Supporting Information

Aryldiazonium Promoted Gold-Redox Catalysis: C-Br, C-P and C-S Bond Formation through Catalytic Sandmeyer Coupling

Haihui Peng, Rong Cai, Chang Xu, Hao Chen and Xiaodong Shi

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I. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. PPh₃AuCl, PPh₃AuNTf₂ were synthesized according to literature report. ¹H NMR, ¹³C NMR, ³¹P NMR, and ¹⁹F NMR spectra were recorded on Agilent 400 MHz or Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl₃ (δ 7.26 ppm) for ¹H and CDCl₃ (δ 77.0 ppm) for ¹³C. Flash column chromatography was performed on 230-430 mesh silica gel.

II. General Procedures

A. General procedure of conditions for Au(I) catalyzed C-X bond formation

\[
\text{[ArN₂][BF₄]} + \text{MX} \xrightarrow{\text{cat. Au}} \text{CH₃CN} \rightarrow \text{F} - \text{X} + \text{F} - \text{H} \rightarrow \text{X} \rightarrow \text{4a} \rightarrow \text{3a}
\]

In a dried glass tube, 1a (0.1 mmol), [Au] (0.005 mmol, 5 mol %) and MX (0.3 mmol, 3 equiv) were dissolved in CH₃CN (0.3 mL). The reaction mixture was stirred at 50 °C for 5-12 h. After the reaction completed, the reaction was filtrate through a pad of silica gel. After evacuation of the solvents, the NMR yields were obtained by ¹⁹F NMR analysis of the crude mixture with the internal standard of benzotrifluoride. The results were summarized in Table S1.

Table S1. Screening of conditions

<table>
<thead>
<tr>
<th>entry</th>
<th>cat.Au(%)</th>
<th>MX</th>
<th>Solvent</th>
<th>Time/h</th>
<th>convn (%)</th>
<th>yield (%)abc</th>
<th>5a</th>
<th>3a</th>
<th>4a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>LiCl</td>
<td>CH₃CN</td>
<td>50 °C, 12 h</td>
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<td>&lt;10</td>
<td>Trace</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>2</td>
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<td>CH₃CN</td>
<td>50 °C, 12 h</td>
<td>70</td>
<td>5a*,&lt;5</td>
<td>Trace</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>3</td>
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<td>LiCl</td>
<td>CH₃CN</td>
<td>50 °C, 12 h</td>
<td>77</td>
<td>5a*,&lt;5</td>
<td>Trace</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5% Ph₃PAuCl</td>
<td>NaBr</td>
<td>CH₃CN</td>
<td>50 °C, 12 h</td>
<td>100</td>
<td>5a,51</td>
<td>11</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>5</td>
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<td>NaBr</td>
<td>CH₃CN</td>
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<td>5a,58</td>
<td>9</td>
<td>18</td>
<td></td>
</tr>
<tr>
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<td>CH₃CN</td>
<td>50 °C, 12 h</td>
<td>100</td>
<td>5a,68</td>
<td>6</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5% Ph₃PAuNTf₂</td>
<td>LiBr</td>
<td>CH₃CN</td>
<td>20% bpy, 50 °C, 5 h</td>
<td>100</td>
<td>5a,63</td>
<td>8</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5% Ph₃PAuCl</td>
<td>LiBr</td>
<td>CH₃CN</td>
<td>50 °C, 5 h</td>
<td>100</td>
<td>5a,83</td>
<td>7</td>
<td>Trace</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>3% Ph₃PAuCl</td>
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<td>50 °C, 5 h</td>
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<td>5a,81</td>
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<td>&lt;5</td>
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</tr>
<tr>
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<td>1% Ph₃PAuCl</td>
<td>LiBr</td>
<td>CH₃CN</td>
<td>50 °C, 5 h</td>
<td>100</td>
<td>5a,63</td>
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<td>9</td>
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</tr>
<tr>
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<td>5a,11</td>
<td>37</td>
<td>Trace</td>
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*Reaction conditions: 1a (0.1 mmol), Au (5 mol%), MX (0.3 mmol), additives and solvent (0.33M); b Determined by ¹⁹F NMR using benzotrifluoride as internal standard; c The major byproduct is biaryl; d Yield of biaryl: 37%.
B. General procedure of conditions for Au(I) catalyzed C-P bond formation

In a dried glass tube, 1a (0.2 mmol, 2 equiv), [Au] (0.005 mmol, 5 mol %), HP(O)(OEt)$_2$ (0.1 mmol, 1 equiv) and additives (2 equiv) were dissolved in CH$_3$CN (0.3 mL). The reaction mixture was stirred at 50 °C for 5-12 h. After the reaction completed, the reaction was filtrate through a pad of silica gel. After evacuation of the solvents, the NMR yields were obtained by $^{19}$F NMR analysis of the crude mixture with the internal standard of benzotrifluoride. The results were summarized in Table S2.

