Organic & Biomolecular Chemistry

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2013, **11**, 8476

Development and applications of remote stereocontrol using allylic organobismuth reagents†

Norazah Basar,[a] Sam Donnelly,[b] Hasnah M. Sirat[a] and Eric J. Thomas*[b]

Received 23rd September 2013,
Accepted 30th October 2013

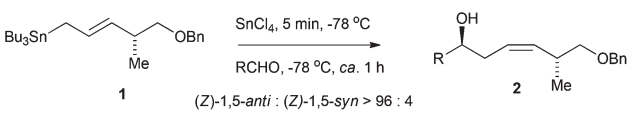
DOI: 10.1039/c3ob41931b

www.rsc.org/obc

Reactions of 5-benzyloxy-4-methylpent-2-enyl(tributyl)stannane with aldehydes promoted by bismuth(III) iodide were usefully stereoselective in favour of the (*E*)-1,5-*anti*-6-benzyloxy-5-methylalk-3-en-1-ols. Similar stereoselectivity was observed for reactions of analogous 5-benzyloxy-4-methylpent-2-enyl bromides with aldehydes when promoted by a low valency bismuth species prepared by reduction of bismuth(III) triiodide with powdered zinc so providing a "tin-free" procedure. The analogous reactions of 4-benzyloxypent-2-enyl(tributyl)stannane with aldehydes promoted by bismuth(III) iodide were also stereoselective but gave lower yields. Attempted 1,6-stereocontrol using these reactions resulted in only modest stereoselectivities. Aspects of the chemistry of the products were studied in particular their stereoselective conversion into aliphatic compounds with methyl bearing stereogenic centres at 1,5,9,13- and 1,3,5-positions along the aliphatic chain. Mechanistically, allylic organobismuth species may be involved in both sets of reactions but this was not confirmed although the similar stereoselectivities observed for both the bismuth(III) iodide mediated reactions of the pent-2-enylstannanes and the low-valency bismuth promoted reactions of the pent-2-enyl bromides are consistent with participation of similar intermediates.

Introduction

Transmetallation of 4- and 5-heterosubstituted alk-2-enyl-(trialkyl)stannanes using tin(IV) halides is stereoselective and generates allyltin trihalides that react with aldehydes and with imines with useful 1,5-, 1,6- and 1,7-stereocontrol.[1,2] For example the 5-benzyloxy-4-methylpent-2-enyl(tributyl)stannane **1** gives the (*Z*)-1,5-*anti*-alkenols **2** following transmetallation with tin(IV) chloride at −78 °C and reaction of the intermediate allyltin trichloride with aldehydes.[2b] This chemistry has been used to complete syntheses of several natural products[3–5] and analogous chemistry has been developed for the corresponding organogermanium compounds so avoiding the use of organotin starting materials.[6]



Following on from this work, it was of interest to study transmetallation of the allylstannanes with other Lewis acids to see whether similar or complementary stereoselectivity was observed. The development of "tin-free" procedures would also be of interest. We here report studies of reactions of allylstannanes, including the pent-2-enylstannane **1**, with aldehydes promoted by bismuth(III) iodide together with analogous reactions of alk-2-enyl bromides promoted by a low valency bismuth species prepared by reduction of bismuth(III) iodide with powdered zinc.[7,8]

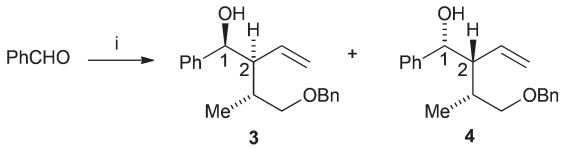
Results and discussion

Preliminary studies and 1,5-stereocontrol in reactions of 4- and 5-benzyloxypent-2-enylstannanes with aldehydes promoted by bismuth(III) iodide

Strong Lewis acids catalyse reactions of allylstannanes with aldehydes by coordination to the aldehyde leading to an SE′ reaction with the stannane. $BF_3{\cdot}Et_2O$ has been widely used in this context with useful 1,2-*syn*-stereoselectivities found for reactions of but-2-enylstannanes with aldehydes at −78 °C.[9] The $BF_3{\cdot}Et_2O$ promoted reaction of the racemic stannane **1** with benzaldehyde followed this pattern and gave a mixture of two SE′ products identified as the 1,2-*syn*-adducts **3** and **4**, ratio 70 : 30, see Scheme 1. The relative configurational assignments shown were provisionally assigned on the basis of the

[a]*Chemistry Department, Faculty of Science, Universiti Teknologi Malaysia Skudai, 81310 Skudai, Johor Bahru, Malaysia*
[b]*School of Chemistry, The University of Manchester, Manchester, M13 9PL, UK. E-mail: e.j.thomas@manchester.ac.uk; Fax: +44 (0)161 275 4939; Tel: +44 (0)161 275 4613*

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ob41931b



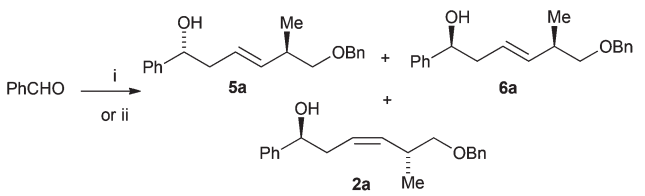
Scheme 1 Reaction of stannane **1** with benzaldehyde catalysed by $BF_3{\cdot}Et_2O$. Reagents and conditions: (i) PhCHO, $BF_3{\cdot}Et_2O$, DCM, −78 °C, 10 min, add **1**, −78 °C to 0 °C (51%, **3** : **4** = 70 : 30).

