Supporting Information

Reactivity of a Coordinated Inorganic Acetylene Unit, HBNH, and the Azidoborane Cation $[HB(N_3)]^+$

Anindya K. Swarnakar, Christian Hering-Junghans, Michael J. Ferguson, Robert McDonald, and Eric Rivard*

Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada T6G 2G2.

Contents

Experimental Procedures

Materials and Instrumentation.

All reactions were performed using standard Schlenk line techniques under an atmosphere of nitrogen or in an inert atmosphere glovebox (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system[1] manufactured by Innovative Technology, Inc., degassed (freeze-pump-thaw method), and stored under an atmosphere of nitrogen prior to use. $NaBAr^F_4$ (Ar^F = 3,5-$(F_3C)_2C_6H_3$) was purchased from Matrix Chemicals and dried under vacuum at 110 °C for 48 hrs. Na, K, $H_3B{\bullet}SMe_2$ (2.0 M in THF), HCl (2.0 M in Et_2O [diluted to 0.2 M in Et_2O]), I_2, $Me_2NH{\bullet}BH_3$, NaN_3, Me_3SiOTf, MeOTf, $^tBu_3P$, $B(C_6F_5)_3$, and PhN=NPh were purchased from Sigma-Aldrich and were used as received. $ImMe_2{}^iPr_2$,[2] $ImMe_2{}^iPr_2{\bullet}BH_3$,[3] $Me_2ND{\bullet}BH_3$,[4] $IPr{\bullet}BH_2N_3$,[5] BAr^F_3,[6] Ph_3COTf,[7] Ph_3SiOTf,[8] and KC_8[9] were prepared according to literature procedures. ^1H, ^{11}B, $^{13}C\{^1H\}$ and ^{19}F NMR spectra were recorded on a Varian iNova 400 spectrometer and referenced externally to $SiMe_4$ (^1H and $^{13}C\{^1H\}$), $F_3B{\bullet}OEt_2$ (^{11}B) and $CFCl_3$ (^{19}F), respectively. Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Infrared spectra were recorded on a Nicolet IR100 FTIR spectrometer as Nujol mulls between NaCl plates. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected. Mass spectra were obtained on Agilent Technology 6220 TOF (for ESI) and Kratos MS50G (for EI) spectrometers.

X-ray Crystallography. Crystals of suitable quality for X-ray diffraction studies were removed from a vial in a glovebox and immediately covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was selected, mounted on a glass fiber, and quickly placed in a low-temperature stream of nitrogen on an X-ray diffractometer.[10] All data were collected at the University of Alberta using a Bruker APEX II CCD detector/D8 diffractometer using Cu Kα radiation with the crystals cooled to −100 °C. The data were corrected for absorption through Gaussian integration from the indexing of the crystal faces.[11] Structures were solved using intrinsic phasing SHELXT.[12] Structure refinement was accomplished using either SHELXL-97 or SHELXL-2013.[13] All carbon-bound hydrogen atoms were assigned positions on the basis of the sp^2 or sp^3 hybridization geometries of their attached carbon atoms, and were given thermal parameters 20 % greater than those of their parent atoms.

Synthetic details

*$ImMe_2^iPr_2$•BH_2I (**1**).* A solution of I_2 (718 mg, 2.83 mmol) in 10 mL of benzene was added dropwise to a 15 mL benzene solution of $ImMe_2^iPr_2$•BH_3 (1.09 g, 5.61 mmol), and the mixture was stirred for 2 hrs. The volatiles were removed from the mixture under vacuum to yield $ImMe_2^iPr_2$•BH_2I as a yellow powder (1.61 g, 90 %). $^1H\{^{11}B\}$ NMR (400 MHz, C_6D_6): δ = 5.43 (br, 2H, C*H*$(CH_3)_2$), 3.27 (br, 2H, B*H*), 1.45 (s, 6H, Im-C*H*$_3$), 1.10 (d, $^3J_{HH}$ = 6.4 Hz, 12H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 124.8 (N-*C*-CH_3), 50.5 (*C*H$(CH_3)_2$), 20.8 (CH(*C*H$_3)_2$), 9.7 (Im-*C*H$_3$). ^{11}B NMR (128 MHz, C_6D_6): δ = -30.1 (br). Anal calcd. for $C_{11}H_{22}BIN_2$: C, 41.28; H, 6.93; N, 8.75. Found: C, 41.30; H, 6.89; N, 8.49 %. Mp (°C): 185-190.

*$ImMe_2^iPr_2$•BH_2N_3 (**2**).* 5 mL of DMSO was added to a mixture of $ImMe_2^iPr_2$•BH_2I (**1**) (2.05 g, 6.41 mmol) and NaN_3 (500 mg, 7.69 mmol) followed by stirring for 24 hrs. 100 mL of ethyl acetate was then added to the mixture and the organic layer was washed with water (3 × 70 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under vacuum to yield **2** as a white solid (1.02 g, 68 %). The product was further purified by crystallization from Et_2O/hexanes at -35 °C. $^1H\{^{11}B\}$ NMR (400 MHz, C_6D_6): δ = 5.34 (br, 2H, C*H*$(CH_3)_2$), 3.47 (br, 2H, B*H*), 1.46 (s, 6H, Im-C*H*$_3$), 1.09 (d, $^3J_{HH}$ = 7.2 Hz, 12H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 162.7 (br, N-*C*-N), 124.5 (N-*C*-CH_3), 50.4 (*C*H$(CH_3)_2$), 21.4 (CH(*C*H$_3)_2$), 9.7 (Im-*C*H$_3$). ^{11}B NMR (160 MHz, C_6D_6): δ = -16.9 (t, $^1J_{BH}$ = 98.0 Hz). IR (Nujol, cm^{-1}): 2324 (w, υ_{BH}), 2118 (m, υ_{N3}), 2085 (s, υ_{N3}). HR-MS (EI) $(C_{11}H_{22}BN_5)^+$: m/z: Calcd: 235.1968; Found: 235.1967 (Δ ppm = 0.7). Anal calcd. for $C_{11}H_{22}BN_5$: C, 56.19; H, 9.43; N, 29.78. Found: C, 56.63; H, 9.54; N, 29.25 %. Mp (°C): 90-94.

*$ImMe_2^iPr_2$•HB=NH•BAr^F_3 (**3**).* A solution of BAr^F_3 (440 mg, 0.68 mmol) in 5 mL CH_2Cl_2 was added dropwise to a 3 mL CH_2Cl_2 solution of $ImMe_2^iPr_2$•BH_2N_3 (**2**) (159 mg, 0.68 mmol). The mixture was stirred for 1 hr and the volatiles were removed under vacuum. The product was then dissolved in 10 mL of toluene and heated to 80 °C for 12 hrs to give a colorless solution. The solvent was removed under vacuum to yield a colorless oil. A 3 mL portion of Et_2O was then added to the oil and the resulting mixture was layered with 3 mL of hexanes to precipitate out a white solid. The mother liquor was decanted from the resulting precipitate and the solid was dried under vacuum to afford **3** as a white powder (374 mg, 64 %). Crystals suitable for X-ray

diffraction were grown from hexanes/CH_2Cl_2 at -35 °C. $^1H\{^{11}B\}$ NMR (400 MHz, C_6D_6): δ = 8.19 (s, 6H, *o*-$C_6H_3(CF_3)_2$), 7.79 (s, 3H, *p*-$C_6H_3(CF_3)_2$), 5.42 (d, $^3J_{HH}$ = 10.0 Hz, 1H, N*H*), 4.62 (br, 1H, B*H*), 3.75 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 1.12 (s, 6H, Im-CH_3), 0.79 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C$H_3)_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 159.8 (br, N-*C*-N), 133.9 (*o*-$C_6H_3(CF_3)_2$), 130.4 (q, $^2J_{CF}$ = 31.8 Hz, *m*-$C_6H_3(CF_3)_2$), 125.6 (N-*C*-CH_3), 125.1 (q, $^1J_{CF}$ = 272.6 Hz, *C*F_3), 119.2 (*p*-$C_6H_3(CF_3)_2$), 51.6 (*C*H$(CH_3)_2$), 21.5 (CH(*C*$H_3)_2$), 8.6 (Im-*C*H_3). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6): δ = 32.6 (br, *B*H), -3.9 (s, *B*Ar^F_3). ^{19}F NMR (376 MHz, C_6D_6): δ = -62.3 (s, C*F*$_3$). IR (Nujol, cm^{-1}): 3367 (w, υ_{NH}), 2489 (w, υ_{BH}). Anal calcd. for $C_{35}H_{31}B_2F_{18}N_3$: C, 49.04; H, 3.65; N, 4.90. Found: C, 48.63; H, 4.03; N, 4.45 %. Mp (°C): 142-146.

*ImMe$_2$^{i}Pr$_2$•H(Cl)B-NH$_2$•BAr$^F_3$(**4**).* To a 5 mL Et_2O solution of ImMe$_2$^{i}Pr$_2$•HB=NH•BAr^F_3 (**3**) (205 mg, 0.24 mmol) was added HCl (1.6 mL, 0.2 M solution in Et_2O, 0.3 mmol) and the mixture was stirred for 2 hrs. The solvent was removed from the mixture under vacuum to yield a white powder. The product (**4**) was further purified by crystallization from Et_2O/ hexanes at -35 °C (128 mg, 60 %). $^1H\{^{11}B\}$ NMR (500 MHz, C_6D_6): δ = 7.83 (s, 6H, *o*-$C_6H_3(CF_3)_2$), 7.66 (s, 3H, *p*-$C_6H_3(CF_3)_2$), 4.53 (br, 2H, C*H*$(CH_3)_2$), 3.75 (br, 1H, B*H*), 3.61 (d, $^3J_{HH}$ = 13.0 Hz, 1H, N*H*), 3.40 (br, 1H, N*H*), 1.36 (s, 6H, Im-CH_3), 0.69 (br, 12H, CH(C$H_3)_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 154.1 (br, N-*C*-N), 133.4 (*o*-$C_6H_3(CF_3)_2$), 130.9 (q, $^2J_{CF}$ = 32.1 Hz, *m*-$C_6H_3(CF_3)_2$), 124.5 (q, $^1J_{CF}$ = 272.9 Hz, *C*F_3), 120.4 (*p*-$C_6H_3(CF_3)_2$), 51.3 (*C*H$(CH_3)_2$), 20.5 (CH(*C*$H_3)_2$), 9.6 (Im-*C*H_3). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6): δ = -3.7 (s, *B*Ar^F_3), -9.5 (br, *B*HCl). ^{19}F NMR (376 MHz, C_6D_6): δ = -62.6 (s, C*F*$_3$). Anal calcd. for $C_{35}H_{32}B_2ClF_{18}N_3$: C, 47.04; H, 3.61; N, 4.70. Found: C, 47.03; H, 3.69; N, 4.68 %. Mp (°C): 117-121.

*ImMe$_2$^{i}Pr$_2$•H$_2$B-NH$_2$•BAr$^F_3$ (**5**).* To a 5 mL Et_2O solution of ImMe$_2$^{i}Pr$_2$•HB=NH•BAr^F_3 (**3**) (131 mg, 0.15 mmol) was added $Me_2NH•BH_3$ (9 mg, 0.2 mmol) and the mixture was stirred for 12 hrs. The solvent was removed from the mixture under vacuum and the remaining residue washed three times with hexanes (3 × 5 mL). The product was then dried under vacuum to yield **5** as a white solid. Crystals suitable for X-ray diffraction were grown from hexanes/CH_2Cl_2 at -35 °C (110 mg, 85 %). $^1H\{^{11}B\}$ NMR (400 MHz, C_6D_6): δ = 7.98 (s, 6H, *o*-$C_6H_3(CF_3)_2$), 7.72 (s, 3H, *p*-$C_6H_3(CF_3)_2$), 4.41 (br, 2H, C*H*$(CH_3)_2$), 2.43 (br, 2H, N*H*), 2.29 (br, 2H, B*H*), 1.34 (s, 6H, Im-CH_3), 0.73 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C$H_3)_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 160.5 (br,

N-*C*-N), 155.4 (br, *ipso*-$C_6H_3(CF_3)_2$), 133.6 (*o*-$C_6H_3(CF_3)_2$), 130.7 (q, $^2J_{CF}$ = 32.1 Hz, *m*-$C_6H_3(CF_3)_2$), 125.4 (N-*C*-CH_3), 124.4 (q, $^1J_{CF}$ = 272.2 Hz, *C*F_3), 120.0 (*p*-$C_6H_3(CF_3)_2$), 50.7 (*C*H$(CH_3)_2$), 20.7 (CH(*C*$H_3)_2$), 9.5 (Im-*C*H_3). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6): δ = -3.9 (s, *B*Ar^F_3), -21.6 (br, *B*H_2). ^{19}F NMR (376 MHz, C_6D_6): δ = -62.5 (s, C*F*$_3$). Anal calcd. for $C_{35}H_{33}B_2F_{18}N_3$: C, 48.92; H, 3.87; N, 4.89. Found: C, 48.24; H, 3.83; N, 4.89 %. Mp (°C): 175-179.

To identify the amine-borane by-product a similar reaction was performed by combining Im$Me_2{}^iPr_2$•HB=NH•BAr^F_3 (**3**) (52 mg, 0.06 mmol) and Me_2NH•BH_3 (4 mg, 0.06 mmol) in 5 mL of C_6D_6. The identified dimethyl amine-borane by-products by ^{11}B NMR spectroscopy were $[Me_2N\text{-}BH_2]_2$ (84 %)[14] and $Me_2NH\text{-}BH_2\text{-}NMe_2\text{-}BH_3$ (14 %).[14]

*Im$Me_2{}^iPr_2$•H_2B-N(D)H•BAr^F_3 (**5-d**).* To a 5 mL Et_2O solution of Im$Me_2{}^iPr_2$•HB=NH•BAr^F_3 (**3**) (191 mg, 0.2 mmol) was added Me_2ND•BH_3 (13 mg, 0.2 mmol) and the mixture was stirred for 12 hrs. The solvent was removed from the mixture under vacuum and the remaining residue was washed three times with hexanes (3 × 5 mL). The product was then dried under vacuum to yield **5-d** as a white solid (120 mg, 70 %). $^1H\{^{11}B\}$ NMR: similar to **5** except the signal at 2.43 (br) ppm, which integrates as one N-*H* proton. ^{11}B NMR: similar to **5**. $^2H\{^1H\}$ NMR (61.4 MHz, C_6H_6): δ = 2.36 (br, ND).

*[Im$Me_2{}^iPr_2$]$_2$•HB-NH•BAr^F_3 (**6**).* A solution of Im$Me_2{}^iPr_2$ (28 mg, 0.16 mmol) in 5 mL of Et_2O was added dropwise to a 5 mL Et_2O solution of Im$Me_2{}^iPr_2$•HB=NH•BAr^F_3 (**3**) (130 mg, 0.15 mmol). The mixture was stirred for 12 hrs and the solvent was removed under vacuum to yield **6** as a light yellow powder (155 mg, 88 %). Crystals suitable for X-ray diffraction were grown from hexanes/CH_2Cl_2 at -35 °C. $^1H\{^{11}B\}$ NMR (400 MHz, C_6D_6): δ = 8.17 (br, 6H, *o*-$C_6H_3(CF_3)_2$), 7.77 (br, 3H, *p*-$C_6H_3(CF_3)_2$), 5.52 (br, 2H, N*H*), 3.80 (br, 2H, C*H*$(CH_3)_2$), 0.60-1.70 (br, 36H, Im-CH_3 and CH(C$H_3)_2$). $^{13}C\{^1H\}$ NMR spectrum was not obtained due to the low solubility and dynamic behavior in solution. $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6): δ = -3.6 (s, *B*Ar^F_3), -14.3 (br, *B*H). $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6): δ = -62.3 to -62.0 (m, C*F*$_3$). Anal calcd. for $C_{46}H_{51}B_2F_{18}N_5$: C, 53.25; H, 4.95; N, 6.75. Found: C, 52.84; H, 4.88; N, 6.41 %. Mp (°C): 147-151.

*Reaction of [ImMe$_2$^{i}Pr$_2$]$_2$•HB-NH•BAr$^F_3$ (**6**) with Me$_2$S•BH$_3$.* To a solution of *[ImMe$_2$^{i}Pr$_2$]$_2$•HB-NH•BAr$^F_3$ (**6**)* (76 mg, 0.07 mmol) in 10 mL of Et_2O was added 37 μL of $Me_2S•BH_3$ (2.0 M solution in THF). The mixture was stirred for 12 hrs and the solvent was removed under vacuum to yield a white powder. $^1H\{^{11}B\}$ and ^{11}B NMR confirmed the presence of $ImMe_2{}^iPr_2•BH_3$[3] and $ImMe_2{}^iPr_2•HB{=}NH•BAr^F_3$ (**3**).

*IPr•BH(OTf)N$_3$ (**7**).* A 5 mL CH_2Cl_2 solution of Ph_3COTf (224 mg, 0.56 mmol) was added dropwise to a 10 mL CH_2Cl_2 solution of IPr•BH_2N_3 (253 mg, 0.56 mmol), and the mixture was stirred for 1 hrs. The volatiles were removed from the mixture under vacuum and the product was washed with hexanes (3 × 5 mL). The residue was then dried under vacuum to give **7** as yellow solid (323 mg, 95 %). Crystals suitable for X-ray diffraction were grown from PhF/hexanes at -35 °C. $^1H\{^{11}B\}$ (400 MHz, C_6D_6): δ = 7.22 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 7.05-7.07 (m, 4H, Ar*H*), 6.29 (s, 2H, N-C*H*), 3.94 (br, 1H, B*H*), 2.53 (sept, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*(CH_3)$_2$), 2.48 (sept, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*(CH_3)$_2$), 1.38 (d, $^3J_{HH}$ = 10.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.36 (d, $^3J_{HH}$ = 10.0 Hz, 6H, CH(C*H*$_3$)$_2$), 0.95 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 145.1 (s, N-*C*H), 145.0 (s, N-*C*H), 132.7 (s, Ar*C*), 131.4 (s, Ar*C*), 124.6 (s, Ar*C*), 124.5 (s, Ar*C*), 124.1 (s, Ar*C*), 119.6 (q, $^1J_{C\text{-}F}$ = 318.9 Hz, *C*F_3), 29.4 (s, *C*H(CH_3)$_2$), 29.3 (s, *C*H(CH_3)$_2$), 25.6 (s, CH(*C*H_3)$_2$), 25.4 (s, CH(*C*H_3)$_2$), 22.5 (s, CH(*C*H_3)$_2$), 22.4 (s, CH(*C*H_3)$_2$). ^{11}B NMR (128 MHz, C_6D_6): δ = -2.0 (br). ^{19}F NMR (376 MHz, C_6D_6): δ = -76.9 (s, C*F*$_3$). IR (Nujol, cm^{-1}): 2462 (m, υ_{BH}), 2201 (w, υ_{N3}), 2117 (s, υ_{N3}). Anal calcd. for $C_{28}H_{37}BF_3N_5O_3S$: C, 56.86; H, 6.31; N, 11.84; S, 5.42. Found: C, 56.37; H, 6.22; N, 10.82; S, 5.06 %. Mp (°C): >195.

