Supporting Information

I₂-Mediated [3 + 2] cycloaddition of methyl-azaarenes with alkyl 2-isocyanoacetates or amino acid ester hydrochlorides: selective synthesis of iodine-functionalized and non-iodine-functionalized fused imidazoles

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1. General information

**Materials and General Experimental:** Methyl-azaheteroarenes, isocyanoacetates and alkyl glycinates were purchased from Shanghai Shaoyuan Co. Ltd. Cholesterol, palladium acetate, phenylacetylene and diphenyl diselenide were purchased from Energy Chemical. Bis(triphenylphosphine)palladium chloride was purchased from Laajoo. Ethyl acrylate was purchased from Aladdin. Cuprous iodide was purchased from Innochem. Unless stated otherwise, all solvents and commercially available reagents were obtained from commercial suppliers and used without further purification. In addition, petroleumether (b.p. 60-90 °C), which was used for column chromatography, was distilled prior to use. Non-commercial starting materials were prepared as described below or according to literature procedures. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel HF254 glass plates. Column chromatography was performed using silica gel (200-300 mesh).

**Instrumentation:** Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance 400 MHz spectrometer at ambient temperature using the non or partly deuterated solvent as internal standard (1H: δ 7.26 ppm and 13C{1H}: δ 77.0 ppm for CDCl3). Chemical shifts (δ) are reported in ppm, relative to the internal standard of tetramethylsilane (TMS). The coupling constants (J) are quoted in hertz (Hz). Resonances are described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or combinations thereof. High resolution mass spectra were obtained on Thermo Scientific Q-Exactive (ESI mode). Melting points were determined using SGW X-4 apparatus and not corrected. IR spectra were obtained on a Thermo Fisher Scientific Nicolet iS10 FTIR infrared spectrometer as KBr pellets and was reported in terms of frequency of transmittance (cm⁻¹).

2. Experimental Procedures

2.1 General procedure

2.1.1 General procedure for synthesis of 3 (3a as an example)

A 25 mL pressure vial was charged with 2-methylquinoline (1a) (0.2 mmol, 1.0 equiv.), I2 (0.32 mmol, 1.6 equiv.) and TFA (0.3 mmol, 1.5 equiv.) in DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 120 °C for 4-6 h under an air atmosphere, after disappearance of the reactant (monitored by TLC), then ethyl 2-isocyanoacetate (2a) (0.4 mmol, 2.0 equiv.) and TBAI (0.1 mmol, 0.5 equiv.) were added at 120 °C for another 6 h. After the reaction completed, and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% Na2S2O3 solution (w/w), dried over anhydrous Na2SO4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product 3a.

2.1.2 General procedure for synthesis of 4 (4a as an example)

A 25 mL pressure vial was charged with 2-methylquinoline (1a) (0.2 mmol, 1.0 equiv.), I2 (0.32 mmol, 1.6 equiv.) and TFA (0.3 mmol, 1.5 equiv.) in DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 120 °C for 4-6 h under an air atmosphere, after disappearance of the reactant (monitored by TLC), then ethyl 2-isocyanoacetate (2a) (0.4 mmol, 2.0 equiv.) and TBAI (0.1 mmol, 0.5 equiv.) were added at 120 °C for another 6 h. After the reaction completed, and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% Na2S2O3 solution (w/w), dried over anhydrous Na2SO4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product 3a.
equiv.), I₂ (0.32 mmol, 1.6 equiv.) and TFA (0.3 mmol, 1.5 equiv.) in DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 120 °C for 4-6 h under an air atmosphere, after disappearance of the reactant (monitored by TLC), then ethyl 2-isocyanoacetate (2a) (0.4 mmol, 2.0 equiv.) was added at 80 °C for another 6 h. After the reaction completed, and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% Na₂S₂O₃ solution (w/w), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product 4a.

### 2.2 Reaction Optimization

We optimized the reaction conditions using 2-methylquinoline (1a) (0.2 mmol, 1.0 equiv.) and ethyl 2-isocyanoacetate (2a) (0.4 mmol, 2.0 equiv.) as model substrates. Initially, the reaction was carried out with various acid (0.3 mmol, 1.5 equiv.) by using I₂ (0.4 mmol, 2.0 equiv.), such as HCl, TsOH, HOAc, TfOH and TFA (Table S1, entries 1-5). The results show that TFA is the best choice giving the product 3a and 4a in 55% and 30% yield (Table S1, entry 5). Next, the amount of I₂ was examined and the results showed that 1.6 equivalents of the I₂ provided 3a in 60% yield (Table S1, entries 5-7). Surprisingly, when 1a, I₂ and TFA were heated in DMSO at 120 °C for 4-6 h, followed by 2a for another 6 h, the yield of 3a increasing to 66% (Table S1, entry 8). When additives were added, such as NH₄I, KI, NaI, NIS, TBAI, the yield of 3a was increased to 78% by using TBAI (Table S1, entries 9-14).

#### Table S1 Optimization of the product 3a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant (eq.)</th>
<th>Acid (eq.)</th>
<th>Additive (eq.)</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>Yield (%)</th>
<th>3a</th>
<th>4a</th>
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<tr>
<td>1</td>
<td>I₂ (2.0)</td>
<td>HCl (1.5)</td>
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<td>DMSO</td>
<td>120</td>
<td>20</td>
<td>15</td>
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<td>TsOH (1.5)</td>
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<td>120</td>
<td>35</td>
<td>20</td>
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<td>HOAc (1.5)</td>
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<td>40</td>
<td>25</td>
<td></td>
</tr>
<tr>
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<td>TfOH (1.5)</td>
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<td>45</td>
<td>35</td>
<td></td>
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<tr>
<td>5</td>
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<td>TFA (1.5)</td>
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<td>DMSO</td>
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<td>55</td>
<td>30</td>
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<td>6</td>
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<td>TFA (1.5)</td>
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<td>DMSO</td>
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<td>58</td>
<td>30</td>
<td></td>
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<td>7</td>
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<td>TFA (1.5)</td>
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<td>DMSO</td>
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<td>60</td>
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<td>8</td>
<td>I₂ (1.6)</td>
<td>TFA (1.5)</td>
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<td>DMSO</td>
<td>120</td>
<td>66</td>
<td>15</td>
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<tr>
<td>9</td>
<td>I₂ (1.6)</td>
<td>TFA (1.5)</td>
<td>NH₄I (1.0)</td>
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<td>68</td>
<td>22</td>
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<td>I₂ (1.6)</td>
<td>TFA (1.5)</td>
<td>KI (1.0)</td>
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<td>TFA (1.5)</td>
<td>NaI (1.0)</td>
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<tr>
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<td>TFA (1.5)</td>
<td>NIS (1.0)</td>
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<td>72</td>
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<td>13</td>
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<td>TFA (1.5)</td>
<td>TBAI (1.0)</td>
<td>DMSO</td>
<td>120</td>
<td>75</td>
<td>5</td>
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</table>
14 b I₂ (1.6) TFA (1.5) TBAI (0.5) DMSO 120 78 5

a Reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), oxidant and acid in solvent (2.0 mL), at different temperatures for 12 h under air atmosphere. b 1a (0.2 mmol), I₂ (1.6 equiv.) and TFA (1.5 equiv.) were heated in DMSO (2 mL) at 120 °C for 4-6 h, followed by 2a (0.4 mmol) and additive were added for another 6 h. c Isolated yield.

We optimized the reaction conditions using 2-methylquinoline (1a) (0.2 mmol, 1.0 equiv.) and glycine ethyl ester hydrochloride (2a') (0.4 mmol, 2.0 equiv.) as model substrates. Initially, the reaction was carried out with different equivalents of I₂ by using TFA (0.3 mmol, 1.5 equiv.) and TBAI (0.5 equiv.) in DMSO (2 mL) at 120 °C (Table S2, entries 1-3). The results show that 2.0 equivalents of I₂ is the best choice giving the major product 3a in 72% yield. Next, a series of acid were examined and the results showed that TFA is the best choice (Table S2, entries 3-6). Finally, 1a (0.2 mmol), 2a’ (0.4 mmol), I₂ (2.0 equiv.), TFA (1.5 equiv.) and TBAI (0.5 equiv.) were heated in DMSO (2 mL) at 120 °C for 12 h in one pot giving the product 3a and 4a in 40% and 30% yields (Table S2, entry 7).

