Supporting Information for Highly Selective Aziridination of Imines Using Trimethylsilyldiazomethane (TMSD) and Applications of *C*-Silylaziridines in Synthesis

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General methods: Flash chromatography was performed on silica gel (Merck Kiesegel 60 F_{254} 230-400 mesh). TLC was performed on aluminium backed silica plates (60 F_{254}) which were developed using standard visualizing agents: UV fluorescence (254 and 366 nm), molybdic acid / Δ, anisaldehyde / Δ, permanganate / Δ. Melting points were determined on a Khofler hot stage. Infrared spectra were recorded as solutions (in $CDCl_3$, unless otherwise specified) on a Perkin-Elmer 157G Grating FT-IR spectrometer. Only selected absorbencies (ν_{max}) are reported. ^{1}H NMR spectra were recorded at either 250 or 400 MHz on Bruker AC-250, or Bruker AM-400 instruments, respectively. Chemical shifts (δ_H) are quoted in parts per million (ppm), referenced to the appropriate residual solvent peak. ^{1}H NMR spectra were recorded at 250 MHz, unless otherwise specified. ^{13}C NMR spectra were recorded at either 63 or 101 MHz on Bruker AC-250, or Bruker AM-400 instruments, respectively. Chemical shifts (δ_C) are quoted in parts per million (ppm), referenced to the appropriate residual solvent peak and are assigned as s, d, t, q for C, CH, CH_2 and CH_3. Degenerate peaks are prefixed by the number of carbons. ^{13}C NMR spectra were recorded at 63 MHz, unless otherwise specified. Low resolution mass spectra (m/z) were recorded on either VG Platform or VG Prospec spectrometers, with only molecular ions (M^+), and major peaks being reported with intensities quoted as percentages of the base peak. High-resolution mass spectra were recorded on a VG Prospec spectrometer. Microanalyses were performed using a Perkin Elmer 2400 CHN elemental analyzer by A.H. Jones, Department of Chemistry, University of Sheffield.

Imines **1a**-**e**,[1] **1f**-**g**,[2] **1h**,[3] **1i**[1,4] were prepared according to literature procedures.

TMSD and TBAT were purchased from Aldrich; TMSD was titrated prior to use.

Representative Procedure for the Aziridination of Imines Using TMSD. To a solution of *N*-tosyl-benzaldimine (**1a**) (259.3 mg, 1.0 mmol) in 1,4-dioxane (5 mL) was added a 1.8 M solution of TMSD in hexanes (2.5 equiv.). After stirring for 7 h at 40•C, the solvent was removed and the crude mixture was purified by flash chromatography on silica gel (eluent petroleum ether/ethyl acetate 20:1) to afford *trans*-**2a** (12.4 mg, 4%) and *cis*-**2a** (236.3 mg, 68%).

(2*R,3*S**)-1-[(4-Methylphenyl)sulfonyl]-2-phenyl-3-(1,1,1-trimethylsilyl)aziridine** (*cis*-**2a**)**:** White solid; eluent petroleum ether/ethyl acetate 5:1, R_f = 0.53; m.p. 108-110•C (from petroleum ether/ethyl acetate); ^{1}H NMR ($CDCl_3$) • –0.38 [9H, s, Si(C*H*$_3$)$_3$], 2.18 (1H, d, *J* = 8.5 Hz, C*H*Si), 2.38 (3H, s, C*H*$_3$C$_6$H$_4$), 3.96 (1H, d, *J* = 8.5 Hz, C*H*Ph), 7.16 (5H, br s, Ph), 7.28 (2H, d, *J* = 8.1 Hz, Ts), 7.83 (2H, d, *J* = 8.1 Hz, Ts); ^{13}C NMR ($CDCl_3$) • –2.5 (3q), 21.6 (q), 37.6 (d), 44.8 (d), 127.4 (2d), 127.7 (d), 128.2 (2d), 128.2 (2d), 129.7 (2d), 135.0 (s), 135.3 (s), 144.5 (s); IR •$_{max}$/ cm^{-1} (CH_2Cl_2) 3066, 3032, 2959, 1599, 1496, 1450, 1323, 1159; MS m/z (EI) 345 (M^+, 6), 190 (100), 73 (68); HRMS: found 345.1230, $C_{18}H_{23}NO_2SSi$ requires 345.1219. Anal. Calcd for

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$C_{18}H_{23}NO_2SSi$: C, 62.57; H, 6.71; N, 4.05. Found: C, 62.64; H, 6.85; N, 4.10.

(2*R,3*R**)-1-[(4-Methylphenyl)sulfonyl]-2-phenyl-3-(1,1,1-trimethylsilyl)aziridine** (*trans*-**2a**)**:** Colourless oil; eluent petroleum ether/ethyl acetate 5:1, R_f = 0.57; ^{1}H NMR ($CDCl_3$) • 0.15 [9H, s, Si(CH_3)$_3$], 1.91 (1H, d, *J* = 6.1 Hz, C*H*Si), 2.23 (3H, s, CH_3C$_6$H$_4$), 3.56 (1H, d, *J* = 6.1 Hz, C*H*Ph), 6.97-7.01 (2H, m, Ph), 7.08-7.12 (3H, m, Ph), 7.11 (2H, d, *J* = 8.6 Hz, Ts), 7.66 (2H, d, *J* = 8.6 Hz, Ts); IR •$_{max}$/ cm^{-1} (CH_2Cl_2) 3068, 2958, 1599, 1497, 1456, 1323, 1160; MS m/z (EI) 345 (M^+, 9), 190 (100), 73 (79); HRMS: found 345.1224, $C_{18}H_{23}NO_2SSi$ requires 345.1219.

