Supporting Information for:

Palladium-Catalyzed Intra- and Intermolecular C–H Arylation Using Mesylates: Synthetic Scope and Mechanistic Studies

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

**Materials and Methods:** Rubidium carbonate, cesium pivalate, 2,4,6-trimethyl pyridine, mesic anhydride, methanesulfonyl chloride, pyridine, para-methoxy phenol, 3,4-dimethoxy phenol, sesamol, 3,4,5-trimethoxy phenol, 5-methyl benzoxazole, benzothiazole, para-methyl phenol, para-fluoro phenol, ortho-methyl phenol, 2-naphthol, 3,4,5-trimethoxy phenol and 1,2-bis(dicyclohexylphosphino)ethane (dcype) were obtained from Aldrich and used as received. Benzoxazole and 3,4-dimethoxy phenol were obtained from TCI America and used as received. Pd(OAc)$_2$ was obtained from Strem chemical and used as received. Anhydrous cesium carbonate was obtained from Acros and used as received. The mesylates for intermolecular arylations were prepared using literature procedures. Anhydrous xylene was obtained from Aldrich and used as received. Anhydrous dichloromethane was purified using Glass Contour solvent purification system column composed of neutral alumina. Toluene was purified using Glass Contour solvent purification system column composed of neutral alumina and a copper catalyst. Other solvents were obtained from Fisher Chemical or VWR Chemical and used without further purification. Flash chromatography was performed on EM Science silica gel 60 (0.040–0.063 mm particle size, 230–400 mesh) and thin layer chromatography was performed on Analtech TLC plates pre-coated with silica gel 60 F$_{254}$. 

S2
Synthesis and characterization of mesylate substrates (Table 1):

![Chemical structure](image)

To a Schlenk flask containing a solution of alcohol 5-OH (75.1 mg, 0.347 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (0.32 mL) was added pyridine (0.14 mL, 1.74 mmol, 5.0 equiv), and methanesulfonyl chloride (0.040 mL, 0.521 mmol, 1.5 equiv) and the resulting mixture was stirred at room temperature overnight. The reaction mixture was quenched with H$_2$O (4 mL) and CH$_2$Cl$_2$ (20 mL) and transferred to a separatory funnel. The resulting mixture was extracted with 10% aqueous HCl (2 x 20 mL), saturated aqueous NaHCO$_3$ (1 x 20 mL) and brine (1 x 20 mL). The organic layer was dried over MgSO$_4$, filtered, concentrated and chromatographed on a silica gel column using 80/20 hexanes/EtOAc (R = 0.26 in 80% hexanes/20% ethyl acetate) to afford the product as a clear oil (52.6 mg, 51% yield).

$^1$H NMR (CDCl$_3$): $\delta$ 7.42 (d, $J = 8.1$ Hz, 1H), 7.27-7.24 (multiple peaks, 2H), 7.16 (t, $J = 7.7$ Hz, 1H), 7.03 (d, $J = 8.1$ Hz, 1H), 6.69 (d, $J = 8.3$ Hz, 1H), 6.60-6.56 (multiple peaks, 2H), 3.79 (s, 3H), 3.18 (s, 3H). $^{13}$C{[H]} NMR (CDCl$_3$): $\delta$ 161.1, 157.5, 148.5, 140.3, 130.4, 128.3, 125.1, 124.4, 120.6, 110.4, 109.5, 104.6, 55.4, 38.5. IR (neat): 2939, 1587, 1486, 1451, 1364, 1266, 1243, 1193, 1158, 1135, 1099, 1036, 951, 874, 809, 759, 685 cm$^{-1}$. HRMS [M+Na] Calcd for C$_{12}$H$_{15}$O$_3$ 317.0454; Found: 317.0461.

![Chemical structure](image)

To a Schlenk flask containing a solution of alcohol 6-OH (67.0 mg, 0.272 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (0.25 mL) was added pyridine (0.11 mL, 1.36 mmol, 5.0 equiv), and methanesulfonyl chloride (0.03 mL, 0.408 mmol, 1.5 equiv) and the resulting mixture was stirred at room temperature overnight. The reaction mixture was quenched with H$_2$O (4 mL) and CH$_2$Cl$_2$ (20 mL) and transferred to a separatory funnel. The resulting mixture was extracted with 10% aqueous HCl (2 x 20 mL), saturated aqueous NaHCO$_3$ (1 x 20 mL) and brine (1 x 20 mL). The organic layer was dried over MgSO$_4$, filtered, concentrated and chromatographed on a silica gel column using 70/30 hexanes/EtOAc (R = 0.29 in 70% hexanes/30% ethyl acetate) to afford the product as a white solid (47.1 mg, 53% yield); mp = 162-164 °C.

$^1$H NMR (CDCl$_3$): $\delta$ 7.39 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.21 (t, $J = 7.9$ Hz, 1H), 7.09 (t, $J = 7.6$ Hz, 1H), 6.90 (dd, $J = 8.2$, 1.6 Hz, 1H), 6.83 (d, $J = 8.7$ Hz, 1H), 6.65 (d, $J = 2.7$ Hz, 1H), 6.57 (dd, $J = 8.7$, 2.8 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.23 (s, 3H). $^{13}$C{[H]} NMR (CDCl$_3$): $\delta$ 150.0, 149.5, 146.0, 139.5,
128.2, 124.9, 123.4, 118.8, 111.7, 110.5, 104.1, 56.3, 56.0, 38.6 [One of the carbons is coincidentally overlapping]. IR (neat): 2924, 1510, 1487, 1468, 1353, 1338, 1265, 1248, 1228, 1189, 1163, 1145, 1126, 1097, 980, 970, 957, 875, 846, 807, 788, 753, 733, 695, 645 cm⁻¹. HRMS [M+Na] Calcd for C₁₅H₁₁F₆O₆S₃ 305.0525; Found: 305.0526.

To a Schlenk flask containing a solution of alcohol 7-OH (458 mg, 2.24 mmol, 1.0 equiv) in CH₂Cl₂ (2.0 mL) was added pyridine (0.90 mL, 11.2 mmol, 5.0 equiv), and methanesulfonyl chloride (0.26 mL, 3.36 mmol, 1.5 equiv) and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with CH₂Cl₂ (25 mL) and transferred to a separatory funnel. The resulting mixture was extracted with 10% aqueous HCl (2 x 20 mL), saturated aqueous NaHCO₃ (1 x 20 mL) and brine (1 x 20 mL). The organic layer was dried over MgSO₄, filtered, concentrated and chromatographed on a silica gel column using 85/15 hexanes/EtOAc (Rf = 0.16 in 90% hexanes/10% ethyl acetate) to afford the product as a white solid (445 mg, 70% yield); mp = 82-83 °C.

¹H NMR (CDCl₃): δ 7.41 (dd, J = 8.1, 1.7 Hz, 1H), 7.24 (td, J = 8.1, 1.7 Hz, 1H), 7.14 (td, J = 7.8, 1.6 Hz, 1H), 7.08-6.98 (multiple peaks, 4H), 6.93 (dd, J = 8.2, 1.5 Hz, 1H), 3.20 (s, 3H).

¹³C{¹H} NMR (CDCl₃): δ 159.1 (J_C-F = 241 Hz), 152.0 (J_C-F = 2.5 Hz), 149.3, 139.8, 128.3, 125.0, 124.1, 120.2 (J_C-F = 8.4 Hz), 119.6, 116.6 (J_C-F = 23 Hz), 38.5. IR (neat): 3079, 3037, 1501, 1488, 1360, 1274, 1259, 1223, 1181, 1160, 1150, 1100, 1091, 966, 894, 863, 852, 784, 752, 733, 705, 686, 598 cm⁻¹. HRMS [M+Na] Calcd for C₁₅H₁₁F₆O₆S₃ 305.0525; Found: 305.0526.

Synthesis and characterization of mesylate substrates (Table 2):

To a Schlenk flask containing a solution of alcohol 8-OH (679 mg, 3.41 mmol, 1.0 equiv) in CH₂Cl₂ (3.1 mL) was added pyridine (1.4 mL, 17.0 mmol, 5.0 equiv), and methanesulfonyl chloride (0.39 mL, 5.11 mmol, 1.5 equiv) and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with H₂O (10 mL) and CH₂Cl₂ (25 mL) and transferred to a separatory funnel. The resulting mixture was extracted with saturated aqueous NH₄Cl (3 x 20 mL), dried over MgSO₄ and filtered through a pad of celite/charcoal using a 60 mL frit and eluting with EtOAc (80 mL). The filtrate was concentrated and
chromatographed on a silica gel column using 85/15 hexanes/EtOAc (R, = 0.32 in 85% hexanes/15% ethyl acetate) to afford the product as a light yellow clear oil (441 mg, 47% yield). 

\[ \text{\textsuperscript{1}H NMR (CDCl₃): } \delta 7.42 (dt, J = 8.0, 1.0 Hz, 1H), 7.32-7.30 (multiple peaks, 2H), 7.25-7.19 (multiple peaks, 3H), 6.83 (tt, J = 7.3, 1.1 Hz, 1H), 6.78-6.75 (multiple peaks, 2H), 3.29 (s, 3H), 2.87 (s, 3H). \] 

\[ \text{\textsuperscript{13}C\{\textsuperscript{1}H\} NMR (CDCl₃): } \delta 148.2, 145.2, 141.0, 129.0, 128.6, 128.4, 126.4, 124.6, 119.0, 114.8, 39.7, 38.2. \]

IR (neat): 2936, 1592, 1493, 1349, 1194, 1163, 1109, 1091, 967, 889, 844, 785, 747, 722, 691 cm\(^{-1}\). HRMS [M+Na] Calcd for C\(_{14}\)H\(_{15}\)N\(_2\)O\(_3\)S 300.0665; Found: 300.0662.

