Azaborines: Synthesis and Use in the Generation of Stabilized Boro-substituted Carbocations

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Supplementary Information

Contents

General remarks

Synthesis and techniques

All preparative scale reactions were conducted in oven dried (160 °C) glassware with magnetic stirring using Schlenk-line techniques or in a glove box under an atmosphere of dry dinitrogen if not mentioned otherwise. Experiments on NMR tube scale were carried out in Teflon cap sealed NMR tubes (ø 5 mm). Solvents were purified by passage over an activated aluminum oxide column, followed by distillation from Na-benzophenone ketal (toluene, benzene, THF, hexanes) or P_2O_5 (pentanes) and degassed prior to use. Dichloromethane, CD_2Cl_2, and α,α,α-trifluorotoluene were distilled from CaH_2 (followed by 3 freeze-pump-thaw cycles and stored over a mixture of 4 Å molecular sieves and dry basic alumina for usage in a glove box). Toluene-d_8 and benzene-d_6 were degassed by 3 freeze-pump-thaw cycles and stored over activated 4 Å molecular sieves. DMF and MeCN were of DrySolv-quality and used as received. Solvents for chromatography and other syntheses were used as received from commercial sources and were at least of ACS reagent grade. Solvents for routine NMR spectroscopy experiments were used as received. Silica gel 60 (particle size 0.040 - 0.063 mm, 230 - 400 mesh) was purchased from Silicycle. TLCs were run on silica gel coated aluminum plates with UV indicator (F254) obtained by EMD Chemicals, Inc. and analyzed by UV/VIS and stained using a cerium ammonium molybdate solution.

Reagents and materials

Reagents for azaborinine synthesis were used as received without further purification unless noted otherwise. 9-Borabicyclo[3.3.1]nonane dimer, sodium bis(trimethylsilyl)amide (NaHMDS) and triethylphosphine oxide were

purchased from Aldrich, stored in a glove box, and used as received. $Ph_3C^+B(C_6F_5)_4^-$, was purchased from Strem or synthesized as reported in the literature.[1] Diphenyliodonium tetrafluoroborate,[2] and bis(4-methoxyphenyl)iodonium tetrafluoroborate,[3] *N*-phenylimidazole and *N*-(4-methoxyphenyl)imidazole[4] were synthesized as described in the literature. 1,3-Diphenylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane,[5] Ender's carbene (1,3,4-triphenyl-1,2,4-triazol-5-ylidene)[6], 1,3-di(4-methoxyphenyl)imidazolium tetrafluoroborate[7], and N,N'-diphenylbenzimidazolium tetrafluoroborate[7] was synthesized as reported in the literature.

Characterization

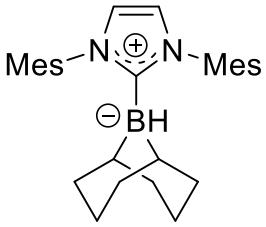
Melting points were measured on an Electrothermal Mel-temp® melting point apparatus connected to a Fluke 51II thermometer. Temperatures are given in degree Celsius (°C) and are uncorrected. ***IR spectra*** were collected on a Bruker ALPHA Platinum ATR as neat solids and absorption bands ($\tilde{\nu}$, s = strong, m = medium, w = weak) are given in cm^{-1}. ***NMR spectra*** were recorded on Bruker Avance 300 (^{1}H: 300.13 ^{13}C: 75.47; QXI probe), Bruker Avance 400 (^{1}H: 400.13, ^{11}B: 128.38, ^{13}C: 100.62, ^{19}F: 376.50, ^{31}P: 161.98; BBI, BBFO and QNP probes), Bruker Avance 500 (^{1}H: 500.19, ^{11}B: 160.27, ^{13}C: 125.62; BBI and BBFO probes), or Bruker Avance 600 (^{1}H: 600.17, ^{11}B: 192.56, ^{13}C: 150.93; ^{31}P: 242.94, TBI probe) instruments operating at the denoted spectrometer frequency given in mega Hertz (MHz) for the specified nucleus. The samples were measured as solutions in the stated solvent at ambient temperature in non-spinning mode if not mentioned otherwise. To specify the signal multiplicity, the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, sept = septet, oct = octet, and m = multiplet; br. indicates a broad resonance; app = apparent. Shifts δ are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an external standard for ^{1}H- and ^{13}C NMR spectra and calibrated against the solvent residual peak or in case of proteo-solvents against known solvent resonances.[8] ^{11}B signals are calibrated against external $BF_3{\cdot}OEt_2$ and ^{19}F against $CFCl_3$. Coupling constants *J* are given in Hertz (Hz). ***GC-MS*** measurements were performed on an Agilent Technologies GC 6850N/ MS 5975N VL MSD equipped with an Agilent Technologies HP-5MS column (length: 30 m, 0.25 mm inner diameter, 0.25 μm coating thickness) coupled to a quadrupole mass filter. Helium was used as the carrier gas with a constant flow of 1.2 mL/min. Separation of the injected species was achieved using the denoted temperature program and retention times t_R are given in minutes (min). High resolution mass-spectra (***HRMS***) were measured by the Queen's Mass Spectrometry and Proteomics Unit (MSPU) at Queen's University, Kingston, Ontario, Canada. Mass spectra were measured on Applied Biosystems/MDS Sciex QStar XL QqTOF or Waters ZQ Single Quad. Fragment signals are given in mass per charge number (m/z). Elemental analysis (***EA***) were performed on a FLASH 2000 Organic Elemental Analyzer. The content of the specified element is expressed in percent (%). ***X-ray*** data collection was performed on a Bruker SMART APEX II X-ray diffractometer at Queen's University, Kingston, Ontario, Canada.

General procedure for carbene borane synthesis (*GP1*).
In a glove box, a vial was charged with azolium salt (1 eq.), base (1 eq.), and 9-borabicyclo[3.3.1]nonane-dimer (0.5 eq.). After the addition of THF, the reaction mixture was stirred at ambient temperature for the indicated time. ^{1}H NMR and ^{11}B NMR spectroscopy of an aliquot confirmed clean formation of the product. The reaction mixture was filtered, the solvent was evaporated in vacuo, and the remainder was crystallized or otherwise purified as indicated.

General procedure for 2 step azaborinine synthesis (*GP2*), Path B
In a glove box, a reaction tube with a Teflon stopper or a J. Young NMR tube was charged with a solution of carbene borane in the designated solvent. The NMR tube was removed from the glove box and placed in a preheated oil bath and the reaction progress was monitored by ^{1}H NMR and ^{11}B NMR spectroscopy. After the indicated time the reaction mixture was cooled to ambient temperature and the solvent was evaporated in vacuo and the product was isolated.

General procedure for 1-pot azaborinine synthesis (*GP3*), Path A
In a glove box, a vial was charged with azolium salt (1 eq.), base (1 eq.), and 9-borabicyclo[3.3.1]nonane-dimer (0.5 eq.). After the addition of THF, the reaction mixture was stirred at ambient temperature for the indicated time. The reaction mixture was filtered and the solvent was evaporated in vacuo. The resulting solid/oil was redissolved in the designated solvent and added to a reaction tube with a Teflon stopper or a J. Young NMR tube. The NMR tube was removed from the glove box and placed in a preheated oil bath and the reaction progress was monitored by ^{1}H NMR and ^{11}B NMR spectroscopy. After the indicated, time the reaction mixture was cooled to ambient temperature and the solvent was evaporated in vacuo and the product was isolated.

Synthesis of carbene-boranes



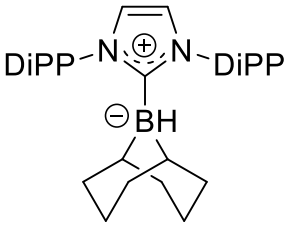
1,3-Dimesityl-imidazol-2-ylidene-9-borabicyclo[3.3.1]nonane 2c, Synthesized following *GP1* from 1,3-dimesityl-1*H*-imidazolium tetrafluoroborate (393.5 mg, 1.00 mmol), NaHMDS (95% Aldrich, 193.5 mg, 1.00 mmol), and 9-borabicyclo[3.3.1]nonane-dimer (122.5 mg, 0.50 mmol) in THF (5 mL) for 23 h. The reaction mixture was filtered, the solvent was evaporated in vacuo, and the remainder was crystallized from CH_2Cl_2/hexanes at –25 °C. The supernatant solution was decanted and the crystals were washed with pentane (3 x 2 mL) and dried in vacuo, traces of hexanes are trapped in the crystal lattice as evident from ^{1}H- and ^{13}C{^{1}H} NMR spectroscopy.

Yield: 255 mg (0.597 mmol, 59%).

^{1}H NMR (C_6D_6, 600 MHz) δ 0.79 (s, 2H, *C*H), 1.61 (m, 3H, C*H*$_2$), 1.72 – 1.81 (m, 3H, C*H*$_2$), 1.94 (m, 2H, C*H*$_2$), 2.05 (s, 6H, C*H*$_3$), 2.07 – 2.17 (m, 17H, C*H*$_2$, C*H*$_3$ and B*H*), 5.90 (s, 2H, NC*H*=), 6.70 (s, 4H, C*H*$_{arom.}$); ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz) δ 18.4, 21.2 (*C*H$_3$), 22.0 (br. s, B*C*H), 25.1, 26.7, 33.0, 38.0 (*C*H$_2$), 121.7 (N*C*H=), 129.3 (*C*H$_{arom.}$), 135.6, 136.0, 139.2 (*C*$_{arom.}$), CB resonance not detected

^{11}B NMR (C_6D_6, 192 MHz): δ −15.8 (d, $^1J_{B,H}$ = 80.8 Hz);

HRMS(TOF EI$^+$): m/z calc. 449.3098 (M$^+$), found 449.3076 (M$^+$)



1,3-Bis(2,6-diisopropylphenyl)-imidazol-2-ylidene-9-borabicyclo[3.3.1]nonane 2e, Synthesized following *GP1* from 1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazolium tetrafluoroborate (426.0 mg, 1.00 mmol), NaHMDS (95% Aldrich, 193.5 mg, 1.00 mmol), and 9-borabicyclo[3.3.1]nonane-dimer (122.4 mg, 0.50 mmol) in THF (5 mL) for 14 h. The reaction mixture was filtered, the solvent was evaporated in vacuo, and the remainder was taken up in the minimal amount of CH_2Cl_2 and hexanes (approx. 7-8 mL) are added. After evaporation of 2/3 of the solvent and storing at –25 °C the obtained crystals were decanted and washed with pentane (3 x 1 mL) and dried in vacuo, traces of hexanes are trapped in the crystal lattice as evident from ^{1}H- and ^{13}C{^{1}H} NMR spectroscopy.

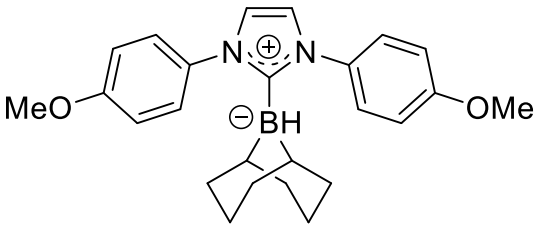
Yield: 283 mg (0.554 mmol, 55%).

^{1}H NMR (C_6D_6, 500 MHz) δ 0.74 (s, 2H, *C*H), 1.01 (d, $^3J_{H,H}$ = 6.9 Hz, 12H, C*H*$_3$), 1.39 (d, $^3J_{H,H}$ = 6.7 Hz, 12H, C*H*$_3$), 1.52 (m, 2H, C*H*$_2$), 1.67 – 2.22 (m, 11H, C*H*$_2$ and B*H*), 2.91 (sept, $^3J_{H,H}$ = 6.6 Hz, 4H), 6.38 (s, 2H, NC*H*=), 7.06 (d, $^3J_{H,H}$ = 7.6 Hz, 4H, C*H*$_{arom.}$) 7.20 (t, $^3J_{H,H}$ = 7.7 Hz, 2H, C*H*$_{arom.}$);

^{13}C{^{1}H} NMR (C_6D_6, 125 MHz) δ 21.8 (br. s, B*C*H), 22.4 (*C*H$_3$), 25.9 (*C*H$_2$), 26.1 (*C*H$_3$), 26.5 (*C*H$_2$), 29.2 (*C*H(CH$_3$)$_2$), 33.4, 37.1 (*C*H$_2$), 122.9 (N*C*H=), 123.9, 130.4 (*C*H$_{arom.}$), 135.7, 146.0 (*C*$_{arom.}$), 178.8 (br. S, *C*B);

^{11}B NMR (C_6D_6, 160 MHz): δ −15.4 (d, $^1J_{B,H}$ = 83.6 Hz)

HRMS(FTMS+pESI): m/z calc. 533.4038 (M$^+$+ Na), found 533.4043 (M$^+$ + Na)



(1,3-Bis(4-methoxyphenyl)-imidazol-2-ylidene-9-borabicyclo[3.3.1]nonane 2f, Synthesized following *GP1* from 1,3-bis(4-methoxyphenyl)-1*H*-imidazolium tetrafluoroborate (297.0 mg, 0.80 mmol), NaHMDS (95% Aldrich, 156.1 mg, 0.80 mmol), and 9-borabicyclo[3.3.1]nonane-dimer (102.0 mg, 0.41 mmol) in THF (4 mL) for 24 h. The reaction mixture was filtered, the solvent was evaporated in vacuo, and the remainder was crystallized from CH_2Cl_2/hexanes at –25 °C. The supernatant solution was decanted and the crystals were washed with pentane (3 x 2 mL) and dried in vacuo.

Yield: 260 mg (0.646 mmol, 80%).

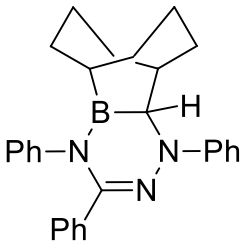
^{1}H NMR (C_6D_6, 500 MHz) δ 0.89 (s, 2H, C*H*), 1.62 (br. s, 3H, C*H*$_2$), 1.75 – 1.77 (m, 2H, C*H*$_2$), 1.92 – 1.97 (m, 1H, C*H*$_2$), 2.04 (br. s, 2H, C*H*$_3$), 2.16 - 2.30 (m, 2H, C*H*$_2$), 2.34 – 2.40 (m, 2H, C*H*$_2$), 2.65 (br. s, 1H, B*H*) 3.16 (s, 6H, C*H*$_3$), 6.22 (s, 2H, C*H*), 6.65 (d, $^3J_{H,H}$ = 10 Hz 4H, C*H*), 7.35 (d, $^3J_{H,H}$ = 5.0 Hz 4H, C*H*)

^{13}C{^{1}H} NMR (C_6D_6, 125 MHz) δ 21.5 (br. s, B*C*H), 25.6, 26.1, 32.5, 36.8 (*C*H$_2$), 54.9 (*C*H$_3$), 114.1 (*C*H$_{arom.}$), 122.2 (N*C*H=), 127.6 (*C*H$_{arom.}$), 132.9, 160.2 (*C*$_{arom.}$), 176.6 (*C*B)

^{11}B NMR (C_6D_6, 160 MHz): δ −16.7 (d, $^1J_{B,H}$ = 84.3 Hz)

HRMS(TOF EI$^+$): m/z calc. 402.2479 (M$^+$), found 402.2483 (M$^+$)

Synthesis of azaborinines



1,3,4-Triphenyl-6-hydro-1,2,4,5-triazaborinine 3a, In a glove box, a 4-dram vial was charged with Ender's carbene (**1a**, 1,3,4-triphenyl-1*H*-1,2,4-triazol-5-ylidene, 298.4 mg, 1.003 mmol) and 9-borabicyclo[3.3.1]nonane-dimer (122.3 mg, 0.501 mmol). After the addition of THF (4 mL), the reaction mixture was stirred at ambient temperature over night (24 h). ^{1}H NMR spectroscopy of an aliquot confirmed clean formation of **3a** with traces of 9-BBN present. The reaction mixture was filtered, the solvent was evaporated in vacuo, and the remainder was crystallized from CH_2Cl_2/hexanes at –25 °C. A few crystals suitable for a single crystal X-ray study were separated. The supernatant solution was decanted and the crystals were washed with pentane (3 x 2 mL) and dried in vacuo. Yield: 228 mg (0.543 mmol, 54%).

Mp: 203-206 °C (CH_2Cl_2/hexanes)

^{1}H NMR (CD_2Cl_2, 500 MHz) δ 1.29 (m, 1H, CH_2), 1.37 (m, 1H, CH_2), 1.53 (m, 1H, CH_2), 1.58 – 1.91 (m, 9H, CH_2 and BCH(CH$_2$)$_2$), 2.00 (m, 1H, CH_2), 2.21 (m, 1H, NCHCH(CH$_2$)$_2$), 3.57 (d, $^{3}J_{H,H}$ = 2.7 Hz, 1H, NCHB), 7.06 (d, $^{3}J_{H,H}$ = 7.1 Hz, 2H, C$H_{arom.}$), 7.10 – 7.15 (m, 5H, C$H_{arom.}$), 7.21 (t, $^{3}J_{H,H}$ = 7.6 Hz, 2H, C$H_{arom.}$), 7.27 (m, 2H, C$H_{arom.}$), 7.37 (m, 4H, C$H_{arom.}$)

^{13}C{^{1}H} NMR (CD_2Cl_2, 150 MHz) δ 23.1, 24.3 (CH$_2$), 24.8 (br. s, BCH(CH$_2$)$_2$), 27.0, 28.5, 29.7, 32.7 (CH$_2$), 34.4 (NCHCH(CH$_2$)$_2$), 56.8 (br. s, NCHB), 123.3, 124.5, 126.5, 127.8, 127.9, 129.0, 129.1, 129.2, 129.4 (CH$_{arom.}$), 136.2, 142.5, 143.5, 150.7 ($C_{arom.}$)

^{11}B NMR (CD_2Cl_2, 160 MHz): δ 48.2 (br. s)

IR: $\tilde{\nu}$ 3082 (w), 3057 (w), 3033 (w), 2982 (w), 2920 (m), 2903 (m), 2884 (m), 2863 (m), 2844 (m), 2801 (m), 1625 (w), 1593 (s), 1574 (m), 1485 (s), 1467 (m), 1447 (m), 1411 (w), 1389 (m), 1371 (m), 1350 (m), 1309 (m), 1271 (s), 1235 (m), 1216 (m), 1191 (m), 1175 (m), 1161 (m), 1152 (m), 1118 (m), 1095 (m), 1070 (m), 1059 (m), 1035 (m), 1003 (m), 991 (w), 961 (w), 934 (w), 909 (m), 899 (w), 881 (w), 857 (w), 835 (w), 769 (w), 746 (s), 692 (s), 669 (m), 652 (m), 616 (w), 599 (w), 553 (w), 518 (w), 500 (w), 471 (w), 449 (w)

HRMS(TOF EI^{+}): m/z calc. 419.2533 (M^{+}), found 419.2532 (M^{+})

Anal. Calcd. (%) for $C_{28}H_{30}BN_3$: C, 80.19; H, 7.21; N, 10.02; Found: C, 79.66; H, 7.29; N, 10.00.

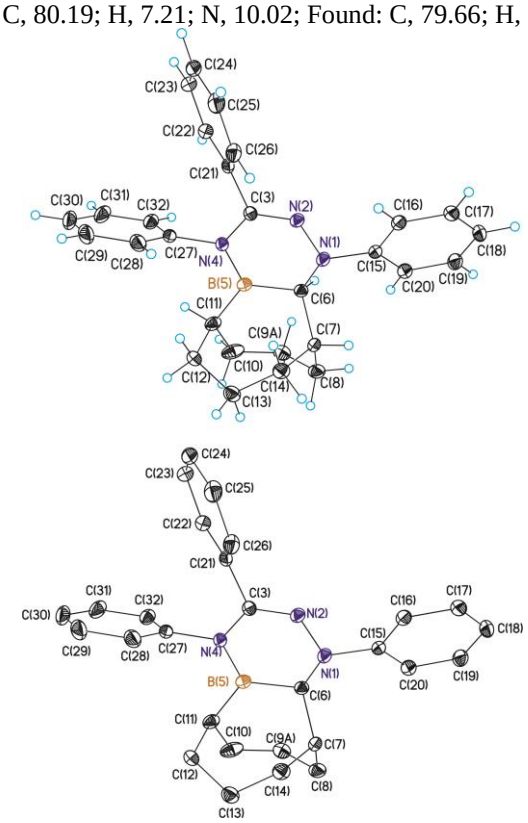
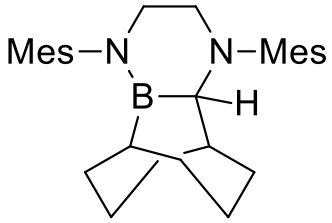


Figure S1: Crystal structure of compound 3a

1,4-Dimesityl-2,3,6-trihydro-1,4,2-diazaborinine 3b, Synthesized following *GP3*: In a glove box a vial was charged with 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (396.1 mg, 1.004 mmol), NaHMDS (95%, 194.4 mg, 1.007 mmol), and 9-borabicyclo[3.3.1]nonane-dimer (124.3 mg, 0.509 mmol). After the addition of THF (5 mL) the reaction mixture was stirred at ambient temperature for 22 h. ^{1}H NMR and ^{11}B NMR spectroscopy of an aliquot confirmed formation of a mixture of carbene-borane and product. The reaction mixture was filtered, the solvent was evaporated in vacuo, and the remainder was taken up in benzene (5 mL) and transferred to a J. Young tube. The vessel was removed from the glove box and placed in a preheated oil bath (80 ºC) for 2 d. The reaction mixture was cooled to ambient temperature and the solvent was evaporated in vacuo. The remainder was taken up in a mixture of CH_2Cl_2/hexanes 5:1, filtered and the solution evaporated to about 1/5 of its original volume, the supernatant was decanted and the remaining solid was washed with pentane. After drying in vacuo the product was isolated as an ochre solid.



Yield: 135 mg (0.313 mmol, 31%).

^{1}H NMR (C_6D_6, 400 MHz) δ 1.29-1.36 (m, 1H), 1.36-1.65 (m, 7H), 1.66-1.82 (m, 3H), 1.85-1.96 (m, 2H), 2.07-2.13 (m, 1H), 2.16 (s, 3H), 2.18 (s, 3H), 2.19 (s, 3H), 2.33 (s, 3H), 2.37 (s, 3H), 2.45 (s, 3H), 2.75 (dt, J = 11.6, 3.7 Hz, 1H), 3.16 (dt, J = 12.3, 4.2 Hz, 1H), 3.29 (m, 1H), 3.35 (br. s, 1H), 3.41 (m, 1H), 6.76 (s, 1H), 6.82 (s, 2H), 6.91 (s, 1H)

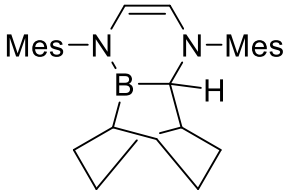
^{13}C{^{1}H} NMR (C_6D_6, 150 MHz) δ 18.0, 18.9, 19.7, 20.2, 20.9, 21.0 (*C*H$_3$), 22.5 (*C*H$_2$), 23.8 (br. s, B*C*H), 24.9, 27.1, 29.4, 30.6 (*C*H$_2$), 35.6 (BCH*C*H), 36.0 (*C*H$_2$), 51.2 (BN*C*H$_2$), 53.0 (BCHN*C*H$_2$), 59.5 (br. s, B*C*HN), 129.4, 129.6, 129.9, 130.0 (*C*H$_{arom.}$), 134.1, 134.4, 134.7, 135.0, 137.0, 138.7 (*C*$_{arom.}$), 143.9, 145.2, (N*C*$_{arom.}$);

^{11}B NMR (C_6D_6, 192 MHz): δ 45.0 (br. s)

HRMS(TOF EI$^+$): m/z calc. 428.3363 (M$^+$), found 428.3368 (M$^+$)

1,4-Dimesityl-6-hydro-1,4,2-diazaborinine 3c,

GP2: 1,3-Dimesityl-imidazol-2-ylidene-9-borabicyclo[3.3.1]nonane (**2c**, 149.6 mg, 0.35 mmol) in xylenes (2 mL) for 46 h at 150 °C. The reaction mixture was cooled to ambient temperature and all volatiles were evaporated and the product was treated with a mixture of CH_2Cl_2/hexanes (1:4) filtered and the solvent evaporated to give the product as an ochre solid. Yield: 130 mg (0.304 mmol, 87%).



GP3: In a glove box, a vial was charged with 1,3- bis(2,4,6-trimethylphenyl)-imidazolium tetrafluoroborate (784 mg, 1.99 mmol), NaHMDS (95%, 386 mg, 2.11 mmol), and 9-borabicyclo[3.3.1]nonane-dimer (244 mg, 1.00 mmol). After the addition of THF (5 mL), the reaction mixture was stirred at ambient temperature for 22 h. ^{1}H NMR and ^{11}B NMR spectroscopy of an aliquot confirmed formation of a mixture of carbene-borane and product. The reaction mixture was filtered, the solvent was evaporated in vacuo, and the remainder was taken up in xylenes (5 mL) and transferred to a J. Young tube. The vessel was removed from the glove box and placed in a preheated oil bath (150 ºC) for 46 h. The reaction mixture was cooled to ambient temperature and the solvent was evaporated in vacuo. The remainder was taken up in a mixture of CH_2Cl_2/hexanes 5:1, filtered and the solution evaporated to about 1/5 of its original volume, the supernatant was decanted and the remaining solid was washed with pentane. After drying in vacuo the product was isolated as an ochre solid. Yield: 746 mg (1.749 mmol, 87%)

^{1}H NMR (CD_2Cl_2, 600 MHz) δ 1.14 (m, 1H, BC*H*), 1.39 – 1.28 (m, 2H, C*H*$_2$), 1.54 – 1.39 (m, 5H, C*H*$_2$); 1.57 (m, 1H, C*H*$_2$), 1.78 – 1.63 (m, 3H, *C*H$_2$), 1.85 (m, 1H, BCHC*H*), 2.02 (m, 1H, C*H*$_2$), 2.21 (s, 3H, C*H*$_3$), 2.25 (s, 3H, C*H*$_3$), 2.27 (s, 3H, C*H*$_3$), 2.29 (s, 3H, C*H*$_3$), 2.31 (s, 3H, C*H*$_3$), 2.33 (s, 3H, C*H*$_3$), 3.69 (d, $^{3}J_{H,H}$ = 2.9 Hz, 1H, BC*H*N), 4.96 (d, $^{3}J_{H,H}$ = 5.8 Hz, 1H, BNC*H*=), 5.44 (d, $^{3}J_{H,H}$ = 5.8 Hz, 1H, BCHNC*H*=), 6.80 (s, 1H, C*H*$_{arom.}$), 6.90 (s, 1H, C*H*$_{arom.}$), 6.91 (s, 2H, C*H*$_{arom.}$);

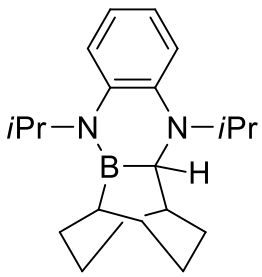
^{13}C{^{1}H} NMR (CD_2Cl_2, 150 MHz) δ 18.1, 18.7, 18.9, 20.1, 21.1, 21.2 (*C*H$_3$), 22.4 (*C*H$_2$), 24.3 (br. s, B*C*H), 24.8, 27.4, 28.7, 30.3 (*C*H$_2$), 34.1 (BCH*C*H), 34.8 (*C*H$_2$), 57.1 (br. s, B*C*HN), 110.1 (BN*C*H=), 124.3 (BCHN*C*H=), 129.0, 129.5, 129.6, 129.6 (*C*H$_{arom.}$), 135.4, 135.7, 135.8, 136.0, 138.3, 138.8 (*C*$_{arom.}$), 141.4, 142.9, (N*C*$_{arom.}$)

^{11}B NMR (CD_2Cl_2, 192 MHz): δ 43.1 (br. s);

HRMS(FTMS+pESI): m/z calc. 426.3206 (M$^+$), found 425.3136 (M$^+$ - H);

Anal. Calcd. (%) for $C_{29}H_{39}BN_2$: C, 81.68; H, 9.22; N, 6.57; Found: C, 82.74; H, 9.24; N, 7.53.

1,4-diisopropyl-1,2,3,4-tetrahydrobenzo[e]-1,4,2-diazaborinine 3d, Synthesized following *GP3*: In a glove box, a 3-dram vial was charged with 1,3-diisopropyl-1*H*-benzo[*d*]imidazolium iodide (660.4 mg, 2.001 mmol), NaHMDS (95%, 386 mg, 2.11 mmol) and 9-borabicyclo[3.3.1]nonane-dimer (244.0 mg, 1.00 mmol). After the



addition of THF (4 mL), the reaction mixture was stirred at ambient temperature over night (24 h). ^{1}H NMR and ^{11}B NMR spectroscopy of an aliquot confirmed formation of the carbene-borane. The reaction mixture was filtered, the solvent was evaporated in vacuo, and the remainder was taken up in benzene (5 mL) and transferred to a J. Young tube and the vessel was removed from the glove box and placed in a preheated oil bath (85 ºC) for 20 h. The reaction mixture was cooled to ambient temperature and the solvent was evaporated in vacuo to give an oil. Yield: 91 mg (0.281 mmol, 84%).

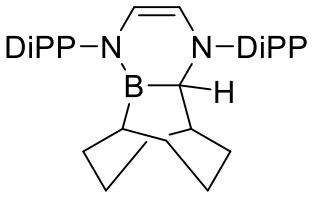
^{1}H NMR (C_6D_6, 500 MHz) δ 1.24 (d, 3H, CH_3), 1.27-1.31 (m, 9H), 1.45-1.61 (m, 6H), 1.68-1.76 (m, 4H), 1.82-1.86 (m, 2H), 2.07 (m, 1H), 2.37 (m, 1H), 2.86 (br. s, 1H), 3.71 (sep, $^{3}J_{H\text{-}H}$ = 7.05 Hz, 1H), 4.06 (sep, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 1H), 6.75 (dd, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 7.0 Hz, 1H), 6.89-6.99 (m, 3H)

^{13}C{^{1}H} NMR (C_6D_6, 125 MHz) δ 18.8, 20.0, 22.1, 22.6, 23.2, 24.7, 27.2, 28.8, 29.3, 34.1, 36.6, 49.3, 49.4, 116.7, 117.1, 121.4, 127.3, 127.5, 127.7, 136.6, 142.1

^{11}B NMR (C_6D_6, 160 MHz): δ 49.2 (br. s)

HRMS(FTMS+pESI): m/z calc. 324.2737 (M^+), found 325.2812 (M^+ + H)

1,4-Bis(2,6-diisopropylphenyl)-6-hydro-1,4,2-diazaborinine 3e,



Synthesized following *GP2*: 1,3-Bis(2,6-diisopropylphenyl)-imidazol-2-ylidene-9-borabicyclo[3.3.1]nonane (101.9 mg, 0.199 mmol) in xylenes (2 mL) for 7 d at 175 °C. The reaction mixture was cooled to ambient temperature and all volatiles were evaporated and the product were treated with a mixture of CH_2Cl_2/hexanes (1:4) filtered and the solvent evaporated to give the product as an ochre solid foam. Yield: 89 mg (0.174 mmol, 87%).

Synthesized following *GP3*: In a glove box a 3-dram vial was charged with 1,3-(2,6-diisopropylphenyl)-imidazolium chloride (306 mg, 0.720 mmol), NaHMDS (95%, 138.9 mg, 0.757 mmol) and 9-borabicyclo[3.3.1]nonane-dimer (88.5 mg, 0.363 mmol). After the addition of THF (3 mL) the reaction mixture was stirred at ambient temperature over night (24 h). ^{1}H NMR and ^{11}B NMR spectroscopy of an aliquot confirmed formation of the carbene-borane. The reaction mixture was filtered, the solvent was evaporated in vacuo, and the remainder was taken up in xylenes (3 mL) and transferred to a J. Young tube. The vessel was removed from the glove box and placed in a preheated oil bath (175 ºC) for 8 d. The reaction mixture was cooled to ambient temperature and the solvent was evaporated in vacuo to give an oil. Yield = 327 mg (0.640 mmol, 88%)

^{1}H NMR (CD_2Cl_2, 600 MHz) δ 1.18 (d, $^{3}J_{H,H}$ = 7.0 Hz, 3H, CH_3), 1.19 (d, $^{3}J_{H,H}$ = 7.0 Hz, 3H, CH_3), 1.20 – 1.34 (m, 21H, 6 x CH_3, CH_2, and BC*H*), 1.41 – 1.56 (m, 6H, CH_2), 1.66 – 1.78 (m, 3H, CH_2); 1.88 – 1.94 (m, 1H, *C*H$_2$), 1.98 (m, 1H, BCHC*H*), 3.28 (sept, $^{3}J_{H,H}$ = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 3.35 (sept, $^{3}J_{H,H}$ = 6.7 Hz, 1H, C*H*(CH$_3$)$_2$), 3.47 (sept, $^{3}J_{H,H}$ = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 3.69 (d, $^{3}J_{H,H}$ = 2.8 Hz, 1H, BC*H*N), 3.80 (sept, $^{3}J_{H,H}$ = 7.0 Hz, 1H, C*H*(CH$_3$)$_2$), 5.06 (d, $^{3}J_{H,H}$ = 5.7 Hz, 1H, BNC*H*=), 5.53 (d, $^{3}J_{H,H}$ = 5.7 Hz, 1H, BCHNC*H*=), 7.21 – 7.12 (m, 4H, C$H_{arom.}$), 7.26 (m, 2H, C$H_{arom.}$);

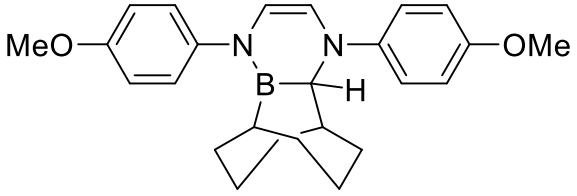
^{13}C{^{1}H} NMR (CD_2Cl_2, 150 MHz) δ 22.4 (*C*H$_2$), 23.2, 23.3, 23.4 (*C*H$_3$), 23.9 (br. s, B*C*H), 24.2 (*C*H$_3$), 24.9 (*C*H$_2$), 25.8, 26.1, 26.2, 27.0 (*C*H$_3$), 27.1 (*C*H$_2$), 28.4, 28.5 (*C*H(CH$_3$)$_2$), 28.5 (*C*H$_2$), 28.8, 28.9 (*C*H(CH$_3$)$_2$), 29.9 (*C*H$_2$), 33.9 (BCH*C*H), 35.0 (*C*H$_2$), 59.9 (br. s, B*C*HN), 112.4 (BN*C*H=), 123.8, 124.1, 124.1, 124.3 (*C*H$_{arom.}$), 125.3 (BCHN*C*H=), 127.3, 127.6 (*C*H$_{arom.}$), 141.2, 142.3, (N*C*$_{arom.}$) 145.9, 147.0, 150.3, 150.6 (*C*$_{arom.}$)

^{11}B NMR (CD_2Cl_2, 192 MHz): δ 42.4 (br. s);

HRMS(FTMS+pESI): m/z calc. 510.4145 (M^+), found 509.4077 (M^+ - H);

Anal. Calcd. (%) for $C_{35}H_{51}BN_2$: C, 82.33; H, 10.07; N, 5.49; Found: C, 82.60; H, 10.06; N, 6.33.

1,4-(4-Methoxyphenyl)-6-hydro-1,4,5-diazaborinine 3f,



Synthesized following *GP2* from 1,3-bis(4-methoxyphenyl)-imidazol-2-ylidene-9-borabicyclo[3.3.1]nonane (**2f**, 41.0 mg, 0.101 mmol) in benzene-d_6 (0.5 mL) for 25 h at 80 °C.

