Supporting information

Substituted Aziridines by Lithiation–Electrophile Trapping of Terminal Aziridines

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(I)	General details	S1
(II)	Characterization data for aziridines 1 and 3 (entries 2–8)	S3
(III)	Characterization data for α,β -aziridinylsilanes 2 and 4 (entries 2–8)	S9
(IV)	Characterization data for substituted aziridines 5 , 6 and 7 (a–j)	S16
(V)	^1H and ^{13}C NMR spectra of aziridines 1 and 3 (entries 2–8)	S28
(VI)	^1H and ^{13}C NMR spectra of α,β -aziridinylsilanes 2 and 4 (entries 2–8)	S36
(VII)	^1H and ^{13}C NMR spectra of substituted aziridines 5 , 6 and 7 (a–j)	S44

(I) General details

Reactions were performed in flame-dried glassware under an atmosphere of argon. Et_2O , THF and MeCN were degassed and dried over alumina under argon.¹ TMP was distilled from CaH_2 . Me_3SiCl and Bu_3SnCl were distilled over K_2CO_3 . All other reagents were used as received. Column chromatography was performed using the solvent systems indicated. Petroleum ether refers to the fraction that boils at 30–40 °C. The stationary phase used was silica gel 60 unless otherwise indicated. ^1H , ^{13}C

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

and ^{119}Sn NMR spectra were recorded in CDCl_3 or $(\text{CD}_3)_2\text{SO}$ at ambient temperature or $65\text{ }^\circ\text{C}$ as indicated. Data are expressed as chemical shifts in parts per million (ppm) relative to residual chloroform (^1H δ 7.27), CDCl_3 (^{13}C δ 77.0), residual dimethyl sulfoxide (^1H δ 2.50) or $(\text{CD}_3)_2\text{SO}$ (^{13}C δ 39.5) as the internal standard on the δ scale. The multiplicity of each signal is designated by the following abbreviations; s, singlet; d, doublet; dd, doublet of doublets; dt, doublet of triplets; ddt, doublet of doublet of triplets; t, triplet; br, broad. Coupling constants J are given in Hz. For ^{119}Sn NMR spectra, only selected $J_{\text{Sn-H}}$ or $J_{\text{Sn-C}}$ coupling constants are reported. 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). HRMS data for Sn-containing compounds are quoted for the most abundant Sn isotope, i.e. ^{120}Sn . Specific rotations $[\alpha]_D^T$ were measured using a polarimeter with a cell of path length 1.0 cm, at $T\text{ }^\circ\text{C}$ and are given in $10^{-1}\text{ deg cm}^2\text{ g}^{-1}$. Concentrations (c) are given in g/100 mL.

(II) Characterization data for aziridines 1 and 3 (entries 2–8)**General procedure A:** Bus-protected aziridine preparation²

The appropriate alkene (4.3 mmol) was added to a stirred suspension of BusNCINa (1.00 g, 5.3 mmol) and phenyltrimethylammonium tribromide (162 mg, 0.4 mmol) in MeCN (22.5 mL) at room temperature. The mixture was stirred for 12 h, filtered and concentrated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/EtOAc or Et₂O) gave the desired aziridine.

1-(*tert*-Butylsulfonyl)-2-pentylaziridine (1)

Following **General procedure A** using 1-heptene gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), *aziridine 1* as a colourless liquid (890 mg, 89%).

*R*_f 0.72 (petroleum ether/EtOAc 9:1); IR (neat) 2933m, 2861m, 1480m, 1366w, 1305s, 1242w, 1129s and 1106m cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.75-2.69 (1 H, m, CHN), 2.59 (1H, d, *J* = 7, CH(*H*)N, *trans* to alkyl chain), 2.07 (1H, d, *J* = 5, CH(*H*)N, *cis* to alkyl chain), 1.69-1.59 (1H, m, CH(*H*)CHN), 1.49-1.40 (12H, m *t*-Bu, CH₂ and CH(*H*)CHN), 1.34-1.29 (4H, m, 2 × CH₂), 0.90 (3H, t, *J* = 7, Me); ¹³C NMR (100 MHz, CDCl₃) δ 59.2 (SC), 38.7 (CHN), 33.9 (CH₂N), 31.3 (CH₂), 31.2 (CH₂), 25.9 (CH₂), 24.2 (SCMe₃), 22.5 (CH₂), 13.9 (Me); MS CI *m/z* (rel. int.) 234 (*M* + H⁺,

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

100), 114 (100), 112 (30); HRMS m/z calcd for $C_{11}H_{24}NO_2S$, 234.1528, found 234.1520.

2-(But-3-enyl)-1-(*tert*-butylsulfonyl)aziridine (3, entry 2)

1,5-Hexadiene (367 mg, 4.5 mmol) was added dropwise to a stirred suspension of BusNClNa (581 mg, 3.0 mmol) and phenyltrimethylammonium tribromide (169 mg, 0.45 mmol) in MeCN (22.5 mL) at room temperature. After stirring for 48 hours, the reaction mixture was filtered and concentrated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/EtOAc 9:1) gave *aziridine* **3** (entry 2) as a colourless oil (387 mg, 59%).

R_f 0.54 (petroleum ether/EtOAc 17:3); IR (neat) 3079w, 2983m, 2934m, 1642m (C=C), 1481m, 1456m, 1397m, 1366w, 1307s, 1238m, 1211w, 1131s and 1064w cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.84 (1H, ddt, $J = 13, 7$ and 6 , =CH), 5.09-4.99 (2H, m, $\text{H}_2\text{C=}$), 2.78-2.72 (1H, m, CHN), 2.60 (1H, d, $J = 7$, CH(*H*)N, *trans* to alkyl chain), 2.34-2.18 (2H, m, =CHCH₂), 2.09 (1H, d, $J = 4$, CH(*H*)N, *cis* to alkyl chain), 1.77-1.68 (1H, m, CH(*H*)), 1.65-1.56 (1H, m, CH(*H*)), 1.49 (9H, s, *t*-Bu); ^{13}C NMR (100 MHz, CDCl_3) δ 137.1 (=CH), 115.5 ($\text{H}_2\text{C=}$), 59.2 (SC), 37.9 (CHN), 34.2 (CH_2N), 30.7 (CH_2), 30.5 (CH_2), 24.2 (SCMe_3); MS CI m/z (rel. int.) 218 ($\text{M} + \text{H}^+$, 100), 98 (80); HRMS m/z calcd for $C_{10}H_{20}NO_2S$, 218.1215, found 218.1209.

1-(*tert*-Butylsulfonyl)-2-phenethylaziridine (3, entry 3)

Following **General procedure A** using 4-phenyl-1-butene gave, following purification of the resulting residue by column chromatography (petroleum ether/EtOAc 24:1), *aziridine 3* (entry 3) as a white solid (965 mg, 84%).

(mp = 62-65 °C); R_f 0.45 (petroleum ether/EtOAc 9:1); IR (KBr) 2930s, 1602s, 1453s, 1408m, 1362s, 1292s, 1111s, 1055w, 1002s and 719s ($C_{Ar}-H$) cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (2H, m, $2 \times C_{Ar}H$), 7.23-7.19 (3H, m, $3 \times C_{Ar}H$), 2.85-2.72 (3H, m, $ArCH_2$ and CHN), 2.59 (1H, d, $J = 7$, $CH(H)N$, *trans* to alkyl chain), 2.05 (1H, d, $J = 5$, $CH(H)N$, *cis* to alkyl chain), 2.00-1.91 (1H, m, $CH(H)$), 1.87-1.78 (1H, m, $CH(H)$), 1.50 (9H, s, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8 (C_{Ar} quat), 129.3 ($2 \times C_{Ar}$), 128.4 ($2 \times C_{Ar}$), 126.1 (C_{Ar}), 59.3 (SC), 37.8 (CHN), 34.4 (CH_2N), 33.3 ($ArCH_2$), 32.7 (CH_2), 24.2 ($SCMe_3$); MS CI m/z (rel. int.) 268 ($M + H^+$, 80), 212 (50), 148 (100), 131 (75), 106 (60); HRMS m/z calcd for $C_{14}H_{22}NO_2S$, 268.1371, found 268.1375.

