Supplementary Material (ESI) for Chemical Communications

Bimetallic Catalytic Synthesis of Annelated Benzazepines

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Electronic Supplementary Information

General experimental procedures

Nuclear magnetic resonance spectra were recorded on a Bruker DPX500 operating at 500 MHz, ^{13}C NMR spectra were recorded at 75 MHz. Chemical shifts are given in parts per million (δ) downfield from tetramethylsilane (TMS, δ 0.00) used as an internal standard. Coupling constants are given in hertz (Hz). Unless otherwise stated deuteriochloroform ($CDCl_3$) was used as solvent. In assignment of the ^1H NMR spectra, s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublets of doublets, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, sep = septet, m = multiplet.

Melting points were determined on a Reichart hot-stage apparatus and are uncorrected. Mass spectra data were obtained from a VG Autospec instrument operating at 70 eV (EI) or ZD 2000 electrospray instrument (ES). High resolution mass spectra (H.R.M.S) were obtained from the EPSRC National Mass Spectrometry Service Centre, Swansea. Infra-red spectroscopy was recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. A solution of the compound in dichloromethane was allowed to evaporate onto a KBr disc to give a thin film, except where stated, or a golden gate solid phase apparatus was used. Column chromatography was performed using flash silica gel 60 and t.l.c on plastic backed silica gel 60 F254 (Merck). *N*,*N*-DMF used was standard analytical grade unless otherwise stated, other solvents were used as purchased without further drying. All compounds were named according to the IUPAC system and were obtained using ACD/I-lab vs. 8.05.

General procedure for Pd/In class 2 capture of iminium ions (A)

Isoquinoline (1 mmol) and 2-iodobenzyl bromide (1 mmol), were heated in DMF (AR) at 80 ^oC for 2h in a Schlenk tube. The mixture was then cooled to ~ RT over 1 h and indium powder (1.5 mol eq.), $Pd(OAc)_2$ (0.1 mol eq.), TFP (0.2 mol eq.), and copper (I) iodide (0.2 mol eq.) added sequentially. The Schlenk tube was then sealed, subjected to two freeze/pump/thaw cycles followed by an addition of allene gas (~ 1 bar), heated at 40 ^oC for 20 h, cooled to room temperature, vented, ether (20 ml) and H_2O (10 ml) added and the mixture stirred for 20 min. The aqueous layer was separated extracted with ether (3 x 15 ml) and the combined ether extracts washed with H_2O (4 x 10 ml), dried over $MgSO_4$, filtered and the filtrate evaporated to afford the crude product which was either reacted without purification or purified by column chromatography.

General Procedure for Reduction of Enamines (B)

A stirred solution of crude benzazepine (1 mol eq.) in EtOH (5 ml) was cooled to 0 ^oC, sodium cyanoborohydride (3 mol eq.) added, the suspension was acidified to pH 2 (conc. HCl) and allowed to warm to RT over 3 h then 1M NaOH (5 ml) added, the mixture was extracted into ether (3 x 25 ml), the combined organics dried over Na_2SO_4 and evaporated to dryness *in vacuo*. The crude amine was purified by column chromatography.

13-Methylene-8,13,14,14a-tetrahydroisoquinoline[2,1-*b*][2] benzazepine (6a)
Prepared by general method **A**, isoquinoline (152 mg, 1.2 mmol) and 2-iodobenzyl bromide (296 mg, 1.0 mmol), gave a crude product which was purified by column chromatography eluting with DCM to give a pale yellow oil (230 mg, 70 %). R_f = 0.79 (DCM)
δ_H($CDCl_3$, 500 MHz) 7.62 (d, 1H, ArH, J, 7.5 Hz), 7.21 (dd, 1H, ArH, J, 2.4, 6.3 Hz), 7.18 (d, 1H, ArH, J, 6.8 Hz), 7.10 (td, 2H, ArH, J, 2.4, 7.5 Hz), 7.04 (d, 2H, ArH, J, 6.8 Hz), 6.88 (d, 1H, ArH, J, 7.5 Hz), 6.06 (dd, 1H, 6-H, J, 0.9, 7.4 Hz), 5.21 (d, 1H, 5-H, J, 7.4 Hz), 5.14 (s, 1H, 13a-H), 5.05 (s, 1H, 13b-H), 4.65 (d, 1H, 14a -H, J, 10.9 Hz), 4.20 (d, 1H, 8b-H, J, 15.3 Hz), 4.06 (d, 1H, 8a-H, J, 15.3 Hz), 2.92 (t, 1H, 14'-H, J 12.2 Hz), 2.05 (dd, 1H, 14-H, J, 2.2, 12.2 Hz), δ_C($CDCl_3$, 75 MHz) 150.33, 143.68, 137.12, 134.95, 132.75, 131.73, 129.12, 128.41, 127.89, 126.03, 125.40, 123.32, 116.96 (CH_2), 98.66, 66.35, 58.73 (CH_2), 42.28 (CH_2), ν_{max}(film)/cm^{-1} 3059, 3010, 2926, 2851, 1616, 1563, 1486, 1462, H.R.M.S [MH^+] $C_{19}H_{18}N$ Calculated 260.1439, found 260.1428

13-Methylene-5,6,8,13,14,14a-hexahydroisoquino [2,1-b][2] benzazepine (7a)
Prepared by general method **B,** 13-methylene-8,13,14,14a-tetrahydroisoquinoline [2,1-*b*][2] benzazepine (230 mg, 0.89 mmol) in EtOH (5 ml) and sodium cyanoborohydride (196 mg, 3.11 mmol) gave the crude amine was purified by column chromatography eluting with 8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine to afford the product as a colourless needles (85 mg, 58 %); R_f= 0.133 (8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine). Mpt 74 – 75 ^oC
δ_H($CDCl_3$, 500 MHz) 7.25 – 7.11 (m, 7H, ArH), 7.08 (d, 1H, ArH, J, 6.7 Hz), 5.25 (s, 1H, 13a-H), 5.15 (d, 1H, 13b-H, J, 1.5 Hz), 4.34 (dd, 1H, 14a-H, J, 2.6, 11.1 Hz) 4.29 (d, 1H, 8b-H, J, 14.8 Hz), 3.95 (d, 1H, 8a-H, J, 14.8 Hz), 3.02 (dd, 1H, 6-H, J, 6.5, 9.4 Hz), 2.88 (dt, 1H, 6-H, J, 4.3, 9.4 Hz), 2.82 (dd, 2H, 5-H, J, 4.3 Hz), 2.78 (dd, 1H, 14-H, J, 3.5, 14.1 Hz), 2.63 (dd, 1H, 14-H, J, 2.6, 14.1 Hz), δ_C($CDCl_3$, 75 MHz) 149.72, 144.02, 139.84, 136.37, 134.43, 129.55, 129.47, 128.03, 127.63, 127.43, 126.71, 125.94, 115.42 (CH_2), 65.34 (14a-CH), 60.93 (8-CH_2), 43.85 (14-CH_2), 41.04 (CH_2), 29.47 (CH_2), ν_{max}(film)/cm^{-1} 3063, 3019, 2914, 2834, 1714, 1630, 1485, m/z (ES) 262 (M+H, 100), H.R.M.S [M + H^+] $C_{19}H_{20}N$ Calculated 262.1590, found 260.1587

n.O.e for **7a**

Irradiated Proton	**Enhancement**								
	H-4	**H-6**	**H-8a**	**H-8b**	**H-9**	**H-12**	**H-13a**	**H-13b**	**H-14b**
H-13a	-	-	-	-	-	-	-	25.9	4.14
H-13b	-	-	-	-	-	5.67	24.12	-	-
H-8a	-	-	-	22.43	-	-	-	-	-
H-8b	-	4.88	20.13	-	8.26	-	-	-	-
H-5	3.23	4.04	-	-	-	-	-	-	-