To a Schlenk flask containing a solution of alcohol \(2\) (500 mg, 2.70 mmol, 1.0 equiv) in CHCl\(_3\) (2.5 mL) was added pyridine (1.1 mL, 13.5 mmol, 5.0 equiv), and methanesulfonyl chloride (0.23 mL, 2.97 mmol, 1.1 equiv) and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with H\(_2\)O (10 mL) and CHCl\(_3\) (25 mL) and transferred to a separatory funnel. The resulting mixture was extracted with saturated aqueous NH\(_4\)Cl (3 x 20 mL), dried over MgSO\(_4\), and filtered. The filtrate was concentrated and chromatographed on a silica gel column using 80/20 hexanes/EtOAc (R, = 0.30 in 80% hexanes/20% ethyl acetate) to afford the product as a light yellow solid (620 mg, 87% yield). 

\[ \text{\textsuperscript{1}H NMR (CDCl₃): } \delta 7.37-7.27 (multiple peaks, 4H), 7.19 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 8.4 Hz, 2H), 7.01 (t, J = 7.4 Hz, 1H), 6.92 (t, J = 7.8 Hz, 1H), 6.21 (br s, 1H), 3.17 (s, 3H). \] 

\[ \text{\textsuperscript{13}C\{\textsuperscript{1}H\} NMR (CDCl₃): } \delta 141.6, 138.5, 136.8, 129.4, 128.0, 123.5, 122.2, 120.8, 119.2, 118.0, 37.6. \]

HRMS [M+Na] Calcd for C\(_{13}\)H\(_{13}\)N\(_2\)O\(_3\)S 286.0508; Found: 286.0497.

To a Schlenk flask containing a solution of alcohol \(9\)-OH (554 mg, 2.60 mmol, 1.0 equiv) in CHCl\(_3\) (2.4 mL) was added pyridine (1.0 mL, 13.0 mmol, 5.0 equiv), and methanesulfonyl chloride (0.30 mL, 3.90 mmol, 1.5 equiv) and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with H\(_2\)O (10 mL) and CHCl\(_3\) (25 mL) and transferred to a separatory funnel. The resulting mixture was extracted with saturated aqueous NH\(_4\)Cl (3 x 20 mL), dried over MgSO\(_4\), filtered, concentrated and chromatographed on a silica gel column using 90/10 hexanes/EtOAc (R, = 0.22 in 90% hexanes/10% ethyl acetate) to afford the product as a light purple clear oil (582 mg, 77% yield).
H NMR (CDCl₃): δ 7.41 (d, J = 7.9 Hz, 1H), 7.33-7.20 (multiple peaks, 3H), 7.05 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 8.6 Hz, 2H), 3.27 (s, 3H), 2.93 (s, 3H), 2.28 (s, 3H). ¹³C{¹H} NMR (CDCl₃): δ 146.1, 145.0, 141.5, 129.6, 128.7, 128.3, 127.9, 125.9, 124.7, 115.5, 39.8, 38.3, 20.4. IR (neat): 2936, 1512, 1493, 1362, 1193, 1162, 1109, 1092, 967, 889, 848, 794, 763, 706 cm⁻¹. HRMS [M+H] Calcd for C₁₅H₁₇NO₃S 292.1002; Found: 292.1002.

To a Schlenk flask containing a solution of alcohol 10-OH (500 mg, 2.18 mmol, 1.0 equiv) in CH₂Cl₂ (2.0 mL) was added pyridine (0.88 mL, 10.9 mmol, 5.0 equiv), and methanesulfonyl chloride (0.25 mL, 3.27 mmol, 1.5 equiv) and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with H₂O (5 mL) and CH₂Cl₂ (15 mL) and transferred to a separatory funnel. The resulting mixture was extracted with 10% HCl (2 x 20 mL), saturated aqueous NaHCO₃ (1 x 20 mL) and brine (1 x 20 mL), dried over MgSO₄, filtered, concentrated and chromatographed on a silica gel column using 80/20 hexanes/EtOAc (Rf = 0.18 in 80% hexanes/20% ethyl acetate) to afford the product as a yellow clear oil (519 mg, 77% yield).

H NMR (CDCl₃): δ 7.38 (d, J = 8.1, 1.5 Hz, 1H), 7.30-7.22 (multiple peaks, 2H), 7.17 (td, J = 7.6, 1.9 Hz, 1H), 6.84-6.78 (multiple peaks, 4H), 3.78 (s, 3H), 3.26 (s, 3H), 2.96 (s, 3H). ¹³C{¹H} NMR (CDCl₃): δ 153.6, 144.4, 142.6, 142.1, 128.3, 126.9, 125.2, 117.7, 114.5, 55.6, 40.3, 38.3. IR (neat): 2936, 1507, 1493, 1362, 1239, 1193, 1161, 1108, 1091, 1033, 967, 889, 849, 793, 762, 706, 574 cm⁻¹. HRMS [M+H] Calcd for C₁₅H₁₇NO₄S 308.0951; Found: 308.0954.

To a Schlenk flask containing a solution of alcohol 11-OH (469 mg, 2.16 mmol, 1.0 equiv) in CH₂Cl₂ (2.0 mL) was added pyridine (0.87 mL, 10.8 mmol, 5.0 equiv), and methanesulfonyl chloride (0.25 mL, 3.24 mmol, 1.5 equiv) and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with H₂O (10 mL) and CH₂Cl₂ (25 mL) and transferred to a separatory funnel. The resulting mixture was extracted with saturated aqueous NH₄Cl (3 x 20 mL), dried over MgSO₄, filtered, concentrated and chromatographed on a silica gel column using 85/15 hexanes/EtOAc (R = 0.24 in 85% hexanes/15% ethyl acetate) to afford the product as a light pink clear oil (426 mg, 67% yield).
\( \text{H NMR (CDCl): } \delta 7.39 \text{ (dd, } J = 8.0, 1.5 \text{ Hz, 1H), 7.32-7.19 } \text{(multiple peaks, 3H), 6.92 (t, } J = 8.7 \text{ Hz, 2H), 6.75-6.70 } \text{(multiple peaks, 2H), 3.26 (s, 3H), 2.93 (s, 3H).} \text{-C{[H] NMR (CDCl): } \delta 156.8 (J_\text{C-H} = 237 \text{ Hz), 144.82, 144.79, 141.5, 128.5, 127.9, 126.1, 124.6, 116.5 (J_\text{C-H} = 7.5 \text{ Hz), 115.5 (J_\text{C-H} = 22 \text{ Hz), 40.2, 38.3.} \text{ IR (neat): 2939, 1505, 1362, 1222, 1194, 1162, 1108, 1092, 967, 890, 853, 823, 805, 782, 763, 707, 567 \text{ cm}.} \text{ HRMS [M+H] Calcd for C,H,F,NOS 296.0751; Found: 296.0740.} \)

\[
\begin{array}{c}
\text{F}_3\text{C} & \text{Me} & \text{OH} \\
(12-\text{OH})
\end{array}
\xrightarrow{\text{MsCl, pyridine}}
\begin{array}{c}
\text{F}_3\text{C} & \text{Me} & \text{OMs} \\
(12-\text{OMs})
\end{array}
\]

To a Schlenk flask containing a solution of alcohol **12-OH** (326 mg, 1.22 mmol, 1.0 equiv) in CHCl, (1.1 mL) was added pyridine (0.49 mL, 6.09 mmol, 5.0 equiv), and methanesulfonyl chloride (0.14 mL, 1.83 mmol, 1.5 equiv) and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with H2O (10 mL) and CHCl, (25 mL) and transferred to a separatory funnel. The resulting mixture was extracted with saturated aqueous NH4Cl (3 x 20 mL), dried over MgSO4, and filtered through a pad of celite/charcoal using a 60 mL frit. The filtrate was concentrated and chromatographed on a silica gel column using 85/15 hexanes/EtOAc (Rf = 0.21 in 85% hexanes/15% ethyl acetate) to afford the product as a light orange clear oil (337 mg, 80% yield).

\( \text{H NMR (CDCl): } \delta 7.45 \text{ (d, } J = 8.1 \text{ Hz, 1H), 7.40-7.27 } \text{(multiple peaks, 4H), 7.06 (d, } J = 7.6 \text{ Hz, 1H), 6.96 (s, 1H), 6.86 (dd, } J = 8.4, 2.4 \text{ Hz, 1H), 3.33 (s, 3H), 2.90 (s, 3H).} \text{-C{[H] NMR (CDCl): } \delta 148.4, 145.2, 140.1, 131.4 (J_\text{C-H} = 31 \text{ Hz), 129.4, 129.0, 128.7, 127.3, 124.5, 124.2 (J_\text{C-H} = 271 \text{ Hz), 117.6, 115.1 (J_\text{C-H} = 3.8 \text{ Hz), 110.1 (J_\text{C-H} = 3.7 \text{ Hz), 39.8, 38.3.} \text{ IR (neat): 2941, 1494, 1454, 1355, 1320, 1162, 1114, 1096, 1068, 968, 910, 860, 794, 764, 721, 697, 656, 590 \text{ cm}.} \text{ HRMS [M+Na] Calcd for C,H,F,NOS 368.0539; Found: 368.0539.} \)

\[
\begin{array}{c}
\text{N} & \text{OH} \\
(13-\text{OH})
\end{array}
\xrightarrow{\text{MsCl, pyridine}}
\begin{array}{c}
\text{N} & \text{OMs} \\
(13-\text{OMs})
\end{array}
\]

To a Schlenk flask containing a solution of alcohol **13-OH** (469 mg, 2.10 mmol, 1.0 equiv) in CHCl, (1.9 mL) was added pyridine (0.85 mL, 10.5 mmol, 5.0 equiv), and methanesulfonyl chloride (0.17 mL, 2.21 mmol, 1.05 equiv) and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with H2O (10 mL) and CHCl, (25 mL) and transferred to a separatory funnel. The resulting mixture was extracted with 10% aqueous HCl (2 x 20 mL), saturated aqueous NaHCO3, (1 x 20 mL) and brine (1 x 20 mL), dried over MgSO4, filtered, concentrated and chromatographed on a silica gel column using 80/20
hexanes/EtOAc (R = 0.28 in 80% hexanes/20% ethyl acetate) to afford the product as a white solid (314 mg, 50% yield); mp = 117-118 °C.

\[ \text{H NMR (CDCl₃): } \delta 7.67 \text{ (d, } J = 8.0 \text{ Hz, 1H)}, 7.39-7.29 \text{ (multiple peaks, 3H)}, 7.22-7.12 \text{ (multiple peaks, 4H)}, 6.83 \text{ (d, } J = 7.9 \text{ Hz, 1H)}, 6.59 \text{ (d, } J = 2.9 \text{ Hz, 1H)}, 5.48 \text{ (s, 2H)}, 3.14 \text{ (s, 3H)}. \]

\[ \text{^13}C \text{ NMR (CDCl₃): } \delta 146.2, 136.2, 131.2, 129.1, 128.6, 128.3, 127.7, 122.2, 121.9, 121.0, 119.7, 109.6, 102.0, 45.2, 38.1. \]

IR (neat): 2934, 1483, 1463, 1449, 1434, 1409, 1365, 1320, 1180, 1147, 1087, 960, 869, 798, 771, 753, 723, 690 cm⁻¹. HRMS [M+Na] Calcd for C₁₆H₁₇NO₂S: 324.0662; Found: 324.0662.

