Supporting Information
for
Cationic Pd(II)-catalyzed C–H activation/cross-coupling reactions
at room temperature: synthetic and mechanistic studies

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Experimental procedures and characterization of all new compounds

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For TLC analyses precoated Kieselgel 60 F<sub>254</sub> plates (Merck, 0.25 mm thick) were used; for column chromatography Silica Flash<sup>®</sup> P60 (SiliCycle, 40–63 μm) was used. Reactions were monitored using an Hewlett-Packard HP6890 gas chromatograph. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Varian UNITY INOVA 400 MHz NMR spectrometer. High resolution mass spectral analyses were obtained using a VG70 double-focusing magnetic sector instrument (VG Analytical) for EI and a PE Sciex QStar Pulsar quadrupole/TOF instrument (API) for ESI.

*Compounds 1a,1b, 1d, 1f, 1j, 1l, 1n, 3a–3hh, 5a–5c were previously reported<sup>1-5</sup>.

I. The synthesis of arylureas

Table 1. Starting materials.

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>ArNHNMe₂</td>
<td>OMe</td>
</tr>
<tr>
<td>1a</td>
<td>84%</td>
</tr>
<tr>
<td>1b</td>
<td>94%</td>
</tr>
<tr>
<td>1c</td>
<td>99%</td>
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<td>1f</td>
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<td>1i</td>
<td>87% (48h)</td>
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<td>1j</td>
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<td>1k</td>
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<td>1m</td>
<td>98%</td>
</tr>
<tr>
<td>1n</td>
<td>99%</td>
</tr>
<tr>
<td>1o</td>
<td>81%</td>
</tr>
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</table>

General procedure A [similar as described in ref. 3].

Anilines (1 mmol), N,N-dimethylcarbamoyl chloride (2 mmol), DMAP (1 mmol), and pyridine (4 mmol) were sequentially added under air to a reaction tube equipped with a stir bar and a septum. CH₂Cl₂ (2 mL) was added by syringe and the resulting mixture vigorously stirred for 36–48 h at ambient temperature. After this time, the contents of the flask were extracted with
EtOAc. The solution obtained was filtered through the plug of silica gel and anhydrous MgSO₄, and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting with hexane/EtOAc to afford the product.

Following the general procedure A, using aniline (0.11 mL, 1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), N,N-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and CH₂Cl₂ (2 mL), yielded the product 1a (164 mg, 84%): ¹H NMR (CDCl₃) δ: 3.02 (s, 6H), 3.79 (s, 3H), 6.36 (brs, 1H), 6.57 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 7.5 Hz, 1H), 7.14-7.19 (m, 2H); ¹³C NMR (CDCl₃), δ: 36.66, 55.46, 105.39, 109.22, 111.94, 129.63, 140.72, 155.80, 160.40; HRESIMS calcd. for C₁₀H₁₄N₂O₂Na (M+Na⁺): 217.0953; found 217.0948.

Following the general procedure A, using m-toluidine (1.07 mL, 10 mmol), DMAP (1.22 g, 10 mmol), pyridine (3.24 mL, 40 mmol), N,N-dimethylcarbamoyl chloride (1.84 mL, 20 mmol), and CH₂Cl₂ (20 mL), yielded the product 1b (1.68 g, 94%): ¹H NMR (CDCl₃) δ: 2.32 (s, 3H), 3.02 (s, 6H), 6.26 (brs, 1H), 6.83-6.85 (m, 1H), 7.14-7.26 (m, 3H); ¹³C NMR (CDCl₃), δ: 21.57, 36.50, 117.12, 120.80, 123.76, 128.65, 138.67, 139.33, 156.01; HRESIMS calcd. for C₁₀H₁₄N₂O₂Na (M+Na⁺): 201.1004; found 201.0999.

Following the general procedure A, using aniline (0.14 mL, 1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), N,N-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and CH₂Cl₂ (2 mL), yielded the product 1c (204 mg, 99%): ¹H NMR (CDCl₃) δ: 1.24 (d, J = 7.2 Hz, 6H), 2.87 (sept, J = 7.2 Hz, 1H), 3.04 (s, 6H), 6.26 (brs, 1H), 6.89-6.92 (m, 1H), 7.16-7.26 (m, 2H), 7.29 (s, 1H); ¹³C NMR (CDCl₃), δ: 24.12, 34.34, 36.64, 117.53, 118.20, 121.28, 128.89, 139.32, 149.93, 155.99; HRESIMS calcd. for C₁₂H₁₈N₂O₂Na (M+Na⁺): 229.1317; found 229.1314.
Following the general procedure A, using aniline (121 mg, 1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), N,N-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and CH$_2$Cl$_2$ (2 mL), yielded the product 1d (187 mg, 97%); $^1$H NMR (CDCl$_3$) δ: 2.20 (s, 3H), 2.23 (s, 3H), 3.02 (s, 6H), 6.18 (brs, 1H), 7.03 (d, $J$ = 8.4 Hz, 1H), 7.07 (dd, $J$ = 2.0 and 8.4 Hz, 1H), 7.20 (d, $J$ = 1.6 Hz, 1H); $^{13}$C NMR (CDCl$_3$), δ: 19.24, 20.08, 36.64, 117.65, 121.70, 130.02, 131.40, 137.04, 137.19, 156.12; HRESIMS calcd. for C$_{11}$H$_{16}$N$_2$ONa (M+Na$^+$): 215.1160; found 215.1157.

Following the general procedure A, using aniline (199 mg, 1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), N,N-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and CH$_2$Cl$_2$ (2 mL), yielded the product 1e (244 mg, 91%); $^1$H NMR (CDCl$_3$) δ: 3.04 (s, 6H), 5.06 (s, 2H), 6.29 (brs, 1H), 6.66 (dd, $J$ = 2.4 and 8.4 Hz, 1H), 6.84 (d, $J$ = 7.2 Hz, 1H), 7.17 (t, $J$ = 8.0 Hz, 1H), 7.28-7.44 (m, 6H); $^{13}$C NMR (CDCl$_3$), δ: 36.63, 70.10, 106.38, 109.97, 112.27, 127.67, 128.02, 128.68, 129.64, 137.28, 140.73, 155.79, 159.58; HRESIMS calcd. for C$_{16}$H$_{18}$N$_2$O$_2$Na (M+Na$^+$): 293.1266; found 293.1269.

Following the general procedure A, using aniline (153 mg, 1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), N,N-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and CH$_2$Cl$_2$ (2 mL), yielded the product 1f (216 mg, 96%); $^1$H NMR (CDCl$_3$) δ: 3.03 (s, 6H), 3.85 (s, 3H), 3.88 (s, 3H), 6.20 (brs, 1H), 6.69 (dd, $J$ = 2.8 and 8.8 Hz, 1H), 6.78 (d, $J$ = 8.8 Hz, 1H), 7.26 (d, $J$ = 2.8 Hz, 1H); $^{13}$C NMR (CDCl$_3$), δ: 36.54, 55.33, 95.51, 97.95, 141.39, 155.81, 160.97; HRESIMS calcd. for C$_{11}$H$_{16}$N$_2$O$_3$Na (M+Na$^+$): 247.1059; found 247.1057.

Following the general procedure A, using aniline (153 mg, 1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), N,N-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and CH$_2$Cl$_2$ (2 mL), yielded the product 1g (209 mg, 93%); $^1$H NMR (CDCl$_3$) δ: 3.02 (s, 6H), 3.76 (s, 6H), 6.16 (s, 1H), 6.31 (brs, 1H), 6.65 (s, 2H); $^{13}$C NMR (CDCl$_3$), δ: 36.48, 55.33, 95.51, 97.95, 141.39, 155.81, 160.97; HRESIMS calcd. for C$_{11}$H$_{16}$N$_2$O$_3$Na (M+Na$^+$): 247.1059; found 247.1058.
Following the general procedure A, using aniline (250 mg, 1.8 mmol), DMAP (1.8 mmol, 223 mg), pyridine (7.3 mmol, 0.6 mL), N,N-dimethylcarbamoyl chloride (3.6 mmol, 0.34 mL), and CH₂Cl₂ (3.6 mL), yielded the product 1h (344 mg, 90%): ¹H NMR (CDCl₃) δ: 2.15 (s, 3H), 3.03 (s, 6H), 3.83 (s, 3H), 6.26 (brs, 1H), 6.60 (dd, J = 2 and 8 Hz, 1H), 6.99 (d, J = 8 Hz, 1H), 7.28 (s, 1H); ¹³C NMR (CDCl₃), δ: 15.68, 36.43, 55.25, 103.17, 111.44, 120.84, 130.15, 138.46, 156.10, 157.84; HRESIMS calcd. for C₁₁H₁₆N₂O₂Na (M+Na⁺): 231.1109; found 231.1107.

Following the general procedure A, using aniline (0.14 mL, 1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), N,N-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and CH₂Cl₂ (2 mL), yielded the product 1i (150 mg, 67%): ¹H NMR (CDCl₃) δ: 3.05 (s, 6H), 3.855 (s, 3H), 3.859 (s, 3H), 6.57 (dd, J = 1.2 and 8.4 Hz, 1H), 7.00 (t, J = 8.4 Hz, 1H), 7.19 (brs, 1H), 7.81 (dd, J = 1.2 and 8.4 Hz, 1H); ¹³C NMR (CDCl₃), δ: 36.21, 55.67, 60.29, 105.74, 111.59, 124.02, 133.52, 136.89, 151.77, 155.25; HRESIMS calcd. for C₁₁H₁₆N₂O₃Na (M+Na⁺): 247.1059; found 247.1057.

