Supporting Information

for

Halodifluoroacetates as Formylation Reagents with Various Amines via Unprecedented Quadruple Cleavage

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1. **General information**

All chemicals were purchased from Adamas Reagent, energy chemical company, J&K Scientific Ltd, Bide Pharmatech Ltd and Tansoole. Unless otherwise stated, all experiments were conducted in a sealed tube under N\textsubscript{2} atmosphere. CH\textsubscript{3}CN was a optional solvent. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

\textsuperscript{1}H-NMR and \textsuperscript{13}C-NMR spectra were recorded in CDCl\textsubscript{3} on a Bruker Avance 500 spectrometer (500 MHz \textsuperscript{1}H, 125 MHz \textsuperscript{13}C, 470 MHz \textsuperscript{19}F) at room temperature. Chemical shifts were reported in ppm on the scale relative to CDCl\textsubscript{3} (\(\delta = 7.26\) for \textsuperscript{1}H-NMR, \(\delta = 77.00\) for \textsuperscript{13}C-NMR) as an internal reference. Coupling constants (\(J\)) were reported in Hertz (Hz).
2. Optimization of experiment conditions for 3

Table S1. Optimization of the bases

<table>
<thead>
<tr>
<th>entry</th>
<th>base</th>
<th>solvent</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K₂CO₃</td>
<td>CH₃CN</td>
<td>86</td>
</tr>
<tr>
<td>2</td>
<td>NaHCO₃</td>
<td>CH₃CN</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>K₃PO₄</td>
<td>CH₃CN</td>
<td>78</td>
</tr>
<tr>
<td>4</td>
<td>Na₃PO₄</td>
<td>CH₃CN</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>Cs₂CO₃</td>
<td>CH₃CN</td>
<td>76</td>
</tr>
<tr>
<td>6</td>
<td>t-BuOK</td>
<td>CH₃CN</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
<td>KOAc</td>
<td>CH₃CN</td>
<td>57</td>
</tr>
<tr>
<td>8</td>
<td>NaOH</td>
<td>CH₃CN</td>
<td>65</td>
</tr>
<tr>
<td>9</td>
<td>Na₂CO₃</td>
<td>CH₃CN</td>
<td>&gt;99 (96)</td>
</tr>
</tbody>
</table>

Reaction condition: a N-Methyl aniline (1a) (0.2 mmol), ethyl bromodifluoroacetate (2) (1.5 equiv), base (2 equiv), CH₃CN (1.5 mL) under N₂ atmosphere at 100 °C for 16 h. b GC yield. c Isolated yield.

Table S2. Optimization of the solvent

<table>
<thead>
<tr>
<th>entry</th>
<th>base</th>
<th>solvent</th>
<th>yield (%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Na₂CO₃</td>
<td>THF</td>
<td>89</td>
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<td>2</td>
<td>Na₂CO₃</td>
<td>DCE</td>
<td>78</td>
</tr>
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<td>3</td>
<td>Na₂CO₃</td>
<td>dioxane</td>
<td>85</td>
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<tr>
<td>4</td>
<td>Na₂CO₃</td>
<td>DMF</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>Na₂CO₃</td>
<td>DMSO</td>
<td>trace</td>
</tr>
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<td>6</td>
<td>Na₂CO₃</td>
<td>toluene</td>
<td>67</td>
</tr>
<tr>
<td>7</td>
<td>Na₂CO₃</td>
<td>H₂O</td>
<td>55</td>
</tr>
<tr>
<td>8</td>
<td>Na₂CO₃</td>
<td>CH₃OH</td>
<td>69</td>
</tr>
<tr>
<td>9</td>
<td>Na₂CO₃</td>
<td>CH₃CN</td>
<td>&gt;99 (96)</td>
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<tr>
<td>10</td>
<td>Na₂CO₃</td>
<td>hexane</td>
<td>77</td>
</tr>
</tbody>
</table>

Reaction condition: a N-Methyl aniline (1a) (0.2 mmol), ethyl bromodifluoroacetate (2) (1.5 equiv), base (2 equiv), solvent (1.5 mL) under N₂ atmosphere at 100 °C for 16 h. b GC yield. c Isolated yield.
3. Crystal data of 3t

Crystallographic data for compound 3t (CCDC-1820711) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email: deposit@ccdc.cam.ac.uk).
4. Optimization of experiment conditions for C source of 3

Table S4. Screening of the different difluoromethyl compounds for 3

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BrCF₂COOEt</td>
<td>96⁺</td>
</tr>
<tr>
<td>2</td>
<td>BrCHFCOOEt</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>CF₂COOEt</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>ClCF₂COONa</td>
<td>62</td>
</tr>
<tr>
<td>5</td>
<td>BrCF₂P(O)(OEt)₂</td>
<td>54</td>
</tr>
<tr>
<td>6</td>
<td>BrCF₂C(O)NR₁R²</td>
<td>trace-32⁺</td>
</tr>
</tbody>
</table>

Reaction condition: 1 (0.2 mmol), substrate C source (1.5 equiv), Na₂CO₃ (2 equiv), GC yield. ⁺isolated yield, ⁺R¹ = R² = cyclohexyl (32%); R¹ = H, R² = Ph (trace); R¹(R²) = pyrrolidinly (trace); R²(R¹) = piperazinly (trace).

