

## SUPPORTING INFORMATION

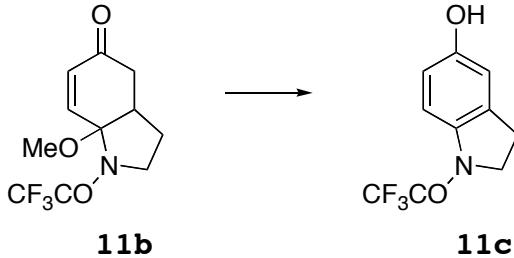
### Oxidation of p-Aminophenols and Formal Radical Cyclization onto Benzene Rings: Formation of Benzo-fused Nitrogen Heterocycles

Stephen P. Fletcher, Derrick L. J. Clive,\* Jianbiao Peng, and David A. Wingert

*Chemistry Department, University of Alberta, Edmonton, Alberta, Canada T6G 2G2  
e-mail: derrick.clive@ualberta.ca*

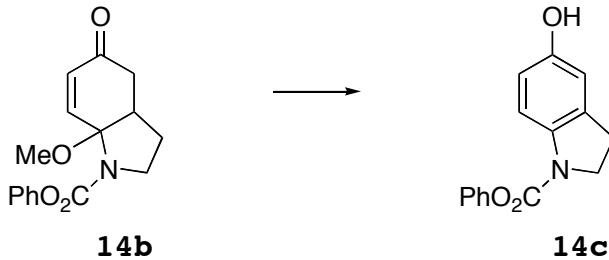
The symbols s, d, t, and q used for  $^{13}\text{C}$  NMR indicate 0, 1, 2, or 3 attached hydrogens. Because of restricted rotation many signals were distorted. If "m" appears before s, d, t, or q, this indicates many signals in close proximity. The use of "br" indicates that the signal is broad.

#### **1-(Trifluoroacetyl)-2,3-dihydro-1*H*-indol-5-ol (**11c**).**



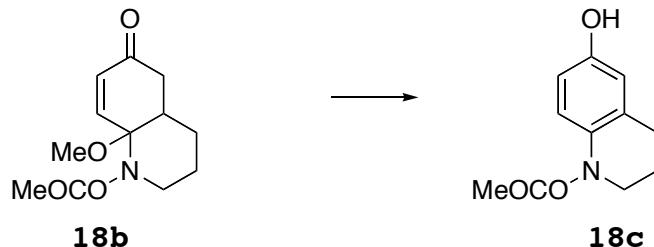
Compound **11c** had: FTIR (CHCl<sub>3</sub>, cast) 3347, 1667, 1616, 1605, 1493, 1462 cm<sup>-1</sup>;  $^1\text{H}$  NMR (CD<sub>3</sub>OD, 500 MHz)  $\delta$  3.17 (t,  $J$  = 8.1 Hz, 2 H), 4.24 (t,  $J$  = 8.6 Hz, 2 H), 6.63 (apparent dd,  $J$  = 8.8, 2.5 Hz, 1 H), 6.71–6.73 (m, 1 H), 7.92 (d,  $J$  = 8.8 Hz, 1 H);  $^{13}\text{C}$  NMR (CD<sub>3</sub>OD, 125 MHz)  $\delta$  29.4 (t), 49.4 (t), 112.9 (d), 114.7 (d), 117.8 (s split into q,  $J_{\text{CF}}$  = 286.0 Hz), 119.6 (d), 135.2 (s), 135.5 (s), 154.5 (s split into q,  $J_{\text{CF}}$  = 37.1 Hz), 157.2 (s); exact mass  $m/z$  calcd for C<sub>10</sub>H<sub>8</sub>F<sub>3</sub>NO<sub>2</sub> 231.05072, found 231.05061.

**Phenyl 5-Hydroxy-2,3-dihydroindole-1-carboxylate (14c).**



Compound **14c** had: mp 190–195 °C; FTIR (CDCl<sub>3</sub> cast) 3390, 1694, 1601 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>OD, 499.8 MHz) δ 3.12 (t, *J* = 9.5 Hz, 2 H), 4.17 (t, *J* = 10 Hz, 2 H), 6.59–7.59 (m, 8 H); <sup>13</sup>C NMR (acetone-d<sub>6</sub>, 100 MHz) δ 28.4 (t), 48.8 (t), 113.2 (d), 114.3 (d), 116.2 (d), 123.0 (d), 126.2 (d), 130.2 (d), 134.0 (s), 135.9 (s), 152.4 (s), 154.6 (s), 206.4 (s); exact mass *m/z* calcd for C<sub>15</sub>H<sub>13</sub>NO<sub>3</sub> 255.08954, found 255.08906.

