Stereoselective synthesis of 4-alkoxy-3-methylidenealkanols using reactions between 2-(1-alkoxyalkyl)propenylstannanes and aldehydes: X-ray crystal structure of (1*R*,4*R*)-3-methylidene-1-(4-nitrophenyl)-pentane-1,4-diol

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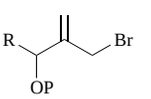
The 2-(1-hydroxy- and 1-alkoxy-alkyl)propenylstannanes 9 and 11–15, react with aldehydes to form 4-hydroxy- and 4-alkoxy-3-methylidenealkanols 23, 24 and 36–53. The stereoselectivity of these reactions has been investigated. If the reactions are carried out by transmetallation of the stannane using a tin(IV) halide before addition of the aldehyde, modest stereoselectivity in favour of the 1,4-*anti*-products 23, 36 and 37 is observed for the hydroxystannane 9, whereas the alkoxystannanes 11–15 give rise preferentially to the 1,4-*syn*-diastereoisomers 47–53, selectivity 75–85 : 25–15. It should be noted that these stereochemical assignments are the reverse of those reported in the preliminary communication on this work. The structure of the 1,4-*anti*-product 36 from the reaction between the hydroxystannane 9 and *p*-nitrobenzaldehyde was established by X-ray diffraction. The stereoselectivity of BINOL–titanium(IV) catalysed reactions of the (*R*)-SEM-stannane (*R*)-12 with benzaldehyde is controlled by the configuration of the BINOL and can be used to synthesize either the 1,4-*anti*- or 1,4-*syn*-isomers 40 and 47.

Introduction

Reactions of propenylmetal reagents with aldehydes are of considerable interest.[1] For example, useful 1,4-asymmetric induction in favour of the 1,4-*syn*-product **2** over the 1,4-*anti*-isomer **3** has been observed for the chromium(II) and indium mediated coupling of 1-bromo-2-(1-alkoxyalkyl)propenes **1** with aldehydes (selectivity 85–95 : 15–5).[2] 2-(1-Substituted-alkyl)propenyl-stannanes and -silanes **4** (M = $SiMe_3$, $SnBu_3$) react with aldehydes to give preferentially either the 1,4-*syn*- or 1,4-*anti*-products **2** or **3** depending on the 1′-substituent and the Lewis acid used to promote the reaction.[3,4] Very high asymmetric induction has been observed for reactions between the propenylstannane **5** and aldehydes in the presence of BINOL–titanium(IV) and related metal catalysts.[5–7] For example the homoallylic alcohols **6** were obtained with excellent ees using the catalyst formed from (*S*)-BINOL and $TiCl_2(OPr^i)_2$ in the presence of molecular sieves.[5] We now report full details of a study of the stereoselectivity of reactions between 2-(1-alkoxyalkyl)prop-2-enylstannanes **4** (M = $SnBu_3$) and aldehydes promoted by tin(IV) halides together with preliminary results on the influence of BINOL–metal catalysts on the stereoselectivity of these reactions.†[8]



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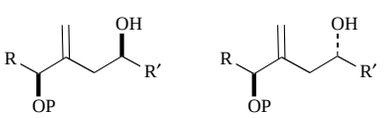
(P = Bn, $SiMe_2Bu^t$, MOM)



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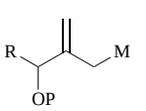

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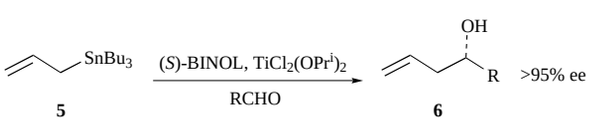
M = $SiMe_3$, $SnBu_3$;
P = Ac, Me

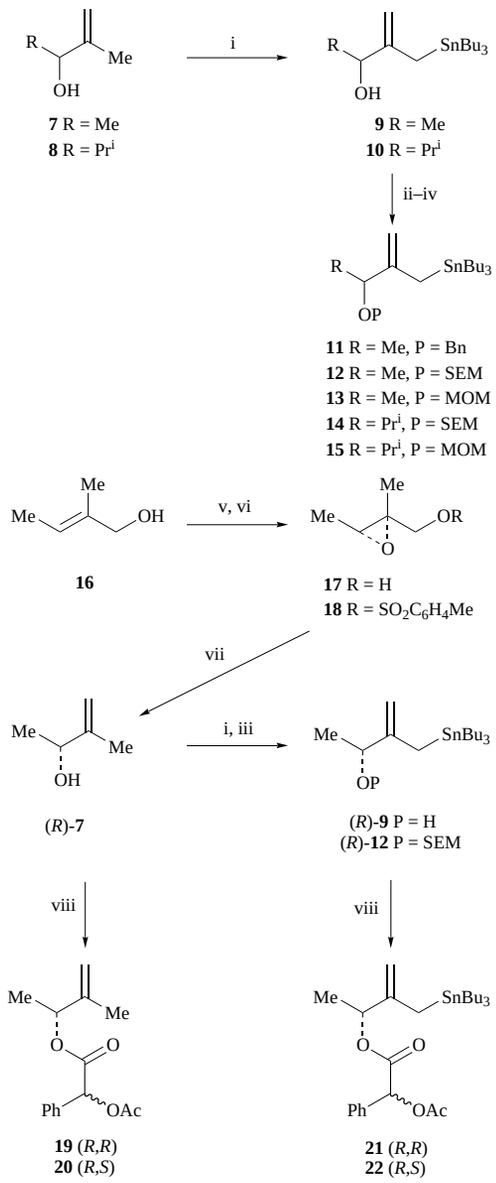


5 **6**

Results and discussion

Racemic 2-(1-hydroxyethyl)- and 2-(1-hydroxy-2-methylpropyl)-prop-2-enyl(tributyl)stannanes **9**[9] and **10** were prepared by stannylation of the alkenols **7** and **8**, and were converted into the benzyl, (2-trimethylsilylethoxy)methoxy (SEM) and methoxymethoxy (MOM) ethers **11**–**15**, respectively (Scheme 1). The (*R*)-enantiomer of the alcohol (*R*)-**7** was prepared from 2-methylbut-2-enol **16** *via* Sharpless epoxidation using (−)-diisopropyl tartrate, formation of the toluene-*p*-sulfonate, and reductive elimination, following the procedure reported in the literature.[4] Stannylation gave the (*R*)-enantiomer of the hydroxyalkylstannane (*R*)-**9**. The absolute configurations of both the alkenol (*R*)-**7** and the stannane (*R*)-**9** were assigned on the basis that (−)-diisopropyl tartrate had been used in the Sharpless epoxidation,[10] and were checked by comparison of the ^{1}H

† The stereochemical assignments made in this paper are the reverse of those reported in the preliminary publication.[8] The original assignments were made by correlation of the racemic products with known compounds prepared following a literature reaction[3] and were supported by preliminary results of an X-ray crystal structure of the major diol from the reaction of the racemic hydroxystannane **9** with benzaldehyde. However, these X-ray data were found to be unreliable because of disorder in the crystals and when the chemistry reported in this paper was carried out using enantiomerically enriched stannanes it was apparent that the structures of the products assigned previously had to be revised. The results reported herein, including the stereochemical assignments, are entirely consistent with the results of Maguire *et al.*,[2] the X-ray crystal structure for the 1,4-*anti*-diol **36**, and the results of Nishigaichi.[3] It should be noted that the relative ^{1}H NMR chemical shift of the benzylic protons for the 1,4-*syn*- and 1,4-*anti*-alkoxyalcohols referred to in the text[2] is a useful check of relative stereochemistry.

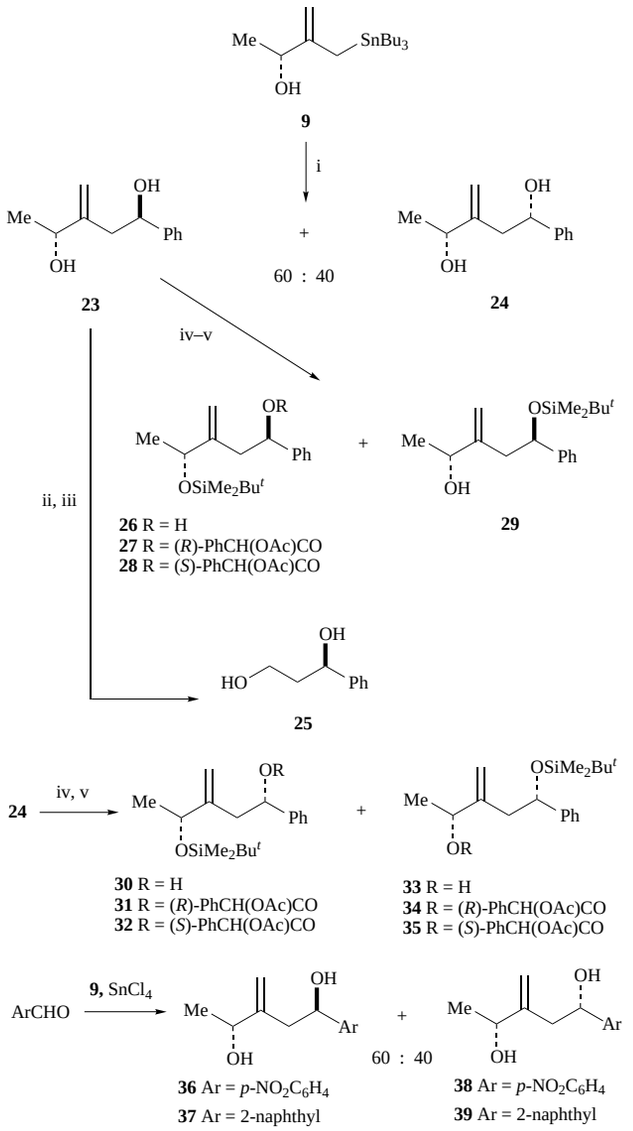


Scheme 1 *Reagents and conditions:* i, 2 BuLi, Bu_3SnCl (**9**, 46%; **10**, 40%); ii, NaH, Bu_4NI, BnBr; iii, SEMCl, Pr^i_2NEt (**12**, 89%; **14**, 70%); iv, MOMCl, Pr^i_2NEt (**13**, 76%; **15**, 65%); v, $Ti(OPr^i)_4$, (−)-diisopropyl tartrate, Bu^tOOH, CH_2Cl_2, −20 °C (55%); vi, toluene-*p*-sulfonyl chloride, Et_3N; vii, NaI, Zn–Cu, ethylene glycol, 80 °C (35% from **17**); viii, (*R*)- or (*S*)-acetylmandelic acid, dicyclohexylcarbodiimide (DCC) (**19**, 80%; **20**, 80%; **21**, 70%; **22**, 70%)

NMR spectra of their (*R*)- and (*S*)-acetylmandelates **19**–**22**, which indicated that the ee of the (*R*)-stannane (*R*)-**9** was *ca.* 92%.[11]

Tin(IV) halide promoted reactions of the propenylstannanes

The tin(IV) halide promoted reactions of the propenylstannanes with aldehydes were carried out by adding the tin halide to a solution of the stannane in dichloromethane at −78 °C and stirring for a few minutes at this temperature to effect transmetallation before the addition of the aldehyde. Using either tin(IV) bromide or tin(IV) chloride, 2-(1-hydroxyethyl)propenylstannane **9** reacted with benzaldehyde to give a mixture of the 1,4-*anti*- and 1,4-*syn*-diastereoisomers **23** and **24** with modest stereoselectivity in favour of the 1,4-*anti*-isomer **23** (**23**:**24** = 60:40), see Scheme 2. The structures of these products were established by chemical correlation of the optically active compounds prepared using the (*R*)-stannane (*R*)-**9**. Ozonolysis of the major product with a reductive work-up gave a mixture of the epimeric diols which were cleaved using sodium periodate followed by reduction using sodium borohydride to give dextrorotatory



Scheme 2 *Reagents and conditions:* i, SnX_4, CH_2Cl_2, −78 °C, 5 min, then PhCHO (70%); ii, O_3, Me_2S, MeOH, −78 °C, then $NaBH_4$ (70%); iii, $NaIO_4$ followed by $NaBH_4$ (70%); iv, *tert*-butyldimethylsilyl trifluoromethanesulfonate, 2,6-lutidine (**26**, 54%; **29**, 12%; **30**, 25%; **33**, 25%); v, (*R*)- or (*S*)-acetylmandelic acid, dicyclohexylcarbodiimide (**27**, 70%; **28**, 76%; **31**, 70%; **32**, 72%; **34**, 70%; **35**, 70%)

1-phenylpropane-1,3-diol which is known to correspond to the (*R*)-enantiomer **25**.[12] Comparisons of the ^{1}H NMR spectra of the (*R*)- and (*S*)-acetylmandelates **27** and **28**, prepared from the monosilyl ether **26** of the major product, and the regioisomeric monosilyl ethers **30** and **33** of the minor product **24** were also consistent with the assigned structures.

Similar stereoselectivity in favour of the 1,4-*anti*-products was observed for reactions of the propenylstannane **9** with *p*-nitrobenzaldehyde and 2-naphthaldehyde. The structure of the major product from the reaction with *p*-nitrobenzaldehyde was confirmed by X-ray diffraction. Fig. 1 shows a projection of the major product as determined by an X-ray crystal study which clearly establishes the structure as the 1,4-*anti*-diastereoisomer **36**.†

In contrast to the stereoselectivity observed with the 2-(2-hydroxyethyl)propenylstannane **9**, the 2-(1-alkoxyethyl)propenylstannanes **11**, **12** and **13** were found to react with aldehydes after transmetallation with either tin(IV) bromide or chloride to give mixtures of the 1,4-*syn*- and 1,4-*anti*-products in which the 1,4-*syn*-diastereoisomers **47**–**51** accounted for 75–85% of the products formed. The results obtained are summarised in Table 1. Similar stereoselectivity was observed using the 2-(1-alkoxy-2-methylpropyl)propenylstannanes **14** and **15**.

