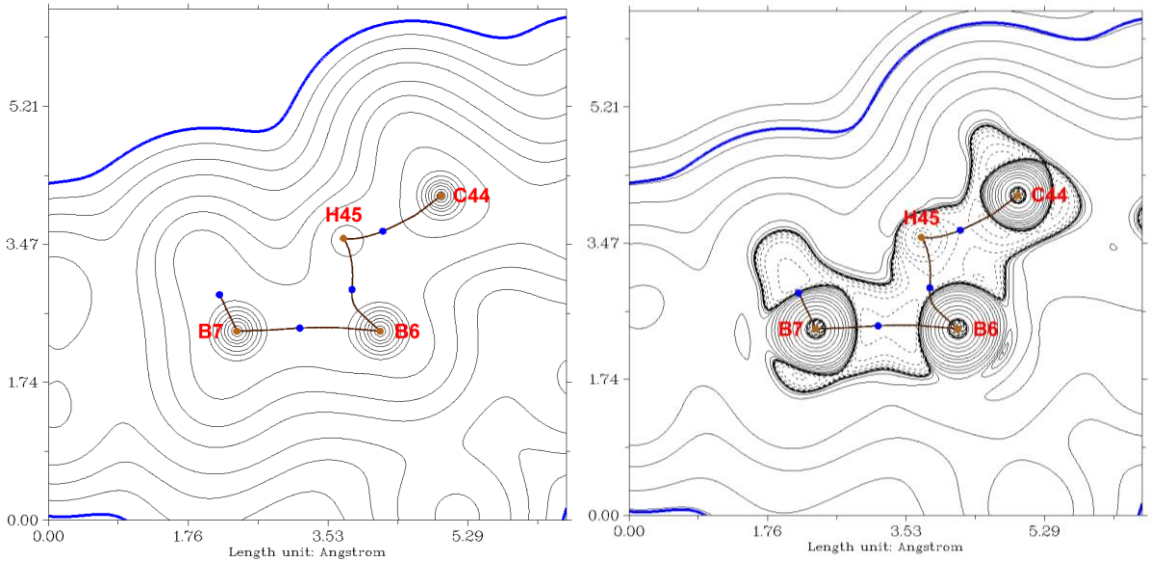
B6–B7: $\rho(\mathbf{r})$ = 0.1558; $\nabla^2\rho(\mathbf{r})$ = −0.3896; $G(\mathbf{r})$ = 0.0400; $V(\mathbf{r})$ = −0.1774; ε = 0.1425.

B6–H45: $\rho(\mathbf{r})$ = 0.0139; $\nabla^2\rho(\mathbf{r})$ = 0.0372; $G(\mathbf{r})$ = 0.0089; $V(\mathbf{r})$ = −0.0085; ε = 0.7661.

H45–C44: $\rho(\mathbf{r})$ = 0.2660; $\nabla^2\rho(\mathbf{r})$ = −0.8924; $G(\mathbf{r})$ = 0.0445; $V(\mathbf{r})$ = −0.3122; ε = 0.0148.

*Diborane(4) Cation C–H insertion TS **15***



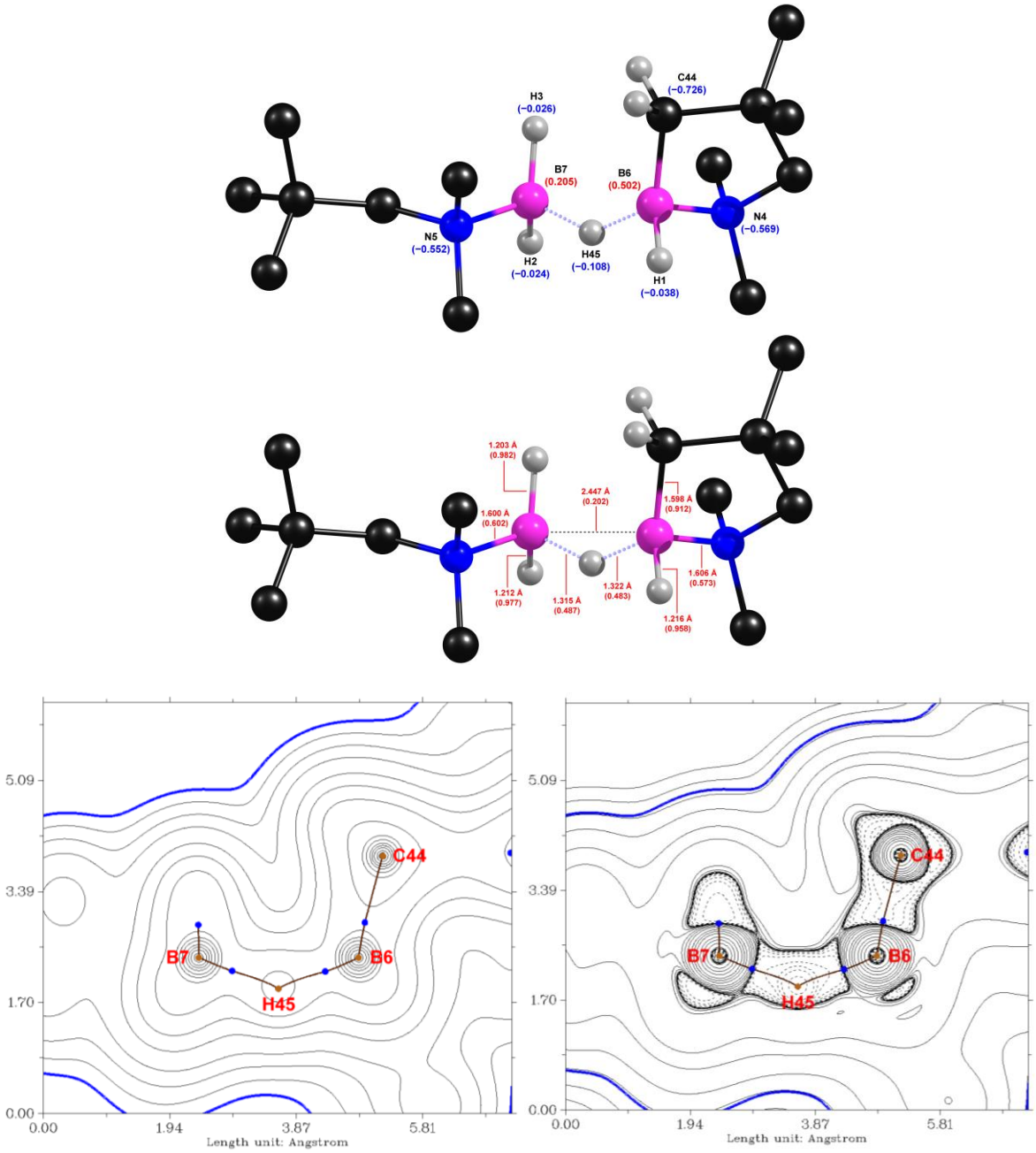


B6–B7: $\rho(\mathbf{r})$ = 0.1263; $\nabla^2\rho(\mathbf{r})$ = −0.2387; $G(\mathbf{r})$ = 0.0194; $V(\mathbf{r})$ = −0.0984; ε = 0.2395.

B6–H45: $\rho(\mathbf{r})$ = 0.1289; $\nabla^2\rho(\mathbf{r})$ = −0.1438; $G(\mathbf{r})$ = 0.0706; $V(\mathbf{r})$ = −0.1772; ε = 1.2103.

H45–C44: $\rho(\mathbf{r})$ = 0.1578; $\nabla^2\rho(\mathbf{r})$ = −0.1986; $G(\mathbf{r})$ = 0.0482; $V(\mathbf{r})$ = −0.1460; ε = 0.4716.

Diborane(4) C–H Insertion Product ***16***

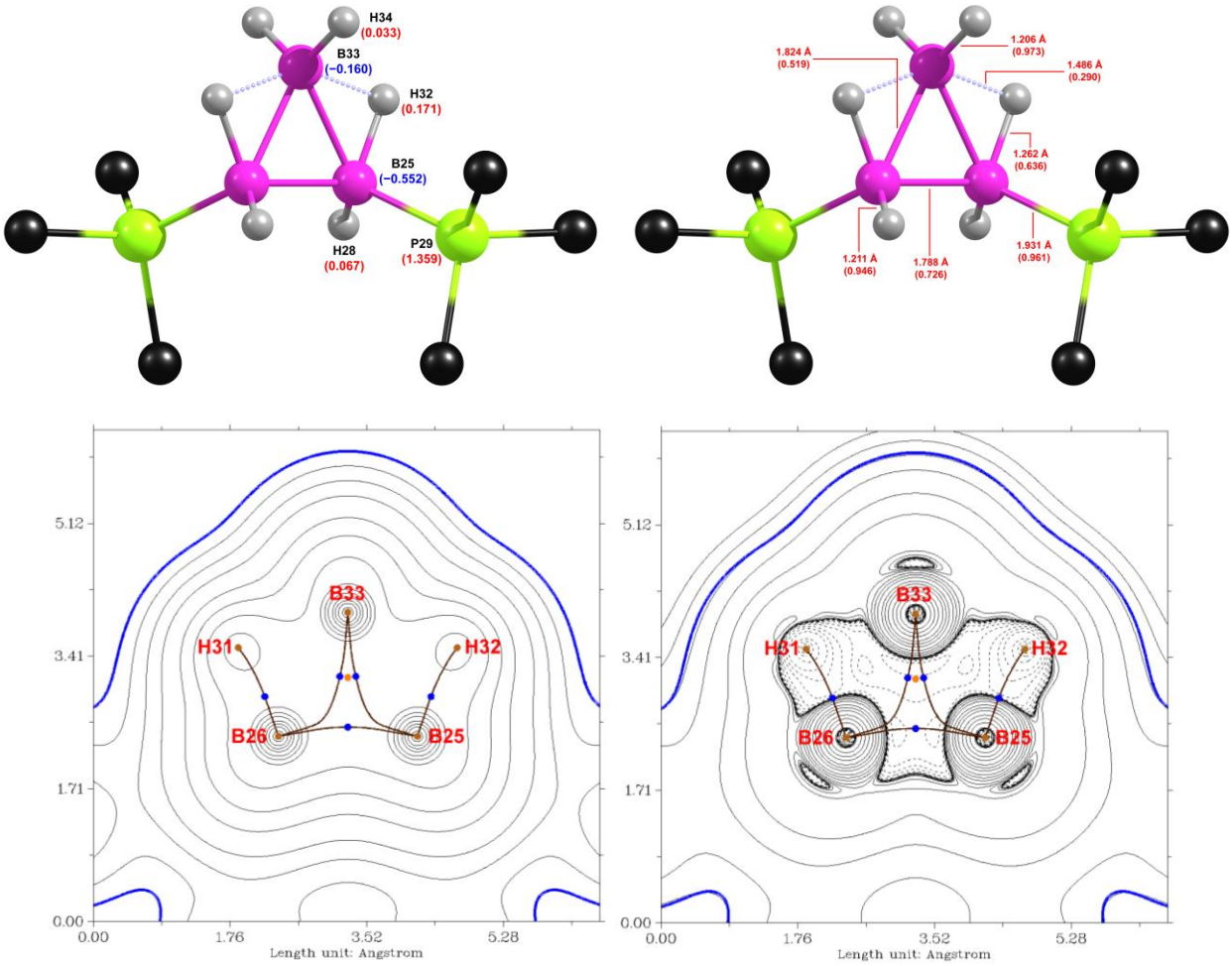


B6–C44: $\rho(\mathbf{r})$ = 0.1800; $\nabla^2\rho(\mathbf{r})$ = −0.3748; $G(\mathbf{r})$ = 0.0976; $V(\mathbf{r})$ = −0.2889; ε = 0.0713.

B6–H45: $\rho(\mathbf{r})$ = 0.1021; $\nabla^2\rho(\mathbf{r})$ = 0.0511; $G(\mathbf{r})$ = 0.0967; $V(\mathbf{r})$ = −0.1806; ε = 0.4466.

B7–H45: $\rho(\mathbf{r})$ = 0.1040; $\nabla^2\rho(\mathbf{r})$ = 0.0677; $G(\mathbf{r})$ = 0.1030; $V(\mathbf{r})$ = −0.1891; ε = 0.3768.

Triboron Cation ***20a***



Contour maps plotted in the plane containing B25, B26 and B33 atoms. An additional (3,+1) critical point is shown in orange.

B25–B26: $\rho(\mathbf{r})$ = 0.1213; $\nabla^2\rho(\mathbf{r})$ = −0.1724; $G(\mathbf{r})$ = 0.0231; $V(\mathbf{r})$ = −0.0893; ε = 0.6615.

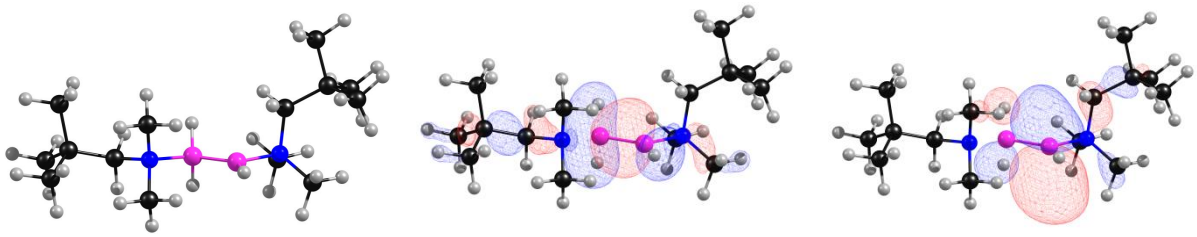
B25–B33: $\rho(\mathbf{r})$ = 0.1014; $\nabla^2\rho(\mathbf{r})$ = −0.0713; $G(\mathbf{r})$ = 0.0330; $V(\mathbf{r})$ = −0.0839; ε = 86.0008.

B25–H32: $\rho(\mathbf{r})$ = 0.1409; $\nabla^2\rho(\mathbf{r})$ = −0.0336 ; $G(\mathbf{r})$ = 0.1245; $V(\mathbf{r})$ = −0.2573; ε = 0.3743.

Conformational Analysis of 14

For diborane(4) cation **14**, three conformations were explored in detail. Gas phase energies listed below are relative to the lowest energy conformation 2. The relative ordering of the energies is preserved upon including either PhMe or PhBr solvation in the computational model.

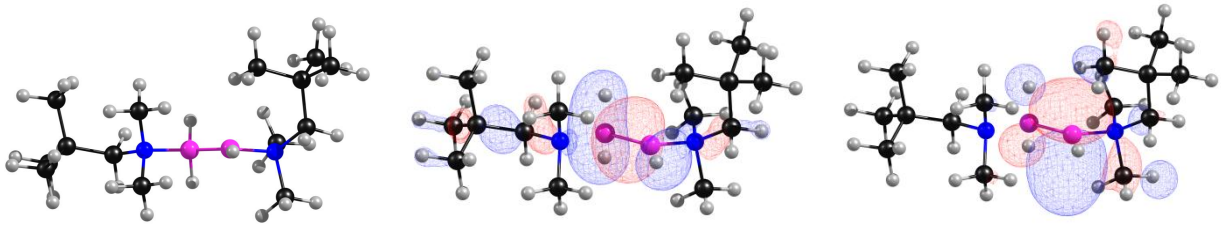
1) Conformation 1, G_{rel} = +4.5 kcal/mol



HOMO LUMO

This sp^2–sp^3 diborane(4) (open borenium) conformation was obtained by following the IRC path from the borenium B–H insertion TS **13**. The borenium center of this structure does not experience stabilization from adjacent C–H or B–H bonds, as the other two conformers do. This structure is also characterized by the lowest LUMO energy (−0.13868 a.u.).

2) Conformation 2, G_{rel} = 0 kcal/mol

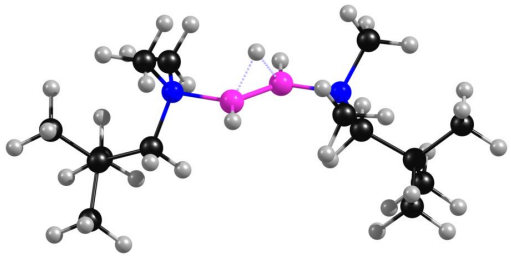


HOMO LUMO

This conformation was obtained by following the IRC path backwards from the C–H insertion TS **15**, and also by C–N bond rotation in Conformation 1. This in another open borenium form of the sp^2–sp^3 diborane(4) cation, although in this case the borenium center is involved in a

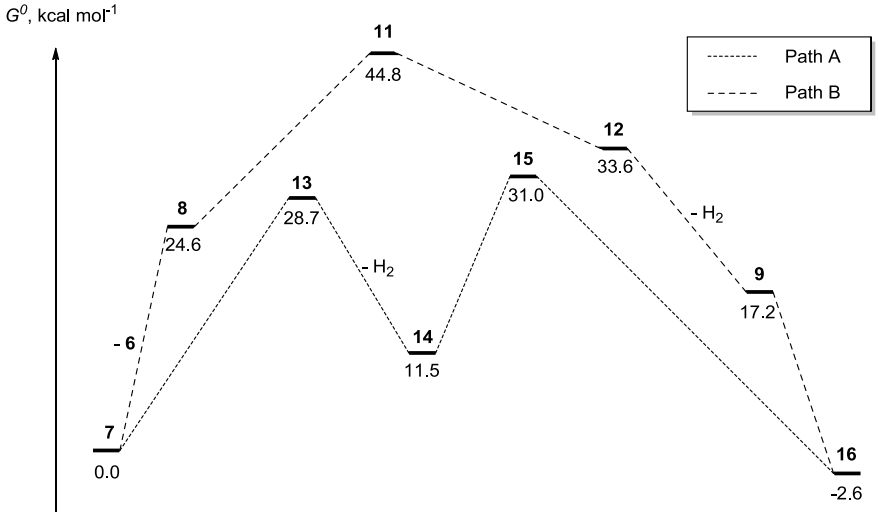
stabilizing interaction with the adjacent C–H bond, and LUMO of this conformer is thus of higher energy (−0.12847 a.u.).

3) Conformation 3, G_{rel} = +1.4 kcal/mol



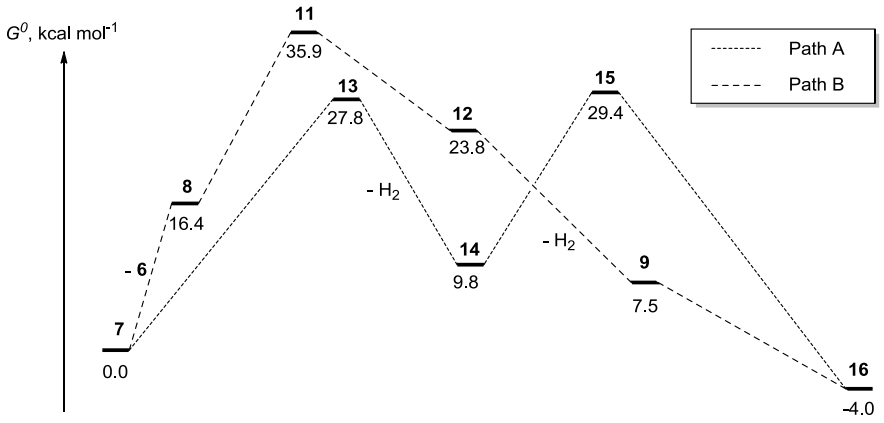
The third conformation is characterized by a C_2 symmetrical B–H–B bridge, thus eliminating the borenium center, and raising LUMO energy to −0.10525 a.u. It should be noted that while this is not the most stable conformation of cation **14**, in related species where the borenium center cannot be stabilized by a proximal C–H bond (such as in Me_3N derivatives), the B–H–B bridged form is of lowest energy.

