ELECTRONIC SUPPLEMENTARY MATERIAL

Synthesis of the ABC tricyclic fragment of the pectenotoxins via stereocontrolled cyclization of a γ-hydroxyepoxide appended to the AB spiroacetal unit.

Rosliana Halim, Margaret A. Brimble* and Jörn Merten

Department of Chemistry, University of Auckland, 23 Symonds St., Auckland, New Zealand.

FAX: +64 9 3737422; EMAIL: m.brimble@auckland.ac.nz

Experimental

General

All reactions were carried out under an N_2 atmosphere using oven-dried glassware using standard syringe and septum techniques, unless otherwise stated. Diethyl ether and tetrahydrofuran were distilled from Na/benzophenone under N_2. Hexane, CH_2Cl_2, and NEt_3 were distilled from CaH_2 under N_2. Butyllithium (1.6 M in hexane) was purchased from the Aldrich Chemical Co. Flash chromatography was performed using Riedel-de Häen or Merck 0.032-0.063mm silica gel and preparative layer chromatography with Merck silica gel 60 PF on glass plates, with the indicated solvents. Analytical TLC was performed with 0.20mm silica gel 60 aluminium-backed plates and analyzed using 365 nm ultraviolet irradiation followed by staining with either alkaline permanganate or vanillin solution. High resolution mass spectra were obtained using EI, CI and FAB techniques on a VG70-SE spectrometer. NMR spectra were recorded on either a Bruker DRX300 spectrometer operating at 300 MHz for ^1H nuclei and 75 MHz for ^{13}C nuclei or on a Bruker DRX400 spectrophotometer operating at 400 MHz for ^1H nuclei and 100 MHz for ^{13}C nuclei. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were determined on a Perkin-Elmer 341 polarimeter.

(2'*R*, 3'*S*, 4*R*, 5*S*)-(+)-3-(7'-Benzyloxy-3'-hydroxy-2'-methylheptanoyl)-4-methyl-5-phenyloxazolidin-2-one (*syn*-adduct 17)

To a solution of (4*R*, 5*S*)-(+)-4-methyl-3-(1'-oxopropyl)-5-phenyloxazolidin-2-one[i] (1.22 g, 5.2 mmol) in dry CH_2Cl_2 (40 mL) at 0 ˚C under N_2 was slowly added $TiCl_4$ (5.0 mL, 1 M solution in CH_2Cl_2, 5 mmol). The orange mixture was stirred at 0 ˚C for 5 min followed by the addition of (–)-sparteine (1.20 mL, 5.2 mmol) to form a dark red enolate. The mixture was stirred at 0 ˚C for 20 min then cooled to –78 ˚C. *N*-Methyl-2-pyrrolidone (0.50, 5.2 mmol) was added and the mixture was stirred for 10 min followed by the addition of 5-benzyloxypentanal[ii] (1.18 g, 6.1 mmol) in dry CH_2Cl_2 (25 mL). The mixture was stirred at –78˚C for 1 h, warmed to 0˚C then stirred for 1 hr. During this time, the colour of the mixture changed from dark red to light brown. The reaction was quenched with 50% aqueous NH_4Cl (15 mL) and warmed to room temperature. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The organic layers were combined, washed with brine (2 × 30 mL) and dried over Na_2SO_4. The solvent was evaporated to give a residual pale yellow oil. The crude product was purified by flash chromatography using hexane-ethyl acetate (4:1) to afford the *title compound* **17** (1.92 g, 90%) as a colourless oil; $[\alpha]_D$ +7.7° (c=1.02, CH_2Cl_2); Found: MH^+, 426.2261, $C_{25}H_{32}NO_5$ requires 426.2281; ν_{max} (film)/cm^{-1} 3518 (OH), 1780s (OC=O), 1698m (NC=O), 1364m; δ_H (300 MHz, $CDCl_3$) 0.87 (3H, d, *J* 6.6 Hz, 4-Me), 1.23 (3H, d, *J* 6.9 Hz, 2'-Me), 1.44-1.67 (6H, m, H-4', H-5', H-6'), 3.0 (1H, br, OH), 3.48 (2H, t, *J* 6.3 Hz, H-7'), 3.78 (1H, dq, *J* 3.0, 6.9 Hz, H-2'), 3.95 (1H, m, H-3'), 4.49 (2H, s, *CH*$_2$Ph), 4.76 (1H, pentet, *J* 6.6 Hz, H-4), 5.64 (1H, d, *J* 7.3 Hz, H-5), 7.26-7.40 (10H, m, 2 × Ph); δ_C (75 MHz, $CDCl_3$) 10.2 (CH_3, Me), 14.2 (CH_3, Me), 20.8 (CH_2, C-5'), 29.4 (CH_2, C-4'), 33.6 (CH_2, C-6'), 42.2 (CH, C-2'), 54.6 (CH, C-4), 70.1 (CH_2, C-7'), 71.4 (CH, C-3'), 72.7 (CH_2, *CH*$_2$Ph), 78.7 (CH, C-5), 125.5 (CH, Ph), 127.3 (CH, *p*-Ph), 127.4 (CH, Ph), 128.2 (CH, Ph), 128.5 (CH, Ph), 128.6 (CH, *p*-Ph), 133.0 (C, Ph), 138.5 (C, Ph), 152.5 (C, C-2), 176.9 (C, C-1'); *m/z* 426 (MH^+, 0.05%), 319 (MH-OCH_2Ph, 0.5%), 107 (OCH_2Ph, 56%), 91 (CH_2Ph, 100%).

