Supporting Information

Intramolecular Cyclopropanation of Unsaturated Terminal Aziridines

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(I) General details

Reactions were performed in flame-dried glassware under an atmosphere of argon. Et₂O, THF and MeCN were degassed and dried over alumina under nitrogen.¹ 2,2,6,6-Tetramethylpiperidine, diisopropylamine, Cy₂NH and *t*-BuOMe were distilled from CaH₂. All other reagents were used as received. Reactions were monitored by tlc (thin layer chromatography) using silica 60 gel aluminium-backed plates. The plates were visualised using ultraviolet light and developed in basic potassium permanganate solution. Column chromatography was performed using the solvent systems indicated. Petroleum ether refers to the fraction that boils at 30–40 °C. The stationary

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(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

phase used was silica gel 60. ^1H and ^{13}C spectra were recorded in CDCl_3 at ambient temperature. Data are expressed as chemical shifts in parts per million (ppm) relative to residual chloroform and CDCl_3 (^1H δ 7.27, ^{13}C δ 77.0 respectively) as the internal standard on the δ scale. The multiplicity of each signal is designated using the following abbreviations; s, singlet; d, doublet; dd, doublet of doublets; dt, doublet of triplets; ddt, doublet of doublet of triplets; t, triplet; sept, septuplet; br, broad. Coupling constants J are given in Hz. Infra-red spectra of the compounds were recorded neat, as a film, or KBr disc as indicated. The intensity of the peaks are reported as s, strong; m, medium; w, weak; br, broad. High-resolution mass spectra were obtained using chemical ionisation techniques (NH_3 and Na^+) or by gas chromatography analysis with a BPX5 column-HP 6890 (dimethylsilicon capillary column, 30 m, 0.25 mm i.d.) equipped with a reflectron TOF mass spectrometer operating at 60 eV (flow rate (He) = 1 mL/min). Specific rotations $[\alpha]_D^T$ were measured using a polarimeter with a cell of path length 10.0 cm, at T °C and are given in $10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$. Concentrations (c) are given in g/100 mL. Chiral gas chromatography was carried out using a CE instruments Trace GC (Thermoquest) with a SGE Cydex B-column.

(II) Synthesis and characterization data for aziridines

General procedure A: *N*-Bus aziridine preparation from epoxides²

Benzyltriethylammonium chloride (0.1 equiv) was added to a stirred suspension of epoxide (1 equiv), *tert*-butylsulfonamide (1.5 equiv) and potassium carbonate (0.1 equiv) in 1,4-dioxane (0.25 mL per mmol of epoxide). The suspension was heated at 90 °C for 16 h, then following cooling, CH₂Cl₂ (25 mL) was added. Following filtration through a short plug of celite and washing with CH₂Cl₂ (2 × 20 mL), the solvent was removed by rotary evaporation. Purification of the residue by column chromatography (petroleum ether/Et₂O, SiO₂) gave the β-hydroxysulfonamide, which was used directly in the next step.

β-Hydroxysulfonamide (1 equiv) was dissolved in CH₂Cl₂ (6 mL per mmol β-hydroxysulfonamide) and pyridine (2 equiv). DMAP (0.1 equiv) and Ms₂O (1.5 equiv) were added and the resultant orange suspension was stirred for 45 min. Et₂O (20 mL) and sat. aqueous CuSO₄ (20 mL) were added and the organic phase was washed with CuSO₄ (20 mL). The combined aqueous phase was washed with Et₂O (3 × 30 mL) and the combined organic phases were washed with brine (50 mL), dried (MgSO₄) and evaporated under reduced pressure to give the crude mesylate which was used directly in the next step.

The crude mesylate was dissolved in THF (9 mL per mmol crude mesylate) and sat. aqueous potassium carbonate (1 mL per mmol crude mesylate) was added. Following stirring at 85 °C for 16 h, the reaction was cooled and Et₂O (30 mL) and H₂O (30 mL) were added. The aqueous phase was washed with Et₂O (3 × 30 mL), the combined

(2) Hodgson, D. M.; Fleming, M. J.; Stanway, S. J. *Org. Lett.* **2005** 7, 3295–3298.

organic phases were dried (MgSO_4) and concentrated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/ Et_2O , Si_2O) gave the *N*-Bus aziridine.

2-(But-3-enyl)-1-tosylaziridine **6**^{3,4}

1,5-Hexadiene (0.89 mL, 7.5 mmol) was added dropwise to a stirred suspension of anhydrous chloramine-T (1.14 g, 5.0 mmol) and PTAB (282 mg, 0.75 mmol) in MeCN (37.5 mL) at room temperature. The mixture was stirred for 48 h, filtered and then evaporated under reduced pressure. Purification of the resulting residue by column chromatography (petroleum ether/ EtOAc 9:1), gave *aziridine 6* as a colourless oil (614 mg, 49%).

R_f 0.42 (petroleum ether/ EtOAc 17:3); ν_{max} (neat)/ cm^{-1} 3077m, 3000m, 2926s, 1923w, 1642m ($\text{C}=\text{C}$), 1598s, 1495m, 1451s, 1401m, 1322s ($\text{S}=\text{O}$), 1233m, 1160s ($\text{S}=\text{O}$) and 1092s; δ_{H} (400 MHz, CDCl_3) 7.85 (2H, d, J 9, $2 \times \text{ArCH}$), 7.36 (2H, d, J 9, $2 \times \text{ArCH}$), 5.74 (1H, ddt, J 13, 7, 6, $=\text{CH}$), 5.00-4.85 (2H, m, $\text{H}_2\text{C}=\text{}$), 2.81-2.75 (1H, m, CHN), 2.65 (1H, d, J 7, $\text{CH}(\text{H})\text{N}$, *trans* to alkyl chain), 2.46 (3H, s, Me), 2.09 (1H, d, J 5, $\text{CH}(\text{H})\text{N}$, *cis* to alkyl chain), 2.08-2.00 (2H, m, $=\text{CHCH}_2$), 1.70-1.62 (1H, m, $\text{CH}(\text{H})$), 1.50-1.41 (1H, m, $\text{CH}(\text{H})$); δ_{C} (100 MHz, CDCl_3) 144.5 ($\text{SC}_{\text{Ar quat}}$), 136.9 ($2 \times \text{C}_{\text{Ar}}$), 134.9 (ArCMe), 130.1 ($2 \times \text{C}_{\text{Ar}}$), 128.1 ($=\text{CH}$), 115.5 ($\text{H}_2\text{C}=\text{}$), 39.7 (CHN), 33.7 (CH_2N), 30.7 (CH_2), 30.5 ($=\text{CHCH}_2$), 21.5 (Me); MS CI m/z (rel. int.) 252 ($\text{M} + \text{H}^+$, 100); HRMS m/z calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_2\text{S}$, 252.1058, found 252.1051.

(3) Jeong, J. U.; Tao, B.; Sagasser, I.; Henniges, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1998**, *120*, 6844–6845.

(4) Lapinsky, D. J.; Bergmeier, S. C. *Tetrahedron*, **2002**, *58*, 7109–7117.

(S)-2-(But-3-enyl)-1-(tert-butylsulfonyl)aziridine 12a **(R)-1,2-Epoxy-5-hexene⁵**

AcOH (47 μ L, 0.82 mmol) was added to a stirring suspension of (*R,R*)-(-)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt (123 mg, 0.20 mmol) and 1,2-epoxy-5-hexene (4.60 mL, 40.8 mmol) in THF (0.40 mL). The reaction was cooled to 0 °C and H₂O (0.40 mL, 22.44 mmol) was added in one portion. The flask was warmed to 25 °C and following stirring for 24 h, the volatiles were removed under reduced pressure (8 mbar) and collected in a cooled (-78 °C) receiving flask. The volatiles were passed through a short plug of silica to remove H₂O, washed with Et₂O (10 mL) and evaporated under reduced pressure to give (*R*)-1,2-epoxy-5-hexene as a colourless oil (1.47 g, 37%) (74% based on theoretical maximum of 50% yield).

$[\alpha]_D^{25} = +8.4$ (*c* 1.0, CHCl₃); Data matches that of commercial racemic 1,2-epoxy-5-hexene. Chiral HPLC analysis of 2-naphthalene thiol derivative shows ee >99% when compared to racemate.

Chiral HPLC analysis, Chiralpax OD column, 0.4 mL/min, Heptane:EtOH 98.5:1.5

(5) Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, T.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 1307–1315.

Area percent report		
RT	Area	Area%
78.84	6098233	99.860

Area percent report		
RT	Area	Area%
62.60	3874014	49.897
73.56	3880847	49.985

(S)-2-(But-3-enyl)-1-(tert-butylsulfonyl)aziridine 12a

Following **General procedure A** using (*R*)-1,2-epoxy-5-hexene (1.13 g, 11.46 mmol) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 6:4 to 4:1), the corresponding *β*-hydroxysulfonamide as a pale yellow oil (1.21 g, 45%). Reaction of the *β*-hydroxysulfonamide gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), *aziridine 12a* as a colourless oil (935 mg, 86%).

