Supporting Information

Low-Valent Cobalt-Catalyzed C–H Allylation

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1. Materials and Methods

**General.** All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still.¹ NMR spectra were measured on a Bruker AV-400 spectrometer and reported in parts per million. ¹H NMR spectra were recorded at 400 MHz in CDCl₃ were referenced internally to tetramethylsilane as a standard, and ¹³C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. Analytical gas chromatography (GC) was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector. Mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer. High resolution (HR MS) mass spectra were recorded by ESI-TOF.

**Materials.** Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., and other commercial suppliers and used as received. Co(acac)₃ (>98.0%), Co(acac)₂ (>99.0%), CoCl₂ (99.9%), and CoBr₂ (99.0%) were purchased from Aldrich Inc. and Tokyo Chemical Industry Co., and used as received. Co(OAc)₂ (>98.0%) were purchased from Alfa Aesar and used as received. Solvents were dried over sodium (for THF, Et₂O) by refluxing for overnight and freshly distilled prior to use. 2-Phenylpyridines², aromatic imines³ and allyl carbonate⁴ was prepared according to the corresponding literatures. Grignard reagents were purchased or were prepared from the corresponding halides and magnesium turnings in anhydrous THF, and titrated prior to use.

2. Investigation of the Key Reaction Parameters

The reactions were carried out according to the general procedure for cobalt catalyzed ortho-C–H allylation by the related parameter optimization shown in Tables S1, S2, and S3.
**Table S1. Investigation of the effect of allylic oxygen electrophiles (2) for the synthesis of (E)-2-(2-cinnamylphenyl)pyridine (3a)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>OR</th>
<th>Cobalt salt</th>
<th>RMgX</th>
<th>Solvent</th>
<th>3a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-OH</td>
<td>Co(acac)_3</td>
<td>TMSCH&lt;sub&gt;2&lt;/sub&gt;MgCl</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>n.d.</td>
</tr>
<tr>
<td>2</td>
<td>-OAc</td>
<td>Co(acac)_3</td>
<td>TMSCH&lt;sub&gt;2&lt;/sub&gt;MgCl</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>-OMe</td>
<td>Co(acac)_3</td>
<td>TMSCH&lt;sub&gt;2&lt;/sub&gt;MgCl</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>-OBoc</td>
<td>Co(acac)_3</td>
<td>TMSCH&lt;sub&gt;2&lt;/sub&gt;MgCl</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>-P(O)(OEt)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Co(acac)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>TMSCH&lt;sub&gt;2&lt;/sub&gt;MgCl</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>30</td>
</tr>
</tbody>
</table>

*Reactions conditions: 1a (0.2 mmol), 2 (0.3 mmol), Co(acac)<sub>3</sub> (10 mol %), TMSCH<sub>2</sub>MgCl (0.4 mmol), 25 ºC, 12 h, isolated yield. n.d. = Not detected by GC-MS and TLC analyses.*

**Table S2. Investigation of the effect of Cobalt catalysts for the synthesis of (E)-2-(2-cinnamylphenyl)pyridine (3a)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>OR</th>
<th>Cobalt salt</th>
<th>RMgX</th>
<th>Solvent</th>
<th>3a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-OBoc</td>
<td>Co(acac)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>TMSCH&lt;sub&gt;2&lt;/sub&gt;MgCl</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>-OBoc</td>
<td>CoCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>TMSCH&lt;sub&gt;2&lt;/sub&gt;MgCl</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>-OBoc</td>
<td>CoBr&lt;sub&gt;2&lt;/sub&gt;</td>
<td>TMSCH&lt;sub&gt;2&lt;/sub&gt;MgCl</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>-OBoc</td>
<td>Co(acac)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>TMSCH&lt;sub&gt;2&lt;/sub&gt;MgCl</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>62</td>
</tr>
<tr>
<td>5</td>
<td>-OBoc</td>
<td>Co(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>TMSCH&lt;sub&gt;2&lt;/sub&gt;MgCl</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>9</td>
</tr>
</tbody>
</table>

*Reactions conditions: 1a (0.2 mmol), 2a (0.3 mmol), [Co] (10 mol %), TMSCH<sub>2</sub>MgCl (0.4 mmol), 25 ºC, 12 h, isolated yield.
Table S3. Investigation of the effect of RMgX for the synthesis of (E)-2-(2-cinnamylphenyl)pyridine (3a)\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>OR</th>
<th>Cobalt salt</th>
<th>RMgX</th>
<th>Solvent</th>
<th>3a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-OBoc</td>
<td>Co(acac)(_3)</td>
<td>TMSCH(_2)MgCl</td>
<td>Et(_2)O</td>
<td>70</td>
</tr>
<tr>
<td>2(^b)</td>
<td>-OBoc</td>
<td>Co(acac)(_3)</td>
<td>TMSCH(_2)MgCl</td>
<td>Et(_2)O</td>
<td>95 (3a/3a(_{di}) = 10/1)(^c)</td>
</tr>
<tr>
<td>3</td>
<td>-OBoc</td>
<td>Co(acac)(_3)</td>
<td>PhMgBr</td>
<td>THF</td>
<td>&lt;10</td>
</tr>
<tr>
<td>4</td>
<td>-OBoc</td>
<td>Co(acac)(_3)</td>
<td>CH(_3)MgCl</td>
<td>THF</td>
<td>&lt;10</td>
</tr>
<tr>
<td>5</td>
<td>-OBoc</td>
<td>Co(acac)(_3)</td>
<td>i-PrMgCl</td>
<td>THF</td>
<td>n.d.</td>
</tr>
<tr>
<td>6</td>
<td>-OBoc</td>
<td>Co(acac)(_3)</td>
<td>n-BuMgBr</td>
<td>THF</td>
<td>n.d.</td>
</tr>
<tr>
<td>7</td>
<td>-OBoc</td>
<td>Co(acac)(_3)</td>
<td>CyMgBr</td>
<td>THF</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>-OBoc</td>
<td>Co(acac)(_3)</td>
<td>t-BuMgBr</td>
<td>THF</td>
<td>trace</td>
</tr>
</tbody>
</table>

