Supporting Information. Directed Borylation by Electrophilic Activation of Benzylamine Boranes

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Experimental

The following chemicals were commercially available and used as received: dimethylbenzylamine (Aldrich); borane tetrahydrofuran, 1.0 M solution in tetrahydrofuran ($BH_3 \cdot THF$, Aldrich); trityl tetrakis(pentafluorophenyl)borate (TrTPFPB, Strem); lithium tetrakis(pentafluorophenyl)borate, ethyl ether complex (TCI America); tetrabutylammonium borohydride (Aldrich); 4-methylbenzyl bromide (Acros); dimethylamine, 5.6 M solution in ethanol (Fluka); 3-methylbenzyl bromide (Aldrich); 2-methylbenzyl bromide (Aldrich); 4-bromobenzyl bromide (Aldrich); 4-chlorobenzyl bromide (Aldrich); 4-fluorobenzyl bromide (Aldrich); 3-fluorobenzyl bromide (Acros); 3-chlorobenzyl bromide (Aldrich); 2-bromobenzyl bromide (Aldrich); 2-chlorobenzyl bromide (Aldrich); 2-fluorobenzyl bromide (Aldrich); (2-bromoethyl)benzene (Aldrich); (3-bromopropyl)benzene (Matheson). Bromobenzene, fluorobenzene, C_6D_5Br and CD_2Cl_2 were dried by storing over activated 4Å molecular sieves; dichloromethane (DCM), ethyl ether (Et_2O) and tetrahydrofuran (THF) were dried by passing through a column of activated alumina; toluene and chlorotrimethylsilane were distilled from CaH_2 under an N_2 atmosphere. Commercially available organolithium reagents (Acros or Aldrich) were titrated with N-benzylbenzamide prior to use.[1] All reactions were performed at room temperature under an N_2 atmosphere unless otherwise stated. Nuclear magnetic resonance experiments were performed on Varian Inova 500 and Inova 400 spectrometers at the following frequencies: ^1H 500 MHz or 400 MHz; $\{^1H\}^{13}C$ 101 MHz or 126 MHz; ^{11}B 160 MHz or 128 MHz; ^{19}F 377 MHz. All spectra were recorded in $CDCl_3$ and referenced to the ^1H signal of internal Me_4Si (unless otherwise stated) according to recommendations,[2] using a Ξ of 25.145020 for Me_4Si (^{13}C), a Ξ of 32.083974 for $BF_3 \cdot OEt_2$ (^{11}B), and a Ξ of 94.094011 for CCl_3F (^{19}F).

Preparation of Dimethylbenzylamine Borane (13a)

$BH_3 \cdot THF$ (9.0 mL, 9.0 mmol) was added by syringe under an N_2 atmosphere to neat dimethylbenzylamine (1.2 mL, 8.0 mmol). After 1 h, the solution was filtered through a plug of silica gel, flushing with DCM and removing solvent by rotary evaporation. The solid product was further dried under high vacuum, yielding 1.12 g **5a** (94%). ^{1}H, ^{13}C and ^{11}B NMR spectral data matched those reported for **5a**.[3]

General Procedure for Preparation of Borane Complexes for Directed Borylation (13b-l, 23, 25)

A solution of 3-methylbenzyl bromide (1.02 g, 5.5 mmol) in DCM (used without drying, 2 x 2 mL) was added to dimethylamine (5.6 M solution in ethanol, 2.0 mL, 11 mmol) diluted with DCM (used without drying, 25 mL) with stirring. After 3 h the reaction was quenched by addition of 5% aq. NaOH (20 mL), separating the layers and extracting the aqueous layer with 2 x 10 mL DCM. The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4 and reduced by rotary evaporation. The crude product was dissolved in anhydrous DCM (10 mL) and reacted with BH_3·THF (1.0 M in THF, 6.0 mL, 6.0 mmol), stirring 1 h before filtering the solution through a plug of silica gel, flushing with 20 mL DCM. The filtrate was reduced under a stream of N2, giving 395 mg **13c** as a slightly yellowish oil (44% y). 3-Methylbenzyldimethylamine borane (**13c**): analytical thin layer chromatography (TLC) on K6F silica gel 60Å, 4:1 hexanes/EtOAc, Rf = 0.49. Molecular ion calculated for $C_{10}H_{18}BNNa$: 186.1430; [M+Na], ESMS found *m*/*z* = 186.1423; IR (neat, cm^{-1}) 2366, B–H; 2319, B–H; 2273, B–H; 1466, B–N; 1167, C–N; ^{1}H NMR: δ 7.29 (1H, t, J = 7.5 Hz), 7.22 (1 H, d, J = 7.7 Hz), 7.13-7.10 (2H, m), 3.95 (2H, s), 2.50 (6H, s), 2.38 (3H, s), 2.2-1.4 (3H, br m); ^{13}C NMR: δ 138.1, 132.9, 131.1, 129.8, 129.2, 128.3, 67.4, 49.6, 21.3; ^{11}B NMR: δ -8.2 (q, J = 94 Hz).

4-Methylbenzyldimethylamine borane (**13b**, 54% y): TLC on K6F silica gel 60Å, 4:1 hexanes/EtOAc, Rf = 0.44. Molecular ion calculated for $C_{10}H_{18}BNNa$: 186.1430; [M+Na], ESMS found *m*/*z* = 186.1436; IR (neat, cm^{-1}) 2362, B–H; 2312, B–H; 2271, B–H; 1465, B–N; 1167, C–N; ^{1}H NMR: δ 7.20 (4H, s), 3.95 (2H, s), 2.49 (6H, s), 2.38 (3H, s), 2.2-1.4 (3H, br m); ^{13}C NMR: δ 139.1, 132.1, 129.1, 128.2, 67.2, 49.5, 21.2; ^{11}B NMR: δ -8.3 (q, J = 91 Hz).

2-Methylbenzyldimethylamine borane (**13d**, 79% y): TLC on K6F silica gel 60Å, 4:1 hexanes/EtOAc, Rf = 0.39. Molecular ion calculated for $C_{10}H_{18}BNNa$: 186.1430; [M+Na], ESMS found *m*/*z* =

186.1431; IR (neat, cm^{-1}) 2364, B–H; 2315, B–H; 2271, B–H; 1470, B–N; 1165, C–N; ^{1}H NMR: δ 7.33-7.20 (4H, m), 4.09 (2H, s), 2.53 (6H, s), 2.43 (3H, s), 2.2-1.4 (3H, br m); ^{13}C NMR: δ 139.0, 133.3, 131.3, 129.8, 129.2, 125.8, 63.6, 49.7, 20.3; ^{11}B NMR: δ -8.0 (q, J = 95 Hz).

4-Bromobenzyldimethylamine borane (**13e**, 77% y): TLC on K6F silica gel 60Å, 4:1 hexanes/EtOAc, Rf = 0.30. Molecular ion calculated for $C_9H_{15}BBrNNa$: 250.0379; [M+Na], ESMS found *m*/*z* = 250.0389; IR (neat, cm^{-1}) 2366, B–H; 2321, B–H; 2269, B–H; 1463, B–N; 1167, C–N; ^{1}H NMR: δ 7.54 (2H, d, J = 8.8 Hz), 7.22 (2H, d, J = 8.8 Hz), 3.93 (2H, s), 2.51 (6H, s), 2.2-1.4 (3H, br m); ^{13}C NMR: δ 133.8, 131.7, 130.2, 123.7, 66.9, 49.9; ^{11}B NMR: δ -8.3 (q, J = 90 Hz).

4-Chlorobenzyldimethylamine borane (**13f**, 91% y): TLC on K6F silica gel 60Å, 4:1 hexanes/EtOAc, Rf = 0.28. Molecular ion calculated for $C_9H_{15}BClNNa$: 206.0884; [M+Na], ESMS found *m*/*z* = 206.0876; IR (neat, cm^{-1}) 2368, B–H; 2315, B–H; 2279, B–H; 1461, B–N; 1169, C–N; ^{1}H NMR: δ 7.38 (2H, d, J = 8.4 Hz), 7.29 (2H, d, J = 8.4 Hz), 3.94 (2H, s), 2.51 (6H, s), 2.2-1.4 (3H, br m); ^{13}C NMR: δ 135.4, 133.5, 129.6, 128.6, 66.8, 49.9; ^{11}B NMR: δ -8.4 (q, J = 90 Hz).

