Supporting Information for:
Palladium Catalyzed Fluorination of Carbon–Hydrogen Bonds

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General Procedures: NMR spectra were obtained on a Varian Inova 500 (499.90 MHz for ^1H ; 125.70 MHz for ^{13}C) or a Varian Inova 400 (399.96 MHz for ^1H ; 100.57 MHz for ^{13}C ; 376.34 MHz for ^{19}F) spectrometer. ^1H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference; ^{19}F NMR are referenced based on the residual solvent peak in the ^1H NMR. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), doublet of quartets (dq), triplet (t), triplet of doublets (td), quartet (q), quartet of doublets (qd), and multiplet (m).

Materials and Methods: Substrates **1**, **14**, and 2-phenylpyridine were obtained from commercial sources and used as received. Quinoline substrates **5-7** were prepared through the reaction of substituted 2-methylanilines and glycerol according to a literature procedure.ⁱ Substrates **4**, **8-13**, and **15** were prepared by Suzuki cross coupling of the respective aryl boronic acid with 2-bromopyridine or 2-bromo-6-methoxypyridine.ⁱⁱ The fluorinating reagents *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (**2**) and *N*-fluoropyridinium tetrafluoroborate (**3**) were obtained from TCI America or Aldrich and used as received. Iodotoluene difluoride, *N*-fluorobenzenesulfonimide, and Selectfluor® were obtained from Aldrich and used without further purification. $\text{Pd}(\text{OAc})_2$ was obtained from Pressure Chemical or Frontier Scientific and used as received. Microwave heating was carried out using a CEM Discovery microwave reactor. The microwave reactions were run in closed reaction vessels with magnetic stirring and with the temperature controlled via IR detection. The GC yields reported for **1a** and **4a** are corrected GC yields based on calibration curves against an internal standard (naphthalene for **1a** and methylnaphthalene for **4a**). The GC yields reported in the experimentals for **5a-7a** and **8a-15a** are approximate, and are based on the calibration curves for **1a** and **4a**, respectively. 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 Merck TLC plates pre-coated with silica gel 60 F₂₅₄. HPLC was performed on a Varian ProStar 210 HPLC using Waters μ Porasil® 10 μm silica (19 x 300 mm) columns. Gas chromatography was performed on a Shimadzu GC-17A equipped with a Restek Rtx®-5 column (15 m, 0.25 mm ID, 0.25 μm df) and an FID detector. GC analysis of all of the products reported herein was carried out using the following method: 100 °C start temperature, ramp 15 °C/min to 240 °C, and hold for 10 min. GCMS analysis was performed on a Shimadzu GCMS QP-5000 equipped with a Restek Rtx®-5 column (30 m, 0.25 mm ID, 0.25 μm df). IR spectra were obtained on a Perkin-Elmer “Spectrum BX” spectrometer. Control reactions (in the absence of Pd catalyst) were run for each substrate, and showed none of the desired fluorinated product under our standard reaction conditions.

I. Experimental Procedures

8-Methylquinoline (**1**) (95.2 μ L, 0.69 mmol, 1 equiv), *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (**2**) (242.6 mg, 1.07 mmol, 1.5 equiv) and Pd(OAc)₂ (15.6 mg, 0.069 mmol, 10 mol %) were combined in benzene (4.5 mL) in an 80 mL microwave reaction vessel equipped with a Teflon stirbar. The reaction mixture was heated in the microwave at 110 °C for 1 h (250 W, 110 °C, 1 h, 10 min ramp). The resulting pale yellow/brown suspension was cooled to room temperature, naphthalene was added as an internal standard, and the reaction was analyzed by gas chromatography (which showed 65% GC yield on this scale). The reaction was then diluted with methanol (10 mL) and methylene chloride (10 mL) and filtered through a plug of Na₂CO₃ (~2 g) and Celite (0.5 g), and the plug was washed with copious methylene chloride (3 x 50 mL). The resulting solution was evaporated to dryness, and the brown solid was purified by chromatography on silica gel (R_f = 0.1 in 95% hexanes/5% ethyl acetate). Product **1a** was isolated as a pale yellow oil (66.1 mg, 59% yield). Note: GC-MS of the crude reaction mixture also showed unreacted starting material (5% GC yield), as well as traces of the acetoxylated product **1c** (6% GC yield)ⁱⁱⁱ and the phenylated product **1b** (2% GC yield).⁴ ¹H NMR (400 MHz, CDCl₃): δ 8.94 (dd, J = 4.0, 2.0 Hz, 1H), 8.18 (dd, J = 8.4, 2.0 Hz, 1H), 7.85-7.80 (multiple peaks, 2H), 7.58 (t, J = 3.4 Hz, 1H), 7.45 (dd, 8.4, J = 4.4 Hz, 1H), 6.15 (d, $^2J_{\text{HF}}$ = 47.6 Hz, 2H); ¹⁹F NMR (376 MHz, CDCl₃): δ -219.3 (t, $^2J_{\text{FH}}$ = 47.2 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 149.53, 145.11 (d, J_{CF} = 3.8 Hz), 135.83, 134.36 (d, J_{CF} = 16.7 Hz), 127.91 (d, J_{CF} = 2.3 Hz), 127.63, 127.04 (d, J_{CF} = 9.8 Hz), 125.94, 121.05, 81.50 (d, J_{CF} = 164.7 Hz). HRMS EI (m/z): [M^+] calcd for C₁₀H₈NF, 161.0641; found, 161.063. Anal. Calcd for C₁₀H₈NF: C, 74.52, H, 5.00, N, 8.69; Found: C, 74.67, H, 5.10, N, 8.53.