(2'*R*, 3'*S*, 4*R*, 5*S*)-(+)-3-(7'-Benzyloxy-3'-hydroxy-2'-methylheptanoyl)-4-methyl-5-phenyloxazolidin-2-thione (Evans *syn*-adduct 18), (2'*S*, 3'*R*, 4*R*, 5*S*)-(+)-3-(7'-Benzyloxy-3'-hydroxy-2'-methylheptanoyl)-4-methyl-5-phenyloxazolidin-2-thione (non-Evans *syn*-adduct 19) and (2'*S*, 3'*S*, 4*R*, 5*S*)-(+)-3-(7'-Benzyloxy-3'-hydroxy-2'-methylheptanoyl)-4-methyl-5-phenyloxazolidin-2-thione (*anti*-adduct 20)

To a solution of oxazolidinethione **15**[iii] (120 mg, 0.48 mmol) in dry CH_2Cl_2 (2 mL) at 0 ˚C was slowly added neat $TiCl_4$ (0.053 mL, 0.48 mmol). The orange mixture was stirred at 0 ˚C for 5 min followed by the addition of (–)-sparteine (0.28 mL, 1.2 mmol) to form a dark red enolate. The red mixture was stirred at 0˚C for 20 min then cooled to –78 ˚C. 5-Benzyloxypentanal[ii] (110 mg, 0.57 mmol) in dry CH_2Cl_2 (2 mL) was added slowly and the mixture was stirred at –78 ˚C for 1 h and then at 0 °C for 1 hr. The reaction was quenched with 50% aqueous NH_4Cl (5 mL) and warmed to room temperature. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The organic layers were combined, washed with brine (2 × 20 mL) and dried over $MgSO_4$. The solvent was evaporated to give the crude mixture which was purified by flash chromatography using hexane-ethyl acetate (4:1) to afford the Evans *syn*-isomer **18** (96 mg, 46%) as yellow oil together with the non-Evans *syn*-isomer **19** (43 mg, 20%) and *anti*-isomer **20** (20 mg, 10%);