Gas phase reaction profile



Computational modeling in PhMe solution

To assess the effects of the condensed phase on the reaction path, single point calculations were performed using PhMe as the solvent in SMD solvation model. Gas phase geometries and vibrational frequencies were used. Solution free energies were corrected for change in concentrations relative to the gas phase. Thus, for all species except H_2, concentrations of 1 M were assumed, resulting in 1.9 kcal/mol free energy corrections. The concentration of H_2 in the actual reaction mixture was limited by H_2 solubility in toluene. Assuming the actual experimental setup for the catalytic reaction,[2] the maximum H_2 pressure attained in the reaction vessel can be approximated to be ca. 250 kPa. At that pressure the maximum solution concentration of H_2 can be estimated to be below 7.4 mM,[S10] resulting in the free energy correction of −1.0 kcal/mol. The resulting free energy profile is given below.

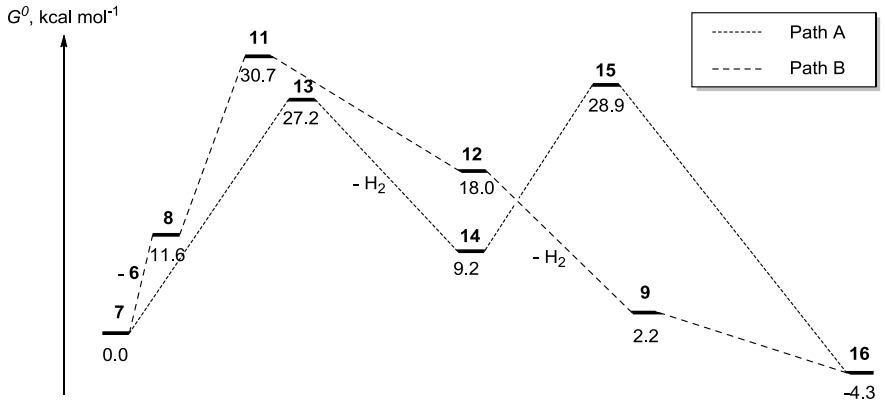


While including solvation in the computational model lowers the barriers in the borenium route (Path B) more so than in the diborane(4) route (Path A), the diborane(4) pathway still appears to be favored. Also, most substrates used in the actual intramolecular borylations[2] were less sterically hindered than **6**, making the $L_2B_2H_5^+$ species even less prone to dissociation into the free borenium and amine borane, further increasing the preference for the diborane(4) pathway. Also, in some high-temperature catalytic experiments[2] H_2 byproduct was allowed to leave the reaction vessel, which could be expected to further increase the preference for the diborane(4) pathway .

Computational modeling in PhBr solution

As suggested by a reviewer, the calculations were also performed using more polar bromobenzene as the solvent. It should be noted, however, that calculations in halobenzene solvents are of limited relevance, since PhMe was the solvent of choice in the previously reported high-temperature catalytic borylations of activated amine boranes.[2b,c]

In this case the same computational approach was used as for PhMe, except for a slightly different free energy correction for H_2 (−1.2 kcal/mol) due to somewhat lower solubility of hydrogen in PhBr (solution concentration of H_2 in the actual experiment estimated to be below 5.6 mM).[S11] The resulting free energy profile is given below.



In this case, the diborane(4) route (Path A) is still favored, albeit the difference between both pathways is only 1.8 kcal/mol. It is thus plausible that the use of bulky amine boranes and halobenzene solvents in the catalytic process may result in some contribution from the borenium pathway.

Calculated Geometries and Energies

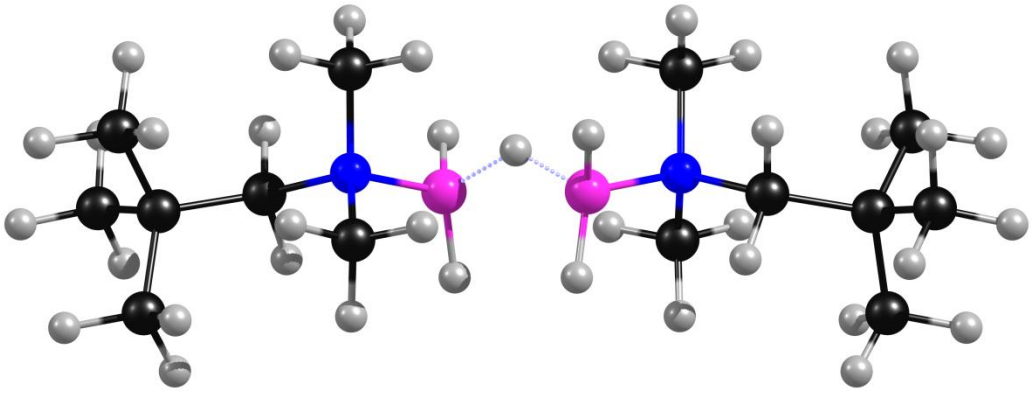
H_2

```
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (gas phase, Hartree) = -1.16872136960
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -1.16829694675
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -1.16822115642
E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -1.1630219876
E(MP4(SDTQ)/cc-pVTZ//MP2/cc-pVDZ) (gas phase, Hartree) = -1.1716172178
```

```
Enthalpy correction (kcal/mol) = 8.361
Entropy (cal/mol·K) = 31.193
Gibbs free energy correction (kcal/mol) = -0.939

H        0.000000000      0.000000000      0.377181113
H        0.000000000      0.000000000     -0.377181113
```

H-Bridged Cation 7



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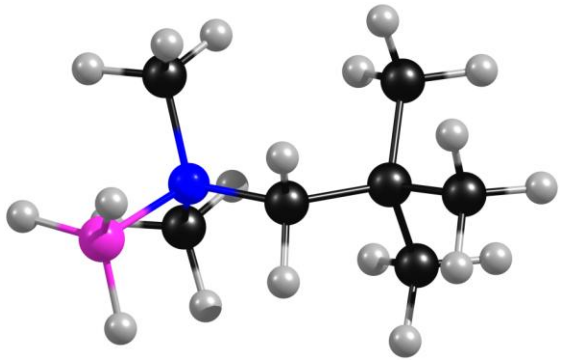
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (gas phase, Hartree) = -715.858971625
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -715.910018619
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -715.927155880
E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -713.8997653604
Enthalpy correction (kcal/mol) = 345.122
Entropy (cal/mol·K) = 163.096
Gibbs free energy correction (kcal/mol) = 296.495