\(^a\) Reactions conditions: 1a (0.2 mmol), 2a (0.3 mmol), Co(acac)\(_3\) (10 mol%), TMSCH\(_2\)MgCl (0.4 mmol), 25 ºC, 12 h, isolated yield. \(^b\) 2a (0.4 mmol) was used. \(^c\) The ratio was detected by \(^1\)H NMR spectroscopy. n.d. = Not detected by GC-MS and TLC analyses.

3. General Procedure for Cobalt-Catalyzed ortho-C–H Allylation

General Procedure A

In a 10 mL Schlenk tube were placed 2-arylpyridine 1 (0.20 mmol), allyl carbonates 2 (0.40 mmol), Co(acac)\(_3\) (10 mol%), and TMSCH\(_2\)MgCl (0.4 mmol) in Et\(_2\)O. The reaction mixture was stirred at rt for 12 h.
mmol), Co(acac)₃ (7 mg, 0.02 mmol), and Et₂O (0.2 mL). To the mixture was added a solution of TMSCH₂MgCl (1.0 M, 0.40 mL, 0.40 mmol) in Et₂O dropwise at 0 °C under N₂. The reaction mixture was stirred at 25 °C for 12 h, and then quenched by the addition of saturated NH₄Cl aqueous solution (2.0 mL). The resulting mixture was stirred at room temperature for 10 min, and then extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to provide the product 3.

**General Procedure B**

![Chemical structure](image)

In a 10 mL Schlenk tube were placed aromatic imines 4 (0.20 mmol), allyl carbonate 2a (0.40 mmol), Co(acac)₃ (7 mg, 0.02 mmol), and Et₂O (0.2 mL). To the mixture was added a solution of TMSCH₂MgCl (1.0 M, 0.40 mL, 0.40 mmol) in Et₂O dropwise at 0 °C under N₂. The reaction mixture was stirred at 25 °C for 12 h, and then quenched by the addition of saturated 3 M HCl aqueous solution (2.0 mL). The resulting mixture was stirred at room temperature for 3 h, and then extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to provide the product 5.

**(E)-2-(2-Cinnamylphenyl)pyridine (Table 2, 3a)**

The general procedure A was applied to 2-phenylpyridine (31 mg, 0.2 mmol), (E)-tert-butyl
cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)$_3$ (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (46.5 mg, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.71$ (d, $J$ = 4.4 Hz, 1H), 7.40 (d, $J$ = 7.6 Hz, 2H), 7.37–7.32 (m, 3H), 7.26–7.24 (m, 5H), 7.17–7.16 (m, 1H), 6.29–6.18 (m, 2H), 3.65 (d, $J$ = 5.2 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 159.5, 149.0, 139.1, 140.5, 137.9, 137.5, 136.2, 130.8, 130.2, 129.9, 129.5, 128.4, 128.0, 126.4, 126.1, 124.5, 121.9, 36.7. HRMS (ESI$^+$): calcd for C$_{20}$H$_{18}$N [M+H]$^+$ 272.1439, found 272.1435.

(E)-2-(2-Cinnamyl-4-methylphenyl)pyridine (Table 2, 3b)

The general procedure A was applied to 2-(p-tolyl)pyridine (34 mg, 0.2 mmol), (E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)$_3$ (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (47 mg, 82% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.68$ (d, $J$ = 4.4 Hz, 1H), 7.67 (t, $J$ = 7.6 Hz, 1H), 7.37 (d, $J$ = 7.6 Hz, 1H), 7.31–7.19 (m, 6H), 7.16–7.11 (m, 3H), 6.29–6.19 (m, 2H), 3.62 (d, $J$ = 5.6 Hz, 2H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 159.9, 149.0, 138.2, 137.7, 137.6, 136.1, 130.8, 130.6, 129.8, 129.6, 128.4, 127.1, 126.9, 126.0, 124.2, 121.5, 36.6, 21.2. HRMS (ESI$^+$): calcd for C$_{21}$H$_{20}$N [M+H]$^+$ 286.1596, found 286.1589.

(E)-2-(2-Cinnamyl-6-methylphenyl)pyridine (Table 2, 3c)

The general procedure A was applied to 2-(o-tolyl)pyridine (34 mg, 0.2 mmol), (E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)$_3$ (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15)
to afford the title compound (44.5 mg, 78% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.65 (d, $J$ = 3.6 Hz, 1H), 7.63 (t, $J$ = 7.6 Hz, 1H), 7.18–7.07 (m, 10H), 6.12–6.05 (m, 1H), 5.99 (d, $J$ = 16.0 Hz, 1H), 3.20 (d, $J$ = 5.2 Hz, 2H), 2.00 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 159.3, 149.5, 140.2, 137.9, 137.5, 136.2, 136.1, 130.5, 129.2, 128.4, 128.2, 128.1, 127.0, 126.9, 126.0, 124.9, 121.8, 36.8, 20.3. HRMS (ESI$^+$): calcd for C$_{21}$H$_{20}$N [M+H]$^+$ 286.1596, found 286.1590.