Yield: 37 mg (0.0919 mmol, 90%)

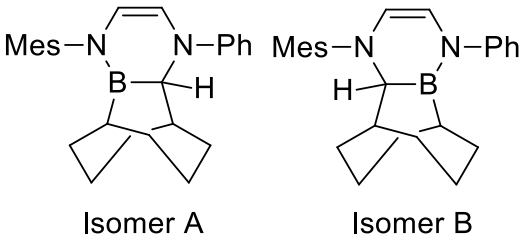
^{1}H NMR (C_6D_6, 400 MHz) δ 1.42-1.56 (m, 4H. CH_2), 1.59-1.70 (m, 4H, BC*H*, CH_2), 1.74-1.84 (m, 3H, CH_2), 1.95-2.04 (m, 1H, CH_2), 2.07-2.15 (m, 1H, CH_2), 2.47 (br. s, 1H, NCHC*H*), 3.29 (s, 3H, CH_3), 3.35 (s, 3H, CH_3), 3.87 (br. d, $^{2}J_{B\text{-}H}$ = 1.9 Hz, 1H, BC*H*N), 5.32 (d, $^{3}J_{H\text{-}H}$ = 6.2 Hz, 1H, BNC*H*=), 5.73 (d, $^{3}J_{H\text{-}H}$ = 6.2 Hz, 1H, BCHNC*H*=), 6.68-6.73 (m, 2H, CH_{arom}), 6.76-6.82 (m, 2H, CH_{arom}), 7.03-7.12 (m, 4H, CH_{arom})

^{13}C{^{1}H} NMR (C_6D_6, 100 MHz) δ 23.0, 23.9, 24.1, 28.0, 28.5, 29.7, 33.2 (*C*H), 34.1, 55.0, 55.1, 56.2, 112.2 (BN*C*H=), 114.6, 114.7, 123.5 (*C*H$_{arom.}$), 123.5 (BCHN*C*H=), 128.3 (*C*H$_{arom.}$), 140.8, 142.2 (N*C*$_{arom.}$), 156.3, 158.1 (O*C*H$_{arom.}$)

^{11}B NMR (C_6D_6, 128 MHz): δ 43.4 (br. s)

HRMS(FTMS+pESI): m/z calc. 402.2479 (M^+), found 401.2393 (M^+ - H)

1-(2,4,6-trimethylphenyl)-3-phenyl-6-hydro-1,4,2-triazaborinine 3gA, 1-(2,4,6-trimethylphenyl)-3-phenyl-6-hydro-1,4,3-triazaborinine 3gB



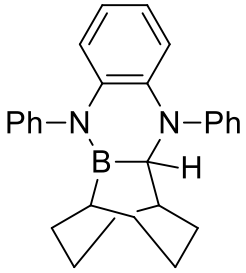
Synthesized following *GP2* from 1-(2,4,6-trimethylphenyl)-3-phenyl-imidazol-2-ylidene-9-borabicyclo[3.3.1]nonane (37.7 mg, 0.098 mmol) in benzene-d6 (0.5 mL) for 13 h at 80 °C. The reaction mixture was cooled to ambient temperature and all volatiles were evaporated and the product was treated with a mixture of CH_2Cl_2/hexanes (1:4) filtered and the solvent evaporated to give the product as an orange oil. Yield: 37 mg (0.096 mmol, 98%).

^{1}H NMR (C_6D_6, 600 MHz) δ 1.01-1.57 (m, 1H, B), 1.88-1.95 (m, 1H, A), 1.24-1.30 (m, A+B), 1.37-1.83 (m, A+B), 2.03-2.12 (m, A+B), 2.15 (s, 3H, A), 2.16 (s, 3H, B), 2.22 (s, 3H, A), 2.28 (s, 3H, B), 2.38 (s, 3H, A), 2.44 (s, 3H, B), 2.50 (m, 1H, A), 3.89 (d, $^2J_{B\text{-}H}$ = 2.5 Hz, 1H, B, BC*H*N), 4.02 (s, 1H, A, BC*H*N), 4.85 (d, $^3J_{H\text{-}H}$ = 6.2 Hz, 1H, A, BN*C*H=), 5.37 (s, 2H, B, BN*C*H=), 5.81 (d, $^3J_{H\text{-}H}$ = 6.2 Hz, 1H, A, BN*C*H=), 6.72 (s, 1H, B, CH_{arom}), 6.80 (s, 1H, A, CH_{arom}), 6.82 (s, 1H, A, CH_{arom}), 6.85 (s, 1H, B, CH_{arom}), 6.90 (t, J = 7.3 Hz, 1H, A, CH_{arom}), 6.99 (t, J = 7.3 Hz, 1H, B, CH_{arom}), 7.07 (d, J= 8.1 Hz, A, CH_{arom}), 7.11 (t, J = 7.7 Hz, A, CH_{arom}), 7.14-7.20 (m, A+B)

^{11}B NMR (C_6D_6, 192 MHz) δ 45.1 (br. s with shoulder)

HRMS(TOF EI$^+$): m/z calc. 384.2737 (M^+), found 384.2742 (M^+)

1,4-diphenyl-1,2,3,4-tetrahydrobenzo[e]-1,4,2-diazaborinine 3h



Synthesized following a modified *GP3* procedure: In a glove box a vial was charged with 1,3-diphenyl-1*H*-benzo[*d*]imidazolium tetrafluoroborate (77.0 mg, 0.215 mmol), NaHMDS (95%, 41.5 mg, 0.215 mmol), and 9-borabicyclo[3.3.1]nonane-dimer (26.2 mg, 0.108 mmol). After the addition of THF (4 mL) the reaction mixture was stirred at ambient temperature for 16 h. The reaction mixture was filtered, the solvent was evaporated in vacuo, and the resulting oil was recrystallized in CH_2Cl_2/pentane at -40 ºC. Washing with additional pentane and drying in vacuo gave the product as a white solid. Yield: 35 mg (0.089 mmol, 41%)

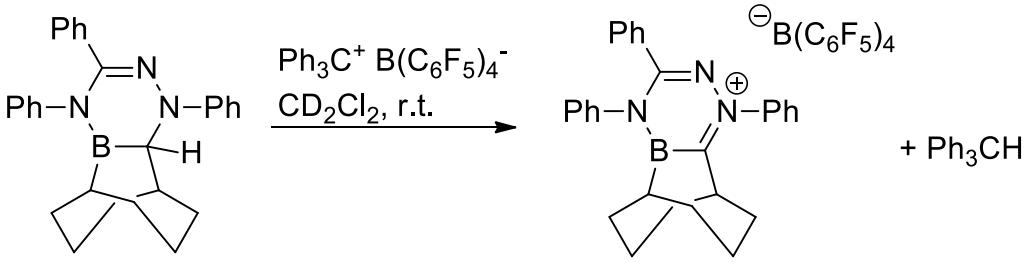
^{1}H NMR (C_6D_6, 400 MHz) δ 1.41-1.55 (m, 4H), 1.62-1.91 (m, 7H), 2.10-2.24 (m, 2H), 2.41-2.44 (m, 1H, NCHC*H*), 3.71 (d, 1H, $^2J_{B\text{-}H}$ = 3.0 Hz, 1H, BC*H*N), 6.30 (dd, J= 8.1, 1.1 Hz, 1H, CH_{arom}), 6.55 (dd, J= 7.9, 1.1 Hz, 1H, CH_{arom}), 6.61 (td, J= 7.6, 1.3 Hz, 1H, CH_{arom}), 6.79 (td, J= 7.6, 1.1 Hz, 1H, CH_{arom}), 7.00-7.10 (m, 1H, CH_{arom}), 7.12-7.38 (m, 9H, CH_{arom})

^{13}C{^{1}H} NMR (C_6D_6, 150 MHz) δ 22.4, 24.2, 25.0, 27.2, 27.7, 29.7, 33.6, 34.0, 57.7, 116.4, 118.3, 118.6, 123.0, 126.6, 126.8, 128.5, 129.5, 130.1, 130.2, 136.0, 143.1, 145.0, 146.9

^{11}B NMR (C_6D_6, 192 MHz): δ 44.5 (br. s)

HRMS(TOF EI$^+$): m/z calc. 392.2424 (M^+), found 392.2435 (M^+)

Generation of 4a

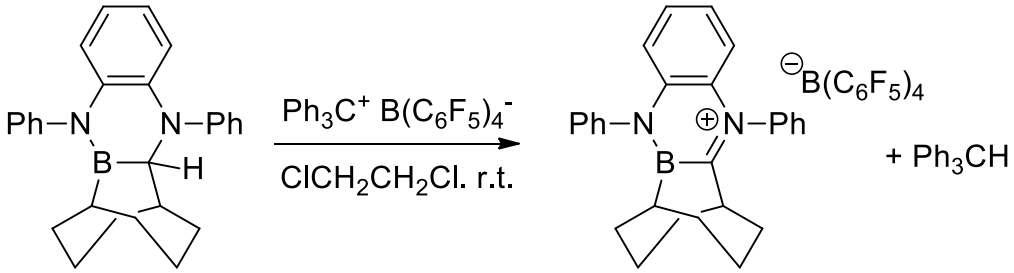


In a glove box, a vial was charged with **3a** (42.0 mg, 0.100 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (92.2 mg, 0.100 mmol) and were allowed to mix in CD_2Cl_2 for 16 h at room temperature. The Gutmann Beckett study[10] and spectroscopic identification were carried out in situ without further purification due to sensitivity of the cation.^{11}B NMR spectroscopy indicated a broad resonance at 42.3 ppm, shifted from 48.2 ppm in **3a**. ^{1}H NMR spectroscopy showed the generation of triphenylmethane at 5.58 ppm indicative of hydride abstraction. An unidentified by-product gave inflated integrations in the some regions of the ^{1}H NMR spectrum. The 1H-COSY NMR showed coupling between

the by-product and underlying aliphatic region, suggesting that the inflated integrations in the aromatic and aliphatic regions are a result of this by-product.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ 1.50-1.54 (m, 3H), 1.79-1.85 (m, 5H), 1.92-1.94 (m, 4H), 2.08-2.18 (m, 4h), 3.47-3.51 (m, 1H), 7.11 (m, 9H), 7.30-7.32 (m, 18H), 7.40-7.44 (m, 5H), 7.51 (m, 3H), 7.70-7.74 (m, 3H)
^{13}C{^{1}H} NMR (C_6D_6, 150 MHz) δ 23.97, 28.85, 31.46, 43.50, 123.72, 127.32, 128.55, 129.09, 130.07, 130.22, 130.66, 131.05, 131.16, 131.47, 132.00, 132.7, 136.1 (dm), 139.0 (dm), 148.8 (dm), 160.26.
B*C*H, B*C*N and C_{ipso} of [$B(C_6F_5)_4$] resonances could not be identified due to the effect of the adjacent boron atom.
^{11}B NMR (CD_2Cl_2, 192 MHz): δ -16.6 (s), 42.3 (br. s)

Generation of 4h

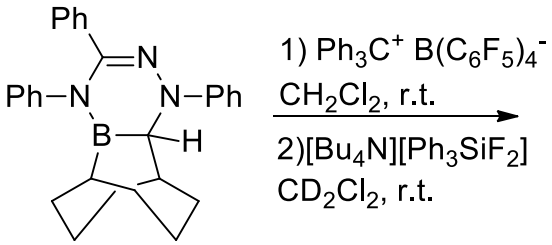


In a glove box, a vial was charged with **3h** (5.4 mg, 0.0138 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (12.7 mg, 0.0138 mmol) and were allowed to mix in CD_2Cl_2 (0.5 mL) in a J. Young tube for 30 minutes at room temperature. ^{11}B NMR spectroscopy of the crude mixture indicated a broad resonance at 38.8 ppm, shifted from 44.5 ppm in **3h** with the counterion $B(C_6F_5)_4^-$ appearing at -16.9 ppm. ^{1}H NMR spectroscopy showed the generation of triphenylmethane at 5.59 ppm indicative of hydride abstraction. Compound **4h** was less cleanly generated compared to compound **4a**, with inflated integrations in the ^{1}H NMR spectrum. The 1H-COSY NMR indicates coupling between the by-product and underlying aliphatic region, suggesting that the inflated integrations in the aromatic and aliphatic regions are a result of this by-product.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ 1.45-1.61 (m, 6H), 1.73-1.84 (m, 10H), 2.01-2.09 (m, 4H), 3.34-3.37 (m, 1H), 7.01-7.53 (m, 30H), 7.62-7.73 (m, 6H), 7.81-7.87 (m, 5H)
^{11}B NMR (CD_2Cl_2, 192 MHz): δ -16.9 (s), 38.8 (br. s)

Cation Reactivity Studies

Reaction of compound 4a with Fluoride



In a glove box, a vial was charged with **3a** (21.0 mg, 0.05 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (46.1 mg, 0.05 mmol) and were allowed to mix in CH_2Cl_2 (0.5 mL) for 30 minutes at room temperature. The solvent was evaporated and the residue was washed with hexanes (1 mL) then decanted and the resulting oil was dried in vacuo. This was repeated 3 more times. After the final drying, the resulting foam was dissolved in CD_2Cl_2 (0.5 mL). In a vial, $[Bu_4N][Ph_3SiF_2]$ (27.0 mg, 0.05 mmol) was dissolved in CD_2Cl_2 (0.2 mL) and added to the solution. Immediately, the solution changed from orange to yellow. In ^{11}B NMR, the broad singlet occurring at 44.1 ppm shifted to -0.4 ppm, indicative of a 4-coordinate boron species, while the anion $^-B(C_6F_5)_4$ remained unchanged at -16.9 ppm. In ^{19}F NMR, a chemical shift of -170.7 ppm appeared, attributed to Ph_3SiF generated as a by-product. A broad resonance also appeared at -162.4 ppm with a small shoulder. This pattern is due to coupling to the two different NMR-active boron isotopes. Peaks at -133.7, -164.3, and -169.2 ppm are attributed to the C_6F_5 rings in $^-B(C_6F_5)_4$.

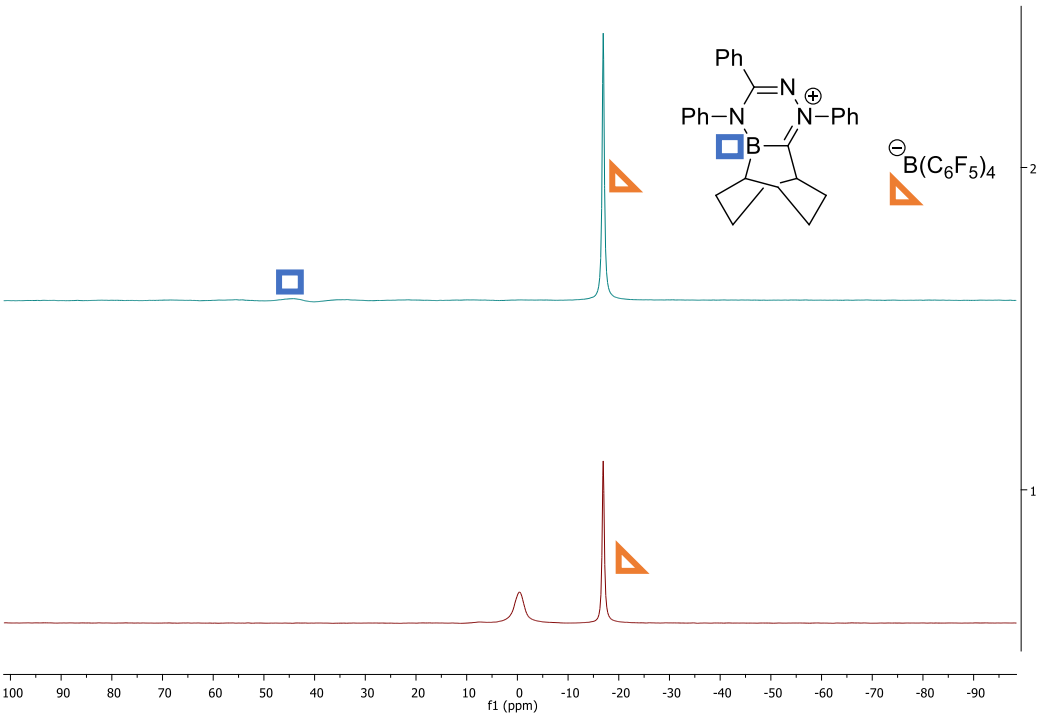


Figure S2: ^{11}B-NMR (128 MHz, top, blue trace before $[Bu_4N][Ph_3SiF_2]$ addition, red trace after $[Bu_4N][Ph_3SiF_2]$ addition) of compound 4a reaction with $[Bu_4N][Ph_3SiF_2]$ in CD_2Cl_2

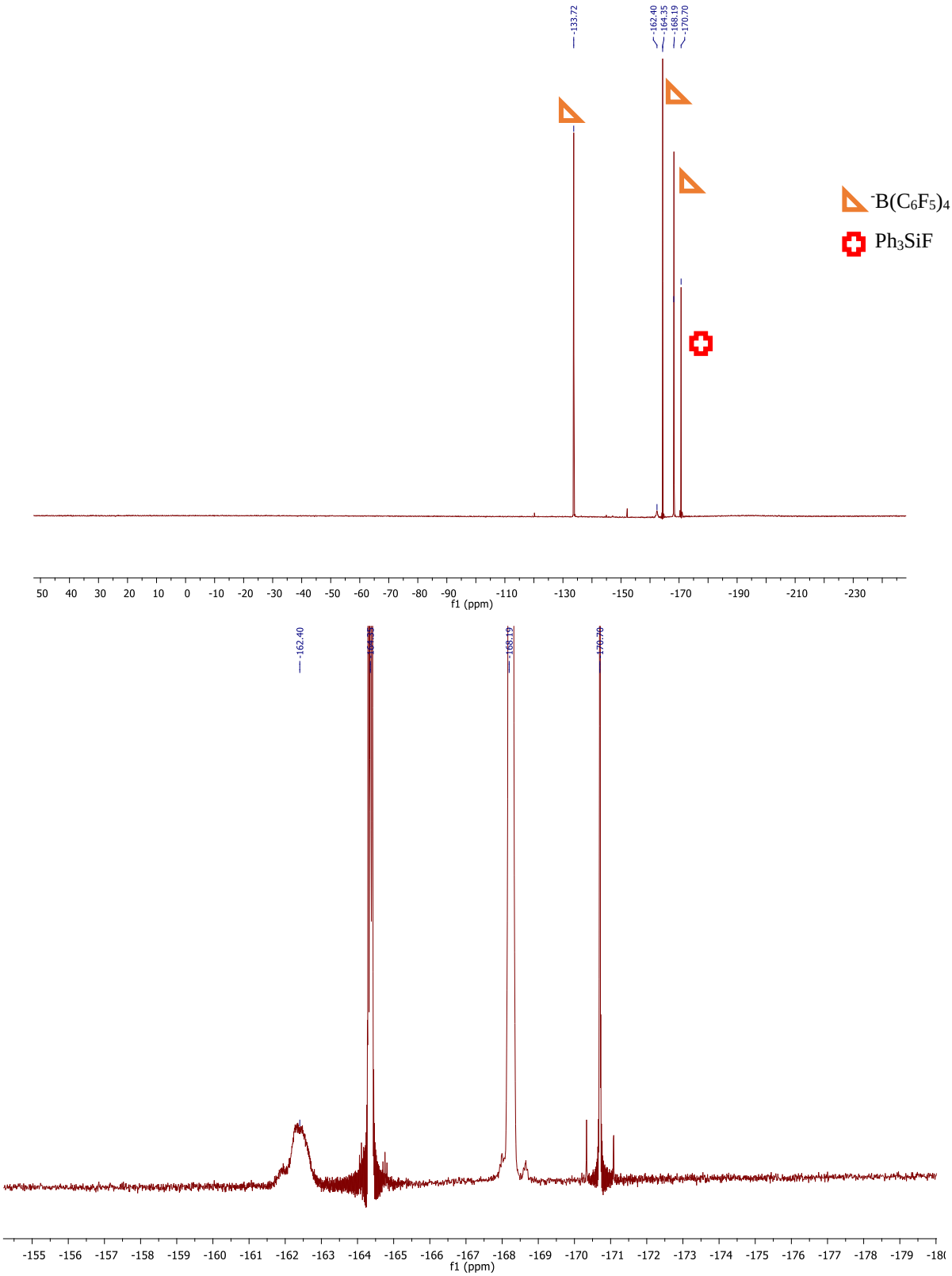


Figure S3: ^{19}F-NMR (376 MHz, top, after $[Bu_4N][Ph_3SiF_2]$ addition), ^{19}F-NMR (376 MHz, bottom, after $[Bu_4N][Ph_3SiF_2]$ addition, zoomed in) of compound 4a reaction with $[Bu_4N][Ph_3SiF_2]$ in CD_2Cl_2

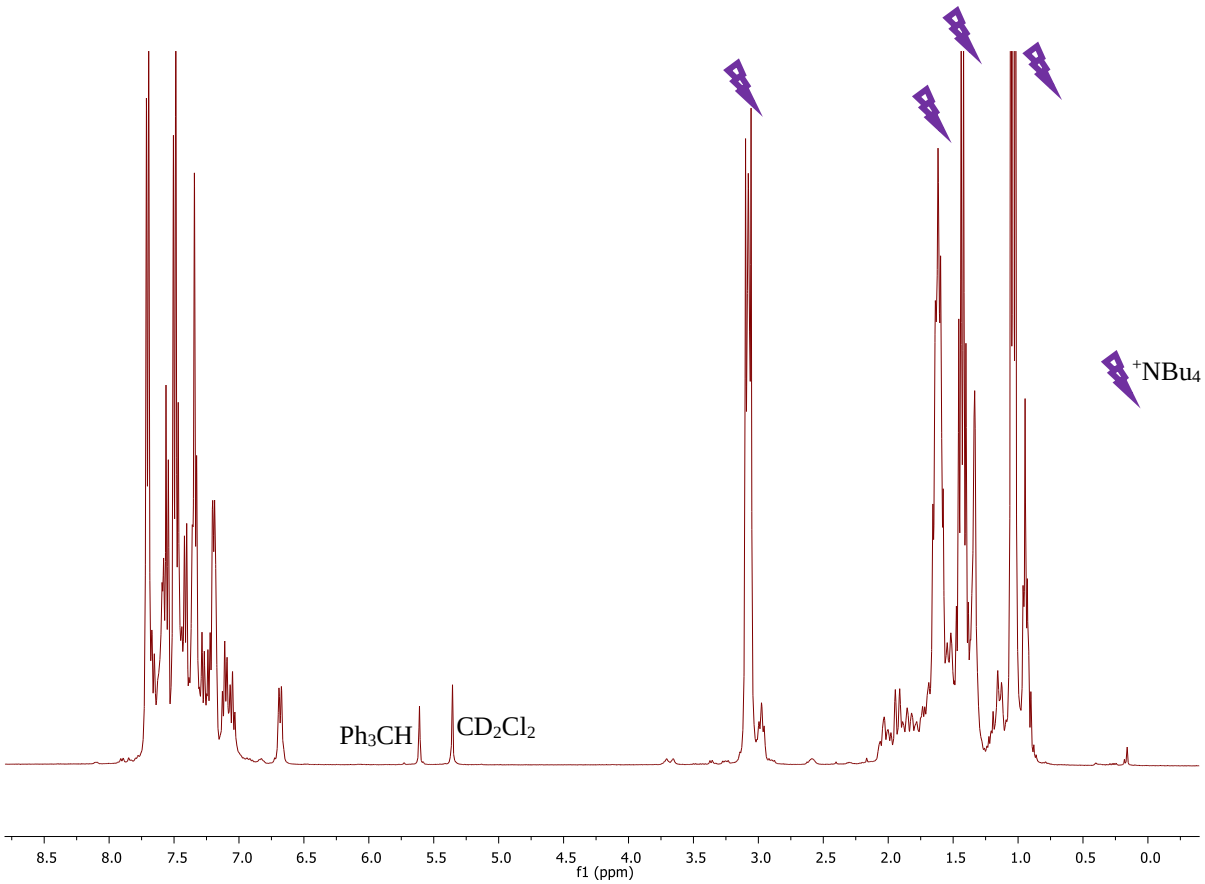
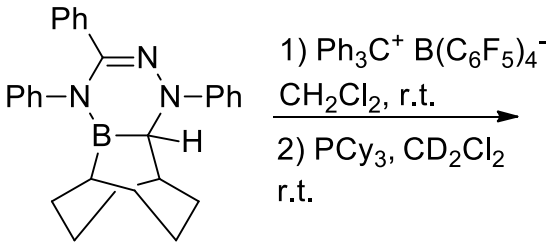


Figure S4: ^{1}H-NMR (400 MHz, bottom) of compound 4a reaction with $[Bu_4N][Ph_3SiF_2]$ in CD_2Cl_2.

Reaction of 4a with Tricyclohexylphosphine



In a glove box, a vial was charged with **3a** (21.0 mg, 0.05 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (46.1 mg, 0.05 mmol) and were allowed to mix in CH_2Cl_2 (0.5 mL) for 30 minutes at room temperature. The solvent was evaporated and the residue was washed with hexanes (1 mL) then decanted and the resulting oil was dried in vacuo. This was repeated 3 more times. After the final drying, the resulting foam was dissolved in CD_2Cl_2 (0.5 mL). In a vial, PCy_3 (14.0 mg, 0.05 mmol) was dissolved in CD_2Cl_2 (0.2 mL) and added to the solution. Immediately, the solution changed from orange to clear. ^{1}H NMR showed an upfield shift for the aliphatic proton alpha to the carbocation, moving from 3.51 ppm to 3.20 ppm. In the ^{31}P NMR, two broad peaks are present at 11.56 and 34.62 ppm, attributed to the free phosphine and the bound phosphine from adduct formation, respectively. The ^{11}B NMR shows only the anion $B(C_6F_5)_4^-$ at -16.9 ppm.

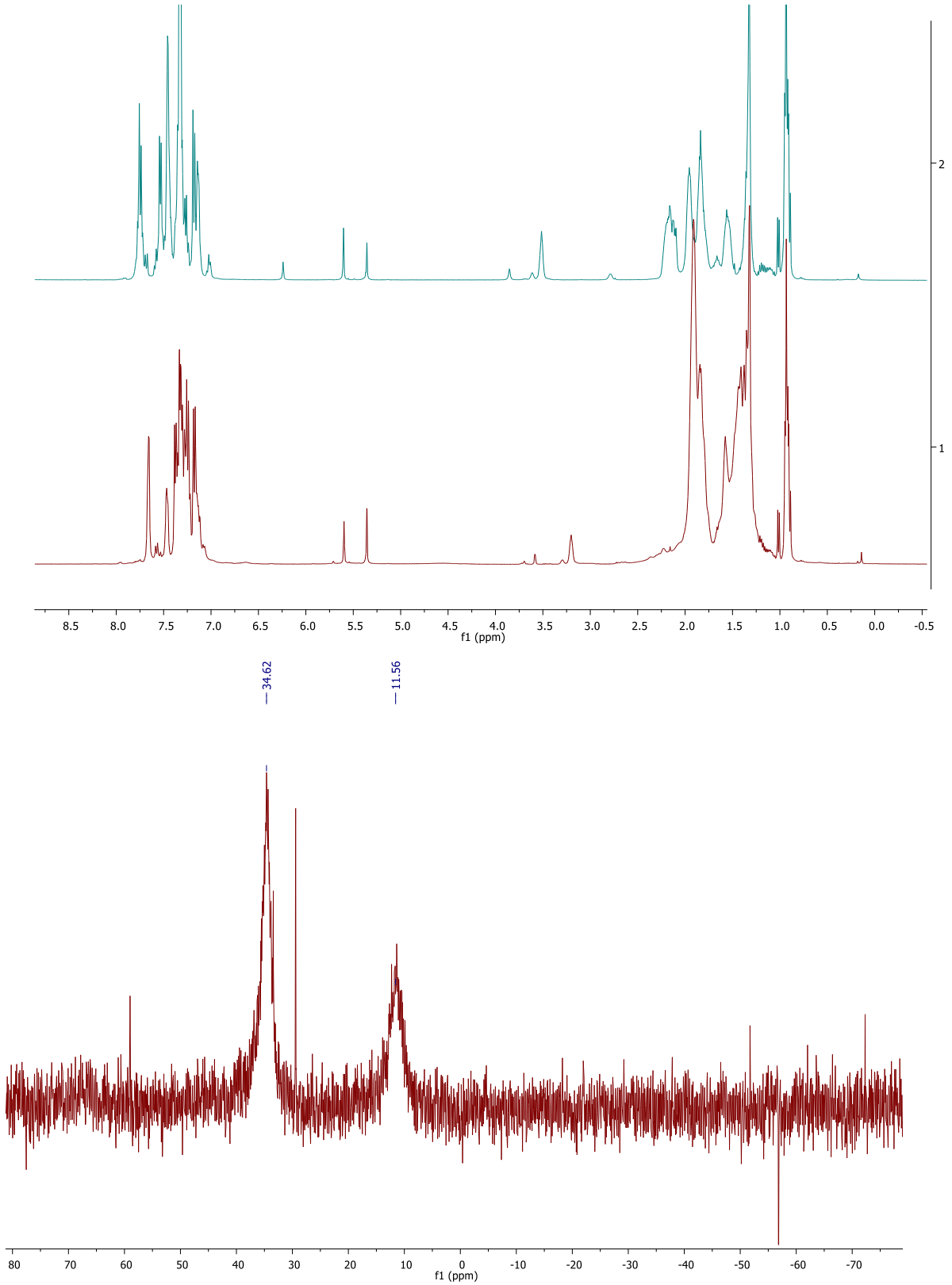


Figure S5: ^{1}H-NMR (400 MHz, top, blue trace before PCy_3 addition, red trace after PCy_3 addition), ^{31}P-NMR (162 MHz, bottom, after PCy_3 addition) of compound 4a reaction with PCy_3 in CD_2Cl_2.

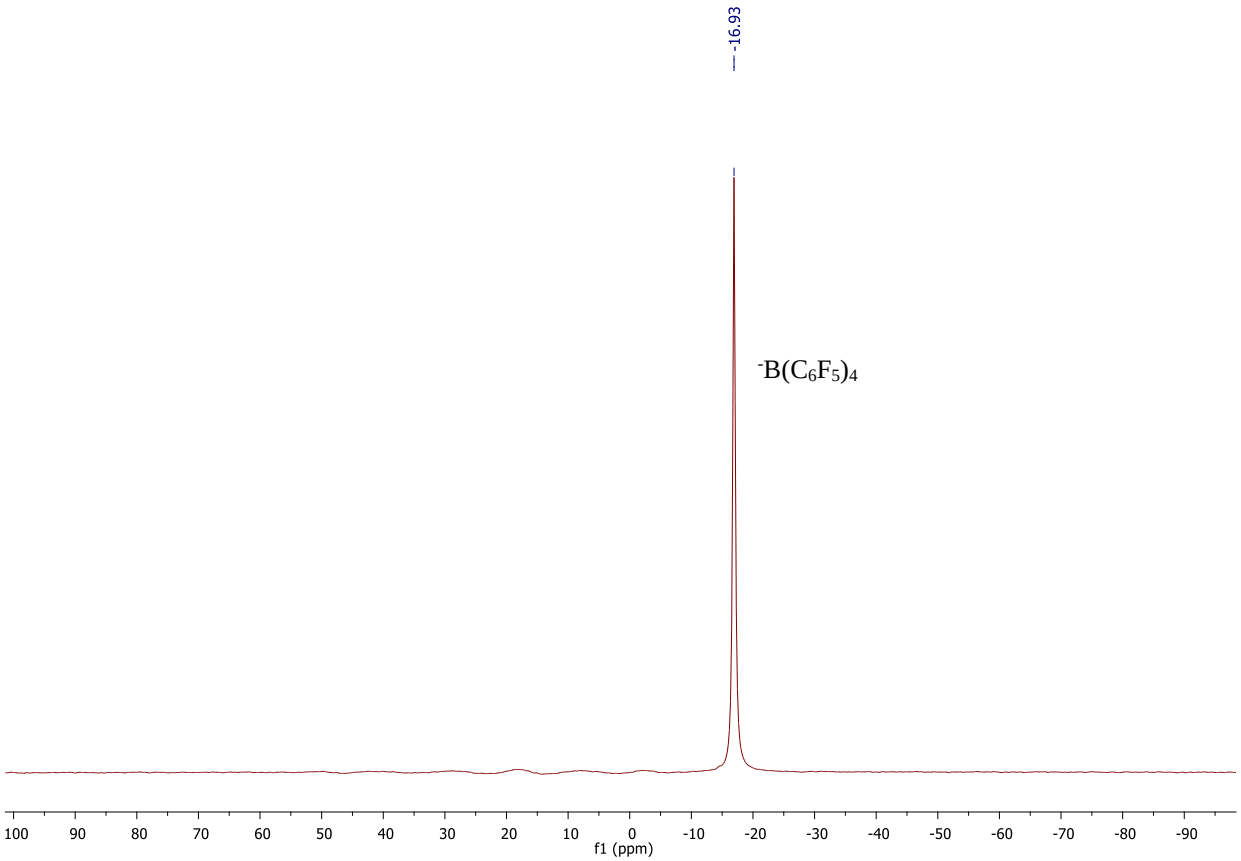
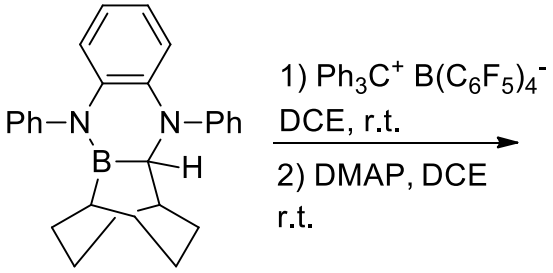


Figure S6: ^{11}B-NMR (128 MHz) of compound 4a reaction with PCy_3 in CD_2Cl_2.

Reaction of 4h with 4-(Dimethylamino)pyridine (DMAP)



In a separate experiment, in a glove box a vial was charged with **3h** (8.6 mg, 0.0219 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (20.2 mg, 0.219 mmol) and were allowed to mix in 1,2-dichloroethane (0.6 mL) in a J. Young tube for 30 minutes at room temperature. The solvent was evaporated *in vacuo* and the sample was washed with pentane (8 x 1 mL) to give an off white solid. The sample was dissolved in 1,2-dichloroethane (0.6 mL) and ^{1}H NMR showed no evidence of triphenylmethane. To this sample, a solution of 4-(dimethylamino)pyridine (2.68mg, 0.0219 mmol) in 1,2-dichloroethane (0.1 mL) was added yielding a dark yellow solution. A change in the ^{11}B NMR chemical shift was observed, shifting upfield to 1.14 ppm from 39.3 ppm.