$[\alpha]_D^{25} = +66.0$ (*c* 1.0, CHCl₃); Data matches that of racemic 2-(but-3-enyl)-1-(tert-butylsulfonyl)aziridine.⁶

(E)-1-(tert-Butylsulfonyl)-2-(hex-3-enyl)aziridine 12b

Following **General procedure A** using (*E*)-2-(hex-3-enyl)oxirane⁷ (1.84 g, 14.58 mmol) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 1:1, *R*_f = 0.26), the corresponding *β*-hydroxysulfonamide as a crude yellow oil (2.18 g, 57%) Reaction of the *β*-hydroxysulfonamide gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), *aziridine 12b* as a colourless oil (1.37 g, 67%).

*R*_f 0.41 (petroleum ether/Et₂O 9:1); IR (neat) 2963s, 1675w (C=C), 1481m, 1457s, 1397m, 1366m, 1306s (S=O), 1237m, 1131s (S=O), 1065m and 1009s cm⁻¹; ¹H NMR

(6) Hodgson, D. M.; Humphreys, P. G.; Ward, J. G. *Org. Lett.* **2005** *7*, 1153–1156.

(7) Hodgson, D. M.; Chung, Y. K.; Paris, J.-M. *J. Am. Chem. Soc.* **2004**, *126*, 8664–8665.

(400 MHz, CDCl₃) δ 5.55 (1H, dt, *J* 15, 6, =CH), 5.43 (1H, dt, *J* 15, 7, =CH), 2.76-2.70 (1H, m, CHN), 2.59 (1H, d, *J* 7, CH(*H*)N, *trans* to alkyl chain), 2.16-2.11 (2H, m, =CHCH₂), 2.08 (1H, d, *J* 5, CH(*H*)N, *cis* to alkyl chain), 2.04-1.96 (2H, m, =CHCH₂), 1.75-1.67 (1H, m, CH(*H*)CHN), 1.57-1.46 (10H, m, CH(*H*)CHN, *t*Bu), 0.96 (3H, t, *J* 7, Me); ¹³C NMR (100 MHz, CDCl₃) δ 133.3 (=CH), 127.3 (=CH), 59.2 (SC), 38.2 (CHN), 34.0 (CH₂N), 31.4 (CH₂), 29.3 (=CHCH₂), 25.5 (=CHCH₂), 24.2 (SCMe₃), 13.8 (Me); MS CI *m/z* (rel. int.) 263 (M + NH₄⁺, 10), 246 (M + H⁺, 95), 190 (20), 126 (100), 109 (35); HRMS *m/z* calcd for C₁₂H₂₇N₂O₂S, 263.1793, found 263.1794.

(*Z*)-1-(*tert*-Butylsulfonyl)-2-(hex-3-enyl)aziridine 12c

Following **General procedure A** using (*Z*)-2-(hex-3-enyl)oxirane⁷ (908 mg, 7.19 mmol) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 1:1, *R*_f = 0.26), the corresponding β -hydroxysulfonamide as a crude white solid (1.44 g, 76%) Reaction of the β -hydroxysulfonamide gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), aziridine **12c** as a colourless oil (940mg, 72%).

*R*_f 0.41 (petroleum ether/Et₂O 9:1); IR (neat) 2963s, 1481m, 1457s, 1397m, 1366w, 1308s (S=O), 1237m, 1131s (S=O), 1068w and 1009w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.41 (1H, dt, *J* 10, 7, =CH), 5.33 (1H, dt, *J* 10, 7, =CH), 2.75-2.69 (1H, m, CHN), 2.58 (1H, d, *J* 7, CH(*H*)N, *trans* to alkyl chain), 2.19-2.14 (2H, m, =CHCH₂), 2.08-2.00 (3H, m, =CHCH₂, CH(*H*)N, *cis* to alkyl chain), 1.76-1.67 (1H, m,

CH(*H*)CHN), 1.55-1.48 (10H, m, CH(*H*)CHN, *t*Bu), 0.95 (3H, t, *J* 8, CH₂Me); ¹³C NMR (100 MHz, CDCl₃) δ 132.9 (=CH), 127.1 (=CH), 59.2 (SC), 38.2 (CHN), 33.9 (CH₂N), 31.5 (CH₂CHN), 24.1 (SCMe₃), 23.9 (=CHCH₂), 20.4 (=CHCH₂), 14.2 (CH₂Me); MS CI *m/z* (rel. int.) 263 (M + NH₄⁺, 5), 246 (M + H⁺, 35), 190 (10), 126 (100), 109 (45); HRMS *m/z* calcd for C₁₂H₂₄NO₂S, 246.1528, found 246.1525.

1-(*tert*-Butylsulfonyl)-2-(4-methylpent-3-enyl)aziridine **12d**

Grubbs 2nd generation catalyst (17 mg, 0.02 mmol) was added to a stirred solution of aziridine **9**⁶ (435 mg, 2.00 mmol) in 2-methyl-2-butene (4.40 mL).⁸ Following stirring for 12 h, the dark brown solution was evaporated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/Et₂O 9:1) gave aziridine **12d** as a pale brown oil (395 mg, 80%).

*R*_f 0.32 (petroleum ether/Et₂O 9:1); IR (neat) 2931s, 1455s, 1397m, 1366m, 1307s, 1238m, 1131s and 1067w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.13 (1H, t, *J* 7, =CH), 2.76-2.71 (1H, m, CHN), 2.59 (1H, d, *J* 7, CH(*H*)N, *trans* to alkyl chain), 2.16-2.10 (2H, m, CH₂), 2.08 (1H, d, *J* 5, CH(*H*)N, *cis* to alkyl chain), 1.75-1.54 (8H, m, CH₂, =CMe₂), 1.49 (9H, s, *t*Bu); ¹³C NMR (100 MHz, CDCl₃) δ 132.7 (=CMe₂), 122.8 (=CH), 59.2 (SC), 38.5 (CHN), 33.9 (CH₂N), 31.6 (CH₂), 25.7 (CH₂), 24.9 (Me), 24.2 (SCMe₃), 17.7 (Me); MS CI *m/z* (rel. int.) 246 (M + H⁺, 50), 190 (30), 126 (100), 109 (55); HRMS *m/z* calcd for C₁₂H₂₄NO₂S, 246.1528, found 246.1531.

(8) Chatterjee, A. K.; Sanders, D. P.; Grubbs, R. H. *Org. Lett.* **2002**, *4*, 1939–1942.

1-(*tert*-Butylsulfonyl)-2-(3-methylbut-3-enyl)aziridine 12e

Following **General procedure A** using 2-(3-methylbut-3-enyl)oxirane⁹ (410 mg, 3.66 mmol) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 1:1 (R_f = 0.21)), the corresponding β -hydroxysulfonamide as a crude white solid (858 mg, 94%). Reaction of the β -hydroxysulfonamide gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), **aziridine 12e** as a colourless oil (503 g, 63%).

R_f 0.31 (petroleum ether/Et₂O 9:1); IR (neat) 3077m, 2983s, 2936s, 1650m (C=C), 1481m, 1455s, 1397m, 1367m (S=O), 1307s, 1239m, 1131s (S=O) and 1070w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.74 (1H, s, H(*H*)C=), 4.71 (1H, s, H(*H*)C=), 2.76-2.71 (1H, m, CHN), 2.59 (1H, d, J 7, CH(*H*)N, *trans* to alkyl chain), 2.14 (2H, t, J 8, =CCH₂), 2.09 (1H, d, J 5, CH(*H*)N, *cis* to alkyl chain), 1.81-1.73 (4H, m, CH(*H*)CHN, =CMe), 1.68-1.59 (1H, m, CH(*H*)CHN), 1.48 (9H, s, ^{*t*}Bu); ¹³C NMR (100 MHz, CDCl₃) δ 144.2 (=C), 110.6 (H₂C=), 59.2 (SC), 38.1 (CHN), 34.2 (=CCH₂), 34.1 (CH₂N), 29.4 (CH₂), 24.1 (SCMe₃), 22.4 (=CMe); MS CI m/z (rel. int.) 249 (M + NH₄⁺, 5), 232 (M + H⁺, 5), 112 (100), 95 (25); HRMS m/z calcd for C₁₁H₂₂NO₂S, 232.1371, found 232.1362.

1-(*tert*-Butylsulfonyl)-2-(2,2-dimethylbut-3-enyl)aziridine 12f

Following **General procedure A** using 2-(2,2-dimethylbut-3-enyl)oxirane⁹ (1.06 g, 8.40 mmol) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 1:1 (*R_f* = 0.14) to 4:6), the corresponding *β*-hydroxysulfonamide as a crude white solid (1.62 g, 73%). Reaction of the *β*-hydroxysulfonamide gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), aziridine **12f** as a white solid (790 mg, 52%).

(mp = 43-45 °C); *R_f* 0.27 (petroleum ether/Et₂O 9:1); IR (film) 2963s, 1641w (C=C), 1480m, 1366m, 1307s (S=O), 1239m, 1130s (S=O) and 1067w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.87 (1H, dd, *J* 17, 10, =CH), 5.03-4.97 (2H, m, H₂C=), 2.73-2.67 (1H, m, CHN), 2.62 (1H, d, *J* 7, CH(*H*)N, *trans* to alkyl chain), 2.03 (1H, d, *J* 5, CH(*H*)N, *cis* to alkyl chain), 1.84 (1H, dd, *J* 14, 5, CH(*H*)CHN), 1.48 (9H, s, ^{*t*}Bu), 1.33 (1H, dd, *J* 14, 8, CH(*H*)CHN), 1.11 (3H, s, CMe(*Me*)), 1.09 (3H, s, CMe(*Me*)); ¹³C NMR (100 MHz, CDCl₃) δ 146.9 (=CH), 111.5 (H₂C=), 59.2 (SC), 44.3 (CH₂), 36.4 (CMe₂), 35.9 (CHN), 34.8 (CH₂N), 26.9 (CMe(*Me*)), 26.6 (CMe(*Me*)), 24.1 (SCMe₃); MS CI *m/z* (rel. int.) 246 (M + H⁺, 60), 126 (100), 109 (30); HRMS *m/z* calcd for C₁₂H₂₄NO₂S, 246.1528, found 246.1518.