![Chemical structures of 3d and 3d']

(E)-2-(2-Cinnamyl-5-methylphenyl)pyridine (Table 2, 3d) and (E)-2-(2-cinnamyl-3-methylphenyl)pyridine (Table 2, 3d')

The general procedure A was applied to 2-(m-tolyl)pyridine (34 mg, 0.2 mmol), (E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)$_3$ (7 mg, 0.02 mmol) at 25 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title mixed compounds (49 mg, 86% yield). The ratio of 3d/3d' (1/1.8) was determined by $^1$H NMR. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.69 (m, 1H), 7.71–7.65 (m, 1H), 7.38 (d, $J$ = 7.6 Hz, 1H), 7.23–7.16 (m, 9H), 6.27–6.17 (m, 0.7H, 3d'), 6.27–6.17 (m, 0.7H, 3d), 6.06 (d, $J$ = 16.0 Hz, 0.7H, 3d), 3.59 (m, 2H), 2.40 (s, 2H, 3d'), 2.37 (s, 1.1H, 3d); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 160.5, 159.9, 149.2, 149.1, 141.4, 140.3, 137.61, 137.59, 136.02, 135.97, 135.89, 135.5, 134.7, 130.54, 130.50, 130.13, 130.08, 129.7, 129.2, 128.7, 128.4, 127.8, 126.8, 126.2, 125.98, 125.94, 124.1, 121.7, 36.2, 33.2, 20.9, 20.0. HRMS (ESI$^+$): calcd for C$_{21}$H$_{20}$N [M+H]$^+$ 286.1596, found 286.1591.

![Chemical structure of 3e]

(E)-2-(2-Cinnamyl-4-methoxyphenyl)pyridine (Table 2, 3e)

The general procedure A was applied to 2-(4-methoxyphenyl)pyridine (37 mg, 0.2 mmol),
(E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (47 mg, 78% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.67 (d, J = 4.4 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.38–7.37 (m, 2H), 7.26–7.17 (m, 7H), 6.90 (s, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.32–6.08 (m, 2H), 3.83 (s, 3H), 3.65 (d, J = 2.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 159.7, 149.1, 139.5, 137.5, 136.1, 133.3, 131.2, 130.9, 129.3, 128.4, 126.9, 126.0, 124.2, 121.4, 115.6, 111.6, 55.3, 36.8. HRMS (ESI⁺): calcd for C₂₁H₂₀NO [M+H]⁺ 302.1545, found 302.1538.

(E)-2-(2-Cinnamyl-3-methoxyphenyl)pyridine (Table 2, 3f)
The general procedure A was applied to 2-(3-methoxyphenyl)pyridine (37 mg, 0.2 mmol), (E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (50.5 mg, 84% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.69 (d, J = 4.0 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.31–7.23 (m, 6H), 7.15 (m, 1H), 7.01 (d, J = 7.6 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.31–6.24 (m, 1H), 6.06 (d, J = 16.0 Hz, 1H), 3.88 (s, 3H), 3.58 (d, J = 6.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 159.7, 157.9, 149.2, 142.1, 137.9, 135.9, 129.7, 129.4, 128.3, 127.1, 126.6, 126.4, 125.9, 124.3, 122.2, 121.8, 110.6, 55.7, 30.2. HRMS (ESI⁺): calcd for C₂₁H₂₀NO [M+H]⁺ 302.1545, found 302.1536.

(E)-2-(2-Cinnamyl-4-fluorophenyl)pyridine (Table 2, 3g)
The general procedure A was applied to 2-(4-fluorophenyl)pyridine (35 mg, 0.2 mmol), (E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25
°C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (42 mg, 73% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.69 (d, J = 4.4 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.40–7.36 (m, 2H), 7.27–7.19 (m, 6H), 7.06 (d, J = 10.0 Hz, 1H), 6.98 (t, J = 8.4 Hz, 1H), 6.28–6.13 (m, 2H), 3.63 (d, J = 5.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 161.5 (d, J = 246.0 Hz), 158.9, 149.2, 140.6 (d, J = 7.0 Hz), 137.2, 136.5, 136.3, 131.5 (d, J = 8.0 Hz), 131.4, 128.4, 127.1, 126.1, 124.2, 121.9, 116.5 (d, J = 11.0 Hz), 113.2 (d, J = 21.0 Hz), 36.6; ¹⁹F NMR (377 MHz, CDCl₃): δ = –113.85. HRMS (ESI⁺): calcd for C₂₀H₁₇FN [M+H]⁺ 290.1345, found 290.1337.

