Supporting Information

for

Photocatalytic sequential C–H functionalization expediting acetoxyomalonylation of imidazo heterocycles

Deepak Singh, Shyamal Pramanik and Soumitra Maity


Experimental section and characterization of synthesized compounds
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1. General

All commercially available chemicals and reagents were used without further purification unless otherwise stated. Solvents for extraction or column chromatography were of technical quality. All water used was purified via a Merck Millipore reverse osmosis purification system prior to use. All reactions were performed in oven-dried glassware under a positive pressure of nitrogen with freshly distilled anhydrous solvents.\(^1\) Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. Solvents were removed under reduced pressure using IKA and Büchi rotary evaporator.

**Thin-layer chromatography (TLC):** The progress of the reaction was monitored by thin-layer chromatography (TLC) using SiO\(_2\)-60 UV254 coated aluminum sheets (Merck, TLC Silica gel 60 F\(_{254}\)). Visualization was achieved using UV light, iodine, and/or chemical staining with vanillin or basic potassium permanganate solutions as appropriate.

**Flash column chromatography (FC):** Purification of reaction mixtures was carried out with flash column chromatography on silica gel 230-400 mesh (Merck, 37–63 µm). Solvents for extraction and chromatography were of technical quality. Eluting solvent mixtures are individually reported in parenthesis.

**NMR spectra:** Proton, carbon, and fluorine nuclear magnetic resonance (\(^1\)H, \(^{13}\)C, and \(^{19}\)F NMR) spectra were recorded on a Bruker Avance III HD (400, 101, and 377 MHz) spectrometer at 25 °C. Chemical shifts (\(\delta\)) are given in ppm and reported as follows: multiplicity (s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), and m (multiplet)), coupling constants (\(J\)) in Hz, number of protons; suggested assignment. The residual deuterated solvent was used as internal standard (CDCl\(_3\): \(\delta_{\text{H}} = 7.26\) ppm; \(\delta_{\text{C}} = 77.16\) ppm).

**Melting point (Mp):** Melting points were measured using Tempstar melting point instrument Remco-Kolkata apparatus using open glass capillaries and are reported uncorrected.

**High-resolution mass spectrometry (HRMS):** HRMS were recorded using a QTOF micro MS system by ESI technique.

**GC–MS:** GC–MS analysis was done by a Thermo Scientific ISQ 7000 single quadrupole mass spectrometer fitted with TRACE 1310 gas chromatograph using a TG-5MS column (30 m \(\times\) 0.25 mm \(\times\) 0.25 µm).

**Photoreactions:** Photoreactions were carried out in borosilicate made culture tube using light source (PAR38 12W blue LED bulb / Kessil violet LEDs 390 nm).

**UV–vis spectroscopy:** UV–vis absorption spectra were recorded using a Shimadzu UV Spectrophotometer (model: UV-1800).

**Luminescence spectrometer:** Fluorescence quenching studies were carried out using a Shimadzu RF-6000 spectrophotometer (model no.- A40246002251SA).

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2. Preparation of starting materials

2.1. General procedure for the synthesis of 2-arylimidazo[1,2-a]pyridines: All 2-arylimidazo[1,2-a]pyridines were prepared either from the corresponding methyl ketone and 2-aminopyridines (or compounds 1a–q and w also prepared following the same procedure), or from the corresponding 2-bromoacetophenone and 2-aminopyridines (for compounds 1r, 1u and v) following the reported procedure.

3. Reaction optimization a:

General procedure for optimization of reaction conditions: An oven-dried culture tube equipped with a magnetic stirring bar was charged with 2-phenylimidazo[1,2-a]pyridine (1a, 39 mg, 0.2 mmol, 1.0 equiv), diethyl bromomalonate (2a, 96 mg, 0.4 mmol, 2.0 equiv), photocatalyst (5 mol %), additive (0.4 mmol, 2.0 equiv), and dry solvent (2 mL). The resulting reaction mixture was stirred at room temperature under open atmosphere conditions using 12 W blue LEDs or 390 nm violet LEDs for 10 h. A fan cooling was also included to maintain the reaction at room temperature.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>solvent</th>
<th>additive</th>
<th>yield (%)</th>
<th>3a:4a:5:6</th>
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<td>4-CzIPN</td>
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<td>2</td>
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<td>CH₃CN</td>
<td>-</td>
<td>47: 0: 0: 22</td>
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<tr>
<td>3</td>
<td>4-CzIPN</td>
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<td>Zn(OAc)₂</td>
<td>0: 38: 0: 0</td>
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<td>4</td>
<td>Rose Bengal</td>
<td>CH₃CN</td>
<td>Zn(OAc)₂</td>
<td>-</td>
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<tr>
<td>5</td>
<td>Eosin-Y</td>
<td>CH₃CN</td>
<td>Zn(OAc)₂</td>
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<td>6</td>
<td>Rhodamine-B</td>
<td>CH₃CN</td>
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<tr>
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<tr>
<td>8</td>
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<td>Zn(OAc)₂</td>
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</tr>
<tr>
<td>9</td>
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<td>DMF</td>
<td>Zn(OAc)₂</td>
<td>0: 25: 0: 0</td>
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<tr>
<td>10</td>
<td>PTH</td>
<td>Toluene</td>
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<tr>
<td>11</td>
<td>PTH</td>
<td>1,2-DCE</td>
<td>Zn(OAc)₂</td>
<td>0: 70: 0: 0</td>
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<tr>
<td>12c</td>
<td>PTH</td>
<td>1,2-DCE</td>
<td>Zn(OAc)₂</td>
<td>0: 94: 0: 0</td>
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</tr>
<tr>
<td>13f</td>
<td>PTH</td>
<td>1,2-DCE</td>
<td>Zn(OAc)₂</td>
<td>0: 52: 0: 0</td>
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<tr>
<td>14g</td>
<td>PTH</td>
<td>1,2-DCE</td>
<td>Zn(OAc)₂</td>
<td>0: 88: 0: 0</td>
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<td>AcOH</td>
<td>0: 64: 0: 0</td>
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<tr>
<td>16</td>
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<td>Zn(OAc)₂</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>17h</td>
<td>PTH</td>
<td>1,2-DCE</td>
<td>Zn(OAc)₂</td>
<td>-</td>
<td></td>
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</tbody>
</table>

4. Experimental procedures & compound characterization data

4.1. General procedure for the synthesis of acetoxymalonylated imidazo-heterocycles: An oven-dried culture tube equipped with a magnetic stirring bar was charged with 2-substituted imidazo-heterocycles 1 (0.2 mmol, 1.0 equiv), active bromo-methylene 2 (0.4 mmol, 2.0 equiv), additive Zn(OAc)$_2$ (132 mg, 0.6 mmol, 3.0 equiv) and photocatalyst PTH (5 mol %) in dry 1,2-DCE (2 mL). The resulting reaction mixture was stirred at room temperature under open atmosphere using 390 nm violet LEDs for 10 h. A fan cooling was also included to maintain the reaction at room temperature. Completion of the reaction was confirmed by TLC. Then, the crude reaction mixture was poured into H$_2$O (10 mL) and extracted with CH$_2$Cl$_2$ (3 x 6 mL). The combined organic layer was washed with brine solution and dried using oven dried anhydrous Na$_2$SO$_4$. Then the mixture was concentrated in a rotary evaporator under reduced pressure. The crude residue was then purified by column chromatography to obtain the desired product 4.

