

# Supporting Information

## Visible-Light-Induced Aerobic Dearomatic Reaction of Indole Derivatives: Access to Heterocycle Fused or Spirocyclo Indolones

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## General Information

All reactions were carried out under Ar atmosphere unless otherwise noted. All reagents and solvents were obtained from commercial suppliers and used without further purification. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on 400 MHz spectrometer at room temperature. Chemical shifts ( $\delta$ ) are reported in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and are reported as wavenumber ( $\text{cm}^{-1}$ ). UV-vis spectra was obtained on JASCO J-810 spectropolarimeter. High resolution mass spectra were obtained using an Agilent 6210 Series TOFLC-MS equipped with electrospray ionization (ESI) probe operating in positive ion mode. All the substrates were prepared according to the literature<sup>[1][2][3]</sup>. The 36W fluorescent light bulb was directly got from the supermarket.

## 2. Experimental details for products

### 2.1 General procedure A for substrates 2

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **2a-2o** (0.2 mmol, 1.0 equiv), Ru (bpy)<sub>3</sub>Cl<sub>2</sub> (2.0 mol%), CsOAc (0.4mmol, 2.0 equiv). 1 mL dry CH<sub>3</sub>CN was added with syringe and the

flask was filled with O<sub>2</sub>. The tube was placed at a distance (app. 5 cm) from a 36W fluorescent light bulb, and the resulting solution was stirred at ambient temperature under visible-light irradiation. After the reaction was finished, the reaction mixture was diluted by adding EtOAc and brine. The aqueous layer was extracted with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the **3a-o**.

## 2.2 Optimization of Reaction Conditions for **4a**<sup>a</sup>

Entry	Catalyst	Base	solvent	Yield( % ) <sup>b</sup>
1	Ru (bpy) <sub>3</sub> Cl <sub>2</sub>	CsOAc	CH <sub>3</sub> CN	45
2	Ru (bpy) <sub>3</sub> Cl <sub>2</sub>	TMG	CH <sub>3</sub> CN	40
3	Ru (bpy) <sub>3</sub> Cl <sub>2</sub>	DBU	CH <sub>3</sub> CN	13
4	Ru (bpy) <sub>3</sub> Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	47
5	Ru (bpy) <sub>3</sub> Cl <sub>2</sub>	DABCO	CH <sub>3</sub> CN	65
6	[Ir(ppy) <sub>2</sub> (dtbbpy)]PF <sub>6</sub>	DABCO	CH <sub>3</sub> CN	59
7	Ru (bpy) <sub>3</sub> Cl <sub>2</sub>	DABCO	CH <sub>3</sub> CN	68
8	Ru (bpy) <sub>3</sub> Cl <sub>2</sub>	/	CH <sub>3</sub> CN	trace
9 <sup>c</sup>	none	CsOAc	CH <sub>3</sub> CN	trace
10 <sup>d</sup>	Ru (bpy) <sub>3</sub> Cl <sub>2</sub>	CsOAc	CH <sub>3</sub> CN	trace

<sup>a</sup> Reaction conditions: **4a** (0.2mmol, 1.0 equiv), base (0.4mmol, 2.0 equiv), air and photocatalyst (0.004 mmol, 2.0 mol%) in dry CH<sub>3</sub>CN(1.0 mL) were irradiated with a 36W CFL for 24h. <sup>b</sup> Isolated yield. <sup>c</sup> Without

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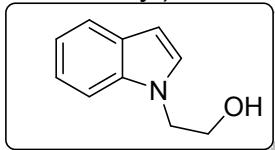
photocatalyst irradiation. <sup>d</sup> Without visible light irradiation.

### 2.3 General procedure B for substrates 4

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **4a-f** (0.2 mmol, 1.0 equiv), Ru (bpy)<sub>3</sub>Cl<sub>2</sub> (2.0 mol%), DABCO (0.4mmol, 2.0 equiv). 1 mL dry CH<sub>3</sub>CN was added with syringe and the flask was filled with air. The tube was placed at a distance (app.5 cm) from a 36W fluorescent light bulb, and the resulting solution was stirred at ambient temperature under visible- light irradiation. After the reaction was finished, the reaction mixture was diluted by adding EtOAc and brine. The aqueous layer was extracted with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the **5a-f**.

### Characterization data of compounds

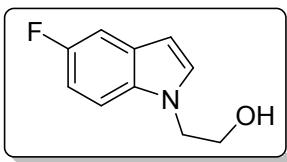
#### 2-(1*H*-indol-1-yl)ethan-1-ol **2a**



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.61-7.58 (m, 1H), 7.30-7.27 (m, 1H), 7.20-7.16 (m, 1H), 7.10-7.04 (m, 2H), 6.46 - 6.45 (m, 1H), 4.10 (t, *J* = 5.3 Hz, 2H), 3.73 (t, *J* = 5.3 Hz, 2H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 136.11, 128.74, 128.46, 121.70, 121.11, 119.61, 109.42, 101.44, 61.80, 48.68.