Table S2 Optimization of the product 3a (Glycine ethyl ester hydrochloride as substrate) a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant (eq.)</th>
<th>Acid (eq.)</th>
<th>Additive (eq.)</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>Yield (%) c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I₂ (1.6)</td>
<td>TFA (1.5)</td>
<td>TBAI (0.5)</td>
<td>DMSO</td>
<td>120</td>
<td>55 5 25</td>
</tr>
<tr>
<td>2</td>
<td>I₂ (1.8)</td>
<td>TFA (1.5)</td>
<td>TBAI (0.5)</td>
<td>DMSO</td>
<td>120</td>
<td>60 18</td>
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<tr>
<td>3</td>
<td>I₂ (2.0)</td>
<td>TFA (1.5)</td>
<td>TBAI (0.5)</td>
<td>DMSO</td>
<td>120</td>
<td>70 trace</td>
</tr>
<tr>
<td>4</td>
<td>I₂ (2.0)</td>
<td>TfOH (1.5)</td>
<td>TBAI (0.5)</td>
<td>DMSO</td>
<td>120</td>
<td>62 15</td>
</tr>
<tr>
<td>5</td>
<td>I₂ (2.0)</td>
<td>HOAc (1.5)</td>
<td>TBAI (0.5)</td>
<td>DMSO</td>
<td>120</td>
<td>52 22</td>
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<tr>
<td>6</td>
<td>I₂ (2.0)</td>
<td>TsOH (1.5)</td>
<td>TBAI (0.5)</td>
<td>DMSO</td>
<td>120</td>
<td>42 25</td>
</tr>
<tr>
<td>7 b</td>
<td>I₂ (2.0)</td>
<td>TFA (1.5)</td>
<td>TBAI (0.5)</td>
<td>DMSO</td>
<td>120</td>
<td>40 30</td>
</tr>
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</table>

a Reaction conditions: 1a (0.2 mmol), I₂ and acid (1.5 equiv.) were heated in DMSO (2 mL) at 120 °C for 4-6 h, followed by 2a’ (0.4 mmol) and additive were added for another 6 h. b 1a (0.2 mmol), 2a’ (0.4 mmol), I₂ (2.0 equiv.), TFA (1.5 equiv.) and TBAI (0.5 equiv.) were heated in DMSO (2 mL) at 120 °C for 12 h c Isolated yield.

We optimized the reaction conditions using 2-methylquinoline (1a) (0.2 mmol, 1.0 equiv.) and glycine ethyl ester hydrochloride (2a’) (0.4 mmol, 2.0 equiv.) as model substrates. Firstly, the reaction of 2-methylquinoline (1a) (0.2 mmol, 1.0 equiv.) and glycine ethyl ester hydrochloride (2a’) (0.4 mmol, 2.0 equiv.) was carried out under standard condition C, giving the major product 4a in 40% yield (Table S3, entry 1).
Surprisingly, when 2 equivalents of K$_2$CO$_3$ were added to the reaction system, the yield of 4a increased to 50%. Next, a series of base were examined, such as Na$_2$CO$_3$, TEA, K$_3$PO$_4$ and Cs$_2$CO$_3$ (Table S3, entries 3-7). The results show that 2.0 equivalents of K$_2$CO$_3$ is the best choice giving the product 4a in 83% yield (Table S3, entry 3). Finally, 1a (0.2 mmol), 2a’ (0.4 mmol), I$_2$ (1.6 equiv.), and K$_2$CO$_3$ (2.0 equiv.) were heated in DMSO (2 mL) at 80 °C for 12 h in one pot, giving the product 4a in 63% (Table S3, entry 8).

**Table S3 Optimization of the product 4a (Glycine ethyl ester hydrochloride as substrate)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant (eq.)</th>
<th>Acid (eq.)</th>
<th>Additive (eq.)</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I$_2$ (1.6)</td>
<td>TFA (1.5)</td>
<td>DMSO</td>
<td>80</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>I$_2$ (1.6)</td>
<td>TFA (1.5)</td>
<td>K$_2$CO$_3$ (2.0)</td>
<td>80</td>
<td>15</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>I$_2$ (1.6)</td>
<td>TFA (1.5)</td>
<td>K$_2$CO$_3$ (2.0)</td>
<td>DMSO</td>
<td>80</td>
<td>trace 83</td>
</tr>
<tr>
<td>4</td>
<td>I$_2$ (1.6)</td>
<td>Na$_2$CO$_3$ (2.0)</td>
<td>DMSO</td>
<td>80</td>
<td>10</td>
<td>56</td>
</tr>
<tr>
<td>5</td>
<td>I$_2$ (1.6)</td>
<td>TEA (2.0)</td>
<td>DMSO</td>
<td>80</td>
<td>trace 30</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>I$_2$ (1.6)</td>
<td>K$_3$PO$_4$ (2.0)</td>
<td>DMSO</td>
<td>80</td>
<td>15</td>
<td>54</td>
</tr>
<tr>
<td>7</td>
<td>I$_2$ (1.6)</td>
<td>Cs$_2$CO$_3$ (2.0)</td>
<td>DMSO</td>
<td>80</td>
<td>trace 70</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>I$_2$ (1.6)</td>
<td>K$_2$CO$_3$ (2.0)</td>
<td>DMSO</td>
<td>80</td>
<td>trace 63</td>
<td></td>
</tr>
</tbody>
</table>

* Reaction conditions: 1a (0.2 mmol), I$_2$ (1.6 equiv.) and acid (1.5 equiv.) were heated in DMSO (2 mL) at 120 °C for 4-6 h, followed by 2a’ (0.4 mmol) and additive (2.0 equiv.) were added for another 6 h at 80 °C. * 1a (0.2 mmol), 2a’ (0.4 mmol), I$_2$ (1.6 equiv.), and K$_2$CO$_3$ (2.0 equiv.) were heated in DMSO (2 mL) at 80 °C for 12 h. * Isolated yield.

### 2.3 The scope of substrates

**Table S4 Substrate scope of iodine-functionalized products. (Amino acid ester hydrochloride as substrate)**

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With the optimized conditions established, the scope of the iodine-functionalized products was tested using various substituted 2-methylquinolines and other methyl azaheterocycles with amino acid ester hydrochlorides as shown in Table S4. At first, we investigated a series of 2-methylquinolines bearing electron-rich substituents on the aryl ring (e.g., 6-Me, 6-OMe, 6-OEt, 8-OMe). To our delight, the reactions could afford the desired products 3b-3e in 62%-68% yields. And the 2-methylquinolines attached with halogen atoms (e.g., 6-F, 6-Cl, 7-Cl, 6-Br) were also tolerated in the reaction, giving the corresponding products 3f-3i in 61%-67% yields. In addition, esterified and amidated 2-methylquinoline carboxylic acids could proceed well in the reaction, affording the desired products 3j-3l in 58%-62% yields. Various methyl azaarenes, such as 2-methylpyridine, 3-methylbenzo[f]quinoline, 2-
methylbenzo[d]thiazole and 2-methylnaphtho[1,2-d]thiazole, were all well tolerated in the protocol and giving the corresponding products 3m-3p in moderate yields. When glycine ethyl ester hydrochloride was replaced by glycine methyl ester hydrochloride and benzyl glycinate hydrochloride, generating the desired products 3q and 3u in good yields. However, 2-methylbenzo[d]oxazole, 1,2-dimethyl-1H-benzo[d]imidazole and 1,3,7,8-tetramethyl-3,7-dihydro-1H-purine-2,6-dione were not suitable for this reaction to generate the iodine-functionalized products.

Table S5 Substrate scope of non-iodine-functionalized products.

(Amino acid ester hydrochloride as substrate) \(^{a,b}\)

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\(^a\) Reaction conditions: 1a (0.2 mmol), I\(_2\) (1.6 equiv.) were heated in DMSO (2 mL) at 120 °C for 4-6 h, followed by 2a\(^{2'}\) (0.4 mmol) and K\(_2\)CO\(_3\) (2.0 equiv.) were added for another 6 h at 80 °C. \(^b\) Isolated yield.

We next examined the scope of this reaction for non-iodine-functionalized products.
(Table S5). Firstly, we studied the 2-methylquinolines in which the phenyl ring had electron-rich substituents (e.g., 6-Me, 6-OMe 6-OEt) the annulation reactions proceeded smoothly to deliver products 4b-4d in good yields. When the phenyl ring of 2-methylquinolines bearing halogen groups (e.g., 6-F, 7-F, 6-Cl, 7-Cl, 6-Br), the reactions could also perform smoothly to afford the desired products 4e-4i in 72%-83% yields. Esterified and amidated 2-methylquinoline carboxylic acids could also proceed well in this reaction, affording the desired products 4j-4l in moderate yields. In addition, other methyl azaarenes, such as 3-methylbenzo[f]quinoline, 2-methylquinoxaline, and 2-methylbenzo[d]thiazole, were all well tolerated in the strategy and giving the corresponding products 4m-4o in moderate yields. In addition, 2-methylquinoline carboxylic acid modified by natural product (cholesterol) was also suitable for this reaction giving the desired product 4p in 43% yield. When glycine ethyl ester hydrochloride was replaced by glycine methyl ester hydrochloride, glycine tert-butyl ester hydrochloride and benzyl glycinate hydrochloride to generate the desired products 4q-4s in moderate to good yields. However, 2-methylbenzo[d]oxazole, 1,2-dimethyl-1H-benzo[d]imidazole and 1,3,7,8-tetramethyl-3,7-dihydro-1H-purine-2,6-dione were still not suitable for this reaction to generate the desired products.

