–Supporting Information for–

Tetrahydrofuran Ring Opening and Related Reactions with Lewis Acidic N-Heterocyclic Carbene-Boryl Trifluoromethanesulfonate

*Andrey Solovyev, Emmanuel Lacôte, and Dennis P. Curran*

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General Remarks: Chemicals were purchased from commercial suppliers and used as received. THF, toluene, and CH₂Cl₂ were dried by passing through an activated alumina column. Reactions were monitored by TLC analysis. Visualization was accomplished with a 254 nm UV lamp or by staining with a vanillin solution. The CombiFlash®Rf flash chromatography system (Teledyne ISCO) and prepacked RediSep®Rf columns were used for purification of products. Melting points (mp) were determined with a Mel-Temp II apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer as thin films (CH₂Cl₂) on NaCl plates. Proton (¹H) and carbon (¹³C) nuclear magnetic resonance (NMR) spectra were measured on Bruker Avance III 400 and Bruker Avance III 500 instruments at 400 (500) and 100 (125) MHz, respectively. The chemical shifts in spectra were measured in parts per million (ppm) on the delta (δ) scale relative to the resonance of the solvent peak (CDCl₃: ¹H = 7.27 ppm, ¹³C = 77.0 ppm). Boron (¹¹B) NMR spectra were measured on a Bruker Avance III 400 instrument at 128.4 MHz. The ¹¹B chemical shifts are given relative to BF₃·OEt₂ (¹¹B = 0 ppm). All NMR spectra were recorded at 293 K. The following abbreviations are used to describe coupling: s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; m = multiplet; br = broad; app = apparent. The resonances of hydrogen atoms connected to the boron atom often cannot be observed in ¹H NMR spectra because of quadrupole broadening. For the same reason, the resonances of carbene carbon atoms connected to the boron atom were not observed in ¹³C NMR spectra of all NHC-boranes. High resolution mass spectra (HRMS) were obtained on a Q-Tof Ultima API, Micromass UK Limited instrument by electrospray ionization (ESI).

Compounds 1¹ and 2² have been prepared according to the literature procedures. Their spectroscopic data were consistent with those previous reported.
Experimental Procedures and Compound Characterization:

**General procedure: THF ring-opening reactions (GP):** A solution of a base (0.2 mmol) was added to a solution of ArOH (0.2 mmol) in THF (0.5 mL) or toluene (0.5 mL) at rt under argon. After 5 min of stirring, the formation of the phenoxide ArOM was assumed. In a separate flask, triflic acid (10 µL, 0.1 mmol) was added to a solution of dipp-Imd-BH$_3$ (40.5 mg, 0.10 mmol) in CH$_2$Cl$_2$ (1 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH$_2$OTf was assumed. In several cases, CH$_2$Cl$_2$ was removed by rotary evaporation and the white residue was dissolved in THF (1 mL). Then the solution of ArOM was added to the resulting solution of dipp-Imd-BH$_2$OTf. The reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The products were purified by flash chromatography.

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-phenoxybutyloxy)borane (dipp-Imd-BH$_2$O(CH$_2$)$_4$OPh) (4a): Following GP with LiHMDS (1 M in toluene, 0.2 mL, 0.2 mmol) and
PhOH (19 mg, 0.20 mmol) in THF (2 mL)–toluene (0.4 mL), elution with hexane:EtOAc = 90:10 gave dipp-Imd-BH₂O(CH₂)₄OPh 4a as a white solid (28.9 mg, 51%): mp 121–122 °C; IR (thin film, cm⁻¹) ν_max 3071, 2964, 2928, 2870, 2250 (B–H), 1689, 1599, 1586, 1538, 1497, 1470, 1387, 1368, 1332, 1301, 1246, 1208, 1172, 1061, 954, 936, 883, 803, 755; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (t, J = 7.8 Hz, 2H), 7.30–7.22 (m, 6H), 7.00 (s, 2H), 6.91 (dt, J = 7.3, 1.0 Hz, 1H), 6.85 (dd, J = 8.6, 1.0 Hz, 1H), 3.70 (t, J = 7.0 Hz, 2H), 2.85 (t, J = 6.6 Hz, 2H), 2.65 (septet, J = 6.9 Hz, 4H), 1.32 (d, J = 6.8 Hz, 12H), 1.29 (app quintet, J = 7.8 Hz, 2H), 1.18 (d, J = 6.8 Hz, 12H), 1.07 (app quintet, J = 7.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 145.2, 134.2, 129.7, 129.2, 123.6, 122.3, 120.0, 114.5, 68.8, 68.2, 28.7, 28.4, 25.8, 24.8, 22.9; ¹¹B NMR (128.4 MHz, CDCl₃) δ –9.2 (t, J_B–H = 92 Hz); HRMS (ESI) calcd. for C₃₇H₅₂¹¹BN₂O₂ ([M + H]⁺) 567.4122, found 567.4144.