(9) Hodgson, D. M.; Chung, Y. K.; Paris, J.-M. *Synthesis* **2005**, 2264–2266.

1-(*tert*-Butylsulfonyl)-2-(1,1-diphenylbut-3-enyl)aziridine 12g

Following **General procedure A** using 2-(1,1-diphenylbut-3-enyl)oxirane⁷ (3.36 g, 13.42 mmol) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 1:1, *R_f* = 0.42), the corresponding *β*-hydroxysulfonamide as a crude yellow solid (4.32 g, 83%). Reaction of the *β*-hydroxysulfonamide gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), **aziridine 12g** as a colourless oil (2.00 g, 48%).

R_f 0.48 (petroleum ether/Et₂O 9:1); IR (neat) 3059m, 2986s, 1639m (C=C), 1600m, 1496w, 1446m, 1307s (S=O), 1247m, 1133s (S=O), 1035w and 702s (C_{Ar-H}) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.13 (10H, m, 10 × C_{Ar}H), 5.52 (1H, ddt, *J* 14, 7, 7, =CH), 5.27-5.22 (1H, m, =CH(*H*)), 5.03-5.00 (1H, m, =CH(*H*)), 3.56 (1H, dd, *J* 7, 5, CHN), 3.26 (1H, dd, *J* 14, 7, =CHCH(*H*)), 2.99 (1H, dd, *J* 14, 7, =CHCH(*H*)), 2.59 (1H, d, *J* 7, CH(*H*)N, *trans* to alkyl chain), 1.74 (1H, d, *J* 5, CH(*H*)N, *cis* to alkyl chain), 1.38 (9H, s, *t*Bu); ¹³C NMR (100 MHz, CDCl₃) δ 143.5 (C_{Ar} quat), 143.1 (C_{Ar} quat), 133.5 (=CH), 129.3 (2 × C_{Ar} ortho), 128.6 (2 × C_{Ar} ortho), 127.9 (2 × C_{Ar}), 127.2 (2 × C_{Ar}), 126.6 (2 × C_{Ar}), 126.5 (2 × C_{Ar}), 119.3 (H₂C=), 59.6 (SC), 50.0 (CPh₂), 43.4 (=CHCH₂), 39.8 (CHN), 33.3 (CH₂N), 24.1 (SCMe₃); MS CI *m/z* (rel. int.) 387 (M + NH₄⁺, 20), 370 (M + H⁺, 15), 250 (100), 221 (45), 220 (40), 167 (55); HRMS *m/z* calcd for C₂₂H₂₈NO₂S, 370.1841, found 370.1846.

1-(*tert*-Butylsulfonyl)-2-(hepta-1,6-dien-4-yl)aziridine 12h

Following **General procedure A** using 2-(hepta-1,6-dien-4-yl)oxirane⁷ (724 mg, 5.24 mmol) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 1:1, *R*_f = 0.25), the corresponding *β*-hydroxysulfonamide as a crude yellow solid (1.12 g, 78%) Reaction of the *β*-hydroxysulfonamide gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), aziridine **12h** as a colourless oil (584 mg, 56%).

*R*_f 0.46 (petroleum ether/Et₂O 9:1); IR (neat) 3077m, 2980s, 2924m, 1641m (C=C), 1481m, 1442w, 1396w, 1366w, 1308s (S=O), 1242m, 1131s (S=O) and 997m cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.89-5.72 (2H, m, 2 × =CH), 5.12-5.02 (4H, m, 2 × H₂C=), 2.69-2.64 (1H, m, CHN), 2.59 (1H, d, *J* 7, CH(*H*)N, *trans* to alkyl chain), 2.35-2.29 (1H, m, =CHCH(*H*)), 2.23-2.06 (4H, m, =CHCH(*H*), =CHCH₂, CH(*H*)N, *cis* to alkyl chain), 1.49 (9H, s, *t*Bu), 1.46-1.37 (1H, m, CHCHN); ¹³C NMR (100 MHz, CDCl₃) δ 135.7 (=CH), 135.4 (=CH), 117.2 (H₂C=), 117.0 (H₂C=), 59.4 (SC), 40.3 (CHN), 39.7 (CHCHN), 36.3 (CH₂N), 35.8 (=CHCH₂), 35.1 (=CHCH₂), 24.2 (SCMe₃); MS CI *m/z* (rel. int.) 275 (M + NH₄⁺, 45), 258 (M + H⁺, 90), 140 (55), 138 (100); HRMS *m/z* calcd for C₁₃H₂₄NO₂S, 258.1519, found 258.1522.

1-(*tert*-Butylsulfonyl)-2-(4-isopropylhepta-1,6-dien-4-yl)aziridine 12i

Following **General procedure A** using *2-(4-isopropylhepta-1,6-dien-4-yl)oxirane*⁷ (1.46 g, 8.10 mmol), except that the reaction was stirred for 72 h gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 1:1, *R_f* = 0.35), the corresponding *β*-hydroxysulfonamide as an orange oil (734 mg, 29%) Reaction of the *β*-hydroxysulfonamide gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), *aziridine 12i* as a colourless oil (403 mg, 58%).

R_f 0.56 (petroleum ether/Et₂O 9:1); IR (neat) 3075m, 2977s, 1638m (C=C), 1480m, 1393w, 1368w, 1309s (S=O), 1257w, 1133s (S=O) and 998m cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.01-5.79 (2H, m, 2 × =CH), 5.13-5.02 (4H, m, 2 × H₂C=), 2.79 (1H, dd, *J* 7, 5, CHN), 2.51 (1H, d, *J* 7, CH(*H*)N, *trans* to alkyl chain), 2.31 (1H, d, *J* 5, CH(*H*)N, *cis* to alkyl chain), 2.22-2.12 (3H, m, =CHCH₂, =CHCH(*H*)), 2.03 (1H, dd, *J* 14, 8, =CHCH(*H*)), 1.81 (1H, sept., *J* 7, CHMe₂), 1.49 (9H, s, *t*Bu), 1.02 (3H, d, *J* 7, CHMe(*Me*)), 0.99 (3H, d, *J* 7, CHMe(*Me*)); ¹³C NMR (100 MHz, CDCl₃) δ 134.7 (=CH), 134.4 (=CH), 117.5 (H₂C=), 117.3 (H₂C=), 59.6 (SC), 40.4 (CHN), 40.0 (C^{*i*}Pr), 37.4 (=CHCH₂), 36.8 (=CHCH₂), 33.3 (CH₂N), 33.2 (CHMe₂), 24.2 (SCMe₃), 17.0 (CHMe₂); MS CI *m/z* (rel. int.) 300 (M + H⁺, 20), 180 (100), 138 (20); HRMS *m/z* calcd for C₁₆H₃₀NO₂S, 300.1997, found 300.1992.

1-(*tert*-Butylsulfonyl)-2-(2-(cyclohexa-1,4-dienyl)ethyl)aziridine 12j

Following **General procedure A** using 2-(2-(cyclohexa-1,4-dienyl)ethyl)oxirane⁷ (1.21 g, 8.03 mmol) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 1:1, R_f = 0.19), the corresponding β -hydroxysulfonamide as a crude white solid (1.09 g, 47%) Reaction of the β -hydroxysulfonamide gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), aziridine **12j** as a colourless oil (452 mg, 44%).

R_f 0.26 (petroleum ether/Et₂O 9:1); IR (neat) 2933s, 1455m (C=C), 1306s (S=O), 1238w, 1130s (S=O) and 1034m cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.74-5.66 (2H, m, 2 $\times$ =CH), 5.48 (1H, s, =CH), 2.81-2.67 (3H, m, CHN, =CHCH₂), 2.62-2.57 (3H, m, =CHCH₂, CH(*H*)N, *trans* to alkyl chain), 2.13-2.08 (3H, m, =CCH₂, CH(*H*)N, *cis* to alkyl chain), 1.81-1.72 (1H, m, CH(*H*)CHN), 1.57-1.60 (1H, m, CH(*H*)CHN), 1.49 (9H, s, *t*Bu); ¹³C NMR (100 MHz, CDCl₃) δ 133.4 (=C), 124.3 (=CH), 124.0 (=CH), 119.2 (=CH), 59.2 (SC), 38.3 (CHN), 34.1 (CH₂N), 33.9 (CH₂CHN), 29.2 (=CCH₂), 29.0 (=CHCH₂), 26.7 (=CHCH₂), 24.2 (SCMe₃); MS CI m/z (rel. int.) 287 (M + NH₄⁺, 5), 270 (M + H⁺, 15), 150 (100); HRMS m/z calcd for C₁₄H₂₄NO₂S, 270.1528, found 270.1527.