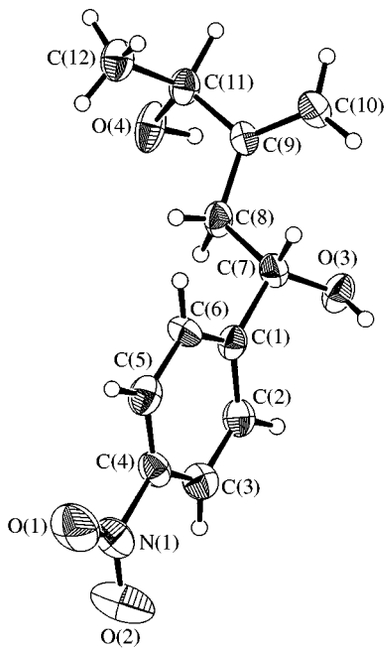
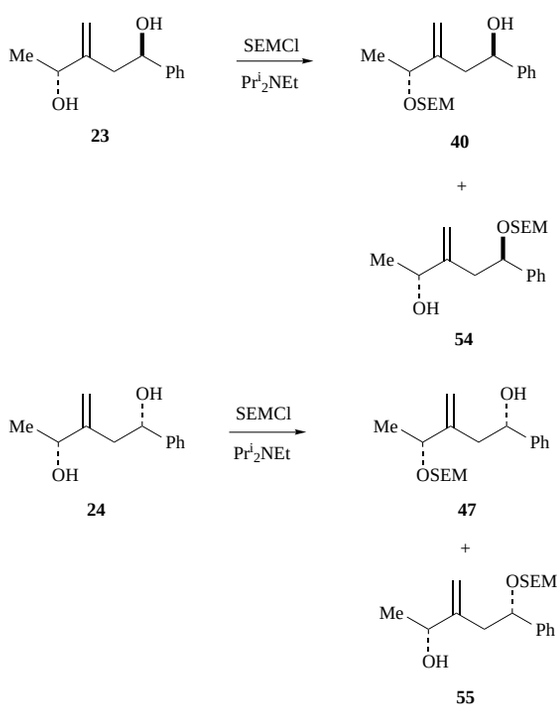


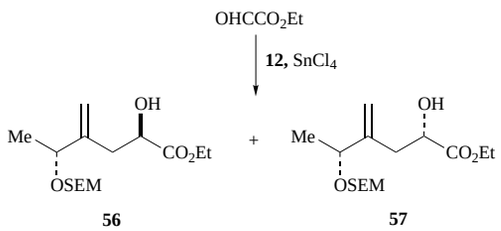
Fig. 1 Projection of a molecule of the 1,4-*anti*-diol **36** as determined by X-ray crystallography

The *syn*- and *anti*-products prepared using the 2-(1-alkoxyalkyl)propenylstannanes could not be separated and were characterised as mixtures. For the products prepared from aromatic aldehydes, stereochemical assignments were made by ^{1}H NMR spectroscopy since it is known that for any pair of *syn*- and *anti*-diastereoisomers, the benzylic (1-H) hydrogen of the *syn*-isomer is *ca.* 0.1–0.2 ppm downfield of the analogous hydrogen of the *anti*-isomer.[2] This assignment of stereochemistry was confirmed for the products **40** and **47** by SEM-protection of the *anti*- and *syn*-1,4-diols **23** and **24**. The *anti*-



diol **23** (the major diol from the reaction of the hydroxystannane **9** and benzaldehyde) gave **40** (*i.e.* the minor product from the reaction of the SEM-stannane **12**) together with its regioisomer **54**. Conversely, the minor *syn*-diol **24** gave the major product from the reaction of the SEM-stannane, *i.e.* **47**, and its regioisomer **55**. These stereochemical assignments are consistent with those established independently by chemical correlation for the enantiotopically enriched products obtained using the (*R*)-stannane (*R*)-**12** and reactions catalysed by BINOL catalysts, *vide infra*.

It would appear that 2-(1-alkoxyalkyl)propenylstannanes are transmetallated with tin(IV) halides to generate propenyltin trihalides which react with aldehydes with reasonable levels, 80(±5):20(±5), of 1,4-asymmetric induction in favour of the *syn*-diastereoisomer. For the stannanes **11**–**15**, this stereoselectivity is not affected significantly by the nature of the 2-(1-alkoxyalkyl) group or by the choice of tin(IV) halide. However, reactions with functionalised aldehydes are less stereoselective. For example, ethyl glyoxalate, on treatment with the (*R*)-SEM-stannane (*R*)-**12** and tin(IV) chloride, gave rise to the *anti*- and *syn*-products **56** and **57**, ratio 37:63, with the use of



(+)- and (−)-menthyl glyoxalates having little effect on the stereoselectivity.

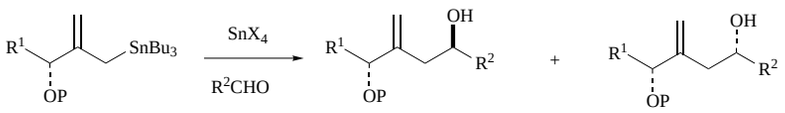
Asymmetric catalysis of reactions of 2-(1-alkoxyalkyl)-propenylstannanes with aldehydes

Since excellent asymmetric induction is observed for reactions between propenylstannane **5** and aromatic and α,β-unsaturated aldehydes in the presence of BINOL-based catalysts,[5–7] it was decided to see whether these catalysts would control the stereoselectivity of reactions of 2-(1-alkoxyalkyl)propenylstannanes with aldehydes. Would the stereoselectivity be controlled by the catalyst, in which case either the 1,4-*syn*- or the 1,4-*anti*-isomer should be the major product depending on the choice of catalyst and chirality of the stannane, or would the configuration of the stannane control the facial selectivity, in which case matching and mis-matching with the catalyst would be observed?

In the event, useful stereocontrol by the catalyst was observed, but the reactions were slow with only modest conversions to products, although slightly better conversions were obtained using the catalyst prepared using titanium(IV) bromide rather than titanium(IV) chloride.[5] The catalyst prepared from (*R*)-BINOL and equimolar amounts of titanium(IV) isopropoxide and titanium(IV) bromide promoted the reaction between the (*R*)-SEM-stannane (*R*)-**12** and benzaldehyde to give predominantly the 1,4-*anti*-product, **40**:**47** = 92:8, whereas (*S*)-BINOL, under the same conditions, gave mainly the 1,4-*syn*-product, **40**:**47** = 12:88 (Table 2). Since the enantiomeric excess of the stannane is only of the order of 92%, these catalysed reactions are proceeding with *ca.* 95% asymmetric induction by the catalyst with the chirality of the stannane having little effect on the overall stereoselectivity.

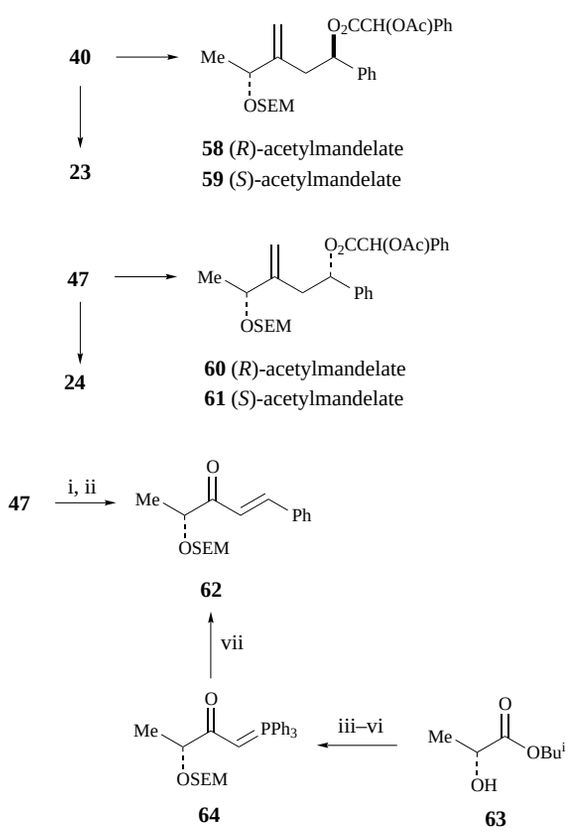
The structures of the products **40** and **47** from the catalysed reactions were identified by comparison of their spectroscopic data with those of products obtained from the tin(IV) chloride promoted reactions, and the absolute configurations of the alcohol groups were consistent with the asymmetric induction previously observed for BINOL–titanium(IV) catalysed allylstannane reactions.[5–7] Since these products could not be separated, the (*R*)-BINOL-based catalysts provided the first access to the SEM-*anti*-product **40** of reasonable diastereoisomeric purity. The structures of products **40** and **47** were checked by conversion into their acetylmandelates whose ^{1}H NMR spectra were consistent with the assigned configurations at the alcohol centres, and by deprotection which gave the *anti*- and *syn*-diols **23** and **24**, respectively (Scheme 3). The enantiomeri-

Table 1 *syn/anti*-Stereoselectivity in tin(IV) halide promoted reactions of 2-(1-alkoxyalkyl)propenylstannanes with aldehydes



11–15 **40–46** **47–53**

					Product			
Stannane	R^1	R^2	P	SnX_4	*anti*	*syn*	Yield (%)	*anti*:*syn*
12	Me	Ph	SEM	$SnBr_4$	**40**	**47**	71	15:85
12	Me	Ph	SEM	$SnCl_4$	**40**	**47**	79	17:83
13	Me	Ph	MOM	$SnBr_4$	**41**	**48**	70	14:86
13	Me	Ph	MOM	$SnCl_4$	**41**	**48**	82	20:80
11	Me	Ph	Bn	$SnBr_4$	**42**	**49**	62	15:85
12	Me	H_2C=CH	SEM	$SnBr_4$	**43**	**50**	77	23:77
12	Me	Me_2CH	SEM	$SnBr_4$	**44**	**51**	75	13:87
14	Pr^i	Ph	SEM	$SnBr_4$	**45**	**52**	69	14:86
15	Pr^i	Ph	MOM	$SnBr_4$	**46**	**53**	60	19:81



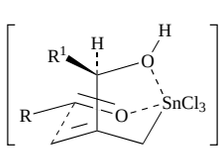
Scheme 3 *Reagents and conditions:* i, O_3, Me_2S; ii, methanesulfonyl chloride, Et_3N; iii, SEMCl, Pr^i_2NEt; iv, LiOH, THF, H_2O; v, Me_3C-COCl; vi, Ph_3P=CH_2; vii, PhCHO, benzene, reflux

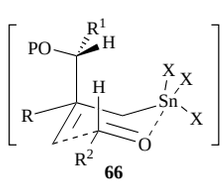
cally enriched *syn*-SEM-product **47** containing *ca.* 15% of its *anti*-isomer **40** was prepared using the (*R*)-SEM-stannane (*R*)-**12** and tin(IV) chloride, and had the same optical rotation as the sample prepared using (*S*)-BINOL. The absolute configuration at C(4) in this compound was also checked by ozonolysis and dehydration to give the unsaturated ketone **62** which was also prepared from (*R*)-isobutyl lactate **63** by way of the keto ylide **64**.

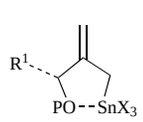
Although the stereoselectivities of the BINOL–$TiBr_2(OPr^i)_2$ catalysed reactions of the (*R*)-SEM-stannane **12** and benzaldehyde were very promising, the conversions and yields were rather modest (30–40%). Preliminary investigations using other published catalyst systems and reaction conditions, including (*R*)-BINOL–$Ti(OPr^i)_4$,[6] (*R*)-BINOL–$Zr(OPr^i)_4$[13] and (*R*)-BINAP–AgO_2CCF_3,[14] in some cases in the presence of Pr^iSiMe_3,[15] gave similar results. Reactions with ethyl glyoxalate[7] gave *ca.* 75:25 mixtures of the 1,4-*syn*- and *anti*-diastereoisomers **57** and **56** (the configuration of the major product depending upon the chirality of the BINOL- or BINAP-containing catalyst used).

Conclusions

This work has shown that modest 1,4-asymmetric induction is possible in reactions between 2-(1-hydroxy- and 1-alkoxyalkyl)-propenylstannanes and aldehydes promoted by an initial transmetallation using a tin(IV) halide. Of interest is the different stereoselectivity observed for the hydroxy- and alkoxy-substituted stannanes. The preferred formation of the 1,4-*syn*-products **47**–**53** from the reactions of the alkoxystannanes and aldehydes is inconsistent with participation of the bicyclic transition structure **65** involving the co-ordinated allyltin trihalide **67**. It may be that the co-ordinated tin trihalide **67** is unable, without undue strain, to align its C–Sn bond parallel to the π-orbitals of the double-bond as would be required for reaction







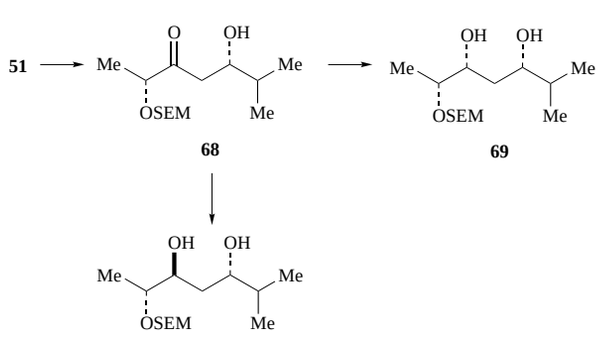
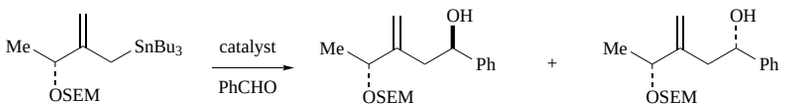


Table 2 Stereoselectivity using BINOL-based catalysts



(*R*)-**12** **40** **47**

Catalyst	Yield (%)	Selectivity **40**:**47**
(*R*)-BINOL, $TiBr_2(OPr^i)_2$	40	92:8
(*S*)-BINOL, $TiBr_2(OPr^i)_2$	30	12:88

with an aldehyde. However, the 1,4-*syn*-stereoselectivity is consistent with participation of the transition structure **66** involving a non-coordinated allyltin trihalide. The reactions controlled by BINOL-based catalysts proceed with excellent stereoselectivity, and have the major advantage that either the 1,4-*syn*- or the 1,4-*anti*-products are obtained depending upon the choice of catalyst. However, further work is required to optimise the chemical conversions and yields in these reactions.

To illustrate the use of this chemistry in synthesis, the *syn*-product **51** was ozonolysed with a reductive work-up using dimethyl sulfide to give the hydroxy ketone **68**. Reduction of the ketone with sodium borohydride–methoxydiethylborane[16] and with tetramethylammonium triacetoxyborohydride[17] then gave the 1,3-*syn*- and 1,3-*anti*-diols **69** and **70**, selectively.