2-[(*tert*-Butyldimethylsilyloxy)methyl]-1-(*tert*-butylsulfonyl)aziridine (3, entry 4)

Following **General procedure A** using allyloxy(*tert*-butyl)dimethylsilane³ gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 24:1), *aziridine 3* (entry 4) as a colourless oil (418 mg, 32%).

(3) Lygo, B.; O'Connor, N.; Wilson, P. R. *Tetrahedron* **1988**, *44*, 6881–6888.

R_f 0.62 (petroleum ether/EtOAc 9:1); IR (neat) 2931m, 1463m, 1392w, 1964w, 1311s, 1254m, 1130s and 1101m (C–O–Si) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.81 (1H, dd, $J = 11$ and 3, OCH(H)), 3.68 (1H, dd, $J = 11$ and 5, OCH(H)), 2.92–2.87 (1H, m, CHN), 2.59 (1H, d, $J = 7$, CH(H)N, *trans* to alkyl chain), 2.21 (1H, d, $J = 5$, CH(H)N, *cis* to alkyl chain), 1.51 (9H, s, *St*-Bu), 0.89 (9H, s, *Sit*-Bu), 0.07 (6H, s, SiMe_2); ^{13}C NMR (100 MHz, CDCl_3) δ 62.4 (OCH₂), 59.5 (SC), 40.2 (CHN) 29.6 (CH₂N), 25.8 (SiCMe_3), 24.2 (SCMe_3), 18.3 (SiC), -5.4 (SiMe_2); MS CI m/z (rel. int.) 308 ($\text{M} + \text{H}^+$, 100), 188 (45), 130 (55); HRMS m/z calcd for $\text{C}_{13}\text{H}_{30}\text{NO}_3\text{SSi}$, 308.1716, found 308.1713.

2-[4-(*tert*-Butyldimethylsilyloxy)butyl]-1-(*tert*-butylsulfonyl)aziridine (3, entry 5)

Following **General procedure A** using *tert*-butyl(hex-5-enyloxy)dimethylsilane⁴ gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), *aziridine 3* (entry 5) as a colourless oil (1.01 g, 68%).

R_f 0.18 (petroleum ether/Et₂O 9:1); IR (neat) 2932s, 2858s, 1462m, 1395w, 1310s, 1254m, 1132s and 1102m (C–O–Si) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.62 (2H, t, $J = 6$, OCH₂), 2.76–2.71 (1H, m, CHN), 2.59 (1H, d, $J = 7$, CH(H)N, *trans* to alkyl chain), 2.07 (1H, d, $J = 5$, CH(H)N, *cis* to alkyl chain), 1.68–1.49 (15H, m, $3 \times \text{CH}_2$ and *St*-Bu), 0.89 (9H, s, *Sit*-Bu), 0.05 (6H, s, SiMe_2); ^{13}C NMR (100 MHz, CDCl_3) δ 62.8 (OCH₂), 59.2 (SC), 38.6 (CHN), 33.8 (CH₂N), 32.3 (CH₂), 31.1 (CH₂), 25.9 (SiCMe_3), 24.2 (SCMe_3), 22.7 (CH₂), 18.3 (SiC), -5.3 (SiMe_2); MS CI m/z (rel. int.)

(4) Brosius, A. D.; Overman, L. E.; Schwink, L. *J. Am. Chem. Soc.* **1999**, *121*, 700–709.

350 ($M + H^+$, 100), 236 (40), 230 (70), 172 (100); HRMS m/z calcd for $C_{16}H_{36}NO_3SSi$, 350.2185, found 350.2174.

1-(*tert*-Butylsulfonyl)-2-(4-chlorobutyl)aziridine (3, entry 6)

Following **General procedure A** using 6-chloro-1-hexene gave, following purification of the resulting residue by column chromatography (petroleum ether/EtOAc 24:1), *aziridine 3* (entry 6) as a colourless oil (433 mg, 40%).

R_f 0.27 (petroleum ether/EtOAc 9:1); IR (neat) 2989s, 2938s, 2869s, 1737w, 1481m, 1458m, 1397, 1366m, 1306s, 1237m, 1130s, 1016w and 654m (C–Cl) cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 3.55 (2H, t, $J = 7$, $ClCH_2$), 2.75–2.70 (1H, m, CHN), 2.60 (1H, d, $J = 7$, $CH(H)N$, *trans* to alkyl chain), 2.09 (1H, d, $J = 5$, $CH(H)N$, *cis* to alkyl chain), 1.89–1.81 (2H, m, CH_2), 1.61–1.59 (4H, m, $2 \times CH_2$), 1.49 (9H, s, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 59.3 (SC), 44.6 ($ClCH_2$), 37.7 (CHN), 34.3 (CH_2N), 31.8 (CH_2), 30.5 (CH_2), 24.2 ($SCMe_3$), 23.7 (CH_2); MS CI m/z (rel. int.) 256 ($^{37}ClM + H^+$, 5), 254 ($^{35}ClM + H^+$, 20), 198 (20), 136 (30), 134 (100), 98 (20); HRMS m/z calcd for $C_{10}H_{21}NO_2SCl$, 254.0982, found 254.0989.

1-(*tert*-Butylsulfonyl)-1-aza-spiro[2.11]tetradecane (3, entry 7)

Following **General procedure A** using methylenecyclododecane⁵ gave, following purification of the resulting residue by column chromatography (petroleum ether/EtOAc 24:1), *aziridine 3* (entry 7) as a white solid (221 mg, 16%).

(mp = 96-97 °C); R_f 0.65 (petroleum ether/EtOAc 9:1); IR (film) 2931s, 2863w, 1471m, 1304s, 1157m, 1128s and 1106s cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.38 (2H, s, CH_2N), 1.84-1.77 (2H, m, CH_2), 1.63-1.55 (4H, m, $2 \times \text{CH}_2$), 1.45 (9H, s, *t*-Bu), 1.43-1.30 (16H, br s, $8 \times \text{CH}_2$); ^{13}C NMR (100 MHz, CDCl_3) δ 60.6 (SC), 51.9 (C), 42.6 (CH_2N), 25.8 ($3 \times \text{CH}_2$), 24.1 (SCMe_3), 22.3 ($2 \times \text{CH}_2$), 21.5 (CH_2); MS CI m/z (rel. int.) 333 ($\text{M} + \text{NH}_4^+$, 25), 316 ($\text{M} + \text{H}^+$, 10), 194 (60), 179 (100); HRMS m/z calcd for $\text{C}_{17}\text{H}_{34}\text{NO}_2\text{S}$, 316.2310, found 316.2310.

(*S*)-1-(*tert*-Butylsulfonyl)-2-decylaziridine (3, entry 8)⁶

(*R*)-1,2 Epoxydodecane was synthesised with >99% ee (as confirmed by chiral HPLC analysis) *via* a hydrolytic kinetic resolution of 1,2-epoxydodecane (90% based on a theoretical maximum of 50%).⁷ (*R*)-1,2 Epoxydodecane ring opening with *tert*-butylsulfonamide (*t*-BuSO₂NH₂, K₂CO₃, BTEAC, dioxane, 90 °C, 16 h, 85%),⁸ followed by alcohol mesylation (Ms₂O, pyridine, DMAP, CH₂Cl₂, rt, 20 min) and ring

(5) Krafft, M. E.; Cheung, Y. Y.; Abboud, K. A. *J. Org. Chem.* **2001**, *66*, 7443–7448.

