Supporting Information for:

Oxidative C–H Activation/C–C Bond Forming Reactions: Synthetic Scope and Mechanistic Insights

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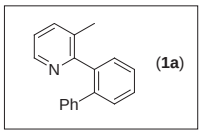
General Procedures: NMR spectra were obtained on a Varian Inova 500 (499.90 MHz for ^{1}H; 125.70 MHz for ^{13}C) or a Varian Inova 400 (399.96 MHz for ^{1}H; 100.57 MHz for ^{13}C) spectrometer. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent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

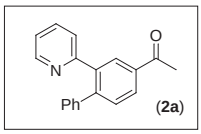
Materials and Methods: Substrates **5**, **7**, **8**, **11**, **12**, and **13** were obtained from commercial sources and used as received. Substrate **1** was prepared by Suzuki cross-coupling of phenyl boronic acid and 2-bromo-3-methylpyridine according to a literature procedure.[1] Pyridine substrates **2**, **3** and **4** were prepared by Stille cross-coupling of 2-tributylpyridyltin with the corresponding aryl bromides.[2] Amide substrates **9** and **10** were prepared by palladium-catalyzed arylation of the corresponding lactam.[3] Phenyl iodonium salts were prepared by the reaction of $PhI(OAc)_2$ with $ArB(OH)_2$ in the presence of $BF_3 \bullet Et_2O$ (for $[Ph_2I]BF_4$, $[Ph–I–p\text{-}FC_6H_4]BF_4$, $[Ph–I–p\text{-}ClC_6H_4]BF_4$, $[Ph–I–o\text{-}CH_3C_6H_5]BF_4$, $[Ph–I–p\text{-}CH_3C_6H_5]BF_4$)[4] or trifluoromethanesulfonic acid (for $[Ph–I–p\text{-}MeOC_6H_4]BF_4$ and [Ph–I–thienyl]BF_4).[5] Mesityl iodonium salts were prepared by the reaction of $MesI(OAc)_2$[6] with $ArB(OH)_2$ in the presence of $BF_3 \bullet Et_2O$ (for $[Mes–I–p\text{-}FC_6H_4]BF_4$, $[Mes–I–p\text{-}ClC_6H_4]BF_4$, $[Mes–I–o\text{-}CH_3C_6H_5]BF_4$, $[Mes–I–p\text{-}CH_3C_6H_5]BF_4$, [Mes–I–(1-napthyl)]$BF_4$, by reaction of $PhI(OAc)_2$ with mesitylene in H_2SO_4,[7] or by reaction of $MesI(OAc)_2$ with anisole in CH_2Cl_2/trifluoroacetic acid.[8] $Pd(OAc)_2$ was obtained from Pressure Chemical and used as received and $PhI(OAc)_2$ was obtained from Acros and used as received. Mercury (electrochemical grade, 99.9999%) was obtained from Aldrich and used as received. Solvents were obtained from Fisher 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 Merck TLC plates pre-coated with silica gel 60 F_{254}. Control reactions (in the absence of Pd catalyst) were run for

each substrate, and generally showed no reaction under our standard conditions. In general, crude reaction mixtures were filtered through glass wool or Celite to remove insoluble materials that form at the end of the reaction before workup.

I. Experimental Procedures



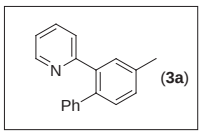
Product 1a. Substrate **1** (200 mg, 1.18 mmol, 1 equiv), $[Ph_2I]BF_4$ (500 mg, 1.36 mmol, 1.15 equiv) and $Pd(OAc)_2$ (13.2 mg, 0.059 mmol, 5 mol%) were combined in acetic acid (10 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 100°C for 12 hours. The reaction mixture was filtered through a plug of Celite and then concentrated under vacuum. The resulting crude oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (2 x 30 mL) and brine (1 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford an orange oil, which was purified by chromatography on silica gel (R_f = 0.2 in 95% CH_2Cl_2/5% ethyl acetate). The product was obtained as a viscous yellow oil (255 mg, 88% yield); ^1H NMR (d_6-acetone): δ 8.47 (d, *J* = 4.8 Hz, 1H), 7.55-7.43 (multiple peaks, 3H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.37-7.35 (m, 1H), 7.21-7.10 (multiple peaks, 6H), 1.75 (s, 3H). $^{13}C\{^1H\}$ NMR (d_6-acetone): δ 161.29, 148.19, 142.99, 142.40, 141.62, 139.03, 133.06, 131.80, 131.32, 130.92, 130.04, 129.58, 128.98, 128.48, 124.00, 19.95. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13, H, 6.16, N, 5.71; Found: C, 88.15, H, 6.17, N, 5.43. IR (thin film) 1418 cm^{-1}.



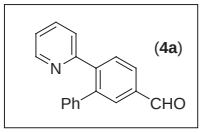
Product 2a. Substrate **2** (150 mg, 0.76 mmol, 1 equiv), $[Ph_2I]BF_4$ (420 mg, 1.14 mmol, 1.5 equiv), and $Pd(OAc)_2$ (8.5 mg, 0.038 mmol, 5 mol%) were combined in acetic acid (6 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap and the reaction was heated at 100°C for 2 days. The reaction mixture was filtered through a plug of Celite and then evaporated to dryness. The resulting oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (2 x 30 mL) and brine (1 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford an orange oil, which was purified by chromatography on silica gel (R_f = 0.25 in 88% CH_2Cl_2/12% ethyl acetate). The product was obtained as an orange/brown solid (189 mg, 91% yield); mp 77-78°C. ^1H NMR (acetone-d_6): δ 8.59-8.57 (m, 1H), 8.07 (dd, *J* = 8.0, 1.9 Hz, 1H), 8.24 (d, *J* = 1.8 Hz, 1H), 7.55 (d, *J* = 8.0, 1H), 7.50 (td, *J* = 7.7, 1.8 Hz, 1H), 7.26-7.25 (m, 3H), 7.21-7.18 (m, 1H), 7.16-7.13 (m, 2H), 6.96-6.93 (m, 1H), 2.63 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ

197.80, 158.50, 149.81, 145.36, 140.37, 139.93, 136.43, 135.63, 131.12, 129.64, 128.44, 128.18, 127.64, 125.49, 122.99, 26.96. HRMS-electrospray (*m/z*): [M^+ + H] calcd for $C_{19}H_{15}NO$, 274.1232; found, 274.1233. Anal. Calcd for $C_{19}H_{15}NO$: C, 83.94, H, 5.53, N, 5.12; Found: C, 83.56, H, 5.45, N, 5.04. IR (KBr) 1683, 1586 cm^{-1}.