*ImMe$_2$^{i}Pr$_2$•BH(OTf)N$_3$ (**8**).* A 5 mL CH_2Cl_2 solution of Ph_3COTf (369 mg, 0.94 mmol) was added dropwise to a 10 mL CH_2Cl_2 solution of $ImMe_2{}^iPr_2•BH_2N_3$ (**2**) (220 mg, 0.94 mmol), and the mixture was stirred for 1 hr. The volatiles were removed from the mixture under vacuum and the product was washed with hexanes (3 × 5 mL). The residue was then dried under vacuum to afford **8** as white powder (237 mg, 66 %). Crystals suitable for X-ray diffraction were grown from hexanes/CH_2Cl_2 at -35 °C. $^1H\{^{11}B\}$ NMR (400 MHz, C_6D_6): δ = 5.12 (br, 2H, C*H*(CH_3)$_2$), 4.56 (br, 1H, B*H*), 1.31 (s, 6H, Im-C*H*$_3$), 1.00 (br, 12H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 125.9 (N-*C*-CH_3), 50.9 (*C*H(CH_3)$_2$), 21.1 (CH(*C*H_3)$_2$), 9.6 (Im-*C*H_3), *C*F_3 and ^{Im}*C*-B

resonances could not be located. ^{11}B NMR (128 MHz, C_6D_6): δ = -1.6 (br). ^{19}F NMR (376 MHz, C_6D_6): δ = -76.3 (s, OTf). IR (Nujol, cm^{-1}): 2478 (m, υ_{BH}), 2116 (s, υ_{N3}). Anal calcd. for $C_{12}H_{21}BF_3N_5O_3S$: C, 37.61; H, 5.52; N, 18.28; S, 8.37. Found: C, 37.01; H, 5.45; N, 15.91; S, 8.88 %. Mp (°C): 74-77. Despite repeated attempts, analyses for N content were always low; for copies of the NMR spectra of **8**, see Figures S2-S5.

Reaction of IPr•BH_2N_3 with R_3SiOTf (R = Me or Ph). A 5 mL of CH_2Cl_2 solution of Ph_3SiOTf (33 mg, 0.08 mmol) or Me_3SiOTf (22 μL, 0.12 mmol) was dropwise added to a 5 mL CH_2Cl_2 solution of IPr•BH_2N_3 (35 mg, 0.08 mmol) or (54 mg, 0.12 mmol) and stirred for 12 hrs. The volatiles were removed under vacuum to yield a white solid. Upon washing with hexanes (3 × 5 mL) and dried under vacuum affords IPr•BH_2OTf as a white powder (27 mg, 61 %) or (60 mg, 90 %). The ^{1}H{^{11}B}, ^{11}B and ^{19}F NMR in spectra in $CDCl_3$ confirmed the product as IPr•BH_2OTf.[4] Also ^{13}C{^{1}H} NMR analysis of the hexanes soluble fraction (with Ph_3SiOTf as a reagent) confirmed the presence of Ph_3SiN_3.[15]

*[IPr(Im$Me_2{}^iPr_2$)•$BH(N_3)$](OTf) (**9**).* A solution of Im$Me_2{}^iPr_2$ (57 mg, 0.32 mmol) and IPr•BH(OTf)N_3 (**7**) (186 mg, 0.31 mmol) in 10 mL of toluene was heated at 80 °C for 12 hrs to give a white slurry. The resulting precipitate was separated from the mother liquor and dried under vacuum to give **9** as a white powder. The product was further purified by washing with 10 mL of fluorobenzene (168 mg, 68 %). ^{1}H{^{11}B} (400 MHz, $CDCl_3$): δ = 7.56 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 7.45 (s, 2H, N-C*H*), 7.38 (d, 2H, $^3J_{HH}$ = 7.6 Hz, Ar*H*), 7.28 (d, 2H, $^3J_{HH}$ = 7.2 Hz, Ar*H*), 4.49 (sept, $^3J_{HH}$ = 7.2 Hz, 1H, C*H*(CH_3)$_2$), 4.23 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 3.69 (br, 1H, B*H*), 2.40-2.55 (m, 4H, C*H*(CH_3)$_2$), 2.28 (s, 3H, Im-CH_3), 2.13 (s, 3H, Im-CH_3), 1.47 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CH(CH_3)$_2$), 1.40 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.37 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH(CH_3)$_2$), 1.18-1.24 (m, 9H, CH(CH_3)$_2$), 1.09 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 0.81 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 145.1 (N-*C*H), 145.0 (br, C_{NHC}-B), 133.2 (Ar*C*), 131.9 (Ar*C*), 127.6 (Ar*C*), 127.4 (Ar*C*), 127.1 (Ar*C*), 125.0 (N-*C*-CH_3, 124.6 (N-*C*-CH_3), 121.1 (q, $^1J_{C\text{-}F}$ = 321.3 Hz, *C*F_3), 52.3 (*C*H(CH_3)$_2$), 51.6 (*C*H(CH_3)$_2$), 29.3 (*C*H(CH_3)$_2{}^{IPr}$), 29.1 (*C*H(CH_3)$_2{}^{IPr}$), 26.5 (CH(*C*H_3)$_2{}^{IPr}$), 25.9 (CH(*C*H_3)$_2{}^{IPr}$), 23.3 (*C*H(CH_3)$_2$), 22.9 (*C*H(CH_3)$_2{}^{IPr}$), 22.0 (*C*H(CH_3)$_2{}^{IPr}$), 20.1 (*C*H(CH_3)$_2$), 11.1 (Im-*C*H_3), 10.9 (Im-*C*H_3). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = -14.3 (br, *B*H). ^{19}F NMR (376 MHz, $CDCl_3$): δ = -78.1

(s, CF_3). IR (Nujol, cm^{-1}): 2400 (w, υ_{BH}), 2186 (w, υ_{N3}), 2107 (s, υ_{N3}). HR-MS (ESI) $(C_{37}H_{57}BN_7)^+$: m/z: Calcd: 622.4763; Found: 622.4756 (Δ ppm = 1.2). Anal calcd. for $C_{39}H_{57}BF_3N_7O_3S$: C, 60.69; H, 7.44; N, 12.70; S, 4.15. Found: C, 59.50; H, 7.01; N, 11.33; S, 4.10 %. Mp (°C): >195. Despite repeated attempts, analyses for C and N content were always low; for copies of the NMR spectra of **9**, see Figures S6-S9.

*[(ImMe$_2$^{i}Pr$_2$)$_2$•BH(N$_3$)](OTf) (**10**).* A solution of ImMe$_2$^{i}Pr$_2$ (85 mg, 0.47 mmol) and ImMe$_2$^{i}Pr$_2$•BH(OTf)N$_3$ (**8**) (179 mg, 0.47 mmol) in 10 mL of toluene was heated at 80 °C for 12 hrs. The solvent was removed under from mixture vacuum and the residue was washed with Et_2O (3 × 5 mL). The product was then dried under vacuum to yield a white solid (195 g, 74 %). $^1H\{^{11}B\}$ NMR (500 MHz, $CDCl_3$): δ = 5.05 (br, 4H, C*H*$(CH_3)_2$), 3.92 (s, 1H, B*H*), 2.34 (s, 12H, Im-CH_3), 1.45 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 1.43 (d, $^3J_{HH}$ = 7.2 Hz, 12H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 127.6 (N-*C*-CH_3), 50.8 (*C*H$(CH_3)_2$), 21.5 (CH(*C*H_3)$_2$), 21.3 (CH(*C*H_3)$_2$), 10.9 (Im-*C*H_3), CF_3 group was not located. ^{11}B NMR (128 MHz, $CDCl_3$): δ = -14.5 (d, $^1J_{B-H}$ = 94.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = -78.1 (s, OTf). IR (Nujol, cm^{-1}): 2379 (m, υ_{BH}), 2105 (s, υ_{N3}). HR-MS (ESI) $(C_{22}H_{41}BN_7)^+$: m/z: Calcd: 414.3511; Found: 414.3514 (Δ ppm = 0.8). Anal calcd. for $C_{23}H_{41}BF_7N_7O_3S$: C, 49.03; H, 7.33; N, 17.40, S, 5.69 %. Found: C, 49.02; H, 7.20; N, 16.42; S, 5.78 %. Mp (°C): 97-101. Despite repeated attempts, analyses for N content were always low; for copies of the NMR spectra of **10**, see Figures S10-S13.

*[(ImMe$_2$^{i}Pr$_2$)$_2$•BH(N$_3$)]BAr$^F_4$ (**11**).* [(ImMe$_2$^{i}Pr$_2$)$_2$•BH(N$_3$)](OTf) (**10**) (87 mg, 0.15 mmol) and NaBAr$^F_4$ (137 mg, 0.15 mmol) were combined in 10 mL of Et_2O. The mixture was stirred for 2 hrs and filtered. The volatiles were removed from the filtrate under vacuum to yield a white solid as **12** (173 mg, 87 %). Crystals suitable for X-ray diffraction were grown from hexanes/CH_2Cl_2 at -35 °C (110 mg, 85 %). $^1H\{^{11}B\}$ NMR (500 MHz, $CDCl_3$): δ = 7.68 (s, 8H, *o*-$C_6H_3(CF_3)_2$), 7.52 (s, 4H, *p*-$C_6H_3(CF_3)_2$), 5.04 (br, 4H, C*H*$(CH_3)_2$), 3.90 (s, 1H, B*H*), 2.22 (s, 12H, Im-CH_3), 1.37 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 1.36 (d, $^3J_{HH}$ = 7.5 Hz, 12H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 161.8 (q, $^1J_{BC}$ = 49.8 Hz, B-*C*$_6H_3(CF_3)_2$), 134.9 (*o*-*C*$_6H_3(CF_3)_2$), 129.0 (q, $^2J_{CF}$ = 32.2 Hz, *m*-*C*$_6H_3(CF_3)_2$), 127.4 (N-*C*-CH_3), 124.7 (q, $^1J_{CF}$ = 272.5 Hz, *C*F_3), 117.6 (*p*-*C*$_6H_3(CF_3)_2$), 50.7 (*C*H$(CH_3)_2$), 21.2 (CH(*C*H_3)$_2$), 21.1 (CH(*C*H_3)$_2$), 10.6 (Im-*C*H_3). ^{11}B NMR

(128 MHz, $CDCl_3$): δ = -6.6 (s, BAr^F_4), -14.6 (d, $^1J_{BH}$ = 92.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.4 (s, CF_3). IR (Nujol, cm^{-1}): 2384 (m, υ_{BH}), 2193 (w, υ_{N3}), 2110 (s, υ_{N3}). HR-MS (ESI) $(C_{22}H_{41}BN_7)^+$: m/z: Calcd: 414.3511; Found: 414.3507 (Δ ppm = 0.9). Anal calcd. for $C_{54}H_{53}B_2F_{24}N_7$: C, 50.76; H, 4.18; N, 7.67. Found: C, 50.95; H, 4.19; N, 6.67 %. Mp (°C): 130-134. Despite repeated attempts, analyses for N content were always low; for copies of the NMR spectra of **11**, see Figures S14-S17.

*Reduction of $ImMe_2{}^iPr_2$•$BH(N_3)OTf$ (**8**) with KC_8.* $ImMe_2{}^iPr_2$•$BH(N_3)OTf$ (**8**) (131 mg, 0.34 mmol) was combined with KC_8 (92 mg, 0.68 mmol) in 10 mL of toluene. The mixture was stirred for 24 hrs and filtered. All the volatiles were removed under vacuum from the filtrate to give a white solid. The ^{1}H and ^{11}B NMR spectra of the resulting solid indicated the formation of $ImMe_2{}^iPr_2$ (44 %), $ImMe_2{}^iPr_2$•BH_2N_3 (20 %), $ImMe_2{}^iPr_2$•BH_3 (13 %) with some other minor unidentified products (*ca.* 23 %). The IR spectrum of the insoluble part showed the formation of K[OTf] and $K[N_3]$ (Figure S18).

*Reduction of $ImMe_2{}^iPr_2$•$BH(N_3)OTf$ (**8**) with K.* $ImMe_2{}^iPr_2$•$BH(N_3)OTf$ (**8**) (450 mg, 1.1 mmol) was combined with K (215 mg, 5.3 mmol) in 20 mL of toluene and the mixture was stirred for 24 hrs. The solution was separated from the precipitate by filtration. The volatiles were removed under vacuum from the filtrate to afford a white solid. The ^{1}H NMR spectrum of the resulting toluene soluble solid revealed the presence of free $ImMe_2{}^iPr_2$ (>90 %) with some other minor unidentified products. The IR spectrum of the insoluble fraction was consistent with the formation of K[OTf] and $K[N_3]$ (Figure S19).

Table S1: Crystallographic data for compound **3**•0.5 C_7H_8

A. Crystal Data

formula	$C_{38.50}H_{35}B_2F_{18}N_3$
formula weight	903.31
crystal dimensions (mm)	0.25×0.13×0.10
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	12.2423 (2)
b (Å)	22.6420 (4)
c (Å)	14.6138 (2)
β (deg)	92.7542 (11)
V (Å^3)	4046.12 (11)
Z	4
ρ_{calcd} (g cm^{-3})	1.483
μ (mm^{-1})	1.290

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ[Å])	Cu Kα(1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	148.69
total data collected	28779 (-15 ≤ h ≤ 15, -28 ≤ k ≤ 28, -18 ≤ l ≤ 17)
independent reflections	8210 (R_{int} = 0.0306)
number of observed reflections (*NO*)	6089 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d,e])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9208–0.7840

Table S1: Crystallographic data for compound **3** (continued).

data/restraints/parameters	8210 / 60[f] / 653
goodness-of-fit (S)[g] [all data]	1.058
final R indices[h]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0633
wR_2 [all data]	0.1957
largest difference peak and hole	0.355 and –0.369 e Å^{-3}

[a]Obtained from least-squares refinement of 9872 reflections with $7.20° < 2\theta < 143.00°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]G. M. Sheldrick, *Acta Crystallogr.* 2015, **A71**, 3–8. (*SHELXT-2014*)

[d]G. M. Sheldrick, *Acta Crystallogr.* 2015, **C71**, 3–8. (*SHELXL-2014*)

[e]Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent toluene carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure as implemented in *PLATON* (A. L. Spek, *Acta Crystallogr.* 2015, **C71**, 9–18. *PLATON* - a multipurpose crystallographic tool. Utrecht University, Utrecht, The Netherlands). A total solvent-accessible void volume of 379 Å^3 with a total electron count of 97 (consistent with 2 molecules of solvent toluene, or 0.5 molecules per formula unit of the [($C_3N_2Me_2{}^iPr_2$)BHNH(B{$C_6H_3(CF_3)_2$}$_3$)] molecule) was found in the unit cell.

[f]The C–F distances within the disordered CF_3 groups were restrained to be the same by use of the *SHELXL* **SADI** instruction.

[g]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0928P)^2 + 1.2643P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[h]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S2: Crystallographic data for compound **4**.

A. Crystal Data

formula	$C_{35}H_{32}B_2ClF_{18}N_3$
formula weight	893.70
crystal dimensions (mm)	0.41×0.26×0.18
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	11.3790 (6)
b (Å)	22.2822 (12)
c (Å)	16.4411 (9)
β (deg)	107.567 (4)
V (Å^3)	3974.2 (4)
Z	4
ρ_{calcd} (g cm^{-3})	1.494
μ (mm^{-1})	1.910

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	148.41
total data collected	27726 (-14 ≤ h ≤ 14, -27 ≤ k ≤ 27, -20 ≤ l ≤ 20)
independent reflections	8048 (R_{int} = 0.0333)
number of observed reflections (NO)	6920 $[F_o^2 \geq 2\sigma(F_o^2)]$
structure solution method	intrinsic phasing (*SHELXT*-2014[c])
refinement method	full-matrix least-squares on F^2(*SHELXL*–2014[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.8573–0.5485

Table S2: Crystallographic data for compound **4** (continued).

data/restraints/parameters	8048 / 0 / 546
goodness-of-fit (S)[e] [all data]	1.047
final R indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0762
wR_2 [all data]	0.2120
largest difference peak and hole	0.858 and –0.570 e Å^{-3}

[a]Obtained from least-squares refinement of 9221 reflections with 6.90° < 2θ <147.22°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]G. M. Sheldrick, *Acta Crystallogr*. 2015, **A71**, 3–8. (*SHELXT*-2014)

[d]G. M. Sheldrick, *Acta Crystallogr*. 2015, **C71**, 3–8. (*SHELXL*-2014)

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0860P)^2 + 7.9803P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S3: Crystallographic data for compound **5**•0.375 CH_2Cl_2.

A. Crystal Data

formula	$C_{35.38}H_{33.75}B_2Cl_{0.75}F_{18}N_3$
formula weight	891.11
crystal dimensions (mm)	0.35×0.31×0.25
crystal system	monoclinic
space group	*I*2/*a* (an alternate setting of *C*2/*c* [No. 15])
unit cell parameters[a]	
a (Å)	25.1883 (19)
b (Å)	12.1920 (9)
c (Å)	26.4276 (18)
β (deg)	98.253 (3)
V (Å^3)	8031.8 (10)
Z	8
ρ_{calcd} (g cm^{-3})	1.474
μ (mm^{-1})	1.738

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	148.06
total data collected	28202 (-29 ≤ h ≤ 25, -15 ≤ k ≤ 15, -32 ≤ l ≤ 32)
independent reflections	7870 (R_{int} = 0.0197)
number of observed reflections (NO)	7250 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT*-2014[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL*–2014[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.6769–0.5450

Table S3: Crystallographic data for compound **5** (continued)

data/restraints/parameters	7870 / 56[e] / 670
extinction coefficient (x)[f]	0.00034(4)
goodness-of-fit (S)[g] [all data]	1.062
final *R* indices[h]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0608
wR_2 [all data]	0.1632
largest difference peak and hole	0.780 and –0.682 e Å^{-3}

[a]Obtained from least-squares refinement of 9457 reflections with 6.76° < 2θ <147.74°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]G. M. Sheldrick, *Acta Crystallogr.* 2015, **A71**, 3–8. (*SHELXT*-2014)

[d]G. M. Sheldrick, *Acta Crystallogr*. 2015, **C71**, 3–8. (*SHELXL*-2014)

[e]The following distance restraints were applied to the minor components of the disordered CF3 groups: C–F, 1.35(1) Å; F···F, 2.20(1) Å. The minor component of the disordered aryl group (atoms C21B to C26B) was constrained to be a hexagon with C–C distances of 1.39 Å, and the C_{aryl}–CF_3 distances were restrained to be 1.50(1) Å. Finally, the C–Cl distance of the solvent dichloromethane molecule was restrained to be approximately the same by use of the *SHELXL* **SADI** instruction.

[f]$F_c^* = kF_c[1 + x\{0.001F_c^2\lambda^3/\sin(2\theta)\}]^{-1/4}$ where k is the overall scale factor.

[g]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; w = $[\sigma^2(F_o^2) + (0.0760P)^2 + 13.2755P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3)$.

[h]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S4: Crystallographic data for compound **6**.

A. Crystal Data

formula	$C_{46}H_{51}B_2F_{18}N_5$
formula weight	1037.53
crystal dimensions (mm)	0.21×0.20×0.13
crystal system	monoclinic
space group	*C*2/*c* (No. 15)
unit cell parameters[a]	
a (Å)	12.9360 (4)
b (Å)	18.7832 (6)
c (Å)	41.0326 (12)
β (deg)	94.5442 (15)
V (Å^3)	9938.7 (5)
Z	8
ρ_{calcd} (g cm^{-3})	1.387
μ (mm^{-1})	1.133

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ[Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	144.77
total data collected	34208 (-15 ≤ h ≤ 15, -23 ≤ k ≤ 22, -50 ≤ l ≤ 50)
independent reflections	9814 (R_{int} = 0.0327)
number of observed reflections (NO)	8438 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT*-2014[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL*–2014[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9085–0.7916

Table S4: Crystallographic data for compound **6** (continued)

data/restraints/parameters	9814 / 108[e] / 741
extinction coefficient (x)[f]	0.000110(17)
goodness-of-fit (S)[g] [all data]	1.037
final R indices[h]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0543
wR_2 [all data]	0.1447
largest difference peak and hole	0.509 and –0.422 e Å^{-3}

[a]Obtained from least-squares refinement of 9992 reflections with 8.46° < 2θ <144.28°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]G. M. Sheldrick, *Acta Crystallogr.* 2015, **A71**, 3–8. (*SHELXT*-2014)

[d]G. M. Sheldrick, *Acta Crystallogr.* 2015, **C71**, 3–8. (*SHELXL*-2014)

[e]The disordered CF_3 groups had the following restraints applied: C–F distances (**DFIX**) restrained to be 1.32 (1) Å (total of 18 restraints); rigid-bond restraint (**RIGU**) applied to the carbon and fluorine anisotropic displacement parameters (total of 90 restraints).

