New route to azaspirocycles via the organolithium-mediated conversion of β-alkoxy aziridines into cyclopentyl amines

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Supporting Information Available: Experimental procedures and full characterisation data.

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General

All reactions were carried out under oxygen free N_2 or Ar using oven-dried and/or flame dried glassware. Organolithium reagents were titrated against *N*-benzylbenzamide before use.[1] Et_2O, THF, toluene and CH_2Cl_2 were dried on an Mbraun SPS solvent purification system, whereas TBME was freshly distilled from benzophenone ketyl. Petrol refers to the fraction of petroleum ether with a boiling point range of 40-60 °C. MeCN and MeOH were purchased in Winchester quantities and used as supplied. Brine refers to a saturated aqueous solution of NaCl. Water is distilled water.

Flash column chromatography was carried out using Fluka Chemie GmbH silica (220-440 mesh). Thin layer chromatography was carried out using commercially available Merck F_{254} aluminium-backed silica plates.

Proton (400 MHz) and carbon (100.6 MHz) NMR spectra were recorded on a Jeol ECX-400 instrument using an internal deuterium lock. For samples recorded as solutions in $CDCl_3$, chemical shifts are quoted in parts per million relative to $CHCl_3$ (δ_H 7.27) and $CDCl_3$ (δ_C 77.0, central line). For samples recorded as solutions in C_6D_6, chemical shifts are quoted in parts per million relative to C_6D_5H (δ_H 7.16) and C_6D_6 (δ_C 128.0, central line). Carbon NMR spectra were recorded with broadband proton decoupling and were assigned using DEPT experiments. Coupling constants (J) are quoted in Hertz. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. For Kugelrohr distillation, the temperatures quoted correspond to the oven temperatures. Infra-red spectra were recorded on an ATI Matteson Genesis FT-IR or a Nicolet IR100 FT-IR machine. Chemical ionisation and high resolution mass spectra were recorded on a Fisons Analytical (VG) Autospec spectrometer.

General procedure A: Reductive alkylation of β-methoxy aziridines

Alkyllithium (2.5 equiv.) was added dropwise to a stirred solution of methoxy aziridine (0.4 mmol) in Et_2O (5 mL) at –78 °C under N_2. After stirring at –78 °C for 5 min, the resulting solution was allowed to warm to rt and stirred for 1 h. Saturated $NH_4Cl_{(aq)}$ (5 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 5 mL) and the combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product.

General procedure B: Hydroboration of allylic sulfonamides

9-BBN (0.50 M solution in THF, 2.0 equiv.) was added dropwise to a stirred solution of allylic sulfonamide (0.3 mmol) in THF (5 mL) at 0 °C under N_2. The resulting solution was allowed to warm to rt and stirred at rt for 2 h. After cooling to 0 °C, 2.0 M $NaOH_{(aq)}$ (6.0 equiv.) and 35% $H_2O_{2(aq)}$ (2.0 equiv.) were added cautiously. The resulting mixture was warmed to rt and stirred for 2 h. Then, Et_2O (10 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 5 mL) and the combined organic extracts were washed with brine (10 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product.

General procedure C: Mitsunobu cyclisation

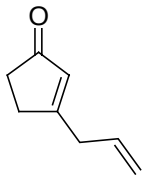
DIAD or DEAD (1.2 equiv.) was added dropwise to a stirred solution of sulfonamido alcohol (0.2 mmol) and PPh_3 (1.2 equiv.) in THF (5 mL) at 0 °C under N_2. The resulting solution was allowed to warm to rt and stirred at rt for 3 h. Then, the solvent was evaporated under reduced pressure to give the crude product.

General procedure D: Lithium-halogen exchange in reductive alkylation

A solution of β-methoxy aziridine (0.3 mmol) in THF, Et_2O or TBME (5 mL) was added *via* canula to a stirred solution of the aryllithium, [3.0 equiv., freshly prepared by adding a solution

of *n*-butyllithium in hexanes (3.0 equiv.) to a stirred solution of aryl bromide (3.0 equiv.) in THF, Et_2O or TBME (3 mL) at –78 °C and stirring for 1 h], at –78 °C under nitrogen. After 5 min, the reaction mixture was allowed to warm to rt and then stirred for 1 h. Saturated $NH_4Cl_{(aq)}$ (5 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 5 mL) and the combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product.

3-Allyl-2-cyclopenten-1-one 4

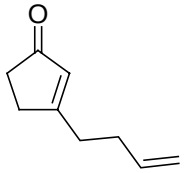


A solution of cyclopentenone (5.1 mL, 60.9 mmol) in THF (10 mL) was added dropwise *via* canula to a stirred solution of allylmagnesium chloride (36.5 mL of a 2.00 M solution in THF, 73.1 mmol) in THF (40 mL) at 0 °C under N_2. After being allowed to warm to rt, the reaction mixture was stirred for 2 h. Then, the reaction mixture was cooled to 0 °C and saturated $NH_4Cl_{(aq)}$ (40 mL) was added. The resulting mixture was stirred at rt for 15 min and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 40 mL) and the combined organic extracts were washed with brine (40 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by Kugelrohr distillation gave 1-allyl-2-cyclopenten-1-ol (7.13 g, 94%) as a colourless oil, bp 120-125 °C/1.2 mm Hg.

PDC (41.3 g, 110.0 mmol) was added in one portion to a stirred solution of 1-allyl-2-cyclopenten-1-ol (6.82 g, 54.9 mmol) in CH_2Cl_2 (60 mL) at rt under N_2. The resulting brown suspension was stirred at rt for 6 h and then Et_2O (50 mL) was added. The solids were removed by filtration through a plug of silica and washed with Et_2O (300 mL). The filtrate was evaporated under reduced pressure to give the crude product. Purification by Kugelrohr distillation gave enone **4** (4.11 g, 61%) as a pale yellow oil, bp 120-125 °C/1.2 mm Hg; R_F(1:1 hexane-EtOAc)

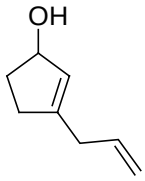
0.4; ^{1}H NMR (400 MHz, C_6D_6) δ 5.84 (s, 1H, =CH), 5.51 (ddt, J = 18.0, 10.0, 7.0 Hz, 1H, C*H*=CH_2), 4.95 (dq, J = 10.0, 2.0 Hz, 1H, CH=CH_AH_B), 4.88 (dq, J = 18.0, 2.0 Hz, 1H, CH=CH_AH_B), 2.52 (d, J = 7.0 Hz, 2H, CH_2-CH=CH_2), 2.04-2.01 (m, 2H), 1.82-1.80 (m, 2H). Spectroscopic data comparable with those recorded in $CDCl_3$.[2]

3-(3-Butenyl)-2-cyclopenten-1-one 5



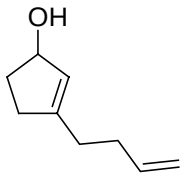
Magnesium turnings (457 mg, 18.8 mmol) were stirred for 30 min in a flame-dried flask at rt under Ar. THF (10 mL) was added and the resulting mixture stirred at rt for 15 min. Then, a solution of 4-bromo-1-butene (1.1 mL, 10.9 mmol) in THF (10 mL) was added dropwise *via* canula in order to maintain a gentle reflux. The resulting suspension was stirred and heated at reflux for 10 min, then cooled to 0 ºC. A solution of 3-ethoxycyclopent-2-enone (1.0 mL, 8.4 mmol) in THF (5 mL) was added dropwise via canula and the reaction mixture was heated at reflux for 30 min. The reaction mixture was allowed to cool to rt and saturated $NH_4Cl_{(aq)}$ (15 mL) was added. The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by Kugelrohr distillation gave enone **5** (758 mg, 67%) as a colourless oil, bp 140-150 ºC/20 mm Hg, R_F(1:1 petrol-Et_2O) 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92-5.90 (m, 1H, =CH), 5.71-5.61 (m, 1H, C*H*=CH_2), 5.04 (ddt, J = 10.0, 2.0, 1.0 Hz, 1H, CH=CH_AH_B), 5.01 (app. dq, J = 17.0, 2.0 Hz, 1H, CH=CH_AH_B), 2.14-2.12 (m, 2H), 2.02-1.92 (m, 4H), 1.88-1.85 (m, 2H). Spectroscopic data consistent with those reported in the literature.[3]

3-Allyl-2-cyclopenten-1-ol 9



$NaBH_4$ (294 mg, 7.8 mmol) was added portionwise over 45 min to a stirred solution of enone **4** (792 mg, 6.5 mmol) and $CeCl_3 \cdot 7H_2O$ (2.90 g, 7.8 mmol) in MeOH (20 mL) at 0 ºC under N_2. The resulting solution was stirred at 0 ºC for 2 h. After being allowed to warm to rt, saturated $NH_4Cl_{(aq)}$ (10 mL) was added. The mixture was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic extracts were washed with water (50 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by Kugelrohr distillation gave allylic alcohol **9** (693 mg, 86%) as a colourless oil, bp 105-110 °C/1.9 mm Hg; R_F(1:1 petrol-EtOAc) 0.5; IR ($CHCl_3$) 3599 (OH), 3012, 2935, 2850, 1637, 1452, 1429, 1388 (SO_2), 1142 (SO_2), 1026, 920, 669 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 5.79 (ddt, J = 17.0, 9.5, 7.0 Hz, 1H, C*H*=CH_2), 5.46 (s, 1H, =CH), 5.05-5.01 (m, 2H, CH=CH_2), 4.71 (br s, 1H, CHO), 2.68-2.65 (br m, 2H), 2.28-2.20 (m, 1H), 2.13-2.05 (m, 1H), 2.00-1.90 (m, 1H), 1.70-1.62 (m, 1H), 1.45 (s, 1H, OH); ^{13}C NMR (100.6 MHz, C_6D_6) δ 146.1 (=C), 134.7 (=*C*H), 129.0 (=CH), 115.8 (=CH_2), 76.4 (CHO), 34.8 (CH_2), 32.9 (CH_2), 32.4 (CH_2); MS (CI, NH_3) *m/z* 107 [$(M - H_2O + H)^+$, 100], 83(6); HRMS (CI, NH_3) *m/z* calcd for $C_8H_{12}O$ $(M - H_2O + H)^+$ 107.0861, found 107.0865.

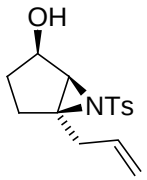
3-(3-Butenyl)-2-cyclopenten-1-ol 10



$NaBH_4$ (622 mg, 16.5 mmol) was added portionwise over 45 min to a stirred solution of enone **5** (1.95 g, 14.3 mmol) and $CeCl_3 \cdot 7H_2O$ (6.40 g, 17.2 mmol) in MeOH (60 mL) at 0 ºC under N_2. The resulting solution was stirred at 0 ºC for 2 h. After being allowed to warm to rt, saturated $NH_4Cl_{(aq)}$ (20 mL) was added. The mixture was extracted with CH_2Cl_2 (3 x 30 mL) and the

combined organic extracts were washed with water (50 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by Kugelrohr distillation gave allylic alcohol **10** (1.76 g, 89%) as a colourless oil, bp 120-140 ºC/8 mm Hg, R_F(1:1 petrol-Et_2O) 0.3; IR (film) 3340 (OH), 2927, 2847, 1642, 1448, 1329, 1039, 910 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 5.72 (ddt, J = 17.0, 10.0, 6.0 Hz, 1H, C*H*=CH_2), 5.35 (app. sextet, J = 2.0 Hz, 1H, =CH), 4.99 (app. dq, J = 17.0, 2.0 Hz, 1H, CH=CH_AH_B), 4.96 (ddt, J = 10.0, 2.0, 1.0 Hz, 1H, CH=CH_AH_B), 4.67-4.63 (m, 1H, CHO), 2.20-2.12 (m, 1H), 2.10-1.94 (m, 5H), 1.91-1.83 (m, 1H), 1.59 (dddd, J = 13.5, 8.5, 5.0, 3.5 Hz, 1H), 0.98 (br s, 1H, OH); ^{13}C NMR (100.6 MHz, C_6D_6) δ 147.9 (=C), 138.4 (=CH), 127.9 (=CH), 114.7 (=CH_2), 77.6 (CHO), 34.3 (CH_2), 33.6 (CH_2), 32.0 (CH_2), 30.7 (CH_2); MS (CI, NH_3) *m/z* 138 [$(M - H_2O + NH_4)^+$, 30], 121 (100); HRMS (CI, NH_3) *m/z*: $[M - H_2O + NH_4]^+$ calcd for $C_9H_{14}O$, 138.1283; found, 138.1284.