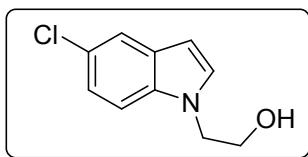
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**2-(5-fluoro-1*H*-indol-1-yl)ethan-1-ol **2b****



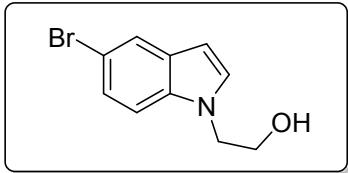
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.26-7.21 (m, 2H), 7.15-7.14 (m, 1H), 6.97- 6.92 (m, 1H), 6.44- 6.43(m, 1H), 4.18 (t, *J* = 5.2 Hz, 2H), 3.84 (t, *J* = 5.2 Hz, 2H).<sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 159.06, 156.73 , 132.77, 129.92, 128.91 (d, *J* = 10.3 Hz), 110.35-109.68 (m), 105.72, (d, *J* = 23.2 Hz), 101.44 (d, *J* = 4.7 Hz), 61.89 , 48.94.

**2-(5-chloro-1*H*-indol-1-yl)ethan-1-ol **2c****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 1.9 Hz, 1H), 7.23-7.21 (m, 1H), 7.15- 7.11 (m, 2H), 6.41 (dd, *J* = 3.1, 0.7 Hz, 1H), 4.16 (t, *J* = 5.2 Hz, 2H), 3.82 (t, *J* = 5.2 Hz, 2H).<sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 134.56, 129.67, 125.30, 121.96, 120.37, 110.41, 101.17, 61.85, 48.83.

**2-(5-bromo-1*H*-indol-1-yl)ethan-1-ol **2d****

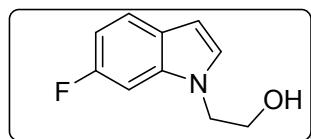


<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 1.6 Hz, 1H), 7.27-7.24 (m,1H), 7.19-7.17 (m,1H), 7.09 (d, *J* = 3.1 Hz, 1H), 6.41 (dd, *J* = 3.1, 0.7 Hz,1H), 4.15 (t, *J* = 5.2 Hz, 2H), 3.81 (t, *J* = 5.2 Hz, 2H).<sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 134.82, 130.34, 129.53, 124.50,123.48, 112.86,

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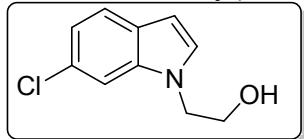
110.88, 101.10, 61.83, 48.81.

**2-(6-fluoro-1*H*-indol-1-yl)ethan-1-ol **2e****



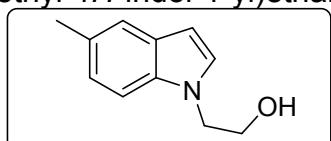
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.48 (dd, *J* = 8.6, 5.4 Hz, 1H), 7.05 (d, *J* = 3.2 Hz, 1H), 6.99 (dd, *J* = 9.9, 2.2 Hz, 1H), 6.88 - 6.83 (m, 1H), 6.44 (dd, *J* = 3.2, 0.7 Hz, 1H), 4.08 (t, *J* = 5.2 Hz, 2H), 3.77 (t, *J* = 5.2 Hz, 2H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 159.82 (d, *J* = 237.4 Hz), 136.16 (d, *J* = 11.9 Hz), 128.80 (d, *J* = 3.7 Hz), 125.08, 121.74 (d, *J* = 10.3 Hz), 108.35 (d, *J* = 24.6 Hz), 101.65, 95.89 (d, *J* = 26.4 Hz), 61.69 , 48.79 .

**2-(6-chloro-1*H*-indol-1-yl)ethan-1-ol **2f****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.4 Hz, 1H), 7.36-7.34 (m, 1H), 7.13 (d, *J* = 3.2 Hz, 1H), 7.07 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.48-6.47 (m, 1H), 4.20 (t, *J* = 5.2 Hz, 2H), 3.90 (t, *J* = 5.2 Hz, 2H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 136.54, 129.07, 127.74, 127.23, 121.87, 120.28, 109.43, 101.77, 61.83 , 48.78.

**2-(5-methyl-1*H*-indol-1-yl)ethan-1-ol **2g****

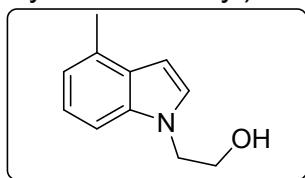


<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.37 (s, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.02-7.00 (m, 2H), 6.37 (d, *J* = 3.0 Hz, 1H), 4.08 (t, *J* = 5.2 Hz, 2H),

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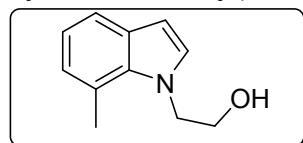
3.74 (t,  $J = 5.2$  Hz, 2H), 2.43 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  134.51, 129.01, 128.82, 128.47, 123.35, 120.74, 109.09, 100.89, 61.85, 48.74, 21.43.