1,2-*syn*-stereoselectivity usually observed for $BF_3{\cdot}Et_2O$ catalysed reactions of alk-2-enylstannanes with aldehydes[9] and the facial selectivities found for reactions of analogous allylsilanes, but these were not confirmed.[10] The regioselectivity was established by ^{1}H NMR.

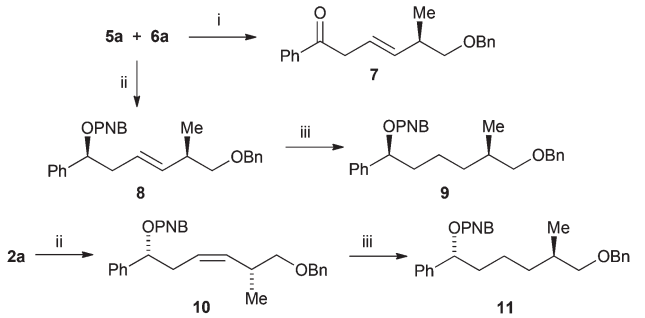
Transmetallation of allyl- and allenylstannanes with indium(III) chloride has been widely studied and subsequent reactions of the organo-indium species with aldehydes developed into a useful synthesis of 1,2-*anti*-products.[11] Moreover 1,6-remote stereocontrol was observed in reactions of butadienyl 2,3-di-indium compounds with aldehydes.[11l] Preliminary studies of the reaction of the racemic stannane **1** with benzaldehyde promoted by indium(III) chloride were carried out at room temperature with the stannane added to a mixture of indium(III) chloride and benzaldehyde in either DCM, acetonitrile or acetone as the solvent. Mixtures of linear products were formed with the major products being the (*E*)-hex-3-enols **5a** and **6a**, ratio *ca.* 70 : 30, together with a small amount of the separable (*Z*)-isomer **2a**,[2b] see Scheme 2. The best yield, 72%, was obtained in DCM at room temperature with lower temperatures resulting in lower yields. Indium(III) bromide and iodide in acetonitrile, gave slightly better stereoselectivities, 78 : 22 and 80 : 20, respectively, but with slightly lower yields.

Although these indium(III) halide promoted reactions of the stannane **1** with benzaldehyde were of interest in that the (*E*)-hexenol **5a** was the major product, the relatively modest 1,5-stereoselectivity observed mitigated against these reactions being useful in synthesis. Bismuth(III) bromide and triflate have been used to promote reactions of allylstannanes with aldehydes with the advantage that organobismuth compounds are supposedly relatively non-toxic.[12]

The reaction between the racemic stannane **1** and benzaldehyde in acetonitrile promoted by bismuth(III) bromide



Scheme 2 Reactions of stannane **1** with benzaldehyde promoted by indium(III) and bismuth(III) halides. Reagents and conditions: (i) InX_3, PhCHO, r.t., add **1**, r.t. (X = Cl, DCM, **5a**:**6a** = 70 : 30, 72%; X = Br, MeCN, **5a**:**6a** = 78 : 22, 66%; X = I, DCM, **5a**:**6a** = 80 : 20, 42%; **2a**, *ca.* 5% in all cases); (ii) BiX_3, PhCHO, MeCN, 15 min, r.t., add **1**, r.t., 30 min (X = Br, **5a**:**6a** = 90 : 10, 58%; X = I, **5a**:**6a** = 92 : 8, 72%; **2a**, *ca.* 5% in both cases).



Scheme 3 Confirmation of the structures of hexenols **5a** and **6a**. Reagents and conditions: (i) Dess Martin periodinane, DCM, r.t., 30 min (75%); (ii) Ph_3P, 4-$NO_2C_6H_4CO_2H$, THF, DIAD, 0 °C, 10 min then r.t., 30 min (**8** with 30% epimer, 63%; **10**, 68%); (iii) NaOAc, $TsNHNH_2$, DME, reflux, 6 h (**9** with 30% **11**, 68%; **11**, 62%).

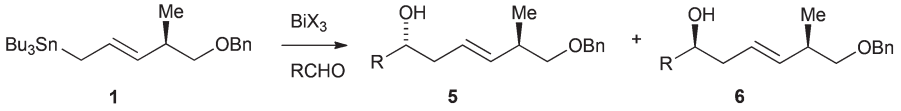
gave a 90 : 10 mixture of the epimeric 1,5-*anti*- and 1,5-*syn*-(*E*)-hexenols **5a** and **6a** together with *ca.* 5% of the (*Z*)-1,5-*anti*-alkenol **2a**.[2b] Since indium(III) iodide had given slightly improved stereoselectivity for the reaction between the stannane **1** and benzaldehyde, the use of bismuth(III) iodide was investigated. A reasonable yield of the (*E*)-products was obtained and the stereoselectivity was slightly improved, **5a**:**6a** = 92 : 8.

The hexenols **5a** and **6a** could not be separated. The ^{1}H NMR spectrum of the ketone **7** prepared by oxidation of a 70 : 30 mixture of these alcohols using the Dess Martin periodinane, see Scheme 3, showed a distinctive 16 Hz coupling between the vinylic protons consistent with the (*E*)-configuration shown. The 1,5-*anti*-configuration of the major hexenol **5a** was established *via* the 4-nitrobenzoate **8** prepared with inversion of configuration from the 70 : 30 mixture of products **5a** and **6a** by a Mitsunobu reaction.[13] Reduction of the alkene **8** containing *ca.* 30% of its epimer using diimide gave the saturated hexane **9** as the major product together with a minor component. This minor component was shown by ^{1}H and ^{13}C NMR to be the 4-nitrobenzoate **11** prepared from the 1,5-*anti*-(*Z*)-product **2a**[2b] *via* its inverted 4-nitrobenzoate **10** followed by reduction using diimide.

