Supporting Information

Functionalized Heterocyclic Scaffolds Derived from Morita-Baylis-Hillman Acetates

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I. General Remarks

DMF was distilled from calcium hydride. Purifications of reaction products were carried out by chromatography using silica gel (200–300 mesh). Melting points were measured on a Perkin-Taike X-4 apparatus and have been corrected. High resolution MS data were recorded on an Agilent 6200 Series TOF spectrometer. NMR spectra were recorded on Bruker AVIII for $^1$H NMR at 500 MHz and for $^{13}$C NMR at 125 MHz. For $^1$H NMR, tetramethylsilane (TMS) served as internal standard ($\delta$). The spectra data presented here are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hertz. For $^{13}$C NMR TMS ($\delta = 0$) or CDCl$_3$ ($\delta = 77.26$) was used as internal standard and spectra were obtained with complete proton decoupling. The starting materials MBHAs were prepared according to literature methods. Compounds 6–10 are commercially available.

II. Optimization of Reaction Conditions

Initially we optimized the reaction of MBHAs with bifunctional nucleophilies. Ethyl-2-acetoxy-3-nitro-4-phenylbut-3(E)-enoate (M1) was used as the model reactant of MBHAs. Different solvents, bases and temperature were examined and the results were shown in Table 1–5. The most successful entry is highlighted in bold and used as the reaction system to form the heterocycles.

Table 1: Optimization of reaction conditions for imidazo[1,2-a]pyridines.$^{[a]}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Base</th>
<th>T (°C)</th>
<th>Yield (%)$^{[b]}$</th>
</tr>
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<td>K$_2$CO$_3$</td>
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<td>K$_2$CO$_3$</td>
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<td>15</td>
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$^{[a]}$ Reaction conditions: M1 (0.2 mmol), 6 (0.2 mmol), K$_2$CO$_3$ (0.2 mmol), solvent (2 mL) were stirred at rt for 30 min, then heated to corresponding temperature. $^{[b]}$ Determined by high-performance liquid chromatography based on the disappearance of the starting M1.
Table 2: Optimization of reaction conditions for indolizines.^[a]

<table>
<thead>
<tr>
<th>Entry</th>
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<th>Base</th>
<th>T (°C)</th>
<th>Yield (%)^[b]</th>
</tr>
</thead>
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<td>Na₂CO₃</td>
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<td>60</td>
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<td>9</td>
<td>MeCN</td>
<td>Et₃N</td>
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<td>88</td>
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</tbody>
</table>

^[a] Reaction conditions: M₁ (0.2 mmol), 7a (0.2 mmol), base (0.3 mmol), solvent (2 mL) were stirred overnight. [b] Determined by high-performance liquid chromatography based on the disappearance of the starting M₁.

Table 3: Optimization of reaction conditions for pyrroles.^[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Base</th>
<th>T (°C)</th>
<th>Yield (%)^[b]</th>
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<td>70</td>
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<td>Na₂CO₃</td>
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<td>9</td>
<td>toluene</td>
<td>Et₃N</td>
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<td>0</td>
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</table>

^[a] Reaction conditions: M₁ (0.2 mmol), 8 (0.2 mmol), base (0.2 mmol), solvent (2 mL) were stirred for 2h. [b] Determined by high-performance liquid chromatography based on the disappearance of the starting M₁.
Table 4: Optimization of reaction conditions for pyrazoles.\(^{[a]}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Base</th>
<th>(T) (°C)</th>
<th>Yield (%(^{[b]}))</th>
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<td>90</td>
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<td>80</td>
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<td>(\text{K}_2\text{CO}_3)</td>
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<td>79</td>
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<td>DABCO</td>
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<td>41</td>
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<td>11</td>
<td>toluene</td>
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<td>65</td>
<td>trace</td>
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</table>

\(^{[a]}\) Reaction conditions: \(\text{M1}\) (0.2 mmol), \(\text{9}\) (0.2 mmol), base (0.2 mmol) or absence, solvent (2 mL) were stirred overnight. \(^{[b]}\) Determined by high-performance liquid chromatography based on the disappearance of the starting \(\text{M1}\).

Table 5: Optimization of reaction conditions for benzo[b][1,6]oxazocin-2-ones.\(^{[a]}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Base</th>
<th>(T) (°C)</th>
<th>Yield (%(^{[b]}))</th>
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<td>trace</td>
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<tr>
<td>6</td>
<td>MeOH</td>
<td>(\text{Et}_3\text{N})</td>
<td>40</td>
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<td>7</td>
<td>MeOH</td>
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<td>25</td>
<td>0</td>
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<tr>
<td>8</td>
<td>MeCN</td>
<td>(\text{Na}_2\text{CO}_3)</td>
<td>40</td>
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<tr>
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<td>DMF</td>
<td>(\text{Na}_2\text{CO}_3)</td>
<td>40</td>
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<td>toluene</td>
<td>(\text{Na}_2\text{CO}_3)</td>
<td>40</td>
<td>trace</td>
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</table>

\(^{[a]}\) Reaction conditions: \(\text{M1}\) (0.2 mmol), \(\text{10}\) (0.2 mmol), solvent (2 mL) were stirred at rt for 15 min. Then base (0.2 mmol) was added and the mixture was heated to corresponding temperature for 2h. \(^{[b]}\) Determined by high-performance liquid chromatography based on the disappearance of the starting \(\text{M1}\).
III. General Procedure for the Synthesis of Imidazo[1,2-a]pyridines

A mixture of MBHAs (0.3 mmol, 1.0 equiv), 2-amino-1-ethoxycarbonylmethyl-pyridium (6, 0.3 mmol, 1.0 equiv) and K$_2$CO$_3$ (0.3 mmol, 1.0 equiv) was stirred in DMF (2.0 mL) at room temperature for 30 min, then the mixture was heated to 115 °C for 1h. Water (5 mL) was added to it and the mixture was extracted three times with EtOAc (10 mL × 3). The combined organic layers were washed with water (10 mL × 3) and brine (10 mL), dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuum. Purification of the residue by chromatography (silica gel) affords the product.

Ethyl 2-phenylimidazo[1,2-a]pyridine-3-carboxylate (1a):

![Chemical structure of ethyl 2-phenylimidazo[1,2-a]pyridine-3-carboxylate](image)

Yellow solid. m.p.: 70 – 72 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 9.41 (1H, d, $J = 7.0$ Hz), 7.75 (3H, m), 7.43 (4H, m), 7.03 (1H, td, $J = 7.0, 1.5$ Hz), 4.30 (2H, q, $J = 7.0$ Hz), 1.22 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 161.2, 153.6, 147.1, 134.5, 130.2, 128.7, 128.3, 127.9, 127.5, 117.5, 114.1, 111.9, 60.5, 13.9. HRMS Calcd. For C$_{16}$H$_{14}$N$_2$O$_2$ + H$: 267.1134, found: 267.1146.

Ethyl 2-(4-chlorophenyl)imidazo[1,2-a]pyridine-3-carboxylate (1b):

![Chemical structure of ethyl 2-(4-chlorophenyl)imidazo[1,2-a]pyridine-3-carboxylate](image)

Yellow solid. m.p.: 110 – 112 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 9.41 (1H, d, $J = 7.0$ Hz), 7.73 (3H, m), 7.45 (1H, t, $J = 7.5$ Hz), 7.41 (2H, d, $J = 8.5$ Hz), 7.05 (1H, t, $J = 7.0$ Hz), 4.32 (2H, q, $J = 7.0$ Hz), 1.25 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 160.9, 152.3, 147.1, 134.8, 132.9, 131.6, 128.4, 128.2, 127.8, 117.5, 114.3, 112.0, 60.6, 14.1. HRMS Calcd. For C$_{16}$H$_{13}$ClN$_2$O$_2$ + H$: 301.0744, found: 301.0738.

