Supporting Information

"A Convenient Method for 3-Pyrroline Synthesis"

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Experimental

Melting points were recorded on Koffler hot stage apparatus and are uncorrected. Proton NMR spectra were recorded on Bruker AM400 MHz, AV400 MHz or DPX250 MHz, spectrometers. Carbon NMR spectra were recorded on Jeol EX 270 MHz, Bruker AV400, or DPX250 MHz spectrometers. Fluorine NMR spectra were recorded using a Bruker DPX400 spectrometer. Chemical shifts were recorded on the δ-scale. In proton and carbon NMR residual solvent was used as an internal standard. In the case of fluorine NMR, trifluoroacetic acid was used as an external standard at –78.50 ppm. Infrared spectra were recorded on a Perkin-Elmer 1600 FT spectrophotometer. High-resolution mass spectra were acquired on VG micromass 70E and AIMS 902 instruments, using electron ionisation (EI), fast atom bombardment (FAB) or electrospray, as stated. Optical rotations were measured on a JASCO (DIP-370) polarimeter and concentrations are given as g/100 mL. Elemental analysis was performed by the microanalysis service of Nottingham University. Chiral HPLC was carried out using Hewlett-Packard 1100 series apparatus with a Diacel Chrialpak OD column (hexane:isopropanol (99:1) with a flow rate of 0.5 mL/min). Reactions were performed in flame-dried glassware under an atmosphere of nitrogen. Solvents were dried before use according to standard procedures:¹ Diethylether and tetrahydrofuran
were distilled from sodium/benzophenone, and dichloromethane was distilled from calcium hydride. Thin layer chromatography (t.l.c.) was carried out on Merck silica gel glass-backed plates. Plates were visualised by exposure to UV light followed by staining with basic potassium permanganate. Flash column chromatography was carried out using Merck silica gel 60 as the stationary phase.

**General procedure A: N-alkylation with 1,3-dibromo-2-methylpropene.**

A solution of the amine or protected amine in dry DMF was added dropwise to a stirring suspension of NaH (60% suspension in mineral oil) in DMF. After 10 minutes, 1,3-dibromo-2-methylpropene\(^2\) was added dropwise (evolution of H\(_2\) was observed) and this solution was stirred for 8 hours at room temperature before being quenched with saturated NH\(_4\)Cl. Water was added and the product extracted into Et\(_2\)O.

**Benzyl-(3-bromo-2-methyl-allyl)-amine 6**

\[
\text{Ph} \quad \text{N} \quad \text{Br} \quad \text{H}
\]

General procedure A was followed using: benzylamine (0.099 g, 0.93 mmol) in dry DMF (3 mL), NaH (0.037 g, 0.93 mmol) in DMF (3 mL) and 1,3-dibromo-2-methylpropene (0.109 g, 0.51 mmol). The organic fractions were combined, washed with brine (20 mL), dried over Na\(_2\)SO\(_4\) and concentrated. The crude material was purified by flash column chromatography on silica using petrol and Et\(_2\)O as eluant (1:2) to give 6 (0.093 g, 76%) \([R_f 0.2; \text{petrol:Et}_2\text{O (1:2)] (trans:cis 2.4:1, by } ^1\text{H NMR) as a colourless oil (Found: C, 55.16; H, 5.74; N, 5.68; C}_{11}\text{H}_{14}\text{NBr requires C, 55.02; H, 5.88; N, 5.83%}; \nu_{\max}/\text{cm}^{-1} \text{ (solution in chloroform) 3330 (NH), 2914, 2847, 1633, 1455, 1376, 1361 and 1101; } \delta_{\text{H}}(400 \text{ MHz; CDCl}_3) \text{ trans: 7.35-7.26 (5 H, m, Ph), 6.15 (1 H, q, J 1, CHBr), 3.75 (2 H, s, CH}_2\text{), 3.27 (2 H, s, CH}_2\text{), 1.85 (3H, d, J 1, CH}_3\text{), 1.52 (1 H, br s, NH); cis: 7.35-7.26 (5 H, m, Ph), 6.02 (1 H, s, CHBr), 3.77 (2 H, s, CH}_2\text{), 3.44 (2 H, s, CH}_2\text{), 1.89 (3H, s, CH}_3\text{), 1.52 (1 H, br s, NH); } \delta_{\text{C}}(67 \text{ MHz; CDCl}_3) \text{ trans: 140.2, 139.9, 128.4 (CH), 128.1 (CH), 126.9 (CH), 103.5 (CH), 55.0 (CH}_3\text{), 53.1 (CH}_2\text{), 21.1 (CH}_3\text{); cis: 140.2, 139.9, 128.4 (CH), 128.1 (CH), 126.9 (CH), 103.5 (CH), 55.0 (CH}_3\text{), 53.1 (CH}_2\text{), 21.1 (CH}_3\text{);}\)
126.9 (CH), 102.6 (CH), 52.7 (CH₃), 51.4 (CH₂), 17.9 (CH₃); m/z (ES⁺) 240 (M⁺ + 1); (C₁₁H₁₄NBr requires 240.0378. Found 240.0371).

(3-Bromo-2-methyl-allyl)-((R)-1-phenyl-ethyl)-amine 8

General procedure A was followed using: (R)-α-methylbenzylamine (0.202 g, 1.67 mmol) in dry DMF (2 mL), NaH (0.081 g, 2.04 mmol) in DMF (3 mL) and 1,3-dibromo-2-methylpropene (0.334 g, 1.56 mmol). The organic fractions were combined, washed with brine (20 mL), dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography, using Et₂O as eluant to give 8 (0.296 g, 70%) %) [R f 0.4; Et₂O] (trans:cis 2.3:1, by ¹H NMR) as a colourless oil (Found: C, 56.92; H, 6.23; N, 5.12. C₁₂H₁₆NBr requires C, 56.71; H, 6.35; N, 5.51%); ν_max(solution in chloroform)/cm⁻¹ 3366 (NH), 2913, 2851, 1632, 1602, 1492, 1455, 1373, 1354, 1307, 1110 and 1077; δ_H(400 MHz; CDCl₃) trans: 7.31-7.20 (5 H, m, Ph), 6.02 (1 H, s, CHBr), 3.69 (1 H, m, CHCH₃), 3.05 (2 H, s, CH₂), 1.76 (3 H, s, CH₃), 1.45 (1 H, br s, NH), 1.31 (3 H, d, J 6.5, CH₂CH); cis: 7.31-7.20 (5 H, m, Ph), 5.91 (1 H, s, CHBr), 3.28 (1 H, d, J 13, CHH), 3.12 (1 H, d, J 13, CHH), 1.79 (3 H, s, CH₃), 1.45 (1 H, br s, NH), 1.35 (3 H, m, CH₃CH); δ_C(67 MHz; CDCl₃) trans: 145.0, 139.0, 128.5 (CH), 127.1 (CH), 126.6 (CH), 103.8 (CH), 57.1 (CH), 53.3 (CH₂), 24.2 (CH₃), 18.0 (CH₃); cis: 145.0, 139.0, 128.5 (CH), 127.1 (CH), 126.6 (CH), 102.0 (CH), 57.5 (CH), 48.8 (CH₂), 29.7 (CH₃), 2.0 (CH₃); m/z (ES⁺) 254 (M⁺ +1); (C₁₂H₁₇NBr requires 254.0544. Found 254.0528).

(3-Bromo-2-methyl-allyl)-(1-naphthalen-1-yl-ethyl)-amine 10

General procedure A was followed using: 1-(1-napthyl)ethylamine (0.200 g, 1.17 mmol) in dry DMF (3 mL), NaH (0.056 g, 1.40 mmol) in DMF (3
mL) and 1,3-dibromo-2-methylpropene (0.238 g, 1.11 mmol). The organic fractions were combined, washed with brine (20 mL), dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography, using petrol and Et₂O (1:1) as eluant to give 10 (0.14 g, 41%) %) [Rf 0.4; petrol:Et₂O (1:1)] (trans:cis 2.3:1, by ¹H NMR) as a colourless oil (Found: C, 63.24; H, 5.83; N, 4.62%. C₁₆H₁₇NBr requires C, 63.17; H, 5.96; N, 4.62%); ν max(film)/cm⁻¹ 3330 (NH), 3061, 2965, 2919, 2864, 1633, 1594, 1509, 1439, 1372, 1286, 1130, 1114, 800 and 779; δ H(400 MHz; CDCl₃) trans: 8.28 (1 H, d, J 9, Ar), 7.94 (1 H, d, J 9.5, Ar), 7.82 (1 H, d, J 8, Ar), 7.74 (1 H, d, J 7, Ar), 7.60-7.52 (3 H, m, Ar), 6.15 (1 H, q, J 1, CHBr), 4.66 (1 H, q, J 6.5, CHN), 3.23 (2 H, s, CHH), 1.90 (3 H, d, J 1, CH₃), 1.55 (3H, d, J 6.5, CHCH₃); cis: 8.30 (1 H, d, J 9, Ar), 7.94 (1 H, d, J 9.5, Ar), 7.81 (1 H, d, J 9.5, Ar), 7.81 (1 H, d, J 7, Ar), 7.74 (1 H, d, J 7, Ar), 7.60-7.52 (3 H, m, Ar), 6.03 (1 H, q, J 1, CHBr), 4.71 (1 H, q, J 6.5, CHN), 3.49 (1 H, d, J 12.5, CHH), 3.36 (1H, d, J 12.5, CHH), 1.92 (3 H, d, J 1, CH₃), 1.59 (3H, d, J 6.5, CHCH₃); δ C(67 MHz; CDCl₃) trans: 140.5, 133.9, 131.2, 128.9 (CH), 127.2 (CH), 125.7 (CH), 125.6 (CH), 125.3 (CH), 123.0 (CH), 122.9 (CH), 122.8 (CH), 103.4 (CH), 53.7 (CH₂), 52.7 (CH), 23.6 (CH₃), 18.0 (CH₃); cis: 140.5, 133.9, 131.2, 128.9 (CH), 127.2 (CH), 125.7 (CH), 125.6 (CH), 125.3 (CH), 123.0 (CH), 122.9 (CH), 122.8 (CH), 102.3 (CH), 53.3 (CH), 50.2 (CH₂), 23.5 (CH₃), 21.5 (CH₃); m/z (ES⁺) 304 (M⁺ +1); (C₁₆H₁₉NBr requires 304.0701. Found 304.0685).