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-phenoxybutyloxy)borane (dipp-Imd-BH₂O(CH₂)₄OPh) (4a): Following GP with NaHMDS (0.6 M in toluene, 0.35 mL, 0.2 mmol) and PhOH (19 mg, 0.20 mmol) in THF (2 mL)–toluene (0.35 mL), elution with hexane:EtOAc = 90:10 gave dipp-Imd-BH₂O(CH₂)₄OPh 4a as a white solid (26.4 mg, 46%). The NMR data of the isolated product were identical to those of the previously prepared sample of 4a.
Following GP with KHMDs (0.5 M in toluene, 0.4 mL, 0.2 mmol) and PhOH (19 mg, 0.20 mmol) in THF (2 mL), elution with hexane:EtOAc = 90:10 first gave dipp-Imd-BH$_2$OPh 3a as a white solid (14.9 mg, 30%): mp 166–168 °C; IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 3129, 2963, 2927, 2869, 2282 (B–H), 1596, 1496, 1471, 1460, 1427, 1385, 1364, 1331, 1293, 1173, 1158, 1070, 998, 955, 878, 803, 759; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (t, $J$ = 7.8 Hz, 2H), 7.29 (d, $J$ = 8.0 Hz, 4H), 7.07 (s, 2H), 6.92 (t, $J$ = 8.0 Hz, 2H), 6.48 (t, $J$ = 7.2 Hz, 1H), 6.18 (d, $J$ = 7.6 Hz, 2H), 2.80 (br q, 2H), 2.65 (septet, $J$ = 6.9 Hz, 4H), 1.23 (d, $J$ = 6.8 Hz, 12H), 1.20 (d, $J$ = 6.8 Hz, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.1, 145.2, 134.1, 129.9, 128.1, 123.7, 122.5, 116.4, 115.5, 28.8, 24.7, 23.0; $^{11}$B NMR (128.4 MHz, CDCl$_3$) $\delta$ −11.3 (t, $J_{\text{B-H}}$ = 93 Hz); HRMS (ESI) calcd. for C$_{33}$H$_{43}$BN$_2$NaO ([M + Na]$^+$) 517.3366, found 517.3386.

Slightly more polar dipp-Imd-BH$_2$O(CH$_2$)$_4$OPh 4a was eluted next and isolated as a white solid (23 mg, 40%). The NMR data of the isolated product were identical to those of the previously prepared sample of 4a.
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(2,6-dimethylphenoxy)butyloxy]borane (dipp-Imd-BH₂O(CH₂)₄O(2,6-Me₂C₆H₃) (4b): Following GP with KHMDS (0.5 M in toluene, 0.4 mL, 0.2 mmol) and 2,6-dimethylphenol (25 mg, 0.20 mmol) in THF (2 mL)–toluene (0.4 mL), elution with hexane:EtOAc = 90:10 gave 4b as a white solid (36.1 mg, 60%): mp 108–110 °C; IR (thin film, cm⁻¹) νmax 3162, 3134, 3070, 3035, 2962, 2928, 2869, 2712, 2225 (B–H), 1699, 1593, 1562, 1472, 1426, 1384, 1361, 1332, 1296, 1262, 1207, 1172, 1123, 1108, 1091, 1060, 1044, 983, 949, 938, 863, 802, 760; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (t, J = 7.8 Hz, 2H), 7.26 (d, J = 8.0 Hz, 4H), 7.00 (s, 2H), 6.99 (d, J = 6.4 Hz, 2H), 6.89 (t, J = 7.4 Hz, 1H), 3.52 (t, J = 6.8 Hz, 2H), 2.86 (t, J = 6.6 Hz, 2H), 2.65 (septet, J = 6.8 Hz, 4H), 2.23 (s, 6H), 1.40–1.30 (m, 2H), 1.32 (d, J = 6.8 Hz, 12H), 1.29 (app quintet, J = 7.8 Hz, 2H), 1.18 (d, J = 6.8 Hz, 12H), 1.12 (app quintet, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 145.2, 134.2, 131.0, 129.7, 128.5, 123.6, 123.2, 122.3, 72.8, 69.1, 28.7, 28.7, 27.0, 24.8, 24.8, 22.9, 16.3; ¹¹B NMR (128.4 MHz, CDCl₃) δ −9.2 (t, J_B-H = 91 Hz); HRMS (ESI) calcd. for C₉₉H₅₅BN₂NaO₂ ([M + Na⁺]) 617.4254, found 617.4227.

