Supporting Information for:

Nickel-Catalyzed Decarboxylative Cross-Coupling of Perfluorobenzoates with Aryl Halides and Sulfonates

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General Procedures: NMR spectra were obtained on a Bruker 400 (399.96 MHz for ^{1}H; 100.57 MHz for ^{13}C) spectrometer. ^{1}H 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 multiple peaks. Melting points were obtained on a Thomas Hoover melting point apparatus. IR spectra were obtained on a Thermo Scientific Nicolet iS5 iD5 ATR spectrometer.

Materials and Methods: Ni(COD)$_2$ was obtained from Strem chemical and used as received. PtBu$_3$HBF$_4$, PCy$_3$HBF$_4$, CMPhos, and anhydrous diglyme were obtained from Aldrich and used as received. Diphenylphosphinoferrocene was obtained from Strem and used as received. The perfluorobenzoate salts were prepared using literature procedures.[1] Aryl iodides, bromides, chlorides and triflates were obtained from Aldrich and used as received. Aryl tosylates were prepared from the corresponding phenols 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 F$_{254}$.

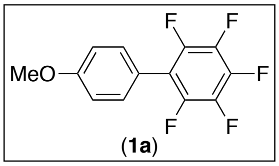
General procedures for Cross-Coupling (Scheme 1-6):

General Procedure (A) for obtaining isolated yields with solid halides or tosylates: Perfluorobenzoate salt was weighed into an oven dried 20 mL scintillation vial equipped with an oven dried stir bar. The vial was taken into the glove box and Ni(COD)$_2$, ligand (none, PtBu$_3$HBF$_4$, CMPhos, or dppf), aryl halide (or tosylate) and 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 inch plug of silica gel, eluting with Et$_2$O (100 mL). The filtrate was transferred to the separatory funnel and washed with H$_2$O (3 x 25 mL) and brine (1 x 25 mL). The organic layer was dried over MgSO$_4$, filtered, concentrated and chromatographed on a silica gel column to afford the product. The product was air dried overnight after concentration on the rotary evaporator to remove trace solvent.

General Procedure (B) for obtaining isolated yields with liquid halides, triflates or tosylates: Perfluorobenzoate salt was weighed into an oven dried 20 mL scintillation vial equipped with an oven dried stir bar. The vial was taken into the glove box and Ni(COD)$_2$, ligand (none, PtBu$_3$HBF$_4$, CMPhos, or dppf), and diglyme were added. Aryl halide (tosylate or triflate) was added to the reaction mixture. 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 inch plug of silica gel, eluting with Et_2O (100 mL). The filtrate was transferred to the separatory funnel and washed with H_2O (3 x 25 mL) and brine (1 x 25 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated and chromatographed on a silica gel column to afford the product. The product was air dried overnight after concentration on the rotary evaporator to remove trace solvent.

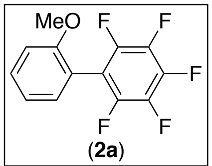
General Procedure for obtaining GC yields: Reactions were run using procedures A or B detailed above. However, instead of purification and isolation, the reaction mixture was diluted using EtOAc and hexadecane was added to it. The calibrated yield of the product against hexadecane as the standard was obtained using GC/MS spectroscopic analysis of the crude reaction mixture.

Procedures and spectral characterization of products using aryl iodides (Scheme 2)



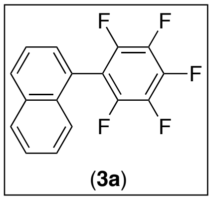
(**1a**)

Following general procedure A, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), $Ni(COD)_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), 4-iodoanisole (117 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 18 h. Chromatography on a silica gel column using 98/2 hexanes/CH_2Cl_2 (R_f = 0.34 in 98% hexanes/2% CH_2Cl_2) yielded product **1a** as a white solid (105 mg, 76% yield). ^{1}H NMR ($CDCl_3$): δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H). ^{19}F NMR ($CDCl_3$): δ -143.6, -156.5, -162.5. The spectroscopic data is consistent with previous literature reports.[1]



