Supporting Information for:

A Highly Selective Catalytic Method for the Oxidative Functionalization of C-H 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) 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), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m), and broad resonance (br).

Materials and Methods: 5,8-Dimethylquinoline was prepared according to a literature procedure.¹ 2-Naphthalen-2-yl-pyridine was prepared via Suzuki coupling of 2-naphthalene boronic acid and 2-bromopyridine as described for closely analogous compounds.² All other substrates as well as $\text{PhI}(\text{OAc})_2$, *N*-chlorosuccinimide and *N*-bromosuccinimide were obtained from Aldrich or Acros and used as received. Solvents were obtained from Fisher Chemical and used without further purification. $\text{Pd}(\text{OAc})_2$ was obtained from Strem Chemicals and used as received. 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. Control reactions (in the absence of Pd catalyst) were run for each substrate, and showed only traces (generally <5%) of non-specific oxidation.

Complex **2** was prepared by a modification of a literature procedure.³ Benzo[*h*]quinoline (114 mg, 0.63 mmol) and $\text{Pd}(\text{OAc})_2$ (141 mg, 0.63 mmol) were stirred in methanol (10 mL) at room temperature for 4 hours, precipitating a bright yellow solid. The solid was collected and washed with hexanes to yield **2** (161 mg, 75%). ^1H NMR (CDCl_3): δ 7.77 (d, J = 6.0 Hz, 1H), 7.39 (d J = 10.0 Hz, 1H), 7.21–7.16 (m, 3H), 7.06 (dd, J = 7.5 Hz, 2.5 Hz, 1H), 6.92 (d, J = 10.5 Hz, 1H), 6.43 (dd, J = 10.0 Hz, 6.5 Hz, 1H). Anal. Calcd for $\text{C}_{30}\text{H}_{22}\text{N}_2\text{O}_4\text{Pd}_2$: C, 52.42, H, 3.23, N, 4.08; Found: C, 52.23, H, 3.25, N, 3.93.

Benzo[*h*]quinoline (159 mg, 0.89 mmol), $\text{PhI}(\text{OAc})_2$ (586 mg, 1.8 mmol), and $\text{Pd}(\text{OAc})_2$ (3.8 mg, 0.017 mmol) were dissolved in CH_3CN (7.5 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap and the mixture stirred at 75 °C for 12 hours. The crude product obtained after evaporation of the solvent was purified by flash chromatography on silica gel (R_f = 0.25 in 4:1

hexanes: ethyl acetate) eluting with 10% ethyl acetate in hexanes to 25% ethyl acetate in hexanes. Although GC analysis of the crude reaction mixture showed **3a** was the major product, with only traces of **3b**, the product was isolated as a mixture of ~11:1 **3a**:**3b**, suggesting hydrolysis on silica gel. This mixture was obtained as a yellow oil (178 mg, 86%), which solidified upon trituration with hexanes. Pure material for elemental analysis was obtained by repeated column chromatography and isolation of only fractions containing **3a**. ^1H NMR (CDCl_3): δ 8.97 (dd, J = 4.0 Hz, 2.0 Hz, 1H), 8.14 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.84 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.82 (d, J = 10.0 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.49 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 7.42 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 2.61 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 171.09, 148.73, 148.08, 145.57, 136.06, 135.77, 128.14, 128.04, 127.27, 126.73, 126.42, 123.30, 122.18, 121.58, 21.79. Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{NO}_2$: C, 75.94, H, 4.67, N, 5.90; Found: C, 75.95, H, 4.77, N, 5.68.

Pure hydroxy product (**3b**) was obtained by dissolving a mixture of **3a** and **3b** in methanolic NaOH. After stirring at room temperature for 3 hr, the mixture was acidified with concentrated HCl to neutral pH, and the methanol was evaporated. The solid thus obtained was extracted between ethyl acetate and water to remove sodium chloride, and the organic layer was dried over sodium sulfate and removed under vacuum to yield pure **3b** (R_f = 0.48 in 4:1 hexanes: ethyl acetate). ^1H NMR (CDCl_3): δ 8.84 (dd, J = 4.5 Hz, 2.0 Hz, 1H), 8.27 (dd, J = 8.0 Hz, 1.5 Hz, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.64 (d, J = 9.5 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.57 (dd, J = 8.0 Hz, 5.0 Hz, 1H), 7.42 (dd, J = 7.5 Hz, 1.0 Hz, 1H), 7.26 (dd, J = 8.0 Hz, 1.0 Hz, 1H), -1.09 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 159.52, 148.41, 145.08, 136.29, 135.14, 129.98, 129.21, 126.34, 124.65, 120.89, 118.20, 116.02, 114.04. Anal. Calcd for $\text{C}_{13}\text{H}_9\text{NO}$: C, 79.98, H, 4.65, N, 7.17; Found: C, 79.62, H, 4.65, N, 7.01.