5-Allyl-6-[(4-methylphenyl)sulfonyl]-6-azabicyclo[3.1.0]pentan-2-ol *cis*-11

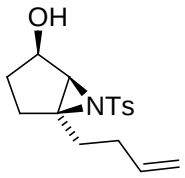


$PhMe_3NBr_3$ (121 mg, 0.3 mmol) was added to a stirred suspension of Chloramine-T trihydrate (1.0 g, 3.5 mmol) and allylic alcohol **9** (400 mg, 3.2 mmol) in MeCN (10 mL) at rt under N_2. After stirring for 18 h, the solids were removed by filtration through a plug of silica and washed with EtOAc. The filtrate was evaporated under reduced pressure to give the crude product, which contained a 70:30 mixture (by ^1H NMR spectroscopy) of hydroxy aziridines *cis*-**11** and *trans*-**11**. Purification by flash column chromatography on silica with hexane-EtOAc (1:1) as eluent gave a 45:55 mixture of hydroxy aziridine *trans*-**11** and $TsNH_2$ (289 mg) as a white solid and hydroxy aziridine *cis*-**11** (451 mg, 48%) as a colourless oil, R_F(1:1 hexane-EtOAc) 0.3; IR ($CDCl_3$) 3577 (OH), 3065, 2928, 1321 (SO_2), 1092 (SO_2), 986, 878, 686, 577 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.32 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 5.88 (ddt, J = 17.0, 10.0, 7.0 Hz, 1H, C*H*=CH_2), 5.17 (dq, J = 17.0, 1.5 Hz, 1H, CH=CH_AH_B), 5.16-5.13 (m,

1H, CH=CH_AH$_B$), 4.26 (br qd, J = 7.5, 2.5 Hz, 1H, CHO), 3.45 (d, J = 2.5 Hz, 1H, CHN), 2.97 (dd, J = 15.0, 7.0 Hz, 1H), 2.90 (dd, J = 15.0, 7.0 Hz, 1H) 2.43 (s, 3H, Me), 2.08-2.02 (dd, J = 14.0, 8.0 Hz, 1H), 1.91 (dt, J = 13.0, 7.5, 1H), 1.72-1.64 (ddd, J = 14.0, 10.5, 8.0 Hz, 1H), 1.27-1.23 (br m, 1H), 1.23-1.13 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.0 (*ipso*-$C_6H_4SO_2$), 137.6 (*ipso*-C_6H_4Me), 133.3 (=CH), 129.6 (*o*-$C_6H_4SO_2$), 127.1 (*m*-$C_6H_4SO_2$), 118.6 (=CH_2), 73.0 (CHO), 60.1 (CN), 54.7 (CHN), 33.7 (CH_2), 29.9 (CH_2), 29.3 (CH_2), 21.6 (Me); MS (CI, NH_3) *m/z* 294 [(M + H)$^+$, 100], 276 (25), 138 (36); HRMS (CI, NH_3) *m/z* calcd for $C_{15}H_{19}NO_3S$ (M + H)$^+$ 294.1164, found 294.1162.

Diagnostic signal for hydroxy aziridine *trans*-**11**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.35 (s, 1H, CHN).

5-(3-Butenyl)-6-[(4-methylphenyl)sulfonyl]-6-azabicyclo[3.1.0]hexan-2-ol *cis*-12

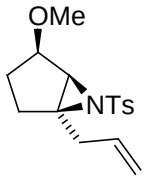


$PhMe_3NBr_3$ (97 mg, 0.3 mmol) was added to a stirred suspension of Chloramine-T trihydrate (796 mg, 2.8 mmol) and allylic alcohol **10** (355 mg, 2.6 mmol) in MeCN (12 mL) at rt under N_2. After stirring for 8 h, the solids were removed by filtration through a plug of silica and washed with Et_2O. The filtrate was evaporated under reduced pressure to give the crude product, which contained a 75:25 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**12** and *trans*-**12**. Purification by flash column chromatography on silica with hexane-EtOAc (2:1) as eluent gave a 65:35 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridine *trans*-**12** and $TsNH_2$ (209 mg) as a white solid and hydroxy aziridine *cis*-**12** (418 mg, 53%) as a colourless oil, R_F(2:1 hexane-EtOAc) 0.1; IR (film) 3507 (OH), 2976, 2927, 1317 (SO_2), 1155 (SO_2), 1089, 998, 884, 687 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5 Hz, 2H, *o*-$C_6H_4SO_2$), 7.33 (d, J = 8.5 Hz, 2H, *m*-$C_6H_4SO_2$), 5.83 (ddt, J = 17.0, 10.0, 6.0 Hz, 1H, C*H*=CH_2), 5.07 (app. dq, J = 17.0, 1.5 Hz, 1H, CH=CH_AH$_B$), 5.01 (app. dq, J = 10.0, 1.5 Hz, 1H, CH=CH_AH$_B$), 4.24 (td, J = 8.0, 2.5 Hz,

1H, CHO), 3.42 (d, J = 2.5 Hz, 1H, CHN), 2.47-2.39 (m, 1H), 2.46 (s, 3H, Me), 2.46-2.20 (m, 3H), 2.11 (dd, J = 14.0, 8.0 Hz, 1H), 1.94 (dt, J = 13.0, 8.0 Hz, 1H), 1.70 (ddd, J = 14.0, 10.5, 8.0 Hz, 1H), 1.20 (ddt, J = 13.0, 10.5, 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.0 (*ipso*-$C_6H_4SO_2$), 137.9 (*ipso*-C_6H_4Me), 137.3 (=CH), 129.6 (*o*-$C_6H_4SO_2$), 127.1 (*m*-$C_6H_4SO_2$), 115.5 (=CH_2), 72.9 (CHO), 61.1 (CN), 55.4 (CHN), 30.8 (CH_2), 29.9 (CH_2), 29.4 (CH_2), 28.2 (CH_2), 21.6 (Me); MS (CI, NH_3) *m/z* 308 [$(M + H)^+$, 70], 290 (20), 152 (100); HRMS (CI, NH_3) *m/z*: [$M + H]^+$ calcd for $C_{16}H_{21}NO_3S$, 308.1320; found, 308.1312.

Diagnostic signals for hydroxy aziridine *trans*-**12**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (br t, J = 4.0 Hz, 1H, CHO) and 3.31 (s, 1H, CHN).

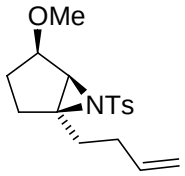
1-Allyl-4-methoxy-6-[(4-methylphenyl)sulfonyl]-6-azabicyclo[3.1.0]pentane *cis*-13



KHMDS (2.5 mL of a 0.50 M solution in toluene, 1.1 mmol) was added dropwise to a stirred solution of hydroxy aziridine *cis*-**11** (333 mg, 1.1 mmol) in THF (10 mL) at –78 °C under N_2. After stirring at –78 °C for 30 min, MeI (0.1 mL, 2.3 mmol) was added dropwise. After stirring at –78 °C for 1 h, the resulting solution was allowed to warm to over 16 h. The reaction mixture was then poured into water (10 mL) and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 10 mL) and the combined organic extracts were washed with water (10 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (1:1) as eluent gave methoxy aziridine *cis*-**13** (325 mg, 93%) as a white solid, mp 73-75 °C; R_F(1:1 petrol-Et_2O) 0.3; IR ($CDCl_3$) 2984, 2930, 2863, 1356 (SO_2), 1186 (SO_2), 1021, 928, 863, 617, 583 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.30 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 5.91 (ddt, J = 17.5, 10.0, 7.0 Hz, 1H, C*H*=CH_2), 5.18 (dq, J = 18.0, 1.5 Hz, 1H, CH=CH_AH_B),

5.15 (ddt, J = 10.0, 1.0 Hz, 1H, CH=CH_AH_B), 3.86 (ddd, J = 9.0, 7.5, 2.5 Hz, 1H, CHO), 3.48 (d, J = 2.5 Hz, 1H, CHN), 3.12 (s, 3H, OMe), 3.03 (dd, J = 15.0, 7.0 Hz, 1H), 2.93 (dd, J = 15.0, 7.0 Hz, 1H), 2.42 (s, 3H, Me), 2.05 (dd, J = 14.0, 8.0 Hz, 1H), 1.81 (dt, J = 12.5, 8.0 Hz, 1H), 1.72-1.65 (m, 1H), 1.41-1.31 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.6 (*ipso*-$C_6H_4SO_2$), 137.9 (*ipso*-C_6H_4Me), 133.6 (=CH), 129.2 (*o*-$C_6H_4SO_2$), 127.1 (*m*-$C_6H_4SO_2$), 118.4 (=CH_2), 81.0 (CHO), 59.1 (CN), 56.9 (CHN), 50.6 (OMe), 33.8 (CH_2), 29.4 (CH_2), 25.9 (CH_2), 21.5 (Me); MS (CI, NH_3) *m/z* 308 [(M + H)$^+$, 100], 276 (41), 266 (7), 152 (25), 137 (86), 120 (9); HRMS (CI, NH_3) *m/z* calcd for $C_{17}H_{21}NO_3S$ (M + H)$^+$ 308.1320, found 308.1321.

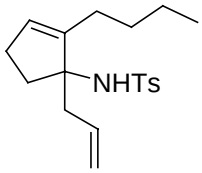
1-(3-Butenyl)-4-methoxy-6-[(4-methylphenyl)sulfonyl]-6-azabicyclo[3.1.0]hexane *cis*-14



KHMDS (2.4 mL of a 0.50 M solution in toluene, 1.2 mmol) was added dropwise to a stirred solution of hydroxy aziridine *cis*-**12** (280 mg, 0.9 mmol) in THF (20 mL) at –78 °C under N_2. After stirring at –78 °C for 30 min, MeI (0.1 mL, 1.8 mmol) was added dropwise. After stirring at –78 °C for 1 h, the resulting solution was allowed to warm to over 16 h. The reaction mixture was then poured into water (10 mL) and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 10 mL) and the combined organic extracts were washed with water (10 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (1:1) as eluent gave methoxy aziridine *cis*-**14** (215 mg, 73%) as a colourless oil, R_F(1:1 petrol-Et_2O) 0.3; IR (film) 2928, 2857, 1319 (SO_2), 1156 (SO_2), 1117, 1091, 986 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.5 Hz, 2H, *o*-$C_6H_4SO_2$), 7.30 (d, J = 8.5 Hz, 2H, *m*-$C_6H_4SO_2$), 5.84 (dddd, J = 17.0, 10.0, 7.0, 6.0 Hz, 1H, C*H*=CH_2), 5.08 (app. dq, J = 17.0, 2.0 Hz, 1H, CH=CH_AH_B), 5.02 (ddt, J = 10.0, 2.0, 1.0 Hz, 1H, CH=CH_AH_B), 3.84 (ddd, J = 8.5, 8.0, 2.5 Hz, 1H, CHO), 3.45 (d, J = 2.5

Hz, 1H, CHN), 3.12 (s, 3H, OMe), 2.55-2.36 (m, 2H), 2.43 (s, 3H, Me), 2.33-2.21 (m, 2H), 2.10 (dd, J = 13.5, 8.0 Hz, 1H), 1.82 (dt, J = 12.5, 8.0 Hz, 1H), 1.68 (ddd, J = 13.5, 10.5, 8.0 Hz, 1H), 1.38 (ddt, J = 12.5, 10.5, 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.8 (*ipso*-$C_6H_4SO_2$), 138.1 (*ipso*-C_6H_4Me), 137.4 (=CH), 129.3 (*o*-$C_6H_4SO_2$), 127.1 (*m*-$C_6H_4SO_2$), 115.1 (=CH_2), 80.9 (CHO), 60.0 (CN), 57.0 (OMe), 51.2 (CHN), 31.0 (CH_2), 29.3 (CH_2), 28.4 (CH_2), 25.9 (CH_2), 21.6 (Me); MS (CI, NH_3) *m/z* 322 [$(M + H)^+$, 30], 290 (25), 166 (100), 151 (60), 134 (40); HRMS (CI, NH_3) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{23}NO_3S$, 322.1469; found, 322.1477.

_N_-(1-Allyl-2-butyl-2-cyclopenten-1-yl)-4-methylbenzenesulfonamide 15a

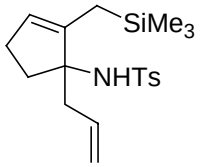


Using general procedure A, methoxy aziridine *cis*-**13** (103 mg, 0.3 mmol) and *n*-butyllithium (0.4 mL of a 1.89 M solution in hexanes, 0.8 mmol) in Et_2O (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (2:1) as eluent gave allylic sulfonamide **15a** (80 mg, 71%) as a white solid, mp 68-70 °C; R_F(2:1 petrol-Et_2O) 0.2; IR ($CDCl_3$) 3372 (NH), 2959, 2931, 2859, 1373 (SO_2), 1184 (SO_2), 1019, 815, 663, 579 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.25 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 5.61 (m, 1H, C*H*=CH_2), 5.43 (br t, J = 2.0 Hz, 1H, =CH), 5.14-5.08 (m, 2H, =CH2), 4.88 (s, 1H, NH), 2.47-2.43 (m, 1H), 2.41 (s, 3H, Me), 2.39-2.20 (m, 3H), 2.12-2.05 (m, 1H), 1.94 (ddd, J = 13.5, 8.5, 5.0 Hz, 1H), 1.74-1.64 (br m, 1H), 1.59-1.51 (m, 1H), 1.37-1.00 (m, 4H), 0.84 (t, J = 7.0 Hz, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.2 (=C), 142.7 (*ipso*-$C_6H_4SO_2$), 139.7 (*ipso*-C_6H_4Me), 132.8 (*C*H=CH_2), 129.2 (*o*-$C_6H_4SO_2$), 127.9 (=CH), 127.0 (*m*-$C_6H_4SO_2$), 119.2 (CH=*C*H_2), 72.2 (CN), 43.4 (CH_2), 34.2 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 25.8 (CH_2), 22.8 (CH_2), 21.4 (Me), 14.0 (Me); MS (CI, NH_3) *m/z* 334 [$(M + H)^+$, 2], 292 (38), 189

(21), 163 (100); HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{27}NO_2S$ $(M + NH_4)^+$ 351.2106, found 351.2100.

Using general procedure A, methoxy aziridine *cis*-**13** (123 mg, 0.4 mmol) and *n*-butyllithium (0.5 mL of a 1.89 M solution in hexanes, 1.0 mmol) in TBME (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (2:1) as eluent gave allylic sulfonamide **15a** (108 mg, 81%) as a white solid.

