Supporting information for

One-Carbon Homologation of *N*-Sulfonylaziridines to Allylic Amines using Dimethylsulfonium Methylide

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(1) General Directions

All reactions were conducted in oven-dried glassware under an atmosphere of nitrogen. THF and MeCN were degassed and dried over alumina under nitrogen.¹ Trimethylsulfonium iodide was dried under high vacuum prior to use. Column chromatography was carried out on Kieselgel 60 (40-63 μm) silica gel. Petrol refers to the fraction of petroleum ether boiling between 30 °C and 40 °C. Melting points were recorded on a Kofler hot block. IR spectra were recorded as thin films or KBr discs, using a 1750 FTIR spectrophotometer. ¹H and ¹³C NMR spectra were recorded at 25 °C, with DPX400 and AV400 spectrometers. ¹H and ¹³C NMR spectra were recorded in CDCl₃. Data are expressed as chemical shifts in parts per million (ppm) relative to residual chloroform (¹H δ 7.27), CDCl₃ (¹³C δ 77.0) as the internal standard on the δ scale. The multiplicity of each signal is designated by the following abbreviations; s, singlet; d, doublet; t, triplet; br, broad. Coupling constants *J* are given in Hz. Mass spectra were obtained using a GCT spectrometer or by the EPSRC National Mass Spectrometry Service Centre at the University of Swansea using a high resolution double focusing mass spectrometer with tandem

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ion trap. Specific rotations $[\alpha]_{\text{D}}^{\text{T}}$ were measured using a polarimeter with a cell of path length 1.0 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.

(II) Procedures and data for aziridines

N-Sulfonyl aziridines **5e**,² **7b**,² **7d**,² **7h**,³ **7i**,³ **9b**,³ **9c**,⁴ **11a**,⁵ **11b**³ and **11c**⁶ were prepared using literature procedures. *N*-Sulfonyl aziridines **5c**, **7e**, **7f**, **7j**, **9a**, **11d**, *cis/trans*-**13a** and *cis/trans*-**13b** were prepared from the corresponding alkene using general procedure A. Aziridines **7a**, **7c**, and **7g** were prepared from the corresponding epoxide using general procedure B.

General Procedure A.^{3,5} The appropriate alkene (1 equiv) was added to a stirred suspension of BusNCINa (1.2 equiv) or chloroamine-T (1.2 equiv) and phenyltrimethylammonium tribromide (PTAB) (0.1 equiv) in MeCN at room temperature. The mixture was stirred for 12–24 h, filtered and concentrated under reduced pressure. Purification of the residue by column chromatography (petrol/ Et₂O) gave the desired aziridine.

General Procedure B.^{7,8} The appropriate epoxide (1 equiv), *tert*-butylsulfonamide (1 equiv), benzyltrimethylammonium chloride (0.1 equiv), K₂CO₃ (0.1 equiv) and dioxane were heated at 95 °C for 16 h. The reaction was allowed to cool, filtered and concentrated under reduced pressure. Purification of the residue by column chromatography (MeOH/Et₂O/petrol) gave the corresponding β-hydroxysulfonamide. The resulting β-hydroxysulfonamide (1 equiv), Ms₂O (1.5 equiv), pyridine (2 equiv) and DMAP (0.1 equiv) were stirred at rt for 20 min. The reaction was diluted with Et₂O, washed with CuSO₄ solution and then brine. The organic layer was separated, dried (MgSO₄) and concentrated under reduced pressure. The resulting mesylated alcohol was heated to reflux in 10% saturated K₂CO₃ solution in THF for 12 h. The organic layer was separated, dried (MgSO₄) and concentrated under reduced pressure. Purification of the residue by column chromatography (Et₂O/petrol) gave the corresponding aziridine.

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1-Benzyl-2-pentylaziridine **5a**

1,2-epoxyheptane⁹ (1.66 g, 14.5 mmol) and benzylamine (4.66 g, 43.5 mmol) were dissolved in MeOH (15 mL) and heated to 130 °C in a sealed tube for 3 h. The solvent was evaporated *in vacuo* and the residue purified by bulb-to-bulb distillation (175 °C/0.1 torr) to give 1-(benzylamino)heptan-2-ol (2.73 g, 85%) as a colorless oil. IR (neat, cm⁻¹) 3311br, 3028m, 2929s, 1604w, 1455s, 1116m; ¹H NMR (400 MHz) δ 7.37-7.24 (m, 5H), 3.84 (d, *J* = 13, 1H), 3.79 (d, *J* = 13, 1H), 3.66-3.60 (m, 1H), 2.77 (dd, *J* = 12, 3, 1H), 2.47 (dd, *J* = 12, 9.5, 1H), 2.31 (br s, 1H), 1.49-1.24 (m, 8H), 0.90 (t, *J* = 7, 3H); ¹³C NMR (100 MHz) δ 140.0, 128.5, 128.1, 127.1, 69.6, 54.8, 53.6, 35.0, 31.9, 25.3, 22.6, 14.0; MS *m/z* (CI) 222 (M+H⁺, 100), 220 (27), 204 (22), 120 (31), 108 (30), 52 (29); HRMS calcd for C₁₄H₂₄NO (M+H⁺) 222.1852, found 222.1852.

To a solution of 1-(benzylamino)heptan-2-ol (600 mg, 2.71 mmol) and PPh₃ (782 mg, 2.98 mmol) in THF (8 mL) at 0 °C was added DEAD (0.54 mL, 2.98 mmol) dropwise. The reaction was left stirring for 3 h and then filtered through a pad of celite using CH₂Cl₂ : petrol (1:1). The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (Et₃N deactivated SiO₂, 30% Et₂O in petrol) to give aziridine **5a** (413 mg, 75%) as a colorless oil; R_f 0.30 (30% Et₂O in petrol). IR (neat, cm⁻¹) 3031w, 2958s, 2928s, 2856m, 1495m, 1454s, 1355s; ¹H NMR (400 MHz) δ 7.37-7.25 (m, 5H), 3.51 (d, *J* = 13, 1H), 3.32 (d, *J* = 13, 1H), 1.61 (d, *J* = 3, 1H), 1.48-1.21 (m, 10H), 0.86 (t, *J* = 7, 3H); ¹³C NMR (100 MHz) δ 139.5, 128.3, 128.2, 126.9, 65.1, 39.8, 34.1, 33.0, 31.6, 27.1, 22.6, 14.0; MS *m/z* (CI) 204 (M+H⁺, 100), 160 (29), 91 (44); HRMS calcd for C₁₄H₂₂N (M+H⁺) 204.1752, found 204.1759.

1-Boc-2-pentylaziridine **5b**

1,2-Epoxyheptane⁹ (1.66 g, 14.54 mmol) and NH₄OH (35%, 8.44 mL) in MeCN (3 mL) were heated in a sealed tube to 100 °C for 1 h. The reaction was cooled, then the solvent was evaporated *in vacuo* and the residue purified by bulb-to-bulb distillation (125 °C/0.2 torr) to give 1-aminoheptan-2-ol¹⁰ (1.56 g, 82%) as a colorless oil. IR (neat, cm⁻¹) 3353br, 2928s, 2858m, 1577m, 1467m, 1074w; ¹H NMR (400 MHz) δ 3.51-3.45 (m, 1H), 2.78 (dd, *J* = 12, 3, 1H), 2.49 (dd, *J* = 12, 8, 1H), 2.09 (br, 3H), 1.43-1.25 (m, 8H), 0.87 (t, *J* = 7, 3H); ¹³C NMR (100 MHz) δ 72.0, 47.5, 34.8, 31.9, 25.4, 22.6, 14.0; MS *m/z* (CI) 132 (M+H⁺, 100), 114 (18), 52 (23); HRMS calcd for C₇H₁₈NO (M+H⁺) 132.1383, found 132.1383.

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1-Aminoheptan-2-ol (500 mg, 3.81 mmol) in CH_2Cl_2 (10 mL) was added to a solution of di-*tert*butyl dicarbonate (832 mg, 3.81 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction was allowed to warm to rt and stirred for 6 h. After quenching with brine solution (15 mL), the layers were separated. The aqueous layer was extracted with Et_2O (2 x 10 mL), the combined organic layers dried (MgSO_4) and solvent removed *in vacuo* to give the crude Boc-protected amine (880 mg). The Boc-protected amine (880 mg) was dissolved in THF (14 mL) and powdered KOH (745 mg, 18.6 mmol) and TsCl (1.02 g, 5.33 mmol) were added. The reaction was stirred for 18 h, filtered and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography (5% Et_2O in petrol) to give aziridine **5b** (601 mg, 74%) as a colorless oil; R_f 0.15 (5% Et_2O in petrol). IR (neat, cm^{-1}) 2932s, 2860m, 1722s, 1469m, 1393m, 1311s, 1163s; ^1H NMR (400 MHz) δ 2.37-2.32 (m, 1H), 2.23 (dd, $J = 6, 2$, 1H), 1.89 (dd, $J = 4.5, 2$, 1H), 1.52-1.41 (m, 13H), 1.36-1.29 (m, 4H), 0.89 (t, $J = 7$, 3H); ^{13}C NMR (100 MHz) δ 162.7, 80.8, 38.2, 32.2, 31.6, 31.4, 27.9, 26.6, 22.6, 14.0; MS m/z (CI) 214 ($\text{M}+\text{H}^+$, 3), 158 (11), 114 (100); HRMS calcd for $\text{C}_{12}\text{H}_{24}\text{NO}_2$ ($\text{M}+\text{H}^+$) 214.1807, found 214.1807.