Methanol (7.5 mL) was added to a mixture of benzo[*h*]quinoline (151 mg, 0.84 mmol), $\text{PhI}(\text{OAc})_2$ (541 mg, 1.7 mmol), and $\text{Pd}(\text{OAc})_2$ (2.2 mg, 0.0098 mmol) in a 20 mL vial. The vial was sealed with a Teflon lined cap and the solution was heated with stirring to 100 °C for 22 hours. The crude mixture was filtered through Celite and the solvent evaporated to yield a dark orange oil which was extracted between ethyl acetate and 10% sodium hydroxide. The organic layers were dried over sodium sulfate and the solvent was removed under vacuum to yield **3c** (171 mg, 95%) as a light yellow solid. ^1H NMR (CDCl_3): δ 9.14 (dd, J = 4.0 Hz, 2.0 Hz, 1H), 8.17 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.79 (d, J = 8.5 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.56 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.50 (dd, J = 8.0 Hz, 4.5 Hz, 1H), 7.27 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 4.19 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 159.23, 148.75, 147.46, 136.52, 135.80, 128.37, 127.30, 126.46, 121.33, 120.74, 109.96, 56.96. HRMS (EI): Calcd for $\text{C}_{14}\text{H}_{11}\text{NO}$ m/z 209.0840, Observed m/z 209.0837.

Benzo[*h*]quinoline (154 mg, 0.86 mmol), $\text{PhI}(\text{OAc})_2$ (562 mg, 1.7 mmol), and $\text{Pd}(\text{OAc})_2$ (10 mg, 0.044 mmol) were combined in a 20 mL vial and absolute ethanol (7.5 mL) added. The vial was

sealed with a Teflon lined cap and the solution stirred at 100 °C for 24 hours. The mixture was filtered through Celite to remove an insoluble black solid, leaving a yellow liquid. After evaporation of the solvent, the crude material was purified by flash chromatography on silica gel (R_f = 0.47 in 9:1 methylene chloride: methanol) eluting with 5% methanol in methylene chloride. The thick oil that resulted was dissolved in methylene chloride and triturated several times with hexanes to yield **3d** (152 mg, 80%) as a light yellow solid. ^1H NMR (CDCl_3): δ 9.11 (dd, J = 4.0 Hz, 2.0 Hz, 1H), 8.15 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.77 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.56 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.49 (dd, J = 8.0 Hz, 4.5 Hz, 1H), 7.29 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 4.36 (q, J = 7.0 Hz, 2H), 1.67 (t, J = 7.0 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 158.74, 148.48, 147.25, 136.48, 135.62, 128.43, 128.36, 127.13, 126.22, 121.93, 121.66, 120.80, 113.18, 66.23, 15.12. Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}$: C, 80.69, H, 5.87, N, 6.27; Found: C, 80.57, H, 5.94, N, 6.06.

Benzo[*h*]quinoline (141 mg, 0.79 mmol), $\text{PhI}(\text{OAc})_2$ (657 mg, 2.0 mmol), and **2** (9 mg, 0.013 mmol) were dissolved in a mixture of isopropanol (4.0 mL) and acetic acid (4.0 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap and the resulting solution was heated to 100 °C for 27 hours. The solvent was removed under vacuum, and the resulting crude material was purified by flash chromatography on silica gel (R_f = 0.5 in 9:1 methylene chloride: methanol) eluting with 5% methanol in methylene chloride to 15% methanol in methylene chloride. The product (**3e**) (135 mg, 72%) was obtained as a brown oil. ^1H NMR (CDCl_3): δ 9.09 (dd, J = 4.5 Hz, 2.0 Hz, 1H), 8.11 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.62-7.57 (m, 3H), 7.46 (dd, J = 8.0 Hz, 4.5 Hz, 1H), 7.34 (dd, J = 6.5 Hz, 3.0 Hz, 1H), 4.64 (septet, J = 6.0 Hz, 1H), 1.50 (d, J = 6.0 Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 157.04, 148.34, 147.11, 136.65, 135.47, 128.45, 128.13, 127.02, 126.04, 123.85, 122.88, 120.89, 119.58, 74.03, 22.35. Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}$: C, 80.98, H, 6.37, N, 5.90; Found: C, 80.72, H, 6.23, N, 5.73.

