Supporting information

Substituted Aziridines by Lithiation–Electrophile Trapping of 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 argon.¹ TMP was distilled from CaH₂. Me₃SiCl and Bu₃SnCl were distilled over K₂CO₃. 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, ¹³C

and $^{119}$Sn NMR spectra were recorded in CDCl$_3$ or (CD$_3$)$_2$SO at ambient temperature or 65 °C as indicated. Data are expressed as chemical shifts in parts per million (ppm) relative to residual chloroform ($^1$H \( \delta \) 7.27), CDCl$_3$ ($^{13}$C \( \delta \) 77.0), residual dimethyl sulfoxide ($^1$H \( \delta \) 2.50) or (CD$_3$)$_2$SO ($^{13}$C \( \delta \) 39.5) as the internal standard on the \( \delta \) 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 $[\alpha]^T_D$ were measured using a polarimeter with a cell of path length 1.0 cm, at T °C and are given in $10^{-1}$ deg cm$^2$ 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 preparation

![Chemical structure](image)

The appropriate alkene (4.3 mmol) was added to a stirred suspension of BusNClNa (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%).

\[ R_f 0.72 \text{ (petroleum ether/EtOAc 9:1)}; \text{ IR (neat) } 2933 \text{m, } 2861 \text{m, } 1480 \text{m, } 1366 \text{w, } 1305 \text{s, } 1242 \text{w, } 1129 \text{s and } 1106 \text{cm}^{-1}; \] ¹H NMR (400 MHz, CDCl₃) \( \delta \) 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 \times CH₂), 0.90 (3H, t, \( J = 7 \), Me); ¹³C NMR (100 MHz, CDCl₃) \( \delta \) 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 Cl \( m/z \) (rel. int.) 234 (M + H⁺), 226 (M + H₂O).

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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$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.84 (1H, ddt, $J$ = 13, 7 and 6, $=\text{CH}$), 5.09-4.99 (2H, m, $H_2C=), 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, $=\text{CHCH}_2$), 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$_3$) $\delta$ 137.1 (=$\text{CH}$), 115.5 (H$_2$C=), 59.2 (SC), 37.9 (CHN), 34.2 (CH$_2$N), 30.7 (CH$_2$), 30.5 (CH$_2$), 24.2 (SCMe$_3$); MS CI m/z (rel. int.) 218 (M + H$^+$, 100), 98 (80); HRMS m/z calcd for C$_{10}$H$_{20}$NO$_2$S, 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); \(R_t\) 0.45 (petroleum ether/EtOAc 9:1); IR (KBr) 2930s, 1602s, 1453s, 1408m, 1362s, 1292s, 1111s, 1055w, 1002s and 719s (C₈–H) cm \(^{-1}\); \(^1\)H NMR (400 MHz, CDCl \(_3\)) \(\delta\) 7.31-7.27 (2H, m, 2 × C₈H), 7.23-7.19 (3H, m, 3 × C₈H), 2.85-2.72 (3H, m, ArCH₂ and CHN), 2.59 (1H, d, \(J = 7\), CH(H)N, \textit{trans} to alkyl chain), 2.05 (1H, d, \(J = 5\), CH(H)N, \textit{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 \(_3\)) \(\delta\) 140.8 (C₈quat), 129.3 (2 × C₈), 128.4 (2 × C₈), 126.1 (C₈), 59.3 (SC), 37.8 (CHN), 34.4 (CH₂N), 33.3 (ArCH₂), 32.7 (CH₂), 24.2 (SCMe₃); 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\(_2\)S, 268.1371, found 268.1375.

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

Following **General procedure A** using allyloxy(*tert*-butyl)dimethylsilane\(^3\) 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%).

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$R_f$ 0.62 (petroleum ether/EtOAc 9:1); IR (neat) 2931m, 1463m, 1392m, 1311s, 1254m, 1130s and 1101m (C–O–Si) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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, St-Bu), 0.07 (6H, s, SiMe$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 62.4 (OCH$_2$), 59.5 (SC), 40.2 (CHN) 29.6 (CH$_2$N), 25.8 (SiCMe$_3$), 24.2 (SCMe$_3$), 18.3 (SiC), −5.4 (SiMe$_2$); MS CI m/z (rel. int.) 308 (M + H$^+$, 100), 188 (45), 130 (55); HRMS m/z calcd for C$_{13}$H$_{30}$NO$_3$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)dimethylsilane$^4$ gave, following purification of the resulting residue by column chromatography (petroleum ether/Et$_2$O 9:1), aziridine 3 (entry 5) as a colourless oil (1.01 g, 68%).