(3-Bromo-2-methyl-allyl)-cyclooctyl-amine 12

General procedure A was followed using: octylamine (0.300 g, 2.36 mmol) in dry DMF (3 mL), NaH (0.093 g, 2.36 mmol) in DMF (3 mL) and 1,3-dibromo-2-methylpropene (0.505 g, 2.36 mmol). The organic fractions were combined, washed with brine (20 mL), dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography, using Et₂O as eluant to give 12 (0.37 g, 60%) %) [Rf 0.2; Et₂O] (trans:cis 2.5:1, by ¹H NMR) as a colourless oil; ν max(film)/cm⁻¹ 3419 (NH), 2878, 2811, 1949, 1631, 1489, 1456, 1383, 1351, 1299, 1097 and 1044; δ H(400 MHz; CDCl₃) trans: 6.14 (1 H, s, CHBr),
3.25 (2 H, s, NCH₂), 2.64 (1 H, m, CH), 1.82 (3 H, s, CH₃), 1.80-1.30 (14 H, m, 7 x CH₂), 1.25 (1 H, br s NH); cis: 5.99 (1 H, s, CHBr), 3.40 (2 H, s, NCH₂), 2.64 (1 H, m, CH), 1.85 (3 H, s, CH₃), 1.80-1.30 (14 H, m, 7 x CH₂), 1.25 (1 H, br s NH); δ_C(100 MHz; CDCl₃) 140.3, 103.6 (CH), 56.6 (CH₂), 53.1 (CH₂), 32.2 (CH₂), 27.2 (CH₂), 25.8 (CH₂), 18.0 (CH₃); cis: 139.7, 102.8 (CH), 56.8 (CH₂), 49.1 (CH₂), 32.2 (CH₂), 27.2 (CH₂), 25.8 (CH₂), 24.0 (CH₂), 21.3(CH₃); m/z (ES⁺) 206 (M⁺ + 1); C₁₂H₂₃NBr requires 260.1014. Found 206.1001).

(3-Bromo-2-methyl-allyl)-decyl-amine 14

General procedure A was followed using: decylamine (0.549 g, 3.32 mmol) in dry DMF (3 mL), NaH (0.159 g, 3.98 mmol) in DMF (3 mL) and 1,3-dibromo-2-methylpropene (0.603 g, 2.82 mmol). The organic fractions were combined, washed with brine (20 mL), dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography, using EtOAc as eluant to give 14 (0.431 g, 53%) [%] [R_f 0.2; EtOAc] (trans:cis 2.3:1, by ¹H NMR) as a colourless oil (Found: C, 57.86; H, 9.67; N, 4.78. C₁₄H₂₈NBr requires C, 57.93; H, 9.72; N, 4.83%); v_max(film)/cm⁻¹ 3316 (NH), 2924, 2853, 1633, 1458, 1376, 1289, 1117, 1026, 834, 778 and 716; δ_H(400 MHz; CDCl₃) trans: 6.10-6.08 (1 H, m, CH), 3.22 (2 H, s, CH₂), 2.56-2.49 (2H, m, CH₂), 1.79 (3 H, d, J 2, CH₃), 1.46-1.41 (1 H, m, NH), 1.26-1.24 (16 H, m, 8 x CH₂), 0.87 (3 H, t, J 7, CH₃); cis: 5.97 (1 H, s, CH), 3.37 (2 H, s, CH₂), 2.56-2.49 (2H, m, CH₂), 1.79 (3 H, d, J 2, CH₃), 1.46-1.41 (1 H, m, NH), 1.26-1.24 (16 H, m, 8 x CH₂), 0.87 (3 H, t, J 7, CH₃); δ_C(67 MHz; CDCl₃) trans: 140.6, 103.3 (CH), 56.0 (CH₂), 52.0 (CH₂), 49.2 (CH₂), 32.0 (CH₂), 30.2 (CH₂), 29.7 (CH₂), 29.7 (CH₂), 29.4 (CH₂), 27.4 (CH₂), 22.8 (CH₂), 21.4 (CH₂), 18.0 (CH₃), 14.2 (CH₃); cis: 140.2, 102.5 (CH), 56.0 (CH₂), 52.0 (CH₂), 49.3 (CH₂), 32.0 (CH₂), 30.2 (CH₂), 29.7 (CH₂), 29.7 (CH₂), 29.4 (CH₂), 27.4 (CH₂), 22.8 (CH₂), 21.4 (CH₂), 18.0 (CH₃), 14.2 (CH₃); m/z (ES⁺) 289 (M⁺ +1); C₁₄H₂₉NBr requires 290.1484. Found 290.1455).
(3-Bromo-2-methyl-allyl)-[(S)-1-(tert-butyl-dimethyl-silanyloxymethyl)-3-methyl-buty1]-amine 16

General procedure A was followed using: TBS-leucinol (5.00 g, 21.6 mmol) in DMF (5 mL), NaH (0.86 g, 21.6 mmol) in DMF (20 mL) and 1,3-dibromo-2-methylpropene (4.62g, 21.6 mmol). The organic fractions were combined, washed with brine (20 mL), dried over Na2SO4 and concentrated. The crude material was purified by flash column chromatography using isohexane and EtOAc (6:1) as eluant to give 16 (6.50 g, 86% %) [Rf 0.3; hexanes:EtOAc (6:1)] (trans:cis 2.2:1 by 1H NMR) as a colourless oil. (Found: C, 52.80; H, 9.10; N, 3.85. C16H34NOSiBr requires C, 52.73; H, 9.40; N, 3.84%); νmax(film)/cm⁻¹ 3342 (NH), 2954, 2928, 1632, 2857, 1470, 1384, 1362, 1254, 1100, 836, 775; δH(250 MHz; CDCl3) trans: 6.14 (1 H, s, CHBr), 3.62 (1 H, dd, J 10 and 4, CHHO), 3.42 (1 H, dd, J 10 and 4, CHHO), 3.25 (2 H, s, CH2), 2.61-2.57 (1 H, m, CHN), 1.83 (3 H, s, CH3) 1.77-1.59 (1 H, m), 1.32-1.13 (1 H, m), 0.93- 0.83 (6 H, m, CH(CH)2), 0.90 (9 H, s, SiCH(CH)3), 0.06 (6 H, s, Si(CH3)2; cis: 5.98 (1 H, s, CHBr), 3.70 (2 H, m, CH2O), 3.25 (2 H, s, CH2), 2.61-2.57 (1 H, m, CHN), 1.83 (3 H, s, CH3) 1.77-1.59 (1 H, m), 1.32-1.13 (1 H, m), 0.93- 0.83 (6 H, m, CH(CH)2), 0.90 (9 H, s, iBu), 0.06 (6 H, s, Si(CH3)2; δC(62 MHz; CDCl3) trans: 141.1, 103.7 (CH), 65.4 (CH2), 56.6 (CH), 53.4 (CH2), 41.2 (CH2), 26.3 (CH3), 25.3 (CH3), 23.5 (CH3), 23.2 (CH3), 21.2 (CH3), 18.6 (CH3), 18.1; cis: 140.6, 102.7 (CH), 65.2 (CH2), 56.3 (CH), 49.3 (CH2), 41.0 (CH2), 26.3 (CH3), 25.3 (CH3), 23.5 (CH3), 23.2 (CH3), 21.2 (CH3), 18.6 (CH3), 18.1; m/z (ES⁺) 394 (M⁺ + 1); (C16H35NOSiBr requires 364.1671. Found 364.1684).

