Stereoselective synthesis of *cis*- and *trans*-2,6-disubstituted 5,6-dihydro-2*H*-pyrans based on 1,5-asymmetric induction in reactions between allylstannanes and aldehydes promoted by tin(IV) chloride

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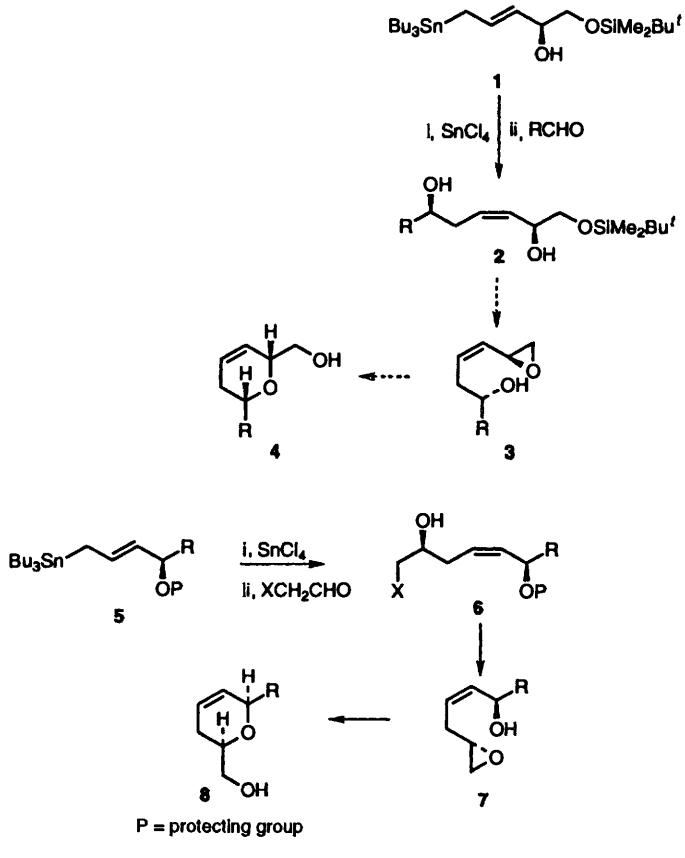
The allyltin trichloride formed by treating [(4*S*)-5-(*tert*-butyldimethylsilyloxy)-4-(2-trimethylsilylethoxy methoxy)]pent-2-enyl(tributyl)stannane **9** with tin(IV) chloride, reacts stereoselectively with 2-oxoethyl toluene-*p*-sulfonate to give the *syn*-6-(2-trimethylsilylethoxymethoxy)hept-4-en-2-ol **10** which was converted into the epoxide **11** by treatment with potassium carbonate in methanol. After replacing the *tert*-butyldimethylsilyl ether by a benzyl ether, removal of the 2-trimethylsilylethoxymethoxy group using trifluoroacetic acid, gave the 2,6-*cis*- and 2,6-*trans*-disubstituted 5,6-dihydro-2*H*-pyrans **14** and **15**, ratio 80:20, which were separated as their *tert*-butyldimethylsilyl ethers **16** and **17** and characterised as their acetates **18** and **19**. The 5,6-dihydro-2*H*-pyrans **24** and **26**, ratio 80:20, were similarly prepared from (4*S*)-4-(2-trimethylsilylethoxymethoxy)pent-2-enyl(tributyl)stannane **21**. A complementary route to the *trans*-2,6-disubstituted 5,6-dihydro-2*H*-pyran **15** was developed from 2-oxoethyl benzoate which gave the *syn*-hydroxy ether **28** under the usual conditions. Mesylation and ester saponification gave the *anti*-epoxide **30** and, after replacing the *tert*-butyldimethylsilyl ether by a benzyl ether, treatment with trifluoroacetic acid gave the 5,6-dihydro-2*H*-pyrans **14** and **15**, in favour of the *trans*-isomer, ratio **14**:**15** = 20:80. Improved stereoselectivity in these dihydropyran syntheses was obtained if the stannane **9** was treated with butyl glyoxylate in the first step. The *cis*-2,6-disubstituted 5,6-dihydro-2*H*-pyran **16** was converted into the tetrahydropyran-3-one **37** by hydroboration–oxidation, and into the tetrahydropyran-4-one **43** by treatment with bromine water, reductive debromination and oxidation.

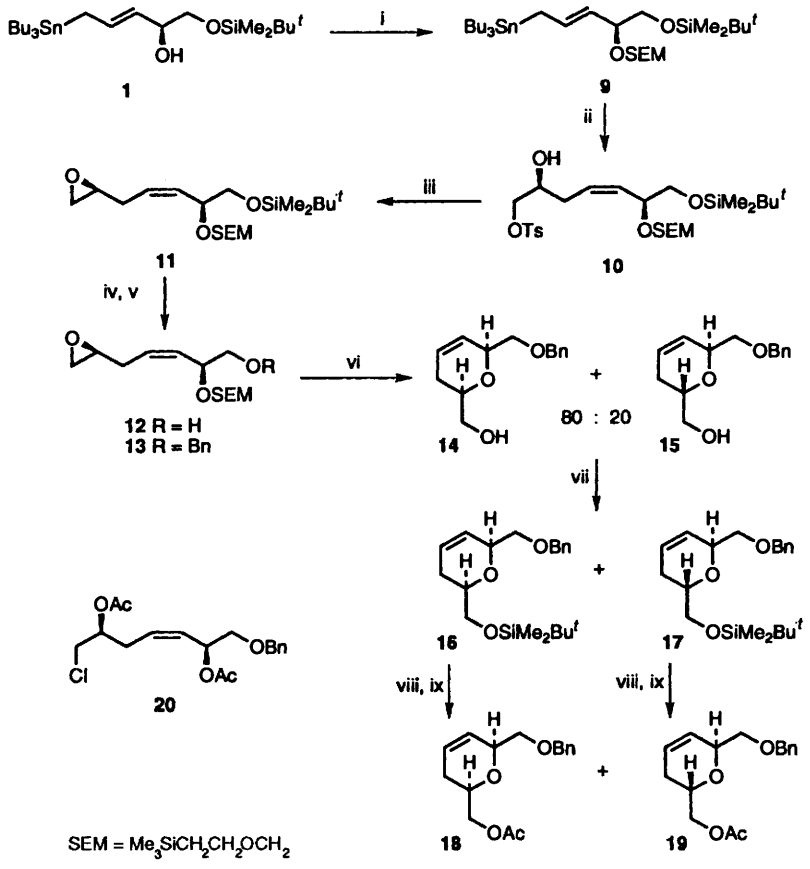
During the course of a preliminary study concerned with a proposed natural product synthesis, we had cause to develop a stereoselective synthesis of a series of *cis*-2,6-disubstituted 5,6-dihydro-2*H*-pyrans. One approach to these compounds investigated was based on the stereoselective formation of *syn*-hex-3-ene-1,5-diols **2** from the reaction between the 5-(*tert*-butyldimethylsilyloxy)-4-hydroxypent-2-enylstannane **1** and aldehydes.[1] However, attempts to convert the diols **2** into the 5,6-dihydro-2*H*-pyrans **4**, *e.g. via* the hydroxy epoxides **3**, were not successful. A complementary strategy was recognised in which a 4-alkoxyalkenylstannane **5** would be treated with a functionalised aldehyde to give access to a homoallylic epoxide **7** (*via* **6**) in which the epoxide group had been introduced using the aldehyde functionality. Acid catalysed isomerisation could then give access to the 2,6-*cis*-difunctionalised 5,6-dihydro-2*H*-pyrans **8**. We report a synthesis of 5,6-dihydro-2*H*-pyrans using this approach and aspects of their chemistry.



Results and discussion

(4*S*)-5-(*tert*-Butyldimethylsilyloxy)-4-hydroxypent-2-enyl-(tributyl)stannane **1** was converted into its 2-trimethylsilyl-ethoxymethoxy (SEM) ether **9**.[1,2] Transmetallation of this stannane by tin(IV) chloride and reaction of the allyltin trichloride so obtained with 2-oxoethyl toluene-*p*-sulfonate gave the *syn*-6-(2-trimethylsilylethoxymethoxy)hept-4-en-2-ol **10** (81%). The ratio of the *syn* to *anti* products from this reaction was not established at this stage, although the stereochemistry of later products in the reaction sequence, Scheme 1, suggest that the *syn*:*anti* ratio must have been *ca.* 85:15. The *syn*-configuration of the major product was assigned by comparison with that obtained from analogous reactions of 4-substituted pent-2-enylstannanes and aldehydes,[1,3] and was confirmed by the stereochemistry of products prepared further along the reaction sequence, see Scheme 1.

Treatment of the tosyloxy alcohol **10** with potassium carbonate in methanol[4] gave the *syn*-epoxide **11** which



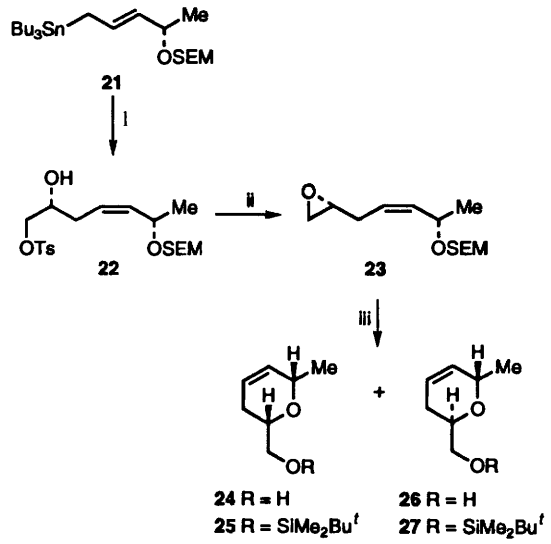
Scheme 1 *Reagents:* i, 2-trimethylsilylethoxymethyl chloride, *N,N*-diisopropylethylamine, dichloromethane (98%); ii, tin(IV) chloride, 2-oxoethyl toluene-*p*-sulfonate, dichloromethane (81%); iii, anhydrous potassium carbonate, methanol (95%); iv, tetrabutylammonium fluoride, tetrahydrofuran (89%); v, sodium hydride, benzyl bromide, NBu_4I, tetrahydrofuran (89%); vi, trifluoroacetic acid, dichloromethane (89%); vii, *tert*-butyldimethylsilyltrifluoromethanesulfonate, triethylamine (**16**, 61%; **17**, 19%); viii, tetrabutylammonium fluoride, tetrahydrofuran, then acetic anhydride, 4-dimethylaminopyridine (**18**, 89%; **19**, 85%)

appeared to contain about 15% of a minor component believed to be its *anti*-epimer. It was decided to replace the *tert*-butyldimethylsilyl group with a more robust protecting group before studying the epoxide–dihydro-2*H*-pyran isomerisation. Selective removal of the *tert*-butyldimethylsilyl group was carried out using tetrabutylammonium fluoride, and benzylation of the primary hydroxy group gave the benzyl ether **13**.[5] Several acids were evaluated for the removal of the SEM group and formation of the dihydropyran. The use of aqueous hydrogen chloride was found to be complicated by the formation of a chlorohydrin characterised as its bis-acetate **20**, and aqueous sulfuric acid gave only modest yields of products. However, it was found that deprotection and rearrangement could be carried out simultaneously in dichloromethane using trifluoroacetic acid as a catalyst giving a mixture of the 2,6-*cis*- and 2,6-*trans*-disubstituted 5,6-dihydro-2*H*-pyrans **14** and **15**, ratio 80:20, yield 89%.[6]