Ethyl 2-(4-fluorophenyl)imidazo[1,2-a]pyridine-3-carboxylate (1c):

![Chemical structure of ethyl 2-(4-fluorophenyl)imidazo[1,2-a]pyridine-3-carboxylate](image)

Yellow solid. m.p.: 95 – 97 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 9.41(1H, d, $J = 7.0$ Hz), 7.74 (3H, m), 7.44(1H, m), 7.12 (2H, t, $J = 9.0$ Hz), 7.05 (1H, td, $J = 7.0, 1.0$ Hz), 4.32 (2H, q, $J = 7.0$ Hz), 1.24 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 163.2 (d, $J = 247$ Hz), 161.0, 152.6, 147.1, 132.1 (d, $J = 8$ Hz), 130.5 (d, $J = 4$ Hz), 128.4, 128.1, 117.5, 114.6 (d, $J = 21$ Hz), 114.2, 111.9, 60.6, 14.1. HRMS Calcd. For C$_{16}$H$_{13}$FN$_2$O$_2$ + H$: 285.1039, found: 285.1035.
Ethyl 2-(4-bromophenyl)imidazo[1,2-a]pyridine-3-carboxylate (1d):

![Structural formula of 1d]

Yellow solid. m.p.: 120 – 122 ºC; \( ^1 \text{H} \) NMR (500 MHz, CDCl\(_3\)): \( \delta \) 9.40 (1H, dt, \( J = 7.0, 1.0 \) Hz), 7.30 (1H, dt, \( J = 9.0, 1.0 \) Hz), 7.66 (2H, dt, \( J = 7.5, 2.0 \) Hz), 7.56 (1H, dt, \( J = 8.5, 2.0 \) Hz), 7.45 (1H, m), 7.05 (1H, td, \( J = 7.0, 1.5 \) Hz), 4.32 (2H, q, \( J = 7.0 \) Hz), 1.25 (3H, t, \( J = 7.0 \) Hz); \( ^{13} \text{C} \) NMR (125 MHz, CDCl\(_3\)): \( \delta \) 160.9, 152.3, 147.1, 133.4, 131.9, 130.8, 128.4, 128.2, 123.1, 117.5, 114.3, 112.0, 60.6, 14.1. HRMS Calcd. For C\(_{16}\)H\(_{13}\)BrN\(_2\)O\(_2\) + H\(^+\): 345.0239, found: 345.0229.

Ethyl 2-(3-bromophenyl)imidazo[1,2-a]pyridine-3-carboxylate (1e):

![Structural formula of 1e]

Yellow solid. m.p.: 107 – 109 ºC; \( ^1 \text{H} \) NMR (500 MHz, CDCl\(_3\)): \( \delta \) 9.43 (1H, dt, \( J = 7.0, 2.0 \) Hz), 7.93 (1H, t, \( J = 7.0 \) Hz), 7.74 (1H, d, \( J = 9.0 \) Hz), 7.71 (1H, dt, \( J = 7.0, 2.0 \) Hz), 7.55 (1H, ddd, \( J = 8.0, 2.0, 1.0 \) Hz), 7.46 (1H, ddd, \( J = 9.0, 7.0, 1.5 \) Hz), 7.31 (1H, d, \( J = 7.5 \) Hz), 7.06 (1H, td, \( J = 7.0, 1.0 \) Hz), 4.33 (2H, q, \( J = 7.0 \) Hz), 1.27 (3H, t, \( J = 7.0 \) Hz); \( ^{13} \text{C} \) NMR (125 MHz, CDCl\(_3\)): \( \delta \) 160.9, 151.7, 147.1, 136.5, 133.3, 129.2, 128.8, 128.4, 128.2, 121.5, 117.6, 114.4, 112.1, 60.7, 14.0. HRMS Calcd. For C\(_{16}\)H\(_{13}\)BrN\(_2\)O\(_2\) + H\(^+\): 345.0239, found: 345.0229.

Ethyl 2-(3-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine-3-carboxylate (1f):

![Structural formula of 1f]

Yellow solid. m.p.: 108 – 110 ºC; \( ^1 \text{H} \) NMR (500 MHz, CDCl\(_3\)): \( \delta \) 9.45 (1H, d, \( J = 7.0 \) Hz), 8.05 (1H, s), 7.97 (1H, d, \( J = 7.5 \) Hz), 7.76 (1H, d, \( J = 9.0 \) Hz), 7.68 (1H, d, \( J = 7.5 \) Hz), 7.57 (1H, t, \( J = 8.0 \) Hz), 7.47 (1H, t, \( J = 7.5 \) Hz), 7.07 (1H, t, \( J = 7.0 \) Hz), 4.31 (2H, q, \( J = 7.0 \) Hz), 1.21 (3H, t, \( J = 7.0 \) Hz); \( ^{13} \text{C} \) NMR (125 MHz, CDCl\(_3\)): \( \delta \) 160.8, 151.8, 147.2, 135.3, 133.5, 129.9 (d, \( J = 33 \) Hz), 128.4, 128.3, 128.2, 127.3 (q, \( J = 4 \) Hz), 125.4 (q, \( J = 4 \) Hz), 125.3 (q, \( J = 271 \) Hz), 117.6, 114.5, 112.2, 60.7, 13.8. HRMS Calcd. For C\(_{17}\)H\(_{13}\)F\(_3\)N\(_2\)O\(_2\) + H\(^+\): 335.1007, found: 335.1004.

Ethyl 2-(4-methoxyphenyl)imidazo[1,2-a]pyridine-3-carboxylate (1g):

![Structural formula of 1g]

Yellow oil. \( ^1 \text{H} \) NMR (500 MHz, CDCl\(_3\)): \( \delta \) 9.39 (1H, d, \( J = 7.0 \) Hz), 7.75 (2H, d, \( J = 8.5 \) Hz), 7.71 (1H, d, \( J = 9.5 \) Hz), 7.39 (1H, t, \( J = 7.5 \) Hz), 7.00 (1H, t, \( J = 6.5 \) Hz), 6.96 (2H, d, \( J = 8.5 \) Hz), 4.32 (2H, q, \( J = 7.0 \) Hz), 3.85 (3H, s), 1.26 (3H, t, \( J = 7.0 \) Hz); \( ^{13} \text{C} \) NMR (125 MHz, CDCl\(_3\)): \( \delta \) 161.2, 160.1, 153.4, 147.1, 131.6, 128.4, 127.9, 126.7, 117.3, 113.9, 113.0, 111.6, 60.4, 55.3, 14.1.
HRMS Calcd. For C_{17}H_{16}N_{2}O_{3} + H^+: 297.1239, found: 297.1230.

**Ethyl 2-(4-acetoxyphenyl)imidazo[1,2-a]pyridine-3-carboxylate (1h):**

![Chemical Structure](attachment:image.png)

Yellow solid. m.p.: 112 – 114 °C; ^1^H NMR (500 MHz, CDCl_3): \( \delta \) 9.42 (1H, d, \( J = 7.0 \) Hz), 7.80 (2H, d, \( J = 9.0 \) Hz), 7.74 (1H, d, \( J = 9.0 \) Hz), 7.45 (1H, m), 7.18 (2H, d, \( J = 8.5 \) Hz), 7.05 (1H, td, \( J = 7.0, 1.0 \) Hz), 4.32 (2H, q, \( J = 7.0 \) Hz), 2.33 (3H, s), 1.24 (3H, t, \( J = 7.0 \) Hz) \( ; \ ^{13} \)C NMR (125 MHz, CDCl_3): \( \delta \) 169.3, 161.1, 152.6, 151.1, 147.1, 132.0, 131.4, 128.4, 128.1, 120.7, 117.5, 114.2, 95.9, 60.6, 21.3, 14.0 \( ; \) HRMS Calcd. For C_{18}H_{16}N_{2}O_{4} + H^+: 325.1188, found: 325.1182.

**Ethyl 2-(4-(dimethylamino)phenyl)imidazo[1,2-a]pyridine-3-carboxylate (1i):**

Yellow oil. ^1^H NMR (500 MHz, CDCl_3): \( \delta \) 9.39 (1H, d, \( J = 7.0 \) Hz), 7.75 (2H, d, \( J = 8.5 \) Hz), 7.71 (1H, d, \( J = 8.5 \) Hz), 7.39 (1H, m), 6.98 (1H, t, \( J = 7.0 \) Hz), 6.76 (1H, d, \( J = 8.5 \) Hz), 4.35 (2H, q, \( J = 7.0 \) Hz), 1.32 (3H, t, \( J = 7.0 \) Hz) \( ; \ ^{13} \)C NMR (125 MHz, CDCl_3): \( \delta \) 163.5, 154.1, 150.8, 147.1, 131.3, 128.4, 127.7, 121.7, 117.1, 113.6, 111.2, 111.1, 60.4, 40.4, 14.3. HRMS Calcd. For C_{18}H_{16}N_{2}O_{4} + H^+: 310.1556, found: 310.1555.

**Ethyl 2-(furan-2-yl)imidazo[1,2-a]pyridine-3-carboxylate (1j):**

Yellow oil. ^1^H NMR (500 MHz, CDCl_3): \( \delta \) 9.36 (1H, d, \( J = 7.0 \) Hz), 7.74 (1H, d, \( J = 9.0 \) Hz), 7.62 (1H, d, \( J = 1.5 \) Hz), 7.41 (2H, m), 7.01 (1H, td, \( J = 7.0, 1.0 \) Hz), 6.56 (1H, dd, \( J = 3.5, 2.0 \) Hz), 4.50 (2H, q, \( J = 7.0 \) Hz), 1.47 (3H, t, \( J = 7.0 \) Hz) \( ; \ ^{13} \)C NMR (125 MHz, CDCl_3): \( \delta \) 160.6, 147.6, 147.2, 143.7, 143.1, 128.5, 128.3, 117.6, 114.2, 113.9, 111.6, 110.9, 60.9, 14.5. HRMS Calcd. For C_{14}H_{12}N_{2}O_{3} + H^+: 257.0926, found: 257.0917.