Following the general procedure A, using aniline (123 mg, 1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), N,N-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and CH₂Cl₂ (2 mL), yielded the product 1j (163 mg, 84%): ¹H NMR (CDCl₃) δ: 3.01 (s, 6H), 6.19 (brs, 1H), 6.83 (d, J = 9.2 Hz, 2H), 7.26 (d, J = 9.2 Hz, 2H); ¹³C NMR (CDCl₃), δ: 36.21, 55.67, 60.29, 105.74, 111.59, 124.02, 133.52, 136.89, 151.77, 155.25; HRESIMS calcd. for C₁₀H₁₄N₂O₂Na (M+Na⁺): 217.0953; found 217.0947.

Following the general procedure A, using m-toluidine (0.91 mL, 10 mmol), DMAP (1.22 g, 10 mmol), pyridine (3.24 mL, 40 mmol), N,N-dimethylcarbamoyl chloride (1.84 mL, 20 mmol), and CH₂Cl₂ (20 mL), yielded the product 1k (1.46 g, 89%): ¹H NMR (CDCl₃) δ: 3.03 (s, 6H), 6.32 (brs, 1H), 7.02 (t, J = 7.2 Hz, 1H), 7.26-7.31 (m, 2H), 7.35-7.38 (m, 2H); ¹³C NMR (CDCl₃), δ: 36.56, 120.10, 122.99, 128.89, 139.44, 155.97; HRESIMS calcd. for C₁₀H₁₄N₂O₂Na (M+Na⁺): 187.0847; found 187.0839.
Following the general procedure A, using aniline (0.11 mL, 1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), N,N-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and CH$_2$Cl$_2$ (2 mL), yielded the product 1l (138 mg, 77%): \textsuperscript{1}H NMR (CDCl$_3$) δ: 2.25 (s, 3H), 3.04 (s, 6H), 6.12 (brs, 1H), 6.98-7.02 (m, 1H), 7.14-7.21 (m, 2H), 7.71 (d, $J = 8$ Hz, 1H); \textsuperscript{13}C NMR (CDCl$_3$), δ: 17.94, 36.64, 122.70, 123.93, 126.91, 128.50, 130.41, 137.39, 156.10; HRESIMS calcd. for C$_{10}$H$_{14}$N$_2$ONa (M+Na$^+$): 201.1004; found 201.1000.

Following the general procedure A, using aniline (135 mg, 1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), N,N-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and CH$_2$Cl$_2$ (2 mL), yielded the product 1m (201 mg, 98%): \textsuperscript{1}H NMR (CDCl$_3$) δ: 2.60 (s, 3H), 3.06 (s, 6H), 6.46 (brs, 1H), 7.39 (t, $J = 8$ Hz, 1H), 7.61 (d, $J = 8$ Hz, 1H), 7.76 (d, $J = 8$ Hz, 1H), 7.89 (s, 1H); \textsuperscript{13}C NMR (CDCl$_3$), δ: 26.83, 36.62, 119.43, 122.91, 124.77, 129.18, 137.73, 140.10, 155.89, 198.47; HRESIMS calcd. for C$_{11}$H$_{14}$N$_2$O$_2$Na (M+Na$^+$): 229.0953; found 229.0948.

Following the general procedure A, using aniline (0.11 mL, 1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), N,N-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and CH$_2$Cl$_2$ (2 mL), yielded the product 1n (189 mg, 99%): \textsuperscript{1}H NMR (CDCl$_3$) δ: 2.93 (s, 6H), 3.02 (t, $J = 8$ Hz, 2H), 3.90 (t, $J = 8$ Hz, 2H), 6.87-6.94 (m, 2H), 7.11-7.18 (m, 2H); \textsuperscript{13}C NMR (CDCl$_3$), δ: 28.15, 38.17, 50.37, 113.36, 121.34, 124.84, 127.01, 131.40, 144.37, 160.30; HRESIMS calcd. for C$_{11}$H$_{14}$N$_2$ONa (M+Na$^+$): 213.1004; found 213.0997.

Following the general procedure A, using aniline (1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), N,N-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and CH$_2$Cl$_2$ (2 mL), yielded the product 1q (81%): \textsuperscript{1}H NMR (acetone-$d_6$) δ: 2.99 (s, 6H), 3.81 (s, 3H), 3.84 (s, 3H), 7.09 (dd, $J = 2.4$ and 8.7 Hz, 1H), 7.18 (d, $J = 8.7$ Hz, 1H), 7.51 (d, $J = 2.4$ Hz, 1H), 7.89 (brs, 1H); \textsuperscript{13}C NMR (acetone-$d_6$) δ: 35.57, 56.25, 105.02, 112.78, 115.07, 130.15, 142.08, 155.78, 156.44; HRESIMS calcd. for C$_{10}$H$_{13}$N$_2$O$_2$Na (M+Na$^+$): 251.0563; found 251.0569.
Following the general procedure A, using aniline (1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), \(N,N\)-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and \(\text{CH}_2\text{Cl}_2\) (2 mL), yielded the product 1q (79%); 
\[\text{1H NMR (acetone-}\text{d}_6\text{): } \delta: 2.99 (s, 6H), 7.08-7.18 (m, 2H), 7.48 (d, \text{ } J = 8.0 \text{ Hz}, 1H), 7.90-7.91 (m, 2H).\]
\[\text{13C NMR (acetone-}\text{d}_6\text{): } \delta: 36.52, 118.77, 122.47, 122.84, 125.16, 130.88, 143.53, 156.22; \text{HRESIMS calcd. for } \text{C}_9\text{H}_{11}\text{N}_2\text{ONa (M+Na}^+\text{): 264.9952; found 264.9953.}\]

Following the general procedure A, using aniline (1 mmol), DMAP (122 mg, 1 mmol), pyridine (0.32 mL, 4 mmol), \(N,N\)-dimethylcarbamoyl chloride (0.18 mL, 2 mmol), and \(\text{CH}_2\text{Cl}_2\) (2 mL), yielded the product 1q (90%); 
\[\text{1H NMR (CDCl}_3\text{): } \delta: 0.80 (t, \text{ } J = 7.6 \text{ Hz}, 3H), 1.29 (d, \text{ } J = 6.8 \text{ Hz}, 3H), 1.56 (m, 2H), 2.53 (m, 1H), 3.03 (s, 6H), 6.22 (brs, 1H), 7.09 (d, \text{ } J = 8.4 \text{ Hz}, 1H), 7.28 (d, \text{ } J = 8.4 \text{ Hz}, 1H); \text{13C NMR (CDCl}_3\text{): } \delta: 12.13, 21.86, 31.11, 36.25, 40.93, 120.52, 126.98, 137.13, 141.96, 156.28; \text{HRESIMS calcd. for } \text{C}_{13}\text{H}_{20}\text{N}_2\text{ONa (M+Na}^+\text{): 243.1473; found 243.1471.}\]

II. C–H arylations with aryl iodide

General procedure B [analogous as described in ref 3].
Aryl urea 1 (0.25 mmol), aryl iodide 2 (0.5 mmol), AgOAc (0.5 mmol, 83 mg), and Pd(OAc)\(_2\) (0.025 mmol, 5.6 mg) were sequentially added under air to a reaction tube equipped with a stir bar and a septum. An aqueous solution containing the surfactant (1.0 mL, 2 wt %), and 48 wt % HBF\(_4\) (1.25 mmol, 0.16 mL) was added by syringe and the resulting mixture vigorously stirred for 20 h at ambient temperature. After this time, the contents of the flask were quenched with aqueous NaHCO\(_3\) and extracted with EtOAc. The solution obtained was filtered through the plug of silica gel and anhydrous MgSO\(_4\), and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting with hexane/EtOAc to afford the product. All products are reported previously (See also section III).\(^1\)^\(^2\)

Following the general procedure above, using 1d (48 mg, 0.25 mmol), \textit{m}-tolyl-I (109 mg, 0.50 mmol), AgOAc (0.5 mmol, 83 mg), and Pd(OAc)\(_2\) (0.025 mmol, 5.6 mg), 2 wt % Brij 35 solution (1.0 mL) 48 wt % aqueous HBF\(_4\) (1.25 mmol, 0.16 mL), the product 3r was obtained (56 mg, 79%); 
\[\text{1H NMR (CDCl}_3\text{): } \delta: 2.23 (s, 3H), 2.29 (s, 3H), 2.39 (s, 3H), 2.81 (s, 6H), 6.44 (brs, 1H), 6.96 (s, 1H), 7.15-7.17 (m, 3H), 7.33 (dd, \text{ } J = 7.2 \text{ and 8.2 Hz}, 1H), 7.94 (s, 1H).\]
Following the general procedure above, using 1q (55 mg, 0.25 mmol), p-An-I (117 mg, 0.50 mmol), AgOAc (0.5 mmol, 83 mg), and Pd(OAc)$_2$ (0.025 mmol, 5.6 mg), 2 wt % Brij 35 solution (1.0 mL) 48 wt % aqueous HBF$_4$ (1.25 mmol, 0.16 mL), the product 3cc was obtained (58 mg, 71%): $^1$H NMR (CDCl$_3$) $\delta$: 0.83 (t, $J = 7.4$ Hz, 3H), 1.22 (t, $J = 6.9$ Hz, 3H), 1.54-1.61 (m, 2H), 2.55 (sext, $J = 6.9$ Hz, 1H), 2.81 (s, 6H), 3.85 (s, 3H), 6.43 (brs, 1H), 6.98 (brs, 1H), 7.00 (d, $J = 8.4$ Hz, 2H), 7.13 (dd, $J = 2.1$ and 8.4 Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 2H), 8.01 (d, $J = 8.4$ Hz, 1H).

