Effective 1,5-Asymmetric Induction in Tin(IV) Chloride Promoted Reactions Between Aldehydes and (4-Alkoxy-2-alkenyl)tributylstannanes

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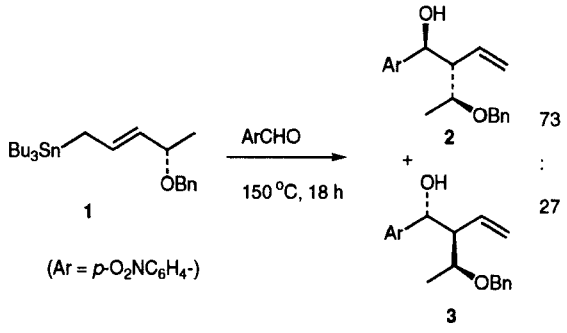
Transmetallation of (*S*)-4-benzyloxy-2-pentenyl(tributyl)stannane (**1**) using tin(IV) chloride generates an allyltin trichloride which reacts in situ with aldehydes to give 1-substituted *syn*-(3*Z*)-5-benzyloxyhexenols with excellent stereoselectivity. With chiral aldehydes, the stereoselectivity of the reaction is dominated by the reagent, except for 2-alkoxyaldehydes which show matching and mismatching consistent with preferred Felkin–Anh diastereofacial selectivity.

Reactions of allylstannanes and aldehydes are being developed for the stereoselective synthesis of homoallylic alcohols.[1] Noncatalysed reactions require high temperatures and proceed via six-membered, cyclic transition states.[2] In contrast, open-chain processes are believed to be involved in Lewis acid catalysed reactions.[3] Transmetallation to generate more reactive allylmetal species is also well established.[4] For 1-substituted allylstannanes, effective diastereofacial selectivity is found for both non catalysed (thermal) and Lewis acid catalysed reactions.[5]

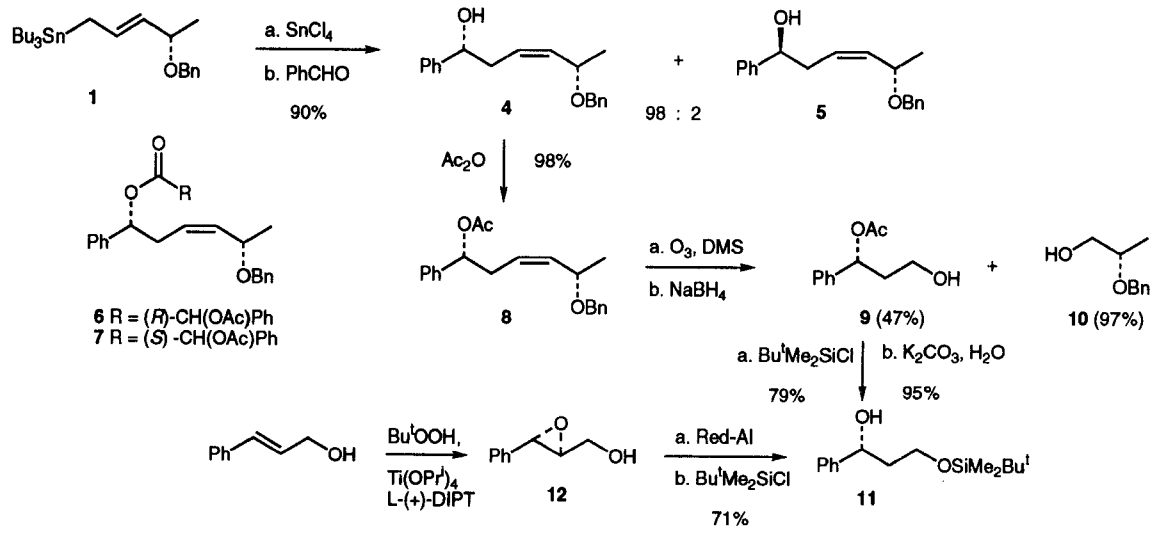


However, the noncatalysed reaction of (*S*)-4-benzyloxy-2-pentenyl(tributyl)stannane (**1**) and *p*-nitrobenzaldehyde at 150°C shows only modest diastereofacial selectivity giving a mixture of the two 1,2-*anti*-products **2** and **3**, ratio 73:27.[6] We now report details of tin(IV) chloride promoted reactions between aldehydes and the stannane **1**. These are believed to involve transmetallation to generate a reactive allyltin trichloride, and proceed with excellent 1,5-asymmetric induction.[7]

Reactions with Achiral Aldehydes

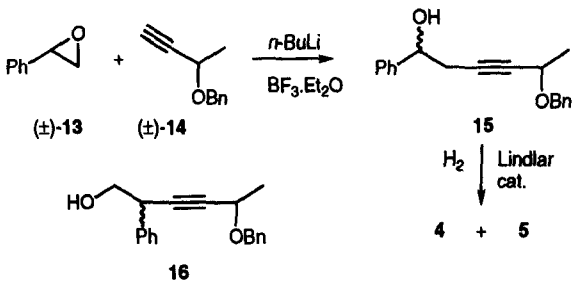
Preliminary studies of reactions between stannane **1** and benzaldehyde promoted by boron trifluoride–diethyl ether complex gave only low yields of products, 1,4-elimination to give benzyl alcohol and penta-1,3-diene dominating the reaction. However, reactions promoted by tin(IV) chloride gave completely different results. Optimum conditions were to add a cooled solution of tin(IV) chloride to a solution of the stannane at − 78 °C followed, after 5 min, by benzaldehyde. Workup after 1 h gave the *syn*-(3*Z*)-5-benzyloxyhexenol **4** (90 %) containing only traces (ca. 2 %) of its *anti*-diastereoisomer **5**.

The structure of the *syn*-(3*Z*)-product **4** was consistent with spectroscopic data. This *cis*-geometry of the double bond was established by the observation of NOE enhancements between the allylic protons. The configuration of the hydroxy-bearing carbon C-1 was initially assigned by the relative ^{1}H NMR chemical shifts of the corre-



sponding (*R*)- and (*S*)-acetylmandelates **6** and **7**,[8] and was confirmed by ozonolysis, with a reductive workup, of the acetate **8**. This gave a mixture of the alcohols **9** and **10** in yields of 47 and 97%, respectively. The configuration of the alcohol **9** was established by conversion into the known (+)-hydroxysilyl ether **11**, $[\alpha]_D$ + 27.4 (c = 0.76, $CHCl_3$) [cf. lit.[9] + 24.7 (c = 0.76, $CHCl_3$)]. To check the absolute configuration of the silyl ether, cinnamyl alcohol was converted into the epoxide **12** using L-(+)-diisopropyl tartrate following the Sharpless procedure.[10] Reduction of the epoxide with Red-Al and selective silylation of the primary alcohol also gave the (+)-hydroxysilyl ether **11**.

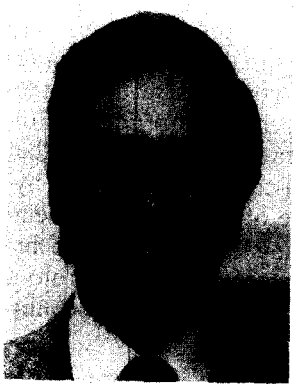
A mixture of the 1,5-*syn*- and 1,5-*anti*-products **4** and **5** was prepared to check that the two isomers could be distinguished by NMR. Lithiation of (±)-3-benzyloxybutyne (**14**) and reaction with the (±)-styrene epoxide **13** gave the hexynol **15** as a mixture of diastereoisomers together a mixture of side-products, possibly the regioisomers **16**. Hydrogenation of **15** using a Lindlar catalyst gave a mixture of the *syn*- and (3*Z*)-*anti*-5-benzyloxyhexenols **4** and **5** which, although inseparable by chromatography, were clearly different by ^{1}H NMR. Comparison with the product mixture obtained from the reaction of the stannane **1** with benzaldehyde, confirmed that the minor (ca. 2%) component was the *anti*-isomer **5**.



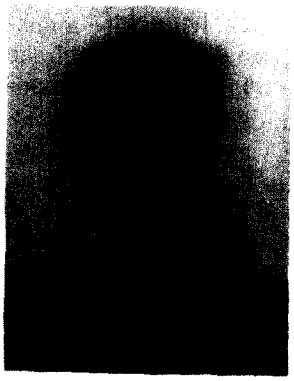
The use of other conditions for the reaction between benzaldehyde and the stannane **1** was less satisfactory. To get good yields of product, it is important to add the aldehyde to the reaction mixture at − 78 °C approximately 5 min after the addition of the tin(IV) chloride. If the addition of the aldehyde is delayed, say by 20 min, lower yields are obtained. Similarly if the stannane is added to a mixture of the aldehyde and tin(IV) chloride, less satisfactory results are obtained with elimination of benzyl alcohol from the stannane becoming more important.

The stereoselective formation of 1-substituted *syn*-(3*Z*)-5-benzyloxyhexenols using stannane **1** and tin(IV) chloride was found to be general for a wide range of aldehydes, see Table 1.[7] Excellent stereoselectivity in favour

Biographical Sketches



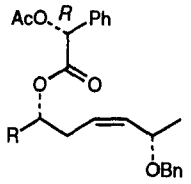
Eric J. Thomas studied for his B.A. and Ph.D. in Cambridge, the latter under the supervision of Dr. I. Fleming. In 1971, he went to Oxford, where he worked as a Departmental Post-doctoral Research Assistant in the Dyson Perrins Laboratory carrying out research under the supervision of Dr. G. H. Whitham into the synthesis of *trans*-cyclooctenes. In 1973, he was appointed as a University Lecturer in Organic Chemistry at King's College, London, where he carried out research into aspects of the chemistry of β-lactams (in collaboration with the late Dr. D. I. John) and embarked on several natural product syntheses. In 1979, he moved back to Oxford as a University Lecturer in Organic Chemistry and Official Tutorial Fellow of Exeter College. In 1988, he was appointed Professor of Organic Chemistry at the University of Manchester. His research interests are concerned with synthetic organic chemistry, both the total synthesis of natural products and the development of new methods, particularly for asymmetric synthesis. He was awarded the Hickinbottom Fellowship of the Royal Society of Chemistry in 1982 and a Pfizer Prize in 1986.



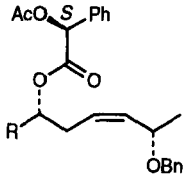
Alan H. McNeill was born in 1963 in Dundee, Scotland, and received his B.Sc. in Chemistry from Dundee in 1985. After 4 years in industry, he moved to Manchester University and completed his Ph.D. in 1992. He is currently a Post-doctoral Research Assistant at Nottingham University.

of the 1,5-*syn*-products **17a–j** was observed with only minor amounts of the *anti*-isomers **18a–j** being detected.