![Chemical structure](image)

(E)-2-(2-Cinnamyl-3-fluorophenyl)pyridine (Table 2, 3h)

The general procedure A was applied to 2-(3-fluorophenyl)pyridine (35 mg, 0.2 mmol), (E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (48 mg, 83% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.71 (d, J = 4.4 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.41–7.20 (m, 7H), 7.16–7.09 (m, 2H), 6.28–6.21 (m, 1H), 6.12 (d, J = 6.0 Hz, 1H), 3.64 (d, J = 6.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 160.4 (d, J = 244.0 Hz), 158.6, 149.3, 142.7 (d, J = 4.0 Hz), 137.5, 136.3, 130.5, 128.3, 128.1, 127.5 (d, J = 9.0 Hz), 126.9, 126.0, 125.5 (d, J = 3.0 Hz), 125.3 (d, J = 16.0 Hz), 124.1, 122.2, 115.2 (d, J = 23.0 Hz), 29.3; ¹⁹F NMR (377 MHz, CDCl₃): δ = –116.83. HRMS (ESI⁺): calcd for C₂₀H₁₇FN [M+H]⁺ 290.1345, found 290.1337.

![Chemical structure](image)

(E)-2-(2-Cinnamyl-4,6-difluorophenyl)pyridine (Table 2, 3i)

The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol),
(E)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (49 mg, 80% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.74 (d, J = 4.0 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.31–7.21 (m, 6H), 6.90 (d, J = 9.2 Hz, 1H), 6.77 (t, J = 8.8 Hz, 1H), 6.19–6.07 (m, 2H), 3.46 (d, J = 6.0 Hz, 2H), ¹³C NMR (100 MHz, CDCl₃): δ = 158.1, 157.7, 155.3, 137.1, 136.3, 132.3, 128.5, 127.5, 127.4, 127.3, 126.1, 126.0, 122.6, 122.2 (dd, J = 12.0, 4.0 Hz), 101.7 (t, J = 26.0 Hz), 36.4; ¹⁹F NMR (377 MHz, CDCl₃): δ = –110.05 (s, 1F), –112.27 (s, 1F). HRMS (ESI⁺): calcd for C₂₀H₁₆F₂N [M+H]⁺ 308.1251, found 308.1243.

![Structure of (E)-2-(2-Cinnamyl-5-(trifluoromethyl)phenyl)pyridine](image)

(E)-2-(2-Cinnamyl-5-(trifluoromethyl)phenyl)pyridine (Table 2, 3j)

The general procedure A was applied to 2-(3-(trifluoromethyl)phenyl)pyridine (45 mg, 0.2 mmol), (E)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (44 mg, 65% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.73 (d, J = 4.8 Hz, 1H), 7.75 (td, J = 7.6, 1.6 Hz, 1H), 7.68 (s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.33–7.29 (m, 1H), 7.27–7.26 (m, 4H), 7.22–7.17 (m, 1H), 6.27–6.17 (m, 2H), 3.66 (d, J = 4.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 158.4, 149.4, 142.2, 141.0, 137.2, 136.5, 131.6, 130.6, 128.5, 128.2, 127.2, 126.8 (q, J = 3.0 Hz), 126.1, 125.5 (q, J = 270.0 Hz), 125.1 (q, J = 4.0 Hz), 124.2, 122.2, 36.5; ¹⁹F NMR (377 MHz, CDCl₃): δ = –63.01. HRMS (ESI⁺): calcd for C₂₁H₁₇F₃N [M+H]⁺ 340.1313, found 340.1313.
(E)-2-(5-Chloro-2-cinnamylphenyl)pyridine (Table 2, 3k)
The general procedure A was applied to 2-(3-chlorophenyl)pyridine (38 mg, 0.2 mmol), 
(E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (45 mg, 74% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.70 (d, J = 3.6 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.30–7.23 (m, 7H), 7.17–7.16 (m, 1H), 6.26–6.19 (m, 1H), 6.05 (d, J = 16.0 Hz, 1H), 3.73 (d, J = 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 159.2, 149.3, 142.9, 137.6, 136.2, 135.5, 135.4, 130.8, 129.6, 128.6, 128.4, 127.5, 127.4, 126.9, 126.0, 124.2, 122.3, 33.7. HRMS (ESI⁺): calcd for C₂₀H₁₇Cl [M+H]⁺ 306.1050, found 306.1043.

(E)-2-(2-Cinnamylphenyl)-3-methylpyridine (Table 2, 3l)
The general procedure A was applied to 3-methyl-2-phenylpyridine (34 mg, 0.2 mmol), 
(E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (43 mg, 75% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.72 (d, J = 4.0 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.27–7.24 (m, 7H), 7.19–7.14 (m, 3H), 6.20–6.13 (m, 1H), 6.06 (d, J = 16.0 Hz, 1H), 3.27 (d, J = 5.6 Hz, 2H), 2.06 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 159.4, 149.6, 140.3, 137.9, 137.6, 136.1, 136.0, 130.5, 129.2, 128.4, 128.1, 127.0, 126.9, 126.0, 124.9, 121.8, 37.1, 20.3. HRMS (ESI⁺): calcd for C₂₁H₂₀N [M+H]⁺ 286.1596, found 286.1591.