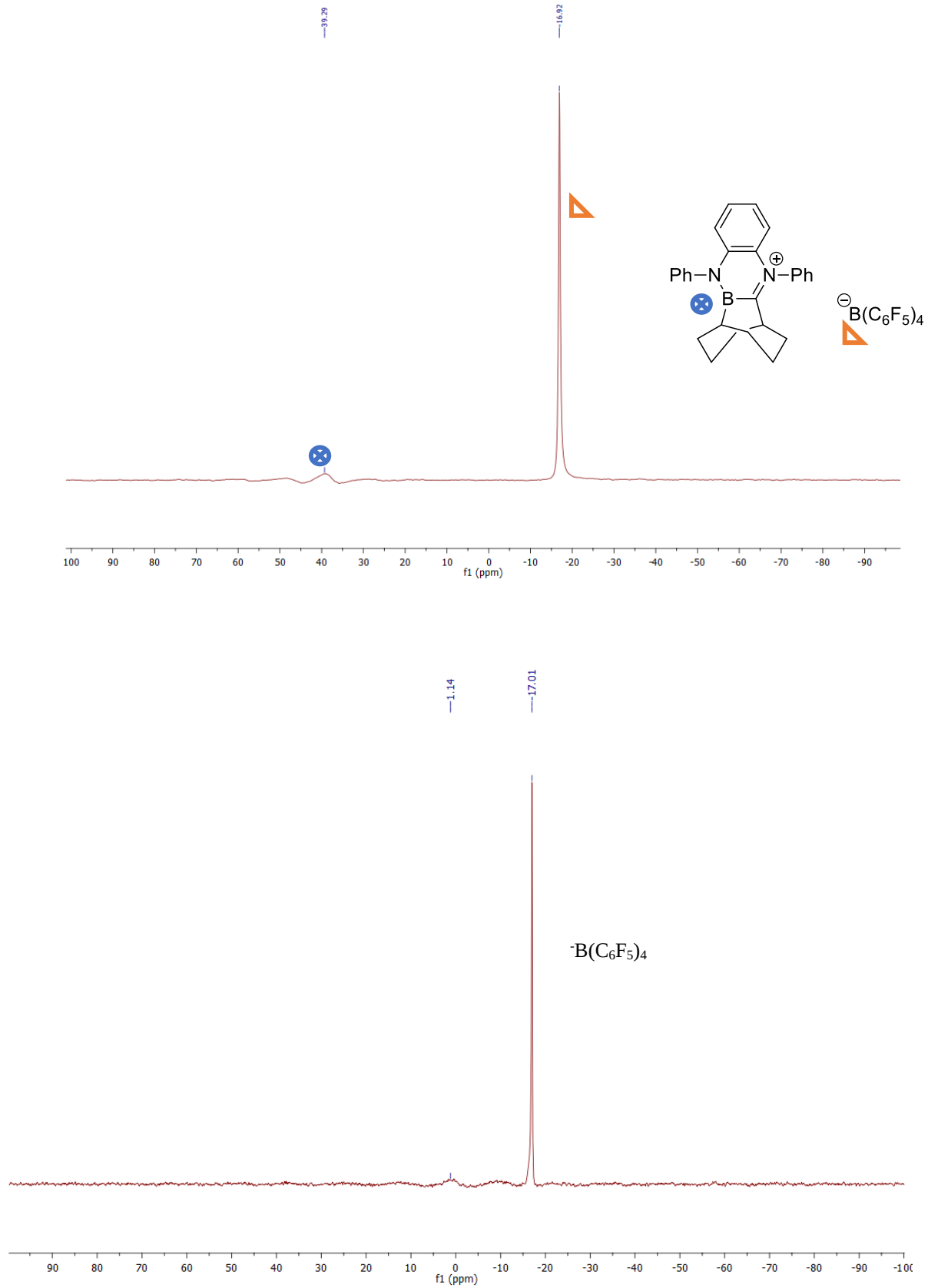
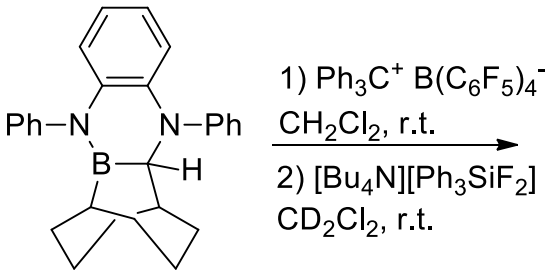


Figure S7: ^{11}B-NMR (192 MHz, top, before DMAP addition, ^{11}B-NMR (192 MHz, bottom, after DMAP addition), of compound 4a reaction with DMAP in 1,2-dichloroethane.

Reaction of 4a with Fluoride



In a glove box, a vial was charged with **3h** (19.6 mg, 0.05 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (46.1 mg, 0.05 mmol) and were allowed to mix in CH_2Cl_2 (0.5 mL) for 30 minutes at room temperature. The solvent was evaporated and the residue was washed with hexanes (1 mL) then decanted and the resulting oil was dried in vacuo. This was repeated 3 more times. After the final drying, the resulting foam was dissolved in CD_2Cl_2 (0.5 mL). In a vial, $[Bu_4N][Ph_3SiF_2]$ (27.0 mg, 0.05 mmol) was dissolved in CD_2Cl_2 (0.2 mL) and added to the solution. Immediately, the solution changed from orange to yellow. In ^{11}B NMR, the broad singlet occurring at 38.8 ppm shifted to -0.02 ppm, indicative of a 4-coordinate boron species, while the anion $^-B(C_6F_5)_4$ remained unchanged at -16.9 ppm. In ^{19}F NMR, a chemical shift of -170.7 ppm appeared, attributed to Ph_3SiF generated as a by-product. A broad resonance also appeared at -166.7 ppm. Peaks at -133.7, -164.4, and -168.2 ppm are attributed to the C_6F_5 rings in $^-B(C_6F_5)_4$.

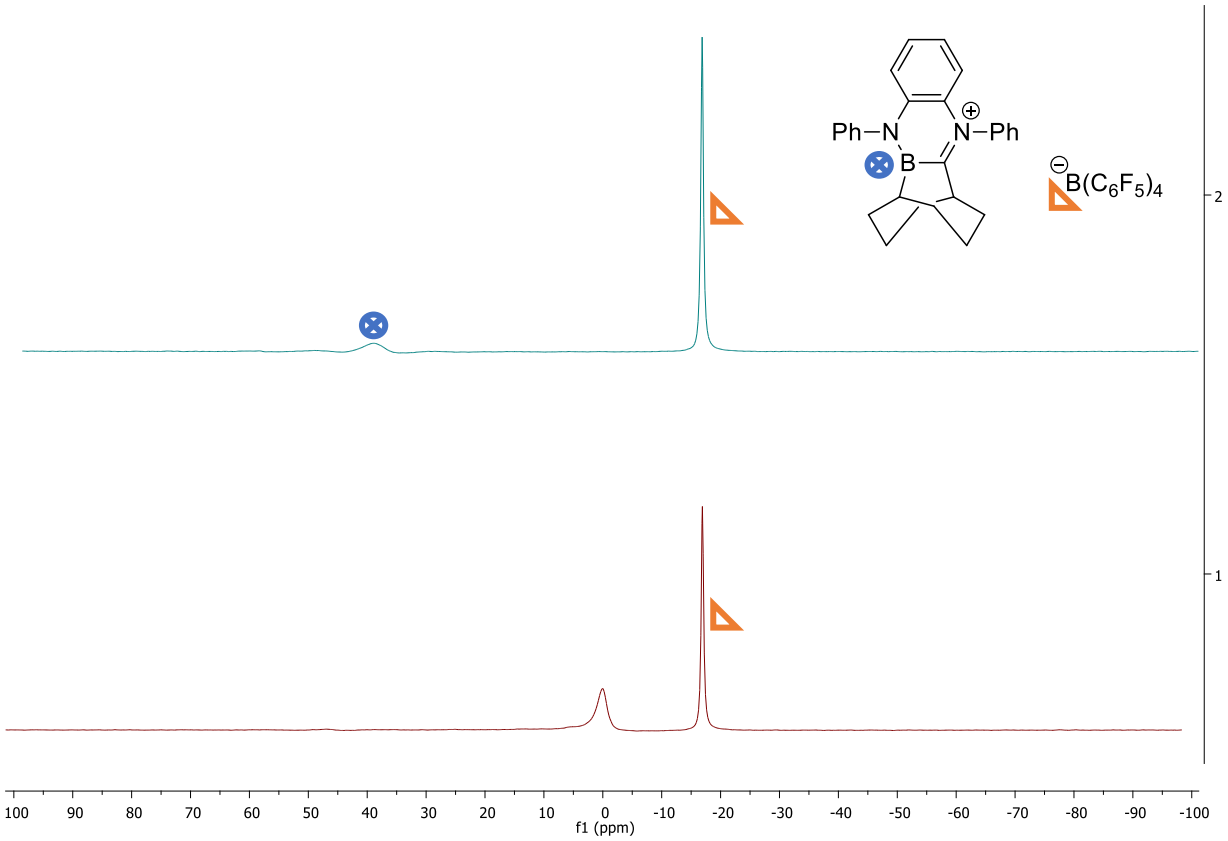


Figure S8: ^{11}B-NMR (128 MHz, blue trace before $[Bu_4N][Ph_3SiF_2]$ addition, red trace after $[Bu_4N][Ph_3SiF_2]$ addition) of compound 4h reaction with $[Bu_4N][Ph_3SiF_2]$ in CD_2Cl_2.

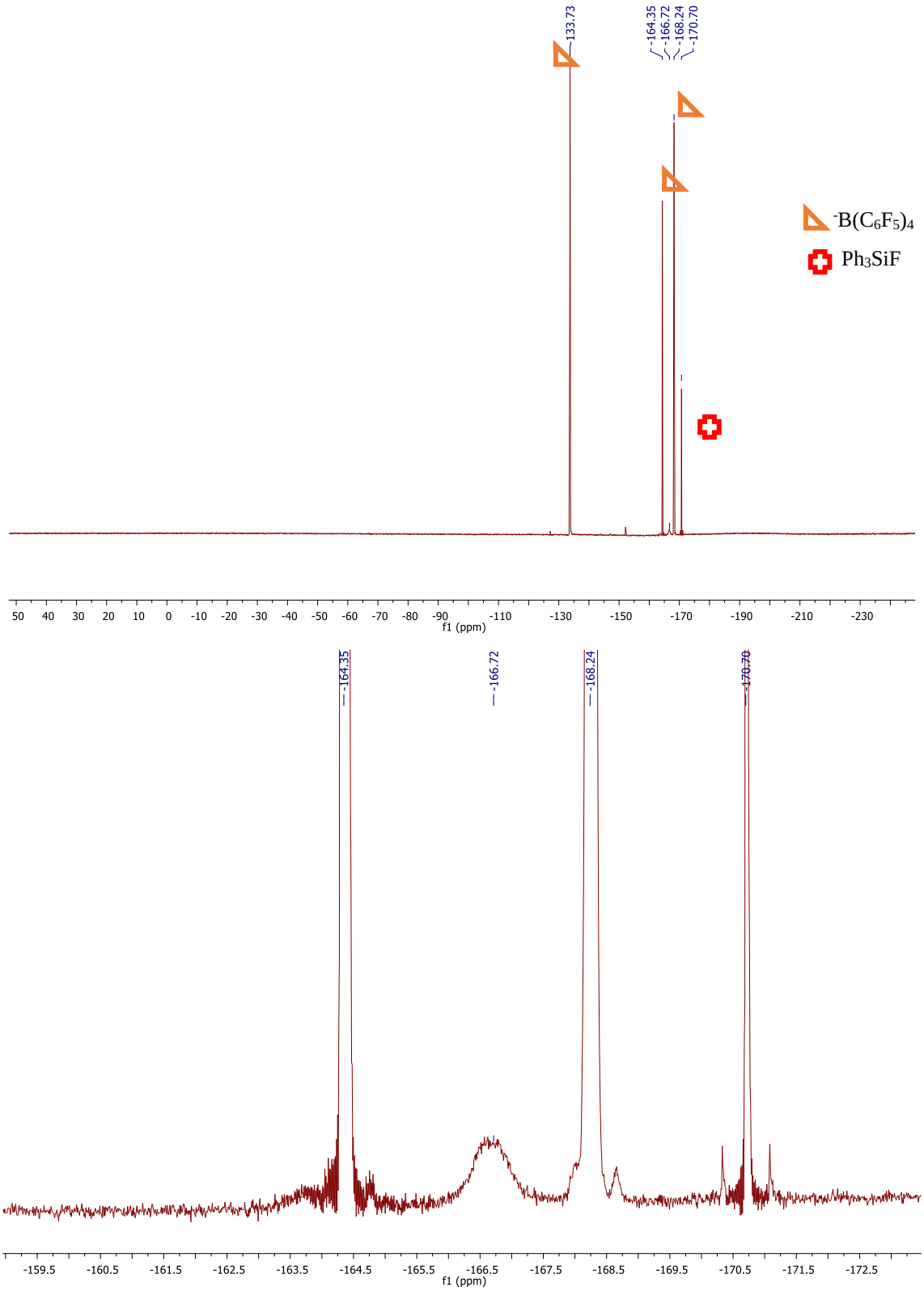


Figure S9: ^{19}F-NMR (376 MHz, top, after [Bu_4N][Ph_3SiF_2] addition), ^{19}F-NMR (376 MHz, bottom, after [Bu_4N][Ph_3SiF_2] addition, zoomed in) of compound 4h reaction with [Bu_4N][Ph_3SiF_2] in CD_2Cl_2.

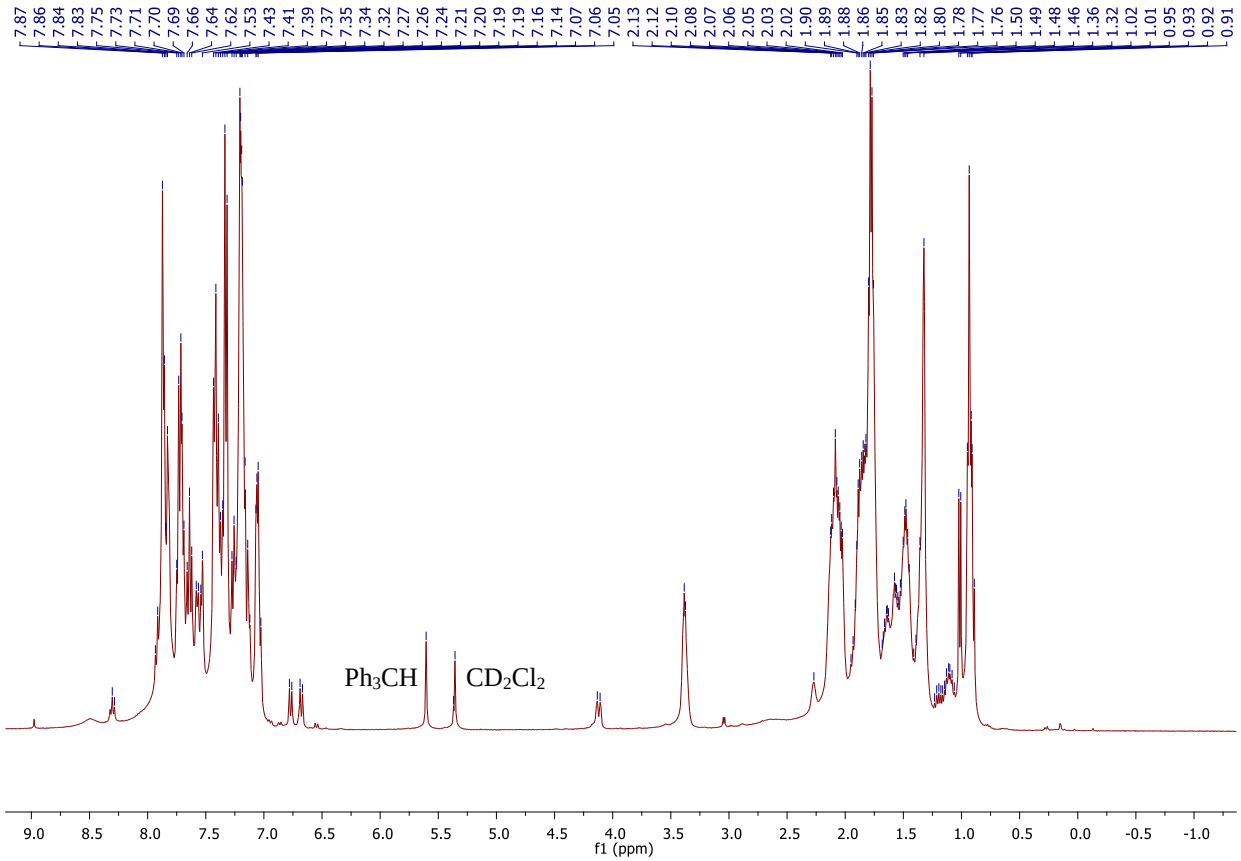
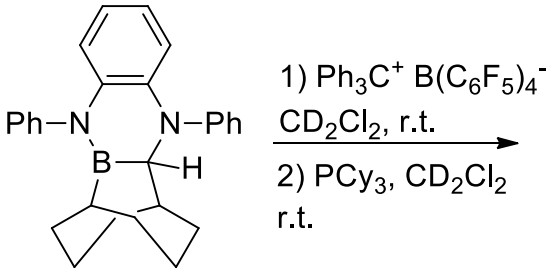


Figure S10: ^{1}H-NMR (400 MHz) of compound 4h reaction with $[Bu_4N][Ph_3SiF_2]$ in CD_2Cl_2.

Reaction of 4h with Tricyclohexylphosphine



In a glove box, a vial was charged with **3h** (19.6 mg, 0.05 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (46.1 mg, 0.05 mmol) and were allowed to mix in CH_2Cl_2 (0.5 mL) for 30 minutes at room temperature. In a vial, PCy_3 (14.0 mg, 0.05 mmol) was dissolved in CD_2Cl_2 (0.2 mL) and added to the solution. Immediately, the solution changed from orange to clear then to yellow. By ^{31}P NMR there are two major broad signals, at 11.36 and 34.57 ppm, characteristic of free phosphine and bound phosphine, respectively. ^{11}B NMR shows only the anion, $B(C_6F_5)_4^-$ at -16.97 ppm.

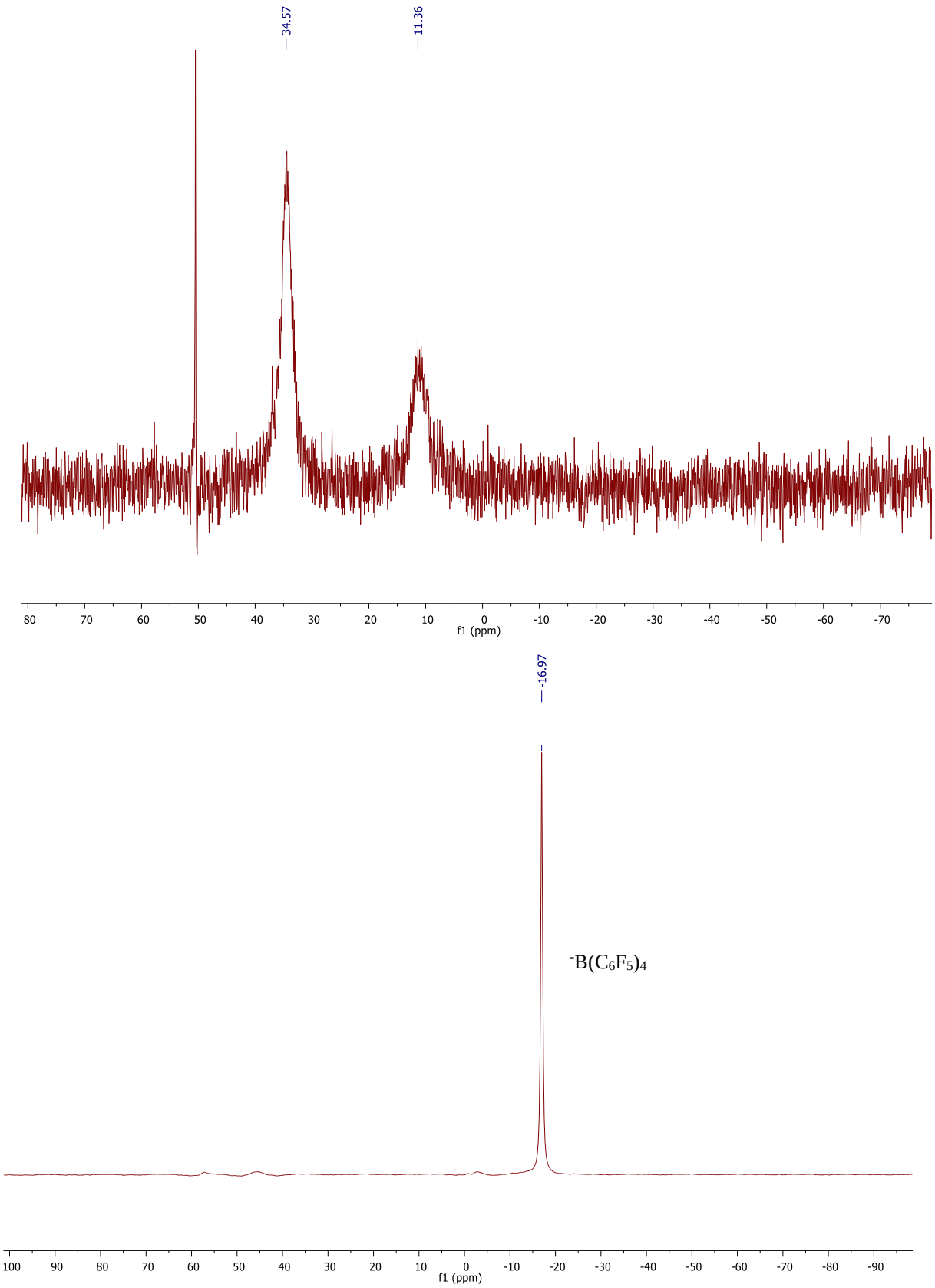


Figure S11: ^{31}P-NMR (162 MHz, top), ^{11}B-NMR (128 MHz, bottom) of compound 4h reaction with PCy_3 in CD_2Cl_2.

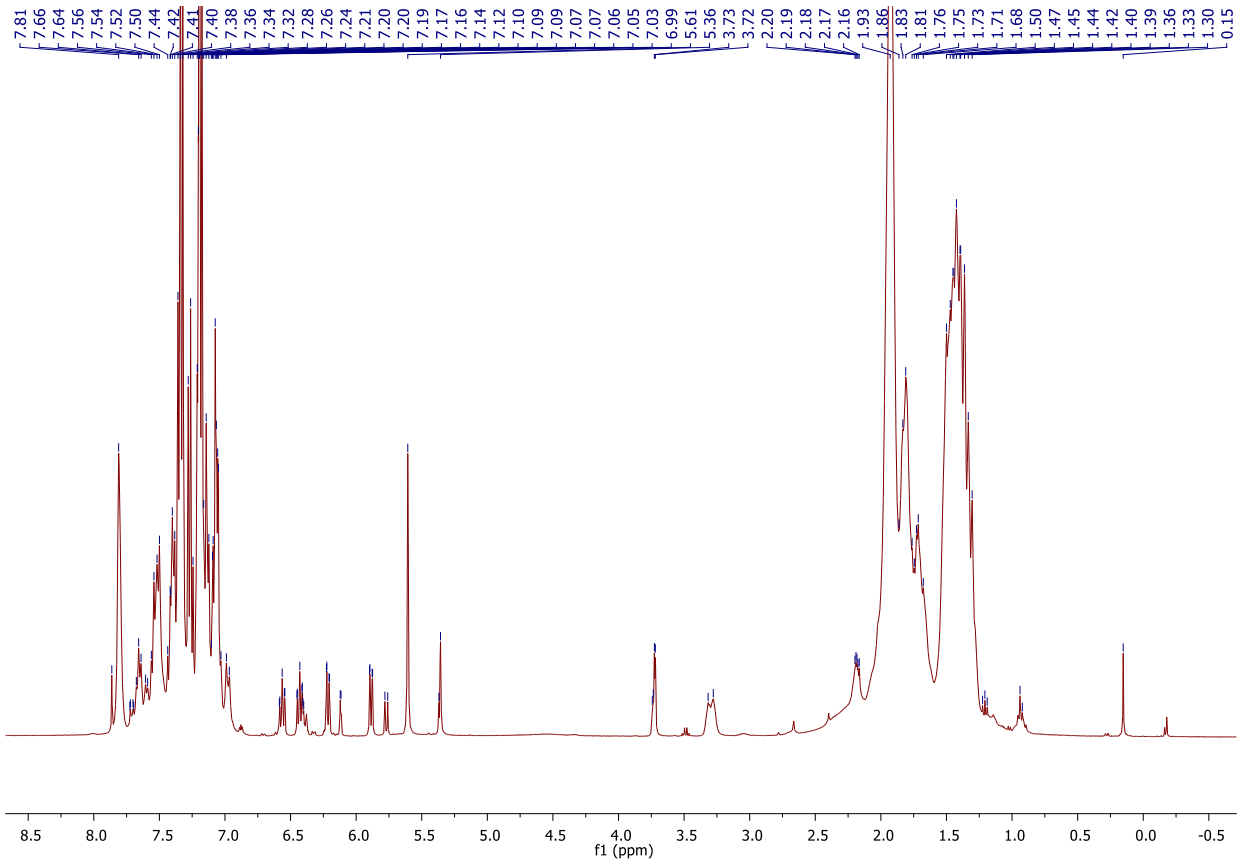


Figure S12: ^{1}H-NMR (400 MHz) of compound 4h reaction with PCy_3 in CD_2Cl_2.

Estimation of Lewis-acidity of 4a

A modified method proposed by Gutmann and Beckett was employed.[10] $^{31}P\{^{1}H\}$ resonances of solutions of Ph_3PO and Et_3PO in CD_2Cl_2 were compared to 3:1 mixtures of **4a** and the indicated Lewis base in CD_2Cl_2 at 298 K. [Sample preparation in a glove box using a J. Young NMR tube: 0.06 mmol **3a** and 0.06 mmol Ph_3C^+ $B(C_6F_5)_4^-$ mixed in CD_2Cl_2 until colorless then solution of 0.02 mmol R_3PO added; total solvent amount ~0.5 mL CD_2Cl_2.] The samples were referenced to external 85% H_3PO_4. $\Delta\delta P$ were calculated using $\Delta\delta P = \delta P(\text{Lewis acid}\bullet R_3PO) - \delta P(R_3PO)$. Relative Lewis acidities (%LA) compared to $B(C_6F_5)_3$ were calculated using $\%LA = \Delta\delta P(\text{Lewis acid}) / \Delta\delta P(B(C_6F_5)_3)*100$. To allow comparisons to values reported in the literature for Gutmann's acceptor numbers (AN), the following equation was used $AN = [\delta P(\text{Lewis acid}\bullet Et_3PO) - 41.0] * [100/(86.14 - 41.0]$.[10b] The following chemical shifts for phosphine oxides in CD_2Cl_2 were measured: $\delta P(Ph_3PO) = 27.6$ ppm, $\delta P(Et_3PO) = 51.1$ ppm

Lewis acid•R_3PO	δ_P/ ppm	$\Delta\delta_P$/ ppm	*%LA*	AN	Reference
$B(C_6F_5)_3\bullet Ph_3PO$	45.6	18.3	—	—	[11]
$B(C_6F_5)_3\bullet Et_3PO$	77.0	26.3	—	79.8	[11]
$B(C_6F_5)_3\bullet Et_3PO$	78.0	27.0	—	82	[10a]
4a•Et_3PO	75.5	24.4	0.904	76.4	This work

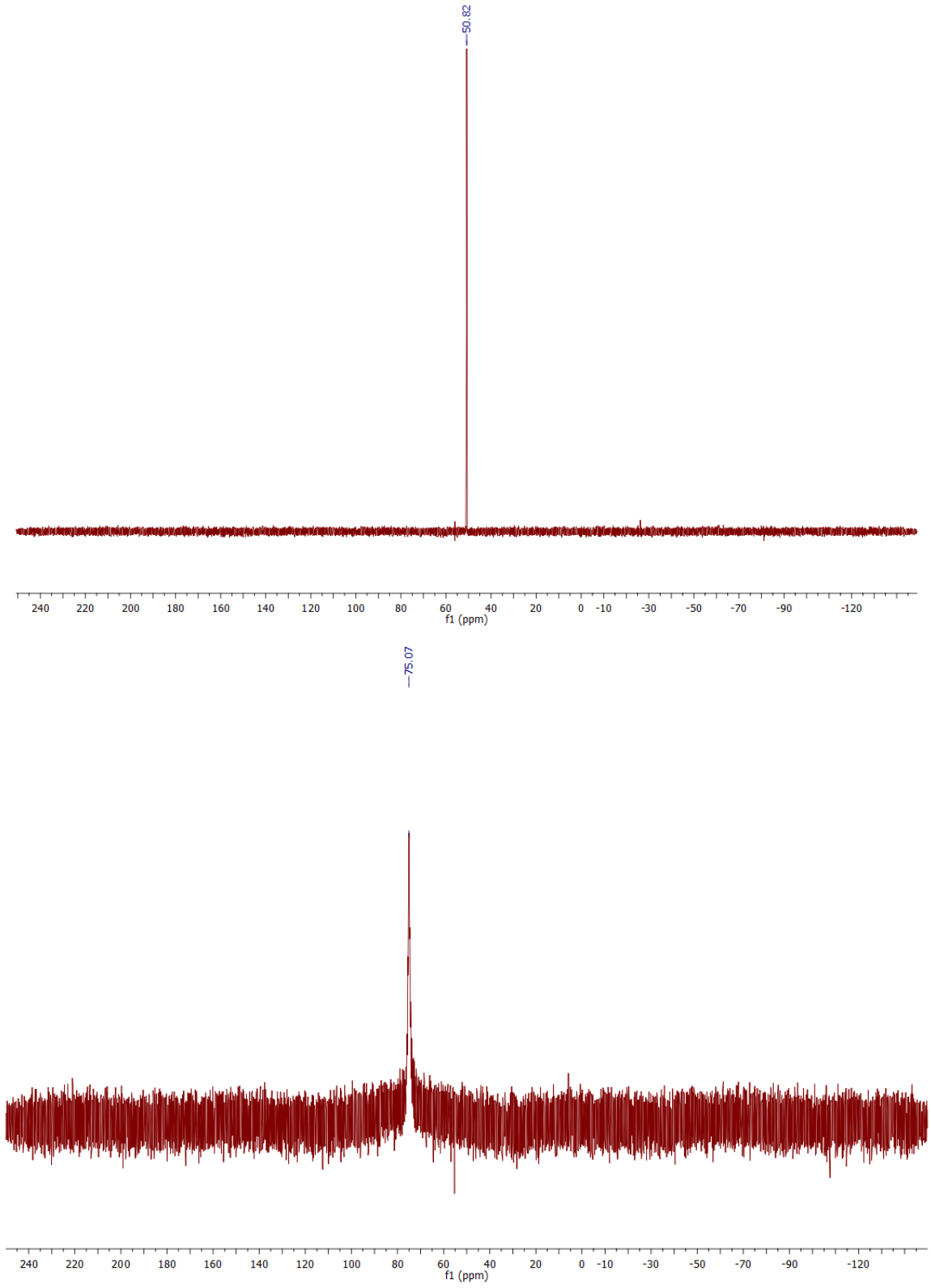


Figure S13: ^{31}P-NMR (162 MHz, top), reaction of compound 3a with Et_3PO and ^{31}P-NMR (162 MHz, bottom) reaction of compound 4a with Et_3PO in CD_2Cl_2.

Single Crystal Data

Formula	$C_{28}H_{30}B_1N_3$
M_r / g mol^{-1}	419.36
T / K	180(2)
Wavelength / Å	0.71073
Crystal dimensions / mm^3	0.179 × 0.139 × 0.129
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell metrics	
a / Å	12.1379(4)
b / Å	9.8806(4)
c / Å	18.5754(6)
α / °	90
β / °	90.151(2)
γ / °	90
V / Å^3	2227.74(14)
Z	4
ρ / g cm^{-3}	1.250
μ / mm^{-1}	0.073
F(000)	896
Correction type	multi-scan
Abs coeff T_{min}, T_{max}	0.706, 0.7455
h, k, l limits	–14, 14; –12, 9; –22, 20
θ-range / °	2.002, 25.678
Reflections collected, unique	16691, 4218
R_{int}	0.0299
Refinement method	full-matrix least-squares on F^2
Data, restraints, parameters	4218, 2, 297
Data completeness	0.998
R	0.0473
wR^2	0.1164
GOF S	1.029
min., max., rmsd residual / e·Å^{-3}	–0.519, 0.484, 0.049

Computational Details

All calculations were carried out using the Gaussian 16 program package[9] using the High Performance Computing Virtual Laboratory (HPCVL), Kingston, Ontario, Canada. Structures were optimized at HF/3-21G followed by further optimization at the M06-2X/3-611G(d,p) level of theory using a PCM solvent model for the corresponding solvent (tetrahydrofuran, benzene, or CH_2Cl_2). The thus obtained structures were subjected to a frequency calculation under standard conditions (p = 1 atm, T = 298.15 K) and their lowest energy structure confirmed by the absence of virtual frequencies. Units for energies are given in Hartree/particle if not otherwise specified. Dipole moments are given in Debye. The reference structures $HBEt_3^-$ and BEt_3 required for the calculation of isodesmic hydride ion affinities (ΔH_{HIA}) were taken from the literature[12] and reoptimized at the M06-2X/3-611G(d,p) level of theory using a PCM solvent model for CH_2Cl_2 followed by a frequency calculation.