4.2. Compound characterization data

**Diethyl 2-acetoxy-2-(2-phenylimidazo[1,2-α]pyridin-3-yl)malonate (4a):**

| Yield: 94% (77 mg). |
| Nature: yellow solid |
| Mp: 121-123 °C |
| $R_f$ value = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)]. |

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.28 (dd, $J = 4.6$, 3.5 Hz, 1H), 7.73 (d, $J = 9.1$ Hz, 1H), 7.60 – 7.58 (m, 2H), 7.41 (d, $J = 7.1$ Hz, 3H), 7.33 (ddd, $J = 9.1$, 6.8, 1.1 Hz, 1H), 6.90 (td, $J = 6.9$, 1.2 Hz, 1H), 3.88 (tdd, $J = 10.7$, 7.1, 3.6 Hz, 4H), 2.14 (s, 3H), 1.13 (t, $J = 7.1$ Hz, 6H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ (ppm): 168.8, 164.2, 146.0, 145.1, 133.7, 130.3, 128.7, 127.9, 126.4, 126.3, 117.8, 113.4, 113.3, 80.0, 63.3, 20.5, 13.8.

HRMS (ESI) $m/z$ calcd for C$_{25}$H$_{23}$N$_2$O$_6$[M+H]$: 411.1556; found: 411.1554
<table>
<thead>
<tr>
<th>Diethyl 2-acetoxyl-2-(2-p-toly)imidazo[1,2-a]pyrin-3-yl)malonate (4b):</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Yield:</strong> 95% (81 mg).</td>
</tr>
<tr>
<td><strong>Nature:</strong> white solid</td>
</tr>
<tr>
<td><strong>Mp:</strong> 168-170 °C</td>
</tr>
<tr>
<td><strong>Rf value</strong> = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)].</td>
</tr>
<tr>
<td><strong>1H NMR (400 MHz, CDCl3) δ (ppm):</strong> 8.27 (d, J = 7.1 Hz, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.48 (d, J = 8.1 Hz, 2H), 7.32 (ddd, J = 8.8, 6.7, 1.0 Hz, 1H), 7.22 (d, J = 7.9 Hz, 2H), 6.89 (td, J = 6.9, 1.2 Hz, 1H), 3.94 – 3.85 (m, 4H), 2.38 (s, 3H), 2.14 (s, 3H), 1.13 (t, J = 7.1 Hz, 6H).</td>
</tr>
<tr>
<td><strong>13C{1H} NMR (101 MHz, CDCl3) δ (ppm):</strong> 168.8, 164.2, 146.1, 145.0, 138.5, 130.6, 130.2, 128.5, 126.4, 126.2, 117.7, 113.3, 113.2, 80.1, 63.3, 21.5, 20.5, 13.8.</td>
</tr>
<tr>
<td><strong>HRMS (ESI) m/z calcld for C23H25N2O6 [M+H]+:</strong> 425.1713; found: 425.1710</td>
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<table>
<thead>
<tr>
<th>Diethyl 2-acetoxyl-2-(2-(4-bromophenyl)imidazo[1,2-a]pyrin-3-yl)malonate (4c):</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Yield:</strong> 92% (90 mg).</td>
</tr>
<tr>
<td><strong>Nature:</strong> white solid</td>
</tr>
<tr>
<td><strong>Mp:</strong> 160-162 °C</td>
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<td><strong>Rf value</strong> = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)].</td>
</tr>
<tr>
<td><strong>1H NMR (400 MHz, CDCl3) δ (ppm):</strong> 8.27 (dd, J = 8.1, 0.9 Hz, 1H), 7.70 (dd, J = 5.6, 4.5 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.49 – 7.46 (m, 2H), 7.33 (ddd, J = 9.1, 6.8, 1.1 Hz, 1H), 6.90 (td, J = 6.9, 1.2 Hz, 1H), 3.98 – 3.89 (m, 4H), 2.14 (s, 3H), 1.14 (t, J = 7.1 Hz, 6H).</td>
</tr>
<tr>
<td><strong>13C{1H} NMR (101 MHz, CDCl3) δ (ppm):</strong> 168.7, 164.2, 146.1, 145.3, 144.9, 132.9, 131.9, 131.0, 126.4, 126.3, 123.1, 117.8, 113.5, 113.3, 79.9, 63.4, 20.5, 13.8.</td>
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<tr>
<td><strong>HRMS (ESI) m/z calcld for C22H22BrN2O6 [M+H]+:</strong> 489.0661; found: 489.0668</td>
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<table>
<thead>
<tr>
<th>Diethyl 2-acetoxyl-2-(2-(4-fluorophenyl)imidazo[1,2-a]pyrin-3-yl)malonate (4d):</th>
</tr>
</thead>
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<tr>
<td><strong>Yield:</strong> 81% (70 mg).</td>
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<tr>
<td><strong>Nature:</strong> white solid</td>
</tr>
<tr>
<td><strong>Mp:</strong> 134-136 °C</td>
</tr>
<tr>
<td><strong>Rf value</strong> = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)].</td>
</tr>
<tr>
<td><strong>1H NMR (400 MHz, CDCl3) δ (ppm):</strong> 8.26 (d, J = 7.2 Hz, 1H), 7.68 (d, J = 9.1 Hz, 1H), 7.57 (dd, J = 8.7, 5.5 Hz, 2H), 7.31 (ddd, J = 8.9, 6.7, 1.0 Hz, 1H), 7.10 (t, J = 8.7 Hz, 2H), 6.88 (td, J = 7.0, 1.1 Hz, 1H), 3.97 – 3.87 (m, 4H), 2.14 (s, 3H), 1.14 (t, J = 7.2 Hz, 6H).</td>
</tr>
<tr>
<td><strong>13C{1H} NMR (101 MHz, CDCl3) δ (ppm):</strong> 168.8, 164.2, 163.1 (d, J = 248.8 Hz), 145.3 (d, J = 4.2 Hz), 132.1 (d, J = 8.6 Hz), 130.1, 126.3 (d, J = 21.3 Hz), 117.8, 114.9, 114.7, 113.4, 113.2, 79.9, 63.4, 20.5, 13.8.</td>
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<tr>
<td><strong>19F NMR (376 MHz, CDCl3) δ (ppm):</strong> −113.1</td>
</tr>
<tr>
<td><strong>HRMS (ESI) m/z calcld for C22H22FNN2O6 [M+H]+:</strong> 429.1462; found: 429.1461</td>
</tr>
</tbody>
</table>
Diethyl 2-acetoxy-2-(2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-yl)malonate (4e):

| Yield: | 89% (79 mg). |
| Nature: | white solid |
| Mp: | 158-160 °C |
| R<sub>t</sub> value | 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)]. |

| ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): | 8.28 – 8.26 (m, 1H), 7.68 (dd, J = 10.0, 0.9 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.41 – 7.38 (m, 2H), 7.31 (ddd, J = 9.1, 6.8, 1.2 Hz, 1H), 6.89 (td, J = 6.9, 1.2 Hz, 1H), 3.97 – 3.89 (m, 4H), 2.14 (s, 3H), 1.14 (t, J = 7.1 Hz, 6H). |
| ¹³C{¹H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm): | 168.7, 164.1, 145.3, 145.0, 134.8, 132.6, 131.63, 128.0, 126.4, 126.3, 117.9, 113.5, 113.2, 79.9, 63.4, 20.5, 13.8. |
| HRMS (ESI) m/z calcld for C<sub>22</sub>H<sub>22</sub>ClN<sub>2</sub>O<sub>6</sub> [M+H]<sup>+</sup>: 445.1166; found: 445.1165 |