H       -0.330663000      1.196443000      1.162434000
H        0.330663000     -1.196443000      1.162434000
H        0.841935000     -1.707545000     -0.776029000
N        1.417739000      1.766809000     -0.259766000
N       -1.417739000     -1.766809000     -0.259766000
B       -0.055480000      1.194637000     -0.008052000
B        0.055480000     -1.194637000     -0.008052000
H        0.000000000      0.000000000     -0.571278000
H       -0.841935000      1.707545000     -0.776029000
C        1.264631000      3.258040000      0.022917000
C       -1.264631000     -3.258040000      0.022917000
H        0.615504000      3.315302000      0.913826000
H       -0.615504000     -3.315302000      0.913826000
H        0.678870000      3.630352000     -0.833989000
H       -0.678870000     -3.630352000     -0.833989000
C        2.470615000      4.202328000      0.259153000
C       -2.470615000     -4.202328000      0.259153000
C        1.820802000      5.603864000      0.219294000
C       -1.820802000     -5.603864000      0.219294000
H        1.390762000      5.819600000     -0.773789000
H       -1.390762000     -5.819600000     -0.773789000
H        2.580767000      6.371799000      0.437078000
H       -2.580767000     -6.371799000      0.437078000
H        1.019690000      5.697194000      0.973016000
H       -1.019690000     -5.697194000      0.973016000
C        3.553839000      4.150016000     -0.829166000
C       -3.553839000     -4.150016000     -0.829166000
H        4.261985000      4.981033000     -0.671322000
H       -4.261985000     -4.981033000     -0.671322000
H        3.125253000      4.268638000     -1.839245000
H       -3.125253000     -4.268638000     -1.839245000
H        4.145434000      3.219664000     -0.800291000
H       -4.145434000     -3.219664000     -0.800291000
C        3.109025000      4.032990000      1.650380000
C       -3.109025000     -4.032990000      1.650380000
H        2.340431000      4.020219000      2.443182000
H       -2.340431000     -4.020219000      2.443182000
H        3.774234000      4.890200000      1.848667000
H       -3.774234000     -4.890200000      1.848667000
H        3.721773000      3.124333000      1.743807000
H       -3.721773000     -3.124333000      1.743807000
C        1.820802000      1.520090000     -1.678940000
C       -1.820802000     -1.520090000     -1.678940000
H        2.819619000      1.929369000     -1.870122000
```

H	-2.819619000	-1.929369000	-1.870122000
H	1.082952000	1.994782000	-2.340901000
H	-1.082952000	-1.994782000	-2.340901000
H	-1.830212000	-0.434104000	-1.851927000
H	1.830212000	0.434104000	-1.851927000
H	2.113737000	1.311714000	1.691862000
H	-2.113737000	-1.311714000	1.691862000
H	3.407966000	1.464194000	0.442972000
H	-3.407966000	-1.464194000	0.442972000
H	-2.351734000	-0.015856000	0.472776000
H	2.351734000	0.015856000	0.472776000
C	2.394069000	1.099317000	0.651739000
C	-2.394069000	-1.099317000	0.651739000

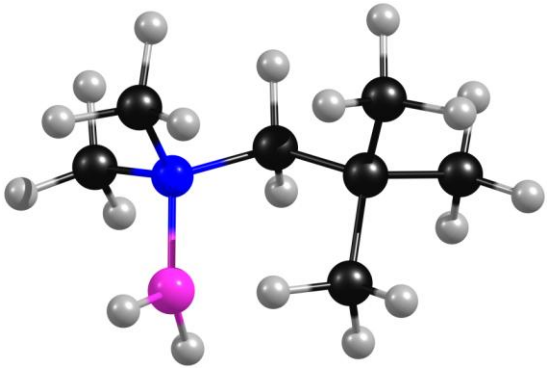
*Amine Borane **6***



E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (gas phase, Hartree) = -358.315891023
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -358.327069520
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -358.330834036
E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -357.3311581062
E(MP4(SDTQ)/cc-pVTZ//MP2/cc-pVDZ) (gas phase, Hartree) = -357.7214553261
Enthalpy correction (kcal/mol) = 173.990
Entropy (cal/mol·K) = 102.233
Gibbs free energy correction (kcal/mol) = 143.509

C	0.024213617	-0.020040295	0.776333936
H	0.020069071	-0.913671612	1.422313154
H	0.088422671	0.853618230	1.446574818
C	-1.330297156	0.058671435	0.024693720
C	-2.375582842	-0.194420671	1.131737655
H	-2.265538241	0.531846820	1.955966286
H	-3.394964363	-0.093964459	0.721853338
H	-2.272033333	-1.209372848	1.552927869
C	-1.614120135	1.454772530	-0.559504333
H	-2.670701855	1.513372807	-0.874934806
H	-1.445573146	2.241064700	0.197243506
H	-0.997570111	1.686681731	-1.440414247
C	-1.527442254	-1.006534348	-1.064422254
H	-1.315462716	-2.020486605	-0.683681193
H	-2.577307996	-0.989302679	-1.406538204
H	-0.895536550	-0.825128241	-1.949365384
C	1.511725118	0.952663113	-0.974751921
H	0.877303015	0.721706203	-1.844698428
H	1.251452386	1.934974947	-0.558522447
H	2.568550013	0.963298453	-1.277221750
H	2.304778300	-0.610766236	2.125533664
H	3.580226270	0.085850388	0.683164607
H	2.295155055	1.374206622	1.622271317
H	1.545790737	-2.161083892	0.313072642
H	0.962353418	-1.653145657	-1.317470965
H	2.681312381	-1.412364919	-0.844462706
N	1.358181249	-0.072868920	0.084486960
C	1.642070289	-1.414620412	-0.487688156
B	2.505549111	0.225370817	1.253667317

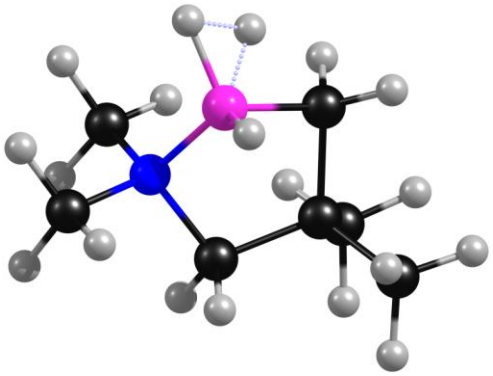
*Primary Borenium Cation **8***



E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (gas phase, Hartree) = -357.480287966
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -357.536233824
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -357.557188836
E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -356.5056331304
E(MP4(SDTQ)/cc-pVTZ//MP2/cc-pVDZ) (gas phase, Hartree) = -356.8849700075
Enthalpy correction (kcal/mol) = 168.146
Entropy (cal/mol·K) = 100.619
Gibbs free energy correction (kcal/mol) = 138.146

C	-0.028892267	-0.286046052	-0.833790708
H	-0.061640558	-1.357216257	-1.092803336
H	-0.115669478	0.301641136	-1.764229000
C	1.280480470	0.008537739	-0.081092591
C	2.396503402	-0.721136026	-0.857038581
H	2.493610825	-0.308794629	-1.875568276
H	3.362944769	-0.584381464	-0.345548911
H	2.196427293	-1.803079676	-0.935036095
C	1.646960507	1.502910471	-0.015359958
H	2.695774518	1.602285799	0.309739156
H	1.561654662	1.975452079	-1.008528807
H	1.039013909	2.078933999	0.698012064
C	1.178677725	-0.592500334	1.325041053
H	1.208685486	-1.690863578	1.333850879
H	1.967793988	-0.214884312	1.998291797
H	0.254028655	-0.227372610	1.882412630
C	-1.586595002	1.417564715	0.162733538
H	-0.886818116	1.853179641	0.882196056
H	-1.503850608	1.927025526	-0.808702317
H	-2.609456422	1.510765857	0.552776948
C	-2.453021970	-0.659330375	-0.762270811
H	-2.235686448	-1.717098724	-0.960233933
H	-3.358199665	-0.566415515	-0.144024426
H	-2.588506314	-0.110760853	-1.706125992
N	-1.287689382	-0.042599428	-0.021959380
B	-1.208640087	-0.805767971	1.335742438
H	-1.691167023	-0.245835048	2.279407747
H	-1.096241869	-1.991169107	1.237864819

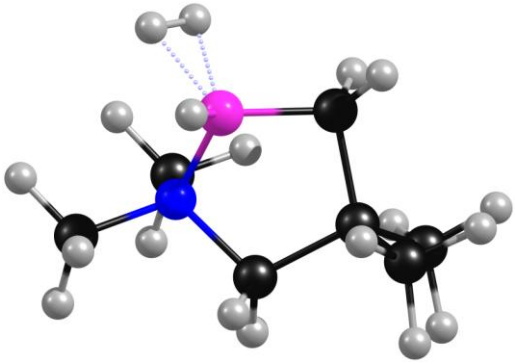
*Borenium C–H Insertion TS **11***



E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (gas phase, Hartree) = -357.446906086
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -357.504036577
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -357.525630210
E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -356.4722952383
E(MP4(SDTQ)/cc-pVTZ//MP2/cc-pVDZ) (gas phase, Hartree) = -356.8533479283
Enthalpy correction (kcal/mol) = 166.264
Entropy (cal/mol·K) = 96.635
Gibbs free energy correction (kcal/mol) = 137.453

C	-0.052090903	0.054674226	-1.011274118
H	-0.063352494	-0.856687532	-1.629675717
H	-0.192066887	0.927795415	-1.670216021
C	1.242406310	0.117659699	-0.153725610
C	2.214561447	-0.964839929	-0.652056814
H	2.440918355	-0.813956020	-1.721460077
H	3.163843722	-0.915617031	-0.094138878
H	1.786638956	-1.974526408	-0.528291047
C	1.915568351	1.496253828	-0.243690506
H	2.812839991	1.524681187	0.396371713
H	2.233814609	1.701645297	-1.279795986
H	1.242470660	2.310654343	0.074486295
C	0.853947412	-0.204125960	1.337453337
H	1.548970738	-0.924280813	1.795804506
H	0.901598467	0.722437250	1.941791151
H	-0.437618274	-0.356885738	2.148966643
C	-1.665081681	1.307492314	0.380560852
H	-0.816278148	1.809468755	0.862055602
H	-1.994192055	1.896758514	-0.488210572
H	-2.495715920	1.199836857	1.092985872
C	-2.405350897	-0.701063076	-0.783313746
H	-2.114727795	-1.717797317	-1.079940117
H	-3.256699271	-0.743305248	-0.089074267
H	-2.670680611	-0.105167038	-1.669581879
N	-1.247767479	-0.052483184	-0.087463914
B	-0.670073779	-0.950331051	1.062570600
H	-1.421603796	-0.837263705	2.101736544
H	-0.546035749	-2.119135856	0.844648552

*Borenium H_2 Complex **12***

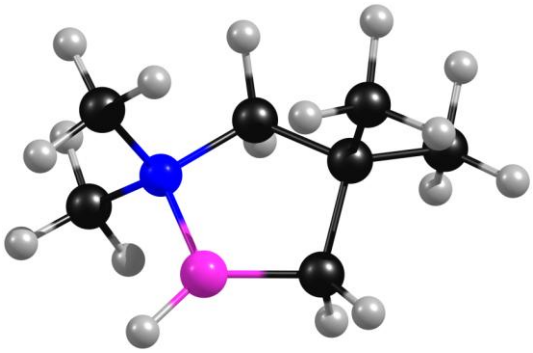


E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (gas phase, Hartree) = -357.464311919
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -357.522822240
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -357.545423019
E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -356.4880648746
E(MP4(SDTQ)/cc-pVTZ//MP2/cc-pVDZ) (gas phase, Hartree) = -356.8689914346
Enthalpy correction (kcal/mol) = 166.504
Entropy (cal/mol·K) = 98.434
Gibbs free energy correction (kcal/mol) = 137.156

C	-0.048868218	0.042740266	-1.007146106
H	-0.070451466	-0.875872843	-1.615338099
H	-0.196489555	0.908433829	-1.674202216
C	1.256559759	0.110809894	-0.151526342
C	2.230516478	-0.956047540	-0.677687323
H	2.449234064	-0.793941619	-1.747446623
H	3.182875213	-0.906901900	-0.124943681
H	1.815277994	-1.972204891	-0.559490754
C	1.914042862	1.495214301	-0.245673067
H	2.815090694	1.528029899	0.388774016

H	2.221363450	1.712023799	-1.283306397
H	1.238229418	2.301983270	0.086076046
C	0.838752880	-0.228302718	1.322424988
H	1.572964538	-0.896569749	1.798530230
H	0.799207433	0.693364027	1.928155718
H	-1.199236987	-0.441645313	2.333730924
C	-1.659206195	1.323860011	0.366586728
H	-0.811254334	1.820999939	0.853166859
H	-1.972344169	1.903084878	-0.514835258
H	-2.504505435	1.240329342	1.066282767
C	-2.408772076	-0.701679549	-0.763392312
H	-2.117458725	-1.716947422	-1.063598975
H	-3.260478543	-0.746333299	-0.068105398
H	-2.686765168	-0.108234961	-1.647399248
N	-1.252126883	-0.047932631	-0.076527881
B	-0.576881006	-0.913322237	1.068248601
H	-1.639984215	-1.072607168	2.108368804
H	-0.700068927	-2.098741723	0.899756937

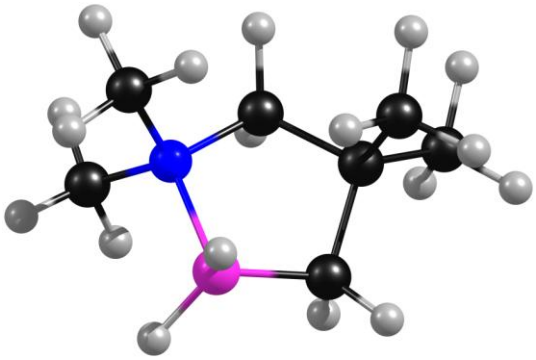
*Cyclic Borenium Cation **9***



E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (gas phase, Hartree) = -356.301490640
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -356.358681441
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -356.380266207
E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -355.3326634136
E(MP4(SDTQ)/cc-pVTZ//MP2/cc-pVDZ) (gas phase, Hartree) = -355.7030362477
Enthalpy correction (kcal/mol) = 154.430
Entropy (cal/mol·K) = 97.487
Gibbs free energy correction (kcal/mol) = 125.364

C	0.014876699	-0.024067689	-1.059320181
H	-0.071946346	-0.997362212	-1.569771199
H	-0.065552422	0.777421703	-1.811573438
C	1.308329733	0.014236910	-0.215904961
C	2.436831954	-0.693513473	-0.975439894
H	2.674891345	-0.163957719	-1.913804591
H	3.350698938	-0.714668466	-0.359709656
H	2.164650952	-1.733937034	-1.222286777
C	1.742145044	1.450095345	0.124669411
H	2.694784982	1.426569077	0.679363743
H	1.898053570	2.046252981	-0.790402428
H	1.017248770	1.979459438	0.767762553
C	0.890885510	-0.722938613	1.083731853
H	0.871130825	-1.826902350	0.908917138
H	1.564470084	-0.569740340	1.942094244
C	-1.754567746	1.455060988	-0.044421131
H	-0.961853864	2.178587007	0.181723843
H	-2.195508076	1.679606426	-1.027217426
H	-2.530689754	1.483349768	0.733861279
C	-2.267677727	-0.890562997	-0.493821786
H	-1.884035642	-1.920656150	-0.447588024
H	-3.112319003	-0.769156170	0.198994862
H	-2.580121251	-0.655628439	-1.522426918
N	-1.171829855	0.066768152	-0.101861106
B	-0.600330771	-0.363580583	1.286294897
H	-1.368151591	-0.396822326	2.204188537

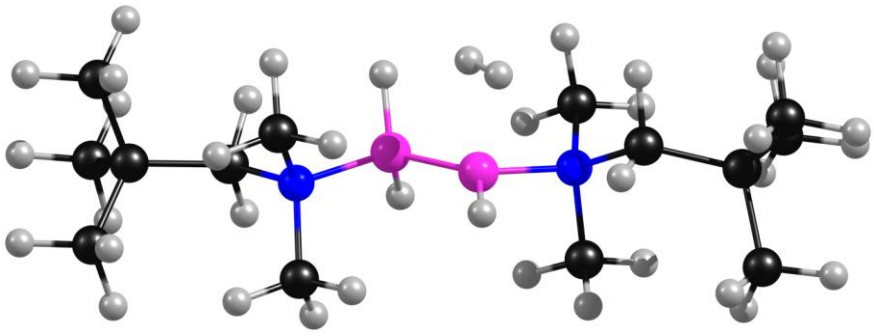
*Cyclic Borylation Product **10***



E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (gas phase, Hartree) = -357.129761216
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -357.139908503
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -357.142939256
E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -356.1544600376
E(MP4(SDTQ)/cc-pVTZ//MP2/cc-pVDZ) (gas phase, Hartree) = -356.5345676772
Enthalpy correction (kcal/mol) = 160.633
Entropy (cal/mol·K) = 95.743
Gibbs free energy correction (kcal/mol) = 132.088

C	0.004576015	-0.016399990	-1.019992059
H	-0.076156047	-0.986148437	-1.540153214
H	-0.052643218	0.783876642	-1.781101276
C	1.302336859	-0.009332409	-0.193761393
C	2.424493398	-0.654236163	-1.018079453
H	2.639515360	-0.080146574	-1.938946299
H	3.352564876	-0.696517572	-0.422738803
H	2.160139872	-1.686741256	-1.306962367
C	1.730937383	1.415913287	0.190783799
H	2.696564999	1.378519339	0.724588297
H	1.865362867	2.048797762	-0.706008823
H	1.006419527	1.898327906	0.864517292
C	0.903974948	-0.827425605	1.055233534
H	0.895020366	-1.902300259	0.780867941
H	1.657496859	-0.710648766	1.855759172
C	-1.777828310	1.437872951	-0.127277898
H	-1.003012571	2.183250131	0.089482972
H	-2.215306523	1.628300664	-1.123808387
H	-2.558614287	1.499664958	0.644376435
C	-2.216530869	-0.899418716	-0.487280027
H	-1.807806402	-1.912961242	-0.374933641
H	-3.084427015	-0.789197132	0.178057712
H	-2.519228862	-0.725395361	-1.535567790
N	-1.177345376	0.081435416	-0.084503035
B	-0.577890722	-0.284983427	1.461221917
H	-1.357031802	-1.093554683	1.947170968
H	-0.579722570	0.780865341	2.064238160

*Borenium B–H Insertion TS **13***

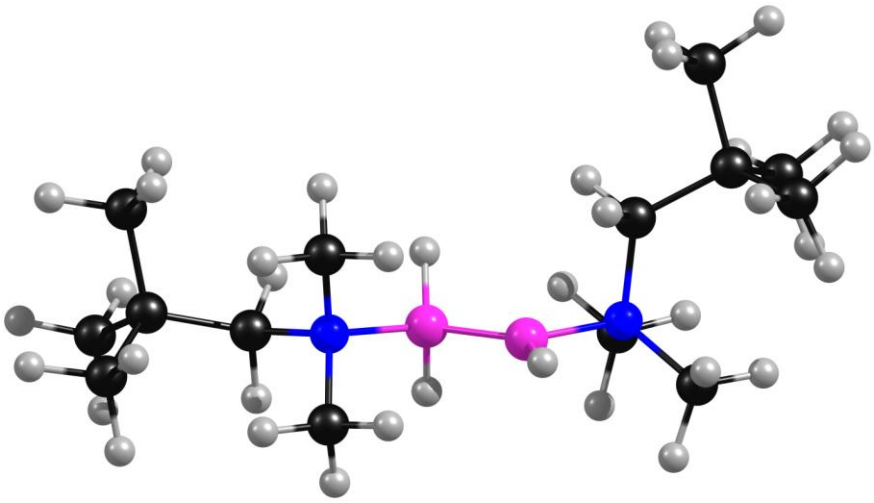


E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (gas phase, Hartree) = -715.807828468
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -715.860226667
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -715.878387327

E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -713.8468560305
Enthalpy correction (kcal/mol) = 341.437
Entropy (cal/mol·K) = 162.205
Gibbs free energy correction (kcal/mol) = 293.076

H	-0.885588000	-1.572965000	0.192778000
H	0.721226000	1.318220000	0.774256000
H	0.889265000	1.102750000	-1.211725000
N	-2.088767000	0.372494000	0.048413000
N	2.104010000	-0.372365000	0.075233000
B	-0.709836000	-0.415131000	-0.114186000
B	0.745021000	0.509530000	-0.150081000
H	-0.635468000	-0.515173000	-1.912792000
H	-1.151749000	-1.084919000	-1.850852000
C	-2.179312000	0.502453000	1.545512000
H	-3.014001000	1.168821000	1.795500000
H	-2.337759000	-0.492646000	1.982707000
H	-1.236321000	0.934323000	1.909952000
C	3.251350000	0.623948000	0.075016000
H	3.017549000	1.321197000	-0.745733000
H	3.114829000	1.180424000	1.017391000
C	-1.995174000	1.742977000	-0.554854000
H	-1.123928000	2.251673000	-0.122934000
H	-1.858229000	1.640223000	-1.640792000
H	-2.911760000	2.304917000	-0.343037000
C	-3.264319000	-0.408452000	-0.530791000
H	-3.190646000	-0.233475000	-1.617556000
H	-3.027499000	-1.468780000	-0.340166000
C	2.228084000	-1.380109000	-1.011988000
H	1.320278000	-2.001565000	-1.015345000
H	2.325131000	-0.857368000	-1.973874000
H	3.100055000	-2.026559000	-0.842308000
C	2.017167000	-1.080479000	1.385593000
H	1.131985000	-1.731812000	1.373922000
H	2.912154000	-1.689764000	1.561772000
H	1.910306000	-0.329396000	2.181064000
C	4.741883000	0.218395000	-0.062404000
C	-4.736990000	-0.175856000	-0.103000000
C	5.131074000	-0.162712000	-1.503334000
H	6.230756000	-0.192011000	-1.587182000
H	4.760398000	-1.152257000	-1.809760000
H	4.763092000	0.586998000	-2.225860000
C	5.221223000	-0.867800000	0.912938000
H	4.824562000	-1.867529000	0.668498000
H	6.320915000	-0.940599000	0.859082000
H	4.956457000	-0.626192000	1.956716000
C	5.488779000	1.526701000	0.280808000
H	6.573951000	1.383844000	0.149500000
H	5.173143000	2.353407000	-0.379196000
H	5.306760000	1.829411000	1.326308000
C	-5.218458000	1.280558000	-0.190684000
H	-4.785085000	1.924553000	0.592705000
H	-5.002289000	1.725547000	-1.177145000
H	-6.312303000	1.304362000	-0.050618000
C	-5.523823000	-1.000927000	-1.147291000
H	-6.600385000	-0.960492000	-0.915669000
H	-5.379128000	-0.603985000	-2.166783000
H	-5.216463000	-2.061254000	-1.138369000
C	-5.067903000	-0.759648000	1.283520000
H	-6.163457000	-0.810037000	1.399584000
H	-4.677424000	-1.787225000	1.389896000
H	-4.687441000	-0.151853000	2.117624000

*Borenium B–H Insertion Product **14**, Conformation 1 (from IRC of **13**)*

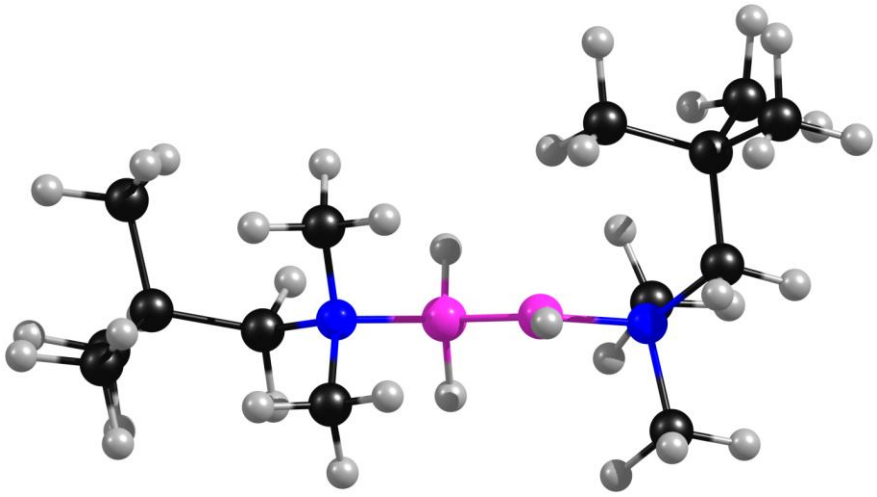


E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (gas phase, Hartree) = -714.642070978
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -714.694619971
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -714.712610247
E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -712.6886073599
Enthalpy correction (kcal/mol) = 331.430
Entropy (cal/mol·K) = 161.779
Gibbs free energy correction (kcal/mol) = 283.195

H	0.961558283	0.288710641	1.838610461
H	-0.776627739	-1.695560422	-0.155687524
H	-0.340745416	-0.171984442	-1.382158310
N	2.195459845	-0.801669851	0.281518708
N	-1.912724219	0.273834148	0.252649567
B	0.800331898	-0.239869184	0.761896131
B	-0.552326866	-0.485700637	-0.216021500
C	3.014940106	-1.234501386	1.456193026
H	3.968274882	-1.655650684	1.111042908
H	3.184700926	-0.375119788	2.116074407
H	2.448053778	-2.007852930	1.996493251
C	-3.009969031	-0.211277713	-0.680979490
H	-2.542404466	-0.227638018	-1.678910193
H	-3.163675150	-1.261546505	-0.381108590
C	2.065231843	-1.945943261	-0.678203282
H	1.567441679	-2.774748142	-0.155813953
H	1.447369433	-1.629096395	-1.527199235
H	3.060609070	-2.259046054	-1.015125178
C	2.703212768	0.466194944	-0.409556440
H	2.142826274	0.493515314	-1.357868162
H	2.343671487	1.310504188	0.214575220
C	-1.702730312	1.745078298	0.166463122
H	-0.818574404	2.003535424	0.768451201
H	-1.525539535	2.018942343	-0.882591980
H	-2.576411932	2.283293113	0.559130306
C	-2.218917645	-0.092027878	1.667237701
H	-1.381088301	0.229098248	2.301895265
H	-3.138355908	0.399677100	2.007156046
H	-2.329137041	-1.183911167	1.729420930
C	-4.389332306	0.483475851	-0.819539272
C	4.206673269	0.713600608	-0.696478723
C	-4.326402431	1.789509209	-1.633881081
H	-5.349780080	2.093936983	-1.911634703
H	-3.882029417	2.629572262	-1.079552572
H	-3.757030711	1.647935118	-2.569495599
C	-5.139267270	0.726537898	0.499345206
H	-4.685862176	1.526925550	1.107900520
H	-6.171137844	1.045332317	0.273350387
H	-5.202775053	-0.191005924	1.109262326
C	-5.205723848	-0.532975069	-1.648852133
H	-6.201487526	-0.117576238	-1.874862918
H	-4.707634024	-0.760556586	-2.607405730
H	-5.345798403	-1.478953003	-1.098140460
C	4.876873655	-0.422641645	-1.483662396
H	5.022460794	-1.332198288	-0.877776687
H	4.303360459	-0.685554759	-2.389050933
H	5.877831294	-0.092508962	-1.808892644
C	4.182395370	1.974245334	-1.588979306
H	5.214666012	2.270294778	-1.836443463
H	3.644030758	1.789277898	-2.534232064
H	3.702125050	2.824070488	-1.073179560
C	5.025997299	1.049128088	0.562204303
H	5.999421197	1.466395380	0.254780001

```
H        4.520326902      1.812127771      1.180126744
H        5.238877995      0.171996167      1.190530428
```

*Borenium B–H Insertion Product **14**, Conformation 2 (Minimum, from IRC of **15**)*



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E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (gas phase, Hartree) = -714.649413264
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -714.701934472
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -714.719892640
E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -712.6957824826
Enthalpy correction (kcal/mol) = 331.358
Entropy (cal/mol·K) = 161.211
Gibbs free energy correction (kcal/mol) = 283.293
```
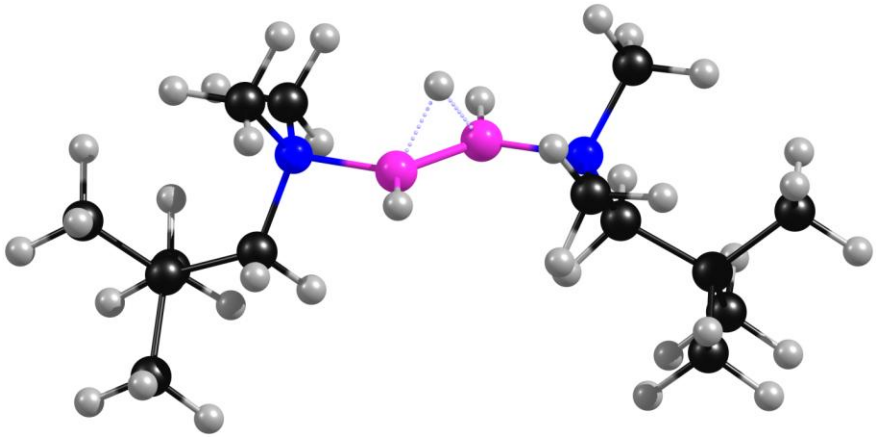

```
H        4.122450789     -0.245945609      1.577641353
H        1.438502717     -0.689808160      3.526502774
H        1.498284844      1.297427937      3.276585250
N        2.099472501     -0.249292383      0.564792566
N        3.146153021      0.407404051      4.623958442
B        2.969766066     -0.007015094      1.854612638
B        2.174307895      0.277382881      3.323557412
C        2.103505660     -1.756827455      0.453727756
H        1.475500090     -2.038772833     -0.404823858
H        3.134007173     -2.105705694      0.298793485
H        1.688400754     -2.181272023      1.379415620
C        2.226230988      0.545378953      5.825892424
H        1.430590662      1.231524725      5.492840521
H        1.769040147     -0.453829507      5.921925735
C        0.673725846      0.188672128      0.706511822
H        0.206035863     -0.411697784      1.497433101
H        0.641986496      1.242078425      0.997684346
H        0.156889585      0.032930862     -0.252744369
C        2.745640182      0.287129818     -0.700137492
H        3.725003619     -0.217184059     -0.744437875
H        2.130318749     -0.077496075     -1.543136400
C        4.035317565      1.588476947      4.449722657
H        4.579296341      1.475073701      3.500038560
H        3.418099694      2.496779312      4.413013273
H        4.758577640      1.651832532      5.274450604
C        3.985869129     -0.821279370      4.735259446
H        4.590037024     -0.916189160      3.821905535
H        4.651963049     -0.762881023      5.604688615
H        3.320458042     -1.691422991      4.827735316
C        2.703441548      1.020585912      7.222611497
C        2.963956636      1.808642768     -0.816622568
C        2.953047047      2.539190731      7.288584967
H        3.038110563      2.847817839      8.344366544
H        3.881457223      2.851922071      6.787887737
H        2.111208407      3.100209211      6.845718415
C        3.913900242      0.267207907      7.795407383
H        4.856016457      0.516032774      7.278641605
H        4.047349611      0.551121130      8.853267019
H        3.768520809     -0.826296360      7.762351224
C        1.486168070      0.718187948      8.124883706
H        1.679934853      1.079260558      9.148254087
H        0.576927231      1.222438626      7.753786119
H        1.284764246     -0.365619384      8.176109916
C        3.610180126      2.372972336      0.455659126
```

