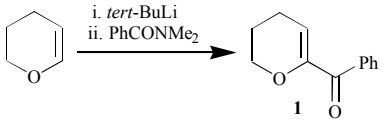
Supplementary Experimental:

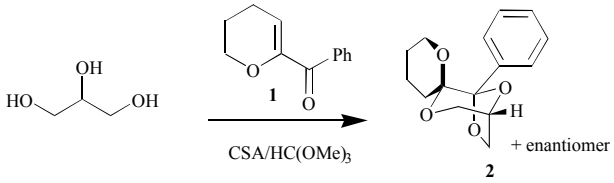
6-Benzoyl-3,4-dihydro-(*2H)*-pyran 1.[6]



A solution of *tert*-butyl lithium (20 mL, 34 mmol; 1.7 M in pentane) was added slowly to a gently stirred solution of 3,4-dihydro-(2*H*)-pyran (3.0 mL, 32.9 mmol) in dry THF (12 mL) precooled to -30°C. The reaction mixture was warmed to 0° C for 30 minutes, then cooled to -78°C. A solution (at 20 °C) of *N,N*-dimethylbenzamide (4.60 g, 30.8 mmol) in THF (3 mL) was added dropwise to the above vinyl anion at –78 °C. The reaction mixture was allowed to warm to 20 °C over 30 mins, and stirred for 30 min. Ammonium chloride solution (10% w/v; 50 mL) was added and the reaction mixture extracted with diethyl ether (3 x 75 mL). The combined organic fractions were dried (Na_2SO_4), filtered and solvent removed under reduced pressure to give an oil which was distilled at 2-4 mmHg, T *ca* 65 °C. Yield 70%, containing <5% impurities.

δ_H (300 MHz; $CDCl_3$) 1.9 (2 H, m), 2.25 (2 H, m), 4.15 (2 H, m), 5.8 (1 H, m, =C*H*), 7.4 (2 H, m), 7.45 (1 H, m), 7.7 (2 H, m). δ_c (62.9 MHz;$CDCl_3$) 21.4 (CH_2), 21.9 (CH_2), 66.9 (CH_2), 116.0 (=CH), 128.4 (2 C, ArH), 129.7 (2 C, ArH), 132.4 (ArH); HRMS (EI) 188.08370 $C_{12}H_{12}O_2$ requires 188.08373.

***racemic*-(1*R*,4(2')*S*,5*S*)-Spiro[5-phenyl-3,6,8-trioxabicyclo[3.2.1]octane-4,2'-tetrahydropyran] 2**



'Orthoformate conditions'. To a solution of glycerol (0.250 g, 2.72 mmol) in dry methanol (20 ml), a solution of 10-camphorsulfonic acid (1.274 g, 5.48 mmol) in dry methanol (10 ml), a solution of 6-benzoyldihydro-(2*H*)-pyran (1.048 g, 5.52 mmol) in dry methanol (10 ml), and a solution of trimethyl orthoformate (0.58 g, 5.48 mmol) in dry methanol (10 ml) was added and the reaction mixture refluxed (calcium choride tube) for 18 h.

After cooling, the reaction mixture was neutralised with saturated sodium hydrogen carbonate and the volatiles removed *in vacuo*, to give a viscous brown residue which was dissolved in water (30 ml) and extracted with dichloromethane (1 × 50 ml and 2 × 30 ml). The organic layers were combined, dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to give a viscous brown residue (1.2 g) which was crystallised (EtOAc/hexane) to give *the title compound* **2** as a crystalline solid (0.299 g, 42%).

Mp 135-137°C

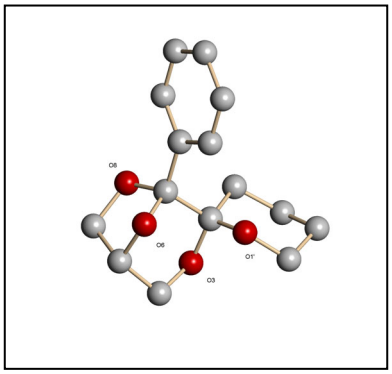
ν_{max}/(film)/cm^{-1} 2905vs, 1435vs, 1380s, 1310w.

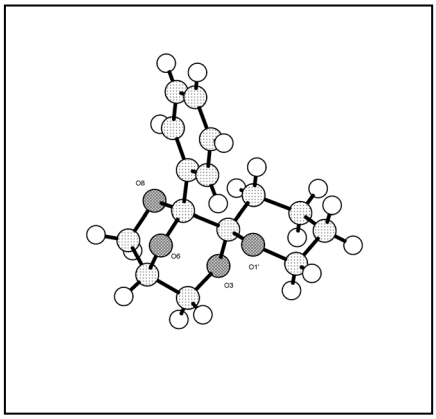
δ_H(250 MHz; $CDCl_3$) 1.05-1.50 (4 H, m), 1.55 (1 H, s), 1.60-1.80 (2 H, m), 3.40 (1 H, d), 3.65-3.85 (2 H, m), 3.90-4.05 (1 H, m), 4.25-4.35 (2 H, m), 4.60 (1 H, m), 7.20 (1 H, s), 7.25-7.35 (3 H, m), 7.65 (2 H, m).

δ_C (100.6 MHz; $CDCl_3$) 18.0 (CH_2), 25.1 (CH_2), 29.3 (CH_2), 61.5 (CH_2), 64.4 (CH_2), 67.6 (CH_2), 75.7 (CH), 97.7, 108.1s, 127.7 (2C, ArH), 128.7 (2C, ArH), 137.0 (Ar). HRMS (FAB) 263.12827 $C_{15}H_{19}O_4$ $(M+H)^+$ requires 263.12833.

m/z (ES+) 285 (40%, $[M + Na]^+$), 263 (50, $[M+H]^+$), 243 (30), 189 (100).

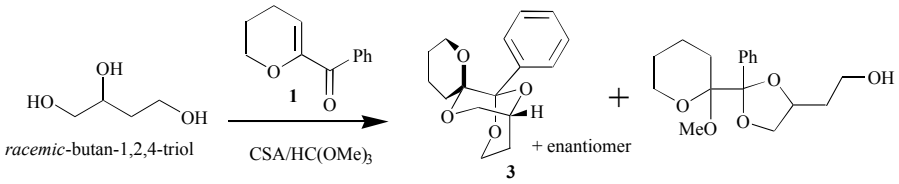
The crystal obtained for X-ray analysis of **2** was found to be centric (racemic).