$R_f$ 0.18 (petroleum ether/Et$_2$O 9:1); IR (neat) 2932s, 2858s, 1462m, 1395w, 1310s, 1254m, 1132s and 1102m (C–O–Si) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.62 (2H, t, $J = 6$, OCH$_2$), 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 × CH$_2$ and St-Bu), 0.89 (9H, s, St-Bu), 0.05 (6H, s, SiMe$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 62.8 (OCH$_2$), 59.2 (SC), 38.6 (CHN), 33.8 (CH$_2$N), 32.3 (CH$_2$), 31.1 (CH$_2$), 25.9 (SiCMe$_3$), 24.2 (SCMe$_3$), 22.7 (CH$_2$), 18.3 (SiC), −5.3 (SiMe$_2$); MS CI m/z (rel. int.)

350 (M + H⁺, 100), 236 (40), 230 (70), 172 (100); HRMS m/z calcld for C₁₆H₃₆NO₃SSi, 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, CDCl₃) δ 3.55 (2H, t, $J = 7$, ClCH₂), 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, CH₂), 1.61-1.59 (4H, m, 2 × CH₂), 1.49 (9H, s, t-Bu); ¹³C NMR (100 MHz, CDCl₃) δ 59.3 (SC), 44.6 (ClCH₂), 37.7 (CHN), 34.3 (CH₂N), 31.8 (CH₂), 30.5 (CH₂), 24.2 (SCMe₃), 23.7 (CH₂); MS CI m/z (rel. int.) 256 ($^{35}$ClM + H⁺, 5), 254 ($^{35}$ClM + H⁺, 20), 198 (20), 136 (30), 134 (100), 98 (20); HRMS m/z calcld for C₁₆H₂₁NO₂SCl, 254.0982, found 254.0989.
1-(*tert*-Butylsulfonyl)-1-aza-spiro[2.11]tetradecane (3, entry 7)

Following General procedure A using methylenecyclododecane\(^5\) 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%).

\((\text{mp} = 96-97 \, ^\circ\text{C}); \, R_f \, 0.65 \, (\text{petroleum ether/EtOAc} \, 9:1); \, \text{IR} \, (\text{film}) \, 2931\text{s}, \, 2863\text{w}, \, 1471\text{m}, \, 1304\text{s}, \, 1157\text{m}, \, 1128\text{s} \, \text{and} \, 1106\text{s} \, \text{cm}^{-1}; \, \text{\textsuperscript{1}H NMR} \, (400 \, \text{MHz}, \, \text{CDCl}_3) \, \delta \, 2.38 \, (2\text{H}, \, s, \, \text{CH}_2\text{N}), \, 1.84-1.77 \, (2\text{H}, \, m, \, \text{CH}_2), \, 1.63-1.55 \, (4\text{H}, \, m, \, 2 \times \, \text{CH}_2), \, 1.45 \, (9\text{H}, \, s, \, \text{t-Bu}), \, 1.43-1.30 \, (16\text{H}, \, \text{br} \, s, \, 8 \times \, \text{CH}_2); \, \text{\textsuperscript{13}C NMR} \, (100 \, \text{MHz}, \, \text{CDCl}_3) \, \delta \, 60.6 \, (\text{SC}), \, 51.9 \, (\text{C}), \, 42.6 \, (\text{CH}_2\text{N}), \, 25.8 \, (3 \times \, \text{CH}_2), \, 24.1 \, (\text{SCMe}_3), \, 22.3 \, (2 \times \, \text{CH}_2), \, 21.5 \, (\text{CH}_2); \, \text{MS CI} \, m/z \, (\text{rel. int.}) \, 333 \, (\text{M} + \text{NH}_4^+, \, 25), \, 316 \, (\text{M} + \text{H}^+, \, 10), \, 194 \, (60), \, 179 \, (100); \, \text{HRMS} \, m/z \, \text{calcd for} \, \text{C}_{17}\text{H}_{34}\text{NO}_2\text{S}, \, 316.2310, \, \text{found} \, 316.2310.\)

(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-BuSO\(_2\)NH\(_2\), K\(_2\)CO\(_3\), BTEAC, dioxane, 90 °C, 16 h, 85%),\(^8\) followed by alcohol mesylation (Ms\(_2\)O, pyridine, DMAP, CH\(_2\)Cl\(_2\), rt, 20 min) and ring

\((\text{6}) \, \text{We thank S. Miles for providing a sample.}\)
closure (K₂CO₃, THF, H₂O, reflux, 48 h, 97% over 2 steps)⁹ gave **aziridine** 3 (entry 8) as a colourless oil (82% over 3 steps).

