Electronic Supplementary Material (ESI) for ChemComm.

Contents

Experimental section

General

^{1}H NMR, ^{13}C NMR, ^{11}B NMR, ^{29}Si NMR, and ^{19}F NMR spectra were measured on a Bruker Avance 300 (300 MHz) spectrometer. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from $CHCl_3$ as an internal standard (δ = 7.26) in $CDCl_3$. Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ as an internal standard (δ = 77.16) in $CDCl_3$. Chemical shifts of ^{11}B NMR were expressed in parts per million downfield from $BF_3{\cdot}OEt_2$ as an external standard (δ = 0) in $CDCl_3$. Chemical shifts of ^{29}Si NMR were expressed in parts per million downfield from Me_4Si as an external standard (δ = 0) in $CDCl_3$. Chemical shifts of ^{19}F NMR were expressed in parts per million downfield from benzotrifluoride as an internal standard (δ = –63.24) in $CDCl_3$. Mass spectra were measured on a JEOL JMS-T100LC spectrometer. Analytical thin layer chromatography (TLC) was performed on a glass plates pre-coated with silica-gel (Merck Kieselgel 60 F_{254}, layer thickness 0.25 mm). Visualization was accomplished by UV light (254 nm) and anisaldehyde, Column chromatography was performed on KANTO Silica Gel 60N (spherical, neutral).

Preparation of 3a

To a mixture of 2-bromo-1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-1,3,2-diazaborole[S1,2] (467.3 mg, 1.0 mmol, 82% purity) and naphthalene (64.0 mg, 0.50 mmol) in THF (3 mL) was added lithium powder (41.6 mg, 6.0 mmol) at –40 °C. After the reaction suspension was stirred for 12 h at –40 °C, gaseous HCF_3 (**2a**, 112 μL, 5.0 mmol) was bubbled into the suspension at –78 °C. After stirring for 3 h at this temperature, the mixture was quenched with 2-propanol, and the solvent was removed *in vacuo*. Purification by deactivated silica-gel column (hexane/NEt_3 = 200/1) gave the product **3a** as a colourless solid (202.2 mg, 56% yield). In this reaction, the B-H compound was obtained as a colourless solid (17.9 mg, 23% yield). NMR spectra of the B-H compound corresponded reasonably well with that reported.[S2]

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.20 (d, $^{3}J_{HH}$= 6.9 Hz, 24H), 2.96 (sept, $^{3}J_{HH}$ = 6.9 Hz, 4H), 5.74 (t, $^{2}J_{HF}$ = 47.2 Hz, 1H), 6.25 (s, 2H), 7.22 (d, $^{2}J_{HH}$ = 7.8 Hz, 4H), 7.34 (t, $^{2}J_{HH}$ = 7.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –131.8 (d, $^{2}J_{FH}$ = 47.2 Hz); ^{11}B NMR ($CDCl_3$, 96 MHz) δ 21.5 (brs); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.8, 25.2, 28.7, 120.3,

123.7, 128.2, 137.2, 146.3 (CF_2H was not characterized). HRMS (APCI-TOF) calcd for $C_{27}H_{37}BF_2N_2$ $[M+H]^+$: 439.3096, found: 439.3106. Mp 112–113 °C.

Preparation of 3b

To a mixture of 2-bromo-1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro–1*H*-1,3,2-diazaborole [S1,2] (46.7 mg, 0.10 mmol, 82% purity) and naphthalene (6.4 mg, 0.050 mmol) in THF (1 mL) was added lithium powder (7.4 mg, 1.0 mmol) at –40 °C and stirred for 15 min. After the reaction suspension was stirred for 12 h at –40 °C, $TMSCF_3$ (**2b**, 30 μL, 0.2 mmol) was added at once to the suspension at –78 °C. After stirring for 3 h at this temperature, the mixture was quenched with 2-propanol, and the solvent was removed *in vacuo*. Purification by silica-gel column (hexane/AcOEt = 50/1) gave the product **3b** as a brownish oil (30.1 mg, 73% yield).