(E)-1-(tert-Butylsulfonyl)-2-(4-phenylbut-3-enyl)aziridine 12k

Styrene (2.29 mL, 20.00 mmol) was added to a stirred solution of *aziridine 9*⁶ (435 mg, 2.00 mmol) and Grubbs 2nd generation catalyst (85 mg, 0.10 mmol) in CH₂Cl₂ (20 mL). Following heating to reflux, the reaction was stirred for 12 h, then cooled to room temperature and then evaporated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/Et₂O 9:1) gave *aziridine 12k* as a pale brown oil (442 mg, 75%).

*R*_f 0.24 (petroleum ether/Et₂O 9:1); IR (film) 2989m, 2934m, 1598w, 1480m, 1451m, 1366m, 1305s, 1236w, 1130s and 710s (C_{Ar-H}) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.21 (5H, m, 5 × C_{Ar}H), 6.47 (1H, d, *J* 16, ArCH=), 6.28-6.21 (1H, m, =CH), 2.83-2.77 (1H, m, CHN), 2.63 (1H, d, *J* 7, CH(*H*)N, *trans* to alkyl chain), 2.41-2.36 (2H, m, =CHCH₂), 2.13 (1H, d, *J* 5, CH(*H*)N, *cis* to alkyl chain), 1.84-1.67 (2H, m, CH₂), 1.51 (9H, s, ^{*t*}Bu); ¹³C NMR (100 MHz, CDCl₃) δ 137.4 (C_{Ar} quat), 130.9 (ArCH=), 128.8 (=CH), 128.5 (2 × C_{Ar}), 127.1 (C_{Ar}), 126.0 (2 × C_{Ar} ortho), 59.3 (SC), 37.8 (CHN), 34.4 (CH₂N), 31.3 (=CHCH₂), 29.9 (CH₂), 24.2 (SCMe₃); MS CI *m/z* (rel. int.) 311 (M + NH₄⁺, 5), 294 (M + H⁺, 10), 238 (20), 174 (100), 157 (60), 91 (30); HRMS *m/z* calcd for C₁₆H₂₇N₂O₂S, 311.1793, found 311.1798.

1-(tert-Butylsulfonyl)-2-(3-phenylbut-3-enyl)aziridine 12l

2-(3-Phenylbut-3-enyl)oxirane

n-BuLi (1.6 M in hexanes, 6.25 mL, 10.00 mmol) was added dropwise to a stirred solution of *t*-BuOK (1.12 g, 10.00 mmol) in THF (40 mL) at −78 °C. After 5 min, α-

methylstyrene (1.30 mL, 10.00 mmol) was added dropwise and following further stirring for 30 min, epichlorohydrin (0.39 mL, 5.00 mmol) was added in one portion. Following stirring for 90 min, sat. aqueous NH_4Cl (5 mL) and Et_2O (5 mL) were added and the phases separated. The aqueous phase was washed with Et_2O (3×10 mL), the combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/ Et_2O 97:3) gave a crude colourless oil. Bulb-to-bulb distillation of the crude oil gave *2-(3-phenylbut-3-enyl)oxirane* as a colourless oil (454 mg, 52%).

(bp. 75 °C, 0.07 mbar); R_f 0.20 (petroleum ether/ Et_2O 97:3); IR (neat) 3082w, 3053m, 2987m, 2923s, 1627s (C=C), 1600m, 1495s, 1444m, 1410m, 1079w, and 706 ($\text{C}_{\text{Ar-H}}$) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.28 (5H, m, $5 \times \text{C}_{\text{ArH}}$), 5.33 (1H, d, J 1, =CH(H)), 5.13 (1H, d, J 1, =CH(H)), 2.99-2.95 (1H, m, CHO), 2.76-2.62 (3H, m, CH(H)O, =CHCH $_2$), 2.48 (1H, dd, J 5, 3, CH(H)O), 1.78-1.65 (2H, m, CH $_2$ CHO); ^{13}C NMR (100 MHz, CDCl_3) δ 147.5 (=C), 140.1 ($\text{C}_{\text{Ar quat}}$), 128.4 ($2 \times \text{C}_{\text{Ar ortho}}$), 127.5 ($2 \times \text{C}_{\text{Ar}}$), 126.1 (C_{Ar}), 112.8 (=CH $_2$), 51.9 (CHO), 47.2 (CH $_2$ O), 31.7 (CH $_2$), 31.2 (CH $_2$); MS CI m/z (rel. int.) 192 ($\text{M} + \text{NH}_4^+$, 35), 175 ($\text{M} + \text{H}^+$, 95), 157 (100); HRMS m/z calcd for $\text{C}_{12}\text{H}_{15}\text{O}$, 175.1123, found 175.1129.

1-(*tert*-Butylsulfonyl)-2-(3-phenylbut-3-enyl)aziridine **121**

Following **General procedure A** using *2-(3-phenylbut-3-enyl)oxirane* (1.36 g, 7.79 mmol) gave, following purification of the resulting residue by column chromatography (petroleum ether/ Et_2O 1:1 (R_f = 0.15) to 4.5:5.5 to 4:6), the corresponding β -hydroxysulfonamide as a crude white solid (2.08 g, 86%). Reaction of the β -hydroxysulfonamide gave, following purification of the resulting residue by

column chromatography (petroleum ether/Et₂O 9:1), *aziridine* **121** as a colourless oil (1.08 g, 47%).

R_f 0.24 (petroleum ether/Et₂O 9:1); IR (neat) 2988m, 2935m, 1627w (C=C), 1480m, 1306s (S=O), 1237w, 1130s (S=O), 1006w and 707s (C_{Ar-H}) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.28 (5H, m, 5 $\times$ C_{Ar-H}), 5.33 (1H, s, =CH(H)), 5.13 (1H, s, =CH(H)), 2.79-2.61 (3H, m, CH₂, CHN), 2.58 (1H, d, J 7, CH(H)N, *trans* to alkyl chain), 2.05 (1H, d, J 5, CH(H)N, *cis* to alkyl chain), 1.82-1.63 (2H, m, CH₂), 1.48 (9H, s, *t*Bu); ¹³C NMR (100 MHz, CDCl₃) δ 146.9 (=C), 140.5 (C_{Ar quat}), 128.4 (2 $\times$ C_{Ar ortho}), 127.5 (2 $\times$ C_{Ar}), 126.0 (C_{Ar}), 113.2 (=CH₂), 59.2 (SC), 38.0 (CHN), 34.2 (CH₂N), 32.1 (CH₂), 30.0 (CH₂), 24.2 (SCMe₃); MS CI m/z (rel. int.) 311 (M + H⁺, 100), 294 (35), 230 (25); HRMS m/z calcd for C₁₆H₂₄NO₂S, 294.1522, found 294.1522.

1-(*tert*-Butylsulfonyl)-2-(pent-4-enyl)aziridine **14a**¹⁰

1,6-Heptadiene (1.40 mL, 10.39 mmol) was added dropwise to a stirred suspension of BusNCI₂Na (1.34 g, 6.93 mmol) and PTAB (391 mg, 1.04 mmol) in MeCN (52 mL) at room temperature. After stirring for 16 h, the reaction mixture was filtered and then evaporated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/Et₂O 95:5) gave *aziridine* **14a** as a colourless oil (802 mg, 50%).

R_f 0.22 (petroleum ether/Et₂O 95:5); IR (neat) 3077w, 2980s, 2935s, 1641m (C=C), 1481m, 1458m, 1397w, 1366w, 1307s (S=O), 1240m, 1131s (S=O) and 935m cm⁻¹;

(10) Gontcharov, A. V.; Liu, H.; Sharpless, K. B. *Org. Lett.* **1999**, *1*, 783–786.

^1H NMR (400 MHz, CDCl_3) δ 5.83 (1H, ddt, J 13, 7, 7, =CH), 5.05-4.96 (2H, m, $\text{H}_2\text{C=}$), 2.75-2.69 (1H, m, CHN), 2.59 (1H, d, J 7, CH(*H*)N, *trans* to alkyl chain), 2.14-2.09 (2H, m, =CHCH₂), 2.07 (1H, d, J 5, *cis* to alkyl chain), 1.65-1.48 (13H, 2 $\times$ CH₂, *t*Bu); ^{13}C NMR (100 MHz, CDCl_3) δ 138.0 (=CH), 115.0 ($\text{H}_2\text{C=}$), 59.2 (SC), 38.3 (CHN), 34.0 (CH₂N), 33.1 (=CHCH₂), 30.6 (CH₂), 25.5 (CH₂), 24.2 (SCMe₃); MS CI m/z (rel. int.) 249 ($\text{M} + \text{NH}_4^+$, 30), 232 ($\text{M} + \text{H}^+$, 40), 176 (30), 112 (100); HRMS m/z calcd for $\text{C}_{11}\text{H}_{22}\text{NO}_2\text{S}$, 232.1371, found 232.1362.

1-(*tert*-Butylsulfonyl)-2-(3-methylenepent-4-enyl)aziridine 14b

2-(3-Methylenepent-4-enyl)oxirane¹¹

*n*BuLi (1.6 M in hexanes, 28.13 mL, 45.00 mmol) was added dropwise to a stirred solution of TMP (7.59 mL, 45.00 mmol) in THF (90 mL) at $-78\text{ }^\circ\text{C}$. Following warming to $25\text{ }^\circ\text{C}$ for 30 min, the solution was cooled to $-78\text{ }^\circ\text{C}$ and a solution of *t*BuOK (5.05 g, 45.00 mmol) in THF (30 mL) was added. Following stirring for 5 min at $-78\text{ }^\circ\text{C}$, isoprene (7.59 mL, 30.00 mmol) was added dropwise. The resultant red solution was stirred at $-78\text{ }^\circ\text{C}$ for 30 min, then epichlorohydrin (4.69 mL, 60.00 mmol) was added in one portion. The resultant orange solution was warmed to $0\text{ }^\circ\text{C}$ and stirred for 90 min at this temperature. Sat. aqueous NH_4Cl (10 mL) was added and the aqueous phase was washed with Et_2O ($3 \times 50\text{ mL}$). The combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/ Et_2O 98:2) gave 2-(3-methylenepent-4-enyl)oxirane as a colourless oil (1.51 g, 41%).