3-Chlorobenzyldimethylamine borane (**13g**, 86% y): Molecular ion calculated for $C_9H_{12}ClN$: 169.0658; [M-BH3], EIMS found *m*/*z* = 169.0652; IR (thin film in $CDCl_3$, cm^{-1}) 2378, B–H; 2323, B–H; 2251, B–H; 1468, B–N; 1169, C–N; ^{1}H NMR: δ 7.42-7.39 (1H, m), 7.37-7.32 (2H, m), 7.26-7.22 (1H, m), 3.95 (2H, s), 2.53 (6H, s), 2.2-1.4 (3H, br m); ^{13}C NMR: δ 134.2, 133.1, 132.1, 130.5, 129.7, 129.3, 66.8, 50.0; ^{11}B NMR: δ -8.2 (q, J = 95 Hz).

4-Fluorobenzyldimethylamine borane (**13h**, 91% y): TLC on K6F silica gel 60Å, 2:1 hexanes/EtOAc, Rf = 0.47. Molecular ion calculated for $C_{10}H_{19}BFNNaO$: 222.1441; [M+Na+MeOH], ESMS found *m*/*z* = 222.1435; IR (neat, cm^{-1}) 2366, B–H; 2319, B–H; 2277, B–H; 1468, B–N; 1162, C–N; ^{1}H NMR: δ 7.35-7.30 (2H, m), 7.16-7.12 (2H, m), 3.95 (2H, s), 2.51 (6H, s), 2.2-1.4 (3H, br m); ^{13}C NMR: δ 163.2 (d, J

= 249 Hz), 134.0 (d, J = 9 Hz), 127.2 (d, J = 4 Hz), 115.5 (d, J = 21 Hz), 66.7, 49.8; ^{11}B NMR: δ -8.5 (q, J = 95 Hz); ^{19}F NMR: δ -112.2 (m).

3-Fluorobenzyldimethylamine borane (**13i**, 68% y): TLC on K6F silica gel 60Å, 4:1 hexanes/EtOAc, Rf = 0.41. Molecular ion calculated for $C_9H_{12}FN$: 153.0954; [M-BH3], EIMS found *m/z* = 153.0948; IR (thin film in $CDCl_3$, cm^{-1}) 2376, B–H; 2324, B–H; 2273, B–H; 1468, B–N; 1169, C–N; ^{1}H NMR: δ 7.39 (1H, td, J = 8.0, 5.9 Hz), 7.16-7.10 (2H, m), 7.08-7.04 (1H, m), 3.97 (2H, s), 2.53 (6H, s), 2.3-1.3 (3H, br m); ^{13}C NMR: δ 162.4 (d, J = 247 Hz), 133.5 (d, J = 7 Hz), 130.0 (d, J = 8 Hz), 128.0 (d, J = 3 Hz), 119.0 (d, J = 21 Hz), 116.1 (d, J = 21 Hz), 66.9 (d, J = 1 Hz), 49.9; ^{11}B NMR: δ -8.2 (q, J = 95 Hz); ^{19}F NMR: δ -112.6 (td, J = 9.0, 5.9 Hz).

2-Bromobenzyldimethylamine borane (**13j**, 81% y): TLC on K6F silica gel 60Å, 4:1 hexanes/EtOAc, Rf = 0.31. Molecular ion calculated for $C_9H_{15}BBrNNa$: 250.0379; [M+Na], ESMS found *m/z* = 250.0373; IR (neat, cm^{-1}) 2360, B–H; 2315, B–H; 2271, B–H; 1465, B–N; 1167, C–N; ^{1}H NMR: δ 7.66 (1H, dd, J = 8.1, 1.5 Hz), 7.52 (1H, dd, J = 7.9, 1.9 Hz), 7.37 (1H, td, J = 7.8 Hz, 1.5 Hz), 7.27 (1H, td, J = 7.7, 1.9 Hz), 4.24 (2H, s), 2.61 (6H, s), 2.2-1.4 (3H, br m); ^{13}C NMR: δ 134.7, 133.7, 131.1, 130.8, 127.3, 127.2, 65.4, 50.2; ^{11}B NMR: δ -8.1 (q, J = 98 Hz).

2-Chlorobenzyldimethylamine borane (**13k**, 73% y): TLC on K6F silica gel 60Å, 9:1 hexanes/Et_2O, Rf = 0.19. Molecular ion calculated for $C_9H_{15}BClNNa$: 206.0884; [M+Na], ESMS found *m/z* = 206.0876; IR (neat, cm^{-1}) 2364, B–H; 2317, B–H; 2273, B–H; 1466, B–N; 1167, C–N; ^{1}H NMR: δ 7.49 (1H, dd, J = 7.3, 2.0 Hz), 7.46 (1H, dd, J = 7.8, 1.5 Hz), 7.36 (1H, td, J = 7.8 Hz, 1.9 Hz), 7.32 (1H, td, J = 7.3, 1.5 Hz), 4.21 (2H, s), 2.59 (6H, s), 2.2-1.4 (3H, br m); ^{13}C NMR: δ 136.4, 134.8, 130.7, 130.3, 129.4, 126.7, 63.1, 50.1; ^{11}B NMR: δ -8.1 (q, J = 95 Hz).

2-Fluorobenzyldimethylamine borane (**13l**, 32% y): TLC on K6F silica gel 60Å, 9:1 hexanes/Et_2O, Rf = 0.17. Molecular ion calculated for $C_9H_{15}BFNNa$: 190.1179; [M+Na], ESMS found *m/z* = 190.1186; IR (neat, cm^{-1}) 2364, B–H; 2317, B–H; 2271, B–H; 1470, B–N; 1169, C–N; ^{1}H NMR: δ 7.44-7.39 (1H, m), 7.37 (1H, td, J = 7.5, 1.9 Hz), 7.20 (1H, td, J = 7.3 Hz, 1.0 Hz), 7.14 (1H, ddd, J = 9.8, 8.3, 1.0 Hz), 4.07 (2H, s), 2.54 (6H, s), 2.2-1.4 (3H, br m); ^{13}C NMR: δ 161.9 (d, J = 248 Hz), 134.6 (d, J = 4 Hz), 131.4 (d, J = 8 Hz), 124.1 (d, J = 4 Hz), 118.6 (d, J = 15 Hz), 115.9 (d, J = 23 Hz), 60.2 (d, J = 2 Hz), 49.9 (d, J = 2 Hz); ^{11}B NMR: δ -8.1 (q, J = 95 Hz); ^{19}F NMR: δ -113.7 (m).

N,*N*-Dimethylphenethylamine borane (**23**, 93% y): TLC on K6F silica gel 60Å, 4:1 hexanes/EtOAc, Rf = 0.31. Molecular ion calculated for $C_{10}H_{18}BNNa$: 186.1430; [M+Na], ESMS found *m*/*z* = 186.1424; IR (neat, cm^{-1}) 2362, B–H; 2314, B–H; 2277, B–H; 1453, B–N; 1167, C–N; ^{1}H NMR: δ 7.31 (2H, t, J = 7.3 Hz), 7.26-7.19 (3H, m), 3.09-2.94 (4H, m), 2.66 (6H, s), 2.1-1.3 (3H, br m); ^{13}C NMR: δ 138.0, 128.8, 126.7, 66.1, 51.8, 30.9; ^{11}B NMR: δ -10.0 (q, J = 98 Hz).

1-(Dimethylamino)-3-phenylpropane borane (**25**, 91% y): TLC on K6F silica gel 60Å, 2:1 hexanes/EtOAc, Rf = 0.49. Molecular ion calculated for $C_{11}H_{20}BNNa$: 200.1586; [M+Na], ESMS found *m*/*z* = 200.1588; IR (neat, cm^{-1}) 2366, B–H; 2319, B–H; 2271, B–H; 1463, B–N; 1167, C–N; ^{1}H NMR: δ 7.31 (2H, t, J = 7.8 Hz), 7.24-7.18 (3H, m), 2.81-2.76 (2H, m), 2.63 (t, J = 7.8 Hz), 2.56 (6H, s), 2.11-2.03 (2H, m), 2.1-1.3 (3H, br m); ^{13}C NMR: δ 140.7, 128.6, 128.3, 126.3, 64.2, 51.4, 33.3, 25.5; ^{11}B NMR: δ -9.9 (q, J = 95 Hz).

