Supporting Information for:

**Catalytic Diboration of Aldehydes via Insertion into the Copper–
Boron Bond**

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Experimental:

General Considerations. All synthetic manipulations were carried out using standard Schlenk techniques under an argon atmosphere, or in an Innovative Technologies glovebox under an atmosphere of purified nitrogen. Reactions were carried out in oven- or flame-dried glassware cooled under vacuum. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Anhydrous tetrahydrofuran and dichloromethane were purchased from Aldrich in 18-L Pure-Pac™ solvent delivery kegs and sparged vigorously with argon for 40 minutes prior to first use. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina and for tetrahydrofuran, a third column packed with activated 4Å molecular sieves. Benzene and pentane, anhydrous, were purchased from Aldrich in Sure-Seal™ bottles, and stored in a glovebox over 4Å molecular sieves. All non-dried solvents used were reagent grade or better.

NMR solvents were obtained from Cambridge Isotope Laboratories. C₆D₆ was dried over sodium benzophenone ketyl, and CD₂Cl₂ was dried over CaH₂. Both solvents were degassed by three freeze-pump-thaw cycles, and vacuum-transferred prior to use. ¹H NMR spectra were recorded on a Varian 300 MHz or 500 MHz instrument, with shifts reported relative to the residual solvent peak. ¹⁹F NMR spectra were recorded on a Varian 300 MHz instrument, with shifts referenced to an external standard of CFCl₃ (0 ppm). ¹¹B NMR spectra were recorded

on a Varian 500 MHz instrument, with shifts referenced to an external standard of 0.5 M BF₃ in diethyl ether (0 ppm). ¹³C NMR spectra were recorded on a Varian 500 MHz instrument, with shifts referenced relative to the solvent peak.

The starting compounds [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) methyl,¹ [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) *tert*-butoxide,² [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) (pinacol)boryl,³ and 1,3-dicyclohexylimidazolium chloride⁴ were synthesized as described previously. Benzaldehyde (Aldrich), *n*-butyraldehyde (Alfa Aesar), *p*-anisaldehyde (Aldrich), mesitaldehyde (Aldrich), *p*-tolualdehyde (Aldrich), isobutyraldehyde (Aldrich), 2-thiophenecarboxaldehyde (Alfa Aesar), cyclohexanecarboxaldehyde (Aldrich), 2-pyridinecarboxaldehyde (TCI America), 3-pyridinecarboxaldehyde (Aldrich), and 4-pyridinecarboxaldehyde (TCI America) were degassed and stored over 4 Å molecular sieves prior to use. Bis(pinacolato)diboron (Frontier Scientific), 4-chlorobenzaldehyde (Aldrich), 4-bromobenzaldehyde (Aldrich), *o*-anisaldehyde (Aldrich), sodium *tert*-butoxide (Aldrich), and copper(I) chloride were used as received.

[1,3-Dicyclohexylimidazol-2-ylidene]copper(I) chloride.⁵ In a glovebox, a round-bottomed flask equipped with a Teflon-coated magnetic stirbar was charged with CuCl (1.62 g, 16.4 mmol), NaOt-Bu (1.50 g, 15.6 mmol), and ICy•HCl (4.03 g, 14.6 mmol). THF (40 mL) was added, and the reaction mixture was stirred for 1.5 hours. The resulting cloudy solution was filtered through Celite, and concentrated *in vacuo*. The resulting yellow foam was taken up in CH₂Cl₂ (30 mL) and filtered through Celite. Upon concentration, the title compound was isolated as a white foam (4.07 g, 82%). ¹H NMR (CD₂Cl₂): δ 6.95 (s, 2H, NCH), 4.28 (tt, *J* =

12.1 Hz, $J = 3.9$ Hz, 2H), 2.06 (m, 4H), 1.89 (m, 4H), 1.77–1.61 (6H) 1.46 (m, 4H), 1.25 (m, 2H). ^{13}C NMR (CD_2Cl_2): 173.8 ($\text{N}_2\text{C}\text{Cu}$), 118.0, 61.7, 35.2, 26.0, 25.6. Anal. Calcd. $\text{C}_{15}\text{H}_{24}\text{N}_2\text{CuCl}$: C, 54.37; H, 7.30. Found: C, 54.44; H, 7.30.

[1,3-Dicyclohexylimidazol-2-ylidene]copper(I) *tert*-butoxide. In a glovebox, a 20-mL scintillation vial equipped with a Teflon-coated magnetic stirbar was charged with (ICy)CuCl (1.25 g, 3.76 mmol) and NaOt-Bu (0.363 g, 3.78 mmol). Tetrahydrofuran (10 mL) was added, and the resulting solution was stirred for 1 hour. After filtering through Celite, the pale yellow solution is concentrated *in vacuo* to give a cream colored foam (1.05 g, 76%). ^1H NMR (C_6D_6): δ 6.38 (s, 2H, NCH), 4.32 (m, 2H), 1.88 (s, 9H), 1.81 (m, 4H), 1.48 (4H), 1.41–1.26 (6H) 1.07 (m, 4H), 0.91 (m, 2H). ^{13}C NMR (C_6D_6): 177.5 ($\text{N}_2\text{C}\text{Cu}$), 117.4, 69.7 (br), 61.0, 37.7 (br), 34.9, 26.0, 25.7 Small amounts (*ca.* 9 mol%) of residual THF, not easily removed, did not prevent effective catalysis. ^1H and ^{13}C NMR spectra of this complex are included as a measure of its purity (Figure S1).

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) α -[(pinacol)boroxy]-2,4,6-trimethylbenzyl.

Method A. In a glovebox, a 20-mL scintillation vial equipped with a Teflon-coated magnetic stirbar was charged with (IPr)CuOt-Bu (0.300 g, 0.571 mmol), and bis(pinacolato)diboron (0.145 g, 0.571 mmol). Pentane was added (5 mL) followed by mesitaldehyde (0.091 mL, 0.628 mmol). The mixture was stirred for 1 hour, and the resulting white precipitate was collected by filtration to afford **1** (0.368 g, 89%).

Method B. In a glovebox, a solution of (ICy)CuOt-Bu (8.4 mg, 0.023 mmol) in benzene (3.0 mL) was added to a flame-dried Schlenk flask containing bis(pinacolato)diboron (0.254 g, 1.00 mmol) and mesitaldehyde (0.148 mL, 1.00 mmol) dissolved in benzene (4.0 mL). The reaction mixture was stirred at room temperature for 22 hours and then concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography (7 : 3 CH_2Cl_2 : diethyl ether, R_f = 0.6), without protection from oxygen or water, to give α -hydroxy-2,4,6-trimethylbenzyl(pinacol)boronate as a colorless oil (0.228 g, 83%). ^1H NMR (C_6D_6): δ 6.77 (s, 2H), 5.16 (d, J = 2.1 Hz, 1H, $\text{CHB}(\text{pin})$), 2.46 (s, 6H), 2.12 (s, 3H), 1.55 (s, 1H, OH), 0.98 (s, 6H, pinacol- CH_3), 0.94 (s, 6H, pinacol- CH_3). ^{13}C NMR (C_6D_6): δ 137.2, 136.9, 136.2, 130.1,

84.5 (OC(CH₃)₂), 60.3 (CB(pin)), 25.2 (pinacol-CH₃), 25.0 (pinacol-CH₃), 21.29. ¹¹B NMR (C₆D₆): δ 33.0 (C-B).

In a glovebox, a 20-mL scintillation vial equipped with a Teflon-coated magnetic stirbar was charged with (IPr)CuMe (0.100 g, 0.205 mmol) and a solution of α-hydroxy-2,4,6-trimethylbenzyl(pinacol)boronate (0.066 g, 0.239 mmol) dissolved in benzene (3 mL) was added. After stirring for 12 hours, the reaction mixture was filtered through Celite, and concentrated *in vacuo*. The resulting solid was washed with pentanes (3 x 3 mL) and collected by filtration to afford **1** as an off-white solid (0.121 g, 81%). ¹H NMR (C₆D₆): δ 7.23 (t, *J* = 7.8 Hz, 2H, *para*-CH), 7.07 (d, *J* = 7.9 Hz, 2H, *meta*-CH), 7.06 (d, *J* = 7.6 Hz, 2H, *meta*-CH), 6.73 (s, 2H, *meta*-CH (mes)), 6.22 (s, 2H, NCH), 5.54 (s, 1H, CuCH(OB(pin))mes), 2.49 (m, 4H, CH(CH₃)₂), 2.28 (s, 3H, *para*-CH₃ (mes)), 2.18 (s, 6H, *ortho*-CH₃ (mes)), 1.29 (d, *J* = 7.0 Hz, 6H, CH(CH₃)₂), 1.23 (d, *J* = 7.0 Hz, 6H, CH(CH₃)₂), 1.06 (d, *J* = 6.7 Hz, 12H, CH(CH₃)₂), 1.00 (s, 6H, pinacol-CH₃), 0.99 (s, 6H, pinacol-CH₃). ¹³C NMR (C₆D₆): δ 185.5 (N₂CCu), 146.2 (*ortho*-C, mes), 146.1 (*ortho*-C, IPr), 146.1 (*ortho*-C, IPr), 135.6 (*ipso*-C, IPr), 132.2 (*ipso*-C, mes), 130.8 (*para*-CH, IPr), 129.1 (*para*-CH, mes), 129.0 (*meta*-CH, mes), 124.5 (*meta*-CH, IPr), 124.5 (*meta*-CH, IPr), 122.6 (NCH), 80.9 (B(OC(CH₃)₂)₂), 77.9 (CuCH), 29.3 (CH(CH₃)₂), 29.3 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 25.4 (pinacol-CH₃), 25.3 (pinacol-CH₃), 25.1 (CH(CH₃)₂), 24.1 (CH(CH₃)₂), 22.6 (*ortho*-CH₃ (mes)), 21.5 (*para*-CH₃ (mes)). ¹¹B NMR (C₆D₆): δ 21.8. Anal. Calcd. C₄₃H₆₀N₂O₃BCu: C, 71.01; H, 8.32. Found: C, 71.03; H, 8.05.

