Supporting Information

Rhodium-Catalyzed Pyridine N-oxide-Assisted Suzuki-Miyaura Coupling Reaction via C(O)-C Bond Activation

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I. General remarks

NMR spectra were obtained on an Agilent 400-MR DD2 or a Bruker AV II-400 spectrometer. The $^1$H NMR (400 MHz) chemical shifts were measured relative to CDCl$_3$ or DMSO-$d_6$ as the internal reference (CDCl$_3$: $\delta = 7.26$ ppm, DMSO-$d_6$: $\delta = 2.50$ ppm). The $^{13}$C NMR (100 MHz) chemical shifts were given using CDCl$_3$ or DMSO-$d_6$ as the internal standard (CDCl$_3$: $\delta = 77.16$ ppm, DMSO-$d_6$: $\delta = 39.52$ ppm). High resolution mass spectra (HR-MS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). IR spectra were obtained on a Thermo Scientific Nicolet 6700. Melting points were determined in open glass capillaries and were uncorrected. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. 2-Benzoylpyridine N-oxides derivatives were prepared according to the literature procedures.$^{1,2}$ Toluene, 1,4-dioxane, dichloromethane (DCM), dimethyl sulfoxide (DMSO), ether (Et$_2$O), chlorobenzene (PhCl) and tetrahydrofuran (THF) were dried before used.

II. Synthesis of starting materials

2.1 Synthesis of aryl N-heteroaryl ketones$^{[1]}$

A solution of the appropriate bromide derivatives (10.0 mmol, 1.0 equiv.) in 20 mL of THF was treated with magnesium (12.0 mmol, 1.2 equiv.) and 10 mg I$_2$. After the formation of the Grignard reagent, the solution was cooled to room temperature, and added into the solution of 2-cyanopyridine (10 mmol, 1.0 equiv.) in THF (15 mL) at 0 °C dropwise. After the reaction was complete monitored by TLC, the mixture was quenched by addition of a solution of saturated NH$_4$Cl. The organic layer was separated and extracted twice with ethyl acetate. After evaporation, the residue was dissolved in Et$_2$O (80.0 mL), and 6 M HCl (10.0 mL) was added. After 30 min, the organic layer was separated. The aqueous layer was basified with saturated NaHCO$_3$, and then extracted three times with ethyl acetate. The combined organic layers were dried over Na$_2$SO$_4$ and evaporated in vacuo. The residue was purified by column chromatography with petroleum ether and ethyl acetate.

2.2 Synthesis of Pyridine N-oxide$^{[2]}$

Oxidation of 2-benzoylpyridines with $m$-CPBA: $m$-chloroperbenzoic acid ($m$-CPBA, 2.58 g, 15 mmol) was added to a solution of ketone (10 mmol) in CH$_2$Cl$_2$ (100 mL) at 0 °C. The mixture was stirred at room temperature until completion (monitored by TLC). After that, the solvent was extracted with saturated NaHCO$_3$ (30 mL x 3). The organic layer was extracted with DCM. The
combined organic layers were dried over Na$_2$SO$_4$ and evaporated in vacuo. The residue chromatographed on silica gel eluting with DCM-MeOH mixtures to give compound.

**III. General procedures**

**3.1 Rhodium-catalyzed C–C activation reaction**

\[
\text{R}^1 \text{R}^2 \text{C} = \text{O} \quad + \quad \text{R}^1 \text{R}^2 \text{C}^\text{H} \quad \xrightarrow{[\text{Rh(CO)}_2(\text{acac})] \quad \text{H}_2\text{O} \ \text{air} \ 24\text{h}} \quad \text{R}^1 \text{R}^2 \text{C} \text{C} \text{R}^1 \text{R}^2
\]

A Schlenk tube with a magnetic stir bar was charged with 1 (0.2 mmol), 2 (0.5 mmol), [Rh(CO)$_2$(acac)] (5.2 mg, 10 mol%, 0.02 mmol), H$_2$O (30 uL) and 1,4-dioxane (2.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 140 °C for 24 hours under air (oil bath). The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH$_2$Cl$_2$, filtered through a celite pad and washed with 10 mL of CH$_2$Cl$_2$. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel with DCM-MeOH = 50:1 to provide the desired product 3.

**3.2 Mechanistic studies**

**3.2.1 Synthesis of biaryl byproduct**

A Schlenk tube with a magnetic stir bar was charged with 1a (39.8 mg, 0.2 mmol), 2a (76.0 mg, 0.5 mmol), [Rh(CO)$_2$(acac)] (5.2 mg, 10 mol%, 0.02 mmol) and 1,4-dioxane (2.0 mL). The Schlenk tube was then sealed with a teflon lined cap and the mixture was heated at 140 °C for 24 hours under air (oil bath). The reaction solution was then cooled to ambient temperature, the reaction mixture was then passed through a short column to obtain a mixture of product 3a (29.8 mg, 65%), 4-methoxyl-1,1'-biphenyl (5) (4.4 mg, 12%), and 4,4'-dimethoxybiphenyl (6) (7.3 mg, 17%) in GC yield.

A Schlenk tube with a magnetic stir bar was charged with 3u (57.8 mg, 0.2 mmol), 2a (62.0 mg, 0.5 mmol), [Rh(CO)$_2$(acac)] (5.2 mg, 10 mol%, 0.02 mmol) and 1,4-dioxane (2.0 mL). The Schlenk tube was then sealed with a teflon lined cap and the mixture was heated at 140 °C for 24 hours under air (oil bath). The reaction solution was then cooled to ambient temperature, the
reaction mixture was then passed through a short column to obtain a mixture of product 1a (34.6 mg, 87%), 7 (25.5 mg, 76%) and 8 (3.9 mg, 8%) in GC yield.

### 3.2.2 Synthesis of deuterated phenylboronic acid

D$_2$O (20 mL) was heated to 75 °C in a 50 mL round-bottomed flask (oil bath). Triphenyl boroxine (5.0 mmol, 1.56 g) was added until the solution was saturated. The resulting solution was stirred at this temperature for 6 h. The solution was filtered while it was still hot. The filtrate was cooled to room temperature, and deuterated phenylboronic acid was obtained as a white solid. After filtration, the white solid was dried in an infrared drying oven under vacuum for 3 h (note: drying for a long period will lead to decomposiion back to triphenyl boroxine).[3] Deuterated phenylboronic acid (2aa-d$_2$) (1.02 g, 56%, >85% D) was obtained. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 7.93 – 7.73 (m, 2H), 7.45 – 7.25 (m, 3H), 8.02 (s, 0.30).

