Supporting Information for

'Diethylphosphine Oxide (DEPO): High-Yielding and Facile Preparation of Indolones in Water' by J. A. Murphy *et al.*

Melting points were recorded using either a Griffin or a Gallenkamp melting point apparatus.

Mass spectra were obtained either from a Jeol JMS-AX 505 HA instrument using electron impact ionization (EI), chemical ionization (CI) or fast atom bombardment (FAB), or from the EPSRC National Spectrometry Service based in Swansea, where different instruments are used according to the analysis that is required. The Finnigan MAT 900 XLT (EI, CI, ESI and APcI analyses as well as exact mass measurements). The Micromass Quatro II (EI, CI, ESI, APcI analyses). Proton NMR (^1H) spectra were recorded at 400 MHz on a Bruker DPX400 spectrometer. Carbon NMR (^{13}C) spectra were similarly recorded at 100.61 MHz on a Bruker DPX400 spectrometer, using a broadband decoupled mode with the multiplicities obtained using a JMOD or DEPT sequence.

Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane. NMR experiments were carried out in deuteriochloroform (CDCl_3). The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet for proton spectra, CH_3 : methyl, CH_2 : methylene, CH: methine, C: quaternary carbon for carbon spectra. Coupling constants (J) are reported in Hertz (Hz).

Infrared spectra were either recorded on a Nicolet "Impact 400D" spectrometer, or on a Perkin Elmer "spectrum One FT-IR" spectrometer.

Flash chromatography was performed using Prolabo 35-75 μm particle sized silica gel 60 (200-400 mesh). Thin layer chromatography (tlc) was carried out on a Merck silica gel 60 F₂₅₄ precoated aluminium plates. Visualization was achieved under a UVP mineralight UVG-11 lamp, and by developing the plates with potassium permanganate (KMnO_4), phosphomolybdic acid (PMA) or acid methanolic vanillin solutions.

All reagents were obtained from commercial suppliers unless otherwise stated. Where necessary, organic solvents were routinely dried and/or distilled prior to use and stored over molecular sieves under nitrogen. Diethyl ether was dried over sodium wire. Other solvents were dried by distillation from the following: tetrahydrofuran (sodium/benzophenone); dichloromethane (calcium hydride); ethyl acetate (magnesium sulfate). All reactions requiring anhydrous conditions were performed in flame-dried apparatus under a nitrogen atmosphere. Organic extracts were, in general, dried over anhydrous magnesium sulfate (MgSO_4) or sodium sulfate (Na_2SO_4).

General procedure for amide precursor preparation

N-Methyl-2-iodoaniline (2.33 g, 10 mmol, 1 equiv.) and triethylamine (1.40 ml, 10 mmol, 1 equiv.) were dissolved in dry dichloromethane (20 ml), under a nitrogen atmosphere. Then the commercial acid chloride (12 mmol, 1.2 equiv.) in dry dichloromethane (15 ml) was added dropwise at room temperature. The reaction was stopped on completion (2-3h) by addition of water (20 ml). The mixture was extracted with dichloromethane, washed with hydrochloric acid (2N, 30ml) and saturated sodium hydrogencarbonate solution (20ml). Organic extracts were then dried over sodium sulfate and the solvent was removed under vacuum. The crude product was purified by column chromatography (90:10, hexanes-ethyl acetate) and recrystallized (hexanes, dichloromethane) except **2d** (oil).

N-(2-Iodophenyl)-*N*-methylcyclohexanecarboxamide **1a**:

N-(2-Iodophenyl)-*N*-methylcyclohexanecarboxamide **1a** was obtained as white flakes (2.12 g, 62%); mp 109-111°C (Found: C, 49.11; H, 5.29; N, 4.00. $\text{C}_{14}\text{H}_{18}\text{INO}$ requires C, 48.97; H, 5.29; N, 4.08%) (Found (ESI): $[\text{MH}^+]$ 344.0511. $\text{C}_{14}\text{H}_{18}\text{INO}$ requires MH 344.0511); ν_{max} (KBr)/ cm^{-1} 2941, 2927, 2852, 1642 (C=O), 1465; δ_{H} (400 MHz, CDCl_3) 0.88-1.92 (11H, m, ring), 3.16 (3H, s, Me), 7.09 (1H, ddd, J 7.9, 7.4, 1.4, ArH), 7.26 (1H, dd, J 7.8, 1.4, ArH), 7.42 (1H, ddd, J 7.8, 7.4, 1.4, ArH), 7.95 (1H, dd, J 7.9, 1.4, ArH); δ_{C} (100.61 MHz, CDCl_3) 25.5 (CH_2), 25.7 (CH_2), 25.9 (CH_2), 29.4

(CH₂), 30.0 (CH₂), 36.2 (CH₃), 42.5 (CH), 100.3 (C), 129.1 (CH), 129.8 (CH), 130.0 (CH), 140.4 (CH), 146.6 (C), 176.4 (C); *m/z* (CI⁺) 361 [(MNH₄⁺), 8%], 344 [(MH⁺), 100], 233 (26), 218 (41) and 216 (57).