Experimental

Melting points were determined on a Buchi 510 apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer 297 and 1710 spectrometers as liquid films unless otherwise stated. Low and high resolution mass spectra were taken on a Kratos Concept mass spectrometer using the chemical ionisation mode (CI) unless otherwise stated. Characteristic clumps of isotope peaks were observed for the propenylstannanes; those quoted correspond to ^{120}Sn. ^{1}H NMR spectra were recorded on a Varian Unity 500 (500 MHz), Bruker AC-300 or Varian INOVA 300 (300 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker AC 300 or INOVA 300 instrument. Optical rotations were measured at 20 °C and are given in units of 10^{-1} deg cm^2 g^{-1}. Flash chromatography was carried out using Merck silica gel 60 (40–63 μm, 230–400 mesh) or May and Baker Sorbsil C60 silica gel (40–60 μm). All solvents were dried and distilled before use. HPLC was carried out using a Pump Controlled Gilson Assembly with a Rainin Dynamax 60A silica column with dimensions of 21.4 × 250 mm and a guard column, monitoring at 254 nm using a Gilson 115 UV detector. Light petroleum refers to the fraction boiling in the range 40–60 °C. Ether refers to diethyl ether.

The (2*R*,3*R*)-hydroxy epoxide **17** was prepared from 2-methylbut-2-enol following the literature procedure[18] and had $[\alpha]_D$ +19.4 (*c* 2.3, CH_2Cl_2) {lit.,[18] [for the (2*S*,3*S*)-enantiomer] −22.2 (*c* 3, CH_2Cl_2)}. (*R*)-3-Methylbut-3-en-2-ol **7** was prepared from the toluene-*p*-sulfonate **18** by reductive elimination using a zinc–copper couple and oven dried sodium iodide in ethylene glycol at 80 °C following the literature procedure[4] and had $[\alpha]_D$ +5.8 (*c* 1, $CHCl_3$) [lit.,[19] +6.2 (*c* 2.1, $CHCl_3$)]. The (*R*)-stannane **9** was prepared from (*R*)-3-methylbut-3-en-2-ol **7** by using the procedure reported in the literature for the racemic compound[9] and had $[\alpha]_D$ −17.0 (*c* 1, CH_2Cl_2).

3-Hydroxy-4-methyl-2-methylidenepentyl(tributyl)stannane 10

2,4-Dimethylpent-1-en-3-ol (2.65 g, 23.2 mmol) was added to a solution of butyllithium (10 M in hexane; 61.5 mmol) and tetramethylethylenediamine (8.47 g, 72.9 mmol) in ether (30 cm^3) at 0 °C. The reaction mixture was stirred at 0 °C for 6 h then tributyltin chloride (8.58 g, 26.4 mmol) in tetrahydrofuran (7 cm^3) was added rapidly at 0 °C. The solution became clear, was allowed to warm to room temp. and was stirred for 30 min. The reaction mixture was added to ether (210 cm^3) and washed with saturated aqueous copper sulfate (2 × 40 cm^3), water (50 cm^3) and brine (2 × 40 cm^3). The organic layer was dried (K_2CO_3) and concentrated under reduced pressure. Chromatography of the residue using light petroleum–ether (50:1 containing 1% of triethylamine) as eluent gave the *title compound* **10** (3.74 g, 40%) as a colourless oil (Found: $M^+ - C_4H_9$, 347.1396. $C_{15}H_{31}OSn$ requires *M*, 347.1397); ν_{max}/cm^{-1} 3487, 1627, 1464, 1377, 1291, 1248, 1073, 1003 and 874; δ_H 0.83 (18 H, m, 3 × CH_2CH_3 and CH_3), 1.25 (9 H, m, 3 × CH_2 and CH_3), 1.41 (7 H, m, 3 × CH_2 and OH), 1.54 and 1.71 (each 1 H, d, *J* 11, 1-H), 1.74 (1 H, m, 4-H), 3.59 (1 H, dd, *J* 6.5, 4, 3-H) and 4.58 and 4.64 (each 1 H, s, 1′-H); δ_C 10.5, 14.4, 15.2, 17.8, 20.5, 28.1, 29.8, 32.1, 82.0, 106.6, 152.3; *m/z* 405 (M^+ + 1, 1%), 347 (97) and 291 (95).

3-Benzyloxy-2-methylidenebutyl(tributyl)stannane 11

The hydroxybutylstannane **9**[9] (1 g, 2.67 mmol) was added to a suspension of sodium hydride (60% in mineral oil; 114 mg, 2.86 mmol) in anhydrous *N*,*N*-dimethylformamide (1.6 cm^3) at 0 °C. The mixture was stirred for 1 h at 20 °C then a solution of tetrabutylammonium iodide (39 mg, 0.103 mmol) and benzyl bromide (499 mg, 2.86 mmol) in tetrahydrofuran was added. The reaction mixture was stirred for 12 h, poured into water (40 cm^3) and extracted with ethyl acetate (3 × 40 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum containing 1% of triethylamine gave the *title compound* **11** (124 mg, 10%) as a colourless oil (Found: $M^+ - C_4H_9$, 409.1548. $C_{20}H_{33}OSn$ requires *M*, 409.1553); ν_{max}/cm^{-1} 1629, 1455, 1075, 875, 733 and 697; δ_H 0.94 (15 H, m, 3 × CH_2CH_3), 1.35 (9 H, m, 3 × CH_2 and CH_3), 1.52 (6 H, m, 3 × CH_2), 1.74 and 1.87 (each 1 H, d, *J* 12, 1-H), 3.90 (1 H, q, *J* 6.5, 3-H), 4.38 and 4.58 (each 1 H, d, *J* 12, PhC*H*H), 4.73 and 4.87 (each 1 H, s, 1′-H) and 7.30 (5 H, m, aromatic H); δ_C 9.8, 13.0, 13.7, 20.4, 27.4, 29.1, 70.0, 78.9, 106.8, 127.3, 127.6, 128.4, 139.0 and 155.4; *m/z* 409 (M^+ − 57, 50%) and 291 (40).

2-Methylidene-3-(2-trimethylsilylethoxymethoxy)butyl-(tributyl)stannane 12

N,*N*-Diisopropylethylamine (950 mg, 7.35 mmol) was added to a solution of the hydroxyalkylstannane **9** (540 mg, 1.44 mmol) in dichloromethane (2 cm^3). The solution was cooled at 0 °C then 2-trimethylsilylethoxymethyl chloride (753 mg, 4.52 mmol) was added and the reaction mixture was stirred at 0 °C for 2 h. The reaction mixture was added to light petroleum and extracted twice with cooled aqueous hydrogen chloride (0.5 M), water and saturated aqueous sodium hydrogen carbonate. The organic layer was dried (K_2CO_3) and concentrated under reduced pressure. Chromatography of the residue using light petroleum–ether (100:1 containing 1% triethylamine) as eluent gave the *title compound* **12** (647 mg, 89%) as a colourless oil (Found: $M^+ - C_4H_9$, 449.1903. $C_{19}H_{41}O_2SiSn$ requires *M*, 449.1898); ν_{max}/cm^{-1} 1630, 1464, 1377, 1249, 1101, 1030, 861 and 836; δ_H 0.09 [9 H, s, $Si(CH_3)_3$], 0.92 (17 H, m, 3 × CH_2CH_3

and CH_2Si), 1.33 (9 H, m, 3 × CH_2 and CH_3), 1.51 (6 H, m, 3 × CH_2), 1.68 and 1.81 (each 1 H, d, *J* 12, 1-H), 3.58 and 3.75 [each 1 H, m, OHC*H*$CH_2Si(CH_3)_3$], 4.11 (1 H, q, *J* 6.5, 3-H), 4.64 and 4.79 (each 1 H, s, 1′-H) and 4.66 (2 H, s, OC*H*HO); δ_C −1.4, 9.7, 13.9, 13.7, 18.1, 20.3, 27.4, 29.1, 65.0, 75.8, 92.4, 106.6 and 150.2; *m/z* 507 ($M^+ + 1$, 34%), 449 (61) and 306 (100).

The (*R*)-stannane (*R*)-**12** was prepared following this procedure and had $[a]_D$ +28.4 (*c* 2.6, $CHCl_3$).

3-(Methoxymethoxy)-2-methylidenebutyl(tributyl)stannane 13

N,*N*-Diisopropylethylamine (1.76 g, 13.6 mmol) was added to a solution of the hydroxystannane **9** (1 g, 2.67 mmol) in dichloromethane (4 cm^3). The solution was cooled at 0 °C, methoxymethyl chloride was added (870 mg, 10.8 mmol) and the reaction mixture was allowed to warm to room temp. and stirred for 1 h. The reaction mixture was added to light petroleum and extracted twice with cooled aqueous hydrogen chloride (0.5 M), water and saturated aqueous sodium hydrogen carbonate. The organic layer was dried (K_2CO_3) and concentrated under reduced pressure. Chromatography of the residue using light petroleum–ether (100:1 containing 1% triethylamine) as eluent gave the *title compound* **13** (848 mg, 76%) as a colourless oil (Found: $M^+ - C_4H_9$, 363.1343. $C_{15}H_{31}O_2Sn$ requires *M*, 363.1346); ν_{max}/cm^{-1} 1630, 1464, 1376, 1157, 1098, 1039, 957, 921 and 875; δ_H 0.92 (15 H, m, 3 × CH_2CH_3), 1.31 (9 H, m, 3 × CH_2 and CH_3), 1.50 (6 H, m, 3 × CH_2), 1.69 and 1.82 (each 1 H, d, *J* 12, 1-H), 3.40 (3 H, s, OCH_3), 4.09 (1 H, q, *J* 6.5, 3-H), 4.59 and 4.66 (each 1 H, d, *J* 7, OC*H*HO) and 4.65 and 4.80 (each 1 H, s, 1′-H); δ_C 9.7, 13.4, 13.7, 20.3, 27.4, 29.0, 55.2, 75.9, 94.1, 106.6 and 150.1; *m/z* 421 ($M^+ + 1$, 65%) and 308 (100).

4-Methyl-3-(2-trimethylsilylethoxymethoxy)-2-methylidenepentyl(tributyl)stannane 14

Following the procedure outlined for the synthesis of the stannane **12**, the hydroxyalkylstannane **10** (500 mg, 1.24 mmol) in dichloromethane (3 cm^3), *N*,*N*-diisopropylethylamine (801 mg, 6.20 mmol) and 2-trimethylsilylethoxymethyl chloride (620 mg, 3.72 mmol) gave, after chromatography using light petroleum–ether (100:1 containing 1% triethylamine) as eluent, the *title compound* **14** (529 mg, 80%) as a colourless oil (Found: $M^+ - C_4H_9$, 477.2216. $C_{21}H_{45}O_2SiSn$ requires *M*, 477.2211); ν_{max}/cm^{-1} 1627, 1463, 1377, 1248, 1095, 1030, 860 and 835; δ_H 0.05 [9 H, s, $Si(CH_3)_3$], 0.97 (23 H, m, 3 × CH_2CH_3, CH_2Si and 2 × CH_3), 1.34 (6 H, m, 3 × CH_2), 1.52 (6 H, m, 3 × CH_2), 1.61 and 1.72 (each 1 H, d, *J* 12.5, 1-H), 1.85 (1 H, m, 4-H), 3.52 [1 H, ddd, *J* 10, 10, 6.5, OC*H*H$CH_2Si(CH_3)_3$], 3.61 (1 H, d, *J* 7, 3-H), 3.85 [1 H, ddd, *J* 10, 10, 6.5, OCH*H*$CH_2Si(CH_3)_3$], 4.60 and 4.63 (each 1 H, d, *J* 7, OC*H*HO) and 4.76 (2 H, narrow m, 1′-H); δ_C −1.4, 9.6, 12.8, 13.7, 17.8, 18.1, 19.9, 27.4, 29.1, 30.1, 65.0, 85.8, 92.1, 110.0 and 147.2; *m/z* 535 ($M^+ + 1$, 2%), 477 (20) and 308 (100).

3-(Methoxymethoxy)-4-methyl-2-methylidenepentyl(tributyl)-stannane 15

Following the procedure outlined for the synthesis of the stannane **13**, the hydroxyalkylstannane **10** (778 mg, 1.93 mmol) in dichloromethane (3 cm^3), *N*,*N*-diisopropylethylamine (1.27 g, 9.87 mmol) and methoxymethyl chloride (615 mg, 7.64 mmol) gave, after chromatography using light petroleum–ethyl acetate (100:1 containing 1% triethylamine) as eluent, the *title compound* **15** (560 mg, 65%) as a colourless oil (Found: $M^+ - C_4H_9$, 391.1662. $C_{17}H_{35}O_2Sn$ requires *M*, 391.1659); ν_{max}/cm^{-1} 1627, 1463, 1377, 1154, 1092, 1039 and 878; δ_H 0.92 (18 H, m, 3 × CH_2CH_3 and CH_3), 1.01 (3 H, d, *J* 7, CH_3), 1.35 (6 H, m, 3 × CH_2), 1.5 (7 H, m, 3 × CH_2 and 1-H), 1.73 (1 H, d, *J* 12.5, 1-H), 1.86 (1 H, m, 4-H), 3.42 (3 H, s, OCH_3), 3.59 (1 H, d, *J* 7, 3-H), 4.48 and 4.65 (each 1 H, d, *J* 6.5, OC*H*HO) and 4.77 (2 H, m, vinylic H); δ_C 9.7, 12.9, 13.7, 18.2, 19.9, 27.4, 29.1, 30.1, 55.7, 85.9, 94.0, 110.1 and 147.1; *m/z* 449 ($M^+ + 1$, 24%), 391 (50) and 308 (100).

(2*R*,3*R*)-2,3-Epoxy-2-methylbutyl toluene-*p*-sulfonate 18

A solution of toluene-*p*-sulfonyl chloride (2.65 g, 14 mmol) and triethylamine (2.82 g, 30 mmol) in dichloromethane (25 cm^3) was added dropwise to a stirred solution of the alcohol **17** (1.40 g, 14 mmol) in dichloromethane (25 cm^3) at 0 °C and the mixture was stirred for 12 h at room temperature. The organic phase was washed with water (2 × 5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with ether–light petroleum (4:6), gave the toluene *p*-sulfonate **18** (2.81 g, 80%); ν_{max}/cm^{-1} 1598, 1360, 1177, 1097, 974, 953, 840, 816 and 773; δ_H(200 MHz) 1.25 (3 H, d, *J* 6.5, CH_3), 1.29 (3 H, s, CH_3), 2.44 (3 H, s, ArCH_3), 2.92 (1 H, q, *J* 6.5, CH), 3.94 (2 H, s, CH_2) and 7.36 and 7.8 (each 2 H, d, *J* 8, ArH); *m/z* 274 ($M^+ + 18$, 100%) and 257 ($M^+ + 1$, 38).