The 5,6-dihydro-2*H*-pyrans **14** and **15** were separated as their *tert*-butyldimethylsilyl ethers **16** and **17**.[7] Desilylation and acetylation gave the acetates **18** and **19** the ^1H NMR spectra of which confirmed the structures of the products as 5,6-dihydro-2*H*-pyrans rather than the isomeric oxepanes. For example, comparison of the ^1H NMR spectrum of the 2-hydroxymethyl-5,6-dihydro-2H-pyran **14** with that of its acetate **16** showed that two protons had moved downfield, from δ 3.51 and 3.55 to 4.18, showing that a primary hydroxy group had been acetylated. The *cis*-2,6-stereochemistry of the 6-acetoxymethyldihydropyran **18** was confirmed by ^1H NOE experiments. In particular, the enhancement of the multiplet due to 2-H on irradiation of 6-H and *vice versa*, which was not observed for the minor acetate **19**. The formation of the 2,6-*cis*-disubstituted dihydropyran **14** as the major product is consistent with the preferred formation of the *syn*-alcohol **10** from the reaction of the stannane **9** with the 2-oxoethyl toluene-*p*-sulfonate, as had been expected on the basis of precedent.

This approach to 5,6-dihydro-2*H*-pyrans was applied to the synthesis of the 2-methyl-5,6-dihydro-2*H*-pyrans **24** and **26**. In this case, the 4-(2-trimethylsilylethoxymethoxy)pent-2-enylstannane **21** was taken through to the *syn*-product **22** by treatment with tin(IV) chloride and 2-oxoethyl toluene-*p*-sulfonate (Scheme 2). Cyclisation was effected by treatment of the toluene-*p*-sulfonate **22** with potassium carbonate in methanol which gave the epoxide **23** together with a minor component believed to be its *anti*-isomer, yield 85%, ratio *syn*:*anti* = 84:16 (^1H NMR). Deprotection of the SEM-ether and cyclisation were carried out simultaneously using trifluoroacetic acid in dichloromethane to give the 2,6-*cis*-disubstituted 5,6-dihydro-2*H*-pyran **24** and its 2,6-*trans*-epimer **26**, ratio 80:20, separated as their *tert*-butyldimethylsilyl ethers **25** and **27**. The structures of these products were assigned on the basis of the known[3] stereochemistry of reactions of stannane **21** with aldehydes, and by comparison of the spectra of the products with those obtained earlier (Scheme 1).

To develop a stereoselective synthesis of 2,6-*trans*-disubstituted 5,6-dihydro-2*H*-pyrans, 2-oxoethyl benzoate was coupled with the allyltin trichloride generated from the 4,5-difunctionalised pentenylstannane **9** and tin(IV) chloride to give the *syn*-alcohol **28** (Scheme 3).[8] Mesylation[9] and methanolysis of the benzoyl group with concomitant displacement of the methylsulfonyloxy group[4] gave the *anti*-epoxide **30** (*via* **29**)



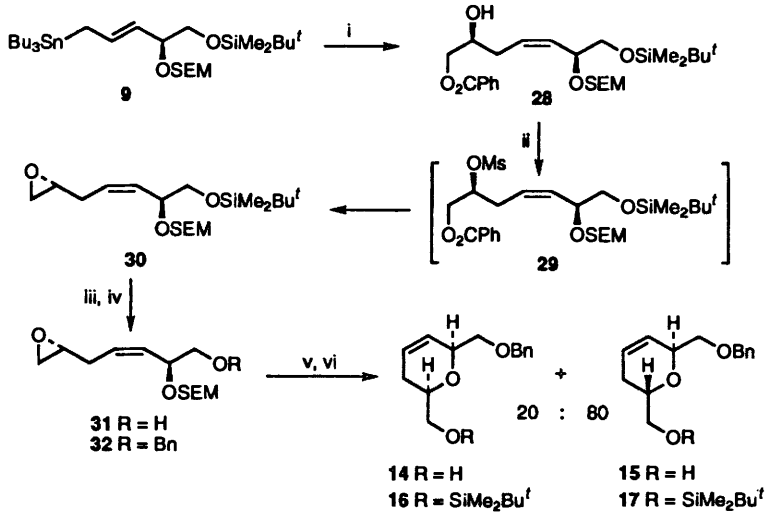
Scheme 2 *Reagents:* i, tin(IV) chloride, 2-oxoethyl toluene-*p*-sulfonate (68%); ii, anhydrous potassium carbonate, methanol (85%); iii, trifluoroacetic acid, dichloromethane, then *tert*-butyldimethylsilyl trifluoromethanesulfonate, triethylamine (74%)

which was isolated as a mixture with its *syn*-epimer **11**, ratio **30**:**11** = 86:14. Replacing the *tert*-butyldimethylsilyl ether by a benzyl ether gave **32** which was converted into the 2,6-*trans*- and 2,6-*cis*-5,6-dihydro-2*H*-pyrans **15** and **14**, separated as their *tert*-butyldimethylsilyl ethers **17** and **16**, ratio 80:20, by treatment with trifluoroacetic acid. These products were identified by comparison with samples prepared earlier (Scheme 1).

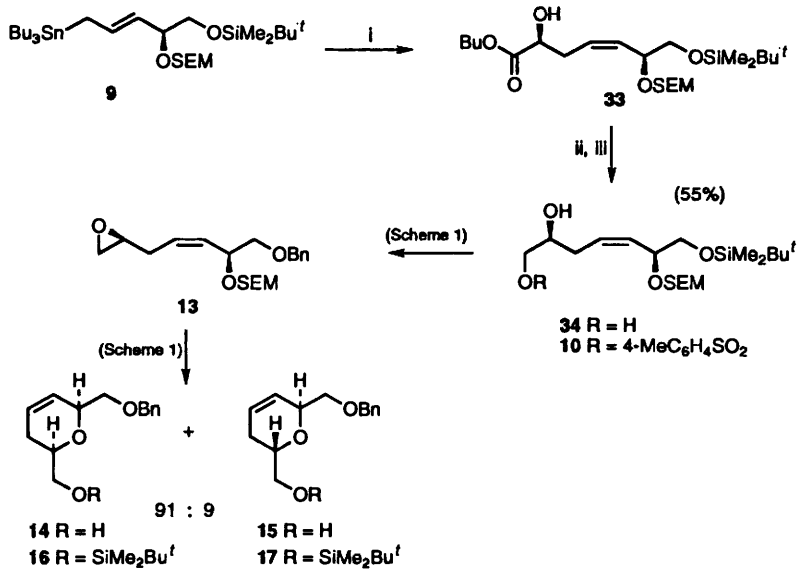
Although this work provided syntheses of 2,6-*cis*- and 2,6-*trans*-5,6-dihydro-2*H*-pyrans, the overall stereoselectivity was slightly disappointing when compared with the high levels of 1,5-asymmetric induction, *ca.* 97:3,[3] normally observed for reactions between 4-alkoxypent-2-enylstannanes and aldehydes. This loss of stereospecificity may be due to lower than usual stereoselectivity in the reactions of the pentenylstannane **9** with aldehydes, either because transmetallation of the 4,5-difunctionalised pentenylstannane is inherently less stereoselective than transmetallation of a monosubstituted allylstannane, or because the reactive α-acyloxyaldehydes react with reduced stereoselectivity. Alternatively, the acid catalysed conversion of the hydroxyepoxides into dihydropyrans may not be proceeding with full inversion of configuration. To get a feel for the relative importance of these effects, pentenylstannane **9** was coupled with butyl glyoxylate to give the butyl *syn*-7-(*tert*-butyldimethylsilyloxy)-2-hydroxy-6-(2-trimethylsilylethoxymethoxy)hept-4-enoate **33** together with two minor products, ratio 95:4:1 (Scheme 4). The stereoselectivity of this reaction shows that the difunctionalised pentenylstannane **9** can react with aldehydes with high stereoselectivity. The ester **33** was reduced to give the diol **34** which was converted regioselectively into the toluene-*p*-sulfonate **10**. Following the sequence of reactions outlined in Scheme 1, this toluene-*p*-sulfonate was converted into the epoxide **13** which now contained only a trace of its *anti*-isomer. Treatment with trifluoroacetic acid in dichloromethane gave the *cis*-2,6-disubstituted 5,6-dihydro-2*H*-pyran **14** containing less than 10% of its *trans*-isomer **15**, the ratio of these products being obtained by HPLC analysis of the acetates **18** and **19**. It would appear that some loss of stereoselectivity is occurring in the epoxide rearrangement, perhaps accounting for 5% of the *trans*-isomer **15** in the product mixture.

Finally, aspects of the chemistry of the 5,6-dihydro-2*H*-pyran **16** were investigated. Hydroboration using borane–methyl sulfide complex followed by oxidation gave a mixture of the epimers of the 3- and 4-hydroxytetrahydropyrans **36** and **35**, ratio 77:23, yield 73%, the structure of the major epimers **36** being confirmed by oxidation[10] to the tetrahydropyran-3-one **37**. Attempts to reverse the regioselectivity of hydroboration using the more hindered 9-borabicyclononane[11] were unsuccessful as only unchanged starting material was obtained, and catechol borane in the presence of lithium borohydride[12] gave only a modest yield of the hydroxytetrahydropyrans **36** and **35**, ratio *ca.* 60:40.