(6) We thank S. Miles for providing a sample.

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

(8) Albanese, D.; Landini, D.; Penso, M.; Petricci, S. *Tetrahedron* **1999**, *55*, 6387–6394.

closure (K_2CO_3 , THF, H_2O , reflux, 48 h, 97% over 2 steps)⁹ gave *aziridine 3* (entry 8) as a colourless oil (82% over 3 steps).

$[\alpha]^{25}_{\text{D}} = +47.5$ (c 1.00, CHCl_3); R_f 0.38 (petroleum ether/ Et_2O 9:1); IR (neat) 2926s, 2855s, 1481m, 1463m, 1396w, 1366w, 1310s, 1261w, 1131s, 1110m and 1021w cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.78-2.66 (1H, m, CH_2CHN), 2.59 (1H, d, $J = 7$, CH(H)N , *trans* to alkyl chain), 2.07 (1H, d, $J = 4$, CH(H)N , *cis* to alkyl chain), 1.68-1.27 (27H, m, $9 \times \text{CH}_2$ and *t*-Bu), 0.88 (3H, t, $J = 7$, Me); ^{13}C NMR (125 MHz, CDCl_3) δ 59.1 (SC), 38.6 (CHN), 33.8 (CH_2N), 31.8 (CH_2), 31.2 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 26.3 (CH_2), 24.2 (SCMe_3), 22.7 (CH_2), 14.1 (Me); MS CI m/z (rel. int.) 321 ($\text{M} + \text{NH}_4^+$, 30), 304 ($\text{M} + \text{H}^+$, 100), 184 (80); HRMS m/z calcd for $\text{C}_{16}\text{H}_{34}\text{NO}_2\text{S}$, 304.2310, found 304.2300.

(III) Characterization data for α,β -aziridinylsilanes **2** and **4** (entries 2–8)

General procedure B: *trans*- α,β -aziridinylsilane preparation at -78°C

n-BuLi (1.6 M in hexanes, 0.94 mL, 1.5 mmol) was added dropwise to a stirred solution of 2,2,6,6-tetramethylpiperidine (0.25 mL, 1.5 mmol) in THF (3.75 mL) at -78°C under argon. The mixture was warmed to room temperature over 30 min and then cooled to -78°C . To this solution, Me_3SiCl (0.19 mL, 1.5 mmol) was added, followed rapidly by a solution of aziridine (0.5 mmol) in THF (1.5 mL). Following stirring for 1 h at -78°C , sat. aqueous NH_4Cl (5 mL) and Et_2O (5 mL) were added. The phases were separated and the aqueous layer extracted with Et_2O (2×15 mL).

(9) Kim, S., K.; Jacobsen, E., N. *Angew. Chem. Int. Ed.* **2004**, *43*, 3952–3954.

The combined organic layers were dried (MgSO_4) and concentrated under reduced pressure. Purification of the residue by column chromatography (SiO_2) gave the α,β -aziridinylsilane.

(2*R,3*R**)-1-(*tert*-Butylsulfonyl)-2-pentyl-3-(trimethylsilyl)aziridine (2)**

Following **General procedure B** using *aziridine 1* gave, following purification of the resulting residue by column chromatography (petroleum ether/ Et_2O 24:1), *trans*- α,β -aziridinylsilane **2** as a colourless oil (131 mg, 86%).

R_f 0.38 (petroleum ether/ Et_2O 19:1); IR (neat) 2956s, 2931s, 2859m, 2359w, 1409w, 1365w, 1309s, 1249m, 1130m and 1049w cm^{-1} ; ^1H NMR (250 MHz, $(\text{CD}_3)_2\text{SO}$, 65 $^\circ\text{C}$) δ 2.62-2.55 (1H, m, CHN), 1.95-1.82 (1H, m, CH(*H*)CHN), 1.73 (1H, d, $J = 6$, CHSi), 1.44-1.26 (16H, m, CH(*H*)CHN, $3 \times \text{CH}_2$ and *t*-Bu), 0.88 (3H, t, $J = 7$, Me), 0.13 (9H, s, SiMe_3); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ 58.6 (SC), 44.0 (CHN), 38.6 (CHSi), 31.6 (CH_2), 30.8 (CH_2), 25.9 (CH_2), 23.7 (SCMe_3), 21.9 (CH_2), 13.8 (Me), -1.9 (SiMe_3); MS CI m/z (rel. int.) 306 ($\text{M} + \text{H}^+$, 50), 250 (40), 186 (100), 184 (90), 114 (35), 112 (40), 90 (50); HRMS m/z calcd for $\text{C}_{14}\text{H}_{32}\text{NO}_2\text{SSi}$, 306.1923, found 306.1910.

(2*R,3*R**)-2-(But-3-enyl)-1-(*tert*-butylsulfonyl)-3-(trimethylsilyl)aziridine (4, entry 2)**

Following **General procedure B** using *aziridine 3* (entry 2) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 97:3), *trans*- α,β -aziridinylsilane **4** (entry 2) as a colourless oil (115 mg, 80%).

R_f 0.80 (petroleum ether/EtOAc 9:1); IR (neat) 3079w, 2955s, 1642m (C=C), 1481m, 1454m, 1411m, 1365w, 1309s, 1250m, 1130s and 1052w cm⁻¹; ¹H NMR (250 MHz, (CD₃)₂SO, 65 °C) δ 5.86 (1H, ddt, J = 13, 7 and 6, =CH), 5.01-4.97 (2H, m, H₂C=), 2.66-2.57 (1H, m, CHN), 2.21-2.12 (2H, m, =CHCH₂), 2.07-1.94 (1H, m, CH(*H*)CHN), 1.76 (1H, d, J = 6, CHSi), 1.59-1.45 (1H, m, CH(*H*)CHN), 1.39 (9H, s, *t*-Bu), 0.13 (9H, s, SiMe₃); ¹³C NMR (100 MHz, (CD₃)₂SO) δ 137.6 (=CH), 115.4 (H₂C=), 58.7 (SC), 43.7 (CHN), 38.5 (CHSi), 30.9 (CH₂), 30.6 (CH₂), 23.7 (SCMe₃), -1.79 (SiMe₃); MS CI m/z (rel. int.) 290 (M + H⁺, 50), 234 (70), 170 (100), 168 (75), 90 (65); HRMS m/z calcd for C₁₃H₂₈NO₂SSi, 290.1610, found 290.1602.

(2*R,3*R**)-1-(*tert*-Butylsulfonyl)-2-phenethyl-3-(trimethylsilyl)aziridine (4, entry 3)**

Following **General procedure B** using *aziridine 3* (entry 3) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 49:1), *trans*- α,β -aziridinylsilane **4** (entry 3) as a white solid (135 mg, 79%).

