Oxidative 1,2-Difunctionalization of Activated Alkenes with Benzylic C(sp\(^3\))-H Bonds and Aryl C(sp\(^2\))-H Bonds

Ming-Bo Zhou, Cheng-Yong Wang, Ren-Jie, Song, Yu, Liu, Wen-Ting Wei, and Jin-Heng Li*

State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

jhli@hnu.edu.cn

Supporting Information

List of Contents

(A) Typical experimental procedure

(B) Analytical data

(C) Reference

(D) Spectra
(A) Typical experimental procedure

(a) Typical Procedures for the Synthesis of Substrates 1:

Substrates 1 were synthesized according to the literatures.¹

(b) Typical Experimental Procedure for the Organomediated Oxidative 1,2-Difunctionalization of Activated Alkenes:

To a Schlenk tube were added N-arylacrylamide 1 (0.5 mmol), arylmethane 2 (7.5 mmol), IrCl₃ (3 mol%), and DTBP (2 equiv). Then the tube was charged with argon, and was stirred at 120 °C for the indicated time until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na₂SO₄, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10 : 1) to afford the desired product.

(c) Table S1: Screening the optimal conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Lewis acid (mol%)</th>
<th>[O]</th>
<th>Solvent</th>
<th>Isolated Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>⎯</td>
<td>DTBP</td>
<td>neat</td>
<td>53</td>
</tr>
<tr>
<td>2</td>
<td>⎯</td>
<td>TBHP</td>
<td>neat</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>⎯</td>
<td>BPO</td>
<td>neat</td>
<td>22</td>
</tr>
<tr>
<td>4</td>
<td>⎯</td>
<td>PhI(OAc)₂</td>
<td>neat</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>FeCl₃ (10)</td>
<td>DTBP</td>
<td>neat</td>
<td>68</td>
</tr>
<tr>
<td>6</td>
<td>Fe(acac)₃ (10)</td>
<td>DTBP</td>
<td>neat</td>
<td>62</td>
</tr>
<tr>
<td>7</td>
<td>CuCl₂ (10)</td>
<td>DTBP</td>
<td>neat</td>
<td>63</td>
</tr>
<tr>
<td>8</td>
<td>ZnCl₂ (10)</td>
<td>DTBP</td>
<td>neat</td>
<td>65</td>
</tr>
<tr>
<td>9</td>
<td>InBr₃ (10)</td>
<td>DTBP</td>
<td>neat</td>
<td>67</td>
</tr>
<tr>
<td>10</td>
<td>CoCl₂ (10)</td>
<td>DTBP</td>
<td>neat</td>
<td>64</td>
</tr>
<tr>
<td>11</td>
<td>PdCl₂ (10)</td>
<td>DTBP</td>
<td>neat</td>
<td>81</td>
</tr>
<tr>
<td>12</td>
<td>RuCl₃ (10)</td>
<td>DTBP</td>
<td>neat</td>
<td>78</td>
</tr>
<tr>
<td>13</td>
<td>RhCl₃ (10)</td>
<td>DTBP</td>
<td>neat</td>
<td>79</td>
</tr>
</tbody>
</table>

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013
14 IrCl₃ (10) DTBP neat 85
15b IrCl₃ (10) DTBP neat 80
16c IrCl₃ (10) DTBP neat 8
17d IrCl₃ (3) DTBP neat 83
18d IrCl₃ (3) DCP neat 81
19de IrCl₃ (3) DTBP DMSO 79
20de IrCl₃ (3) DTBP NMP trace
21ef IrCl₃ (3) DTBP neat 75
22ef IrCl₃ (3) DTBP neat 86

a Reaction conditions: 1a (0.5 mmol), 2a (7.5 mmol), Lewis acid and [O] (1.0 mmol) at 120 °C under argon atmosphere for 12 h.
b At 130 °C. c At 90 °C. d For 24 h. e 2a (5 mmol) in solvent (anhydrous, 0.5 mL). f DTBP (0.6 mmol). g 1a (10 mmol) and 2a (15 equiv) for 48 h.

(d) The control experiments

As shown in Scheme S1, some control experiments were carried out to understand the mechanism. The results demonstrated that no kinetic isotope effect (k_H/k_D = 1.0) in either intramolecular or intermolecular experiments was discovered, implying that the iron-catalyzed oxidative difunctionalization proceeds via either the SEAr mechanism or the free radical mechanism ((a) W. D. Jones, Acc. Chem. Res. 2003, 36, 140; (b) A. Pinto, L. Neuville, P. Retailleau and J. Zhu, Org. Lett. 2006, 8, 4927; (c) W. D. Jones and F. J. Feher, J. Am. Chem. Soc. 1986, 108, 4814; (d) X. Chen, X.-S. Hao, C. E. Goodhue and J.-Q. Yu, J. Am. Chem. Soc. 2006, 128, 6790.). The deuterated experiment between toluene and toluene-D₈ (k_H/k_D = 9.0) supports that benzyl C-H bond cleavage is the rate-limiting step (Eq S1). Notably, two radical inhibitors, TEMPO (Eq 3) and 2,6-di-tert-butylphenol, were added to the difunctionalization reaction: a stoichiometric amount of radical inhibitor (2 equiv) results in no conversion of amide 1a; however, mesitylene (2g) was transferred by TEMPO into 1-(3,5-dimethylbenzyloxy)-2,2,6,6-tetramethylpiperidine (6ag) in 88% yield (Eq S2). The results suggest that a mesitylene radical is yielded and the current reaction includes a radical process.
The data of the reaction between 1a and 2a in-situ determined by GC-MS analysis showed that a DCP could be converted into a methyl group, a ketone and an alcohol (Eqs S3 and S4).