Crystal data for 2 $C_{15}H_{18}O_4$, $M = 262.29$, orthorhombic, space group $P2_12_12_1$, $a = 8.5600(16)$, $b = 12.140(2)$, $c = 25.374(5)$ Å, V = 2636.8(8) Å^3, $T = 150(2)$ K, $Z = 8$, μ(Mo-Kα) = 0.095 mm^{-1}, 18818 data collected, 4634 unique data (Rint = 0.0660) $R_1 = 0.0624$ for 3234 observed data and $wR_2 = 0.01375$ for all data, CCDC 257570.

racemic-(1*R*,5*R*,8(2')*R*)-Spiro[1-phenyl-2,7,9-trioxabicyclo[3.3.1]nonane-8,2'-tetrahydropyran] **3** and **[2-(2-methoxyoxan-2-yl)-2-phenyl-1,3-dioxolan-4-yl]ethanol**

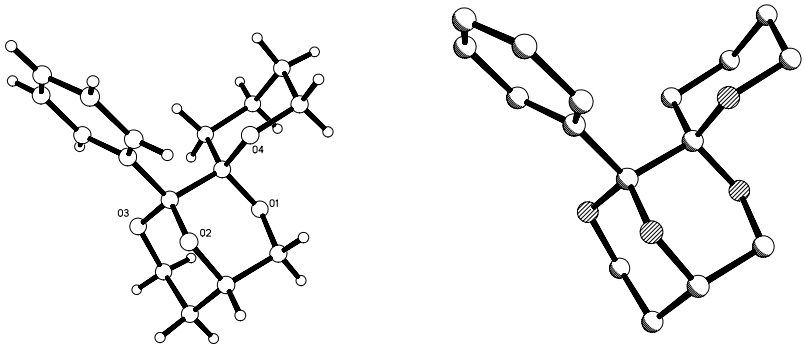


To a solution of *racemic*-1,2,4-butanetriol (1.08 g, 10 mmol) in dry methanol (20 mL) a solution of 10-camphorsulfonic acid (1.24 g, 5.4 mmol) in dry methanol (10 mL), a solution of 6-benzoyl-3,4-dihydro-(2*H*)-pyran **1** (1.00 g, 5.4 mmol) in dry methanol (10 mL), and a solution of trimethyl orthoformate (0.57 g, 5.4 mmol) in dry methanol (10 mL) was added and the reaction mixture refluxed for 3 days.

After cooling, the reaction mixture was neutralised with saturated sodium hydrogen carbonate and the volatiles removed *in vacuo*, to give a viscous residue that was dissolved in water (30 mL) and extracted with dichloromethane (3 × 30 mL). The organic layers were combined, dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to give a crude residue (1.93 g) that contained two products (R_f value 0.55 and 0.05, 25% EtOAc in hexane), that were separated using column chromatography (EtOAc/hexane) to give a white crystalline (EtOH) solid **3** (98 mg 6.5%). Mp 120-122°C (from EtOH) (Rf 0.55) ν_{max}/(film)/cm^{-1} 2910vs, 1470s, 1380m; δ_H (250 MHz; $CDCl_3$) 1.15-1.55 (4 H, m), 1.65-1.90 (3 H, m), 2.35-2.55 (1 H, m), 3.55-3.80 (3 H, m), 4.05-4.15 (2 H, m), 4.48 (1 H, *ca*. dt), 4.9 (1 H, *ca*. dt), 7.30 (3 H, m), 7.60 (2 H, m) [minor isomer (< 5%): 2.0 (m), 2.2 (m), 4.3 (dt), 4.7 (m)]; δ_C (62.9 MHz; $CDCl_3$) 17.9 (CH_2), 24.6 (CH_2), 28.3, (CH_2), 28.8 (CH_2), 60.6 (CH_2), 61.2 (OCH_2), 62.8 (OCH_2), 67.0 (OCH), 95.8, 96.4, 127.2 (ArH), 127.5 (ArH), 128.1 (ArH), 140.7 (Ar); *m/z* (ES), 299 (3%, $[M+Na]^+$), 277 (30%, $[MH]^+$), 189 (100);

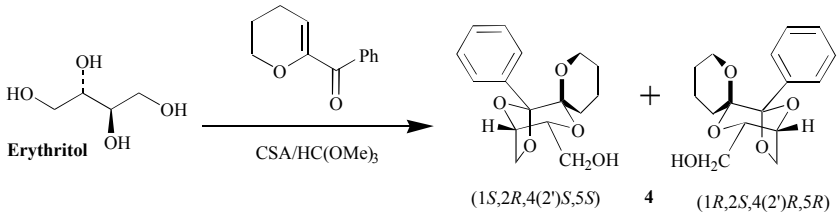
and an orange oil [2-(2-methoxyoxan-2-yl)-2-phenyl-1,3-dioxolan-4-yl]methanol as a mixture of two diastereoisomers (990 mg, 60%). ν_{max}/(film)/cm^{-1} 2920vs, 1470sh, 1450s, 1380m, 1360m, 760w and 705w; δ_H (250 MHz; $CDCl_3$) 1.20 (2 H, m), 1.35-1.45 (2 H, m), 1.55-1.95 (4 H, m) 2.90 (1 H, br s, O*H*), 3.08 and 3.10 (2 x 3 H, 2 x s, 2 x OMe) 3.5-3.9 (6 H, m), 4.35 (1 H, m), 7.3 (3 H, m), 7.50 (2 H, m); δ_C (62.9 MHz; $CDCl_3$) 18.3 (CH_2), 18.4 (CH_2), 24.9 (CH_2), 28.5 (CH_2), 28.6 (CH_2), 33.6 (CH_2), 33.6 (CH_2), 49.7 (CH), 60.9 (CH_2), 61.0 (CH_2), 61.2 (CH_2), 61.3 (CH_2), 62.5 (CH_2), 64.2 (CH_2), 66.1 (CH), 68.3 (CH), 95.9, 97.0, 100.3, 101.2, 127.6 (ArH), 127.7 (ArH), 128.3 (ArH), 129.0 (ArH), 129.1 (ArH), 137.3, 137.4; *m/z* (ES) 331 (100%, $[M+Na]^+$) 277.

The crystal obtained for X-ray analysis of 3 was found to be centric (racemic).



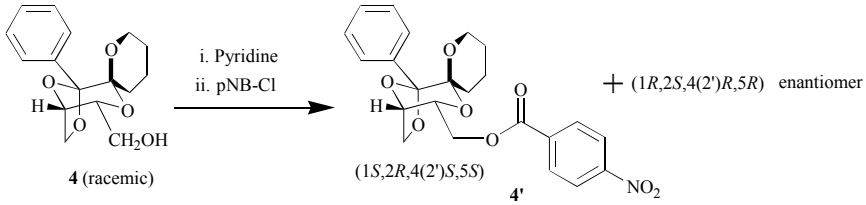
Crystal data for 3 $C_{16}H_{20}O_4$, M = 276.32, monoclinic, space group $P2_1/n$, a = 6.320(6), b = 23.154(16), c = 9.673(6) Å, β = 105.89(6) °, V = 1361.4(18) Å^3, T = 190(2) K, Z = 4, μ(Mo-Kα) = 0.096 mm^{-1}, 4587 data collected, 2143 unique data (Rint = 0.0723), R_1 = 0.0601 for 1435 observed data and wR_2 = 0.1657 for all data, CCDC 257573.

racemic-(1_R_,2_S_,4(2')_R_,5_R_)-Spiro-[2-hydroxymethyl-5-phenyl-3,6,8-trioxabicyclo[3.2.1]octane-4,2'-tetrahydropyran]