***N*-(2-Iodophenyl)-*N*-methylcyclopentanecarboxamide 1b:**

N-(2-Iodophenyl)-*N*-methylcyclopentanecarboxamide **1b** was obtained as white flakes (3.26 g, 99%); mp 108-110°C (Found: C, 47.40; H, 4.94; N, 4.21. C₁₃H₁₆INO requires C, 47.41; H, 4.90; N, 4.26%) (Found (ESI): [MH⁺] 330.0363. C₁₃H₁₆INO requires *MH* 330.0355); $\nu_{\max}$ (KBr)/cm⁻¹ 2963, 2868, 1643 (C=O), 1466, 1425, 1389; δ_{H} (400 MHz, CDCl₃) 1.34-1.79 (7H, m, ring), 1.92-2.01 (1H, m, ring), 2.27-2.35 (1H, m, ring), 3.18 (3H, s, Me), 7.08 (1H, ddd, *J* 7.9, 7.4, 1.5, ArH), 7.25 (1H, dd, *J* 7.8, 1.5, ArH), 7.42 (1H, ddd, *J* 7.8, 7.4, 1.2, ArH), 7.94 (1H, dd, *J* 7.9, 1.2, ArH); δ_{C} (100.61 MHz, CDCl₃) 26.7 (CH₂), 26.8 (CH₂), 31.3 (CH₂), 32.0 (CH₂), 36.6 (CH₃), 43.1 (CH), 100.7 (C), 129.8 (CH), 130.1 (CH), 130.3 (CH), 140.6 (CH), 147.0 (C), 177.2 (C); *m/z* (CI⁺) 330 [(MH⁺), 58%], 288 (100), 260 (48) and 245 (62).

***N*-(2-Iodophenyl)-*N*-methylisobutyramide 1c:**

N-(2-Iodophenyl)-*N*-methylisobutyramide **1c** was obtained as white flakes (2.93 g, 97%); mp 94-95°C (Found: C, 43.81; H, 4.67; N, 4.60. C₁₁H₁₄INO requires C, 43.56; H, 4.66; N, 4.62%) (Found (ESI): [MH⁺] 304.0201. C₁₁H₁₄INO requires *MH* 304.0198); $\nu_{\max}$ (KBr)/cm⁻¹ 2967, 2928, 2869, 1653 (C=O), 1471, 1382; δ_{H} (400 MHz, CDCl₃) 0.99 (3H, d, *J* 6.8, CH₃), 1.13 (3H, d, *J* 6.7, CH₃), 2.18-2.25 (1H, m, CH), 3.17 (3H, s, Me), 7.06 (1H, ddd, *J* 7.9, 7.4, 1.6, ArH), 7.26 (1H, dd, *J* 7.8, 1.6, ArH), 7.41 (1H, ddd, *J* 7.8, 7.4, 1.3, ArH), 7.92 (1H, dd, *J* 7.9, 1.3, ArH); δ_{C} (100.61 MHz, CDCl₃) 20.1 (CH₃), 20.4 (CH₃), 32.4 (CH), 36.5 (CH₃), 100.5 (C), 129.3 (CH), 130.1 (CH), 130.3 (CH), 140.7 (CH), 146.9 (C), 177.6 (C); *m/z* (CI⁺) 304 [(MH⁺), 11%], 193 (100), 176 (97), and 108 (18).

2-Ethylhexanoic acid (2-iodophenyl)methylamide **1d**:

2-Ethylhexanoic acid (2-iodophenyl)methylamide **1d** was obtained as a pale yellow oil (3.52 g, 98%); (Found: C, 50.21; H, 6.27; N, 4.02. C₁₅H₂₂INO requires C, 50.13; H, 6.17; N, 3.9%) (Found (ESI): [MH⁺] 360.0822. C₁₅H₂₂INO requires *MH* 360.0824); ν_{max} (film)/cm⁻¹ 2959, 2931, 2871, 1662 (C=O), 1470, 1388; δ_{H} (400 MHz, CDCl₃) 0.80-0.89 (6H, m, 2 x CH₃), 1.15-1.25 (4H, m, side chain), 1.40-1.44 (2H, m, side chain), 1.57-1.95 (3H, m, side chain), 3.21 (3H, s, Me), 7.06 (1H, ddd, *J* 8.0, 7.4, 1.6, ArH), 7.23 (1H, dd, *J* 7.8, 1.6, ArH), 7.40 (1H, ddd, *J* 7.8, 7.4, 1.4, ArH), 7.94 (1H, dd, *J* 8.0, 1.4, ArH); δ_{C} (100.61 MHz, CDCl₃) 12.2 (CH₃), 12.9 (CH₃), 14.1 (CH₃), 14.2 (CH₃), 23.0 (CH₂), 23.1 (CH₂), 25.0 (CH₂), 26.0 (CH₂), 29.8 (CH₂), 30.3 (CH₂), 31.8 (CH₂), 32.2 (CH₂), 36.3 (CH₃), 36.4 (CH₃), 44.2 (CH), 44.4 (CH), 99.7 (C), 99.8 (C), 129.6 (CH), 129.7 (CH), 129.9 (CH), 140.5 (CH), 140.6 (CH), 146.5 (C), 174.3 (C); *m/z* (Cl⁺) 360 [(MH⁺), 100%] and 232 (61).