To a Schlenk flask containing a solution of alcohol 14-OH (452 mg, 1.88 mmol, 1.0 equiv) in CH₂Cl₂ (1.7 mL) was added pyridine (0.76 mL, 9.38 mmol, 5.0 equiv), and methanesulfonyl chloride (0.15 mL, 1.97 mmol, 1.05 equiv) and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with H₂O (10 mL) and CH₂Cl₂ (25 mL) and transferred to a separatory funnel. The resulting mixture was extracted with 10% aqueous HCl (2 x 20 mL), saturated aqueous NaHCO₃ (1 x 20 mL) and brine (1 x 20 mL), dried over MgSO₄, filtered, concentrated and chromatographed on a silica gel column using 80/20 hexanes/EtOAc (R = 0.29 in 80% hexanes/20% ethyl acetate) to afford the product as a pale yellow solid (290 mg, 48% yield); mp = 92-93 °C.

\[ \text{H NMR (CDCl₃): } \delta 7.69 \text{ (d, } J = 7.9 \text{ Hz, 1H)}, 7.34 \text{ (dd, } J = 8.9, 4.6 \text{ Hz, 1H)}, 7.27 \text{ (d, } J = 7.9 \text{ Hz, 1H)}, 7.23-7.14 \text{ (multiple peaks, 3H)}, 7.00 \text{ (td, } J = 8.2, 3.1 \text{ Hz, 1H)}, 6.61 \text{ (d, } J = 3.1 \text{ Hz, 1H)}, 6.46 \text{ (dd, } J = 8.7, 3.1 \text{ Hz, 1H)}, 5.46 \text{ (s, 2H)}, 3.21 \text{ (s, 3H)}. \]

\[ \text{^13}C \text{ NMR (CDCl₃): } \delta 161.3 \text{ (J₁₂ = 247 Hz)}, 141.4 \text{ (J₁₂ = 2.9 Hz), 136.1, 134.0 \text{ (J₁₂ = 7.5 Hz), 128.6, 128.1, 124.1, (J₁₂ = 8.8 Hz), 122.1, 121.1, 119.9, 115.7 \text{ (J₁₂ = 24 Hz), 115.5 \text{ (J₁₂ = 25 Hz), 109.4, 102.5, 45.1, 38.1. IR (neat): 3025, 1489, 1462, 1438, 1340, 1310, 1269, 1259, 1189, 1150, 1081, 979, 860, 850, 817, 786, 748, 731, 681 cm⁻¹. HRMS [M+Na] Calcd for C₁₆H₁₁FNO₃S: 342.0571; Found: 342.0573.} \]

**Synthesis and characterization of mesylate substrates for mechanistic studies:**

![Mesylate Substrate Diagram](image-url)
To a Schlenk flask containing a solution of alcohol 26-OH (1.00 g, 4.99 mmol, 1.0 equiv) in CHCl₃ (4.5 mL) was added pyridine (2.0 mL, 25.0 mmol, 5.0 equiv). The resulting solution was cooled to 0 °C, methanesulfonyl chloride (0.58 mL, 7.49 mmol, 1.5 equiv) and the resulting mixture was stirred at room temperature overnight. The reaction mixture was quenched with H₂O (10 mL) and CHCl₃ (25 mL) and transferred to a separatory funnel. The resulting mixture was extracted with 10% aqueous HCl (2 x 20 mL), saturated aqueous NaHCO₃, (1 x 20 mL) and brine (1 x 20 mL). The organic layer was dried over MgSO₄, filtered, concentrated and chromatographed on a silica gel column using 85/15 hexanes/EtOAc (Rₐ = 0.36 in 85% hexanes/15% ethyl acetate) to afford the product as a white solid (908 mg, 65% yield); mp = 67-68 °C.

¹H NMR (CDCl₃): δ 7.33 (t, J = 8.1 Hz, 2H), 7.23 (d, J = 2.0 Hz, 1H), 7.11 (t, J = 7.4 Hz, 1H), 7.06 (dd, J = 8.3, 2.0 Hz, 1H), 6.97 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 8.4 Hz, 1H), 3.15 (s, 3H), 2.36 (s, 3H).

¹C{¹H} NMR (CDCl₃): δ 156.8, 145.9, 140.1, 134.8, 129.8, 128.8, 125.4, 123.5, 120.6, 117.8, 38.4, 20.7.

IR (neat): 3030, 1505, 1489, 1367, 1292, 1282, 1265, 1213, 1176, 1101, 973, 946, 857, 837, 830, 813, 765, 751, 688 cm⁻¹.

HRMS [M+Na] Calcd for C_{14}H_{14}O_{4}S 301.0505; Found: 301.0503.

To a Schlenk flask containing a solution of alcohol 26-OH-d₅ (500 mg, 2.44 mmol, 1.0 equiv) in CHCl₃ (2.2 mL) was added pyridine (0.98 mL, 12.2 mmol, 5.0 equiv). The resulting solution was cooled to 0 °C, methanesulfonyl chloride (0.28 mL, 3.65 mmol, 1.5 equiv) and the resulting mixture was stirred at room temperature overnight. The reaction mixture was quenched with H₂O (10 mL) and CHCl₃ (25 mL) and transferred to a separatory funnel. The resulting mixture was extracted with 10% aqueous HCl (2 x 20 mL), saturated aqueous NaHCO₃, (1 x 20 mL) and brine (1 x 20 mL). The organic layer was dried over MgSO₄, filtered, concentrated and chromatographed on a silica gel column using 85/15 hexanes/EtOAc (Rₐ = 0.24 in 85% hexanes/15% ethyl acetate) to afford the product as a white solid (400 mg, 58% yield); mp = 67-68 °C.

¹H NMR (CDCl₃): δ 7.23 (s, 1H), 7.06 (d, J = 8.2 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 3.15 (s, 3H), 2.36 (s, 3H) (90% D). ¹C{¹H} NMR (CDCl₃): δ 156.7, 145.9, 140.1, 134.8, 129.4 (t), 128.8, 125.4, 123.0 (t), 120.6, 117.4 (t), 38.4, 20.7. HRMS [M+Na] Calcd for C₂₆H₂₀D₅O₄S 306.0819; Found: 306.0830.
To a Schlenk flask containing a solution of alcohol 1-OH-d (1.01 g, 5.40 mmol, 1.0 equiv) in CH₂Cl₂ (4.9 mL) was added pyridine (2.2 mL, 27.0 mmol, 5.0 equiv). The resulting solution was cooled to 0 °C, methanesulfonyl chloride (0.63 mL, 8.10 mmol, 1.5 equiv) was added dropwise, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was quenched with H₂O (10 mL) and CH₂Cl₂ (25 mL) and transferred to a separatory funnel. The resulting mixture was extracted with 10% aqueous HCl (2 x 20 mL), saturated aqueous NaHCO₃ (1 x 20 mL) and brine (1 x 20 mL). The aqueous layers were combined and extracted once with CH₂Cl₂ (20 mL). The combined organic layers was dried over MgSO₄, filtered, concentrated and chromatographed on a silica gel column using 80/20 hexanes/EtOAc (R₁f = 0.24 in 85% hexanes/15% ethyl acetate) to afford the product as a white solid (846 mg, 59% yield) mp = 69-70°C.

¹H NMR (CDCl₃): δ 7.42 (dd, J = 8.1, 1.7 Hz, 1H), 7.38-7.34 (multiple peaks, 2H), 7.25 (td, J = 7.8, 1.7 Hz, 1H), 7.15 (t, J = 7.8 Hz, 2H), 7.00 (t, J = 8.9 Hz, 2H), 3.18 (s, 3H) (100% D).

¹³C{¹H} NMR (CDCl₃): δ 156.2, 148.8, 140.2, 129.9, 129.8, 128.3, 125.1, 124.2, 124.0, 120.3, 118.4, 118.1 (t), 38.4.

IR (neat): 3025, 1488, 1469, 1455, 1358, 1332, 1305, 1254, 1207, 1186, 1166, 1150, 1118, 1098, 1097, 976, 948, 894, 880, 855, 837, 793, 760, 743, 734, 686, 624 cm⁻¹.

HRMS [M+Na] Calcd for C₁₃H₁₁DOS 288.0411; Found: 288.0412.

To a Schlenk flask containing a solution of alcohol 27-OH (1.13 g, 3.89 mmol, 1.0 equiv) in CH₂Cl₂ (3.5 mL) was added pyridine (1.6 mL, 19.4 mmol, 5.0 equiv). The resulting solution was cooled to 0 °C, methanesulfonyl chloride (0.45 mL, 5.83 mmol, 1.5 equiv) was added, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was quenched with H₂O (10 mL) and CH₂Cl₂ (25 mL) and transferred to a separatory funnel. The resulting mixture was extracted with saturated aqueous NH₄Cl (3 x 20 mL), dried over MgSO₄, filtered, concentrated and chromatographed on a silica gel column using 80/20 hexanes/EtOAc (R₁ = 0.29 in 80% hexanes/20% ethyl acetate) to afford the product as a clear yellow viscous oil (985 mg, 69% yield).
H NMR (CDCl₃): δ 7.40-7.37 (m, 1H), 7.25-7.12 (multiple peaks, 6H), 7.06-6.99 (multiple peaks, 3H), 6.64-6.55 (multiple peaks, 3H), 3.71 (s, 3H), 2.79 (s, 3H). ¹³C{¹H} NMR (CDCl₃): δ 160.4, 148.5, 147.0, 144.1, 139.5, 129.8, 129.5, 129.2, 128.1, 125.6, 124.3, 122.9, 122.8, 115.2, 108.6, 108.0, 55.2, 38.2. IR (neat): 2970, 1586, 1483, 1338, 1324, 1271, 1233, 1195, 1160, 1154, 1148, 1100, 1038, 976, 870, 851, 813, 783, 765, 754, 714, 696, 687 cm⁻¹. HRMS [M+Na]⁺ Calcd for C₂₀H₁₉N₄O₃ 392.0927; Found: 392.0926.

