

Supporting Information for:

Nickel-Catalyzed Decarboxylative Arylation of Azoles with Perfluoro- and Nitrobenzoates

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General Procedures: NMR spectra were obtained on a Bruker 400 (399.96 MHz for ^1H ; 100.57 MHz for ^{13}C) spectrometer. ^1H NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet of doublets (td), triplet (t), doublet of triplets (dt), doublet of multiplets (dm), multiplet (m), and broad resonance (br). IR spectra were obtained on a Thermo scientific Nicolet iS5 iD5 ATR spectrometer. Only the medium to strong peaks in the IR spectra are reported. Melting points were obtained on a Thomas Hoover melting point apparatus.

Materials and Methods: 5-methyl benzoxazole, 5-chloro benzoxazole, Li_2CO_3 , anhydrous DMA, and anhydrous diglyme were obtained from Aldrich and used as received. 6-nitrobenzoxazole was obtained from Matrix Scientific and used as received. $\text{Ni}(\text{OTf})_2$ and AgOTf were obtained from Strem Chemicals and used as received. 6-methoxy benzoxazole,¹ 4-nitrophenyloxazole² and the benzoates³ were prepared using literature procedures. Other solvents were obtained from Fisher Chemical or VWR Chemical and used without further purification. Flash chromatography was performed on EM Science silica gel 60 (0.040–0.063 mm particle size, 230–400 mesh) and thin layer chromatography was performed on Analtech TLC plates pre-coated with silica gel 60 F₂₅₄.

General procedures

General Procedure for synthesis of potassium benzoate salts

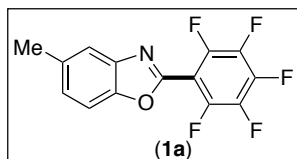
Benzoate salts were prepared using literature procedures.³ To a solution of benzoic acid (1 equiv, 17 mmol) derivative in anhydrous ethanol (17 mL) was added a solution of potassium tert-butoxide (1 equiv, 17 mmol) (in anhydrous ethanol, 17 mL) under a nitrogen atmosphere. The resulting mixture was allowed to stir at room temperature for 1.5 hours. The reaction mixture was concentrated to about half the volume on a rotary evaporator. The solution was cooled to 0 °C and the immediate precipitate was collected using suction filtration. The collected benzoate salt was washed with ice-cold ether (2 x 10 mL) and ice-cold ethanol (2 x 5 mL) sequentially. The salt was then dried under high vacuum and analyzed by NMR spectroscopy prior to use.

General Procedure for C–H Arylations (Schemes 3-5):

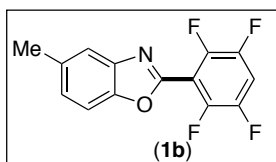
Perfluorobenzoate or nitrobenzoate was weighed into an oven dried 20 mL scintillation vial. The vial was taken into the glove box andazole, $\text{Ni}(\text{OTf})_2$, Li_2CO_3 , AgOTf and anhydrous solvent

(diglyme or DMA/diglyme) were added. The vial was sealed with a Teflon lined cap, taken out of the glove box and the reaction mixture was allowed to stir at the indicated temperature for the indicated time. The reaction mixture was cooled to room temperature and filtered through a 1.5/1.5 inch plug of silica gel (top)/celite (bottom), eluting with EtOAc (100 mL). The crude product was concentrated and chromatographed on a silica gel column to afford the product.

Procedures and Spectral Characterization of Arylation Products in Scheme 3

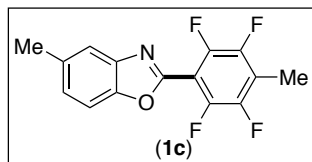


Following general procedure, pentafluorophenyl potassium carboxylate (375 mg, 1.50 mmol, 3.0 equiv), 5-methylbenzoxazole (66.6 mg, 0.500 mmol, 1.0 equiv), Ni(OTf)₂ (2.68 mg, 0.0075 mmol, 0.015 equiv), Li₂CO₃ (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), and anhydrous diglyme (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 20 h. Chromatography on a silica gel column using 2/98 EtOAc/hexanes (*R_f* = 0.27 in 2% EtOAc/98% hexanes) yielded product **1a** as a light yellow solid (61.6 mg, 41% yield). mp = 114-115 °C. ¹H NMR (CDCl₃): δ 7.65 (s, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 2.51 (s, 3H). ¹³C NMR (CDCl₃): δ 152.3 (m), 148.7, 145.6 (dm, *J_{C-F}* = 258 Hz), 142.8 (dm, *J_{C-F}* = 258 Hz), 141.3, 138.1 (dm, *J_{C-F}* = 249 Hz), 135.2, 127.8, 120.6, 110.3, 104.2 (td, *J_{C-F}* = 14, 4 Hz), 21.5. ¹⁹F NMR (CDCl₃): δ -136.8, -148.7, -160.3. IR (neat): 2929, 1522, 1516, 1492, 1476, 1418, 1182, 1143, 1107, 1081, 1013, 996, 950, 861, 816, 808, 802, 745 cm⁻¹. HRMS [M+H⁺] Calcd for C₁₄H₆F₅NO 300.0442; Found: 300.0452.