Representative Procedure for Directed Borylation (Table 1)

Method A, large scale. Dimethylbenzylamine borane (**13a**, 179 mg, 1.20 mmol) was dissolved in anhydrous bromobenzene (12 mL) and activated by addition of a solution of TrTPFPB (1.00 g, 1.08 mmol) in bromobenzene (4 + 1 mL) under an N_2 atmosphere. After 4 h the reaction was quenched with a solution of Bu_4NBH_4 (297 mg, 1.15 mmol) in bromobenzene (2 + 1 mL), added by syringe. The solvent was removed by a stream of N_2, and the residue was purified either by flash chromatography (FC) on silica gel (15 cm x 20 mm diameter) as in the case of **17a** (4:1 hexanes EtOAc) or by PLC (K6F silica gel 60Å, 1000 μm thickness), isolating 115 mg product (Rf = 0.28, 72% y based on TrTPFPB) and recovering 30 mg **13a** (Rf = 0.41, 17%). ^{1}H and ^{11}B NMR spectral data matched those reported for **17a**.[4]

Method B, small scale (approximately 0.1 mmol). TrTPFPB (0.9 eq) was dissolved in anhydrous bromobenzene (1 mL) and treated with a solution of an amine borane (1 eq) in bromobenzene (0.2 + 0.1 mL) under an N_2 atmosphere. After the required time the reaction was quenched with a solution of Bu_4NBH_4 (0.95 eq) in bromobenzene (0.2 + 0.1 mL), added by syringe. The solvent was removed by a stream of N_2, and the residue was purified by by PLC (K6F silica gel 60Å, 1000 μm thickness).

Method **B** was used to prepare the following compounds:

2,2,5-Trimethyl-2,3-benzazaborolidine (**17b**): Purified by FC (4:1 hexanes/EtOAc, Rf = 0.32, 41% y of **17b**, recovered 21% of **13b**). Molecular ion calculated for $C_{10}H_{16}BNNa$: 184.1273; [M+Na], ESMS found *m/z* = 184.1276; IR (neat, cm^{-1}) 2339, B–H; 2306, B–H; 1463, B–N; 1071, C–N; ^{1}H NMR: δ 7.25 (1H, s), 6.97 (1H, d, J = 7.4 Hz), 6.90 (1H, d, J = 7.4 Hz), 4.01 (2H, s), 3.2-2.4 (2H, br m), 2.76 (6H, s), 2.32 (3H, s); ^{13}C NMR: δ 136.5, 135.8, 130.4, 125.6, 121.4, 69.5, 50.9, 21.5; ^{11}B NMR: δ -1.4 (t, J = 99 Hz).

2,2,4-Trimethyl-2,3-benzazaborolidine and 2,2,6-trimethyl-2,3-benzazaborolidine (**17c**): Purified by PLC (4:1 hexanes/EtOAc, Rf = 0.34, 79% y of **17c** as inseparable mixture of regioisomers in a 3:1 ratio, recovered 13% of **13c**). Molecular ion calculated for $C_{10}H_{15}BN$: 160.1298; [M-H], EIMS found *m/z* = 160.1305; IR (neat, cm^{-1}) 2341, B–H; 2294, B–H; 1459, B–N; 1055, C–N; ^{1}H NMR: δ 7.31 (1H-minor isomer, d, J = 7.3 Hz), 7.04-6.97 (2H-major isomer + 1H-minor isomer, m), 6.91-6.88 (1H-major isomer + 1H-minor isomer, m), 4.05 (2H-major isomer, s), 4.01 (2H-minor isomer, s), 3.2-2.4 (2H-major isomer + 2H-minor isomer, br m), 2.77 (6H-major isomer, s), 2.76 (6H-minor isomer, s), 2.30 (3H-minor isomer, s), 2.29 (3H-major isomer, s); ^{13}C NMR: δ 139.5, 139.0, 138.2, 134.3, 129.5, 128.0, 127.5, 125.3, 122.4, 118.7, 69.9, 69.6, 51.1, 50.9, 21.7, 21.3; ^{11}B NMR: δ -1.9 (major isomer, t, J = 97 Hz).

2,2,7-Trimethyl-2,3-benzazaborolidine (**17d**): Purified by FC (4:1 hexanes/EtOAc, Rf = 0.29, 76% y of **17d**, recovered 10% of **13d**). Molecular ion calculated for $C_{10}H_{16}BNNa$: 184.1273; [M+Na], ESMS found *m*/*z* = 184.1268; IR (neat, cm^{-1}) 2342, B–H; 2298, B–H; 1461, B–N; 1061, C–N; ^{1}H NMR: δ 7.24 (1H, d, J = 7.2 Hz), 7.11 (1H, t, J = 7.3 Hz), 6.89 (1H, d, J = 7.2 Hz), 4.03 (2H, s), 3.2-2.4 (2H, br m), 2.77 (6H, s), 2.19 (3H, s); ^{13}C NMR: δ 137.4, 130.9, 127.3, 126.9, 126.1, 68.4, 51.3, 18.9; ^{11}B NMR: δ -1.4 (t, J = 99 Hz).

5-Bromo-2,2-dimethyl-2,3-benzazaborolidine (**17e**): Purified by PLC (4:1 hexanes/EtOAc, Rf = 0.15, 53% y of **17e**, recovered 15% of **13e**). Molecular ion calculated for $C_9H_{12}BBrN$: 224.0246; [M-H], EIMS found *m*/*z* = 224.0254; IR (neat, cm^{-1}) 2344, B–H; 2298, B–H; 1455, B–N; 1069, C–N; ^{1}H NMR: δ 7.52 (1H, br s), 7.20 (1H, dd, J = 7.9, 1.9 Hz), 6.94 (1H, d, J = 7.9 Hz), 3.98 (2H, s), 3.1-2.3 (2H, br m), 2.75 (6H, s); ^{13}C NMR: δ 137.4, 132.5, 127.7, 123.4, 122.1, 69.1, 50.9; ^{11}B NMR: δ -1.7 (t, J = 99 Hz).

5-Chloro-2,2-dimethyl-2,3-benzazaborolidine (**17f**): Purified by PLC (4:1 hexanes/EtOAc, Rf = 0.14, 73% y of **17f**, recovered 17% of **13f**). Molecular ion calculated for $C_9H_{12}BClN$: 180.0751; [M-H], EIMS found *m*/*z* = 180.0753; IR (neat, cm^{-1}) 2352, B–H; 2302, B–H; 1455, B–N; 1077, C–N; ^{1}H NMR: δ 7.36 (1H, br s), 7.20 (1H, dd, J = 8.0, 1.9 Hz), 6.94 (1H, d, J = 8.0 Hz), 4.00 (2H, s), 3.1-2.3 (2H, br m), 2.75 (6H, s); ^{13}C NMR: δ 136.9, 133.3, 129.6, 124.8, 122.9, 69.0, 50.9; ^{11}B NMR: δ -1.7 (t, J = 100 Hz).

Compounds **17g-1** and **17g-2** were obtained in 67% combined yield, 1:1.3 ratio.

6-Chloro-2,2-dimethyl-2,3-benzazaborolidine (**17g-1**): Purified by PLC (4:1 hexanes/EtOAc, Rf = 0.38, 29% y of **17g-1**). Molecular ion calculated for $C_9H_{12}BClN$: 180.0751; [M-H], EIMS found *m*/*z* = 180.0752; IR (thin film in $CDCl_3$, cm^{-1}) 2360, B–H; 2298, B–H; 1460, B–N; 1079, C–N; ^{1}H NMR: δ

7.33 (1H, d, J = 7.9 Hz), 7.15 (1H, dd, J = 7.9, 1.8 Hz), 7.06 (1H, d, J = 1.8 Hz), 4.01 (2H, s), 3.2-2.2 (2H, br m), 2.76 (6H, s); ^{13}C NMR: δ 140.5, 130.9, 130.6, 127.2, 121.9, 69.1, 50.9; ^{11}B NMR: δ -1.7 (t, J = 100 Hz).

4-Chloro-2,2-dimethyl-2,3-benzazaborolidine (**17g-2**): Purified by PLC (4:1 hexanes/EtOAc, Rf = 0.23, 38% y of **17g-2**). Molecular ion calculated for $C_9H_{12}BClN$: 180.0751; [M-H], EIMS found *m/z* = 180.0753; IR (thin film in $CDCl_3$, cm^{-1}) 2363, B–H; 2253, B–H; 1471, B–N; 1074, C–N; ^{1}H NMR: δ 7.16 (1H, d, J = 7.8 Hz), 7.03 (1H, t, J = 7.8 Hz), 6.95 (1H, d, J = 7.8 Hz), 4.07 (2H, s), 3.2-2.4 (2H, br m), 2.78 (6H, s); ^{13}C NMR: δ 140.3, 136.1, 127.5, 126.8, 120.0, 69.6, 51.2; ^{11}B NMR: δ -2.0 (t, J = 100 Hz).