5,8-Dimethylquinoline (**5**) (105.7 mg, 0.669 mmol, 1 equiv), *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (**2**) (237.9 mg, 1.05 mmol, 1.6 equiv) and Pd(OAc)₂ (15.6 mg, 0.069 mmol, 10 mol %) were combined in benzene (4.5 mL) in an 80 mL microwave reaction vessel equipped with a Teflon stirbar. The reaction mixture was heated in the microwave at 110 °C for 1 h (250 W, 110 °C, 1 h, 10 min ramp). The resulting yellow suspension was cooled to room temperature, naphthalene was added as an internal standard, and the reaction was analyzed by gas chromatography (which showed ~57% GC yield). The reaction was then diluted with acetonitrile (10 mL), filtered through a plug of Na₂CO₃ (2.5 mg) and Celite (0.5 mg), and the plug was washed with copious acetonitrile (3 x 50 mL). The resulting solution was evaporated to dryness, and the brown solid was purified by chromatography on silica gel (R_f = 0.07 in

90% toluene/10% hexanes). Product **5a** was obtained as a yellow oil (67 mg, 57% yield). Note: GC-MS analysis of the crude reaction mixture also showed unreacted material (~4% GC yield), as well as traces of the corresponding acetoxyated product (~5% GC yield), the corresponding phenylated product (~2% GC yield), and the corresponding difluorinated product (~4% GC yield). ^1H NMR (400 MHz, acetone- d_6): δ 8.90 (dd, $J = 4.0, 1.6$ Hz, 1H), 8.43 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.70 (d, $J = 7.2$ Hz, 1H), 7.54 (dd, $J = 8.4, 4.0$ Hz, 1H), 7.44 (d, $J = 7.2$ Hz, 1H), 6.06 (d, $^2J_{\text{HF}} = 48.0$ Hz, 2H), 2.67 (s); ^{19}F NMR (376 MHz, acetone- d_6): δ -217.03 (t, $J_{\text{FH}} = 48.0$ Hz); ^{13}C NMR (100 MHz, acetone- d_6): δ 149.43, 145.70 (d, $J_{\text{CF}} = 3.6$), 135.45 (d, $J_{\text{CF}} = 2.2$), 132.78 (d, $J_{\text{CF}} = 16.1$), 132.54, 127.31 (d, $J_{\text{CF}} = 8.8$), 127.17, 126.4, 121.11, 81.12 (d, $J_{\text{CF}} = 161.9$), 17.70. HRMS EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{11}\text{H}_{10}\text{NF}$, 175.0797; found, 175.0789. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{NF}$: C, 75.41, H, 5.75, N, 7.99; Found: C, 75.20, H, 5.93, N, 7.73.

nOe conformation of regiochemistry of oxidation:

5-Fluoro-8-methylquinoline (**6**) (100 mg, 0.62 mmol, 1 equiv), *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (**2**) (211.0 mg, 0.93 mmol, 1.5 equiv) and $\text{Pd}(\text{OAc})_2$ (9.7 mg, 0.043 mmol, 7.0 mol %) were combined in benzene (2.0 mL) in a 10 mL microwave reaction vessel equipped with a Teflon stirbar. The reaction mixture was heated in the microwave at 100 °C for 4 h (200 W, 100 °C, 4 h, 10 min ramp). The resulting yellow suspension was cooled to room temperature, naphthalene was added as an internal standard, and the reaction was analyzed by gas chromatography (which showed ~54% GC yield). The reaction was then diluted with acetonitrile (10 mL), filtered through a plug of Na_2CO_3 (2.5 mg) and Celite (0.5 mg), and the plug was washed with copious acetonitrile (3 x 50 mL). The resulting solution was evaporated to dryness, and the brown solid was purified by chromatography on silica gel ($R_f = 0.07$ in 70% toluene/30% hexanes). Product **6a** was obtained as an off-white crystalline solid (54 mg, 49% yield). $\text{Mp} = 52.8\text{--}54.7$ °C. Note: GC-MS analysis of the crude reaction mixture also showed traces of the corresponding acetoxyated product (~7% GC yield), the corresponding phenylated product (~25% GC yield), and the corresponding difluorinated product (~6% GC yield). ^1H NMR (500 MHz, acetone- d_6): δ

9.00 (dd, $J = 4.3, 1.8$ Hz, 1H), 8.49 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.84 (m, 1H), 7.66 (dd, $J = 8.5, 4.0$ Hz, 1H), 7.39 (dd, $J = 10.0, 8.0$ Hz, 1H), 6.03 (d, $^2J_{\text{HF}} = 47.5$ Hz); ^{19}F NMR (376 MHz, acetone- d_6): δ -123.65 - -123.75 (m), -215.83 (td, $J = 48.0, 5.1$); ^{13}C NMR (125 MHz, acetone- d_6): δ 158.75 (dd, $J_{\text{CF}} = 254.3, 6.4$ Hz), 152.07, 147.06 (d, $J_{\text{CF}} = 3.6$), 132.03 (dd, $J_{\text{CF}} = 16.3, 4.9$ Hz), 129.97 (d, $J_{\text{CF}} = 4.5$ Hz), 129.01 (t, $J_{\text{CF}} = 9.43$ Hz), 122.92 (d, $J_{\text{CF}} = 2.8$ Hz), 119.45 (d, $J_{\text{CF}} = 16.2$ Hz), 110.70 (d, $J_{\text{CF}} = 20.24$ Hz), 81.51 (dt, $J_{\text{CF}} = 163.87, 4.8$ Hz). HRMS EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{10}\text{H}_7\text{NF}_2$, 179.0547; found, 179.0552. Anal. Calcd for $\text{C}_{10}\text{H}_7\text{NF}_2$: C, 67.04, H, 3.94, N, 7.82; Found: C, 67.49, H, 4.27, N, 7.46.