General procedures for Arylations (Tables 1-2 and 4-6):

General Procedure (A) for intramolecular C–H Arylations:
Pd(OAc)₂ was weighed into a 20 mL scintillation vial. The vial was taken into the glove box and dctype, Rb₂CO₃, and CsOPiv (with or without as indicated) were added. A solution of substrate in toluene (or xylene) was added to this mixture. The vial was sealed with a Teflon lined cap, taken out of the glove box and the reaction mixture was allowed to stir at the indicated temperature for the indicated time. The reaction mixture was cooled to room temperature and filtered through a 1.5 inch plug of silica gel, eluting with Et₂O (100 mL). The filtrate was concentrated and chromatographed on a silica gel column to afford the product.

General Procedure (B) for intramolecular C–H Arylations:
Pd(OAc)₂ was weighed into in a 20 mL scintillation vial. The vial was taken into the glove box and dctype, Rb₂CO₃, CsOPiv (with or without as indicated) and a solution of substrate in toluene (or xylene) were added. The vial was sealed with a Teflon lined cap, taken out of the glove box and the reaction mixture was allowed to stir at the indicated temperature for the indicated time. The reaction mixture was cooled to room temperature and filtered through a 1.5 inch plug of silica gel, eluting with EtOAc (100 mL). The filtrate was concentrated and chromatographed on a silica gel column to afford the product.

General Procedure (C) for intermolecular C–H Arylations with preformed mesylates:
Mesylate and Pd(OAc)₂ were weighed into in a 20 mL scintillation vial. The vial was taken into the glove box and dctype, Cs₂CO₃, CsOPiv, azole substrate and toluene were added. The vial was sealed with a Teflon lined cap, taken out of the glove box and the reaction mixture was allowed to stir at 120 °C for the indicated time. The reaction mixture was cooled to room temperature and filtered through a 1.5 inch plug of silica gel, eluting with EtO (100 mL). The filtrate was concentrated and chromatographed on a silica gel column to afford the product.
General Procedure (D) for intermolecular sequential Mesylation/C–H Arylations:
To a 20 mL scintillation vial containing the aryl alcohol and a magnetic stirbar was added mesic anhydride and solvent (toluene or xylene) in the glove box. To the mixture was added 2,4,6-trimethylpyridine. The vial was sealed with a Teflon lined cap and taken out of the glove box and allowed to stir at 120 °C for 3 h. The sealed vial was allowed to cool to room temperature and taken into the glove box.
To another 20 mL scintillation vial containing Pd(OAc)$_2$, was added dcype, Cs$_2$CO$_3$, CsOPiv, azole substrate and toluene in the glove box. To this mixture was added the solution of the mesylate obtained in the first step (mesylate solution was filtered through a pipet plug of celite). The vial containing all the reagents was sealed with a Teflon lined cap, taken out of the glove box and the reaction mixture was allowed to stir at 120 °C for the indicated time. The reaction mixture was cooled to room temperature and filtered through a 1.5 inch plug of silica gel, eluting with EtO (100 mL). The filtrate was concentrated and chromatographed on a silica gel column to afford the product.

General Procedure (E) for Intramolecular sequential Mesylation/C–H Arylations:
To a 20 mL scintillation vial containing the alcohol and a magnetic stirbar was added mesic anhydride and solvent (toluene or xylene) in the glove box. To the mixture was added 2,4,6-trimethylpyridine. The vial was sealed with a Teflon lined cap and taken out of the glove box and allowed to stir at 120 °C for 3 h. The sealed vial was allowed to cool to room temperature and taken into the glove box.
To another 20 mL scintillation vial containing Pd(OAc)$_2$, was added dcype, Rb$_2$CO$_3$, and solvent (toluene or xylene) in the glove box. To this mixture was added the solution of the mesylate obtained in the first step (mesylate solution was filtered through a pipet plug of celite). The vial containing all the reagents was sealed with a Teflon lined cap, taken out of the glove box and the reaction mixture was allowed to stir at the indicated temperature for the indicated time. The reaction mixture was cooled to room temperature and filtered through a 1.5 inch plug of silica gel, eluting with EtO (100 mL). The filtrate was concentrated and chromatographed on a silica gel column to afford the product.

Procedures and Spectral Characterization of Arylation products in Table 1

Following general procedure A, 5-OMs (109 mg, 0.369 mmol, 1.0 equiv), Pd(OAc)$_2$ (8.27 mg, 0.037 mmol, 0.10 equiv), dcype (31.2 mg, 0.074 mmol, 0.20 equiv), Rb.CO$_3$ (128 mg, 0.554 mmol,
1.5 equiv) and anhydrous toluene (1.5 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 19 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (Rf = 0.46 in 98% hexanes/2% ethyl acetate) yielded product 5a as a white solid (65.7 mg, 90% yield). 1H NMR (CDCl3): δ 7.86 (d, J = 7.4 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.37 (td, J = 7.7, 1.4 Hz, 1H), 7.34 (td, J = 7.4, 1.1 Hz, 1H), 7.10 (d, J = 2.2 Hz, 1H), 6.95 (dd, J = 8.5, 2.2 Hz, 1H), 3.91 (s, 3H). The spectroscopic data is consistent with previous literature reports:

Following general procedure A, 6-OMs (38.7 mg, 0.119 mmol, 1.0 equiv), Pd(OAc)2 (2.67 mg, 0.012 mmol, 0.10 equiv), dcyte (10.1 mg, 0.024 mmol, 0.20 equiv), Rb.CO (41.3 mg, 0.179 mmol, 1.5 equiv) and anhydrous toluene (0.48 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17.5 h. Chromatography on a silica gel column using 90/10 hexanes/EtOAc (Rf = 0.23 in 90% hexanes/10% ethyl acetate) yielded product 6a as a light yellow solid (24.2 mg, 89% yield); mp = 114-115 °C. 1H NMR (CDCl3): δ 7.84 (d, J = 7.7 Hz, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.38 (s, 1H), 7.37 (td, J = 7.7, 1.4 Hz, 1H), 7.31 (td, J = 7.5, 1.2 Hz, 1H), 7.13 (s, 1H), 4.00 (s, 3H), 3.99 (s, 3H). 13C{1H} NMR (CDCl3): δ 156.3, 151.0, 149.8, 146.1, 125.4, 124.8, 122.5, 119.5, 115.5, 111.4, 102.2, 95.6, 56.5, 56.3 IR (neat): 2922, 1474, 1459, 1439, 1300, 1281, 1219, 1186, 1165, 1139, 1026, 961, 861, 848, 839, 826, 815, 745, 720 cm−1. HRMS [M+Na] Calcd for C19H16O6 251.0679; Found: 251.0685.

Following general procedure A, 7-OMs (141 mg, 0.500 mmol, 1.0 equiv), Pd(OAc)2 (11.2 mg, 0.050 mmol, 0.10 equiv), dcyte (42.3 mg, 0.100 mmol, 0.20 equiv), Rb.CO (173 mg, 0.750 mmol, 1.5 equiv), CsOPiv (122 mg, 0.519 mmol, 1.04 equiv) and anhydrous xylene (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 19 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (Rf = 0.46 in 98% hexanes/2% ethyl acetate) yielded product 7a as a pale yellow solid (68.9 mg, 74% yield). 1H NMR (CDCl3): δ 7.92 (d, J = 7.7 Hz, 1H), 7.61 (dd, J = 8.2, 2.7 Hz, 1H), 7.57 (d, J = 8.3 Hz, 1H), 7.52-7.46 (multiple peaks, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.17 (td, J = 9.0, 2.7 Hz, 1H). The spectroscopic data is consistent with previous literature reports.
Procedures and Spectral Characterization of Arylation products in Table 2

Following general procedure **A, 8-OMs** (100 mg, 0.361 mmol, 1.0 equiv), Pd(OAc), (8.08 mg, 0.036 mmol, 0.10 equiv), dcype (30.5 mg, 0.072 mmol, 0.20 equiv), Rb.CO. (125 mg, 0.541 mmol, 1.5 equiv), CsOPiv (84.4 mg, 0.361 mmol, 1.0 equiv) and anhydrous toluene (1.4 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 1 °C for 20 h. Chromatography on a silica gel column using 95/5 hexanes/EtOAc (R = 0.57 in 95% hexanes/5% ethyl acetate) yielded product **8a** as a light brown solid (61.4 mg, 94% yield). H NMR (CDCl): δ 8.11 (d, J = 7.8 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.24 (t, J = 7.5 Hz, 2H), 3.87 (s, 3H). The spectroscopic data is consistent with previous literature reports.

Following general procedure **A, 9-OMs** (100 mg, 0.343 mmol, 1.0 equiv), Pd(OAc), (7.69 mg, 0.034 mmol, 0.10 equiv), dcype (29.0 mg, 0.069 mmol, 0.20 equiv), Rb.CO. (119 mg, 0.515 mmol, 1.5 equiv), CsOPiv (80.3 mg, 0.343 mmol, 1.0 equiv) and anhydrous toluene (1.4 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 1 °C for 16 h. Chromatography on a silica gel column using 95/5 hexanes/EtOAc (R = 0.48 in 95% hexanes/5% ethyl acetate) yielded product **9a** as a light yellow solid (63.6 mg, 95% yield). H NMR (CDCl): δ 8.06 (d, J = 7.6 Hz, 1H), 7.90 (s, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.31-7.27 (multiple peaks, 2H), 7.20 (t, J = 7.4 Hz, 1H), 3.83 (s, 3H), 2.54 (s, 3H). The spectroscopic data is consistent with previous literature reports.

Following general procedure **A, 10-OMs** (100 mg, 0.325 mmol, 1.0 equiv), Pd(OAc), (7.29 mg, 0.033 mmol, 0.10 equiv), dcype (27.5 mg, 0.065 mmol, 0.20 equiv), Rb.CO. (113 mg, 0.488 mmol, 1.5 equiv), CsOPiv (76.1 mg, 0.325 mmol, 1.0 equiv) and anhydrous toluene (1.3 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 1 °C for 20 h. Chromatography on a silica gel column using 95/5 hexanes/EtOAc (R = 0.35 in 95% hexanes/5% ethyl acetate) yielded product **10a** as a white solid (63.0 mg, 92 % yield). H NMR (CDCl): 8.05 (d, J = 7.9 Hz, 1H), 7.59 (d, J = 2.5 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 8.2
Hz, 1H), 7.31 (d, J = 8.8 Hz, 1H), 7.20 (t, J = 7.2 Hz, 1H), 7.13 (dd, J = 8.8, 2.5 Hz, 1H), 3.94 (s, 3H), 3.84 (s, 3H). The spectroscopic data is consistent with previous literature reports.