4-Methoxy-13-methylene-8,13,14,14a-tetrahydroisoquino[2,1-*b*][2] benzazepine (6b)
Prepared by general method **A** on a 1 mmol scale using 5-methoxyisoquinoline (191 mg, 1.2 mmol) gave a crude product, which was partially purified by column chromatography eluting with 7 : 3 (v/v), hexane : DCM, as a pale yellow oil, 314 mg R_f = 0.21 (7 : 3 (v/v) Hexane : DCM)
δ_H($CDCl_3$, 500 MHz) 7.25 (s, 2H, ArH), 7.23 (d, 1H, ArH, J, 2.4 Hz), 7.20 (d, 1H, ArH, J, 2.4 Hz), 7.03 (t, 1H, ArH, J, 7.9 Hz),6.78 (d, 2H, ArH, J, 7.9 Hz), 6.15 (dd, 1H, 6-H, J, 0.9, 7.6 Hz), 5.59 (d, 1H, 5-H, J, 7.6 Hz), 5.21(s, 1H, 13a-H), 5.12 (d, 1H, 13b-H, J, 2.1 Hz), 4.69 (d, 1H, 14a-H, J, 11.0 Hz), 4.26 (d, 1H, 8b-H, J, 15.4 Hz), 4.14 (d,1H, 8a-H, J, 15.4 Hz), 3.80 (s, 3H, OCH_3), 3.00 (t, 1H,

14c-H, J 11.0 Hz), 2.12 (dd, 1H, 14b-H, J, 2.2, 13.0 Hz), δ_C($CDCl_3$, 75 MHz) 152.99, 150.46, 143.68, 137.15, 134.34, 133.21, 132.89, 130.57, 129.11, 128.55, 127.66, 125.87, 116.87 (CH_2), 114.91, 109.49, 92.85, 69.37, 66.30, 58.69, 55.92, 41.75 (CH_2), 41.55 (CH_2), ν_{max}(film)/cm^{-1} 3065, 3000, 2928, 2829, 1654, 1611, 1566, 1514, 1478, 1467, m/z (ES) 290.8 (M+, 22), 290.0 (M, 100) 162.8 (38), 156.6 (61), H.R.M.S [MH^+] $C_{20}H_{19}NO$, Calculated 290.1545, found 290.1552

4-Methoxy-13-methylene-5,6,8,13,14,14a-hexahydroisoquino[2,1-*b*][2] benzazepine (7b)
Prepared by general method **B** using 4-methoxy-13-methylene-8,13,14,14a-tetrahydroisoquino [2,1-*b*][2] benzazepine (156 mg, 0.54 mmol), sodium cyanoborohydride (101 mg, 0.62 mmol), EtOH (3 ml), gave the crude product which was purified by column chromatography eluting with 8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine to afford the product as a colourless glass sheets (148 mg, 94 %); R_f = 0.18 (8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine). Mpt 92 – 95 ^oC, δ_H($CDCl_3$, 500 MHz) 7.24 (dd, 2H, 10,11-H, J, 1.2, 5.6 Hz), 7.21 (dd, 1H, ArH, J, 5.6 Hz), 7.19 (t, 1H, ArH, J, 5.6), 7.13 (t, 1H, 1-H, J, 7.9 Hz), 6.79 (d, 1H, 2-H, J, 7.9 Hz), 6.67 (d, 1H, 3-H, J, 7.9 Hz), 5.25 (s, 1H, 13a-H), 5.14 (d, 1H, 13b-H, J, 1.8 Hz), 4.32 (dd, 1H, 14a-H, J, 2.8, 11.2 Hz), 4.28 (d, 1H, 8b-H, J, 14.8 Hz), 3.95 (d, 1H, 8a-H, J, 14.8 Hz), 3.80 (s, 3H, OCH3), 2.83-2.73 (m, 3H, 14-H, 5-H_2), 2.82 (dd, 2H, 6-H, J, 2.8, 6.6 Hz), 2.78 (dd, 1H, 6-H, J, 2.8, 6.6 Hz), 2.63 (dd, 1H, 14-H, J, 2.8, 13.8 Hz), δ_C($CDCl_3$, 75 MHz) 157.62, 149.72, 144.02, 141.05, 136.27, 129.59, 127.98, 127.61, 126.41, 123.43, 119.60, 115.38 (CH_2), 107.72, 65.14 (14a-CH), 60.76 (8-CH_2), 55.70 (CH_3), 43.32 (CH_2), 40.64 (CH_2), 23.82 (CH_2), ν_{max}(film)/cm^{-1} 3070, 3005, 2929, 2835, 2241, 1714, 1630, 1589, 1469, 1383, m/z (ES) 292 (M+H, 100), H.R.M.S [M + H^+] $C_{20}H_{21}NO$ Calculated 292.1696, found 292.1697

4-Phenyl-13-methylene-5,6,8,13,14,14a-hexahydroisoquino[2,1-*b*][2] benzazepine (7d)
Prepared by general method **A** then **B** on a 1 mmol scale using 5-phenyl isoquinoline (241 mg, 1.2 mmol) to give a crude product which was purified by column chromatography eluting with 8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine to afford the product as a colourless sheets (167 mg, 85 %); R_f = 0.10, (8:2:0.01 (v/v/v) hexane / diethylether / triethylamine), Mpt 102 – 104 ^oC, δ_H($CDCl_3$, 500 MHz) 7.37 (t, 2H, ArH, J, 7.3 Hz), 7.31 (tt, 1H, ArH, J, 1.7, 7.3 Hz), 7.27 (d, 1H, ArH, J, 1.4 Hz), 7.25 (s, 1H, ArH), 7.24, (s, 1H, ArH), 7.22 (d, 1H, ArH, 1.4 H), 7.19 (dt, 3H, ArH, J, 1.9, 7.9 Hz), 7.15 (d, 1H, ArH, J, 6.9 Hz), 7.05 (dd, 1H, ArH, J, 1.9, 6.9 Hz), 5.28 (s, 1H, 13a-H), 5.15 (d, 1H, 13b-H, J, 1.8 Hz), 4.40 (dd, 1H, 14a-H, J, 2.6, 11.1 Hz), 4.28 (d, 1H, 8b-H, J, 14.7 Hz), 3.92 (d, 1H, 8aH, J, 14.7 Hz), 2.76-2.89 (m, 2H, 5-H, 14-H), 2.56 (dt, 1H, 5-H, J, 3.3, 16.0 Hz), 2.69 (dt, 2H, 6-H, J, 3.3, 12.8 Hz), 2.62 (dd, 1H, 5-H, J, 3.3, 13.8 Hz), δ_C($CDCl_3$, 75 MHz)149.29, 143.53, 142.15, 141.63, 139.59, 135.75, 131.68, 129.04, 128.29, 128.06, 127.79, 127.57, 127.22, 126.80, 126.40, 125.37, 115.06 (CH_2), 65.35 (14a-CH), 60 53 (8-CH_2), 43.76 (CH_2), 40.83 (CH_2), 28.33, ν_{max}(film)/cm^{-1} 3063, 3029, 2925, 2846, 2252, 1630, 1588, 1463, 1435, m/z (ES) 339 (M+2, 71), 338 (M+H, 100)**,** H.R.M.S [M + H^+] $C_{25}H_{23}N$ Calculated 338.1903, found 338.1900