III. C–H Suzuki–Miyaura

General procedure C [analogous as described in ref 4].

Arylurea 1 (0.25 mmol), arylboronic acid 2 (1.5–3 equiv), 1,4-benzoquinone (2–5 equiv), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.025 mmol, 11 mg) were sequentially added in air to a reaction tube equipped with a stir bar and a septum. EtOAc was added by syringe and the resulting mixture vigorously stirred for 20 h at ambient temperature. After this time, the contents of the flask were quenched with aqueous NaOH (to remove 1,4-hydroxybenzene) and extracted with EtOAc. The solution obtained was filtered through the plug of silica gel and anhydrous MgSO$_4$, and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting with hexane/EtOAc to afford the product. All products are reported previously except 3ii.

Following the general procedure above, using arylurea (53 mg, 0.25 mmol), $p$-tolylB(OH)$_2$ (102 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3ii (73 mg, 97%): $^1$H NMR (CDCl$_3$) $\delta$: 2.41 (s, 3H), 2.91 (s, 6H), 6.02 (brs, 1H), 7.25 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.8$ Hz, 2H), 7.43 (d, $J = 8.1$ Hz, 1H), 7.46-7.56 (m, 2H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.83 (d, $J = 8.8$ Hz, 1H), 7.99 (d, $J = 8.8$ Hz, 1H). $^{13}$C NMR (CDCl$_3$) $\delta$: 20.85, 36.18, 123.96, 125.45, 126.05, 126.38, 127.29, 127.50, 128.69, 128.81, 130.80, 133.25, 134.71, 136.38, 136.73, 157.26; HRESIMS calcd. for C$_{20}$H$_{20}$N$_2$ONa (M+Na$^+$): 327.1473; found 327.1479.

Following the general procedure above, using 1b (44 mg, 0.25 mmol), PhB(OH)$_2$ (96 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3a (61 mg, 96%): $^1$H NMR (CDCl$_3$) $\delta$: 2.38 (s, 3H), 2.79 (s, 6H), 6.48 (brs,
1H), 6.90 (dd, J = 1.0 and 7.7 Hz, 1H), 7.08 (d, J = 7.7 Hz, 1H), 7.35-7.38 (m, 3H), 7.43-7.47 (m, 2H), 8.02 (brs, 1H).

Following the general procedure above, using 1b (44 mg, 0.25 mmol), p-AnB(OH)₂ (114 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3b (53 mg, 75%); ¹H NMR (CDCl₃): δ: 2.37 (s, 3H), 2.81 (s, 6H), 3.84 (s, 3H), 6.50 (brs, 1H), 6.87 (dd, J = 1.0 and 7.7 Hz, 1H), 6.98 (d, J = 8.7 Hz, 2H), 7.05 (d, J = 7.7 Hz, 1H), 7.28 (d, J = 8.7 Hz, 2H), 8.01 (brs, 1H).

Following the general procedure above, using 1b (44 mg, 0.25 mmol), p-tolylB(OH)₂ (102 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3c (60 mg, 90%); ¹H NMR (CDCl₃): δ: 2.38 (s, 3H), 2.40 (s, 3H), 2.81 (s, 6H), 6.52 (brs, 1H), 6.88 (dd, J = 1.0 and 7.7 Hz, 1H), 7.07 (d, J = 7.7 Hz, 1H), 7.26 (brs, 4H), 8.02 (s, 1H).

Following the general procedure above, using 1b (44 mg, 0.25 mmol), p-MeCO₂C₆H₄B(OH)₂ (135 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3d (73 mg, 94%); ¹H NMR (CDCl₃): δ: 2.38 (s, 3H), 2.82 (s, 6H), 3.94 (s, 3H), 6.37 (brs, 1H), 6.92 (dd, J = 1.2 and 8.4 Hz, 1H), 7.09 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 7.8 Hz, 2H), 7.95 (brs, 1H), 8.12 (d, J = 8.4 Hz, 2H).

Following the general procedure above, using 1b (44 mg, 0.25 mmol), p-AcC₆H₄B(OH)₂ (123 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3e (63 mg, 86%); ¹H NMR (CDCl₃): δ: 2.38 (s, 3H), 2.64 (s, 3H), 2.83 (s,
Following the general procedure above, using 1b (44 mg, 0.25 mmol), p-ClC₆H₄B(OH)₂ (117 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3f (67 mg, 94%); ¹H NMR (CDCl₃) δ:  2.37 (s, 3H), 2.83 (s, 6H), 6.33 (brs, 1H), 6.91 (d, J = 7.7 Hz, 1H), 7.05 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.93 (brs, 1H).

Following the general procedure above, using 1b (44 mg, 0.25 mmol), 2,5-(MeO)₂C₆H₃B(OH)₂ (136 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3g (77 mg, 98%); ¹H NMR (CDCl₃) δ:  2.38 (s, 3H), 2.83 (s, 6H), 3.74 (s, 3H), 3.77 (s, 3H), 6.79 (d, J = 3.0 Hz, 1H), 6.89 (dd, J = 3.0 and 8.9 Hz, 1H), 6.89-6.90 (m, 2H), 7.03 (brs, 1H), 7.10 (d, J = 7.8 Hz, 1H), 7.78 (brs, 1H).

Following the general procedure above, using 1a (48 mg, 0.25 mmol), p-AnB(OH)₂ (114 mg, 0.75 mmol), BQ (0.5 mmol, 54 mg), and [Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3h (60 mg, 81%); ¹H NMR (CDCl₃) δ:  2.81 (s, 6H), 3.84 (s, 6H), 6.60 (brs, 1H), 6.61 (dd, J = 2.6 and 8.3 Hz, 1H), 6.98 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 8.3 Hz, 1H), 7.27 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 2.6 Hz, 1H).

Following the general procedure above, using 1a (48 mg, 0.25 mmol), p-tolylB(OH)₂ (102 mg, 0.75 mmol), BQ (0.5 mmol, 54 mg), and [Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3i (61 mg, 87%); ¹H NMR (CDCl₃) δ:  2.40 (s, 3H), 2.81 (s, 6H), 3.85 (s, 3H), 6.63 (dd, J = 2.7 and 8.5 Hz, 1H), 6.64 (brs, 1H), 7.02 (d, J = 8.5 Hz, 1H), 7.25 (brs, 4H), 7.94 (d, J = 2.7 Hz, 1H).
Following the general procedure above, using 1a (48 mg, 0.25 mmol), PhB(OH)$_2$ (96 mg, 0.75 mmol), BQ (0.5 mmol, 54 mg), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3j (62 mg, 70%); $^1$H NMR (CDCl$_3$) $\delta$: 2.96 (s, 6H), 3.85 (s, 3H), 6.60 (brs, 1H), 6.63 (dd, $J=2.6$ and 8.4 Hz, 1H), 7.08 (d, $J=8.6$ Hz, 1H), 7.34-7.38 (m, 3H), 7.43-7.47 (m, 2H), 7.94 (d, $J=2.6$ Hz, 1H).

Following the general procedure above, using 1a (48 mg, 0.25 mmol), 2d (135 mg, 0.75 mmol), BQ (0.5 mmol, 54 mg), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3k (60 mg, 70%); $^1$H NMR (CDCl$_3$) $\delta$: 1.41 (t, $J=7.1$ Hz, 3H), 2.82 (s, 6H), 3.84 (s, 3H), 4.39 (q, $J=7.1$ Hz, 2H), 6.49 (brs, 1H), 6.65 (dd, $J=2.6$ and 8.4 Hz, 1H), 7.08 (d, $J=8.4$ Hz, 1H), 7.44 (d, $J=8.4$ Hz, 2H), 7.88 (d, $J=2.6$ Hz, 1H), 8.11 (d, $J=8.4$ Hz, 2H).

Following the general procedure above, using 1o (57 mg, 0.25 mmol), p-tolylB(OH)$_2$ (102 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3l (77 mg, 97%); $^1$H NMR (CDCl$_3$) $\delta$: 2.40 (s, 3H), 2.81 (s, 6H), 5.11 (s, 2H), 6.65 (brs, 1H), 6.70 (dd, $J=2.6$ and 8.4 Hz, 1H), 7.08 (d, $J=8.4$ Hz, 1H), 7.26 (brs, 4H), 7.32 (d, $J=7.2$ Hz, 1H), 7.39 (t, $J=7.2$ Hz, 2H), 7.47 (d, $J=7.2$ Hz, 2H), 8.05 (d, $J=2.6$ Hz, 1H).
Following the general procedure above, using arylurea (63 mg, 0.25 mmol), \( p\)-tolylB(OH)\(_2\) (102 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)\(_4\)](BF\(_4\))\(_2\) (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3n (69 mg, 80%); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) : 2.38 (s, 3H), 2.79 (s, 6H), 3.98 (s, 2H), 6.54 (brs, 1H), 6.85 (dd, \( J = 1.7 \) and 7.8 Hz, 1H), 7.07 (d, \( J = 7.8 \) Hz, 1H), 7.14-7.19 (m, 1H), 7.24-7.27 (m, 8H), 8.11 (d, \( J = 1.7 \) Hz, 1H).