Table S2. Screening of conditions

<table>
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<tr>
<th>entry</th>
<th>cat. Au(%)</th>
<th>Additive(2 equiv)</th>
<th>Solvent</th>
<th>Time/h</th>
<th>convn (%)$^c$</th>
<th>yield (%)$^{c,d}$</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>None</td>
<td>CH$_3$CN</td>
<td>10 h</td>
<td>50</td>
<td>0 31 0</td>
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<tr>
<td>2</td>
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<td>CH$_3$CN</td>
<td>10 h</td>
<td>100</td>
<td>0 70 0</td>
</tr>
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<td>3</td>
<td>1 eq Cu(OAc)$_2$</td>
<td>Na$_2$CO$_3$</td>
<td>CH$_3$CN</td>
<td>10 h</td>
<td>100</td>
<td>0 75 0</td>
</tr>
<tr>
<td>4</td>
<td>5% PPh$_3$AuCl</td>
<td>None</td>
<td>CH$_3$CN</td>
<td>10 h</td>
<td>50</td>
<td>25 13 0</td>
</tr>
<tr>
<td>5</td>
<td>5% PPh$_3$AuCl</td>
<td>Na$_2$CO$_3$</td>
<td>CH$_3$CN</td>
<td>10 h</td>
<td>100</td>
<td>11 38 0</td>
</tr>
<tr>
<td>6</td>
<td>5% PPh$_3$AuNTf$_2$</td>
<td>20% bpy, Na$_2$CO$_3$</td>
<td>CH$_3$CN</td>
<td>10 h</td>
<td>100</td>
<td>&lt;5 53 11</td>
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<td>7</td>
<td>5% PPh$_3$AuNTf$_2$</td>
<td>3-Cl-py</td>
<td>CH$_3$CN</td>
<td>5 h</td>
<td>100</td>
<td>67 16 0</td>
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<td>5 h</td>
<td>100</td>
<td>73 15 0</td>
</tr>
<tr>
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<td>None$^d$</td>
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<td>CH$_3$CN</td>
<td>10 h</td>
<td>69</td>
<td>0 5 44</td>
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<tr>
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<td>CH$_3$CN</td>
<td>10 h</td>
<td>&gt;90</td>
<td>0 25 4</td>
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<td>2 h</td>
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<td>3 h</td>
<td>100</td>
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<td>0.5 h</td>
<td>100</td>
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<td>3-Cl-py</td>
<td>CH$_3$CN/EtOH = 6:1</td>
<td>3 h</td>
<td>100</td>
<td>83 7 0</td>
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<td>15</td>
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<td>3-Cl-py</td>
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<td>5 h</td>
<td>100</td>
<td>70 13 0</td>
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<td>CH$_3$CN/EtOH = 6:1</td>
<td>7 h</td>
<td>100</td>
<td>51 18 0</td>
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</table>

$^a$ Reaction conditions: 1a (0.2 mmol), Au (5 mol%), HP(O)(OEt)$_2$ (0.1 mmol), additives and solvent (0.33M); $^c$ Determined by $^{19}$F NMR using benzotrifluoride as internal standard; $^d$ The major byproduct is biaryl, yield of biaryl:37%; $^d$ room temperature.

S3
C. General procedure for Au(I) catalyzed C-Br bond formation

\[ [\text{ArN}_2]^+(\text{BF}_4^-) + \text{LiBr} \rightarrow \text{Ar} - \text{Br} \]

In a dried glass tube, 1 (0.2 mmol), PPh\(_3\)AuCl (0.010 mmol, 5 mol %) and LiBr (0.6 mmol, 3 equiv) were dissolved in CH\(_3\)CN (0.5 mL). The reaction mixture was stirred at 50 °C for 5 h. After the reaction completed, the reaction mixture was directly put on the column to obtain the product.

D. General procedure for Au(I) catalyzed C-S bond formation

\[ [\text{ArN}_2]^+(\text{BF}_4^-) + \text{HS}\text{COOMe} \rightarrow \text{ArS}\text{COOMe} \]

In a dried glass tube, 1 (0.4 mmol, 2 equiv), PPh\(_3\)AuCl (0.010 mmol, 5 mol %), Na\(_2\)CO\(_3\) (2 equiv) and 4 (0.2 mmol, 1 equiv) were dissolved in CH\(_3\)CN (0.5 mL). The reaction mixture was stirred at room temperature for 3 h. After the reaction completed, the reaction mixture was directly put on the column to obtain the product.

E. General procedure for Au(I) catalyzed C-P bond formation

\[ [\text{ArN}_2]^+(\text{BF}_4^-) + \text{HPOEt} \rightarrow \text{ArP}OEt \]

In a dried glass tube, 1 (0.4 mmol, 2 equiv), PPh\(_3\)AuCl (0.010 mmol, 5 mol %), diethyl phosphite (0.2 mmol, 1 equiv) and 3-Cl-Py (0.4 mmol, 1 equiv) were dissolved in CH\(_3\)CN (0.5 mL). The reaction mixture was stirred at 50 °C for 8 h. After the reaction completed, the reaction mixture was directly put on the column to obtain the product.
III. Stoichiometric experiment with PPh₃Au complex

A. Stoichiometric experiments of diazonium with PPh₃AuCl

In a dried glass tube, 1a (0.036 mmol, 1.1 equiv), Nu⁻ (1 equiv) and PPh₃AuCl (0.033 mmol, 1 equiv) were dissolved in CD₃CN (0.3 mL). The reaction mixture was stirred at 50 °C for 10h. The results were summarized in Figure S1. By using bpy as nucleophile, the reaction kinetics was also monitored with ³¹P NMR, the results were summarized in Figure S2.

**Figure S1.** ³¹P NMR of PPh₃AuCl with diazonium 1a in the presence of nucleophiles

**Figure S2.** ³¹P NMR of PPh₃AuCl with diazonium 1a in the presence of bpy
B. Stoichiometric experiments of diazonium with PPh₃AuNTf₂

In a dried glass tube, 1a (0.05 mmol, 1.5 equiv) and PPh₃AuNTf₂ (0.033 mmol, 1 equiv) were dissolved in CD₃CN (0.3 mL). The reaction mixture was stirred at 50 °C for 10 h. The reaction was monitored by ³¹P NMR and ¹⁹F NMR. The results were summarized in Figure S3 and Figure S4.