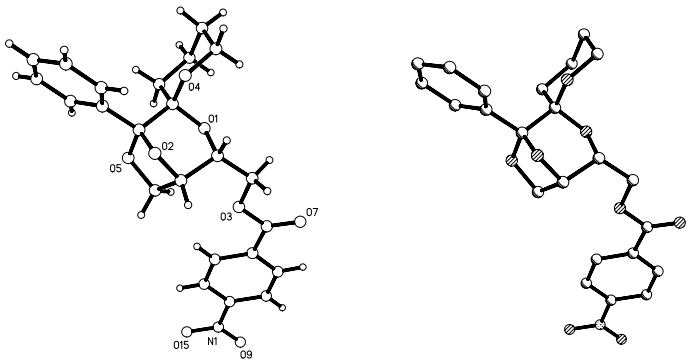


meso-Erythritol (1.804 g, 15.1 mmol), 6-benzoyl-3,4-dihydro-(2*H*)-pyran (1.43 g, 7.60 mmol), camphorsulfonic acid (1.86 g, 8.01 mmol) and trimethylorthoformate (0.804 g, 7.58 mmol) were added to dry methanol (80 mL) and the solution refluxed for 24 h. After cooling, the solution was neutralised by the addition of saturated sodium hydrogen carbonate and extracted with dichloromethane (3 x 30 mL). The combined organic fractions were dried (Na_2SO_4) and the volatiles removed *in vacuo* to give a brown residue (2.00 g) which was purified (including separation from a small amount of a less polar isomer) by flash chromatography (20-50% EtOAc in hexane) to give *the title compound* (R_f 0.45) as a sticky white solid (1.36 g, 68%). δ_H (250 MHz; $CDCl_3$) 1.08-1.52 (4 H, m), 1.60-1.88 (2 H, m), 3.60-3.90 (4 H, m), 3.98-4.20 (1 H, m), 4.25-4.45 (2 H, m), 4.55 (1 H, m), 7.32 (3 H, m), 7.65 (2 H, m); δ_C (62.9 MHz; $CDCl_3$) 16 (CH_2), 23.5 (CH_2), 27.5 (CH_2), 59.5 (CH_2), 60 (CH_2), 63 (CH_2), 70 (CH), 96 (C), 106 (C), 126 (CH), 127 (CH), 135 (C); m/z 315 (100%, $[M+Na]^+$).

racemic-(1_R_,2_S_,4(2')_R_,5_R_)-Spiro[2-(4-nitrobenzoyloxymethyl)-5-phenyl-3,6,8-trioxabicyclo[3.2.1]octane-4,2'-tetrahydropyran] and 4'

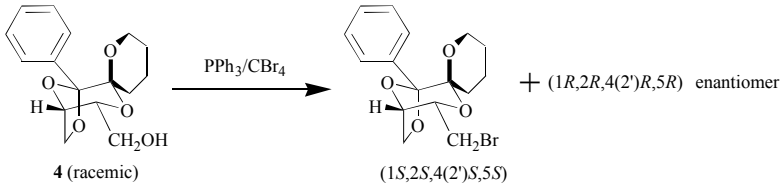


Pyridine (2.65 mL) and 4-nitrobenzoyl chloride (2.03g, 10.9 mmol) were added sequentially to a solution of racemic alcohol **4** (1.35 g, 4.64 mmol) in dichloromethane (5 mL) at 0 ^{o}C, and allowed to warm to room temperature over 18 h. The reaction mixture was poured into ice-water (50 mL) and and extracted (CH_2Cl_2; 3 x 30 mL). The solvent was removed *in vacuo* from the combined organic fractions to give a solid (2 g) which was purified by flash chromatography (ethyl acetate-hexane gradiant) and recrystallised to give orange crystals (310 mg, 18%). ν_{max} /cm^{-1} 2891, 1724, 1516, 1464, 1376; δ_H (250 MHz; $CDCl_3$) 1.1-1.9 (6 H, m), 3.7-3.9 (2 H, m), 3.9-4.0 (1 H, m), 4.35-4.5 (3 H, m), 4.6-4.75(2 H, m), 7.35 (3 H, m), 7.65 (2 H, m), 8.25 (2 H, m), 8.35 (2 H, m); δ_C (75 MHz; $CDCl_3$) 17.9, 25.0, 29.0, 61.6, 64.3, 64.7, 69.4, 76.4, 98.5, 107.8, 124.2, 127.76, , 128.1, 128.9, 131.2, 135.3, 136.4, 151.1, 164.7; m/z (ES), 464 (100, [M+Na]$^+$), 413 (60). The crystal used was found to be centric/racemic. The 1S enantiomer **4'** is shown.



Crystal data for 4' $C_{23}H_{23}NO_8$, M = 441.42, monoclinic, space group C2/c, a = 34.238(8), b = 6.778(2), c = 18.623(10) Å, β = 109.64(2) ^{o}, V = 4070(3) Å^3, T = 140(2) K, Z = 8, μ(Mo-Kα) = 0.110 mm^{-1}, 4409 data collected, 3571 unique data (Rint = 0.0443), R_1 = 0.0521 for 2530 observed data and wR_2 = 0.1377 for all data, CCDC 257574.

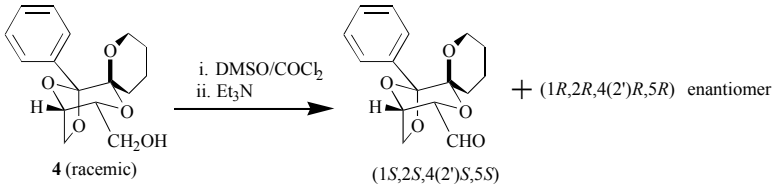
***racemic*-(1*R*,2*R*,4(2')*R*,5*R*)-Spiro-[2-bromomethyl-5-phenyl-3,6,8-trioxabicyclo[3.2.1]octane-4,2'-tetrahydropyran]**



Triphenylphosphine (4.884 g, 18.6 mmol) and carbon tetrabromide (6.654 g, 20.1 mmol) were added sequentially to a suspension of the racemic alcohol **4** (1.36 g, 4.65 mmol) in dry dichloromethane (160 mL) at 25 ^{O}C, and stirred for 48 h. The volatiles were removed *in vacuo* and the resulting solid extracted with diethyl ether (20 mL), and then dichloromethane (20 mL), and the solvent removed *in vacuo*. Purification by flash chromatography (80% ethyl acetate in hexane), gave *the title bromide* as a white solid (1.28 g, 74%); δ_H (250 MHz; $CDCl_3$) 1.08-1.52 (4 H, m), 1.65-1.85 (2 H, m), 3.32 (2 H, ddd), 3.68-3.82 (2 H, m), 3.86 (1 H, m), 4.25 (1

H, dd), 4.55 (1 H, t), 4.74 (1 H, dd), 7.32 (3 H, m), 7.65 (2 H, m); δ_C (62.9 MHz; $CDCl_3$) 17.9 (CH_2), 25.1 (CH_2), 29.1 (CH_2), 29.4 (CH_2), 61.6 (CH_2), 64.2 (CH_2), 71.9 (CH), 76.8 (CH), 98.6, 107.6, 127.7 (2 C, ArH), 127.8 (2 C, ArH), 128.9 (ArH), 136.4 (Ar); Found (FAB) 355.05443 $C_{16}H_{20}O_4{}^{79}Br$ requires 355.05450; *m/z* (EI) 355 (16%, $[M+H]^+$), 353 (10), 293 (92), 279 (54), 161 (41).