^{1}H NMR ($CDCl_3$, 300 MHz) δ –0.26 (s, 9H), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 12H), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 12H), 3.10 (sept, $^3J_{HH}$ = 6.8 Hz, 4H), 6.20 (s, 2H), 7.23 (d, $^2J_{HH}$ = 7.2 Hz, 4H), 7.34 (t, $^2J_{HH}$ = 7.2 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –124.5; ^{11}B NMR ($CDCl_3$, 96 MHz) δ 22.7 (brs); ^{29}Si NMR ($CDCl_3$, 60 MHz) δ 2.75 (t, $^2J_{SiF}$ = 32.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ –4.8 (t, $^3J_{CF}$ = 2.6 Hz), 23.2, 26.1, 28.4, 120.8, 123.4, 127.7, 139.0, 145.9 ($\underline{C}F_2TMS$ was not characterized). HRMS (ESI-TOF) calcd for $C_{30}H_{45}BF_2N_2Si$ $[M+K]^+$: 549.3050, found: 549.3038.

X-ray Crystallography

X-ray diffraction data were collected on a Rigaku RAXIS-Rapid diffractometer. The structures were solved by a direct method (SHELXL-2014).[S3] The X-ray structure solution and refinement were carried out using the Yadokari-XG software.[S4]

3a: $C_{27}H_{37}BF_2N_2$, colourless prisms (THF), M_W = 438.39, crystal dimensions = 0.26 × 0.22 × 0.19 mm^3, triclinic, space group $P2_1/n$ (#14), a = 19.382(3), b = 14.1960(15), c = 19.505(2) Å, β = 103.166(3)°, V = 5225.6(10) Å^3, Z = 8, λ = 0.71075 Å, T = 153 K, ρ_{calcd} = 1.114 g cm^{-3}, $\mu_{MoK\alpha}$ = 0.074 mm^{-1}, F_{000} = 1888, 49617 total reflections ($2\theta_{max}$ = 54.97°), index ranges = $-25 \le h \le 25$, $-18 \le k \le 18$, $-25 \le l \le 24$, 11970 unique reflections (R_{int} = 0.112), $R1$ = 0.0775 ($I > 2\sigma(I)$), 0.1734 (all data), $wR2$ = 0.1728 ($I > 2\sigma(I)$), 0.2159 (all data), S = 1.006 (857 parameters). CCDC-1530683.

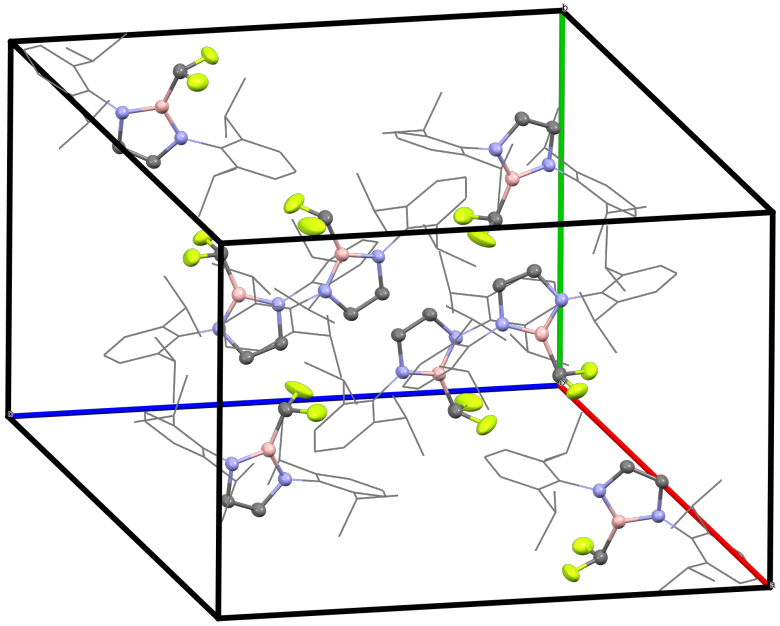
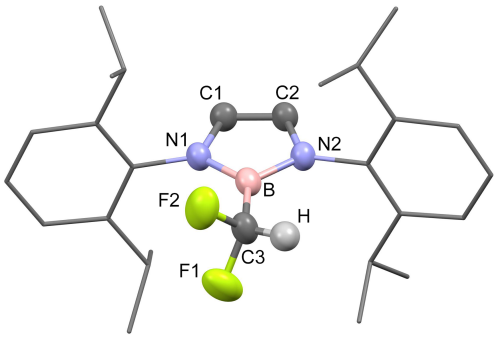