The reactions of other aldehydes with the stannane **1** promoted by bismuth(III) iodide were studied and in all cases useful stereoselectivities in favour of the 1,5-*anti*-(*E*)-products were obtained. Most reactions were carried out in acetonitrile as solvent, but later it was found that significantly better yields were obtained using a mixed solvent system of acetonitrile and DCM without any loss of stereoselectivity, see Table 1.

The product ratios were determined by integration of the $CHCH_3$ peaks in ^{1}H NMR spectra. The 1,5-*anti*-configuration of the major product **5f** from the reaction with butanal was confirmed by Mitsunobu esterification with inversion of configuration using 4-nitrobenzoic acid followed by reduction of the resulting unsaturated ester **12** with diimide. The saturated ester **13** so obtained was compared with the *anti*-isomer **15** prepared using the same chemistry from the known 1,5-*anti*-(*Z*)-alkenol **2f**.[2b] The two epimers **13** and **15** could not be distinguished using ^{1}H NMR but there were slight differences in

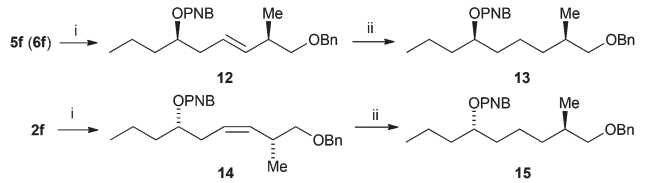
Table 1 Reactions of stannane **1** with aldehydes promoted by bismuth(III) halides



1 5 6

X	R	Solvent	Yield[a] (%)	Products[b]	1,5-*anti* : 1,5-*syn*
Br	Ph	MeCN	58	**5a, 6a**	90 : 10
I	Ph	MeCN	72 (66)	**5a, 6a**	92 : 8
I	4-$O_2NC_6H_4$	MeCN	53	**5b, 6b**	95 : 5
I	4-$MeOC_6H_4$	MeCN	56	**5c, 6c**	92 : 8
I	MeCH=CH	MeCN	45	**5d, 6d**	90 : 10
I	^{i}Pr	MeCN	55	**5e, 6e**	93 : 7
I	^{n}Pr	MeCN	61 (82)	**5f, 6f**	93 : 7
I	Ph	MeCN–DCM	80	**5a, 6a**	92 : 8
I	^{i}Pr	MeCN–DCM	87	**5e, 6e**	93 : 7
I	^{n}Pr	MeCN–DCM	92	**5f, 6f**	93 : 7

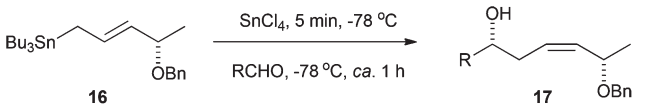
[a] Yields based on the stannane with stannane–aldehyde–BiI_3 = 1 : 3 : 1. Yields in parenthesis are based on the aldehyde with stannane–aldehyde–BiI_3 = 1.3 : 1 : 1.4. [b] In all cases *ca.* 5% of *anti*-(*Z*)-alkenols **2** were isolated.



Scheme 4 Confirmation of the structure of alkenol **5f**. Reagents and conditions: (i) Ph_3P, 4-$NO_2C_6H_4CO_2H$, THF, DIAD, 0 °C, 10 min then r.t., 30 min (**12**, 92%; **14**, 68%); (ii) NaOAc, $TsNHNH_2$, DME, reflux, 6 h (**13**, 64%; **15**, 51%).

their ^{13}C NMR spectra with six peaks being distinguished in a spectrum of a mixture. The 1,5-*anti*-configurations of the other major products **5** were assigned by analogy (Scheme 4).

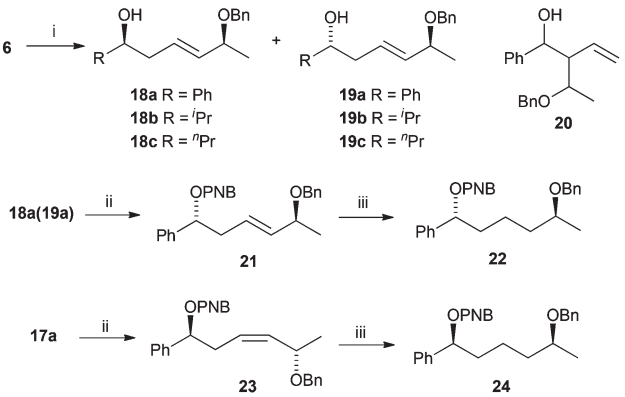
High 1,5-stereocontrol in favour of the (*Z*)-1,5-*syn*-products **17** had been observed for the tin(IV) chloride promoted reactions of the 4-benzyloxypent-2-enyl(tributyl)stannane **16** with aldehydes,[2a] and so it was of interest to study the bismuth(III) iodide promoted reaction of this stannane with aldehydes.



16 17

(*Z*)-1,5-*syn* : (*Z*)-1,5-*anti* > 97 : 3

Useful stereoselectivities, *ca.* 93 : 7, in favour of the (*E*)-1,5-*syn*-products **18** were observed, see Scheme 5, although the yields were only modest. In the reaction with benzaldehyde a minor side-product was identified as a branched isomer **20**. The relative 1,5-configuration was established by conversion of the benzaldehyde derived products **18a(19a)** to the 4-nitrobenzoate **21** by esterification with inversion using a Mitsunobu reaction. Reduction using diimide gave the 1,5-*anti*-5-benzyloxyhex-1-yl 4-nitrobenzoate **22** that was compared with the *syn*-epimer **24**, prepared from the known (*Z*)-1,5-*syn*-5-benzyloxy-1-phenylhex-3-enol **17a** using the same chemistry, see Scheme 5. The esters **22** and **24** were distinguishable by ^{1}H and ^{13}C NMR. Structures were assigned to the other products **18b,c** by analogy.

