Ruthenium-catalyzed ortho-arylation of acetanilides with aromatic boronic acids: an easy route to phenanthridines and carbazoles

Ravi Kiran Chinnagolla and Masilamani Jeganmohan*

Department of Chemistry, Indian Institute of Science Education and Research, Pune 411021, India
Email: mjeganmohan@iiserpune.ac.in

Electronic Supplementary Information

Table of Contents
Page 2 Experimental Section
Pages 3 – 4 Optimization Studies
Pages 5 – 23 Spectral Data of all Compounds 3a-z, 4a-h and 5a-d
Pages 24 – 59 Copies of $^1$H and $^{13}$C NMR Spectra of All Compounds
Experimental Section

General Procedure for the Coupling of Acetanilides 1 with Aromaticboronic Acids 2 Catalyzed by Ruthenium Complex.

A 15-mL pressure tube equipped with a magnetic stirrer and septum containing acetanilide (1) (100 mg, if it is solid), \([\{\text{RuCl}_2(p\text{-cymene})\}_2]\) (0.03 equiv), Ag_2O (1.0 equiv), Cu(OTf)_2 (0.20 equiv) and aromaticboronic acid 2 (1.5 equiv) was evacuated and purged with nitrogen gas three times. To the tube was added AgSbF_6 (0.12 mmol inside the glove box. Then, dry THF (3.0 mL) was added in the tube via syringe (If the acetanilide (1) is liquid, 100 mg of acetanilide (1) was dissolved in the dry THF (3.0 mL) and added to the tube via syringe).

Then, the pressure tube was covered with a screw cap and the reaction mixture was allowed to stir at 110 °C for 20 h. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure 3.

Note: The reaction is moisture sensitive. Dry THF should be used in order to get good conversation.

General Procedure for the Preparation of Phenanthridines.

Note: For Phenanthridines synthesis, crude product 3 was taken directly without column purification. In the reaction, pure as well as crude product 3 worked equally.

To a solution of Ph_3PO (3.0 equiv) in dry CH_2Cl_2 (5.0 mL), was added Tf_2O (1.5 equiv) under the nitrogen atmosphere at 0 °C. After 15 min, the above crude arylated anilides 3 (1.00 mmol) was dissolved in CH_2Cl_2 (2.0 mL) and added to the solution via syringe. The reaction was then warmed to r.t. and stirred until the complete completion (approx. 3 h). After completion, the reaction mixture was quenched by addition of sat. aq. NaHCO_3. The mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined extracts were washed with brine, dried anhydrous Na_2SO_4 and concentrated it under the reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of hexanes and EtOAc as eluent to afford phenanthidine derivatives 4.
### Optimization Studies

![Diagram](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Oxidant (1.0 equiv)</th>
<th>Additive (12 mol %)</th>
<th>Co-catalyst (20 mol %)</th>
<th>Yield of 3a (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>Ag$_2$O</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>MeOH</td>
<td>Ag$_2$O</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>nr</td>
</tr>
<tr>
<td>3</td>
<td>AcOH</td>
<td>Ag$_2$O</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>nr</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>Ag$_2$O</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>nr</td>
</tr>
<tr>
<td>5</td>
<td>DCE</td>
<td>Ag$_2$O</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>nr</td>
</tr>
<tr>
<td>6</td>
<td>DME</td>
<td>Ag$_2$O</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>nr</td>
</tr>
<tr>
<td>7</td>
<td>DMF</td>
<td>Ag$_2$O</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>nr</td>
</tr>
<tr>
<td>8</td>
<td>THF</td>
<td>AgOTf</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>15</td>
</tr>
<tr>
<td>9</td>
<td>THF</td>
<td>AgOAc</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>THF</td>
<td>AgF</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>5</td>
</tr>
<tr>
<td>11</td>
<td>THF</td>
<td>K$_2$S$_2$O$_8$</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>nr</td>
</tr>
<tr>
<td>12</td>
<td>THF</td>
<td>(NH$_4$)$_2$S$_2$O$_8$</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>nr</td>
</tr>
<tr>
<td>13</td>
<td>THF</td>
<td>oxone</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>nr</td>
</tr>
<tr>
<td>14</td>
<td>THF</td>
<td>Cu(OAc)$_2$</td>
<td>AgSbF$_6$</td>
<td>--</td>
<td>nr</td>
</tr>
<tr>
<td>15</td>
<td>THF</td>
<td>Ag$_2$O</td>
<td>AgBF$_4$</td>
<td>--</td>
<td>60</td>
</tr>
<tr>
<td>16</td>
<td>THF</td>
<td>Ag$_2$O</td>
<td>AgOTf</td>
<td>--</td>
<td>55</td>
</tr>
<tr>
<td>17</td>
<td>THF</td>
<td>Ag$_2$O</td>
<td>KPF$_6$</td>
<td>--</td>
<td>nr</td>
</tr>
<tr>
<td>18</td>
<td>THF</td>
<td>Ag$_2$O</td>
<td>AgSbF$_6$</td>
<td>Cu(OTf)$_2$ (1.0 equiv)</td>
<td>82</td>
</tr>
<tr>
<td>19</td>
<td>THF</td>
<td>Ag$_2$O</td>
<td>AgSbF$_6$</td>
<td>Cu(OTf)$_2$</td>
<td>83</td>
</tr>
<tr>
<td>20</td>
<td>THF</td>
<td>Ag$_2$O</td>
<td>-</td>
<td>Cu(OTf)$_2$</td>
<td>68</td>
</tr>
</tbody>
</table>
All reactions were carried out using 1a (100 mg), phenylboronic acid (2a) (1.5 equiv), [{RuCl\(_2\)(p-cymene)}\(_2\)] (0.03 equiv), AgSbF\(_6\) (0.12 equiv), Ag\(_2\)O (1.0 equiv) and Cu(OTf)\(_2\) (0.20 equiv) in THF (3.0 mL) at 110 °C for 20 h. \(^{\text{b}}\)GC yield

