Ruthenium (II)-catalyzed C-O/C-S Cyclization for Synthesis of 5-member O-Containing and S-Containing Heterocycles

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I. General information

Reagents and solvents were purchased from various commercial sources and were used directly without any further purification unless otherwise stated. Column chromatography was performed with 200-300 mesh silica gel. $^1$H spectra were recorded at 400 and 500 MHz, and $^{13}$C spectra were recorded at 100 and 125 MHz. Chemical shifts are reported in parts per million (d) using TMS and chloroform as internal standards and coupling constants are expressed in Hertz. Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, m=multiplet, br=broad singlet), coupling constants (Hz), and integration. IR spectra were recorded on an FT-IR spectrometer and are reported in cm$^{-1}$. Melting points were recorded using an electro thermal capillary melting point apparatus and are uncorrected. HR-MS were recorded using the ESI-TOF.

II. Experimental Section

1. Optimization of Reaction Conditions

Table S1. Optimization Studies for Catalyst$^{[a]}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Oxidant</th>
<th>Additive</th>
<th>Solvent</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[RuCl$_2$(p-cymene)]$_2$</td>
<td>AgOAc</td>
<td>AgSbF$_6$</td>
<td>DCE</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>[RuCl$_2$(p-cymene)]$_2$</td>
<td>Ag$_2$CO$_3$</td>
<td>AgSbF$_6$</td>
<td>DCE</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>[RuCl$_2$(p-cymene)]$_2$</td>
<td>CsOAc</td>
<td>AgSbF$_6$</td>
<td>DCE</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>[RuCl$_2$(p-cymene)]$_2$</td>
<td>Cu(OAc)$_2$·H$_2$O</td>
<td>AgSbF$_6$</td>
<td>DCE</td>
<td>96</td>
</tr>
<tr>
<td>5$^{[b]}$</td>
<td>[RuCl$_2$(p-cymene)]$_2$</td>
<td>Cu(OAc)$_2$·H$_2$O</td>
<td>AgSbF$_6$</td>
<td>DCE</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>[Cp*RhCl$_2$]$_2$</td>
<td>Cu(OAc)$_2$·H$_2$O</td>
<td>-</td>
<td>DCE</td>
<td>-</td>
</tr>
</tbody>
</table>
Table S2. Optimization Studies for Solvent^[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCE</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>DCM</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>CCl₄</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>DME</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>H₂O</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>HOAc</td>
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</tr>
<tr>
<td>8</td>
<td>toluene</td>
<td>24</td>
</tr>
<tr>
<td>9</td>
<td>n-BuOH</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>DMF</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>1,4-Dioxane</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>EtOH</td>
<td>-</td>
</tr>
</tbody>
</table>

^[a]Standard reaction conditions: 1a (0.3 mmol), Ru (0.015 mmol), Oxidant (2.0 eq.), Additive (0.7 eq.), Solvent (5 mL). The reaction mixture was stirring at 90 °C for 12 h under air.

Table S3. Optimization Studies for Oxidant and Additive^[a]
Standard reaction conditions: 1a (0.3 mmol), Ru (0.015 mmol), Oxidant (2.0 eq.), Additive (0.7 eq.), Solvent (5 ml). The reaction mixture was stirring at 90 °C for 12 h under air.

Table S4. Optimization Studies for the reactants ratio $^{[a]}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant</th>
<th>Additive</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(OAc)$_2$·H$_2$O</td>
<td>AgSbF$_6$</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>Cu(OAc)$_2$·H$_2$O</td>
<td>KPF$_6$</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>AgOAc</td>
<td>AgSbF$_6$</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>(NH$_4$)$_2$S$_2$O$_8$</td>
<td>AgSbF$_6$</td>
<td>-</td>
</tr>
<tr>
<td>5$^b$</td>
<td>Ag$_2$CO$_3$</td>
<td>AgSbF$_6$</td>
<td>trace</td>
</tr>
</tbody>
</table>

$^a$ Standard reaction conditions: 1a (0.3 mmol), Ru (0.015 mmol), Oxidant (2.0 eq.), Additive (0.7 eq.), Solvent (5 ml). The reaction mixture was stirring at 90 °C for 12 h under air.
The reaction mixture was stirring at 90 °C for 12 h under air.

Table S5. Control Experiment [a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Oxidant</th>
<th>Additive</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[RuCl₂(p-cymene)]₂</td>
<td>Cu(OAc)₂·H₂O</td>
<td>AgSbF₆</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>Cu(OAc)₂·H₂O</td>
<td>AgSbF₆</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>[RuCl₂(p-cymene)]₂</td>
<td>-</td>
<td>AgSbF₆</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>[RuCl₂(p-cymene)]₂</td>
<td>Cu(OAc)₂·H₂O</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

[a] The reaction mixture was stirring at 90 °C for 12 h under air.

2. Experimental Procedures

General Procedure for the preparation of N-vinylbenzamides.

Procedure A¹: A suspension of Hippuric acid (5.0 g, 27.9 mmol), sodium acetate (4.2 g, 30.7 mmol), and acetic anhydride (30 mL) was stirred at room temperature for 30 min. Benzaldehydes (3.3 g, 30.7 mmol) was added. The resulting suspension was stirred at room temperature for 1 h and then at 60 °C for 5 h. The reaction mixture became a brown solution that upon cooling to room temperature again became a suspension. This suspension was mixed with water (1 L) and stirred at room temperature for a 0.5 h.
insoluble material was separated by filtration. The methanol (20 mL) solution of crude product (4.6 g, 17.5 mmol) and sodium methoxide in methanol (2 mL of 25% CH$_3$ONa in CH$_3$OH) was stirred at room temperature for 15 min. Solvent was evaporated, and the residue was partitioned between 10% aqueous ammonium chloride (100 mL) and methylene chloride (150 mL). The organic layer was washed with water (3 x 100 mL), dried over anhydrous sodium sulfate, and evaporated to an oily residue. The residue was purified by flash column chromatography (Petroleum ether /ethyl acetate) to afford the N-vinylbenzamides.

**Procedure B**: (Z)-4- (2-naphthylmethylene)-2-phenyl-5(4H)-oxazolone were added to a given alcohols (60 mL) containing TEA (5.0 mmol) and the resulting solution was refluxed for 1-2 h. After removal of the solvent under reduced pressure, the reaction mixture obtained was dissolved in chloroform (50-100 mL) and then washed twice with hydrochloric acid (3 mol/L, 50 mL), and finally dried over sodium sulfate. Evaporation of chloroform in vacuo gave the crystalline solid, and and the resulting residue was purified by column chromatography (Petroleum ether /ethyl acetate) to give the desired products N-vinylbenzamides.

**General Procedure for Ru(II) Catalytic C-O Cyclization for Synthesis of Oxazoles**

**Procedure C**: [RuCl$_2$(p-cymene)]$_2$ (0.015 mmol), AgSbF$_6$ (0.21 mmol) and Cu(OAc)$_2$·H$_2$O (0.6 mmol) were added to a solution of N-vinylbenzamides (0.3 mmol) in DCE. The reaction mixture then heated at 90 °C under air until the N-vinylbenzamides was completely converted into the corresponding oxazole derivatives as evidenced by monitoring with TLC. The reaction mixture was then extracted with ethyl acetate and the ethyl acetate layer was washed with a brine solution. The organic layer was separated, dried over anhydrous MgSO$_4$ and concentrated under vacuum to give the crude product. The crude product was then further purified by column
Mechanistic Studies

a) 

\[
\text{RuC}_2(p\text{-cymene})_2(0.05 \text{ eq.}) \quad \text{AgSbF}_5 (0.7 \text{ eq.}) \\
\text{Cu(}\text{OAc})_2\cdot\text{H}_2\text{O (2.0 eq)} \\
\text{DCE-d}_4, 2\text{h, 90}^\circ\text{C, sealed tube} \\
\rightarrow \text{MeO}_2\text{C} \\
\]

\[
\text{H} + \text{H}^\text{NMR} \\
\text{1a (53%) (10% D)} \\
\]

\[
\text{2a (47%)} \\
\]

\[
\text{1a-D/1} \quad \text{2a-D/1} \\
\]

\[
\text{f}1 \text{ (ppm)} \\
\]