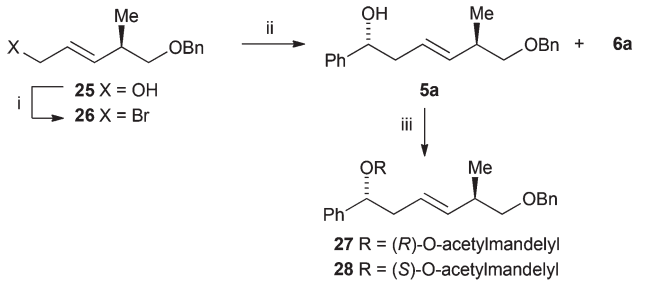


Scheme 5 Reactions of the 4-benzyloxypent-2-enylstannane **16** with aldehydes promoted by bismuth(III) iodide. Reagents and conditions: (i) RCHO, BiI_3, DCM, MeCN, r.t., add stannane in DCM, 30 min (**18a**/**19a**, 56%, **18a**:**19a** = 93 : 7; **18b**/**19b**, 48%, **18b**:**19b** = 93 : 7; **18c**/**19c**, 62%; **18c**:**19c** = 92 : 8); (ii) Ph_3P, 4-$NO_2C_6H_4CO_2H$, DIAD, THF, 0 °C to r.t., 30 min (**21**, 49%; **23**, 63%); (iii) NaOAc, $TsNHNH_2$, DME, H_2O, reflux, 16 h (**22**, 40%; **24**, 48%).

These bismuth(III) iodide promoted reactions of the pent-2-enylstannanes **1** and **16** with aldehydes are of interest since they proceed with stereoselectivity different from that observed for the tin(IV) halide promoted reactions. However, this chemistry is still based on the use of an organotin starting material and the development of a "tin-free" procedure remained of interest.

1,5-Stereocontrol in reactions of 4- and 5-benzyloxypent-2-enyl bromides with aldehydes

Reactions of allylic bromides with aldehydes have been promoted by activated bismuth(0) prepared by reduction of bismuth(III) iodide using powdered zinc, iron or aluminium.[14] Since allylic organobismuth intermediates related to those generated in the bismuth(III) iodide promoted reactions of stannane **1** with aldehydes may be involved, *vide infra*, it was of interest to repeat this chemistry using 4-methylpent-2-enyl bromide **26** to see whether useful 1,5-stereocontrol could be achieved.



Scheme 6 Reactions of benzaldehyde with the (*R*)-pent-2-enyl bromide **26** promoted by bismuth(0). Reagents and conditions: (i) Ph_3P, CBr_4, DCM, r.t., 2 h (92%); (ii) BiI_3, activated zinc powder, THF, r.t., 1 h, then add **26** and PhCHO, reflux 2 h or r.t., 16 h (83%; **5a**:**6a** = 96 : 4); (iii) (*R*)- or (*S*)-*O*-acetylmandelyl chloride, py., DMAP, DCM, 0 °C, r.t. 2 h (**27**, 60%; **28**, 39%).

Following the published procedure, activated zinc powder was suspended in a solution of bismuth(III) iodide in THF and the mixture stirred vigorously at room temperature for 1 h during which time a black precipitate developed. The (*R*)-4-methylpent-2-enyl bromide **26** was prepared from the known alcohol **25**,[2b] see Scheme 6. It was added to the black suspension followed by benzaldehyde and the mixture was heated under reflux for 2 h. After work-up and chromatography, an 83% yield of the (*E*)-hex-3-enols **5a** and **6a** was obtained with a useful diastereoselectivity, 96 : 4, in favour of the (*E*)-1,5-*anti*-product **5a**. Lower yields were obtained if iron or aluminium were used to reduce the bismuth(III) iodide. At room temperature, the reaction of the pent-2-enyl bromide **26** with benzaldehyde gave similar yields and stereoselectivity, but 16 h was required for completion.

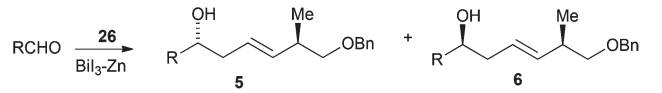
The products **5a** and **6a** were identified by comparison with samples prepared earlier but, in this case, as enantiomerically enriched (*R*)-pent-2-enyl bromide **26** had been used, the major product **5a**, still containing *ca.* 4% of its *syn*-epimer **6a**, was converted into the (*R*)- and (*S*)-*O*-acetylmandelates **27** and **28**. The relative chemical shifts of these derivatives were consistent with the major product **5a** from the bismuth promoted reaction being the (1*R*,5*R*)-diastereoisomer as shown.[15]

The reactions of other aldehydes with the pent-2-enyl bromide **26** mediated by bismuth(0) were then investigated. In all cases usefully stereoselective reactions in favour of the (*E*)-1,5-*anti*-products **5** were observed, see Table 2. In this work, the products that had been made previously were identified by comparison with earlier samples. The structures of the new products were assigned by analogy and the ratios of the products **5** and **6** were estimated by ^{1}H NMR using their CHCH_3 doublets.

As the bismuth(0) promoted reactions of the pentenyl bromide **26** with aldehydes proceeded with useful 1,5-stereocontrol it was of interest to see whether structurally related alk-2-enyl bromides also reacted with viable stereoselectivity and the 2,4-dimethylpent-2-enyl bromide **30** was selected for study.