To optimize the arylation reaction, various additives, solvents and oxidants were examined in the reaction of 1a with 2a in the presence of [{RuCl\(_2\)(p-cymene)}\(_2\)] (3 mol %) at 110 °C for 20 h. First, the catalytic reaction was tested with various solvents such as THF, MeOH, AcOH, Toluene, DCE, DME, and DMF in the presence of catalyst, AgSbF\(_6\) (12 mol %) and Ag\(_2\)O (1.0 equiv). Among them, THF solvent was the best, providing coupling product 3a in 71% GC yield. The remaining solvents were totally ineffective. Next, the catalytic reaction was tested with various oxidants such as Ag\(_2\)O, AgOTf, AgOAc, AgF, K\(_2\)S\(_2\)O\(_8\), (NH\(_4\))\(_2\)S\(_2\)O\(_8\), oxone and Cu(OAc)\(_2\). Among them, Ag\(_2\)O was very effective, giving 3a in 71% GC yield. AgOTf, AgOAc and AgF were less effective, giving 3a in 15, 10, and 5% GC yields, respectively. Remaining oxidants were totally ineffective. A variety of additives such as AgSbF\(_6\), AgBF\(_4\), AgOTf and KPF\(_6\) were also tested. Among them, AgSbF\(_6\) was very effective, giving 3a in 71% GC yield. AgBF\(_4\) and AgOTf were moderately effective, giving 3a in 60% and 55% GC yields, respectively. But, KPF\(_6\) was totally ineffective. Further, the reaction was tested with 1.0 equiv and 20 mol % of Cu(OTf)\(_2\). In the reaction, 3a was observed 82 and 83% GC yields, respectively. It is believed that Cu(OTf)\(_2\) increases the rate of C-H bond activation and stabilizes the active catalyst. The catalytic reaction was also tested without AgSbF\(_6\), only with Ag\(_2\)O (1.0 equiv) and Cu(OTf)\(_2\) (20 mol %). In the reaction, 3a was observed in 68% GC yield.

Spectral data and copies of \(^1\)H, \(^{13}\)C and DEPT NMR spectra of all compounds 3a-z, 4a-h and 5a-d are listed below.
Spectral Data of Compounds 3a-z, 4a-h and 5a-d

_N-(1,1'-biphenyl)-2-yl)acetamide (3a).

```
    Me C
    O  \    \N
    H   \   \   
   /\    /\   
  /  \  /  \  
```

Colorless solid; Rf value: 0.3 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).

_1H NMR (CDCl₃, 400 MHz):_ \( \delta \) 8.26 (d, \( J = 8.0 \) Hz, 1 H), 7.49 (t, \( J = 8.0 \) Hz, 2 H), 7.44 – 7.35 (m, 4 H), 7.25 (d, \( J = 8.0 \) Hz, 1 H), 7.18 (t, \( J = 8.0 \) Hz, 1 H), 7.14 (bs, 1 H), 2.02 (s, 3 H).

_13C NMR (CDCl₃, 100 MHz):_ \( \delta \) 168.2, 138.1, 134.6, 132.1, 130.0, 129.2, 129.1, 128.4, 127.9, 124.3, 121.6, 24.6.

_HRMS (ESI):_ calc. for [(C₁₄H₁₃NO)H] (M+H) 212.1075, measured 212.1073.

_N-(5-Methoxy-[1,1'-biphenyl]-2-yl)acetamide (3b).

```
    Me C
    O  \    \N
    H   \   \   
   /\    /\   
  /  \  /  \  
```

Colorless solid; Rf value: 0.33 in 50% ethyl acetate in hexanes; eluent (50% ethyl acetate in hexanes).

_1H NMR (CDCl₃, 400 MHz):_ \( \delta \) 8.00 (d, \( J = 8.0 \) Hz, 1 H), 7.48 (t, \( J = 8.0 \) Hz, 2 H), 7.42 (d, \( J = 8.0 \) Hz, 1 H), 7.37 (d, \( J = 8.0 \) Hz, 2 H), 6.98 (bs, 1 H), 6.91 (dd, \( J = 8.0 \), 4.0, Hz, 1 H), 6.81 (s, 1 H), 3.81 (s, 3 H), 2.00 (s, 3 H).
$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.4, 156.4, 138.2, 134.7, 129.0, 128.9, 127.9, 127.6, 124.3, 115.4, 113.4, 55.5, 24.2.

HRMS (ESI): calc. for [(C$_{15}$H$_{15}$NO$_2$)$_2$H] (M+H) 242.1181, measured 242.1184.

$N$-(5-Methyl-[1,1'-biphenyl]-2-yl)acetamide (3c).

\[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{Me} \\
\text{Me}
\end{array}
\]

Colorless solid; Rf value: 0.33 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.09 (d, $J$ = 8.0 Hz, 1 H), 7.48 (t, $J$ = 8.0 Hz, 2 H), 7.42 (d, $J$ = 8.0 Hz, 1 H), 7.37 (d, $J$ = 8.0, Hz, 2 H), 7.18 (d, $J$ = 8.0, Hz, 1 H), 7.07 (s, 2 H), 2.36 (s, 3 H), 2.02 (s, 3 H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.3, 138.3, 134.1, 132.5, 132.0, 130.6, 129.1, 128.9, 128.9, 127.8, 122.0, 24.4, 20.8.

HRMS (ESI): calc. for [(C$_{15}$H$_{15}$NO)$_2$H] (M+H) 226.1232, measured 226.1235.

$N$-(5-Bromo-[1,1'-biphenyl]-2-yl)acetamide (3d).

\[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{Me} \\
\text{Br}
\end{array}
\]

Colorless solid; Rf value: 0.34 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).
$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.16 (d, $J$ = 8.0 Hz, 1 H), 7.48 – 7.40 (m, 4 H), 7.34 – 7.30 (m, 3 H), 7.08 (bs, 1 H), 1.97 (s, 3 H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.2, 136.6, 133.8, 132.6, 131.2, 129.2, 129.0, 128.5, 122.9, 116.9, 24.6.

