Sc(OTf)₃ Catalyzed Dehydrogenative Reaction of Electron-rich (hetero)aryl Nucleophiles with 9-Aryl-fluoren-9-ols

Chen Zhou, Chen Hu, Gang Hong, Yuchen He, Zhicong Tang and Limin Wang *
* Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China. Fax & Tel: +86-21-64253881. Email: wanglimin@ecust.edu.cn

1. General Information S2
2. Preparation of the starting materials S2
3. Optimization of The Reaction Conditions S3
4. General Procedure A S4
5. Procedure B S17
6. Quantum Yields Measurements. S18
7. References S19
8. Copies of ¹H NMR, ¹³C NMR, ¹⁹F NMR S20
9. DSC and TGA curves S70
10. UV and PL Spectra of Pyrene and Product 8 S71
1. General Information

$^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded at 400 MHz, 100 MHz and 376 MHz respectively using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in parts per million and hertz, respectively. Melting points were uncorrected. High-resolution mass spectrometry (HRMS) was performed on an ESI-TOF spectrometer. Chemicals were commercially available and used without purification. Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM). Emission spectra were recorded on a Shimadzu RF-530XPC luminescence spectrometer upon excitation at the absorption maxima in the degassed CH$_2$Cl$_2$ solvent after saturating with argon. Absorption spectra were measured with a Shimadzu UV-3150 spectrometer at 25 °C. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer DSC 8500. Thermogravimetric analyses (TGA) were conducted on a PerkinElmer TGA 8000.

2. Preparation of The Starting Materials

In an over-dried, argon purged round flask, the Grignard solution was prepared from magnesium turnings (15 mmol) reacting with bromobenzene (15 mmol) in anhydrous THF (30 mL). 9-fluorenone (5 mmol) was dissolved in anhydrous THF (15 mL) at room temperature and then added dropwise to Grignard solution. The reaction was allowed to stir overnight at 50 °C. After cooling to room temperature, the reaction was quenched by addition of saturated aqueous ammonium chloride (40 mL) and extracted with dichloromethane (3×40 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and the solvent was evaporated under vacuum, the residue was purified by flash column chromatography on silica gel to give white solid 9-phenyl-fluoren-9-ol.\(^1\)
In an over-dried, argon purged round flask, the Grignard solution was prepared from magnesium turnings (15 mmol) reacting with bromobenzene (15 mmol) in anhydrous THF (30 mL). Xanthenone (5 mmol) was dissolved in anhydrous THF (15 mL) at room temperature and then added quickly dropwise to Grignard solution which was chilled to 0 °C in an ice-water bath, over 20 min. The mixture was removed from the ice water bath to room temperature and stirred for 24h. After complication, the reaction was quenched by addition of saturated aqueous ammonium chloride (40 mL) and extracted with dichloromethane (3×40 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and the solvent was evaporated under vacuum, the residue was purified by flash column chromatography on silica gel to give white solid xanthen-9-ol.

3. Optimization of The Reaction Conditions

Initially, the reaction of 9-phenyl-fluoren-9-ol 1a and indole 2a was carried out with 10 mol % Sc(OTf)₃ in dichloromethane (DCM) at 60 °C for 12 h (Table S1, entry 1). To our delight, the desired product 3a was isolated in 97% yield. Then other rare earth Lewis acids were tested in this reaction system, and it was found that Sc(OTf)₃ was the most efficient in providing the desired product (Table S1, entries 2-7). Also, AlCl₃ and FeCl₃ were researched and produced 3a in 88% and 79% yield respectively (Table S1, entries 8-9). Subsequently, optimization by variation of solvents and temperatures turned out to be futile (Table S1, entries 10-17). Gratifyingly, shortening the reaction time to only 4 h could still afford the product in 97% yield (Table S1, entries 18-20). Further investigation on the reaction conditions revealed that the ratio of 1a to 2a (1:1.2) led to a leap in the yield to 99% (Table S1, entry 21-22). Moreover, it was found that the yield remained intact when the catalyst amount was reduced to 2 mol % (Table S1, entry 23-24). Notably, using BF₃·Et₂O or CF₃SO₂H system led to 33% and 9% yields, respectively.

Table S1 Optimization of the reaction conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol %)</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sc(OTf)₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>12</td>
<td>97</td>
</tr>
</tbody>
</table>