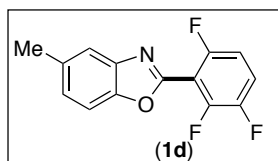


Following general procedure, 2,3,5,6-tetrafluorophenyl potassium carboxylate (348 mg, 1.50 mmol, 3.0 equiv), 5-methylbenzoxazole (66.6 mg, 0.500 mmol, 1.0 equiv), Ni(OTf)₂ (2.68 mg, 0.0075 mmol, 0.015 equiv), Li₂CO₃ (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), and anhydrous diglyme (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 20 h. Chromatography on a silica gel column using 6/94 EtOAc/hexanes (*R_f* = 0.32 in 6% EtOAc/94% hexanes) yielded product **1b** as a white solid (60.9 mg, 43% yield). mp = 108-109 °C. ¹H NMR (CDCl₃): δ 7.67 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.32-7.23 (multiple peaks, 2H), 2.52 (s, 3H). ¹³C NMR (CDCl₃): δ 153.0 (t, *J_{C-F}* =

3.7 Hz), 148.8, 146.2 (dm, $J_{C-F} = 240$ Hz), 145.0 (dm, $J_{C-F} = 251$ Hz), 141.3, 135.1, 127.8, 120.7, 110.4, 109.2 (t, $J_{C-F} = 13$ Hz), 108.5 (t, $J_{C-F} = 22$ Hz), 21.5. ^{19}F NMR (CDCl_3): δ -137.4, -137.8. IR (neat): 3059, 3031, 1498, 1447, 944, 933, 711 cm^{-1} . HRMS [M^+] Calcd for $\text{C}_{14}\text{H}_7\text{F}_4\text{NO}$ 281.0464; Found: 281.0464.

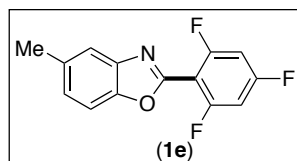


Following general procedure, 2,3,5,6-tetrafluoro-4-toluic potassium carboxylate (369 mg, 1.50 mmol, 3.0 equiv), 5-methylbenzoxazole (66.6 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (2.7 mg, 0.0075 mmol, 0.015 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), and anhydrous diglyme (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 $^\circ\text{C}$ for 20 h. Chromatography on a silica gel column using 8/92 EtOAc/hexanes ($R_f = 0.47$ in 8% EtOAc/92% hexanes) yielded product **1c** as a pale yellow solid (73.8 mg, 50% yield). ^1H NMR (CDCl_3): δ 7.65 (s, 1H), 7.51 (d, $J = 8.4$ Hz, 1H), 7.24 (dd, $J = 8.3, 1.6$ Hz, 1H), 2.50 (s, 3H), 2.37 (t, $J = 2.2$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 153.5 (t, $J_{C-F} = 4.2$ Hz), 148.7, 145.4 (dm, $J_{C-F} = 244$ Hz), 144.9 (ddt, $J_{C-F} = 256, 16, 4$ Hz), 141.4, 134.9, 127.5, 120.5, 119.6 (t, $J_{C-F} = 19$ Hz), 110.3, 105.8 (t, $J_{C-F} = 13.5$ Hz), 21.5, 8.11-7.95 (m). ^{19}F NMR (CDCl_3): δ -139.5, -142.3. HRMS [$\text{M}+\text{H}^+$] Calcd for $\text{C}_{15}\text{H}_9\text{F}_4\text{NO}$ 296.0699; Found: 296.0700.