Preparation of *O*-acetylmandelates

General procedure: preparation of (*R*)-3-methylbut-3-en-2-yl (*R*)-*O*-acetylmandelate 19. (*R*)-*O*-Acetylmandelic acid (49 mg, 0.25 mmol) and 4-dimethylaminopyridine (DMAP, cat.) were added to a solution of (*R*)-3-methylbut-3-en-2-ol **7** (20 mg, 0.23 mmol) in dichloromethane (0.5 cm^3) followed by a solution of dicyclohexylcarbodiimide (DCC) (95 mg, 0.46 mmol) in dichloromethane (0.5 cm^3) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The solvent was removed under reduced pressure and ether was added. The mixture was filtered and the filtrate concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (3:7) as eluent gave the *title compound* **19** as a colourless oil (49 mg, 80% yield) (Found: $M^+ + NH_4$, 280.1559. $C_{15}H_{22}NO_4$ requires *M*, 280.1549); $[a]_D$ −89.7 (*c* 3.5, CH_2Cl_2); ν_{max}/cm^{-1} 1746, 1374, 1233, 1211, 1179, 1085, 1054, 910, 740 and 697; δ_H 1.38 (3 H, d, *J* 6.5, 1-H_3), 1.51 (3 H, s, 3-CH_3), 2.24 (3 H, s, $OCOCH_3$), 4.74 (2 H, s, vinylic H), 5.33 (1 H, q, *J* 6.5, 2-H), 5.96 (1 H, s, C*H*$OCOCH_3$), 7.41 (3 H, m, ArH) and 7.5 (2 H, m, ArH); δ_C 17.9, 18.9, 20.7, 74.7, 74.8, 111.9, 127.7, 128.7, 129.2, 133.9, 143.7, 168.0 and 170.4; *m/z* 281 ($M^+ + 19$, 40%), 280 ($M^+ + 18$, 100) and 263 ($M^+ + 1$, 10).

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

(*R*)-3-Methylbut-3-en-2-yl (*S*)-*O*-acetylmandelate 20. (80%) (Found: $M^+ + NH_4$, 280.1561. $C_{15}H_{22}NO_4$ requires *M*, 280.1549); $[a]_D$ +108.3 (*c* 2.3, CH_2Cl_2); ν_{max}/cm^{-1} 1746, 1374, 1233, 1211, 1179, 1085, 1052, 738 and 697; δ_H 1.24 (3 H, d, *J* 6.5, 1-H_3), 1.77 (3 H, s, 3-CH_3), 2.24 (3 H, s, $OCOCH_3$), 4.91 and 5.02 (each 1 H, s, vinylic H), 5.33 (1 H, q, *J* 6.5, 2-H), 5.96 (1 H, s, C*H*$OCOCH_3$), 7.43 (3 H, m, ArH) and 7.52 (2 H, m, ArH); δ_C 18.2, 18.7, 20.7, 74.7, 74.9, 112.1, 127.5, 128.7, 129.1, 133.9, 143.7, 168.1 and 170.3; *m/z* 280 ($M^+ + 18$, 100%), 263 ($M^+ + 1$, 5) and 212 (70).

(*R*)-3-(Tributylstannylmethyl)but-3-en-2-yl (*R*)-*O*-acetylmandelate 21. (70%) (Found: $M^+ - C_4H_9$, 495.1560. $C_{23}H_{35}O_4Sn$ requires *M*, 495.1556); $[a]_D$ −53.3 (*c* 1, CH_2Cl_2); ν_{max}/cm^{-1} 1748, 1633, 1455, 1373, 1233, 1210, 1056, 875, 745 and 695; δ_H 0.80–1.54 [32 H, m, $Sn(CH_2CH_2CH_2CH_3)_3$, 1′-H_2 and 1-H_3], 2.24 (3 H, s, $OCOCH_3$), 4.48 (2 H, s, vinylic H), 5.17 (1 H, q, *J* 6.5, 2-H), 5.96 (1 H, s, C*H*$OCOCH_3$), 7.40 (3 H, m, ArH) and 7.51 (2 H, m, ArH); δ_C 9.5, 13.7, 14.7, 19.3, 27.3, 29.0, 74.3, 74.7, 77.2, 105.8, 127.8, 128.7, 129.2, 133.9, 148.3, 168.0 and 170.4; *m/z* (EI) 495 ($M^+ - 57$, 8%), 427 (10) and 179 (100).

(*R*)-3-(Tributylstannylmethyl)but-3-en-2-yl (*S*)-*O*-acetylmandelate 22. (70%) (Found: $M^+ - C_4H_9$, 495.1549. $C_{23}H_{35}O_4Sn$ requires *M*, 495.1556); $[a]_D$ +28.4 (*c* 2.7, CH_2Cl_2); ν_{max}/cm^{-1} 2120, 1748, 1632, 1453, 1372, 1231, 1178, 1048, 876 and 695; δ_H 0.85–1.99 [32 H, m, $Sn(CH_2CH_2CH_2CH_3)_3$, 1′-H_2 and 1-H_3], 2.22 (3 H, s, $OCOCH_3$), 4.67 and 4.82 (each 1 H, s, vinylic H), 5.22 (1 H, q, *J* 6.5, 2-H), 5.97 (1 H, s, C*H*$OCOCH_3$), 7.41 (3 H, m, ArH) and 7.51 (2 H, m, ArH); δ_C 9.6, 13.7, 24.7, 25.5, 29.0, 34.9, 55.8, 74.5, 74.6, 106.3, 127.6, 128.7, 129.1, 134.0, 148.3, 168.1 and 170.1; *m/z* (EI) 495 ($M^+ - 57$, 8%), 149 (90) and 49 (100).

(1*R*,4*R*)-3-Methylidene-1-phenyl-4-(*tert*-butyldimethylsilyloxy)pentyl (*R*)-*O*-acetylmandelate 27. Eluted using ether–light petroleum (2:8) (70%) (Found: $M^+ + NH_4$, 500.2843. $C_{28}H_{42}NO_5Si$ requires *M*, 500.2832); $[\alpha]_D$ −40.0 (*c* 0.2, CH_2Cl_2); ν_{max}/cm^{-1} 1755, 1253, 1231, 1116, 1085, 1058 and 836; δ_H −0.03 and −0.02 (each 3 H, s, CH_3Si), 0.85 [9 H, s, $SiC(CH_3)_3$], 1.14 (3 H, d, *J* 5, 5-H_3), 2.14 (3 H, s, $OCOCH_3$), 2.41 (1 H, dd, *J* 11.5, 4, 2-H), 2.65 (1 H, dd, *J* 11.5, 6.5, 2-H′), 4.12 (1 H, q, *J* 5, 4-H), 4.78 and 5.06 (each 1 H, s, vinylic H), 5.89 (1 H, dd, *J* 6.5, 4, 1-H), 5.95 (1 H, s, C*H*$OCOCH_3$), 6.94 (2 H, m, ArH), 7.14 (3 H, m, ArH) and 7.32 (5 H, m, ArH); *m/z* 500 ($M^+ + 18$, 12%) and 351 (60).

(1*R*,4*R*)-3-Methylidene-1-phenyl-4-(*tert*-butyldimethylsilyloxy)pentyl (*S*)-*O*-acetylmandelate 28. Eluted using ether–light petroleum (2:8) (76%) (Found: $M^+ + NH_4$, 500.2837. $C_{28}H_{42}NO_5Si$ requires *M*, 500.2832); $[\alpha]_D$ +97.9 (*c* 0.4, CH_2Cl_2); ν_{max}/cm^{-1} 1752, 1372, 1231, 1175, 1117, 1084, 1056, 909 and 697; δ_H −0.09 and −0.06 (each 3 H, s, CH_3Si), 0.82 [9 H, s, $SiC(CH_3)_3$], 1.02 (3 H, d, *J* 5, 5-H_3), 2.12 (3 H, s, $OCOCH_3$), 2.37 (1 H, dd, *J* 11, 4, 2-H), 2.52 (1 H, dd, *J* 11, 6.5, 2-H′), 4.01 (1 H, q, *J* 5, 4-H), 4.40 and 4.76 (each 1 H, s, vinylic H), 5.87 (1 H, dd, *J* 6.5, 4, 1-H), 5.93 (1 H, s, C*H*$OCOCH_3$) and 7.37 (10 H, m, ArH); *m/z* 500 ($M^+ + 18$, 14%), 351 (70) and 157 (100).

(1*S*,4*R*)-3-Methylidene-1-phenyl-4-(*tert*-butyldimethylsilyloxy)pentyl (*R*)-*O*-acetylmandelate 31. Eluted using ether–light petroleum (2:8) (70%) (Found: $M^+ + NH_4$, 500.2846. $C_{28}H_{42}NO_5Si$ requires *M*, 500.2832); $[\alpha]_D$ −180.0 (*c* 0.2, CH_2Cl_2); ν_{max}/cm^{-1} 1752, 1371, 1232, 1055, 979, 836, 776, 745 and 697; δ_H 0.00 and 0.03 (each 3 H, s, CH_3Si), 0.89 [9 H, s, $SiC(CH_3)_3$], 1.11 (3 H, d, *J* 6.5, 5-H_3), 2.19 (3 H, s, $OCOCH_3$), 2.53 (2 H, d, *J* 6.5, 2-H_2), 4.15 (1 H, q, *J* 6.5, 4-H), 4.40 and 4.73 (each 1 H, s, vinylic H), 5.97 (1 H, m, 1-H), 5.99 (1 H, s, C*H*$OCOCH_3$) and 7.44 (10 H, m, ArH); *m/z* 500 ($M^+ + 18$, 22%) and 351 (70).

(1*S*,4*R*)-3-Methylidene-1-phenyl-4-(*tert*-butyldimethylsilyloxy)pentyl (*S*)-*O*-acetylmandelate 32. Eluted using ether–light petroleum (2:8) (72%) (Found: $M^+ + NH_4$, 500.2844. $C_{28}H_{42}NO_5Si$ requires *M*, 500.2832); $[\alpha]_D$ −6.9 (*c* 0.3, CH_2Cl_2); ν_{max}/cm^{-1} 1750, 1371, 1231, 1175, 1083, 1056, 836, 776 and 697; δ_H 0.00 and 0.03 (each 3 H, s, CH_3Si), 0.87 [9 H, s, $SiC(CH_3)_3$], 1.20 (3 H, d, *J* 6.5, 5-H_3), 2.16 (3 H, s, $OCOCH_3$), 2.48 (2 H, m, 2-H_2), 4.23 (1 H, q, *J* 6.5, 4-H), 4.78 and 5.06 (each 1 H, s, vinylic H), 5.91 (1 H, dd, *J* 8, 5.5, 1-H), 5.97 (1 H, s, C*H*$OCOCH_3$), 6.97 (2 H, m, ArH), 7.15 (3 H, m, ArH) and 7.32 (5 H, m, ArH); *m/z* 500 ($M^+ + 18$, 22%) and 351 (96).

(2*R*,5*S*)-3-Methylidene-5-phenyl-5-(*tert*-butyldimethylsilyloxy)pentan-2-yl (*R*)-*O*-acetylmandelate 34. Eluted using ether–light petroleum (2:8) (70%) (Found: $M^+ + NH_4$, 500.2841. $C_{28}H_{42}NO_5Si$ requires *M*, 500.2832); δ_H −0.31 and −0.12 (each 3 H, s, CH_3Si), 0.79 [9 H, s, $SiC(CH_3)_3$], 1.32 (3 H, d, *J* 6.5, 1-H_3), 1.96 (1 H, dd, *J* 14, 4.5, 4-H), 2.17 (3 H, s, $OCOCH_3$), 2.18 (1 H, dd, *J* 14, 7.5, 4-H′), 4.56 (1 H, dd, *J* 8.5, 4.5, 5-H), 4.72 and 4.84 (each 1 H, s, vinylic H), 5.34 (1 H, q, *J* 6.5, 2-H), 5.87 (1 H, s, C*H*$OCOCH_3$), 7.08 (2 H, m, ArH), 7.2 (3 H, m, ArH), 7.28 (3 H, m, ArH) and 7.43 (2 H, m, ArH); *m/z* 500 ($M^+ + 18$, 5%), 368 (10) and 157 (100).

(2*R*,5*S*)-3-Methylidene-5-phenyl-5-(*tert*-butyldimethylsilyloxy)pentan-2-yl (*S*)-*O*-acetylmandelate 35. Eluted using ether–light petroleum (2:8) (70%) $[\alpha]_D$ +21.0 (*c* 0.8, CH_2Cl_2); ν_{max}/cm^{-1} 1746, 1454, 1372, 1232, 1178, 1084, 1068, 836, 777 and 699; δ_H −0.25 and −0.05 (each 3 H, s, CH_3Si), 0.82 [9 H, s, $SiC(CH_3)_3$], 1.16 (3 H, d, *J* 6.5, 1-H_3), 2.18 (3 H, s, $OCOCH_3$), 2.31 (1 H, dd, *J* 14.5, 4.5, 4-H), 2.35 (1 H, dd, *J* 14.5, 8, 4-H′), 4.74 (1 H, dd, *J* 8, 4.5, 5-H), 4.91 and 5.10 (each 1 H, s, vinylic H), 5.40 (1 H, q, *J* 6.5, 2-H), 5.88 (1 H, s, C*H*$OCOCH_3$), 7.24 (5 H, m, ArH), 7.35 (3 H, m, ArH) and 7.45 (2 H, m, ArH); *m/z* 500 ($M^+ + 18$, 10%), 368 (28) and 351 (100).

(1*R*,4*R*)-3-Methylidene-1-phenyl-4-(2-trimethylsilylethoxymethoxy)pentyl (*R*)-*O*-acetylmandelate 58. Eluted with ether–light petroleum (4:6) (85%) (Found: $M^+ + NH_4$, 516.2791. $C_{28}H_{42}NO_6Si$ requires *M*, 516.2781); $[\alpha]_D$ +36.0 (*c* 1.2, CH_2Cl_2); ν_{max}/cm^{-1} 1751, 1455, 1373, 1232, 1207, 1175, 1103, 1082, 1056, 1028, 920, 860, 836, 755 and 697; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.90 [2 H, m, C$H_2$$Si(CH_3)_3$], 1.19 (3 H, d, *J* 6.5, 5-H_3), 2.14 (3 H, s, $OCOCH_3$), 2.42 (1 H, dd, *J* 15.5, 5.5, 2-H), 2.61 (1 H, dd, *J* 15.5, 8.5, 2-H′), 3.49 and 3.67 [each 1 H, td, *J* 10, 7, OCH-*H*$CH_2Si(CH_3)_3$], 4.11 (1 H, q, *J* 6.5, 4-H), 4.51 and 4.55 (each 1 H, d, *J* 7, OC*H*HO), 4.92 and 5.09 (each 1 H, s, vinylic H), 5.92 (1 H, m, 1-H), 5.94 (1 H, s, C*H*$OCOCH_3$), 6.96 (2 H, m, ArH), 7.14 (3 H, m, ArH) and 7.33 (5 H, m, ArH); δ_C −1.4, 18.1, 20.1, 20.7, 37.4, 65.1, 74.4, 75.2, 76.2, 92.2, 114.6, 126.2, 127.9, 128.0, 128.2, 128.7, 129.1, 133.6, 139.5, 144.3, 167.8 and 170.2; *m/z* 516 ($M^+ + 18$, 40%) and 370 (10).