The regioselectivity of this reaction could not be definitively determined from the ^1H NMR spectrum of **2a** due to overlapping aromatic resonances. As a result, a deuterated version of this product was prepared by reaction of **2** with [Mes–I–C_6D_5]BF_4 under analogous conditions to those described above. The ^1H NMR data for the deuterated product (**2a-*d*$_5$**) was as follows: ^1H NMR (d_6-acetone): δ 8.69-8.67 (m, 1H), 8.30 (d, *J* = 2.0 Hz, 1H), 8.17 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.68 (d, *J* = 8 Hz, 1H), 7.63 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.34-7.32 (m, 1H), 7.15-7.13 (m, 1H).

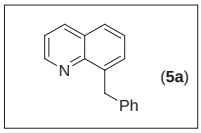


Product 3a. Substrate **3** (150 mg, 0.89 mmol, 1 equiv), [Ph_2I]BF_4 (489 mg, 1.33 mmol, 1.5 equiv), and $Pd(OAc)_2$ (9.9 mg, 0.044 mmol, 5 mol%) were combined in acetic acid (4 mL) and acetic anhydride (4 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap and the reaction was heated at 100°C for 12 hours. The reaction mixture was filtered through a plug of Celite and then evaporated to dryness. The resulting oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (2 x 30 mL) and brine (1 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford a yellow oil, which was purified by chromatography on silica gel (R_f = 0.24 in 97.5% CH_2Cl_2/2.5% ethyl acetate). The product was obtained as a brown solid (156 mg, 74% yield); mp 80-84 °C . ^1H NMR (C_6D_6): δ 8.58 (d, *J* = 4.8 Hz, 1H), 7.79 (s, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.22-7.20 (m, 2H), 7.04-6.95 (multiple peaks, 4H), 6.83-6.79 (m, 2H), 6.77-6.75 (m, 1H), 2.17 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.88, 148.94, 140.85, 138.76, 137.36, 136.92, 134.68, 130.66, 130.03, 129.28, 128.86, 127.59, 126.08, 125.04, 120.84, 20.66. HRMS-electrospray (*m/z*): [M^+ + H] calcd for $C_{18}H_{15}N$, 246.1283; found, 246.1290. IR (KBr) 1584 cm^{-1}.

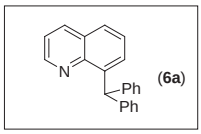


Product 4a. Substrate **4** (200 mg, 1.09 mmol, 1 equiv), [Ph_2I]BF_4 (441 mg, 1.20 mmol, 1.1 equiv), and $Pd(OAc)_2$ (12.2 mg, 0.054 mmol, 5 mol%) were combined in AcOH (9 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was heated at 100°C overnight. GC analysis at the completion of the reaction showed 11% starting material (**4**), 67% mono-arylated product (**4a**) and 21% of the analogous diarylated product. The reaction mixture was filtered through a plug of Celite and

evaporated to dryness. The resulting oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (2 x 30 mL) and brine (1 x 30 mL). The organic extracts were dried over $MgSO_4$ and concentrated under vacuum to afford a yellow oil, which was purified by chromatography on silica gel (R_f = 0.25 in 65% hexanes/35% ethyl acetate). The product was obtained as pale yellow solid (142 mg, 51% yield); mp 90-94 °C. ^{1}H NMR (C_6D_6): δ 9.71 (s, 1H), 8.51-8.49 (m, 1H), 7.87 (d, *J* = 9.7 Hz, 1H), 7.74 (d, *J* = 1.5 Hz, 1H), 7.61 (dd, *J* = 7.9, 1.5, 1H), 7.04-7.01 (m, 2H), 6.99-6.96 (multiple peaks, 3H), 6.74-6.66 (m, 2H), 6.52-6.28 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 191.60, 157.49, 149.32, 144.64, 141.15, 139.63, 135.77, 135.11, 131.60, 131.08, 129.17, 128.14, 127.97, 127.01, 124.97, 121.78. HRMS-electrospray (*m/z*): [M^+ – H] calcd for $C_{18}H_{13}NO$, 258.0919; found, 258.0922. IR (KBr): 1696, 1585 cm^{-1}.

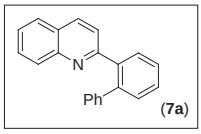


Product 5a. Substrate **5** (619 mg, 4.32 mmol, 2 equiv), $[Ph_2I]BF_4$ (794 mg, 2.16 mol, 1 equiv) and $Pd(OAc)_2$ (24 mg, 0.108 mmol, 5 mol%) were combined in a solution of benzene (9 mL) and acetic anhydride (9 mL) in a sealed container with a Teflon lined cap, and the reaction was stirred at 100°C for 12 hours. The reaction mixture was filtered through a plug of glass wool, and the resulting solution was concentrated under vacuum to afford a yellow oil, which was purified by chromatography on silica gel (R_f = 0.22 in 70% CH_2Cl_2/30% hexanes). The product was obtained as a brown-orange solid (337 mg, 72% yield based on $[Ph_2I]BF_4$); mp: 52-53 °C. ^{1}H NMR (d_6-acetone): δ 8.96 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.26 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.78 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.58-7.55 (m, 1H), 7.50-7.45 (multiple peaks, 2H), 7.38-7.36 (m, 2H), 7.26-7.22 (m, 2H), 7.17-7.12 (m, 1H), 4.69 (s, 2H). ^{13}C{^{1}H} NMR (d_6-acetone): δ 151.36, 148.41, 143.67, 142.07, 137.91, 131.17, 130.88, 130.29, 129.96, 128.23, 128.12, 127.48, 122.97, 38.18. Anal. Calcd for $C_{16}H_{13}N$: C, 87.64, H, 5.98, N, 6.39; Found: C, 87.63, H, 5.91, N, 6.35. IR (KBr) 1497, 1491 cm^{-1}.

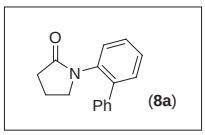


Product 6a. Substrate **5a** (182 mg, 0.83 mmol, 1 equiv), $[Ph_2I]BF_4$ (367 mg, 1.00 mmol, 1.2 equiv), and $Pd(OAc)_2$ (9.3 mg, 0.042 mmol, 5 mol%) were combined in acetic acid (3.5 mL) and acetic anhydride (3.5 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap and the reaction was heated at 100°C for 12 hours. The reaction mixture was filtered through a plug of Celite and then evaporated to dryness. The resulting oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (2 x 30 mL) and

brine (1 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford a pale yellow oil, which was purified by chromatography on silica gel (R_f = 0.22 in 50% CH_2Cl_2/50% hexanes). The product was obtained as a white solid (147 mg, 60% yield); mp 135-137 °C. ^{1}H NMR ($CDCl_3$): δ 8.97 (d, *J* = 3.9 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.41-7.35 (multiple peaks, 6H) 7.32-7.27 (multiple peaks, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.33, 145.98, 144.14, 142.37, 135.79, 130.01, 129.31, 128.01, 127.82, 126.20, 125.73, 125.67, 120.68, 49.67. Anal. Calcd for $C_{22}H_{17}N$: C, 89.46, H, 5.80, N, 4.74; Found: C, 89.24, H, 5.96, N, 4.63. IR (KBr) 1492 cm^{-1}. Note: Product **6a** is formed in 16% yield by GC in the absence of Pd catalyst.