S3
<table>
<thead>
<tr>
<th></th>
<th>Substituent</th>
<th>Lewis Acid</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Yb(OTf)₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>12</td>
<td></td>
<td>74</td>
</tr>
<tr>
<td>3</td>
<td>Y(OTf)₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>12</td>
<td></td>
<td>53</td>
</tr>
<tr>
<td>4</td>
<td>La(OTf)₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>12</td>
<td></td>
<td>N.D.</td>
</tr>
<tr>
<td>5</td>
<td>Yb(Pfb)₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>12</td>
<td></td>
<td>N.D.</td>
</tr>
<tr>
<td>6</td>
<td>Y(Pfb)₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>12</td>
<td></td>
<td>N.D.</td>
</tr>
<tr>
<td>7</td>
<td>Dy(Pfb)₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>12</td>
<td></td>
<td>N.D.</td>
</tr>
<tr>
<td>8</td>
<td>AlCl₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>12</td>
<td></td>
<td>88</td>
</tr>
<tr>
<td>9</td>
<td>FeCl₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>12</td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>10</td>
<td>Sc(OTf)₃ (10)</td>
<td>CH₃CN</td>
<td>60</td>
<td>12</td>
<td></td>
<td>96</td>
</tr>
<tr>
<td>11</td>
<td>Sc(OTf)₃ (10)</td>
<td>CHCl₃</td>
<td>60</td>
<td>12</td>
<td></td>
<td>94</td>
</tr>
<tr>
<td>12</td>
<td>Sc(OTf)₃ (10)</td>
<td>DMF</td>
<td>60</td>
<td>12</td>
<td></td>
<td>N.D.</td>
</tr>
<tr>
<td>13</td>
<td>Sc(OTf)₃ (10)</td>
<td>Toluene</td>
<td>60</td>
<td>12</td>
<td></td>
<td>91</td>
</tr>
<tr>
<td>14</td>
<td>Sc(OTf)₃ (10)</td>
<td>EtOH</td>
<td>60</td>
<td>12</td>
<td></td>
<td>N.D.</td>
</tr>
<tr>
<td>15</td>
<td>Sc(OTf)₃ (10)</td>
<td>DCM</td>
<td>80</td>
<td>12</td>
<td></td>
<td>96</td>
</tr>
<tr>
<td>16</td>
<td>Sc(OTf)₃ (10)</td>
<td>DCM</td>
<td>40</td>
<td>12</td>
<td></td>
<td>86</td>
</tr>
<tr>
<td>17</td>
<td>Sc(OTf)₃ (10)</td>
<td>DCM</td>
<td>25</td>
<td>12</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>18</td>
<td>Sc(OTf)₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>1</td>
<td></td>
<td>91</td>
</tr>
<tr>
<td>19</td>
<td>Sc(OTf)₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>3</td>
<td></td>
<td>95</td>
</tr>
<tr>
<td>20</td>
<td>Sc(OTf)₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>4</td>
<td></td>
<td>97</td>
</tr>
<tr>
<td>21</td>
<td>Sc(OTf)₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>4</td>
<td></td>
<td>99</td>
</tr>
<tr>
<td>22</td>
<td>Sc(OTf)₃ (10)</td>
<td>DCM</td>
<td>60</td>
<td>4</td>
<td></td>
<td>87</td>
</tr>
<tr>
<td>23</td>
<td>Sc(OTf)₃ (2)</td>
<td>DCM</td>
<td>60</td>
<td>4</td>
<td></td>
<td>99</td>
</tr>
<tr>
<td>24</td>
<td>Sc(OTf)₃ (1)</td>
<td>DCM</td>
<td>60</td>
<td>4</td>
<td></td>
<td>84</td>
</tr>
</tbody>
</table>

*a Standard reaction conditions: 1a (0.25 mmol), 2a (0.25 mmol), Lewis acid (x mol %), and solvent (2 mL), at 60 °C. N.D. = Not Detected

*b Yield of isolated product. c 1a (0.25 mmol), 2a (0.3 mmol).

d 1a (0.25 mmol), 2a (0.2 mmol)

4. General Procedure A

Substituted tertiary alcohols (0.25 mmol, 1 equiv), substituted indoles (0.3 mmol, 1.2 equiv), Sc(OTf)₃ (2 mol %), CH₂Cl₂ (2 mL) and a stir bar were added to a sealed tube. After being stirred at 60 °C for 4 h, the mixture was evaporated under vacuum. The desired product was isolated by silica gel column chromatography with an ethyl acetate/petroleum ether mixture as eluent.
3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3a)

General procedure A was followed using 9-phenyl-fluoren-9-ol (64.58 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)₃ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH₂Cl₂ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded 3a (88.38 mg, 99% yield) as a white solid (mp 169-171 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 7.7 Hz, 3H), 7.54 (d, J = 7.6 Hz, 2H), 7.37–7.25 (m, 5H), 7.23–7.16 (m, 5H), 7.14–7.04 (m, 2H), 6.97–6.87 (m, 1H), 6.62 (d, J = 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 151.9, 144.4, 139.8, 137.2, 128.2, 127.6, 127.4, 126.6, 126.4, 125.7, 123.1, 121.9, 121.8, 120.6, 120.5, 120.1, 119.2, 111.3, 60.3; HRMS (ESI-TOF) m/z: [M - H]⁻ Calcd for C₂₇H₁₈N 356.1439; Found 356.1437.

3-(9-(p-tolyl)-9H-fluoren-9-yl)-1H-indole (3b)

General procedure A was followed using 9-(p-tolyl)-9H-fluoren-9-ol (68.09 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)₃ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH₂Cl₂ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate: petroleum ether = 2:100) afforded 3b (88.97 mg, 96% yield) as a white solid (mp 182-184 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 8.0 Hz, 3H), 7.53 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.26 (d, J = 8.2 Hz, 1H), 7.22–7.07 (m, 6H), 6.99 (d, J = 7.9 Hz, 2H), 6.92 (t, J = 7.7 Hz, 1H), 6.62 (s, 1H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.1, 141.4, 139.7, 137.2, 136.1, 129.0, 127.6, 127.5, 127.3, 126.5, 125.7, 123.1, 122.0, 121.8, 120.6, 120.0, 119.2, 111.3, 60.0, 21.1; HRMS (ESI-TOF) m/z: [M - H]⁻ Calcd for C₂₈H₂₀N 370.1596; Found 370.1597.

3-(9-(4-methoxyphenyl)-9H-fluoren-9-yl)-1H-indole (3c)
General procedure A was followed using 9-(4-methoxyphenyl)-9H-fluoren-9-ol (72.09 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate: petroleum ether = 5:100) afforded 3c (93.80 mg, 97% yield) as a white solid (mp 104-106 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79–7.71 (m, 3H), 7.56–7.48 (m, 2H), 7.35–7.29 (m, 2H), 7.25–7.15 (m, 5H), 7.13–7.07 (m, 2H), 6.95–6.90 (m, 1H), 6.75–6.68 (m, 2H), 6.62–6.56 (m, 1H), 3.71 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.3, 152.2, 139.7, 137.2, 136.5, 128.7, 127.6, 127.3, 126.5, 125.6, 123.0, 122.0, 121.8, 120.7, 120.1, 119.2, 113.6, 111.3, 59.6, 55.2; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for C$_{28}$H$_{20}$NO 386.1545; Found 386.1547.