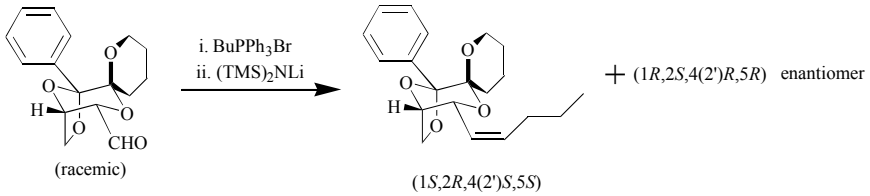
racemic-(1_R_,2_R_,4(2')_R_,5_R_)-Spiro[2-formyl-5-phenyl-3,6,8-trioxabicyclo[3.2.1]octane-4,2'-tetrahydropyran]



4 (racemic) (1*S*,2*S*,4(2')*S*,5*S*)

A solution of dimethyl sulfoxide (2.66 g, 2.5 mL, 34.1 mmol) in dry dichloromethane (10 mL) was added dropwise to a solution of oxalyl chloride (2.164 g, 8.5 mL, 17.0 mmol) in dichloromethane (20 mL) at –78 ^{0}C. The reaction mixture was stirred at –78 ^{0}C for 30 min, then a solution of the alcohol (2.492 g, 8.52 mmol) in dry dichloromethane was added dropwise, followed by stirring at –78 ^{0}C for 15 min. A solution of triethylamine (3.45 g, 4.75 mL, 34.1 mmol) in CH_2Cl_2 (10 mL) was added dropwise and the reaction mixture allowed to warm to room temperature for 1.5 h, then washed with water (10 mL), hydrochloric acid (1 M; 10 mL), and saturated sodium hydrogencarbonate (10 mL), dried (Na_2SO_4) and solvent removed *in vacuo* to give a brown crystalline crude product that was purified using flash chromatography (20% to 50% ethyl acetate in hexane) to give *the title aldehyde* (0.65 g, 26%). δ_H (250 MHz; $CDCl_3$) 1.15-1.52 (4 H, m), 1.70-1.95 (2 H, m), 3.78 (2 H, m), 3.90 (1 H, m), 4.10 (1 H, d), 4.70 (1 H, dd), 4.85 (1 H, dd), 7.32 (3 H, m), 7.65 (2 H, m), 9.68 (1 H, s); δ_C (62.9 MHz, $CDCl_3$) 17.7 (CH_2), 24.9 (CH_2), 28.9 (CH_2), 61.7 (CH_2), 66.5 (CH_2), 75.6 (CH), 76.4 (CH), 98.8, 108.1, 127.6 (2 C, ArH), 127.7 (2 C, ArH) 128.9 (ArH), 136.3, 200.4 (CHO); Found (FAB) 291.12326. $C_{16}H_{19}O_5$ requires 291.12325.

racemic-(1_R_,2_S_,4(2')_R_,5_R_)-Spiro[2-(pent-(1_Z_)-enyl)-5-phenyl-3,6,8-trioxabicyclo[3.2.1]octane-4,2'-tetrahydropyran]

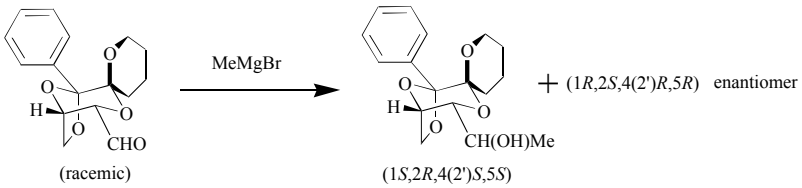


(racemic) (1*S*,2*R*,4(2')*S*,5*S*)

A solution of lithium bis(trimethylsilyl)amide (3.0 mL, 3.0 mmol; 1 M in THF) in THF (20 mL) was added dropwise to a suspension of butyltriphenylphosphonium bromide (0.547 g, 1.37 mmol) in dry THF (20 mL) which turned from clear to a bright orange solution. After stirring for 15 min, a solution of aldehyde (0.799 g, 2.75 mmol) in THF (30 mL) was added dropwise resulting after 10 min in a crimson solution which was stirred for 1 h, then added to ether (100 mL), and washed with water (2 x 20 mL), the organic fraction was dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to give an orange sticky solid (1.24 g) that was purified by flash chromatography (15-25% EtOAc in hexane) to give *the title alkene* as a yellow oil (0.394 g, 44%). δ_H (250 MHz; $CDCl_3$) 0.8 (3 H, t), 0.90-1.35 (6 H, m), 1.50-1.70 (2 H, m), 2 H, m), 3.60 (2 H, m), 3.70 (1 H, m), 4.35 (1

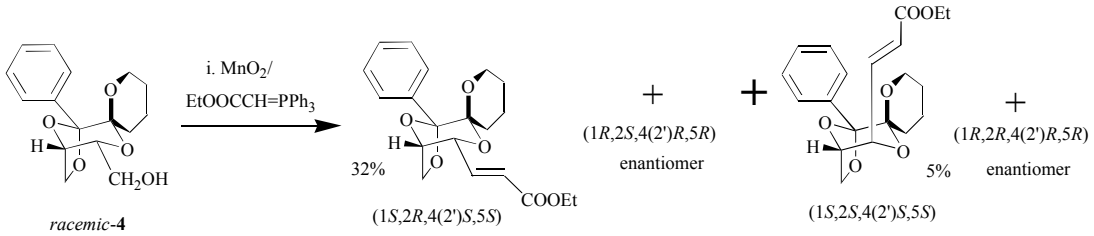
H, dd), 4.40 (1 H, dd), 4.96 (1 H, d, J 8), 5.23 (1 H, dd, *J* 8, 11), 5.55 (1 H, dt, *J* 11, 7) 7.20 (3 H, m), 7.50 (2 H, m); δ_C (62.9 MHz; $CDCl_3$) 14.1, 17.9, 23.1, 25.2, 29.4, 30.8, 61.6, 65.0, 68.5, 78.8, 97.9, 107.5, 125.2, 127.7, 127.8, 128.9, 136.3, 136.9; m/z (ES): 353 (18%, $[M+Na]^+$), 331 (29, $[M+H]^+$), 279 (42), 161 (100), 102 (98). Found (FAB) 331.19083, $C_{20}H_{27}O_4$ requires 331.19093.

***racemic*-(1*R*,2*S*,4(2')*R*,5*R*)-Spiro[2-(1-hydroxyethyl)-5-phenyl-3,6,8-trioxabicyclo[3.2.1]octane-4,2'-tetrahydropyran]**



Methyl magnesium bromide (2.2 mL; 3 M in THF) in dry THF (30 mL) was added dropwise over 15 min to a suspension of aldehyde in THF (100 mL) at –78 ^{O}C and then allowed to warm to room temperature for 1.5 h. Saturated ammonium chloride solution (10 mL) and ether (80 mL) were added, and the resulting mixture washed with water (2 x 30 mL). The organic fraction was dried (Na_2SO_4), filtered, and the solvent removed in vacuo to give crude product (1.18 g) which was purified by flash chromatography (25-50% EtOAc in hexane) to give *the title secondary alcohol* (of unknown alcohol stereochemistry; 0.27 g, 27%). δ_H (250 MHz; $CDCl_3$) 1.08-1.58 (4 H, m), 1.40 (3 H, d), 1.60-1.95 (2 H, m), 3.70-3.80 (2 H, m), 3.80 (2 H, dq), 3.90 (1 H, m), 4.00 (1 H, dd), 4.40 (1 H, dd), 4.85 (1 H, dd), 7.32 (3 H, m), 7.65 (2 H, m); δ_C (62.9 MHz; $CDCl_3$): 17.9 (CH_2), 20.8 (CH_3), 25.1 (CH_2), 29.2 (CH_2), 61.5 (CH_2), 64.9 (CH_2), 67.4 (CH), 75.3 (CH), 76.3 (CH), 98.2, 107.4, 127.7 (ArH), 127.8 (ArH), 128.7 (ArH), 136.8; m/z (ES) 329 (37%, $[M+Na]^+$), 123 (100); Found (FAB) 307.15452, $C_{17}H_{23}O_5$ requires 307.15455.