2,3-Dimethoxy-13-methylene-5,6,8,13,14,14a-hexahydroisoquino[2,1-*b*][2] benzazepine (7e)
Prepared by general method **A** then **B** on a 1 mmol scale using 6,7-dimethyoxyisoquinoline (227 mg, 1.2 mmol) to give a crude product which was purified by column chromatography eluting with 8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine to afford the product as a colourless square prisms (109 mg, 69 %); R_f = 0.12 (8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine), Mpt 96 - 99 ^oC, δ_H($CDCl_3$, 500 MHz) 7.25 (d, 1H, ArH, J, 6.5 Hz), 7.24 (dd, 1H, ArH, J, 1.0, 6.5 Hz), 7.21 (td, 1H, ArH, J, 2.7, 6.5 Hz), 7.17 (d, 1H, ArH, J, 6.5 Hz), 6.63 (s, 1H, 1-H), 6.56 (s, 1H, 4-H), 5.26 (s, 1H, 13a-H), 5.15 (d, 1H, 13b-H, J, 1.7 Hz), 4.32 (dd, 1H, 14a-H, J, 2.8, 11.0 Hz), 4.26 (d, 1H, 8b-H, J, 14.8 Hz), 3.94 (d, 1H, 8a-H, J, 14.8 Hz), 3.88 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 2.93 (ddd, 1H, 5-H, J, 7.2, 9.4, 16.0 Hz), 2.84-2.78 (m, 3H, 5-H, 6-H_2), 2.69 (dt, 2H, 14-H, J, 3.3, 12.8 Hz), 2.62 (dd, 1H, 14-H, J, 2.8 , 13.8Hz), δ_C($CDCl_3$, 75 MHz)149.16, 147.61, 147.04, 143.50,

135.85, 131.31, 129.10, 127.56, 127.21, 126.03, 114.89 (CH_2), 111.37, 109.89, 64.35(14a-CH), 60.31 (8-CH_2), 56.09 (CH_3), 55.79 (CH_3), 43.49 (14-CH_2), 40.44 (CH_2), 28.62 (CH_2), ν_{max}(film)/cm^{-1} 3071, 3008, 2936, 2837, 2253, 2192, 1629, 1612, 1518, 1405, m/z (ES) 323(M+2, 55), 322(M+H, 100), H.R.M.S [M + H^+] $C_{21}H_{23}NO_2$ Calculated 322.1802, found 322.1801

5-(2-Furyl)-13-methylene-5,6,8,13,14,14a-hexahydroisoquino[2,1-*b*][2] benzazepine (7f)
Prepared by general method **A** then **B** on a 1 mmol scale using 4-furyl isoquinoline (160 mg, 1.2 mmol) to give a crude product which was purified by column chromatography eluting with 8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine to afford the product as a colourless prisms (119 mg, 68 %); R_f = 0.14 (8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine). Mpt 111 - 113 ^oC, δ_H($CDCl_3$, 500 MHz) 7.34 (s, 1H, ArH), 7.25 (d, 1H, ArH, J, 3.2 Hz), 7.23 (d 2H, ArH, J, 3.2 Hz), 7.21 (dd, 2 H, ArH, J, 2.0, 5.0 Hz), 7.17 (s, 2H, ArH), 7.15 (d, 1H, ArH, J, 2.0 Hz), 6.26 (dd, 1H, ArH, J, 2.0, 2.9), 5.86 (d, 1H, furan H, J, 2.9 Hz), 5.26 (s, 1H, 13a-H), 5.16 (d, 1H, 13b-H, J, 1.6 Hz), 4.42 (dd, 1H, 14a-H, J, 3.3, 10.9 Hz), 4.26 (d, 1H, 8b-H, J, 15.0 Hz), 4.12 (t, 1H, 5-H, J, 3.3 Hz), 3.87 (d, 1H, 8a-H, J, 15.0 Hz), 3.14 (dd, 1H, 14-H, J, 4.6, 12.5 Hz), 3.10 (dd, 1H, 6-H, J, 3.3, 12.5 Hz), 2.79 (t, 1H, 6-H, J, 12.5 Hz), 2.79 (t, 1H, 14-H, J, 12.5 Hz), 2.68 (dd, 1H, 14-H, J, 3.3, 12.5 Hz), δ_C($CDCl_3$, 75 MHz) 159.05, 149.46, 143.82, 141.43, 139.91, 136.60, 134.40, 130.41, 129.40, 128.03, 127.89, 127.60, 127.40, 126.89, 126.73, 115.45 (CH_2), 110.63, 106.86, 77.66, 65.22, 60.62 (CH_2), 48.88 (CH_2), 40.95 (CH_2), ν_{max}(film)/cm^{-1} 3063, 3029, 2925, 2846, 2252, 2194, 1817, 1791, 1630, 1612, 1588, 1496, 1384, m/z (ES) 339.0 (M+2, 71), 338.0 (M+1, 100), H.R.M.S [M + H^+] $C_{23}H_{21}NO$ Calculated 328.1696, found 328.1696

n.O.e for **7f**

Enhanced proton															
Irradiated proton	**H-1**	**H-4**	**H-5b**	**H-5c**	**H-5d**	**H-6**	**H-8a**	**H-8b**	**H9**	**H-12**	**H-13a**	**H-13b**	**H-14a**	**H-14b**	**H-14c**
H-5a	-	7.64	1.35	-	-	6.82	-	-	-	-	-	-	-	-	-
H-5b	-	-	-	4.74	-	-	-	-	-	-	-	-	-	-	-
H-5c	-	-	4.47	-	2.69	-	-	-	-	-	-	-	-	-	-
H-8a	-	-	-	-	-	-	-	23.34	7.16	-	-	-	-	-	-
H-8b	-	-	-	-	-	-	21.07	-	-	-	-	-	8.79	-	-
H-13a	-	-	-	-	-	-	-	-	-	-	-	28.21	-	-	-
H-13b	-	-	-	-	-	-	-	-	-	6.10	23.52	-	-	-	-
H-14b	-	-	8.12	-	-	-	-	1.92	-	-	-	-	-	-	2.14
H-14c	12.07	-	-	-	-	-	-	-	-	-	-	5.23	7.01	-	-

13-Methylene-5-(4-methylphenyl)-5,6,8,13,14,14a-hexahydroisoquino[2,1-b][2]benzazepine (7g)
Prepared by general method **A** then **B** on a 1mmol scale using 4-(4-methylphenyl) isoquinoline (228 mg, 1.05 mmol) to give a crude product which was purified by column chromatography eluting with 8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine to afford the product as a colourless amorphous solid (146 mg, 66 %); R_f = 0.37 (8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine). Mpt 96 - 98 ^oC, δ_H($CDCl_3$, 500 MHz) 7.26 (t, 2H, ArH, J, 7.3 Hz), 7.20 (dd, 1H, ArH, J, 1.0, 7.5 Hz), 7.16 (t, 2H, ArH, J, 7.3 Hz), 7.10 (d, 2H, ArH, J, 8.3 Hz), 7.07 (d, 2H, ArH, J, 8.3 Hz), 7.05-7.06 (m, 2H, ArH), 6.92 (d, 1H, ArH, J, 7.5 Hz), 5.27 (s, 1H, 13a-H), 5.18 (d, 1H, 13b-H, J, 1.7 Hz), 4.44 (dd, 1H, 14a-H, J, 4.4, 9.8 Hz), 4.22 (d, 1H, 8b-H, J, 15.0 Hz), 4.03 (t, 1H, 5-H, J, 4.4 Hz), 3.80 (d, 1H, 8a-H, J, 15.0 Hz), 3.23 (dd, 1H, 6-H, J, 5.1, 12.4 Hz), 2.80-2.82 (m, 2H, 14b, 14c-H), 2.78 (t, 1H, 6a-H, J, 4.4 Hz), 2.31 (s, 3H, Me), δ_C($CDCl_3$, 75 MHz) 149.11, 143.88, 143.22, 139.34, 137.39, 136.55, 135.61, 130.24, 128.86, 128.52, 127.63, 127.32, 127.12, 126.52, 126.40, 125.84, 114.84 (CH_2), 65.05 (14a-CH), 60.10 (CH_2), 52.83 (CH_2), 44.00 (CH),