C. Stoichiometric experiments of diazonium with PPh₃AuCl

In a dried glass tube, 1a (0.05 mmol, 1.5 equiv) and PPh₃AuCl (0.033 mmol, 1 equiv) were dissolved in CD₃CN (0.3 mL). The reaction mixture was stirred at 50 °C for 10 h. The reaction was monitored by ³¹P NMR and ¹⁹F NMR. The results were summarized in Figure S3 and Figure S4.

D. Stoichiometric experiments of diazonium with PPh₃AuNTf₂ and 1 equiv LiCl

In a dried glass tube, 1a (0.05 mmol, 1.5 equiv), PPh₃AuNTf₂ (0.033 mmol, 1 equiv) and LiCl (0.033 mmol, 1 equiv) were dissolved in CD₃CN (0.3 mL). The reaction mixture was stirred at 50 °C for 10 h. The reaction was monitored by ³¹P NMR and ¹⁹F NMR. The results were summarized in Figure S3 and Figure S4.

E. Stoichiometric experiments of diazonium with PPh₃AuNTf₂ and 10 equiv LiCl

In a dried glass tube, 1a (0.05 mmol, 1.5 equiv), PPh₃AuNTf₂ (0.033 mmol, 1 equiv) and LiCl (0.33 mmol, 10 equiv) were dissolved in CD₃CN (0.3 mL). The reaction mixture was stirred at 50 °C for 10 h. The reaction was monitored by ³¹P NMR and ¹⁹F NMR. The results were summarized in Figure S3 and Figure S4.
Figure S3. $^{31}$P NMR analysis of stoichiometric experiments

Figure S4. $^{19}$F NMR analysis of stoichiometric experiments
IV. Kinetics Experiments for C-S bond formation

A. Kinetics Experiments for Au-catalyzed C-S bond formation

In a dried glass tube, 1a (0.4 mmol, 2 equiv), PPh$_3$AuCl (0.010 mmol, 5 mol %), Na$_2$CO$_3$ (0.4 mmol, 2 equiv) and 4 (0.2 mmol, 1 equiv) were dissolved in CD$_3$CN (0.5 mL). The reaction mixture was stirred at room temperature for 3 h. The reaction was monitored by $^{19}$F NMR analysis with the internal standard of benzotrifluoride with different reaction time. The results were summarized in Figure S5.

![Figure S5. PPh$_3$AuCl catalyzed C-S bond formation](image-url)
B. Kinetics Experiments for C-S bond formation without gold catalyst

In a dried glass tube, 1a (0.4 mmol, 2 equiv), Na$_2$CO$_3$ (0.4 mmol, 2 equiv) and 4 (0.2 mmol, 1 equiv) were dissolved in CD$_3$CN (0.5 mL). The reaction mixture was stirred at room temperature for 3 h. The reaction was monitored by $^{19}$F NMR analysis with the internal standard of benzotrifluoride with different reaction time. The results were summarized in Figure S6.

![Figure S6](image_url)

**Figure S6.** Na$_2$CO$_3$ promoted C-S bond formation
C. Kinetics Experiments for C-S bond formation without base and catalyst

![Chemical reaction diagram]

In a dried glass tube, 1a (0.4 mmol, 2 equiv) and 4 (0.2 mmol, 1 equiv) were dissolved in CD$_3$CN (0.5 mL). The reaction mixture was stirred at room temperature for 3 h. The reaction was monitored by $^{19}$F NMR analysis with the internal standard of benzotrifluoride with different reaction time. The results were summarized in Figure S7.

![Graph showing percentage vs. time]

**Figure S7.** No metal or base promoted reaction
V. Exploring the Au(III) intermediate in Au(I) oxidation by electrospray ionization mass spectrometry (ESI-MS).

ESI-MS spectra were collected using a Waters Xevo QTof mass spectrometer (Milford, MA, USA) in the positive ion mode. The samples were infused and sprayed at a flow rate of 10 μL/min with an applied high voltage of 5 kV.

20 mM PPh₃AuCl was reacted with NaBr at a 1:3 ratio in CH₃CN and was stirred at room temperature for 12 h. The solution was further stirred at 50 °C for 1 h on the next day. Then 20 mM of aryldiazonium 2a was added to the reaction mixture and stirred for 1 h. The reaction solution was diluted to 500 μM using CH₃CN and subsequently analyzed using ESI-MS. The acquired MS data is shown in Figure S8. Besides the aruldiazonium ion [Ar-N₂⁺] (m/z 123) seen in the spectrum, a Au(III) complex ion [Ph₃PAuAr(Br)₂ + Ar-N₂⁺] is also detected at m/z 835 (Figure S8).