[α]²⁵₅ = +47.5 (c 1.00, CHCl₃); Rₚ 0.38 (petroleum ether/Et₂O 9:1); IR (neat) 2926s, 2855s, 1481m, 1463m, 1396w, 1366w, 1310s, 1261w, 1131s, 1110m and 1021w cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.78-2.66 (1H, m, CH₂CN), 2.59 (1H, d, J = 7, CH(CH₃)₂N, trans to alkyl chain), 2.07 (1H, d, J = 4, CH(H)N, cis to alkyl chain), 1.68-1.27 (27H, m, 9 × CH₂ and t-Bu), 0.88 (3H, t, J = 7, Me); ¹³C NMR (125 MHz, CDCl₃) δ 59.1 (SC), 38.6 (CHN), 33.8 (CH₂N), 31.8 (CH₂), 31.2 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 26.3 (CH₂), 24.2 (SCMe₃), 22.7 (CH₂), 14.1 (Me); MS Cl m/z (rel. int.) 321 (M + NH₄⁺, 30), 304 (M + H⁺, 100), 184 (80); HRMS m/z calcd for C₁₆H₃₄NO₂S, 304.2310, found 304.2300.

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

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

\[
\begin{align*}
\text{Bus} & \quad \text{R} \quad \text{N} \quad \text{SiMe₃} \\
\text{n-BuLi} (1.6 \text{ M in hexanes, 0.94 mL, 1.5 mmol}) & \text{was added dropwise to a stirred solution of 2,2,6,6-tetramethylpiperidine (0.25 mL, 1.5 mmol) in THF (3.75 mL) at –78 °C under argon. The mixture was warmed to room temperature over 30 min and then cooled to –78 °C. To this solution, Me₃SiCl (0.19 mL, 1.5 mmol) was added, followed rapidly by a solution of aziridine (0.5 mmol) in THF (1.5 mL). Following stirring for 1 h at –78 °C, sat. aqueous NH₄Cl (5 mL) and Et₂O (5 mL) were added. The phases were separated and the aqueous layer extracted with Et₂O (2 × 15 mL).}
\end{align*}
\]

The combined organic layers were dried (MgSO₄) and concentrated under reduced pressure. Purification of the residue by column chromatography (SiO₂) gave the α,β-aziridinylsilane.

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

\[
\begin{align*}
\text{C}_8\text{H}_{11} & \text{N} \quad \text{Bus} \\
& \quad \text{SiMe}_3
\end{align*}
\]

Following **General procedure B** using aziridine 1 gave, following purification of the resulting residue by column chromatography (petroleum ether/Et₂O 24:1), trans-α,β-aziridinylsilane 2 as a colourless oil (131 mg, 86%).

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

Rf 0.80 (petroleum ether/EtOAc 9:1); IR (neat) 3079w, 2955s, 1642m (C=C), 1481m, 1454m, 1411m, 1365w, 1250m, 1130s and 1052w cm⁻¹; ¹H NMR (250 MHz, (CD₃)₂SO, 65 ºC) δ 5.86 (1H, ddt, J = 13, 7 and 6, =CH), 5.01-4.97 (2H, m, H 2C=), 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.

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\(^{-1}\);
\(^1\)H NMR (250 MHz, (CD\(_3\))\(_2\)SO, 65 °C) \(\delta\) 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(CH\(_2\)CHN), 1.81 (1H, d, \(J = 6\), CHSi), 1.75-1.69 (1H, m, CH(CH\(_2\)CHN), 1.39 (9H, s, t-Bu), 0.09 (9H, s, SiMe\(_3\)); \(^{13}\)C NMR (100 MHz, (CD\(_3\))\(_2\)SO) \(\delta\) 140.9 (C\(_{Ar}\) quart), 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\(_2\)SSi, 340.1767, found 340.1765.

\((2R^*,3R^*)-2-[(\text{tert}-\text{Butyldimethylsilyloxy})\text{methyl}]\text{-1-(\text{tert}-\text{butylsulfonyl})-3-}(\text{trimethylsilyl})\text{aziridine (4, entry 4)}\\

\begin{center}
\text{[TBSO]}_N^{\text{Bus}} \text{SiMe}_3
\end{center}

Following General procedure B using aziridine 3 (entry 4) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et\(_2\)O 49:1), trans-\(\alpha,\beta\)-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\(^{-1}\); \(^1\)H NMR (250 MHz, (CD\(_3\))\(_2\)SO, 65 °C) \(\delta\) 3.76 (2H, d, \(J = 5\), CH\(_2\)), 2.79-2.73 (1H, m, CH\(_2\)CHN), 1.78 (1H, d, \(J = 6\), CHSi), 1.40 (9H, s, S\_t-Bu), 0.88 (9H, s, S\_t-Bu), 0.15 (9H, s, SiMe\(_3\)), 0.06 (6H, s, SiMe\(_2\)); \(^{13}\)C NMR (100 MHz, (CD\(_3\))\(_2\)SO) \(\delta\) 63.9 (OCH\(_2\)), 58.9 (SC), 44.9 (CHN), 34.9 (CHSi), 25.6 (SiCM\(_3\)), 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\(_3\)SSi\(_2\), 380.2111, found 380.2128.
(2R*,3R*)-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%).