General procedure for the diboration of aldehydes:

In a glovebox, a flame-dried Schlenk flask equipped with a Teflon-coated magnetic stirbar was charged with bis(pinacolato)diboron (0.127 g, 0.5 mmol). Benzene was added, followed by aldehyde (0.5 mmol). A solution of (ICy)CuOt-Bu in benzene was added via syringe. The

reaction mixture was stirred at room temperature for 22 hours, and then concentrated *in vacuo*. In a glovebox the product was extracted from the crude solid into pentane (4 x 5 mL). The extracts were combined, filtered through Celite, and concentrated *in vacuo* to give the title compounds. The yields reported are for individual runs, and may differ slightly from those reported in Table 1 of the manuscript which are averages of two runs.

For reactions run at 1% (ICy)CuOt-Bu: A solution of (ICy)CuOt-Bu (5 μ mol; 1.8 mL of a 2.7 mM stock solution in benzene) was added to the Schlenk flask containing a solution bis(pinacolato)diboron and aldehyde in benzene (4 mL).

For reactions run at 2.3% (ICy)CuOt-Bu: A solution of (ICy)CuOt-Bu (11.5 μ mol; 4.6 mL of a 2.5 mM stock solution in benzene) was added to the Schlenk flask containing a solution of bis(pinacolato)diboron and aldehyde in benzene (1.4 mL).

α -[(Pinacol)boroxy]benzyl(pinacol)boronate. The general procedure was followed using 1% (ICy)CuOt-Bu to give a white solid (0.153 g, 85%, mp 94–97 °C). ^1H NMR (C_6D_6): δ 7.66 (d, J = 7.2 Hz, 2H, *ortho*-CH), 7.16 (t, J = 7.3 Hz, 2H, *meta*-CH), 7.01 (t, J = 7.3 Hz, 1H, *para*-CH), 5.40 (s, 1H, $\text{CHB}(\text{pin})$), 1.08 (s, 6H, pinacol- CH_3), 1.07 (s, 6H, pinacol- CH_3), 0.97 (s, 6H, pinacol- CH_3), 0.96 (s, 6H, pinacol- CH_3). ^{13}C NMR (C_6D_6): δ 141.7 (*ipso*-C), 128.9 (*meta*-CH), 127.1 (*para*-CH), 126.7 (*ortho*-CH), 84.4 ($\text{B}(\text{OC}(\text{CH}_3)_2)_2$), 83.0 ($\text{B}(\text{OC}(\text{CH}_3)_2)_2$), 67.6 (BCH), 25.2 (pinacol- CH_3), 25.0 (pinacol- CH_3), 24.9 (pinacol- CH_3). ^{11}B NMR (C_6D_6): δ 31.8 (C-B), 22.6 (O-B). IR (KBr pellet, cm^{-1}): 2977, 1456, 1327, 1140, 973, 849, 706. Anal. Calcd. $\text{C}_{19}\text{H}_{30}\text{O}_5\text{B}_2$: C, 63.38; H, 8.40. Found: C, 63.29; H, 8.55.

α -[(Pinacol)boroxy]-4-methoxybenzyl(pinacol)boronate. The general procedure was followed using 1% (ICy)CuO*t*-Bu, except that during the work-up, the extraction was carried out using pentane (4 x 5 mL) and benzene (2 mL). The product was isolated as a tan solid (0.158 g, 81%, mp 74–76 °C). ^1H NMR (C_6D_6): δ 7.59 (d, J = 8.7 Hz, 2H), 6.79 (d, 8.7 Hz, 2H), 5.38 (s, 1H, CHB(pin)), 3.23 (s, 3H, ArOCH₃), 1.10 (s, 6H, pinacol-CH₃), 1.06 (s, 6H, pinacol-CH₃), 1.02 (s, 6H, pinacol-CH₃), 1.00 (s, 6H, pinacol-CH₃). ^{13}C NMR (C_6D_6): δ 159.4, 133.6, 128.4, 114.5, 84.3 (OC(CH₃)₂), 83.0 (OC(CH₃)₂), 67.4 (CB(pin)), 55.0 (ArOCH₃), 25.3 (pinacol-CH₃), 25.0 (pinacol-CH₃), 25.0 (pinacol-CH₃), 25.0 (pinacol-CH₃). ^{11}B NMR (C_6D_6): δ 31.7 (C–B), 22.4 (O–B). IR (KBr pellet, cm^{-1}): 2978, 1437, 1331, 1449, 964, 849. Anal. Calcd. $\text{C}_{20}\text{H}_{32}\text{O}_6\text{B}_2$: C, 61.58; H, 8.27. Found: C, 61.43; H, 7.99.

α -[(Pinacol)boroxy]-4-methylbenzyl(pinacol)boronate. The general procedure using 1% (ICy)CuO*t*-Bu was followed to afford the title compound as a white solid (0.172 g, 92%, mp 84–86 °C). ^1H NMR (C_6D_6): δ 7.60 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 5.40 (s, 1H, CHB(pin)), 2.05 (s, 3H), 1.09 (s, 6H), 1.08 (s, 6H), 1.00 (s, 6H), 0.98 (s, 6H). ^{13}C NMR (C_6D_6): δ 138.7, 136.3, 129.6, 126.9, 84.3, 83.0, 67.6 (CB(pin)), 25.2, 25.0, 25.0, 25.0, 21.4. ^{11}B NMR

(C₆D₆): δ 31.7 (C–B), 22.5 (O–B). IR (KBr pellet, cm^{–1}): 2979, 1499, 1368, 1322, 1142, 971, 848. Anal. Calcd. C₂₀H₃₂O₅B₂: C, 64.21; H, 8.62. Found: C, 64.12; H, 8.62.

α -[(Pinacol)boroxy]-4-bromobenzyl(pinacol)boronate. The general procedure using 2.3% (ICy)CuOt-Bu was followed except that the extraction was carried out with pentane (4 x 5 mL) and benzene (2 mL). After concentration of the combined extracts, the product was further purified by recrystallization from pentane at –40 °C to give colorless crystals (0.182 g, 83%, mp 108–109 °C). ¹H NMR (C₆D₆): δ 7.34 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 5.22 (s, 1H, CHB(pin)), 1.08 (s, 6H, pinacol-CH₃), 1.07 (s, 6H, pinacol-CH₃), 0.96 (s, 6H, pinacol-CH₃), 0.94 (s, 6H, pinacol-CH₃). ¹³C NMR (C₆D₆): δ 140.7, 131.9, 128.3, 120.9, 84.5 (OC(CH₃)₂), 83.2 (OC(CH₃)₂), 66.9 (CB(pin)), 25.2 (pinacol-CH₃), 24.95 (pinacol-CH₃), 24.93 (pinacol-CH₃), 24.92 (pinacol-CH₃). ¹¹B NMR (C₆D₆): δ 31.7 (C–B), 22.5 (O–B). IR (KBr pellet, cm^{–1}): 3449, 2966, 1263, 1009, 805. Repeated attempts at elemental analysis failed to give satisfactory results; ¹H and ¹³C NMR spectra for this compound are included to attest to its purity (Figure S2).