18: $[\alpha]_D$ +35.6° (c=0.82, $CHCl_3$); Found: MH^+, 442.2062, $C_{25}H_{32}NO_4S$ requires 442.2052; ν_{max} (cm^{-1}) 3435br (OH), 1692s (C=O), 1377s; δ_H (300 MHz, $CDCl_3$) 0.94 (3H, d, *J* 6.6 Hz, Me), 1.23 (3H, d, *J* 7.0 Hz, Me), 1.45-1.71 (6H, m, H-4', H-5' and H-6'), 2.79 (1H, d, *J* 2.4 Hz, OH), 3.49 (2H, t, *J* 6.2 Hz, H-7'), 4.09 (1H, m, H-3'), 4.51 (2H, s, *CH*$_2$Ph), 4.81 (1H, dq, *J* 2.6, 7.0 Hz, H-3'), 5.00 (1H, pentet, *J* 6.6 Hz, H-4), 5.75 (1H, d, *J* 7.2 Hz, H-5), 7.25-7.43 (10H, m, 2 × Ph); δ_C (75 MHz, $CDCl_3$) 10.4 (CH_3, Me), 14.2 (CH_3, Me), 22.6 (CH_2, C-5'), 29.6 (CH_2, C-4'), 33.5 (CH_2, C-6'), 41.9 (CH, C-2'), 59.1 (CH, C-4), 70.2 (CH_2, C-7'), 71.2 (CH, C-3'), 72.9 (CH_2, *CH*$_2$Ph), 83.0 (CH, C-5), 125.8 (CH, Ph), 127.5 (CH, Ph), 127.6 (CH, Ph), 128.3 (CH, Ph), 128.7 (CH, Ph), 129.0 (CH, Ph), 132.2 (C, Ph), 138.5 (C, Ph), 178.2 (C, C-1'), 184.9 (C, C-2); *m/z* (CI) 442 (MH^+, 1%), 250 (36%), 194 (45%), 91 (CH_2Ph, 43%), 85 (SCNCO, 100%).

19: $[\alpha]_D$ +53.6° (c=1.2, $CHCl_3$); Found: MH^+, 442.2043, $C_{25}H_{32}NO_4S$ requires 442.2052; ν_{max} (cm^{-1}) 3432br (OH), 1698s (C=O), 1375s; δ_H (300 MHz, $CDCl_3$) 0.92 (3H, d, *J* 6.6 Hz, Me), 1.26 (3H, d, *J* 6.9 Hz, Me), 1.44-1.68 (6H, m, H4', H-5' and H-6'), 2.91 (1H, d, *J* 21Hz, OH), 3.50 (2H, t, *J* 6.2 Hz, H-7'), 4.05 (1H, m, H-3'), 4.51 (2H, s, *CH*$_2$Ph), 4.68 (1H, dq, *J* 2.8, 6.9 Hz, H-2'), 5.00 (1H, pentet, *J* 6.6 Hz, H-4), 5.75 (1H, d, *J* 7.2 Hz, H-5), 7.25-7.43 (10H, m, 2 × Ph); δ_C (75 MHz, $CDCl_3$) 10.1 (CH_3, Me), 14.0 (CH_3, Me), 22.7 (CH_2, C-5'), 29.6 (CH_2, C-4'), 33.8 (CH_2, C-6'), 42.1 (CH, C-2'), 59.0 (CH, C-4), 70.2 (CH_2, C-7'), 71.4 (CH, C-3'), 72.9 (CH_2, *CH*$_2$Ph), 83.1 (CH, C-5), 125.8 (CH, Ph), 127.5 (CH, Ph), 127.6 (CH, Ph), 128.3 (CH, Ph), 128.7 (CH, Ph), 129.0 (CH, Ph), 132.3 (C, Ph), 138.6 (C, Ph), 178.3 (C, C-2'), 184.8 (C, C-2); *m/z* (CI) 442 (MH^+, 1.5%), 427 (MH-CH_3, 2%), 250 (38%), 194 (100%), 178 (87%), 91 (CH_2Ph, 84%), 84 (SCNCO, 99%).

