Supporting Information

DABO Boronates: Stable Heterocyclic Boronic Acid Complexes for Use in Suzuki-Miyaura Cross-Coupling Reactions

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For a procedure to prepare DABO boronates please follow the link http://www.youtube.com/watch?v=jnw-bEjKcOU
I. General Experimental Details

All reactions were performed under an atmosphere of argon unless stated otherwise. Reactions were carried out in microwave vials with PFT crimp-on caps. All glassware was oven- or flame-dried and cooled under an inert atmosphere of argon unless stated otherwise. All commercially available reagents were used as received except the following: tetrahydrofuran, dichloromethane, toluene, and ether were degassed with argon and dried by vacuum filtration through activated alumina according to the procedure by Grubbs.¹ DI water, ethanol, butanol, and 1,4-dioxane were degassed by freeze-pump-thawing. Thin-layer chromatography (TLC) was performed on 250 µm layer 6 Å glass-backed silica gel plates. Eluted plates were visualized using UV light, vanillin, p-anisaldehyde, ceric ammonium molybdate, or potassium permanganate stains. Silica gel chromatography was performed according to the method by Still, Kahn, and Mitra² with silica gel 60 (230-400 mesh). Boronic acids were purchased and used as received. Potassium phosphate was ground into a fine powder before use.

II. Instrumentation

Infrared spectra were recorded on an FTIR. ¹H, ¹³C, and ¹¹B NMR spectra were recorded at 500, 125, and 160 MHz, respectively. ¹H NMR spectra were reported in ppm on the δ scale and referenced to residual solvent signal (CDCl₃ at 7.26 ppm, CD₃CN at 1.94 ppm, DMSO at 2.50 ppm). The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad, app = apparent), coupling constant(s) in Hertz (Hz), and integration. ¹³C NMR spectra were reported in ppm relative to CDCl₃ (77.16 ppm). ¹¹B NMR spectra were recorded using quartz NMR tubes and referenced with BF₃·Et₂O (0.00 ppm) as an external standard. NMR spectra were collected at 25 °C. Melting points were obtained using an Electrothermal melting point apparatus and are uncorrected.

III. Characterization

Phenyl DABO boronate 1.\(^3\)-\(^5\) This reaction was run on a 41.8 mmol scale with 5.10 g (41.8 mmol) of phenylboronic acid and provided 7.77 g (40.7 mmol) of phenyl DABO boronate as a light beige solid (97% yield). Decomposition point 213–215 °C; \(^1\)H NMR (500 MHz, CD\(_3\)CN) \(\delta\) 7.48 (d, \(J = 7.0\) Hz, 2H), 7.20 (m, 3H), 5.12 (br s, 1H), 3.96 (m, 2H), 3.86 (m, 2H), 3.21 (m, 2H), 2.84 (m, 2H); \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 7.43 (d, \(J = 6.5\) Hz, 2H), 7.17 (m, 3H), 6.87 (br s, 1H), 3.87 (m, 2H), 3.78 (m, 2H), 3.08 (m, 2H), 2.84 (m, 2H); \(^{11}\)B NMR (160 MHz, CD\(_3\)CN) \(\delta\) +10.09 (br s); \(^{13}\)C NMR (125 MHz, CD\(_3\)CN) \(\delta\) 132.6, 127.0, 126.7, 63.1, 51.2 (missing boronate carbon); \(^{13}\)C NMR (125 MHz, DMSO) \(\delta\) 132.6, 126.7, 126.3, 63.0, 50.7 (missing boronate carbon); IR (KBr) 3116 (br), 3020, 2985, 2931, 2866, 1458 cm\(^{-1}\).

4-Chlorophenyl DABO boronate 2. This reaction was run on an 11.1 mmol scale with 1.74 g (11.1 mmol) of 4-chlorophenylboronic acid and provided 2.51 g (11.1 mmol) of 4-chlorophenyl DABO boronate as an off-white solid (99% yield). Decomposition point 230–233 °C; \(^1\)H NMR (500 MHz, CD\(_3\)CN) \(\delta\) 7.46 (d, \(J = 8.0\) Hz, 2H), 7.22 (d, \(J = 8.0\) Hz, 2H), 5.17 (br s, 1H), 3.95 (m, 2H), 3.85 (m, 2H), 3.19 (m, 2H), 2.84 (m, 2H); \(^{13}\)C NMR (125 MHz, CD\(_3\)CN) \(\delta\) 135.3, 133.0, 127.7, 64.2, 52.0 (missing boronate carbon); IR (KBr) 3146 (br), 3004, 2964, 2857, 1920, 1660, 1584, 1562 cm\(^{-1}\).