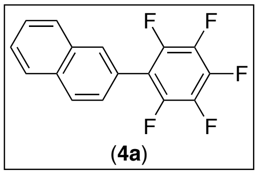
(**2a**)

Following general procedure B, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), $Ni(COD)_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), *ortho*-iodoanisole (117 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 24 h. Chromatography on a silica gel column using hexanes (R_f = 0.34 in hexanes) yielded product **2a** as a white solid (88.9 mg, 65% yield). ^{1}H NMR (CDCl$_3$): δ 7.48-7.43 (m, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.08-7.02 (multiple peaks, 2H), 3.81 (s, 3H). ^{19}F NMR (CDCl$_3$): δ -140.2, -156.2, -163.2. The spectroscopic data is consistent with previous literature reports.[1]



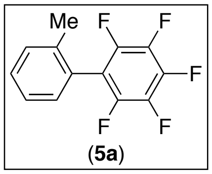
(**3a**)

Following general procedure B, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), 1-iodonaphthalene (127 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 24 h. Chromatography on a silica gel column using hexanes (R_f = 0.47 in hexanes) yielded product **3a** as a white solid (105.6 mg, 72% yield). ^{1}H NMR (CDCl$_3$): δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.60-7.44 (multiple peaks, 5H). ^{19}F NMR (CDCl$_3$): δ -139.4, -154.6, -161.9. The spectroscopic data is consistent with previous literature reports.[1]



(**4a**)

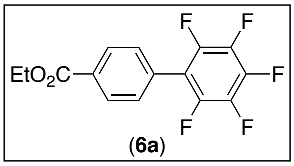
Following general procedure A, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), 2-iodonaphthalene (127 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 18 h. Chromatography on a silica gel column using hexanes (R_f = 0.53 in hexanes) yielded product **4a** as a white solid (108 mg, 74% yield). ^{1}H NMR (CDCl$_3$): δ 7.97-7.89 (multiple peaks, 4H), 7.60-7.48 (multiple peaks, 3H). ^{19}F NMR (CDCl$_3$): δ -143.0, -155.4, -162.9. The spectroscopic data is consistent with previous literature reports.[2]



(**5a**)

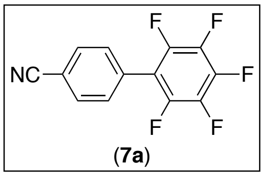
Following general procedure B, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), 2-iodotoluene (109 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120

°C for 24 h. Chromatography on a silica gel column using hexanes (R_f = 0.60 in hexanes) yielded product **5a** as a white solid (95.0 mg, 74% yield). ^{1}H NMR ($CDCl_3$): δ 7.40-7.27 (multiple peaks, 3H), 7.18 (d, *J* = 7.6 Hz, 1H), 2.18 (s, 3H). ^{19}F NMR ($CDCl_3$): δ -140.6, -155.4, -162.2. The spectroscopic data is consistent with previous literature reports.[1]



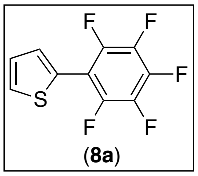
(**6a**)

Following general procedure B, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), $Ni(COD)_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), ethyl-4-iodobenzoate (138 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 24 h. Chromatography on a silica gel column using 2/4/94 acetone/CH_2Cl_2/hexanes (R_f = 0.25 in 2% acetone/4% CH_2Cl_2/94% hexanes) yielded product **6a** as a white solid (119 mg, 76% yield). ^{1}H NMR ($CDCl_3$): δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.52-7.50 (m, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR ($CDCl_3$): δ -142.8, -154.2, -161.6. The spectroscopic data is consistent with previous literature reports.[1]



(**7a**)

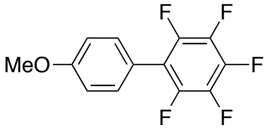
Following general procedure A, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), $Ni(COD)_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), 4-iodobenzonitrile (114 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 18 h. Chromatography on a silica gel column using 2/4/94 acetone/CH_2Cl_2/hexanes (R_f = 0.23 in 2% acetone/4% CH_2Cl_2/94% hexanes) yielded product **7a** as a white solid (85.0 mg, 63% yield). ^{1}H NMR ($CDCl_3$): δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H). The spectroscopic data is consistent with previous literature reports.[1]



