Supporting Information

2-Pyridylmethyl ether: a readily removable and efficient directing group for amino acid ligand accelerated ortho-C–H olefination of phenols

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I. General remarks

The $^1$H NMR (400 MHz or 600 MHz) chemical shifts were measured relative to TMS, CDCl$_3$ or DMSO-$d_6$ as the internal reference. The $^{13}$C NMR (100 MHz) chemical shifts are given using CDCl$_3$ or DMSO-$d_6$ as the internal standard. High resolution mass spectra (HR-MS) were recorded by ESI-TOF. Melting points were determined with XRC-1 and are uncorrected. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. L-Val-OH, L-Leu-OH and L-Ile-OH were used to synthesize the N-protected amino acid ligands according to known procedures.$^{1,2,3}$ Solvents were dried by refluxing for at least 24 h over CaH$_2$ (DMF, DCE, DCM) and freshly distilled prior to use. t-AmyloH was obtained from commercial suppliers and used directly without further purification. Py = 2-pyridyl, $^4$Py = 4-pyridyl.

II. Optimization of the reaction condition

![Chemical reaction diagram]

Table 1 Optimization of the reaction conditions.$^a$

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<th>Entry</th>
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<th>Oxidant</th>
<th>Additive</th>
<th>Yield (%)$^b$</th>
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<td>KHCO$_3$</td>
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<td>7</td>
<td>Boc-Val-OH</td>
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<td>KHCO$_3$</td>
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$^a$Electronic Supplementary Material (ESI) for Chemical Communications

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<th>Reaction Code</th>
<th>Reaction Details</th>
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<td>Boc-Val-OH + O&lt;sub&gt;2&lt;/sub&gt; + KHCO&lt;sub&gt;3&lt;/sub&gt; = 29</td>
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<tr>
<td>15&lt;sup&gt;e&lt;/sup&gt;</td>
<td>- + K&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt; + - = Trace</td>
</tr>
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</table>

<sup>a</sup> Reactions were carried out using 1<sup>a</sup> (0.5 mmol) and 2<sup>a</sup> (0.75 mmol), Pd(OAc)<sub>2</sub> (10 mol%), ligand (20 mol%) and additive (2.0 equiv) in t-AmylOH (2 mL) for 12 hours under 1 atm O<sub>2</sub>.<sup>b</sup> Yield of isolated product. <sup>c</sup> 10 mol% BQ used. <sup>d</sup> At 60 °C. <sup>e</sup> Reaction was carried out using 1<sup>a</sup> (0.5 mmol) and 2<sup>a</sup> (0.75 mmol), Pd(OAc)<sub>2</sub> (10 mol%), additive (2.0 equiv) and oxidant (1.0 mmol) in DCE (2 mL) at 110 °C for 24 hours under N<sub>2</sub>. DCE = 1,2-dichloroethane, t-AmylOH = tert-amyl alcohol, Py = 2-pyridyl.

### III. Preparation of starting materials and characterization

A mixture of phenols (10.0 mmol), 2-(chloromethyl)pyridine hydrochloride (10.0 mmol), and K<sub>2</sub>CO<sub>3</sub> (4.14 g, 30.0 mmol) was dissolved in CH<sub>3</sub>CN (20 mL) and heated to reflux under nitrogen for 8 hours. After being cooled to room temperature, the reaction mixture was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

A mixture of 3,4-dimethylphenol (10.0 mmol), 4-(chloromethyl)pyridine hydrochloride (10.0 mmol), and K<sub>2</sub>CO<sub>3</sub> (4.14 g, 30.0 mmol) was dissolved in CH<sub>3</sub>CN...
(20 mL) and heated to reflux under nitrogen for 8 hours. After being cooled to room temperature, the reaction mixture was filtered and washed with CH₂Cl₂. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to provide the desired product 1,2-dimethyl-4-(pyridin-4-ylmethoxy)benzene.

A mixture of 3,4-dimethylphenol (10.0 mmol), Benzyl chloride (10.0 mmol), and K₂CO₃ (2.07 g, 15.0 mmol) was dissolved in CH₃CN (20 mL) and heated to reflux under nitrogen for 8 hours. After being cooled to room temperature, the reaction mixture was filtered and washed with CH₂Cl₂. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

2-(Pyridin-2-ylmethoxy)toluene

The title compound was obtained as colorless oil (1.8 g, 90%). ¹H NMR (400 MHz, CDCl₃): δ = 2.34 (s, 3H), 5.22 (s, 2H), 6.85-6.90 (m, 2H), 7.12-7.22 (m, 3H), 7.55 (d, J = 7.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 8.58 (d, J = 4.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.5, 70.5, 111.5, 120.9, 121.0, 122.6, 126.9, 127.0, 130.9, 136.9, 149.2, 156.5, 157.9 ppm.

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene

The title compound was obtained as colorless oil (1.9 g, 89%). ¹H NMR (400 MHz, CDCl₃): δ = 2.18 (s, 3H), 2.22 (s, 3H), 5.17 (s, 2H), 6.70 (d, J = 8.0 Hz, 1H), 6.81 (s,
1H), 7.01 (d, J = 8.0 Hz, 1H), 7.18 (t, J = 6.4 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 8.57 (d, J = 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.9, 20.1, 70.7, 111.8, 116.5, 121.3, 122.6, 129.2, 130.5, 136.9, 137.9, 149.2, 156.6, 157.8$ ppm.

1,2-Dimethyl-4-(pyridin-4-ylmethoxy)benzene

The title compound was obtained as a white solid (1.77 g, 83%). M.p.: 44-46 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.20$ (s, 3H), 2.24 (s, 3H), 5.05 (s, 1H), 6.66 (d, J = 8.0 Hz, 1H), 6.78 (s, 1H), 7.02 (d, J = 8.4 Hz, 1H), 7.34(d, J = 5.6 Hz, 2H), 8.59 (d, J = 6.0 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.9, 20.2, 68.3, 111.7, 116.5, 121.6, 129.6, 130.5, 138.1, 146.8, 150.1, 156.5$ ppm.

4-(Benzyloxy)-1,2-dimethylbenzene

The title compound was obtained as colorless oil (1.8 g, 85%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.22$ (s, 3H), 2.26 (s, 3H), 5.05 (s, 2H), 6.73 (d, J = 8.4 Hz, 1H), 6.83 (s, 1H), 7.04 (d, J = 8.4 Hz, 1H), 7.32-7.46 (m, 5H), ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.9, 20.2, 70.2, 111.9, 116.6, 127.6, 127.9, 128.7, 129.0, 130.4, 137.5, 137.9, 157.1$ ppm.

3-(Pyridin-2-ylmethoxy)toluene

The title compound was obtained as colorless oil (1.75 g, 88%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.32$ (s, 3H), 5.19 (s, 2H), 6.78-6.82 (m, 3H), 7.14-7.22 (m, 2H), 7.51 (d,
\[ J = 7.6 \text{ Hz, 1H}, 7.68 \text{ (t, } J = 7.6 \text{ Hz, 1H)}, 8.58 \text{ (d, } J = 4.4 \text{ Hz, 1H)} \text{ ppm.} \]
\[ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 21.6, 70.6, 111.7, 115.8, 121.3, 122.1, 122.6, 129.4, 136.9, 139.7, 149.3, 157.6, 158.5 \text{ ppm.} \]

**tert-Butyl-2-(pyridin-2-ylmethoxy)benzene**

The title compound was obtained as colorless oil (2.2 g, 91%). \(^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 1.50 \text{ (s, 9H)}, 5.32 \text{ (s, 2H)}, 6.94-6.99 \text{ (m, 2H)}, 7.18 \text{ (t, } J = 7.6 \text{ Hz, 1H)}, 7.25 \text{ (t, } J = 6.0 \text{ Hz, 1H)}, 7.36 \text{ (d, } J = 7.6 \text{ Hz, 1H)}, 7.61 \text{ (d, } J = 7.6 \text{ Hz, 1H)}, 7.75 \text{ (t, } J = 7.6 \text{ Hz, 1H)}, 8.64 \text{ (d, } J = 4.8 \text{ Hz, 1H)} \text{ ppm.} \]
\[ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 30.0, 35.0, 71.0, 112.9, 121.0, 121.3, 122.6, 126.9, 127.3, 137.0, 138.4, 149.3, 157.2, 157.9 \text{ ppm.} \]