40.73 (CH_2), 21.08 (CH_3), ν_{max}(film)/cm^{-1} 3060, 3020, 2921, 2818, 2247, 1702, 1630, 1509, 1449, m/z (ES) 353.0 (M, 94), 351.9 (M, 100), H.R.M.S [M + H$^+$] $C_{26}H_{25}N$ Calculated 352.2060, found 352.2058

5-(4-Isopropoxyphenyl)-13-methylene-5,6,8,13,14,14a-hexahydroisoquino[2,1-b][2]benzazepine (7h)

Prepared by general method **A** then **B** on a 1mmol scale using 4-(4-Isopropoxyphenyl) isoquinoline (264 mg, 1 mmol) to give a crude product which was purified by column chromatography eluting with 8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine to afford the product as a colourless prisms (217 mg, 73 %); R_f = 0. 32 (8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine). Mpt 50-51 ^oC, δ_H($CDCl_3$, 500 MHz) 7.27 (s, 1H, ArH), 7.24 (s, 1H, ArH), 7.20 (td, 1H, ArH, J, 1.1, 7.3 Hz), 7.17 (td, 2H , ArH, J, 1.5, 7.3 Hz), 7.16 (t, 1H, ArH, J, 7.1 Hz), 7.10 (d, 2H, ArH, J, 8.6 Hz), 7.06-7.09 (m, 2H, ArH), 6.95 (d, 1H, ArH, J, 7.6 Hz), 6.77 (d, 2H, ArH, J, 8.6 Hz), 5.27 (s, 1H, 13a-H), 5.18 (d, 1H, 13b-H, J, 1.7 Hz), 4.49 (sep, 1H, 5d, J, 6.1 Hz), 4.43 (dd, 1H, 14a-H, J, 4.4, 9.7 Hz), 4.22 (d, 1H, 8b, J, 15.0 Hz), 4.00 (t, 1H, 5a-H, J, 4.4 Hz), 3.81 (d, 1H, 8a-H, J, 15.0 Hz), 3.21 (dd, 1H, 6-H, J, 5.1, 12.3 Hz), 2.80 (dd, 3H, 6,14b,14c-H, J, 3.7, 12.3 Hz), 1.32 (dd, 6H, $CH(CH_3)_2$, J, 2.2, 6.1 Hz), δ_C($CDCl_3$, 75 MHz) 156.68, 149.53, 139.71, 139.25, 138.01, 136.99, 130.69, 129.95, 129.23, 128.05, 125.75, 127.55, 126.92, 126.23, 115.74, 115.27 (CH_2), 70.10, 65.49, 60.57 (CH_2), 44.00, 41.16 (CH_2), 32.28 (CH_2), 22.58, ν_{max}(film)/cm^{-1} 3060, 3021, 2925, 2853, 2248, 1608, 1505, 1242, m/z (ES) 397 (M+2, 96), 396 (M+1, 100), H.R.M.S [M + H$^+$] $C_{28}H_{29}NO$ Calculated 396.2322, found 396.2324.

14-Methylene-5,6,8,14,15,15a-hexahydro[1,3]dioxolo[4,5-*h*]isoquino[2,1-*b*]benzazepine (7i)

Prepared by general method A then B on a 1 mmol scale using 3,4-methylenedioxy-2-iodobenzyl bromide (341 mg, 1 mmol) to give a crude product which was purified by column chromatography eluting with 1:1 (v/v) hexane / ethyl acetate to afford the product as a pale yellow oil (91 mg, 75 %); R_f = 0.41, 1:1 (v/v) hexane / ethyl acetate), δ_H($CDCl_3$, 500 MHz) 7.17 - 7.08 (m, 4H, 1-4H), 6.75 (s, 1H, ArH), 6.69 (s, 1H, ArH), 5.94 (dd, 2H,11-H_2, J, 1.5, 4.6 Hz), 5.22 (s, 1H, 14a-H), 5.09 (d, 1H, 14b-H, J, 1.8 Hz), 4.29 (dd, 1H, 15a-H, J, 3.0, 11.1 Hz), 4.20 (d, 1H, 8b-H, J, 14.8 Hz), 3.83 (d, 1H, 8a, J, 14.8 Hz), 3.00 (ddd, 1H, 5-H, J, 6.4, 9.4, 15.8 Hz), 2.88 (td, 1H, 5-H, J, 5.3, 12.0 Hz), 2.74-2.80 (m, 2H, 6-H, 15-H), 2.80 (d, 1H, 6-H, J, 5.1 Hz), 2.59 (dd, 1H, 15-H, J, 3.0, 13.8 Hz), δ_C($CDCl_3$, 75 MHz) 149.45, 146.90, 139.71, 134.38, 130.00, 129.43, 127.39, 126.69, 1255.93, 124.10, 115.27 (CH_2), 110.13, 108.98, 101.40 (CH_2), 65.12 (CH), 60.52 (CH_2), 43.72 (CH_2), 40.99 (CH_2), 29.44 (CH_2), ν_{max}(film)/cm^{-1} 3075, 3019, 2906, 2837, 2246, 1630, 1611, 1501, 1482, 1338, 1236. H.R.M.S [M + H$^+$] $C_{21}H_{19}NO_4$, Calculated, 306.1494, found 306.1500.

10,11-Dimethoxy-13-methylene-5,6,8,13,14,14a-hexhydroisoquin[2,1-b] benzazepine (7j)

Prepared by general method A then B on a 0.5 mmol scale using 3,4-dimethoxy-2-iodobenzyl bromide (178 mg, 0.5 mmol) and 6,7-dimethyoxyisoquinoline (94 mg, 0.5 mmol) to give a crude product which was purified by column chromatography eluting with 1:1 (v/v) hexane : ether to afford the product as a pale yellow oil (60 mg, 74 %); R_f = 0.11 (Ether), δ_H($CDCl_3$, 500 MHz) 7.08-7.16 (m, 4H, ArH), 6.81 (s, 1H, 9-H), 6.71 (s, 1H, 12-H), 5.22 (s, 1H, 13a-H), 5.12 (d, 1H, 13b-H, J, 1.8 Hz), 4.30 (dd, 1H, 14a-H, J, 3.0, 11.0 Hz), 4.23 (s, 1H, 8b-H, J, 14.8 Hz), 3.89 (s, 3H, OMe), 3.88 (s, 3H, OMe), 3.87 (d, 1H, 8a-H, J, 14.8 Hz), 2.77-3.05 (m, 5H, 5-H_2, 6-H_2, 14-H), 2.63 (dd, 1H, 14-H, J, 3.0, 13.8 Hz), δ_C($CDCl_3$, 75 MHz) 149.57, 148.21, 139.82, 136.17, 134.44, 129.11, 128.68, 127.43, 125.97, 120.89, 114.85 (CH_2), 113.09, 111.90, 65.01 (CH), 60.62 (CH_2), 56.43, 56.30 (CH_2), 44.05 (CH_2), 41.23 (CH_2), 29.40 (CH_2), ν_{max}(film)/cm^{-1} 3061, 3001, 2932, 2909, 2832, 2253, 1627, 1603, 1572, 1463, 1250, H.R.M.S [M + H$^+$] $C_{21}H_{23}NO_2$, Calculated, 322.1802 found 322.1802

2,3,10,11-Tetramethoxy-13-methylene-5,6,8,13,14,14a-hexahydroisoquino[2,1-b][2] benzazepine (7k)