H	2.978272398	2.207646664	1.352448779
H	4.607145448	1.935978312	0.632578265
H	3.733478498	3.465667679	0.365097075
C	3.943447778	1.972890864	-1.997226207
H	4.158866752	3.041698819	-2.158386759
H	4.898797876	1.455595149	-1.804087539
H	3.512290663	1.571617977	-2.930804369
C	1.683726202	2.592014064	-1.160744760
H	1.960267672	3.611938863	-1.476169312
H	1.139931109	2.122466908	-1.998895723
H	0.992792276	2.697947619	-0.311437403

*Borenium B–H Insertion Product **14**, Conformation 3 (C_2 Symmetrical)*

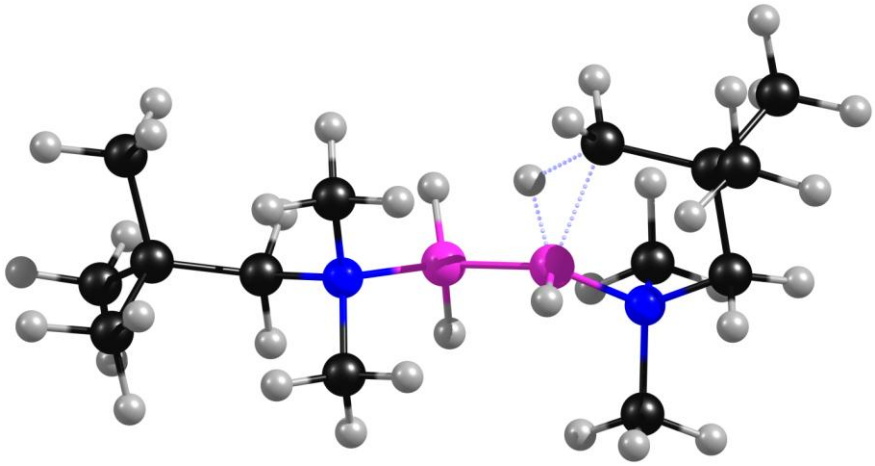


E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (gas phase, Hartree) = -714.649714857
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -714.701119213
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -714.718333740
E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -712.6972494254
Enthalpy correction (kcal/mol) = 331.875
Entropy (cal/mol·K) = 157.519
Gibbs free energy correction (kcal/mol) = 284.911

C	2.661340695	0.555420394	-0.343414737
C	-2.661340695	-0.555420394	-0.343414737
H	1.868308304	0.320264421	-1.075464331
H	-1.868308304	-0.320264421	-1.075464331
H	2.668223476	1.649767948	-0.206443473
H	-2.668223476	-1.649767948	-0.206443473
C	4.015915858	0.115405912	-0.954432275
C	-4.015915858	-0.115405912	-0.954432275
C	4.209302302	1.117169819	-2.115018322
C	-4.209302302	-1.117169819	-2.115018322
H	4.310607207	2.150553502	-1.741416614
H	-4.310607207	-2.150553502	-1.741416614
H	5.124376203	0.864777391	-2.675092604
H	-5.124376203	-0.864777391	-2.675092604
H	3.360794038	1.083783295	-2.820537478
H	-3.360794038	-1.083783295	-2.820537478
C	5.221410662	0.243175369	-0.010406156
C	-5.221410662	-0.243175369	-0.010406156
H	6.148639094	0.102586496	-0.591373016
H	-6.148639094	-0.102586496	-0.591373016
H	5.272029482	1.241448756	0.457229912
H	-5.272029482	-1.241448756	0.457229912
H	5.225052369	-0.522648411	0.783013633
H	-5.225052369	0.522648411	0.783013633
C	3.973347643	-1.296037167	-1.568516561
C	-3.973347643	1.296037167	-1.568516561
H	-3.087974780	1.422852627	-2.216331031
H	3.087974780	-1.422852627	-2.216331031
H	4.867465030	-1.443038872	-2.197530057
H	-4.867465030	1.443038872	-2.197530057
H	-3.974282455	2.099730875	-0.817595907
H	3.974282455	-2.099730875	-0.817595907
C	2.832977757	0.650865306	2.151953918
C	-2.832977757	-0.650865306	2.151953918
H	3.884690467	0.341543100	2.179722418
H	-3.884690467	-0.341543100	2.179722418
H	2.756779700	1.743001946	2.062642257
H	-2.756779700	-1.743001946	2.062642257

H	2.325402807	0.322884843	3.070982594
H	-2.325402807	-0.322884843	3.070982594
H	-1.798563726	1.923519341	0.210228471
H	1.798563726	-1.923519341	0.210228471
H	-3.305515256	1.739668619	1.187113176
H	3.305515256	-1.739668619	1.187113176
H	-1.705203784	1.782346868	1.996206932
H	1.705203784	-1.782346868	1.996206932
N	2.131532846	0.022820244	0.985367194
N	-2.131532846	-0.022820244	0.985367194
C	-2.247997535	1.459625133	1.096461321
C	2.247997535	-1.459625133	1.096461321
B	0.617117329	0.517587399	0.969453842
B	-0.617117329	-0.517587399	0.969453842
H	0.573963886	1.721984264	1.015006136
H	-0.573963886	-1.721984264	1.015006136
H	0.000000000	0.000000000	2.118219128

*Diborane(4) Cation C–H insertion TS **15***



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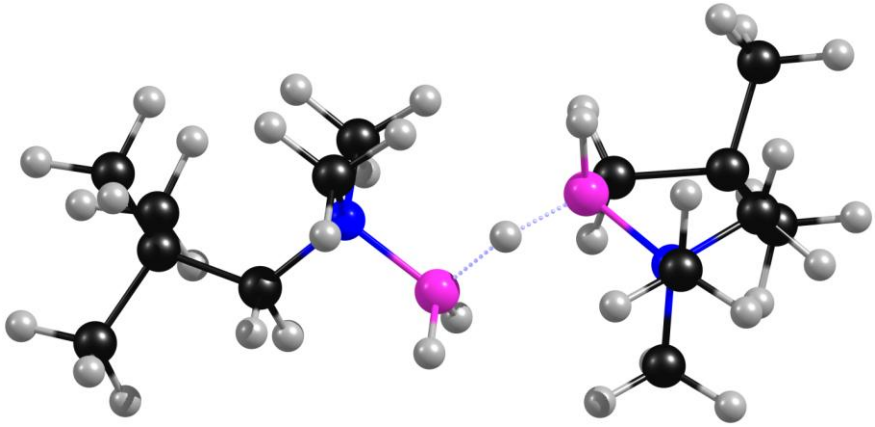
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -714.671408482
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -714.689146457
E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -712.6697465472
Enthalpy correction (kcal/mol) = 329.913
Entropy (cal/mol·K) = 154.950
Gibbs free energy correction (kcal/mol) = 283.715

H	4.025937034	0.235319166	1.703758947
H	1.436083499	-0.502384230	3.477824603
H	1.312302495	1.498077826	3.593746262
N	1.987423846	-0.157218295	0.662813792
N	3.116739096	0.552538511	4.645267594
B	2.865678480	0.546872902	1.782122801
B	2.063223853	0.544641203	3.401525910
C	2.087550845	-1.643584755	0.777666530
H	1.559283257	-2.107513888	-0.069811946
H	3.149508442	-1.926328938	0.760719340
H	1.630424638	-1.954046915	1.726639284
C	2.262887224	0.532322861	5.905347853
H	1.442453941	1.238841706	5.701602539
H	1.823704761	-0.479398005	5.905988370
C	0.545223956	0.230644032	0.740074697
H	0.131786855	-0.145644236	1.684708342
H	0.455296976	1.323928273	0.713014254
H	0.009334631	-0.207534927	-0.116411116
C	2.593162560	0.298240912	-0.635038613
H	3.512046682	-0.295768507	-0.760787537
H	1.904475088	0.060279236	-1.464664105
C	3.980140144	1.761913488	4.565284861
H	4.500938297	1.751397183	3.596119325
H	3.348313809	2.658356352	4.643935271
H	4.728055638	1.755265540	5.369758523
C	3.978487182	-0.664981575	4.578646441
H	4.515542614	-0.661245029	3.621162014
H	4.700220259	-0.674093590	5.404224470
H	3.331320833	-1.551643612	4.633323119
C	2.811479508	0.848763350	7.321476457
C	2.938835425	1.804257280	-0.541074290

C	3.036659623	2.354845406	7.554144280
H	3.177500608	2.538918470	8.632761989
H	3.928315501	2.748478979	7.043634780
H	2.160116231	2.942696663	7.229099747
C	4.064440550	0.062608100	7.737076052
H	4.973174834	0.393671090	7.206856290
H	4.248761359	0.222672140	8.813127942
H	3.937637823	-1.022429631	7.580973683
C	1.651073607	0.413184848	8.244239358
H	1.894180218	0.657402410	9.291358022
H	0.713647474	0.934522920	7.983284099
H	1.473092532	-0.673883515	8.178056260
C	2.938635565	2.226232250	0.963630008
H	2.414155896	1.691977402	2.086119390
H	3.898871225	2.663832951	1.275528037
H	2.161550456	2.998943267	1.139778386
C	4.353937243	2.010075895	-1.108948281
H	4.619513706	3.080201306	-1.107517709
H	5.101146018	1.460224210	-0.511166810
H	4.409411772	1.648150663	-2.150205393
C	1.948177048	2.663311158	-1.346614766
H	2.212356541	3.730522126	-1.259845478
H	1.986450264	2.393155561	-2.415762558
H	0.907605587	2.541587501	-1.003053444

*Diborane(4) C–H Insertion Product **16***

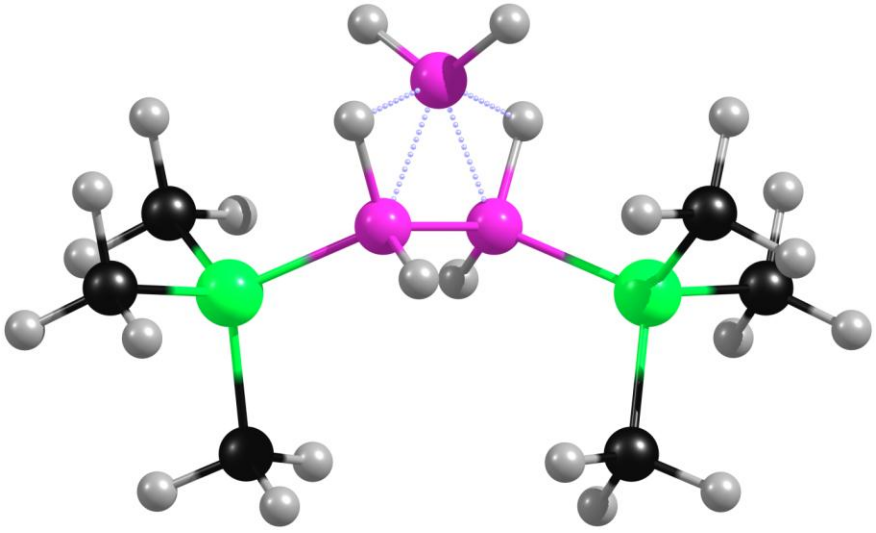


E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (gas phase, Hartree) = -714.672940663
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhMe, SMD, Hartree)= -714.724920446
E(M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ) (PhBr, SMD, Hartree)= -714.742266742
E(MP4(SDTQ)/cc-pVDZ//MP2/cc-pVDZ) (gas phase, Hartree) = -712.7225532321
Enthalpy correction (kcal/mol) = 331.311
Entropy (cal/mol·K) = 158.939
Gibbs free energy correction (kcal/mol) = 283.924

H	4.115941685	-0.165642483	1.368750723
H	1.272547565	-0.730148182	3.806833631
H	1.392120521	1.310267942	3.449197393
N	2.031906520	-0.255596673	0.377629161
N	3.061900959	0.376862836	4.776961803
B	3.039228377	0.395012328	1.446136341
B	1.949971279	0.259963925	3.632770731
C	2.181816105	-1.728622752	0.217763730
H	1.550789118	-2.076883445	-0.615146131
H	3.236743628	-1.957782884	0.016220238
H	1.865343359	-2.218385179	1.150795785
C	2.237957787	0.538436424	6.050614732
H	1.419829868	1.226987447	5.776842766
H	1.790881018	-0.457906454	6.203786630
C	0.597641883	0.053117248	0.661369376
H	0.291610844	-0.480046902	1.572032689
H	0.475805073	1.132543323	0.807653047
H	-0.014821656	-0.281597450	-0.190608073
C	2.485891970	0.478040642	-0.864887683
H	3.354944222	-0.081953916	-1.246019499
H	1.680733538	0.429899045	-1.618448656
C	3.956647114	1.540270576	4.507921800
H	4.417025754	1.398778310	3.519710817
H	3.357526009	2.460642583	4.508063273
H	4.743415584	1.591796175	5.271620036
C	3.881354927	-0.874431174	4.809903709

H	4.371291436	-0.991887147	3.832150402
H	4.642796407	-0.813112360	5.596278296
H	3.213033550	-1.727238739	4.993652613
C	2.840913873	1.033783552	7.389467968
C	2.898699392	1.930306444	-0.470092994
C	3.111589713	2.549722640	7.406170358
H	3.291332369	2.872776514	8.445379755
H	3.996434091	2.843558055	6.822483609
H	2.240418157	3.114583004	7.030036661
C	4.088646090	0.268618377	7.856523522
H	4.982327416	0.496962290	7.251870475
H	4.323588128	0.563228447	8.893332462
H	3.924909649	-0.822777469	7.852251039
C	1.704857129	0.758313823	8.400124518
H	1.995710933	1.129915131	9.396126208
H	0.772428011	1.271153186	8.106581675
H	1.495697216	-0.321810790	8.485229348
C	2.967194918	1.951928647	1.093829823
H	2.659829252	-0.132764420	2.597484497
H	3.843491788	2.535525527	1.421752961
H	2.076047798	2.454354194	1.508209300
C	4.286743061	2.212258281	-1.067020076
H	4.591368038	3.249819478	-0.850321093
H	5.046327998	1.532899414	-0.642488548
H	4.280756185	2.082520796	-2.163808783
C	1.898085709	2.960975108	-1.013074612
H	2.191746355	3.975387625	-0.694971817
H	1.874067423	2.945021594	-2.117040597
H	0.873357706	2.777358160	-0.647362101

*Triboron Cation **20a***



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Entropy (cal/mol·K) = 134.066
Gibbs free energy correction (kcal/mol) = 157.635

C	3.503977365	1.477018538	-0.078303818
C	-3.503977365	-1.477018538	-0.078303818
H	3.111596074	2.349971833	-0.623936433
H	-3.111596074	-2.349971833	-0.623936433
H	3.682143650	1.763502744	0.970534189
H	-3.682143650	-1.763502744	0.970534189
H	4.451924483	1.151719508	-0.536240970
H	-4.451924483	-1.151719508	-0.536240970
C	3.008516439	-1.288630312	0.735869020
C	-3.008516439	1.288630312	0.735869020
H	2.305850485	-2.136274540	0.716146984
H	-2.305850485	2.136274540	0.716146984
H	3.952156793	-1.577637959	0.245684901
H	-3.952156793	1.577637959	0.245684901
H	3.207647697	-1.013211382	1.783358606
H	-3.207647697	1.013211382	1.783358606
C	2.115654046	-0.338250989	-1.887207798
C	-2.115654046	0.338250989	-1.887207798
H	1.432272787	-1.197189282	-1.975576641
H	-1.432272787	1.197189282	-1.975576641

H	1.707834210	0.513155065	-2.455752635
H	-1.707834210	-0.513155065	-2.455752635
H	3.101300336	-0.610290331	-2.298003616
H	-3.101300336	0.610290331	-2.298003616
B	0.573109617	0.686213126	0.592744148
B	-0.573109617	-0.686213126	0.592744148
H	-0.136880477	-1.659974500	0.019269211
H	0.136880477	1.659974500	0.019269211
P	2.274175471	0.132406975	-0.133282219
P	-2.274175471	-0.132406975	-0.133282219
H	-0.867343706	-1.122353470	1.739979225
H	0.867343706	1.122353470	1.739979225
B	0.000000000	0.000000000	2.183132765
H	0.804657608	-0.654989813	2.797891735
H	-0.804657608	0.654989813	2.797891735

References

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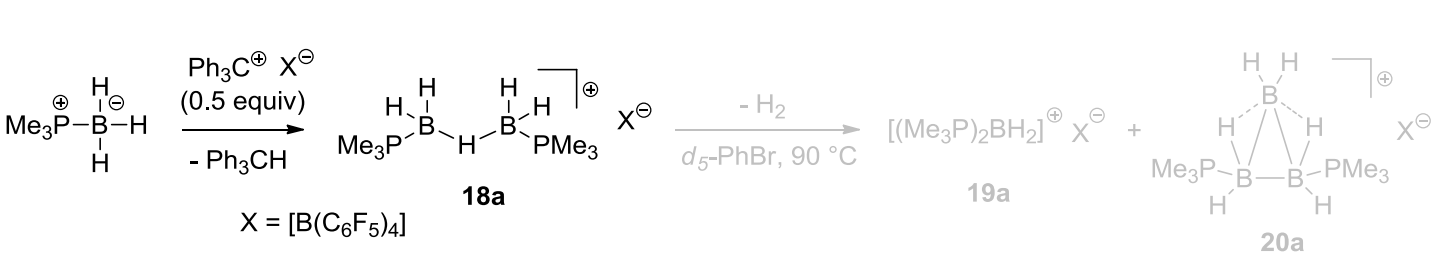
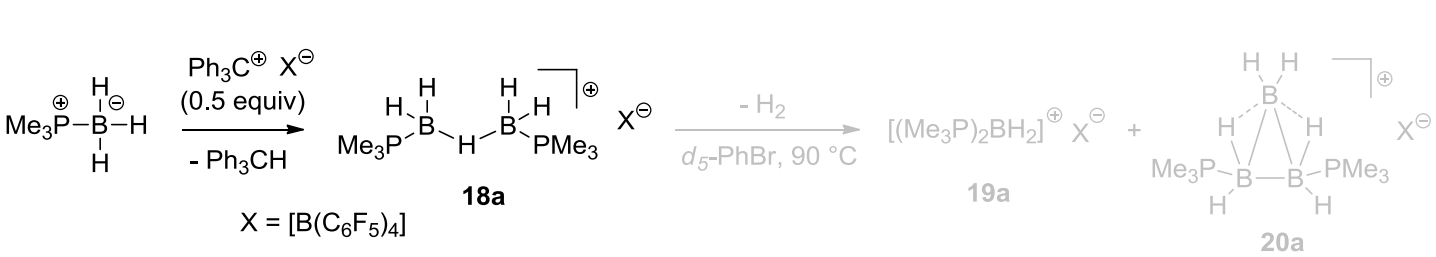
Selected NMR Spectra