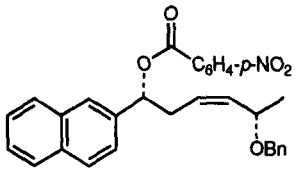
The *syn*- and *anti*-products obtained from aromatic aldehydes and methyl glyoxalate were distinguished by ^{1}H NMR, whereas the products from the reactions with aliphatic aldehydes could only be distinguished by ^{13}C NMR. A mixture of **17g** and **18g** was prepared by hydrogenation of the corresponding alkyne and were separated by chromatography. The configuration of the hydroxy-bearing carbon for the major products **17d,f,g,i** obtained from furfural, butanal, 2-methylpropanal, and methyl glyoxalate, was established by comparison of the ^{1}H NMR spectra of their (*R*)- and (*S*)-acetylmandelates **19d,f,g,i** and **20d,f,g,i**.[8] In all cases the relative chemical shifts were consistent with the major products having the 1,5-*syn*-stereochemistry, see Table 2. The *cis*-geometry of the double bonds in **17a–j** was consistent with absorptions at ν = 696–699 cm^{-1} in their IR spectra, and vinylic coupling constants of ca. 11 Hz in the ^{1}H NMR spectra of their acetylmandelates. The structures of the other products were assigned by analogy. Finally, the structure of the *p*-nitrobenzoate **21** of the product **17j** prepared from 2-naphthaldehyde, was confirmed by X-ray difraction.[11]



19d, R = 2-furyl
19f, R = *n*-Pr
19g, R = *i*-Pr
19i, R = MeO_2C



20d, R = 2-furyl
20f, R = *n*-Pr
20g, R = *i*-Pr
20i, R = MeO_2C



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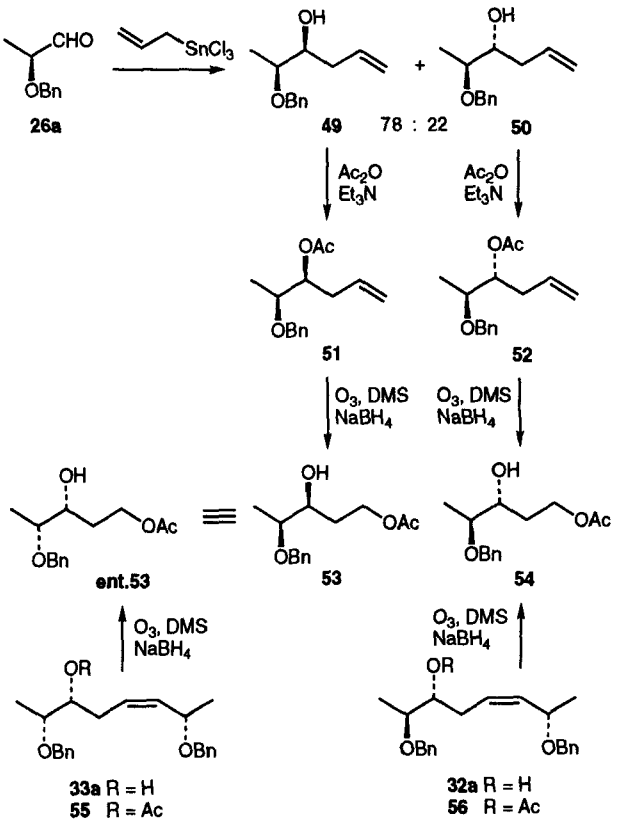
Reactions with Chiral Aldehydes

Tin(IV) chloride promoted reactions of the (4*S*)-stannane **1** and a series of chiral aldehydes were investigated to see whether the stereochemical preference of the reagent or the diastereofacial bias of the aldehyde would determine the overall stereoselectivity of the reactions.[12] Reactions with 2- and 3-alkoxyaldehydes with chiral centres at both the 2- and 3-positions were investigated, and the results are shown in Table 3.

Excellent stereoselectivity in favour of the 1,5-*syn*-products was observed in all cases except for reactions with the (2*R*)-2-alkoxypropanals **27a–c**. These each gave a mixture of two products in a ratio of about 70:30, the major product corresponding to the (3*Z*)-*syn*-diastereoisomer **33a–c**, the minor product being identified as the (3*Z*)-*anti*-isomer **34a–c**.



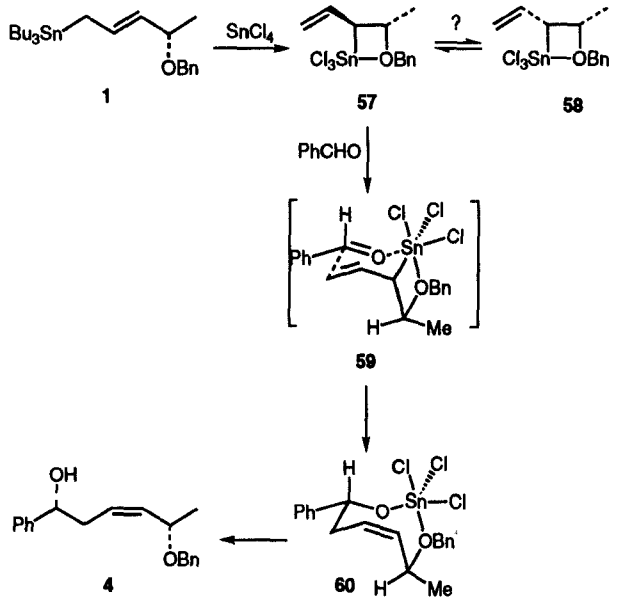
The (*R*)- and (*S*)-acetylmandelates **35–48** were synthesised to establish the configurations of the hydroxy-bearing carbons in the products **28–34**. The relative ^{1}H chemical shifts observed for protons near to the hydroxy bearing chiral centre are shown in Table 2.[8] The acetylmandelates obtained from the *minor* products from reactions with the (2*R*)-2-alkoxypropanals **27a–c** show a reversal in relative chemical shift compared with the acetylmandelates prepared from all the other products. Following the mnemonic in the literature,[8] this suggests that the minor products have the (*S*)-configuration at the hydroxy-bearing carbon indicative of 1,5-*anti*-stereochemistry, all the other products having the 1,5-*syn*-stereochemistry. Coupling constants between the vinylic protons of 11 Hz were observed for the acetylmandelates confirming the *cis*-alkene geometry.

The structures of the major products **32a** and **33a** obtained from the (2*S*)- and (2*R*)-2-benzyloxypropanals **26a** and **27a** and the (4*S*)-benzyloxystannane **1** were confirmed by correlation with known compounds. The tin(IV) chloride promoted reaction between 2-benzyloxypropanal **26a** and allyltrimethylsilane is known to give a mixture of the *syn*- and *anti*-alcohols **49** and **50** in which the chelation-controlled *syn*-product **49** is the major component, **49**:**50** = 35:1.[13] In our hands, the analogous reaction using allyltributylstannane was less stereoselective but still gave the *syn*-alcohol **49** as the major component, **49**:**50** = 78:22, and was useful in that it gave access to both stereoisomers which could be separated. Acetylation and ozonolysis with a reductive workup gave the acetates **53** and **54** in which the acetyl group had migrated to the primary position. Ozonolysis of the acetates **55** and **56**, prepared from the major products **33a** and **32a** of the

reactions of stannane **1** with the (2*R*)- and (2*S*)-2-benzyloxypropanals **27a** and **26a**, gave the enantiomer of acetate **53**, and the acetate **54**, respectively. These correlations confirmed the stereochemical assignments made to the products of the reactions from the 2-alkoxypropanals **26** and **27**.

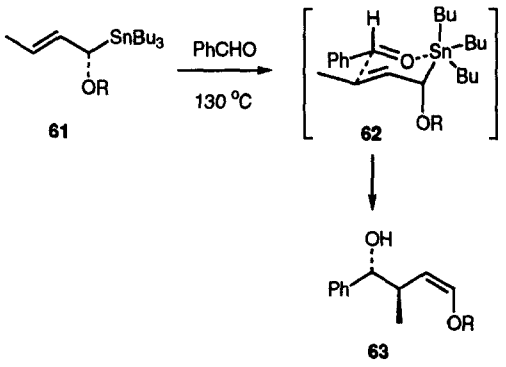
Mechanistic Discussion

The major products in the reactions of stannane **1** and aldehydes promoted by tin(IV) chloride are 1-substituted *syn*-(3*Z*)-5-benzyloxyhexenols, i.e. **4**, **17a–j**, and **28–33**, see Tables 1 and 3, most reactions proceeding with excellent stereoselectivity. The formation of these products is consistent with transmetallation of the allyltributylstannane **1** to give the allyltin trichloride **57** which then reacts with the aldehyde via the cyclic transition state **59**. It is suggested that this intermediate allyltin trichloride is stabilised by coordination of the oxygen of the benzyloxy group to the electron-deficient tin,[14] and that it is formed stereoselectively so that the methyl and vinyl groups are *trans*-disposed about the 4-membered ring. The 4-membered ring is not excessively strained because the pentacoordinated tin is trigonal bipyramidal with the allyl fragment equatorial and the oxygen ligand axial. Indeed an X-ray structure of a 4-membered ring oxastannane has recently been published.[15] The allyltin trichloride **57** reacts with aldehydes via the cyclic transition state **59** in which the group α to tin is in the pseudo-axial position. This preference leads to the formation of products which have *cis*-double bonds, and controls the facial selectivity of the attack on the aldehyde.



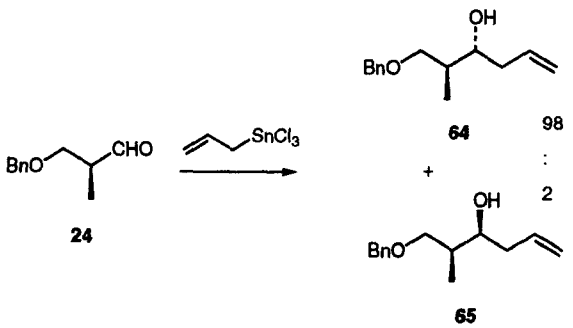
The origin of the stereoselectivity of the first step in this sequence, the formation of the allyltin trichloride **57**, has not been studied. It may be that **57** is more stable than its *cis*-diastereoisomer **58**, and that an initially formed *cis–trans* mixture equilibrates to give more of the *trans*-stereoisomer which then reacts with the aldehyde. Moreover, the reaction of the *trans*-allyltin trichloride **57** with an aldehyde may be faster than the analogous reaction of its *cis*-diastereoisomer **58** due to less steric hindrance to the approaching aldehyde. Alternatively, the stereoselectivity of transmetallation may be due to kinetic control, the greater stability of the *trans*-allyltin trichloride intermediate being reflected in the transition state for its formation if, for example, the tin(IV) chloride is delivered to the double bond of the tributylstannane **1** by the oxygen of the benzyloxy substituent.

The preference of the group α to tin to adopt the axial position in the transition state **59** has precedent in the noncatalysed reactions of α-substituted allylstannanes, e.g. **61**, and aldehydes.[5] However, in the transition states **62** of these latter reactions, the tin is pentacoordinated, not hexacoordinated as it is in transition state **59**, and so may not provide a very convincing analogy.



The first formed product of the reaction between the allyltin trihalide **57** and an aldehyde is likely to be the 8-membered-ring-containing intermediate **60**. This would be hydrolysed on workup and is probably much more stable than its *trans*-double-bond-containing isomer. It is possible that this difference in stability is reflected in the transition states for reactions of the allyltin trihalide **57** with aldehydes. Preliminary molecular modelling calculations on analogues of **60** and its *trans*-double-bond isomer, indicate that the *cis*-isomer **60** is the much more stable.

The tin(IV) chloride promoted reactions of the stannane **1** and chiral alkoxyaldehydes show a strong preference for the formation of the 1,5-*syn*-isomer, i.e. for the reagent-controlled product, irrespective of the configuration of the aldehyde. This is surprising when compared with the high degree of chelation control observed in reactions of alkoxyaldehydes and unsubstituted allyltin trihalides. For example, the 3-benzyloxypropanal **24** reacts with prop-2-enyltin trichloride to give the *anti*- and *syn*-prod-



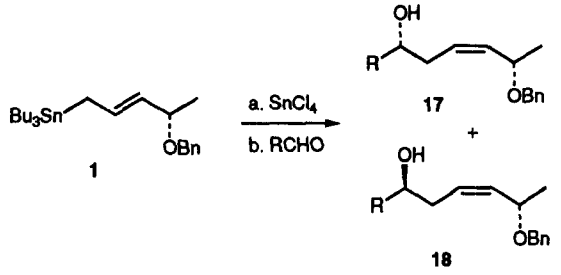
ucts **64** and **65**, ratio **64**:**65** = 98:2.[16] This preference for chelation control is not observed in reactions of the alkoxyallyltin trihalide **57**. It would appear that the internal coordination proposed for the allyltin trichloride precludes chelation control in reactions with alkoxyaldehydes.

Indeed, the matching and mismatching observed for the 2-alkoxypropanals **26a–c** and **27a–c** is consistent with a preference for Cram (Felkin–Anh) selectivity.[17] The minor products **34a–c** from the mismatched (2*R*)-aldehydes **27a–c** may have been formed by equilibration of the allyltin trihalide **57** with its epimer **58**. This can then react with the (2*R*)-aldehydes via the Felkin–Anh mode to give the observed minor products.