1a

Zero-point correction=0.530231 (Hartree/Particle)
Thermal correction to Energy=0.555716
Thermal correction to Enthalpy=0.556660
Thermal correction to Gibbs Free Energy=0.474100
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Imaginary Frequencies 0
Dipole Moment 2.4241

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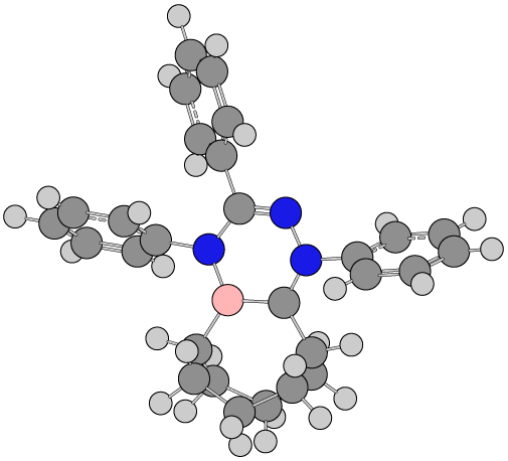
3a



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Thermal correction to Enthalpy	0.546919
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Sum of electronic and thermal Free Energies	-1272.725547
Imaginary Frequencies	0
Dipole Moment	2.3397

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9	6	4.482462	2.534017	1.226048
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12	1	5.704588	3.940751	0.160853
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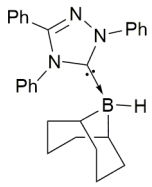

2a

PCM solvent model for THF
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Thermal correction to Enthalpy = 0.553949
Thermal correction to Gibbs Free Energy = 0.470602
Sum of electronic and zero-point Energies = −1273.404269
Sum of electronic and thermal Energies = −1273.378400
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Imaginary Frequencies 0
Dipole Moment 7.8471
Coordinates (Å)
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H,0,-4.6288544422,-0.7557179011,-2.4089258033
C,0,-2.6600292744,-1.5406795718,-2.0597154877
H,0,-2.8162854716,-2.4246818702,-2.6651216485
C,0,-1.4381240931,-1.3460998056,-1.4282369701
H,0,-0.625305493,-2.0540007329,-1.5369372889
C,0,5.5917697381,0.9808631718,1.0341199073
H,0,6.1721738754,1.8078078321,1.42336334
C,0,-3.4806473874,0.5305456753,-1.1289264166
H,0,-4.2747389577,1.2573072776,-1.012258619
C,0,2.827927639,-0.7146674995,3.4961976955
H,0,3.3592154164,-1.3467181801,2.7955151544
C,0,0.5085512498,0.8623712752,-3.0622359076
H,0,-0.4714648184,0.380648235,-3.0063013982
C,0,3.0036033571,1.0167396037,-2.38488724
H,0,3.8709673907,0.6438903418,-1.8330920445
C,0,6.2311990933,-0.14793479,0.5303240605
H,0,7.3130719253,-0.1981170758,0.5268541891
C,0,2.5314286979,0.115710764,5.7411238852
H,0,2.8417556059,0.1403912801,6.7786425334
C,0,3.4046508678,0.9045874439,-3.8701856059

H,0,4.3007522838,1.5088026571,-4.068246963
H,0,3.6918288528,-0.1392664414,-4.0469935201
C,0,0.9251765916,0.7406323875,-4.5423210102
H,0,0.8974620051,-0.3257421001,-4.7985579215
H,0,0.1847343734,1.2329189763,-5.1877025126
C,0,2.3196748935,1.2838399624,-4.8902580073
H,0,2.612286413,0.9058587926,-5.8762666446
H,0,2.2766582421,2.3683603397,-4.9996276621
C,0,3.2170446933,-0.6815529363,4.8292583082
H,0,4.0555009946,-1.2838759867,5.1561317462
C,0,1.5703320391,3.1824452344,-2.5358099142
H,0,1.3558973949,4.0881760653,-1.9575763293
H,0,1.8271785454,3.5327042216,-3.5359928142
C,0,2.7792185895,2.4663097571,-1.9114927415
H,0,2.6357858341,2.448621751,-0.821861659
H,0,3.6787950414,3.0735348519,-2.0831078425
C,0,0.2995856659,2.3177540045,-2.5972569739
H,0,-0.1410376807,2.2911788629,-1.5909418965
H,0,-0.4413659217,2.8225110525,-3.2323944759
B,0,1.6501684948,0.1206531468,-2.1486398068
H,0,1.814770458,-1.0496547565,-2.4797623438
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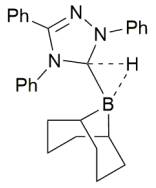
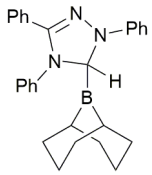
N,0,2.0425521573,0.0396412153,0.539427350



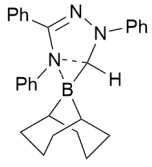
TS1

PCM solvent model for THF
Zero-point correction = 0.524602
Thermal correction to Energy = 0.550586
Thermal correction to Enthalpy = 0.551530
Thermal correction to Gibbs Free Energy = 0.466245
Sum of electronic and zero-point Energies = −1273.361660
Sum of electronic and thermal Energies = −1273.335676
Sum of electronic and thermal Enthalpies = −1273.334731
Sum of electronic and thermal Free Energies = −1273.420016
Imaginary Frequencies 1
Dipole Moment 4.6667
Coordinates (Å)
N,0,0.0095839868,0.0301410925,0.0001590264
N,0,0.0088718688,0.0090330659,1.4118137008
C,0,3.5324630751,0.0117564111,0.7116497003
C,0,-0.9717528869,0.871781654,-0.579856581
C,0,4.3302606296,1.1404214837,0.8461215361
H,0,3.8588854359,2.110080254,0.9513699125
C,0,1.3338150772,-0.0963061373,-0.4888330069
C,0,0.7861790672,0.8591433853,4.0497925628
H,0,-0.1049194706,1.3202731086,3.6431502263
C,0,1.6378813262,0.1586544809,3.1887421276
C,0,4.1046520095,-1.251561514,0.5721423351
H,0,3.4657428449,-2.1233967011,0.4786591499
C,0,-0.6389832158,1.8735340881,-1.4886858702
H,0,0.398090659,2.0341658797,-1.7572359246
C,0,1.0839081413,0.9623702915,5.4011785388
H,0,0.4197774239,1.5116919956,6.0572520382
C,0,5.4874772791,-1.3802499795,0.5562266984
H,0,5.9366032936,-2.3596316217,0.4448269393
C,0,-2.9679875469,2.4870225641,-1.6770348728
H,0,-3.7427016207,3.1095141926,-2.1072146628
C,0,-3.292799937,1.5005581307,-0.7483603976
H,0,-4.3245923049,1.3525297643,-0.4522481415
C,0,-2.3048434345,0.6909923415,-0.2049342187
H,0,-2.5463536607,-0.0810871646,0.5145769767
C,0,5.7156211122,1.0054307281,0.8385684721
H,0,6.3420051234,1.8824843565,0.9458317905
C,0,-1.6384511956,2.668159706,-2.0414006603
H,0,-1.3689403785,3.4409394262,-2.7520609546
C,0,2.7889691606,-0.4427598139,3.7040536769
H,0,3.4522192477,-1.0058658313,3.0622548334
C,0,0.7024524638,-0.7513210652,-3.0530924683
H,0,-0.3309252312,-0.7693733344,-2.6913670393
C,0,3.2210289538,-0.2953103182,-2.52579137
H,0,3.9935295078,-0.0193842333,-1.806058314
C,0,6.2934412853,-0.2509284196,0.6875510249
H,0,7.3717801366,-0.3525702593,0.6756171385
C,0,2.2355120146,0.3670291185,5.9093126354
H,0,2.4705643973,0.4501327647,6.9635835607
C,0,3.5810990626,-1.6955101331,-3.0744209794
H,0,4.5297751397,-1.6481228461,-3.6230779333
H,0,3.7626727281,-2.341887921,-2.2066157745
C,0,1.0703070976,-2.1924026887,-3.4818085424
H,0,0.8983325297,-2.855096271,-2.6245937927
H,0,0.3887442632,-2.5287889434,-4.2721290304
C,0,2.5189578484,-2.3692375247,-3.9656155023
H,0,2.7414892124,-3.4393962985,-4.02094736
H,0,2.6031689569,-2.0037633093,-4.9888745379
C,0,3.0819888542,-0.3360911925,5.0597092563
H,0,3.9744493772,-0.809096019,5.4508416498
C,0,2.1743406766,0.6249882237,-4.7236194017
H,0,2.1083563759,1.5494476528,-5.305657602
H,0,2.5408627434,-0.1303392009,-5.4184365132
C,0,3.2018214063,0.8219109184,-3.6002260379
H,0,2.996512289,1.7744206745,-3.0939236715
H,0,4.2008067545,0.9193257768,-4.0405188754
C,0,0.7629331854,0.2583209689,-4.2259045075
H,0,0.2626265281,1.1774905461,-3.9057100563
H,0,0.174208595,-0.1281239983,-5.0664285007
B,0,1.7505043401,-0.3223636356,-1.9348908531
H,0,1.5296832144,-1.2980329711,-0.8039324979
C,0,1.2429103015,0.0687463106,1.7667975658
N,0,2.1140860574,0.1502511287,0.6842001929



Carbene Insertion Intermediate

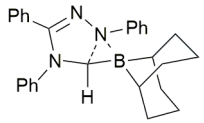
PCM solvent model for THF
Zero-point correction = 0.528264
Thermal correction to Energy = 0.554449
Thermal correction to Enthalpy = 0.555393
Thermal correction to Gibbs Free Energy = 0.471336
Sum of electronic and zero-point Energies = −1273.384148
Sum of electronic and thermal Energies = −1273.357964
Sum of electronic and thermal Enthalpies = −1273.357019
Sum of electronic and thermal Free Energies = −1273.441076
Imaginary Frequencies 0
Dipole Moment 4.2666
Coordinates (Å)
N,0,0.012915205,-0.0512104458,-0.0271978246
N,0,0.0098631153,-0.027778319,1.3613022899
C,0,3.5332393663,-0.0337532408,0.7285845441
C,0,-1.0468437845,0.4964370285,-0.7307465459
C,0,4.1388354395,0.7543056788,1.7119038622
H,0,3.5412802774,1.2044646112,2.4938935316
C,0,1.3844484756,0.0811111028,-0.5537699426
C,0,0.9273992802,0.3384180963,4.1436318264
H,0,0.18272465,1.0709877466,3.85716012
C,0,1.5887068952,-0.3841362422,3.1496014321
C,0,4.3222255633,-0.5960406113,-0.2798072499
H,0,3.8562823386,-1.215325934,-1.0373361701
C,0,-2.1969829282,0.978980063,-0.0892327192
H,0,-2.2607453598,0.9234866199,0.9887421058
C,0,1.2317364988,0.1178889059,5.481454394
H,0,0.7197097306,0.6845804634,6.2496162249
C,0,5.691327643,-0.3664403912,-0.3089218851
H,0,6.2881299322,-0.8046888424,-1.0997844977
C,0,-3.1330748689,1.6257717736,-2.2303873111
H,0,-3.9372177654,2.0684127355,-2.8043026307
C,0,-1.9993174004,1.132328026,-2.8654900432
H,0,-1.9134146325,1.1826007957,-3.9449680427
C,0,-0.962563661,0.5684047956,-2.1304875658
H,0,-0.096604144,0.1685149155,-2.6457375043
C,0,5.513862694,0.9617766804,1.6854466455
H,0,5.9706841046,1.5717699648,2.4555110016
C,0,-3.2209627398,1.5361840358,-0.8409033228
H,0,-4.0996625079,1.9147722106,-0.3312189847
C,0,2.552077761,-1.3318912798,3.503407124
H,0,3.0596322325,-1.8993442616,2.7318892668
C,0,1.1214613494,2.8440060336,-0.2661806359
H,0,0.3796917583,2.5772231222,0.4942852988
C,0,2.8024826895,1.996592329,-2.0645692104
H,0,3.2778820098,1.134869367,-2.5458392857
C,0,6.2957237649,0.4106892661,0.6757535371
H,0,7.3642547566,0.585088172,0.6554793166
C,0,2.1947574909,-0.8236886718,5.8330089148
H,0,2.4334399949,-0.9919915799,6.8762078566
C,0,1.9716840008,2.7435251604,-3.1481251629
H,0,2.6405768428,3.0527772711,-3.9588785299
H,0,1.2616899842,2.0351426964,-3.5917531907
C,0,0.4041571174,3.7180167259,-1.3315119898
H,0,-0.5402252877,3.2258449708,-1.5836100246
H,0,0.1415502242,4.6820255938,-0.8804050931
C,0,1.1950638264,3.9650206516,-2.6321900642
H,0,0.4918545318,4.2814392954,-3.4086517181
H,0,1.8837549015,4.7997929877,-2.5038380282
C,0,2.85031421,-1.5500173224,4.8424491695
H,0,3.59439425,-2.2892325389,5.1128986797
C,0,3.4474048015,3.9822899029,-0.480717511
H,0,4.2953113163,4.2880228933,0.1403481399
H,0,3.1710747915,4.8666958329,-1.0544934287
C,0,3.9204725915,2.8577500474,-1.4216230669
H,0,4.5649973339,2.1818429863,-0.8494675062
H,0,4.5475715078,3.2862712539,-2.2121583655
C,0,2.2829836514,3.5899039675,0.4411718396
H,0,2.6656665125,2.9520294104,1.2448154704
H,0,1.8867012009,4.488868688,0.9266565639
B,0,1.7544111375,1.5959977985,-0.9773187849
N,0,2.137377471,-0.2655307902,0.6812333421
C,0,1.2298444575,-0.1709100392,1.7361546931
H,0,1.5648101593,-0.6725783054,-1.3273816968



TS$_2$

PCM solvent model for THF
Zero-point correction = 0.526521
Thermal correction to Energy = 0.552112
Thermal correction to Enthalpy = 0.553056
Thermal correction to Gibbs Free Energy = 0.469739
Sum of electronic and zero-point Energies = −1273.370296
Sum of electronic and thermal Energies = −1273.344705
Sum of electronic and thermal Enthalpies = −1273.343760
Sum of electronic and thermal Free Energies =−1273.427077
Imaginary Frequencies 1
Dipole Moment 4.8455
Coordinates (Å)
N,0,0.0103693399,-0.0039487268,-0.0123521545
N,0,0.0115888186,-0.0073463449,1.3652027671
C,0,3.5313348531,-0.0178243613,1.0662004593
C,0,-0.7574698697,-1.01248588,-0.644134961

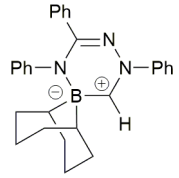
C,0,4.441221507,0.6204345407,1.9054241292
H,0,4.1468414672,1.5292026277,2.4175529577
C,0,1.1388744136,0.5419357987,-0.5980366683
C,0,0.7838451624,0.942195373,4.1200507011
H,0,0.1040843227,1.6710737208,3.6941627416
C,0,1.4655645588,0.0678812756,3.2718075168
C,0,3.8762912113,-1.1985433994,0.4176868318
H,0,3.15017105,-1.6850956454,-0.2240655724
C,0,-1.3065508759,-2.0704817306,0.0817549602
H,0,-1.1410004782,-2.1284782668,1.1483966385
C,0,0.9830305601,0.8784608958,5.4946689367
H,0,0.4532461498,1.5625697667,6.1462884653
C,0,5.1435322432,-1.742065958,0.6052699944
H,0,5.4145952809,-2.6592901548,0.0970329147
C,0,-2.2474524667,-2.9670825912,-1.9576587091
H,0,-2.8267744919,-3.7274378939,-2.4663729762
C,0,-1.6978099413,-1.9084462435,-2.6737911292
H,0,-1.853617943,-1.8345732884,-3.7432127123
C,0,-0.9688740718,-0.9219213276,-2.0214985119
H,0,-0.587615362,-0.0691477306,-2.5712105525
C,0,5.7010815793,0.0669953482,2.0976547412
H,0,6.4061963996,0.5567673256,2.7580327885
C,0,-2.0556041133,-3.0353369355,-0.5808030725
H,0,-2.4818462221,-3.8544829133,-0.0141072766
C,0,2.3414623519,-0.8782155004,3.8098528049
H,0,2.8627037068,-1.5713439046,3.1603326476
C,0,1.0296684376,3.001884166,0.6731871001
H,0,0.1969781385,2.6461423469,1.2926893905
C,0,3.0212003374,2.4285898317,-0.9133107351
H,0,3.6543452424,1.648744825,-1.3591096496
C,0,6.0549058713,-1.1121973503,1.446587796
H,0,7.0393514705,-1.5386218916,1.5954818413
C,0,1.8600592956,-0.0597802733,6.0286109343
H,0,2.0162185549,-0.109319166,7.0994481355
C,0,2.3055223157,3.1622674674,-2.0684113818
H,0,3.0396720754,3.5956226543,-2.758550387
H,0,1.7334378491,2.4248744668,-2.6468635769
C,0,0.3984243123,3.8416312151,-0.4618588084
H,0,-0.399942269,3.23142198,-0.9031403486
H,0,-0.0901895679,4.7341297499,-0.0511377317
C,0,1.3489254152,4.2698407042,-1.5978289129
H,0,0.7459758268,4.6037428482,-2.4485428371
H,0,1.9311711101,5.1406891762,-1.2943569343
C,0,2.5341358426,-0.9381935667,5.1850657038
H,0,3.2100697744,-1.6771826912,5.5977563032
C,0,3.2399393565,4.3341581818,0.8794968522
H,0,3.9661427598,4.6496918543,1.6360739733
H,0,2.9573643027,5.2473304683,0.3542295925
C,0,3.9409635756,3.3598694547,-0.0941139558
H,0,4.6252380593,2.7312553892,0.4818033202
H,0,4.576205106,3.9436481247,-0.7729532496
C,0,1.9977133754,3.769416141,1.5906005696
H,0,2.3183892123,3.0799570316,2.3843927548
H,0,1.4818423802,4.5933097245,2.0995136361
B,0,1.8398877697,1.8167972989,-0.023676554
N,0,2.212243282,0.5261366186,0.9020107387
C,0,1.2084064249,0.1695086661,1.813644608
H,0,1.4928098351,-0.0125039273,-1.4700778937



TS_2'

PCM solvent model for THF
Zero-point correction = 0.526723
Thermal correction to Energy = 0.552228
Thermal correction to Enthalpy = 0.553172
Thermal correction to Gibbs Free Energy = 0.470384
Sum of electronic and zero-point Energies = −1273.379777
Sum of electronic and thermal Energies = −1273.354271
Sum of electronic and thermal Enthalpies = −1273.353327
Sum of electronic and thermal Free Energies = −1273.436115
Imaginary Frequencies 1
Dipole Moment 5.9130
Coordinates (Å)
N,0,-0.0470339049,0.033060224,-0.1603461283
C,0,0.0439243066,-0.0300963271,3.5503697557
C,0,1.0854602799,-0.0166438255,-1.0435860749
C,0,-0.3963032799,-0.9836615426,4.4692527401
H,0,-1.1336137652,-1.7142525624,4.1623469892
C,0,-0.1753105855,1.0900028731,0.7214418624
C,0,1.0031752123,0.9074128778,3.9162074897
H,0,1.3625472166,1.6205817406,3.1849274194
C,0,2.0332977538,-1.0335319195,-0.9539872523
H,0,1.9242321013,-1.8144125409,-0.2105838982
C,0,1.4993432966,0.9135808396,5.2165278522
H,0,2.2437345874,1.6483506979,5.4985934119
C,0,3.2726146725,-0.010188093,-2.7550221044
H,0,4.1244700343,-0.0105618495,-3.4237305204
C,0,2.3291242479,1.009296109,-2.8281413228
H,0,2.4410314428,1.80479318,-3.5545117879
C,0,1.2281797495,1.0040701068,-1.9787836101
H,0,0.4714695147,1.7778743897,-2.0403952954
C,0,0.1141615091,-0.9758240929,5.7606660577
H,0,-0.2321436825,-1.7141293402,6.4740685086
C,0,3.1207093552,-1.0295036735,-1.8190738064
H,0,3.8576720976,-1.8203595278,-1.752147462
C,0,-2.8957782813,0.7664565161,1.1478697454
H,0,-2.8857136755,-0.1154800974,0.4949807846
C,0,-1.5746499655,2.5005414042,2.5769332301
H,0,-0.6125723003,2.8466525702,2.9740049211
C,0,1.0558674872,-0.0231637968,6.1429467164
H,0,1.4466746586,-0.0181439301,7.1529386708
C,0,-2.1092058167,3.6325135899,1.6736039419
H,0,-2.2327215737,4.5550353373,2.2543904321
H,0,-1.3443940517,3.8460497762,0.9152308771
C,0,-3.4594903701,1.9234974664,0.2954044449
H,0,-2.8589708809,1.9694867633,-0.622924506

H,0,-4.4860095022,1.7003815116,-0.0217818932
C,0,-3.4294615965,3.3142843668,0.9537291368
H,0,-3.6026301604,4.0716699184,0.1819824636
H,0,-4.2607430941,3.4156455228,1.6519690792
C,0,-3.8180520767,1.4974268038,3.4626684201
H,0,-4.214634015,1.0570488544,4.383542648
H,0,-4.5546760919,2.2417656062,3.1583496183
C,0,-2.4771484153,2.1856380031,3.7882834763
H,0,-1.911832652,1.5309526011,4.4622577473
H,0,-2.680373644,3.1025154759,4.3564383325
C,0,-3.7303035127,0.3981038116,2.3890036445
H,0,-3.2703112374,-0.4926160985,2.8376950471
H,0,-4.7476737215,0.1048766754,2.1007080908
B,0,-1.4367626326,1.2022367659,1.6480965332
N,0,-0.5304539117,0.0060546567,2.2412212387
H,0,0.6968155087,1.7452151076,0.7443673413
C,0,-0.5453802685,-1.1662682555,0.372794896
N,0,-0.6822436516,-1.2167752688,1.6530303899
C,0,-0.8125968153,-2.3291071282,-0.4919516986
C,0,-1.1317260817,-2.1453693597,-1.8381046077
C,0,-0.7735945294,-3.6185285408,0.0441160791
C,0,-1.4022690138,-3.2456953777,-2.6435410815
H,0,-1.1740083192,-1.1430235052,-2.2488528681
C,0,-1.0416893482,-4.7131522507,-0.765438498
H,0,-0.5299066637,-3.7486863032,1.0913377905
C,0,-1.3552212555,-4.5297081991,-2.1106496635
H,0,-1.6524827956,-3.0984765656,-3.6869987869
H,0,-1.0048902541,-5.712055129,-0.3481287202
H,0,-1.5638057811,-5.3861043958,-2.7404031142



N(1)-Attack ylide

PCM solvent model for THF
Zero-point correction = 0.528339
Thermal correction to Energy = 0.554090
Thermal correction to Enthalpy = 0.555035
Thermal correction to Gibbs Free Energy = 0.472126
Sum of electronic and zero-point Energies = −1273.400445
Sum of electronic and thermal Energies = −1273.374693
Sum of electronic and thermal Enthalpies = −1273.373749
Sum of electronic and thermal Free Energies = −1273.456658
Imaginary Frequencies 0
Dipole Moment 4.4350
Coordinates (Å)

N,0,-0.0055194483,-0.0047837591,-0.0100775092
N,0,-0.0069494269,-0.0085255968,1.3758757058
N,0,2.3461045615,-0.0057111491,1.3020090528
C,0,1.18019521,-0.146111537,1.9358299136
C,0,1.0259494744,0.2622783216,-0.7517005783
C,0,-1.2823712673,-0.3966289774,-0.5647653708
C,0,-1.7567797109,0.2533119358,-1.697704911
H,0,-1.1983707692,1.0753431184,-2.1291269393
C,0,-2.9701059959,-0.1443190433,-2.2477625221
H,0,-3.349091991,0.3623090493,-3.1264263654
C,0,-3.6996693009,-1.1731284843,-1.6617072217
H,0,-4.6465678961,-1.477507404,-2.09012193
C,0,-3.2187731922,-1.8023719657,-0.5165696543
H,0,-3.7875560059,-2.5998764455,-0.0549128267
C,0,-2.0083461614,-1.4137930438,0.0432423661
H,0,-1.6220724141,-1.8810075832,0.9385712391
C,0,1.1054933615,-0.4823267361,3.3921959381
C,0,1.543217618,-1.7141993378,3.8772820697
H,0,1.9650904756,-2.4451258837,3.1969355251
C,0,1.4474569012,-1.9970405264,5.2346443438
H,0,1.7874348397,-2.955293162,5.6083116854
C,0,0.9206132836,-1.0523951675,6.1113103396
H,0,0.8532874107,-1.2733777895,7.1697617848
C,0,0.4781917459,0.1738687515,5.6260920573
H,0,0.0641269686,0.910412631,6.3040334917
C,0,0.5640053992,0.4573045362,4.2667259624
H,0,0.215918151,1.4075947311,3.8785909298
C,0,3.5510558878,-0.5178530129,1.8780223297
C,0,4.1280532462,0.0602069269,3.0076894963
H,0,3.6319267095,0.8883028582,3.4988714141
C,0,5.3280641132,-0.4353385317,3.5038393171
H,0,5.770655372,0.0185985274,4.3823936947
C,0,5.9612287166,-1.504414964,2.8759074383
H,0,6.9001419655,-1.8830187363,3.2611872144
C,0,5.3772818866,-2.0895501845,1.7566423786
H,0,5.8574138088,-2.9291032495,1.2682113433
C,0,4.1718132855,-1.6025842379,1.2624372002
H,0,3.703608015,-2.0513844121,0.3944585538
B,0,2.3441984737,0.8538829764,-0.0533498614
H,0,0.8530159601,0.0753705404,-1.8092949328
C,0,2.0752025298,2.4378649986,0.2502257142
H,0,1.1687496691,2.5672824729,0.8594381464
C,0,3.6887589055,0.7963161862,-0.9579620292
H,0,3.9897332578,-0.2325810278,-1.1966078494
C,0,1.8249421277,3.1696985972,-1.0847444061
H,0,1.7134640299,4.2485369637,-0.9158917674
H,0,0.857568656,2.8297247753,-1.4791801086
C,0,3.3736916273,1.4900052104,-2.3019556489
H,0,4.261986776,1.4723291857,-2.9456295549
H,0,2.6109940623,0.911827837,-2.8369756044
C,0,4.8928497065,1.4595236628,-0.2477486102
H,0,5.7186441454,1.5690733458,-0.963179496
H,0,5.2592466203,0.7784259114,0.5244495352
C,0,3.2512615649,3.0002214127,1.0629582392
H,0,3.0933807979,4.0648171814,1.2806852408
H,0,3.2560941715,2.4935332669,2.0340363044
C,0,4.6330887727,2.8353507762,0.4054885708
C,0,2.8931561693,2.9459218933,-2.1724479331
H,0,2.4897361082,3.2739667167,-3.1362402095

H,0,3.7519913155,3.5906665331,-1.9834280222
H,0,4.770918117,3.6281141633,-0.3310675456
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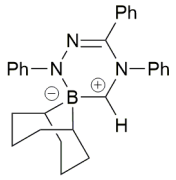
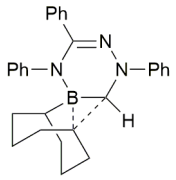


N(4)-Attack ylide

PCM solvent model for THF
Zero-point correction = 0.527570
Thermal correction to Energy = 0.553401
Thermal correction to Enthalpy = 0.554345
Thermal correction to Gibbs Free Energy = 0.471471
Sum of electronic and zero-point Energies = −1273.388802
Sum of electronic and thermal Energies = −1273.362971
Sum of electronic and thermal Enthalpies = −1273.362027
Sum of electronic and thermal Free Energies = −1273.444901
Imaginary Frequencies 0
Dipole Moment 7.3431
Coordinates (Å)
N,0,0.0496829975,0.1051475159,-0.0759445324
N,0,0.0923981045,-0.0957996923,2.5560606835
C,0,1.235942954,0.0252693915,0.4816624593
C,0,-0.1825435228,-0.4477223191,-1.3961616367
C,0,0.5917557339,0.0102131604,-2.4532407021
H,0,1.3228517981,0.7932679149,-2.2874330337
C,0,0.3973371862,-0.5341497844,-3.7182456325
H,0,0.9933402311,-0.1803379113,-4.5500537331
C,0,-0.5649767938,-1.518815801,-3.9136046044
H,0,-0.7181390471,-1.9371241022,-4.9006207867
C,0,-1.3335555827,-1.966756615,-2.8421810579
H,0,-2.07947516,-2.7371632041,-2.9918323782
C,0,-1.1466435405,-1.4323105878,-1.5739531936
H,0,-1.7358483646,-1.772431005,-0.7306435346
C,0,-0.0212237788,-0.714765478,3.8295238319
C,0,-0.8983426521,-0.2162817166,4.7951010431
H,0,-1.5190655752,0.6374015417,4.5523957584
C,0,-0.9595372562,-0.8137937658,6.0477324321
H,0,-1.6360059593,-0.4164315995,6.7953610092
C,0,-0.1514438066,-1.9075562619,6.3495921945
H,0,-0.1982975682,-2.3660274952,7.3297475092
C,0,0.7066138695,-2.4140043309,5.3784374869
H,0,1.3257458471,-3.2762351799,5.5962236838
C,0,0.7662847972,-1.8283397244,4.1187074024
H,0,1.4152044744,-2.2293539452,3.3504385571
B,0,1.3916000017,0.6150779818,1.9654416328
H,0,1.9617984536,-0.5174715634,-0.1244012846
C,0,1.2240531842,2.2396726759,1.9614701338
H,0,0.2882537923,2.55623164,1.4803668555
C,0,2.8055307529,0.3092880788,2.6879744807
H,0,3.0115781309,-0.765023383,2.7769887561
C,0,2.3657680559,2.8487407142,1.1210483934
H,0,2.3229252817,3.9451507187,1.1505233728
H,0,2.1861947855,2.5710800806,0.0729498547
C,0,3.9142572336,0.8900696334,1.7824973379
H,0,4.8988538846,0.6969745048,2.2263448443
H,0,3.9078874371,0.3505267903,0.8268263684
C,0,2.8490791936,0.8940503586,4.118715232
H,0,3.8670692884,0.8060082811,4.5206959103
H,0,2.2187413788,0.2730728281,4.7619403463
C,0,1.1630682311,2.7302336137,3.4170988435
H,0,1.0269770298,3.8189496527,3.4540585142
H,0,0.2668216126,2.295548806,3.8775288587
C,0,2.3853397862,2.3571225303,4.2715286983
C,0,3.7891181467,2.3954540996,1.4957096201
H,0,4.4692682783,2.6582607318,0.678554442
H,0,4.1434641525,2.9582236549,2.3595831924
H,0,3.2053015787,3.0384427228,4.0415900187
H,0,2.1468228971,2.5359152754,5.3253518208
N,0,-1.0665415649,0.1976955946,1.9912175924
C,0,-1.0836830348,0.4506270672,0.7208001643
C,0,-2.303547815,0.9613689344,0.0702264335
C,0,-3.561517564,0.6301180347,0.5819969019
C,0,-2.2163258733,1.8162384376,-1.0316281145
C,0,-4.7107910633,1.1359637522,-0.0094970117
H,0,-3.6236285914,-0.0257822867,1.4417040051
C,0,-3.3703635896,2.3177347711,-1.6225623854
H,0,-1.2444238942,2.0980881887,-1.4216132371
C,0,-4.6203115802,1.9775821175,-1.1161097843
H,0,-5.6815762326,0.8681667916,0.3901404571
H,0,-3.2907090041,2.9807488246,-2.4755546765
H,0,-5.5190607796,2.3679268427,-1.5778755079



TS$_3$

PCM solvent model for THF
Zero-point correction = 0.528151
Thermal correction to Energy = 0.553454
Thermal correction to Enthalpy = 0.554398
Thermal correction to Gibbs Free Energy = 0.472582
Sum of electronic and zero-point Energies = −1273.378174
Sum of electronic and thermal Energies = −1273.352872
Sum of electronic and thermal Enthalpies = −1273.351928
Sum of electronic and thermal Free Energies = −1273.433743

Imaginary Frequencies 1
Dipole Moment 1.8801
Coordinates (Å)
N,0,0.0031411239,0.0047346027,0.0005148361
N,0,0.0027790251,0.0107839328,1.4016025677
N,0,2.3897655596,0.0102063963,1.4313536765
C,0,1.1388387504,0.0067791955,2.0086147534
C,0,1.1386617597,-0.1589581576,-0.7106910317
C,0,-1.2682829318,0.2164995828,-0.5842666248
C,0,-1.3801238368,0.7533311016,-1.8694074746
H,0,-0.4988147678,1.0722098736,-2.4099757309
C,0,-2.6332929746,0.9146042125,-2.4493973954
H,0,-2.703281912,1.3342924946,-3.4458166922
C,0,-3.7856883722,0.564550496,-1.7552844447
H,0,-4.7601341334,0.6980751954,-2.2081175774
C,0,-3.6707383696,0.0532721133,-0.465219307
H,0,-4.5599801119,-0.218106524,0.0914357708
C,0,-2.4259368002,-0.1220963374,0.1234946221
H,0,-2.3318280919,-0.5163949187,1.1247156123
C,0,1.0130512236,-0.0096560218,3.5010557504
C,0,1.4746519363,-1.0914162158,4.2518220979
H,0,1.9482392151,-1.9298722195,3.7552866303
C,0,1.3247838178,-1.0945151263,5.6328767101
H,0,1.6795344287,-1.9401153138,6.2097408758
C,0,0.7215919248,-0.015143262,6.2738877188
H,0,0.6130990873,-0.0160975245,7.3518689097
C,0,0.2542665954,1.0605722605,5.5268613067
H,0,-0.2212830518,1.8999384972,6.0198972637
C,0,0.3928981161,1.0600653628,4.1421463356
H,0,0.0233772609,1.8894523264,3.5506936609
C,0,3.537855647,-0.0497414195,2.2851811289
C,0,3.9274742735,1.0521247847,3.044569693
H,0,3.3358382615,1.95955606,3.0093186965
C,0,5.0561492452,0.9807071742,3.8542315576
H,0,5.3496431925,1.8427894618,4.4411996768
C,0,5.8058195404,-0.1901368333,3.9099825707
H,0,6.6878527348,-0.2423532498,4.5366301105
C,0,5.4091525124,-1.2978516143,3.1658987521
H,0,5.9778021982,-2.2188003738,3.2159752824
C,0,4.2755684577,-1.2305633848,2.36437187
H,0,3.9480949863,-2.0943488834,1.7977181589
B,0,2.4983501703,-0.0446027075,-0.0901751454
H,0,0.9772204334,-0.3579480066,-1.7625221949
C,0,2.1879266978,1.6255032166,-0.9960022324
H,0,1.2362187051,2.1205476894,-0.7858703929
C,0,3.8693059593,-0.4732067448,-0.7934102092
H,0,4.1600768728,-1.455084941,-0.4004108003
C,0,2.4238846083,1.6152536209,-2.5133705283
H,0,2.6433310626,2.6433293598,-2.830420557
H,0,1.4878983952,1.3529400952,-3.0140735795
C,0,3.6988850695,-0.6385151275,-2.3151410301
H,0,4.5839198354,-1.1406509109,-2.7218889053
H,0,2.851747293,-1.3001856242,-2.5253456317
C,0,5.0322498213,0.495691393,-0.4548839337
H,0,5.8747969028,0.2818649136,-1.1235609036
H,0,5.3882470732,0.2741279133,0.5518068245
C,0,3.2677535511,2.402295898,-0.2172074166
H,0,3.1408772015,3.4614225871,-0.4756862685
H,0,3.0700637532,2.3289909483,0.8532637599
C,0,4.714863016,2.0064405245,-0.5329281572
C,0,3.5319127952,0.6900478514,-3.0596332696
H,0,3.3183243289,0.4887881874,-4.1132227797
H,0,4.4915293094,1.2086752962,-3.0500464668
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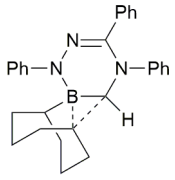
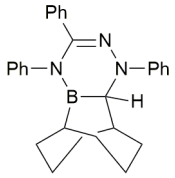


TS$_3$'

PCM solvent model for THF
Zero-point correction = 0.527253
Thermal correction to Energy = 0.552692
Thermal correction to Enthalpy = 0.553636
Thermal correction to Gibbs Free Energy = 0.471495
Sum of electronic and zero-point Energies = −1273.368869
Sum of electronic and thermal Energies = −1273.343430
Sum of electronic and thermal Enthalpies = −1273.342486
Sum of electronic and thermal Free Energies = −1273.424627
Imaginary Frequencies 1
Dipole Moment 5.6181
Coordinates (Å)
N,0,0.022263363,-0.1676822631,-0.0388960421
N,0,0.0497574966,0.1348857811,2.7085949888
C,0,1.2269707155,-0.2616570221,0.5792849534
C,0,-0.112291385,-0.4801433737,-1.4307052997
C,0,0.7725291798,0.0623256492,-2.3581584463
H,0,1.5424116372,0.7518802735,-2.0298988612
C,0,0.6421458035,-0.2623598844,-3.7039040341
H,0,1.3294703713,0.1629329648,-4.4248560585
C,0,-0.3753473756,-1.1130155824,-4.1235960727
H,0,-0.4799582738,-1.358013202,-5.1731981924
C,0,-1.2585219854,-1.6485612512,-3.1899966308
H,0,-2.0496512714,-2.3154771127,-3.5099089408
C,0,-1.1259898165,-1.341250275,-1.8419105943
H,0,-1.8040715998,-1.7583832476,-1.1067515805
C,0,-0.1758893234,0.2512258755,4.0988925852
C,0,-0.9051106526,1.3141920754,4.6437807041
H,0,-1.3174834627,2.0627562261,3.979008381
C,0,-1.100015449,1.3994725279,6.0170429
H,0,-1.6607478202,2.2334948461,6.4234646177
C,0,-0.5749676316,0.4323744024,6.8703414428
H,0,-0.7255112157,0.5055983601,7.9404609366
C,0,0.1284915456,-0.6398303883,6.329196966
H,0,0.5211118065,-1.4147605803,6.9774690933

