Electronic supplementary information for
3-hydroxypyrrolidines from epoxysulfonamides and
dimethylsulfoxonium methylide

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(I) General Directions

All reactions were conducted in flame-dried glassware under an atmosphere of argon. THF was distilled under an atmosphere of argon from sodium benzophenone ketyl, while CH$_2$Cl$_2$ was degassed and dried over alumina under nitrogen. Column chromatography was carried out on Kieselgel 60 (40–63 μm) silica gel. Petrol refers to the fraction of petroleum ether boiling between 30 and 40 °C. Melting points were recorded on a Kofler hot block. IR spectra were recorded as thin films or KBr discs, using a 1750 FTIR spectrophotometer. $^1$H and $^{13}$C NMR spectra were recorded at 25 °C in CDCl$_3$, using DPX400, AV400 or AMX500 spectrometers. Data are expressed as chemical shifts in parts per million (ppm) relative to residual CHCl$_3$ ($^1$H δ 7.27) or

CDCl$_3$ ($^{13}$C $\delta$ 77.0) as the internal standard on the $\delta$ scale. The multiplicity of each signal is designated by the following abbreviations; s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; br, broad singlet. Coupling constants $J$ are given in Hz. Mass spectra were obtained from the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea with a Micromass ZAB-E instrument, or 900 XLT high resolution double focusing mass spectrometer with tandem ion trap. Alternatively they were recorded in-house using a VG Mass Lab TRIO1 or Micromass platform APCI spectrometer using chemical ionization (CI) or electrospray ionization (ESI) techniques.

(II) Procedures and data for epoxysulfonamide preparation

**General Procedure A.** Aza-Payne rearrangement of N-Ts 2-aziridinemethanols to epoxysulfonamides.\(^2\)

A suspension of KH (4 equiv) in THF was cooled to $-78$ °C and a solution of the appropriate N-Ts 2-aziridinemethanol (1 equiv) in THF was added dropwise. The reaction was warmed to 0 °C over 5 min and left to stir at this temperature for 2 h. The reaction was carefully quenched with sat. aq. NH$_4$Cl solution (30 mL) and the organic layer separated. The aqueous layer was extracted with Et$_2$O (3 x 30 mL); the combined organic layers were dried (MgSO$_4$) and solvent evaporated \textit{in vacuo}. The residue was purified by column chromatography (Et$_2$O/petrol) to give the corresponding epoxysulfonamide.

4-Methyl-N-[(R*)-1-((R*)-oxiran-2-yl)butyl]benzenesulfonamide *anti*-7a

 Following general procedure A, the addition of *trans*-3-propyl-1-tosylaziridin-2-yl)methanol\(^3\) (600 mg, 2.23 mmol) in THF (18 mL) to KH (30% w/w, 1.19 g, 8.91 mmol) in THF (18 mL) gave after work-up and column chromatography (50% Et\(_2\)O in petrol) *anti*-epoxide 7a (550 mg, 92%) as a colorless oil, which solidified on standing; \(R_f\) 0.16 (50% Et\(_2\)O in petrol); mp 55–57 °C; IR (neat)/cm\(^{-1}\) 3278br, 2961m, 2874m, 1599w, 1455m, 1328s, 1160s, 1093m; \(^1\)H NMR (400 MHz) \(\delta\) 7.76 (d, \(J = 8, 2\)H), 7.30 (d, \(J = 8, 2\)H), 5.11 (d, \(J = 7.5, 1\)H), 2.97–2.94 (m, 1H), 2.78 (ddd, \(J = 6.5, 3.5, 3, 1\)H), 2.61 (dd, \(J = 4.5, 3.5, 1\)H), 2.52 (dd, \(J = 4.5, 3, 1\)H), 2.43 (s, 3H), 1.61–1.10 (m, 4H), 0.78 (t, \(J = 7, 3\)H); \(^13\)C NMR (100 MHz) \(\delta\) 143.5, 137.8, 129.6, 127.1, 53.9, 46.7, 34.5, 21.5, 18.2, 13.6; MS \(m/z\) (Cl) 287 (M+NH\(_4\)\(^+\), 100), 271 (18), 270 (12), 189 (17), 52 (24); HRMS calcd for C\(_{13}\)H\(_{20}\)N\(_2\)O\(_3\)S (M+H\(^+\)) 270.1164, found 270.1161.

4-Methyl-N-[(R*)-1-((S*)-oxiran-2-yl)butyl]benzenesulfonamide *syn*-7a

 Following general procedure A, the addition of *cis*-3-propyl-1-tosylaziridin-2-yl)methanol\(^3\) (500 mg, 1.86 mmol) in THF (15 mL) to KH (30% w/w, 993 mg, 7.43 mmol) in THF (15 mL) gave after work-up and column chromatography (50% Et\(_2\)O in petrol) *syn*-epoxide 7a (400 mg, 80%) as a white solid; \(R_f\) 0.16 (50% Et\(_2\)O in petrol); mp 98–99 °C; IR (KBr)/cm\(^{-1}\) 3244br, 2964m, 2863m, 1597m, 1431m, 1329s, 1152s, 1094s; \(^1\)H NMR (400 MHz) \(\delta\) 7.75 (d, \(J = 8, 2\)H), 7.30 (d, \(J = 8, 2\)H), 4.55 (d, \(J = 9, 1\)H), 3.53–3.48 (m, 1H), 2.96 (ddd, \(J = 5, 4, 2.5, 1\)H), 2.66 (dd, \(J = 4.5, 4, 1\)H), 2.60 (dd, \(J = 4.5, 2.5, 1\)H), 2.43 (s, 3H), 1.58–1.19 (m, 4H), 0.81 (t, \(J = 7, 3\)H); \(^13\)C NMR (100 MHz) \(\delta\) 143.4, 138.2, 129.6, 126.9, 53.5, 52.5, 44.4, 35.7, 21.5, 18.5, 13.7; MS \(m/z\) (Cl) 287 (M+NH\(_4\)\(^+\), 100), 271 (35), 189 (18), 72 (88); HRMS calcd for C\(_{13}\)H\(_{20}\)N\(_2\)O\(_3\)S (M+NH\(_4\)\(^+\)) 287.1429, found 287.1424.