5-Fluoro-2,2-dimethyl-2,3-benzazaborolidine (**17h**): Purified by PLC (2:1 hexanes/EtOAc, Rf = 0.31, 59% y of **17h**, recovered 22% of **13h**). Molecular ion calculated for $C_9H_{12}BFN$: 164.1047; [M-H], EIMS found *m/z* = 164.1045; IR (neat, cm^{-1}) 2356, B–H; 2317, B–H; 1461, B–N; 1063, C–N; ^{1}H NMR: δ 7.08 (1H, d, J = 8.9 Hz), 7.00 (1H, dd, J = 8.2, 4.9 Hz), 6.74 (1H, td, J = 8.8, 2.5 Hz), 4.01 (2H, s), 3.1-2.3 (2H, br m), 2.76 (6H, s); ^{13}C NMR: δ 162.9 (d, J = 244 Hz), 133.9 (d, J = 2 Hz), 122.8 (d, J = 7 Hz), 116.0 (d, J = 19 Hz), 111.5 (d, J = 23 Hz), 69.0, 50.9; ^{11}B NMR: δ -1.6 (t, J = 102 Hz) ; ^{19}F NMR: δ -117.0 (m).

Compounds **17i-1** and **17i-2** were obtained in 67% combined yield, 4:1 ratio.

6-Fluoro-2,2-dimethyl-2,3-benzazaborolidine (**17i-1**): Purified by PLC (4:1 hexanes/EtOAc, Rf = 0.31, 54% y of **17i-1**). Molecular ion calculated for $C_9H_{12}BFN$: 164.1047; [M-H], EIMS found *m/z* = 164.1049; IR (thin film in $CDCl_3$, cm^{-1}) 2359, B–H; 2298, B–H; 1472, B–N; 1066, C–N; ^{1}H NMR: δ 7.33 (1H, unres. dd, J = 7.8, 6.3 Hz), 6.89 (1H, ddd, J = 9.8, 7.8, 2.2 Hz), 6.79 (1H, dd, J = 9.4, 2.2 Hz), 4.01 (2H, s), 3.1-2.3 (2H, br m), 2.76 (6H, s); ^{13}C NMR: δ 161.6 (d, J = 241 Hz), 140.1 (d, J = 7 Hz), 130.7 (d, J = 7 Hz), 113.9 (d, J = 20 Hz), 109.0 (d, J = 22 Hz), 69.3 (d, J = 3 Hz), 50.9; ^{11}B NMR: δ -1.6 (t, J = 100 Hz) ; ^{19}F NMR: δ -119.4 (m).

4-Fluoro-2,2-dimethyl-2,3-benzazaborolidine (**17i-2**): Purified by PLC (4:1 hexanes/EtOAc, Rf = 0.23, 13% y of **17i-2**). Molecular ion calculated for $C_9H_{12}BFN$: 164.1047; [M-H], EIMS found *m/z* = 164.1053; IR (thin film in $CDCl_3$, cm^{-1}) 2376, B–H; 2302, B–H; 1459, B–N; 1075, C–N; ^1H NMR: δ 7.08 (1H, td, J = 7.4, 5.6 Hz), 6.90-6.82 (2H, m), 4.05 (2H, s), 3.2-2.4 (2H, br m), 2.78 (6H, s); ^{13}C NMR: δ 163.9 (d, J = 241 Hz), 141.9 (d, J = 14 Hz), 127.2 (d, J = 7 Hz), 117.7 (d, J = 3 Hz), 113.9 (d, J = 25 Hz), 69.4 (d, J = 1 Hz), 51.0; ^{11}B NMR: δ -2.9 (t, J = 100 Hz) ; ^{19}F NMR: δ -107.1 (m).

7-Bromo-2,2-dimethyl-2,3-benzazaborolidine (**17j**): Purified by FC (9:1 hexanes/Et_2O, Rf = 0.24, 55% y of **17j**, recovered 16% of **13j**). Molecular ion calculated for $C_9H_{12}BBrN$: 224.0246; [M-H], EIMS found *m/z* = 224.0255; IR (neat, cm^{-1}) 2356, B–H; 2296, B–H; 1443, B–N; 1071, C–N; ^1H NMR: δ 7.31 (1H, d, J = 7.4 Hz), 7.21 (1H, d, J = 7.9 Hz), 7.06 (1H, t, J = 7.5 Hz), 4.12 (2H, s), 3.2-2.4 (2H, br m), 2.79 (6H, s); ^{13}C NMR: δ 138.2, 129.2, 128.2, 127.9, 117.4, 70.2, 51.2; ^{11}B NMR: δ -1.0 (t, J = 103 Hz).

7-Chloro-2,2-dimethyl-2,3-benzazaborolidine (**17k**): Purified by FC (9:1 hexanes/Et_2O, Rf = 0.24, 55% y of **17k**, recovered 20% of **13k**). Molecular ion calculated for $C_9H_{12}BClN$: 180.0751; [M-H], EIMS found *m/z* = 180.0749; IR (neat, cm^{-1}) 2354, B–H; 2298, B–H; 1447, B–N; 1073, C–N; ^1H NMR: δ 7.28 (1H, d, J = 7.3 Hz), 7.13 (1H, t, J = 7.6 Hz), 7.05 (1H, d, J = 8.1 Hz), 4.14 (2H, s), 3.2-2.4 (2H, br m), 2.78 (6H, s); ^{13}C NMR: δ 136.2, 128.9, 128.3, 127.7, 125.0, 68.3, 51.3; ^{11}B NMR: δ -1.1 (t, J = 100 Hz).

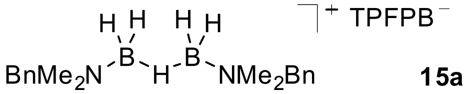
7-Fluoro-2,2-dimethyl-2,3-benzazaborolidine (**17l**): Purified by PLC (9:1 hexanes/Et_2O, Rf = 0.19, 33% y of **17l**, recovered 36% of **13l**). Molecular ion calculated for $C_9H_{13}BFN$: 164.1047; [M-H], EIMS found *m/z* = 164.1044; IR (neat, cm^{-1}) 2352, B–H; 2314, B–H; 1465, B–N; 1075, C–N; ^1H NMR: δ 7.18-7.15 (2H, m), 6.79-6.73 (1H, m), 4.13 (2H, s), 3.2-2.4 (2H, br m), 2.79 (6H, s); ^{13}C NMR: δ 158.2 (d, J = 248 Hz), 129.2 (d, J = 5 Hz), 125.0 (d, J = 3 Hz), 114.6 (d, J = 22 Hz), 111.3 (d, J = 19 Hz), 65.4, 51.1; ^{11}B NMR: δ -1.4 (t, J = 100 Hz) ; ^{19}F NMR: δ -121.1 (m).

2,2-Dimethyl-2,1-benzazaborinane (**24**): Purified by FC (4:1 hexanes/EtOAc, Rf = 0.18, 74% y of **24**, recovered 17% of **23**). Molecular ion calculated for $C_{10}H_{16}BNNa$: 184.1273; [M+Na], ESMS found *m/z*

= 184.1279; IR (neat, cm^{-1}) 2314, B–H; 1436, B–N; 1084, C–N; ^{1}H NMR: δ 7.26 (1H, d, J = 6.9 Hz), 7.12 (1H, td, J = 6.9, 1.9 Hz), 7.08-7.01 (2H, m), 3.07 (4H, s), 3.0-2.2 (2H, br m), 2.66 (6H, s); ^{13}C NMR: δ 134.1, 132.9, 126.9, 125.6, 124.5, 59.2, 50.5, 28.4; ^{11}B NMR: δ -5.2 (t, J = 96 Hz).

2,2-Dimethyl-2,1-benzazaborepane (**26**): Purified by PLC (2:1 hexanes/EtOAc, Rf = 0.43, 42% y of **26**, recovered 31% of **25**). Molecular ion calculated for $C_{11}H_{18}BNNa$: 198.1430; [M+Na], ESMS found *m/z* = 198.1425; IR (neat, cm^{-1}) 2329, B–H; 1455, B–N; 1102, C–N; ^{1}H NMR: δ 7.44 (1H, t, J = 4.1 Hz), 7.11-7.06 (2H, m), 7.02-6.97 (1H, m), 3.1-2.3 (2H, br m), 3.08 (2H, br s), 2.97 (2H, br s), 2.52 (6H, s), 1.87 (2H, pentet, J = 5.6 Hz); ^{13}C NMR: δ 146.9, 137.0, 126.8, 126.0, 125.3, 67.5, 51.4, 36.5, 26.0; ^{11}B NMR: δ -1.8 (t, J = 93 Hz).