α -[(Pinacol)boroxy]-4-chlorobenzyl(pinacol)boronate. The general procedure was followed using 2.3% (ICy)CuOt-Bu except that the extraction was carried out with pentane (4 x 5 mL) and benzene (2 mL). After concentration of the combined extracts, the product was recrystallized

from pentane at $-40\text{ }^{\circ}\text{C}$ to give colorless crystals (0.157 g, 80%, mp $94\text{--}96\text{ }^{\circ}\text{C}$). ^1H NMR (C_6D_6): δ 7.40 (d, $J = 8.0\text{ Hz}$, 2H), 7.11 (d, $J = 8.0\text{ Hz}$, 2H), 5.25 (s, 1H, $\text{CHB}(\text{pin})$), 1.08 (s, 6H, pinacol- CH_3), 1.07 (s, 6H, pinacol- CH_3), 0.96 (s, 6H, pinacol- CH_3), 0.89 (s, 6H, pinacol- CH_3). ^{13}C NMR (C_6D_6): δ 140.2, 132.8, 129.0, 128.0, 84.5 ($\text{OC}(\text{CH}_3)_2$), 83.2 ($\text{OC}(\text{CH}_3)_2$), 66.9 ($\text{CB}(\text{pin})$), 25.7 (pinacol- CH_3), 25.2 (pinacol- CH_3), 24.9 (pinacol- CH_3), 24.9 (pinacol- CH_3). ^{11}B NMR (C_6D_6): δ 31.6 (C-B), 22.5 (O-B). IR (KBr pellet, cm^{-1}): 3449, 2978, 1339, 1147, 966, 850. Repeated attempts at elemental analysis failed to give satisfactory results; ^1H and ^{13}C NMR spectra for this compound are included to attest to its purity (Figure S3).

α -[(Pinacol)boroxy]-4-trifluoromethylbenzyl(pinacol)boronate. The general procedure using 2.3% (ICy)CuOt-Bu was followed to give a white solid (0.187 g, 87%, mp = $99\text{--}100\text{ }^{\circ}\text{C}$). ^1H NMR (C_6D_6): δ 7.52 (d, $J = 8.1\text{ Hz}$, 2H), 7.35 (d, $J = 8.2\text{ Hz}$, 2H), 5.29 (s, 1H, $\text{CHB}(\text{pin})$), 1.09 (s, 6H, pinacol- CH_3), 1.08 (s, 6H, pinacol- CH_3), 0.96 (s, 6H, pinacol- CH_3), 0.94 (s, 6H, pinacol- CH_3). ^{13}C NMR (C_6D_6): δ 145.9, 128.8 (q, $J_{\text{C-F}} = 31.7\text{ Hz}$, CCF_3), 126.6, 125.7 (q, $J_{\text{C-F}} = 4.0\text{ Hz}$), 125.5 (q, $J_{\text{C-F}} = 271.8\text{ Hz}$, CF_3), 84.7 ($\text{OC}(\text{CH}_3)_2$), 83.3 ($\text{OC}(\text{CH}_3)_2$), 67.1 ($\text{CB}(\text{pin})$), 25.2 (pinacol- CH_3), 24.94 (pinacol- CH_3), 24.9 (pinacol- CH_3), 24.9 (pinacol- CH_3). ^{19}F NMR (C_6D_6): δ -62.3 . ^{11}B NMR (C_6D_6): δ 31.6 (C-B), 22.5 (O-B). IR (KBr pellet, cm^{-1}): 2982, 1933, 1619, 1326, 1121, 851. Anal. Calcd. $\text{C}_{20}\text{H}_{29}\text{O}_5\text{F}_3\text{B}_2$: C, 56.12; H, 6.83. Found: C, 55.81; H, 7.07.

α -[(Pinacol)boroxy]-2-methoxybenzyl(pinacol)boronate. The general procedure using 1% (ICy)CuOt-Bu was followed to give a colorless oil which solidified after several days (0.180 g, 92%, mp = 58–60 °C). ^1H NMR (C_6D_6): δ 7.80 (m, 1H), 7.04 (m, 1H), 6.91 (m, 1H), 6.51 (m, 1H), 5.81 (s, 1H, $\text{CHB}(\text{pin})$), 3.30 (s, 3H, ArOCH_3), 1.08 (s, 6H, pinacol- CH_3), 1.06 (s, 6H, pinacol- CH_3), 1.05 (s, 6H, pinacol- CH_3), 1.02 (s, 6H, pinacol- CH_3). ^{13}C NMR (C_6D_6): δ 157.0, 131.0, 128.8, 128.2, 121.3, 110.9, 83.9, 82.8, 62.9 ($\text{CB}(\text{pin})$), 55.4 (ArOCH_3), 25.2, 25.1, 25.0, 25.0. ^{11}B NMR (C_6D_6): δ 31.9 (C-B), 22.8 (O-B). IR (KBr pellet, cm^{-1}): 2980, 1493, 1371, 1143, 968, 849, 752, 668, 533. Anal. Calcd. $\text{C}_{19}\text{H}_{30}\text{O}_6\text{B}_2$: C, 60.68; H, 8.04. Found: C, 60.33; H, 7.93.

α -[(Pinacol)boroxy]-2,4,6-trimethylbenzyl(pinacol)boronate. The general procedure using 2.3% (ICy)CuOt-Bu was followed except that the product was further purified by recrystallization from pentane at -40 °C to give colorless crystals (0.143 g, 71%, mp = 103–105 °C). ^1H NMR (C_6D_6): δ 6.77 (s, 2H), 5.85 (s, 1H, $\text{CHB}(\text{pin})$), 2.63 (s, 6H), 2.09 (s, 3H), 1.05 (s, 6H, pinacol- CH_3), 1.03 (s, 6H, pinacol- CH_3), 1.03 (s, 6H, pinacol- CH_3), 0.98 (s, 6H, pinacol- CH_3). ^{13}C NMR (C_6D_6): δ 137.6, 136.6, 135.5, 130.1, 84.4 ($\text{OC}(\text{CH}_3)_2$), 82.8 ($\text{OC}(\text{CH}_3)_2$), 63.7

(CB(pin)), 25.20 (pinacol-CH₃), 25.19 (pinacol-CH₃), 25.1 (pinacol-CH₃), 25.0 (pinacol-CH₃), 21.4, 21.3. ¹¹B NMR (C₆D₆): δ 32.7 (C-B), 22.6 (O-B). IR (KBr pellet, cm⁻¹): 2989, 1497, 1429, 1371, 1141, 851. Repeated attempts at elemental analysis failed to give satisfactory results; ¹H and ¹³C NMR spectra for this compound are included to attest to its purity (Figure S4).

α-[(Pinacol)boroxy]-3-pyridylmethyl(pinacol)boronate. A Schlenk flask equipped with a Teflon-coated magnetic stirbar was charged with bis(pinacolato)diboron (0.127 g, 0.500 mmol) dissolved in benzene (4 mL). 3-pyridinecarboxaldehyde (0.047 mL, 0.500 mmol) was added via syringe followed by a solution of (ICy)CuOt-Bu (0.0184 g, 0.05 mmol) dissolved in benzene (2 mL), and the reaction mixture was stirred for 22 hours. The reaction mixture was concentrated *in vacuo*, and the crude product was recrystallized from CH₂Cl₂ at -40 °C to afford the title compound as a white solid (0.110 g, 61%, mp = 120 °C dec). ¹H NMR (CD₂Cl₂): δ 8.41 (m, 2H), 7.69 (m, 1H), 7.24 (m, 1H), 4.90 (s, 1H, CHB(pin)), 1.22 (s, 6H, pinacol-CH₃), 1.21 (s, 6H, pinacol-CH₃), 1.19 (s, 6H, pinacol-CH₃), 1.17 (s, 6H, pinacol-CH₃). ¹³C NMR (C₆D₆): δ 147.6, 147.5, 137.4, 134.4, 123.7, 84.6, 83.5, 66.0, 25.1, 25.0, 24.9. ¹¹B NMR (C₆D₆): δ 29.6 (C-B), 22.1 (O-B). IR (KBr pellet, cm⁻¹): 2980, 1482, 1422, 1309, 1153, 1062, 964, 850, 564. Anal. Calcd. C₁₈H₂₉O₅B₂N: C, 59.88; H, 8.10. Found: C, 60.23; H, 7.49.

α -[(Pinacol)boroxy]-2-thienylmethyl(pinacol)borate. The general procedure using 1% (ICy)CuOt-Bu was followed to afford the title compound as a pale yellow oil (0.167 g, 91%). ^1H NMR (C_6D_6): δ 7.15 (m, 1H), 6.84 (m, 1H), 6.73 (m, 1H), 5.61 (s, 1H, $\text{CHB}(\text{pin})$), 1.06 (s, 12H, pinacol- CH_3), 1.02 (s, 6H, pinacol- CH_3), 1.01 (s, 6H, pinacol- CH_3). ^{13}C NMR (C_6D_6): δ 144.6, 127.2, 125.3, 125.1, 84.7 ($\text{OC}(\text{CH}_3)_2$), 83.2 ($\text{OC}(\text{CH}_3)_2$), 63.1 ($\text{CB}(\text{pin})$), 25.2 (pinacol- CH_3), 25.04 (pinacol- CH_3), 24.98 (pinacol- CH_3), 24.94 (pinacol- CH_3). ^{11}B NMR (C_6D_6): δ 31.4 ($\text{C}-\text{B}$), 22.5 ($\text{O}-\text{B}$). IR (KBr plate, neat, cm^{-1}): 2981, 1439, 1270, 1143, 1033, 967. Anal. Calcd. $\text{C}_{17}\text{H}_{28}\text{O}_5\text{B}_2\text{S}$: C, 55.77; H, 7.71. Found: C, 55.87; H, 7.40.