5. Optimization of experiment conditions for 6

Table S5. Screening of the different difluoromethyl compounds for 6

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BrCF₂COOEt</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td>BrCHFCOOEt</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>CF₂COOEt</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>ClCF₂COONa</td>
<td>88⁺</td>
</tr>
<tr>
<td>5</td>
<td>BrCF₂P(O)(OEt)₂</td>
<td>51</td>
</tr>
<tr>
<td>6</td>
<td>BrCF₂C(O)NR₁R²</td>
<td>trace-43⁺</td>
</tr>
</tbody>
</table>

Reaction condition: 1 (0.2 mmol), substrate C source (1.5 equiv), Na₂CO₃ (2 equiv), GC yield. ⁺isolated yield, ⁺R¹ = R² = cyclohexyl (43%); R¹ = H, R² = Ph (trace); R¹(R²) = pyrrolidinly (trace); R²(R¹) = piperazinly (trace).
6. General process for the synthesis of 3 and 6

\[
\begin{align*}
\text{R}^1 & \quad \text{X} \\
\text{N} \quad \text{R}^2 & + \\
\text{R}^1 \quad \text{N} \quad \text{R}^2
\end{align*}
\]

In a dried Schlenk tube were placed 1 (0.2 mol, 1 equiv), Na$_2$CO$_3$ (0.4 mol, 2 equiv), B$_2$pin$_2$ (0 - 0.1 equiv). 2 or 5 (0.3 mmol, 1.5 equiv) and solvent is added to the mixture under N$_2$ atmosphere. The resulting mixture was stirred at 100 °C for 16 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 50:1, v/v) to give the desired product 3 or 6.

7. Control experiments of mechanistic studies

\[
\begin{align*}
\text{R}^1 \text{N} \quad \text{R}^2 & + \\
\text{R}^1 \text{N} \quad \text{R}^2
\end{align*}
\]

1a 0.2 mmol 2 equiv 2 1.5 equiv

90% (GC yield)

1a 0.2 mmol 2 equiv 2 1.5 equiv

88% (GC yield)

1a 0.2 mmol 2 1.5 equiv

93% (83%) (GC yield)
Mechanistic studies

8. General process for the synthesis of 16

In a dried Schlenk tube were placed 15 (0.2 mol, 1 equiv), Na₂CO₃ (0.4 mol, 2 equiv), DMAP (50 mmol%), 2 (0.3 mmol, 1.5 equiv) and solvent is added the mixture under N₂ atmosphere. The resulting mixture was stirred at 100 °C for 16 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 50:1, v/v) to give the desired product 16 in 38% yield.
9. Characterization data for products

**N-methyl-N-phenylformamide (3a)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (20:1). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.48 (s, 1H), 7.44 – 7.39 (m, 2H), 7.28 (ddt, $J$ = 8.6, 7.1, 1.1 Hz, 1H), 7.19 – 7.13 (m, 2H), 3.34 – 3.26 (m, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.2, 142.1, 129.5, 126.3, 122.3, 31.9.

**N-methyl-N-(p-tolyl)formamide (3b)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a white solid (20:1). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.41 (s, 1H), 7.22 – 7.18 (m, 2H), 7.05 (d, $J$ = 8.3 Hz, 2H), 3.28 (s, 3H), 2.35 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.3, 139.6, 136.3, 130.1, 122.5, 32.2, 20.8.

**N-(4-methoxyphenyl)-N-methylformamide (3c)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (10:1). $^1$H NMR (500 MHz, DMSO) δ 8.35 (s, 1H), 7.26 (d, $J$ = 9.0 Hz, 2H), 6.98 (d, $J$ = 9.0 Hz, 2H), 3.76 (s, 3H), 3.16 (s, 3H). $^{13}$C NMR (125 MHz, DMSO) δ 162.4, 157.9, 135.6, 124.3, 115.0, 55.8, 32.1.

**N-(4-chlorophenyl)-N-methylformamide (3d)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (25:2). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.42 (s, 1H), 7.38 – 7.33 (m, 2H), 7.12 – 7.03 (m, 2H), 3.27 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.9, 140.7, 131.9, 129.7, 123.4, 32.0.

**N-(4-bromophenyl)-N-methylformamide (3e)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as a white solid (50:7). $^1$H NMR (500 MHz, DMSO) δ
8.55 (s, 3H), 7.59 (d, \( J = 8.9 \) Hz, 7H), 7.32 (d, \( J = 8.9 \) Hz, 6H), 3.20 (s, 9H). \(^{13}\)C NMR (125 MHz, DMSO) \( \delta \) 162.4, 141.9, 132.6, 123.8, 118.3, 31.3.