(1*R*,4*R*)-3-Methylidene-1-phenyl-4-(2-trimethylsilylethoxymethoxy)pentyl (*S*)-*O*-acetylmandelate 59. Eluted with ether–light petroleum (4:6) (85%) (Found: $M^+ + NH_4$, 516.2790. $C_{28}H_{42}NO_6Si$ requires *M*, 516.2781); $[\alpha]_D$ +132.9 (*c* 0.9, CH_2Cl_2); ν_{max}/cm^{-1} 1749, 1497, 1373, 1232, 1208, 1175, 1105, 1081, 1056, 1029, 860, 836, 754 and 697; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.88 [2 H, m, C$H_2$$Si(CH_3)_3$], 1.09 (3 H, d, *J* 6.5, 5-H_3), 2.13 (3 H, s, $OCOCH_3$), 2.35 (1 H, dd, *J* 15.5, 4.5, 2-H), 2.51 (1 H, dd, *J* 15.5, 9, 2-H′), 3.44 and 3.63 [each 1 H, td, *J* 10, 7, OCH-*H*$CH_2Si(CH_3)_3$], 3.97 (1 H, q, *J* 6.5, 4-H), 4.31 and 4.42 (each 1 H, d, *J* 7, OC*H*HO), 4.52 and 4.75 (each 1 H, s, vinylic H), 5.92 (1 H, m, 1-H), 5.93 (1 H, s, C*H*$OCOCH_3$), 7.31 (5 H, m, ArH), 7.35 (3 H, m, ArH) and 7.44 (2 H, m, ArH); δ_C −1.3, 18.2, 20.2, 20.8, 37.6, 65.1, 74.5, 74.8, 75.7, 92.0, 114.1, 126.2, 127.7, 128.0, 128.3, 128.6, 129.1, 133.7, 139.5, 143.8, 167.8 and 169.9; *m/z* 516 ($M^+ + 18$, 12%).

(1*S*,4*R*)-3-Methylidene-1-phenyl-4-(2-trimethylsilylethoxymethoxy)pentyl (*R*)-*O*-acetylmandelate 60. Eluted with ether–light petroleum (4:6) (90%) (Found: $M^+ + NH_4$, 516.2770. $C_{28}H_{42}NO_6Si$ requires *M*, 516.2781); $[\alpha]_D$ −48.1 (*c* 1.1, CH_2Cl_2); ν_{max}/cm^{-1} 1750, 1455, 1373, 1232, 1208, 1175, 1102, 1081, 1055, 1028, 920, 860, 836, 754 and 697; δ_H −0.02 [9 H, s, $Si(CH_3)_3$], 0.86 [2 H, m, C$H_2$$Si(CH_3)_3$], 1.09 (3 H, d, *J* 6.5, 5-H_3), 2.13 (3 H, s, $OCOCH_3$), 2.41 (1 H, dd, *J* 15.5, 10.5, 2-H), 2.48 (1 H, dd, *J* 15.5, 9.0, 2-H′), 3.42 and 3.62 [each 1 H, td, *J* 10, 7, OCH-*H*$CH_2Si(CH_3)_3$], 4.02 (1 H, q, *J* 6.5, 4-H), 4.29 and 4.39 (each 1 H, d, *J* 7, OC*H*HO), 4.52 and 4.73 (each 1 H, s, vinylic H), 5.92 (1 H, m, 1-H), 5.93 (1 H, s, C*H*$OCOCH_3$), 7.30 (5 H, m, ArH), 7.35 (3 H, m, ArH) and 7.43 (2 H, m, ArH); δ_C −1.3, 18.2, 19.9, 20.8, 37.7, 65.1, 74.5, 74.8, 75.6, 92.0, 114.5, 126.3, 127.7, 128.0, 128.3, 128.6, 129.1, 133.8, 139.6, 143.8, 167.9 and 169.9; *m/z* 516 ($M^+ + 18$, 12%).

(1*S*,4*R*)-3-Methylidene-1-phenyl-4-(2-trimethylsilylethoxymethoxy)pentyl (*S*)-*O*-acetylmandelate 61. Eluted with ether–light petroleum (4:6) (90%) (Found: $M^+ + NH_4$, 516.2782. $C_{28}H_{42}NO_6Si$ requires *M*, 516.2781); $[\alpha]_D$ +56.3 (*c* 1.4, CH_2Cl_2); ν_{max}/cm^{-1} 1750, 1455, 1372, 1232, 1207, 1175, 1102, 1081, 1056, 1027, 919, 860, 836, 755 and 697; δ_H −0.02 [9 H, s, $Si(CH_3)_3$], 0.90 [2 H, m, C$H_2$$Si(CH_3)_3$], 1.24 (3 H, d, *J* 6.5, 5-H_3), 2.14 (3 H, s, $OCOCH_3$), 2.46 (1 H, dd, *J* 15.5, 5, 2-H), 2.55 (1 H, dd, *J* 15.5, 9, 2-H′), 3.46 and 3.67 [each 1 H, td, *J* 9, 8, OCH-*H*$CH_2Si(CH_3)_3$], 4.17 (1 H, q, *J* 6.5, 4-H), 4.44 and 4.46 (each 1 H, d, *J* 7, OC*H*HO), 4.93 and 5.09 (1 H, s, vinylic H), 5.9 (1 H, m, 1-H), 5.95 (1 H, s, C*H*$OCOCH_3$), 6.96 (2 H, m, ArH), 7.13 (3 H, m, ArH) and 7.33 (5 H, m, ArH); δ_C −1.3, 18.2, 20.2, 20.8, 37.6, 65.1, 74.4, 74.9, 76.3, 92.0, 114.6, 126.0, 127.8, 128.0, 128.5, 129.0, 129.1, 133.4, 139.5, 144.3, 167.6 and 169.9; *m/z* 516 ($M^+ + 18$, 55%) and 237 (50).

Tin(IV) halide promoted reactions between allylstannanes and aldehydes

General procedure: preparation of 1-phenyl-3-methylidenepentane-1,4-diols 23 and 24. A cooled solution of tin(IV) chloride (367 mg, 1.41 mmol) in dichloromethane (1.41 cm^3) was added dropwise to a stirred solution of the racemic hydroxyalkylstannane **9** (530 mg, 1.41 mmol) in dichloromethane (14.1 cm^3) at −78 °C. After 5 min, a cooled solution of benzaldehyde

(1.41 mmol) in dichloromethane (0.4 cm^3) was added and the mixture stirred for 1 h at −78 °C. Saturated aqueous sodium hydrogen carbonate (15 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 light petroleum–ethyl acetate as eluent gave a mixture of the diols **23** and **24** (55%) which were separated by HPLC. The less polar product was identified as the (1*RS*,4*RS*)-diastereoisomer of the *title compound* **23**, a white solid, mp 66 °C (ethyl acetate–hexane) (Found: M^+, 192.1148. $C_{12}H_{16}O_2$ requires *M*, 192.1146); ν_{max}/cm^{-1} 3341, 1649, 1492, 1455, 1103, 1041, 915, 893, 766 and 702; δ_H 1.28 (3 H, d, *J* 6.5, 5-H_3), 2.41 (1 H, dd, *J* 14.5, 3, 2-H), 2.56 (1 H, dd, *J* 14.5, 10, 2-H′), 3.04 and 3.37 (each 1 H, br s, OH), 4.37 (1 H, q, *J* 6.5, 4-H), 4.79 (1 H, dd, *J* 9.5, 3, 1-H), 4.99 and 5.17 (each 1 H, s, vinylic H) and 7.35 (5 H, m, ArH); δ_C 22.4, 41.8, 70.9, 74.6, 113.8, 125.8, 127.5, 128.4, 144.4 and 149.6; *m/z* 210 (M^+ + 18, 20%) and 192 (M^+, 100). The more polar product was identified as the (1*RS*,4*SR*)-diastereoisomer of the *title compound* **24**, a white solid, mp 47 °C (hexane) (Found: M^+, 192.1149. $C_{12}H_{16}O_2$ requires *M*, 192.1146); ν_{max}/cm^{-1} 3344, 1646, 1494, 1453, 1040, 911, 756 and 700; δ_H 1.33 (3 H, d, *J* 6.5, 5-H_3), 2.43 (1 H, dd, *J* 14.5, 9, 2-H), 2.63 (1 H, dd, *J* 14.5, 3.5, 2-H′), 2.65 and 3.65 (each 1 H, br s, OH), 4.28 (1 H, q, *J* 6.5, 4-H), 4.91 (2 H, m, vinylic H and 1-H), 5.14 (1 H, s, vinylic H) and 7.40 (5 H, m, ArH); δ_C 21.8, 42.9, 70.7, 73.7, 113.6, 125.8, 127.4, 128.3, 144.2 and 148.8; *m/z* 210 ($M^+ + NH_4$, 8%), 192 (M^+, 100) and 175 (42).

Following the above procedure, the stannane (*R*)-**9** gave the (1*R*,4*R*)-diol **23** (Found: M^+, 192.1148. $C_{12}H_{16}O_2$ requires *M*, 192.1146); $[\alpha]_D$ +68.8 (*c* 0.2, CH_2Cl_2) and the (1*S*,4*R*)-diol **24** (Found: M^+, 192.1149. $C_{12}H_{16}O_2$ requires *M*, 192.1146); $[\alpha]_D$ −52.0 (*c* 0.2, CH_2Cl_2).

The following 1-substituted-3-methylidenepentane-1,4-diols were prepared using this procedure:

(1*RS*,4*RS*)- and (1*SR*,4*RS*)-3-Methylidene-1-(*p*-nitrophenyl)-pentane-1,4-diols 36 and 38. The (1*RS*,4*RS*)-diol **36** (38%) was a yellow solid, mp 118–120 °C (CH_2Cl_2–hexane) (Found: $M^+ + NH_4$, 255.1341. $C_{12}H_{19}N_2O_4$ requires *M*, 255.1345); ν_{max}/cm^{-1} 3341, 1604, 1519, 1347, 1106, 1071, 1038, 1015, 913 and 699; δ_H 1.39 (3 H, d, *J* 6.5, 5-H_3), 2.39 (1 H, br s, OH), 2.54 (2 H, d, *J* 6.5, 2-H_2), 4.04 (1 H, br s, OH), 4.49 (1 H, q, *J* 6.5, 4-H), 4.94 (1 H, t, *J* 6.5, 1-H), 5.04 and 5.24 (each 1 H, s, vinylic H), 7.62 (2 H, d, *J* 9, ArH) and 8.25 (2 H, d, *J* 9, ArH); *m/z* 255 (M^+ + 18, 47%), 237 (M^+, 10) and 190 (100). The (1*SR*,4*RS*)-diol **38** was an oil (53 mg, 22%) (Found: $M^+ + NH_4$, 255.1355. $C_{12}H_{19}N_2O_4$ requires *M*, 255.1345); ν_{max}/cm^{-1} 3343, 1604, 1519, 1347, 1106, 1070, 1037, 1013, 913 and 854; δ_H 1.43 (3 H, d, *J* 6.5, 5-H_3), 2.11 (1 H, br s, OH), 2.44 (1 H, dd, *J* 14.5, 8.5, 2-H), 2.80 (1 H, dd, *J* 14.5, 3.5, 2-H′), 3.70 (1 H, br s, OH), 4.41 (1 H, q, *J* 6.5, 4-H), 4.87 (1 H, s, vinylic H), 5.08 (1 H, m, 1-H), 5.19 (1 H, s, vinylic H), 7.59 (2 H, d, *J* 9, ArH) and 8.24 (2 H, d, *J* 9, ArH); *m/z* 255 (M^+ + 18, 100%) and 237 (M^+, 10).

(1*RS*,4*RS*)- and (1*SR*,4*RS*)-3-Methylidene-1-(2-naphthyl)-pentane-1,4-diols 37 and 39. The (1*RS*,4*RS*)-diol **37** was an oil (32%) (Found: M^+, 242.1302. $C_{16}H_{18}O_2$ requires *M*, 242.1307); ν_{max}/cm^{-1} 3300, 3055, 1645, 1602, 1509, 1451, 1434, 1368, 1320, 1270, 1122, 1106, 1069, 1038, 904, 859, 821 and 748; δ_H 1.39 (3 H, d, *J* 6.5, 5-H_3), 2.58 (1 H, dd, *J* 14.5, 3.5, 2-H), 2.70 (1 H, dd, *J* 14.5, 9.5, 2-H′), 2.81 and 3.3 (each 1 H, br s, OH), 4.46 (1 H, q, *J* 6.5, 4-H), 5.01 (1 H, dd, *J* 9.5, 3.5, 1-H), 5.08 and 5.24 (each 1 H, s, vinylic H), 7.55 (3 H, m, ArH) and 7.89 (4 H, m, ArH); *m/z* 260 ($M^+ + NH_4$, 8%), 243 (M^+ + 1, 18) and 242 (M^+, 100). The (1*SR*,4*RS*)-diol **39** was an oil (20%) (Found: M^+, 242.1300. $C_{16}H_{18}O_2$ requires *M*, 242.1307); ν_{max}/cm^{-1} 3307, 1644, 1602, 1509, 1453, 1435, 1368, 1270, 1121, 1102, 1071, 1039, 902, 859, 820 and 748; δ_H 1.42 (3 H, d, *J* 6.5, 5-H_3), 2.29 (1 H, br s, OH), 2.58 (1 H, dd, *J* 14.5, 9, 2-H), 2.82 (1 H, dd, *J* 14.5, 4, 2-H′), 3.02 (1 H, br s, OH), 4.39 (1 H, q, *J* 6.5, 4-H), 4.98 (1 H, s, vinylic H), 5.15 (1 H, dd, *J* 9, 3.5, 1-H), 5.21 (1 H, s, vinylic H), 7.53 (3 H, m, ArH) and 7.87 (4 H, m, ArH); *m/z* 260 (M^+ + 18, 10%), 243 (M^+ + 1, 20) and 242 (M^+, 100).

The following 1-substituted-4-alkoxy-3-methylidenepentanols were prepared similarly. In some cases the (1*RS*,4*SR*)- and (1*SR*,4*RS*)-diastereoisomers could not be separated. The ^1H NMR peaks are given for the major isomer only (see Table 1).