Present work is concerned with extending the scope of the tin(IV) halide promoted reactions of (alkoxyallyl)stannanes to include 1,6- and 1,7-asymmetric induction,[18,19] and to apply this chemistry to develop new strategies for the stereoselective synthesis of open-chain compounds.[20] Allylstannanes with 4-amino and 5-thiosubstituents have also been found to react with efficient 1,5-asymmetric induction.[21,22]

^{1}H NMR spectra were recorded on a Bruker AC-300 or a Varian XL-300 spectrometer and ^{13}C spectra on the Bruker AC-300 operating at 75 MHz in solution in $CDCl_3$. ^{19}F spectra were recorded on a Varian Unity-500 operating at 470 MHz. IR spectra were measured on a Perkin-Elmer 1710 FT spectrometer as evaporated

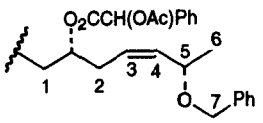
Table 1. Tin(IV) Chloride Promoted Reactions of Stannane 1 and Aldehydes



R	Products	Yield (%)	1,5-*syn* : 1,5-*anti*
Ph	**4, 5**	90	98 : 2[a]
p-ClC_6H_4	**17a, 18a**	77	94 : 6[a]
p-$O_2NC_6H_4$	**17b, 18b**	77	95 : 5[a]
p-$MeOC_6H_4$	**17c, 18c**	77	97 : 3[a]
2-furyl	**17d, 18d**	72	95 : 5[a]
PhCH=CH	**17e, 18e**	64	95 : 5[b]
Pr	**17f, 18f**	84	95 : 5[c]
i-Pr	**17g, 18g**	84	93 : 7[c]
cyclohexyl	**17h, 18h**	78	92 : 8[c]
MeO_2C	**17i, 18i**	68	98 : 2[c]
2-naphthyl	**17j, 18j**	72	95 : 5[a]

[a] Determined by ^{1}H NMR.
[b] By analogy.
[c] Determined by ^{13}C NMR.

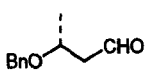
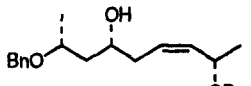
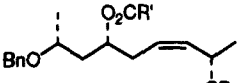
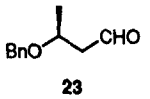
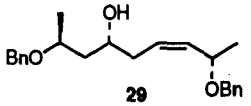
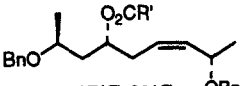
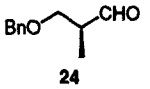
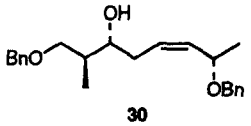
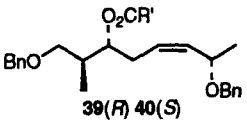
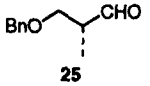
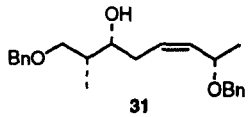
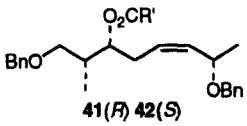
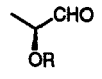
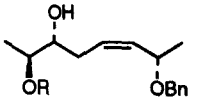
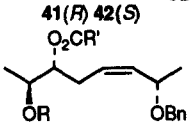
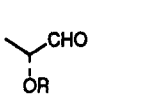
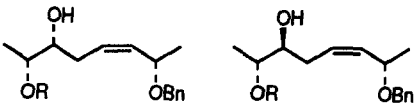
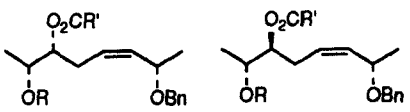
Table 2. Relative ^{1}H Chemical Shifts of (*R*)- and (S)-Acetylmandelates; δ (*R*-mandelate)-δ (*S*-mandelate)



Parent Alcohol	1-H, 1′-H	2-H, 2′-H	3-H	4-H	5-H	6-H	7-H, 7′-H
4	–	0.19, 0.05	0.2	0.2	0.09	0.03	0.12, 0.10
17d	–	0.22, 0.22	0.23	0.37	0.18	0.11	0.19, 0.18
17f	– 0.12	0.16, 0.16	0.22	0.34	0.15	0.07	0.17, 0.14
17g	– 0.24	0.18, 0.18	0.41	0.27	0.21	0.08	0.22, 0.20
17i	–	0.00, 0.00	0.19	0.03	0.01	0.01	0.00, 0.03
28	– 0.10	0.22, 0.22	0.34	0.21	0.18	0.04	– –[a]
29	– 0.12, – 0.15	0.19, 0.19	0.33	0.02	0.17	0.02	– –[a]
30	– 0.15 (– 0.22)[b]	0.18, 0.18	0.41	0.31	0.16	0.12	– –[a]
31	– 0.06 (– 0.2)[b]	0.24, 0.24	0.33	0.33	0.18	0.1	– –[a]
32a	– 0.25 (– 0.27)[b]	0.07, 0.07	0.37	0.26	0.1	0.02	– –[a]
32b	– 0.21 (– 0.25)[b]	0.03, 0.03	0.47	0.32	0.16	0.09	0.2, 0.21
32c	– 0.22 (– 0.24)[b]	0.12, 0.12	0.4	0.26	0.15	0.09	0.23, 0.18
33a	– 0.19 (– 0.31)[b]	0.16, 0.16	0.41	0.27	0.15	0.03	– –[a]
33b	– 0.2 (– 0.38)[b]	0.27, 0.06	0.45	0.28	0.15	0.09	0.17, 0.17
33c	– 0.22 (– 0.33)[b]	0.12, 0.12	0.41	0.24	0.16	0.05	0.19, 0.14
34a	0.23 (0.19)[b]	– 0.09, – 0.09	– 0.4	– 0.27	– 0.17	– 0.12	– –[a]
34b	0.21 (0.25)[b]	– 0.22, – 0.06	– 0.49	– 0.34	– 0.17	– 0.08	– 0.2, – 0.21
34c	0.23 (0.22)[b]	– 0.05, – 0.05	– 0.4	– 0.28	– 0.16	– 0.12	– 0.16, – 0.14

[a] Presence of two $PhCH_2$ groups made comparison of δ (*CH*HPh) unreliable.
[b] The relative chemical shift of the methyl group attached to C(1) (numbering as in the Table).

Table 3. Products and Their Acetylmandelates from Tin(IV) Chloride Promoted Reactions of Allylstannane **1** and Chiral Aldehydes

Aldehyde	Products	Yield (%)	1,5-*syn* : 1,5-*anti*	Acetylmandelates (R' = CH(OAc)Ph
 **22**	 **28**	76	96 : 4	 **35(*R*) 36(*S*)**
 **23**	 **29**	85	96 : 4	 **37(*R*) 38(*S*)**
 **24**	 **30**	55	96 : 4[a]	 **39(*R*) 40(*S*)**
 **25**	 **31**	66	96 : 4[a]	 **41(*R*) 42(*S*)**
 **26a** R = Bn **26b** R = $SiMe_2Bu^t$ **26c** R = MOM	 **32a** R = Bn **32b** R = $SiMe_2Bu^t$ **32c** R = MOM	90 72 72	96 : 4 96 : 4 96 : 4	 **43a (*R*) 44a (*S*)** R = Bn **43b (*R*) 44b (*S*)** R = $SiMe_2Bu^t$ **43c (*R*) 44c (*S*)** R = MOM
 **27a** R = Bn **27b** R = $SiMe_2Bu^t$ **27c** R = MOM	 **33a** R = Bn **33b** R = $SiMe_2Bu^t$ **33c** R = MOM **34a** R = Bn **34b** R = $SiMe_2Bu^t$ **34c** R = MOM	89 65 68	70 : 30[b] 70 : 30[b] 65 : 35[b]	 **45a (*R*) 46a (*S*)** **47a (*R*) 48a (*S*)** R = Bn **45b (*R*) 46b (*S*)** **47b (*R*) 48b (*S*)** R = $SiMe_2Bu^t$ **45c (*R*) 46c (*S*)** **47c (*R*) 48c (*S*)** R = MOM

[a] Partial racemisation of aldehydes **24** and **25** gave 5–7% of crossover products.
[b] Ratio corresponds to **33** : **34**.

Table 4. Physical Data for 1-Substituted *syn*-(3*Z*)-5-Benzyloxy-3-hexenols[a]

Product	IR ν_{max} (cm^{-1})	^1H NMR ($CDCl_3$) δ, J (Hz)	MS *m/z* (%)
4	3408, 3029, 1071, 736, 699	1.12 (3H, d, J = 7.5, 6-H_3), 2.21 (1H, d, J = 2.5, OH), 2.50 (2H, m, 2-H_2), 4.23 (1H, m, 5-H), 4.36 and 4.51 (each 1H, d, J = 12, C*H*HPh), 4.71 (1H, m, 1-H), 5.58 (2H, m, 3-H, 4-H), 7.35 (10H, m, aromatic H)	300 (M^+ + 18, 36), 197 (39), 192 (100), 157 (100)
17a	3408, 3029, 1090, 831, 737, 698	1.18 (3H, d, J = 7.5, 6-H_3), 2.30 (1H, br s, OH), 2.41 and 2.50 (each 1H, m, 2-H), 4.22 (1H, m, 5-H), 4.38 and 4.50 (each 1H, d, J = 12, C*H*HPh), 4.69 (1H, dd, J = 8, 5, 1-H), 5.57 (2H, m, 3-H, 4-H), 7.20–7.38 (9H, m, aromatic H)	334 (M^+ + 18, 1), 317 (M^+ + 1, 1), 207 (32), 139 (99), 113 (100)
17b	3410, 1605, 1520, 1346, 1070, 856, 741, 699	1.21 (3H, d, J = 7.5, 6-H_3), 2.49 (2H, m, 2-H_2), 2.74 (1H, br s, OH), 4.25 (1H, m, 5-H), 4.44 and 4.49 (each 1H, d, J = 12, C*H*HPh), 4.80 (1H, m, 1-H), 5.61 (2H, m, 3-H, 4-H), 7.35 (5H, m, aromatic H), 7.45 and 8.18 (each 2H, d, J = 7.5, aromatic H)	345 (M^+ + 18, 61), 328 (M^+ + 1, 3), 310 (42), 108 (100)
17c	3418, 3063, 1722, 1611, 1513, 1248, 1072, 737, 699	1.13 (3H, d, J = 7.5, 6-H_3), 2.04 (1H, br s, OH), 2.42 and 2.52 (each 1H, m, 2-H), 3.80 (3H, s, OCH_3), 4.23 (1H, m, 5-H), 4.36 and 4.50 (each 1H, d, J = 12, C*H*HPh), 4.69 (1H, t, J = 7.5, 1-H), 5.55 (2H, m, 3-H, 4-H), 6.88 and 7.25 (each 2H, d, J = 9, aromatic H), 7.35 (5H, m, aromatic H)	312 (M^+, 2), 187 (100), 137 (97)
17d	3411, 1067, 1026, 731, 696	1.22 (3H, d, J = 7.5, 6-H_3), 2.18 (1H, br s, OH), 2.62 (2H, m, 2-H_2), 4.30 (1H, m, 5-H), 4.41 and 4.56 (each 1H, d, J = 12, C*H*HPh), 4.73 (1H, t, J = 7.5, 1-H), 5.58 (2H, m, 3-H, 4-H), 6.23 (1H, d, J = 3), 6.33 (1H, dd, J = 2, 3.5), 7.25–7.40 (6H, m, aromatic H)	290 (M^+ + 18, 3), 255 (4), 147 (100)
17e	3397, 3062, 3027, 1495, 1453, 1071, 1028, 967, 749, 696	1.28 (3H, d, J = 7.5, 8-H_3), 1.93 (1H, br s, OH), 2.41 (2H, m, 4-H_2), 4.32 (2H, m, 3-H and 7-H), 4.41 and 4.56 (each 1H, d, J = 12, C*H*HPh), 5.2 (2H, m, H-5 and 6-H), 6.22 (1H, dd, J = 6.5, 16, 2-H), 6.59 (1H, d, J = 16, 1-H), 7.30 (10H, m, aromatic H)	326 (M^+ + 18, 2), 199 (29), 183 (100)

Table 4. (Continued)