General procedure for EPHP reaction

The amide precursor (2 mmol, 1 equiv.) was dissolved in dry toluene (16 ml) at reflux, under nitrogen atmosphere. Then 1-ethylpiperidinium hypophosphite (3.584 g, 20 mmol, 10 equiv.) and AIBN (0.192 g, 0.8 mmol, 0.4 equiv.) in dry toluene (4 ml) were added through a syringe pump, at the slowest possible speed, over 12 h, with several additions of AIBN (0.05g) until completion. On completion, water was added. Toluene was evaporated, the crude product was then diluted in dichloromethane (30 ml), then washed with hydrochloric acid (2N, 30 ml), saturated sodium hydrogencarbonate solution (20 ml) and brine (20 ml). The organic phase was dried over sodium sulfate and evaporated under reduced pressure. The bulk crude mixture was then purified by column chromatography (90:10, hexanes-ethyl acetate) A small portion was separated by HPLC chromatography (90:10 hexane-ethyl acetate), using a flow rate of 6 ml/min for all compounds.

1-Methyl-3-spirocyclohexyloxindole **2a** and cyclohexanecarboxylic acid

methylphenylamide 3a: **2a** and **3a** were prepared with the general EPHP procedure (**2a**: 58% yield, **3a**: 21% yield).

1-Methyl-3-spirocyclohexyloxindole **2a** was obtained as a yellow oil (0.251 g, 58%); ν_{max} (film)/cm⁻¹ 2932, 2851, 1708 (C=O), 1612, 1470; δ_{H} (400 MHz, CDCl₃) 1.55-1.99 (10H, m, CH₂), 3.21 (3H, s, Me), 6.85 (1H, dd, *J* 7.7, 0.9, ArH), 7.05 (1H, ddd, *J* 7.8, 7.3, 0.9, ArH), 7.28 (1H, ddd, *J* 7.8, 7.7, 1.1, ArH), 7.46 (1H, dd, *J* 7.3, 1.1, ArH); δ_{C} (100.61 MHz, CDCl₃) 21.4 (CH₂), 25.4 (CH₂), 26.3 (CH₃), 33.2 (CH₂), 47.6 (C), 108.0 (CH), 122.1 (CH), 124.0 (CH), 127.6 (CH), 135.6 (C), 143.0 (C) and 180.9 (C); *m/z* (EI⁺) 215 [(M⁺), 31%], 160 (100), 159 (30) and 130 (49).

Cyclohexanecarboxylic acid methylphenylamide¹ **3a** was obtained as white flakes (0.093 g, 21%); mp 63-64°C (lit.² 63°C); ν_{max} (KBr)/cm⁻¹ 2934, 2859, 1653 (C=O), 1496, 1386; δ_{H} (400 MHz, CDCl₃) 0.99-1.09 (2H, m, CH₂), 1.21-1.33 (1H, m, CH₂), 1.56-1.75 (7H, m, CH₂), 2.24-2.30 (1H, m, CH), 3.32 (3H, s, Me), 7.26 (2H, dd, *J* 7.9, 1.4, ArH), 7.41-7.45 (1H, m, ArH), 7.48-7.52 (2H, m, ArH); δ_{C} (100.61 MHz, CDCl₃) 25.7 (CH₂), 25.8 (CH₂), 29.6 (CH₂), 37.6 (CH₃), 41.5 (CH), 127.4 (CH), 127.8 (CH), 129.9 (CH), 144.5 (C), 176.6 (C); *m/z* (EI⁺) 217 [(M⁺), 18%], 107 (100), 83 (66), 77 (17), and 55 (59).

1'-Methylspiro[cyclopentane-1,3'-indolin]-2'-one **2b** and cyclopentanecarboxylic acid methylphenylamide **3b**:

2b and **3b** were accessed through the general EPHP protocol (**2b**: 49% yield, **3b**: 21% yield).