Benzyl-(3-bromo-2-methyl-allyl)-carbamic acid tert-butyl ester 18

General procedure A was followed using: benzylcarbamic acid tert-butyl ester (0.96 mg, 4.6 mmol) in dry DMF (5 mL), NaH (0.23 g, 5.6 mmol) in DMF (5 mL) and 1,3-dibromo-2-methylpropene (1.2 mg, 0.56 mmol). The organic fractions were combined, washed
with brine (20 mL), dried over MgSO₄ and concentrated. The crude material was purified by flash column chromatography, using petrol and Et₂O (3:1) as eluant to give 10 (1.28 g, 82%) [Rₐ 0.4; petrol:Et₂O (3:1)] colourless oil as a mixture of isomers (2.3:1, trans:cis by ^1H NMR) (Found: C, 56.81; H, 6.57; N, 3.99. C₁₆H₂₂NO₂ requires C, 56.48; H, 6.52; N, 4.12%); ν max(solution in CHCl₃)/cm⁻¹ 2916, 1694, 1488, 1456, 1360, 1316, 1107, 1076, 967 and 834; δH(400 MHz; C₆D₆, 340K) trans: 7.58-7.34 (5 H, m, Ph), 5.94 (1 H, s, CHBr), 4.58 (2 H, s, PhCH₂) 4.38 (2 H, s, CH₂), 1.78 (3 H, s, CH₃), 1.70 (9 H, s, (CH₃)₃); cis: 7.58-7.34 (5 H, m, Ph), 6.07 (1 H, s, CHBr), 4.51 (2 H, s, PhCH₂) 3.94 (2 H, s, CH₂), 1.92 (3 H, s, CH₃), 1.68 (9 H, s, (CH₃)₃); δC(67 MHz; CDCl₃) 155.7, 155.5, 138.0, 137.5, 128.2 (CH), 127.7 (CH), 127.1 (CH), 104.3 (CH), 102.0 (CH), 80.1, 80.0, 51.3 (CH₂) 49.6 (CH₂), 28.2 (CH₃); m/z (ES⁺) 362 (M⁺ + 23, 100%); (C₁₆H₂₂NO₂Na requires 362.0732. Found 362.0713).

**N-Benzyl-N-(3-bromo-2-methyl-allyl)-4-methyl-benzenesulfonamide 20**

General procedure A was followed using: N-Benzyl-4-sulfonamide (0.300 g, 1.15 mmol) in dry DMF (5 mL), NaH (0.061 g, 1.52 mmol) in DMF (5 mL) and 1,3-dibromo-2-methylpropene (0.321 g, 1.46 mmol). The organic fractions were combined, washed with brine (20 mL), dried over MgSO₄ and concentrated. The crude material was purified by flash column chromatography, using petrol and Et₂O (3:1) as eluant to give 20 (0.28 g, 61%) [Rₐ 0.3; petrol:Et₂O (3:1)] (trans:cis 2.3:1, by ^1H NMR) as white crystals; mp 40-42 °C; ν max(solution in CHCl₃)/cm⁻¹ 2923, 2856, 1633, 1598 (SO), 1495, 1455, 1353, 1145, 1097, 1013 and 894; δH(400 MHz; CDCl₃) trans: 7.72 (2 H, d, J 8, 2 x CH (Ts)), 7.34-7.16 (7 H, m, Ar), 5.89 (1 H, q, J 1, CHBr), 4.24 (2 H, s, CH₂Ph), 3.74 (2 H, s, CH₂), 2.50 (3 H, s, CH₃ (Ts)), 1.54 (3 H, J 1, CH₃); cis: 7.72 (2 H, d, J 8, 2 x CH (Ts)), 7.34-7.16 (7 H, m, Ar), 5.81 (1 H, app d, J 1.5, CHBr), 4.30 (2 H, s, CH₂Ph), 3.94 (2 H, s, CH₂=C=C), 2.50 (3 H, s, CH₃ (Ts)), 1.62 (3 H, J 1.5, CH₃); δC(100 MHz; CDCl₃) trans: 143.5, 136.8, 136.3, 135.6, 129.7 (CH), 128.6 (CH), 128.4 (CH), 127.3 (CH), 127.1 (CH) 106.7 (CH), 53.4 (CH₂), 51.4 (CH₂), 21.5
Benzyl-(3-bromo-2-methylallyl)-((R)-1-phenyl-ethyl)-carbamic acid tert-butyl ester 22

General procedure A was followed using: (R)-α-methylbenzylcarbamic acid tert-butyl ester (1.49 g, 6.74 mmol) in dry DMF (15 mL), NaH (0.269 g, 6.74 mmol) in DMF (15 mL) and 1,3-dibromo-2-methylpropene (1.44 g, 6.74 mmol). The organic fractions were combined, washed with brine (20 mL), dried over MgSO₄ and concentrated. The crude material was purified by flash column chromatography, using petrol and Et₂O (3:1) as eluant to give 22 (1.22 g, 51%) [Rf 0.5; petrol:Et₂O (3:1)] (trans:cis 2.3:1, by ¹H NMR) as a colourless oil (Found: C, 57.58; H, 6.91; N, 4.19. C₁₇H₂₄NO₂Br requires C, 57.63; H, 6.83; N, 3.95%); νmax(solution in CHCl₃)/cm⁻¹ 2919, 1698, 1490, 1457, 1360, 1320, 1048, 988, 907 and 870; δH(400 MHz; d-6 DMSO, 353K) trans: 7.38-7.24 (5 H, m, Ph), 6.08 (1 H, br s, CHBr), 5.16 (1 H, q, J 7, CH), 3.83 (1 H, d, J 16, CHH), 3.74 (1 H, d, J 16, CHH), 1.66 (3 H, s, CH₃), 1.52 (3 H, d, J 7, CH₃CH), 1.39 (9 H, s, CH₃) ; cis: 7.38-7.24 (5 H, m, Ph), 6.08 (1 H, br s, CHBr), 5.22 (1 H, q, J 8, CH), 3.95 (1 H, d, J 16, CHH), 3.87 (1 H, d, J 16, CHH), 1.66 (3 H, s, CH₃), 1.52 (3 H, d, J 8, CH₃CH), 1.42 (9 H, s, CH₃); δC(67 MHz; C₆D₆) 166, 155, 142, 138, 128.5, 128.4 (CH), 127.6 (CH), 127.4 (CH), 104 (CH), 79.6, 54.0 (CH), 49.9 (CH₂), 28.0 (CH₃), 20.0 (CH₃) 17.3 (CH₃); m/z (ES⁺) 417 (M + CH₃CN + Na⁺. C₁₉H₂₇N₂O₂BrNa requires 417.1154. Found 417.1189).

N-(3-Bromo-2-methylallyl)-4-methyl-N-((R)-1-phenyl-ethyl)benzenesulfonamide 24
General procedure A was followed using: 4-Methyl-N-(1-phenyl-ethyl)-benzenesulfonamide (0.19 g, 0.69 mmol) in dry DMF (5 mL), NaH (0.040 g, 1.02 mmol) in DMF (5 mL) and 1,3-dibromo-2-methylpropene (0.218 g, 1.01 mmol).

The organic fractions were combined, washed with brine (20 mL), dried over MgSO₄ and concentrated. The crude material was purified by flash column chromatography, using petrol and Et₂O (2:1) as eluant to give 24 (0.24 g, 85%) [Rf 0.3; petrol:Et₂O (2:1)] (trans:cis 2.3:1, by ¹H NMR) as a colourless oil; ν_max(solution in chloroform)/cm⁻¹ 2931, 1633, 1598 (SO), 1495, 1453, 1381, 1333, 1305, 1158, 1119, 1091, 1045, 1027, 992 and 884; δ_H(400 MHz; CDCl₃) trans: 7.76 (2 H, d, J 8, 2 x CH (Ts)), 7.30-7.23 (3 H, m, Ph), 7.16-7.13 (2 H, m, Ph), 5.87 (1 H, q, J 1, CHBr), 5.25 (1 H, q, J 1, CH₃), 5.14 (1 H, dd, J 15 and 1, CHH), 3.60 (1 H, dd, J 15 and 1, CHH), 2.48 (3 H, s, CH₃ (Ts)), 1.49 (3 H, d, J 1, CH₃), 1.47 (3 H, d, J 7, CH₂CH); cis: 7.76 (2 H, d, J 8, 2 x CH (Ts)), 7.34 (2 H, d, J 8, 2 x CH (Ts)), 7.30-7.23 (3 H, m, Ph), 7.16-7.13 (2 H, m, Ph), 5.69 (1 H, q, J 1.5, CHBr), 5.25 (1 H, q, J 1.5, CH₃), 1.50 (3 H, d, J 1.5, CH₃), 1.38 (3 H, d, J 6.5, CH₂CH); δ_C(100 MHz; CDCl₃) trans: 143.2, 139.1, 137.9, 129.6 (CH), 128.1, 127.9 (CH), 127.7 (CH), 127.3 (CH), 127.0 (CH), 106.1 (CH), 55.6 (CH), 49.6 (CH₂), 21.4 (CH₃), 20.0 (CH₃), 16.7 (CH₃); cis: 143.2, 139.1, 137.6, 129.5 (CH), 128.1, 127.9 (CH), 127.7 (CH), 127.3 (CH), 127.0 (CH), 101.8 (CH), 55.5 (CH), 46.1 (CH₂), 21.4 (CH₃), 15.2 (CH₃), 16.8 (CH₃); m/z (ES⁺) 408 (M⁺ + 1); (C₁₉H₂₃NSO₂Br requires 408.0633. Found 408.0632).