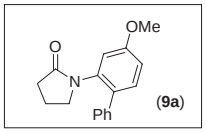


Product 7a. Substrate **7** (200 mg, 0.97 mmol, 1 equiv), $[Ph_2I]BF_4$ (428 mg, 1.16 mmol, 1.2 equiv), and $Pd(OAc)_2$ (10.9 mg, 0.054 mmol, 5 mol%) were combined in AcOH (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was heated at 100°C overnight. GC analysis at the completion of the reaction showed 19% starting material (**7**), 71% mono-arylated product (**7a**) and 10% of the analogous diarylated product. The reaction mixture was filtered through a plug of Celite and then evaporated to dryness. The resulting oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (2 x 30 mL) and brine (1 x 30 mL). The organic extracts were dried over $MgSO_4$ and concentrated under vacuum to afford a yellow oil, which was purified by chromatography on silica gel (R_f = 0.22 in 94% hexanes/6% ethyl acetate). The product was obtained as a pale yellow solid (157 mg, 58% yield); mp 134-138 °C. ^{1}H NMR (C_6D_6): δ 8.38 (d, *J* = 8.4 Hz, 1H), 8.14 (dd, *J* = 7.60, 1.45, 1H), 7.39-7.34 (m, 2H), 7.31-7.28 (m, 2H), 7.26-7.16 (multiple peaks, 6H), 6.95-6.90 (m, 2H), 6.88-6.86 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.60, 147.94, 140.86, 140.46, 139.45, 134.43, 130.62, 130.21, 129.52, 129.26, 129.06, 128.62, 128.04, 127.88, 127.59, 127.18, 126.60, 126.27, 123.13. HRMS-electrospray (*m/z*): [M^+ – H] calcd for $C_{21}H_{15}N$, 280.1126; found, 280.1127. IR (KBr) 1699, 1589 cm^{-1}.



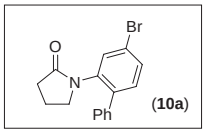
Product 8a. Substrate **8** (152 mg, 0.94 mmol, 1 equiv), $[Ph_2I]BF_4$ (521 mg, 1.41 mmol, 1.5 equiv), $NaHCO_3$ (119 mg, 1.14 mmol, 1.5 equiv) and $Pd(OAc)_2$ (11.9 mg, 0.053 mmol, 5 mol%) were combined in toluene (8 mL) in a 20 mL vial fitted with a Teflon lined cap, and the reaction was stirred at 100°C for 24 hours. The reaction mixture was filtered through a plug of Celite and concentrated under vacuum to afford a yellow

oil, which was purified by chromatography on silica gel (R_f = 0.1 in 50% ethyl acetate/50% hexanes). The product was obtained as an orange oil (170 mg, 75% yield). ^{1}H NMR ($CDCl_3$): δ 7.44-7.35 (multiple peaks, 6H), 7.34-7.33 (m, 2H), 7.32 (t, *J* = 1.7 Hz, 1H), 3.21 (t, *J* = 7.0 Hz, 2H), 2.43 (t, *J* = 8.1 Hz, 2H), 1.90-1.83 (m, 2H). ^{13}C{^{1}H} NMR (d_6-acetone): δ 174.18, 140.09, 140.03, 137.60, 130.95, 129.13, 128.78, 128.59, 128.44, 127.71, 127.59, 49.65, 31.06, 18.99. Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98, H, 6.37, N, 5.90; Found: C, 80.67, H, 6.46, N, 5.67. IR (thin film) 1715, 1377 cm^{-1}.



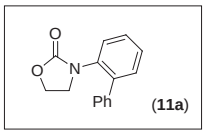
Product 9a. Substrate **9** (180 mg, 0.94 mmol, 1 equiv), $[Ph_2I]BF_4$ (692 mg, 1.88 mmol, 2 equiv), $Pd(OAc)_2$ (10.5 mg, 0.047 mmol, 5 mol%) and $NaHCO_3$ (158 mg, 1.88 mmol, 2 equiv) were combined in toluene (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap and the reaction was heated at 100°C for 12 hours. The reaction mixture was evaporated to dryness, and the residue was redissolved in CH_2Cl_2 and filtered through a plug of Celite. The solution was concentrated to afford a yellow oil, which was purified by chromatography on silica gel (R_f = 0.25 in 70% ethyl acetate/30% hexanes). The product was obtained as a yellow solid (211 mg, 84% yield); mp 61-64 °C. ^{1}H NMR (C_6D_6): δ 7.41-7.39 (m, 2H), 7.18-7.16 (m, 1H), 7.14-7.05 (multiple peaks, 4H), 6.73 (dd, *J* = 8.5, 2.6 Hz, 1H), 3.30 (s, 3H), 2.78 (t, *J* = 6.9 Hz, 2H), 2.03 (t, *J* = 8.0 Hz, 2H), 1.19-1.12 (m, 2H). ^{13}C{H} NMR ($CDCl_3$): δ 175.15, 159.10, 138.41, 136.62, 131.46, 131.09, 127.92, 127.89, 126.74, 113.70, 112.89, 54.95, 49.66, 30.74, 18.46. HRMS-electrospray (*m/z*): [M^+ + Na] calcd for $C_{17}H_{17}NO_2$, 290.1157; found, 290.1167. IR (KBr) 1687, 1609 cm^{-1}.

The regioselectivity of this reaction could not be definitively determined from the ^{1}H NMR spectrum of **9a** due to overlapping aromatic resonances. As a result, a deuterated version of this product was prepared by reaction of **9** with $[Mes–I–C_6D_5]BF_4$ under analogous conditions to those described above. The ^{1}H NMR data for the deuterated product (**9a-*d*$_5$**) was as follows: ^{1}H NMR (d_6-acetone): δ 7.31 (d, *J* = 8.5 Hz, 1H), 6.98 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.92 (d, *J* = 2.6 Hz, 1H), 3.84 (s, 3H), 3.26 (t, *J* = 6.9 Hz, 2H), 2.26 (t, *J* = 8.0 Hz, 2H), 1.91-1.84 (m, 2H).