(mp = 77-79 °C); R_f 0.84 (petroleum ether/EtOAc 9:1); IR (KBr) 2984s, 1602s, 1482m, 1455m, 1410s, 1363w, 1305s, 1129s, 1052m, 1027w and 711s ($C_{Ar}-H$) cm^{-1} ; 1H NMR (250 MHz, $(CD_3)_2SO$, 65 °C) δ 7.32-7.16 (5H, m, $5 \times C_{Ar}H$), 2.76-2.58 (3H, m, CH_2 and CHN), 2.29-2.15 (1H, m, $CH(H)CHN$), 1.81 (1H, d, $J = 6$, $CHSi$), 1.75-1.69 (1H, m, $CH(H)CHN$), 1.39 (9H, s, *t*-Bu), 0.09 (9H, s, $SiMe_3$); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 140.9 ($C_{Ar\text{ quat}}$), 128.4 ($2 \times C_{Ar}$), 128.2 ($2 \times C_{Ar}$), 125.9 (C_{Ar}), 58.8 (SC), 43.8 (CHN), 38.6 ($CHSi$), 33.5 (CH_2), 32.4 (CH_2), 23.7 ($SCMe_3$), -1.9 ($SiMe_3$). MS CI m/z (rel. int.) 340 ($M + H^+$, 55), 285 (35), 220 (100), 218 (60), 90 (55); HRMS m/z calcd for $C_{17}H_{30}NO_2SSi$, 340.1767, found 340.1765.

(2*R,3*R**)-2-[(*tert*-Butyldimethylsilyloxy)methyl]-1-(*tert*-butylsulfonyl)-3-(trimethylsilyl)aziridine (4, entry 4)**

Following **General procedure B** using *aziridine 3* (entry 4) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 49:1), *trans- α,β -aziridinylsilane 4* (entry 4) as a yellow oil (98 mg, 52%).

R_f 0.71 (petroleum ether/EtOAc 23:2); IR (neat) 2956s, 2859s, 2257w, 1472m, 1395m, 1363m, 1311s, 1252s, 1120s and 1103m ($C-O-Si$) cm^{-1} ; 1H NMR (250 MHz, $(CD_3)_2SO$, 65 °C) δ 3.76 (2H, d, $J = 5$, CH_2), 2.79-2.73 (1H, m, CH_2CHN), 1.78 (1H, d, $J = 6$, $CHSi$), 1.40 (9H, s, *St*-Bu), 0.88 (9H, s, *Sit*-Bu), 0.15 (9H, s, $SiMe_3$), 0.06 (6H, s, $SiMe_2$); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 63.9 (OCH_2), 58.9 (SC), 44.9 (CHN), 34.9 ($CHSi$), 25.6 ($SiCMe_3$), 23.7 ($SCMe_3$), 17.8 (SiC), -1.63 ($SiMe_3$), -5.5 ($SiMe_2$); MS CI m/z (rel. int.) 380 ($M + H^+$, 100), 202 (65), 176 (45); HRMS m/z calcd for $C_{16}H_{38}NO_3SSi_2$, 380.2111, found 380.2128.

(2*R,3*R**)-2-[4-(*tert*-Butyldimethylsilyloxy)butyl]-1-(*tert*-butylsulfonyl)-3-(trimethylsilyl)aziridine (4, entry 5)**

Following **General procedure B** using *aziridine 3* (entry 5) gave, following purification of the resulting residue by column chromatography (petroleum ether/EtOAc 49:1), *trans- α,β -aziridinylsilane 4* (entry 5) as a colourless oil (175 mg, 83%).

R_f 0.61 (petroleum ether/EtOAc 19:1); IR (neat) 2932s, 2858m, 1472m, 1394m, 1363w, 1311s, 1251s, 1132s, 1102m (C–O–Si) and 1006w cm^{-1} ; ^1H NMR (250 MHz, $(\text{CD}_3)_2\text{SO}$, 65 $^\circ\text{C}$) δ 3.60 (2H, t, $J = 6$, OCH_2), 2.62–2.55 (1H, m, CH_2CHN), 1.97–1.84 (1H, m, $\text{CH}(H)\text{CHN}$), 1.72 (1H, d, $J = 6$, CHSi), 1.53–1.38 (14H, m, $\text{CH}(H)\text{CHN}$, $2 \times \text{CH}_2$ and *St*-Bu), 0.87 (9H, s, *Si**t*-Bu), 0.13 (SiMe_3), 0.03 (SiMe_2); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ 62.2 (OCH_2), 58.6 (SC), 44.1 (CHN), 38.5 (CHSi), 31.7 ($2 \times \text{CH}_2$), 25.8 (SiCMe_3), 23.7 (SCMe_3), 22.8 (CH_2), 17.9 (SiC), -1.86 (SiMe_3), -5.4 (SiMe_2); MS CI m/z (rel. int.) 422 ($\text{M} + \text{H}^+$, 25), 228 (70), 155 (70), 98 (60), 90 (70), 74 (100); HRMS m/z calcd for $\text{C}_{19}\text{H}_{44}\text{NO}_3\text{SSi}_2$, 422.2580, found 422.2563.

(2*R,3*R**)-1-(*tert*-Butylsulfonyl)-2-(4-chlorobutyl)-3-(trimethylsilyl)aziridine (4, entry 6)**

Following **General procedure B** using *aziridine 3* (entry 6) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 49:1), *trans- α,β -aziridinylsilane 4* (entry 6) as a colourless oil (129 mg, 79%).

R_f 0.59 (petroleum ether/EtOAc 9:1); IR (neat) 2955s, 2869m, 1481w, 1457w, 1365w, 1307s, 1250m, 1130s and 640m (C–Cl) cm^{-1} ; ^1H NMR (250 MHz, $(\text{CD}_3)_2\text{SO}$, 65 °C) δ 3.63 (2H, t, J = 7, ClCH_2), 2.64-2.57 (1H, m, CH_2CHN), 1.98-1.72 (4H, $\text{CH}(H)\text{CHN}$, CHSi and CH_2), 1.59-1.43 (3H, m, $\text{CH}(H)\text{CHN}$ and CH_2), 1.39 (9H, s, *t*-Bu), 0.34 (9H, s, SiMe_3); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ 58.7 (SC), 45.1 (ClCH_2), 43.7 (CHN), 38.6 (CHSi), 31.5 ($2 \times \text{CH}_2$), 30.9 (CH_2), 23.7 (SCMe_3), -1.84 (SiMe_3); MS CI m/z (rel. int.) 328 ($^{37}\text{ClM} + \text{H}^+$, 5), 326 ($^{35}\text{ClM} + \text{H}^+$, 15), 218 (85), 134 (100), 98 (70), 90 (55); HRMS m/z calcd for $\text{C}_{13}\text{H}_{29}\text{NO}_2\text{SSiCl}$, 326.1377, found 326.1373.

1-(*tert*-Butylsulfonyl)-2-trimethylsilyl-1-aza-spiro[2.11]tetradecane (4, entry 7)

(Representative of the general procedure for *trans*- α,β -aziridinylsilane preparation at 0 °C)

n-BuLi (1.6 M in hexanes, 0.81 mL, 1.3 mmol) was added dropwise to a stirred solution of 2,2,6,6-tetramethylpiperidine (0.22 mL, 1.3 mmol) in THF (3.23 mL) at 0 °C under argon. The mixture was warmed to room temperature over 30 min and then cooled to 0 °C. To this solution, Me_3SiCl (0.17 mL, 1.3 mmol) was added, followed rapidly by a solution of *aziridine 3* (entry 7) (138 mg, 0.43 mmol) in THF (1.30 mL). Following stirring for 16 h at 0 °C, sat. aqueous NH_4Cl (5 mL) and Et_2O (5 mL) were added. The phases were separated and the aqueous layer extracted with Et_2O (2×15 mL). The combined organic layers were dried (MgSO_4) and concentrated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/ Et_2O 49:1) gave *α,β -aziridinylsilane 4* (entry 7) as a colourless oil (107 mg, 63%).