Prepared by general method **A** then **B** on a 0.5 mmol scale using 3,4-dimethoxy-2-iodobenzyl bromide (178 mg, 0.5 mmol) to give a crude product which was purified by column chromatography eluting with ethyl acetate to afford the product as a pale yellow oil (60 mg, 74 %); R_f= 0.06 (Ethyl acetate), δ_H($CDCl_3$, 500 MHz) 6.81 (s, 1H, 4-H), 6.71 (s, 1H, 1-H), 6.62 (s, 1H, 9-H), 6.57 (s, 1H, 12-H), 5.23 (s, 1H, 13a-H), 5.13 (d, 1H, 13b-H, J, 1.8 Hz), 4.23 (dd, 1H, 14a-H, J, 2.9, 10.8 Hz), 4.22 (d, 1H, 8b-H, J, 14.8 Hz), 3.91 (s, 6 H, OMe), 3.88 (s, 6 H, OMe), 3.84 (d, 8a-H, J, 14.8 Hz), 2.92 (s, 1H, 5-H), 2.89 (d, 1H, 5-H, J, 2.9 Hz), 2.83 (d, 1H, 14-H, J, 13.8 Hz), 2.77 (s, 1H, 6-H), 2.70 (dd, 1H, 6-H, J, 2.9, 10.8 Hz), 2.61 (dd, 1H, 14-H, J, 2.9, 13.8 Hz), δ_C($CDCl_3$, 75 MHz) 149.48, 148.21, 148.0, 147.44, 136.07, 131.75, 128.67, 126.49, 114.73 (CH_2), 113.05, 111.85, 111.56, 110.28, 64.46, 60.46, 56.50, 56.20, 44.10, 41.03, 30.72, 28.99, ν_{max}(film)/cm^{-1} 2996, 2933, 2908, 2832, 1603, 1512, 1463, H.R.M.S [M + H^+] $C_{23}H_{27}NO_4$, Calculated, 382.2013, found 382.2015.

13-Methyl-15-methylene-7,8-13-13b,14,15-hexahydro-5*H*-indolo[2',3',:3,4]pyrido[1,2-*b*][2]benzazepine (9a)

Prepared by general method **A** then **B** on a 0.6 mmol scale using N-methyl-β-carboline (111 mg, 0.6 mmol) to give a crude product which was purified by column chromatography eluting with 1:1 (8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine) to afford the product as a white amorphous solid (47 mg, 65 %), R_f= 0.11 (8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine), Mpt 155-157 ^oC, δ_H($CDCl_3$, 500 MHz) 7.46 (d, 1H, ArH, J, 7.9 Hz), 7.28 (d, 1H, ArH, J, 7.9 Hz), 7.24-7.26 (m, 4H, ArH), 7.18 (t, 1H, ArH, J, 7.3 Hz), 7.07 (t, 1H, ArH, J, 7.3 Hz), 5.27 (s, 1H, 15a-H), 5.19 (s, 1H, 15b-H), 4.47 (d, 1H, 14a-H, J, 10.9 Hz), 4.40 (d, 1H, 5b-H, J, 14.7 Hz), 4.02 (d, 1H, 5a-H, J, 14.7 Hz), 3.71 (s, 3H, 13-Me), 2.93 (d, 1H, 6-H, J, 9.0 Hz), 2.92 (dd, 1H, 14-H, J, 10.9, 14.1 Hz), 2.87 (dd, 1H, 6-H, J, 3.4, 9.0 Hz), 2.82 (t, 1H, 7-H, J, 13.7 Hz), 2.72(d, 1H, 7-H, J, 13.7 Hz), 2.59 (dd, 1H, 14-H, J, 1.6, 14.1 Hz), δ_C($CDCl_3$, 75 MHz) 148.73, 143.71, 137.36, 135.44, 129.44, 127.79, 127.58, 127.42, 126.86, 121.11, 118.89, 118.20, 115.85, 115.12 (CH2), 108.75, 106.92, 61.04 (CH_2), 59.63 (CH), 42.94 (CH2), 37.71 (CH_2), 29.57 (CH_3), 21.79 (CH_2), ν_{max}(film)/cm^{-1} 3059, 2922, 2845, 2251, 1632, 1613, 1469, 1433, 1318, 1139, m/z (ES) 315 (M+H, 100), H.R.M.S [M + H^+] $C_{22}H_{22}N_2$, Calculated, 315.1856, found 315.1856.

15-methylene-13-[(4-methylphenyl)sulfonyl]-7,8,13,13b,14,15,hexahydro-5*H*-indolo [2'3':3:4] pyrdido[1,2 *b*][2] benzazepine(9b)

Prepared by general method **A** then **B** on a 0.5 mmol scale using N-tosyl- β-carboline (161 mg, 0.5 mmol) to give a crude product which was purified by column chromatography eluting with 1:1 (ether) to afford the product as a pale yellow oil, recrystallised in ether to give pale yellow needles (59 mg, 64 %); R_f= 0.37 (EtOAc) Mpt 187 – 190 ^oC, δ_H($CDCl_3$, 500 MHz) 8.11 (d, 1H, ArH, J, 8.1 Hz), 7.59 (d, 1H, ArH, J, 8.1 Hz), 7.30 (d, 1H, ArH, J, 7.6 Hz), 7.19-7.27 (m, 6H, ArH), 7.13 (d, 2H, ArH, J, 8.1 Hz), 5.48 (s, 1H, 15a-H), 5.18 (d, 1H, 15b-H, J, 1.4 Hz), 4.96 (d, 1H, 16-H, J, 10.1 Hz), 4.46 (d, 1H, 9b-H, J, 14.7 Hz), 4.00 (d, 1H, 9a-H, J, 14.7 Hz), 3.22 (d, 1H, 15c-H, J, 12.2 Hz), 2.88 (d, 1H, 5-H, J, 4.9 Hz), 2.83 (d, 1H, 15b-H, J, 8.5 Hz), 2.66 (d, 1H, 6-H, J, 11.1 Hz), 2.60 (t, 1H, 6-H, J, 11.1 Hz), 2.29 (s, 3H, Me), δ_C($CDCl_3$, 75 MHz) 148.76, 145.01, 137.16, 135.50, 130.75, 132.23, 129.73, 128.25, 128.01, 127.48, 127.48, 126.77, 124.86, 124.10, 118.00, 116.18 (CH_2), 115.69, 61.66 (CH_2), 41.79 (CH_2), 38.33 (CH_2), 22.02 (CH_2), 21.97, ν_{max}(film)/cm^{-1} 3060, 2923, 2846, 1627, 1597, 1453, 1366, 1172, m/z (ES) 455 (M+H, 100), H.R.M.S [M + H^+] $C_{28}H_{26}N2O_2S$ Calculated, 455.1788, found 455.1789

Note: Compounds **12a-d**, are prepared via general procedure **A**, using thiophene (2 mol eq.) as an additional additive to promote the reaction.