Following general procedure A, 11-OMs (100 mg, 0.339 mmol, 1.0 equiv), Pd(OAc)₂ (7.58 mg, 0.034 mmol, 0.10 equiv), dcype (28.6 mg, 0.068 mmol, 0.20 equiv), Rb.CO₂ (117 mg, 0.508 mmol, 1.5 equiv), CsOPiv (79.2 mg, 0.339 mmol, 1.0 equiv) and anhydrous toluene (1.4 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 1 °C for 1.5 h. Chromatography on a silica gel column using 95/5 hexanes/EtOAc (Rf = 0.38 in 95% hexanes/5% ethyl acetate) yielded product 11a as a pale yellow solid (67.3 mg, 99.8% yield). ¹H NMR (CDCl₃): δ 8.04 (d, J = 7.9 Hz, 1H), 7.75 (dd, J = 8.9, 2.5 Hz, 1H), 7.50 (t, J = 7.7 Hz, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.32 (dd, J = 8.8, 4.2 Hz, 1H), 7.26-7.19 (multiple peaks, 2H), 3.85 (s, 3H). The spectroscopic data is identical to that previously reported in the literature.

Following general procedure A, 12-OMs (100 mg, 0.290 mmol, 1.0 equiv), Pd(OAc)₂ (6.49 mg, 0.029 mmol, 0.10 equiv), dcype (24.5 mg, 0.058 mmol, 0.20 equiv), Rb.CO₂ (100 mg, 0.434 mmol, 1.5 equiv), CsOPiv (67.8 mg, 0.290 mmol, 1.0 equiv) and anhydrous toluene (1.2 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 19 h. Chromatography on a silica gel column using 95/5 hexanes/EtOAc (Rf = 0.52 in 95% hexanes/5% ethyl acetate) yielded product 12a as a pale yellow solid (68.5 mg, 95% yield); mp = 118-119 °C. ¹H NMR (CDCl₃): δ 8.17 (d, J = 8.1 Hz, 1H), 8.14 (d, J = 7.9 Hz, 1H), 7.67 (s, 1H), 7.56 (t, J = 7.7 Hz, 1H), 7.50-7.45 (multiple peaks, 2H), 7.29 (t, J = 7.4 Hz, 1H), 3.91 (s, 3H). ¹C NMR (CDCl₃): δ 141.9, 140.0, 127.4 (Jₙ = 32 Hz), 127.0, 125.3, 125.0 (Jₙ = 270 Hz), 121.8, 120.9, 120.5, 119.5, 115.5 (Jₙ = 4.0 Hz), 108.8, 105.7 (Jₙ = 4.2 Hz), 29.2. IR (neat): 2924, 1473, 1455, 1359, 1314, 1283, 1248, 1241, 1229, 1155, 1132, 1107, 1064, 1051, 902, 861, 828, 818, 747, 737, 726, 663, 642 cm⁻¹. HRMS M Calcd for C₂₇H₂₈F₁₆N₂: 581.1988; Found: 581.1982.
Following general procedure **B, 13-OMs** (151 mg, 0.500 mmol, 1.0 equiv), Pd(OAc), (11.2 mg, 0.050 mmol, 0.10 equiv), dcype (42.3 mg, 0.100 mmol, 0.20 equiv), Rb.CO, (173 mg, 0.750 mmol, 1.5 equiv), CsOPiv (117 mg, 0.500 mmol, 1.0 equiv) and anhydrous xylene (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 145 °C for 16 h. Chromatography on a silica gel column using 98/2 to 85/15 hexanes/EtOAc (R = 0.19 in 98% hexanes/2% ethyl acetate) yielded product **13a** as a light brown solid (74.5 mg, 73% yield). \( \text{H NMR (CDCl}_3\):} \delta 7.72 (d, \( J = 7.5 \) Hz, 1H), 7.66 (d, \( J = 7.9 \) Hz, 1H), 7.48 (d, \( J = 7.5 \) Hz, 1H), 7.41 (t, \( J = 7.4 \) Hz, 1H), 7.37 (d, \( J = 8.2 \) Hz, 1H), 7.31 (t, \( J = 7.5 \) Hz, 1H), 7.20 (t, \( J = 7.6 \) Hz, 1H), 7.11 (t, \( J = 7.5 \) Hz, 1H), 6.63 (br s, 1H), 5.09 (s, 2H). The spectroscopic data is consistent with previous literature reports.

![Image](14a.png)

Following general procedure **B, 14-OMs** (100 mg, 0.313 mmol, 1.0 equiv), Pd(OAc), (7.01 mg, 0.031 mmol, 0.10 equiv), dcype (26.5 mg, 0.063 mmol, 0.20 equiv), Rb.CO, (109 mg, 0.470 mmol, 1.5 equiv), CsOPiv (36.6 mg, 0.157 mmol, 0.5 equiv) and anhydrous xylene (1.3 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 145 °C for 17.5 h. Chromatography on a silica gel column using 98/2 to 0/100 hexanes/EtOAc (R = 0.15 in 98% hexanes/2% ethyl acetate) yielded product **14a** as a light yellow solid (54.0 mg, 77% yield). \( \text{H NMR (CDCl}_3\):} \delta 7.66-7.63 (multiple peaks, 2H), 7.35 (d, \( J = 8.1 \) Hz, 1H), 7.21-7.18 (multiple peaks, 2H), 7.14-7.09 (multiple peaks, 2H), 6.58 (s, 1H), 5.08 (s, 2H). The spectroscopic data is consistent with previous literature reports.

**Procedures and Spectral Characterization of Arylation products in Table 4**

![Image](15a.png)

Following general procedure **C, 4-methoxy phenyl mesylate (15-OMs)** (152 mg, 0.750 mmol, 1.5 equiv), benzoazoxole (59.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc), (5.60 mg, 0.025 mmol, 0.05 equiv), dcype (21.1 mg, 0.050 mmol, 0.10 equiv), Cs.CO, (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv), and anhydrous toluene (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 90/10 hexanes/EtOAc (R = 0.22 in 90% hexanes/10% ethyl acetate) yielded product **15a** as a white solid (109.4 mg, 97% yield). \( \text{H NMR (CDCl}_3\):} \delta 8.20 (d, \( J = 8.6 \) Hz,
Following general procedure C, 3,4-dimethoxy phenyl mesylate (16-OMs) (174 mg, 0.750 mmol, 1.5 equiv), benzoxazole (59.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc), (5.60 mg, 0.025 mmol, 0.05 equiv), dcy (21.1 mg, 0.050 mmol, 0.10 equiv), Cs,CO. (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv), and anhydrous toluene (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 18 h. Chromatography on a silica gel column using 70/30 hexanes/EtOAc (R = 0.36 in 70% hexanes/30% ethyl acetate) yielded product 16a as a white solid (120 mg, 94% yield). H NMR (CDCl): δ 7.86 (dd, J = 8.3, 2.0 Hz, 1H), 7.77-7.73 (multiple peaks, 2H), 7.58-7.55 (m, 1H), 7.36-7.32 (multiple peaks, 2H), 6.99 (d, J = 8.4 Hz, 1H), 4.02 (s, 3H), 3.97 (s, 3H). The spectroscopic data is identical to that previously reported in the literature:

Following general procedure C, 3,4,5-trimethoxy phenyl mesylate (17-OMs) (197 mg, 0.750 mmol, 1.5 equiv), benzoxazole (59.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc), (5.60 mg, 0.025 mmol, 0.05 equiv), dcy (21.1 mg, 0.050 mmol, 0.10 equiv), Cs,CO. (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv), and anhydrous toluene (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 75/25 hexanes/EtOAc (R = 0.33 in 75% hexanes/25% ethyl acetate) yielded product 17a as a white solid (137 mg, 96% yield). H NMR (CDCl): δ 7.79-7.76 (m, 1H), 7.60-7.58 (m, 1H), 7.51 (s, 2H), 7.37-7.35 (multiple peaks, 2H), 4.00 (s, 6H), 3.94 (s, 3H). The spectroscopic data is consistent with previous literature reports:

Following general procedure C, 3,4-methylenedioxyphenyl mesylate (18-OMs) (162 mg, 0.750 mmol, 1.5 equiv), benzoxazole (59.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc), (5.60 mg, 0.025 mmol, 0.05 equiv), dcy (21.1 mg, 0.050 mmol, 0.10 equiv), Cs,CO. (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv), and anhydrous toluene (2.0 mL) were combined in a 20
mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 85/15 hexanes/EtOAc (R = 0.38 in 85% hexanes/15% ethyl acetate) yielded product 18a as a light yellow solid (116 mg, 97% yield). H NMR (CDCl₃): δ 7.83 (dd, J = 8.1, 1.7 Hz, 1H), 7.75-7.72 (m, 1H), 7.70 (d, J = 1.7 Hz, 1H), 7.56-7.53 (m, 1H), 7.36-7.31 (multiple peaks, 2H), 6.95 (d, J = 8.2 Hz, 1H), 6.08 (s, 2H). The spectroscopic data is consistent with previous literature reports.

Following general procedure C, 4-methoxyphenyl mesylate (15-OMs) (152 mg, 0.750 mmol, 1.5 equiv), 5-methyl benzoazole (66.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc)₂ (5.60 mg, 0.025 mmol, 0.05 equiv), dicype (21.1 mg, 0.050 mmol, 0.1 equiv), Cs₂CO₃ (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv), and anhydrous toluene (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 90/10 hexanes/EtOAc (R = 0.27 in 90% hexanes/10% ethyl acetate) yielded product 15b as a white solid (117 mg, 98% yield). H NMR (CDCl₃): 8.18 (d, J = 8.8 Hz, 2H), 7.51 (s, 1H), 7.42 (d, J = 8.1 Hz, 1H), 7.12 (d, J = 8.2 Hz, 1H), 7.02 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 2.48 (s, 3H). The spectroscopic data is consistent with previous literature reports.