HRMS (ESI): calc. for [(C$_{14}$H$_{12}$BrNO)H] (M+H) 290.0181, measured 290.0182.

$N$-(5-Chloro-[1,1'-biphenyl]-2-yl)acetamide (3e).

Colorless solid; Rf value: 0.33 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.25 (d, $J$ = 8.0 Hz, 1 H), 7.53 – 7.45 (m, 3 H), 7.37 – 7.32 (m, 3 H), 7.24 (s, 1 H), 7.11 (bs, 1 H), 2.02 (s, 3 H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.2, 136.8, 133.6, 133.3, 129.8, 129.3, 129.3, 129.0, 128.5, 128.2, 127.6, 122.7, 24.6.

HRMS (ESI): calc. for [(C$_{14}$H$_{12}$ClNO)H] (M+H) 246.0686, measured 246.0681.

$N$-(5-Fluoro-[1,1'-biphenyl]-2-yl)acetamide (3f).
Colorless solid; Rf value: 0.29 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).

\[ \text{H NMR (CDCl}_3, 400 \text{ MHz):} \delta 8.14 (s, 1 H), 7.52 – 7.42 (m, 3 H), 7.36 (d, \text{J} = 8.0 \text{ Hz, 2 H}), 7.06 (t, \text{J} = 8.0 \text{ Hz, 2 H}), 7.36 (dd, \text{J} = 8.0, 4.0 \text{ Hz, 1 H}), 2.02 (s, 3 H). \]

\[ \text{C NMR (CDCl}_3, 100 \text{ MHz):} \delta 160.4, 158.0, 137.1, 130.7, 129.1, 129.0, 128.3, 124.1, 124.0 (\text{due to F-coupling}), 116.7 \text{ and } 116.5 (\text{due to F-coupling}), 114.9 \text{ and } 114.7 (\text{due to F-coupling}), 24.4. \]

HRMS (ESI): calc. for [(C\textsubscript{14}H\textsubscript{12}FNO)H] (M+H) 230.0981, measured 230.0980.

**N-(5-Cyano-[1,1'-biphenyl]-2-yl)acetamide (3g).**

![Chemical Structure](image)

Colorless solid; Rf value: 0.25 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).

\[ \text{H NMR (CDCl}_3, 400 \text{ MHz):} \delta 8.57 (d, \text{J} = 8.0 \text{ Hz 1 H}), 7.65 (d, \text{J} = 8.0 \text{ Hz 1 H}), 7.57 – 7.50 (m, 4 H), 8.35 (d, \text{J} = 8.0 \text{ Hz 3 H}), 2.06 (s, 3 H). \]

\[ \text{C NMR (CDCl}_3, 100 \text{ MHz):} \delta 168.4, 138.9, 135.6, 133.7, 132.5, 131.9, 129.6, 129.0, 128.9, 120.7, 118.7, 107.0, 24.7. \]

HRMS (ESI): calc. for [(C\textsubscript{15}H\textsubscript{12}N\textsubscript{2}O)H] (M+H) 237.1028, measured 237.1025.
N-(5-Nitro-[1,1'-biphenyl]-2-yl)acetamide (3h).

![Chemical structure of N-(5-Nitro-[1,1'-biphenyl]-2-yl)acetamide](image)

Colorless solid; Rf value: 0.3 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.65 (d, $J$ = 8.0 Hz, 1 H), 8.24 (dd, $J$ = 8.0, 4.0 Hz, 1 H), 8.14 (s, 1 H), 7.59 – 7.52 (m, 3 H), 7.46 (bs, 1 H), 7.40 (d, $J$ = 8.0 Hz, 2 H), 2.08. (s, 3 H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.4, 148.6, 141.3, 141.0, 137.9, 130.2, 129.1, 129.0, 128.5, 125.1, 122.4, 26.8.

HRMS (ESI): calc. for [(C$_{14}$H$_{12}$N$_{2}$O$_{3}$)H] (M+H) 257.0926, measured 257.0924.

Methyl 6-acetamido-[1,1'-biphenyl]-3-carboxylate. (3i).

![Chemical structure of Methyl 6-acetamido-[1,1'-biphenyl]-3-carboxylate](image)

Colorless solid; Rf value: 0.2 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.49 (d, $J$ = 8.0 Hz, 1 H), 8.03 (dd, $J$ = 8.0, 4.0 Hz, 1 H), 7.92 (s, 1 H), 7.54 (t, $J$ = 8.0 Hz, 2 H), 7.46 (t, $J$ = 8.0 Hz, 1 H), 8.49 (dd, $J$ = 8.0, 4.0 Hz, 2 H), 7.36 (bs, 1 H), 3.90 (s, 3 H), 2.05 (s, 3 H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.3, 166.5, 138.9, 137.0, 131.5, 131.1, 130.0, 129.6, 129.2, 128.5, 135.3, 120.0, 52.0, 24.8.
HRMS (ESI): calc. for \([\text{C}_{16}\text{H}_{15}\text{NO}_{3}]\)H (M+H) 270.1130, measured 270.1133.

\textbf{N-(4-Bromo-[1,1'-biphenyl]-2-yl)acetamide (3j).}

\[
\begin{align*}
&\text{Me} \\
&\text{O} \\
&\text{NH} \\
&\text{Br} \\
&\text{Ph}
\end{align*}
\]

Colorless solid; Rf value: 0.33 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).

\textbf{\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz):} \delta 8.53 (s, 1 H), 7.50 (t, \(J = 8.0\) Hz, 2 H), 7.44 (t, \(J = 8.0\) Hz, 1 H), 7.34 (d, \(J = 8.0\) Hz, 2 H), 7.30 (d, \(J = 8.0\) Hz, 1 H), 7.17 (s, 1 H), 7.10 (d, \(J = 8.0\) Hz, 1 H), 2.02 (s, 3 H).