This bromide was prepared both as its racemate and as its (*R*)-and (*S*)-enantiomers (*ca.* 95% ee) from the corresponding alcohol **29**.[2b] With benzaldehyde, an inseparable mixture of

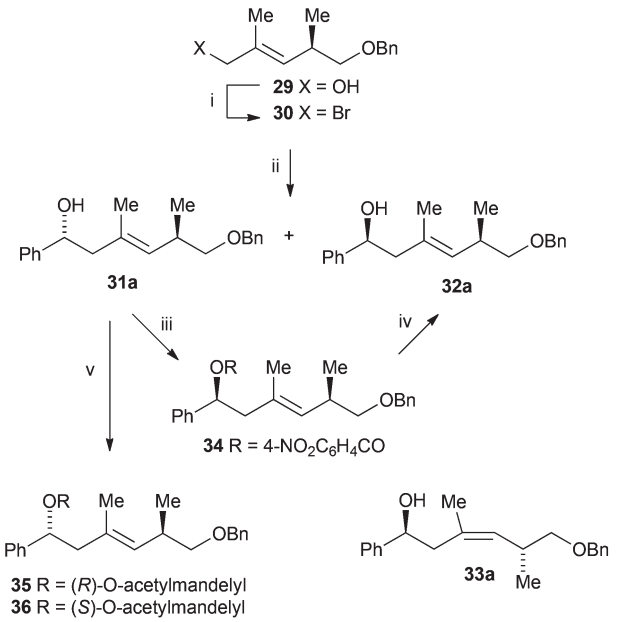
Table 2 Reactions of aldehydes with (*R*)-pent-2-enyl bromide **26** mediated by Bi(0)



R	Yield (%)	Products	1,5-*anti* : 1,5-*syn*
Ph	83	**5a, 6a**	96 : 4
MeCH=CH	86	**5d, 6d**	93 : 7
^{i}Pr	82	**5e, 6e**	95 : 5
^{n}Pr	92	**5f, 6f**	93 : 7
$BnOCH_2$	63	**5g, 6g**	87 : 13
$BnOCH_2CH_2$	87	**5h, 6h**	95 : 5
$TBSOCH_2$	66	**5i, 6i**	95 : 5
$TBSOCH_2CH_2$	63	**5j, 6j**	95 : 5

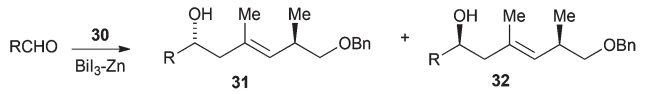
the (*E*)-1,5-*anti*- and (*E*)-1,5-*syn*-hex-3-enols **31a** and **32a**, 65%, **31a** : **32a** = 95 : 5, together with *ca.* 10% of the known (*Z*)-1,5-*anti*-product **33a**,[2b] was obtained, see Scheme 7.

The structures of these products were initially assigned by analogy with the reactions of the pent-2-enyl bromide **26**. The products **31a** and **32a** could be distinguished by ^{1}H NMR, the doublets attributed to the 5-CH_3 groups being used to estimate the 1,5-stereoselectivity. The (*E*)-double-bond geometry of the major product **31a** and the (*Z*)-double-bond geometry of the minor product **33a** were confirmed by nOe studies. The minor (*E*)-product **32a** was prepared from the major epimer **31a** by a Mitsunobu reaction with inversion of configuration followed



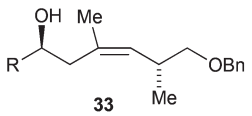
Scheme 7 1,5-Stereocontrol in reactions of the (*R*)-2,4-dimethylpent-2-enyl bromide **30** with benzaldehyde. Reagents and conditions: (i) Ph_3P, CBr_4, DCM, r.t., 2 h (90%); (ii) BiI_3, activated zinc powder, THF, r.t., 1 h, then add **30** and PhCHO, reflux 2 h or r.t., 16 h (65%, **31a**:**32a** = 95 : 5; **33a**, 10%); (iii) Ph_3P, 4-$NO_2C_6H_4CO_2H$, DIAD, THF, 0 °C to r.t., 30 min (60%); (iv) NaOH, MeOH, r.t., 2 h (43%); (v) (*R*)- or (*S*)-*O*-acetylmandelic acid, py., DMAP, DCC, DCM, 0 °C, r.t. 16 h (**35**, 78%; **36**, 75%).

Table 3 Reactions of aldehydes with (*R*)-2,4-dimethylpent-2-enyl bromide **30** mediated by Bi(0)



R	Yield (%)	Products	1,5-*anti* : 1,5-*syn*[a]
Ph	65	**31a**, **32a**	95 : 5
MeCH=CH	80	**31b**, **32b**	91 : 9
^{i}Pr	72	**31c**, **32c**	90 : 10
^{n}Pr	78	**31d**, **32d**	96 : 4
4-$O_2NC_6H_4$	63	**31e**, **32e**	95 : 5
$TBSOCH_2$	50	**31f**, **32f**	95 : 5[b]

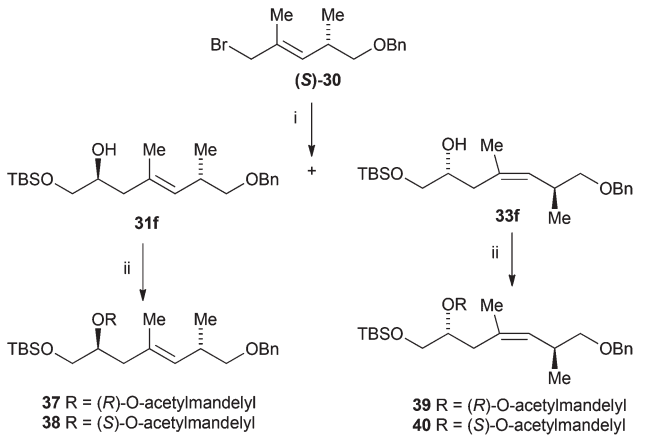
[a] In all cases 5–10% of the (*Z*)-1,5-*anti*-isomer **33** was isolated. [b] In this case, *ca.* 20% of the (*Z*)-1,5-*anti*-isomer **33f** was isolated.