4-Bromophenyl DABO boronate 3.\(^5\) This reaction was run on a 2.49 mmol scale with 500 mg (2.49 mmol) of 4-bromophenylboronic acid and provided 599 mg (2.21 mmol) of 4-bromophenyl DABO boronate as an off-white solid (89% yield). Decomposition point 275–277 °C; \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 7.36 (m, 4H), 6.91 (br s, 1H), 3.86 (m, 2H), 3.77 (m, 2H), 3.07 (m, 2H), 2.85 (m, 2H); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.41 (d, \(J = 8.0\) Hz, 2H), 7.38 (d, \(J = 8.0\) Hz, 2H), 5.17 (br s, 1H), 3.95 (m, 2H), 3.85 (m, 2H), 3.20 (m, 2H), 2.84 (m, 2H); \(^{13}\)C NMR (125 MHz, DMSO) \(\delta\) 134.9, 129.4, 120.1, 63.0, 50.7 (missing the ipso carbon); IR (KBr) 3116 (br), 2857, 1577, 1481, 1460 cm\(^{-1}\).

2-Methoxyphenyl DABO boronate 4. This reaction was run on a 3.29 mmol scale with 500 mg (3.29 mmol) of 2-methoxyphenylboronic acid and provided 720 mg (3.26 mmol) of 2-methoxyphenyl DABO boronate as an off-white solid (99% yield). Decomposition point 170–172 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.64 (d, \(J = 6.0\) Hz, 1H), 7.23 (t, \(J = 6.5\) Hz, 1H), 6.97 (t, \(J = 7.0\) Hz, 1H), 6.80 (d, \(J = 8.0\) Hz, 1H), 5.53 (br s, 1H), 4.11 (m, 2H), 3.91 (m, 2H), 3.81 (s, 3H), 3.44 (m, 2H), 2.89 (m, 2H); \(^{13}\)C NMR (125 MHz, CD\(_3\)CN) \(\delta\) 161.8, 134.5, 128.8, 121.3, 109.4, 62.8, 55.3, 51.8 (missing boronate carbon signal); IR (KBr) 3100 (br), 2848, 2690, 1592, 1573 cm\(^{-1}\).

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4-Methoxyphenyl DABO boronate 5. This reaction was run on a 3.29 mmol scale with 500 mg (3.29 mmol) of 4-methoxyphenylboronic acid and provided 608 mg (2.75 mmol) of 4-methoxyphenyl DABO boronate as a white solid (84% yield). Decomposition point 218–220 °C; 1H NMR (500 MHz, DMSO) δ 7.32 (d, J = 8.5 Hz, 2H), 6.75 (d and br s, J = 8.5 Hz, 3H), 3.86 (m, 2H), 3.76 (m, 2H), 3.69 (s, 3H) 3.06 (m, 2H), 2.80 (m, 2H); 1H NMR (500 MHz, CDCl3) δ 7.40 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 5.02 (br s, 1H), 3.94 (m, 2H), 3.85 (m, 2H), 3.74 (s, 3H), 3.19 (m, 2H), 2.84 (m, 2H); 13C NMR (125 MHz, DMSO) δ 158.4, 133.7, 112.3, 62.9, 54.7, 50.6 (missing boronate carbon); IR (KBr) 3141 (br), 3032, 2880, 2714, 2674, 1903, 1569, 1508 cm-1.

4-Nitrophenyl DABO boronate 6. This reaction was run on a 3.40 mmol scale with 500 mg (3.40 mmol) of 4-nitrophenylboronic acid and provided 716 mg (3.31 mmol) of 4-nitrophenyl DABO boronate as a light yellow solid (97% yield). Decomposition point 277–278 °C; 1H NMR (500 MHz, DMSO) δ 7.61 (m, 4H), 7.04 (br s, 1H), 3.88 (m, 2H), 3.78 (m, 2H), 3.11 (m, 2H), 2.89 (m, 2H); 1H NMR (500 MHz, CDCl3) δ 7.65 (d, J = 7.5 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 5.29 (br s, 1H), 3.99 (m, 2H), 3.88 (m, 2H), 3.22 (m, 2H), 2.88 (m, 2H); 13C NMR (125 MHz, CD3CN) δ 135.3, 133.0, 127.7, 64.2, 52.0 (missing boronate carbon); IR (KBr) 3138 (br), 3040, 2970, 2932, 2218, 1545 cm-1.

