On the stereoselectivity of reactions of alkoxyallylstannanes and alkoxy aldehydes

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Different behaviour is observed in tin(IV) halide promoted reactions between the 2-(1-alkoxyethyl)prop-2-enylstannane 10 and the 4-alkoxypent-2-enylstannanes 1 with 2-alkoxy aldehydes. The chirality of the aldehyde would appear to dominate the stereoselectivity in the former case with the preferred addition following the chelation controlled mode, whereas the stannane dominates the stereoselectivity in the latter. The different behaviour of these two types of stannane may be a reflection of the coordination of the tin in the intermediate allyltin trihalides which are believed to be the reactive species involved in the reactions with the aldehydes.

Alkoxyalk-2-enylstannanes are transmetallated by tin(IV) halides to generate allyltin trihalides which react with aldehydes and imines with useful levels of 1,5-, 1,6- and 1,7-asymmetric induction.[1] For example, in reactions with aldehydes, the (*S*)-4-benzyloxypent-2-enylstannane **1** gives the 1,5-*syn*-diastereoisomers **2**† with excellent stereoselectivity (*ca.* 97:3).[2] With chiral aldehydes, the 1,5-*syn*-diastereoisomers **2** remain the dominant products, although some matching and mis-matching is observed with chiral 2-alkoxy aldehydes, *e.g.* (*S*)- and (*R*)-2-benzyloxypropanal (*S*)- and (*R*)-**3** give the 1,5-*syn*-product **4** (*syn*:*anti* = 96:4) and the *syn*- and *anti*-products **5** and **6** (70:30), respectively (Scheme 1).[2,3]

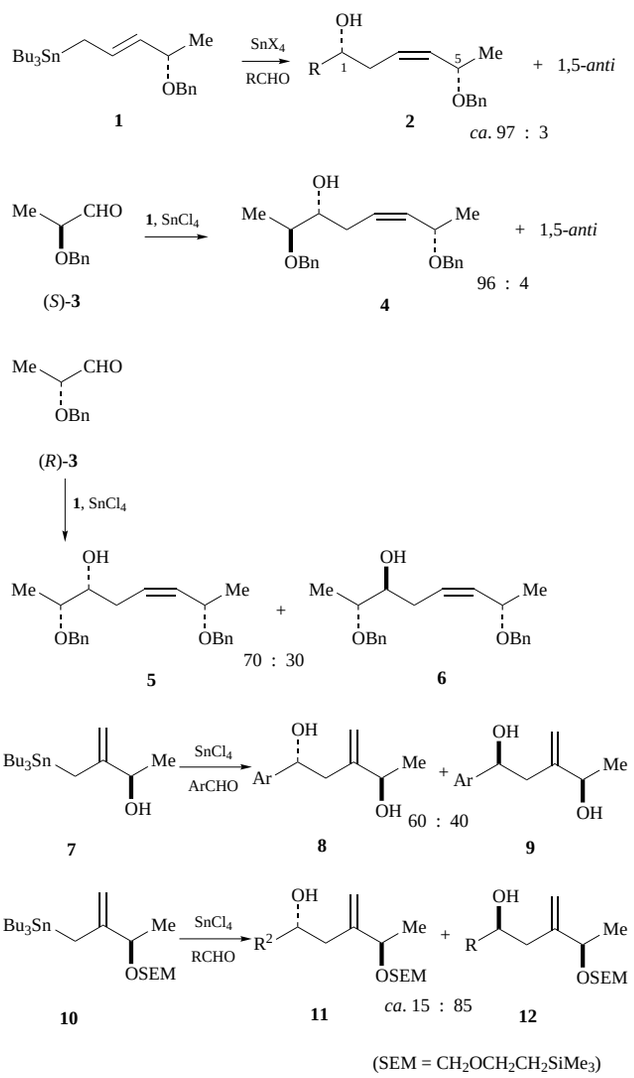
In the preceding paper, the stereoselectivities of reactions between simple aldehydes and the 2-substituted propenylstannanes **7** and **10** are reported.[4] After treatment with a tin(IV) halide, 2-(1-hydroxyethyl)propenylstannane **7** reacts with aldehydes with modest selectivity in favour of the 1,4-*anti*-diols **8** whereas the analogous alkoxystannane **10** gives more of the 1,4-*syn*-products **12**.†

We now report a comparison of the reactions of the allyltin trihalides generated from the (*S*)-4-benzyloxypent-2-enylstannane **1** and the 2-(1-alkoxyethyl)propenylstannane **10** with 2-alkoxy aldehydes. The results obtained may have some bearing on the differing structures of the reactive species which are involved.

Results and discussion

The stereoselectivities of reactions of the (*S*)- and (*R*)-2,3-*O*-isopropylidenepropanal **13** with the allyltin tribromide generated from the 2-(1-alkoxyethyl)prop-2-enylstannane **10** were found to be controlled by the chirality of the aldehyde, not by the stannane. Thus the (*S*)-aldehyde (*S*)-**13**[5] gave a mixture of adducts in which the usually observed 1,4-*syn*-preference of the stannane was reversed in favour of the 1,4-*anti*-isomer **14** (1,4-*anti*:1,4-*syn* = 95:5) and the (*R*)-aldehyde (*R*)-**13**[6] gave the 1,4-*syn*-diastereoisomer **19** (1,4-*syn*:1,4-*anti* = 85:15).†

The configurations of the alcohol groups of the major products **14** and **19** were established by comparison of the ^{1}H NMR chemical shifts of acetylmandelates **15**, **16** and **20**, **21** (Scheme 2).[7] The major products **14** and **19** were converted *via* a Mitsunobu reaction with inversion into the *p*-nitrobenzoates **18** and **23** which were saponified to give the alcohols **17** and **22**, so confirming that the minor products were epimers of the major products at the alcoholic carbon centre.[8]

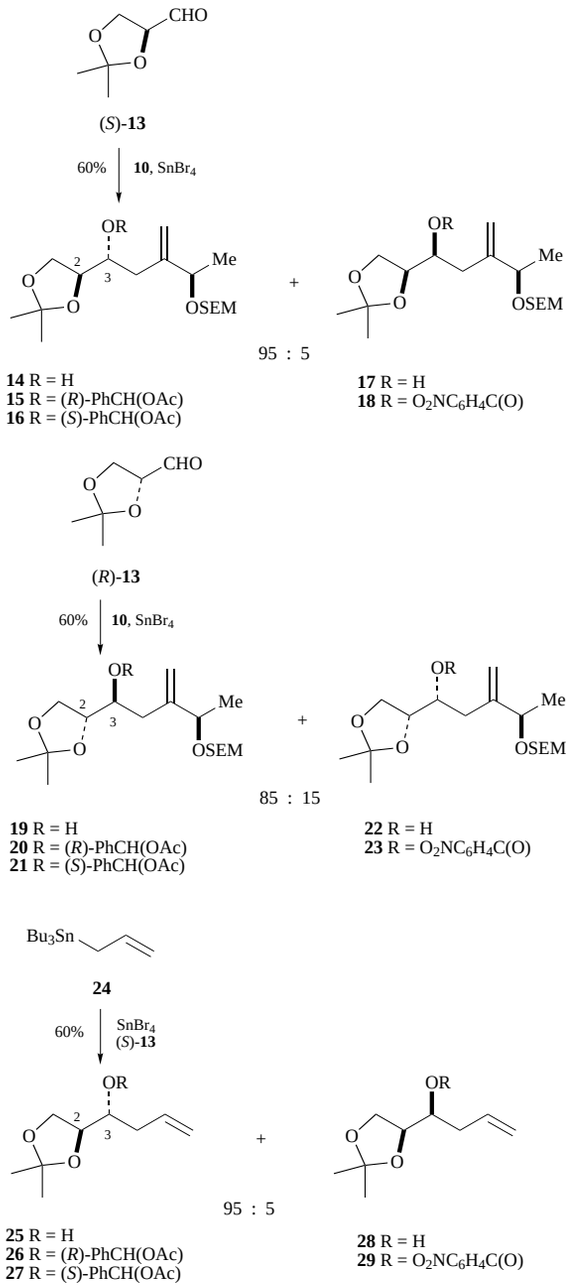


Scheme 1

In these cases, the reactions with the chiral aldehydes are giving the 2,3-*anti*-isomers‡ as the major products irrespective of the chirality of the aldehyde. This selectivity was also observed for reactions with the achiral stannane, prop-2-

† Relative numbering system between the alcoholic carbon and the alkoxy substituent (see compound **2**, Scheme 1).

‡ Absolute numbering system is used, *i.e.* numbering used for construction of names (see compound **14**, Scheme 2).



Scheme 2

enyl(tributyl)stannane **24**, which gave the 2,3-*anti*-product **25** on reaction with the (*S*)-aldehyde (*S*-**13**, selectivity *ca.* 95:5 (*anti*:*syn*). Again the configuration of the 2,3-*anti*-product **25** at the alcoholic carbon was confirmed by comparison of the ^{1}H NMR spectra of the acetylmandelates **26** and **27** and a Mitsunobu inversion followed by saponification to convert the 2,3-*anti*-isomer **25** into the minor product **28** *via* the *p*-nitrobenzoate **29**.

The preference for the formation of the 2,3-*anti*-products **14**, **19** and **25** in reactions of the stannanes **10** and **24** with the (*S*)- and (*R*)-dioxolanyl aldehydes **13** contrasts with the control exercised by the stannane in reactions between the (*S*)- and (*R*)-2-benzyloxypropanals **3** with the chiral stannane **1**.[2,3] To help to establish the causes of this change in stereoselectivity, reactions between the stannane **1** and the (*S*)- and (*R*)-dioxolanyl aldehydes **13** were examined.

The reaction between (*S*)-aldehyde (*S*)-**13** and the allyltin tribromide generated from the pentenylstannane **1**[2] gave two major products which were separated and identified as the regioisomeric hydroxy acetonides **30** and **35** (Scheme 3). The non-rearranged hydroxy acetonide **30** also contained a minor component which was identified as the 1,5-*anti*-product **33** (1,5-*syn*:1,5-*anti* = 95:5).† The enantiomeric (*R*)-aldehyde (*R*)-**13** similarly reacted with the pentenylstannane **1** to give two major products identified as the regioisomeric hydroxy acetonides **37** and **42**, with the 3-hydroxy compound **37** containing *ca.* 10% of its 1,5-*anti*-isomer **40** (1,5-*syn*:1,5-*anti* = 90:10).