[f]$F_c^* = kF_c[1 + x\{0.001F_c^2\lambda^3/\sin(2\theta)\}]^{-1/4}$ where k is the overall scale factor.

[g]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; w = $[\sigma^2(F_o^2) + (0.0543P)^2 + 11.5528P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[h]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S5: Crystallographic data for compound **7**•0.5 C_6H_5F.

A. Crystal Data

formula	$C_{31}H_{39.50}BF_{3.50}N_5O_3S$
formula weight	639.54
crystal dimensions (mm)	0.27×0.24×0.12
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters[a]	
a (Å)	9.3972 (2)
b (Å)	12.2337 (3)
c (Å)	16.8072 (4)
α (deg)	73.1735 (10)
β (deg)	77.1382 (11)
γ (deg)	68.1258 (10)
V (Å^3)	1701.94 (7)
Z	2
ρ_{calcd} (g cm^{-3})	1.248
μ (mm^{-1})	1.333

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ[Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	144.69
total data collected	11942 (-15 ≤ h ≤ 15, -23 ≤ k ≤ 22, -50 ≤ l ≤ 50)
independent reflections	6460 (R_{int} = 0.0327)
number of observed reflections (NO)	5942 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT*-2014[c])

Table S4: Crystallographic data for compound **7** (continued)

refinement method	full-matrix least-squares on F^2 (*SHELXL*–2014[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9050–0.7372
data/restraints/parameters	6460 / 20[e] / 523
goodness-of-fit (S)[f] [all data]	1.063
final *R* indices[g]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0434
wR_2 [all data]	0.1255
largest difference peak and hole	0.276 and –0.264 e Å^{-3}

[a]Obtained from least-squares refinement of 9106 reflections with $5.54° < 2\theta < 144.38°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]G. M. Sheldrick, *Acta Crystallogr.* 2015, **A71**, 3–8. (*SHELXT*-2014)

[d]G. M. Sheldrick, *Acta Crystallogr.* 2015, **C71**, 3–8. (*SHELXL*-2014)

[e]The N4A–N5A and N4B–N5B distances were restrained to be approximately the equal by use of the *SHELXL* **SADI** instruction. Additionally, the geometry of the two orientations of the disorderd triflate group was restrained to be approximately equal by use of the *SHELXL* **SAME** instruction.

[f]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0634P)^2 + 0.4987P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

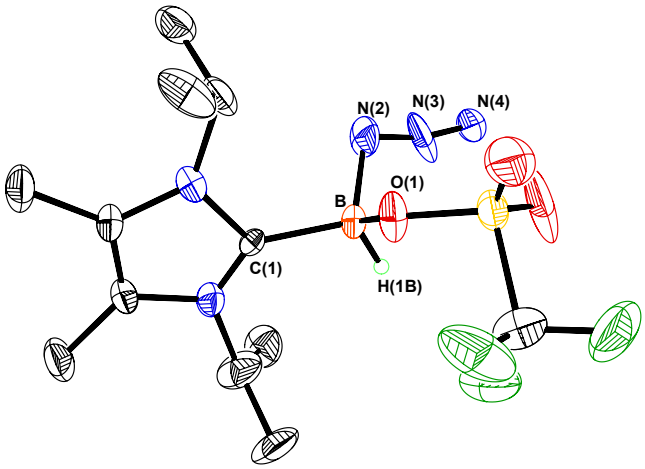


Figure S1: Molecular structure of $ImMe_2{}^iPr_2{\bullet}BHN_3(OTf)$ (**8**) with thermal ellipsoids presented at a 30 % probability level. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)−B 1.636(9), B−N(2) 1.519(19), B−O(1) 1.609(16), N(2)−N(3) 1.261(19), N(3)−N(4) 1.157(15); C(1)−B−N(2) 110.9(11), B−N(2)−N(3) 112.5(14), N(2)−N(3)−N(4) 169(3).

Table S5: Crystallographic data for compound **8**.

A. Crystal Data

formula	$C_{12}H_{21}BF_3N_5O_3S$
formula weight	383.21
crystal dimensions (mm)	0.56×0.14×0.08
crystal system	orthorhombic
space group	*Cmc*2$_1$ (No. 36)
unit cell parameters[a]	
a (Å)	13.5787 (3)
b (Å)	12.2769 (2)
c (Å)	11.1774 (2)
V (Å^3)	1863.32 (6)
Z	4

Table S5: Crystallographic data for compound **8** (continued).

β_{calcd} (g cm^{-3})	1.366
μ (mm^{-1})	2.013
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ[Å])	Cu Kα[a] (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 or 10 s exposures)
data collection 2θ limit (deg)	140.55
total data collected	5885 (-16 ≤ h ≤ 14, -14 ≤ k ≤ 14, -13 ≤ l ≤ 13)
independent reflections	1850 (R_{int} = 0.0452)
number of observed reflections (NO)	1733 [$F_o^2 \geq 2\,\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT*-2014[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL*–2014[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9689–0.4591
data/restraints/parameters	1850 / 7[e] / 201
Flack absolute structure parameter[f]	0.09(6)
goodness-of-fit (S)[g] [all data]	1.061
final R indices[h]	
R_1 [$F_o^2 \geq 2\,\sigma(F_o^2)$]	0.0684
wR_2 [all data]	0.1940
largest difference peak and hole	0.536 and –0.385 e Å^{-3}

[a]Obtained from least-squares refinement of 9953 reflections with 7.90° < 2θ < 140.38°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]G. M. Sheldrick, *Acta Crystallogr*. 2015, **A71**, 3–8.

[d]G. M. Sheldrick, Acta Crystallogr. 2015, **C71**, 3–8.

Table S5: Crystallographic data for compound **8** (continued).

[e]The distances d(N1–C3) and d(N1'–C7) were constrained to be equal (within 0.03 Å) during refinement. The C–C distances within the disordered isopropyl groups were constrained to be equal to target values during refinement: d(C3–C4) = d(C3–C5) = d(C7–C8) = d(C7–C9) = 1.50(1) Å; d(C4···C5) = d(C8···C9) = 2.50(1) Å.

[f]H. D. Flack, *Acta Crystallogr*. 1983, **A39**, 876–881; H. D. Flack and G. Bernardinelli, *Acta Crystallogr*. 1999, **A55***,* 908–915; H. D. Flack, G. Bernardinelli, *J. Appl. Cryst.* 2000, **33**, 1143–1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration. The low anomalous scattering power of the atoms in this structure (none heavier than fluorine) implies that the data cannot be used for absolute structure assignment, thus the Flack parameter is provided for informational purposes only. Both enantiomers of the molecule are present in the unit cell, so the Flack parameter is only refining the polarity of the non-centrosymmetric space group.

[g]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.1687P)^2 + 0.0029P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[h]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S5: Crystallographic data for compound **11**.

A. Crystal Data	
formula	$C_{54}H_{53}B_2F_{24}N_7$
formula weight	1277.65
crystal dimensions (mm)	0.33×0.17×0.15
crystal system	monoclinic
space group	$P2_12_12_1$ (No. 19)
unit cell parameters[a]	
a (Å)	12.6084 (3)
b (Å)	19.7795 (6)
c (Å)	24.1204 (6)
V (Å^3)	6015.3 (3)
Z	4
β_{calcd} (g cm^{-3})	1.411
μ (mm^{-1})	1.206
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2 θ limit (deg)	144.70
total data collected	42409 (-15 ≤ h ≤ 15, -23 ≤ k ≤ 21, -29 ≤ l ≤ 29)
independent reflections	11860 (R_{int} = 0.0192)
number of observed reflections (NO)	11579 [$F_o^2 \geq 2\ \sigma s(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT*-2014[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL*–2014[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.8737–0.7102
data/restraints/parameters	11860 / 3[e] / 812

Table S5: Crystallographic data for compound **11** (continued).

Flack absolute structure parameter[f]	0.008(16)
goodness-of-fit (S)[g] [all data]	1.045
final R indices[h]	
R_1 [$F_o^2 \geq 2\,\sigma(F_o^2)$]	0.0480
wR_2 [all data]	0.1337
largest difference peak and hole	0.480 and –0.351 e Å^{-3}

[a]Obtained from least-squares refinement of 9410 reflections with 7.92° < 2 θ < 144.42°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]G. M. Sheldrick, *Acta Crystallogr*. 2015, **A71**, 3–8.

[d]G. M. Sheldrick, Acta Crystallogr. 2015, **C71**, 3–8.

[e]The following distances restraints were applied to the minor (25% occupancy) orientation of the BH-N3 group: B1B–N5B, 1.50(1) Å; N5B–N6B, 1.20(1) Å; N6B–N7B, 1.15(1) Å.

[f]H. D. Flack, *Acta Crystallogr*. 1983, **A39**, 876–881; H. D. Flack, G. Bernardinelli, *Acta Crystallogr*. 1999, **A55**, 908–915; H. D. Flack, G. Bernardinelli, *J. Appl. Cryst.* 2000, **33**, 1143–1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration.

[g]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0800P)^2 + 2.1043P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[h]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

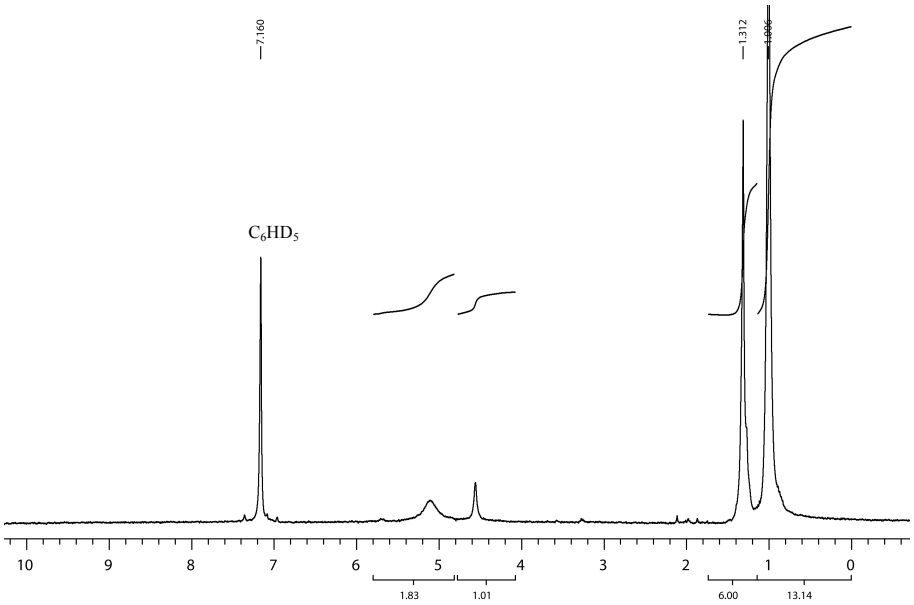


Figure S2: $^{1}H\{^{11}B\}$ NMR spectrum (C_6D_6) of $ImMe_2{}^{i}Pr_2{\bullet}BH(OTf)N_3$ (**8**).

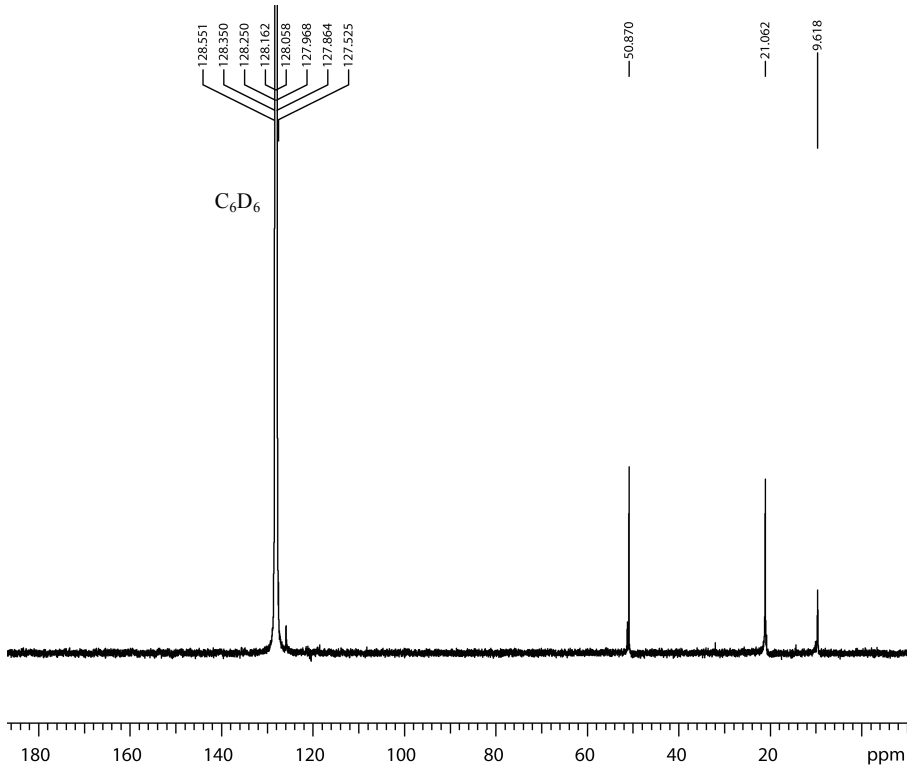


Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6) of $ImMe_2{}^{i}Pr_2{\bullet}BH(OTf)N_3$ (**8**).

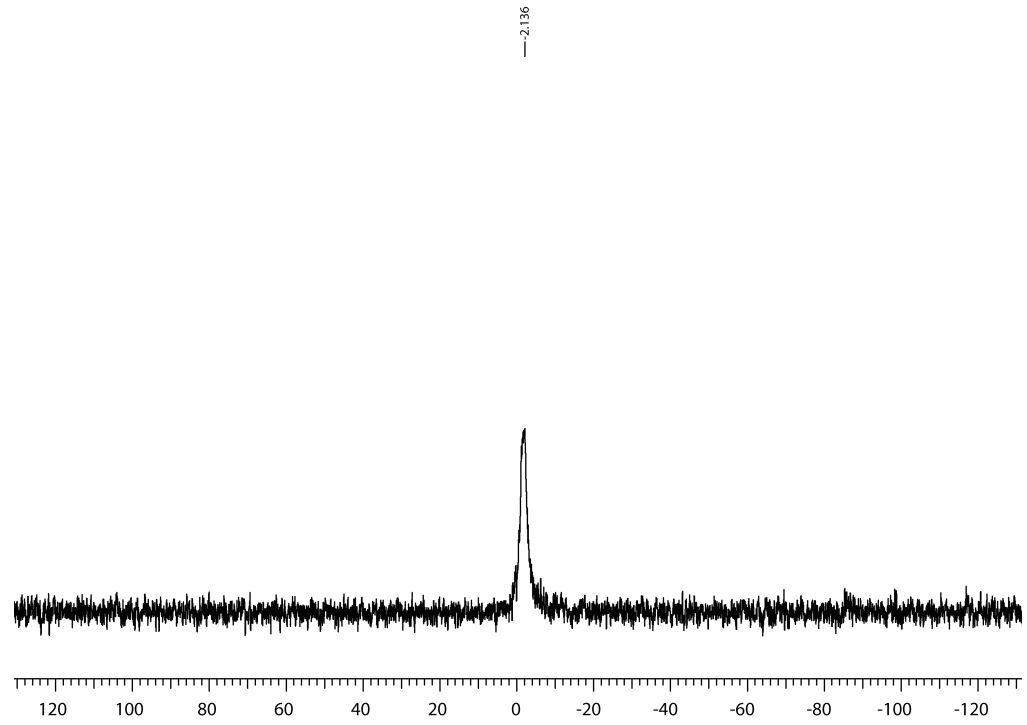


Figure S4: ^{11}B NMR spectrum (C_6D_6) of $ImMe_2{}^{i}Pr_2{\bullet}BH(OTf)N_3$ (**8**).

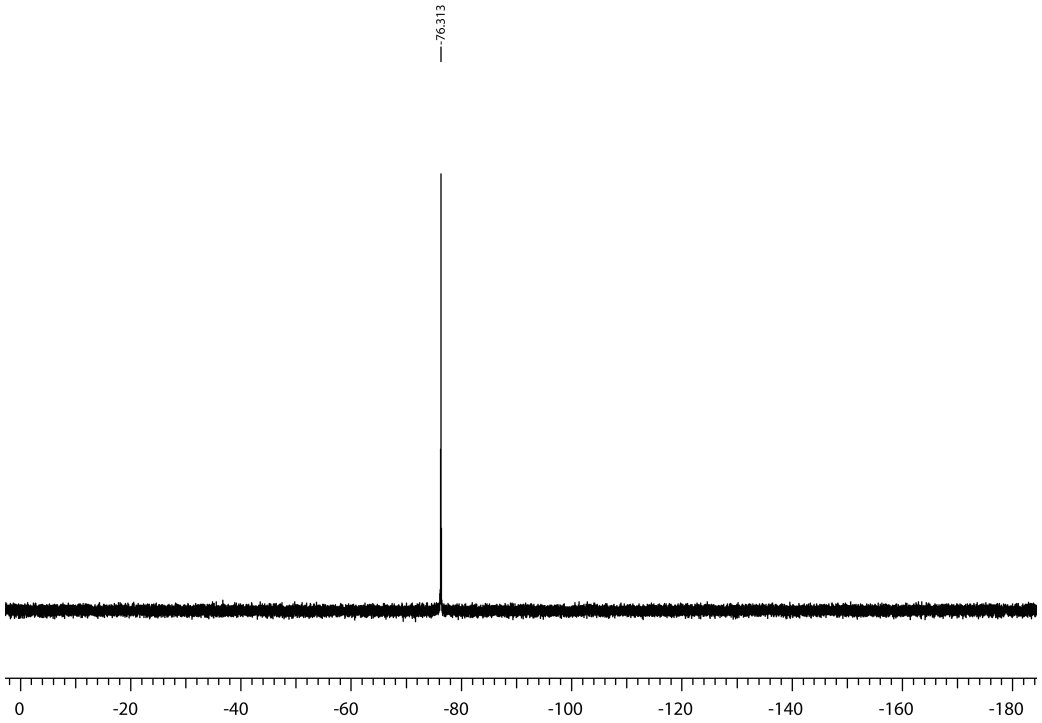


Figure S5: ^{19}F NMR spectrum (C_6D_6) of $ImMe_2{}^{i}Pr_2{\bullet}BH(OTf)N_3$ (**8**).