![Figure S8. ESI-MS spectrum of the reaction mixture with NaBr.](image)

Tandem MS analysis (MS/MS) was used to characterize the structures of assigned ions. Upon collision induced dissociation (CID), m/z 835 gave rise to fragment ions [Ph₃PAu⁺] (m/z 459), [Ar-PPh₃] (m/z 357), [Ar-N₂⁺] (m/z 123), consistent with the assigned Au(III) ion structure for m/z 835. (Figure S9).
The reaction was also examined using LiBr to replace NaBr. In the experiment, 20 mM PPh₃AuCl was reacted with LiBr in ACN at a 1:3 ratio and was stirred at room temperature for 12 h. The solution was stirred at 50 °C for 1 h on the next day. Then 20 mM of aryl diazonium 2a was added to the reaction mixture and stirred for 1 hr. The reaction solution was diluted to 500 µM using CH₃CN and subsequently analyzed using ESI-MS. The acquired MS data is shown in Figure S10. Beside [Ph₃PAuBr⁺] (m/z 545), [Ar-PPh₃⁺] (m/z 357), [Ar-N₂⁺] (m/z 123) seen in the spectrum, two solid (III) complex ions, [Ph₃PAuAr(Br)₂⁺ Li⁺] (m/z 719), [Ph₃PAuAr(Br)₂⁺ ArN₂⁺] (m/z 835) are also detected.
Figure S10. ESI-MS spectrum of the reaction mixture with LiBr

4 mM PPh₃AuCl was reacted with equal concentration of aryl diazonium and 2,2'-bipyridyl (bpy) at a 1:1:1 ratio in CH₃CN and was stirred at room temperature for 30 min. The reaction solution was diluted to 50 µM using CH₃CN and subsequently analyzed using ESI-MS and the sample injected flow rate was 5 µL/min. In addition to [Ar-N₂⁺] (m/z 123), [bpy+H⁺] (m/z 157), [bpy+Ar-N₂⁺] (m/z 279), [bpy+PPh₃Au⁺] (m/z 615), and [Cl⁺+2(PPh₃Au⁺)] (m/z 953) observed in the acquired MS spectrum (Figure S-X), an Au(III) complex ion [Ph₃PAuAr(Cl)(bpy)]⁺ was also detected at m/z 745.
Tandem MS analysis (MS/MS) was used to characterize the structures of assigned ions. Upon collision induced dissociation (CID), m/z 745 gave rise to fragment ions [Ar-PPh₃⁺] (m/z 357) and [Ar-AuCl(bpy)]⁺ (m/z 483), consistent with the assigned Au(III) ion structure for m/z 745. (Figure S-Y).
Figure S12. CID MS-MS spectrum of m/z 745
V. Compounds Characterization

Compounds 5a, 5b, 5c, 5d, 5e, 5f, and 5g are commercially available and volatile compounds. 5h, 5i, 5j, 5k, 5l, 5m, 5n, 5o, 5p, 5q, 5r, 5s, 5t, 5u, 5v, 5w, 5x, 5y, 5z, 5aa, 5ab were reported in literature.

![5a](image)

CAS: 460-00-4, GC-MS: 174.0, 95.1, 87.1, 75.1, 68.1, 50.1.

![5b](image)

CAS: 104-92-7, GC-MS: 187.8, 170.8, 142.9, 118.9, 92.0, 77.0, 63.0.

![5c](image)

CAS: 106-38-7, GC-MS: 169.9, 91.0, 65.0.

![5d](image)

CAS: 402-43-7, GC-MS: 223.8, 204.8, 173.8, 144.9, 125.0, 95.0, 75.0.

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CAS: 589-87-7, GC-MS: 281.6, 154.8, 140.9, 126.8, 75.0.

CAS: 106-37-6, GC-MS: 235.7, 154.8, 117.9, 75.0.

CAS: 108-86-1, GC-MS: 155.8, 77.0, 51.0.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.82 (dt, $J = 1.6$, 8.4 Hz, 2H), 7.61 (dt, $J = 1.6$, 8.8 Hz, 2H), 2.61 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 197.0, 135.8, 131.9, 129.8, 128.3, 26.5.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.77 (d, $J = 7.2$ Hz, 2H), 7.67 (dt, $J = 2.0$, 8.8 Hz, 2H), 7.61 (m, 3H), 7.49 (t, $J = 7.6$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 195.6, 137.1, 136.3, 132.6, 131.6, 131.5, 129.9, 128.4, 127.5.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.81 (dd, $J = 1.2$, 8.4 Hz, 2H), 7.63 (m, 2H), 7.45 (m, 3H), 7.35 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 195.9, 140.7, 136.1, 133.8, 133.2, 131.2, 130.3, 129.0, 128.7, 127.2, 119.5.
$^{1}$H NMR (400 MHz, CDCl$_3$): δ 7.04 (s, 1H), 7.03 (s, 1H), 6.04 (s, 2H), 2.61 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 199.4, 150.3, 147.3, 134.2, 113.8, 109.8, 102.4, 33.8, 30.2.

$^{1}$H NMR (400 MHz, CDCl$_3$): δ 7.45 (m, 3H), 6.29 (q, $J = 1.6$ Hz, 1H), 2.38 (q, $J = 1.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 159.9, 153.7, 151.8, 127.5, 125.6, 125.5, 120.1, 118.9, 115.2, 18.5.

HRMS: m/z (ESI) Calculated for [M+H]$^+$ 238.9708, Found 238.9688.

$^{1}$H NMR (400 MHz, CDCl$_3$): δ 9.13 (d, $J = 2.0$ Hz, 1H), 8.84 (d, $J = 2.0$ Hz, 1H), 8.43 (d, $J = 2.0$ Hz, 1H), 3.97 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 164.5, 154.5, 148.8, 139.5, 127.3, 120.6, 52.7.
$\textbf{5p}$

$1^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.20 (d, $J = 2.0$ Hz, 1H), 8.04 (d, $J = 3.0$ Hz, 1H), 7.53 (dd, $J = 2.0$, 9.0 Hz, 1H), 7.47 (ddd, $J = 1.0$, 7.0 Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.26 (m, 2H), 4.34 (q, $J = 7.5$ Hz, 2H), 1.4 (t, $J = 7.5$ Hz, 3H).