2-Pentyl-1-tosylaziridine **5c**¹¹

Following general procedure A, 1-heptene (3.49 g, 35.5 mmol), chloroamine-T (9.71 g, 42.7 mmol) and PTAB (1.34 g, 3.55 mmol) in MeCN (150 mL) gave after column chromatography (20% Et_2O in petrol) aziridine **5c** (6.08 g, 64%) as a colorless oil; R_f 0.16 (20% Et_2O in petrol). IR (neat, cm^{-1}) 2931s, 2859s, 1598s, 1456s, 1324s, 1162s, 1020m; ^1H NMR (400 MHz) δ 7.82 (d, $J = 8.5$, 2H), 7.32 (d, $J = 8.5$, 2H), 2.72-2.68 (m, 1H), 2.63 (d, $J = 7$, 1H), 2.44 (s, 3H), 2.05 (d, $J = 4.5$, 1H), 1.55-1.50 (m, 1H), 1.34-1.19 (m, 7H), 0.81 (t, $J = 7$, 3H); ^{13}C NMR (100 MHz) δ 144.4, 135.2, 129.6, 128.0, 40.4, 33.7, 31.2, 31.1, 26.4, 22.4, 21.6, 13.8; MS m/z (CI) 268 ($\text{M}+\text{H}^+$, 100), 112 (19); HRMS calcd for $\text{C}_{14}\text{H}_{22}\text{NO}_2\text{S}$ ($\text{M}+\text{H}^+$) 268.1371, found 268.1364.

2-Pentyl-1-*para*-nosylaziridine **5d**

1-Heptene (393 mg, 4.00 mmol) was added to a suspension of $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$ ¹² (64 mg, 0.2 mmol), $\text{PhI}=\text{NSO}_2\text{C}_6\text{H}_4\text{pNO}_2$ ¹³ (2.44 g, 6.00 mmol) and activated 4Å MS (1.20 g) in MeCN (10 mL) and stirred for 14 h. The reaction mixture was then filtered and solvent evaporated *in vacuo*. The residue was purified by column chromatography (20% petrol in Et_2O) to give aziridine **5d** (716 mg, 60%) as a yellow oil; R_f

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0.17 (20% Et₂O in petrol). IR (neat, cm⁻¹) 3107m, 2932s, 2860s, 1608m, 1532s, 1351s, 1231m, 1199m; ¹H NMR (400 MHz) δ 8.40 (d, *J* = 9, 2H), 8.16 (d, *J* = 9, 2H), 2.92-2.86 (m, 1H), 2.74 (d, *J* = 7, 1H), 2.16 (d, *J* = 4.5, 1H), 1.63-1.54 (m, 1H), 1.43-1.19 (m, 7H), 0.84 (t, *J* = 7, 3H); ¹³C NMR (100 MHz) δ 150.6, 144.2, 129.3, 124.2, 41.4, 34.6, 31.2, 31.1, 26.4, 22.4, 13.9; MS *m/z* (CI) 316 (M+NH₄⁺, 32), 299 (78), 269 (100); HRMS calcd for C₁₃H₂₂N₃O₄S (M+NH₄⁺) 316.1331, found 316.1342.

(*S*)-1-(*tert*-Butylsulfonyl)-2-(trityloxymethyl)aziridine **7a**¹⁴

Following general procedure B, (*R*)-tritylglycidyl ether (411 mg, 1.30 mmol) gave *aziridine 7a* (487 mg, 86%, over 3 steps) as a white foam; R_f 0.64 (25% Et₂O in petrol), [α]_D²⁵ -45.8 (c = 1.0, CHCl₃). IR (KBr, cm⁻¹) 3059m, 3032m, 2953s, 1597m, 1366s, 1156s, 1131s; ¹H NMR (400 MHz) δ 7.44 (dd, *J* = 8, 1.5, 6H), 7.32-7.22 (m, 9H), 3.34 (dd, *J* = 11, 4., 1H), 3.14 (dd, *J* = 11, 7, 1H), 2.94 (m, 1H), 2.59 (d, *J* = 7, 1H), 2.20 (d, *J* = 4.5, 1H), 1.54 (s, 9H); ¹³C NMR (100 MHz) δ 143.6, 128.7, 128.0, 127.3, 87.0, 63.2, 59.6, 38.9, 29.9, 24.3; MS *m/z* (CI) 436 (M+H⁺, 1), 243 (100), HRMS calcd for C₂₆H₃₀NO₃S (M+H⁺) 436.1946, found 436.1954.

1-(*tert*-Butylsulfonyl)-2-(hex-5-yn-1-yl)aziridine **7c**

Following general procedure B, 2-(hex-5-ynyl)oxirane¹⁵ (100 mg, 0.81 mmol) gave *aziridine 7c* (167 mg, 85%, over 3 steps) as a colorless oil; R_f 0.15 (20% Et₂O in petrol). IR (neat, cm⁻¹) 2988m, 2938s, 1481m, 1304s, 1238m, 1130s; ¹H NMR (400 MHz) δ 2.75-2.70 (m, 1H), 2.59 (d, *J* = 7, 1H), 2.23-2.19 (m, 2H), 2.07 (d, *J* = 4.5, 1H), 1.95 (t, *J* = 2.5, 1H), 1.66-1.53 (m, 6H), 1.49 (s, 9H); ¹³C NMR (100 MHz) δ 84.0, 68.5, 59.3, 38.2, 34.1, 30.8, 27.8, 25.4, 24.2, 18.2; MS *m/z* (CI) 261 (M+NH₄⁺, 55), 170 (26), 124 (100), 95 (60); HRMS calcd for C₁₂H₂₅N₂O₂S (M+NH₄⁺) 261.1637, found 261.1640.

2-Benzyl-1-(*tert*-butylsulfonyl)aziridine **7e**

Following general procedure A, allylbenzene (138 mg, 1.17 mmol), BusNCINa (271 mg, 1.40 mmol) and PTAB (0.44 mg, 0.12 mmol) in MeCN (4 mL) gave after column chromatography (20% Et₂O in petrol) *aziridine 7e* (205 mg, 69%) as a colorless oil; R_f 0.18 (20% Et₂O in petrol). IR (neat, cm⁻¹) 3030w, 2988m, 2934m, 1497m, 1480m, 1305s, 1130s; ¹H NMR (400 MHz) δ 7.34-7.23 (m, 5H), 3.06-2.97 (m, 2H), 2.83-2.78 (m, 1H), 2.62 (d, *J* = 7, 1H), 2.10 (d, *J* = 4.5, 1H), 1.45 (s, 9H); ¹³C NMR (100 MHz)

(14) We thank S. Miles for the characterization of this compound.

(15) Prepared in 2 steps (lithium acetylide substitution then epoxidation using *m*CPBA) from 6-bromo-hexene in 64% yield.

δ 136.5, 129.1, 128.6, 126.9, 59.3, 39.3, 37.4, 32.9, 24.1; MS m/z (CI) 271($M+NH_4^+$, 14), 254 (92), 215 (70), 198 (100), 134 (85), 132 (45); HRMS calcd for $C_{13}H_{23}N_2O_2S$ ($M+NH_4^+$) 271.1480, found 271.1485.

2-(4-Bromobutyl)-1-(*tert*-butylsulfonyl)aziridine **7f**

Following general procedure A, 6-bromo-1-hexene (527 mg, 3.23 mmol), BusNCINa (751 mg, 3.88 mmol) and PTAB (120 mg, 0.32 mmol) in MeCN (11 mL) gave after column chromatography (15% Et₂O in petrol) *aziridine 7f* (530 mg, 55%) as a colorless oil; R_f 0.15 (20% Et₂O in petrol). IR (neat, cm^{-1}) 2937s, 1481s, 1457s, 1305s, 1130s, 1068m, 1013m; ¹H NMR (400 MHz) δ 3.42 (t, $J = 7$, 2H), 2.75-2.70 (m, 1H), 2.59 (d, $J = 7$, 1H), 2.09 (d, $J = 4.5$, 1H), 1.97-1.90 (m, 2H), 1.64-1.57 (m, 4H), 1.50 (s, 9H); ¹³C NMR (100 MHz) δ 59.3, 37.7, 34.3, 33.4, 32.0, 30.4, 25.0, 24.2; MS m/z (CI) 298 ($M+H^+$, 100), 261 (42), 260 (40), 178 (17), 98 (39); HRMS calcd for $C_{10}H_{21}NO_2BrS$ ($M+H^+$) 298.0476, found 298.0469.