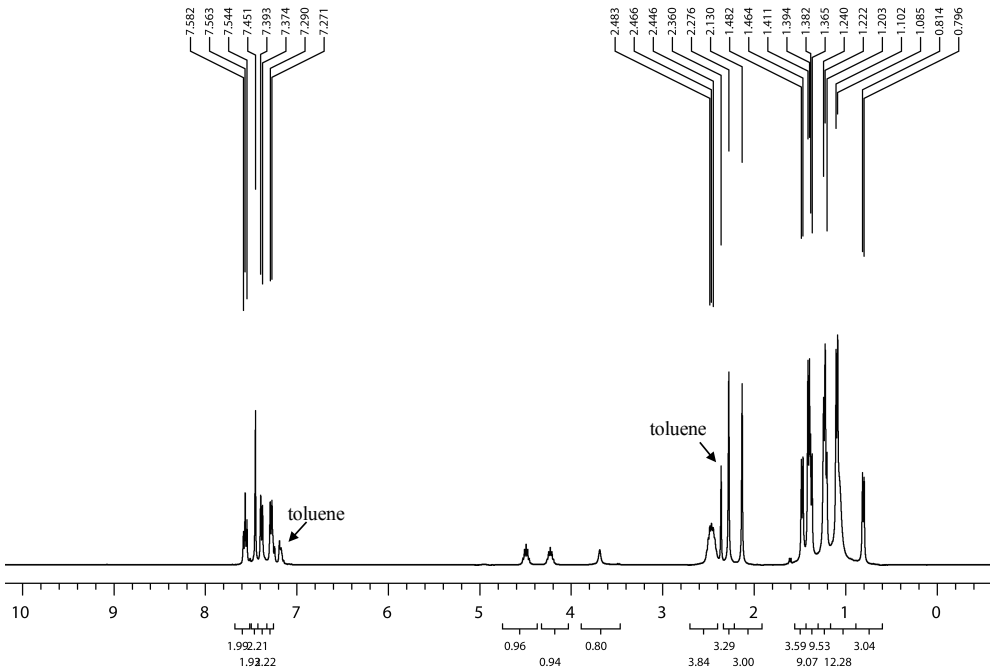


Figure S6: $^{1}H\{^{11}B\}$ NMR spectrum ($CDCl_3$) of [IPr($ImMe_2{}^{i}Pr_2$)•$BH(N_3)$]OTf (**9**).

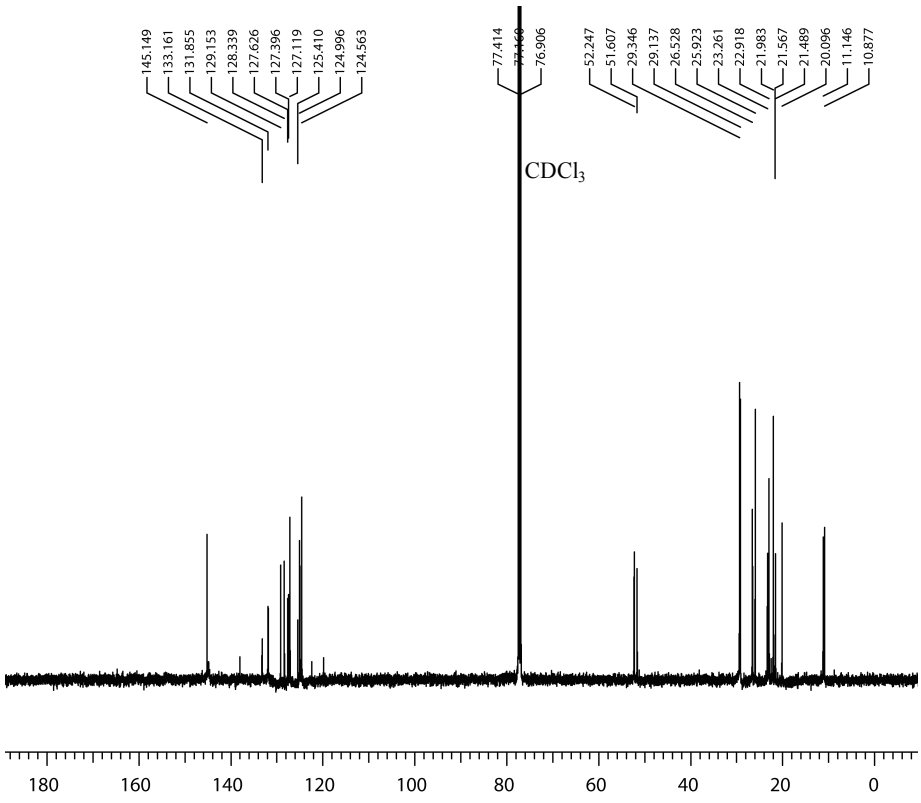


Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of [IPr($ImMe_2{}^{i}Pr_2$)•$BH(N_3)$]OTf (**9**).

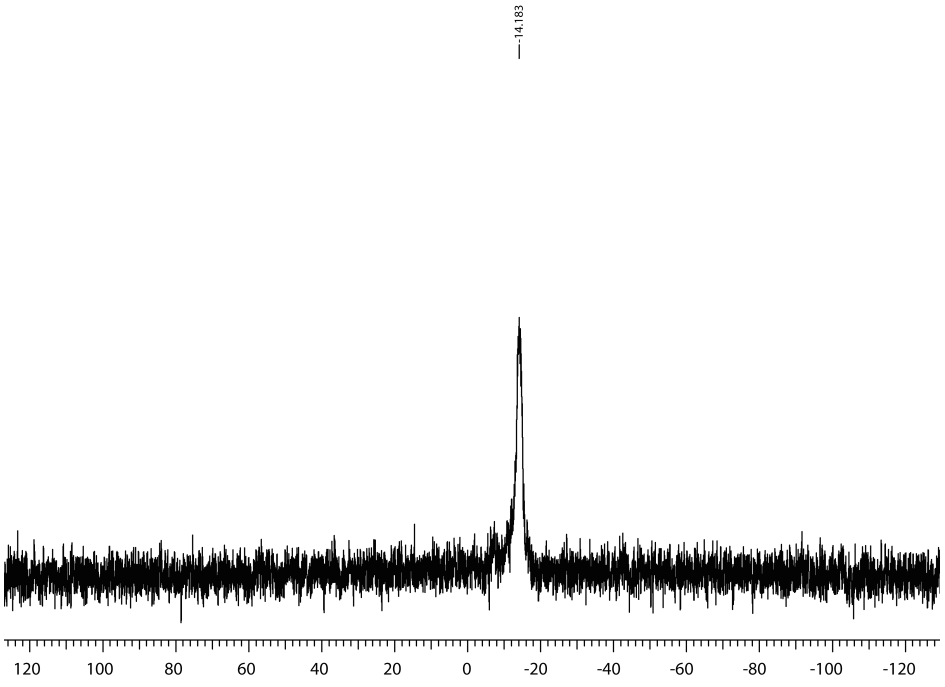


Figure S8: ^{11}B NMR spectrum ($CDCl_3$) of [IPr($ImMe_2{}^iPr_2$)•$BH(N_3)$]OTf (**9**).

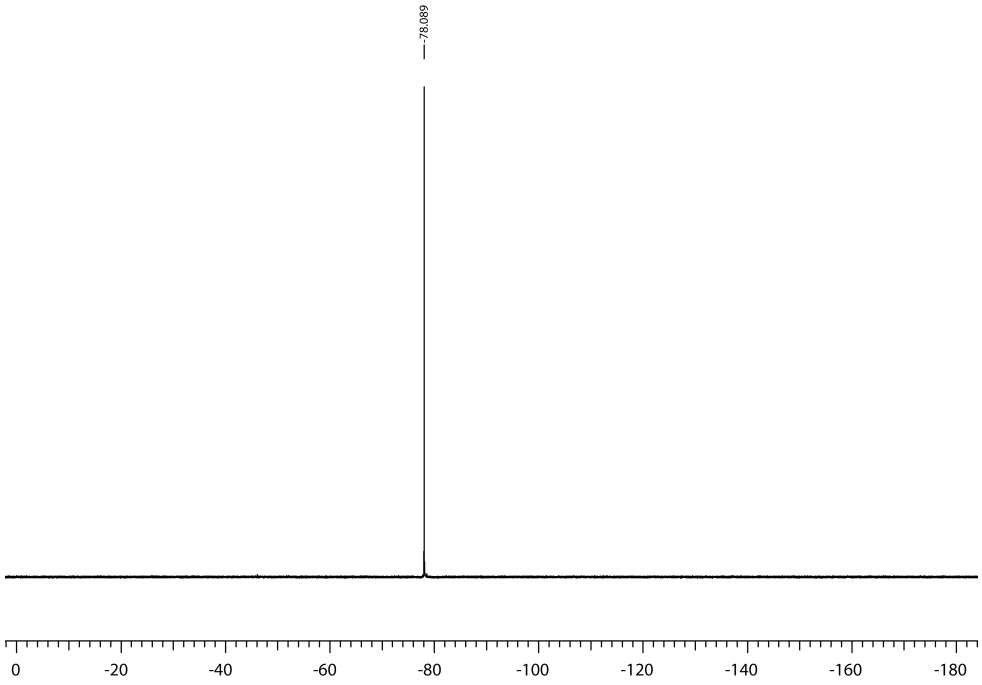


Figure S9: ^{19}F NMR spectrum ($CDCl_3$) of [IPr($ImMe_2{}^iPr_2$)•$BH(N_3)$]OTf (**9**).

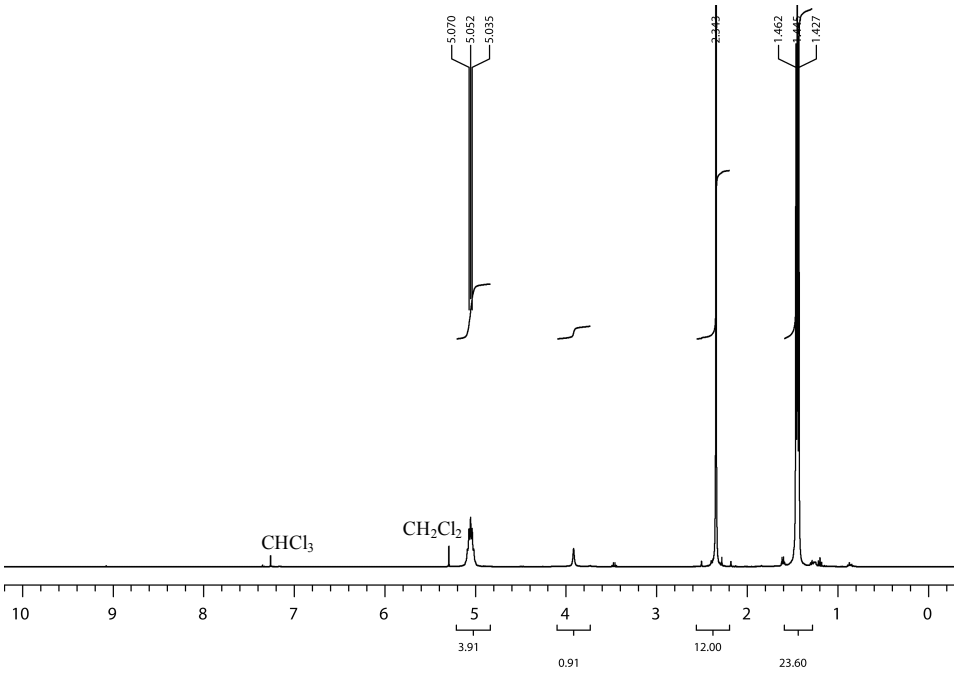


Figure S10: $^{1}H\{^{11}B\}$ NMR spectrum ($CDCl_3$) of $[(ImMe_2{}^{i}Pr_2)_2{\bullet}BH(N_3)]OTf$ (**10**).

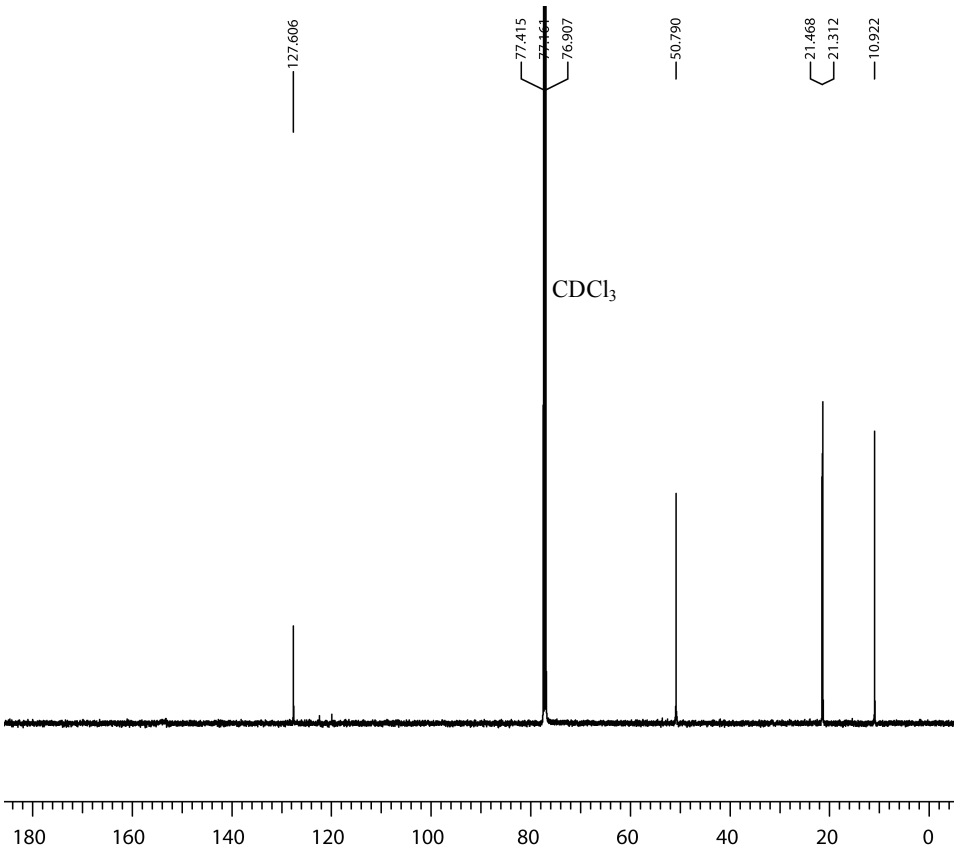


Figure S11: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of $[(ImMe_2{}^{i}Pr_2)_2{\bullet}BH(N_3)]OTf$ (**10**).

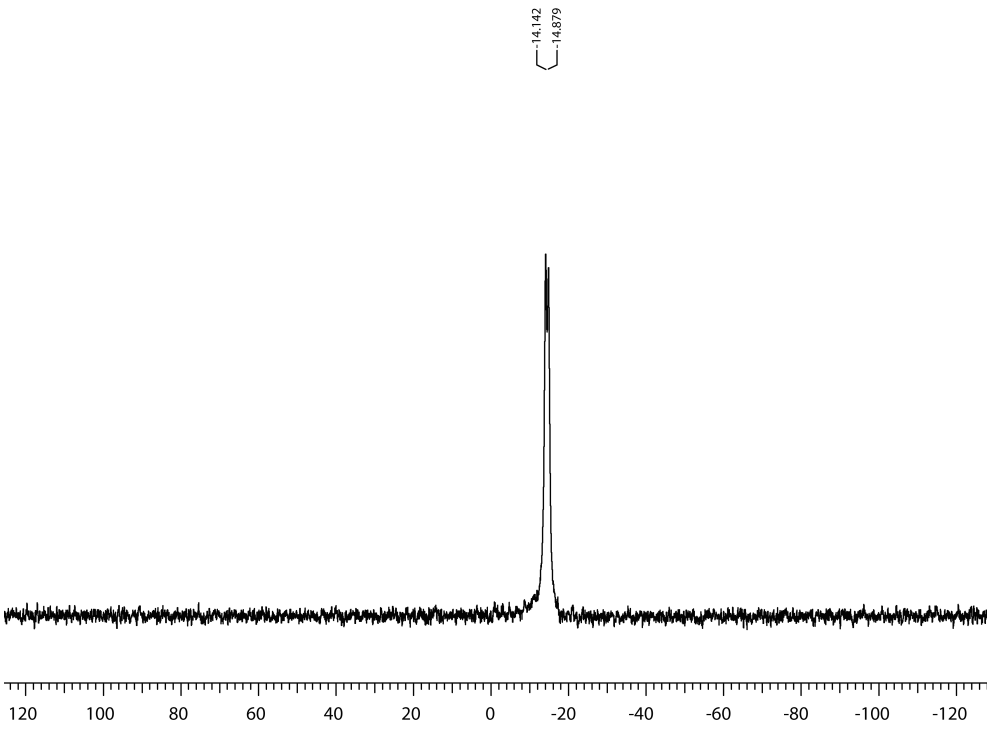


Figure S12: ^{11}B NMR spectrum ($CDCl_3$) of [($ImMe_2{}^iPr_2)_2$•$BH(N_3)$]OTf (**10**).

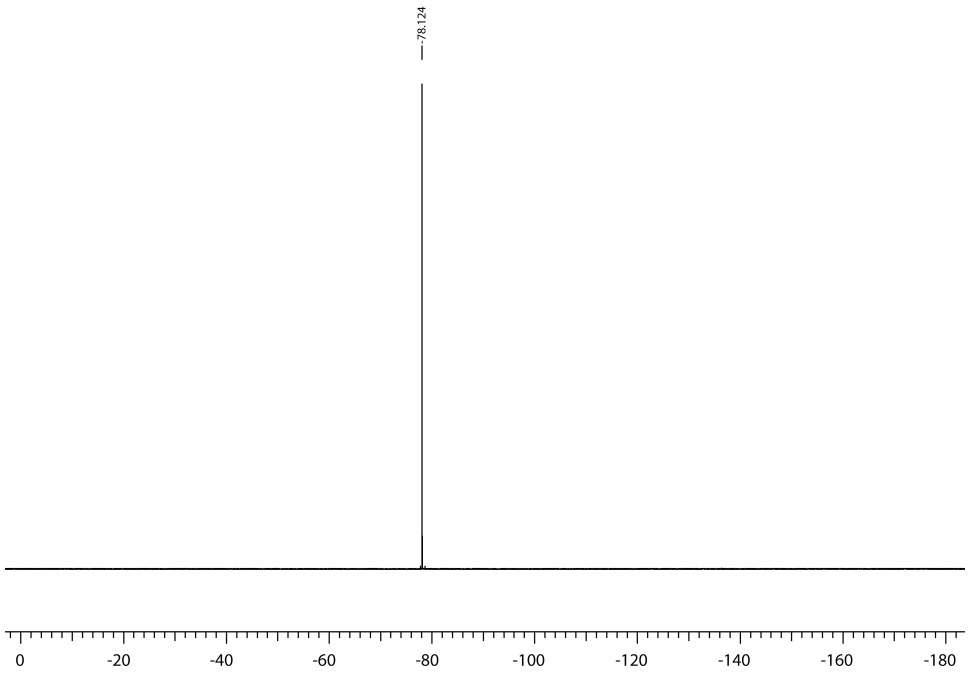


Figure S13: ^{19}F NMR spectrum ($CDCl_3$) of [($ImMe_2{}^iPr_2)_2$•$BH(N_3)$]OTf (**10**).