2.4 Synthesis of starting materials

![Scheme S1](image)

**Scheme S1** Synthesis of α-isocyanoacetates

**General procedure A:** Followed the procedure in the literature.¹ Acetic anhydride (22.0 mL, 242.1 mmol, 8.0 equiv.) was added dropwise to a solution of methyl phenylalaninate (25.0 mmol, 1.0 equiv.) in HCOOH (50.0 mL) at 0 °C. After the addition was complete, the reaction mixture was stirred at room temperature for an additional 1 h. Ice-water (20.0 mL) was added and then the solvent was evaporated at reduced pressure to give the N-formamide as a colorless oil. A stirred solution of amide (18.5 mmol, 1.0 equiv.) and Et₃N (12.8 mL, 92.0 mmol, 5.0 equiv.) in CH₂Cl₂ (90.0 mL) was cooled to –30 °C. Phosphorus oxychloride (2.6 mL, 27.5 mmol, 1.5 equiv.) was added dropwise and the reaction mixture was stirred for 3 h at –30 °C. A saturated aqueous solution of Na₂CO₃ was added dropwise and the temperature of the mixture was maintained at –30 °C. The mixture was stirred at –30 °C for 0.5 h and then raised to room temperature. The aqueous layer was separated and extracted with CH₂Cl₂. The organic extracts were combined, washed with brine, dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to provide the isocyanide.

![Scheme S2](image)

**Scheme S2** Synthesis of isocyanides

**General procedure B:** Followed the procedure in the literature.² In an oven-dried 25
mL Schlenk tube equipped with a magnetic stir bar were added a primary amine R-NH₂ (0.4 mmol), sodium chlorodifluoroacetate (0.8 mmol) and K₂CO₃ (0.8 mmol). The Schlenk tube was evacuated and refilled with dry nitrogen. Dry DMF (5 mL) was then added by syringe. The contents in the tube were vigorously stirred for 12 hours at 100 °C (heated in an oil bath). The reaction mixture was then allowed to cool to room temperature. The resulting mixture was extracted by dichloromethane. The combined organic layers were washed with a large amount of water for 4 times, with brine for once and then dried over magnesium sulfate. The solvent was removed under vacuum and the residuals were purified by column chromatography on silica using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent to give purified isocyanide.

Scheme S3 Synthesis of α-isocyanoacetamides

General procedure C: Followed the procedure in the literature.³ To 30 mmol of amine was added 30 mmol of methyl 2-isocyanoacetate and the mixture was stirred overnight at room temperature. If the product precipitated during the reaction, it was filtered off, washed three times with cold diethyl ether, and dried under vacuum overnight. If no precipitation was observed, cold diethylether was added to the reaction mixture, and the product was allowed to crystallize in the freezer at –20 °C. In the rare cases, the product was formed as an oil or no crystallization occurred, the product was purified by preparative chromatography with silica gel and ethyl acetate as eluent.

2.5 The further application of iodinated products

Scheme S4 Arylation of iodinated product

Adapting a literature procedure,⁴ potassium carbonate (0.4 mmol, 2.0 equiv.), phenylboronic acid (0.26 mmol, 1.3 equiv.) and Pd(PPh₃)₂Cl₂ (5 mol%) were added to a solution of 3a (0.2 mmol, 1.0 equiv.) in a 5:1 solvent mixture of dioxane and water. The reaction mixture was heated to 90 °C and stirred at this temperature until complete consumption of 3a was observed (monitored by TLC). After cooling to room temperature, the mixture was diluted with a mixture of EA and water and the aqueous layer was extracted with EtOAc (3 × 50 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired 5 in 76% yield.
Adapting a literature procedure,\textsuperscript{5} \(3a\) (0.2 mmol, 1 equiv.), \(\text{Pd(PPh}_3\text{)}_2\text{Cl}_2\) (5 mol%), CuI (10 mol%) and phenylacetylene (0.24 mmol, 1.2 equiv.) were added to a 25 mL Schlenk flask with a stir bar under an Ar atmosphere. Then tetrahydrofuran (2 mL) and triethylamine (1 mL) were added sequentially. The reaction mixture was then stirred at 50 °C. Afterwards 15 mL of water were added and the reaction mixture was extracted with EtOAc (3 × 50 mL). The combined organic fractions were washed with brine and dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. After filtration, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate as the eluent to afford the desired \(6\) in 78% yield.

Adapting a literature procedure,\textsuperscript{6} \(3a\) (0.2 mmol, 1 equiv.), \(\text{Pd(OAc)}_2\) (10 mol%), \(\text{PPh}_3\) (20 mol%) and ethyl acrylate (0.3 mmol, 1.5 equiv.) were added to a 25 mL Schlenk flask with a stir bar under an Ar atmosphere. Then dioxane (2 mL) and triethylamine (1 mL) were added sequentially. The reaction mixture was then stirred at 90 °C. Afterwards 50 mL of water were added and the reaction mixture was extracted with EtOAc (3 × 50 mL). The combined organic fractions were washed with brine and dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. After filtration, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate as the eluent to afford the desired \(7\) in 85% yield.

Adapting a literature procedure,\textsuperscript{7} a 25 mL pressure vial was charged with \(3a\) (0.2 mmol, 1.0 equiv.), diphenyl diselenide (0.12 mmol, 0.6 equiv.) in DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 110 °C for 24 h under an air atmosphere. After the reaction completed, and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired \(8\) in 80% yield.
70% yield.

3. Molecular structure and crystallographic data

![X-ray crystal structure of compound 3j](image)

**Figure S1** X-ray crystal structure of compound 3j

**Table S6. Crystal data and structure refinement for compound 3j**

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4. Characterization of Products

Ethyl 3-iodoimidazo[1,5-a]quinoline-1-carboxylate (3a), 57 mg, 78%, yellow solid, m.p. 101-102 °C. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.71-8.59 (m, 1H), 7.80-7.70 (m, 1H), 7.64-7.57 (m, 1H), 7.52 (dd, $J$ = 7.8, 7.3, 1.1 Hz, 1H), 7.35 (d, $J$ = 4.7 Hz, 2H), 4.58 (q, $J$ = 7.1 Hz, 2H), 1.52 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.2, 135.3, 135.0, 131.9, 128.9, 128.6, 126.3, 125.8, 119.5, 116.4, 79.6, 62.5, 14.3. IR (KBr, cm$^{-1}$): 2831, 1706, 1597, 1364, 1191, 776. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{14}$H$_{12}$IN$_2$O$_2$: 366.9865, found: 366.9866.

Ethyl 3-iodo-7-methylimidazo[1,5-a]quinoline-1-carboxylate (3b), 60 mg, 78%, yellow solid, m.p. 140-142 °C. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.56 (d, $J$ = 8.8 Hz, 1H), 7.53-7.49 (m, 1H), 7.40 (dd, $J$ = 8.8, 1.7 Hz, 1H), 7.29 (s, 2H), 4.56 (q, $J$ = 7.1 Hz, 2H), 2.49 (s, 3H), 1.51 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.1, 136.7, 135.2, 134.7, 129.9, 129.8, 128.5, 126.1, 125.7, 119.3, 116.2, 79.4, 62.4, 20.9, 14.3. IR (KBr, cm$^{-1}$): 2832, 1690, 1597, 1364, 1200, 1065, 776. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{15}$H$_{14}$IN$_2$O$_2$: 381.0022, found: 381.0023.

Ethyl 3-iodo-7-methoxyimidazo[1,5-a]quinoline-1-carboxylate (3c), 55 mg, 70%, yellow solid, m.p. 148-150 °C. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.66 (d, $J$ = 9.4 Hz, 1H), 7.30-7.24 (m, 2H), 7.15 (ddd, $J$ = 9.4, 2.9, 1.0 Hz, 1H), 7.10 (d, $J$ = 2.9 Hz, 1H), 4.55 (q, $J$ = 7.1 Hz, 2H), 3.90 (s, 3H), 1.50 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.0, 157.6, 134.9, 134.4, 127.2, 126.2, 126.0, 121.0, 116.7, 116.6, 110.0, 79.6, 62.4, 55.6, 14.3. IR (KBr, cm$^{-1}$): 2832, 1687, 1597, 1364, 1200, 1065, 776. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{15}$H$_{14}$IN$_2$O$_3$: 396.9971, found: 396.9974.