**2-(4-methyl-1*H*-indol-1-yl)ethan-1-ol **2h****



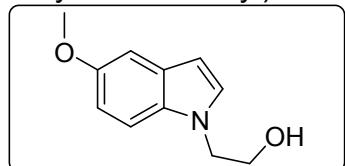
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.23-7.10(m, 3H), 6.92 (d,  $J = 7.0$  Hz, 1H), 6.52 (d,  $J = 3.1$  Hz, 1H), 4.23 (t,  $J = 5.2$  Hz, 2H), 3.89 (t,  $J = 5.2$  Hz, 2H), 2.55 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  135.76, 130.62, 128.63, 127.77, 121.88, 119.79, 106.96, 100.04, 61.97, 48.87, 18.76.

**2-(7-methyl-1*H*-indol-1-yl)ethan-1-ol **2i****



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.46-7.44 (m, 1H), 7.05 (d,  $J = 3.1$  Hz, 1H), 6.98 (t,  $J = 7.5$  Hz, 1H), 6.91 (d,  $J = 7.0$  Hz, 1H), 6.47 (d,  $J = 3.1$  Hz, 1H), 4.42 (t,  $J = 5.3$  Hz, 2H), 3.81 (t,  $J = 5.3$  Hz, 2H), 2.67 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  134.64, 129.89, 129.86, 124.90, 120.74, 119.80, 119.27, 101.95,

**2-(5-methoxy-1*H*-indol-1-yl)ethan-1-ol **2j****

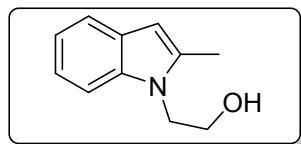


$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.17 (d,  $J = 8.9$  Hz, 1H), 7.05 (d,  $J = 8.9$  Hz, 1H), 6.91 (t,  $J = 7.5$  Hz, 1H), 6.47 (d,  $J = 3.1$  Hz, 1H), 4.42 (t,  $J = 5.3$  Hz, 2H), 3.81 (t,  $J = 5.3$  Hz, 2H), 3.65 (s, 3H), 3.25 (s, 3H).

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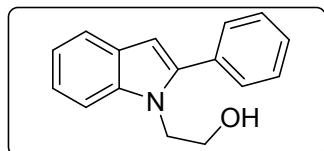
= 2.4 Hz, 1H), 7.04 (d,  $J$  = 3.1 Hz, 1H), 6.82 (s, 1H), 6.37 (s, 1H), 4.08 (t,  $J$  = 5.2 Hz, 2H), 3.80 (s, 3H), 3.74 (t,  $J$  = 5.2 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  154.08, 131.44, 129.06, 128.97, 112.02, 110.16, 102.70, 100.96, 61.84, 55.94, 48.86.

**2-(2-methyl-1*H*-indol-1-yl)ethan-1-ol **2k****



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.49 (d,  $J$  = 7.8 Hz, 1H), 7.25 (d,  $J$  = 8.1 Hz, 1H), 7.14-7.04 (m, 2H), 6.22 (s, 1H), 4.15 (t,  $J$  = 5.5 Hz, 1H), 3.80 (t,  $J$  = 5.5 Hz, 1H), 2.41 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  137.05, 136.83, 128.17, 120.69, 119.80, 119.57, 109.03, 100.32, 61.72, 45.31, 12.98.

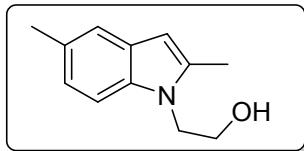
**2-(2-phenyl-1*H*-indol-1-yl)ethan-1-ol **2l****



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.62 (d,  $J$  = 7.8 Hz, 1H), 7.52-7.50 (m, 2H), 7.47-7.38 (m, 4H), 7.23 (t,  $J$  = 7.6 Hz, 1H), 7.14 (t,  $J$  = 7.4 Hz, 1H), 6.54 (s, 1H), 4.30 (t,  $J$  = 5.8 Hz, 2H), 3.79 (t,  $J$  = 5.8 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  141.66, 137.68, 132.89, 129.73, 128.59, 128.26, 128.15, 121.86, 120.68, 120.16, 110.13, 102.79, 61.74, 45.97.

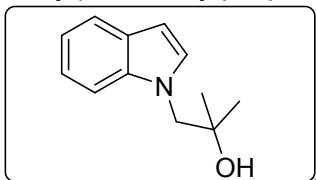
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**2-(2,5-dimethyl-1*H*-indol-1-yl)ethan-1-ol **2m****



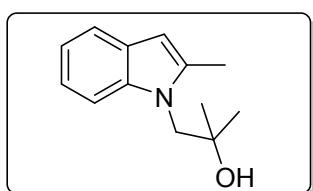
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.28 (s, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 6.94 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.13 (t, *J* = 1.0 Hz, 1H), 4.13 (t, *J* = 5.8 Hz, 1H), 3.80 (t, *J* = 5.8 Hz, 1H), 2.42 (s, 3H), 2.39 (s, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 137.04, 135.22, 128.74, 128.43, 122.17, 119.60, 108.68, 99.84, 61.76, 45.35, 21.40, 12.96.