20: $[\alpha]_D$ +1.86° (c=1.05, $CHCl_3$); Found: MH^+, 442.2045, $C_{25}H_{32}NO_4S$ requires 442.2052; ν_{max} (cm^{-1}) 3436br (OH), 1680s (C=O); δ_H (300 MHz, $CDCl_3$) 0.95 (3H, d, *J* 6.6 Hz, Me), 1.15 (3H,

d, *J* 6.9 Hz, Me), 1.22-1.70 (6H, m, H-4', H-5' and H-6'), 2.85 (1H, d, *J* 9.3 Hz, OH), 3.49 (2H, t, *J* 6.1 Hz, H-7'), 3.74 (1H, q, *J* 7.6 Hz, H-3'), 4.51 (2H, s, CH_2Ph), 4.89 (1H, pentet, *J* 6.9 Hz, H-2'), 5.02 (1H, pentet, *J* 6.6 Hz, H-4), 5.75 (1H, d, *J* 7.1 Hz, H-5), 7.25-7.44 (10H, m, 2 × Ph); δ_C (75 MHz, $CDCl_3$) 14.1 (CH_3, Me), 14.9 (CH_3, Me), 22.2 (CH_2, C-5'), 29.6 (CH_2, C-4'), 34.6 (CH_2, C-6'), 43.1 (CH, C-2'), 59.3 (CH, C-4), 70.2 (CH_2, C-7'), 72.9 (CH, C-3'), 72.9 (CH_2, CH_2Ph) 83.2 (CH, C-5), 125.8 (CH, Ph), 127.6 (CH, Ph), 127.7 (CH, Ph), 128.3 (CH, Ph), 128.7 (CH, Ph), 129.0 (CH, Ph), 132.1 (C, Ph), 138.5 (C, Ph), 177.5 (C, C-1'), 185.6 (C, C-2); *m/z* (CI) 442 (MH^+, 0.2%), 194 (63%), 91(CH_2Ph, 100%), 85 (SCNCO, 99%).

(2*S*, 3*S*)-(+)-7-Benzyloxy-2-methylheptane-1,3-diol 21

To a solution of *syn*-adduct **17** (310 mg, 0.73 mmol) in dry THF (4 mL) at 0 °C was added $LiBH_4$ (23 mg, 1.1 mmol) and the reaction mixture was stirred at room temperature for 5 min. Water (2 mL) was added and the mixture concentrated under reduced pressure. The residue was extracted with ethyl acetate (3 × 5 mL), dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The crude product was purified by flash chromatography using hexane-ethyl acetate (3:2) as eluent to afford the *title compound* **21** (160 mg, 87%) as a yellow oil; $[\alpha]_D$ +11.5° (c=0.8, $CHCl_3$); Found: MH^+, 253.1804, $C_{15}H_{26}O_3$ requires 253.1803; ν_{max} (film)/cm^{-1} 3390 (br, OH); δ_H (300 MHz, $CDCl_3$) 0.89 (3H, d, *J* 7.1 Hz, Me), 1.26 (1H, m, H-2), 1.41-1.67 (6H, m, H-4, H-5, H-6), 2.50 (2H, br, OH), 3.49 (2H, t, *J* 6.3 Hz, H-7), 3.68 (2H, d, *J* 5.4 Hz, H-1), 3.81 (1H, m, H-3), 4.50 (2H, s, CH_2Ph), 7.26-7.39 (5H, m, Ph); δ_C (75 MHz, $CDCl_3$) 10.1 (CH_3, Me), 22.9 (CH_2, C-5), 29.6 (CH_2, C-4), 33.7 (CH_2, C-6), 39.1 (CH, C-2), 67.1 (CH_2, C-1), 70.3 (CH_2, C-7), 72.9 (CH_2, CH_2Ph), 74.3 (CH, C-3), 127.5 (CH, p-Ph), 127.6 (CH, Ph), 128.3 (CH, Ph), 138.5 (C, Ph); *m/z* (CI) 253 (MH^+, 72%), 235 (MH-H_2O, 37%), 217 (MH-H_2O-H_2O, 28%), 145 (M-OCH_2Ph, 27%), 91 (CH_2Ph, 100%).