2-Furyl DABO boronate 7. This reaction was run on a 26.8 mmol scale with 3.00 g (26.8 mmol) of 2-furylboronic acid and provided 3.68 g (20.3 mmol) of 2-furyl DABO boronate as an off-white solid (76% yield). This moderate yield might have been a result of the poor quality of the 2-furylboronic acid, whose proton NMR indicated significant decomposition. Decomposition point 192–193 °C; 1H NMR (500 MHz, CD3CN) δ 7.51 (s, 1H), 6.34 (d, J = 3.0 Hz, 1H), 6.30 (m, 1H), 5.42 (br s, 1H), 3.92 (m, 2H), 3.83 (m, 2H), 3.22 (m, 2H), 2.82 (m, 2H); 13C NMR (125 MHz, CD3CN) δ 144.1, 114.4, 110.0, 63.6, 51.6 (missing boronate carbon); IR (KBr) 3085 (br), 2855, 1638, 1593, 1567 cm-1.

2-Thiophenyl DABO boronate 8. This reaction was run on a 23.4 mmol scale with 3.00 g (23.4 mmol) of 2-thiopheneboronic acid and provided 4.13 g (23.1 mmol) of 2-thiophene DABO boronate as a light beige solid (99% yield). Decomposition point 180–182 °C; 1H NMR (500 MHz, DMSO) δ 7.39 (m, 1H), 7.01 (m, 2H), 3.82 (m, 2H), 3.77 (m, 2H), 3.07 (m, 2H), 2.83 (m, 2H); 13C NMR (125 MHz, DMSO) δ 130.0, 127.7, 126.9, 63.3, 50.8 (missing boronate carbon); IR (KBr) 3109 (br), 2870, 1507, 1459 cm-1.

4-Pyridyl DABO boronate 9. This reaction was run on a 24.4 mmol scale with 3.00 g (24.4 mmol) of 4-pyridylboronic acid and provided 4.61 g of a yellow solid containing a small amount of diethanolamine as an impurity (100:8.8 mol ratio of product:diethanolamine). The yield was calculated to reflect the amount of DABO complex (4.40 g, 22.9 mmol, 94% yield). Decomposition point 200–203 °C; 1H NMR (500
MHz, DMSO) δ 8.35 (d, J = 5.5 Hz, 2H), 7.36 (d, J = 5.5 Hz, 2H), 7.08 (br s, 1H), 3.88 (m, 2H), 3.79 (m, 2H), 3.10 (m, 2H), 2.88 (m, 2H); 13C NMR (125 MHz, DMSO) δ 147.8, 128.0, 63.1, 50.8 (missing boronate carbon); IR (KBr) 3117 (br), 2878, 2699, 1597 cm⁻¹.

2-Benzofuranyl DABO boronate 10. This reaction was run on a 123 mmol scale with 20.0 g (123 mmol) of 2-benzofuranboronic acid and provided 28.2 g (122 mmol) of 2-benzofuran DABO boronate as a white solid (99% yield). Decomposition point 225–227 °C; 1H NMR (500 MHz, CD₃CN) δ 7.52 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.19 (dt, J = 1.5, 7.5 Hz, 1H), 7.14 (dt, J = 1.5, 8.0 Hz, 1H), 6.74 (s, 1H), 5.56 (br s, 1H), 3.97 (m, 2H), 3.89 (m, 2H), 3.25 (m, 2H), 2.86 (m, 2H); 1H NMR (500 MHz, DMSO) δ 7.51 (d, J = 7.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.30 (br s, 1H), 7.16–7.10 (m, 2H), 6.70 (s, 1H), 3.86 (m, 2H), 3.81 (m, 2H), 3.14 (m, 2H), 2.86 (m, 2H); 13C NMR (125 MHz, DMSO) δ 156.2, 128.9, 122.7, 121.6, 120.2, 110.7, 110.1, 62.7, 50.4 (missing boronate carbon); IR (KBr) 3093 (br), 2871, 1950, 1908, 1639, 1552 cm⁻¹.