(1*RS*,4*SR*)-3-Methylidene-1-phenyl-4-(2-trimethylsilyl-ethoxymethoxy)pentan-1-ol 47. Light petroleum–ethyl acetate (10:1) as eluent (Found: M^+ + H, 323.2051. $C_{18}H_{31}O_3Si$ requires *M*, 323.2043); ν_{max}/cm^{-1} 3443, 1647, 1494, 1453, 1375, 1249, 1105, 1024, 861, 836, 756 and 700; δ_H 0.06 [9 H, s, $Si(CH_3)_3$], 0.97 [2 H, m, CH_2Si$(CH_3)_3$], 1.36 (3 H, d, *J* 6.5, 5-H_3), 2.47 (1 H, dd, *J* 15, 8, 2-H), 2.64 (1 H, dd, *J* 15, 4, 2-H′), 3.00 (1 H, br s, OH), 3.70 [2 H, m, OCH_2CH_2Si$(CH_3)_3$], 4.27 (1 H, q, *J* 6.5, 4-H), 4.66 (2 H, s, OC*H*HO), 4.94 (1 H, dd, *J* 7, 4, 1-H), 5.04 and 5.19 (each 1 H, m, vinylic H) and 7.40 (5 H, m, aromatic H); δ_C −1.4, 18.1, 20.0, 42.1, 65.4, 72.8, 75.8, 92.6, 115.1, 125.8, 127.3, 128.3, 144.3 and 146.4; *m/z* 323 (M^+ + H, 2%), 277 (12) and 247 (40). The (1*S*,4*R*)-enantiomer **47** (Found: $M^+ + NH_4$, 340.2298. $C_{14}H_{20}O_3$ requires *M*, 340.2308) had $[\alpha]_D$ −2.0 (*c* 0.5, CH_2Cl_2).

(1*RS*,4*SR*)-3-Methylidene-1-phenyl-4-(methoxymethoxy)-pentan-1-ol 48. Light petroleum–ethyl acetate (5:1) as eluent (Found: M^+ + H, 237.1489. $C_{14}H_{21}O_3$ requires *M*, 237.1491); ν_{max}/cm^{-1} 3449, 1648, 1494, 1453, 1374, 1217, 1157, 1037, 917, 757 and 702; δ_H 1.37 (3 H, d, *J* 6.5, 5-H_3), 2.45 (1 H, dd, *J* 14.5, 9, 2-H), 2.63 (1 H, dd, *J* 14.5, 4, 2-H′), 2.93 (1 H, br s, OH), 3.41 (3 H, s, OCH_3), 4.26 (1 H, q, *J* 6.5, 4-H), 4.61 and 4.64 (each 1 H, d, *J* 7, OC*H*HO), 4.94 (1 H, dd, *J* 9, 4, 1-H), 5.08 and 5.22 (each 1 H, s, vinylic H) and 7.40 (5 H, m, ArH); δ_C 19.46, 41.96, 55.53, 72.75, 75.83, 94.28, 115.18, 125.82, 127.38, 128.36, 144.33 and 146.24; *m/z* 254 (M^+ + 18, 10%), 237 (M^+ + 1, 5), 219 (100) and 192 (42).

(1*RS*,4*SR*)-4-Benzyloxy-3-methylidene-1-phenylpentan-1-ol 49. Light petroleum–ethyl acetate (10:1) as eluent (Found: M^+ + H, 283.1693. $C_{19}H_{23}O_2$ requires *M*, 283.1698); ν_{max}/cm^{-1} 3416, 3063, 3030, 1647, 1495, 1453, 1091, 912, 754 and 700; δ_H 1.41 (3 H, d, *J* 6.5, 5-H_3), 2.50 (1 H, dd, *J* 15, 9, 2-H), 2.69 (1 H, dd, *J* 15, 4, 2-H′), 2.85 (1 H, br s, OH), 4.05 (1 H, q, *J* 6.5, 4-H), 4.43 and 4.54 (each 1 H, d, *J* 12, PhC*H*HO), 4.98 (1 H, dd, *J* 8.5, 4, 1-H), 5.10 and 5.21 (each 1 H, s, vinylic H) and 7.40 (10 H, m, ArH); δ_C 19.7, 41.6, 70.3, 72.7, 78.5, 115.3, 125.9, 127.4, 127.6, 127.7, 128.4, 128.5, 138.4, 144.4 and 146.2; *m/z* 300 (M^+ + 18, 5%), 283 (M^+ + 1, 4) and 265 (100).

(3*RS*,6*SR*)-5-Methylidene-6-(2-trimethylsilylethoxy-methoxy)hept-1-en-3-ol 50. Light petroleum–ethyl acetate (5:1) as eluent (Found: M^+ + H, 273.1883. $C_{14}H_{29}O_3Si$ requires *M*, 273.1886); ν_{max}/cm^{-1} 3438, 1645, 1422, 1375, 1249, 1103, 1025, 920, 859 and 835; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.88 [2 H, m, CH_2Si$(CH_3)_3$], 1.25 (3 H, d, *J* 6.5, 7-H_3), 2.15 (1 H, dd, *J* 14.5, 8, 4-H), 2.39 (1 H, dd, *J* 14.5, 4.5, 4-H′), 2.87 (1 H, d, *J* 4, OH), 3.52 and 3.62 [each 1 H, m, OC*H*HCH_2Si$(CH_3)_3$], 4.17 (1 H, q, *J* 6.5, 6-H), 4.26 (1 H, m, 3-H), 4.58 and 4.60 (each 1 H, d, *J* 6.5, OC*H*HO), 4.96 (1 H, s, 1′-H), 5.04 (1 H, d, *J* 11, 1-H), 5.09 (1 H, s, 1′-H′), 5.21 (1 H, d, *J* 17.5, 1-H′) and 5.82 (1 H, ddd, *J* 17.5, 11, 6, 2-H); δ_C −1.4, 18.1, 19.9, 39.8, 65.3, 71.1, 75.5, 92.4, 114.3, 115.3, 140.6 and 145.9; *m/z* 290 (M^+ + 18, 8%) and 273 (M^+ + 1, 10).

(3*RS*,6*RS*)- and (3*RS*,6*SR*)-2-Methyl-5-methylidene-6-(2-trimethylsilylethoxymethoxy)heptan-3-ols 44 and 51. In this case, chromatography [light petroleum–ethyl acetate (10:1)] separated the (3*RS*,6*RS*)- and (3*RS*,6*SR*)-diastereoisomers. The (3*RS*,6*RS*)-isomer of the *title compound* **44** was an oil (Found: M^+ + H, 289.2195. $C_{15}H_{33}O_3Si$ requires *M*, 289.2199); ν_{max}/cm^{-1} 3463, 1644, 1467, 1376, 1249, 1103, 1024, 860 and 836; δ_H −0.02 [9 H, s, $Si(CH_3)_3$], 0.82 [2 H, m, CH_2Si$(CH_3)_3$], 0.91 and

0.93 (each 3 H, d, *J* 6, CH_3), 1.25 (3 H, d, *J* 6.5, 7-H_3), 1.67 (1 H, m, 2-H), 2.07 (1 H, dd, *J* 14.5, 10, 4-H), 2.21 (1 H, d, *J* 14.5, 4-H′), 2.85 (1 H, d, *J* 2.5, OH), 3.42 (1 H, m, 3-H), 3.55 and 3.64 [each 1 H, m, OC*H*HCH_2Si$(CH_3)_3$], 4.18 (1 H, q, *J* 6.5, 6-H), 4.63 (2 H, m, OCH_2O) and 4.96 and 5.09 (each 1 H, s, vinylic H); δ_C −1.4, 17.7, 18.0, 18.7, 20.4, 33.7, 36.7, 65.4, 75.2, 75.5, 92.4, 114.5 and 147.8; *m/z* 306 (M^+ + 18, 8%), 289 (M^+ + 1, 10) and 243 (32). The (3*RS*,6*SR*)-isomer of the *title compound* **51** was also an oil (Found: M^+ + H, 289.2201. $C_{15}H_{33}O_3Si$ requires *M*, 289.2199); ν_{max}/cm^{-1} 3474, 1645, 1467, 1375, 1249, 1103, 1027, 860 and 836; δ_H −0.02 [9 H, s, Si$(CH_3)_3$], 0.91 [8 H, m, CH$(CH_3)_2$ and CH_2Si$(CH_3)_3$], 1.26 (3 H, d, *J* 6.5, 7-H_3), 1.64 (1 H, m, 2-H), 2.00 (1 H, dd, *J* 14.5, 10, 4-H), 2.32 (1 H, d, *J* 14.5, 4-H′), 2.38 (1 H, d, *J* 3, OH), 3.49 (1 H, m, 3-H), 3.54 and 3.63 [each 1 H, m, OCH*H*CH_2Si$(CH_3)_3$], 4.18 (1 H, q, *J* 6.5, 6-H), 4.63 (2 H, m, OCH_2O) and 4.97 and 5.10 (each 1 H, s, vinylic H); δ_C −1.4, 17.5, 18.1, 18.8, 20.0, 33.6, 37.1, 65.4, 74.8, 75.8, 92.6, 114.3 and 147.5; *m/z* 306 (M^+ + 18, 6%) and 289 (M^+ + 1, 10).

(1*RS*,4*SR*)-3-Methylidene-1-phenyl-4-(2-trimethylsilylethoxymethoxy)-5-methylhexan-1-ol 52. Light petroleum–ethyl acetate (10:1) as eluent (Found: M^+ + H, 351.2363. $C_{20}H_{35}O_3Si$ requires *M*, 351.2355); ν_{max}/cm^{-1} 3443, 1644, 1493, 1454, 1384, 1250, 1132, 1026, 861, 836, 757 and 700; δ_H 0.06 [9 H, s, Si$(CH_3)_3$], 0.88 and 1.05 (each 3 H, d, *J* 6.5, CH_3), 0.98 [2 H, m, CH_2Si$(CH_3)_3$], 1.90 (1 H, m, 5-H), 2.41 (1 H, dd, *J* 15, 9, 2-H), 2.56 (1 H, dd, *J* 15, 4, 2-H′), 3.10 (1 H, br s, OH), 3.57 [1 H, m, OCH*H*CH_2Si$(CH_3)_3$], 3.67 (1 H, d, *J* 8.5, 4-H), 3.77 [1 H, m, OCH*H*CH_2Si$(CH_3)_3$], 4.55 and 4.61 (each 1 H, d, *J* 7, OC*H*HO), 4.95 (1 H, dd, *J* 8.5, 4, 1-H), 5.14 and 5.15 (each 1 H, s, vinylic H) and 7.40 (5 H, m, ArH); δ_C −1.4, 18.1, 19.0, 19.3, 30.8, 42.0, 65.5, 72.9, 86.9, 92.7, 117.3, 125.8, 127.3, 128.4, 144.1 and 144.4; *m/z* 368 (M^+ + 18, 10%), 351 (M^+ + 1, 12), 305 (100), 275 (70) and 220 (67).

(1*RS*,4*SR*)-4-(Methoxymethoxy)-5-methyl-3-methylidene-1-phenylhexan-1-ol 53. Light petroleum–ethyl acetate (8:1) as eluent (Found: M^+ + H, 265.1809. $C_{16}H_{25}O_3$ requires *M*, 265.1804); ν_{max}/cm^{-1} 3443, 1644, 1493, 1453, 1385, 1157, 1092, 1033, 915, 757 and 701; δ_H 0.88 and 1.06 (each 3 H, d, *J* 6.5, CH_3), 1.90 (1 H, m, 5-H), 2.42 (1 H, dd, *J* 14.5, 8, 2-H), 2.55 (1 H, dd, *J* 14.5, 4.5, 2-H′), 2.97 (1 H, br s, OH), 3.41 (3 H, s, OCH_3), 3.64 (1 H, d, *J* 8.5, 4-H), 4.45 and 4.58 (each 1 H, d, *J* 7, OC*H*HO), 4.95 (1 H, dd, *J* 8, 4.5, 1-H), 5.13 and 5.16 (each 1 H, s, vinylic H) and 7.40 (5 H, m, ArH); δ_C 19.1, 19.3, 30.6, 41.7, 55.8, 72.8, 86.9, 94.4, 117.5, 125.9, 127.4, 128.4, 143.8 and 144.4; *m/z* 282 (M^+ + 18, 8%), 265 (M^+ + 1, 7), 247 (100) and 220 (70).

Ethyl (2*S*,5*R*)-2-hydroxy-4-methylidene-5-(2-trimethylsilylethoxymethoxy)hexanoate 57. (71%) (Found: $M^+ + NH_4$, 336.2199. $C_{15}H_{34}NO_5Si$ requires *M*, 336.2206); $[\alpha]_D$ +35.2 (*c* 3, $CHCl_3$); ν_{max}/cm^{-1} 3448, 1738, 1372, 1249, 1197, 1102, 1025, 860 and 836; δ_H 0.05 [9 H, s, Si$(CH_3)_3$], 0.96 [2 H, m, CH_2Si(CH_3)], 1.32 (6 H, m, 6-H_3 and CH_3CH$_2$), 2.48 (1 H, dd, *J* 15, 7, 3-H), 2.6 (1 H, dd, *J* 15, 4, 3-H′), 3.39 (1 H, d, *J* 5.5, OH), 3.53–3.82 [2 H, m, OCH_2CH_2Si$(CH_3)_3$], 4.20–4.43 (4 H, m, 2-H, CH_3CH_2 and 5-H), 4.67 and 4.68 (each 1 H, d, *J* 7, OCH*H*O) and 5.09 and 5.19 (each 1 H, s, vinylic H); *m/z* 336 (M^+ + 18, 14%) and 243 (100).

Deprotection of 2-trimethylsilylethoxymethyl ethers

Magnesium bromide–diethyl ether (359 mg, 1.39 mmol), potassium carbonate (169 mg, 1.22 mmol) and butanethiol (75 μl, 0.70 mmol) were added to a stirred solution of the SEM ether **40** (28 mg, 0.087 mmol) in ether (3 cm^3) at room temperature. After 16 h the reaction mixture was partitioned between diethyl ether and water. The aqueous phase was extracted with ether (3 × 10 cm^3) and the combined organic phases were washed with brine (1 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with diethyl ether–light petroleum (8:2) as eluent gave the diol **23** (12.5 mg, 75%).

Following the above procedure, the SEM ether **47** gave the diol **24** (12.5 mg, 75%).