**1,3-Dimethyl-4-(pyridin-2-ylmethoxy)benzene**

The title compound was obtained as a slight yellow solid (2.0 g, 94%). M.p.: 60-62 °C. \(^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 2.26 \text{ (s, 3H)}, 2.31 \text{ (s, 3H)}, 5.20 \text{ (s, 2H)}, 6.74 \text{ (d, } J = 7.6 \text{ Hz, 1H)}, 6.92 \text{ (d, } J = 8.0 \text{ Hz, 1H)}, 6.99 \text{ (s, 1H)}, 7.20 \text{ (t, } J = 6.4 \text{ Hz, 1H)}, 7.55 \text{ (d, } J = 8.0 \text{ Hz, 1H)}, 7.70 \text{ (t, } J = 7.6 \text{ Hz, 1H)}, 8.58 \text{ (d, } J = 4.4 \text{ Hz, 1H)} \text{ ppm.} \]
\[ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 16.5, 20.6, 70.8, 111.6, 121.1, 122.6, 126.7, 127.2, 130.2, 131.8, 137.0, 149.1, 154.5, 158.1 \text{ ppm.} \]

**Pyridin-2-ylmethoxybenzene**

The title compound was obtained as colorless oil (1.7 g, 92%). \(^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 5.21 \text{ (s, 2H)}, 6.95-7.00 \text{ (m, 3H)}, 7.20 \text{ (t, } J = 6.0 \text{ Hz, 1H)}, 7.27-7.31 \text{ (m,}
2H), 7.52 (d, J = 7.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 8.59 (d, J = 4.8 Hz, 1H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 70.6, 115.0, 121.3, 121.4, 122.7, 129.7, 137.0, 149.3, 157.5, 158.5 ppm.

1,3-Di-tert-butyl-4-(pyridin-2-ylmethoxy)benzene

The title compound was obtained as a white solid (2.6 g, 88%). M.p.: 78-80 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$= 1.31 (s, 9H), 1.47 (s, 9H), 5.25 (s, 2H), 6.82 (d, J = 8.4 Hz, 1H), 7.15 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 6.0 Hz, 1H), 7.37 (s, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 8.59 (d, J = 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 30.1, 31.7, 34.4, 35.2, 71.1, 112.2, 121.3, 122.5, 123.6, 124.2, 137.0, 137.5, 143.2, 149.2, 155.0, 158.2 ppm.

2-(Pyridin-2-ylmethoxy)anisole

The title compound was obtained as a white solid (1.8 g, 84%). M.p.: 50-52 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.91 (s, 3H), 5.29 (s, 2H), 6.85-6.93 (m, 4H), 7.19 (t, J = 6.0 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 8.57 (d, J = 4.8 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 56.1, 71.6, 112.1, 114.0, 121.0, 121.4, 121.7, 122.7, 137.0, 148.0, 149.2, 149.7, 157.6 ppm.

1-(Pyridin-2-ylmethoxy)naphthalene

The title compound was obtained as a white solid (1.9 g, 81%). M.p.: 46-48 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 5.40 (s, 2H), 6.85 (d, J = 7.6 Hz, 1H), 7.21 (t, J = 6.0 Hz,
1H), 7.32 (t, J = 8.0 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.49-7.52 (m, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.80-7.82 (m, 1H), 8.39 (t, J = 6.0 Hz, 1H), 8.61 (d, J = 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 70.9, 105.5, 120.9, 121.2, 122.1, 122.7, 125.4, 125.8, 126.0, 126.6, 127.7, 134.7, 137.0, 149.3, 154.1, 157.5 ppm.

4-(Pyridin-2-ylmethoxy)anisole

The title compound was obtained as a white solid (1.75 g, 81%). M.p.: 39-41 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.76 (s, 3H), 5.16 (s, 2H), 6.82 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 9.2 Hz, 2H), 7.20 (t, J = 6.4 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 8.58 (d, J = 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 55.8, 71.4, 114.8, 115.9, 121.4, 122.7, 136.9, 149.3, 152.7, 154.2, 157.7 ppm.

4-(Pyridin-2-ylmethoxy)toluene

The title compound was obtained as colorless oil (1.7 g, 85%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.28 (s, 3H), 5.18 (s, 2H), 6.87 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 7.19 (t, J = 6.4 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 8.58 (d, J = 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 20.6, 70.8, 114.8, 121.4, 122.6, 130.1, 130.5, 136.9, 149.3, 156.4, 157.7 ppm.

*tert*-Butyl-4-(pyridin-2-ylmethoxy)benzene
The title compound was obtained as colorless oil (2.0 g, 83%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.30\) (s, 9H), 5.20 (s, 2H), 6.92 (d, \(J = 8.4\) Hz, 2H), 7.20 (t, \(J = 6.4\) Hz, 1H), 7.30 (d, \(J = 8.4\) Hz, 2H), 7.53 (d, \(J = 8.0\) Hz, 1H), 7.68 (t, \(J = 7.6\) Hz, 1H), 8.59 (d, \(J = 4.4\) Hz, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 31.6, 34.2, 70.8, 114.4, 121.4, 122.7, 126.4, 136.9, 144.0, 149.3, 156.3, 157.8\) ppm.

**4-(Pyridin-2-ylmethoxy)chlorobenzene**

The title compound was obtained as a white solid (1.9 g, 88%). M.p.: 54-56 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.28\) (s, 2H), 6.90 (t, \(J = 7.6\) Hz, 1H), 6.96 (d, \(J = 8.0\) Hz, 1H), 7.17-7.24 (m, 2H), 7.39 (d, \(J = 8.0\) Hz, 1H), 7.64 (d, \(J = 7.6\) Hz, 1H), 7.72 (t, \(J = 7.6\) Hz, 1H), 8.58 (d, \(J = 4.8\) Hz, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 71.3, 113.9, 121.3, 122.0, 122.8, 123.2, 127.9, 130.5, 137.1, 149.2, 154.0, 157.0\) ppm.

**1,3-Dichloro-4-(pyridin-2-ylmethoxy)benzene**

The title compound was obtained as a white solid (2.3 g, 91%). M.p.: 100-102 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.25\) (s, 2H), 6.89 (d, \(J = 8.8\) Hz, 1H), 7.14 (d, \(J = 10.0\) Hz, 1H), 7.22 (t, \(J = 6.0\) Hz, 1H), 7.39 (s, 1H), 7.59 (d, \(J = 7.6\) Hz, 1H), 7.72 (t, \(J = 7.6\) Hz, 1H), 8.58 (d, \(J = 4.0\) Hz, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 71.7, 114.7, 121.3, 123.0, 124.0, 126.4, 127.8, 130.2, 137.2, 149.3, 152.8, 156.5\) ppm.

**2-(Pyridin-2-ylmethoxy)nitrobenzene**

The title compound was obtained as a slight yellow solid (2.0 g, 87%). M.p.: 76-78 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.34\) (s, 2H), 7.05 (t, \(J = 7.6\) Hz, 1H), 7.16 (d, \(J = 8.4\) Hz, 1H), 8.59 (d, \(J = 4.4\) Hz, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 31.6, 34.2, 70.8, 114.4, 121.4, 122.7, 126.4, 136.9, 144.0, 149.3, 156.3, 157.8\) ppm.
Hz, 1H), 7.23 (t, J = 6.4 Hz, 1H), 7.51 (t, J = 8.4 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 8.58 (d, J = 4.0 Hz, 1H) ppm. $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$): $\delta$ = 71.6, 115.0, 121.0, 121.4, 123.1, 126.0, 134.5, 137.3, 140.1, 149.2, 151.8, 156.0 ppm.

2,2'-Bis(pyridin-2-ylmethoxy)-1,1'-binaphthyl

The title compound was obtained as a white solid (3.2 g, 71%). M.p.: 124-126 °C. $^1\text{H}$ NMR (400 MHz, CDCl$_3$): $\delta$ = 5.20 (s, 4H), 6.69 (d, J = 8.0 Hz, 2H), 6.99 (t, J = 6.4 Hz, 2H), 7.22-7.24 (m, 6H), 7.31-7.34 (m, 2H), 7.44 (d, J = 9.2 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 8.8 Hz, 2H), 8.42 (d, J = 4.4 Hz, 2H) ppm. $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$): $\delta$ = 71.6, 115.2, 120.3, 120.9, 122.3, 124.0, 125.6, 126.6, 128.1, 129.5, 129.7, 134.3, 136.6, 148.7, 153.8, 157.8 ppm.