3-(9-(4-(tert-butyl)phenyl)-9H-fluoren-9-yl)-1H-indole (3d)

General procedure A was followed using 9-(4-(tert-butyl)phenyl)-9H-fluoren-9-ol (78.61 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate: petroleum ether = 2:100) afforded 3d (93.85 mg, 91% yield) as a white solid (mp 103-105 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.70 (d, $J$ = 7.7 Hz, 3H), 7.47 (d, $J$ = 7.6 Hz, 2H), 7.26 (t, $J$ = 7.6 Hz, 2H), 7.22–7.19 (m, 1H), 7.16–7.10 (m, 6H), 7.06–7.00 (m, 1H), 6.95–6.90 (m, 1H), 6.86–6.80 (m, 1H), 6.63–6.59 (m, 1H), 6.2 (t, $J$ = 0.9 Hz, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.1, 149.3, 141.2, 139.8, 137.1, 127.5, 127.3, 127.2, 126.5, 125.9, 125.1, 123.2, 121.9, 121.8, 120.7, 120.0, 119.1, 111.3, 59.9, 34.4, 31.4. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for C$_{31}$H$_{26}$N 412.2065; Found 412.2064.

3-(9-(4-fluorophenyl)-9H-fluoren-9-yl)-1H-indole (3e)

General procedure A was followed using 9-(4-fluorophenyl)-9H-fluoren-9-ol (69.08 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate: petroleum ether = 2:100) afforded 3e (82.80 mg, 88% yield) as a white solid (mp 188-190 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.78 (t, $J$ = 7.4 Hz, 3H), 7.52 (d, $J$ = 7.6 Hz, 2H), 7.34 (t, $J$ = 7.5 Hz, 2H), 7.28 (d, $J$ = 8.2 Hz, 1H), 7.24–7.06 (m, 6H), 6.95 (t, $J$ =
7.6 Hz, 1H), 6.91–6.82 (m, 2H), 6.61 (d, J = 2.5 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.0 (d, J$_{C-F}$ = 243.4 Hz), 151.8, 140.2, 139.7, 137.2, 129.2 (d, J$_{C-F}$ = 7.8 Hz), 127.7, 127.5, 126.3, 125.6, 123.0, 122.0 (d, J$_{C-F}$ = 13.2 Hz), 120.3, 120.2, 119.3, 115.1, 114.9, 111.4, 59.7; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -116.68; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for C$_{27}$H$_{17}$NF 374.1345; Found 374.1346.

3-(9-(4-chlorophenyl)-9H-fluoren-9-yl)-1H-indole (3f)

![Image of 3f](image1)

General procedure A was followed using 9-(4-chlorophenyl)-9H-fluoren-9-ol (73.19 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 2:100) afforded 3f (87.35 mg, 89% yield) as a white solid (mp 82–84 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.78–7.67 (m, 3H), 7.44 (d, J = 7.6 Hz, 2H), 7.30–7.20 (m, 3H), 7.16–7.02 (m, 8H), 6.93–6.86 (m, 1H), 6.55 (d, J = 2.5 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.4, 142.0, 138.6, 136.2, 131.4, 128.0, 127.3, 126.7, 126.5, 125.2, 124.5, 122.0, 120.9, 120.7, 119.1, 118.9, 118.3, 110.4, 58.7; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for C$_{27}$H$_{17}$NF 390.1050; Found 390.1049.

3-(9-(3,4-dimethylphenyl)-9H-fluoren-9-yl)-1H-indole (3g)

![Image of 3g](image2)

General procedure A was followed using 9-(3,4-dimethylphenyl)-9H-fluoren-9-ol (71.59 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 2:100) afforded 3g (94.50 mg, 98% yield) as a white solid (mp 116–118 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.76 (d, J = 7.2 Hz, 3H), 7.53 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.26–7.16 (m, 3H), 7.13–7.03 (m, 3H), 7.00–6.88 (m, 3H), 6.63 (t, J = 2.0 Hz, 1H), 2.18 (s, 3H), 2.09 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.2, 141.7, 139.7, 137.2, 136.3, 134.8, 129.5, 128.5, 127.6, 127.3, 126.6, 125.7, 125.3, 123.0, 122.0, 121.8, 120.8, 120.0, 119.1, 111.3, 60.0, 20.0, 19.4; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for C$_{29}$H$_{22}$N 384.1752; Found 384.1753.

3-(2-bromo-9-phenyl-9H-fluoren-9-yl)-1H-indole (3h)
General procedure A was followed using 2-bromo-9-phenyl-9H-fluoren-9-ol (84.30 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)₃ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH₂Cl₂ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 3:100) afforded 3h (62.07 mg, 57% yield) as a white solid (mp 97-99 °C). ¹H NMR (400 MHz, DMSO-d₆) δ 10.99 (s, 1H), 8.10–7.87 (m, 2H), 7.64–7.54 (m, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.44–7.35 (m, 2H), 7.32–7.21 (m, 6H), 7.07–6.99 (m, 1H), 6.85–6.77 (m, 1H), 6.76–6.66 (m, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ 159.0, 156.5, 148.9, 143.9, 143.3, 142.5, 135.8, 133.7, 133.4, 133.3, 132.9, 132.3, 132.1, 130.8, 130.6, 129.0, 127.7, 126.3, 126.0, 125.6, 125.5, 123.8, 122.8, 117.3, 65.2; HRMS (ESI-TOF) m/z: [M - H]⁻ Calcd for C₂₇H₁₇NBr 434.0544; Found 434.0545.