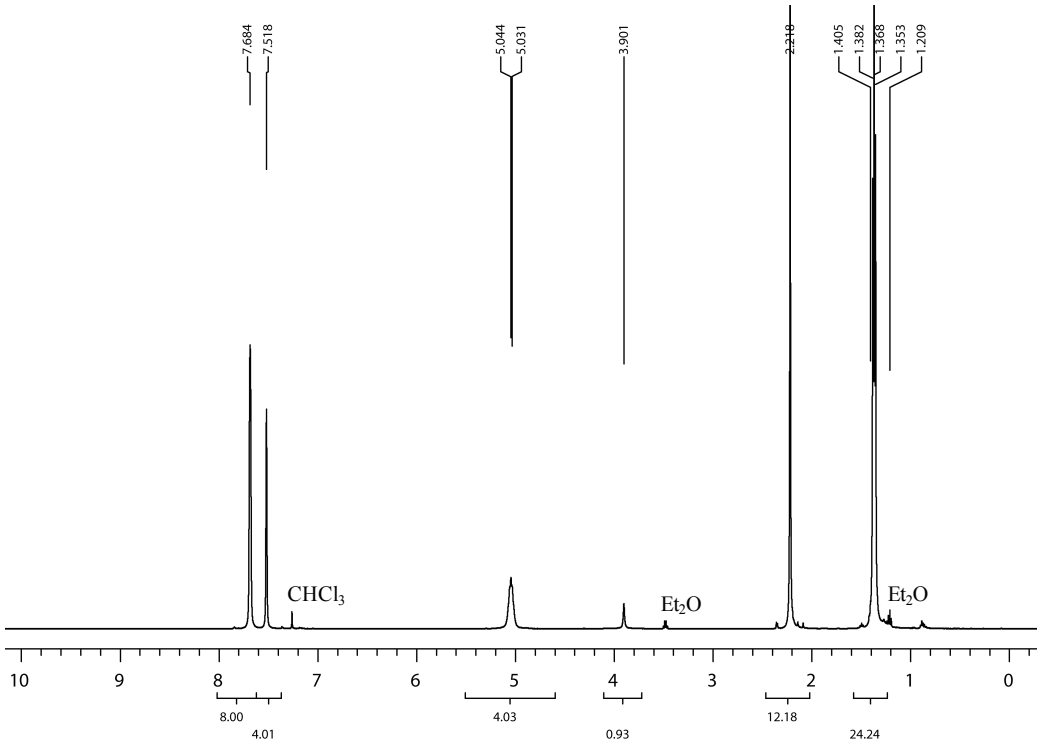


Figure S14: $^{1}H\{^{11}B\}$ NMR spectrum ($CDCl_3$) of $[(ImMe_2{}^{i}Pr_2)_2{\bullet}BH(N_3)]BAr^{F}{}_4$ (**11**).

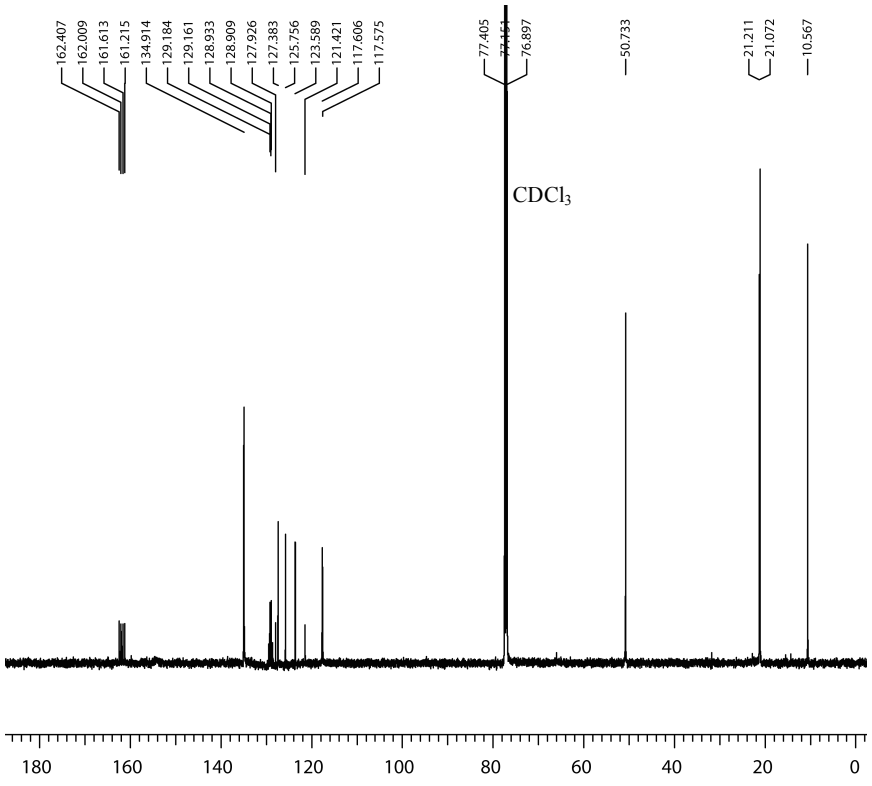


Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of $[(ImMe_2{}^{i}Pr_2)_2{\bullet}BH(N_3)]BAr^{F}{}_4$ (**11**).

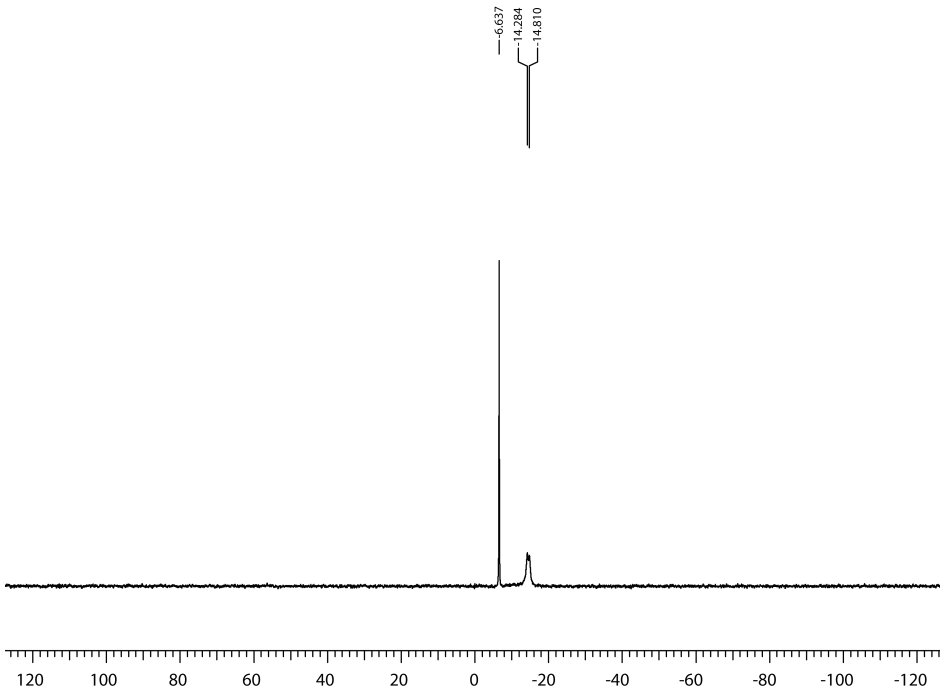


Figure S16: ^{11}B NMR spectrum ($CDCl_3$) of $[(ImMe_2{}^iPr_2)_2{\bullet}BH(N_3)]BAr^F{}_4$ (**11**).

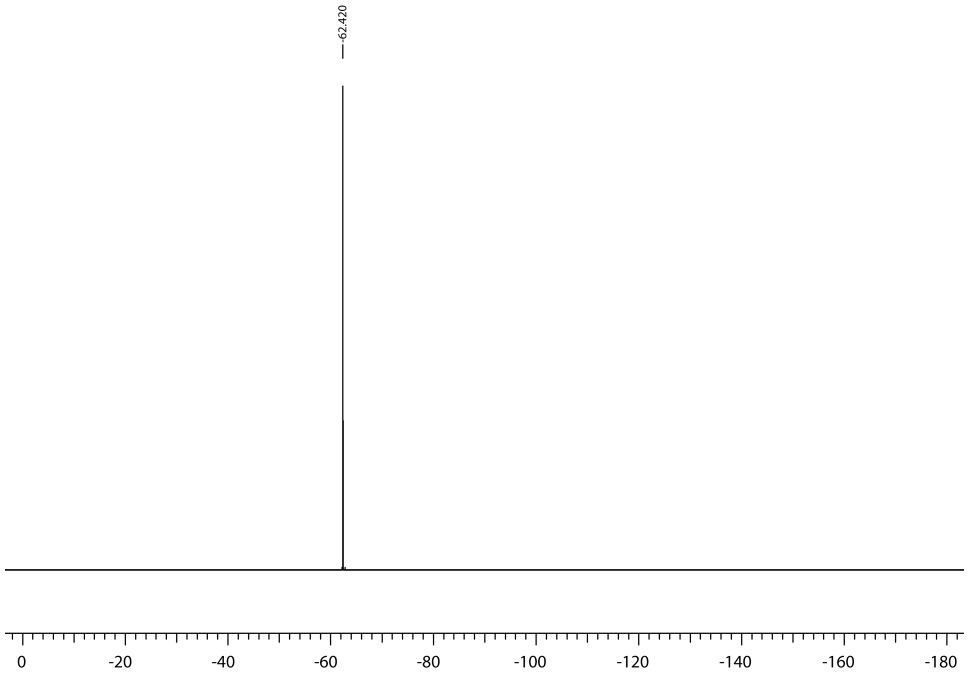


Figure S17: ^{19}F NMR spectrum ($CDCl_3$) of $[(ImMe_2{}^iPr_2)_2{\bullet}BH(N_3)]BAr^F{}_4$ (**11**).

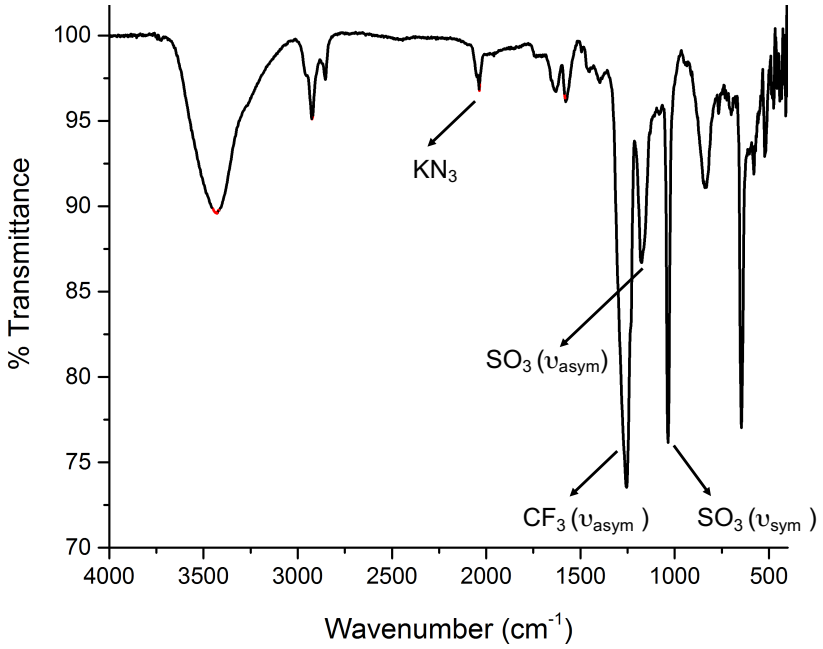


Figure S18: IR spectrum of the insoluble part from the reduction of $ImMe_2{}^iPr_2$•BH(OTf)N_3 (**8**) with KC_8.

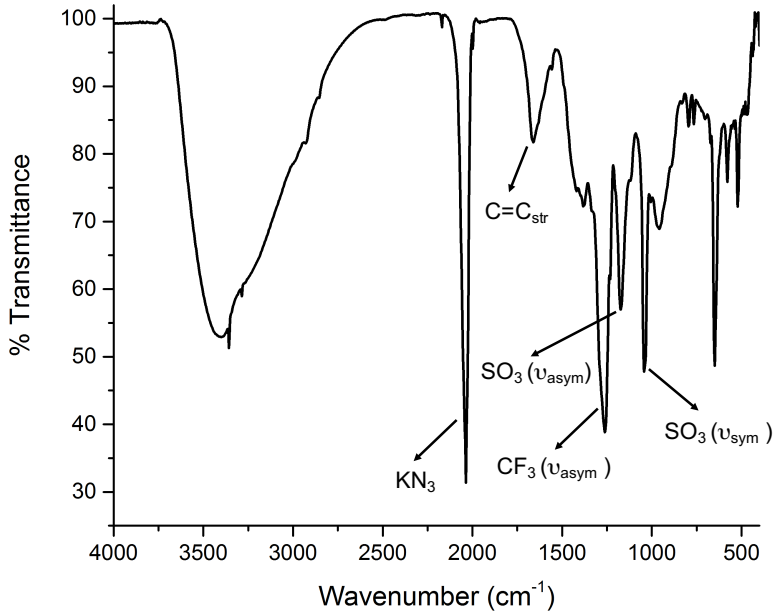


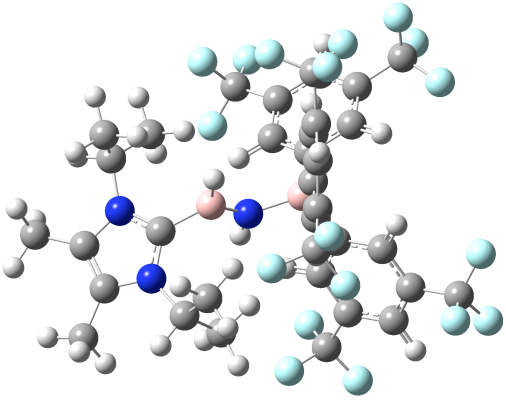
Figure S19: IR spectrum of the insoluble part from the reduction of $ImMe_2{}^iPr_2$•BH(OTf)N_3 (**8**) with K.

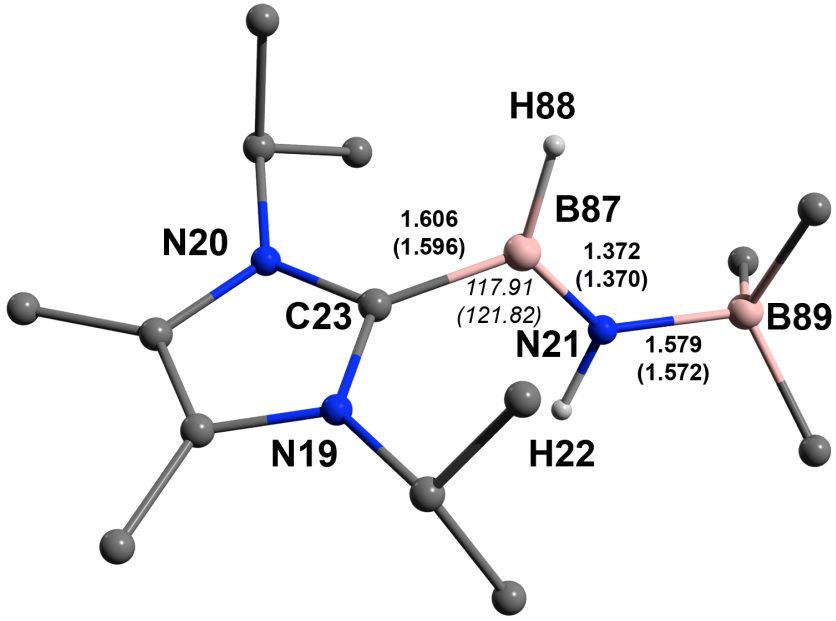
2. Computational Studies

Density Functional theory (DFT) calculations (full geometry optimisation) was carried out on **3**, **4**, **5**, **6**, **$ImMe_2$•$BH(OTf)N_3$** (as a truncated model for **7** and **8**) and **$[(ImMe_2)_2$•$B(H)N_3]^+$** (as a truncated model for the cation in **9**) starting from the geometries of their respective crystal structures with the Gaussian09 program package[16] (M062X functional with 6-31G(d,p))).[17] The optimized structures were in reasonable agreement with the observed molecular structures, frequency analyses were carried out to verify the absence of imaginary frequencies. The optimized structures were subjected to natural bond orbital (NBO) analysis[18] and the Kohn-Sham orbitals were obtained from the formatted checkpoint files.

It should be emphasized that the computation was carried out for a single, isolated (gas phase) species. There may well be significant differences among gas-phase, solution, and solid-state data.[19]

Figure S20: POV-ray depiction of the optimized structure of **3** (top), with a detailed view (bottom) in which H-atoms on the $ImMe_2{}^iPr_2$ and the $-C_6H_3(CF_3)_2$ groups have been omitted for clarity; atom numbers as they appear in the output-file, bond lengths, and C-B-N angle in italics (experimental values in brackets). xyz-coordinates for the optimized structure of **3**, checked to be a minimum on the energy hyper-surface by a frequency analysis.





F	5.10600570	2.26031259	-0.67875877
F	4.51446760	4.10321869	0.27337349
F	4.82080678	4.05224359	-1.85862054
F	0.34464727	5.52951389	-3.10363568
F	-1.16557991	3.97751047	-3.14579908
F	-0.95679786	5.22541851	-1.40621116
F	-1.24105704	-3.33397738	-3.96374763

F	-0.25162342	-1.77842515	-5.07463645
F	0.55105632	-3.78812213	-5.08620763
F	3.40122503	-4.76845322	-0.32873435
F	4.67011528	-3.03615818	-0.51337270
F	4.36866199	-4.34699138	-2.21041042
F	0.55376086	2.47608996	4.80234121
F	2.61418599	2.34541045	4.19130726
F	1.91186377	1.18911411	5.88105433
F	0.61982277	-4.09755407	3.09226618
F	-1.21328117	-3.23614450	3.82206554
F	0.51594660	-3.32890086	5.11338414
N	-4.28134214	-0.99608530	-0.02160849
N	-4.53145386	1.14246840	0.13449255
N	-1.14087077	0.06093470	-0.22766037
H	-1.49459597	-0.10369197	-1.16517182
C	-3.63988998	0.14610428	0.29195912
C	-5.58965536	-0.71899650	-0.39563318
C	-5.74955378	0.63078258	-0.29046393
C	-6.55791357	-1.76952194	-0.82541922
H	-6.15370174	-2.37542788	-1.64131952
H	-7.47434648	-1.29996412	-1.18397756
H	-6.82602117	-2.43870474	-0.00242331
C	-6.94700045	1.48058598	-0.55294486
H	-7.24775993	2.03843830	0.33881646
H	-7.78689042	0.85095313	-0.84735547
H	-6.76705468	2.19689236	-1.35983352
C	-3.73760864	-2.37716137	0.08230433
H	-4.62893174	-3.00814840	0.05265489
C	-3.04990313	-2.60121283	1.42442577
H	-2.77802081	-3.65576292	1.51308480
H	-2.12758510	-2.02324904	1.51439067
H	-3.70654258	-2.34419429	2.25908872
C	-2.85012600	-2.73116472	-1.10847947
H	-2.68743259	-3.81148358	-1.12862806
H	-3.30967452	-2.43968248	-2.05716480
H	-1.87308858	-2.25177846	-1.02096686
C	-4.31725156	2.56607754	0.49218802
H	-5.16641163	3.08937773	0.04641369
C	-4.37370752	2.72197862	2.00918480
H	-4.29686148	3.77937844	2.27267004
H	-5.31182825	2.32956696	2.41087004
H	-3.54189735	2.19060564	2.47931600
C	-3.04308994	3.14137308	-0.11246861
H	-3.03807442	4.22250866	0.04224973
H	-2.14267972	2.74122741	0.36151329
H	-2.98912577	2.95806018	-1.18897515

C	1.03097880	1.45770191	-0.66527350
C	2.39001856	1.78979286	-0.54529446
H	3.07635699	1.09015008	-0.07244023
C	2.89104813	2.99654900	-1.02150772
C	2.05797034	3.92833177	-1.63990478
H	2.45275706	4.86691073	-2.01306242
C	0.71590532	3.61036639	-1.77558446
C	0.22036886	2.39579854	-1.30313609
H	-0.83392945	2.18084817	-1.44288942
C	4.33799309	3.34762832	-0.82257366
C	-0.25365927	4.58781598	-2.36594400
C	0.98859612	-1.16462117	-1.08048708
C	0.36331710	-1.48009575	-2.29086521
H	-0.48851996	-0.89909406	-2.64367689
C	0.78931861	-2.53045426	-3.10012318
C	1.90262106	-3.28392619	-2.75727378
H	2.24448391	-4.09624578	-3.38794471
C	2.57366364	-2.95608468	-1.58334356
C	2.12035101	-1.92931954	-0.75914256
H	2.66029174	-1.72603549	0.16302561
C	-0.02522464	-2.86028488	-4.31377732
C	3.75928075	-3.77588036	-1.15989719
C	0.76698668	-0.23546288	1.44971136
C	1.14718890	0.75435134	2.35958404
H	1.37156616	1.75692830	2.00215282
C	1.23148196	0.49669478	3.72907029
C	0.92662693	-0.75627549	4.24326826
H	0.98517361	-0.95016283	5.30782725
C	0.55393978	-1.75659890	3.35088981
C	0.49200934	-1.50178759	1.98545888
H	0.20942799	-2.31276157	1.31497336
C	1.58473876	1.62431123	4.65523003
C	0.13238702	-3.10603761	3.85019085
B	-2.10050935	0.27794764	0.72857358
H	-1.85775446	0.54223661	1.86655835
B	0.43512093	0.04324968	-0.12073916

Summary of Natural Population Analysis:

Atom	No	Charge
N	19	-0.35947
N	20	-0.36043
N	**21**	**-1.02080**
H	**22**	**0.40958**
C	23	0.24496
B	**87**	**0.50598**

H 88 -0.02585
B 89 0.59438

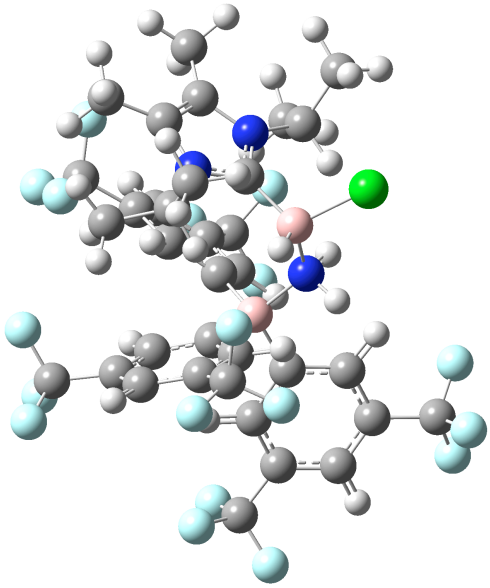
Selected NBOs of **3**.