Benzo[*h*]quinoline (146 mg, 0.82 mmol), $\text{PhI}(\text{OAc})_2$ (531 mg, 1.6 mmol), and **2** (2 mg, 0.0055 mmol) were dissolved in trifluoroethanol (7.5 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap and the mixture was stirred at 100 °C for 21 hours. Following evaporation of the solvent, the crude dark orange oil was purified by flash chromatography on silica gel (R_f = 0.48 in 4:1 hexanes: ethyl acetate), eluting with methylene chloride to 5% methanol in methylene chloride. The product was obtained as an orange oil which was taken up in diethyl ether and filtered through a plug of Celite. After addition of hexanes to the mixture and evaporation of the solvent, **3f** (161 mg, 71%) was obtained as a light orange solid. The orange impurity was removed by further chromatography eluting with 5% ethyl acetate in hexanes, leaving a white solid. ^1H NMR (CDCl_3): δ 9.09 (dd, J = 4.5 Hz, 2.0 Hz, 1H), 8.18 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.75 (dd, J = 7.5 Hz, 1.0 Hz, 1H), 7.69 (d, J = 9.0 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.53 (dd, J = 8.0 Hz, 4.5 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 4.66 (q, J = 9.0 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$

NMR (CDCl₃): δ 156.97, 148.93, 146.15, 136.61, 135.84, 128.52, 128.34, 127.41, 126.50, 125.47, 123.77, 123.32, 121.55, 120.90, 70.70 (q, J_{C-F} = 34.0 Hz). Anal. Calcd for C₁₅H₁₀F₃NO: C, 64.98, H, 3.64, N, 5.05; Found: C, 64.93, H, 3.67, N, 4.97.

Benzo[*h*]quinoline (159 mg, 0.89 mmol), *N*-chlorosuccinimide (137 mg, 1.0 mmol), and **2** (5.4 mg, 0.0079 mmol) were dissolved in CH₃CN (7.5 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap and the resulting solution was stirred at 100 °C for 3 days. The solvent was evaporated, and the crude solid was purified by flash chromatography on silica gel (R_f = 0.41 in 4:1 hexanes: ethyl acetate) eluting with 10% ethyl acetate in hexanes. The product (180 mg, 95%) was obtained as a white solid. ¹H NMR (CDCl₃): δ 9.12 (dd, J = 4.0 Hz, 2.0 Hz, 1H), 8.18 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.85-7.82 (m, 2H), 7.69 (d, J = 9.0 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.58-7.55 (m, 2H). ¹³C{¹H} NMR (CDCl₃): δ 147.68, 146.52, 136.37, 135.70, 132.40, 131.58, 128.18, 127.75, 127.65, 127.59, 126.68, 121.76. Anal. Calcd for C₁₃H₈ClN: C, 73.08, H, 3.77, N, 6.56; Found: C, 72.97, H, 3.84, N, 6.57.

Benzo[*h*]quinoline (159 mg, 0.89 mmol), *N*-bromosuccinimide (168 mg, 0.94 mmol), and **2** (3.0 mg, 0.0044 mmol) were dissolved in CH₃CN (7.5 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap and the mixture stirred at 100 °C for 1.5 days. After evaporation of the solvent, the crude solid was purified by flash chromatography on silica gel (R_f = 0.43 in 4:1 hexanes: ethyl acetate), eluting with 10% ethyl acetate in hexanes. The product (215 mg, 93%) was obtained as a white solid. ¹H NMR (CDCl₃): δ 9.12 (dd, J = 4.0 Hz, 2.0 Hz, 1H), 8.18 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 8.11 (dd, J = 7.5 Hz, 1.0 Hz, 1H), 7.89 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 9.0 Hz, 1H), 7.57 (dd, J = 7.0 Hz, 4.0 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H). ¹³C{¹H} NMR (CDCl₃): δ 147.11, 146.09, 136.36, 135.71, 135.59, 128.48, 128.45, 128.23, 128.02, 127.44, 126.64, 121.97, 119.58. Anal. Calcd for C₁₃H₈BrN: C, 60.49, H, 3.12, N, 5.43 Found: C, 60.66, H, 3.20, N, 5.27.