α -[(Pinacol)boroxy]-*n*-butyl(pinacol)boronate. The general procedure using 1% (ICy)CuOt-Bu was followed to afford the title compound as a yellow oil (0.158 g, 97%). ^1H NMR (C_6D_6): δ 4.33 (dd, $J = 5.0, 8.5$ Hz, 1H, $\text{CHB}(\text{pin})$), 1.93 (m, 1H), 1.84 (m, 1H), 1.64 (sextet, $J = 7.5$ Hz, 2H), 0.92 (t, 7.5 Hz, 3H). ^{13}C NMR (C_6D_6): δ 84.1, 82.7, 64.3 ($\text{CB}(\text{pin})$), 36.0, 25.2, 25.2, 25.1, 25.0, 25.0, 20.4, 14.6. ^{11}B NMR (C_6D_6): δ 32.7 ($\text{C}-\text{B}$), 22.6 ($\text{O}-\text{B}$). IR (KBr plate, neat, cm^{-1}): 2978, 1507, 1390, 1268, 1146, 970, 850. Anal. Calcd. $\text{C}_{16}\text{H}_{32}\text{O}_5\text{B}_2$: C, 58.94; H, 9.89. Found: C, 58.75; H, 9.51.

α -[(Pinacol)boroxy]-isobutyl(pinacol)boronate. The general procedure using 1% (ICy)CuOt-Bu was followed afford the title compound as a colorless oil (0.152 g, 93%). ^1H NMR (C_6D_6): δ 4.14 (d, $J = 5.0$ Hz, 1H, $\text{CHB}(\text{pin})$), 2.20 (septet, $J = 6.8$ Hz, 1H, $(\text{CH}_3)_2\text{CH}$), 1.16 (dd, $J = 1.8$ Hz, 6.8 Hz), 6H, $(\text{CH}_3)_2\text{CH}$), 1.11 (s, 12H, pinacol- CH_3), 1.06 (s, 12H, pinacol- CH_3). ^{13}C NMR (C_6D_6): δ 84.0 ($\text{B}(\text{OC}(\text{CH}_3)_2)_2$), 82.6 ($\text{B}(\text{OC}(\text{CH}_3)_2)_2$), 70.5 ($\text{CB}(\text{pin})$), 32.5 ($(\text{CH}_3)_2\text{C}$), 25.3 (pinacol- CH_3), 25.3 (pinacol- CH_3), 25.2 (pinacol- CH_3), 25.0 (pinacol- CH_3), 20.3 ($(\text{CH}_3)_2\text{C}$), 19.6 ($(\text{CH}_3)_2\text{C}$). ^{11}B NMR (C_6D_6): δ 32.4 (C-B), 22.3 (O-B). IR (KBr plate, neat, cm^{-1}): 2933, 1507, 1272, 1114, 970, 850. Anal. Calcd. $\text{C}_{16}\text{H}_{32}\text{O}_5\text{B}_2$: C, 58.94; H, 9.89. Found: C, 58.86; H, 10.28.

α -Hydroxyneopentyl(pinacol)boronate. The general procedure was followed using 1% (ICy)CuOt-Bu, except that the crude reaction mixture was concentrated and purified by column chromatography (7 : 3 dichloromethane : diethyl ether, $R_f = 0.5$), without protection from oxygen or water, to afford the title compound as a colorless oil (0.076 g, 71%). ^1H NMR (C_6D_6): δ 3.30 (s, 1H, $\text{CHB}(\text{pin})$), 2.04 (s, 1H, OH), 1.13 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.99 (s, 12H, pinacol- CH_3). ^{13}C NMR (C_6D_6): δ 84.4 ($\text{OC}(\text{CH}_3)_2$), 70.3 ($\text{CB}(\text{pin})$), 35.4 ($\text{C}(\text{CH}_3)_3$), 27.6 ($\text{C}(\text{CH}_3)_3$), 25.2 (pinacol- CH_3), 25.1 (pinacol- CH_3). ^{11}B NMR: δ 32.8 (C-B). IR (KBr film, cm^{-1}): 3613, 2979, 2952, 1324, 1143, 1047, 845. Repeated attempts at elemental analysis failed to give satisfactory results; ^1H and ^{13}C NMR spectra for this compound are included to attest to its purity (Figure S5).

α -[(Pinacol)boroxy]-cyclohexylmethyl(pinacol)boronate. The general procedure using 1% (ICy)CuOt-Bu was followed to afford the title compound as a white solid (0.175 g, 96%, mp = 85–86 °C). ^1H NMR (C_6D_6): δ 4.14 (d, J = 5.0 Hz, 1H, $\text{CHB}(\text{pin})$), 1.97 (m, 1H), 1.90 (m, 2H), 1.71 (m, 2H), 1.55 (m, 2H), 1.40 (m, 1H), 1.21 (m, 3H), 1.11 (s, 12H), 1.09 (s, 12H). ^{13}C NMR (C_6D_6): δ 84.0 ($\text{OC}(\text{CH}_3)_2$), 82.6 ($\text{OC}(\text{CH}_3)_2$), 69.9 ($\text{CB}(\text{pin})$), 42.3, 31.0, 30.0, 27.24, 27.20, 27.18, 25.32 (pinacol- CH_3), 25.27 (pinacol- CH_3), 25.1 (pinacol- CH_3). ^{11}B NMR (C_6D_6): δ 32.5 (C-B), 22.4 (O-B). IR (KBr pellet, cm^{-1}): 3000, 2928, 1450, 1142, 972, 673. Anal. Calcd. $\text{C}_{19}\text{H}_{35}\text{O}_5\text{B}_2$: C, 62.33; H, 9.91. Found: C, 62.10; H, 9.75.

Di(2'-pyridyl)-1,2-bis[(pinacol)boroxy]ethane. The reaction was set up according to the general procedure except that 0.25 mmol of bis(pinacolato)diboron and a catalyst loading of 10% (ICy)CuOt-Bu catalyst loading were used. After 22 hours, the precipitated product was collected by filtration and dried *in vacuo*. The resulting white solid (0.069 g, 59%, mp = 240 °C dec) comprised a 12:1 mixture of the *meso* and *rac* isomers as judged by ^1H NMR spectroscopy. For comparison, a 3:1 ratio of *meso* and *rac* isomers was observed by ^1H NMR spectroscopy of the concentrated crude reaction mixture. ^1H NMR (CD_2Cl_2) for the *meso* isomer: δ 8.61 (m, 2H), 8.17 (m, 2H), 8.09 (m, 2H), 7.63 (m, 2H), 4.73 (s, 2H), 1.34 (s, 12H), 1.26 (s, 12H). ^{13}C NMR

(CD₂Cl₂): δ 160.9, 141.6, 140.7, 125.3, 124.3, 80.2 (OC(CH₃)₂), 78.3 (OCH), 26.7 (pinacol-CH₃), 25.9 (pinacol-CH₃). ¹¹B NMR (CD₂Cl₂): δ 11.0 (O-B). IR (KBr pellet, cm⁻¹): 2976, 1621, 1479, 1027, 900, 811, 767, 543. Anal. Calcd. C₂₄H₃₄N₂B₂O₆: C, 61.57; H, 7.32. Found: C, 61.29; H, 7.14.

Stoichiometric reaction of **1 with (pin)BB(pin):** In a glovebox, C₆D₆ was added to a 20-mL scintillation vial containing **1** (0.025 g, 0.034 mmol), bis(pinacolato)diboron (8.7 mg, 0.034 mmol) and 1,4-dimethoxybenzene (2.5 mg, 0.017 mmol). The solution was transferred to an NMR tube, and the tube was sealed and taken out of the glove box. An initial ¹H NMR spectrum was taken to determine the ratio of **1** and the internal standard (specifically, the benzyl proton of **1** (5.55 ppm) was compared to the methoxy groups of 1,4-dimethoxybenzene). Another ¹H NMR spectrum was taken after 20 hours which indicated that 10% of **1** was converted to **2** and (IPr)CuB(pin) based on comparison of the benzyl proton of **2** (5.85 ppm) and an isopropyl group of (IPr)CuB(pin) (1.48 ppm) with the internal standard.