3-(9-methyl-9H-fluoren-9-yl)-1H-indole (3i)

General procedure A was followed using 9-methyl-9H-fluoren-9-ol (49.06 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)₃ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH₂Cl₂ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 2:100) afforded 3i (55.50 mg, 75% yield) as a white solid (mp 180-182 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.95–7.76 (m, 3H), 7.38–7.30 (m, 3H), 7.24–7.14 (m, 5H), 6.97 (t, J = 7.6 Hz, 1H), 6.63 (t, J = 7.6 Hz, 1H), 6.30 (d, J = 8.1 Hz, 1H), 1.87 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.1, 139.6, 136.8, 127.6, 127.2, 125.6, 124.0, 121.8, 121.7, 120.2, 120.1, 120.0, 119.2, 110.8, 50.3, 26.7; HRMS (ESI-TOF) m/z: [M - H]⁻ Calcd for C₂₂H₁₆N 294.1283; Found 294.1281.

3-(9-(naphthalen-1-yl)-9H-fluoren-9-yl)-1H-indole (3j)

General procedure A was followed using 9-(naphthalen-1-yl)-9H-fluoren-9-ol (77.10 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)₃ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH₂Cl₂ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 2:100) afforded 3j (96.67 mg, 95% yield) as a white solid (mp 120-
122 °C. $^1$H NMR (400 MHz, DMSO-$_d$6) δ 10.88 (s, 1H), 8.02 (d, $J = 7.6$ Hz, 2H), 7.93–7.46 (m, 5H), 7.42–7.14 (m, 9H), 7.06–6.96 (m, 2H), 6.86–6.77 (m, 1H), 6.50–6.28 (m, 1H); $^{13}$C NMR (100 MHz, DMSO-$_d$6) δ 144.1, 142.6, 139.8, 134.1, 133.9, 133.7, 133.6, 132.8, 132.7, 131.1, 130.3, 130.2 (2C), 130.1 (2C), 130.0 (2C), 126.3, 126.1 (2C), 125.1, 123.7, 117.3, 66.1; HRMS (ESI-TOF) m/z: [M - H] Calcd for C$_{31}$H$_{20}$N 406.1596; Found 406.1597.

**4-methoxy-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3k)**

![Diagram](image)

General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 4-methoxy-1H-indole (44.15 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 2:100) afforded 3k (69.56 mg, 72% yield) as a white solid (mp 96–98 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.89–7.57 (m, 5H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.24–7.06 (m, 8H), 6.91 (d, $J = 8.1$ Hz, 1H), 6.43 (d, $J = 7.1$ Hz, 2H), 3.24 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.6, 152.4, 147.6, 139.9, 139.2, 127.7, 127.6, 126.7, 126.2, 125.4, 123.0, 122.3, 120.4, 119.8, 117.0, 104.5, 100.7, 60.7, 54.4; HRMS (ESI-TOF) m/z: [M - H] Calcd for C$_{28}$H$_{20}$NO 386.1545; Found 386.1543.

**4-chloro-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3l)**

![Diagram](image)

General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 4-chloro-1H-indole (45.48 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 2:100) afforded 3l (95.91 mg, 98% yield) as a white solid (mp 258-260 °C). $^1$H NMR (400 MHz, DMSO-$_d$6) δ 11.32 (s, 1H), 7.92 (d, $J = 7.5$ Hz, 2H), 7.73–7.64 (m, 1H), 7.45–7.32 (m, 4H), 7.29 (t, $J = 7.4$ Hz, 2H), 7.22–6.97 (m, 7H), 6.71–6.60 (m, 1H); $^{13}$C NMR (100 MHz, DMSO-$_d$6) δ 151.8, 147.2, 139.6, 139.1, 128.2, 127.7, 127.3, 126.3 (2C), 126.1, 125.6, 124.3, 122.6, 122.0, 121.2, 120.3, 117.7, 111.3, 60.3; HRMS (ESI-TOF) m/z: [M - H] Calcd for C$_{28}$H$_{17}$NCl 390.1050; Found 390.1051.

**4-fluoro-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3m)**
General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 4-fluoro-1H-indole (40.54 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 2:100) afforded 3m (92.69 mg, 99% yield) as a white solid (mp 228-230 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86–7.74 (m, 3H), 7.59 (d, $J$ = 7.6 Hz, 2H), 7.34 (td, $J$ = 7.5, 1.1 Hz, 2H), 7.26–7.22 (m, 2H), 7.21–7.14 (m, 5H), 7.10–7.05 (m, 2H), 6.73–6.66 (m, 1H), 6.52 (d, $J$ = 2.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.0 (d, $J$$_{C-F}$ = 246.1 Hz), 151.8, 145.8 (d, $J$$_{C-F}$ = 3.4 Hz), 140.2 (d, $J$$_{C-F}$ = 11.1 Hz), 139.8, 128.1, 127.8, 127.4, 126.6, 126.3, 126.0 (d, $J$$_{C-F}$ = 5.4 Hz), 123.4, 122.9 (d, $J$$_{C-F}$ = 8.0 Hz), 120.1, 119.3 (d, $J$$_{C-F}$ = 4.0 Hz), 115.2 (d, $J$$_{C-F}$ = 19.5 Hz), 107.5 (d, $J$$_{C-F}$ = 3.6 Hz), 105.6 (d, $J$$_{C-F}$ = 21.4 Hz), 60.2; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -111.69; HRMS (ESI-TOF) m/z: [M-H]$^-$ Calcd for C$_{27}$H$_{17}$NF 374.1345; Found 374.1347.