11-methylene-1-(2-thienyl)-3,4,6,11,12,12a-hexahydro[1,2-*b*][2]benzazepine (13a)
Prepared by general method **A** then **B** on a 0.16 mmol scale using 2-thienyl pyridine (27 mg, 0.16 mmol) to give a crude product which was purified by column chromatography eluting with 1:1 (v/v) hexane : ether to afford the product as a pale yellow oil (19 mg, 60 %); R_f= 0.21(Ether : Hexane) δ_H($CDCl_3$, 500 MHz) 7.24-7.19 (m, 4H, ArH + Thiophene-H), 7.15 (dd, 1H, ArH, J, 1.2, 5.0 Hz), 7.00 (t, 1H, Thiophene-H, J, 2.4 Hz), 6.99 (d, 1H, Thiophene-H, J, 2.4 Hz), 6.09 (dd, 1H, 2-H, J, 2.4, 3.6 Hz), 5.14 (s, 1H, 11a-H), 5.09 (s, 1H, 11b-H), 4.34 (d, 1H, 6b-H, J, 14.6 Hz), 4.14 (d, 1H, 12a-H, J, 10.3 Hz), 3.92 (d, 1H, 6a-H, J, 14.6 Hz), 2.68 (dd, 1H, 3-H, J, 2.6, 9.0 Hz), 2.63 (d, 1H, 12-H, J, 10.3 Hz), 2.59 (dd, 1H, 12-H, J, 2.6, 14.1 Hz), 2.52 (dd, 1H, 4-H, J, 9.0, 18.0 Hz), 2.15 (d, 1H, 4-H, J, 18 Hz), δ_C($CDCl_3$, 75 MHz) 129.37, 127.68, 127.45, 127.31, 127.22, 123.24, 122.74, 121.87, 114.61 (CH_2), 63.80 (CH), 60.67 (CH_2), 41.27 (CH_2), 36.03 (CH_2), 26.36 (CH_2), ν_{max}(film)/cm^{-1} 3071, 2909, 2247, 1632, 1484, 1434, 1038, m/z (ES) 294 (M+H, 100 %), H.R.M.S [M + H^+] $C_{19}H_{19}NS$, Calculated, 294.1311, found 294.1311.

1-(2-furyl)-11-methylene-3,4,6,11,12,12a-hexahydro[1,2-*b*][2]benzazepine (13b)
Prepared by general method **A** then **B** on a 0.5 mmol scale using 2-furyl pyridine (73 mg, 0.5 mmol) to give a crude product which was purified by column chromatography eluting with ether to afford the product as a colourless oil (65 mg, 63 %); R_f= 0.25 (ether), δ_H($CDCl_3$, 500 MHz) 7.35 (s, 1H, furan-H), 7.24 (d, 2H, ArH, J, 7.3 Hz), 7.22 (d, 2H, ArH, J, 7.3 Hz), 6.40 (dd, 1H, furan-H, J, 1.0, 3.0 Hz), 6.24 (d, 2-H, J, 3.0 Hz), 6.23 (s, 1H, furan-H), 5.20 (s, 1H, 11a-H), 5.13 (s, 1H, 11b-H), 4.37 (d, 1H, 6b-H, J, 14.5 Hz), 4.15 (d, 1H, 12a-H, J, 10.3 Hz), 3.95 (d, 1H, 6a-H, J, 14.5 Hz), 2.79 (dd, 1H, 3-H, J, 7.7, 11.8 Hz), 2.73 (dd, 2H, 12-H, J, 4.6, 10.3 Hz), 2.67 (app dd, 1H, 3-H, J, 3.4, 11.8 Hz), 2.59 (dd, 1H, 4b-H, J, 10.3, 18.6 Hz), 2.19 (td, 1H, 4a-H, J, 4.6, 18.6 Hz), δ_C($CDCl_3$, 75 MHz) 148.81, 141.32, 134.28, 132.08, 131.01, 129.69, 127.97, 127.40, 120.72, 114.95 (CH_2), 111.00, 104.24 (CH), 60.82 (CH), 60.03 (CH_2), 41.21 (CH_2), 36.40 (CH_2), 25.47 (CH_2), ν_{max}(film)/cm^{-1} 3065, 3027, 2907, 2831, 1704, 1631, 1488, 1434, 1314, m/z (ES) 278 (M+H, 100 %), H.R.M.S [M + H^+] $C_{19}H_{19}NO$, Calculated, 278.1539, found 278.1537.

11-methylene-1-(1-methyl-1*H*-pyrrol-2-yl)-3,4,6,11,12,12a-hexahydro[1,2-*b*][2]benzazepine (13c)
Prepared by general method **A** then **B** on a 0.5 mmol scale using β-nicotinamide (81 mg, 0.5 mmol) to give a crude product which was purified by column chromatography eluting with 1:1(hexane : EtOAc) to afford the product as a colourless oil (72 mg, 61 %); R_f= 0.06 (8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine). δ_H($CDCl_3$, 500 MHz) 7.24-7.18 (m, 4H, ArH), 6.61 (dd, 1H, Pyrrole-H, J, 1.8, 2.6 Hz), 6.12 (dd, 1H, Pyrrole-H, J, 2.6, 3.6 Hz), 6.05 (dd, 1H, Pyrrole-H, J, 1.8, 3.6 Hz), 5.72 (s, 1H, 12-H), 5.30 (s, 1H, 11a-H), 5.06 (s, 1H, 11b-H), 4.31 (d, 1H, 6b-H, J, 14.4 Hz), 3.95 (d, 1H, 6a-H, J, 14.4 Hz), 3.58 (s, 3H, N-Me), 2.77-2.27 (m, 5H, 4-H_2, 3-H_2, 12-H), 2.27-2.17 (m, 1H, 12-H), δ_C($CDCl_3$, 75 MHz) 129.94, 128.41, 127.83, 125.94, 123.34, 115.51 (CH2), 11.03, 108.12, 107.65, 60.49 (CH), 42.69 (CH_2), 36.54 (CH_2), 35.23 (CH_3), 26.30 (CH_2), 15.68 (CH_2), ν_{max}(film)/cm^{-1} 3065, 2905, 2829, 1717, 1631, 1482, 1467, 1432, 1303, m/z (ES) 291 (M+H, 100 %), H.R.M.S [M + H^+] $C_{20}H_{22}N_2$, Calculated, 291.1856, found 291.1856.

1-(3-furyl)-11-methylene-3,4,6,11,12,12a-hexahydro[1,2-*b*][2]benzazepine (13d)
Prepared by general method A then B on a 0.5 mmol scale using 3-furyl pyridine (95 mg, 0.5 mmol) to give a crude product which was purified by column chromatography eluting with ether to afford the product as a colourless oil, which was recrystallised in ether to give colourless plates (65 mg, 63 %); R_f= 0.31(Ether), Mpt 94 -95 ^oC, δ_H($CDCl_3$, 500 MHz) 7.35 (s, 1H, ArH), 7.31 (t, 1H, ArH, J, 1.5 Hz), 7.19 (s, 1H, ArH), 7.15 (s, 1H, ArH), 7.14 (dd, 1H, furan-H, J, 2.3, 6.3 Hz), 7.11 (d, 1H, furan-H, J, 6.3 Hz), 6.48 (s, 1H, furan-H), 5.92 (d, 1H, 2-H, J, 3.3 Hz), 5.14 (s, 1H, 11a-H),