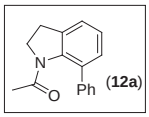
Product 10a. Substrate **10** (180 mg, 0.75 mmol, 1 equiv), $[Ph_2I]BF_4$ (689 mg, 1.87 mmol, 2.5 equiv), and $Pd(OAc)_2$ (8.4 mg, 0.038 mmol, 5 mol%) were combined in toluene (6.25 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap and the reaction was heated at 100°C for 12 hours. The reaction mixture

was filtered through a plug of Celite and then evaporated to dryness. The resulting oil was dissolved in methylene chloride and extracted with saturated aqueous $NaHCO_3$ (2 x 30 mL) and brine (1 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford an orange oil, which was purified by chromatography on silica gel (R_f = 0.23 in 96% CH_2Cl_2/4% ethyl acetate). The product was obtained as an orange-brown solid (180 mg, 78% yield); mp 116-118 ^oC. ^1H NMR (C_6D_6): δ 7.52 (s, 1H), 7.23 (d, *J* = 7.3 Hz, 2H), 7.13-7.06 (multiple peaks, 4H), 6.79 (d, *J* = 8.1 Hz, 1H), 2.59 (t, *J* = 6.8 Hz, 2H), 1.93 (t, *J* = 8.0 Hz, 2H), 1.13-1.06 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 175.39, 138.49, 137.84, 137.38, 131.89, 131.26, 130.90, 128.39, 127.93, 127.75, 121.44, 49.77, 30.85, 18.79. Anal. Calcd for $C_{16}H_{14}BrNO$: C, 60.78, H, 4.46, N, 4.43; Found: C, 61.08, H, 4.66, N, 4.19. IR (KBr) 1697, 1413 cm^{-1}.



(**11a**)

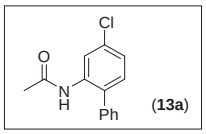
Product 11a. Substrate **11** (150 mg, 0.92 mmol, 1 equiv), $[Ph_2I]BF_4$ (676 mg, 1.84 mmol, 2 equiv), $Pd(OAc)_2$ (10.2 mg, 0.046 mmol, 5 mol%) and $NaHCO_3$ (155 mg, 1.84 mmol, 2 equiv) were combined in benzene (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap and the reaction was heated at 100°C for 12 hours. The reaction mixture was filtered through a plug of Celite and then evaporated to dryness. The resulting oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (2 x 30 mL) and brine (1 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford an orange oil, which was purified by chromatography on silica gel (R_f = 0.23 in 97.5% CH_2Cl_2/2.5% ethyl acetate). The product was obtained as a yellow solid (182 mg, 83% yield); mp 107-109 ^oC. ^1H NMR (C_6D_6): δ 7.38 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.32-7.30 (m, 2H), 7.14-7.12 (m, 1H), 7.10-7.06 (multiple peaks, 3H), 7.05-6.99 (m, 2H) 3.24 (dd, *J* = 8.6, 7.2 Hz, 2H), 2.55 (dd, *J* = 8.5, 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.78, 139.62, 139.00, 135.08, 131.10, 128.89, 128.87, 128.58, 128.41, 128.25, 127.99, 62.43, 47.13. Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30, H, 5.48, N, 5.85; Found: C, 75.50, H, 5.66, N, 5.68. IR (KBr) 1740, 1483 cm^{-1}.



(**12a**)

Product 12a. Substrate **12** (150 mg, 0.93 mmol, 1 equiv), $[Ph_2I]BF_4$ (685 mg, 1.86 mmol, 2 equiv), and $Pd(OAc)_2$ (10.4 mg, 0.047 mmol, 5 mol%) were combined in AcOH (5 mL) and Ac_2O (5 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was heated at 100°C overnight. GC analysis at the completion of the reaction showed 29% starting material (**12**) and 71% of the mono-arylated product (**12a**). Notably, attempts to optimize the reaction conditions did not lead to further conversion with this substrate. The reaction mixture was evaporated to dryness, and the remaining solid

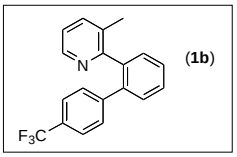
residue was taken up in MeOH (20 mL) and filtered through a plug of Celite. The methanol was removed under vacuum and the solids were taken up in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (3 x 30 mL). The organic extracts were concentrated under vacuum to afford a red oil, which was purified by chromatography on silica gel (R_f = 0.2 in 70% hexanes/30% ethyl acetate). The product was obtained as pale yellow solid (108 mg, 49% yield); mp 117-119 °C. ^{1}H NMR (d_6-acetone): δ 7.52-7.14 (multiple peaks, 8H), 4.23 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 1.50 (br s, 3H). ^{13}C{^{1}H} NMR (d_6-acetone): δ 141.58, 129.77, 128.16, 127.78, 126.02, 124.67,51.15, 22.89. (The ^{13}C NMR peaks of **12a** are broad and several are missing, presumably as a result of fluxional motion of the amide.) Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98, H, 6.37, N, 5.90; Found: C, 80.89, H, 6.52, N, 5.58. IR (KBr) 1648 cm^{-1}.



(**13a**)

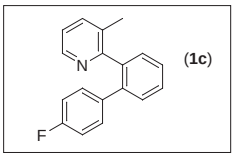
Product 13a. Substrate **13** (250 mg, 1.47 mmol, 1 equiv), $[Ph_2I]BF_4$ (1.08 g, 2.95 mmol, 2 equiv), and $Pd(OAc)_2$ (16.5 mg, 0.074 mmol, 5 mol%) were combined in benzene (12 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap and the reaction was heated at 100°C for 12 hours. The reaction mixture was filtered through a plug of Celite and then evaporated to dryness. The resulting oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (2 x 30 mL) and brine (1 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford an orange oil, which was purified by chromatography on silica gel (R_f = 0.28 in 55% diethyl ether/45% hexanes). The product was obtained as an orange-brown solid (240 mg, 67% yield); mp 125-126 °C. ^{1}H NMR (C_6D_6): δ 9.02 (s, 1H), 7.10-7.05 (multiple peaks, 3H), 6.97-6.95 (m, 2H), 6.91 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.64 (s, 1H), 1.25 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 167.96, 136.65, 135.27, 133.40, 130.55, 130.19, 128.82, 128.66, 127.88, 123.94, 121.24, 24.04. Anal. Calcd for $C_{14}H_{12}ClNO$: C, 68.44, H, 4.92, N, 5.70; Found: C, 68.38, H, 4.99, N, 5.47. IR (KBr) 3224, 3026, 1648, 1532 cm^{-1}.