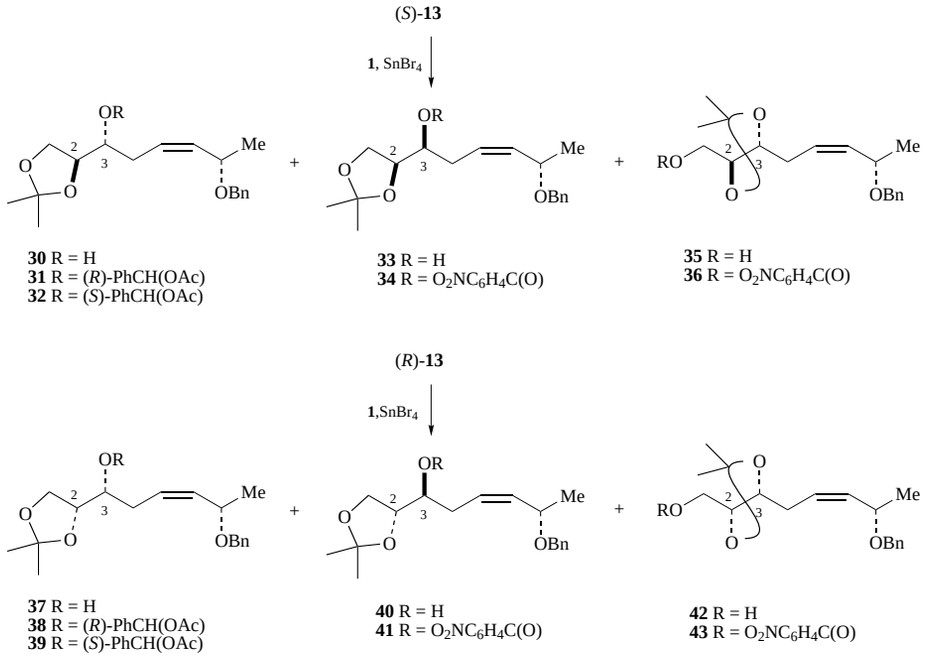
Structures were assigned to these products on the basis of spectroscopic data and chemical correlation. The configurations at the alcoholic carbon centres of the hydroxy acetonides **30** and **37** were established by comparison of the ^{1}H NMR spectra of their acetylmandelates.[7] The minor 3-hydroxy acetonides **33** and **40** were identified by comparison with samples prepared by a Mitsunobu inversion of the major isomers **30** and **37** giving the *p*-nitrobenzoates **34** and **41**, respectively, followed by hydrolysis. The rearranged 1-hydroxy 2,3-acetonides‡ **35** and **42** were shown to be primary alcohols by esterification using *p*-nitrobenzoic acid which gave the *p*-nitrobenzoates **36** and **43**, respectively, in which the 1-H_2 protons had been deshielded by *ca.* 0.5 ppm relative to the parent alcohols. Treatment of the major 3-hydroxy acetonide **30** with tin(IV) bromide established an equilibrium with the 1-hydroxy isomer **35** showing that these products had the same configurations at their stereogenic centres. The configuration of the 1-hydroxy 2,3-acetonide **42** was assigned by analogy. The NMR data for the acetonides **35** and **42** were also consistent with the assigned structures, *e.g.* an NOE enhancement of H(3) on irradiation of H(2), and *vice versa* for isomer **35**, were consistent with these protons being *cis*-disposed about the acetonide ring.

The 4-benzyloxypent-2-enylstannane **1** therefore reacts with the aldehydes **13** with the stereoselectivity being dominated by the stannane, as observed in its reactions with the 2-benzyloxypropanals **3**.[2,3]

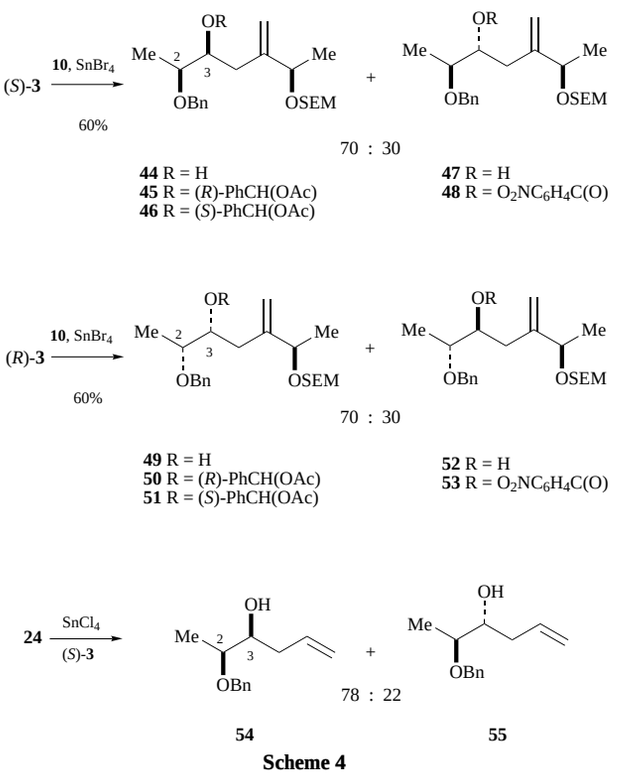
It remained to establish the stereoselectivity of reactions between the 2-(alkoxyethyl)prop-2-enylstannane **10** and the (*S*)- and (*R*)-2-benzyloxypropanals **3** (Scheme 4).[9] In the event, both aldehydes reacted with the propenyltin tribromide generated from the stannane **10** to give the 2,3-*syn*-product‡ with modest selectivity *ca.* 70:30, even though in the case of the reaction with the (*R*)-aldehyde this meant that the 1,4-*anti*-isomer **49**† was the major product. The structure of this major product from the reaction with the (*R*)-aldehyde (*R*)-**3** was established by comparison of the ^{1}H NMR spectra of its acetylmandelates **50** and **51**,[7] and the minor product **52** was identified by comparison with an authentic sample prepared from the major product by a Mitsunobu reaction followed by hydrolysis. The products **44** and **47** from the reaction with the (*S*)-aldehyde (*S*)-**3** could not be separated. Nevertheless, comparison of the ^{1}H NMR spectra of mixtures containing predominantly the (*R*)- and (*S*)-mandelates **45** and **46** confirmed the stereochemistry as shown, and a Mitsunobu reaction interconverted the major and minor products. The preferred formation of the 2,3-*syn*-products‡ **44** and **49** follows the selectivity observed in reactions of 2-benzyloxypropanal (*S*)-**3** with the achiral propenylstannane **24** which is known to give the *syn*- and *anti*-products **54** and **55** (78:22).[2]

It would appear that the stereocontrol is exercised by the aldehyde in reactions between the allyltin trihalide generated from the 2-(1-alkoxyethyl)propenylstannane **10** and the 2-alkoxy aldehydes (*S*)- and (*R*)-**3** and -**13**, whereas the stannane controls the stereoselectivities of the analogous reactions of the 4-benzyloxypent-2-enylstannane **1**.

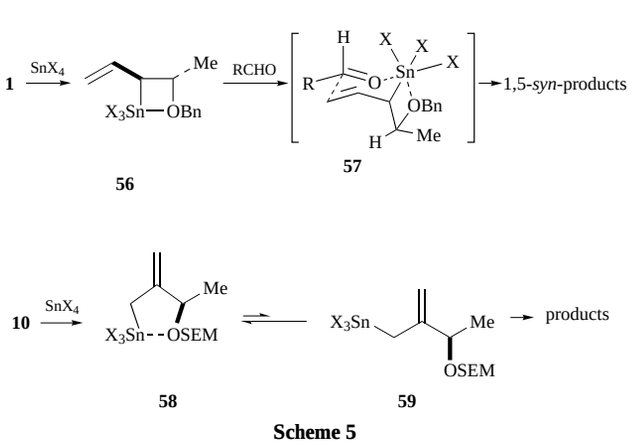
The stereoselectivity of tin(IV) halide promoted reactions of stannane **1** with aldehydes is believed to be controlled by participation of the allyltin trihalide **56**, which reacts with aldehydes *via* the six-membered, cyclic, chair-like transition structure **57**. The formation of the allyltin trihalide **56** is believed to be stereoselective for the isomer shown in which the vinyl and methyl groups are *trans*-disposed about the four-membered oxastannane ring. In the reaction of this intermediate with an aldehyde *via* the chair-like transition structure **57**, the formation



Scheme 3



Scheme 4



Scheme 5

of *cis*-alkenes is predominant, and controls the facial selectivity of the reaction with the aldehyde and the overall 1,5-*syn*-stereoselectivity† which overwhelms any intrinsic facial preference of a chiral aldehyde.[1,2]

The tin(IV) halide promoted reactions of the 2-(1-alkoxyethyl)propenylstannane **10** may involve the non-coordinated allyltin trihalides **59** as the reactive species even though they may be the minor components of an equilibrium with the coordinated tin trihalides **58**. It has been suggested that it is difficult for the C–Sn bond in the coordinated tin halides **58** to align with the π-orbitals of the double-bond and so that the coordinated species are less reactive than the more flexible non-coordinated species **59**. Moreover the non-coordinated tin halides **59** are able to coordinate to the alkoxy group of an alkoxyaldehyde and so undergo chelation controlled addition which would not be possible for the coordinated species **58**. Chelation controlled additions to the dioxolanyl aldehydes (*S*)- and (*R*)-**13** are known to give 2,3-*anti*-products selectively,[10,11] and the reactions with the allyltin trihalides **58**, and the equivalent achiral tin trihalides derived from propenylstannane **24**, would appear to conform to this pattern. Similarly the preferred formation of the 2,3-*syn*-products in reactions between the stannanes **10** and **24** and the 2-benzyloxypropanals (*S*)- and (*R*)-**3** is consistent with chelation control.

This difference in behaviour of the allyltin trihalides derived from stannanes **1** and **10** or **24** may be due to structural differences in the allyltin trihalide involved in the reaction, perhaps in the extent of coordination of any alkoxy substituent to the tin. If the electron deficient tin is coordinated to an alkoxy substituent, as in the allyltin trihalide **56**, the tin may be unable to coordinate to the alkoxy substituent of an alkoxy aldehyde and the stereoselectivity is consequently controlled by the allyltin trihalide with participation of transition structures analogous to **57**. However, if the alkoxy group in the stannane is not coordinated to the electron deficient tin, chelation controlled addition to an alkoxy aldehyde may occur as observed for reactions of the stannanes **10** and **24** with aldehydes **3** and **13**. Differences in reactivity of coordinated and non-coordinated allylic tin trihalides in reactions with hydroxy and alkoxy ketones have been noted before.[12]

More work is required to characterise further the allyltin trihalides involved as intermediates in these reactions, *e.g.* by

using ^{119}Sn NMR spectroscopy. The suggestion that the reactive species involved in the reactions of the allylstannane **10** and aldehydes promoted by tin(IV) halides have structures in which the electron deficient tin is not coordinated by the alkoxy substituent is presently made to explain the stereoselectivity of the reactions of **10** with aldehydes reported in this and the proceeding paper.[4] Notwithstanding this mechanistic dichotomy, the different behaviour of the alkoxyallylstannanes **1** and **10** reported herein is significant and will have a bearing on their application in organic synthesis.

Experimental

For general experimental details see the previous paper in this series. (*S*)- and (*R*)-2,2-Dimethyl-4-formyl-1,3-dioxolane (*S*)- and (*R*)-**13** had $[\alpha]_D$ −71.7 (*c* 2, benzene) [lit.,[5] $[\alpha]_D$ −75.4 (*c* 8, benzene)] and $[\alpha]_D$ 78.0 (*c* 2, benzene) [lit.,[6] $[\alpha]_D$ 80.1 (*c* 1.5, benzene)], respectively. (*R*) and (*S*)-2-(benzyloxy)propanal **3** had $[\alpha]_D$ +50.8 (*c* 3, $CHCl_3$) and $[\alpha]_D$ −51.3 (*c* 3, $CHCl_3$), respectively [lit.,[9] $[\alpha]_D$ −52.2 (*c* 6.5, $CHCl_3$)].