**Scheme S1. Control Experiments.**

1,3-Dimethyl-5-(((2,2,6,6-tetramethylcyclohexyl)oxy)methyl)benzene (4aa):
3-Ethyl-1,3-dimethylindolin-2-one (5aa):

\[
\begin{align*}
\text{Yellow oil; } ^1\text{H NMR (500 MHz, CDCl}_3\text{) } & \delta: 7.26 (t, J = 7.5 \text{ Hz, 1H}), 7.17 (d, J = 7.5 \text{ Hz, 1H}), 7.07 (t, J = 7.5 \text{ Hz, 1H}), 6.84 (d, J = 8.0 \text{ Hz, 1H}), 3.22 (s, 3H), 1.97-1.89 (m, 1H), 1.81-1.74 (m, 1H), 1.35 (s, 3H), 0.59 (t, J = 7.5 \text{ Hz, 3H});
\end{align*}
\]

\[
\begin{align*}
^1\text{C NMR (125 MHz, CDCl}_3\text{) } & \delta: 180.7, 143.4, 133.9, 127.6, 122.5, 122.4, 107.8, 48.9, 31.4, 26.0, 23.3, 8.8; 
\text{IR (KBr, cm}^{-1}\text{): 1722, 1461; LRMS (EI, 70 eV) } m/z (\%) : 189 (M^+, 21), 161 (100); 
\text{HRMS } m/z (ESI) \text{ calcd for } C_{12}H_{16}NO ([M+H]^+) 190.1308, \text{ found 190.1312.}
\end{align*}
\]

(B) Analytical data

1,3-Dimethyl-3-phenethylindolin-2-one (3aa):

\[
\begin{align*}
\text{Yellow oil; } ^1\text{H NMR (400 MHz, CDCl}_3\text{) } & \delta: 7.30 (t, J = 7.6 \text{ Hz, 1H}), 7.25-7.19 (m, 3H), 7.15-7.09 (m, 2H), 7.03 (d, J = 7.6 \text{ Hz, 2H}), 6.87 (d, J = 7.6 \text{ Hz, 1H}), 3.21 (s, 3H), 2.33-2.23 (m, 2H), 2.15-1.97 (m, 2H), 1.39 (s, 3H); 
\end{align*}
\]

\[
\begin{align*}
^1\text{C NMR (100 MHz, CDCl}_3\text{) } & \delta: 131.3, 131.0, 122.5, 118.8, 72.1, 53.3, 33.1, 26.5, 14.9, 13.8, 10.5.
\end{align*}
\]
1,3-Dimethyl-3-(4-methylphenethyl)indolin-2-one (3ab):

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.29 (t, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 9.2$ Hz, 1H), 7.10 (t, $J = 7.2$ Hz, 1H), 7.01 (d, $J = 8.0$ Hz, 2H), 6.91 (d, $J = 8.0$ Hz, 2H), 6.86 (d, $J = 7.6$ Hz, 1H), 3.20 (s, 3H), 2.29-2.20 (m, 2H), 2.24 (s, 3H), 2.10-1.95 (m, 2H), 1.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 180.4, 143.3, 138.2, 135.2, 133.7, 128.9, 128.1, 127.7, 122.5, 122.4, 108.0, 48.4, 40.4, 30.4, 26.1, 23.9, 20.9; IR (KBr, cm$^{-1}$): 1716, 1684, 1481; LRMS (EI, 70 eV) m/z (%): 279 (M$^+$, 1), 161 (100); HRMS m/z (ESI) calcd for C$_{19}$H$_{22}$NO ([M+H]$^+$) 280.1696, found 280.1702.

3-(4-Methoxyphenethyl)-1,3-dimethylindolin-2-one (3ac):

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.30-7.22 (m, 2H), 7.11 (t, $J = 6.0$ Hz, 1H), 6.94 (d, $J = 6.8$ Hz, 2H), 6.86 (d, $J = 6.0$ Hz, 1H), 6.75 (d, $J = 6.8$ Hz, 2H), 3.75 (s, 3H), 3.21 (s, 3H), 2.26-2.20 (m, 2H), 2.09-1.95 (m, 2H), 1.39 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 180.3, 157.8, 143.4, 133.8, 133.5, 129.1, 127.8,
122.5 (2C), 113.7, 107.9, 55.2, 48.3, 40.5, 30.0, 26.1, 23.9; IR (KBr, cm⁻¹): 1723, 1668, 1413; LRMS (EI, 70 eV) m/z (%): 295 (M⁺, 3), 161 (100); HRMS m/z (ESI) calcd for C₁₉H₂₂NO₂ ([M+H]⁺) 296.1645, found 296.1654.