(E)-2-(2,4-Difluoro-6-(3-(p-tolyl)allyl)phenyl)pyridine (Table 3, 3m)
The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol),
(E)-tert-butyl (3-(p-tolyl)allyl) carbonate (99 mg, 0.4 mmol) and Co(acac)_3 (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (51 mg, 79% yield). 1H NMR (400 MHz, CDCl_3): δ = 8.73 (d, J = 4.4 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.27 (t, J = 6.0 Hz, 1H), 7.13 (d, J = 7.6 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 9.2 Hz, 1H), 6.76 (t, J = 9.2 Hz, 1H), 6.11 (d, J = 16.0 Hz, 1H), 6.08–6.01 (m, 1H), 3.44 (d, J = 6.4 Hz, 2H), 2.31 (s, 3H); 13C NMR (100 MHz, CDCl_3): δ = 161.0 (dd, J = 248.0, 13.0 Hz), 159.1 (dd, J = 246.0, 13.0 Hz), 153.2, 149.6, 143.1 (dd, J = 9.0, 4.0 Hz), 137.0, 136.2, 134.3, 131.6, 129.2, 126.3, 126.0, 124.4 (dd, J = 15.0, 4.0 Hz), 122.6, 112.2 (dd, J = 21.0, 3.0 Hz), 101.6 (t, J = 26.0 Hz), 36.4, 21.1; 19F NMR (377 MHz, CDCl_3): δ = -110.09– -110.13 (m, 1F), -112.34– -112.38 (m, 1F). HRMS (ESI^+): calcd for C_21H_18F_2N [M+H]^+ 322.1407, found 322.1411.

(E)-2-(2,4-Difluoro-6-(3-(4-methoxyphenyl)allyl)phenyl)pyridine (Table 3, 3n)

The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (E)-tert-butyl (3-(4-methoxyphenyl)allyl) carbonate (106 mg, 0.4 mmol) and Co(acac)_3 (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound (58 mg, 86% yield). 1H NMR (400 MHz, CDCl_3): δ = 8.73 (d, J = 4.8 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.27 (t, J = 6.0 Hz, 1H), 7.17 (d, J = 7.6 Hz, 2H), 6.89 (d, J = 10.6 Hz, 1H), 6.82–6.76 (m, 3H), 6.09 (d, J = 15.6 Hz, 1H), 6.00–5.93 (m, 1H), 3.78 (s, 3H), 3.43 (d, J = 6.8 Hz, 2H); 13C NMR (100 MHz, CDCl_3): δ = 161.1 (dd, J = 247.0, 13.0 Hz), 159.0 (dd, J = 246.0, 13.0 Hz), 158.9, 149.6, 143.2 (dd, J = 9.0, 3.0 Hz), 136.2, 131.2, 129.9, 127.2, 125.9, 125.1, 124.4 (dd, J = 15.0, 3.0 Hz), 122.5, 113.9, 112.2 (dd, J = 21.0, 3.0 Hz), 101.6 (t, J = 26.0 Hz), 55.2, 36.4; 19F NMR (377 MHz, CDCl_3): δ = -110.13 (d, J = 7.5 Hz, 1F), -112.38 (d, J = 7.5 Hz, 1F). HRMS (ESI^+): calcd for C_21H_18F_2NO [M+H]^+ 338.1356, found 338.1358.
(E)-2-(2,4-Difluoro-6-(3-(4-methoxyphenyl)allyl)phenyl)pyridine (Table 3, 3o)

The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (E)-tert-butyl (3-(2-methoxyphenyl)allyl) carbonate (106 mg, 0.4 mmol) and Co(acac)_3 (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound (61 mg, 91% yield). ^1H NMR (400 MHz, CDCl_3): δ = 8.73 (d, J = 4.4 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.31-7.25 (m, 2H), 7.16 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 9.2 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.72 (t, J = 9.2 Hz, 1H), 6.53 (d, J = 16.0 Hz, 1H), 6.16-6.08 (m, 1H), 3.81 (s, 3H), 3.46 (d, J = 6.8 Hz, 2H); ^13C NMR (100 MHz, CDCl_3): δ = 161.1 (dd, J = 248.0, 13.0 Hz), 159.0 (dd, J = 247.0, 13.0 Hz), 156.4, 153.2, 143.3 (dd, J = 9.0, 4.0 Hz), 136.2, 128.3, 128.0, 126.7, 126.6, 126.1, 126.0, 125.9, 124.3 (dd, J = 16.0, 4.0 Hz), 122.5, 120.5, 112.1 (dd, J = 22.0, 3.0 Hz), 110.7, 101.5 (t, J = 27.0 Hz), 55.3, 36.9; ^19F NMR (377 MHz, CDCl_3): δ = -110.20 (d, J = 7.9 Hz, 1F), -112.46 (d, J = 7.2 Hz, 1F). HRMS (ESI^+) calcd for C_{27}H_{18}F_{2}NO [M+H]^+ 338.1356, found 338.1357.

(E)-2-(2,4-Difluoro-6-(3-(4-methoxyphenyl)allyl)phenyl)pyridine (Table 3, 3p)

The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (E)-tert-butyl (3-(3,4-dimethoxyphenyl)allyl) carbonate (118 mg, 0.4 mmol) and Co(acac)_3 (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/7) to afford the title compound (36 mg, 49% yield). ^1H NMR (400 MHz, CDCl_3): δ = 8.74 (d, J = 2.8 Hz, 1H), 7.73 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.29 (t, J = 6.4 Hz, 1H), 7.26 (s, 1H), 6.90 (d, J = 9.2 Hz, 1H), 6.81-6.78 (m, 4H), 6.09 (d, J = 16.0 Hz, 1H), 6.02-5.94 (m, 1H), 3.86 (m, 6H), 3.44 (d, J = 6.4 Hz, 2H); ^13C NMR
(100 MHz, CDCl$_3$): $\delta = 161.1$ (dd, $J = 248.0, 14.0$ Hz), 159.1 (dd, $J = 246.0, 12.0$ Hz), 153.2, 149.7, 149.0, 148.6, 143.1 (dd, $J = 9.0, 4.0$ Hz), 136.2, 131.4, 130.2, 126.0, 125.5, 122.6, 119.2, 112.2 (dd, $J = 21.0, 3.0$ Hz), 111.1, 108.6, 101.6 (t, $J = 26.0$ Hz), 55.9, 55.8, 36.3; $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta = -110.09$ (d, $J = 7.5$ Hz, 1F), $-112.29$ (d, $J = 7.5$ Hz, 1F). HRMS (ESI$^+$): calcd for C$_{22}$H$_{20}$F$_2$NO$_2$ [M+H]$^+$ 368.1462, found 368.1464.