Dipp-Imd-BH₂O(2,6-Me₂C₆H₃) 3b was isolated as impure solid (1.3 mg, 2%) and was not characterized.
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(4-chlorophenoxy)butyloxy]borane (dipp-Imd-BH$_2$O(CH$_2$)$_4$OC$_6$H$_4$Cl) (4c): Following GP with NaHMDS (1 M in THF, 0.2 mL, 0.2 mmol) and 4-chlorophenol (25 mg, 0.20 mmol) in THF (1.5 mL)–CH$_2$Cl$_2$ (1 mL), elution with hexane:EtOAc = 6:1 gave 4c as a light yellow solid (30.5 mg, 50%): mp 115–120 °C; IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 3073, 2963, 2929, 2869, 2359 (B–H), 2222 (B–H), 1695, 1596, 1580, 1492, 1471, 1426, 1385, 1364, 1332, 1286, 1245, 1211, 1161, 1123, 1104, 1092, 1060, 1005, 824, 823, 759; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.42 (t, $J = 7.5$ Hz, 2H), 7.26 (d, $J = 7.5$ Hz, 4H), 7.20 (d, $J = 9.0$ Hz, 2H), 7.00 (s, 2H), 6.76 (d, $J = 9.0$ Hz, 2H), 3.66 (t, $J = 6.9$ Hz, 2H), 2.84 (t, $J = 6.5$ Hz, 2H), 2.64 (septet, $J = 6.9$, 4H), 1.31 (d, $J = 6.9$ Hz, 12H), 1.30–1.20 (m, 2H), 1.18 (d, $J = 7.2$ Hz, 12H), 1.06 (app quintet, $J = 7.1$ Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 157.9, 145.2, 134.2, 129.7, 129.1, 124.7, 123.6, 122.3, 115.7, 68.7, 68.6, 28.7, 28.3, 25.6, 24.8, 22.9; $^{11}$B NMR (96.3 MHz, CDCl$_3$) $\delta$ −9.3 (t, $J_{\text{B-H}} = 84$ Hz); HRMS (ESI) cakd. for C$_{37}$H$_{50}$$^{11}$B$_{35}$ClN$_2$NaO$_2$ ([M + Na$^+$]) 623.3552, found 623.3535.
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-cyanophenoxy)borane (dipp-Imd-BH$_2$OC$_6$H$_4$CN) (3d) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(4-cyanophenoxy)butyloxy]borane (dipp-Imd-BH$_2$O(CH$_2$)$_4$OC$_6$H$_4$CN) (4d): Following GP with NaHMDS (1 M in THF, 0.2 mL, 0.2 mmol) and 4-cyanophenol (24 mg, 0.20 mmol) in THF (1.5 mL)–CH$_2$Cl$_2$ (1 mL), elution with hexane:EtOAc = 8:1 to 3:1 gave dipp-Imd-BH$_2$OC$_6$H$_4$CN 3d as a white solid (10.6 mg, 20%): mp 181–182 °C; IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 2966, 2929, 2871, 2306, 2212, 1600, 1511, 1471, 1385, 1366, 1325, 1174, 1155, 1125, 1101, 1086, 1061, 937, 839, 762, 740; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.51 (t, $J = 7.8$ Hz, 2H), 7.30 (d, $J = 7.5$, 4H), 7.19 (d, $J = 8.7$ Hz, 2H), 7.11 (s, 2H), 6.17 (d, $J = 9.0$ Hz, 2H), 2.60 (septet, $J = 6.9$, 4H), 1.21 (d, $J = 6.9$ Hz, 12H), 1.20 (d, $J = 6.9$ Hz, 12H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 165.8, 145.2, 133.7, 133.0, 130.2, 123.8, 122.8, 121.2, 117.1, 97.8, 28.8, 24.7, 23.0; $^{11}$B NMR (96.3 MHz, CDCl$_3$) $\delta$ −11.2 (br s); HRMS (ESI) calcd. for C$_{34}$H$_{42}$BN$_3$NaO ([M + Na]$^+$) 542.3319, found 542.3342.