(11) Klusener, P. A. A.; Hommes, H. H.; Verkruijsse, H. D.; Brandsma, L. *J. Chem. Soc., Chem. Commun* **1985**, 1677–1678.

R_f 0.38 (petroleum ether/Et₂O 98:2); IR (neat) cm⁻¹ 3089w, 2980s, 2925s, 1596s (C=C), 1410w, 1261m and 994m; ¹H NMR (400 MHz, CDCl₃) δ 6.39 (1H, dd, J 18, 11, =CH), 5.27 (1H, app. d, J 18, =CH(*H*)), 5.09 (1H, app. d, J 11, =CH(*H*)), 5.05-5.03 (2H, m, =CH₂), 2.99-2.95 (1H, m, CHO), 2.78-2.76 (1H, m, CH(*H*)O), 2.51 (1H, dd, J 5, 3, CH(*H*)O), 2.47-2.31 (2H, m, =CHCH₂), 1.82-1.68 (2H, m, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 145.3 (=C), 138.5 (=CH), 116.1 (=CH₂), 113.5 (=CH₂), 52.0 (CHO), 47.2 (CH₂O), 31.0 (CH₂), 27.6 (=CHCH₂); MS CI m/z (rel. int.) 142 (M + NH₄⁺, 100), 125 (M + H⁺, 95), 107 (95), 81 (35); HRMS m/z calcd for C₈H₁₃O, 125.0966, found 125.0968.

1-(*tert*-Butylsulfonyl)-2-(3-methylenepent-4-enyl)aziridine **14b**

Following **General procedure A** using 2-(3-methylenepent-4-enyl)oxirane (1.50 g, 12.14 mmol) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 1:1, R_f = 0.34), the corresponding β -hydroxysulfonamide as a crude yellow solid (1.56 g, 49%) Reaction of the β -hydroxysulfonamide gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), aziridine **14b** as a colourless oil (889 mg, 60%).

R_f 0.36 (petroleum ether/Et₂O 9:1); IR (neat) 3088m, 2987s, 2955s, 1596s (C=C), 1481s, 1458s, 1397m, 1306s (S=O), 1238m, 1131s (S=O) and 1070w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.40 (1H, dd, J 18, 11, =CH), 5.24 (1H, app. d, J 18, =CH(*H*)), 5.09 (1H, app. d, J 11, =CH(*H*)), 5.05-5.03 (2H, m, =CH₂), 2.80-2.74 (1H, m, CHN), 2.61 (1H, d, J 7, CH(*H*)N, *trans* to alkyl chain), 2.44-2.31 (2H, m, =CCH₂), 2.11 (1H, d, J 5, CH(*H*)N, *cis* to alkyl chain), 1.85-1.68 (2H, m, CH₂), 1.49 (9H, s, ^{*t*}Bu); ¹³C NMR (100 MHz, CDCl₃) δ 114.8 (=C), 138.3 (=CH), 116.5 (=CH₂), 113.5 (=CH₂),

59.2 (SC), 38.1 (CHN), 34.2 (CH₂N), 29.9 (CH₂), 28.1 (=CCH₂), 24.2 (SCMe₃); MS
CI *m/z* (rel. int.) 261 (M + NH₄⁺, 5), 244 (M + H⁺, 15), 124 (100); HRMS *m/z* calcd
for C₁₂H₂₂NO₂S, 244.1371, found 244.1378.

(II) Synthesis and characterization data for amines**General procedure B:** Bicyclic amine preparation

ⁿBuLi (1.6 M in hexanes, 0.94 mL, 1.5 mmol) was added dropwise to a stirred solution of dicyclohexylamine (0.30 mL, 1.5 mmol) in ^tBuOMe (5 mL) at $-78\text{ }^{\circ}\text{C}$ under argon. Following warming to room temperature for 30 min, the reaction was cooled to $0\text{ }^{\circ}\text{C}$ and a solution of aziridine (0.5 mmol) in ^tBuOMe (10 mL) at $0\text{ }^{\circ}\text{C}$ was added dropwise over 1 h *via* cannula and the reaction was left to stir at $0\text{ }^{\circ}\text{C}$. On completion of the reaction (tlc monitoring), sat. NH_4Cl (5 mL) and Et_2O (5 mL) were added. The phases were separated and the aqueous layer extracted with Et_2O ($2 \times 15\text{ mL}$). The organic layers were combined, dried (MgSO_4) and evaporated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/ Et_2O or EtOAc, SiO_2) gave the bicyclic amine.

N*-[(1*R**,2*R**,5*S**)-Bicyclo[3.1.0]hexan-2-yl]-4-methylbenzenesulfonamide **8*

Following **General procedure B** using **aziridine 6** (126 mg, 0.5 mmol) (reaction time = 16 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/EtOAc 9:1 to 17:3), *bicyclic amine 8* as a colourless oil (59 mg, 47%).

R_f 0.23 (petroleum ether/EtOAc 9:1); IR (neat) 3272br.s (N–H), 3039w (cyclopropane), 2930m, 2870m, 1599m, 1495w, 1428m, 1322s (S=O), 1157s (S=O), 1093s, 1012m and 736m ($\text{C}_{\text{Ar-H}}$) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (2H, d, J 9,

2 × C_{Ar}H), 7.33 (2H, d, *J* 9, 2 × C_{Ar}H), 4.66 (1H, d, *J* 8, NH), 3.73-3.66 (1H, m, NCH), 2.43 (3H, s, Me), 1.82-1.68 (1H, m, CH(*H*)), 1.62 (1H, dd, *J* 13, 8, CH(*H*)), 1.49 (1H, dd, *J* 14, 8, CH(*H*)), 1.38-1.25 (2H, m, CH(*H*) and NCHCH), 1.13-1.05 (1H, m, CH), 0.41-0.29 (1H, m, cyclopropane-CH(*H*)_{exo}), 0.08-0.02 (1H, m, cyclopropane-CH(*H*)_{endo}); ¹³C NMR (100 MHz, CDCl₃) δ 143.2 (C_{Ar} quatMe), 138.1 (SC), 129.7 (2 × C_{Ar}), 127.0 (2 × C_{Ar}), 56.0 (NCH), 28.3 (CH₂), 24.4 (CH₂), 22.2 (CH), 21.5 (Me), 16.3 (NCHCH), 6.7 (cyclopropane-CH₂); MS CI *m/z* (rel. int.) 269 (M + NH₄⁺, 55), 252 (M + H⁺, 100), 189 (90), 172 (30), 155 (30), 98 (55), 96 (50); HRMS *m/z* calcd for C₁₃H₁₈NO₂S, 252.1058, found 252.1050; nOe experiments: irradiation at 3.73 (CHNH) saw reciprocal signal enhancement at 0.08 (cyclopropane-CH(*H*)_{endo}), no signal enhancement was observed at 0.41 (cyclopropane-CH(*H*)_{exo}).

N*-[(1*R**,2*R**,5*S**)-Bicyclo[3.1.0]hexan-2-yl]-2-methylpropane-2-sulfonamide **10*

Following **General procedure B** using **aziridine 9** (109 mg, 0.5 mmol) (reaction time = 2 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 7:3), *bicyclic amine 10* as a white solid (82 mg, 75%).

(mp = 101-102 °C); *R*_f 0.38 (petroleum ether/Et₂O 4:1); IR (film) 3273s (N–H), 3036m (cyclopropane), 2935s, 1454m, 1364w (S=O), 1297s, 1131s (S=O), 1108m, 1058w and 1025m cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.16 (1H, d, *J* 9, NH), 3.88-3.84 (1H, m, NHCH), 1.89-1.79 (1H, m, CH(*H*)), 1.73-1.63 (2H, m, CH(*H*)),

CH(*H*)CHN), 1.52-1.46 (1H, m, CH(*H*)CHN), 1.44-1.41 (2H, m, CH₂CH, NCHCH), 1.40 (9H, s, ^{*t*}Bu), 0.48-0.42 (1H, m, cyclopropane-CH(*H*)_{exo}), 0.13-0.10 (1H, m, cyclopropane-CH(*H*)_{endo}); ¹³C NMR (100 MHz, CDCl₃) δ 59.6 (SC), 57.6 (CHN), 29.6 (CH₂CHN), 24.4 (CH₂), 24.3 (SCMe₃), 23.1 (NHCH), 16.4 (CH₂CH), 7.0 (cyclopropane-CH₂); MS CI *m/z* (rel. int.) 235 (M + NH₄⁺, 45), 218 (M + H⁺, 30), 98 (100), 81 (50); HRMS *m/z* calcd for C₁₀H₂₀NO₂S, 218.1215, found 218.1209.