Diboration of mesitaldehyde using complex **1 as precatalyst:** In a glovebox, mesitaldehyde (0.074 mL, 0.5 mmol) was added via syringe to a 20-mL scintillation vial containing bis(pinacolato)diboron (0.127 g, 0.5 mmol) dissolved in benzene (1 mL). The resulting solution was transferred to a 20-mL scintillation vial containing **1** (0.0727 g, 0.1 mmol) and a Teflon coated magnetic stirbar. Additional benzene (1 mL) was used to ensure complete transfer. The reaction mixture was stirred for 24 hours, transferred to a Schlenk flask, and concentrated *in vacuo*. An internal standard, 1,4-dimethoxybenzene (0.0414 g, 0.3 mmol) was added, and the crude reaction mixture was dissolved in C₆D₆ (2 mL) or CD₂Cl₂ (2 mL). The yield of **2** (90%, average of two runs) was determined by ¹H NMR spectroscopy through integration of the benzylic proton of **2** relative to the methoxy protons of 1,4-dimethoxybenzene.

Determination of the catalyst resting state for the diboration of mesitaldehyde with (IPr)CuOt-Bu precatalyst: In a glovebox, C₆D₆ was added to a vial charged with (IPr)CuOt-Bu (0.0125 g, 0.024 mmol) and bis(pinacolato)diboron (0.0242 g, 0.095 mmol). Mesitaldehyde was added via syringe (0.014 mL, 0.095 mmol), and the solution was transferred to an NMR tube. Analysis by ¹H NMR spectroscopy after 15 and 90 minutes indicated that **1** was the major complex in solution (>95% of observed ligand resonances can be assigned to **1**).

Control Reactions: No reaction was observed between bis(pinacolato)diboron and benzaldehyde, 2-pyridinecarboxaldehyde, or 3-pyridinecarboxaldehyde using the general procedure in the absence of (ICy)CuOt-Bu.

Figure S1. ^1H and ^{13}C NMR spectra of (ICy)CuOt-Bu.

Figure S2. ^1H and ^{13}C NMR spectra of α -[(pinacol)boroxy]-4-bromobenzyl(pinacol)boronate.

Figure S3. ^1H and ^{13}C NMR spectra of α -[(pinacol)boroxy]-4-chlorobenzyl(pinacol)boronate.

Figure S4. ^1H and ^{13}C NMR spectra of **2**.

Figure S5. ^1H and ^{13}C NMR spectra of α -hydroxyneopentyl(pinacol)boronate.

X-ray Diffraction Studies: Experiments were performed on single crystals of **1** (grown by the vapor diffusion of pentane into a concentrated diethyl ether solution at $-40\text{ }^{\circ}\text{C}$) and **2** (grown from a saturated hexamethyldisiloxane/toluene solution at $-40\text{ }^{\circ}\text{C}$). Colorless crystals were removed from the supernatant and transferred onto a microscope slide coated with Paratone N oil. A crystal was affixed to a glass fiber or a cryoloop using the oil, frozen in a nitrogen stream, and optically centered. The data were collected on a Siemens three-circle platform goniometer equipped with a Bruker Smart Apex CCD detector with graphite-monochromated MoK α radiation ($\lambda = 0.71073\text{ \AA}$), using both phi and omega scans at $-173\text{ }^{\circ}\text{C}$. The structures were solved by direct methods (SHELXS)⁶ and refined against F^2 on all data by full matrix least squares with SHELXL-97 (Sheldrick, G. M. *SHELXL 97*; Universität Göttingen: Göttingen, Germany, 1997). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model.

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) α -[(pinacol)boroxy]-2,4,6-trimethylbenzyl (1). The (pinacol)borate group in this complex was found to be disordered over two positions; however, attempts to model the minor component ($\sim 9\%$ of the total occupancy) led to unstable refinements even with strong restraints; for this reason, the minor component was not included in the final model. One peak of significant electron density ($1.12\text{ e/\AA}^3$) remained after convergence which corresponds to O(1) of the minor component of the disordered (pinacol)borate group.

Figure S6. X-ray crystal structure of **1**. For clarity in labeling, hydrogen atoms have been omitted and structure shown as a stick representation.

Table S1. Crystal data and structure refinement for **1**.

Identification code	05091	
Empirical formula	C ₄₃ H ₆₀ N ₂ O ₃ BCu	
Formula weight	727.28	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>n</i>	
Unit cell dimensions	<i>a</i> = 11.8285(13) Å	$\alpha = 90^\circ$.
	<i>b</i> = 20.610(2) Å	$\beta = 101.158(4)^\circ$.
	<i>c</i> = 17.6358(18) Å	$\gamma = 90^\circ$.
Volume	4218.1(8) Å ³	
Z	4	
Density (calculated)	1.145 g/cm ³	
Absorption coefficient	0.555 mm ⁻¹	
F(000)	1560	
Crystal size	0.15 x 0.15 x 0.15 mm ³	
Theta range for data collection	1.91 to 28.70°.	
Index ranges	-15 ≤ <i>h</i> ≤ 15, -27 ≤ <i>k</i> ≤ 27, -23 ≤ <i>l</i> ≤ 23	
Reflections collected	88667	
Independent reflections	10890 [R(int) = 0.0439]	
Completeness to theta = 28.70°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9213 and 0.9213	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10890 / 0 / 466	
Goodness-of-fit on F ²	1.092	
Final R indices [I > 2σ(I)]	R1 = 0.0499, wR2 = 0.1231	
R indices (all data)	R1 = 0.0625, wR2 = 0.1303	
Largest diff. peak and hole	1.121 and -0.186 e/Å ³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	1794(1)	1991(1)	9704(1)	22(1)
O(1)	1404(1)	2116(1)	8009(1)	34(1)
O(2)	2367(1)	1674(1)	7071(1)	38(1)
O(3)	1865(1)	968(1)	7967(1)	32(1)
N(1)	2556(1)	1577(1)	11321(1)	24(1)
N(2)	3511(1)	2396(1)	11051(1)	23(1)
C(1)	2638(2)	1992(1)	10735(1)	21(1)
C(2)	3368(2)	1717(1)	11978(1)	30(1)
C(3)	3973(2)	2231(1)	11809(1)	29(1)
C(4)	1737(2)	1051(1)	11255(1)	24(1)
C(5)	2022(2)	460(1)	10957(1)	26(1)
C(6)	1219(2)	−41(1)	10901(1)	32(1)
C(7)	179(2)	47(1)	11136(1)	38(1)
C(8)	−81(2)	645(1)	11420(1)	37(1)
C(9)	689(2)	1161(1)	11494(1)	29(1)
C(10)	3171(2)	346(1)	10717(1)	30(1)
C(11)	3021(2)	168(2)	9868(2)	59(1)
C(12)	3849(2)	−169(2)	11226(2)	58(1)
C(13)	374(2)	1821(1)	11778(1)	38(1)
C(14)	−321(3)	2209(1)	11102(2)	51(1)
C(15)	−282(4)	1773(2)	12441(2)	77(1)
C(16)	3873(2)	2942(1)	10647(1)	24(1)
C(17)	4683(2)	2836(1)	10181(1)	28(1)
C(18)	5008(2)	3372(1)	9790(1)	32(1)
C(19)	4548(2)	3980(1)	9870(1)	34(1)
C(20)	3745(2)	4069(1)	10338(1)	32(1)
C(21)	3390(2)	3548(1)	10741(1)	28(1)
C(22)	5195(2)	2170(1)	10107(1)	36(1)
C(23)	5031(3)	1958(2)	9264(2)	59(1)
C(24)	6462(2)	2150(1)	10507(2)	43(1)
C(25)	2504(2)	3645(1)	11254(1)	33(1)

C(26)	1353(2)	3872(1)	10780(2)	45(1)
C(27)	2965(2)	4101(1)	11924(1)	42(1)
C(28)	840(2)	2038(1)	8673(1)	27(1)
C(29)	98(2)	2621(1)	8740(1)	26(1)
C(30)	494(2)	3265(1)	8706(1)	33(1)
C(31)	−239(3)	3777(1)	8811(1)	44(1)
C(32)	−1342(3)	3681(1)	8951(1)	47(1)
C(33)	−1702(2)	3051(1)	9005(1)	42(1)
C(34)	−1009(2)	2522(1)	8905(1)	30(1)
C(35)	1699(2)	3405(1)	8598(2)	48(1)
C(36)	−2131(4)	4247(2)	9029(2)	79(1)
C(37)	−1467(2)	1849(1)	8988(2)	39(1)
C(38)	2898(2)	1062(1)	6968(1)	33(1)
C(39)	2819(2)	944(2)	6099(1)	47(1)
C(40)	4163(2)	1104(1)	7353(1)	32(1)
C(41)	2203(2)	565(1)	7357(1)	31(1)
C(42)	1104(2)	335(2)	6849(2)	50(1)
C(43)	2888(2)	−6(1)	7751(1)	36(1)
B(1)	1873(2)	1601(1)	7709(1)	33(1)

Table S3. Bond lengths [Å] and angles [°] for **1**.