(1-tert-Butoxycarbonyl)-2-indolyl DABO boronate 11. This reaction was run on a 7.66 mmol scale with 2.00 g (7.66 mmol) of (1-tert-butoxycarbonyl)-2-indoleboronic acid and provided 2.08 g (6.30 mmol) of (1-tert-butoxycarbonyl)-2-indole DABO boronate as a faint pink solid (82% yield). Decomposition point 218–221 °C; 1H NMR (500 MHz, DMSO) δ 7.83 (d, J = 8.5 Hz, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.15 (t, J = 7.0 Hz, 1H), 7.10 (t, J = 6.5 Hz, 1H), 6.86 (br s, 1H), 6.72 (s, 1H), 3.84 (m, 2H), 3.71 (m, 2H), 3.37 (m, 2H), 2.82 (m, 2H), 1.65 (s, 9H); 13C NMR (125 MHz, DMSO) δ 150.9, 137.3, 130.3, 122.7, 121.6, 119.9, 115.1, 114.4, 82.7, 62.5, 51.0, 27.9 (missing boronate carbon); IR (KBr) 3018 (br), 2976, 2891, 2861, 1718, 1534 cm⁻¹.

(1-tert-Butoxycarbonyl)-2-pyrrolyl DABO boronate 12. This reaction was run on a 9.48 mmol scale with 2.00 g (9.48 mmol) of (1-tert-butoxycarbonyl)-2-pyrroleboronic acid and provided 2.61 g (9.33 mmol) of (1-tert-butoxycarbonyl)-2-pyrrole DABO boronate as a white solid (98% yield). Decomposition point 169–171 °C; 1H NMR (500 MHz, DMSO) δ 7.16 (s, 1H), 6.64 (br s, 1H), 6.26 (s, 1H), 6.03 (t, J = 3.0 Hz, 1H), 3.76 (m, 2H), 3.63 (m, 2H), 3.33 (m, 2H), 2.75 (m, 2H), 1.53 (s, 9H); 13C NMR (125 MHz, DMSO) δ 149.7, 122.5, 119.6, 110.4, 81.9, 62.2, 51.1, 27.7 (missing boronate carbon); IR (KBr) 3123 (br), 2983, 1745, 1546 cm⁻¹.

(E)-Styryl DABO boronate 13. This reaction was run on a 13.5 mmol scale with 2.00 g (13.5 mmol) of (E)-styrylboronic acid and provided 1.45 g (6.68 mmol) of (E)-styryl DABO boronate as a white solid (49% yield). The boronic acid was dissolved in 7.0 mL ethyl acetate before adding DEA dropwise. After the addition, the reaction mixture turned off-white with the formation of a fine solid. The reaction mixture
was concentrated to give a pink mixture. About 3 mL of ethyl acetate was added to the mixture, which was sonicated for 1 min to provide a suspension of a light pink solid. The colored impurities were removed by sequential sonication in ethyl acetate and filtration. Additional product was isolated by concentration of the filtrate followed by sonication in ethyl acetate and filtration. Residual solvent was removed under high vacuum. Melting point 190–193 °C; \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 7.36 (d, \(J = 7.5\) Hz, 2H), 7.28 (t, \(J = 7.5\) Hz, 2H), 7.15 (t, \(J = 7.0\) Hz, 1H), 6.85 (br s, 1H), 6.65 (d, \(J = 18.0\) Hz, 1H), 6.24 (d, \(J = 18.0\) Hz, 1H), 3.76–3.80 (m, 2H), 3.66–3.70 (m, 2H), 3.02–3.06 (m, 2H), 2.75–2.77 (m, 2H); \(^{13}\)C NMR (125 MHz, DMSO) \(\delta\) 139.4, 136.1, 128.4, 126.5, 125.7, 62.5, 51.6 (missing boronate carbon); IR (KBr) 3078, 3057, 3021, 2970, 2855, 1621, 1597, 1573, 1494 cm\(^{-1}\).

3-(Trifluoromethyl)-1,1′-biphenyl (14).\(^6\) The reaction was run on a 1.0 mmol scale with 144 \(\mu\)L (1.0 mmol) 3-trifluoromethyliodophenyl and provided 205.3 mg (0.92 mmol) 3-trifluoromethylbiphenyl (92% yield). This reaction was run with 7 mol % Pd(OAc)\(_2\) (15.7 mg, 0.07 mmol) and JohnPhos (25 mg, 0.07 mmol) in THF:H\(_2\)O (5:1, 7.50 mL total). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.85 (s, 1H), 7.77 (d, \(J = 8.0\) Hz, 1H), 7.61 (m, 3H), 7.57 (t, \(J = 7.5\) Hz, 1H), 7.49 (t, \(J = 7.0\) Hz, 2H), 7.41 (t, \(J = 7.0\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 142.2, 139.9, 131.3 (q), 130.6, 129.4, 129.1, 128.2, 127.3, 124.11, 124.09, 124.06.