1'-Methylspiro[cyclopentane-1,3'-indolin]-2'-one¹ **2b** was obtained as white flakes (0.197 g, 49%); mp 59°C (lit.,³ 58-59°C); ν_{max} (KBr)/cm⁻¹ 3050, 2953, 2869, 1709 (C=O), 1612, 1468; δ_{H} (400 MHz, CDCl₃) 1.87-1.92 (2H, m, CH₂), 2.01-2.04 (2H, m,

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² A. J. Birch, J. Cymerman-Craig and M. Slaytor, *Aust. J. Chem.*, **1955**, 38, 512.

CH₂), 2.13-2.23 (4H, m, 2 x CH₂), 3.24 (3H, s, CH₃), 6.84 (1H, dd, *J* 7.7, 1.0, ArH), 7.06 (1H, ddd, *J* 7.7, 7.4, 1.0, ArH), 7.23 (1H, ddd, *J* 7.7, 7.4, 1.5, ArH), 7.28 (1H, dd, 7.7, 1.5, ArH); ¹³C (100.61 MHz, CDCl₃) 26.7 (CH₃), 27.2 (CH₂), 39.0 (CH₂), 54.6 (C), 108.1 (CH), 122.7 (CH), 123.0 (CH), 127.9 (CH), 137.5 (C), 143.8 (C), 182.4 (C); *m/z* (EI⁺) 201 [(M⁺), 42%], 160 (100), 153 (48), 136 (35), 130 (15) and 106 (30).

Cyclopentanecarboxylic acid methylphenylamide¹ **3b** was obtained as a colorless oil (0.087 g, 21%); ν_{max} (film)/cm⁻¹ 3052, 2956, 2870, 1651 (C=O), 1428, 1387; ¹H (400 MHz, CDCl₃) 1.44-1.54 (2H, m, CH₂), 1.67-1.72 (2H, m, CH₂), 1.76-1.94 (4H, m, 2 x CH₂), 2.65-2.73 (1H, m, CH), 3.34 (3H, s, CH₃), 7.25 (2H, dd, *J* 7.9, 1.4, ArH), 7.33-7.40 (1H, m, ArH), 7.45-7.49 (2H, m, ArH); ¹³C (100.61 MHz, CDCl₃) 26.4 (CH₂), 31.4 (CH₂), 37.8 (CH₃), 42.1 (CH), 127.7 (CH), 127.8 (CH), 127.9 (CH), 129.7 (CH), 129.8 (CH), 144.7 (C) and 177.1 (C); *m/z* (EI⁺) 203 [(M⁺), 15%], 167 (28), 149 (62), 107 (100) and 81 (27).

1,3,3-Trimethyl-1,3-dihydroindol-2-one **2c** and *N*-methyl-*N*-phenylisobutyramide **3c**:

1,3,3-Trimethyl-1,3-dihydroindol-2-one¹ **2c** was obtained as colorless flakes (0.179 g, 51%); mp 54-55°C (lit.⁴ 54-55°C); ν_{max} (KBr)/cm⁻¹ 3050, 2971, 2929, 1705 (C=O), 1614, 1472; ¹H (400 MHz, CDCl₃) 1.38 (6H, s, CH₃), 3.23 (3H, s, CH₃), 6.85 (1H, dd, *J* 7.8, 0.9, ArH), 7.07 (1H, ddd, *J* 7.6, 7.3, 0.9, ArH), 7.21 (1H, dd, *J* 7.3, 0.7, ArH), 7.27 (1H, ddd, *J* 7.8, 7.6, 0.7, ArH); ¹³C (100.61 MHz, CDCl₃) 24.6 (CH₃), 26.4 (CH₃), 44.4 (C), 108.2 (CH), 122.5 (CH), 122.7 (CH), 127.9 (CH), 136.1 (C), 142.9 (C), 181.6 (C); *m/z* (EI⁺) 175 [(M⁺), 96%], 160 (100), 132 (32) and 117 (20).

N-Methyl-*N*-phenylisobutyramide¹ **3c** was obtained as a colorless flakes (0.082 g, 23%); mp 77-78°C (lit.⁵ 78.7-79.2°C); ν_{max} (KBr)/cm⁻¹ 2983, 2962, 2934, 1653 (C=O), 1496, 1268; ¹H (400 MHz, CDCl₃) 1.03 (3H, m, CH₃), 1.04 (3H, m, CH₃), 2.49-

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⁴ K. H. Shaughnessy, B. C. Hamann and J. F. Hartwig, *J. Org. Chem.*, **1998**, 63, 6546.

⁵ K. Dietliker and H. Heimgartner, *Helv. Chim. Acta*, **1983**, 66, 262

2.53 (1H, m, CH), 3.26 (3H, s, CH₃), 7.19 (2H, dd, *J* 8.0, 1.4, ArH), 7.33-7.37 (1H, m, ArH), 7.41-7.45 (2H, m, ArH); δ_{C} (100.61 MHz, CDCl₃) 19.9 (CH₃), 31.2 (CH), 37.6 (CH₃), 127.5 (CH), 127.9 (CH), 129.9 (CH), 144.5 (C), 177.6 (C); *m/z* (EI⁺) 177 (100%, M⁺), 107 (92), 77 (23) and 69 (20).

