

Decarbonylative Borylation of Aryl Anhydrides via Rhodium Catalysis

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List of Known Compounds/General Methods

All starting materials reported in the manuscript have been prepared according to the method reported previously¹⁻⁸. Unless stated otherwise, all compounds reported in this manuscript have been previously reported. Spectroscopic data matched literature values. All experiments involving palladium were performed using standard Schlenk techniques under argon atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ¹H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ¹H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on Bruker spectrometers at 400 (¹H NMR) and 101 MHz (¹³C NMR). All shifts are reported in parts per million (ppm) relative to residual CHCl₃ peak (7.26 and 77.0 ppm, ¹H NMR and ¹³C NMR, respectively). All coupling constants (*J*) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5973A inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 220 °C, then hold at 220 °C for 15 min (splitless mode of injection, total run time of 22.0 min). High-resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument (for HRMS). Melting point was measured on MeltEMP (laboratory devices). All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions. ¹H NMR and ¹³C NMR data are given for all compounds in the Supporting Information. ¹H NMR, ¹³C NMR and HRMS data are reported for all new compounds.

Experimental Procedures

General Procedure for Anhydride Synthesis.¹ An oven-dried flask (25 mL) equipped with a stir bar was charged with aryl carboxylic acid (typically, 3.0 mmol, 1.0 equiv), triethylamine (typically, 6.0 mmol, 2.0 equiv), dichloromethane (typically, 0.50 M) and placed under a positive pressure of argon. Acyl chloride (typically, 1.0 equiv) was added portions to the reaction mixture with vigorous stirring at room temperature, and the reaction mixture was stirred for 15 h. After the indicated time, the reaction mixture was diluted with dichloromethane (30 mL). The reaction mixture was washed with 5% HCl (1 x 30 mL), 5% NaHCO₃ (1 x 30 mL), and H₂O (1 x 30 mL), dried, and concentrated to get crude product. Unless stated otherwise, the crude product was purified by chromatography on silica gel (ethyl acetate/hexane) to give an analytically pure product.

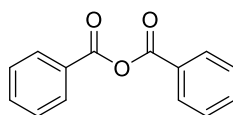
General Procedure for Rhodium-Catalyzed Decarbonylative Borylation of Anhydrides. An oven-dried vial equipped with a stir bar was charged with anhydride substrate (neat, 1.0 equiv), B₂pin₂ (typically, 2.5 equiv), Rh(PPh₃)₃Cl (typically, 2 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. 1,4-Dioxane (typically, 0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C or 120 °C, and stirred for the indicated time at 160 °C or 120 °C. After the indicated time, the reaction mixture was diluted with CH₂Cl₂ (10 mL), filtered, and concentrated. The sample was analyzed by ¹H NMR (CDCl₃, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexanes/ethyl acetate) afforded the title product.

Representative Procedure for Rhodium-Catalyzed Decarbonylative Borylation of Anhydrides. An oven-dried vial equipped with a stir bar was charged with benzoic anhydride (neat, 45.2 mg, 0.20 mmol, 1.0 equiv), B₂pin₂ (127.0 mg, 0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (3.7 mg, 0.004 mmol, 2 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. 1,4-Dioxane (1.0 mL, 0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C or 120 °C, and stirred for 1 h at 160 °C or 15 h at 120 °C. After the indicated time, the

reaction mixture was cooled down to room temperature, diluted with CH₂Cl₂ (10 mL), filtered, and concentrated. A sample was analyzed by ¹H NMR (CDCl₃, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexanes/ethyl acetate) afforded the title product. Yield 86% (35.1 mg, 0.172 mmol). White solid. Characterization data are included in the section below.

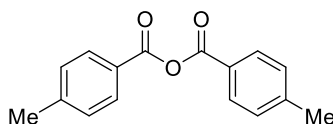
Characterization Data for Starting Materials

Note: All starting materials have been prepared according to the previously published procedure.¹⁻² The yields have not been optimized.



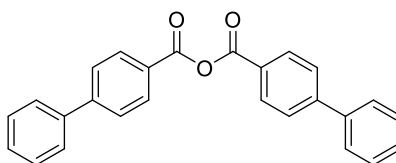
1a

Benzoic anhydride (1a). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.18-8.15 (m, 4H), 7.70-7.66 (m, 2H), 7.53 (t, *J* = 7.7 Hz, 4H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.32, 134.52, 130.53, 128.85, 128.79.