1,4-Bis-[(1-*tert*-butylsulfonyl)aziridine-2-yl]butane **7g**

Following general procedure B (except equiv of reagents doubled), 1,2,7,8-diepoxyoctane (186 mg, 1.31 mmol) gave *aziridine 7g* (324 mg, 65%, over 3 steps, 1:1 diastereoisomers by GCMS analysis, $t_R = 14.03$ min, $t_R = 14.14$ min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 20 °C/min) as a colorless oil; R_f 0.15 (50% Et₂O in petrol). IR (neat, cm^{-1}) 2988m, 2937m, 1481m, 1459m, 1302s, 1130s; ¹H NMR (400 MHz) δ 2.72-2.69 (m, 2H), 2.57 (d, $J = 7$, 2H), 2.07 (d, $J = 4.5$, 2H), 1.64-1.48 (m, 8H), 1.48 (s, 18H); ¹³C NMR (100 MHz) δ 59.3, 38.0, 34.3, 31.2, 26.0, 24.2; MS m/z (CI) 381 ($M+H^+$, 89), 325 (30), 261 (100), 110 (36); HRMS calcd for $C_{16}H_{33}N_2O_4S_2$ ($M+H^+$) 381.1882, found 381.1872.

1-(*tert*-Butylsulfonyl)-2-methyl-2-phenylaziridine **7j**

Following general procedure A, α -methylstyrene (118 mg, 1.00 mmol), BusNCINa (232 mg, 1.20 mmol) and PTAB (38 mg, 0.1 mmol) in MeCN (3 mL) gave after column chromatography (10% Et₂O in petrol) *aziridine 7j* (170 mg, 67%) as a colorless oil; R_f 0.17 (10% Et₂O in petrol). IR (neat, cm^{-1}) 3506m, 3062m, 2987s, 2934s, 1604w, 1448m, 1305s, 1115s; ¹H NMR (400 MHz) δ 7.49-7.28 (m, 5H), 2.94 (s, 1H), 2.51 (s, 1H), 2.01 (s, 3H), 1.52 (s, 9H); ¹³C NMR (100 MHz) δ 141.6, 128.4, 127.6, 126.4, 60.9, 49.2, 43.4, 24.2, 20.9; MS m/z (CI) 271 ($M+NH_4^+$, 35), 254 (41), 134 (100), 133 (68), 132 (70); HRMS calcd for $C_{13}H_{23}N_2O_2S$ ($M+NH_4^+$) 271.1480, found 271.1470.

1-(*tert*-Butylsulfonyl)-1,1a,6,6a-tetrahydro-1-azacyclopropaindene **9a**

Following general procedure A, indene (116 mg, 1.0 mmol), BusNCINa (232 mg, 1.2 mmol) and PTAB (38 mg, 0.1 mmol) in MeCN (3 mL) gave after column chromatography (20% Et₂O in petrol) *aziridine 9a* (133 mg, 53%) as a yellow solid; *R_f* 0.15 (30% Et₂O in petrol), mp 54-55 °C. IR (KBr, cm⁻¹) 2975s, 2930s, 1475m, 1305s, 1293m, 1122s; ¹H NMR (400 MHz) δ 7.48 (d, *J* = 7.5, 1H), 7.32-7.21 (m, 3H), 4.18 (d, *J* = 5, 1H), 3.89 (ddd, *J* = 5, 3, 3, 1H), 3.22 (d, *J* = 3, 2H), 1.46 (s, 9H); ¹³C NMR (100 MHz) δ 143.8, 138.7, 128.6, 126.6, 125.6, 124.8, 59.6, 50.1, 43.1, 34.8, 24.1; MS *m/z* (CI) 252 (M+H⁺, 67), 132 (47), 131 (100), 130 (42); HRMS calcd for C₁₃H₁₈NO₂S (M+H⁺) 252.1058, found 252.1050.

trans-2-Phenyl-1-tosyl-3-[(triethylsilanyloxy)methyl]-aziridine **9d**

To a solution of (3-phenyl-1-tosylaziridin-2-yl)methanol⁴ (200 mg, 0.66 mmol) and imidazole (50 mg, 0.73 mmol) in DMF (0.7 mL) at 0 °C was added chlorotriethylsilane (130 mg, 0.86 mmol) dropwise. The reaction was allowed to warm to rt and stirred for 30 min. Et₂O (5 mL) was added to the reaction mixture and the organic layer was separated, dried (MgSO₄) and solvent evaporated *in vacuo*. The residue was purified by column chromatography (10% Et₂O in petrol) to give *aziridine 9d* (248 mg, 90%) as a colorless oil; *R_f* 0.19 (10% Et₂O in petrol). IR (neat, cm⁻¹) 2956s, 2877s, 1599m, 1498s, 1458m, 1325s, 1185s, 1089s; ¹H NMR (400 MHz) δ 7.84 (d, *J* = 8, 2H), 7.28-7.20 (m, 7H), 4.38 (dd, *J* = 11, 4.5, 1H), 4.14 (dd, *J* = 11, 7.5, 1H), 3.90 (d, *J* = 4.5, 1H), 3.15-3.10 (m, 1H), 2.41 (s, 3H), 0.98 (t, *J* = 8, 9H), 0.65 (q, *J* = 8, 6H); ¹³C NMR (100 MHz) δ 144.0, 137.3, 134.7, 129.5, 128.5, 128.2, 127.4, 126.9, 60.4, 52.3, 47.7, 21.6, 6.7, 4.4; MS *m/z* (CI) 418 (M+H⁺, 67), 388 (92), 286 (100), 262 (95), 132 (90), 120 (66); HRMS calcd for C₂₂H₃₂NO₃SSi (M+H⁺) 418.1872, found 418.1885.

cis-2-Isopropyl-1-tosyl-3-vinylaziridine **9e**

Following a related procedure,¹⁶ a solution of LDA (0.25 M in THF; 6.40 mL, 1.60 mmol) was added to allyl bromide (161 mg, 1.33 mmol) and dry ZnCl₂ (254 mg, 1.86 mmol) in THF (6.0 mL) at -78 °C and allowed to stir for 30 min. 4-Methyl-*N*-(2-methylpropylidene)benzenesulfonamide¹⁷ (300 mg, 1.33 mmol) in THF (1.0 mL) was added and the reaction stirred for 30 min at -78 °C then 5 h at rt. Brine (15 mL) was added to the reaction mixture and the organic layer was separated, dried (MgSO₄) and solvent evaporated *in vacuo*. The residue was purified by column chromatography (15%→25% Et₂O in petrol) to give

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aziridine 9e (88 mg, 25%) as a colorless oil; R_f 0.24 (20% Et₂O in petrol). IR (neat, cm⁻¹) 2964s, 2874w, 1599m, 1495m, 1325s, 1159s; ¹H NMR (400 MHz) δ 7.83 (d, J = 8, 2H), 7.30 (d, J = 8, 2H), 6.15 (ddd, J = 17, 10, 9.5, 1H), 5.50 (d, J = 17, 1H), 5.38 (d, J = 10, 1H), 3.12 (dd, J = 9.5, 4.5, 1H), 2.79 (dd, J = 7, 4.5, 1H), 2.43 (s, 3H), 1.51 (octet, J = 7.0, 1H), 0.90 (d, J = 7, 3H), 0.77 (d, J = 7, 3H); ¹³C NMR (100 MHz) δ 144.0, 137.1, 132.0, 129.4, 127.8, 121.7, 54.1, 51.4, 30.2, 21.6, 19.7, 19.2; MS m/z (CI) 266 (M+H⁺, 100), 110 (48); HRMS calcd for C₁₄H₂₀NO₂S (M+H⁺) 266.1215, found 266.1212. The *cis*-configuration was determined by NOSEY experiments.