3-(2-Methoxyphenethyl)-1,3-dimethylindolin-2-one (3ad):

Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ: 7.29-7.22 (m, 2H), 7.12-7.07 (m, 2H), 6.91 (d, J = 7.6 Hz, 1H), 6.84 (d, J = 7.6 Hz, 1H), 6.79-6.73 (m, 2H), 3.74 (s, 3H), 3.20 (s, 3H), 2.36-2.16 (m, 3H), 2.07-1.97 (m, 1H), 1.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 180.5, 157.4, 143.5, 134.0, 129.9, 129.7, 127.6, 127.1, 122.7, 122.3, 120.2, 110.1, 107.8, 55.1, 48.4, 38.1, 26.1, 25.6, 24.0; IR (KBr, cm⁻¹): 1716, 1614, 1471; LRMS (EI, 70 eV) m/z (%): 295 (M⁺, 1), 161 (100); HRMS m/z (ESI) calcd for C₁₉H₂₂NO₂ ([M+H]⁺) 296.1645, found 296.1654.

3-(2-Bromophenethyl)-1,3-dimethylindolin-2-one (3ae):

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.44 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.17-7.07 (m, 3H), 7.00 (t, J = 7.0 Hz, 1H), 6.88 (d, J = 7.0 Hz, 1H), 3.25 (s, 3H), 2.41-2.28 (m, 2H), 2.20-2.13 (m, 1H), 2.08-2.02 (m, 1H), 1.40 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 180.2, 143.3, 140.7, 133.4, 132.6, 130.4, 127.8, 127.6, 127.4, 124.1, 122.7, 122.5, 107.9, 48.3, 38.3, 31.5, 26.2, 23.8; IR (KBr,
cm\(^{-1}\): 1719, 1623, 1422; LRMS (EI, 70 eV) \(m/z\) (%): 345 (M\(^{+}\)+2, 2), 343 (M\(^{+}\), 2), 161 (100); HRMS \(m/z\) (ESI) calcd for C\(_{18}\)H\(_{19}\)BrNO ([M+H\(^{+}\)]\(^{+}\)) 344.0652, found 344.0658.

3-(2-Iodophenethyl)-1,3-dimethylindolin-2-one (3af):

![Structure of 3af](image)

Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.72 (d, \(J = 8.0\) Hz, 1H), 7.34-7.26 (m, 2H), 7.20 (t, \(J = 7.2\) Hz, 1H), 7.11-7.08 (m, 2H), 6.88 (d, \(J = 7.6\) Hz, 1H), 6.82 (t, \(J = 7.2\) Hz, 1H), 3.23 (s, 3H), 2.44-2.36 (m, 1H), 2.30-2.27 (m, 1H), 2.15-1.99 (m, 2H), 1.41 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 180.2, 144.0, 143.2, 139.3, 133.3, 129.5, 128.3, 127.9, 127.8, 123.0, 122.5, 107.9, 100.0, 48.2, 38.6, 36.0, 26.2, 23.7; IR (KBr, cm\(^{-1}\)): 1708, 1633, 1413; LRMS (EI, 70 eV) \(m/z\) (%): 391 (M\(^{+}\), 3), 161 (100); HRMS \(m/z\) (ESI) calcd for C\(_{18}\)H\(_{19}\)INO ([M+H\(^{+}\)]\(^{+}\)) 392.0513, found 392.0519.

3-(3,5-Dimethylphenethyl)-1,3-dimethylindolin-2-one (3ag):

![Structure of 3ag](image)

Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.29 (t, \(J = 7.6\) Hz, 1H), 7.23 (d, \(J = 7.2\) Hz, 1H), 7.10 (d, \(J = 7.6\) Hz, 1H), 6.86 (d, \(J = 7.6\) Hz, 1H), 6.77 (s, 1H), 6.66 (s, 2H), 3.22 (s, 3H), 2.29-2.17 (m, 2H), 2.23 (s, 6H), 2.08-1.95 (m, 2H), 1.39 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 180.4, 143.3, 141.3, 137.6, 133.7, 127.7, 127.4, 126.1, 122.5, 122.4, 107.9, 48.4, 40.4, 30.7, 26.1, 23.9, 21.1; IR (KBr, cm\(^{-1}\)):
1703, 1621, 1406; LRMS (EI, 70 eV) \(m/z\) (%): 293 \((M^+, 8)\), 161 \((100)\); HRMS \(m/z\) (ESI) calcd for \(C_{20}H_{24}NO\) \([M+H]^+\) 294.1832, found 294.1828.

**1,3-Dimethyl-3-(2-(pyridin-2-yl)ethyl)indolin-2-one (3ah):**

![Image](image1)

Yellow oil; \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.45 \((d, J = 4.8 \text{ Hz}, 1H)\), 7.51 \((t, J = 7.6 \text{ Hz}, 1H)\), 7.29-7.20 \((m, 2H)\), 7.09-7.04 \((m, 2H)\), 7.00 \((d, J = 7.6 \text{ Hz}, 1H)\), 6.86 \((d, J = 7.6 \text{ Hz}, 1H)\), 3.24 \((s, 3H)\), 2.53-2.19 \((m, 4H)\), 1.42 \((s, 3H)\); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\): 180.3, 160.9, 148.9, 143.1, 136.3, 133.5, 127.8, 122.7 \((2C)\), 121.1, 107.9, 48.2, 37.8, 33.2, 26.1, 23.8; IR (KBr, cm\(^{-1}\)): 1716, 1618, 1431; LRMS (EI, 70 eV) \(m/z\) (%): 266 \((M^+, 12)\), 161 \((100)\); HRMS \(m/z\) (ESI) calcd for \(C_{17}H_{19}N_2O\) \([M+H]^+\) 267.1492, found 267.1498.

