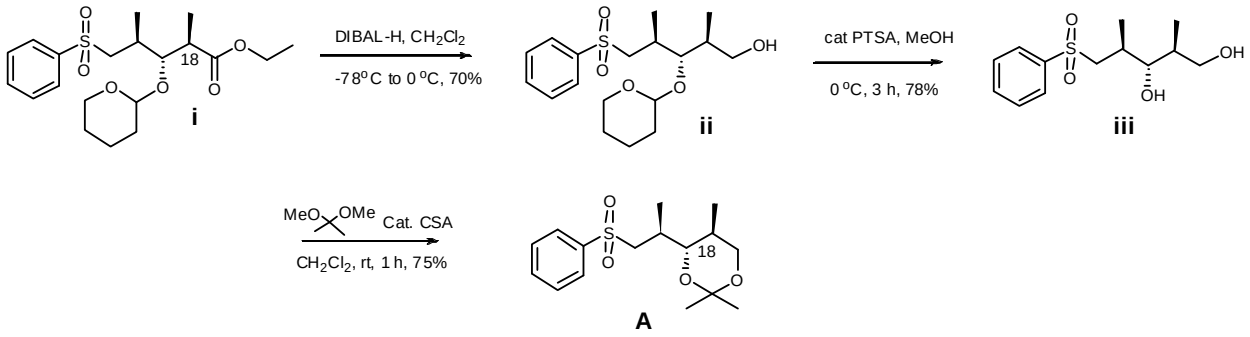
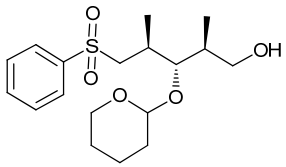
Supplementary Information

The relative stereochemistry at C17-C18 in **16** was established by conversion to acetonide '**A**' as depicted in the Scheme below.

Scheme



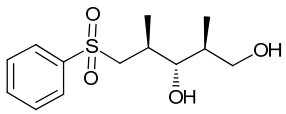
(2*S*,3*S*,4*S*)-2,4-Dimethyl-5-(phenylsulfonyl)-3-((tetrahydro-2*H*-pyran-2-yl)oxy)pentane-1-ol (ii)



To the solution of sulfone **i**, prepared from sulfoxide **16** as detailed above, (198 mg, 0.5 mmol, 1 eq) in anhydrous dichloromethane (5 mL) under N_2 atmosphere, cooled at -78 °C, DIBAL-H (1.4 M in toluene, 0.7 mL, 1 mmol, 2 eq) was added. The reaction mixture was stirred for 30 min at 0 °C before being quenched with MeOH (2 mL). The mixture was allowed to warm to ambient temperature and an aq solution of Rochelle's salt was added (10 mL). The aq phase was extracted with dichloromethane (3 x 5 mL) and the combined organic extracts were dried on Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography on silica gel using hexanes-EtOAc (6:4, v/v) gave alcohol **ii** (124 mg, 0.35 mmol) in 70% yield. **TLC** $\mathbf{R_f}$ = 0.12 (20% EtOAc-hexanes). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.91 (d, *J* = 6.8 Hz, 2H), 7.66-7.49 (m, 3H), 4.41 (dd, *J* = 6.8, 1.5 Hz, 1H), 3.91-3.78 (m, 2H), 3.59-3.78 (m, 4H) 2.84 (dd, *J* = 14.3, 9.0 Hz, 1H), 2.36-2.21 (m, 1H), 2.19-1.89 (br,

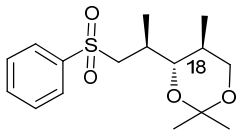
1H), 1.85-1.56 (m, 3H), 1.53-1.30 (m, 4H), 1.18 (d, J = 6.7 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H).

(2*S*,3*S*,4*S*)-2,4-Dimethyl-5-(phenylsulfonyl)pentane-1,3-diol (iii)



To the solution of alcohol **ii** (107 mg, 0.3 mmol, 1 eq) in methanol (5 mL) under N_2 atmosphere, *p*-toluenesulfonic acid (6 mg, 0.03 mmol, 0.1 eq) was added at 0 °C. The resulting mixture was warmed to rt and stirred for 1 h. An aq saturated solution of $NaHCO_3$ (5 mL) was added, the aq layer was extracted with dichloromethane and the combined organic layers were washed with brine, dried over on anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography using hexanes-EtOAc (7:3, v/v) as the eluent to afford the alcohol **iii** (65 mg, 0.24mmol) in 78% yield. **TLC R_f** =0.1 (30% EtOAc-hexanes). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.89 (d, J = 7.1 Hz, 2H), 7.63 (d, J = 7.0 Hz, 1H), 7.54 (d, J = 7.1 Hz, 2H), 3.73 (dd, J = 10.1, 2.2 Hz, 1H), 3.52 (dd, J = 10.1, 7.1 Hz, 1H), 3.38-3.25 (m, 2H), 2.88 (dd, J = 14.3, 9.0 Hz, 1H), 2.34-2.2 (m, 1H), 1.74-1.61 (m, 1H), 1.13 (d, J = 6.8 Hz, 3H), 0.76 (d, J = 6.8 Hz, 3H).

(*4S,5S*)-2,2,5-trimethyl-4-((*S*)-*1*-(phenylsulfonyl)propan-2-yl)-1,3-dioxane (A)



To a solution of 1,3-diol **iii** (60 mg, 0.2 mmol, 1 eq) in anhydrous dichloromethane (3 mL), 2,2-dimethoxypropane (0.1 mL, 0.5 mmol, 2.5 eq) was added followed by CSA (6 mg, 0.03 mmol, 0.1 eq) at 0 °C. The reaction mixture was stirred at room temperature for 3 h. An aq saturated solution of $NaHCO_3$ (2 mL) was added, the aqueous layer was extracted with dichloromethane (2 x 4 mL) and the combined organic layers were washed with brine, dried

over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography using hexanes-EtOAc (9.5:0.5, v/v) as the eluent to afford the acetonide A (46 mg, 0.15 mmol) in 75% yield. **TLC R_f** = 0.2 (5% EtOAc-hexanes). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.95-7.92 (m, 2H), 7.67-7.63 (m, 1H), 7.6-7.56 (m, 2H), 3.64 (dd, *J* = 11.5, 5.1 Hz, 1H), 3.44 (t, *J* = 11.1, 1H), 3.34 (dd, *J* = 10.3, 1.5 Hz, 1H) 3.31 (dd, *J* = 14.8, 1.5 Hz, 1H), 2.88 (dd, *J* = 14.8, 9.0 Hz, 1H), 2.36-2.29 (m, 1H), 1.62-1.53 (m, 1H), 1.36 (s, 3H), 1.29 (s, 3H), 1.17 (d, *J* = 6.8 Hz, 3H), 0.58 (d, *J* = 6.7 Hz, 3H).