(*R*)-1-Phenylpropane-1,3-diol 25

Ozonolysed air was bubbled through a solution of the diol **23** (20 mg, 0.10 mmol) in methanol (3 cm^3) at −78 °C for 30 min. Air was then blown through the solution for 10 min, and dimethyl sulfide (65 mg, 1.0 mmol) was added. The reaction was allowed to warm to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in methanol (3 cm^3), sodium borohydride (15 mg, 0.4 mmol) was added at 0 °C and the mixture was stirred for 2 h at room temperature. Aqueous hydrogen chloride (1 M; 1 cm^3) was added at 0 °C, the layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 3 cm^3). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Chromatography of the residue eluting with light petroleum–ethyl acetate (9.8:0.2), gave (1*R*,3*RS*,4*R*)-1-phenylpentane-1,3,4-triol (15.3 mg, 75%) (Found: M^+, 196.1099. $C_{11}H_{16}O_3$ requires *M*, 196.1099); $[\alpha]_D$ +92.0 (*c* 0.4, CH_2Cl_2); ν_{max}/cm^{-1} 3383, 3063, 3030, 1453, 1433, 1377, 1058, 760 and 701; δ_H 1.15 (3 H, d, *J* 7, 5-H_3), 1.65 (1 H, br s, OH), 1.71–2.04 (2 H, m, 2-H_2), 2.30 and 3.19 (each 1 H, br s, OH), 3.57–3.93 (2 H, m, 3-H and 4-H), 4.96 (0.6 H, dd, *J* 10, 4, 1-H), 5.07 (0.4 H, t, *J* 6, 1-H) and 7.32 (5 H, m, ArH); δ_C 17.1, 39.3, 70.2, 74.4, 75.3, 125.7, 127.6, 128.5 and 144.2; *m/z* 197 (M^+ + 1, 12%) and 196 (M^+, 100).

Saturated aqueous sodium hydrogen carbonate (15 μl) was added to a solution of the triol (30 mg, 0.15 mmol), maintaining the temperature below 25 °C. Solid sodium periodate (66 mg, 0.30 mmol) was added over a 10 min period with vigorous stirring and the reaction was allowed to proceed for 2 h while the temperature was maintained below 25 °C. The solid was removed by filtration, the filtrate dried ($MgSO_4$) and dichloromethane removed under reduced pressure. The crude product was dissolved in methanol (5 cm^3), sodium borohydride (46 mg, 1.22 mmol) was added at 0 °C and the mixture was stirred for 2 h at room temperature. Aqueous hydrogen chloride (1 M; 1 cm^3) was added at 0 °C, the layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 3 cm^3). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Chromatography of the residue, eluting with ether–light petroleum (6:4), gave (*R*)-1-phenylpropane-1,3-diol **25** (15.3 mg, 75%) (Found: M^+, 152.0841. $C_9H_{12}O_2$ requires *M*, 152.0837); $[\alpha]_D$ +52.9 (*c* 1.2, $CHCl_3$) [lit.,[12] +69.0 (*c* 1.51, $CHCl_3$)].

(1*R*,4*R*)-3-Methylidene-1-phenyl-4-(*tert*-butyldimethylsilyloxy)-pentan-1-ol 26 and (2*R*,5*R*)-3-methylidene-5-phenyl-5-(*tert*-butyldimethylsilyloxy)pentan-2-ol 29

tert-Butyldimethylsilyl trifluoromethanesulfonate (37 mg, 0.14 mmol) was added dropwise to a stirred solution of (1*R*,4*R*)-3-methylidene-1-phenylpentane-1,4-diol **23** (25 mg, 0.13 mmol) and 2,6-lutidine (28 mg, 0.26 mmol) in dichloromethane (1 cm^3) at 0 °C under argon. The reaction was allowed to warm to room temperature and was stirred for 3 h. Water (1 cm^3) and dichloromethane (5 cm^3) were added. The organic extract was washed with brine (1 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with light petroleum–ether (8:2) gave the *title compound* **26** as a colourless oil (21.5 mg, 54%) (Found: M^+ − OH, 289.1985. $C_{18}H_{29}OSi$ requires *M*, 289.1988); $[\alpha]_D$ +11.1 (*c* 0.5, CH_2Cl_2); ν_{max}/cm^{-1} 3450, 1643, 1471, 1255, 1197, 1116, 1087, 975, 836, 777 and 700; δ_H 0.17 and 0.18 (each 3 H, s, CH_3Si), 0.97 [9 H, s, SiC$(CH_3)_3$], 1.36 (3 H, d, *J* 6.5, 5-H_3), 2.49 (1 H, dd, *J* 14.5, 3, 2-H), 2.57 (1 H, dd, *J* 14.5, 9.5, 2-H′), 4.14 (1 H, s, OH), 4.44 (1 H, q, *J* 6.5, 4-H), 4.76 (1 H, br d, *J* 9.5, 1-H), 5.00 and 5.15 (each 1 H, s, vinylic H) and 7.30–7.48 (5 H, m, ArH); δ_C −4.7,

18.2, 23.1, 25.9, 43.0, 72.9, 74.2, 114.4, 125.8, 127.3, 128.3, 144.7 and 149.8; *m/z* 289 ($M^+ - 17$, 12%) and 157 (100). A second fraction was isolated and identified as the *title compound* **29** (4.5 mg, 12%) (Found: M^+, 306.2019. $C_{18}H_{30}O_2Si$ requires *M*, 306.2015); $[\alpha]_D$ +86.8 (*c* 0.4, CH_2Cl_2); ν_{max}/cm^{-1} 3432, 1644, 1471, 1454, 1363, 1256, 1085, 1065, 1026, 939, 855, 836, 777 and 700; δ_H −0.20 and −0.04 (each 3 H, s, CH_3Si), 0.84 [9 H, s, $SiC(CH_3)_3$], 1.20 (3 H, d, *J* 6.5, 1-H_3), 2.31 (1 H, dd, *J* 14, 4, 4-H), 2.59 (1 H, dd, *J* 14, 9, 4-H′), 3.37 (1 H, d, *J* 2, OH), 4.27 (1 H, q, *J* 6.5, 2-H), 4.74 (1 H, dd, *J* 9, 4, 5-H), 4.86 and 5.06 (each 1 H, s, vinylic H) and 7.30 (5 H, m, ArH); *m/z* 306 (M^+, 10%) and 175 (100).

(1*S*,4*R*)-3-Methylidene-1-phenyl-4-(*tert*-butyldimethylsilyloxy)-pentan-1-ol 30 and (2*R*,5*S*)-3-methylidene-5-phenyl-5-(*tert*-butyldimethylsilyloxy)pentan-2-ol 33

Following the above procedure, the (1*S*,4*R*)-diol **24** gave the title compound **30** (10 mg, 25%) (Found: M^+, 306.2011. $C_{18}H_{30}O_2Si$ requires *M*, 306.2015); $[\alpha]_D$ −58.0 (*c* 1.0, CH_2Cl_2); ν_{max}/cm^{-1} 3432, 1645, 1471, 1463, 1453, 1370, 1254, 1114, 1087, 1055, 907, 836 and 776; δ_H 0.07 and 0.8 (each 3 H, s, CH_3Si), 0.90 [9 H, s, $SiC(CH_3)_3$], 1.28 (3 H, d, *J* 5, 5-H_3), 2.38 (1 H, dd, *J* 11, 7, 2-H), 2.62 (1 H, dd, *J* 11, 2.5, 2-H′), 3.01 (1 H, d, *J* 2.5, OH), 4.33 (1 H, q, *J* 5, 4-H), 4.83 and 5.08 (each 1 H, s, vinylic H), 4.92 (1 H, m, 1-H) and 7.36 (5 H, m, ArH); *m/z* 306 (M^+, 4%), 305 ($M^+ - H$, 5), 289 (20) and 157 (100). This was followed by the *title compound* **33** (10 mg, 25%) (Found: M^+, 306.2018. $C_{18}H_{30}O_2Si$ requires *M*, 306.2015); $[\alpha]_D$ −115.5 (*c* 0.1, CH_2Cl_2); ν_{max}/cm^{-1} 3454, 1650, 1493, 1472, 1463, 1363, 1256, 1087, 1068, 940, 836, 770 and 770; δ_H −0.18 and −0.02 (each 3 H, s, CH_3Si), 0.85 [9 H, s, $SiC(CH_3)_3$], 1.24 (3 H, d, *J* 5, 1-H_3), 2.39 (1 H, dd, *J* 10.5, 5.5, 4-H), 2.54 (1 H, dd, *J* 10.5, 3.5, 4-H′), 2.70 (1 H, d, *J* 3, OH), 4.18 (1 H, m, 2-H), 4.67 and 5.03 (each 1 H, s, vinylic H), 4.84 (1 H, dd, *J* 5.5, 3.5, 5-H) and 7.24 (5 H, m, ArH); *m/z* 306 (M^+, 6%) and 192 (100).

(2*RS*,5*RS*)-3-Methylidene-5-phenyl-5-(2-trimethylsilylethoxymethoxy)pentan-2-ol 54

N,*N*-Diisopropylethylamine (267 mg, 2.07 mmol) was added to the diol **23** (132 mg, 0.687 mmol) in dichloromethane (4 cm^3). The solution was cooled to 0 °C, 2-trimethylsilylethoxymethyl chloride (122 mg, 0.734 mmol) was added, and the reaction mixture stirred at room temperature for 12 h. The reaction was diluted with dichloromethane (5 cm^3) and washed with water (1 cm^3) and brine (1 cm^3). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using diethyl ether–light petroleum (3:7) as eluent gave the SEM ether **40** (33 mg, 15%) followed by the *title compound* **54** (33 mg, 15%) (Found: $M^+ + NH_4$, 340.2304. $C_{18}H_{34}NO_3Si$ requires *M*, 340.2308); ν_{max}/cm^{-1} 3475, 1454, 1249, 1103, 1058, 1021, 916, 860, 836, 756 and 700; δ_H 0.04 [9 H, s, $Si(CH_3)_3$], 0.88 [2 H, m, $CH_2Si(CH_3)_3$], 1.29 (3 H, d, *J* 6.5, 1-H_3), 2.40 (1 H, dd, *J* 14.5, 4, 4-H), 2.71 (1 H, dd, *J* 14.5, 10, 4-H′), 3.33 (1 H, d, *J* 2.5, OH), 3.45 and 3.77 [each 1 H, m, $OCHHCH_2Si(CH_3)_3$], 4.36 (1 H, m, 2-H), 4.54 and 4.63 (each 1 H, d, *J* 7, OC*H*HO), 4.77 (1 H, dd, *J* 10, 4, 5-H), 5.01 and 5.15 (each 1 H, s, vinylic H) and 7.36 (5 H, m, ArH); *m/z* 340 ($M^+ + 18$, 14%), 323 ($M^+ + 1$, 8) and 192 (100). Further elution gave recovered diol **23** (24 mg, 18%).

(2*RS*,5*SR*)-3-Methylidene-5-phenyl-5-(2-trimethylsilylethoxymethoxy)pentan-2-ol 55

Chromatography of the products obtained by treatment of the (1*RS*,4*SR*)-diol **24** with 2-trimethylsilylethoxymethyl chloride following the above procedure gave the SEM ether **47** (35 mg, 16%) followed by the *title compound* **55** (33 mg, 15%) (Found: $M^+ + NH_4$, 340.2299. $C_{18}H_{34}NO_3Si$ requires *M*, 340.2308); ν_{max}/cm^{-1} 3451, 1454, 1249, 1152, 1102, 1057, 1023, 938, 916, 860, 836, 757 and 701; δ_H 0.04 [9 H, s, $Si(CH_3)_3$], 0.90 [2 H, m, $CH_2Si(CH_3)_3$], 1.34 (3 H, d, *J* 6.5, 1-H_3), 2.58 (2 H, m, 4-H_2), 2.70 (1 H, d, *J* 4, OH), 3.46 and 3.77 [each 1 H, m, $OCHHCH_2Si(CH_3)_3$], 4.32 (1 H, m, 2-H), 4.57 and 4.66 (each 1 H, d, *J* 7, OC*H*HO), 4.88 (1 H, dd, *J* 8, 5.5, 5-H), 4.95 and 5.16 (each 1 H, s, vinylic H) and 7.35 (5 H, m, ArH); *m/z* 340 ($M^+ + 18$, 30%) and 323 ($M^+ + 1$, 20). Further elution gave unchanged diol **24** (16%).

Asymmetric catalysis of reactions between (*R*)-2-[1-(2-trimethylsilylethoxymethoxy)ethyl]prop-2-enyl(tributyl)stannane 12 and benzaldehyde

A solution of titanium(IV) dibromide diisopropoxide (7.8 mg, 0.024 mmol) in toluene (0.12 cm^3) was added dropwise to a stirred solution of powdered 4 Å molecular sieves (50 mg) and (*R*)-BINOL (3.4 mg, 0.012 mmoles) in dichloromethane (1 cm^3) at room temperature under argon. After stirring 2 h at room temperature a solution of benzaldehyde (12 mg, 0.12 mmol) in dichloromethane (50 cm^3) was added to it. The reaction was cooled at −78 °C and a solution of (*R*)-2-[1-(2-trimethylsilylethoxymethoxy)ethyl]prop-2-enyl(tributyl)stannane **12** (60 mg, 0.12 mmol) in dichloromethane (0.5 cm^3) was added. The reaction was stirred for 30 min at −78 °C and 3 days at −20 °C. Saturated aqueous $NaHCO_3$ (0.5 cm^3) was added and the mixture was filtered through a plug of Celite, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with diethyl ether–light petroleum (4:6) gave (1*R*,4*R*)-3-methylidene-1-phenyl-4-(2-trimethylsilylethoxymethoxy)pentan-1-ol **40** (15.3 mg, 40%) containing *ca.* 8% (by ^1H NMR spectroscopy) of its epimer **47**, $[\alpha]_D$ +83.1 (*c* 1.0, CH_2Cl_2) (Found: $M^+ + NH_4$, 340.2317. $C_{18}H_{34}NO_3Si$ requires *M*, 340.2308); ν_{max}/cm^{-1} 3443, 1493, 1453, 1375, 1248, 1023, 859, 836, 755 and 699; δ_H 0.06 [9 H, s, $Si(CH_3)_3$], 1.00 [2 H, m, $CH_2Si(CH_3)_3$], 1.35 (3 H, d, *J* 6.5, 5-H_3), 2.45 (2 H, m, 2-H_2), 3.46 (1 H, d, *J* 2.5, OH), 3.70 [2 H, m, $OCH_2CH_2Si(CH_3)_3$], 4.27 (1 H, q, *J* 6.5, 4-H), 4.73 (2 H, s, OCH_2O), 4.85 (1 H, dd, *J* 7.5, 4.5, 1-H), 5.12 and 5.22 (each 1 H, s, vinylic H) and 7.40 (5 H, m, ArH); δ_C −1.4, 18.1, 20.2, 42.4, 65.5, 73.3, 75.7, 92.5, 115.3, 125.8, 127.4, 128.4, 144.5 and 146.9; *m/z* 340 ($M^+ + 18$, 82%) and 323 ($M^+ + 1$, 60).