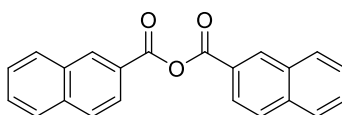
1b

4-Methylbenzoic anhydride (1b).¹ Yield 79% (602.2 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.04 (d, *J* = 8.2 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 2.46 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.51, 145.54, 130.58, 129.53, 126.13, 21.81.



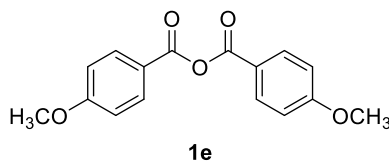
1c

[1,1'-Biphenyl]-4-carboxylic anhydride (1c).² Yield 85% (964.2 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.25 (d, *J* = 8.0 Hz, 4H), 7.76 (d, *J* = 8.1 Hz, 4H), 7.66 (d, *J* = 7.5 Hz, 4H), 7.51 (t, *J* = 7.4 Hz, 4H), 7.46-7.42 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.30, 147.27, 139.50, 131.12, 129.02, 128.54, 127.49, 127.45, 127.32.

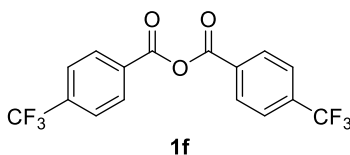


1d

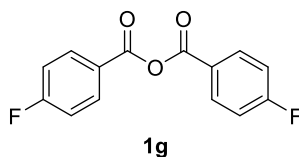
2-Naphthoic anhydride (1d).¹ Yield 90% (880.4 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.78 (s, 2H), 8.21-8.18 (m, 2H), 8.04-7.93 (m, 6H), 7.70-7.68 (m, 2H), 7.63-7.59 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.74, 136.21, 132.80, 132.42, 129.65, 129.23, 128.84, 127.91, 127.12, 126.05, 125.38.



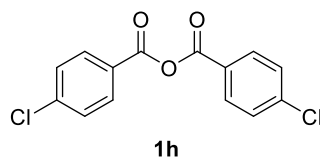
4-Methoxybenzoic anhydride (1e).¹ Yield 81% (695.2 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.10 (d, J = 8.9 Hz, 4H), 6.98 (d, J = 8.9 Hz, 4H), 3.90 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 164.53, 162.25, 132.78, 121.20, 114.09, 55.56.



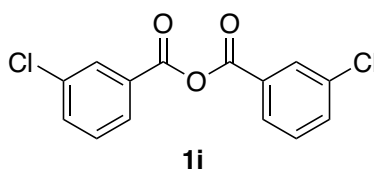
4-(Trifluoromethyl)benzoic anhydride (1f).¹ Yield 76% (830.4 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.28 (d, J = 8.2 Hz, 4H), 7.82 (d, J = 8.2 Hz, 4H). **¹³C NMR (101 MHz, CDCl₃)** δ 160.75, 136.09 (q, J = 33.3 Hz), 131.65, 130.95, 126.05 (q, J = 3.7 Hz), 123.28 (q, J = 273.7 Hz). **¹⁹F NMR (376 MHz, CDCl₃)** δ -63.24.



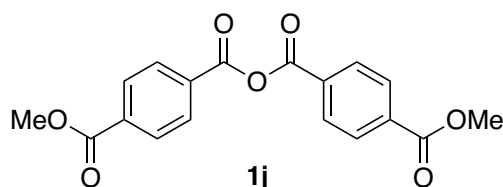
4-Fluorobenzoic anhydride (1g).¹ Yield 78% (613.2 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.19-8.15 (m, 4H), 7.21 (t, J = 8.5 Hz, 4H). **¹³C NMR (101 MHz, CDCl₃)** δ 116.70 (d, J = 258.6 Hz), 161.18, 133.29 (d, J = 10.1 Hz), 124.95 (d, J = 3.0 Hz), 116.26 (d, J = 22.2 Hz). **¹⁹F NMR (376 MHz, CDCl₃)** δ -101.94.



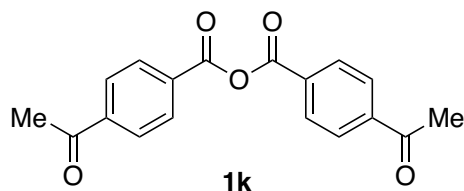
4-Chlorobenzoic anhydride (1h).¹ Yield 82% (723.2 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.07 (d, $J = 8.4$ Hz, 4H), 7.51 (d, $J = 8.4$ Hz, 4H). **¹³C NMR (101 MHz, CDCl₃)** δ 161.27, 141.40, 131.86, 129.35, 127.04.