7-(*tert*-Butylsulfonyl)-7-azabicyclo[4.1.0]heptane **11d**

Following general procedure A, cyclohexene (154 mg, 1.87 mmol), BusNCINa (435 mg, 2.24 mmol) and PTAB (70 mg, 0.19 mmol) in MeCN (6 mL) gave after column chromatography (20% Et₂O in petrol) *aziridine 11d* (289 mg, 71%) as a colorless oil; R_f 0.35 (30% Et₂O in petrol). IR (neat, cm⁻¹) 2938s, 2866s, 1480m, 1305s, 1241m, 1125s, 968s; ¹H NMR (400 MHz) δ 2.94 (s, 2H), 1.94-1.82 (m, 4H), 1.47 (s, 9H), 1.46-1.40 (m, 2H), 1.32-1.23 (m, 2H); ¹³C NMR (100 MHz) δ 58.7, 39.1, 24.1, 22.9, 19.6; MS m/z (CI) 218 (M+H⁺, 100), 98 (29), 96 (29); HRMS calcd for C₁₀H₂₀NO₂S (M+H⁺) 218.1215, found 218.1212.

trans-2,3-Dibutyl-1-tosylaziridine **trans-13a**¹⁸

Following general procedure A, *trans*-5-decene (421 mg, 3.0 mmol), chloroamine-T (820 mg, 3.60 mmol) and PTAB (113 mg, 0.3 mmol) in MeCN (10 mL) gave after column chromatography (10% Et₂O in petrol) *aziridine trans-13a* (566 mg, 61%) as a colorless oil; R_f 0.25 (20% Et₂O in petrol). IR (neat, cm⁻¹) 2958s, 1598m, 1496s, 1322s, 1239m, 1128s, 1092m; ¹H NMR (400 MHz) δ 7.83 (d, J = 8, 2H), 7.30 (d, J = 8, 2H), 2.65-2.60 (m, 2H), 2.43 (s, 3H), 1.79-1.63 (m, 4H), 1.33-1.21 (m, 8H), 0.85 (t, J = 7, 6H); ¹³C NMR (100 MHz) δ 143.7, 138.0, 129.4, 127.4, 49.9, 29.6, 29.5, 22.2, 21.5, 14.0; MS m/z (CI) 310 (M+H⁺, 44), 154 (100); HRMS calcd for C₁₇H₂₈NO₂S (M+H⁺) 310.1841, found 310.1848.

trans-2,3-Dibutyl-1-(*tert*-butylsulfonyl)aziridine **trans-13b**

Following general procedure A, *trans*-dec-5-ene (281 mg, 2.0 mmol), BusNCINa (465 mg, 2.4 mmol) and PTAB (75 mg, 0.2 mmol) in

(18) Bäckvall, J. E.; Oshima, K.; Palermo, R. E.; Sharpless, K. B. *J. Org. Chem.* **1979**, 44, 1953–1957.

MeCN (7 mL) gave after column chromatography (10% Et₂O in petrol) *aziridine trans-13b* (413 mg, 75%) as a colorless oil; R_f 0.35 (20% Et₂O in petrol). IR (neat, cm⁻¹) 2932s, 1462m, 1306s, 1119s, 1016m; ¹H NMR (400 MHz) δ 2.55-2.52 (m, 2H), 2.09-2.01 (m, 2H), 1.55-1.32 (m, 19H), 0.92 (t, *J* = 7.5, 6H); ¹³C NMR (100 MHz) δ 59.7, 48.6, 29.7, 29.2, 24.1, 22.4, 13.9; MS *m/z* (CI) 276 (M+NH₄⁺, 43), 220 (31), 156 (48), 154 (100); HRMS calcd for C₁₄H₃₀NO₂S (M+H⁺) 276.1997, found 276.2000.

cis-2,3-Dibutyl-1-tosylaziridine ***cis*-13a**¹⁸

Following general procedure A, *cis*-5-decene¹⁹ (421 mg, 3.00 mmol), chloroamine-T (820 mg, 3.6 mmol) and PTAB (113 mg, 0.30 mmol) in MeCN (10 mL) gave after column chromatography (10% Et₂O in petrol) *aziridine cis-13a* (631 mg, 68%) as a colorless oil; R_f 0.25 (20% Et₂O in petrol). IR (neat, cm⁻¹) 2957s, 1598m, 1495s, 1324s, 1241m, 1160s, 1092m; ¹H NMR (400 MHz) δ 7.83 (d, *J* = 8, 2H), 7.33 (d, *J* = 8, 2H), 2.80-2.74 (m, 2H), 2.44 (s, 3H), 1.54-1.17 (m, 12H), 0.82 (t, *J* = 7, 6H); ¹³C NMR (100 MHz) δ 144.2, 135.4, 129.5, 128.1, 45.2, 29.4, 26.4, 22.3, 21.6, 13.9; MS *m/z* (CI) 310 (M+H⁺, 100), 154 (68); HRMS calcd for C₁₇H₂₈NO₂S (M+H⁺) 310.1841, found 310.1832.

cis-2,3-Dibutyl-1-(*tert*-butylsulfonyl)aziridine ***cis*-13b**

Following general procedure A, *cis*-dec-5-ene¹⁹ (620 mg, 4.42 mmol), BusNCINa (1.00 g, 5.30 mmol) and PTAB (165 mg, 0.44 mmol) in MeCN (15 mL) gave after column chromatography (5% Et₂O in petrol) *aziridine cis-13b* (743 mg, 61%) as a colorless oil; R_f 0.35 (20% Et₂O in petrol). IR (neat, cm⁻¹) 2958s, 2873s, 1466m, 1395w, 1366w, 1309s, 1257w, 1129s; ¹H NMR (400 MHz) δ 2.75-2.70 (m, 2H), 1.59-1.49 (m, 4H), 1.43 (s, 9H), 1.42-1.32 (m, 8H), 0.89 (t, *J* = 7, 6H); ¹³C NMR (100 MHz) δ 58.7, 44.2, 29.1, 26.6, 24.1, 22.4, 13.9; MS *m/z* (CI) 276 (M+H⁺, 100), 156 (20); HRMS calcd for C₁₄H₃₀NO₂S (M+H⁺) 276.1997, found 276.1994.

(19) Prepared by Lindlar reduction of dec-5-yne.

(III) General procedure and data for allylic *N*-sulfonyl amines

General procedure C. *n*-BuLi (1.6 M in hexanes; 3 – 6 equiv) was added dropwise to a stirred suspension of trimethylsulfonium iodide (3 – 6 equiv) in THF at –10 °C and left stirring for 15 min. The aziridine (1 equiv) in THF was added dropwise and the reaction was allowed to warm to 5 °C over 3 h. After quenching with brine solution, the layers were separated. The aqueous layer was extracted with Et₂O, the combined organic layers were dried (MgSO₄) and solvent evaporated *in vacuo*. The residue was purified by column chromatography (SiO₂, petrol/Et₂O) to give the allylic sulfonamide.

4-Methyl-*N*-(oct-1-en-3-yl)benzenesulfonamide **6c**²⁰

Following general procedure C, the addition of aziridine **5c** (100 mg, 0.37 mmol) in THF (0.5 mL) to a solution of dimethylsulfonium methylide (1.85 mmol) in THF (4 mL) gave after workup and column chromatography (30% Et₂O in petrol) *allylic sulfonamide 6c* (95 mg, 91%) as a colorless oil; *R*_f 0.19 (30% Et₂O in petrol). IR (neat, cm⁻¹) 3281br, 2930s, 1599w, 1429m, 1327s, 1159s, 1094m; ¹H NMR (400 MHz) 7.74 (d, *J* = 8, 2H), 7.27 (d, *J* = 8, 2H), 5.53 (ddd, *J* = 17, 10.5, 6.5, 1H), 5.07 (d, *J* = 8, 1H), 4.97 (ddd, *J* = 17, 1.5, 1, 1H), 4.92 (ddd, *J* = 10.5, 1.5, 1, 1H), 3.75-3.68 (m, 1H), 2.41 (s, 3H), 1.43 (q, *J* = 7, 2H), 1.27-1.10 (m, 6H), 0.82 (t, *J* = 7, 3H); ¹³C NMR (100 MHz) δ 143.1, 138.2, 137.9, 129.4, 127.2, 115.7, 56.3, 35.5, 31.3, 24.9, 22.4, 21.5, 13.9; MS *m/z* (CI) 299 (M+NH₄⁺, 14), 282 (23), 210 (24), 128 (30), 100 (100); HRMS calcd for C₁₅H₂₇N₂O₂S (M+NH₄⁺) 299.1793, found 299.1790.

4-Nitro-*N*-(oct-1-en-3-yl)benzenesulfonamide **6d**

Following general procedure C (except reaction was left at –15 °C for 18 h), the addition of aziridine **5d** (80 mg, 0.27 mmol) in THF (0.3 mL) to a solution of dimethylsulfonium methylide (0.80 mmol) in THF (3 mL) gave after workup and column chromatography (30% petrol in Et₂O) *allylic sulfonamide 6d* (38 mg, 45%) as a yellow oil; *R*_f 0.11 (30% petrol in Et₂O). IR (neat, cm⁻¹) 3285br, 2932m, 1607w, 1531s, 1349s, 1165s; ¹H NMR (400 MHz) δ 8.34 (d, *J* = 9, 2H), 8.04 (d, *J* = 9, 2H), 5.50 (ddd, *J* = 17, 10.5, 7, 1H), 4.98 (ddd, *J* = 17, 1.5, 1, 1H), 4.97 (ddd, *J* = 10.5, 1.5, 1, 1H), 4.73 (d, *J* = 8, 1H), 3.90-3.83 (m, 1H), 1.50 (q, *J* = 6.5, 2H), 1.29-1.18 (m, 6H), 0.85 (t, *J* = 7, 3H); ¹³C NMR (100 MHz) δ 149.9, 147.0, 137.2, 128.4, 124.2, 116.4, 56.9, 35.6, 31.2, 25.0, 22.4, 13.9; MS *m/z* (CI) 330 (M+NH₄⁺,

(20) Mordini, A.; Russo, F.; Valacchi, M.; Zani, L.; Degl'Innocenti, A.; Reginato, G. *Tetrahedron* **2002**, *58*, 7153–7163.