Room Temperature Activation of Dimethylbenzylamine Borane (13a) with TrTPFPB: Isolation of *H*-Bridged Compound 15a

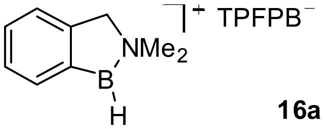


$[\mathrm{BnMe_2N{-}BH_2{-}H{-}BH_2{-}NMe_2Bn}]^+\ \mathrm{TPFPB}^-$

15a

Solid TrTPFPB (0.103 g, 0.112 mmol) was added in small portions to a solution of **13a** (41.7 mg, 0.280 mmol) in anhydrous PhH (1 mL). The resulting mixture was diluted with 1 mL of dry hexanes. The top layer of the resulting two-layer mixture was discarded, and the bottom layer (dark brown oil) was washed with 3 x 1.5 mL of anhydrous PhH, followed by 2 x 1 mL of anhydrous hexanes. The residue was dried in vacuum to give 61.3 mg (67%) of a glassy solid. C_6D_5Br and CD_2Cl_2 solutions of **15a** were found to be stable at room temperature for weeks if kept under inert conditions. ^{1}H NMR (C_6D_5Br): δ 7.32-7.14 (6H, m), 6.96-6.90 (4H, m), 3.52 (4H, s), 2.9-1.9 (4H, br m), 2.10 (12H, s), -2.3 (1H, br s); ^{11}B NMR (C_6D_5Br): δ 0 (br s), -16.2 (s); ^{13}C NMR (CD_2Cl_2): δ 148.6 (d, J = 240 Hz), 138.7 (d, J = 245 Hz), 136.7 (d, J = 245 Hz), 132.8, 131.0, 129.6, 128.2, 125.6-123.1 (br m), 67.5, 49.2; ^{19}F NMR (C_6D_5Br): δ -131.7 (unres d), -161.8 (t, J = 21 Hz), -165.8 (m).

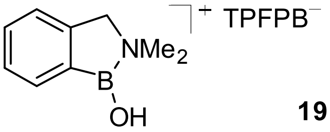
Room Temperature Activation of the Cyclic Amine Borane 17a: Independent Generation of the Cationic Trivalent Boron Intermediate 16a



16a

A mixture of solid **17a** (24.3 mg, 0.165 mmol) and TrTPFPB (0.145 g, 0.157 mmol) was covered with 1 mL of dry PhH in a nitrogen-filled glovebox. After stirring at room temperature for several minutes the top layer was removed, and the bottom layer was washed with 3 x 1 mL PhH, followed by 1 mL hexanes. The resulting oil solidified upon trituration with hexanes. Removal of the hexanes gave 0.117 g (91%) of a yellowish powder. The ^{13}C NMR spectrum could not be obtained due to instability of the product in C_6D_5Br. ^{1}H NMR (C_6D_5Br): δ 7.62 (1H, d, J = 7.0 Hz), 7.43 (1H, m), 7.18-7.11 (1H, m), 6.94 (1H, d, J = 7.0 Hz), 5.9-4.9 (1H, br s; sharper in a ^{11}B decoupling experiment), 3.87 (2H, s), 2.35 (6H, s); ^{11}B NMR: δ 58.9 (br s), -16.2 (s); ^{19}F NMR: δ -131.8 (m), -161.5 (t, J = 21 Hz), -165.6 (m).

Structure Assignment for 19 (*B*-Hydroxy Analogue of 16a)

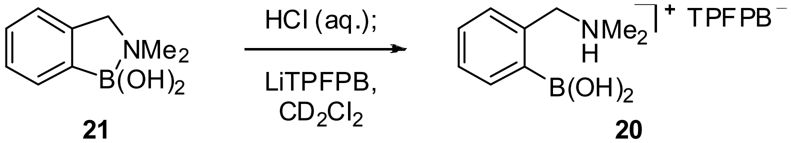


19

A mixture of TrTPFPB (0.113 g, 123 μmol) and **17a** (18.1 mg, 123 μmol) was layered with anhydrous benzene (1 mL) under an N_2 atmosphere. The mixture was stirred at rt for 10 minutes, then water (2.2 μL, 123 μmol) was added. After stirring for 10 minutes at rt the top layer was separated and discarded. The resulting brown oil was washed with 4 x 1 ml of dry benzene, and dried in vacuum. The residue was dissolved in CD_2Cl_2 and transferred into a nitrogen flushed NMR tube. Assay by ^{1}H NMR shows **19** containing **17a** as a trace impurity. Peak at 39 ppm in ^{11}B NMR is consistent with that previously reported for **16a**.[4] Cation **19**: ^{1}H NMR: δ 7.93-7.86 (2H, m), 7.64 (1H, t, J = 7.6 Hz), 7.49 (1H, d, J = 7.9 Hz), 7.46 (1H, s), 4.68 (2H, s), 3.18 (6H, s); ^{11}B NMR: δ 39 (s), -16.7 (s).

In order to investigate reaction of **19** with an additional equivalent of water, the cation **19** was generated *in situ*, without removing the byproduct Ph_3CH. Activation of **17a** (32 mg, 220 μmol) with

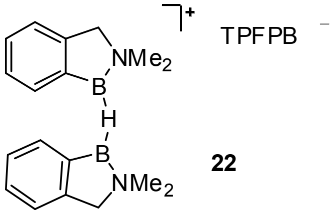
TrTPFPB (224 mg, 243 μmol) in CD_2Cl_2 (3.0 mL total) was performed, followed by addition of water (4.0 μL, 220 μmol) before transferring an aliquot to an NMR tube. Both ^{1}H and ^{11}B NMR spectra were found to be consistent with the spectral data given above for the pure **19**. An aliquot of this solution (1.2 mL, ca. 90 μmol) was added an additional equivalent of water (2.0 μL, 110 μmol) before transferring to an NMR tube, giving major ^{11}B NMR signals at δ 29 ppm as well as major signals by ^{1}H NMR identical with chemical shifts assigned to **20** as reported below.



21 **20**

The known 2-dimethylaminobenzeneboronic acid (**21**, 9.9 mg, 55 μmol)[5] was protonated by addition of 0.5 M HCl (1.0 mL, 1.0 mmol) with stirring for 1 h at rt. Next, solid $Li(OEt_2)_nB(C_6F_5)_4$ (50 mg, ca. 60 μmol) was added with vigorous stirring for 10 min followed by extraction with 0.7 mL CD_2Cl_2. Assay by ^{1}H NMR showed compound **20** and Et_2O in a ratio of ca. 1.5:1. Ammonium salt **20**: ^{1}H NMR: δ 8.3-7.9 (1H, br m), 7.90-7.86 (1H, m), 7.65-7.59 (2H, m), 7.37-7.32 (1H, m), 5.9 (2H, br s), 4.28 (2H, d, J = 5.9 Hz), 2.89 (6H, d, J = 5.4 Hz); ^{11}B NMR: δ 29 (br s), -16.7 (s).

Room Temperature Activation of 2,2-Dimethyl-2,3-Benzazaborolidine (17a) with TrTPFPB: Observation of *H*-Bridged Compound 22



22

A dry NMR tube was charged in a nitrogen flushed glovebox with a solution of TrTPFPB (46.5 mg, 50.4 μmol) in dry C_6D_5Br (0.6 mL). Variable amounts of **17a** solution in dry C_6D_5Br were added, and the mixture was analyzed by ^{1}H and ^{11}B NMR spectroscopy. The following observations were made:

at 1:1 TrTPFPB:**17a** ratio the only compound observed besides Ph_3CH is the borenium ion **16a**.

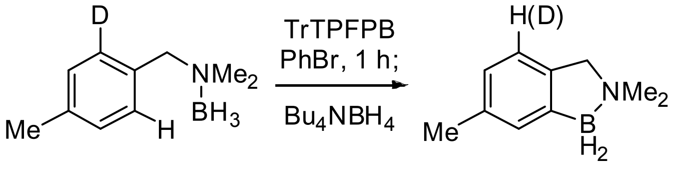
at 1:1.5 TrTPFPB:**17a** ratio ^{11}B NMR shows two distinct peaks, assigned as **16a** (59 ppm) and **22** (11 ppm). ^{1}H NMR, however, shows only one set of broadened peaks.

at 1:2 TrTPFPB:**17a** ratio ^{11}B NMR shows only one peak at 11 ppm, assigned as **22**. ^{1}H NMR shows only one set of peaks.

at 1:3 TrTPFPB:**17a** ratio ^{11}B NMR shows two distinct peaks, assigned as **22** (11 ppm) and **17a** (-1 ppm). ^{1}H NMR shows only one set of peaks.