The regioselectivity of this reaction could not be definitively assigned from the ^{1}H NMR spectrum of **13a** due to overlapping aromatic resonances. As a result, a deuterated version of this product was prepared by reaction of **13** with [Mes–I–C_6D_5]BF_4 under analogous conditions to those described above. The ^{1}H NMR data for the deuterated product (**13a**-d_5) was as follows: ^{1}H NMR (C_6D_6): δ 9.02 (br. s, 1H), 6.92 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.64 (br. s, 1H), 1.25 (s, 3H).



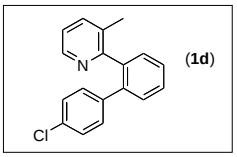
(**1b**)

Product 1b. Substrate **1** (150 mg, 0.89 mmol, 1 equiv), [Mes–I–*p*-$CF_3C_6H_5$]BF_4 (466 mg, 0.98 mmol, 1.1 equiv) and $Pd(OAc)_2$ (10 mg, 0.044 mmol, 5 mol%) were combined in acetic acid (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 100°C for 12 hours. The reaction mixture was filtered through a plug of glass wool and concentrated under vacuum. The resulting oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (1 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford an orange oil, which was purified by chromatography on silica gel (R_f = 0.25 in 75% hexanes/25% ethyl acetate). The product was obtained as a yellow oil (242 mg, 87% yield). ^{1}H NMR (d_6-acetone): δ 8.42 (d, *J* = 4.2 Hz, 1H), 7.57-7.53 (multiple peaks, 5H), 7.46-7.40 (multiple peaks, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.18 (dd, *J* = 8.0 Hz, 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (d_6-acetone): δ 159.83, 147.84, 146.27, 140.87, 140.13, 138.42, 132.21, 131.06, 130.76, 130.59, 129.34, 129.08 (d, *J* = 32 Hz), 128.99, 125.59 (q, *J* = 4 Hz), 124.43 (q, 270 Hz), 123.39, 19.08. Anal. Calcd for $C_{18}H_{14}FN$: C, 72.83, H, 4.50, N, 4.47**;** Found: C, 72.53, H, 4.60, N, 4.36.



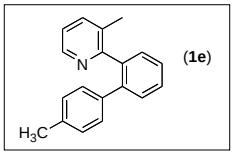
(**1c**)

Product 1c. Substrate **1** (153 mg, 0.91 mmol, 1 equiv), [Mes–I–*p*-FC_6H_5]BF_4 (446 mg, 1.04 mmol, 1.15 equiv) and $Pd(OAc)_2$ (10.1 mg, 0.043 mmol, 5 mol%) were combined in acetic acid (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 100°C for 12 hours. The reaction mixture was filtered through a plug of glass wool and concentrated under vacuum. The resulting oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (1 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford an orange oil, which was purified by chromatography on silica gel (R_f = 0.3 in 75% hexanes/25% ethyl acetate). The product was obtained as a yellow solid (210 mg, 88% yield); mp 135-137 °C. ^{1}H NMR (d_6-acetone): δ 8.43 (d, *J* = 4.0 Hz, 1H), 7.57-7.32 (multiple peaks, 5H), 7.22-7.12 (multiple peaks, 3H), 6.97-6.93 (m, 2H), 1.77 (s, 3H). ^{13}C{^{1}H} NMR (d_6-acetone): δ 162.60 (d, $^1J_{CF}$ = 243 Hz), 160.15, 147.34, 140.76, 140.35, 138.29 (d, $^4J_{CF}$ = 3.0 Hz), 138.12, 131.99, 131.82 (d, $^3J_{CF}$ = 7.6 Hz), 130.79, 130.30, 129.07, 128.16, 123.10, 115.35 (d, $^2J_{CF}$ = 21 Hz), 18.91**.** Anal. Calcd for $C_{18}H_{14}FN$: C, 82.11, H, 5.36, N, 5.32**;** Found: C, 81.86, H, 5.52, N, 5.15. IR (KBr) 1482 cm^{-1}.



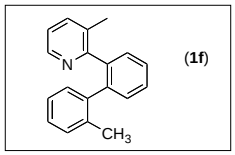
(**1d**)

Product 1d. Substrate **1** (150 mg, 0.89 mmol, 1 equiv), [Mes–I–*p*-ClC_6H_5]BF_4 (453 mg, 1.02 mmol, 1.15 equiv) and $Pd(OAc)_2$ (10 mg, 0.044 mmol, 5 mol%) were combined in acetic acid (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 100°C for 12 hours. The reaction mixture was filtered through a plug of glass wool and concentrated under vacuum. The resulting oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (1 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford an orange oil, which was purified by chromatography on silica gel (R_f = 0.25 in 75% hexanes/25% ethyl acetate). The product was obtained as a yellow solid (205 mg, 83% yield); mp 106-107 °C. ^{1}H NMR (d_6-acetone): δ 8.42 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.55-7.46 (multiple peaks, 3H), 7.43 (dt, *J* = 7.5, 0.8 Hz, 1H), 7.38-7.36 (m, 1H), 7.21-7.12 (multiple peaks, 5H), 1.79 (s, 3H). ^{13}C{^{1}H} NMR (d_6-acetone): δ 160.11, 147.48, 140.84, 140.82, 140.25, 138.31, 133.25, 132.12, 131.71, 130.95, 130.39, 129.25, 128.81, 128.53, 123.27, 19.07. Anal. Calcd for $C_{18}H_{14}FN$: C, 77.28, H, 5.04, N, 5.01**;** Found: C, 77.59, H, 4.91, N, 4.63. IR (KBr) 1477, 1449 cm^{-1}.



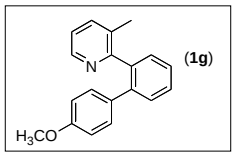
(**1e**)

Product 1e. Substrate **1** (150 mg, 0.89 mmol, 1 equiv), [Mes–I–*p*-$CH_3C_6H_5$]BF_4 (432 mg, 1.02 mmol, 1.15 equiv) and $Pd(OAc)_2$ (10 mg, 0.044 mmol, 5 mol%) were combined in acetic acid (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 100°C for 12 hours. The reaction mixture was filtered through a plug of glass wool and concentrated under vacuum. The resulting oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (1 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford an orange oil, which was purified by chromatography on silica gel (R_f = 0.25 in 80% hexanes/20% ethyl acetate). The product was obtained as a yellow solid (193 mg, 84% yield); mp 59-62 °C. ^{1}H NMR (d_6-acetone): δ 8.45 (d, *J* = 4.4 Hz, 1H), 7.50-7.43 (multiple peaks, 3H), 7.39-7.33 (multiple peaks, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.04-6.98 (multiple peaks, 4H), 2.23 (s, 3H), 1.74 (s, 3H). ^{13}C{^{1}H} NMR (d_6-acetone): δ 159.68, 146.39, 140.49, 139.81, 138.29, 137.15, 136.14, 131.16, 129.95, 129.43, 128.98, 128.46, 128.13, 126.91, 122.12. Anal. Calcd for $C_{18}H_{14}FN$: C, 87.99, H, 6.61, N, 5.40**;** Found: C, 87.73, H, 6.45, N, 5.11. IR (KBr) 1449 cm^{-1}.