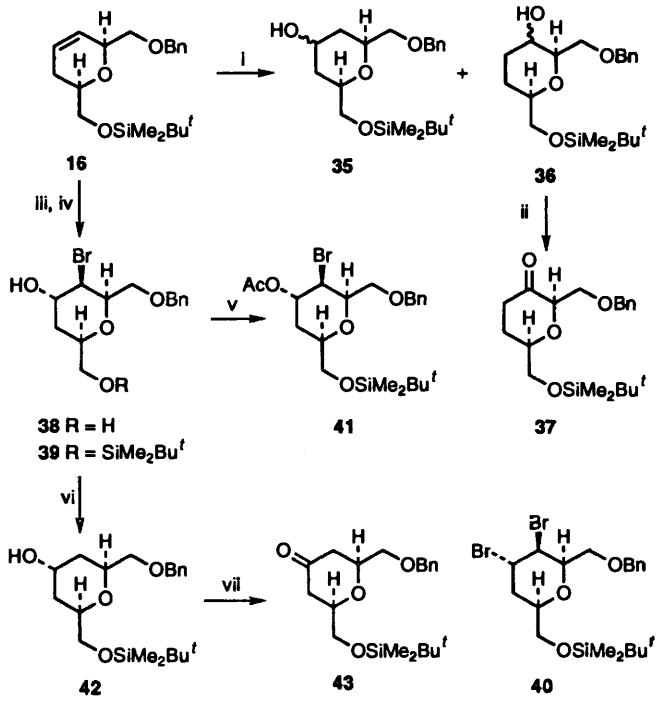
Treatment of the dihydropyran **16** with *N*-bromosuccinimide in wet 1,2-dimethoxymethane[13] gave the bromohydrin **38** in which the *tert*-butyldimethylsilyl group had been lost. When this reaction was repeated in the presence of a buffer at pH 7, a mixture of the bromohydrin **39** and the dibromide **40**, ratio 80:20, was obtained. The stereochemistry of the bromohydrin **39** was confirmed as diaxial on the basis of ^{1}H NMR NOE data for the acetate **41**, and the regiochemistry was established by



Scheme 3 *Reagents:* i, tin(IV) chloride, 2-oxoethyl benzoate (72%); ii, methanesulfonyl chloride, triethylamine (47%), then potassium carbonate, methanol (**30**, 47%); iii, tetrabutylammonium fluoride, tetrahydrofuran (84%); iv, sodium hydride, benzyl bromide, NBu_4I, tetrahydrofuran (59%); v, trifluoroacetic acid, dichloromethane (64%); vi, *tert*-butyldimethylsilyl trifluoromethanesulfonate (**16**, 15%; **17**, 60%)



Scheme 4 *Reagents:* i, tin(IV) chloride, butyl glyoxylate (78%); ii, sodium boranuide ($NaBH_4$) (87%); iii, dibutyltin oxide, methanol, reflux, then toluene-*p*-sulfonyl chloride, triethylamine (55%)



Scheme 5 *Reagents:* i, borane–methyl sulfide complex then 30% aqueous hydrogen peroxide, sodium hydroxide (**35**, 17%; **36**, 56%); ii, *N*-methylmorpholine *N*-oxide, tetrapropylammonium perruthenate (78%); iii, *N*-bromosuccinimide, 1,2-dimethoxyethane, water (**38**, 68%); iv, *N*-bromosuccinimide, 1,2-dimethoxyethane, pH 7 buffer (**39**, 65%; **40**, 17%); v, acetic anhydride, triethylamine, 4-dimethylaminopyridine (80%); vi, tributyltin hydride, AIBN (cat.) (91%); vii, dimethyl sulfoxide, oxalyl chloride (86%)

reductive debromination using tributyltin hydride followed by oxidation[14] to the tetrahydropyran-4-one **43**.

This work establishes stereoselective syntheses of *cis*- and *trans*-2,6-disubstituted 5,6-dihydro-2*H*-pyrans demonstrating a use of remote asymmetric induction using (alkoxyalkenyl)-stannanes in synthesis. The incorporation of the 5,6-dihydro-2*H*-pyrans into the synthesis of natural products is under investigation.

Experimental

For general experimental details, see the previous paper in this series.[1]

(4*S*)-5-(*tert*-Butyldimethylsilyloxy)-4-(2-trimethylsilylethoxymethoxy)pent-2-enyl(tributyl)stannane 9

N,*N*-Diisopropylethylamine (17 cm^3, 98 mmol) and 2-(trimethylsilylethoxy)methyl chloride (17 cm^3, 96 mmol) were added dropwise to a solution of the (hydroxypentenyl)stannane **1** (24.4 g, 48 mmol) in dichloromethane (300 cm^3) at 0 °C. The solution was allowed to warm to ambient temperature and stirred for 18 h before being cooled to 0 °C when water (20 cm^3) was added to it. The mixture was separated and the organic phase was washed with water. The aqueous extracts were extracted with dichloromethane and then the combined organic extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography on silica gel using gradient elution, light petroleum–ether (100:1, 1% triethylamine) to (20:1, 1% triethylamine) gave the *title compound* **9** (30.0 g, 98%) (Found: $M^+ - C_4H_9$, 579.2713. $C_{25}H_{55}O_3Si_2{}^{120}Sn$ requires *M*, 579.2712); ν_{max}/cm^{-1} 1652, 1463, 1250, 1027 and 836; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.10 [6 H, s, $Si(CH_3)_2$], 0.94 [26 H, m, $SiC(CH_3)_3$, $(CH_3CH_2CH_2CH_2)_3Sn$ and $CH_2Si(CH_3)_3$], 1.25–1.85 [14 H, m, $(CH_3CH_2CH_2CH_2)_3Sn$ and 1-H_2], 3.63 [3 H, m, 5-H_2 and $OCHHCH_2Si(CH_3)_3$], 3.71 [1 H, m, $OCHHCH_2Si(CH_3)_3$], 4.09 (0.8 H, m, 4-H), 4.50 (0.2 H, m, 4-H), 4.70 and 4.78 (each 1 H, d, *J* 6.5, OCHO), 4.99 (0.2 H, m, 3-H), 5.10 (0.8 H, dd, *J* 15, 7.5, 3-H) and 5.89 (1 H, dt, *J* 15.5, 6.5, 2-H); *m*/*z* (EI) 579 ($M^+ - C_4H_9$, 0.3%) and 549 (0.5).

(2*S*,6*S*,4*Z*)-7-(*tert*-Butyldimethylsilyloxy)-2-hydroxy-6-(2-trimethylsilylethoxymethoxy)hept-4-enyl toluene-*p*-sulfonate 10

Tin(IV) chloride (1 mol dm^{-3} in dichloromethane; 24 cm^3) was added dropwise to a solution of stannane **9** (15 g, 23.6 mmol) in dichloromethane (254 cm^3) at −78 °C, and the mixture stirred for 5 min at −78 °C. 2-Oxoethyl toluene-*p*-sulfonate (1 mol dm^{-3} in dichloromethane; 25 cm^3) was added dropwise to it and then the solution was stirred for 1 h at −78 °C. Saturated aqueous $NaHCO_3$ (100 cm^3) was added to the mixture which was then allowed to warm to ambient temperature. The aqueous phase was extracted with dichloromethane and the

combined organic extracts were washed with saturated aqueous NH_4Cl, dried ($MgSO_4$), and then concentrated under reduced pressure. Chromatography on silica gel, using light petroleum–ethyl acetate (4:1, 1% triethylamine) as eluent, gave the *title compound* **10** (10.71 g, 81%) (Found: $M^+ + NH_4$, 578.3004. $C_{26}H_{52}NO_7SSi$ requires *M*, 578.3003); ν_{max}/cm^{-1} 3448, 2858, 1599, 1364, 1251, 1178, 1099, 1057 and 837; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.10 [6 H, s, $Si(CH_3)_2$], 0.92 [9 H, s, $SiC(CH_3)_3$], 0.97 [2 H, m, $CH_2Si(CH_3)_3$], 2.31 (1 H, m, 3-H), 2.49 (4 H, m, 3-H′ and CH_3Ar), 3.32 (1 H, d, *J* 6.5, OH), 3.58 and 3.72 (each 2 H, m, 7-H_2 and $OCH_2CH_2Si(CH_3)_3$], 3.87 (1 H, m, 2-H), 3.99 (2 H, m, 1-H_2), 4.43 (1 H, m, 6-H), 4.65 and 4.77 (each 1 H, d, *J* 7, OCHO), 5.44 (1 H, t, *J* 10.5, 5-H), 5.72 (1 H, dt, *J* 10.5, 6, 4-H) and 7.39 and 7.83 (each 2 H, d, *J* 7, ArH); δ_C −5.3, −5.2, −1.4, 18.0, 18.5, 21.7, 26.0, 31.8, 65.2, 65.8, 68.7, 71.9, 73.0, 91.9, 128.0, 129.9, 130.0, 130.8, 132.8 and 144.9; *m*/*z* (CI) 578 ($M^+ + NH_4$, 15%).

Preparation from diol 34. Dibutyltin oxide (0.466 g, 1.87 mmol) was added to a solution of diol **34** (0.724 g, 1.78 mmol) in methanol (45 cm^3), and the solution was heated under reflux for 1 h before being cooled to 0 °C when triethylamine (0.78 cm^3, 5.6 mmol) and toluene-*p*-sulfonyl chloride (1.03 g, 5.4 mmol) were added to it. The solution was allowed to warm to ambient temperature, stirred for 18 h, and then filtered though Celite. The precipitate was washed with ethyl acetate, and the filtrate concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (6:1) as eluent gave the *title compound* **10** (0.546 g, 55%); $[\alpha]_D^{22}$ +41.7 (*c* 1.8, $CHCl_3$).

(2*S*,6*S*,3*Z*)-1-(*tert*-Butyldimethylsilyloxy)-6,7-epoxy-2-(2-trimethylsilylethoxymethoxy)hept-3-ene 11

Anhydrous K_2CO_3 (0.3 g, 2.21 mmol) was added in portions to a solution of the toluene-*p*-sulfonate **10** (1.15 g, 2.05 mmol) in methanol (14 cm^3). The slurry was stirred at ambient temperature for 18 h then partitioned between ether (30 cm^3) and water (30 cm^3). The aqueous phase was extracted with ether, and the combined organic extracts were washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure to give the *title compound* **11** (0.76 g, 95%) which was used without further purification (Found: $M^+ + NH_4$, 406.2813. $C_{19}H_{44}NO_4Si_2$ requires *M*, 406.2809); $[\alpha]_D^{22}$ +59.1 (*c* 2.2, $CHCl_3$); ν_{max}/cm^{-1} 2859, 1251, 1104, 1028 and 837; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.10 [6 H, s, $Si(CH_3)_2$], 0.94 [9 H, s, $SiC(CH_3)_3$], 0.97 [2 H, m, $CH_2Si(CH_3)_3$], 2.48 (2 H, m, 5-H_2), 2.56 (1 H, dd, *J* 5, 2.5, 7-H), 2.78 (1 H, t, *J* 4.5, 7-H′), 3.02 (1 H, m, 6-H), 3.60 and 3.74 [each 2 H, m, 1-H_2 and $OCH_2CH_2Si(CH_3)_3$], 4.47 (1 H, dt, *J* 9.5, 5.5, 2-H), 4.70 and 4.74 (each 1 H, d, *J* 7, OCHO), 5.44 (1 H, m, 3-H) and 5.73 (1 H, dt, *J* 11, 7.5, 4-H); δ_C −5.3, −5.2, −1.4, 18.1, 18.5, 26.0, 30.6, 46.4, 51.4, 65.0, 66.1, 72.0, 92.3, 128.4 and 130.2; *m*/*z* (CI) 406 ($M^+ + NH_4$, 8%) and 389 ($M^+ + H$, 3).