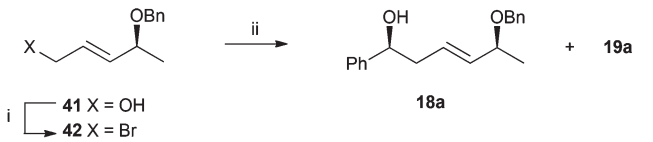
by saponification of the resulting 4-nitrobenzoate ester **34**. The 1,5-*anti*-configuration of the major product **31a** prepared using the (*R*)-enantiomer of the pent-2-enyl bromide **(*R*)-30** was established by comparison of the ^{1}H NMR spectra of the (*R*)- and (*S*)-*O*-acetylmandelates **35** and **36**, see Scheme 7.[15]

Reactions of the 2,4-dimethylpent-2-enyl bromide **30** with other aldehydes were then investigated, see Table 3. In all cases the major products were the (*E*)-products **31** and **32** formed with useful stereoselectivities, >90 : 10, in favour of the 1,5-*anti*-epimers **31**. The ratios of the products **31** and **32** in the (*E*)-alkene manifold were determined by ^{1}H NMR using their CHCH_3 doublets. Typically, 5–10% of the (*Z*)-1,5-*anti*-alkenols **33** were also isolated and identified by comparison with known compounds.[2b] The only exception to this useful stereoselectivity was the reaction with 2-*tert*-butyldimethylsilyloxyethanal. In this case the 1,5-stereoselectivity in the (*E*)-manifold was 95 : 5 as expected, but the yield was only 50% and about 20% of the (*Z*)-1,5-*anti*-isomer **33f** was isolated. Because of this reduced (*E*)/(*Z*)-stereoselectivity, the structures of the (*E*)- and (*Z*)-1,5-*anti*-isomers **31f** and **33f**, in this case prepared from the (*S*)-enantiomer of the 2,4-dimethylpentenyl bromide **(*S*)-30**, were confirmed by comparison of the ^{1}H NMR spectra of their (*R*)- and (*S*)-*O*-acetylmandelates **37**/**38** and **39**/**40**, see Scheme 8.[15] The structures of the other products were assigned by analogy.

Following the studies of the reactions of 4-benzyloxypent-2-enylstannane **16** with aldehydes it was of interest to study the bismuth(0) promoted reactions with aldehydes of the corresponding bromide **42**. This was prepared from the alcohol **41**[2a] and was found to undergo the bismuth(0) mediated reaction with benzaldehyde to give mainly the (*E*)-1,5-*syn*-hex-3-enol **18a** prepared earlier. Although useful stereoselectivity, 1,5-*syn* : 1,5-*anti* = 94 : 6, was observed, the yield was only 46%, perhaps due to a competing elimination, see Scheme 9.



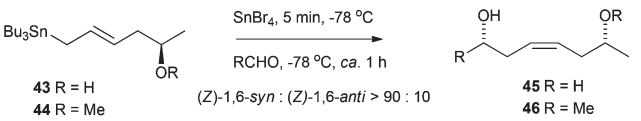
Scheme 8 Reaction of the bromide **(*S*)-30** with *tert*-butyldimethylsilyloxyethanal. Reagents and conditions: (i) BiI_3, activated zinc powder, THF, r.t., 1 h, then add **(*S*)-30** and $TBSOCH_2CHO$, reflux 2 h (50%, **31f**:**32f** = 95 : 5; **33f**, 20%); (ii) (*R*)- or (*S*)-*O*-acetylmandelyl chloride, py., DMAP, DCM, 0 °C, r.t. 2 h (**37**, 62%; **38**, 76%; **39**, 72%; **40**, 80%).



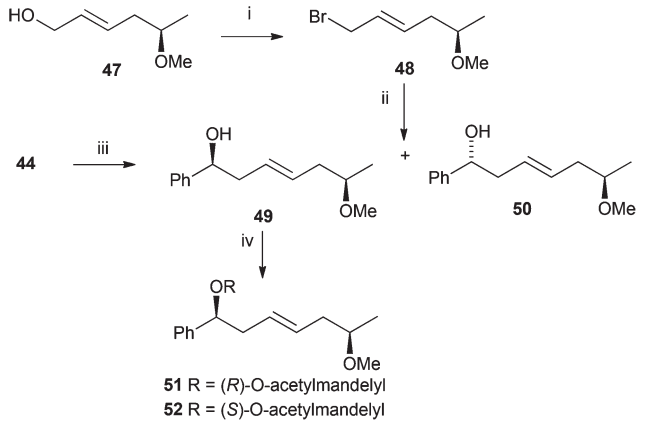
Scheme 9 The bismuth(0) promoted reaction of the pent-2-enyl bromide **42** with benzaldehyde. Reagents and conditions: (i) Ph_3P, CBr_4, DCM, r.t., 2 h (90%); (ii) BiI_3, activated zinc powder, THF, r.t., 1 h, then add **42** and PhCHO, reflux 2 h (46%, **18a**:**19a** = 94 : 6).