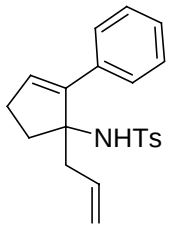
_N_-[1-Allyl-2-(trimethylsilyl)methyl-2-cyclopenten-1-yl]-4-methylbenzenesulfonamide 15b



Using general procedure A, methoxy aziridine *cis*-**13** (122 mg, 0.4 mmol) and (trimethylsilyl)methyllithium (1.3 mL of a 0.77 M solution in pentane, 1.0 mmol) in Et_2O (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (2:1) as eluent gave allylic sulfonamide **XX** (90 mg, 63%) as a white solid, mp 49-51 °C; R_F(2:1 petrol-Et_2O) 0.3; IR ($CDCl_3$) 3367 (NH), 3055, 2988, 1267 (SO_2), 1155 (SO_2), 843, 815, 574 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.26 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 5.64-5.54 (m, 1H, C*H*=CH_2), 5.39 (s, 1H, =CH), 5.09 (d, J = 17.0 Hz, 1H, CH=CH_AH_B), 5.07 (d, J = 9.0 Hz, 1H, CH=CH_AH_B), 4.79 (s, 1H, NH), 2.45-2.41 (m, 1H), 2.43 (s, 3H, Me), 2.27-2.02 (m, 4H), 1.97-1.86 (m, 1H), 1.14 (d, J = 16.0 Hz, 1H, CH_AH_BSi), 1.06 (d, J = 16.0 Hz, 1H, CH_AH_BSi), 0.01 (s, 9H, $SiMe_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 142.7 (*ipso*-$C_6H_4SO_2$), 141.5 (=C), 140.0 (*ipso*-C_6H_4Me), 132.9 (*C*H=CH_2), 129.3 (*o*-$C_6H_4SO_2$), 127.5 (=CH), 127.0 (*m*-$C_6H_4SO_2$), 119.0 (CH=*C*H_2), 72.9 (CN), 42.8 (CH_2), 33.4 (CH_2), 29.8 (CH_2), 21.4 (Me), 14.1 (CH_2Si), –0.88 ($SiMe_3$); MS (CI, NH_3) *m/z* 364 [$(M + H)^+$, 82], 348 (15), 338 (10), 322 (100), 306 (27), 244 (27), 228 (9), 193 (60), 91 (10), 73 (32); HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{29}NO_2SSi$ $(M + H)^+$ 364.1765, found 354.1764.

Using general procedure A, methoxy aziridine *cis*-**13** (141 mg, 0.5 mmol) and (trimethylsilyl)methyllithium (1.8 mL of a 0.65 M solution in pentane, 1.2 mmol) in TBME (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (2:1) as eluent gave allylic sulfonamide **15b** (128 mg, 77%) as a white solid.

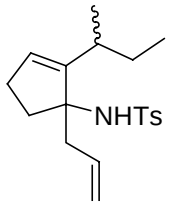
***N*-(1-Allyl-2-phenyl-2-cyclopenten-1-yl)-4-methylbenzenesulfonamide 15c**



Using general procedure A, methoxy aziridine *cis*-**13** (204 mg, 0.7 mmol) and phenyllithium (1.3 mL of a 1.31 M solution in dibutyl ether, 1.6 mmol) in Et_2O (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (2:1) as eluent gave allylic sulfonamide **15c** (137 mg, 58%) as a white solid, mp 85-86 °C; R_F(2:1 petrol-Et_2O) 0.2; IR ($CDCl_3$) 3369 (NH), 2927, 2853, 1388 (SO_2), 1155 (SO_2), 981, 607 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.28 (m, 2H, Ar), 7.15-7.11 (m, 5H, Ar), 6.05 (t, J = 2.5 Hz, 1H, =CH), 5.42 (ddt, J = 18.0, 9.5, 5.5 Hz, 1H, =CH), 4.94 (d, J = 18.0, 1H, $CH{=}CH_AH_B$), 4.94 (m, 3H, $=CH_2$ and NH), 2.61 (dd, J = 14.0, 9.0 Hz, 1H), 2.48-2.40 (m, 2H), 2.33- 2.26 (m, 1H), 2.30 (s, 3H, Me), 2.22-2.14 (m, 1H), 2.10-2.04 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.6 (=C), 142.9 (*ipso*-$C_6H_4SO_2$), 139.5 (*ipso*-C_6H_4Me), 135.0 (*ipso*-Ph), 133.6 ($CH{=}CH_2$), 132.8 (=CH), 129.3 (*o*-$C_6H_4SO_2$), 128.1 (CH, Ph), 127.2 (CH, Ph), 127.0 (*m*-$C_6H_4SO_2$), 126.9 (CH, Ph), 119.3 ($CH{=}CH_2$), 72.0 (CN), 42.7 (CH_2), 35.7 (CH_2), 29.9 (CH_2), 21.4 (Me); MS (CI, NH_3) *m/z* 371 [$(M + NH_4)^+$, 14], 354 (20), 312 (30), 183 (100), 158 (5); HRMS (CI, NH_3) *m/z* calcd for $C_{21}H_{24}NO_2S$ $(M + H)^+$ 354.1528, found 354.1532.

Using general procedure A, methoxy aziridine *cis*-**13** (106 mg, 0.3 mmol) and phenyllithium (0.5 mL of a 1.78 M solution in dibutyl ether, 0.9 mmol) in TBME (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (2:1) as eluent gave allylic sulfonamide **15c** (83 mg, 68%) as a white solid.

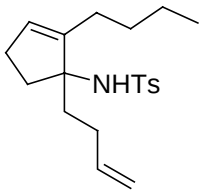
_N_-(1-Allyl-2-*sec*-butyl-2-cyclopenten-1-yl)-4-methylbenzenesulfonamide 15d



Using general procedure A, methoxy aziridine *cis*-**13** (112 mg, 0.4 mmol) and *s*-butyllithium (0.8 mL of a 1.10 M solution in cyclohexanes, 0.9 mmol) in Et_2O (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (2:1) as eluent gave allylic sulfonamide **15d** (95 mg, 85%) as a white solid, mp 61-63 °C; R_F(2:1 petrol-Et_2O) 0.3; IR ($CDCl_3$) 3369 (NH), 2965, 2930, 1330 (SO_2), 1154 (SO_2), 1056, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (~50:50 mixture of diastereoisomers) δ 7.75 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.28 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 5.65-5.53 (m, 2H, 2 x =CH), 5.13-5.07 (m, 2H, CH=CH_2), 4.75 and 4.68 (s, 1H, NH), 2.60-2.50 (m, 1H), 2.42 (s, 3H, Me), 2.33-2.20 (m, 2H), 2.14-2.00 (m, 3H), 1.94-1.83 (m, 1H), 1.56-1.45 (m, 1H), 1.40-1.26 (m, 1H), 1.07 and 1.02 (d, J = 7.0 Hz, 3H, CH*Me*), 0.89 and 0.85 (t, J = 7.5, 3H, CH_2*Me*); ^{13}C NMR (100.6 MHz, $CDCl_3$) (~50:50 mixture of diastereoisomers) δ 151.2 and 150.9 (=C), 142.8 (*ipso*-$C_6H_4SO_2$), 140.4 (*ipso*-C_6H_4Me), 133.2 (*C*H=CH_2), 129.5 (*o*-$C_6H_4SO_2$), 127.4 and 127.1 (=CH), 126.8 (*m*-$C_6H_4SO_2$), 119.0 (CH=*C*H_2), 73.0 and 72.8 (CN), 42.7 and 42.5 (CH_2), 34.6 and 34.0 (CH_2), 32.1 and 32.0 (CH), 30.7 and 30.3 (CH_2), 29.6 and 29.4 (CH_2), 21.3 (Me), 21.0 (Me) 11.9 (Me); MS (CI, NH_3) *m/z* 351 [(M + $NH_4)^+$, 9], 334 (4), 292 (74), 189 (23), 163 (100); HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{27}NO_2S$ (M + $NH_4)^+$ 351.2106, found 351.2105.

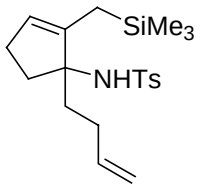
Using general procedure A, methoxy aziridine *cis*-**13** (104 mg, 0.3 mmol) and *s*-butyllithium (0.9 mL of a 1.15 M solution in cyclohexanes, 0.9 mmol) in TBME (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (2:1) as eluent gave allylic sulfonamide **15d** (92 mg, 82%) as a white solid.

_N_-[1-(3-Butenyl)-2-butyl-2-cyclopenten-1-yl]-4-methylbenzenesulfonamide 16a



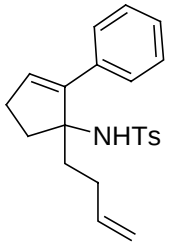
Using general procedure A, *n*-butyllithium (1.0 mL of a 1.20 M solution in hexanes, 1.2 mmol) and methoxy aziridine *cis*-**14** (150 mg, 0.5 mmol) in Et_2O (7 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (7:3) as eluent gave allylic sulfonamide **16a** (131 mg, 80%) as a white solid, mp 66-67 ºC; R_F(7:3 petrol-Et_2O) 0.2; IR (Nujol) 3258 (NH), 1325 (SO_2), 1152 (SO_2) cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.87 (d, J = 8.0, 2H, *o*-$C_6H_4SO_2$), 6.77 (d, J = 8.0, 2H, *m*-$C_6H_4SO_2$), 5.71-5.62 (m, 1H, C*H*=CH_2), 5.37 (s, 1H, NH), 5.23 (app. quintet, J = 2.0, 1H, =CH), 4.96 (app. dq, J = 17.0, 2.0, 1H, CH=CH_AH_B), 4.92 (app. dt, J = 11.0, 1.0, 1H, CH=CH_AH_B), 2.60 (ddd, J = 13.5, 9.0, 3.5, 1H), 2.51-2.42 (m, 1H), 2.03-1.95 (m, 2H), 1.91 (s, 3H, Me), 1.83-1.74 (m, 3H), 1.56-1.52 (m, 2H), 1.43-1.34 (m, 1H), 1.26-1.03 (m, 3H), 0.99-0.89 (m, 1H), 0.82 (t, J = 7.0, 3H, Me); ^{13}C NMR (100.6 MHz, C_6D_6) δ 144.6 (=C), 142.2 (*ipso*-$C_6H_4SO_2$), 141.1 (*ipso*-C_6H_4Me), 138.3 (*C*H=CH_2), 129.2 (*o*-$C_6H_4SO_2$), 127.6 and 127.5 (*m*-$C_6H_4SO_2$ and =CH), 114.7 (=CH_2), 73.2 (CN), 38.3 (CH_2), 34.4 (CH_2), 30.2 (CH_2), 29.8 (CH_2), 28.5 (CH_2), 26.1 (CH_2), 23.2 (CH_2), 21.0 (Me), 14.3 (Me); MS (CI, NH_3) *m/z* 365 [$(M + NH_4)^+$, 20], 348 (30), 292 (45), 177 (100); HRMS (CI, NH_3) *m/z*: [$M + H]^+$ calcd for $C_{20}H_{29}NO_2S$, 348.1997; found, 348.2002.

***N*-{1-(3-Butenyl)-2-[(trimethylsilyl)methyl]-2-cyclopenten-1-yl}-4-methylbenzenesulfonamide 16b**



Using general procedure A, (trimethylsilyl)methyllithium (0.6 mL of a 0.63 M solution in pentane, 0.4 mmol) and methoxy aziridine *cis*-**14** (50 mg, 0.2 mmol) in Et_2O (3 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (7:3) as eluent gave allylic sulfonamide **16b** (48 mg, 82%) as a colourless oil, R_F(7:3 petrol-Et_2O) 0.3; IR (film) 3263 (NH), 2950, 2854, 1419, 1322 (SO_2), 1248, 1155 (SO_2), 1095 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.5, 2H, *o*-$C_6H_4SO_2$), 7.27 (d, J = 8.5, 2H, *m*-$C_6H_4SO_2$), 5.80-5.70 (m, 1H, C*H*=CH_2), 5.42-5.40 (m, 1H, =CH), 4.98-4.91 (m, 1H, CH=CH_AH_B), 4.95-4.92 (m, 1H, CH=CH_AH_B), 4.45 (s, 1H, NH), 2.43 (s, 3H, Me), 2.33-2.08 (m, 3H), 2.00-1.80 (m, 4H), 1.52-1.44 (m, 1H), 1.12 (dq, J = 16.0, 1.5, 1H, CH_AH_BSi), 1.05 (dq, J = 16.0, 2.0, 1H, CH_AH_BSi), 0.08 (br s, 9H, $SiMe_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 142.8 (*ipso*-$C_6H_4SO_2$), 141.1 (=C), 137.9 (*C*H=CH_2), 137.9 (*ipso*-C_6H_4Me), 129.3 (*o*-$C_6H_4SO_2$), 127.6 (=CH), 127.0 (*m*-$C_6H_4SO_2$), 114.6 (=CH_2), 74.1 (CN), 37.1 (CH_2), 33.7 (CH_2), 30.0 (CH_2), 28.2 (CH_2), 21.5 (Me), 14.1 (CH_2Si), −0.8 ($SiMe_3$); MS (CI, NH_3) *m/z* 378 [$(M + H)^+$, 35], 322 (30), 244 (45), 207 (100); HRMS (CI, NH_3) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{31}NO_2SSi$, 378.1923; found, 378.1909.