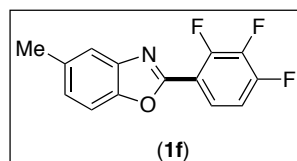


Following general procedure, 2,3,6-trifluorophenyl potassium carboxylate (321 mg, 1.50 mmol, 3.0 equiv), 5-methylbenzoxazole (66.6 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (2.7 mg, 0.0075 mmol, 0.015 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL) and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 $^\circ\text{C}$ for 20 h. Chromatography on a silica gel column using 5/95 EtOAc/hexanes ($R_f = 0.24$ in 5% EtOAc/95% hexanes) yielded product **1d** as a white solid (71.4 mg, 54% yield). mp = 105-106 $^\circ\text{C}$. ^1H NMR (CDCl_3): δ 7.66 (s, 1H), 7.52 (d, $J = 8.4$ Hz, 1H), 7.38-7.30 (m, 1H), 7.26-7.24 (m, 1H), 7.08-7.02 (m, 1H), 2.51 (s, 3H). ^{13}C NMR (CDCl_3): δ 156.3 (dt, $J_{C-F} = 254, 3.5$ Hz), 153.9-153.8 (m), 149.1 (ddd, $J_{C-F} = 260, 15, 6.1$ Hz), 148.7, 147.3 (ddd, $J_{C-F} = 245, 12, 3.6$ Hz), 141.4, 134.8, 127.3, 120.5, 119.5 (dd, $J_{C-F} = 20, 10$ Hz), 112.0-111.6 (m), 110.2, 108.1 (dd, $J_{C-F} = 17,$

12 Hz), 21.5. ^{19}F NMR (CDCl_3): δ -113.5, -131.7, -140.6. IR (neat): 3101, 3041, 1492, 1449, 1239, 1023, 1006, 884, 822, 734 cm^{-1} . HRMS [$\text{M}+\text{H}^+$] Calcd for $\text{C}_{14}\text{H}_8\text{F}_3\text{NO}$ 264.0636; Found: 264.0638.

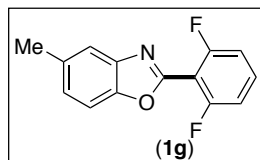


Following general procedure, 2,4,6-trifluorophenyl potassium carboxylate (321 mg, 1.50 mmol, 3.0 equiv), 5-methylbenzoxazole (66.6 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (8.9 mg, 0.025 mmol, 0.05 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 20 h. Chromatography on a silica gel column using 5/95 EtOAc/hexanes (R_f = 0.25 in 5% EtOAc/95% hexanes) yielded product **1e** as a pale yellow solid (62.3 mg, 47% yield). mp = 111-112 °C. ^1H NMR (CDCl_3): δ 7.64 (s, 1H), 7.50 (d, J = 8.3 Hz, 1H), 7.23 (d, J = 8.3 Hz, 1H), 6.87 (t, J = 8.4 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (CDCl_3): δ 164.1 (dt, $J_{\text{C-F}}$ = 254, 15 Hz), 161.7 (ddd, $J_{\text{C-F}}$ = 259, 15, 8.4 Hz), 154.1 (t, $J_{\text{C-F}}$ = 3.8 Hz), 148.7, 141.4, 134.7, 127.0, 120.3, 110.1, 103.5 (td, $J_{\text{C-F}}$ = 16, 5 Hz), 101.5 (td, $J_{\text{C-F}}$ = 26, 4 Hz), 21.5. ^{19}F NMR (CDCl_3): δ -101.8, -104.7. IR (neat): 3075, 2928, 1644, 1609, 1597, 1480, 1460, 1441, 1354, 1180, 1127, 1041, 1005, 867, 843, 825, 802 cm^{-1} . HRMS [$\text{M}+\text{H}^+$] Calcd for $\text{C}_{14}\text{H}_8\text{F}_3\text{NO}$ 264.0636; Found: 264.0636.

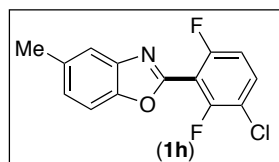


Following general procedure, 2,3,4-trifluorophenyl potassium carboxylate (321 mg, 1.50 mmol, 3.0 equiv), 5-methylbenzoxazole (66.6 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (8.93 mg, 0.025 mmol, 0.05 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 20 h. Chromatography on a silica gel column using 4/96 EtOAc/hexanes (R_f = 0.22 in 4% EtOAc/96% hexanes) yielded product **1f** as a light yellow solid (91.4 mg, 70% yield). mp = 109-111 °C. ^1H NMR (CDCl_3): δ 8.01-7.95 (m, 1H), 7.60 (s, 1H), 7.49 (d, J = 8.2 Hz, 1H), 7.22 (d, J = 8.3 Hz, 1H), 7.17-7.10 (m, 1H), 2.50 (s, 3H). ^{13}C NMR (CDCl_3): δ 157.8 (m), 152.9 (ddd, $J_{\text{C-F}}$ = 255, 9.8, 2.7 Hz), 150.3 (ddd, $J_{\text{C-F}}$ = 262, 11, 3.1), 148.7, 141.6, 140.7 (dt, $J_{\text{C-F}}$ = 251, 15), 134.9, 127.0, 124.2-124.1 (m), 120.3, 113.5 (dd, $J_{\text{C-F}}$ = 8.0, 3.7 Hz), 112.8 (dd, $J_{\text{C-F}}$ = 18, 4 Hz), 110.1,

21.5. ^{19}F NMR (CDCl_3): δ -128.5, -131.1, -158.5. IR (neat): 3085, 2926, 1487, 1282, 1262, 1179, 1031, 945, 889, 805, 797 cm^{-1} . HRMS [M^+] Calcd for $\text{C}_{14}\text{H}_8\text{F}_3\text{NO}$ 263.0558; Found: 263.0557.