Diethyl 2-acetoxy-2-(2-(4-cyanophenyl)imidazo[1,2-a]pyridin-3-yl)malonate (4f):

| Yield: | 79% (69 mg). |
| Nature: | yellow solid |
| Mp: | 133-135 °C |
| R<sub>t</sub> value | 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)]. |

| ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): | 8.33 – 8.31 (m, 1H), 7.79 – 7.72 (m, 5H), 7.40 (ddd, J = 8.8, 6.9, 1.0 Hz, 1H), 6.97 (td, J = 6.9, 1.1 Hz, 1H), 3.99 – 3.91 (m, 4H), 2.12 (s, 3H), 1.15 (t, J = 7.2 Hz, 6H). |
| ¹³C{¹H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm): | 168.6, 163.9, 145.1, 143.5, 138.4, 131.7, 131.1, 127.2, 126.6, 118.7, 117.8, 114.2, 113.9, 112.5, 79.6, 63.6, 20.4, 13.8. |
| HRMS (ESI) m/z calcld for C<sub>23</sub>H<sub>22</sub>N<sub>3</sub>O<sub>6</sub> [M+H]<sup>+</sup>: 436.1509; found: 436.1503 |

Diethyl 2-acetoxy-2-(2-(4-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl)malonate (4g):

| Yield: | 85% (75 mg). |
| Nature: | white solid |
| Mp: | 177-179 °C |
| R<sub>t</sub> value | 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)]. |

| ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): | 8.34 (d, J = 7.1 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.58 – 7.56 (m, 2H), 7.51 – 7.47 (m, 1H), 7.04 (t, J = 7.0 Hz, 1H), 7.00 – 6.96 (m, 2H), 3.99 – 3.90 (m, 4.3 Hz, 4H), 3.85 (s, 3H), 2.16 (s, 3H), 1.15 (t, J = 7.2 Hz, 6H). |
| ¹³C{¹H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm): | 168.8, 164.3, 160.0, 146.0, 145.2, 131.5, 126.4, 126.2, 126.0, 117.7, 113.3, 113.2, 113.0, 80.1, 63.3, 55.5, 20.5, 13.8. |
| HRMS (ESI) m/z calcld for C<sub>23</sub>H<sub>22</sub>N<sub>3</sub>O<sub>7</sub> [M+H]<sup>+</sup>: 441.1662; found: 441.1677 |
Diethyl 2-acetoxy-2-(2-(2-fluorophenyl)imidazo[1,2-α]pyridin-3-yl)malonate (4h):

**Yield:** 93% (80 mg).

**Nature:** yellow solid  
**Mp:** 94-96 °C  
**R<sub>f</sub> value** = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)].

<table>
<thead>
<tr>
<th>NMR</th>
<th>ppm</th>
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<tbody>
<tr>
<td>&lt;sup&gt;1&lt;/sup&gt;H NMR (400 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>8.32 – 8.30 (m, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.46 (dd, J = 7.4, 1.8 Hz, 1H), 7.39 (tdd, J = 7.2, 5.1, 1.8 Hz, 1H), 7.33 (ddd, J = 8.8, 6.8, 1.0 Hz, 1H), 7.17 (ddd, J = 18.5, 8.6, 0.9 Hz, 2H), 6.91 (td, J = 7.0, 1.1 Hz, 1H), 3.92 (b, 4H), 2.06 (s, 3H), 1.14 (t, J = 7.1 Hz, 6H).</td>
</tr>
<tr>
<td>&lt;sup&gt;13&lt;/sup&gt;C{&lt;sup&gt;1&lt;/sup&gt;H} NMR (101 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>168.8, 164.2, 160.7 (d, J = 249.5 Hz), 145.5, 140.1, 132.9 (d, J = 2.0 Hz), 130.7 (d, J = 8.4 Hz), 126.1 (d, J = 10.4 Hz), 123.4 (d, J = 3.2 Hz), 122.3 (d, J = 15.9 Hz), 118.0, 115.4 (d, J = 21.7 Hz), 114.7, 113.2, 79.8, 63.2, 20.3, 13.7.</td>
</tr>
<tr>
<td>&lt;sup&gt;19&lt;/sup&gt;F NMR (376 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>-112.4</td>
</tr>
<tr>
<td>HRMS (ESI)</td>
<td>m/z calcd for C&lt;sub&gt;22&lt;/sub&gt;H&lt;sub&gt;22&lt;/sub&gt;F&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt; [M+H]&lt;sup&gt;+&lt;/sup&gt;: 429.1462; found: 429.1464</td>
</tr>
</tbody>
</table>

Diethyl 2-acetoxy-2-(2-(3-bromophenyl)imidazo[1,2-α]pyridin-3-yl)malonate (4i):

**Yield:** 74% (73 mg).

**Nature:** yellow gummy liquid  
**R<sub>f</sub> value** = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)].

<table>
<thead>
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<th>NMR</th>
<th>ppm</th>
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<tbody>
<tr>
<td>&lt;sup&gt;1&lt;/sup&gt;H NMR (400 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>8.30 – 8.28 (m, 1H), 7.77 (t, J = 1.8 Hz, 1H), 7.71 (dd, J = 5.5, 4.5 Hz, 1H), 7.54 (ddt, J = 6.7, 3.1, 1.0 Hz, 2H), 7.35 – 7.30 (m, 2H), 6.90 (td, J = 6.9, 1.3 Hz, 1H), 3.96 (m, 4H), 2.14 (s, 3H), 1.19 (t, J = 7.1 Hz, 6H).</td>
</tr>
<tr>
<td>&lt;sup&gt;13&lt;/sup&gt;C{&lt;sup&gt;1&lt;/sup&gt;H} NMR (101 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>168.7, 164.2, 145.3, 144.5, 136.0, 133.3, 131.6, 129.5, 128.9, 126.4, 126.3, 121.8, 117.9, 113.7, 113.4, 79.8, 63.5, 20.4, 13.8.</td>
</tr>
<tr>
<td>HRMS (ESI)</td>
<td>m/z calcd for C&lt;sub&gt;22&lt;/sub&gt;H&lt;sub&gt;22&lt;/sub&gt;BrN&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt; [M+H]&lt;sup&gt;+&lt;/sup&gt;: 489.0661; found: 489.0695</td>
</tr>
</tbody>
</table>

Diethyl 2-((1,1'-biphenyl)-4-yl)imidazo[1,2-α]pyridin-3-yl)-2-acetoxymalonate (4j):

**Yield:** 77% (75 mg).

**Nature:** white solid  
**Mp:** 197-199 °C  
**R<sub>f</sub> value** = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)].

<table>
<thead>
<tr>
<th>NMR</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;sup&gt;1&lt;/sup&gt;H NMR (400 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>8.30 – 8.28 (m, 1H), 7.73 – 7.71 (m, 1H), 7.68 (s, 4H), 7.66 – 7.63 (m, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.39 – 7.30 (m, 2H), 6.90 (td, J = 6.9, 1.2 Hz, 1H), 3.97 – 3.88 (m, 4H), 2.15 (s, 3H), 1.15 (t, J = 7.2 Hz, 6H).</td>
</tr>
</tbody>
</table>
**13C[1]H NMR (101 MHz, CDCl₃) δ (ppm):** 168.8, 164.3 145.9, 145.3, 141.3, 140.8, 133.0, 130.7, 128.9, 127.6, 127.2, 126.5, 126.4, 126.0, 117.9, 113.4, 113.1, 80.1, 63.3, 20.5, 13.8.

**HRMS (ESI) m/z calcd for C₂₈H₂₇N₂O₆ [M+H]⁺: 487.1869; found: 487.1865**

**Diethyl 2-acetoxy-2-(2-(naphthalen-2-yl)imidazo[1,2-a]pyridin-3-yl)malonate (4k):**

<table>
<thead>
<tr>
<th>Yield: 82% (75 mg).</th>
<th><img src="image" alt="4k" /></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nature:</strong> white solid</td>
<td><strong>Rf value</strong> = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)].</td>
</tr>
<tr>
<td><strong>Mp:</strong> 158-160 °C</td>
<td></td>
</tr>
</tbody>
</table>

**1H NMR (400 MHz, CDCl₃) δ (ppm):** 8.32 (d, J = 7.2 Hz, 1H), 8.08 (s, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.77 – 7.73 (m, 2H), 7.52 – 7.50 (m, 2H), 7.34 (ddd, J = 9.0, 6.8, 1.1 Hz, 1H), 6.92 (td, J = 6.9, 1.2 Hz, 1H), 3.79 (q, J = 7.1 Hz, 4H), 2.12 (s, 3H), 1.10 (t, J = 7.2 Hz, 6H).