(**8a**)

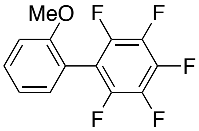
Following general procedure B, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), $Ni(COD)_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), 2-iodothiophene (105 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 24 h. Chromatography on a silica gel column using hexanes (R_f = 0.63 in hexanes) yielded product **8a** as a white solid (88.9 mg, 71% yield). ^{1}H NMR ($CDCl_3$): δ 7.56-7.52 (multiple peaks, 2H), 7.19 (t, *J* = 4.5 Hz, 1H). ^{19}F NMR ($CDCl_3$): δ -139.9, -155.9, -162.1. The spectroscopic data is consistent with previous literature reports.[1]

Procedures and spectral characterization of products using aryl bromides and chlorides (Scheme 3)



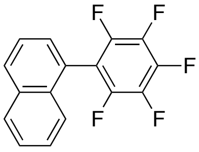
(**1a**)

Following general procedure B, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), $Ni(COD)_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), CMPhos (40.4 mg, 0.10 mmol, 0.2 equiv), 4-bromoanisole (93.5 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 18 h. Chromatography on a silica gel column using 2/98 CH_2Cl_2/hexanes (R_f = 0.34 in 2% CH_2Cl_2/98% hexanes) yielded product **1a** as a white solid (91.8 mg, 67% yield). The spectroscopic data is identical to that of the product isolated using **1-I**.



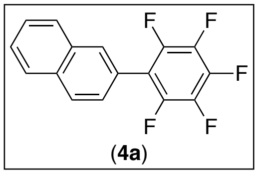
(**2a**)

Following general procedure B, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), $Ni(COD)_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), CMPhos (40.4 mg, 0.10 mmol, 0.2 equiv), 2-bromoanisole (93.5 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 18 h. Chromatography on a silica gel column using 2/1/97 CH_2Cl_2/acetone/hexanes (R_f = 0.43 in 2% CH_2Cl_2/1%acetone/97% hexanes) yielded product **2a** as a white solid (92.2 mg, 67% yield). The spectroscopic data is identical to that of the product isolated using **2-I**.

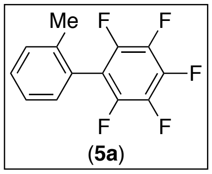


(**3a**)

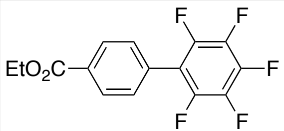
Following general procedure B, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), $Ni(COD)_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), $PtBu_3HBF_4$ (29.0 mg, 0.10 mmol, 0.2 equiv), 1-bromonaphthalene (103 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 18 h. Chromatography on a silica gel column using hexanes (R_f = 0.53 in hexanes) yielded product **3a** as a white solid (125 mg, 85% yield). The spectroscopic data is identical to that of the product isolated using **3-I**.


(**4a**)

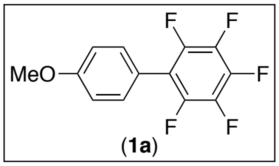
Following general procedure A, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), $Ni(COD)_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), CMPhos (40.4 mg, 0.10 mmol, 0.2 equiv), 2-bromonaphthalene (103 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using 0.2/98.8 CH_2Cl_2/hexanes (R_f = 0.51 in 0.2% CH_2Cl_2/98.8% hexanes) yielded product **4a** as a white solid (123 mg, 84% yield). The spectroscopic data is identical to that of the product isolated using **4-I**.


(**5a**)

Following general procedure B, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), $Ni(COD)_2$ (13.8 mg, 0.050 mmol, 0.10 equiv), CMPhos (40.4 mg, 0.10 mmol, 0.2 equiv), *ortho*-bromotoluene (85.5 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using 1/99 CH_2Cl_2/hexanes (R_f = 0.62 in 99% hexanes/1% CH_2Cl_2) yielded product **5a** as a white solid (68.1 mg, 53% yield). The spectroscopic data of **5a** is identical to that isolated from the reaction with **5-I**.