4-Methyl-N-[(R*)-(4-bromophenyl)((R*)-oxiran-2-yl)methyl]benzenesulfonamide 7e

To a mixture of (E)-3-(4-bromophenyl)-2-propen-1-ol 4 (1.10 g, 5.16 mmol) and anhydrous chloramine-T (1.30 g, 5.68 mmol) in MeCN (60 mL) was added PTAB (196 mg, 0.52 mmol) at rt. After stirring for 16 h, the mixture was filtered and the solvent evaporated in vacuo. Purification of the residue by column chromatography (50% Et₂O in petrol) gave trans-[3-(4-bromophenyl)-1-tosylaziridin-2-yl]methanol (1.34 g, 68%) as a colorless oil; Rf 0.21 (50% Et₂O in petrol); IR (neat)/cm⁻¹ 3521, 3064, 3039, 2950, 2885, 1598, 1497, 1456, 1323, 1161, 1088; ¹H NMR (400 MHz) δ 7.82 (d, J = 8, 2H), 7.39 (d, J = 8, 2H), 7.30 (d, J = 8, 2H), 7.02 (d, J = 8, 2H), 4.32–4.28 (m, 1H), 4.18–4.14 (m, 1H), 3.98 (d, J = 4, 1H), 3.12–3.18 (m, 2H), 2.42 (s, 3H); ¹³C NMR (100 MHz) δ 144.6, 136.8, 131.7, 131.8, 129.8, 128.1, 127.1, 122.4, 60.4, 54.7, 45.6, 21.7; MS m/z (ESI) 382 (M+H⁺, 100); HRMS calcd for C₁₆H₁₇BrNO₃S (M+H⁺) 382.0113, found 382.0105.

Following general procedure A, the addition of trans-(3-(4-bromophenyl)-1-tosylaziridin-2-yl)methanol (370 mg, 0.97 mmol) in THF (8 mL) to KH (30% w/w, 517 mg, 3.88 mmol) in THF (8 mL) gave after work-up and column chromatography (50% Et₂O in petrol) anti-epoxide 7e (290 mg, 78%) as a white solid; Rf 0.19 (50% Et₂O in petrol); mp 113–114 °C; IR (KBr)/cm⁻¹ 3263, 2960, 2898, 1599, 1490, 1445, 1330, 1164, 1093, 1074; ¹H NMR (400 MHz) δ 7.56 (d, J = 8, 2H), 7.32 (d, J = 8.5, 2H), 7.18 (d, J = 8, 2H), 6.98 (d, J = 8.5, 2H), 5.29 (d, J = 6.5, 1H), 4.39 (dd, J = 6.5, 5, 1H), 3.21–3.18 (m, 1H), 2.70 (dd, J = 4, 1H), 2.41–2.35 (m, 4H); ¹³C NMR (100 MHz) δ 143.7, 137.0, 134.9, 131.6, 129.5, 129.2, 127.1, 122.4, 57.5, 53.6, 45.5, 21.6; MS m/z (ESI) 382 (M+H⁺, 100); HRMS calcd for C₁₆H₁₇BrNO₃S (M+H⁺) 382.0113, found 382.0103.

4-Methyl-N-[(R*)-1-((R*)-2-methyloxiran-2-yl)pentyl]-benzenesulfonamide 7f

Following general procedure A (except reaction left at rt for 24 h), the addition of (E)-(3-butyl-2-methyl-1-tosylaziridin-2-yl)methanol\(^3\) 5 (140 mg, 0.47 mmol) in THF (4 mL) to KH (30% w/w, 251 mg, 1.88 mmol) in THF (4 mL) gave after work-up and column chromatography (20%→40% Et\(_2\)O in petrol) epoxide 7f (112 mg, 80%) as a colorless oil, which solidified on standing; mp 71–73 °C; \(R_f\) 0.19 (50% Et\(_2\)O in petrol); IR (KBr)/cm\(^{-1}\) 3257br, 2926s, 2868m, 1598m, 1497m, 1431m, 1399m, 1326s, 1163s, 1095m; \(^1\)H NMR (400 MHz) \(\delta\) 7.75 (d, \(J = 8, 2\)H), 7.30 (d, \(J = 8, 2\)H), 5.25 (d, \(J = 10, 1\)H), 2.83–2.77 (m, 1H), 2.66 (d, \(J = 4.5, 1\)H), 2.48 (d, \(J = 4.5, 1\)H), 2.43 (s, 3H), 1.64–1.57 (m, 1H), 1.42–1.31 (m, 1H), 1.21 (s, 3H), 1.20–0.99 (m, 4H), 0.76 (t, \(J = 7, 3\)H); \(^{13}\)C NMR (100 MHz) \(\delta\) 145.6, 137.6, 129.6, 127.1, 58.6, 57.7, 54.7, 31.1, 27.6, 22.2, 21.5, 16.1, 13.8; MS \(m/z\) (ESI) 296 (M−H\(^-\), 100); HRMS calcd for C\(_{15}\)H\(_{22}\)NO\(_3\)S (M−H\(^-\)) 296.1322, found 296.1314.