$13^1$C NMR (125 MHz, CDCl$_3$): $\delta$ 140.2, 138.5, 128.2, 126.3, 124.7, 123.1, 121.9, 120.6, 119.2, 111.5, 109.9, 108.7, 37.7, 13.7.

$\textbf{5q}$

$1^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55 (s, 1H), 7.59 (m, 3H), 7.31 (m, 2H), 7.23 (m, 1H), 2.69 (s, 3H), 2.46 (s, 3H).

$13^1$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.0, 150.6, 138.8, 138.3, 133.0, 131.4, 131.2, 127.6, 126.5, 125.3, 121.4, 115.4, 23.1, 17.6.


$\textbf{5r}$

$1^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.52 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 0.33 (s, 9H).

$13^1$C NMR (125 MHz, CDCl$_3$): $\delta$ 133.4, 131.5, 122.7, 122.1, 103.8, 95.6, 29.7, -0.1.

$\textbf{5s}$

$1^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.20 (d, $J = 2.0$ Hz, 1H), 8.04 (d, $J = 3.0$ Hz, 1H), 7.61 (d, $J = 16.0$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 6.42 (d, $J = 16.0$ Hz, 1H), 4.26 (q, $J = 7.5$ Hz, 2H), 1.33 (t, $J = 7.5$ Hz, 3H).

$13^1$C NMR (125 MHz, CDCl$_3$): $\delta$ 166.7, 143.2, 133.4, 132.1, 129.4, 124.4, 119.0, 60.6, 14.3.
\( \text{H NMR (400 MHz, CDCl}_3\text{): } \delta 7.94 (dd, J = 2.0, 6.4 \text{ Hz}, 2H), 7.53 (dd, J = 2.0, 6.4 \text{ Hz}, 2H), 7.23 (d, J = 8.4 \text{ Hz}, 1H), 6.88 (dd, J = 2.8, 8.4 \text{ Hz}, 1H), 6.84 (d, J = 2.8 \text{ Hz}, 1H), 2.83 (dd, J = 4.4 \text{ Hz}, 2H), 2.42 (d, J = 8.4 \text{ Hz}, 1H), 2.32 (m, 2H), 2.20 (m, 1H), 1.97 (m, 4H), 1.41 (m, 6H), 0.83 (s, 3H). \)

\( \text{13C NMR (100 MHz, CDCl}_3\text{): } \delta 220.5, 164.5, 148.5, 138.0, 137.5, 131.7, 131.5, 131.4, 128.5, 126.4, 121.4, 118.6, 50.4, 47.9, 44.2, 38.0, 35.9, 31.5, 29.4, 26.3, 25.7, 21.6, 13.8. \)

HRMS: m/z (ESI) Calculated for [M+H]\(^+\) 453.1065, Found 453.1061.

\( \text{1H NMR (400 MHz, CDCl}_3\text{): } \delta 7.39 (dd, J = 5.6, 9.2 \text{ Hz}, 2H), 6.96 (t, J = 8.8 \text{ Hz}, 2H), 5.35 (d, J = 7.6 \text{ Hz}, 1H), 4.50 (m, 1H), 3.53 (s, 3H), 3.27 (m, 2H), 1.38 (s, 9H). \)

\( \text{13C NMR (100 MHz, CDCl}_3\text{): } \delta 170.9, 162.1 (d, J = 246.0 \text{ Hz}), 154.8, 133.9 (dd, J = 8.0, 13.2 \text{ Hz}), 129.6, 116.0 (d, J = 21.7 \text{ Hz}), 80.0, 53.2, 52.2 (d, J = 12.2 \text{ Hz}), 38.1, 28.1 (d, J = 6.8 \text{ Hz}). \)

HRMS: m/z (ESI) Calculated for [M+Na]\(^+\) 352.0995, Found 352.0983.

\( \text{1H NMR (400 MHz, CDCl}_3\text{): } \delta 7.39 (dt, J = 2.0, 7.2 \text{ Hz}, 2H), 6.83 (dt, J = 2.0, 7.2 \text{ Hz}, 2H), 5.35 (d, J = 6.0 \text{ Hz}, 1H), 4.50 (m, 1H), 3.78 (s, 3H), 3.54 (s, 3H), 3.25 (d, J = 4.0 \text{ Hz}, 2H), 1.42 (s, 9H). \)

\( \text{13C NMR (125 MHz, CDCl}_3\text{): } \delta 171.1, 159.4, 154.9, 134.4, 124.7, 114.6, 79.9, 55.2, 53.1, 52.2, 38.7, 28.2. \)

HRMS: m/z (ESI) Calculated for [M+Na]\(^+\) 364.1195, Found 364.1185.

\( \text{1H NMR (500 MHz, CDCl}_3\text{): } \delta 7.31 (d, J = 8.0 \text{ Hz}, 2H), 7.09 (d, J = 8.0, \text{ Hz}, 2H), 5.37 (d, J = 7.0 \text{ Hz}, 1H), 4.53 (m, 1H), 3.54 (s, 3H), 3.31 (d, J = 5.0 \text{ Hz}, 2H), 2.31 (s, 3H), 1.41 (s, 9H). \)
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 171.0, 154.9, 137.1, 131.6, 130.8, 129.7, 79.9, 53.2, 52.2, 37.7, 28.1, 20.9.