\( N-(4\text{-fluorophenyl})-N\text{-methylformamide (3f)} \)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as a yellow oil (20:3). \(^1\)H NMR (500 MHz, DMSO) \( \delta \) 8.44 (s, 1H), 7.51 – 7.36 (m, 2H), 7.25 (t, \( J = 8.8 \) Hz, 2H), 3.19 (s, 3H). \(^{13}\)C NMR (125 MHz, DMSO) \( \delta \) 162.5, 160.4 (d, \( J = 241.3 \) Hz) 138.98 (d, \( J = 2.7 \) Hz), 124.45 (d, \( J = 7.7 \) Hz), 116.54 (d, \( J = 22.5 \) Hz), 31.9.

\( N\text{-methyl-}N\text{-}(m\text{-tolyl})\text{formamide (3g)} \)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (20:1). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.45 (s, 1H), 7.28 (t, \( J = 7.6 \) Hz, 1H), 7.08 (d, \( J = 7.4 \) Hz, 1H), 6.96 (d, \( J = 7.7 \) Hz, 2H), 3.29 (s, 3H), 2.38 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 162.3, 142.1, 139.6, 129.3, 127.1, 123.1, 119.4, 32.1, 21.4.

\( N-(3\text{-chlorophenyl})-N\text{-methylformamide (3h)} \)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (20:3). \(^1\)H NMR (500 MHz, DMSO) \( \delta \) 8.59 (s, 1H), 7.69 (t, \( J = 1.9 \) Hz, 1H), 7.46 (dt, \( J = 16.1, 5.1 \) Hz, 2H), 7.31 (dd, \( J = 15.5, 8.0 \) Hz, 2H), 3.21 (s, 3H). \(^{13}\)C NMR (125 MHz, DMSO) \( \delta \) 162.6, 144.0, 134.3, 131.4, 125.7, 121.5, 120.2, 31.3.

\( N-(3\text{-bromophenyl})-N\text{-methylformamide (3i)} \)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (20:3). \(^1\)H NMR (500 MHz, DMSO) \( \delta \) 8.57 (s, 1H), 7.83 – 7.57 (m, 1H), 7.53 – 7.34 (m, 3H), 3.20 (s, 3H). \(^{13}\)C NMR (125 MHz, DMSO) \( \delta \) 162.6, 144.2, 131.6, 128.7, 124.3, 122.7, 120.7, 31.3.

\( N\text{-methyl-}N\text{-}(o\text{-tolyl})\text{formamide (3j)} \)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as a yellow oil (10:3). \(^1\)H NMR (500 MHz, DMSO) \( \delta \) 8.07 (s, 6H), 7.38 – 7.21 (m, 31H), 7.18 (dd, \( J = 5.2, 4.0 \) Hz, 2H), 3.09 (s, 19H), 2.21 (s, 19H).
$^{13}$C NMR (125 MHz, DMSO) δ 163.0, 141.2, 135.5, 131.7, 128.5, 128.2, 127.6, 33.0, 17.8.

$N$-(2-fluorophenyl)-$N$-methylformamide (3k)$^6$
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (22:5). $^1$H NMR (500 MHz, DMSO) δ 8.26 (d, $J = 2.4$ Hz, 1H), 7.47 (td, $J = 8.0$, 1.5 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.34 – 7.24 (m, 2H), 3.16 (d, $J = 0.7$ Hz, 3H). $^{13}$C NMR (125 MHz, DMSO) δ 163.2, 157.0 (d, $J = 245$ Hz), 130.0 (d, $J = 113.0$ Hz), 129.4 (d, $J = 8.8$ Hz), 128.2, 125.8, 117.2 (d, $J = 20$ Hz), 32.8.

$N$-benzyl-$N$-phenylformamide (3l)$^5$
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (25:3). $^1$H NMR (500 MHz, DMSO) δ 8.67 (s, 1H), 7.39 – 7.17 (m, 10H), 5.04 (s, 2H). $^{13}$C NMR (125 MHz, DMSO) δ 162.9, 141.2, 137.4, 129.9, 128.9, 127.7, 127.5, 126.5, 123.2, 47.1.

$N$-ethyl-$N$-phenylformamide (3m)$^4$
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (50:3). $^1$H NMR (500 MHz, DMSO) δ 8.32 (s, 1H), 7.40 – 7.35 (m, 2H), 7.26 (t, $J = 6.9$ Hz, 1H), 7.21 – 7.05 (m, 2H), 3.83 (q, $J = 7.2$ Hz, 2H), 1.13 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.9, 140.7, 129.5, 126.7, 124.1, 39.9, 12.9.

$N$-isopropyl-$N$-phenylformamide (3n)$^4$
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (10:3). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.29 (s, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 6.93 (d, $J = 8.0$ Hz, 2H), 3.80 (q, $J = 7.2$ Hz, 2H), 2.34 (s, 3H), 1.11 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.4, 138.9, 129.7, 128.9, 128.3, 45.8, 21.1.

$N$-ethyl-$N$-(m-tolyl)formamide (3o)$^4$
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a
yellow oil (25:2). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.45 (s, 1H), 7.28 (t, \(J = 7.6\) Hz, 1H), 7.08 (d, \(J = 7.4\) Hz, 1H), 6.96 (d, \(J = 7.7\) Hz, 2H), 3.29 (s, 3H), 2.38 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 161.9, 140.6, 139.5, 129.2, 127.4, 124.8, 121.1, 39.9, 21.2, 12.9.