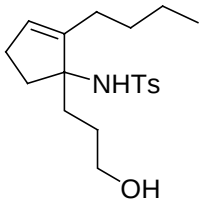
***N*-[1-(3-Butenyl)-2-phenyl-2-cyclopenten-1-yl]-4-methylbenzenesulfonamide 16c**



Using general procedure A, phenyllithium (1.0 mL of a 1.14 M solution in dibutyl ether, 1.2 mmol) and methoxy aziridine *cis*-**14** (150 mg, 0.5 mmol) in Et_2O (7 mL) gave the crude product.

Purification by flash column chromatography on silica with petrol-Et_2O (7:3) as eluent gave allylic sulfonamide **16c** (109 mg, 63%) as a white solid, mp 85-88 ºC; R_F(7:3 petrol-Et_2O) 0.1; IR (CH_2Cl_2) 3330 (NH), 3054, 2986, 1422, 1340 (SO_2), 1269, 1155 (SO_2), 896 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.76 (d, J = 8.0, 2H, *o*-$C_6H_4SO_2$), 7.28-7.26 (m, 2H, Ph), 7.05-6.99 (m, 3H, Ph), 6.68 (d, J = 8.0, 2H, *m*-$C_6H_4SO_2$), 5.77 (t, J = 2.5, 1H, =CH), 5.52-5.42 (m, 1H, C*H*=CH_2), 4.81-4.76 (m, 2H, =CH_2), 4.68 (s, 1H, NH), 2.56-2.51 (m, 1H), 2.45-2.37 (m, 1H), 2.02-1.83 (m, 3H), 1.86 (s, 3H, Me), 1.78-1.64 (m, 3H); ^{13}C NMR (100.6 MHz, C_6D_6) δ 143.9 (=C), 142.4 (*ipso*-$C_6H_4SO_2$), 141.0 (*ipso*-C_6H_4Me), 138.0 (*C*H=CH_2), 135.7 (*ipso*-Ph), 133.5 (Ph), 129.3 (*o*-$C_6H_4SO_2$), 128.3 (Ph), 127.4, 127.3 and 127.2 (*m*-$C_6H_4SO_2$, Ph, =CH), 114.7 (=CH_2), 73.1 (CN), 37.5 (CH_2), 36.1 (CH_2), 30.1 (CH_2), 28.7 (CH_2), 21.0 (Me); MS (CI, NH_3) *m/z* 385 [$(M + NH_4)^+$, 35], 368 (25), 312 (50), 197 (100); HRMS (CI, NH_3) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{25}NO_2S$, 348.1997; found, 348.1997.

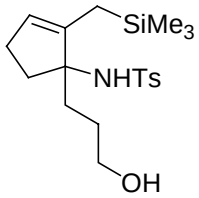
***N*-{2-Butyl-[1-(3-hydroxypropyl)]-2-cyclopenten-1-yl}-4-methylbenzenesulfonamide 17a**



Using general procedure B, allylic sulfonamide **15a** (167 mg, 0.5 mmol) and 9-BBN (2.0 mL of a 0.50 M solution in THF, 1.0 mmol) in THF (5 mL) gave the crude product. Purification by flash column chromatography on silica with hexane-EtOAc (1:1) as eluent gave sulfonamido alcohol **17a** (62 mg, 35%) as a colourless oil, R_F(1:1 hexane-EtOAc) 0.2; IR ($CDCl_3$) 3524 (OH), 3379 (NH), 2957, 2873, 1380 (SO_2), 1094 (SO_2), 979, 651 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.28 (d, J = 8.0 Hz, *m*-$C_6H_4SO_2$), 5.58 (d, J = 3.5 Hz, 1H, =CH), 5.40 (s, 1H, NH), 3.71-3.58 (m, 2H, C*H*$_2$OH), 2.49-2.35 (m, 1H), 2.45 (s, 3H, Me), 2.18-2.09 (m, 2H), 1.93-1.79 (m, 2H), 1.68-1.54 (m, 2H), 1.47-1.39 (m, 2H), 1.30-1.10 (m, 3H), 0.97-0.93 (m, 2H), 0.86 (t, J = 7.5 Hz, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.4 (=C), 142.6

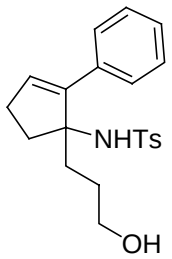
(*ipso*-$C_6H_4SO_2$), 139.7 (*ipso*-C_6H_4Me), 129.7 (*o*-$C_6H_4SO_2$), 127.0 (=CH) 126.9 (*m*-$C_6H_4SO_2$), 72.9 (CN), 62.5 (CH_2OH), 35.5 (CH_2), 34.0 (CH_2), 29.8 (CH_2), 29.4 (CH_2), 26.8 (CH_2), 25.8 (CH_2), 22.8 (CH_2), 21.4 (Me), 14.0 (Me); MS (CI, NH_3) *m/z* 292 [$(M - C_3H_7O)^+$, 51], 196 (5), 189 (17), 181 (100); HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{29}NO_3S$ (M - NHTs)$^+$ 181.1592, found 181.1600.

_N_-{1-(3-Hydroxypropyl)-2-[(trimethylsilyl)methyl]-2-cyclopenten-1-yl}-4-methylbenzenesulfonamide 17b



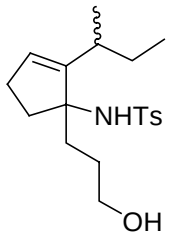
Using general procedure B, allylic sulfonamide **15b** (90 mg, 0.3 mmol) and 9-BBN (1.0 mL of a 0.50 M solution in THF, 0.5 mmol) in THF (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (1:4) as eluent gave sulfonamido alcohol **17b** (81 mg, 86%) as a colourless oil, R_F(1:4 petrol-Et_2O) 0.2; IR ($CHCl_3$) 3626 (OH), 3375 (NH), 3022, 2954, 1400, 1321 (SO_2), 1250, 1153 (SO_2), 862, 773, 665 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 7.94 (d, *J* = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 6.85 (d, *J* = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 6.27 (s, 1H, =CH), 5.28 (s, 1H, NH), 3.61-3.55 (m, 1H, C*H*$_A$H$_B$OH), 3.53-3.47 (m, 1H, CH$_A$*H*$_B$OH), 2.79 (br s, 1H, OH), 2.51 (ddd, *J* = 13.0, 9.0, 4.0 Hz, 1H), 2.43-2.34 (br m, 1H), 2.02-1.98 (m, 2H), 1.94 (s, 3H, Ar*Me*), 1.78 (ddd, *J* = 13.0, 9.0, 5.0 Hz, 1H), 1.71-1.62 (br m, 1H), 1.47-1.38 (br m, 2H), 1.20 (d, *J* = 16.0 Hz, 1H, C*H*$_A$H$_B$Si), 1.09 (d, *J* = 16.0 Hz, 1H, CH$_A$*H*$_B$Si), 0.04 (s, 9H, $SiMe_3$); ^{13}C NMR (100.6 MHz, C_6D_6) δ 142.8 (*ipso*-$C_6H_4SO_2$), 142.3 (=C), 141.3 (*ipso*-C_6H_4Me), 129.3 (*o*-$C_6H_4SO_2$), 127.5 (*m*-$C_6H_4SO_2$), 126.9 (=CH), 73.8 (CN), 62.7 (CH_2OH), 36.4 (CH_2), 33.4 (CH_2), 30.2 (CH_2), 27.4 (CH_2), 21.1 (Me), 14.4 (CH_2Si), –0.70 ($SiMe_3$); MS (CI, NH_3) *m/z* 382 [$(M + H)^+$, 10], 364 (10), 322 (13), 244 (27), 211 (100), 90 (7); HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{31}NO_3SSi$ $(M + H)^+$ 382.1872, found 382.1874.

***N*-[1-(3-Hydroxypropyl)-2-phenyl-2-cyclopenten-1-yl]-4-methylbenzenesulfonamide 17c**



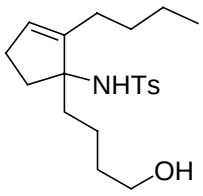
Using general procedure B, allylic sulfonamide **15c** (100 mg, 0.3 mmol) and 9-BBN (1.1 mL of a 0.50 M solution in THF, 0.6 mmol) in THF (3 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-EtOAc (1:1) as eluent gave sulfonamido alcohol **17c** (82 mg, 79%) as a colourless oil, R_F(1:1 petrol-EtOAc) 0.2; IR ($CDCl_3$) 3628 (OH), 3370 (NH), 2929, 1323 (SO_2), 1154 (SO_2), 815, 661, 581 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.34 (d, J = 8.0 Hz, 2H, Ar), 7.22-7.18 (m, 5H, Ar), 6.11 (t, J = 2.5 Hz, 1H, =CH), 5.20 (s, 1H, NH), 3.48 (m, 2H, CH_2OH), 2.54 (dddd, J = 17.0, 8.5, 5.5, 2.5 Hz, 1H), 2.43 (ddd, J = 13.5, 8.5, 3.5 Hz, 1H), 2.38 (s, 3H, Me), 2.30 (m, 1H), 2.11-2.01 (m, 2H), 1.79 (ddd, J = 13.5, 11.5, 5.0 Hz, 1H), 1.68 (br s, 1H, OH), 1.53-1.46 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.8 (=C), 142.9 (*ipso*-$C_6H_4SO_2$), 139.6 (*ipso*-C_6H_4Me), 135.1 (*ipso*-Ph), 133.2 (=CH), 129.3 (*o*-$C_6H_4SO_2$), 128.1 (CH, Ph), 127.2 (CH, Ph), 126.9 (*m*-$C_6H_4SO_2$), 126.9 (CH, Ph), 72.8 (CN), 62.5 (CH_2OH), 35.7 (CH_2), 34.9 (CH_2), 29.9 (CH_2), 27.2 (CH_2), 21.4 (Me); MS (CI, NH_3) *m/z* 372 [$(M + H)^+$, 42], 312 (36), 201 (100), 189 (48); HRMS (CI, NH_3) *m/z* calcd for $C_{21}H_{25}NO_3S$ $(M + H)^+$ 372.1633, found 372.1634.

***N*-{2-*sec*-Butyl-[1-(3-hydroxypropyl)]-2-cyclopenten-1-yl}-4-methylbenzenesulfonamide 17d**



Using general procedure B, allylic sulfonamide **15d** (90 mg, 0.3 mmol) and 9-BBN (1.1 mL of a 0.50 M solution in THF, 0.5 mmol) in THF (5 mL) gave the crude product. Purification by flash column chromatography on silica with hexane-EtOAc (2:1) as eluent gave sulfonamido alcohol **17d** (57 mg, 60%) as a colourless oil, R_F(2:1 hexane-EtOAc) 0.3; IR ($CDCl_3$), 3628 (OH), 3380 (NH), 2963, 2875, 1380 (SO_2), 1120 (SO_2), 791, 728, 610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (~50:50 mixture of diastereoisomers) δ 7.75 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.28 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 5.54-5.52 (m, 1H, =CH), 5.36 and 5.16 (s, 1H, NH), 3.66-3.54 (m, 2H, C*H*$_2$OH), 2.43 (s, 3H, Me), 2.33-2.23 (m, 1H), 2.22-1.74 (m, 5H), 1.60-1.25 (m, 5H), 1.04 and 1.01 (d, J = 7.0 Hz, 3H, CH*Me*), 0.88 and 0.85 (t, J = 7.0 Hz, 3H, CH_2*Me*); ^{13}C NMR (100.6 MHz, $CDCl_3$) (~50:50 mixture of diastereoisomers) δ 151.4 and 151.2 (=C), 142.7 (*ipso*-$C_6H_4SO_2$), 140.5 and 140.4 (*ipso*-C_6H_4Me), 129.4 (*o*-$C_6H_4SO_2$), 126.7 (*m*-$C_6H_4SO_2$), 126.5 (=CH), 73.7 and 73.6 (CN), 62.6 (CH_2OH), 34.8 and 34.7 (CH_2), 34.3 (CH_2), 33.8 (CH_2), 32.0 and 31.9 (CH), 30.5 and 30.3 (CH_2), 29.7 and 29.5 (CH_2), 27.2 and 27.1 (CH_2), 21.4 (Me), 21.2 (Me), 12.0 and 11.8 (Me); MS (CI, NH_3) *m/z* 292 [(M – $C_3H_7O)^+$, 42], 189 (24), 181 (100); HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{29}NO_3S$ (M - NHTs)$^+$ 181.1592, found 181.1594.