5-methyl-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3n)

General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 5-methyl-1H-indole (39.35 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 1:100) afforded 3n (87.15 mg, 94% yield) as a white solid (mp 137-139 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80–7.67 (m, 3H), 7.56–7.51 (m, 2H), 7.34 (td, $J$ = 7.5, 1.1 Hz, 2H), 7.29–7.22 (m, 3H), 7.21–7.17 (m, 5H), 6.98–6.93 (m, 1H), 6.85–6.81 (m, 1H), 6.61 (d, $J$ = 2.5 Hz, 1H), 2.28 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.0, 144.4, 139.8, 135.6, 131.5, 130.8, 129.8, 128.2, 127.6, 127.3, 126.7, 126.6, 125.8, 123.5, 123.2, 121.6, 120.0, 111.0, 60.3, 21.7; HRMS (EI) Calcd for C$_{28}$H$_{21}$N [M]$^+$ m/z: 371.1674; Found 371.1678.

5-bromo-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3o)
General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 5-bromo-1H-indole (58.81 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 2:100) afforded 3o (99.15 mg, 91% yield) as a white solid (mp 220-222 °C).$^1$H NMR (400 MHz, CDCl$_3$) δ 7.88–7.72 (m, 3H), 7.49 (d, $J = 7.6$ Hz, 2H), 7.35 (t, $J = 7.6$ Hz, 2H), 7.26–7.18 (m, 8H), 7.13 (d, $J = 7.5$ Hz, 2H), 6.63 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.5, 143.8, 139.7, 135.8, 128.4, 128.2, 127.7, 127.5, 127.4, 126.9, 125.6, 124.8, 124.3, 120.4, 120.2, 112.7, 112.6, 60.1; HRMS (ESI-TOF) m/z: [M - H] Calcd for C$_{27}$H$_{17}$N$_8$1Br 436.0524; Found 436.0526.

3-(9-phenyl-9H-fluoren-9-yl)-5-(trifluoromethyl)-1H-indole (3p)

General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 5-(trifluoromethyl)-1H-indole (55.54 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 2:100) afforded 3p (105.63 mg, 99% yield) as a white solid (mp 249–251 °C).$^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.44 (s, 1H), 8.00–7.95 (m, 2H), 7.55 (d, $J = 8.5$ Hz, 1H), 7.46 (d, $J = 7.6$ Hz, 2H), 7.44–7.39 (m, 2H), 7.32–7.26 (m, 8H), 6.96 (d, $J = 2.5$ Hz, 1H), 6.87 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 151.1, 144.1, 139.2, 138.5, 128.3, 127.7, 127.6, 127.1, 126.8, 126.6 (q, $J_{C-F} = 269.5$), 126.1, 125.4, 124.9, 120.5, 119.7, 119.3 (q, $J_{C-F} = 30.5$), 117.5, 117.3, 112.7, 59.5. $^{19}$F NMR (376 MHz, DMSO-d$_6$) δ -58.78; HRMS (ESI-TOF) m/z: [M - H] Calcd for C$_{28}$H$_{17}$NF$_3$ 424.1313; Found 424.1312.

5-nitro-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3q)

General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 5-nitro-1H-indole (48.64 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (dichloromethane/petroleum ether = 2:5) afforded 3q (99.59 mg, 99% yield) as a yellow solid (mp 268-270 °C).$^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.73 (s, 1H), 7.99 (d, $J = 7.5$ Hz, 2H), 7.97–7.89 (m, 1H), 7.60–7.47 (m, 4H), 7.46–7.39 (m, 2H), 7.34–7.25 (m, 7H), 7.05 (d, $J = 2.5$ Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 150.6, 143.9, 140.3, 140.1, 139.2, 128.5, 127.9, 127.8, 127.6, 127.1, 127.0, 125.4, 124.9, 121.4, 120.6,
117.2, 116.4, 112.4, 59.4; HRMS (ESI-TOF) m/z: [M - H]\(^+\) Calcd for C\(_{27}\)H\(_{17}\)N\(_2\)O\(_2\) 401.1290; Found 401.1291

**6-bromo-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3r)**

![Chemical Structure](image)

General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 6-bromo-1H-indole (58.81 mg, 0.3 mmol) and Sc(OTf)\(_3\) (2.46 mg, 0.005 mmol, 0.02 equiv) in CH\(_2\)Cl\(_2\) (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 2:100) afforded 3r (100.18 mg, 92% yield) as a white solid (mp 221–223 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 (t, \(J = 7.6\) Hz, 3H), 7.49 (d, \(J = 7.6\) Hz, 2H), 7.43–7.31 (m, 3H), 7.25–7.15 (m, 7H), 7.02 (d, \(J = 8.6\) Hz, 1H), 6.88 (d, \(J = 8.6\) Hz, 1H), 6.60 (d, \(J = 2.4\) Hz, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 151.5, 144.1, 139.7, 138.0, 128.3, 127.7, 127.6, 127.5, 126.8, 125.6, 123.6, 123.0, 122.6, 120.9, 120.2, 115.5, 114.2, 60.1; HRMS (ESI-TOF) m/z: [M - H]\(^+\) Calcd for C\(_{27}\)H\(_{17}\)NBr 434.0544; Found 434.0542.

**7-methyl-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3s)**

![Chemical Structure](image)

General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 7-methyl-1H-indole (39.35 mg, 0.3 mmol) and Sc(OTf)\(_3\) (2.46 mg, 0.005 mmol, 0.02 equiv) in CH\(_2\)Cl\(_2\) (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 1:100) afforded 3s (91.72 mg, 99% yield) as a white solid (mp 65-67 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80–7.67 (m, 3H), 7.56–7.52 (m, 2H), 7.34 (td, \(J = 7.5, 1.1\) Hz, 2H), 7.30–7.26 (m, 2H), 7.24–7.16 (m, 5H), 6.95–6.90 (m, 2H), 6.89–6.83 (m, 1H), 6.64 (d, \(J = 2.5\) Hz, 1H), 2.40 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 151.9, 144.4, 139.8, 136.8, 128.2, 127.6, 127.4, 126.6, 126.0, 125.7, 122.8, 122.4, 121.1, 120.4, 120.1, 119.8, 119.4, 60.3, 16.6; HRMS (ESI-TOF) m/z: [M - H]\(^+\) Calcd for C\(_{28}\)H\(_{20}\)N 370.1596; Found 370.1595.