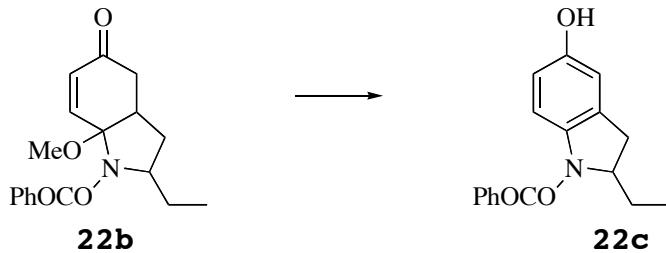
**Methyl 6-Hydroxy-3,4-dihydro-2H-quinoline-1-carboxylate (18c).**



Compound **18c** had: FTIR (CH<sub>2</sub>Cl<sub>2</sub>, cast) 2950, 1706, 1616, 1582, 1502 cm<sup>-1</sup>; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz) δ 1.42 (quintet, *J* = 6.4 Hz, 2 H), 2.30 (t, *J* = 6.6 Hz, 2 H), 3.49 (s, 3 H), 3.52 (t, *J* = 6.2 Hz, 2 H), 6.66 (s, 1 H), 6.89 (d, *J* = 8.4 Hz, 1 H), 7.93 (d, *J* = 8.4 Hz, 1 H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz) δ 20.7 (q), 23.5 (t), 27.5 (t), 44.9 (t), 52.3 (q), 124.2 (d), 127.0 (d), 129.2 (d), 129.5 (s), 132.7 (s), 136.5 (s), 155.1 (s); exact mass *m/z* calcd for C<sub>12</sub>H<sub>15</sub>NO<sub>2</sub> 205.11028, found 205.11051.

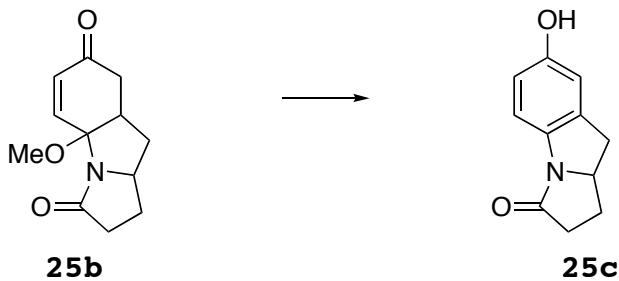
**Phenyl 2-Ethyl-5-hydroxy-2,3-dihydroindole-1-carboxylate**

(22c).



Compound **22c** had: FTIR (CHCl<sub>3</sub>, cast) 3380, 2966, 2876, 1716, 1689, 1605 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 0.95 (br t, *J* = 5.5 Hz, 3 H), 1.58-1.78 (br m, 2 H), 1.85-1.95 (br s, 1 H), 2.72-2.82 (br d, 1 H), 3.35 (br dd, *J* = 15.5, 10.0 Hz, 1 H), 4.50-4.63 (apparent br s, 1 H), 4.97 (br s, 1 H), 6.61 (dd, *J* = 9.0, 2.5 Hz, 1 H), 6.68 (br s, 1 H), 7.17-7.25 (m, 3 H), 7.39 (t, *J* = 8.0 Hz, 2.3 H), 7.64-7.71 (br s, 0.55 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 9.1 (q), 27.8 (br t), 33.3 (t), 61.2 (br d), 112.2 (br d), 113.9 (d), 116.2 (br d), 121.8 (d), 125.5 (d), 129.4 (d), 135.5 (br s), 150.9 (br s), 152.0 (s); exact mass *m/z* calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>3</sub> 283.12085, found 283.12038.

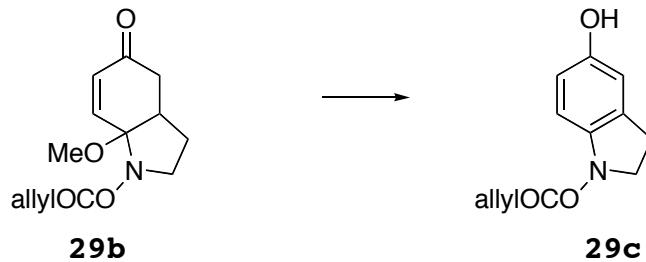
**6-Hydroxy-1,2,8a-tetrahydro-3a-azacyclopenta[a]inden-3-one (25c).**



Compound **25c** had: FTIR (microscope) 3203, 2975, 1651, 1610, 1500, 1453 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz) δ 1.94-2.02 (m, 1 H), 2.44 (quintet of m, *J* = 7.3 Hz, 1 H), 2.50 (ddd, *J* = 16.6, 8.6, 0.7 Hz, 1 H), 2.79-2.90 (m, 2 H), 3.10 (dd, *J* = 15.7, 8.2 Hz, 1 H), 3.30 (quintet, *J* = 1.6 Hz, 2 H), 4.64 (tdd, *J* = 9.8, 8.3, 6.2 Hz, 2 H), 6.60 (dd, *J* = 8.4, 2.5 Hz, 1 H), 6.67-6.69