R_f 0.13 (petroleum ether/Et₂O 49:1); IR (film) 2932s, 2864m, 1641w, 1472m, 1392w, 1306s, 1251s and 1124s cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.44-2.38 (1H, m, CH(*H*)), 2.07 (1H, s, CHSi), 1.96-1.89 (1H, m, CH(*H*)), 1.81-1.71 (1H, m, CH(*H*)), 1.62-1.27 (27H, m, 9 $\times$ CH₂, *t*-Bu), 0.99-0.86 (1H, m, CH(*H*)), 0.15 (9H, s, SiMe₃); ¹³C NMR (100 MHz, CDCl₃) δ 60.3 (CN), 55.1 (SC), 45.8 (CHSi), 29.9 (CH₂), 29.6 (CH₂), 26.3 (CH₂), 26.0 (CH₂), 25.9 (CH₂), 24.3 (SCMe₃), 22.7 (CH₂), 22.2 (CH₂), 22.0 (2 $\times$ CH₂), 21.9 (CH₂), 21.4 (CH₂), -1.27 (SiMe₃); MS CI m/z (rel. int.) 388 (M + H⁺, 30), 316 (100), 314 (50), 196 (70), 184 (50), 90 (60); HRMS m/z calcd for C₂₀H₄₂NO₂SSi, 388.2706, found 388.2702.

(2*S*, 3*S*)-1-(*tert*-Butylsulfonyl)-2-decyl-3-(trimethylsilyl)aziridine (4, entry 8)

Following **General procedure B** using *aziridine 3* (entry 8) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 49:1), *trans*- α,β -aziridinylsilane **4** (entry 8) as a colourless oil (152 mg, 81%).

$[\alpha]_D^{25} = +45.4$ (c 1.0, CHCl₃); R_f 0.74 (petroleum ether/Et₂O 9:1); IR (neat) 2927s, 2855m, 1481w, 1459m, 1365w, 1311s, 1250s, 1130s, 1102w and 1022w cm⁻¹; ¹H NMR (250 MHz, (CD₃)₂SO, 65 °C) δ 2.61-2.54 (1H, m, CH₂CHN), 1.95-1.82 (1H, m, CH(*H*)CHN), 1.73 (1H, d, J = 6, CHSi), 1.42-1.22 (26H, m, CH(*H*)CHN), 8 $\times$ CH₂ and *t*-Bu), 0.87 (3H, t, J = 7, Me), 0.13 (9H, s, SiMe₃); ¹³C NMR (125 MHz, (CD₃)₂SO) δ 58.7 (SC), 44.1 (CHN), 39.0 (CHSi), 31.2 (CH₂CHN), 28.9, (CH₂), 28.8 (CH₂), 28.6 (CH₂), 28.5 (2 $\times$ CH₂), 26.2 (2 $\times$ CH₂), 23.7 (SCMe₃), 22.0 (CH₂), 13.9 (Me), -1.89 (SiMe₃); MS CI m/z (rel. int.) 376 (M + H⁺, 100), 256 (30), 184 (95), 182 (45); HRMS m/z calcd for C₁₉H₄₂NO₂SiS, 376.2706, found 376.2712.

Confirmation of ee

TBAF (1.0 M in THF, 0.20 mL, 0.20 mmol) was added dropwise to a stirred solution of α,β -aziridinylsilane **4** (entry 8) (68 mg, 0.18 mmol) in THF (3.5 mL) at room temperature. Following stirring for 1 h at room temperature, H₂O (5 mL) was added and the mixture extracted with Et₂O (3 x 15 mL). The combined organic layers were dried (MgSO₄) and concentrated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/Et₂O 19:1) gave *aziridine 3* (entry 8) as a colourless oil (49 mg, 89%).

$[\alpha]_D^{25} = +45.6$ (*c* 1.00, CHCl₃); spectroscopic data matched those reported above.

(IV) Characterization data for substituted aziridines 5, 6 and 7 (a-j)**General procedure C: Substituted aziridine preparation**

n-BuLi (1.6 M in hexanes, 0.47 mL, 0.75 mmol) was added dropwise to a stirred solution of 2,2,6,6-tetramethylpiperidine (0.13 mL, 0.75 mmol) in THF (1.9 mL) at –78 °C. Following warming to room temperature over 20 min, the reaction was cooled to –78 °C and a solution of aziridine (0.25 mmol) in THF (0.75 mL) added, followed after 90 s by the electrophile (0.75 mmol). Following stirring for time *t* at –78 °C, sat. aqueous NH₄Cl (5 mL) and Et₂O (5 mL) were added. The phases were separated and the aqueous layer extracted with Et₂O (2 × 15 mL). The combined organic layers were dried (MgSO₄) and concentrated under reduced pressure.

Purification of the residue by column chromatography (SiO₂ unless indicated otherwise) gave the substituted aziridines.

(2*R,3*R**)-1-(*tert*-Butylsulfonyl)-2-pentyl-3-(tributylstannyl)aziridine (5)**

n-BuLi (1.6 M in hexanes, 0.47 mL, 0.75 mmol) was added dropwise to a stirred solution of 2,2,6,6-tetramethylpiperidine (0.13 mL, 0.75 mmol) in THF (1.9 mL) at -78°C . Following warming to room temperature over 20 min, the reaction was cooled to -78°C and then a solution of *aziridine 1* (58 mg, 0.25 mmol) in THF (0.75 mL) was added, followed after 90 s by Bu₃SnCl (0.20 mL, 0.75 mmol). Following stirring for 1 h at -78°C , MeOH (0.5 mL) was added and the solution concentrated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/Et₂O 49:1 (Florisil[®])) gave α,β -aziridinylstannane **5** as a colourless oil (114 mg, 87%).

*R*_f 0.40 (petroleum ether/Et₂O 49:1); IR (neat) 2926s, 2856s, 1463m, 1395w, 1377w, 1305s, 1242w and 1160m cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 2.62-2.51 (1H, m, CHN), 1.86-1.80 (1H, m, CH(*H*)CHN), 1.77 (1H, d, *J* = 6, CHSn), 1.62-1.29 (28H, m, *t*-Bu, CH(*H*)CHN, 3 × CH₂, 3 × SnCH₂CH₂ and 3 × SnCH₂CH₂CH₂), 1.11-0.85 (18H, m, Me, 3 × SnCH₂ and 3 × SnCH₂CH₂CH₂Me); ¹³C NMR (100 MHz, CDCl₃) δ 59.1 (SC), 44.5 (CHN), 36.0 (CHSn), 33.8 (CH₂), 31.6 (CH₂), 28.9 (*J*_{Sn-C} = 20, SnCH₂CH₂), 27.4 (*J*_{Sn-C} = 62, SnCH₂CH₂CH₂), 26.1 (CH₂), 24.3 (SCMe₃), 22.6 (CH₂), 13.9 (Me), 13.7 (SnCH₂CH₂CH₂Me), 10.8 (*J*_{Sn-C} = 336, SnCH₂); ¹¹⁹Sn NMR (93MHz, CDCl₃) δ -18.76; MS EI *m/z* (rel. int.) 524 (60), 522 (M + H⁺, 50), 520 (30),

308 (100), 306 (80), 251 (60), 114 (30); HRMS m/z calcd for $C_{23}H_{50}NO_2SSn$, 524.2579, found 524.2583.

(2*R,3*R**)-1-(*tert*-Butylsulfonyl)-2-pentyl-3-deuterioaziridine (6)**

Following **General procedure C** using CD_3OD (0.5 mL) ($t = 90$ s) gave, following purification of the resulting residue by column chromatography (petroleum ether/ Et_2O 9:1), *substituted aziridine 6* as a colourless oil (50 mg, 86%) (91% deuterium incorporation as judged by 1H NMR spectroscopy).