**13C[1]H NMR (101 MHz, CDCl₃) δ (ppm):** 168.8, 164.30, 146.0, 145.3, 132.7, 131.1, 129.9, 128.4, 127.8, 127.7, 127.6, 126.6, 126.5, 126.4, 126.3, 117.8, 113.8, 113.3, 80.1, 63.3, 20.5, 13.7.

**HRMS (ESI) m/z calcd for C₂₆H₂₅N₂O₆ [M+H]⁺: 461.1713; found: 461.1714**

**Diethyl 2-acetoxy-2-(8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)malonate (4l):**

<table>
<thead>
<tr>
<th>Yield: 78% (66 mg).</th>
<th><img src="image" alt="4l" /></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nature:</strong> light yellow oil</td>
<td><strong>Rf value</strong> = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)].</td>
</tr>
<tr>
<td><strong>Mp:</strong> 158-160 °C</td>
<td></td>
</tr>
</tbody>
</table>

**1H NMR (400 MHz, CDCl₃) δ (ppm):** 8.13 (d, J = 7.0 Hz, 1H), 7.58 (dd, J = 7.9, 1.6 Hz, 2H), 7.43 – 7.36 (m, 3H), 7.09 (dd, J = 6.9, 0.9 Hz, 1H), 6.78 (t, J = 7.0 Hz, 1H), 3.91 – 3.81 (m, 4H), 2.64 (s, 3H), 2.13 (s, 3H), 1.13 (t, J = 7.2 Hz, 6H).

**13C[1]H NMR (101 MHz, CDCl₃) δ (ppm):** 168.8, 164.3, 145.8, 145.6, 134.2, 130.5, 128.5, 127.9, 127.8, 124.8, 124.0, 113.7, 113.1, 80.2, 63.2, 20.5, 17.4, 13.8.

**HRMS (ESI) m/z calcd for C₂₃H₂₃N₂O₆ [M+H]⁺: 425.1713; found: 425.1707**

**Diethyl 2-acetoxy-2-(7-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)malonate (4m):**

<table>
<thead>
<tr>
<th>Yield: 82% (70 mg).</th>
<th><img src="image" alt="4m" /></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nature:</strong> light yellow solid</td>
<td><strong>Rf value</strong> = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)].</td>
</tr>
<tr>
<td><strong>Mp:</strong> 135-137 °C</td>
<td></td>
</tr>
</tbody>
</table>

**S8**
**H NMR (400 MHz, CDCl₃) δ (ppm):** 8.15 (d, J = 7.1 Hz, 1H), 7.59 – 7.57 (m, 2H), 7.50 (s, 1H), 7.43 – 7.37 (m, 3H), 6.74 (dd, J = 7.2, 1.7 Hz, 1H), 3.93 – 3.82 (m, 4H), 2.43 (s, 3H), 2.13 (s, 3H), 1.12 (t, J = 7.1 Hz, 6H).

**13C{¹H} NMR (101 MHz, CDCl₃) δ (ppm):** 168.8, 164.2, 145.5, 145.4, 137.7, 133.6, 130.3, 128.7, 127.9, 125.6, 116.0, 112.9, 80.0, 63.3, 21.4, 20.5, 13.8.

HRMS (ESI) m/z calcd for C₂₃H₂₅N₂O₆ [M+H]⁺: 425.1713; found: 425.1707

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**Diethyl 2-acetoxy-2-(6-iodo-2-phenylimidazo[1,2-a]pyridin-3-yl)malonate (4n):**

| Yield: | 58% (62 mg). |
| Nature: | white solid |
| Mp: | 143-145 °C |
| Rf value: | 0.2 [EtOAc: Petroleum ether = 2:8 (v/v)]. |

**H NMR (400 MHz, CDCl₃) δ (ppm):** 8.60 (s, 1H), 7.67 (d, J = 9.2 Hz, 1H), 7.61 – 7.57 (m, 3H), 7.45 – 7.43 (m, 3H), 3.94 (q, J = 7.1 Hz, 4H), 2.12 (s, 3H), 1.17 (t, J = 7.1 Hz, 6H).

**13C{¹H} NMR (101 MHz, CDCl₃) δ (ppm):** 168.6, 163.7, 144.4, 142.6, 135.7, 131.9, 131.3, 130.3, 129.5, 128.2, 117.9, 113.9, 79.5, 63.7, 20.4, 13.8.

HRMS (ESI) m/z calcd for C₂₂H₂₁IN₂O₆ [M+H]⁺: 537.0523; found: 537.0517

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**Diethyl 2-acetoxy-2-(6-bromo-2-phenylimidazo[1,2-a]pyridin-3-yl)malonate (4o):**

| Yield: | 79% (77 mg). |
| Nature: | white solid |
| Mp: | 96-98 °C |
| Rf value: | 0.2 [EtOAc: Petroleum ether = 2:8 (v/v)]. |

**H NMR (400 MHz, CDCl₃) δ (ppm):** 8.48 (s, 1H), 7.74 (d, J = 9.5 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.44 (ddd, J = 9.5, 5.3, 1.9 Hz, 4H), 3.93 (m, 4H), 2.12 (s, 3H), 1.16 (t, J = 7.2 Hz, 6H).

**13C{¹H} NMR (101 MHz, CDCl₃) δ (ppm):** 168.7, 163.9, 146.6, 143.5, 133.2, 130.2, 129.8, 128.1, 127.9, 126.7, 118.3, 114.0, 107.9, 79.7, 63.5, 20.4, 13.8.

HRMS (ESI) m/z calcd for C₂₂H₂₂BrN₂O₆ [M+H]⁺: 489.0661; found: 489.0656
Diethyl 2-acetoxy-2-(6-bromo-7-methyl-2-phenylimidazo[1,2-α]pyridin-3-yl)malonate (4p):

<table>
<thead>
<tr>
<th>Yield: 59% (60 mg).</th>
<th>![Structure Diagram]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nature: light yellow solid</td>
<td>Me</td>
</tr>
<tr>
<td>Mp: 137-139 °C</td>
<td>EtO₂C</td>
</tr>
<tr>
<td>R&lt;sub&gt;f&lt;/sub&gt; value = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)].</td>
<td>CO₂Et</td>
</tr>
</tbody>
</table>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.15 (d, J = 7.1 Hz, 1H), 7.58 (dd, J = 7.8, 1.7 Hz, 2H), 7.50 (s, 1H), 7.41 – 7.39 (m, 2H), 6.73 (dd, J = 7.2, 1.7 Hz, 1H), 3.93 – 3.82 (m, 4H), 2.43 (s, 3H), 2.13 (s, 3H), 1.13 (t, J = 7.1 Hz, 6H).

<sup>13</sup>C<sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm): 168.8, 164.3, 145.6, 145.4, 137.7, 133.7, 130.3, 128.7, 127.8, 125.6, 116.0, 115.9, 112.8, 80.0, 63.2, 21.4, 20.5, 13.8.