5-Bromo-8-methylquinoline (**7**) (100 mg, 0.45 mmol, 1 equiv), *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (**2**) (204.3 mg, 0.90 mmol, 2 equiv), and $\text{Pd}(\text{OAc})_2$ (10.1 mg, 0.045 mmol, 10 mol %) were combined in benzene (10 mL) in an 80 mL microwave reaction vessel equipped with a Teflon stirbar. The vessel was sealed with a Teflon lined cap, and the reaction mixture was heated in the microwave at 110 °C for 4 h (250 W, 110 °C, 4 h, 10 min ramp). The resulting yellow suspension was cooled to room temperature, then diluted with CH_2Cl_2 (50 mL) and washed three times with water. The organic layer was then dried over magnesium sulfate and concentrated. The resulting brown solid was purified by chromatography on silica gel ($R_f = 0.15$ in 80% toluene/20% hexanes). Product **7a** was isolated as a white crystalline solid (57 mg, 53% yield). Mp = 67.9-69.4 °C. Note: isolated samples of **7a** were contaminated with traces (~1.5-2.5%) of the phenylated product (which partially co-eluted with **7a**). GC-MS analysis of the crude reaction mixture also showed 52% GC yield of **7a**, along with traces of the corresponding difluorinated product (~6% GC yield), acetoxylated product (~6% GC yield), and the corresponding phenylated product (~14% GC yield). ^1H NMR (400 MHz, acetone- d_6): δ 8.97 (dd, $J = 4.0, 1.6$ Hz, 1H), 8.56 (dd, $J = 8.6, 1.4$ Hz, 1H), 7.96 (d, $J = 7.6$ Hz, 1H), 7.75 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.70 (dd, $J = 8.4, 4.2$ Hz, 1H), 6.16 (dd, $J = 47.6, 0.8$ Hz, 2H); ^{19}F NMR (376 MHz, acetone- d_6): δ -223.09 (t, $^2J_{\text{FH}} = 47.8$ Hz); ^{13}C NMR (100 MHz, acetone- d_6): δ 151.74, 146.73 (d, $J_{\text{CF}} = 3.7$ Hz), 136.23 (d, $J_{\text{CF}} = 16.94$ Hz), 136.06, 131.12, 128.45 (d, $J_{\text{CF}} = 11.1$ Hz), 127.91, 123.94, 122.34 (d, $J_{\text{CF}} = 2.9$ Hz), 81.80 (d, $J_{\text{CF}} = 165.0$ Hz). HRMS EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{10}\text{H}_7\text{BrNF}$, 238.9746; found, 238.9756.

2-(2-Fluorophenyl)-pyridine (**4**) (100 mg, 0.58 mmol, 1 equiv), *N*-fluoropyridinium tetrafluoroborate (**3**) (267 mg, 1.44 mmol, 2.5 equiv), and Pd(OAc)₂ (13 mg, 0.058 mmol, 10 mol %) were combined in trifluorotoluene (26.2 mL) and acetonitrile (0.5 mL) in an 80 mL microwave reaction vessel equipped with a Teflon stirbar. The reaction mixture was heated in the microwave to 150 °C for 1.5 h (300W, 150 °C, 1.5 h, 20 min ramp). The light brown suspension was cooled to room temperature, methylnaphthalene was added as an internal standard, and the reaction was analyzed by gas chromatography (which showed 82% GC yield). The reaction mixture was then diluted with acetonitrile (20 mL) and filtered through a plug of Na₂CO₃ (~2 g) and Celite (~0.5 g) and the plug was washed with an additional 100 mL of acetonitrile. The solvent was removed under vacuum, and the resulting brown solid was purified by chromatography on silica gel (*R*_f = 0.2 in 80% hexanes/20% ethyl acetate). Product **4a** was isolated as a pale yellow oil (75.6 mg, 69% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.76 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.78 (td, *J* = 7.7, 1.9 Hz, 1H), 7.52-7.48 (m, 1H), 7.37-7.28 (multiple peaks, 2H), 7.03-6.96 (m, 2H); ¹⁹F NMR (376 MHz, CDCl₃): δ -114.78 - -114.88 (m); ¹³C NMR (100 MHz, acetone-*d*₆): δ 161.30 (dd, *J*_{CF} = 247.25, 7.0 Hz), 150.68, 150.34, 137.25, 131.52 (t, *J*_{CF} = 10.3 Hz), 126.70, 124.06, 119.33 (t, *J*_{CF} = 18.88 Hz), 112.64 (dd, *J*_{CF} = 19.2, 6.6 Hz). HRMS EI (*m/z*): [*M*⁺] calcd for C₁₁H₇NF₂, 191.0457; found, 191.0546. Anal. Calcd for C₁₁H₇NF₂: C, 69.11, H, 3.69, N, 7.33; Found: C, 69.07, H, 3.84, N, 7.17.

2-Phenylpyridine (82.5 μL, 0.58 mmol, 1 equiv), *N*-fluoropyridinium tetrafluoroborate (**3**) (480.9 mg, 2.60 mmol, 4.5 equiv), and Pd(OAc)₂ (13 mg, 0.058 mmol, 10 mol %) were combined in trifluorotoluene (26.2 mL) and acetonitrile (0.5 mL) in an 80 mL microwave reaction vessel equipped with a Teflon stirbar. The reaction mixture was heated in the microwave to 150 °C for 1.5 h (150 °C, 20 min ramp, 300 W maximum). The resulting light brown suspension was cooled to room temperature, methylnaphthalene was added as an internal standard, and the reaction was analyzed by gas chromatography (which showed 57% GC yield). The reaction mixture was then diluted with acetonitrile (20 mL) and filtered through a plug of Na₂CO₃ (~2 g) and Celite (~0.5 g) and the plug was washed with an additional 100 mL of acetonitrile. The solvent was removed under vacuum, and the resulting brown solid was purified by chromatography on silica gel (*R*_f = 0.2 in 80% hexanes/20% ethyl acetate). Product **4a** was isolated as a pale yellow oil (69.0 mg, 62% yield). For characterization data, see previous entry (above).

2-(2-Methylphenyl)-pyridine (**8**) (97.8 mg, 0.58 mmol, 1 equiv), *N*-fluoropyridinium tetrafluoroborate (**3**) (300 mg, 1.62 mmol, 2.8 equiv), and Pd(OAc)₂ (13 mg, 0.058 mmol, 10 mol%) were combined in trifluorotoluene (26.2 mL) and acetonitrile (0.25 mL) in an 80 mL microwave reaction vessel equipped with a Teflon stirbar. The reaction mixture was heated in the microwave to 150 °C for 1.5 h (150 °C, 20 min ramp, 300 W maximum). The resulting light brown suspension was cooled to room temperature, methylnaphthalene was added as an internal standard, and the reaction was analyzed by gas chromatography (which showed ~72% GC yield). The reaction mixture was then diluted with acetonitrile (20 mL) and filtered through a plug of Na₂CO₃ (~2 g) and Celite (~0.5 g) and the plug was washed with an additional 100 mL of acetonitrile, 10 mL of methylene chloride, and 10 mL of methanol. The solvent was removed under vacuum, and the resulting brown solid was purified by chromatography on silica gel (*R*_f = 0.2 in 80% hexanes/20% ethyl acetate). Product **8a** was isolated as a pale yellow oil (56 mg, 52% yield). ¹H NMR (400 MHz, acetone-*d*₆): δ 8.71 (ddd, *J* = 4.8, 1.7, 1.0 Hz, 1H), 7.88 (td, *J* = 7.7, 1.9 Hz, 1H), 7.42 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.37 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 7.34-7.29 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 9.2 Hz, 1H), 2.18 (s, 3 H); ¹⁹F NMR (376 MHz, acetone-*d*₆): δ -113.79 (dd, *J* = 8.8, 6.3); ¹³C NMR (100 MHz, acetone-*d*₆): δ 161.02 (d, *J*_{C-F} = 241.7 Hz), 155.14 (d, *J*_{CF} = 1.1 Hz), 150.45, 140.06 (d, *J* = 2.9 Hz), 137.11, 130.26 (s, *J*_{CF} = 9.5 Hz), 129.59 (d, *J*_{CF} = 15.6 Hz), 126.87 (d, *J*_{CF} = 2.9 Hz), 126.35 (d, *J*_{CF} = 1.5 Hz), 123.38, 113.65 (d, *J*_{CF} = 22.7 Hz). HRMS EI (*m/z*): [M-H⁺] calcd for C₁₂H₁₀FN, 186.0719; found, 186.0714. Anal. Calcd for C₁₂H₁₀FN: C, 76.99, H, 5.38, N, 7.48; Found: C, 76.90, H, 5.62, N, 7.32.