Product	IR ν_{max} (cm^{-1})	^1H NMR ($CDCl_3$) δ, J (Hz)	MS m/z (%)
17f	3397, 1069, 735, 697	0.94 (3H, t, J = 7, 1-H_3), 1.28 (3H, d, J = 6.5, 9-H_3), 1.43 (4H, m, 2-H_2 and 3-H_2), 1.60 (1H, br s, OH), 2.20 (2H, t, J = 6.5, 5-H_2), 3.63 (1H, m, 4-H), 4.31 (1H, m, 8-H), 4.41 and 4.56 (each 1H, d, J = 12, C*H*HPh), 5.59 (2H, m, 6-H and 7-H), 7.30 (5H, m, aromatic H)	266 (M^+ + 18, 6), 249 (M^+ + 1, 35), 158 (69), 141 (100)
17g	3452, 1072, 736, 698	0.93 (6H, d, J = 7, CH*Me*$_2$), 1.28 (3H, d, J = 6.5, 8-H_3), 1.68 (2H, m, 2-H and OH), 2.19 (2H, t, J = 6.5, 4-H_2), 3.39 (1H, q, J = 6, 3-H), 4.31 (1H, m, 7-H), 4.42 and 4.56 (each 1H, d, J = 12, C*H*HPh), 5.60 (2H, m, 5-H and 6-H), 7.30 (5H, m, aromatic H)	266 (M^+ + 18, 4), 228 (32), 139 (99)
17h	3451, 1071, 735, 698	0.95–1.35 (6H, m), 1.27 (3H, d, J = 6.5, 6-H_3), 1.61–1.85 (6H, m), 2.21 (2H, t, J = 6.5, 2-H_2), 3.38 (1H, m, 1-H), 4.31 (1H, m, 5-H), 4.41 and 4.56 (each 1H, d, J = 12, C*H*HPh), 5.60 (2H, m, 3-H and 4-H), 7.32 (5H, m, aromatic H)	306 (M^+ + 18, 31), 289 (M^+ + 1, 10), 198 (26), 181 (26), 179 (100)
17i	3434, 1737, 1210, 1088, 736, 698	1.28 (3H, d, J = 7.5, 7-H_3), 2.50 (2H, m, 3-H_2), 2.83 (1H, d, J = 6.5, OH), 3.79 (3H, s, OMe), 4.28 (2H, m, 2-H and 6-H), 4.38 and 4.54 (each 1H, d, J = 12, C*H*HPh), 5.58 (2H, m, 4-H and 5-H), 7.31 (5H, m, aromatic H)	282 (M^+ + 18, 27), 265 (M^+ + 1, 3), 174 (100)
17j	3406, 3059, 1071, 858, 820, 747, 698	1.14 (3H, d, J = 6.5, 6-H_3), 2.32 (1H, br s, OH), 2.50–2.70 (2H, m, 2-H_2), 4.27 (1H, m, 5-H), 4.37 and 4.50 (each 1H, d, J = 12, C*H*HPh), 4.89 (1H, t, J = 6.5, 1-H), 5.54 (1H, dd, J = 9, 11, 4-H), 5.65 (1H, dt, J = 11, 7, 3-H), 7.29–7.88 (12H, m, aromatic H)	350 (M^+ + 18, 12), 332 (M^+, 12), 207 (100)
28	3465, 3030, 1092, 736, 698	1.25 (6H, d, J = 6.5, 1-H_3 and 9-H_3), 1.62 (2H, m, 3-H_2), 2.10–2.30 (2H, m, 5-H_2), 2.83 (1H, d, J = 2, OH), 3.83 (1H, m, 2-H), 3.95 (1H, m, 4-H), 4.26 (1H, m, 8-H), 4.36, 4.44, 4.53 and 4.61 (each 1H, d, J = 12, C*H*HPh), 5.50 (1H, m, 7-H), 5.60 (1H, dt, J = 11, 7, 6-H), 7.30 (10H, m, aromatic H)	355 (M^+ + 1, 14), 337 (24), 247 (100)
29	3470, 3029, 1092, 736, 698	1.23–1.24 (6H, overlapping d, each J = 6.5, 1-H_3, 9-H_3), 1.61 (2H, m, 3-H_2), 2.17 (2H, m, 5-H_2), 3.80 (3H, m, 2-H, 4-H and OH), 4.27 (1H, m, 8-H), 4.35, 4.41, 4.53, and 4.65 (each 1H, d, J = 12, C*H*HPh), 5.49 (1H, m, 7-H), 5.60 (1H, dt, J = 11, 7, 6-H), 7.30 (10H, m, aromatic H)	355 (M^+ + 1, 28), 247 (100)
30	3450, 3030, 1093, 736, 698	0.87 (3H, d, J = 7, 2-CH_3), 1.22 (3H, d, J = 6.5, 8-H_3), 1.83 (1H, m, 2-H), 2.20 (2H, m, 4-H_2), 3.30 (1H, d, J = 3, OH), 3.39–3.58 (3H, m, 1-H_2 and 3-H), 4.25 (1H, m, 7-H), 4.35 (1H, d, J = 12, C*H*HPh), 4.48 (2H, s, C*H*$_2$Ph), 4.52 (1H, d, J = 12, C*H*HPh), 5.49 (1H, dd, J = 11, 9, 6-H), 5.66 (1H, dt, J = 11, 7, 5-H), 7.30 (10H, m, aromatic H)	355 (M^+ + 1, 12), 247 (100)
31	3458, 1093, 736, 698	0.93 (3H, d, J = 7, 2-CH_3), 1.25 (3H, d, J = 6.5, 8-H_3), 1.88 (1H, m, 2-H), 2.07–2.32 (2H, m, 4-H_2), 2.63 (1H, d, J = 3, OH), 3.50 (2H, m, 1-H_2), 3.81 (1H, m, 3-H), 4.28 (1H, m, 7-H), 4.38 (1H, d, J = 12, C*H*HPh), 4.50 (2H, s, CH_2Ph), 4.55 (1H, d, J = 12, C*H*HPh), 5.50 (1H, dd, J = 11, 9, 6-H), 5.63 (1H, dt, J = 11, 7, 5-H), 7.30 (10H, m, aromatic H)	372 (M^+ + 18, 1), 355 (M^+ + 1, 5), 196 (82), 91 (100)
32a	3451, 1074, 736, 698	1.09 (3H, d, J = 6.5, 1-H_3), 1.18 (3H, d, J = 6.5, 8-H_3), 1.62 (1H, br s, OH), 2.13 (2H, m, 4-H_2), 3.42 (1H, qd, J = 6.5, 4, 2-H), 3.64 (1H, m, 3-H), 4.2 (1H, m, 7-H), 4.31, 4.41, 4.47, and 4.53 (each 1H, d, J = 12, C*H*HPh), 5.44 (1H, dd, J = 11, 9, 6-H), 5.55 (1H, dt, J = 11, 7, 5-H), 7.21 (10H, m, aromatic H)	358 (M^+ + 18, 59), 233 (100)
32b	3432, 1257, 1088, 836, 776, 734, 697	0.07 and 0.08 (each 3H, s, SiMe), 0.90 (9H, s, $SiCMe_3$), 1.09 (3H, d, J = 6.5, 1-H_3), 1.28 (3H, d, J = 6.5, 8-H_3), 1.61 (1H, br s, OH), 2.18 (2H, m, 4-H_2), 3.51 (1H, m, 2-H), 3.77 (1H, m, 3-H), 4.30 (1H, m, 7-H), 4.40 and 4.58 (each 1H, d, J = 12, C*H*HPh), 5.52 (1H, dd, J = 11, 9, 6-H), 5.65 (1H, dt, J = 11, 7, 5-H), 7.23–7.33 (5H, m, aromatic H)	365 (M^+ + 1, 7), 73 (100)[b]
32c	3456, 1100, 1035, 919, 737, 698	1.15 (3H, d, J = 6.5, 1-H_3), 1.28 (3H, d, J = 6.5, 8-H_3), 2.20 (2H, m, 4-H_2), 2.45 (1H, br s, OH), 3.38 (3H, s, OMe), 3.66 (2H, m, 2-H and 3-H), 4.30 (1H, m, 7-H), 4.41 and 4.58 (each 1H, d, J = 12, C*H*HPh), 4.67 and 4.70 (each 1H, d, J = 7, OCH*H*O), 5.53 (1H, dd, J = 11, 9, 6-H), 5.68 (1H, dt, J = 11, 7, 5-H), 7.30 (5H, m, aromatic H)	295 (M^+ + 1, 1), 91 (100)[c]
33a	3450, 3064, 1073, 736, 698	1.17 (3H, d, J = 6.5, 1-H_3), 1.25 (3H, d, J = 6.5, 8-H_3), 2.23 (2H, m, 4-H_2), 2.40 (1H, br s, OH), 3.38–3.52 (2H, m, 2-H and 3-H), 4.28 (1H, m, 7-H), 4.38, 4.43, 4.55 and 4.65 (each 1H, d, J = 12, C*H*HPh), 5.51 (1H, dd, J = 11, 9, 6-H), 5.66 (1H, dt, J = 11, 7, 5-H), 7.30 (10H, m, aromatic H)	358 (M^+ + 18, 9), 281 (42), 233 (59), 91 (100)
33b	3473, 1072, 837, 777, 735, 697	0.08 and 0.09 (each 3H, s, SiMe), 0.90 (9H, s, $SiCMe_3$), 1.14 (3H, d, J = 6.5, 1-H_3), 1.27 (3H, d, J = 6.5, 8-H_3), 2.20 (2H, t, J = 6.5, 4-H_2), 3.32 (1H, q, J = 6.5, 3-H), 3.68 (1H, m, 2-H), 4.29 (1H, m, 7-H), 4.40 and 4.57 (each 1H, d, J = 12, C*H*HPh), 5.52 (1H, dd, J = 11, 9, 6-H), 5.68 (1H, dt, J = 11, 7, 5-H), 7.25–7.35 (5H, m, aromatic H)	365 (M^+ + 1, 5), 257 (34), 239 (42), 131 (100)[b]
33c	3455, 1100, 1036, 919, 737, 699	1.17 (3H, d, J = 6.5, 1-H_3), 1.28 (3H, d, J = 6.5, 8-H_3), 2.21 (2H, m, 4-H_2), 2.72 (1H, d, J = 2, OH), 3.39 (3H, s, OMe), 3.47 (1H, m, 3-H), 3.55 (1H, m, 2-H), 4.30 (1H, m, 7-H), 4.41 and 4.53 (each 1H, d, J = 12, C*H*HPh), 4.67 and 4.72 (each 1H, d, J = 7, OC*H*HO), 5.52 (1H, m, 6-H), 5.68 (1H, dt, J = 11, 7, 5-H), 7.30 (5H, m, aromatic H).	312 (M^+ + 18, 8), 295 (M^+ + 1, 13), 155 (100)

Table 4. (Continued)

Product	IR ν_{max} (cm^{-1})	^1H NMR ($CDCl_3$) δ, J (Hz)	MS m/z (%)
34a	3452, 1072, 736, 698	1.17 (3H, d, J = 6.5, 1-H_3), 1.28 (3H, d, J = 6.5, 8-H_3), 2.05 (1H, br s, OH), 2.22 (2H, t, J = 6.5, 4-H_2), 3.50 (1H, m, 2-H), 3.73 (1H, td, J = 6.5, 4, 3-H), 4.30 (1H, m, 7-H), 4.38, 4.50, 4.54 and 4.62 (each 1H, d, J = 12, C*H*HPh), 5.52 (1H, m, 6-H), 5.63 (1H, dt, J = 11, 7, 5-H), 7.30 (10H, m, aromatic H)	358 (M^+ + 18, 15), 341 (M^+ + 1, 2), 233 (100)
34b	3461, 1256, 1093, 837, 777, 736, 698	0.08 (6H, s, $SiMe_2$), 0.90 (9H, s, $SiCMe_3$), 1.08 (3H, d, J = 6.5, 1-H_3), 1.27 (3H, d, J = 6.5, 8-H_3), 1.58 (1H, br s OH), 2.18 (2H, m, 4-H_2), 3.50 (1H, m, 2-H), 3.78 (1H, m, 3-H), 4.32 (1H, m, 7-H), 4.40 and 4.54 (each 1H, d, J = 12, C*H*HPh), 5.52 (1H, dd, J = 11, 9, 6-H), 5.65 (1H, dt, J = 11, 7, 5-H), and 7.24–7.33 (5H, m, aromatic H)	365 (M^+ + 1, 4), 239 (43), 43 (100)[b]
34c	3464, 1100, 1036, 919, 737, 699	1.18 (3H, d, J = 6.5, 1-H_3), 1.31 (3H, d, J = 6.5, 8-H_3), 2.25 (2H, m, 4-H_2), 3.41 (3H, s, OMe), 3.70 (2H, m, 2-H and 3-H), 4.30 (1H, m, 7-H), 4.45 and 4.60 (each 1H, d, J = 12, C*H*HPh), 4.70 and 4.73 (each 1H, d, J = 7, OC*H*HO), 5.8 (1H, dd, J = 11, 9, 6-H), 5.69 (1H, dt, J = 11, 7, 5-H), and 7.30 (5H, m, aromatic H)	312 (M^+ + 18, 17), 295 (M^+ + 1, 26), 155 (100)

[a] All compounds except **17e** gave HRMS $m/z \pm 0.0014$.
[b] FAB.
[c] EI.