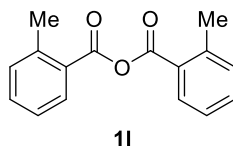
3-Chlorobenzoic anhydride (1i).¹ Yield 85% (749.7 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.11 (t, $J = 1.8$ Hz, 2H), 8.05-8.02 (m, 2H), 7.68-7.65 (m, 2H), 7.49 (t, $J = 7.9$ Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 160.82, 135.16, 134.73, 130.45, 130.26, 130.23, 128.65.



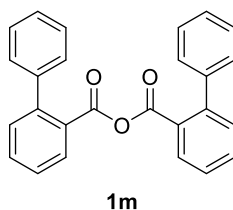
4-(Methoxycarbonyl)benzoic anhydride (1j).¹ Yield 77% (790.2 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.21 (d, $J = 8.5$ Hz, 4H), 8.17 (d, $J = 8.5$ Hz, 4H), 3.97 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 165.78, 161.20, 135.38, 132.12, 130.46, 129.96, 52.62.



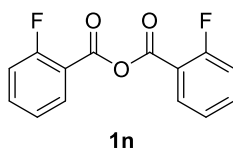
4-Acetylbenzoic anhydride (1k).¹ Yield 71% (660.5 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.23 (d, $J = 8.5$ Hz, 4H), 8.08 (d, $J = 8.5$ Hz, 4H), 2.67 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 197.19, 161.15, 141.40, 132.03, 130.76, 128.59, 26.91.



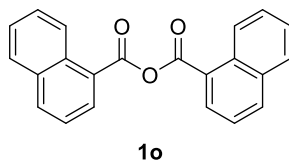
2-Methylbenzoic anhydride (1l).¹ Yield 70% (533.6 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.06-8.05 (m, 2H), 7.51 (t, *J* = 8.1 Hz, 2H), 7.35-7.30 (m, 4H), 2.71 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.88, 142.56, 133.57, 132.20, 131.39, 127.69, 126.06, 21.98.



[1,1'-Biphenyl]-2-carboxylic anhydride (1m).³ Yield 84% (952.9 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.54 (t, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.38-7.29 (m, 14H). **¹³C NMR (101 MHz, CDCl₃)** δ 163.17, 143.60, 140.52, 132.46, 131.06, 131.01, 128.57, 128.19, 127.45, 127.12.

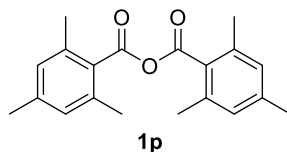


2-Fluorobenzoic anhydride (1n).¹ Yield 81% (636.8 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.10-8.06 (m, 2H), 7.67-7.62 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.18 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.53 (d, *J* = 264.6 Hz), 159.34 (d, *J* = 2.0 Hz), 136.32 (d, *J* = 9.1 Hz), 132.92, 124.45 (d, *J* = 4.0 Hz), 117.46 (d, *J* = 1.0 Hz), 117.18 (d, *J* = 13.1 Hz). **¹⁹F NMR (376 MHz, CDCl₃)** δ -107.52.

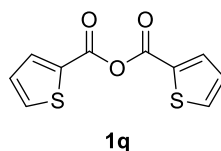


1-Naphthoic anhydride (1o).¹ Yield 88% (860.9 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 9.16 (d, *J* = 8.1 Hz, 2H), 8.45-8.43 (m, 2H), 8.15 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 2H),

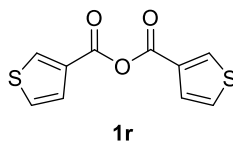
7.74-7.69 (m, 2H), 7.63-7.59 (m, 2H), 7.58-7.55 (m, 2H). **^{13}C NMR (101 MHz, CDCl_3)** δ 162.92, 135.53, 133.93, 132.10, 131.87, 128.81, 128.79, 126.76, 125.63, 124.85, 124.45.



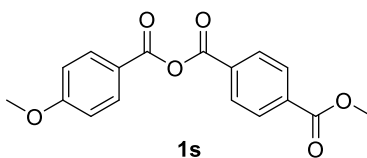
2,4,6-Trimethylbenzoic anhydride (1p).⁴ Yield 60% (558.3 mg). White solid. **^1H NMR (400 MHz, CDCl_3)** δ 6.88 (s, 4H), 2.40 (s, 12H), 2.29 (s, 6H). **^{13}C NMR (101 MHz, CDCl_3)** δ 165.36, 140.73, 136.28, 135.89, 128.83, 21.17, 20.04.