Cu(1)–C(1)	1.8975(18)	C(2)–C(3)	1.344(3)
Cu(1)–C(28)	1.9473(19)	C(4)–C(5)	1.393(3)
O(1)–B(1)	1.352(3)	C(4)–C(9)	1.402(3)
O(1)–C(28)	1.464(2)	C(5)–C(6)	1.394(3)
O(2)–B(1)	1.373(3)	C(5)–C(10)	1.518(3)
O(2)–C(38)	1.436(3)	C(6)–C(7)	1.384(3)
O(3)–B(1)	1.382(3)	C(7)–C(8)	1.387(4)
O(3)–C(41)	1.473(2)	C(8)–C(9)	1.390(3)
N(1)–C(1)	1.360(2)	C(9)–C(13)	1.521(3)
N(1)–C(2)	1.385(2)	C(10)–C(12)	1.515(3)
N(1)–C(4)	1.444(2)	C(10)–C(11)	1.519(3)
N(2)–C(1)	1.359(2)	C(13)–C(15)	1.527(4)
N(2)–C(3)	1.384(2)	C(13)–C(14)	1.536(4)
N(2)–C(16)	1.442(2)	C(16)–C(17)	1.395(3)

C(16)–C(21)	1.396(3)	C(3)–N(2)–C(16)	124.72(16)
C(17)–C(18)	1.396(3)	N(2)–C(1)–N(1)	103.47(15)
C(17)–C(22)	1.515(3)	N(2)–C(1)–Cu(1)	127.69(13)
C(18)–C(19)	1.385(3)	N(1)–C(1)–Cu(1)	128.79(14)
C(19)–C(20)	1.386(3)	C(3)–C(2)–N(1)	107.00(17)
C(20)–C(21)	1.397(3)	C(2)–C(3)–N(2)	106.19(17)
C(21)–C(25)	1.524(3)	C(5)–C(4)–C(9)	123.17(18)
C(22)–C(23)	1.525(4)	C(5)–C(4)–N(1)	118.62(17)
C(22)–C(24)	1.529(3)	C(9)–C(4)–N(1)	118.20(18)
C(25)–C(27)	1.526(3)	C(4)–C(5)–C(6)	117.59(18)
C(25)–C(26)	1.527(3)	C(4)–C(5)–C(10)	122.46(18)
C(28)–C(29)	1.506(3)	C(6)–C(5)–C(10)	119.94(19)
C(29)–C(34)	1.410(3)	C(7)–C(6)–C(5)	121.0(2)
C(29)–C(30)	1.414(3)	C(6)–C(7)–C(8)	119.8(2)
C(30)–C(31)	1.400(3)	C(7)–C(8)–C(9)	121.8(2)
C(30)–C(35)	1.501(4)	C(8)–C(9)–C(4)	116.7(2)
C(31)–C(32)	1.388(4)	C(8)–C(9)–C(13)	121.2(2)
C(32)–C(33)	1.375(4)	C(4)–C(9)–C(13)	122.05(19)
C(32)–C(36)	1.517(4)	C(12)–C(10)–C(5)	110.06(19)
C(33)–C(34)	1.397(3)	C(12)–C(10)–C(11)	111.3(2)
C(34)–C(37)	1.505(3)	C(5)–C(10)–C(11)	111.91(18)
C(38)–C(40)	1.522(3)	C(9)–C(13)–C(15)	112.8(2)
C(38)–C(39)	1.536(3)	C(9)–C(13)–C(14)	109.82(19)
C(38)–C(41)	1.554(3)	C(15)–C(13)–C(14)	110.7(2)
C(41)–C(42)	1.506(3)	C(17)–C(16)–C(21)	123.65(18)
C(41)–C(43)	1.519(3)	C(17)–C(16)–N(2)	118.20(18)
		C(21)–C(16)–N(2)	118.15(18)
C(1)–Cu(1)–C(28)	175.46(8)	C(16)–C(17)–C(18)	116.92(19)
B(1)–O(1)–C(28)	120.80(17)	C(16)–C(17)–C(22)	121.63(19)
B(1)–O(2)–C(38)	105.88(17)	C(18)–C(17)–C(22)	121.5(2)
B(1)–O(3)–C(41)	105.77(16)	C(19)–C(18)–C(17)	121.0(2)
C(1)–N(1)–C(2)	111.40(16)	C(18)–C(19)–C(20)	120.5(2)
C(1)–N(1)–C(4)	123.84(15)	C(19)–C(20)–C(21)	120.7(2)
C(2)–N(1)–C(4)	124.75(16)	C(16)–C(21)–C(20)	117.17(19)
C(1)–N(2)–C(3)	111.94(16)	C(16)–C(21)–C(25)	122.16(18)
C(1)–N(2)–C(16)	123.29(15)	C(20)–C(21)–C(25)	120.67(19)

C(17)–C(22)–C(23)	111.5(2)	C(32)–C(33)–C(34)	122.1(2)
C(17)–C(22)–C(24)	110.95(19)	C(33)–C(34)–C(29)	120.3(2)
C(23)–C(22)–C(24)	111.7(2)	C(33)–C(34)–C(37)	118.4(2)
C(21)–C(25)–C(27)	110.93(19)	C(29)–C(34)–C(37)	121.28(19)
C(21)–C(25)–C(26)	110.99(18)	O(2)–C(38)–C(40)	108.04(18)
C(27)–C(25)–C(26)	112.41(19)	O(2)–C(38)–C(39)	108.76(18)
O(1)–C(28)–C(29)	109.73(16)	C(40)–C(38)–C(39)	108.60(19)
O(1)–C(28)–Cu(1)	118.74(14)	O(2)–C(38)–C(41)	103.92(16)
C(29)–C(28)–Cu(1)	101.94(12)	C(40)–C(38)–C(41)	113.49(17)
C(34)–C(29)–C(30)	118.26(19)	C(39)–C(38)–C(41)	113.7(2)
C(34)–C(29)–C(28)	118.64(18)	O(3)–C(41)–C(42)	106.71(18)
C(30)–C(29)–C(28)	122.91(19)	O(3)–C(41)–C(43)	107.44(17)
C(31)–C(30)–C(29)	118.9(2)	C(42)–C(41)–C(43)	110.5(2)
C(31)–C(30)–C(35)	120.0(2)	O(3)–C(41)–C(38)	101.11(16)
C(29)–C(30)–C(35)	121.1(2)	C(42)–C(41)–C(38)	114.4(2)
C(32)–C(31)–C(30)	123.0(2)	C(43)–C(41)–C(38)	115.56(17)
C(33)–C(32)–C(31)	117.4(2)	O(1)–B(1)–O(2)	120.5(2)
C(33)–C(32)–C(36)	121.0(3)	O(1)–B(1)–O(3)	125.6(2)
C(31)–C(32)–C(36)	121.5(3)	O(2)–B(1)–O(3)	113.8(2)

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	22(1)	26(1)	16(1)	4(1)	−1(1)	0(1)
O(1)	37(1)	39(1)	25(1)	6(1)	6(1)	6(1)
O(2)	40(1)	46(1)	28(1)	8(1)	9(1)	10(1)
O(3)	33(1)	38(1)	25(1)	0(1)	7(1)	2(1)
N(1)	25(1)	27(1)	18(1)	4(1)	−1(1)	−4(1)
N(2)	25(1)	25(1)	18(1)	1(1)	1(1)	−2(1)
C(1)	23(1)	22(1)	18(1)	2(1)	1(1)	−1(1)
C(2)	32(1)	37(1)	18(1)	3(1)	−4(1)	−5(1)
C(3)	31(1)	35(1)	18(1)	0(1)	−3(1)	−4(1)
C(4)	24(1)	27(1)	18(1)	5(1)	0(1)	−4(1)
C(5)	23(1)	28(1)	25(1)	7(1)	1(1)	0(1)