**1,3-Dimethyl-3-(2-(pyridin-3-yl)ethyl)indolin-2-one (3ai):**

![Image](image2)

Yellow oil; \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.38 \((d, J = 4.0 \text{ Hz}, 1H)\), 8.21 \((s, 1H)\), 7.38 \((t, J = 7.6 \text{ Hz}, 1H)\), 7.32 \((t, J = 7.6 \text{ Hz}, 1H)\), 7.23 \((t, J = 7.2 \text{ Hz}, 1H)\), 7.16-7.10 \((m, 2H)\), 6.88 \((d, J = 7.6 \text{ Hz}, 1H)\), 3.20 \((s, 3H)\), 2.34-2.26 \((m, 2H)\), 2.25-2.10 \((m, 1H)\), 2.09-1.99 \((m, 1H)\), 1.40 \((s, 3H)\); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\): 180.1, 149.7, 147.5, 143.3, 136.5, 135.8, 133.3, 128.1, 123.2, 122.8, 122.5, 108.2, 48.3, 39.6, 28.3, 26.2, 24.1; IR (KBr, cm\(^{-1}\)): 1721, 1632, 1431; LRMS (EI, 70 eV) \(m/z\) (%): 266
(M⁺, 4), 161 (100); HRMS m/z (ESI) calcd for C₁₇H₁₉N₂O ([M+H⁺]⁺) 267.1492, found 267.1496.

1,3-Dimethyl-3-(2-(pyridin-4-yl)ethyl)indolin-2-one (3aj):

Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ: 8.41 (d, J = 5.6 Hz, 2H), 7.34-7.28 (m, 1H), 7.22 (d, J = 6.8 Hz, 1H), 7.12 (t, J = 3.6 Hz, 1H), 6.96 (d, J = 6.0 Hz, 2H), 6.89 (d, J = 7.6 Hz, 1H), 3.22 (s, 3H), 2.33-2.24 (m, 2H), 2.17-1.98 (m, 2H), 1.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 180.0, 150.2, 149.5, 143.2, 133.1, 128.0, 123.7, 122.7, 122.4, 108.1, 48.2, 38.7, 30.3, 26.1, 23.9; IR (KBr, cm⁻¹): 1723, 1646, 1406; LRMS (EI, 70 eV) m/z (%): 266 (M⁺, 17), 161 (100); HRMS m/z (ESI) calcd for C₁₇H₁₉N₂O ([M+H⁺]⁺) 267.1492, found 267.1480.

1,3-Dimethyl-3-(2-(thiophen-2-yl)ethyl)indolin-2-one (3ak):

Brown oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.29 (d, J = 7.5 Hz, 1H), 7.21 (d, J = 7.0 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.04 (t, J = 5.0 Hz, 1H), 6.87-6.82 (m, 2H), 6.64 (d, J = 3.5 Hz, 1H), 3.21 (s, 3H), 2.57-2.49 (m, 1H), 2.40-2.30 (m, 2H), 2.14-2.07 (m, 1H), 1.41 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 180.0, 144.1, 143.3, 133.4, 127.9, 126.5, 124.0, 123.0, 122.6, 122.5, 108.0, 48.1, 40.1, 26.1, 25.0, 23.8; IR (KBr, cm⁻¹): 1731, 1651, 1422, 896; LRMS (EI, 70 eV) m/z (%): 271 (M⁺, 2), 161 (100); HRMS m/z (ESI) calcd for C₁₆H₁₈NOS ([M+H⁺]⁺) 272.1111, found 272.1116.
1,3-Dimethyl-3-(2-(quinolin-8-yl)ethyl)indolin-2-one (3al):  

Brown oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 8.86 (d, $J = 4.0$ Hz, 1H), 8.04 (d, $J = 8.0$ Hz, 1H), 7.57 (d, $J = 4.5$ Hz, 1H), 7.35-7.23 (m, 5H), 7.06 (t, $J = 7.5$ Hz, 1H), 6.82 (d, $J = 7.5$ Hz, 1H), 3.21 (s, 3H), 3.00-2.94 (m, 2H), 2.44-2.38 (m, 1H), 2.32-2.26 (m, 1H), 1.41 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 180.6, 149.1, 146.6, 143.3, 140.3, 136.0, 133.9, 128.6, 128.1, 127.6, 126.0 (2C), 122.8, 122.3, 120.7, 107.8, 48.5, 38.7, 26.8, 26.1, 24.1; IR (KBr, cm$^{-1}$): 1703, 1632, 1418, 982; LRMS (EI, 70 eV) m/z (%): 316 (M$^+$, 1), 156 (100); HRMS m/z (ESI) calcd for C$_{21}$H$_{21}$N$_2$O ([M+H]$^+$) 317.1656, found 317.1648.