Thiophene-2-carboxylic anhydride (1q).¹ Yield 84% (599.7 mg). White solid. **^1H NMR (400 MHz, CDCl_3)** δ 7.99-7.98 (m, 2H), 7.75-7.74 (m, 2H), 7.21-7.19 (m, 2H). **^{13}C NMR (101 MHz, CDCl_3)** δ 156.61, 136.02, 135.31, 131.99, 128.44.

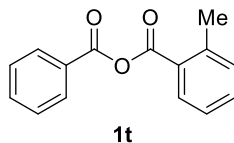


Thiophene-3-carboxylic anhydride (1r).⁵ Yield 87% (621.1 mg). White solid. **^1H NMR (400 MHz, CDCl_3)** δ 8.30 (d, $J = 3.0$ Hz, 2H), 7.62 (d, $J = 5.1$ Hz, 2H), 7.41-7.38 (m, 2H). **^{13}C NMR (101 MHz, CDCl_3)** δ 157.50, 135.56, 132.15, 128.13, 126.97.

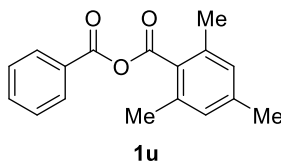


4-Methoxybenzoic 4-(methoxycarbonyl)benzoic anhydride (1s).⁶ Yield 81% (763.2 mg). White solid. **^1H NMR (400 MHz, CDCl_3)** δ 8.21 (d, $J = 8.7$ Hz, 2H), 8.17 (d, $J = 8.7$ Hz, 2H), 8.09 (d, $J = 9.0$ Hz, 2H), 6.99 (d, $J = 9.0$ Hz, 2H), 3.97 (s, 3H), 3.90 (s, 3H). **^{13}C NMR (101**

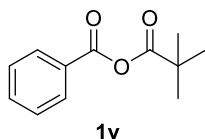
MHz, CDCl₃ δ 165.93, 161.81, 161.62, 135.05, 132.97, 132.70, 130.34, 129.87, 120.62, 114.26, 114.09, 55.61, 52.58.



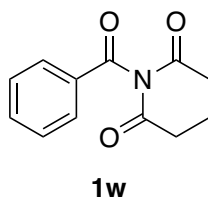
Benzoic 2-methylbenzoic anhydride (1t).¹ Yield 70% (504.2 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.18-8.14 (m, 2H), 8.07 (d, $J = 7.9$ Hz, 1H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.55-7.49 (m, 3H), 7.35-7.32 (m, 2H), 2.72 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.69, 162.42, 142.63, 134.37, 133.69, 132.23, 131.40, 130.46, 128.94, 128.79, 127.54, 126.05, 21.98.



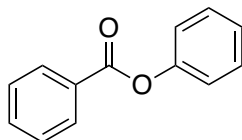
Benzoic 2,4,6-trimethylbenzoic anhydride (1u).¹ Yield 77% (619.3 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.15-8.13 (m, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 2H), 6.90 (s, 2H), 2.43 (s, 6H), 2.31 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 175.85, 172.31, 140.03, 136.07, 133.81, 130.19, 129.34, 129.29, 128.76, 128.48, 21.13, 20.28.



Benzoic pivalic anhydride (1v).¹ Yield 87% (537.9 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.04 (d, $J = 7.1$ Hz, 2H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.49 (t, $J = 7.8$ Hz, 2H), 1.37 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 173.74, 162.47, 134.30, 130.34, 128.74, 40.31, 26.56.

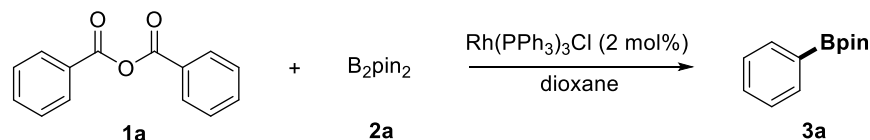


1-Benzoylpiperidine-2,6-dione (1w).¹ Yield 78% (507.9 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.86 (d, J = 7.8 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 2.74 (t, J = 6.5 Hz, 4H), 2.13-2.09 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 171.98, 170.81, 134.94, 131.67, 130.09, 129.09, 32.28, 17.39.