(3-Bromo-2-methyl-allyl)-sec-butyl-carbamic acid tert-butyl ester 26

General procedure A was followed using: sec-Butyl-carbamic acid tert-butyl ester (0.490 g, 2.83 mmol) in dry DMF (5 mL), NaH (0.158 g, 3.96 mmol) in DMF (5 mL) and 1,3-dibromo-2-methylpropene (0.726 g, 3.40 mmol). The
organic fractions were combined, washed with brine (20 mL), dried over MgSO₄ and concentrated. The crude material was purified by flash column chromatography, using pentane and Et₂O (9:1) as eluant to give 25 (0.34 g, 40%) [Rf 0.4; pentane:Et₂O (9:1)] (trans:cis 2.3:1, by ¹H NMR) as a colourless oil; νmax(film)/cm⁻¹ 2970, 2932, 2360, 2341, 1690 (CO), 1455, 1404, 1334, 1250 and 1162; δH(400 MHz; d-DMSO, 371K) trans: 6.25 (1 H, m, CHBr), 3.80-3.60 (3 H, m, CH₂N and CHN), 1.75 (3 H, m, CH₃C=C), 1.65-1.55 (2 H, m, CH₂CH₃), 1.50 (9 H, s, (CH₃)₃), 1.20-1.10 (3 H, m, CH₃CH), 0.90-0.80 (3 H, m, CH₃CH₂); cis: 6.20 (1 H, m, CHBr), 3.80-3.60 (3 H, m, CH₂N and CHN), 1.75 (3 H, m, CH₃C=C), 1.65-1.55 (2 H, m, CH₂CH₃), 1.50 (9 H, s, (CH₃)₃), 1.20-1.10 (3 H, m, CH₃CH), 0.90-0.80 (3 H, m, CH₃CH₂); δC(400 MHz; C₆D₆, 340K) trans: 156.0, 140.7, 104.3 (CH), 79.8, 55.1 (CH), 50.8 (CH₂), 29.1 (CH₃), 28.6 (CH₂), 20.5 (CH₃), 18.0 (CH₃), 11.9 (CH₃); cis: 156.0, 140.7, 101.7 (CH), 798.8, 55.1 (CH), 47.1 (CH₂), 29.1 (CH₃), 28.6 (CH₂), 21.1 (CH₃), 19.0 (CH₃), 10.7 (CH₃); m/z (ES⁺) 305 (M⁺ + 1); (C₁₃H₂₅NO₂Br requires 305.0990. Found 305.0975).

**N-(3-Bromo-2-methyl-allyl)-N-sec-butyl-4-methyl-benzenesulfonamide 28**

General procedure A was followed using: N-sec-butyl-4-methyl-benzenesulfonamide (0.300 g, 1.34 mmol) in dry DMF (5 mL), NaH (0.070 g, 1.74 mmol) in DMF (5 mL) and 1,3-dibromo-2-methylpropene (0.375 g, 1.75 mmol). The organic fractions were combined, washed with brine (20 mL), dried over MgSO₄ and concentrated. The crude material was purified by flash column chromatography, using petrol and Et₂O (2:1) as eluant to give 28 (0.41 g, 85%) [Rf 0.6; petrol:Et₂O (2:1)] (trans:cis 2.5:1, by ¹H NMR) as white crystals; mp 67-69°C. (Found: C, 49.98; H, 5.96; N, 3.75. C₁₅H₂₂NSO₂Br requires C, 50.00; H, 6.15; N, 3.89%). νmax(film)/cm⁻¹ 2974, 2970, 1598 (SO), 1335, 1154, 1093 and 890; δH(400 MHz; CDCl₃) trans: 7.67 (2 H, d, J 8, 2 x CH (Ts)), 7.29 (2 H, d, J 8, 2 x CH (Ts)), 6.17 (1 H, q, J 1, CHBr), 3.82-3.74 (3 H, m, CH₂N and CHN), 2.43 (3 H, t, J 3.5, CH₃ (Ts)), 1.82 (3 H, d, J 1, CH₃C=C), 1.47-
1.33 (2 H, m, CH\(_2\)CH\(_3\)), 0.99 (3 H, d, \(J\) 7.6, \(CH\(_2\)CH\(_2\)), 0.80 (3 H, t, \(J\) 7.5, \(CH\(_2\)CH\(_2\)); cis: 7.71 (2 H, d, \(J\) 8, 2 \(CH\) (Ts)), 7.28 (2 H, d, \(J\) 8, 2 \(CH\) (Ts)), 5.96 (1 H, q, \(J\) 1, CHBr), 3.99 (2 H, s, \(CH\(_2\)N)) 3.82-3.74 (1 H, m, CHN), 2.43 (3 H, t, \(J\) 3.5, \(CH\(_3\)) (Ts)), 1.97 (3 H, d, \(J\) 1, \(CH\(_2\)C=C)), 1.47-1.33 (2 H, m, \(CH\(_2\)\)CH\(_3\)), 0.99 (3 H, d, \(J\) 7.6, \(CH\(_2\)CH\(_2\)), 0.80 (3 H, t, \(J\) 7.5, \(CH\(_2\)CH\(_2\)); \(\delta\)\(_C\) (100 MHz; CDCl\(_3\)) trans: 143.1, 138.0, 129.6 (CH), 127.0 (CH), 105.5 (CH), 56.0 (CH), 49.1 (CH\(_2\)), 28.1 (CH\(_2\)), 21.5 (CH\(_3\)), 18.1 (CH\(_3\)); cis: 143.1, 138.0, 129.6 (CH), 127.0 (CH), 105.5 (CH), 56.0 (CH), 49.1 (CH\(_2\)), 28.1 (CH\(_2\)), 21.5 (CH\(_3\)), 17.4 (CH\(_3\)); \(m/z\) (ES\(^+\)) 360 (M\(^+\) + 1); (C\(_{15}\)H\(_{23}\)NO\(_2\)Br requires 360.0633. Found 360.0658).

\(\text{N-(3-Bromo-2-methyl-allyl)-N-cyclohexyl-4-methyl-benzenesulfonamide 30}\)

General procedure A was followed using: \(\text{N-Cyclohexyl-4-methyl-benzenesulfonamide (0.300 g, 1.19 mmol) in dry DMF (5 mL), NaH (0.062 g, 1.54 mmol) in DMF (5 mL) and 1,3-dibromo-2-methylpropene (0.33 g, 1.54 mmol). The organic fractions were combined, washed with brine (20 mL), dried over MgSO\(_4\) and concentrated. The crude material was purified by flash column chromatography, using petrol and Et\(_2\)O (2:1) as eluant to give 30 (0.37 g, 81\%) [\(R_f\) 0.5; petrol:Et\(_2\)O (2:1)] (trans:cis 2.5:1, by \(^1\)H NMR) as a colourless, viscous oil (Found: C, 52.77; H, 6.15; N, 3.48. C\(_{17}\)H\(_{24}\)NSO\(_2\)Br requires C, 52.85; H, 6.26; N, 3.63%); \(\nu\)\(_{\text{max}}\) (solution in chloroform)/cm\(^{-1}\) 3695, 3604, 2936, 2859, 1600 (SO), 1452, 1332, 1305, 1154, 1093, 1004 and 883; \(\delta\)\(_H\) (400 MHz; CDCl\(_3\)) trans: 7.64 (2 H, d, \(J\) 8, 2 \(CH\) (Ts)), 7.27 (2 H, d, \(J\) 8, 2 \(CH\) (Ts)), 6.16 (1 H, s, CHBr), 3.80 (2 H, s, CH\(_2\)), 3.64-3.62 (1 H, m, CH), 2.40 (3 H, s, CH\(_3\) (Ts)), 1.79 (3 H, s, CH\(_3\)), 1.70-0.94 (10 H, m, 5 \(CH\)\(_2\)); cis: 7.68 (2 H, d, \(J\) 8, 2 \(CH\) (Ts)), 7.27 (2 H, d, \(J\) 8, 2 \(CH\) (Ts)), 5.93 (1 H, s, CHBr), 4.01 (2 H, s, CH\(_2\)), 3.64-3.62 (1 H, m, CH), 2.40 (3 H, s, CH\(_3\) (Ts)), 1.91 (3 H, s, CH\(_3\)), 1.70-0.94 (10 H, m, 5 \(CH\)\(_2\); \(\delta\)\(_C\) (100 MHz; CDCl\(_3\)) trans: 143.0, 139.3, 138.3, 129.6 (CH), 105.1 (CH), 58.3 (CH), 49.4 (CH\(_2\)), 31.3 (CH\(_2\)), 26.2 (CH\(_2\)), 21.5 (CH\(_3\)), 17.3 (CH\(_3\)); cis: 143.0, 139.3, 138.3, 129.6 (CH), 101.7 (CH), 58.3 (CH), 46.3 (CH\(_2\)), 30.9 (CH\(_2\)), 25.3
(CH₂), 21.5 (CH₃), 20.6 (CH₃); m/z (ES⁺) 368 (M⁺ + 1). (C₁₇H₂₅NSO₂Br requires 386.0789. Found 386.0793).