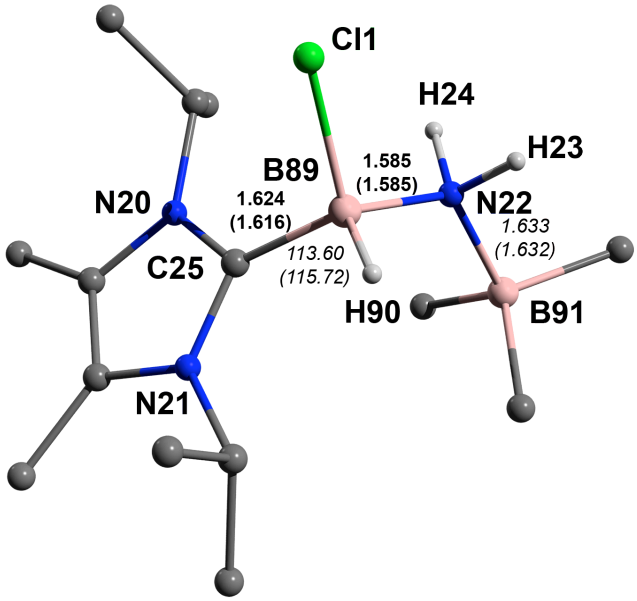
26. (1.97415) BD (1) N 21 - H 22 (WBI = 0.7876)
(70.99%) 0.8426* N 21 s(22.25%)p 3.49(77.71%)d 0.00(0.04%)
(29.01%) 0.5386* H 22 s(99.91%)p 0.00(0.09%)
27. (1.95368) BD (1) N 21 - B 87 (WBI = 1.3322)
(79.47%) 0.8914* N 21 s(0.38%)p99.99(99.59%)d 0.08(0.03%)
(20.53%) 0.4531* B 87 s(0.40%)p99.99(99.24%)d 0.92(0.37%)
28. (1.79996) BD (2) N 21 - B 87 (WBI = 1.3322)
(78.03%) 0.8833* N 21 s(76.39%)p 0.31(23.59%)d 0.00(0.02%)
(21.97%) 0.4687* B 87 s(30.96%)p 2.22(68.87%)d 0.01(0.17%)
29. (1.96622) BD (1) C 23 - B 87 (WBI = 0.8479)
(69.43%) 0.8333* C 23 s(44.91%)p 1.23(55.09%)d 0.00(0.00%)
(30.57%) 0.5529* B 87 s(32.60%)p 2.06(67.30%)d 0.00(0.10%)
103. (1.97257) BD (1) B 87 - H 88 (WBI = 0.9612)
(48.30%) 0.6950* B 87 s(36.04%)p 1.77(63.91%)d 0.00(0.04%)
(51.70%) 0.7190* H 88 s(99.96%)p 0.00(0.04%)
217. (1.62040) LP (1) N 21 s(0.95%)p99.99(99.05%)d 0.00(0.00%)
218. (0.46372) LP*(1) B 89 s(23.15%)p 3.31(76.73%)d 0.01(0.12%)

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
From ($ImMe_2{}^iPr_2$)BHNH to $BAr^F{}_3$

Donor NBO (i)	Acceptor NBO (j)	kcal/mol
26. BD (1) N 21 - H 22	/218. LP*(1) B 89	18.06
28. BD (2) N 21 - B 87	/218. LP*(1) B 89	192.59
217. LP (1) N 21	/218. LP*(1) B 89	217.46

Figure S21: POV-ray depiction of the optimized structure of **4** (top), with a detailed view (bottom) in which H-atoms on the $ImMe_2{}^iPr_2$ and the $C_6H_3(CF_3)_2$- groups have been omitted for clarity; atom numbers as they appear in the output-file, bond lengths, and C-B-N angle in italics (experimental values in brackets). xyz-coordinates for the optimized structure of **4**, checked to be a minimum on the energy hyper-surface by a frequency analysis.





Cl	1.02621188	-0.46962075	4.41792720
F	-6.25054954	1.59941471	-2.02823781
F	-4.99079157	0.27385488	-3.17214132
F	-4.29479670	2.25478904	-2.68677307
F	-4.91336301	-2.06861821	2.79079069
F	-5.54292636	-0.07739074	3.31554733
F	-6.69168571	-1.22250167	1.89006505
F	1.65332029	4.62306431	2.50741097
F	0.75509572	6.18753892	1.31666865
F	-0.47343569	4.96496169	2.61334184
F	2.52793250	3.15029045	-3.07829341
F	0.56131118	2.80117042	-3.89117828
F	1.15402448	4.79869179	-3.30090931
F	2.88175622	-2.17898488	-3.87367605
F	3.89551388	-2.59432956	-2.02316410
F	3.39545689	-0.55833803	-2.53363881
F	-2.50480666	-4.25895044	-1.66632817
F	-0.90659106	-5.11189902	-2.85279593
F	-0.89879727	-5.33232440	-0.70531962
N	2.57400389	-1.92593017	1.75018778
N	3.28090818	0.02766953	1.14692280
N	-0.34010787	-0.13346417	2.00294746
H	-0.97588736	0.39970462	2.60191846
H	-0.60798430	-1.10446288	2.17653470
C	2.29655718	-0.60790854	1.82142151
C	3.74014420	-2.13051669	1.03279470
C	4.19458410	-0.89520150	0.66068800
C	1.75896329	-2.97727211	2.40213579
H	0.86312838	-2.45443945	2.73497234
C	1.34249192	-4.07474978	1.42560952
H	0.44575243	-4.57005596	1.80568262
H	1.10660069	-3.65921972	0.44474363
H	2.11430649	-4.83866632	1.31219239
C	2.45497155	-3.51460477	3.64906699
H	1.77185521	-4.19113607	4.16938430
H	3.35577866	-4.07864450	3.39652777
H	2.71570745	-2.70029793	4.32606349
C	3.34402287	1.50866348	1.00475429
H	2.31097494	1.83372793	1.11171744
C	3.80992843	1.97406506	-0.37240523
H	3.50296576	3.01634303	-0.48795634
H	4.89429288	1.93672795	-0.48838268
H	3.34570052	1.40811943	-1.18382813
C	4.16205311	2.10533714	2.14309847
H	4.11441006	3.19560959	2.08676259
H	3.76089754	1.79234280	3.11048582

H	5.21119695	1.79943305	2.08018073
C	4.32397028	-3.46867686	0.72214498
H	4.40343603	-4.10030896	1.60845243
H	5.32491740	-3.34085077	0.30988267
H	3.72817450	-3.99140678	-0.02905892
C	5.44899322	-0.56544292	-0.08077829
H	6.01744944	0.21650383	0.42795701
H	5.24847728	-0.24548203	-1.10447659
H	6.07813110	-1.45474574	-0.12661892
C	-2.37075970	0.17824421	0.36336928
C	-2.99574319	0.70341666	-0.77895600
H	-2.39186632	1.15363988	-1.56357296
C	-4.37502835	0.68172235	-0.93762631
C	-5.20024988	0.13825138	0.04385951
H	-6.27714043	0.12846407	-0.07739694
C	-4.60454377	-0.38515646	1.17975102
C	-3.21648694	-0.36719228	1.33367239
H	-2.81898005	-0.80963478	2.24550598
C	-4.98097490	1.20772619	-2.20866403
C	-5.44663785	-0.94072733	2.29229425
C	-0.17756298	1.65269788	0.04279822
C	-0.13555729	2.69495285	0.97848623
H	-0.48194413	2.53476293	1.99639661
C	0.37822245	3.94997252	0.66531697
C	0.81392172	4.24303980	-0.62111159
H	1.20783592	5.22298276	-0.86715467
C	0.71521187	3.24642250	-1.58390625
C	0.23730656	1.97887113	-1.25688129
H	0.19221289	1.23173237	-2.04520331
C	0.56844478	4.94328548	1.77354792
C	1.23206407	3.50365215	-2.97015507
C	-0.13854566	-1.03228741	-0.47536296
C	1.13147566	-0.97009546	-1.07052837
H	1.75501621	-0.09779440	-0.90678911
C	1.60942134	-1.97070341	-1.91006453
C	0.84718493	-3.10729250	-2.16594746
H	1.20428927	-3.88452933	-2.83381010
C	-0.39713346	-3.20895525	-1.55821143
C	-0.88547852	-2.18703894	-0.74246426
H	-1.88521954	-2.29207228	-0.32702914
C	2.94207457	-1.82396077	-2.58636222
C	-1.18636104	-4.47779743	-1.70634348
B	1.09381497	0.13188046	2.62373674
H	1.29099428	1.30491513	2.67189192
B	-0.73989249	0.18051353	0.45072139

Summary of Natural Population Analysis:
Atom No Charge

Cl	**1**	**-0.28980**
N	20	-0.35477
N	21	-0.35538
N	**22**	**-1.01753**
H	**23**	**0.45452**
H	**24**	**0.43949**
C	25	0.25697
B	**89**	**0.27108**
H	**90**	**-0.02117**
B	91	0.61082

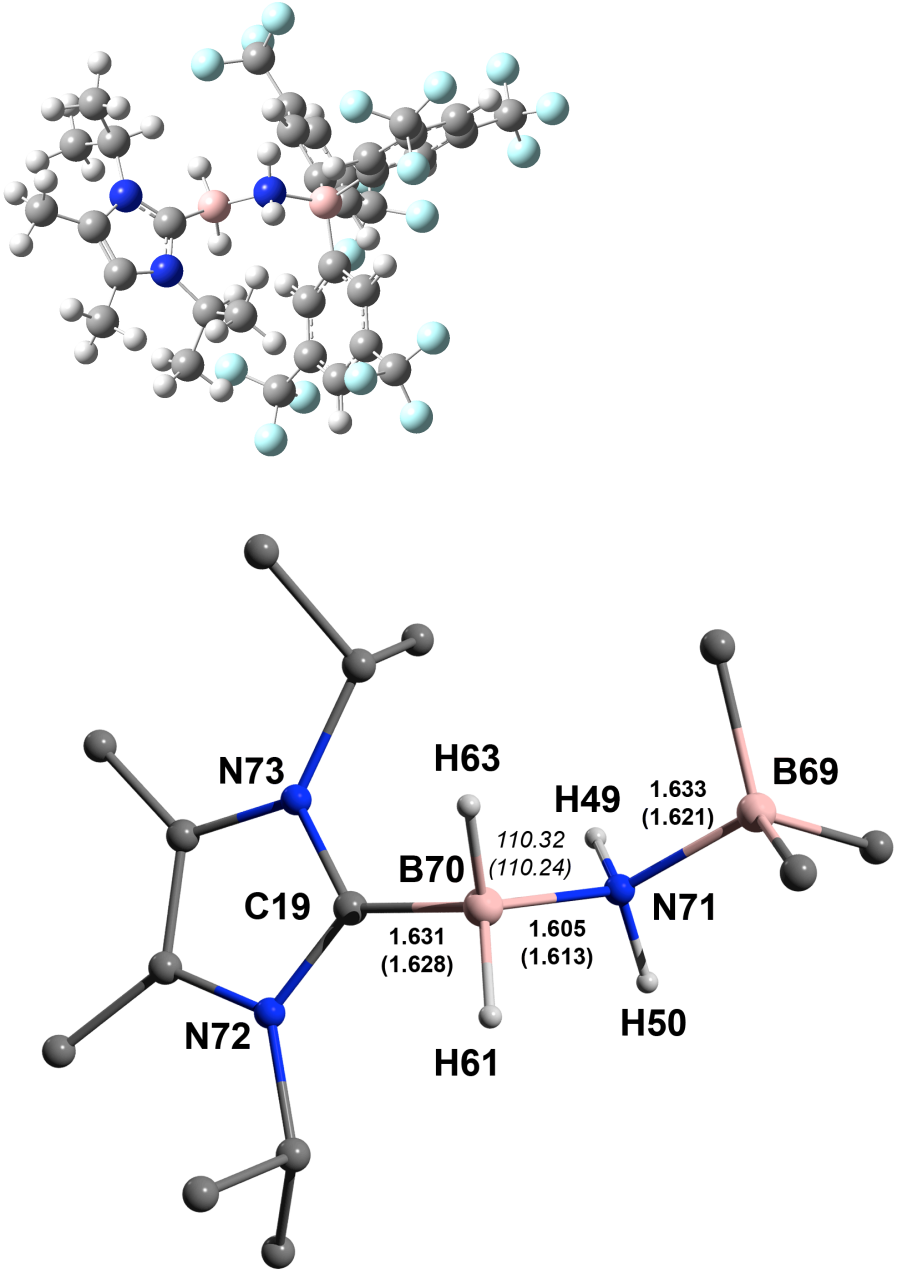
Selected NBOs of **4**.

1. (1.98638) BD (1)Cl 1 - B 89 (WBI = 0.9264)
(69.58%) 0.8341*Cl 1 s(27.15%)p 2.67(72.59%)d 0.01(0.25%)
(30.42%) 0.5516* B 89 s(23.12%)p 3.32(76.68%)d 0.01(0.20%)
27. (1.9593) BD (1) N 22 - H 23 (WBI = 0.7609)
(72.99%) 0.8543* N 22 s(19.79%)p 4.05(80.16%)d 0.00(0.05%)
(27.01%) 0.5197* H 23 s(99.90%)p 0.00(0.10%)
28. (1.97818) BD (1) N 22 - H 24 (WBI = 0.7728)
(72.33%) 0.8505* N 22 s(20.25%)p 3.94(79.70%)d 0.00(0.05%)
(27.67%) 0.5260* H 24 s(99.91%)p 0.00(0.09%)
29. (1.82957) BD (1) N 22 - B 89 (WBI = 0.6766)
(80.76%) 0.8987* N 22 s(59.12%)p 0.69(40.86%)d 0.00(0.02%)
(19.24%) 0.4386* B 89 s(21.60%)p 3.62(78.19%)d 0.01(0.21%)
30. (1.96705) BD (1) C 25 - B 89 (WBI = 0.8428)
(68.48%) 0.8276* C 25 s(45.76%)p 1.19(54.23%)d 0.00(0.00%)
(31.52%) 0.5614* B 89 s(25.30%)p 2.95(74.60%)d 0.00(0.10%)
103. (1.97109) BD (1) B 89 - H 90 (WBI = 0.9531)
(48.73%) 0.6981* B 89 s(29.92%)p 2.34(70.02%)d 0.00(0.06%)
(51.27%) 0.7160* H 90 s(99.96%)p 0.00(0.04%)
225. (1.62753) LP (1) N 22 s(0.77%)p99.99(99.23%)d 0.00(0.00%)
228. (0.44014) LP*(1) B 91 s(19.55%)p 4.11(80.33%)d 0.01(0.12%)

Second Order Perturbation Theory Analysis of the Fock Matrix in NBO Basis
From ($ImMe_2{}^iPr_2$)BHClNH$_2$ to $BAr^F{}_3$

Donor NBO (i)	Acceptor NBO (j)	kcal/mol
27. BD (1) N 22 - H 23	/228. LP*(1) B 91	19.38
28. BD (1) N 22 - H 24	/228. LP*(1) B 91	21.15
29. BD (1) N 22 - B 89	/228. LP*(1) B 91	154.21
225. LP (1) N 22	/228. LP*(1) B 91	202.71

Figure S22: POV-ray depiction of the optimized structure of **5** (top), with a detailed view (bottom) in which H-atoms on the $ImMe_2{}^iPr_2$ and the $-C_6H_3(CF_3)_2$ groups have been omitted for clarity; atom numbers as they appear in the output-file, bond lengths, and C-B-N angle in italics (experimental values in brackets). xyz-coordinates for the optimized structure of **5**, checked to be a minimum on the energy hyper-surface by a frequency analysis.