1,3-Dimethyl-3-(2-phenylpropyl)indolin-2-one (3am):  

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.14 (t, $J = 7.6$ Hz, 1H), 7.08-7.00 (m, 3H), 6.93-6.85 (m, 4H), 6.72 (d, $J = 8.0$ Hz, 1H), 3.21 (s, 3H), 2.42-2.37 (m, 1H), 2.33-2.28 (m, 1H), 2.20-2.15 (m, 1H), 1.30 (s, 3H), 1.04 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 180.7, 147.3, 143.0, 133.4, 128.0, 127.4, 126.6, 125.7, 122.9, 122.3, 107.8, 48.2, 46.1, 37.2, 26.1, 26.0, 22.7; IR (KBr, cm$^{-1}$): 1709, 1665, 1412; LRMS (EI, 70 eV) m/z (%): 279 (M$^+$, 6), 161 (100); HRMS m/z (ESI) calcd for C$_{19}$H$_{22}$NO ([M+H]$^+$) 280.1696, found 280.1694.

1,3-Dimethyl-3-(2-methyl-2-phenylpropyl)indolin-2-one (3an):
Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.13-7.02 (m, 4H), 6.97 (d, $J = 7.6$ Hz, 2H), 6.72-6.63 (m, 3H), 2.99 (s, 3H), 2.54 (d, $J = 14.4$ Hz, 1H), 2.29 (d, $J = 14.4$ Hz, 1H), 1.23 (s, 3H), 1.10 (s, 3H), 1.05 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 180.4, 148.2, 142.5, 132.7, 127.4, 126.9, 125.9, 125.3, 123.9, 121.7, 107.5, 51.5, 47.4, 37.8, 31.0, 28.3, 28.1, 26.0; IR (KBr, cm$^{-1}$): 1721, 1653, 1401; LRMS (EI, 70 eV) $m/z$ (%): 293 (M$^+$, 5), 161 (100); HRMS $m/z$ (ESI) calcd for C$_{20}$H$_{24}$NO ([M$+\text{H}^+$]) 294.1781, found 294.1798.

1-Benzyl-3-(3,5-dimethylphenethyl)-3-methylindolin-2-one (3bg):

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.30-7.21 (m, 6H), 7.18 (d, $J = 7.6$ Hz, 1H), 7.13 (t, $J = 7.6$ Hz, 1H), 7.07-6.68 (m, 4H), 4.99 (d, $J = 16.0$ Hz, 1H), 4.87 (d, $J = 16.0$ Hz, 1H), 2.34-2.20 (m, 2H), 2.23 (s, 6H), 2.09-2.00 (m, 2H), 1.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 180.4, 142.5, 141.4, 137.7, 133.8, 128.7, 127.6, 127.5 (2C), 127.2, 126.2, 126.1, 122.5 (2C), 109.0, 48.4, 43.6, 40.5, 30.9, 24.2, 21.1; IR (KBr, cm$^{-1}$): 1703, 1651, 1406; LRMS (EI, 70 eV) $m/z$ (%): 369 (M$^+$, 1), 237 (100); HRMS $m/z$ (ESI) calcd for C$_{26}$H$_{28}$NO ([M$+\text{H}^+$]) 370.2165, found 370.2166.

3-(3,5-Dimethylphenethyl)-1,3,5-trimethylindolin-2-one (3eg):
Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.08 (d, $J = 6.0$ Hz, 1H), 7.03 (s, 1H), 6.75 (t, $J = 6.4$ Hz, 2H), 6.67 (s, 2H), 3.20 (s, 3H), 2.37 (s, 3H), 2.27-2.19 (m, 2H), 2.20 (s, 6H), 2.08-1.94 (m, 2H), 1.37 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$) $\delta$: 180.3, 141.4, 140.9, 137.6, 133.7, 132.0, 127.4, 126.1, 123.3, 107.6, 48.4, 40.4, 30.7, 26.9, 23.9, 21.1 (2C); IR (KBr, cm$^{-1}$): 1711, 1655, 1432; LRMS (EI, 70 eV) $m/z$ (%): 307 (M$^+$, 5), 175 (100); HRMS $m/z$ (ESI) calcd for C$_{21}$H$_{26}$NO ([M+H]$^+$) 308.2009, found 308.2008.

3-(3,5-Dimethylphenethyl)-5-methoxy-1,3-dimethylindolin-2-one (3fg):

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 6.83-6.79 (m, 2H), 6.75 (d, $J = 8.4$ Hz, 2H), 6.65 (s, 2H), 3.82 (s, 3H), 3.19 (s, 3H), 2.92-2.19 (m, 2H), 2.20 (s, 6H), 2.08-1.92 (m, 2H), 1.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 180.0, 156.2, 141.3, 137.6, 137.0, 135.3, 127.4, 126.1, 111.7, 110.3, 108.1, 55.8, 48.9, 40.5, 30.8, 26.2, 24.0, 21.1; IR (KBr, cm$^{-1}$): 1708, 1621, 1493; LRMS (EI, 70 eV) $m/z$ (%): 323 (M$^+$, 12), 191 (100); HRMS $m/z$ (ESI) calcd for C$_{23}$H$_{28}$NO$_2$ ([M+H]$^+$) 324.1965, found 324.1968.