HRMS (ESI) m/z calcd for C<sub>23</sub>H<sub>24</sub>BrN<sub>2</sub>O<sub>6</sub> [M+H]<sup>+</sup>: 503.0818; found: 503.0812

Diethyl 2-acetoxy-2-(6,8-dibromo-2-phenylimidazo[1,2-α]pyridin-3-yl)malonate (4q):

<table>
<thead>
<tr>
<th>Yield: 51% (58 mg).</th>
<th>![Structure Diagram]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nature: yellow gummy liquid</td>
<td>Br</td>
</tr>
<tr>
<td>R&lt;sub&gt;f&lt;/sub&gt; value = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)].</td>
<td>EtO₂C</td>
</tr>
</tbody>
</table>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.43 (d, J = 1.5 Hz, 1H), 7.66 (d, J = 1.5 Hz, 1H), 7.59 – 7.56 (m, 2H), 7.40 (dd, J = 5.0, 2.1 Hz, 3H), 3.94 – 3.89 (m, 4H), 2.11 (s, 3H), 1.16 (t, J = 7.1 Hz, 6H).

<sup>13</sup>C<sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm): 168.6, 163.8, 147.9, 142.1, 133.5, 131.0, 130.5, 128.9, 127.9, 125.9, 115.7, 112.4, 106.4, 79.8, 63.5, 20.4, 13.8.

HRMS (ESI) m/z calcd for C<sub>22</sub>H<sub>21</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>6</sub> [M+H]<sup>+</sup>: 503.0818; found: 503.0812

Diethyl 2-acetoxy-2-(2-(ethoxycarbonyl)imidazo[1,2-α]pyridin-3-yl)malonate (4r):

<table>
<thead>
<tr>
<th>Yield: 56% (45 mg).</th>
<th>![Structure Diagram]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nature: light yellow oil</td>
<td>EtO₂C</td>
</tr>
<tr>
<td>R&lt;sub&gt;f&lt;/sub&gt; value = 0.3 [EtOAc: Petroleum ether = 6:4 (v/v)]</td>
<td>CO₂Et</td>
</tr>
</tbody>
</table>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.18 – 8.16 (m, 1H), 7.75 – 7.72 (m, 1H), 7.32 (ddd, J = 9.0, 6.6, 1.1 Hz, 1H), 6.90 (td, J = 7.0, 1.2 Hz, 1H), 4.42 (t, J = 7.2 Hz, 2H), 4.38 – 4.25 (m, 4H), 2.20 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 6H).

<sup>13</sup>C<sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm): 168.8, 164.3, 163.4, 145.2, 136.6, 126.8, 126.6, 119.9, 119.2, 113.9, 79.7, 63.6, 61.8, 20.8, 14.4, 13.9.

HRMS (ESI) m/z calcd for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>NaO<sub>8</sub> [M+Na]<sup>+</sup>: 429.1274; found: 429.1280
<table>
<thead>
<tr>
<th><strong>Dimethyl 2-acetoxy-2-(2-phenylimidazo[1,2-α]pyridin-3-yl)malonate (4s):</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Yield:</strong> 92% (70 mg).</td>
</tr>
<tr>
<td><strong>Nature:</strong> white solid</td>
</tr>
<tr>
<td><strong>Mp:</strong> 125-127 °C</td>
</tr>
<tr>
<td><strong>R&lt;sub&gt;f&lt;/sub&gt; value</strong> = 0.2 [EtOAc: Petroleum ether = 4:6 (v/v)].</td>
</tr>
<tr>
<td><strong>&lt;sup&gt;1&lt;/sup&gt;H NMR (400 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;) δ (ppm):</strong> 8.23 (dd, J = 4.6, 3.5 Hz, 1H), 7.68 (dd, J = 5.5, 4.5 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.41 (tdd, J = 6.8, 4.6, 2.5 Hz, 3H), 7.32 – 7.27 (m, 1H), 6.88 (td, J = 6.9, 1.3 Hz, 1H), 3.47 (s, 6H), 2.15 (s, 3H).</td>
</tr>
<tr>
<td><strong>&lt;sup&gt;13&lt;/sup&gt;C{&lt;sup&gt;1&lt;/sup&gt;H} NMR (101 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;) δ (ppm):</strong> 168.9, 164.8, 146.8, 145.5, 134.1, 130.2, 128.5, 127.9, 126.1, 125.8, 118.1, 113.1, 112.9, 79.9, 53.7, 20.5.</td>
</tr>
<tr>
<td><strong>HRMS (ESI) m/z calcd for C&lt;sub&gt;20&lt;/sub&gt;H&lt;sub&gt;19&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;[M+H]&lt;sup&gt;+&lt;/sup&gt;:</strong> 383.1243; found: 383.1245</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Diisopropyl 2-acetoxy-2-(2-phenylimidazo[1,2-α]pyridin-3-yl)malonate (4t):</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Yield:</strong> 72% (63 mg).</td>
</tr>
<tr>
<td><strong>Nature:</strong> light yellow oil</td>
</tr>
<tr>
<td><strong>R&lt;sub&gt;f&lt;/sub&gt; value</strong> = 0.3 [EtOAc: Petroleum ether = 4:6 (v/v)].</td>
</tr>
<tr>
<td><strong>&lt;sup&gt;1&lt;/sup&gt;H NMR (400 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;) δ (ppm):</strong> 8.30 (dt, J = 7.1, 1.1 Hz, 1H), 7.66 – 7.61 (m, 3H), 7.42 – 7.37 (m, 3H), 7.29 – 7.24 (m, 1H), 6.84 (td, J = 6.9, 1.3 Hz, 1H), 4.70 (dt, J = 12.5, 6.3 Hz, 2H), 2.08 (s, 3H), 1.12 (d, J = 6.3 Hz, 6H), 1.07 (d, J = 6.3 Hz, 6H).</td>
</tr>
<tr>
<td><strong>&lt;sup&gt;13&lt;/sup&gt;C{&lt;sup&gt;1&lt;/sup&gt;H} NMR (101 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;) δ (ppm):</strong> 168.7, 163.9, 146.5, 145.5, 134.6, 130.3, 128.4, 127.8, 126.5, 125.6, 117.9, 113.4, 112.6, 80.5, 71.8, 21.4, 21.3, 20.4.</td>
</tr>
<tr>
<td><strong>HRMS (ESI) m/z calcd for C&lt;sub&gt;28&lt;/sub&gt;H&lt;sub&gt;19&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;[M+H]&lt;sup&gt;+&lt;/sup&gt;:</strong> 439.1869; found: 439.1859</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Diethyl 2-acetoxy-2-(6-phenylimidazo[2,1-b]thiazol-5-yl)malonate (4u):</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Yield:</strong> 84% (70 mg).</td>
</tr>
<tr>
<td><strong>Nature:</strong> light yellow oil</td>
</tr>
<tr>
<td><strong>R&lt;sub&gt;f&lt;/sub&gt; value</strong> = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)].</td>
</tr>
<tr>
<td><strong>&lt;sup&gt;1&lt;/sup&gt;H NMR (400 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;) δ (ppm):</strong> 7.62 (d, J = 4.6 Hz, 1H), 7.57 – 7.55 (m, 2H), 7.41 – 7.35 (m, 3H), 6.85 (d, J = 4.7 Hz, 1H), 4.02 – 3.92 (m, 4H), 2.03 (s, 3H), 1.14 (t, J = 7.1 Hz, 6H).</td>
</tr>
<tr>
<td><strong>&lt;sup&gt;13&lt;/sup&gt;C{&lt;sup&gt;1&lt;/sup&gt;H} NMR (101 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;) δ (ppm):</strong> 169.2, 164.1, 150.7, 147.6, 133.8, 130.1, 128.5, 127.9, 121.5, 115.7, 112.0, 79.5, 63.3, 20.4, 13.7.</td>
</tr>
<tr>
<td><strong>HRMS (ESI) m/z calcd for C&lt;sub&gt;28&lt;/sub&gt;H&lt;sub&gt;21&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;S [M+H]&lt;sup&gt;+&lt;/sup&gt;:</strong> 417.1120; found: 417.1115</td>
</tr>
</tbody>
</table>
Diethyl 2-acetoxy-2-(2-phenylbenzo[d]imidazo[2,1-b]thiazol-3-yl)malonate (4v):

Yield: 65% (60 mg).
Nature: light yellow oil

Rf value = 0.2 [EtOAc: Petroleum ether = 2:8 (v/v)].