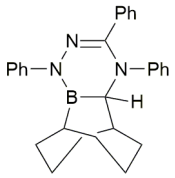
C,0,0.3132627541,-0.7402691391,4.9553850232
H,0,0.8297702546,-1.5927088877,4.5321321848
B,0,1.4123770558,0.1054388248,2.0206416661
H,0,2.029686498,-0.5489498987,-0.0922068385
C,0,1.8951335063,1.7174797007,1.1600654694
H,0,1.1575125725,2.085476161,0.4420757447
C,0,2.7585722144,-0.1712126177,2.8476443704
H,0,2.6435602461,-1.1177094368,3.388915301
C,0,3.280372503,1.7281674926,0.4978321985
H,0,3.6072829565,2.7720331557,0.3991415164
H,0,3.1801593509,1.3556640349,-0.5259945889
C,0,3.9609670802,-0.3548614868,1.9020306782
H,0,4.8142028632,-0.7298250869,2.4785379966
H,0,3.7344969263,-1.1322025861,1.1642617192
C,0,3.0267483679,0.9155380248,3.9176598235
H,0,4.0350665072,0.7727134112,4.3251598755
H,0,2.3407560167,0.7549441639,4.7507842428
C,0,1.7989754354,2.6225323624,2.4042206351
H,0,1.8850519072,3.6582309217,2.0497026909
H,0,0.8057908658,2.5333319705,2.8505536013
C,0,2.8823524081,2.3818888129,3.4586629342
C,0,4.4050805109,0.932354484,1.1958511632
H,0,5.1659122096,0.6877056494,0.4490086359
H,0,4.9087186726,1.5648759626,1.927873543
H,0,3.8295653983,2.7606270831,3.0711568929
H,0,2.6545048341,2.9997279876,4.3323551252
N,0,-1.0279178868,0.5621726568,1.9716561487
C,0,-1.0569465545,0.4005832464,0.7073189943
C,0,-2.2521004709,0.9041132067,-0.0202457476
C,0,-2.1309337072,1.7285020688,-1.1420146245
C,0,-3.522249322,0.5928313845,0.4662085344
C,0,-3.2661175198,2.2254511076,-1.7698774838
H,0,-1.149545967,1.9890608247,-1.52101562
C,0,-4.6567936641,1.0877214457,-0.1668182758
H,0,-3.6082752933,-0.0379340028,1.3426701895
C,0,-4.5316685571,1.9017268665,-1.2881306413
H,0,-3.1618399219,2.8687654203,-2.6352092879
H,0,-5.638628229,0.8344021482,0.2146526366
H,0,-5.4156095479,2.2849286525,-1.7835601537



3a

PCM solvent model for THF
Zero-point correction = 0.530231
Thermal correction to Energy = 0.555716
Thermal correction to Enthalpy = 0.556660
Thermal correction to Gibbs Free Energy = 0.474100
Sum of electronic and zero-point Energies = −1273.429045
Sum of electronic and thermal Energies = −1273.403561
Sum of electronic and thermal Enthalpies = −1273.402616
Sum of electronic and thermal Free Energies = −1273.485177
Imaginary Frequencies 0
Dipole Moment 2.4241
Coordinates (Å)
N,0,-0.0138471887,-0.0344408725,-0.0032136269
N,0,-0.0092152092,-0.0228597227,1.3841264341
N,0,2.3622455233,-0.0233847177,1.3037303167
C,0,1.1178702403,-0.0137486713,1.9846896288
C,0,0.9848404371,-0.9843156917,-0.5736071814
H,0,0.7789253192,-1.9807598367,-0.1351618288
C,0,0.8642898733,-1.1409360993,-2.0971505961
H,0,-0.1747894789,-1.4209267766,-2.2982555345
C,0,1.695106737,-2.3464558084,-2.5875509582
H,0,1.2477208696,-2.6839448189,-3.5279526786
H,0,1.5720434379,-3.1740491846,-1.8784157181
C,0,3.1843224035,-2.1213737413,-2.8443423581
C,0,4.0264809087,-1.734169342,-1.6308463474
H,0,5.0729266556,-1.6892193259,-1.952444741
H,0,3.9723747362,-2.5383295588,-0.8856599951
C,0,3.6806070174,-0.3831295622,-0.9591037778
H,0,4.5439123249,-0.1334287311,-0.3398351433
C,0,3.5138730936,0.7816626064,-1.9766761212
C,0,2.0696250878,1.197432793,-2.2913252961
C,0,1.1354120028,0.1484757848,-2.909609782
H,0,1.507668048,-0.1347471107,-3.9002193612
H,0,0.179033313,0.6460176967,-3.0891409967
C,0,-1.3648145029,-0.2287094807,-0.4687350193
C,0,-1.9184636293,0.7035366658,-1.3367871447
H,0,-1.3337378146,1.5736022409,-1.6114019704
C,0,-3.2094152733,0.5178648766,-1.8272352896
H,0,-3.6383779329,1.247289644,-2.5039421434
C,0,-3.9482763419,-0.594288498,-1.4402586285
H,0,-4.9533947752,-0.7373887665,-1.8184080299
C,0,-3.3977209613,-1.5190847787,-0.5540610796
H,0,-3.9758290494,-2.3805167696,-0.2410049818
C,0,-2.1089661755,-1.338061563,-0.0687937048
H,0,-1.6738383166,-2.0430898223,0.630627278
C,0,1.1013801437,0.0033474487,3.4717839832
C,0,1.9946498815,-0.7799266046,4.2059773771
H,0,2.7235240695,-1.3928680509,3.6891623981
C,0,1.9425702791,-0.7858434785,5.5946029743
H,0,2.6355185718,-1.4015222223,6.1553990331
C,0,1.0029802622,-0.0058369265,6.2627051705
H,0,0.9678768052,-0.0060579334,7.3455382396
C,0,0.1080131386,0.7729322391,5.5345802572
H,0,-0.6254655457,1.3821156203,6.049167089
C,0,0.155001479,0.7762878942,4.1456490852
H,0,-0.539110501,1.3748411454,3.568545041
C,0,3.4656068015,0.6336370601,1.9459118943
C,0,3.3431580125,1.96718301,2.3266897732
H,0,2.4150214129,2.4926246821,2.129146784
C,0,4.4024631263,2.6082159837,2.9593238018
H,0,4.3004445749,3.6447022356,3.2572816971

C,0,5.5895051546,1.9243867401,3.2030234712
H,0,6.4147587389,2.4252870773,3.6940847405
C,0,5.7117157575,0.5932218632,2.8154104254
H,0,6.6315538025,0.053391642,3.0052281594
C,0,4.649924501,-0.054862002,2.1945138112
H,0,4.7271009214,-1.097501108,1.9059356802
B,0,2.396163337,-0.4662915149,-0.0513202479
H,0,4.0114374799,1.663641548,-1.5631363821
H,0,4.0455815927,0.5410958268,-2.9038353141
H,0,1.6037455325,1.568958944,-1.3704863408
H,0,2.1039756471,2.052910544,-2.9731371691
H,0,3.5948546114,-3.04662633,-3.2607671251
H,0,3.3085280069,-1.3674533204,-3.6273291685



Not observed triazaborinine

PCM solvent model for THF
Zero-point correction = 0.530226
Thermal correction to Energy = 0.555842
Thermal correction to Enthalpy = 0.556786
Thermal correction to Gibbs Free Energy = 0.473492
Sum of electronic and zero-point Energies = −1273.427849
Sum of electronic and thermal Energies = −1273.402233
Sum of electronic and thermal Enthalpies = −1273.401288
Sum of electronic and thermal Free Energies = −1273.484582
Imaginary Frequencies 0
Dipole Moment 2.7991
Coordinates (Å)
N,0,0.0474271276,-0.1347499582,-0.0144388741
N,0,0.0376710852,-0.0958392451,2.7854586927
C,0,1.3864067319,-0.016265277,0.6235565848
H,0,1.8752992333,-1.0039136298,0.5414144353
C,0,2.2851359149,0.9729597936,-0.145527699
H,0,2.144081939,0.7472609423,-1.2054008038
C,0,3.7843477914,0.7017479498,0.086802938
H,0,4.3228696621,1.1264329665,-0.766702558
H,0,3.9549668151,-0.3809047617,0.0455418156
C,0,4.4143806384,1.2619814752,1.3571045999
C,0,3.838199278,0.7283105221,2.6658773568
H,0,4.4474840906,1.1286119709,3.4838388622
H,0,3.9671388127,-0.360927667,2.6956267781
C,0,2.3648544932,1.0809920654,2.960856944
H,0,2.2342361173,0.9322688045,4.0334043657
C,0,2.0206152256,2.5789871618,2.6820260846
C,0,1.2534933174,2.8653747369,1.3777244172
C,0,1.893555714,2.458060781,0.0415644744
H,0,2.7773491698,3.0776187514,-0.1466169862
H,0,1.1732148778,2.7265446216,-0.7377471344
C,0,0.0695197438,-0.743203095,-1.3200258241
C,0,0.1213936746,0.0432205402,-2.4670973346
H,0,0.1149040445,1.1229008912,-2.3679624516
C,0,0.159435029,-0.5571780894,-3.7213790857
H,0,0.1953255013,0.0597941654,-4.6110936432
C,0,0.1412988698,-1.944047364,-3.8333075743
H,0,0.1637969417,-2.409945957,-4.8109691355
C,0,0.0902285247,-2.7310295527,-2.6865158923
H,0,0.0716370417,-3.8111468137,-2.7680319094
C,0,0.0606697245,-2.1322010678,-1.432185493
H,0,0.0174166383,-2.7365717291,-0.5317410013
C,0,-0.2529453033,0.0303945454,4.1768632213
C,0,-1.3479895824,0.7850609579,4.596186922
H,0,-1.9759978935,1.2565230348,3.8507316447
C,0,-1.6232815582,0.9126036521,5.9519824102
H,0,-2.4738451176,1.5028628629,6.2717591057
C,0,-0.8105385967,0.2915351982,6.8972352033
H,0,-1.0271648951,0.3937073193,7.9536131961
C,0,0.2747095219,-0.4699989009,6.4762046175
H,0,0.9040946693,-0.9694955916,7.2030633146
C,0,0.5479010491,-0.6108454943,5.119307197
H,0,1.3775550345,-1.2213209494,4.7813025262
B,0,1.2573970317,0.2730271216,2.1803291225
H,0,1.3845643428,2.93312673,3.4985987976
H,0,2.932617828,3.1837255166,2.7215347761
H,0,0.2650451309,2.3916476646,1.4434728008
H,0,1.0528959103,3.9400404673,1.3334888972
H,0,5.4844172142,1.0330873166,1.333416367
H,0,4.3466134044,2.3541914058,1.3444488102
C,0,-1.0578373141,-0.4102838974,0.7768315057
N,0,-1.1218887289,-0.406157099,2.0575458344
C,0,-2.3605334259,-0.6651332345,0.0906680216
C,0,-3.1660879898,-1.7238515878,0.5068278502
C,0,-2.8072316182,0.1798100457,-0.9267795768
C,0,-4.3989770618,-1.9449529962,-0.0973354949
H,0,-2.8174495321,-2.3672222319,1.3053096674
C,0,-4.0434720408,-0.036891746,-1.5226618712
H,0,-2.1903964616,1.0132087344,-1.2408796674
C,0,-4.8395990626,-1.1035242266,-1.1140157683
H,0,-5.0150830785,-2.7753769488,0.2261965693
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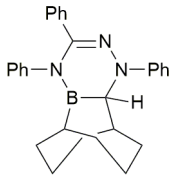
H,0,-5.8001255622,-1.2759299099,-1.5846358054



3a

PCM solvent model for CH_2CH_2
Zero-point correction = 0.530192
Thermal correction to Energy = 0.555684
Thermal correction to Enthalpy = 0.556628
Thermal correction to Gibbs Free Energy = 0.474042
Sum of electronic and zero-point Energies = −1273.429521
Sum of electronic and thermal Energies = −1273.404029
Sum of electronic and thermal Enthalpies = −1273.403085
Sum of electronic and thermal Free Energies = −1273.485671
Imaginary Frequencies 0
Dipole Moment 2.4658
Coordinates (Å)

N,0,-0.0006741363,-0.0005529444,-0.0002916749
N,0,-0.0007909497,-0.0005433035,1.3872612967
N,0,2.3708579343,0.0002327941,1.3146847747
C,0,1.124450498,0.0041341604,1.9914428466
C,0,1.0002992019,-0.9453036246,-0.5754736952
H,0,0.7929566239,-1.9456780367,-0.1468759518
C,0,0.8851783609,-1.0877945611,-2.1008134951
H,0,-0.1533049921,-1.3653708,-2.3082645893
C,0,1.7169728091,-2.2892533522,-2.5994219284
H,0,1.2728638856,-2.617485635,-3.5446419462
H,0,1.5907154229,-3.1233377743,-1.8985179705
C,0,3.2072663196,-2.0628294554,-2.84850037
C,0,4.0449933158,-1.6874576093,-1.6282457469
H,0,5.0927254577,-1.6405304365,-1.9453208551
H,0,3.9872095829,-2.4981614671,-0.8905113392
C,0,3.6977339346,-0.3421637975,-0.945717261
H,0,4.5588746489,-0.0989133786,-0.320844143
C,0,3.5356040909,0.8318343416,-1.9534000326
C,0,2.0927333773,1.2515321085,-2.2692094494
C,0,1.1597872287,0.2090140605,-2.9002240296
H,0,1.5350564542,-0.0651918441,-3.8922258404
H,0,0.2043536664,0.7090378647,-3.078080516
C,0,-1.3499853695,-0.1916922865,-0.4719328462
C,0,-1.9020500618,0.748580876,-1.332368376
H,0,-1.3173692967,1.6217521764,-1.5970984508
C,0,-3.1914504792,0.5665173435,-1.8283708175
H,0,-3.6191261212,1.302135438,-2.4991546765
C,0,-3.9302967622,-0.5502311592,-1.4546496103
H,0,-4.934135102,-0.690609495,-1.8371862552
C,0,-3.3812629425,-1.4834348512,-0.5762683872
H,0,-3.9592358329,-2.348731884,-0.2738080404
C,0,-2.0940489449,-1.3059421462,-0.0854947596
H,0,-1.6600420642,-2.0180334487,0.6074663229
C,0,1.1036813063,0.0092973544,3.4785745386
C,0,1.9921661574,-0.7835247743,4.2083590341
H,0,2.7198214974,-1.3951072893,3.6881604236
C,0,1.9366628382,-0.8007143013,5.5968155698
H,0,2.625730253,-1.4238391095,6.1541579909
C,0,0.9984825843,-0.0224907971,6.2690956977
H,0,0.9607282854,-0.0315378448,7.3517966744
C,0,0.1084102831,0.7659560094,5.5453073995
H,0,-0.6237253353,1.3739584398,6.0631869607
C,0,0.1588121309,0.7805918623,4.1564995085
H,0,-0.5311392282,1.3873359202,3.5829282159
C,0,3.4719762828,0.6518297687,1.9662898689
C,0,3.3487809951,1.9829240777,2.3554267019
H,0,2.4220718794,2.510579117,2.1569695052
C,0,4.4056876397,2.6188529519,2.9973090181
H,0,4.3032114295,3.6534484926,3.3016293598
C,0,5.5910358277,1.9322929327,3.2418897221
H,0,6.4144308659,2.4291822207,3.7401022552
C,0,5.7139889856,0.6036297646,2.8457983958
H,0,6.6325103658,0.0617784958,3.0362045407
C,0,4.6545646126,-0.0394122475,2.2155676659
H,0,4.7322897793,-1.0800993985,1.9202093972
B,0,2.4098168302,-0.4321569941,-0.043673386
H,0,4.0324179521,1.7097257037,-1.5303306695
H,0,4.0702389202,0.5990968289,-2.880857149
H,0,1.6240199271,1.6149876601,-1.3465776458
H,0,2.1299639389,2.1131817912,-2.9430336947
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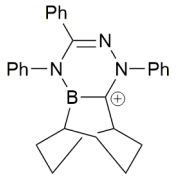

Triazaborenium

PCM solvent model for CH_2CH_2
Zero-point correction = 0.520182
Thermal correction to Energy = 0.545994
Thermal correction to Enthalpy = 0.546939
Thermal correction to Gibbs Free Energy = 0.462321
Sum of electronic and zero-point Energies = −1272.669022
Sum of electronic and thermal Energies = −1272.643210
Sum of electronic and thermal Enthalpies = −1272.642266
Sum of electronic and thermal Free Energies = −1272.726884
Imaginary Frequencies 0
Dipole Moment 2.3158
Coordinates (Å)

N,0,0.0011806936,-0.0228871811,0.0030300703
N,0,-0.0002314284,-0.0198547222,1.3660700487

N,0,2.3630335026,-0.0144306468,1.3670330229
C,0,1.1377779392,-0.0307475576,1.9949352544
C,0,1.062982845,-0.1006871398,-0.7583719871
C,0,-1.3564352707,0.0391665463,-0.5213039885
C,0,-1.7999130633,1.2249071125,-1.0852493637
H,0,-1.1474774227,2.0885855136,-1.1291410433
C,0,-3.1011356958,1.2766590896,-1.5737203809
H,0,-3.46952368,2.1931487792,-2.0163865823
C,0,-3.9237085064,0.1578831011,-1.4885151684
H,0,-4.9353806958,0.2033551145,-1.871628139
C,0,-3.4562234239,-1.0180459564,-0.9077821432
H,0,-4.1001911463,-1.8853639807,-0.8387367611
C,0,-2.1601381667,-1.0844757112,-0.4108523213
H,0,-1.7751905883,-1.9851792114,0.0508637334
C,0,1.0275818563,-0.0461772668,3.477378963
C,0,1.7174209509,-0.9854200864,4.2468836562
H,0,2.3662539168,-1.7123730118,3.775016441
C,0,1.5556221235,-0.9956466103,5.6253749323
H,0,2.0831686723,-1.7303204649,6.2205619987
C,0,0.7192938292,-0.0667998016,6.2393035114
H,0,0.6044204965,-0.0722930741,7.3163145561
C,0,0.0269991664,0.8633218048,5.4712085455
H,0,-0.6277092805,1.5833988411,5.9457885936
C,0,0.1707835586,0.8684179224,4.0891438385
H,0,-0.3707078077,1.5814608373,3.4798650515
C,0,3.5638702332,0.1384119023,2.165295785
C,0,3.7893411248,1.3340275848,2.8340207643
H,0,3.0647196292,2.1374870641,2.7684945487
C,0,4.9472181627,1.4750246007,3.590471709
H,0,5.1301076313,2.4015232065,4.1199284972
C,0,5.8664660161,0.4330545501,3.6644110121
H,0,6.7662536415,0.5472169806,4.2558123692
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H,0,6.3496394969,-1.5644877713,3.0281901204
C,0,4.4772945112,-0.9057956418,2.2200026976
H,0,4.2753797679,-1.8273030644,1.6855380733
B,0,2.4486701722,-0.0479642796,-0.0604478416
C,0,3.7553857236,0.0835803167,-0.9032227193
C,0,0.9605372525,-0.2535997133,-2.244436874
H,0,-0.0932491057,-0.3746564715,-2.499206953
H,0,4.5887459335,0.2037074745,-0.2054976203
C,0,3.7041922851,1.4097177247,-1.710819839
C,0,4.0836565407,-1.1946518367,-1.714195309
C,0,1.4163301436,1.0343484184,-2.9774162222
C,0,1.6481905829,-1.5856451456,-2.6523807142
H,0,0.8415243532,1.8623146216,-2.5498271788
H,0,1.0706054239,0.9346408925,-4.010325595
C,0,2.9009932795,1.4337232275,-3.0162602172
H,0,4.7331368272,1.6845892229,-1.9619761228
H,0,3.3398657613,2.2055929246,-1.0487795765
H,0,3.4257251382,0.8470259945,-3.7670944581
H,0,2.9285290772,2.4614784595,-3.3901385897
H,0,1.1752883295,-1.8954199679,-3.5882033684
H,0,1.3687558643,-2.3467795486,-1.9143874438
C,0,3.1643684653,-1.6127375787,-2.8746691853
H,0,3.3990801573,-1.0410981596,-3.7701909593
H,0,3.4199045131,-2.6466167614,-3.124889458
H,0,5.0953719046,-1.0854421547,-2.1183148714
H,0,4.1367580143,-2.0269560768,-1.0028362813

$B(C_6F_5)_3$

Tris(pentafluorophenyl)borane

PCM solvent model for CH_2CH_2
Zero-point correction = 0.157245
Thermal correction to Energy = 0.185424
Thermal correction to Enthalpy = 0.186368
Thermal correction to Gibbs Free Energy = 0.098048
Sum of electronic and zero-point Energies = −2208.005440
Sum of electronic and thermal Energies = −2207.977261
Sum of electronic and thermal Enthalpies = −2207.976317
Sum of electronic and thermal Free Energies = −2208.064637
Imaginary Frequencies 0
Dipole Moment 0.0105
Coordinates (Å)
C,0,0.0004568747,-0.0002244462,-0.0011491112
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C,0,2.4395311324,-0.019974813,1.4103316084
C,0,2.3876069043,-0.0480492965,0.0161814931
C,0,1.2007229346,-0.0295840161,-0.6920294277
B,0,3.7956315071,-0.0315474021,2.1949604635
C,0,5.0245259575,-0.8167460045,1.6227186204
C,0,4.8769987118,-1.9957694699,0.8909901607
C,0,5.9499791426,-2.7057069121,0.3858491237
C,0,7.2342780721,-2.2289870139,0.5912906991
C,0,7.4318071328,-1.0578685489,1.3042053118
C,0,6.3373055411,-0.3825557707,1.81074574
F,0,3.6650855462,-2.5014963705,0.6608313279
F,0,6.5880873508,0.7377520727,2.4885218674
F,0,5.7634538981,-3.8314783435,-0.2938764175
F,0,8.6639025296,-0.600183656,1.4957226139
F,0,8.2710428025,-2.8914840228,0.107113346
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F,0,3.510792547,-0.077520576,-0.7015011473
F,0,-1.1524312917,0.042781608,2.0442839826
F,0,1.1989462079,-0.0433681976,-2.0202175198
F,0,-1.1438723748,0.0089066008,-0.6634683989
C,0,3.921826533,0.7420719198,3.5514091508
C,0,4.7326613801,0.2892181104,4.5929157794
C,0,4.8464168929,0.9535140176,5.7997235155
C,0,4.144544996,2.132042608,5.9925657058
C,0,3.3332541544,2.6271037285,4.9848034779
C,0,3.2286058543,1.9279435692,3.7970655163
F,0,5.4310034052,-0.839124484,4.4641213061
F,0,2.4324601325,2.451169706,2.8643729529
F,0,5.6197879618,0.4782728838,6.7693934563
F,0,2.665182079,3.7599639359,5.1704506818
F,0,4.2489286513,2.7841949406,7.1380111096

$HB(C_6F_5)_3^-$

Tris(pentafluorophenyl)hydridoborate

PCM solvent model for CH_2CH_2
Zero-point correction = 0.165274
Thermal correction to Energy = 0.193980
Thermal correction to Enthalpy = 0.194924
Thermal correction to Gibbs Free Energy = 0.104488
Sum of electronic and zero-point Energies = −2208.753216
Sum of electronic and thermal Energies = −2208.724511
Sum of electronic and thermal Enthalpies = −2208.723567
Sum of electronic and thermal Free Energies = −2208.814002
Imaginary Frequencies 0
Dipole Moment 1.3190
Coordinates (Å)

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C,0,-1.2142920516,-0.6589064434,2.4648042641
C,0,0.4465725295,-0.6501314289,4.6350958055
C,0,-1.6083096469,-1.3118448943,3.6208288782
C,0,-0.7661421238,-1.3080273113,4.7186535988
C,0,1.8909466178,1.106464593,0.6806746528
C,0,2.8264664365,0.0846154869,0.804274492
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B,0,0.3093340587,0.7564868491,0.8983945378
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F,0,5.0283154579,-0.7835112824,0.7367141744
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F,0,1.9889122541,0.6154305433,3.4693927449
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F,0,-1.1225548229,-1.9279942866,5.844897225
F,0,-2.7868337441,-1.9381961432,3.6922806678
F,0,-2.0851789156,-0.6832224655,1.4421016899
F,0,-1.9579593396,1.2822073687,-0.9794346308
F,0,-3.6120233146,3.367480179,-0.8717903221
F,0,-3.2798420332,5.2983604843,1.0086126235
F,0,-1.2424422353,5.1089663113,2.7983646825
F,0,0.4379738326,3.0114761212,2.7038441687

BEt_3

Triethylborane

PCM solvent model for CH_2CH_2
Zero-point correction = 0.201027
Thermal correction to Energy = 0.211453
Thermal correction to Enthalpy = 0.212397
Thermal correction to Gibbs Free Energy = 0.165577
Sum of electronic and zero-point Energies = −262.258937
Sum of electronic and thermal Energies = −262.248511
Sum of electronic and thermal Enthalpies = −262.247567
Sum of electronic and thermal Free Energies = −262.294387
Imaginary Frequencies 0
Dipole Moment 0.1271
Coordinates (Å)

B,0,-0.0006318084,-0.0022351742,-0.000326792
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H,0,-0.4934466706,0.8905414057,1.9798362658
H,0,1.5589351248,0.0089315304,3.1151550932
H,0,2.0048577375,-0.8812834849,1.6603053291
H,0,2.0027281536,0.8834705887,1.6489186941
C,0,-0.15661576,-1.3692563522,-0.7668002387
C,0,0.185353954,-1.3958089273,-2.2587703124
H,0,-1.2124426963,-1.6499542649,-0.6196422151
H,0,0.3956593089,-2.1494280942,-0.2267687127
H,0,-0.0007436182,-2.3754550674,-2.7045404282
H,0,-0.4064998835,-0.6626357089,-2.813004863
H,0,1.2378790148,-1.1518701733,-2.4238571638
C,0,0.0996401712,1.366217147,-0.7713687798
C,0,-1.3544820823,1.7757476858,-1.1113131676
H,0,0.6693545006,1.2912132531,-1.702326652
H,0,0.5530448688,2.153916575,-0.1614600116
H,0,-1.3836902512,2.7327258914,-1.6356792485
H,0,-1.8378700329,1.0314919632,-1.7498888184
H,0,-1.959109505,1.8760960217,-0.2058592656

$HBEt_3^-$

Hydridotriethylborate

PCM solvent model for CH_2CH_2
Zero-point correction = 0.207986
Thermal correction to Energy = 0.218222
Thermal correction to Enthalpy = 0.219167
Thermal correction to Gibbs Free Energy = 0.173542
Sum of electronic and zero-point Energies = −262.943802
Sum of electronic and thermal Energies = −262.933566
Sum of electronic and thermal Enthalpies = −262.932622

Sum of electronic and thermal Free Energies = −262.978246
Imaginary Frequencies 0
Dipole Moment 2.5564
Coordinates (Å)
H,0,-0.0010045231,0.0054134489,-0.0126036535
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C,0,1.7116230644,1.413757807,0.8021328745
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H,0,2.4324176059,-1.4004240352,1.6782946954
C,0,2.6812571859,-1.3158833207,-0.4587483232
H,0,3.3818512979,-0.4741684649,-0.4436261017
H,0,3.2743322571,-2.2315000919,-0.5727830238
H,0,2.0755408544,-1.2027474491,-1.3649762302
C,0,-0.9515591659,-1.1935279056,2.5186457869
H,0,-1.6810829324,-1.2255925889,1.7015608136
H,0,-0.3994453212,-2.1383166532,2.4866142537
H,0,-1.5146086703,-1.1798960298,3.459984268
C,0,2.8711662981,1.5185445622,1.8039866028
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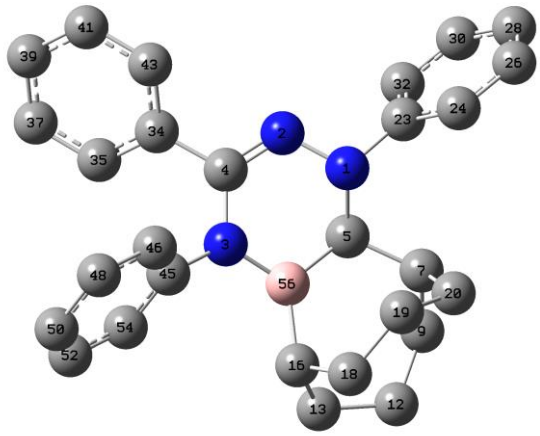
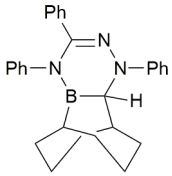
Charge Distribution

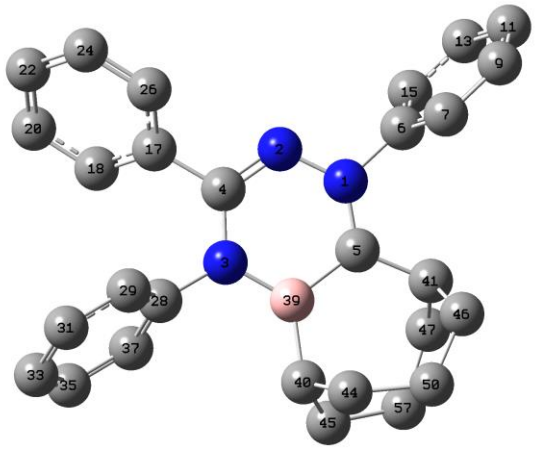


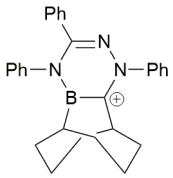


Sum of APT charges = 0.00000
APT charges with hydrogens summed into heavy atoms:

1	N	-0.753254
2	N	-0.295005
3	N	-1.206335
4	C	0.801227
5	C	-0.044632
7	C	0.049692
9	C	0.005397
12	C	-0.011388
13	C	0.043642
16	C	-0.331511
18	C	0.023310
19	C	0.002365
20	C	-0.000779
23	C	0.461091
24	C	-0.050332
26	C	0.011736
28	C	-0.032507
30	C	0.022244
32	C	-0.079467

34 C 0.041402
35 C -0.039943
37 C -0.002147
39 C -0.023640
41 C 0.012308
43 C -0.014818
45 C 0.510095
46 C -0.089200
48 C 0.037839
50 C -0.030188
52 C 0.033772
54 C -0.066152
56 B 1.015180





Sum of APT charges = 1.00000
APT charges with hydrogens summed into heavy atoms:
1 N 0.275670
2 N -1.001070
3 N -0.893337
4 C 1.203297
5 C 0.128574
6 C 0.295852
7 C -0.027541
9 C 0.020672
11 C 0.057515
13 C 0.013085
15 C 0.006234
17 C -0.185350
18 C 0.035386
20 C -0.038252
22 C 0.061921
24 C -0.028466
26 C 0.059001
28 C 0.390337
29 C -0.043602
31 C 0.025191
33 C 0.031031
35 C 0.029700
37 C -0.046938
39 B 0.863714
40 C -0.350311

41 C -0.105563
44 C 0.034467
45 C 0.075553
46 C 0.063143
47 C 0.019146
50 C 0.017379
57 C 0.013564

^{1}H, ^{11}B, and $^{13}C\{^{1}H\}$ spectra

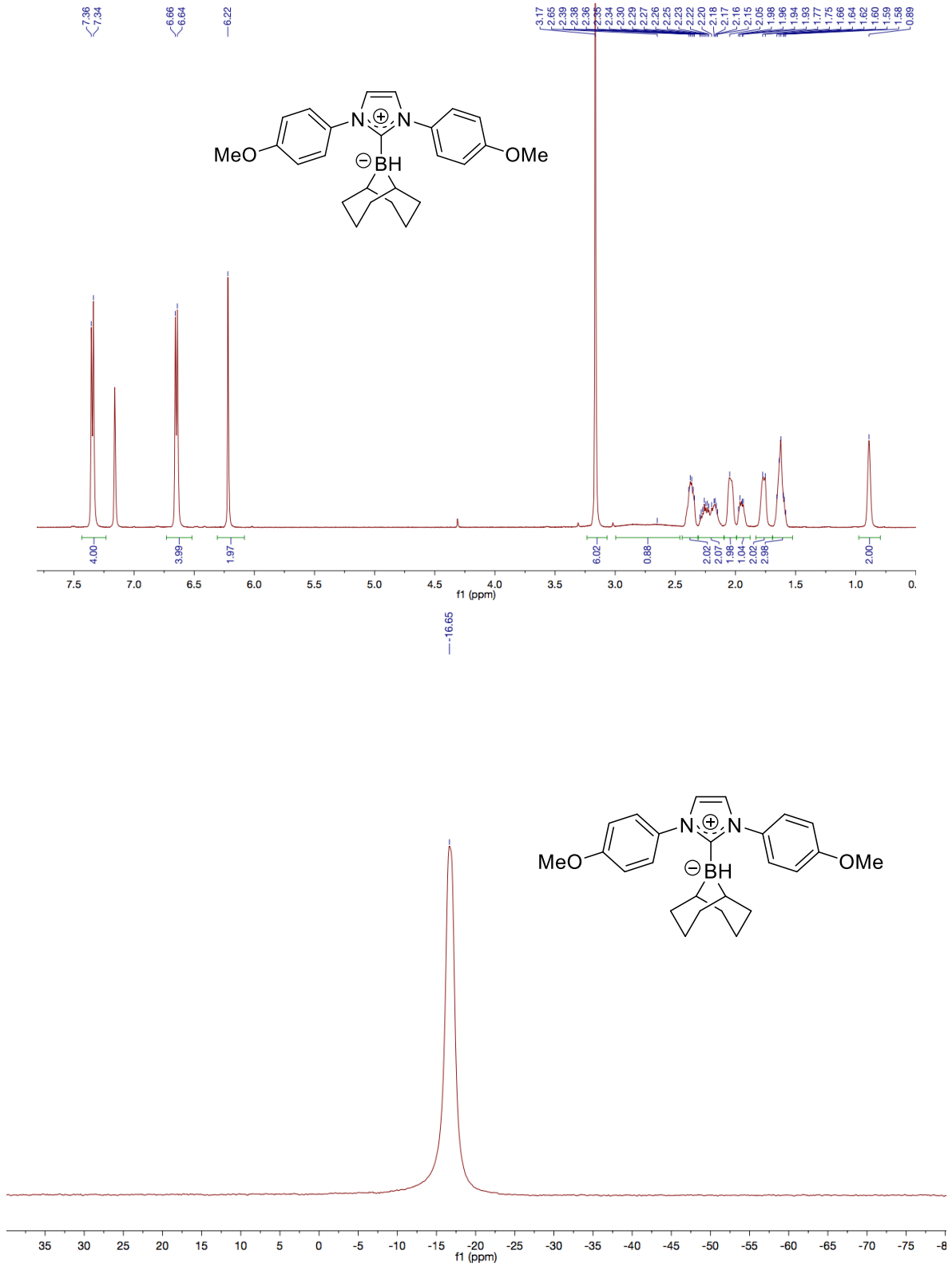


Figure S14: ^{1}H-NMR (500 MHz, top), ^{11}B-NMR (160 MHz, bottom) of compound 2f in C_6D_6