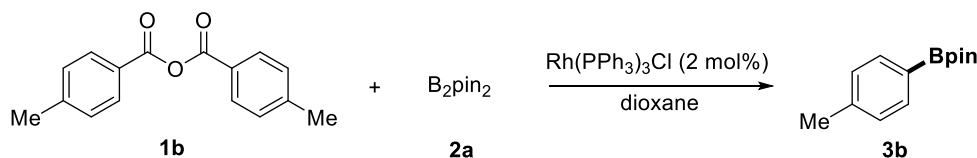
**1x**

Phenyl benzoate (1x). Yield 90% (534.8 mg).⁶ White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.23-8.21 (m, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 7.44 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 7.26-7.22 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 165.19, 150.93, 133.56, 130.15, 129.54, 129.47, 128.55, 125.87, 121.70.

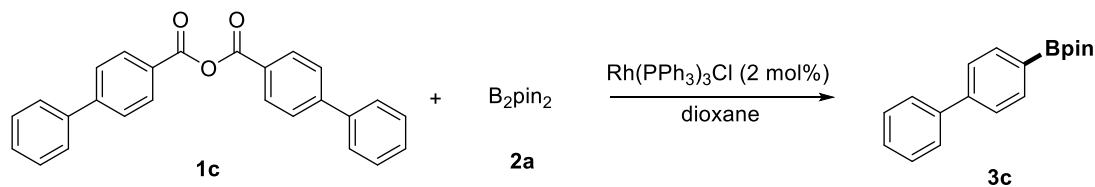
Characterization Data for Desired Products

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (Scheme 1, 3a)¹

According to the general procedure, the reaction of benzoic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 86% yield (35.1 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.81 (d, *J* = 7.1 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 1.35 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 134.72, 131.24, 127.69, 83.76, 24.86.

4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (Scheme 1, 3b)¹

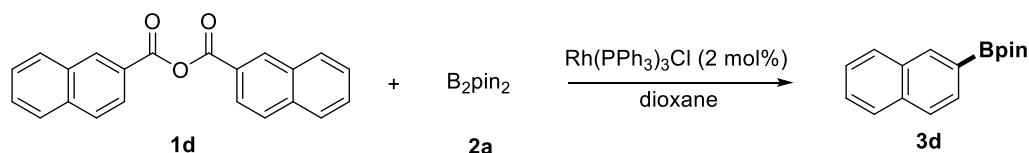
According to the general procedure, the reaction of 4-methylbenzoic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 81% yield (35.3 mg) or 73% yield (31.8 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.70 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 1.34 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 141.39, 134.78, 128.50, 83.60, 24.84, 21.71.

2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3c)⁷

According to the general procedure, the reaction of [1,1'-biphenyl]-4-carboxylic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-

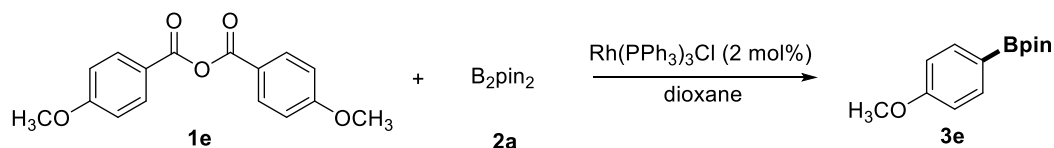
dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 88% yield (49.3 mg) or 83% yield (46.5 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.63-7.61 (m, 4H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 1.37 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 143.87, 140.99, 135.23, 128.75, 127.54, 127.22, 126.45, 83.81, 24.86.

4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (Scheme 1, 3d)¹



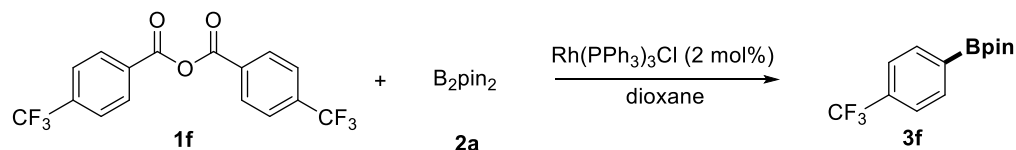
According to the general procedure, the reaction of 2-naphthoic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 89% yield (45.2 mg) or 81% yield (41.2 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.38 (s, 1H), 7.90-7.88 (m, 1H), 7.86-7.83 (m, 3H), 7.54-7.46 (m, 2H), 1.40 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 136.22, 135.00, 132.78, 130.37, 128.63, 127.68, 126.96, 125.77, 83.91, 24.91.