\textbf{\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz):} \delta 168.2, 137.0, 135.8, 131.1, 130.6, 129.2, 129.0, 128.3, 127.2, 124.0, 122.0, 24.6.

HRMS (ESI): calc. for \([\text{C}_{14}\text{H}_{12}\text{BrNO}]\)H (M+H) 290.0181, measured 290.0182.

\textbf{N-(3-Phenylnapthalen-2-yl)acetamide (3k).}

\[
\begin{align*}
&\text{O} \\
&\text{Me} \\
&\text{NH} \\
&\text{Ph}
\end{align*}
\]

Colorless solid; Rf value: 0.34 in 25% ethyl acetate in hexanes; eluent (25% ethyl acetate in hexanes).

\textbf{\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz):} \delta 8.84 (s, 1 H), 7.88 (d, \(J = 8.0\) Hz, 1 H), 7.78 (d, \(J = 8.0\) Hz, 1 H), 7.72 (s, 1 H), 7.56 – 7.41 (m, 7 H), 7.30 (bs, 1 H), 2.07 (s, 3 H).
$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.3, 137.9, 133.6, 132.5, 132.0, 130.2, 129.4, 129.1, 128.2, 127.7, 127.4, 126.5, 125.4, 118.0, 24.8.

HRMS (ESI): calc. for [(C$_{18}$H$_{15}$NO)H] (M+H) 262.1232, measured 262.1230.

$N$-([1,1'-biphenyl]-2-yl)propionamide (3l).

\[ \text{Colorless solid; Rf value: 0.3 in 30\% ethyl acetate in hexanes; eluent (30\% ethyl acetate in hexanes).} \]

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.32 (d, $J$ = 8.0 Hz, 1 H), 7.50 (t, $J$ = 8.0, 4.0 Hz, 2 H), 7.43 (d, $J$ = 8.0 Hz, 1 H), 7.39-7.35 (m, 3 H), 7.25 (d, $J$ = 8.0 Hz, 1 H), 7.20-7.16 (m, 2 H), 2.24 (q, $J$ = 8.0 Hz, 2 H), 1.12 (t, $J$ = 8.0 Hz, 3 H)

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 171.8, 138.1, 134.7, 132.0, 129.9, 129.2, 129.0, 128.4, 127.9, 124.1, 121.4, 30.8, 9.5.

HRMS (ESI): calc. for [(C$_{15}$H$_{15}$NO)H] (M+H) 226.1232, measured 226.1233.

$N$-([4',5-Dichloro-[1,1'-biphenyl]-2-yl]acetamide (3o).

\[ \text{Colorless solid; Rf value: 0.33 in 30\% ethyl acetate in hexanes; (30\% ethyl acetate in hexanes).} \]
$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.19 (d, $J = 8.0$ Hz, 1 H), 7.48 (d, $J = 8.0$ Hz, 2 H), 7.34 (d, $J = 8.0$ Hz, 1 H), 7.30 (d, $J = 8.0$ Hz, 2 H), 7.21 (s, 1 H), 6.98 (bs, 1 H), 2.01 (s, 3 H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.3, 135.3, 134.7, 133.2, 132.7, 130.4, 129.7, 129.5, 128.6, 123.4, 24.5.

HRMS (ESI): calc. for [(C$_{14}$H$_{11}$Cl$_2$NO)H] (M+H) 280.0296, measured 280.0293.

$N$-(4'-Bromo-5-chloro-[1,1'-biphenyl]-2-yl)acetamide (3p).

![Chemical structure of 3p]

Colorless solid; Rf value: 0.34 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.14 (d, $J = 8.0$ Hz, 1 H), 7.62 (d, $J = 8.0$ Hz, 2 H), 7.33 (dd, $J = 8.0$, 4.0 Hz, 1 H), 7.23 (d, $J = 8.0$ Hz, 2 H), 7.20 (s, 1 H), 7.03 (bs, 1 H), 2.03 (s, 3 H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.3, 135.7, 133.1, 132.8, 132.4, 130.6, 129.6, 128.6, 123.5, 122.8, 24.4.

HRMS (ESI): calc. for [(C$_{14}$H$_{11}$ClBrNO)H] (M+H) 323.9791, measured 323.9794.

$N$-(5-Chloro-4'-iodo-[1,1'-biphenyl]-2-yl)acetamide (3q).

![Chemical structure of 3q]
Colorless solid; Rf value: 0.35 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).

\[ ^1H \text{ NMR (CDCl}_3, 400 \text{ MHz)}: \delta 8.15 (d, J = 8.0 \text{ Hz}, 1 \text{ H}), 7.83 (d, J = 8.0 \text{ Hz}, 2 \text{ H}), 7.33 (dd, J = 8.0, 4.0 \text{ Hz}, 1 \text{ H}), 7.20 (s, 1 \text{ H}), 7.10 (d, J = 8.0 \text{ Hz}, 2 \text{ H}), 7.01 (bs, 1 \text{ H}), 2.04 (s, 3 \text{ H}). \]

\[ ^{13}C \text{ NMR (CDCl}_3, 100 \text{ MHz)}: \delta 168.3, 138.6, 136.3, 133.1, 132.8, 130.8, 129.6, 129.5, 128.6, 123.5, 94.5, 24.5. \]

HRMS (ESI): calc. for \([C_{14}H_{11}ClINO]H\) (M+H) 371.9652, measured 371.9651.

\[ N-(4-\text{Chloro-2-(naphthalen-2-yl)phenyl})\text{acetamide (3r).} \]

Colorless solid; Rf value: 0.39 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).