(2*S*, 3*S*)-(–)-7-Benzyloxy-1-*tert*-butyldiphenylsilyloxy-2-methylheptan-3-ol 22

To a solution of *tert*-butyldiphenylsilyl chloride (0.20 mL, 0.77 mmol) and imidazole (81 mg, 1.2 mmol) in dry dichloromethane (5 mL) at 0 °C was added a solution of diol **21** (150 mg, 0.60 mmol) in dry dichloromethane (5 mL). The reaction mixture was stirred at room temperature overnight. The mixture was diluted with dichloromethane (20 mL), washed with saturated solution of $NaHCO_3$ (1 × 5 mL), brine (2 × 5 mL) and dried over $MgSO_4$. The solvent was

evaporated under reduced pressure to give the crude product which was purified by flash chromatography using hexane-ethyl acetate (9:1) as eluent to afford the *title compound* **22** (220 mg, 77%) as a colourless oil; $[\alpha]_D$ –3.0° (c=0.73, $CHCl_3$); Found: MH^+, 491.2982, $C_{31}H_{43}O_3Si$ requires 491.3007; ν_{max} (film)/cm^{-1} 3479br (OH), 1265s (Si-O-C); δ_H (300 MHz, $CDCl_3$) 0.89 (3H, d, *J* 7.1 Hz, Me), 1.06 (9H, s, ^{t}Bu), 1.25-1.66 (7H, m, H-2, H-4, H-5, H-6), 2.74 (1H, br, OH), 3.49 (2H, t, *J* 6.4 Hz, H-7), 3.67 (1H, dd, *J* 5.9, 10.0 Hz, H-1A), 3.75 (1H, dd, *J* 4.3, 10.0 Hz, H-1B), 3.86 (1H, m, H-3), 4.50 (2H, s, *CH*$_2$Ph), 7.25-7.44 (11H, m, Ph), 7.64-7.69 (4H, m, Ph); δ_C (75 MHz, $CDCl_3$) 10.2 (CH_3, Me), 19.2 (C, ^{t}Bu), 22.9 (CH_2, C-5), 26.9 (CH_3, ^{t}Bu), 29.8 (CH_2, C-4), 34.0 (CH_2, C-6), 39.1 (CH, C-2), 68.7 (CH_2, C-1), 70.4 (CH_2, C-7), 72.9 (CH_2, *CH*$_2$Ph), 74.1 (CH, C-3), 127.5 (CH, p-Ph), 127.6 (CH, Ph), 127.8 (CH, Ph), 128.3 (CH, Ph), 129.78 (CH, p-Ph), 129.82 (CH, p-Ph), 133.0 (C, Ph), 133.1 (C, Ph), 135.6 (CH, Ph), 135.7 (CH, Ph), 138.7 (C, Ph); *m/z* (CI) 491 (MH^+, 23%), 196 (100%), 91 (CH_2Ph, 81%).

(2*S*, 3*S*)-(+)-7-Benzyloxy-1-*tert*-butyldiphenylsilyloxy-3-*tert*-butyldimethylsilyloxy-2-methylheptane 23