\(\text{N-butyl-N-phenylformamide (3p)}\)^5

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (50:7). \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 8.40 (s, 4H), 7.48 – 7.22 (m, 23H), 3.79 (t, \(J = 7.2\) Hz, 8H), 1.44 – 1.14 (m, 21H), 0.82 (t, \(J = 7.4\) Hz, 14H). \(^{13}\)C NMR (125 MHz, DMSO) \(\delta\) 162.4, 141.2, 130.0, 126.6, 123.8, 43.4, 29.6, 19.8, 14.0.

\(\text{N-allyl-N-phenylformamide (3q)}\)^4

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (25:3). \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 8.54 (s, 1H), 7.45 – 7.31 (m, 4H), 7.30 – 7.22 (m, 1H), 5.78 (ddt, \(J = 17.2, 10.4, 5.3\) Hz, 1H), 5.12 (tq, \(J = 10.2, 1.6\) Hz, 2H), 4.40 (dt, \(J = 5.2, 1.6\) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 161.7, 137.6, 129.9, 127.4, 124.4, 117.4, 45.9, 27.1, 22.2.

\(\text{3,4-dihydroquinoline-1(2H)-carbaldehyde (3r)}\)^4

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (20:3). \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 8.84 (s, 1H), 8.20 (d, \(J = 8.3\) Hz, 1H), 7.43 – 7.34 (m, 1H), 7.25 – 7.13 (m, 2H), 7.11 – 7.02 (m, 1H), 3.73 – 3.65 (m, 2H), 2.76 (t, \(J = 6.4\) Hz, 2H), 1.83 (dt, \(J = 12.4, 6.3\) Hz, 2H). \(^{13}\)C NMR (125 MHz, DMSO) \(\delta\) 161.7, 137.6, 129.9, 128.7, 127.4, 124.4, 117.4, 45.9, 27.1, 22.2.

\(\text{3,4-dihydroisoquinoline-2(1H)-carbaldehyde (3s)}\)^4

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as a yellow oil (5:3). \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 8.17 (s, 1H), 7.36 – 6.95 (m, 4H), 4.55 (s, 2H), 3.63 (td, \(J = 6.0, 2.8\) Hz, 2H), 3.44 (s, 7H), 2.83 (t, \(J = 5.9\) Hz, 2H). \(^{13}\)C NMR (125 MHz, DMSO) \(\delta\) 162.2, 134.5, 132.6, 129.4, 127.0, 126.8, 126.4, 42.7, 41.9, 29.6.
**N-isopropyl-N-(4-(phenylamino)phenyl)formamide (3t)**

![Structure of N-isopropyl-N-(4-(phenylamino)phenyl)formamide](image)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a white solid (25:4). \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.16 (s, 1H), 7.37 – 7.23 (m, 2H), 7.19 – 6.92 (m, 7H), 4.82 (dt, \(J = 13.6, 6.8\) Hz, 1H), 1.18 (d, \(J = 6.8\) Hz, 5H). \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 162.9, 143.7, 142.2, 130.4, 129.9, 129.5, 121.9, 118.9, 116.8, 45.3, 20.9.

HRMS (EI, m/z) calcd for [C\(_{16}\)H\(_{19}\)N\(_2\)O]: 255.1497.; found: 255.1493.

**indoline-1-carbaldehyde (3u)**

![Structure of indoline-1-carbaldehyde](image)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a yellow oil (10:3). \(^{1}H\) NMR (500 MHz, DMSO) \(\delta\) 9.01 (s, 1H), 7.40 (d, \(J = 8.0\) Hz, 1H), 7.25 (d, \(J = 7.4\) Hz, 1H), 7.22 – 7.12 (m, 1H), 7.09 – 6.90 (m, 1H), 4.18 – 3.82 (t, \(J = 8.5\) Hz, 2H), 3.09 (t, \(J = 8.5\) Hz, 2H). \(^{13}C\) NMR (125 MHz, DMSO) \(\delta\) 165.4, 163.6, 146.3, 137.9, 137.0, 132.5, 132.2, 131.0, 130.4, 129.3, 128.9, 120.8, 115.1, 51.7, 49.4, 32.4, 31.8.

**N,N-dicyclohexylformamide (3v)**

![Structure of N,N-dicyclohexylformamide](image)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as a yellow oil (>20:1). \(^{1}H\) NMR (500 MHz, DMSO) \(\delta\) 8.14 (s, 1H), 3.68 (tt, \(J = 11.8, 3.4\) Hz, 1H), 3.15 (tt, \(J = 12.1, 3.7\) Hz, 1H), 1.80 – 1.61 (m, 8H), 1.61 – 1.40 (m, 6H), 1.36 – 1.15 (m, 5H), 1.14 – 1.03 (m, 2H). \(^{13}C\) NMR (126 MHz, DMSO) \(\delta\) 161.6, 54.5, 51.8, 33.7, 29.9, 25.8, 25.7, 25.1, 24.9.