Following the general procedure above, using 1c (51 mg, 0.25 mmol), \( p\)-tolylB(OH)\(_2\) (102 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)\(_4\)](BF\(_4\))\(_2\) (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3o (66 mg, 89%); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) : 1.29 (t, \( J = 7.0 \) Hz, 6H), 2.40 (s, 3H), 2.82 (s, 6H), 2.95 (sept, \( J = 7.0 \) Hz, 1H), 6.57 (brs, 1H), 6.93 (dd, \( J = 1.7 \) and 8.7 Hz, 1H), 7.11 (d, \( J = 8.7 \) Hz, 1H), 7.26 (brs, 4H), 8.10 (d, \( J = 1.7 \) Hz, 1H).

Following the general procedure above, using 1d (48 mg, 0.25 mmol), \( p\)-AnB(OH)\(_2\) (114 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)\(_4\)](BF\(_4\))\(_2\) (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3p (64 mg, 86%); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) : 2.22 (s, 3H), 2.28 (s, 3H), 2.39 (s, 3H), 2.81 (s, 6H), 3.85 (s, 3H), 6.38 (brs, 1H), 6.95 (brs, 1H), 6.98 (dd, \( J = 8.8 \) Hz, 2H), 7.28 (d, \( J = 8.8 \) Hz, 2H), 7.91 (s, 1H).

Following the general procedure above, using 1d (48 mg, 0.25 mmol), \( p\)-tolylB(OH)\(_2\) (102 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)\(_4\)](BF\(_4\))\(_2\) (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3q (67 mg, 96%); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) : 2.22 (s, 3H), 2.29 (s, 3H), 2.39 (s, 3H), 2.81 (s, 6H), 6.42 (brs, 1H), 6.96 (s, 1H), 7.25 (brs, 4H), 7.92 (s, 1H).

Following the general procedure above, using 1d (48 mg, 0.25 mmol), PhB(OH)\(_2\) (96 mg, 0.75 mol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)\(_4\)](BF\(_4\))\(_2\) (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3r (67 mg, 96%); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) : 2.22 (s, 3H), 2.29 (s, 3H), 2.39 (s, 3H), 2.81 (s, 6H), 6.42 (brs, 1H), 6.96 (s, 1H), 7.25 (brs, 4H), 7.92 (s, 1H).
mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)_4](BF_4)_2 (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3s (64 mg, 95%); 1H NMR (CDCl_3) δ: 2.23 (s, 3H), 2.30 (s, 3H), 2.80 (s, 6H), 6.37 (brs, 1H), 6.98 (s, 1H), 7.34-7.38 (m, 3H), 7.43-7.47 (m, 2H), 7.93 (s, 1H).

Following the general procedure above, using 1l (44 mg, 0.25 mmol), p-tolylB(OH)_2 (102 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)_4](BF_4)_2 (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3t (43 mg, 65%); 1H NMR (CDCl_3) δ: 2.32 (s, 3H), 2.39 (s, 3H), 2.85 (s, 6H), 5.71 (brs, 1H), 7.12 (dd, J = 1.8 and 7.5 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.20-7.26 (m, 5H).

Following the general procedure above, using 1h (52 mg, 0.25 mmol), p-tolylB(OH)_2 (102 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)_4](BF_4)_2 (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3u (60 mg, 80%); 1H NMR (CDCl_3) δ: 2.18 (s, 3H), 2.39 (s, 3H), 2.82 (s, 6H), 3.89 (s, 3H), 6.59 (brs, 1H), 6.94 (s, 1H), 7.24 (brs, 4H), 7.87 (s, 1H).

Following the general procedure above, using 1n (47 mg, 0.25 mmol), PhB(OH)_2 (96 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)_4](BF_4)_2 (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3v (60 mg, 90%); 1H NMR (CDCl_3) δ: 2.51 (s, 6H), 3.07 (t, J = 8.0 Hz, 2H), 3.94 (t, J = 8.0 Hz, 2H), 6.99 (t, J = 7.8 Hz, 1H), 7.12 (t, J = 8.1 Hz, 2H), 7.20-7.24 (m, 2H), 7.32 (d, J = 7.8 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H).

Following the general procedure above, using 1n (47 mg, 0.25 mmol), p-tolylB(OH)_2 (102 mg, 0.75 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)_4](BF_4)_2 (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3w (62 mg, 89%); 1H NMR (CDCl_3) δ: 2.34 (s, 3H), 2.57 (s, 6H), 3.09 (t, J = 7.9 Hz, 2H), 3.96 (t, J = 7.9 Hz, 2H), 6.99 (t, J = 7.8 Hz, 1H), 6.98-7.02 (m, 4H), 7.26 (brs, 1H), 7.32 (d, J = 8.0 Hz, 2H).
Following the general procedure above, using 1j (48 mg, 0.25 mmol), p-tolylB(OH)$_2$ (51 mg, 0.375 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3aa (58 mg, 82%). $^1$H NMR (CDCl$_3$) $\delta$: 2.39 (s, 3H), 2.80 (s, 6H), 3.78 (s, 3H), 6.29 (brs, 1H), 6.75 (d, $J = 3.0$ Hz, 1H), 6.87 (dd, $J = 3.0$ and 9.0 Hz, 1H), 7.28 (brs, 4H), 7.93 (d, $J = 9.0$ Hz, 1H).

Following the general procedure above, using 1j (48 mg, 0.25 mmol), PhB(OH)$_2$ (46 mg, 0.375 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3bb (60 mg, 89%). $^1$H NMR (CDCl$_3$) $\delta$: 2.79 (s, 6H), 3.79 (s, 3H), 6.24 (brs, 1H), 6.77 (d, $J = 3.0$ Hz, 1H), 6.89 (dd, $J = 3.0$ and 9.0 Hz, 1H), 7.26-7.40 (m, 3H), 7.44-7.48 (m, 2H), 7.93 (d, $J = 9.0$ Hz, 1H).

Following the general procedure above, using 1q (55 mg, 0.25 mmol), p-tolylB(OH)$_2$ (51 mg, 0.375 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3dd (68 mg, 88%). $^1$H NMR (CDCl$_3$) $\delta$: 0.83 (t, $J = 7.3$ Hz, 3H), 1.22 (t, $J = 7.0$ Hz, 3H), 1.52-1.61 (m, 2H), 2.40 (s, 3H), 2.56 (sext, $J = 7.0$ Hz, 1H), 2.81 (s, 6H), 6.47 (brs, 1H), 6.99 (d, $J = 2.2$ Hz, 1H), 7.13 (dd, $J = 2.2$ and 8.4 Hz, 1H), 7.25-7.30 (m, 4H), 8.01 (d, $J = 8.4$ Hz, 1H).

Following the general procedure above, using 1q (55 mg, 0.25 mmol), PhB(OH)$_2$ (46 mg, 0.375 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3ee (59 mg, 80%). $^1$H NMR (CDCl$_3$) $\delta$: 0.83 (t, $J = 7.5$ Hz, 3H), 1.22 (t, $J = 6.9$ Hz, 3H), 1.56 (sept, $J = 7.5$ Hz, 2H), 2.54-2.62 (m, 1H), 2.79 (s, 6H), 6.42 (brs, 1H), 7.00 (d, $J = 1.9$ Hz, 1H), 7.15 (dd, $J = 1.9$ and 8.5 Hz, 1H), 7.35-7.40 (m, 3H), 7.44-7.48 (m, 2H), 8.02 (t, $J = 8.5$ Hz, 1H).
Following the general procedure above, using 1k (41 mg, 0.25 mmol), p-tolylB(OH)$_2$ (51 mg, 0.375 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3gg (50 mg, 78%): $^1$H NMR (CDCl$_3$) $\delta$: 2.40 (s, 3H), 2.80 (s, 6H), 6.55 (brs, 1H), 7.05 (t, $J=7.4$ Hz, 1H), 7.17 (d, $J=7.4$ Hz, 1H), 7.27 (brs, 4H), 7.31 (t, $J=8.3$ Hz, 1H), 8.17 (d, $J=8.3$ Hz, 1H).

Following the general procedure above, using 1k (41 mg, 0.25 mmol), PhB(OH)$_2$ (46 mg, 0.375 mmol), BQ (1.25 mmol, 135 mg), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.025 mmol, 11 mg), EtOAc (1.0 mL), yielded the product 3hh (50 mg, 83%): $^1$H NMR (CDCl$_3$) $\delta$: 2.78 (s, 6H), 6.51 (brs, 1H), 7.06 (dt, $J=1.2$ and 7.5 Hz, 1H), 7.19 (dd, $J=1.6$ and 7.5 Hz, 1H), 7.31-7.40 (m, 4H), 7.45-7.49 (m, 2H), 8.16 (dd, $J=1.2$ and 7.4 Hz, 1H).