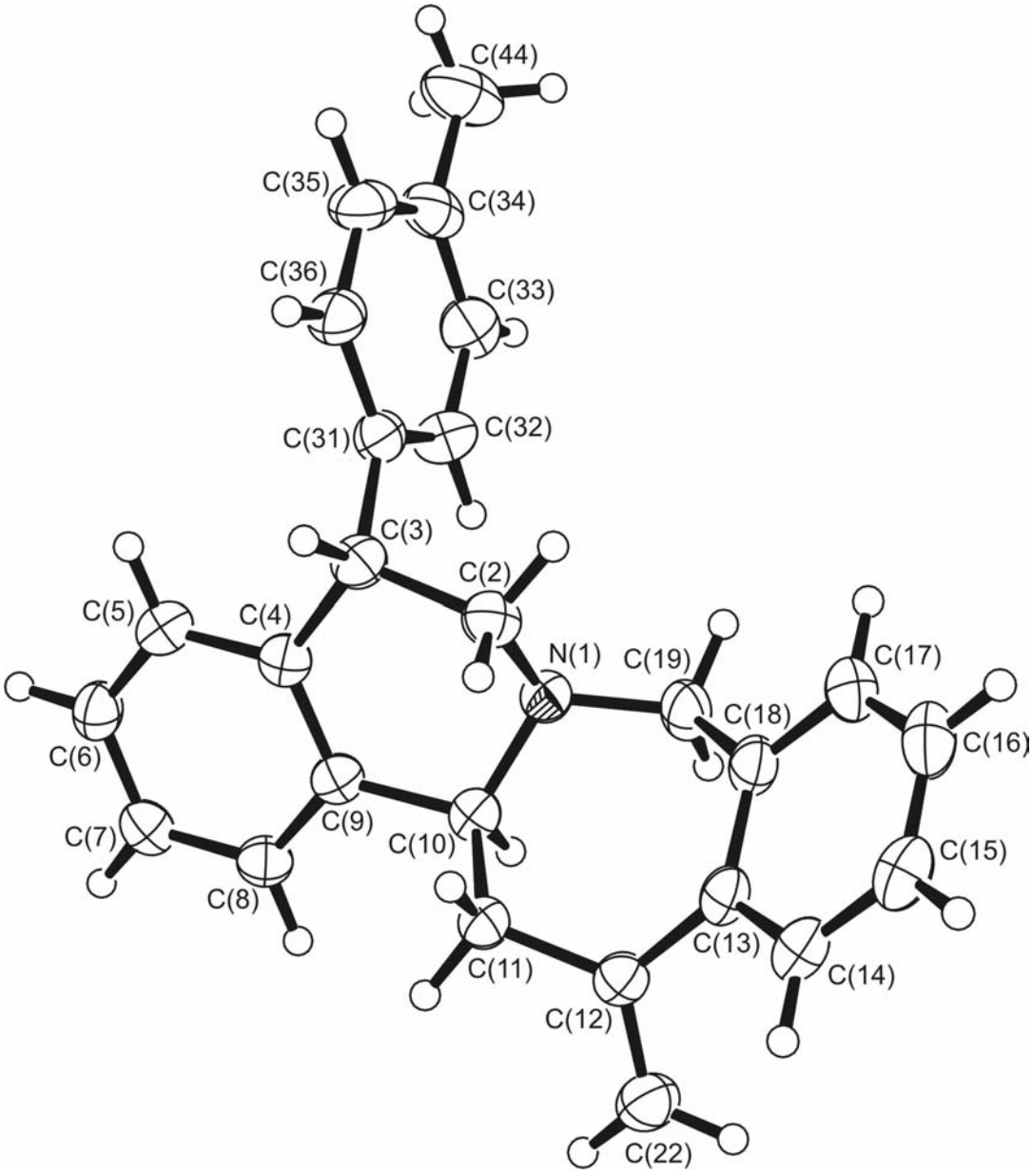
5.09 (d, 1H, 11b-H, J, 1.5 Hz), 4.30 (d, 1H, 6b-H, J, 14.6 Hz), 3.95 (d, 1H, 12a-H, J, 10.7 Hz), 3.90 (d, 1H, 6a-H, J, 14.6 Hz), 2.67 (dd, 1H, 3-H, J, 3.3, 10.7 Hz), 2.58 (d, 1H, 3-H, J, 10.7 Hz), 2.56 (dd, 2H, 12-H, J, 2.2, 14.0 Hz), 2.43 (tdd, 1H, 4-H, J, 2.3, 10.7, 18.0 Hz), 2.12 (td, 1H, 4-H, J, 2.3, 18.0 Hz), δ_C($CDCl_3$, 75 MHz) 149.85, 144.43, 143.58, 138.02, 135.67, 132.92, 129.81, 128.09, 127.85, 127.66, 125.90, 121.60, 114.87 (CH_2), 108.58, 63.60 (CH), 61.09 (CH_2), 41.92 (CH_2), 36.50 (CH_2), 26.53 (CH_2), ν_{max}(film)/cm^{-1} 3068, 3052, 2923, 1955, 1584, 1477, 1433, m/z (ES) 278 (M+H, 100 %), H.R.M.S [M + H^+] $C_{19}H_{19}NO$, Calculated, 278.1539, found 278.1538

Methyl 4-{1-[(2-benzyl-1,2,3,4-tetrahydroisoquinolin-1-yl)methyl]vinyl}benzoate (17a)
Prepared by general procedure **A** then **B**, benzyl bromide (171 mg, 1 mmol), isoquinoline (126 mg, 1 mmol) and methyl-4-iodobenzoate (393 mg, 1.5 mmol) gave a crude product which was purified by column chromatography eluting with 8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine to afford the product as a pale yellow oil (92 mg, 47 %); R_f = 0. 19 (8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine), δ_H($CDCl_3$, 500 MHz) 7.94 (d, 2H, ArH, J, 8.3 Hz), 7.42 (d, 2H, ArH, J, 8.3 Hz), 7.19 (d, 4H, ArH, J, 8.3 Hz), 7.12 (dd, 2H, ArH, J, 3.8, 7.1 Hz), 7.09 (d, 1H, ArH, J, 7.1 Hz), 6.93 (d, 1H, ArH, J, 7.1 Hz), 5.38 (s, 1H, 10a-H), 5.09 (s, 1H, 10b-H), 3.92 (s, 3H, OMe), 3.72 (t, 1H, 1-H, J, 6.3 Hz), 3.67 (d, 1H, 11b-H, J, 13.3 Hz), 3.55 (d, 1H, 11a-H, 13.3 Hz), 3.25 (ddd, 1H, 3-H , J, 5.1, 11.1, 13.3 Hz), 3.04 (dd, 1H, 3-H, J, 7.9, 14.5 Hz), 2.94 (ddd, 1H, 4-H , J, 6.3, 11.1, 16.9 Hz), 2.82 (dd, 2H, 3-H, J, 6.3, 14.5 Hz), 2.53 (dd, 1H, 4-H, J, 2.9, 16.9 Hz), δ_C($CDCl_3$, 75 MHz) 167.42, 146.00, 139.71, 138.42, 134.66, 130.07, 129.49, 129.24, 129.17, 128.57, 127.27, 126.72, 125.97, 125.85, 117.13 (CH_2), 59.84 (CH), 58.06 (CH_2), 52.49 (CH_3), 43.12 (CH_2), 42.64 (CH_2), 24.01 (CH_2), ν_{max}(film)/cm^{-1} 2925, 2840, 2253, 1716, 1608, 1437, 1286, m/z (ES) 398 (M+H, 100 %), H.R.M.S [M + H^+] $C_{27}H_{27}NO_2$, Calculated, 398.2115, found 398.2115.