3-(3,5-Dimethylphenethyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3gg):
Yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.56 (d, $J = 8.0$ Hz, 1H), 7.41 (s, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 6.77 (s, 1H), 6.62 (s, 2H), 3.24 (s, 3H), 2.32-2.18 (m, 2H), 2.22 (s, 6H), 2.09-2.00 (m, 2H), 1.41 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 180.2, 146.3, 140.6, 137.7, 134.3, 127.6, 126.0, 125.6 (d, $J = 12.8$ Hz, 1C), 124.1 (q, $J = 186.6$ Hz, 1C), 119.5 (d, $J = 3.5$ Hz, 1C), 107.6, 48.4, 40.0, 30.7, 26.3, 23.9, 21.1; IR (KBr, cm$^{-1}$): 1716, 1624, 1416; LRMS (EI, 70 eV) $m/z$ (%): 361 (M$^+$, 1), 229 (100); HRMS $m/z$ (ESI) calcd for C$_{21}$H$_{23}$F$_3$NO ([M+H]$^+$) 362.1730, found 362.1726.

3-(3,5-Dimethylphenethyl)-1,3,7-trimethylindolin-2-one (3hg):

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.05 (d, $J = 6.4$ Hz, 1H), 7.02-6.96 (m, 2H), 6.77 (s, 1H), 6.66 (s, 2H), 3.50 (s, 3H), 2.60 (s, 3H), 2.27-2.13 (m, 2H), 2.22 (s, 6H), 2.09-1.90 (m, 2H), 1.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 181.1, 141.3, 141.0, 137.6, 134.3, 131.4, 127.4 (2C), 126.1 (2C), 122.4, 120.3, 119.5, 47.7, 40.7, 30.7, 29.4, 24.3, 21.1, 19.0; IR (KBr, cm$^{-1}$): 1715, 1662, 1413; LRMS (EI, 70 eV) $m/z$ (%): 307 (M$^+$, 4), 175 (100); HRMS $m/z$ (ESI) calcd for C$_{20}$H$_{26}$NO ([M+H]$^+$) 308.2009, found 308.2008.
7-Chloro-3-(3,5-dimethylphenethyl)-1,3-dimethylindolin-2-one (3ig):

Yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.20 (d, $J = 8.0$ Hz, 1H), 7.08 (d, $J = 7.0$ Hz, 1H), 6.99 (d, $J = 7.5$ Hz, 1H), 6.77 (s, 1H), 6.64 (s, 2H), 3.57 (s, 3H), 2.30-2.18 (m, 2H), 2.25 (s, 6H), 2.07-1.92 (m, 2H), 1.37 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 180.5, 140.8, 139.2, 137.7, 136.5, 130.0, 127.5, 126.1, 123.3, 120.9, 115.4, 48.1, 40.5, 30.7, 29.4, 24.3, 21.1; IR (KBr, cm$^{-1}$): 1716, 1635, 1423; LRMS (EI, 70 eV) $m/z$ (%): 327 (M$^+$, 1), 197 (32), 195 (100); HRMS $m/z$ (ESI) calcd for C$_{20}$H$_{23}$ClNO ([M$^+$H$^+$]$^+$) 328.1463, found 328.1461.

3-(3,5-Dimethylphenethyl)-7-iodo-1,3-dimethylindolin-2-one (3jg):

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.67 (d, $J = 7.6$ Hz, 1H), 7.14 (d, $J = 7.2$ Hz, 1H), 6.78 (t, $J = 7.6$ Hz, 2H), 6.63 (s, 2H), 3.58 (s, 3H), 2.30-2.14 (m, 2H), 2.23 (s, 6H), 2.07-1.91 (m, 2H), 1.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 180.9, 143.6, 140.8, 140.3, 137.7, 136.8, 127.5, 126.1 (2C), 124.2, 122.2, 71.6, 47.9, 40.4, 30.7, 29.9, 24.3, 21.2; IR (KBr, cm$^{-1}$): 1716 1489, 1460; LRMS (EI, 70 eV) $m/z$ (%): 419 (M$^+$, 1), 287 (100); HRMS $m/z$ (ESI) calcd for C$_{20}$H$_{23}$INO ([M$^+$H$^+$]$^+$) 420.0826, found 420.0833.
3-(3,5-Dimethylphenethyl)-1,3,6-trimethylindolin-2-one (3kg) and 3-(3,5-Dimethylphenethyl)-1,3,4-trimethylindolin-2-one (3kg’)

\[
\text{3kg : 3kg’ = 2-1}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.22-7.16 (m, 1H), 7.09 (d, \(J = 7.6\) Hz, 0.5H), 6.90 (d, \(J = 7.2\) Hz, 0.5H), 6.86-6.82 (m, 1H), 6.76 (s, 1.5H), 6.70-6.62 (m, 4.5H), 3.19 (s, 1.5H), 3.18 (s, 3H), 2.39 (s, 1.5H), 2.35 (s, 3H), 2.34-2.17 (m, 12H), 2.14-1.91 (m, 3H), 1.45 (s, 1.5H), 1.35 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 180.6, 180.3, 143.5, 143.3(2C), 141.1, 137.6, 137.5, 137.4, 134.0, 130.6, 130.0, 127.5, 127.3, 126.0 (2C), 124.9, 122.9, 122.1, 108.8, 105.6, 49.3, 48.1, 40.4, 38.2, 30.7, 31.2, 26.0, 25.9, 23.9, 22.3, 21.0, 20.9, 18.1, 14.1.