(2*R,3*S**)-2-(4-Methoxyphenyl)-1-[(4-methylphenyl)sulfonyl]-3-(1,1,1-trimethylsilyl)aziridine** (*cis*-**2b**)**:** Pale yellow oil; eluent petroleum ether/ethyl acetate 2:1, R_f = 0.53; ^{1}H NMR ($CDCl_3$) • –0.31 [9H, s, Si(CH_3)$_3$], 2.18 (1H, d, *J* = 8.4 Hz, C*H*Si), 2.43 (3H, s, CH_3C$_6$H$_4$), 3.74 (3H, s, CH_3O), 3.95 (1H, d, *J* = 8.4 Hz, C*H*CHSi), 6.76 (2H, d, *J* = 8.4 Hz, C$_6$H$_4$OMe), 7.12 (2H, d, *J* = 8.4 Hz, C$_6$H$_4$OMe), 7.32 (2H, d, *J* = 8.1 Hz, Ts), 7.87 (2H, d, *J* = 8.1 Hz, Ts); ^{13}C NMR ($CDCl_3$) • –2.3 (3q), 21.7 (q), 37.8 (d), 44.5 (d), 55.2 (q), 113.5 (2d), 127.3 (s), 128.2 (2d), 128.5 (2d), 128.5 (2d), 129.6 (2d), 135.1 (s), 144.4 (s), 159.1 (s); IR •$_{max}$/ cm^{-1} 3036, 2959, 1613, 1515, 1321, 1252, 1159; MS m/z (EI) 375 (M^+, 24), 220 (100); HRMS: found 375.1329, $C_{19}H_{25}NO_3SSi$ requires 375.1324. Anal. Calcd for $C_{19}H_{25}NO_3SSi$: C, 60.77; H, 6.71; N, 3.73. Found: C, 60.92; H, 6.83; N, 3.43.

(2*R,3*S**)-2-(4-Chlorophenyl)-1-[(4-methylphenyl)sulfonyl]-3-(1,1,1-trimethylsilyl)aziridine** (*cis*-**2c**)**:** Pale yellow oil; eluent petroleum ether/ethyl acetate 10:1, R_f = 0.53; ^{1}H NMR ($CDCl_3$) • –0.41 [9H, s, Si(CH_3)$_3$], 2.11 (1H, d, *J* = 8.4 Hz, C*H*Si), 2.34 (3H, s, CH_3C$_6$H$_4$), 3.86 (1H, d, *J* = 8.4 Hz, C*H*CHSi), 7.00-7.23 (4H, m, C$_6$H$_4$Cl), 7.24 (2H, d, *J* = 8.1 Hz, Ts), 7.77 (2H, d, *J* = 8.1 Hz, Ts); ^{13}C NMR ($CDCl_3$) • –2.3 (3q), 21.7 (q), 37.9 (d), 44.1 (d), 128.2 (2d), 128.4 (2d), 128.8 (2d), 129.7 (2d), 133.6 (s), 133.9 (s), 134.9 (s), 144.6 (s); IR •$_{max}$/ cm^{-1} 3035, 2959, 1599, 1494, 1323, 1252, 1159; MS m/z (EI) 379 (M^+, 1524), 224 (68), 86 (69), 84 (100). Anal. Calcd for $C_{18}H_{22}ClNO_2SSi$: C, 56.90; H, 5.84; N, 3.69. Found: C, 57.20; H, 5.95; N, 3.57.

(2*R,3*R**)-2-(4-Chlorophenyl)-1-[(4-methylphenyl)sulfonyl]-3-(1,1,1-trimethylsilyl)aziridine** (*trans*-**2c**)**:** Pale yellow oil; eluent petroleum ether/ethyl acetate 10:1, R_f = 0.60; ^{1}H NMR ($CDCl_3$) (selection of signals) • 0.29 [9H, s, Si(CH_3)$_3$], 2.02 (1H, d, *J* = 6.1 Hz, C*H*Si), 2.40 (3H, s, CH_3C$_6$H$_4$), 3.66 (1H, d, *J* = 6.1 Hz, C*H*CHSi), 7.80 (2H, d, *J* = 8.2 Hz, Ts).

(2*R,3*S**)-1-[(4-Methylphenyl)sulfonyl]-2-(4-nitrophenyl)-3-(1,1,1-trimethylsilyl)aziridine**

(*cis*-**2d**)**:** Pale yellow oil; eluent petroleum ether/ethyl acetate 10:1, R_f = 0.23; ^{1}H NMR ($CDCl_3$) • –0.24 [9H, s, Si(CH_3)$_3$], 2.37 (1H, d, *J* = 8.6 Hz, C*H*Si), 2.53 (3H, s, CH_3C$_6$H$_4$), 4.14 (1H, d, *J* = 8.6 Hz, C*H*CHSi), 7.44 (2H, d, *J* = 8.3 Hz, Ts), 7.51 (2H, d, *J* = 8.6 Hz, C$_6$H$_4$NO$_2$), 7.96 (2H, d, *J* = 8.3 Hz, Ts), 8.20 (2H, d, *J* = 8.6 Hz, C$_6$H$_4$NO$_2$); ^{13}C NMR ($CDCl_3$) • –2.3 (3q), 21.7 (q), 38.3 (d), 44.0 (d), 123.5 (2d), 128.2 (2d), 128.4 (2d), 129.8 (2d), 134.5 (s), 142.9 (s), 145.0 (s), 147.5 (s); IR •$_{max}$/ cm^{-1} 3067, 2959, 1603, 1525, 1347, 1253, 1161; MS m/z (EI) 390 (M^+, 6), 235 (100); HRMS: found 390.1077, $C_{18}H_{22}N_2O_4SSi$ requires 390.1070. Anal. Calcd for $C_{18}H_{22}N_2O_4SSi$: C, 55.36; H, 5.68; N, 7.17. Found: C, 55.35; H, 5.80; N, 6.89.