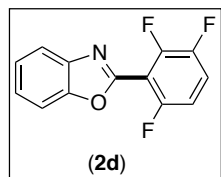
Following general procedure, 2,6-difluorophenyl potassium carboxylate (294 mg, 1.50 mmol, 3.0 equiv), 5-methylbenzoxazole (66.6 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (17.8 mg, 0.05 mmol, 0.10 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 $^\circ\text{C}$ for 20 h. Chromatography on a silica gel column using 4/96 EtOAc/hexanes (R_f = 0.21 in 4% EtOAc/96% hexanes) yielded product **1g** as a white solid (58.7 mg, 48% yield). mp = 72-73 $^\circ\text{C}$. ^1H NMR (CDCl_3): δ 7.65 (s, 1H), 7.52-7.47 (multiple peaks, 2H), 7.23 (d, J = 8.1 Hz, 1H), 7.10 (t, J = 8.6 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (CDCl_3): δ 161.1 (dd, $J_{\text{C-F}}$ = 257, 5.2 Hz), 154.7 (t, $J_{\text{C-F}}$ = 3.6 Hz), 148.7, 141.5, 134.5, 132.6 (t, $J_{\text{C-F}}$ = 11 Hz), 126.9, 120.3, 112.4-112.2 (m), 110.1, 106.5 (t, $J_{\text{C-F}}$ = 16 Hz), 21.4. ^{19}F NMR (CDCl_3): δ -108.4. IR (thin film, CH_2Cl_2): 3066, 2922, 1627, 1583, 1470, 1453, 1231, 1200, 1044, 1006, 929, 828, 789, 743, 689, 594, 566 cm^{-1} .



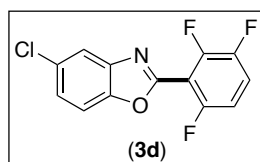
Following general procedure, 3-chloro-2,6-difluorophenyl potassium carboxylate (346 mg, 1.50 mmol, 3.0 equiv), 5-methylbenzoxazole (66.6 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (2.68 mg, 0.0075 mmol, 0.015 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 $^\circ\text{C}$ for 20 h. Chromatography on a silica gel column using 5/95 EtOAc/hexanes (R_f = 0.27 in 5% EtOAc/95% hexanes) yielded product **1h** as a white solid (72.1 mg, 52% yield). mp = 114-115 $^\circ\text{C}$. ^1H NMR (CDCl_3): δ 7.66 (s, 1H), 7.58-7.54 (m, 1H), 7.52 (d, J = 8.7 Hz, 1H), 7.26-7.24 (m, 1H), 7.08 (td, J = 9.2, 1.9 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (CDCl_3): δ 159.4 (dd, $J_{\text{C-F}}$ = 257, 4.3 Hz), 156.5 (dd, $J_{\text{C-F}}$ = 259, 5.8 Hz), 153.8 (t, $J_{\text{C-F}}$ = 3.9 Hz), 148.8, 141.4, 134.8, 132.8 (d, $J_{\text{C-F}}$ = 9.8 Hz), 127.3, 120.5, 117.9 (dd, $J_{\text{C-F}}$ = 18, 4.3 Hz), 112.9 (dd, $J_{\text{C-F}}$ = 23, 4.3 Hz), 110.2, 108.0 (t, $J_{\text{C-F}}$ = 16 Hz), 21.5. ^{19}F NMR (CDCl_3): δ -107.9, -109.3. IR (neat): 3098, 2967, 2925, 1608, 1579,

1484, 1455, 1441, 1217, 1197, 1020, 933, 842, 820, 802 cm^{-1} . HRMS $[\text{M}+\text{H}^+]$ Calcd for $\text{C}_{14}\text{H}_8\text{ClF}_2\text{NO}$ 280.0341; Found: 280.0341.