4-Methyl-N-(2-(oxiran-2-yl)propan-2-yl]benzenesulfonamide 7g

Following general procedure A, the addition (3,3-dimethyl-1-tosylazirin-2-yl)methanol\(^3\) (255 mg, 1.00 mmol) in THF (8 mL) to KH (30% w/w, 533 mg, 4.00 mmol) in THF (8 mL) gave after work-up and column chromatography (50% Et\(_2\)O in petrol) epoxide 7g (160 mg, 63%) as a white solid; mp 74–75 °C; \(R_f\) 0.19 (50% Et\(_2\)O in petrol); IR (KBr)/cm\(^{-1}\) 3276br, 2983m, 1599m, 1324s, 1152s, 1094s; \(^1\)H NMR (400 MHz) \(\delta\) 7.77 (d, \(J = 8, 2\)H), 7.29 (d, \(J = 8, 2\)H), 4.75 (s, 1H), 2.91 (dd, \(J = 4, 2.5, 1\)H), 2.74 (dd, \(J = 4, 2.5, 1\)H), 2.68 (dd, \(J = 4, 4, 1\)H), 2.43 (s, 3H), 1.23 (s, 3H), 1.22 (s, 3H); \(^{13}\)C NMR (100 MHz) \(\delta\) 143.2, 140.1, 129.6, 127.0, 58.4, 54.8, 44.6, 25.0, 23.4, 21.5; MS \(m/z\) (ESI) 278 (M+Na\(^+\), 100); HRMS calcd for C\(_{12}\)H\(_{17}\)NNaO\(_3\)S (M+Na\(^+\)) 278.0827, found 278.0826.

4-Methyl-N-[(3R*,4R*)-1-oxaspiro[2.5]octan-4-yl]benzenesulfonamide anti-9b

![Structure](structure.png)

To a mixture of cyclohexenyl-1-methanol (820 mg, 7.32 mmol) and anhydrous chloramine-T (1.80 g, 8.10 mmol) in MeCN (100 mL) was added PTAB (275 mg, 0.73 mmol) at rt. After stirring for 16 h, the mixture was filtered and the solvent evaporated in vacuo. Purification of the residue by column chromatography (50% Et₂O in petrol) gave (7-tosyl-7-azabicyclo[4.1.0]heptan-1-yl)methanol (1.60 g, 78%) as a colorless oil; Rₙ 0.20 (50% Et₂O in petrol); IR (KBr)/cm⁻¹ 3519br, 2940m, 1598m, 1439m, 1329m, 1303s, 1150s, 1090s; ¹H NMR (400 MHz) δ 7.83 (d, J = 8, 2H), 7.33 (d, J = 8, 2H), 4.05–4.02 (m, 2H), 3.25 (dd, J = 5, 1, 1H), 3.04–3.00 (m, 1H), 2.45 (s, 3H), 2.27 (ddd, J = 15, 6, 6, 1H), 1.83–1.76 (m, 2H), 1.69–1.62 (m, 1H), 1.42–1.18 (m, 4H); ¹³C NMR (100 MHz) δ 143.8, 138.2, 129.6, 126.8, 65.9, 56.4, 45.4, 27.4, 22.8, 21.6, 19.7, 19.3; MS m/z (CI) 282 (M+H⁺, 80), 264 (40), 252 (30), 189 (100), 155 (38), 128 (50), 108 (55), 91 (30); HRMS calc for C₁₄H₂₀NO₃S (M+H⁺) 282.1164, found 282.1154.

Following general procedure A, the addition of (7-tosyl-7-azabicyclo[4.1.0]heptan-1-yl)methanol (230 mg, 0.82 mmol) in THF (7 mL) to KH (30% w/w, 437 mg, 3.28 mmol) in THF (7 mL) gave after work-up and column chromatography (50% Et₂O in petrol) anti-epoxide 9b (210 mg, 91%) as a colorless oil; Rₙ 0.19 (50% Et₂O in petrol); IR (neat)/cm⁻¹ 3201br, 3069m, 2939s, 1597m, 1452m, 1329s, 1288m, 1160s, 1094s; ¹H NMR (400 MHz) δ 7.75 (d, J = 8, 2H), 7.29 (d, J = 8, 2H), 5.42 (d, J = 6, 1H), 3.04–2.99 (m, 1H), 2.66 (d, J = 4.5, 1H), 2.44 (d, J = 4.5, 1H), 2.42 (s, 3H), 1.92–1.85 (m, 1H), 1.74–1.33 (m, 7H); ¹³C NMR (100 MHz) δ 143.5, 137.3, 129.7, 127.1, 59.4, 54.6, 51.8, 31.0, 30.6, 23.8, 21.6, 21.5; MS m/z (CI) 282 (M+H⁺, 65), 252 (30), 189 (40), 128 (100), 112 (45), 110 (50), 98 (55); HRMS calc for C₁₄H₂₀NO₃S (M+H⁺) 282.1164, found 282.1154.

4-Methyl-N-[(3R*,4S*)-1-oxaspiro[2.5]octan-4-yl]benzenesulfonamide syn-9b

![Chemical structure](attachment:image.png)