(2*R,3*R**)-1-[(4-Methylphenyl)sulfonyl]-2-(4-nitrophenyl)-3-(1,1,1-trimethylsilyl)aziridine**

(trans-**2d**)**:** Pale yellow oil; eluent petroleum ether/ethyl acetate 10:1, R_f = 0.33; ^{1}H NMR ($CDCl_3$) • 0.25 [9H, s, Si(CH_3)$_3$], 1.96 (1H, d, *J* = 6.1 Hz, C*H*Si), 2.34 (3H, s, CH_3C$_6$H$_4$), 3.69 (1H, d, *J* = 6.1 Hz, C*H*CHSi), 7.21 (2H, d, *J* = 9.0 Hz, C$_6$H$_4$NO$_2$), 7.25 (2H, d, *J* = 8.6 Hz, Ts), 7.75 (2H, d, *J* = 8.6 Hz, Ts), 8.05 (2H, d, *J* = 9.0 Hz, C$_6$H$_4$NO$_2$); ^{13}C NMR ($CDCl_3$) (selection of signals) • –1.1 (3q), 21.6 (q), 44.5 (d), 45.6 (d), 123.9 (2d), 127.0 (2d), 127.5 (2d), 129.7 (2d), 144.4 (s), 144.5 (s); IR •$_{max}$/ cm^{-1} 2956, 1602, 1524, 1348, 1161; MS m/z (EI) 390 (M^+, 16), 235 (100), 73 (46); HRMS: found 390.1066, $C_{18}H_{22}N_2O_4SSi$ requires 390.1070.

(2*R,3*S**)-1-[(4-Methylphenyl)sulfonyl]-2-[(*E*)-2-phenyl-1-ethenyl]-3-(1,1,1-trimethylsilyl)aziridine**

(*cis*-**2e**)**:** Yellow solid; eluent petroleum ether/ethyl acetate 5:1 + 1% NEt_3, R_f = 0.53; m.p. 90-92•C (from petroleum ether/ethyl acetate); ^{1}H NMR ($CDCl_3$) • 0.00 [9H, s, Si(CH_3)$_3$], 2.16 (1H, d, *J* = 8.2 Hz, C*H*Si), 2.45 (3H, s, CH_3C$_6$H$_4$), 3.61 (1H, t, *J* = 8.4 Hz, C*H*CHSi), 5.90 (1H, dd, *J* = 15.9, 7.9 Hz, C*H*CHPh), 6.72 (1H, d, *J* = 15.9 Hz, C*H*Ph), 7.29-7.37 (5H, m, Ph), 7.34 (2H, d, *J* = 8.4 Hz, Ts), 7.85 (2H, d, *J* = 8.4 Hz, Ts); ^{13}C NMR (C_6D_6) • –1.8 (3q), 21.1 (q), 37.0 (d), 45.2 (d), 124.8 (d), 126.6 (2d), 128.2 (d), 128.4 (d), 128.9 (2d), 129.7 (2d), 134.8 (2d), 136.5 (s), 136.7 (s), 144.0 (s); IR •$_{max}$/ cm^{-1} (CH_2Cl_2) 3063, 3031, 2959, 1599, 1322, 1268, 1159; MS m/z (EI) 371 (M^+, 11), 216 (100), 73 (93); HRMS: found 371.1373, $C_{20}H_{25}NO_2SSi$ requires 371.1375. Anal. Calcd for $C_{20}H_{25}NO_2SSi$: C, 64.65; H, 6.78; N, 3.77. Found: C, 65.12; H, 6.79; N, 3.59.

(2*R,3*S**)-2-Butyl-1-[(4-methylphenyl)sulfonyl]-3-(1,1,1-trimethylsilyl)aziridine** (*cis*-**2f**)**:** Colourless liquid; eluent petroleum ether/ethyl acetate 5:1, R_f = 0.56; ^{1}H NMR ($CDCl_3$) • 0.00 [9H, s, Si(CH_3)$_3$], 0.86 (3H, t, *J* = 6.7 Hz, CH_3CH$_2$), 1.20-1.45 (5H, m, C*H*HCH_2CH_2CH$_3$), 1.46-1.60 (1H, m, C*H*HCH), 1.93 (1H, d, *J* = 8.2 Hz, C*H*Si), 2.47 (3H, s, CH_3C$_6$H$_4$), 2.86 (1H, td, *J* = 7.9, 4.9 Hz, C*H*CH$_2$), 7.35 (2H, d, *J* = 8.3 Hz, Ts), 7.84 (2H, d, *J* = 8.3 Hz, Ts); ^{13}C NMR ($CDCl_3$) • –1.7 (3q), 13.9 (q), 21.6 (q), 22.2 (t), 29.8 (t), 29.9 (t), 36.1 (d), 44.7 (d), 128.2 (2d), 129.4 (2d), 135.4 (s), 144.1 (s); IR •$_{max}$/ cm^{-1} 2960, 1599, 1317, 1252, 1158; MS m/z (EI) 325 (M^+, 5), 170 (100), 121 (56), 119 (62); HRMS: found 325.1546, $C_{16}H_{27}NO_2SSi$ requires 325.1532. Anal.