^1H NMR (400 MHz, CDCl₃) δ (ppm): 8.02 (d, J = 8.1 Hz, 1H), 7.72 (dd, J = 7.9, 1.1 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.47 – 7.35 (m, 5H), 3.84 (bs, 4H), 2.16 (s, 3H), 1.15 (t, J = 7.2 Hz, 6H).

^13C{^1H} NMR (101 MHz, CDCl₃) δ (ppm): 168.1, 164.7, 149.3, 147.4, 133.7, 133.5, 130.3, 128.7, 127.8, 126.3, 125.2, 124.3, 118.7, 116.2, 80.4, 63.4, 21.1, 13.7.

HRMS (ESI) m/z calcd for C₂₄H₂₃N₂O₆S [M+H]^+: 467.1277; found: 467.1271

Diethyl 2-acetoxy-2-(2-phenylimidazo[1,2-a]pyrimidin-3-yl)malonate (4w):

Yield: 85% (70 mg).
Nature: white solid
Mp: 119-121 °C

Rf value = 0.3 [EtOAc: Petroleum ether = 6:4 (v/v)].

^1H NMR (400 MHz, CDCl₃) δ (ppm): 8.66 (dt, J = 4.8, 1.9 Hz, 2H), 7.64 (dd, J = 7.5, 1.9 Hz, 2H), 7.42 (dd, J = 4.9, 2.5 Hz, 3H), 6.96 (dd, J = 7.0, 4.1 Hz, 1H), 3.94 (q, J = 7.2 Hz, 4H), 2.09 (s, 3H), 1.14 (t, J = 7.1 Hz, 6H).

^13C{^1H} NMR (101 MHz, CDCl₃) δ (ppm): 168.8, 163.9, 151.2, 148.1, 134.9, 133.4, 130.4, 128.9, 127.9, 112.1, 109.0, 79.7, 63.5, 20.4, 13.8.

HRMS (ESI) m/z calcd for C₂₁H₂₁N₃NaO₆ [M+Na]^+: 434.1328; found: 434.1319

Ethyl 2-acetoxy-2-cyano-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (4x):

Yield: 48% (35 mg).
Nature: yellow gummy liquid

Rf value = 0.2 [EtOAc: Petroleum ether = 3:7 (v/v)].

^1H NMR (400 MHz, CDCl₃) δ (ppm): 8.53 (dd, J = 6.1, 0.9 Hz, 1H), 7.73 (d, J = 9.1 Hz, 1H), 7.55 – 7.53 (m, 2H), 7.44 – 7.39 (m, 4H), 7.03 (td, J = 7.0, 1.1 Hz, 1H), 3.98 (dq, J = 10.6, 7.1 Hz, 1H), 3.75 (dq, J = 10.7, 7.1 Hz, 1H), 2.15 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H).

^13C{^1H} NMR (101 MHz, CDCl₃) δ (ppm): 168.5, 161.1, 147.8, 146.1, 133.4, 130.4, 128.9, 127.7, 126.7, 125.9, 118.2, 113.6, 112.5, 108.3, 83.3, 64.5, 20.1, 13.6.

HRMS (ESI) m/z calcd for C₂₀H₁₃N₃O₄ [M+H]^+: 364.1297; found: 364.1293
Ethyl 2-acetoxy-3-oxo-2-(2-phenylimidazo[1,2-α]pyridin-3-yl)butanoate (4y):

Yield: 83% (63 mg).
Nature: white solid
Mp: 114-116 °C
Rf value = 0.3 [EtOAc: Petroleum ether = 4:6 (v/v)]

1H NMR (400 MHz, CDCl₃) δ (ppm): 8.13 (d, J = 7.0 Hz, 1H), 7.66 (dd, J = 5.6, 4.5 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.43 (dd, J = 5.1, 2.2 Hz, 3H), 7.32 (ddd, J = 8.8, 6.8, 1.1 Hz, 1H), 6.88 (td, J = 6.9, 1.2 Hz, 1H), 3.65 (dd, J = 10.7, 7.2 Hz, 1H), 3.39 (dd, J = 10.7, 7.2 Hz, 1H), 2.34 (s, 3H), 2.17 (s, 3H), 1.02 (t, J = 7.1 Hz, 3H).

13C{1H} NMR (101 MHz, CDCl₃) δ (ppm): 196.3, 169.1, 164.2, 147.2, 145.8, 134.2, 130.3, 128.6, 128.3, 126.6, 126.3, 117.9, 113.3, 111.6, 85.2, 62.6, 27.3, 20.5, 14.1.

HRMS (ESI) m/z calcd for C₂₁H₂₁N₂O₅ [M+H]+: 381.1450; found: 381.1452

Diethyl 2-(2-phenylimidazo[1,2-α]pyridin-3-yl)malonate (5):

Yield: 66% (46 mg).
Nature: yellow oil
Rf value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)].

1H NMR (400 MHz, CDCl₃) δ (ppm): 8.35 – 8.33 (m, 1H), 7.76 (dd, J = 8.3, 1.3 Hz, 2H), 7.68 – 7.65 (m, 1H), 7.51 – 7.47 (m, 2H), 7.41 (dt, J = 9.4, 4.4 Hz, 1H), 7.25 – 7.22 (m, 1H), 6.82 (td, J = 6.9, 1.2 Hz, 1H), 5.40 (s, 1H), 4.23 (qd, J = 7.2, 3.1 Hz, 4H), 1.24 (t, J = 7.2 Hz, 6H).

13C{1H} NMR (101 MHz, CDCl₃) δ (ppm): 166.8, 146.4, 145.9, 133.9, 129.2, 128.8, 128.3, 126.3, 125.3, 117.7, 112.1, 111.9, 62.5, 49.3, 14.1.

5. Mechanistic studies and control experiments:

5.1. Radical trapping with TEMPO: An oven-dried culture tube equipped with a magnetic stirring bar was charged with 2-phenylimidazo[1,2-α]pyridine (1a, 39 mg, 0.2 mmol, 1.0 equiv), diethyl bromomalonate (2a, 96 mg, 0.4 mmol, 2.0 equiv), Zn(OAc)₂ (132 mg, 0.6 mmol, 3.0 equiv), photocatalyst PTH (5 mol %) in dry 1,2-DCE (2 mL) followed by the addition of TEMPO (94 mg, 0.6 mmol, 3.0 equiv). The resulting reaction mixture was stirred at room temperature under an open atmosphere using 390 nm violet LED for 10 h. A fan cooling was also included to maintain the reaction at room temperature. After the reaction, it was found that the formation of acetoxymalonylated product 4a was suppressed significantly, and the TEMPO-DEM adduct 7 and TEMPO-OAc adduct 8 were detected by HRMS analysis of the crude reaction mixture, indicating the involvement of a malonyl radical and acetyl radical during the reaction.