2-(2-Methoxyphenyl)-pyridine (**9**) (107 mg, 0.578 mmol, 1 equiv), *N*-fluoropyridinium tetrafluoroborate (**3**) (267 mg, 1.44 mmol, 2.5 equiv), and Pd(OAc)₂ (13 mg, 0.0578 mmol, 10 mol %) were combined in trifluorotoluene (26 mL) and acetonitrile (0.25 mL) in an 80 mL microwave reaction vessel equipped with a Teflon stirbar. The reaction mixture was heated in the microwave at 150 °C for 2 h (150 °C, 2 h, 20 min ramp, 300 W maximum). The resulting light brown suspension was cooled to room temperature, methylnaphthalene was added as an internal standard, and the reaction was analyzed by gas chromatography (which showed ~35% GC yield). The reaction mixture was then diluted with acetonitrile (20 mL) and filtered through a plug of Na₂CO₃ (~2 g) and Celite (~0.5 g) and the plug was washed with an additional 100 mL of acetonitrile, 10 mL of methylene chloride, and 10 mL of methanol. The solvent was removed under vacuum, and the resulting brown solid was purified by chromatography on silica gel (*R*_f = 0.21 in 50% hexanes/50% ethyl acetate). Product **9a** was isolated as a clear oil (39 mg, 33% yield). ¹H NMR (400 MHz, acetone-*d*₆): δ 8.66 (ddd, *J* = 4.7, 1.5, 1.1 Hz, 1H), 7.83 (td, *J* = 7.7, 1.9 Hz, 1H), 7.44-7.37 (multiple peaks, 2H), 7.33 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.83 (td, *J* = 8.8, 0.8 Hz, 1H), 3.77 (s, 3H). ¹⁹F NMR (376 MHz, acetone-*d*₆): δ -117.19 (dd, *J*_{FH} = 9.2, 6.6 Hz). ¹³C NMR (100 MHz, acetone-*d*₆): δ 161.61 (d, ¹*J*_{CF} = 243.2 Hz), 159.34 (d, *J*_{CF} = 6.6 Hz), 152.97, 150.24, 136.60, 130.98 (d, ³*J*_{CF} = 10.3 Hz), 126.92, 123.22, 119.73 (d, ²*J*_{CF} = 17.6 Hz), 108.73 (d, *J*_{CF} = 22.7 Hz), 108.06 (d, ⁴*J*_{CF} = 2.9 Hz), 56.53. HRMS EI (*m/z*): [*M*⁺] calcd for C₁₂H₁₀FNO, 203.0746; found, 203.0737. Anal. Calcd for C₁₂H₁₀FNO: C, 70.93, H, 4.96, N, 6.89; Found: C, 70.53, H, 5.21, N, 6.46.

2-(3-Trifluoromethylphenyl)-pyridine (**10**) (129 mg, 0.58 mmol, 1 equiv), *N*-fluoropyridinium tetrafluoroborate (**3**) (300 mg, 1.6 mmol, 2.8 equiv), and Pd(OAc)₂ (13 mg, 0.058 mmol, 10 mol %) were combined in trifluorotoluene (26.2 mL) and acetonitrile (0.25 mL) in an 80 mL microwave reaction vessel equipped with a Teflon stirbar. The reaction mixture was heated in the microwave at 150 °C for 2 h (150 °C, 2 h, 20 min ramp, 300 W maximum). The resulting light brown suspension was cooled to room temperature, methylnaphthalene was added as an internal standard, and the reaction was analyzed by gas chromatography (which showed ~88% GC yield). The reaction mixture was then diluted with acetonitrile (20 mL) and filtered through a plug of Na₂CO₃ (~2 g) and Celite (~0.5 g) and the plug was washed with an additional 100 mL of acetonitrile, 10 mL of methylene chloride, and 10 mL of methanol. The solvent was removed under vacuum, and the resulting brown solid was purified by chromatography on silica gel (*R*_f = 0.17 in 90% hexanes/10% ethyl acetate). Product **10a** was isolated as a clear oil (105 mg, 75% yield). The regioselectivity of this reaction was confirmed through COSY and HMQC experiments as well as ¹³C NMR coupling constant analysis. ¹H NMR (400 MHz, acetone-*d*₆): δ 8.76 (dt, *J* = 4.8, 1.4 Hz, 1H), 8.44 (dd, *J* = 7.0, 2.2 Hz, 1H), 7.96-7.90 (multiple peaks, 2H), 7.83 (dddd, *J* = 8.7, 4.4, 2.6, 0.7 Hz, 1H), 7.51 (dd, *J* = 11.1, 8.7 Hz, 1H), 7.46-7.40 (m, 1H); ¹⁹F NMR (376 MHz, acetone-*d*₆): δ -62.61 (d, *J* = 1.1 Hz), -112.40 - -112.51 (m); ¹³C NMR (100 MHz, acetone-*d*₆): δ 163.33 (d, *J*_{CF} = 253.5 Hz), 152.09 (d, *J*_{CF} = 2.6 Hz), 151.04, 137.85, 129.39 (dq, *J* = 4.4, 3.7), 129.09 (d, *J*_{CF} = 13.2 Hz), 128.69 (dq, *J*_{CF} = 10.3, 3.7 Hz), 127.56 (qd, *J*_{CF} = 32.6, 3.3 Hz), 125.33 (d, *J*_{CF} = 11.0 Hz), 125.07 (q, *J*_{CF} = 269.6 Hz), 124.43, 118.49 (d, *J*_{CF} = 24.9 Hz). HRMS EI (*m/z*): [*M*⁺] calcd for C₁₂H₇F₄N, 241.0515; found, 241.0503. Anal. Calcd for C₁₂H₇F₄N: C, 59.76, H, 2.93, N, 5.81; Found: C, 60.22, H, 3.03, N, 5.55.