\[
\text{7.30} \quad 7.35 \quad 7.40 \quad 7.45 \quad 7.50 \quad 7.55 \quad 7.60 \quad 7.65 \quad 7.70 \quad 7.75 \quad 7.80 \quad 7.85 \quad 7.90 \quad 7.95 \quad 8.00 \quad 8.05 \quad 8.10 \quad 8.15 \\
\text{2.00} \quad 1.90 \quad 1.80 \quad 1.70 \quad 1.60 \quad 1.50 \quad 1.40 \quad 1.30 \quad 1.20 \quad 1.10 \quad 1.00 \quad 0.90 \quad 0.80 \quad 0.70 \quad 0.60 \quad 0.50 \quad 0.40 \quad 0.30 \\
\]

\[
\text{N} \quad \text{O} \\
\text{O} \\
\text{C} \quad \text{H}_3 \\
\]

\[
\text{7.35} \quad 7.38 \quad 7.39 \quad 7.40 \quad 7.42 \quad 7.44 \quad 7.46 \quad 7.53 \quad 7.55 \quad 7.57 \quad 7.61 \quad 7.62 \quad 7.64 \quad 7.69 \quad 7.71 \quad 8.01 \quad 8.03 \quad 8.05 \\
\text{2.00} \quad 1.90 \quad 1.80 \quad 1.70 \quad 1.60 \quad 1.50 \quad 1.40 \quad 1.30 \quad 1.20 \quad 1.10 \quad 1.00 \quad 0.90 \quad 0.80 \quad 0.70 \quad 0.60 \quad 0.50 \quad 0.40 \quad 0.30 \\
\]

\[
\text{N} \quad \text{O} \\
\text{O} \\
\text{C} \quad \text{H}_3 \\
\]

\[
\text{7.35} \quad 7.38 \quad 7.39 \quad 7.40 \quad 7.42 \quad 7.44 \quad 7.46 \quad 7.53 \quad 7.55 \quad 7.57 \quad 7.61 \quad 7.62 \quad 7.64 \quad 7.69 \quad 7.71 \quad 8.01 \quad 8.03 \quad 8.05 \\
\text{2.00} \quad 1.90 \quad 1.80 \quad 1.70 \quad 1.60 \quad 1.50 \quad 1.40 \quad 1.30 \quad 1.20 \quad 1.10 \quad 1.00 \quad 0.90 \quad 0.80 \quad 0.70 \quad 0.60 \quad 0.50 \quad 0.40 \quad 0.30 \\
\]

\[
\text{N} \quad \text{O} \\
\text{O} \\
\text{C} \quad \text{H}_3 \\
\]

\[
\text{7.35} \quad 7.38 \quad 7.39 \quad 7.40 \quad 7.42 \quad 7.44 \quad 7.46 \quad 7.53 \quad 7.55 \quad 7.57 \quad 7.61 \quad 7.62 \quad 7.64 \quad 7.69 \quad 7.71 \quad 8.01 \quad 8.03 \quad 8.05 \\
\text{2.00} \quad 1.90 \quad 1.80 \quad 1.70 \quad 1.60 \quad 1.50 \quad 1.40 \quad 1.30 \quad 1.20 \quad 1.10 \quad 1.00 \quad 0.90 \quad 0.80 \quad 0.70 \quad 0.60 \quad 0.50 \quad 0.40 \quad 0.30 \\
\]

\[
\text{N} \quad \text{O} \\
\text{O} \\
\text{C} \quad \text{H}_3 \\
\]

\[
\text{7.35} \quad 7.38 \quad 7.39 \quad 7.40 \quad 7.42 \quad 7.44 \quad 7.46 \quad 7.53 \quad 7.55 \quad 7.57 \quad 7.61 \quad 7.62 \quad 7.64 \quad 7.69 \quad 7.71 \quad 8.01 \quad 8.03 \quad 8.05 \\
\text{2.00} \quad 1.90 \quad 1.80 \quad 1.70 \quad 1.60 \quad 1.50 \quad 1.40 \quad 1.30 \quad 1.20 \quad 1.10 \quad 1.00 \quad 0.90 \quad 0.80 \quad 0.70 \quad 0.60 \quad 0.50 \quad 0.40 \quad 0.30 \\
\]

\[
\text{N} \quad \text{O} \\
\text{O} \\
\text{C} \quad \text{H}_3 \\
\]

\[
\text{7.35} \quad 7.38 \quad 7.39 \quad 7.40 \quad 7.42 \quad 7.44 \quad 7.46 \quad 7.53 \quad 7.55 \quad 7.57 \quad 7.61 \quad 7.62 \quad 7.64 \quad 7.69 \quad 7.71 \quad 8.01 \quad 8.03 \quad 8.05 \\
\text{2.00} \quad 1.90 \quad 1.80 \quad 1.70 \quad 1.60 \quad 1.50 \quad 1.40 \quad 1.30 \quad 1.20 \quad 1.10 \quad 1.00 \quad 0.90 \quad 0.80 \quad 0.70 \quad 0.60 \quad 0.50 \quad 0.40 \quad 0.30 \\
\]
The general procedure A and B was followed by using benzaldehyde-α-d₁. Purification by column chromatography (Petroleum ether/EtOAc, 5:1) yielded 1a-d₁ (73%). ¹H NMR (500 MHz, DMSO-d₆) δ 10.12 (s, 1H), 7.99 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 7.0 Hz, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.45-7.35 (m, 3H), 3.74 (s, 3H). Two separate Round-bottomed flask containing [RuCl₂(p-cymene)]₂ (3.06 mg, 0.005 mmol), AgSbF₆ (24.05 mg, 0.07 mmol) and Cu(OAc)₂·H₂O (9.98 mg 0.2 mmol) were added to a solution of 1a (28.13 mg, 0.1 mmol) or 1a-d₁ (28.23 mg, 0.1 mmol) in DCE. Then, the reaction mixture was heated at 90 °C under air. The corresponding yield of each times was determined by HPLC. A kinetic isotope effect value k_H/k_D = 1.58 was obtained.
<table>
<thead>
<tr>
<th>Time (h)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a-d1→2a (%)</td>
<td>39.16</td>
<td>60.87</td>
<td>72.06</td>
<td>77.78</td>
<td>81.49</td>
<td>84.91</td>
<td>87.15</td>
<td>87.76</td>
<td>90.49</td>
</tr>
<tr>
<td>1a→2a (%)</td>
<td>25.65</td>
<td>47.29</td>
<td>62.74</td>
<td>71.71</td>
<td>78.06</td>
<td>82.84</td>
<td>85.98</td>
<td>89.87</td>
<td>92.24</td>
</tr>
</tbody>
</table>
III. Spectra data of products

methyl 2,5-diphenyloxazole-4-carboxylate (2a)

The title compound was prepared from 1a following general procedure C, and purified by column chromatography as white solid (80.7 mg, 96%). Melting point: 86-87 °C.

$^1$$H$ NMR (400 MHz, DMSO-$d_6$) : δ 8.14-8.03 (m, 4H), 7.61 (dd, $J = 5.1, 1.9$ Hz, 3H), 7.59-7.55 (m, 3H), 3.87 (s, 3H).

$^{13}$$C$ NMR (100 MHz, DMSO-$d_6$) : δ 162.5, 159.4, 154.9, 131.9, 131.0, 129.7, 129.0, 128.8, 128.0, 127.0, 126.9, 126.3, 52.5.

FT-IR: 3063.10, 2950.68, 1711.58, 1563.44, 1491.11, 1446.72, 1357.56, 1216.44, 1098.64, 708.12.

HRMS (ESI): calcd for C$_{17}$H$_{13}$NO$_3$ (M+H)$^+ = 280.0968$, found 280.0980.

methyl 2-(4-methoxyphenyl)-5-phenyloxazole-4-carboxylate (2b)

The title compound was prepared from 1b following general procedure C, and purified by column chromatography as white solid (63.6 mg, 69%). Melting point: 146-147 °C.

$^1$$H$ NMR (400 MHz, DMSO-$d_6$) : δ 8.10 (dd, $J = 7.6, 1.9$ Hz, 2H), 8.03 (d, $J = 8.8$ Hz, 2H), 7.55 (d, $J = 7.2$ Hz, 3H), 7.12 (d, $J = 8.8$ Hz, 2H), 3.86 (s, 6H).