R_f 0.36 (petroleum ether/ Et_2O 9:1); IR (neat) 2933s, 2861m, 1459w, 1366w, 1307s, 1219w and 1126s cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 2.72-2.68 (1H, m, CHN), 2.57 (0.1H, d, $J = 7$, CH(*H*)N, *trans* to alkyl chain), 2.05 (1H, d, $J = 5$, CH(*H*)N, *cis* to alkyl chain), 1.70-1.58 (1H, m, CH(*H*)CHN), 1.48-1.41 (12H, m, *t*-Bu, CH_2 and CH(*H*)CHN), 1.33-1.31 (4H, m, $2 \times CH_2$), 0.88 (3H, t, $J = 7$, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 59.2 (SC), 38.7 (CHN), 33.7 (CHDN, t, $J = 26$), 31.3 (CH_2), 31.2 (CH_2), 25.9 (CH_2), 24.2 ($SCMe_3$), 22.4 (CH_2), 13.9 (Me); MS CI m/z (rel. int.) 235 (M + H^+ , 100), 179 (20), 115 (70); HRMS m/z calcd for $C_{11}H_{23}NO_2SD$, 235.1591, found 235.1585.

(*R*^{*})-[(2*R*^{*},3*R*^{*})-1-(*tert*-Butylsulfonyl)-3-pentylaziridin-2-yl]-phenylmethanol**(7a)**

Following **General procedure C** using benzaldehyde (80 μ L, 0.75 mmol) ($t = 90$ s) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), *aziridinyl alcohol* **7a** as a white solid (31 mg, 38%).

(mp = 65-67 °C); R_f 0.51 (petroleum ether/Et₂O 4:1); IR (film) 3490br s (O–H), 2932m, 2680w, 1642m, 1454m, 1366w, 1294s, 1198w, 1117s, 1023w and 717s (C_{Ar-H}) cm^{-1} ; 1H NMR (400 MHz, CDCl₃) δ 7.45-7.29 (5H, m, $5 \times C_{Ar-H}$), 4.86-4.83 (1H, dd, $J = 9$ and 2, $CHOH$), 3.99 (1H, br s, OH), 2.97-2.93 (1H, m, CH_2CHN), 2.78 (1H, dd, $J = 9$ and 5, $CHNCHO$), 1.83-1.75 (1H, m, $CH(H)CHN$), 1.51 (9H, s, *t*-Bu), 1.19-1.01 (7H, m, $CH(H)CHN$ and $3 \times CH_2$), 0.75 (3H, t, $J = 7$, Me); ^{13}C NMR (100 MHz, CDCl₃) δ 139.9 ($C_{Ar\text{ quat}}$), 128.6 ($2 \times C_{Ar\text{ ortho}}$), 128.2 ($2 \times C_{Ar}$), 126.0 (C_{Ar}), 73.2 ($CHOH$), 60.3 (SC), 55.5 ($CHNCHO$), 46.0 (CH_2CHN), 31.0 (CH_2), 30.5 (CH_2), 25.4 (CH_2), 23.9 ($SCMe_3$), 22.3 (CH_2), 13.7 (Me); MS CI m/z (rel. int.) 357 ($M + NH_4^+$, 5), 340 ($M + H^+$, 10), 220 (100), 202 (60), 100 (70); HRMS m/z calcd for C₁₈H₃₀NO₃S, 340.1946, found 340.1941.

(*R*^{*})-1-[(2*S*^{*},3*R*^{*})-1-(*tert*-Butylsulfonyl)-3-penyylaziridin-2-yl]-2,2-dimethylpropan-1-ol (7b)

Following **General procedure C** using pivalaldehyde (80 μ L, 0.75 mmol) ($t = 90$ s) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), *aziridinyl alcohol 7b* as a colourless oil (43 mg, 54%).

R_f 0.69 (petroleum ether/Et₂O 4:1); IR (neat) 3508br s (O–H), 2958s, 1481m, 1405w, 1365m, 1293s, 1245w, 1117s (C–O), 1043w and 1012m cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ 3.71 (1H, br s, OH), 3.39 (1H, dd, $J = 10$ and 3, *CHOH*), 2.88–2.84 (1H, m, *CH₂CHN*), 2.73 (1H, dd, $J = 10$ and 5, *CHNCHO*), 1.76–1.52 (2H, m, *CH₂CHN*), 1.48–1.29 (15H, s, 3 $\times$ CH₂ and *St*-Bu), 1.00 (9H, s, *OCHt*-Bu), 0.89 (3H, t, $J = 7$, Me); ¹³C NMR (100 MHz, CDCl₃) δ 77.3 (*CHOH*), 60.3 (SC), 52.7 (*CHNCHO*), 46.7 (*CH₂CHN*), 35.1 (*OCHCMe₃*), 31.6 (*CH₂CHN*), 30.3 (CH₂), 26.2 (*OCHCMe₃*), 25.2 (CH₂), 24.0 (SCMe₃), 22.4 (CH₂), 13.9 (Me); MS CI m/z (rel. int.) 320 ($M + H^+$, 15), 220 (45), 183 (100), 125 (50), 100 (40); HRMS m/z calcd for C₁₆H₃₄NO₃S, 320.2259, found 320.2267.

(*R*^{*})-1-[(2*S*^{*},3*R*^{*})-1-(*tert*-Butylsulfonyl)-3-pentylaziridin-2-yl]-2-methylpropan-1-ol (7c)

Following **General procedure C** using isobutyraldehyde (70 μ L, 0.75 mmol) ($t = 90$ s) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), *aziridinyl alcohol 7c* as a colourless oil (33 mg, 43%).

R_f 0.64 (petroleum ether/Et₂O 4:1); IR (neat) 3512br m (O–H), 2960s, 2933s, 1467m, 1366w, 1296s, 1258m, 1124s, 1089m and 1034w cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ 3.62 (1H, br s, OH), 3.50–3.46 (1H, m, CHOH), 2.84–2.80 (1H, m, CH₂CHN), 2.68 (1H, dd, $J = 9$ and 5, CHNCHO), 1.90–1.70 (2H, m, CHMe₂, CH(*H*)CHN), 1.47 (9H, s, *t*-Bu), 1.43–1.31 (7H, m, CH(*H*)CHN and 3 $\times$ CH₂), 1.03 (3H, d, $J = 7$, CHMe), 1.01 (3H, d, $J = 7$, CHMe), 0.89 (3H, t, $J = 7$, CH₂Me); ¹³C NMR (100 MHz, CDCl₃) δ 74.9 (CHOH), 60.2 (SC), 53.6 (CHNCHO), 45.9 (CH₂CHN), 32.7 (CHMe₂), 31.5 (CH₂CHN), 30.5 (CH₂), 25.3 (CH₂), 24.0 (SCMe₃), 22.4 (CH₂), 18.9 (CHMe), 17.9 (CHMe), 13.9 (CH₂Me); MS CI m/z (rel. int.) 306 ($M + H^+$, 15), 220 (50), 169 (100), 155 (55), 100 (50); HRMS m/z calcd for C₁₅H₃₂NO₃S, 306.2103, found 306.2097.

(*R*^{*})-1-[(2*S*^{*},3*R*^{*})-(1-(*tert*-Butylsulfonyl)-3-pentylaziridin-2-yl)]butan-1-ol (7d)

Following **General procedure C** using butyraldehyde (70 μ L, 0.75 mmol) ($t = 90$ s) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1), *aziridinyl alcohol 7d* as a colourless oil (41 mg, 54%).