**2-methyl-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3t)**

S12
General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 2-methyl-1H-indole (39.35 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 1:100) afforded 3t (60.10 mg, 65% yield) as a yellow solid (mp 182-184 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.76 (d, $J = 7.5$ Hz, 2H), 7.64 (s, 1H), 7.50 (d, $J = 7.6$ Hz, 2H), 7.39–7.28 (m, 4H), 7.25–7.16 (m, 6H), 7.01 (t, $J = 7.5$ Hz, 1H), 6.77 (t, $J = 7.6$ Hz, 1H), 6.65–6.24 (m, 1H), 1.40–1.23 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.8, 145.6, 139.7, 135.2, 132.2, 128.4, 127.6, 127.4, 127.3, 126.5, 126.1, 121.4, 120.6, 120.0, 118.8, 113.8, 110.0, 60.5, 14.1; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for C$_{28}$H$_{20}$N 370.1596; Found 370.1594.

3-methyl-2-(9-phenyl-9H-fluoren-9-yl)-1H-indole(3u)

General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 3-methyl-1H-indole (39.35 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 2:100) afforded 3u (89.51 mg, 96% yield) as a yellow solid (mp 77-79 °C); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.77 (d, $J = 7.5$ Hz, 2H), 7.64–7.42 (m, 4H), 7.42–7.30 (m, 4H), 7.31–7.18 (m, 5H), 7.16–7.01 (m, 3H), 1.89 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.8, 143.6, 140.1, 135.8, 134.1, 130.4, 128.6, 128.1, 127.4, 127.2, 126.1, 121.6, 120.4, 119.2, 118.9, 118.3, 110.5, 108.8, 61.4, 10.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{28}$H$_{22}$N 372.1752; Found 372.1753.

1-methyl-3-(9-phenyl-9H-fluoren-9-yl)-1H-indole (3v)

General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), N-methyl-indole (39.35 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/
petroleum ether = 1:100) afforded 3v (91.70 mg, 99% yield) as a white solid (mp 190-192 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.78 (d, \(J = 7.5\) Hz, 2H), 7.55 (d, \(J = 7.6\) Hz, 2H), 7.33 (q, \(J = 8.6\) Hz, 3H), 7.28–7.12 (m, 8H), 7.07 (d, \(J = 8.1\) Hz, 1H), 6.93 (t, \(J = 7.6\) Hz, 1H), 6.50 (s, 1H), 3.60 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 152.1, 144.5, 139.7, 138.0, 128.2, 127.7, 127.6, 127.3, 126.9, 126.6, 125.7, 122.0, 121.4, 120.0, 118.8, 118.7, 109.4, 60.3, 32.6; HRMS (EI) Calcd for C\(_{28}\)H\(_{21}\)N \([M]^+\) m/z: 371.1674; Found 371.1676.

3-trityl-1H-indole (3w)

![3-trityl-1H-indole](image)

General procedure A was followed using triphenylmethanol (65.08 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)_3 (2.46 mg, 0.005 mmol, 0.02 equiv) in CH\(_2\)Cl\(_2\) (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 1:100) afforded 3w (79.38 mg, 88% yield) as a white solid (mp 207-209 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.87 (s, 1H), 7.29 (d, \(J = 8.2\) Hz, 1H), 7.23–7.19 (m, 15H), 7.10–7.06 (m, 1H), 6.80–6.76 (m, 2H), 6.68–6.65 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.5, 137.0, 130.8, 127.8, 127.4, 126.0, 125.5, 123.9, 122.8, 121.7, 119.2, 110.9, 59.4; HRMS (ESI-TOF) m/z: [M - H]^\pm Calcd for C\(_{27}\)H\(_{20}\)N 358.1596; Found 358.1598.

2-(9-phenyl-9H-fluoren-9-yl)benzofuran (5a)

![2-(9-phenyl-9H-fluoren-9-yl)benzofuran](image)

General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), benzofuran (35.44 mg, 0.3 mmol) and Sc(OTf)_3 (2.46 mg, 0.005 mmol, 0.02 equiv) in CH\(_2\)Cl\(_2\) (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 2:100) afforded 5a (49.20 mg, 55% yield) as a white solid (mp 202-204 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82–7.76 (m, 2H), 7.69–7.64 (m, 2H), 7.47–7.39 (m, 4H), 7.32 (td, \(J = 7.5, 1.2\) Hz, 2H), 7.23–7.19 (m, 4H), 7.15 (td, \(J = 7.5, 1.1\) Hz, 1H), 7.06–7.02 (m, 2H), 6.40 (d, \(J = 0.9\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.9, 155.7, 148.4, 143.0, 140.3, 128.5, 128.2, 128.1, 127.9, 127.2, 127.1, 126.4, 123.9, 122.7, 120.8, 120.3, 111.3, 105.1, 61.1; HRMS (EI) Calcd for C\(_{27}\)H\(_{18}\)O \([M]^+\) m/z: 358.1358; Found 358.1355.