To a mixture of 2,6-lutidine (0.09 mL, 0.8 mmol), 4-(dimethylamino)pyridine (49 mg, 0.4 mmol) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.12 mL, 0.5 mmol) in dry DMF (5 mL) at 0 °C was added a solution of alcohol **22** (217 mg, 0.4 mmol) in dry DMF (10 mL). The mixture was stirred at room temperature overnight then the solvent was evaporated under reduced pressure. The residue was diluted with Et_2O (20 mL), washed with brine (2 × 10 mL), water (2 × 10 mL) and dried over Na_2SO_4. Removal of the solvent by evaporation under reduced pressure yielded the crude product that was purified by flash chromatography using hexane-ethyl acetate (95:5) as eluent to afford the *title compound* **23** (230 mg, 95%) as a colourless oil; $[\alpha]_D$ +1.8° (c = 1.025, $CHCl_3$); Found: MH^+, 605.3846, $C_{37}H_{57}O_3Si_2$ requires 605.3846; ν_{max} (cm^{-1}) 1252s (Si-O-C); δ_H (300 MHz, $CDCl_3$) –0.02 (3H, s, *Me*$_2$^{t}BuSi), 0.01 (3H, s, *Me*$_2$^{t}BuSi), 0.81 (3H, d, *J* 7.1 Hz, Me), 0.84 (9H, s, Me$_2$*^{t}Bu*Si), 1.05 (9H, s, *^{t}Bu*Ph$_2$Si), 1.25-1.41 (6H, m, H-4, H-5, H-6), 1.58 (1H, m, H-2), 3.45 (2H, t, *J* 6.5 Hz, H-7), 3.48 (1H, dd, *J* 6.7, 9.8 Hz, H-1A), 3.61 (1H, dd, *J* 6.7, 9.8 Hz, H-1B), 3.81 (1H, dt, *J* 3.0, 6.2 Hz, H-3), 4.49 (2H, s, *CH*$_2$Ph), 7.2-7.4 (11H, m, Ph), 7.6-7.7 (4H, m, Ph); δ_C (75 MHz, $CDCl_3$) –4.6 (CH_3, *Me*$_2$^{t}BuSi), –4.1 (CH_3, *Me*$_2$^{t}BuSi), 10.6 (CH_3, Me), 18.1 (C, *^{t}Bu*Me$_2$Si), 19.3 (C, *^{t}Bu*Ph$_2$Si), 22.4 (CH_2, C-5), 25.9 (CH_3, *^{t}Bu*Me$_2$Si), 26.9 (CH_3, *^{t}Bu*Ph$_2$Si), 29.9 (CH_2, C-4), 34.4 (CH_2, C-6), 39.9 (CH, C-2), 66.3 (CH_2, C-1), 70.4 (CH_2, C-7), 72.0 (CH, C-3), 72.9 (CH_2, *CH*$_2$Ph), 127.6

(CH, Ph), 128.3 (CH, p-Ph), 129.5 (CH, p-Ph), 134.08 (CH, Ph), 134.1 (C, Ph), 135.6 (CH, Ph), 138.7 (C, Ph); *m/z* (CI) 605 (MH^+, 18%), 547 (M-^{t}Bu, 4%), 217 (100%), 91 (CH_2Ph, 56%).

(5*S*, 6*S*)-(+)–5-*tert*-Butyldimethylsilyloxy-1-*tert*-butyldiphenylsilyloxy-6-methylheptan-1-ol 24