Table 5. Yields and Physical Data for Representative *O*-Acetylmandelates

Product	Yield (%)	IR ν_{max} (cm^{-1})	^1H NMR δ, J (Hz)	MS m/z (%)
6	82	3033, 1747, 1372, 1232, 1207, 1175, 1057, 739, 698	1.05 (3H, d, J = 7.5, 6-H_3), 2.19 (3H, s, CH_3CO), 2.54 and 2.68 (each 1H, m, 2-H), 4.11 (1H, m, 5-H), 4.27 and 4.46 (each 1H, d, J = 12, C*H*HPh), 5.48 (2H, m, 3-H and 4-H), 5.77 (1H, t, J = 7, 1-H), 6.00 (1H, s, C*H*OAc), 6.95 (2H, m), 7.18 (3H, m), 7.35 (10H, m, aromatic H)	476 (M^+ + 18, 69), 351 (35), 157 (100)
7[a]	85	3033, 1746, 1230, 1207, 1174, 1056, 737, 697	1.02 (3H, d, J = 7.5, 6-H_3), 2.19 (3H, s, CH_3CO), 2.49 (2H, m, 2-H_2), 4.02 (1H, m, 5-H), 4.15 and 4.36 (each 1H, d, J = 12, C*H*HPh), 5.28 (2H, m, 3-H and 4-H), 5.77 (1H, t, J = 7, 1-H), 6.00 (1H, s, C*H*OAc), 7.30 (10H, m, aromatic H), 7.40 (3H, m), 7.50 (2H, m)	476 (M^+ + 18, 16), 351 (18), 197 (14), 157 (100)
19d	86	1747, 1372, 1232, 1206, 1175, 1055, 741, 698	1.21 (3H, d, J = 6.5, 6-H_3), 2.22 (3H, s, CH_3CO), 2.80 (2H, t, J = 7, 2-H_2), 4.31 (1H, m, 5-H), 4.40 and 4.58 (1H, d, J = 12, C*H*HPh), 5.53 (2H, m, 3-H and 4-H), 5.92 (1H, t, J = 7, 1-H), 5.97 (1H, s, C*H*OAc), 6.14 (1H, d, J = 3), 6.29 (1H, dd, J = 3, 2), 7.30–7.42 (11H, m, aromatic H)	466 (M^+ + 18, 4), 147 (100)
20d	92	1747, 1372, 1231, 1206, 1175, 1055, 741, 698	1.10 (3H, d, J = 6.5, 6-H_3), 2.17 (3H, s, CH_3CO), 2.58 (2H, m, 2-H_2), 4.13 (1H, m, 5-H), 4.21 and 4.40 (1H, d, J = 12, C*H*HPh), 5.16 (1H, dt, J = 11, 7, 3-H), 5.30 (1H, dd, J = 11, 9, 4-H), 5.83 (1H, t, J = 7, 1-H), 5.91 (1H, s, CHOAc), 6.31 (2H, s, furyl H), 7.21–7.47 (11H, m, aromatic H)	466 (M^+ + 18, 5), 147 (100)
19f[b]	76	1746, 1372, 1233, 1211, 1179, 1058, 737, 698	0.71 (3H, t, J = 7.5, 1-H_3), 0.97 (2H, m, 2-H_2), 1.25 (3H, d, J = 7.5, 9-H_3), 1.39 (2H, m, 3-H_2), 2.20 (3H, s, $COCH_3$), 2.34 (2H, m, 5-H_2), 4.27 (1H, m, 8-H), 4.38 and 4.56 (each 1H, d, J = 12, C*H*HPh), 4.91 (1H, m, 4-H), 5.51 (2H, m, 6-H and 7-H), 5.88 (1H, s, C*H*OAc), 7.25–7.50 (10H, m, aromatic H)	442 (M^+ + 18, 17), 317 (76), 123 (100)
20f[b]	59	1746, 1372, 1233, 1211, 1179, 1058, 737, 698	0.90 (3H, t, J = 7.5, 1-H_3), 1.18 (3H, d, J = 7.5, 9-H_3), 1.31 and 1.51 (each 2H, m), 2.18 (2H, t, J = 7, 5-H_2), 2.20 (3H, s, CH_3CO), 4.12 (1H, m, 8H), 4.21 and 4.42 (each 1H, d, J = 12, C*H*HPh), 4.92 (1H, m, 4-H), 5.17 and 5.29 (each 1H, m, 6-H, 7-H), 5.88 (1H, s, C*H*OAc), 7.25–7.50 (10H, m, aromatic H)	442 (M^+ + 18, 18), 317 (93), 123 (100)
19g[b]	86	1746, 1371, 1233, 1210, 1179, 1058, 737, 698	0.60 and 0.62 (each 3H, d, J = 6.5, CH*Me*), 1.24 (3H, d, J = 6.5, 8-H_3), 1.59 (1H, m, 2-H), 2.20 (3H, s, CH_3CO), 2.30 (2H, m, 4-H_2), 4.28 (1H, m, 7-H), 4.38 and 4.58 (each 1H, d, J = 12, C*H*HPh), 4.79 (1H, dt, J = 7.5, 5, 3-H), 5.51 (2H, m, 5-H and 6-H), 5.91 (1H, s, CHOAc), 7.21–7.48 (10H, m, aromatic H)	442 (M^+ + 18, 19), 317 (90), 123 (100)
20g[b]	93	1746, 1372, 1234, 1210, 1179, 1056, 738, 698	0.89 (6H, d, J = 6.5, CHMe_2), 1.16 (3H, d, J = 6.5, 8-H_3), 1.83 (1H, m, 2-H), 2.12 (2H, t, J = 6.5, 4-H_2), 2.19 (3H, s, CH_3CO), 4.09 (1H, m, 7-H), 4.16 and 4.38 (each 1H, d, J = 12, C*H*HPh), 4.77 (1H, q, J = 6, 3-H), 5.10 (1H, dt, J = 11, 7, 5-H), 5.23 (1H, dd, J = 11, 9, 6-H), 5.90 (1H, s, C*H*OAc), 7.20–7.49 (10H, m, aromatic H)	442 (M^+ + 18, 9), 317 (60), 123 (100)
19i[b]	79	1752, 1372, 1231, 1203, 1173, 1053, 738, 698	1.23 (3H, d, J = 6.5, 7-H_3), 2.20 (3H, s, CH_3CO), 2.60 (2H, m, 3-H_2), 3.58 (3H, s, OMe), 4.22 (1H, m, 6-H), 4.32 and 4.52 (each 1H, d, J = 12, C*H*HPh), 5.11 (1H, dd, J = 7.5, 2-H), 5.52 (2H, m, 4-H and 5-H), 5.98 (1H, s, C*H*OAc), 7.22–7.50 (10H, m, aromatic H)	458 (M^+ + 18, 90), 333 (100)

Table 5. (Continued)