2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3e)¹



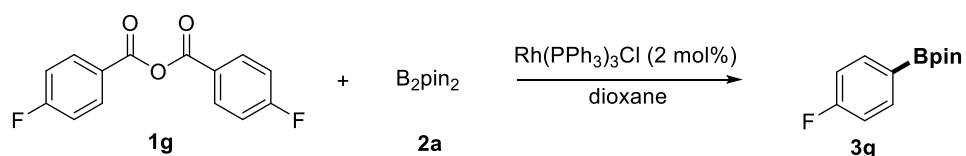
According to the general procedure, the reaction of 4-methoxybenzoic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 87% yield (40.7 mg) or 75% yield (35.1 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.75 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 1.33 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.12, 136.49, 113.29, 55.08, 24.84.

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (Scheme 1, 3f)¹



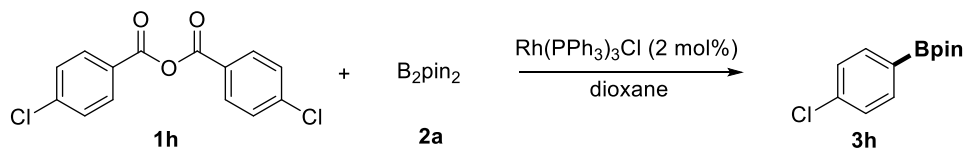
According to the general procedure, the reaction of 4-(trifluoromethyl)benzoic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 78% yield (42.5 mg) or 79% yield (43.0 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.9 Hz, 2H), 1.36 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 134.99, 132.80 (q, *J* = 32.3 Hz), 124.30 (q, *J* = 3.7 Hz), 124.12 (q, *J* = 273.7 Hz), 84.26, 24.84. **¹⁹F NMR (376 MHz, CDCl₃)** δ -63.90.

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3g)¹



According to the general procedure, the reaction of 4-fluorobenzoic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 85% yield (37.8 mg) or 84% yield (37.3 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.81-7.78 (m, 2H), 7.07-7.02 (m, 2H), 1.34 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 165.07 (d, *J* = 251.5 Hz), 136.95 (d, *J* = 9.1 Hz), 114.83 (d, *J* = 20.2 Hz), 83.89, 24.85. **¹⁹F NMR (376 MHz, CDCl₃)** δ -108.34.

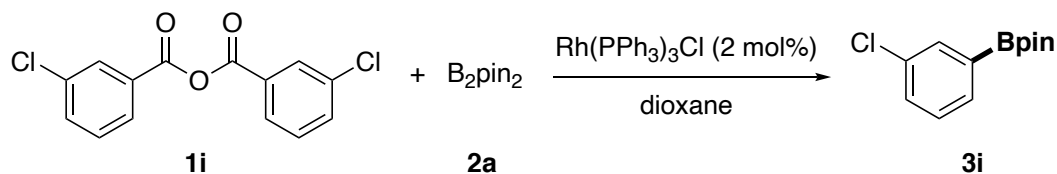
2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3h)¹



According to the general procedure, the reaction of 4-chlorobenzoic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title

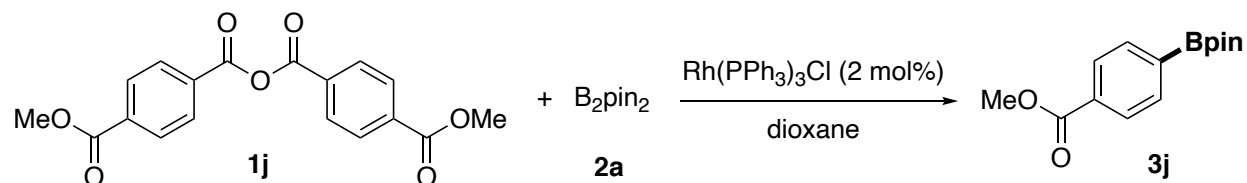
compound in 87% yield (37.8 mg) or 85% yield (37.3 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 1.34 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 137.51, 136.10, 127.99, 83.99, 24.84.