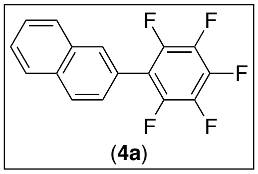

(**6a**)

Following general procedure A, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), $Ni(COD)_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), CMPhos (40.4 mg, 0.10 mmol, 0.2 equiv), ethyl-4-bromobenzoate (114.5 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using 30/70 CH_2Cl_2/hexanes (R_f = 0.21 in 30% CH_2Cl_2/70% hexanes) yielded product **10a** as a white solid (99.6 mg, 63% yield). The spectroscopic data of **6a** is identical to that isolated from the reaction with **6**-**I**.



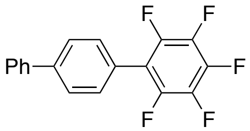
(**1a**)

Following general procedure B, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), dppf (55.4 mg, 0.10 mmol, 0.2 equiv), 4-chloroanisole (71.3 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using 20/80 CH_2Cl_2/hexanes yielded product **1a** as a white solid (68.2 mg, 50% yield). The spectroscopic data is identical to that of the product isolated using **1-I**.



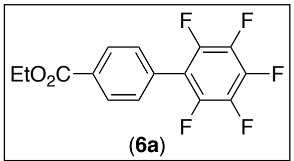
(**4a**)

Following general procedure A, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), dppf (34.6 mg, 0.06 mmol, 0.12 equiv), 2-chloronaphthalene (81.3 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using hexanes (R_f = 0.53 in hexanes) yielded product **4a** as a white solid (94.6 mg, 64% yield). The spectroscopic data is identical to that of the product isolated using **4-I**.



(**9a**)

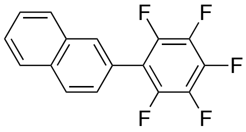
Following general procedure A, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), dppf (34.6 mg, 0.06 mmol, 0.12 equiv), 4-chlorobiphenyl (94.3 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using hexanes (R_f = 0.33 in hexanes) yielded product **9a** as a white solid (70.6 mg, 44% yield). ^{1}H NMR ($CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.52-7.46 (multiple peaks, 4H), 7.39 (t, *J* = 7.4 Hz, 1H). ^{19}F NMR ($CDCl_3$): δ -143.1, -155.5, -162.2. The spectroscopic data is consistent with previous literature reports.[1]



(**6a**)

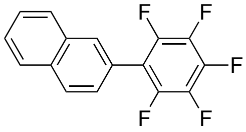
Following general procedure A, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), dppf (34.6 mg, 0.06 mmol, 0.12 equiv), ethyl-4-chlorobenzoate (92.3 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using 4/96 (acetone/hexanes) yielded product **6a** as a white solid (86.9 mg, 55% yield). The spectroscopic data is identical to that of the product isolated using **6-I**.

Procedures and spectral characterization of products using aryl tosylates and triflates (Scheme 4)



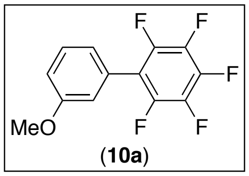
(**4a**)

Following general procedure B, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), dppf (34.6 mg, 0.06 mmol, 0.12 equiv), 2-naphthyltriflate (138.1 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using hexanes yielded product **4a** as a white solid (91.2 mg, 62% yield). The spectroscopic data is identical to that of the product isolated using **4-I**.



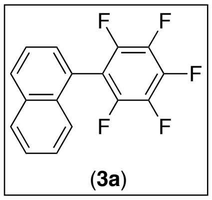
(**4a**)

Following general procedure A, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), dppf (34.6 mg, 0.06 mmol, 0.12 equiv), 2-naphthyltosylate (149.2 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using hexanes yielded product **4a** as a white solid (88.9 mg, 60% yield). The spectroscopic data is identical to that of the product isolated using **4-I**. The spectroscopic data is identical to that of the product isolated using **4-I**.