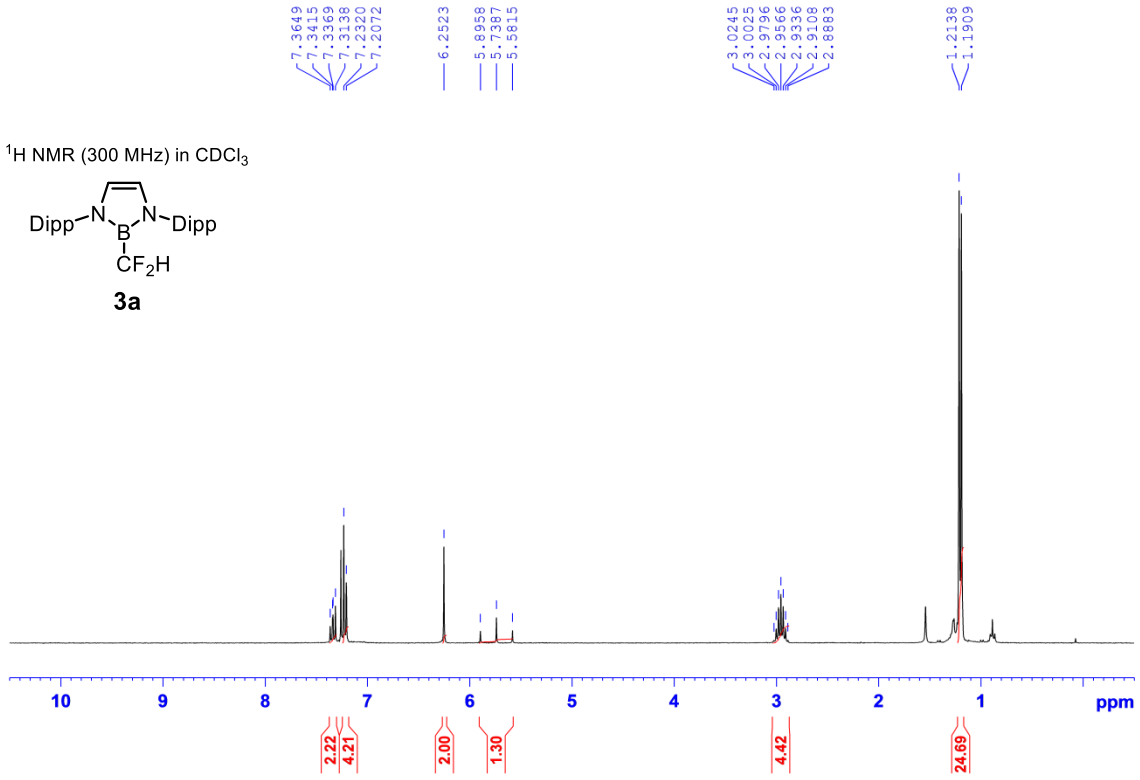
Figure S1. Crystal structure of **3a**.