(3)-2-(2,4-Difluoro-6-(3-(4-fluorophenyl)allyl)phenyl)pyridine (Table 3, 3q)

The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (E)-$tert$-butyl (3-(4-fluorophenyl)allyl) carbonate (101 mg, 0.4 mmol) and Co(acac)$_3$ (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (59 mg, 91% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.75$ (d, $J = 4.4$ Hz, 1H), 7.74 (t, $J = 7.6$ Hz, 1H), 7.35 (d, $J = 8.0$ Hz, 1H), 7.29 (t, $J = 6.0$ Hz, 1H), 7.21–7.18 (m, 2H), 6.97–6.88 (m, 3H), 6.77 (t, $J = 9.2$ Hz, 1H), 6.10 (d, $J = 16.0$ Hz, 1H), 6.05–5.98 (m, 1H), 3.45 (d, $J = 6.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 161.2$ (dd, $J = 248.0$, 13.0 Hz), 160.9 (d, $J = 245.0$ Hz), 159.1 (dd, $J = 246.0$, 12.0 Hz), 152.9, 149.5, 142.8 (dd, $J = 9.0$, 3.0 Hz), 136.4, 133.2 (d, $J = 4.0$ Hz), 130.6, 127.5 (d, $J = 8.0$ Hz), 127.1 (d, $J = 2.0$ Hz), 126.0, 124.1 (dd, $J = 15.0$, 3.0 Hz), 122.7, 115.2 (d, $J = 22.0$ Hz), 112.2 (dd, $J = 21.0$, 3.0 Hz), 101.7 (t, $J = 27.0$ Hz), 36.4; $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta = -109.84$ (t, $J = 7.5$ Hz, 1F), $-112.14$ (t, $J = 7.9$ Hz, 1F), $-114.93$ (d, $J = 7.5$ Hz, 1F). HRMS (ESI$^+$): calcd for C$_{20}$H$_{18}$F$_3$N [M+H]$^+$ 326.1157, found 326.1150.

(3)-2-(2,4-Difluoro-6-(3-(3-(trifluoromethyl)phenyl)allyl)phenyl)pyridine (Table 3, 3r)

The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (E)-$tert$-butyl (3-(3-(trifluoromethyl)phenyl)allyl) carbonate (121 mg, 0.4 mmol) and
Co(acac)$_3$ (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (64 mg, 85% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ = 8.75 (d, $J$ = 4.4 Hz, 1H), 7.73 (t, $J$ = 7.6 Hz, 1H), 7.46–7.29 (m, 6H), 6.89 (d, $J$ = 9.2 Hz, 1H), 6.78 (t, $J$ = 9.2 Hz, 1H), 6.22–6.14 (m, 2H), 3.50 (d, $J$ = 3.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 161.2 (dd, $J$ = 248.0, 13.0 Hz), 159.1 (dd, $J$ = 247.0, 13.0 Hz), 153.0, 149.6, 142.4 (dd, $J$ = 8.0, 3.0 Hz), 137.8, 136.3, 131.3, 131.0, 130.7, 130.3, 129.5, 129.2, 128.9, 126.0, 125.4 (q, $J$ = 270.0 Hz), 124.4 (dd, $J$ = 16.0, 4.0 Hz), 123.7 (q, $J$ = 4.0 Hz), 122.8 (q, $J$ = 4.0 Hz), 122.7, 112.3 (dd, $J$ = 22.0, 3.0 Hz), 101.9 (t, $J$ = 27.0 Hz), 36.4; $^{19}$F NMR (377 MHz, CDCl$_3$): δ = -62.77 (s, 3F), -109.79 (d, $J$ = 7.5 Hz, 1F), -112.01 (d, $J$ = 7.5 Hz, 1F). HRMS (ESI$^+$): calcd for C$_{21}$H$_{15}$F$_3$N [M+H]$^+$ 376.1125, found 376.1124.

(E)-2-(2-(3-(4-Chlorophenyl)allyl)-4,6-difluorophenyl)pyridine (Table 3, 3s)