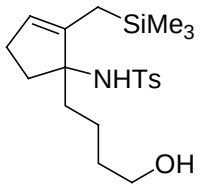
_N_-[2-Butyl-1-(4-hydroxybutyl)-2-cyclopenten-1-yl]-4-methylbenzenesulfonamide 18a



Using general procedure B, 9-BBN (1.0 mL of a 0.50 M solution in THF, 0.5 mmol) and allylic sulfonamide **16a** (83 mg, 0.2 mmol) in THF (8 mL) gave the crude product. Purification by flash column chromatography on silica with Et_2O as eluent gave alcohol **18a** (56 mg, 64%) as a white solid, mp 96-98 ºC; R_F(Et_2O) 0.3; IR (CH_2Cl_2) 3619 (OH), 3372 (NH), 3053, 2986, 1422, 1340 (SO_2), 1264, 1154 (SO_2), 896 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.82 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 6.77 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 5.23 (br s, 1H, =CH), 4.82 (s, 1H, NH), 3.30-

3.24 (m, 2H, CH_2O), 2.58 (ddd, J = 13.5, 9.0, 3.5 Hz, 1H), 2.52-2.43 (m, 1H), 2.04-1.95 (m, 1H), 1.91 (s, 3H, Me), 1.81 (ddd, J = 13.5, 9.5, 5.0 Hz, 1H), 1.56-1.38 (m, 4H), 1.24-1.15 (m, 7H), 0.97-0.89 (m, 1H), 0.83 (t, J = 7.5 Hz, 3H, Me), 0.72 (br s, 1H, OH); ^{13}C NMR (100.6 MHz, C_6D_6) δ 145.2 (=C), 142.3 (*ipso*-$C_6H_4SO_2$), 141.3 (*ipso*-C_6H_4Me), 129.3 (*o*-$C_6H_4SO_2$), 127.5 (*m*-$C_6H_4SO_2$), 127.2 (=CH), 73.5 (CN), 62.3 (CH_2O), 39.3 (CH_2), 34.5 (CH_2), 33.2 (CH_2), 30.2 (CH_2), 29.9 (CH_2), 26.3 (CH_2), 23.2 (CH_2), 21.1 (Me), 20.4 (CH_2), 14.3 (Me); MS (CI, NH_3) *m/z* 383 [$(M + NH_4)^+$, 15], 292 (25), 195 (100); HRMS (CI, NH_3) *m/z*: $[M + NH_4]^+$ calcd for $C_{20}H_{31}NO_3S$, 383.2368; found, 383.2367.

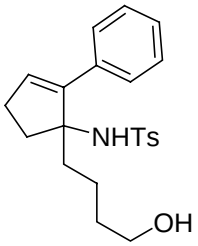
_N_-{1-(4-Hydroxybutyl)-2-[(trimethylsilyl)methyl]-2-cyclopenten-1-yl}-4-methylbenzenesulfonamide 18b



Using general procedure B, 9-BBN (0.7 mL of a 0.50 M solution in THF, 0.3 mmol) and allylic sulfonamide **16b** (64 mg, 0.2 mmol) in THF (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (7:3) as eluent gave alcohol **18b** (47 mg, 71%) as a colourless oil, R_F(3:7 petrol-Et_2O) 0.1; IR (film) 3482 (OH), 3271 (NH), 2949, 2860, 1418, 1323 (SO_2), 1248, 1155 (SO_2), 1093, 860 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.5 Hz, 2H, *o*-$C_6H_4SO_2$), 7.26 (d, J = 8.5 Hz, 2H, *m*-$C_6H_4SO_2$), 5.37-5.34 (br m, 1H, =CH), 4.76 (s, 1H, NH), 3.60 (t, J = 6.5 Hz, 2H, CH_2O), 2.43 (s, 3H, Me), 2.31-2.06 (m, 3H), 1.89-1.76 (m, 3H), 1.50 (app. quintet, J = 6.5 Hz, 2H, CH_2), 1.40-1.15 (m, 3H), 1.10 (dq, J = 16.0, 1.5 Hz, 1H, CH_AH$_B$Si), 0.99 (dq, J = 16.0, 2.0 Hz, 1H, CH$_A$$H_B$Si), 0.10 (s, 9H, $SiMe_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 142.8 (*ipso*-$C_6H_4SO_2$), 141.7 (=C), 140.0 (*ipso*-C_6H_4Me), 129.3 (*o*-$C_6H_4SO_2$), 127.3 (=CH), 127.0 (*m*-$C_6H_4SO_2$), 74.1 (CN), 62.5 (CH_2O), 38.0 (CH_2), 33.7 (CH_2), 32.7 (CH_2), 29.9 (CH_2), 21.4 (Me), 20.1 (CH_2), 14.2 (CH_2Si), −0.9 ($SiMe_3$); MS (CI, NH_3) *m/z* 396 [(M +

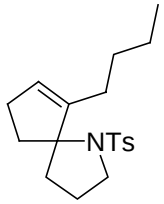
H)$^+$, 5], 322 (30), 244 (35), 225 (100); HRMS (CI, NH_3) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{33}NO_3SSi$, 396.2029; found, 396.2025.

***N*-[1-(4-Hydroxybutyl)-2-phenyl-2-cyclopenten-1-yl]-4-methylbenzenesulfonamide 18c**



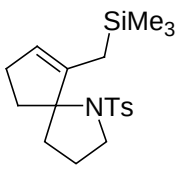
Using general procedure B, 9-BBN (1.0 mL of a 0.50 M solution in THF, 0.5 mmol) and allylic sulfonamide **16c** (90 mg, 0.2 mmol) in THF (8 mL) gave the crude product. Purification by flash column chromatography on silica with Et_2O as eluent gave alcohol **18c** (65 mg, 69%) as a white solid, mp 85-88 ºC; $R_F(Et_2O)$ 0.3; IR (CH_2Cl_2) 3620 (OH), 3378 (NH), 3051, 2986, 1422, 1339 (SO_2), 1265, 1153 (SO_2), 896 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.79 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.31 (dd, J = 8.0 Hz, 1.5, 2H, Ph), 7.04-6.99 (m, 3H, Ph), 6.70 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 5.79 (t, J = 2.5 Hz, 1H, =CH), 4.80 (s, 1H, NH), 3.12-3.04 (m, 2H, CH_2O), 2.56-2.50 (m, 1H), 2.48-2.41 (m, 1H), 2.01-1.79 (m, 3H), 1.86 (s, 3H, Me), 1.62-1.55 (m, 1H), 1.15-0.89 (m, 4H), 0.40 (t, J = 5.0 Hz, 1H, OH); ^{13}C NMR (100.6 MHz, C_6D_6) δ 144.3 (=C), 142.3 (*ipso*-$C_6H_4SO_2$), 141.1 and 141.0 (*ipso*-C_6H_4Me and *ipso*-Ph), 136.0, 133.3 and 133.2 (3 x Ph), 129.3 (*o*-$C_6H_4SO_2$), 127.4 (*m*-$C_6H_4SO_2$), 127.2 (=CH), 73.4 (CN), 62.1 (CH_2O), 38.4 (CH_2), 36.0 (CH_2), 32.8 (CH_2), 30.2 (CH_2), 21.0 (Me), 20.6 (CH_2); MS (CI, NH_3) *m/z* 403 $[(M + NH_4)^+$, 50], 386 (15), 312 (20), 215 (100); HRMS (CI, NH_3) *m/z*: $[M + NH_4]^+$ calcd for $C_{22}H_{27}NO_3S$, 403.2055; found, 403.2051.

1-Butyl-6-[(4-methylphenyl)sulfonyl]-6-azaspiro[4.4]non-1-ene 19a



Using general procedure C, sulfonamido alcohol **17a** (60 mg, 0.2 mmol), PPh_3 (54 mg, 0.2 mmol) and DIAD (38 μL, 0.2 mmol) in THF (2 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-EtOAc (8:1) as eluent gave aza-spirocycle **19a** (37 mg, 65%) as a colourless oil, R_F(8:1 petrol-EtOAc) 0.3; IR ($CHCl_3$) 2960, 2931, 2860, 1334 (SO_2), 1154 (SO_2), 1092, 754, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.26 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 5.48 (br t, J = 2.0 Hz, 2H, =CH), 3.55-3.50 (m, 1H, CH_AH$_B$N), 3.41-3.35 (m, 1H, CH$_A$$H_B$N), 2.56-2.49 (m, 2H), 2.41 (s, 3H, Me), 2.20-2.12 (m, 1H), 1.98-1.92 (m, 1H), 1.89-1.70 (m, 4H), 1.44-1.33 (m, 3H), 1.27-1.19 (m, 3H), 0.88 (t, J = 7.5 Hz, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 146.0 (=C), 142.5 (*ipso*-$C_6H_4SO_2$), 138.6 (*ipso*-C_6H_4Me), 129.2 (*o*-$C_6H_4SO_2$), 127.0 (*m*-C_6H_4Me), 125.4 (=CH), 80.4 (CN), 49.4 (CH_2N), 39.1 (CH_2), 37.4 (CH_2), 29.9 (CH_2), 29.4 (CH_2), 26.3 (CH_2), 23.2 (CH_2), 22.9 (CH_2), 21.6 (Me), 14.1 (Me); MS (CI, NH_3) *m/z* 334 [$(M + H)^+$, 100], 178 (12); HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{27}NO_2S$ $(M + H)^+$ 334.1839, found 334.1834.

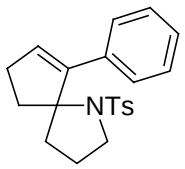
6-[(4-Methylphenyl)sulfonyl]-1-[(trimethylsilyl)methyl]-6-azaspiro[4.4]non-1-ene 19b



Using general procedure C, sulfonamido alcohol **17b** (73 mg, 0.2 mmol), PPh_3 (60 mg, 0.2 mmol) and DIAD (45 μL, 0.2 mmol) in THF (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-EtOAc (20:1) as eluent gave aza-spirocycle **19b** (53 mg, 76 %) as a white solid, mp 60-61 °C; R_F(20:1 petrol-EtOAc) 0.2; IR ($CHCl_3$) 3020,

2956, 1456, 1334 (SO_2), 1250, 1153 (SO_2),1095, 862, 671 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.82 (d, J = 8.0 Hz, 2H, *o*-$C_6H_6SO_2$), 6.82 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 5.46 (app. quintet, J = 2.0 Hz, 1H, =CH), 3.37-3.32 (m, 1H, C$H_A$$H_B$N), 3.27 (m, 1H, C$H_A$$H_B$N), 2.64-2.48 (m, 2H), 2.11-2.02 (br m, 1H), 1.92 (s, 3H, Me), 1.69 (dq, J = 16.0, 2.0 Hz, 1H, C$H_A$$H_B$Si), 1.61-1.54 (m, 2H, CH and C$H_A$$H_B$Si), 1.33-1.23 (m, 4H), 0.11 (s, 9H, $SiMe_3$); ^{13}C NMR (100.6 MHz, C_6D_6) δ 143.8 (=C), 142.1 (*ipso*-$C_6H_4SO_2$), 140.0 (*ipso*-C_6H_4Me), 129.3 (*o*-$C_6H_4SO_2$), 127.6 (*m*-$C_6H_4SO_2$), 125.0 (=CH), 81.5 (CN), 49.4 (CH_2N), 38.4 (CH_2), 36.3 (CH_2), 29.6 (CH_2), 23.2 (CH_2), 21.0 (Me), 14.9 (CH_2Si), –0.6 ($SiMe_3$); MS (CI, NH_3) *m/z* 364 [$(M + H)^+$, 100], 226 (17), 90 (6); HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{29}NO_2SSi$ $(M + H)^+$ 364.1767, found 354.1763.

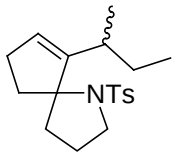
6-[(4-Methylphenyl)sulfonyl]-1-phenyl-6-azaspiro[4.4]non-1-ene 19c



Using general procedure C, sulfonamido alcohol **17c** (40 mg, 0.1 mmol), PPh_3 (34 mg, 0.1 mmol) and DIAD (30 μL, 0.1 mmol) in THF (4 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-EtOAc (8:1) as eluent gave aza-spirocycle **19c** (23 mg, 61%) as a white solid, mp 108-110 °C; R_F(8:1 petrol-EtOAc) 0.2; IR ($CHCl_3$) 2977, 2878, 1495, 1339 (SO_2), 1155 (SO_2), 1094 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.36-7.33 (m, 2H, Ph), 7.20-7.18 (m, 3H, Ph), 7.11 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 6.19 (t, J = 2.5 Hz, 1H, =CH), 3.67-3.63 (td, J = 8.5, 2.5 Hz, 1H, C$H_A$$H_B$N), 3.37-3.31 (m, 1H, C$H_A$$H_B$N), 2.79-2.67 (m, 2H), 2.37-2.26 (m, 2H), 2.36 (s, 3H, Me), 2.29-1.94 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) 144.5 (=C), 142.5 (*ipso*-$C_6H_4SO_2$), 137.9 (*ipso*-C_6H_4Me), 135.7 (*ipso*-Ph), 130.7 (=CH), 129.1 (*o*-$C_6H_4SO_2$), 127.9 (CH, Ph), 127.1 (CH, Ph), 127.0 (CH, Ph), 126.7 (*m*-$C_6H_4SO_2$), 79.7 (CN), 48.8 (CH_2N), 39.1 (CH_2), 38.9 (CH_2), 29.5 (CH_2), 23.3

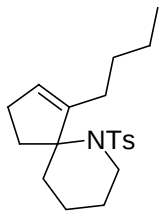
(CH_2), 21.4 (Me); MS (CI, NH_3) *m/z* 354 [$(M + H)^+$, 100], 198 (6); HRMS (CI, NH_3) *m/z* calcd for $C_{21}H_{23}NO_2S$ $(M + H)^+$ 354.1528, found 354.1525.