Further elution gave dipp-Imd-BH$_2$O(CH$_2$)$_4$OC$_6$H$_4$CN 4d as yellow oil (8.2 mg, 14%). The compound 4d was only about 75% pure and was not stable enough to be fully characterized: IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 2965, 2929, 2871, 2224, 1698, 1651, 1605, 1508, 1470, 1386, 1367, 1331, 1303, 1259, 1207, 1171, 1114, 1061; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.55 (t, $J = 6.9$ Hz, 2H), 7.40 (d, $J = 7.2$ Hz, 2H), 7.25 (d, $J = 7.8$ Hz, 4H), 7.08 (s, 2H), 6.87 (d, $J = 9.0$ Hz, 2H), 3.74 (t, $J = 6.9$ Hz, 2H), 2.84 (t, $J = 6.3$ Hz, 2H), 2.65 (septet, $J = 6.9$, 4H), 1.30 (d, $J = 6.9$ Hz,
12H), 1.30–1.20 (m, 2H), 1.17 (d, J = 6.9 Hz, 12H), 1.06 (app quintet, J = 6.9 Hz, 2H); \(^{11}\)B NMR (96.3 MHz, CDCl\(_3\)) \(\delta\) –9.3 (t, \(J_{B-H} = 92\) Hz); HRMS (ESI) calcd. for C\(_{38}\)H\(_{50}\)\(^{11}\)BN\(_3\)NaO\(_2\) ([M + Na\(^+\)]\(^{+}\)) 614.3894, found 614.3888.

\[
\begin{array}{c}
\text{dipp} \\
\text{O}_2\text{N} \quad \text{Na} \\
\text{dipp}
\end{array}
\text{BH}_2\text{OTf} \quad \text{(2 equiv)} \quad \text{THF, rt, 20 h}
\begin{array}{c}
\text{dipp} \\
\text{NO}_2 \\
\text{dipp}
\end{array}
\]

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-nitrophenoxy)borane (dipp-Imd-BH\(_2\)-OC\(_6\)H\(_4\)NO\(_2\)) (3e): Following GP with NaHMDS (0.6 M in toluene, 0.35 mL, 0.2 mmol) and 4-nitrophenol (28 mg, 0.20 mmol) in THF (2 mL)–toluene (0.4 mL), elution with hexane:EtOAc = 80:20 gave 3e as a light yellow solid (23.5 mg, 43%): mp 175–178 °C; IR (thin film, cm\(^{-1}\)) \(v_{\text{max}}\) 2965, 2929, 2871, 2328 (B–H), 1594, 1500, 1471, 1429, 1386, 1365, 1313, 1257, 1178, 1158, 1104, 1089, 952, 938, 849, 804, 758; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.87–7.83 (m, 2H), 7.52 (t, \(J = 7.8\) Hz, 2H), 7.31 (d, \(J = 7.8\) Hz, 4H), 7.12 (s, 2H), 6.16–6.12 (m, 2H), 2.61 (septet, \(J = 6.9\) Hz, 4H), 1.22 (d, \(J = 6.9\) Hz, 12H), 1.21 (d, \(J = 6.9\) Hz, 12H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.4, 145.2, 137.7, 133.7, 130.3, 125.5, 123.9, 122.9, 116.1, 28.9, 24.7, 23.0; \(^{11}\)B NMR (96.3 MHz, CDCl\(_3\)) \(\delta\) –10.9 (br s); HRMS (ESI) calcd. for C\(_{33}\)H\(_{42}\)^{11}BN\(_3\)NaO\(_3\) ([M + Na\(^+\)]\(^{+}\)) 562.3217, found 562.3209.
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene phenoxylborane (dipp-Imd-BH$_2$OPh) (3a): A solution of KHMDS (0.5 M in toluene, 0.2 mL, 0.2 mmol) was added to a solution of PhOH (19 mg, 0.20 mmol) and 18-crown-6 ether (53 mg, 0.20 mmol) in toluene (0.1 mL) at rt under argon. After 5 min of stirring, the formation of PhOK was assumed. In a separate flask, triflic acid (10 µL, 0.1 mmol) was added to a solution of dipp-Imd-BH$_3$ (40.5 mg, 0.10 mmol) in toluene (1 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH$_2$OTf was assumed. Then the solution of dipp-Imd-BH$_2$OTf was added to a suspension of PhOK followed by toluene (1.5 mL). The cloudy reaction mixture was stirred at rt for 2 days. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The products were purified by flash chromatography. Elution with hexane:Et$_2$O = 95:5 gave dipp-Imd-BH$_2$OPh 3a as a white solid (31.9 mg, 64%). The NMR data of the isolated product were identical to those of the previously prepared sample of 3a.