The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (E)-tert-butyl (3-(4-chlorophenyl)allyl) carbonate (107 mg, 0.4 mmol) and Co(acac)$_3$ (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (48 mg, 70% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ = 8.74 (d, $J$ = 2.8 Hz, 1H), 7.73 (t, $J$ = 7.6 Hz, 1H), 7.33 (d, $J$ = 8.0 Hz, 1H), 7.28 (t, $J$ = 6.0 Hz, 1H), 7.22 (d, $J$ = 7.6 Hz, 2H), 7.15 (d, $J$ = 7.6 Hz, 2H), 6.88 (d, $J$ = 9.2 Hz, 1H), 6.77 (t, $J$ = 9.2 Hz, 1H), 6.18–6.04 (m, 2H), 3.47 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 161.2 (dd, $J$ = 248.0, 13.0 Hz), 159.1 (dd, $J$ = 247.0, 13.0 Hz), 153.1, 149.7, 142.6 (dd, $J$ = 9.0, 4.0 Hz), 136.2, 135.6, 132.9, 130.5, 128.6, 128.2, 127.3, 125.9, 124.4 (dd, $J$ = 16.0, 4.0 Hz), 122.6, 112.3 (dd, $J$ = 21.0, 3.0 Hz), 101.8 (t, $J$ = 25.0 Hz), 36.4; $^{19}$F NMR (377 MHz, CDCl$_3$): δ = -109.95 (d, $J$ = 6.8 Hz, 1F), -112.16 (d, $J$ = 7.5 Hz, 1F). HRMS (ESI$^+$): calcd for C$_{20}$H$_{15}$ClF$_2$N [M+H]$^+$ 342.0861, found 342.0856.
(E)-2-(2-(3-(4-Bromophenyl)allyl)-4,6-difluorophenyl)pyridine (Table 3, 3t)

The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (E)-tert-butyl (3-(4-bromophenyl)allyl) carbonate (125 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (60 mg, 78% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.73 (d, J = 3.2 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.38–7.29 (m, 4H), 7.08 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 9.2 Hz, 1H), 6.77 (t, J = 9.2 Hz, 1H), 6.15–6.05 (m, 2H), 3.46 (d, J = 3.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 161.1 (dd, J = 247.0, 13.0 Hz), 159.1 (dd, J = 247.0, 12.0 Hz), 153.1, 149.7, 142.5 (dd, J = 9.0, 4.0 Hz), 136.2, 136.0, 131.5, 130.5, 128.3, 127.6, 125.9, 124.4 (dd, J = 16.0, 4.0 Hz), 122.6, 121.0, 112.2 (dd, J = 21.0, 4.0 Hz), 101.8 (t, J = 27.0 Hz), 36.4; ¹⁹F NMR (377 MHz, CDCl₃): δ = --109.90 (d, J = 7.9 Hz, 1F), –112.12 (d, J = 7.9 Hz, 1F). HRMS (ESI⁺): calcd for C₂₀H₁₅BrF₂N [M+H]⁺ 386.0356 and 388.0335, found 386.0364 and 388.0343.

(E)-2-(2-Allylphenyl)pyridine (Table 3, 3u)⁵

The general procedure A was applied to 2-phenylpyridine (31 mg, 0.2 mmol), (E)-tert-butyl allyl carbonate (63 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (16 mg, 40% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.69 (d, J = 4.8 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.40–7.28 (m, 5H), 7.26–7.23 (m, 1H), 5.93–5.83 (m, 1H), 4.94 (d, J = 10.4 Hz, 1H), 4.87 (d, J = 17.2 Hz, 1H), 3.48 (d, J = 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 159.9, 149.2, 140.5, 137.8, 137.7, 136.3, 130.1, 130.0, 128.6, 126.4, 124.3, 121.8, 115.7, 37.5, 27.3. HRMS (ESI⁺): calcd for C₁₄H₁₄N [M+H]⁺ 196.1126, found
The general procedure B was applied to (E)-4-methoxy-N-(1-phenylethylidene)aniline (45 mg, 0.2 mmol), (E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/40) to afford the title compound (28.5 mg, 60% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.56 (d, J = 7.6 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.26–7.24 (m, 3H), 7.20–7.14 (m, 3H), 7.07 (t, J = 7.2 Hz, 1H), 6.38–6.24 (m, 2H), 3.71 (d, J = 5.2 Hz, 2H), 2.48 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 202.0, 140.0, 137.9, 137.5, 131.5, 131.2, 131.0, 129.2, 129.1, 128.4, 127.0, 126.2, 126.1, 37.2, 29.8. HRMS (ESI⁺): calcd for C₁₇H₁₇O [M+H]⁺ 237.1279, found 237.1276.

(E)-1-(2-Cinnamyl-4-methylphenyl)ethanone (Scheme 2, 5b)

The general procedure B was applied to (E)-4-methoxy-N-(1-(p-tolyl)ethylidene)aniline (48 mg, 0.2 mmol), (E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/40) to afford the title compound (29 mg, 58% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.61 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.25 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.14 (s, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.48–6.34 (m, 2H), 3.80 (d, J = 4.8 Hz, 2H), 2.56 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 201.3, 142.2, 140.6, 137.6, 134.8, 132.1, 130.8, 129.8, 129.5, 128.4, 126.9, 126.8, 126.1, 37.4, 29.6, 21.4. HRMS (ESI⁺): calcd for C₁₈H₁₉O [M+H]⁺ 251.1436, found 251.1444.
(E)-1-(2-Cinnamyl-4-methoxyphenyl)ethanone (Scheme 2, 5c)

The general procedure B was applied to (E)-4-methoxy-N-(1-(4-methoxyphenyl)ethylidene)-aniline (51 mg, 0.2 mmol), (E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound (37 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, J = 8.8 Hz, 1H), 7.33 (d, J = 7.6 Hz, 2H), 7.29–7.26 (m, 2H), 7.16 (t, J = 7.2 Hz, 1H), 6.85 (s, 1H), 6.78 (d, J = 8.8 Hz, 1H), 6.46–6.35 (m, 2H), 3.86 (d, J = 4.8 Hz, 2H), 3.84 (s, 3H), 2.56 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 199.7, 162.1, 143.9, 137.6, 132.5, 131.0, 129.9, 129.2, 128.4, 127.0, 126.2, 116.9, 110.8, 55.3, 37.9, 29.3. HRMS (ESI⁺): calcd for C₁₈H₁₉O₂ [M+H]⁺ 267.1385, found 267.1380.