To a solution of 4-methyl-N-(2-methylene cyclohexyl)benzenesulfonamide\(^7\) (145 mg, 0.55 mmol) in CH\(_2\)Cl\(_2\) (5.5 mL) was added NaHCO\(_3\) (92 mg, 1.09 mmol) and mCPBA (188 mg, 1.09 mmol) and the reaction mixture was then stirred at rt for 24 h. The reaction mixture was washed with sat. aq. Na\(_2\)SO\(_4\) solution (2 x 20 mL) and then sat. aq. Na\(_2\)CO\(_3\) solution (2 x 20 mL). The organic layer was dried (MgSO\(_4\)) and solvent evaporated in vacuo. Analysis of the \(^1\)H NMR of the crude reaction mixture revealed d.r. = 96:4. The residue was purified by column chromatography (30%→50% Et\(_2\)O in petrol) to give only the syn-isomer of epoxide 9b (119 mg, 77%) as a white solid; mp 140–142 °C; \(R_t\) 0.15 (50% Et\(_2\)O in petrol); IR (KBr)/cm\(^{-1}\) 3201br, 3069w, 2939s, 1598m, 1450m, 1328m, 1288m, 1162s, 1092; \(^1\)H NMR (400 MHz) \(\delta\) 7.72 (d, \(J = 8, 2\)H), 7.27 (d, \(J = 8, 2\)H), 4.85 (d, \(J = 10, 1\)H), 3.49 (ddd, \(J = 11.5, 10, 4.5, 1\)H), 2.75 (d, \(J = 4.5, 1\)H), 2.45 (d, \(J = 4.5, 1\)H), 2.40 (s, 3H), 1.85–1.21 (m, 8H); \(^{13}\)C NMR (100 MHz) \(\delta\) 143.2, 138.5, 129.7, 126.7, 59.6, 52.4, 51.0, 32.8, 32.1, 24.7, 22.9, 21.5; MS m/z (Cl) 282 (M+H\(^+\), 30), 252 (15), 189 (28), 128 (100), 112 (70), 110 (73), 98 (95); HRMS calcd for C\(_{14}\)H\(_{26}\)NO\(_3\)S (M+H\(^+\)) 282.1164, found 282.1160.

\[N-[(R*)-1-((2S*,3S*)-3-(4-Chlorophenyl)oxiran-2-yl)hexyl]-4-methylbenzenesulfonamide 11\]

![Chemical structure](attachment:image.png)

To a solution of 4-methyl-N-(1-octen-3-yl)benzenesulfonamide\(^7\) (200 mg, 0.71 mmol) and 4-chlorostyrene (1.48 g, 10.7 mmol) in CH\(_2\)Cl\(_2\) (7 mL) was added Grubbs’ 2nd generation catalyst (17 mg, 20 \(\mu\)mol). The reaction was heated to reflux for 12 h then cooled and filtered through a short silica plug. The solvent was evaporated in vacuo and the residue was purified by column chromatography (20%→50% Et\(_2\)O in petrol) to give (E)-N-[(1-(4-chlorophenyl)-1-octen-3-yl]-4-methylbenzenesulfonamide (231 mg,

83%, E:Z=95:5 by $^1$H NMR analysis of isomeric vinylic protons in the $\delta$ 6.50–5.50 region) as a colorless oil, which solidified on standing; mp 99–100 °C; $R_f$ 0.19 (30% Et$_2$O in petrol); IR (neat)/cm$^{-1}$ 3268w, 2924s, 2858s, 1597w, 1491m, 1318m, 1161s, 1091m; $^1$H NMR (400 MHz) $\delta$ 7.75 (d, $J$ = 8, 2H), 7.19 (d, $J$ = 8.5, 2H), 7.16 (d, $J$ = 8, 2H), 7.01 (d, $J$ = 8.5, 2H), 6.15 (d, $J$ = 15.5, 1H), 5.71 (dd, $J$ = 15.5, 8, 1H), 5.31 (d, $J$ = 8, 1H), 3.89 (quint, $J$ = 8, 1H), 2.29 (s, 3H), 1.60–1.45 (m, 2H), 1.32–1.14 (m, 6H), 0.82 (t, $J$ = 8, 3H); $^{13}$C NMR (100 MHz) $\delta$ 143.2, 138.2, 134.9, 133.1, 129.9, 129.9, 129.5, 128.5, 127.5, 127.3, 56.4, 35.7, 31.3, 25.1, 22.4, 21.4, 14.0; MS m/z (ESI) 414 (M+Na$^+$, 100); HRMS calcd for C$_{21}$H$_{26}$ClNNaO$_2$S (M+Na$^+$) 414.1270, found 414.1275.

To a solution of (E)-N-[1-(4-chlorophenyl)-1-octen-3-yl]-4-methylbenzenesulfonamide (200 mg, 0.51 mmol) in CH$_2$Cl$_2$ (5 mL) was added NaHCO$_3$ (86 mg, 1.02 mmol) and mCPBA (176 mg, 1.02 mmol) and the reaction was then stirred at rt for 24 h. The reaction mixture was washed with sat. aq. Na$_2$SO$_3$ solution (2 x 15 mL) and then sat. aq. Na$_2$CO$_3$ solution (2 x 15 mL). The organic layer was dried (MgSO$_4$) and solvent evaporated in vacuo. The residue was purified by column chromatography (40% Et$_2$O in petrol) to give epoxide 11 (154 mg, 74%, d.r. = 65:35 by $^1$H NMR analysis of isomeric N-H protons in the $\delta$ 5.50–4.50 region). Further purification by column chromatography (20% Et$_2$O in petrol) gave partial separation of the major syn diastereoisomer of epoxide 11 (58 mg, 28%) as a colorless oil which solidified on standing; mp 119–120 °C; $R_f$ 0.24 (30% Et$_2$O in petrol); IR (KBr)/cm$^{-1}$ 3281br, 2926s, 1599w, 1495m, 1427m, 1318m, 1160m, 1089m; $^1$H NMR (400 MHz) $\delta$ 7.78 (d, $J$ = 8, 2H), 7.32 (d, $J$ = 8.5, 2H), 7.27 (d, $J$ = 8, 2H), 7.04 (d, $J$ = 8.5, 2H), 4.79 (d, $J$ = 9, 1H), 3.69 (d, $J$ = 2, 1H), 3.65 (dtd, $J$ = 9, 8, 2.5, 1H), 2.92 (dd, $J$ = 2.5, 2, 1H), 2.45 (s, 3H), 1.63–1.43 (m, 2H), 1.28–1.08 (m, 6H), 0.81 (t, $J$ = 8, 3H); $^{13}$C NMR (100 MHz) $\delta$ 143.5, 138.1, 135.0, 134.0, 129.8, 128.6, 127.0, 126.9, 63.9, 55.1, 52.3, 33.4, 31.4, 25.0, 22.4, 21.5, 13.9; MS m/z (ESI) 430 (M+Na$^+$, 100); HRMS calcd for C$_{21}$H$_{26}$ClNNaO$_2$S (M+Na$^+$) 430.1220, found 430.1214.
(III) General procedure and data for 3-hydroxypyrrolidines