Procedures and Spectral Characterization of Arylation Products in Scheme 4

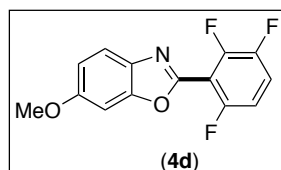


Following general procedure, 2,3,6-trifluorophenyl potassium carboxylate (321 mg, 1.50 mmol, 3.0 equiv), benzoxazole (59.6 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (2.7 mg, 0.0075 mmol, 0.015 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 20 h. Chromatography on a silica gel column using 5/95 EtOAc/hexanes ($R_f = 0.24$ in 5% EtOAc/95% hexanes) yielded product **2d** as a white solid (70.6 mg, 57% yield). mp = 73-74 °C. ^1H NMR (CDCl_3): δ 7.88 (d, $J = 7.9$ Hz, 1H), 7.64 (d, $J = 7.6$ Hz, 1H), 7.45-7.29 (multiple peaks, 3H), 7.07-7.01 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 156.3 (dt, $J_{\text{C-F}} = 254$, 3.0 Hz), 153.8 (m), 150.4, 149.1 (ddd, $J_{\text{C-F}} = 260$, 15, 6 Hz), 147.5 (ddd, $J_{\text{C-F}} = 244$, 13, 4 Hz), 141.2, 126.1, 124.9, 120.7, 119.6 (dd, $J_{\text{C-F}} = 20$, 10 Hz), 111.8, (dm, $J_{\text{C-F}} = 24$ Hz), 110.9, 108.0 (dd, $J_{\text{C-F}} = 17$, 12 Hz). ^{19}F NMR (CDCl_3): δ -113.4, -131.6, -140.5. IR (neat): 3092, 3046, 1612, 1557, 1492, 1449, 1295, 1244, 1206, 1023, 1005, 945, 885, 821, 812, 734 cm^{-1} . HRMS $[\text{M}+\text{H}^+]$ Calcd for $\text{C}_{13}\text{H}_6\text{F}_3\text{NO}$ 250.0480; Found: 250.0483.

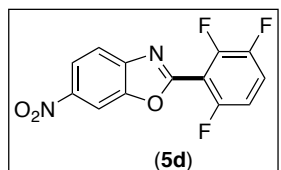


Following general procedure, 2,3,6-trifluorophenyl potassium carboxylate (321 mg, 1.50 mmol, 3.0 equiv), 5-chlorobenzoxazole (76.8 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (2.68 mg, 0.0075 mmol, 0.015 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), and anhydrous diglyme (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 20 h. Chromatography on a silica gel column using 5/95 EtOAc/hexanes ($R_f = 0.27$ in 5% EtOAc/95% hexanes) yielded product **3d** as a pale yellow solid (77.0 mg, 54% yield). mp = 109-110.5 °C. ^1H NMR (CDCl_3): δ 7.87 (d, $J = 2.2$ Hz, 1H), 7.58 (d, $J = 8.7$ Hz, 1H), 7.42 (dd, $J = 8.7$, 2.0 Hz, 1H), 7.40-7.33 (m, 1H), 7.10-7.04 (m,

1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 156.1 (dt, $J_{\text{C-F}} = 255, 3.4$ Hz), 155.3-155.2 (m), 149.3 (ddd, $J_{\text{C-F}} = 261, 15, 5.7$ Hz), 149.0, 147.5 (ddd, $J_{\text{C-F}} = 245, 12, 3.7$ Hz), 142.3, 130.5, 126.6, 120.7, 120.1 (dd, $J_{\text{C-F}} = 19, 10$ Hz), 112.2-111.8 (dm), 111.7, 107.6 (dd, $J_{\text{C-F}} = 17, 12$ Hz). ^{19}F NMR (CDCl_3): δ -113.1, -131.2, -140.2. IR (neat): 3035, 1554, 1498, 1462, 1450, 1441, 1330, 1260, 1252, 1203, 1056, 1016, 966, 928, 881, 824, 804, 735, 708, 699, 627 cm^{-1} . HRMS [M^+] Calcd for $\text{C}_{13}\text{H}_5\text{ClF}_3\text{NO}$ 283.0012; Found: 283.0014.