General procedure for reactions between allylstannanes and aldehydes

(2*S*,3*R*,6*R*)-1,2-*O*-isopropylidene-5-methylidene-6-(2-trimethylsilylethoxymethoxy)heptan-3-ol 14. A cooled solution of tin(IV) bromide (107 mg, 0.24 mmol) in dichloromethane (0.24 cm^3) was added dropwise to a stirred solution of the stannane **10** (100 mg, 0.20 mmol) in dichloromethane (3 cm^3) at −78 °C. After 10 min, a cooled solution of 2,3-*O*-isopropylidene-L-glyceraldehyde (*S*)-**13** (26 mg, 0.20 mmol) in dichloromethane (0.4 cm^3) was added and the mixture stirred for 1 h at −78 °C. Saturated aqueous sodium hydrogen carbonate (3 cm^3) was added, and the mixture allowed to warm to room temp. before being partitioned between dichloromethane and water. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue using diethyl ether–light petroleum (6:4) as eluent gave the *title compound* **14** (41 mg, 60%) as a colourless oil, containing *ca.* 5% (^{1}H NMR spectroscopy) of its epimer **17** (Found: $M^+ + H$, 347.2244. $C_{17}H_{35}O_5Si$ requires *M*, 347.2254); $[\alpha]_D$ +40.7 (*c* 3, CH_2Cl_2); ν_{max}/cm^{-1} 3475, 1374, 1252, 1217, 1159, 1105, 1068, 1026, 922, 861 and 837; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.90 (2 H, m, CH_2Si), 1.28 (3 H, d, *J* 6.5, 7-H_3), 1.34 and 1.40 (each 3 H, s, CH_3), 2.13 (1 H, dd, *J* 14.5, 10, 4-H), 2.44 (1 H, d, *J* 14.5, 4-H′), 3.39 (1 H, d, *J* 2, OH), 3.56 (1 H, m, OCH*H*CH_2Si), 3.64 and 3.93 (each 2 H, m), 4.05 (1 H, m), 4.21 (1 H, q, *J* 6.5, 6-H), 4.64 and 4.66 (each 1 H, d, *J* 7, OC*H*HO) and 5.03 and 5.13 (each 1 H, s, vinylic H); δ_C −1.4, 18.0, 20.1, 25.3, 26.7, 36.0, 65.5, 66.6, 71.9, 75.7, 78.7, 92.4, 109.2, 115.3 and 146.5; *m*/*z* 364 ($M^+ + 18$, 10%), 347 ($M^+ + 1$, 12) and 229 (100).

The following compounds were prepared by this procedure using the appropriate stannane.

(2*R*,3*S*,6*R*)-1,2-*O*-Isopropylidene-5-methylidene-6-(2-trimethylsilylethoxymethoxy)heptan-3-ol 19. (41 mg, 60%) Containing *ca.* 15% of its epimer **22** (Found: $M^+ + H$, 347.2260. $C_{17}H_{35}O_5Si$ requires *M*, 347.2254); $[\alpha]_D$ +48.4 (*c* 1.1, CH_2Cl_2); ν_{max}/cm^{-1} 3470, 1374, 1249, 1214, 1159, 1105, 1065, 1028, 922, 861 and 837; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.90 (2 H, m, CH_2Si), 1.28 (3 H, d, *J* 6.5, 7-H_3), 1.33 and 1.40 (each 3 H, s, CH_3), 2.09 (1 H, dd, *J*. 15, 9, 4-H), 2.47 (1 H, dd, *J* 15, 2.5, 4-H′), 2.98 (1 H, d, *J* 3.5, OH), 3.55 and 3.63 (each 1 H, m, OCH*H*CH_2Si), 3.78 (1 H, m), 3.93 (2 H, m), 4.03 (1 H, m), 4.20 (1 H, q, *J* 6.5, 6-H), 4.63 and 4.65 (each 1 H, d, *J* 7, OC*H*HO) and 5.03 and 5.13 (each 1 H, s, vinylic H); δ_C −1.4, 18.1, 19.9, 25.3, 26.7, 35.9, 65.5, 66.3, 70.8, 76.1, 78.4, 92.6, 109.2, 115.3 and 146.0; *m*/*z* 364 ($M^+ + 18$, 12%), 347 ($M^+ + 1$, 10) and 229 (100).

(2*S*,3*R*)-1,2-*O*-Isopropylidenehex-5-en-3-ol 25.[11] Obtained as a colourless oil (234 mg, 60%) containing *ca.* 5% (^{1}H NMR spectroscopy) of its epimer **28** (Found: $M^+ + H$, 173.1184. $C_9H_{17}O_3$ requires *M*, 173.1178); $[\alpha]_D$ −56.2 (*c* 1, CH_2Cl_2); ν_{max}/cm^{-1} 3465, 1642, 1372, 1253, 1216, 1159, 1065, 996, 919 and 856; δ_H 1.34 and 1.41 (each 3 H, s, CH_3), 1.96 (1 H, d, *J* 3, OH), 2.20 and 2.31 (each 1 H, m, 4-H), 3.76 and 3.91 (each 1 H, m), 4.00 (2 H, m), 5.13 (2 H, m, 6-H_2) and 5.82 (1 H, m, 5-H); δ_C 25.3, 26.6, 37.6, 65.2, 70.4, 78.1, 109.1, 118.4 and 134.0; *m*/*z* 173 ($M^+ + 1$, 20%), 164 (10) and 96 (100).

(2*S*,3*S*,6*R*)-2-Benzyloxy-5-methylidene-6-(2-trimethylsilylethoxymethoxy)heptan-3-ol 44. Obtained as a colourless oil (57 mg, 75%) containing *ca.* 30% (^{1}H NMR spectroscopy) of its epimer **47** (Found: $M^+ + H$, 381.2467. $C_{21}H_{37}O_4Si$ requires *M*, 381.2461); $[\alpha]_D$ +52.6 (*c* 5.4, CH_2Cl_2); ν_{max}/cm^{-1} 3466, 1454, 1377, 1251, 1201, 1101, 1027, 936, 925, 863, 839, 739 and 698; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.91 (2 H, m, CH_2Si), 1.22 (3 H, d, *J* 6, 1-H_3), 1.27 (3 H, d, *J* 6.5, 7-H_3), 2.15 (1 H, dd, *J* 15, 10, 4-H), 2.35 (1 H, dd, *J* 15, 2, 4-H′), 2.96 (1 H, d, *J* 3, OH), 3.47 and 3.55 (each 1 H, m, OC*H*HCH_2Si), 3.67 (2 H, m, 2-H and 3-H), 4.20 (1 H, q, *J* 6.5, 6-H), 4.52 and 4.62 (each 1 H, d, *J* 12, OC*H*HPh), 4.61 and 4.64 (each 1 H, d, *J* 7, OC*H*HO), 5.01 and 5.11 (each 1 H, s, vinylic H), 7.27 (1 H, m, ArH) and 7.33 (4 H, m, ArH); δ_C −1.4, 14.8, 18.1, 20.3, 35.1, 65.4, 70.9, 73.0, 75.5, 77.8, 92.4, 114.4, 127.6, 127.8, 128.4, 138.5 and 147.0; *m*/*z* 398 ($M^+ + 18$, 28%), 381 ($M^+ + 1$, 20) and 280 (100).

(2*R*,3*R*,6*R*)-2-Benzyloxy-5-methylidene-6-(2-trimethylsilylethoxymethoxy)heptan-3-ol 49. (40 mg, 53%) (Found: $M^+ + H$, 381.2465. $C_{21}H_{37}O_4Si$ requires *M*, 381.2461); $[\alpha]_D$ +43.7 (*c* 1, CH_2Cl_2); ν_{max}/cm^{-1} 3459, 1454, 1374, 1249, 1100, 1074, 1056, 1027, 860 and 836; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.92 (2 H, m, CH_2Si), 1.21 (3 H, d, *J* 6, 1-H_3), 1.27 (3 H, d, *J* 6.5, 7-H_3), 2.20 (1 H, dd, *J* 15, 9, 4-H), 2.26 (1 H, dd, *J* 15, 3, 4-H′), 3.00 (1 H, d, *J* 3.5, OH), 3.49 and 3.54 (each 1 H, m), 3.68 (2 H, m), 4.21 (1 H, q, *J* 6.5, 6-H), 4.47 and 4.64 (each 1 H, d, *J* 11.5, OC*H*HPh), 4.62 and 4.65 (each 1 H, d, *J* 7, OC*H*HO), 4.99 and 5.10 (each 1 H, s, vinylic H), 7.27 (1 H, m, ArH) and 7.32 (4 H, m, ArH); δ_C −1.4, 15.3, 18.1, 20.4, 34.9, 65.3, 71.1, 73.3, 75.3, 77.5, 92.3, 114.1, 127.7, 127.8, 128.4, 138.6 and 146.9; *m*/*z* 398 ($M^+ + 18$, 10%), 381 ($M^+ + 1$, 4) and 280 (100).

General procedure for the Mitsunobu inversion and hydrolysis

(2*S*,3*S*,6*R*)-1,2-*O*-Isopropylidene-5-methylidene-6-(2-trimethylsilylethoxymethoxy)heptan-3-ol 17. Diethyl azodicarboxylate (30 mg, 0.174 mmol) was added to a stirred solution of the heptan-3-ol **14** (40 mg, 0.116 mmol), triphenylphosphine (46 mg, 0.175 mmol) and *p*-nitrobenzoic acid (29 mg, 0.174 mmol) in anhydrous toluene (2 cm^3) at −35 °C under argon. The reaction was allowed to warm to room temp. and was stirred for 12 h, before being partitioned between diethyl ether and water. The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue, eluting with diethyl ether–light petroleum (1:1), gave the *p*-nitrobenzoate **18** (27 mg, 48%) as a yellow oil (Found: $M^+ + NH_4$, 513.2637. $C_{24}H_{41}N_2O_8Si$ requires *M*, 513.2632); ν_{max}/cm^{-1} 1734, 1610, 1532, 1371 and 1352; *m*/*z* 513 ($M^+ + 18$, 20%) and 348 (12).

A solution of this *p*-nitrobenzoate **18** (28 mg, 0.057 mmol), lithium hydroxide (7 mg, 0.17 mmol) in tetrahydrofuran (THF) (3 cm^3) and H_2O (0.3 cm^3) was stirred at room temperature for 12 h. Saturated aqueous ammonium chloride (1 cm^3) was added. The aqueous phase was extracted with diethyl ether (3 × 5 cm^3), and the combined organic extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with diethyl ether–light petroleum (1:1) gave the *title compound* **17** (19 mg, 95%) (Found: $M^+ + H$, 347.2255. $C_{17}H_{35}O_5Si$ requires *M*, 347.2254); $[\alpha]_D$ +33.8 (*c* 1, CH_2Cl_2); ν_{max}/cm^{-1} 3478, 1372, 1249, 1212, 1158, 1101, 1065, 1025, 919, 859 and 836; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.91 (2 H, m, CH_2Si), 1.27 (3 H, d, *J* 6.5, 7-H_3), 1.35 and 1.42 (each 3 H, s, CH_3), 2.14 (1 H, dd, *J* 15, 9, 4-H), 2.23 (1 H, dd, *J* 15, 3, 4-H′), 2.62 (1 H, d, *J* 5, OH), 3.54 and

3.66 (each 1 H, m, OCH*H*CH_2Si), 3.75 and 4.02 (each 2 H, m), 4.21 (1 H, q, *J* 6.5, 6-H), 4.62 and 4.65 (each 1 H, d, *J* 7, OC*H*HO) and 5.03 and 5.13 (each 1 H, s, vinylic H); δ_C −1.4, 18.1, 20.1, 25.3, 26.6, 35.9, 65.3, 66.1, 70.8, 75.6, 78.7, 92.5, 109.5, 114.6 and 146.0; *m*/*z* 364 (M^+ + 18, 5%), 347 (M^+ + 1, 5) and 246 (60).