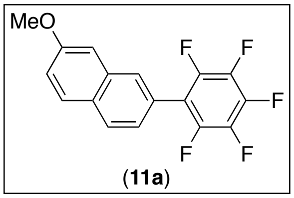
(**10a**)

Following general procedure A, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), dppf (34.6 mg, 0.06 mmol, 0.12 equiv), 3-methoxyphenyl 4-methylbenzenesulfonate (139.2 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using 10/90 CH_2Cl_2/hexanes (R_f = 0.33 in 10/90 CH_2Cl_2/hexanes) yielded product **10a** as a white solid (86.6 mg, 63% yield). ^{1}H NMR ($CDCl_3$): δ 7.41 (t, *J* = 8.0 Hz, 1H), 7.02-6.98 (multiple peaks, 2H), 6.94 (s, 1H), 3.85 (s, 3H). ^{19}F NMR ($CDCl_3$): δ -142.8, -155.5, -162.2. The spectroscopic data is consistent with previous literature reports.[1]



(**3a**)

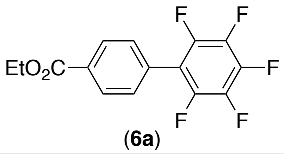
Following general procedure A, salt **A** (313 mg, 1.25 mmol, 2.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), dppf (34.6 mg, 0.06 mmol, 0.12 equiv), 1-naphthyltosylate (149.2 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using hexanes yielded product **3a** as a white solid (102 mg, 69% yield). The spectroscopic data is identical to that of the product isolated using **3-I**.



(**11a**)

Following general procedure A, salt **A** (313 mg, 1.25 mmol, 2.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), dppf (34.6 mg, 0.06 mmol, 0.12 equiv), 7-methoxynaphthalen-2-yl-4-methylbenzenesulfonate (164.2 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using 20/80 CH_2Cl_2/hexanes yielded product **11a** as a light yellow solid (91.2 mg, 56% yield). mp = 117-119 °C. ^{1}H NMR ($CDCl_3$): δ 7.88 (d, *J* = 8.6 Hz, 1H), 7.81 (s, 1H), 7.79 (d, *J* = 9.2 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.23 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.17 (d, *J* = 2.6 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 158.2, 144.3 (dm, $^1J_{C-F}$ = 248 Hz), 140.4

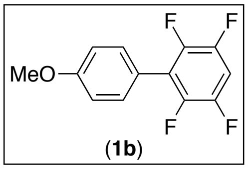
(dm, $^{1}J_{C\text{-}F}$ = 252 Hz), 137.9 (dm, $^{1}J_{C\text{-}F}$ = 248 Hz), 134.3, 129.2, 128.8, 128.1, 124.8, 124.2, 120.2, 116.1 (td, $J_{C\text{-}F}$ = 17, 4.0 Hz), 106.0, 55.3. One of the carbon resonances is coincidentally overlapping. ^{19}F NMR ($CDCl_3$): δ -142.9, -155.6, -162.2. IR (neat): 3007, 2964, 1629, 1606, 1510, 1491, 1467, 1424, 1389, 1254, 1217, 1172, 1060, 1031, 985, 958, 899, 846, 833, 706, 629 cm^{-1}. HRMS Calcd for $C_{17}H_9F_5O$ 324.0574; Found: 324.0568.



(**6a**)

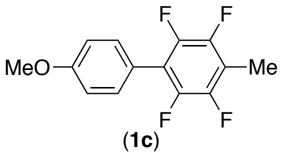
Following general procedure A, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), dppf (34.6 mg, 0.06 mmol, 0.12 equiv), ethyl-4-(tosyloxy)benzoate (160.2 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using 35/65 CH_2Cl_2/hexanes yielded product **6a** as a white solid (82.7 mg, 52% yield). The spectroscopic data is identical to that of the product isolated using **6-I**.