\[ ^1H \text{ NMR (CDCl}_3, 400 \text{ MHz)}: \delta 8.27 (d, J = 8.0 \text{ Hz}, 1 \text{ H}), 7.98 (d, J = 8.0 \text{ Hz}, 1 \text{ H}), 7.94 – 7.88 (m, 2 \text{ H}), 7.84 (s, 1 \text{ H}), 7.60 – 7.57 (m, 2 \text{ H}), 7.45 (d, J = 8.0 \text{ Hz}, 1 \text{ H}), 7.36 (d, J = 8.0 \text{ Hz}, 1 \text{ H}), 7.34 (s, 1 \text{ H}), 7.18 (bs, 1 \text{ H}), 1.98 (s, 3 \text{ H}). \]

\[ ^{13}C \text{ NMR (CDCl}_3, 100 \text{ MHz)}: \delta 168.3, 134.2, 133.6, 133.5, 133.4, 132.1, 129.9, 129.3, 129.0, 128.34, 128.32, 128.0, 127.8, 126.9, 126.8, 126.5, 122.9, 24.5. \]

HRMS (ESI): calc. for \([C_{18}H_{14}ClNO]H\) (M+H) 296.0842, measured 296.0842.
**N-(5-Chloro-3',4'-dimethoxy-[1,1'-biphenyl]-2-yl)acetamide.(3s).**

![Chemical structure](image)

Colorless solid; Rf value: 0.35 in 50% ethyl acetate in hexanes; eluent (50% ethyl acetate in hexanes).

**¹H NMR (CDCl₃, 400 MHz):** δ 8.34 (d, J = 8.0 Hz, 1 H), 7.39 (d, J = 8.0 Hz, 1 H), 7.21 (s, 2 H), 6.97 (d, J = 8.0 Hz, 1 H), 6.89 (d, J = 8.0 Hz, 1 H), 6.83 (s, 1 H), 3.94 (s, 3 H), 3.89 (s, 3 H), 2.03 (s, 3 H).

**¹³C NMR (CDCl₃, 100 MHz):** δ 173.2, 168.1, 149.4, 149.0, 133.5, 129.7, 129.1, 129.0, 127.9, 122.5, 121.2, 112.0, 111.5, 55.97, 55.91, 24.6.

**HRMS (ESI):** calc. for [(C₁₆H₁₆ClNO₃)H] (M+H) 306.0897, measured 306.0894.

**N-(2-(Benzo[d][1,3]dioxol-5-yl)-4-chlorophenyl)acetamide (3t).**

![Chemical structure](image)

Colorless solid; Rf value: 0.37 in 50% ethyl acetate in hexanes; eluent (50% ethyl acetate in hexanes).

**¹H NMR (CDCl₃, 400 MHz):** δ 8.18 (d, J = 8.0 Hz, 1 H), 7.26 (dd, J = 8.0, 4.0 Hz, 1 H), 7.16 (s, 2 H), 6.88 (d, J = 8.0 Hz, 1 H), 6.77 (s, 1 H), 6.76 (d, J = 8.0 Hz, 1 H), 6.01 (s, 2 H), 2.01 (s, 3 H).

**¹³C NMR (CDCl₃, 100 MHz):** δ 168.2, 148.3, 147.7, 133.4, 130.3, 129.8, 129.1, 128.0, 122.7, 122.5, 120.9, 109.4, 108.9, 101.4, 24.5.
HRMS (ESI): calc. for [(C_{15}H_{12}ClNO_{3})H] (M+H) 290.0584, measured 290.0583.

\(N\)-(3'-Bromo-5-chloro-[1,1'-biphenyl]-2-yl)acetamide (3u).

\[
\begin{array}{c}
\text{O} \\
\text{Me} \\
\text{NH} \\
\text{Br} \\
\text{Cl}
\end{array}
\]

Colorless solid; Rf value: 0.34 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).

\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 8.15 (d, \(J = 8.0\) Hz, 1 H), 7.58 (d, \(J = 8.0\) Hz, 1 H), 7.52 (s, 1 H), 7.39 – 7.28 (m, 3 H), 7.22 (s, 1 H), 7.05 (bs, 1 H), 2.04 (s, 3 H).

\(^{13}\)C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 168.3, 138.9, 133.1, 132.5, 132.1, 131.5, 130.6, 129.6, 128.7, 127.5, 123.6, 123.3, 24.4.

HRMS (ESI): calc. for [(C_{14}H_{11}BrCINO)H] (M+H) 323.9791, measured 323.9790.

\((E)-N\)-(4-bromo-2-styrylphenyl)acetamide (3v).

\[
\begin{array}{c}
\text{O} \\
\text{Me} \\
\text{NH} \\
\text{Br}
\end{array}
\]

Colorless solid; Rf value: 0.35 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).

\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 7.67 (d, \(J = 8.0\) Hz, 1 H), 7.64 (s, 1 H), 7.49 (d, \(J = 8.0\) Hz, 2 H), 7.41 – 7.31 (m, 5 H), 7.33 (dd, \(J = 16.0, 8.0\) Hz, 2 H), 2.19 (s, 3 H).
$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.7, 136.4, 133.6, 132.2, 130.9, 129.4, 128.8, 128.5, 126.8, 125.8, 121.9, 118.7, 24.2.

HRMS (ESI): calc. for [(C$_{16}$H$_{14}$BrNO)H] (M+H) 316.0337, measured 316.0338.

$N$-(4'-acetyl-5-methoxy-[1,1'-biphenyl]-2-yl)acetamide (3w).

Colorless solid; Rf value: 0.29 in 50% ethyl acetate in hexanes; eluent (50% ethyl acetate in hexanes).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.04 (d, $J = 8.0$ Hz, 2 H), 7.88 (d, $J = 8.0$, Hz, 1 H), 7.48 (d, $J = 8.0$ Hz, 2 H), 6.95 (dd, $J = 8.0$, 4.0 Hz, 1 H), 6.94 (bs, 1 H), 6.81 (s, 1 H), 3.82 (s, 3 H), 2.65 (s, 3 H), 2.02 (s, 3 H).

$^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$ 197.7, 168.9, 157.4, 143.9, 137.7, 135.5, 129.5, 128.9, 128.2, 127.7, 114.8, 113.9, 55.4, 26.8, 22.8.

HRMS (ESI): calc. for [(C$_{17}$H$_{17}$NO$_3$)H] (M+H) 284.1287, measured 284.1287.