49), 300 (47), 128 (38), 120 (40), 100 (100), 52 (66); HRMS calcd for $C_{14}H_{24}N_3O_4S$ ($M+NH_4^+$) 330.1488, found 330.1479.

2-Methyl-*N*-(oct-1-en-3-yl)propane-2-sulfonamide **6e**

Following general procedure C, the addition of aziridine **5e** (80 mg, 0.34 mmol) in THF (0.5 mL) to a solution of dimethylsulfonium methylide (1.02 mmol) in THF (3 mL) gave after workup and column chromatography (30% Et₂O in petrol) *allylic sulfonamide 6e* (83 mg, 99%) as a colorless oil; *R*_f 0.21 (30% Et₂O in petrol). IR (neat, cm⁻¹) 3281br, 3083w, 2933s, 1645w, 1455m, 1304s, 1126s; ¹H NMR (400 MHz) 5.77 (ddd, *J* = 17, 10.5, 6.5, 1H), 5.21 (ddd, *J* = 17, 1.5, 1, 1H), 5.13 (ddd, *J* = 10.5, 1.5, 1, 1H), 4.24 (d, *J* = 9.5, 1H), 3.92-3.84 (m, 1H), 1.63-1.50 (m, 2H), 1.45-1.21 (m, 15H), 0.86 (t, *J* = 7, 3H); ¹³C NMR (100 MHz) δ 138.9, 115.2, 59.6, 57.3, 37.0, 31.5, 25.1, 24.2, 22.4, 13.9; MS *m/z* (CI) 265 ($M+NH_4^+$, 100), 248 (28), 176 (21), 128 (79), 111 (42), 56 (43); HRMS calcd for $C_{12}H_{29}N_2O_2S$ ($M+NH_4^+$) 265.1950, found 265.1958.

(*S*)-2-Methyl-*N*-[1-(trityloxy)but-3-en-2-yl]propane-2-sulfonamide **8a**

Following general procedure C, the addition of aziridine **7a** (80 mg, 0.18 mmol) in THF (0.3 mL) to a solution of dimethylsulfonium methylide (0.54 mmol) in THF (2 mL) gave after workup and column chromatography (30% Et₂O in petrol) *allylic sulfonamide 8a* (73 mg, 90%) as a colorless gum; *R*_f 0.20 (30% Et₂O in petrol), [*α*]_D²⁵ = -17 (*c* 1.00, CHCl₃); IR (neat, cm⁻¹) 3277br, 3059m, 3024m, 2976m, 2872m, 1597w, 1449s, 1312s, 1129s, 922m; ¹H NMR (400 MHz) δ 7.43 (d, *J* = 8, 6H), 7.34-7.24 (m, 9H), 5.97 (ddd, *J* = 17, 10.5, 6.5, 1H), 5.38 (ddd, *J* = 17, 1.5, 1, 1H), 5.28 (ddd, *J* = 10.5, 1.5, 1, 1H), 4.29 (d, *J* = 9.0, 1H), 4.12-4.09 (m, 1H), 3.28 (d, *J* = 4, 2H), 1.35 (s, 9H); ¹³C NMR (100 MHz) δ 143.5, 136.9, 128.6, 127.9, 127.2, 116.4, 86.7, 66.3, 59.8, 56.9, 24.2; MS *m/z* (EI-) 448 (*M*-H, 8), 313 (7), 239 (11), 206 (100); HRMS calcd for $C_{27}H_{30}NO_3S$ (*M*-H) 448.1946, found 448.1939.

The *ee* of the *allylic sulfonamide 8a* was determined to be >99% by chiral HPLC analysis; Chiralcel AD, 99:1 heptane:EtOH, 0.5 mL/min, 210nm, *t*_r (minor) = 29 min, *t*_r (major) = 37 min.

N-(Hepta-1,6-dien-3-yl)-2-methylpropane-2-sulfonamide **8b**

Following general procedure C, the addition of aziridine **7b** (50 mg, 0.23 mmol) in THF (0.3 mL) to a solution of dimethylsulfonium methylide (0.69 mmol) in THF (2 mL) gave after workup and column chromatography (20% Et₂O in petrol) *allylic sulfonamide 8b* (52 mg, 99%) as a colorless oil; *R*_f 0.22 (30% Et₂O in petrol). IR (neat, cm⁻¹) 3566w, 3278br, 3079s, 2982s, 1842w, 1642s, 1435s, 1304s, 1127s; ¹H NMR (400 MHz) δ

5.87-5.75 (m, 2H), 5.24 (ddd, $J = 17, 1.5, 1, 1\text{H}$), 5.19 (ddd, $J = 10, 1.5, 1, 1\text{H}$), 5.05 (ddt, $J = 17, 1.5, 1, 1\text{H}$), 5.00 (ddt, $J = 10, 1.5, 1, 1\text{H}$), 4.04 (d, $J = 10, 1\text{H}$), 4.00-3.92 (m, 1H), 2.18-2.13 (m, 2H), 1.78-1.64 (m, 2H), 1.39 (s, 9H); ^{13}C NMR (100 MHz) δ 138.5, 137.5, 115.6, 115.3, 59.8, 56.8, 36.1, 29.7, 24.2; MS m/z (CI) 249 ($\text{M}+\text{NH}_4^+$, 65), 232 (50), 176 (100), 112 (67), 95 (81) 56 (45); HRMS calcd for $\text{C}_{11}\text{H}_{25}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{NH}_4^+$) 249.1637, found 249.1631.

2-Methyl-*N*-(non-1-en-8-yn-3-yl)propane-2-sulfonamide **8c**

Following general procedure C, the addition of aziridine **7c** (50 mg, 0.22 mmol) in THF (0.3 mL) to a solution of dimethylsulfonium methylide (0.62 mmol) in THF (2.0 mL) gave after workup and column chromatography (30% Et_2O in petrol) *allylic sulfonamide 8c* (51 mg, 94%) as a colorless oil; R_f 0.24 (40% Et_2O in petrol). IR (neat, cm^{-1}) 3282br, 2940m, 2865m, 1645w, 1432m, 1302s, 1127s, 1019m; ^1H NMR (400 MHz) δ 5.79 (ddd, $J = 17, 10.5, 7, 1\text{H}$), 5.24 (ddd, $J = 17, 1.5, 1, 1\text{H}$), 5.17 (ddd, $J = 10.5, 1.5, 1, 1\text{H}$), 3.98-3.90 (m, 2H), 2.23-2.15 (m, 2H), 1.95 (t, $J = 2, 1\text{H}$), 1.73-1.43 (m, 6H), 1.39 (s, 9H); ^{13}C NMR (100 MHz) δ 138.6, 115.5, 84.1, 68.5, 59.8, 57.1, 36.5, 28.1, 24.6, 24.2, 18.2; MS m/z (CI) 275 ($\text{M}+\text{NH}_4^+$, 17), 56 (100); HRMS calcd for $\text{C}_{13}\text{H}_{27}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{NH}_4^+$) 275.1793, found 275.1783.

N-(7-Chlorohept-1-en-3-yl)-2-methylpropane-2-sulfonamide **8d**

Following general procedure C, the addition of aziridine **7d** (80 mg, 0.32 mmol) in THF (0.5 mL) to a solution of dimethylsulfonium methylide (0.96 mmol) in THF (3.0 mL) gave after workup and column chromatography (30% Et_2O in petrol) *allylic sulfonamide 8d* (84 mg, 98%) as a colorless oil; R_f 0.20 (40% Et_2O in petrol). IR (neat, cm^{-1}) 3280br, 3084w, 2940s, 2870s, 1645w, 1480s, 1305s, 1127s, 925s; ^1H NMR (400 MHz) δ 5.78 (ddd, $J = 17, 10.5, 7, 1\text{H}$), 5.21 (ddd, $J = 17, 1.5, 1, 1\text{H}$), 5.17 (ddd, $J = 10, 1.5, 1, 1\text{H}$), 4.20 (d, $J = 10, 1\text{H}$), 3.95-3.87 (m, 1H), 3.53 (t, $J = 7, 2\text{H}$), 1.83-1.74 (m, 2H), 1.65-1.49 (m, 4H), 1.37 (s, 9H); ^{13}C NMR (100 MHz) δ 138.4, 115.6, 59.7, 57.0, 44.7, 36.3, 32.1, 24.2, 22.8; MS m/z (CI) 285 ($\text{M}+\text{NH}_4^+$, 66), 268 (21), 176 (100), 56 (47); HRMS calcd for $\text{C}_{11}\text{H}_{26}\text{N}_2\text{O}_2\text{SCl}$ ($\text{M}+\text{NH}_4^+$) 285.1404, found 285.1405.