C(6)	32(1)	26(1)	36(1)	4(1)	4(1)	-1(1)
C(7)	32(1)	39(1)	42(1)	7(1)	7(1)	-12(1)
C(8)	28(1)	50(1)	35(1)	2(1)	11(1)	-7(1)
C(9)	29(1)	37(1)	20(1)	0(1)	4(1)	-2(1)
C(10)	25(1)	31(1)	34(1)	4(1)	4(1)	3(1)
C(11)	34(1)	105(3)	40(1)	-8(2)	11(1)	9(1)
C(12)	37(1)	67(2)	69(2)	28(2)	11(1)	21(1)
C(13)	37(1)	46(1)	33(1)	-11(1)	9(1)	0(1)
C(14)	53(2)	51(2)	49(2)	-13(1)	7(1)	18(1)
C(15)	112(3)	79(2)	54(2)	-19(2)	53(2)	-4(2)
C(16)	26(1)	25(1)	20(1)	1(1)	0(1)	-5(1)
C(17)	25(1)	32(1)	25(1)	-2(1)	0(1)	-3(1)
C(18)	27(1)	45(1)	26(1)	3(1)	5(1)	-7(1)
C(19)	37(1)	36(1)	26(1)	9(1)	-1(1)	-11(1)
C(20)	37(1)	27(1)	30(1)	1(1)	1(1)	-2(1)
C(21)	33(1)	27(1)	23(1)	-2(1)	3(1)	-3(1)
C(22)	32(1)	37(1)	39(1)	-3(1)	10(1)	4(1)
C(23)	55(2)	62(2)	52(2)	-28(1)	-9(1)	17(1)
C(24)	40(1)	53(2)	35(1)	-1(1)	4(1)	12(1)
C(25)	41(1)	31(1)	30(1)	-2(1)	11(1)	2(1)
C(26)	37(1)	60(2)	37(1)	-7(1)	8(1)	-1(1)
C(27)	50(1)	46(1)	29(1)	-5(1)	3(1)	10(1)
C(28)	30(1)	32(1)	17(1)	2(1)	1(1)	6(1)
C(29)	34(1)	27(1)	13(1)	-1(1)	-2(1)	4(1)
C(30)	48(1)	31(1)	16(1)	3(1)	-5(1)	-5(1)
C(31)	83(2)	22(1)	20(1)	1(1)	-4(1)	-1(1)
C(32)	82(2)	35(1)	26(1)	3(1)	18(1)	22(1)
C(33)	56(2)	40(1)	34(1)	6(1)	22(1)	16(1)
C(34)	41(1)	28(1)	22(1)	0(1)	9(1)	7(1)
C(35)	53(2)	44(1)	40(1)	11(1)	-10(1)	-17(1)
C(36)	142(3)	46(2)	59(2)	10(1)	44(2)	49(2)
C(37)	44(1)	33(1)	44(1)	-2(1)	18(1)	-3(1)
C(38)	30(1)	42(1)	24(1)	5(1)	3(1)	5(1)
C(39)	44(1)	70(2)	25(1)	0(1)	6(1)	9(1)
C(40)	28(1)	39(1)	29(1)	4(1)	6(1)	1(1)
C(41)	28(1)	37(1)	28(1)	-5(1)	6(1)	0(1)

C(42)	37(1)	70(2)	41(1)	−17(1)	3(1)	−8(1)
C(43)	38(1)	33(1)	39(1)	0(1)	13(1)	0(1)
B(1)	40(1)	38(1)	19(1)	3(1)	0(1)	5(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**.

	x	y	z	U(eq)
H(2)	3477	1492	12457	36
H(3)	4593	2440	12143	35
H(6)	1389	−449	10698	38
H(7)	−355	−301	11103	45
H(8)	−805	703	11567	44
H(10)	3620	759	10799	36
H(11A)	2559	−228	9767	89
H(11B)	3779	96	9736	89
H(11C)	2629	523	9552	89
H(12A)	3936	−40	11769	86
H(12B)	4611	−216	11093	86
H(12C)	3437	−584	11146	86
H(13)	1107	2061	11972	46
H(14A)	145	2271	10704	77
H(14B)	−524	2633	11288	77
H(14C)	−1025	1972	10881	77
H(15A)	−1034	1569	12255	115
H(15B)	−395	2209	12636	115
H(15C)	161	1510	12858	115
H(18)	5554	3319	9464	39
H(19)	4784	4340	9602	41
H(20)	3433	4488	10385	38
H(22)	4769	1854	10379	43
H(23A)	4212	1979	9026	89
H(23B)	5310	1512	9238	89
H(23C)	5468	2248	8986	89
H(24A)	6905	2454	10251	65
H(24B)	6763	1709	10475	65

H(24C)	6532	2273	11051	65
H(25)	2372	3213	11480	40
H(26A)	1461	4286	10530	67
H(26B)	798	3929	11122	67
H(26C)	1061	3547	10385	67
H(27A)	3165	4519	11720	63
H(27B)	3652	3910	12246	63
H(27C)	2373	4167	12236	63
H(28)	337	1644	8588	33
H(31)	31	4209	8785	52
H(33)	−2446	2974	9115	50
H(35A)	1755	3320	8059	72
H(35B)	2242	3125	8940	72
H(35C)	1885	3861	8722	72
H(36A)	−2679	4308	8542	118
H(36B)	−1671	4642	9153	118
H(36C)	−2553	4157	9444	118
H(37A)	−2240	1878	9109	59
H(37B)	−954	1621	9407	59
H(37C)	−1504	1611	8503	59
H(39A)	2015	983	5831	70
H(39B)	3104	508	6018	70
H(39C)	3289	1267	5893	70
H(40A)	4512	1485	7158	48
H(40B)	4564	712	7236	48
H(40C)	4227	1143	7914	48
H(42A)	638	101	7163	75
H(42B)	1288	45	6450	75
H(42C)	669	709	6604	75
H(43A)	3502	153	8164	54
H(43B)	3229	−247	7371	54
H(43C)	2376	−293	7971	54

Figure S7. X-ray crystal structure of **2** shown as 50% ellipsoids.

Table S6. Crystal data and structure refinement for **2**.

Identification code	05179fin	
Empirical formula	C ₂₂ H ₃₆ B ₂ O ₅	
Formula weight	402.13	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pbca</i>	
Unit cell dimensions	<i>a</i> = 16.6596(5) Å	$\alpha = 90^\circ$.
	<i>b</i> = 13.4080(6) Å	$\beta = 90^\circ$.
	<i>c</i> = 20.9886(9) Å	$\gamma = 90^\circ$.
Volume	4688.3(3) Å ³	
<i>Z</i>	8	
Density (calculated)	1.139 g/cm ³	
Absorption coefficient	0.077 mm ⁻¹	
<i>F</i> (000)	1744	
Crystal size	0.10 x 0.10 x 0.10 mm ³	
θ range for data collection	1.94 to 29.57°.	
Index ranges	-23 ≤ <i>h</i> ≤ 23, -18 ≤ <i>k</i> ≤ 18, -29 ≤ <i>l</i> ≤ 28	

Reflections collected	100005
Independent reflections	6578 [R(int) = 0.0451]
Completeness to $\theta = 29.57^\circ$	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9923 and 0.9923
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6578 / 0 / 273
Goodness-of-fit on F^2	1.070
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0603$, $wR2 = 0.1571$
R indices (all data)	$R1 = 0.0696$, $wR2 = 0.1655$
Largest diff. peak and hole	0.648 and $-0.193 \text{ e/\AA}^3$

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
B(1)	3028(1)	4199(1)	2092(1)	17(1)
B(2)	2069(1)	4575(1)	3295(1)	18(1)
C(1)	2086(1)	4342(1)	2166(1)	15(1)
C(2)	1626(1)	3785(1)	1653(1)	14(1)
C(3)	1632(1)	2737(1)	1625(1)	16(1)
C(4)	1217(1)	2255(1)	1136(1)	20(1)
C(5)	783(1)	2778(1)	682(1)	22(1)
C(6)	785(1)	3813(1)	716(1)	21(1)
C(7)	1205(1)	4327(1)	1187(1)	17(1)
C(8)	2050(1)	2106(1)	2118(1)	22(1)
C(9)	328(1)	2238(2)	167(1)	34(1)
C(10)	1183(1)	5455(1)	1175(1)	23(1)
C(11)	4216(1)	4020(1)	1590(1)	20(1)
C(12)	4329(1)	3884(1)	2323(1)	21(1)
C(13)	4134(1)	3033(1)	1237(1)	28(1)
C(14)	4829(1)	4678(1)	1267(1)	29(1)
C(15)	4799(1)	2967(1)	2519(1)	30(1)
C(16)	4662(1)	4812(1)	2648(1)	30(1)
C(17)	2395(1)	4947(1)	4311(1)	24(1)

C(18)	2483(1)	5891(1)	3886(1)	22(1)
C(19)	3190(1)	4418(1)	4427(1)	32(1)
C(20)	1954(1)	5118(2)	4936(1)	37(1)
C(21)	3254(1)	6472(1)	3974(1)	31(1)
C(22)	1764(1)	6592(1)	3918(1)	35(1)
O(1)	1814(1)	4023(1)	2792(1)	17(1)
O(2)	3426(1)	4497(1)	1554(1)	19(1)
O(3)	3498(1)	3768(1)	2542(1)	21(1)
O(4)	2475(1)	5461(1)	3244(1)	21(1)
O(5)	1911(1)	4285(1)	3911(1)	22(1)

Table S8. Bond lengths [Å] and angles [°] for **2**.