$^{13}$$C$ NMR (100 MHz, DMSO-$d_6$): δ 162.59, 162.14, 159.58, 154.33, 130.80, 129.00, 128.72, 128.66, 127.88, 127.09, 118.83, 115.16, 55.95, 52.40.

FT-IR: 3007.33, 2950.68, 1723.37, 1614.98, 1562.17, 1505.74, 1494.07, 1355.41, 1214.20, 1023.56, 737.68.

HRMS (ESI): calcd for C$_{18}$H$_{15}$NO$_4$ (M+H)$^+ = 310.1074$, found 310.1075.
methyl 2-(4-(tert-butyl)phenyl)-5-phenyloxazole-4-carboxylate \((2c)\)

The title compound was prepared from \(1c\) following general procedure C, and purified by column chromatography as white solid (70.2 mg, 70%). Melting point: 94-95 °C.

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 8.10 (dd, \(J = 7.6, 2.0\) Hz, 2H), 8.02 (d, \(J = 8.5\) Hz, 2H), 7.61 (d, \(J = 8.5\) Hz, 2H), 7.58-7.53 (m, 3H), 3.86 (s, 3H), 1.33 (s, 9H).

\(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) 162.49, 159.48, 154.59, 130.79, 128.93, 128.64, 127.99, 127.03, 126.67, 126.39, 123.65, 52.33, 35.14, 31.25.

FT-IR: 3057.58, 2960.42, 2361.26, 1721.04, 1565.30, 1354.63, 1321.48, 1093.19, 817.53, 748.73.

HRMS (ESI): calcd for C\(_{21}\)H\(_{21}\)NO\(_3\) (M+H)\(^+=\) 336.1594, found 336.1598.

methyl 5-phenyl-2-(p-tolyl)oxazole-4-carboxylate \((2d)\)

The title compound was prepared from \(1d\) following general procedure C, and purified by column chromatography as white solid (70.9 mg, 81%). Melting point: 103-104 °C.

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 8.10 (dd, \(J = 7.3, 2.1\) Hz, 2H), 7.97 (d, \(J = 8.0\) Hz, 2H), 7.59-7.55 (m, 3H), 7.38 (d, \(J = 8.0\) Hz, 2H), 3.86 (s, 3H), 2.39 (s, 9H).

\(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) 162.51, 159.48, 154.59, 141.87, 130.84, 130.21, 128.97, 128.65, 127.90, 126.98, 126.79, 123.58, 52.3, 21.52.

FT-IR: 3247.45, 2953.79, 1725.36, 1564.00, 1501.88, 1356.79, 1108.49, 1093.19, 817.53, 748.73.

HRMS (ESI): calcd for C\(_{18}\)H\(_{15}\)NO\(_3\) (M+H)\(^+=\) 294.1125, found 294.1122.
methyl 5-phenyl-2-(3,4,5-trimethoxyphenyl)oxazole-4-carboxylate \((2e)\)

The title compound was prepared from \(1e\) following general procedure C, and purified by column chromatography as white solid (85.1 mg, 77%). Melting point: 168-169 °C.

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 8.13 (dd, \(J = 7.6, 2.1\) Hz, 2H), 7.60-7.55 (m, 3H), 7.35 (s, 2H), 3.91 (s, 6H), 3.86 (s, 3H), 3.76 (s, 3H).

\(^1^3\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) 162.49, 159.37, 154.82, 153.88, 140.75, 130.94, 129.01, 128.82, 128.05, 126.96, 121.60, 104.26, 60.69, 56.65, 52.44.

FT-IR: 2999.39, 2948.02, 2837.00, 1723.01, 1587.26, 1498.01, 1415.40, 1213.98, 1127.63, 728.92.

HRMS (ESI): calcd for C\(_{20}\)H\(_{19}\)NO\(_6\) (M+H) \(^+\) = 370.1285, found 370.1280.

methyl 2-(3,5-dimethoxyphenyl)-5-phenyloxazole-4-carboxylate \((2f)\)

The title compound was prepared from \(1f\) following general procedure C, and purified by column chromatography as white solid (80.5 mg, 79%). Melting point: 158-159 °C.

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 8.14-7.57 (m, 2H), 7.56 (dd, \(J = 1.9\) Hz, 1.9 Hz, 3H), 7.21 (d, \(J = 2.3\) Hz, 2H), 6.73 (t, \(J = 2.3\) Hz, 1H), 3.86 (d, \(J = 2.8\) Hz, 7H).

\(^1^3\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) 162.43, 161.41, 159.19, 154.95, 131.00, 129.01, 128.84, 128.21, 128.10, 104.60, 104.05, 56.06, 52.46.

FT-IR: 3483.87, 2846.88, 1718.45, 1601.68, 1562.48, 1316.62, 1221.20, 834.47.

HRMS (ESI): calcd for C\(_{19}\)H\(_{17}\)NO\(_5\) (M+H) \(^+\) = 340.1179, found 340.1186.
methyl 2-(4-chlorophenyl)-5-phenyloxazole-4-carboxylate (2g)

The title compound was prepared from 1g following general procedure C, and purified by column chromatography as light yellow solid (23.5 mg, 25%). Melting point: 120-121°C.

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.12 (dd, 4H), 7.66 (dd, $J = 1.9$ Hz, 1.9 Hz, 2H), 7.60-7.56 (m, 3H), 3.86 (s, 3H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): 162.36, 158.51, 155.05, 136.56, 131.02, 129.84, 129.00, 128.78, 128.63, 128.12, 126.84, 125.16, 52.46.

FT-IR: 3072.54, 2955.24, 1723.70, 1606.99, 1481.83, 1405.32, 1221.33, 1088.54, 1010.82, 730.55.

HRMS (ESI): calcd for C$_{17}$H$_{12}$NO$_3$Cl (M+H)$^+$ = 314.0578, found 314.0586.

methyl 2-(4-nitrophenyl)-5-phenyloxazole-4-carboxylate (2h)

The title compound was prepared from 1h following general procedure C, and purified by column chromatography as yellow solid (37.1 mg, 38%). Melting point: 172-173°C.

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 8.41 (d, $J = 9.0$ Hz, 2H), 8.36 (d, $J = 9.0$ Hz, 2H), 8.16-8.14 (m, 2H), 7.62-7.58 (m, 3H), 3.88 (s, 3H).

$^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta$ 162.21, 157.66, 155.98, 149.18, 131.76, 131.36, 129.08, 128.98, 128.62, 128.15, 126.63, 124.97, 52.60.

FT-IR: 3107.03, 3051.76, 2950.25, 1723.82, 1517.84, 1495.24, 1322.97, 1217.84, 1111.18, 1090.64, 712.13.
HRMS (ESI): calcd for C\textsubscript{17}H\textsubscript{12}N\textsubscript{2}O\textsubscript{5} (M+H) \textsuperscript{+} = 325.0819, found 325.0814.

methyl 5-phenyl-2-(4-(trifluoromethyl)phenyl)oxazole-4-carboxylate (2i)

The title compound was prepared from 1i following general procedure C, and purified by column chromatography as light yellow solid (18.0 mg, 17%). Melting point: 112-113 °C.

\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \delta 8.31 (d, J = 8.2 Hz, 2H), 8.13 (dd, J = 6.5, 3.2 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.58 (dd, J = 5.1, 1.8 Hz, 3H), 3.87 (s, 3H).

\textsuperscript{13}C NMR (125 MHz, DMSO-\textit{d}_6): \delta 162.29, 158.11, 155.59, 131.52, 131.26, 131.23, 129.07, 128.93, 128.33, 127.69, 126.72 (q, J = 3.8 Hz), 124.33 (q, J = 270.7 Hz), 52.55.

FT-IR: 2952.74, 1723.06, 1434.47, 1326.01, 1221.05, 1156.98, 1063.63, 1012.23, 763.64.

HRMS (ESI): calcd for C\textsubscript{18}H\textsubscript{12}N\textsubscript{2}O\textsubscript{3}F\textsubscript{3}(M+H) \textsuperscript{+} = 348.0842, found 348.0845.

methyl 2-(4-fluorophenyl)-5-phenyloxazole-4-carboxylate (2j)

The title compound was prepared from 1j following general procedure C, and purified by column chromatography as white solid (13.7 mg, 15%). Melting point: 131-132 °C.