Procedures and spectral characterization of products using different perfluorobenzoates (Scheme 5)



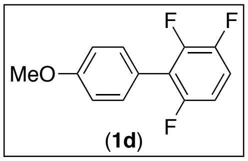
(**1b**)

Following general procedure A, salt **B** (174 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), $PtBu_3HBF_4$ (29.0 mg, 0.10 mmol, 0.2 equiv), 4-iodoanisole (117 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 20 h. Chromatography on a silica gel column using hexanes (R_f = 0.27 in hexanes) yielded product **1b** as a white solid (71.5 mg, 56% yield). ^{1}H NMR ($CDCl_3$): δ 7.40 (d, J = 8.3 Hz, 2H), 7.05-6.98 (multiple peaks, 3H), 3.87 (s, 3H). ^{19}F NMR ($CDCl_3$): δ -139.4, -144.3. The spectroscopic data is consistent with previous literature reports.[1]



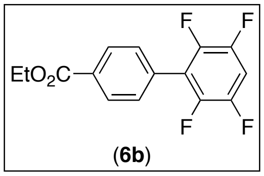
(**1c**)

Following general procedure A, salt **C** (185 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), $PtBu_3HBF_4$ (29.0 mg, 0.10 mmol, 0.2 equiv), 4-iodoanisole (117 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 20 h. Chromatography on a silica gel column using hexanes (R_f = 0.24 in hexanes) yielded product **1c** as a white solid (99 mg, 73% yield). ^{1}H NMR ($CDCl_3$): δ 7.41-7.37 (multiplet, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 2.31 (t, *J* = 2.1 Hz, 3H). ^{19}F NMR ($CDCl_3$): δ -144.0, -146.0. The spectroscopic data is consistent with previous literature reports.[1]



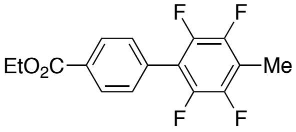
(**1d**)

Following general procedure A, salt **D** (161 mg, 0.75 mmol, 1.5 equiv), $Ni(COD)_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), $PtBu_3HBF_4$ (29.0 mg, 0.10 mmol, 0.2 equiv), 4-iodoanisole (117 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 18 h. Chromatography on a silica gel column using 1.5/98.5 Et_2O/hexanes (R_f = 0.27 in 1.5% Et_2O/98.5% hexanes) yielded product **1d** as a white solid (52 mg, 44% yield). ^{1}H NMR ($CDCl_3$): δ 7.41 (d, *J* = 8.8 Hz, 2H), 7.12-7.04 (m, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.93-6.87 (m, 1H), 3.86 (s, 3H). ^{19}F NMR ($CDCl_3$): δ -120.0, -138.2, -142.2. The spectroscopic data is consistent with previous literature reports.[1]



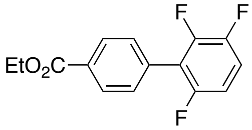
(**6b**)

Following general procedure B, salt **B** (174 mg, 0.75 mmol, 1.5 equiv), $Ni(COD)_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), $PtBu_3HBF_4$ (29.0 mg, 0.10 mmol, 0.2 equiv), ethyl-4-iodobenzoate (138 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 18 h. Chromatography on a silica gel column using 3/97 Et_2O/hexanes (R_f = 0.22 in 3% Et_2O/97% hexanes) yielded product **6b** as a white solid (88.6, 59% yield). mp = 110-112 °C. ^{1}H NMR ($CDCl_3$): δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.15-7.07 (m, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 165.9, 146.2 (dm, $^1J_{C\text{-}F}$ = 247 Hz), 143.6 (ddt, $^1J_{C\text{-}F}$ = 247, 14, 4 Hz), 131.8 (t, $J_{C\text{-}F}$ = 2.6 Hz), 131.1, 130.1 (t, $J_{C\text{-}F}$ = 2.3 Hz), 129.7, 120.5 (t, $J_{C\text{-}F}$ = 16 Hz), 105.5 (t, $J_{C\text{-}F}$ = 22 Hz), 61.2, 14.3. ^{19}F NMR ($CDCl_3$): δ -138.6, -143.5. IR (neat): 2992, 2906, 1714, 1496, 1485, 1450, 1404, 1389, 1362, 1271, 1184, 1169, 1127, 1105, 1022, 931, 884, 863, 851, 832, 772, 731, 713, 702, 687 cm^{-1}. HRMS Calcd for $C_{15}H_{10}F_4O_2$ 298.0617; Found: 298.0617.