\[ RF \, 0.61 \text{ (petroleum ether/EtOAc 19:1)}; \] IR (neat) 2932s, 2858m, 1472m, 1394m, 1363w, 1311s, 1251s, 1132s, 1102m (C–O–Si) and 1006w cm\(^{-1}\); \( ^1\)H NMR (250 MHz, (CD\(_3\))\(_2\)SO, 65 °C) \( \delta \) 3.60 (2H, t, \( J = 6 \), OCH\(_2\)), 2.62-2.55 (1H, m, CH\(_2\)CHN), 1.97-1.84 (1H, m, CH\(_2\) and St-Bu), 0.87 (9H, s, St-Bu), 0.13 (SiMe\(_3\)), 0.03 (SiMe\(_2\)); \( ^{13}\)C NMR (100 MHz, (CD\(_3\))\(_2\)SO) \( \delta \) 62.2 (OCH\(_2\)), 58.6 (SC), 44.1 (CHN), 38.5 (CHSi), 31.7 (2 × 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 (M + H\(^+\), 25), 228 (70), 155 (70), 98 (60), 90 (70), 74 (100); HRMS m/z calcd for C\(_{19}\)H\(_{44}\)NO\(_3\)SSi\(_2\), 422.2580, found 422.2563.

(2R*,3R*)-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/Et\(_2\)O 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$^{-1}$; $^1$H NMR (250 MHz, (CD$_3$)$_2$SO, 65 ºC) δ 3.63 (2H, t, $J = 7$, ClCH$_2$), 2.64-2.57 (1H, m, CH$_2$CHN), 1.98-1.72 (4H, CH(H)CHN, CHSi and CH$_2$), 1.59-1.43 (3H, m, CH(H)CHN and CH$_2$), 1.39 (9H, s, t-Bu), 0.34 (9H, s, SiMe$_3$); $^{13}$C NMR (100 MHz, (CD$_3$)$_2$SO) δ 58.7 (SC), 45.1 (ClCH$_2$), 43.7 (CHN), 38.6 (CHSi), 31.5 (2 × CH$_2$), 30.9 (CH$_2$), 23.7 (SCMe$_3$), –1.84 (SiMe$_3$); MS CI m/z (rel. int.) 328 ($^{37}$ClM + H+, 5), 326 ($^{35}$ClM + H+, 15), 218 (85), 134 (100), 98 (70), 90 (55); HRMS m/z calcd for C$_{13}$H$_{29}$NO$_2$SSiCl, 326.1377, found 326.1373.

1-(tert-Butylsulfonyl)-2-trimethylsilanyl-1-aza-spiro[2.11]tetradecane (4, entry 7) (Representative of the general procedure for trans-$\alpha$,-$\beta$-aziridinylsilane preparation at 0 ºC)

`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 ºC under argon. The mixture was warmed to room temperature over 30 min and then cooled to 0 ºC. To this solution, Me$_3$SiCl (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 ºC, sat. aqueous NH$_4$Cl (5 mL) and Et$_2$O (5 mL) were added. The phases were separated and the aqueous layer extracted with Et$_2$O (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$_2$O 49:1) gave $\alpha$,$\beta$-aziridinylsilane 4 (entry 7) as a colourless oil (107 mg, 63%).`
$R_f$ 0.13 (petroleum ether/Et$_2$O 49:1); IR (film) 2932s, 2864m, 1641w, 1472m, 1392w, 1306s, 1251s and 1124s cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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 $\times$ CH$_2$, t-Bu), 0.99-0.86 (1H, m, CH(H)), 0.15 (9H, s, SiMe$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 60.3 (CN), 55.1 (SC), 45.8 (CHSi), 29.9 (CH$_2$), 29.6 (CH$_2$), 26.3 (CH$_2$) 26.0 (CH$_2$), 25.9 (CH$_2$), 24.3 (SCMe$_3$), 22.7 (CH$_2$), 22.2 (CH$_2$), 22.0 (2 $\times$ CH$_2$), 21.9 (CH$_2$), 21.4 (CH$_2$), $-1.27$ (SiMe$_3$); 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 C$_{20}$H$_{42}$NO$_2$SSi, 388.2706, found 388.2702.

(2S, 3S)-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/Et$_2$O 49:1), trans-$\alpha,\beta$-aziridinylsilane 4 (entry 8) as a colourless oil (152 mg, 81%).