The following compounds were prepared following these procedures;

(2*R*,3*R*,6*R*)-1,2-*O*-Isopropylidene-5-methylidene-6-(2-trimethylsilylethoxymethoxy)hept-3-yl *p*-nitrobenzoate 23. Obtained as a yellow oil (28 mg, 49%) (Found: $M^+ + NH_4$, 513.2631. $C_{24}H_{41}N_2O_8Si$ requires *M*, 513.2632); $[\alpha]_D$ +63.1 (*c* 0.6, CH_2Cl_2); ν_{max}/cm^{-1} 1733, 1610, 1533, 1374, 1350, 1276, 1116, 1105, 1063, 1026, 858, 837 and 720; δ_H −0.02 [9 H, s, $Si(CH_3)_3$], 0.89 (2 H, m, CH_2Si), 1.28 (3 H, d, *J* 6.5, 7-H_3), 1.33 and 1.43 (each 3 H, s, CH_3), 2.44 (1 H, dd, *J* 15, 5, 4-H), 2.52 (1 H, dt, *J* 15, 9, 4-H′), 3.48 and 3.66 [each 1 H, m, OC*H*-$HCH_2Si(CH_3)_3$], 3.79 (1 H, dd, *J* 8.5, 6, 1-H), 4.05 (1 H, dd, *J* 8.5, 7, 1-H′), 4.21 (1 H, q, *J* 6.5, 6-H), 4.29 (1 H, m, 2-H), 4.54 and 4.55 (each 1 H, d, *J* 7, OC*H*HO), 4.98 and 5.07 (each 1 H, s, vinylic H), 5.42 (1 H, m, 3-H) and 8.19 and 8.27 (each 2 H, d, *J* 9, ArH); *m*/*z* 513 (M^+ + 18, 28%) and 320 (28).

(2*R*,3*R*,6*R*)-1,2-*O*-Isopropylidene-5-methylidene-6-(2-trimethylsilylethoxymethoxy)heptan-3-ol 22. (19 mg, 95%) (Found: M^+ + H, 347.2252. $C_{17}H_{35}O_5Si$ requires *M*, 347.2254); $[\alpha]_D$ +80.7 (*c* 1, CH_2Cl_2); ν_{max}/cm^{-1} 3475, 1374, 1252, 1215, 1159, 1100, 1066, 1028, 922, 861 and 840; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.90 (2 H, m, CH_2Si), 1.27 (3 H, d, *J* 6.5, 7-H_3), 1.35 and 1.42 (each 3 H, s, CH_3), 2.13 (1 H, dd, *J* 14.5, 3.5, 4-H), 2.23 (1 H, dd, *J* 14.5, 9.5, 4-H′), 3.00 (1 H, d, *J* 4.5, OH), 3.54 and 3.65 (each 1 H, m, OC*H*HCH_2Si), 3.71 (1 H, m, 3-H), 3.77 (1 H, dd, *J* 8, 7, 1-H), 3.99 (1 H, dd, *J* 8, 7, 1-H′), 4.06 (1 H, m, 2-H), 4.21 (1 H, q, *J* 6.5, 6-H), 4.62 and 4.64 (each 1 H, d, *J* 7, OC*H*HO) and 5.01 and 5.11 (each 1 H, s, vinylic H); δ_C −1.4, 18.1, 20.3, 25.3, 26.6, 35.5, 65.4, 65.9, 71.1, 75.4, 78.5, 92.4, 109.4, 114.9 and 146.2; *m*/*z* 364 (M^+ + 18, 20%) and 347 (M^+ + 1, 15).

(2*S*,3*S*)-1,2-*O*-Isopropylidenehex-5-en-3-yl *p*-nitrobenzoate 29. (22 mg, 60%); $[\alpha]_D$ −23.8 (*c* 0.5, CH_2Cl_2); ν_{max}/cm^{-1} 1726, 1608, 1530, 1372, 1349, 1276, 1118, 1103, 1067, 873, 842 and 720; δ_H 1.34 and 1.43 (each 3 H, s, CH_3), 2.50 (2 H, m, 4-H_2), 3.78 (1 H, dd, *J* 8.5, 6, 1-H), 4.06 (1 H, dd, *J* 8.5, 6.5, 1-H′), 4.31 (1 H, q, *J* 6, 2-H), 5.07 (1 H, dd, *J* 10.5, 1.5, 6-H), 5.13 (1 H, dd, *J* 17, 1.5, 6-H′), 5.24 (1 H, td, *J* 7.5, 5, 3-H), 5.77 (1 H, m, 5-H) and 8.20 and 8.27 (each 2 H, dt, *J* 9, 2, ArH); *m*/*z* (EI) 319 (4%), 291 (22) and 120 (100).

(2*S*,3*S*)-1,2-*O*-Isopropylidenehex-5-en-3-ol 28.[11] (9 mg, 92%) (Found: M^+ + H, 173.1178. $C_9H_{17}O_3$ requires *M*, 173.1178); $[\alpha]_D$ −50.0 (*c* 1, CH_2Cl_2); ν_{max}/cm^{-1} 3464, 1642, 1372, 1252, 1215, 1160, 1065, 993, 917 and 855; δ_H 1.35 and 1.42 (each 3 H, s, CH_3), 2.23 (3 H, m, 4-H_2 and OH), 3.58 and 3.74 (each 1 H, m), 4.01 (2 H, m, 1-H_2), 5.12 (2 H, m) and 5.84 (1 H, m, 5-H); *m*/*z* 190 (M^+ + 1, 18%) and 173 (M^+ + 1, 100).

(2*S*,3*S*,7*S*,5*Z*)-7-Benzyloxy-1,2-*O*-isopropylideneoct-5-en-3-yl *p*-nitrobenzoate 34. (25 mg, 48%) (Found: $M^+ + NH_4$, 473.2274. $C_{25}H_{33}N_2O_7$ requires *M*, 473.2288); $[\alpha]_D$ +128.9 (*c* 0.1, CH_2Cl_2); ν_{max}/cm^{-1} 1726, 1607, 1529, 1454, 1371, 1347, 1274, 1102, 1069, 873, 842 and 720; δ_H 1.16 (3 H, d, *J* 6.5, 8-H_3), 1.33 and 1.44 (each 3 H, s, CH_3), 2.51 (2 H, t, *J* 6.5, 4-H_2), 3.74 (1 H, dd, *J* 8.5, 6, 1-H), 4.03 (1 H, dd, *J* 8.5, 7, 1-H′), 4.30 (2 H, m, 2-H and 7-H), 4.34 and 4.50 (each 1 H, d, *J* 12, OC*H*HPh), 5.18 (1 H, dt, *J* 7, 5.5, 3-H), 5.51 (1 H, dd, *J* 11, 9, 6-H), 5.56 (1 H, dt, *J* 11, 7, 5-H), 7.30 (5 H, m, ArH) and 8.19 and 8.27 (each 2 H, d, *J* 9, ArH); *m*/*z* 473 (M^+ + 18, 12%), 443 (40) and 318 (100).

(2*S*,3*S*,7*S*,5*Z*)-7-Benzyloxy-1,2-*O*-isopropylideneoct-5-en-3-ol 33. (17 mg, 95%) (Found: M^+ + H, 307.1912. $C_{18}H_{27}O_4$ requires *M*, 307.1909); $[\alpha]_D$ +23.9 (*c* 0.8, CH_2Cl_2); ν_{max}/cm^{-1} 3470, 1454, 1371, 1258, 1215, 1069, 857 and 739; δ_H 1.25 (3 H, d, *J* 6.5, 8-H_3), 1.33 and 1.42 (each 3 H, s, CH_3), 2.20 (3 H, m, 4-H_2 and OH), 3.51 (1 H, m, 3-H), 3.71 (1 H, m, 2-H), 3.98 (2 H, m, 1-H_2), 4.27 (1 H, m, 7-H), 4.35 and 4.53 (each 1 H, d, *J* 12, OC*H*HPh), 5.53 (1 H, dd, *J* 11, 9, 6-H), 5.62 (1 H, dt, *J* 11, 7, 5-H) and 7.29 (5 H, m, ArH); δ_C 21.4, 25.3, 26.6, 32.2, 66.0, 69.9, 70.2, 71.6, 78.3, 109.5, 127.1, 127.5, 127.7, 128.4, 135.0 and 138.7; *m*/*z* 324 (M^+ + 18, 18%), 307 (M^+ + 1, 22) and 199 (100).

(2*R*,3*S*,7*S*,5*Z*)-7-Benzyloxy-1,2-*O*-isopropylideneoct-5-en-3-yl *p*-nitrobenzoate 41. (25 mg, 48%) (Found: $M^+ + NH_4$, 473.2286. $C_{25}H_{33}N_2O_7$ requires *M*, 473.2288); $[\alpha]_D$ +26.7 (*c* 0.1, CH_2Cl_2); ν_{max}/cm^{-1} 1727, 1607, 1529, 1454, 1371, 1273, 1101, 1064, 844, 719 and 698; δ_H 1.16 (3 H, d, *J* 6.5, 8-H_3), 1.54 (6 H, s, 2 × CH_3), 2.51 (2 H, dt, *J* 6.5, 1, 4-H_2), 3.84 (1 H, dd, *J* 8.5, 6, 1-H), 4.03 (1 H, dd, *J* 8.5, 6.5, 1-H′), 4.25 (2 H, m, 7-H and 2-H), 4.30 and 4.48 (each 1 H, d, *J* 12, OC*H*HPh), 5.24 (1 H, q, *J* 6, 3-H), 5.50 (1 H, dd, *J* 11, 9, 6-H), 5.57 (1 H, dt, *J* 11, 7, 5-H), 7.29 (5 H, m, ArH) and 8.16 and 8.25 (each 2 H, d, *J* 9, ArH); *m*/*z* 473 (M^+ + 18, 20%) and 348 (22).