IV. General procedure for 2-pyridylmethyl ether directed C–H ortho-olefination of phenols

A mixture of phenol ethers 1 (0.5 mmol), alkenes 2 (0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 10 mol%), KHCO$_3$ (100 mg, 1.0 mmol) and ligand (20 mol%) was dissolved in $\tau$-AmylOH (2 mL) in a 50 mL Schlenk-type sealed tube. The reaction tube was filled with O$_2$. Subsequently, the reaction mixture was stirred for 10 min at room temperature, and then heated at 90 ºC for 12 h. After being cooled to room temperature, the reaction mixture was diluted with 5 mL of CH$_2$Cl$_2$, filtered through a plug of celite, and washed with 10-20 mL of CH$_2$Cl$_2$. The combined organic extracts
were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product 3.

A mixture of phenol ethers 1 (0.5 mmol), alkenes 2 (2.5 mmol), Pd(OAc)$_2$ (11.2 mg, 10 mol%), KHCO$_3$ (200 mg, 2.0 mmol) and Boc-Val-OH (21.7 mg, 20 mol%) was dissolved in $t$-AmylOH (2 mL) in a 50 mL Schlenk-type sealed tube. The reaction tube was filled with O$_2$. Subsequently, the reaction mixture was stirred for 10 min at room temperature, and then heated at 90 ºC for 20 h. After being cooled to room temperature, the reaction mixture was diluted with 5 mL of CH$_2$Cl$_2$, filtered through a plug of celite, and washed with 10-20 mL of CH$_2$Cl$_2$. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product 4.

A mixture of 4-(pyridin-2-ylmethoxy)anisole (0.5 mmol), $N,N$-dimethylacrylamide (0.5 mmol), Pd(OAc)$_2$ (11.2 mg, 10 mol%), KHCO$_3$ (200 mg, 2.0 mmol) and Boc-Val-OH (21.7 mg, 20 mol%) was dissolved in $t$-AmylOH (2 mL) in a 50 mL Schlenk-type sealed tube. The reaction tube was filled with O$_2$. Subsequently, the reaction mixture was stirred for 10 min at room temperature, and then heated at 90 ºC for 10 h. After being cooled to room temperature, $n$-butyl acrylate was added into the mixture under the oxygen environment, and then the mixture was heated at 90 ºC for another 10 h. After being cooled to room temperature, the reaction mixture was diluted with 5 mL of CH$_2$Cl$_2$, filtered through a plug of celite, and washed with 10-20 mL of CH$_2$Cl$_2$. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired
product.

V. Experimental data for the described substances

\(\text{(E)-N,N-Dimethyl-3-(3-methyl-2-(pyridin-2-ylmethoxy)phenyl)acrylamide (3a)}\)

2-(Pyridin-2-ylmethoxy)toluene (100 mg, 0.5 mmol), \(N,N\)-dimethylacrylamide (75 mg, 0.75 mmol), Pd(OAc)\(_2\) (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO\(_3\) (100 mg, 1.0 mmol) in \(t\)-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O\(_2\). Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (134 mg, 90% yield). M.p.: 104-106 ºC. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.31\) (s, 3H), 3.02 (s, 3H), 3.06 (s, 3H), 4.96 (s, 2H), 6.97 (d, \(J = 15.6\) Hz, 1H), 7.05 (t, \(J = 7.6\) Hz, 1H), 7.19 (d, \(J = 7.2\) Hz, 1H), 7.24 (t, \(J = 6.0\) Hz, 1H), 7.39 (d, \(J = 7.6\) Hz, 1H), 7.73 (d, \(J = 7.6\) Hz, 1H), 7.78 (t, \(J = 7.6\) Hz, 1H), 7.90 (d, \(J = 15.6\) Hz, 1H), 8.57 (d, \(J = 4.4\) Hz, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 16.3, 36.0, 37.4, 75.7, 119.4, 121.8, 122.9, 124.6, 126.5, 129.2, 132.2, 132.6, 137.0, 137.7, 149.3, 156.1, 157.2, 167.0\) ppm. HRMS (ESI\(^+\)): calcd for C\(_{18}\)H\(_{20}\)N\(_2\)O\(_2\) [M+H]\(^+\) 297.1603, found 297.1609.

\(\text{(E)-N,N-Dimethyl-3-(4-methyl-2-(pyridin-2-ylmethoxy)phenyl)acrylamide (3b)}\)

3-(Pyridin-2-ylmethoxy)toluene (100 mg, 0.5 mmol), \(N,N\)-dimethylacrylamide (75 mg, 0.75 mmol), Pd(OAc)\(_2\) (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO\(_3\) (100 mg, 1.0 mmol) in \(t\)-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O\(_2\). Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (126 mg, 85% yield). M.p.: 132-134 ºC. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.33\) (s, 3H), 3.02 (s, 3H), 3.06 (s, 3H), 4.96 (s, 2H), 6.79-6.80 (m,
(E)-3-(4,5-Dimethyl-2-(pyridin-2-ylmethoxy)phenyl)-N,N-dimethylacrylamide (3c)

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), N,N-dimethylacrylamide (75 mg, 0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in $t$-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (143 mg, 92% yield). M.p.: 108-110 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.20 (s, 3H), 2.23 (s, 3H), 3.05 (s, 3H), 3.09 (s, 3H), 5.24 (s, 2H), 6.76 (s, 1H), 6.98 (d, $J$ = 15.6 Hz, 1H), 7.22-7.28 (m, 2H), 7.57 (d, $J$ = 7.6 Hz, 1H), 7.72 (t, $J$ = 7.2 Hz, 1H), 7.96 (d, $J$ = 15.6 Hz, 1H), 8.58 (d, $J$ = 4.0 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 18.9, 20.4, 36.0, 37.5, 71.2, 114.3, 117.5, 121.6, 122.1, 122.8, 129.2, 130.3, 137.1, 138.0, 139.8, 149.2, 155.2, 157.3, 167.7 ppm. HRMS (ESI$^+$): calcd for C$_{19}$H$_{22}$N$_2$O$_2$ [M+H]$^+$ 311.1760, found 311.1756.

(E)-3-(3,5-Dimethyl-2-(pyridin-2-ylmethoxy)phenyl)-N,N-dimethylacrylamide (3d)

1,3-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (107 mg, 0.5 mmol),
N,N-dimethylacrylamide (75 mg, 0.75 mmol), Pd(OAc)\textsubscript{2} (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO\textsubscript{3} (100 mg, 1.0 mmol) in t-AmylOH (2 mL) at 90 °C for 12 h under 1 atm O\textsubscript{2}. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded colorless oil (141 mg, 91% yield). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{δ} = 2.25 (s, 3H), 2.28 (s, 3H), 3.00 (s, 3H), 3.05 (s, 3H), 4.90 (s, 2H), 6.94 (d, \textit{J} = 15.6 Hz, 1H), 7.00 (s, 1H), 7.18 (s, 1H), 7.20 (t, \textit{J} = 6.0 Hz, 1H), 7.70-7.78 (m, 2H), 7.86 (d, \textit{J} = 15.6 Hz, 1H), 8.54 (d, \textit{J} = 4.4 Hz, 1H) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \textit{δ} = 16.1, 20.8, 35.9, 37.3, 75.6, 118.9, 121.8, 122.8, 126.5, 128.5, 131.6, 133.4, 133.9, 137.1, 137.7, 149.0, 153.8, 157.0, 166.9 ppm. HRMS (ESI\textsuperscript{+}): calced for C\textsubscript{19}H\textsubscript{22}N\textsubscript{2}O\textsubscript{2} [M+H]\textsuperscript{+} 311.1760, found 311.1764.

\[ \text{(E)-3-(3-tert-Butyl-2-(pyridin-2-ylmethoxy)phenyl)-N,N-dimethylacrylamide (3e)} \]