Ethyl 7-ethoxy-3-iodoimidazo[1,5-a]quinoline-1-carboxylate (3d), 59 mg, 72%, yellow solid, m.p. 152-153 °C. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.67 (dd, $J$ = 9.4, 1.8
Hz, 1H), 7.33-7.26 (m, 2H), 7.17 (ddd, $J = 9.4, 2.8, 1.9$ Hz, 1H), 7.12 (t, $J = 2.7$ Hz, 1H), 4.56 (q, $J = 7.1$ Hz, 2H), 4.14 (qd, $J = 7.0, 1.2$ Hz, 2H), 1.53-1.49 (m, 3H), 1.49-1.44 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.1, 157.1, 135.0, 134.5, 127.3, 126.2, 126.1, 121.1, 117.2, 116.6, 110.8, 79.6, 63.9, 62.3, 14.7, 14.3. IR (KBr, cm$^{-1}$): 2832, 1699, 1597, 1364, 1196, 1065, 776. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{16}$H$_{16}$IN$_2$O$_3$: 411.0127, found: 411.0128.

Ethyl 3-iodo-9-methoxyimidazo[1,5-$a$]quinoline-1-carboxylate (3e), 52 mg, 66%, yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (t, $J = 8.0$ Hz, 1H), 7.27 (dd, $J = 7.7, 0.9$ Hz, 1H), 7.22-7.14 (m, 2H), 7.04 (dd, $J = 8.1, 1.2$ Hz, 1H), 4.41 (q, $J = 7.2$ Hz, 2H), 3.87 (s, 3H), 1.37 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.2, 149.5, 139.4, 133.9, 127.6, 126.8, 124.5, 122.4, 120.1, 116.7, 110.4, 61.7, 55.3, 14.2. IR (KBr, cm$^{-1}$): 2832, 1654, 1597, 1364, 776. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{15}$H$_{14}$IN$_2$O$_3$: 396.9971, found: 396.9973.

Ethyl 7-fluoro-3-iodoimidazo[1,5-$a$]quinoline-1-carboxylate (3f), 54 mg, 71%, yellow solid, m.p. 175-176 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.79 (dd, $J = 9.4, 4.7$ Hz, 1H), 7.42-7.34 (m, 2H), 7.34-7.26 (m, 2H), 4.56 (q, $J = 7.1$ Hz, 2H), 1.51 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.5, 160.0, 159.0 (d, $J = 12.0$ Hz), 128.4 (d, $J = 3.0$ Hz), 127.6 (d, $J = 9.0$ Hz), 125.4 (d, $J = 4.0$ Hz), 121.9 (d, $J = 8.0$ Hz), 117.63, 116.3 (d, $J = 23.0$ Hz), 113.6 (d, $J = 23.0$ Hz), 80.2, 62.6, 14.3. IR (KBr, cm$^{-1}$): 2832, 1711, 1698, 1478, 1234, 1192, 776. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{14}$H$_{11}$FIN$_2$O$_2$: 384.9771, found: 384.9773.

Ethyl 7-chloro-3-iodoimidazo[1,5-$a$]quinoline-1-carboxylate (3g), 60 mg, 75%, yellow solid, m.p. 192-193 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.85 (d, $J = 1.9$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 1H), 7.48 (dd, $J = 8.4, 1.9$ Hz, 1H), 7.30 (d, $J = 2.8$ Hz, 2H), 4.59 (q, $J = 7.1$ Hz, 2H), 1.52 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.8, 135.2, 135.0, 134.2, 132.2, 129.7, 127.3, 125.4, 124.1, 119.8, 116.5, 80.0, 62.7, 14.2. IR (KBr, cm$^{-1}$): 2832, 1695, 1597, 1363, 1192, 776. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{14}$H$_{11}$ClIN$_2$O$_2$: 400.9475, found: 400.9477.
**Ethyl 8-chloro-3-iodoimidazo[1,5-a]quinoline-1-carboxylate (3h),** 64 mg, 80%, yellow solid, m.p. 161-162 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.71 (d, $J = 9.2$ Hz, 1H), 7.70 (d, $J = 2.4$ Hz, 1H), 7.52 (dd, $J = 9.2, 2.5$ Hz, 1H), 7.35 (d, $J = 9.4$ Hz, 1H), 7.24 (s, 1H), 4.57 (q, $J = 7.1$ Hz, 2H), 1.51 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.9, 135.1, 132.4, 130.3, 128.5, 127.8, 127.1, 125.1, 121.2, 117.6, 80.3, 62.6, 14.3. IR (KBr, cm$^{-1}$): 2832, 1710, 1601, 1437, 1364, 1190, 1066, 829, 776. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{14}$H$_{11}$ClIN$_2$O$_2$: 400.9475, found: 400.9476.

**Ethyl 7-bromo-3-iodoimidazo[1,5-a]quinoline-1-carboxylate (3i),** 65 mg, 74%, yellow solid, m.p. 182-183 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.61 (d, $J = 9.4$ Hz, 1H), 7.83 (d, $J = 2.3$ Hz, 1H), 7.64 (dd, $J = 9.2, 2.3$ Hz, 1H), 7.32 (d, $J = 9.4$ Hz, 1H), 7.21 (d, $J = 9.3$ Hz, 1H), 4.56 (q, $J = 7.1$ Hz, 2H), 1.51 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.9, 135.1, 135.0, 131.3, 130.9, 130.6, 127.4, 124.9, 121.3, 120.2, 117.59, 80.3, 62.6, 14.3. IR (KBr, cm$^{-1}$): 2832, 1710, 1601, 1437, 1364, 1190, 1066, 829, 776. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{14}$H$_{11}$BrIN$_2$O$_2$: 444.8970, found: 444.8974.

**Diethyl 3-iodoimidazo[1,5-a]quinoline-1,7-dicarboxylate (3j),** 61 mg, 70%, yellow solid, m.p. 193-194 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.73 (d, $J = 9.0$ Hz, 1H), 8.45 (d, $J = 2.0$ Hz, 1H), 8.23 (dd, $J = 9.0, 2.0$ Hz, 1H), 7.48-7.33 (m, 2H), 4.58 (q, $J = 7.1$ Hz, 2H), 4.45 (q, $J = 7.1$ Hz, 2H), 1.52 (t, $J = 7.1$ Hz, 3H), 1.45 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.3, 160.0, 135.5, 134.3, 130.6, 129.1, 128.7, 126.1, 125.6, 119.7, 117.3, 80.1, 62.8, 61.5, 14.3. IR (KBr, cm$^{-1}$): 2979, 2832, 1711, 1693, 1600, 1428, 1364, 1287, 1186, 1059, 776. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{17}$H$_{16}$IN$_2$O$_4$: 439.0076, found: 439.0078.
7-(sec-butyl) 1-Ethyl 3-iodimidazo[1,5-a]quinoline-1,7-dicarboxylate (3k), 68 mg, 73%, yellow solid, m.p. 130-131 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.71 (d, \(J = 9.0\) Hz, 1H), 8.43 (d, \(J = 2.0\) Hz, 1H), 8.23 (dd, \(J = 9.0, 2.0\) Hz, 1H), 7.40 (q, \(J = 9.4\) Hz, 2H), 5.15 (dt, \(J = 12.6, 6.2\) Hz, 1H), 4.58 (q, \(J = 7.1\) Hz, 2H), 1.81-1.69 (m, 2H), 1.51 (t, \(J = 7.1\) Hz, 3H), 1.38 (d, \(J = 6.3\) Hz, 3H), 1.00 (t, \(J = 7.5\) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.9, 159.9, 135.4, 134.2, 130.5, 129.1, 126.1, 125.5, 119.6, 117.2, 80.0, 73.6, 28.9, 19.5, 14.3, 9.7. IR (KBr, cm\(^{-1}\)): 2970, 2831, 1579, 1362, 1328, 1282, 793, 763. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{19}\)H\(_{20}\)IN\(_2\)O\(_4\): 467.0390, found: 467.0392.