^{11}B NMR (225 MHz),
d_5-PhBr

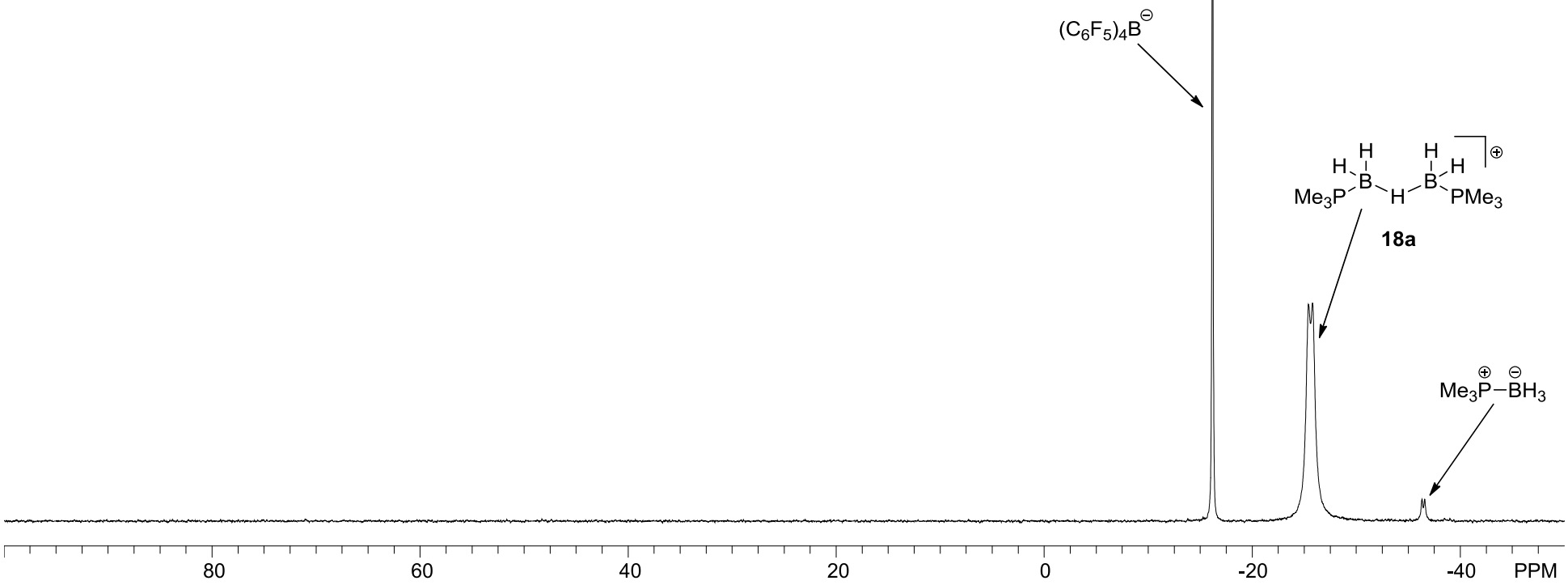


Step 1. Generation of **18a** from $Me_3P–BH_3$

$^{11}B\{^{1}H\}$ NMR (225 MHz),
d_5-PhBr



Step 1. Generation of **18a** from $Me_3P–BH_3$



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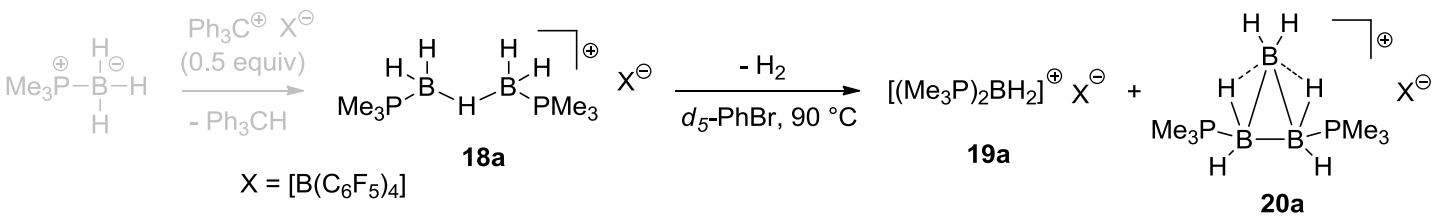
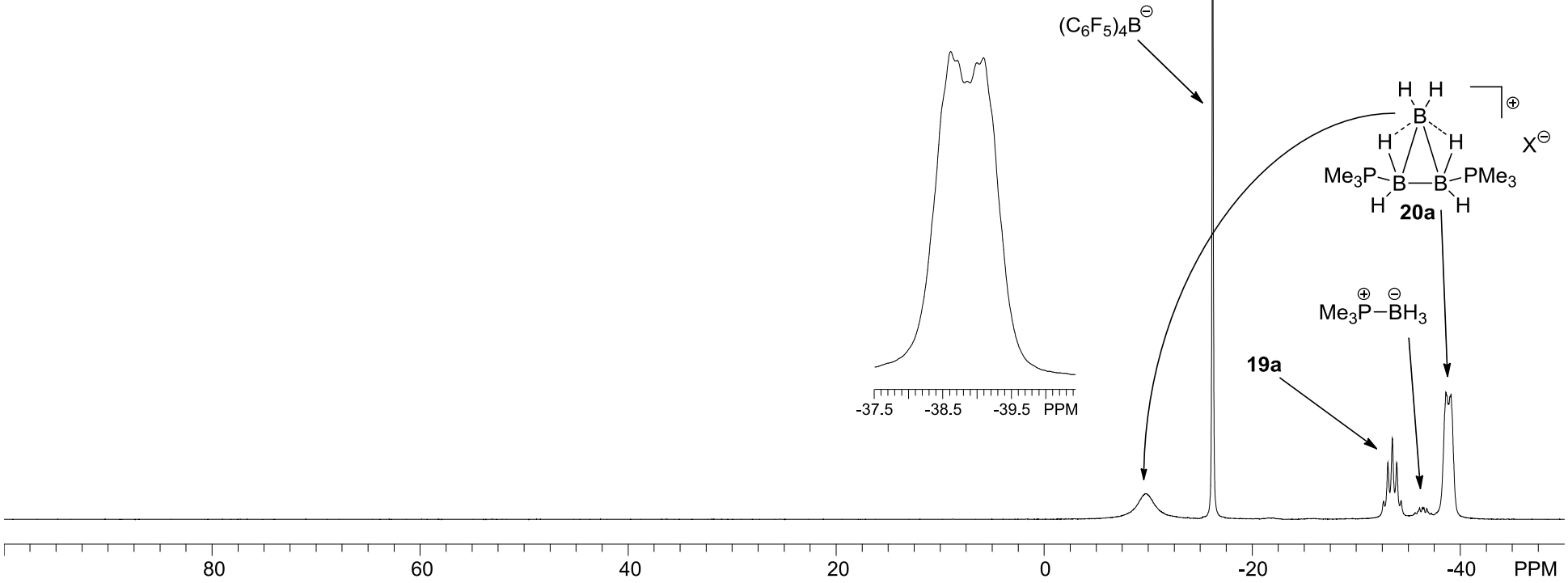
d_5-PhBr



Step 2. Thermolysis of **18a**



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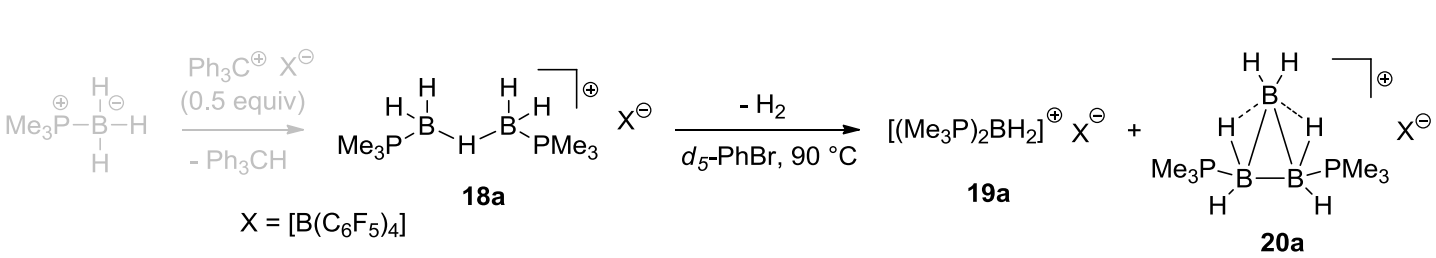
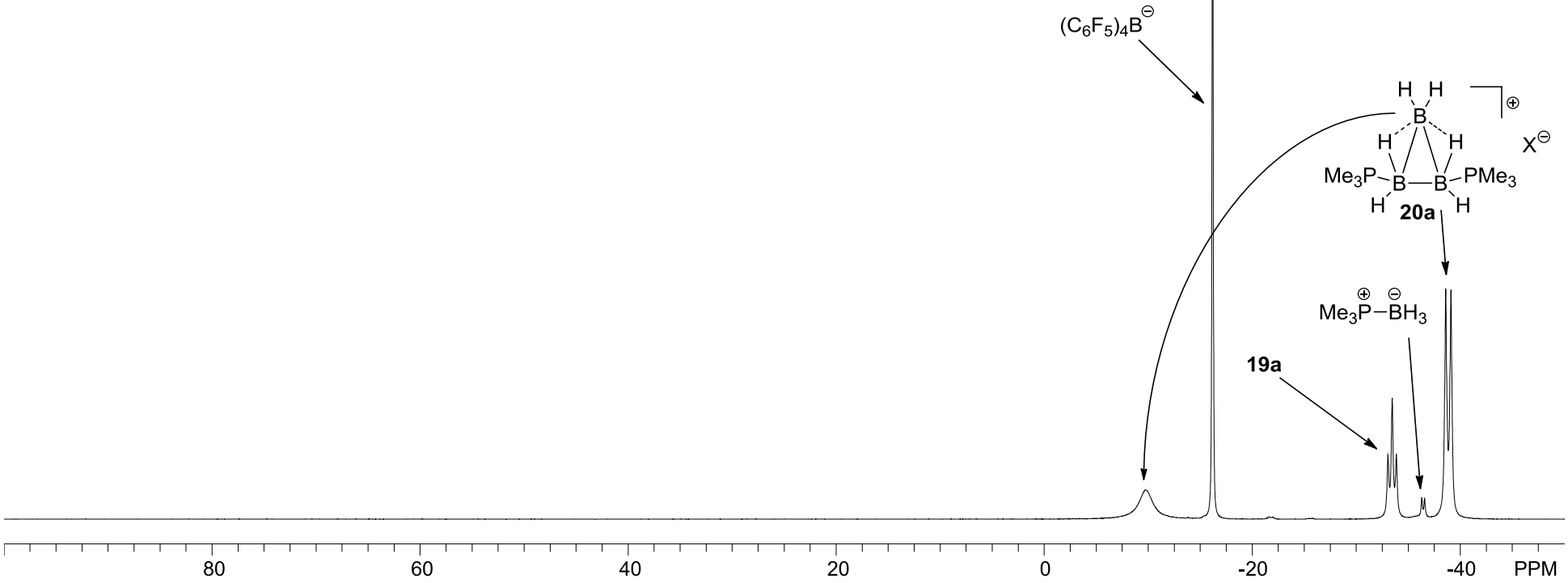


Step 2. Thermolysis of **18a**



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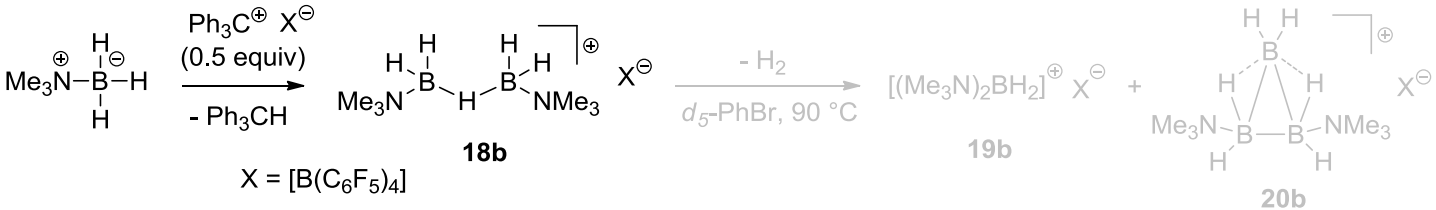
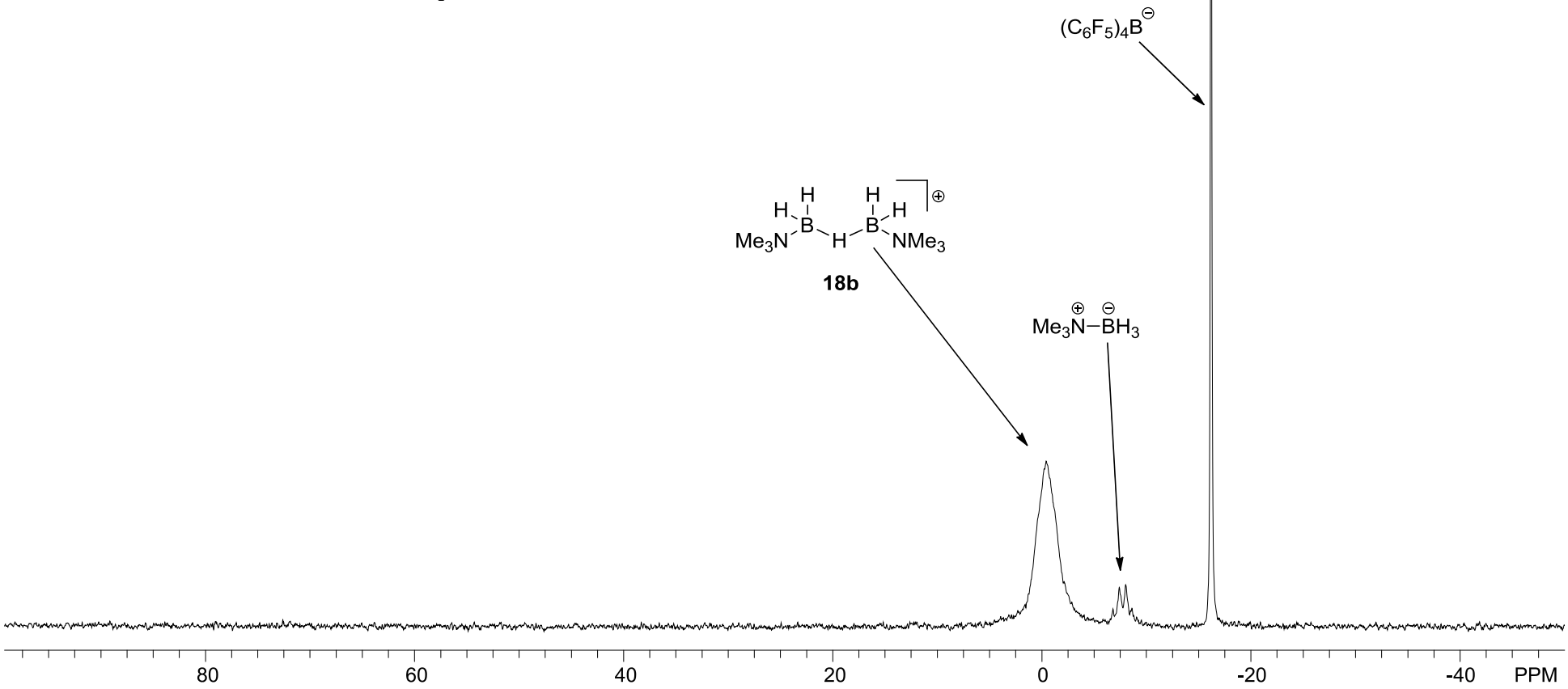
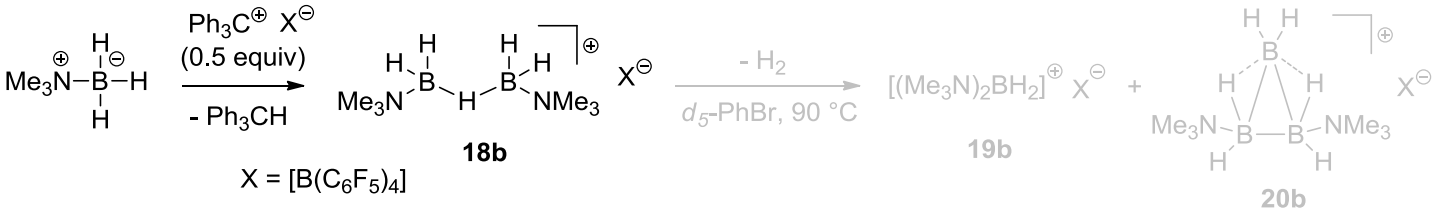