1,6-Stereocontrol in reactions of allylic organobismuth reagents with aldehydes

Useful 1,6-stereocontrol in favour of the (*Z*)-1,6-*syn*-isomers **45** and **46** was observed for tin(IV) bromide promoted reactions of the 5-hydroxy- and 5-methoxy-hex-2-enylstannanes **43** and **44** with aldehydes.[2b] The bismuth(III) iodide promoted reactions of these stannanes, and the bismuth(0) induced reaction of the bromide **48**, with aldehydes, were therefore briefly investigated.



The bismuth(III) iodide promoted reaction of the (*R*)-5-methoxyhex-2-enylstannane **44**, and the bismuth(0) induced reaction of the (*R*)-bromide **48**, available from the alcohol **47**,[2b] with benzaldehyde, gave only modest 1,6-stereocontrol, 80 : 20 and 74 : 26, respectively, in favour of the (*E*)-1,6-*syn*-diastereoisomer **49**, see Scheme 10. The (*E*)-configuration of the major product followed from its ^{1}H NMR spectrum and the 1,6-*syn*-configuration was deduced from the ^{1}H NMR chemical shifts of the (*R*)- and (*S*)-*O*-acetyl mandelates **51** and **52**. The ratio of the epimers **49** and **50** was estimated by integration of the 7-H_3 peaks in the ^{1}H NMR spectra of the product mixtures.



Scheme 10 1,6-Stereocontrol in bismuth-mediated reactions of the hex-2-enylstannane **44** and the hex-2-enyl bromide **48** with benzaldehyde. Reagents and conditions: (i) Ph_3P, CBr_4, DCM, r.t., 2 h (92%); (ii) BiI_3, activated zinc powder, THF, r.t., 1 h, then add **48** and PhCHO, reflux 2 h (69%; **49** : **50** = 74 : 26); (iii) PhCHO, BiI_3, DCM, MeCN, r.t., add **44** in DCM, 30 min (80%; **49** : **50** = 80 : 20); iv, (*R*)- or (*S*)-*O*-acetylmandelyl chloride, py., DMAP, DCM, 0 °C, r.t. 2 h (**51**, 59%; **52**, 62%).

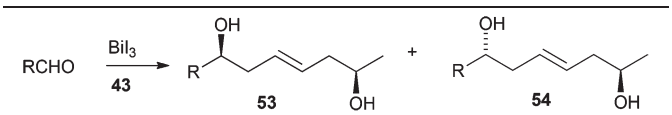
Similar results were observed for the bismuth(III) iodide promoted reactions of the 5-hydroxyhex-2-enylstannane **43** with several aldehydes, see Table 4. In this series, the ratios of the products were estimated by ^{13}C with the 1,5-*syn*-(*E*)-stereochemistry of the major product **53** assigned by analogy with the analogous reaction of the 5-methoxyhexenylstannane **44** with benzaldehyde.

Low valency bismuth promoted reactions of the (*R*)-pent-2-enyl bromide 26 with chiral aldehydes

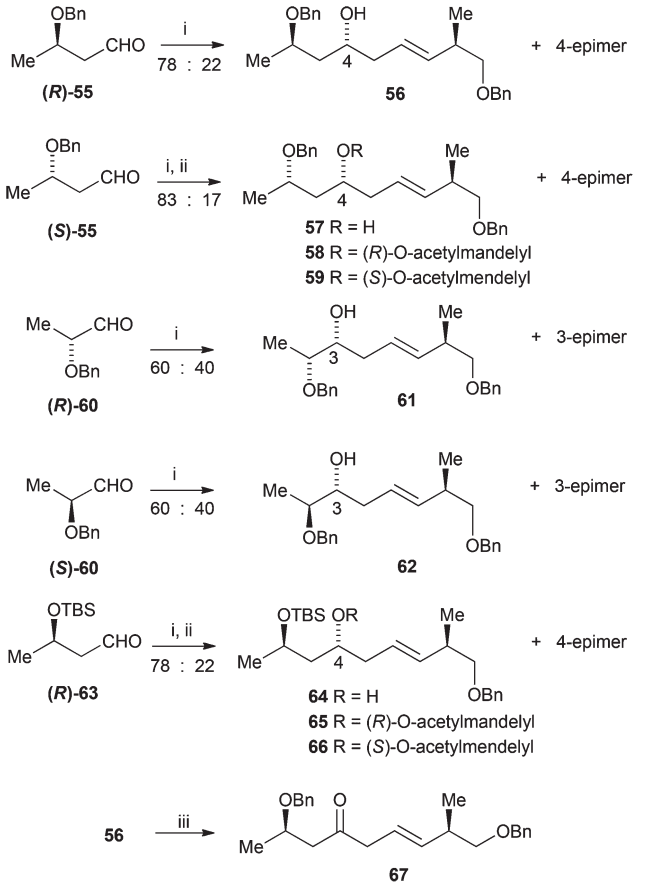
The low valency bismuth promoted reactions between the (*R*)-pent-2-enyl bromide **26** and chiral α- and β-alkoxyaldehydes were briefly examined to see whether the chirality of the aldehyde or that of the bromide influenced the diastereoselectivity of the reaction. Rather disappointingly, only modest stereoselectivities, 83 : 17 at best, were observed for these reactions and no significant matching or mismatching was observed for enantiomeric aldehydes, see Scheme 11.