**IV. General Procedure for the Synthesis of Indolizines**

A mixture of MBHAs (0.3 mmol, 1.0 equiv), ethyl 2-pyridylacetate (7a, 0.3 mmol, 1.0 equiv) and Et_3N (0.45 mmol, 1.5 equiv) was stirred in MeCN (2 mL) at room temperature overnight. Once starting material was consumed (monitored by TLC), the organic solvent was removed and the residue was purified by column chromatography (silica gel) to give the product. The same method can also be used to prepare indolizines with cyano group from 2-pyridylacetonitrile (7b).
Ethyl 3-(2-ethoxy-2-oxoethyl)-2-phenyldizine-1-carboxylate (2a):

Brown oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.32 (1H, d, $J = 8.5$ Hz), 7.97 (1H, d, $J = 7.0$ Hz), 7.38 (5H, m), 7.12 (1H, ddd, $J = 9.5$, 7.0, 1.0 Hz), 6.82 (1H, td, $J = 7.0$, 1.0 Hz), 4.17 (4H, m), 3.75 (2H, s), 1.23 (3H, t, $J = 7.5$ Hz), 1.10 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.7, 164.9, 136.2, 134.8, 131.8, 130.5, 127.5, 127.1, 123.1, 122.3, 120.2, 116.5, 112.8, 102.2, 61.4, 59.2, 30.9, 14.1. HRMS Calcd. For C$_{21}$H$_{21}$NO$_4$ + H$: 352.1549$, found: 352.1537.

Ethyl 2-(4-chlorophenyl)-3-(2-ethoxy-2-oxoethyl)dizine-1-carboxylate (2b):

Brown oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.31 (1H, d, $J = 9.0$ Hz), 7.98 (1H, d, $J = 7.0$ Hz), 7.38 (2H, m), 7.32 (2H, m), 7.13 (1H, ddd, $J = 9.5$, 7.0, 1.0 Hz), 6.83 (1H, td, $J = 7.0$, 1.0 Hz), 4.17 (4H, m), 3.73 (2H, s), 1.24 (3H, t, $J = 7.0$ Hz), 1.16 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.6, 164.8, 136.3, 133.4, 133.3, 132.0, 130.4, 127.9, 123.3, 122.6, 120.4, 116.7, 113.1, 102.2, 61.6, 59.4, 30.9, 14.3, 14.2. HRMS Calcd. For C$_{21}$H$_{20}$ClNO$_4$ + H$: 386.1159$, found: 386.1155.

Ethyl 3-(2-ethoxy-2-oxoethyl)-2-(4-fluorophenyl)dizine-1-carboxylate (2c):

Brown oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.31 (1H, d, $J = 9.0$ Hz), 7.98 (1H, d, $J = 7.0$ Hz), 7.35 (2H, m), 7.12 (3H, m), 6.82 (1H, d, $J = 6.5$, 1.0 Hz), 4.17 (4H, m), 3.73 (2H, s), 1.23 (3H, t, $J = 7.0$ Hz), 1.15 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.5, 164.8, 162.3 (d, $J = 244$ Hz), 136.2, 132.1 (d, $J = 8$ Hz), 130.7, 130.6 (d, $J = 4$ Hz), 123.1, 122.5, 120.2, 116.6, 114.4 (d, $J = 21$ Hz), 112.9, 102.2, 61.4, 59.2, 30.8, 14.2, 14.1. HRMS Calcd. For C$_{21}$H$_{20}$FNO$_4$ + H$: 370.1455$, found: 370.1449.

Ethyl 2-(4-bromophenyl)-3-(2-ethoxy-2-oxoethyl)dizine-1-carboxylate (2d):
Brown oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.31 (1H, d, $J = 9.0$ Hz), 7.98 (1H, d, $J = 7.0$ Hz), 7.53 (2H, d, $J = 8.0$ Hz), 7.27 (2H, d, $J = 8.0$ Hz), 7.13 (1H, ddd, $J = 8.0$, 7.0, 1.0 Hz), 6.83 (1H, td, $J = 7.0$, 1.0 Hz), 4.19 (2H, q, $J = 7.0$ Hz), 4.15 (2H, q, $J = 7.0$ Hz), 1.24 (3H, t, $J = 7.0$ Hz), $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.6, 164.8, 136.3, 133.8, 132.4, 130.8, 130.6, 123.3, 122.7, 121.6, 120.4, 116.6, 113.1, 102.2, 61.6, 59.4, 30.9, 14.3, 14.2. HRMS Calcd. For C$_{21}$H$_{20}$BrNO$_4$ + H$: 430.0654$, found: 430.0652.

Ethyl 2-(3-bromophenyl)-3-(2-ethoxy-2-oxoethyl)indolizine-1-carboxylate (2e):

Brown oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.32 (1H, d, $J = 9.5$ Hz), 8.00 (1H, d, $J = 7.0$ Hz), 7.56 (1H, t, $J = 1.5$ Hz), 7.49 (1H, dt, $J = 8.0$, 1.0 Hz), 7.33 (1H, d, $J = 7.5$ Hz), 7.27 (1H, t, $J = 7.5$ Hz), 7.13 (1H, ddd, $J = 8.0$, 7.0 Hz), 6.83 (1H, td, $J = 7.0$, 1.0 Hz), 4.16 (4H, m), 3.74 (2H, s), 1.25 (3H, t, $J = 7.0$ Hz), 1.13 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.5, 164.8, 137.1, 136.4, 133.7, 130.3, 129.4, 129.1, 123.3, 122.7, 121.6, 120.3, 116.7, 113.2, 102.2, 61.6, 59.4, 31.0, 14.3, 14.2. HRMS Calcd. For C$_{21}$H$_{20}$BrNO$_4$ + H$: 430.0654$, found: 430.0652.

Ethyl 2-(2-bromophenyl)-3-(2-ethoxy-2-oxoethyl)indolizine-1-carboxylate (2f):

Brown oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.32 (1H, d, $J = 9.0$ Hz), 8.00 (1H, d, $J = 7.0$ Hz), 7.65 (1H, dd, $J = 8.0$, 1.0 Hz), 7.33 (2H, m), 7.23 (1H, td, $J = 8.0$, 2.0 Hz), 7.12 (1H, ddd, $J = 8.0$, 7.0, 1.0 Hz), 6.82 (1H, td, $J = 7.0$, 1.0 Hz), 4.11 (4H, m), 3.70 (1H, d, $J = 16.5$ Hz), 3.66 (1H, d, $J = 16.5$ Hz), 1.19 (3H, t, $J = 7.0$ Hz), 1.03 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.3, 164.7, 136.5, 136.1, 132.2, 131.9, 130.3, 129.0, 126.8, 125.2, 123.4, 122.5, 120.3, 116.5, 112.9, 102.8, 61.4, 59.2, 30.8, 14.2, 14.0. HRMS Calcd. For C$_{21}$H$_{20}$BrNO$_4$ + H$: 430.0654$, found: 430.0652.

Ethyl 3-(2-ethoxy-2-oxoethyl)-2-(3-(trifluoromethyl)phenyl)indolizine-1-carboxylate (2g):

Brown oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.38 (1H, d, $J = 9.0$ Hz), 8.03 (1H, d, $J = 7.0$ Hz), 7.69 (1H, s), 7.63 (1H, d, $J = 7.5$ Hz), 7.60 (1H, d, $J = 7.5$ Hz), 7.53 (1H, t, $J = 7.5$ Hz), 7.16 (1H, m), 6.86 (1H, td, $J = 7.0$, 1.0 Hz), 4.16 (4H, m), 3.72 (2H, s), 1.24 (3H, t, $J = 7.0$ Hz), 1.06 (3H, t, $J =
7.0 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.3, 164.6, 136.4, 135.7, 134.0, 130.0, 129.9 (d, $J = 32$ Hz), 127.9, 127.5 (q, $J = 4$ Hz), 125.4, 123.9 (q, $J = 4$ Hz), 123.2, 122.7, 120.3, 116.6, 113.2, 102.2, 61.5, 59.3, 30.9, 14.0, 13.9. HRMS Calcd. For C$_{22}$H$_{20}$F$_3$NO$_4$ + H$^+$: 420.1423, found: 420.1416.

Ethyl 3-(2-ethoxy-2-oxoethyl)-2-(4-methoxyphenyl)indolizine-1-carboxylate (2h):

Brown oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.30 (1H, d, $J = 9.0$ Hz), 7.96 (1H, d, $J = 7.0$ Hz), 7.32 (2H, dt, $J = 8.5, 2.0$ Hz), 7.11 (1H, dd, $J = 9.0, 6.5$ Hz), 6.95 (2H, dt, $J = 8.5, 2.0$ Hz), 6.81 (1H, td, $J = 8.5, 2.0$ Hz), 4.20 (2H, q, $J = 7.5$ Hz), 4.15 (2H, q, $J = 7.5$ Hz), 3.86 (3H, s), 3.76 (2H, s), 1.23 (3H, t, $J = 7.0$ Hz), 1.18 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.7, 164.9, 158.8, 136.1, 131.7, 131.5, 126.9, 122.2, 120.2, 116.6, 113.0, 112.7, 102.2, 61.3, 59.2, 55.3, 30.9, 14.3, 14.2. HRMS Calcd. For C$_{22}$H$_{23}$NO$_5$ + H$^+$: 382.1654, found: 382.1645.