2-Methyl-*N*-(1-phenylbut-3-en-2-yl)propane-2-sulfonamide **8e**

Following general procedure C, the addition of aziridine **7e** (100 mg, 0.39 mmol) in THF (0.5 mL) to a solution of dimethylsulfonium methylide (1.18 mmol) in THF (4.0 mL) gave after workup and column chromatography (30% Et_2O in petrol) *allylic sulfonamide 8e* (103 mg, 99%) as a white solid; R_f 0.16 (30% Et_2O in petrol), mp 77-78

$^{\circ}\text{C}$. IR (KBr, cm^{-1}) 3280br, 3031m, 2980m, 1620w, 1605w, 1305s, 1290s, 1128s; ^1H NMR (400 MHz) 7.34-7.21 (m, 5H), 5.86 (ddd, $J = 17, 10, 6.5$, 1H), 5.20 (ddd, $J = 17, 1.5, 1$, 1H), 5.17 (ddd, $J = 10, 1.5, 1$, 1H), 4.28-4.20 (m, 1H), 3.89 (d, $J = 10$, 1H), 2.95 (d, $J = 6$, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz) δ 138.1, 136.5, 130.0, 128.4, 126.8, 115.5, 60.0, 58.1, 43.1, 24.0; MS m/z (CI) 285 ($\text{M}+\text{NH}_4^+$, 79), 268 (38), 176 (100), 132 (52), 91 (98); HRMS calcd for $\text{C}_{14}\text{H}_{25}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{NH}_4^+$) 285.1637, found 285.1643.

2-Methyl-*N*-(octa-1,7-dien-3-yl)propane-2-sulfonamide **8f**

Following general procedure C, the addition of aziridine **7f** (50 mg, 0.17 mmol) in THF (0.3 mL) to a solution of dimethylsulfonium methylide (0.85 mmol) in THF (2.0 mL) gave after workup and column chromatography (20% Et_2O in petrol) *allylic sulfonamide* **8f** (35 mg, 85%) as a colorless oil; R_f 0.11 (20% Et_2O in petrol). IR (neat, cm^{-1}) 3280m, 2936s, 1642m, 1432m, 1305s, 1127s, 994m; ^1H NMR (400 MHz) δ 5.84-5.74 (m, 2H), 5.24 (ddd, $J = 17, 1.5, 1$, 1H), 5.18 (ddd, $J = 10.5, 1.5, 1$, 1H), 5.02 (ddt, $J = 17, 1.5, 1$, 1H), 4.96 (ddt, $J = 10.5, 1.5, 1$, 1H), 3.98-3.91 (m, 1H), 3.84 (d, $J = 10$, 1H), 2.12-2.06 (m, 2H), 1.65-1.41 (m, 4H), 1.39 (s, 9H); ^{13}C NMR (100 MHz) δ 138.8, 138.2, 115.4, 115.0, 59.8, 57.1, 36.4, 33.3, 24.7, 24.2; MS m/z (CI) 263 ($\text{M}+\text{NH}_4^+$, 11), 126 (37), 109 (100), 56 (63); HRMS calcd for $\text{C}_{12}\text{H}_{27}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{NH}_4^+$) 263.1793, found 263.1788.

N,N-(deca-1,9-diene-3,8-diyl)bis(2-methylpropane)-2-sulfonamide **8g**

Following general procedure C, the addition of aziridine **7g** (40 mg, 0.11 mmol) in THF (0.3 mL) to a solution of dimethylsulfonium methylide (0.66 mmol) in THF (1 mL) gave after workup and column chromatography (60% Et_2O in petrol) *allylic sulfonamide* **8g** (44 mg, 99%, 1:1 diastereoisomers by GCMS analysis, $t_R = 12.25$ min, $t_R = 12.48$ min, initial temp. = 120°C , max. temp. = 280°C , rate = $20^{\circ}\text{C}/\text{min}$) as a white solid; R_f 0.15 (60% Et_2O in petrol), mp $92-94^{\circ}\text{C}$. IR (KBr, cm^{-1}) 3267br, 2985m, 2932m, 2855m, 1644w, 1457m, 1306s, 1128s; ^1H NMR (400 MHz) δ 5.83-5.74 (m, 2H), 5.23 (d, $J = 17$, 2H), 5.16 (d, $J = 11$, 2H), 4.16 (d, $J = 10$, 1H), 3.99-3.91 (m, 3H), 1.64-1.62 (m, 4H), 1.49-1.42 (m, 4H), 1.39 (s, 9H); ^{13}C NMR (100 MHz) δ 138.7, 138.5, 115.4, 115.3, 59.7, 59.7, 57.1, 57.0, 36.7, 36.3, 25.0, 25.0, 24.2, 24.2; MS m/z (CI) 426 ($\text{M}+\text{NH}_4^+$, 23), 289 (35), 176 (65), 155 (100), 154 (90), 137 (58), 135 (46), 114 (42); HRMS calcd for $\text{C}_{18}\text{H}_{40}\text{N}_3\text{O}_4\text{S}_2$ ($\text{M}+\text{NH}_4^+$) 426.2460, found 426.2475.

2-Methyl-*N*-(1-phenylallyl)propane-2-sulfonamide **8h(i)** and 2-Methyl-*N*-(2-phenylallyl)propane-2-sulfonamide **8h(ii)**

8h(i) and **8h(ii)**

Following general procedure C, the addition of aziridine **7h** (74 mg, 0.31 mmol) in THF (0.5 mL) to a solution of dimethylsulfonium methylide (0.93 mmol) in THF (3 mL) gave after workup and column chromatography (30% Et₂O in petrol) *allylic sulfonamides* **8h(i)** and **8h(ii)** (75 mg, 95%, **8h(i):8h(ii)** = 82:18 by GCMS analysis, *t_R* **7h(i)** = 11.73 min, *t_R* **7h(ii)** = 12.63 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 15 °C/min) as a white solid; *R_f* 0.13 (30% Et₂O in petrol). IR (KBr, cm⁻¹) 3290br, 2981s, 1638m, 1605w, 1458s, 1302s, 1118s (combined compounds).

Data for **8h(i)** - ¹H NMR (400 MHz) δ 7.43-7.30 (m, 5H), 6.04 (ddd *J* = 16.5, 10.5, 6.5, 1H), 5.28 (ddd, *J* = 16.5, 1.5, 1, 1H), 5.25 (ddd, *J* = 10.5, 1.5, 1, 1H), 5.13 (dddd, *J* = 10.0, 6.5, 1, 1, 1H), 4.63 (d, *J* = 10, 1H), 1.35 (s, 9H); ¹³C NMR (100 MHz) δ 140.6, 138.5, 128.7, 127.7, 127.0, 116.1, 60.3, 59.9, 24.1; MS *m/z* (CI) 271 (M+NH₄⁺, 100), 134 (24), 132 (42), 117 (100); HRMS calcd for C₁₃H₂₃N₂O₂S (M+NH₄⁺) 271.1480, found 271.1481.

Data for **8h(ii)** - ¹H NMR (400 MHz) δ 7.43-7.30 (m, 5H), 5.48 (s, 1H), 5.37 (s, 1H), 4.23 (s, 3H), 1.39 (s, 9H); ¹³C NMR (100 MHz) δ 144.4, 138.3, 128.6, 128.2, 126.1, 114.2, 60.0, 48.0, 24.2; MS *m/z* (CI) 271 (M+NH₄⁺, 100), 254 (32), 155 (55), 134 (88), 132 (74), 120 (48), 119 (30); HRMS calcd for C₁₃H₂₃N₂O₂S (M+NH₄⁺) 271.1480, found 271.1476.

2-Methyl-*N*-(1-vinylcyclohexyl)propane-2-sulfonamide **8i**

Following general procedure C, the addition of aziridine **7i** (86 mg, 0.37 mmol) in THF (0.5 mL) to a solution of dimethylsulfonium methylide (1.85 mmol) in THF (4 mL) gave after workup and column chromatography (20% Et₂O in petrol) *allylic sulfonamide* **8i** (88 mg, 97%) as a white solid; *R_f* 0.22 (20% Et₂O in petrol), mp 44–45 °C. IR (KBr, cm⁻¹) 3277br, 2930s, 1642w, 1455m, 1305m, 1121m; ¹H NMR (400 MHz) 6.03 (dd, *J* = 18, 10.5, 1H), 5.25 (dd, *J* = 18, 1, 1H), 5.23 (dd, *J* = 10.5, 1, 1H), 3.68 (s, 1H), 1.95-0.82 (m, 4H), 1.65-1.41 (m, 6H), 1.38 (s, 9H); ¹³C NMR (100 MHz) δ 142.6, 114.9, 60.2, 59.7, 36.6, 25.4, 24.4, 22.3; MS *m/z* (CI) 246 (M+H⁺, 3), 124 (25), 109 (100), 82 (23); HRMS calcd for C₁₂H₂₄NO₂S (M+H⁺) 246.1528, found 246.1538.