**N-(3-Bromo-2-methyl-allyl)-N-hexyl-4-methyl-benzenesulfonamide 32**

N-(3-Bromo-2-methyl-allyl)-N-hexyl-4-methyl-benzenesulfonamide (0.300 g, 1.18 mmol) in dry DMF (5 mL), NaH (0.062 g, 1.54 mmol) in DMF (5 mL) and 1,3-dibromo-2-methylpropene (0.33 g, 1.54 mmol). The organic fractions were combined, washed with brine (20 mL), dried over MgSO₄ and concentrated. The crude material was purified by column chromatography on silica using petrol and Et₂O (2:1) as eluant to give 32 (0.36 g, 79%) [Rf 0.4; petrol:Et₂O (2:1)] (trans: cis 1.85:1, by ¹H NMR) as a viscous oil (Found: C, 52.07; H, 6.35; N, 3.54. C₁₇H₂₆NSO₂Br requires C, 52.57; H, 6.75; N, 3.61%); νmax(film)/cm⁻¹ 2953, 2928, 2858, 1632, 1598 (SO), 1494, 1454, 1397, 1338, 1304, 1159, 1091, 1019, 988 and 915; δH(400 MHz; CDCl₃) **trans**: 7.66 (2 H, d, J 8, 2x CH (Ts)), 7.28 (2 H, d, J 8, 2 x CH (Ts)), 6.12 (1 H, q, J 1, CHBr), 3.72 (2 H, d, J 1, NCH₂C=C), 3.05-3.00 (2 H, m, NCH₂CH₂), 2.42 (3 H, t, J 3, CH₃ (Ts)), 1.77 (3 H, d, J 1, CH₃C=C), 1.46- 1.38 (2 H, m, NCH₂CH₂), 1.25-1.16 (6 H, m, 3 x CH₂), 0.85 (3 H, t, J 7,CH₃CH₂); **cis**: 7.69 (2 H, d, J 8, 2x CH (Ts)), 7.30 (2 H, d, J 8, 2 x CH (Ts)), 6.04 (1 H, q, J 1, CHBr), 3.94 (2 H, d, J 1, NCH₂C=C), 3.05-3.00 (2 H, m, NCH₂CH₂), 2.42 (3 H, t, J 3, CH₃ (Ts)), 1.85 (3 H, d, J 1, CH₃C=C), 1.46- 1.38 (2 H, m, NCH₂CH₂), 1.25-1.16 (6 H, m, 3 x CH₂), 0.85 (3 H, t, J 7,CH₃CH₂); δc(100 MHz; CDCl₃) **trans**: 143.5, 137.6, 136.7, 129.7 (CH), 127.4 (CH), 105.7 (CH), 54.2 (CH₂), 47.4 (CH₂), 31.2 (CH₂), 27.8 (CH₂), 26.4 (CH₂), 22.4 (CH₃), 21.4 (CH₃), 13.9 (CH₃); **cis**: 143.2, 137.5, 136.7, 129.6 (CH), 127.0 (CH), 103.8 (CH), 50.6 (CH₂), 48.2 (CH₂), 31.8 (CH₂), 28.0 (CH₂), 26.3 (CH₂), 22.4 (CH₃), 20.4 (CH₃), 17.2 (CH₃); m/z (ES⁺) 388 (M⁺ + 1); (C₁₇H₂₇NSO₂Br requires 388.0945. Found 388.0973).
General procedure B: Cyclisation of Vinylbromides:

A solution of KHMDS (2.0 equivs of a 0.5 M solution in toluene), was added dropwise to a stirring solution of the vinylbromide in dry Et₂O at room temperature. The resulting brown solution was stirred for 2 hours and then the reaction was quenched with saturated NH₄Cl solution. The product was extracted into Et₂O and the combined organic layers were washed with water, brine and then dried with MgSO₄. Removal of the solvent in vacuo left the crude product which was purified by column chromatography.

4-Methyl-2-phenyl-2,5-dihydro-1H-pyrrole 7 and Benzyl-but-2-ynyl-amine

General procedure B was followed using: KHMDS (0.5 M in toluene) (1.6 mL, 0.74 mmol), vinylbromide 6 (0.09 g, 0.37 mmol) in dry Et₂O (5 mL). The crude product was purified by flash column chromatography, using DCM and MeOH (9:1) as eluant to give 7 (0.032 g, 55%) a colourless oil and acetylene (0.007 g, 8%) as an isolated by-product. 3-Pyrroline 7; [Rf 0.3; DCM:MeOH (9:1)] νₓ(solution in CHCl₃)/cm⁻¹ 3367 (NH), 2844, 2510, 1664, 1602, 1490, 1380, 1350, 1074, 985 and 891; δₓ(400 MHz; CDCl₃) 7.35-7.25 (5 H, m, Ph), 5.47 (1 H, app sextet, J 1.5, CHBr), 5.03 (1 H, m, CHPh), 3.85 (1 H, ddq, J 14, 4.5 and 1 CHH), 3.71 (1 H, br d, J 14, CHH), 2.48 (1 H, br s, NH), 1.84 (s, 3H, CH₃); δₓ(67 MHz; CDCl₃) 144.9, 138.8, 128.4 (CH), 127.1 (CH), 126.8 (CH), 125.9 (CH), 69.5 (CH), 57.5 (CH₂), 13.9 (CH₃); m/z (FAB⁺) 160 (M⁺ + 1); (C₁₁H₁₄N requires 160.1126. Found 160.1129). Acetylene: [Rf 0.5; DCM:MeOH (9:1)] νₓ(solution in CHCl₃)/cm⁻¹ 3323 (NH), 2923, 2855, 1713, 1495, 1454, 1360, 1128 and 1089; δₓ(400 MHz; CDCl₃) 7.40-7.25 (5 H, m, Ph), 3.85 (2 H, s, CH₂), 3.38 (2 H, s, CH₂), 1.85 (3 H, s, CH₃), 1.60 (1 H, br s, NH); m/z (EI) 159 (M⁺, 5%), 158 (12.8), 156 (10), 144 (9) and 91 (100).
General procedure B was followed using: KHMS (0.5 M in toluene) (0.8 mL, 0.4 mmol), vinylbromide 8 (0.075 g, 0.29 mmol) in dry Et₂O (3 mL). The crude product was purified by flash column chromatography, using DCM and MeOH (9:1) as eluant to give 9 (0.028 g, 56%) as and acetylene (0.005 g, 9%) as colourless oils. 3-Pyrroline: [Rf 0.3; DCM:MeOH (9:1)] [α]D22 −71.23 (c 0.47 in CHCl₃); νmax(solution in chloroform)/cm⁻¹ 3357(NH), 2918, 2846, 1666, 1598, 1492, 1450, 1368, 1069, 1027, 996 and 971; δH(400 MHz; CDCl₃) 7.47-7.19 (5 H, m, Ph), 5.83 (1 H, app q, J 2, CHBr), 3.73 (1 H, dq, J 14 and 1, CHH), 3.68 (1 H, dq, J 14 and 1, CHH), 2.05 (1 H, br s, NH), 1.80 (m, 3H, CH₃C=C), 1.57 (3 H, s, CH₃); δC(67 MHz; CDCl₃) 148.0, 137.0, 131.0 (CH), 128.2 (CH), 126.3 (CH), 125.3 (CH), 71.0, 56.9 (CH₂), 29.2 (CH₃), 14.0 (CH₃); m/z (FAB⁺) 174.1289 (M + H⁺). C₁₂H₁₆N requires 174.1282. Acetylene: [Rf 0.6; DCM:MeOH (9:1)] νmax(solution in CHCl₃)/cm⁻¹ 3323 (NH), 2925, 2855, 1721, 1495, 1375, 1104, 1076 and 908; δH(400 MHz; CDCl₃) 7.39-7.25 (5 H, m, Ph), 4.04 (1 H, q, J 6.5, CHCH₃), 3.34 (1 H, dq, J 16.5 and 2.5, CHH), 3.15 (1 H, dq, J 16.5 and 2.5, CHH), 1.85 (3 H, t, J 2.5, CH₃), 1.44 (3 H, d, J 6.5, CH₃CH); m/z (FAB⁺) 174 (M + H⁺).

2,4-Dimethyl-2-naphthalen-1-yl-2,5-dihydro-1H-pyrrole 11 and but-2-ynyl-(1-naphthalen-1-yl-ethyl)-amine

![Diagram](image-url)
General procedure B was followed using: KHMDS (0.5 M in toluene) (1.3 mL, 0.66 mmol), vinylbromide 10 (0.099 g, 0.33 mmol) in dry Et₂O (6 mL). The addition of veratrole (10µL) to the crude reaction mixture (66 mg, 90%), followed by integration of the ¹H NMR spectrum of this mixture allowed the yields of the 3-pyrroline 11 (47 mg, 65%) and the acetylene (7 mg, 10%) to be determined.

3-Pyrroline 11; νₘₐₓ(film)/cm⁻¹ 3046 (NH), 2957, 2919, 2849, 1727, 1596, 1508, 1445, 1255, 1117, 1078, 1000, 804 and 778; δₜₗ(400 MHz; CDCl₃) 8.59 (1 H, d, J 8, Ar), 7.87 (1 H, dd, J 8 and 1.5, Ar), 7.74 (1 H, d, J 8, Ar), 7.65 (1 H, dd, J 6 and 1, Ar), 7.55-7.45 (2 H, m, Ar), 7.40 (1 H, dd, J 8 and 7.5, Ar), 6.04-6.03 (1 H, m, CH), 3.77 (1 H, dq, J 15 and 1, CHH), 3.71 (1 H, dq, J 15 and 1, CHH), 2.34 (1 H, s, NH), 1.85 (3 H, q, J 1, CH₃), 1.79 (3 H, s, CH₃); δᵥ(100 MHz; CDCl₃) 143.8, 137.4, 135.0, 131.3 (CH), 130.5, 129.2 (CH), 127.8 (CH), 126.7 (CH), 125.2 (CH), 125.0 (CH), 123.1 (CH), 72.6, 56.9 (CH₂), 29.7 (CH₃), 14.1 (CH₃); m/z (EI) 223 (M⁺); (C₁₆H₁₇N requires 223.1361. Found 223.1361).