![Chemical Structure](image1)

Ethyl 7-((3,4-dimethylphenyl)carbamoyl)-3-iodimidazo[1,5-a]quinoline-1-carboxylate (3l), 68 mg, 67%, yellow solid, m.p. 230-231 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.59 (d, \(J = 9.0\) Hz, 1H), 8.35 (s, 1H), 8.08 (d, \(J = 1.7\) Hz, 1H), 7.86 (d, \(J = 1.8\) Hz, 1H), 7.52 (s, 1H), 7.45 (d, \(J = 8.0\) Hz, 1H), 7.24-7.15 (m, 2H), 7.13 (d, \(J = 8.1\) Hz, 1H), 4.56 (q, \(J = 7.1\) Hz, 2H), 2.28 (s, 3H), 2.25 (s, 3H), 1.50 (t, \(J = 7.1\) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.5, 159.9, 137.3, 135.6, 135.2, 133.6, 133.2, 132.9, 130.1, 127.9, 126.6, 125.8, 125.4, 121.6, 119.7, 117.8, 117.1, 80.2, 62.8, 19.9, 19.2, 14.3. IR (KBr, cm\(^{-1}\)): 2832, 1712, 1583, 1504, 1362, 1248, 1184, 1051, 867. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{23}\)H\(_{21}\)IN\(_3\)O\(_3\): 514.0549, found: 514.0551.

![Chemical Structure](image2)

Ethyl 1-iodimidazo[1,5-a]pyridine-3-carboxylate (3m), 38 mg, 60%, yellow solid, m.p. 110-111 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.39-9.23 (m, 1H), 7.53 (dt, \(J = 9.1, 1.2\) Hz, 1H), 7.15 (ddd, \(J = 9.1, 6.6, 0.9\) Hz, 1H), 6.97 (td, \(J = 7.1, 1.2\) Hz, 1H), 4.50 (q, \(J = 7.1\) Hz, 2H), 1.46 (t, \(J = 7.1\) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.7, 136.2, 129.5, 125.9, 123.8, 118.7, 116.3, 61.5, 14.5. IR (KBr, cm\(^{-1}\)): 2917, 2832, 1712, 1583, 1504, 1362, 1248, 1184, 1051, 867. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{10}\)H\(_{10}\)IN\(_2\)O\(_2\): 316.9781, found: 316.9781.

![Chemical Structure](image3)
Ethyl 1-iodobenzo[f]imidazo[1,5-a]quinoline-3-carboxylate (3n), 57 mg, 68%, yellow solid, m.p. 188-189 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.51-8.30 (m, 2H), 8.10 (d, \(J = 9.5\) Hz, 1H), 7.90 (d, \(J = 8.7\) Hz, 2H), 7.62 (dq, \(J = 14.7, 7.1\) Hz, 2H), 7.42 (d, \(J = 9.5\) Hz, 1H), 4.60 (q, \(J = 7.0\) Hz, 2H), 1.54 (t, \(J = 7.0\) Hz, 3H). \(\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\)) \(\delta\) 160.1, 135.3, 134.2, 131.2, 129.9, 129.2, 129.1, 128.6, 127.7, 126.9, 123.0, 121.3, 120.6, 118.0, 116.2, 78.6, 62.4, 14.3. IR (KBr, cm\(^{-1}\)): 2832, 1659, 1592, 1363, 775. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{18}\)H\(_{14}\)IN\(_2\)O\(_2\): 417.0022, found: 417.0024.

![](attachment:3n.png)

Ethyl 3-iodobenzo[d]imidazo[5,1-b]thiazole-1-carboxylate (3o), 51 mg, 68%, white solid, m.p. 176-177 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.15 (dd, \(J = 8.4, 1.3\) Hz, 1H), 7.66 (dd, \(J = 7.9, 1.5\) Hz, 1H), 7.51-7.46 (m, 1H), 7.43 (td, \(J = 7.6, 1.4\) Hz, 1H), 4.52 (q, \(J = 7.1\) Hz, 2H), 1.48 (t, \(J = 7.1\) Hz, 3H). \(\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\)) \(\delta\) 157.8, 140.2, 134.1, 133.8, 132.3, 126.8, 126.4, 123.9, 119.2, 70.6, 62.1, 14.4. IR (KBr, cm\(^{-1}\)): 2831, 1705, 1597, 1363, 1171, 775. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{12}\)H\(_{10}\)IN\(_2\)O\(_2\): 372.9429, found: 372.9430.

![](attachment:3o.png)

Ethyl 8-iodoimidazo[5,1-b]naphtho[1,2-d]thiazole-10-carboxylate (3p), 54 mg, 64%, yellow solid, m.p. 183-184 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03-7.98 (m, 1H), 7.95 (d, \(J = 8.7\) Hz, 1H), 7.80-7.74 (m, 1H), 7.71 (d, \(J = 8.7\) Hz, 1H), 7.65-7.58 (m, 2H), 4.51 (q, \(J = 7.1\) Hz, 2H), 1.37 (t, \(J = 7.1\) Hz, 3H). \(\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\)) \(\delta\) 158.4, 139.9, 135.5, 132.4, 130.7, 128.7, 128.5, 128.5, 126.4, 126.1, 123.5, 122.1, 120.5, 69.9, 62.4, 14.2. IR (KBr, cm\(^{-1}\)): 2831, 1711, 1597, 1363, 775. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{16}\)H\(_{12}\)IN\(_2\)O\(_2\): 422.9586, found: 422.9588.

![](attachment:3p.png)

Ethyl 3-iodoimidazo[1,5-a]quinoline-1-carboxylate (3q), 55 mg, 79%, yellow solid, m.p. 192–193 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.76 (d, \(J = 8.7\) Hz, 1H), 7.75 (dd, \(J = 7.8, 1.6\) Hz, 1H), 7.61 (ddd, \(J = 8.8, 7.2, 1.7\) Hz, 1H), 7.56-7.50 (m, 1H), 7.36 (q, \(J = 9.3\) Hz, 2H), 4.09 (s, 3H). \(\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\)) \(\delta\) 160.4, 135.6, 134.6, 131.9, 128.9, 128.7, 126.9, 126.5, 125.8, 119.6, 116.3, 79.7, 53.2. IR (KBr, cm\(^{-1}\)): 2831, 1710, 1593, 1363, 1188, 775. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{13}\)H\(_{10}\)IN\(_2\)O\(_2\): 352.9709, found: 352.9710.
Benzyl 3-iodoimidazo[1,5-a]quinoline-1-carboxylate (3r), 56 mg, 65%, yellow solid, m.p. 135–136 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.60 – 8.46 (m, 1H), 7.74 – 7.68 (m, 1H), 7.57 – 7.54 (m, 2H), 7.52 – 7.47 (m, 2H), 7.40 (ddd, $J = 7.3$, 6.1, 1.6 Hz, 2H), 7.38 – 7.34 (m, 1H), 7.34 – 7.28 (m, 2H), 5.55 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.9, 135.4, 135.3, 134.7, 131.7, 128.8, 128.6, 128.6, 128.5, 126.8, 126.3, 125.7, 119.4, 79.7, 67.8. IR (KBr, cm$^{-1}$): 2831, 1705, 1597, 1366, 1176, 774. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{19}$H$_{14}$IN$_2$O$_2$: 428.0022, found: 428.0024.

N-benzyl-3-iodoimidazo[1,5-a]quinoline-1-carboxamide (3s), 47 mg, 55%, yellow solid, m.p. 146–147 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.50 – 9.42 (m, 1H), 7.90 (s, 1H), 7.72 (dd, $J = 7.8$, 1.6 Hz, 1H), 7.63 (ddd, $J = 8.8$, 7.2, 1.7 Hz, 1H), 7.51 (td, $J = 7.5$, 1.1 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 3H), 4.72 (d, $J = 6.1$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.1, 138.5, 137.9, 135.2, 128.8, 128.7, 128.5, 127.9, 127.6, 126.7, 125.8, 125.7, 121.1, 116.2, 43.9. IR (KBr, cm$^{-1}$): 2831, 1597, 1537, 1363, 774. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{19}$H$_{15}$IN$_3$: 428.0182, found: 428.0184.

3-Iodo-N-(1-phenylethyl)imidazo[1,5-a]quinoline-1-carboxamide (3t), 44 mg, 50%, yellow solid, m.p. 156–157 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.45 – 9.35 (m, 1H), 7.86 (d, $J = 7.9$ Hz, 1H), 7.70 – 7.67 (m, 1H), 7.58 (ddd, $J = 8.8$, 7.2, 1.7 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.40 – 7.35 (m, 2H), 7.29 (s, 2H), 7.27 (s, 1H), 5.34 (p, $J = 7.1$ Hz, 1H), 1.68 (d, $J = 7.0$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.3, 143.1, 138.6, 135.2, 132.4, 128.7, 128.6, 128.4, 127.4, 126.7, 126.2, 125.7, 121.2, 116.2, 49.6, 22.2. IR (KBr, cm$^{-1}$): 2917, 2831, 1601, 1531, 1363, 791, 774, 756, 700. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{20}$H$_{17}$IN$_3$: 442.0338, found: 442.0342.
3-Iodo-N-(thiophen-2-ylmethyl)imidazo[1,5-a]quinoline-1-carboxamide (3u), 39 mg, 45%, yellow solid, m.p. 164–165 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.63 – 9.31 (m, 1H), 7.93 (s, 1H), 7.71 (dd, $J$ = 7.8, 1.5 Hz, 1H), 7.64 (ddd, $J$ = 8.8, 7.2, 1.6 Hz, 1H), 7.51 (td, $J$ = 7.8, 1.0 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.26 – 7.24 (m, 1H), 7.10 (dd, $J$ = 3.5, 1.0 Hz, 1H), 6.99 (dd, $J$ = 5.1, 3.5 Hz, 1H), 4.96 – 4.75 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.8, 140.5, 138.2, 135.3, 132.3, 128.8, 128.5, 126.9, 126.8, 126.3, 125.9, 125.7, 125.4, 121.1, 116.2, 38.6. IR (KBr, cm$^{-1}$): 2917, 2831, 1601, 1509, 1363, 790, 774, 753, 702. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{17}$H$_{13}$IN$_2$OS: 433.9746, found: 433.9750.