**IV. Fujiwara–Moritani reactions**

**General procedure D in water [analogous as described in ref 5].**

 Arylurea 1 (0.25 mmol), acrylate ester (0.5 mmol), 1,4-benzoquinone (0.25 mmol, 27 mg), AgOAc (0.5 mmol, 85 mg), and Pd(OAc)$_2$ (0.025 mmol, 5.6 mg) were sequentially added under air to a reaction tube equipped with a stir bar and a septum. An aqueous solution containing the surfactant (1.0 mL, 2 wt %), and 48 wt % HBF$_4$ (1.25 mmol, 0.16 mL) was added by syringe and the resulting mixture vigorously stirred for 20 h at ambient temperature. After this time, the contents of the flask were quenched with aqueous NaHCO$_3$ and extracted with EtOAc. The solution obtained was filtered through the plug of silica gel and anhydrous MgSO$_4$, and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting with hexane/EtOAc to afford the product. All products are reported except 5d–5h.$^3$

Following the general procedure above, using 1a (48 mg, 0.25 mmol), acrylate ester (92 mg, 0.50 mmol), 1,4-benzoquinone (0.25 mmol, 27 mg), AgNO$_3$ (0.5 mmol, 85 mg), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.025 mmol, 11 mg), 2 wt % PTS solution (1.0 mL), yielded the product 5a (69 mg, 74%), $^1$H NMR (CDCl$_3$) $\delta$: 0.90 (t, $J=6.8$ Hz, 3H), 0.91 (t, $J=7.5$ Hz, 3H), 1.25-1.45 (m, 8H), 1.60-1.67 (m,
1H), 3.06 (s, 6H), 3.82 (s, 3H), 4.08 (dd, J = 6.0 and 11 Hz, 1H), 4.11 (dd, J = 5.7 and 11 Hz, 1H),
6.28 (d, J = 15.7 Hz, 1H), 6.45 (brs, 1H), 6.67 (dd, J = 2.6 and 8.7 Hz, 1H), 7.40 (d, J = 2.5 Hz, 1H),
7.46 (d, J = 8.7 Hz, 1H), 7.75 (d, J = 15.7 Hz, 1H).

Following the general procedure above, using 1a (48 mg, 0.25 mmol), acrylate ester (120 mg,
0.50 mmol), 1,4-benzoquinone (0.25 mmol, 27 mg), AgNO₃ (0.5 mmol, 85 mg), and
[Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), 2 wt % PTS solution (1.0 mL), yielded the product 5b
(71 mg, 76%), ¹H NMR (CDCl₃) δ: 0.88 (t, J = 7.2 Hz, 3H), 1.26-1.49 (m, 12H), 1.55-1.61 (m, 1H),
3.07 (s, 6H), 3.82 (s, 3H), 5.00 (sext, J = 6.2 Hz, 1H), 6.28 (d, J = 15.7 Hz, 1H), 6.43 (brs, 1H), 6.67
(dd, J = 2.6 and 8.7 Hz, 1H), 7.41 (d, J = 2.6 Hz, 1H), 7.45 (d, J = 8.7 Hz, 1H), 7.75 (d, J = 15.7 Hz, 1H).

Following the general procedure above, using 1g (56 mg, 0.25 mmol), acrylate ester (106 mg,
0.50 mmol), 1,4-benzoquinone (0.25 mmol, 27 mg), AgNO₃ (0.5 mmol, 85 mg), and
[Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), 2 wt % PTS solution (1.0 mL), yielded the product 5c
(86 mg, 80%), ¹H NMR (CDCl₃) δ: 0.86 (d, J = 6.5 Hz, 6H), 0.92 (d, J = 6.5 Hz, 3H), 1.11-1.17 (m, 3H),
1.31 (d, J = 6.8 Hz, 6H), 1.23-1.33 (m, 3H), 1.45-1.54 (m, 3H), 1.69-1.77 (m, 1H), 2.57 (sept, J =
6.8 Hz, 1H), 3.83 (s, 3H), 3.84 (s, 3H), 4.19-4.25 (m, 2H), 6.25 (s, 1H), 6.48 (d, J = 16.2 Hz, 1H),
7.35 (s, 1H), 7.38 (brs, 1H), 7.75 (d, J = 16.2 Hz, 1H).

Following the general procedure above, using using 1b (44 mg, 0.25 mmol), acrylate ester (92 mg,
0.50 mmol), 1,4-benzoquinone (0.25 mmol, 27 mg), AgOAc (0.5 mmol, 83 mg), and
[Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), 2 wt % Brij 35 solution (1.0 mL), yielded the product 5d
(77 mg, 86%), ¹H NMR (CDCl₃) δ: 0.89-0.92 (m, 6H), 1.25-1.43 (m, 8H), 1.54-1.64 (m, 1H), 2.33 (s, 3H),
3.03 (s, 6H), 4.03 (dd, J = 6.0 and 11.0 Hz, 1H), 4.07 (dd, J = 5.7 and 11.0 Hz, 1H), 6.34 (d, J =
15.8 Hz, 1H), 6.46 (brs, 1H), 6.94 (d, J = 8.1 Hz, 1H), 7.42-7.44 (m, 2H), 7.75 (d, J = 15.8 Hz, 1H).
¹³C NMR (CDCl₃) δ: 11.16, 14.19, 21.63, 23.11, 29.07, 30.58, 36.64, 38.95, 67.04, 118.89, 124.94,
125.75, 125.87, 126.94, 137.60, 139.83, 141.42, 156.12, 167.41; HRESIMS calcd. for
C₂₁H₂₅N₂O₃Na (M+Na⁺): 383.2310; found 383.2311.
Following the general procedure above, using using 1a (48 mg, 0.25 mmol), acrylate ester (81 mg, 0.50 mmol), 1,4-benzoquinone (0.25 mmol, 27 mg), AgOAc (0.5 mmol, 83 mg), and [Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), 2 wt % Brij 35 solution (1.0 mL), yielded the product 5e (88 mg, 99%), ¹H NMR (CDCl₃) δ: 2.99 (s, 6H), 3.78 (s, 3H), 5.18 (s, 2H), 6.29 (d, J = 15.7 Hz, 1H), 6.60 (brs, 1H), 6.65 (dd, J = 2.6 and 8.8 Hz, 1H), 7.26 (d, J = 2.6 Hz, 1H), 7.31-7.37 (m, 5H), 7.42 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 15.9 Hz, 1H). ¹³C NMR (CDCl₃) δ: 36.63, 55.55, 66.37, 109.11, 111.96, 116.48, 119.71, 128.25, 128.31, 128.53, 128.69, 136.24, 139.63, 140.19, 155.96, 161.91, 167.19; HRESIMS calcd. for C₂₀H₂₂N₂O₄Na (M+Na⁺): 377.1477; found 377.1478.

Following the general procedure above, using using 1h (52 mg, 0.25 mmol), acrylate ester (43 mg, 0.50 mmol), 1,4-benzoquinone (0.25 mmol, 27 mg), AgOAc (0.5 mmol, 83 mg), and [Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), 2 wt % Brij 35 solution (1.0 mL), yielded the product 5f (65 mg, 89%), ¹H NMR (CDCl₃) δ: 2.15 (s, 3H), 3.04 (s, 6H), 3.74 (s, 3H), 3.81 (s, 3H), 6.24 (d, J = 15.8 Hz, 1H), 6.58 (brs, 1H), 7.18 (s, 1H), 7.26 (s, 1H), 7.74 (d, J = 15.8 Hz, 1H). ¹³C NMR (CDCl₃) δ: 15.94, 36.66, 51.69, 55.59, 106.68, 116.05, 119.04, 123.50, 128.53, 137.43, 139.89, 156.15, 159.96, 167.96; HRESIMS calcd. for C₁₅H₂₀N₂O₄Na (M+Na⁺): 315.1321; found 315.1322.

Following the general procedure above, using 1a (48 mg, 0.25 mmol), acrylamide (80 mg, 0.50 mmol), 1,4-benzoquinone (0.25 mmol, 27 mg), AgOAc (0.5 mmol, 83 mg), and [Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), 2 wt % Brij 35 solution (1.0 mL), yielded the product 5g (73 mg, 83%), ¹H NMR (CDCl₃) δ: 3.05 (s, 6H), 3.28 (s, 3H), 3.76 (s, 3H), 6.17 (d, J = 15.3 Hz, 1H), 6.52 (dd, J = 2.6 and 8.8 Hz, 1H), 6.87 (brs, 1H), 7.07 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 7.2 Hz, 1H), 7.33-7.43 (m, 4H), 7.77 (d, J = 15.3 Hz, 1H). ¹³C NMR (CDCl₃) δ: 36.69, 37.56, 55.50, 108.19, 111.59, 117.75, 119.58, 127.40, 127.77, 127.95, 129.76, 136.56, 139.40, 143.57, 155.87, 161.30, 166.42; HRESIMS calcd. for C₂₀H₂₃N₃O₄Na (M+Na⁺): 376.1637; found 376.1639.
Following the general procedure above, using 1a (48 mg, 0.25 mmol), acrylamide (123 mg, 0.50 mmol), 1,4-benzoquinone (0.25 mmol, 27 mg), AgOAc (0.5 mmol, 83 mg), and [Pd(MeCN)₄](BF₄)₂ (0.025 mmol, 11 mg), 2 wt % Brij 35 solution (1.0 mL), yielded the product 5h (75 mg, 69%), ¹H NMR (CDCl₃) δ: 1.21 (t, J = 7.2 Hz, 3H), 3.02 (s, 6H), 3.11 (d, J = 6.0 Hz, 2H), 3.78 (s, 3H), 4.15 (q, J = 7.1 Hz, 2H), 4.84-4.89 (m, 1H), 6.20 (d, J = 16.2 Hz, 1H), 6.30-6.34 (m, 1H), 6.60 (dd, J = 2.5 and 8.7 Hz, 1H), 6.77 (brs, 1H), 7.10 (dd, J = 1.6 and 7.9 Hz, 1H), 7.20-7.28 (m, 2H), 7.33 (s, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 16.2 Hz, 1H). ¹³C NMR (CDCl₃) δ: 14.23, 36.69, 38.07, 53.56, 55.54, 61.67, 108.56, 111.79, 119.17, 119.39, 127.18, 127.87, 129.47, 136.11, 136.43, 139.43, 155.95, 161.49, 165.65, 171.83, HRESIMS calcd. for C₂₄H₂₉N₃O₅Na (M+Na⁺): 462.2005; found 462.2005.