(**1f**)

Product 1f. Substrate **1** (150 mg, 0.89 mmol, 1 equiv), [Mes–I–*p*-$CH_3C_6H_5$]BF_4 (489 mg, 1.15 mmol, 1.3 equiv) and $Pd(OAc)_2$ (10 mg, 0.044 mmol, 5 mol%) were combined in acetic acid (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 100°C for 12 hours. The reaction mixture was filtered through a plug of glass wool and concentrated under vacuum. The resulting oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (1 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford an orange oil, which was purified by chromatography on silica gel (R_f = 0.25 in 80% hexanes/20% ethyl acetate). The product was obtained as a white solid (165 mg, 72% yield**);** mp 73-77 °C. ^{1}H NMR (d_6-acetone): δ 8.30 (d, *J* = 3.6 Hz, 1H), 7.48-7.44 (multiple peaks, 2H), 7.39-7.36 (multiple peaks, 2H), 7.32-7.30 (m, 1H), 7.10-7.03 (multiple peaks, 3H), 6.96-6.92 (multiple peaks, 2H), 2.16 (s, 3H), 1.95 (s, 3H). ^{13}C{^{1}H} NMR (d_6-acetone): δ 160.12, 147.01, 141.58 (br), 141.42, 137.95, 136.67 (br), 131.97, 131.13, 130.67, 130.63, 128.35, 127.81, 125.53, 122.81, 20.74, 19.34. (Several of the ^{13}C NMR peaks of **1h** are broad and three are missing – this is believed to be the result of fluxional motion about the aryl-aryl bonds.) Anal. Calcd for $C_{18}H_{14}FN$: C, 87.99, H, 6.61, N, 5.40**;** Found: C, 88.09, H, 6.51, N, 5.24. IR (KBr) 1418 cm^{-1}.



(**1g**)

Product 1g. Substrate **1** (150 mg, 0.89 mmol, 1 equiv), [Mes–I–*p*-$MeOC_6H_5$]BF_4 (449 mg, 1.02 mmol, 1.1 equiv) and $Pd(OAc)_2$ (10 mg, 0.044 mmol, 5 mol%) were combined in acetic acid (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 120°C for 12 hours. The reaction mixture was filtered through a plug of glass wool and concentrated under vacuum. The resulting oil was dissolved in CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ (1 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford an orange oil, which was purified by chromatography on silica gel (R_f = 0.20 in 80% hexanes/20% ethyl acetate). The product was obtained as a clear oil (197 mg, 81% yield); ^{1}H NMR (d_6-acetone): δ 8.42 (d, *J* = 4.4 Hz, 1H), 7.46-7.28 (multiple peaks, 5H), 7.14-7.11 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 3.68 (s, 3H), 1.70 (s, 3H). ^{13}C{^{1}H} NMR (d_6-acetone): δ 159.73, 158.68, 146.42, 140.22, 139.73, 137.18, 133.40, 131.17, 130.17, 129.94, 129.33, 128.13, 126.68, 122.12, 113.22, 54.49, 18.09. HRMS (electrospray) [M$^+$] calcd for $C_{19}H_{19}NO$, 275.1310; found, 275.1303. IR (KBr) 1609, 1516 cm^{-1}.

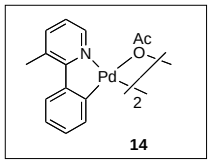
Reaction of 1 with Ph–I. Substrate **1** (15.0 mg, 0.09 mmol, 1 equiv), Ph–I (21.7 mg, 0.11 mmol, 1.20 equiv), and $Pd(OAc)_2$ (1.00 mg, 0.004 mmol, 5 mol%) were combined in AcOH (1.04 mL) in a 2 mL vial equipped with a small magnetic stir bar. The vial was sealed with a Teflon-lined cap and heated at 100°C for 12 hr. The reaction was cooled to room temperature and analyzed by gas chromatography, which showed only starting material and Ph–I with <1% of product **1a**.

Reaction of 1 with Ph–OTf. Substrate **1** (15.0 mg, 0.09 mmol, 1 equiv), Ph–OTf (24.1 mg, 0.11 mmol, 1.20 equiv), and $Pd(OAc)_2$ (1.00 mg, 0.0044 mmol, 5 mol%) were combined in AcOH (1.04 mL) in a 2 mL vial equipped with a small magnetic stir bar. The vial was sealed with a Teflon-lined cap and heated at 100°C for 12 hr. The reaction was cooled to room temperature and analyzed by gas chromatography, which showed only starting material (**1**) and Ph–OTf with <1% of product **1a**.

Reaction of 1 with $[Ph_2I]BF_4$ in the Presence of Hg. Substrate **1** (10.0 mg, 0.059 mmol, 1 equiv), $[Ph_2I]BF_4$ (26.1 mg, 0.071 mmol, 1.20 equiv), and $Pd(OAc)_2$ (0.700 mg, 0.0031 mmol, 5 mol%) were combined in AcOH (0.50 mL) in a 2 mL vial equipped with a small magnetic stir bar. Metallic Hg (>500 equiv) was added to the reaction mixture, and the vial was sealed with a Teflon-lined cap and heated at 100°C for 12 hr. The reaction was cooled to room temperature and analyzed by gas chromatography, which revealed quantitative conversion to product **1a**. **SAFETY NOTE: These reactions should be handled with extreme caution, as the reaction of excess $[Ph_2I]BF_4$ is known to generate highly toxic phenyl mercury compounds![9]**

Reaction of 1 with $[Ph_2I]BF_4$ in the Presence of MEHQ. Substrate **1** (10.0 mg, 0.059 mmol, 1 equiv), $[Ph_2I]BF_4$ (26.1 mg, 0.071 mmol, 1.20 equiv), and $Pd(OAc)_2$ (0.700 mg, 0.0031 mmol, 5 mol%) were combined in AcOH (0.50 mL) in a 2 mL vial equipped with a small magnetic stir bar. MEHQ (1.83 mg, 0.015 mmol, 25 mol%) was added to the reaction mixture, and the vial was sealed with a Teflon-lined cap and heated at 100°C for 12 hr. The reaction was cooled to room temperature and analyzed by gas chromatography, which revealed quantitative conversion to product **1a**.