Acetylene: δₜₗ(400 MHz; CDCl₃) 8.32 (1 H, d, J 8.5, Ar), 7.91 (1 H, d, J 8, Ar), 7.79 (1 H, d, J 8, Ar), 7.74 (1 H, d, J 7, Ar), 7.58-7.49 (3 H, m, Ar), 4.90 (1 H, q, J 6.5, CH), 3.45 (1 H, dq, J 16.5 and 2.5, CHH), 3.32 (1 H, dq, J 16.5 and 2.5, CHH), 1.88 (3 H, t, J 2.5, CH₃), 1.73 (1 H, s, NH), 1.55 (3 H, d, J 6.5, CH₃); δᵥ(67 MHz; CDCl₃) 140.3, 133.9, 131.2, 128.8 (CH), 127.2 (CH), 125.6 (CH), 125.4 (CH), 125.2 (CH), 122.9 (CH), 78.9, 77.5, 51.8 (CH), 36.4 (CH₂), 23.0 (CH₃), 3.4 (CH₃).

3-Methyl-1-aza-spiro[4.7]dodec-3-ene 13 and But-2-ynyl-cyclooctyl-amine

![3-Methyl-1-aza-spiro[4.7]dodec-3-ene 13](image1.png)  
[3-Methyl-1-aza-spiro[4.7]dodec-3-ene 13](image2.png)
General procedure B was followed using: KHMDS (0.5 M in toluene) (1.6 mL, 0.82 mmol), vinyl bromide 12 (0.084 g, 0.41 mmol) in dry Et₂O (3 mL). The combined ether layers were extracted with 2 M HCl (2 x 10 mL), the organic layer was discarded and the aqueous layer washed with a further portion of Et₂O (10 mL). 1 M NaOH was added until the solution was basic and then the product was extracted under reduced pressure to leave the 3-pyrroline 13 and acetylene (2:1 by ¹H NMR) (0.035 g, 64%) as an inseparable mixture. 3-pyrroline: δH(400 MHz; CDCl₃) 5.44 (1 H, q, J 2, CH), 3.57 (2 H, t, J 1, CH₂N), 1.71 (3 H, d, J 1, CH₃), 1.76-1.42 (15 H, m, cyclooctyl); δC(100MHz; CDCl₃) 135.9, 131.2 (CH), 72.3, 55.6 (CH₂), 36.0 (CH₂), 31.9 (CH₂), 27.3 (CH₂), 24.8 (CH₂), 23.8 (CH₂), 23.0 (CH₂), 14.1 (CH₃); Acetylene: δH(400 MHz; CDCl₃) 3.34 (2 H, q, J 1.5, CH₂), 1.80 (3 H, t, J 1.5, CH₃), 1.76-1.42 (15 H, m, cyclooctyl); δC(100MHz; CDCl₃) 164.4, 154.4, 78.5 (CH₂), 56.1 (CH), 41.9 (CH₂), 35.8 (CH₂), 30.7 (CH₂), 29.7 (CH₂), 28.3 (CH₂), 25.6 (CH₂), 14.1 (CH₂), 3.5 (CH₃).

4-Methyl-2-nonyl-2,5-dihydro-1H-pyrrole 15 and but-2-ynyl-decyl-amine

General procedure B was followed using: KHMDS (0.5 M in toluene) (1.3 mL, 0.65 mmol), vinyl bromide 14 (0.098 g, 0.33 mmol) in dry Et₂O (3 mL). The addition of veratrole (10µL) to the crude reaction mixture (64 mg, 91%), followed by integration of the ¹H NMR spectrum of this mixture allowed the yields of the 3-pyrroline 15 (46 mg, 65%) and the acetylene (10 mg, 14%) to be determined. 3-Pyrroline 15: νmax(film)/cm⁻¹ 3317 (NH), 2924, 2854, 1542, 1458, 1402, 966, 812 and 722; δH(400 MHz; CDCl₃) 6.36 (1 H, s, CH), 3.90 (1 H, s, CHN), 3.65-3.57 (2 H, m, CH₂N), 2.09 (1 H, s, NH), 1.73 (3 H, s, CH₃), 1.24-1.26 (16 H, m, 8 x CH₂), 0.87 (3 H, t, J 6.5, CH₃); δC(67 MHz; CDCl₃)
137.7, 126.5 (CH), 65.8 (CH), 35.7 (CH₂), 36.3 (CH₂), 31.9 (CH₂), 29.8 (CH₂), 29.6 (CH₂), 29.3 (CH₂), 27.3 (CH₂), 26.5 (CH₂), 22.6 (CH₂), 14.1 (CH₃); m/z (El) 209 (M⁺); (C₁₄H₂₇N requires 209.2144. Found 209.2134).

Acetylene: δₚ(67MHz; CDCl₃) 3.34 (2 H, q, J 2.5, CH₂CC), 2.63 (2 H, t, J 7, CH₂), 1.80 (3 H, t, J 2.5 CCCH₃), 1.48-1.42 (1 Hx, m, NH), 1.24-1.26 (16 H, m, 8 x CH₂), 0.87 (3 H, t, J 7, CH₃CH₂); δc(67 MHz; CDCl₃) 78.7, 76.9, 48.9 (CH₂), 38.6 (CH₂), 31.9 (CH₂), 30.2 (CH₂), 29.9 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 27.3 (CH₂), 22.6 (CH₂), 14.0 (CH₃), 3.4 (CH₃).

(R)-2-(tert-Butyl-dimethyl-silanyloxy)methyl)-2-isobutyl-4-methyl-2,5-dihydro-1H-pyrrole 17 and [(S)-1-(tert-Butyl-dimethyl-silanyloxy)methyl]-3-methyl-butyl]-but-2-ynyl-amine

General procedure B was followed using: KHMDs (0.5 M in toluene) (46 mL, 23 mmol), vinylbromide 16 (5.56 g, 15.3 mmol) in Et₂O (40 mL) at 0°C. The crude material, a mixture of 3-pyrroline and acetylene (2.3:1 by ¹H NMR) was purified by flash column chromatography using isohexane and Et₂O as eluant (6:1) to yield 17 (2.34 g, 53%) and acetylene (1.10 g, 25%) as colourless oils. Pyrroline: [Rf 0.2; hexanes:Et₂O (2:1)] (Found: C, 67.78; H, 11.61; N, 4.85. C₁₆H₃₃NOSi requires C, 67.78; H, 11.73; N, 4.95%); [α]D²³ +16.70 (c 0.48 in CHCl₃); ν max(film)/cm⁻¹ 3367 (NH), 2953, 2929, 2857, 1665, 1471, 1463, 1406, 1384, 1362, 1255, 1097, 836, 775; δₚ(250 MHz; CDCl₃) 5.27 (1 H, m, CH), 3.61 (2 H, m, CH₂O), 3.40 (2 H, s, CH₂), 1.85 (1 H, s, NH), 1.73 (3 H, s, CH₃) 1.75-1.70 (1 H, m, CH(CH₃)₂), 1.46 (1 H, dd, J 14 and 6, CHH), 1.43 (1 H, dd, J 14 and 6, CHH), 0.92-0.89 (6 H, m, CH(CH₃)₂), 0.86 (9 H, s, Si(CH₃)₃), 0.00 (6 H, s, Si(CH₃)₂); δc(62 MHz; CDCl₃) 136.6, 126.4 (CH), 71.8 (CH₂), 68.1, 55.7 (CH₂), 44.4 (CH₂), 24.3 (CH₃), 23.3 (CH₃), 23.1 (CH₃), 22.9 (CH), 16.7, 12.6 (CH₃), -7.0 (CH₃); m/z (ES⁺) 284 (M⁺ + 1); (C₁₆H₃₄NOSi requires 284.2410. Found 284.2398). Acetylene: [Rf 0.4;
hexanes:Et$_2$O (2:1) [α]$_D^{23}$ –1.20 (c 0.58 in CHCl$_3$); $\nu_{\text{max}}$(film)/cm$^{-1}$ 3331 (NH), 2955, 2857, 1470;
$\delta_h$(250 MHz; CDCl$_3$) 3.62 (1 H, dd, J 10, 4, CHHO), 3.48-3.43 (1 H, m, CHHO), 3.42 (2 H, q, J 2.5, CH$_2$N), 2.88-2.80 (1H, m, CHN), 1.81 (3 H, q, J 2.5, CH$_3$) 1.30-1.10 (3 H, m, CH$_2$ and CH(CH$_3$_2)), 0.94-0.93 (6 H, m, CH(CH$_3$_2)), 0.91 (9 H, s, SiC(CH$_3$_3)), 0.07 (6 H, s, Si(CH$_3$_2); $\delta_c$(62 MHz; CDCl$_3$) 138.0, 127.9, 65.4 (CH$_2$), 55.7 (CH), 40.7 (CH$_2$), 36.2 (CH$_2$), 25.8 (CH$_3$), 25.0 (CH), 23.0 (CH$_3$), 22.9 (CH$_3$), 18.2, 3.4(CH$_3$), -5.4 (CH$_3$); m/z (ES$^+$) 284 (M$^+$ + 1); (C$_{16}$H$_{34}$NOSi requires 284.2410. Found 284.2402).