$[\alpha]_{25}^D = +45.4$ (c 1.0, CHCl$_3$); $R_f$ 0.74 (petroleum ether/Et$_2$O 9:1); IR (neat) 2927s, 2855m, 1481w, 1459m, 1365w, 1311s, 1250s, 1130s, 1102w and 1022w cm$^{-1}$; $^1$H NMR (250 MHz, (CD$_3$)$_2$SO, 65 °C) $\delta$ 2.61-2.54 (1H, m, CH$_2$CHN), 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 $\times$ CH$_2$ and t-Bu), 0.87 (3H, t, J = 7, Me), 0.13 (9H, s, SiMe$_3$); $^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO) $\delta$ 58.7 (SC), 44.1 (CHN), 39.0 (CHSi), 31.2 (CH$_2$CHN), 28.9, (CH$_2$), 28.8 (CH$_2$), 28.6 (CH$_2$), 28.5 (2 $\times$ CH$_2$), 26.2 (2 $\times$ CH$_2$), 23.7 (SCMe$_3$), 22.0 (CH$_2$), 13.9 (Me), $-1.89$ (SiMe$_3$); MS CI $m/z$ (rel. int.) 376 (M + H$^+$, 100), 256 (30), 184 (95), 182 (45); HRMS $m/z$ calcd for C$_{10}$H$_{21}$NO$_2$SiS, 376.2706, found 376.2712.
Confirmation of ee

\[
\text{Bus} \quad \text{C}_{10}\text{H}_{21}\text{SiMe}_3 \quad \text{Bus}
\]

TBAF (1.0 M in THF, 0.20 mL, 0.20 mmol) was added dropwise to a stirred solution of \(\alpha,\beta\)-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, H\(_2\)O (5 mL) was added and the mixture extracted with Et\(_2\)O (3 \times 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\(_2\)O 19:1) gave aziridine 3 (entry 8) as a colourless oil (49 mg, 89%).

\([\alpha]_{D}^{25} = +45.6 \text{ (c 1.00, CHCl}_3\text{); spectroscopic data matched those reported above.}\)

(IV) Characterization data for substituted aziridines 5, 6 and 7 (a-j)

**General procedure C: Substituted aziridine preparation**

\[
\text{Bus} \quad \text{C}_5\text{H}_{11}\text{E}
\]

\(n\)-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 NH\(_4\)Cl (5 mL) and Et\(_2\)O (5 mL) were added. The phases were separated and the aqueous layer extracted with Et\(_2\)O (2 \times 15 mL). The combined organic layers were dried (MgSO\(_4\)) and concentrated under reduced pressure.
Purification of the residue by column chromatography (SiO₂ unless indicated otherwise) gave the substituted aziridines.

\((2R^*,3R^*)-1-\text{( tert-Butylsulfonyl)}-2\text{-pentyl-3-(tributylstannyl)aziridine (5)}\)

\[
\begin{array}{c}
\text{C}_9\text{H}_{11} \\
\text{N} \\
\text{SnBu}_3 \\
\text{Bus}
\end{array}
\]

\(n\)-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) \(\delta\) 59.1 (SC), 44.5 (CHN), 36.0 (CHSn), 33.8 (CH₂), 31.6 (CH₂), 28.9 (\(J_{\text{Sn-C}} = 20\), SnCH₂CH₂), 27.4 (\(J_{\text{Sn-C}} = 62\), SnCH₂CH₂CH₂), 26.1 (CH₂), 24.3 (SCMe₃), 22.6 (CH₂), 13.9 (Me), 13.7 (SnCH₂CH₂CH₂Me), 10.8 (\(J_{\text{Sn-C}} = 336\), SnCH₂); ¹¹⁹Sn NMR (93MHz, CDCl₃) \(\delta\) −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 \( \text{C}_{23}\text{H}_{50}\text{NO}_{2}\text{SSn} \), 524.2579, found 524.2583.

\((2R^*3R^*)-1-(\text{tert-Butylsulfonyl})-2\text{-pentyl}-3\text{-deuteroaziridine (6)}\)

Following **General procedure C** using \( \text{CD}_3\text{OD} \) (0.5 mL) \( (t = 90 \text{ s}) \) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et\(_2\)O 9:1), **substituted aziridine 6** as a colourless oil \( (50 \text{ mg}, 86\%) \) \( (91\% \text{ deuteration incorporation as judged by } ^1\text{H NMR spectroscopy}) \).

\( R_f 0.36 \) (petroleum ether/Et\(_2\)O 9:1); IR (neat) 2933s, 2861m, 1459w, 1366w, 1307s, 1219w and 1126s cm\(^{-1}\); \(^1\text{H NMR (400 MHz, CDCl}_3\) \( \delta 2.72-2.68 \) (1H, m, CHN), 2.57 (0.1H, d, \( J = 7\), CH(H)N, \text{trans to alkyl chain}), 2.05 (1H, d, \( J = 5\), CH(H)N, \text{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); \(^{13}\text{C NMR (100 MHz, CDCl}_3\) \( \delta 59.2 \) (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 Cl m/z (rel. int.) 235 (M + H\(^+\), 100), 179 (20), 115 (70); HRMS m/z calcd for \( \text{C}_{11}\text{H}_{23}\text{NO}_{2}\text{SD} \), 235.1591, found 235.1585.
Following General procedure C using benzaldehyde (80 µL, 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%).