\textit{tert}-Butyl-2-(pyridin-2-ylmethoxy)benzene (121 mg, 0.5 mmol), N,N-dimethylacrylamide (75 mg, 0.75 mmol), Pd(OAc)\textsubscript{2} (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO\textsubscript{3} (100 mg, 1.0 mmol) in t-AmylOH (2 mL) at 90 °C for 12 h under 1 atm O\textsubscript{2}. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded colorless oil (159 mg, 94% yield). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{δ} = 1.39 (s, 9H), 2.98 (s, 3H), 3.05 (s, 3H), 5.03 (s, 2H), 6.88 (d, \textit{J} = 15.6 Hz, 1H), 7.06 (t, \textit{J} = 7.6 Hz, 1H), 7.21 (t, \textit{J} = 5.6 Hz, 1H), 7.36 (d, \textit{J} = 7.6 Hz, 1H), 7.40 (d, \textit{J} = 7.6 Hz, 1H), 7.78-7.84 (m, 2H), 7.89 (d, \textit{J} = 15.6 Hz, 1H), 8.54 (d, \textit{J} = 4.4 Hz, 1H) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \textit{δ} = 30.9, 35.2, 35.9, 37.4, 76.7, 119.0, 121.3, 122.7, 124.1, 126.8, 128.7, 130.0, 137.2, 138.5, 143.5, 148.9, 157.0, 157.3, 166.7 ppm. HRMS (ESI\textsuperscript{+}): calced for C\textsubscript{21}H\textsubscript{26}N\textsubscript{2}O\textsubscript{2} [M+H]\textsuperscript{+} 339.2073, found 339.2069.
(E)-3-(3,5-Di-tert-butyl-2-(pyridin-2-ylmethoxy)phenyl)-N,N-dimethylacrylamide (3f)

1,3-Di-tert-butyl-4-(pyridin-2-ylmethoxy)benzene (149 mg, 0.5 mmol), N,N-dimethylacrylamide (75 mg, 0.75 mmol), Pd(OAc)₂ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO₃ (100 mg, 1.0 mmol) in t-AmylOH (2 mL) at 90 °C for 12 h under 1 atm O₂. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (188 mg, 95% yield). M.p.: 106-108 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.34 (s, 9H), 1.40 (s, 9H), 2.99 (s, 3H), 3.05 (s, 3H), 5.05 (s, 2H), 6.87 (d, J = 15.6 Hz, 1H), 7.26 (m, 1H), 7.37 (s, 1H), 7.40 (s, 1H), 7.85-7.89 (m, 3H), 8.55 (d, J = 4.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 31.1, 31.6, 34.7, 35.4, 35.9, 37.4, 76.2, 118.8, 121.4, 122.7, 123.9, 126.1, 129.1, 137.5, 139.3, 142.5, 146.4, 148.6, 154.6, 157.4, 166.9 ppm. HRMS (ESI⁺): calcd for C₂₅H₃₄N₂O₂ [M+H]⁺ 395.2699, found 395.2690.

(E)-3-(3-Methoxy-2-(pyridin-2-ylmethoxy)phenyl)-N,N-dimethylacrylamide (3g)

2-(Pyridin-2-ylmethoxy)anisole (108 mg, 0.5 mmol), N,N-dimethylacrylamide (75 mg, 0.75 mmol), Pd(OAc)₂ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO₃ (100 mg, 1.0 mmol) in t-AmylOH (2 mL) at 90 °C for 12 h under 1 atm O₂. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded colorless oil (125 mg, 80% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.98 (s, 3H), 3.01 (s, 3H), 3.80 (s, 3H), 5.12 (s, 2H), 6.88 (d, J = 7.6 Hz, 1H), 6.93 (d, J = 15.6 Hz, 1H), 7.02 (t, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 7.18-7.19 (m, 1H), 7.70-7.75 (m, 2H), 7.87 (d, J = 15.6 Hz, 1H), 8.50 (d, J = 4.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 35.7, 37.2, 55.7, 75.2, 113.1, 119.4, 119.8, 121.9, 122.5, 124.3, 129.5, 136.8, 137.0, 146.5, 148.7, 153.0, 157.3, 166.7 ppm. HRMS (ESI⁺): calcd for C₁₈H₂₀N₂O₃ [M+H]⁺ 313.1552, found 313.1553.
**OCH2Py**

**NMe2**

**O**

(E)-N,N-Dimethyl-3-(1-(pyridin-2-ylmethoxy)naphthalen-2-yl)acrylamide (3h)

1-(Pyridin-2-ylmethoxy)naphthalene (118 mg, 0.5 mmol), N,N-dimethylacrylamide (75 mg, 0.75 mmol), Pd(OAc)2 (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO3 (100 mg, 1.0 mmol) in t-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (146 mg, 88% yield). M.p.: 120-122 ºC. 1H NMR (400 MHz, CDCl3): δ = 3.06 (s, 3H), 3.14 (s, 3H), 5.17 (s, 2H), 7.05 (d, J = 15.6 Hz, 1H), 7.29 (t, J = 5.2 Hz, 1H), 7.48-7.51 (m, 2H), 7.63-7.67 (m, 2H), 7.82-7.89 (m, 3H), 8.15-8.19 (m, 2H), 8.63 (d, J = 3.6 Hz, 1H) ppm. 13C NMR (100 MHz, CDCl3): δ = 36.0, 37.3, 77.4, 119.1, 122.2, 122.9, 123.2, 124.3, 124.4, 124.9, 126.8, 127.3, 128.1, 128.3, 135.5, 136.8, 137.5, 149.1, 154.1, 156.7, 166.9 ppm. HRMS (ESI⁺): calcd for C21H20N2O2 [M+H]⁺ 333.1603, found 333.1601.

**OCH2Py**

**NMe2**

**(E)-N,N-Dimethyl-3-(2-(pyridin-2-ylmethoxy)phenyl)acrylamide (3i)**

Pyridin-2-ylmethoxybenzene (93 mg, 0.5 mmol), N,N-dimethylacrylamide (75 mg, 0.75 mmol), Pd(OAc)2 (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO3 (100 mg, 1.0 mmol) in t-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (88 mg, 62% yield). M.p.: 108-110 ºC. 1H NMR (400 MHz, CDCl3): δ = 3.06 (s, 3H), 3.10 (s, 3H), 5.31 (s, 2H), 6.96-7.00 (m, 2H), 7.02 (d, J = 15.6 Hz, 1H), 7.26-7.31 (m, 2H), 7.53 (d, J = 7.2 Hz, 1H), 7.61 (t, J = 6.4 Hz, 1H), 7.76-7.81 (m, 1H), 8.02 (d, J = 15.6 Hz, 1H), 8.59 (d, J = 4.4 Hz, 1H) ppm. 13C NMR (100 MHz, CDCl3): δ = 36.0, 37.5, 70.9, 112.6, 118.8, 121.3, 121.7, 123.0, 124.8, 129.2, 130.8, 137.4, 137.8, 149.1, 156.86, 156.93, 167.3 ppm. HRMS (ESI⁺): calcd for C17H18N2O2 [M+H]⁺ 283.1447, found 283.1443.
(E)-3-(3-Chloro-2-(pyridin-2-ylmethoxy)phenyl)-N,N-dimethylacrylamide (3j)

2-(Pyridin-2-ylmethoxy)chlorobenzene (110 mg, 0.5 mmol), N,N-dimethylacrylamide (75 mg, 0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Ac-Ile-OH (17.3 mg, 0.1 mmol) or Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in $t$-AmylOH (2 mL) at 90 °C for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded colorless oil (124 mg, 78% yield) or (81 mg, 51% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.02 (s, 3H), 3.05 (s, 3H), 5.10 (s, 2H), 7.03 (d, $J$ = 15.6 Hz, 1H), 7.08 (t, $J$ = 8.0 Hz, 1H), 7.25-7.27 (m, 1H), 7.39 (d, $J$ = 8.0 Hz, 1H), 7.43 (d, $J$ = 8.0 Hz, 1H), 7.77-7.79 (m, 2H), 7.81 (d, $J$ = 15.6 Hz, 1H), 8.56 (d, $J$ = 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 35.9, 37.3, 75.6, 120.8, 122.2, 123.0, 125.4, 127.4, 129.0, 131.25, 131.29, 136.5, 137.1, 149.0, 153.3, 156.4, 166.5 ppm. HRMS (ESI$^+$): calcd for C$_{17}$H$_{17}$ClN$_2$O$_2$ [M+H]$^+$ 317.1057, found 317.1054.