2,4,6-Triisopropyl-1,1′-biphenyl (15).\(^7\) To a reaction vial equipped with a stir bar was added all solid reactants, including Pd(OAc)\(_2\) (11 mg, 0.05 mmol, 5 mol %), PPh\(_3\) (52 mg, 0.20 mmol, 20 mol %), K\(_3\)PO\(_4\) (575 mg, 2.5 mmol, 2.5 equiv), and phenyl DABO boronate (477 mg, 2.5 mmol, 2.5 equiv). A PFT crimp-on septum cap was then placed on the reaction vial, and the system was evacuated on high vacuum and backfilled with argon twice. 1,4-Dioxane (6.25 mL) and H\(_2\)O (1.25 mL) were added via syringe followed by 2,4,6-triisopropylbromobenzene (0.253 mL, 1.0 mmol, 1.0 equiv). The vial was then placed in a pre-heated heating block at 100 °C. After 38 h, the vial was removed from the heating block and allowed to cool to room temperature. The reaction mixture was filtered through a pad of Celite, rinsing with methylene chloride. The resulting orange/brown solution was concentrated by under reduced pressure to give a viscous liquid. Methanol (5 mL) was added, and a white solid appeared. Vacuum filtration of the solid and rinsing with methanol provided 98 mg of white crystals. Additional product was isolated by concentrating the filtrate under reduced pressure and adding methanol (3 mL). Vacuum filtration of the mixture and rinsing with methanol provided 50 mg more of product. The final yield of 2,4,6-triisopropylbiphenyl was 149 mg, 0.530 mmol (53% yield): \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.38 (t, \(J = 7.0\) Hz, 2H), 7.34 (t, \(J = 7.0\) Hz, 1H), 7.18 (d, \(J = 8.0\) Hz, 2H), 7.06 (s, 2H), 2.94 (quint, \(J = 6.5\) Hz,

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1H), 2.60 (sept, J = 7.0 Hz, 2H), 1.32 (d, J = 6.5 Hz, 6H), 1.08 (d, J = 7.0 Hz, 12H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 148.0, 146.7, 141.1, 137.3, 130.0, 128.1, 126.6, 120.7, 34.5, 30.5, 24.4, 24.3.

2-(4-Methoxyphenyl)benzofuran (16).\(^8\) This reaction conducted run on a 1.44 mmol scale with 270 mg (181 µL, 1.44 mmol) of 4-bromoanisole and provided 313 mg (1.40 mmol) of 2-benzophenone-4-methoxyphenyl (97% yield). It was run using 1 mol % Pd(OAc)\(_2\) (3.3 mg, 0.014 mmol), 4 mol % PPh\(_3\) (15 mg, 0.057 mmol), and 2.5 equiv of Na\(_2\)CO\(_3\) (380 mg, 3.6 mmol) at 70 °C for 21 h in THF:H\(_2\)O (2:1, 15 mL total). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.80 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 7.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.27–7.20 (m, 2H), 6.98 (d, J = 8.5 Hz, 2H), 6.89 (s, 1H), 3.87 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 160.1, 156.2, 154.8, 129.6, 126.6, 123.9, 123.5, 123.0, 120.7, 114.4, 111.1, 99.8, 55.5.

Large-scale procedure for the Suzuki-Miyaura reaction of 2-benzofuran DABO boronate: 2-(4-methoxyphenyl)benzofuran (16).\(^8\) To a 500 mL, 1-neck round bottom flask was added 2-benzofuran DABO boronate (11.4 g, 49.1 mmol), Pd(OAc)\(_2\) (50 mg, 0.223 mmol), PPh\(_3\) (234 mg, 0.892 mmol), and Na\(_2\)CO\(_3\) (11.8 g, 112 mmol). The flask was then fitted with a reflux condenser, and the system was evacuated under high vacuum and refilled with argon twice. Tetrahydrofuran (150 mL) and H\(_2\)O (75 mL) were added to the round bottom followed by 4-bromoanisole (5.60 mL, 44.6 mmol) via syringe. The reaction flask was placed in a pre-heated oil bath at 65 °C. The reaction was stirred and heated for 19 h before cooling to room temperature and transferring to a separatory funnel with ether. The organic layer was separated, and the aqueous layer was extracted twice with ether (2 x 40 mL). The organic layers were combined and washed with brine, dried (MgSO\(_4\)), and concentrated to give a dark brown mixture. Upon the addition of methanol (15 mL), a white solid crashed out and was filtered (7.56 g). Additional material was isolated by concentrating the filtrate, adding a small amount of methanol, and filtration of the resulting solid. The total mass of white solid obtained was 8.90 g (39.7 mmol) of product 17 in 89% yield.