(2*S*,6*S*,3*Z*)-6,7-Epoxy-2-(2-trimethylsilylethoxymethoxy)hept-3-en-1-ol 12

Tetrabutylammonium fluoride (1.1 mol dm^{-3} in tetrahydrofuran; 0.53 cm^3) was added dropwise to a solution of epoxide **11** (0.207 g, 0.53 mmol) in tetrahydrofuran (3 cm^3) and the solution stirred at ambient temperature for 18 h. Methanol (3 cm^3) and water (*ca.* 0.15 cm^3) were added to it, and the stirring continued for 30 min before the solution was dissolved in ethyl acetate, washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (3:1) as eluent gave the *title compound* **12** as a colourless oil (0.13 g, 89%) (Found: $M^+ + NH_4$, 292.1946. $C_{13}H_{30}NO_4Si$ requires *M*, 292.1944); $[\alpha]_D^{22}$ +84.6 (*c* 2.4, $CHCl_3$); ν_{max}/cm^{-1} 3455, 2893, 1249, 1103, 1056, 1025 and 836; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.97 [2 H, m, $CH_2Si(CH_3)_3$], 2.48 (2 H, m, 5-H_2), 2.55 (1 H, dd, *J* 5, 2.5, 7-H), 2.72 (1 H, br s, OH), 2.76 (1 H, t, *J* 4.5, 7-H′), 3.02 (1 H, m, 6-H), 3.59 [3 H, m, 1-H_2 and $OCHHCH_2Si(CH_3)_3$], 3.77 [1 H, m, $OCHHCH_2Si(CH_3)_3$], 4.43 (1 H, m, 2-H), 4.70 and 4.75 (each 1 H, d, *J* 8, OCHO), 5.47 (1 H, t, *J* 10.5, 3-H) and 5.72 (1 H, dt, *J* 10.5, 7, 4-H); δ_C −1.4, 18.1, 30.2, 46.1, 51.1, 65.3, 65.5, 73.9, 92.8, 128.6 and 129.5; *m*/*z* (CI) 292 ($M^+ + NH_4$, 100%) and 275 ($M^+ + H$, 23).

(2*S*,6*S*,3*Z*)-1-Benzyloxy-6,7-epoxy-2-(2-trimethylsilylethoxymethoxy)hept-3-ene 13

The alcohol **12** (1.71 g, 6.24 mmol) in tetrahydrofuran (16 cm^3) was added dropwise to sodium hydride (60% suspension in oil; 0.5 g, 12.5 mmol; washed with light petroleum) suspended in tetrahydrofuran (10 cm^3) at 0 °C, and the mixture allowed to warm to ambient temperature and stirred for 1 h. The mixture was cooled to 0 °C and benzyl bromide (1.5 cm^3, 12.6 mmol) was added dropwise to it followed by tetrabutylammonium iodide (cat.). The mixture was allowed to warm to ambient temperature and stirred for 18 h. Saturated aqueous NH_4Cl (10 cm^3) was added to it and the mixture partitioned between ethyl acetate (30 cm^3) and water (30 cm^3). The aqueous phase was extracted with ethyl acetate and the organic extracts were washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel, using light petroleum–ethyl acetate (10:1) as eluent gave the *title compound* **13** (2.03 g, 89%) (Found: $M^+ + NH_4$, 382.2418. $C_{20}H_{36}NO_4Si$ requires *M*, 382.2414); $[\alpha]_D^{22}$ +73.7 (*c* 2.1, $CHCl_3$); ν_{max}/cm^{-1} 1740, 1249, 1027 and 836; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.97 [2 H, m, $CH_2Si(CH_3)_3$], 2.46 (2 H, m, 5-H_2), 2.51 (1 H, dd, *J* 5, 2.5, 7-H), 2.73 (1 H, t, *J* 4.5, 7-H′), 2.98 (1 H, m, 6-H), 3.57 [3 H, m, 1-H_2 and $OCHHCH_2Si(CH_3)_3$], 3.80 [1 H, m, $OCHHCH_2Si(CH_3)_3$], 4.61 (2 H, s, OCH_2Ph), 4.64 (1 H, m, 2-H), 4.71 and 4.75 (each 1 H, d, *J* 8, OCHO), 5.51 (1 H, dd, *J* 10.5, 9, 3-H), 5.73 (1 H, dt, *J* 10.5, 7.5, 4-H) and 7.38 (5 H, m, ArH); δ_C −1.4, 18.1, 30.5, 46.4, 51.3, 65.1, 70.2, 72.7, 73.3, 92.1, 127.6, 128.4, 128.5, 129.8 and 138.3; *m*/*z* (CI) 382 ($M^+ + NH_4$, 70%) and 307(16).

(2*S*,6*R*)-2-Benzyloxymethyl-6-hydroxymethyl-5,6-dihydro-2*H*-pyran 14

Trifluoroacetic acid (0.8 cm^3) was added dropwise to a solution of epoxide **13** (65 mg, 0.18 mmol) in dry dichloromethane (0.4 cm^3) at 0 °C, and the mixture stirred at 0 °C for 25 min. Aqueous NaOH (10%; 5 cm^3) and ethyl acetate (5 cm^3) were added to the mixture, the phases separated, and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (3:2) as eluent gave the *title compound* **14** (37 mg, 89%) containing *ca.* 20% of its epimer at C6 (Found: $M^+ + NH_4$, 252.1602. $C_{14}H_{22}NO_3$ requires *M*, 252.1600); $[\alpha]_D^{22}$ −27.1 (*c* 1.4, $CHCl_3$); ν_{max}/cm^{-1} 3439, 3032, 2862, 1656, 1454, 1367, 1091 and 738; δ_H 1.92 (1 H, m, 5-H), 2.14 (1 H, m, 5-H′), 2.43 (1 H, br s, OH), 3.49–3.84 (5 H, m, CH_2OCH_2Ph, CH_2OH and 6-H), 4.44 (1 H, m, 2-H), 4.60 and 4.67 (each 1 H, d, *J* 12, OCHPh), 5.72 (1 H, br d, *J* 10.5, 3-H), 5.95 (1 H, m, 4-H) and 7.38 (5 H, m, ArH); δ_C 26.6, 65.6, 72.8, 73.5, 74.2, 74.3, 125.6, 127.1, 127.7, 127.8, 128.4 and 138.2; *m*/*z* (CI) 252 ($M^+ + NH_4$, 100%).

On a larger scale (*ca.* 0.7 g), the reaction was more conveniently quenched by the addition of water and ethyl acetate, followed by the careful (effervescence) addition of anhydrous potassium carbonate in portions until effervescence ceased. The yields of the larger scale reactions were *ca.* 65%.

(2*S*,6*R*)- and (2*S*,6*S*)-2-Benzyloxymethyl-6-(*tert*-butyldimethylsilyloxymethyl)- 5,6-dihydro-2*H*-pyran 16 and 17

Triethylamine (0.403 cm^3, 2.89 mmol) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.53 cm^3, 2.31 mmol) were

added dropwise to the alcohol **14** containing *ca.* 20% of **15** (0.271 g, 1.16 mmol) in dichloromethane (5 cm^3) at 0 °C, and the mixture was stirred at 0 °C for 1 h. Saturated aqueous $NaHCO_3$ was added to it followed by ethyl acetate (20 cm^3) and water (20 cm^3). The organic phase was washed with water and brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography on silica gel, using light petroleum–ether (29:1) as eluent gave the (2*S*,6*R*)-isomer of the *title compound* **16** (0.245 g, 61%) (Found: $M^+ + NH_4$, 366.2462. $C_{20}H_{36}NO_3Si$ requires *M*, 366.2464); $[\alpha]_D^{22}$ −11.2 (*c* 2.4, $CHCl_3$); ν_{max}/cm^{-1} 3033, 1472, 1254, 1183 and 837; δ_H 0.10 [6 H, s, $Si(CH_3)_2$], 0.95 [9 H, s, $SiC(CH_3)_3$], 2.1 (2 H, m, 5-H_2), 3.51 (1 H, dd, *J* 10, 5, 1″-H), 3.55–3.66 (2 H, m, 1″-H′ and 1′-H), 3.73 (1 H, m, 6-H), 3.83 (1 H, dd, *J* 10, 5.5, 1′-H′), 4.41 (1 H, m, 2-H), 4.60 and 4.67 (each 1 H, d, *J* 12, *H*CHPh), 5.72 (1 H, m, 3-H), 5.95 (1 H, m, 4-H) and 7.38 (5 H, m, ArH); δ_C −5.2, −5.1, 18.4, 26.0, 27.9, 66.4, 72.8, 73.5, 74.4, 74.5, 125.9, 127.7, 127.6, 127.8, 128.4 and 138.3; *m*/*z* (CI) 366 ($M^+ + NH_4$, 88%) and 349 ($M^+ + H$, 25); together with the (2*S*,6*S*)-isomer of the *title compound* **17** (0.078 g, 19%) (Found: $M^+ + NH_4$, 366.2474. $C_{20}H_{36}NO_3Si$ requires *M*, 366.2464); $[\alpha]_D^{22}$ −81.4 (*c* 2.0, $CHCl_3$); ν_{max}/cm^{-1} 3033, 1472, 1254, 1190, 837 and 778; δ_H 0.10 [6 H, s, $Si(CH_3)_2$], 0.91 [9 H, s, $SiC(CH_3)_3$], 2.10 (2 H, m, 5-H_2), 3.51 (1 H, dd, *J* 10, 4, 1″-H), 3.64 (2 H, m, 1″-H′ and 1′-H), 3.80 (1 H, m, 1′-H′), 3.86 (1 H, m, 6-H), 4.46 (1 H, m, 2-H), 4.61 and 4.68 (each 1 H, d, *J* 12, *H*CHPh), 5.73 (1 H, m, 3-H), 5.98 (1 H, m, 4-H) and 7.38 (5 H, m, ArH); δ_C −5.3, −5.2, 18.4, 26.0, 27.2, 66.0, 69.4, 71.4, 72.4, 73.3, 125.8, 126.1, 127.6, 127.7, 128.4 and 138.3; *m*/*z* (CI) 366 ($M^+ + NH_4$, 100%) and 349 ($M^+ + H$, 25).