Calcd for $C_{16}H_{27}NO_2SSi$: C, 59.03; H, 8.36; N, 4.30. Found: C, 59.00; H, 8.45; N, 4.26.

(2*R,3*R**)-2-Butyl-1-[(4-methylphenyl)sulfonyl]-3-(1,1,1-trimethylsilyl)aziridine** (*trans*-**2f**)**:** Colourless liquid; eluent petroleum ether/ethyl acetate 5:1, R_f = 0.59; ^{1}H NMR ($CDCl_3$) (selection of signals) • 0.06 [9H, s, Si(C*H*$_3$)$_3$], 1.86 (1H, d, *J* = 6.1 Hz, C*H*Si), 2.46 (3H, s, C*H*$_3$C$_6$H$_4$), 2.62 (1H, dt, *J* = 7.3, 6.0 Hz, C*H*CH$_2$).

(2*R,3*S**)-2-Cyclohexyl-1-[(4-methylphenyl)sulfonyl]-3-(1,1,1-trimethylsilyl)aziridine** (*cis*-**2g**)**:** Colourless liquid; eluent petroleum ether/ethyl acetate 5:1, R_f = 0.54; ^{1}H NMR ($CDCl_3$) • 0.00 [9H, s, Si(C*H*$_3$)$_3$], 0.90-1.25 (6H, m, CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_2$), 1.53-1.79 (6H, m, C*H*$_2$C*H*CH*H*$_2$), 1.93 (1H, d, *J* = 8.2 Hz, C*H*Si), 2.46 (3H, s, C*H*$_3$C$_6$H$_4$), 2.61 (1H, t, *J* = 8.4 Hz, CHC*H*CH), 7.34 (2H, d, *J* = 8.1 Hz, Ts), 7.83 (2H, d, *J* = 8.1 Hz, Ts); ^{13}C NMR ($CDCl_3$) • –1.6 (3q), 21.6 (q), 25.5 (t), 25.5 (t), 26.1 (t), 30.3 (t), 31.6 (t), 36.2 (d), 38.6 (d), 50.0 (d), 128.3 (2d), 129.4 (2d), 135.2 (s), 144.1 (s); IR •$_{max}$/ cm^{-1} 2931, 1598, 1318, 1252, 1158; MS m/z (EI) 351 (M^+, 14), 196 (100); HRMS: found 351.1700, $C_{18}H_{29}NO_2SSi$ requires 351.1688. Anal. Calcd for $C_{18}H_{29}NO_2SSi$: C, 61.49; H, 8.31; N, 3.98. Found: C, 61.26; H, 8.53; N, 3.95.

(2*R,3*R**)-2-Cyclohexyl-1-[(4-methylphenyl)sulfonyl]-3-(1,1,1-trimethylsilyl)aziridine** (*trans*-**2g**)**:** Colourless liquid; eluent petroleum ether/ethyl acetate 5:1, R_f = 0.56; ^{1}H NMR ($CDCl_3$) (selection of signals) • -0.16 [9H, s, Si(C*H*$_3$)$_3$], 1.61 (1H, d, *J* = 6.4 Hz, C*H*Si), 2.46 (3H, s, C*H*$_3$C$_6$H$_4$).

Ethyl (2*R,3*S**)-1-[(4-methylphenyl)sulfonyl]-3-(1,1,1-trimethylsilyl)aziridine-2-carboxylate** (*cis*-**2h**)**:**[5] Colourless liquid; ^{1}H NMR ($CDCl_3$) • 0.00 [9H, s, Si(C*H*$_3$)$_3$], 1.26 (3H, m, C*H*$_3$CH$_2$), 2.12 (1H, d, *J* = 8.7 Hz, C*H*Si), 2.44 (3H, s, C*H*$_3$C$_6$H$_4$), 3.43 (1H, d, *J* = 8.7 Hz, NC*H*C), 4.17 (2H, m, C*H*$_2$), 7.33 (2H, d, *J* = 8.1 Hz, Ts), 7.83 (2H, d, *J* = 8.1 Hz, Ts); ^{13}C NMR ($CDCl_3$) • –2.4 (3q), 14.0 (q), 21.6 (q), 35.6 (d), 40.4 (d), 61.8 (t), 128.2 (2d), 129.6 (2d), 134.4 (s), 144.9 (s), 167.1 (s).

Ethyl (2*R,3*R**)-1-[(4-methylphenyl)sulfonyl]-3-(1,1,1-trimethylsilyl)aziridine-2-carboxylate** (*trans*-**2h**)**:**[5] Colourless liquid; ^{1}H NMR ($CDCl_3$) • 0.26 [9H, s, Si(C*H*$_3$)$_3$], 1.23 (3H, m, C*H*$_3$CH$_2$), 2.32 (1H, d, *J* = 6.0 Hz, C*H*Si), 2.44 (3H, s, C*H*$_3$C$_6$H$_4$), 3.22 (1H, d, *J* = 8.7 Hz, NC*H*C), 4.17 (2H, m, C*H*$_2$), 7.33 (2H, d, *J* = 8.1 Hz, Ts), 7.86 (2H, d, *J* = 8.1 Hz, Ts); ^{13}C NMR ($CDCl_3$) • –1.5 (3q), 14.0 (q), 21.6 (q), 39.4 (d), 41.1 (d), 61.8 (t), 127.7 (2d), 129.6 (2d), 136.2 (s), 144.4 (s), 167.8 (s).