2,5-bis(9-phenyl-9H-fluoren-9-yl)thiophene (5b)

S14
General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), thiophene (25.24 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/ petroleum ether = 1:100) afforded 5b (59.08 mg, 84% yield) as a white solid (mp 254-256 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.77–7.67 (m, 4H), 7.48–7.41 (m, 4H), 7.34 (td, J = 7.5, 1.2 Hz, 4H), 7.27–7.22 (m, 4H), 7.20–7.08 (m, 10H), 6.59 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.9, 148.0, 145.6, 139.8, 128.1, 127.7, 127.6, 127.5, 126.9, 126.2, 125.6, 120.2, 62.3; HRMS (EI) Calcd for C$_{42}$H$_{28}$S [M]$^+$ m/z: 564.1912; Found 564.1916. Spectral data match those previously reported.

4-(9-phenyl-9H-fluoren-9-yl) phenol (5f)

General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), phenol (28.23 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/ petroleum ether = 4:100) afforded 5f (66.80 mg, 71% yield) as a white solid (mp 185–187 °C); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.74 (d, J = 7.5 Hz, 2H), 7.46–7.12 (m, 12H), 7.10–7.01 (m, 2H), 6.69–6.61 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.3, 151.5, 146.1, 140.1, 138.1, 129.4, 128.2, 128.1, 127.7, 127.4, 126.6, 126.1, 120.2, 115.0, 64.8; HRMS (ESI-TOF) m/z: [M - H]$^-^$ Calcd for C$_{25}$H$_{17}$O$_3$ 333.1279; Found 333.1278.

9-phenyl-9-(2,4,6-trimethoxyphenyl)-9H-fluorene (5g)

General procedure A was followed using 9-phenyl-9H-fluoren-9-ol (64.58 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (50.46 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/ petroleum ether = 2:100) afforded 5g (101.40 mg, 99% yield) as a white solid (mp 150-152 °C); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.70 (d, J = 7.4 Hz, 2H), 7.50 (d, J =
7.6 Hz, 2H), 7.28–7.24 (m, 2H), 7.21–7.13 (m, 2H), 7.11–6.98 (m, 5H), 6.09 (s, 2H), 3.77 (s, 3H), 3.18 (s, 6H); $^1$H NMR (100 MHz, CDCl$_3$) δ 160.2, 159.7, 152.2, 148.9, 139.5, 127.6, 127.0, 126.3, 125.7, 124.9, 124.4, 119.4, 114.5, 92.9, 61.2, 55.6, 55.2; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{28}$H$_{24}$NaO$_3$ 431.1623; Found 431.1624.

3-(9-phenyl-9H-xanthen-9-yl)-1H-indole (7a)

![3-(9-phenyl-9H-xanthen-9-yl)-1H-indole (7a)](image)

General procedure A was followed using 9-phenyl-9H-xanthen-9-ol (68.58 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 4:100) afforded 7a (88.85 mg, 95% yield) as a white solid (mp 249–251 °C).

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.07 (s, 1H), 7.43–7.39 (m, 1H), 7.33–7.28 (m, 2H), 7.27–7.17 (m, 5H), 7.06–6.98 (m, 3H), 6.97–6.89 (m, 4H), 6.71–6.65 (m, 1H), 6.54 (d, $J$ = 8.0 Hz, 1H), 6.48 (d, $J$ = 2.5 Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 151.8, 145.6, 137.4, 129.4, 128.7, 128.0, 127.9, 127.1, 126.4, 125.1, 123.1, 121.0, 120.7, 118.9, 118.4, 116.1, 111.8, 48.3; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for C$_{27}$H$_{18}$NO 372.1388; Found 372.1390.

3-(9-(p-tolyl)-9H-xanthen-9-yl)-1H-indole (7b)

![3-(9-(p-tolyl)-9H-xanthen-9-yl)-1H-indole (7b)](image)

General procedure A was followed using 9-(p-tolyl)-9H-xanthen-9-ol (72.09 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 4:100) afforded 7b (95.13 mg, 98% yield) as a white solid (mp 298–300 °C).

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 10.87 (s, 1H), 7.36 (d, $J$ = 8.2 Hz, 1H), 7.24 (t, $J$ = 7.2 Hz, 2H), 7.14 (d, $J$ = 8.1 Hz, 2H), 7.02–6.90 (m, 7H), 6.78 (d, $J$ = 7.9 Hz, 2H), 6.68–6.55 (m, 2H), 6.44 (d, $J$ = 2.5 Hz, 1H), 2.23 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 151.8, 142.6, 137.4, 135.2, 129.3, 128.9, 128.2, 127.9, 127.6, 127.0, 125.1, 122.6, 120.9, 120.8, 119.1, 118.1, 115.9, 111.5, 48.0, 20.4; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for C$_{28}$H$_{20}$NO 386.1545; Found 386.1546.

3-(9-(4-fluorophenyl)-9H-xanthen-9-yl)-1H-indole (7c)

![3-(9-(4-fluorophenyl)-9H-xanthen-9-yl)-1H-indole (7c)](image)
General procedure A was followed using 9-(4-fluorophenyl)-9H-xanthen-9-ol (73.08 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 4:100) afforded 7c (92.18 mg, 94% yield) as a white solid (mp 226-228 °C). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 11.12 (s, 1H), 7.42 (d, $J$ = 8.2 Hz, 1H), 7.31 (t, $J$ = 7.7 Hz, 2H), 7.24 (d, $J$ = 8.1 Hz, 2H), 7.12–6.99 (m, 5H), 6.98–6.88 (m, 4H), 6.68 (t, $J$ = 7.6 Hz, 1H), 6.59–6.48 (m, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 160.5 (d, $J$$_{C-F}$ = 242.2 Hz), 151.8, 141.7 (d, $J$$_{C-F}$ = 2.9 Hz), 137.5, 129.9 (d, $J$$_{C-F}$ = 7.9 Hz), 129.2, 128.6, 128.2, 127.0, 125.0, 123.2, 121.1, 120.7, 118.9, 118.5, 116.2, 114.7 (d, $J$$_{C-F}$ = 21.1 Hz), 111.8, 47.9; $^{19}$F NMR (376 MHz, DMSO-$d_6$) δ -116.56; HRMS (ESI-TOF) $m/z$: [M - H] $-$ Calcd for C$_{27}$H$_{17}$NOF 390.1294; Found 390.1293.