**1-(1*H*-indol-1-yl)-2-methylpropan-2-ol **2n****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.61-7.59 (m, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.20-7.06 (m, 3H), 6.49 (d, *J* = 3.1, 1H), 3.99 (s, 2H), 1.18 (s, 6H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 137.11, 129.47, 128.36, 121.72, 120.91, 119.46, 110.21, 101.65, 72.16, 56.90, 27.43.

**2-methyl-1-(2-methyl-1*H*-indol-1-yl)propan-2-ol **2o****

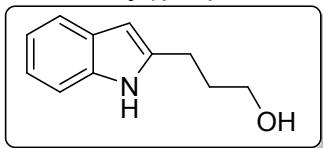


<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.47 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.38-7.33 (m, 1H), 7.13-7.01 (m, 2H), 6.23 (d, *J* = 1.2 Hz, 1H), 3.99 (s, 2H), 2.41 (s, 3H), 1.23 (s, 6H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 138.03, 137.76, 128.22, 120.61, 119.57, 119.53, 110.55, 100.99, 72.93, 53.71,

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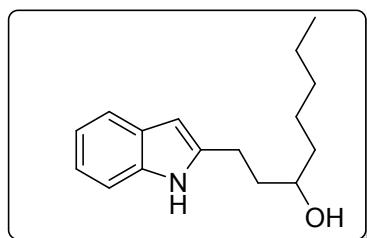
27.95, 13.58.

**3-(1*H*-indol-2-yl)propan-1-ol **4a****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.53-7.52 (m, 1H), 7.29-7.24 (m, 1H), 7.15-7.02 (m, 2H), 6.24 (s, 1H), 3.72 (t, *J* = 6.0 Hz, 2H), 2.85 (t, *J* = 6.0 Hz, 2H), 1.98-1.91(m, 2H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 139.14, 135.95, 128.77, 121.06, 119.79, 119.61, 110.45, 99.59, 62.12, 31.75, 24.69.

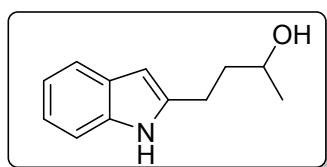
**1-(1*H*-indol-2-yl)octan-3-ol **4b****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.28 (s, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.13-7.03 (m, 2H), 6.23 (s, 1H), 3.73-3.62 (m, 1H), 2.95 – 2.81 (m, 2H), 1.93-1.88 (m, 1H), 1.81-1.73 (m, 1H), 1.53 – 1.42 (m, 3H), 1.33-1.26 (m, 5H), 0.89 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 139.60, 135.93, 128.79, 120.98, 119.75, 119.55, 110.43, 99.44, 71.49, 37.84, 36.49, 31.88, 25.37, 24.55, 22.66, 14.07.

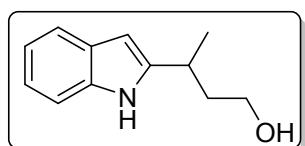
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**4-(1*H*-indol-2-yl)butan-2-ol **4c****



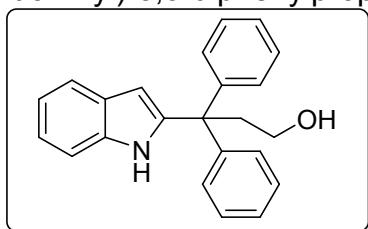
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.39 (brs, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.27-7.26 (m, 1H), 7.15- 6.99 (m, 2H), 6.22 (s, 1H), 3.93-3.79 (m, 1H), 2.88 – 2.78 (m, 1H), 1.89-1.73 (m, 2H), 1.22 (d, *J* = 6.2 Hz, 1H). <sup>13</sup>C NMR (100MHz, Chloroform-*d*) δ 139.55, 135.96, 128.77, 120.95, 119.73, 119.52, 110.49, 99.37, 67.49, 38.25, 24.55, 23.82.

**3-(1*H*-indol-2-yl)butan-1-ol **4d****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 7.54-7.52 (m, 1H), 7.29-7.27 (m, 1H), 7.15-7.03 (m, 2H), 6.25 (d, *J* = 2.1 Hz, 1H), 3.71-3.59 (m, 2H), 3.14-3.05 (m, 1H), 1.90-1.83 (m, 2H), 1.36 (d, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (100MHz, Chloroform-*d*) δ 144.17, 135.72, 128.58, 121.08, 119.90, 119.59, 110.54, 98.01, 60.85, 39.73, 29.94, 20.70.

**3-(1*H*-indol-2-yl)-3,3-diphenylpropan-1-ol **4e****

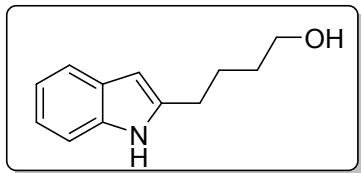


<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.71 (s, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.31-7.19 (m, 12H), 7.13-7.04 (m, 2H), 6.20-6.19 (m, 1H), 3.69 (t, *J* = 6.7 Hz, 2H), 2.95 (t, *J* = 6.7 Hz, 2H), 2.04 (s, 1H). <sup>13</sup>C NMR (100 MHz,

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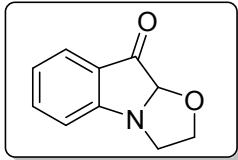
Chloroform-*d*) δ 145.91, 143.64, 136.09, 128.56, 128.26, 127.92, 121.57, 120.34, 119.64, 110.82, 102.52, 60.16, 52.31, 42.68.