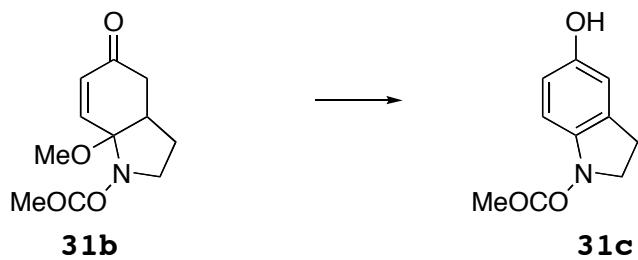
(m, 1 H), 7.29 (d,  $J$  = 8.4 Hz, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  29.8 (t), 36.7 (t), 37.2 (t), 65.4 (d), 113.8 (d), 114.5 (d), 116.2 (d), 132.6 (s), 138.0 (s), 156.1 (s); exact mass  $m/z$  calcd for  $\text{C}_{11}\text{H}_{11}\text{NO}_2$  189.07898, found 189.07917.

**Allyl 5-Hydroxy-2,3-dihydroindole-1-carboxylate (29c).**



Compound **29c** had: FTIR ( $\text{CHCl}_3$ , cast) 3360, 2950, 1670, 1604, 1497, 1435  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.06 (t,  $J$  = 7.5 Hz, 2 H), 4.03 (t,  $J$  = 8.5 Hz, 2 H), 4.70 (br s, 1.3 H), 4.78 (br s, 0.7 H), 5.23-5.41 (br m, 2 H), 5.70 (br s, 1 H), 5.99 (br s, 1 H), 6.66 (d,  $J$  = 8.4 Hz, 1 H), 6.70-6.71 (m, 1 H), 7.34 (br s, 0.4 H), 7.67-7.73 (br m, 0.6 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  27.6 (m t), 47.5 (m t), 65.8 (m t), 112.2 (m d), 113.8 (d), 117.6 (m s), 132.7 (m d), 135.9 (m t); exact mass  $m/z$  calcd for  $\text{C}_{12}\text{H}_{12}\text{NO}_3$  219.08954, found 219.08958.

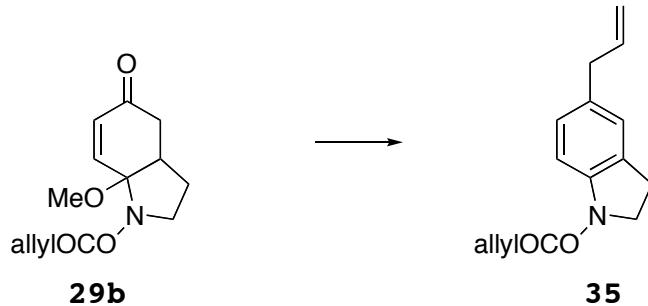
**Methyl 5-Hydroxy-2,3-dihydroindole-1-carboxylate (31c).**



Compound **31c** had: FTIR (microscope) 3275, 2961, 1708, 1671, 1600, 1484  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 500 MHz)  $\delta$  3.02 (t,  $J$  = 8.6 Hz, 2 H), 3.74-3.86 (br s, 3 H), 3.93 (t,  $J$  = 8.4 Hz, 2 H), 6.56 (dd,  $J$  = 8.6, 2.4 Hz, 1 H), 6.63 (apparent t,  $J$  = 1.3 Hz, 1 H),

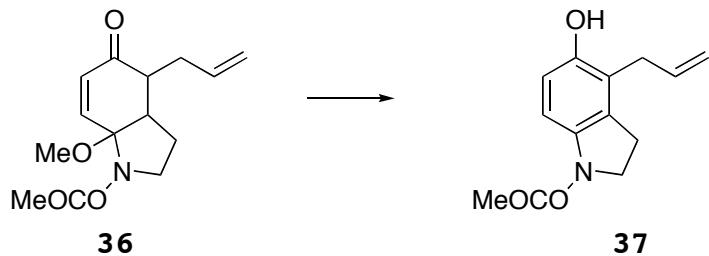
7.18–7.32 (br s, 0.3 H), 7.48–7.60 (br s, 0.7 H);  $^{13}\text{C}$  NMR (acetone-d<sub>6</sub>, 100 MHz)  $\delta$  28.2 (br t), 47.5 (br t), 52.2 (q), 112.9 (d), 114.0 (d), 115.7 (br d), 154.0 (s); exact mass *m/z* calcd for C<sub>10</sub>H<sub>11</sub>NO<sub>3</sub> 193.07390, found 193.07356.