$N$-(4'-formyl-5-methoxy-[1,1'-biphenyl]-2-yl)acetamide (3x).

Colorless semisolid; Rf value: 0.28 in 50% ethyl acetate in hexanes; eluent (50% ethyl acetate in hexanes).
\(^1\)H NMR (DMSO-\(d_6\), 400 MHz): \(\delta\) 10.05 (s, 1 H), 9.30 (s, 1 H), 7.96 (d, \(J = 8.0\) Hz, 2 H), 7.61 (d, \(J = 8.0\) Hz, 2 H), 7.29 (d, \(J = 8.0\) Hz, 1 H), 6.98 (dd, \(J = 8.0, 4.0\) Hz, 1 H), 6.93 (s, 1 H), 3.79 (s, 3 H), 1.84 (s, 3 H).

\(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz): \(\delta\) 192.9, 168.9, 157.4, 145.4, 137.6, 134.9, 129.5, 129.4, 127.8, 120.6, 114.8, 114.2, 55.4, 22.8.

HRMS (ESI): calc. for [(C\(_{16}\)H\(_{15}\)NO\(_3\))H] (M+H) 270.1130, measured 270.1132.

\(N\)-(3-Phenylthiophen-2-yl)acetamide (3y).

\[
\begin{align*}
\text{Me} & \quad \text{O} \\
\text{S} & \quad \text{NH} \\
\text{O Me} & \quad \text{Me}
\end{align*}
\]

Colorless solid; Rf value: 0.32 in 25% ethyl acetate in hexanes; eluent (25% ethyl acetate in hexanes).

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.96 (bs, 1 H), 7.49 (t, \(J = 8.0\) Hz, 2 H), 7.41 (d, \(J = 8.0\) Hz, 2 H), 7.38 (t, \(J = 8.0\) Hz, 1 H), 6.96 – 6.92 (m, 2 H), 2.16 (s, 3 H).

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 166.5, 135.2, 133.4, 129.4, 128.3, 127.4, 126.0, 125.7, 117.8, 23.3.

HRMS (ESI): calc. for [(C\(_{12}\)H\(_{11}\)NOS)H] (M+H) 218.0640, measured 218.0634.

\(N\)-(3-(4-methoxyphenyl)thiophen-2-yl)acetamide (3z).

\[
\begin{align*}
\text{Me} & \quad \text{O} \\
\text{S} & \quad \text{NH} \\
\text{O Me} & \quad \text{Me}
\end{align*}
\]

Colorless solid; Rf value: 0.35 in 30% ethyl acetate in hexanes; eluent (30% ethyl acetate in hexanes).
$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.85 (bs, 1 H), 7.73 (d, $J = 8.0$, Hz, 2 H), 7.02 (d, $J = 8.0$, Hz, 2 H), 6.94 (d, $J = 8.0$, Hz, 1 H), 6.89 (d, $J = 8.0$, Hz, 1 H), 3.87 (s, 3 H), 2.16 (s, 3 H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 166.5, 158.9, 132.9, 129.5, 127.5, 125.8, 125.8, 117.6, 114.8, 55.4, 23.4.

HRMS (ESI): calc. for [(C$_{13}$H$_{13}$NO$_2$S)H] (M+H) 248.0745, measured 248.0744.

6-Methylphenanthridine (4a).

![6-Methylphenanthridine (4a)](image)

Colorless solid; Rf value: 0.4 in 10% ethyl acetate in hexanes; eluent (10% ethyl acetate in hexanes).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.62 (d, $J = 8.0$ Hz, 1 H), 8.54 (d, $J = 8.0$ Hz, 1 H), 8.22 (d, $J = 8.0$ Hz, 1 H), 8.13 (d, $J = 8.0$ Hz, 1 H), 7.85 (t, $J = 8.0$ Hz, 1 H), 7.74 – 7.68 (m, 2 H), 7.63 (t, $J = 8.0$ Hz, 1 H), 3.06 (s, 3 H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 158.9, 143.4, 132.5, 130.6, 129.1, 128.7, 127.3, 126.6, 126.4, 125.8, 123.7, 122.3, 121.9, 23.2.

HRMS (ESI): calc. for [(C$_{14}$H$_{11}$N)H] (M+H) 194.0970, measured 194.0972.

2-Methoxy-6-methylphenanthridine (4b).

![2-Methoxy-6-methylphenanthridine (4b)](image)

Colorless solid; Rf value: 0.36 in 15% ethyl acetate in hexanes; eluent (15% ethyl acetate in hexanes).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.56 (d, $J = 8.0$ Hz, 1 H), 8.22 (d, $J = 8.0$ Hz, 1 H), 8.11 (d, $J = 8.0$ Hz, 1 H), 7.87 (s, 1 H), 7.85 (t, $J = 8.0$ Hz, 1 H), 7.71 (t, $J = 8.0$ Hz, 1 H), 7.35 (dd, $J = 8.0$, 4.0 Hz, 1 H), 4.02 (s, 3 H), 3.06 (s, 3 H).
$^{13}$C NMR (CDCl$_3$, 100 MHz): δ 158.1, 156.2, 137.9, 132.2, 130.6, 130.1, 127.6, 126.7, 125.8, 124.8, 122.4, 118.5, 103.1, 55.6, 22.6.

HRMS (ESI): calc. for [(C$_{15}$H$_{13}$NO)H] (M+H) 224.1075, measured 224.1081.

2,6-Dimethylphenanthridine (4c).

![Figure: 2,6-Dimethylphenanthridine](image)

Colorless solid; Rf value: 0.4 in 10% ethyl acetate in hexanes; eluent (10% ethyl acetate in hexanes).