R_f 0.35 (petroleum ether/Et₂O 4:1); IR (film) 3517br m (O–H), 2933s, 2873s, 1459m, 1366w, 1294s, 1124s, 1084m and 1013m cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.78-3.71 (1H, m, *CHOH*), 3.61 (1H, br s, OH), 2.79-2.75 (1H, m, *CH₂CHN*), 2.58 (1H, dd, *J* 9 and 5, *CHNCHO*), 1.82-1.77 (1H, m, *CH(H)CHN*), 1.67-1.31 (20H, m, *CH(H)CHN*, 5 $\times$ CH₂ and *t*-Bu), 0.94 (3H, t, *J* 7, Me), 0.89 (3H, t, *J* 7, Me); ¹³C NMR (100 MHz, CDCl₃) δ 70.2 (*CHOH*), 60.1 (SC), 54.8 (*CHNCHO*), 45.5 (*CH₂CHN*), 36.9 (*OCHCH₂*), 31.5 (CH₂), 30.7 (CH₂), 25.5 (CH₂), 23.9 (SCMe₃), 22.4 (CH₂), 18.6 (CH₂), 14.0 (Me), 13.9 (Me); MS CI *m/z* (rel. int.) 306 (*M* + H⁺, 100), 250 (25), 186 (50), 184 (55); HRMS *m/z* calcd for C₁₅H₃₂NO₃S, 306.2103, found 306.2092.

3-[(2*S**,3*R**)-1-(*tert*-Butylsulfonyl)-3-pentylaziridin-2-yl]pentan-3-ol (**7e**)

Following **General procedure C** using 3-pentanone (80 μ L, 0.75 mmol) (*t* = 1 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 9:1 $\rightarrow$ 4:1), *aziridinyl alcohol 7e* as a white solid (61 mg, 76%). (mp = 65-67 °C); R_f 0.19 (petroleum ether/Et₂O 4:1); IR (film) 3509br m (O–H), 2964s, 2929s, 1458m, 1367m, 1297s, 1128m, 1110s (C–O) and 1022m cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.84-2.79 (2H, m, *CH₂CHN*, *CHCO*), 2.04-1.96 (1H, m, *CH(H)CHN*), 1.86-1.78 (1H, m, *CH(H)CHN*), 1.66-1.31 (19H, 3 $\times$ CH₂, 2 $\times$ OCCH₂ and *t*-Bu.), 0.96-0.87 (9H, m, 2 $\times$ OCCH₂Me and Me); ¹³C NMR (100 MHz, CDCl₃) δ 71.5 (CO), 60.0 (SC), 50.7 (*CHCO*), 48.1 (*CH₂CHN*), 31.5 (*CH₂CHN*), 30.6 (2 $\times$ OCCH₂), 28.4 (CH₂), 27.6 (CH₂), 24.4 (CMe₃), 22.4 (CH₂), 13.9 (Me), 7.7 (OCCH₂Me), 7.5 (OCCH₂Me); MS CI *m/z* (rel. int.) 320 (*M* + H⁺, 20), 198 (60), 182

(90), 112 (100), 100 (95); HRMS m/z calcd for $C_{16}H_{34}NO_3S$, 320.2259, found 320.2260.

1-[(2*S,3*R**)-1-(*tert*-Butylsulfonyl)-3-pentylazirdin-2-yl]cyclopentanol (7f)**

Following **General procedure C** using cyclopentanone (70 μ L, 0.75 mmol) ($t = 1$ h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 4:1), *aziridinyl alcohol* **7f** as a colourless oil (47 mg, 59%).

R_f 0.20 (petroleum ether/Et₂O 4:1); IR (film) 3506br s (O–H), 2958s, 2872m, 1455m, 1300s, 1205w, 1123s and 1001w cm^{-1} ; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ 4.45 (1H, s, OH), 2.74 (1H, d, $J = 5$, CHNCO), 2.61–2.58 (1H, m, CH_2CHN), 2.03–1.97 (1H, m, $\text{CH}(H)\text{CHN}$), 1.73–1.25 (24H, m, $\text{CH}(H)\text{CHN}$, $7 \times \text{CH}_2$ and *t*-Bu), 0.87 (3H, t, $J = 7$, Me); ^{13}C NMR (125 MHz, $(\text{CD}_3)_2\text{SO}$) δ 78.9 (CO), 59.4 (SC), 52.8 (CH_2CHN), 45.4 (CHNCO), 37.6 (COCH_2), 35.9 (COCH_2), 30.9 (CH_2CHN), 28.2 (CH_2), 27.1 (CH_2), 23.8 (SCMe_3), 23.6 (COCH_2CH_2), 23.2 (COCH_2CH_2), 21.9 (CH_2), 13.8 (Me); MS CI m/z (rel. int.) 335 ($\text{M} + \text{NH}_4^+$, 10), 318 ($\text{M} + \text{H}^+$, 10), 300 (35), 232 (90), 198 (50), 181 (80), 155 (60), 112 (100); HRMS m/z calcd for $C_{16}H_{32}NO_3S$, 318.2103, found 318.2115.

[(2*S,3*R**)-1-(*tert*-Butylsulfonyl)-3-pentylazirdin-2-yl](phenyl)methanone (7g)**

Following **General procedure C** using *N*, *N*-dimethylbenzamide (223 mg, 1.5 mmol) in THF (0.50 mL) ($t = 1$ h) gave, following purification of the resulting residue by

column chromatography (petroleum ether/Et₂O 24:1), *substituted aziridine 7g* as a colourless oil (48 mg, 57%).

R_f 0.30 (petroleum ether/Et₂O 4:1); IR (neat) 2931s, 2861m, 1693s (C=O), 1598w, 1523w, 1482m, 1451m, 1311s, 1227s, 1129s and 736s (C_{Ar}-H) cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 8.10 (2H, d, $J = 7$, 2 $\times$ C_{Ar}H), 7.68-7.65 (1H, m, C_{Ar}H), 7.56-7.52 (2H, m, 2 $\times$ C_{Ar}H), 4.14 (1H, d, $J = 4$, CHNCO), 3.06-3.02 (1H, m, CH₂CHN), 2.37-2.28 (1H, m, CH(*H*)CHN), 1.98-1.89 (1H, m, CH(*H*)CHN), 1.65-1.44 (11H, CH₂ and *t*-Bu), 1.37-1.32 (4H, m, 2 $\times$ CH₂), 0.87 (3H, t, $J = 7$, Me); ¹³C NMR (63 MHz, CDCl₃) δ 192.1 (CO), 135.8 (C_{Ar} quat), 134.2 (C_{Ar}), 128.9 (2 $\times$ C_{Ar} ortho), 128.5 (2 $\times$ C_{Ar}), 61.0 (SC), 49.6 (CH₂CHN), 46.9 (CHNCO), 31.4 (CH₂CHN), 28.8 (CH₂), 27.6 (CH₂), 23.9 (CMe₃), 22.4 (CH₂), 13.9 (Me); MS CI m/z (rel. int.) 355 (M + NH₄⁺, 100), 338 (M + H⁺, 20), 220 (20); HRMS m/z calcd for C₁₈H₃₁N₂O₃S, 355.2050, found 355.2052.

(2*S,3*R**)-1-(*tert*-Butylsulfonyl)-3-pentylaziridine-2-carbaldehyde (7h)**

Following **General procedure C** using *N*, *N*-dimethylformamide (60 μ L, 0.75 mmol) ($t = 1$ h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 4:1 (Florisil[®])), *substituted aziridine 7h* as a colourless oil (41 mg, 63%).