### 3.2.3 Deuterium-labeling experiment
A Schlenk tube with a magnetic stir bar was charged with 3ab (0.2 mmol, 48.4 mg), 2aa-d2 (0.5 mmol, 63.0 mg), [Rh(CO)2(acac)] (5.2 mg, 10 mol%, 0.02 mmol), 1,4-dioxane (2.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 140 °C for 24 hours under air (oil bath). The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH2Cl2, filtered through a celite pad and washed with 10 mL of CH2Cl2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel with PE-EA = 100:1 to provide the desired product 9a-d1 (17.1 mg, 70%, >80% D).

### 3.3 Gram scale transformation

A Schlenk tube with a magnetic stir bar was charged with 1a (0.99 g, 5.0 mmol), 2a (1.90 g, 12.5 mmol), [Rh(CO)2(acac)] (0.13 g, 10 mol%, 0.5 mmol), H2O (0.75 mL) and 1,4-dioxane (50 mL). The Schlenk tube was then sealed with a teflon lined cap and the mixture was heated at 140 °C for 24 hours under air (oil bath). The reaction solution was then cooled to ambient temperature and basified with saturated NaHCO3, and then extracted three times with ethyl acetate. The combined organic layers were dried over Na2SO4 and evaporated in vacuo. The residue was purified by column chromatography on silica gel to provide the desired product 3a (0.83 g, 3.62 mmol) in 72% yield.

### 3.4 Catalytic C-C activation and removal of traceless directing group

A magnetic stir bar was charged with 2-benzoylpyridine 1-oxide 1a (0.99 g, 5.0 mmol), 4-methoxyphenylboronic acid 2a (1.90 g, 12.5 mmol), [Rh(CO)2(acac)] (0.13 g, 10 mol%, 0.5
mmol), H₂O (0.75 mL) in 1,4-dioxane (50 mL). The mixture was heated at 140 °C for 24 hours under air (oil bath). After the reaction solution was cooled to 50 °C, PBr₃ (5.4 g, 20 mmol) was added dropwise. The reaction medium was stirred 1 hour. The reaction solution was basified with saturated NaHCO₃, and then extracted three times with ethyl acetate. The combined organic layers were dried over Na₂SO₄ and evaporated in vacuo. The residue was purified by column chromatography with petroleum ether/ethyl acetate = 10/1 to provide the product 4a (0.63 g, 3.46 mmol) in 69% yield.

IV. Supporting data of extra experiments

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Additive</th>
<th>Yield[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>K₂CO₃ (1.2 eq)</td>
<td>51%</td>
</tr>
<tr>
<td>2</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>Na₂CO₃ (1.2 eq)</td>
<td>41%</td>
</tr>
<tr>
<td>3</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>Cs₂CO₃ (1.2 eq)</td>
<td>13%</td>
</tr>
<tr>
<td>4</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>NaOAc (1.2 eq)</td>
<td>32%</td>
</tr>
<tr>
<td>5</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>KOAc (1.2 eq)</td>
<td>36%</td>
</tr>
<tr>
<td>6</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>AgOAc (1.2 eq)</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>AgSbF₆ (1.2 eq)</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>K₃PO₄ (1.2 eq)</td>
<td>42%</td>
</tr>
<tr>
<td>9</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>K₂HPO₄ (1.2 eq)</td>
<td>40%</td>
</tr>
<tr>
<td>10</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>CF₃COOK (1.2 eq)</td>
<td>21%</td>
</tr>
<tr>
<td>11</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>NaF (1.2 eq)</td>
<td>50%</td>
</tr>
<tr>
<td>12</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>KOAc+K₂CO₃ (1.2 eq)</td>
<td>35%</td>
</tr>
<tr>
<td>13</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>K₂CO₃+Cul (1.2 eq)</td>
<td>31%</td>
</tr>
<tr>
<td>14</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>HOAc (1.2 eq)</td>
<td>N.R.</td>
</tr>
<tr>
<td>15[^c]</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>DPPB (0.2 eq)</td>
<td>36%</td>
</tr>
<tr>
<td>16[^d]</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>DPPE (0.2 eq)</td>
<td>trace</td>
</tr>
<tr>
<td>17[^e]</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>DPPP (0.2 eq)</td>
<td>N.R.</td>
</tr>
<tr>
<td>18[^f]</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>BINAP (0.2 eq)</td>
<td>38%</td>
</tr>
<tr>
<td>19[^g]</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>PCy₃ (0.2 eq)</td>
<td>trace</td>
</tr>
<tr>
<td>20[^h]</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>P(o-tol)₁ (0.2 eq)</td>
<td>40%</td>
</tr>
<tr>
<td>21[^i]</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>X-Phos (0.2 eq)</td>
<td>25%</td>
</tr>
<tr>
<td>22[^j]</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>Xanthos (0.2 eq)</td>
<td>trace</td>
</tr>
<tr>
<td>23[^k]</td>
<td>[Rh(CO)₂(acac)]</td>
<td>1,4-dioxane</td>
<td>ICy (0.2 eq)</td>
<td>N.R.</td>
</tr>
</tbody>
</table>

[^a]: General conditions: 1a (0.2 mmol), 2a (0.5 mmol), [Rh] (10 mol%), additive, solvent (1.0 mL) were stirred at 140 °C for 24 h in air.[^b]: Isolated yields.[^c]: DPPB: 1,4-Bis(diphenylphosphino)butane.[^d]: DPPE:
1,4-Bis(diphenylphosphino)ethane.  \[^{[c]}\]DPPP: 1,4-Bis(diphenylphosphino)propane.  \[^{[b]}\]BINAP: 1,1'-Binaphthyl-2,2'-diphenylphosphine.  \[^{[d]}\]PCy\textsubscript{3}: Tricyclohexylphosphine.  \[^{[i]}\]P(o-tol)\textsubscript{3}: Tri(o-tolyl)phosphine.  \[^{[j]}\]X-PHOS: 2-(Dicyclohexylphosphino)-2',4',6'-tri-i-propyl-1,1'-biphenyl.  \[^{[k]}\]Xantphos: 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene.  \[^{[l]}\]ICy: 1,3-dicyclohexylimidazolium chloride.