8-Methylquinoline (162 μ L, 1.4 mmol), PhI(OAc)₂ (433.3 mg, 1.3 mmol), and Pd(OAc)₂ (2.66 mg, 0.012 mmol) were combined in AcOH (10 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction mixture was heated at 100°C for 22 hr. The solvent was removed under vacuum, and the resulting oil was purified by chromatography on silica gel (R_f = 0.2 in 80% hexanes/20% ethyl acetate). The product (**4a**) was obtained as a white solid (211 mg, 88% yield). ¹H NMR (CDCl₃): δ 8.93 (dd, J = 4.4 Hz, 2.0 Hz, 1H), 8.14 (dd, J = 8.4 Hz, 2 Hz,

1H), 7.75 (m, 2H), 7.55 (dd, $J = 8.2$ Hz, 7.4 Hz, 1H), 7.44 (dd, $J = 8.6$ Hz, 4.2 Hz, 1H), 5.86 (s, 2H), 2.16 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 171.12, 150.02, 146.24, 136.34, 134.31, 128.88, 128.25, 126.31, 121.41, 62.88, 21.26. Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_2$: C, 71.63, H, 5.51, N, 6.96; Found: C, 71.79, H, 5.91, N, 6.65.

8-Methylquinoline (162 μL , 1.2 mmol), $\text{PhI}(\text{OAc})_2$ (419 mg, 1.3 mmol), and $\text{Pd}(\text{OAc})_2$ (5.3 mg, 0.023 mmol) were combined in MeOH (10 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction mixture was heated at 100°C for 18 hr. The solvent was removed under vacuum, and the resulting oil was purified by chromatography on silica gel ($R_f = 0.1$ in 90% hexanes/10% ethyl acetate). The product (**4b**) was obtained as a yellow oil (167 mg, 80% yield). ^1H NMR (CDCl_3): δ 8.93 (dd, $J = 4.4$ Hz, 2.0 Hz, 1H), 8.15 (dd, $J = 8.2$ Hz, 1.8 Hz, 1H), 7.83 (dd, $J = 7.0$ Hz, 1.0 Hz, 1H), 7.75 (d, $J = 8$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 1H), 7.41 (dd, $J = 8.2$ Hz, 4.2 Hz, 1H), 5.20 (s, 2H), 3.60 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 149.66, 145.98, 136.43, 128.18, 127.62, 127.26, 126.49, 121.14, 70.87, 59.00. Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{NO}$: C, 76.28, H, 6.40, N, 8.09; Found: C, 76.30, H, 6.16, N, 8.10.

5,8-Dimethylquinoline (186 mg, 1.186 mmol), $\text{PhI}(\text{OAc})_2$ (419 mg, 1.3 mmol), $\text{Pd}(\text{OAc})_2$ (10.6 mg, 0.047 mmol) were combined in $\text{CH}_3\text{CO}_2\text{H}$ (10 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction mixture was heated at 100°C for 20 hr. The solvent was removed under vacuum, and the resulting oil was purified by chromatography on silica gel ($R_f = 0.05$ in 90% hexanes/10% ethyl acetate). The product (**5**) was obtained as a white solid (231 mg, 80% yield). ^1H NMR (CDCl_3): δ 8.95 (dd, $J = 4.2$ Hz, 1.4 Hz, 1H), 8.32 (dd, $J = 8.4$ Hz, 2 Hz, 1H), 7.65 (d, $J = 6.8$ Hz, 1H), 7.45 (dd, $J = 8.4$ Hz, 4.0 Hz, 1H), 7.36 (d, $J = 6.8$ Hz, 1H), 5.81 (s, 2H), 2.57 (s, 3H), 2.13 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 171.27, 149.62, 146.63, 135.28, 133.79, 132.37, 128.98, 127.73, 126.76, 121.04, 63.13, 21.37, 18.84. Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_2$: C, 72.54, H, 6.09, N, 6.51; Found: C, 72.34, H, 6.40, N, 6.40.

nOe confirmation of regiochemistry of oxidation:

Azobenzene (1.01 g, 5.5 mmol), $\text{PhI}(\text{OAc})_2$ (3.57 g, 11.1 mmol), and $\text{Pd}(\text{OAc})_2$ (27 mg, 0.12 mmol) were weighed into a 50 mL Schlenk flask. The flask was flushed with nitrogen and CH_3CN (30 mL) was added. The flask was sealed and the reaction was stirred at 75 °C for 3 days. After evaporation of the solvent, the crude purple oil was purified by flash chromatography on silica gel (R_f = 0.38 in 4:1 hexanes: ethyl acetate) eluting with 5% ethyl acetate in hexanes to 20% ethyl acetate in hexanes. The product (**6**) (824 mg, 62% overall yield, 79% based on converted azobenzene) was obtained as a viscous bright red oil. A mixture of diacetoxymethyl isomers (2,2- and 2,5-) was obtained as the major byproduct as an orange solid (~15%). ^1H NMR (CDCl_3): δ 7.87-7.85 (m, 2H), 7.82 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.53-7.48 (m, 4H), 7.37-7.34 (m, 1H), 7.25 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 2.40 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 169.49, 152.77, 149.00, 143.90, 132.08, 131.35, 129.09, 126.52, 123.32, 122.95, 117.58, 20.69. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$: C, 69.99, H, 5.03, N, 11.66. Found: C, 70.13, H, 5.04, N, 11.64.