2-Methyl-*N*-(2-phenylbut-3-en-2-yl)propane-2-sulfonamide **8j**

Following general procedure C, the addition of aziridine **7j** (78 mg, 0.31 mmol) in THF (0.5 mL) to a solution of dimethylsulfonium methylide (1.54 mmol) in THF (3 mL) gave after workup and column chromatography (20%

Et₂O in petrol) *allylic sulfonamide 8j* (77 mg, 93%) as a colorless oil; R_f 0.14 (30% Et₂O in petrol). IR (neat, cm⁻¹) 3519s, 3277br, 2987s, 1639m, 1601m, 1446m, 1300s, 1122s; ¹H NMR (400 MHz) δ 7.51-7.48 (m, 2H), 7.38-7.34 (m, 2H), 7.30-7.26 (m, 1H), 6.31 (dd, *J* = 17, 11, 1H), 5.28 (dd, *J* = 11, 1, 1H), 5.23 (dd, *J* = 17, 1, 1H), 4.18 (s, 1H), 1.89 (s, 3H), 1.42 (9H); ¹³C NMR (100 MHz) δ 145.1, 143.1, 128.4, 127.4, 126.0, 114.2, 63.6, 60.0, 26.5, 24.4; MS *m/z* (CI) 285 (M+NH₄⁺, 10), 147, (69), 146 (28), 132 (62), 131 (100), 130 (28); HRMS calcd for C₁₄H₂₅N₂O₂S (M+NH₄⁺) 285.1637, found 285.1624.

2-Methyl-*N*-(1-methylene-2,3-dihydro-1*H*-inden-2-yl)propane-2-sulfonamide **10a**

Following general procedure C, the addition of aziridine **9a** (44 mg, 0.18 mmol) in THF (0.3 mL) to a solution of dimethylsulfonium methylide (0.54 mmol) in THF (2 mL) gave after workup and column chromatography (35% Et₂O in petrol) *allylic sulfonamide 10a* (45 mg, 95%) as a pale yellow solid; R_f 0.18 (35% Et₂O in petrol), mp 38-39 °C. IR (KBr, cm⁻¹) 3286br, 2977m, 1462m, 1301s, 1126s; ¹H NMR (400 MHz) δ 7.50-7.47 (m, 1H), 7.30-7.22 (m, 3H), 5.63 (d, *J* = 1.5, 1H), 5.40 (d, *J* = 1.5, 1H), 4.78-4.70 (m, 1H), 4.12 (d, *J* = 10, 1H), 3.50 (dd, *J* = 16, 8, 1H), 2.93 (dd, *J* = 16, 6, 1H), 1.48 (s, 9H); ¹³C NMR (100 MHz) δ 150.4, 141.7, 138.4, 129.3, 127.2, 125.2, 121.0, 105.5, 59.0, 58.4, 40.6, 24.3; MS *m/z* (CI) 283 (M+NH₄⁺, 17), 266 (70), 155 (41), 146 (100), 145 (72), 144 (79), 130 (70), 129 (60), 128 (97), 115 (34); HRMS calcd for C₁₄H₂₃N₂O₂S (M+NH₄⁺) 283.1480, found 283.1475.

2-Methyl-*N*-(3-phenylbut-3-en-2-yl)propane-2-sulfonamide **10b** and 2-methyl-*N*-(2-methyl-1-phenylallyl)propane-2-sulfonamide **10b(ii)**

10b and

10b(ii)

Following general procedure C, the addition of aziridine **9b** (68 mg, 0.27 mmol) in THF (0.3 mL) to a solution of dimethylsulfonium methylide (1.35 mmol) in THF (3 mL) gave after workup and column chromatography (20% Et₂O in petrol) *allylic sulfonamide 10b* (58 mg, 81%) as a white solid; R_f 0.13 (20% Et₂O in petrol), mp 50-52 °C. IR (KBr, cm⁻¹) 3277br, 3082w, 2979m, 1625w, 1479m, 1305s, 1127s; ¹H NMR (400 MHz) δ 7.38-7.31 (m, 5H), 5.33 (s, 1H), 5.29 (s, 1H), 4.56 (dq, *J* = 10, 7, 1H), 4.05 (d, *J* = 10, 1H), 1.38 (d, *J* = 7, 3H), 1.37 (s, 9H); ¹³C NMR (100 MHz) δ 151.5, 140.0, 128.5, 127.9, 126.9, 112.7, 59.9, 54.2, 24.1, 23.8; MS *m/z* (CI) 285 (M+NH₄⁺, 63), 268 (47), 252 (26), 164 (56), 146 (41), 132 (84), 131 (100); HRMS calcd for C₁₄H₂₅N₂O₂S (M+NH₄⁺) 285.1637, found 285.1633.

Also isolated was *allylic sulfonamide 10b(ii)* (9 mg, 12%) as a white solid; R_f 0.17 (20% Et₂O in petrol), mp 46-48 °C. IR (KBr, cm⁻¹) 3292br, 2967s, 1657w, 1456m, 1299s, 1123s; ¹H NMR (400 MHz) δ 7.40-7.28 (m, 5H), 5.11 (s, 1H), 5.08 (s, 1H), 5.01 (d, J = 10, 1H), 4.35 (d, J = 10, 1H), 1.69 (s, 3H), 1.36 (s, 9H); ¹³C NMR (100 MHz) δ 144.6, 140.2, 128.8, 127.7, 127.0, 113.2, 63.4, 60.0, 24.1, 20.1; MS m/z (CI) 285 (M+NH₄⁺, 39), 226 (19), 147 (35), 146 (88), 106 (100); HRMS calcd for C₁₄H₂₅N₂O₂S (M+NH₄⁺) 285.1637, found 285.1630.

N-(1-hydroxy-3-phenylbut-3-en-2-yl)tosylsulfonamide **10c**

Following general procedure C, the addition of aziridine **9c** (60 mg, 0.20 mmol) in THF (0.5 mL) to a solution of dimethylsulfonium methylide (1.2 mmol) in THF (2.0 mL) gave after workup and column chromatography (Et₂O) *allylic sulfonamide 10c* (54 mg, 85%) as a colorless oil; R_f 0.24 (Et₂O). IR (neat, cm⁻¹) 3507br, 3282br, 3061m, 2926m, 1598m, 1495m, 1322s, 1158s; ¹H NMR (400 MHz) δ 7.74 (d, J = 8.5, 2H), 7.28-7.23 (m, 5H), 7.17-7.14 (m, 2H), 5.53 (d, J = 8, 1H), 5.27 (s, 1H), 5.21 (d, J = 1.5, 1H), 4.44-4.40 (m, 1H), 3.62 (dd, J = 11.5, 6, 1H), 3.54 (d, J = 11.5, 6, 1H), 2.41 (s, 3H), 2.27 (br, 1H); ¹³C NMR (100 MHz) δ 145.5, 143.5, 139.2, 137.3, 129.6, 128.5, 128.0, 127.1, 126.6, 115.7, 64.2, 58.5, 21.5; MS m/z (CI) 335 (M+NH₄⁺, 100), 305 (38), 189 (40), 133 (41), 52 (61); HRMS calcd for C₁₇H₂₃NO₃S (M+NH₄⁺) 335.1424, found 335.1425.

4-Methyl-*N*-(2-phenyl-1-triethylsilanyloxymethyl-allyl)benzenesulfonamide **10d**

Following general procedure C, the addition of aziridine **9d** (84 mg, 0.20 mmol) in THF (0.3 mL) to a solution of dimethylsulfonium methylide (1.00 mmol) in THF (2.0 mL) gave after workup and column chromatography (30% Et₂O in petrol) *allylic sulfonamide 10d* (68 mg, 79%) as a colorless oil; R_f 0.25 (30% Et₂O in petrol). IR (neat, cm⁻¹) 3290br, 2955m, 2876m, 1634w, 1599w, 1414m, 1329s, 1163s 1095m; ¹H NMR (400 MHz) δ 7.75 (d, J = 8, 2H), 7.33-7.25 (m, 7H), 5.27 (s, 2H), 5.20 (d, J = 7.5, 1H), 4.32 (ddd, J = 7.5, 5, 4, 1H), 3.53 (dd, J = 10, 5, 1H), 3.42 (dd, J = 10, 4, 1H), 2.41 (s, 3H), 0.85 (t, J = 7, 9H), 0.46 (q, J = 7, 6H); ¹³C NMR (100 MHz) δ 145.7, 143.2, 139.9, 137.6, 129.5, 128.3, 127.7, 127.2, 126.8, 115.9, 63.7, 58.2, 21.5, 6.6, 4.2; MS m/z (CI) 432 (M+H⁺, 100), 402 (57), 286 (14); HRMS calcd for C₂₃H₃₄NO₃SiS (M+H⁺) 432.2029, found 432.2022.