Ethyl imidazo[1,5-a]quinoline-1-carboxylate (4a), 38 mg, 80%, yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.76 (d, $J$ = 8.7 Hz, 1H), 7.70 (dd, $J$ = 7.8, 1.6 Hz, 1H), 7.61-7.54 (m, 2H), 7.50-7.45 (m, 1H), 7.38 (d, $J$ = 9.3 Hz, 1H), 7.26 (d, $J$ = 9.3 Hz, 1H), 4.56 (q, $J$ = 7.1 Hz, 2H), 1.52 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.8, 133.5, 131.8, 128.5, 126.2, 125.9, 124.9, 123.7, 119.7, 116.0, 62.1, 14.2. IR (KBr, cm$^{-1}$): 2831, 1708, 1605, 1364, 774. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{14}$H$_{13}$N$_2$O$_2$: 240.0899, found: 240.0890.

Ethyl 7-methylimidazo[1,5-a]quinoline-1-carboxylate (4b), 39 mg, 76%, yellow solid, m.p. 79-80 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.61 (d, $J$ = 8.8 Hz, 1H), 7.52 (s, 1H), 7.43-7.40 (m, 1H), 7.33 (dd, $J$ = 8.8, 2.0 Hz, 1H), 7.30 (d, $J$ = 9.3 Hz, 1H), 7.14 (d, $J$ = 9.2 Hz, 1H), 4.53 (q, $J$ = 7.1 Hz, 2H), 2.43 (s, 3H), 1.49 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.8, 133.5, 129.9, 129.4, 128.3, 125.6, 124.9, 123.6, 119.6, 115.9, 61.9, 20.9, 14.3. IR (KBr, cm$^{-1}$): 2831, 1601, 1364, 774. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{15}$H$_{13}$N$_2$O$_2$: 254.1055, found: 254.1057.
**Ethyl 7-methoxyimidazo[1,5-\(a\)]quinoline-1-carboxylate (4c)**, 45 mg, 84%, yellow solid, m.p. 107-108 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.81 (d, \(J = 9.4\) Hz, 1H), 7.58 (s, 1H), 7.40 (d, \(J = 9.3\) Hz, 1H), 7.24 (d, \(J = 9.3\) Hz, 1H), 7.19 (dd, \(J = 9.4, 3.0\) Hz, 1H), 7.12 (d, \(J = 2.9\) Hz, 1H), 4.55 (q, \(J = 7.1\) Hz, 2H), 3.92 (s, 3H), 1.52 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.9, 157.4, 133.3, 132.8, 127.1, 126.5, 124.8, 123.9, 121.5, 116.4, 110.1, 62.0, 55.6, 14.4. IR (KBr, cm\(^{-1}\)): 2831, 1596, 1487, 1363, 1245, 774. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{15}\)H\(_{15}\)N\(_2\)O\(_3\): 271.1004, found: 271.1005.

**Ethyl 7-ethoxyimidazo[1,5-\(a\)]quinoline-1-carboxylate (4d)**, 47 mg, 82%, yellow solid, m.p. 96-97 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.76 (d, \(J = 9.4\) Hz, 1H), 7.54 (s, 1H), 7.33 (d, \(J = 9.3\) Hz, 1H), 7.20-7.10 (m, 2H), 7.05 (d, \(J = 2.8\) Hz, 1H), 4.53 (q, \(J = 7.1\) Hz, 2H), 4.10 (q, \(J = 7.0\) Hz, 2H), 1.50 (t, \(J = 7.1\) Hz, 3H), 1.44 (t, \(J = 7.0\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.8, 156.6, 133.3, 132.6, 127.0, 126.3, 124.8, 123.8, 121.3, 116.6, 116.3, 110.7, 63.8, 61.9, 14.7, 14.3. IR (KBr, cm\(^{-1}\)): 2980, 2832, 1579, 1371, 776. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{16}\)H\(_{17}\)N\(_2\)O\(_3\): 285.1161, found: 285.1163.

**Ethyl 7-fluoroimidazo[1,5-\(a\)]quinoline-1-carboxylate (4e)**, 37 mg, 72%, yellow solid, m.p. 86-87 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.88 (dd, \(J = 9.5, 4.8\) Hz, 1H), 7.61 (s, 1H), 7.42 (d, \(J = 9.3\) Hz, 1H), 7.35 (dd, \(J = 8.5, 3.0\) Hz, 1H), 7.28 (dd, \(J = 9.4, 7.7, 3.0\) Hz, 1H), 7.20 (d, \(J = 9.3\) Hz, 1H), 4.55 (q, \(J = 7.1\) Hz, 2H), 1.51 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.8, 160.0 (d, \(J = 247.0\) Hz), 133.3, 132.6, 127.0, 126.3, 124.8, 123.8, 121.3, 116.6, 116.3, 110.7, 63.8, 61.9, 14.7, 14.3. IR (KBr, cm\(^{-1}\)): 2832, 1706, 1593, 1483, 1366, 1190, 777. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{14}\)H\(_{12}\)FN\(_2\)O\(_2\): 259.0805, found: 259.0807.

**Ethyl 8-fluoroimidazo[1,5-\(a\)]quinoline-1-carboxylate (4f)**, 36 mg, 70%, yellow solid, m.p. 97-98 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.77 (dd, \(J = 11.7, 2.4\) Hz, 1H), 7.70 (dd, \(J = 8.7, 6.3\) Hz, 1H), 7.60 (s, 1H), 7.37 (d, \(J = 9.3\) Hz, 1H), 7.29-7.24 (m, 2H), 4.57 (q, \(J = 7.1\) Hz, 2H), 1.52 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\)
161.5 (d, $J = 247.0 \text{ Hz}$), 160.6, 133.4 (d, $J = 10.0 \text{ Hz}$), 123.8 (d, $J = 1.0 \text{ Hz}$), 122.2 (d, $J = 2.0 \text{ Hz}$), 115.3 (d, $J = 3.0 \text{ Hz}$), 114.7 (d, $J = 3.0 \text{ Hz}$), 107.3 (d, $J = 29.0 \text{ Hz}$), 62.3, 14.3. IR (KBr, cm$^{-1}$): 2832, 1709, 1593, 1486, 1363, 1187, 776. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{14}$H$_{12}$FN$_2$O$_2$: 259.0805, found: 259.0806.

**Ethyl 7-chloroimidazo[1,5-a]quinoline-1-carboxylate (4g),** 43 mg, 79%, yellow solid, m.p. 153-154 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.68 (d, $J = 9.2 \text{ Hz}$, 1H), 7.67 (d, $J = 2.3 \text{ Hz}$, 1H), 7.50 (dd, $J = 9.2, 2.4 \text{ Hz}$, 1H), 7.32 (d, $J = 9.4 \text{ Hz}$, 1H), 7.21 (d, $J = 9.4 \text{ Hz}$, 1H), 4.56 (q, $J = 7.1 \text{ Hz}$, 2H), 1.51 (t, $J = 7.1 \text{ Hz}$, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.9, 135.1, 135.1, 132.4, 130.2, 128.5, 127.8, 127.1, 125.0, 121.1, 117.6, 80.3, 62.6, 14.3. IR (KBr, cm$^{-1}$): 2831, 1712, 1697, 1598, 1470, 1363, 1318, 1193, 775. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{14}$H$_{12}$ClN$_2$O$_2$: 275.0509; found: 275.0511.