**4-(1*H*-indol-2-yl)butan-1-ol **4f****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.13 (brs, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.36-7.17 (m, 1H), 7.12-7.04 (m, 2H), 6.21 (s, 1H), 3.63 (t, *J* = 6.3 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 1.79-1.71 (m, 1H), 1.65-1.53 (m, 1H).  
<sup>13</sup>C NMR (100MHz, Chloroform-*d*) δ 139.64, 135.92, 128.78, 120.94, 119.75, 119.56, 110.44, 99.50, 62.53, 32.01, 27.89, 25.55.

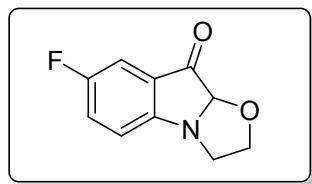
**2,3-dihydrooxazolo[3,2-*a*]indol-9(9*aH*)-one **3a****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.56-7.63 (m, 2H), 7.02-7.05 (m, 2H), 4.88 (s, 1H), 4.03-4.08 (m, 1H), 3.87-3.92 (m, 2H), 3.55-3.88 (m, 2H). <sup>13</sup>C NMR (100MHz, Chloroform-*d*) δ 198.10, 137.86, 124.96, 122.40, 115.23, 92.56, 77.34, 67.40, 50.85. FTIR (film): ν 2921, 1721, 1609, 1474, 1317cm<sup>-1</sup>. UV-vis spectra (methanol): λ<sub>1</sub>=386nm, λ<sub>2</sub>=334nm. HRMS (ESI, m/z): Calculated for [C<sub>10</sub>H<sub>9</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 176.0706, found 176.0706.

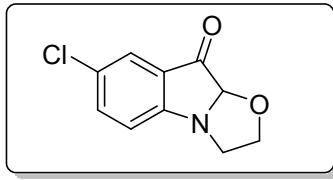
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**7-fluoro-2,3-dihydrooxazolo[3,2-*a*]indol-9(9*aH*)-one **3b****



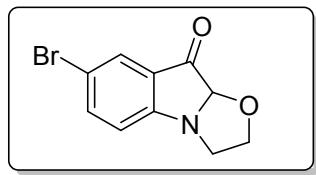
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.35-7.24 (m, 2H), 6.98-7.01 (m, 1H), 4.90 (s, 1H), 4.04-4.08 (m, 1H), 3.86-3.92 (m, 1H), 3.48-3.58 (m, 2H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 197.51 (d, *J* = 2.9 Hz), 161.21 (d, *J* = 1.0 Hz), 159.68, 157.25, 130.22-119.76 (m), 116.53 (d, *J* = 7.7 Hz), 110.29 (d, *J* = 23.0 Hz), 96.73-84.53 (m), 67.40, 51.19. HRMS (ESI, m/z): Calculated for [C<sub>10</sub>H<sub>9</sub>FNO<sub>2</sub>] (M+H)<sup>+</sup> 194.0612, found 194.0613.

**7-chloro-2,3-dihydrooxazolo[3,2-*a*]indol-9(9*aH*)-one **3c****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.62-7.48 (m, 2H), 6.97 (dd, *J* = 8.6, 0.5 Hz, 1H), 4.88 (s, 1H), 4.09-4.04 (m, 1H), 3.94-3.88 (m, 1H), 3.63-3.46 (m, 2H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 196.80, 163.21, 137.65, 128.01, 125.46, 124.42, 116.43, 92.83, 67.57, 50.82. HRMS (ESI, m/z): Calculated for [C<sub>10</sub>H<sub>9</sub>ClNO<sub>2</sub>] (M+H)<sup>+</sup> 210.0316, found 210.0317.

**7-bromo-2,3-dihydrooxazolo[3,2-*a*]indol-9(9*aH*)-one **3d****

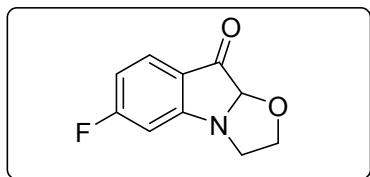


<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.65-7.65 (m, 3H), 4.80 (s, 1H), 4.03-3.97 (m, 1H), 3.89-3.81 (m, 1H), 3.53-3.41 (m, 2H). <sup>13</sup>C NMR

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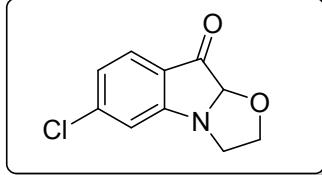
(100MHz, Chloroform-*d*)  $\delta$  195.62, 162.55, 139.32, 126.49, 124.89, 115.79, 114.05, 91.61, 66.56, 49.70. HRMS (ESI, m/z): Calculated for [C<sub>10</sub>H<sub>9</sub>BrNO<sub>2</sub>] (M+H)<sup>+</sup> 253.9811, found 253.9811.