(2*R,3*S**)-2-Phenyl-3-(1,1,1-trimethylsilyl)-1-[2-(1,1,1-trimethylsilyl)ethyl]sulfonylaziridine** (*cis*-**2i**)**:** Colourless oil; eluent petroleum ether/ethyl acetate 5:1, R_f = 0.62; ^{1}H NMR ($CDCl_3$) • –0.21 [9H, s, Si(C*H*$_3$)$_3$], 0.00 [9H, s, Si(C*H*$_3$)$_3$], 1.11-1.19 (2H, m, C*H*$_2$Si), 2.20 (1H, d, *J* = 8.4 Hz, C*H*Si), 3.05-3.12 (2H, m, C*H*$_2$S), 3.91 (1H, d, *J* = 8.4 Hz, C*H*Ph), 7.17-7.31 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) • –2.1 (3q), -2.0 (3q), 9.9 (t), 36.9 (d), 44.3 (d), 48.7 (t), 127.3 (2d), 127.9 (d), 128.3 (2d), 135.3 (s); IR •$_{max}$/ cm^{-1} (CH_2Cl_2) 3033, 2957, 1606, 1321, 1253, 1141; MS m/z (CI with NH_3) 356 ([M+H]$^+$, 21), 190 (100); HRMS: found [M+H]$^+$ 356.1536, $C_{16}H_{30}NO_2SSi$ requires 356.1536. Anal. Calcd for $C_{16}H_{29}NO_2SSi$: C, 54.04; H, 8.22; N, 3.94. Found: C, 54.15; H, 8.26; N, 3.81.

(2*R,3*R**)-2-Phenyl-3-(1,1,1-trimethylsilyl)-1-[2-(1,1,1-trimethylsilyl)ethyl]sulfonylaziridine** (*trans*-**2i**)**:** Colourless oil; eluent petroleum ether/ethyl acetate 5:1, R_f = 0.72; ^{1}H NMR ($CDCl_3$) (selection of signals) • 0.00 [9H, s, Si(C*H*$_3$)$_3$], 0.30 [9H, s, Si(C*H*$_3$)$_3$], 1.06-1.15 (2H, m, C*H*$_2$Si), 2.01 (1H, d, *J* = 6.0 Hz, C*H*Si), 3.06-3.12 (2H, m, C*H*$_2$S), 3.67 (1H, d, *J* = 6.0 Hz, C*H*Ph).

Representative Procedure for the Coupling of Si-aziridines with Electrophiles. To a solution of *cis*-**2a** (86.4 mg, 0.25 mmol) and TBAT (135.0 mg, 0.25 mmol, 1 equiv.) in THF (2.5 mL) was added benzaldehyde (76 •L, 0.75 mmol, 3 equiv.). After stirring for 12 h at 40•C, saturated NH_4Cl solution was added (5 mL), the organic solvent was removed and the reaction mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic extracts were washed by saturated NaCl solution (5 mL), dried with anhydrous Na_2SO_4 and evaporated. The crude mixture was purified by flash chromatography on silica gel (eluent petroleum ether/ethyl acetate 5:1) to afford *cis*-**5a** major diastereoisomer (55.8 mg, 59%) and *cis*-**5a** minor diastereoisomer (1.1 mg, 1%).

(*R){(2*R**,3*R**)-1-[(4-Methylphenyl)sulfonyl]-3-phenylaziridin-2-yl}(phenyl)methanol** (*cis*-**5**, major diastereoisomer)**:** White solid; eluent petroleum ether/ethyl acetate 2:1, R_f = 0.46; m.p. 112-114•C (from petroleum ether/ethyl acetate); ^{1}H NMR ($CDCl_3$) • 2.06 (1H, br d, *J* = 2.1 Hz, O*H*), 2.45 (3H, s, C*H*$_3$C$_6$H$_4$), 3.33 (1H, dd, *J* = 8.9, 7.3 Hz, NC*H*CHOH), 4.02 (1H, d, *J* = 7.3 Hz, NC*H*Ph), 4.16 (1H, br d, *J* = 8.9 Hz, C*H*OH), 6.90-6.94 (2H, m, Ph), 7.19-7.32 (8H, m, Ph), 7.37 (2H, d, *J* = 8.1 Hz, Ts), 7.94 (2H, d, *J* = 8.1 Hz, Ts); ^{13}C NMR ($CDCl_3$) • 21.8 (q), 46.0 (d), 51.2 (d), 70.7 (d), 126.2 (2d), 127.4 (2d), 128.3 (2d), 128.5 (4d), 130.0 (2d), 132.1 (s), 134.4 (s), 139.0 (s), 145.0 (s); IR •$_{max}$/ cm^{-1} 3587, 3035, 1599, 1329, 1163, 1092; MS m/z (CI with NH_3) 380 ([M+H]$^+$, 6), 274 (48), 224 (100); HRMS: found [M+H]$^+$ 380.1305, $C_{22}H_{22}NO_3S$ requires 380.1320. Anal. Calcd for $C_{22}H_{21}NO_3S$: C, 69.63; H, 5.58; N, 3.69. Found: C, 69.36; H, 5.62; N, 3.57.