Following this procedure, a mixture of the alcohols **14** and **15** prepared from the *anti*-epoxide **32** (17 mg), see Scheme 3, gave the (2*S*,6*R*)-isomer of the title compound **16** (3.8 mg, 15%) and the (2*S*,6*S*)-isomer of the title compound **17** (15 mg, 60%).

(2*S*,6*R*)-6-Acetoxymethyl-2-benzyloxymethyl-5,6-dihydro-2*H*-pyran 18

Tetrabutylammonium fluoride (1.1 mol dm^{-3} in tetrahydrofuran; 0.13 cm^3) was added dropwise to a solution of the silyl ether **16** (0.044 g, 0.13 mmol) in tetrahydrofuran (0.65 cm^3) at 0 °C, and the mixture allowed to warm to ambient temperature and stirred for 18 h. Methanol (0.5 cm^3) and water (*ca.* 0.05 cm^3) were added to it and the mixture was stirred for 30 min before being dissolved in ethyl acetate, washed with brine, dried ($MgSO_4$), and then concentrated under reduced pressure. The residue was immediately dissolved in dry dichloromethane (1 cm^3), cooled to 0 °C, and triethylamine (0.070 cm^3, 0.5 mmol), acetic anhydride (0.050 cm^3, 0.53 mmol), and 4-dimethylaminopyridine (cat.) were added to it. The mixture was stirred at 0 °C for 1 h and then saturated $NaHCO_3$ (1 cm^3) was added to it. The mixture was extracted with ethyl acetate, and the organic extracts were washed with water and brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel, using light petroleum–ethyl acetate (10:1) as eluent, gave the *title compound* **18** (31 mg, 89%) (Found: $M^+ + NH_4$, 294.1708. $C_{16}H_{24}NO_4$ requires *M*, 294.1705); $[\alpha]_D^{22}$ −34.4 (*c* 1.2, $CHCl_3$); ν_{max}/cm^{-1} 1740, 1236, 1097 and 1043; δ_H 1.93–2.22 (2 H, m, 5-H_2), 2.12 (3 H, s, CH_3CO_2), 3.51 (1 H, dd, *J* 10, 5, 1′-H), 3.62 (1 H, dd, *J* 10, 6, 1′-H′), 3.91 (1 H, m, 6-H), 4.18 (2 H, m, 1″-H_2), 4.43 (1 H, m, 2-H), 4.61 and 4.67 (each 1 H, d, *J* 12, *H*CHPh), 5.77 (1 H, dt, *J* 10, 1, 3-H), 5.93 (1 H, m, 4-H) and 7.38 (5 H, m, ArH); δ_C 21.0, 27.3, 66.8, 71.7, 72.5, 73.5, 74.5, 125.0, 127.5, 127.6, 127.8, 128.4, 138.3 and 171.1; *m*/*z* (CI) 294 ($M^+ + NH_4$, 100%) and 277 ($M^+ + H$, 50).

(2*S*,6*S*)-6-Acetoxymethyl-2-benzyloxymethyl-5,6-dihydro-2*H*-pyran 19

Following the procedure outlined for the synthesis of **18**, the silyl ether **17** (37 mg, 0.10 mmol) gave the *title compound* **19** (25 mg, 85%) (Found: $M^+ + NH_4$, 294.1702. $C_{16}H_{24}NO_4$ requires *M*, 294.1705); $[\alpha]_D^{22}$ −83.0 (*c* 1.2, $CHCl_3$); ν_{max}/cm^{-1} 3017, 1739, 1239, 1191, 1109, 1048 and 756; δ_H 2.01–2.11 (2 H, m, 5-H_2), 2.13 (3 H, s, CH_3CO_2), 3.53 (1 H, dd, *J* 10, 5, 1′-H), 3.65 (1 H, dd, *J* 10, 7, 1′-H′), 4.09 (1 H, m, 6-H), 4.19 (2 H, m, 1″-H_2), 4.50 (1 H, m, 2-H), 4.53 and 4.58 (each 1 H, d, *J* 12, *H*CHPh), 5.76 (1 H, dt, *J* 10, 1, 3-H), 5.97 (1 H, m, 4-H) and 7.38 (5 H, m, ArH); δ_C 21.0, 26.5, 29.8, 66.4, 66.8, 71.1, 72.5, 73.3, 125.2, 126.2, 127.6, 128.4, 138.3, and 171.1; *m*/*z* (CI) 294 ($M^+ + NH_4$, 100%) and 277 ($M^+ + H$, 55).

(2*S*,6*S*,3*Z*)-2,6-Diacetoxy-1-benzyloxy-7-chlorohept-3-ene 20

Concentrated hydrochloric acid (*ca.* 0.05 cm^3) was added to a solution of the epoxide **13** (42 mg, 0.12 mmol) in acetonitrile (0.5 cm^3) at 0 °C, and the mixture stirred at 0 °C for 30 min. Saturated aqueous $NaHCO_3$ (1 cm^3) was added to it and the mixture partitioned between ethyl acetate (10 cm^3) and water (10 cm^3). The aqueous layer was extracted with ethyl acetate and the combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (3:2) as eluent gave the chlorohydrin (26 mg, 83%) which was dissolved in pyridine (0.5 cm^3) and the solution cooled to 0 °C. 4-Dimethylaminopyridine (cat.) and acetic anhydride (0.03 cm^3, 0.32 mmol) were added to the mixture and the solution was allowed to warm to ambient temperature and stirred for 1 h. Saturated aqueous $NaHCO_3$ was added to it and the mixture partitioned between ethyl acetate (5 cm^3) and water (5 cm^3). The aqueous layer was extracted with ethyl acetate, and the combined organic extracts were washed with saturated aqueous $CuSO_4$ and water, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel, using light petroleum–ethyl acetate (5:1) as eluent, gave the *title compound* **20** (27 mg, 79%) (Found: $M^+ + NH_4^+$, 372.1584. $C_{18}H_{27}{}^{35}ClNO_5$ requires *M*, 372.1578); ν_{max}/cm^{-1} 1739, 1371, 1235 and 1030; δ_H 2.09 and 2.10 (each 3 H, s, CH_3CO_2), 2.63 (2 H, m, 5-H_2), 3.55 (2 H, m), 3.65 (2 H, m), 4.57 and 4.64 (each 1 H, d, *J* 12, O*H*CHPh), 5.11 (1 H, m, 6-H), 5.56 (1 H, m, 3-H), 5.63 (1 H, m, 4-H), 5.75 (1 H, m, 2-H) and 7.38 (5 H, m, ArH); δ_C 20.9, 21.2, 30.2, 45.0, 69.0, 71.2, 72.0, 73.3, 127.7, 127.8, 128.4, 128.6, 137.9 and 170.3; *m*/*z* (CI) 374 ($M^+ + NH_4$, 33%), 372 ($M^+ + NH_4$, 100), 297 (12) and 295 (36).

(2*S*,6*R*,3*Z*)-6-(2-Trimethylsilylethoxymethoxy)-2-hydroxyhept-4-enyl toluene-*p*-sulfonate 22

Following the procedure outlined for the synthesis of **10**, the stannane **21** (0.52 g, 1.03 mmol) gave the *title compound* **22** (0.3 g, 68%); ν_{max}/cm^{-1} 3432, 1599, 1364, 1249, 1178, 1098, 1021 and 836; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.98 [2 H, m, $CH_2Si(CH_3)_3$], 1.27 (3 H, d, *J* 6, 7-H_3), 2.40 (2 H, m, 3-H_2), 2.49 (3 H, s, CH_3Ar), 3.59 and 3.71 [each 1 H, m, $OCHHCH_2Si(CH_3)_3$], 3.86 (1 H, m, 2-H), 4.01 (2 H, m, 1-H_2), 4.53 (1 H, m, 6-H), 4.64 and 4.78 (each 1 H, d, *J* 7, O*H*CHO), 5.45 (1 H, m, 5-H), 5.59 (1 H, m, 4-H), 7.39 and 7.84 (each 2 H, d, *J* 8, ArH); δ_C −1.4, 18.0, 21.3, 21.6, 31.8, 65.1, 66.8, 68.6, 73.4, 91.6, 127.9, 128.0, 129.9, 130.0, 134.4 and 145.0; *m*/*z* (CI) 448 ($M^+ + NH_4$, 6%).

(2*S*,6*R*,3*Z*)-6,7-Epoxy-2-(2-trimethylsilylethoxymethoxy)hept-3-ene 23

Anhydrous K_2CO_3 (51 mg, 0.37 mmol) was added to a solution of the toluene-*p*-sulfonate **22** (0.145 g, 0.34 mmol) in methanol (1 cm^3). The slurry was stirred for 1 h, then water (1 cm^3) was added to it and the mixture partitioned between ethyl acetate (10 cm^3) and water (10 cm^3). The organic phase was washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure to afford the *title compound* **23** (74 mg, 85%) which was used without further purification (Found: $M^+ + NH_4$, 276.1999. $C_{13}H_{30}NO_3Si$ requires *M*, 276.1995);

ν_{max}/cm^{-1} 1249, 1101, 1026 and 836; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.96 [2 H, m, $CH_2Si(CH_3)_3$], 1.27 (3 H, d, *J* 6.5, 1-H_3), 2.43 (2 H, m, 5-H_2), 2.54 (1 H, dd, *J* 5, 2.5, 7-H), 2.77 (1 H, t, *J* 4.5, 7-H'), 3.00 (1 H, m, 6-H), 3.56 and 3.74 [each 1 H, m, $OCHHCH_2Si(CH_3)_3$], 4.56 (1 H, m, 2-H), 4.63 and 4.69 (each 1 H, d, *J* 7, OHCHO), 5.46 (1 H, t, *J* 10, 3-H) and 5.60 (1 H, m, 4-H); δ_C −1.4, 18.1, 21.4, 30.2, 46.3, 51.3, 65.0, 66.7, 91.8, 125.7 and 134.4; *m/z* (CI) 276 ($M^+ + NH_4$, 9%).