Completed metric parameters of **3a**



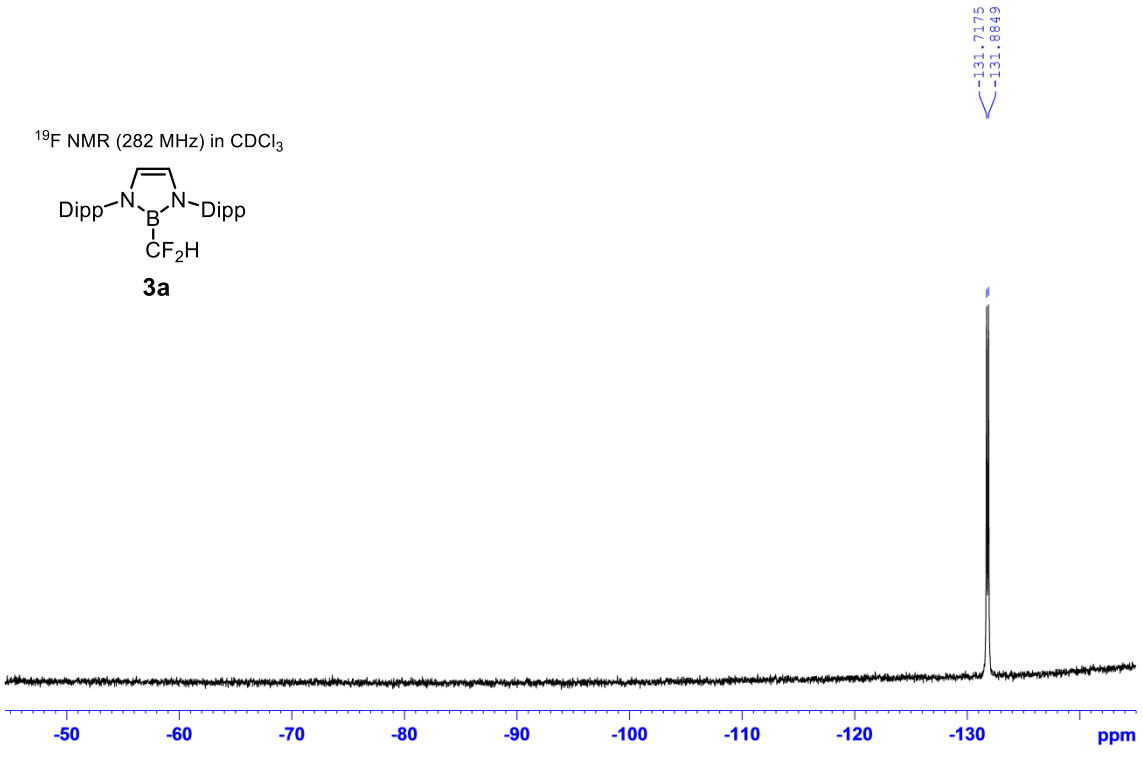
Parameter (Å, °)	Molecule 1	Molecule 2
B–N1	1.414(4)	1.420(4)
B–N2	1.420(4)	1.424(4)
N1–C1	1.406(4)	1.413(3)
N2–C2	1.412(3)	1.413(3)
C1–C2	1.326(4)	1.337(4)
N1–C_{Dipp}	1.446(4)	1.443(3)
N2–C_{Dipp}	1.446(3)	1.442(3)
B–C3	1.589(4)	1.578(4)
C3–F1	1.378(4)	1.357(4)
C3–F2	1.378(3)	1.361(5)
C3–H	1.00(3)	0.97(3)
N1–B–N2	107.3(2)	105.9(2)
N1–B–C3	128.0(3)	129.4(3)
N2–B–C3	126.0(3)	124.8(3)
B–N1–C1	105.9(2)	107.7(2)
B–N2–C2	107.3(2)	107.9(2)
N1–C1–C2	109.3(2)	109.6(2)
N2–C2–C1	109.5(2)	108.9(2)
B–C3–F1	111.7(2)	112.1(3)
B–C3–F2	110.7(2)	112.2(3)
F1–C3–F2	103.3(2)	102.8(3)

