Supporting Information

PALLADIUM-CATALYZED BORYLATION OF ARYL IODIDES WITH 2,3-DIHYDRO-1*H*-BENZO[*d*][1,3,2]DIAZABOROLES

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General Considerations.

All experiments were carried out under a nitrogen atmosphere using oven-dried (120 °C) glassware. NMR spectra were recorded on a JEOL JNM-A500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz) or a JEOL ECX-400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz). Chemical shifts of ^{1}H NMR and ^{13}C NMR signals reported δ ppm referenced to the solvent or an internal $SiMe_4$. Mass spectra were obtained at an ionization potential of 70 eV with a JEOL JMS-T100GCV spectrometer. GLC analyses were carried out with a Shimadzu GC-14B equipped with a glass column (OV-17 on Chromosorb W, 2 m). GLC yields were determined using suitable hydrocarbons as internal standards.

Materials.

Toluene and 1,4-dioxane were distilled from sodium benzophenone ketyl before use. Aryl halides **2**, $Pd[P(t\text{-}Bu)_3]_2$ (TCI Co., Inc.) and Et_3N (Kanto Chemical Co., Inc.) were purchased from commercial sources, and used without purification. 1,3,5,6-Tetramethyl-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (**1**) was prepared by the literature methods.[1] $PdCl_2$(dtbpf) (DtBPF = 1,1′-bis(di-*tert*-butylphosphino)ferrocene) was prepared by the treatment of $PdCl_2(MeCN)_2$ with DtBPF.[2]

Procedure for Arylboronate Synthesis (Tables 1 and 2)

In a glove box, **1** (0.375 mmol), **2** (0.25 mmol), and Pd catalyst (7.5 μmol), and Et_3N (104 μL, 0.75 mmol) were placed in a screw-capped vial containing a stir bar, and dissolved in 1.0 mL of solvent. The vial was sealed with a cap equipped and removed from the glove box. The reaction mixture was then stirred at 80 °C for 3–6 h, and then cooled to room temperature. Pinacol (35.4 mg, 0.3 mmol) and 6 M aq HCl (0.5 mL)

were added to the mixture. After stirring for 15 h at room temperature, the GC analysis of the resulting mixture indicated the formation of the corresponding pinacol boronate esters.

Borylation of Electron-Rich Aryl Iodides – General Procedure A (Table 3)

In a glove box, **1** (65.3 mg, 0.375 mmol), **2** (0.25 mmol), and $PdCl_2$(dtbpf) (4.9 mg, 7.5 μmol) were placed in a screw-capped vial containing a stir bar, and dissolved in 1,4-dioxane (1.0 mL) and Et_3N (104 μL, 0.75 mmol). The vial was sealed with a cap equipped and removed from the glove box. The reaction mixture was then stirred at 80 °C for 6 h. The resulting mixture was allowed to cool to room temperature, diluted with toluene, washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography to give the desired product **3**.

Borylation of Electron-Deficient Aryl Iodides – General Procedure B (Table 3)

In a glove box, **1** (0.375 mmol), **2** (0.25 mmol), and $Pd[P(t\text{-}Bu)_3]_2$ (3.8 mg, 7.5 μmol) were placed in a screw-capped vial containing a stir bar, and dissolved in toluene (1.0 mL) and Et_3N (0.75 mmol). The vial was sealed with a cap equipped and removed from the glove box. The reaction mixture was then stirred at 80 °C for 3 h. The resulting mixture was allowed to cool to room temperature, diluted with toluene, washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography to give the desired product **3**.

2-(4-Methoxyphenyl)-1,3,5,6-tetramethyl-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (3a). Following the general procedure A, the title compound was prepared starting from **2a** (57.7 mg, 0.247 mmol). Silica gel chromatography afforded the analytically pure product (55.3 mg, 80% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 6 H), 3.34 (s, 6 H), 3.87 (s, 3 H), 6.84 (s, 2 H), 7.02 (d, *J* = 8.5 Hz, 2 H), 7.54 (d, *J* = 9.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ = 19.96, 29.73, 55.03, 109.44, 113.61, 126.46, 135.43, 136.56, 159.91. HRMS (EI): *m/z* calcd for $C_{17}H_{21}BN_2O$ [M^+]: 280.1747; found: 280.1740.