1-*sec*-Butyl-6-[(4-methylphenyl)sulfonyl]-6-azaspiro[4.4]non-1-ene 19d



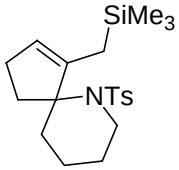
Using general procedure C, sulfonamido alcohol **17d** (36 mg, 0.1 mmol), PPh_3 (31 mg, 0.1 mmol) and DIAD (24 μL, 0.1 mmol) in THF (2 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-EtOAc (8:1) as eluent gave aza-spirocycle **19d** (24 mg, 71%) as a colourless oil, R_F(8:1 petrol-EtOAc) 0.3; IR ($CHCl_3$) 2964, 1456, 1336 (SO_2), 1153 (SO_2), 787, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (~50:50 mixture of diastereoisomers) δ 7.75-7.72 (m, 2H, *o*-$C_6H_4SO_2$), 7.28-7.26 (m, 2H, *m*-$C_6H_4SO_2$), 5.55-5.52 (m, 1H, =CH), 3.42-3.33 (m, 2H, CH_2N), 2.55-2.44 (m, 2H), 2.42 (s, 3H, Me), 2.22-2.07 (m, 2H), 2.04-1.90 (m, 1H), 1.86-1.74 (m, 2H), 1.61-1.49 (m, 1H), 1.44-1.27 (m, 3H), 1.23 and 1.07 (d, *J* = 7.0 Hz, 3H, CH*Me*), 0.96 and 0.89 (t, *J* = 7.5 Hz, 3H, CH_2*Me*); ^{13}C NMR (100.6 MHz, $CDCl_3$) (~50:50 mixture of diastereoisomers) δ 153.2 and 152.2 (=C), 142.6 (*ipso*-$C_6H_4SO_2$), 138.6 (*ipso*-C_6H_4Me), 129.4 (*o*-$C_6H_4SO_2$), 127.2 and 127.1 (*m*-$C_6H_4SO_2$), 124.7 and 124.4 (=CH), 81.3 (CN), 49.3 (CH_2N), 39.2 and 38.9 (CH_2), 36.6 (CH_2), 32.4 and 32.3 (CH), 31.6 (CH_2), 29.8 and 29.1 (CH_2), 23.3 (CH_2), 22.6 and 22.1 (Me), 21.6 and 21.4 (Me), 12.3 and 11.8 (Me); MS (CI, NH_3) *m/z* 334 [$(M + H)^+$, 100], 178 (10); HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{27}NO_2S$ $(M + H)^+$ 334.1841, found 334.1841.

1-Butyl-6-[(4-methylphenyl)sulfonyl]-6-azaspiro[4.5]dec-1-ene 20a



Using general procedure C, PPh_3 (46 mg, 0.2 mmol), DIAD (34 μL, 0.2 mmol) and sulfonamido alcohol **18a** (53 mg, 0.1 mmol) in THF (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (8:2) as eluent gave aza-spirocycle **20a** (40 mg, 79%) as a colourless oil, R_F(8:2 petrol-Et_2O) 0.2; IR (CH_2Cl_2) 3082, 3037, 2937, 1341 (SO_2), 1265, 1160 (SO_2) cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.74 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 6.79 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 5.41 (app. quintet, J = 2.0 Hz, 1H, =CH), 3.86 (dtd, J = 12.0, 4.5, 1.5 Hz, 1H, C$H_A$$H_B$N), 2.75-2.66 (m, 1H), 2.51 (td, J = 12.0, 3.0 Hz, 1H, C$H_A$$H_B$N), 2.13-1.98 (m, 2H), 1.93-1.78 (m, 2H), 1.90 (s, 3H, Me), 1.75-1.54 (m, 4H), 1.52-1.42 (m, 2H), 1.36-1.22 (m, 3H), 1.14-1.05 (m, 1H), 1.02-0.98 (m, 1H), 1.01 (t, J = 7.5 Hz, 3H, Me); ^{13}C NMR (100.6 MHz, C_6D_6) δ 150.0 (=C), 142.4 (*ipso*-$C_6H_4SO_2$), 138.8 (*ipso*-C_6H_4Me), 129.2 (*o*-$C_6H_4SO_2$), 128.1 (*m*-$C_6H_4SO_2$), 123.0 (=CH), 75.4 (CN), 46.3 (CH_2N), 37.8 (CH_2), 31.5 (CH_2), 30.1 (CH_2), 29.7 (CH_2), 28.1 (CH_2), 25.8 (CH_2), 23.7 (CH_2), 21.1 (Me), 21.0 (CH_2), 14.5 (CH_2); MS (CI, NH_3) *m/z* 348 [$(M + H)^+$, 100], 192 (15); HRMS (CI, NH_3) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{29}NO_2S$, 348.1997; found, 348.1993.

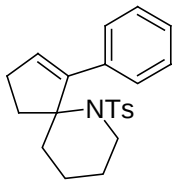
6-[(4-Methylphenyl)sulfonyl]-1-[(trimethylsilyl)methyl]-6-azaspiro[4.5]dec-1-ene 20b



Using general procedure C, PPh_3 (35 mg, 0.1 mmol), DEAD (17 μL, 0.1 mmol) and sulfonamido alcohol **18b** (44 mg, 0.1 mmol) in THF (2 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (9:1) as eluent gave aza-spirocycle **20b** (36

mg, 87%) as a white solid, mp 64-66 ºC, R_F(9:1 petrol-Et_2O) 0.1; IR (Nujol mull) 1345 (SO_2), 1247, 1161 (SO_2), 1092, 861 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.76 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 6.80 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 5.38-5.36 (br m, 1H, =CH), 3.84-3.81 (m, 1H, CH_AH$_B$N), 2.54-2.48 (m, 1H, CH$_A$$H_B$N), 2.24-2.18 (m, 1H), 2.15-2.06 (m, 1H), 2.01-1.93 (m, 1H), 1.92 (s, 3H, Me), 1.74-1.64 (m, 2H), 1.61-1.55 (m, 2H), 1.36-1.21 (m, 3H), 1.14-1.02 (m, 1H, CH_AH$_B$Si), 0.97 (br d, J = 13.0 Hz, 1H, CH$_A$$H_B$Si), 0.19 (s, 9H, $SiMe_3$); ^{13}C NMR (100.6 MHz, C_6D_6) δ 146.6 (=C), 142.4 (*ipso*-$C_6H_4SO_2$), 138.8 (*ipso*-C_6H_4Me), 129.3 (*o*-$C_6H_4SO_2$), 128.2 (*m*-$C_6H_4SO_2$), 123.1 (=CH), 75.9 (CN), 46.4 (CH_2N), 37.6 (CH_2), 29.7 (CH_2), 29.3 (CH_2), 25.7 (CH_2), 21.1 (Me), 21.0 (CH_2), 16.8 (CH_2Si), −0.2 ($SiMe_3$); MS (CI, NH_3) *m/z* 378 [(M + H)$^+$, 100]; HRMS (CI, NH_3) *m/z*: [M + H]$^+$ calcd for $C_{20}H_{31}NO_2SSi$, 378.1923; found, 378.1916.

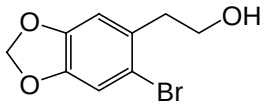
6-[(4-Methylphenyl)sulfonyl]-1-phenyl-6-azaspiro[4.5]dec-1-ene 20c



Using general procedure C, PPh_3 (51 mg, 0.2 mmol), DIAD (37 μL, 0.2 mmol) and sulfonamido alcohol **18c** (62 mg, 0.2 mmol) in THF (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (8:2) as eluent gave aza-spirocycle **20c** (45 mg, 76%) as a white solid, mp 109-110 ºC, R_F(8:2 petrol-Et_2O) 0.1; IR (CH_2Cl_2) 3073, 3004, 2966, 1342 (SO_2), 1266, 1161 (SO_2) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 8.0, 1.0 Hz, 2H, *o*-Ph), 7.49 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.30 (dd, J = 8.0, 7.5 Hz, 2H, *m*-Ph), 7.23 (tt, J = 7.5, 1.0 Hz, 1H, *p*-Ph), 7.19 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 6.19 (t, J = 2.5 Hz, 1H, =CH), 3.75 (dtd, J = 12.0, 3.5, 1.5 Hz, 1H, CH_AH$_B$N), 2.90 (td, J = 12.0, 3.0 Hz, 1H, CH$_A$$H_B$N), 2.46 (dddd, J = 17.5, 9.0, 3.5, 3.0 Hz, 1H), 2.40 (s, 3H, Me), 2.39-2.07 (m, 4H), 1.79-1.66 (m, 2H), 1.64-1.52 (m, 2H), 1.44-1.40 (m, 1H); ^{13}C NMR (100.6 MHz, C_6D_6) δ 147.4 (=C), 143.0 (*ipso*-$C_6H_4SO_2$), 136.9 and 135.9 (*ipso*-C_6H_4Me and *ipso*-Ph), 129.1, (*o*-$C_6H_4SO_2$), 128.0, 127.8

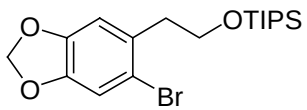
and 127.6 (*m*-$C_6H_4SO_2$, *m*-Ph, and *o*-Ph), 126.6 and 126.5 (=CH and *p*-Ph), 74.1 (CN), 46.2 (CH_2N), 36.6 (CH_2), 32.0 (CH_2), 29.3 (CH_2), 25.4 (CH_2), 21.5 (Me), 20.9 (CH_2); MS (CI, NH_3) *m/z* 368 [$(M + H)^+$, 100], 212 (15); HRMS (CI, NH_3) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{25}NO_2S$, 368.1684; found, 368.1684.

2-(6-Bromo-1,3-benzodioxol-5-yl)ethanol[4]



Br_2 (0.7 mL, 14.4 mmol) was added dropwise to a stirred solution of 2-(1,3-benzodioxol-5-yl)-1-ethanol (1.7 g, 10.3 mmol), in CH_2Cl_2 (20 mL) ar rt under N_2. After stirring at rt for 30 min, saturated $Na_2SO_{3(aq)}$ (20 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with petrol-EtOAc (3:2) as eluent gave alcohol 2-(6-Bromo-1,3-benzodioxol-5-yl)ethanol (2.1 g, 82%) as a white solid, mp 79-80 °C; R_F(2:1 petrol-EtOAc) 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 1H, CH, Ar), 6.78 (s, 1H, CH, Ar), 5.96 (s, 2H, OCH_2O), 3.86 (t, *J* = 6.5 Hz, 2H, CH_2O), 2.94 (t, *J* = 6.5 Hz, 2H, CH_2), 1.49 (s, 1H, OH); Spectroscopic data consistent with that reported in the literature.[4]

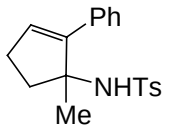
[2-(6-Bromo-1,3-benzodioxol-5-yl)-ethoxy]-triisopropyl-silane 27



TIPSCl (0.6 mL, 2.9 mmol) was added dropwise to a stirred solution of 2-(6-Bromo-1,3-benzodioxol-5-yl)ethanol (650 mg, 2.7 mmol) and imidazole (380 mg, 5.6 mmol) in DMF (10 mL) at rt under N_2. The resulting solution was stirred at rt for 72 h. Water (10 mL) and EtOAc (10 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 10 mL) and the combined organic extracts were washed with water (3 x 20 mL) and brine

(10mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with petrol-EtOAc (99:1) as eluent gave aryl bromide **27** (960 mg, 90%) as a colourless oil, R_F(99:1 petrol-EtOAc) 0.2; IR ($CHCl_3$) 3020, 2943, 2868, 1504, 1477, 1217, 1109, 1045, 937, 881, 862, 783, 675 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H, CH, Ar), 6.80 (s, 1H, CH, Ar), 5.94 (s, 2H, OCH_2O), 3.85 (t, J = 7.0 Hz, 2H, CH_2OH), 2.92 (t, J = 7.0 Hz, 2H, $ArCH_2$), 1.12-1.01 (m, 21H, C*H*Me and CH*Me*); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 147.0 (*ipso*-C_6H_2O), 146.8 (*ipso*-C_6H_2O), 131.4 (*ipso*-$C_6H_2CH_2$), 114.5 (*ipso*-C_6H_2Br), 112.5 (CH, Ar), 111.1 (CH, Ar), 101.5 (OCH_2O), 62.8 (CH_2O), 39.6 (Ar*C*H_2), 17.9 (CH*Me*$_2$), 11.9 (SiCH); MS (CI, NH_3) *m/z* 401 [$(M + H)^+$, 12] 376 (56), 374 (55), 359 (34), 357 (33), 244 (16), 242 (16), 229 (98), 227 (100); HRMS (CI, NH_3) *m/z* calcd for $C_{18}H_{29}O_3{}^{79}BrSi$ $(M + H)^+$ 401.1148, found 401.1145.

***N*-(1-Methyl-2-phenyl-2-cyclopenten-1-yl)-4-methylbenzenesulfonamide 24a**

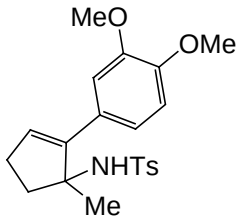


Using general procedure A, methoxy aziridine *cis*-**2** (105 mg, 0.4 mmol) and phenyllithium (0.6 mL of a 1.70 M solution in dibutylether, 0.9 mmol) in Et_2O (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (1:1) as eluent gave allylic sulfonamide **24a** (83 mg, 69%) as a pale yellow solid, mp 104-108 °C; R_F(1:1 petrol-Et_2O) 0.3; IR ($CHCl_3$) 3369 (NH), 3024, 1599, 1495, 1331 (SO_2), 1215, 1153 (SO_2), 1090, 974, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.29-7.26 (m, 2H, *m*-$C_6H_4SO_2$), 7.17-7.13 (m, 5H, Ph), 5.96 (s, 1H, =CH), 4.89 (s, 1H, NH), 2.41-2.17 (m, 3H), 2.38 (s, 3H, Me), 1.92-1.84 (m, 1H), 1.41 (s, 3H, Me); ^{13}C NMR (400 MHz, $CDCl_3$) δ 146.3 (=C), 142.7 (*ipso*-$C_6H_4SO_2$), 139.5 (*ipso*-C_6H_4Me), 134.5 (*ipso*-Ph), 131.2 (=CH), 129.2 (*o*-$C_6H_4SO_2$), 127.9 (CH, Ph), 127.6 (CH, Ph), 127.0 (CH, Ph), 126.9 (*m*-$C_6H_4SO_2$), 69.2 (CN), 40.2 (CH_2), 29.1 (CH_2), 24.6 (Me), 21.2 (Me); MS (CI, NH_3) *m/z* 328 [$(M + H)^+$, 9], 312 (59),

189 (7), 157 (100); HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{21}NO_2S$ $(M + H)^+$ 328.1371, found 328.1368.

n-Butyllithium (0.6 mL of a 1.54 M solution in hexanes, 0.9 mmol) was added dropwise to a stirred solution of bromobenzene (94 μL, 0.9 mmol) in THF (3 mL) at –78 °C under N_2. The resulting solution was stirred at –78 °C for 1 h. Then, this solution was added *via* canula to a stirred solution of methoxy aziridine *cis*-**2** (100 mg, 0.4 mmol) in Et_2O (5 mL) at –78 °C under N_2. After 5 min, the reaction mixture was allowed to warm to rt and stirred at rt for 1 h. Saturated $NH_4Cl_{(aq)}$ (5 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 5 mL) and the combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (2:1) as eluent gave allylic sulfonamide **24a** (54 mg, 46%) as a white solid.