Cation **22**: ^{1}H NMR(only two characteristic aliphatic peaks can be unambiguously identified): δ 3.53 (2H, s), 2.23 (6H, s); ^{11}B NMR: δ 11 (s), -16.2 (s).

Kinetic Isotope Effect Study: Preparation and Reaction of 13b-D$_1$



13b-*d*$_1$

17b-*d*$_1$: **17b** = 2.8 : 1

4-Methylbenzyldimethylamine (170 mg, 1.14 mmol), prepared from dimethylamine and 4-methylbenzyl bromide,[6] was dissolved in Et$_2$O (0.3 mL) in a 5 ML round bottom flask fused to a reflux condenser and reacted with n-BuLi in hexane (2.14 M, 0.80 mL, 1.7 mmol) under an N$_2$ atmosphere, heating to reflux (bath temperature: 75 °C) for 2 h with stirring.[7] The orange solution was then cooled to rt and diluted with anhydrous THF (1 mL), and the resulting reddish solution was transferred by cannula (rinsing the flask with 1 mL THF) to a flask containing a mixture of D$_2$O (0.30 mL, 17 mmol) and THF (1 mL) with vigorous stirring. After 1 h the layers were separated, the supernatant was filtered, the flask rinsed with 2 x 5 mL Et$_2$O, and the combined filtrate was dried over MgSO$_4$ and reduced by a stream of N$_2$.

The crude product from the deuteration was taken up in 2 mL anhydrous DCM and treated with BH$_3$·THF (1.0 M, 1.5 mL, 1.5 mmol) under an N$_2$ atmosphere. After 2 h the solution was filtered through a plug of silica gel, flushing with 20 mL DCM, and the sample was reduced under a stream of

N_2, collecting 129 mg **13b-D$_1$** (69% y over two steps). The ^{1}H NMR spectrum of a sample shows peaks consistent with the desired product (see spectroscopic data for **5b** below), the aromatic region integrating for 3.05H, indicating 95% deuteration.

Borane complex **13b-D$_1$** (17.8 mg, 108 μmol) was dissolved in anhydrous PhBr (1.2 mL) and activated with a solution of TrTPFPB (91 mg, 99 μmol) in PhBr (2 x 0.4 mL) under an N_2 atmosphere. After stirring 1 h the reaction was quenched by addition of a solution of Bu_4NBH_4 (33 mg, 130 μmol) in PhBr (2 x 0.4 mL), and the solvent was then removed under a stream of N_2. The residue was purified by preparative thin layer chromatography (PLC) on silica gel (20 cm x 20 cm x 1000 μm, 4:1 hexanes/EtOAc) recovering 2.1 mg product **17b** with ^{1}H NMR data matching that reported earlier for **17b**. The ^{1}H NMR peak corresponding to the *ortho*-C–H integrates for 0.27H, indicating 73% deuteration. Substrate **13b** was chosen for this study rather than the simpler **13a** because the ^{1}H NMR signal for the *ortho*-C–H of **17a** overlaps with another aromatic proton signal. All aromatic proton signals for **17b** are fully resolved in the 500 MHz ^{1}H NMR spectrum.

Preparation and Reaction of 28

$BH_3{\cdot}THF$ (2.2 mL, 2.2 mmol) was added by syringe to a solution of 2-(trimethylsilyl)-N,N-dimethylbenzylamine[7] (0.415 g , 2.0 mmol) in 1 mL of dry DCM. After 5 min, the solution was filtered through a plug of silica gel, flushing with DCM and removing solvent by rotary evaporation. The solid product was further dried under high vacuum, yielding 0.403 g **28** (91%). Molecular ion calculated for $C_{12}H_{21}NSi$: 207.1443; [M-BH_3], EIMS found *m/z* = 207.1446; IR (thin film in $CDCl_3$, cm^{-1}) 2376, B–H; 2272, B–H; 1469, B–N; 1168, C–N; ^{1}H NMR: δ 7.65-7.60 (1H, m), 7.41-7.35 (3H, m), 4.22 (2H, s), 2.4-1.4 (3H, br m), 2.50 (6H, s), 0.39 (9H, s); ^{13}C NMR: δ 142.8, 137.0, 136.0, 132.0, 128.6, 128.1, 66.1, 49.9, 1.6; ^{11}B NMR: δ -7.8 (t, J = 90 Hz).

Following method **B** (page S-7) on 0.115 mmol TrTPFPB scale, compound **34** was converted to **17a** in 96% isolated yield based on **28**. Crude ^{1}H NMR assay showed no traces of any byproducts derived from **28**.

Preparation of 2-*tert*-Butylbenzaldehyde (32)

A dry flask was charged with fluorobenzene (dried over 4Å MS) (0.307 g, 3.19 mmol) in anhydrous Et_2O (3 mL) under an N_2 atmosphere. The solution was cooled to -78 °C, and a solution of *t*-BuLi in pentane (8.0 mL, 1.6M, 12.8 mmol) was added dropwise. After a few minutes, the mixture was allowed to warm to -55 °C, and was stirred for 3h. Dry DMF (1.0 mL, 13.1 mmol) was added dropwise while keeping the temperature below 0 °C. After warming to rt the mixture was quenched with saturated NH_4Cl solution. The solids were dissolved by adding 1M HCl, and the clear solution was extracted with Et_2O. The combined extracts were dried with $MgSO_4$, filtered and concentrated in vacuum. Flash chromatography (19:1 Hexanes:EtOAc) gave 0.259 g (50%) of a colorless oil. Spectral data matched those reported elsewhere.[8]

Preparation and Reaction of 34

A mixture of the aldehyde **32** (0.256 g, 1.58 mmol), dimethylamine hydrochloride (0.386 g, 4.74 mmol) and sodium cyanoborohydride (0.298 g, 4.74 mmol) in 3 mL MeOH was acidified with AcOH to reach pH 5. After stirring at rt for 45 h the mixture was made strongly acidic by adding ca. 1 mL of 6M HCl. The mixture was extracted with 3 x 5 mL Hex, and the organic extracts were discarded. The aqueous layer was made strongly basic by adding 10% NaOH solution, and then extracted with Et_2O. After drying the extracts with $MgSO_4$, filtering and concentration in vacuum, the residue was treated with excess BH_3-THF (10 mL, 1M, 10 mmol). Flash chromatography (19:1 Hexanes:EtOAc) gave 0.127 g of a colorless oil (39% over two steps). Molecular ion calculated for $C_{13}H_{22}N$: 192.1752; [M-BH_3+H], ESMS found *m*/*z* = 192.1748; IR (thin film in $CDCl_3$, cm^{-1}) 2375, B–H; 2323, B–H; 2273, B–H; 1469, B–N; 1170, C–N; ^{1}H NMR: δ 7.51 (1H, dd, J = 8.0, 1.2 Hz), 7.46 (1H, dd, J = 6.2, 1.6 Hz), 7.34-7.28

(1H, m), 7.25-7.19 (1H, m), 4.49 (2H, s), 2.55 (6H, s), 2.4-1.3 (3H, br m), 1.45 (9H, s); ^{13}C NMR: δ 150.2, 132.6, 131.2, 128.7, 127.8, 125.5, 63.4, 50.7, 36.2, 33.0; ^{11}B NMR: δ -7.3 (q, J = 95 Hz).

Following method **B** (page S-7) on 0.11 mmol TrTPFPB scale, compound **34** was converted to 7-*tert*-butyl-2,2-dimethyl-2,3-benzazaborolidine (**35**) in 66% isolated yield. Crude ^{1}H NMR assay after borohydride quench showed no traces of **17a**. Purified by PLC (4:1 hexanes/EtOAc, Rf = 0.48). Molecular ion calculated for $C_{13}H_{21}BN$: 202.1767; [M-H], EIMS found *m*/*z* = 202.1771; IR (neat, cm^{-1}) 2347, B–H; 2292, B–H; 1471, B–N; 1066, C–N; ^{1}H NMR: δ 7.28 (1H, d, J = 7.0 Hz), 7.18-7.08 (2H, m), 4.26 (2H, s), 3.2-2.2 (2H, br m), 2.77 (6H, s) , 1.32 (9H, s); ^{13}C NMR: δ 144.3, 136.0, 127.5, 127.2, 122.1, 70.4, 50.6, 35.0, 30.6; ^{11}B NMR: δ -2.6 (t, J = 90 Hz).