**General procedure E in EtOAc [similar as described in ref. 5].**

Arylurea 1 (0.25 mmol), acrylate ester (0.5 mmol), 1,4-benzoquinone (0.75 mmol, 81 mg), and Pd(OAc)₂ (0.025 mmol, 5.6 mg) were sequentially added under air to a reaction tube equipped with a stir bar and a septum. EtOAc (1.0 mL) and 48 wt % HBF₄ (0.25 mmol, 32 uL) were added by syringe and the resulting mixture vigorously stirred for 20 h at ambient temperature. After this time, the contents of the flask were quenched with aqueous NaHCO₃ and extracted with EtOAc. The solution obtained was filtered through the plug of silica gel and anhydrous MgSO₄, and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting with hexane/EtOAc to afford the product.

Following the general procedure above, using aryl urea 1b (44.6 mg, 0.25 mmol), acrylate ester (43 mg, 0.5 mmol), 1,4-benzoquinone (0.75 mmol, 81 mg), Pd(OAc)₂ (0.025 mmol, 5.6 mg), 48 wt % HBF₄ (0.25 mmol, 32 uL), and EtOAc (1 mL), yielded the product 5i (61.2 mg, 93%); ¹H NMR (CDCl₃) δ: 2.34 (s, 3H), 3.06 (s, 6H), 3.79 (s, 3H), 6.26 (brs, 1H), 6.36 (d, J = 15.5 Hz, 1H), 6.94 (d, J = 8 Hz, 1H), 7.41 (d, J = 8 Hz, 1H), 7.48 (s, 1H), 7.80 (d, J = 15.5 Hz, 1H); ¹³C NMR (CDCl₃), δ: 21.53, 36.57, 51.68, 118.02, 125.21, 125.90, 126.06, 126.84, 137.76, 140.38, 141.33, 156.26, 167.72; HRESIMS calcd. for C₁₄H₁₈N₂O₃Na (M+Na⁺): 285.1215; found 285.1206.
Following the general procedure above, using aryl urea 1d (48.1 mg, 0.25 mmol), acrylate ester (43 mg, 0.5 mmol), 1,4-benzoquinone (0.75 mmol, 81 mg), Pd(OAc)$_2$ (0.025 mmol, 5.6 mg), 48 wt % HBF$_4$ (0.25 mmol, 32 uL), and EtOAc (1 mL), yielded the product 5j (68.3 mg, 99%); $^1$H NMR (CDCl$_3$) $\delta$: 2.23 (s, 3H), 2.24 (s, 3H), 3.05 (s, 6H), 3.78 (s, 3H), 6.19 (brs, 1H), 6.36 (d, $J = 15.5$ Hz, 1H), 7.30 (s, 1H), 7.35 (s, 1H), 7.80 (d, $J = 15.5$ Hz, 1H); $^{13}$C NMR (CDCl$_3$), $\delta$: 19.33, 19.96, 36.62, 51.69, 117.71, 125.85, 127.09, 127.71, 133.57, 135.60, 140.10, 140.49, 156.53, 167.72; HRESIMS calcd. for C$_{15}$H$_{20}$N$_2$O$_3$Na (M+Na$^+$): 299.1372; found 299.1364.

Following the general procedure above, using aryl urea 1c (51.6 mg, 0.25 mmol), acrylate ester (43 mg, 0.5 mmol), 1,4-benzoquinone (0.75 mmol, 81 mg), Pd(OAc)$_2$ (0.025 mmol, 5.6 mg), 48 wt % HBF$_4$ (0.25 mmol, 32 uL), and EtOAc (1 mL), yielded the product 5k (69.4 mg, 96%); $^1$H NMR (CDCl$_3$) $\delta$: 1.24 (d, $J = 7$ Hz, 6H), 2.89 (sept, $J = 7$ Hz, 1H), 3.06 (s, 6H), 3.79 (s, 3H), 6.28 (brs, 1H), 6.37 (d, $J = 16$ Hz, 1H), 7.01 (d, $J = 8$ Hz, 1H), 7.46 (d, $J = 8$ Hz, 1H), 7.52 (s, 1H), 7.81 (d, $J = 16$ Hz, 1H); $^{13}$C NMR (CDCl$_3$), $\delta$: 23.75, 34.19, 36.67, 51.74, 118.33, 123.17, 123.35, 125.39, 127.13, 137.85, 140.40, 152.29, 156.20, 167.64; HRESIMS calcd. for C$_{16}$H$_{22}$N$_2$O$_3$Na (M+Na$^+$): 313.1528; found 313.1517.

Following the general procedure above, using 1a (48 mg, 0.25 mmol), acrylate ester (92 mg, 0.50 mmol), 1,4-benzoquinone (0.75 mmol, 81 mg), Pd(OAc)$_2$ (0.025 mmol, 5.6 mg), 48 wt % HBF$_4$ (0.25 mmol, 32 uL), and EtOAc (1 mL), yielded the product 5l (91 mg, 97%); $^1$H NMR (CDCl$_3$) $\delta$: 0.90 (t, $J = 6.8$ Hz, 3H), 0.91 (t, $J = 7.5$ Hz, 3H), 1.25-1.41 (m, 8H), 1.58-1.63 (m, 1H), 2.99 (s, 6H), 3.80 (s, 3H), 4.02 (dd, $J = 6.0$ and 11 Hz, 1H), 4.07 (dd, $J = 5.6$ and 11 Hz, 1H), 6.33 (d, $J = 15.7$ Hz, 1H), 6.47 (brs, 1H), 6.88 (dd, $J = 2.6$ and 8.7 Hz, 1H), 7.03 (d, $J = 2.6$ Hz, 1H), 7.29 (d, $J = 8.7$ Hz, 1H), 7.77 (d, $J = 15.7$ Hz, 1H); $^{13}$C NMR (CDCl$_3$), $\delta$: 10.95, 14.02, 22.91, 23.77, 28.89, 30.38, 36.42, 38.76, 55.45, 66.88, 110.72, 116.82, 119.42, 128.18, 130.35, 130.91, 140.08, 156.63, 157.01, 167.04; HRESIMS calcd. for C$_{21}$H$_{32}$N$_2$O$_4$Na (M+Na$^+$): 399.2260; found 399.2260.
Following the general procedure above, using aryl urea 1k (41.1 mg, 0.25 mmol), acrylate ester (43 mg, 0.5 mmol), 1,4-benzoquinone (0.75 mmol, 81 mg), Pd(OAc)$_2$ (0.025 mmol, 5.6 mg), 48 wt % HBF$_4$ (0.25 mmol, 32 uL), and EtOAc (1 mL), yielded the product 5m (82 mg, 95%); $^1$H NMR (CDCl$_3$) &delta;: 0.91 (t, $J$ = 7.2 Hz, 3H), 0.92 (t, $J$ = 7.6 Hz, 3H), 1.25-1.45 (m, 8H), 1.61-1.66 (m, 1H), 3.07 (s, 6H), 4.08-4.16 (m, 2H), 6.27 (br s, 1H), 6.42 (d, $J$ = 15.6 Hz, 1H), 7.12-7.16 (m, 1H), 7.34-7.39 (m, 1H), 7.53 (d, $J$ = 7.6 Hz, 1H), 7.67 (d, $J$ = 8.4 Hz, 1H), 7.83 (d, $J$ = 15.6 Hz, 1H); $^{13}$C NMR (CDCl$_3$), &delta;: 11.56, 14.18, 23.10, 23.97, 29.07, 30.58, 36.62, 38.96, 67.10, 119.90, 124.86, 125.41, 127.05, 127.98, 130.73, 137.84, 140.03, 156.14, 167.20; HRESIMS calcd. for C$_{20}$H$_{30}$N$_2$O$_3$Na (M+Na$^+$): 369.2154; found 369.2162.

Following the general procedure above, using aryl urea 1q (0.25 mmol), acrylate ester (0.5 mmol), 1,4-benzoquinone (0.75 mmol, 81 mg), and Pd(OAc)$_2$ (0.025 mmol, 5.6 mg), EtOAc (1.0 mL) and 48 wt % HBF$_4$ (0.25 mmol, 32 uL) yielded the product 5n (99 mg, 99%); $^1$H NMR (CDCl$_3$) &delta;: 0.81 (t, $J$ = 7.3 Hz, 3H), 0.90 (t, $J$ = 7.0 Hz, 6H), 1.31 (d, $J$ = 7.0 Hz, 3H), 1.41-1.43 (m, 8H), 1.54-1.62 (m, 3H), 2.57 (sext, $J$ = 7.0 Hz, 1H), 3.01 (s, 3H), 4.04 (dd, $J$ = 6.0 and 11.0 Hz, 1H), 4.07 (dd, $J$ = 5.6 and 11.0 Hz, 1H), 6.38 (d, $J$ = 15.9 Hz, 1H), 6.51 (brs, 1H), 7.16 (dd, $J$ = 2.0 and 8.4 Hz, 1H), 7.33 (d, $J$ = 1.9 Hz, 1H), 7.44 (d, $J$ = 8.4 Hz, 1H), 7.83 (d, $J$ = 15.9 Hz, 1H). $^{13}$C NMR (CDCl$_3$), &delta;: 10.99, 12.17, 14.03, 21.74, 22.95, 23.77, 28.91, 30.39, 31.01, 36.45, 38.79, 41.18, 66.85, 119.20, 125.24, 125.60, 127.82, 129.46, 135.45, 140.29, 144.20, 156.17, 167.16; HRESIMS calcd. for C$_{24}$H$_{38}$N$_2$O$_3$Na (M+Na$^+$): 425.2780; found 425.2774.