**6-fluoro-2,3-dihydrooxazolo[3,2-*a*]indol-9(9a*H*)-one **3e****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.64-7.60 (m, 1H), 6.75-6.66 (m, 2H), 4.88 (s, 1H), 4.11-4.06 (m, 1H), 3.99-3.93 (m, 1H), 3.61-3.48 (m, 2H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*)  $\delta$  195.94, 169.44 (d, *J* = 257.8 Hz), 167.02 (d, *J* = 13.1 Hz), 127.30 (d, *J* = 12.0 Hz), 120.68 (d, *J* = 1.5 Hz), 110.73 (d, *J* = 24.3 Hz), 102.21 (d, *J* = 25.5 Hz), 92.91, 67.72, 50.56 . HRMS (ESI, m/z): Calculated for [C<sub>10</sub>H<sub>9</sub>FNO<sub>2</sub>] (M+H)<sup>+</sup> 194.0612, found 194.0612.

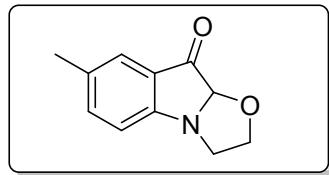
**6-chloro-2,3-dihydrooxazolo[3,2-*a*]indol-9(9a*H*)-one **3f****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.54 (d, *J* = 8.0 Hz, 1H), 7.01-6.99 (m, 2H), 4.88 (s, 1H), 4.10-4.05 (m, 1H), 3.97-3.92 (m, 1H), 3.61-3.50 (m, 2H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*)  $\delta$  196.46, 165.56, 144.24, 125.94, 123.11, 122.73, 115.42, 92.68, 67.71, 50.59 .HRMS(ESI, m/z): Calculated for [C<sub>10</sub>H<sub>9</sub>ClNO<sub>2</sub>] (M+H)<sup>+</sup> 210.0316, found 210.0315.

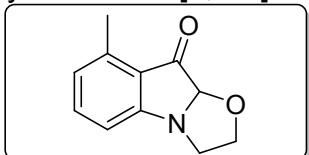
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**7-methyl-2,3-dihydrooxazolo[3,2-*a*]indol-9(9*aH*)-one **3g****



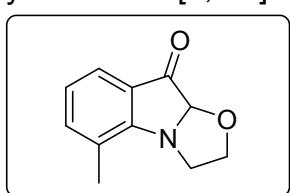
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.41-7.39 (m, 2H), 6.96-6.93 (m, 1H), 4.87 (s, 1H), 4.05-4.01 (m, 1H), 3.87-3.81 (m, 1H), 3.54-3.51 (m, 2H), 2.33 (s, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 198.35, 163.19, 139.10, 132.26, 124.54, 124.46, 115.15, 92.98, 67.14, 51.10, 20.62. HRMS (ESI, m/z): Calculated for [C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 190.0863, found 190.0863.

**8-methyl-2,3-dihydrooxazolo[3,2-*a*]indol-9(9*aH*)-one **3h****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.41 (t, *J* = 7.8 Hz, 1H), 6.76-6.83 (m, 2H), 4.81 (s, 1H), 4.05-4.00 (m, 1H), 3.90-3.84 (m, 1H), 3.68-3.39 (m, 2H), 2.56 (s, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 198.73, 165.52, 140.58, 137.14, 123.97, 122.13, 112.33, 92.46, 67.08, 50.96, 18.12. HRMS (ESI, m/z): Calculated for [C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 190.0863, found 190.0863.

**5-methyl-2,3-dihydrooxazolo[3,2-*a*]indol-9(9*aH*)-one **3i****

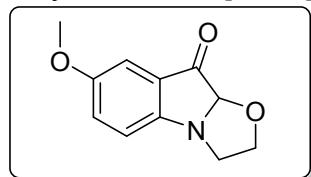


<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.41-7.39

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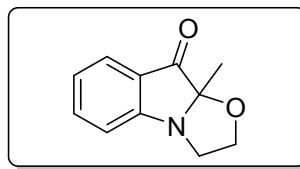
(m, 1H), 6.99 (t,  $J = 7.5$  Hz, 1H), 4.93 (s, 1H), 4.12-4.01 (m, 2H), 3.66-3.60 (m, 1H), 3.43-3.37 (m, 1H), 2.40 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  199.10, 139.39, 126.49, 125.15, 122.99, 122.35, 93.26, 68.33, 50.57, 17.38. HRMS (ESI, m/z): Calculated for [C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 190.0863, found 190.0865.

**7-methoxy-2,3-dihydrooxazolo[3,2-*a*]indol-9(9*a*H)-one 3j**



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.28-7.20 (m, 1H), 7.06 (d,  $J = 2.7$  Hz, 1H), 6.99 (d,  $J = 8.8$  Hz, 1H), 4.90 (s, 1H), 4.06-4.02 (m, 1H), 3.86-3.79 (m, 4H), 3.54-3.47 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  198.58, 159.86, 155.72, 127.62, 124.89, 116.72, 93.48, 67.04, 55.83, 51.36. HRMS (ESI, m/z): Calculated for [C<sub>11</sub>H<sub>11</sub>NO<sub>3</sub>] (M+H)<sup>+</sup> 206.0812, found 206.0812.