Preparation of Amine-Borane 46

A mixture of TrTPFPB (0.108 g, 0.117 mmol) and **17a** (17.2 mg, 0.117 mmol) in 1 mL of dry PhH was refluxed for 24h. During that time the amount of a dark oil on the bottom of the reaction flask decreased substantially. After quenching with a solution of n-Bu_4NBH_4 (36.1 mg, 0.140 mmol) in 1.5 mL of dry PhH the top layer of the two-layer mixture was separated, and the bottom layer was extracted with 3 x 1.5 mL PhH. The top layer was combined with the extracts, and the resulting solution was concentrated in vacuum. Purification by PLC (4:1 hexanes/EtOAc) gave 16.8 mg of a colorless oil (46%) as the only non-polar product besides Ph_3CH. Molecular ion calculated for $C_{15}H_{12}BNF_5$: 312.0983; [M-H], ESMS found *m*/*z* = 312.0989; IR (thin film in $CDCl_3$, cm^{-1}) 2253, B–H; 1467, B–N; ^{1}H NMR: δ 7.28 (1H, d, J = 7.2 Hz), 7.24-7.20 (1H, m), 7.19-7.15 (1H, m), 7.13 (1H, d, J = 7.2 Hz), 4.27 (1H, d, J = 13 Hz), 4.08 (1H, d, J = 13 Hz), 4.0-3.2 (1H, br m), 2.88 (3H, s), 2.46 (3H, s); ^{11}B NMR: δ -1.6 (q, J = 90 Hz); ^{13}C NMR: δ 149.2 (d, J = 240 Hz), 150.0 (br m), 140.3 (d, J = 250 Hz), 138.2, 137.2 (d, J = 255 Hz), 129.7, 127.2, 125.6, 121.7, 115.3, 69.5, 50.8, 46.5; ^{19}F NMR: δ -128.6 (d, J = 16 Hz), -156.3 (d, J = 20 Hz), -163.5 (m).

Et_3SiD Exchange Experiment

Et_3SiD (25.0 µL, 18.5 mg, 0.158 mmol) was added to a suspension of **16a** in 0.1 mL of dry PhH in a nitrogen-filled glovebox. After stirring at room temperature for 10 minutes the reaction mixture was diluted with 1 mL of dry hexanes. The precipitate was separated, washed with 2 x 1 mL hexanes, and dried in the glovebox overnight. ^1H NMR assay indicated that B-$\underline{H}$(D) signal intensity was only 8% of the starting value, and other signals in the spectrum were found to be unaffected. The $\underline{B}$-H(D) peak in ^{11}B NMR spectrum was found to be ca. 1 ppm upfield compared to starting borenium ion **16a** due to interaction with residual Et_3SiD / Et_3SiH.

D_2 Exchange Experiment

A dry thick-wall Schlenk tube was charged with **16a** (16.7 mg, 20.2 µmol) in 0.5 mL of dry benzene in a glove box. The contents of the tube were frozen in liquid N_2, the tube was evacuated and filled with D_2 (2-3 atm). The tube was then sealed and the contents were stirred at room temperature for 30 days. After quenching with excess n-Bu_4NBH_4 the reaction mixture was filtered through a short plug of silica, and concentrated in vacuum. Purification by PLC (4:1 hexanes/EtOAc) gave two compounds:
46: 1.1 mg of a colorless oil, $R_f = 0.5$. ^1H NMR assay of the δ 4.0-3.2 ppm signal indicates ca. 40% D incorporation with the entire label centered on the boron atom. No D incorporation in the o'-position was observed.

17a: 0.5 mg of a colorless solid, $R_f = 0.6$. Significant D incorporation was apparent from comparing CI-MS (CH_4 ionization) spectra of the authentic unlabeled **17a** and **17a** recovered from above. Approximate calculations show ca. 40±10 % D incorporation assuming exclusive B-$\underline{H}$ labeling (no exchange of C-$\underline{H}$).

Catalytic Cyclization from 13a to 17a

A dry thick-wall 12 mL Schlenk tube with a Teflon stopper was charged with a solution of **13a** (0.197 g, 1.32 mmol) and TrTPFPB (61.1 mg, 66.2 μmol) in 3 mL of dry toluene in a glove box. The tube was sealed and heated in an oil bath for 5.5 h, bath temperature 160 °C behind a safety shield. After cooling to room temperature the reaction mixture was quenched by adding solid n-Bu_4NBH_4 (30 mg, 0.117 mmol), and then diluted with CH_2Cl_2. The resulting mixture was filtered though a short plug of silica gel while eluting with CH_2Cl_2, and the solvents were evaporated under vacuum. Flash chromatography on silica gel (4:1 Hexanes:EtOAc) gave 0.175 g (90%) of a white crystalline solid. Spectral data matched those reported for **17a**.[4]

References for Supporting Information

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Computational Details

The structure of all species was fully optimized at the standard B3LYP/6-31G* level of theory using the Gaussian 03[A] program package. Vibrational frequencies at the optimized geometries were computed at the same level of theory, and used to verify the nature of the stationary points and to generate a correction for zero-point energy. All energies presented in the manuscript paper are electronic energies, including a correction for zero point energy.

Complete text ref. 38: Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Additional single-point energy calculations were carried out for the B3LYP/6-31G* geometries at the MP2/cc-pVTZ level of theory, using the MOLPRO program package. These calculations used density fitting methods (DF-MP2) for greater efficiency (see H.-J. Werner, F. R. Manby and P. J. Knowles, *J. Chem. Phys.* 2003, **118**, 8149-8160.)

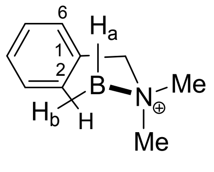
Complete text ref. 39: MOLPRO, version 2008.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, A. Mitrushenkov, G. Rauhut, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F.

Eckert, E. Goll, C. Hampel, G. Hetzer, T. Hrenar, G. Knizia, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, and A. Wolf, , see http://www.molpro.net.

Table S1. Structures from Fig. 4; energies and interatomic distances

Structure	E_{rel} + zpe^{a} (kcal/mol)	E_{rel} + zpe^{b} (kcal/mol)	$r_{C(1)B}$^{c}	$r_{C(2)B}$^{c}	r_{BN}^{c}	$r_{C(2)H}$^{c}	$r_{(2)HB}$^{c}	r_{BHa}^{c}	r_{BHb}^{c}
Min$_{\mathbf{A}}$	**0.0**	**0.0**	**2.38**	**2.55**	**1.57**	**1.09**	**2.73**	**1.18**	**1.18**
TS$_{\mathbf{AB}}$	**0.27**	**–0.08**	**2.34**	**2.21**	**1.61**	**1.09**	**2.47**	**1.18**	**1.19**
Min$_{\mathbf{B}}$	**0.43**	**–0.32**	**2.31**	**2.01**	**1.63**	**1.09**	**2.33**	**1.19**	**1.19**
TS$_{\mathbf{BC}}$	**18.0**	**13.3**	**2.48**	**1.66**	**1.59**	**1.51**	**1.28**	**1.30**	**1.19**
Min$_{\mathbf{C}}$	**-9.3**	**–7.2**	**2.37**	**1.50**	**1.57**	**--**	**--**	**--**	**1.19**
TS$_{\mathbf{Cexch}}$	**22.4**	**17.2**	**2.37**	**1.57**	**1.59**	**2.40**	**1.27**	**1.27**	**1.25**

a. B3LYP/6-31G* energies are corrected for zero point energy (zpe)
b. DF-MP2 relative energies including the B3LYP/6-31G* correction for zero point energy (zpe)
c. interatomic distances r_{xy} are given in units of Å



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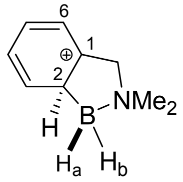

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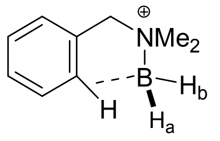

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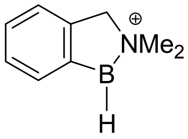
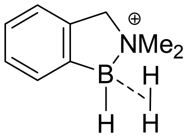
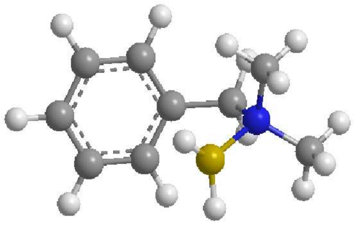


16a (Min$_C$)