C	1.59070682	-3.30467266	3.94614897
C	2.11117184	-2.45460365	2.82437284
C	3.45325999	-2.49465096	2.47878654
C	1.21159579	-1.66988213	2.10231169
C	3.87226616	-1.73209696	1.39235833
C	5.32923057	-1.70054313	1.02431883
C	-0.84551051	-4.52170333	-1.92377151
C	-3.71542726	2.81112507	4.34057220
C	-6.33493256	1.81795803	3.02269404
C	1.61054871	-0.89459115	1.00770177
C	2.97262009	-0.95202031	0.67490772
C	-0.08029280	-2.28490831	-1.08161336
C	-6.54246344	-0.53542678	0.85163232
C	-3.54964578	-2.18078000	0.14805152
C	-5.26049474	1.29271578	2.12711549
C	-0.73057447	-3.03136470	-2.06238006
C	-5.34677422	0.28768071	1.20747139
C	-3.38627767	2.89245138	2.85183678
C	-3.25615278	1.11369603	1.12328059
C	-0.01848400	-0.88469371	-1.13742516
C	-3.68035606	-0.77562074	-0.43364015
C	-1.36469581	-2.40807054	-3.13150947
C	-3.77244761	4.22476156	2.21971338
C	1.28250134	1.38301329	-0.33701917
C	1.37881782	2.46179027	0.55077206
C	-0.62858040	-0.27790381	-2.24553704
C	-4.56689542	-0.71158336	-1.67329169
C	-1.30870004	-1.02152483	-3.20815548
C	1.91341854	1.54597751	-1.57576550
C	2.02353070	3.64547338	0.20986998
C	2.03724648	4.76080149	1.21277610
C	-2.00637862	-0.29539464	-4.32232227
C	2.57813135	2.72439716	-1.91449341
C	2.63266854	3.79340800	-1.03120537
C	3.21237828	2.82077148	-3.27204724
H	4.15525630	-3.10235317	3.03780055
H	0.17182090	-1.68634414	2.42633093
H	-3.60709412	1.79111518	4.71869715
H	-6.19149521	1.51344619	4.06262886
H	-4.71953206	3.17127314	4.57007681
H	-3.01113947	3.44794705	4.88104659
H	0.39203229	-2.81329022	-0.25716941
H	-2.87539658	-2.19267891	1.01079123
H	-7.30050096	1.43641091	2.68917457
H	-7.28257403	-0.46779937	1.64979064
H	-6.29407934	-1.58993722	0.72663538

H	-4.51111877	-2.58744618	0.47142008
H	-6.38895061	2.90868028	2.99171429
H	-1.20944300	-0.56818267	1.14421622
H	-0.39424364	0.54694975	1.97725260
H	-3.13816995	-2.85172126	-0.60880700
H	3.34284798	-0.36900757	-0.16529171
H	-2.30987767	2.76624050	2.74081885
H	-7.00919979	-0.18656292	-0.07386483
H	-4.85506680	4.38049883	2.24429246
H	-3.29786630	5.04255875	2.76768106
H	-1.88977142	-2.98766741	-3.88324515
H	-2.68825173	-0.43401951	-0.73227228
H	0.93626120	2.39349312	1.54249134
H	-5.54857702	-1.16080523	-1.50946836
H	-1.39231609	2.52006278	0.98343622
H	-3.43517579	4.26216878	1.18134780
H	-1.83444040	1.47924472	-0.63354640
H	-4.07954622	-1.26639053	-2.47910147
H	1.89297840	0.73580494	-2.30224815
H	-0.60727818	0.80390834	-2.34325202
H	-4.69012862	0.32107973	-2.00790921
H	3.13958241	4.71270330	-1.29852575
B	0.57778642	-0.00652730	0.10560207
B	-1.76071025	1.45283260	0.56781770
N	-0.72253767	0.32274880	1.03634486
N	-3.95756508	1.77114312	2.07206548
N	-4.10047665	0.19462761	0.60430179
F	0.97546014	-4.40588636	3.48580841
F	2.56496003	-3.70923618	4.77044134
F	0.68281998	-2.64163179	4.68491900
F	5.97772495	-2.78706988	1.46963896
F	0.14780986	-5.04089321	-1.19629906
F	-1.99993317	-4.86387205	-1.31148821
F	-0.85061517	-5.13464908	-3.11489707
F	5.94550526	-0.63058593	1.55000047
F	5.50294676	-1.63801809	-0.30261146
F	2.63556072	4.39253254	2.35717814
F	0.78785845	5.13554536	1.54468502
F	-2.93204522	-1.06923441	-4.91544606
F	4.04874439	1.79557287	-3.49482708
F	2.67324401	5.84790142	0.75829307
F	-2.64183641	0.79501283	-3.85758116
F	-1.16353085	0.11899544	-5.27392546
F	3.91172651	3.95376431	-3.42557393
F	2.29127497	2.78347936	-4.24810602

Summary of Natural Population Analysis:
Atom No Charge

H 49 0.42857
H 50 0.43737
H 61 -0.02026
H 63 -0.00910
B 69 0.62008
B 70 -0.00227
N 71 -0.98595
N 72 -0.36946
N 73 -0.36750
C 19 0.30567

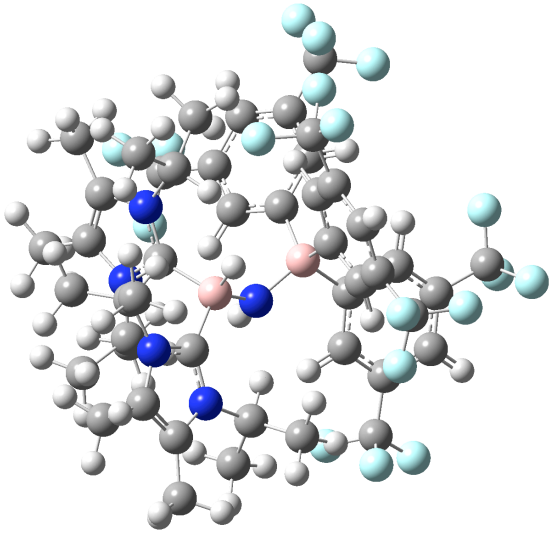
Selected NBOs of **5**.

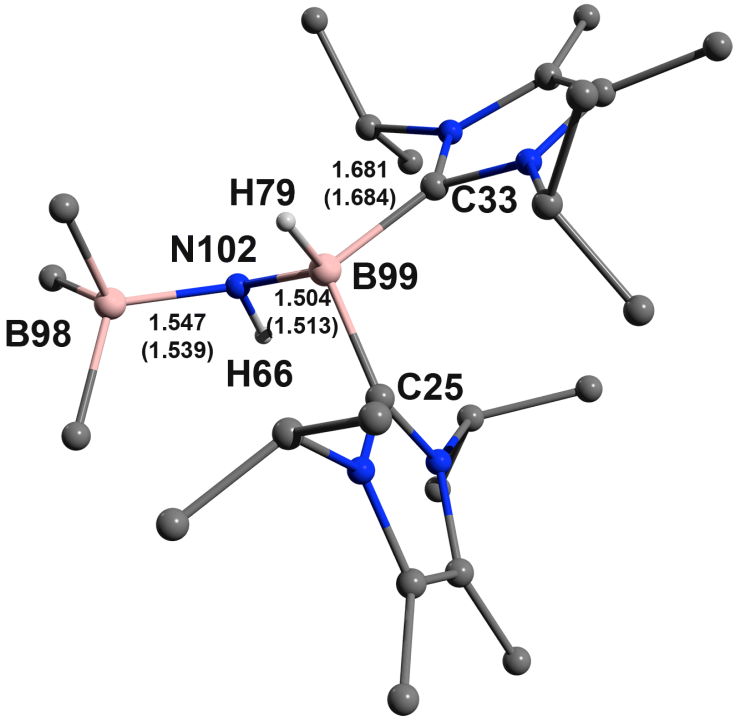
55. (1.96853) BD (1) C 19 - B 70 (WBI = 0.8647)
(68.82%) 0.8296* C 19 s(46.52%)p 1.15(53.48%)d 0.00(0.00%)
(31.18%) 0.5584* B 70 s(24.22%)p 3.13(75.69%)d 0.00(0.09%)
56. (1.97901) BD (1) C 19 - N 72
(35.91%) 0.5992* C 19 s(27.05%)p 2.69(72.83%)d 0.00(0.12%)
(64.09%) 0.8006* N 72 s(34.46%)p 1.90(65.50%)d 0.00(0.04%)
57. (1.88803) BD (2) C 19 - N 72
(26.68%) 0.5166* C 19 s(0.00%)p 1.00(99.71%)d 0.00(0.29%)
(73.32%) 0.8563* N 72 s(0.00%)p 1.00(99.96%)d 0.00(0.04%)
58. (1.97895) BD (1) C 19 - N 73
(35.93%) 0.5994* C 19 s(26.64%)p 2.75(73.23%)d 0.00(0.12%)
(64.07%) 0.8004* N 73 s(34.36%)p 1.91(65.60%)d 0.00(0.04%)
100. (1.97885) BD (1) H 49 - N 71 (WBI = 0.7861)
(28.27%) 0.5317* H 49 s(99.91%)p 0.00(0.09%)
(71.73%) 0.8469* N 71 s(20.93%)p 3.78(79.02%)d 0.00(0.05%)
101. (1.98050) BD (1) H 50 - N 71 (WBI = 0.7786)
(27.80%) 0.5273* H 50 s(99.91%)p 0.00(0.09%)
(72.20%) 0.8497* N 71 s(20.20%)p 3.95(79.74%)d 0.00(0.05%)
102. (1.97155) BD (1) H 61 - B 70 (WBI = 0.9653)
(51.57%) 0.7181* H 61 s(99.96%)p 0.00(0.04%)
(48.43%) 0.6959* B 70 s(28.59%)p 2.49(71.34%)d 0.00(0.06%)
103. (1.96022) BD (1) H 63 - B 70 (WBI = 0.9522)
(51.22%) 0.7157* H 63 s(99.96%)p 0.00(0.04%)
(48.78%) 0.6985* B 70 s(26.98%)p 2.70(72.96%)d 0.00(0.06%)
104. (1.85612) BD (1) B 70 - N 71 (WBI = 0.6860)
(20.01%) 0.4473* B 70 s(20.15%)p 3.95(79.65%)d 0.01(0.20%)
(79.99%) 0.8944* N 71 s(57.20%)p 0.75(42.78%)d 0.00(0.02%)
163. (0.43801) LP*(1) B 69 s(19.35%)p 4.16(80.53%)d 0.01(0.12%)
164. (1.62156) LP (1) N 71 s(1.60%)p61.38(98.40%)d 0.00(0.00%)
165. (1.51054) LP (1) N 73 s(0.02%)p99.99(99.95%)d 1.71(0.03%)

Second Order Perturbation Theory Analysis of the Fock Matrix in NBO Basis
From ($ImMe_2{}^iPr_2$)BH_2NH_2 to $BAr^F{}_3$

Donor NBO (i)	Acceptor NBO (j)	kcal/mol
100. BD (1) H 49 - N 71	/163. LP*(1) B 69	23.43
101. BD (1) H 50 - N 71	/163. LP*(1) B 69	19.64
104. BD (1) B 70 - N 71	/163. LP*(1) B 69	135.47
164. LP (1) N 71	/163. LP*(1) B 69	230.04

Figure S23: POV-ray depiction of the optimized structure of **6** (top), with a detailed view (bottom) in which H-atoms on the $ImMe_2{}^iPr_2$ and the $-C_6H_3(CF_3)_2$ groups have been omitted for clarity; atom numbers as they appear in the output-file and bond lengths (experimental values in brackets). xyz-coordinates for the optimized structure of **6**, checked to be a minimum on the energy hyper-surface by a frequency analysis.





C	-0.16331895	3.99684006	-3.02564677
C	1.35241588	4.34623596	-1.08477523
C	0.57191119	3.46615715	-1.83252938
C	-3.71972655	2.70999810	-3.45011608
C	-2.03344364	0.16326303	-4.13750749
C	2.03598337	3.83380437	0.00787345
C	2.83787317	4.73935265	0.89639216
C	0.46565318	2.12694097	-1.47104893
C	-3.39781296	4.33992188	-0.70427710
C	6.14367774	-0.70179997	-0.58293948
C	-3.24458637	2.20678185	-2.12668542
C	4.56838817	-2.15872918	-1.83202996
C	-3.12280123	2.89391762	-0.95480365
C	1.95381587	2.47962832	0.34024152
C	4.74101909	-1.08806975	-0.95273891
C	-2.74077982	-0.20796456	-2.83572749
C	1.15219337	1.57970981	-0.37454087
C	2.99072903	-3.68575014	-3.05472359
C	3.27326158	-2.52995246	-2.14672721
C	-4.12011277	-0.82162183	-3.06613671
C	3.64997202	-0.42262197	-0.41015978
C	-1.33822279	3.50426800	1.52915575
C	2.18031765	-1.85324463	-1.59947224
C	2.32550737	-0.78559458	-0.71504742
C	-2.41314724	0.78943593	-0.57857415
C	-2.29931423	2.32314244	1.40048421
C	-1.21964026	-3.95803287	-2.67122735
C	-3.55923716	2.53545298	2.23757688
C	1.03067106	-0.32274357	1.58135994
C	-1.15871096	-3.48483951	-1.22320398
C	-5.52026837	0.04499920	0.32207307
C	0.63200214	0.61004285	2.53882389
C	-2.67253883	-1.84678023	-0.12103070
C	-4.52752136	-0.77608787	1.14404850
C	1.22578961	-1.63357975	2.04156588
C	-3.62409743	-3.83127585	-0.61352484
C	-0.48884052	-4.47463187	-0.27690588
C	-4.55113701	-3.09160725	0.05576501
C	0.37876190	0.25314008	3.86353348
C	-0.20309291	1.29331529	4.76726185
C	-3.77290463	-5.20215466	-1.18847027
C	-5.94761398	-3.47787524	0.42419485
C	0.99442572	-1.99165873	3.36595852
C	-5.11899477	-1.26158071	2.46726244
C	0.55251633	-1.05242630	4.29631223
C	1.24642963	-3.40126359	3.81263050

H	1.43443395	5.39412394	-1.35103820
H	-2.88331770	2.88963859	-4.12882717
H	-4.24135689	3.65734811	-3.30974131
H	-2.67128201	0.73835563	-4.81091580
H	-4.41700489	2.01731253	-3.92689482
H	-1.75803775	-0.76025524	-4.65383268
H	-1.12154479	0.73361841	-3.94872054
H	-2.46693136	4.90543898	-0.62915170
H	-3.95982288	4.75115398	-1.54367070
H	-0.17134233	1.48094476	-2.06899405
H	5.42159004	-2.67698430	-2.25642747
H	-4.82494010	-0.08901291	-3.46968720
H	-1.85197500	4.46434090	1.44459552
H	-3.98315449	4.50321946	0.20168167
H	-0.54651545	3.45248076	0.77860578
H	-4.03570102	-1.63987228	-3.78727144
H	3.83817136	0.40314549	0.27106693
H	2.51553203	2.13183549	1.20600486
H	-2.12391547	-0.95799341	-2.34107960
H	-0.28088650	-0.57702077	-1.59601465
H	1.18487619	-2.18187863	-1.88255575
H	-1.79690179	-3.26302313	-3.29134592
H	-0.87796263	3.46870085	2.52105696
H	-4.53195821	-1.22582235	-2.13709958
H	-0.20044726	-3.99966930	-3.06620968
H	-4.11939415	3.41918418	1.92379479
H	-5.03227863	0.54333350	-0.52028763
H	-1.78938980	1.43131055	1.76724947
H	-1.65053609	-4.95655433	-2.77717446
H	0.47642077	1.64648764	2.24884994
H	-0.57122845	-2.56811430	-1.16020947
H	-3.25785756	2.67945455	3.27720338
H	-1.57100126	-0.41239283	1.25126808
H	-5.97156120	0.81364152	0.95575747
H	-4.23007325	1.67526043	2.19638358
H	-3.66919692	-0.15241872	1.39117158
H	-6.32932572	-0.57880214	-0.06839705
H	-3.88312076	-5.17445860	-2.27635753
H	0.52772940	-4.65599753	-0.63764626
H	1.54092944	-2.39888064	1.33440519
H	-6.65600911	-2.66180887	0.27006419
H	-1.00313163	-5.43846587	-0.22270382
H	-0.42071368	-4.05302589	0.72875890
H	-2.91875494	-5.83813832	-0.95231156
H	-4.66096712	-5.67818132	-0.77067570
H	-6.26894638	-4.30985537	-0.20399667

H	-5.22164603	-0.40373275	3.13741991
H	-4.45637809	-1.98649898	2.94625148
H	-6.11000276	-1.70340348	2.34807899
H	-6.02191422	-3.79705821	1.46760979
H	0.34463389	-1.33447534	5.32213515
B	1.02858694	-0.03416013	-0.02915132
B	-1.63258869	-0.53763741	0.04999899
N	-2.80087278	0.91224339	-1.87150334
N	-2.61531873	2.00148255	-0.01438511
N	-0.27286609	-0.66460169	-0.57943439
N	-2.47846330	-3.04931102	-0.70588152
N	-3.94079643	-1.87834677	0.35936296
F	0.57131764	4.87225294	-3.72220687
F	-0.53374034	3.01766669	-3.87578805
F	-1.30179604	4.64539699	-2.69197621
F	2.88016306	5.99824899	0.43339016
F	6.91907445	-0.56221734	-1.67205577
F	4.10179606	4.31698202	1.03301949
F	2.15252854	-3.34276139	-4.05391236
F	6.19395059	0.45132910	0.09622532
F	2.30952141	4.78677265	2.13187010
F	4.09309818	-4.19552495	-3.61471745
F	6.72927466	-1.63990087	0.18078777
F	2.37624103	-4.69513978	-2.39897134
F	0.43454795	2.47000387	4.66887812
F	-1.49571725	1.54808696	4.43680989
F	-0.20010589	0.93244916	6.05497949
F	1.00854690	-4.28855427	2.82928460
F	2.51567099	-3.58965931	4.20188081
F	0.46558772	-3.74371818	4.85214860

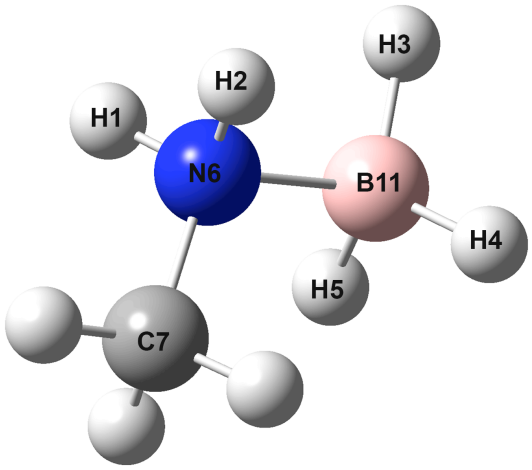
Summary of Natural Population Analysis:

Atom	No	Charge
H	**66**	**0.36890**
H	**79**	**-0.00326**
B	98	0.60246
B	**99**	**0.23993**
N	100	-0.38330
N	101	-0.36882
N	**102**	**-1.13857**
N	103	-0.37042
N	104	-0.38120
C	25	0.30196
C	33	0.32137

Selected NBOs of **6**.

68. (1.95644) BD (1) C 25 - B 99 (WBI = 0.8029)
(69.74%) 0.8351* C 25 s(46.83%)p 1.14(53.17%)d 0.00(0.00%)
(30.26%) 0.5501* B 99 s(22.70%)p 3.40(77.21%)d 0.00(0.09%)
95. (1.96011) BD (1) C 33 - B 99 (WBI = 0.8176)
(69.40%) 0.8331* C 33 s(46.82%)p 1.14(53.18%)d 0.00(0.00%)
(30.60%) 0.5532* B 99 s(22.23%)p 3.49(77.68%)d 0.00(0.09%)
135. (1.97093) BD (1) H 66 - N 102 (WBI = 0.8211)
(31.19%) 0.5585* H 66 s(99.92%)p 0.00(0.08%)
(68.81%) 0.8295* N 102 s(17.65%)p 4.66(82.30%)d 0.00(0.06%)
136. (1.93891) BD (1) H 79 - B 99 (WBI = 0.9268)
(51.35%) 0.7166* H 79 s(99.96%)p 0.00(0.04%)
(48.65%) 0.6975* B 99 s(27.99%)p 2.57(71.95%)d 0.00(0.06%)
137. (1.96336) BD (1) B 98 - N 102 (WBI = 0.7669)
(24.03%) 0.4902* B 98 s(24.05%)p 3.15(75.80%)d 0.01(0.14%)
(75.97%) 0.8716* N 102 s(39.44%)p 1.53(60.54%)d 0.00(0.02%)
138. (1.96794) BD (1) B 99 - N 102 (WBI = 0.8529)
(26.71%) 0.5168* B 99 s(27.00%)p 2.70(72.86%)d 0.00(0.13%)
(73.29%) 0.8561* N 102 s(37.64%)p 1.66(62.34%)d 0.00(0.02%)
213. (1.82670) LP (1) N 102 s(5.24%)p18.09(94.74%)d 0.00(0.02%)

Figure S24: POV-ray depiction of the optimized structure of **$MeNH_2$•BH_3**; atom numbers as they appear in the output-file and bond lengths (experimental values in brackets).