Following the general procedure above, using aryl urea 1n (47.6 mg, 0.25 mmol), acrylate ester (43 mg, 0.5 mmol), 1,4-benzoquinone (0.75 mmol, 81 mg), Pd(OAc)$_2$ (0.025 mmol, 5.6 mg), 48
wt % HBF$_4$ (0.25 mmol, 32 uL), and EtOAc (1 mL), yielded the product 5o (92.5 mg, 99%): $^1$H NMR (CDCl$_3$) δ: 0.90-0.93 (m, 6H), 1.30-1.43 (m, 8H), 1.57-1.61 (m, 1H), 3.01 (s, 6H), 3.09 (t, $J$ = 8 Hz, 2H), 3.94 (t, $J$ = 8 Hz, 2H), 4.02-4.12 (m, 2H), 6.33 (d, $J$ = 16 Hz, 1H), 7.00 (t, $J$ = 7.6 Hz, 1H), 7.19 (d, $J$ = 7.2 Hz, 1H), 7.38 (d, $J$ = 7.6 Hz, 1H), 7.51 (d, $J$ = 16 Hz, 1H); $^{13}$C NMR (CDCl$_3$), δ: 11.15, 14.13, 23.04, 23.96, 29.05, 30.01, 30.55, 37.56, 38.93, 52.74, 66.59, 117.31, 123.62, 123.72, 125.56, 126.00, 134.30, 141.39, 144.85, 161.68, 167.39; HRESIMS calcd. for C$_{22}$H$_{32}$N$_{2}$O$_{3}$Na (M+Na$^+$): 395.2311; found 395.2305.

Following the general procedure above, using aryl urea 1o (57.2 mg, 0.25 mmol), acrylate ester (43 mg, 0.5 mmol), 1,4-benzoquinone (0.75 mmol, 81 mg), Pd(OAc)$_2$ (0.025 mmol, 5.6 mg), 48 wt % HBF$_4$ (0.25 mmol, 32 uL), and EtOAc (1 mL), yielded the product 5p (91.2 mg, 89%): $^1$H NMR (acetone-d$_6$) δ: 0.88-0.94 (m, 6H), 1.31-1.42 (m, 8H), 1.61-1.65 (m, 1H), 3.08 (s, 6H), 3.93 (s, 3H), 4.08-4.14 (m, 2H), 6.32 (d, $J$ = 16 Hz, 1H), 6.43 (brs, 1H), 7.52 (s, 1H), 7.59 (s, 1H), 7.68 (d, $J$ = 16 Hz, 1H); $^{13}$C NMR (acetone-d$_6$), δ: 11.14, 14.19, 23.11, 23.95, 29.07, 30.57, 36.66, 38.97, 56.41, 67.16, 107.91, 118.45, 118.51, 119.74, 128.01, 137.97, 155.64, 156.65, 167.24; HRESIMS calcd. for C$_{21}$H$_{31}$N$_{2}$O$_{4}$NaCl (M+Na$^+$): 433.1870; found 433.1870.

Following the general procedure above, using aryl urea 1p (61 mg, 0.25 mmol), acrylate ester (43 mg, 0.5 mmol), 1,4-benzoquinone (0.75 mmol, 81 mg), Pd(OAc)$_2$ (0.025 mmol, 5.6 mg), 48 wt % HBF$_4$ (0.25 mmol, 32 uL), and EtOAc (1 mL), yielded the product 5q (88.7 mg, 83%): $^1$H NMR (acetone-d$_6$) δ: 0.88-0.94 (m, 6H), 1.30-1.42 (m, 8H), 1.61-1.65 (m, 1H), 3.06 (s, 6H), 4.08-4.14 (m, 2H), 6.33 (brs, 1H), 6.39 (d, $J$ = 16 Hz, 1H), 7.24 (dd, $J$ = 1.6 and 8.4 Hz, 1H), 7.36 (d, $J$ = 8.4 Hz, 1H), 7.71 (d, $J$ = 16 Hz, 1H), 7.95 (d, $J$ = 1.6 Hz, 1H); $^{13}$C NMR (acetone-d$_6$), δ: 11.17, 14.21, 23.12, 23.97, 29.09, 30.58, 36.65, 38.96, 67.26, 120.38, 124.51, 126.41, 127.80, 127.85, 128.17, 138.83, 138.92, 155.65, 166.99; HRESIMS calcd. for C$_{20}$H$_{29}$N$_{2}$O$_{3}$NaBr (M+Na$^+$): 447.1259; found 427.1255.
Following the general procedure above, using aryl urea 1l (44.6 mg, 0.25 mmol), acrylate ester (43 mg, 0.5 mmol), 1,4-benzoquinone (0.75 mmol, 81 mg), Pd(OAc)$_2$ (0.025 mmol, 5.6 mg), 48 wt % HBF$_4$ (0.25 mmol, 32 uL), and EtOAc (1 mL), yielded the product 5r (78.3 mg, 87%); $^1$H NMR (CDCl$_3$) $\delta$: 0.89-0.94 (m, 6H), 1.31-1.43 (m, 8H), 1.61-1.64 (m, 1H), 3.07 (s, 6H), 4.06-4.14 (m, 2H), 5.85 (brs, 1H), 6.40 (d, $J=16.5$ Hz, 1H), 7.18 (t, $J=7.5$ Hz, 1H), 7.26 (d, $J=7.5$ Hz, 1H), 7.50 (d, $J=7.5$ Hz, 1H), 7.88 (d, $J=16.5$ Hz, 1H); $^{13}$C NMR (CDCl$_3$), $\delta$: 11.15, 14.18, 18.37, 23.09, 23.96, 29.06, 30.55, 36.64, 38.94, 66.89, 119.16, 124.45, 126.76, 132.38, 132.58, 136.41, 136.77, 141.27, 156.60, 167.45; HRESIMS calcd. for C$_{21}$H$_{32}$N$_2$O$_3$Na (M+Na$^+$): 383.2311; found 383.2309.

Following the general procedure above, using aryl urea 1o (57.2 mg, 0.25 mmol), acrylamide (123 mg, 0.5 mmol), 1,4-benzoquinone (0.75 mmol, 81 mg), Pd(OAc)$_2$ (0.025 mmol, 5.6 mg), 48 wt % HBF$_4$ (0.25 mmol, 32 uL), and EtOAc (1 mL), yielded the product 5s (84 mg, 71%); $^1$H NMR (CDCl$_3$) $\delta$: 1.22 (t, $J=7.1$ Hz, 3H), 3.02 (s, 6H), 3.05-3.08 (m, 2H), 3.86 (s, 3H), 4.14 (q, $J=7.1$ Hz, 2H), 6.11 (dd, $J=8.6$ and 15.3 Hz, 1H), 6.51 (dd, $J=7.8$ and 11.8 Hz, 1H), 7.09-7.14 (m, 3H), 7.20-7.28 (m, 3H), 7.35 (d, $J=6.5$ Hz, 1H), 7.59 (d, $J=15.3$ Hz, 1H); $^{13}$C NMR (CDCl$_3$), $\delta$: 14.31, 36.77, 38.18, 53.73, 56.48, 61.84, 108.30, 108.31, 108.32, 118.22, 120.02, 127.35, 127.59, 128.78, 129.52, 135.35, 136.12, 138.14, 155.95, 156.33, 165.43, 171.78, 171.80; HRESIMS calcd. for C$_{24}$H$_{28}$N$_3$O$_5$ClNa (M+Na$^+$): 496.1615; found 496.1620.

Following the general procedure above, using aryl urea 1q (0.25 mmol), acrylamide (81 mg, 0.5 mmol), 1,4-benzoquinone (0.75 mmol, 81 mg), and Pd(OAc)$_2$ (0.025 mmol, 5.6 mg), EtOAc (1.0 mL) and 48 wt % HBF$_4$ (0.25 mmol, 32 uL) yielded the product 5t (49 mg, 52%); $^1$H NMR (CDCl$_3$) $\delta$: 0.73 (t, $J=7.4$ Hz, 3H), 1.10 (d, $J=7.4$ Hz, 3H), 1.43-1.50 (m, 2H), 2.40-2.49 (m, 1H), 3.03 (s, 6H), 3.31 (s, 3H), 6.26 (d, $J=15.3$ Hz, 1H), 6.59 (brs, 1H), 6.91 (brs, 1H), 7.10 (dd, $J=2.0$ and 8.4 Hz, 1H), 7.17 (dd, $J=1.5$ and 6.9 Hz, 2H), 7.34-7.44 (m, 3H), 7.54 (d, $J=8.4$ Hz, 1H), 7.83 (d, $J=$
15.3 Hz, 1H). $^{13}$C NMR (CDCl$_3$) $\delta$: 12.33, 21.88, 31.15, 36.76, 37.63, 41.20, 120.31, 125.36, 125.61, 127.47, 127.82, 127.92, 128.93, 129.78, 135.62, 137.66, 143.63, 143.73, 156.32, 166.28; HRESIMS calcd. for C$_{23}$H$_{29}$N$_3$O$_2$Na (M+Na$^+$): 402.2157; found 402.2159.