Product	Yield (%)	IR ν_{max} (cm^{-1})	^1H NMR δ, J (Hz)	MS m/z (%)
20i[b]	85	1752, 1372, 1229, 1137, 1086, 740, 699	1.22 (3H, d, J = 6.5, 7-H_3), 2.21 (3H, s, CH_3CO), 2.60 (2H, m, 3-H_2), 3.76 (3H, s, OMe), 4.21 (1H, m, 6-H), 4.32 and 4.49 (each 1H, d, J = 12, C*H*HPh), 5.11 (1H, dd, J = 7, 5, 2-H), 5.33 (1H, dt, J = 11, 7, 4-H), 5.49 (1H, dd, J = 11, 9, 5-H), 6.10 (1H, s, C*H*OAc), 7.30–7.55 (10H, m, aromatic H)	458 (M^+ + 18, 100)
35[b]	86	1745, 1373, 1233, 1210, 1178, 1060, 738, 698	1.00 (3H, d, J = 6.5, 1-H_3), 1.25 (3H, d, J = 6.5, 9-H_3), 1.60 (2H, m, 3H_2), 2.20 (3H, s, CH_3CO), 2.40 (2H, m, 5-H_2), 2.97 (1H, m, 2-H), 3.82 and 4.19 (each 1H, d, J = 12, C*H*HPh), 4.28 (1H, m, 8-H), 4.36 and 4.54 (each 1H, d, J = 12, C*H*HPh), 5.24 (1H, m, 4-H), 5.53 (2H, m, 6-H and 7-H), 5.90 (1H, s, C*H*OAc), 7.20–7.50 (15H, m, aromatic H)	548 (M^+ + 18, 6), 529 (M^+ − 1, 12), 91 (100)[c]
36[b]	77	1743, 1372, 1233, 1209, 1178, 1059, 737, 697	1.17 (3H, d, J = 6.5, 1-H_3), 1.21 (3H, d, J = 6.5, 9-H_3), 1.70 (2H, t, J = 6.5, 3-H_2), 2.18 (2H, m, 5-H_2), 2.20 (3H, s, CH_3CO), 3.61 (1H, sex, J = 6.5, 2-H), 4.10 (1H, dq, J = 9, 6.5, 8-H), 4.20, 4.32, 4.40 and 4.49 (each 1H, d, J = 12, C*H*HPh), 5.19 (1H, dt, J = 11.5, 7, 6-H), 5.27–5.37 (2H, m, 4-H and 7-H), 5.90 (1H, s, C*H*OAc), 7.31–7.52 (15H, m, aromatic H)	548 (M^+ + 18, 29), 229 (46), 106 (100)
37[b]	75	1745, 1373, 1232, 1209, 1178, 1059, 737, 697	0.98 (3H, d, J = 6.5, 1-H_3), 1.23 (3H, d, J = 6.5, 9-H_3), 1.51 (1H, ddd, J = 14, 7.5, 5, 3-H), 1.86 (1H, m, 3-H), 2.18 (3H, s, CH_3CO), 2.37 (2H, m, 5-H_2), 3.05 (1H, sex, J = 6.5, 2-H), 4.13 (1H, d, J = 12, C*H*HPh), 4.22 (1H, m, 8-H), 4.28, 4.35, and 4.54 (each 1H, d, J = 12, C*H*HPh), 5.02 (1H, m, 4-H), 5.50 (2H, m, 6-H and 7-H), 5.85 (1H, s, C*H*OAc), 7.21–7.48 (15H, m, aromatic H)	548 (M^+ + 18, 66), 229 (100)
38[b]	83	1745, 1373, 1233, 1210, 1178, 1059, 737, 698	1.14 (3H, d, J = 6.5, 1-H_3), 1.21 (3H, d, J = 6.5, 9-H_3), 1.63 and 2.01 (each 1H, m, 3-H), 2.18 (2H, m, 5-H_2), 2.20 (3H, s, CH_3CO), 3.55 (1H, sex, J = 6.5, 2-H), 4.05 (1H, m, 8-H), 4.19, 4.37, 4.39, and 4.54 (each 1H, d, J = 12, C*H*HPh), 5.04 (1H, m, 4-H), 5.17 (1H, dt, J = 11, 7, 6-H), 5.30 (1H, m, 7-H), 5.85 (1H, s, CHOAc), 7.23–7.48 (15H, m, aromatic H)	548 (M^+ + 18, 54), 229 (100)
39[b]	61	1745, 1371, 1232, 1210, 1178, 1059, 737, 698	0.71 (3H, d, J = 6.5, 2-Me), 1.23 (3H, d, J = 6.5, 8-H_3), 1.96 (1H, m, 2-H), 2.13 (3H, s, CH_3CO), 2.38 (2H, t, J = 6, 4-H_2), 2.97 (1H, m, 1-H), 3.11 (1H, dd, J = 9.5, 5.5, 1′-H), 4.20 (2H, s, CH_2Ph) 4.24 (1H, m, 7-H), 4.36 and 4.55 (each 1H, d, J = 12, C*H*HPh), 4.98 (1H, q, J = 6, 3-H), 5.52 (2H, m, 5-H and 6-H), 5.89 (1H, s, C*H*OAc), 7.21–7.48 (15H, m, aromatic H)	548 (M^+ + 18, 19), 91 (100)
40[b]	67	1745, 1372, 1233, 1210, 1178, 1088, 737, 698	0.93 (3H, d, J = 6.5, 2-Me), 1.13 (3H, d, J = 6.5, 8-H_3), 2.11 (1H, m, 2-H), 2.16 (3H, s, CH_3CO), 2.20 (2H, m, 4-H_2), 3.30 and 3.41 (each 1H, dd, J = 9, 6, 1-H), 4.08 (1H, m, 7-H), 4.16, 4.38, 4.41 and 4.45 (each 1H, d, J = 12, C*H*HPh), 4.99 (1H, m, 3-H), 5.11 and 5.21 (each 1H, m, 5-H, 6-H), 5.88 (1H, s, C*H*OAc), 7.21–7.49 (15H, m, aromatic H)	548 (M^+ + 18, 28), 229 (100)
41[b]	72	1745, 1327, 1233, 1210, 1179, 1088, 1060, 738, 698	0.72 (3H, d, J = 7, 2-Me), 1.23 (3H, d, J = 6.5, 8-H_3), 1.89 (1H, m, 2-H), 2.20 (3H, s, CH_3CO), 2.25–2.52 (2H, m, 4-H_2), 2.79 (1H, t, J = 9, 1-H), 2.97 (1H, dd, J = 9, 6.5, 1′-H), 4.13 and 4.19 (each 1H, d, J = 12, C*H*HPh), 4.25 (1H, m, 7-H), 4.36 and 4.55 (each 1H, d, J = 12, C*H*HPh), 5.17 (1H, m, 3-H), 5.49 (2H, m, 5-H and 6-H), 5.90 (1H, s, C*H*OAc), 7.15–7.49 (15H, m, aromatic H)	548 (M^+ + 18, 12), 229 (54), 106 (100)
42[b]	76	1744, 1371, 1233, 1209, 1178, 1058, 737, 698	0.92 (3H, d, J = 7, 2-Me), 1.13 (3H, d, J = 6.5, 8-H_3), 1.95 (1H, m, 2-H), 2.14 (2H, m, 4-H_2), 2.17 (3H, s, CH_3CO), 3.20 (2H, d, J = 7, 1-H_2), 4.07 (1H, m, 7-H), 4.15, 4.33, 4.35 and 4.43 (each 1H, d, J = 12, C*H*HPh), 5.06–5.26 (3H, m, 3-H, 5-H, 6-H), 5.86 (1H, s, C*H*OAc), 7.36–7.48 (15H, m, aromatic H)	548 (M^+ + 18, 10), 229 (91), 91 (100)
43a[b]	90	1746, 1372, 1232, 1209, 1179, 1057, 737, 698	0.91 (3H, d, J = 6.5, 1-H_3), 1.22 (3H, d, J = 6.5, 8-H_3), 2.16 (3H, s, CH_3CO), 2.40 (2H, m, 4-H_2), 3.41 (1H, dq, J = 4, 6.5, 2-H), 4.18–4.26 (3H, m, 7-H and CH_2Ph), 4.34 and 4.54 (each 1H, d, J = 12, C*H*HPh), 5.00 (1H, m, 3-H), 5.50 (2H, m, 5-H and 6-H), 5.89 (1H, s, C*H*OAc), 7.07–7.46 (15H, m, aromatic H)	534 (M^+ + 18, 35), 91 (100)
44a[b]	82	1746, 1372, 1233, 1209, 1179, 1088, 736, 697	1.18 (3H, d, J = 6.5, 1-H_3), 1.20 (3H, d, J = 6.5, 8-H_3), 2.20 (3H, s, CH_3CO), 2.33 (2H, t, J = 6.5, 4-H_2), 3.66 (1H, m, 2-H), 4.12 (1H, m, 7-H), 4.18 and 4.39 (each 1H, d, J = 12, C*H*HPh), 4.54 (2H, s, CH_2Ph), 4.95 (1H, m, 3-H), 5.13 (1H, dt, J = 11, 7, 5-H), 5.24 (1H, dd, J = 11, 9, 6-H), 5.90 (1H, s, C*H*OAc), 7.19–7.49 (15H, m, aromatic H)	534 (M^+ + 18, 8), 106 (100)
45a[b]	93	1746, 1372, 1232, 1209, 1179, 1057, 737, 698	0.84 (3H, d, J = 6.5, 1-H_3), 1.23 (3H, d, J = 6.5, 8-H_3), 2.19 (3H, s, CH_3CO), 2.42 (2H, m, 4-H_2), 3.48 (1H, m, 2-H), 4.27 (1H, m, 7-H), 4.28, 4.35, 4.41 and 4.56 (each 1H, d, J = 12, C*H*HPh), 4.99 (1H, m, 3-H), 5.50 (2H, m, 5-H and 6-H), 5.92 (1H, s, C*H*OAc), 7.16–7.50 (15H, m, aromatic H)	534 (M^+ + 18, 31), 91 (100)
46a[b]	85	1746, 1372, 1233, 1209, 1179, 1056, 737, 698	1.15 (3H, d, J = 6.5, 1-H_3), 1.20 (3H, d, J = 6.5, 8-H_3), 2.20 (3H, s, CH_3CO), 2.26 (2H, m, 4-H_2), 3.67 (1H, m, 2-H), 4.12 (1H, m, 7-H), 4.18, 4.38, 4.49 and 4.61 (each 1H, d, J = 12, C*H*HPh), 4.99 (1H, m, 3-H), 5.09 (1H, dt, J = 11, 7, 5-H), 5.23 (1H, dd, J = 11, 9, 6-H), 5.92 (1H, s, C*H*OAc), 7.22–7.51 (15H, m, aromatic H)	534 (M^+ + 18, 32), 91 (100)

Table 5. (Continued)

Product	Yield (%)	IR ν_{max} (cm^{-1})	^1H NMR δ, J (Hz)	MS m/z (%)
47a[b]	92	1745, 1372, 1232, 1209, 1178, 1064, 737, 699	1.10 (3H, d, J = 6.5, 1-H_3), 1.16 (3H, d, J = 6.5, 8-H_3), 2.19 (3H, s, CH_3CO), 2.32 (2H, m, 4-H_2), 3.64 (1H, m, 2-H), 4.12 (1H, m, 7-H), 4.24 and 4.45 (each 1H, d, J = 12, C*H*HPh), 4.53 (2H, s, CH_2Ph), 4.95 (1H, m, 3-H), 5.12 (1H, dt, J = 11, 7, 5-H), 5.25 (1H, dd, J = 11, 9, 6-H), 5.88 (1H, s, C*H*OAc), 7.22–7.50 (15H, m, aromatic H)	534 (M^+ + 18, 5), 91 (100)
48a[b]	82	1746, 1372, 1232, 1209, 1179, 1060, 737, 698	0.91 (3H, d, J = 6.5, 1-H_3), 1.28 (3H, d, J = 6.5, 8-H_3), 2.18 (3H, s, CH_3CO), 2.41 (2H, m, 4-H_2), 3.41 (1H, m, 2-H), 4.23 and 4.28 (each 1H, d, J = 12, C*H*HPh), 4.29 (1H, m, 7-H), 4.34 and 4.54 (each 1H, d, J = 12, C*H*HPh), 5.00 (1H, m, 3-H), 5.52 (2H, m, 5-H and 6-H), 5.92 (1H, s, CHOAc), 7.13–7.51 (15H, m, aromatic H)	534 (M^+ + 18, 96), 91 (100)

[a] Mp 85 °C; C, H, N ± 0.3 %.
[b] HRMS m/z ± 0.0035.
[c] FAB.

films. Mass spectra were recorded on a Kratos Concept mass spectrometer using chemical ionisation (NH_3) unless otherwise stated. Melting points were determined on a Koffler block apparatus, and are uncorrected. Optical rotations were measured on an Optical Activity AA100 polarimeter.

Chromatography refers to flash chromatography using Merck silica gel 60 H (40–63 mm^3; 230–400 mesh) or May and Baker Sorbsil C60 silica gel (40–60 mm^3). Light petroleum refers to the fraction which distills at 40–60 °C. All nonaqueous reactions were carried out under argon.

1-Substituted (3*Z*)-5-Benzyloxy-3-hexenols 4, 17a–j, 28–34; General Procedure:
A cooled solution of tin(IV) chloride (28 mg, 0.108 mmol) in anhydr. CH_2Cl_2 (0.3–0.5 mL) was added dropwise to a solution of the (4-benzyloxypent-2-enyl)tributylstannane (**1**) (50 mg, 0.108 mmol) in anhydr. CH_2Cl_2 (3 mL) at − 78 °C, and the mixture stirred for 5 min. A cooled solution of the aldehyde (0.108 mmol) in CH_2Cl_2 was then added, and the mixture stirred at − 78 °C for 1 h. Sat. aq $NaHCO_3$ was added, the mixture was allowed to warm to r.t. and was then extracted with CH_2Cl_2. The organic extracts were combined and washed twice with water and brine, and dried ($MgSO_4$). After concentration under reduced pressure, flash chromatography of the residue, using Et_2O–light petroleum (1:3) as eluant, gave the products as colourless oils. Spectroscopic data are listed in Table 4. Product ratios were obtained by analysis of samples of the crude reaction products before chromatography, and are given in Tables 1 and 3.

Acetylmandelates 6, 7, 19, 20, 35–48; General Procedure:
(*R*)- or (*S*)-*O*-Acetylmandelic acid (2 mol equiv) and DMAP (2 mg) were added to a solution of the alcohol (typically 20 mg) in anhydr. CH_2Cl_2 (ca. 0.25 mL) followed by a solution of DCC (2 mol equiv) in anhydr. CH_2Cl_2 (ca. 0.25 mL) at 0 °C. After being stirred for 5 min, the reaction mixture was allowed to warm to r.t. and stirred for 24 h. The mixture was then filtered, the filtrate washed with hexane, and the combined organic extracts washed with aqueous HCl (1 N) and sat. aq $NaHCO_3$, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue using Et_2O – light petroluem (1:2) as eluant gave the acetylmandelate (Tables 2 and 5).

(1*R*,5*S*,3*Z*)-1-Acetoxy-5-benzyloxy-1-phenyl-3-hexene (8):
Ac_2O (72 mg, 7.10 mmol), Et_3N (179 mg, 17.73 mmol) and DMAP (2 mg, 0.002 mmol) were added to a solution of the alcohol **4** (100 mg, 3.55 mmol) in anhydr. CH_2Cl_2 at 0 °C. The mixture was allowed to warm to r.t., and was stirred for 4 h before being poured into water (5 mL). The mixture was extracted with CH_2Cl_2 (2 × 100 mL), and the combined organic extracts were washed with aq HCl (1 N; 2 × 10 mL), water (15 mL), and brine (2 × 10 mL). After drying ($MgSO_4$), the extracts were concentrated under reduced pressure, and the residue was purified by chromatography using Et_2O–light petroleum (1:3) as eluant to give the acetate **8** (114 mg, 98 %) as an oil.