(*S){(2*R**,3*R**)-1-[(4-Methylphenyl)sulfonyl]-3-phenylaziridin-2-yl}(phenyl)methanol** (*cis*-**5**, minor diastereoisomer)**:** Colourless oil; eluent petroleum ether/ethyl acetate 2:1, R_f = 0.41; ^{1}H NMR ($CDCl_3$) (selection of signals) • 2.32 (3H, s, C*H*$_3$C$_6$H$_4$), 3.17 (1H, dd, *J* = 8.9, 7.0 Hz, NC*H*CHOH), 4.00 (1H, d, *J* = 8.9 Hz, NC*H*Ph or C*H*OH), 4.16 (1H, d, *J* = 7.0 Hz, NC*H*Ph or C*H*OH).

(1*R)-1-{(2*R**,3*R**)-1-[(4-Methylphenyl)sulfonyl]-3-phenylaziridin-2-yl}pentan-1-ol** (*cis*-**6**, major diastereoisomer)**:** Colourless oil; eluent petroleum

(5) Juhl, K.; Hazell, R. G.; Jørgensen, K. A. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2293.

ether/ethyl acetate 2:1, R_f = 0.52; ^{1}H NMR ($CDCl_3$) • 0.63 (3H, m, C*H*$_3$CH$_2$), 0.77-1.46 (6H, m, CH$_2$C*H*$_2$C*H*$_2$), 2.37 (3H, s, C*H*$_3$C$_6$H$_4$), 2.94-3.06 (2H, m, C*H*C*H*OH), 3.97 (1H, d, *J* = 6.7 Hz, C*H*Ph), 7.14-7.25 (5H, m, Ph), 7.29 (2H, d, *J* = 8.1 Hz, Ts), 7.84 (2H, d, *J* = 8.1 Hz, Ts); ^{13}C NMR ($CDCl_3$) • 13.7 (q), 21.7 (q), 22.2 (t), 26.7 (t), 33.1 (t), 45.8 (d), 50.8 (d), 68.2 (d), 127.1 (2d), 128.1 (3d), 128.4 (2d), 129.9 (2d), 132.3 (s), 134.5 (s), 144.9 (s); IR •$_{max}$/ cm^{-1} 3592, 2960, 2953, 1599, 1329, 1163, 1093; MS m/z (CI with NH_3) 360 ([M+H]$^+$, 12), 204 (100), 91 (41); HRMS: found [M+H]$^+$ 360.1618, $C_{20}H_{26}NO_3S$ requires 360.1633. Anal. Calcd for $C_{20}H_{25}NO_3S$: C, 66.82; H, 7.01; N, 3.90. Found: C, 66.78; H, 7.28; N, 3.66.

(1*S)-1-{(2*R**,3*R**)-1-[(4-Methylphenyl)sulfonyl]-3-phenylaziridin-2-yl}pentan-1-ol** (*cis*-**6**, minor diastereoisomer)**:** Colourless oil; eluent petroleum ether/ethyl acetate 2:1, R_f = 0.43; ^{1}H NMR ($CDCl_3$) • 0.56-1.37 (9H, m, C*H*$_3$C*H*$_2$C*H*$_2$C*H*$_2$), 2.38 (3H, s, C*H*$_3$C$_6$H$_4$), 2.91 (1H, dd, *J* = 8.9, 6.9 Hz, C*H*CHOH), 2.96-3.07 (1H, m, C*H*CH), 3.98 (1H, d, *J* = 6.9 Hz, C*H*Ph), 7.20-7.26 (5H, m, Ph), 7.29 (2H, d, *J* = 8.1 Hz, Ts), 7.82 (2H, d, *J* = 8.1 Hz, Ts).

(*R)Phenyl((2*R**,3*R**)-3-phenyl-1-{[2-(1,1,1-trimethylsilyl)ethyl]sulfonyl}aziridin-2-yl)methanol** (*cis*-**7**, major diastereoisomer)**:** Colourless oil; eluent petroleum ether/ethyl acetate 5:1, R_f = 0.28; ^{1}H NMR ($CDCl_3$) • 0.00 [9H, s, Si(C*H*$_3$)$_3$], 1.07-1.27 (2H, m, C*H*$_2$Si), 1.69 (1H, br s, O*H*), 3.08-3.27 (2H, m, C*H*$_2$S), 3.21 (1H, dd, *J* = 8.9, 7.3 Hz, NC*H*CHOH), 3.93 (1H, d, *J* = 7.3 Hz, NC*H*Ph), 4.19 (1H, d, *J* = 8.9 Hz, C*H*OH), 6.82-6.88 (2H, m, Ph), 7.14-7.37 (8H, m, Ph); ^{13}C NMR ($CDCl_3$) • –2.0 (3q), 9.8 (t), 45.3 (d), 49.0 (t), 50.1 (d), 71.0 (d), 126.1 (2d), 127.4 (2d), 128.4 (d), 128.5 (d), 128.6 (4d), 132.3 (s), 139.4 (s); IR •$_{max}$/ cm^{-1} 3603, 2958, 1325, 1253, 1145; MS m/z (CI with NH_3) 390 ([M+H]$^+$, 4), 224 (100); HRMS: found [M+H]$^+$ 390.1564, $C_{20}H_{28}NO_3SSi$ requires 390.1559.