3-Butyl-3-ethyl-1-methyl-1,3-dihydroindol-2-one 2d and 2-ethylhexanoic acid methylphenylamide 3d:

3-Butyl-3-ethyl-1-methyl-1,3-dihydroindol-2-one **2d** was obtained as a pale yellow oil (0.176 g, 38%); (Found: C, 77.37; H, 9.04; N, 6.54. C₁₅H₂₁NO requires C, 77.77; H, 9.16; N, 6.06%) (Found (ESI): [MH⁺] 232.1711. C₁₅H₂₁INO requires *MH* 232.1701); ν_{max} (film)/cm⁻¹ 2961, 2932, 2874, 1713 (C=O), 1613, 1469; δ_{H} (400 MHz, CDCl₃) 0.55 (3H, t, *J* 7.4, CH₃), 0.74-0.79 (4H, m, CH₃ and CH₂), 0.92-0.97 (1H, m, CH₂), 1.14-1.26 (2H, m, CH₂), 1.69-1.81 (2H, m, CH₂), 1.84-1.94 (2H, m, CH₂), 3.21 (3H, s, CH₃), 6.83 (1H, dd, *J* 7.7, 0.9, ArH), 7.07 (1H, ddd, *J* 7.5, 7.3, 0.9, ArH), 7.13 (1H, dd, *J* 7.3, 1.2, ArH), 7.26 (1H, ddd, *J* 7.7, 7.5, 1.2, ArH); δ_{C} (100.61 MHz, CDCl₃) 8.7 (CH₃), 13.9 (CH₃), 23.1 (CH₂), 26.1 (CH₃), 26.6 (CH₂), 31.2 (CH₂), 37.7 (CH₂), 53.9 (C), 107.8 (CH), 122.6 (CH), 122.9 (CH), 127.7 (CH), 132.6 (C), 144.4 (C), 180.4 (C); *m/z* (EI⁺) 231 [(M⁺), 18%], 175 (96), 160 (92), 146 (100), 130 (85), 49 (67) and 41 (96).

2-Ethylhexanoic acid methylphenylamide **3d** was obtained as a colorless oil (0.056 g, 12%); (Found: C, 76.71; H, 9.89; N, 6.17. C₁₅H₂₃NO requires C, 77.19; H, 9.94; N, 6.01%) (Found (ESI): [MH⁺] 234.1865. C₁₅H₂₃NO requires *MH* 234.1858); ν_{max} (film)/cm⁻¹ 2959, 2929, 2873, 1652 (C=O), 1496, 1117; δ_{H} (400 MHz, CDCl₃) 0.79-0.86 (6H, m, 2 x CH₃), 1.09-1.20 (4H, m, CH₂), 1.26-1.40 (2H, m, CH₂), 1.56-1.65 (2H, m, CH₂), 2.19-2.26 (1H, m, CH), 3.28 (3H, s, CH₃), 7.17 (2H, d, *J* 7.2, ArH), 7.32-7.36 (1H, m, ArH), 7.42-7.44 (2H, m, ArH); δ_{C} (100.61 MHz, CDCl₃) 12.7 (CH₃), 14.5 (CH₃), 23.3 (CH₂), 26.7 (CH₂), 30.3 (CH₂), 33.3 (CH₂), 38.0 (CH₃), 44.0 (CH), 128.1 (CH), 128.4 (CH), 130.1 (CH), 144.8 (C), 176.9 (C); *m/z* (CI⁺) 234 [(MH⁺), 100%] and 107 (20).

General procedure for the cyclization reactions with DEPO in water

Water (3-10 ml) was deoxygenated by boiling under nitrogen for 10 min. The amide precursor (1 eq., 0.8 -1.5 mmol) was added to the deoxygenated water under nitrogen. DEPO (20 eq.) and V-501 (3-4 eq.) were added in portions during the experiment and the mixture was heated for 6-10 days at 80°C with stirring. The mixture was cooled and sodium hydroxide solution (2N, 20 ml) was added; then the mixture was extracted by diethyl ether. The organic layers were dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The products were frequently very pure, but if impurities were present, then the product was purified by column chromatography on silica gel [ethyl acetate/petroleum ether 1:10-2:8].

1-Methyl-3-spirocyclohexyloxindole 2a

N-(2-Iodophenyl)-*N*-methylcyclohexanecarboxamide **1a** (0.054 g, 0.157 mmol), DEPO (3.14 mmol) and V-501 (0.471 mmol) in portions, were added to the deoxygenated water under nitrogen, and mixture was heated for 6 days at 80°C. Following work-up, 1-methyl-3-spirocyclohexyloxindole was obtained as a colorless oil (0.033 g, 97% yield).