2-Phenyl pyrazole (200 mg, 1.39 mmol), $\text{PhI}(\text{OAc})_2$ (514 mg, 1.59 mmol), and $\text{Pd}(\text{OAc})_2$ (7.8 mg, 0.035 mmol) were combined in $\text{CH}_3\text{CO}_2\text{H}$ (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction mixture was heated at 100°C for 12 hr. The solvent was removed under vacuum, and the resulting oil was purified by chromatography on silica gel (R_f = 0.40 in 90% hexanes/10% ethyl acetate). The product (**7**) was obtained as a clear oil (154 mg, 54% yield). ^1H NMR (CDCl_3): δ 7.68 (dd, J = 10.8 Hz, J = 2.8 Hz, 2H), 7.57 (dd, J = 7.2 Hz, J = 2.4 Hz, 1H), 7.35-7.27 (multiple peaks, 2H), 7.17 (m, 1H), 6.39 (t, J = 2 Hz, 1H), 2.15 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 168.86, 143.39, 141.13, 133.24, 130.27, 128.47, 126.92, 125.76, 124.12, 107.14, 20.88. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.11; H, 4.97; N, 13.53.

Benzylidene imine (50 mg, 0.275 mmol), $\text{PhI}(\text{OAc})_2$ (133 mg, 0.414 mmol) and $\text{Pd}(\text{OAc})_2$ (3.1 mg, 0.014 mmol) were combined in CH_3CN (2 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction mixture was heated at 100°C for 12 hr. The yield of this reaction (47%) was determined by gas chromatography (versus standard of hexadecane) by comparison to an authentic sample of the product (**8**). GC and GCMS analysis showed that the remainder of the material was composed of the dioxidized product (~25%) and the starting imine (~25%).

2-Naphthalen-2-yl-pyridine (84 mg, 0.409 mmol), $\text{PhI}(\text{OAc})_2$ (158 mg, 0.49 mmol), and $\text{Pd}(\text{OAc})_2$ (5.5 mg, 0.025 mmol) were combined in CH_3CN (3 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction mixture was heated at 100°C for 12 hr. The solvent was removed under vacuum, and the resulting oil was purified by chromatography on silica gel ($R_f = 0.15$ in 80% hexanes/20% ethyl acetate). The product (**9**) was obtained as a clear oil (108 mg, 73% yield). ^1H NMR (CDCl_3): δ 8.75 (d, $J = 4.8$ Hz, 1H), 8.19 (s, 1H), 7.92 (d, $J = 8$ Hz, 1H), 7.84 (d, $J = 8$ Hz, 1H), 7.78 (dt, $J = 7.6$ Hz, $J = 2$ Hz, 1H), 7.66 (d, $J = 8$ Hz, 1H), 7.65 (s, 1H), 7.58–7.49 (multiple peaks, 2H), 7.29 (m, 1H), 2.22 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 169.81, 156.21, 149.76, 146.15, 136.59, 133.85, 132.63, 131.84, 130.88, 128.45, 127.49, 127.24, 126.33, 123.98, 122.43, 120.72, 21.18. Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{NO}_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.67; H, 5.31; N, 5.02.