2-(2-Trifluoromethylphenyl)-pyridine (**11**) (129 mg, 0.59 mmol, 1 equiv), *N*-fluoropyridinium tetrafluoroborate (**3**) (300 mg, 1.6 mmol, 2.8 equiv), and Pd(OAc)₂ (13 mg, 0.0578 mmol, 10 mol %) were combined in trifluorotoluene (26.2 mL) and acetonitrile (0.25 mL) in an 80 mL microwave reaction vessel equipped with a Teflon stirbar. The reaction mixture was heated in the microwave at 150 °C for 2 h (150 °C, 20 min ramp, 300 W maximum). The resulting light brown suspension was cooled to room temperature, methylnaphthalene was added as an internal standard, and the reaction was analyzed by gas chromatography (which showed ~62% GC yield). The reaction mixture was then diluted with acetonitrile (20 mL) and filtered through a plug of Na₂CO₃ (~2 g) and Celite (~0.5 g) and the plug was washed with an additional 100 mL of acetonitrile and 10 mL of methanol. The solvent was removed under vacuum, and the resulting brown solid was purified by chromatography on silica gel (*R*_f = 0.08 in 90% hexanes/10% ethyl acetate). Product **11a** was isolated as a clear oil (77 mg, 55% yield). ¹H NMR (400 MHz, acetone-*d*₆): δ 8.70 (ddd, *J* = 4.8, 1.6, 1.0 Hz, 1H), 7.91 (td, *J* = 7.7, 1.7 Hz, 1H), 7.76-7.68 (multiple peaks, 2H), 7.60-7.45 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.45 (ddd, *J* = 7.7, 4.9, 1.1 Hz, 1H); ¹⁹F NMR (376 MHz, acetone-*d*₆): δ -57.85 (s), -114.50 - -114.58 (m); ¹³C NMR (100 MHz, acetone-*d*₆): δ 161.27 (d, *J*_{CF} = 244.6 Hz), 152.56, 150.27, 137.01, 131.61 (d, *J*_{CF} = 8.8 Hz), 131.05 (qd, *J*_{CF} = 28.8, 3.0 Hz), 129.23 (app. dd, *J*_{CF} = 19.8, 2.2 Hz), 126.05, 124.51 (qd, *J*_{CF} = 271.95, 3.7 Hz), 124.18, 122.98 (dq, *J*_{CF} = 5.4, 3.7 Hz), 120.62 (d, *J*_{CF} = 23.4 Hz). HRMS EI (*m/z*): [*M*⁺] calcd for C₁₂H₇F₄N, 241.0515; found, 241.0517.

2-(2-Chlorophenyl)-pyridine (**12**) (107 mg, 0.578 mmol, 1 equiv), *N*-fluoropyridinium tetrafluoroborate (**3**) (333 mg, 1.8 mmol, 3.1 equiv), and Pd(OAc)₂ (13 mg, 0.0578 mmol, 10 mol %) were combined in trifluorotoluene (26 mL) and acetonitrile (0.25 mL) in an 80 mL microwave reaction vessel equipped with a Teflon stirbar. The reaction mixture was heated in the microwave to 150 °C for 2 h (150 °C, 2 h, 20 min ramp, 300 W maximum). The resulting light brown suspension was cooled to room temperature, methylnaphthalene was added as an internal standard, and the reaction was analyzed by gas chromatography (which showed ~66% GC yield). The reaction mixture was then diluted with acetonitrile (20 mL) and filtered through a plug of Na₂CO₃ (~2 g) and Celite (~0.5 g) and the plug was washed with an additional 100 mL of acetonitrile, 10 mL of methylene chloride, and 10 mL of methanol. The solvent was removed under vacuum, and the resulting brown solid was purified by chromatography on silica gel (*R*_f = 0.32 in 80% hexanes/20% ethyl acetate). Product **12a** was isolated as a pale yellow oil (59 mg, 50% yield). ¹H NMR (400 MHz, acetone-*d*₆): δ 8.72 (ddd, *J* = 4.9, 1.8, 1 Hz, 1H), 7.93 (td, *J* = 7.7, 1.8 Hz, 1H), 7.56–7.46 (multiple peaks, 2H), 7.44 (ddd, *J* = 7.6, 5.0, 1.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.26 (td, *J* = 8.7, 0.8, 1H); ¹⁹F NMR (376 MHz, acetone-*d*₆): δ –118.51 (ddd, *J*_{FH} = 9.7, 5.9, 1.5 Hz); ¹³C NMR (100 MHz, acetone-*d*₆): δ 161.48 (d, *J*_{CF} = 246.9 Hz), 153.07, 150.56, 137.26, 134.74 (*J*_{CF} = 5.2 Hz), 131.51 (d, *J*_{CF} = 9.5 Hz), 129.18 (d, *J*_{CF} = 19.0 Hz), 126.44, 124.40, 124.14, 115.41 (*J*_{CF} = 22.0 Hz). HRMS EI (*m/z*): [*M*⁺] calcd for C₁₁H₇ClFN, 207.0251; found, 207.0252.