Reaction of 1 with $[Ph_2I]BF_4$ in the Presence of Galvinoxyl. Substrate **1** (10.0mg, 0.059 mmol, 1 equiv), $[Ph_2I]BF_4$ (26.1 mg, 0.071 mmol, 1.20 equiv), and $Pd(OAc)_2$ (0.700 mg, 0.0031 mmol, 5 mol%) were combined in AcOH (0.50 mL) in a 2 mL vial equipped with a small magnetic stir bar. Galvinoxyl (6.23 mg, 0.015 mmol, 25 mol%) was added to the reaction mixture, and the vial was sealed with a Teflon-lined cap and heated at 100°C for 12 hr. The reaction was cooled to room temperature and analyzed by gas chromatography, which revealed quantitative conversion to product **1a**.



14

Synthesis of Palladacycle 14. Substrate 1 (1.07 g, 6.30 mmol, 1.4 equiv), and $Pd(OAc)_2$ (1.01 g, 4.50 mmol, 1 equiv) were combined in MeOH (63 mL) in a 200 mL flask equipped with a magnetic stir bar and stirred at room temperature for 12 hr. The reaction mixture was then filtered, and the precipitate was washed with diethyl ether (100 mL), collected and dried. The product was obtained as a yellow solid (918 mg, 61% yield). ^{1}H NMR (d_6-acetone): δ 7.92 (d, *J* = 5.2 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 2H), 6.94 (d, *J* = 7.4 Hz, 2H), 6.88-6.78 (multiple peaks, 4H), 6.53 (dd, *J* = 7.6, 2.0 Hz, 2H), 2.44 (s, 6H), 2.09 (s, 6H). Anal. Calcd for $C_{28}H_{26}N_2O_4Pd_2$: C, 50.39, H, 3.93, N, 4.20; Found: C, 50.27, H, 3.98, N, 4.10.

Stoichiometric Reaction of 14 with $[Ph_2I]BF_4$. Complex **14** (15.0 mg, 0.02 mmol, 1 equiv), $[Ph_2I]BF_4$ (61.1 mg, 0.17 mmol, 3.2 equiv per Pd), and **3** (19.0 mg, 0.11 mmol, 2.5 equiv per Pd) were combined in AcOH (0.37 mL) in a 2 mL vial equipped with a small magnetic stir bar. The vial was sealed with a Teflon-lined cap and heated at 100°C for 12 hr. The reaction was cooled to room temperature and analyzed by gas chromatography, which showed 90 % yield of **1a** (determined relative to an internal standard). Significant quantities of phenylated **3** (product **3a**) were also observed by GC (as expected since an excess of oxidant was utilized). Importantly, when $[Ph_2I]BF_4$ was replaced with Ph–I or Ph–OTf under otherwise identical conditions <1% of product **1a** was observed by GC.

When the stoichiometric reaction between **14** and $[Ph_2I]BF_4$ reaction was conducted in the absence of added substrate **3** (under the following conditions: complex **14** (1 equiv, 0.02 mmol), $[Ph_2I]BF_4$ (1.2 equiv per Pd, 0.05 mmol), AcOH (0.37 mL), 12 hr, 100°C) product **1a** was obtained in 20% yield (determined relative to an internal standard) as the major product detectable by GC analysis. ^{1}H NMR spectroscopy and electrospray mass spectrometry revealed a complex mixture of additional high molecular weight organic products, and the MS data is consistent with the formation of a mixture of polyphenylated momomers and dimers of **1**. While the origin of these products and the details of this reactivity remains under investigation, we hypothesize that added **3** may act to trap reactive cationic palladium species (generated after initial C–C bond forming reductive elimination) that may be responsible for producing these polyphenylated products. Notably, under catalytic conditions, a large excess of substrate is present relative to catalyst, so such reactive species are expected to be trapped rapidly in a productive manner.

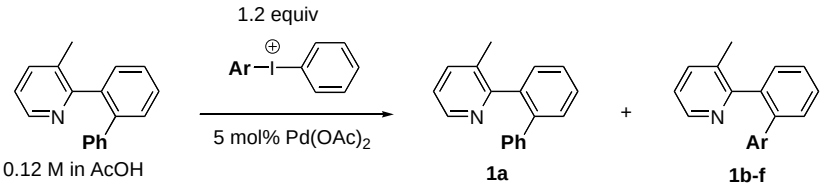
II. Reactions with Mixed Iodonium Reagents [Ph–I–Ar]BF_4

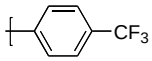
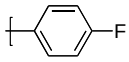
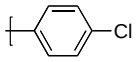
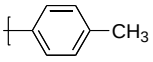
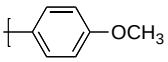
Reaction of 1 with [Ph–I–Ar]BF_4. Substrate **1** (10.0 mg, 0.059 mmol, 1 equiv), [Ph–I–Ar]BF_4 (0.071 mmol, 1.20 equiv), and $Pd(OAc)_2$ (0.700 mg, 0.0031 mmol, 5 mol%) were combined in AcOH (0.49 mL) in a 2 mL vial equipped with a small magnetic stir bar. The vial was sealed with a Teflon-lined cap and heated at 100°C for 12 hr. The reaction was cooled to room temperature and analyzed by gas chromatography. The yields of the products were determined by integration relative to a GC standard (2-phenylpyridine) and are ± approximately 10%.

Preliminary experiments were conducted to compare the electronic effects of aryl transfer in our C–H activation/arylation reactions to those in a reaction reported to proceed by a Pd(II)/Pd(0) catalytic cycle. We selected the Suzuki reaction between phenyl boronic acid and [Ph–I–Ar]BF_4 for these studies.[10] This reaction was first examined under our standard C–H activation/arylation conditions (0.12 M in AcOH, 100°C, 12 hr), in order to allow direct comparison between the results; however, no coupling products were observed by GC under these conditions. As such, we examined the selectivity of this reaction in DME/H_2O at room temperature (see below) with the series of iodonium salts examined in Table S1. Notably, our reaction conditions differ somewhat from those in the original paper, as we used the BF_4 salts of the iodonium reagents; however, we feel that these were more relevant for direct comparison to the C–H activation/arylation reactions. As summarized in Table S1, the Suzuki reactions proceed with different selectivity for transfer of Ar versus Ph relative to the C–H activation/arylation reactions; however, a similar general trend in reactivity (where electron poor Ar groups are transferred in higher yield than electron rich Ar groups) is observed in both transformations.