***racemic*-(1*R*,2*S*,4(2')*R*,5*R*)-Spiro-[((1*E*)-2-ethoxycarbonylethenyl)-5-phenyl-3,6,8-trioxabicyclo[3.2.1]octane-4,2'-tetrahydropyran]** and ***racemic*-(1*R*,2*R*,4(2')*R*,5*R*)-spiro-[((1*E*)-2-ethoxycarbonylethenyl)-5-phenyl-3,6,8-trioxabicyclo[3.2.1]octane-4,2'-tetrahydropyran]**

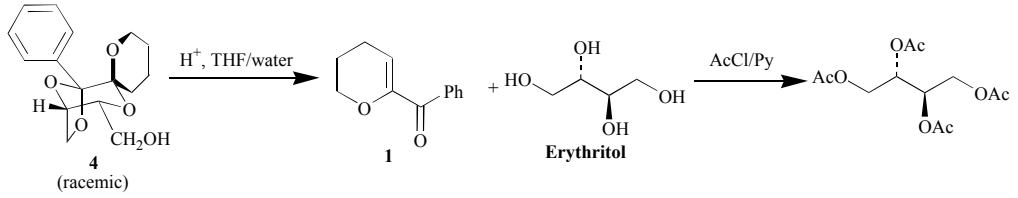


Manganese (IV) oxide (1.197 g, 13.8 mmol) was added to a stirred solution of the alcohol (1.198 g, 4.10 mmol) and ethoxycarbonylmethylenetriphenylphosphorane (1.722 g, 4.94 mmol) in toluene (100 mL) and the reaction mixture was then heated to reflux. Two further portions of manganese (IV) oxide were added during the first hour, and the mixture then refluxed for 24 h. After cooling, the reaction mixture was filtered through Celite, and the Celite washed with toluene (200 mL). The organic fractions were combined and the solvent removed in vacuo. The crude product (1.59 g) was purified by flash chromatography (25-50% EtOAc in hexane) to give the equatorially substituted (2R) compound as a yellow oil (0.472 g, 32%). δ_H (250 MHz; $CDCl_3$) 1.08-1.42 (4 H, m), 1.25 (3 H, t), 1.60-1.80 (2 H, m), 3.62 (1 H, m), 3.70 (2 H, m), 4.1 (2 H, q), 4.20 (1 H, m), 4.42 (1 H, d), 4.95 (1 H, t), 6.18 (1 H, dd, *J* 16, 2), 6.75 (1 H, dd, *J* 16 4), 7.22 (3 H, m), 7.52 (2 H, m); δ_C (62.9 MHz; CDC_3): 14.6

(CH_3), 17.8 (CH_2), 25.0 (CH_2), 29.2 (CH_2), 61.1 (CH_2), 61.2 (CH_2), 64.4 (CH_2), 70.7 (CH), 77.3 (CH), 98.3, 107.7, 123.6 (=CH), 127.7 (ArH), 127.8 (ArH), 128.9 (ArH), 136.4 (Ar), 142.2 (=CH), 166.4; *m/z* (ES) 383 (54%, $[M+Na]^+$), 361 (45, $[M+H]^+$), 189 (44), 161 (100), 155 (85); Found (FAB) 361.16507, $C_{20}H_{25}O_6$ ($[M+H]^+$) requires 361.16511

and the axially substituted 2S-substituted isomer as a sticky solid (74 mg, 5%) δ_H (250 MHz; $CDCl_3$) 1.08-1.42 (4 H, m), 1.22 (3 H, t), 1.55-1.82 (2 H, m), 3.55 (1 H, m, 2-C*H*), 3.69 (2 H, m), 4.12 (1 H, m), 4.22 (2 H, q), 4.40 (1 H, d, 1-H), 4.70 (1 H, t), 6.20 (1 H, dd, *J* 16, 2), 7.20 (1 H, dd, *J* 16, 7), 7.28 (3 H, m), 7.52 (2 H, m); δ_C (62.9 MHz; $CDCl_3$): 14.6 (CH_3), 17.9 (CH_2), 25.1 (CH_2), 29.3 (CH_2), 61.0 (2 x OCH_2), 61.6 (OCH_2), 78.3 (OCH), 78.6 (OCH), 97.3, 108.9, 125.1 (=CH), 127.6 (ArH), 127.8 (ArH), 128.9 (ArH), 136.8 (Ar), 142.8 (=CH), 166.3 (C=O).

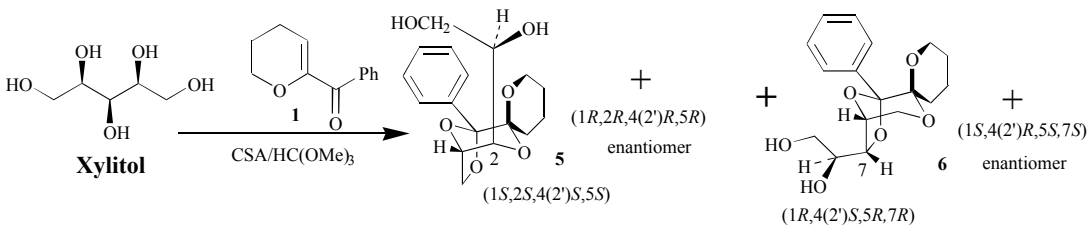
Deprotection of *racemic*-(1*R*,2*R*,4(2')*R*,5*R*)-Spiro[2-hydroxymethyl-5-phenyl-3,6,8-trioxabicyclo[3.2.1]octane-4,2'-tetrahydropyran] 4 to erythritol tetraacetate.



Alcohol **4** (0.987 g, 3.376 mmol) and camphorsulfonic acid (0.401 g, 1.727 mmol) was added to a solution of THF (20 mL) and water (25 mL) and the reaction mixture was refluxed for 48 h. After cooling, the volatiles were removed *in vacuo* and water (8 mL) added to the residue. The resulting mixture was extracted with dichloromethane (3 x 15 mL). The organic fractions were combined, and the solvent removed *in vacuo* to leave a brown oil (0.315 g) that was shown by NMR to contain a mixture of **1** and **4**.

The aqueous fraction was freeze dried to give a white solid (0.70 g) which was then suspended in dichloromethane (60 mL). Pyridine (1.368 g, 17.3 mmol), then acetyl chloride (1.804 g, 23.0 mmol) an then a crystal of 4-(dimethylamino)pyridine were added slowly to the suspension which was stirred at room temperature overnight. The reaction mixture was added to ice-water (100 mL) and extracted with dichloromethane (3 x 40 mL). The solvent was removed *in vacuo* from the combined organic layers to give a white solid (0.733 g, 2.53 mmol) that was recrystallised (chloroform) to give a crystalline solid (0.733 g, 75%) δ_H (250 MHz; $CDCl_3$) 2.08 (12 H, 2 x s), 4.15-4.40 (4 H, m), 5.20 (2 H, m), δ_C (62.9 MHz; $CDCl_3$) 20.9 (CH_3), 21.1 (CH_3), 62.1 (CH_2), 68.6 (CH), 170.4, 170.8.