Following general procedure C, 4-methoxyphenyl mesylate (15-OMs) (152 mg, 0.750 mmol, 1.5 equiv), 6-methoxy benzoazole substrate (74.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc)₂ (11.2 mg, 0.050 mmol, 0.1 equiv), dicype (42.3 mg, 0.100 mmol, 0.20 equiv), Cs₂CO₃ (224 mg, 0.689 mmol, 1.4 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv), and anhydrous toluene (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 19.5 h. Chromatography on a silica gel column using 90/10 hexanes/EtOAc (R = 0.26 in 90% hexanes/10% ethyl acetate) yielded product 15c as a white solid (109 mg, 86% yield); mp = 109-110 °C. H NMR (CDCl₃): 8.13 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.7 Hz, 1H), 7.09 (d, J = 2.4 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 6.93 (dd, J = 8.8, 2.4 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H). C{H} NMR (CDCl₃): δ 162.4, 161.9, 157.9, 151.5, 136.0, 128.9, 119.9, 119.5, 114.3, 112.4, 95.4, 55.9, 55.4. IR (neat): 2936, 1615, 1504, 1484, 1325, 1301, 1258, 1218, 1189, 1175, 1144, 1112, 1048, 1031, 1019,
1004, 916, 946, 832, 821, 808, 793, 736, 646 cm⁻¹. HRMS [M+Na] Calcd for C₁₅H₁₃NO₂ 278.0788; Found: 278.0791.

Following general procedure C, 4-methoxyphenyl mesylate (15-OMs) (152 mg, 0.750 mmol, 1.5 equiv), benzothiazole (67.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc)₃ (5.60 mg, 0.025 mmol, 0.05 equiv), dcype (21.1 mg, 0.050 mmol, 0.10 equiv), Cs₂CO₃ (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv), and anhydrous toluene (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 9/1 cm⁷ 7 hexanes/EtOAc (R₉ = 0.24 in 93% hexanes/7% ethyl acetate) yielded product 15d as a white solid (103 mg, 86% yield). 1H NMR (CDCl₃): δ 8.06-8.02 (multiple peaks, 3H), 7.88 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H). The spectroscopic data is consistent with previous literature reports.

**Procedures and Spectral Characterization of Arylation products in Table 5**

Following general procedure D, 4-methoxy phenol (15-OH) (93.1 mg, 0.750 mmol, 1.5 equiv), mesic anhydride (133 mg, 0.765 mmol, 1.53 equiv), 2,4,6-trimethylpyridine (90.9 mg, 0.750 mmol, 1.5 equiv), and toluene (3.0 mL) were combined for the first step. Following general procedure D, the solution of the mesylate obtained in the first step was combined with benzothiazole (59.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc)₃ (11.2 mg, 0.050 mmol, 0.10 equiv), dcype (42.3 mg, 0.100 mmol, 0.20 equiv), Cs₂CO₃ (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 90/10 hexanes/EtOAc (R₉ = 0.22 in 90% hexanes/10% ethyl acetate) yielded product 15a as a white solid (108 mg, 96% yield). 1H NMR (CDCl₃): δ 8.20 (d, J = 8.6 Hz, 2H), 7.75-7.73 (m, 1H), 7.57-7.55 (m, 1H), 7.36-7.30 (multiple peaks, 2H), 7.04 (d, J = 8.6 Hz, 2H), 3.90 (s, 3H). The spectroscopic data is consistent with previous literature reports.
Following general procedure D, 3,4-dimethoxy phenol (16-OH) (116 mg, 0.750 mmol, 1.5 equiv), mesic anhydride (133 mg, 0.765 mmol, 1.53 equiv), 2,4,6-trimethylpyridine (90.9 mg, 0.750 mmol, 1.5 equiv), and toluene (3.0 mL) were combined for the first step.

Following general procedure D, the solution of the mesylate obtained in the first step was combined with benzoxazole (59.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc) (11.2 mg, 0.050 mmol, 0.10 equiv), dcyphos (42.3 mg, 0.100 mmol, 0.20 equiv), CsCO (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 75/25 hexanes/EtOAc (R = 0.32 in 75% hexanes/25% ethyl acetate) yielded product 16a as a white solid (121 mg, 95% yield). 

\[
\text{H NMR (CDCl}_3\text{): } \delta 7.86 (dd, J = 8.3, 2.0 Hz, 1H), 7.77-7.73 (multiple peaks, 2H), 7.58-7.55 (m, 1H), 7.36-7.32 (multiple peaks, 2H), 6.99 (d, J = 8.4 Hz, 1H), 4.02 (s, 3H), 3.97 (s, 3H)
\]

The spectroscopic data is consistent with previous literature reports.

![Diagram](17a)

Following general procedure D, 3,4,5-trimethoxy phenol (17-OH) (138 mg, 0.750 mmol, 1.5 equiv), mesic anhydride (133 mg, 0.765 mmol, 1.53 equiv), 2,4,6-trimethylpyridine (90.9 mg, 0.750 mmol, 1.5 equiv), and toluene (3.0 mL) were combined for the first step.

Following general procedure D, the solution of the mesylate obtained in the first step was combined with benzoxazole (59.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc) (11.2 mg, 0.050 mmol, 0.10 equiv), dcyphos (42.3 mg, 0.100 mmol, 0.20 equiv), CsCO (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 75/25 hexanes/EtOAc (R = 0.33 in 75% hexanes/25% ethyl acetate) yielded product 17a as a white solid (125 mg, 88% yield). 

\[
\text{H NMR (CDCl}_3\text{): } \delta 7.79-7.76 (m, 1H), 7.60-7.58 (m, 1H), 7.51 (s, 2H), 7.37-7.35 (multiple peaks, 2H), 4.00 (s, 6H), 3.94 (s, 3H)
\]

The spectroscopic data is consistent with previous literature reports.

![Diagram](18a)

Following general procedure D, 3,4-methylenedioxy phenol (18-OH) (104 mg, 0.750 mmol, 1.5 equiv), mesic anhydride (133 mg, 0.765 mmol, 1.53 equiv), 2,4,6-trimethylpyridine (90.9 mg, 0.750 mmol, 1.5 equiv), and toluene (3.0 mL) were combined for the first step.
Following general procedure D, the solution of the mesylate obtained in the first step was combined with benzoxazole (59.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc)₂, (11.2 mg, 0.050 mmol, 0.10 equiv), dicyclopentadiene (42.3 mg, 0.100 mmol, 0.20 equiv), Cs₂CO₃ (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 18.5 h. Chromatography on a silica gel column using 85/15 hexanes/EtOAc (R = 0.38 in 85% hexanes/15% ethyl acetate) yielded product 18a as a white solid (112 mg, 93% yield). ¹H NMR (CDCl₃): δ 7.83 (dd, J = 8.1, 1.7 Hz, 1H), 7.75-7.72 (m, 1H), 7.70 (d, J = 1.7 Hz, 1H), 7.56-7.53 (m, 1H), 7.36-7.31 (multiple peaks, 2H), 6.95 (d, J = 8.2 Hz, 1H), 6.08 (s, 2H). The spectroscopic data is consistent with previous literature reports.

![Product 18a](image1)

Following general procedure D, 4-methyl phenol (19-OH) (81.1 mg, 0.750 mmol, 1.5 equiv), mesic anhydride (133 mg, 0.765 mmol, 1.53 equiv), 2,4,6-trimethylpyridine (90.9 mg, 0.750 mmol, 1.5 equiv), and toluene (3.0 mL) were combined for the first step. Following general procedure D, the solution of the mesylate obtained in the first step was combined with benzoxazole (59.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc)₂, (11.2 mg, 0.050 mmol, 0.10 equiv), dicyclopentadiene (42.3 mg, 0.100 mmol, 0.20 equiv), Cs₂CO₃ (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 95/5 hexanes/EtOAc (R = 0.34 in 95% hexanes/5% ethyl acetate) yielded product 19a as a white solid (96 mg, 92% yield). ¹H NMR (CDCl₃): δ 8.15 (d, J = 8.2 Hz, 2H), 7.77-7.75 (m, 1H), 7.59-7.56 (m, 1H), 7.35-7.32 (multiple peaks, 4H), 2.45 (s, 3H). The spectroscopic data is consistent with previous literature reports.

![Product 19a](image2)

Following general procedure D, 4-fluoro phenol (20-OH) (84.1 mg, 0.750 mmol, 1.5 equiv), mesic anhydride (133 mg, 0.765 mmol, 1.53 equiv), 2,4,6-trimethylpyridine (90.9 mg, 0.750 mmol, 1.5 equiv), and toluene (3.0 mL) were combined for the first step. Following general procedure D, the solution of the mesylate obtained in the first step was combined with benzoxazole (59.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc)₂, (11.2 mg, 0.050 mmol, 0.10 equiv), dicyclopentadiene (42.3 mg, 0.100 mmol, 0.20 equiv), Cs₂CO₃ (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 20 h. Chromatography on a silica gel column using 95/5 hexanes/EtOAc (R = 0.23 in 95% hexanes/5% ethyl acetate) yielded product 20a as a
white solid (101 mg, 95% yield). H NMR (CDCl₃): δ 8.29-8.24 (m, 2H), 7.79-7.74 (m, 1H), 7.59-7.56 (m, 1H), 7.38-7.34 (multiple peaks, 2H), 7.22 (t, J = 8.6 Hz, 2H). The spectroscopic data is consistent with previous literature reports.

![Image](image1)

Following general procedure D, o-tolyl phenol (21-OH) (81.1 mg, 0.750 mmol, 1.5 equiv), mesic anhydride (133 mg, 0.765 mmol, 1.53 equiv), 2,4,6-trimethylpyridine (90.9 mg, 0.750 mmol, 1.5 equiv), and toluene (3.0 mL) were combined for the first step. Following general procedure D, the solution of the mesylate obtained in the first step was combined with benzoxazole (59.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc)₂ (11.2 mg, 0.050 mmol, 0.10 equiv), dcyte (42.3 mg, 0.100 mmol, 0.20 equiv), Cs₂CO₃ (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 19 h. Chromatography on a silica gel column using 95/5 hexanes/EtOAc (Rₛ = 0.41 in 95% hexanes/5% ethyl acetate) yielded product 21a as a light yellow solid (98.8 mg, 94% yield). H NMR (CDCl₃): δ 8.18 (d, J = 7.2 Hz, 1H), 7.82-7.80 (m, 1H), 7.61-7.59 (m, 1H), 7.43-7.33 (multiple peaks, 5H), 2.82 (s, 3H). The spectroscopic data is consistent with previous literature reports.