**Ethyl 8-chloroimidazo[1,5-a]quinoline-1-carboxylate (4h),** 41 mg, 75%, yellow solid, m.p. 97-98 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.00 (s, 1H), 7.64 (dd, $J = 8.4, 2.7 \text{ Hz}$, 1H), 7.60 (d, $J = 2.2 \text{ Hz}$, 1H), 7.49-7.43 (m, 1H), 7.40 (dd, $J = 9.3, 2.7 \text{ Hz}$, 1H), 7.28-7.23 (m, 1H), 4.58 (q, $J = 7.1 \text{ Hz}$, 2H), 1.53 (t, $J = 7.1 \text{ Hz}$, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.6, 133.9, 133.5, 133.4, 132.5, 129.5, 126.8, 124.2, 124.1, 124.0, 120.20, 116.4, 62.4, 14.3. IR (KBr, cm$^{-1}$): 2831, 1704, 1606, 1419, 1366, 1293, 1212, 864, 836, 775. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{14}$H$_{12}$ClN$_2$O$_2$: 275.0509; found: 275.0510.

**Ethyl 7-bromoimidazo[1,5-a]quinoline-1-carboxylate (4i),** 48 mg, 75%, yellow solid, m.p. 99-100 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.75 (d, $J = 9.2 \text{ Hz}$, 1H), 7.83 (d, $J = 2.3 \text{ Hz}$, 1H), 7.65 (dd, $J = 9.2, 2.3 \text{ Hz}$, 1H), 7.60 (s, 1H), 7.42 (d, $J = 9.3 \text{ Hz}$, 1H), 7.17 (d, $J = 9.3 \text{ Hz}$, 1H), 4.55 (q, $J = 7.1 \text{ Hz}$, 2H), 1.51 (t, $J = 7.1 \text{ Hz}$, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.7, 133.3, 131.0, 130.9, 130.6, 127.3, 124.3, 123.7, 121.7, 119.6, 117.3, 62.3, 14.3. IR (KBr, cm$^{-1}$): 2831, 1703, 1596, 1442, 1365, 1293, 1212, 864, 802, 665. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{14}$H$_{12}$BrN$_2$O$_2$: 319.0004, found: 319.0005.
Diethyl imidazo[1,5-a]quinoline-1,7-dicarboxylate (4j), 44 mg, 70%, yellow solid, m.p. 137-138 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.83 (d, $J = 9.0$ Hz, 1H), 8.41 (d, $J = 2.0$ Hz, 1H), 8.22 (dd, $J = 9.0, 2.0$ Hz, 1H), 7.62 (s, 1H), 7.45 (d, $J = 9.3$ Hz, 1H), 7.34 (d, $J = 9.3$ Hz, 1H), 4.57 (q, $J = 7.1$ Hz, 2H), 4.44 (q, $J = 7.1$ Hz, 2H), 1.52 (t, $J = 7.1$ Hz, 3H), 1.44 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.5, 160.8, 134.5, 133.8, 133.6, 130.4, 128.9, 128.2, 125.4, 124.8, 124.1, 119.9, 116.9, 62.4, 61.4, 14.3. IR (KBr, cm$^{-1}$): 2831, 1723, 1698, 1596, 1363, 1280, 1196, 775, 765. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{17}$H$_{17}$N$_2$O$_4$: 313.1110, found: 313.1112.

7-(sec-butyl) 1-Ethyl imidazo[1,5-a]quinoline-1,7-dicarboxylate (4k), 49 mg, 73%, yellow solid, m.p. 106-107 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.81 (d, $J = 9.0$ Hz, 1H), 8.40 (d, $J = 2.0$ Hz, 1H), 8.22 (dd, $J = 9.0, 2.0$ Hz, 1H), 7.61 (s, 1H), 7.45 (d, $J = 9.3$ Hz, 1H), 7.34 (d, $J = 9.3$ Hz, 1H), 5.14 (dt, $J = 12.6, 6.3$ Hz, 1H), 4.57 (q, $J = 7.1$ Hz, 2H), 1.79-1.70 (m, 2H), 1.52 (t, $J = 7.1$ Hz, 3H), 1.00 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.1, 160.8, 134.4, 133.6, 130.3, 128.8, 128.6, 125.3, 124.9, 124.1, 119.9, 116.9, 73.5, 62.3, 28.9, 19.5, 14.3, 9.7. IR (KBr, cm$^{-1}$): 2975, 2831, 1723, 1698, 1596, 1363, 1280, 1196, 775, 764, 734. HR-MS (ESI): m/z [M+H]$^+$ calcd for C$_{19}$H$_{21}$N$_2$O$_4$: 341.1423, found: 341.1424.

Ethyl 7-((3,4-dimethylphenyl)carbamoyl)imidazo[1,5-a]quinoline-1-carboxylate (4l), 53 mg, 69%, yellow solid, m.p. 154–155 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.74 (d, $J = 9.0$ Hz, 1H), 8.24 (s, 1H), 8.15 (d, $J = 2.1$ Hz, 1H), 7.91 (dd, $J = 9.0, 2.1$ Hz, 1H), 7.58 (s, 1H), 7.49 (s, 1H), 7.42 (dd, $J = 8.2, 1.8$ Hz, 1H), 7.36 (d, $J = 9.3$ Hz, 1H), 7.19 (d, $J = 9.3$ Hz, 1H), 7.12 (d, $J = 8.1$ Hz, 1H), 4.56 (q, $J = 7.1$ Hz, 2H), 2.26 (d, $J = 8.4$ Hz, 6H), 1.52 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.5, 160.8, 137.4, 135.5, 133.6, 133.5, 133.4, 133.2, 132.8, 130.1, 127.9, 126.1, 125.5, 124.7, 124.1, 121.6, 120.1, 117.8, 117.1, 62.4, 19.9, 19.2, 14.3. IR (KBr, cm$^{-1}$): 2832, 1702,
1597, 1541, 1363, 1329, 1188, 776. HR-MS (ESI): m/z [M+H]^+ calced for C_{23}H_{22}N_{3}O_{3}: 388.1583, found: 388.1584.

N\_N\_EtO\_2\_C\_4m
Ethyl benzo[f]imidazo[1,5-a]quinoline-3-carboxylate (4m), 35 mg, 65%, yellow solid, m.p. 140-141 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.65 (d, J = 9.4 Hz, 1H), 8.55 (d, J = 9.6 Hz, 1H), 8.23 (d, J = 9.6 Hz, 1H), 8.04-7.95 (m, 2H), 7.74 – 7.60 (m, 4H), 4.60 (q, J = 7.1 Hz, 2H), 1.55 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.0, 133.8, 132.6, 131.3, 129.6, 128.9, 128.7, 127.6, 126.7, 123.4, 123.2, 121.2, 119.7, 118.8, 116.3, 62.1, 14.4. IR (KBr, cm⁻¹): 2832, 1592, 1363, 775. HR-MS (ESI): m/z [M+H]^+ calcd for C_{18}H_{15}N_{2}O_{2}: 291.1055, found: 291.1057.

N\_N\_EtO\_2\_C\_4n
Ethyl imidazo[1,5-a]quinoxaline-1-carboxylate (4n), 29 mg, 60%, yellow solid, m.p. 101-102 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.08-8.73 (m, 2H), 8.08-8.00 (m, 1H), 7.95-7.87 (m, 1H), 7.68-7.53 (m, 2H), 4.58 (q, J = 7.1 Hz, 2H), 1.57-1.46 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.3, 144.4, 137.6, 134.4, 130.4, 128.6, 127.9, 127.6, 127.3, 126.3, 119.3, 62.8, 14.2. IR (KBr, cm⁻¹): 2977, 2831, 1719, 1592, 1459, 1365, 1256, 1203, 1147, 1053, 879, 776, 749. HR-MS (ESI): m/z [M+H]^+ calcd for C_{13}H_{12}N_{2}O_{2}: 242.0851, found: 242.0852.

N\_S\_EtO\_2\_C\_4o
Ethyl benzo[d]imidazo[5,1-b]thiazole-1-carboxylate (4o), 33 mg, 68%, white solid, m.p. 107-108 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.27-9.21 (m, 1H), 7.67-7.62 (m, 1H), 7.48 (ddd, J = 8.5, 7.4, 1.4 Hz, 1H), 7.45-7.39 (m, 1H), 7.33 (s, 1H), 4.52 (q, J = 7.1 Hz, 2H), 1.50 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.8, 133.1, 126.4, 126.2, 123.7, 120.0, 118.9, 61.8, 14.4. IR (KBr, cm⁻¹): 2957, 2832, 1592, 1414, 1359, 777. HR-MS (ESI): m/z [M+H]^+ calcd for C_{12}H_{11}N_{2}O_{2}S: 247.0463, found: 247.0464.