2-(3-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3i)¹



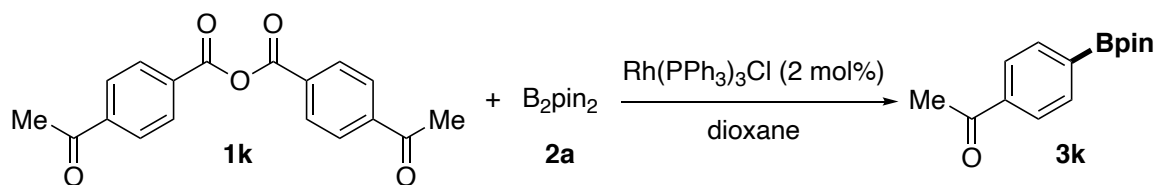
According to the general procedure, the reaction of 3-chlorobenzoyl anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 78% yield (37.1 mg) or 76% yield (36.2 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.78 (s, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 10.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 1.34 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 134.54, 134.01, 132.62, 131.26, 129.17, 84.13, 24.83.

Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Scheme 1, 3j)¹



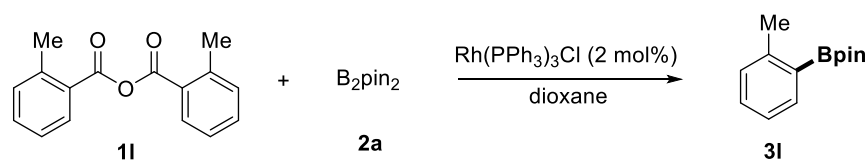
According to the general procedure, the reaction of 4-(methoxycarbonyl)benzoic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 91% yield (47.7 mg) or 86% yield (45.1 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 2H), 3.92 (s, 3H), 1.35 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 167.13, 134.63, 132.26, 128.57, 52.14, 24.86.

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (Scheme 1, 3k)¹



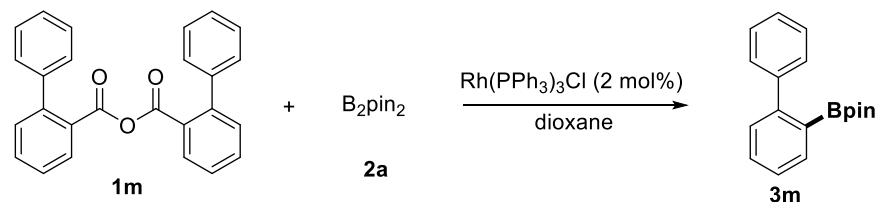
According to the general procedure, the reaction of 4-acetylbenzoic anhydride (0.20 mmol, 1.0 equiv), B_2pin_2 (0.50 mmol, 2.5 equiv), $Rh(PPh_3)_3Cl$ (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 81% yield (39.9 mg) or 78% yield (38.4 mg). White solid. **1H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, $J = 8.3$ Hz, 2H), 7.89 (d, $J = 8.3$ Hz, 2H), 2.62 (s, 3H), 1.36 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.52, 138.96, 134.90, 127.28, 84.21, 26.77, 24.86.

4,4,5,5-Tetramethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (Scheme 1, **3l**)¹



According to the general procedure, the reaction of 2-methylbenzoic anhydride (0.20 mmol, 1.0 equiv), B_2pin_2 (0.50 mmol, 2.5 equiv), $Rh(PPh_3)_3Cl$ (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 76% yield (33.2 mg) or 72% yield (31.4 mg). White solid. **1H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, $J = 6.8$ Hz, 1H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.16 (t, $J = 6.8$ Hz, 2H), 2.54 (s, 3H), 1.34 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.81, 135.82, 130.77, 129.75, 124.68, 83.39, 24.87, 22.20.

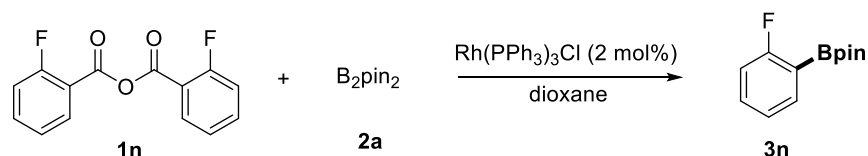
2-([1,1'-Biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, **3m**)⁸



According to the general procedure, the reaction of [1,1'-biphenyl]-2-carboxylic anhydride (0.20 mmol, 1.0 equiv), B_2pin_2 (0.50 mmol, 2.5 equiv), $Rh(PPh_3)_3Cl$ (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and

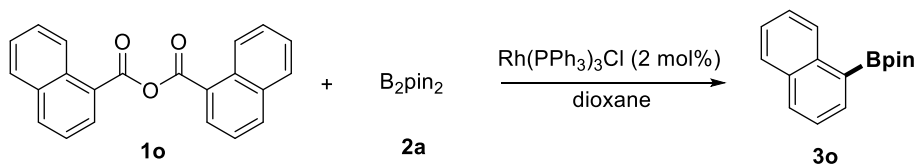
chromatography the title compound in 89% yield (49.9 mg) or 79% yield (44.2 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.72 (d, *J* = 7.3 Hz, 1H), 7.47-7.34 (m, 8H), 1.21 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 147.47, 143.21, 134.41, 130.05, 129.10, 128.94, 127.75, 126.81, 126.25, 83.71, 24.56.