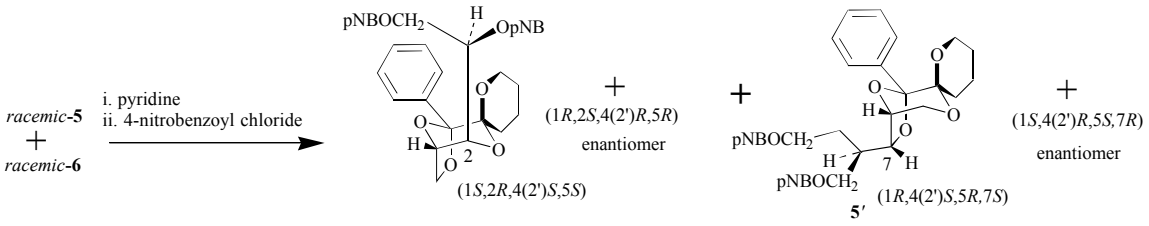
***racemic*-(1*R*,2*R*,4(2')*R*,5*R*)-Spiro[2-[(1*S*)-1,2-dihydroxyethyl]-5-phenyl-3,6,8-trioxa[3.2.1]octane-4(2')-tetrahydropyran] 5** and ***racemic*-(1*R*,4(2')*S*,5*R*,7*R*)-spiro[7-[(1*S*)-1,2-dihydroxyethyl]-5-phenyl-3,6,8-trioxa[3.2.1]octane-4(2')-tetrahydropyran 6**



Xylitol (4.04 g, 26.6 mmol), 6-benzoyl-3,4-dihydro-(2*H*)-pyran (2.51 g, 13.7 mmol), camphorsulfonic acid (3.04 g, 13.1 mmol) and trimethylorthoformate (1.38 g, 13.0 mmol) were added to dry methanol (130 mL) and refluxed for 72 h.

After cooling, the reaction mixture was neutralised (saturated $NaHCO_3$) and the volatiles removed *in vacuo*. Water (30 mL) and dichloromethane (60 mL) was added to the resulting brown residue, the organic layer was separated, and the aquous extracted dichloromethane (2 x 30 mL) The combined organic fractions were dried (Na_2SO_4) and the solvent removed *in vacuo*. The crude product (2.81 g) was purified by flash chromatography (EtOAc) to give a mixture of the 2-axially substituted racemic diol **5** and the 7-substituted isomer **6** (1.62 g, 5.0 mmol, 37%). δ_H (300 MHz; $CDCl_3$) 7.60 (2 H, m), 7.31 3 H, m), 4.50-4.58 (2 H, m), 4.25 (1 H, dd), 3.65-3.82 (3 H, m), 3.45-3.58 (2 H, m), 1.6-1.85 (2 H, m), 1.1-1.45 (4 H, m); δ_C (62.9 MHz; $CDCl_3$) 137.0, 136.5, 128.9, 128.8, 127.9, 127.8, 127.6, 127.5, 108.8, 108.6, 97.8, 97.3, 79.7, 78.7, 72.6, 64.0, 63.9, 63.6, 63.1, 62.4, 61.5, 29.7, 29.2, 25.0, 21.4, 17.9, 14.5; *m/z* (ES) 496 (15%), 495 (59), 345 (100; $[M+Na]^+$), 334 (53), 205 (66), 151 (55), 137 (100).

***racemic*-(1*R*,2*S*,4(2')*R*,5*R*)-Spiro-[2-(1,2-*bis*-4-nitrobenzoyloxyethyl)-5-phenyl-3,6,8-trioxa[3.2.1]octane-4(2')-tetrahydropyran]** and ***racemic*-(1*R*,4(2')*S*,5*R,7S*)-spiro-[7-(1,2-*bis*-4-nitrobenzoyloxyethyl)-5-phenyl-3,6,8-trioxa[3.2.1]octane-4(2')-tetrahydropyran]**

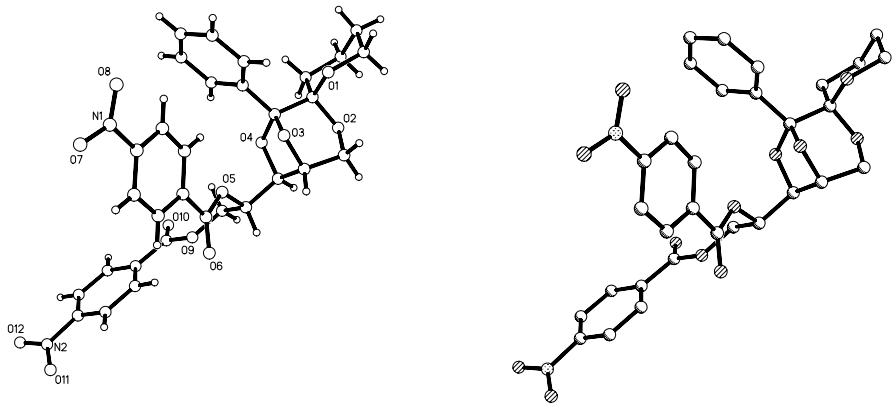


Pyridine (2.78 mL, 36.0 mmol) and 4-nitrobenzoyl chloride (5.85 g, 31.5 mmol) was added to a solution of crude mixed diol (**5** and **6**) (2.89 g) in dry dichloromethane (10 mL) at 0 ^oC, and then the reaction mixture was allowed to warm to room temperature and stirred for 24 h. The reaction mixture was poured into ice-water (50 mL) and extracted (CH_2Cl_2; 3 x 30 mL), the solvent was removed *in vacuo* from the combined organic fractions, and the residue purified by flash chromatography (10% to 100% EtOAc in hexane) to give the 2-substituted compound (Rf = 0.34) and the 7-substituted compound (Rf = 0.2).

The Rf = 0.34 fraction gave the axially substituted 2 isomer (0.196 g, 10%). Mp 193-198 ^oC ν_{max} /cm^{-1} 1719, 1525, 1272, 1103, 717; δ_H (250 MHz; $CDCl_3$) 8.2-8.35 (4 H, m), 7.85-8.10 (4 H, m), 7.77 (2 H, m), 7.28-7.32 93 H, m), 4.95-5.1 (2 H, 2 x dd), 4.78 (1 H,dd), 4.66 (1 H, s), 4.45-4.58 (2 H, 2 x dd), 4.12 (1 H, dd), 3.70-3.95 (2 H, m), 1.65-1.78 (2 H, m), 1.18-1.54 (4 H, m); d_C (62.9 MHz; $CDCl_3$) 164.9, 164.8, 151.1, 150.8, 136.6, 135.4, 131.2, 131.1, 128.9, 128.0, 127.6, 124.1, 123.7, 109.8, 97.7, 77.2, 76.9, 73.3, 66.2, 65.3, 62.4, 29.8, 25.0, 18.1; m/z (ES) 643 (24%; $[M+Na]^+$), 408 (100), 102 (41).