General Procedure B. Synthesis of 3-hydroxypyrrolidines from epoxysulfonamides.

{nBuLi (3.3 equiv) was added dropwise to a stirred suspension of trimethylsulfoxonium iodide (3 equiv) in THF at −78 °C and stirred at this temperature for 15 min and then at 0 °C for 15 min. The solution was recooled to −78 °C and a solution of the epoxysulfonamide (1 equiv) in THF and then DMPU (20 equiv) were added dropwise. The reaction was warmed to rt over 5 min and then refluxed for 2 h. After quenching with 5% aq. NH₄Cl solution (10 mL) and dilution with EtOAc (10 mL), the layers were separated. The aqueous layer was extracted with EtOAc (3 x 20 mL); the combined organic layers were dried (MgSO₄), and solvent was evaporated in vacuo. The residue was purified by column chromatography (petrol/Et₂O) to give the corresponding 3-hydroxypyrrolidine.

\[(2R^*,3S^*)-2\text{-Propyl-1-tosylpyrrolidin-3-ol trans-8a}\]

Following general procedure B, the addition of anti-epoxysulfonamide 7a (50 mg, 0.19 mmol) in THF (0.5 mL) and then DMPU (0.45 mL, 3.74 mmol) to dimethylsulfoxonium methyldide [prepared from nBuLi (1.6 M in hexanes; 0.38 mL, 0.61 mmol) and trimethylsulfoxonium iodide (123 mg, 0.56 mmol) in THF (1.4 mL)] gave after work-up and column chromatography (60% Et₂O in petrol) trans-pyrrolidinol 8a (45 mg, 86%) as a colorless oil; Rᵣ 0.18 (70% Et₂O in petrol); IR (neat)/cm⁻¹ 3510br, 2960s, 1599s, 1494s, 1336s, 1156s; \(^1\)H NMR (400 MHz) δ 7.74 (d, J = 8, 2H), 7.31 (d, J = 8, 2H), 4.05 (d, J = 3, 1H), 3.49–3.44 (m, 2H), 3.24 (ddd, J = 10.5, 9.5, 7, 1H), 2.41 (s, 3H), 2.06–1.97 (m, 1H), 1.77–1.67 (m, 3H), 1.50–1.33 (m, 2H), 1.26 (br, 1H), 0.94 (t, J = 7, 3H); \(^13\)C NMR (100 MHz) δ 143.4, 134.2, 129.5, 127.7, 74.8, 69.1, 46.2, 37.3, 32.4, 21.5, 19.5, 14.0; MS m/z (CI) 301 (M+NH⁴⁺, 100), 284 (68), 130 (50), 48 (33), 86 (29), 72 (30); HRMS calcd for C₁₄H₂₅N₂O₅S (M+NH⁴⁺) 301.1586, found 301.1577.
(2R*,3R*)-2-Propyl-1-tosylpyrrolidin-3-ol cis-8a

Following general procedure B, the addition of syn-epoxysulfonamide 7a (50 mg, 0.19 mmol) in THF (0.5 mL) and then DMPU (0.45 mL, 3.74 mmol) to dimethylsulfoxonium methyldi [prepared from nBuLi (1.6 M in hexanes; 0.38 mL, 0.61 mmol) and trimethylsulfoxonium iodide (123 mg, 0.56 mmol) in THF (1.4 mL)] gave after work-up and column chromatography (60% Et₂O in petrol) cis-pyrrolidinol 8a (44 mg, 83%) as a colorless oil, which solidified on standing; mp 97–98 °C; Rₖ 0.18 (70% Et₂O in petrol); IR (KBr)/cm⁻¹ 3484br, 2959m, 1597m, 1457m, 1327m, 1156m, 1090m; ¹H NMR (400 MHz) δ 7.71 (d, J = 8, 2H), 7.31 (d, J = 8, 2H), 4.06 (dddd, J = 10, 8, 5, 5, 1H), 3.54–3.39 (m, 3H), 2.43 (s, 3H), 1.92–1.83 (m, 1H), 1.79–1.68 (m, 2H), 1.61–1.51 (m, 2H), 1.43 (app. sextet, J = 7, 2H), 0.98 (t, J = 7, 3H); ¹³C NMR (100 MHz) δ 143.4, 134.8, 129.7, 127.4, 71.7, 63.9, 46.3, 32.5, 31.5, 21.5, 19.6, 14.3; MS m/z (ESI) 306 (M+Na⁺, 45), 284 (100); HRMS calcd for C₁₄H₂₁NNaO₃S (M+Na⁺) 306.1140, found 306.1137.