Ethyl 2-(4-acetoxyphenyl)-3-(2-ethoxy-2-oxoethyl)indolizine-1-carboxylate (2i):

Brown oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.32 (1H, d, $J = 9.0$ Hz), 7.96 (1H, d, $J = 7.0$ Hz), 7.40 (2H, d, $J = 8.5$ Hz), 7.13 (3H, m), 6.82 (1H, t, $J = 7.0$ Hz), 4.16 (4H, m), 3.76 (2H, s), 2.33 (3H, s), 1.24 (3H, t, $J = 7.0$ Hz), 1.12 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.7, 169.6, 165.0, 150.1, 136.4, 132.4, 131.7, 130.8, 123.2, 122.6, 120.7, 120.3, 116.7, 113.1, 102.3, 61.5, 59.4, 30.9, 21.4, 14.2, 14.2. HRMS Calcd. For C$_{23}$H$_{23}$NO$_6$ + H$^+$: 410.1604, found: 410.1600.

Ethyl 2-(4-(dimethylamino)phenyl)-3-(2-ethoxy-2-oxoethyl)indolizine-1-carboxylate Late (2j):

Brown oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.29 (1H, d, $J = 9.0$ Hz), 7.95 (1H, d, $J = 7.0$ Hz), 7.28 (2H, dt, $J = 8.5, 3.0$ Hz), 7.09 (1H, m), 6.79 (3H, m), 4.23 (2H, q, $J = 7.0$ Hz), 4.16 (2H, q, $J = 7.0$ Hz), 3.80 (2H, s), 2.99 (6H, s), 1.23 (6H, m); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 170.1, 165.2, 149.9, 136.3, 132.4, 131.5, 123.2, 122.5, 122.0, 120.3, 116.6, 112.7, 111.9, 102.3, 61.4, 59.2, 10.8, 31.2, 14.5, 14.3. HRMS Calcd. For C$_{23}$H$_{26}$N$_2$O$_4$ + H$^+$: 395.1971, found: 395.1970.
Ethyl 3-(2-ethoxy-2-oxoethyl)-2-(furan-2-yl)indolizine-1-carboxylate (2k):

\[
\text{\begin{tikzpicture}
  \node[draw] (n1) at (0,0) {\text{H}};
  \node[draw] (n2) at (1,0) {\text{O}};
  \node[draw] (n3) at (2,0) {\text{H}};
  \node[draw] (n4) at (3,0) {\text{O}};
  \node[draw] (n5) at (4,0) {\text{H}};
  \draw (n1) -- (n2) -- (n3) -- (n4) -- (n5);
\end{tikzpicture}}
\]

Brown oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.28 (1H, d, $J = 9.0$ Hz), 7.98 (1H, d, $J = 7.0$ Hz), 7.56 (1H, m), 7.10 (1H, d, $J = 8.0$ Hz), 6.80 (1H, d, $J = 6.0$ Hz), 6.68 (1H, d, $J = 8.0$ Hz), 6.52 (1H, d, $J = 7.0$ Hz), 4.29 (2H, q, $J = 7.0$ Hz), 4.15 (2H, q, $J = 7.0$ Hz), 3.96 (2H, s), 1.28 (3H, t, $J = 7.0$ Hz), 1.23 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.4, 164.5, 147.4, 142.4, 136.4, 123.2, 122.5, 120.4, 120.3, 117.7, 113.0, 110.8, 110.8, 102.1, 61.4, 59.4, 31.2, 14.4, 14.1. HRMS Calcd. For C$_{19}$H$_{19}$NO$_5$ H$^+$: 342.1341, found: 342.1333.

Ethyl 2-(1-cyano-2-phenylindolizin-3-yl)acetate (2l):

\[
\text{\begin{tikzpicture}
  \node[draw] (n1) at (0,0) {\text{CN}};
  \node[draw] (n2) at (1,0) {\text{H}};
  \node[draw] (n3) at (2,0) {\text{O}};
  \node[draw] (n4) at (3,0) {\text{H}};
  \node[draw] (n5) at (4,0) {\text{O}};
  \draw (n1) -- (n2) -- (n3) -- (n4) -- (n5);
\end{tikzpicture}}
\]

Brown solid. m.p.: 134 – 136 ºC; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.04 (1H, d, $J = 7.0$ Hz), 7.70 (1H, d, $J = 8.0$ Hz), 7.58 (2H, d, $J = 8.0$ Hz), 7.50 (2H, t, $J = 7.0$ Hz), 7.14 (1H, t, $J = 7.5$ Hz), 6.86 (1H, t, $J = 7.0$ Hz), 4.22 (2H, q, $J = 7.0$ Hz), 3.92 (2H, s), 1.28 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.4, 164.5, 147.4, 142.4, 136.4, 123.2, 122.5, 120.4, 120.3, 117.7, 113.0, 110.8, 110.8, 102.1, 61.4, 59.4, 31.2, 14.4, 14.1. HRMS Calcd. For C$_{19}$H$_{16}$N$_2$O$_2$ H$^+$: 305.1290, found: 305.1278.

Ethyl 2-(2-(4-chlorophenyl)-1-cyanoindolizin-3-yl)acetate (2m):

\[
\text{\begin{tikzpicture}
  \node[draw] (n1) at (0,0) {\text{CN}};
  \node[draw] (n2) at (1,0) {\text{H}};
  \node[draw] (n3) at (2,0) {\text{Cl}};
  \node[draw] (n4) at (3,0) {\text{O}};
  \node[draw] (n5) at (4,0) {\text{H}};
  \draw (n1) -- (n2) -- (n3) -- (n4) -- (n5);
\end{tikzpicture}}
\]

Brown solid. m.p.: 139 – 141 ºC; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.05 (1H, d, $J = 7.0$ Hz), 7.69 (1H, d, $J = 8.5$ Hz), 7.53 (2H, d, $J = 8.5$ Hz), 7.47 (2H, d, $J = 8.5$ Hz), 7.15 (1H, dd, $J = 8.5$, 7.0 Hz), 6.87 (1H, d, $J = 7.0$, 1.0 Hz), 4.23 (2H, q, $J = 7.0$ Hz), 3.88 (2H, s), 1.28 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.3, 138.1, 132.0, 131.8, 129.6, 128.9, 128.2, 123.8, 122.5, 117.9, 116.7, 115.3, 113.4, 81.9, 61.7, 31.1, 14.4. HRMS Calcd. For C$_{19}$H$_{15}$ClN$_2$O$_2$ H$^+$: 339.0900, found: 339.0898.

Ethyl 2-(1-cyano-2-(4-fluorophenyl)indolizin-3-yl)acetate (2n):

\[
\text{\begin{tikzpicture}
  \node[draw] (n1) at (0,0) {\text{CN}};
  \node[draw] (n2) at (1,0) {\text{H}};
  \node[draw] (n3) at (2,0) {\text{F}};
  \node[draw] (n4) at (3,0) {\text{O}};
  \node[draw] (n5) at (4,0) {\text{H}};
  \draw (n1) -- (n2) -- (n3) -- (n4) -- (n5);
\end{tikzpicture}}
\]
Brown solid. m.p.: 109 – 111 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.05 (1H, d, \(J = 7.0\) Hz), 7.69 (1H, d, \(J = 9.0\) Hz), 7.56 (2H, m), 6.87 (1H, td, \(J = 7.0, 1.0\) Hz), 4.22 (2H, q, \(J = 7.0\) Hz), 3.88 (2H, s), 1.28 (3H, t, \(J = 7.0\) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 169.2, 162.77 (d, \(J = 247\) Hz), 138.1, 131.4 (d, \(J = 8\) Hz), 130.4, 128.0 (d, \(J = 4\) Hz), 123.8, 122.7, 117.8, 116.6, 115.9 (d, \(J = 21\) Hz), 115.3, 113.5, 81.9, 61.8, 31.0, 14.2. HRMS Calcd. For C\(_{19}\)H\(_{15}\)FN\(_2\)O\(_2\) + H\(^+\): 323.1196, found: 323.1191.

**Ethyl 2-(2-(4-bromophenyl)-1-cyanoindolizin-3-yl)acetate (2o):**

Brown solid. m.p.: 128 – 130 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.05 (1H, d, \(J = 7.0\) Hz), 7.69 (1H, d, \(J = 9.0\) Hz), 7.63 (2H, d, \(J = 8.5\) Hz), 7.46 (2H, d, \(J = 8.0\) Hz), 7.15 (1H, dd, \(J = 8.5, 7.0\) Hz), 6.87 (1H, t, \(J = 7.0\) Hz), 4.22 (2H, q, \(J = 7.0\) Hz), 3.88 (2H, s), 1.28 (3H, t, \(J = 7.0\) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 169.1, 138.2, 132.1, 131.2, 130.9, 130.6, 123.9, 122.8, 122.7, 117.9, 116.5, 115.3, 113.6, 81.8, 61.9, 31.0, 14.2. HRMS Calcd. For C\(_{19}\)H\(_{15}\)BrN\(_2\)O\(_2\) + H\(^+\): 383.0395, found: 383.0386.