(2*S*,6*S*)- and (2*S*,6*R*)-6-(*tert*-Butyldimethylsilyloxymethyl-2-methyl-5,6-dihydro-2*H*-pyran 25 and 27

Trifluoroacetic acid (0.15 cm^3) was added dropwise to a solution of the epoxide **23** (62 mg, 0.24 mmol) in dichloromethane (0.5 cm^3) at 0 °C, and the mixture allowed to warm to ambient temperature and stirred for 1 h. Methanol and anhydrous potassium carbonate (50 mg, 0.36 mmol) were added to it and stirring was continued for 20 min before the mixture was partitioned between dichloromethane (5 cm^3) and water (5 cm^3). The aqueous layer was extracted with dichloromethane and the organic extracts were washed with brine, dried ($MgSO_4$), and then concentrated under reduced pressure. The residue was dissolved in dichloromethane (1 cm^3) and cooled to 0 °C, triethylamine (0.12 cm^3, 0.86 mmol) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.165 cm^3, 0.72 mmol) were added to it and the mixture stirred at 0 °C for 30 min. Saturated aqueous $NaHCO_3$ (1 cm^3) was added to it and the mixture partitioned between ethyl acetate (10 cm^3) and water (10 cm^3). The organic layer was washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel, using light petroleum–ether (10:1) as eluent, gave a mixture of the title compounds **25** and **27** (43 mg, 74%). Further chromatography on silica gel, using light petroleum–ether (80:1) as eluent, gave (2*S*,6*S*)-isomer of the *title compound* **25** (15 mg) (Found: $M^+ + NH_4$, 260.2044. $C_{13}H_{30}NO_2Si$ requires *M*, 260.2046); $[\alpha]_D^{22}$ −22.7 (*c* 0.7, $CHCl_3$); ν_{max}/cm^{-1} 1256, 1189, 1130, 1089 and 836; δ_H 0.13 [6 H, s, $Si(CH_3)_2$], 0.94 [9 H, s, $SiC(CH_3)_3$], 1.26 (3 H, d, *J* 6.5, 1-CH_3), 2.01 (2 H, m, 5-H_2), 3.59 (1 H, dd, *J* 10, 5.5, 1'-H), 3.70 (1 H, m, 6-H), 3.79 (1 H, dd, *J* 10, 5.5, 1'-H'), 4.28 (1 H, m, 1-H), 5.64 (1 H, m, 4-H) and 5.83 (1 H, m, 3-H); δ_C −5.2, −5.1, 18.4, 21.3, 26.0, 27.8, 66.6, 70.9, 74.8, 123.9 and 131.6; *m/z* (CI) 260 ($M^+ + NH_4$, 31%) and 243 ($M^+ + H$, 100); together with the (2*S*,6*R*)-isomer of the *title compound* **27** (5 mg) (Found: $M^+ + H$, 243.1784. $C_{13}H_{27}O_2Si$ requires *M*, 243.1780); ν_{max}/cm^{-1} 2855, 1258, 1098 and 837; δ_H 0.10 [6 H, s, $Si(CH_3)_2$], 0.94 [9 H, s, $SiC(CH_3)_3$], 1.29 (3 H, d, *J* 7, 1-CH_3), 2.05 (2 H, m, 5-H_2), 3.62 and 3.76 (each 1 H, dd, *J* 10, 5.5, 1'-H), 3.83 (1 H, m, 6-H), 4.41 (1 H, m, 1-H), 5.72 (1 H, m, 4-H) and 5.84 (1 H, m, 3-H); δ_C −5.3, −5.1, 18.4, 20.0, 26.0, 27.2, 66.1, 68.3, 68.7, 123.2 and 131.0: *m/z* (CI) 260 ($M^+ + NH_4$, 18%) and 243 (MH^+, 59).

(2*S*,6*S*,4*Z*)-7-(*tert*-Butyldimethylsilyloxy)-2-hydroxy-6-(2-trimethylsilylethoxymethoxy)hept-4-enyl benzoate 28

Tin(IV) chloride (1 mol dm^{-3} in dichloromethane; 1.9 cm^3) was added dropwise to a solution of the stannane **9** (1.18 g, 1.86 mmol) in dichloromethane (20 cm^3) at −78 °C, and the reaction stirred at −78 °C for 5 min. 2-Oxoethyl benzoate (1 mol dm^{-3} in dichloromethane; 2 cm^3) was added to the mixture and stirring continued at −78 °C for 1 h, before saturated aqueous $NaHCO_3$ was added to it and the mixture allowed to warm to ambient temperature. The mixture was extracted with ethyl acetate and the organic extracts were washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (10:1, 1% triethylamine) as eluent gave the *title compound* **28** (0.68 g, 72%); ν_{max}/cm^{-1} 3443, 1724, 1251, 1102, 1057, 1027 and 837; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.11 [6 H, s, $Si(CH_3)_2$], 0.93 [9 H, s, $SiC(CH_3)_3$], 0.98 [2 H, m, $CH_2Si(CH_3)_3$], 2.46 and 2.54 (each 1 H, m, 3-H), 3.2 (1 H, br d, *J* 5, OH), 3.58–3.84 [4 H, m, 7-H_2 and $OCH_2CH_2Si(CH_3)_3$], 4.07 (1 H, m, 2-H), 4.36 (2 H, m, 1-H_2), 4.53 (1 H, m, 6-H), 4.71 and 4.83 (each 1 H, d, *J* 7, OHCHO), 5.50 (1 H, t, *J* 10, 5-H), 5.84 (1 H, m, 4-H), 7.49 (2 H, t, *J* 7.5, ArH), 7.61 (1 H, t, *J* 7.5, ArH) and 8.11 (2 H, d, *J* 7.5, ArH); δ_C −5.3, −5.2, −1.4, 18.0, 18.5, 26.0, 32.5, 65.2, 65.9, 68.5, 69.2, 72.1, 92.1, 128.4, 129.7, 130.0, 130.3, 130.8, 133.1 and 166.6; *m/z* (CI) 364 (53%).

(2*S*,6*R*,3*Z*)-1-(*tert*-Butyldimethylsilyloxy-6,7-epoxy-2-(2-trimethylsilylethoxymethoxy)hept-3-ene 30

Triethylamine (0.23 cm^3, 1.65 mmol) and methanesulfonyl chloride (0.12 cm^3, 1.55 mmol) were added dropwise to a solution of the alcohol **28** (0.26 g, 0.51 mmol) in dichloromethane (2 cm^3) at 0 °C and the solution allowed to warm to ambient temperature and stirred for 18 h. Saturated aqueous $NaHCO_3$ (2 cm^3) was added to it and the mixture partitioned between ethyl acetate (10 cm^3) and water (10 cm^3). The aqueous layer was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure. The residue was dissolved in dry methanol (3 cm^3), anhydrous K_2CO_3 (0.18 g, 1.30 mmol) was added to it, and the slurry stirred at ambient temperature for 2 h before being partitioned between ethyl acetate (10 cm^3) and water (10 cm^3). The organic layer was washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel afforded the *title compound* **30** as a colourless oil (93 mg, 47%) (Found: $M^+ + NH_4$, 406.2809. $C_{19}H_{44}NO_4Si_2$ requires *M*, 406.2809); ν_{max}/cm^{-1} 1250, 1104, 1027 and 836; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.10 [6 H, s, $Si(CH_3)_2$], 0.93 [9 H, s, $SiC(CH_3)_3$], 0.97 [2 H, m, $CH_2Si(CH_3)_3$], 2.45 (2 H, m, 5-H_2), 2.58 (1 H, dd, *J* 5, 2.5, 7-H), 2.78 (1 H, t, *J* 4.5, 7-H'), 3.01 (1 H, m, 6-H), 3.56 (1 H, dd, *J* 10, 8, 1-H), 3.63 (1 H, dd, *J* 10, 5, 1-H'), 3.74 [2 H, m, $OCH_2CH_2Si(CH_3)_3$], 4.47 (1 H, m, 2-H), 4.69 and 4.73 (each 1 H, d, *J* 7, OHCHO), 5.43 (1 H, t, *J* 10, 1.5, 3-H) and 5.76 (1 H, m, 4-H); δ_C −5.3, −5.2, −1.4, 18.1, 18.5, 26.0, 30.9, 46.7, 51.5, 65.0, 66.1, 71.9, 92.1, 128.7 and 130.0; *m/z* (CI) 406 ($M^+ + NH_4$, 20%), 389 ($M^+ + H$, 3) and 241 (100).

(2*S*,6*R*,3*Z*)-6,7-Epoxy-2-(2-trimethylsilylethoxymethoxy)hept-3-enol 31

Following the procedure used for the preparation of **12**, the epoxide **30** (0.145 g, 0.4 mmol) gave the *title compound* **31** (91 mg, 84%) (Found: $M^+ + NH_4$, 292.1944. $C_{13}H_{30}NO_4Si$ requires *M*, 294.1944); ν_{max}/cm^{-1} 3460, 1249, 1102, 1024 and 836; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.99 [2 H, m, $CH_2Si(CH_3)_3$], 2.36 and 2.49 (each 1 H, m, 5-H), 2.59 (1 H, dd, *J* 5, 2.5, 7-H), 2.62 (1 H, br s, OH), 2.81 (1 H, t, *J* 5, 7-H'), 3.01 (1 H, m, 6-H), 3.61 [3 H, m, 1-H_2 and $OCHHCH_2Si(CH_3)_3$], 3.80 [1 H, m, $OCHHCH_2Si(CH_3)_3$], 4.48 (1 H, m, 2-H), 4.72 and 4.76 (each 1 H, d, *J* 7, OHCHO), 5.49 (1 H, dd, *J* 11, 9, 3-H) and 5.79 (1 H, dt, *J* 11, 8.5, 4-H); δ_C −1.4, 18.1, 30.9, 46.9, 51.3, 65.4, 65.5, 73.8, 92.7, 129.2 and 129.3; *m/z* (CI) 292 ($M^+ + NH_4$, 13%) and 275 ($M^+ + H$, 5).

(2*S*,6*R*,3*Z*)-1-Benzyloxy-6,7-epoxy-2-(2-trimethylsilylethoxymethoxy)hept-3-ene 32

Following the procedure used for the preparation of **13**, the alcohol **31** (79 mg, 0.29 mmol) gave the *title compound* **32** (64 mg, 59%) (Found: $M^+ + NH_4$, 382.2410. $C_{20}H_{36}NO_4Si$ requires *M*, 382.2414); ν_{max}/cm^{-1} 1249, 1102, 1027 and 836; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.99 [2 H, m, $CH_2Si(CH_3)_3$], 2.44 (2 H, m, 5-H_2), 2.56 (1 H, dd, *J* 5, 2.5, 7-H), 2.76 (1 H, t, *J* 5, 7-H'), 2.98 (1 H, m, 6-H), 3.57 [3 H, m, 1-H_2 and $OCHHCH_2Si(CH_3)_3$], 3.79 [1 H, m, $OCHHCH_2Si(CH_3)_3$], 4.65 (3 H, m, 2-H and CH_2Ph), 4.71 and 4.75 (each 1 H, d, *J* 7, OHCHO),

5.51 (1 H, dd, *J* 11, 9, 3-H), 5.76 (1 H, dt, *J* 11, 7.5, 4-H) and 7.38 (5 H, m, ArH); δ_C −1.4, 18.1, 30.8, 46.7, 51.4, 65.1, 70.0, 72.8, 73.3, 92.0, 127.6, 128.4, 128.8, 129.6 and 138.3; *m/z* (CI) 382 ($M^+ + NH_4$, 10%).