(7a)

Following General procedure C using benzaldehyde (80 µL, 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); Rf 0.51 (petroleum ether/Et₂O 4:1); IR (film) 3490br s (O–H), 2932m, 2680w, 1642m, 1454m, 1366w, 1294s, 1198w, 1117s, 1023w and 717s (CAr–H) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.45-7.29 (5H, m, 5 × C ArH), 4.86-4.83 (1H, dd, J = 9 and 2, CHO), 3.99 (1H, br s, OH), 2.97-2.93 (1H, m, CH₂CHN), 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 × CH₂), 0.75 (3H, t, J = 7, Me); ¹³C NMR (100 MHz, CDCl₃) δ 139.9 (CAr quat), 128.6 (2 × C Ar ortho), 128.2 (2 × C Ar ), 126.0 (C Ar ), 73.2 (CHOH), 60.3 (SC), 55.5 (CHNCHO), 46.0 (CH₂CHN), 31.0 (CH₂), 30.5 (CH₂), 25.4 (CH₂), 23.9 (SCMe₃), 22.3 (CH₂), 13.7 (Me); MS CI m/z (rel. int.) 357 (M + NH₄⁺, 5), 340 (M + H⁺, 10), 220 (100), 202 (60), 100 (70); HRMS m/z calcd for C₁₈H₃₀NO₃S, 340.1946, found 340.1941.
(R*)-1-[(2S*,3R*)-1-(tert-Butylsulfonyl)-3-penylaziridin-2-yl]-2-2-dimethylpropan-1-ol (7b)

Following **General procedure C** using pivalaldehyde (80 µL, 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$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.71 (1H, br s, OH), 3.39 (1H, dd, $J = 10$ and 3, CH$_2$OH), 2.88-2.84 (1H, m, CH$_2$CHN), 2.73 (1H, dd, $J = 10$ and 5, CHNCHO), 1.76-1.52 (2H, m, CH$_2$CHN), 1.48-1.29 (15H, s, 3 × CH$_2$ and St-Bu), 1.00 (9H, s, OCH$_3$-Bu), 0.89 (3H, t, $J = 7$, Me); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 77.3 (CHOH), 60.3 (SC), 52.7 (CHNCHO), 46.7 (CH$_2$CHN), 35.1 (OCHCMe$_3$), 31.6 (CH$_2$CHN), 30.3 (CH$_2$), 26.2 (OCHCMe$_3$), 25.2 (CH$_2$), 24.0 (SCMe$_3$), 22.4 (CH$_2$), 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 C$_{16}$H$_{34}$NO$_3$S, 320.2259, found 320.2267.
Following **General procedure C** using isobutyraldehyde (70 µL, 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 \text{(petroleum ether/Et}_2\text{O 4:1); IR (neat) 3512br m (O–H), 2960s, 2933s, 1467m, 1366w, 1258s, 1124s, 1089m and 1034w cm}^{-1}; {^1}\text{H NMR (400 MHz, CDCl}_3\text{) }\delta 3.62 (1H, br s, OH), 3.50-3.46 (1H, m, CHOH), 2.84-2.80 (1H, m, CH\text{CHN}), 2.68 (1H, dd, \text{J} = 9 \text{ and } 5, \text{CHNCHO}), 1.90-1.70 (2H, m, CHMe\text{e}_2, \text{CH(H)CHN}), 1.47 (9H, s, t-\text{Bu}), 1.43-1.31 (7H, m, CH(H)CHN and 3 × CH\text{e}_2), 1.03 (3H, d, \text{J} = 7, \text{CHMe}), 1.01 (3H, d, \text{J} = 7, \text{CHMe}), 0.89 (3H, t, \text{J} = 7, \text{CH}_2\text{Me}); {^{13}}\text{C NMR (100 MHz, CDCl}_3\text{) }\delta 74.9 (\text{CHOH}), 60.2 (\text{SC}), 53.6 (\text{CHNCHO}), 45.9 (\text{CH}_2\text{CHN}), 32.7 (\text{CHMe}_2), 31.5 (\text{CH}_2\text{CHN}), 30.5 (\text{CH}_2), 25.3 (\text{CH}_2), 24.0 (\text{SCMe}_3), 22.4 (\text{CH}_2), 18.9 (\text{CHMe}), 17.9 (\text{CHMe}), 13.9 (\text{CH}_2\text{Me}); \text{MS CI } m/z \text{ (rel. int.) 306 (M + H}^+, 15), 220 (50), 169 (100), 155 (55), 100 (50); \text{HRMS } m/z \text{ calcd for C}_{15}\text{H}_{32}\text{NO}_3\text{S, 306.2103, found 306.2097.}