**Ethyl 2-(2-(3-bromophenyl)-1-cyanoindolizin-3-yl)acetate (2p):**

Brown solid. m.p.: 107 – 109 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.09 (1H, d, \(J = 7.0\) Hz), 7.60 (1H, t, \(J = 2.0\) Hz), 7.70 (1H, d, \(J = 9.0\) Hz), 7.55 (2H, m), 7.37 (1H, t, \(J = 8.0\) Hz), 7.16 (1H, dd, \(J = 8.5, 7.0\) Hz), 6.88 (1H, td, \(J = 7.0, 1.0\) Hz), 4.23 (2H, q, \(J = 7.0\) Hz), 3.89 (2H, s), 1.31 (3H, t, \(J = 7.0\) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 169.0, 138.2, 134.1, 132.5, 131.3, 130.4, 130.1, 128.4, 123.9, 122.9, 122.8, 117.9, 116.3, 115.6, 81.9, 61.9, 31.1, 14.2. HRMS Calcd. For C\(_{19}\)H\(_{15}\)BrN\(_2\)O\(_2\) + H\(^+\): 383.0395, found: 383.0386.

**Ethyl 2-(2-(2-bromophenyl)-1-cyanoindolizin-3-yl)acetate (2q):**

Brown oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.01 (1H, d, \(J = 7.0\) Hz), 7.70 (2H, m), 7.39 (2H, m), 7.29 (1H, td, \(J = 7.0, 2.5\) Hz), 7.14 (1H, ddd, \(J = 9.0, 7.0, 0.5\) Hz), 6.86 (1H, td, \(J = 7.0, 1.0\) Hz), 4.12 (2H, m), 3.76 (2H, s), 1.21 (3H, t, \(J = 7.0\) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 168.8, 137.7, 133.1, 133.0, 132.6, 130.7, 130.2, 127.5, 124.4, 124.0, 122.6, 117.9, 116.5, 116.2, 113.3, 81.2, 61.6, 30.9, 14.1. HRMS Calcd. For C\(_{19}\)H\(_{15}\)BrN\(_2\)O\(_2\) + H\(^+\): 383.0395, found: 383.0386.
Ethyl 2-(1-cyano-2-(3-(trifluoromethyl)phenyl)indolizin-3-yl)acetate (2r):

Brown oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 8.14 (1H, d, $J = 7.0$ Hz), 7.89 (1H, s), 7.82 (1H, d, $J = 7.5$ Hz), 7.70 (2H, m), 7.64 (1H, t, $J = 7.5$ Hz), 7.18 (1H, ddd, $J = 9.0, 7.0, 0.5$ Hz), 6.90 (1H, td, $J = 7.0, 1.0$ Hz), 4.24 (2H, q, $J = 7.0$ Hz), 3.88 (2H, s), 1.29 (3H, t, $J = 7.0$ Hz);

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 168.9, 138.2, 133.1, 132.9, 131.2 (q, $J = 33$ Hz), 130.1, 129.5, 126.4 (q, $J = 4$ Hz), 125.1 (q), 124.9 (q), 124.0, 123.0, 117.9, 116.3, 115.6, 113.7, 81.9, 62.0, 31.2, 14.0. HRMS Calcd. For C$_{20}$H$_{15}$F$_3$N$_2$O$_2$ + H$: 373.1164, found: 373.1154.

Ethyl 2-(1-cyano-2-(4-methoxyphenyl)indolizin-3-yl)acetate (2s):

Brown solid. m.p.: 132 – 134 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 8.03 (1H, d, $J = 7.0$ Hz), 7.67 (1H, d, $J = 9.0$ Hz), 7.52 (2H, d, $J = 8.5$ Hz), 7.11 (1H, ddd, $J = 9.0, 7.0, 0.5$ Hz), 7.02 (2H, d, $J = 9.0$ Hz), 6.84 (1H, td, $J = 7.0, 1.0$ Hz), 4.22 (2H, q, $J = 7.0$ Hz), 3.90 (2H, s), 3.86 (3H, s), 1.28 (3H, t, $J = 7.0$ Hz);

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 169.4, 159.6, 138.0, 131.6, 130.8, 124.3, 123.8, 122.4, 117.7, 116.9, 115.0, 114.4, 113.2, 81.8, 61.7, 55.4, 31.1, 14.2. HRMS Calcd. For C$_{20}$H$_{18}$N$_2$O$_3$ + H$: 335.1396, found: 335.1394.

Ethyl 2-(2-(4-acetoxyphenyl)-1-cyanoindolizin-3-yl)acetate (2t):

Brown oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 8.04 (1H, d, $J = 7.0$ Hz), 7.70 (1H, d, $J = 9.0$ Hz), 7.62 (2H, d, $J = 8.5$ Hz), 7.23 (2H, d, $J = 8.5$ Hz), 7.15 (1H, m), 6.87 (1H, td, $J = 7.0, 1.0$ Hz), 4.22 (2H, q, $J = 7.0$ Hz), 3.92 (2H, s), 2.34 (3H, s), 1.28 (3H, t, $J = 7.0$ Hz);

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 169.5, 169.2, 150.6, 138.2, 130.7, 129.6, 123.8, 122.7, 122.1, 117.9, 116.6, 115.4, 114.0, 113.5, 81.9, 61.8, 29.7, 21.2, 14.2. HRMS Calcd. For C$_{21}$H$_{18}$N$_2$O$_4$ + H$: 363.1345, found: 363.1338.

Ethyl 2-(1-cyano-2-(furan-2-yl)indolizin-3-yl)acetate (2u):

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Brown solid. m.p.: 130 – 132 ºC; ¹H NMR (500 MHz, CDCl₃): δ 7.98 (1H, d, J = 7.0 Hz), 7.64 (1H, d, J = 8.5 Hz), 7.55 (1H, dd, J = 2.0, 0.5 Hz), 7.11 (1H, ddd, J = 8.5, 7.0, 1.0 Hz), 7.04 (1H, dd, J = 3.5, 0.5 Hz), 6.83 (1H, td, J = 7.0, 1.0 Hz), 6.54 (1H, dd, J = 3.5, 2.0 Hz), 4.24 (2H, s), 4.18 (2H, q, J = 7.0 Hz), 1.24 (3H, t, J = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 169.1, 147.2, 142.5, 138.5, 123.5, 122.8, 120.5, 117.7, 116.7, 114.6, 113.5, 111.7, 119.3, 79.2, 61.6, 31.2, 14.1.

HRMS Calcd. For C₁₇H₁₄N₂O₃ + H⁺: 295.1083, found: 295.1077.

V. General Procedure for the Synthesis of Pyrroles

To a solution of 2-isocyanatoacetate (8, 0.3 mmol, 1.0 equiv) and DBU (0.3 mmol, 1.0 equiv) in toluene (1 mL) was added MBHAs (0.3 mmol, 1.0 equiv) in toluene (1 mL) dropwise and then the mixture was stirred at room temperature for 2h. Water (5 mL) was added to it and the mixture was extracted three times with EtOAc (10 mL × 3). The combined organic layers were washed with water (10 mL × 3) and brine (10 mL), dried over anhydrous Na₂SO₄ and concentrated in vacuum. Purification of the residue by chromatography (silica gel) affords the product.

**Diethyl 3-phenyl-1H-pyrrole-2,5-dicarboxylate (3a):**

![Chemical Structure](image)

Yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 9.50 (1H, s), 7.59 (1H, d, J = 3.5 Hz), 7.32 (5H, m), 4.12 (4H, m), 1.10 (3H, t, J = 7.5 Hz), 1.07 (3H, t, J = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 163.8, 160.9, 133.7, 132.3, 130.1, 127.1, 126.9, 126.7, 121.0, 117.3, 60.5, 59.8, 13.9, 13.8. HRMS Calcd. For C₁₆H₁₇NO₄ + H⁺: 288.1236, found: 288.1239.