(2R*,3S*)-2-(Benzylxymethyl)-1-tosylpyrrolidin-3-ol trans-8b

Following general procedure B, the addition of N-[(R*)-2-(benzylxylo)-1-(S*)-(oxiran-2-yl)ethyl]-4-methylbenzenesulfonamide (anti-7b)²³ (50 mg, 0.14 mmol) in THF (0.5 mL) and then DMPU (0.35 mL, 2.91 mmol) to dimethylsulfoxonium methyldi [prepared from nBuLi (1.6 M in hexanes; 0.30 mL, 0.48 mmol) and trimethylsulfoxonium iodide (95 mg, 0.43 mmol) in THF (1 mL)] gave after work-up and column chromatography (70% Et₂O in petrol) trans-pyrrolidinol 8b (39 mg, 74%) as a colorless oil; Rₖ 0.18 (70% Et₂O in petrol); IR (neat)/cm⁻¹ 3223br, 3038w, 2932s, 1598s, 1454m, 1346m, 1162m; ¹H NMR (400 MHz) δ 7.74 (d, J = 8, 2H), 7.39–7.30 (m, 7H), 4.56 (dd, J = 18.5, 12, 2H), 4.32 (s, 1H), 3.88 (dd, J = 9.5, 4, 1H), 3.54–3.40 (m, 3H), 3.26
Spectra and physical properties matched commercially available material (Aldrich, cat. no. 53,215–0).
(1.6 M in hexanes; 0.55 mL, 0.88 mmol) and trimethylsulfoxonium iodide (174 mg, 0.79 mmol) in THF (2 mL) gave after work-up and column chromatography (35% EtOAc in petrol) pyrrolidinol 8c (46 mg, 72%) as a colorless oil, which solidified on standing; mp 60–61 °C (lit8 61–65 °C); Rf 0.18 (35% EtOAc in petrol); IR (neat)/cm\(^{-1}\) 3486br, 2948m, 1597m, 1446m, 1326s, 1161s, 1090s; \(^{1}\)H NMR (400 MHz) \(\delta\) 7.71 (d, \(J = 8\), 2H), 7.32 (d, \(J = 8\), 2H), 3.38–3.33 (m, 3H), 3.23 (ddd, \(J = 11\), 2.5, 1.5, 1H), 2.42 (s, 3H), 1.23 (br, 1H), 1.92–1.82 (m, 2H); \(^{13}\)C NMR (100 MHz) \(\delta\) 143.6, 133.5, 129.7, 127.6, 127.4, 126.2, 78.7, 71.9, 46.8, 31.2, 21.6; MS m/z (ESI) 264 (M+Na\(^+\), 100); HRMS calcd for C\(_{11}\)H\(_{15}\)NNaO\(_3\)S (M+Na\(^+\)) 264.0670, found 264.0668.

(2\(R^*,3S^*\))-2-Phenyl-1-tosylpyrrolidin-3-ol 8d

Following general procedure B, the addition of 4-methyl-N-\([(R^*,R^*)\)-oxiran-2-yl(phenyl)methyl\]benzenesulfonamide (7d)\(^{2,3}\) (40 mg, 0.13 mmol) in THF (0.5 mL) and then DMPU (0.32 mL, 2.66 mmol) to dimethylsulfoxonium methyldie [prepared from nBuLi (1.6 M in hexanes; 0.27 mL, 0.43 mmol) and trimethylsulfoxonium iodide (87 mg, 0.40 mmol) in THF (0.8 mL)] gave after work-up and column chromatography (70% Et\(_2\)O in petrol) pyrrolidinol 8d (37 mg, 88%) as a white solid; mp 137–138 °C; Rf 0.17 (70% Et\(_2\)O in petrol); IR (KBr)/cm\(^{-1}\) 3514br, 2949m, 1598m, 1451m, 1328s, 1254w, 1155s, 1091m; \(^{1}\)H NMR (400 MHz) \(\delta\) 7.73 (d, \(J = 8\), 2H), 7.33–7.25 (m, 7H), 4.68 (s, 1H), 4.11 (br, 1H), 3.69 (ddd, \(J = 10, 9, 2\), 1H), 3.48 (ddd, \(J = 10, 7, 6.5\), 1H), 2.41 (s, 3H), 2.03–1.84 (m, 2H), 1.74–1.69 (m, 1H); \(^{13}\)C NMR (100 MHz) \(\delta\) 143.5, 139.9, 134.4, 129.6, 128.5, 127.7, 127.4, 126.2, 78.7, 71.9, 46.8, 31.2, 21.6; MS m/z (ESI) 340 (M+Na\(^+\), 100); HRMS calcd for C\(_{17}\)H\(_{19}\)NNaO\(_3\)S (M+Na\(^+\)) 340.0983, found 340.0978.
Following general procedure B, the addition of anti-epoxysulfonamide 7e (50 mg, 0.13 mmol) in THF (0.5 mL) and then DMPU (0.31 mL, 2.66 mmol) to dimethylsulfoxonium methyldide [prepared from nBuLi (1.6 M in hexanes; 0.27 mL, 0.43 mmol) and trimethylsulfoxonium iodide (86 mg, 0.39 mmol) in THF (0.8 mL)] gave after work-up and column chromatography (35% EtOAc in petrol) pyrrolidinol 8e (43 mg, 82%) as a white solid; mp 143–144 °C; Rf 0.20 (35% EtOAc in petrol); IR (KBr)/cm⁻¹ 3510s, 2942m, 2875w, 1540w, 1488m, 1445w, 1403m, 1330s, 1253w, 1157s, 1093m, 1008 m; ¹H NMR (400 MHz) δ 7.72 (d, J = 8, 2H), 7.43 (d, J = 8, 2H), 7.29 (d, J = 8, 2H), 7.21 (d, J = 8, 2H), 4.61 (s, 1H), 4.09–4.07 (m, 1H), 3.68 (ddd, J = 10, 9, 2, 1H), 3.48 (ddd, J = 10, 7, 6.5, 1H), 2.42 (s, 3H), 2.00–1.91 (m, 2H), 1.76–1.69 (m, 1H); ¹³C NMR (100 MHz) δ 143.8, 139.1, 134.1, 131.6, 129.7, 128.0, 127.7, 121.4, 84.4, 71.3, 46.8, 31.3, 21.6; MS m/z (ESI) 396 (M+H⁺, 100); HRMS calcd for C₁₇H₁₉BrNO₃S (M+H⁺) 396.0269, found 396.0268.