\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \delta 8.17-8.10 (m, 4H), 7.56 (dd, J = 5.2, 1.9 Hz, 3H), 7.43 (t, J = 8.8 Hz, 2H), 3.86 (s, 3H).

\textsuperscript{13}C NMR (125 MHz, DMSO-\textit{d}_6): \delta 164.32 (d, J = 248.2 Hz), 162.44, 158.69, 154.95, 131.00, 129.54 (d, J = 2.9 Hz), 129.02, 128.79, 128.02, 126.91, 123.02 (d, J = 2.9 Hz), 117.03, 116.85, 52.48.

FT-IR: 3063.82, 3046.09, 2956.64, 1725.96, 1611.92, 1496.11, 1362.58, 1107.10,
methyl 2-(4-bromophenyl)-5-phenyloxazole-4-carboxylate (2k)

The title compound was prepared from 1k following general procedure C, and purified by column chromatography as white solid (40.0 mg, 34%). Melting point: 115-116 °C.

\[ ^1H\text{ NMR (500 MHz, DMSO-}d_6\text{:} \delta 8.14-8.05 (m, 2H), 8.05 (d, } J = 8.6 \text{ Hz, 2H), 7.81 (d, } J = 8.6 \text{ Hz, 2H), 7.60-7.56 (m, 3H), 3.87 (s, 3H).} \]

\[ ^{13}C\text{ NMR (125 MHz, DMSO-}d_6\text{:} \delta 162.38, 158.67, 155.13, 132.82, 131.09, 129.05, 128.84, 128.15, 126.85, 125.53, 125.47, 52.52.} \]

\[ \text{FT-IR:} \text{ 2923.29, 2852.04, 1723.65, 1492.33, 1480.82, 1399.47, 1222.38, 1008.43, 727.05.} \]

\[ \text{HRMS (ESI):} \text{ calcd for } C_{17}H_{12}NO_3F (M+H)^+ = 298.0874, \text{ found } 298.0879. \]

methyl 2-(3-methoxyphenyl)-5-phenyloxazole-4-carboxylate (2l)

The title compound was prepared from 1l following general procedure C, and purified by column chromatography as white solid (25.2 mg, 27%).

\[ ^1H\text{ NMR (500 MHz, DMSO-}d_6\text{:} \delta 8.14-8.08 (m, 2H), 7.67 (d, } J = 7.8 \text{ Hz, 1H), 7.55 (m, 4H), 7.49 (t, } J = 8.0 \text{ Hz, 1H), 7.16 (dd, } J = 8.2 \text{, 2.1 Hz, 1H), 3.86 (s, 6H).} \]

\[ ^{13}C\text{ NMR (125 MHz, DMSO-}d_6\text{:} \delta 162.45, 160.10, 159.24, 154.90, 130.97, 129.00, 128.79, 128.02, 127.51, 126.92, 119.22, 117.98, 111.46, 55.86, 52.44.} \]

\[ \text{HRMS (ESI):} \text{ calcd for } C_{18}H_{15}NO_4 (M+H)^+ = 310.1001, \text{ found } 310.0864. \]
methyl 2-(3-nitrophenyl)-5-phenyloxazole-4-carboxylate (2m)

![Structure](image)

The title compound was prepared from 1m following general procedure C, and purified by column chromatography as white solid (61.5 mg, 68%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 8.74 (s, 1H), 8.51 (d, $J = 7.8$ Hz, 1H), 8.42 (dd, $J = 7.9$, 1.9 Hz, 1H), 8.14 (dd, $J = 6.5$, 3.1 Hz, 2H), 7.88 (t, $J = 8.0$ Hz, 1H), 7.58 (dd, $J = 5.1$, 1.9 Hz, 3H), 3.87 (s, 3H).

$^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta$ 162.20, 157.50, 155.64, 148.63, 132.81, 131.60, 131.29, 129.06, 128.88, 128.12, 127.60, 126.52, 126.10, 121.17, 52.58.

HRMS (ESI): calcd for C$_{17}$H$_{12}$N$_2$O$_5$ (M+H)$^+$ = 325.0746, found 325.0627.

methyl 2-(3-chlorophenyl)-5-phenyloxazole-4-carboxylate (2n)

![Structure](image)

The title compound was prepared from 1n following general procedure C, and purified by column chromatography as white solid (62.3 mg, 66%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 8.13 (dd, $J = 6.7$, 3.0 Hz, 2H), 8.07 (s, 1H), 8.04 (d, $J = 7.7$ Hz, 1H), 7.66 (d, $J = 7.1$ Hz, 1H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.58-7.54 (m, 3H), 3.86 (s, 3H).

$^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta$ 162.32, 158.02, 155.27, 134.45, 131.71, 131.60, 131.10, 129.00, 128.86, 128.18, 128.12, 126.75, 126.34, 125.51, 52.50.

HRMS (ESI): calcd for C$_{17}$H$_{12}$ClNO$_3$ (M+H)$^+$ = 314.0506, found 314.0367.

methyl 2-(2-fluorophenyl)-5-phenyloxazole-4-carboxylate (2o)
The title compound was prepared from 1o following general procedure C, and purified by column chromatography as white solid (18.9 mg, 21%). Melting point: 102-103 °C.

**1H NMR (500 MHz, DMSO-\textit{d}_6):** \( \delta 8.15 \) (t, \( J = 8.3 \) Hz, 3H), \( 8.09 \) (dd, \( J = 7.5, 1.9 \) Hz, 2H), \( 7.67 \) (q, \( J = 7.3 \) Hz, 1H), 7.69-7.57 (m, 3H), 7.50-7.42 (m, 2H), 3.87 (s, 3H).

**13C NMR (125 MHz, DMSO-\textit{d}_6):** \( \delta 162.38, 159.87 \) (d, \( J = 155.97 \) Hz), \( 155.07, 134.00 \) (d, \( J = 8.5 \) Hz), 131.11, 130.20, 129.09, 128.78, 127.97, 126.82, 125.68 (d, \( J = 3.6 \) Hz), 117.59 (d, \( J = 20.7 \) Hz), 114.49 (d, \( J = 10.8 \) Hz), 52.52.

**FT-IR:** 3055.64, 2952.59, 1716.99, 1620.07, 1594.19, 1574.33, 1555.44, 1239.31, 1219.98, 737.32.

**HRMS (ESI):** calcd for C\textsubscript{17}H\textsubscript{12}NO\textsubscript{3}F (M+H) \(^+= \) 298.0874, found 298.0871.

**methyl 2-(2-chlorophenyl)-5-phenyloxazole-4-carboxylate** (2p)

The title compound was prepared from 1p following general procedure C, and purified by column chromatography as light yellow solid (18.4 mg, 19%). Melting point: 105-106 °C.

**1H NMR (500 MHz, DMSO-\textit{d}_6):** \( \delta 8.13-8.09 \) (m, 3H), 7.70 (d, \( J = 8.0 \) Hz, 1H), 7.63-7.60 (m, 1H), 7.59-7.55 (m, 4H), 3.87 (s, 3H).

**13C NMR (125 MHz, DMSO-\textit{d}_6):** \( \delta 162.36, 157.45, 155.29, 133.09, 131.93, 131.80, 131.69, 131.14, 129.11, 128.78, 128.24, 127.85, 126.77, 125.14, 52.54.

**FT-IR:** 3066.55, 2950.45, 1720.04, 1590.68, 1493.44, 1443.18, 1365.04, 1230.97, 1110.28, 743.31

**HRMS (ESI):** calcd for C\textsubscript{17}H\textsubscript{12}NO\textsubscript{3}Cl (M+H) \(^+= \) 314.0578, found 314.0582.
methyl 2-(2-methoxyphenyl)-5-phenyloxazole-4-carboxylate  \((2q)\)

The title compound was prepared from 1q following general procedure C, and purified by column chromatography as white solid (60.5 mg, 45%). Melting point: 146-147 °C.