V. Experimental data for the described substances

2-Benzoylpyridine 1-oxide (1a) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 1a as a yellowish solid (1.69 g, 85%). \(^1\)H NMR (400 MHz, Chloroform-\text{d}) δ 8.27 – 8.23 (m, 1H), 7.86 – 7.81 (m, 2H), 7.64 – 7.58 (m, 1H), 7.50 – 7.45 (m, 2H), 7.44 – 7.38 (m, 3H). \(^{13}\)C NMR (100 MHz, Chloroform-\text{d}) δ 189.34, 147.06, 140.01, 135.05, 134.23, 129.26, 128.87, 127.08, 125.68, 125.64. HRMS (ESI\textsuperscript{+}): calcd for C\textsubscript{12}H\textsubscript{10}NO\textsubscript{2} [M+H]\textsuperscript{+} 200.0712, found 200.0721.

2-Acetylpyridine 1-oxide (1b) : Purification by column chromatography on silica gel (DCM/MeOH = 80/1, v/v) afforded 1b as a red liquid (1.21 g, 87%). \(^1\)H NMR (400 MHz, Chloroform-\text{d}) δ 8.22 – 8.17 (m, 1H), 7.69 (dd, \(J = 7.8, 2.3\) Hz, 1H), 7.36 (ddd, \(J = 7.6, 6.4, 2.3\) Hz, 1H), 7.30 (td, \(J = 7.7, 1.3\) Hz, 1H), 2.80 (s, 3H). \(^{13}\)C NMR (100 MHz, Chloroform-\text{d}) δ 194.96, 146.84, 140.66, 128.06, 126.82, 125.51, 30.71. HRMS (ESI\textsuperscript{+}): calcd for C\textsubscript{7}H\textsubscript{8}NO\textsubscript{2} [M+H]\textsuperscript{+} 138.0555, found 138.0521.

6-Benzoyl-2-methylpyridine 1-oxide (1c) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 1c as a brown solid (1.60 g, 75%). \(^1\)H NMR (400 MHz, Chloroform-\text{d}) δ 8.09 (q, \(J = 6.3, 5.5\) Hz, 1H), 7.84 – 7.73 (m, 2H), 7.60 – 7.50 (m, 1H), 7.46 – 7.38 (m, 2H), 7.17 (d, \(J = 9.5\) Hz, 2H), 2.36 (dd, \(J = 9.0, 4.7\) Hz, 3H). \(^{13}\)C NMR (100 MHz, Chloroform-\text{d}) δ 189.48, 146.37, 139.28, 137.70, 135.11, 134.15, 129.31, 128.83, 127.77, 126.02, 20.38. HRMS (ESI\textsuperscript{+}): calcd for C\textsubscript{13}H\textsubscript{12}NO\textsubscript{2} [M+H]\textsuperscript{+} 214.0868, found 214.0857.
6-Benzoyl-3-methylpyridine 1-oxide (1d) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 1d as a brown solid (1.75 g, 82%). $^1$H NMR (400 MHz, Chloroform-d$_2$) δ 8.07 (d, $J = 3.3$ Hz, 1H), 7.85 – 7.76 (m, 2H), 7.57 (dddt, $J = 7.0, 5.5, 2.8, 1.4$ Hz, 1H), 7.44 (tt, $J = 7.5, 1.9$ Hz, 2H), 7.30 (dt, $J = 8.1, 2.3$ Hz, 1H), 7.19 (d, $J = 9.0$ Hz, 1H), 2.45 – 2.33 (m, 3H). $^{13}$C NMR (100 MHz, Chloroform-d$_2$) δ 189.55, 144.42, 139.77, 138.22, 135.36, 134.02, 129.23, 128.78, 127.06, 125.19, 18.42. IR(KBr)/cm$^{-1}$: 3040, 1660, 1610, 1450, 1300, 1260, 1180, 931, 702. HRMS (ESI$^+$): calcd for C$_{13}$H$_{12}$NO$_2$ [M+H]$^+$ 214.0868, found 214.0857.

6-Benzoyl-4-methylpyridine 1-oxide (1e) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 1e as a brown solid (1.77 g, 83%). $^1$H NMR (400 MHz, Chloroform-d$_2$) δ 8.15 – 8.10 (m, 1H), 7.86 – 7.80 (m, 2H), 7.62 – 7.55 (m, 1H), 7.46 (dd, $J = 8.4, 7.1$ Hz, 2H), 7.20 (dt, $J = 5.3, 1.6$ Hz, 2H), 2.39 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-d$_2$) δ 189.47, 146.39, 139.30, 137.75, 135.09, 134.18, 129.33, 128.84, 127.76, 126.04, 20.40. HRMS (ESI$^+$): calcd for C$_{13}$H$_{12}$NO$_2$ [M+H]$^+$ 214.0868, found 214.0857.

2-Benzoylquinoline 1-oxide (1f) : Purification by column chromatography on silica gel (DCM/MeOH = 100/1, v/v) afforded 1f as a brown solid (1.61 g, 65%). $^1$H NMR (400 MHz, Chloroform-d$_2$) δ 8.69 (d, $J = 8.8$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.83 (dd, $J = 8.3, 1.5$ Hz, 3H), 7.78 (dd, $J = 8.7, 6.9, 1.4$ Hz, 1H), 7.69 (dd, $J = 8.2, 6.9, 1.3$ Hz, 1H), 7.61 – 7.54 (m, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.39 (d, $J = 8.6$ Hz, 1H). $^{13}$C NMR (100 MHz, Chloroform-d$_2$) δ 190.29, 142.74, 141.61, 135.27, 134.11, 131.02, 130.67, 129.59, 129.17, 128.94, 128.37, 125.94, 120.40, 119.73. HRMS (ESI$^+$): calcd for C$_{16}$H$_{12}$NO$_2$ [M+H]$^+$ 250.0868, found 250.0861.
6-Benzoyl-4-methoxypyridine 1-oxide (1g) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 1g as a yellowish solid (0.55 g, 24%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.13 (d, $J$ = 7.2 Hz, 1H), 7.85 (dt, $J$ = 8.5, 1.6 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.49 – 7.44 (m, 2H), 6.94 (dd, $J$ = 7.2, 3.5 Hz, 1H), 6.89 (d, $J$ = 3.4 Hz, 1H), 3.88 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 188.85, 157.78, 147.62, 140.81, 134.86, 134.27, 129.44, 128.87, 113.58, 110.23, 56.38. HRMS (ESI$^+$): calcd for C$_{13}$H$_{12}$NO$_3$ [M+H]$^+$ 230.0817, found 230.0835.