$^1$H NMR (CDCl$_3$, 400 MHz): δ 8.60 (d, $J = 8.0$ Hz, 1 H), 8.30 (s, 1 H), 8.19 (d, $J = 8.0$ Hz, 1 H), 8.00 (d, $J = 8.0$ Hz, 1 H), 7.81 (t, $J = 8.0$ Hz, 1 H), 7.67 (t, $J = 8.0$ Hz, 1 H), 7.53 (dd, $J = 8.0$, 4.0 Hz, 1 H), 3.03 (s, 3 H), 2.61 (s, 3 H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): δ 157.7, 141.8, 136.0, 132.25, 130.24, 130.2, 128.9, 127.0, 126.4, 125.7, 123.5, 122.2, 121.5, 23.2, 21.8.

HRMS (ESI): calc. for [(C$_{15}$H$_{13}$N)H] (M+H) 208.1126, measured 208.1128.

2-Chloro-6-methylphenanthridine (4d).

![Figure: 2-Chloro-6-methylphenanthridine](image)

Colorless solid; Rf value: 0.39 in 10% ethyl acetate in hexanes; eluent (10% ethyl acetate in hexanes).

$^1$H NMR (CDCl$_3$, 400 MHz): δ 8.53 (d, $J = 8.0$ Hz, 1 H), 8.47 (s, 1 H), 8.23 (d, $J = 8.0$ Hz, 1 H), 8.04 (d, $J = 8.0$ Hz, 1 H), 7.87 (t, $J = 8.0$ Hz, 1 H), 7.74 (t, $J = 8.0$ Hz, 1 H), 7.64 (dd, $J = 8.0$, 4.0 Hz, 1 H), 3.04 (s, 3 H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): δ 159.2, 141.8, 132.2, 131.5, 130.8, 130.6, 129.1, 128.0, 126.6, 125.9, 124.8, 122.3, 121.6, 23.23.

HRMS (ESI): calc. for [(C$_{14}$H$_{10}$ClN)H] (M+H) 228.0580, measured 228.0584.
6-methylphenanthridine-2-carbonitrile (4e).

\[
\begin{array}{c}
\text{NC} \\
\text{N} \\
\text{Me}
\end{array}
\]

Colorless solid; Rf value: 0.34 in 10% ethyl acetate in hexanes; eluent (10% ethyl acetate in hexanes).

\(^1\text{H NMR (CDCl}_3, 400 \text{ MHz)}: \delta 8.87 \text{ (s, 1 H), 8.59 (d, } J = 8.0 \text{ Hz, 1 H), 8.29 (d, } J = 8.0 \text{ Hz, 1 H), 8.16 (d, } J = 8.0 \text{ Hz, 1 H), 7.94 (t, } J = 8.0 \text{ Hz, 1 H), 7.90 (dd, } J = 8.0, 4.0 \text{ Hz, 1 H), 7.81 (t, } J = 8.0 \text{ Hz, 1 H), 3.09 (s, 3 H).}
\]

\(^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz):} \delta 162.5, 145.4, 131.5, 131.4, 130.6, 130.3, 128.7, 127.7, 126.9, 126.2, 123.9, 122.3, 119.2, 109.7, 23.6.

\text{HRMS (ESI):} \text{ calc. for } [(C_{15}H_{10}N_2)H] (M+H) 219.0922, \text{ measured } 219.0923.

3-Bromo-6-methylphenanthridine (4f).

\[
\begin{array}{c}
\text{Br} \\
\text{N} \\
\text{Me}
\end{array}
\]

Colorless solid; Rf value: 0.4 in 10% ethyl acetate in hexanes; eluent (10% ethyl acetate in hexanes).

\(^1\text{H NMR (CDCl}_3, 400 \text{ MHz):} \delta 8.57 \text{ (d, } J = 8.0 \text{ Hz, 1 H), 8.37 (dd, } J = 8.0, 4.0 \text{ Hz, 1 H), 8.29 (s, 1 H), 8.23 (d, } J = 8.0 \text{ Hz, 1 H), 7.87 (t, } J = 8.0 \text{ Hz, 1 H), 7.76 - 7.69 \text{ (m, 2 H), 3.05 (s, 3 H).}
\]

\(^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz):} \delta 160.3, 144.3, 132.2, 131.6, 131.0, 129.6, 127.8, 126.7, 125.8, 123.4, 122.6, 122.3, 23.2.

\text{HRMS (ESI):} \text{ calc. for } [(C_{14}H_{10}BrN)H] (M+H) 272.0075, \text{ measured } 272.0078.
5-Methylbenzo[b]phenanthridine (4g).

![Structure of 5-Methylbenzo[b]phenanthridine](image)

Colorless solid; Rf value: 0.42 in 10% ethyl acetate in hexanes; eluent (10% ethyl acetate in hexanes).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.99 (s, 1 H), 8.75 (d, $J = 8.0$ Hz, 1 H), 8.58 (s, 1 H), 8.18 (d, $J = 8.0$ Hz, 1 H), 8.11 – 8.08 (m, 2 H), 7.86 (t, $J = 8.0$ Hz, 1 H), 7.70 (t, $J = 8.0$ Hz, 1 H), 7.58 – 7.56 (m, 2 H), 3.04 (s, 3 H)

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 159.7, 141.2, 133.3, 132.5, 131.5, 130.7, 128.2, 128.1, 127.7, 127.0, 126.7, 126.0, 125.9, 123.0, 122.5, 121.0, 23.7.

HRMS (ESI): calc. for [(C$_{18}$H$_{13}$N)H] (M+H) 244.1126, measured 244.1125.

5-Methylthieno[2,3-c]isoquinoline (4h).

![Structure of 5-Methylthieno[2,3-c]isoquinoline](image)

Colorless solid; Rf value: 0.43 in 10% ethyl acetate in hexanes; eluent (10% ethyl acetate in hexanes).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.27 (d, $J = 8.0$ Hz, 1 H), 8.23 (d, $J = 8.0$ Hz, 1 H), 7.82 - 7.78 (m, 2 H), 7.64 (t, $J = 8.0$ Hz, 1 H), 7.54 (d, $J = 8.0$ Hz, 1 H), 3.05 (s, 3 H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 156.1, 131.9, 130.3, 126.6, 126.0, 124.7, 124.4, 123.3, 119.7, 22.8.