Reaction of Phenylboronic acid with [Ph–I–Ar]BF_4. Phenylboronic acid (20 mg, 0.16 mmol, 1.1 equiv), [Ph–I–Ar]BF_4 (0.15 mmol, 1.0 equiv), Na_2CO_3 (40 mg, 0.30 mmol, 2 equiv), and $Pd(PPh_3)_4$ (4.3 mg, 0.0037 mmol, 2.5 mol%) were combined in DME (1.69 mL) and H_2O (0.43 mL) in a Schlenk flask under an N_2 atmosphere. The reaction was stirred for 1 hr at room temperature then analyzed by gas chromatography to determine the ratio of phenylated to arylated product (which is reported in Table S1, column 6 for each of the iodonium salts). These ratios are uncorrected for small differences in the response factors between the substituted biphenyl products. This assumption (of small differences in response factor) was made based on the small difference in response factor measured for the arylated phenyl pyridine products (**1a-1f**) in Table S1.

Table S1. Selectivity for Ph versus Ar Transfer in C–H Activation/Arylation of **1** with [Ph–I–Ar]BF_4

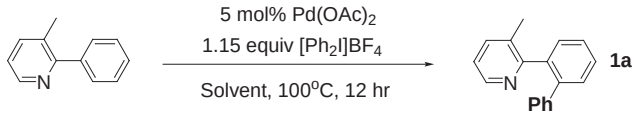


Entry	Ar	Yield (**1a**)[b]	Yield (**1b-1f**)[b]	Ratio (Ph/Ar Transfer)	Ratio (Ph/Ar Suzuki)[c]
1		86%[d]	———	———	———
2		26%	68%	1 : 2.6	1 : 1.5
3		75%	25%	1 : 0.33	1 : 1.1
4		45%	37%	1 : 0.83	1: 1.3
5		63%	44%	1 : 0.71	1 : 1.1
6		75%	25%	1 : 0.33	———
7		73%	23%	1 : 0.31	1 : 0.77

[a]Conditions: Substrate **1** (1.0 equiv, 0.12 M in AcOH), [Ph–I–Ar]BF_4 (1.1 equiv), $Pd(OAc)_2$, 100°C, 12 hr. [b]Yields determined by GC based on integration versus an internal standard (errors ± ~10%) and were calibrated versus authentic samples of each of the products. [c]Ratio of phenylated to arylated product observed in Suzuki cross-coupling of Ph–$B(OH)_2$ with [Ph–I–Ar]BF_4 under the following conditions: Ph–$B(OH)_2$ (1.1 equiv, 0.07 M in 3/1 DME/H_2O), [Ph–I–Ar]BF_4 (1 equiv), K_2CO_3 (2 equiv), $Pd(PPh_3)_4$ (2.5 mol%) at 25°C for 1 hr. Ratio determined by GC integration. [d]GC analysis shows traces of the diarylated product.

III. Solvent Optimization Studies

Table S2. Solvent Optimization Studies with Substrate **1**



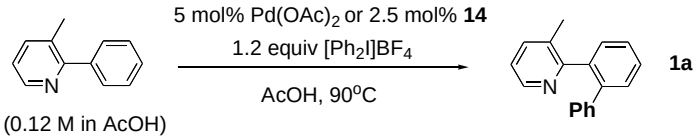
Entry	Solvent	% Conversion (GC)[a]
1	AcOH	100%
2	50% AcOH/50% Ac_2O	100%
3	Benzene	43%
4	Toluene	11%
5	CH_2Cl_2	16%
6	CH_3CN	14%
7	$CHCl_3$	18%
8	DMF	15%

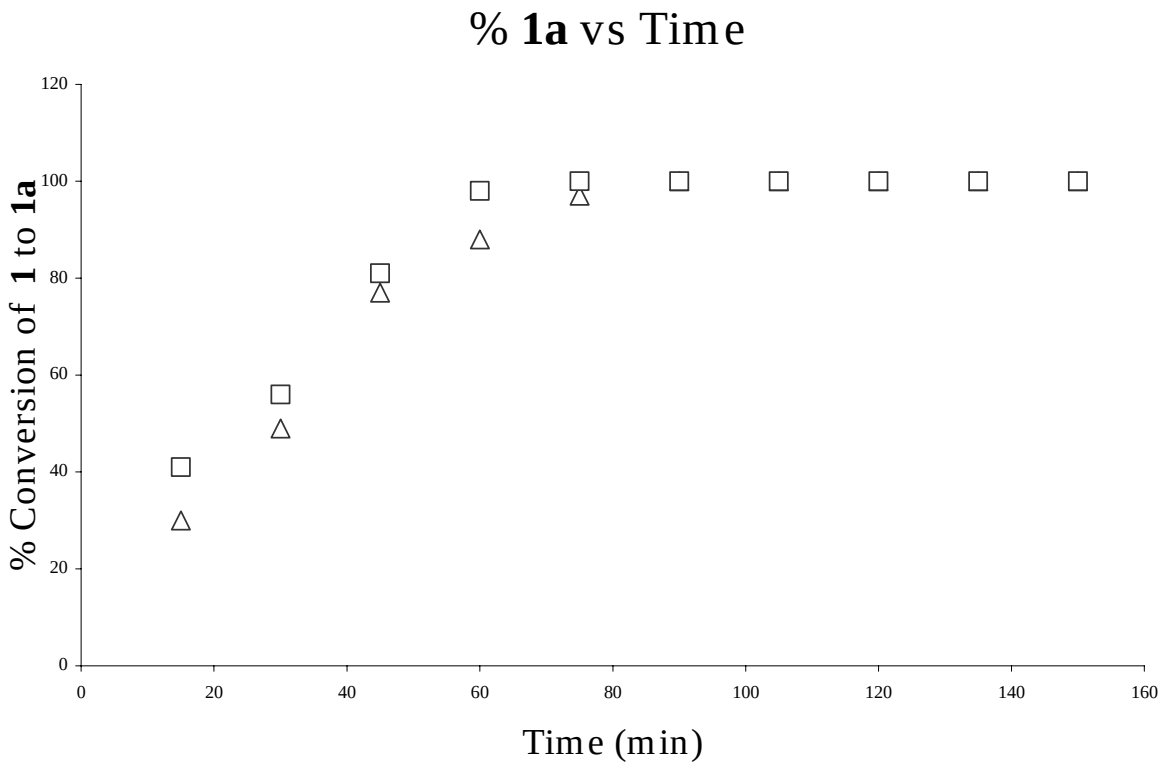
[a] % conversion estimated by integration of GC peak areas (not corrected for differences in response factor)

Note: The optimal solvent/reaction conditions (*eg,* equiv of $[Ph_2I]BF_4$) required for these reactions was found to vary somewhat as a function of substrate

IV. Time Course – Reaction of $Pd(OAc)_2$ or Catalyst 14 with Substrate 1

Table S4. Time Course of Reaction with $Pd(OAc)_2$ versus **14** as Catalyst





Legend
Squares = Catalyst **14**
Triangles = $Pd(OAc)_2$

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