7d
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.41 (d, $J$ = 8.0 Hz, 2H), 7.28 (t, $J$ = 8.0 Hz, 2H), 7.21 (t, $J$ = 7.5 Hz, 1H), 5.39 (d, $J$ = 7.0 Hz, 1H), 4.56 (m, 1H), 3.53 (s, 3H), 3.37 (m, 2H), 1.42 (s, 9H).
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 171.0, 155.0, 134.7, 131.0, 129.0, 127.0, 80.1, 53.2, 52.3, 37.2, 28.2.

7e
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.52 (d, $J$ = 8.4 Hz, 2H), 7.46 (d, $J$ = 8.4 Hz, 2H), 5.34 (d, $J$ = 6.4 Hz, 1H), 4.56 (m, 1H), 3.59 (s, 3H), 3.35 (m, 2H), 1.41 (s, 9H).
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 170.7, 154.9, 140.5, 129.3, 128.5 (q, $J$ = 26.2 Hz), 125.7, (d, $J$ = 2.7 Hz), 124.0 (q, $J$ = 216.3 Hz), 80.3, 53.3, 52.5, 36.0, 28.2.

7f
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (dd, $J$ = 2.0, 6.8 Hz, 2H), 7.14 (dt, $J$ = 1.6, 6.8 Hz, 2H), 5.29 (d, $J$ = 8.0 Hz, 1H), 4.57 (m, 1H), 3.60 (s, 3H), 3.37 (m, 2H), 1.42 (s, 9H).
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 170.8, 154.8, 138.0, 132.5, 92.1, 80.2, 53.3, 52.5, 37.0, 28.2.
$$\text{Br}$$

$$\text{NHBOc}$$

$$\text{COOMe}$$

$$7g$$

$${}^1\text{H NMR (500 MHz, CDCl}_3\text{:}$$ δ 7.40 (dt, J = 2.5, 9.0 Hz, 2H), 7.27 (dt, J = 2.0, 8.5 Hz, 2H), 5.35 (d, J = 7.5 Hz, 1H), 4.56 (m, 1H), 3.59 (s, 3H), 3.35 (m, 2H), 1.41 (s, 9H).

$${}^{13}\text{C NMR (125 MHz, CDCl}_3\text{:}$$ δ 170.8, 154.8, 134.0, 132.4, 132.0, 120.9, 80.1, 53.2, 52.4, 37.1, 28.2.


$$\text{O}$$

$$\text{NHBOc}$$

$$\text{COOMe}$$

$$7h$$

$${}^1\text{H NMR (500 MHz, CDCl}_3\text{:}$$ δ 7.87 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 5.32 (d, J = 7.5 Hz, 1H), 4.57 (m, 1H), 3.56 (s, 3H), 3.37 (m, 2H), 2.57 (s, 3H), 1.41 (s, 9H).

$${}^{13}\text{C NMR (125 MHz, CDCl}_3\text{:}$$ δ 197.0, 170.7, 154.9, 142.4, 134.7, 128.8, 128.1, 80.3, 53.2, 52.6, 35.4, 28.2, 26.5.


$$\text{Ph}$$

$$\text{O}$$

$$\text{NHBOc}$$

$$\text{COOMe}$$

$$7i$$

$${}^1\text{H NMR (400 MHz, CDCl}_3\text{:}$$ δ 7.76 (d, J = 7.6 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 5.41 (d, J = 6.8 Hz, 1H), 4.65 (m, 1H), 3.66 (s, 3H), 3.47 (m, 2H), 1.43 (s, 9H).

$${}^{13}\text{C NMR (125 MHz, CDCl}_3\text{:}$$ δ 195.6, 170.8, 154.9, 141.6, 137.5, 135.0, 132.4, 130.6, 129.8, 128.3, 127.9, 80.3, 53.2, 52.5, 35.4, 28.2.


$$\text{O}$$

$$\text{NHBOc}$$

$$\text{COOMe}$$

$$7j$$

$${}^1\text{H NMR (400 MHz, CDCl}_3\text{:}$$ δ 6.97 (d, J = 2.0 Hz, 1H), 6.92 (dd, J = 2.0, 6.4 Hz, 1H), 6.78 (d, J = 6.8 Hz, 1H), 5.34 (d, J = 5.6 Hz, 1H), 4.51 (m, 1H), 4.23 (s, 4H), 3.61 (s, 3H), 3.26 (m, 2H), 1.42 (s, 9H).

$${}^{13}\text{C NMR (125 MHz, CDCl}_3\text{:}$$ δ 171.1, 154.9, 143.6, 143.4, 125.8, 121.4, 117.8, 79.9, 64.3, 64.2, 53.2, 52.3, 38.4, 28.2.

**7k**

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.05 (s, 1H), 8.76 (d, $J = 1.5$ Hz, 1H), 8.31 (s, 1H), 5.39 (d, $J = 7.5$ Hz, 1H), 4.60 (m, 1H), 3.96 (s, 3H), 3.64 (s, 3H), 3.46 (m, 2H), 1.41 (s, 9H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 170.6, 165.1, 154.6, 148.7, 138.6, 132.7, 126.1, 80.4, 53.2, 52.6, 36.9, 28.2.