(E)-1-(2-Cinnamyl-4-fluorophenyl)ethanone (Scheme 2, 5d)

The general procedure B was applied to (E)-N-(1-(4-fluorophenyl)ethylidene)-4-methoxyaniline (49 mg, 0.2 mmol), (E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/40) to afford the title compound (32.5 mg, 64% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.75–7.72 (m, 1H), 7.34 (d, J = 7.6 Hz, 2H), 7.30–7.26 (m, 2H), 7.18 (t, J = 7.2 Hz, 1H), 7.04 (d, J = 10.0 Hz, 1H), 6.98 (t, J = 8.4 Hz, 1H), 6.45–6.30 (m, 2H), 3.82 (d, J = 6.4 Hz, 2H), 2.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 200.2, 163.0 (d, J = 252.0 Hz), 144.3 (d, J = 8.0 Hz), 137.3, 133.8 (d, J = 3.0 Hz), 131.9 (d, J = 9.0 Hz), 131.7, 128.5, 128.2, 127.2, 126.1, 118.0 (d, J = 21.0 Hz), 112.9 (d, J = 21.0 Hz), 37.3, 29.7; ¹⁹F NMR (377 MHz, CDCl₃): δ = -107.20. HRMS (ESI⁺): calcd for C₁₇H₁₆FO [M+H]⁺ 255.1185, found 255.1180.
(E)-1-(2-cinnamyl-3-methoxyphenyl)ethanone (Scheme 2, 5e)

The general procedure B was applied to (E)-3-methoxy-N-(1-(4-methoxyphenyl)ethyldiene)-aniline (51 mg, 0.2 mmol), (E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound (33 mg, 62% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.32–7.22 (m, 5H), 7.17–7.13 (m, 2H), 6.98 (d, J = 8.0 Hz, 1H), 6.41–6.29 (m, 2H), 3.86 (s, 3H), 3.74 (d, J = 5.2 Hz, 2H), 2.53 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 203.2, 158.2, 140.7, 138.0, 130.4, 129.2, 128.5, 127.6, 127.1, 126.9, 126.2, 120.3, 113.3, 56.0, 30.7, 29.4. GC-MS (EI): calcd for C₁₈H₁₉O₂ [M] 266.13, found 266.15.

(E)-1-(2-Cinnamyl-3-fluorophenyl)ethanone (Scheme 2, 5f)

The general procedure B was applied to (E)-N-(1-(3-fluorophenyl)ethyldiene)-4-methoxyaniline (49 mg, 0.2 mmol), (E)-tert-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and Co(acac)₃ (7 mg, 0.02 mmol) at 25 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/40) to afford the title compound (33 mg, 65% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.42 (d, J = 7.6 Hz, 1H), 7.30–7.15 (m, 7H), 6.45–6.30 (m, 2H), 3.78 (d, J = 5.2 Hz, 2H), 2.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 201.4, 160.6 (d, J = 245.0 Hz), 140.4 (d, J = 4.0 Hz), 137.6, 131.2, 128.6, 127.9, 127.5 (d, J = 8.0 Hz), 127.2, 127.0 (d, J = 16.0 Hz), 126.3, 124.6 (d, J = 4.0 Hz), 118.5 (d, J = 24.0 Hz), 30.2, 28.8 (d, J = 5.0 Hz); ¹⁹F NMR (377 MHz, CDCl₃): δ = −115.64. GC-MS (EI): calcd for C₁₇H₁₆FO [M] 254.11, found 254.11.

4. Cobalt-Catalyzed ortho-C–H Allylation of 2-Phenylpyridine with Allyl Carbonate (Z)-2a and 2b
The general procedure A was applied to 2-arylpyridine 1a (31.0 mg, 0.20 mmol), allyl carbonate 2b or (Z)-2a (93.6 mg, 0.40 mmol), and Co(acac)₃ (7.1 mg, 0.02 mmol) at 25 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE =1/15) to provide the product 3a. ((Z)-2a: 89% yield; 2b: 80% yield)

5. Intermolecular Kinetic Isotopic Effect Experiment

The general procedure A was applied to 2-arylpyridine 1a (31.0 mg, 0.20 mmol), 1a-d₅ (32.0 mg, 0.20 mmol), (E)-tert-butyl cinnamyl carbonate (93.6 mg, 0.4 mmol), and Co(acac)₃ (7.1 mg, 0.02 mmol) at 25 ºC for 1 h. The crude residue was analyzed by ¹H NMR and then purified by column chromatography on silica gel (EtOAc/PE =1/15) to provide the mixed compounds 3a and 3a-d₄. The ¹H NMR data of the mixture suggest that the related KIE value is 4.0 (Figure S1). The KIE measurements were performed three runs giving the same result.
Figure S1. $^1$H NMR spectrum of the mixed 3a and 3a-$d_4$ measured in CDCl$_3$.

References


6. $^1\text{H}$, $^{13}\text{C}$ and $^{19}\text{F}$ NMR Spectra
$3g$
$^{1}H-H$ COSY spectrum
$5c$

$5c$
$^1$H-$^1$H COSY spectrum