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (ethylthio)borane (dipp-Imd-BH$_2$SEt) (3f) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(ethylthio)butyloxy]borane (dipp-Imd-BH$_2$O(CH$_2$)$_4$SEt) (4f): A solution of LiHMDS (1 M in toluene, 0.2 mL, 0.2 mmol) was added to a solution of EtSH (15 µL, 0.20 mmol) in THF (0.5 mL) at rt. After 5 min of
stirring, the formation of EtSLi was assumed. In a separate flask, triflic acid (10 µL, 0.1 mmol) was added to a solution of dipp-Imd-BH$_3$ 1 (40.5 mg, 0.10 mmol) in toluene (1 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH$_2$OTf 2 was assumed. Toluene was removed by rotary evaporation and the white residue was dissolved in THF (1.5 mL). Then the solution of EtSLi was added to the resulting solution of dipp-Imd-BH$_2$OTf 2. The cloudy reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography. Elution with hexane:EtOAc = 95:5 to 90:10 gave dipp-Imd-BH$_2$SEt 3f as a white solid (7.3 mg, 16%): mp 204–207 °C; IR (thin film, cm$^{-1}$) $v_{\text{max}}$ 3156, 3053, 2963, 2926, 2869, 2365 (B–H), 1565, 1471, 1429, 1383, 1364, 1333, 1258, 1233, 1173, 1061, 1038, 937, 803, 763; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (t, $J = 7.8$ Hz, 2H), 7.29 (d, $J = 7.8$ Hz, 4H), 7.04 (s, 2H), 2.62 (septet, $J = 6.8$ Hz, 4H), 1.53 (q, $J = 7.3$ Hz, 2H), 1.34 (d, $J = 6.8$ Hz, 12H), 1.16 (d, $J = 6.8$ Hz, 12H), 0.85 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.5, 133.9, 130.1, 123.8, 122.4, 28.8, 27.1, 25.3, 22.7, 17.3; $^{11}$B NMR (128.4 MHz, CDCl$_3$) $\delta$ –24.0 (t, $J = 99$ Hz); HRMS (ESI) calcd. for C$_{29}$H$_{44}^{11}$BN$_2$S ([M + H]$^+$) 463.3318, found 463.3301.

Further elution gave dipp-Imd-BH$_2$O(CH$_2$)$_4$SEt 4f as a white solid (29.3 mg, 54%): mp 66–68 °C; IR (thin film, cm$^{-1}$) $v_{\text{max}}$ 3075, 2963, 2928, 2869, 2708, 2218 (B–H), 1596, 1471, 1459, 1426, 1384, 1364, 1332, 1259, 1211, 1173, 1121, 1107, 1060, 1037, 981, 949, 937, 802, 759; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (t, $J = 7.8$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 4H), 6.98 (s, 2H), 2.78 (t, $J = 6.6$, 2H), 2.63 (septet, $J = 6.8$ Hz, 4H), 2.45 (q, $J = 7.5$ Hz, 2H), 2.26 (t, $J = 7.8$ Hz, 2H), 1.31 (d, $J = 6.8$ Hz, 12H), 1.20 (t, $J = 7.4$ Hz, 3H), 1.17 (d, $J = 6.8$ Hz, 12H), 1.12 (app. quintet, $J = 8.0$ Hz, 2H), 0.99 (app. quintet, $J = 7.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.2, 134.2, 129.7, 123.6, 122.3, 68.9, 31.8, 31.7, 28.7, 26.4, 25.7, 24.8, 22.9, 14.8; $^{11}$B NMR
(128.4 MHz, CDCl$_3$) δ –9.3 (t, $J = 94$ Hz); HRMS (ESI) calcd. for C$_{33}$H$_{50}$$_{11}$BN$_2$O$_2$ ([M – H]$^+$) 533.3737, found 533.3749.