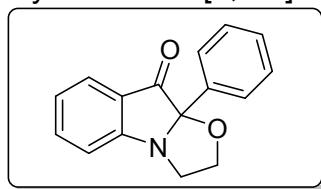
**9a-methyl-2,3-dihydrooxazolo[3,2-*a*]indol-9(9*a*H)-one 3k**



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.65-7.57 (m, 2H), 7.06-7.02 (m, 2H), 4.07-4.03 (m, 1H), 3.71-3.53 (m, 3H), 1.51 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  163.36, 137.75, 125.14, 124.03, 122.55, 115.29, 98.08, 66.76, 50.53, 19.38. HRMS (ESI, m/z): Calculated for [C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 190.0863, found 190.0863.

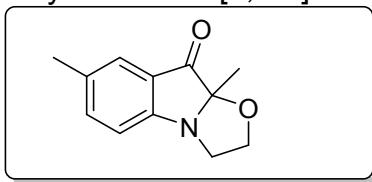
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**9a-phenyl-2,3-dihydrooxazolo[3,2-*a*]indol-9(9*aH*)-one **3l****



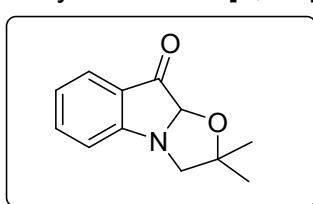
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.68-7.58 (m, 4H), 7.40-7.36 (m, 3H), 7.10-7.04 (m, 2H), 4.09-4.01(m, 2H), 3.66-3.62 (m, 1H), 3.56-3.50 (m, 1H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 197.15, 163.96, 137.78, 136.06, 128.95, 128.40, 126.52, 125.64, 122.79, 122.61, 114.81, 67.96, 50.12. HRMS (ESI, m/z): Calculated for [C<sub>16</sub>H<sub>13</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 252.1019, found 252.1013.

**7,9a-dimethyl-2,3-dihydrooxazolo[3,2-*a*]indol-9(9*aH*)-one **3m****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.55-7.35 (m, 2H), 6.95 (d, *J* = 8.2 Hz, 1H), 4.05-4.01 (m, 1H), 3.68-3.51 (m, 3H), 2.33 (s, 3H), 1.50 (s, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 199.62, 161.50, 138.99, 132.38, 124.71, 124.18, 115.20, 98.48, 66.61, 50.77, 20.64, 19.48. HRMS (ESI, m/z): Calculated for [C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 204.1019, found 204.1022.

**2,2-dimethyl-2,3-dihydrooxazolo[3,2-*a*]indol-9(9*aH*)-one **3n****

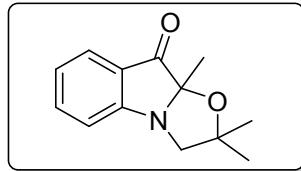


<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.62-7.53 (m, 2H), 7.01- 6.92 (m, 1H).

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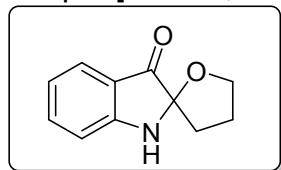
2H), 5.01 (s, 1H), 3.46-3.30 (m, 2H), 1.42 (s, 3H), 1.14 (s, 3H).<sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 199.51, 165.72, 137.90, 125.17, 123.30, 121.80, 114.50, 92.40, 84.77, 61.66, 27.88, 26.32. HRMS (ESI, m/z): Calculated for [C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 204.1019, found 204.1020.

**2,2,9a-trimethyl-2,3-dihydrooxazolo[3,2-*a*]indol-9(*aH*)-one **3o****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.74-7.41 (m, 2H), 7.01- 6.93 (m, 2H), 3.68-3.30 (m, 2H), 1.48 (s, 3H), 1.37 (s, 3H), 0.88 (s, 3H).<sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 201.25, 164.15, 137.78, 125.47, 122.34, 121.73, 114.06, 98.63, 83.84, 60.71, 28.21, 28.16, 20.69. HRMS (ESI, m/z): Calculated for [C<sub>13</sub>H<sub>15</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 218.1176, found 218.1178.

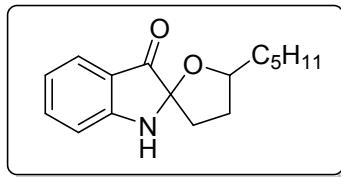
**4,5-dihydro-3*H*-spiro[furan-2,2'-indolin]-3'-one **5a****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.58-7.56 (m, 1H), 7.45-7.41 (m, 1H), 6.86 - 6.72 (m, 2H), 4.87 (s, 1H), 4.22-3.97 (m, 2H), 2.35-2.22 (m, 2H), 2.17-2.06 (m, 1H), 2.03-1.94 (m, 1H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 200.99, 159.72, 137.90, 125.09, 119.69, 112.22, 95.10, 69.28, 34.06, 25.79. HRMS (ESI, m/z): Calculated for [C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 190.0863, found 190.0864.