(E)-3-(3,5-Dichloro-2-(pyridin-2-ylmethoxy)phenyl)-N,N-dimethylacrylamide (3k)

1,3-Dichloro-4-(pyridin-2-ylmethoxy)benzene (127 mg, 0.5 mmol), N,N-dimethylacrylamide (75 mg, 0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Ac-Ile-OH (17.3 mg, 0.1 mmol) or Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in $t$-AmylOH (2 mL) at 90 °C for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (126 mg, 72% yield) or (47 mg, 27% yield). M.p.: 108-110 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.03 (s, 3H), 3.09 (s, 3H), 5.09 (s, 2H), 6.98 (d, $J$ = 15.6 Hz, 1H), 7.26 (t, $J$ = 6.0 Hz, 1H), 7.40-7.42 (m, 2H), 7.74-7.83 (m,
3H), 8.56 (d, J = 4.8 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 36.0, 37.5, 75.9, 121.9, 122.3, 123.2, 126.8, 129.9, 130.2, 130.8, 132.4, 135.3, 137.3, 149.0, 152.1, 156.1, 166.1$ ppm. HRMS (ESI$^+$): calcld for C$_{17}$H$_{16}$Cl$_2$N$_2$O$_2$ [M+H]$^+$ 351.0667, found 351.0669.

(E)-N,N-Dimethyl-3-(3-nitro-2-(pyridin-2-ylmethoxy)phenyl)acrylamide (3l)

2-(Pyridin-2-ylmethoxy)nitrobenzene (115 mg, 0.5 mmol), N,N-dimethylacrylamide (75 mg, 0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Ac-Ile-OH (17.3 mg, 0.1 mmol) or Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in $\ell$-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (98 mg, 60% yield) or (50 mg, 31% yield). M.p.: 110-112 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.04$ (s, 3H), 3.08 (s, 3H), 5.18 (s, 2H), 7.10 (d, J = 15.6 Hz, 1H), 7.25-7.31 (m, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.76-7.86 (m, 4H), 8.56 (d, J = 4.8 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 36.1, 37.4, 77.5, 122.5, 123.4, 124.9, 125.9, 132.6, 133.4, 135.3, 137.5, 145.2, 148.88, 148.93, 150.3, 155.6, 166.1$ ppm. HRMS (ESI$^+$): calcld for C$_{17}$H$_{17}$N$_3$O$_4$ [M+H]$^+$ 328.1297, found 328.1296.

(E)-Butyl 3-(4,5-dimethyl-2-(pyridin-2-ylmethoxy)phenyl)acrylate (3m)

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106.0 mg, 0.5 mmol), butyl acrylate (96.0 mg, 0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in $\ell$-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded colorless oil (146 mg, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.94$ (t, J = 7.6 Hz, 3H), 1.39-1.49 (m, 2H), 1.65-1.72 (m, 2H), 2.19 (s,
3H), 2.22 (s, 3H), 4.18 (t, $J = 6.4$ Hz, 2H), 5.26 (s, 2H), 6.49 (d, $J = 16.0$ Hz, 1H), 6.73 (s, 1H), 7.24-7.26 (m, 1H), 7.31 (s, 1H), 7.54 (d, $J = 7.6$ Hz, 1H), 7.71-7.73 (m, 1H), 8.06 (d, $J = 16.4$ Hz, 1H), 8.59 (d, $J = 4.0$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 13.9, 18.9, 19.4, 20.5, 30.9, 64.3, 71.0, 114.3, 117.7, 121.2, 121.3, 122.8, 129.4, 129.6, 137.3, 139.8, 140.9, 149.1, 155.2, 157.2, 167.9 ppm. HRMS (ESI$^+$): calcd for C$_{21}$H$_{25}$NO$_3$ [M+H]$^+$ 340.1913, found 340.1914.

(E)-tert-Butyl 3-(4,5-dimethyl-2-(pyridin-2-ylmethoxy)phenyl)acrylate (3n)

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), tert-butyl acrylate (96 mg, 0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in t-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (128 mg, 75% yield). M.p.: 70-72 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.53 (s, 9H), 2.19 (s, 3H), 2.22 (s, 3H), 5.26 (s, 2H), 6.41 (d, $J = 16.4$ Hz, 1H), 6.73 (s, 1H), 7.24-7.26 (m, 1H), 7.31 (s, 1H), 7.56 (d, $J = 7.2$ Hz, 1H), 7.72-7.74 (m, 1H), 8.00 (d, $J = 16.4$ Hz, 1H), 8.58 (d, $J = 4.4$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 18.9, 20.5, 28.4, 71.0, 80.2, 114.3, 119.5, 121.3, 122.8, 129.4, 137.3, 138.7, 140.6, 149.0, 155.1, 157.3, 167.1 ppm. HRMS (ESI$^+$): calcd for C$_{21}$H$_{25}$NO$_3$ [M+H]$^+$ 340.1913, found 340.1909.

(E)-4,5-Dimethyl-1-(pyridin-2-ylmethoxy)-2-styrylbenzene (3o)

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), styrene (78 mg, 0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in t-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O$_2$. 

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Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (131 mg, 83% yield). M.p.: 70-72 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.24 (s, 6H), 5.29 (s, 2H), 6.74 (s, 1H), 7.11 (d, $J$ = 16.4 Hz, 1H), 7.22-7.26 (m, 2H), 7.34 (t, $J$ = 7.2 Hz, 2H), 7.40 (s, 1H), 7.52-7.60 (m, 4H), 7.73 (t, $J$ = 7.6 Hz, 1H), 8.61 (d, $J$ = 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.1, 20.2, 71.2, 114.5, 121.3, 122.7, 123.5, 124.2, 126.5, 127.3, 127.8, 128.3, 128.7, 129.3, 137.2, 137.5, 138.3, 149.0, 153.9, 157.7 ppm. HRMS (ESI$^+$): calcd for C$_{22}$H$_{21}$NO [M+H]$^+$ 316.1701, found 316.1704.

**OCH$_2$Py(E)-4,5-Dimethyl-1-(pyridin-2-ylmethoxy)-2-(4-methylstyryl)benzene (3p)**

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), 4-methylstyrene (89 mg, 0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in t-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (147 mg, 89% yield). M.p.: 116-118 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.23 (s, 3H), 2.24 (s, 3H), 2.36 (s, 3H), 5.28 (s, 2H), 6.74 (s, 1H), 7.09 (d, $J$ = 16.4 Hz, 1H), 7.16 (d, $J$ = 7.6 Hz, 2H), 7.23 (t, $J$ = 6.4 Hz, 1H), 7.39-7.44 (m, 3H), 7.48 (d, $J$ = 16.4 Hz, 1H), 7.58 (d, $J$ = 7.6 Hz, 1H), 7.72 (t, $J$ = 7.6 Hz, 1H), 8.61 (d, $J$ = 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.1, 20.2, 21.3, 71.2, 114.5, 121.3, 122.5, 122.7, 124.4, 126.5, 127.7, 128.3, 129.3, 129.4, 135.5, 137.1, 137.2, 149.0, 153.8, 157.8 ppm. HRMS (ESI$^+$): calcd for C$_{23}$H$_{23}$NO [M+H]$^+$ 330.1858, found 330.1856.

**OCH$_2$PyCl(E)-4,5-Dimethyl-1-(pyridin-2-ylmethoxy)-2-(4-chlorostyryl)benzene (3q)**
1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), 4-chlorostyrene (104 mg, 0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in $\tau$-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (152 mg, 87% yield). M.p.: 124-126 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.23$ (s, 6H), 5.28 (s, 2H), 6.73 (s, 1H), 7.05 (d, $J = 16.4$ Hz, 1H), 7.23 (t, $J = 6.0$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.37(s, 1H), 7.43 (d, $J = 8.0$ Hz, 2H), 7.48-7.56 (m, 2H), 7.72 (t, $J = 7.6$ Hz, 1H), 8.62 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 19.1, 20.2, 71.3, 114.5, 121.3, 122.8, 123.8, 124.2, 127.0, 127.7, 127.8, 128.9, 129.4, 132.8, 136.8, 137.2, 137.8, 149.2, 154.0, 157.7 ppm. HRMS (ESI$^+$): calcd for C$_{22}$H$_{20}$ClNO [M+H]$^+$ 350.1312, found 350.1312.