TS$_{\mathbf{Cexch}}$

Cationic structures for Table S1



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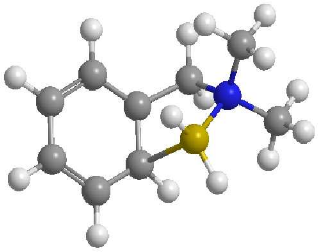

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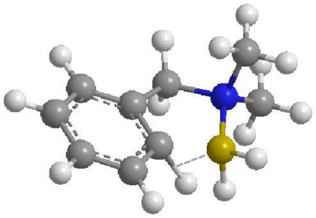

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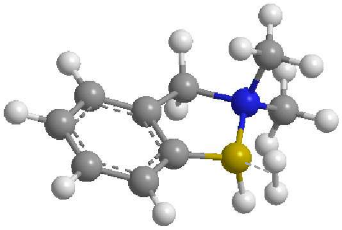
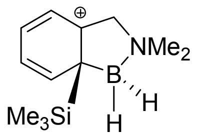


TS$_{Cexch}$

Table S2. Structures from Fig. 5; energies and interatomic distances[a]

Structure	E_{rel} + zpe (kcal/mol)	$r_{C(1)B}$	$r_{C(2)B}$	$r_{C(2)H}$	r_{BN}	$r_{C(2)Si}$	r_{SiHa}	r_{BHa}
Min$_{\mathbf{D}}$	**0.00**	**2.50**	**1.67**	**--**	**1.67**	**2.19**	**2.80**	**1.20**
TS$_{\mathbf{DE}}$	**5.9**	**2.47**	**1.63**	**--**	**1.64**	**2.52**	**2.02**	**1.23**
Min$_{\mathbf{E}}$	**-14.2**	**2.40**	**1.56**	**--**	**1.62**	**3.59**	**1.61**	**1.41**
TSEG	**-2.3**	**2.42**	**1.59**	**--**	**1.63**	**3.64**	**1.92^{Ha}** **1.98^{Hb}**	**1.23**
Min$_{\mathbf{G}}$	**6.3**	**2.32**	**1.90**	**1.09**	**1.63**	**--**	**--**	**1.19**
TS$_{\mathbf{GH}}$	**23.5**	**2.49**	**1.65**	**1.52**	**1.59**	**--**	**--**	**1.28 1.19**
Min$_{\mathbf{H}}$	**-4.0**	**2.38**	**1.49**	**--**	**1.56**	**--**	**--**	**1.19**

a. LYP/6-31G* energies are corrected for zero point energy (zpe); interatomic distances r_{xy} are given in units of Å



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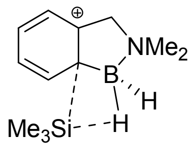

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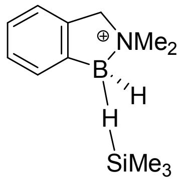
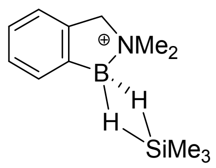
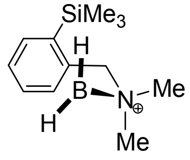


Min$_{\mathbf{E}}$



TS$_{\mathbf{E\mathit{ent}E}}$



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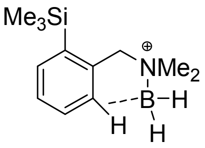

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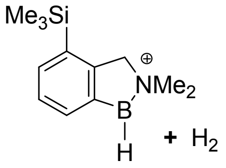
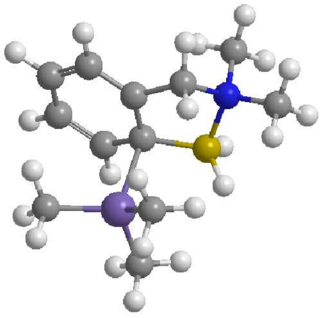
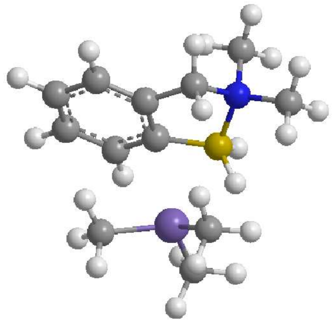


Min$_{\mathbf{H}}$

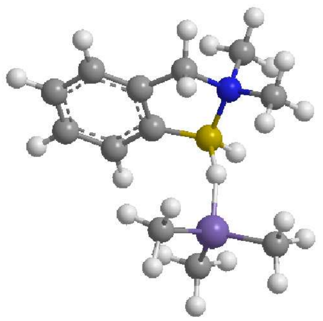
Cationic structures for Table S2



Min$_{\mathrm{D}}$



TS$_{\mathrm{DE}}$



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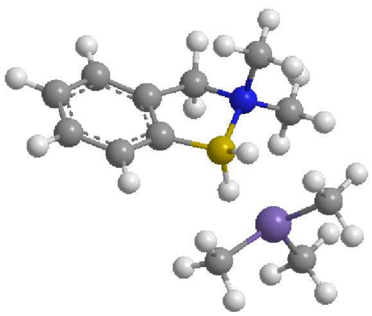
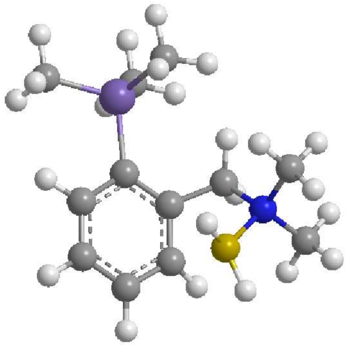
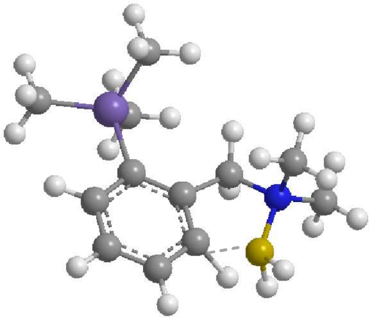


TS$_{\mathbf{E}\textit{ent}\mathbf{E}}$



Min$_{\mathbf{G}}$



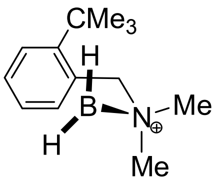
TS$_{\mathbf{GH}}$

Table S3. Structures from **40** to **35**; energies and interatomic distances[a]

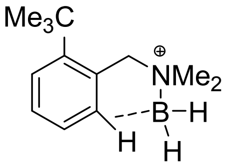
Structure	E_{rel} + zpe (kcal/mol)	$r_{C(1)B}$	$r_{C(2)B}$	r_{BN}	$r_{C(2)H}$	$r_{(2)HB}$	$r_{(2)HHa}$	r_{BHa}	r_{BHb}
Min_J	**0.0**	**2.34**	**1.88**	**1.63**	**1.09**	**2.22**	**2.43**	**1.19**	**1.19**
TS_{JK}	**16.1**	**2.49**	**1.65**	**1.59**	**1.52**	**1.28**	**1.05**	**1.30**	**1.19**
Min_k	**-11.1**	**1.50**	**2.37**	**1.57**	**--**	**--**	**0.74**	**--**	**1.19**

a. B3LYP/6-31G* energies are corrected for zero point energy (zpe);

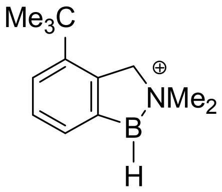
interatomic distances r_{xy} are given in units of Å



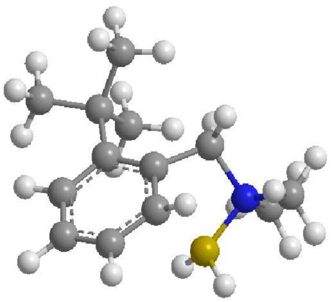
Min_J



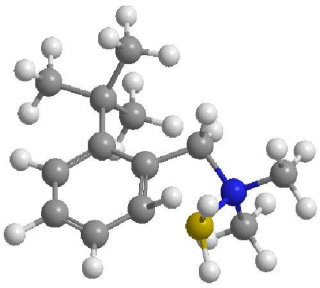
TS_{JK}



Min_K



Min$_J$



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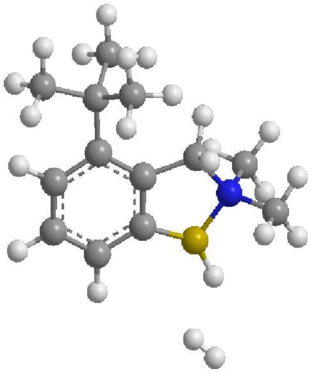

Min$_K$