A mixture of (2*S*, 3*S*)-(+)-7-benzyloxy-1-*tert*-butyldiphenylsilyloxy-3-*tert*-butyldimethylsilyloxy-2-methylheptane **23** (0.441 g, 0.73 mmol) and 10% palladium on carbon (catalytic amount) in methanol (10 mL) was stirred under a hydrogen atmosphere overnight. The mixture was filtered through Celite® and the solvent evaporated under reduced pressure. The crude product was purified by flash chromatography using hexane-ethyl acetate (95:5) as eluent to give the *title compound* **24** (0.37 g, 99%) as a colourless oil; $[\alpha]_D$ +3.1° (c=0.88, $CHCl_3$); Found: MH^+, 515.3383, $C_{30}H_{51}O_3Si_2$ requires 515.3377; ν_{max} (cm^{-1}) 3369br (OH), 1252s (Si-O-C); δ_H (300 MHz, $CDCl_3$) –0.02 (3H, s, Me_2^{t}BuSi), 0.02 (3H, s, Me_2^{t}BuSi), 0.84 (12H, s, Me_2^{t}*Bu*Si and Me), 1.05 (9H, s, ^{t}*Bu*Ph_2Si), 1.04-1.60 (6H, m, H-2, H-3, H-4), 1.74 (1H, m, H-6), 3.47 (1H, dd, *J* 6.7, 9.8 Hz, H-7A), 3.59-3.64 (2H, m, H-7B, H-1), 3.81 (1H, td, *J* 6.2, 3.2 Hz, H-5), 7.33-7.42 (6H, m, Ph), 7.63-7.68 (4H, m, Ph); δ_C (75MHz, $CDCl_3$) –4.6 (CH_3, Me_2^{t}BuSi), –4.1 (CH_3, Me_2^{t}BuSi), 10.7 (CH_3, Me), 18.1 (C, ^{t}*Bu*Me_2Si), 19.3 (C, ^{t}*Bu*Ph_2Si), 25.9 (CH_3, ^{t}*Bu*Me_2Si), 26.9 (CH_3, ^{t}*Bu*Ph_2Si), 29.7 (CH_2, C-4), 32.9 (CH_2, C-3), 34.3 (CH_2, C-2), 29.9 (CH, C-6), 63.0 (CH_2, C-1), 66.2 (CH_2, C-7), 72.0 (CH, C-5), 127.6 (CH, Ph), 129.5 (CH, Ph), 134.07 (C, Ph), 135.6 (CH, Ph); *m/z* (CI) 515 (MH^+, 1%), 325 (65%), 109 (100%).

(5*S*, 6*S*)-(+)–5-*tert*-Butyldimethylsilyloxy-1-*tert*-butyldiphenylsilyloxy-6-methylheptan-1-al 12

A mixture of alcohol **24** (0.643 g, 1.25 mmol), pyridinium chlorochromate (0.40 g, 1.87 mmol) and potassium carbonate (0.5 g) in dry dichloromethane (20 mL) was stirred at room temperature. After 3 h, the mixture was filtered through a pad of Celite® and silica gel. The solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography using hexane-ethyl acetate (95:5) as eluent to afford the *title compound* **12** (0.63 g, 99%) as a colourless oil, $[\alpha]_D$ +1.7° (c = 1.39, $CHCl_3$); Found: MH^+, 513.3230, $C_{30}H_{49}O_3Si_2$ requires 513.3230; ν_{max} (cm^{-1}) 1727s (C=O), 1252s (Si-O-C); δ_H (300 MHz, $CDCl_3$) –0.01 (3H, s, Me_2^{t}BuSi), 0.02 (3H, s, Me_2^{t}BuSi), 0.81 (3H, s, Me), 0.84 (9H, s,

$Me_2{}^tBu$Si), 1.05 (9H, s, ^tBuPh$_2$Si), 1.35-1.60 (4H, m, H-3, H-4), 1.74 (1H, m, H-6), 2.38 (2H, td, *J* 7.2, 1.7 Hz, H-2), 3.47 (1H, dd, *J* 6.6, 9.9 Hz, H-7A), 3.62 (1H, dd, *J* 6.6, 9.9 Hz, H-7B), 3.81 (1H, td, *J* 3.4, 5.9 Hz, H-5), 7.33-7.44 (6H, m, Ph), 7.62-7.67 (4H, m, Ph), 9.73 (1H, t, *J* 1.7 Hz, H-1); δ_C (75 MHz, $CDCl_3$) –4.6 (CH_3, $Me_2{}^tBu$Si), –4.2 (CH_3, $Me_2{}^tBu$Si), 10.9 (CH_3, Me), 18.1 (C, $Me_2{}^tBu$Si), 18.4 (CH_2, C-3), 19.2 (C, ^tBuPh$_2$Si), 25.9 (CH_3, ^tBuMe$_2$Si), 26.9 (CH_3, ^tBuPh$_2$Si), 34.0 (CH_2, C-4), 40.0 (CH, C-6), 43.9 (CH_2, C-2), 66.0 (CH_2, C-7), 71.9 (CH, C-5), 127.58 (CH, Ph), 127.60 (CH, Ph), 129.52 (CH, Ph), 129.54 (CH, Ph), 134.0 (C, Ph), 135.6 (CH, Ph), 202.4 (CH, C-1); *m/z* 513 (MH^+, 27%), 455 (M-^{t}Bu, 54%), 381 (M-^{t}BuMe$_2$SiO, 100).