N*-[*(1S,2S,5R)*-Bicyclo[3.1.0]hexan-2-yl]-2-methylpropane-2-sulfonamide **13a*

Following **General procedure B** using (*S*)-aziridine **12a** (109 mg, 0.5 mmol) (reaction time = 2 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 7:3), *bicyclic amine 13a* as a white solid (81 mg, 74%).

[α]_D²⁵ = −13.7 (*c* 1.1, CHCl₃); Data matches that of racemic *N*-[(1*R**,2*R**,5*S**)-bicyclo[3.1.0]hexan-2-yl]-2-methylpropane-2-sulfonamide **10** above. The enantiomeric excess (>99%) was confirmed by chiral GC (Cydex-B column, 100 °C, 0.5 mLmin^{−1}).

----Area percent report----

RT	Area	Area%
874.85	1202648	100

----Area percent report----

RT	Area	Area%
863.02	656644	49.69
879.99	665578	50.31

N*-[*(1R*,2R*,5S*,6R*)*-6-Ethylbicyclo[3.1.0]hexan-2-yl]-2-methylpropane-2-sulfonamide **13b*

Following **General procedure B** using **aziridine 12b** (123 mg, 0.5 mmol) (reaction time = 3 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 4:1), **bicyclic amine 13b** as a white solid (105 mg, 85%).

(mp = 73-75 °C); *R*_f 0.19 (petroleum ether/Et₂O 4:1); IR (film) 3275br.s (N–H), 3020m (cyclopropane), 2960s, 2872s, 1455m, 1396w, 1366w, 1298s (S=O), 1172m,

1128s (S=O), 1062m and 1016s cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.03 (1H, d, J 10, NH), 3.88 (1H, dd, J 10, 6, CHNH), 1.84-1.63 (3H, m, CH(*H*)CHN, CH_2), 1.52-1.40 (10H, m, CH(*H*)CHN, ^tBu), 1.27-1.11 (4H, m, NCHCH, CH_2CH , CH_2Me), 0.91 (3H, t, J 7, CH_2Me), 0.44 (1H, app. sept, J 3, cyclopropane-CH); ^{13}C NMR (100 MHz, CDCl_3) δ 59.6 (SC), 57.6 (CHN), 31.2 (NCHCH), 30.4 (CH_2CHN), 25.3 (CH_2), 24.7 (CH_2Me), 24.3 (SCMe_3), 23.8 (CH_2CH), 22.3 (cyclopropane-CH), 13.5 (CH_2Me); MS CI m/z (rel. int.) 263 ($\text{M} + \text{NH}_4^+$, 15), 246 ($\text{M} + \text{H}^+$, 5), 126 (30), 109 (100); HRMS m/z calcd for $\text{C}_{12}\text{H}_{27}\text{N}_2\text{O}_2\text{S}$, 263.1793, found 263.1802; nOe experiments: irradiation at 3.88 (CHNH) saw reciprocal signal enhancement at 0.44 (cyclopropane-CH), no signal enhancement was observed at 1.27-1.11 (CH_2Me).

N*-[(1*R**,2*R**,5*S**,6*R**)-6-Ethylbicyclo[3.1.0]hexan-2-yl]-2-methylpropane-2-sulfonamide **13c*

Following **General procedure B** using *aziridine 12c* (123 mg, 0.5 mmol) (reaction time = 4 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/ Et_2O 4:1), *bicyclic amine 13c* as a white solid (56 mg, 46%).

(mp = 69-71 $^{\circ}\text{C}$); R_f 0.20 (petroleum ether/ Et_2O 4:1); IR (film) 3273br.s (N-H), 3041w (cyclopropane), 2963s, 2872m, 1454m, 1337w, 1299s (S=O), 1177w, 1129s

(S=O), 1063w and 1018m cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.22 (1H, d, J 10, NH), 3.81-3.76 (1H, m, CHNH), 2.04-1.94 (1H, m, CH(*H*)CHN), 1.85-1.78 (2H, m, CH_2), 1.57-1.50 (2H, m, CH(*H*)CHN, CHNCH), 1.42-1.40 (10H, m, CH_2CH , *t*Bu), 1.25-1.19 (2H, m, CH_2Me), 0.98 (3H, t, J 7, CH_2Me), 0.78-0.69 (1H, m, cyclopropane-CH); ^{13}C NMR (100 MHz, CDCl_3) δ 59.7 (SC), 56.7 (CHN), 37.6 (NCHCH), 28.8 (CH_2CHN), 24.3 (SCMe_3), 22.8 (CH_2), 22.6 (CH_2Me), 22.2 (CH_2CH), 17.0 (cyclopropane-CH), 14.6 (CH_2Me); MS CI m/z (rel. int.) 263 ($\text{M} + \text{NH}_4^+$, 10), 246 ($\text{M} + \text{H}^+$, 5), 155 (35), 109 (100), 108 (25); HRMS m/z calcd for $\text{C}_{12}\text{H}_{27}\text{N}_2\text{O}_2\text{S}$, 263.1793, found 263.1787; nOe experiments: irradiation at 3.81 (CHNH) saw reciprocal signal enhancement at 1.25 (CH_2Me), no signal enhancement was observed at 0.78 (cyclopropane-CH).

N*-[(1*R**,2*S**,5*S**)-6,6-Dimethylbicyclo[3.1.0]hexan-2-yl]-2-methylpropane-2-sulfonamide **13d*

Following **General procedure B** using *aziridine 12d* (123 mg, 0.5 mmol) (reaction time = 2 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/ Et_2O 4:1), *bicyclic amine 13d* as a pale yellow solid (69 mg, 56%).

(mp = 100-102 °C); R_f 0.19 (petroleum ether/Et₂O 4:1); IR (film) 3286br.s (N–H), 2959m, 2942m, 2867s, 1454m, 1398w, 1364w, 1293s (S=O), 1129s (S=O), 1072w and 1022w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.25 (1H, d, J 10, NH), 3.77-3.72 (1H, m, CHNH), 2.03-1.91 (2H, m, CH₂), 1.84-1.79 (1H, m, CH(H)), 1.58-1.49 (1H, m, CH(H)), 1.39 (9H, s, ^{*t*}Bu), 1.28 (1H, t, J 6, CH₂CH), 1.16 (1H, d, J 7, NCHCH), 0.97 (3H, s, cyclopropane-Me), 0.94 (3H, s, cyclopropane-Me); ¹³C NMR (100 MHz, CDCl₃) δ 59.6 (SC), 56.9 (CHNH), 38.0 (CH₂), 37.5 (NCHCH), 31.2 (CH₂CH), 28.0 (cyclopropane-CMe(Me)), 24.3 (SCMe₃), 23.2 (CH₂), 19.3 (cyclopropane-C), 14.8 (cyclopropane-CMe(Me)); MS CI m/z (rel. int.) 263 (M + NH₄⁺, 25), 246 (M + H⁺, 5), 109 (100); HRMS m/z calcd for C₁₂H₂₇N₂O₂S, 263.1793, found 263.1805.

2-Methyl-*N*-[(1*R**,2*R**,5*S**)-5-methylbicyclo[3.1.0]hexan-2-yl]propane-2-sulfonamide **13e**

Following **General procedure B** using **aziridine 12e** (116 mg, 0.5 mmol) (reaction time = 2 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 4:1), **bicyclic amine 13e** as a white solid (94 mg, 81%).

(mp = 104-106 °C); R_f 0.32 (petroleum ether/Et₂O 4:1); IR (film) 3271br.s (N–H), 3031m (cyclopropane), 2924s, 14452m, 1365m, 1294s (S=O), 1168w, 1127s (S=O), 1052m and 1021w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.41 (1H, br.s, NH), 3.79 (1H, dd, J 10, 6, CHNH), 1.77-1.65 (3H, m, CH₂CHN, CH(H)C), 1.56-1.47 (1H, m, CH(H)C), 1.38 (9H, s, ^{*t*}Bu), 1.26 (3H, s, CMe), 1.09 (1H, dd, J 8, 4, NCHCH), 0.37-

0.29 (2H, m, cyclopropane-CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 59.6 (SC), 58.5 (CHN), 31.4 (CH₂CHN), 30.6 (CH₂C), 30.0 (NCHCH), 24.6 (CMe), 24.3 (SCMe₃), 21.1 (CMe), 14.2 (cyclopropane-CH₂); MS CI *m/z* (rel. int.) 249 (M + NH₄⁺, 10), 232 (M + H⁺, 5), 155 (10), 112 (30), 95 (100), 94 (30); HRMS *m/z* calcd for C₁₁H₂₅N₂O₂S, 249.1637, found 249.1626.

N*-[(1*R**,2*R**,5*S**)-4,4-Dimethylbicyclo[3.1.0]hexan-2-yl]-2-methylpropane-2-sulfonamide **13f*

Following **General procedure B** using *aziridine 12f* (123 mg, 0.5 mmol) (reaction time = 1.5 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 4:1), *bicyclic amine 13f* as a white solid (122 mg, 99%).