5.2. Radical trapping with alkene: An oven-dried culture tube equipped with a magnetic stirring bar was charged with 2-phenylimidazo[1,2-α]pyridine (1a, 39 mg, 0.2 mmol, 1.0 equiv), diethyl bromomalonate (2a, 96 mg, 0.4 mmol, 2.0 equiv), 5-hexene-1-ol (47 μL, 0.4 mmol, 2.0 equiv), photocatalyst PTH (5 mol %) in dry 1,2-DCE (2 mL). The resulting reaction mixture was stirred at room temperature under an open atmosphere using 390 nm violet LED for 15 h. A fan cooling was also included to maintain the reaction at room temperature. After the reaction, ATRA product 9 was isolated via column chromatography. This further confirms the involvement of a malonyl radical during the reaction.

Diethyl 2-(2-bromo-6-hydroxyhexyl)malonate (9):¹

Yield: 46% (31 mg).
Nature: colourless oil.
Rf value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)].

5.3. Reaction of 2-phenylimidazo[1,2-α]pyridine and bromomalonate without Zn(OAc)₂:

An oven-dried culture tube equipped with a magnetic stirring bar was charged with 2-phenylimidazo[1,2-α]pyridine (1a, 39 mg, 0.2 mmol, 1.0 equiv), diethyl bromomalonate (2a, 96 mg, 0.4 mmol, 2.0 equiv) and photocatalyst PTH (5 mol %) in dry 1,2-DCE (2 mL). The resulting reaction mixture was stirred at room temperature under open atmosphere in using 390 nm violet LED for 10 h. A fan cooling was also included to maintain the reaction at room temperature. The completion of the reaction was confirmed by TLC. Then, the crude reaction mixture was poured into H₂O (10 mL) and extracted with CH₂Cl₂ (3 × 6 mL). The combined organic layer was washed with brine solution and dried using oven dried anhydrous Na₂SO₄. Then, the mixture was concentrated in a rotary evaporator under reduced pressure and the crude residue was purified by column chromatography to obtain the products 3a and 6.

**Diethyl 2-hydroxy-2-(2-phenylimidazo[1,2-α]pyridin-3-yl)malonate (3a):**

| Yield: | 57% (42 mg). |
| Nature: | white solid |
| Mpt: | 147-149 °C |
| Rf value | = 0.2 [EtOAc: Petroleum ether = 4:6 (v/v)]. |

**1H NMR (400 MHz, CDCl₃) δ (ppm):**

8.08 – 8.06 (m, 1H), 7.67 – 7.65 (m, 1H), 7.53 (dd, J = 8.2, 1.5 Hz, 2H), 7.41 – 7.34 (m, 3H), 7.25 (q, J = 5.7 Hz, 1H), 6.81 (td, J = 6.9, 1.2 Hz, 1H), 4.68 (s, 1H), 3.94 (dq, J = 10.6, 7.0 Hz, 2H), 3.67 (dq, J = 10.6, 7.1 Hz, 2H), 1.02 (t, J = 7.1 Hz, 6H).

**13C{1H} NMR (101 MHz, CDCl₃) δ (ppm):**

168.7, 146.2, 145.2, 135.0, 129.8, 128.3, 128.1, 125.7, 125.5, 117.9, 115.6, 112.6, 76.9, 63.5, 13.7.
3-Bromo-2-phenylimidazo[1,2-a]pyridine (6)*:

Yield: 24% (13 mg).

Nature: yellow liquid

R<sub>f</sub> value = 0.6 [EtOAc: Petroleum ether = 4:6 (v/v)].

H<sup>1</sup> NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.16 – 8.12 (m, 3H), 7.63 (dd, J = 10.1, 0.9 Hz, 1H), 7.49 (dd, J = 10.4, 4.6 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.24 – 7.22 (m, 1H), 6.91 (td, J = 6.8, 0.9 Hz, 1H).

C<sup>13</sup>{H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm): 145.5, 142.7, 132.9, 128.6, 128.4, 127.9, 125.2, 124.0, 117.7, 113.1, 91.8.

5.4. Competitive acylation reaction with benzoic acid

An oven-dried culture tube equipped with a magnetic stirring bar was charged with diethyl 2-(2-phenylimidazo[1,2-a]pyridin-3-yl)malonate (5, 70 mg, 0.2 mmol, 1.0 equiv), benzoic acid (24 mg, 0.2 mmol, 1.0 equiv), Zn(OAc)<sub>2</sub> (44 mg, 0.2 mmol, 1.0 equiv) and photocatalyst PTH (5 mol %). The resulting reaction mixture was stirred at rt under open atmosphere condition using 390 nm violet LED for 10 h. The completion of the reaction was confirmed by TLC. Then, the crude reaction mixture was poured into H<sub>2</sub>O (10 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 6 mL). The combined organic layer was washed with brine solution and dried using oven dried anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then, the mixture was concentrated in a rotary evaporator under reduced pressure and the crude residue was purified by column chromatography to obtain the desired products 4a and 10.

Diethyl 2-(benzoyloxy)-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)malonate (10):

Yield: 40% (38 mg).

Nature: yellow gummy liquid

R<sub>f</sub> value = 0.3 [EtOAc: Petroleum ether = 4:6 (v/v)].

H<sup>1</sup> NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.43 (dd, J = 8.1, 0.9 Hz, 1H), 7.92 (dd, J = 8.4, 1.1 Hz, 2H), 7.73 (d, J = 8.9 Hz, 1H), 7.64 (dd, J = 7.9, 1.6 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.43 – 7.39 (m, 5H), 7.33 (ddd, J = 9.1, 6.8, 1.1 Hz, 1H), 6.90 (tt, J = 12.9, 6.5 Hz, 1H), 3.98 – 3.86 (m, 4H), 1.13 (t, J = 7.1 Hz, 6H).

C<sup>13</sup>{H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm): 164.4, 164.3, 146.8, 145.5, 134.3, 133.9, 130.3, 130.2, 128.9, 128.7, 128.6, 127.9, 126.4, 125.8, 118.2, 113.7, 113.1, 80.4, 63.3, 13.8.

HRMS (ESI) m/z calc for C<sub>27</sub>H<sub>25</sub>N<sub>2</sub>O<sub>6</sub> [M+H]<sup>+</sup>: 473.1713; found: 473.1711.

5.5. **Stern–Volmer fluorescence quenching experiments**

All emission spectra were recorded using a Shimadzu RF-6000 Spectrophotometer (model no. A40246002251SA). Photocatalyst PTH and different concentrations of added quenchers were prepared in dry and degassed acetonitrile in quartz cuvettes. For the quenching experiments, the concentration of PTH was 4.0 × 10⁻⁵ M. The solutions were excited at 320 nm, and the emission intensity was measured at 445 nm for PTH. Plots were derived according to the Stern–Volmer equation, and $K_{sv}$ was calculated.

Stern–Volmer equation: \[ \frac{I_0}{I} = 1 + K_{sv}[Q] \]

Where $I_0$ is the luminescence intensity of the photocatalyst in the absence of a quencher, $I$ is the intensity of the photocatalyst in the presence of quenchers, $[Q]$ is the concentration of added quencher, and $K_{sv}$ is the Stern–Volmer quenching constant. All emission spectra were recorded after each addition of the quencher. The obtained spectra (Figure S2) show that diethyl bromomalonate (2a) is the prominent quencher here and suggested a mechanism started with radical engagement of 2a.

![Figure S2: The fluorescence emission spectra of PTH with different concentrations of added quenchers diethyl bromomalonates (2a), 2-phenylimidazo[1,2-a]pyridine (1a), and diethyl 2-(2-phenylimidazo[1,2-a]pyridin-3-yl)malonate (5).](image)
5.6. Analysis of the aqueous extract of the crude reaction mixture
After completion of the reaction, the crude reaction mixture was extracted with CH$_2$Cl$_2$ (3 × 6 mL) and water (10 mL). The water extract was evaporated on a rotary evaporator under reduced pressure and then dried by a high vacuum pump with temperature to get an off-white solid. The solid material is highly hygroscopic and liquified upon exposure to air. HRMS spectra of the material clearly indicated that it is nothing but the zinc bromide (ZnBr$_2$). In addition, the aqueous part of crude reaction mixture has vinegar-like smell, which indicates in situ generation of acetic acid, which was further confirmed by GC–MS analysis.