Ethyl 3-(pyridin-2-yl)benzoate (**13**) (131.4 mg, 0.58 mmol, 1 equiv), *N*-fluoropyridinium tetrafluoroborate (**3**) (333 mg, 1.8 mmol, 3.1 equiv), and Pd(OAc)₂ (13 mg, 0.058 mmol, 10 mol %) were combined in trifluorotoluene (26.2 mL) and acetonitrile (0.25 mL) in an 80 mL microwave reaction vessel equipped with a Teflon stirbar. The reaction mixture was heated in the microwave at 150 °C for 2 h (150 °C, 2 h, 20 min ramp, 300 W maximum). The resulting yellow suspension was cooled to room temperature, methylnaphthalene was added as an internal standard, and the reaction was analyzed by gas chromatography (which showed ~84% GC yield). The reaction mixture was then diluted with acetonitrile (20 mL) and filtered through a plug of Na₂CO₃ (~2 g) and Celite (~0.5 g) and the plug was washed with an additional 100 mL of acetonitrile and 10 mL of methanol. The solvent was removed under vacuum, and the resulting brown solid was dried onto silica gel and purified by chromatography on silica gel (*R*_f = 0.27 in 90% hexanes/10% ethyl acetate). Product **13a** was isolated as a white crystalline solid (77 mg, 54% yield). Note: the sample obtained from column chromatography was contaminated with traces (7% by GC analysis) of the starting material. Samples for microanalysis were obtained after further purification by HPLC (90% hexanes/ 10% ethyl acetate, 20 mL/min, Waters μ -porasil 19.1 mm). The regioselectivity of this reaction was confirmed through COSY and HMQC experiments as well as ¹³C NMR coupling constant analysis. Mp = 36.5-37.8 °C. ¹H NMR (400 MHz, acetone-*d*₆): δ 8.78-8.73 (multiple peaks, 2H), 8.11 (ddd, *J* = 8.5, 4.9, 2.3 Hz, 1H), 7.96-7.86 (multiple peaks, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, acetone-*d*₆): δ -111.86 - -111.93 (m); ¹³C NMR (100 MHz, acetone-*d*₆): δ 137.97, 164.11 (d, *J*_{CF} = 254.2 Hz), 152.82 (d, *J*_{CF} = 2.9 Hz), 150.99, 137.70, 133.71 (d, *J*_{CF} = 4.4 Hz), 123.79 (d, *J*_{CF} = 9.5 Hz), 128.49 (d, *J*_{CF} = 12.4 Hz), 128.27 (d, *J*_{CF} = 3.7 Hz), 125.23 (d, *J*_{CF} = 10.2 Hz), 124.12, 117.63 (d, *J*_{CF} = 24.1 Hz), 33.97, 13.20. IR (KBr): 1713 cm⁻¹. Anal. Calcd for C₁₄H₁₂FN O₂: C, 68.56, H, 4.93, N, 5.71; Found: C, 68.78, H, 5.14, N, 5.68.

2-Benzoylpyridine (**14**) (105.9 mg, 0.58 mmol, 1 equiv), *N*-fluoropyridinium tetrafluoroborate (**3**) (350 mg, 1.8 mmol, 3.3 equiv), and Pd(OAc)₂ (13 mg, 0.058 mmol, 10 mol %) were combined in trifluorotoluene (26.2 mL) and acetonitrile (0.125 mL) in an 80 mL microwave reaction vessel equipped with a Teflon stirbar. The reaction mixture was heated in the microwave at 150 °C for 2 h (150 °C, 20 min ramp, 2 h, 300 W maximum). The resulting yellow suspension was cooled to room temperature, methylnaphthalene was added as an internal standard, and the reaction was analyzed by gas chromatography (which showed ~80% GC yield). The reaction mixture was then diluted with acetonitrile (20 mL) and filtered through a plug of Na₂CO₃ (~2 g) and Celite (~0.5 g) and the plug was washed with an additional 100 mL of acetonitrile and 10 mL of methanol. The solvent was removed under vacuum, and the resulting brown solid was dried onto silica gel and purified by chromatography on silica gel (*R*_f = 0.12 in 80% hexanes/20% ethyl acetate). Product **14a** was isolated as a white solid (55 mg, 48% yield). Mp = 35.3-36.5 °C. Note: samples of **14a** obtained by chromatography generally passed elemental analysis; nonetheless, GC and ¹H NMR spectroscopy showed that they were often contaminated with traces (3-5%) of the 2-benzoylpyridine starting material (which partially co-elutes with **14a**). ¹H NMR (400 MHz, acetone-*d*₆): δ 8.65 (dt, *J* = 3.7, 0.9 Hz, 1H), 8.10-8.05 (multiple peaks, 2H), 7.70-7.62 (multiple peaks, 3H), 7.36 (td, *J* = 6.0, 0.8 Hz, 1H), 7.24 (ddd, *J* = 8.4, 6.8, 0.4 Hz, 1H); ¹⁹F NMR (376 MHz, acetone-*d*₆): δ -111.60 (ddd, *J* = 10.1, 6.9, 5.0 Hz); ¹³C NMR (100 MHz, acetone-*d*₆): δ 194.06, 161.64 (d, *J*_{CF} = 249.8 Hz), 155.33, 150.06, 138.21, 134.38 (d, *J*_{CF} = 8.8 Hz), 131.84 (d, *J*_{CF} = 3.0 Hz), 128.22, 128.03 (d, *J* = 14.9), 125.11 (d, *J*_{CF} = 3.7 Hz), 123.70, 116.68 (d, *J*_{CF} = 22.0). IR (KBr): 1668 cm⁻¹. HRMS EI (*m/z*): [*M*⁺] calcd for C₁₂H₉FNO, 201.0590; found, 201.0595. Anal. Calcd for C₁₂H₉FNO: C, 71.64, H, 4.01, N, 6.96; Found: C, 71.49, H, 4.01, N, 6.90.