Butyl (2*S*,6*S*,4*Z*)-7-(*tert*-butyldimethylsilyloxy)-2-hydroxy-6-(2-trimethylsilylethoxymethoxy)hept-4-enoate 33

Following the procedure used for the synthesis of the alcohol **10**, the stannane **9** (2.23 g, 3.51 mmol) and butyl glyoxylate (3.8 mmol) gave, after chromatography on silica gel using light petroleum–ethyl acetate (10:1, 1% triethylamine) as eluent, the *title compound* **33** (1.3 g, 78%) (Found: $M^+ + NH_4$, 494.3339. $C_{23}H_{52}NO_6Si_2$ requires *M*, 494.3333); $[\alpha]_D^{22}$ +31.4 (*c* 5.3, $CHCl_3$); ν_{max}/cm^{-1} 3451, 1738, 1250, 1201, 1103, 1026 and 837; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.10 [6 H, s, $Si(CH_3)_2$], 0.95 [14 H, m, $SiC(CH_3)_3$, $CH_3CH_2CH_2CH_2O$ and $CH_2Si(CH_3)_3$], 1.41 (2 H, sextet, *J* 7, $CH_3CH_2CH_2CH_2O$), 1.67 (2 H, quintet, *J* 7, $CH_3CH_2CH_2CH_2O$), 2.62 (2 H, m, 3-H_2), 3.38 (1 H, d, *J* 8, OH), 3.54 (1 H, dd, *J* 11, 8, 7-H), 3.61 (1 H, dd, *J* 11, 5.5, 7-H′), 3.76 [2 H, m, $OCH_2CH_2Si(CH_3)_3$], 4.20 (2 H, t, *J* 7, $CH_3CH_2CH_2CH_2O$), 4.25 (1 H, m, 2-H), 4.49 (1 H, dt, *J* 9.5, 6, 6-H), 4.66 and 4.75 (each 1 H, d, *J* 7, OHCHO), 5.45 (1 H, t, *J* 10.5, 5-H) and 5.73 (1 H, dt, *J* 10.5, 8, 6-H); δ_C −5.3, −1.4, 13.7, 18.0, 18.5, 19.1, 26.0, 30.6, 33.0, 65.1, 65.3, 65.9, 70.0, 71.5, 91.8, 129.2, 131.1 and 174.3; *m/z* (CI) 494 ($M^+ + NH_4$, 11%), 401 (33), 346 (56) and 329 (100).

(2*S*,6*S*,4*Z*)-7-(*tert*-Butyldimethylsilyloxy)-6-(2-trimethylsilylethoxymethoxy)hept-4-ene-1,2-diol 34

Sodium boranuide ($NaBH_4$) (0.19 g, 5.02 mmol) was added to a solution of the ester **33** (1.2 g, 2.52 mmol) in absolute ethanol (12 cm^3) at 0 °C. The mixture was allowed to warm to ambient temperature and stirred for 18 h. Saturated aqueous NH_4Cl was added to it followed by ethyl acetate (50 cm^3). The layers were separated and the aqueous phase extracted with ethyl acetate. The combined organic extracts were washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Filtration though a silica plug, using light petroleum–ethyl acetate (2:1) as eluent, gave the *title compound* **34** (0.89 g, 87%) which was used without further purification (Found: $M^+ + H$, 407.2649. $C_{19}H_{43}O_5Si_2$ requires *M*, 407.2649); $[\alpha]_D^{22}$ +64.6 (*c* 1.8, $CHCl_3$); ν_{max}/cm^{-1} 3407, 2859, 1251, 1102, 1026 and 837; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.10 [6 H, s, $Si(CH_3)_2$], 0.95 [9 H, s, $SiC(CH_3)_3$], 0.97 [2 H, m, $CH_2Si(CH_3)_3$], 2.25 (1 H, m, 3-H), 2.48 (1 H, dt, *J* 14, 9, 3-H′), 2.62 and 3.2 (each 1 H, br s, OH), 3.46–3.82 [7 H, m, 7-H_2, $OCH_2CH_2Si(CH_3)_3$, 1-H_2, and 2-H], 4.49 (1 H, dt, *J* 9.5, 5, 6-H), 4.69 and 4.80 (each 1 H, d, *J* 7, OHCHO), 5.43 (1 H, t, *J* 10.5, 5-H) and 5.78 (1 H, td, *J* 10.5, 6.5, 4-H); δ_C −5.3, −5.2, −1.4, 18.0, 18.5, 26.0, 32.0, 65.2, 65.9, 66.4, 71.4, 72.4, 92.3, 130.2 and 130.6; *m/z* (CI) 424 ($M^+ + NH_4$, 3%) and 407 ($M^+ + H$, 4).

2-Benzyloxymethyl-6-(*tert*-butyldimethylsilyloxymethyl)-3- and -4-hydroxytetrahydropyrans 36 and 35

Dihydropyran **16** (34 mg, 0.10 mmol) in tetrahydrofuran (0.4 cm^3) was added dropwise to borane–dimethyl sulfide complex (10.0–10.2 mol dm^{-3} in dimethyl sulfide; 0.030 cm^3) in tetrahydrofuran (0.2 cm^3) at 0 °C, and the solution stirred for 1 h. The mixture was allowed to warm slowly to ambient temperature and stirred for 18 h before being cooled to 0 °C when tetrahydrofuran (0.5 cm^3), water (0.5 cm^3), 10% aqueous NaOH (0.5 cm^3) and 30% hydrogen peroxide solution (0.25 cm^3) were added to it, and the mixture was stirred at 0 °C for 2 h. The mixture was partitioned between ethyl acetate (10 cm^3) and water (10 cm^3), and the aqueous phase extracted with ethyl acetate. The combined organic extracts were washed with water and brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (5:1) as eluent gave the *3-hydroxytetrahydropyran* **36** (20 mg, 56%) as a mixture of epimers (Found: $M^+ + H$, 367.2298. $C_{20}H_{35}O_4Si$ requires *M*, 367.2305); ν_{max}/cm^{-1} 3432, 2857, 1457, 1254, 1106 and 838; δ_H 0.10 [6 H, s, $Si(CH_3)_2$], 0.93 [9 H, s, $SiC(CH_3)_3$], 1.23–1.76 (3 H, m, 4-H and 5-H_2), 2.17 (1 H, m, 4-H′), 3.01 (1 H, br s, OH), 3.35–3.85 (7 H, m, 1′-H_2, 1″-H_2, 2-H, 3-H and 6-H), 4.59 and 4.66 (each 1 H, d, *J* 12, HC*H*Ph) and 7.38 (5 H, m, ArH); *m/z* (CI) 384 ($M^+ + NH_4$, 100%) and 367 ($M^+ + H$, 49); followed by the *4-hydroxytetrahydropyran* **35** (6 mg, 17%) as a mixture of epimers (Found: $M^+ + H$, 367.2301. $C_{20}H_{35}O_4Si$ requires *M*, 367.2305); ν_{max}/cm^{-1} 3430, 2858, 1255, 1122, 1074 and 837; *m/z* (CI) 367 ($M^+ + H$, 2%).

(2*R*,6*R*)-2-Benzyloxymethyl-6-(*tert*-butyldimethylsilyloxymethyl)tetrahydropyran-3-one 37

N-Methylmorpholine *N*-oxide (13 mg, 0.11 mmol), powdered 4 Å molecular sieves (*ca.* 5 mg) and tetrapropylammonium perruthenate (cat.) were added to a solution of the alcohol **36** (18 mg, 0.049 mmol) dichloromethane (0.5 cm^3) and the slurry stirred for 18 h before being filtered though silica using ethyl acetate as eluent. The filtrate was concentrated under reduced pressure, and chromatography on silica gel using light petroleum–ethyl acetate (8:1) as eluent, gave the *title compound* **37** (14 mg, 78%) (Found: $M^+ + NH_4$, 382.2425. $C_{20}H_{36}NO_4Si$ requires *M*, 382.2414); $[\alpha]_D^{22}$ +44.8 (*c* 0.9, $CHCl_3$); ν_{max}/cm^{-1} 2857, 1726, 1253, 1109, 838 and 778; δ_H 0.10 [6 H, s, $Si(CH_3)_2$], 0.94 [9 H, s, $SiC(CH_3)_3$], 2.02 and 2.17 (each 1 H, m, 5-H), 2.48 (1 H, ddd, *J* 16, 10, 7, 4-H), 2.68 (1 H, ddd, *J* 16, 6.5, 5.5, 4-H′), 3.72 (2 H, m), 3.89 (3 H, m), 4.13 (1 H, dd, *J* 5.5, 2.5, 2-H), 4.52 (2 H, s, CH_2Ph) and 7.38 (5 H, m, ArH); δ_C −5.3, −5.2, 18.4, 25.9, 27.0, 37.0, 65.7, 69.1, 73.7, 76.0, 82.5, 127.6, 127.7, 128.4, 138.0 and 208.5; *m/z* (CI) 382 ($M^+ + NH_4$, 31%) and 296 (24).

(2*R*,3*R*,4*S*,6*R*)-2-Benzyloxymethyl-3-bromo-6-hydroxymethyltetrahydropyran-4-ol 38

N-Bromosuccinimide (43 mg, 0.24 mmol) was added to the dihydropyran **16** (42 mg, 0.12 mmol) in 1,2-dimethoxyethane (0.9 cm^3) and water (0.3 cm^3), and the mixture stirred in the dark for 18 h before being diluted with ethyl acetate (10 cm^3), washed with 5% aqueous sodium thiosulfate and water, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (1:1) as eluent gave the *title compound* **38** (27 mg, 68%) (Found: M^+, 330.0470. $C_{14}H_{19}O_4{}^{79}Br$ requires *M*, 330.0467); ν_{max}/cm^{-1} 3399, 1184, 1078 and 743; δ_H 1.52 (1 H, br d, *J* 14, 5-H_{eq}), 2.24 (1 H, ddd, *J* 16, 11.5, 3, 5-H_{ax}), 2.51 and 2.78 (each 1 H, br s, OH), 3.56–3.74 (4 H, m, 1″-H_2 and 1′-H_2), 4.01 (1 H, m, 6-H), 4.07 (1 H, m, 4-H), 4.16 (1 H, td, *J* 6, 1.5, 2-H), 4.31 (1 H, br s, 3-H), 4.56 and 4.62 (each 1 H, *J* 12, OHC*H*Ph) and 7.38 (5 H, m, ArH); δ_C 29.6, 52.7, 65.7, 68.8, 71.5, 72.0, 73.0, 73.7, 127.9, 128.0, 128.5 and 137.7; *m/z* (CI) 350 ($M^+ + NH_4$, 13%) and 348 ($M^+ + NH_4$, 12).