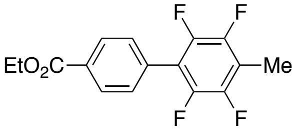
(**6c**)

Following general procedure B, salt **C** (92.3 mg, 0.375 mmol, 1.5 equiv), Ni(COD)$_2$ (6.9 mg, 0.025 mmol, 0.1 equiv), PtBu$_3$HBF$_4$ (14.5 mg, 0.10 mmol, 0.2 equiv), ethyl-4-iodobenzoate (69.0 mg, 0.250 mmol, 1.0 equiv) and anhydrous diglyme (0.5 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 18 h. Chromatography on a silica gel column using 1/2/97 acetone/CH$_2$Cl$_2$/hexanes (R$_f$ = 0.22 in 1% acetone/2% CH$_2$Cl$_2$/97% hexanes) yielded product **6c** as a white solid (53.0 mg, 68% yield). ^{1}H NMR (CDCl$_3$): δ 8.15 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 2.33 (t, J = 2.1 Hz, 3H), 1.41 (t, J = 7.1 Hz, 3H). ^{19}F NMR (CDCl$_3$): δ -143.6, -145.2. The spectroscopic data is consistent with previous literature reports.[3]



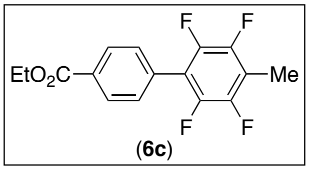
(**6d**)

Following general procedure B, salt **D** (161 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), PtBu$_3$HBF$_4$ (29.0 mg, 0.10 mmol, 0.2 equiv), ethyl-4-iodobenzoate (138 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 18 h. Chromatography on a silica gel column using 2/4/94 acetone/CH$_2$Cl$_2$/hexanes (R$_f$ = 0.24 in 2% acetone/4% CH$_2$Cl$_2$/94% hexanes) yielded product **6d** as a white solid (76.2 mg, 54% yield). mp = 53-55 °C. ^{1}H NMR (CDCl$_3$): δ 8.15 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.21-7.13 (m, 1H), 6.98-6.92 (m, 1H), 4.41 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). ^{13}C NMR (CDCl$_3$): δ 166.1, 155.1 (dm, $^1J_{C\text{-}F}$ = 243 Hz), 147.8 (ddd, $J_{C\text{-}F}$ = 250, 14, 7 Hz), 147.5 (ddd, $J_{C\text{-}F}$ = 244, 13, 3.7 Hz), 132.8, 130.6, 130.2 (t, $J_{C\text{-}F}$ = 2.2 Hz), 129.5, 119.3 (dd, $J_{C\text{-}F}$ = 20, 15 Hz), 116.4 (ddd, $J_{C\text{-}F}$ = 19, 10 Hz), 111.1 (ddd, $J_{C\text{-}F}$ = 254, 6.6, 4.3 Hz), 61.1, 14.3. ^{19}F NMR (CDCl$_3$): δ -119.4, -137.4, -141.6. IR (neat): 2986, 2911, 1709, 1485, 1403, 1361, 1268, 1229, 1184, 1127, 1113, 1102, 1088, 1024, 999, 891, 849, 800, 773, 735, 698, 604 cm^{-1}. HRMS Calcd for $C_{15}H_{11}F_3O_2$ 280.0711; Found: 280.0712.



(**6c**)

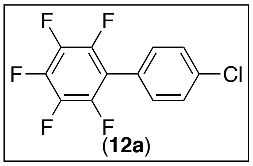
Following general procedure B, salt **C** (185 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), CMPhos (40.4 mg, 0.10 mmol, 0.2 equiv), ethyl-4-bromobenzoate (114.5 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 24 h. Chromatography on a silica gel column using 20/80 CH$_2$Cl$_2$/hexanes (R$_f$ = 0.13 in 20% CH$_2$Cl$_2$/80% hexanes) yielded product **6c** as a white solid (48.2 mg, 31% yield). The spectroscopic data is identical to that isolated using **6-I**.