Copies of NMR charts



^{1}H NMR (300 MHz) in $CDCl_3$

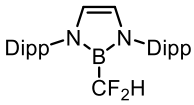
3a



^{19}F NMR (282 MHz) in $CDCl_3$

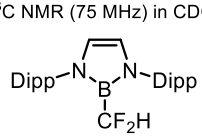
3a

^{11}B NMR (96 MHz) in $CDCl_3$



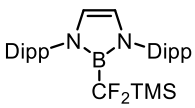
3a

^{13}C NMR (75 MHz) in $CDCl_3$



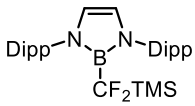
3a

^{1}H NMR (300 MHz) in $CDCl_3$



3b

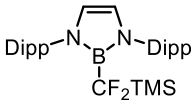
^{19}F NMR (282 MHz) in $CDCl_3$



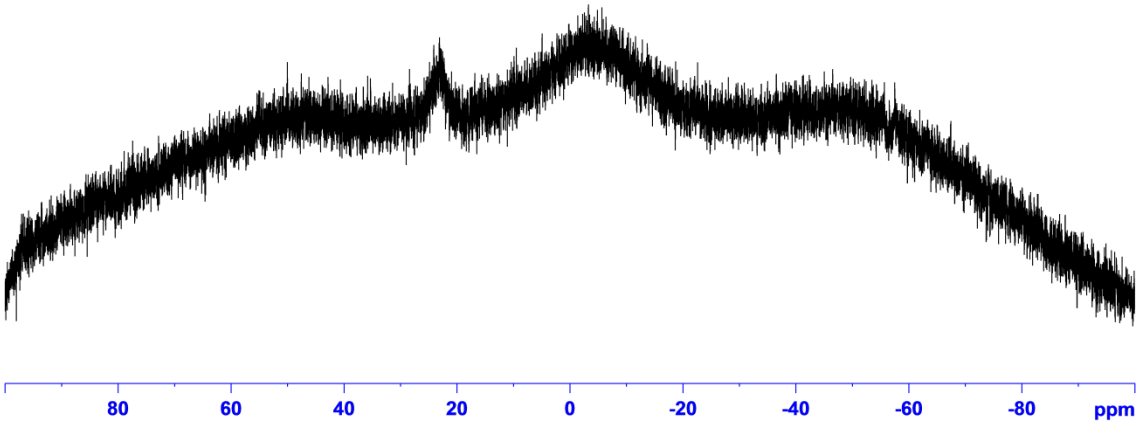
3b

22.71

^{11}B NMR (96 MHz) in $CDCl_3$

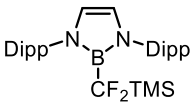


3b

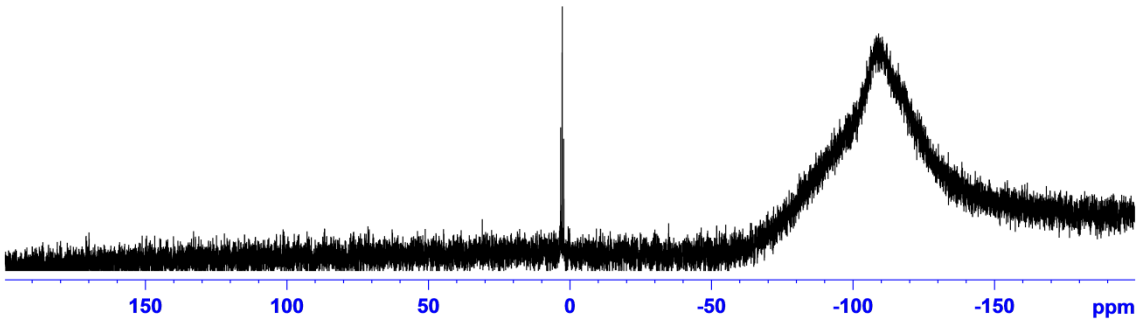


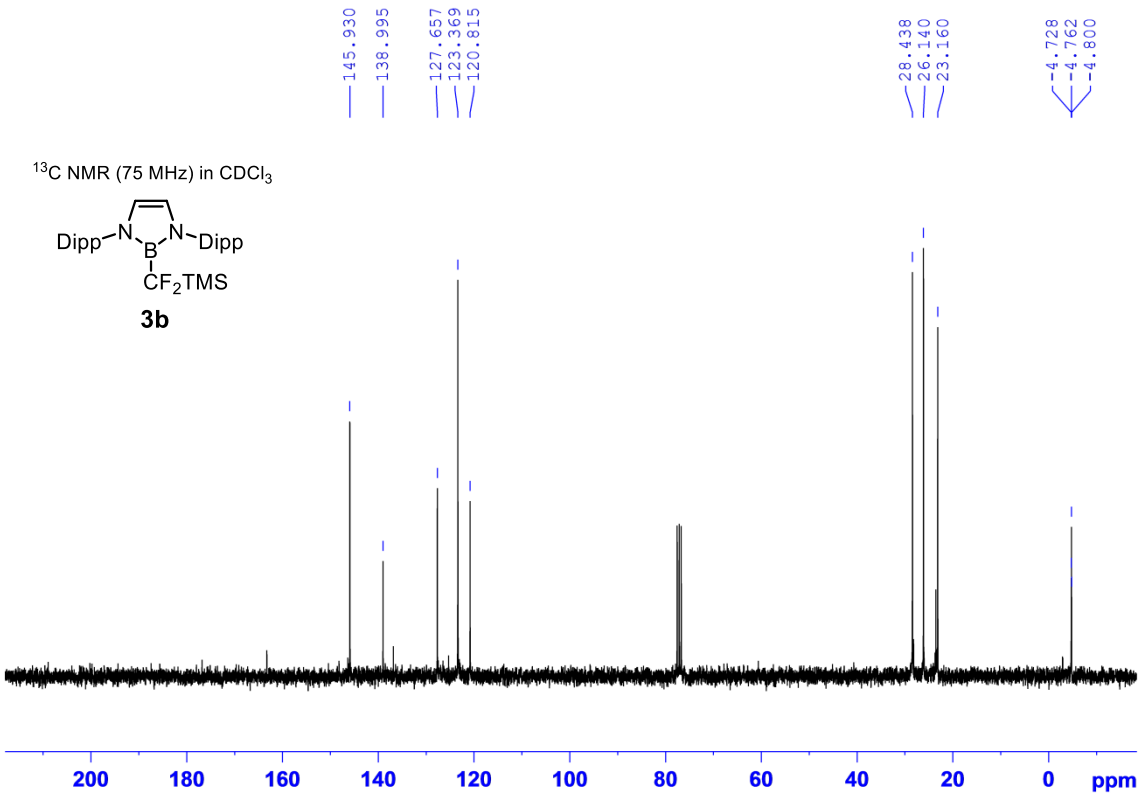
3.29
2.75
2.20

^{29}Si NMR (60 MHz) in $CDCl_3$



3b




145.930
138.995
127.657
123.369
120.815
28.438
26.140
23.160
-4.728
-4.762
-4.800
13C NMR (75 MHz) in CDCl3
Dipp
N
B
N
Dipp
CF2TMS
3b
200
180
160
140
120
100
80
60
40
20
0
ppm

References

S1 A. J. Arduengo III , R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, *Tetrahedron*, 1999, **55**, 14523.

S2 Y. Segawa, Y. Suzuki, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2008, **130**, 16069.

S3 G. Sheldrick, T. Schneider, *Acta Cryst. C*, 2015, **71**, 3.

S4 Yadokari-XG, Software for Crystal Structure Analyses, K. Wakita (2001); Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses, C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218.