**Electronic Supplementary Material (ESI) for Chemical Communications**

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$\text{(E)-4,5-Dimethyl-1-(pyridin-2-ylmethoxy)-2-(4-fluorostyryl)benzene (3r)}$

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), 4-fluorostyrene (92 mg, 0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in $\tau$-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (130 mg, 78% yield). M.p.: 114-116 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.23$ (s, 6H), 5.28 (s, 2H), 6.73 (s, 1H), 7.02-7.11 (m, 3H), 7.23 (t, $J = 6.0$ Hz, 1H), 7.37(s, 1H), 7.43-7.50 (m, 3H), 7.55 (d, $J = 7.6$ Hz, 1H), 7.72 (t, $J = 7.6$ Hz, 1H), 8.61 (d, $J = 4.4$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 19.1, 20.2, 71.3, 114.5, 115.5, 115.7, 121.3, 122.7, 123.32, 123.34, 124.0, 127.1, 127.7, 127.9, 128.0, 129.4, 134.45, 134.49, 137.1, 137.5, 149.1, 153.9, 157.7, 161.0, 163.5 ppm. HRMS (ESI$^+$): calcd for C$_{22}$H$_{20}$FNO [M+H]$^+$ 334.1607, found 334.1606.
(E)-4,5-Dimethyl-1-(pyridin-2-ylmethoxy)-2-(3-chlorostyryl)benzene (3s)

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), 3-chlorostyrene (276 mg, 2.0 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in t-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (126 mg, 72% yield). M.p.: 104-106 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.23 (s, 6H), 5.28 (s, 2H), 6.73 (s, 1H), 7.04 (d, $J$ = 16.4 Hz, 1H), 7.18-7.26 (m, 3H), 7.36-7.38 (m, 2H), 7.51-7.55 (m, 3H), 7.72 (t, $J$ = 7.6 Hz, 1H), 8.61 (d, $J$ = 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.1, 20.3, 71.4, 114.6, 121.3, 122.8, 123.7, 124.8, 125.1, 126.3, 126.8, 127.1, 127.9, 129.4, 129.9, 134.7, 137.2, 138.0, 140.2, 149.2, 154.1, 157.6 ppm. HRMS (ESI$^+$): calcd for C$_{22}$H$_{20}$ClNO $[M+H]^+$ 350.1312, found 350.1307.

\[ \text{OCH}_2\text{Py} \]

\[ \text{OMe} \]

\[ \text{OMe} \]

(E)-4,5-Dimethyl-1-(pyridin-2-ylmethoxy)-2-(3,4-dimethoxystyryl)benzene (3t)

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), 3,4-dimethoxystyrene (123 mg, 0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in t-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (141 mg, 75% yield). M.p.: 58-60 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.22 (s, 6H), 3.90 (s, 3H) 3.93 (s, 3H), 5.28 (s, 2H), 6.72 (s, 1H), 6.85 (d, $J$ = 8.4 Hz, 1H), 7.05-7.09 (m, 3H), 7.22 (t, $J$ = 6.0 Hz, 1H), 7.38-7.42 (m, 2H), 7.57 (d, $J$ = 8.0 Hz, 1H), 7.69 (t, $J$ = 7.6 Hz, 1H), 8.60 (d, $J$ = 4.0 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.1, 20.2, 55.9, 56.1, 71.3, 108.9, 111.4, 114.5, 119.7, 121.3, 121.7, 122.7, 124.4, 127.6, 128.1, 129.4, 131.5, 137.1, 148.7, 149.1, 149.2, 153.8, 157.8 ppm. HRMS (ESI$^+$): calcd for C$_{24}$H$_{25}$NO$_3$ $[M+H]^+$ 376.1913, found 376.1914.
1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), n-decene (105 mg, 0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in t-AmylOH (2 mL) at 90 °C for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a mixture as colorless oil (132 mg, 75% yield). The two products could not be isolated by silica gel column chromatography, but a single ortho-alkyl phenol 3ua could be obtained by catalytic hydrogenation of the mixture (3u+3u’, 1:1.5).

2-Decyl-4,5-dimethylphenol (3ua)

To a stirred solution of the mixture (3u+3u’, 0.3 mmol) and absolute EtOH (6.0 mL) was added Pd/C (100 mg, 10% Pd). After being stirred under an atmosphere of H$_2$ (balloon) for overnight, the mixture was filtered over a pad of celite with EtOAc (20 mL) and concentrated under reduce pressure. The residue was purified by flash chromatography over silica gel to give desired product 3ua as colorless oil (71 mg, 90% Yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.86 (t, $J = 7.2$ Hz, 3H), 1.20-1.32 (m, 14H), 1.56-1.61 (m, 2H), 2.16 (s, 3H), 2.17 (s, 3H), 2.50 (t, $J = 7.6$ Hz, 2H), 4.47 (br. s., 1H), 6.56 (s, 1H), 6.86 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 14.3, 18.9, 19.45, 19.48, 22.8, 29.5, 29.7, 29.8, 29.9, 30.0, 30.3, 32.1, 116.8, 125.7, 128.6, 131.4, 135.2, 151.4 ppm. HRMS (ESI$^+$): calcd for C$_{18}$H$_{30}$O [M+Na]$^+$ 285.2194, found 285.2196.
mg, 0.75 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (100 mg, 1.0 mmol) in t-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a mixture as colorless oil (125 mg, 66% yield). The two products could not be isolated by silica gel column chromatography, but a single ortho-alkyl phenol 3va could be obtained by catalytic hydrogenation of the mixture (3v+3v′, 1:2.5).

2-Dodecyl-4,5-dimethylphenol (3va)

To a stirred solution of the mixture (3v+3v′, 0.3 mmol) and absolute EtOH (6.0 mL) was added Pd/C (100 mg, 10% Pd). After being stirred under an atmosphere of H$_2$ (balloon) for overnight, the mixture was filtered over a pad of celite with EtOAc (20 mL) and concentrated under reduce pressure. The residue was purified by flash chromatography over silica gel to give desired product 3va as colorless oil (75 mg, 86% Yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.86 (t, $J$ = 6.8 Hz, 3H), 1.20-1.32 (m, 18H), 1.54-1.59 (m, 2H), 2.16 (s, 3H), 2.17 (s, 3H), 2.50 (t, $J$ = 8.0 Hz, 2H), 4.48 (br. s., 1H), 6.56 (s, 1H), 6.86 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 14.3, 18.9, 19.45, 19.48, 22.8, 27.9, 29.5, 29.71, 29.77, 29.80, 29.83, 30.0, 30.3, 32.1, 116.7, 125.7, 128.6, 131.4, 135.2, 151.4 ppm. HRMS (ESI$^+$): calcd for C$_{20}$H$_{34}$O [M+Na]$^+$ 313.2507, found 313.2510.

(2E,2′E)-3,3′-(2-(Pyridin-2-ylmethoxy)-1,3-phenylene)bis(N,N-dimethylacrylamide) (4a)

Pyridin-2-ylmethoxybenzene (93 mg, 0.5 mmol), N,N-dimethylacrylamide (248 mg, 2.5 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (200 mg, 2.0 mmol) in t-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O$_2$. 
Purification via silica gel column chromatography using 50% acetone in petroleum ether afforded a slight yellow solid (139 mg, 73% yield). M.p.: 38-40 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.01 (s, 6H), 3.05 (s, 6H), 4.95 (s, 2H), 7.02 (d, $J$ = 15.6 Hz, 2H), 7.16 (t, $J$ = 7.6 Hz, 1H), 7.21 (t, $J$ = 6.0 Hz, 1H), 7.53 (d, $J$ = 7.6 Hz, 2H), 7.73-7.79 (m, 2H), 7.86 (d, $J$ = 15.6 Hz, 2H), 8.54 (d, $J$ = 4.8 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 36.0, 37.4, 76.8, 120.3, 122.2, 123.1, 125.1, 130.0, 130.1, 137.0, 137.2, 149.2, 156.3, 156.4, 166.7 ppm. HRMS (ESI$^+$): calcd for C$_{22}$H$_{25}$N$_3$O$_3$ [M+H]$^+$ 380.1974, found 380.1967.