4-Methyl-2-phenyl-2,5-dihydro-pyrrole-1-carboxylic acid tert-butyl ester 19

General procedure B was followed using: KHMDS (0.5 M in toluene) (1.6 mL, 0.8 mmol), vinylbromide 18 (0.230 g, 0.68 mmol) in dry Et$_2$O (3 mL). The crude product was purified by flash column chromatography, using petrol and Et$_2$O (3:1) as eluant to give 19 (0.11 g, 63%) [Rf 0.3; petrol:Et$_2$O (3:1)] as a colourless oil (Found: C, 73.90; H, 8.25; N, 5.52. C$_{16}$H$_{21}$NO$_2$ requires C, 74.10; H, 8.16; N, 5.40%); $\nu_{\text{max}}$(solution in chloroform)/cm$^{-1}$ 2973, 2916, 2886, 2858, 1682 (CO), 1455, 1385, 1366, 1345, 1114, 1076, 1030, 968, 894; $\delta_h$(400 MHz; d-6 DMSO, 383K) 7.34-7.20 (5 H, m, Ph), 5.44-5.43 (1 H, m, CH), 5.36 (1 H, br, CH), 4.20-4.10 (2 H, m, CH$_2$), 1.82 (3 H, d, J 1.5, CH$_3$), 1.28 (9 H, s, (CH$_3$_3)); $\delta_c$(67 MHz; CDCl$_3$) 154, 143, 134.2, 128.3 (CH) 128.0 (CH), 127.0 (CH), 126.5 (CH), 126.3 (CH) 125.2 (CH), 79.3, 68.5 (CH) 68.1 (CH), 57.0 (CH$_2$) 56.7 (CH$_2$), 28.4 (CH$_3$), 28.0 (CH$_3$), 14.1 (CH$_3$); m/z (ES$^+$) 282 (M + 23); C$_{16}$H$_{21}$NO$_2$Na requires 282.1470. Found 282.1470).

4-Methyl-2-phenyl-1-(toluene-4-sulfonyl)-2,5-dihydro-$1H$-pyrrole 21

General procedure B was followed using: KHMDS (0.5 M in toluene) (0.8 mL, 0.4 mmol), vinylbromide 20 (0.081 g, 0.21 mmol) in dry Et$_2$O (3 mL). The crude product
was purified by flash column chromatography, using petrol and diethyl ether (3:1) as eluant to give 21 (0.04 g, 64%) [Rf 0.2; petrol:Et2O (3:1)] as a viscous oil; \( \nu_{\text{max}}(\text{solution in CHCl}_3)/\text{cm}^{-1} \) 2918, 2861, 1559 (SO), 1494, 1455, 1383, 1348, 1305, 1159, 1098 and 1074; \( \delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3) \) 7.51 (2 H, d, J 6.5, 2x CH (Ts)), 7.28-7.20 (5 H, m, Ph), 7.18 (2 H, d, J 6.5, 2x CH (Ts)), 5.48 (1 H, app sextet, J 2, CHC=C), 5.28 (1 H, app septet, J 2, CHN), 4.20 (1 H, app d of sextets, J 15 and 1, CHH), 4.16 (1 H, ddq, J 15, 5 and 1, CHH), 2.40 ((3 H, s, CH 3), 1.75 (3 H, m, CH 3C=C); \( \delta_{\text{C}}(100 \text{ MHz; CDCl}_3) \) 143.0, 141.1, 135.6, 134.2, 129.4 (CH), 128.3 (CH), 127.6 (CH), 127.3 (CH), 127.2 (CH), 124.7 (CH), 70.6 (CH), 58.2 (CH 2), 21.4 (CH 3), 13.9 (CH 3); \( m/z \) (ES\(^+\)) 314 (M\(^+\) + 1); \( \text{C}_{18}\text{H}_{20}\text{NSO}_2 \) requires 314.1214. Found 314.1229.

\( \text{(S)-2,4,-Dimethyl-2-phenyl-2,5-dihydro-pyrrole-1-carboxylic acid tert-butyl ester 23} \)

General procedure B was followed using: KHMDS (0.5 M in toluene) (1.1 mL, 0.55 mmol), vinylbromide 21 (0.154 g, 0.435 mmol) in dry Et2O (3 mL). The crude product was purified by flash column chromatography, using petrol and Et2O as eluant to give 23 (0.07 g, 59%) [Rf 0.3; petrol:Et2O (3:1)] as a colourless oil; \( [\alpha]_D^{22} \) –105.77 (c 0.60 in CHCl 3); \( \nu_{\text{max}}(\text{film})/\text{cm}^{-1} \) 2855, 1698 (CO), 1488, 1456, 1356, 1318, 1084, 1056, 995, 958, 890 and 8714; \( \delta_{\text{H}}(400 \text{ MHz, d}_6\text{-DMSO, 373K}) \) 7.33–7.18 (5 H, m, Ph), 5.32 (1 H, s, CH), 4.24 (1 H, d, J 15, CHH), 4.13 (1 H, d, J 15 Hz, CHH), 1.80 (3 H, s, CH 3), 1.77 (3 H, s, CH 3), 1.38 (9 H, s, C(CH 3) 3); \( \delta_{\text{C}}(100 \text{ MHz, CDCl}_3) \) 150.6, 139.6, 132.0 (CH), 130.4, 128.5 (CH), 128.0 (CH), 127.8 (CH), 127.5 (CH), 127.1 (CH), 126.3 (CH), 125.8 (CH), 125.6 (CH), 125.3 (CH), 125.3 (CH), 82.5, 79.2, 57.5 (CH 2), 28.4, 27.9 (CH 3), 23.9, 22.6 (CH 3), 14.0, (CH 3) 10.6 (CH 3); \( m/z \) (ES\(^+\)) 296 (M\(^+\) + 23); \( \text{C}_{17}\text{H}_{23}\text{NO}_2\text{Na}^+ \) requires 296.1626. Found 296.1630.

\( \text{(S)-2,4-Dimethyl-2-phenyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrole 25} \)
General procedure B was followed using: KHMDS (0.5 M in toluene) (0.63 mL, 0.32 mmol), vinylbromide 24 (0.064 g, 0.157 mmol) in dry Et₂O (3 mL). The crude product was purified by flash column chromatography, using petrol and Et₂O (3:1) as eluant to give 25 (15 mg, 29%) [Rf 0.3; petrol:Et₂O (3:1)] as a colourless oil; ν max(solution in CHCl₃)/cm⁻¹ 2978, 2919, 2852, 1599 (SO), 1495, 1450, 1373, 1340, 1305, 1156, 1119, 1097 and 1062; δH(400 MHz; CDCl₃) 7.26 (5 H, m, Ph), 7.15 (2 H, d, J, 2 x CH (Ar)), 7.03 (2 H, d, J 8, 2 x CH (Ar), 5.21 (1 H, app septet, J 2, CHC=C), 4.26 (1 H, dq, J 13 and 1, CHH), 4.06 (1 H, dq, J 13 and 1 CHH), 2.35 (3 H, s, CH₃ (Ts)), 2.01 (3 H, s, CH₃), 1.79 (3 H, s, CH₃); δC(100 MHz; CDCl₃) 142.4, 142.2, 137.2, 131.6 (CH), 131.2, 128.9 (CH), 127.9 (CH), 127.2 (CH), 127.1 (CH), 127.0 (CH), 74.7, 58.3 (CH₃), 25.6 (CH₃), 21.4 (CH₃), 13.9 (CH₃); m/z (ES⁺) 328 (M⁺ + 1); (C₁₈H₂₂NSO₂ requires 328.1371. Found 328.1386).

2-Ethyl-2,4-dimethyl-2,5-dihydro-pyrrole-1-carboxylic acid tert-butyl ester 27

General procedure B was followed using: KHMDS (0.5 M in toluene) (1.3 mL, 0.65 mmol), vinylbromide 26 (0.097 g, 0.316 mmol) in dry Et₂O (3 mL). The crude product was purified by flash column chromatography on silica using petrol and Et₂O (3:1) as eluant to give 27 (19 mg, 27%) [Rf 0.3; petrol:Et₂O (3:1)] as an oil; δH(400 MHz; CDCl₃) 5.10-5.00 (1 H, m, CH), 4.05-3.90 (2 H, m, CH₂), 1.80-1.70 (3 H, m, CH₃), 1.50-1.40 (9 H, m, (CH₃)₃), 0.95-0.90 (2 H, m, CH₂), 0.75-0.70 (3 H, m, CH₃).

2-Ethyl-2,4-dimethyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrole 29

General procedure B was followed using: KHMDS (0.5 M in toluene) (0.7 mL, 0.35 mmol), vinylbromide 28 (0.060 g, 0.166 mmol) in dry Et₂O (3 mL). The crude product was purified by flash column chromatography, using petrol and Et₂O (2:1) as eluant to
give 29 (15 mg, 32%) [Rf 0.3; petrol:Et₂O (2:1)] as a colourless oil; ν_max(solution in chloroform)/cm⁻¹ 3156, 2971, 2930, 1794, 1644, 1599 (SO), 1461, 1381, 1342, 1327, 1157, 1097 and 892; δ_H(400 MHz; CDCl₃) 7.77 (2 H, d, J 8, 2 x CH (Ts)), 7.28 (2 H, d, J 8, 2 x CH (Ts)), 5.02 (1 H, app q, J 2, CHC≡C), 3.97 (1 H, dd, J 13 and 1, CHH), 3.94 (1 H, dd, J 13 and 1, CHH), 2.42 (3 H, s, CH₃ (Ts)), 1.69 (3 H, d, J 1, CH₂C≡C), 1.45 (3 H, s, CH₃C₆H₄N), 0.85 (2 H, m, CH₂CH₃), 0.80 (3 H, t, J 7.5, CH₃CH₂); δ_C(100 MHz; CDCl₃) 142.6, 138.4, 131.8, 129.3 (CH), 129.1 (CH), 127.2 (CH), 77.3, 55.8 (CH₂), 33.4 (CH₂), 26.5 (CH₃), 21.5 (CH₃), 13.9 (CH₃), 9.0 (CH₃); m/z (ES⁺) 280 (M⁺ + 1); (C₁₄H₂₂NSO₂ requires 280.1371. Found 280.1387).