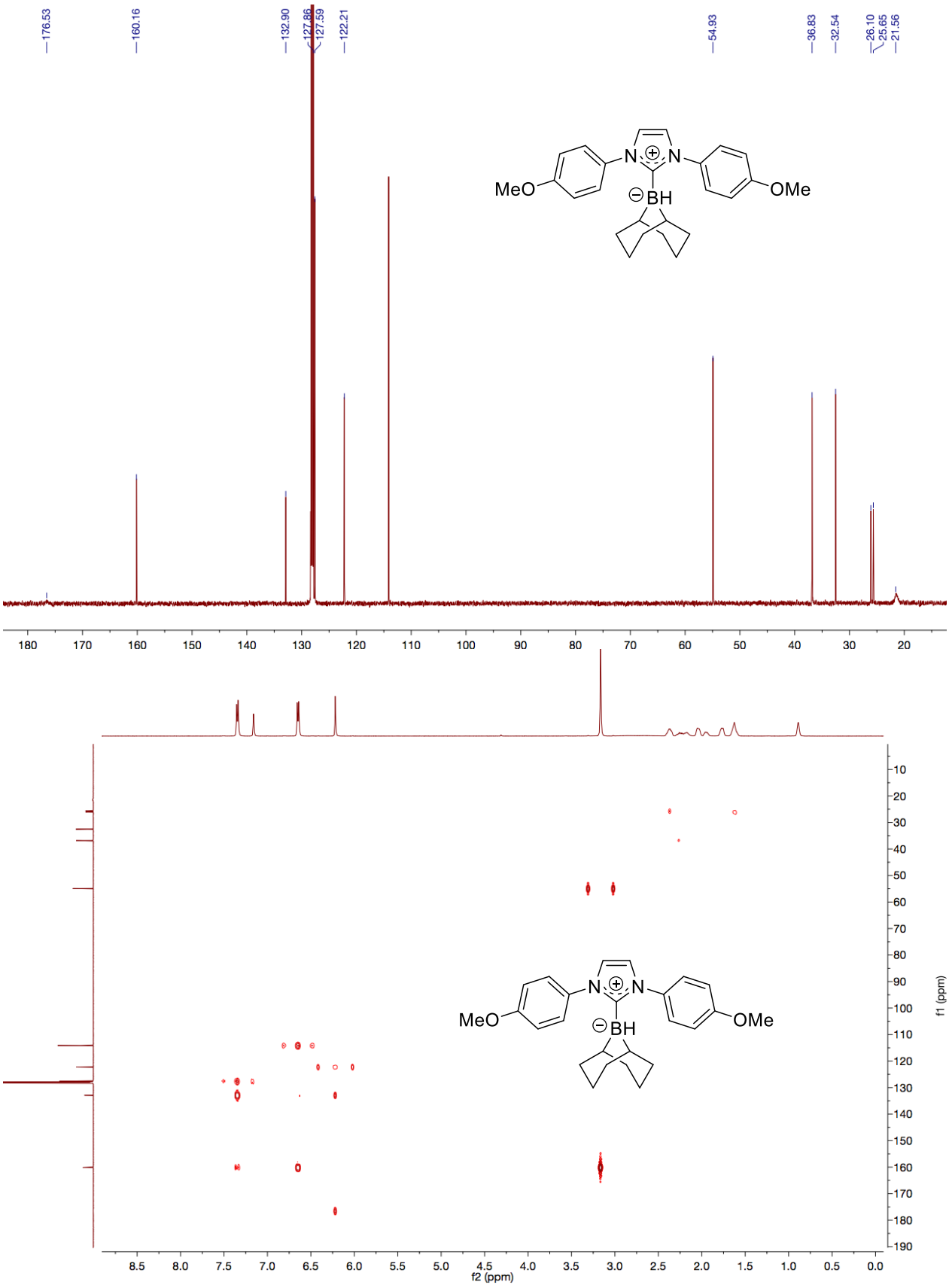


Figure S15: $^{13}C\{^{1}H\}$-NMR (125 MHz, top), HMBC (bottom) of compound 2f in C_6D_6

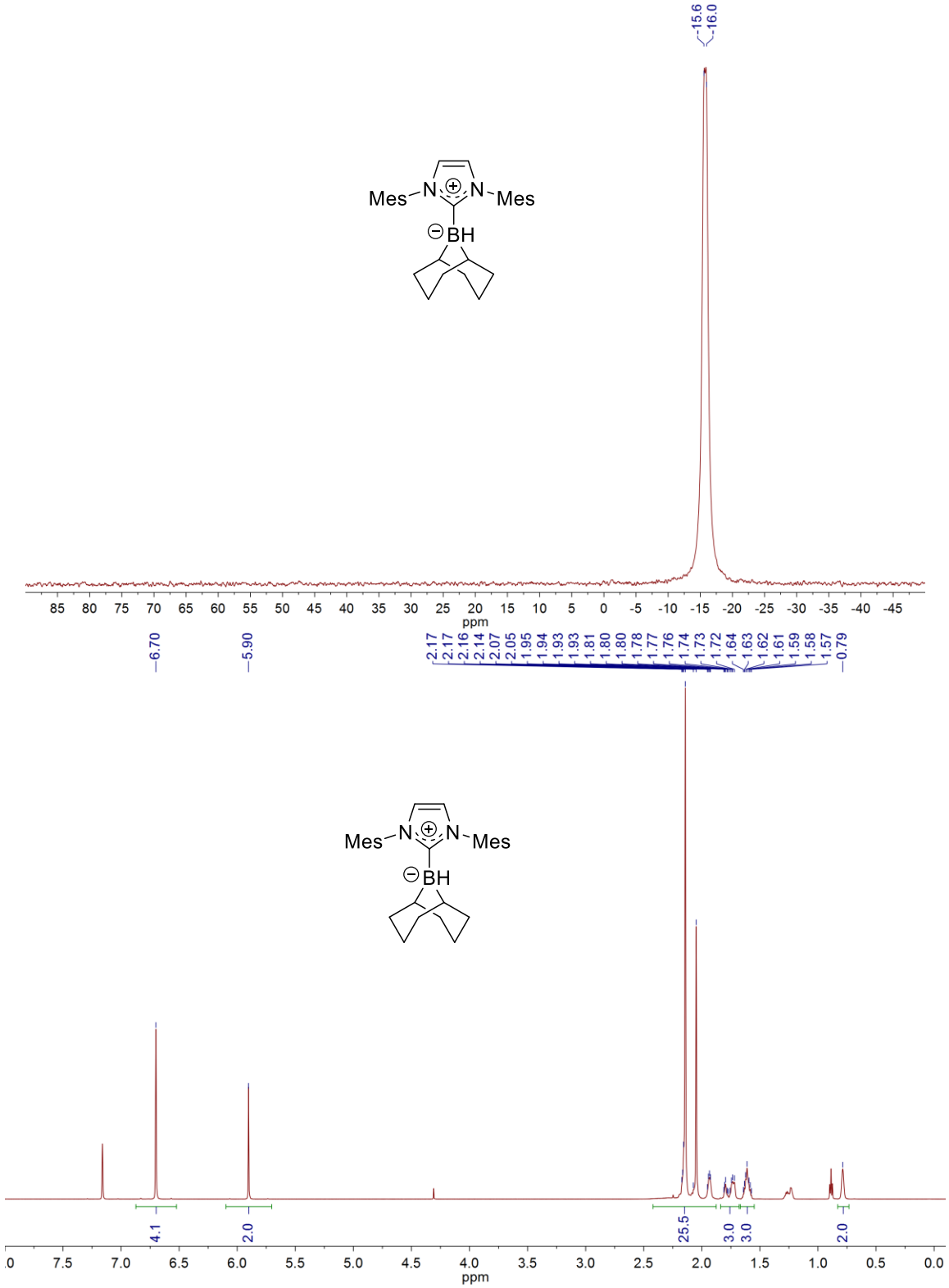


Figure S16: ^{11}B-NMR (160 MHz, top), ^{1}H-NMR (500 MHz, bottom) of compound 2c in C_6D_6

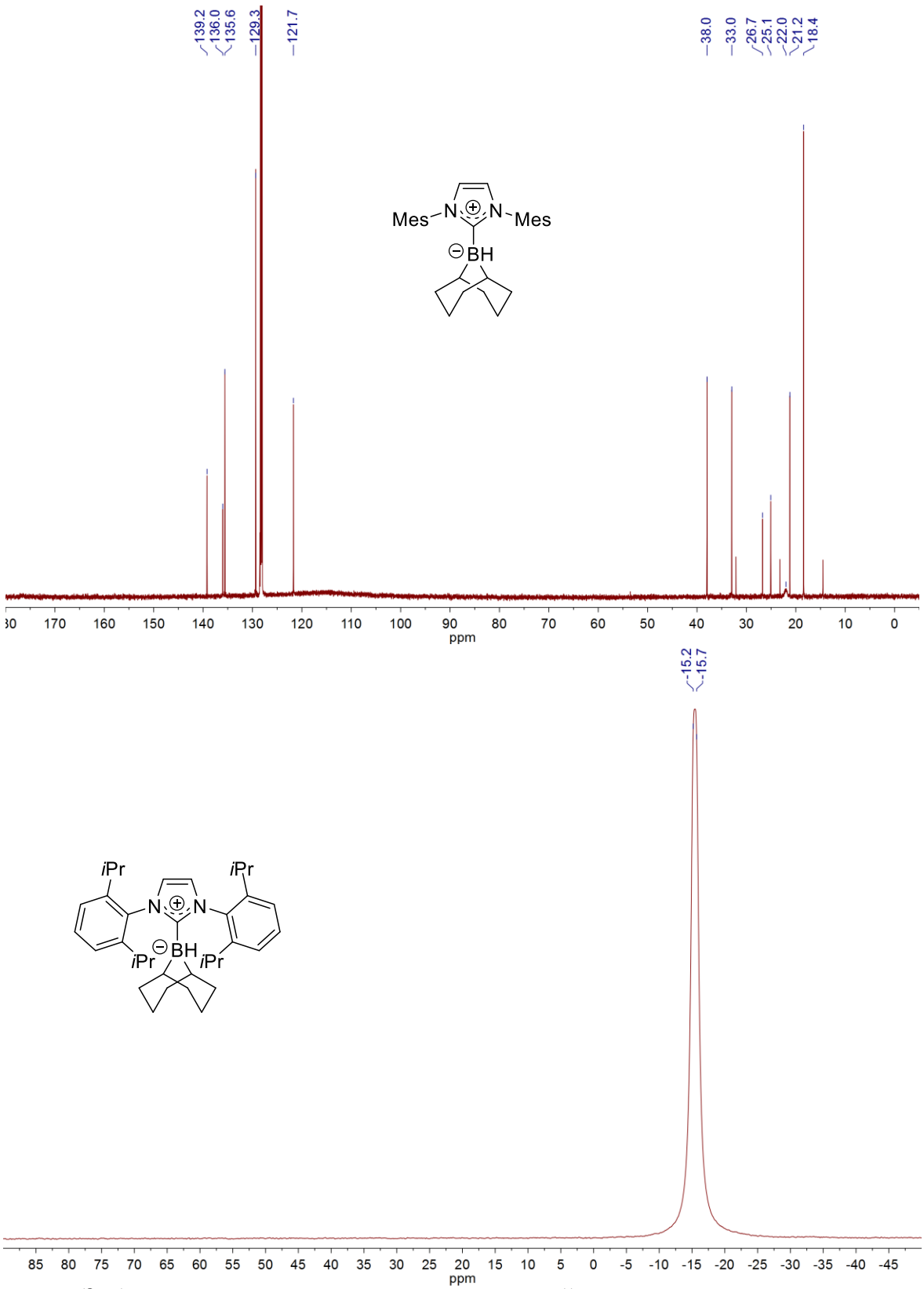


Figure S17: $^{13}C\{^{1}H\}$-NMR (125 MHz, top) of compound 2c in C_6D_6, ^{11}B-NMR (160 MHz, bottom) of compound 2e in C_6D_6

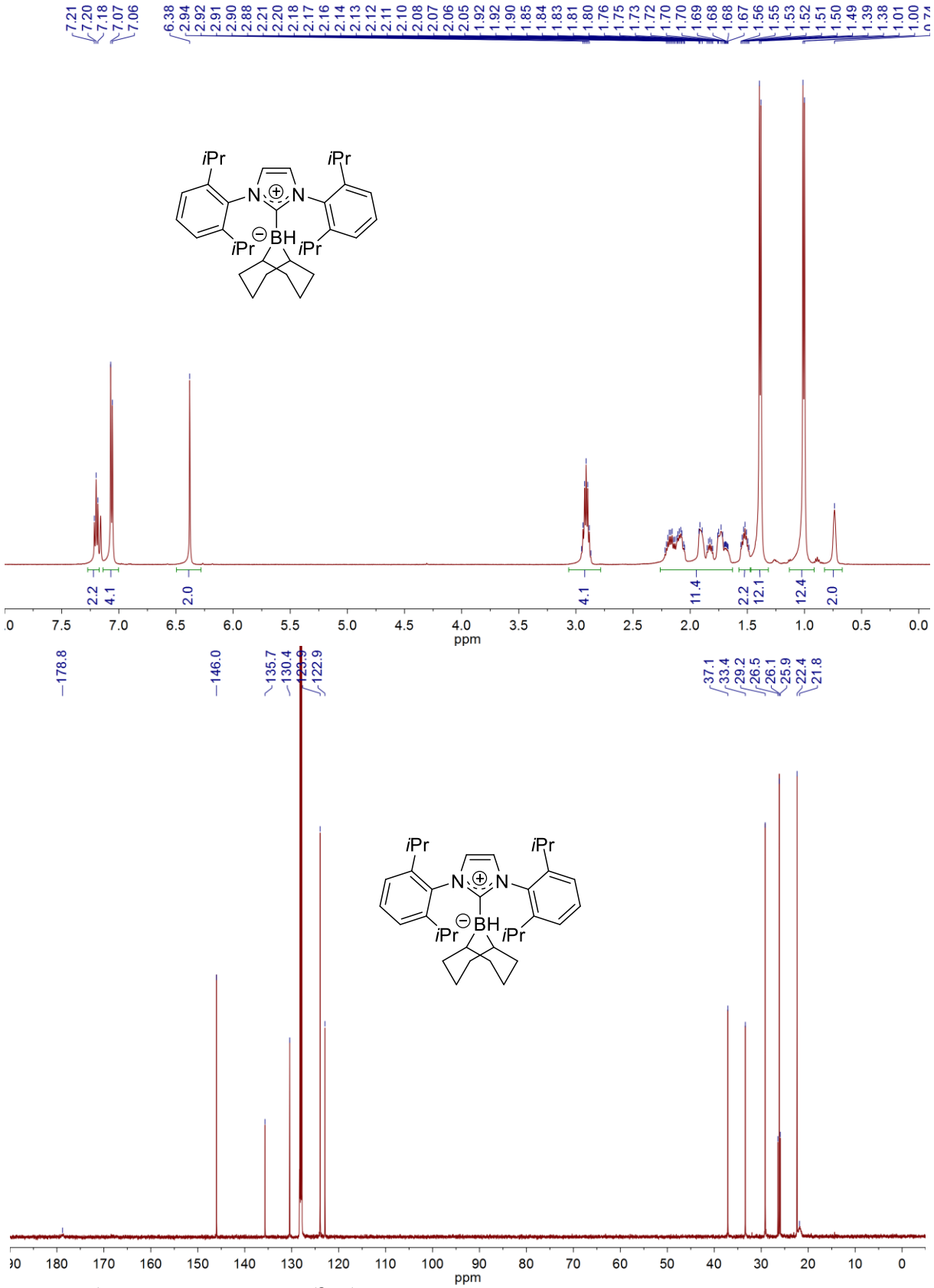


Figure S18: ^{1}H-NMR (500 MHz, top), ^{13}C{^{1}H} -NMR (125 MHz, bottom) of compound 2e in C_6D_6

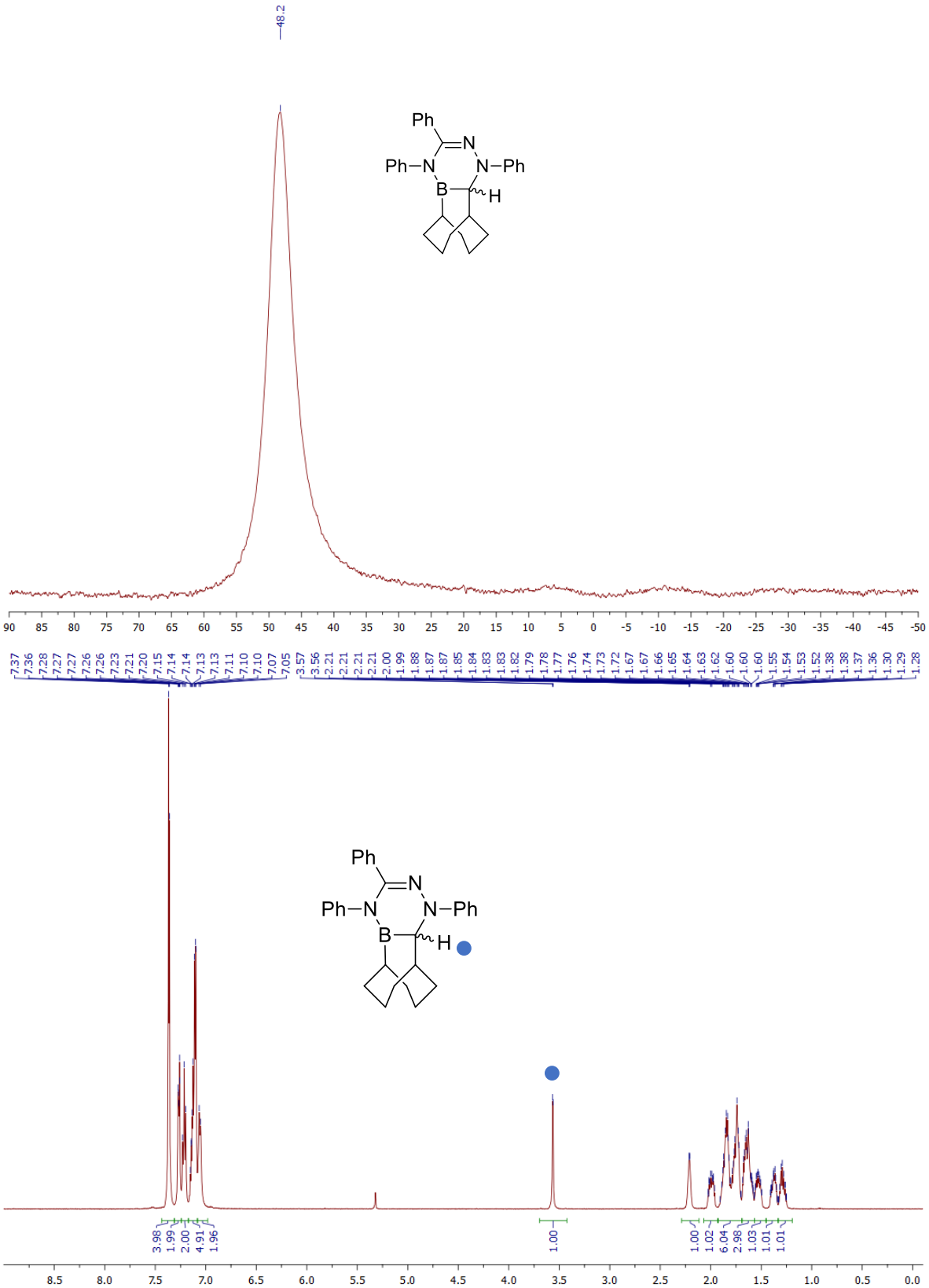


Figure S19: ^{11}B-NMR (160 MHz, top), ^{1}H-NMR (500 MHz, bottom) of compound 3a in CD_2Cl_2

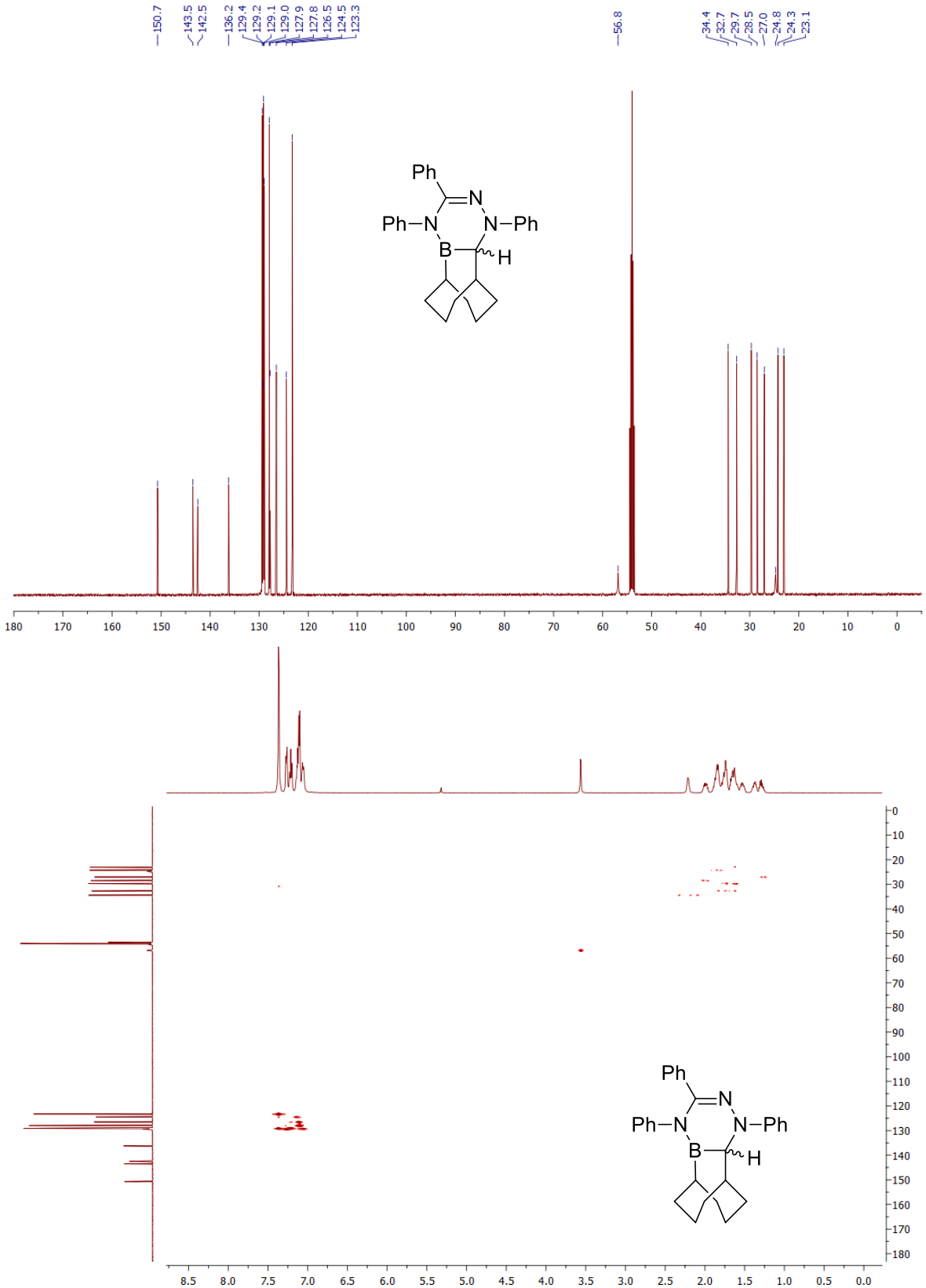


Figure S20: $^{13}C\{^{1}H\}$ NMR (150 MHz, top), HMQC ^{13}C NMR (bottom) of compound 3a in CD_2Cl_2

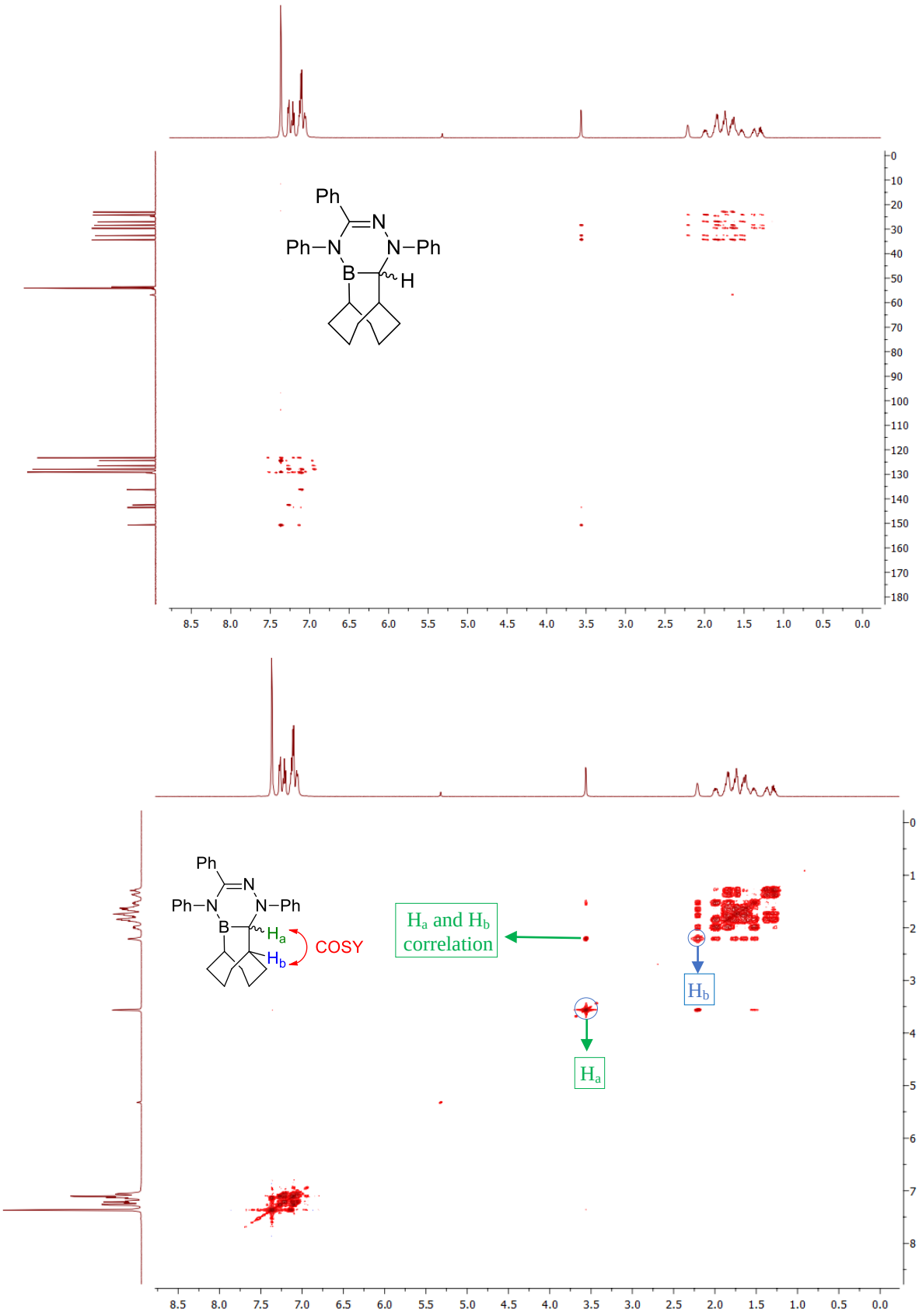


Figure S21: HMBC NMR (top), COSY NMR (bottom) of compound 3a in CD_2Cl_2

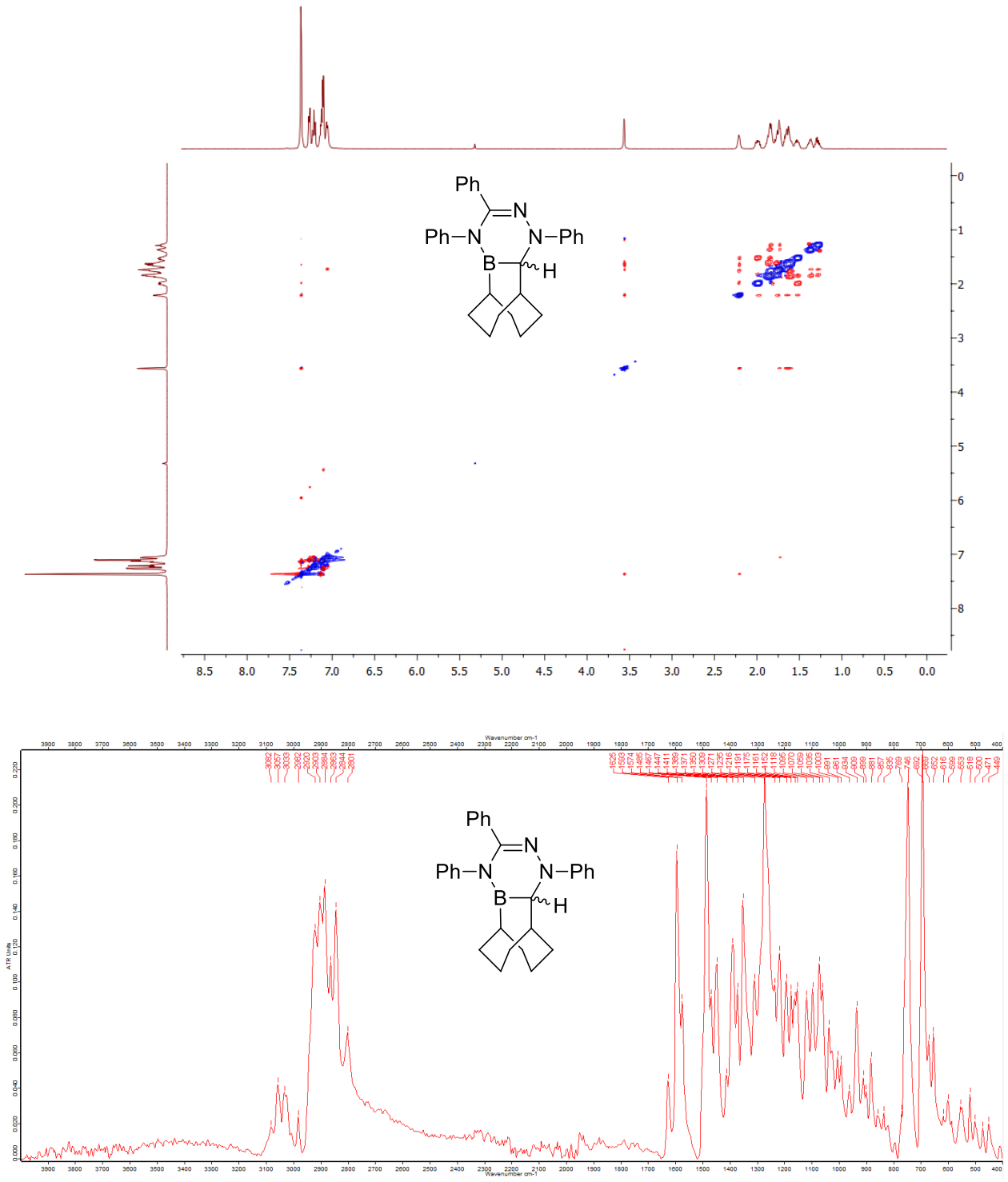


Figure S22: NOESY NMR (top) in CD_2Cl_2, IR spectrum, neat (bottom) of compound 3a

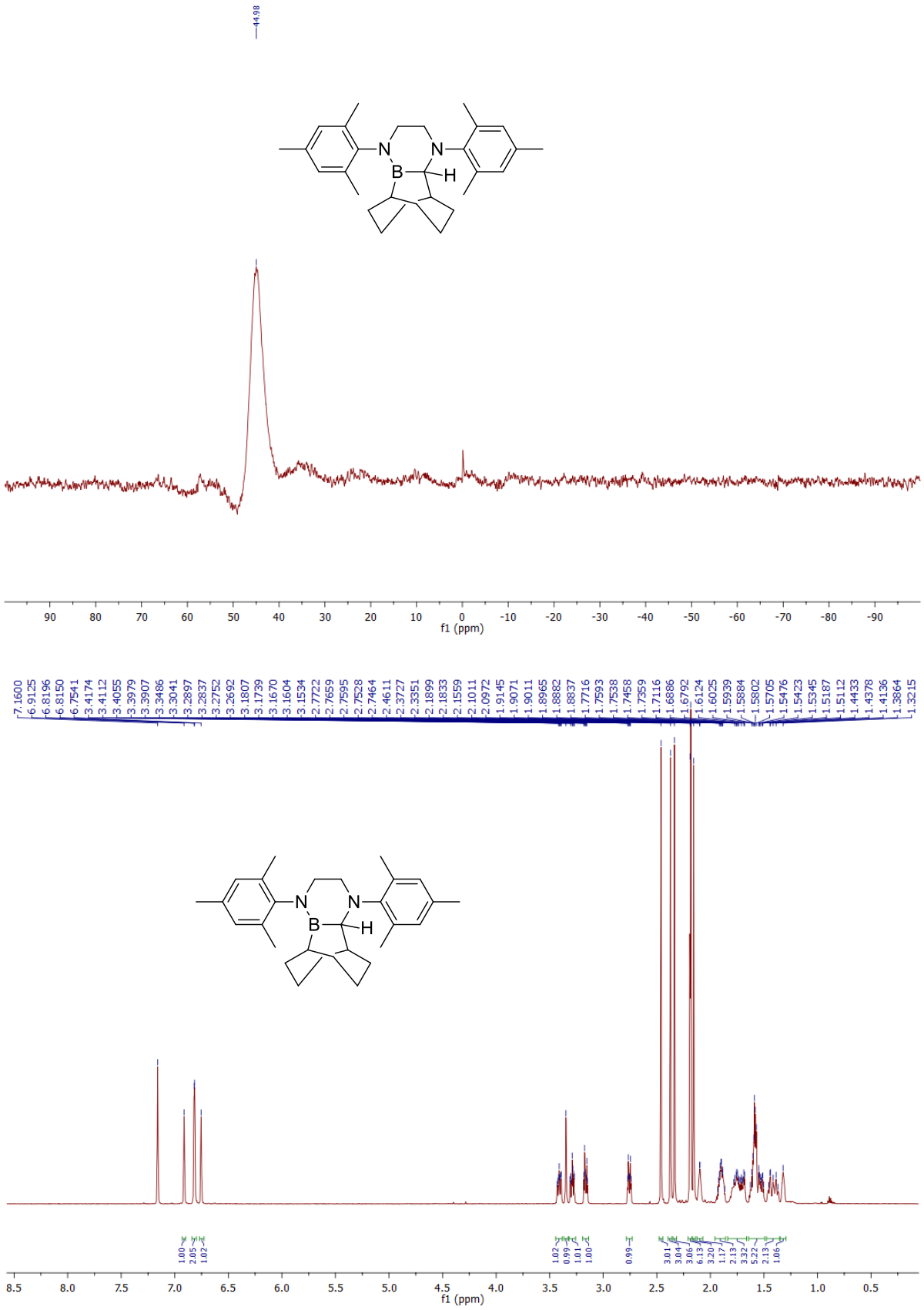


Figure S23: ^{11}B-NMR (192 MHz, top), ^{1}H-NMR (600 MHz, bottom) of compound 3b in C_6D_6