(*S)Phenyl((2*R**,3*R**)-3-phenyl-1-{[2-(1,1,1-trimethylsilyl)ethyl]sulfonyl}aziridin-2-yl)methanol** (*cis*-**7**, minor diastereoisomer)**:** Colourless oil; eluent petroleum ether/ethyl acetate 2:1, R_f = 0.59; ^{1}H NMR ($CDCl_3$) • 0.00 [9H, s, Si(C*H*$_3$)$_3$], 0.88 (1H, td, *J* = 13.8, 4.6 Hz, C*H*HSi), 1.00 (1H, td, *J* = 13.6, 4.2 Hz, C*H*HSi), 2.33 (1H, td, *J* = 13.7, 4.2 Hz, C*H*HS), 2.71 (1H, td, *J* = 14.0, 4.6 Hz, C*H*HS), 3.29 (1H, dd, *J* = 9.1, 7.0 Hz, NC*H*CHOH), 4.24 (1H, d, *J* = 9.1 Hz, NC*H*Ph or C*H*OH), 4.32 (1H, d, *J* = 7.0 Hz, NC*H*Ph or C*H*OH), 7.40-7.64 (10H, m, Ph).

(2*S,3*R**)-2-Deuterium-3-phenyl-1-(phenylsulfonyl)aziridine** (*cis*-**8**)**:**[6] White solid; eluent petroleum ether/ethyl acetate 5:1, R_f = 0.40; m.p. 84-86•C (from petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) • 2.43 (3H, s, C*H*$_3$C$_6$H$_4$), 2.97 (1H, d, *J* = 7.2 Hz, C*H*D), 3.76 (1H, d, *J* = 7.2 Hz, C*H*Ph) 7.19-7.23 (2H, m, Ph), 7.26-7.30 (3H, m, Ph), 7.32 (2H, d, *J* = 8.2 Hz, Ts), 7.86 (2H, d, *J* = 8.2 Hz, Ts); ^{13}C NMR ($CDCl_3$) • 21.5 (q), 35.5 (dt, $J_{C\text{-}D}$ = 27.7 Hz), 40.8 (d), 126.4 (2d), 127.8 (2d), 128.1 (d), 128.4 (2d), 129.5 (2d), 134.8 (s), 134.9 (s), 144.5 (s); IR •$_{max}$/ cm^{-1} 3036, 1600, 1322, 1162, 1093; MS m/z (EI) 274 (M$^+$, 1), 119 (100), 92 (79); HRMS (CI with NH_3): found [M+H]$^+$ 275.0965, $C_{15}H_{15}DNSO_2$ requires 275.0963.

Ring Opening of *cis*-2a with Sodium Azide: To a solution of *cis*-**2a** (41.5 mg, 0.12 mmol) in DMF (3 mL) was added NaN_3 (78.0 mg, 1.20 mmol, 10 equiv.). After stirring for 20 h at r.t. the solvent was removed and the crude mixture was purified by flash chromatography on silica gel (eluent petroleum ether/ethyl acetate 12:1) to afford **9** (45.7 mg, 98%).

***N*1-[(1*R**,2*R**)-2-Azido-1-phenyl-2-(1,1,1-trimethylsilyl)ethyl]-1-benzenesulfonamide** (**9**)**:** White solid; eluent petroleum ether/ethyl acetate 5:1, R_f = 0.46; m.p. 122-124•C (from petroleum ether/ethyl acetate); ^{1}H NMR ($CDCl_3$) • 0.00 [9H, s, Si(C*H*$_3$)$_3$], 2.23 (3H, s, C*H*$_3$C$_6$H$_4$), 2.93 (1H, d, *J* = 5.6 Hz, C*H*Si), 4.50 (1H, dd, *J* = 8.0, 5.6 Hz, C*H*Ph), 5.21 (1H, d, *J* = 8.0 Hz, N*H*), 6.88-7.11 (7H, m, Ph and Ts), 7.32 (2H, d, *J* = 8.2 Hz, Ts); ^{13}C NMR ($CDCl_3$) • –2.6 (3q), 21.4 (q), 58.8 (d), 61.2 (q), 126.9 (2d), 127.0 (2d), 127.7 (d), 128.4 (2d), 129.1 (2d), 137.5 (s), 138.6 (s), 142.9 (s); IR •$_{max}$/ cm^{-1} 3376, 3034, 2959, 2098, 1600, 1412, 1330, 1254, 1161, 1092; MS m/z (CI with NH_3) 406 ([M+NH$_4$]$^+$, 29), 361 (62), 260 (53), 229 (100), 205 (58), 192 (67), 189 (68), 106 (59), 90 (77); HRMS: found [M+NH$_4$]$^+$ 406.1743, $C_{18}H_{28}N_5O_2SSi$ requires 406.1733. Anal. Calcd for $C_{18}H_{24}N_4O_2SSi$: C, 55.64; H, 6.23; N, 14.42. Found: C, 55.46; H, 5.96; N, 14.79.