6-Benzoyl-3-Chloropyridine 1-oxide (1h) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 1h as a brown solid (1.82 g, 78%, mp = 117-119 °C). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.30 (dd, $J$ = 1.6, 0.7 Hz, 1H), 7.81 (dd, $J$ = 8.4, 1.3 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.52 – 7.45 (m, 2H), 7.42 – 7.36 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 188.52, 145.63, 139.33, 134.92, 134.61, 134.40, 129.22, 128.92, 125.99, 125.71. HRMS (ESI$^+$): calcd for C$_{12}$H$_8$NO$_2$ClNa [M+Na]$^+$ 256.0141 found 256.0128.

(4-Methoxyphenyl)(1-oxido-2-pyridinyl)methanone (3a) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3a as a yellowish solid (37.5 mg, 82%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.21 – 8.16 (m, 1H), 7.76 – 7.72 (m, 2H), 7.34 – 7.30 (m, 3H), 6.89 – 6.85 (m, 2H), 3.80 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 187.66, 164.56, 147.50, 140.06, 131.95, 128.07, 126.75, 125.77, 125.56, 114.21, 55.62. HRMS (ESI$^+$): calcd for C$_{13}$H$_{12}$NO$_3$ [M+H]$^+$ 230.0817, found 230.0809.

(4-Methylphenyl)(1-oxido-2-pyridinyl)methanone (3b) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3b as a yellowish liquid (38.7 mg, 91%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.24 (ddd, $J$ = 5.8, 2.7, 1.5 Hz, 1H), 7.77 – 7.69 (m, 2H),
7.46 – 7.34 (m, 3H), 7.28 – 7.25 (m, 2H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 188.91, 147.35, 145.45, 140.05, 132.60, 129.61, 129.47, 126.87, 125.68, 125.59, 21.89. HRMS (ESI$^+$): calcd for C$_{13}$H$_{12}$NO$_2$ [M+H]$^+$ 214.0868, found 214.0857.

(4-Ethylphenyl)(1-oxido-2-pyridinyl)methanone (3c) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3c as a colorless liquid (39.5 mg, 87%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.24 (ddd, $J$ = 5.0, 2.3, 1.5 Hz, 1H), 7.80 – 7.70 (m, 2H), 7.46 – 7.34 (m, 3H), 7.31 – 7.27 (m, 2H), 2.70 (q, $J$ = 7.6 Hz, 2H), 1.24 (t, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 188.91, 151.57, 147.38, 140.05, 132.77, 129.60, 128.47, 126.86, 125.71, 125.58, 29.16, 15.14. HRMS (ESI$^+$): calcd for C$_{14}$H$_{14}$NO$_2$ [M+H]$^+$ 228.1025, found 228.1016.

(4-i-Propylphenyl)(1-oxido-2-pyridinyl)methanone (3d) : Purification by column chromatography on silica gel (DCM/MeOH = 80/1, v/v) afforded 3d as a yellowish liquid (39.0 mg, 81%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.26 – 8.21 (m, 1H), 7.77 – 7.72 (m, 2H), 7.41 – 7.36 (m, 3H), 7.27 – 7.24 (m, 2H), 2.66 – 2.60 (m, 2H), 1.68 – 1.60 (m, 2H), 0.93 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 188.91, 150.11, 147.37, 140.04, 132.77, 129.52, 129.04, 126.85, 125.73, 125.55, 38.22, 24.16, 13.79. HRMS (ESI$^+$): calcd for C$_{15}$H$_{16}$NO$_2$ [M+H]$^+$ 242.1181, found 242.1170.

(4-n-Butylphenyl)(1-oxido-2-pyridinyl)methanone (3e) : Purification by column chromatography on silica gel (DCM/MeOH = 80/1, v/v) afforded 3e as a white solid (40.3 mg, 79%, mp = 135-137 °C). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.27 – 8.19 (m, 1H), 7.78 – 7.70 (m, 2H), 7.44 – 7.34 (m, 3H), 7.27 – 7.24 (m, 2H), 2.73 – 2.60 (m, 2H), 1.64 – 1.54 (m, 2H), 1.33 (dtq, $J$ = 14.6, 7.3 Hz, 2H), 0.90 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 188.90, 150.34, 147.36, 140.03, 132.73, 129.52, 129.00, 126.86, 125.72, 125.54, 35.88, 33.13, 22.30, 13.90. HRMS (ESI$^+$): calcd for C$_{16}$H$_{18}$NO$_2$ [M+H]$^+$ 256.1338, found 256.1334.
(4-Butylphenyl)(1-oxido-2-pyridinyl)methanone (3f) : Purification by column chromatography on silica gel (DCM/MeOH = 80/1, v/v) afforded 3f as a white solid (42.3 mg, 83%). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.26 – 8.21 (m, 1H), 7.76 (d, \(J = 8.5\) Hz, 2H), 7.51 – 7.45 (m, 2H), 7.38 (d, \(J = 1.4\) Hz, 3H), 1.31 (s, 9H). \(^1\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 188.87, 158.24, 147.37, 140.03, 132.43, 129.33, 126.88, 125.94, 125.74, 125.55, 35.32, 31.02. HRMS (ESI\(^+\)): calcd for C\(_{16}\)H\(_{18}\)NO\(_2\) [M+H]\(^+\) 256.1338, found 256.1328.