4-(1,3,5,6-Tetramethyl-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)phenol (3c). Following the general procedure A, the title compound was prepared starting from **2c** (54.8 mg, 0.249 mmol). Silica gel chromatography afforded the analytically pure product (55.7 mg, 84% yield) as a white solid. ^{1}H NMR ($CDCl_3$): δ = 2.35 (s, 6H), 3.33 (s, 6H), 5.01 (s, 1H), 6.84 (s, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 19.96, 29.72, 109.47, 115.027, 126.502, 135.64, 136.54, 155.86. HRMS (EI): *m/z* calcd for $C_{16}H_{19}BN_2O$ [M^+]: 266.1590; found: 266.1556.

4-(1,3,5,6-tetramethyl-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)aniline (3d). Following the general procedure A, the title compound was prepared starting from **2d** (54.0 mg, 0.247 mmol). Silica gel chromatography afforded the analytically pure product (55.6 mg, 85% yield) as a white solid. ^{1}H NMR ($CDCl_3$): δ = 2.34 (s, 6H), 3.33 (s, 6H), 3.73 (s, 2H), 6.76 (d, *J* = 7.7 Hz, 2H), 6.82 (s, 2H), 7.40 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 19.94, 29.74, 109.32, 114.62, 126.25, 135.33, 136.64, 146.74. HRMS (EI): *m/z* calcd for $C_{16}H_{20}BN_3$ [M^+]: 265.1750; found: 265.1775.

1,3,5,6-Tetramethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (3e). Following the general

procedure B, the title compound was prepared starting from **2e** (50.5 mg, 0.248 mmol). Silica gel chromatography afforded the analytically pure product (48.9 mg, 79% yield) as a white solid. ^{1}H NMR ($CDCl_3$): δ = 2.35 (s, 6 H), 3.34 (s, 6 H), 6.85 (s, 2 H), 7.43 (d, *J* = 14.3 Hz, 2 H), 7.46 (t, *J* = 9.2 Hz, 1 H), 7.59 (d, *J* = 9.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ = 19.97, 29.72, 109.55, 109.62, 126.61, 127.88, 128.50, 134.02, 136.50. HRMS (EI): *m/z* calcd for $C_{16}H_{19}BN_2$ [M^+]: 250.1641; found: 250.1642.

Ethyl 4-(1,3,5,6-Tetramethyl-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)benzoate (3b). Following the general procedure B, the title compound was prepared starting from **2b** (68.3 mg, 0.247 mmol). Silica gel chromatography afforded the analytically pure product (55.0 mg, 69% yield) as a white solid. ^{1}H NMR ($CDCl_3$): δ = 1.42 (t, *J* = 7.0 Hz, 3H), 2.36 (s, 6H), 3.34 (s, 6H), 4.42 (q, *J* = 7.1 Hz, 2H), 6.87 (s, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 8.12 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 14.35, 19.98, 29.71, 60.95, 109.71, 123.95, 128.72, 130.30, 133.91, 136.36, 166.81. HRMS (EI): *m/z* calcd for $C_{19}H_{23}BN_2O_2$ [M^+]: 322.1853; found: 322.1848.

1-(4-(1,3,5,6-Tetramethyl-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)phenyl)ethan-1-one (3f). Following the general procedure B, the title compound was prepared starting from **2f** (65.8 mg, 0.267 mmol). Silica gel chromatography afforded the analytically pure product (61.7 mg, 79% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$): δ = 2.36 (s, 6H), 2.65 (s, 6H), 3.34 (s, 6H), 6.88 (s, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 20.01, 26.65, 29.68, 109.66, 127.14, 127.63, 134.28, 136.52, 198.40. HRMS (EI): *m/z* calcd for $C_{18}H_{21}BN_2O$ [M^+]: 292.1747; found: 292.1724.