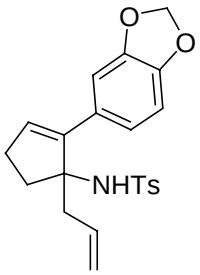
_N_-{[2-(3,4-Dimethoxybenzene)]-1-methyl-2-phenyl-2-cyclopenten-1-yl}-4-methylbenzenesulfonamide 24b



n-Butyllithium (0.6 mL of a 1.54 M solution in hexanes, 0.9 mmol) was added dropwise to a stirred solution of 4-bromoveratrole **25** (0.1 mL, 0.9 mmol) in THF (3 mL) at –78 °C under N_2. The resulting solution was stirred at –78 °C for 1 h. Then, this solution was added *via* canula to a stirred solution of methoxy aziridine *cis*-**2** (100 mg, 0.4 mmol) in Et_2O (5 mL) at –78 °C under N_2. After 5 min, the reaction mixture was allowed to warm to rt and stirred at rt for 1 h. Saturated $NH_4Cl_{(aq)}$ (5 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 5 mL) and the combined organic extracts were dried ($MgSO_4$) and evaporated under

reduced pressure to give the crude product. Purification by flash column chromatography on silica with CH_2Cl_2-acetone (99.5:0.5) as eluent gave allylic sulfonamide **24b** (64 mg, 46%) as a white solid, mp 104-108 °C; R_F(99.5:0.5 CH_2Cl_2-acetone) 0.2; IR ($CHCl_3$) 3367 (NH), 2937, 2839, 1601, 1514, 1464, 1406, 1325 (SO_2), 1151 (SO_2), 1090, 1026, 874, 658 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.23 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 6.95-6.93 (m, 2H, Ar), 6.74 (d, J = 9.0 Hz, 1H, Ar), 5.96 (t, J = 2.5 Hz, 1H,=CH), 5.01 (s, 1H, NH), 3.86 (s, 3H, OMe), 3.78 (s, 3H, OMe), 2.47-2.23 (m, 3H), 2.40 (s, 3H, Me), 1.92 (ddd, J = 13.0, 7.5, 5.5 Hz, 1H), 1.51 (s, 3H, Me); ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.4 (2 x *ipso*-C_6H_4OMe), 146.2 (=C), 142.9 (*ipso*-$C_6H_4SO_2$), 139.8 (*ipso*-C_6H_4Me), 129.9 (=CH), 129.3 (*o*-$C_6H_4SO_2$), 127.5 (*ipso*-Ar), 126.9 (*m*-$C_6H_4SO_2$), 119.5 (*m*-C_6H_3OMe), 110.7 (*o*-C_6H_3OMe), 110.4 (*o*-C_6H_3OMe), 69.4 (CN), 55.8 (OMe), 55.7 (OMe), 40.4 (CH_2), 29.0 (CH_2), 24.9 (Me), 21.4 (Me); MS (CI, NH_3) *m/z* 405 [$(M + NH_4)^+$, 13], 387 (36), 217 (100); HRMS (CI, NH_3) *m/z* calcd for $C_{21}H_{25}NO_4S$ $(M + NH_4)^+$ 405.1848, found 405.1848.

_N_-(1-Allyl-2-1,3-benzodioxol-5-yl-cyclopent-2-enyl)-4-methyl-enzenesulfonamide 15e

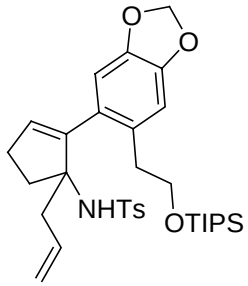


Using general procedure D, methoxy aziridine *cis*-**13** (101 mg, 0.3 mmol), aryl bromide **26** (0.1 mL, 1.0 mmol) and *n*-butyllithium (0.7 mL of a 1.40 M solution in hexanes, 1.0 mmol) in Et_2O (8 mL) gave the crude product. Purification by flash column chromatography on silica with CH_2Cl_2 as eluent gave allylic sulfonamide **15e** (83 mg, 64%) as a white solid, mp 115-116 °C; R_F(CH_2Cl_2) 0.3; IR ($CHCl_3$) 3367 (NH), 3032, 2894, 1504, 1439, 1331 (SO_2), 1154 (SO_2), 1093, 984, 937, 813, 574 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.26 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 6.91 (dd, J = 8.0, 1.5 Hz, 1H, *p*-C_6H_3O), 6.87 (d, J = 1.5 Hz, 1H, *o*-C_6H_3O), 6.71 (d, J = 8.0 Hz, 1H, *m*-C_6H_3O), 6.06 (t, J = 2.5 Hz, 1H, =CH), 5.97 (s,

2H, OCH_2O), 5.55 (ddt, J = 16.0, 9.0, 5.5 Hz, 1H, C*H*=CH_2), 5.10 (d, J = 5.5 Hz, 1H, CH=CH_AH_B), 5.08 (d, J = 16.0 Hz, 1H, CH=CH_AH_B), 5.00 (s, 1H, NH), 2.71 (dd, J = 14.0, 9.0 Hz, 1H), 2.57-2.49 (m, 2H), 2.44 (s, 3H, Me), 2.41-2.37 (m, 1H), 2.31-2.23 (m, 1H), 2.21 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 147.3 (*ipso*-C_6H_3O), 146.7 (*ipso*-C_6H_3O), 143.2 (=C), 142.9 (*ipso*-$C_6H_4SO_2$), 139.5 (*ipso*-C_6H_4Me), 132.8 (=CH), 132.7 (=CH), 129.3 (*o*-$C_6H_4SO_2$), 129.1 (*ipso*-Ar), 127.0 (*m*-$C_6H_4SO_2$), 120.5 (*p*-C_6H_3O), 119.3 (=CH_2), 107.9 (CH, C_6H_3O), 107.6 (CH, C_6H_3O), 100.9 (OCH_2O), 72.0 (CN), 42.8 (CH_2), 35.7 (CH_2), 29.7 (CH_2), 21.4 (Me); MS (CI, NH_3) *m/z* 398 [$(M + H)^+$, 23] 356 (49), 227 (100), 201 (11); HRMS (CI, NH_3) *m/z* calcd for $C_{22}H_{23}NO_4S$ $(M + H)^+$ 398.1426, found 398.1421.

Using general procedure D, methoxy aziridine *cis*-**13** (104 mg, 0.3 mmol), aryl bromide **26** (0.1 mL, 1.0 mmol) and *n*-butyllithium (0.7 mL of a 1.40 M solution in hexanes, 1.0 mmol) in TBME (8 mL) gave the crude product. Purification by flash column chromatography on silica with CH_2Cl_2 as eluent gave allylic sulfonamide **15e** (73 mg, 54%) as a white solid.

_N_-{1-Allyl-2-[6-(2-triisopropylsilanyloxy-ethyl)-1,3-benzodioxol-5-yl]-cyclopent-2-enyl}-4-methyl-benzenesulfonamide 15f

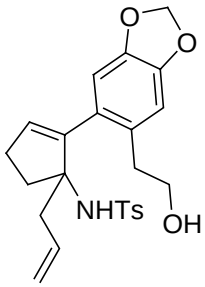


Using general procedure D, methoxy aziridine *cis*-**13** (406 mg, 1.3 mmol), aryl bromide **27** (1.6 g, 4.0 mmol) and *n*-butyllithium (1.6 mL of a 2.52 M solution in hexanes, 4.0 mmol) in Et_2O (20 mL) gave the crude product. Purification by flash column chromatography on silica with CH_2Cl_2 as eluent gave allylic sulfonamide **15f** (262 mg, 43%) as a white solid, mp 138-140 °C; R_F(CH_2Cl_2) 0.3; IR ($CHCl_3$) 3357 (NH), 2945, 2867, 1731, 1484, 1329 (SO_2), 1153 (SO_2), 1094, 909, 714, 680 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.28 (d,

J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 6.82 (s, 1H, CH, Ar), 6.76 (s, 1H, CH, Ar), 5.95 (d, J = 1.5 Hz, 1H, OCH_ACH_BO), 5.94 (d, J = 1.5 Hz, 1H, OCH_ACH_BO), 5.74 (t, J = 2.0 Hz, 1H, =CH), 5.66-5.55 (m, 1H, =C*H*CH_2), 5.13-5.06 (m, 2H, =CH_2), 4.53 (s, 1H, NH), 3.74 (t, J = 7.5 Hz, CH_2O), 2.79-2.67 (m, 2H, CH_2), 2.56 (dd, J = 14.5, 8.0 Hz, 1H), 2.52-2.37 (m, 1H), 2.42 (s, 3H, Me), 2.34-2.26 (m, 3H), 2.14-2.09 (m, 1H), 1.10-0.90 (m, 21H, C*H*Me and CH*Me*); ^{13}C NMR (100.6 MHz, C_6D_6) δ 147.0 (*ipso*-C_6H_2O), 145.7 (*ipso*-C_6H_2O), 142.9 (*ipso*-$C_6H_4SO_2$), 142.9 (=C), 140.3 (*ipso*-C_6H_4Me), 133.7 (=CH), 132.9 (=CH), 131.6 (*ipso*-Ar), 129.5 (*o*-$C_6H_4SO_2$), 127.5 (*ipso*-Ar), 126.7 (*m*-$C_6H_4SO_2$), 119.3 (=CH_2), 110.1 (CH, Ar), 109.1 (CH, Ar), 101.0 (OCH_2O), 72.7 (CN), 65.2 (CH_2O), 44.2 (CH_2), 36.8 (CH_2), 33.7 (CH_2), 30.5 (CH_2), 21.5 (Ar*Me*), 17.9 (3 x CH*Me*$_2$), 11.9 (3 x C*H*Me$_2$); MS (CI, NH_3) *m/z* 598 [$(M + H)^+$, 3] 556 (93), 427 (15), 383 (19), 253 (100), 211 (10), 189 (20), 171 (6), 108 (10); HRMS (CI, NH_3) *m/z* calcd for $C_{33}H_{48}NO_5SiS$ $(M + H)^+$ 599.3101, found 599.3086.

Using general procedure D, methoxy aziridine *cis*-**13** (144 mg, 0.5 mmol), aryl bromide **27** (564 mg, 1.4 mmol) and *n*-butyllithium (1.0 mL of a 1.40 M solution in hexanes, 1.4 mmol) in TBME (10 mL) gave the crude product. Purification by flash column chromatography on silica with CH_2Cl_2 as eluent gave allylic sulfonamide **15f** (103 mg, 37%) as a white solid.

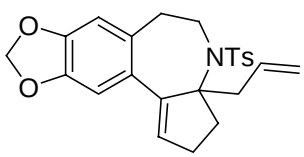
_N_-{1-Allyl-2-[6-(2-hydroxy-ethyl)-1,3-benzodioxol-5-yl]-cyclopent-2-enyl}-4-methyl-benzenesulfonamide



TBAF (0.4 mL of a 1.0 M solution in THF, 0.4 mmol) was added to a stirred solution of allylic sulfonamide **15f** (43 mg, 0.1 mmol) in THF (4 mL) at rt under N_2. The resulting mixture was

heated at reflux for 1 h then cooled to rt. Water (5 mL) and EtOAc (5 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 5 mL) and the combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with petrol-EtOAc (3:2) as eluent gave *N*-{1-Allyl-2-[6-(2-hydroxy-ethyl)-1,3-benzodioxol-5-yl]-cyclopent-2-enyl}-4-methyl-benzenesulfonamide (32 mg, 100%) as a white foam, R_F(3:2 petrol-EtOAc) 0.2; IR ($CHCl_3$) 3619 (OH), 3355 (NH), 2928, 1601, 1374, 1327 (SO_2), 1153 (SO_2), 1043, 937, 752 cm^{-1}: ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.23 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 6.80 (s, 1H, CH, Ar), 6.64 (s, 1H, CH, Ar), 5.96-5.94 (m, 2H, OCH_2O), 5.87 (s, 1H, NH), 5.70 (t, J = 2.0 Hz, 1H, =CH), 5.64 (m, 1H, C*H*=CH_2), 5.12 (d, J = 16.0 Hz, 1H, CH=CH_AH_B), 5.06 (d, J = 10.0 Hz, 1H, CH=CH_AH_B), 3.93-3.88 (m, 1H, CH_AH_B O), 3.85-3.79 (m, 1H, CH_AH_BO), 3.02 (ddd, J = 14.5, 9.0, 6.5 Hz, 1H, CHAr), 2.68-2.62 (m, 2H), 2.44-2.12 (5H), 2.41 (s, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 147.2 (*ipso*-C_6H_2O), 145.6 (*ipso*-C_6H_2O), 142.6 (=C), 142.4 (*ipso*-$C_6H_4SO_2$), 140.7 (*ipso*-C_6H_4Me), 134.7 (=CH), 133.0 (=CH), 131.8 (*ipso*-Ar), 129.4 (*o*-$C_6H_4SO_2$), 128.4 (*ipso*-Ar), 126.6 (*m*-$C_6H_4SO_2$), 119.1 (=CH_2), 109.0 (CH, Ar), 108.9 (CH, Ar), 101.0 (OCH_2O), 72.7 (C-N), 63.6 (CH_2O), 43.4 (CH_2), 35.4 (CH_2), 34.9 (CH_2), 30.7 (CH_2), 21.5 (Me); MS (CI, NH_3) *m/z* 442 [$(M + H)^+$, 23] 286 (13), 271 (100), 246 (13), 189 (42): HRMS (CI, NH_3) *m/z* calcd for $C_{24}H_{27}NO_5S$ $(M + NH_4)^+$ 459.1954, found 459.1956.