**4-(4-chlorophenyl)piperazine-1-carbaldehyde (3w)**

![Structure of 4-(4-chlorophenyl)piperazine-1-carbaldehyde](image)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as a yellow oil (>20:1). \(^{1}H\) NMR (500 MHz, DMSO) \(\delta\) 8.07 (s, 1H), 7.30 – 7.19 (m, 2H), 7.09 – 6.88 (m, 2H), 3.53 – 3.47 (m, 4H), 3.16 – 2.84 (m, 4H). \(^{13}C\) NMR (126 MHz, DMSO) \(\delta\) 161.0, 149.8, 128.8, 123.2, 117.8, 49.3, 48.2, 44.6, 39.1.

HRMS (EI, m/z) calcd for [C\(_{11}\)H\(_{14}\)ClN\(_2\)O]: 255.0795.; found: 255.0790.
4-(4-methoxyphenyl)piperazine-1-carbaldehyde (3x)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as a yellow oil (>20:1). $^1$H NMR (500 MHz, DMSO) $\delta$ 8.05 (s, 1H), 6.95 – 6.87 (m, 2H), 6.86 – 6.80 (m, 2H), 3.68 (s, 3H), 3.54 – 3.47 (m, 4H), 3.03 – 2.96 (m, 2H), 2.96 – 2.90 (m, 2H). $^{13}$C NMR (125 MHz, DMSO) $\delta$ 161.0, 153.6, 145.3, 118.6, 114.4, 55.3, 51.1, 49.9, 44.9, 39.4. HRMS (EI, m/z) calcd for [C$_{12}$H$_{17}$N$_2$O$_2$]: 221.1290.; found: 221.1287.

N-phenylformamide (6a)$^1$

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.71 (s, m H), 8.41 (t, $J = 8.7$ Hz, m H), 7.62 – 7.38 (m, m H), 7.38 – 7.28 (m, m H), 7.25 – 7.10 (m, m H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 162.7, 159.1, 136.9, 136.7, 129.8, 129.1, 125.3, 124.9, 120.0, 118.8.

N-p-tolylformamide (6b)$^1$

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.36 (d, $J = 11.5$ Hz, 1H), 8.36 (d, $J = 15.7$ Hz, 1H), 7.60 – 7.48 (m, 1H), 7.42 (d, $J = 8.4$ Hz, 1H), 7.14 (dd, $J = 13.4$, 8.2 Hz, 2H), 6.99 (d, $J = 8.3$ Hz, 1H), 2.32 (d, $J = 9.2$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 162.9, 159.0, 135.2, 134.5, 134.3, 134.1, 130.2, 129.6, 120.1, 119.2, 20.9.

N-(4-ethylphenyl)formamide (6c)$^8$

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.64 (d, $J = 11.5$ Hz, 1H), 8.45 (d, $J = 9.9$ Hz, 1H), 8.33 (d, $J = 1.8$ Hz, 1H), 7.62 (s, 1H), 7.50 – 7.40 (m, 1H), 7.22 – 7.12 (m, 2H), 7.06 – 6.98 (m, 1H), 7.24 – 2.50 (m, 2H), 1.22 (q, $J = 7.6$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 163.0, 159.1, 141.6, 140.9, 134.5, 134.3, 129.1, 128.4, 120.2, 119.2, 28.3, 15.7.
**N-(4-isopropylphenyl)formamide (6d)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.64 (d, $J = 11.5$ Hz, 1H), 8.44 (d, $J = 10.2$ Hz, 1H), 8.34 (d, $J = 1.8$ Hz, 1H), 7.58 (s, 1H), 7.51 – 7.41 (m, 1H), 7.25 – 7.13 (m, 2H), 7.06 – 6.97 (m, 1H), 3.13 – 2.67 (m, 1H), 1.23 (t, $J = 6.8$ Hz, 6H).

**N-(4-(tert-butyl)phenyl)formamide (6e)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.65 (d, $J = 11.5$ Hz, 1H), 8.35 (d, $J = 1.8$ Hz, 1H), 8.30 (d, $J = 10.4$ Hz, 1H), 7.51 (s, 1H), 7.49 – 7.44 (m, 1H), 7.41 – 7.32 (m, 2H), 7.10 – 6.99 (m, 1H), 1.31 (d, $J = 6.2$ Hz, 9H).

**N-(4-methoxyphenyl)formamide (6f)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.41 (dd, $J = 93.2$, 6.6 Hz, 1H), 7.87 (d, $J = 8.6$ Hz, 1H), 7.48 – 7.39 (m, 1H), 7.28 (s, 1H), 7.07 – 6.98 (m, 1H), 6.94 – 6.83 (m, 2H), 3.80 (d, $J = 6.5$ Hz, 3H).