7-((3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-
cyclopenta[a]phenanthren-3-yl) 1-ethyl imidazo[1,5-a]quinoline-1,7-dicarboxylate (4p), 65 mg, 50%, yellow solid, m.p. 139-141 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.83 (d, \(J = 9.0\) Hz, 1H), 8.42 (d, \(J = 1.8\) Hz, 1H), 8.23 (dd, \(J = 9.0, 1.9\) Hz, 1H), 7.63 (s, 1H), 7.46 (d, \(J = 9.3\) Hz, 1H), 7.35 (d, \(J = 9.4\) Hz, 1H), 5.48-5.40 (m, 1H), 4.91 (ddt, \(J = 12.9, 8.5, 4.2\) Hz, 1H), 4.57 (q, \(J = 7.1\) Hz, 1H), 2.51 (d, \(J = 7.7\) Hz, 2H), 2.08-1.96 (m, 4H), 1.52 (d, \(J = 7.1\) Hz, 7H), 1.39-1.22 (m, 7H), 1.10 (d, \(J = 12.1\) Hz, 7H), 1.05-0.96 (m, 4H), 0.92 (d, \(J = 6.5\) Hz, 4H), 0.87 (dd, \(J = 6.6, 1.7\) Hz, 8H), 0.70 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.9, 160.8, 139.5, 134.5, 133.6, 130.4, 128.9, 128.6, 125.4, 124.9, 124.1, 122.9, 119.9, 116.9, 62.4, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.2, 35.8, 31.9, 31.9, 31.8, 31.4, 28.2, 27.9, 24.3, 23.8, 22.8, 22.6, 21.1, 19.4, 18.7, 14.3, 11.9. IR (KBr, cm\(^{-1}\)): 2950, 2832, 1715, 1581, 1467, 1366, 1330, 1281, 1191, 776. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{42}\)H\(_{57}\)N\(_2\)O\(_4\): 653.4240, found: 653.4242.

Methyl imidazo[1,5-a]quinoline-1-carboxylate (4q), 36 mg, 79%, yellow solid, m.p. 143-144 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.79 (d, \(J = 8.7\) Hz, 1H), 7.68 (dd, \(J = 7.8, 1.6\) Hz, 1H), 7.60 – 7.53 (m, 2H), 7.46 (ddd, \(J = 7.8, 7.3, 1.1\) Hz, 1H), 7.36 (d, \(J = 9.3\) Hz, 1H), 7.24 (s, 1H), 4.07 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 161.1, 133.7, 132.8, 131.9, 128.5, 128.3, 126.3, 125.5, 125.1, 123.8, 119.8, 115.9, 52.9. IR (KBr, cm\(^{-1}\)): 2832, 1704, 1581, 1448, 1363, 1171, 1144, 1137, 777, 759. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{13}\)H\(_{11}\)N\(_2\)O\(_2\): 227.0742, found: 227.0744.

tert-Butyl imidazo[1,5-a]quinoline-1-carboxylate (4r), 38 mg, 70%, yellow solid, m.p. 95-96 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.54 (d, \(J = 8.6\) Hz, 1H), 7.70 (d, \(J = 7.8\) Hz, 1H), 7.69 (d, \(J = 7.7\) Hz, 1H), 7.27 – 7.21 (m, 1H), 1.73 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.6, 134.5, 132.8, 131.8, 128.6, 128.1, 126.1, 125.5, 124.4, 123.3, 119.4, 116.2, 83.3, 28.2. IR (KBr, cm\(^{-1}\)): 2976, 2832, 1704, 1595, 1428, 1363, 1322, 1171, 1148, 1109, 775, 758. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{16}\)H\(_{17}\)N\(_2\)O\(_2\): 269.1212, found: 269.1215.

Benzyl imidazo[1,5-a]quinoline-1-carboxylate (4s), 36 mg, 60%, yellow solid, m.p. 111-112 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.74 – 8.63 (m, 1H), 7.69 (d, \(J = 7.7\) Hz,
$^{1}H$), 7.60 (s, 1H), 7.56 (dt, $J = 7.7$, 1.9 Hz, 2H), 7.52 (dd, $J = 8.6$, 1.6 Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.43 – 7.38 (m, 2H), 7.39 – 7.32 (m, 2H), 7.29 – 7.24 (m, 1H), 5.55 (s, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.7, 135.5, 133.6, 132.9, 131.9, 128.6, 128.5, 128.3, 126.3, 125.6, 125.0, 123.9, 119.8, 116.0, 67.5. IR (KBr, cm$^{-1}$): 2831, 1580, 1358, 1182, 1153, 1105, 775, 753, 739. HR-MS (ESI): m/z [M+H]$^{+}$ calcd for C$_{19}$H$_{15}$N$_2$O$_2$: 303.1055, found: 303.1058.

**Ethyl 3-phenylimidazo[1,5-a]quinoline-1-carboxylate (5)**, 48 mg, 76%, yellow solid, m.p. 78-79 °C. $^{1}H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.55 (d, $J = 8.6$ Hz, 1H), 7.89-7.84 (m, 2H), 7.75-7.70 (m, 2H), 7.60 (ddd, $J = 9.4$ Hz, 1H), 4.62 (q, $J = 7.1$ Hz, 2H), 1.54 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.4, 135.1, 133.6, 132.7, 131.9, 129.4, 128.7, 128.5, 128.4, 127.9, 127.6, 126.3, 125.7, 125.1, 119.5, 116.5, 62.3, 14.4. IR (KBr, cm$^{-1}$): 2831, 1597, 1363, 775, 698. HR-MS (ESI): m/z [M+H]$^{+}$ calcd for C$_{20}$H$_{17}$N$_2$O$_2$: 317.1212, found: 317.1214.

**Ethyl 3-(phenylethynyl)imidazo[1,5-a]quinoline-1-carboxylate (6)**, 53 mg, 78%, yellow solid, m.p. 93-94 °C. $^{1}H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.70 (d, $J = 6.6$ Hz, 1H), 7.76 (dd, $J = 7.7$, 1.5 Hz, 1H), 7.69-7.57 (m, 4H), 7.45-7.32 (m, 4H), 4.59 (q, $J = 7.1$ Hz, 2H), 1.54 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.6, 135.5, 132.8, 131.8, 131.5, 128.8, 128.7, 128.3, 126.7, 126.2, 125.8, 122.9, 119.6, 118.2, 115.8, 93.0, 81.3, 62.5, 14.3. IR (KBr, cm$^{-1}$): 2831, 2193, 1597, 1499, 1363, 1186, 1068, 775. HR-MS (ESI): m/z [M+H]$^{+}$ calcd for C$_{22}$H$_{17}$N$_2$O$_2$: 341.1212, found: 341.1214.

**Ethyl (E)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)imidazo[1,5-a]quinoline-1-carboxylate (7)**, 57 mg, 85%, yellow solid, m.p. 158-159 °C. $^{1}H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.47 (d, $J = 8.7$ Hz, 1H), 7.91 (d, $J = 15.6$ Hz, 1H), 7.75 (dd, $J = 7.8$, 1.5 Hz, 1H), 7.64-7.58 (m, 2H), 7.52 (td, $J = 7.6$, 1.0 Hz, 1H), 7.41 (d, $J = 9.3$ Hz, 1H), 6.87 (d, $J = 15.6$ Hz, 1H), 4.60 (q, $J = 7.1$ Hz, 2H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.53 (t, $J = 7.1$ Hz, 3H), 1.34 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 161.1, 134.0, 132.8, 131.7, 129.9, 128.9, 128.9, 126.7, 126.6, 125.5, 119.2, 117.8, 114.7, 62.7, 60.4, 14.3.
IR (KBr, cm\(^{-1}\)): 2831, 1717, 1693, 1607, 1366, 1294, 1270, 1163, 775. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{19}\)H\(_{19}\)N\(_2\)O\(_4\): 339.1267, found: 339.1268.

**Ethyl 3-(phenylselanyl)imidazo[1,5-a]quinoline-1-carboxylate (8)**, 55 mg, 70%, yellow oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.62 (d, \(J = 8.7\) Hz, 1H), 7.72 (dd, \(J = 7.8, 1.6\) Hz, 1H), 7.60 (ddd, \(J = 8.7, 7.2, 1.6\) Hz, 1H), 7.55-7.46 (m, 2H), 7.35-7.29 (m, 3H), 7.19-7.11 (m, 3H), 4.59 (q, \(J = 7.1\) Hz, 2H), 1.52 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.9, 136.9, 134.1, 132.0, 131.8, 130.1, 129.1, 128.8, 128.6, 126.6, 126.5, 126.3, 125.6, 120.8, 119.4, 116.4, 62.5, 14.3. IR (KBr, cm\(^{-1}\)): 2831, 1713, 1600, 1365, 1181, 1159, 1071, 803, 775, 738, 687. HR-MS (ESI): m/z [M+H]\(^+\) calcd for C\(_{20}\)H\(_{17}\)N\(_2\)O\(_2\)Se: 397.0377, found: 397.0379.

**5. References**


6. Copy of $^1$H and $^{13}$C NMR Spectra of Products