(2*R*,3*S*,7*S*,5*Z*)-7-Benzyloxy-1,2-*O*-isopropylideneoct-5-en-3-ol 40. (17 mg, 95%) (Found: M^+ + H, 307.1917. $C_{18}H_{27}O_4$ requires *M*, 307.1909); $[\alpha]_D$ +2.7 (*c* 0.5, CH_2Cl_2); ν_{max}/cm^{-1} 3452, 1454, 1371, 1254, 1214, 1067, 855, 738 and 698; δ_H 1.26 (3 H, d, *J* 6.5, 8-H_3), 1.34 and 1.40 (each 3 H, s, CH_3), 2.03 (1 H, d, *J* 3.5, OH), 2.17 (1 H, m, 4-H), 2.25 (1 H, m, 4-H′), 3.71 (1 H, m, 3-H), 3.86 (1 H, m, 2-H), 3.96 (2 H, m, 1-H_2), 4.27 (1 H, m, 7-H), 4.36 and 4.52 (each 1 H, d, *J* 12, OC*H*HPh), 5.56 (1 H, dd, *J* 11, 9, 6-H), 5.62 (1 H, dt, *J* 11, 7, 5-H) and 7.29 (5 H, m, ArH); *m*/*z* 324 (M^+ + 18, 20%), 307 (M^+ + 1, 18) and 199 (100).

(2*S*,3*R*,6*R*)-2-Benzyloxy-5-methylidene-6-(2-trimethylsilylethoxymethoxy)hept-3-yl *p*-nitrobenzoate 48. The compound was obtained (28 mg, 46%) containing 30% of its C(3) epimer (Found: $M^+ + NH_4$, 547.2850. $C_{28}H_{43}N_2O_7Si$ requires *M*, 547.2839); $[\alpha]_D$ +38.0 (*c* 0.5, CH_2Cl_2); ν_{max}/cm^{-1} 1726, 1608, 1530, 1274, 1117, 1018, 861, 836 and 719; δ_H −0.02 [9 H, s, $Si(CH_3)_3$], 0.87 (2 H, m, CH_2Si), 1.22 (3 H, d, *J* 6.5, 1-H_3), 1.27 (3 H, d, *J* 6.5, 7-H_3), 2.47 (1 H, dd, *J* 15.5, 10, 4-H), 2.56 (1 H, dd, *J* 15.5, 3.5, 4-H′), 3.48 and 3.66 (each 1 H, m, OC*H*-HCH_2Si), 3.75 (1 H, m, 2-H), 4.21 (1 H, q, *J* 6.5, 6-H), 4.48 and 4.57 (each 1 H, d, *J* 7, OC*H*HO), 4.53 and 4.55 (each 1 H, d, *J* 12, OC*H*HPh), 4.92 and 5.02 (each 1 H, s, vinylic H), 5.45 (1 H, m, 3-H), 7.28 (5 H, m, ArH) and 8.16 and 8.25 (each 2 H, d, *J* 9, ArH); *m*/*z* 547 (M^+ + 18, 18%) and 447 (28).

(2*S*,3*R*,6*R*)-2-Benzyloxy-5-methylidene-6-(2-trimethylsilylethoxymethoxy)heptan-3-ol 47. The compound was obtained (21 mg, 95%) containing 30% of its epimer **44** (Found: M^+ + H, 381.2453. $C_{21}H_{37}O_4Si$ requires *M*, 381.2461); $[\alpha]_D$ +59.8 (*c* 1.4, CH_2Cl_2); ν_{max}/cm^{-1} 3470, 1456, 1376, 1251, 1103, 1028, 925, 864, 837, 740 and 679; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.91 (2 H, m, CH_2Si), 1.21 (3 H, d, *J* 6.5, 1-H_3), 1.28 (3 H, d, *J* 6.5, 7-H_3), 2.15 (1 H, dd, *J* 15, 10, H-4), 2.31 (1 H, dd, *J* 15, 3, H-4′), 2.70 (1 H, d, *J* 4, OH), 3.50 and 3.68 (each 2 H, m), 4.22 (1 H, q, *J* 6.5, 6-H), 4.46 and 4.63 (each 1 H, d, *J* 11.5, OC*H*HPh), 4.61 and 4.64 (each 1 H, d, *J* 7, OC*H*HO), 5.10 and 5.11 (each 1 H, s, vinylic H), 7.27 (1 H, m, ArH) and 7.33 (4 H, m, ArH); δ_C −1.4, 15.6, 18.1, 20.2, 35.3, 65.2, 71.1, 73.4, 75.5, 77.7, 92.5, 113.7, 127.7, 127.8, 128.5, 138.5 and 146.8; *m*/*z* 398 (M^+ + 18, 12%) and 381 (M^+ + 1, 22).

(2*R*,3*S*,6*R*)-2-Benzyloxy-5-methylidene-6-(2-trimethylsilylethoxymethoxy)hept-3-yl *p*-nitrobenzoate 53. (37 mg, 60%) (Found: $M^+ + NH_4$, 547.2832. $C_{28}H_{43}N_2O_7Si$ requires *M*, 547.2839); $[\alpha]_D$ +10.2 (*c* 0.5, CH_2Cl_2); ν_{max}/cm^{-1} 1760, 1540, 1255, 1110, 1030, 860, 840 and 710; δ_H 0.00 [9 H, s, $Si(CH_3)_3$], 0.89 (2 H, m, CH_2Si), 1.28 (3 H, d, *J* 6.5, 1-H_3), 1.30 (3 H, d, *J* 6.5, 7-H_3), 2.50 (2 H, d, *J* 6, 4-H_2), 3.49 and 3.68 (each 1 H, td, *J* 10, 6.5, OC*H*HCH_2Si), 3.78 (1 H, m, 2-H), 4.23 (1 H, q, *J* 6.5, 6-H), 4.53 (2 H, s, OCH_2O), 4.56 and 4.57 (each 1 H, d, *J* 12, OC*H*HPh), 4.97 and 5.05 (each 1 H, s, vinylic H), 5.52 (1 H, td, *J* 7, 3.5, 3-H), 7.27 (5 H, m, ArH) and 8.17 and 8.28 (each 2 H, d, *J* 9, ArH); *m*/*z* 547 (M^+ + 18, 10%) and 354 (100).

(2*R*,3*S*,6*R*)-2-Benzyloxy-5-methylidene-6-(2-trimethylsilylethoxymethoxy)heptan-3-ol 52. (21 mg, 95%) (Found: $M^+ + H$, 381.2454. $C_{21}H_{37}O_4Si$ requires *M*, 381.2461); $[\alpha]_D$ +29.7 (*c* 1.2, CH_2Cl_2); ν_{max}/cm^{-1} 3459, 1454, 1375, 1249, 1203, 1100, 1027, 939, 861, 836 and 750; δ_H 0.00 [9 H, s, $Si(CH_3)_3$], 0.91 (2 H, m, CH_2Si), 1.20 (3 H, d, *J* 6.5, 1-H_3), 1.28 (3 H, d, *J* 6.5, 7-H_3), 2.13 (1 H, dd, *J* 15, 9, 4-H), 2.35 (1 H, dd, *J* 15, 3, 4-H′), 2.59 (1 H, d, *J* 4, OH), 3.58 (3 H, m, 2-H and OCH_2CH_2Si), 3.87 (1 H, m, 3-H), 4.21 (1 H, q, *J* 6.5, 6-H), 4.50 and 4.61 (each 1 H, d, *J* 12, OC*H*HPh), 4.62 and 4.64 (each 1 H, d, *J* 7, OC*H*HO), 5.01 and 5.11 (each 1 H, s, vinylic H) and 7.29 (5 H, m, ArH); *m*/*z* 381 ($M^+ + 1$, 12%) and 354 (10).

General procedure for the preparation of *O*-acetylmandelates

(2*S*,3*R*,6*R*)-1,2-*O*-Isopropylidene-5-methylidene-6-(2-trimethylsilylethoxymethoxy)heptan-3-yl (*R*)-*O*-acetylmandelate 15. (*R*)-*O*-Acetylmandelic acid (20 mg, 0.10 mmol) and 4-dimethylaminopyridine (DMAP) (cat.) were added to a solution of the heptan-3-ol **14** (31 mg, 0.09 mmol) in dichloromethane (0.5 cm^3) followed by a solution of dicyclohexylcarbodiimide (DCC) (37 mg, 0.18 mmol) in dichloromethane (0.5 cm^3) at 0 °C. The reaction mixture was allowed to warm to room temp. and stirred for 16 h. The solvent was removed under reduced pressure and diethyl ether was added. The mixture was then filtered and the filtrate was concentrated under reduced pressure. Chromatography of the residue using diethyl ether–light petroleum (1:1) as eluent gave the *title compound* **15** (34 mg, 72%) (Found: $M^+ + NH_4$, 540.2998. $C_{27}H_{46}NO_8Si$ requires *M*, 540.2993); $[\alpha]_D$ −5.0 (*c* 2.6, CH_2Cl_2); ν_{max}/cm^{-1} 1754, 1456, 1374, 1233, 1177, 1060, 922, 858, 840, 747 and 696; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.91 (2 H, m, CH_2Si), 1.15 and 1.21 (each 3 H, s, CH_3), 1.25 (3 H, d, *J* 6.5, 7-H_3), 2.15 (3 H, s, CH_3COO), 2.29 (1 H, dd, *J* 15.5, 9, 4-H), 2.42 (1 H, dd, *J* 15.5, 4, 4-H′), 3.36 (1 H, dd, *J* 8.5, 6.5, 1-H), 3.50 and 3.70 (each 1 H, td, *J* 10, 7, OC*H*HCH$_2$Si), 3.54 (1 H, dd, *J* 8.5, 6.5, 1-H′), 3.89 (1 H, q, *J* 6.5, 2-H), 4.18 (1 H, q, *J* 6.5, 6-H), 4.57 (2 H, s, OCH_2O), 4.93 and 5.07 (each 1 H, s, vinylic H), 5.11 (1 H, m, 3-H), 5.86 (1 H, s, C*H*Ph), 7.35 (3 H, m, ArH) and 7.43 (2 H, m, ArH); δ_C −1.4, 18.2, 20.3, 20.7, 25.3, 26.2, 32.8, 65.1, 65.8, 73.6, 74.4, 74.8, 76.1, 92.2, 109.5, 114.6, 127.6, 128.8, 129.3, 133.8, 143.9, 168.2 and 170.1; *m*/*z* 540 ($M^+ + 18$, 75%), 376 (20) and 375 (100).

The following acetylmandelates were prepared following the same procedure using the appropriate enantiomer of *O*-acetylmandelic acid.

(2*S*,3*R*,6*R*)-1,2-*O*-Isopropylidene-5-methylidene-6-(2-trimethylsilylethoxymethoxy)hept-3-yl (*S*)-*O*-acetylmandelate 16. (33 mg, 70%) (Found: $M^+ + NH_4$, 540.2998. $C_{27}H_{46}NO_8Si$ requires *M*, 540.2993); $[\alpha]_D$ +78.0 (*c* 3.4, CH_2Cl_2); ν_{max}/cm^{-1} 1751, 1456, 1374, 1233, 1209, 1177, 1060, 1028, 919, 858, 840, 749 and 699; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.88 (2 H, m, CH_2Si), 1.09 (3 H, d, *J* 6.5, 7-H_3), 1.31 and 1.40 (each 3 H, s, CH_3), 2.09 (1 H, dd, *J* 15.5, 10, 4-H), 2.15 (3 H, s, CH_3COO), 2.31 (1 H, dd, *J* 15.5, 2, 4-H′), 3.44 and 3.63 [each 1 H, td, *J* 10, 7, OC*H*HCH$_2$Si(CH$_3$)$_3$], 3.78 (1 H, dd, *J* 8.5, 6, 1-H), 3.95 (1 H, q, *J* 6.5, 6-H), 4.01 (1 H, dd, *J* 8.5, 6.5, 1-H′), 4.08 (1 H, q, *J* 6.5, 2-H), 4.28 and 4.38 (each 1 H, d, *J* 7, OC*H*HO), 4.29 and 4.59 (each 1 H, s, vinylic H), 5.13 (1 H, m, 3-H), 5.79 (1 H, s, C*H*Ph), 7.33 (3 H, m, ArH) and 7.41 (2 H, m, ArH); δ_C −1.4, 18.1, 20.2, 20.7, 25.2, 26.5, 32.3, 65.1, 66.1, 73.2, 74.6, 74.7, 77.2, 92.1, 109.8, 113.9, 128.0, 128.7, 129.4, 133.4, 143.6, 168.3 and 170.3; *m*/*z* 540 ($M^+ + 18$, 100).