![Image](image2)

Following general procedure D, 2-naphthol (22-OH) (108 mg, 0.750 mmol, 1.5 equiv), mesic anhydride (133 mg, 0.765 mmol, 1.53 equiv), 2,4,6-trimethylpyridine (90.9 mg, 0.750 mmol, 1.5 equiv), and toluene (3.0 mL) were combined for the first step. Following general procedure D, the solution of the mesylate obtained in the first step was combined with benzoxazole (59.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc)₂ (11.2 mg, 0.050 mmol, 0.10 equiv), dcyte (42.3 mg, 0.100 mmol, 0.20 equiv), Cs₂CO₃ (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 95/5 hexanes/EtOAc (Rₛ = 0.25 in 95% hexanes/5% ethyl acetate) yielded product 22a as a white solid (106 mg, 87% yield). H NMR (CDCl₃): δ 8.80 (s, 1H), 8.33 (dd, J = 8.6, 1.7 Hz, 1H), 8.01-7.98 (multiple peaks, 2H), 7.92-7.90 (m, 1H), 7.83-7.80 (m, 1H), 7.66-7.55 (multiple peaks, 3H), 7.41-7.36 (multiple peaks, 2H). The spectroscopic data is consistent with previous literature reports.
Following general procedure D, 4-methoxy phenol (15-OH) (93.1 mg, 0.750 mmol, 1.5 equiv), mesic anhydride (133 mg, 0.765 mmol, 1.5 equiv), 2,4,6-trimethylpyridine (90.9 mg, 0.750 mmol, 1.5 equiv), and toluene (3.0 mL) were combined for the first step.

Following general procedure D, the solution of the mesylate obtained in the first step was combined with 5-methyl benzoxazole (66.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc)\(_2\) (11.2 mg, 0.050 mmol, 0.10 equiv), dcype (42.3 mg, 0.100 mmol, 0.20 equiv), CsCO\(_3\) (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 88/12 hexanes/EtOAc (R\(_f\) = 0.34 in 88% hexanes/12% ethyl acetate) yielded product 15b as a white solid (116 mg, 97% yield). \(\text{^1}H\) NMR (CDCl\(_3\)): 8.18 (d, \(J = 8.8 \text{ Hz}, 2\)H), 7.51 (s, 1H), 7.42 (d, \(J = 8.1 \text{ Hz}, 1\)H), 7.12 (d, \(J = 8.2 \text{ Hz}, 1\)H), 7.02 (d, \(J = 8.8 \text{ Hz}, 2\)H), 3.89 (s, 3H), 2.48 (s, 3H). The spectroscopic data is consistent with previous literature reports.

Following general procedure D, 4-methoxyphenol (93.1 mg, 0.750 mmol, 1.5 equiv), mesic anhydride (133 mg, 0.765 mmol, 1.53 equiv), 2,4,6-trimethylpyridine (90.9 mg, 0.750 mmol, 1.5 equiv), and toluene (3.0 mL) were combined for the first step.

Following general procedure D, the solution of the mesylate obtained in the first step was combined with 6-methoxy benzoxazole (74.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc)\(_2\) (11.2 mg, 0.050 mmol, 0.10 equiv), dcype (42.3 mg, 0.100 mmol, 0.20 equiv), CsCO\(_3\) (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 85/15 hexanes/EtOAc (R\(_f\) = 0.27 in 85% hexanes/15% ethyl acetate) yielded product 15c as a white solid (115 mg, 90% yield). \(\text{^1}H\) NMR (CDCl\(_3\)): 8.13 (d, \(J = 8.8 \text{ Hz}, 2\)H), 7.60 (d, \(J = 8.7 \text{ Hz}, 1\)H), 7.09 (d, \(J = 2.4 \text{ Hz}, 1\)H), 7.01 (d, \(J = 8.8 \text{ Hz}, 2\)H), 6.93 (dd, \(J = 8.7, 2.4 \text{ Hz}, 1\)H), 3.88 (s, 3H), 3.87 (s, 3H). The spectroscopic data is identical to that of the product isolated using the preformed mesylate 15-OMs.
Following general procedure D, 4-methoxy phenol (15-OH) (93.1 mg, 0.750 mmol, 1.5 equiv), mesic anhydride (133 mg, 0.765 mmol, 1.53 equiv), 2,4,6-trimethylpyridine (90.9 mg, 0.750 mmol, 1.5 equiv), and toluene (3.0 mL) were combined for the first step.

Following general procedure D, the solution of the mesylate obtained in the first step was combined with benzothiazole (67.6 mg, 0.500 mmol, 1.0 equiv), Pd(OAc), (11.2 mg, 0.050 mmol, 0.10 equiv), dcype (42.3 mg, 0.100 mmol, 0.20 equiv), CsCO (244 mg, 0.750 mmol, 1.5 equiv), CsOPiv (129 mg, 0.550 mmol, 1.1 equiv) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 18 h. Chromatography on a silica gel column using 93/7 hexanes/EtOAc (R = 0.32 in 93% hexanes/7% ethyl acetate) yielded product 15d as a white solid (101 mg, 84% yield). H NMR (CDCl): 8.06-8.02 (multiple peaks, 3H), 7.88 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H). The spectroscopic data is consistent with previous literature reports.

Following general procedure D, 4-methoxy phenol (15-OH) (93.1 mg, 0.750 mmol, 1.5 equiv), mesic anhydride (133 mg, 0.765 mmol, 1.53 equiv), 2,4,6-trimethylpyridine (90.9 mg, 0.750 mmol, 1.5 equiv), and toluene (3.0 mL) were combined for the first step.

Following general procedure D, the solution of the mesylate obtained in the first step was combined with 2-phenyl-1,3,4-oxadiazole (73.6 mg, 0.504 mmol, 1.0 equiv), Pd(OAc), (11.2 mg, 0.050 mmol, 0.10 equiv), dcype (42.3 mg, 0.100 mmol, 0.20 equiv), CsCO (244 mg, 0.750 mmol, 1.49 equiv), CsOPiv (129 mg, 0.550 mmol, 1.09 equiv) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 18 h. Chromatography on a silica gel column using 75/25 to 70/30 hexanes/EtOAc (R = 0.35 in 75% hexanes/25% ethyl acetate) yielded product 15e as a white solid (115 mg, 91% yield). H NMR (CDCl): 8.14-8.11 (multiple peaks, 2H), 8.09 (d, J = 8.8 Hz, 2H), 7.56-7.52 (multiple peaks, 3H), 7.04 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H). The spectroscopic data is consistent with previous literature reports.

**Procedures and Spectral Characterization of Arylation products in Table 6**

Following general procedure E, 1-OH (93.1 mg, 0.500 mmol, 1.0 equiv), mesic anhydride (88.8 mg, 0.510 mmol, 1.02 equiv), 2,4,6-trimethylpyridine (60.6 mg, 0.500 mmol, 1.0 equiv), and xylene (2.0 mL) were combined for the first step.
Following general procedure E, the solution of the mesylate obtained in the first step Pd(OAc),
(11.2 mg, 0.050 mmol, 0.10 equiv), dctype (42.3 mg, 0.100 mmol, 0.20 equiv), Rb.CO. (173 mg,
0.750 mmol, 1.5 equiv), and anhydrous xylene (1.0 mL) were combined in a 20 mL scintillation
vial. The reaction mixture was allowed to stir at 120 °C for 18 h. Chromatography on a silica gel
column using 98/2 hexanes/EtOAc (R = 0.62 in 98% hexanes/2% ethyl acetate) yielded product
1a as a white solid (62.6 mg, 74% yield). H NMR (CDCl₃): δ 7.96 (d, J = 7.8 Hz, 2H), 7.58 (d, J =
8.2 Hz, 2H), 7.46 (t, J = 7.8 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H). The spectroscopic data is consistent
with previous literature reports.

![Image of 2a]

Following general procedure E, 2-OH (108 mg, 0.500 mmol, 1.0 equiv), mesic anhydride (88.8
mg, 0.510 mmol, 1.02 equiv), 2,4,6-trimethylpyridine (60.6 mg, 0.500 mmol, 1.0 equiv), and
xylene (2.0 mL) were combined for the first step.

Following general procedure E, the solution of the mesylate obtained in the first step was
combined with Pd(OAc), (11.2 mg, 0.050 mmol, 0.10 equiv), dctype (42.3 mg, 0.100 mmol, 0.20
equiv), Rb.CO. (173 mg, 0.750 mmol, 1.5 equiv), and anhydrous xylene (1.0 mL) were combined
in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h.
Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R = 0.29 in 98%
hexanes/2% ethyl acetate) yielded product 2a as a light yellow oil (69.5 mg, 70% yield). H NMR
(CDCl₃): δ 7.92 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 8.3 Hz, 1H), 7.48-7.43 (multiple peaks, 3H), 7.33 (td,
J = 7.5, 1.0 Hz, 1H), 7.05 (dd, J = 8.9, 2.7 Hz, 1H), 3.92 (s, 3H). The spectroscopic data is
consistent with previous literature reports.

![Image of 23a]

Following general procedure E, 23-OH (100.1 mg, 0.500 mmol, 1.0 equiv), mesic anhydride (88.8
mg, 0.510 mmol, 1.02 equiv), 2,4,6-trimethylpyridine (60.6 mg, 0.500 mmol, 1.0 equiv), and
anhydrous toluene (2.0 mL) were combined for the first step.

Following general procedure E, the solution of the mesylate obtained in the first step was
combined with Pd(OAc), (11.2 mg, 0.050 mmol, 0.10 equiv), dctype (42.3 mg, 0.100 mmol, 0.20
equiv), Rb.CO. (173 mg, 0.750 mmol, 1.5 equiv), and anhydrous toluene (1.0 mL) were combined
in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 19 h.
Chromatography on a silica gel column using 99/1 hexanes/EtOAc (R = 0.54 in 99%
hexanes/1% ethyl acetate) yielded product 23a as a white solid (64.7 mg, 71% yield). H NMR
(CDCl₃): δ 7.93 (d, J = 7.7 Hz, 1H), 7.76 (s, 1H), 7.56 (d, J = 8.3 Hz, 1H), 7.47-7.44 (multiple peaks,
2H), 7.34 (t, J = 7.5 Hz, 1H), 7.29-7.26 (m, 1H), 2.53 (s, 3H). The spectroscopic data is consistent with previous literature reports.

Following general procedure E, **7-OH** (102 mg, 0.500 mmol, 1.0 equiv), mesic anhydride (88.8 mg, 0.510 mmol, 1.02 equiv), 2,4,6-trimethylpyridine (60.6 mg, 0.500 mmol, 1.0 equiv), and xylene (2.0 mL) were combined for the first step.