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

Following **General procedure C** using butyraldehyde (70 µL, 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/Et$_2$O 4:1); IR (film) 3517 br m (O–H), 2933 s, 2873 s, 1459 m, 1366 w, 1294 s, 1124 s, 1084 m and 1013 m cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.78-3.71 (1H, m, CHOH), 3.61 (1H, br s, OH), 2.79-2.75 (1H, m, CH$_2$CH/N), 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 × CH$_2$ and t-Bu), 0.94 (3H, t, $J$ 7, Me), 0.89 (3H, t, $J$ 7, Me); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 70.2 (CHOH), 60.1 (SC), 54.8 (CHNCHO), 45.5 (CH$_2$CHN), 36.9 (OCHCH$_2$), 31.5 (CH$_2$), 30.7 (CH$_2$), 25.5 (CH$_2$), 23.9 (SCMe$_3$), 22.4 (CH$_2$), 18.6 (CH$_2$), 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 C$_{15}$H$_{32}$NO$_3$S, 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 µL, 0.75 mmol) (t = 1 h) gave, following purification of the resulting residue by column chromatography (petroleum ether/Et$_2$O 9:1→4:1), **aziridinyl alcohol 7e** as a white solid (61 mg, 76%). (mp = 65-67 °C); $R_f$ 0.19 (petroleum ether/Et$_2$O 4:1); IR (film) 3509 br m (O–H), 2964 s, 2929 s, 1458 m, 1367 m, 1297 s, 1128 m, 1110 s (C–O) and 1022 m cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.84-2.79 (2H, m, CH$_2$CH/N, 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 × CH$_2$, 2 × OCH$_2$ and t-Bu), 0.96-0.87 (9H, m, 2 × OCH$_2$Me and Me); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 71.5 (CO), 60.0 (SC), 50.7 (CHCO), 48.1 (CH$_2$CHN), 31.5 (CH$_2$CHN), 30.6 (2 × OCH$_2$), 28.4 (CH$_2$), 27.6 (CH$_2$), 24.4 (SCMe$_3$), 22.4 (CH$_2$), 13.9 (Me), 7.7 (OCH$_2$Me), 7.5 (OCH$_2$Me); MS CI m/z (rel. int.) 320 (M + H$^+$, 20), 198 (60), 182
Following General procedure C using cyclopentanone (70 µL, 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%).

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

Following General procedure C using cyclopentanone (70 µL, 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%).

Following General procedure C using cyclopentanone (70 µL, 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%).

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 4:1), aziridinyl alcohol 7g as a colourless oil (47 mg, 59%).
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 × C ArH), 7.68-7.65 (1H, m, C ArH), 7.56-7.52 (2H, m, 2 × C ArH), 4.14 (1H, d, *J* = 4, CHNCO), 3.06-3.02 (1H, m, CH₂CN), 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 × CH₂), 0.87 (3H, t, *J* = 7, Me); ¹³C NMR (63 MHz, CDCl₃) δ 192.1 (CO), 135.8 (C Ar quatr), 134.2 (C Ar), 128.9 (2 × C Ar ortho), 128.5 (2 × C Ar), 61.0 (SC), 49.6 (CH₂CHN), 46.9 (CHNCO), 31.4 (CH₂CHN), 28.8 (CH₂), 27.6 (CH₂), 23.9 (CMes), 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.

*(25*,*3R*)-1-(tert-Butylsulfonyl)-3-pentylaziridine-2-carbaldehyde (7h)

Following **General procedure C** using *N*, *N*-dimethylformamide (60 µL, 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 × CH₂, CH(H)CHN) and t-Bu).
0.90 (3H, t, \(J = 7\), Me); \(^{13}\)C NMR (63 MHz, CDCl\(_3\)) \(\delta\) 194.3 (CHO), 60.7 (SC), 51.5 (CH\(_2\)CHN), 46.3 (CHCO), 31.2 (CH\(_2\)CHN), 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 (M + NH\(_4^+\), 100), 262 (M + H\(^+\), 40), 198 (35), 142 (40); HRMS \(m/z\) calcld for C\(_{12}\)H\(_{24}\)NO\(_3\)S, 262.1477, found 262.1473.