![Image of HRMS spectra](image1)

**Figure S3:** HRMS and GC–MS spectra of the aqueous extract of the crude reaction mixture.

5.7. NMR experiment

![Image of NMR spectra](image2)

**Figure S4:** $^1$H NMR spectra were taken in CDCl$_3$: 2-phenylimidazo[1,2-$a$]pyridine (1a; black); after interaction of 1a with Zn(OAc)$_2$ (red), in the absence of PTH. $\delta_H = 7.26$ ppm represents the residual solvent signal in CDCl$_3$. 

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**General procedure for the NMR experiment:** To check if Zn(OAc)$_2$ interacts with the 2-phenylimidazo[1,2-$a$]pyridine moiety individual $^1$H NMR spectra of 2-phenylimidazo[1,2-$a$]pyridine and 2-phenylimidazo[1,2-$a$]pyridine with Zn(OAc)$_2$ [1:1] in CDCl$_3$ were recorded. Observations from this study revealed the shifting of peaks in the aromatic region, more specifically the signal for the C-H$_a$ proton was shifted towards the downfield region as clearly indicated above in Figure S4. This is possibly due to coordination type interaction of Zn with the N-atom at C-1 position, which facilitates the reaction process to uplift the overall reaction yield via preactivation of the IP unit.

6. **X-ray crystal data with ORTEP plot for compound 4d.**

![Figure S5: ORTEP plot of compound 4d with 30% ellipsoid probability.](image)

**Crystal data for 4d:** X-ray single crystal data were collected using MoKα ($\lambda = 0.71073$ Å) radiation on a Rigaku SuperNova diffractometer equipped with an Eos S2 detector. Structure solution/refinement were carried out using Shelx-2013. The structure was solved by direct method and refined in a routine manner. Nonhydrogen atoms were treated anisotropically. All hydrogen atoms were geometrically fixed. CCDC (CCDC No: 2221790) contains the supplementary crystallographic data of 4d. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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7. NMR spectra

$^1$H NMR of 3a (400 MHz, CDCl$_3$):

$^{13}$C{$^1$H} NMR of 3a (101 MHz, CDCl$_3$):
$^1$H NMR of 4a (400 MHz, CDCl$_3$):

$^{13}$C{\textsuperscript{1}H} NMR of 4a (101 MHz, CDCl$_3$):
$^1$H NMR of 4b (400 MHz, CDCl$_3$):

$^{13}$C\{$^1$H} NMR of 4b (101 MHz, CDCl$_3$):
$^1$H NMR of 4c (400 MHz, CDCl$_3$):

$^{13}$C{$^1$H} NMR of 4c (101 MHz, CDCl$_3$):
$^1$H NMR of 4d (400 MHz, CDCl$_3$):

$^{13}$C{$^1$H} NMR of 4d (101 MHz, CDCl$_3$):
$^{19}F\{^4H\}$ NMR of 4d (377 MHz, CDCl$_3$):
$^1$H NMR of 4e (400 MHz, CDCl$_3$):

$^{13}$C{$_1^1$H} NMR of 4e (101 MHz, CDCl$_3$):
$^1$H NMR of 4f (400 MHz, CDCl3):

$^{13}$C{${}^1$H} NMR of 4f (101 MHz, CDCl3):
$^1$H NMR of 4g (400 MHz, CDCl$_3$):

$^{13}$C\{$^1$H} NMR of 4g (101 MHz, CDCl$_3$):
$^1$H NMR of 4h (400 MHz, CDCl$_3$):

$^{13}$C $^1$H NMR of 4h (101 MHz, CDCl$_3$):
$^{19}$F-$^1$H NMR of 4h (377 MHz, CDCl$_3$):
$^1$H NMR of 4i (400 MHz, CDCl$_3$):

$^{13}$C\{$^1$H} NMR of 4i (101 MHz, CDCl$_3$):
$^1$H NMR of 4j (400 MHz, CDCl$_3$):

$^{13}$C{${}^1$H} NMR of 4j (101 MHz, CDCl$_3$):
$^1$H NMR of 4k (400 MHz, CDCl$_3$):

$^{13}$C{$_^1$H} NMR of 4k (101 MHz, CDCl$_3$):
$^1$H NMR of 4l (400 MHz, CDCl₃):

$^{13}$C{$^1$H} NMR of 4l (101 MHz, CDCl₃):
$^1$H NMR of 4m (400 MHz, CDCl$_3$):

$^{13}$C-$^1$H NMR of 4m (101 MHz, CDCl$_3$):
$^1$H NMR of 4n (400 MHz, CDCl$_3$):

$^{13}$C$\{^1$H$\}$ NMR of 4n (101 MHz, CDCl$_3$):
$^1$H NMR of 4o (400 MHz, CDCl$_3$):

$^{13}$C$\{^1$H$\}$ NMR of 4o (101 MHz, CDCl$_3$):
$^1$H NMR of 4p (400 MHz, CDCl$_3$):

$^{13}$C{$^1$H} NMR of 4p (101 MHz, CDCl$_3$):
$^1$H NMR of 4q (400 MHz, CDCl$_3$):

$^{13}$C $^1$H NMR of 4q (101 MHz, CDCl$_3$):
$^1$H NMR of 4r (400 MHz, CDCl$_3$):

$^{13}$C$\{^1$H$\}$ NMR of 4r (101 MHz, CDCl$_3$):
$^1$H NMR of 4s (400 MHz, CDCl$_3$):

$^{13}$C{$^1$H} NMR of 4s (101 MHz, CDCl$_3$):
$^1$H NMR of 4t (400 MHz, CDCl$_3$):

$^{13}$C{$^1$H} NMR of 4t (101 MHz, CDCl$_3$):
$^1$H NMR of 4u (400 MHz, CDCl$_3$):

$^{13}$C{$^1$H} NMR of 4u (101 MHz, CDCl$_3$):
$^1$H NMR of 4v (400 MHz, CDCl$_3$):

$^{13}$C{${^1}$H} NMR of 4v (101 MHz, CDCl$_3$):
$^1$H NMR of 4w (400 MHz, CDCl$_3$):

$^{13}$C {$^1$H} NMR of 4w (101 MHz, CDCl$_3$):
$^1$H NMR of 4x (400 MHz, CDCl₃):

$^{13}$C{¹H} NMR of 4x (101 MHz, CDCl₃):
$^1$H NMR of 4y (400 MHz, CDCl$_3$):

$^{13}$C{${^1}$H} NMR of 4y (101 MHz, CDCl$_3$):
$^1$H NMR of 5 (400 MHz, CDCl$_3$):

$^{13}$C{$^1$H} NMR of 5 (101 MHz, CDCl$_3$):
\(^1\)H NMR of 6 (400 MHz, CDCl\(_3\)):

\(^1\)C\(^{\text{(1H)}}\) NMR of 6 (101 MHz, CDCl\(_3\)):
$^1$H NMR of 9 (400 MHz, CDCl$_3$):

$^{13}$C\{$^1$H\} NMR of 9 (101 MHz, CDCl$_3$):
$^1$H NMR of 10 (400 MHz, CDCl$_3$):

$^{13}$C{$^1$H} NMR of 10 (101 MHz, CDCl$_3$):
$^1$H NMR of N-(pyridin-2-yl)benzamide (400 MHz, CDCl$_3$): 

$^{13}$C $^1$H NMR of N-(pyridin-2-yl)benzamide (101 MHz, CDCl$_3$):