(**6c**)

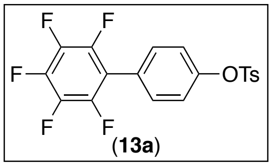
Following general procedure A, salt **C** (185 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), dppf (34.6 mg, 0.06 mmol, 0.12 equiv), ethyl-4-(tosyloxy)benzoate (160 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using 50/50 CH$_2$Cl$_2$/hexanes yielded product **6c** as a white solid (77.9 mg, 50% yield). The spectroscopic data is identical to that isolated using **6-I**.

Procedures and spectral characterization of products in Scheme 6



(**12a**)

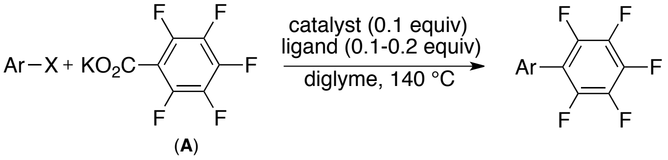
Following general procedure A, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), 1-chloro-4-iodobenzene (119 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 24 h. Chromatography on a silica gel column using hexanes (R$_f$ = 0.65 in hexanes) yielded product **12a** as a white solid (79.0 mg, 57% yield). ^{1}H NMR (CDCl$_3$): δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H). ^{19}F NMR (CDCl$_3$): δ -143.1, -154.7, -161.8. The spectroscopic data is consistent with previous literature reports.[4]



(**13a**)

Following general procedure A, salt **A** (188 mg, 0.75 mmol, 1.5 equiv), Ni(COD)$_2$ (13.8 mg, 0.05 mmol, 0.1 equiv), 4-iodophenyl 4-methylbenzenesulfonate (187 mg, 0.500 mmol, 1.0 equiv) and anhydrous diglyme (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 24 h. Chromatography on a silica gel column using 50/50 CH_2Cl_2/hexanes (R_f = 0.40 in 50/50 CH_2Cl_2/hexanes) yielded product **13a** as a white solid (142 mg, 68% yield). ^{1}H NMR ($CDCl_3$): δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.37-7.33 (multiple peaks, 4H), 7.13 (d, *J* = 8.7 Hz, 2H), 2.46 (s, 3H). ^{19}F NMR ($CDCl_3$): δ -143.0, -154.5, -161.7. The spectroscopic data is consistent with previous literature reports.[1]

Table 1. Exploration of Ni^{II} catalysts in place of Ni(COD)$_2$



ArX	product	catalyst	ligand	yield of product^{a,b}
1-I	1a	$NiCl_2(PCy_3)_2$	$PtBu_3HBF_4$	67%
1-I	1a	$NiBr_2$(DME)	$PtBu_3HBF_4$	86%
1-Br	1a	$NiCl_2(PCy_3)_2$	CM-Phos	35%
1-Br	1a	$NiBr_2$(DME)	CM-Phos	39%
1-Cl	1a	$NiCl_2(PCy_3)_2$	dppf	43%
1-Cl	1a	$NiBr_2$(DME)	dppf	15%
4-OTs	4a	$NiCl_2(PCy_3)_2$	dppf	63%^{c}
4-OTs	4a	$NiBr_2$(DME)	dppf	17%^{c}

[a] ArX (1 equiv), salt A (1.5 equiv), catalyst (0.1 equiv), ligand (0.2 equiv), diglyme, 140 °C, 20 h. [b] Calibrated GC yield against hexadecane as the internal standard. [c] 0.125 equiv ligand used.

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1. Shang, R.; Xu, Q.; Jiang, Y. –Y.; Wang, Y.; Liu, L. *Org. Lett.* **2010**, *12*, 1000-1003.
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3. Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H. –Z.; Liu, L. *Angew. Chem. Int. Ed.* **2009**, *48*, 9350-9354.
4. Wei, Y.; Kan, J.; Wang, M.; Su, W.; Hong, M. *Org. Lett.* **2009**, *11*, 3346-3349.