**7l**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.53 (s, 1H), 7.65 (dd, $J = 1.6$, 7.6 Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 5.38 (d, $J = 6.8$ Hz, 1H), 4.53 (m, 1H), 3.60 (s, 3H), 3.33 (m, 2H), 2.53 (s, 3H), 1.41 (s, 9H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 170.6, 157.4, 154.8, 151.8, 139.8, 128.2, 123.4, 80.1, 53.2, 37.8, 28.2, 23.9.


**7m**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.17 (dd, $J = 1.6$, 7.6 Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 5.38 (d, $J = 6.8$ Hz, 1H), 4.53 (m, 1H), 3.60 (s, 3H), 3.33 (m, 2H), 2.53 (s, 3H), 1.41 (s, 9H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 170.8, 159.8, 154.8, 149.6, 145.9, 123.9, 106.9, 80.3, 54.7, 53.3, 52.5, 38.9, 28.2.


**7n**

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.87 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 6.19 (d, $J = 7.5$ Hz, 1H), 4.75 (dd, $J = 5.5$, 12.0 Hz, 1H), 3.82 (d, $J = 5.0$ Hz, 2H), 3.73 (s, 3H), 1.41 (s, 9H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 170.9, 152.7, 135.5, 127.1, 126.2, 124.6, 121.6, 121.0, 111.8, 80.0, 53.9, 52.7, 35.4, 28.2.

1H NMR (500 MHz, CDCl₃): δ 7.35 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.32 (d, J = 7.5 Hz, 1H), 4.57 (m, 1H), 3.56 (s, 3H), 3.37 (m, 2H), 1.41 (s, 9H), 0.23 (s, 9H).
13C NMR (125 MHz, CDCl₃): δ 170.8, 154.9, 135.8, 132.3, 129.8, 121.5, 104.4, 95.1, 80.2, 53.2, 52.4, 36.6, 28.2, -0.1.

1H NMR (500 MHz, CDCl₃): δ 7.68 (d, J = 16.5 Hz, 1H), 7.58 (s, 4H), 6.47 (d, J = 16.5 Hz, 1H), 5.53 (d, J = 7.5 Hz, 1H), 4.76 (m, 1H), 4.27 (q, J = 7.0 Hz, 2H), 3.96 (m, 2H), 3.73 (s, 3H), 1.42 (s, 9H), 1.34 (t, J = 7.5 Hz, 3H).
13C NMR (125 MHz, CDCl₃): δ 170.9, 166.6, 154.9, 152.1, 143.2, 135.8, 128.8, 122.0, 119.4, 80.1, 60.6, 53.2, 52.6, 36.7, 28.2, 14.2.

1H NMR (500 MHz, CDCl₃): δ 7.62 (d, J = 15.5 Hz, 1H), 7.43 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 6.40 (d, J = 15.5 Hz, 1H), 5.38 (d, J = 7.5 Hz, 1H), 4.60 (m, 1H), 4.26 (q, J = 7.0 Hz, 2H), 3.60 (s, 3H), 3.41 (m, 2H), 1.41 (s, 9H), 1.34 (t, J = 7.0 Hz, 3H).
13C NMR (125 MHz, CDCl₃): δ 170.7, 166.8, 154.8, 152.1, 143.5, 132.6, 129.8, 128.4, 118.1, 80.0, 60.5, 53.2, 52.4, 36.2, 28.2, 14.2.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.73 (s, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.33 (m, 2H), 7.24 (m, 1H), 5.38 (d, $J = 7.6$ Hz, 1H), 4.65 (m, 1H), 3.63 (s, 3H), 3.45 (m, 2H), 2.71 (s, 3H), 2.47 (s, 3H), 1.43 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 170.9, 154.9, 151.2, 150.7, 138.7, 138.0, 131.2, 130.8, 129.2, 129.1, 126.3, 124.4, 121.0, 115.3, 80.2, 53.2, 52.5, 35.8, 29.6, 28.2, 20.6, 17.4.


$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J = 5.6$, 8.4, 13.6 Hz, 2H), 7.15 (ddd, $J = 3.2$, 9.2 Hz, 2H), 4.12 (m, 4H), 1.33 (t, $J = 7.2$ Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.3 (d, $J = 199.3$ Hz), 134.3 (t, $J = 9.1$ Hz), 124.4 (d, $J = 150.7$ Hz), 115.8 (dd, $J = 12.9$, 16.6 Hz), 62.1 (d, $J = 3.8$ Hz), 16.2 (d, $J = 4.9$ Hz).

HRMS: m/z (ESI) Calculated for [M+H]$^+$ 245.0943, Found 245.0931.
**8d**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (dd, $J = 3.6, 8.4$ Hz, 2H), 7.52 (dd, $J = 8.0, 12.8$ Hz, 2H), 4.11 (m, 4H), 1.32 (t, $J = 7.2$ Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 137.7 (d, $J = 15.2$ Hz), 133.1 (d, $J = 10.4$ Hz), 128.0 (d, $J = 188.8$ Hz), 100.1 (d, $J = 3.9$ Hz), 62.3 (d, $J = 5.3$ Hz), 16.3 (d, $J = 6.2$ Hz).

**8e**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.65 (m, 4H), 4.12 (m, 4H), 1.32 (t, $J = 7.2$ Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 133.2 (d, $J = 8.3$ Hz), 131.7 (d, $J = 12.1$ Hz), 127.5 (d, $J = 3.1$ Hz), 127.4 (d, $J = 151.9$ Hz), 62.2 (d, $J = 4.2$ Hz), 16.2 (d, $J = 5.4$ Hz).