(2$E$,$2'E$)-3,3'-(5-Methyl-2-(pyridin-2-ylmethoxy)-1,3-phenylene)bis(N,N-dimethyl acrylamide) (4b)

4-(Pyridin-2-ylmethoxy)toluene (100 mg, 0.5 mmol), N,N-dimethylacrylamide (248 mg, 2.5 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (200 mg, 2.0 mmol) in t-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 50% acetone in petroleum ether afforded a white solid (142 mg, 72% yield). M.p.: 152-154 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.37 (s, 3H), 3.02 (s, 6H), 3.08 (s, 6H), 4.98 (s, 2H), 6.99 (d, $J$ = 15.6 Hz, 2H), 7.30-7.31 (m, 1H), 7.35 (s, 2H), 7.83-7.87 (m, 4H), 8.53 (d, $J$ = 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.0, 36.0, 37.4, 76.5, 120.0, 122.4, 123.2, 129.6, 130.4, 134.5, 137.0, 137.7, 148.7, 154.2, 156.2, 166.8 ppm. HRMS (ESI$^+$): calcd for C$_{23}$H$_{27}$N$_3$O$_3$ [M+H]$^+$ 394.2131, found 394.2130.

(2$E$,$2'E$)-3,3'-(5-tert-Butyl-2-(pyridin-2-ylmethoxy)-1,3-phenylene)bis(N,N-dimethyl acrylamide) (4c)
tert-Butyl-4-(pyridin-2-ylmethoxy)benzene (121 mg, 0.5 mmol), N,N-dimethylacrylamide (248 mg, 2.5 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (200 mg, 2.0 mmol) in t-AmylOH (2 mL) at 90 °C for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 50% acetone in petroleum ether afforded a white solid (164 mg, 75% yield). M.p.: 162-164 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.35 (s, 9H), 3.02 (s, 6H), 3.06 (s, 6H), 4.97 (s, 2H), 7.03 (d, $J$ = 15.6 Hz, 2H), 7.28 (t, $J$ = 6.0 Hz, 1H), 7.53 (s, 2H), 7.80-7.87 (m, 4H), 8.56 (d, $J$ = 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 31.4, 34.6, 36.0, 37.4, 76.0, 120.0, 122.2, 123.1, 127.5, 129.2, 137.6, 137.7, 147.7, 148.8, 154.1, 156.4, 166.9 ppm. HRMS (ESI$^+$): calcd for C$_{26}$H$_{33}$N$_3$O$_3$ [M+H]$^+$ 436.2600, found 436.2603.

(2E,2′E)-3,3′-(5-Methoxy-2-(pyridin-2-ylmethoxy)-1,3-phenylene)bis(N,N-dimethylacrylamide) (4d)

4-(Pyridin-2-ylmethoxy)anisole (108 mg, 0.5 mmol), N,N-dimethylacrylamide (248 mg, 2.5 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (200 mg, 2.0 mmol) in t-AmylOH (2 mL) at 90 °C for 20 h under 1 atm O$_2$. Purification via silica gel column chromatography using 50% acetone in petroleum ether afforded a slight yellow solid (143 mg, 70% yield). M.p.: 167-170 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.02 (s, 3H), 3.07 (s, 6H), 3.85 (s, 6H), 4.97 (s, 2H), 6.99 (d, $J$ = 15.2 Hz, 2H), 7.06 (s, 2H), 7.30 (t, $J$ = 5.6 Hz, 1H), 7.81-7.89 (m, 4H), 8.55 (d, $J$ = 4.8 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 36.0, 37.4, 55.9, 76.5, 114.7, 120.5, 122.5, 123.2, 130.7, 136.9, 137.9, 148.5, 150.2, 156.2, 166.7 ppm. HRMS (ESI$^+$): calcd for C$_{23}$H$_{27}$N$_3$O$_4$ [M+H]$^+$ 410.2080, found 410.2075.
(2E,2′E)-Di-Butyl 3,3′-(5-methoxy-2-(pyridin-2-ylmethoxy)-1,3-phenylene) diacrylate (4e)

4-(Pyridin-2-ylmethoxy)anisole (108 mg, 0.5 mmol), n-butyl acrylate (320 mg, 2.5 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (200 mg, 2.0 mmol) in t-AmloH (2 mL) at 90 °C for 12 h under 1 atm O$_2$. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a slight yellow solid (187 mg, 80% yield). M.p.: 60-62 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.90 (t, $J$ = 7.2 Hz, 6H), 1.33-1.43 (m, 4H), 1.60-1.67 (m, 4H), 3.83 (s, 3H), 4.14 (t, $J$ = 6.4 Hz, 4H), 4.94 (s, 2H), 6.41 (d, $J$ = 16.0 Hz, 2H), 7.12 (s, 2H), 7.26-7.27 (m, 1H), 7.67 (d, $J$ = 7.2 Hz, 1H), 7.78 (m, 1H), 7.90 (d, $J$ = 16.0 Hz, 2H), 8.57 (d, $J$ = 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 13.9, 19.3, 30.8, 55.8, 64.6, 78.2, 114.4, 120.7, 122.2, 123.2, 130.0, 137.4, 138.5, 149.1, 150.7, 156.1, 156.3, 166.8 ppm. HRMS (ESI$^+$): calcd for C$_{27}$H$_{35}$NO$_6$ [M+H]$^+$ 468.2386, found 468.2384.

(E)-Butyl 3-(3-((E)-3-(dimethylamino)-3-oxoprop-1-enyl)-5-methoxy-2-(pyridin-2-ylmethoxy)phenyl)acrylate (4f)

4-(Pyridin-2-ylmethoxy)anisole (108 mg, 0.5 mmol), N,N-dimethylacrylamide (50 mg, 0.5 mmol), Pd(OAc)$_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO$_3$ (200 mg, 2.0 mmol) in t-AmloH (2 mL) at 90 °C for 10 h under 1 atm O$_2$. Subsequently, butyl acrylate (96.0 mg, 0.75 mmol) was added for another 10 h under 1 atm O$_2$. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (105 mg, 48% yield). M.p.: 64-66 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.87 (t, $J$ = 7.6 Hz, 3H), 1.31-1.40 (m, 2H), 1.57-1.64 (m, 2H), 3.00 (s, 3H), 3.05 (s, 3H), 3.81 (s, 3H), 4.12 (t, $J$ = 6.4 Hz, 2H), 4.89 (s, 2H), 6.38 (d, $J$ = 16.0 Hz, 1H), 7.00-7.08 (m, 3H), 7.21 (t, $J$ = 6.0 Hz, 1H), 7.66-7.83 (m, 3H), 7.90 (d, $J$ = 16.0 Hz, 1H), 8.54 (d, $J$ = 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ =
13.9, 19.3, 29.8, 36.1, 37.5, 55.9, 64.6, 77.8, 112.9, 116.4, 120.5, 120.7, 122.2, 123.1, 129.9, 130.9, 136.9, 137.1, 138.8, 149.4, 150.6, 156.2, 156.4, 166.7, 166.9 ppm. HRMS (ESI^+): calcd for C_{25}H_{30}N_2O_5 [M+H]^+ 439.2233, found 439.2232.