Summary of Natural Population Analysis:
Atom No Charge

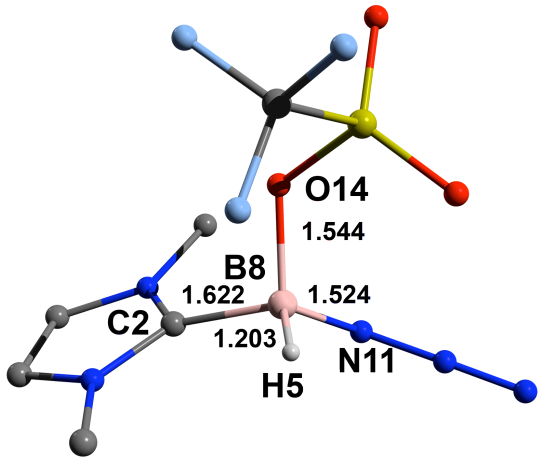
H	1	0.45515
H	2	0.45516
H	3	-0.02973
H	4	-0.03438
H	5	-0.03440
N	6	-0.78117
C	7	-0.47460
H	8	0.25310
H	9	0.22066
H	10	0.25310
B	11	-0.28288

Selected NBOs of **$MeNH_2$•BH_3**:

1. (1.98782) BD (1) H 1 - N 6
(26.63%) 0.5161* H 1 s(99.89%)p 0.00(0.11%)
(73.37%) 0.8565* N 6 s(19.11%)p 4.23(80.84%)d 0.00(0.05%)
2. (1.98782) BD (1) H 2 - N 6
(26.63%) 0.5161* H 2 s(99.89%)p 0.00(0.11%)
(73.37%) 0.8565* N 6 s(19.12%)p 4.23(80.84%)d 0.00(0.05%)
3. (1.98582) BD (1) H 3 - B 11
(51.71%) 0.7191* H 3 s(99.95%)p 0.00(0.05%)
(48.29%) 0.6949* B 11 s(27.08%)p 2.69(72.86%)d 0.00(0.06%)
4. (1.98449) BD (1) H 4 - B 11

(51.98%) 0.7210* H 4 s(99.95%)p 0.00(0.05%)
(48.02%) 0.6930* B 11 s(27.42%)p 2.65(72.52%)d 0.00(0.06%)
5. (1.98449) BD (1) H 5 - B 11
(51.98%) 0.7210* H 5 s(99.95%)p 0.00(0.05%)
(48.02%) 0.6930* B 11 s(27.42%)p 2.64(72.52%)d 0.00(0.06%)
6. (1.99593) BD (1) N 6 - C 7
(63.23%) 0.7952* N 6 s(25.95%)p 2.85(74.01%)d 0.00(0.04%)
(36.77%) 0.6063* C 7 s(22.41%)p 3.46(77.47%)d 0.01(0.12%)
7. (1.98492) BD (1) N 6 - B 11
(79.86%) 0.8936* N 6 s(35.78%)p 1.79(64.22%)d 0.00(0.00%)
(20.14%) 0.4488* B 11 s(18.04%)p 4.53(81.73%)d 0.01(0.23%)

Figure S25: POV-ray depiction of the optimized structure of **ImMe$_2$•BH(OTf)N$_3$**; atom numbers as they appear in the output-file and bond lengths. xyz-coordinates for the optimized structure of **ImMe$_2$•BH(OTf)N$_3$**, checked to be a minimum on the energy hyper-surface by a frequency analysis.



C	-2.31020700	-1.32368100	0.14314400
C	1.96101900	-0.10866600	0.09897600
C	3.71716800	-1.48182400	0.23418000
C	3.78362300	-0.84116900	-0.96075500
H	0.16434300	0.37579500	1.52007400
H	4.36881300	-2.21289600	0.68398500
H	4.50164400	-0.90826000	-1.76185600
B	0.58057600	0.67594200	0.43234300
N	-0.38787800	3.73081100	1.51427800
N	0.17272500	2.94512600	0.92804600
N	0.84061900	2.16671700	0.25380100
O	-2.46232700	0.32984400	-1.89327100
O	-2.22894100	1.30463200	0.42428400
O	-0.33743300	0.13871800	-0.68693000
F	-3.60665600	-1.36847700	0.40964200
F	-2.00401700	-2.28651200	-0.71710900
F	-1.62842400	-1.52994800	1.27097800
S	-1.87993000	0.31514900	-0.57245500
C	2.32331900	0.82831200	-2.16740600
H	3.23148900	1.09424800	-2.70808600
H	1.82751300	1.72531000	-1.79727500
H	1.64428900	0.27213900	-2.81506600
C	2.10947800	-1.46102100	2.17729600

H	2.74786400	-2.27880800	2.50987500
H	1.07911900	-1.80533900	2.09366000
H	2.15948700	-0.63922800	2.89150300
N	2.69434100	-0.00155000	-1.02035300
N	2.58398200	-1.01794300	0.86763800

Summary of Natural Population Analysis:

Atom	No	Charge				
C	1	0.88582	1.99974	3.03033	0.08411	5.11418
C	2	0.29662	1.99909	3.66779	0.03650	5.70338
C	3	-0.07516	1.99916	4.05809	0.01791	6.07516
C	4	-0.06982	1.99915	4.05280	0.01787	6.06982
H	5	-0.04374	0.00000	1.04203	0.00171	1.04374
B	8	0.47939	1.99880	2.49806	0.02375	4.52061
N	9	-0.07419	1.99963	5.04787	0.02669	7.07419
N	10	0.26958	1.99960	4.69584	0.03497	6.73042
N	11	-0.61014	1.99932	5.58864	0.02218	7.61014
O	12	-0.94156	1.99988	6.91649	0.02519	8.94156
O	13	-0.94786	1.99988	6.92321	0.02477	8.94786
O	14	-0.93768	1.99977	6.92690	0.01102	8.93768
F	15	-0.35228	1.99992	7.34382	0.00855	9.35228
F	16	-0.35792	1.99992	7.34944	0.00857	9.35792
F	17	-0.36655	1.99992	7.35844	0.00819	9.36655
S	18	2.42888	9.99863	3.34893	0.22356	13.57112
C	19	-0.49450	1.99946	4.48298	0.01206	6.49450
C	23	-0.48532	1.99948	4.47440	0.01144	6.48532
N	27	-0.35479	1.99927	5.34424	0.01128	7.35479
N	28	-0.36409	1.99927			

Selected NBOs of **$ImMe_2$•BH(OTf)N_3**:

1. (1.95874) BD (1) C 2 - B 8 (WBI = 0.74)
   (69.79%) 0.8354* C 2 s(45.79%)p 1.18(54.21%)d 0.00(0.00%)
   (30.21%) 0.5496* B 8 s(23.29%)p 3.29(76.60%)d 0.00(0.11%)
2. (1.98117) BD (1) H 5 - B 8
   (52.18%) 0.7223* H 5 s(99.96%)p 0.00(0.04%)
   (47.82%) 0.6916* B 8 s(31.78%)p 2.14(68.15%)d 0.00(0.07%)
3. (1.90992) BD (1) B 8 - N 11
   (25.49%) 0.5049* B 8 s(25.25%)p 2.95(74.53%)d 0.01(0.22%)
   (74.51%) 0.8632* N 11 s(33.35%)p 2.00(66.59%)d 0.00(0.06%)
4. (1.97855) BD (1) B 8 - O 14
   (17.72%) 0.4209* B 8 s(19.74%)p 4.04(79.85%)d 0.02(0.40%)
   (82.28%) 0.9071* O 14 s(44.02%)p 1.27(55.95%)d 0.00(0.03%)
5. (1.99586) BD (1) N 9 - N 10
   (43.27%) 0.6578* N 9 s(31.24%)p 2.20(68.58%)d 0.01(0.18%)

(56.73%) 0.7532* N 10 s(47.71%)p 1.10(52.25%)d 0.00(0.04%)
6. (1.99330) BD (2) N   9 - N 10
(48.65%) 0.6975* N   9 s(0.17%)p99.99(99.39%)d 2.52(0.44%)
(51.35%) 0.7166* N 10 s(0.13%)p99.99(99.64%)d 1.76(0.23%)
7. (1.99199) BD (3) N   9 - N 10
(45.17%) 0.6721* N   9 s(1.70%)p57.61(97.85%)d 0.27(0.45%)
(54.83%) 0.7405* N 10 s(1.75%)p56.00(98.06%)d 0.11(0.19%)
8. (1.99248) BD (1) N 10 - N 11
(56.18%) 0.7496* N 10 s(50.38%)p 0.98(49.59%)d 0.00(0.03%)
(43.82%) 0.6619* N 11 s(26.43%)p 2.78(73.42%)d 0.01(0.15%)

Figure S26. Selected molecular orbitals of **$ImMe_2$•BH(OTf)N_3** calculated at the M062X/6-31g(d,p) level of density functional theory.

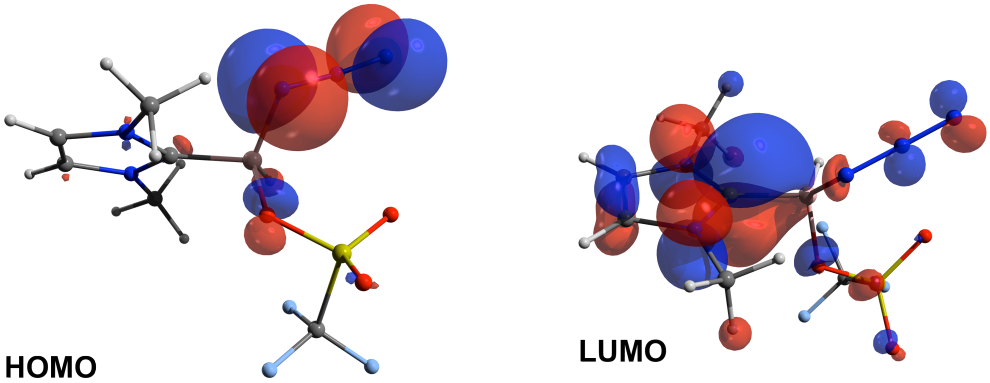
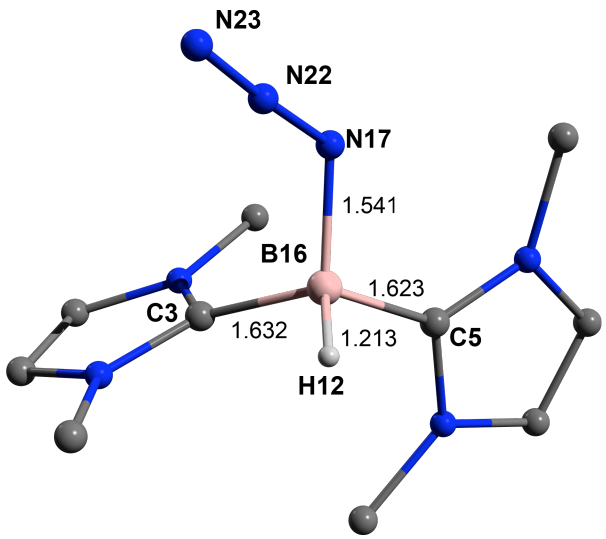


Figure S27: POV-ray depiction of the optimized structure of **[(ImMe$_2$)$_2$•B(H)N$_3$]$^+$**; atom numbers as they appear in the output-file and bond lengths. xyz-coordinates for the optimized structure of **[(ImMe$_2$)$_2$•B(H)N$_3$]$^+$**, checked to be a minimum on the energy hyper-surface by a frequency analysis.



C	2.84316714	-0.24845820	-1.79196143
C	-0.73090583	-2.22637717	-1.34308594
C	1.18688290	-0.26873566	0.07496734
C	3.09852464	-1.36816208	0.44685311
C	-1.40944327	-0.02089568	-0.40835118
C	-2.79570175	1.86395964	0.53041637
C	-3.00274619	-1.59751282	-0.47017396
C	2.34666419	-1.46102485	1.57314830
C	-3.55197637	-0.47024563	0.04287032
C	0.09448406	-0.57292780	2.28261154
H	2.17950649	-0.64845674	-2.55837410
H	0.27349231	0.75474721	-1.78911377
H	-0.13161215	-1.69228473	-2.08175384
H	-2.22938496	2.06314654	1.43849192
H	-0.23499996	0.46550063	2.22001171
B	0.04180318	0.67896619	-0.60099084
N	0.03574931	2.03371858	0.13266998
N	2.36779716	-0.63016296	-0.45993344
N	-1.68508423	-1.29885516	-0.74399585

N	-2.55944734	0.48823519	0.07241412
N	1.17850952	-0.77451243	1.32315631
N	0.93384261	2.81149690	-0.17887563
N	1.73822286	3.56944740	-0.41751417
H	2.54411096	-1.93858291	2.51959682
H	4.08196105	-1.74790380	0.22040246
H	-3.42920931	-2.56694192	-0.67241154
H	-4.55622093	-0.26224371	0.37542754
H	-3.86331072	1.96491412	0.72032459
H	-2.48200216	2.56621177	-0.23848394
H	-1.28511774	-3.02021494	-1.84228566
H	-0.08111990	-2.66217424	-0.57985188
H	3.84241156	-0.65980483	-1.92509560
H	2.88167121	0.83775790	-1.87400789
H	0.47646881	-0.77148829	3.28323400
H	-0.73648682	-1.25030410	2.06962730

Summary of Natural Population Analysis:

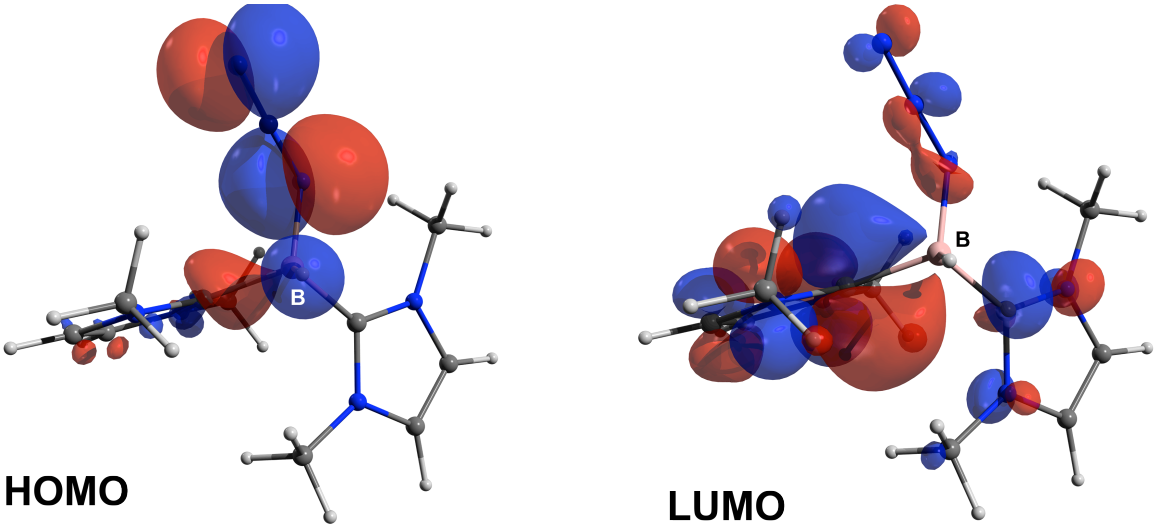
Atom	No	Charge
C	1	-0.48663
C	2	-0.48832
C	3	0.28241
C	4	-0.06292
C	5	0.29797
C	6	-0.48193
C	7	-0.06934
C	8	-0.06482
C	9	-0.06224
C	10	-0.49239
H	11	0.25837
H	12	0.00969
H	13	0.26196
H	14	0.26718
H	15	0.27281
B	16	0.17152
N	17	-0.58306
N	18	-0.36013
N	19	-0.36729
N	20	-0.35776
N	21	-0.36181
N	22	0.25131
N	23	-0.06079
H	24	0.27859
H	25	0.27913

H 26 0.27763
H 27 0.27855
H 28 0.25413
H 29 0.27872
H 30 0.27046
H 31 0.25226
H 32 0.26393
H 33 0.27332
H 34 0.26870
H 35 0.25080

Selected NBOs of **[(ImMe$_2$)$_2$•B(H)N$_3$]$^+$**:

1. (1.95700) BD (1) C 3 - B 16
(68.30%) 0.8264* C 3 s(45.92%)p 1.18(54.08%)d 0.00(0.00%)
(31.70%) 0.5630* B 16 s(23.75%)p 3.21(76.17%)d 0.00(0.08%)
2. (1.95954) BD (1) C 5 - B 16
(67.73%) 0.8230* C 5 s(46.00%)p 1.17(54.00%)d 0.00(0.00%)
(32.27%) 0.5681* B 16 s(23.99%)p 3.16(75.93%)d 0.00(0.08%)
3. (1.95454) BD (1) H 12 - B 16
(50.13%) 0.7080* H 12 s(99.96%)p 0.00(0.04%)
(49.87%) 0.7062* B 16 s(28.59%)p 2.50(71.36%)d 0.00(0.06%)
4. (1.90076) BD (1) B 16 - N 17
(27.16%) 0.5212* B 16 s(23.68%)p 3.22(76.15%)d 0.01(0.17%)
(72.84%) 0.8535* N 17 s(32.93%)p 2.04(67.01%)d 0.00(0.07%)
5. (1.99203) BD (1) N 17 - N 22
(43.76%) 0.6615* N 17 s(26.11%)p 2.82(73.73%)d 0.01(0.16%)
(56.24%) 0.7499* N 22 s(50.41%)p 0.98(49.56%)d 0.00(0.03%)
6. (1.99553) BD (1) N 22 - N 23
(56.86%) 0.7540* N 22 s(48.03%)p 1.08(51.93%)d 0.00(0.04%)
(43.14%) 0.6568* N 23 s(31.13%)p 2.21(68.69%)d 0.01(0.18%)
7. (1.99397) BD (2) N 22 - N 23
(51.02%) 0.7143* N 22 s(0.00%)p 1.00(99.76%)d 0.00(0.24%)
(48.98%) 0.6998* N 23 s(0.00%)p 1.00(99.56%)d 0.00(0.44%)
8. (1.99202) BD (3) N 22 - N 23
(55.79%) 0.7469* N 22 s(1.55%)p63.40(98.27%)d 0.12(0.18%)
(44.21%) 0.6649* N 23 s(1.56%)p62.61(97.97%)d 0.30(0.47%)
9. (1.77484) LP (1) N 17 s(41.02%)p 1.43(58.86%)d 0.00(0.12%)
10. (1.51880) LP (2) N 17 s(0.01%)p99.99(99.78%)d20.05(0.21%)
11. (1.97208) LP (1) N 23 s(67.72%)p 0.48(32.26%)d 0.00(0.03%)

Figure S28. Selected molecular orbitals of **[(ImMe$_2$)$_2$•B(H)N$_3$]$^+$** calculated at the M062X/6-31g(d,p) level of density functional theory.



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