Step 1. Generation of **18b** from $Me_3N–BH_3$

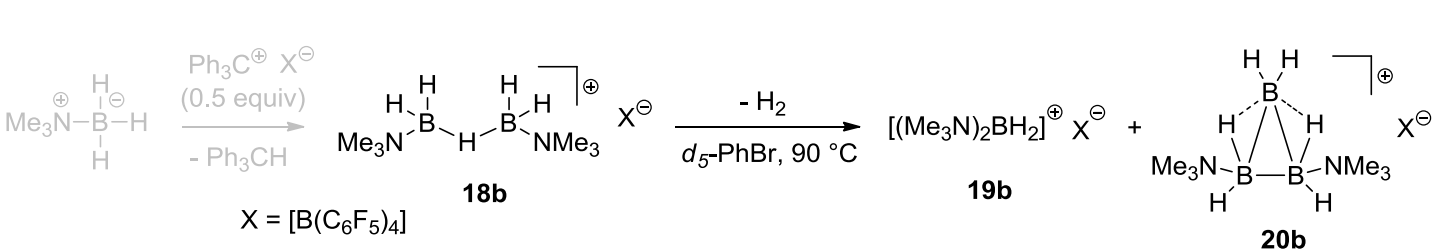


$^{11}B\{^{1}H\}$ NMR (160 MHz),
d_5-PhBr

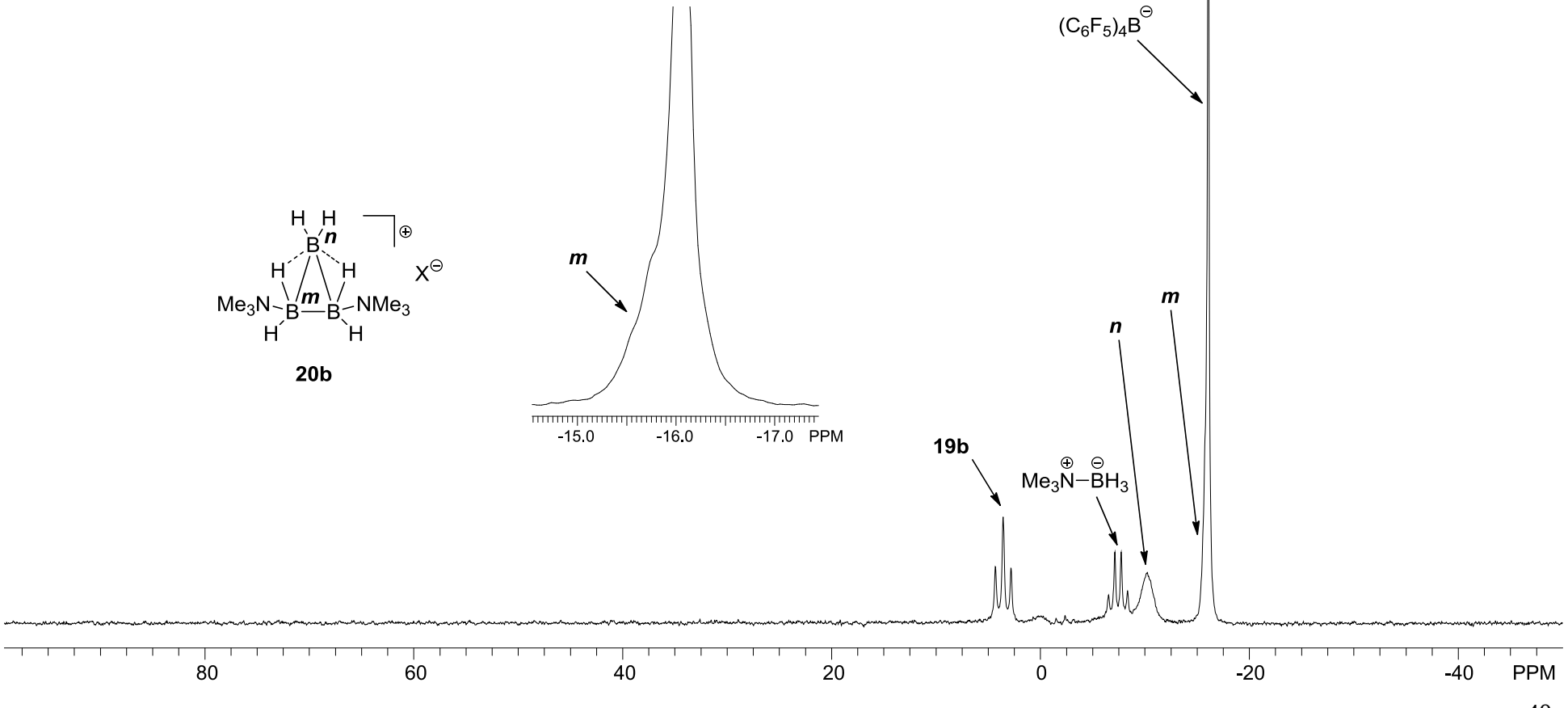


Step 1. Generation of **18b** from $Me_3N–BH_3$

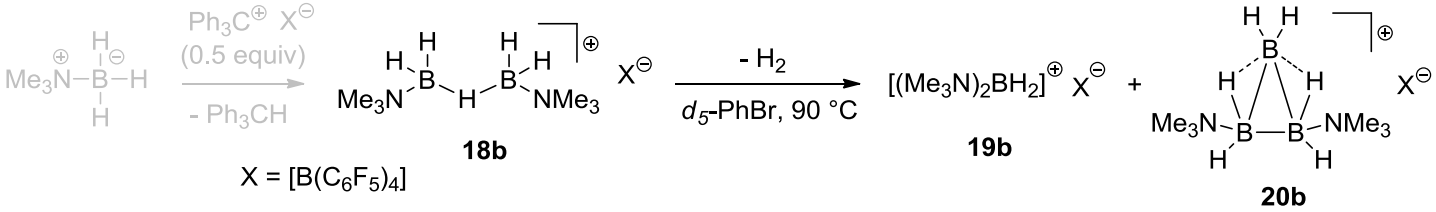
^{11}B NMR (160 MHz),
d_5-PhBr, 90 °C



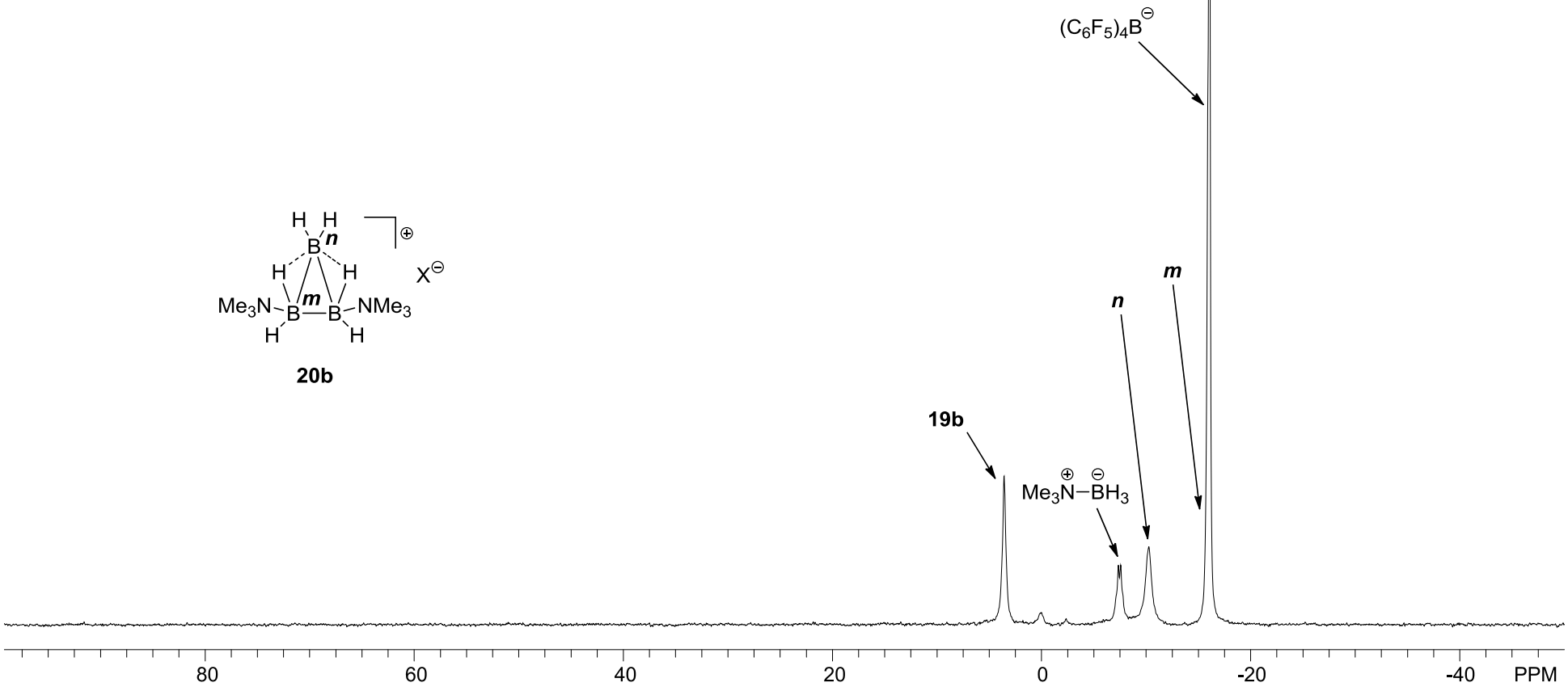
Step 2. Thermolysis of **18b**



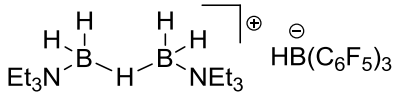
$^{11}B\{^{1}H\}$ NMR (160 MHz),
d_5-PhBr, 90 °C



Step 2. Thermolysis of **18b**



^{1}H NMR (400 MHz),
CD_2Cl_2



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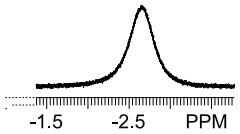
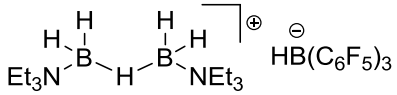


^{11}B NMR (128 MHz),
CD_2Cl_2



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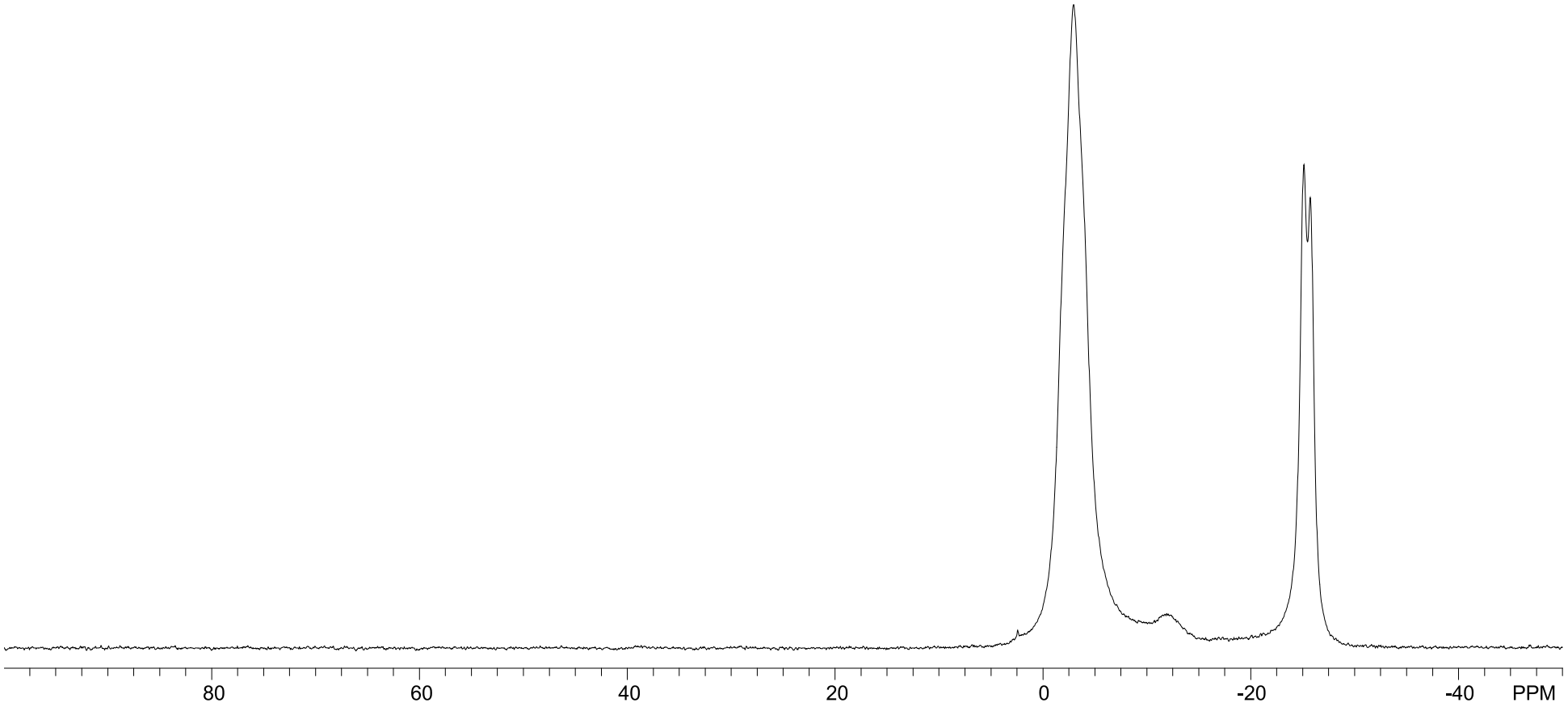
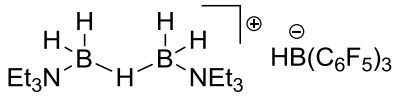


$^{11}B\{^{1}H\}$ NMR (128 MHz),
CD_2Cl_2



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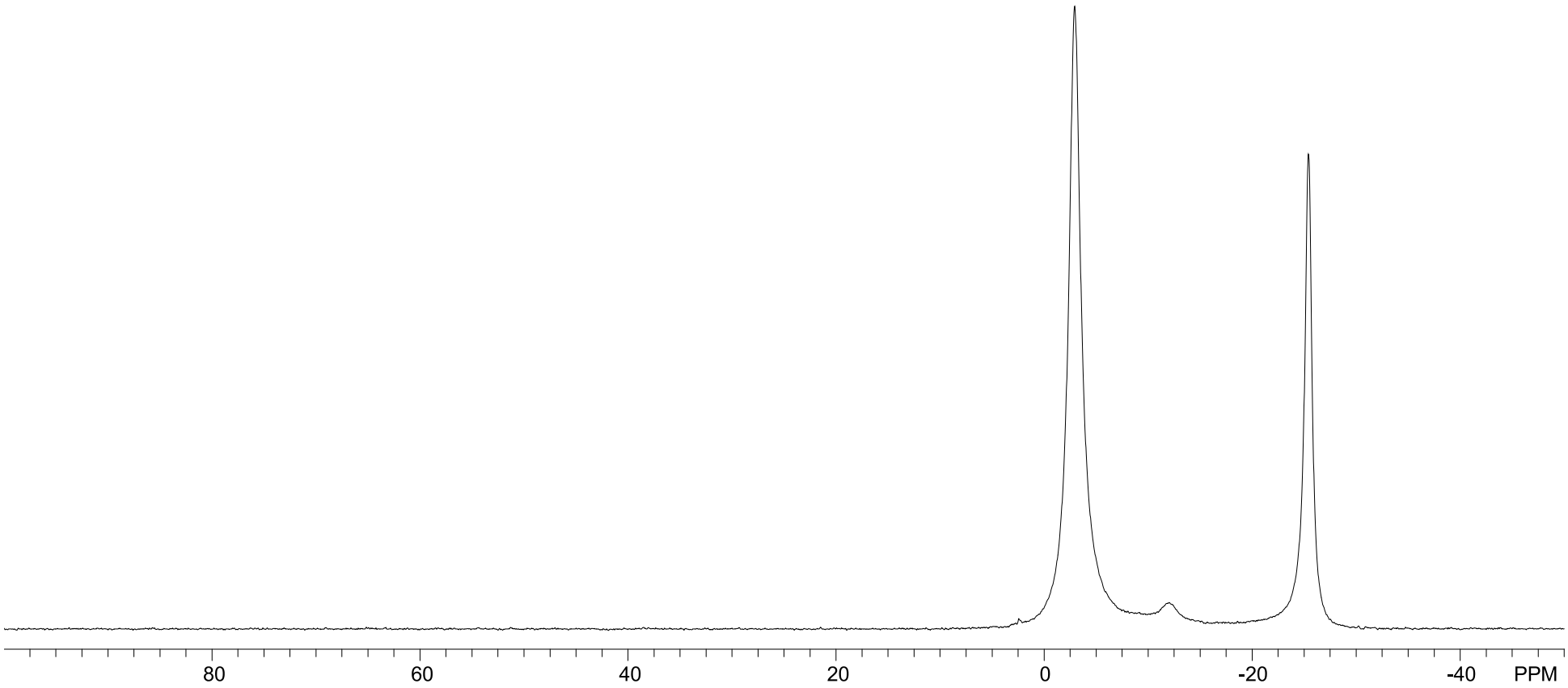
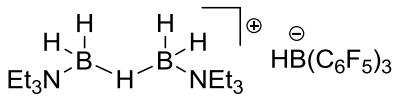


$^{13}C\{^{1}H\}$ NMR (101 MHz),
CD_2Cl_2



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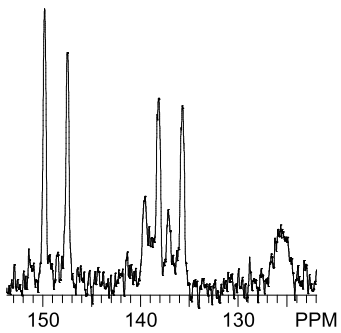
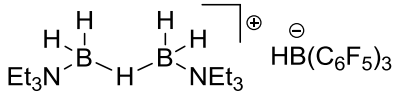


^{19}F NMR (377 MHz),
CD_2Cl_2



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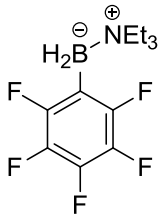
^{1}H NMR (400 MHz),
$CDCl_3$



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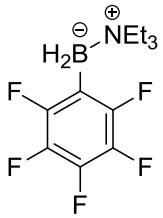
^{11}B NMR (128 MHz),
$CDCl_3$



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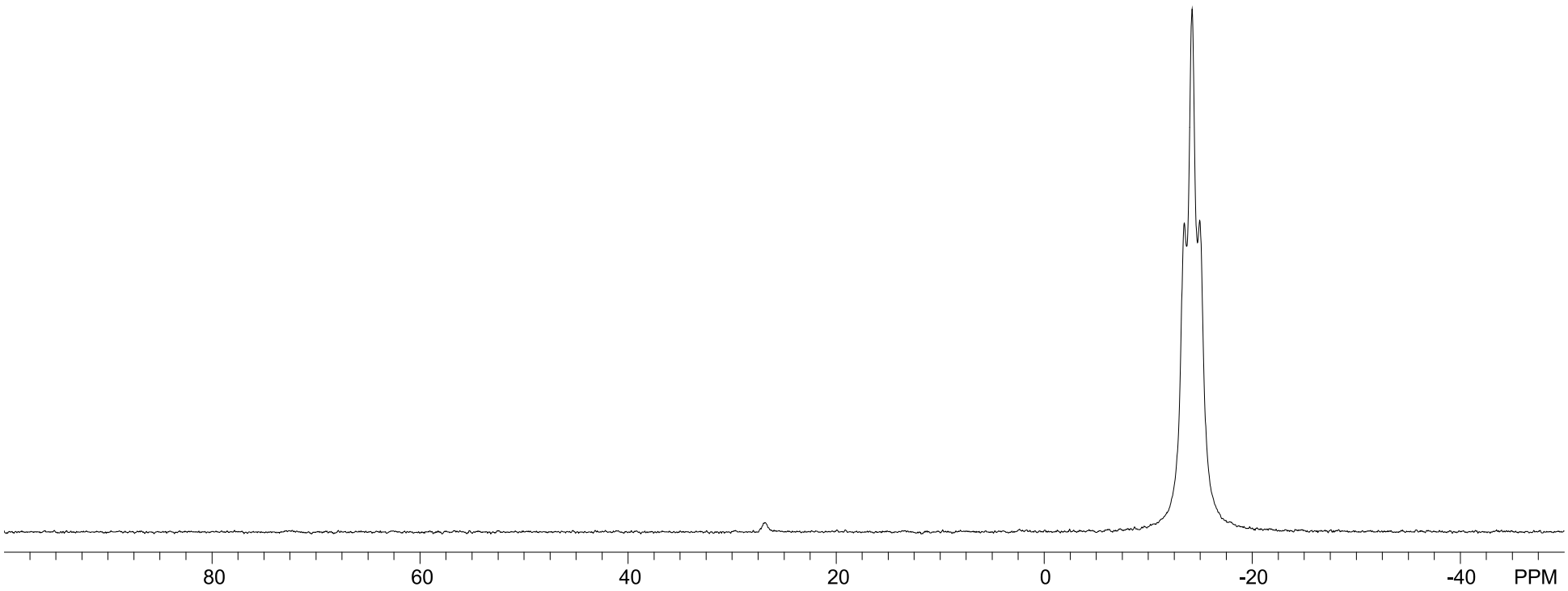
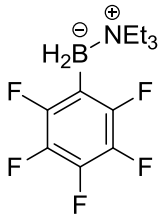