1,3-Bis(2,6-diisoproplyphenyl)imidazol-2-ylidene (4-hydroxybutyloxy)borane (dipp-Imd-BH$_2$O(CH$_2$)$_4$OH) (5): A solution of TMSOK (26 mg, 0.20 mmol) and dipp-Imd-BH$_2$OTf 2 (55 mg, 0.10 mmol) in a THF (2 mL) was stirred for 20 h at rt. The solvent was removed and the residue was loaded on silica gel. Chromatographic separation (elution with hexane : EtOAc = 2 : 1 to 1 : 1) gave dipp-Imd-BH$_2$O(CH$_2$)$_4$OH 5 as a white solid (18.3 mg, 37%): mp 106–108 °C; IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 3159, 3073, 2963, 2928, 2870, 2287, 2228 (B–H), 1683, 1595, 1471, 1460, 1426, 1385, 1364, 1332, 1299, 1271, 1257, 1213, 1171, 1103, 1061, 1043, 949, 937, 871, 803, 759, 733; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (t, $J = 7.8$ Hz, 2H), 7.28 (d, $J = 7.6$ Hz, 4H), 7.02 (s, 2H), 5.41 (t, $J = 6.2$ Hz, 1H), 3.27 (q, $J = 5.5$ Hz, 2H), 2.66 (t, $J = 5.2$ Hz, 2H), 2.62 (septet, $J = 6.9$, 4H), 1.33 (d, $J = 6.8$ Hz, 12H), 1.35–1.25 (m, 2H), 1.16 (d, $J = 6.8$ Hz, 12H), 1.06 (app quintet, $J = 7.3$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.2, 133.9, 129.9, 123.7, 122.4, 70.0, 62.4, 32.2, 30.4, 28.7, 25.0, 22.7; $^{11}$B NMR (128.4 MHz, CDCl$_3$) δ –9.3 (t, $J = 96$ Hz); HRMS (ESI) calcd. for C$_{31}$H$_{48}$$_{11}$BN$_2$O$_2$ ([M]$^+$) 491.3809, found 491.3828.
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene ethoxyborane (dipp-Imd-BH$_2$OEt) (S1): Lithium ethoxide was prepared by the addition of BuLi (1.6 M solution in hexanes, 0.13 mL, 0.21 mmol) to a solution of ethanol (12 µL, 0.20 mmol) in THF (0.5 mL) at 0 °C. Then compound S1 was prepared according to GP from resulting EtOLi (0.20 mmol) and dipp-Imd-BH$_2$OTf 2 (50 mg, 0.09 mmol) in a THF (1.5 mL)–CH$_2$Cl$_2$ (0.5 mL) solution. Chromatographic separation (elution with hexane:EtOAc = 8:1 to 5:1) gave dipp-Imd-BH$_2$OEt S1 as a light yellow solid (14.9 mg, 33%): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.44 (t, $J = 7.8$ Hz, 2H), 7.27 (d, $J = 7.8$ Hz, 4H), 7.00 (s, 2H), 2.82 (q, $J = 6.9$ Hz, 2H), 2.65 (septet, $J = 6.8$ Hz, 4H), 1.32 (d, $J = 6.9$ Hz, 12H), 1.17 (d, $J = 6.9$ Hz, 12H), 0.52 (t, $J = 6.9$ Hz, 6H); $^{11}$B NMR (96.3 MHz, CDCl$_3$) $\delta$ –9.5 (t, $J = 96$ Hz).

The isolated sample of S1 was only 90% pure and decomposed during the attempts to purify it by recrystallization.