(2*R*,3*R*,4*S*,6*R*)-2-Benzyloxymethyl-3-bromo-6-(*tert*-butyldimethylsilyloxymethyl)tetrahydropyran-4-ol 39 and (2*R*,3*R*,4*S*,6*R*)-2-benzyloxymethyl-3,4-dibromo-6-(*tert*-butyldimethylsilyloxymethyl)tetrahydropyran 40

N-Bromosuccinimide (0.105 g, 0.59 mmol) was added to a solution of the dihydropyran **16** (0.103 g, 0.296 mmol) in 1,2-dimethoxyethane (2.25 cm^3) and pH7 buffer solution (0.75 cm^3) and the mixture stirred in the dark for 18 h before being diluted with ethyl acetate (10 cm^3), washed with 5% aqueous sodium thiosulfate and water, dried ($MgSO_4$), and then concentrated under reduced pressure. Chromatography on silica gel, using light petroleum–ethyl acetate (6:1) as eluent, gave the *title compound* **39** (86 mg, 65%) (Found: $M^+ + NH_4$, 462.1668.

$C_{20}H_{37}{}^{79}BrNO_4Si$ requires *M*, 462.1675); $[\alpha]_D^{22}$ +6.5 (*c* 6.5, $CHCl_3$); ν_{max}/cm^{-1} 3426, 2857, 1255, 1128, 1077, 837 and 779; δ_H 0.09 and 0.10 [each 3 H, s, $Si(CH_3)_2$], 0.94 [9 H, s, $SiC(CH_3)_3$], 1.71 (1 H, d, *J* 14.5, 5-H_{eq}), 2.01 (1 H, d, *J* 3.5, OH), 2.20 (1 H, ddd, *J* 14.5, 12, 3, 5-H_{ax}), 3.50 (1 H, dd, *J* 10, 6.5, 1″-H), 3.60 (1 H, dd, *J* 10, 6, 1″-H'), 3.68 (1 H, dd, *J* 10, 6, 1'-H), 3.76 (1 H, dd, *J* 10, 5, 1'-H'), 3.93 (1 H, m, 6-H), 4.13 (2 H, m, 2-H and 4-H), 4.37 (1 H, m, 3-H), 4.56 and 4.64 (each 1 H, d, *J* 12, *H*CHPh) and 7.38 (5 H, m, ArH); δ_C −5.3, −5.2, 18.4, 25.9, 29.7, 53.0, 66.1, 69.2, 71.7, 72.0, 72.9, 73.6, 127.7, 127.9, 128.4 and 138.1; *m/z* (CI) 464 ($M^+ + NH_4$, 12%), 462 ($M^+ + NH_4$, 12) and 268 (100); together with the *title compound* **40** (26 mg, 17%) $[\alpha]_D^{22}$ +22.7 (*c* 0.9, $CHCl_3$); ν_{max}/cm^{-1} 2857, 1254, 1129, 836 and 778; δ_H 0.09 and 0.10 [each 3 H, s, $Si(CH_3)_2$], 0.92 [9 H, s, $SiC(CH_3)_3$], 1.97 (1 H, br d, *J* 15, 5-H_{eq}), 2.53 (1 H, ddd, *J* 15, 11, 3.5, 5-H_{ax}), 3.55 (1 H, dd, *J* 10, 6.5, 1″-H), 3.67 (2 H, m, 1″-H' and 1'-H), 3.78 (1 H, dd, *J* 10.5, 5, 1'-H'), 4.04 (1 H, m, 6-H), 4.32 (1 H, td, *J* 6, 1.5, 2-H), 4.53 (1 H, m, 4-H), 4.56 and 4.63 (each 1 H, d, *J* 12, HC*H*Ph), 4.83 (1 H, dd, *J* 7, 2, 3-H) and 7.38 (5 H, m, ArH); δ_C −5.2, 18.3, 25.9, 30.6, 50.3, 52.5, 65.2, 71.5, 72.0, 73.3, 73.7, 127.8, 127.9, 128.4 and 138.0; *m/z* (CI) 528 ($M^+ + NH_4$, 58%), 526 ($M^+ + NH_4$, 100) and 524 ($M^+ + NH_4$, 57).

(2*R*,3*R*,4*S*,6*R*)-4-Acetoxy-2-benzyloxymethyl-3-bromo-6-(*tert*-butyldimethylsilyloxymethyl)tetrahydropyran 41

Triethylamine (0.03 cm^3, 0.215 mmol) and acetic anhydride (0.016 cm^3, 0.170 mmol) were added to the bromohydrin **39** (25 mg, 0.056 mmol) and 4-dimethylaminopyridine (cat.) in dichloromethane (0.5 cm^3) at 0 °C and the mixture stirred at 0 °C for 90 min. Saturated aqueous $NaHCO_3$ (1 cm^3) and ethyl acetate (10 cm^3) were added to the mixture and the layers were separated, and the organic phase was washed with water and brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (10:1) as eluent gave the *title compound* **41** (22 mg, 80%) (Found: $M^+ + NH_4$, 504.1788. $C_{22}H_{39}{}^{79}BrNO_5Si$ requires *M*, 504.1781); $[\alpha]_D^{22}$ +23.2 (*c* 0.9, $CHCl_3$); ν_{max}/cm^{-1} 2857, 1747, 1371, 1230, 1084 and 837; δ_H 0.09 and 0.10 [each 3 H, s, $Si(CH_3)_2$], 0.94 [9 H, s, $SiC(CH_3)_3$], 1.75 (1 H, br d, *J* 14.5, 5-H_{eq}), 2.13 (3 H, s, CH_3CO_2), 2.24 (1 H, ddd, *J* 14.5, 11.5, 3, 5-H_{ax}), 3.59 (1 H, dd, *J* 10, 6, 1″-H), 3.61 (1 H, dd, *J* 10, 5.5, 1″-H'), 3.67 (1 H, dd, *J* 10, 6, 1'-H), 3.76 (1 H, dd, *J* 10, 5, 1'-H'), 3.84 (1 H, m, 6-H), 3.97 (1 H, td, *J* 6, 1.5, 2-H), 4.20 (1 H, m, 3-H), 4.57 and 4.63 (each 1 H, d, *J* 12, O*H*CHPh), 5.33 (1 H, dd, *J* 5.5, 3, 4-H) and 7.38 (5 H, m, ArH); δ_H −5.2, 18.4, 21.2, 25.9, 27.2, 49.1, 66.0, 70.7, 72.0, 72.8, 73.7, 73.8, 127.8, 127.9, 128.4, 137.9 and 169.6; *m/z* (CI) 506 ($M^+ + NH_4$, 100%) and 504 ($M^+ + NH_4$, 94).

(2*S*,4*R*,6*R*)-2-Benzyloxymethyl-6-(*tert*-butyldimethylsilyloxymethyl)tetrahydropyran-4-ol 42

A solution of bromohydrin **39** (0.196 g, 0.44 mmol) and tributyltin hydride (0.175 cm^3, 0.65 mmol) in toluene (8.6 cm^3) was degassed with argon for 1 h. AIBN (cat.) was added to it and the mixture heated under reflux for 1 h before being cooled and concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (4:1, 1% triethylamine) as eluent, gave the *title compound* **42** (0.146 g, 91%) (Found: $M^+ + H$, 367.2300. $C_{20}H_{35}O_4Si$ requires *M*, 367.2305); $[\alpha]_D^{22}$ +3.2 (*c* 1.4, $CHCl_3$); ν_{max}/cm^{-1} 3434, 2858, 1255, 1122, 1074 and 837; δ_H 0.10 [6 H, s, $Si(CH_3)_2$], 0.92 [9 H, s, $SiC(CH_3)_3$], 1.50–1.75 (4 H, m, 3-H_2 and 5-H_2), 3.47 (1 H, dd, *J* 10, 4, 1″-H), 3.54 (1 H, dd, *J* 10, 5.5, 1″-H'), 3.58 (1 H, dd, *J* 10, 6, 1'-H), 3.76 (1 H, dd, *J* 10, 5, 1'-H'), 3.93 (1 H, dtd, *J* 11, 5, 2, 2-H), 4.09 (1 H, m, 6-H), 4.35 (1 H, m, 4-H), 4.58 and 4.64 (each 1 H, d, *J* 12, OHC*H*Ph) and 7.38 (5 H, m, ArH); δ_C −5.2, 18.4, 26.0, 35.2, 64.3, 66.6, 70.9, 72.2, 73.4, 127.5, 127.7, 128.3 and 138.4; *m/z* (CI) 384 ($M^+ + NH_4$, 8%) and 367 ($M^+ + H$, 12).

(2*S*,6*R*)-2-Benzyloxymethyl-6-(*tert*-butyldimethylsilyloxymethyl)tetrahydropyran-4-one 43

Dimethyl sulfoxide (0.130 cm^3, 1.83 mmol) in dichloromethane (4.2 cm^3) was added dropwise to oxalyl chloride (0.135 cm^3, 1.55 mmol) in dichloromethane (4.2 cm^3) at −50 °C and the mixture stirred at −50 °C for 5 min. The alcohol **42** (0.225 g, 0.61 mmol) in dichloromethane (6 cm^3) was added to it, and the mixture stirred at −50 °C for 20 min. Triethylamine (0.525 cm^3, 3.77 mmol) was added to it and the mixture stirred at −50 °C for 10 min and allowed to warm to 0 °C. Water (5 cm^3) was added to it and the mixture allowed to warm to ambient temperature before being diluted with ethyl acetate (10 cm^3) and the phases separated. The organic layer was washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel, using light petroleum–ethyl acetate (6:1) as eluent gave the *title compound* **43** (0.193 g, 86%) (Found: $M^+ + NH_4$, 382.2413. $C_{20}H_{36}NO_4Si$ requires *M*, 382.2414); $[\alpha]_D^{22}$ +2.9 (*c* 1.0, $CHCl_3$); ν_{max}/cm^{-1} 2857, 1722, 1253, 1117 and 837; δ_H 0.11 [6 H, s, $Si(CH_3)_2$], 0.95 [9 H, s, $SiC(CH_3)_3$], 2.44 (4 H, m, 3-H_2 and 5-H_2), 3.59 (1 H, dd, *J* 11, 4.5, 1″-H), 3.65 (1 H, dd, *J* 11, 5, 1″-H'), 3.78 (3 H, m, 1'-H_2 and 2-H), 3.90 (1 H, m, 6-H), 4.63 (2 H, s, CH_2Ph) and 7.38 (5 H, m, ArH); δ_H −5.2, 15.3, 18.4, 25.9, 44.2, 44.3, 65.8, 72.4, 73.6, 76.2, 127.7, 127.8, 128.4, 138.0 and 207.3; *m/z* (CI) 382 ($M^+ + NH_4$, 100%) and 365 ($M^+ + H$, 5).

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