**N-(4-fluorophenyl)formamide (6g)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.58 (d, $J = 11.4$ Hz, 1H), 8.42 (s, 1H), 8.34 (d, $J = 1.7$ Hz, 1H), 7.55 (s, 1H), 7.53 – 7.47 (m, 2H), 7.11 – 6.98 (m, 4H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 160.6 (d, $J = 242.5$ Hz), 159.0, 132.7 (d, $J = 2.5$ Hz), 121.9 (d, $J = 7.5$ Hz), 115.9 (d, $J = 8.2$ Hz).

**N-(4-chlorophenyl)formamide (6h)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the
product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.75 (s, 1H), 8.50 (dd, $J$ = 148.9, 6.5 Hz, 1H), 7.81 (s, 1H), 7.56 – 7.43 (m, 1H), 7.39 – 7.21 (m, 2H), 7.12 – 6.93 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 162.7, 159.2, 135.9, 135.8, 130.8, 129.1, 121.3, 120.1.

$N$-$(4$-bromophenyl$)$formamide (6i)$^1$

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.68 (d, $J$ = 11.3 Hz, 3H), 8.41 (s, 1H), 8.34 (t, $J$ = 50.2 Hz, 7H), 7.63 – 7.43 (m, 24H), 7.39 (d, $J$ = 2.0 Hz, 7H), 7.03 – 6.97 (m, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 162.2, 158.9, 140.3, 140.0, 138.4, 137.8, 136.1, 135.9, 128.8, 128.4, 127.8, 127.5, 126.9, 120.3, 119.1.

$N$-$(1,1'$-biphenyl$)-4$-yl$)$formamide (6j)$^9$

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.76 (d, $J$ = 11.4 Hz, 1H), 8.42 (t, $J$ = 5.1 Hz, 2H), 7.68 – 7.50 (m, 11H), 7.50 – 7.40 (m, 4H), 7.39 – 7.32 (m, 2H), 7.22 – 7.14 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 162.5, 159.0, 140.3, 140.0, 138.4, 137.8, 136.1, 135.9, 128.8, 128.4, 127.5, 126.9, 120.3, 119.1.

$N$-$(2$-chlorophenyl$)$formamide (6k)$^9$

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.75 (s, 1H), 8.53 (d, $J$ = 1.2 Hz, 1H), 8.43 (dd, $J$ = 8.3, 1.3 Hz, 1H), 7.74 (s, 1H), 7.46 (d, $J$ = 8.0 Hz, 1H), 7.41 (dd, $J$ = 8.0, 1.3 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.16 (dt, $J$ = 8.7, 4.4 Hz, 1H), 7.10 (td, $J$ = 7.9, 1.5 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.4, 158.8, 133.8, 133.7, 130.3, 129.1, 128.0, 127.9, 125.9, 125.2, 124.1, 122.5, 122.0, 118.6.

$N$-$m$-tolylformamide (6l)$^4$

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.71 (d, $J$ = 11.4 Hz, 1H), 8.48 (s, 1H), 8.38 (d, $J$ = 1.8 Hz, 1H), 7.57 – 7.45 (m, 1H), 7.42 (d, $J$ = 12.9 Hz, 1H), 7.34 (d, $J$ = 8.0 Hz, 1H), 7.25 (ddd, $J$ = 15.7, 10.3, 6.5 Hz, 1H), 7.02 (d, $J$ = 7.6 Hz, 1H), 6.98 (d, $J$ = 7.5 Hz, 1H), 6.93 (d, $J$ = 5.3 Hz, 1H), 2.37
(d, J = 8.8 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.8, 159.1, 139.9, 139.1, 136.8, 136.7, 129.6, 128.9, 126.1, 125.6, 120.6, 119.5, 117.1, 115.8, 21.5, 21.4.

N-(3-chlorophenyl)formamide (6m)$^9$

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.56 (dd, J = 159.6, 6.3 Hz, 1H), 8.33 (s, 1H), 7.69 (t, J = 2.0 Hz, 1H), 7.46 (s, 1H), 7.40 (dt, J = 14.7, 7.4 Hz, 1H), 7.35 – 7.25 (m, 1H), 7.01 (dd, J = 8.0, 1.4 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.2, 159.0, 137.9, 139.7, 135.5, 134.8, 130.9, 130.1, 125.4, 124.9, 120.1, 118.8, 117.9, 116.7.

N-(3,4-dimethylphenyl)formamide (6n)$^{11}$

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.63 (d, J = 11.5 Hz, 1H), 8.45 (d, J = 10.0 Hz, 1H), 8.32 (d, J = 1.8 Hz, 1H), 7.53 (d, J = 3.4 Hz, 1H), 7.33 (d, J = 1.9 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.13 – 7.03 (m, 1H), 6.91 – 6.80 (m, 1H), 2.23 (t, J = 9.3 Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 163.0, 159.1, 138.2, 137.4, 134.6, 134.4, 133.8, 133.2, 130.6, 130.0, 121.4, 120.5, 117.5, 116.4, 19.9, 19.8, 19.2, 19.2.

N-tert-butylformamide (6o)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.17 (dd, J = 118.5, 6.9 Hz, 1H), 5.60 (d, J = 278.3 Hz, 1H), 1.38 (d, J = 21.9 Hz, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.9, 160.5, 51.4, 50.4, 31.0, 28.9. HRMS (EI, m/z) calcd for [C$_5$H$_{12}$NO]: 102.0919.; found: 102.0914.