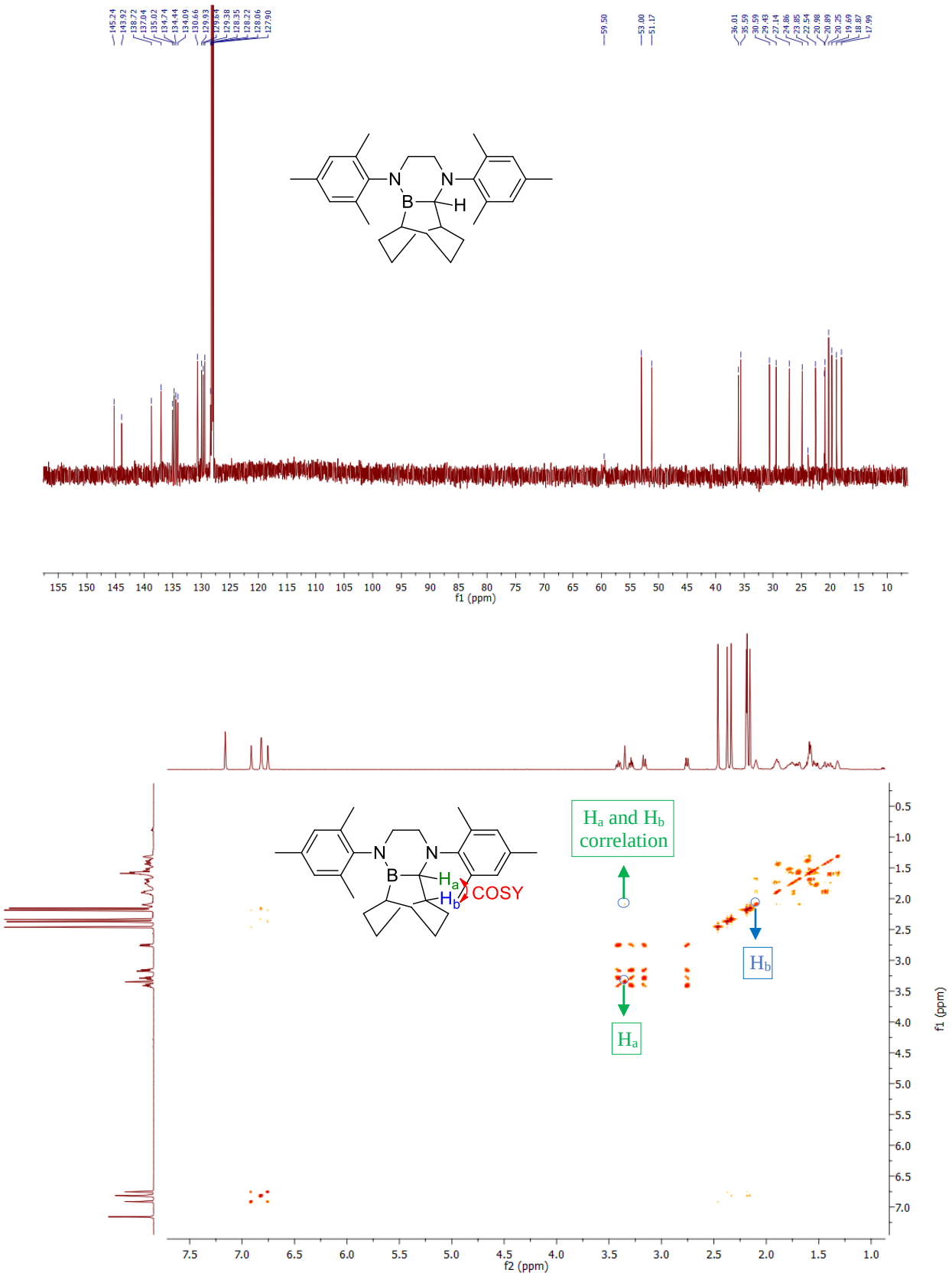


Figure S24: $^{13}C\{^{1}H\}$-NMR (150 MHz, top), COSY NMR (bottom) of compound 3b in C_6D_6

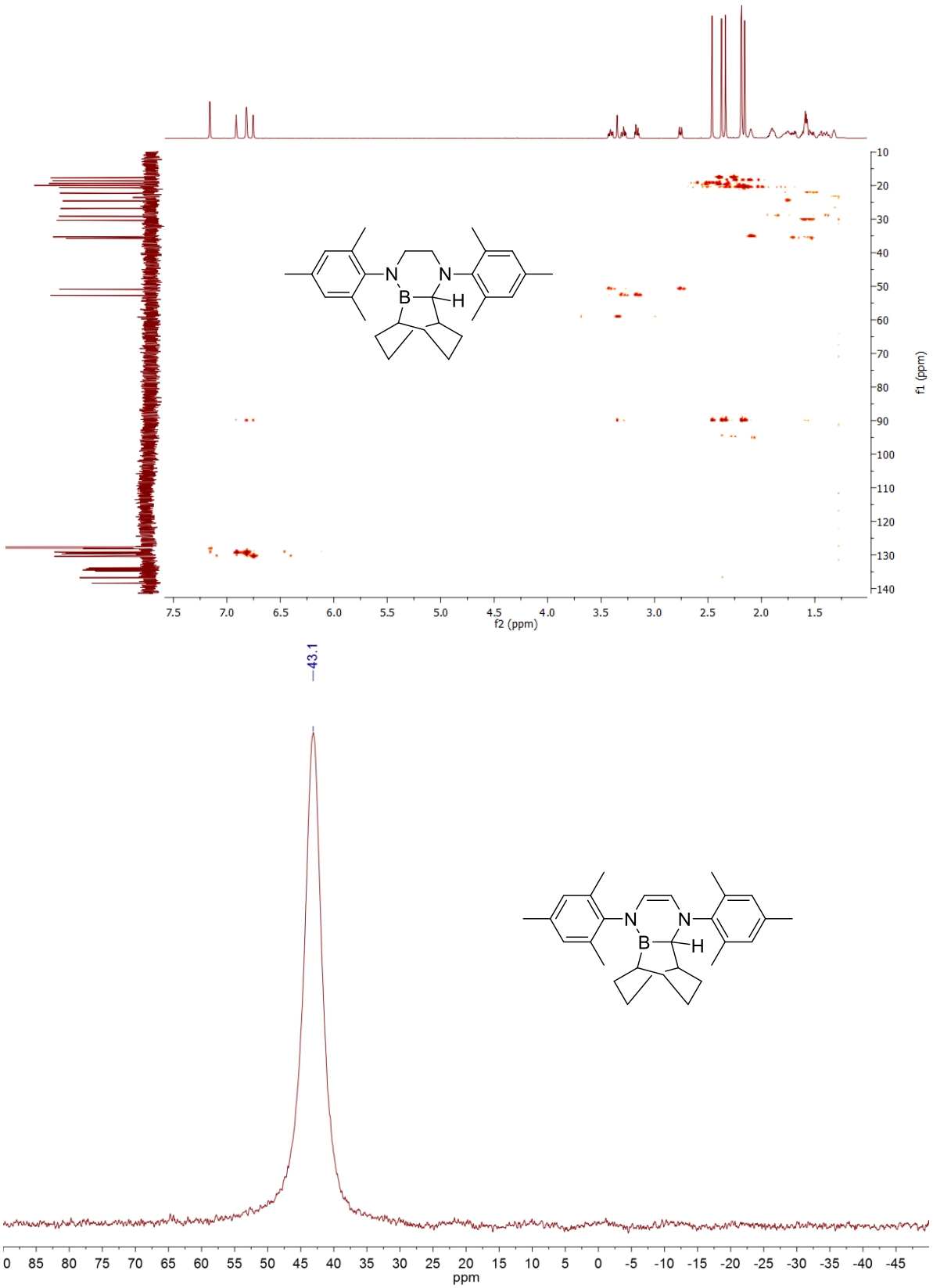


Figure S25: HMQC NMR (top) of 3b in C_6D_6, ^{11}B-NMR (192 MHz, bottom) of compound 3c in CD_2Cl_2

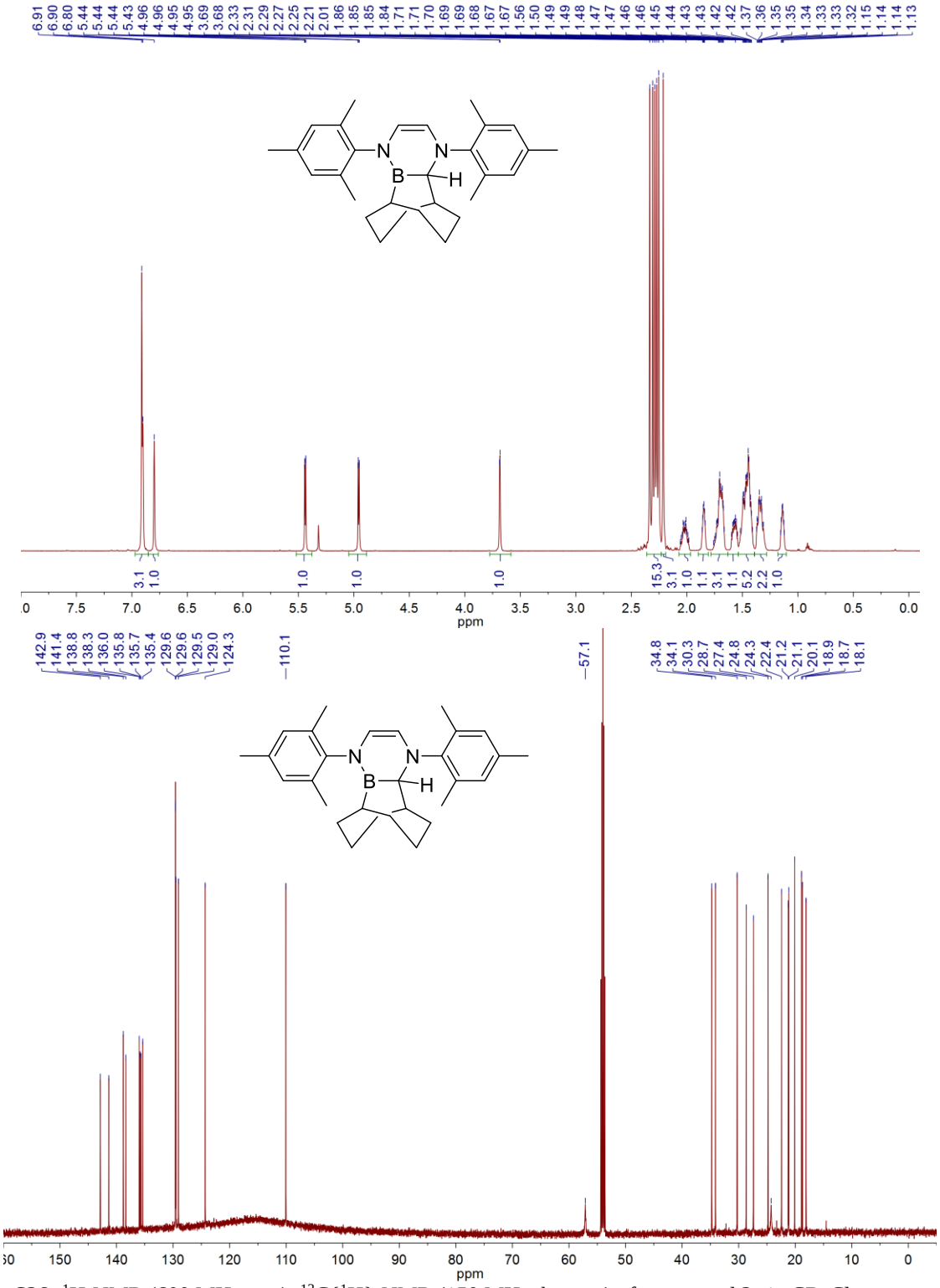


Figure S26: ^{1}H-NMR (600 MHz, top), ^{13}C{^{1}H}-NMR (150 MHz, bottom) of compound 3c in CD_2Cl_2

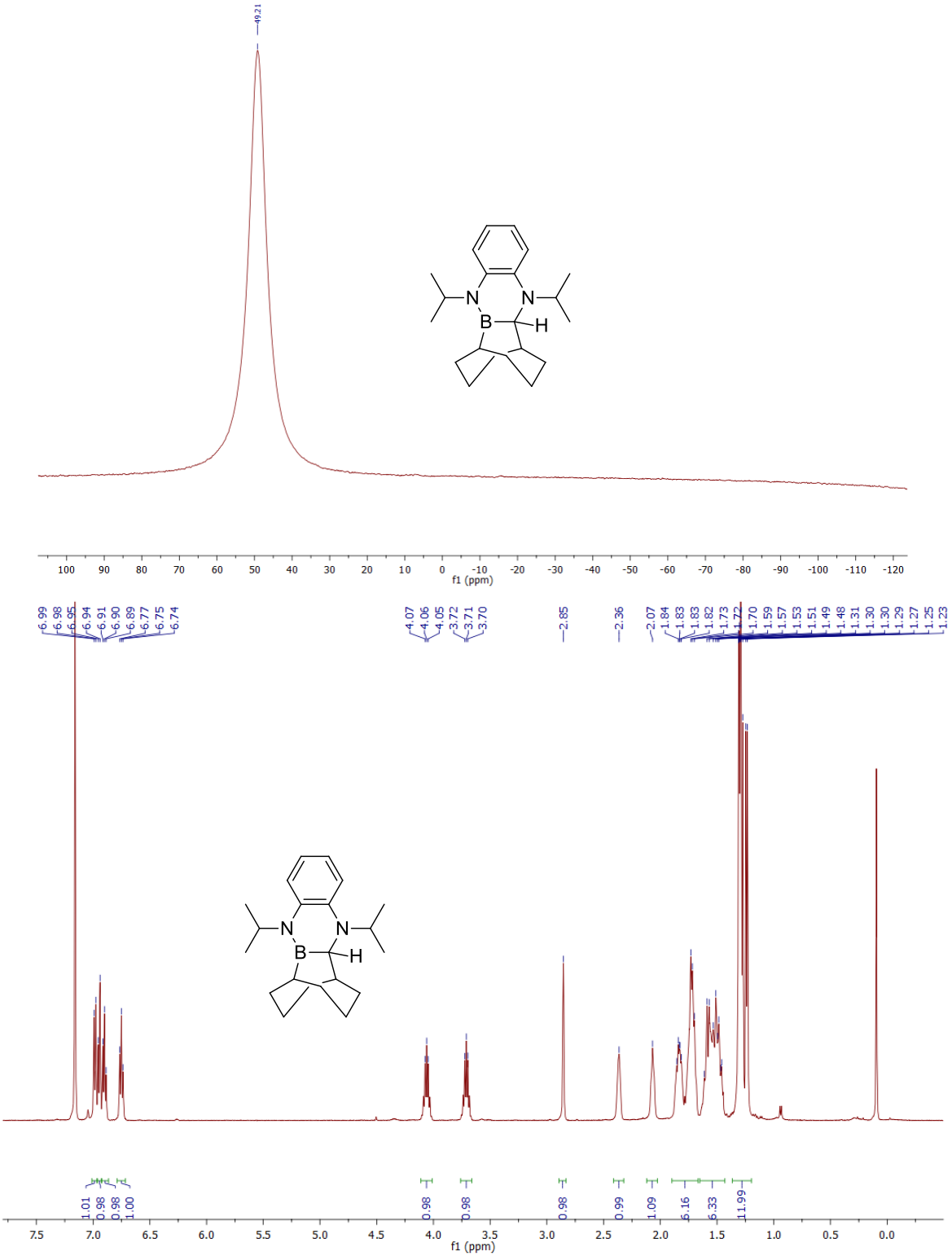


Figure S27: ^{11}B-NMR (160 MHz, top), ^{1}H-NMR (500 MHz, bottom) of compound 3d in C_6D_6

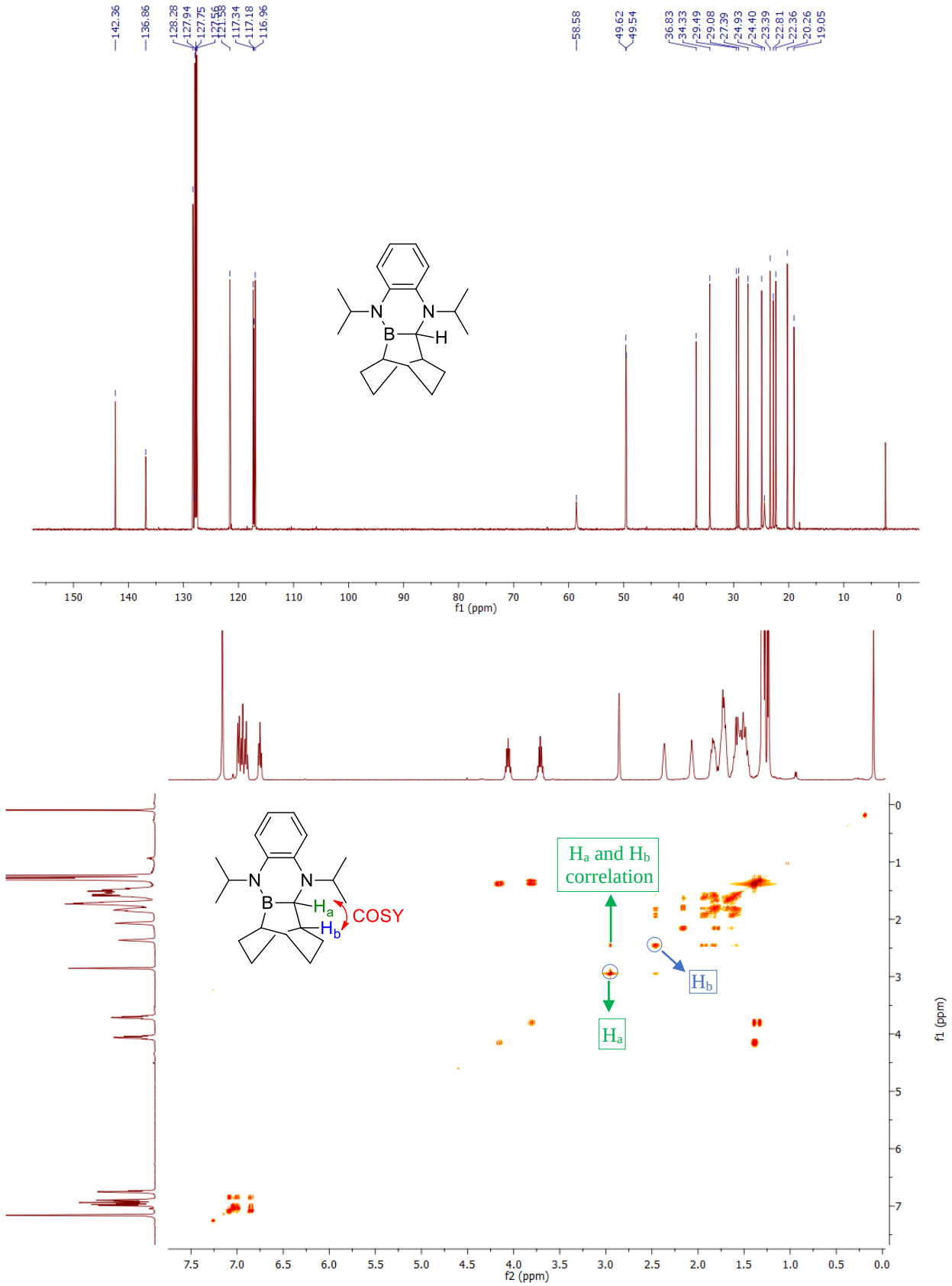


Figure S28: $^{13}C\{^{1}H\}$-NMR (125 MHz, top), COSY NMR (bottom) of compound 3d in C_6D_6

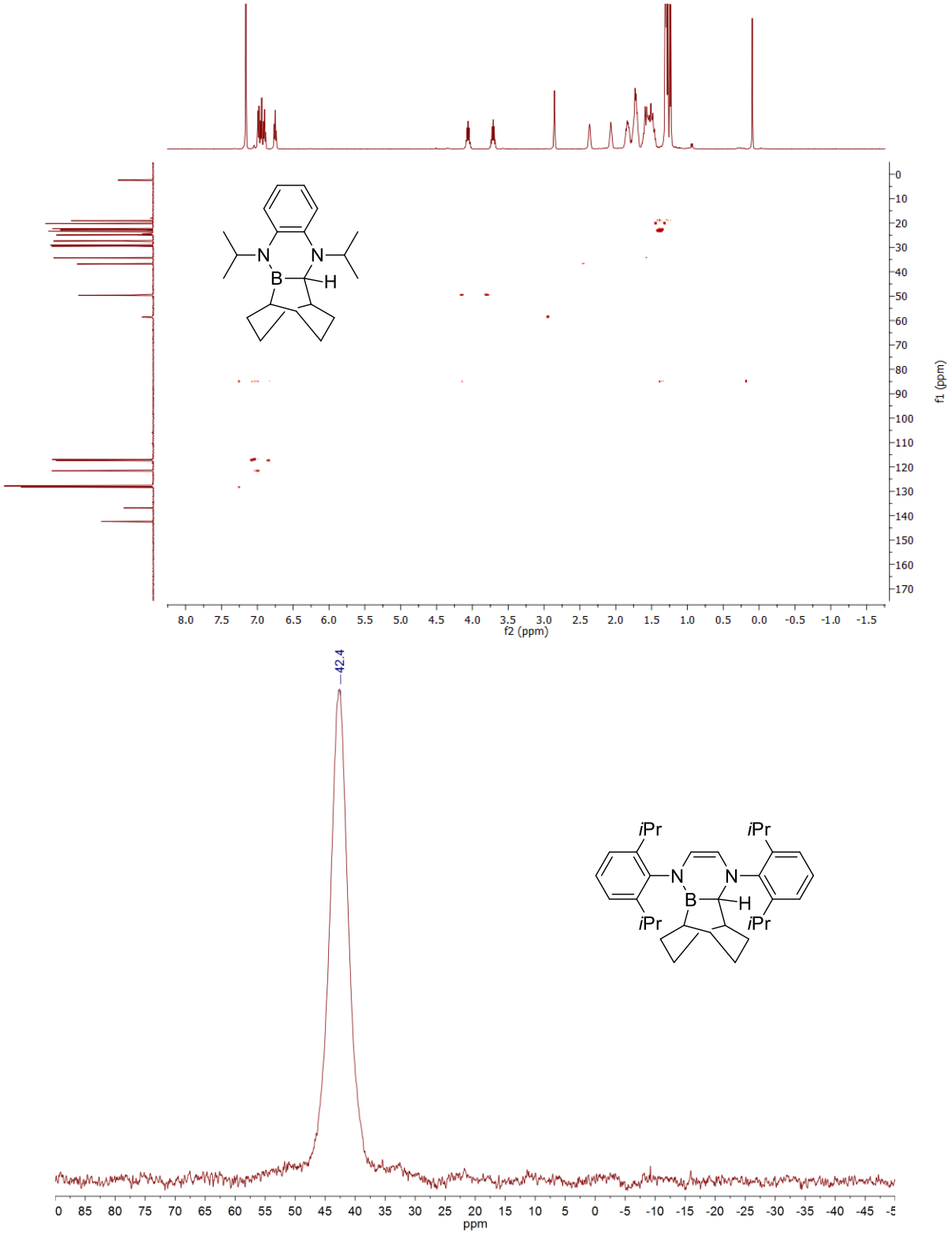


Figure S29: HMQC ^{13}C NMR (top) of compound 3d in C_6D_6, ^{11}B-NMR (192 MHz, bottom) of compound 3e in C_6D_6

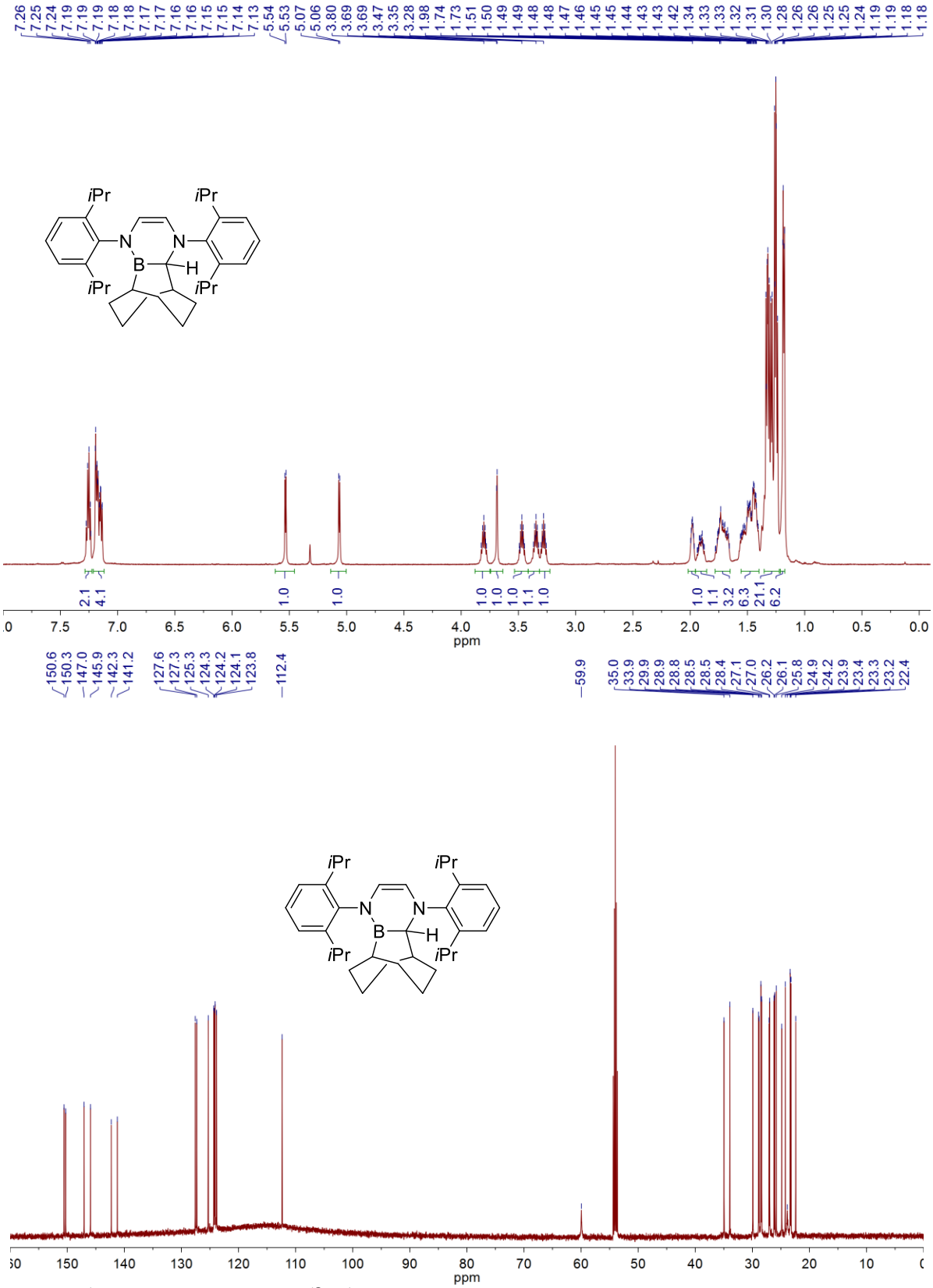


Figure S30: ^{1}H-NMR (600 MHz, top), ^{13}C{^{1}H}-NMR (150 MHz, bottom) of compound 3e in C_6D_6

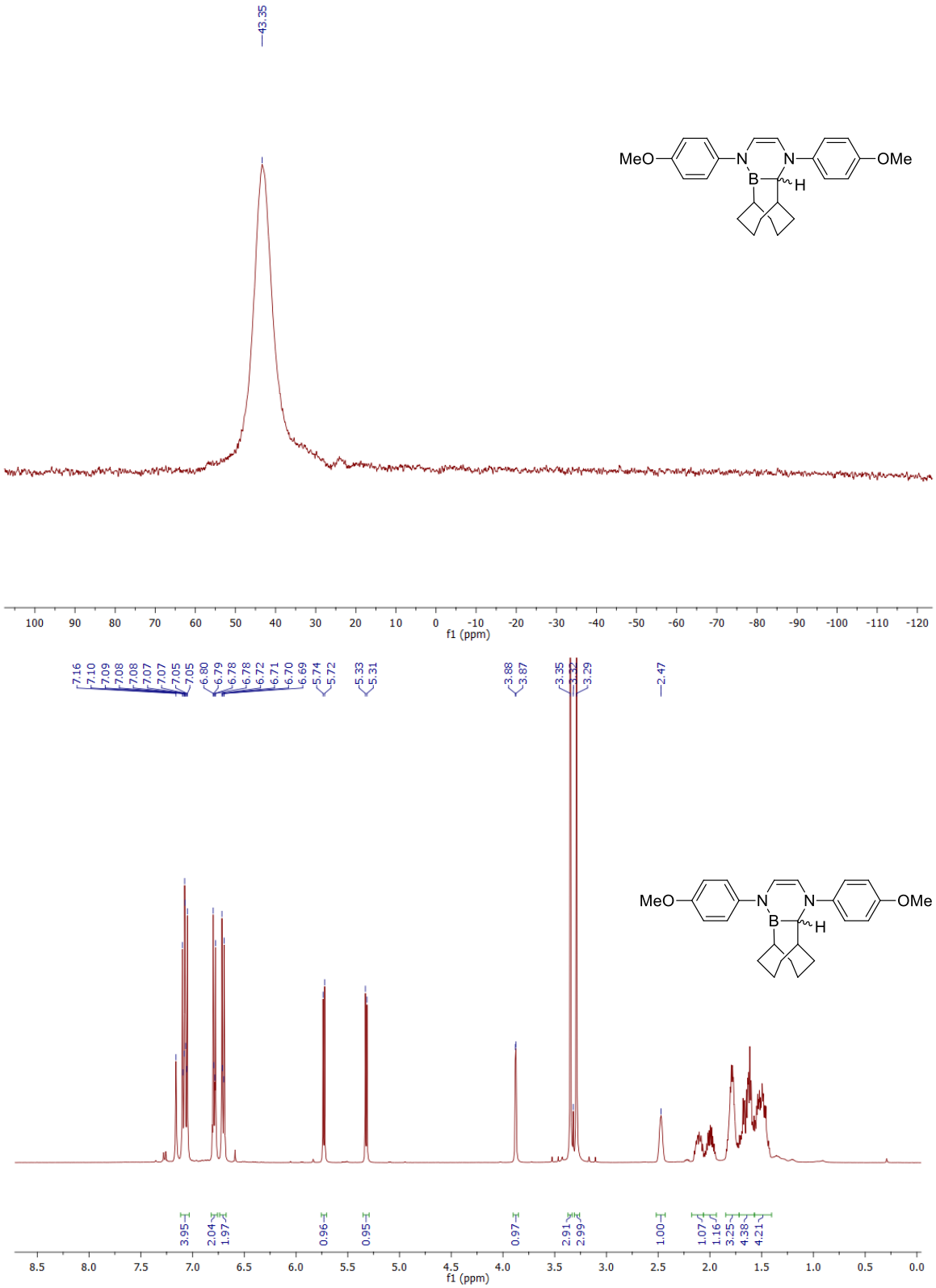


Figure S31: ^{11}B-NMR (160 MHz, top), ^{1}H-NMR (400 MHz, bottom) of compound 3f in C_6D_6

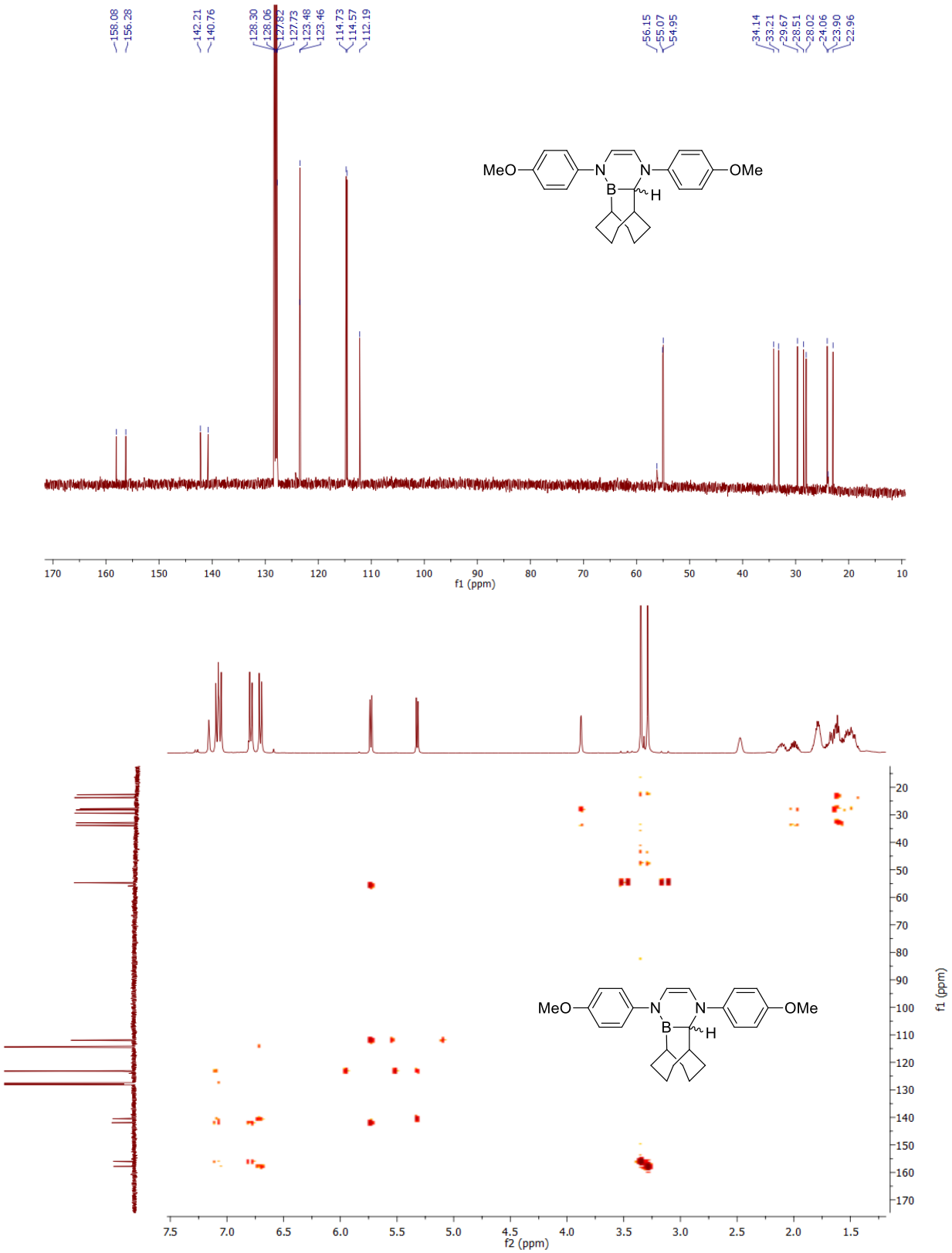


Figure S32: $^{13}C\{^{1}H\}$-NMR (100 MHz, top), COSY NMR (bottom) of compound 3f in C_6D_6