**Methyl 5-Allyl-2,3-dihydroindole-1-carboxylate (35).**



Compound **35** had: FTIR (CHCl<sub>3</sub>, cast) 3078, 2921, 1710, 1638, 1615, 1494 cm<sup>-1</sup>;  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  3.10 (t,  $J$  = 8.6 Hz, 2 H), 3.34 (d,  $J$  = 6.6 Hz, 2 H), 4.04 (t,  $J$  = 8.6 Hz, 2 H), 4.68–4.83 (br m, 2 H), 5.03–5.09 (m, 2 H), 5.24–5.41 (br m, 2 H), 5.95 (ddt,  $J$  = 17.0, 10.2, 6.6 Hz, 1 H), 5.95–6.07 (br s, 1 H), 6.98–7.03 (br s, 1 H), 7.00 (s, 1 H), 7.38–7.52 (br s, 0.35 H), 7.76–7.83 (br s, 0.65 H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  27.5 (br t), 39.7 (t), 47.5 (br t), 114.5 (br d), 115.5 (t), 117.6 (br s), 124.8 (br d), 127.6 (d), 132.7 (br d), 134.4 (t), 137.8 (d); exact mass *m/z* calcd for C<sub>15</sub>H<sub>17</sub>NO<sub>2</sub> 243.12593, found 243.12527.

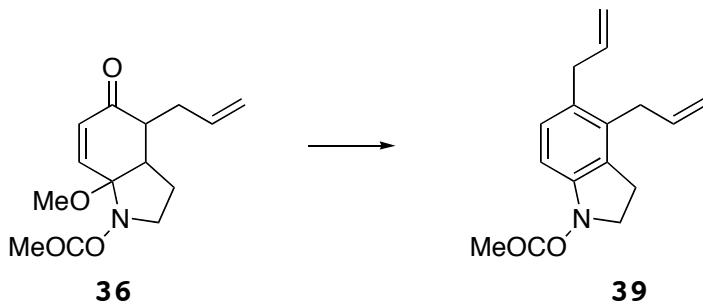
**Methyl 4-Allyl-5-hydroxy-2,3-dihydroindole-1-carboxylate (37).**



Compound **37** had: FTIR (microscope) 3353, 3074, 2959, 2915,

1682, 1638, 1601, 1484  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 500 MHz)  $\delta$  2.97 (t,  $J$  = 8.6 Hz, 2 H), 3.27–3.31 (m, 2 H), 3.72–3.84 (br s, 3 H), 3.92 (t,  $J$  = 8.1 Hz, 2 H), 4.91 (t,  $J$  = 1.3 Hz, 1 H), 4.94 (apparent dq,  $J$  = 7.4, 1.7 Hz, 1 H), 5.87 (dddd,  $J$  = 16.8, 10.7, 6.5, 6.1 Hz, 1 H), 6.58 (d,  $J$  = 8.5 Hz, 1 H), 7.04–7.20 (br s, 0.3 H), 7.38–7.46 (br s, 0.7 H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 125 MHz)  $\delta$  27.2 (br t), 32.1 (t), 52.9 (br q), 113.9 (br d), 114.4 (d), 115.0 (t), 124.2 (s), 133.0 (br s), 136.0 (br s), 136.9 (d), 152.2 (s); exact mass  $m/z$  calcd for  $\text{C}_{13}\text{H}_{15}\text{NO}_3$  233.10519, found 233.10544.

**Methyl 4,5-Diallyl-2,3-dihydroindole-1-carboxylate (39).**



Compound **39** had: FTIR ( $\text{CHCl}_3$ , cast) 2976, 2953, 2918, 1715, 1636, 1476  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz)  $\delta$  3.02 (t,  $J$  = 8.7 Hz, 2 H), 3.29–3.34 (m, 4 H), 3.76–3.83 (br s, 3 H), 3.96 (dd,  $J$  = 9.4, 8.2 Hz, 2 H), 4.89 (qdd,  $J$  = 16.5, 3.7, 1.8 Hz, 2 H), 4.96–5.01 (m, 2 H), 5.81–5.93 (m, 2 H), 6.96 (d,  $J$  = 8.2 Hz, 1 H), 7.20–7.36 (br s, 0.3 H), 7.52–7.62 (br s, 0.7 H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 100 MHz)  $\delta$  27.3 (m t), 35.6 (t), 37.5 (t), 48.7 (br t), 53.1 (br q), 113.7 (br d), 115.59 (t), 115.63 (t), 130.0 (d), 133.9 (d), 135.2 (br s), 136.7 (d), 139.1 (d); exact mass  $m/z$  calcd for  $\text{C}_{16}\text{H}_{19}\text{NO}_2$  257.14157, found 257.14105.