(4-nAmylphenyl)(1-oxido-2-pyridinyl)methanone (3g) : Purification by column chromatography on silica gel (DCM/MeOH = 80/1, v/v) afforded 3g as a yellow liquid (41.4 mg, 77%). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.27 – 8.20 (m, 1H), 7.78 – 7.71 (m, 2H), 7.44 – 7.35 (m, 3H), 7.27 (d, \(J = 1.9\) Hz, 2H), 2.68 – 2.61 (m, 2H), 1.66 – 1.57 (m, 2H), 1.31 (tt, \(J = 5.6, 3.0\) Hz, 4H), 0.90 – 0.84 (m, 3H). \(^1\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 188.89, 150.38, 147.39, 140.04, 132.73, 129.53, 128.99, 126.83, 125.70, 125.56, 36.16, 31.40, 30.70, 22.49, 13.99. HRMS (ESI\(^+\)): calcd for C\(_{17}\)H\(_{20}\)NO\(_2\) [M+H]\(^+\) 270.1494, found 270.1482.

(4-Trimethylsilylphenyl)(1-oxido-2-pyridinyl)methanone (3h): Purification by column chromatography on silica gel (DCM/MeOH = 80/1, v/v) afforded 3h as a green yellow liquid (49.8 mg, 92%). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.25 (ddd, \(J = 4.7, 2.6, 1.3\) Hz, 1H), 7.79 – 7.75 (m, 2H), 7.65 – 7.60 (m, 2H), 7.41 (q, \(J = 3.0\) Hz, 3H), 0.27 (s, 9H). \(^1\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 141.44, 136.46, 135.16, 129.41, 128.38, 127.12, 127.09, 2.43. HRMS (ESI\(^+\)): calcd for C\(_{15}\)H\(_{13}\)NO\(_2\)Si [M+H]\(^+\) 272.1107, found 272.1116.

(4-Phenoxyphenyl)(1-oxido-2-pyridinyl)methanone (3i): Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3i as a white solid (49.4 mg, 85%,
mp = 137-139 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.23 (ddd, $J = 5.2$, 3.1, 1.3 Hz, 1H), 7.85 – 7.76 (m, 2H), 7.45 – 7.35 (m, 5H), 7.23 – 7.15 (m, 1H), 7.10 – 7.02 (m, 2H), 7.02 – 6.95 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 187.74, 163.11, 155.05, 147.27, 140.03, 131.85, 130.10, 129.52, 126.92, 125.85, 125.61, 124.91, 120.43, 117.45. IR(KBr)/cm$^{-1}$: 3440, 3060, 1660, 1590, 1430, 1320, 1240, 1160, 942, 761. HRMS (ESI$^+$): calcd for C$_{18}$H$_{14}$NO$_3$ [M+H]$^+$ 292.0974, found 292.0988.

(4-Hydroxyphenyl)(1-oxido-2-pyridinyl)methanone (3j): Purification by column chromatography on silica gel (DCM/MeOH = 25/1, v/v) afforded 3j as a white solid (30.1 mg, 70%, mp = 141-145 °C). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.66 (s, 1H), 8.32 (d, $J = 6.2$ Hz, 1H), 7.64 – 7.55 (m, 4H), 7.49 (t, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 188.11, 163.70, 146.99, 140.04, 132.37, 127.81, 126.97, 126.34, 125.56, 116.17. HRMS (ESI$^+$): calcd for C$_{12}$H$_{10}$NO$_3$ [M+H]$^+$ 216.0661, found 216.0635.

(4-Chlorophenyl)(1-oxido-2-pyridinyl)methanone (3k): Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3k as a yellowish liquid (28.5 mg, 61%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.25 – 8.21 (m, 1H), 7.76 (dd, $J = 8.8$, 2.2 Hz, 2H), 7.43 (dq, $J = 9.0$, 2.2 Hz, 5H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 188.21, 146.67, 140.64, 140.05, 133.49, 130.56, 129.23, 128.85, 127.33, 125.89. HRMS (ESI$^+$): calcd for C$_{12}$H$_{8}$NO$_2$ClNa [M+Na]$^+$ 256.0141 found 256.0128.

(4-Bromophenyl)(1-oxido-2-pyridinyl)methanone (3l): Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3l as a brown liquid (36.0 mg, 65%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.26 – 8.20 (m, 1H), 7.72 – 7.65 (m, 2H), 7.64 – 7.58 (m, 2H), 7.46 – 7.41 (m, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 188.44, 140.07, 133.91, 132.88, 132.22, 130.59, 129.47, 127.32, 125.93, 125.81. HRMS (ESI$^+$): calcd for C$_{12}$H$_{8}$NO$_2$BrNa [M+Na]$^+$ 299.9636, found 299.9652.
(4-(Trifluoromethyl)phenyl)(1-oxido-2-pyridinyl)methanone (3m): Purification by column chromatography on silica gel (DCM/MeOH = 80/1, v/v) afforded 3m as a yellowish liquid (12.8 mg, 24%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.26 – 8.21 (m, 1H), 7.91 (d, $J$ = 8.1 Hz, 2H), 7.72 (d, $J$ = 8.2 Hz, 2H), 7.51 – 7.41 (m, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 187.55, 145.26, 139.02, 136.91, 134.11 (q, $^1J_{C-F}$ = 32 Hz), 128.22, 126.66, 125.14, 124.96, 124.91 (q, $^2J_{C-F}$ = 4 Hz), 123.81 (q, $^3J_{C-F}$ = 272 Hz). $^{19}$F NMR (400 MHz, Chloroform-$d$) $\delta$ -63.24. HRMS (ESI$^+$): calcd for C$_{13}$H$_8$NO$_2$F$_3$Na $[M+Na]^+$ 290.0405, found 290.0390.

(3-Methylphenyl)(1-oxido-2-pyridinyl)methanone (3n): Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3n as a yellowish liquid (36.6 mg, 86%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.27 – 8.22 (m, 1H), 7.65 (s, 1H), 7.59 (d, $J$ = 7.8 Hz, 1H), 7.44 – 7.31 (m, 5H), 2.38 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 188.48, 146.24, 139.02, 137.75, 134.10, 134.07, 128.50, 127.55, 125.88, 125.60, 124.64, 124.50, 20.29. HRMS (ESI$^+$): calcd for C$_{13}$H$_{12}$NO$_2$ [M+H]$^+$ 214.0868, found 214.0857.