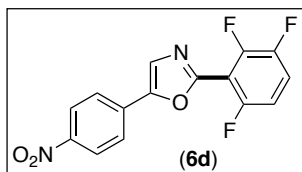


Following general procedure, 2,3,6-trifluorophenyl potassium carboxylate (321 mg, 1.50 mmol, 3.0 equiv), 6-methoxybenzoxazole (74.6 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (8.9 mg, 0.025 mmol, 0.05 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 $^\circ\text{C}$ for 20 h. Chromatography on a silica gel column using 9/91 EtOAc/hexanes ($R_f = 0.21$ in 9% EtOAc/91% hexanes) yielded product **4d** as a off-white solid (73.7 mg, 53% yield). mp = 105-106 $^\circ\text{C}$. ^1H NMR (CDCl_3): δ 7.75 (d, $J = 8.8$ Hz, 1H), 7.37-7.28 (m, 1H), 7.16 (d, $J = 2.4$ Hz, 1H), 7.07-7.01 (m, 1H), 7.02 (dd, $J = 8.8, 2.3$ Hz, 1H), 3.90 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 159.0, 156.2 (dt, $J_{\text{C-F}} = 254, 3.3$ Hz), 152.8-152.7 (m), 151.5, 149.0 (ddd, $J_{\text{C-F}} = 259, 15, 6.1$ Hz), 147.5 (ddd, $J_{\text{C-F}} = 245, 13, 3.7$ Hz), 135.0, 120.8, 119.2 (dd, $J_{\text{C-F}} = 20, 9.6$ Hz), 113.8, 111.8 (ddd, $J_{\text{C-F}} = 24, 6, 5$ Hz), 108.1 (dd, $J_{\text{C-F}} = 17, 12$ Hz), 95.1, 55.9. ^{19}F NMR (CDCl_3): δ -113.7, -131.9, -140.6. IR (neat): 3053, 1622, 1549, 1486, 1304, 1191, 1144, 1117, 1010, 888, 816, 807 cm^{-1} . HRMS [$\text{M}+\text{H}^+$] Calcd for $\text{C}_{14}\text{H}_8\text{F}_3\text{NO}_2$ 280.0585; Found: 280.0588.

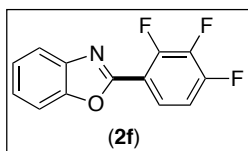


Following general procedure, 2,3,6-trifluorophenyl potassium carboxylate (321 mg, 1.50 mmol, 3.0 equiv), 6-nitrobenzoxazole (81.6 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (2.68 mg, 0.0075 mmol, 0.015 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 $^\circ\text{C}$ for 20 h. Chromatography on a silica gel column using 12/88 EtOAc/hexanes ($R_f = 0.26$ in 12%

EtOAc/88% hexanes) yielded product **5d** as a pale yellow solid (86.5 mg, 59% yield). mp = 152-153 °C. ^1H NMR (CDCl_3): δ 8.59 (d, J = 2.2 Hz, 1H), 8.39 (dd, J = 8.8, 2.2 Hz, 1H), 8.00 (d, J = 8.8 Hz, 1H), 7.48-7.40 (m, 1H), 7.14-7.08 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 158.5-158.4 (m), 156.4 (dt, $J_{\text{C-F}}$ = 257, 3.0 Hz), 149.6, 149.3 (ddd, $J_{\text{C-F}}$ = 262, 16, 5.6 Hz), 147.5 (ddd, $J_{\text{C-F}}$ = 246, 12, 3.7 Hz), 146.1, 145.9, 121.0 (dd, $J_{\text{C-F}}$ = 20, 10 Hz), 121.0, 120.8, 112.2 (ddd, $J_{\text{C-F}}$ = 24, 6.0, 5.0 Hz), 107.7, 106.9 (dd, $J_{\text{C-F}}$ = 17, 11 Hz). ^{19}F NMR (CDCl_3): δ -112.2, -130.4, -139.7. IR (neat): 3113, 3073, 1553, 1528, 1493, 1433, 1351, 1269, 1249, 1235, 1211, 1013, 892, 881, 816, 807, 735 cm^{-1} . HRMS [$\text{M}+\text{H}^+$] Calcd for $\text{C}_{13}\text{H}_5\text{F}_3\text{N}_2\text{O}_3$ 295.0331; Found: 295.0330.