tert-Butyl 2-(4-methoxyphenyl)-1H-indole-1-carboxylate (17).\(^9\) The reaction was run on a 0.50 mmol scale with 94 mg (63 µL, 0.50 mmol) of 4-bromoanisole and provided 157 mg (0.49 mmol) of tert-butyl 2-(4-methoxyphenyl)-1H-indole-1-carboxylate (97% yield). This reaction was run with 7 mol % Pd(OAc)\(_2\) (7.9 mg, 0.035 mmol) and JohnPhos (12 mg, 0.035 mmol) at 70 °C for 6 h. \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 8.18 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.35 (d, J = 8.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 1H), 7.24 (m, 1H), 6.94 (d, J = 7.5 Hz, 2H), 6.51 (s, 1H), 3.86 (s, 3H), 1.37 (s, 9H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 159.4, 150.4, 140.5, 137.4, 130.0, 129.4, 127.6, 124.2, 123.0, 120.4, 115.3, 113.4, 109.6, 83.5, 55.5, 27.8.

Methyl 6,6-dimethyl-2-(trifluoromethylsulfonyloxy)cyclohex-1-enecarboxylate (18). Light yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 3.80 (s, 3H), 2.38 (t, $J = 6.5$ Hz, 2H), 1.83 (quint, $J = 3.5$ Hz, 2H), 1.53–1.50 (m, 2H), 1.20 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 165.9, 147.4, 133.1, 117.8 (q, $J = 315$ Hz), 52.1, 37.3, 35.3, 27.8, 27.3, 18.7; IR (thin film) 2958, 2877, 1739, 1682 cm$^{-1}$; HRMS (ES/MeOH) $m/z$ calcd for C$_{11}$H$_{15}$F$_3$O$_5$SNa (M + Na)$^+$ 339.0490, found 339.0500.

Methyl 2-(furan-2-yl)-6,6-dimethylcyclohex-1-enecarboxylate (19). This reaction was carried out on a 0.304 mmol scale with 92.6 mg (0.304 mmol) of methyl 6,6-dimethyl-2-(trifluoromethylsulfonyloxy)cyclohex-1-enecarboxylate (18) and provided 70.2 mg (0.30 mmol) of methyl 2-(furan-2-yl)-6,6-dimethylcyclohex-1-enecarboxylate (99% yield). This reaction was run with 0.5 mol % of Pd(OAc)$_2$, 10 mol % XPhos in THF:H$_2$O (4:1, 2.2 mL total) for 24 h at 80 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.32 (d, $J = 1.7$ Hz, 1H), 6.34 (dd, $J = 3.2$, 1.7 Hz, 1H), 6.28 (d, $J = 3.5$ Hz, 1H), 3.75 (s, 3H), 2.39 (t, 2H), 1.78 (quint, $J = 6.5$ Hz, 2H), 1.57 (m, 2H), 1.17 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 171.2 (C), 153.4 (C), 142.2 (CH), 135.5 (C), 124.8 (C), 111.1 (CH), 107.7 (CH), 51.6 (CH$_3$), 38.3 (CH$_2$), 33.7 (C), 28.6 (CH$_3$), 26.9 (CH$_2$), 18.7 (CH$_2$); IR (thin film) 3159, 3135, 2962, 2939, 2870, 2854, 1724 cm$^{-1}$; HRMS (ES/MeOH) $m/z$ calcd for C$_{14}$H$_{18}$O$_3$Na (M + Na)$^+$ 257.1154, found 257.1158.