(2*R*,3*S*,6*R*)-1,2-*O*-Isopropylidene-5-methylidene-6-(2-trimethylsilylethoxymethoxy)hept-3-yl (*R*)-*O*-acetylmandelate 20. (32 mg, 68%) (Found: $M^+ + NH_4$, 540.2996. $C_{27}H_{46}NO_8Si$ requires *M*, 540.2993); $[\alpha]_D$ +2.6 (*c* 4.5, CH_2Cl_2); ν_{max}/cm^{-1} 1749, 1456, 1374, 1233, 1212, 1180, 1060, 922, 858, 837, 747 and 699; δ_H 0.04 [9 H, s, $Si(CH_3)_3$], 0.94 (2 H, m, CH_2Si), 1.08 (3 H, d, *J* 6.5, 7-H_3), 1.38 and 1.48 (each 3 H, s, CH_3), 2.13 (1 H, dd, *J* 15.5, 10, 4-H), 2.21 (3 H, s, CH_3COO), 2.42 (1 H, dd, *J* 15.5, 2, 4-H′), 3.52 and 3.70 (each 1 H, td, *J* 10, 7.5, OC*H*HCH$_2$Si), 3.84 (1 H, dd, *J* 8.5, 6, 1-H), 4.06 (2 H, m, 6-H and 1-H′), 4.16 (1 H, q, *J* 6, 2-H), 4.39 and 4.63 (each 1 H, s, vinylic H), 4.44 and 4.53 (each 1 H, d, *J* 7, OC*H*HO), 5.20 (1 H, m, 3-H), 5.87 (1 H, s, C*H*Ph), 7.40 (3 H, m, ArH) and 7.46 (2 H, m, ArH); δ_C −1.4, 18.1, 19.9, 20.7, 25.2, 26.4, 32.0, 65.0, 66.0, 73.2, 74.7, 75.0, 76.8, 92.3, 109.8, 114.3, 128.0, 128.7, 129.3, 133.5, 143.6, 168.4 and 170.3; *m*/*z* 540 ($M^+ + 18$, 30).

(2*R*,3*S*,6*R*)-1,2-*O*-Isopropylidene-5-methylidene-6-(2-trimethylsilylethoxymethoxy)hept-3-yl (*S*-*O*-acetylmandelate 21. (33 mg, 70%) (Found: $M^+ + NH_4$, 540.3011. $C_{27}H_{46}NO_8Si$ requires *M*, 540.2993); $[\alpha]_D$ +76.8 (*c* 3, CH_2Cl_2); ν_{max}/cm^{-1} 1750, 1455, 1372, 1232, 1176, 1058, 920, 859, 837, 749 and 696; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.95 (2 H, m, CH_2Si), 1.20 and 1.27 (each 3 H, s, CH_3), 1.30 (3 H, d, *J* 6.5, 7-H_3), 2.22 (3 H, s, CH_3COO), 2.30 (1 H, dd, *J* 15.5, 9, 4-H), 2.52 (1 H, dd, *J* 15.5, 3.5, 4-H′), 3.49 (1 H, dd, *J* 8.5, 7, 1-H), 3.56 and 3.74 [each 1 H, td, *J* 9.5, 7.5, OC*H*HCH$_2$Si(CH$_3$)$_3$], 3.65 (1 H, dd, *J* 8.5, 6.5, 1-H′), 3.95 (1 H, q, *J* 6.5, 2-H), 4.24 (1 H, q, *J* 6.5, 6-H), 4.63 (2 H, s, OCH_2O), 4.99 and 5.11 (each 1 H, s, vinylic H), 5.20 (1 H, m, 3-H), 5.90 (1 H, s, C*H*Ph), 7.40 (3 H, m, ArH) and (2 H, m, ArH); δ_C −1.4, 18.1, 20.0, 20.7, 25.3, 26.1, 32.5, 65.1, 65.7, 73.6, 74.5, 75.1, 76.4, 92.5, 109.4, 114.6, 127.6, 128.8, 129.3, 133.7, 144.0, 168.2 and 170.1; *m*/*z* 540 ($M^+ + 18$, 14%) and 375 (96).

(2*S*,3*R*)-1,2-*O*-Isopropylidenehex-5-en-3-yl (*R*)-*O*-acetylmandelate 26. (23 mg, 74%) (Found: $M^+ + NH_4$, 366.1919. $C_{19}H_{28}NO_6$ requires *M*, 366.1917); $[\alpha]_D$ −84.3 (*c* 2.7, CH_2Cl_2); ν_{max}/cm^{-1} 1747, 1455, 1373, 1233, 1177, 1060, 922, 856, 746 and 697; δ_H 1.23 and 1.29 (each 3 H, s, CH_3), 2.23 (3 H, s, CH_3COO), 2.40 (1 H, m, 4-H), 2.56 (1 H, m, 4-H′), 3.42 and 3.66 (each 1 H, dd, *J* 8.5, 6.5, 1-H), 4.00 (1 H, q, *J* 6.5, 2-H), 4.99 (1 H, dt, *J* 7, 4.5, 3-H), 5.15 (2 H, m, 6-H_2), 5.80 (1 H, m, 5-H), 5.90 (1 H, s, C*H*Ph), 7.44 (3 H, m, ArH) and 7.49 (2 H, m, ArH); δ_C 20.6, 25.2, 26.2, 35.5, 65.9, 74.3, 74.5, 75.6, 109.4, 118.6, 127.5, 128.7, 129.3, 132.2, 133.6, 168.0 and 170.2; *m*/*z* 366 ($M^+ + 18$, 80%), 349 ($M^+ + 1$, 40) and 291 (100).

(2*S*,3*R*)-1,2-*O*-Isopropylidenehex-5-en-3-yl (*S*)-*O*-acetylmandelate 27. (28 mg, 90%) (Found: $M^+ + NH_4$, 366.1920. $C_{19}H_{28}NO_6$ requires *M*, 366.1917); $[\alpha]_D$ +47.23 (*c* 3.6, CH_2Cl_2); ν_{max}/cm^{-1} 1747, 1456, 1373, 1233, 1177, 1060, 978, 921, 848 and 697; δ_H 1.38 and 1.45 (each 3 H, s, CH_3), 2.21 (1 H, m, 4-H), 2.22 (3 H, s, CH_3COO), 2.40 (1 H, m, 4-H′), 3.82 (1 H, dd, *J* 8.5, 5.5, 1-H), 4.06 (1 H, dd, *J* 8.5, 6.5, 1-H′), 4.15 (1 H, q, *J* 6.5, 2-H), 4.75 (2 H, m, 6-H_2), 5.02 (1 H, m, 3-H), 5.42 (1 H, m, 5-H), 5.89 (1 H, s, C*H*Ph), 7.41 (3 H, m, ArH) and 7.50 (2 H, m, ArH); δ_C 20.6, 25.2, 26.4, 35.1, 65.2, 74.1, 74.5, 75.8, 109.6, 118.2, 127.6, 128.6, 129.2, 131.9, 133.4, 168.1 and 170.2; *m*/*z* 366 ($M^+ + 18$, 100%) and 349 ($M^+ + 1$, 64).

(2*S*,3*R*,7*S*,5*Z*)-7-Benzyloxy-1,2-*O*-isopropylideneoct-5-en-3-yl (*R*)-*O*-acetylmandelate 31. (35 mg, 80%) (Found: $M^+ + NH_4$, 500.2662. $C_{28}H_{38}NO_7$ requires *M*, 500.2648); $[\alpha]_D$ −70.9 (*c* 4, CH_2Cl_2); ν_{max}/cm^{-1} 1748, 1455, 1372, 1231, 1175, 1062, 924, 848, 739 and 698; δ_H 1.18 and 1.21 (each 3 H, s, CH_3), 1.24 (3 H, d, *J* 6.5, 8-H_3), 2.17 (3 H, s, CH_3COO), 2.45 (2 H, m, 4-H_2), 3.29 and 3.55 (each 1 H, dd, *J* 8.5, 6, 1-H), 3.92 (1 H, q, *J* 6, 2-H), 4.28 (1 H, m, 7-H), 4.35 and 4.54 (each 1 H, d, *J* 12, OC*H*HPh), 4.90 (1 H, m, 3-H), 5.54 (2 H, m, 5-H and 6-H), 5.83 (1 H, s, C*H*Ph) and 7.34 (10 H, m, ArH); δ_C 20.7, 21.4, 25.3, 26.3, 29.4, 66.2, 70.0, 70.4, 74.6, 74.9, 75.5, 109.6, 125.4, 127.4, 127.6, 127.8, 128.4, 128.9, 129.5, 133.6, 135.6, 138.9, 168.2 and 170.2; *m*/*z* 500 ($M^+ + 18$, 70%) and 375 (100).

(2*S*,3*R*,7*S*,5*Z*)-7-Benzyloxy-1,2-*O*-isopropylideneoct-5-en-3-yl (*S*)-*O*-acetylmandelate 32. (35 mg, 80%) (Found: $M^+ + NH_4$, 500.2637. $C_{28}H_{38}NO_7$ requires *M*, 500.2648); $[\alpha]_D$ +44.5 (*c* 3, CH_2Cl_2); ν_{max}/cm^{-1} 1747, 1455, 1372, 1232, 1208, 1176, 1062, 846, 739 and 698; δ_H 1.13 (3 H, d, *J* 6.5, 8-H_3), 1.30 and 1.37 (each 3 H, s, CH_3), 2.17 (3 H, s, CH_3COO), 2.28 (2 H, m, 4-H_2), 3.76 (1 H, dd, *J* 8.5, 6, 1-H), 3.99 (1 H, dd, *J* 8.5, 6.5, 1-H′), 4.09 (2 H, m, 2-H and 7-H), 4.16 and 4.37 (each 1 H, d, *J* 12,

OC*H*HPh), 4.94 (1 H, m, 3-H), 5.06 (1 H, dt, *J* 11, 7, 5-H), 5.27 (1 H, dd, *J* 11, 9, 6-H), 5.83 (1 H, s, C*H*Ph) and 7.35 (10 H, m, ArH); δ_C 20.7, 21.3, 25.3, 26.6, 28.8, 66.4, 69.9, 70.1, 74.7, 74.9, 75.8, 109.8, 125.2, 127.5, 127.7, 127.8, 128.3, 128.8, 129.5, 133.4, 135.3, 138.8, 168.4 and 170.4; *m*/*z* 500 (M^+ + 18, 6%), 375 (10) and 302 (100).