3-(3,5-Dimethylphenethyl)-1-methyl-3-phenylindolin-2-one (3lg):

Yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.38-7.34 (m, 3H), 7.30-7.26 (m, 3H), 7.23-7.20 (m, 1H), 7.17-7.14 (m, 1H), 6.92 (d, \(J = 8.0\) Hz, 1H), 6.79 (s, 1H), 6.70 (s, 2H), 3.22 (s, 3H), 2.71 (d, \(J = 4.0\) Hz, 1H), 2.47-2.41 (m, 1H), 2.37-2.31 (m, 1H), 2.24 (s, 6H), 2.15-2.10 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 178.3, 143.9, 141.1, 140.0, 137.7, 131.9, 128.5, 128.2, 127.5, 127.2, 126.8, 126.1, 124.7, 122.7, 108.3, 56.6, 39.8, 30.8, 26.3, 21.1; IR (KBr, cm\(^{-1}\)): 1716, 1681, 1422;
LRMS (EI, 70 eV) m/z (%): 355 (M+, 1), 223 (100); HRMS m/z (ESI) calcd for C_{23}H_{26}NO ([M+H]^+) 356.2016, found 356.2019.

3-(3,5-Dimethylphenethyl)-1-methyl-3-(o-tolyl)indolin-2-one (3mg):

![Chemical structure image]

Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ: 7.66 (d, J = 8.0 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.24 (t, J = 6.4 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.06-7.01 (m, 2H), 6.90 (t, J = 7.6 Hz, 2H), 6.81 (s, 1H), 6.71 (s, 2H), 3.34 (s, 3H), 2.77-2.66 (m, 1H), 2.49-2.29 (m, 2H), 2.25 (s, 6H), 2.04-1.94 (m, 1H), 1.67 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ: 178.7, 144.0, 141.3, 138.1, 137.8, 136.9, 132.8, 132.0, 128.0, 127.6, 127.4, 127.3, 126.2, 125.9, 123.2, 123.1, 107.7, 55.9, 40.5, 29.4, 26.2, 21.2, 19.3; IR (KBr, cm^{-1}): 1709, 1665, 1412; LRMS (EI, 70 eV) m/z (%): 369 (M+, 2), 147 (100); HRMS m/z (ESI) calcd for C_{26}H_{28}NO ([M+H]^+) 370.2165, found 370.2166.

(3-(3,5-Dimethylphenethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate (3ng):

![Chemical structure image]

Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ: 7.32 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 8.8 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 6.86 (d, J = 7.6 Hz, 1H), 6.77 (s, 1H), 6.63 (s, 2H), 4.53 (d, J = 10.8 Hz, 1H), 4.18 (d, J = 10.8 Hz, 1H), 3.22 (s, 3H), 2.28-2.21 (m, 2H), 2.22 (s, 6H), 2.10-2.05 (m, 2H), 1.85 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ: 177.2, 170.2, 144.2, 140.7, 137.7, 129.3, 128.4, 127.6, 126.1, 123.3, 122.6,
3-(3,5-Dimethylphenethyl)-1-methylindolin-2-one (3og):

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.30 (t, $J = 8.0$ Hz, 2H), 7.08 (t, $J = 8.0$ Hz, 1H), 6.85-6.80 (m, 4H), 3.49 (t, $J = 6.4$ Hz, 1H), 3.21 (s, 3H), 2.69-2.52 (m, 2H), 2.29-2.20 (m, 2H), 2.26 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 177.7, 144.4, 141.2, 137.8, 129.0, 127.9, 127.6, 126.3, 123.8, 122.3, 107.9, 45.0, 32.4, 31.8, 26.1, 21.2; IR (KBr, cm$^{-1}$): 1706, 1681, 1415; LRMS (EI, 70 eV) m/z (%): 279 (M$^+$, 2), 147 (100); HRMS m/z (ESI) calcd for C$_{19}$H$_{22}$NO ([M$+$H]$^+$) 280.1696, found 280.1698.

3-(2-(3,5-Dimethylphenyl)-1-phenylethyl)-1-methylindolin-2-one (3pg):

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.37-7.34 (m, 1H), 7.18 (t, $J = 6.0$ Hz, 2H), 7.14-7.10 (m, 4H), 6.87 (d, $J = 6.0$ Hz, 3H), 6.76 (s, 2H), 3.88 (d, $J = 2.0$ Hz, 1H), 3.39 (s, 3H), 3.22-3.19 (m, 1H), 3.02-2.98 (m, 1H), 2.48-2.43 (m, 1H), 2.30 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 171.2, 141.8, 140.0, 138.3, 138.0, 129.9, 128.6, 128.2, 128.0, 127.3, 127.0, 126.7, 126.3, 123.4, 114.7, 50.5, 44.4,
36.0, 29.6, 21.3; IR (KBr, cm⁻¹): 1719, 1665, 1403; LRMS (EI, 70 eV) m/z (%): 355 (M⁺, 3), 236 (100); HRMS m/z (ESI) calcd for C₂₅H₂₆NO ([M+H]⁺) 356.2009, found 356.2006.