\(^1\text{H NMR (500 MHz, DMSO-}d_6\text{):} \delta 8.08-8.06 \text{ (dd, } J = 1.7, 1.7 \text{ Hz, } 2\text{H}), 7.95 \text{ (dd, } J = 7.7, 1.6 \text{ Hz, } 1\text{H}), 7.62 – 7.51 \text{ (m, } 4\text{H}), 7.27 \text{ (d, } J = 8.4 \text{ Hz, } 1\text{H}), 7.13 \text{ (t, } J = 7.3 \text{ Hz, } 1\text{H}), 3.93 \text{ (s, } 3\text{H}), 3.86 \text{ (s, } 3\text{H}).

\(^{13}\text{C NMR (125 MHz, DMSO-}d_6\text{):} \delta 162.62, 158.57, 158.00, 154.57, 133.40, 130.84, 130.75, 129.08, 128.61, 127.61, 127.14, 121.16, 115.26, 113.21, 56.54, 52.41.

\text{FT-IR:} 2943.87, 2849.16, 1713.65, 1589.63, 1560.95, 1482.18, 1437.54, 1223.62, 1112.00, 741.60.

\text{HRMS (ESI):} \text{calcd for C}_{18}\text{H}_{15}\text{NO}_4 (M+H) \text{ }^\dagger = 310.1074, \text{found} 310.1073

methyl 5-phenyl-2-(m-tolyl)oxazole-4-carboxylate  \((2r)\)

The title compound was prepared from 1r following general procedure C, and purified by column chromatography as white solid (75.1 mg, 47%). Melting point: 90-91 °C.

\(^1\text{H NMR (500 MHz, DMSO-}d_6\text{):} \delta 8.11-8.06 \text{ (m, } 3\text{H}), 7.56 \text{ (q, } J = 5.6 \text{ Hz, } 3\text{H}), 7.48 \text{ (t, } J = 7.0 \text{ Hz, } 1\text{H}), 7.41 \text{ (dd, } J = 15.3, 7.4 \text{ Hz, } 2\text{H}), 3.87 \text{ (s, } 3\text{H}), 2.70 \text{ (s, } 3\text{H}).

\(^{13}\text{C NMR (125 MHz, DMSO-}d_6\text{):} \delta 162.59, 159.85, 154.51, 137.68, 132.26, 131.38, 130.91, 129.31, 129.05, 128.73, 127.76, 127.03, 126.86, 125.32, 52.47, 22.00.

\text{FT-IR:} 3058.42, 2950.32, 2924.05, 1718.73, 1605.65, 1588.46, 1490.71, 1266.83, 1224.95, 1107.99, 725.34.

\text{HRMS (ESI):} \text{calcd for C}_{18}\text{H}_{15}\text{NO}_3 (M+H) \text{ }^\dagger = 294.1125, \text{found} 294.1117.
methyl 2-phenyl-5-(p-tolyl)oxazole-4-carboxylate \hspace{1cm} (2s)

\begin{center}
\includegraphics[width=0.5\textwidth]{methyl_2-phenyl-5-(p-tolyl)oxazole-4-carboxylate_2s.png}
\end{center}

The title compound was prepared from 1s following general procedure C, and purified by column chromatography as white solid (18.0 mg, 23%).

$^1$H NMR (500 MHz, DMSO-\textit{d}_6): \(\delta\) 8.10 (dd, \(J = 7.1, 2.6\) Hz, 2H), 8.03 (d, \(J = 8.2\) Hz, 2H), 7.59 (dd, \(J = 5.1, 1.8\) Hz, 3H), 7.38 (d, \(J = 8.1\) Hz, 2H), 3.86 (s, 3H), 2.40 (s, 3H).

$^{13}$C NMR (125 MHz, DMSO-\textit{d}_6): \(\delta\) 162.56, 159.12, 155.13, 140.98, 131.79, 129.72, 129.61, 128.68, 127.51, 126.83, 126.36, 124.18, 52.41, 21.53.

HRMS (ESI): calcd for C\textsubscript{18}H\textsubscript{15}NO\textsubscript{3} (M+H)$^+$ = 294.1052, found 294.0899.

methyl 5-(4-nitrophenyl)-2-phenyloxazole-4-carboxylate \hspace{1cm} (2t)

\begin{center}
\includegraphics[width=0.5\textwidth]{methyl_5-(4-nitrophenyl)-2-phenyloxazole-4-carboxylate_2t.png}
\end{center}

The title compound was prepared from 1t following general procedure C, and purified by column chromatography as white solid (52.2 mg, 65%).

$^1$H NMR (500 MHz, DMSO-\textit{d}_6): \(\delta\) 8.38 (q, \(J = 9.1\) Hz, 4H), 8.12 (d, \(J = 6.3\) Hz, 2H), 7.60 (q, \(J = 6.5\) Hz, 3H), 3.89 (s, 3H).

$^{13}$C NMR (125 MHz, DMSO-\textit{d}_6): \(\delta\) 162.21, 160.45, 152.31, 148.30, 132.76, 132.24, 130.33, 129.82, 129.76, 127.11, 125.95, 124.14, 52.76.

HRMS (ESI): calcd for C\textsubscript{17}H\textsubscript{12}N\textsubscript{2}O\textsubscript{5} (M+H)$^+$ = 325.0746, found 325.0628.

methyl 5-phenyl-2-(thiophen-2-yl)oxazole-4-carboxylate \hspace{1cm} (2u)

\begin{center}
\includegraphics[width=0.5\textwidth]{methyl_5-phenyl-2-(thiophen-2-yl)oxazole-4-carboxylate_2u.png}
\end{center}
The title compound was prepared from **1u** following general procedure C, and purified by column chromatography as white solid (41.3 mg, 48%). Melting point: 103-104 °C.

**\(^1\)H NMR (500 MHz, DMSO-\(d_6\)):** \(\delta\) 8.08 (dd, \(J = 7.5, 2.1\) Hz, 1H), 7.91-7.90 (m, 2H), 7.59-7.56 (m, 3H), 7.29 (t, \(J = 4.8, 3.9\) Hz, 1H), 3.85 (s, 3H).

**\(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)):** \(\delta\) 162.29, 155.83, 154.37, 131.40, 131.01, 130.01, 129.20, 129.04, 128.75, 128.29, 127.82, 126.76, 52.49.

**FT-IR:** 3051.39, 2939.68, 1716.68, 1493.11, 1217.37, 1088.03, 1027.18, 718.15.

**HRMS (ESI):** calcd for C\(_{15}\)H\(_{11}\)NO\(_3\)S (M+H) \(^+\) = 286.0532, found 286.0540.

methyl 2-(furan-2-yl)-5-phenyloxazole-4-carboxylate  
(2v)

The title compound was prepared from **1v** following general procedure C, and purified by column chromatography as white solid (43.1 mg, 53%). Melting point: 91-92 °C.

**\(^1\)H NMR (400 MHz, DMSO-\(d_6\)):** \(\delta\) 8.06-8.02 (m, 3H), 7.56 (dd, \(J = 5.1, 1.9\) Hz, 3H), 7.37 (d, \(J = 3.5\) Hz, 1H), 6.79 (dd, \(J = 3.5, 1.8\) Hz, 1H), 3.85 (s, 3H).

**\(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)):** \(\delta\) 162.26, 154.23, 152.27, 146.82, 141.53, 131.02, 129.02, 128.73, 127.76, 126.69, 113.99, 113.03, 52.47.

**FT-IR:** 3115.80, 2951.30, 1720.40, 1625.84, 1493.27, 1357.05, 1214.34, 1113.37, 1012.37, 765.45.

**HRMS (ESI):** calcd for C\(_{15}\)H\(_{11}\)NO\(_4\) (M+H) \(^+\) = 270.0761, found 270.0758.

methyl 2-(naphthalen-2-yl)-5-phenyloxazole-4-carboxylate  
(2w)

The title compound was prepared from **1w** following general procedure C, and purified by column chromatography as white solid (12.9 mg, 33%). Melting point: 95-96 °C.