(3-Chlorophenyl)(1-oxido-2-pyridinyl)methanone (3o): Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3o as a yellowish liquid (20.5 mg, 44%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.24 (dt, $J$ = 5.6, 1.3 Hz, 1H), 7.79 (t, $J$ = 1.9 Hz, 1H), 7.68 (ddd, $J$ = 7.7, 1.6, 1.1 Hz, 1H), 7.56 (ddd, $J$ = 8.0, 2.1, 1.1 Hz, 1H), 7.48 – 7.38 (m, 4H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 188.24, 146.45, 140.07, 136.72, 135.12, 134.01, 130.19, 128.91, 127.42, 127.29, 125.87, 125.85. HRMS (ESI$^+$): calcd for C$_{12}$H$_8$NO$_2$ClNa $[M+Na]^+$ 256.0141, found 256.0127.

(2-Methoxyphenyl)(1-oxido-2-pyridinyl)methanone (3p): Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3p as a brown liquid (17.4 mg, 38%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.18 – 8.12 (m, 1H), 7.92 (dd, $J$ = 8.0, 1.8 Hz, 1H), 7.51 (ddd, $J$ = 5.6, 1.3 Hz, 1H), 7.48 (ddd, $J$ = 8.0, 2.1, 1.1 Hz, 1H), 7.42 (dt, $J$ = 1.9 Hz, 1H), 7.38 (m, 4H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 188.24, 146.45, 140.07, 136.72, 135.12, 134.01, 130.19, 128.91, 127.42, 127.29, 125.87, 125.85. HRMS (ESI$^+$): calcd for C$_{13}$H$_8$NO$_2$ClNa $[M+Na]^+$ 275.0334, found 275.0334.
\( ^1H \) NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.80 (d, \( J = 5.8 \) Hz, 1H), 7.71 (d, \( J = 7.7 \) Hz, 1H), 7.56 (td, \( J = 7.5, 1.5 \) Hz, 1H), 7.48 (d, \( J = 7.6 \) Hz, 1H), 7.36 – 7.30 (m, 3H), 7.23 – 7.15 (m, 4H), 7.05 (ddd, \( J = 7.0, 3.8, 2.1 \) Hz, 2H). \( ^{13} \)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 198.65, 156.73, 147.07, 141.46, 140.07, 137.46, 131.62, 130.28, 129.20, 128.89, 127.95, 127.64, 127.51, 127.08, 124.64. HRMS (ESI\(^+\)): calcd for \( C_{18}H_{13}NO_2 \) [M+Na]\(^+\) 298.0844, found 298.0828.

(3,4-Dimethoxyphenyl)(1-oxido-2-pyridinyl)methanone (3r) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3r as a yellowish solid (38.8 mg, 75%, mp = 143-144 \(^o\)C). \( ^1H \) NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 8.29 – 8.19 (m, 1H), 7.57 (d, \( J = 2.1 \) Hz, 1H), 7.41 – 7.34 (m, 3H), 7.22 (dd, \( J = 8.4, 2.0 \) Hz, 1H), 6.83 (d, \( J = 8.4 \) Hz, 1H), 3.92 (d, \( J = 5.5 \) Hz, 6H). \( ^{13} \)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 187.76, 154.49, 149.47, 147.32, 140.08, 128.23, 126.73, 125.65, 125.43, 110.32, 110.30, 56.19, 56.06. IR(KBr)/cm\(^{-1}\): 3450, 3070, 1660, 1600, 1430, 1310, 1230, 1140, 1020, 763. HRMS (ESI\(^+\)): calcd for \( C_{14}H_{14}NO_4 \) [M+H]\(^+\) 260.0923, found 260.0912.
(3-Methyl-4-methoxyphenyl)(1-oxido-2-pyridinyl)methanone (3t) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3t as a yellowish liquid (42.7 mg, 88%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.24 (ddd, $J = 4.8, 3.2, 2.0$ Hz, 1H), 7.71 – 7.60 (m, 2H), 7.37 (h, $J = 3.4$ Hz, 3H), 6.84 (d, $J = 9.2$ Hz, 1H), 3.88 (s, 3H), 2.21 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 186.89, 161.90, 146.61, 139.03, 130.70, 129.14, 126.54, 126.42, 125.57, 124.60, 124.40, 108.62, 54.63, 15.22. HRMS (ESI$^+$): calcd for C$_{14}$H$_{14}$NO$_3$ [M+H]$^+$ 244.0974, found 244.0960.

(3,4,5-Methoxyphenyl)(1-oxido-2-pyridinyl)methanone (3u) : Purification by column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded 3u as a yellowish liquid (41.6 mg, 72%, mp = 162-164 °C). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.26 (ddd, $J = 4.2, 2.5, 1.0$ Hz, 1H), 7.40 (tddt, $J = 5.2, 3.5, 2.6, 1.2$ Hz, 3H), 7.07 (d, $J = 1.1$ Hz, 2H), 3.90 (t, $J = 1.0$ Hz, 3H), 3.84 (t, $J = 1.0$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 188.10, 153.38, 147.04, 143.89, 140.08, 130.20, 126.92, 125.70, 125.43, 106.84, 60.98, 56.32. IR(KBr)/cm$^{-1}$: 3360, 3080, 1650, 1580, 1460, 1340, 1230, 1130, 994, 762. HRMS (ESI$^+$): calcd for C$_{15}$H$_{16}$NO$_5$ [M+H]$^+$ 290.1028, found 290.1043.

(4-Methoxyphenyl)(1-oxido-6-methylpyridin-2-yl)methanone (3v) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3v as a yellowish solid (39.3 mg, 81%, mp = 125-128 °C). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.76 – 7.71 (m, 2H), 7.33 (ddd, $J = 7.6, 2.3, 0.7$ Hz, 1H), 7.24 – 7.18 (m, 2H), 6.91 – 6.85 (m, 2H), 3.81 (s, 3H), 2.49 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 188.15, 164.34, 149.87, 147.31, 131.72, 128.43, 127.02, 125.20, 122.80, 114.17, 55.58, 17.47. HRMS (ESI$^+$): calcd for C$_{14}$H$_{14}$NO$_3$ [M+H]$^+$ 244.0974, found 244.0960.