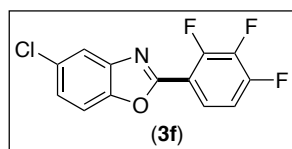


Following general procedure, 2,3,6-trifluorophenyl potassium carboxylate (321 mg, 1.50 mmol, 3.0 equiv), 4-nitrophenyloxazole (95.1 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (17.8 mg, 0.050 mmol, 0.10 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 20 h. Chromatography on a silica gel column using 21/79 EtOAc/hexanes (R_f = 0.24 in 21% EtOAc/79% hexanes) yielded product **6d** as a yellow solid (84.5 mg, 53% yield). ^1H NMR (CDCl_3): δ 8.33 (d, J = 8.9 Hz, 2H), 7.90 (d, J = 8.9 Hz, 2H), 7.78 (s, 1H), 7.37-7.29 (m, 1H), 7.09-7.03 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 155.9 (dt, $J_{\text{C-F}}$ = 254, 3.2), 153.5-153.4 (m), 150.0, 148.6 (ddd, $J_{\text{C-F}}$ = 260, 16, 6.4 Hz), 147.5, 147.6 (ddd, $J_{\text{C-F}}$ = 245, 12, 3.8 Hz), 132.9, 126.5, 124.9, 124.5, 119.2 (dd, $J_{\text{C-F}}$ = 20, 10 Hz), 111.9 (ddd, $J_{\text{C-F}}$ = 24, 6.4, 3.9 Hz), 107.3 (dd, $J_{\text{C-F}}$ = 17, 12 Hz). IR (neat): 2923, 1603, 1537, 1516, 1493, 1335, 1252, 1240, 1139, 1105, 1014, 942, 872, 854, 840, 813, 750, 739, 720, 703, 689, 623, 603, 584 cm^{-1} .



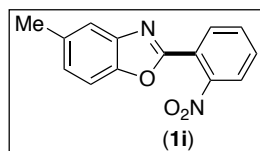
Following general procedure, 2,3,4-trifluorophenyl potassium carboxylate (321 mg, 1.50 mmol, 3.0 equiv), benzoxazole (59.6 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (8.9 mg, 0.025 mmol, 0.05 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 20 h. Chromatography on a silica gel column using 4/96 EtOAc/hexanes (R_f = 0.14 in 4% EtOAc/96%

hexanes) yielded product **2f** as a pale yellow solid (66.8 mg, 54% yield). mp = 128-129.5 °C. ^1H NMR (CDCl_3): δ 8.04-7.98 (m, 1H), 7.85-7.81 (m, 1H), 7.64-7.61 (m, 1H), 7.44-7.38 (multiple peaks, 2H), 7.19-7.12 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 157.8-157.6 (m), 153.1 (ddd, $J_{\text{C-F}} = 255, 10, 2.9$ Hz), 150.4, 150.3 (ddd, $J_{\text{C-F}} = 262, 12, 3.5$ Hz), 141.4, 140.7 (dt, $J_{\text{C-F}} = 251, 15$ Hz), 125.8, 124.9, 124.3-124.1 (m), 120.4, 113.4 (dd, $J_{\text{C-F}} = 7.5, 3.8$ Hz), 112.8 (dd, $J_{\text{C-F}} = 18, 3.7$ Hz), 110.7. ^{19}F NMR (CDCl_3): δ -128.1, -130.9, -158.4. IR (neat): 3060, 1489, 1453, 1292, 1279, 1249, 1239, 1103, 1030, 1001, 938, 892, 798, 763, 746, 713, 701, 646, 629, 592 cm^{-1} . HRMS [M^+] Calcd for $\text{C}_{13}\text{H}_6\text{F}_3\text{NO}$ 249.0401; Found: 249.0404.



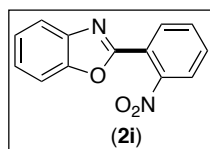
Following general procedure, 2,3,4-trifluorophenyl potassium carboxylate (321 mg, 1.50 mmol, 3.0 equiv), 5-chlorobenzoxazole (76.8 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (8.9 mg, 0.025 mmol, 0.05 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 20 h. Chromatography on a silica gel column using 3/97 EtOAc/hexanes ($R_f = 0.23$ in 3% EtOAc/97% hexanes) yielded product **3f** as a pale yellow solid (74.5 mg, 53% yield). mp = 136-137 °C. ^1H NMR (CDCl_3): δ 8.00-7.94 (m, 1H), 7.77 (d, $J = 2.1$ Hz, 1H), 7.53 (d, $J = 8.6$ Hz, 1H), 7.36 (dd, $J = 8.7, 2.0$ Hz, 1H), 7.18-7.11 (m, 1H). ^{13}C NMR (CDCl_3): δ 159.1-159.0 (m), 153.3 (ddd, $J_{\text{C-F}} = 256, 10, 3$), 150.5 (ddd, $J_{\text{C-F}} = 263, 12, 3.6$), 149.0, 142.5, 140.8 (dt, $J_{\text{C-F}} = 251, 15$), 130.5, 126.2, 124.5-124.3 (m), 120.3, 113.1-112.8 (multiple peaks, 2C), 111.5. ^{19}F NMR (CDCl_3): -127.2, -130.6, -158.1. IR (neat): 3094, 3064, 1551, 1525, 1449, 1347, 1304, 1256, 1056, 803, 719, 712, 702 cm^{-1} . HRMS [$\text{M}+\text{H}^+$] Calcd for $\text{C}_{13}\text{H}_5\text{ClF}_3\text{NO}$ 284.0090; Found: 284.0090.