4-(1,3,5,6-Tetramethyl-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)benzaldehyde (3g). Following the general procedure B, **2g** (56.1 mg, 0.242 mmol) was allowed to react with **1** for 1 h at 80 °C. Silica gel chromatography afforded the analytically pure product (56.5 mg, 84% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$): δ = 2.36 (s, 6H), 3.33 (s, 6H), 6.88 (s, 2H), 7.76 (d, *J*=7.7 Hz 2H), 7.95 (d, *J*=6.8 Hz 2H), 10.08 (s, 1H). ^{13}C NMR ($CDCl_3$): δ = 6.34, 20.01, 29.68, 109.66, 124.60, 127.14, 134.28, 136.32, 192.61. HRMS (EI): *m/z* calcd for $C_{17}H_{19}BN_2O$ [M^+]: 278.1590; found: 278.1578.

3-(1,3,5,6-Tetramethyl-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)benzonitrile (3h). Following the general procedure B, the title compound was prepared starting from **2h** (57.3 mg, 0.250 mmol). Silica gel chromatography afforded the analytically pure product (49.6 mg, 72% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$): δ = 2.36 (s, 6H), 3.33 (s, 6H), 6.85 (s, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.86 (s, 1H). ^{13}C NMR ($CDCl_3$): δ = 19.98, 29.69, 109.84, 112.18, 119.16, 127.22, 128.55, 131.92, 136.12, 137.32, 138.08. HRMS (EI): *m/z* calcd for $C_{17}H_{18}BN_3$ [M^+]: 275.1594; found: 275.1623.

1,3,5,6-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (3i). Following the general procedure B, the title compound was prepared starting from **2i** (66.9 mg, 0.246 mmol). Silica gel chromatography afforded the analytically pure product (64.9 mg, 83% yield) as a white solid. ^{1}H NMR ($CDCl_3$): δ = 2.36 (s, 6H), 3.33 (s, 6H), 6.88 (s, 2H), 7.69 (s, 4H). ^{13}C NMR ($CDCl_3$): δ = 19.99, 29.68, 109.79, 124.34 (q, *J* = 270.78 Hz), 124.49 (q, *J* = 3.81 Hz), 127.08, 130.44 (q, *J* = 32.42 Hz), 134.21, 136.31. HRMS (EI): *m/z* calcd for $C_{17}H_{18}BF_3N_2$ [M^+]: 317.1437; found: 317.1431.

1,3,5,6-Tetramethyl-2-(4-nitrophenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (3j). Following the

general procedure B, the title compound was prepared starting from **2j** (62.6 mg, 0.251 mmol). Silica gel chromatography afforded the analytically pure product (53.4 mg, 72% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$): δ = 2.37 (s, 6H), 3.34 (s, 6H), 6.90 (s, 6H), 7.76 (d, *J* = 9.0 Hz, 2H), 8.30 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 20.01, 29.68, 109.86, 122.85, 127.44, 134.76, 136.32, 147.50. HRMS (EI): *m/z* calcd for $C_{16}H_{18}BN_3O_2$ [M^+]: 295.1492; found: 295.1487.

Procedure for Arylboronic Acid Synthesis (Scheme 2)

To a solution of 1,3,5,6-tetramethyl-2-phenyl-1,3,2-benzodiazaborole (62.8 mg, 0.251 mmol) in ether (1 mL) was added 6 M aq HCl (0.5 mL). After stirring for 15 h at room temperature, the organic extracts were washed with 6 M aq HCl (3 × 0.5 mL), dried over Na_2SO_4 and concentrated. The crude product was dried in vacuo overnight to yield phenyl boronic acid as a white solid (30.4 mg, 99% yield).

Reference

1. J. M. Murphy, J. D. Lawrence, K. Kawamura, C. Incarvito, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 13684.
2. T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, K. Hirotsu, *J. Am. Chem. Soc.* **1984**, *106*, 158.