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**Note:** Please ensure that all the aromatic and heterocyclic rings are correctly represented in the diagrams. The chemical structures and NMR data are critical for confirming the purity and identity of the compounds.
\[ ^1\text{H NMR (400 MHz, DMSO-}d_6\text{): } \delta 8.75 \text{ (s, 1H), 8.19-8.16 (m, 4H), 8.11 (d, } J = 8.7 \text{ Hz, 1H), 8.04-8.01 (m, 1H), 7.67-7.57 (m, 5H), 3.89 (s, 3H).} \]

\[ ^{13}\text{C NMR (100 MHz, DMSO-}d_6\text{): } \delta 162.50, 159.57, 155.01, 134.43, 133.05, 130.98, 129.44, 129.27, 129.02, 128.81, 128.34, 128.29, 128.22, 127.63, 127.06, 127.00, 123.62, 123.39, 52.45. \]

\[ \text{FT-IR: } 3054.44, 1717.88, 1563.37, 1350.65, 1221.14, 1106.55, 1010.35, 748.03. \]

\[ \text{HRMS (ESI): calcld for C}_{21}\text{H}_{15}\text{NO}_3 (M+H)^{\text{+}} = 330.1125, \text{ found 330.1125.} \]

methyl 2-(benzofuran-2-yl)-5-phenyloxazole-4-carboxylate \hspace{1cm} (2x)

The title compound was prepared from 1x following general procedure C, and purified by column chromatography as white solid (70.1 mg, 73%). Melting point: 121-122 °C.

\[ ^1\text{H NMR (500 MHz, DMSO-}d_6\text{): } \delta 8.10-8.08 \text{ (m, 2H), 7.81 (d, } J = 10.8 \text{ Hz, 2H), 7.75 (s, 1H), 7.60-7.57 (m, 3H), 7.49 (t, } J = 8.4 \text{ Hz, 1H), 7.38 (t, } J = 7.8 \text{ Hz, 1H), 3.86 (s, 3H).} \]

\[ ^{13}\text{C NMR (125 MHz, DMSO-}d_6\text{): } \delta 162.13, 155.30, 155.09, 152.14, 142.92, 131.25, 129.07, 128.88, 127.73, 127.43, 126.54, 124.60, 122.99, 112.25, 109.78, 52.57. \]

\[ \text{FT-IR: } 3434.34, 2952.29, 2377.04, 1718.62, 1621.04, 1491.29, 1357.49, 1217.20, 1094.89, 1217.20, 723.56. \]

\[ \text{HRMS (ESI): calcld for C}_{19}\text{H}_{13}\text{NO}_4 (M+H)^{\text{+}} = 320.0917, \text{ found 320.0917.} \]

methyl 2-(benzo[b]thiophen-2-yl)-5-phenyloxazole-4-carboxylate \hspace{1cm} (2y)

The title compound was prepared from 1y following general procedure C, and purified by column chromatography as white solid (78.7 mg, 78%). Melting point: 152-153 °C.
$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 8.28 (s, 1H), 8.13-8.09 (m, 3H), 8.01 (d, $J = 7.0$ Hz, 1H), 7.61-7.58 (m, 3H), 7.50 (m, 2H), 3.87 (s, 3H).

$^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta$ 162.18, 155.66, 155.11, 140.40, 139.61, 131.20, 129.06, 128.86, 127.98, 127.11, 126.80, 126.67, 125.86, 125.59, 123.35, 52.55.

FT-IR: 3052.85, 2947.65, 1716.72, 1602.33, 1556.42, 1495.00, 1322.09, 1218.62, 1087.72, 747.32.

HRMS (ESI): calcd for C$_{19}$H$_{13}$NO$_3$S (M+H)$^+$ = 336.0689, found 336.0683.

**methyl 2-methyl-5-phenyloxazole-4-carboxylate (2z)**

![methyl 2-methyl-5-phenyloxazole-4-carboxylate](image)

The title compound was prepared from 1z following general procedure C, and purified by column chromatography as white solid (25.5 mg, 39%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 7.97-7.91 (m, 2H), 7.52 (m, 3H), 3.80 (s, 3H).

$^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta$ 162.52, 160.45, 154.67, 130.66, 128.96, 128.46, 127.14, 126.65, 52.25, 13.81.

HRMS (ESI): calcd for C$_{12}$H$_{11}$NO$_3$ (M+H)$^+$ = 218.0739, found 218.0570.

**ethyl 2,5-diphenyloxazole-4-carboxylate (5a)**

![ethyl 2,5-diphenyloxazole-4-carboxylate](image)

The title compound 5a was prepared as the general procedure C, and purified by column chromatography as white solid (86.5 mg, 98%). Melting point: 65-66 °C.

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.10 (t, $J = 3.7, 3.5$ Hz, 4H), 7.58 (m, 3H), 4.34 (q, $J = 7.1$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 161.96, 159.45, 154.79, 131.79, 130.90, 129.69, 128.93, 128.87, 128.29, 127.05, 126.88, 126.35, 61.33, 14.49.
FT-IR: 3060.56, 2974.48, 1722.56, 1557.87, 1372.75, 1215.64, 1090.15, 708.36.

HRMS (ESI): calcd for C_{18}H_{15}NO_{3} (M+H) \textsuperscript{+} = 294.1125, found 294.1126.

**propyl 2,5-diphenyloxazole-4-carboxylate (5b)**

![Propyl 2,5-diphenyloxazole-4-carboxylate](image)

The title compound 5b was prepared as the general procedure C, and purified by column chromatography as white solid (79.4 mg, 85%). Melting point: 75-76 °C.

\textbf{\textsuperscript{1}H NMR (500 MHz, DMSO-\textsubscript{d6})}: \(\delta\) 8.11-8.07 (m, 4H), 7.59 (dd, \(J = 5.2, 1.8\) Hz, 3H), 7.56 (dd, \(J = 5.3, 1.8\) Hz, 3H), 4.24 (t, \(J = 6.7\) Hz, 2H), 1.69 (q, \(J = 7.0\) Hz, 2H), 0.91 (t, \(J = 7.4\) Hz, 3H).

\textbf{\textsuperscript{13}C NMR (125 MHz, DMSO-\textsubscript{d6})}: \(\delta\) 162.01, 159.49, 154.81, 131.81, 130.91, 129.71, 128.94, 128.92, 128.29, 127.08, 126.88, 126.35, 66.74, 21.93, 10.75.

FT-IR: 2967.90, 2933.06, 1723.83, 1566.27, 1486.01, 1199.72, 1102.61, 714.89, 698.55.

HRMS (ESI): calcd for C_{19}H_{17}NO_{3} (M+H) \textsuperscript{+} = 308.1281, found 308.1275.

**isopropyl 2,5-diphenyloxazole-4-carboxylate (5c)**

![Isopropyl 2,5-diphenyloxazole-4-carboxylate](image)

The title compound 5c was prepared as the general procedure C, and purified by column chromatography as white solid (76.8 mg, 83%). Melting point: 77-78 °C.

\textbf{\textsuperscript{1}H NMR (500 MHz, DMSO-\textsubscript{d6})}: \(\delta\) 8.11-8.06 (m, 4H), 7.60 (dd, \(J = 5.2, 1.8\) Hz, 1H), 7.58-7.53 (m, 3H), 5.18 (m, 1H), 1.31 (d, \(J = 6.3\) Hz, 6H).

\textbf{\textsuperscript{13}C NMR (125 MHz, DMSO-\textsubscript{d6})}: \(\delta\) 161.46, 159.48, 154.69, 131.80, 130.89, 129.72, 129.01, 128.90, 128.55, 127.11, 126.90, 126.37, 69.09, 22.02.
FT-IR: 3068.64, 2976.78, 1702.90, 1560.66, 1491.07, 1385.50, 1368.60, 1222.09, 1097.28, 1006.05, 705.91, 688.97.

HRMS (ESI): calcd for C_{19}H_{17}NO_3 (M+H)^+ = 308.1281, found 308.1287.

benzyl 2,5-diphenyloxazole-4-carboxylate (5d)

The title compound 5d was prepared as the general procedure C, and purified by column chromatography as white solid (79.4 mg, 75%). Melting point: 84-85 °C.

^1H NMR (400 MHz, DMSO-d_6): δ 8.11-8.07 (m, 4H), 7.59 (dd, J = 5.2, 2.0 Hz, 3H), 7.52 (dd, J = 5.2, 2.0 Hz, 3H), 7.45 (dd, J = 8.1, 1.5 Hz, 2H), 7.43-7.37 (m, 3H), 5.38 (s, 2H).

^13C NMR (100 MHz, DMSO-d_6): δ 161.84, 159.52, 155.08, 136.10, 131.81, 130.93, 129.68, 128.94, 128.90, 128.71, 128.08, 126.91, 126.30, 66.82.