(mp = 91-93 °C); *R*_f 0.23 (petroleum ether/Et₂O 4:1); IR (film) 3300br.s (N-H), 3002m (cyclopropane), 2956s, 1431m, 1365w, 1300s (S=O), 1155w, 1127s (S=O) and 1045m cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.99 (1H, d, *J* 9, NH), 3.92-3.88 (1H, m, CHNH), 1.49-1.44 (3H, m, NCHCH, CH₂CHN), 1.40 (9H, s, ^tBu), 1.28-1.23 (1H, m, CMe₂CH), 1.20 (3H, s, CMe(*Me*)), 1.01 (3H, s, CMe(*Me*)), 0.48-0.43 (1H, m, cyclopropane-CH(*H*)_{exo}), 0.10-0.07 (1H, m, cyclopropane-CH(*H*)_{endo}); ¹³C NMR (100 MHz, CDCl₃) δ 59.6 (SC), 58.4 (CHN), 45.0 (NCHCH), 38.5 (CMe₂), 31.1 (CMe(*Me*)), 30.1 (CMe₂CH), 27.0 (CMe(*Me*)), 24.3 (SCMe₃), 24.2 (CH₂CHN), 6.9 (cyclopropane-CH₂); MS CI *m/z* (rel. int.) 263 (M + NH₄⁺, 20), 246 (M + H⁺, 5), 109 (100); HRMS *m/z* calcd for C₁₂H₂₇N₂O₂S, 263.1793, found 263.1783.

N*-[(1*R**,2*S**,5*R**)-3,3-diphenylbicyclo[3.1.0]hexan-2-yl]-2-methylpropane-2-sulfonamide **13g*

Following **General procedure B** using *aziridine 12g* (185 mg, 0.5 mmol) (reaction time = 2 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 4:1), *bicyclic amine 13g* as a pale yellow solid (157 mg, 85%).

(mp = 192-194 °C); *R*_f 0.20 (petroleum ether/Et₂O 4:1); IR (film) 3274br.s (N–H), 3031m (cyclopropane), 2982s, 1598m, 1495m, 1335m, 1394w, 1365m, 1296s (S=O), 1216w, 1129s (S=O), 1057w and 702s (C_{Ar}–H) cm^{–1}; ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.16 (10H, m, 10 × C_{Ar}H), 4.57 (1H, dd, *J* 10, 2, CHNH), 3.31 (1H, d, *J* 10, NH), 3.04 (1H, dd, *J* 14, 7, CCH(*H*)), 2.07 (1H, dd, *J* 14, 3, CCH(*H*)), 1.78-1.71 (1H, m, CCH₂CH), 1.57-1.52 (1H, m, NCHCH), 1.33 (9H, s, ^{*t*}Bu), 0.97-0.92 (1H, m, cyclopropane-CH(*H*)_{exo}), 0.49-0.47 (1H, m, cyclopropane-CH(*H*)_{endo}); ¹³C NMR (100 MHz, CDCl₃) δ 147.3 (C_{Ar} quat), 144.4 (C_{Ar} quat), 128.9 (2 × C_{Ar} ortho), 128.3 (2 × C_{Ar} ortho), 128.1 (2 × C_{Ar}), 127.3 (2 × C_{Ar}), 126.7 (C_{Ar}), 126.2 (C_{Ar}), 65.2 (CHNH), 62.4 (CPh₂), 59.8 (SC), 42.2 (CCH₂), 25.8 (NCHCH), 24.2 (SCMe₃), 19.5 (CH₂CH), 18.7 (cyclopropane-CH₂); MS CI *m/z* (rel. int.) 387 (M + NH₄⁺, 25), 370 (M + H⁺, 10), 250 (25), 234 (80), 233 (100), 167 (30); HRMS *m/z* calcd for C₂₂H₃₁N₂O₂S, 387.2106, found 387.2099.

N*-[*(1R*,2R*,3S*,5R*)*-3-Allylbicyclo[3.1.0]hexan-2-yl]-2-methylpropane-2-sulfonamide **13h*

Following **General procedure B** using *aziridine 12h* (129 mg, 0.5 mmol) (reaction time = 2 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 4:1), *bicyclic amine 13h* as a white solid (127 mg, 98%).

(mp = 67-69 °C); *R*_f 0.20 (petroleum ether/Et₂O 4:1); IR (film) 3270br.s (N–H), 3076m (cyclopropane), 2982s, 2935s, 1640m (C=C), 1455s, 1396w, 1366m, 1300s (S=O), 1209m, 1129s (S=O), 1056m and 1022w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.76-5.66 (1H, m, =CH), 5.02-4.96 (2H, m, H₂C=), 4.18 (1H, d, *J* 10, NH), 3.52 (1H, dd, *J* 10, 2, CHNH), 2.29-2.14 (3H, m, =CHCH(*H*), NCHCH, =CHCH₂CH), 1.95-1.88 (1H, m, =CHCH(*H*)), 1.49-1.33 (12H, m, ^{*t*}Bu, CH₂, CH₂CH), 0.69-0.64 (1H, m, cyclopropane-CH(*H*)), 0.21-0.18 (1H, m, cyclopropane-CH(*H*)); ¹³C NMR (100 MHz, CDCl₃) δ 136.9 (=CH), 116.0 (H₂C=), 63.6 (CHNH), 59.6 (SC), 50.7 (=CHCH₂CH), 40.4 (=CHCH₂), 31.7 (NCHCH), 25.5 (CH₂), 24.3 (SCMe₃), 18.8 (CH₂CH), 12.9 (cyclopropane-CH₂); MS CI *m/z* (rel. int.) 275 (M + NH₄⁺, 100), 258 (20), 138 (25), 121 (80); HRMS *m/z* calcd for C₁₃H₂₄NO₂S, 258.1521, found 258.1522; nOe experiments: irradiation at 3.52 (CHNH) saw reciprocal signal enhancement at 2.29 (=CHCH(*H*)) and 0.21 (cyclopropane-CH(*H*)_{endo}), no signal enhancement was seen at 0.69 (cyclopropane-CH(*H*)_{exo}).

N*-[(1*R**,2*S**,3*R**,5*R**)-3-Allyl-3-isopropylbicyclo[3.1.0]hexan-2-yl]-2-methylpropane-2-sulfonamide **13i*

Following **General procedure B** using *aziridine 12i* (150 mg, 0.5 mmol) (reaction time = 2 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 4:1), *bicyclic amine 13i* as a white solid (147 mg, 98%).

(mp = 81-83 °C); *R_f* 0.34 (petroleum ether/Et₂O 4:1); IR (film) 3301s (N–H), 3060m (cyclopropane), 2977s, 2878s, 1637m (C=C), 1459m, 1305s (S=O), 1207w, 1130s (S=O), 1089m and 1029w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.22-6.12 (1H, m, =CH), 5.24-5.11 (2H, m, H₂C=), 4.49 (1H, d, *J* 11, NH), 3.51 (1H, dd, *J* 11, 3, CHNH), 2.43-2.37 (1H, m, =CHCH(*H*)), 2.34-2.28 (1H, m, =CHCH(*H*)), 1.85 (1H, dd, *J* 15, 7, CCH(*H*)), 1.69 (1H, sept. *J* 7, CHMe₂), 1.43 (9H, s, ^{*t*}Bu), 1.35-1.21 (3H, m, CCH(*H*), NCHCH, CH₂CH), 1.02-0.97 (1H, m, cyclopropane-CH(*H*)_{exo}), 0.92 (3H, d, *J* 7, CHMe(*Me*)), 0.89 (3H, d, *J* 7, CHMe(*Me*)), 0.22-0.19 (1H, m, cyclopropane-CH(*H*)_{endo}); ¹³C NMR (100 MHz, CDCl₃) δ 137.7 (=CH), 116.8 (H₂C=), 63.8 (CHNH), 60.9 (*C*^{*i*}Pr), 59.5 (SC), 39.3 (=CHCH₂), 36.0 (CCH₂), 33.1 (CHMe₂), 26.9 (NCHCH), 24.4 (SCMe₃), 20.8 (CH₂CH), 18.3 (CHMe(*Me*)), 18.2 (CHMe(*Me*)), 17.8 (cyclopropane-CH₂); MS CI *m/z* (rel. int.) 317 (M + NH₄⁺, 15), 300 (M + H⁺, 30), 180 (30), 163 (100); HRMS *m/z* calcd for C₁₆H₃₃N₂O₂S, 317.2263, found

317.2261; nOe experiments: irradiation at 3.51 (CHNH) saw reciprocal enhancement at 1.69 (CHMe₂) and 0.22 (cyclopropane-CH(H)_{endo}), no signal enhancement was seen at 1.02 (cyclopropane-CH(H)_{exo}), irradiation at 1.69 (CHMe₂) saw reciprocal enhancement at 0.22 (cyclopropane-CH(H)_{endo}), no signal enhancement was seen at 1.02 (cyclopropane-CH(H)_{exo}).

N*-[*(1R*,2R*,5R*, 6R*)*-Hexahydro-1*H*-cyclopenta(1,3)cyclopropa(1,2)benzen-3-yl]-2-methylpropane-2-sulfonamide **13j*

Following **General procedure B** using **aziridine 12j** (135 mg, 0.5 mmol) (reaction time = 3 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 4:1), *tricyclic amine 13j* as a white solid (108 mg, 80%).