4-Methyl-*N*-(2-methylenehex-5-en-3-yl)benzenesulfonamide **10e**

Following general procedure C, the addition of aziridine **9e** (63 mg, 0.24 mmol) in THF (0.3 mL) to a solution of dimethylsulfonium methylide (1.20 mmol) in

THF (2.5 mL) gave after workup and column chromatography (30% Et₂O in petrol) *allylic sulfonamide 10e* (50 mg, 75%) as a white solid; R_f 0.11 (30% Et₂O in petrol), mp 53-55 °C. IR (KBr, cm⁻¹) 3287br, 2956m, 1598s, 1443m, 1348s, 1162s, 1094m; ¹H NMR (400 MHz) δ 7.69 (d, *J* = 8, 2H), 7.23 (d, *J* = 8, 2H), 6.10 (dd, *J* = 17.5, 11, 1H), 5.17 (d, *J* = 17.5, 1H), 5.02 (d, *J* = 11, 1H), 4.96 (s, 1H), 4.85 (d, *J* = 9, 1H), 4.79 (s, 1H), 3.84 (dd, *J* = 9, 7, 1H), 2.41 (s, 3H), 1.84 (octet, *J* = 7, 1H), 0.87 (d, *J* = 7, 3H), 0.86 (d, *J* = 7, 3H); ¹³C NMR (100 MHz) δ 144.9, 143.0, 137.9, 136.1, 129.3, 127.2, 115.8, 114.6, 60.8, 31.5, 21.5, 19.7, 17.6; MS *m/z* (CI) 297 (M+NH₄⁺, 65), 280 (35), 236 (100), 155 (25), 109 (48); HRMS calcd for C₁₅H₂₅N₂O₂S (M+NH₄⁺) 297.1637, found 297.1633.

4-Methyl-*N*-(2-methylenecyclopentyl)benzenesulfonamide **12a**

Following general procedure C, the addition of aziridine **11a** (100 mg, 0.42 mmol) in THF (0.3 mL) to a solution of dimethylsulfonium methylide (2.1 mmol) in THF (4 mL) gave after workup and column chromatography (30% Et₂O in petrol) *allylic sulfonamide 12a* (87 mg, 82%) as a colorless oil; R_f 0.14 (30% Et₂O in petrol). IR (neat, cm⁻¹) 3289br, 2963m, 1659w, 1599w, 1496m, 1435m, 1321m, 1160s; ¹H NMR (400 MHz) δ 7.79 (d, *J* = 9, 2H), 7.30 (d, *J* = 9, 2H), 4.93 (app. q, *J* = 2, 1H), 4.88 (app. q, *J* = 2, 1H), 4.63 (d, *J* = 8, 1H), 4.00-3.94 (m, 1H), 2.43 (s, 3H), 2.31-2.26 (m, 2H), 1.93-1.85 (m, 1H), 1.73-1.63 (m, 1H), 1.55-1.33 (m, 2H); ¹³C NMR (100 MHz) δ 151.4, 143.3, 137.9, 129.6, 127.0, 108.0, 57.4, 34.4, 30.3, 21.9, 21.5; MS *m/z* (CI) 296 (M+NH₄⁺, 11), 252 (20), 96 (43), 81 (100); HRMS calcd for C₁₃H₂₁N₂O₂S (M+NH₄⁺) 269.1324, found 269.1331.

2-Methyl-*N*-(2-methylenecyclopentyl)-propane-2-sulfonamide **12b**

Following general procedure C, the addition of aziridine **11b** (80 mg, 0.39 mmol) in THF (0.5 mL) to a solution of dimethylsulfonium methylide (1.97 mmol) in THF (4 mL) gave after workup and column chromatography (30% Et₂O in petrol) *allylic sulfonamide 12b* (78 mg, 92%) as a white solid; R_f 0.18 (30% Et₂O in petrol), mp 57-58 °C. IR (KBr, cm⁻¹) 3282br, 2959s, 1659w, 1459m, 1368m, 1304s, 1131s, 931m; ¹H NMR (400 MHz) δ 5.21 (app. q, *J* = 2, 1H), 5.05 (app. q, *J* = 2, 1H), 4.19-4.11 (m, 1H), 3.72 (d, *J* = 9, 1H), 2.45-2.22 (m, 3H), 1.81-1.71 (m, 1H), 1.65-1.45 (m, 2H), 1.44 (s, 9H); ¹³C NMR (100 MHz) δ 151.9, 107.5, 59.7, 59.2, 35.7, 30.2, 24.3, 21.5; MS *m/z* (CI) 235 (M+NH₄⁺, 29), 218 (24), 98 (48), 97 (43), 96 (32), 81 (100); HRMS calcd for C₁₀H₂₃N₂O₂S (M+NH₄⁺) 235.1480, found 235.1487.

4-Methyl-*N*-(2-methylenecyclohexyl)benzenesulfonamide **12c**²¹

Following general procedure C, the addition of aziridine **11c** (80 mg, 0.32 mmol) in THF (0.3 mL) to a solution of dimethylsulfonium methylide (1.6 mmol) in THF (3 mL) gave after workup and column chromatography (30% Et₂O in petrol) *allylic sulfonamide* **12c** (73 mg, 86%) as a white solid; R_f 0.15 (30% Et₂O in petrol), mp 75-77 °C. IR (KBr, cm⁻¹) 3269br, 2929s, 2852m, 1651m, 1598m, 1496m, 1318s, 1168s; ¹H NMR (400 MHz) δ 7.77 (d, *J* = 8, 2H), 7.27 (d, *J* = 8, 2H), 5.01 (d, *J* = 8, 1H), 4.74 (s, 1H), 4.66 (s, 1H), 3.77-3.72 (m, 1H), 2.41 (s, 3H), 2.30-2.23 (m, 1H), 1.96 (ddd, *J* = 13, 13, 4, 1H), 1.79-1.53 (m, 3H), 1.47-1.26 (m, 3H); ¹³C NMR (100 MHz) δ 147.4, 143.0, 138.1, 129.5, 127.0, 107.7, 56.1, 35.5, 33.9, 27.2, 24.1, 21.5; MS *m/z* (CI) 283 (M+NH₄⁺, 12), 266 (28), 110 (48), 95 (100), 91 (29); HRMS calcd for C₁₄H₂₃N₂O₂S (M+NH₄⁺) 283.1480, found 283.1489.

2-Methyl-*N*-(2-methylenecyclohexyl)propane-2-sulfonamide **12d**

Following general procedure C, the addition of aziridine **11d** (54 mg, 0.25 mmol) in THF (0.3 mL) to a solution of dimethylsulfonium methylide (1.25 mmol) in THF (2.5 mL) gave after workup and column chromatography (30% Et₂O in petrol) *allylic sulfonamide* **12d** (54 mg, 94%) as a white solid; R_f 0.17 (30% Et₂O in petrol). IR (KBr, cm⁻¹) 3273br, 2990m, 2927s, 2852m, 1654m, 1456m, 1313s, 1109s, 902s; ¹H NMR (400 MHz) δ 4.94 (s, 1H), 4.83 (s, 1H), 3.97 (d, *J* = 10, 1H), 3.82 (ddd, *J* = 10, 10, 4, 1H), 2.42 (d, *J* = 13, 2, 1, 1H), 2.21-2.15 (m, 1H), 2.03 (ddd, *J* = 13, 13, 2, 1H), 1.83-1.70 (m, 2H), 1.58-1.47 (m, 1H), 1.40 (s, 9H), 1.37-1.19 (m, 2H); ¹³C NMR (100 MHz) δ 149.0, 106.6, 59.9, 57.8, 37.9, 35.1, 27.4, 25.3, 24.2; MS *m/z* (CI) 249 (M+NH₄⁺, 50), 112 (32), 111 (46), 95 (100); HRMS calcd for C₁₁H₂₅N₂O₂S (M+NH₄⁺) 249.1637, found 249.1646.

4-Methyl-*N*-(6-methylenedecan-5-yl)benzenesulfonamide **14a**²²

Following general procedure C, the addition of aziridine *cis*-**13a** (100 mg, 0.32 mmol) in THF (0.5 mL) to a solution of dimethylsulfonium methylide (1.6 mmol) in THF (3 mL) gave after workup and column chromatography (20% Et₂O in petrol) *allylic sulfonamide* **14a** (32 mg, 31%) as a colorless oil; R_f 0.19 (30% Et₂O in petrol). IR (neat, cm⁻¹) 3280br, 2957s, 2872m, 1648w, 1599w, 1327m, 1161s; ¹H NMR (400 MHz) δ 7.72 (d, *J* = 8, 2H), 7.27-7.25 (m, 2H), 4.80 (s, 1H), 4.76 (d, *J* = 7, 1H), 4.70 (s, 1H), 3.71 (q, *J* = 7, 1H), 2.41 (s, 3H), 1.74 (t, *J* = 7, 2H), 1.51-1.44 (m, 2H), 1.28-

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1.08 (m, 8H), 0.85-0.80 (m, 6H); ^{13}C NMR (100 MHz) δ 148.0, 143.0, 138.1, 129.3, 127.2, 111.1, 59.0, 34.1, 31.0, 29.5, 27.8, 22.5, 22.2, 21.4, 13.9, 13.8; MS m/z (CI) 341 ($\text{M}+\text{NH}_4^+$, 2), 266 (38), 153 (100), 91 (17); HRMS calcd for $\text{C}_{18}\text{H}_{33}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{NH}_4^+$) 341.2263, found 341.2253.

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NHBus

8f

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S49

S50

S51

S53

S54

S56

12b

12c

S63