V. The synthesis of boscalid

![C-H activation conditions](image)

C–H Suzuki–Miyaura (1st step):
Following the general procedure C, using arylurea (82 mg, 0.5 mmol), p-ClPhB(OH)$_2$ (156 mg, 1.0 mmol), BQ (1.5 mmol, 162 mg), and [Pd(MeCN)$_4$](BF$_4$)$_2$ (0.05 mmol, 22 mg), EtOAc (2.0 mL), yielded the product (125 mg, 91%); $^1$H NMR (CDCl$_3$) $\delta$: 2.83 (s, 6H), 6.35 (brs, 1H), 7.09 (dt, $J = 1.2$ and 7.5 Hz, 1H), 7.16 (dd, $J = 1.5$ and 7.6 Hz, 1H), 7.32-7.37 (m, 3H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.45 (dd, $J = 1.2$ and 8.4 Hz, 1H). $^{13}$C NMR (CDCl$_3$) $\delta$: 36.22, 121.21, 122.95, 128.71, 129.19, 129.61, 130.52, 130.62, 133.83, 136.09, 137.13, 155.42; HRESIMS calcd. for C$_{15}$H$_{15}$N$_2$O$_2$Na (M+Na$^+$): 297.0771; found 297.0773.

Deprotection and 2-chloronicotinoylation (2nd step):
The resulting product (119 mg, 0.43 mmol) from 1st step shown in above was mixed with KOH (364 mg, 6.5 mmol) in 1,4-dioxane/water (1.6 mL/0.8 mL). After stirring under reflux conditions for 20 h, the solution obtained was filtered through the plug of silica gel and anhydrous MgSO$_4$. After evaporation to remove solvents, the crude oil, 2-chloronicotinoyl chloride and (122 mg, 0.69 mmol) were sequentially added under air to a reaction tube equipped with a stir bar and a septum. THF (5 mL), and Et$_3$N (1.39 mmol, 0.19 mL) was added by syringe and the resulting mixture vigorously stirred for 2 h at ambient temperature. After this time, the contents of the flask were quenched with aqueous K$_2$CO$_3$ and extracted with EtOAc. The solution obtained was filtered through the plug of silica gel and anhydrous MgSO$_4$, and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting with hexane/EtOAc to afford Boscalid (145 mg, 98%); $^1$H NMR (CDCl$_3$) $\delta$: 7.27 (brs, 1H), 7.33-7.37 (m, 4H), 7.42-7.48 (m, 3H), 8.14 (dd, $J = 1.9$ and 7.8 Hz, 2H), 8.41 (d, $J = 8.2$ Hz, 1H), 8.45 (dd, $J = 1.9$ and 4.7 Hz, 1H). $^{13}$C NMR (CDCl$_3$) $\delta$: 122.55, 122.91, 125.56, 128.91, 129.27, 130.33, 130.86, 131.25, 132.61, 134.28, 134.35, 136.39, 139.89, 146.73, 151.21, 162.75; HRESIMS calcd. for C$_{18}$H$_{13}$N$_2$O$_2$Na (M+Na$^+$): 365.0224; found 365.0216.
VI. Mechanistic studies

Arylurea 1 (0.1 or 0.11 mmol), and [Pd(MeCN)₄(BF₄)₂] (0.1 mmol) were sequentially added under Ar to a reaction tube equipped with a stir bar and a septum. EtOAc (6 mL, or EtOAc/CH₂Cl₂) was added by syringe and the resulting mixture stirred for 0.5 h at ambient temperature. To complete the reaction, we heat the reaction mixture at 40 °C for 0.5 h. The resulting crystals were filtered off and washed with EtOAc and Et₂O followed by dried under vacuum to give yellow crystals. Single crystals were obtained by the recrystallization from MeCN/toluene. ¹H NMR (acetone-d₆) δ: 2.61 (s, 3H), 3.12 (brs, 9H), 3.72 (s, 3H), 6.42 (dd, J = 2.8 and 8.7 Hz, 1H), 6.67 (d, J = 2.8 Hz, 1H), 6.97 (d, J = 8.7 Hz, 1H), 8.74 (brs, 1H). ¹³C NMR (acetone-d₆) δ: 2.46, 36.94, 54.87, 102.37, 104.30, 109.16, 122.59, 135.50, 135.59, 136.63, 154.72, 158.97. ¹⁹F NMR (acetone-d₆) δ: -88.768. ¹¹B NMR (acetone-d₆) δ: 4.362; ESI/TOF C₁₄H₁₉BF₄N₄O₂Pd (M⁺-BF₄): 381.06.

Arylurea 1 (0.05 mmol), and Pd(OAc)₂ (0.05 mmol) were sequentially added under Ar to a reaction tube equipped with a stir bar and a septum. Acetone-d₆ (1.0 mL), and 48 wt % HBF₄ (0.1 mmol) was added by syringe and the resulting mixture vigorously stirred for 0.5 h at ambient temperature. After this time, MeCN (0.1 mmol) was added and ¹H NMR was carried out to check the structure. The spectrum of the product was matched with the palladacycle shown in above. On the other hand, the reaction without HBF₄ gave no product.

2% Brij 35 was used instead of AcOEt.
Arylurea 1 (0.05 mmol), and Pd(OAc)$_2$ (0.05 mmol) were sequentially added under Ar to a reaction tube equipped with a stir bar and a septum. EtOAc (1.0 mL), and 48 wt % HBF$_4$ (0.15 mmol) was added by syringe and the resulting mixture vigorously stirred for 0.5 h at ambient temperature. After this time, acrylate ester, phenylboronic acid, or iodobenzene (0.1 mmol) was added. After stirring 4 h, the contents of the flask were quenched with aqueous $\text{K}_2\text{CO}_3$ and extracted with EtOAc. The solution obtained was filtered through the plug of silica gel and anhydrous MgSO$_4$, and then concentrated by rotary evaporation and dried under vacuum. $^1$H NMR was carried out to check the yields.

Arylurea 1 (0.05 mmol), and Pd(OAc)$_2$ (0.05 mmol) were sequentially added under Ar to a reaction tube equipped with a stir bar and a septum. EtOAc (1.0 mL), and 48 wt % HBF$_4$ (0.15 mmol) was added by syringe and the resulting mixture vigorously stirred for 0.5 h at ambient temperature. After this time, acrylate ester, phenylboronic acid, or iodobenzene (0.1 mmol) and BQ (0 or 1 mmol) and 1 (0.5 mmol) were added. After stirring 14 h, the contents of the flask were quenched with aqueous $\text{K}_2\text{CO}_3$ and extracted with EtOAc. The solution obtained was filtered through the plug of silica gel and anhydrous MgSO$_4$, and then concentrated by rotary evaporation and dried under vacuum. $^1$H NMR was carried out to check the yields.

Arylurea 1 (0.05 mmol), and Pd(OAc)$_2$ (0.05 mmol) were sequentially added under Ar to a reaction tube equipped with a stir bar and a septum. EtOAc (1.0 mL), and 48 wt % HBF$_4$ (0.15 mmol) was added by syringe and the resulting mixture vigorously stirred for 0.5 h at ambient temperature. After this time, acrylate ester, phenylboronic acid, or iodobenzene (0.1 mmol) and 1 (0.5 mmol) were added. After stirring 14 h, the contents of the flask were quenched with aqueous $\text{K}_2\text{CO}_3$ and extracted with EtOAc. The solution obtained was filtered through the plug of silica gel and anhydrous MgSO$_4$, and then concentrated by rotary evaporation and dried under vacuum. $^1$H NMR was carried out to check the yields.

Arylurea 1 (0.05 mmol), and Pd(OAc)$_2$ (0.05 mmol) were sequentially added under Ar to a reaction tube equipped with a stir bar and a septum. EtOAc (1.0 mL), and 48 wt % HBF$_4$ (0.15 mmol) was added by syringe and the resulting mixture vigorously stirred for 0.5 h at ambient temperature. After this time, acrylate ester, phenylboronic acid, or iodobenzene (0.1 mmol) and 1 (0.5 mmol) were added. After stirring 14 h, the contents of the flask were quenched with aqueous $\text{K}_2\text{CO}_3$ and extracted with EtOAc. The solution obtained was filtered through the plug of silica gel and anhydrous MgSO$_4$, and then concentrated by rotary evaporation and dried under vacuum. $^1$H NMR was carried out to check the yields.

Arylurea 1 (0.05 mmol), and Pd(OAc)$_2$ (0.05 mmol) were sequentially added under Ar to a reaction tube equipped with a stir bar and a septum. EtOAc (1.0 mL), and 48 wt % HBF$_4$ (0.15 mmol) was added by syringe and the resulting mixture vigorously stirred for 0.5 h at ambient temperature. After this time, acrylate ester, phenylboronic acid, or iodobenzene (0.1 mmol) and 1 (0.5 mmol), HBF$_4$ (0 or 2.5 mmol) and

<table>
<thead>
<tr>
<th>AgOAc (equiv)</th>
<th>HBF$_4$ (equiv)</th>
<th>Yield</th>
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<tr>
<td>0</td>
<td>0</td>
<td>41%</td>
<td>0.4</td>
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<td>15</td>
<td>2.5</td>
<td>45%</td>
<td>4.5</td>
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</table>

$^a$Yields were based on Pd.
AgOAc (0 or 0.75 mmol) were added. After stirring 14 h, the contents of the flask were quenched with aqueous K$_2$CO$_3$ and extracted with EtOAc. The solution obtained was filtered through the plug of silica gel and anhydrous MgSO$_4$, and then concentrated by rotary evaporation and dried under vacuum. $^1$H NMR was carried out to check the yields.

Reference