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (3-phenyloxypropoxy)borane (dipp-Imd-BH$_2$O(CH$_2$)$_3$OPh) (6): A solution of BuLi (1.5 M in hexanes, 0.13 mL, 0.2 mmol) was added to a solution of PhOH (19 mg, 0.20 mmol) in PhH (0.5 mL) at rt. After 5 min of stirring, the
formation of a precipitate of PhOLi was observed. In a separate flask, triflic acid (10 µL, 0.1 mmol) was added to a solution of dipp-Imd-BH$_3$ 1 (40.5 mg, 0.10 mmol) in CH$_2$Cl$_2$ (0.5 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH$_2$OTf 2 was assumed. Then the resulting solution of dipp-Imd-BH$_2$OTf 2 was added to the suspension of PhOLi followed by oxetane (0.13 mL, 2.0 mmol). The reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was purified by column chromatography. Elution with hexane:EtOAc = 5:1 gave dipp-Imd-BH$_2$O(CH$_2$)$_3$OPh 6 as yellow oil (24 mg, 43%). The product was about 90% pure: IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 3071, 2963, 2929, 2869, 2224 (B–H), 1691, 1600, 1586, 1497, 1471, 1426, 1384, 1364, 1332, 1300, 1247, 1212, 1172, 1123, 1061, 1032, 937, 803, 755; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.39 (t, $J = 7.8$ Hz, 2H), 7.30–7.20 (m, 6H), 6.99 (s, 2H), 6.90 (t, $J = 7.4$ Hz, 1H), 6.79 (d, $J = 8.4$ Hz, 2H), 3.46 (t, $J = 7.2$ Hz, 2H), 3.00 (t, $J = 6.0$ Hz, 2H), 2.64 (septet, $J = 6.9$, 4H), 1.44 (app. quintet, $J = 6.8$, 2H), 1.31 (d, $J = 6.6$ Hz, 12H), 1.30–1.20 (m, 2H), 1.18 (d, $J = 6.9$ Hz, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.4, 145.2, 134.1, 129.8, 129.0, 123.6, 122.3, 119.8, 114.7, 66.5, 65.7, 32.1, 28.8, 24.8, 24.6, 23.0; $^{11}$B NMR (96.3 MHz, CDCl$_3$) $\delta$ -9.2 (t, $J = 87$ Hz); HRMS (ESI) calcd. for C$_{36}$H$_{49}^{11}$BN$_2$NaO$_2$ ([M + Na]$^+$) 575.3785, found 575.3755.

**1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene acetoxyborane (7):** A solution of BuLi (0.9 M in hexanes, 0.22 mL, 0.2 mmol) was added to a solution of PhOH (19 mg, 0.20 mmol) in EtOAc (0.5 mL) at rt. After 5 min of stirring, the formation of PhOLi was assumed. In a separate
flask, triflic acid (10 µL, 0.1 mmol) was added to a solution of dipp-Imd-BH$_3$ 1 (40.5 mg, 0.10 mmol) in PhH (0.5 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH$_2$OTf 2 was assumed. The solvent was removed by rotary evaporation and the residue was dissolved in EtOAc (0.5 mL). Then the resulting solution of dipp-Imd-BH$_2$OTf 2 was added to the solution of PhOLi. The reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was purified by column chromatography. Elution with hexane:EtOAc = 9:1 to pure EtOAc gave dipp-Imd-BH$_2$OAc 7 as a white solid (14.5 mg, 31%): mp 203–204 °C; IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 3153, 3114, 3082, 2962, 2926, 2872, 2359, 2340, 1682, 1470, 1428, 1372, 1314, 1160, 1106, 802, 760; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.8, 145.1, 133.6, 130.1, 123.8, 122.7, 28.8, 24.8, 22.9, 22.2; $^{11}$B NMR (128.4 MHz, CDCl$_3$) $\delta$ –12.4 (t, $J = 89$ Hz); HRMS (ESI) calcd. for C$_{29}$H$_{41}$BN$_2$NaO$_2$ ([M + Na]$^+$) 483.3159, found 483.3150.
References:


AS63-02, dipp-Imd-BH2O(CH2)4OPh, THF-DCM, Fr. 56-68, CDCl3, 400B, 10/26/10
AS63-02, dipp-Imd-BH2O(CH2)4OPh, THF-DCM, Fr. 56-68, CDCl3, 400B, 10/26/10
AS63-02, dipp-Imd-BH2O(CH2)4OPh, THF-DCM, Fr. 56-68, CDCl3, 400B, 10/26/10

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AS63-81, dipp-Imd-BHOPh, CDCl3, Fr. 49-62, 400B, 03/23/11

3a
AS63-81, dipp-Imd-BHOPh, CDCl3, Fr. 49-62, 400B, 03/29/11

3a
AS63-81, dipp-Imd-BHOPh, CDCl3, Fr. 49-62, 400B, 03/23/11

3a
boron-11 NMR
AS63-87, dipp-Imd-BHO(CH2)4OCH3Me2, Fr. 44-55, 400B, 03/31/11
AS63–87, dipp–Imd–BHO(CH2)4OC6H3Me2, Fr. 44–55, 400B, 03/31/11