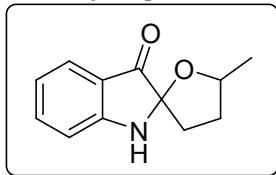
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**5-pentyl-4,5-dihydro-3*H*-spiro[furan-2,2'-indolin]-3'-one **5b****



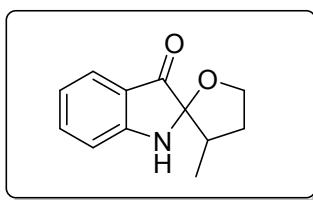
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.56 (d, *J* = 7.7 Hz, 1H), 7.44-7.40 (m, 1H), 6.85 - 6.71 (m, 2H), 4.81 (s, 1H), 4.31- 4.19 (m, 1H), 2.41-2.12 (m, 2H), 2.03-1.98 (m, 1H), 1.78 - 1.61 (m, 2H), 1.59-1.47 (m, 1H), 1.45 -1.21 (m, 6H), 0.88 (t, *J* = 6.5 Hz, 3H). HRMS (ESI, m/z): Calculated for [C<sub>16</sub>H<sub>21</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 260.1645, found 260.1646.

**5-methyl-4,5-dihydro-3*H*-spiro[furan-2,2'-indolin]-3'-one **5c****



$\delta$  7.54 (d, *J* = 7.7 Hz, 1H), 7.44-7.37 (m, 1H), 6.82-6.71 (m, 2H), 5.02 (s, 1H), 4.43-4.37 (m, 1H), 2.39-2.24 (m, 2H), 2.22-2.15 (m, 0.45H), 2.07-1.93 (m, 1.64H), 1.73-1.61 (m, 0.65H), 1.34 (d, *J* = 1.7 Hz, 1.54H), 1.32(d, *J* = 1.7 Hz, 1.42H). HRMS (ESI, m/z): Calculated for [C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 204.1019, found 204.1022.

**3-methyl-4,5-dihydro-3*H*-spiro[furan-2,2'-indolin]-3'-one **5d****

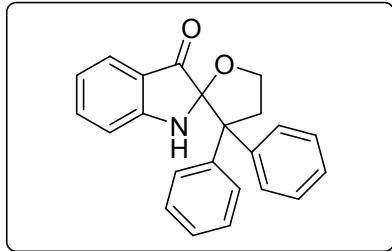


<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.55-7.50 (m, 1H), 7.44 - 7.37 (m, 1H), 6.80- 6.74 (m, 2H), 4.96- 4.87 (m, 1H), 4.28-3.93 (m, 2H), 2.63 - 2.46 (m, 0.76H), 2.41 - 2.23 (m, 1.38H), 2.19-2.11 (m, 0.30H), 1.80-1.65

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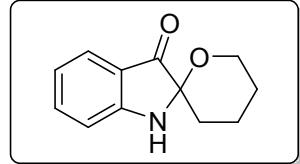
(m, 0.76H), 1.00 (t,  $J = 6.8$  Hz, 3H).HRMS (ESI, m/z): Calculated for [C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 204.1019, found 204.1021.

**3,3-diphenyl-4,5-dihydro-3*H*-spiro[furan-2,2'-indolin]-3'-one **5e****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.42-7.37 (m, 2H), 7.36-7.33 (m, 1H), 7.32-7.26 (m, 3H), 7.21-7.16 (m, 6H), 6.77 (t,  $J = 7.3$  Hz, 1H), 6.69 (d,  $J = 8.1$  Hz, 1H), 4.72 (s, 1H), 4.43 - 4.33 (m, 2H), 3.73-3.65 (m, 1H), 2.73-2.67 (m, 1H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 199.05, 158.79, 145.31, 142.28, 137.40, 128.48, 128.40, 128.18, 127.91, 126.95, 126.88, 125.15, 120.06, 119.67, 111.77, 97.95, 63.21, 56.26, 37.59

**3',4',5',6'-tetrahydrospiro[indoline-2,2'-pyran]-3-one **5f****



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d,  $J = 7.5$  Hz, 1H), 7.47-7.44 (m, 1H), 6.87-6.83 (m, 2H), 5.16 (s, 1H), 4.14-4.09 (m, 1H), 3.85-3.78 (m, 1H), 2.15-2.09 (m, 1H), 2.06-1.99 (m, 1H), 1.86-1.81 (m, 1H), 1.75-1.69 (m, 1H), 1.62-1.54 (m, 2H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 198.96, 159.45, 137.81, 125.48, 120.04, 119.84, 112.75, 87.54, 63.82, 30.58, 24.74, 19.26. HRMS (ESI, m/z): Calculated for [C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 204.1019, found 204.1020.

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## Copies of $^1\text{H}$ NMR, $^{13}\text{C}$ NMR of substrates and products