B(1)–O(3)	1.3571(18)	C(12)–C(15)	1.514(2)
B(1)–O(2)	1.3679(18)	C(12)–C(16)	1.524(2)
B(1)–C(1)	1.588(2)	C(17)–O(5)	1.4632(17)
B(2)–O(1)	1.3578(18)	C(17)–C(20)	1.521(2)
B(2)–O(4)	1.3707(19)	C(17)–C(19)	1.522(2)
B(2)–O(5)	1.3757(19)	C(17)–C(18)	1.555(2)
C(1)–O(1)	1.4563(16)	C(18)–O(4)	1.4660(17)
C(1)–C(2)	1.5182(18)	C(18)–C(21)	1.513(2)
C(2)–C(7)	1.4048(19)	C(18)–C(22)	1.524(2)
C(2)–C(3)	1.4064(19)		
C(3)–C(4)	1.3953(19)	O(3)–B(1)–O(2)	114.73(12)
C(3)–C(8)	1.5079(19)	O(3)–B(1)–C(1)	123.66(12)
C(4)–C(5)	1.387(2)	O(2)–B(1)–C(1)	121.60(13)
C(5)–C(6)	1.388(2)	O(1)–B(2)–O(4)	124.45(13)
C(5)–C(9)	1.506(2)	O(1)–B(2)–O(5)	121.10(13)
C(6)–C(7)	1.3950(19)	O(4)–B(2)–O(5)	114.43(12)
C(7)–C(10)	1.513(2)	O(1)–C(1)–C(2)	109.79(10)
C(11)–O(2)	1.4659(17)	O(1)–C(1)–B(1)	111.13(11)
C(11)–C(14)	1.510(2)	C(2)–C(1)–B(1)	111.70(11)
C(11)–C(13)	1.523(2)	C(7)–C(2)–C(3)	119.46(12)
C(11)–C(12)	1.560(2)	C(7)–C(2)–C(1)	119.36(12)
C(12)–O(3)	1.4671(17)	C(3)–C(2)–C(1)	121.16(12)

C(4)–C(3)–C(2)	119.31(13)	O(3)–C(12)–C(11)	101.97(10)
C(4)–C(3)–C(8)	118.28(12)	C(15)–C(12)–C(11)	115.23(13)
C(2)–C(3)–C(8)	122.39(12)	C(16)–C(12)–C(11)	112.89(13)
C(5)–C(4)–C(3)	121.96(13)	O(5)–C(17)–C(20)	108.62(13)
C(4)–C(5)–C(6)	117.96(13)	O(5)–C(17)–C(19)	106.75(12)
C(4)–C(5)–C(9)	120.85(14)	C(20)–C(17)–C(19)	110.60(14)
C(6)–C(5)–C(9)	121.19(14)	O(5)–C(17)–C(18)	102.53(11)
C(5)–C(6)–C(7)	122.09(13)	C(20)–C(17)–C(18)	114.69(14)
C(6)–C(7)–C(2)	119.19(12)	C(19)–C(17)–C(18)	112.95(14)
C(6)–C(7)–C(10)	118.01(13)	O(4)–C(18)–C(21)	108.84(12)
C(2)–C(7)–C(10)	122.80(12)	O(4)–C(18)–C(22)	106.09(13)
O(2)–C(11)–C(14)	109.27(12)	C(21)–C(18)–C(22)	110.12(14)
O(2)–C(11)–C(13)	105.83(12)	O(4)–C(18)–C(17)	101.90(11)
C(14)–C(11)–C(13)	110.46(13)	C(21)–C(18)–C(17)	115.35(13)
O(2)–C(11)–C(12)	102.13(11)	C(22)–C(18)–C(17)	113.70(14)
C(14)–C(11)–C(12)	115.48(13)	B(2)–O(1)–C(1)	116.36(11)
C(13)–C(11)–C(12)	112.85(13)	B(1)–O(2)–C(11)	105.44(11)
O(3)–C(12)–C(15)	108.43(12)	B(1)–O(3)–C(12)	106.38(11)
O(3)–C(12)–C(16)	106.85(12)	B(2)–O(4)–C(18)	105.82(11)
C(15)–C(12)–C(16)	110.70(13)	B(2)–O(5)–C(17)	105.15(11)

Table S9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\text{h}^2 \text{a}^{*2} \text{U}^{11} + \dots + 2 \text{h k a}^* \text{b}^* \text{U}^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	14(1)	19(1)	16(1)	−4(1)	0(1)	−3(1)
B(2)	16(1)	21(1)	17(1)	−3(1)	0(1)	0(1)
C(1)	15(1)	17(1)	14(1)	−3(1)	1(1)	−2(1)
C(2)	12(1)	18(1)	13(1)	−2(1)	1(1)	−2(1)
C(3)	15(1)	18(1)	15(1)	−1(1)	2(1)	1(1)
C(4)	23(1)	17(1)	18(1)	−4(1)	3(1)	−5(1)
C(5)	21(1)	29(1)	14(1)	−3(1)	0(1)	−10(1)
C(6)	22(1)	28(1)	14(1)	4(1)	−2(1)	−2(1)
C(7)	19(1)	17(1)	14(1)	1(1)	3(1)	−2(1)
C(8)	24(1)	18(1)	24(1)	1(1)	−4(1)	3(1)

C(9)	40(1)	41(1)	21(1)	−5(1)	−7(1)	−17(1)
C(10)	29(1)	19(1)	21(1)	4(1)	0(1)	0(1)
C(11)	15(1)	22(1)	22(1)	0(1)	2(1)	2(1)
C(12)	13(1)	27(1)	22(1)	0(1)	−2(1)	0(1)
C(13)	29(1)	29(1)	26(1)	−7(1)	5(1)	2(1)
C(14)	19(1)	33(1)	34(1)	7(1)	7(1)	2(1)
C(15)	21(1)	33(1)	36(1)	7(1)	−4(1)	5(1)
C(16)	21(1)	36(1)	33(1)	−9(1)	−7(1)	−3(1)
C(17)	32(1)	23(1)	15(1)	−4(1)	−2(1)	−6(1)
C(18)	29(1)	19(1)	18(1)	−6(1)	−1(1)	−3(1)
C(19)	40(1)	30(1)	26(1)	−3(1)	−12(1)	−1(1)
C(20)	52(1)	42(1)	17(1)	−7(1)	8(1)	−10(1)
C(21)	39(1)	30(1)	24(1)	−5(1)	−4(1)	−15(1)
C(22)	43(1)	27(1)	36(1)	−11(1)	−1(1)	5(1)
O(1)	18(1)	20(1)	13(1)	−3(1)	2(1)	−3(1)
O(2)	14(1)	24(1)	19(1)	1(1)	1(1)	1(1)
O(3)	15(1)	29(1)	18(1)	1(1)	−1(1)	−1(1)
O(4)	27(1)	21(1)	15(1)	−4(1)	0(1)	−6(1)
O(5)	28(1)	24(1)	15(1)	−3(1)	1(1)	−8(1)

Table S10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**.

	x	y	z	U(eq)
H(1)	1964	5069	2120	18
H(4)	1232	1548	1114	24
H(6)	490	4181	408	25
H(8A)	1730	2094	2510	33
H(8B)	2580	2389	2210	33
H(8C)	2113	1425	1956	33
H(9A)	708	1965	−144	51
H(9B)	−36	2705	−47	51
H(9C)	17	1694	356	51
H(10A)	1727	5714	1108	35
H(10B)	973	5703	1581	35

H(10C)	834	5678	827	35
H(13A)	3723	2624	1445	42
H(13B)	4649	2680	1245	42
H(13C)	3977	3161	795	42
H(14A)	4688	4755	816	43
H(14B)	5361	4372	1302	43
H(14C)	4835	5334	1472	43
H(15A)	4843	2946	2985	45
H(15B)	5336	2993	2331	45
H(15C)	4520	2367	2370	45
H(16A)	4347	5396	2519	45
H(16B)	5224	4907	2522	45
H(16C)	4630	4731	3111	45
H(19A)	3089	3770	4629	48
H(19B)	3526	4826	4708	48
H(19C)	3466	4316	4020	48
H(20A)	1412	5366	4848	56
H(20B)	2247	5610	5191	56
H(20C)	1920	4488	5171	56
H(21A)	3711	6051	3858	47
H(21B)	3304	6676	4421	47
H(21C)	3245	7065	3701	47
H(22A)	1806	7092	3580	53
H(22B)	1755	6926	4334	53
H(22C)	1268	6208	3863	53

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