(2*R*,3*R*,7*S*,5*Z*)-7-Benzyloxy-1,2-*O*-isopropylideneoct-5-en-3-yl (*R*)-*O*-acetylmandelate 38. (35 mg, 80%) (Found: $M^+ + NH_4$, 500.2666. $C_{28}H_{38}NO_7$ requires *M*, 500.2648); $[\alpha]_D$ −27.8 (*c* 4.5, CH_2Cl_2); ν_{max}/cm^{-1} 1745, 1454, 1372, 1232, 1178, 1062, 858, 739 and 698; δ_H 1.20 and 1.21 (each 3 H, s, CH_3), 1.23 (3 H, d, *J* 6.5, 8-H_3), 2.18 (3 H, s, CH_3COO), 2.40 (1 H, m, 4-H), 2.47 (1 H, m, 4-H′), 3.29 and 3.72 (each 1 H, dd, *J* 8.5, 6.5, 1-H), 4.02 (1 H, td, *J* 6.5, 3.5, 2-H), 4.30 (1 H, m, 7-H), 4.34 and 4.53 (each 1 H, d, *J* 12, OC*H*HPh), 4.88 (1 H, td, *J* 7, 3, 3-H), 5.51 (2 H, m, 5-H and 6-H), 5.87 (1 H, s, C*H*Ph) and 7.35 (10 H, m, ArH); δ_C 20.8, 21.4, 25.2, 26.0, 29.0, 65.1, 70.0, 70.2, 73.6, 74.8, 75.1, 109.4, 125.7, 127.5, 127.8, 127.9, 128.4, 128.8, 129.4, 133.6, 135.7, 138.8, 168.7 and 170.4; *m*/*z* 500 (M^+ + 18, 78%) and 375 (100).

(2*R*,3*R*,7*S*,5*Z*)-7-Benzyloxy-1,2-*O*-isopropylideneoct-5-en-3-yl (*S*)-*O*-acetylmandelate 39. (35 mg, 80%) (Found: $M^+ + NH_4$, 500.2665. $C_{28}H_{38}NO_7$ requires *M*, 500.2648); $[\alpha]_D$ +54.5 (*c* 3.8, CH_2Cl_2); ν_{max}/cm^{-1} 1746, 1454, 1372, 1231, 1177, 1068, 969, 858, 739 and 698; δ_H 1.17 (3 H, d, *J* 6.5, 8-H_3), 1.32 and 1.41 (each 3 H, s, CH_3), 2.17 (3 H, s, CH_3COO), 2.21 (1 H, m, 4-H), 2.32 (1 H, m, 4-H′), 3.72 (1 H, dd, *J* 8.5, 6, 1-H), 3.94 (1 H, dd, *J* 8.5, 7, 1-H′), 4.14 (2 H, m, 2-H and 7-H), 4.18 and 4.38 (each 1 H, d, *J* 12, OC*H*HPh), 4.90 (1 H, m, 3-H), 5.16 (1 H, dt, *J* 11, 7, 5-H), 5.31 (1 H, dd, *J* 11, 9, 6-H), 5.88 (1 H, s, C*H*Ph) and 7.36 (10 H, m, ArH); δ_C 20.7, 21.2, 25.4, 26.2, 28.7, 65.3, 69.8, 69.9, 73.7, 74.8, 75.3, 109.6, 125.6, 127.5, 127.7, 127.8, 128.4, 128.8, 129.4, 133.5, 135.4, 138.7, 168.7 and 170.4; *m*/*z* 500 (M^+ + 18, 60%), 447 (12) and 375 (100).

(2*S*,3*S*,6*R*)-2-Benzyloxy-5-methylidene-6-(2-trimethylsilylethoxymethoxy)hept-3-yl (*R*)-*O*-acetylmandelate 45. This was obtained (35 mg, 70%) containing 30% of its epimer at C(3) (Found: $M^+ + NH_4$, 574.3196. $C_{31}H_{48}NO_7Si$ requires *M*, 574.3200); $[\alpha]_D$ +8.1 (*c* 4.3, CH_2Cl_2); ν_{max}/cm^{-1} 1747, 1455, 1373, 1232, 1179, 1102, 1056, 1028, 920, 859, 836, 744 and 697; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.91 (2 H, m, CH_2Si), 1.11 (3 H, d, *J* 6.5, 1-H_3), 1.20 (3 H, d, *J* 6.5, 7-H_3), 2.16 (3 H, s, CH_3COO), 2.20 and 2.30 (each 1 H, m, 4-H), 3.48 and 3.68 (each 1 H, m, OC*H*HCH$_2$Si), 3.98 (1 H, q, *J* 6.5, 6-H), 4.20 (1 H, m, 2-H), 4.32–4.57 (6 H, overlapping peaks), 5.14 (1 H, m, 3-H), 5.86 (1 H, s, C*H*Ph), 7.28 (8 H, m, ArH) and 7.44 (2 H, m, ArH); δ_C −1.4, 16.0, 18.1, 20.3, 20.8, 30.9, 65.1, 71.4, 74.1, 74.8, 75.6, 75.9, 92.0, 113.5, 127.5, 128.0, 128.4, 128.7, 129.2, 133.7, 138.6, 144.2, 168.5 and 170.2; *m*/*z* 574 (M^+ + 18, 100%) and 409 (25).

(2*S*,3*S*,6*R*)-2-Benzyloxy-5-methylidene-6-(2-trimethylsilylethoxymethoxy)hept-3-yl (*S*)-*O*-acetylmandelate 46. This was obtained (35 mg, 70%) containing 30% of its epimer at C(3) (Found: $M^+ + NH_4$, 574.3191. $C_{31}H_{48}NO_7Si$ requires *M*, 574.3200); $[\alpha]_D$ +57.2 (*c* 6.4, CH_2Cl_2); ν_{max}/cm^{-1} 1746, 1455, 1373, 1232, 1179, 1102, 1056, 1028, 920, 859, 836, 739 and 697; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.92 (2 H, m, CH_2Si), 0.95 (3 H, d, *J* 6.5, 1-H_3), 1.26 (3 H, d, *J* 6.5, 7-H_3), 2.15 (3 H, s, CH_3COO), 2.32 and 2.37 (each 1 H, m, 4-H), 3.48 and 3.70 (each 2 H, m), 3.99–4.58 (4 H, overlapping peaks), 4.94 and 5.08 (each 1 H, s, vinylic H), 5.21 (1 H, m, 3-H), 5.93 (1 H, s, C*H*Ph), 7.29 (8 H, m, ArH) and 7.44 (2 H, m, ArH); δ_C −1.4, 15.5, 18.1, 20.3, 20.8, 30.7, 65.1, 71.0, 74.5, 74.7, 74.9, 75.9, 92.2, 114.1, 127.3, 127.8, 127.9, 128.2, 128.7, 129.2, 133.9, 138.5, 144.6, 168.4 and 170.1; *m*/*z* 574 (M^+ + 18, 100%) and 409 (20).

(2*R*,3*R*,6*R*)-2-Benzyloxy-5-methylidene-6-(2-trimethylsilylethoxymethoxy)hept-3-yl (*R*)-*O*-acetylmandelate 50. (35 mg, 70%) (Found: $M^+ + NH_4$, 574.3186. $C_{31}H_{48}No_7Si$ requires *M*, 574.3200); $[\alpha]_D$ +10.4 (*c* 5, CH_2Cl_2); ν_{max}/cm^{-1} 1751, 1456, 1374, 1235, 1185, 1103, 1060, 1031, 922, 861, 840, 739 and 699; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.82 (3 H, d, *J* 6.5, 1-H_3), 0.92 (2 H, m, CH_2Si), 1.25 (3 H, d, *J* 6.5, 7-H_3), 2.16 (3 H, s, CH_3COO), 2.32 (1 H, dd, *J* 15.5, 9, 4-H), 2.41 (1 H, dd, *J* 15.5, 3.5, 4-H′), 3.49 [2 H, m, 2-H and OC*H*HCH$_2$Si(CH$_3$)$_3$], 3.69 [1 H, td, *J* 10, 6.5, OCH*H*CH$_2$Si(CH$_3$)$_3$], 4.17 (1 H, q, *J* 6.5, 6-H), 4.32 and 4.42 (each 1 H, d, *J* 12, OC*H*HPh), 4.56 (2 H, s, OCH_2O), 4.90 and 5.05 (each 1 H, s, vinylic H), 5.18 (1 H, m, 3-H), 5.92 (1 H, s, C*H*Ph), 7.28 (8 H, m, ArH) and 7.43–7.45 (2 H, m, ArH); δ_C −1.4, 14.7, 18.2, 20.3, 20.7, 30.3, 65.1, 70.9, 74.1, 74.5, 75.0, 75.1, 92.1, 114.1, 127.5, 127.6, 127.7, 128.3, 128.7, 129.2, 134.0, 138.5, 144.7, 168.4 and 170.1; *m*/*z* 574 (M^+ + 18, 40%) and 409 (30).

(2*R*,3*R*,6*R*)-2-Benzyloxy-5-methylidene-6-(2-trimethylsilylethoxymethoxy)hept-3-yl (*S*)-*O*-acetylmandelate 51. (30 mg, 60%) (Found: $M^+ + NH_4$, 574.3185. $C_{31}H_{48}NO_7Si$ requires *M*, 574.3200); $[\alpha]_D$ +68.2 (*c* 3, CH_2Cl_2); ν_{max}/cm^{-1} 1747, 1455, 1373, 1233, 1181, 1102, 1055, 1028, 921, 860, 836, 744 and 697; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.89 (2 H, m, CH_2Si), 1.10 (3 H, d, *J* 6.5, 1-H_3), 1.19 (3 H, d, *J* 6.5, 7-H_3), 2.16 (3 H, s, CH_3COO), 2.18 (1 H, dd, *J* 15.5, 10, 4-H), 2.25 (1 H, dd, *J* 15.5, 3, 4-H′), 3.44 [1 H, td, *J* 10, 6.5, OCH*H*CH$_2$Si(CH$_3$)$_3$], 3.65 [2 H, m, 2-H and OC*H*HCH$_2$Si(CH$_3$)$_3$], 3.95 (1 H, q, *J* 6.5, 6-H), 4.29 and 4.38 (each 1 H, d, *J* 7, OC*H*HO), 4.33 and 4.60 (each 1 H, s, vinylic H), 4.50 and 4.61 (each 1 H, d, *J* 12, OC*H*HPh), 5.17 (1 H, m, 3-H), 5.86 (1 H, s, C*H*Ph), 7.29 (8 H, m, ArH) and 7.43 (2 H, m, ArH); δ_C −1.4, 15.0, 18.1, 20.3, 20.7, 30.5, 65.0, 71.1, 74.5, 74.6, 74.7, 74.8, 92.0, 113.4, 127.6, 127.7, 127.9, 128.4, 128.7, 129.3, 133.6, 138.5, 144.4, 168.6 and 170.3; *m*/*z* 574 (M^+ + 18, 40%) and 409 (12).