HRMS (ESI): calc. for [(C$_{12}$H$_{9}$NS)H] (M+H) 200.0534, measured 200.0530.
1-(9H-Carbazol-9-yl)ethanone (5a).\(^1\)

![Chemical structure of 1-(9H-Carbazol-9-yl)ethanone (5a)](image)

Colorless solid; Rf value: 0.43 in 5% ethyl acetate in hexanes; eluent (5% ethyl acetate in hexanes).

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.22 (d, \(J = 8.0\) Hz, 2 H), 8.00 (d, \(J = 8.0\) Hz, 2 H), 7.49 (t, \(J = 8.0\) Hz, 2 H), 7.40 (t, \(J = 8.0\) Hz, 2 H), 2.89 (s, 3 H).

\(^1\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 170.1, 138.6, 127.3, 126.4, 123.7, 119.8, 116.2, 27.7.


Methyl 9-acetyl-9H-carbazole-3-carboxylate (5b).\(^2\)

![Chemical structure of Methyl 9-acetyl-9H-carbazole-3-carboxylate (5b)](image)

Colorless solid; Rf value: 0.4 in 5% ethyl acetate in hexanes; eluent (5% ethyl acetate in hexanes).

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.65 (s, 1 H), 8.28 (d, \(J = 8.0\) Hz, 1 H), 8.15 (d, \(J = 8.0\) Hz, 2 H), 8.04 (d, \(J = 4.0\) Hz, 1 H), 7.52 (t, \(J = 8.0\) Hz, 1 H), 7.43 (t, \(J = 8.0\) Hz, 1 H), 4.00 (s, 3 H) 2.09 (s, 3 H).

\(^1\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 170.1, 116.9, 141.3, 138.9, 128.7, 127.9, 126.2, 125.8, 125.4, 124.0, 121.6, 120.2, 116.0, 115.9, 52.2, 27.7.

HRMS (ESI): calc. for [(C\(_{16}\)H\(_{13}\)NO\(_3\))H] (M+H) 268.0974, measured 268.0973.
1-(3-Bromo-9H-carbazol-9-yl)ethanone (5c).\(^2\)

Colorless solid; Rf value: 0.44 in 5% ethyl acetate in hexanes; eluent (5% ethyl acetate in hexanes).

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.15 (d, \(J = 8.0\) Hz, 1 H), 8.08 (d, \(J = 8.0\) Hz, 1 H), 8.04 (s, 1 H), 7.91 (t, \(J = 8.0\) Hz, 1 H), 7.54 (d, \(J = 8.0\) Hz, 1 H), 7.50 (t, \(J = 8.0\) Hz, 1 H), 7.39 (t, \(J = 8.0\) Hz, 1 H), 2.85 (s, 3 H).

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 170.0, 138.6, 137.4, 130.1, 128.0, 125.2, 123.6, 122.6, 122.4, 120.0, 117.8, 116.8, 115.7, 27.8.

HRMS (ESI): calc. for [(C\(_{14}\)H\(_{10}\)BrNO)H] (M+H) 288.0024, measured 288.0021.

1-(3-Fluoro-9H-carbazol-9-yl)ethanone (5d).\(^2\)

Colorless solid; Rf value: 0.41 in 5% ethyl acetate in hexanes; eluent (5% ethyl acetate in hexanes).

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.31 (m, 1 H), 8.11 (d, \(J = 8.0\) Hz, 1 H), 7.96 (d, \(J = 8.0\) Hz, 1 H), 7.64 (dd, \(J = 8.0, 4.0\) Hz, 1 H), 7.52 (t, \(J = 8.0\) Hz, 1 H), 7.41 (t, \(J = 8.0\) Hz, 1 H), 7.21 (t, \(J = 8.0\) Hz, 1 H), 2.89 (s, 3 H).

HRMS (ESI): calc. for [(C\(_{14}\)H\(_{10}\)FNO)H] (M+H) 228.0825, measured 228.0823.

The compounds 5a-d was prepared based on the following reported procedure:


$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3a.
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3b.
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3c.
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3d.
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3e.

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2014
$^{1}$$H$, $^{13}$$C$ and DEPT NMR Spectra of Compound 3f.
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3g
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3h
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3i

![NMR Spectra](image)
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3j
\(^1\)H, \(^{13}\)C and DEPT NMR Spectra of Compound 3k

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2014
$^1$H and $^{13}$C NMR Spectra of Compound 31
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3o
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3p

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2014
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3q

[Diagram of NMR spectra with peaks labeled]
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3r

![NMR Spectra](image)
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3s
$^1\text{H}, ^{13}\text{C}$ and DEPT NMR Spectra of Compound 3t
\(^1\)H, \(^{13}\)C and DEPT NMR Spectra of Compound 3u
$^{1}H$, $^{13}C$ and DEPT NMR Spectra of Compound 3v
\(^1\)H and \(^{13}\)C NMR Spectra of Compound 3w

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2014
$^1$H and $^{13}$C NMR Spectra of Compound 3x
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3y
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 3z
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 4a
\(^1\)H, \(^{13}\)C and DEPT NMR Spectra of Compound 4b

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2014
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 4c
$^1$H, $^{13}$C and DEPT NMR Spectra of Compound 4d
$^1$H and $^{13}$C NMR Spectra of Compound 4e
\(^1\text{H}, \text{ }^{13}\text{C} \text{ and DEPT NMR Spectra of Compound } 4f\)
$^1$H and $^{13}$C NMR Spectra of Compound 4g
$^1$H and $^{13}$C NMR Spectra of Compound 4h.
$^1$H and $^{13}$C NMR Spectra of Compound 5a
$^1$H and $^{13}$C NMR Spectra of Compound 5b.
$^1$H and $^{13}$C NMR Spectra of Compound 5c.
$^{1}$H and $^{13}$C NMR Spectra of Compound 5d.