**Diethyl 3-(4-chlorophenyl)-1H-pyrrole-2,5-dicarboxylate (3b):**

![Chemical Structure](image)

Yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 9.64 (1H, s), 7.58 (1H, d, J = 3.0 Hz), 7.32 (2H, d, J = 8.0 Hz), 7.26 (2H, d, J = 8.0 Hz), 4.14 (4H, m), 1.15 (3H, t, J = 7.0 Hz), 1.11 (3H, t, J = 7.5 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 163.7, 160.8, 133.1, 132.2, 131.6, 131.0, 127.2, 126.9, 121.0, 117.1, 60.7, 59.9, 14.1, 13.9. HRMS Calcd. For C₁₆H₁₆ClNO₄ + H⁺: 322.0846, found: 322.0840.
Diethyl 3-(4-fluorophenyl)-1H-pyrrole-2,5-dicarboxylate (3c):

Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.66 (1H, s), 7.58 (1H, d, $J = 3.5$ Hz), 7.29 (2H, m), 7.04 (2H, t, $J = 8.5$ Hz), 4.14 (4H, m), 1.42 (3H, t, $J = 7.0$ Hz), 1.09 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 163.8, 162.3 (d, $J = 244$ Hz), 160.9, 131.9 (d, $J = 8.0$ Hz), 131.2, 129.5 (d, $J = 4.0$ Hz), 126.9, 121.1, 117.2, 113.9 (d, $J = 21$ Hz), 60.7, 59.9, 14.1, 13.9. HRMS Calcd. For C$_{16}$H$_{16}$FNO$_4$ + H$^+$: 306.1142, found: 306.1136.

Diethyl 3-(4-bromophenyl)-1H-pyrrole-2,5-dicarboxylate (3d):

Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.59 (1H, s), 7.58 (1H, d, $J = 3.5$ Hz), 7.47 (2H, d, $J = 8.0$ Hz), 7.21 (2H, d, $J = 8.0$ Hz), 4.15 (4H, m), 1.52 (3H, t, $J = 7.0$ Hz), 1.11 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 163.7, 160.8, 132.7, 131.9, 131.0, 130.1, 126.9, 121.4, 121.0, 117.1, 60.7, 59.9, 14.1, 13.9. HRMS Calcd. For C$_{16}$H$_{16}$BrNO$_4$ + H$^+$: 366.0341, found: 366.0338.

Diethyl 3-(3-bromophenyl)-1H-pyrrole-2,5-dicarboxylate (3e):

Yellow solid. m.p.: 91 – 93 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.52 (1H, s), 7.62 (1H, d, $J = 3.5$ Hz), 7.50 (1H, s), 7.47 (1H, d, $J = 8.0$ Hz), 7.28 (1H, d, $J = 8.0$ Hz), 7.23 (1H, t, $J = 8.0$ Hz), 4.15 (4H, m), 1.13 (6H, m); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 163.6, 160.8, 135.8, 133.2, 130.2, 130.1, 129.0, 128.4, 126.9, 121.2, 120.8, 117.3, 60.8, 60.3, 14.0, 13.8. HRMS Calcd. For C$_{16}$H$_{16}$BrNO$_4$ + H$^+$: 366.0341, found: 366.0338.

Diethyl 3-(2-bromophenyl)-1H-pyrrole-2,5-dicarboxylate (3f):

Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.75 (1H, s), 7.62 (1H, d, $J = 3.0$ Hz), 7.59 (1H, dd, $J =$
8.0, 1.0 Hz), 7.30 (1H, td, \( J = 7.5, 1.0 \) Hz), 7.25 (1H, dd, \( J = 7.5, 2.0 \) Hz), 7.18 (1H, m), 4.09 (4H, m), 1.06 (3H, t, \( J = 7.0 \) Hz), 1.00 (3H, t, \( J = 7.0 \) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 163.6, 160.8, 136.0, 131.7, 131.2, 130.5, 128.6, 126.7, 126.3, 124.2, 121.4, 117.5, 60.6, 59.8, 13.9, 13.7. HRMS Calcd. For C\(_{16}\)H\(_{16}\)BrNO\(_4\) + H\(^+\): 366.0341, found: 366.0338.

**Diethyl 3-(3-(trifluoromethyl)phenyl)-1H-pyrrole-2,5-dicarboxylate (3g):**

![Chemical structure]

Yellow solid. m.p.: 49 – 51 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 9.83 (1H, s), 7.63 (1H, d, \( J = 3.5 \) Hz), 7.59 (2H, m), 7.52 (1H, d, \( J = 7.5 \) Hz), 7.46 (1H, t, \( J = 7.5 \) Hz), 4.11 (4H, m), 1.08 (3H, t, \( J = 7.0 \) Hz), 1.02 (3H, t, \( J = 7.0 \) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 163.7, 161.0, 134.7, 133.7, 130.3, 129.4 (q, \( J = 32 \) Hz), 127.3, 127.2, 124.4 (q, \( J = 271 \) Hz), 123.8 (q, \( J = 4 \) Hz), 122.3, 121.3, 117.2, 60.9, 60.0, 13.9, 13.6. HRMS Calcd. For C\(_{17}\)H\(_{16}\)F\(_3\)NO\(_4\) + H\(^+\): 356.1110, found: 356.1104.

**Diethyl 3-(4-methoxyphenyl)-1H-pyrrole-2,5-dicarboxylate (3h):**

![Chemical structure]

Yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 9.67 (1H, s), 7.58 (1H, d, \( J = 3.5 \) Hz), 7.29 (2H, d, \( J = 9.0 \) Hz), 6.91 (2H, d, \( J = 9.0 \) Hz), 4.16 (4H, m), 3.84 (3H, s), 1.18 (3H, t, \( J = 7.0 \) Hz), 1.13 (3H, t, \( J = 7.0 \) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 163.9, 161.0, 158.8, 132.3, 131.4, 126.9, 125.6, 120.8, 117.0, 112.5, 60.5, 59.8, 55.2, 14.2, 14.0. HRMS Calcd. For C\(_{17}\)H\(_{19}\)NO\(_5\) + H\(^+\): 318.1341, found: 318.1340.

**Diethyl 3-(4-acetoxyphenyl)-1H-pyrrole-2,5-dicarboxylate (3i):**

![Chemical structure]

Yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 9.73 (1H, s), 7.59 (1H, d, \( J = 3.5 \) Hz), 7.32 (2H, d, \( J = 8.5 \) Hz), 7.07 (2H, d, \( J = 8.5 \) Hz), 4.12 (4H, m), 2.30 (3H, s), 2.12 (3H, t, \( J = 7.0 \) Hz), 1.07 (3H, t, \( J = 7.0 \) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 169.4, 163.9, 161.1, 149.9, 131.5, 131.2, 131.1, 127.0, 121.2, 120.1, 117.3, 60.7, 59.9, 21.2, 13.9, 13.7. HRMS Calcd. For C\(_{18}\)H\(_{19}\)NO\(_6\) + H\(^+\): 346.1291, found: 346.1287.
Diethyl 3-(4-(dimethylamino)phenyl)-1H-pyrrole-2,5-dicarboxylate (3j):

![Structure of Diethyl 3-(4-(dimethylamino)phenyl)-1H-pyrrole-2,5-dicarboxylate (3j)]

Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.45 (1H, s), 7.57 (1H, d, $J = 3.5$ Hz), 7.27 (2H, d, $J = 8.5$ Hz), 6.75 (2H, d, $J = 8.5$ Hz), 4.19 (4H, m), 2.98 (6H, s), 1.20 (3H, t, $J = 7.0$ Hz), 1.18 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 163.9, 160.9, 149.9, 133.1, 131.2, 126.9, 120.9, 120.5, 116.9, 111.3, 60.4, 59.7, 40.7, 14.2, 14.1. HRMS Calcd. For C$_{18}$H$_{22}$N$_2$O$_4$ + H$^+$: 331.1658, found: 331.1652.

Diethyl 3-(furan-2-yl)-1H-pyrrole-2,5-dicarboxylate (3k):

![Structure of Diethyl 3-(furan-2-yl)-1H-pyrrole-2,5-dicarboxylate (3k)]

Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.78 (1H, s), 7.56 (1H, d, $J = 3.5$ Hz), 7.50 (1H, dd, $J = 2.0$, 1.0 Hz), 6.54 (1H, dd, $J = 3.0$, 1.0 Hz), 6.48 (1H, dd, $J = 3.0$, 2.0 Hz), 4.24 (2H, q, $J = 7.0$ Hz), 4.20 (2H, q, $J = 7.0$ Hz), 1.22 (6H, m); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 163.5, 160.6, 145.4, 141.8, 126.9, 122.3, 120.3, 117.8, 110.9, 110.7, 60.9, 60.1, 14.2, 14.1. HRMS Calcd. For C$_{14}$H$_{15}$NO$_5$ + H$^+$: 278.1028, found: 278.1020.

VI. General Procedure for the Synthesis of Pyrazoles

A mixture of MBHAs (0.3 mmol, 1.0 equiv) and phenylhydrazine (9, 0.3 mmol, 1.0 equiv) was stirred in MeOH (2 mL) at 65 °C overnight. Once starting material was consumed (monitored by TLC), the organic solvent was removed and the residue was purified by column chromatography (silica gel) to give the target compound.