Tin(IV) halide promoted reactions between (*S*)-4-benzyloxypent-2-enyl(tributyl)stannane 1 and 2,3-*O*-isopropylidenepropanal 13

A cooled solution of tin(IV) bromide (750 mg, 1.71 mmol) in dichloromethane (1.71 cm^3) was added dropwise to a stirred solution of the (*S*)-4-benzyloxypent-2-enyl(tributyl)stannane **1** (650 mg, 1.40 mmol) in dichloromethane (6 cm^3) at −78 °C. After 10 min, a cooled solution of 2,3-*O*-isopropylidene-L-propanal **13** (182 mg, 1.40 mmol) in dichloromethane (1 cm^3) was added and the mixture stirred for 1 h at −78 °C. Saturated aqueous sodium hydrogen carbonate (10 cm^3) was added, and the mixture allowed to warm to room temp. before being partitioned between dichloromethane and water. The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using diethyl ether–light petroleum (7:3) as eluent gave two fractions. The less polar fraction contained (2S,3R,7S,5Z)-7-*benzyloxy*-1,2-O-*isopropylideneoct*-5-*en*-3-*ol* **30** (120 mg, 28%) as a colourless oil, containing *ca.* 5% (^{1}H NMR spectroscopy) of its epimer **33** (Found: M^+ + H, 307.1918. $C_{18}H_{27}O_4$ requires *M*, 307.1909); $[\alpha]_D$ +4.3 (*c* 1.6, CH_2Cl_2); ν_{max}/cm^{-1} 3453, 1454, 1371, 1254, 1214, 1067, 854, 738 and 699; δ_H 1.25 (3 H, d, *J* 6.5, 8-H_3), 1.34 and 1.40 (each 3 H, s, CH_3), 2.22 (3 H, m, 4-H_2 and OH), 3.69 (1 H, m, 3-H), 3.88 (1 H, m), 3.95 (2 H, m), 4.27 (1 H, m, 7-H), 4.39 and 4.53 (each 1 H, d, *J* 12, OC*H*HPh), 5.56 (1 H, dd, *J* 11, 9, 6-H), 5.62 (1 H, dt, *J* 11, 7, 5-H) and 7.31 (5 H, m, ArH); δ_C 21.2, 25.3, 26.6, 31.6, 65.4, 69.9, 70.0, 71.1, 78.3, 109.2, 127.5, 127.6, 127.9, 128.4, 135.4 and 138.6; *m*/*z* 324 (M^+ + 18, 65%), (M^+ + 1, 30) and 199 (100);. The more polar fraction contained (2S,3R,7S,5Z)-7-*benzyloxy*-2,3-O-*isopropylideneoct*-5-*en*-1-*ol* **35** (Found: M^+ + H, 307.1899. $C_{18}H_{27}O_4$ requires *M*, 307.1909); $[\alpha]_D$ −4.6 (*c* 4, CH_2Cl_2); ν_{max}/cm^{-1} 3436, 1455, 1380, 1370, 1248, 1217, 1165, 1096, 1069, 1046, 902, 840, 738 and 697; δ_H 1.25 (3 H, d, *J* 6.5, 8-H_3), 1.34 and 1.45 (each 3 H, s, CH_3), 1.85 (1 H, t, *J* 6, OH), 2.21 (1 H, m, 4-H), 2.38 (1 H, m, 4-H′), 3.58 (2 H, m, 1-H_2), 4.16 (2 H, m, 2-H and 3-H), 4.26 (1 H, m, 7-H), 4.35 and 4.56 (each 1 H, d, *J* 12, OC*H*HPh), 5.50 (1 H, dd, *J* 11, 9, 6-H), 5.59 (1 H, dt, *J* 11, 7, 5-H) and 7.29 (5 H, m, ArH); δ_C 21.4, 25.3, 27.8, 28.1, 61.6, 69.9, 70.1, 77.2, 77.6, 108.3, 127.5, 127.6, 127.8, 128.4, 134.5 and 138.8; *m*/*z* 324 (M^+ + 18, 20%), 307 (M^+ + 1, 10) and 199 (100).

Following this procedure the (*R*)-aldehyde (*R*)-**13** gave (2R,3R,7S,5Z)-7-*benzyloxy*-1,2-O-*isopropylideneoct*-5-*en*-3-*ol*

37 (60 mg, 15%) as a colourless oil, containing *ca.* 10% (^{1}H NMR spectroscopy) of its epimer **40** (Found: $M^+ + H$, 307.1916. $C_{18}H_{27}O_4$ requires *M*, 307.1909); $[\alpha]_D$ +27.4 (*c* 1.3, CH_2Cl_2); ν_{max}/cm^{-1} 3470, 1454, 1371, 1256, 1214, 1158, 1069, 857, 737 and 699; δ_H 1.25 (3 H, d, *J* 6.5, 8-H_3), 1.34 and 1.41 (each 3 H, s, CH_3), 2.22 (3 H, m, 4-H_2 and OH), 3.52 (1 H, m, 3-H), 3.72 (1 H, dd, *J* 7.5, 6, 1-H), 3.97 (2 H, m, 1-H′ and 2-H), 4.28 (1 H, m, 7-H), 4.38 and 4.54 (each 1 H, d, *J* 12, OC*H*HPh), 5.53 (1 H, dd, *J* 11, 9, 6-H), 5.61 (1 H, dt, *J* 11, 7, 5-H) and 7.29 (5 H, m, ArH); δ_C 21.3, 25.3, 26.6, 32.3, 66.0, 69.8, 70.0, 71.5, 78.1, 109.4, 127.3, 127.5, 127.8, 128.4, 135.0 and 138.7; *m*/*z* 324 ($M^+ + 18$, 28%), 307 ($M^+ + 1$, 15) and 199 (100) together with (2R,3R,7S,5Z)-7-*benzyloxy*-2,3-O-*isopropylideneoct*-5-*en*-1-*ol* **42** (98 mg, 25%) (Found: $M^+ + H$, 307.1914. $C_{18}H_{27}O_4$ requires *M*, 307.1909); $[\alpha]_D$ +19.5 (*c* 2.4, CH_2Cl_2); ν_{max}/cm^{-1} 3457, 1454, 1371, 1247, 1217, 1165, 1093, 1070, 904, 843, 738 and 699; δ_H 1.25 (3 H, d, *J* 6.5, 8-H_3), 1.38 and 1.39 (each 3 H, s, CH_3), 1.90 (1 H, m, OH), 2.31 (1 H, m, 4-H), 2.39 (1 H, m, 4-H′), 3.54 (1 H, m, 1-H), 3.73 (2 H, m, 1-H′ and 3-H), 3.93 (1 H, m, 2-H), 4.27 (1 H, m, 7-H), 4.35 and 4.55 (each 1 H, d, *J* 12, OC*H*HPh), 5.52 (1 H, dd, *J* 11, 9, 6-H), 5.61 (1 H, dd, *J* 11, 7, 5-H), 7.26 (1 H, m, ArH) and 7.31 (4 H, m, ArH); δ_C 21.4, 27.0, 27.3, 30.9, 61.9, 69.9, 70.1, 76.2, 80.9, 108.8, 126.6, 127.5, 127.7, 128.4, 135.0 and 138.8; *m*/*z* 324 ($M^+ + 18$, 30%), 307 ($M^+ + 1$, 10) and 199 (100).

Treatment of (2*S*,3*R*,7*S*,5*Z*)-7-Benzyloxy-1,2-*O*-isopropylideneoct-5-en-3-ol 30 with tin(IV) bromide

A cooled solution of tin(IV) bromide (96 mg, 0.22 mmol) in dichloromethane (0.22 cm^3) was added dropwise to a stirred solution of the alkenol **30** (55 mg, 0.18 mmol) in dichloromethane (2 cm^3) at −78 °C and the mixture stirred for 1 h at −78 °C. Saturated aqueous sodium hydrogen carbonate (1 cm^3) was added, and the mixture allowed to warm to room temp. before being partitioned between dichloromethane and water. The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using diethyl ether–light petroleum (7:3) as eluent gave unreacted alkenol **30** (20 mg, 37%) as a colourless oil, and its rearranged isomer **35** (21 mg, 38%) as a colourless oil.

(2*S*,3*R*,7*S*,5*Z*)-7-Benzyloxy-2,3-*O*-isopropylideneoct-5-en-1-yl *p*-nitrobenzoate 36

Following the procedure outlined above for the synthesis of the *p*-nitrobenzoate **18**, the alcohol **35** gave the *title compound* **36** (42 mg, 80%) (Found: $M^+ + NH_4$, 473.2287. $C_{25}H_{33}N_2O_7$ requires *M*, 473.2288); $[\alpha]_D$ −0.5 (*c* 0.7, CH_2Cl_2); ν_{max}/cm^{-1} 1729, 1607, 1530, 1454, 1273, 1218, 1167, 1102, 1078, 1015, 873, 844 and 720; δ_H 1.24 (3 H, d, *J* 6.5, 8-H_3), 1.36 and 1.46 (each 3 H, s, CH_3), 2.29 (1 H, m, 4-H), 2.43 (1 H, m, 4-H′), 4.28 (3 H, m, 2-H, 3-H and 7-H), 4.34 and 4.55 (each 1 H, d, *J* 12, OC*H*HPh), 4.40 (2 H, m, 1-H_2), 5.53 (1 H, dd, *J* 11, 9, 6-H), 5.62 (1 H, dt, *J* 11, 7, 5-H), 7.24 (1 H, m, ArH), 7.30 (4 H, m, ArH) and 8.19 and 8.26 (each 2 H, d, *J* 9, ArH); *m*/*z* 473 ($M^+ + 18$, 92%), 443 (10) and 260 (100).

(2*R*,3*R*,7*S*,5*Z*)-7-Benzyloxy-2,3-*O*-isopropylideneoct-5-enyl *p*-nitrobenzoate 43

Following the procedure outlined above for the synthesis of the *p*-nitrobenzoate **18**, the alcohol **42** gave the *title compound* **43** (42 mg, 80%) (Found $M^+ + NH_4$, 473.2298. $C_{25}H_{33}N_2O_7$ requires *M*, 473.2288); $[\alpha]_D$ +19.2 (*c* 0.4, CH_2Cl_2); ν_{max}/cm^{-1} 1729, 1530, 1454, 1380, 1371, 1348, 1275, 1099, 846, 738, 720 and 698; δ_H 1.24 (3 H, d, *J* 6.5, 8-H_3), 1.39 and 1.42 (each 3 H, s, CH_3), 2.43 (2 H, m, 4-H_2), 3.93 and 3.98 (each 1 H, m), 4.27 (1 H, m, 7-H), 4.33 and 4.53 (each 1 H, d, *J* 12, OC*H*HPh), 4.35 (1 H, dd, *J* 12, 5.5, 1-H), 4.51 (1 H, dd, *J* 12, 3, 1-H′), 5.55 (1 H, dd, *J* 11, 9, 6-H), 5.63 (1 H, dt, *J* 11, 7, 5-H), 7.31 (5 H, m, ArH) and 8.18 and 8.26 (each 2 H, d, *J* 9, ArH); *m*/*z* 473 ($M^+ + 18$, 20%), 348 (30) and 260 (100).

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