$C_{21}H_{28}NO_3$ calc. M, 342.2069. Found: M + NH_4^+, 342.2055.
IR: ν = 1737, 1371, 1235, 1074, 1026, 737, 698 cm^{-1}.
MS: m/z (%) = 342 (M^+ + 18, 43), 217 (27), 197 (33), 157 (100).
^1H NMR: δ = 1.09 (3H, d, J = 7.5, 6-H_3), 2.08 (3H, s, CH_3CO), 2.55 and 2.69 (each 1H, m, 2-H), 4.18 (1H, m, 5-H), 4.31 and 4.49 (each 1H, d, J = 12, C*H*HPh), 5.49 (2H, m, 3-H and 4-H), 5.79 (1H, t, J = 6, 1-H), 7.31 (10H, m, aromatic H).

(2*S*,3*S*)-2-Benzyloxy-5-hexen-3-yl Acetate (51):
Following the above procedure, Ac_2O (62 mg, 0.612 mmol), Et_3N (154 mg, 1.53 mmol), DMAP (3 mg, 0.025 mmol) and the alcohol **49** (63 mg, 0.306 mmol) gave the acetate **51** (69 mg, 91 %) as an oil. $[\alpha]_D$ + 12.8 (c = 1, $CHCl_3$).
IR: ν = 1738, 1643, 1376, 1240, 1072, 1028, 917, 737, 698 cm^{-1}
MS: m/z = 266 (M^+ + 18, 100).
^1H NMR: δ = 1.17 (3H, d, J = 6.5, 1-H_3), 2.06 (3H, s, CH_3CO), 2.28–2.50 (2H, m, 4-H_2), 3.62 (1H, qd, J = 6.5, 4.5, 2-H), 4.50 and 4.64 (each 1H, d, J = 12, C*H*HPh), 4.96–5.10 (3H, m, 6-H_2 and 3-H), 5.72 (1H, ddt, J = 17.5, 10, 7, 5-H), 7.32 (5H, m, aromatic H).

(2S,3R)-2-Benzyloxy-5-hexen-3-yl Acetate (52):
Following the above procedure, Ac_2O (43 mg, 0.417 mmol), Et_3N (105 mg, 1.04 mmol), DMAP (3 mg, 0.025 mmol) and the alcohol **50** (43 mg, 0.209 mmol) gave the acetate **52** (40 mg, 77 %) as an oil. $[\alpha]_D$ − 7.6 (c = 1, $CHCl_3$)
IR: ν = 1739, 1643, 1375, 1240, 1068, 1028, 736, 698 cm^{-1}.
MS: m/z = 266 (M^+ + 18, 70), 249 (100).
^1H NMR: δ = 1.21 (3H, d, J = 6.5, 1-H_3), 2.10 (3H, s, CH_3CO), 2.40 (2H, m, 4-H_2), 3.62 (1H, qd, J = 6.5, 4.5, 2-H), 4.58 (2H, s, CH_2Ph), 5.06 (3H, m, 6-H_2 and 3-H), 5.75 (1H, ddt, J = 17, 10, 7, 5-H), 7.34 (5H, m, aromatic H).

(2*S*,6*R*,7*R*,3*Z*)-6-Acetoxy-2,7-dibenzyloxyoct-3-ene (55):
Following the above procedure, the alcohol **33a** (100 mg, 0.275 mmol) was acetylated using Ac_2O (56 mg, 0.550 mmol), Et_3N (139 mg, 1.38 mmol), and DMAP (3 mg, 0.025 mmol) to give the acetate **55** (100 mg, 95 %). $[\alpha]_D$ − 27.9 (c = 1, $CHCl_3$).
$C_{24}H_{34}NO_4$ calc. M, 400.2488. Found: M + NH_4, 400.2488.
IR: ν = 1738, 1374, 1239, 1094, 1029, 736, 698 cm^{-1}.
MS: m/z = 400 (M^+ + 18, 89), 275 (100).
^1H NMR: δ = 1.19 (3H, d, J = 6.5, 8-H_3), 1.27 (3H, d, J = 6.5, 1-H_3), 2.05 (3H, s, CH_3CO), 2.40 (2H, m, 5-H_2), 3.64 (1H, m,

7-H), 4.30 (1 H, m, 2-H), 4.38, 4.51, 4.54 and 4.67 (each 1 H, d, $J = 12$, C*H*HPh), 5.01 (1 H, m, 6-H), 5.50 (2 H, m, 3-H and 4-H), 7.31 (5 H, m, aromatic).

(2*S*,6*R*,7*S*,3*Z*)-6-Acetoxy-2,7-dibenzyloxyoct-3-ene (56):
Following the above procedure, the alcohol **32a** (114 mg, 0.313 mmol) was acetylated using Ac_2O (64 mg, 0.626 mmol), Et_3N (158 mg, 1.57 mmol), and DMAP (3 mg, 0.025 mmol), to give the acetate **56** (101 mg, 84 %). $[\alpha]_D$ − 10.2 ($c = 1$, $CHCl_3$).

$C_{24}H_{34}NO_4$ calc. M, 400.2488. Found M + NH_4, 400.2481.

IR: ν = 1738, 1372, 1237, 1094, 1028, 736, 698 cm^{-1}.

MS: m/z = 400 (M^+ + 18, 48), 275 (100).

^{1}H NMR: δ = 1.18 (3 H, d, $J = 6.5$, 8-H_3), 1.23 (3 H, d, $J = 6.5$, 1-H_3), 2.04 (3 H, s, CH_3CO), 2.28–2.52 (2 H, m, 5-H_2), 3.60 (1 H, 2d, $J = 6.5$, 4.5, 7-H), 4.28 (1 H, m, 2-H), 4.35 and 4.53 (each 1 H, d, $J = 12$, C*H*HPh), 4.55 (2 H, s, CH_2Ph), 5.03 (1 H, m, 6-H), 5.45–5.58 (2 H, m, 3-H and 4-H), 7.31 (5 H, m, aromatic H).

(3*R*)-3-Acetoxy-3-phenylpropan-1-ol (9):
Ozonolysed air was bubbled through a solution of the acetate **8** (109 mg, 0.336 mmol) in $CHCl_3$ (8 mL) at − 60 °C for 30 min. Air was then blown through the solution for 10 min, and dimethyl sulfide (208 mg, 3.36 mmol) was added. The mixture was allowed to warm to r. t., and was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (5 mL) and a solution of $NaBH_4$ (53 mg, 1.32 mmol) in aq EtOH (3 mL) was added at 0 °C. The mixture was stirred for 2 h at 20 °C, and acidified by the addition of aq HCl (1 N; 3 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by chromatography using Et_2O–light petroleum as eluant (1 : 1) to give the alcohol **9** (30 mg, 47 %), as a colourless oil. $[\alpha]_D$ + 79.2 ($c = 1$, $CHCl_3$).

$C_{11}H_{14}O_3$ calc. M, 194.0943. Found: M, 194.0938.

IR: ν = 3426, 3034, 1736, 1374, 1239, 1048, 1027, 760, 701 cm^{-1}.

MS: m/z = 212 (M^+ + 18, 4), 177 (58), 152 (100), 117 (76).

^{1}H NMR: δ = 2.0–2.2 (3 H, m, 2-H_2 and OH), 2.10 (3 H, s, CH_3CO), 3.62 (2 H, t, $J = 7.5$, 1-H_2), 5.95 (1 H, dd, $J = 7.5$, 9, 3-H), 7.31 (5 H, m, aromatic H).

(2S)-2-Benzyloxypropan-1-ol **10** (54 mg, 97 %) was also isolated as a colourless oil: $[\alpha]_D$ + 44.83 ($c = 6.4$, $CHCl_3$).

(2*S*,3*S*)-5-Acetoxy-2-benzyloxypentan-3-ol (53):
Following the above procedure, ozonolysis of the acetate **51** (65 mg, 0.262 mmol) gave the hydroxyacetate **53** (46 mg, 70 %), as a colourless oil. $[\alpha]_D$ + 4.8 ($c = 1$, $CHCl_3$).

IR: ν = 3451, 1738, 1369, 1245, 1073, 738, 699 cm^{-1}.

MS: m/z = 270 (M^+ + 18, 53), 253 (100).

^{1}H NMR: δ = 1.21 (3 H, d, $J = 6.5$, 1-H_3), 1.68–1.88 (2 H, m, 4-H_2), 2.05 (3 H, s, CH_3CO), 2.70 (1 H, br s, OH), 3.41 (1 H, m, 2-H), 3.57 (1 H, m, 3-H), 4.24 (2 H, m, 5-H_2), 4.44 and 4.68 (each 1 H, d, $J = 12$, C*H*HPh), and 7.31 (5 H, m, aromatic H).

(2*S*,3*R*)-5-Acetoxy-2-benzyloxypentan-3-ol (54):
Following the above procedure, ozonolysis of acetate **52** (36 mg, 0.145 mmol) gave the hydroxyacetate **54** (25 mg, 68 %). $[\alpha]_D$ + 40.1 ($c = 1$, $CHCl_3$).

IR: ν = 3459, 1737, 1370, 1245, 1049, 740, 700 cm^{-1}.

MS: m/z = 270 (M^+ + 18, 55), 253 (100).

^{1}H NMR: δ = 1.19 (3 H, d, $J = 6.5$, 1-H_3), 1.65–1.87 (2 H, m, 4-H_2), 2.05 (3 H, s, CH_3CO), 2.25 (1 H, br s, OH), 3.53 (1 H, qd, $J = 6.5$, 4, 2-H), 3.80 (1 H, dt, $J = 10$, 3.5, 3-H), 4.24 (2 H, m, 5-H_2), 4.50 and 4.63 (each 1 H, d, $J = 12$, C*H*HPh), and 7.30 (5 H, m, aromatic H).

Ozonolysis of Acetate 55:
Following the above procedure, the acetate **55** (95 mg, 0.249 mmol) gave the hydroxyacetate ent-**53** (43 mg, 69 %), $[\alpha]_D$ − 14.8 ($c = 1$, $CHCl_3$), with spectroscopic data identical with those of its enantiomer **53** prepared by ozonolysis of acetate **51**.

$C_{14}H_{21}O_4$ calc. M, 253.1440. Found M + H, 253.1442.

Ozonolysis of Acetate 56:
Following the above procedure, the acetate **56** (86 mg, 0.225 mmol) gave the hydroxyacetate **54** (36 mg, 65 %); $[\alpha]_D$ + 40.4 ($c = 1$, $CHCl_3$) with spectroscopic data identical with those of a sample prepared by ozonolysis of acetate **52**.

$C_{14}H_{21}O_4$ calc. M, 253.1440. Found M + H, 253.1430.

(1*R*)-1-Phenyl-3-tert-butyldimethylsilyloxypropan-1-ol (11):
From Acetoxyalcohol **9**: Imidazole (21 mg, 0.31 mmol) and *tert*-butyldimethylsilyl chloride (28 mg, 0.186 mmol) were added to a solution of the alcohol **9** (24 mg, 0.124 mmol) in anhydr. DMF (2 mL) at 0 °C and the mixture stirred for 12 h at 20 °C. Water (15 mL) and CH_2Cl_2 (20 mL) were added, and the organic layer separated, washed with water (2 × 10 mL), and dried ($MgSO_4$). After concentration under reduced pressure, the residue was purified by chromatography using Et_2O–light petroleum (1 : 10) as eluant to give (1*R*)-1-acetoxy-3-*tert*-butyldimethylsilyloxypropane (30 mg, 79 %) as a colourless oil.

IR: ν = 1742, 1235, 1102, 834, 777, 699 cm^{-1}.

MS: m/z = 266 (M^+ − 43, 100), 117 (92).

^{1}HNMR: δ = 0.00 [6 H, s, $Si(CH_3)_2$], 0.86 [9 H, s, $SiC(CH_3)_3$], 1.95 and 2.10 (each 1 H, m, 2-H), 2.02 (3 H, s, CH_3O), 3.69 (2 H, m, 3-H_2), 5.86 (1 H, dd, $J = 6$, 7.5, 1-H), 7.31 (5 H, m, aromatic H).

Aqueous K_2CO_3 (0.12 N, 0.8 mL) was added to a solution of this acetate (30 mg, 0.097 mmol) in MeOH (4 mL), and the mixture stirred for 2 h at 20 °C. EtOAc (10 mL) and water (10 mL) were added, and the aqueous layer extracted with more EtOAc (2 × 5 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by chromatography using Et_2O–light petroleum (1 : 10) as eluant to give the silyloxypropanol **11** (23 mg, 95 %) as a colourless oil; $[\alpha]_D$ + 27.4 ($c = 0.76$, $CHCl_3$) [lit.[9] + 24.7 ($c = 0.76$, $CHCl_3$).