1-Methyl-3-spirocyclopentyloxindole 2b

N-(2-Iodophenyl)-*N*-methylcyclopentanecarboxamide **1b** (0.12 g, 0.365 mmol), DEPO (0.077 g, 7.31 mmol) and V-501 (0.306 g, 1.09 mmol) in portions, were added to deoxygenated water under nitrogen, and mixture was heated for 6 days at 80°C. Following work-up, 1-methyl-3-spirocyclopentyloxindole was obtained as a pale yellow oil (0.066 g, 90% yield).

1,3,3-Trimethyl-1,3-dihydroindol-2-one 2c

N-(2-Iodophenyl)-*N*-methylisobutyramide **1c** (0.15 g, 0.49 mmol), DEPO (1.04 g, 9.9 mmol) and V-501 (0.548 g, 1.96 mmol) in portions, were added to deoxygenated water

under nitrogen, and the mixture was heated for 7 days at 80°C. Following work-up, 1,3,3-Trimethyl-1,3-dihydroindol-2-one was obtained as colorless viscous oil (0.075 g, 87%).

3-Butyl-3-ethyl-1-methyl-1,3-dihydro-indol-2-one 2d

2-Ethylhexanoic acid (2-iodophenyl)methylamide **1d** (0.055 g, 0.153 mmol), DEPO (3.24 g, 3.06 mmol) and V-501 (0.168 g, 0.612 mmol) in portions, were added to the deoxygenated water under nitrogen, and mixture was heated for 10 days at 80°C. Following work-up, 3-butyl-3-ethyl-1-methyl-1,3-dihydroindol-2-one was obtained as a yellow oil (0.029 g, 82%).

General procedure for radical cyclisation reactions to form indolines

Water (5 ml) was boiled for 10 min. under nitrogen then the appropriate substrate [1 eq. (0.04. mmol- 0.86 mmol)] was added, and then DEPO (20 eq.) and V-501 (3-4 eq.) were added in portions and the mixture was heated for 42 h (except **5a**, where 36 h was used) at 80°C under nitrogen. The mixture was cooled and sodium hydroxide solution (2N, 20 ml) was added and then the mixture was extracted with diethyl ether. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (90/10-85/15). To recover the unused DEPO, the aqueous layer was acidified to pH 6 and extracted with DCM. This was dried and evaporated to yield essentially pure recovered DEPO.

3-Ethyl-1-methanesulfonyl-2,3-dihydro-1 H-indole 5a

3-Ethyl-1-methanesulfonyl-2,3-dihydro-1 H-indole (0.034 g, 75% yield) was obtained as a colorless oil from *N*-but-2-enyl-*N*-(2-iodophenyl)methanesulfonamide (0.071 g). Found: $M+NH_4^+$, 243.1169, $C_{11}H_{15}NO_2S$ requires M , 243.1167. $\nu_{max}(\text{disc})/\text{cm}^{-1}$ 3016, 2963, 2930, 1599, 1478, 1342, 1232, 1161 and 1051. $^1H(400\text{ MHz, }CDCl_3)$ 1.07 (3H, d, J 7.3, CH_3) 1.66 (1H, m, CH_2), 1.90 (1H, m, CH_2), 2.93 (3H, s, CH_3), 3.38 (1H, m, CH), 3.69 (1H, dd, J 10.2, 10.2, CH_2), 4.13 (1H, dd, J 10.2, 10.2, CH_2), 7.11 (1H, m, ArH),

7.27 (2H, m, ArH), 7.46 (1H, d, J 2.8, ArH). $^{\text{C}}$ (100.61 MHz, CDCl_3) 11.3 (CH_3), 27.5 (CH_2), 34.3 (CH_3), 41.4 (CH), 55.9 (CH_2), 113.4 (CH) 123.6 (CH), 124.7 (CH), 128.1 (CH_2), 135.0 (C) and 141.8 (C). m/z , (EI^+) 225 (M^+ , 45%), 196 (50), 146 (78), 130 (79), 118 (100) and 91 (35).