4-(Thiophen-3-yl)pyridine (20). This reaction was run on a 0.50 mmol scale with 82 mg (47 µL, 0.50 mmol) of 3-bromothiophene and provided 75 mg (0.46 mmol) of 4-(thiophen-3-yl)pyridine (92% yield). This reaction was run with 4 mol % Pd$_2$(dba)$_3$ (9.2 mg, 0.01 mmol) and RuPhos (9.3 mmol, 0.02 mmol) and 2.0 equiv K$_3$PO$_4$ (230 mg, 1.0 mmol) in $n$-butanol (2 mL) at 100 °C for 25 h. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.61 (brs, 2H), 7.65 (s, 1H), 7.47 (m, 2H), 7.43 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 150.5, 142.8, 139.6, 127.2, 125.8, 123.2, 120.9.

tert-Butyl 2-(thiophen-3-yl)-1H-pyrrole-1-carboxylate (21). This reaction was run on a 0.50 mmol scale with 82 mg (47 µL, 0.50 mmol) of 3-bromothiophene and provided 81 mg (0.32 mmol) of tert-butyl 2-(thiophen-3-yl)-1H-pyrrole-1-carboxylate (65% yield). This reaction was set up with 7 mol % of Pd(OAc)$_2$ (7.9 mg, 0.035 mmol) and JohnPhos (12 mg, 0.035 mmol) in THF:H$_2$O at 60 °C for 6 h. The product was a clear, colorless oil: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.34 (m, 1H), 7.28–2.24 (m, 2H), 7.10 (d, $J = 4.0$ Hz, 1H), 6.22–6.18 (m, 2H), 1.43 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 149.4, 134.4, 129.9, 129.5, 124.1, 123.0, 122.5, 114.8, 110.6, 83.7, 28.0; IR (thin film) 3151, 3109, 2981, 2935, 2873, 1747 cm$^{-1}$; HRMS (ES/MeOH) $m/z$ calcd for C$_{13}$H$_{15}$NO$_2$SNa (M + Na)$^+$ 272.0721, found 272.0722.

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2-(4-Methoxyphenyl)thiophene (22).\textsuperscript{12} The reaction was set up on a 0.50 mmol scale with 94 mg (63 mL, 0.50 mmol) of 4-bromoanisole and provided 89 mg (0.47 mmol) of 2-(4-methoxyphenyl)thiophene (94% yield). This reaction was run with 7 mol % of Pd(OAc)\textsubscript{2} (8 mg, 0.035 mmol) and JohnPhos (12 mg, 0.035 mmol) in THF:H\textsubscript{2}O at 65 °C for 4 h.\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) $\delta$ 7.53 (d, $J = 8.5$ Hz, 2H), 7.22–7.19 (m, 2H), 7.05 (t, $J = 4.5$ Hz, 1H), 6.91 (d, $J = 8.5$ Hz, 2H), 3.84 (s, 3H); $^{13}$C NMR (125 MHz, CDCl\textsubscript{3}) $\delta$ 159.3, 144.5, 128.1, 127.5, 127.4, 124.0, 122.3, 114.4, 55.5.

(E)-4-Styrylbenzonitrile (23).\textsuperscript{13} This reaction was run on a 0.50 mmol scale with 91 mg (0.50 mmol) of 4-bromobenzonitrile and provided 84 mg (41 mmol) of (E)-4-styrylbenzonitrile (82% yield). This reaction was set up with 5 mol % of Pd(OAc)\textsubscript{2} (5.6 mg, 0.025 mmol) and JohnPhos (8.8 mg, 0.025 mmol) in THF:H\textsubscript{2}O at 100 °C for 7 h. The product was a white solid: $^1$H NMR (500 MHz, CDCl\textsubscript{3}) $\delta$ 7.64 (d, $J = 8.5$ Hz, 2H), 7.58 (d, $J = 8.5$ Hz, 2H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.39 (t, $J = 7.0$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.22 (d, $J = 16.5$ Hz, 1H), 7.09 (d, $J = 16.5$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl\textsubscript{3}) $\delta$ 142.0, 136.4, 132.6, 132.5, 129.0, 128.8, 127.1, 127.0, 126.9, 119.2, 110.7.

(E)-3-Styrylthiophene (24).\textsuperscript{14} This reaction was run on a 0.50 mmol scale with 82 mg (47 µL, 0.50 mmol) of 3-bromothiophene and provided 81 mg (0.43 mmol) of (E)-3-styrylthiophene (87% yield). This reaction was set up with 5 mol % of Pd(OAc)\textsubscript{2} (5.6 mg, 0.025 mmol) and JohnPhos (8.8 mg, 0.025 mmol) in THF:H\textsubscript{2}O at 100 °C for 7 h. The product was a white solid: $^1$H NMR (500 MHz, CDCl\textsubscript{3}) $\delta$ 7.49 (s, 1H), 7.48 (s, 1H), 7.32–7.39 (m, 4H), 7.24–7.27 (m, 2H), 7.13 (d, $J = 16$ Hz, 1H), 6.96 (d, $J = 16$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl\textsubscript{3}) $\delta$ 140.2, 137.5, 128.81, 128.79, 127.6, 126.4, 126.3, 125.0, 123.0, 122.5.