Ring Opening of *cis*-2a with Benzenethiol: To a solution of *cis*-**2a** (41.5 mg, 0.12 mmol) and benzenethiol (15 •L, 0.14 mmol, 1.2 equiv.) in toluene (0.7 mL) was added a 50% NaOH solution and Hex_4NCl (2.4 mg, 6 •mol, 5 mol%). After stirring for 5 h at r.t. the aqueous layer was extracted with diethyl ether (3 × 2 mL). The combined organic extracts were washed by saturated NaCl solution (2 mL), dried with anhydrous $MgSO_4$ and evaporated. The crude mixture was purified by flash chromatography on silica gel (eluent petroleum ether/ethyl acetate 12:1) to afford **10** (41.0 mg, 75%).

***N*1-[(1*R**,2*S**)-1-Phenyl-2-(phenylsulfanyl)-2-(1,1,1-trimethylsilyl)ethyl]-1-benzenesulfonamide** (**10**)**:** White solid; eluent petroleum ether/ethyl acetate 5:1, R_f = 0.53; m.p. 162-164•C (from petroleum ether/ethyl acetate); ^{1}H NMR ($CDCl_3$) • 0.00 [9H, s, Si(C*H*$_3$)$_3$], 2.08 (3H, s, C*H*$_3$C$_6$H$_4$), 2.51 (1H, d, *J* = 3.8 Hz, C*H*S), 4.71 (1H, dd, *J* = 8.9, 3.8 Hz, C*H*N), 5.41 (1H, d, *J* = 8.9 Hz, N*H*), 6.56-6.82 (12H, m, Ar), 7.22 (2H, d, *J* = 8.2 Hz, Ts); ^{13}C NMR ($CDCl_3$) • –2.0 (3q), 21.4 (q), 44.4 (d), 58.0 (d), 15.8 (d), 126.8 (2d), 126.9 (d), 127.0 (2d), 127.8 (2d), 128.4 (2d), 128.9 (2d), 129.0 (2d), 136.6 (s), 137.7 (s), 139.6 (s), 142.8 (s); IR •$_{max}$/ cm^{-1} 3358, 3066, 2956, 1600, 1410, 1346, 1252, 1160, 1091; MS m/z (CI with NH_3) 473 ([M+NH$_4$]$^+$, 4), 332 (45), 260 (100), 244 (73), 190 (44), 106 (44), 91 (70), 73 (76); HRMS: found [M+NH$_4$]$^+$ 473.1745, $C_{24}H_{33}N_2O_2S_2Si$ requires 473.1753.

(6) 5 equiv. of $CDCl_3$ and 0.5 equiv. of TBAT were used in this case.

Anal. Calcd for $C_{24}H_{29}NO_2S_2Si$: C, 63.25; H, 6.41; N, 3.07. Found: C, 63.09; H, 6.39; N, 2.93.

Deprotonation and cyclisation of *cis*-2a: To a solution of *cis*-**2a** (51.8 mg, 0.15 mmol) in THF (1.5 mL) at –78•C was added dropwise a 1.47 M solution of *n*-BuLi in hexanes (108 •L, 0.16 mmol, 1.05 equiv.). After stirring the resulting red solution for 20 min. more at -78•C, MeI (19 •L, 0.30 mmol, 2.0 equiv.) was added. The mixture was allowed to reach r.t. within one hour and saturated NH_4Cl solution was added (1 mL), the organic solvent was removed and the reaction mixture was extracted with diethyl ether (4 × 3 mL). The combined organic extracts were washed by saturated NaCl solution (3 mL), dried with anhydrous $MgSO_4$ and evaporated. The crude mixture was purified by flash chromatography on silica gel (eluent petroleum ether/ethyl acetate 20:1) to afford **11** (40.5 mg, 75%).

(1*S,3a*S**,7a*S**,7b*R**)-3a,6-Dimethyl-7b-phenyl-1-(1,1,1-trimethylsilyl)-3,3a,7a,7b-tetrahydro-1*H*-3λ^6-aziridino[1,2-*b*]benzo[*d*]isothiazole-3,3-dione (11):** White solid; eluent petroleum ether/ethyl acetate 5:1, R_f = 0.63; m.p. 116-118•C (from petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) • –0.25 [9H, s, Si(C*H*$_3$)$_3$], 1.40 (3H, s, C*H*$_3$CSO$_2$), 1.92 (3H, t, *J* = 1.3 Hz, C*H*$_3$CCHC), 2.42 (1H, s, C*H*N), 2.95 (1H, d, *J* = 5.0 Hz, CHC*H*CN), 5.73 (1H, dq, *J* = 5.4, 1.2 Hz, C*H*CHCN), 5.79 (1H, dd, *J* = 9.7, 1.5 Hz, C*H*CHCS), 5.99 (1H, d, *J* = 9.7 Hz, C*H*CS), 7.31-7.38 (3H, m, Ph), 7.38-7.44 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) • –3.1 (3q), 21.7 (q), 23.7 (q), 38.5 (d), 50.4 (d), 60.3 (s), 63.8 (s), 117.6 (d), 125.2 (d), 127.1 (d), 127.8 (2d), 128.5 (3d), 130.9 (s), 137.1 (s); IR •$_{max}$/ cm^{-1} (CH_2Cl_2) 2961, 1448, 1329, 1252, 1162; MS m/z (CI with NH_3) 360 ([M+H]$^+$, 4), 190 (100), 189 (64); HRMS: found [M+H]$^+$ 360.1437, $C_{19}H_{26}NO_2SSi$ requires 360.1454. Anal. Calcd for $C_{19}H_{25}NO_2SSi$: C, 63.47; H, 7.01; N, 3.90. Found: C, 63.53; H, 7.12; N, 4.19.