(2R*, 3S*)-2-Butyl-3-methyl-1-tosylpyrrolidin-3-ol 8f

Following general procedure B, the addition of epoxysulfonamide 7f (50 mg, 0.17 mmol) in THF (0.7 mL) and then DMPU (0.40 mL, 3.33 mmol) to dimethylsulfoxonium methyldide [prepared from nBuLi (1.6 M in hexanes; 0.34 mL, 0.54 mmol) and trimethylsulfoxonium iodide (111 mg, 0.50 mmol) in THF (1 mL)] gave after work-up and column chromatography (70% Et₂O in petrol) pyrrolidinol 8f (42 mg, 80%) as a colorless oil; Rf 0.19 (70% Et₂O in petrol); IR (neat)/cm⁻¹ 3508br, 2957s, 1599m, 1455m, 1329s, 1157s; ¹H NMR (400 MHz) δ 7.74 (d, J = 8, 2H), 7.29 (d, J = 8, 2H), 3.45 (dd, J = 6.5, 6, 1H), 3.39 (ddd, J = 10, 8, 1.5, 1H), 3.25 (ddd, J = 10, 7.5, 7, 1H), 2.40 (s, 3H), 1.88 (ddd, J = 13, 7.5, 1.5, 1H), 1.70 (ddd, J = 13, 8, 7.5, 1H), 1.59–1.28 (m, 7H), 1.24 (s, 3H), 0.91 (t, J = 7, 3H); ¹³C NMR (100 MHz) δ 143.4, 134.6, 129.5, 127.9, 79.7, 70.8,
45.8, 37.6, 33.8, 28.1, 22.9, 22.6, 21.5, 14.0; MS m/z (ESI+) 334 (M+Na⁺, 100); HRMS calcd for C₁₆H₂₅NNaO₃S (M+Na⁺) 334.1453, found 334.1441.

2, 2-Dimethyl-1-tosylpyrrolidin-3-ol 8g

Following general procedure B, the addition of epoxysulfonamide 7g (50 mg, 0.20 mmol) in THF (0.5 mL) and then DMPU (0.47 mmol, 3.91 mmol) to dimethylsulfoxonium methyldide [prepared from nBuLi (1.6 M in hexanes; 0.41 mL, 0.65 mmol) and trimethylsulfoxonium iodide (130 mg, 0.59 mmol) in THF (1.5 mL)] gave after work-up and column chromatography (35% EtOAc in petrol) pyrrolidinol 8g (38 mg, 72%) as a white solid; mp 114–115 °C; Rf 0.16 (35% EtOAc in petrol); IR (KBr)/cm⁻¹ 3440br, 2982m, 1597m, 1331s, 1155s, 1111m; ¹H NMR (400 MHz) δ 7.70 (d, J = 8, 2H), 7.26 (d, J = 8, 2H), 3.80 (dd, J = 5.5, 5.5, 2H), 3.47 (ddd, J = 8.5, 7, 6.5, 1H), 3.39 (ddd, J = 8.5, 6, 5.5, 1H), 2.40 (s, 3H), 2.24 (br, 1H) 2.10 (ddd, J = 8, 7, 6, 5.5, 1H), 1.76 (ddd, J = 8, 6.5, 5.5, 1H), 1.36 (s, 3H), 1.31 (s, 3H); ¹³C NMR (100 MHz) δ 142.8, 138.5, 129.5, 127.0, 79.8, 67.1, 45.5, 29.9, 26.8, 21.5, 21.1; MS m/z (ESI) 292 (M+Na⁺, 100); HRMS calcd for C₁₃H₁₉NNaO₃S (M+Na⁺) 292.0983, found 292.0977.

2,2-Cyclohexyl-1-tosylpyrrolidin-3-ol 10a

Following general procedure B, the addition of 4-methyl-N-(1-(oxiran-2-yl)cyclohexyl)benzenesulfonamide (9a)⁹ (50 mg, 0.17 mmol) in THF (0.5 mL) and then DMPU (0.41 mL, 3.40 mmol) to dimethylsulfoxonium methyldide [prepared from nBuLi (1.6 M in hexanes; 0.35 mL, 0.56 mmol) and trimethylsulfoxonium iodide (112 mg, 0.51 mmol) in THF (1.2 mL)] gave after work-up and column chromatography (70% Et₂O in

petrol) pyrrolidinol 10a (43 mg, 81%) as a colorless oil, which solidified on standing; mp 94–95 °C; Rf 0.19 (70% Et2O in petrol); IR (KBr)/cm⁻¹ 3501br, 2939m, 2863m, 1599w, 1454m, 1295m, 1154s, 1092s; ¹H NMR (400 MHz) δ 7.72 (d, J = 8, 2H), 7.23 (d, J = 8, 2H), 4.35 (br, 1H), 3.66 (ddd, J = 9, 9, 2, 1H), 3.47 (ddd, J = 9, 6.5, 6, 1H), 2.38 (s, 3H), 2.27–2.04 (m, 3H), 1.89–1.52 (m, 7H), 1.37–1.14 (m, 3H); ¹³C NMR (100 MHz) δ 142.4, 139.3, 129.3, 129.7, 73.7, 72.8, 46.7, 36.0, 30.8, 29.6, 24.9, 24.8, 24.5, 21.4; MS m/z (ESI) 332 (M+Na⁺, 90), 310 (100); HRMS calcd for C₁₆H₂₃NNaO₃S (M+Na⁺) 332.1296, found 332.1299.