3-Ethyl-1-methanesulfonyl-6-methoxy-2,3-dihydro-1 *H*-indole 5b

3-Ethyl-1-methanesulfonyl-6-methoxy-2,3-dihydro-1 *H*-indole **5b** (0.022 g, 73% yield) was obtained as a colorless oil from *N*-but-2-enyl-*N*-(2-iodo-5-methoxyphenyl)-methanesulfonamide **4b** (0.045 g). (Found: $\text{M}+\text{H}^+$, 256.1007, $\text{C}_{12}\text{H}_{17}\text{NO}_3\text{S}$ (M) requires MH^+ , 256.1007 $\text{max}(\text{disc})/\text{cm}^{-1}$ 3009, 2963, 2929, 1612, 1467, 1346 and 1160. $^{\text{H}}$ (400 MHz, CDCl_3) 0.96 (3H, t, J 7.3, CH_3) 1.54 (1H, m, CH_2), 1.77 (1H, m, CH_2), 2.87 (3H, s, SCH_3), 3.21 (1H, m, ArCH), 3.60 (1H, m, CH_2), 3.76 (3H, s, OCH_3), 4.06 (1H, m, CH_2), 6.55 (1H, dd, J 8.2, 2.3, ArH), 6.97 (1H, d, J 2.3, ArH), 7.05 (1H, d, J 8.2, ArH). $^{\text{C}}$ (100.61 MHz, CDCl_3) 11.3 (CH_3), 27.9 (CH_2), 34.3 (CH_3), 40.8 (CH), 55.6 (CH_3), 56.7 (CH_2), 100.1 (CH) 109.0 (CH), 125.1 (CH), 127.0 (C), 142.9 (C), and 160.2 (C). m/z , (EI^+) 255 (M^+ , 48%), 226 (100), 146 (88), 132 (82), 104 (45), and 79 (52).

1-Methanesulfonyl-3-methyl-2,3-dihydro-1*H*-indole 5c

1-Methanesulfonyl-3-methyl-2,3-dihydro-1*H*-indole (0.141 g, 78% yield) was formed as a colorless oil [from *N*-allyl-*N*-(2-iodophenyl)methanesulfonamide **4c** (0.29 g)]. [Found; $\text{M}+\text{NH}_4^+$, 229.1004; $\text{C}_{10}\text{H}_{13}\text{NO}_2\text{S}$ (M) requires MNH_4^+ 229.1005. $\text{max}(\text{disc})/\text{cm}^{-1}$ 2932, 1492, 1461, 1345 and 1157. $^{\text{H}}$ (400 MHz, CDCl_3) 1.43 (3H, d, J 5.2, CH_3) 2.96 (3H, s, SCH_3), 3.56 (2H, m, CH_2), 4.23 (1H, m, CH), 7.12-7.16 (1H, m, ArH), 7.27-7.35 (2H, m, ArH), 7.45-7.52 (1H, m, ArH). $^{\text{C}}$ (100.61 MHz, CDCl_3) 19.7 (CH_3), 26.9 (CH), 35.0 (CH_3), 55.2 (CH_2), 113.7 (CH) 124.4 (CH), 128.3 (CH), 135.7 (CH) 136.5 (C) and 143.2 (C). m/z (EI^+) 211 (25%), 199 (30), 130 (52), 86 (60) and 84 (100).

9-Methanesulfonyl-2, 3, 4, 4a, 9, 9a-hexahydro-1H-carbazole-1-carboxylic acid methyl ester 7a

9-Methanesulfonyl-2, 3, 4, 4a, 9, 9a-hexahydro-1H-carbazole-1-carboxylic acid methyl ester **7a** (0.012 g, 98%) was obtained as a white solid from N-cyclohex-2-enyl-N-(2-iodophenyl)methanesulfonamide **6a** (0.017 g). m.p. 142-143 °C. [Found; $M+H^+$ 310.1111 $C_{15}H_{19}NO_4S$, (M) requires, MH^+ 310.1113]. $\nu_{max}(\text{disc})/\text{cm}^{-1}$ 3021, 2929, 1713, 1459, 1343, 1227 and 1164. $^1H(400\text{ MHz}; CDCl_3)$. 1.27-1.20 (1H, m, CH_2), 1.65-1.61 (2H, m, CH_2), 2.20-1.81 (2H, m, CH_2), 2.26 (1H, m, CH_2), 2.5 (1H, m, CH), 2.89 (3H, s, SCH_3), 3.67 (1H, m, ArCH), 3.74 (3H, s, OCH_3), 4.64 (1H, dd, J 9.2, 7.6, NCH), 7.14 (2H, m, ArH), 7.24-7.34 (1H, m, ArH), 7.44 (1H, d, J 7.8, ArH). $^{13}C(100.61\text{ MHz}, CDCl_3)$ 20.0 (CH_2), 24.7 (CH_2), 27.0 (CH_2), 38.8 (CH_3), 41.2 (CH), 46.7 (CH), 52.6 (CH), 65.5 (CH_3), 118.7 (CH), 123.5 (CH), 125.8 (CH), 128.6 (CH), 136.2 (C), 141.3 (C) and 175.2 (C). m/z (EI^+), 309 (8%), 230 (15), 170 (100), 130 (28), 115 (20), 79 (24) and 59 (21).