R_f 0.25 (petroleum ether/Et₂O 4:1); IR (neat) 2958s, 2934s, 2862m, 1723s (C=O), 1481w, 1461m, 1315s, 1217w, 1123s and 1042w cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 9.33 (1H, d, $J = 7$, CHO), 3.28 (1H, br s, CHCO), 3.05-3.03 (1H, m, CH₂CHN), 1.91-1.94 (1H, m, CH(*H*)CHN), 1.62-1.32 (16H, m, 3 $\times$ CH₂, CH(*H*)CHN and *t*-Bu),

0.90 (3H, t, $J = 7$, Me); ^{13}C NMR (63 MHz, CDCl_3) δ 194.3 (CHO), 60.7 (SC), 51.5 (CH_2CHN), 46.3 (CHCO), 31.2 (CH_2CHN), 29.9 (CH_2), 25.9 (CH_2), 24.1 (SCMe_3), 22.4 (CH_2), 13.9 (Me); MS CI m/z (rel. int.) 279 ($\text{M} + \text{NH}_4^+$, 100), 262 ($\text{M} + \text{H}^+$, 40), 198 (35), 142 (40); HRMS m/z calcd for $\text{C}_{12}\text{H}_{24}\text{NO}_3\text{S}$, 262.1477, found 262.1473.

(2*R,3*R**)-1-(*tert*-Butylsulfonyl)-2-pentyl-3-(phenylsulfonyl)aziridine (7i)**

n-BuLi (1.6 M in hexanes, 0.94 mL, 1.50 mmol) was added dropwise to a stirred solution of 2,2,6,6-tetramethylpiperidine (0.25 mL, 1.50 mmol) in THF (1.90 mL) at $-78\text{ }^\circ\text{C}$. Following warming to room temperature over 20 min, the reaction was cooled to $-78\text{ }^\circ\text{C}$ and then a solution of *aziridine* **1** (58 mg, 0.25 mmol) in THF (0.75 mL) was added, followed after 90 s by benzenesulfonyl fluoride (0.12 mL, 1.00 mmol). Following stirring for 1 h at $-78\text{ }^\circ\text{C}$, sat. NH_4Cl (5 mL) and Et_2O (5 mL) were added. The phases were separated and the aqueous layer extracted with Et_2O (2×15 mL). The combined organic layers were dried (MgSO_4) and concentrated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/ Et_2O 4:1) gave *substituted aziridine* **7i** as a pale yellow crystalline solid (86 mg, 92%).

mp = $85\text{--}87\text{ }^\circ\text{C}$; R_f 0.36 (petroleum ether/ Et_2O 4:1); IR (film) 3067w, 2933s, 2872s, 1585m, 1449s, 1401m, 1367m, 1317s (S=O), 1213m, 1157s (S=O), 1087m, 1023w and 706s ($\text{C}_{\text{Ar}}\text{--H}$) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (2H, d, $J = 8$, $2 \times \text{C}_{\text{Ar}}\text{H}$), 7.74–7.71 (1H, m, $\text{C}_{\text{Ar}}\text{H}$), 7.63–7.59 (2H, m, $2 \times \text{C}_{\text{Ar}}\text{H}$), 4.00 (1H, d, $J = 4$, CHSO_2), 3.02–2.97 (1H, m, CH_2CHN), 2.23–2.15 (1H, m, $\text{CH}(H)\text{CHN}$), 1.74–1.64 (1H, m, $\text{CH}(H)\text{CHN}$), 1.45–1.38 (11H, m, CH_2 and *t*-Bu), 1.25–1.17 (4H, m, $2 \times \text{CH}_2$), 0.82

(3H, t, $J = 7$, Me); ^{13}C NMR (100 MHz, CDCl_3) δ 136.7 ($\text{C}_{\text{Ar quat}}$), 134.7 (C_{Ar}), 129.5 ($2 \times \text{C}_{\text{Ar}}$), 128.9 ($2 \times \text{C}_{\text{Ar ortho}}$), 61.7 (CHSO_2), 58.5 (SC), 48.1 (CH_2CHN), 30.9 (CH_2CHN), 27.4 (CH_2), 27.3 (CH_2), 23.9 (CMe_3), 22.3 (CH_2), 13.8 (Me); MS CI m/z (rel. int.) 391 ($\text{M} + \text{NH}_4^+$, 100), 374 ($\text{M} + \text{H}^+$, 10), 232 (20); HRMS m/z calcd for $\text{C}_{17}\text{H}_{31}\text{N}_2\text{O}_4\text{S}_2$, 391.1725, found 391.1739.

(2*S,3*R**)-Methyl 1-(*tert*-butylsulfonyl)-3-pentylaziridine-2-carboxylate (7j)**

n-BuLi (1.6 M in hexanes, 0.47 mL, 0.75 mmol) was added dropwise to a stirred solution of 2,2,6,6-tetramethylpiperidine (0.13 mL, 0.75 mmol) in THF (1.90 mL) at -78°C . Following warming to room temperature over 20 min, the reaction was cooled to -78°C and then a solution of *aziridine 1* (58 mg, 0.25 mmol) in THF (0.75 mL) was added. After 90 s, CO_2 was bubbled through the solution for 10 min, and then sat. aqueous NH_4Cl (5 mL) and Et_2O (5 mL) were added and the phases separated. The aqueous layer was acidified with HCl (2.0 N, 0.50 mL) and extracted with EtOAc (4×10 mL). The combined organic layers were dried (MgSO_4) and concentrated under reduced pressure. The residue was re-dissolved in Et_2O (5 mL) and diazomethane in Et_2O^{10} (approx. 8 mmol in 25 mL) was added dropwise over 30 min to the stirring solution. Following diazomethane addition, argon was bubbled through the solution until the reaction became colorless and then the solvent was concentrated under reduced pressure. Purification of the residue by column chromatography (petroleum ether/ Et_2O 9:1) gave *substituted aziridine 7j* as a colourless oil (45 mg, 63%).

(10) Black, T. H. *Aldrichim. Acta* 1983, 16, 3–10.

R_f 0.62 (petroleum ether/Et₂O 4:1); IR (neat) 2952s, 2933s, 2862m, 1753s (C=O), 1444m, 1366w, 1315s, 1248m, 1207m, 1123s, 1059w, 1025w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.79 (3H, s, OMe), 3.22 (1H, d, J = 4, CHCO), 3.01-2.95 (1H, m, CH₂CHN), 2.20-2.12 (1H, m, CH(*H*)CHN), 1.78-1.69 (1H, m, CH(*H*)CHN), 1.59-1.29 (15H, m, 3 $\times$ CH₂ and *t*-Bu), 0.89 (3H, t, J = 7, Me); ¹³C NMR (100 MHz, CDCl₃) δ 167.9 (CO), 60.9 (SC), 52.7 (OMe), 47.6 (CHCO), 44.2 (CH₂CHN), 31.2 (CH₂CHN), 28.5 (CH₂), 27.2 (CH₂), 23.9 (SCMe₃), 22.4 (CH₂), 13.9 (Me); MS CI m/z (rel. int.) 309 (M + NH₄⁺, 55), 292 (M + H⁺, 45), 172 (100); HRMS m/z calcd for C₁₃H₂₆NO₄S, 292.1583, found 292.1595.

(V) ^1H and ^{13}C NMR spectra of aziridines **1** and **3** (entries 2–8)

S29

S30

S31

S33

S34

S35

(VI) ^1H and ^{13}C NMR spectra of α,β -azirdinylsilanes **2** and **4** (entries 2–8)

S41

S42

S43

S45

S46

S47

S48

S49

S50

S51

S52

S53

S54

S55