(*S*)-(–)-[4-Benzyloxy-3-(*tert*-butyldimethylsilyloxy)butane]-1-sulfonylbenzene 13

To a solution of methyl phenyl sulfone (0.22 g, 1.39 mmol) in dry THF (6 mL) at –78 °C was added BuLi (0.96 mL, 1.6 M solution in hexane, 1.53 mmol) and the light brown solution was stirred at –78 °C for 10 min then at room temperature for 30 min. Hexamethylphosphoramide (0.53 mL, 3.06 mmol) and a solution of epoxide **25**[iv] (0.2 g, 1.22 mmol) in dry THF (2 mL) were added at room temperature. The resultant clear bright yellow solution was stirred for 1.5 hr, then cooled to 0 °C. A premixed solution of *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.35 mL, 1.53 mmol) and 2,6-lutidine (0.24 mL, 2.09 mmol) in dry THF (2 mL, 2 × 1 mL wash) was added to the reaction mixture via cannula. A white precipitate formed that disappeared after 15 min. The mixture was stirred at 0 °C for 2.5 h then quenched with saturated NH_4Cl solution (3 mL). The organic phase was separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine (2 × 20 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the crude mixture was purified by flash chromatography using hexane-ethyl acetate (95:5) as eluent to afford the title compound **13** (0.58 g, 97%) as a yellow oil; $[\alpha]_D$ –14.2° (c=1.6, $CHCl_3$); Found: $M^{+\cdot}$, 434.1943, $C_{22}H_{34}O_4SSi$ requires 434.1947; ν_{max} (cm^{-1}) 1447m, 1307s (SO_2Ph), 1255s (Si-O-C), 1146s (SO_2Ph); δ_H (400 MHz, $CDCl_3$) –0.012 (3H, s, $Me_2{}^tBu$Si), 0.02 (3H, s, $Me_2{}^tBu$Si), 0.82 (9H, s, ^tBu), 1.84-1.96 (2H, m, H-2), 3.17 (2H, m, H-1), 3.23 (1H, dd, *J* 6.6, 9.5 Hz, H-4A), 3.36 (1H, dd, *J* 5.2, 9.5 Hz, H-4B), 3.91 (1H, m, H-3), 4.43 and 4.48 (2H, AB, J_{AB} 11.9 Hz, CH_2Ph), 7.23-7.35 (5H, m, CH_2Ph), 7.55 (2H, m, SO_2Ph), 7.63 (1H, m, SO_2Ph), 7.89 (2H, m, SO_2Ph); δ_C (75 MHz, $CDCl_3$) –4.99 (CH_3, $Me_2{}^tBu$Si), –4.6 (CH_3, $Me_2{}^tBu$Si), 18.0 (C, $Me_2{}^tBu$Si), 25.7 (CH_3, $Me_2{}^tBu$Si), 27.8 (CH_2, C-2), 52.1 (CH_2, C-1), 69.1 (CH, C-3), 73.31 (CH_2, C-4 or CH_2Ph), 73.38 (CH_2, CH_2Ph or C-4), 127.6 (CH, Ph), 127.7 (CH, Ph), 128.1 (CH,

Ph), 128.4 (CH, Ph), 129.2 (CH, Ph), 133.6 (CH, Ph), 137.9 (C, Ph), 139.0 (C, Ph); *m/z* 434 (M^+, 0.3%), 171 (10%), 143 (18%), 91 (CH_2Ph, 100%).

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