(E)-3,3'-Bis(4-chlorostyryl)-2,2'-bis(pyridin-2-ylmethoxy)-1,1'-binaphthyl (4g)

2,2'-Bis(pyridin-2-ylmethoxy)-1,1'-binaphthyl (234 mg, 0.5 mmol), 4-chlorostyrene (345 mg, 2.5 mmol), Pd(OAc)_2 (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and KHCO_3 (200 mg, 2.0 mmol) in t-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 15% EtOAc in petroleum ether afforded a white solid (204 mg, 55% yield). M.p.: 110-112 ºC. 1H NMR (400 MHz, CDCl_3): δ = 4.70 (d, J = 13.2 Hz, 2H), 4.99 (d, J = 13.2 Hz, 2H), 6.79 (d, J = 7.6 Hz, 2H), 7.01 (t, J = 6.4 Hz, 2H), 7.19-7.30 (m, 10H), 7.38-7.41 (m, 8H), 7.49 (d, J = 16.4 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H), 8.18 (s, 2H), 8.30 (d, J = 4.8 Hz, 2H) ppm. 13C NMR (100 MHz, CDCl_3): δ = 76.3, 121.4, 122.4, 124.6, 125.6, 125.8, 125.9, 126.4, 126.9, 128.0, 128.2, 129.0, 129.7, 131.1, 133.5, 133.8, 136.1, 136.7, 136.8, 148.3, 153.8, 157.2 ppm. HRMS (ESI^+): calcd for C_{48}H_{34}Cl_2N_2O_2 [M+H]^+ 741.2076, found 741,2071.

VI. Deprotection of ortho-alkenylated phenols and characterization

General procedure for deprotection by catalytic hydrogenation

Method A (H_2, 1 atm): To a stirred solution of ortho-alkenyl phenol ethers (0.3 mmol) in absolute EtOH (6.0 mL) was added Pd/C (100 mg, 10% Pd). After being stirred under an atmosphere of H_2 (balloon) for overnight, the mixture was filtered over a pad
of celite with EtOAc (20 mL) and concentrated under reduced pressure. The residue was purified by flash chromatography over silica gel to give corresponding phenols.

**Method B** (H₂, 15 atm): To a stirred solution of ortho-alkenyl phenol ethers (0.3 mmol) in absolute EtOH (6.0 mL) was added Pd/C (10 mg, 10% Pd). After being stirred under 15 atm H₂ for overnight, the mixture was filtered over a pad of celite with EtOAc (20 mL) and concentrated under reduced pressure. The residue was purified by flash chromatography over silica gel to give the corresponding phenols.

![Chemical structure](image)

**3-(2-Hydroxy-4,5-dimethylphenyl)-N,N-dimethylpropanamide (3ca)**

The product 3ca was synthesized according to **Method A** (60 mg, 90% yield) or **Method B** (61 mg, 92% yield) as a white solid. M.p.: 122-124 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.15 (s, 3H), 2.17 (s, 3H), 2.66-2.69 (m, 2H), 2.86-2.89 (m, 2H), 2.93 (s, 3H), 2.95 (s, 3H), 6.73 (s, 1H), 6.80 (s, 1H), 9.40 (br. s., 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 18.8, 19.6, 24.3, 35.7, 36.0, 37.2, 119.3, 125.6, 127.9, 131.7, 136.3, 153.4, 174.0 ppm. HRMS (ESI⁺): calcd for C₁₃H₁₉NO₂ [M+Na]+ 244.1313, found 244.1317.

![Chemical structure](image)

**3-(3-tert-Butyl-2-hydroxyphenyl)-N,N-dimethylpropanamide (3ea)**

The product 3ea was synthesized according to **Method A** as colorless oil (63 mg, 83% yield). ¹H NMR (400 MHz, CDCl₃): δ = 1.42 (s, 9H), 2.70 (t, J = 4.2 Hz, 2H), 2.92-2.95 (m, 8H), 6.75 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 7.2 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 9.79 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 24.7, 29.9, 35.1, 35.8, 36.1, 37.2, 119.4, 125.2, 128.6, 129.5, 138.6, 154.6, 174.2 ppm. HRMS (ESI⁺): calcd for C₁₅H₂₃NO₂ [M+Na]+ 272.1626, found 272.1625.
The product 4aa was synthesized according to Method A as a white solid (75 mg, 85% yield). M.p.: 148-150 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.66$ (t, $J = 6.8$ Hz, 4H), 2.93-2.99 (m, 16H), 6.73 (t, $J = 7.6$ Hz, 1H), 6.98 (d, $J = 7.6$ Hz, 2H), 9.87 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 26.2$, 34.9, 35.8, 37.4, 119.9, 128.9, 129.2, 153.8, 173.8 ppm. HRMS (ESI$^+$): calcd for C$_{16}$H$_{24}$N$_2$O$_3$ [M+Na]$^+$ 315.1685, found 315.1683.

**General procedure for deprotection by Mg in methanol**

To a stirred solution of (E)-3-(4,5-dimethyl-2-(pyridin-2-ylmethoxy)phenyl)-N,N-di methylacrylamide (3c, 0.3 mmol) in MeOH (10 mL) was added Mg turnings (50.4 mg, 2.1 mmol) at 0 °C. The suspension then warmed to room temperature and stirred for 24 h. The mixture was filtered over a pad of celite with EtOAc (20 mL). The filtrate was successively washed with aqueous saturated solution of NaHCO$_3$ (10 mL) and brine (10 mL), dried (Na$_2$SO$_4$) and then concentrated under reduced pressure. The residue was purified by flash chromatography to give the corresponding product 3ca as a white solid (47 mg, 70%). M.p.: 122-124 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.15$ (s, 3H), 2.17 (s, 3H), 2.66-2.69 (m, 2H), 2.86-2.89 (m, 2H), 2.93 (s, 3H), 2.95 (s, 3H), 6.73 (s, 1H), 6.80 (s, 1H), 9.40 (br. s., 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.8$, 19.6, 24.3, 35.7, 36.0, 37.2, 119.3, 125.6, 127.9, 131.7, 136.3, 153.4, 174.0 ppm. HRMS (ESI$^+$): calcd for C$_{13}$H$_{19}$NO$_2$ [M+Na]$^+$ 244.1313, found 244.1317.

**General procedure for deprotection by BBr$_3$**

To a solution of ortho-alkenyl phenol ethers (2 mmol) in dry CH$_2$Cl$_2$ (40 mL) at -40 °C was slowly added BBr$_3$ (3 mL, 4.0 M solution in CH$_2$Cl$_2$; 12 mmol) under a
nitrogen atmosphere. The solution was stirred for 15 min at the same temperature and then allowed to worm to room temperature and further stirred 40 h. The reaction was quenched with excess amount of H$_2$O. Then the mixture was neutralized by NaHCO$_3$. Subsequently, the mixture was worked up by an appropriate method to give the desired products.

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(E)-3-(2-Hydroxy-4,5-dimethylphenyl)-N,N\text{-dimethylacrylamide (3cb)}
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The crude product was precipitated after neutralization by NaHCO$_3$, and was purified by flash chromatography to give the corresponding product 3cb as a white solid (341 mg, 78% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 2.13$ (s, 3H), 2.14 (s, 3H), 2.92 (s, 3H), 3.13 (s, 3H), 6.67 (s, 1H), 7.03 (d, $J = 15.6$ Hz, 1H), 7.40 (s, 1H), 7.67 (d, $J = 15.6$ Hz, 1H), 9.62 (s, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 18.3$, 19.5, 35.3, 36.8, 115.8, 117.1, 119.2, 126.7, 128.7, 136.6, 139.1, 154.2, 166.2 ppm. HRMS (ESI$^+$): calcd for C$_{13}$H$_{17}$NO$_2$ [M+Na]$^+$ 242.1157, found 242.1153.

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(E)-2-(4-Chlorostyryl)-4,5\text{-dimethylphenol (3qb)}
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After the neutralization, the mixture was extracted with CH$_2$Cl$_2$, and the organic layers were dried over Na$_2$SO$_4$, filtered, and evaporated to dryness. The residue was purified by column chromatography to give the desired products as a white solid (319 mg, 62% Yield). M.p.: 118-120 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.29$ (s, 3H), 2.32 (s, 3H), 4.70 (br. s, 1H), 7.04 (s, 1H), 7.22 (d, $J = 15.6$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.73 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 19.2$, 20.2, 118.9, 122.3, 128.85, 128.89, 129.00, 129.5, 131.07, 131.10, 133.0, 139.1, 144.4, 150.2 ppm. HRMS (ESI$^+$): calcd for C$_{16}$H$_{15}$ClO [M+Na]$^+$ 281.0709,
found 281.0714.

References:


VII. Copies of $^1$H and $^{13}$C NMR spectra
Electronic Supplementary Material (ESI) for Chemical Communications

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[Diagram of chemical structures and spectra]

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[Chemical structures and spectra]