3-(9-phenyl-9H-thioxanthen-9-yl)-1H-indole (7d)

General procedure A was followed using 9-phenyl-9H-thioxanthen-9-ol (72.60 mg, 0.25 mmol), indole (35.15 mg, 0.3 mmol) and Sc(OTf)$_3$ (2.46 mg, 0.005 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (2 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 4:100) afforded 7d (89.60 mg, 92% yield) as a white solid (mp 230-232 °C). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 11.08 (s, 1H), 7.54–7.44 (m, 3H), 7.27 (t, $J$ = 7.5 Hz, 2H), 7.18–7.10 (m, 4H), 7.06 (t, $J$ = 7.6 Hz, 1H), 6.94 (d, $J$ = 7.8 Hz, 2H), 6.73 (t, $J$ = 7.5 Hz, 1H), 6.63–6.54 (m, 2H), 6.49 (d, $J$ = 8.0 Hz, 1H), 6.15 (d, $J$ = 2.4 Hz, 1H), 5.75 (d, $J$ = 1.7 Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 143.3, 139.5, 137.4, 132.6, 130.3, 128.4, 127.5, 126.9, 126.6, 126.3, 125.8, 125.7, 121.5, 121.2, 119.1, 118.5, 112.0, 55.3. HRMS (ESI-TOF) $m/z$: [M - H]$^-$ Calcd for C$_{27}$H$_{17}$NS 388.1160; Found 388.1159.

5. Procedure B

2-bromo-9-phenyl-9H-fluoren-9-ol (1686.08 mg, 5.0 mmol), indole (702.90 mg, 6 mmol) and Sc(OTf)$_3$ (49.22 mg, 0.1 mmol, 0.02 equiv) in CH$_2$Cl$_2$ (15 mL) at 60 °C for 4 h. Chromatography (ethyl acetate/petroleum ether = 3:100) afforded 3h (809.51 mg, 37% yield) as a white solid. 3h (0.5 mmol, 1 equiv), pyren-1-ylboronic acid (1.5 mmol, 3 equiv), Pd(PPh$_3$)$_4$ (0.05 mmol), aqueous Na$_2$CO$_3$ (2.0 M, 1 mL), ethanol (2 mL), and toluene (4 mL) and a stir bar were added to a sealed tube. After being stirred at 110 °C for 24 h, the mixture was evaporated under vacuum, and the product was extracted with
dichloromethane (3×40 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and the solvent was removed by rotary evaporation. The target product was isolated by silica gel column chromatography with a dichloromethane/petroleum ether mixture as eluent.⁴

3-(9-phenyl-2-(pyren-1-yl)-9H-fluoren-9-yl)-1H-indole (8)

Product 8 was obtained by using 3h (0.5 mmol, 1 equiv), pyren-1-ylboronic acid (1.5 mmol, 3 equiv), Pd(PPh₃)₄ (0.05 mmol), aqueous Na₂CO₃ (2.0 M, 1 mL), ethanol (2 mL), and toluene (4 mL) at 110 °C for 24 h. Chromatography (dichloromethane/petroleum ether = 25:100) afforded 8 (231.70 mg, 83% yield) yellowish white solid (mp 148–150 °C).¹H NMR (400 MHz, CDCl₃) δ 8.19–7.98 (m, 6H), 7.97–7.83 (m, 5H), 7.82–7.69 (m, 2H), 7.60 (t, J = 8.7 Hz, 2H), 7.43–7.33 (m, 3H), 7.28–7.19 (m, 5H), 7.13–7.03 (m, 2H), 6.86 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 2.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 152.2, 152.1, 144.4, 140.3, 139.6, 138.9, 137.8, 137.2, 131.5, 131.0, 130.5, 130.1, 128.4, 128.3, 128.2, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 126.7, 126.4, 126.0, 125.9, 125.3, 125.1, 124.9, 124.7, 124.6, 123.2, 121.9, 121.8, 120.6, 120.3, 120.1, 119.4, 111.3, 60.5; HRMS (ESI-TOF) m/z: [M - H]⁻ Calcd for C₄₃H₂₆N 556.2065; Found 556.2064.

6. Quantum Yields Measurements.⁵

The fluorescence quantum yields of substrates (5a, 5b, 3p, 3m, 3e, 3c, 3a, 3k) were determined by comparing the integrated area of the corrected emission spectrum with the reference for 9,10-diphenylanthracene (Φₑ = 0.90, in cyclohexane). The fluorescence quantum yields of compound 8 was determined by comparing the integrated area of the corrected emission spectrum with the reference for quinine sulfate (Φₑ = 0.55 in 0.1 M H₂SO₄). The quantum yields of a sample was then calculated according to the following equation:

$$\Phi = \Phi' \times \frac{A'}{A} \times \frac{l}{l'} \times \frac{n²}{n'²}$$

where Φ is the fluorescence quantum yield of testing sample, l is the integrated emission intensity of testing sample, n is the refractive index (1.42 for dichloromethane, 1.43 for cyclohexane and 1.33 for water), A is the optical density. The superscript "'" refers to the referenced fluorescence dyes of known quantum yields.
7. References


Copies of $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR, HRMS

3a
3c

S22
3h
3m
3n
3w

S54
7c
DSC and TGA curves

Figure S1: (a) DSC curve of product 8 and (b) TGA curve of product 8
UV and PL Spectra of Pyrene and Product 8

Figure S2 UV and PL spectra of pyrene and product 8 in CH$_2$Cl$_2$ solution