2-Methoxy-6-phenylpyridine (**15**) (107 mg, 0.58 mmol, 1 equiv), *N*-fluoropyridinium tetrafluoroborate (**3**) (481 mg, 2.6 mmol, 4.5 equiv), and Pd(OAc)₂ (13 mg, 0.058 mmol, 10 mol %) were combined in trifluorotoluene (26.2 mL) and acetonitrile (0.5 mL) in an 80 mL microwave reaction vessel equipped with a Teflon stirbar. The reaction mixture was heated in the microwave at 150 °C for 2 h (150 °C, 2 h, 20 min ramp, 300 W maximum). The resulting yellow suspension was cooled to room temperature, methylnaphthalene was added as an internal standard, and the reaction was analyzed by gas chromatography (which showed ~57% GC yield). The reaction mixture was then diluted with acetonitrile (20 mL) and filtered through a plug of Na₂CO₃ (~2 g) and Celite (~0.5 g) and the plug was washed with an additional 100 mL of acetonitrile and 10 mL of methanol. The solvent was removed under vacuum, and the resulting brown solid was dried onto silica gel purified by chromatography on silica gel (*R*_f = 0.4 in 90% hexanes/10% ethyl acetate). Product **15a** was isolated as a clear oil (71 mg, 60% yield). ¹H NMR (400 MHz, acetone-*d*₆): δ 7.81 (dd, *J* = 8.2, 7.4 Hz, 1H), 7.52 (tt, *J* = 8.4, 6.4 Hz, 1H), 7.18-7.09 (multiple peaks, 3H), 6.83 (dd, *J* = 8.4, 0.8 Hz, 1H), 3.89 (s, 3H); ¹⁹F NMR (376 MHz, acetone-*d*₆): δ -115.55 - -115.64 (m); ¹³C NMR (100 MHz, acetone-*d*₆): δ 164.73, 161.36 (dd, *J*_{CF} = 247.6, 7.4 Hz), 147.46, 140.01, 131.45 (t, *J*_{CF} = 10.3 Hz), 119.72, 118.96 (t, *J* = 18.6), 112.70 (dd, *J*_{CF} = 19.4, 6.2 Hz), 111.27, 53.68. HRMS EI (*m/z*): [*M*⁺] calcd for C₁₂H₉F₂NO, 221.0662; found, 221.0652. Anal. Calcd for C₁₂H₉F₂NO: C, 65.16, H, 4.10, N, 6.33; Found: C, 64.95, H, 4.11, N, 6.31.

Data in Table 1 (General Information): All oxidant screening reactions were set up in duplicate and were analyzed by GC analysis with naphthalene as the internal standard.

Thermal Reactions: 8-Methylquinoline (6.1 μL , 0.045 mmol, 1 equiv), "F⁺" reagent (0.067 mmol, 1.5 equiv), and $\text{Pd}(\text{OAc})_2$ (1.0 mg, 0.0045 mmol, 10 mol %) were combined in benzene (0.75 mL) in a 4 mL vial. The vial was sealed with a Teflon lined cap, and the reaction heated at 110 $^\circ\text{C}$ for 13 h. After cooling, naphthalene was added as an internal standard, and the reaction mixture was diluted with CH_3CN and filtered through a plug of Na_2CO_3 and Celite. The yields of **1a**, **1b**, and **1c** were determined through GC analysis.

Microwave Reactions: 8-Methylquinoline (6.1 μL , 0.045 mmol, 1 equiv), "F⁺" reagent (0.067 mmol, 1.5 equiv), and $\text{Pd}(\text{OAc})_2$ (1.0 mg, 0.0045 mmol, 10 mol %) were combined in benzene (0.75 mL) in a 10 mL microwave reaction vessel. The vessel was sealed, and the reaction was heated with microwave irradiation at 110 $^\circ\text{C}$ for 1 h (250 W, 110 $^\circ\text{C}$, 1 h, 10 min ramp). After cooling, naphthalene was added as an internal standard, and the reaction mixture was diluted with CH_3CN and filtered through a plug of Na_2CO_3 and Celite. The yields of **1a**, **1b**, and **1c** were determined through GC analysis.

Table S1. Palladium Catalyzed Fluorination of 4

Entry	"F ⁺ " Source	Yield of 4a
1	(2)	6%
2	(3)	76%
3		33%
4		0%
5		58%

Data in Table S1: All oxidant screening reactions were analyzed by GC analysis with naphthalene as the internal standard.

Substrate **4** (8 mg, 0.045 mmol, 1 equiv), "F⁺" reagent (0.11 mmol, 2.5 equiv), and Pd(OAc)₂ (1.0 mg, 0.005 mmol, 10 mol %) were combined in trifluorotoluene (2.0 mL) and CH₃CN (0.038 mL) in a 10 mL microwave reaction vessel. The vessel was sealed, and the reaction was heated while stirring with microwave irradiation at 150 °C for 1.5 h (300 W, 150 °C, 1.5 h, 20 min ramp). After cooling, methylnaphthalene was added as an internal standard, and the reaction mixture was diluted with CH₃CN and filtered through a plug of Na₂CO₃ and Celite. The yield of **4a** was determined through GC analysis.

Reaction of 1a, 2 and benzene: 8-(Fluoromethyl)quinoline (**1a**) (50 mg, 0.31 mmol, 1 equiv) and *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (**2**) (141 mg, 0.62 mmol, 2 equiv) were combined in benzene (5.2 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was heated at 130 °C for 13 h. The reaction was diluted with 10 mL acetonitrile and filtered through ~2 g sodium carbonate and ~0.5 g Celite, washing with an additional 100 mL acetonitrile, 10 mL methylene chloride, and 10 mL methanol. The washes were concentrated, and the resulting product was purified by chromatography on silica gel (R_f = 0.27 in 90% hexanes/10% ethyl acetate). Product **1b** was isolated as a white solid (37 mg, 54% yield). Spectroscopic data was identical to that previously reported for this compound.^{iv}

Reaction of 1a, 2, and benzene- d_6 : 8-(Fluoromethyl)quinoline (**1a**) (50 mg, 0.31 mmol, 1 equiv) and *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (**2**) (140.7 mg, 0.620, 2 equiv) were combined in benzene- d_6 (2 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was heated at 130 °C for 13 h. The reaction was diluted with 10 mL acetonitrile and filtered through ~2 g sodium carbonate and ~0.5 g Celite, washing with an additional 100 mL acetonitrile, 10 mL methylene chloride, and 10 mL methanol. The crude reaction mixture was then assayed by GCMS [(m/z): [M^+] calcd for $C_{16}H_8D_5N$, 224; found, 224].