**8f**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 (dd, $J = 8.4, 13.2$ Hz, 2H), 7.45 (dd, $J = 3.6, 8.4$ Hz, 2H), 4.11 (m, 4H), 1.32 (t, $J = 7.2$ Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.9 (d, $J = 3.0$ Hz), 133.1 (d, $J = 8.7$ Hz), 128.8 (d, $J = 12.5$ Hz), 126.9 (d, $J = 151.8$ Hz), 62.2 (d, $J = 4.2$ Hz), 16.2 (d, $J = 5.4$ Hz).


**8g**

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.94 (dd, $J = 8.0, 12.8$ Hz, 1H), 7.85 (m, 1H), 7.81 (m, 3H), 7.63 (m, 2H), 7.51 (m, 2H), 4.15 (m, 4H), 1.36 (t, $J = 7.2$ Hz, 6H).

**8h**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 (dd, $J = 8.4, 13.2$ Hz, 2H), 7.45 (dd, $J = 3.6, 8.4$ Hz, 2H), 4.11 (m, 4H), 1.32 (t, $J = 7.2$ Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 138.9 (d, $J = 3.0$ Hz), 133.1 (d, $J = 8.7$ Hz), 128.8 (d, $J = 12.5$ Hz), 126.9 (d, $J = 151.8$ Hz), 62.2 (d, $J = 4.2$ Hz), 16.2 (d, $J = 5.4$ Hz).
8i

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.74 (dd, $J = 8.5$, 13.5 Hz, 2H), 7.54 (dd, $J = 3.5$, 8.5 Hz, 2H), 4.10 (m, 4H), 1.32 (t, $J = 7.2$ Hz, 6H), 0.25 (s, 9H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 131.8 (d, $J = 14.6$ Hz), 131.5 (d, $J = 9.9$ Hz), 128.2 (d, $J = 188.3$ Hz), 127.3 (d, $J = 3.3$ Hz), 103.8, 97.4, 62.2 (d, $J = 5.3$ Hz), 16.3 (d, $J = 6.7$ Hz), -0.2.

HRMS: m/z (ESI) Calculated for [M+H]$^+$ 311.1232, Found 311.1220.

8j

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (dd, $J = 8.0$, 12.8 Hz, 2H), 7.78 (d, $J = 16.0$ Hz, 1H), 7.60 (dd, $J = 3.6$, 8.0 Hz, 2H), 6.51 (d, $J = 16.0$ Hz, 1H), 4.28 (q, $J = 7.2$ Hz, 2H), 4.13 (m, 4H), 1.35 (t, $J = 7.2$ Hz, 3H), 1.33 (t, $J = 7.2$ Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 166.5, 143.1, 138.2 (d, $J = 3.3$ Hz), 132.3 (d, $J = 10.0$ Hz), 127.8 (d, $J = 15.2$ Hz), 120.7, 130.1 (d, $J = 187.9$ Hz), 62.3 (d, $J = 5.6$ Hz), 60.8, 16.3 (d, $J = 6.6$ Hz), 14.3.

HRMS: m/z (ESI) Calculated for [M+H]$^+$ 313.1205, Found 313.1200.

(E)-8k

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.07 (dd, $J = 8.5$, 13.5 Hz, 1H), 7.76 (m, 2H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.38 (m, 2H), 7.27 (dt, $J = 2.0$, 8.0 Hz, 1H), 4.16 (m, 4H), 2.74 (s, 3H), 2.69 (s, 3H), 1.36 (t, $J = 6.5$ Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 155.0 (d, $J = 4.3$ Hz), 150.7, 143.1, 138.7, 135.0 (d, $J = 13.6$ Hz), 130.2 (d, $J = 188.6$ Hz), 131.4, 126.4, 125.4 (d, $J = 19.5$ Hz), 119.4 (d, $J = 19.0$ Hz), 115.4, 62.0 (d, $J = 6.6$ Hz), 21.3(d, $J = 4.2$ Hz), 17.6, 16.3 (d, $J = 7.8$ Hz).

HRMS: m/z (ESI) Calculated for [M+H]$^+$ 347.1525, Found 347.1510.
(Z)-8k

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.72 (dd, $J = 8.0, 13.5$ Hz, 1H), 7.18 (d, $J = 8.0$ Hz, 1H), 7.06 (t, $J = 7.5$ Hz, 1H), 6.91 (t, $J = 8.0$ Hz, 1H), 6.83 (dd, $J = 1.5, 5.0$ Hz, 1H), 6.54 (dt, $J = 2.5, 7.5$ Hz, 1H), 6.19 (d, $J = 8.0$ Hz, 1H), 4.09 (m, 4H), 2.49 (s, 3H), 2.33 (s, 3H), 1.30 (t, $J = 6.5$ Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 156.5 (d, $J = 4.3$ Hz), 152.8, 143.2, 141.4, 134.3 (d, $J = 13.6$ Hz), 131.1 (d, $J = 188.6$ Hz), 128.2, 127.7, 125.9, 123.1 (d, $J = 19.0$ Hz), 117.1, 115.8 (d, $J = 19.5$ Hz), 62.0 (d, $J = 6.6$ Hz), 21.2 (d, $J = 4.2$ Hz), 17.5, 16.2 (d, $J = 7.8$ Hz).

HRMS: m/z (ESI) Calculated for [M+H]$^+$ 347.1525, Found 347.1510.
F

\[ \text{S} \quad \text{NH\text{Boc}} \quad \text{COOMe} \]
$$\text{NHBoc}$$

$$\text{COOMe}$$
\[ \text{Diagram of a molecule with a phosphonate group and ethoxy groups.} \]