Ethyl 1,3-diphenyl-1H-pyrazole-5-carboxylate (4a):

![Structure of Ethyl 1,3-diphenyl-1H-pyrazole-5-carboxylate (4a)]

Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.89 (2H, m), 7.45 (7H, m), 7.36 (1H, tt, $J = 7.0$, 1.5 Hz), 7.34 (1H, s), 4.27 (2H, q, $J = 7.0$ Hz), 1.27 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 159.1, 151.5, 140.4, 134.7, 132.2, 128.8, 128.7, 128.6, 128.4, 126.1, 125.8, 109.4, 61.2, 14.1. HRMS Calcd. For C$_{18}$H$_{16}$N$_2$O$_2$ + H$^+$: 293.1290, found: 293.1282.
Ethyl 3-(4-chlorophenyl)-1-phenyl-1H-pyrazole-5-carboxylate (4b):

Yellow solid. m.p.: 61 – 63 ºC; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 7.45\) (2H, d, \(J = 8.5\) Hz), \(7.48\) (5H, m), \(7.39\) (2H, d, \(J = 8.5\) Hz), \(7.30\) (1H, s), \(4.27\) (2H, q, \(J = 7.0\) Hz), \(1.27\) (3H, t, \(J = 7.0\) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 159.0, 150.4, 140.3, 134.9, 134.2, 130.7, 128.9, 128.8, 128.6, 127.1, 126.1, 109.3, 61.3, 14.0\). HRMS Calcd. For C\(_{18}\)H\(_{15}\)ClN\(_2\)O\(_2\) + H\(^+\): 327.0900, found: 327.0898.

Ethyl 3-(4-fluorophenyl)-1-phenyl-1H-pyrazole-5-carboxylate (4c):

Yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 7.85\) (2H, m), \(7.48\) (5H, m), \(7.28\) (1H, s), \(7.11\) (2H, t, \(J = 9.0\) Hz), \(4.27\) (2H, q, \(J = 7.0\) Hz), \(1.27\) (3H, t, \(J = 7.0\) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 162.9\) (d, \(J = 245\) Hz), \(159.0, 150.6, 140.3, 134.8, 128.7, 128.6, 128.4\) (d, \(J = 4\) Hz), \(127.5\) (d, \(J = 8\) Hz), \(126.1, 115.7\) (d, \(J = 21\) Hz), \(109.2, 61.3, 14.0\). HRMS Calcd. For C\(_{18}\)H\(_{15}\)FN\(_2\)O\(_2\) + H\(^+\): 311.1196, found: 311.1189.

Ethyl 3-(4-bromophenyl)-1-phenyl-1H-pyrazole-5-carboxylate (4d):

Yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 7.75\) (2H, d, \(J = 8.5\) Hz), \(7.55\) (2H, d, \(J = 8.5\) Hz), \(7.48\) (5H, m), \(7.30\) (1H, s), \(4.27\) (2H, q, \(J = 7.0\) Hz), \(1.26\) (3H, t, \(J = 7.0\) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 159.0, 150.4, 140.3, 134.9, 131.9, 131.1, 128.8, 128.5, 127.3, 126.1, 122.4, 109.3, 61.3, 14.0\). HRMS Calcd. For C\(_{18}\)H\(_{15}\)BrN\(_2\)O\(_2\) + H\(^+\): 371.0395, found: 371.0391.

Ethyl 3-(3-bromophenyl)-1-phenyl-1H-pyrazole-5-carboxylate (4e):

Yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 8.05\) (1H, t, \(J = 1.5\) Hz), \(7.79\) (1H, d, \(J = 8.0\) Hz), \(7.48\) (6H, m), \(7.31\) (1H, s), \(7.29\) (1H, t, \(J = 8.0\) Hz), \(4.27\) (2H, q, \(J = 7.0\) Hz), \(1.27\) (3H, t, \(J = 7.0\) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 158.9, 150.0, 140.2, 134.2, 131.3, 130.3, 129.0, 128.8, 128.7,
128.6, 128.2, 126.1, 124.3, 109.5, 61.3, 14.0. HRMS Calcd. For C_{18}H_{13}BrN_{2}O_{2} + H^{+}: 371.0395, found: 371.0391.

**Ethyl 1-phenyl-3-(3-(trifluoromethyl)phenyl)-1H-pyrazole-5-carboxylate (4f):**

Yellow solid. m.p.: 96 – 98 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.15 (1H, s), 8.06 (1H, d, \(J = 7.5\) Hz), 7.61 (1H, d, \(J = 7.5\) Hz), 7.54 (1H, t, \(J = 7.5\) Hz), 7.49 (5H, m), 7.37 (1H, s), 4.28 (2H, q, \(J = 7.5\) Hz), 1.28 (3H, t, \(J = 7.0\) Hz);

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 158.9, 150.0, 140.2, 135.0, 133.0, 131.2 (d, \(J = 32\) Hz), 129.2, 128.9, 128.6, 128.2, 126.1, 124.9 (q, \(J = 4\) Hz), 124.1 (q, \(J = 271\) Hz), 122.5 (q, \(J = 4\) Hz), 109.5, 61.4, 14.0. HRMS Calcd. For C_{19}H_{15}F_{3}N_{2}O_{2} + H^{+}: 361.1164, found: 361.1155.

**Ethyl 3-(4-methoxyphenyl)-1-phenyl-1H-pyrazole-5-carboxylate (4g):**

Yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.89 (2H, d, \(J = 9.0\) Hz), 7.47 (5H, m), 7.26 (1H, s), 6.95 (2H, d, \(J = 9.0\) Hz), 4.26 (2H, q, \(J = 7.0\) Hz), 3.84 (3H, s), 1.26 (3H, t, \(J = 7.0\) Hz);

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 159.8, 159.2, 151.3, 140.4, 134.6, 128.6, 128.5, 127.1, 126.1, 124.9, 114.1, 108.9, 61.2, 55.3, 14.0. HRMS Calcd. For C_{19}H_{18}N_{2}O_{2} + H^{+}: 323.1396, found: 323.1394.

**Ethyl 3-(4-acetoxyphenyl)-1-phenyl-1H-pyrazole-5-carboxylate (4h):**

Yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.89 (2H, d, \(J = 8.5\) Hz), 7.48 (5H, m), 7.29 (1H, s), 7.16 (2H, d, \(J = 8.5\) Hz), 4.26 (2H, q, \(J = 7.0\) Hz), 2.31 (3H, s), 1.26 (3H, t, \(J = 7.0\) Hz);

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 169.4, 159.1, 150.8, 150.7, 140.3, 134.8, 129.9, 128.7, 128.6, 126.9, 126.1, 121.9, 109.3, 61.2, 21.2, 14.0. HRMS Calcd. For C_{20}H_{18}N_{2}O_{2} + H^{+}: 351.1345, found: 351.1338.

**Ethyl 3-(furan-2-yl)-1-phenyl-1H-pyrazole-5-carboxylate (4i):**

Yellow oil.
Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.45 (6H, m), 7.24 (1H, s), 6.78 (1H, d, $J$ = 3.0 Hz), 6.49 (1H, dd, $J$ = 3.0, 2.0 Hz), 4.25 (2H, q, $J$ = 7.0 Hz), 1.26 (3H, t, $J$ = 7.0 Hz);

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 158.9, 147.6, 144.1, 142.4, 140.1, 134.4, 128.8, 128.6, 126.2, 111.5, 109.1, 106.8, 61.3, 14.0.

HRMS Calcd. For C$_{16}$H$_{14}$N$_2$O$_3$ + H$^+$: 283.1083; found: 283.1080.

VII. General Procedure for the Synthesis of Benzo[b][1,6]oxazocin-2-ones

A mixture of MBHAs (0.3 mmol, 1.0 equiv) and 2-aminophenol (10, 0.3 mmol, 1.0 equiv) was stirred in MeOH (2 mL) at room temperature for 15 min. Then Na$_2$CO$_3$ (0.3 mmol, 1.0 equiv) was added and the mixture was heated to 40 °C for 2h. Once the starting MBHAs disappeared, the organic solvent was removed and the residue was purified by column chromatography (silica gel) to give the product.

(3Z,5E)-5-Phenyl-2H-benzo[b][1,6]oxazocin-2-one (5a):

![Chemical Structure](attachment:image.png)

Yellow solid. m.p.: 151 – 153 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.14 (1H, d, $J$ = 16.5 Hz), 7.77 (1H, d, $J$ = 7.5 Hz), 7.67 (2H, d, $J$ = 7.0 Hz), 7.53 (1H, d, $J$ = 16.5 Hz), 7.47 (1H, t, $J$ = 7.0 Hz), 7.40 (4H, m), 7.30 (1H, d, $J$ = 8.0 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 153.1, 149.6, 146.0, 140.4, 135.8, 131.9, 130.6, 129.9, 129.0, 128.9, 128.1, 125.7, 121.2, 116.3. HRMS Calcd. For C$_{16}$H$_{11}$NO$_2$ + H$^+$: 250.0868; found: 250.0867.