Procedures and Spectral Characterization of Arylation Products in Scheme 5

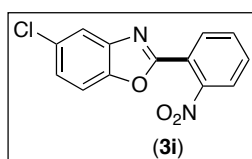


Following general procedure, 2-nitrophenyl potassium carboxylate (308 mg, 1.50 mmol, 3.0 equiv), 5-methylbenzoxazole (66.6 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (8.9 mg, 0.025 mmol,

0.05 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 20 h. Chromatography on a silica gel column using 13/87 EtOAc/hexanes ($R_f = 0.18$ in 13% EtOAc/87% hexanes) yielded product **1i** as an amber solid (61.9 mg, 49% yield). ^1H NMR (CDCl_3): δ 8.14 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.88 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.76-7.66 (multiple peaks, 2H), 7.60 (s, 1H), 7.44 (d, $J = 8.4$ Hz, 1H), 7.21 (dd, $J = 8.5, 1.8$ Hz, 1H), 2.50 (s, 3H). The spectroscopic data is consistent with that previously reported in the literature.⁴

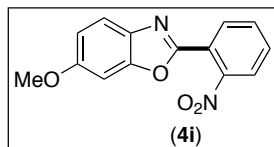


Following general procedure, 2-nitrophenyl potassium carboxylate (308 mg, 1.50 mmol, 3.0 equiv), benzoxazole (59.6 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (8.9 mg, 0.025 mmol, 0.05 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 20 h. Chromatography on a silica gel column using 13/87 EtOAc/hexanes ($R_f = 0.24$ in 13% EtOAc/87% hexanes) yielded product **2i** as an amber solid (77.6 mg, 65% yield). ^1H NMR (CDCl_3): δ 8.15 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.90 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.84-7.80 (m, 1H), 7.77-7.67 (multiple peaks, 2H), 7.62-7.56 (m, 1H), 7.43-7.38 (multiple peaks, 2H). The spectroscopic data is consistent with that previously reported in the literature.⁴



Following general procedure, 2-nitrophenyl potassium carboxylate (308 mg, 1.50 mmol, 3.0 equiv), 5-chlorobenzoxazole (76.8 mg, 0.500 mmol, 1.0 equiv), $\text{Ni}(\text{OTf})_2$ (17.8 mg, 0.050 mmol, 0.10 equiv), Li_2CO_3 (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 20 h. Chromatography on a silica gel column using 13/87 EtOAc/hexanes ($R_f = 0.16$ in 12% EtOAc/88% hexanes) yielded product **3i** as a yellow solid (70.8 mg, 52% yield). ^1H NMR (CDCl_3): δ 8.13 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.92 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.80 (d, $J = 2.0$ Hz, 1H),

7.79-7.70 (multiple peaks, 2H), 7.51 (d, $J = 8.7$ Hz, 1H), 7.39 (dd, $J = 8.7, 2.1$ Hz, 1H). The spectroscopic data is consistent with that previously reported in the literature.⁴



Following general procedure, 2-nitrophenyl potassium carboxylate (308 mg, 1.50 mmol, 3.0 equiv), 6-methoxybenzoxazole (74.6 mg, 0.500 mmol, 1.0 equiv), Ni(OTf)₂ (17.8 mg, 0.050 mmol, 0.10 equiv), Li₂CO₃ (55.4 mg, 0.750 mmol, 1.5 equiv), AgOTf (385 mg, 1.5 mmol, 3.0 equiv), anhydrous *N,N*-dimethylacetamide (0.4 mL), and anhydrous diglyme (1.6 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 20 h. Chromatography on a silica gel column using 9/91 EtOAc/hexanes to 27/73 EtOAc/hexanes ($R_f = 0.20$ in 9% EtOAc/91% hexanes) yielded product **4i** as an amber solid (61.3 mg, 45% yield). mp = 144-145 °C. ¹H NMR (CDCl₃): δ 8.11 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.83 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.72-7.61 (multiple peaks, 3H), 7.07 (d, $J = 2.4$ Hz, 1H), 6.98 (dd, $J = 8.8, 2.4$ Hz, 1H), 3.85 (s, 3H). ¹³C NMR (CDCl₃): δ 158.9, 157.6, 151.9, 148.9, 135.2, 132.2, 131.4, 131.0, 124.0, 121.3, 120.6, 113.7, 95.2, 55.9. IR (neat): 3077, 2831, 1533, 1490, 1435, 1327, 1266, 1024, 820, 765 cm⁻¹. HRMS [M+H⁺] Calcd for C₁₄H₁₀N₂O₄ 271.0719; Found: 271.0718.

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