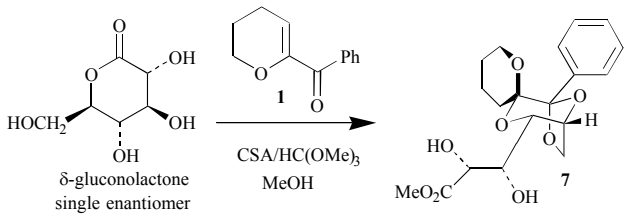
The Rf = 0.2 fraction was recrystallised (EtOAc/Hexane) to give the title 7-substituted compound (0.116 g, 6%); Mp 191-194 ^oC; ν_{max} /cm^{-1} 1720, 1528, 1267, 720; δ_H (250 MHz; $CDCl_3$) 8.13-8.27 (4 H, m), 7.97 (2 H, m), 7.63 (4 H, m), 7.32-7.45 (3 H, m), 5.68 (1 H, m), 4.67-4.80 (2 H, dd), 4.62 (1 H, s), 4.25 (1 H, dd), 3.68-3.85 (2 H, m), 3.62 (1 H, dd), 1.6-1.82 (2 H, m), 1.08-1.48 (4 H, m); δ_C (62.9 MHz; $CDCl_3$) 164.7, 164.6, 151.1, 150.8, 136.4, 135.2, 134.9, 131.3, 131.2, 129.0, 127.9, 127.8, 124.0, 123.6, 109.6, 97.4, 77.8, 76.7, 72.7, 64.7, 63.7, 61.7, 29.2, 25.0, 17.9; m/z (ES), 643 (100%, $[M+Na]^+$)413 (45), 301 (29) 102 (41).

The crystal used for X-ray analysis of **5'**, obtained by very slow diffusion of hexane into ethyl acetate was centric/racemic.



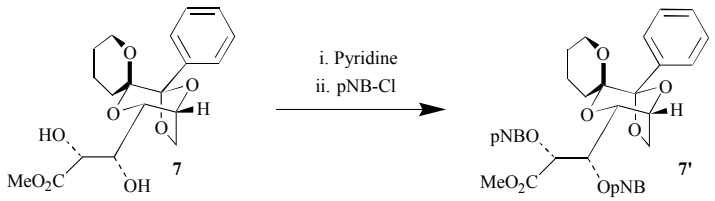
Crystal data for 5' $C_{31}H_{28}N_2O_{12}$, M = 620.55, triclinic, space group P-1, a = 10.110(2), b = 11.449(2), c = 14.007(3) Å, α= 79.04(2), β= 79.75(1), γ= 70.44(1) °, V = 1488.4(5) Å^3, T = 190(2) K, Z = 2, μ(Mo-Kα) = 0.108 mm^{-1}, 6201 data collected, 5850 unique data (Rint = 0.0736), R1 = 0.0476 for 3968 observed data and wR_2 = 0.1269 for all data, CCDC 257569.

Methyl (2*R*,3*R*)-dihydroxy-3-{[1*R*,4(2')R,5*R*]-spiro[5-phenyl-3,6,8-trioxabicyclo[3.2.1]octan-2-yl-4(2')-tetrahydropyran]}propanoate 7

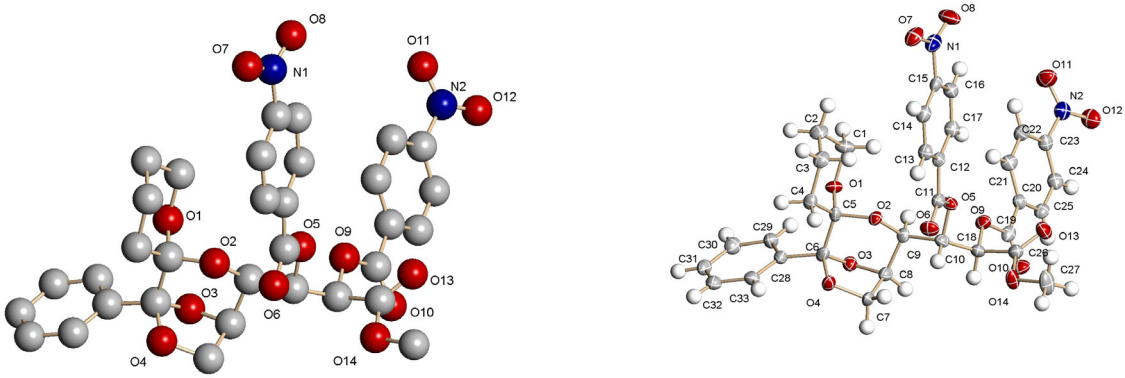


δ-Gluconolactone (890 mg, 5.6 mmol), camphorsulfonic acid (580 mg, 2.5 mmol) and trimethylorthoformate (0.54 mL, 5.0 mmol) was added to a stirred solution of 6-benzoyl-3,4-dihydro-(2*H*)-pyran (470 mg, 2.5 mmol) in dry methanol (40 mL) followed by reflux for 18 h. After cooling to room temperature, the solution was neutralised with saturated sodium hydrogen carbonate and the volatiles removed *in vacuo*. Water (50 mL) was added to the residue, and the resulting mixture extracted (CH_2Cl_2; 3 x 30 mL), the combined extracts were dried, filtered and the solvent removed *in vacuo*. The residue was purified by flash chromatography (75% to 100% EtOAc-hexane) to give *the title compound* **7** as a pale yellow oil (456 mg, 48%) δ_H (250 MHz; $CDCl_3$) 1.34-1.54 (2 H, m), 1.57-1.69 (2 H, m), 1.79-2.06 (2 H, m), 3.26 (1 H, d, J 5), 3.69 (1H, d, *J* 5), 3.88-4.01 (2 H, m), 4.07 (2 H, s), 4.11-4.15 (1 H, m), 4.18-4.24 (1 H, m), 4.47-4.50 (1 H, m), 4.73-4.76 (2 H, m), 4.85 (1 H, m), 7.52-7.56 (3 H, m), 7.83-7.89 (2 H, m); δ_c (62.9 MHz; $CDCl_3$) 18.0 (CH_2), 24.9 (CH_2), 29.0 (CH_2), 53.3 (CH), 61.5 (CH_2), 65.5 (CH_2), 71.9 (2 C, CH), 76.7 (CH), 98.8, 107.5, 127.7 (ArH), 127.8 (ArH), 128.8 (ArH), 136.6 (Ar), 173.2; m/z (FAB) 381.