(3Z,5E)-5-(4-Chlorophenyl)-2H-benzo[b][1,6]oxazocin-2-one (5b):

![Chemical Structure](attachment:image.png)

Yellow solid. m.p.: 148 – 150 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.09 (1H, d, $J$ = 16.5 Hz), 7.77 (1H, d, $J$ = 8.0, 1.5 Hz), 7.59 (2H, dt, $J$ = 9.0, 2.0 Hz), 7.48 (2H, m), 7.37 (3H, m), 7.31 (1H, dd, $J$ = 8.5, 1.0 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 153.0, 149.4, 146.1, 138.9, 135.8, 134.4, 131.9, 130.7, 129.2, 129.0, 125.7, 121.8, 116.3. HRMS Calcd. For C$_{16}$H$_{10}$ClNO$_2$ + H$^+$: 284.0478; found: 284.0468.
(3Z,5E)-5-(4-Fluorophenyl)-2H-benzo[b][1,6]oxazocin-2-one (5c):

Yellow solid. m.p.: 141 – 143 ºC; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.10 (1H, d, \(J = 16.5\) Hz), 7.76 (1H, dd, \(J = 16.5\) Hz), 7.64 (2H, m), 7.47 (1H, td, \(J = 8.5, 2.0\) Hz), 7.43 (1H, d, \(J = 16.5\) Hz), 7.37 (1H, m), 7.30 (1H, dd, \(J = 8.0, 1.0\) Hz), 7.10 (2H, t, \(J = 8.5\) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 163.7 (d, \(J = 249\) Hz), 153.1, 149.4, 146.0, 139.1, 132.0 (d, \(J = 3\) Hz), 131.9, 130.6 129.9 (d, \(J = 8\) Hz), 128.9, 125.7, 120.9 (d, \(J = 2\) Hz), 116.3, 116.1 (d, \(J = 22\) Hz). HRMS Calcd. For C\(_{16}\)H\(_{10}\)FNO\(_2\) + H\(^+\): 268.0774, found: 268.0771.

(3Z,5E)-5-(4-Bromophenyl)-2H-benzo[b][1,6]oxazocin-2-one (5d):

Yellow solid. m.p.: 137 – 139 ºC; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.05 (1H, d, \(J = 16.5\) Hz), 7.76 (1H, dd, \(J = 8.0, 1.0\) Hz), 7.50 (6H, m), 7.38 (1H, t, \(J = 7.5\) Hz), 7.30 (1H, d, \(J = 8.0\) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 153.0, 149.3, 146.0, 138.9, 134.7, 132.2, 131.9, 130.8, 129.4, 129.0, 125.7, 124.1, 121.8, 116.4. HRMS Calcd. For C\(_{16}\)H\(_{10}\)BrNO\(_2\) + H\(^+\): 327.9973, found: 327.9969.

(3Z,5E)-5-(3-Bromophenyl)-2H-benzo[b][1,6]oxazocin-2-one (5e):

Yellow solid. m.p.: >250 ºC; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.05 (1H, d, \(J = 16.5\) Hz), 7.78 (2H, m), 7.57 (1H, d, \(J = 7.5\) Hz), 7.48 (3H, m), 7.39 (1H, t, \(J = 7.5\) Hz), 7.28 (2H, m); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 153.0, 149.1, 146.1, 138.6, 137.8, 132.6, 131.9, 130.9, 130.7, 130.4, 129.1, 126.6, 125.7, 123.1, 122.5, 116.3. HRMS Calcd. For C\(_{16}\)H\(_{10}\)BrNO\(_2\) + H\(^+\): 327.9973, found: 327.9969.
(3Z,5E)-5-(2-Bromophenyl)-2H-benzo[b][1,6]oxazocin-2-one (5f):

Yellow solid. m.p.: 148 – 150 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 8.50 (1H, d, \(J = 16.0 \) Hz), 7.82 (1H, dd, \(J = 8.0, 1.0 \) Hz), 7.79 (1H, dd, \(J = 8.0, 1.0 \) Hz), 7.63 (1H, dd, \(J = 8.0, 1.0 \) Hz), 7.48 (2H, m), 7.38 (2H, m), 7.31 (1H, dd, \(J = 8.0, 1.0 \) Hz), 7.23 (1H, td, \(J = 8.0, 1.0 \) Hz); \(^1\)C NMR (125 MHz, CDCl\(_3\)): δ 153.1, 149.3, 146.1, 138.6, 135.7, 133.4, 131.9, 130.9, 130.8, 129.3, 127.7, 127.6, 125.7, 125.6, 123.6, 116.3. HRMS Calcd. For C\(_{16}\)H\(_{10}\)BrNO\(_2\): 327.9973, found: 327.9969.

(3Z,5E)-5-(3-(Trifluoromethyl)phenyl)-2H-benzo[b][1,6]oxazocin-2-one (5g):

Yellow solid. m.p.: 158 – 160 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 8.17 (1H, d, \(J = 16.0 \) Hz), 7.90 (1H, s), 7.83 (1H, d, \(J = 7.5 \) Hz), 7.79 (1H, dd, \(J = 8.0, 1.5 \) Hz), 7.62 (1H, d, \(J = 7.5 \) Hz), 7.52 (3H, m), 7.40 (1H, td, \(J = 7.5, 1.0 \) Hz), 7.32 (1H, dd, \(J = 8.0, 1.5 \) Hz); \(^1\)C NMR (125 MHz, CDCl\(_3\)): δ 153.0, 149.1, 146.1, 138.6, 136.5, 131.9, 131.5 (d, \(J = 32 \) Hz), 131.1, 130.9, 129.4, 129.2, 126.2 (q, \(J = 4 \) Hz), 125.8, 124.7 (q, \(J = 4 \) Hz), 123.9 (q, \(J = 271 \) Hz), 122.9, 116.4. HRMS Calcd. For C\(_{17}\)H\(_{10}\)F\(_3\)NO\(_2\): 318.0742, found: 318.0733.

(3Z,5E)-5-(4-Methoxyphenyl)-2H-benzo[b][1,6]oxazocin-2-one (5h):

Yellow solid. m.p.: 166 – 168 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 8.10 (1H, d, \(J = 16.0 \) Hz), 7.75 (1H, dd, \(J = 8.0, 1.5 \) Hz), 7.62 (2H, d, \(J = 8.5 \) Hz), 7.44 (1H, td, \(J = 7.5, 1.5 \) Hz), 7.40 (1H, d, \(J = 16.0 \) Hz), 7.36 (1H, td, \(J = 8.0, 1.5 \) Hz), 7.29 (1H, dd, \(J = 8.5, 1.0 \) Hz), 6.94 (2H, d, \(J = 8.5 \) Hz), 3.85 (3H, s); \(^1\)C NMR (125 MHz, CDCl\(_3\)): δ 161.2, 153.3, 149.8, 145.9, 140.1, 132.5, 132.1, 130.1, 129.8, 128.7, 125.6, 118.8, 116.3, 114.5, 55.4. HRMS Calcd. For C\(_{17}\)H\(_{13}\)NO\(_3\): 280.0974, found: 280.0972.
4-((3Z,5E)-2-Oxo-2H-benzo[b][1,6]oxazocin-5-yl)phenyl acetate (5i):

Yellow solid. m.p.: 169 – 171 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.13 (1H, d, $J = 16.0$ Hz), 7.77 (1H, dd, $J = 8.0$, 1.5 Hz), 7.68 (2H, d, $J = 8.5$ Hz), 7.47 (2H, m), 7.38 (1H, td, $J = 8.0$, 1.0 Hz), 7.30 (1H, dd, $J = 8.0$, 1.0 Hz), 7.15 (2H, d, $J = 8.5$ Hz), 2.32 (3H, s); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.2, 153.1, 151.8, 149.5, 146.0, 139.3, 133.6, 131.9, 130.6, 129.2, 128.9, 125.7, 122.2, 121.3, 116.3, 21.2. HRMS Calcd. For C$_{18}$H$_{13}$NO$_4$ + H$^+$: 308.0923, found: 308.0920.

(3Z,5E)-5-(4-(Dimethylamino)phenyl)-2H-benzo[b][1,6]oxazocin-2-one (5j):

Yellow solid. m.p.: 70 – 72 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.10 (1H, d, $J = 16.0$ Hz), 7.72 (1H, dd, $J = 8.0$, 1.5 Hz), 7.57 (2H, d, $J = 9.0$ Hz), 7.39 (1H, td, $J = 8.0$, 1.5 Hz), 7.33 (2H, m), 7.27 (1H, m), 6.70 (2H, d, $J = 9.0$ Hz), 3.04 (6H, s); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 153.6, 151.6, 150.0, 145.8, 141.0, 132.4, 130.0, 129.3, 128.3, 125.5, 123.9, 116.2, 115.8, 111.9, 40.2. HRMS Calcd. For C$_{18}$H$_{16}$N$_2$O$_2$ + H$^+$: 293.1290, found: 293.1285.

VIII. Reference

IX. $^1$H NMR and $^{13}$C NMR Spectra.
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\[ \text{Diagram of molecule} \]

1b

\[ \text{Diagram of molecule} \]

1b

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