From Cinnamyl Alcohol: Activated, powered 4 Å molecular sieves (400 mg), titanium(IV) isopropoxide (106 mg, 0.373 mmol) and *t*-BuOOH (6.0 M in CH_2Cl_2; 2.49 mL) were added to a solution of L-(+)-diisopropyl tartrate (131 mg, 0.560 mmol) in CH_2Cl_2 (70 mL) at − 20 °C. The mixture ws stirred at − 20 °C for 1 h, and a solution of freshly distilled cinnamyl alcohol (1.0 g, 7.46 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 1 h. The reaction mixture was stirred at − 20 °C for 3 h, and NaOH in brine (10 %; 5.6 mL) and Et_2O (8 mL) were added. After allowing the mixture to warm to 10 °C, $MgSO_4$ (5.6 g) and Celite were added, and the mixture stirred for 15 min. The solids were removed by filtration and the filtrate concentrated under reduced pressure. Toluene was added to the residue, and removed under reduced pressure to leave the epoxy alcohol **12** (840 mg, 75 %) which was crystallised from Et_2O–light petroleum, mp 51 °C (lit. 51.5–53 °C); $[\alpha]_D^{26}$ − 47.3 ($c = 2.4$, $CHCl_3$) [lit.[10] − 49.6 ($c = 2.4$, $CHCl_3$)].

Red-Al (3.4 M in toluene; 0.86 mL, 2.94 mmol) was added dropwise to a solution of the epoxide **12** (400 mg, 2.67 mmol) in DME (15 mL) at 0 °C. The reaction mixture was stirred at 20 °C for 3 h, diluted with Et_2O (10 mL), and aq HCl (5 %; 2 mL) was added. After 30 min, the mixture was filtered, and the filtrate extracted with EtOAc. The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to leave a pale yellow oil identified as (1*R*)-1-phenylpropane-1,3-diol (382 mg, 94 %). $[\alpha]_D$ + 49.6 ($c = 1$, $CHCl_3$).

IR: ν = 3349, 1050, 752, 701 cm^{-1}.

MS: m/z = 170 (M^+ + 18, 26), 152 (100).

^{1}H NMR: δ = 2.0 (2 H, m, 2-H_2), 2.52 (2 H, br s, 2 × OH), 3.88 (2 H, t, $J = 5.5$, 3-H_2), 4.98 (1 H, dd, $J = 8.5$, 4, 1-H), 7.3 (5 H, m, aromatic H).

This diol (2.09 mg, 1.51 mmol) was silylated using *tert*-butyldimethylsilyl chloride (288 mg, 1.5 mmol) using the procedure outlined above to give the mono-*tert*-butyldimethylsilyl ether **11** (277 mg, 76 %) with spectroscopic data identical with those of a sample prepared from the alkoxy alcohol **9**; $[\alpha]_D$ + 31.5 ($c = 0.76$, $CHCl_3$).

5-Benzyloxy-1-phenyl-3-hexyn-1-ol (15):
Butyllithium (1.52 M in hexane; 8.36 mL, 12.5 mmol) was added dropwise to a solution of 3-benzyloxybut-1-yne **(14)** (2.01 g, 12.5 mmol) in anhydr. THF (35 mL) at −78 °C. After 20 min, BF_3–Et_2O (1.78 g, 12.5 mmol) was added followed, after 15 min, by a solution of styrene oxide **(13)** (1.66 g, 13.8 mmol) in anhydr. THF (8 mL). After 1.5 h at −78 °C, sat. aq $NaHCO_3$ (2 mL) was added, the mixture allowed to warm to r.t. and added to water (20 mL). The mixture was extracted with Et_2O (2 × 25 mL), and the combined organic extracts were washed with brine (25 mL) and dried ($MgSO_4$). Concentration under reduced pressure gave an oil which was separated by chromatography using Et_2O–light petroleum (1:1) as eluant to give 5-benzyloxy-1-phenyl-3-hexyn-1-ol **(15)** (714 mg, 20%) as an oil.

$C_{19}H_{24}NO_2$ calc. M, 298.1807. Found: M + NH_4, 298.1806.

IR: ν = 3425, 3031, 1372, 1162, 1085, 1050, 740, 699 cm^{-1}.

MS: m/z = 298 (M^+ + 18, 100).

^1H NMR: δ = 1.44 (3 H, d, J = 7.5, 6-H_3), 2.32 (1 H, d, J = 2.5, OH), 2.71 (2 H, d, J = 7.5, 2-H_2), 4.20 (1 H, m, 5-H), 4.41 (1 H, overlapping d, J = 12, C*H*HPh of each diastereoisomer), 4.69 (1 H, d, J = 12, C*H*HPh), 4.89 (1 H, m, 1-H), 7.35 (10 H, m, aromatic H).

Also isolated was a second fraction which was shown to be a mixture of products (430 mg) by ^1H NMR including the regioisomers **16**.

Hydrogenation of Alkyne 15:
A suspension of Lindlar catalyst (10 mg) in a solution of the alkyne **15** (100 mg, 0.357 mmol) in EtOH (2 mL) was stirred vigorously under hydrogen for 8 h. The mixture was filtered through Celite, and the filtrate concentrated under reduced pressure. Flash chromatography of the residue using Et_2O–light petroleum (1:3) as eluant gave a mixture of the *syn*- and *anti*-5-benzyloxy-3-hexenols **4** and **5** (90 mg, 89%).

^1H NMR: δ = 1.13 and 1.22 (each 1.5 H, d, J = 7.5, 6-H_3 of each isomer), 2.20 (1 H, br s, OH), 2.51 (2 H, m, 2-H_2), 4.22 (1 H, m, 5-H), 4.22, 4.37, 4.41 and 4.51 (each 0.5 H, d, J = 12, C*H*HPh of each isomer), 4.71 (1 H, t, J = 7.5, 1-H), 5.48–5.65 (2 H, m, 3-H and 4-H), 7.30 (10 H, m, aromatic H).

***syn*- and *anti*-7-Benzyloxy-2-methyl-5-octen-3-ol (17 g) and (18 g):**
Following the above procedure, 7-benzyloxy-2-methyl-5-octyn-3-ol (20 mg, 0.081 mmol) was hydrogenated to give the alkenols **17 g** and **18 g** (18 mg, 90%) which were separated by flash chromatography using Et_2O–light petroleum (1:3) as eluant. The less polar isomer was identified as the *syn*-isomer **17 g**.

^{13}C NMR: δ = 17.5, 18.9, 21.5, 32.7, 33.4, 70.0, 70.2, 76.2, 127.6, 128.0, 128.5, 128.95, 135.1, 138.9.

The more polar isomer was identified as the *anti*-diastereoisomer **18 g**.

MS: m/z = 266 (M^+ + 18, 26), 249 (M^+ + 1, 25), 196 (100).

^1H NMR: δ = 0.92 and 0.93 (each 3 H, d, J = 6.5, CH_3), 1.29 (3 H, d, J = 6.5, 8-H_3), 1.58 (1 H, br. s, OH), 1.48 (1 H, m, 2-H), 2.20 (2 H, m, 4-H_2), 3.39 (1 H, m, 3-H), 4.30 (1 H, m, 7-H), 4.39 and 4.56 (each 1 H, d, J = 12, C*H*HPh), 5.59 (2 H, m, 5-H and 6-H), 7.30 (5 H, m, aromatic H).

^{13}C NMR: δ = 17.6, 19.0, 21.6, 32.9, 33.4, 70.0, 70.3, 76.4, 127.9, 128.1, 128.6, 128.9, 135.2, 138.9.

(1*R*,5*S*,3*Z*)-5-Benzyloxy-1-(2-naphthyl)-3-hexen-1-ol *p*-Nitrobenzoate (21):
p-Nitrobenzoyl chloride (62 mg, 0.332 mmol) was added to a solution of the 1-(2-naphthyl)hexenol **17j** (50 mg, 0.151 mmol), Et_3N (31 mg, 0.332 mmol), and DMAP (3 mg, 0.025 mmol) in CH_2Cl_2 (0.6 mL) at 0 °C. The solution was stirred for 6 h at 20 °C, and concentrated under reduced pressure. Flash chromatography of the residue using Et_2O–light petroleum (1:3) as eluant gave the *p*-nitrobenzoate **21** (68 mg, 94%) which was recrystallised from CH_2Cl_2–hexane, mp 90–91 °C. $[\alpha]_D$ −47.6 (c = 1, $CHCl_3$).

$C_{30}H_{27}NO_5$	calc.	C 74.8	H 5.6	N 2.9
(481)	found	74.5	5.9	3.1

IR: ν = 1718, 1605, 1525, 1270, 1118, 1102, 748, 719, 699 cm^{-1}.

MS: m/z = 499 (M^+ + 18, 10), 207 (100).

^1H NMR: δ = 1.3 (3 H, d, J = 6.5, 6-H_3), 2.86 and 3.01 (each 1 H, m, 2-H), 4.29 (1 H, m, 5-H), 4.31 and 4.47 (each 1 H, d, J = 12, C*H*HPh), 5.45–5.69 (2 H, m, H-3 and H-4), 6.26 (1 H, t, J = 6.5, 1-H), 7.25–8.30 (16 H, m, aromatic H).

Reaction Between 2-Propenytin Trichloride and (*S*)-2-Benzyloxypropanal (26a):
A cooled solution of tin(IV) chloride (47 mg, 0.182 mol) in anhydr. CH_2Cl_2 (0.21 mL) was added dropwise to a solution of prop-2-enyl(tributyl)stannane (60 mg, 0.182 mmol) in anhydr. CH_2Cl_2 (3 mL) at −78 °C. After 5 min, a cooled solution of (*S*)-2-benzyloxypropanal **(26a)** (30 mg, 0.182 mmol) was added, and the mixture stirred for 1 h at −78 °C. Aq $NaHCO_3$ (1 mL) was added, and the mixture allowed to warm to r.t. The reaction mixture was diluted with CH_2Cl_2 (10 mL), washed with water (2 × 8 mL) and brine (8 mL), and dried ($MgSO_4$). Concentration under reduced pressure gave an oil which on chromatography using Et_2O–light petroleum (1:3) as eluant gave the *syn*- and *anti*-alcohols **49** and **50** (30 mg, 80%).

(2*S*,3*S*)-2-Benzyloxy-5-hexen-3-ol (49):
$[\alpha]_D$ + 27.2 (c = 1, $CHCl_3$).

$C_{13}H_{22}NO_2$ calc. M, 224.1650. Found: M + NH_4, 224.1664.

IR: ν = 3441, 3068, 3031, 1641, 1072, 1029, 993, 914, 736, 698 cm^{-1}.

MS: m/z = 224 (M^+ + 18, 56) 182 (100).

^1H NMR: δ = 1.22 (3 H, d, J = 7, 1-H_3), 2.15–2.41 (2 H, m, 4-H_2), 2.50 (1 H, br. s, OH), 3.46 (1 H, m, 2-H), 3.54 (1 H, m, 3-H), 4.46 and 4.68 (each 1 H, d, J = 12, C*H*HPh), 5.08–5.12 (2 H, m, 6-H_2), 5.89 (1 H, ddt, J = 17, 10, 7, 5-H), and 7.32 (5 H, m, aromatic H).

(2*S*,3*R*)-2-Benzyloxy-5-hexen-3-ol (50):
$[\alpha]_D$ + 23.6 (c = 1, $CHCl_3$).

IR: ν = 3425, 1641, 1071, 1028, 915, 698 cm^{-1}.

MS: m/z = 224 (M^+ + 18, 100).

^1H NMR: δ = 1.20 (3 H, d, J = 7, 1-H_3), 1.82 (1 H, br s, OH), 2.28 (2 H, m, 4-H_2), 3.52 (1 H, m, 2-H), 3.79 (1 H, m, 3-H), 4.52 and 4.64 (each 1 H, d, J = 12, C*H*HPh), 5.14 (2 H, m, 6-H_2), 5.83 (1 H, ddt, J = 17, 10, 7, 5-H), 7.30 (5 H, m, aromatic H).

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