Reaction of 1a, 2, and anisole: 8-(Fluoromethyl)quinoline (**1a**) (50 mg, 0.31 mmol, 1 equiv) and *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (**2**) (141 mg, 0.62 mmol, 2 equiv) were combined in anisole (5.2 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was heated at 110 °C for 13 h. The reaction was diluted with 10 mL acetonitrile and filtered through ~2 g sodium carbonate and ~0.5 g Celite, washing with an additional 100 mL acetonitrile, 10 mL methylene chloride, and 10 mL

methanol. The washes were concentrated, and the resulting product was purified by chromatography on silica gel ($R_f = 0.53$ in 80% hexanes/20% ethyl acetate). The product was isolated as a clear oil (53 mg, 68% yield; $o/p = 1:1.1$ by GC). The two regioisomers were separated by HPLC (90% hexanes, 10% ethyl acetate, 20 mL/min, 19.1 mm Waters μ -Porasil column). (*o*-Methoxybenzyl)quinoline: ^1H NMR (400 MHz, acetone- d_6): δ 8.90 (dd, $J = 4.2, 1.8$ Hz, 1H), 8.25 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.74 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.48 – 7.37 (multiple peaks, 3H), 7.15 (td, $J = 7.7, 1.5$ Hz, 1H), 7.07 (dd, $J = 7.6, 1.2$ Hz, 1H), 6.95 (d, $J = 6.95$ Hz, 1H), 6.77 (td, $J = 7.4, 1.1$ Hz, 1H), 4.63 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, acetone- d_6): δ 158.61, 150.35, 147.84, 140.71, 137.08, 131.53, 130.43, 129.97, 129.33, 128.17, 127.21, 127.09, 122.03, 121.15, 111.32, 55.73, 31.37. (*p*-Methoxybenzyl)quinoline: ^1H NMR (400 MHz, acetone- d_6): δ 8.96 (dd, $J = 4.2, 1.8$ Hz, 1H), 8.29 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.79 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.57 – 7.47 (multiple peaks, 3H), 7.27 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 2H), 4.59 (s, 2H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, acetone- d_6): δ 158.95, 150.49, 147.55, 141.75, 137.09, 134.67, 130.95, 130.14, 129.46, 127.29, 127.26, 122.13, 114.50, 55.44, 36.42. HRMS (EI) $[M^+]$ for $\text{C}_{17}\text{H}_{15}\text{NO}$, 249.1154, found, 249.1163.

8-(Fluoromethyl)quinoline (**1a**) (50 mg, 0.31 mmol, 1 equiv), *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (**2**) (141 mg, 0.62 mmol, 2 equiv), and 1,4-dimethoxybenzene (857 mg, 6.2 mmol, 20 equiv) combined in trifluorotoluene (5 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was heated at 110 °C for 13 h. The reaction was diluted with 10 mL acetonitrile and filtered through ~2 g sodium carbonate and ~0.5 g Celite, washing with an additional 100 mL acetonitrile, 10 mL methylene chloride, and 10 mL methanol. The washes were concentrated, and the resulting product was purified by chromatography on silica gel ($R_f = 0.16$ in 90% hexanes/10% ethyl acetate). The product was isolated as a clear oil (49 mg, 57% yield). ^1H NMR (400 MHz, acetone- d_6): δ 8.95 (dd, $J = 4.0, 2.0$ Hz, 1H), 8.31 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.80 (dd, $J = 7.4, 2.2$ Hz, 1H), 7.53–7.44 (multiple peaks, 3H), 6.91 (dd, $J = 8.0, 1.2$ Hz, 1H), 6.77–6.70 (multiple peaks, 2H), 4.62 (s, 2H), 3.79 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, acetone- d_6): δ 154.56, 152.82, 150.37, 147.78, 140.58, 137.09, 131.70, 130.03, 129.34, 127.23, 127.15, 122.05, 118.17, 112.20, 111.77, 56.29, 55.65, 31.49. HRMS (EI): $[M^+]$ for $\text{C}_{19}\text{H}_{17}\text{NO}_2$, 279.1259, found, 279.1267.

Competition reaction of 1a and 2 with benzene and *p*-dimethoxybenzene: 8-(Fluoromethyl)quinoline (7.2 mg, 0.045 mmol, 1 equiv), *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (2) (15.1 mg, 0.067 mmol, 1.5 equiv), benzene (50 equiv) and *p*-dimethoxybenzene (50 equiv) were combined with trifluorotoluene (1 mL) in a 4 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was heated at 130 °C for 13 h. After cooling, naphthalene was added as an internal standard, and the reaction mixture was diluted with CH₃CN and filtered through a plug of Na₂CO₃ and Celite. The yields of **1b** and the corresponding (*p*-MeO)₂C₆H₃ product were determined by GC analysis to be 3% and 87%, respectively (a 1:29 ratio).

Reaction of 4a with 2 and benzene: 2-(2,6-Difluoro)pyridine (**4a**) (8.5 mg, 0.0445 mmol, 1 equiv) and *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (2) (15.1 mg, 0.067, 1.5 equiv) were combined in benzene (1 mL) in a 4 mL vial. The vial was sealed with a Teflon lined cap, and the reaction heated at 130 °C for 13 h. After cooling, naphthalene was added as an internal standard, and the reaction mixture was diluted with CH₃CN and filtered through a plug of Na₂CO₃ and Celite. The reaction was analyzed by GCMS and no phenylated product was observed.

Reaction of 1a with AcOH: We sought to test whether product **1c** could be formed by reaction of **1a** with HOAc under our reaction conditions. (Notably, the HOAc would be generated in the initial C–H activation reaction of 8-methylquinoline with Pd(OAc)₂). The following experiment was carried out:

8-(Fluoromethyl)quinoline (**1a**) (7.2 mg, 0.045 mmol, 1 equiv), *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (2) (15.1 mg, 0.067 mmol, 1.5 equiv), and AcOH (5 μL, 0.089 mmol, 2 equiv) were

combined in benzene (1 mL) in a 4 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was heated at 110 °C for 13 h. After cooling, naphthalene was added as an internal standard, and the reaction mixture was diluted with CH₃CN and filtered through a plug of Na₂CO₃ and Celite. GC analysis showed that **1c** was formed in 11% yield under these conditions. *Note:* Product **1c** was *not* formed under the same reaction conditions in the absence of **2**. Additionally, the reaction of **1a** with 2 equiv AcOH in the presence of Pd(OAc)₂ but in the absence of **2** also afforded none of product **1c**.

This result clearly shows that **1c** can be generated by direct reaction of **1a** with HOAc in the presence of oxidant **2**. However, product **1c** could also be formed directly by competitive C–F and C–OAc bond forming reductive elimination from the Pd center during the reaction. Such C–O coupling at Pd under oxidative conditions are well-precedented.³ However, it is interesting to note that none of the corresponding acetate product was formed with any of the phenylpyridine substrates. Since competing C–O and C–F bond forming reductive elimination from the Pd catalyst could also occur in these systems, this result suggests that the non-Pd-mediated pathway may be more likely. However, we have thus far been unable to definitively establish the origin of **1c** in these systems.

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