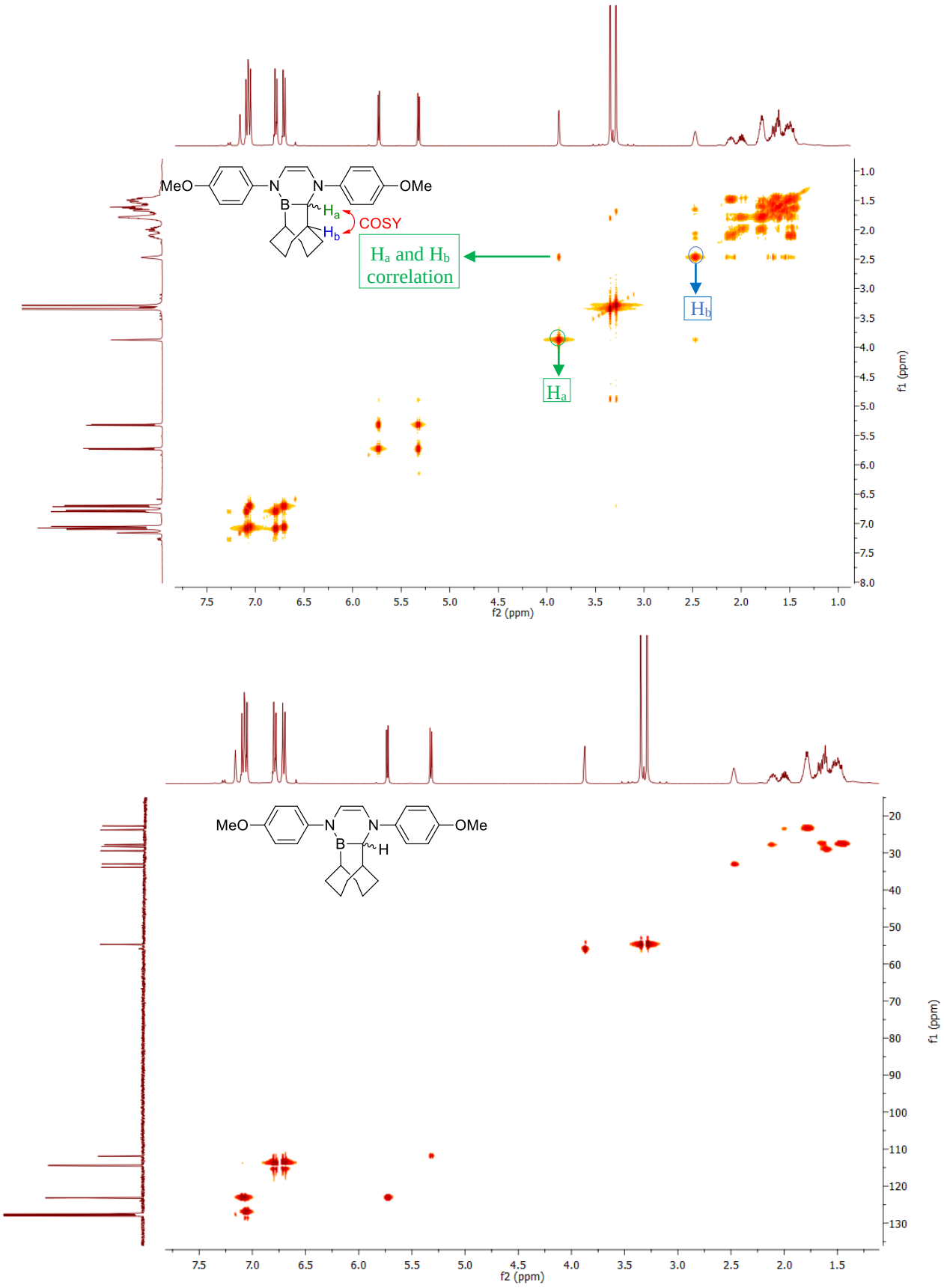


Figure S33: COSY NMR (top), HSQC ^{13}C NMR (bottom) of compound 3f in C_6D_6

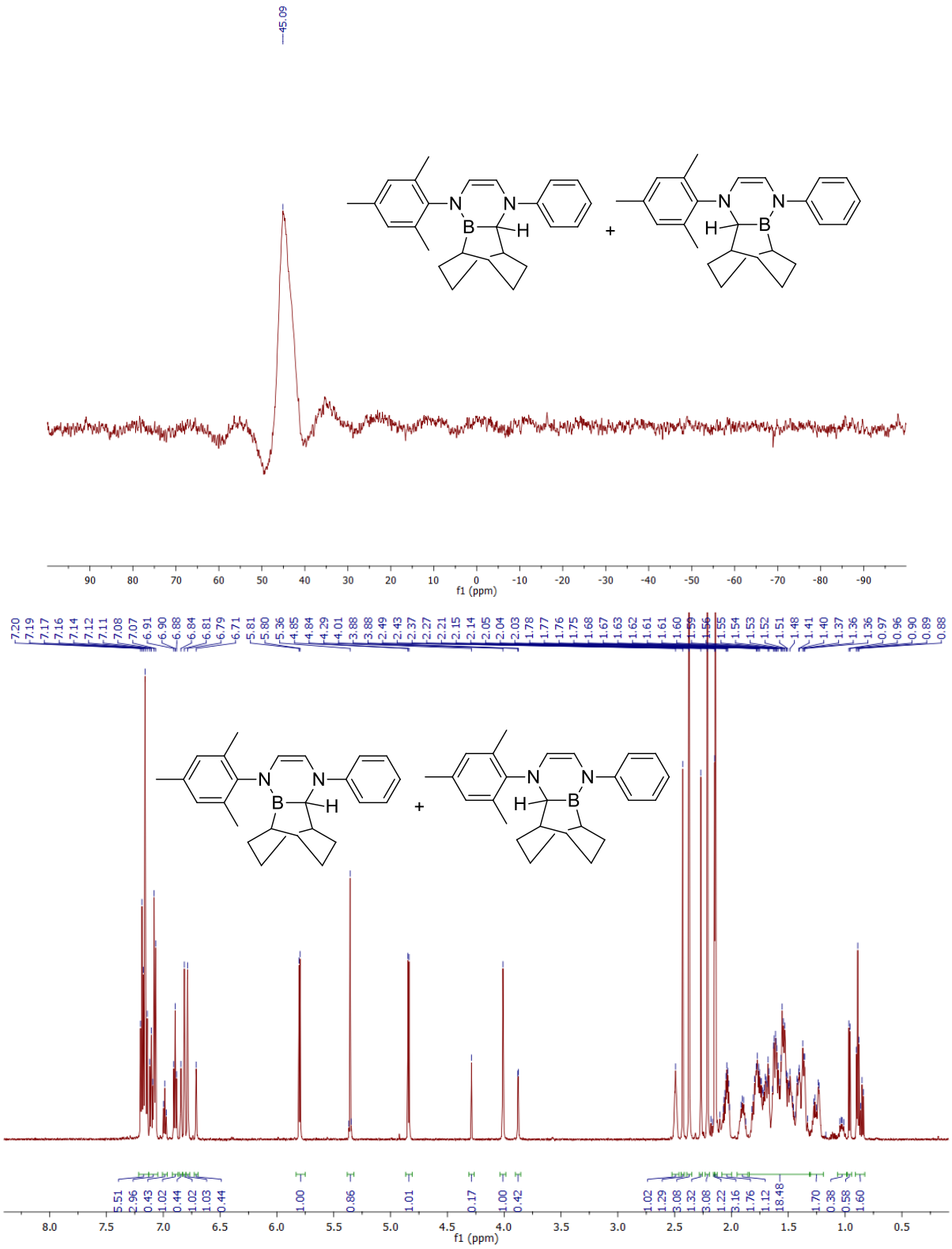


Figure S34: ^{11}B-NMR (192 MHz, top), HSQC ^{13}C NMR (bottom) of compound 3gA and 3gB in C_6D_6

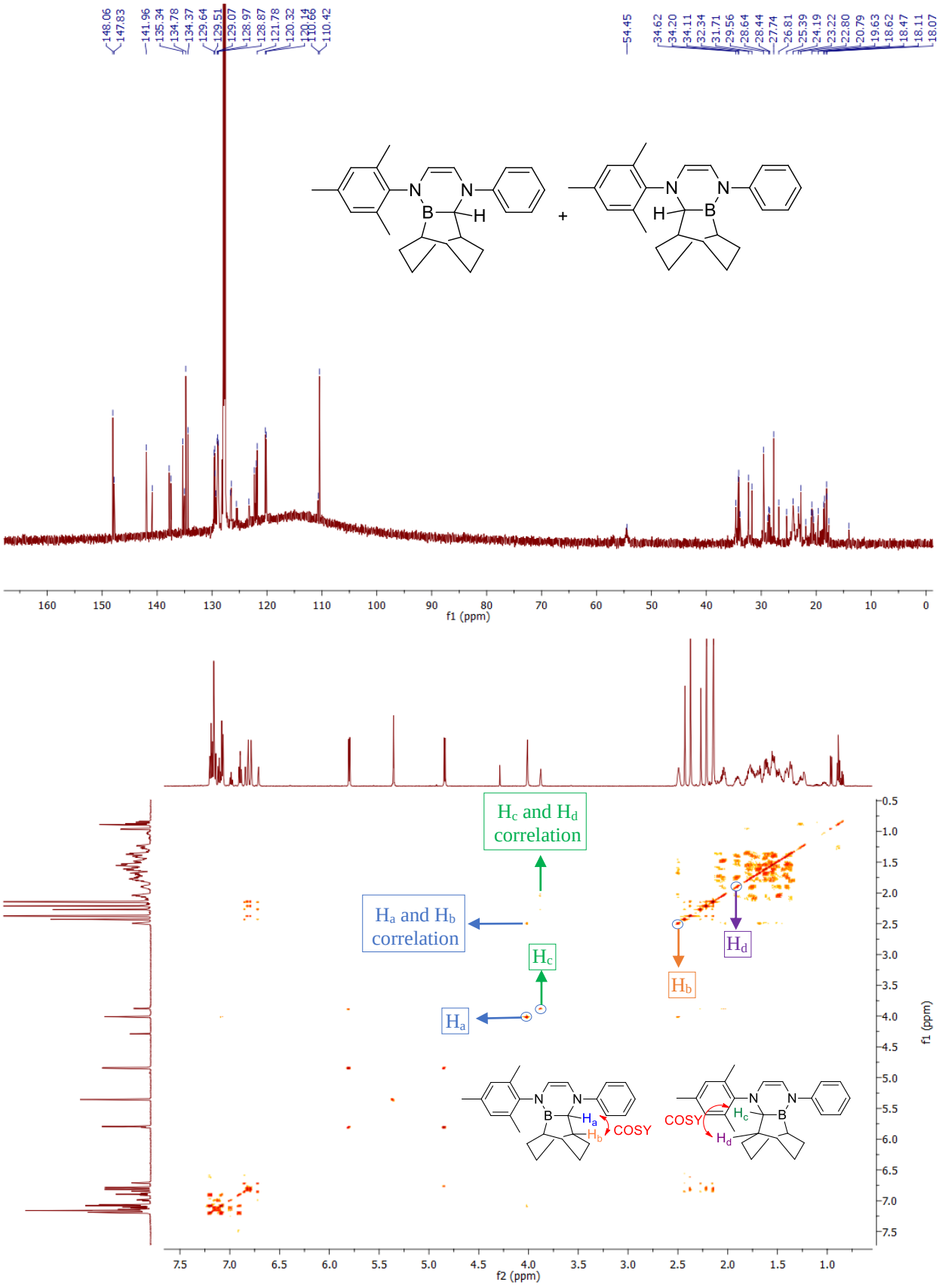


Figure S35: $^{13}C\{^{1}H\}$ -NMR (150 MHz, top), COSY NMR (bottom) of compound 3gA and 3gB in C_6D_6

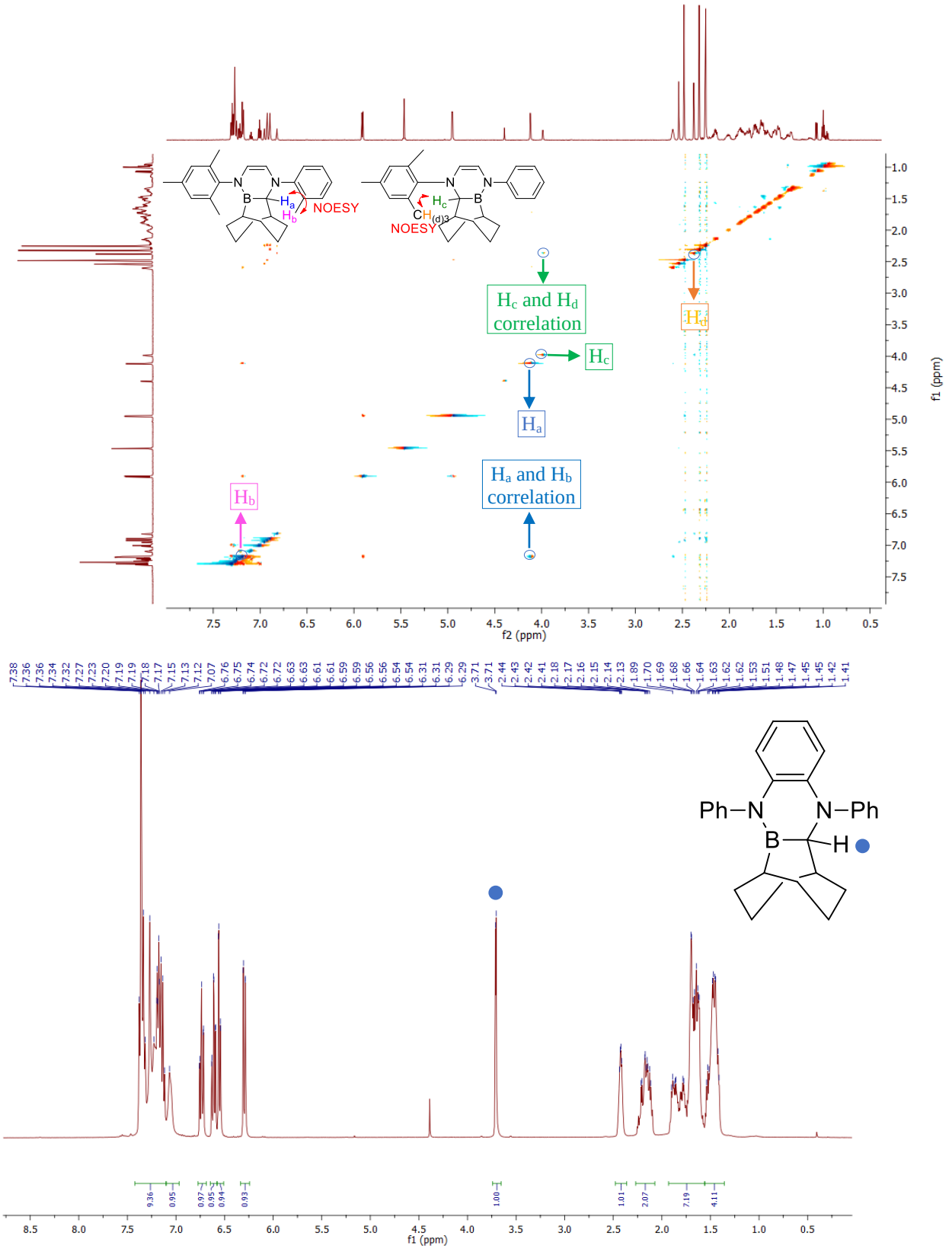


Figure S36: NOESY-NMR (top) of compounds 3gA and 3gB, ^{1}H-NMR (600 MHz, bottom) of compound 3h in C_6D_6

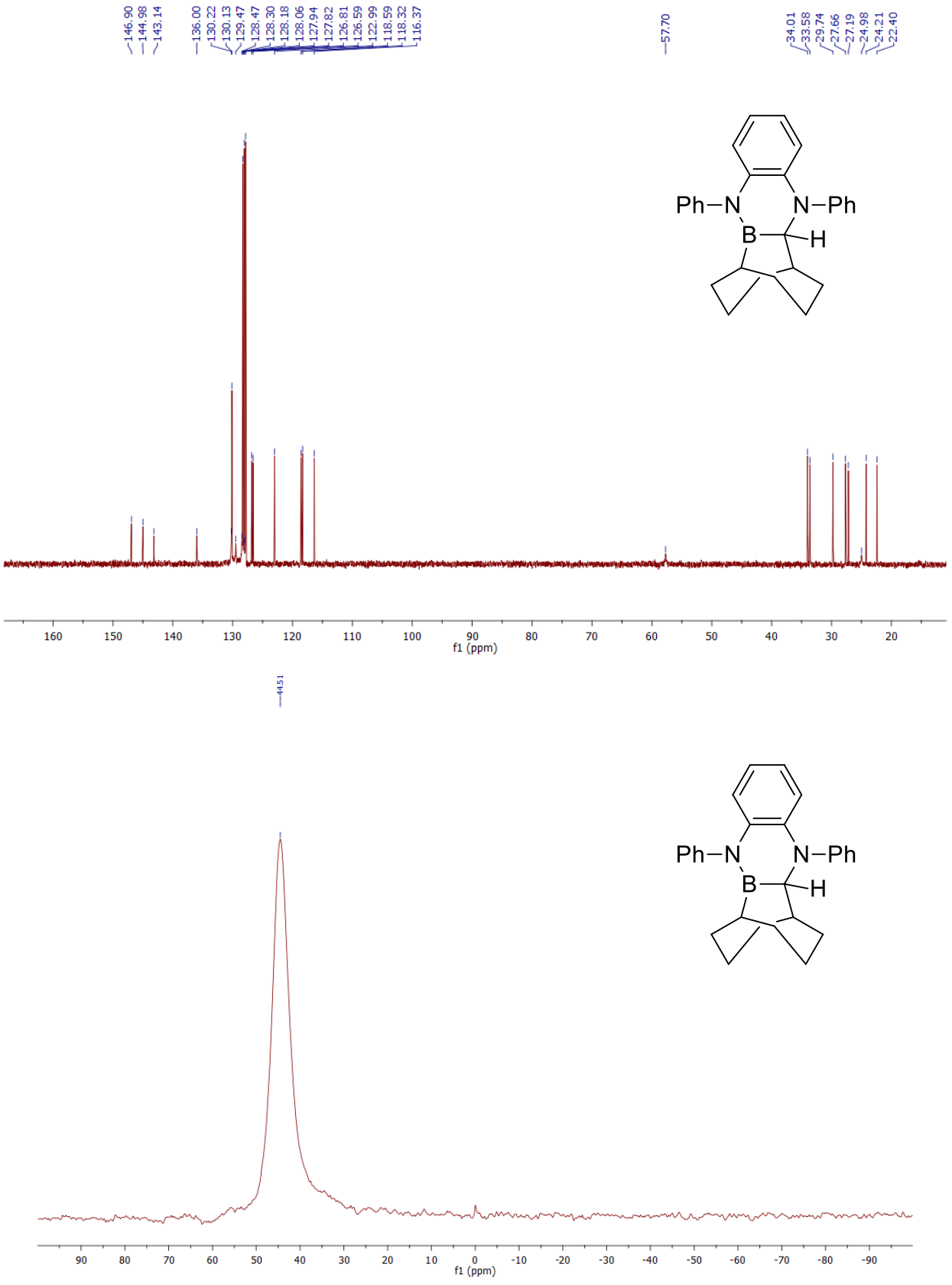


Figure S37: $^{13}C\{^{1}H\}$-NMR (150 MHz, top), ^{11}B-NMR (192 MHz, bottom) of compound 3h in C_6D_6

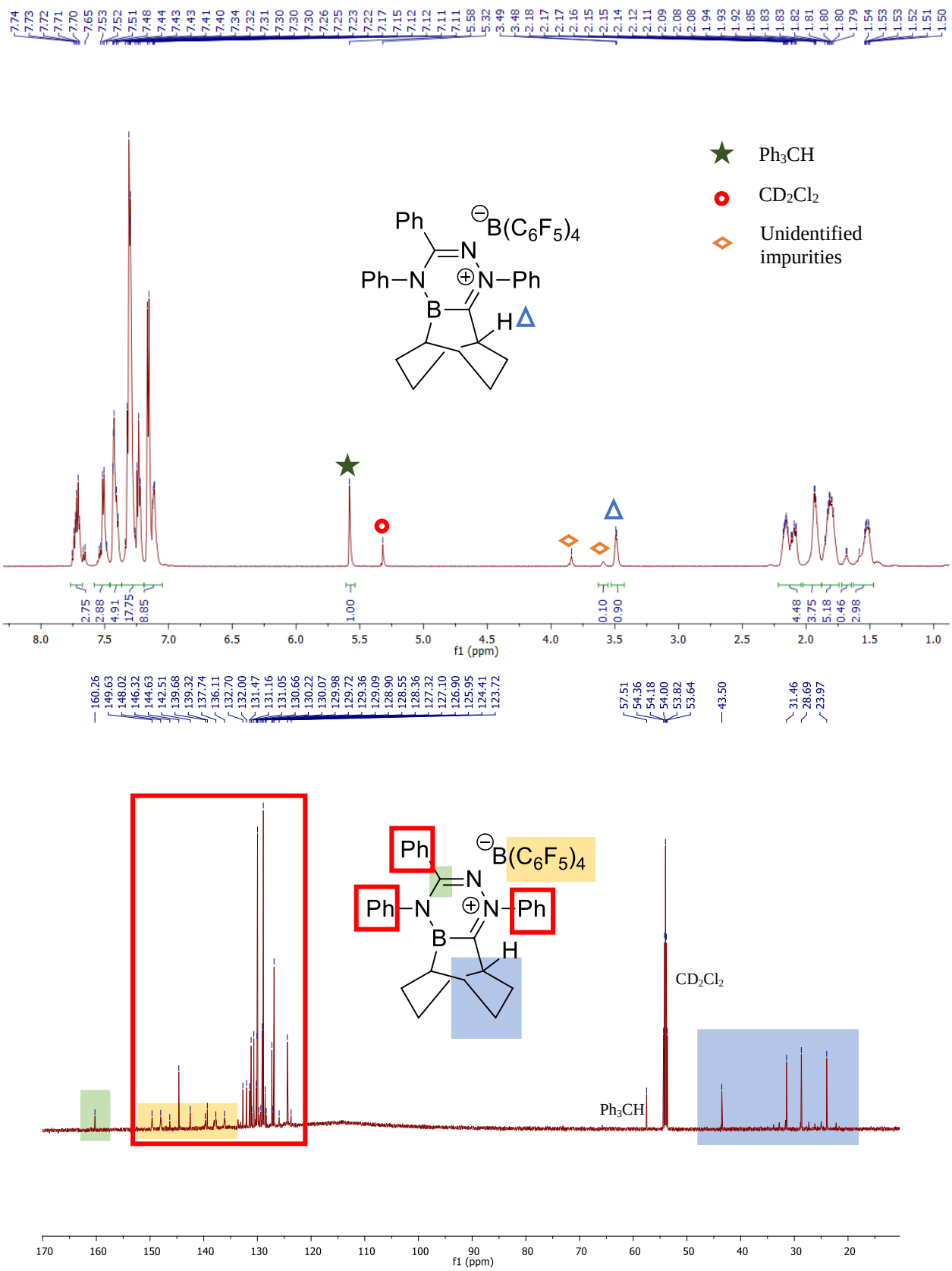


Figure S38: ^{1}H-NMR (600 MHz, top), ^{13}C{^{1}H}-NMR (150 MHz, bottom) of compound 4a in CD_2Cl_2 without purification.

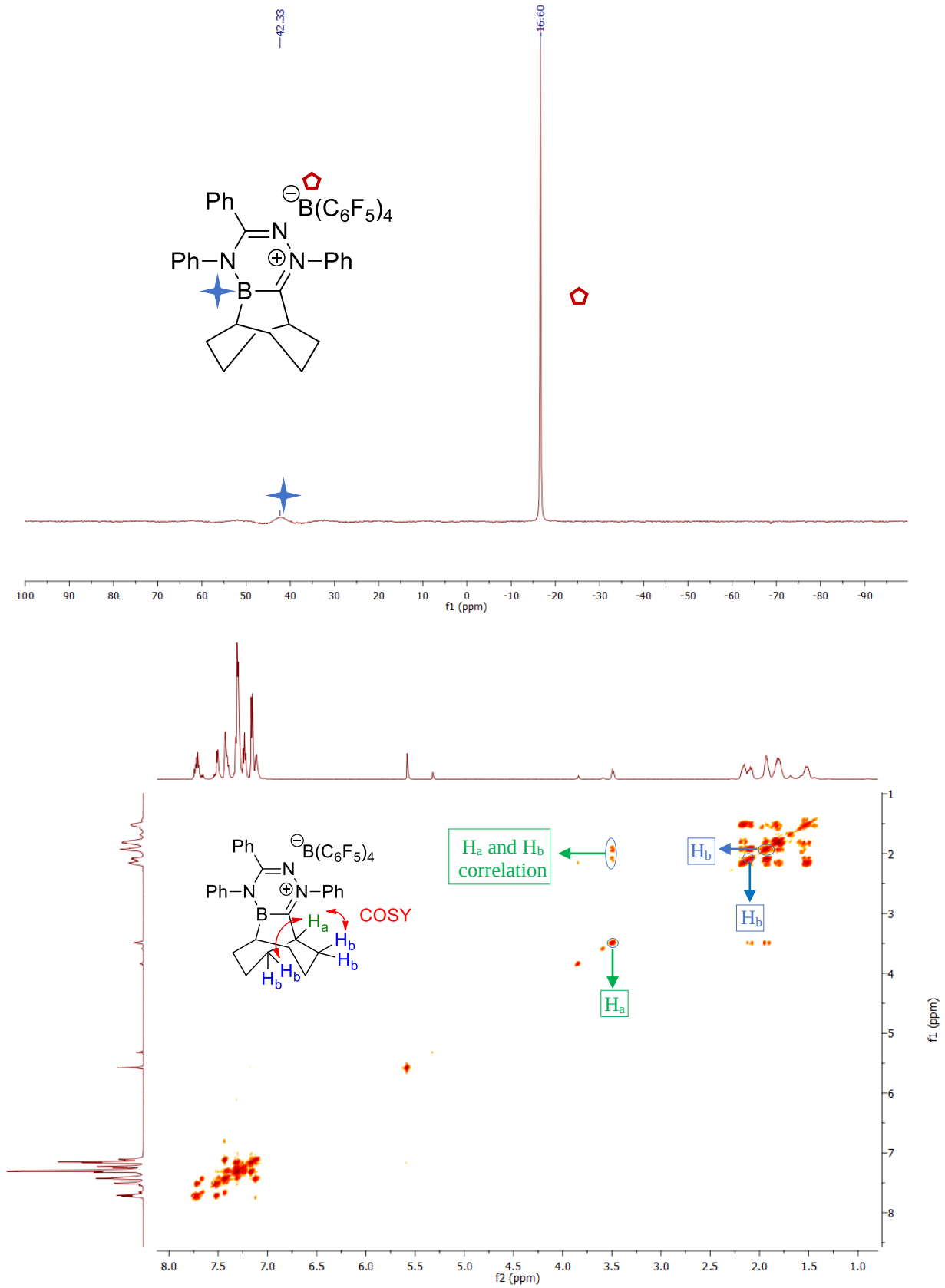


Figure S39: ^{11}B-NMR (192 MHz, top), COSY-NMR (bottom) of compound 4a in CD_2Cl_2 without purification.

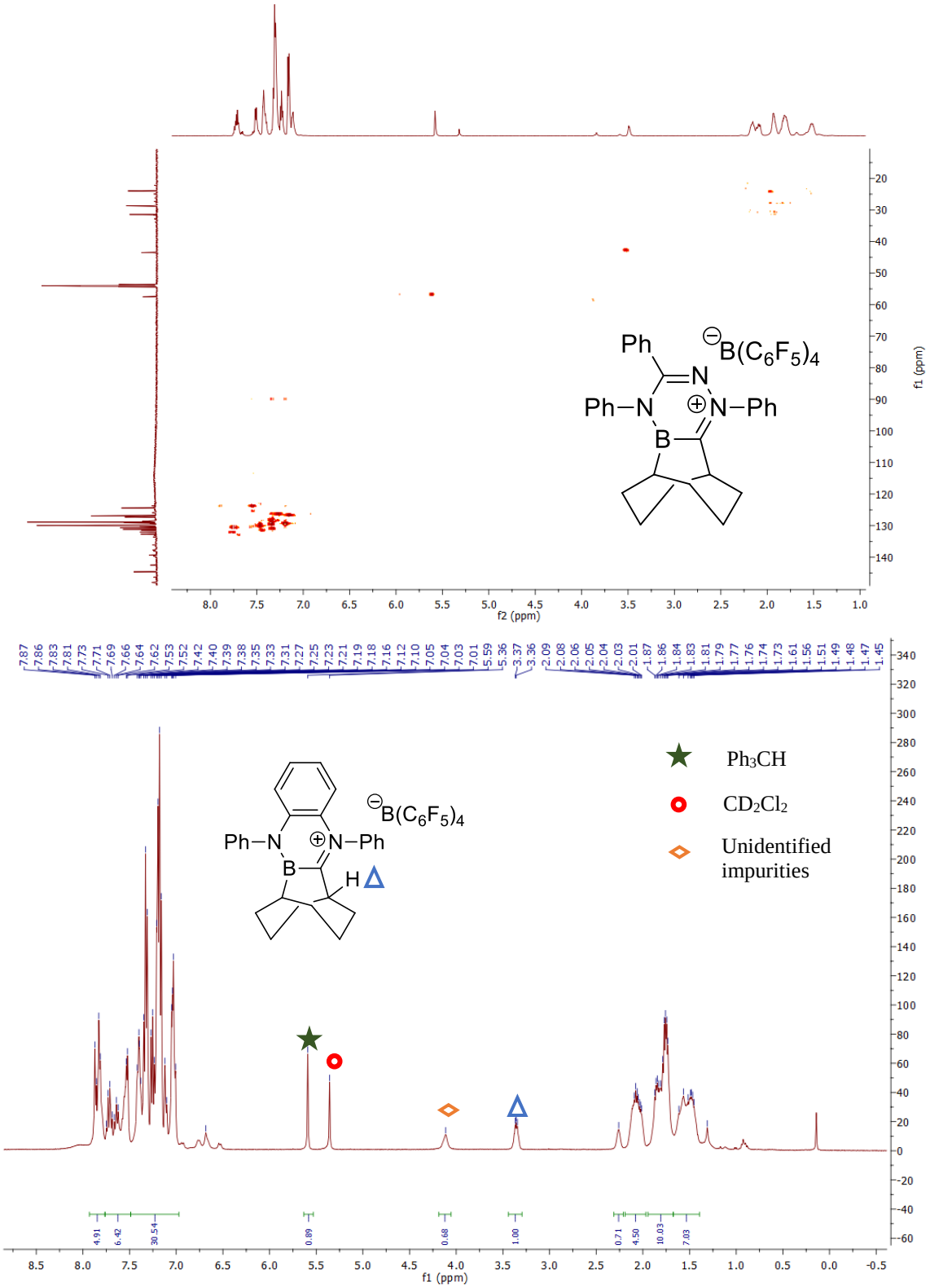


Figure S40: HMQC ^{13}C-NMR (top) of compound 4a in CD_2Cl_2, ^{1}H-NMR (400 MHz, bottom) of compound 4h in CD_2Cl_2 without purification.

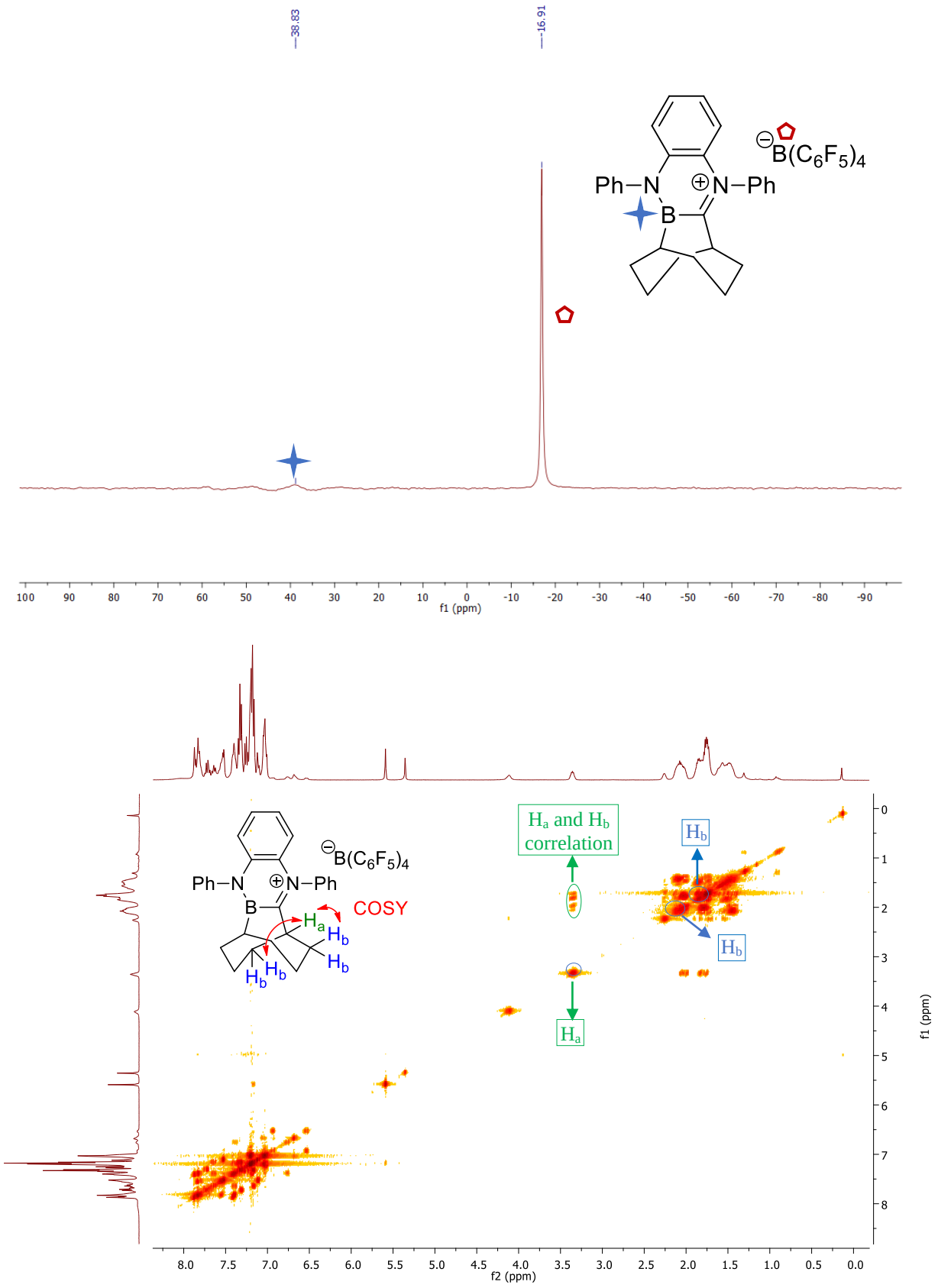


Figure S41: ^{11}B-NMR (128 MHz, top), COSY (bottom) of compound 4h in CD_2Cl_2 without purification.

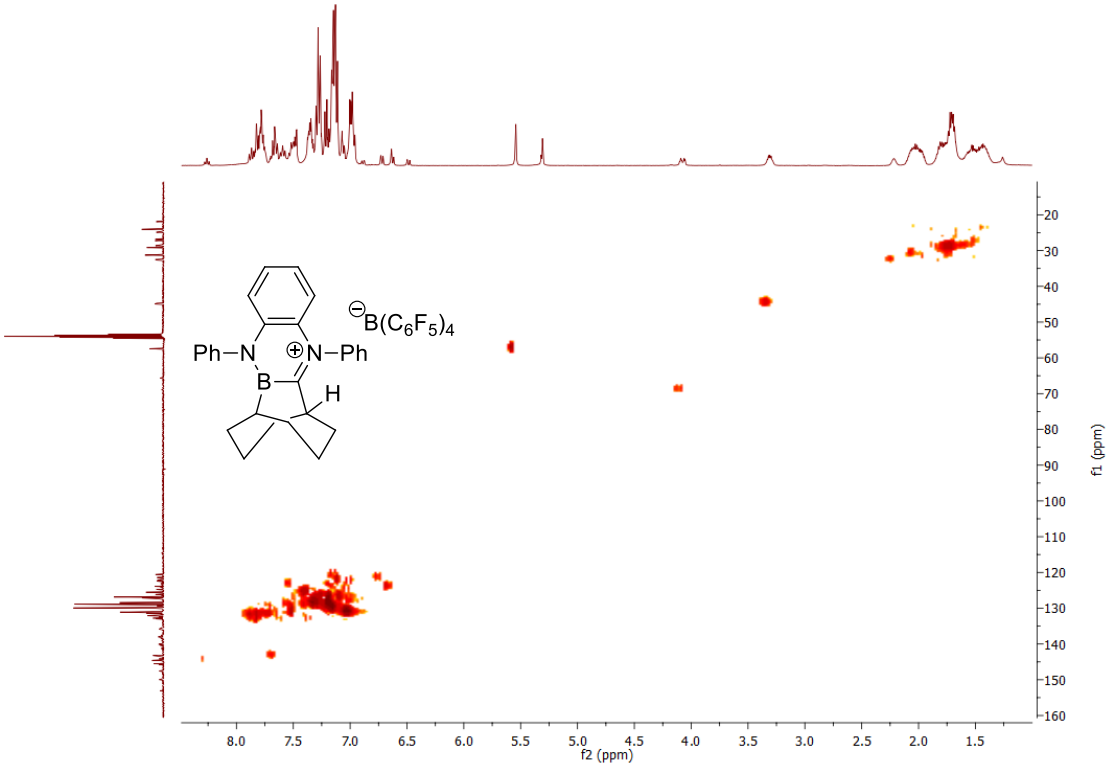


Figure S42: HMQC ^{13}C NMR of compound 4h in CD_2Cl_2 without purification.

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