(4-Methoxyphenyl)(1-oxido-5-methylpyridin-2-yl)methanone (3w) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3w as a white solid (40.3 mg, 83%,
mp = 125-128 °C. $^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 8.07 (s, 1H), 7.82 – 7.75 (m, 2H), 7.28 – 7.25 (m, 1H), 7.18 (dd, $J$ = 7.9, 1.5, 0.8 Hz, 1H), 6.95 – 6.88 (m, 2H), 3.84 (s, 3H), 2.35 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-\textit{d}) $\delta$ 187.88, 164.41, 144.76, 139.76, 137.86, 131.90, 128.34, 127.10, 125.04, 114.11, 55.59, 18.38. IR(KBr)/cm$^{-1}$: 3450, 3040, 2840, 1640, 1600, 1330, 1270, 1160, 1020, 961, 767. HRMS (ESI$^+$): calcd for C$_{14}$H$_{14}$NO$_3$ [M+H]$^+$ 244.0974, found 244.0960.

(4-Methoxyphenyl)(1-oxido-4-methylpyridin-2-yl)methanone (3x) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3x as a yellowish solid (38.9 mg, 80%, mp = 125-128 °C). $^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 8.06 (d, $J$ = 7.1 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.11 (d, $J$ = 6.3 Hz, 2H), 6.90 – 6.83 (m, 2H), 3.79 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-\textit{d}) $\delta$ 187.89, 164.56, 146.81, 139.36, 137.74, 132.04, 128.19, 127.56, 126.00, 114.23, 55.67, 20.44. HRMS (ESI$^+$): calcd for C$_{14}$H$_{14}$NO$_3$ [M+H]$^+$ 244.0974, found 244.0960.

(4-Methoxy-phenyl)-(1-oxy-quinolin-2-yl)-methanone (3y) : Purification by column chromatography on silica gel (DCM/MeOH = 100/1, v/v) afforded 3y as a yellowish liquid (36.8 mg, 66%). $^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 8.73 (d, $J$ = 8.8 Hz, 1H), 7.96 – 7.91 (m, 1H), 7.85 – 7.78 (m, 4H), 7.71 (ddd, $J$ = 8.1, 6.9, 1.3 Hz, 1H), 7.39 (d, $J$ = 8.6 Hz, 1H), 6.96 – 6.91 (m, 2H), 3.85 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-\textit{d}) $\delta$ 187.56, 163.44, 142.17, 140.66, 130.80, 129.93, 129.53, 128.41, 128.41, 127.24, 124.80, 119.44, 118.87, 113.24, 54.56. HRMS (ESI$^+$): calcd for C$_{17}$H$_{14}$NO$_3$ [M+H]$^+$ 280.0974, found 280.0924.

(4-Methoxyphenyl)(1-oxido-4-methoxypyridin-2-yl)methanone (3z) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3z as a yellowish liquid (38.3 mg, 74%). $^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 8.12 (d, $J$ = 7.2 Hz, 1H), 7.83 – 7.79 (m, 2H), 6.95 – 6.90 (m, 3H), 6.86 (d, $J$ = 3.4 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-\textit{d}) $\delta$
187.19, 164.59, 157.82, 148.01, 140.80, 132.10, 127.87, 114.21, 113.35, 110.14, 56.35, 55.62. HRMS (ESI\(^{+}\)): calcd for C\(_{14}\)H\(_{14}\)NO\(_4\) [M+H]\(^{+}\) 260.0923, found 260.0912.

(4-Methoxyphenyl)(1-oxido-5-chloropyridin-2-yl)methanone (3aa) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3aa as a yellowish liquid (37.9 mg, 72%). \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 8.27 (dd, \(J = 1.7, 0.7\) Hz, 1H), 7.81 – 7.77 (m, 2H), 7.38 – 7.32 (m, 2H), 6.96 – 6.92 (m, 2H), 3.87 (s, 3H). \(^{13}\)C NMR (100 MHz, Chloroform-d) \(\delta\) 186.78, 164.72, 146.04, 139.33, 134.24, 131.93, 127.92, 125.96, 125.57, 114.26, 55.64. HRMS (ESI\(^{+}\)): calcd for C\(_{13}\)H\(_{16}\)NO\(_3\)ClNa [M+Na]\(^{+}\) 286.0247, found 286.0271.

(4-Dimethylaminophenyl)(1-oxido-2-pyridinyl)methanone (3ab) : Purification by column chromatography on silica gel (DCM/MeOH = 50/1, v/v) afforded 3ab as a light yellow solid (36.3 mg, 75%). \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 8.25 (t, \(J = 2.1\) Hz, 1H), 7.75 – 7.68 (m, 2H), 7.35 (d, \(J = 2.6\) Hz, 3H), 6.64 (dd, \(J = 8.9, 1.5\) Hz, 2H), 3.06 (s, 6H). \(^{13}\)C NMR (100 MHz, Chloroform-d) \(\delta\) 186.56, 154.33, 148.31, 140.04, 132.11, 126.20, 125.61, 125.49, 122.82, 110.93, 40.05. HRMS (ESI\(^{+}\)): calcd for C\(_{14}\)H\(_{15}\)N\(_2\)O\(_2\) [M+H]\(^{+}\) 243.1134, found 243.1125.

(4-Methoxyphenyl)(2-pyridinyl)methanone (4a) : Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded 4a as a yellowish solid (0.63 g, 69%). \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 8.69 (ddd, \(J = 4.8, 1.8, 1.0\) Hz, 1H), 8.15 – 8.08 (m, 2H), 7.98 (dt, \(J = 7.8, 1.1\) Hz, 1H), 7.87 (tt, \(J = 7.8, 1.5\) Hz, 1H), 7.45 (ddt, \(J = 7.5, 4.8, 1.3\) Hz, 1H), 7.00 – 6.91 (m, 2H), 3.87 (d, \(J = 1.3\) Hz, 3H). \(^{13}\)C NMR (100 MHz, Chloroform-d) \(\delta\) 191.26, 162.54, 154.72, 147.32, 135.98, 132.46, 127.94, 124.80, 123.49, 112.49, 54.46. IR(KBr)/cm\(^{-1}\): 3430, 3010, 1650, 1610, 1260, 1020, 936, 751. HRMS (ESI\(^{+}\)): calcd for C\(_{13}\)H\(_{12}\)NO\(_2\) [M+H]\(^{+}\) 214.0868, found 214.0852.
4-Methoxybiphenyl (5) : Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded 5 as a white solid (4.4 mg, 12%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.58 – 7.51 (m, 4H), 7.42 (dd, J = 8.5, 6.9 Hz, 2H), 7.34 – 7.28 (m, 1H), 7.01 – 6.95 (m, 2H), 3.86 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 158.10, 139.79, 132.74, 127.68, 127.11, 125.70, 125.61, 113.16, 54.31. HRMS (ESI$^+$): calcd for C$_{13}$H$_{13}$O [M+H]$^+$ 185.0966, found 185.0952.