Phenethyl DABO boronate (25). This reaction was run on a 2.3 mmol scale with 0.35 g (2.3 mmol) of phenethylboronic acid and provided 0.22 g (1.0 mmol) of phenethyl DABO boronate as a white solid (44% yield). The boronic acid was dissolved in 1.0 mL ethyl acetate before adding DEA by syringe. After stirring for 20 minutes at room temperature in air, the solution was concentrated to provide a viscous liquid. White solid began to form over the next ten minutes. About 5.0 mL diethyl ether was added, and the mixture was sonotated for 1 min to provide a suspension of white solid. The suspension was filtered to provide the product as a chunky white solid. Residual solvent was removed under high vacuum. Melting point 132–136 °C; $^1$H NMR (500 MHz, CDCl\textsubscript{3}) $\delta$ 7.15–7.33 (m, 5H), 6.14 (br s, 1H), 3.85–3.90 (m, 2H), 3.80–3.83 (m, 2H), 3.10–3.17 (m, 2H), 2.62 (m, 4H), 0.83 (dd, $J = 9.0$, 8.5 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl\textsubscript{3}) $\delta$ 146.5, 128.6, 128.2, 125.7, 63.0, 51.6, 31.7 (missing boronate carbon); IR (KBr) 3119 (br), 3024, 2925, 1601, 1491 cm$^{-1}$.


4-Phenethylbenzonitrile \( (26) \).\textsuperscript{15} This reaction was run on a 0.20 mmol scale, where the limiting reagent is phenethyl DABO boronate \( 25 \) (44 mg, 0.20 mmol), with 40 mg (2.2 mmol) of 4-bromobenzonitrile and provided 21 mg (0.10 mmol) of 4-phenethylbenzonitrile (52% yield). This reaction was set up with 9 mol % of \( \text{PdCl}_2(\text{dppf})\text{CH}_2\text{Cl}_2 \) (15 mg, 0.018 mmol) and \( \text{K}_2\text{CO}_3 \) (83 mg, 0.60 mmol) as the base in THF:H\textsubscript{2}O at 90 °C for 24 h. The product was a clear, colorless liquid: \( ^1\text{H NMR} \) (500 MHz, CDCl\textsubscript{3}) \( \delta \) 7.55 (d, \( J = 8.0 \) Hz, 2H), 7.17–7.32 (m, 5H), 7.12 (d, \( J = 7.5 \) Hz, 2H), 2.99 (m, 2H), 2.92 (m, 2H); \( ^{13}\text{C NMR} \) (125 MHz, CDCl\textsubscript{3}) \( \delta \) 147.4, 140.7, 132.3, 129.5, 128.61, 128.56, 126.4, 119.2, 110.0, 38.1, 37.4.

Z-restored spin-echo 13C spectrum with 1H decoupling
Z-restored spin-echo 13C spectrum with 1H decoupling
Z-restored spin-echo 13C spectrum with 1H decoupling

Br

O

B

NH

3
Z-restored spin-echo 13C spectrum with 1H decoupling
Z–restored spin–echo 13C spectrum with 1H decoupling

[Diagram of a chemical structure with labeled atoms and bonds]

Current Data Parameters

[Text listing acquisition parameters]

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Reilly and Rychnovsky
$\text{Z-restored spin-echo }^{13}\text{C} \text{ spectrum with } 1\text{H decoupling}$
Z–restored spin–echo 13C spectrum with 1H decoupling
Z-restored spin-echo 13C spectrum with 1H decoupling
Z-restored spin-echo 13C spectrum with 1H decoupling

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Z–restored spin-echo 13C spectrum with 1H decoupling

14

Ph

CF₃
1H spectrum
13C spectrum with 1H decoupling

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**Diagram:**

- A chemical structure labeled with atoms and bonds.

**Text:**

- **Reilly and Rychnovsky**

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1H spectrum

Boc

21

N
Z-restored spin-echo 13C spectrum with 1H decoupling
1H spectrum
Z-restored spin-echo 13C spectrum with 1H decoupling