FT-IR: 3033.08, 1708.05, 1564.28, 1489.25, 1453.67, 1219.60, 1106.61, 1007.21, 687.61.

HRMS (ESI): calcd for C_{23}H_{17}NO_3 (M+H)^+ = 356.1281, found 356.1285.

butyl 2,5-diphenyloxazole-4-carboxylate (5e)

The title compound 5e was prepared as the general procedure C, and purified by column chromatography as white solid (78.9 mg, 82%). Melting point: 74-75 °C.

^1H NMR (400 MHz, DMSO-d_6): δ 8.11-8.06 (m, 4H), 7.61-7.55 (m, 6H), 4.29 (t, J = 6.6 Hz, 2H), 1.66 (p, J = 6.8 Hz, 2H), 1.34 (h, J = 7.4 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H).

^13C NMR (100 MHz, DMSO-d_6): δ 161.99, 159.50, 154.80, 154.80, 131.79, 130.88, 129.70, 128.92, 128.31, 127.10, 126.87, 126.36, 64.99, 30.54, 19.11, 13.99.
**FT-IR:** 2997.31, 1584.98, 1491.00, 1353.07, 1211.62, 1095.94, 710.35.

**HRMS (ESI):** calcd for C\textsubscript{20}H\textsubscript{19}NO\textsubscript{3} (M+H)\textsuperscript{+} = 322.1483, found 322.1445.

methyl 2,5-diphenylfuran-3-carboxylate \hspace{1cm} (7)

\[ \text{The title compound 7 was prepared as the general procedure C, and purified by column chromatography as white solid (56.5 mg, 68%).} \]

\[ \text{\textbf{\textsuperscript{1}H NMR (500 MHz, DMSO-}d\textsubscript{6})\hspace{0.5cm}: \delta 8.07-8.02 (m, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.54-7.44 (m, 5H), 7.37 (d, J = 5.2 Hz, 2H), 3.80 (s, 3H).} \]

\[ \text{\textbf{\textsuperscript{13}C NMR (125 MHz, DMSO-}d\textsubscript{6})\hspace{0.5cm}: \delta 163.59, 155.98, 152.47, 130.08, 129.46, 128.85, 128.82, 128.44, 124.38, 115.74, 108.65, 52.22.} \]

methyl 5-(3-methoxyphenyl)-2-phenylfuran-3-carboxylate \hspace{1cm} (7a)

\[ \text{The title compound 7a was prepared as the general procedure C, and purified by column chromatography as white solid (50.8 mg, 75%).} \]

\[ \text{\textbf{\textsuperscript{1}H NMR (500 MHz, DMSO-}d\textsubscript{6})\hspace{0.5cm}: \delta 7.86 (d, J = 7.2 Hz, 2H), 7.71-7.68 (m, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.43 (t, J = 8.0 Hz, 1H), 7.40-7.35 (m, 2H), 7.08-7.03 (m, 1H), 3.83 (s, 3H), 3.81 (s, 3H).} \]

\[ \text{\textbf{\textsuperscript{13}C NMR (125 MHz, DMSO-}d\textsubscript{6})\hspace{0.5cm}: \delta 163.60, 159.48, 155.59, 152.38, 130.59, 129.46, 129.42, 128.86, 124.41, 120.62, 115.95, 115.86, 113.76, 108.78, 55.68, 52.26.} \]

methyl 5-(3-chlorophenyl)-2-phenylfuran-3-carboxylate \hspace{1cm} (7b)
The title compound 7b was prepared as the general procedure C, and purified by column chromatography as white solid (34.6 mg, 47%).

**1H NMR (500 MHz, DMSO-$_d_6$):** $\delta$ 8.00-7.95 (m, 1H), 7.93 (d, $J = 8.3$ Hz, 1H), 7.91-7.85 (m, 2H), 7.59-7.53 (m, 1H), 7.48 (t, $J = 7.7$ Hz, 2H), 7.40 (s, 1H), 7.37 (d, $J = 7.4$ Hz, 1H), 7.35-7.30 (m, 1H), 3.83 (s, 3H).

**13C NMR (125 MHz, DMSO-$_d_6$):** $\delta$ 154.19, 152.83, 129.45, 129.25, 129.03, 124.54, 124.35, 124.33, 116.66, 115.10, 114.90, 108.83, 52.38.

**HRMS (ESI):** calcld for C$_{17}$H$_{13}$NO$_2$S (M+H)$^+$ = 296.0667, found 296.0538.

The title compound 9 was prepared as the general procedure C, and purified by column chromatography as white solid (62.8 mg, 71%).

**1H NMR (500 MHz, DMSO-$_d_6$):** $\delta$ 7.98 (s, 2H), 7.56 (s, 5H), 7.50-7.46 (m, 3H), 3.76 (s, 3H).

**13C NMR (125 MHz, DMSO-$_d_6$):** $\delta$ 165.48, 162.57, 145.63, 140.95, 132.53, 131.45, 130.16, 130.07, 129.88, 129.84, 128.92, 126.75, 52.47.

**HRMS (ESI):** calcld for C$_{17}$H$_{13}$NO$_2$S (M+H)$^+$ = 296.0667, found 296.0538.

The title compound 9a was prepared as the general procedure C, and purified by column chromatography as white solid (53.8 mg, 78%).
**1H NMR (500 MHz, DMSO-\textit{d}_6):** δ 7.80 (d, \(J = 7.5\) Hz, 1H), 7.62-7.57 (m, 2H), 7.51-7.46 (m, 3H), 7.45-7.35 (m, 3H), 3.75 (s, 3H), 2.61 (s, 3H).

**13C NMR (125 MHz, DMSO-\textit{d}_6):** δ 165.15, 162.69, 145.96, 140.34, 136.53, 132.19, 131.81, 130.69, 130.13, 130.08, 130.06, 129.78, 128.91, 127.01, 52.47, 21.59.

**HRMS (ESI):** calcd for C\textsubscript{18}H\textsubscript{15}NO\textsubscript{2}S (M+H) \(=\) 310.0857, found 310.0899.

**methyl 2-(4-fluorophenyl)-5-phenylthiazole-4-carboxylate** (9b)

The title compound 9b was prepared as the general procedure C, and purified by column chromatography as white solid (38.5 mg, 38%).

**1H NMR (500 MHz, DMSO-\textit{d}_6):** δ 8.04 (dd, \(J = 8.7, 5.3\) Hz, 2H), 7.60-7.55 (m, 2H), 7.52-7.47 (m, 3H), 7.40 (t, \(J = 8.8\) Hz, 2H), 3.75 (s, 3H).

**13C NMR (125 MHz, DMSO-\textit{d}_6):** δ 164.28, 164.04 (d, \(J = 247.5\) Hz), 162.50, 145.75, 140.91, 130.08, 129.87, 129.22, 129.15, 128.92, 117.03, 116.86, 52.48.

**HRMS (ESI):** calcd for C\textsubscript{17}H\textsubscript{12}FNO\textsubscript{2}S (M+H) \(=\) 314.0606, found 314.0647.

**methyl 2-phenyl-5-(p-tolyl)thiazole-4-carboxylate** (9c)

The title compound 9c was prepared as the general procedure C, and purified by column chromatography as white solid (47.3 mg, 61%).

**1H NMR (500 MHz, DMSO-\textit{d}_6):** δ 7.99-7.92 (m, 2H), 7.54 (s, 3H), 7.45 (d, \(J = 5.6\) Hz, 2H), 7.28 (d, \(J = 5.2\) Hz, 2H), 3.76 (s, 3H), 2.37 (s, 3H).

**13C NMR (125 MHz, DMSO-\textit{d}_6):** δ 165.10, 162.67, 145.79, 140.67, 139.56, 132.58, 131.35, 129.94, 129.83, 129.48, 127.22, 126.70, 52.43, 21.34.

**HRMS (ESI):** calcd for C\textsubscript{18}H\textsubscript{15}NO\textsubscript{2}S (M+H) \(=\) 310.0857, found 310.0892.
methyl 5-(4-nitrophenyl)-2-phenylthiazole-4-carboxylate  \( \text{9d} \)

The title compound \( \text{9d} \) was prepared as the general procedure C, and purified by column chromatography as white solid (66.5 mg, 75%).