\((2R^*,3R^*)-1-(\text{tert-Butylsulfonyl})-2\text{-pentyl-3-(phenylsulfonyl)aziridine (7i)}\)

\[
\text{Bus} = \text{N} \quad \text{SO}_2\text{Ph}
\]

\(n\)-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 °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 benzenesulfonyl fluoride (0.12 mL, 1.00 mmol). Following stirring for 1 h at –78 °C, sat. NH\(_4\)Cl (5 mL) and Et\(_2\)O (5 mL) were added. The phases were separated and the aqueous layer extracted with Et\(_2\)O (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\(_2\)O 4:1) gave substituted aziridine 7i as a pale yellow crystalline solid (86 mg, 92%).

mp = 85-87 °C; \(R_f\) 0.36 (petroleum ether/Et\(_2\)O 4:1); IR (film) 3067w, 2933s, 2872s, 1585m, 1449s, 1401m, 1367m, 1317s (S=O), 1213m, 1157s (S=O), 1087m, 1023w and 706s (C\(_\text{Ar}\)-H) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 (2H, d, \(J = 8\), 2 × C\(_\text{Ar}\)H), 7.74-7.71 (1H, m, C\(_\text{Ar}\)H), 7.63-7.59 (2H, m, 2 × C\(_\text{Ar}\)H), 4.00 (1H, d, \(J = 4\), CHSO\(_2\)), 3.02-2.97 (1H, m, CH\(_2\)CHN), 2.23-2.15 (1H, m, CH(\(\text{H}\))CHN), 1.74-1.64 (1H, m, CH(\(\text{H}\))CHN), 1.45-1.38 (11H, m, CH\(_2\) and \(t\)-Bu), 1.25-1.17 (4H, m, 2 × CH\(_2\)\), 0.82
(3H, t, J = 7, Me); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.7 (CAr quat), 134.7 (CAr), 129.5 (2 × CAr), 128.9 (2 × CAr ortho), 61.7 (CHSO$_2$), 58.5 (SC), 48.1 (CH$_2$CHN), 30.9 (CH$_2$CHN), 27.4 (CH$_2$), 27.3 (CH$_2$), 23.9 (CMes), 22.3 (CH$_2$), 13.8 (Me); MS CI $m/z$ (rel. int.) 391 (M + NH$_4^+$, 100), 374 (M + H$^+$, 10), 232 (20); HRMS $m/z$ calcd for C$_{17}$H$_{31}$N$_2$O$_4$S$_2$, 391.1725, found 391.1739.

(2S*,3R*)-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 ºC. Following warming to room temperature over 20 min, the reaction was cooled to −78 ºC 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$_4$Cl (5 mL) and Et$_2$O (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$_2$O (5 mL) and diazomethane in Et$_2$O$^{10}$ (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$_2$O 9:1) gave substituted aziridine 7j as a colourless oil (45 mg, 63%).

$R_f$ 0.62 (petroleum ether/Et$_2$O 4:1); IR (neat) 2952s, 2933s, 2862m, 1753s (C=O), 1444m, 1366w, 1315s, 1248m, 1207m, 1123s, 1059w, 1025w cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.79 (3H, s, OMe), 3.22 (1H, d, $J = 4$, CHCO), 3.01-2.95 (1H, m, CH$_2$CHN), 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 × CH$_2$ and t-Bu), 0.89 (3H, t, $J = 7$, Me); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.9 (CO), 60.9 (SC), 52.7 (OMe), 47.6 (CHCO), 44.2 (CH$_2$CHN), 31.2 (CH$_2$CHN), 28.5 (CH$_2$), 27.2 (CH$_2$), 23.9 (SCMe$_3$), 22.4 (CH$_2$), 13.9 (Me); MS CI m/z (rel. int.) 309 (M + NH$_4^+$, 55), 292 (M + H$,^+$, 45), 172 (100); HRMS m/z calcd for C$_{13}$H$_{26}$NO$_4$S, 292.1583, found 292.1595.
(V) $^1$H and $^{13}$C NMR spectra of aziridines 1 and 3 (entries 2–8)
(VI) $^1$H and $^{13}$C NMR spectra of $\alpha,\beta$-azirdinylsilanes 2 and 4 (entries 2–8)
(VII) $^1$H and $^{13}$C NMR spectra of substituted aziridines 5, 6 and 7 (a-j)
$C_6H_{11}$

Chemical Shift (ppm)

- 77.32
- 77.00
- 76.68
- 60.29
- 52.66
- 46.72
- 35.09
- 31.61
- 30.33
- 26.16
- 25.16
- 24.02
- 22.37
- 13.89

Chemical Shift (ppm)

- 3.02
- 15.00
- 2.57
- 0.96
- 0.97
- 0.81

- 7.27
- 3.71
- 3.40
- 3.38
- 3.37
- 2.87
- 2.86
- 2.85
- 2.74
- 2.72
- 2.71
- 2.70
- 1.68
- 1.48
- 1.40
- 1.38
- 1.32
- 1.31
- 1.29
- 1.00
- 0.91
- 0.89

Chemical Shift (ppm)