(C) Reference


(D) Spectra

1,3-Dimethyl-3-phenethylindolin-2-one (3aa)
1,3-Dimethyl-3-phenethylindolin-2-one (3aa)
1,3-Dimethyl-3-(4-methylphenethyl)indolin-2-one (3ab)

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013
3-(4-Methoxyphenethyl)-1,3-dimethylindolin-2-one (3ac)
3-(4-Methoxyphenethyl)-1,3-dimethylindolin-2-one (3ac)
3-(2-Methoxyphenethyl)-1,3-dimethylindolin-2-one (3ad)
3-(2-Bromophenethyl)-1,3-dimethylindolin-2-one (3ae)
3-(2-Bromophenethyl)-1,3-dimethylindolin-2-one (3ae)
3-(2-Iodophenethyl)-1,3-dimethylindolin-2-one (3af)
3-(3,5-Dimethylphenethyl)-1,3-dimethylindolin-2-one (3ag)
1,3-Dimethyl-3-(2-(pyridin-2-yl)ethyl)indolin-2-one (3ah)
1,3-Dimethyl-3-(2-(pyridin-3-yl)ethyl)indolin-2-one (3ai)
1,3-Dimethyl-3-(2-(pyridin-3-yl)ethyl)indolin-2-one (3ai)
1,3-Dimethyl-3-(2-(pyridin-4-yl)ethyl)indolin-2-one (3aj)
1,3-Dimethyl-3-(2-(thiophen-2-yl)ethyl)indolin-2-one (3ak):
1,3-Dimethyl-3-(2-(thiophen-2-yl)ethyl)indolin-2-one (3ak):
1,3-Dimethyl-3-(2-(quinolin-8-yl)ethyl)indolin-2-one (3al):
1,3-Dimethyl-3-(2-(quinolin-8-yl)ethyl)indolin-2-one (3al):
1,3-Dimethyl-3-(2-phenylpropyl)indolin-2-one (3am)
1,3-Dimethyl-3-(2-phenylpropyl)indolin-2-one (3am)
1,3-Dimethyl-3-(2-methyl-2-phenylpropyl)indolin-2-one (3an)
1,3-Dimethyl-3-(2-methyl-2-phenylpropyl)indolin-2-one (3an)
1-Benzyl-3-(3,5-dimethylphenethyl)-3-methylindolin-2-one (3bg)
1-Benzyl-3-(3,5-dimethylphenethyl)-3-methylindolin-2-one (3bg)
3-(3,5-Dimethylphenethyl)-1,3,5-trimethylindolin-2-one (3eg)
3-(3,5-Dimethylphenethyl)-1,3,5-trimethylindolin-2-one (3eg)
3-(3,5-Dimethylphenethyl)-5-methoxy-1,3-dimethylindolin-2-one (3fg)
3-(3,5-Dimethylphenethyl)-5-methoxy-1,3-dimethylindolin-2-one (3fg)
3-(3,5-Dimethylphenethyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3gg)
3-(3,5-Dimethylphenethyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3gg)
3-(3,5-Dimethylphenethyl)-1,3,7-trimethylindolin-2-one (3hg)
3-(3,5-Dimethylphenethyl)-1,3,7-trimethylindolin-2-one (3hg)
7-Chloro-3-(3,5-dimethylphenethyl)-1,3-dimethylindolin-2-one (3ig)
7-Chloro-3-(3,5-dimethylphenethyl)-1,3-dimethylindolin-2-one (3ig)
3-(3,5-Dimethylphenethyl)-7-iodo-1,3-dimethylindolin-2-one (3jg)
3-(3,5-Dimethylphenethyl)-7-iodo-1,3-dimethylindolin-2-one (3jg)
3-(3,5-Dimethylphenethyl)-1,3,6-trimethylindolin-2-one (3kg) and 3-(3,5-Dimethylphenethyl)-1,3,4-trimethylindolin-2-one (3kg')
3-(3,5-Dimethylphenethyl)-1,3,6-trimethylindolin-2-one (3kg) and 3-(3,5-Dimethylphenethyl)-1,3,4-trimethylindolin-2-one (3kg')
3-(3,5-Dimethylphenethyl)-1-methyl-3-phenylindolin-2-one (3lg)
3-(3,5-Dimethylphenethyl)-1-methyl-3-phenylindolin-2-one (3lg)
3-(3,5-Dimethylphenethyl)-1-methyl-3-(o-tolyl)indolin-2-one (3mg)
3-(3,5-Dimethylphenethyl)-1-methyl-3-(o-tolyl)indolin-2-one (3mg)
(3-(3,5-Dimethylphenethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate (3ng)
(3-(3,5-Dimethylphenethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate (3ng)
3-(3,5-Dimethylphenethyl)-1-methylindolin-2-one (3og)
3-(2-(3,5-Dimethylphenyl)-1-phenylethyl)-1-methylindolin-2-one (3pg)
3-(2-(3,5-Dimethylphenyl)-1-phenylethyl)-1-methylindolin-2-one (3pg)
1-((3,5-Dimethylbenzyl)oxy)-2,2,6,6-tetramethylpiperidine (4ag)
1-((3,5-Dimethylbenzyl)oxy)-2,2,6,6-tetramethylpiperidine (4ag)
3-Ethyl-1,3-dimethylindolin-2-one (5aa)
3aa and 3aa-D1