**1H NMR (500 MHz, DMSO-\( d_6 \)):** \( \delta \) 8.33 (d, \( J = 8.8 \) Hz, 2H), 8.02 (dd, \( J = 6.4, 3.1 \) Hz, 2H), 7.89 (d, \( J = 8.8 \) Hz, 2H), 7.61-7.56 (m, 3H), 3.78 (s, 3H).

**13C NMR (125 MHz, DMSO-\( d_6 \)):** \( \delta \) 166.76, 162.17, 148.13, 143.01, 142.17, 137.06, 132.28, 131.80, 131.68, 129.97, 126.90, 123.91, 52.68.

**HRMS (ESI):** calcd for \( \text{C}_{17}\text{H}_{12}\text{N}_{2}\text{O}_{4}\text{S} \) (M+H) \( ^+ \)= 341.0551, found 341.0593.
IV. Copies of $^1$H and $^{13}$C NMR spectra of products

methyl 2,5-diphenyloxazole-4-carboxylate (2a)

400MHz $^1$H in DMSO-$d_6$

100MHz $^{13}$C in DMSO-$d_6$
methyl 2-(4-methoxyphenyl)-5-phenyloxazole-4-carboxylate \( \text{(2b)} \)

400MHz \(^1\)H in DMSO-\(d6\)

100MHz \(^{13}\)C in DMSO-\(d6\)
methyl 2-(4-(tert-butyl)phenyl)-5-phenyloxazole-4-carboxylate (2c)

400MHz $^1$H in DMSO-$d_6$

$^1$H NMR spectrum showing the chemical shifts for the compound.

100MHz $^{13}$C in DMSO-$d_6$

$^{13}$C NMR spectrum showing the chemical shifts for the compound.
methyl 5-phenyl-2-(p-tolyl)oxazole-4-carboxylate (2d)

400MHz $^1$H in DMSO-$d_6$

100MHz $^{13}$C in DMSO-$d_6$
methyl 5-phenyl-2-(3,4,5-trimethoxyphenyl)oxazole-4-carboxylate \( (2e) \)

**400MHz \(^1\)H in DMSO-\(d_6\)**

![400MHz 1H NMR](image_url)

**100MHz \(^{13}\)C in DMSO-\(d_6\)**

![100MHz 13C NMR](image_url)
methyl 2-(3,5-dimethoxyphenyl)-5-phenyloxazole-4-carboxylate (2f)

400MHz $^1$H in DMSO-$d_6$

100MHz $^{13}$C in DMSO-$d_6$
methyl 2-(4-chlorophenyl)-5-phenyloxazole-4-carboxylate (2g)

400MHz $^1$H in DMSO-$d_6$

100MHz $^{13}$C in DMSO-$d_6$
methyl 2-(4-nitrophenyl)-5-phenyloxazole-4-carboxylate (2h)

500MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$
methyl 5-phenyl-2-(4-(trifluoromethyl)phenyl)oxazole-4-carboxylate (2i)

**400MHz $^1$H in DMSO-$d_6$**

**125MHz $^{13}$C in DMSO-$d_6$**
methyl 2-(4-fluorophenyl)-5-phenyloxazole-4-carboxylate (2j)

400MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$
methyl 2-(4-bromophenyl)-5-phenyloxazole-4-carboxylate \( (2k) \)

500MHz \(^1\)H in DMSO-\(d_6\)

125MHz \(^1\)C in DMSO-\(d_6\)
methyl 2-(3-methoxyphenyl)-5-phenyloxazole-4-carboxylate

500MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$
methyl 2-(3-nitrophenyl)-5-phenyloxazole-4-carboxylate (2m)

500MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$
methyl 2-(3-chlorophenyl)-5-phenyloxazole-4-carboxylate (2n)

500MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$
methyl 2-(2-fluorophenyl)-5-phenyloxazole-4-carboxylate  

(2o)  

500MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$
methyl 2-(2-chlorophenyl)-5-phenyloxazole-4-carboxylate \((2p)\)

500MHz \(^1\)H in DMSO-\(d_6\)

125MHz \(^1\)C in DMSO-\(d_6\)
methyl 2-(2-methoxyphenyl)-5-phenyloxazole-4-carboxylate (2q)

500MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$
methyl 5-phenyl-2-(m-tolyl)oxazole-4-carboxylate (2r)

500MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$
methyl 2-phenyl-5-(p-tolyl)oxazole-4-carboxylate \hspace{1cm} (2s)

500MHz $^1$H in DMSO-\textit{d}6

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{spectrum1}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{spectrum2}
\end{figure}

methyl 5-(4-nitrophenyl)-2-phenyloxazole-4-carboxylate \hspace{1cm} (2t)
500MHz $^1$H in DMSO-d$_6$

125MHz $^{13}$C in DMSO-d$_6$

methyl 5-phenyl-2-(thiophen-2-yl)oxazole-4-carboxylate (2u)
500MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$

methyl 2-(furan-2-yl)-5-phenyloxazole-4-carboxylate  

(2v)
400MHz $^1$H in DMSO-$d_6$

100MHz $^{13}$C in DMSO-$d_6$

methyl 2-(naphthalen-2-yl)-5-phenyloxazole-4-carboxylate (2w)
400MHz $^1$H in DMSO-$d_6$

100MHz $^{13}$C in DMSO-$d_6$

methyl 2-(benzofuran-2-yl)-5-phenyloxazole-4-carboxylate (2x)
500MHz ¹H in DMSO-d6

125MHz ¹³C in DMSO-d6

methyl 2-(benzo[b]thiophen-2-yl)-5-phenyloxazole-4-carboxylate  (2y)
500MHz $^1$H in DMSO-$d_6$

![NMR Spectrum](image)

125MHz $^{13}$C in DMSO-$d_6$

![NMR Spectrum](image)

methyl 2-methyl-5-phenyloxazole-4-carboxylate (2z)
500MHz $^1$H in DMSO-d$_6$

125MHz $^{13}$C in DMSO-d$_6$

ethyl 2,5-diphenyloxazole-4-carboxylate \( (5a) \)
400MHz $^1$H in DMSO-$d_6$

100MHz $^{13}$C in DMSO-$d_6$

propyl 2,5-diphenyloxazole-4-carboxylate  

(5b)
500MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$

isopropyl 2,5-diphenyloxazole-4-carboxylate (5c)
500MHz $^1$H in DMSO-$d_6$

benzyl 2,5-diphenyloxazole-4-carboxylate (5d)
400MHz $^1$H in DMSO-$d_6$

100MHz $^{13}$C in DMSO-$d_6$

butyl 2,5-diphenyloxazole-4-carboxylate (5e)
400MHz $^1$H in DMSO-$d_6$

100MHz $^{13}$C in DMSO-$d_6$

methyl 2,5-diphenylfuran-3-carboxylate (7)
500MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$

methyl 5-(3-methoxyphenyl)-2-phenylfuran-3-carboxylate (7a)
**500MHz $^1$H in DMSO-$d_6$**

**125MHz $^{13}$C in DMSO-$d_6$**

methyl 5-(3-chlorophenyl)-2-phenylfuran-3-carboxylate (7b)
500MHz $^1$H in DMSO-$d_6$

![NMR spectrum of methyl 2,5-diphenylthiazole-4-carboxylate (9)](image)

125MHz $^{13}$C in DMSO-$d_6$

![NMR spectrum of methyl 2,5-diphenylthiazole-4-carboxylate (9)](image)
methyl 5-phenyl-2-(o-tolyl)thiazole-4-carboxylate (9a)
methyl 2-(4-fluorophenyl)-5-phenylthiazole-4-carboxylate (9b)
500MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$
methyl 2-phenyl-5-(p-tolyl)thiazole-4-carboxylate (9c)

500MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$
methyl 5-(4-nitrophenyl)-2-phenylthiazole-4-carboxylate (9d)

500MHz $^1$H in DMSO-$d_6$

125MHz $^{13}$C in DMSO-$d_6$
V. Reference

1. Jursic, Branko S.; Sagiraju, Sarada; Ancalade, Dustin K.; Clark, Traneil; Stevens, Edwin D. Synthetic Communications. *2007*, 37, 1709-1714.