This procedure using (*S*)-BINOL gave (1*S*,4*R*)-3-methylidene-1-phenyl-4-(2-trimethylsilylethoxymethoxy)pentan-1-ol **47** (11.5 mg, 30%) containing *ca.* 12% (by ^1H NMR spectroscopy) of its epimer **40** (Found: $M^+ + NH_4$, 340.2298. $C_{18}H_{34}NO_3Si$ requires *M*, 340.2308); $[\alpha]_D$ −2.0 (*c* 0.5, CH_2Cl_2).

(*R*)-1-Phenyl-4-(2-trimethylsilylethoxymethoxy)pent-1-en-3-one 62

Ozonolysed air was bubbled through a solution of the alkene **47** (140 mg, 0.43 mmol) in methanol (5 cm^3) at −78 °C for 30 min. Air was then blown through the solution for 10 min, and dimethyl sulfide (270 mg, 4.34 mmol) was added. The reaction was allowed to warm to room temperature and the solvent was removed under reduced pressure. Methanesulfonyl chloride (30 mg, 0.26 mmol) and triethylamine (66 mg, 0.65 mmol) were added sequentially to the residue at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 3 h, before being partitioned between dichloromethane and water. The organic extract was washed with brine (1 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with diethyl ether–light petroleum (2:8), gave the *title compound* **62** (93 mg, 70%) (Found: $M^+ + H$, 307.1731. $C_{17}H_{27}O_3Si$ requires *M*, 307.1729); $[\alpha]_D$ +69.4 (*c* 3.0, CH_2Cl_2); ν_{max}/cm^{-1} 1692, 1609, 1576, 1450, 1373, 1331, 1249, 1202, 1109, 1060, 1031, 860, 836 and 761; δ_H 0.00 [9 H, s, $Si(CH_3)_3$], 0.93 [2 H, m, $CH_2Si(CH_3)_3$], 1.44 (3 H, d, *J* 7, 5-H_3), 3.67 [2 H, m, $OCH_2CH_2Si(CH_3)_3$], 4.38 (1 H, q, *J* 7, 4-H), 4.75 and 4.82 (each 1 H, d, *J* 7, OC*H*HO), 7.13 (1 H, d, *J* 16, 2-H), 7.42 (3 H, m, ArH), 7.61 (2 H, m, ArH) and 7.76 (1 H, d, *J* 16, 1-H); δ_C 1.6, 17.9, 65.8, 77.8, 94.2, 120.8, 128.4, 128.8, 128.9, 130.5, 134.5, 143.7 and 200.1; *m/z* 307 ($M^+ + 1$, 12%), 279 (20) and 249 (100).

N,*N*-Diisopropylethylamine (3.9 g, 0.03 mol) was added to a solution of isobutyl (*R*)-lactate **63** (1.5 g, 0.01 mol) in dichloromethane (10 cm^3). The solution was cooled at 0 °C, then 2-trimethylsilylethoxymethyl chloride (2.6 g, 0.015 mol) was added and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was washed with water and brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with light petroleum–ethyl acetate, gave isobutyl (*R*)-2-(2-trimethylsilylethoxymethoxy)propionate (2.41 g, 85%) (Found: M^+, 276.4467. $C_{13}H_{28}O_4Si$ requires *M*, 276.4473); $[\alpha]_D$ +70.9 (*c* 3.2, CH_2Cl_2).

A solution of isobutyl (*R*)-2-(2-trimethylsilylethoxymethoxy)propionate (750 mg, 2.71 mmol), lithium hydroxide (0.34 g, 8.15 mmol) in tetrahydrofuran (5 cm^3) and water (0.5 cm^3), was stirred at room temperature for 12 h. After acidification using aqueous hydrogen chloride (1 M; 20 cm^3), extraction with ethyl acetate (3 × 20 cm^3) and drying of the organic extract ($MgSO_4$) gave the acid (598 mg, 80%) as a colourless liquid which was used immediately. Triethylamine (186 mg, 1.83 mmol) and pivaloyl chloride (196 mg, 1.62 mmol) were added dropwise to a solution of the crude acid (370 mg, 1.68 mmol) in tetrahydrofuran (15 cm^3) at −78 °C, and the resulting solution was allowed to warm to 0 °C over 2 h, and then was maintained at 0 °C for 1 h. A solution of butyllithium (10 M in hexane; 0.55 cm^3, 5.5 mmol) was added slowly to a stirred suspension of ethyltriphenylphosphonium bromide (1.96 g, 5.5 mmol) in tetrahydrofuran (15 cm^3) at 0 °C. After being stirred at 0 °C for 30 min, the ylide solution was added dropwise by syringe to the crude mixed anhydride solution, which had been recooled to −78 °C. The reaction was maintained at −78 °C for 1 h, allowed to warm to room temperature for 2 h, and then quenched by the addition of saturated aqueous ammonium chloride (35 cm^3). The organic phase was extracted with ethyl acetate (3 × 20 cm^3), washed sequentially with saturated aqueous sodium hydrogen carbonate (2 × 15 cm^3) and brine (2 × 15 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with light petroleum–ethyl acetate (1:4), gave the ylide **64** (402 mg, 50%) (Found: M^+ + H, 479.2086. $C_{28}H_{36}O_3SiP$ requires *M*, 479.2172); $[\alpha]_D$ +39.6 (*c* 1.1, CH_2Cl_2); ν_{max}/cm^{-1} 3057, 1544, 1438, 1393, 1248, 1189, 1160, 1107, 1029, 861, 837, 749, 716 and 693; δ_H 0.00 [9 H, s, $Si(CH_3)_3$], 0.96 [2 H, m, $CH_2Si(CH_3)_3$], 1.46 (3 H, d, *J* 6.5, 1-H_3), 3.59–3.80 [2 H, m, $OCH_2CH_2Si(CH_3)_3$], 4.13 (2 H, m, 2-H and 4-H), 4.83 and 4.85 (each 1 H, d, *J* 7, OC*H*HO) and 7.56 (15 H, m, ArH); *m/z* 479 (M^+ + 1, 100).

A solution of the ylide **64** (250 mg, 0.52 mmol) and benzaldehyde (58 mg, 0.44 mmol) in benzene (5 cm^3) was heated under reflux for 60 h. The reaction mixture was concentrated under reduced pressure. Chromatography of the residue eluting with diethyl ether–light petroleum (2:8) gave the title compound **62** (128 mg, 80%) (Found: M^+ + H, 307.1726. $C_{17}H_{27}O_3Si$ requires *M*, 307.1729); $[\alpha]_D$ +100.4 (*c* 2.5, CH_2Cl_2).

(2*RS*,5*SR*)-5-Hydroxy-6-methyl-2-(2-trimethylsilylethoxymethoxy)heptan-3-one 68

Ozonolysed air was bubbled through a solution of the alkenol **51** (540 mg, 1.875 mmol) in methanol (80 cm^3) at −78 °C for 30 min. Air was then blown through the solution for 10 min, and dimethyl sulfide (2.06 g, 18.75 mmol) was added. The mixture was allowed to warm to room temp., and was concentrated under reduced pressure. Chromatography of the residue using light petroleum–ethyl acetate as eluent (10:1) gave the *title compound* **68** (326 mg, 60%) (Found: $M^+ + NH_4$, 308.2263. $C_{14}H_{34}NO_4Si$ requires *M*, 308.2257); ν_{max}/cm^{-1} 3492, 1716, 1467, 1379, 1250, 1109, 1058, 1030, 861 and 836; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.9 [8 H, m, 2 × CH_3 and $CH_2Si(CH_3)_3$], 1.29 (3 H, d, *J* 6.5, 1-H_3), 1.68 (1 H, m, 6-H), 2.63 (2 H, m, 4-H_2), 2.97 (1 H, d, *J* 3, OH), 3.59 [2 H, m, $OCH_2CH_2Si(CH_3)_3$], 3.79 (1 H, m, 5-H), 4.10 (1 H, q, *J* 6.5, 2-H), 4.67 and 4.69 (each 1 H, d, *J* 7, OC*H*HO); δ_C −1.4, 17.2, 17.8, 18.0, 18.4, 33.2, 41.8, 65.9, 72.3, 78.8, 94.3 and 213.5; *m/z* 308 ($M^+ + NH_4$, 98%) and 291 (M^+ + H, 30).

(2*RS*,3*RS*,5*SR*)-6-Methyl-2-(2-trimethylsilylethoxymethoxy)-heptane-3,5-diol 69

Methoxydiethylborane (1 M in THF; 0.2 cm^3, 0.198 mmol) was added dropwise to a solution of hydroxy ketone **68** (53 mg, 0.18 mmol) in tetrahydrofuran–methanol (5:1; 2.4 cm^3) at −78 °C and the mixture was stirred for 15 min. Sodium borohydride (0.198 mmol) was added and the mixture was stirred at −78 °C for 5 h before acetic acid (0.21 cm^3) was added. The mixture was then diluted with ethyl acetate, washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was azeotroped with methanol until hydrolysis of the borane was complete. Chromatography using light petroleum–ethyl acetate (5:1) as eluent gave the *title compound* **69** (32 mg, 60%) (Found: M^+ + H, 293.2150. $C_{14}H_{33}O_4Si$ requires *M*, 293.2148); ν_{max}/cm^{-1} 3390, 1466, 1379, 1249, 1102, 1056, 1029, 858 and 836; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.89 [8 H, m, 2 × CH_3 and $CH_2Si(CH_3)_3$], 1.14 (3 H, d, *J* 6, 1-H_3), 1.41 (1 H, dt, *J* 14, 10, 4-H), 1.55 (1 H, dt, *J* 14, 2, 4-H′), 1.66 (1 H, m, 6-H), 3.58 [5 H, m, 2-H, 3-H, 5-H and $OCH_2CH_2Si(CH_3)_3$], 3.71 and 3.78 (each 1 H, br s, OH) and 4.71 (2 H, m, OCH_2O); δ_C −1.4, 16.6, 17.5, 18.1, 18.4, 33.95, 35.3, 65.7, 76.4, 76.9, 78.8 and 94.3; *m/z* 310 ($M^+ + NH_4$, 20%), 293 (M^+ + H, 75) and 247 (28).

(2*RS*,3*SR*,5*SR*)-6-Methyl-2-(2-trimethylsilylethoxymethoxy)-heptane-3,5-diol 70

Anhydrous acetic acid (1.5 cm^3) was added to a solution of tetramethylammonium triacetoxyborohydride (700 mg, 2.68 mmol) in anhydrous acetonitrile (1.5 cm^3) and the mixture stirred at room temp. for 30 min. A solution of hydroxy ketone **68** (97 mg, 0.334 mmol) in anhydrous acetonitrile (0.7 cm^3) was added and the mixture stirred for 75 min at room temp. Water was added, followed by ethyl acetate, and solid potassium carbonate until the pH reached 7. The aqueous solution was extracted with ethyl acetate and the combined organic extracts dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum–ethyl acetate (2:1) as eluent gave the *title compound* **70** (88 mg, 90%) (Found: M^+ + H, 293.2151. $C_{14}H_{33}O_4Si$ requires *M*, 293.2148); ν_{max}/cm^{-1} 3416, 1410, 1249, 1104, 1056, 1029, 859 and 836; δ_H −0.01 [9 H, s, $Si(CH_3)_3$], 0.86 and 0.91 (each 3 H, d, *J* 7, CH_3), 0.87 [2 H, m, $CH_2Si(CH_3)_3$], 1.13 (3 H, d, *J* 6.5, 1-H_3), 1.19 and 1.50 (each 1 H, m, 4-H), 1.66 [1 H, m, $CH(CH_3)_2$], 2.37 and 3.20 (each 1 H, br s, OH), 3.62 (4 H, m), 3.83 (1 H, m) and 4.67 and 4.70 (each 1 H, d, *J* 7, OC*H*HO); δ_C −1.4, 15.8, 17.9, 18.1, 18.8, 33.9, 34.8, 65.6, 70.8, 73.4, 78.6 and 94.2; *m/z* 310 ($M^+ + NH_4$, 13%), 293 (M^+ + H, 70), 247 (38), 235 (30) and 192 (100).

Crystal data for diol 36‡

$C_{12}H_{15}NO_4$, *M* = 237.25, primitive orthorhombic cell, space group *Pbca* (#61), crystal dimensions 0.30 × 0.40 × 0.50 mm, yellow crystal, *a* = 24.251(6), *b* = 14.837(9), *c* = 13.797(2) Å, *U* = 4964(2) $Å^3$ using the setting angles of 25 carefully centred reflections in the range 30.21 < 2θ < 38.52°, *Z* = 16, D_c = 1.27 g cm^{-1}, *F*(000) = 2016.00. Rigaku AFC5R diffractometer, graphite monochromated Mo-Kα radiation (λ = 0.710 69 Å) and a rotating anode generator. The data were collected at a temperature of 23 ± 1 °C using the ω scan technique to a maximum of 2θ value of 50.1°. The weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of three scans) and the counts were accumulated to ensure good counting statistics. A total of 4913

‡ Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/126.

reflections were collected. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 3.5%. A linear correction factor was applied to the data to account for this phenomenon. The linear absorption coefficient, μ, for Mo-Kα radiation is 0.96 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.86 to 1.00. The data were corrected for Lorentz and polarisation effects. The structure was solved by direct methods[20] and expanded using Fourier techniques.[21] The asymmetric unit contains two molecules, which are geometrically the same, within experimental error. Fig. 1 shows molecule 1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were included in calculated positions. Those bonded to oxygen were found by difference Fourier techniques. Some were allowed to refine isotropically in early rounds of refinement, but all were fixed in the final rounds. The final cycle of full-matrix least-squares refinement on F was based on 2226 observed reflections [$I > 2.50\sigma(I)$] and 307 variable parameters and converged (largest parameter shift was 0.00 times its esd), with $R = 0.085$, $R_\omega = 0.069$, weighting scheme $\omega = 1/[\sigma^2 F_o + 0.000\,01\,|F_o|^2]$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.55 and -0.36 e $Å^{-3}$, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[22] Anomalous dispersion effects were included in *F*cal;[23] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[24] The values for the mass attenuation coefficients are those of Creagh and Hubell.[25] All calculations were performed using the teXsan[26] crystallographic software package of Molecular Structure Corporation.

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