$^{11}B\{^{1}H\}$ NMR (128 MHz),
$CDCl_3$



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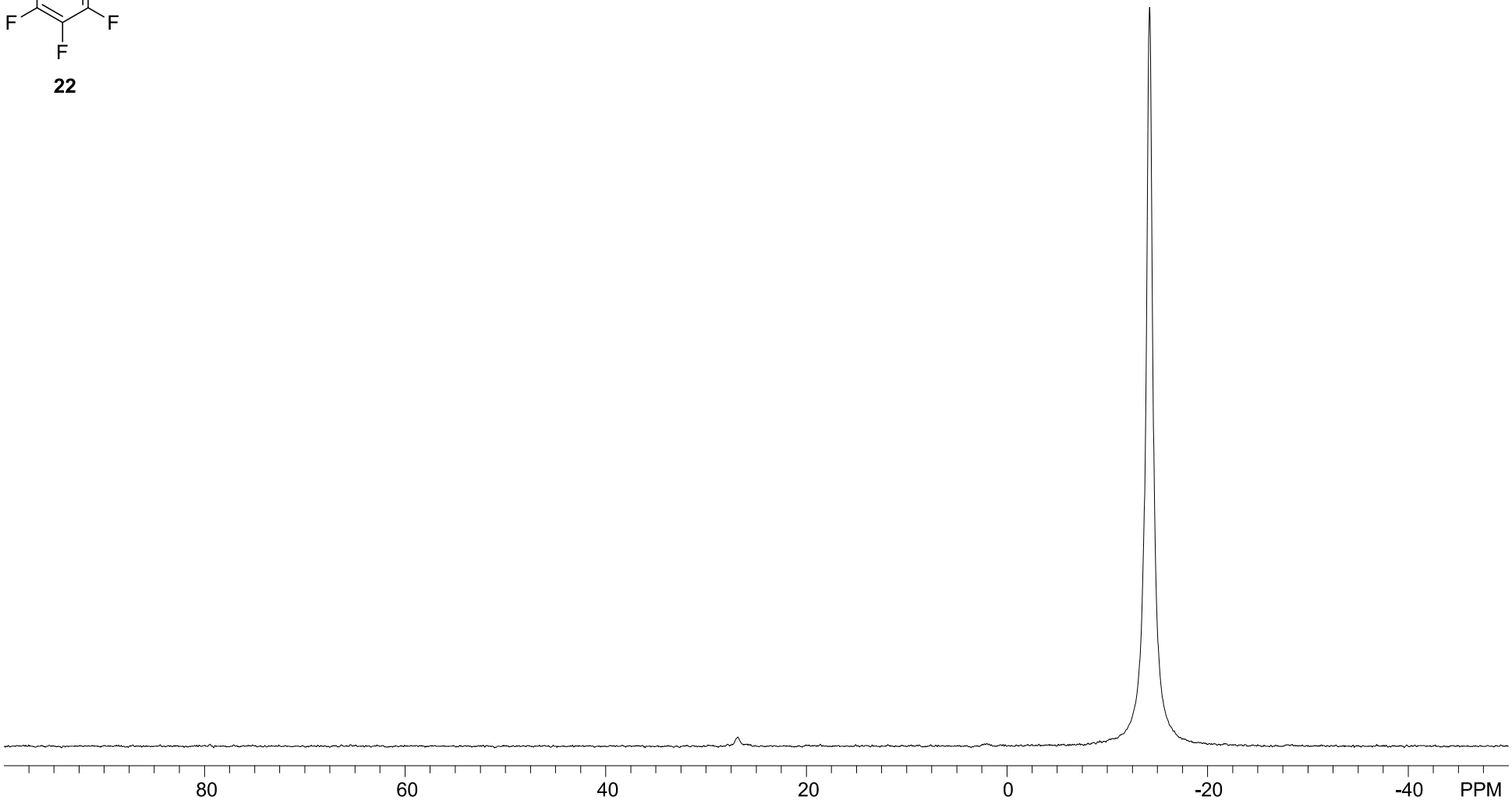
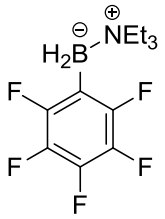


^{13}C NMR (101 MHz),
$CDCl_3$



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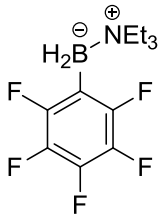
^{19}F NMR (377 MHz),
$CDCl_3$



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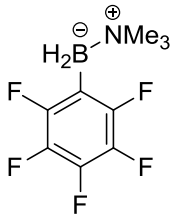
^{1}H NMR (400 MHz),
$CDCl_3$



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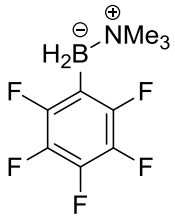
^{11}B NMR (128 MHz),
$CDCl_3$



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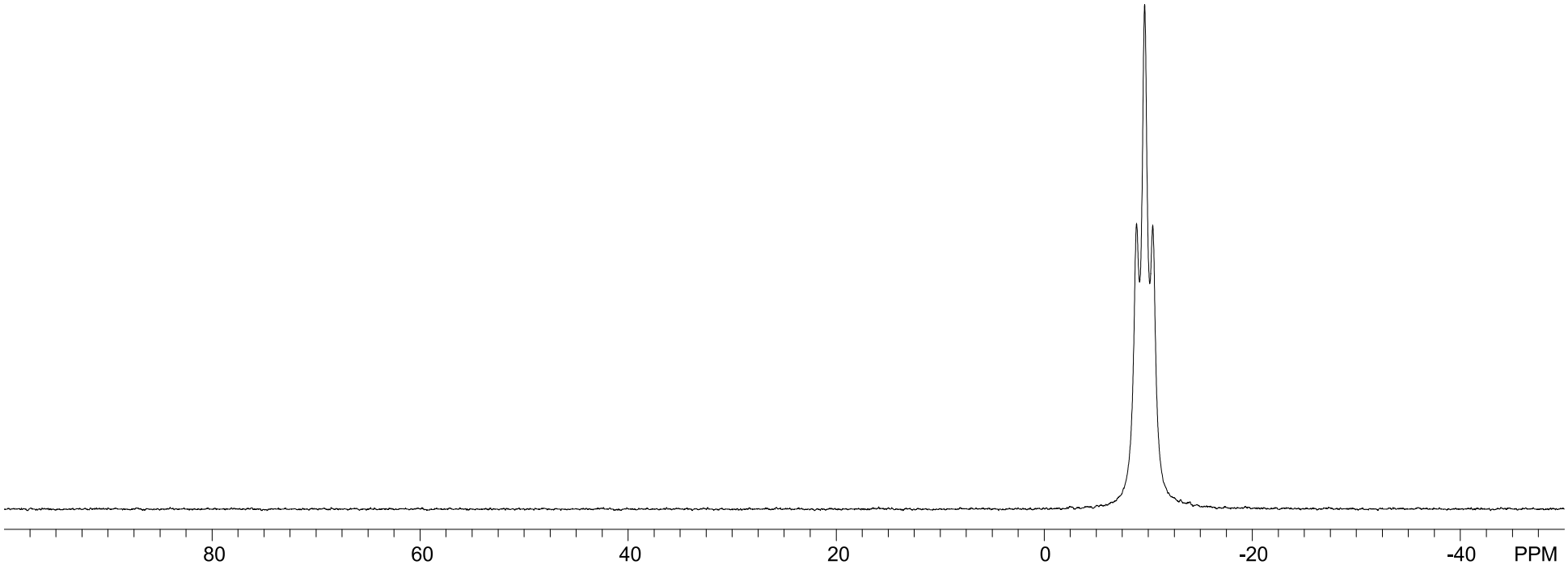
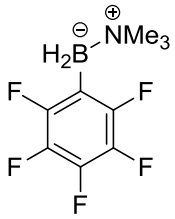


$^{11}B\{^{1}H\}$ NMR (128 MHz),
$CDCl_3$



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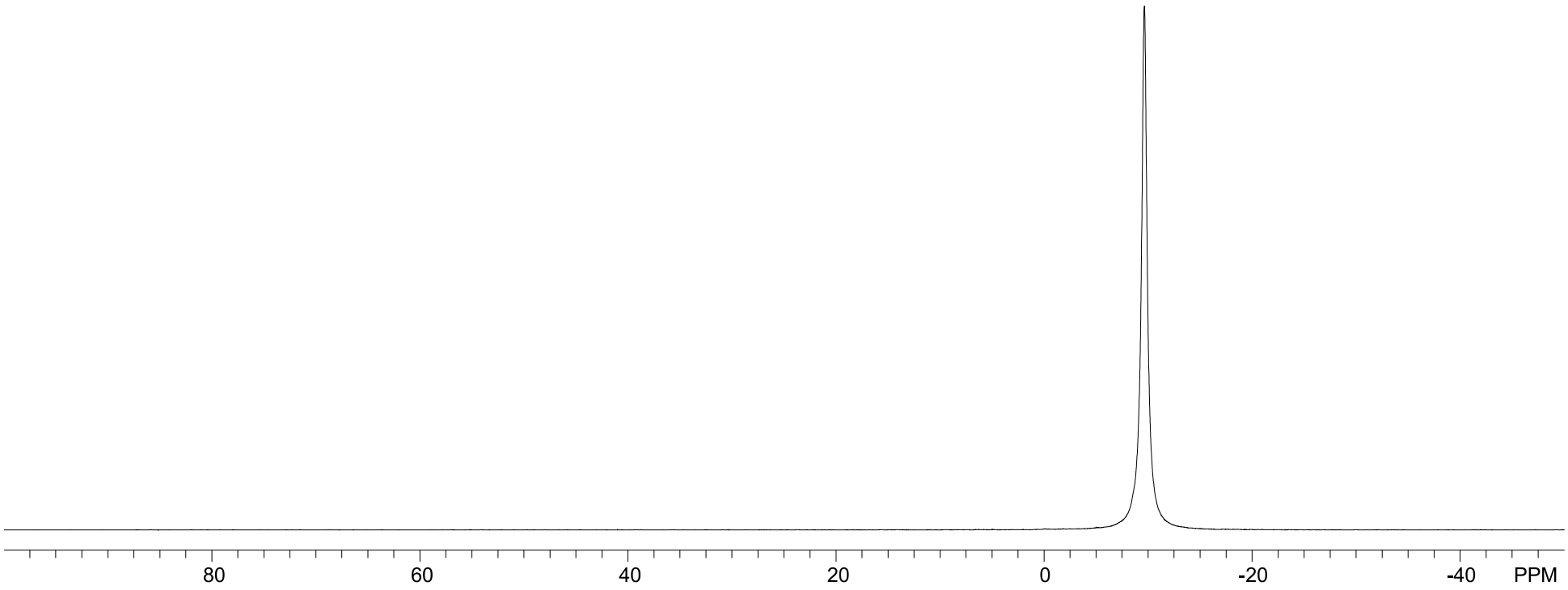
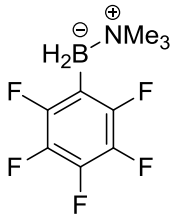


^{13}C NMR (101 MHz),
$CDCl_3$



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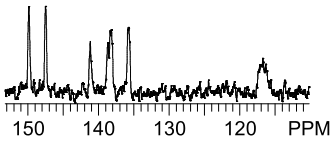
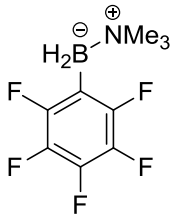
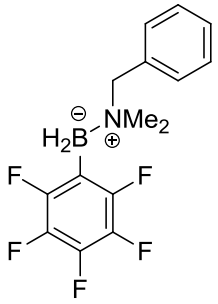


^{19}F NMR (377 MHz),
$CDCl_3$



23

^{1}H NMR (500 MHz),
$CDCl_3$



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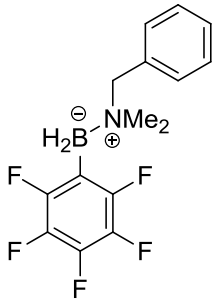
^{11}B NMR (128 MHz),
$CDCl_3$



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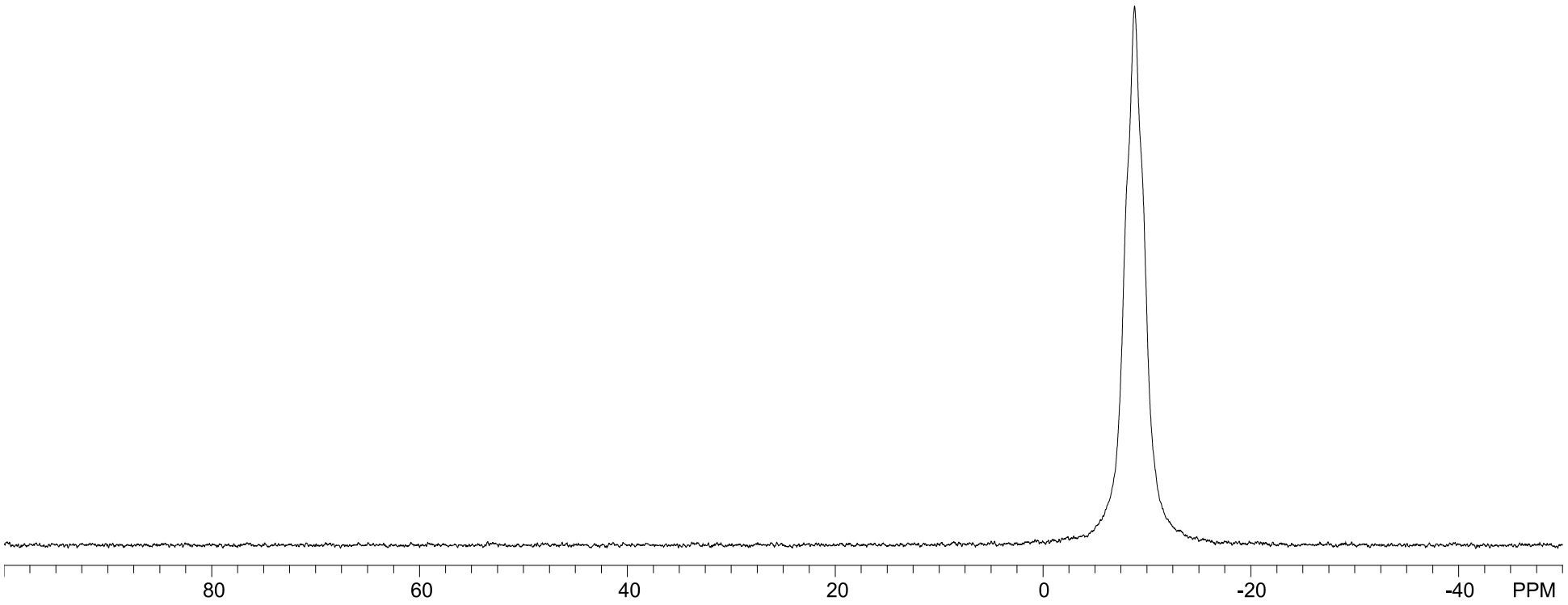
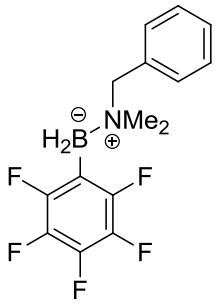


$^{11}B\{^{1}H\}$ NMR (128 MHz),
$CDCl_3$



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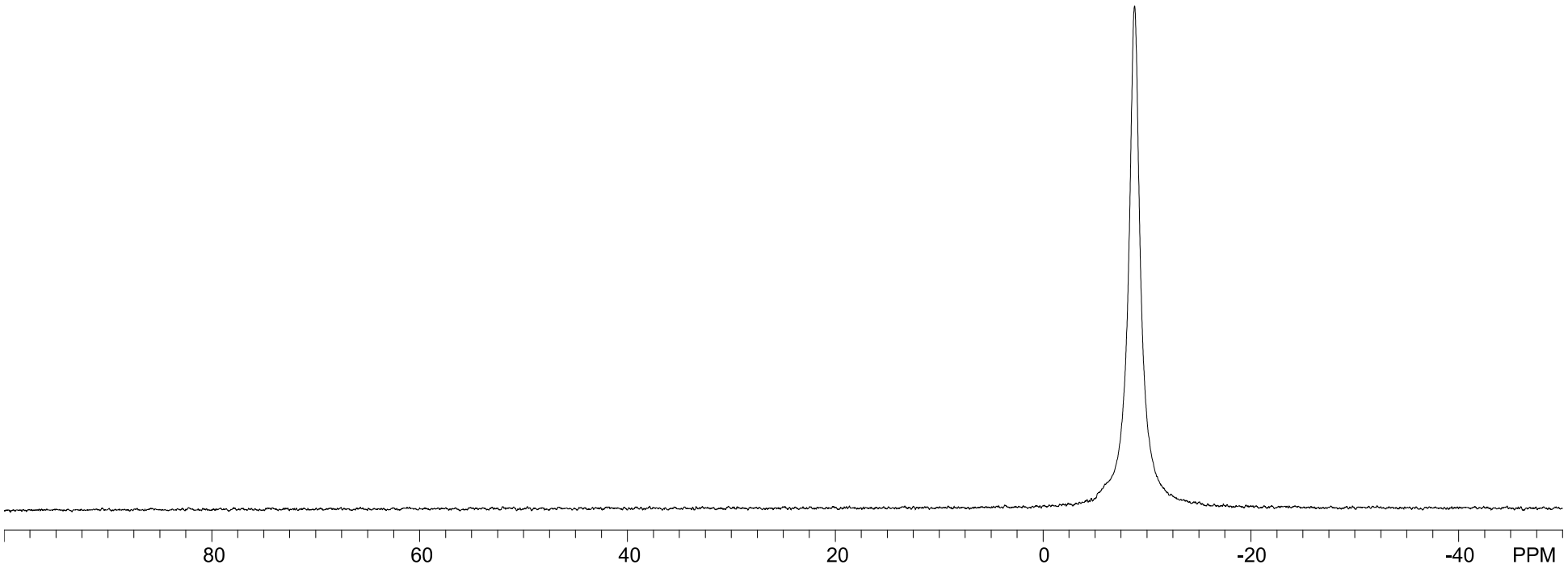
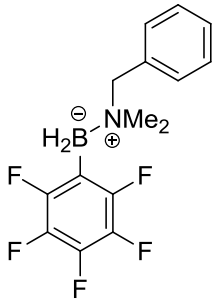