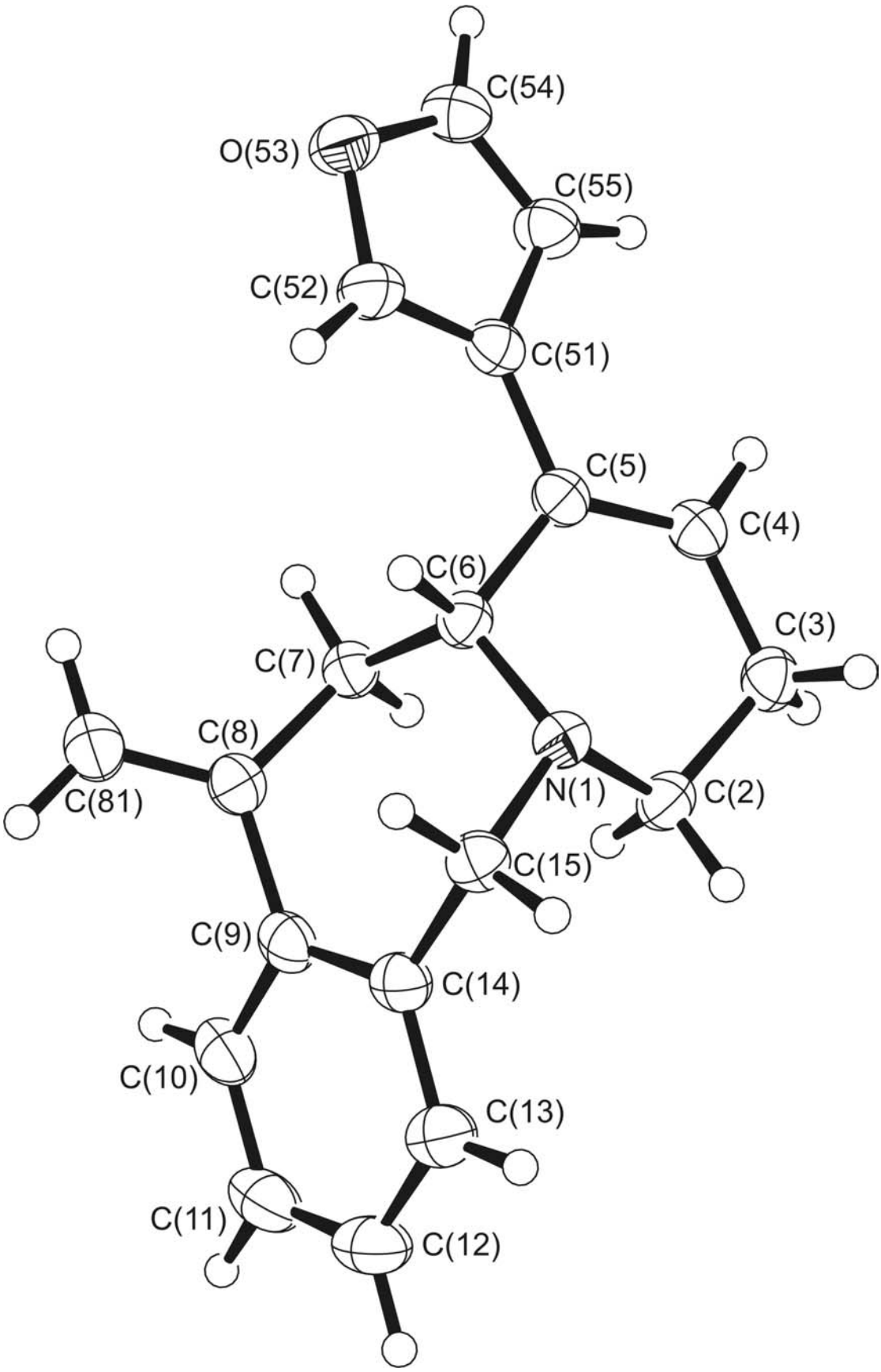
2-Benzyl-1-{2-[4-(trifluoromethyl)phenyl]prop-2-en-1-yl}-1,2,3,4-tetrahydroisoquinoline (17b)
Prepared by general procedure **A** then **B**, benzyl bromide (171 mg, 1 mmol), isoquinoline (0.126 g, 1 mmol) and 4-iodobenzotrifluoride (272 mg, 1.5 mmol) gave a crude product which was purified by column chromatography eluting with 8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine to afford the product as a pale yellow oil (55 mg, 36 %); R_f = 0. 30 (8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine).δ_H($CDCl_3$, 500 MHz) 7.42 (d, 2H, ArH, J, 8.3 Hz), 7.36 (d, 2H, ArH, J, 8.3 Hz), 7.12 (dd, 2H, J, 1.5, 5.3 Hz), 7.08 (app. dd, 2H, J, 3.2, 7.2 Hz), 7.06 (app. dd, 2H, J, 1.5, 5.3 Hz), 7.03 (d, 2H, ArH, J, 7.3 Hz), 6.85 (d, 1H, ArH, J, 7.3 Hz), 5.27 (d, 1H, 10b-H, J, 0.6 Hz), 5.00 (s, 1H, 10a), 3.61 (d, 1H, 1-H, J, 13.6 Hz), 3.60 (d, 1H, 11-H, J, 13.6 Hz), 3.48 (d, 1H, 11-H, J, 13.6 Hz), 3.21 (ddd, 1H, 3-H, J, 5.0, 11.2, 13.4 Hz), 2.96 (dd, 2H, 4-H, J, 7.9, 14.5 Hz), 2.88 (ddd, 1H, 9-H, J, 6.8, 11.2, 16.9 Hz), 2.75 (dd, 1H, 3-H, J, 5.0, 11.2 Hz), 2.47 (dd, 1H, 9-H, J, 3.0, 16.9 Hz), δ_C($CDCl_3$, 75 MHz) 144.24, 138.16, 136.83, 133.21, 128.64, 128.06, 127.10, 125.53, 125.15, 125.03, 124.54, 124.24, 124.14, 115.70 (CH_2), 58.04 (CH), 56.57 (CH_2), 41.78 (CH_2), 41.47 (CH_2), 22.53 (CH_2), ν_{max}(film)/cm^{-1} 3063, 3026, 2939, 2838, 2248, 1616, 1493, 1325
m/z (ES) 408 (M +H, 100 %), H.R.M.S [M + H^+] $C_{26}H_{24}F_3N$, Calculated, 408.1934, found 408.1935.

1-[2-(3,5-dichlorophenyl)prop-2-en-1-yl]-2-[4-(trifluoromethoxy)benzyl]-1,2,3,4-tetrahydroisoquioline (17c)
Prepared by general procedure **A** then **B**, 4-trifluoromethoxybenzyl bromide (255 mg, 0.50 mmol), isoquinoline (63 mg, 0.50 mmol) and 3,5-dichloroiodobenzene (205 mg, 0.75 mmol) gave a crude product which was purified by column chromatography eluting with 8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine to afford the product as a pale yellow oil (83 mg, 48 %); R_f= 0. 20(8 : 2 : 0.01 (v/v/v) hexane / diethylether / triethylamine), δ_H($CDCl_3$, 500 MHz) 7.22 (d, 1H, ArH, J, 7.6 Hz), 7.18 (d, 1H, ArH, J, 8.3 Hz), 7.14-7.10 (m, 4H, ArH), 7.07 (d, 4H, ArH, J, 8.3 Hz), 6.90 (d, 1H, ArH, J, 5.90 Hz), 5.31 (s, 1H, 10a-H), 5.07 (s, 1H, 10b-H), 3.66 (d, 2H, 11b-H, masked 1-H, J, 13.2 Hz), 3.54 (d, 1H, 11b, J, 13.2 Hz), 3.26 (ddd, 1H, , J, 5.3, 11.6, 13.6 Hz), 2.95 (d, 1H, , J, 15.2

Hz), 2.91 (d, 1H, , J, 14.4 Hz), 2.78 (td, 2H, , J, 5.3, 15.2 Hz), 2.53 (dd, 1H, , J, 3.6, 17.0 Hz), δ_C($CDCl_3$, 75 MHz) 148.54, 144.67, 144.61, 138.20, 137.89, 135.20, 134.41, 130.36, 129.62, 128.66, 128.46, 127.56, 126.82, 126.24, 125.30, 121.30, 120.96, 117.43 (CH_2), 59.81 (CH), 57.14 (CH_2), 42.97 (CH_2), 42.62 (CH_2), 23.65 (CH_2), ν_{max}(film)/cm^{-1} 3075, 3018, 2941, 2837, 1583, 1558, 1507, 1260, 1222, m/z (ES) 495 (^{37}Cl) (M+H, 17 %), 494 (^{37}Cl + ^{35}Cl) (M+H, 62 %), 492 (^{35}Cl) (M+H, 91 %), H.R.M.S [M + H^+] (^{35}Cl) $C_{26}H_{24}F_3N$, Calculated, 492.1103, found 492.1103.



View of 7g. Ellipsoid probability: 50%.



View of 13d. Ellipsoid probability: 50%.