N-(adamantan-1-yl)formamide (6p)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.17 (dd, J = 124.2, 7.2 Hz, 1H), 5.73 (s, 1H), 5.14 (s, 1H), 2.09 (dd, J = 43.5, 13.4 Hz, 5H), 1.86 (d, J = 2.5 Hz, 4H), 1.80 – 1.60 (m, 7H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.1, 160.3, 50.7, 44.2, 41.9, 36.2, 35.9, 29.4, 29.3. HRMS (EI, m/z) calcd for [C$_{11}$H$_{18}$NO]: 180.1388; found: 180.1384.
\textbf{N-(isoquinolin-5-yl)formamide (6q)}

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 10:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, DMSO) $\delta$ 10.73 – 10.43 (m, 1H), 9.33 (s, 1H), 8.74 – 8.50 (m, 2H), 8.33 (d, $J = 7.4$ Hz, 1H), 8.02 (t, $J = 6.5$ Hz, 1H), 7.95 (dd, $J = 21.5$, 8.1 Hz, 1H), 7.72 – 7.64 (m, 1H). $^{13}$C NMR (125 MHz, DMSO) $\delta$ 164.6, 160.9, 153.1, 152.9, 143.6, 143.4, 133.5, 132.4, 129.5, 129.1, 128.7, 128.0, 127.8, 125.1, 124.5, 123.0, 121.5, 115.8, 115.2.

HRMS (EI, m/z) calcd for [C$_{10}$H$_9$N$_2$O]: 173.0715; found: 173.0710.

\textbf{4-(2-chlorodibenzo[b,f][1,4]oxazepin-11-yl)piperazine-1-carbaldehyde (8)}

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 10:1, v/v) to give the product as a white solid (>20:1). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.09 (s, 1H), 7.39 (dd, $J = 8.7$, 2.6 Hz, 1H), 7.30 (d, $J = 2.6$ Hz, 1H), 7.18 (d, $J = 8.7$ Hz, 1H), 7.14 (dd, $J = 7.7$, 1.5 Hz, 1H), 7.12 – 7.06 (m, 2H), 7.04 – 6.97 (m, 1H), 3.79 – 3.21 (m, 8H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.0, 159.3, 158.6, 151.7, 139.6, 133.0, 130.5, 128.8, 127.1, 125.9, 125.2, 124.7, 122.9, 120.2, 47.9, 47.3, 45.2, 39.8.

HRMS (EI, m/z) calcd for [C$_{18}$H$_{17}$N$_3$O$_2$Cl]: 342.1009; found: 342.1000.

\textbf{(R)-N-methyl-N-(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)formamide (10)}

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 10:1, v/v) to give the product as a white solid (>10:7). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.00 (d, $J = 15.7$ Hz, 1H), 7.42 (dd, $J = 8.9$, 2.7 Hz, 2H), 7.39 – 7.21 (m, 5H), 6.88 (t, $J = 7.8$ Hz, 2H), 5.16 (dd, $J = 31.2$, 8.9, 4.0 Hz, 1H), 3.64 – 3.30 (m, 2H), 2.91 (d, $J = 16.9$ Hz, 3H), 2.29 – 2.15 (m, 1H), 2.11 (dd, $J = 11.3$, 7.5, 4.0 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 162.8, 162.7, 160.2, 159.9, 140.4, 139.9, 129.1, 128.9, 128.3, 128.1, 126.9 (dq, $J = 14.5$, 3.7 Hz), 125.7, 125.6, 125.8, 115.7, 78.2, 77.0, 46.0, 41.6, 36.9, 35.9, 34.9, 29.6. $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -61.5, -61.6.

HRMS (EI, m/z) calcd for [C$_{18}$H$_{19}$NO$_2$F$_3$]: 338.1368; found: 338.1364.
4-(5-isopropoxy-4-((4-((2-(isopropylsulfonyl)phenyl)amino)pyrimidin-2-yl)(methyl)amino)-2-methylphenyl)piperidine-1-carbaldehyde (12)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow oil (10:1). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.96 (d, $J$ = 177.4 Hz, 1H), 8.10 (s, 1H), 7.95 – 7.69 (m, 2H), 7.56 (s, 1H), 7.27 – 6.74 (m, 4H), 6.73 (s, 1H), 4.65 – 4.59 (m, 1H), 4.29 (dt, $J$ = 12.1, 6.0 Hz, 1H), 3.79 (dd, $J$ = 11.2, 1.8 Hz, 1H), 3.31 – 3.17 (m, 2H), 2.97 (ddd, $J$ = 12.0, 8.9, 3.2 Hz, 1H), 2.76 (td, $J$ = 12.9, 2.7 Hz, 1H), 2.28 (d, $J$ = 14.9 Hz, 3H), 1.89 (dd, $J$ = 23.7, 13.1 Hz, 2H), 1.67 – 1.57 (m, 2H), 1.28 (d, $J$ = 6.8 Hz, 6H), 1.18 (dd, $J$ = 5.9, 4.1 Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 160.9, 157.9, 155.1, 153.5, 152.7, 152., 148.4, 145.0, 144.0, 138.4, 137.5, 134.5, 134.3, 133.3, 131.1, 129.8, 128.0, 126.7, 125.6, 123.9, 123.1, 122.8, 115.9, 111.1, 110.7, 108.6, 108.1, 101.8, 72.4, 70.1, 55.9, 46.8, 40.6, 38.4, 33.6, 32.2, 22.4, 21.9, 18.6, 15.3. HRMS (EI, m/z) calcd for [C$_{30}$H$_{40}$N$_5$O$_4$S]: 566.2801; found: 566.2796.