4,4'-Dimethoxybiphenyl (6) : Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded 6 as a yellowish liquid (7.3 mg, 17%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.51 – 7.45 (m, 4H), 6.99 – 6.93 (m, 4H), 3.85 (s, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 157.65, 132.45, 126.70, 113.13, 54.32. HRMS (ESI$^+$): calcd for C$_{14}$H$_{15}$O$_2$ [M+H]$^+$ 215.1072, found 215.1091.

1,3,5-Trimethoxybenzene (7) : Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1, v/v) afforded 7 as a white solid (25.5 mg, 76%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 6.98 (t, J = 8.4 Hz, 1H), 6.58 (d, J = 8.4 Hz, 2H), 3.85 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 153.53, 138.14, 123.64, 105.23, 60.82, 56.07. HRMS (ESI$^+$): calcd for C$_9$H$_{13}$O$_3$ [M+H]$^+$ 169.0865, found 169.0842.

2-(3,4,5-Trimethoxybenzoyl)quinoline (10b) : Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded 10b as a green yellow liquid (0.75 g, 55%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.36 (d, J = 8.3 Hz, 1H), 8.20 (d, J = 8.2 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.93 (dd, J = 8.2, 1.4 Hz, 1H), 7.80 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.68 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.64 (s, 2H), 3.97 (s, 3H), 3.91 (s, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 191.10, 153.89, 151.70, 145.61, 141.80, 136.16, 129.90, 129.34, 129.22, 127.86, 127.42, 126.69, 120.03, 108.22, 59.96, 55.24. HRMS (ESI$^+$): calcd for C$_{19}$H$_{16}$NO$_4$ [M+H]$^+$ 324.1236, found 324.1278.

VI. X-ray crystal structure of 3f
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<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Empirical formula</td>
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<tr>
<td>Temperature/K</td>
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<td>Crystal system</td>
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<td>Space group</td>
<td>P4_{2}/n</td>
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<tr>
<td>b/Å</td>
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<tr>
<td>c/Å</td>
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</tr>
<tr>
<td>α/°</td>
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<tr>
<td>β/°</td>
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</tr>
<tr>
<td>γ/°</td>
<td>90</td>
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<tr>
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<tr>
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<tr>
<td>F(000)</td>
<td>1088.0</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
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</tr>
</tbody>
</table>
Radiation       MoKα (λ = 0.71073)
2Θ range for data collection/°  6.138 to 52.666
Index ranges       -24 ≤ h ≤ 23, -24 ≤ k ≤ 24, -8 ≤ l ≤ 8
Reflections collected  11605
Independent reflections  2851 [R_int = 0.0347, Rsigma = 0.0343]
Data/restraints/parameters  2851/0/175
Goodness-of-fit on F²  1.022
Final R indexes [I>=2σ (I)]  R₁ = 0.0506, wR₂ = 0.1102
Final R indexes [all data]  R₁ = 0.0882, wR₂ = 0.1280
Largest diff. peak/hole / e Å⁻³  0.15/-0.18

VII. References
VIII. Copies of $^1$H and $^{13}$C spectra

(1a):
(1d):

**$^1$H NMR**

**$^{13}$C NMR**
**1H NMR**

**13C NMR**
(1f):

$^1$H NMR

$^{13}$C NMR
(3b):
H NMR

\[ \begin{array}{c}
1.98 \\
3.31 \\
2.91 \\
1.98 \\
1.98
\end{array} \]

13C NMR

\[ \begin{array}{c}
181.97 \\
41.96 \\
132.77 \\
128.58 \\
128.71 \\
128.82 \\
128.56 \\
\end{array} \]
S33

$^1$H NMR

$^{13}$C NMR
(3e):

$^1$H NMR

$^1$C NMR

$^1$C NMR
(3f): 

**H NMR**

**C NMR**
H NMR

$^{13}$C NMR
(3h): 

$^{1}H$ NMR

$^{13}C$ NMR
**$^{1}H$ NMR**

$^{13}C$ NMR

S38
H NMR

13C NMR
$^{19}$F NMR

(3n):

$^1$H NMR
$^{13}$C NMR

(3p):

$^1$H NMR
$^{13}$C NMR:

(3q):

$^1$H NMR:

$^1$H NMR
$^{13}$C NMR

$^1$H NMR

\[ \text{OMe (3t):} \]

\[ \text{O}^{\text{N}^+} \text{O} \backslash \text{CH}_3 \]

\[ \text{OMe (3t):} \]

\[ \text{O}^{\text{N}^+} \text{O} \backslash \text{CH}_3 \]
$^{13}$C NMR

(3u):

$^1$H NMR
$^1$H NMR

$^1$C NMR

(3v):
$^{13}$C NMR

(3w):

$^1$H NMR
$^{13}$C NMR

(3x):

$^1$H NMR
$^{1}H$ NMR

$^{13}C$ NMR
$^{13}\text{C NMR}$

(3aa):

$^{1}\text{H NMR}$
$\text{C NMR}$

$\text{H NMR}$

\begin{align*}
\text{\textsuperscript{13}C NMR} & \\
\text{H NMR} & \\
\end{align*}


\[ \text{\^{13}C NMR} \]

\[ \text{(4a):} \]

\[ \text{\textbf{H NMR}} \]

S58
$^{13}$C NMR

(5):

$^1$H NMR
$^{13}$C NMR

(6):

$^1$H NMR
$^{13}$C NMR

(7):

$^1$H NMR
$^{13}$C NMR

(10b):
1H NMR

13C NMR