(3aR*,7aS*)-1-Tosyl-octahydro-1H-indol-3a-ol cis-10b

Following general procedure B, the addition of anti-epoxysulfonamide 9b (110 mg, 0.39 mmol) in THF (1.9 mL) and then DMPU (0.94 mL, 7.80 mmol) to dimethylosulfonium methylide [prepared from nBuLi (1.6 M in hexanes; 0.80 mL, 1.28 mmol) and trimethylsulfonium iodide (257 mg, 1.17 mmol) in THF (2 mL)] gave after work-up and column chromatography (35% EtOAc in petrol) cis-pyrrolidinol 10b (80 mg, 69%) as a colorless oil; Rf 0.18 (35% EtOAc in petrol); IR (neat)/cm⁻¹ 3501br, 2975s, 2927s, 1599s, 1454m, 1336m, 1156s, 1094m; ¹H NMR (400 MHz) δ 7.75 (d, J = 8, 2H), 7.30 (d, J = 8, 2H), 3.50 (ddd, J = 9, 8, 7, 1H), 3.38–3.31 (m, 2H), 2.41 (s, 3H), 2.20–2.11 (m, 2H), 1.93 (d, J = 13, 1H), 1.67–1.47 (m, 4H), 1.42–1.19 (m, 3H); ¹³C NMR (100 MHz) δ 143.2, 135.1, 129.5, 127.5, 66.9, 45.3, 35.2, 34.0, 33.2, 23.5, 23.0, 21.5; MS m/z (ESI) 296 (M+H⁺, 100); HRMS calcd for C₁₅H₂₂NOS (M+H⁺) 296.1320, found 296.1318.

(3aR*,7aR*)-1-Tosyl-octahydro-1H-indol-3a-ol trans-10b

Following general procedure B, the addition of syn-epoxysulfonamide 9b (130 mg, 0.46 mmol) in THF (1.6 mL) and then DMPU (1.11 mL, 9.20 mmol) to dimethylosulfonium methylide [prepared from nBuLi (1.6 M in hexanes; 0.95 mL, 1.52 mmol) and trimethylsulfonium iodide (304 mg, 1.38 mmol) in THF (3 mL)] gave
after work-up and column chromatography (70% Et₂O in petrol) *trans*-pyrrolidinol 10b (90 mg, 66%) as a colorless oil, which solidified on standing; mp 121–122 °C; R₉ 0.19 (70% Et₂O in petrol); IR (KBr)/cm⁻¹ 3501br, 2975s, 2925s, 1599m, 1451m, 1331m, 1154s, 1091m; ¹H NMR (500 MHz) δ 7.70 (d, J = 8, 2H), 7.35 (d, J = 8, 2H), 3.59 (ddd, J = 10.5, 10, 2, 1H), 3.20 (ddd, J = 10.5, 10, 2, 1H), 2.46 (s, 3H), 2.43 (ddd, J = 12, 4, 1H), 2.34–2.30 (m, 1H), 1.97–1.59 (m, 6H), 1.50–1.38 (m, 2H), 1.21–1.18 (m, 2H); ¹³C NMR (125 MHz) δ 143.6, 133.1, 129.7, 127.7, 76.3, 66.6, 46.4, 36.1, 34.1, 25.8, 23.9, 21.6, 20.1; MS m/z (ESI) 294 (M−H⁺, 100), 255 (10), 239 (15), 170 (15); HRMS calcd for C₁₅H₂₀NO₃S (M−H⁺) 294.1164, found 294.1164.

(2R⁺,3R⁺,45⁺)-4-(4-Chlorophenyl)-2-pentyl-1-tosylpyrrolidin-3-ol 12

Following general procedure B, the addition of *syn*-epoxysulfonamide 11 (50 mg, 0.12 mmol) in THF (0.5 mL) and then DMPU (0.30 mL, 2.5 mmol) to dimethylsulfoxonium methylique [prepared from nBuLi (1.6 M in hexanes; 0.25 mL, 0.40 mmol) and trimethylsulfoxonium iodide (81 mg, 0.37 mmol) in THF (0.7 mL)] gave after work-up and column chromatography (40% Et₂O in petrol) *pyrrolidinol* 12 (40 mg, 77%) as a colorless oil; R₉ 0.20 (40% Et₂O in petrol); IR (neat)/cm⁻¹ 3499br, 2955s, 2927s, 1598m, 1494m, 1340m, 1161s, 1094m; ¹H NMR (500 MHz) δ 7.74 (d, J = 8, 2H), 7.34 (d, J = 8, 2H), 7.22 (d, J = 8.5, 2H), 6.88 (d, J = 8.5, 2H), 3.88 (ddd, J = 7, 6.5, 6, 1H), 3.80–3.75 (m, 2H), 3.26–3.20 (m, 2H), 2.48 (s, 3H), 1.83–1.26 (m, 9H), 0.92 (t, J = 8, 3H); ¹³C NMR (125 MHz) δ 143.8, 137.0, 134.9, 133.3, 129.8, 129.0, 128.8, 127.5, 77.3, 62.3, 51.3, 48.8, 32.0, 29.5, 25.8, 22.6, 21.6, 14.1; HRMS calcd for C₂₂H₂₉ClNO₃S (M+H⁺) 422.1557, found 422.1550.
trans-8a
cis-8a
trans-8b

Chemical Shift (ppm)
10a

Chemical Shift (ppm)
cis-10b

Chemical Shift (ppm)
cis-10b

Chemical Shift (ppm)
trans-10b