$\text{N-(4-}$(N-(5-methylisoxazol-3-yl)sulfamoyl)phenyl)$\text{)formamide (14)}$

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow oil. $^1$H NMR (500 MHz, DMSO) $\delta$ 10.92 (s, 1H), 7.68 – 7.27 (m, 2H), 6.74 – 6.46 (m, 2H), 6.23 – 5.90 (m, 3H), 2.29 (s, 3H). $^{13}$C NMR (125 MHz, DMSO) $\delta$ 170.3, 158.4, 153.7, 129.3, 123.4, 121.8, 115.9, 111.1, 110.7, 108.6, 108.1, 101.8, 72.4, 70.1, 55.9, 46.8, 40.6, 38.4, 33.6, 32.2, 22.4, 21.9, 18.6, 15.3. HRMS (EI, m/z) calcd for [C$_{11}$H$_{12}$N$_3$O$_4$S]: 282.0549; found: 282.0505.

$\text{4-methoxyphenyl formate (16)}$

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.28 (s, 1H), 7.10 – 7.01 (m, 2H), 6.95 – 6.87 (m, 2H), 3.80 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 159.8, 157.7, 143.3, 122.0, 114.7, 55.6.
10. References

11. NMR spectroscopic data

*N*-methyl-*N*-phenylformamide (3a)
$N$-methyl-$N$-(p-tolyl)formamide (3b)
\[ N-(4\text{-methoxyphenyl})-N\text{-methylformamide (3c)} \]
N-(4-chlorophenyl)-N-methylformamide (3d)
N-(4-bromophenyl)-N-methylformamide (3e)
N-(4-fluorophenyl)-N-methylformamide (3f)
$N$-methyl-$N$-(m-tolyl)formamide (3g)
$N$-(3-chlorophenyl)-$N$-methylformamide (3h)
N-(3-bromophenyl)-N-methylformamide (3i)
$N$-methyl-$N$-(o-tolyl)formamide (3j)
$N$-(2-fluorophenyl)-$N$-methylformamide (3k)
N-benzyl-N-phenylformamide (3I)
N-ethyl-N-phenylformamide (3m)
N-isopropyl-N-phenylformamide (3n)
\textit{N-ethyl-N-(m-tolyl)formamide (3o)}
N-butyl-N-phenylformamide (3p)
$N$-allyl-$N$-phenylformamide (3q)
3,4-dihydroquinoline-1(2H)-carbaldehyde (3r)
3,4-dihydroisoquinoline-2(1H)-carbaldehyde (3s)
N-isopropyl-N-(4-(phenylamino)phenyl)formamide (3t)
indoline-1-carbaldehyde (3u)
N,N-dicyclohexylformamide (3v)
4-(4-chlorophenyl)piperazine-1-carbaldehyde (3w)
4-(4-methoxyphenyl)piperazine-1-carbaldehyde (3x)
N-phenylformamide (6a)
N-p-tolylformamide (6b)
$N$-(4-ethylphenyl)formamide (6c)
N-(4-isopropylphenyl)formamide (6d)
N-(4-(tert-butyl)phenyl)formamide (6e)
$N$-(4-methoxyphenyl)formamide (6f)
N-(4-fluorophenyl)formamide (6g)
$N$-(4-chlorophenyl)formamide (6h)
N-(4-bromophenyl)formamide (6i)
N-([1,1\textquotesingle-biphenyl]-4-yl)formamide (6j)
N-(2-chlorophenyl)formamide (6k)
N-m-tolylformamide(6l)
$N$-(3-chlorophenyl)formamide (6m)
$N$-(3,4-dimethylphenyl)formamide (6n)
$N$-tert-butylformamide (6o)
$N$-(adamantan-1-yl)formamide (6p)
N-(isoquinolin-5-yl)formamide (6q)
4-(2-chlorodibenzo[b,f][1,4]oxazepin-11-yl)piperazine-1-carbaldehyde (8)
(R)-N-methyl-N-(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)formamide (10)
4-(5-isopropoxy-4-((4-((2-(isopropylsulfonyl)phenyl)amino)pyrimidin-2-yl)(methyl)amino)-2-methylphenyl)piperidine-1-carbaldehyde (12)
$N$-$(4$-$(N$-$(5$-methylisoxazol-3-yl)sulfamoyl)phenyl)$formamide$ (14)
4-methoxyphenyl formate (16)