Methyl (2*R*,3*S*)-bis(4-nitrobenzoyloxy)-3-{(1*R*,4(2')*R*,5*R*)-spiro-[5-phenyl-3,6,8-trioxabicyclo[3.2.1]octan-2-yl-4(2')-tetrahydropyran]}propanoate

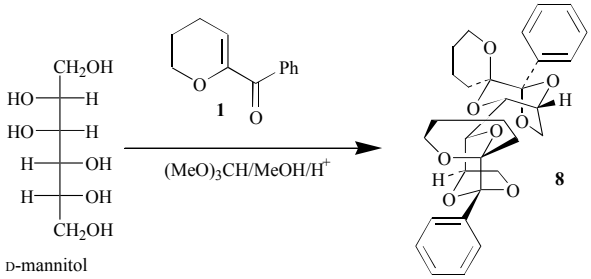


Pyridine (0.3 mL, 3.9 mmol), and 4-nitrobenzoyl chloride (532 mg, 2.9 mmol) were added sequentially to a solution of **7** (310 mg, 0.82 mmol) in dichloromethane at 0 °C. The reaction mixture was allowed to warm to room temperature overnight, and then poured into ice-water (50 mL) and extracted with dichloromethane (3 x 30 mL). The combined organic extracts were dried (Na_2SO_4), filtered and the solvent removed *in vacuo*. The residue was purified by flash chromatography (25-100% EtOAc in hexane) to give the crystalline *title compound* (145 mg, 26%). δ_H (250 MHz; $CDCl_3$) 1.05-1.31 (6 H, m), 1.76-1.81 (1 H, m), 3.64-3.69 (2 H, m), 3.82 (3 H, s), 3.96-4.00 (1 H, m), 4.49-4.51 (1 H, m), 4.68-4.76 (2 H, m), 5.66-5.67 (1 H, m), 5.87-5.91 (1 H, m), 7.26-7.34 (3 H, m), 7.54-7.67 (2 H, m), 8.26-8.37 (8 H, m).



Crystal data for 7' $C_{33}H_{30}N_2O_{14}$, $M = 678.59$, orthorhombic, space group $P2_12_12_1$, $a = 12.6293(16)$, $b = 12.9407(17)$, $c = 12.247(3)$ Å, V = 3145.6(7) Å^3, $T = 150(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.113 mm^{-1}, 23021 data collected, 5554 unique data (Rint = 0.0815), $R_1 = 0.0548$ for 4259 observed data and $wR_2 = 0.1199$ for all data, CCDC 257571.

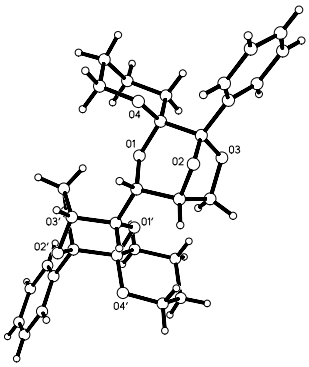
2,2'-Bi{[1*R*,2*R*,4(2'')*R*,5*R*]-spiro[5-phenyl-3,6,8-trioxabicyclo[3.2.1]octan-2-yl-4,2''-tetrahydropyran] 8

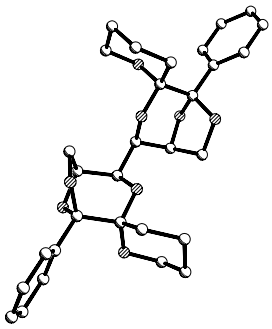


To a solution of D-mannitol (0.511 g, 2.80 mmol) in dry methanol (20 mL) a solution of 10-camphorsulfonic acid (1.274 g, 5.48 mmol) in dry methanol (10 mL), a solution of 6-benzoyldihydro-(2*H*)-pyran **1** (1.05 g, 5.52 mmol) in dry methanol (10 mL), and a solution of trimethyl orthoformate (0.581 g, 5.47 mmol) in dry methanol (10 mL) was added and the reaction mixture refluxed for 18 h.

After cooling, the reaction mixture was neutralised with saturated sodium hydrogen carbonate and the volatiles removed *in vacuo*, to give an oily residue to which was added water (30 mL) and then extracted with dichloromethane (3 × 30 mL). The organic layers were combined, dried (Na_2SO_4), filtered and the solvent

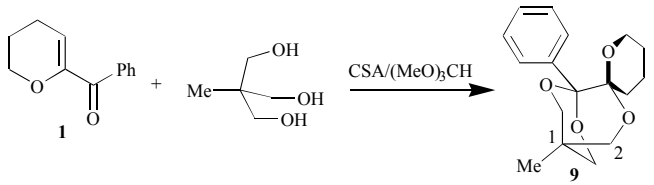
removed *in vacuo* to give a viscous brown residue (1.45 g). Recrystallisation (EtOAc-Hexane) gave *the title compound* **8** as crystals (568 mg, 39%). Mp 279 ^{O}C, $[\alpha]_D$ –106.5^{O}. ν_{max} /cm^{-1} 2910, 1470, 1380, 1000, δ_H (250 MHz; $CDCl_3$) 1.10-1.85 (5 H, m), 1.90 (1 H, *ca*. d, J 13), 3.55-3.75 (2 H, m), 3.95 (1 H, t, J 1.1), 4.45 (1 H, s), 4.55 (1 H, d 4.8), 4.85 (1 H, d *J* 6.9), 7.35 (3 H, m), 7.60 (2 H, m). δ_C (62.9 MHz; $CDCl_3$) 17.9 (CH_2), 24.7 (CH_2), 28.7 (CH_2), 61.4 (OCH_2), 65.7 (OCH_2), 70.9 (OCH), 76.9 (OCH), 98.5, 107.4, 127.4 (2C, ArH), 128.4 (ArH), 136.3 (Ar); m/z (ES) 545 (100%, $[M+Na]^+$), HRMS (FAB) 523.23315 $(M+H)^+$, $C_{30}H_{35}O_8$ requires 523.23319.





Crystal data for 8 $C_{15}H_{17}O_4$, M = 261.29, monoclinic, space group C2, a = 15.354(4), b = 6.0880(9), c = 14.926(2) Å, β = 113.236(17) ^{o}, V = 1282.0(4) Å^3, T = 200(2) K, Z = 4, μ(Mo-Kα) = 0.098 mm^{-1}, 1630 data collected, 1464 unique data (Rint = 0.0316), R_1 = 0.0335 for 1341 observed data and wR_2 = 0.0816 for all data, CCDC 257572.

racemic-Spiro-[1-methyl-5-phenyl-3,6,9-trioxabicyclo[3.2.2]nonane-4(2')-tetrahydropyran] 11



A solution of 1,1,1-tris(hydroxymethyl)ethane (1.03 g, 8.69 mmol), 10-camphorsulfonic acid (0.635 g, 2.73 mmol), trimethyl orthoformate (0.292 g, 2.75 mmol) and 6-benzoyldihydro-(2*H*)-pyran in dry methanol (50 mL) was refluxed for 18 h. After cooling, the reaction mixture was neutralised with saturated sodium hydrogencarbonate and the volatiles removed *in vacuo*. Water (30 mL) was added to the brown residue, and the mixture extracted with dichloromethane (3 x 30 mL). The combined organic fractions were dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to give a viscous brown residue (0.63 g) which was purified by flash chromatography (EtOAc/hexane) to give *the title compound* **9** (39 mg, 5%). Mp 162-164. δ_H 0.75-0.9 (1 H, m), 0.8 (3 H, s), 1.25 (1 H, m), 1.4 (2 H, m), 1.55 (1 H, m), 1.75 (1 H, m), 3.60 (1 H, *ca*. d, *J* 10), 3.7-3.9 (5 H, m), 4.10 (1 H, *ca*. d, *J* 10), 4.4 (1 H, *ca*. dd, *J* 8, 2), 7.30 (3 H, m), 7.55 (2 H, m).

δ_C (62.9 MHz; $CDCl_3$) includes 18.4 (CH_3), 18.7 (CH_2), 24.9 (CH_2), 32.2 (CH_2), 36, 38.9 (C), 61.3 (OCH_2), 70.6 (OCH_2), 71.2 (OCH_2), 126.1 (ArH), 127.3 (ArH), 127.5 (ArH).