Following general procedure E, the solution of the mesylate obtained in the first step was combined with Pd(OAc)$_2$ (11.2 mg, 0.050 mmol, 0.10 equiv), dcype (42.3 mg, 0.100 mmol, 0.20 equiv), Rb$_2$CO$_3$ (173 mg, 0.750 mmol, 1.5 equiv), and anhydrous xylene (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 19 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R$_f$ = 0.63 in 98% hexanes/2% ethyl acetate) yielded product **7a** as a light yellow solid (75.4 mg, 82% yield). H NMR (CDCl$_3$): δ 7.92 (d, J = 7.7 Hz, 1H), 7.61 (dd, J = 8.2, 2.7 Hz, 1H), 7.57 (d, J = 8.3 Hz, 1H), 7.52-7.46 (multiple peaks, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.17 (td, J = 9.0, 2.7 Hz, 1H). The spectroscopic data is consistent with previous literature reports.

Following general procedure E, **24-OH** (100 mg, 0.500 mmol, 1.0 equiv), mesic anhydride (88.8 mg, 0.510 mmol, 1.02 equiv), 2,4,6-trimethylpyridine (60.6 mg, 0.500 mmol, 1.0 equiv), and xylene (2.0 mL) were combined for the first step.

Following general procedure E, the solution of the mesylate obtained in the first step was combined with Pd(OAc)$_2$ (11.2 mg, 0.050 mmol, 0.10 equiv), dcype (42.3 mg, 0.100 mmol, 0.20 equiv), Rb$_2$CO$_3$ (173 mg, 0.750 mmol, 1.5 equiv), and anhydrous xylene (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R$_f$ = 0.67 in 98% hexanes/2% ethyl acetate) yielded product **24a** as a light yellow oil (78.1 mg, 84% yield). H NMR (CDCl$_3$): δ 7.96 (d, J = 7.7 Hz, 1H), 7.81-7.79 (m, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.46 (td, J = 7.8, 1.3 Hz, 1H), 7.35 (td, J = 7.5, 1.0 Hz, 1H), 7.30-7.24 (multiple peaks, 2H), 2.62 (s, 3H). The spectroscopic data is consistent with previous literature reports.
Following general procedure E, **25-OH** (118 mg, 0.500 mmol, 1.0 equiv), mesic anhydride (88.8 mg, 0.510 mmol, 1.02 equiv), 2,4,6-trimethylpyridine (60.6 mg, 0.500 mmol, 1.0 equiv), and xylene (2.0 mL) were combined for the first step.

Following general procedure E, the solution of the mesylate obtained in the first step was combined with Pd(OAc)$_2$ (11.2 mg, 0.050 mmol, 0.10 equiv), dcype (42.3 mg, 0.100 mmol, 0.20 equiv), Rb$_2$CO$_3$ (173 mg, 0.750 mmol, 1.5 equiv), and anhydrous xylene (1.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 140 °C for 19 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R$_f$ = 0.51 in 98% hexanes/2% ethyl acetate) yielded product as a mixture of **25a** and **25b** (25a:25b = 1.5:1) as a light yellow solid (88.2 mg, 81% yield). **Major isomer (25a):** $^1$H NMR (CDCl$_3$): $\delta$ 8.65 (d, $J = 7.9$ Hz, 1H), 8.42 (dd, $J = 7.0$, 1.7 Hz, 1H), 8.05 (d, $J = 8.0$ Hz, 1H), 7.95 (d, $J = 8.7$ Hz, 1H), 7.79 (d, $J = 8.9$ Hz, 1H), 7.77-7.70 (multiple peaks, 2H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.53-7.49 (multiple peaks, 2H). **Minor isomer (25b):** $^1$H NMR (CDCl$_3$): $\delta$ 8.43 (br s, 1H), 8.12-8.02 (multiple peaks, 2H), 7.99 (d, $J = 8.5$ Hz, 1H), 7.94 (br s, 1H), 7.63-7.46 (multiple peaks, 4H), 7.39 (t, $J = 7.3$ Hz, 1H). The spectroscopic data is consistent with previous literature reports.

**Procedures for mechanistic studies:**

Following general procedure A, **1-OMs-d** (100 mg, 0.377 mmol, 1.0 equiv), Pd(OAc)$_2$ (8.40 mg, 0.038 mmol, 0.10 equiv), dcype (31.9 mg, 0.075 mmol, 0.20 equiv), Rb$_2$CO$_3$ (131 mg, 0.565 mmol, 1.5 equiv), CsOPiv (88.2 mg, 0.377 mmol, 1.00 equiv), and anhydrous toluene (1.5 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. Chromatography on a silica gel column using 99/1 hexanes/EtOAc (R$_f$ = 0.42 in 99% hexanes/1% ethyl acetate) yielded product as a mixture of **1a** and **1a-d** (49.7 mg, 78% yield).
Following general procedure A, 26-OMs (49.1 mg, 0.176 mmol, 0.5 equiv) and 26-OMs-d₅ (50.0 mg, 0.176 mmol, 0.5 equiv), Pd(OAc)₂ (7.90 mg, 0.035 mmol, 0.10 equiv), dcppe (29.8 mg, 0.071 mmol, 0.20 equiv), Rb₂CO₃ (122 mg, 0.529 mmol, 1.5 equiv), CsOPiv (82.6 mg, 0.353 mmol, 1.00 equiv), and anhydrous toluene (1.4 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 1.25 h. The crude reaction mixture was allowed to cool to room temperature and diluted with EtOAc. Hexadecane internal standard was added and the resulting reaction mixture was analyzed using GC. The calibrated GC yield against hexadecane was determined to be 10%. The crude reaction mixture was worked up as detailed in procedure A and chromatographed on a silica gel column using 99/1 hexanes/EtOAc (Rᵣ = 0.39 in 99% hexanes/1% ethyl acetate). The isolated product was analyzed using ¹H NMR spectroscopy to obtain the ratio of 26a:26a-d₅ (2.3:1).

Following general procedure A, 27-OMs (185 mg, 0.500 mmol, 1.0 equiv), Pd(OAc)₂ (11.2 mg, 0.050 mmol, 0.10 equiv), dcppe (42.3 mg, 0.100 mmol, 0.20 equiv), Rb₂CO₃ (173 mg, 0.75 mmol, 1.5 equiv), and anhydrous xylene (2.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 22 h. Chromatography on a silica gel column using 90/10 hexanes/EtO₂ yielded product as a mixture of 27a and 27b (50.4 mg, 37% yield). The isolated product was analyzed by ¹H NMR spectroscopy to obtain the ratio of 27a:27b by comparison to the previously reported spectral data for 27a and 27b.
Following general procedure C, 15-OMs (17.0 mg, 0.084 mmol, 1.0 equiv), benzoazole (10.0 mg, 0.084 mmol, 1.0 equiv), 6-methoxy benzoazole (12.5 mg, 0.084 mmol, 1.0 equiv), Pd(OAc)$_2$ (1.9 mg, 0.008 mmol, 0.10 equiv), dcype (7.1 mg, 0.017 mmol, 0.20 equiv), Cs.CO$_3$ (41 mg, 0.126 mmol, 1.5 equiv), CsOPiv (21.6 mg, 0.092 mmol, 1.1 equiv), and anhydrous toluene (0.34 mL) were combined in a 4 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. The reaction mixture was allowed to cool to room temperature and then diluted with EtOAc. Gas chromatographic analysis of the crude reaction mixture showed 56% and 47% calibrated yields (against hexadecane as the internal standard) of 15a and 15c respectively (15a: 15c = 1.2:1).

Following general procedure C, 15-OMs (17.0 mg, 0.084 mmol, 1.0 equiv), $p$-MeC$_6$H$_4$OMs (15.6 mg, 0.084 mmol, 1.0 equiv), benzoazole (10.0 mg, 0.084 mmol, 1.0 equiv), Pd(OAc)$_2$ (1.9 mg, 0.008 mmol, 0.10 equiv), dcype (7.1 mg, 0.017 mmol, 0.20 equiv), Cs.CO$_3$ (41 mg, 0.126 mmol, 1.5 equiv), CsOPiv (21.6 mg, 0.092 mmol, 1.1 equiv), and anhydrous toluene (0.34 mL) were combined in a 4 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. The reaction mixture was allowed to cool to room temperature and then diluted with EtOAc. Gas chromatographic analysis of the crude reaction mixture showed 66% and 50% calibrated yields (against hexadecane as the internal standard) of 15-Ar and 15a respectively (15-Ar: 15a = 1.3:1).
Following general procedure C, 15-OMs (17.0 mg, 0.084 mmol, 1.0 equiv), \textit{p}-F\textit{C}6\textit{H}4\textit{OMs} (16.0 mg, 0.084 mmol, 1.0 equiv), benzoxazole (10.0 mg, 0.084 mmol, 1.0 equiv), \textit{Pd(OAc)}2 (1.9 mg, 0.008 mmol, 0.10 equiv), dctype (7.1 mg, 0.017 mmol, 0.20 equiv), Cs\textsubscript{2}CO\textsubscript{3} (41 mg, 0.126 mmol, 1.5 equiv), CsOPiv (21.6 mg, 0.092 mmol, 1.1 equiv), and anhydrous toluene (0.34 mL) were combined in a 4 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. The reaction mixture was allowed to cool to room temperature and then diluted with EtOAc. Gas chromatographic analysis of the crude reaction mixture showed 56% and 25% calibrated yields (against hexadecane as the internal standard) of 15-Ar and 15a respectively (15-Ar: 15a = 2.2:1).

Following general procedure C, 15-OMs (17.0 mg, 0.084 mmol, 1.0 equiv), \textit{p}-CF\textit{C}6\textit{H}4\textit{OMs} (20.2 mg, 0.084 mmol, 1.0 equiv), benzoxazole (10.0 mg, 0.084 mmol, 1.0 equiv), \textit{Pd(OAc)}2 (1.9 mg, 0.008 mmol, 0.10 equiv), dctype (7.1 mg, 0.017 mmol, 0.20 equiv), Cs\textsubscript{2}CO\textsubscript{3} (41 mg, 0.126 mmol, 1.5 equiv), CsOPiv (21.6 mg, 0.092 mmol, 1.1 equiv), and anhydrous toluene (0.34 mL) were combined in a 4 mL scintillation vial. The reaction mixture was allowed to stir at 120 °C for 17 h. The reaction mixture was allowed to cool to room temperature and then diluted with EtOAc. Gas chromatographic analysis of the crude reaction mixture showed 21% and 5% calibrated yields (against hexadecane as the internal standard) of 15-Ar and 15a respectively (15-Ar: 15a = 4.2:1).
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