9-Methanesulfonyl-6-methoxy-2, 3, 4, 4a, 9, 9a-hexahydro-1H-carbazole 7b

9-Methanesulfonyl-6-methoxy-2, 3, 4, 4a, 9, 9a-hexahydro-1H-carbazole **7b** (0.058g, 91%) was obtained as a yellow oil from N-cyclohex-2-enyl-N-(2-iodo-4-methoxyphenyl)methanesulfonamide (0.092g) **6b**. [Found; $M+NH_4^+$, 299.1424 $C_{14}H_{19}NO_3S$, requires, 299.1424. $\nu_{max}(\text{disc})/\text{cm}^{-1}$ 2933, 2859, 1483, 1341, 1157 and 1031. $^1H(400\text{ MHz}, CDCl_3)$ 1.20-1.28 (2H, m, CH_2), 1.43-1.56 (2H, m, CH_2), 1.62-1.64 (1H, m, CH_2), 1.78-1.85 (1H, m, CH_2), 2.03-2.07 (1H, m, CH_2), 2.13-2.17 (1H, m, CH_2), 2.85 (3H, s, SCH_3), 3.52 (1H, m, ArCH), 3.80 (3H, s, OCH_3), 4.35 (1H, m, NCH), 6.71 (2H, m, ArH), 7.30 (1H, d, J 8.3, ArH). $^{13}C(100.61\text{ MHz}, CDCl_3)$, 20.9 (CH_2), 22.4 (CH_2), 24.9 (CH_2), 28.9 (CH_2), 37.7 (CH), 40.8 (CH_3), 55.8 (CH_3), 64.2 (CH), 110.3 (CH), 112.2 (CH), 117.3 (CH), 134.8 (C), 137.0 (C) and 157.5 (C). m/z (EI^+) 281 (15%), 202 (100), 160 (35) and 79 (42).

9-Methanesulfonyl-2, 3, 4, 4a, 9, 9a-hexahydro-1*H*-carbazole **7c**⁶

9-Methanesulfonyl-2, 3, 4, 4a, 9, 9a-hexahydro-1*H*-carbazole **7c** (0.139 g, 91%) was obtained as a colorless oil from *N*-cyclohex-2-enyl-*N*-(2-iodophenyl)-methanesulfonamide **6c** (0.23 g). $\nu_{\text{max}}(\text{disc})/\text{cm}^{-1}$ 2932, 1602, 1459, 1345.2 and 1159.7. ^1H (400 MHz, CDCl_3) 1.28-1.94 (6H, m, 3 x CH_2), 2.13-2.30 (2H, m, CH_2), 3.0 (3H, s, SCH_3), 3.6 (1H, m, ArCH), 4.62 (1H, m, NCH), 7.16 (1H, dd, J 7.3, 7.3 ArH) 7.25-7.34 (2H, m, ArH), 7.44 (1H, dd, J 7.8, 7.8, ArH). ^{13}C (100.61 MHz, CDCl_3) 20.8 (CH_2), 22.2 (CH_2), 24.7 (CH_2), 28.6 (CH_2), 38.6 (CH_3), 40.5 (CH), 64.1 (CH), 115.5 (CH), 123.6 (CH), 124.2 (CH), 128.0 (CH), 134.7 (C) and 141.4 (C).

7-Ethyl-2,9-dioxabicyclo[4.3.0]nonane **9**⁷

Water (5 ml) was deoxygenated by boiling for 10 min. under nitrogen, and then 2-*O*-2-butenyl-3-bromotetrahydropyran (0.21 g, 0.892 mmol) was added to the water, followed by DEPO (0.945 g, 8.92 mmol) and 4-(3-carboxy-1-cyano-1-methylpropylazo)-4-cyano-4-methylbutyric acid (V-501) (0.075 g, 0.446 mmol), and the mixture was heated for 8 h at 80°C under nitrogen. The mixture was cooled and sodium hydroxide (2N, 20 ml) was added and the mixture was then extracted with diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate, filtered, concentrated *in vacuo*, and purified by short column chromatography (silica gel, petroleum ether/diethyl ether/4:1) to afford 7-ethyl-2,9-dioxabicyclo[4.3.0]nonane (0.104 g, 74%) as a colorless oil. $\nu_{\text{max}}(\text{disc})/\text{cm}^{-1}$ 2932, 1462, 1090, 1059 and 1034.5. ^1H [400 MHz (major diastereomer), CDCl_3] 0.90 (3H, t, J 7.4, CH_3) 1.22-1.84 (7H, m, 4-H, 5-H, 7-H plus 7- CH_2), 2.21-2.27 (1H, m, 6-H), 3.39-3.57 (2H, m, CH_2), 3.85-4.37 (2H, m, CH_2), 5.00 (1H, d, J 3.6, 1-H). ^{13}C [100.61 MHz, (major diastereomer), CDCl_3] 12.9 (CH_3), 20.9 (CH_2), 22.7 (CH_2), 25.7 (CH_2), 39.8 (CH), 44.0 (CH), 64.6 (CH_2), 74.1 (CH_2) and 102.4 (CH).

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