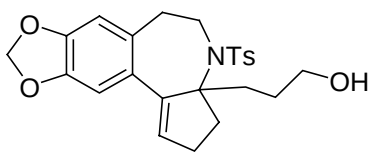
3a-Allyl-4-[(4-methylphenyl)sulfonyl]-2,3,3a,4,5,6-hexahydrocyclopenta[*a*][1,3]dioxolo[4,5-*h*][3]benzazepine 28



DIAD (0.2 mL, 0.9 mmol) was added to a stirred solution of the sulfonamido alcohol (342 mg, 0.8 mmol) and PPh_3 (244 mg, 0.9 mmol) in toluene (10 mL) at 0 °C under N_2. After being

allowed to warm to rt, the resulting solution was stirred for 14 h. Then, the solvent was evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with petrol-EtOAc (6:1) as eluent gave bicyclic sulfonamide **28** (328 mg, 100%) as a white foam, R_F(6:1 petrol-EtOAc) 0.2; IR ($CHCl_3$) 2899, 2254, 1483, 1320 (SO_2), 1247, 1153 (SO_2), 1043, 936 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 7.29 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 6.63 (s, 1H, CH, Ar), 6.48 (s, 1H, CH, Ar), 5.96 (t, J = 2.5 Hz, 1H, =CH), 5.93 (d, J = 1.5 Hz, 1H, OCH_AH_BO), 5.91 (d, J = 1.5 Hz, 1H, OCH_AH_BO), 5.47 (dddd, J = 17.0, 10.0, 8.5, 6.0 Hz, 1H, CH=CH_2), 4.99 (d, J = 17.5 Hz, 1H, CH=CH_AH_B), 4.96 (d, J = 10.5 Hz, 1H, CH=CH_AH_B), 3.70-3.68 (m, 2H), 3.33 (dd, J = 13.5, 8.5 Hz, 1H), 2.90 (dt, J = 18.0, 7.5 Hz, 1H, CH_AH_BN), 2.80 (dt, J = 18.0, 3.0, 1H, CH_AH_BN), 2.62 (ddd, J = 14.5, 9.0, 4.5 Hz, 1H), 2.50-2.45 (m, 3H), 2.43 (s, 3H, Me), 2.31-2.23 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 147.4 (*ipso*-C_6H_2O), 145.8 (*ipso*-C_6H_2O), 145.0 (=C), 142.9 (*ipso*-$C_6H_4SO_2$), 139.5 (*ipso*-C_6H_4Me), 134.0 (=CH), 133.8 (=CH), 129.5 (*ipso*-Ar), 129.5 (*o*-$C_6H_4SO_2$), 127.4 (*ipso*-Ar), 127.2 (*m*-$C_6H_4SO_2$), 118.3 (=CH_2), 110.5 (CH, Ar), 109.0 (CH, Ar), 101.0 (OCH_2O), 80.2 (C-N), 44.1 (CH_2), 43.7 (CH_2), 36.2 (CH_2), 36.1 (CH_2), 31.3 (CH_2), 21.5 (Me); MS (CI, NH_3) *m/z* 424 [$(M + H)^+$, 82] 382 (8), 270 (24), 228 (100), 189 (10), 108 (10); HRMS (CI, NH_3) *m/z* calcd for $C_{24}H_{25}NO_4S$ $(M + H)^+$ 424.1583, found 424.1577.

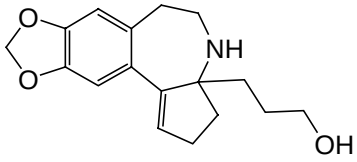
3-[4-[(4-Methylphenyl)sulfonyl]-2,4,5,6-tetrahydrocyclopenta[*a*][1,3]dioxolo[4,5-*h*][3]benzazepin-3(3*H*)-yl]-1-propanol



Using general procedure B, 9-BBN (3.1 mL of a 0.50 M solution in THF, 1.6 mmol) and bicyclic sulfonamide **28** (328 mg, 0.8 mmol) in THF (5 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-EtOAc (5:4) as eluent gave the bicyclic alcohol (320 mg, 94%) as a white foam, R_F(5:4 petrol-EtOAc) 0.2; IR ($CHCl_3$) 3623 (OH), 3020, 2930,

1483, 1322 (SO_2), 1154 (SO_2), 1042, 938, 765, 551 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.85 (d, J = 8.0 Hz, 2H, *o*-$C_6H_4SO_2$), 6.80 (d, J = 8.0 Hz, 2H, *m*-$C_6H_4SO_2$), 6.57 (s, 1H, CH, Ar), 6.23 (s, 1H, CH, Ar), 5.56 (t, J = 2.5 Hz, 1H, =CH), 5.29 (d, J = 1.0 Hz, 1H, OCH_AH$_B$O), 5.25 (d, J = 1.0 Hz, 1H, OCH$_A$$H_B$O), 3.70 (dt, J = 15.5, 3.5 Hz, 1H, CH_AH$_B$N), 3.49 (ddd, J = 15.5, 12.0, 1.5 Hz, 1H, CH$_A$$H_B$N), 3.29-3.20 (m, 2H, CH_2O), 2.92 (ddd, J = 17.5, 12.0, 3.0 Hz, 1H, CHAr), 2.79-2.67 (m, 2H), 2.45-2.35 (m, 2H), 2.22-2.14 (m, 1H), 2.06-1.95 (m, 2H), 1.90 (s, 3H, Me), 1.38-1.26 (m, 2H), 0.99 (br s, 1H, OH); ^{13}C NMR (400 MHz, C_6D_6) δ 147.9 (*ipso*-Ar), 146.4 (*ipso*-Ar), 146.3 (=C), 142.4 (*ipso*-$C_6H_4SO_2$), 140.8 (*ipso*-C_6H_4Me), 133.1 (=CH), 129.9 (*ipso*-Ar), 129.5 (*o*-$C_6H_4SO_2$), 128.2 (*ipso*-Ar), 127.7 (*m*-$C_6H_4SO_2$), 110.4 (CH, Ar), 109.5 (CH, Ar), 101.0 (OCH_2O), 81.2 (CN), 62.8 (CH_2O), 44.4 (CH_2N), 37.4 (CH_2), 36.6 (CH_2), 36.2 (CH_2), 31.3 (CH_2), 28.5 (CH_2), 21.1 (Ar*Me*); MS (CI, NH_3) *m/z* 442 [$(M + H)^+$, 100] 424 (18), 288 (76), 264 (93), 189 (80), 108 (26); HRMS (CI, NH_3) *m/z* calcd for $C_{24}H_{27}NO_5S$ $(M + H)^+$ 442.1689, found 442.1691.

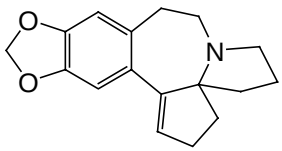
3-[2,4,5,6-tetrahydrocyclopenta[*a*][1,3]dioxolo[4,5-*h*][3]benzazepin-3(3*H*)-yl]-1-propanol 29



A solution of naphthalene (94 mg, 0.7 mmol) in THF (3 mL) was added *via* canula to a stirred suspension of Na metal (17 mg, 0.7 mmol) in THF (1 mL) at rt under Ar and stirred for 4 h. The resulting dark green solution was cooled to -78 ºC, then a solution of the bicyclic alcohol (54 mg, 0.1 mmol) in THF (2 mL) was added *via* canula. The resulting mixture was stirred at -78 ºC for 5 min, MeOH (0.3 mL) was added and the mixture was allowed to warm to rt. Water (2 mL) and CH_2Cl_2 (2 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 2 mL) and the combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with CH_2Cl_2-MeOH-$NH_{3(aq)}$ (90:9.5:0.5) as eluent gave bicyclic amino alcohol **29** (21 mg,

60%) as a cloudy oil, R_F(90:9.5:0.5 CH_2Cl_2-MeOH-$NH_{3(aq)}$) 0.3; IR ($CHCl_3$) 3604 (OH), 3451 (NH), 3030, 2960, 1731, 1482, 1249, 1045, 909, 849, 746, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.61 (s, 1H, CH, Ar), 6.58 (s, 1H, CH, Ar), 5.94 (d, J = 1.5 Hz, 1H, OCH_AH$_B$O), 5.92 (d, J = 1.5 Hz, 1H, OCH$_A$$H_B$O), 5.64 (t, J = 2.0 Hz, 1H, =CH), 3.65-3.60 (m, 1H), 3.47-3.41 (m, 1H), 3.10-2.90 (m, 3H), 2.69-2.59 (m, 2H), 2.36 (ddt, J = 17.0, 9.5, 3.0 Hz, 1H), 2.22 (ddd, J = 13.5, 9.5, 6.5 Hz, 1H), 1.90-1.66 (m, 3H), 1.63-1.57 (m, 1H), 1.42-1.37 (m, 1H), 1.27-1.24 (m, 1H), 0.90-0.83 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 151.4 (=C), 146.5 (*ipso*-Ar), 145.8 (*ipso*-Ar), 132.2 (*ipso*-Ar), 130.8 (*ipso*-Ar), 128.5 (=CH), 109.8 (CH, Ar), 109.5 (CH, Ar), 68.0 (CN), 62.8 (CH_2O), 41.1 (CH_2), 39.6 (CH_2), 37.5 (CH_2), 34.1 (CH_2), 29.5 (CH_2), 28.3 (CH_2); MS (CI, NH_3) *m/z* 288 [$(M + H)^+$, 100] 228 (9), 102 (31), 85 (13); HRMS (CI, NH_3) *m/z* calcd for $C_{17}H_{21}NO_3S$ $(M + H)^+$ 288.1600, found 288.1598.

2,3,5,6,8,9-hexahydro-4*H*-cyclopenta[*a*][1,3]dioxolo[4,5-*h*]pyrrolo[2,1-*b*][3]benzazepine 21



PPh_3 (16 mg, 0.1 mmol) was added in one portion to stirred solution of bicyclic amino alcohol **30** (15 mg, 0.1 mmol), CBr_4 (20 mg, 0.1 mmol), imidazole (4 mg, 0.1 mmol) and Et_3N (15 µL, 0.1 mmol) in CH_2Cl_2 (2 mL) at rt under Ar. The resulting solution was stirred at rt for 20 h, then water (2 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 2 mL) and the combined organics were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with CH_2Cl_2-MeOH-$NH_{3(aq)}$ (95:4.5:0.5) as eluent gave synthetic target **21** (10 mg, 71%) as a pale yellow oil, R_F(95:4.5:0.5 CH_2Cl_2-MeOH-$NH_{3(aq)}$) 0.2; IR ($CHCl_3$) 2937, 1503, 1378, 1219, 1043, 903, 730, 642 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.65 (s, 1H, CH, Ar), 6.60 (s, 1H, CH, Ar), 5.92 (d, J = 1.5 Hz, 1H, OCH_AH$_B$O), 5.90 (d, J = 1.5 Hz, 1H, OCH$_A$$H_B$O), 5.71 (dd, J = 2.5, 2.0 Hz, 1H, =CH), 3.44 (ddd, J = 15.0, 11.0, 4.0 Hz, 1H), 3.25 (ddd, J = 17.0, 11.0, 4.5 Hz,

1H), 3.00 (dt, J = 14.5, 4.5 Hz, 1H), 2.93-2.86 (m, 3H), 2.46-2.39 (m, 1H), 2.24 (dtd, J = 16.0, 8.0, 2.0 Hz, 1H), 1.98-1.94 (m, 2H), 1.83-1.72 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 150.0 (=C), 146.9 (*ipso*-Ar), 145.5 (*ipso*-Ar), 145.5 (*ipso*-Ar), 130.9 (*ipso*-Ar), 129.0 (=CH), 128.9 (*ipso*-Ar), 110.0 (CH, Ar), 109.4 (CH, Ar), 100.9 (OCH_2O), 78.5 (CN), 49.5 (CH_2N), 44.1 (CH_2N), 40.1 (CH_2), 35.2 (CH_2), 32.7 (CH_2), 29.2 (CH_2), 23.9 (CH_2); MS (CI, NH_3) *m/z* 270 [(M + H)$^+$, 100]; HRMS (CI, NH_3) *m/z* calcd for $C_{17}H_{19}NO_2$ (M + H)$^+$ 270.1494, found 270.1491.

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