(mp = 129-131 °C); *R*_f 0.21 (petroleum ether/Et₂O 4:1); IR (film) 3270br.s (N–H), 3056m (cyclopropane), 2973s, 2255m, 1656w (C=C), 1435m, 1366w, 1307s (S=O), 1293s, 1221w, 1127s (S=O), 1071m and 1016w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.60-5.55 (1H, m, =CH), 5.49-5.45 (1H, m, =CH), 4.18 (1H, d, *J* 9, NH), 3.90 (1H, dd, *J* 9, 6, CHNH), 2.50-2.21 (4H, m, 2 × =CHCH₂), 1.83-1.57 (4H, m, CH₂CHN, CH₂), 1.39 (9H, s, ^{*t*}Bu), 1.21 (1H, d, *J* 3, NCHCH), 0.84-0.82 (1H, m, cyclopropane-CH); ¹³C NMR (100 MHz, CDCl₃) δ 124.7 (=CH), 124.0 (=CH), 59.6 (SC), 58.4

(CHN), 31.6 (NCHCH), 31.2 (CH₂CHN), 30.5 (CH₂), 29.0 (=CHCH₂), 27.5 (=CHCH₂C), 24.4 (SCMe₃), 23.6 (=CHCH₂), 18.1 (cyclopropane-CH); MS CI *m/z* (rel. int.) 287 (M + NH₄⁺, 20), 270 (M + H⁺, 5), 150 (15), 133 (100); HRMS *m/z* calcd for C₁₄H₂₇N₂O₂S, 287.1793, found 287.1780.

2-Methyl-N-[(1*R**,2*S**,5*R**,6*R**)-6-phenylbicyclo[3.1.0]hexan-2-yl]propane-2-sulfonamide **13k**

Following **General procedure B** using *aziridine 12k* (146 mg, 0.5 mmol) (reaction time = 2 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 7:3), *bicyclic amine 13k* as a pale yellow solid (69 mg, 47%).

(mp = 161-163 °C); *R_f* 0.25 (petroleum ether/Et₂O 7:3); IR (film) 3275br.s (N-H), 3030m (cyclopropane), 2954m, 1603m, 1449m, 1364w, 1339w, 1294s (S=O), 1213w, 1173w, 1121s (S=O), 1068m, 1030m and 749s (Ar-H) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.24 (2H, m, 2 × C_{Ar}H), 7.18-7.14 (1H, m, C_{Ar}H), 7.03-7.01 (2H, m, 2 × C_{Ar}H), 4.30 (1H, d, *J* 10, NH), 4.09 (1H, dd, *J* 10, 6, CHNH), 2.06-1.91 (2H, m, CH₂CHN), 1.85-1.64 (5H, m, CH₂, 3 × CH), 1.43 (9H, s, ^{*t*}Bu); ¹³C NMR (100 MHz, CDCl₃) δ 141.5 (C_{Ar} quat), 128.3 (2 × C_{Ar}), 125.7 (C_{Ar}), 125.6 (2 × C_{Ar}), 59.7 (SC), 57.8 (CHN), 34.7 (CH₂CHN), 30.9 (CH), 28.4 (CH₂), 25.1 (CHAr), 24.6 (CH), 24.3 (SCMe₃); MS CI *m/z* (rel. int.) 311 (M + NH₄⁺, 5), 157 (100), 156 (30), 91 (30); HRMS *m/z* calcd for C₁₆H₂₇N₂O₂S, 311.1793, found 311.1800.

2-Methyl-N-[(1*R**,2*R**,5*R**)-5-phenylbicyclo[3.1.0]hexan-2-yl]propane-2-sulfonamide **13l**

Following **General procedure B** using *aziridine 12l* (147 mg, 0.5 mmol) (reaction time = 4 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 4:1), *bicyclic amine 13l* as a white solid (132 mg, 90%).

(mp = 129-131 °C); *R*_f 0.21 (petroleum ether/Et₂O 4:1); IR (film) 3269 br. s (N–H), 2973m, 2932m, 2361m, 1450m, 1295s (S=O), 1127s (S=O), 1029m and 719m (C_{Ar}–H) cm^{–1}; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.29 (2H, m, 2 × C_{Ar}H), 7.22-7.17 (3H, m, 3 × C_{Ar}H), 4.03 (1H, dd, *J* 10, 6, CHNH), 3.94 (1H, d, *J* 10, NH), 2.23-2.13 (2H, m, CH₂), 1.92-1.87 (1H, m, CH(*H*)), 1.83 (1H, dd, *J* 9, 4, NCHCH), 1.78-1.69 (1H, m, CH(*H*)), 1.42 (9H, s, ^tBu), 0.97-0.94 (1H, m, cyclopropane-CH(*H*)_{exo}), 0.89-0.86 (1H, m, cyclopropane-CH(*H*)_{endo}); ¹³C NMR (100 MHz, CDCl₃) δ 143.6 (C_{Ar} quat), 128.4 (2 × C_{Ar} ortho), 126.1 (2 × C_{Ar}), 125.8 (C_{Ar}), 59.7 (SC), 58.0 (CHNH), 32.4 (CH₂), 32.3 (NCHCH), 30.9 (CH₂), 29.0 (CC_{Ar}), 24.3 (SCMe₃), 17.9 (cyclopropane-CH₂); MS CI *m/z* (rel. int.) 311 (M + NH₄⁺, 100), 294 (M + H⁺, 5), 157 (90); HRMS *m/z* calcd for C₁₆H₂₇N₂O₂S, 311.1793, found 311.1804; nOe experiments: irradiation at 4.03 (CHNH) saw reciprocal signal enhancement at 0.89 (cyclopropane-CH(*H*)_{endo}), no signal enhancement was observed at 0.97 (cyclopropane-CH(*H*)_{exo}).

N*-[(1*R**,2*R**,6*S**)-Bicyclo[4.1.0]heptan-2-yl]-2-methylpropane-2-sulfonamide **15a*

Following **General procedure B** using *aziridine 14a* (116 mg, 0.5 mmol) (reaction time = 4 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 4:1), *bicyclic amine 15a* as a pale yellow solid (39 mg, 34%).

(mp = 72-74 °C); *R*_f 0.19 (petroleum ether/Et₂O 4:1); IR (film) 3288br.s (N–H), 3065m (cyclopropane), 2935s, 2860s, 1674w, 1454s, 1396w, 1365m, 1304s (S=O), 1209w, 1130s (S=O), 1069w and 1007w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.22 (1H, d, *J* 10, NH), 3.66-3.60 (1H, m, CHNH), 1.86-1.77 (1H, m, CH(*H*)CHN), 1.67-1.60 (2H, m, CH(*H*), CH(*H*)CHN), 1.42 (10H, m, ^tBu, NCHCH), 1.38-1.24 (1H, m, CH(*H*)), 1.16-1.08 (1H, m, CHCH₂), 1.03-0.94 (2H, m, CH₂), 0.71-0.65 (1H, m, cyclopropane-CH(*H*)), 0.08-0.06 (1H, m, cyclopropane-CH(*H*)); ¹³C NMR (100 MHz, CDCl₃) δ 59.6 (SC), 51.4 (CHN), 30.1 (NCHCH), 24.3 (SCMe₃), 22.4 (CH₂CHN), 17.3 (CH₂), 16.8 (CH₂), 10.1 (CHCH₂), 9.5 (cyclopropane-CH₂); MS CI *m/z* (rel. int.) 249 (M + NH₄⁺, 40), 232 (M + H⁺, 10), 112 (80), 95 (100); HRMS *m/z* calcd for C₁₁H₂₂NO₂S, 232.1371, found 232.1375.

2-Methyl-N-[(1*R**,2*R**,5*S**)-5-vinylbicyclo[3.1.0]hexan-2-yl]propane-2-sulfonamide **15b**

Following **General procedure B** using *aziridine 14b* (122 mg, 0.5 mmol) (reaction time = 3 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 4:1), *bicyclic amine 15b* as a white solid (104 mg, 85%).

(mp = 99-101 °C); *R*_f 0.25 (petroleum ether/Et₂O 4:1); IR (film) 3278br.s (N–H), 3067m (cyclopropane), 2974m, 2927s, 2865w, 1631m (C=C), 1451m, 1440m, 1397w, 1365w, 1295s (S=O), 1174w, 1124s (S=O) and 1001w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.73 (1H, dd, *J* 17, 11, =CH), 5.07 (1H, dd, *J* 17, 1, =CH(*H*)), 4.97 (1H, dd, *J* 11, 1, =CH(*H*)), 4.06 (1H, d, *J* 10, NH), 3.89 (1H, app. dd, *J* 10, 6, CHNH), 2.07-1.98 (1H, m, CH(*H*)CHN), 1.83-1.56 (3H, m, CH(*H*)CHN, CH₂), 1.45-1.39 (10H, m, NCHCH, ^tBu), 0.78-0.74 (1H, m, cyclopropane-CH(*H*)_{exo}), 0.67-0.65 (1H, m, cyclopropane-CH(*H*)_{endo}); ¹³C NMR (100 MHz, CDCl₃) δ 141.7 (=CH), 111.4 (=CH₂), 59.7 (SC), 57.8 (NCH), 32.2 (NCHCH), 31.5 (CH₂), 30.6 (CH₂CHN), 25.9 (=CHC), 24.3 (SCMe₃), 15.5 (cyclopropane-CH₂); MS CI *m/z* (rel. int.) 261 (M + NH₄⁺, 55), 244 (M + H⁺, 10), 107 (100); HRMS *m/z* calcd for C₁₂H₂₂NO₂S, 244.1371, found 244.1375.

(IV) ^1H and ^{13}C NMR spectra of aziridines

12e

12h

12i

S45

12j

S46

S47

12I

S48

14a

S49

14b

(V) ^1H and ^{13}C NMR spectra of amines

S52

S53

S54

S55

S56

13i

S61

S63

S64