$\text{dipp} \quad \text{BH}_2 \quad \text{O} \quad \text{Me} \quad \text{Me}$

4b
AS63-87, dipp-Imd-BH\textsubscript{2}(CH\textsubscript{2})\textsubscript{4}OC\textsubscript{6}H\textsubscript{3}Me\textsubscript{2}, Fr. 44-55, 400B, 03/31/11

boron-11 NMR
AS34-37, IPr-IMD-BH2OTf + ClC6H4ONa, Fr. 18-20, CDC13, 301b, 02/07/10
AS34-37, IPr-IMD-BH2OTf + ClC6H4ONa, Fr. 18-20, CDC13, 301b, 02/07/10

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AS34-37, IPr-IMD-BH2OTf + ClC6H4ONa, Fr. 18-20, CDCl3, 301b, 02/07/10

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4c
boron-11 NMR
AS34-36, IPr-IMD-BH2OTf + NCC6H4ONa, Fr. 21-23, CDCl3, 301b, 02/07/10
AS34-36, IPr-IMD-BH2OTf + NCC6H4ONa, Fr. 21-23, CDCl3, 301b, 02/07/10
AS34-36, IPr-IMD-BH2OTf + NCC6H4ONa, Fr. 21-23, CDCl3, 301b, 02/07/10

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3d
boron-11 NMR
AS34-36, IPr-IMD-BH2OTf + NCC6H4ONa, Fr. 27-29, CDC13, 301b, 02/07/10

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AS34-36, IPr-IMD-BH2OTf + NCC6H4ONa, Fr. 27-29, CDCl3, 301b, 02/07/10

boron-11 NMR

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AS34-13, IPr-IMD-BH2OC6H4NO2, Fr. 16-19, CDCl3, 301b, 01/13/10
AS63-95, dipp-Imd-BH2OC6H4NO2, Fr. 27-36, CDCl3, 400B, 04/19/11
AS34-13, IPr-IMD-BH2OC6H4NO2, Fr. 16-19, CDCl3, 301b, 01/13/10

boron-11 NMR
AS82-49, dipp-Imd-BH2SEt, Fr. 35-46, CDCl3, 400B, 10/26/11

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AS82-49, dipp-Imd-BH2SEt, Fr. 35-46, CDCl3, 400B, 10/26/11

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AS82-49, dipp-Imd-BH2SEt, Fr. 35-46, CDCl3, 400B, 10/26/11

3f
boron-11 NMR
AS82-48, dipp-Imd-BH2O(CH2)4SEt, Fr. 38-46, CDCl3, 400B, 10/21/11
AS82-48, dipp-Imd-BH2O(CH2)4SEt, Fr. 38-46, CDCl3, 400B, 10/21/11

4f
boron-11 NMR
AS82-01, dipp-Imd-BH2O(CH2)4OH, Fr. 52-59, CDCl3, 400B, 04/29/11
AS82-01, dipp-Imd-BH2O(CH2)4OH, Fr. 52-59, CDC13, 400B, 04/29/11
AS82-01, dipp-Imd-BH2OTf + TMSOK in THF, Fr. 52-59, CDCl3, 400B, 04/29/11

5
boron-11 NMR
AS22-92, IPr-IMD-BH2OTf + EtOLi, Fr. 23-28, CDCl3, 301b, 12/10/09

[Chemical structure and NMR spectrum image]

S1
AS22-92, IPr-IMD-BH2OTf + EtOLi, Fr. 23-28, CDCl3, 301b, 12/10/09

boron-11 NMR

S1
AS34-10, IPr-IMD-BH2OTf + PhOLi in oxetane, Fr. 15-18, CDCl3, 301b, 01/09/10
AS34-10, IPr-IMD-BH2OTf + PhOLi in oxetane, Fr. 15-18, CDC13, 301b, 01/09/10

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AS34-10, IPr-IMD-BH2OTf + PhOLi in oxetane, Fr. 15-18, CDCl3, 301b, 01/09/10

boron-11 NMR
AS49-68, IPr-IMD-BH2OAc, crystal, CDCl3, 400B, 09/21/10
AS49-68, IPr-IMD-BH2OTf + PhOLi in EtOAc, Fr. 41-48, CDCl3, 400B, 09/16/10

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AS49-68, IPr-IMD-BH2OTf + PhOLi in EtOAc, Fr. 41-48, CDCl3, 400B, 09/16/10

boron-11 NMR