2-Cyclohexyl-4-methyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrole 31

General procedure B was followed using: KHMDS (0.5 M in toluene) (0.8 mL, 0.4 mmol), vinylbromide 30 (0.120 g, 0.31 mmol) in dry Et₂O (3 mL). The crude product was purified by flash column chromatography, using petrol and Et₂O (2:1) as eluant to give the 31 (25 mg, 26%) [Rf 0.3; petrol:Et₂O (2:1)] as a colourless oil; ν_max(solution in CHCl₃)/cm⁻¹ 2926, 2863, 1678, 1598 (SO), 1494, 1454, 1383, 1325, 1149, 1097, 1069, 972 and 906; δ_H(400 MHz; CDCl₃) 7.76 (2 H, d, J 8, 2 x CH (Ts)), 7.27 (2 H, d, J 8, 2 x CH (Ts)), 5.75 (1 H, app q, J 1.5, CHC≡C), 3.97 (2 H, app q, J 1, CH₂), 2.42 (3 H, s, CH₃ (Ts)), 1.72-1.63 (9 H, m, CH₃ + 3 x CH₂), 1.32-1.26 (4 H, m, 2 x CH₂); δ_C(100 MHz; CDCl₃) 142.6, 138.6, 131.7, 129.3 (CH), 127.3 (CH), 126.7 (CH), 76.4, 57.9 (CH₂), 37.3 (CH₂), 25.2 (CH₂), 24.6 (CH₂), 21.4 (CH₃), 14.3 (CH₃); m/z (ES⁺) 306 (M⁺ + 1); (C₁₇H₂₄NSO₂ requires 306.1528. Found 306.1537).

4-Methyl-2-pentyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrole 33

General procedure B was followed using: KHMDS (0.5 M in toluene) (0.7 mL, 0.35 mmol), vinylbromide 32 (0.100 g, 0.26 mmol) in dry Et₂O (3 mL).
The crude product was purified by flash column chromatography, using petrol and Et₂O (3:1) as eluant
to give 33 (95 mg, 64%) \([R_f 0.2; \text{petrol:Et}_2\text{O (3:1)}]\) as a colourless oil; \(v_{\text{max}}\) (film)/cm\(^{-1}\) 3403, 2954, 2926, 2858, 1712, 1598 (SO), 1494, 1465, 1344, 1162, 1096 and 814; \(\delta_H\) (400 MHz; CDCl\(_3\)) 7.70 (2 H, d, \(J 8, 2 \times \text{CH (Ts)}\)), 7.29 (2 H, d, \(J 8, 2 \times \text{CH (Ts)}\)), 5.19 (1 H, app t, \(J 1.5, \text{CHC=C}\)), 4.40 (1 H, m, CHN), 3.99 (1 H, d, \(J 14, \text{CHH}\)), 3.93 (1 H, d, \(J 14, \text{CHHH}\)), 2.42 (3 H, s, CH\(_3\) (Ts)), 1.80-1.64 (2 H, m, CH\(_2\)CHN), 1.63 (3 H, s, CH\(_3\)C=C), 1.32-1.20 (6 H, m, 3 x CH\(_2\)), 0.88 (3 H, t, \(J 7, \text{CH}_3\)CH\(_2\)); \(\delta_C\) (100 MHz; CDCl\(_3\)) 143.1, 135.0, 134.0, 129.6 (CH), 127.3 (CH), 123.6 (CH), 67.7 (CH), 58.5 (CH\(_2\)), 36.3 (CH\(_2\)), 31.8 (CH\(_2\)), 24.2 (CH\(_2\)), 22.6 (CH\(_2\)), 21.5 (CH\(_3\)), 14.0 (CH\(_3\)), 13.9 (CH\(_3\)); \(m/z\) (ES\(^+\)) 308 (M\(^+\) + 1); (C\(_{14}\)H\(_{24}\)NSO\(_2\)) requires 308.1684.  Found 308.1693.

(S)-3,3,3-Trifluoro-2-methoxy-2-phenyl-propionic acid (R)-2-isobutyl-4-methyl-2,5-dihydro-1\(H\)-pyrrol-2-ylmethyl ester

A solution of 3-pyrroline (0.49 g, 1.73 mmol) in THF (3 mL), water (3 mL) and acetic acid (10 mL) was heated at reflux for 2 days. After concentration by rotary evaporation, the residue was dissolved in Et\(_2\)O, washed with 2 M NaOH until basic. The aqueous layer was extracted with Et\(_2\)O (3 x 10 mL), then the organic layers combined and washed with water. 2 M HCl (10 mL) was added and after vigorous shaking, the ether layer was discarded. The acidic aqueous portion was washed with Et\(_2\)O and basified with 2 M NaOH. Finally, the resulting solution was extracted with Et\(_2\)O (3 x 10 mL), the ether fractions combined, washed with water (5 mL), brine (5 mL), dried over Na\(_2\)SO\(_4\) and concentrated, to afford a crude sample of alcohol, which was used in the next step without any further purification.

Following Ward and Rhee,\(^3\) (S)-Methoxytrifluoromethylphenylacetic acid chloride (0.10 g, 0.39 mmol) was added to a stirring solution of 3-pyrroline (0.051 g, 0.30 mmol) DCM (1 mL), DMAP (0.004 g, 0.03 mmol) and NE\(_3\) (0.33 mL, 2.4 mmol) under an atmosphere of N\(_2\). After 1 hour, the red solution was diluted with DCM (10 mL), washed with a saturated solution of NaHCO\(_3\) (5 mL), water (5 mL)
and brine (5 mL), then dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography using isohexane and Et₂O as eluant (1:1) Mosher’s ester (0.034 g, 30%) [Rf 0.2; hexane:Et₂O (1:1)] as a colourless oil. νₘₐₓ(film)/cm⁻¹ 2953, 2896, 2856, 1703, 1674, 1464, 1392, 1364, 1344, 1255, 1169, 1111, 854, 837 and 774; δₜ₁(250 MHz; CDCl₃) 7.60-7.50 (2 H, m, Ph), 7.43-7.39 (3 H, m, Ph), 4.20 (1 H, d, J 10.5, CHH), 4.10 (1 H, d, J 10.5, CHH), 3.64 (1 H, d, J 14.5, CHH), 3.55 (3 H, s, OCH₃), 3.53 (1 H, d, J 14.5, CHH), 1.79 (1 H, s, NH), 1.71 (3 H, s, CH₃) 1.70-1.61 (1 H, m, CH(CH₃)₂), 1.44-1.39 (2 H, m, CH₂CH), 0.90 (3 H, d, J 6.5, CH(CH₃)₂), 0.87 (3 H, d, J 6.5, CH(CH₃)₂); δₐ(62 MHz; CDCl₃) 166.5, 140.2, 132.2, 129.5 (CH), 128.3 (CH), 127.4 (CH), 125.9 (CH), 121.1, 84.6 (q, J 28, CF₃), 72.1 (CH₂), 71.4, 57.2 (CH₂), 55.3 (CH₃), 46.0 (CH₂), 24.6 (CH), 24.4 (CH₃), 24.3 (CH₃), 14.0 (CH₃); δₚ(376 MHz; CDCl₃) –74.44; m/z (ES⁺) 386 (M⁺ + H).

(R/S)-3,3,3-Trifluoro-2-methoxy-2-phenyl-propionic acid (R)-2-isobutyl-4-methyl-2,5-dihydro-1H-pyrrol-2-ylmethyl ester

Oxalyl chloride (0.1 mL, 1.1 mmol) was added to a stirring solution of rac-methoxytrifluoromethyl-phenylacetic acid (0.055 g, 0.24 mmol) and DMF (1 mg) in isohexane (1 mL). After 45 minutes, the solvent was removed in vacuo and to the residue was dissolved in DCM (0.5 mL). A solution of the alcohol (0.030 g, 0.18 mmol), DMAP (0.002 g, 0.018 mmol) and NEt₃ (0.145 g, 1.44 mmol) in DCM (1 mL) were then added and the resulting mixture was stirred for 1 hour. The red solution was diluted with DCM (10 mL), washed with saturated NaHCO₃ solution (5 mL), water (5 mL), brine (5 mL), dried over Na₂SO₄ and then concentrated in vacuo. The crude material was purified by flash column chromatography using isohexane and Et₂O as eluant (1:1). The Mosher’s ester was isolated as a (1:1 mixture of diastereomers); [Rf 0.2; hexane:Et₂O (1:1)] δₚ(376 MHz; CDCl₃) –74.53 and –74.61.