2-Phenyl pyridine (200 mg, 1.29 mmol), $\text{PhI}(\text{OAc})_2$ (581 mg, 1.80 mmol), and $\text{Pd}(\text{OAc})_2$ (14 mg, 0.065 mmol) were combined in CH_3CN (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction mixture was heated at 100°C for 12 hr. The solvent was removed under vacuum, and the resulting oil was purified by chromatography on silica gel ($R_f = 0.30$ in 70% hexanes/30% ethyl acetate). The product (**10**) was obtained as a clear oil (142 mg, 52% yield). A substantial amount of the di-oxidized product (**11**) was also obtained (90 mg, 26% yield). ^1H NMR (CDCl_3): δ 8.71 (d, $J = 6$ Hz, 1H), 7.77–7.70 (multiple peaks, 2H), 7.55 (d, $J = 7.6$ Hz, 1H), 7.44 (dt, $J = 7.6$ Hz, $J = 1.8$ Hz, 1H), 7.37 (dt, $J = 7.2$ Hz, $J = 1.6$ Hz, 1H), 7.27 (m, 1H), 7.17 (d, $J = 8$ Hz, 1H), 2.19 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 169.59, 155.98, 149.73, 148.24, 136.43, 133.30, 130.96, 129.87, 126.54, 123.76, 123.39, 122.35, 21.11. Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.52; H, 4.98; N, 6.34.

2-Phenyl pyridine (100 mg, 0.64 mmol), $\text{PhI}(\text{OAc})_2$ (519 mg, 1.61 mmol), and $\text{Pd}(\text{OAc})_2$ (8.7 mg, 0.039 mmol) were combined in CH_3CN (4 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction mixture was heated at 100°C for 12 hr. The solvent was removed under vacuum, and the resulting oil was purified by chromatography on silica gel ($R_f = 0.40$ in 45% hexanes/55% ethyl acetate). The product (**11**) was obtained as a white solid (144 mg, 83% yield). ^1H NMR (CDCl_3): δ 8.70 (d, $J = 4.8$ Hz, 1H), 7.73 (dt, $J = 7.6$ Hz, $J = 2$ Hz, 1H), 7.44 (t, $J = 8.4$ Hz, 1H), 7.32 (d, $J = 8$ Hz, 1H), 7.27 (t, $J = 7.32$ Hz, 1H), 7.10 (d, $J = 8$ Hz, 1H), 2.02 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 169.10, 152.46, 149.62, 149.26, 136.13, 129.54, 127.68, 125.27, 122.67, 120.84, 20.77. Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_4$: C, 66.34; H, 4.83; N, 5.16. Found: C, 66.34; H, 4.61; N, 5.02.

2-*p*-Tolyl-pyridine (200 mg, 1.18 mmol), $\text{PhI}(\text{OAc})_2$ (875 mg, 2.72 mmol), and $\text{Pd}(\text{OAc})_2$ (15.8 mg, 0.071 mmol) were combined in CH_3CN (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction mixture was heated at 100°C for 12 hr. The solvent was removed under vacuum, and the resulting oil was purified by chromatography on silica gel ($R_f = 0.45$ in 60% hexanes/40% ethyl acetate). The product (**12**) was obtained as a white solid (262 mg, 78% yield). ^1H NMR (CDCl_3): δ 8.67 (d, $J = 6.8$ Hz, 1H), 7.69 (dt, $J = 8$ Hz, $J = 1.6$ Hz, 1H), 7.29 (d, $J = 7.6$ Hz, 1H), 7.21 (m, 1H), 6.91 (s, 2H), 2.39 (s, 3H), 2.00 (s, 6H). ^{13}C NMR (CDCl_3): δ 169.14, 152.54, 149.52, 148.89, 140.19, 135.99, 125.24, 124.74, 122.42, 121.41, 21.39, 20.71. Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.52; H, 5.37; N, 4.71.

nOe confirmation of the regioselectivity of oxidation:

4-(2-Pyridyl)benzaldehyde (200 mg, 1.09 mmol), $\text{PhI}(\text{OAc})_2$ (842 mg, 2.62 mmol), and $\text{Pd}(\text{OAc})_2$ (19.5 mg, 0.087 mmol) were combined in CH_3CN (7.5 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction mixture was heated at 100°C for 12 hr. The solvent was removed under vacuum, and the resulting oil was purified by chromatography on silica gel ($R_f = 0.3$ in 60% hexanes/40% ethyl acetate). The product (**13**) was obtained as a light yellow solid (189 mg, 58% yield). ^1H NMR (CDCl_3): δ 10.00 (s, 1H), 8.72 (d, $J = 6.4$ Hz, 1H), 7.77 (dt, $J = 6.4$ Hz, $J = 2$ Hz, 1H), 7.64 (s, 2H), 7.35–7.30 (multiple peaks, 2H), 2.055 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 190.00, 168.78, 151.56, 149.96, 148.85, 137.29, 136.34, 133.22, 125.16, 123.29, 121.83, 20.71. Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_5$: C, 64.21; H, 4.38; N, 4.68. Found: C, 64.27; H, 4.25; N, 4.63.

nOe confirmation of the regioselectivity of oxidation:

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