^{13}C NMR (101 MHz),
$CDCl_3$



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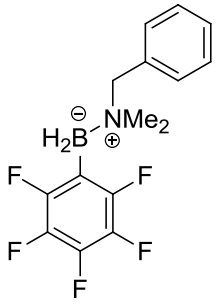
^{19}F NMR (377 MHz),
$CDCl_3$



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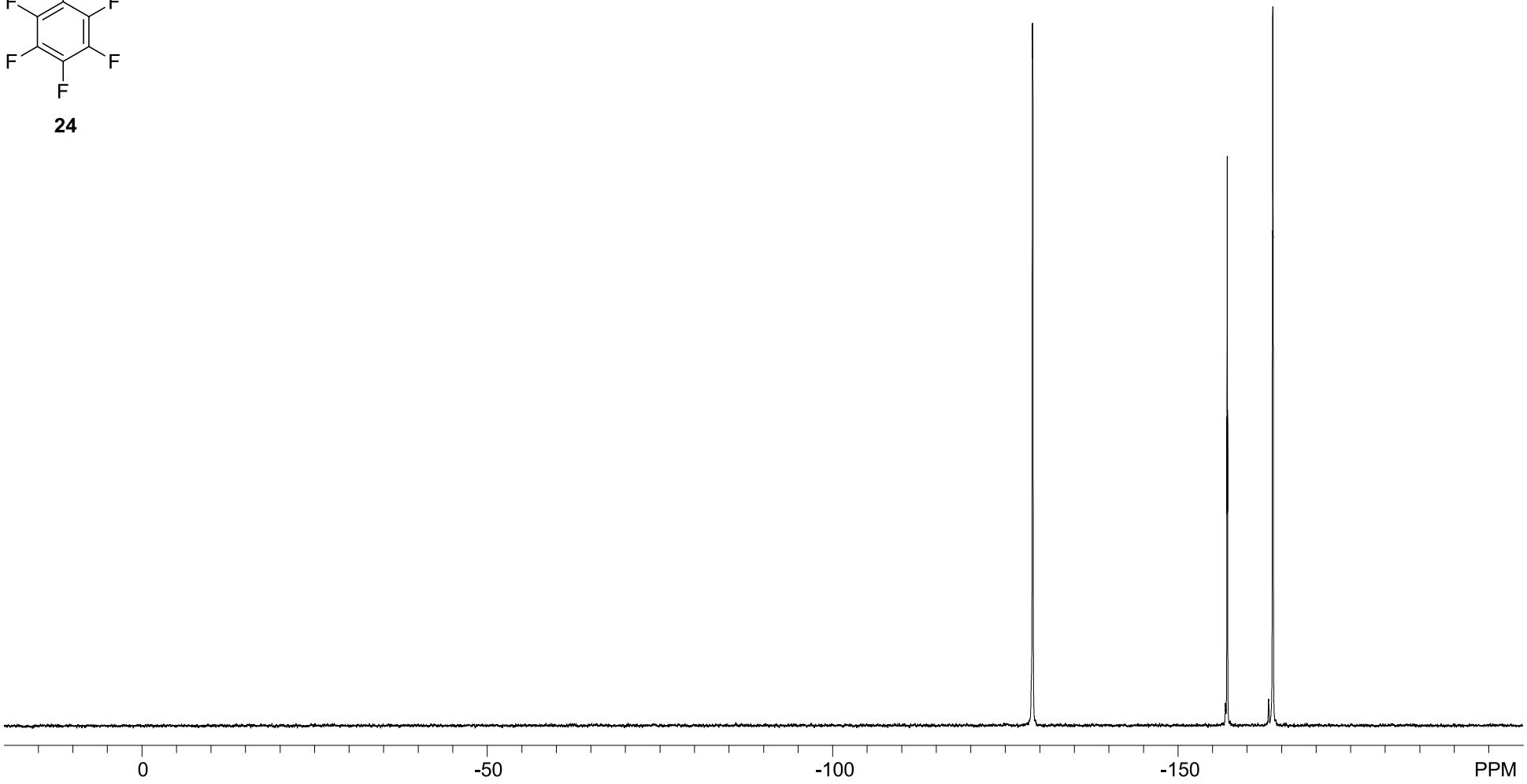
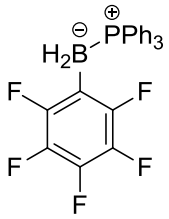


^{1}H NMR (500 MHz),
$CDCl_3$



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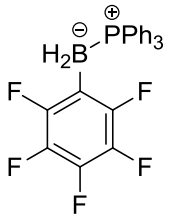
^{11}B NMR (128 MHz),
$CDCl_3$



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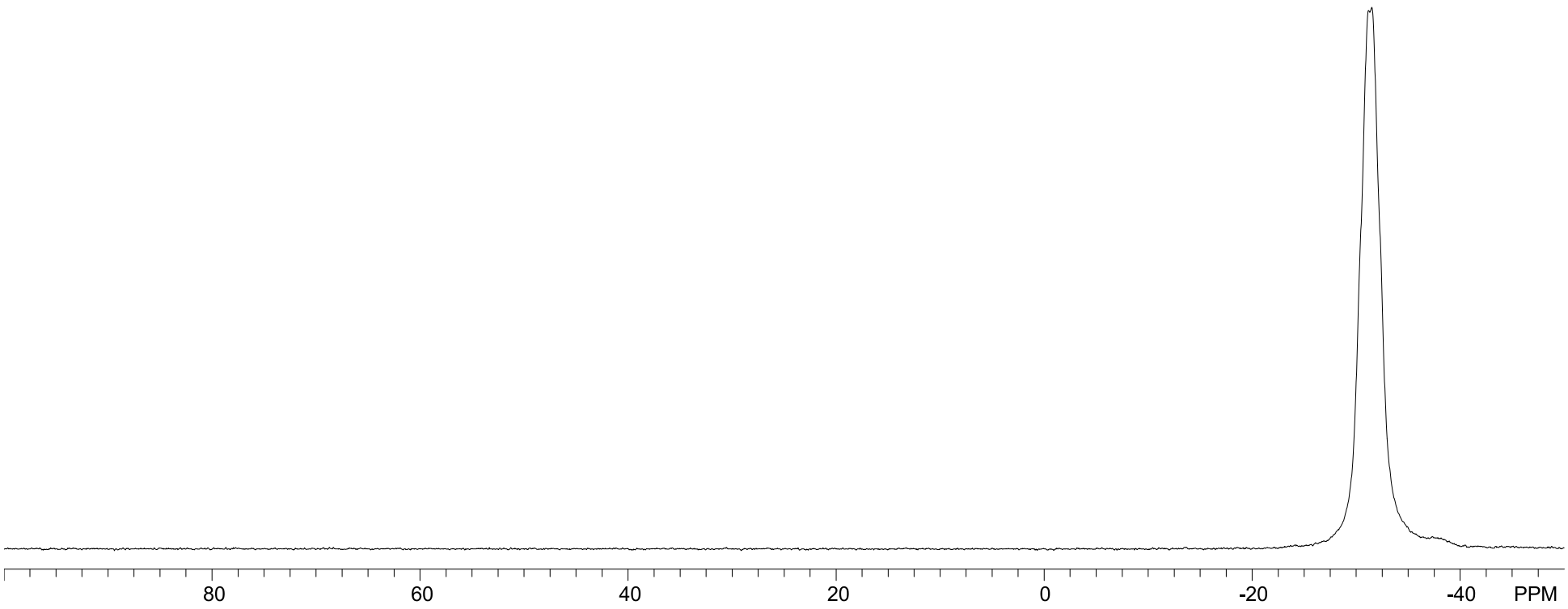
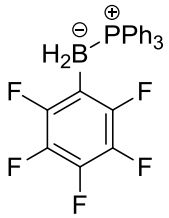


$^{11}B\{^{1}H\}$ NMR (128 MHz),
$CDCl_3$



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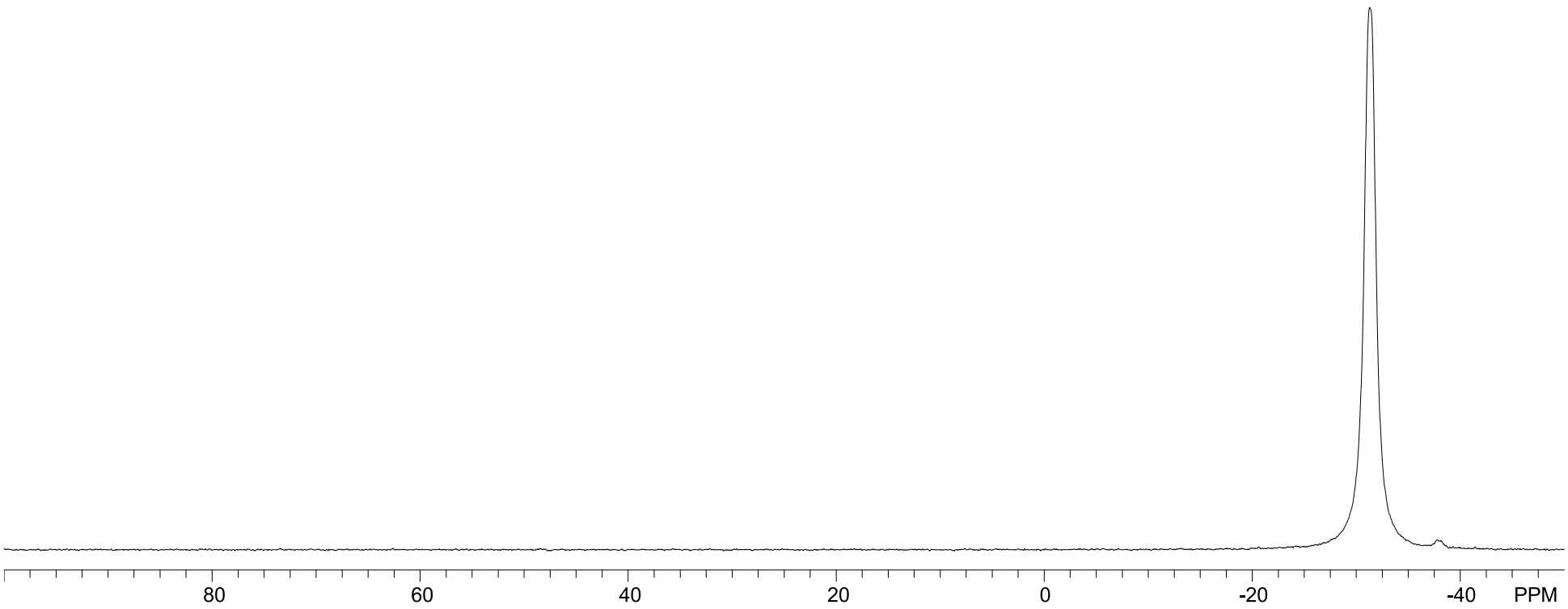
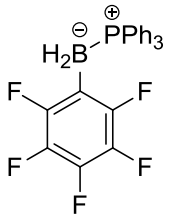


$^{13}C\{^{1}H\}$ NMR (101 MHz),
$CDCl_3$



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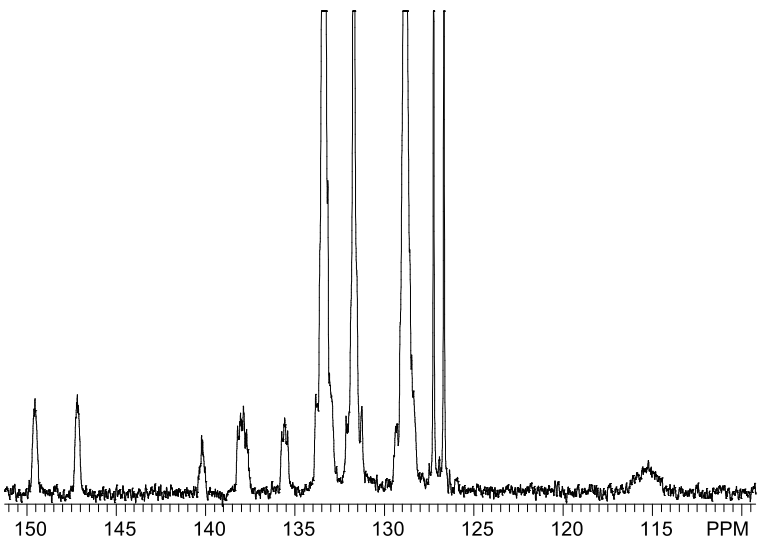
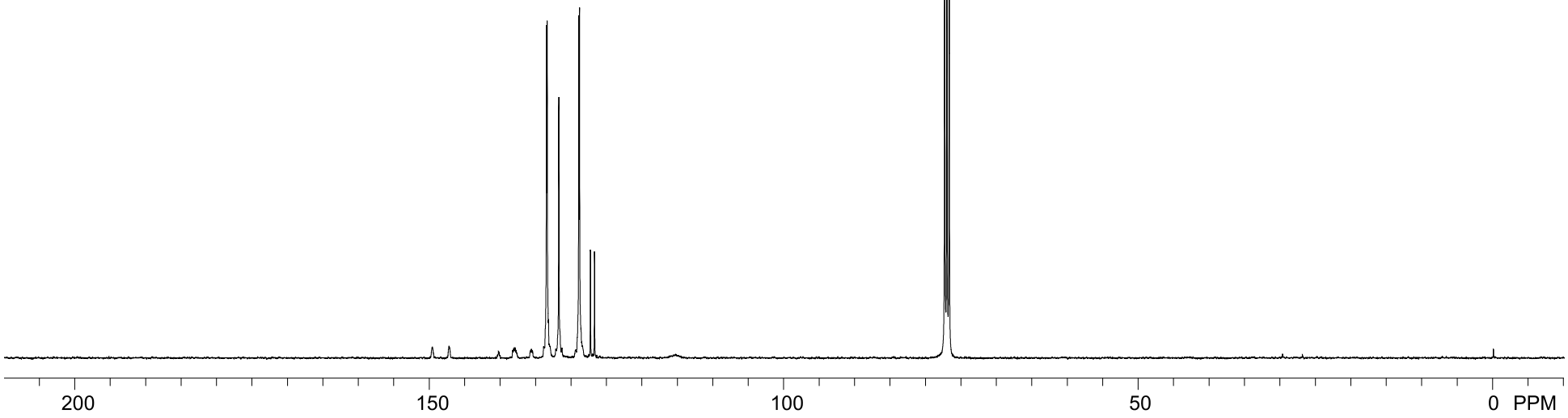
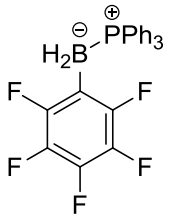




^{19}F NMR (377 MHz),
$CDCl_3$



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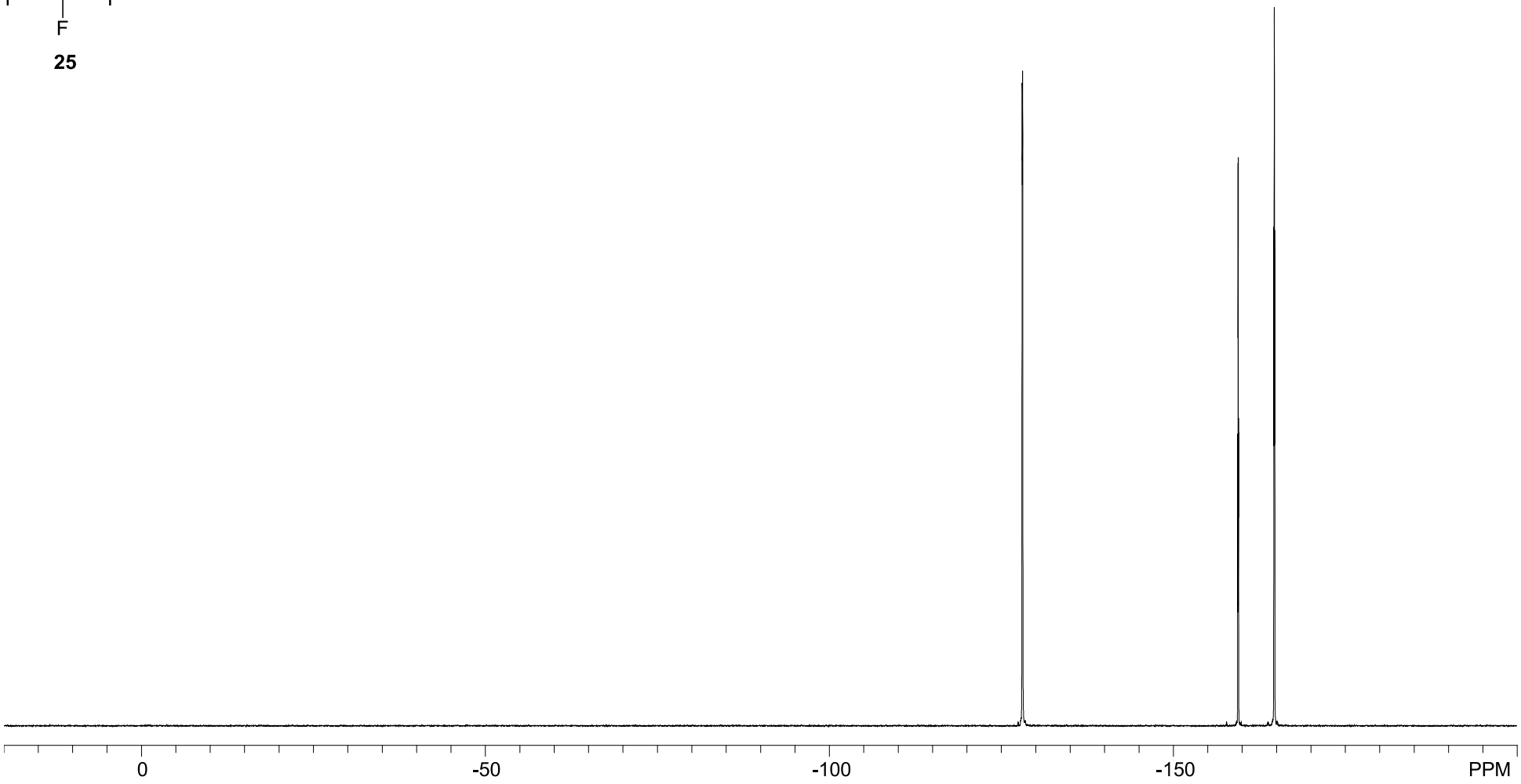
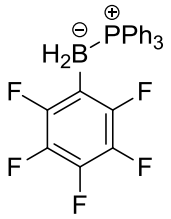


^{31}P NMR (162 MHz),
$CDCl_3$



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