2-(2-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3n)¹

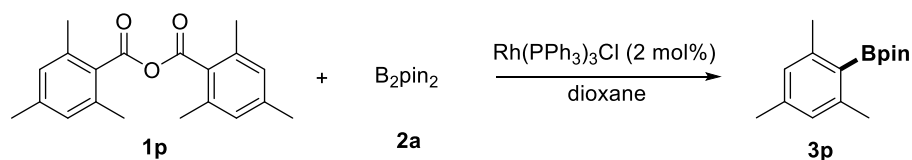


According to the general procedure, the reaction of 2-fluorobenzoic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 86% yield (38.2 mg) or 88% yield (39.1 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.74 (t, *J* = 6.7 Hz, 1H), 7.45-7.40 (m, 1H), 7.13 (t, *J* = 7.1 Hz, 1H), 7.03 (t, *J* = 8.6 Hz, 1H), 1.36 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 167.17 (d, *J* = 251.5 Hz), 136.80 (d, *J* = 8.1 Hz), 133.26 (d, *J* = 8.1 Hz), 123.58 (d, *J* = 3.0 Hz), 115.24 (d, *J* = 24.2 Hz), 83.88, 24.81. **¹⁹F NMR (376 MHz, CDCl₃)** δ -102.54.

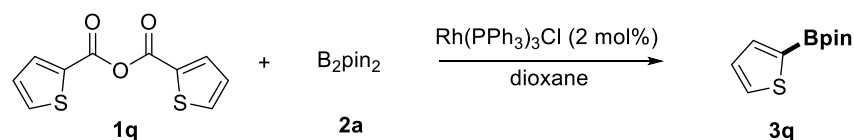
4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (Scheme 1, 3o)¹



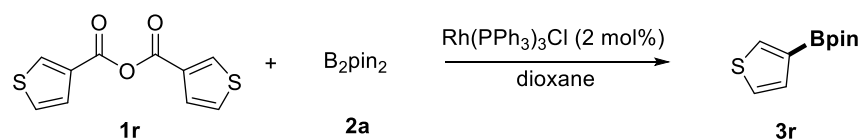
According to the general procedure, the reaction of 1-naphthoic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 81% yield (41.2 mg) or 67% yield (34.1 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.77 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 6.9 Hz, 1H), 7.49-7.46 (m, 2H), 1.43 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 136.88, 135.61, 133.17, 131.58, 128.38, 128.32, 126.31, 125.46, 124.94, 83.71, 24.95.

2-Mesityl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3p)⁷

According to the general procedure, the reaction of 2,4,6-trimethylbenzoic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 45% yield (22.2 mg) or 44% yield (21.7 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 6.77 (s, 2H), 2.36 (s, 6H), 2.24 (s, 3H), 1.37 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 142.09, 138.90, 127.41, 83.44, 24.93, 22.16, 21.22.

4,4,5,5-Tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (Scheme 1, 3q)¹

According to the general procedure, the reaction of thiophene-2-carboxylic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 71% yield (29.8 mg) or 78% yield (32.8 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.66-7.63 (m, 2H), 7.21-7.19 (m, 1H), 1.35 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 137.15, 132.36, 128.21, 84.08, 24.75.

4,4,5,5-Tetramethyl-2-(thiophen-3-yl)-1,3,2-dioxaborolane (Scheme 1, 3r)⁷

According to the general procedure, the reaction of thiophene-3-carboxylic anhydride (0.20 mmol, 1.0 equiv), B₂pin₂ (0.50 mmol, 2.5 equiv), Rh(PPh₃)₃Cl (0.004 mmol, 2 mol%) in 1,4-dioxane (0.20 M) for 1 h at 160 °C or 15 h at 120 °C, afforded after work-up and chromatography the title compound in 98% yield (41.2 mg) or 95% yield (39.9 mg). White solid.

¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 2.7 Hz, 1H), 7.41 (d, *J* = 5.8 Hz, 1H), 7.35-7.33 (m, 1H), 1.34 (s, 12H). **¹³C NMR (101 MHz, CDCl₃)** δ 136.44, 131.99, 125.31, 83.64, 24.81.

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