The structures of these products were initially assigned by analogy with the earlier reactions of the pent-2-enyl bromide **26** with achiral aldehydes. The (*E*)-configurations of the

Table 4 Reactions of aldehydes with the 5-hydroxyhex-2-enylstannane **43** mediated by bismuth(III) iodide



R	Yield (%)	Products	1,6-*syn* : 1,6-*anti*
Ph	63	**53a**, **54a**	80 : 20
^{t}Bu	71	**53b**, **54b**	80 : 20
^{i}Pr	74	**53c**, **54c**	68 : 32
^{n}Pr	78	**53d**, **54d**	50 : 50
4-$O_2NC_6H_4$	78	**53e**, **54e**	82 : 28



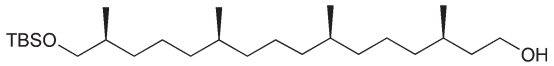
Scheme 11 Reactions of the pent-2-enyl bromide **26** with chiral aldehydes. Reagents and conditions: (i) BiI_3, activated zinc, THF, r.t., 1 h, then add **26** and RCHO, reflux 2 h (**56**, 53%, 1,5-*anti*:1,5-*syn* = 78 : 22; **57**, 63%, 1,5-*anti* : 1,5-*syn* = 83 : 17; **61**, 60%, 1,5-*anti* : 1,5-*syn* = 60 : 40; **62**, 67%, 1,5-*anti* : 1,5-*syn* = 60 : 40; **64**, 51%, 1,5-*anti* : 1,5-*syn* = 78 : 22); (ii) (*R*)- or (*S*)-*O*-acetylmandelyl chloride, py., DMAP, DCM, 0 °C, r.t. 2 h (**58**, 68%; **59** 76%; **65**, 58%; **66**, 69%); (iii) Dess Martin periodinane, DCM, r.t., 2 h (74%).

alkenol **56** and its 1,5-*syn*-epimer were confirmed by oxidation of the mixture of products to the enone **67**. The 1,5-*anti*-configurations of the major products **57** and **64** from the reactions of the (*S*)-3-benzyloxy- and (*R*)-*tert*-butyldimethylsilyloxy-butanals **(*S*)-55** and **(*R*)-63**, were confirmed by comparison of the ^1H NMR spectra of their (*R*)- and (*S*)-*O*-acetylmandelates. The configurations of the other major products were assigned as the 1,5-*anti*-epimers **56**, **61** and **62** by analogy, see Scheme 11. The minor products from these reactions were not separated from the major products. They were assumed to be the (*E*)-1,5-*syn*-isomers by comparison with earlier work. The ratios of the products were estimated from the ^1H and ^{13}C NMR spectra of product mixtures.

Applications of remote stereocontrol using pent-2-enyl bromides in synthesis

Many natural products are known that have all *syn*-methyl substituents at 1,5,9-positions along an aliphatic chain, *e.g.* the all-*syn*-16-*tert*-butyldimethylsilyloxy-3,7,11,15-tetramethylhexadecan-1-ol **68** is a potential intermediate for the synthesis of

lipids found in archaeal cell membranes.[16] It was of interest to see whether this motif could be prepared using organobismuth chemistry.



68

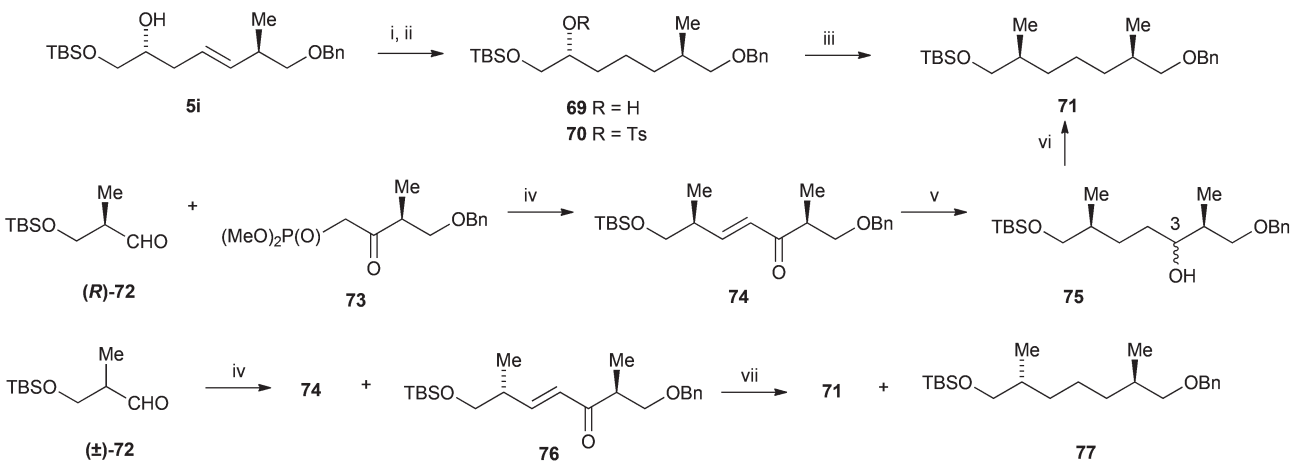
The (*E*)-1,5-*anti*-product **5i** prepared from 2-*tert*-butyldimethylsilyloxyethanal and the (*R*)-4-methylpent-2-enyl bromide (***R*)-26**, see Table 2, was reduced using diimide and the resulting saturated alcohol **69** converted into its toluene *p*-sulfonate **70**. Substitution of the toluene *p*-sulfonyl group by a methyl group with inversion of configuration was achieved using the cuprate formed from methyllithium and copper(I) cyanide,[17] and gave the 2,6-*syn*-dimethylheptane **71**. A minor elimination product was formed during this displacement and was removed by treatment of the crude product mixture with osmium tetraoxide and *N*-methylmorpholine-*N*-oxide, see Scheme 12.

The 2,6-*syn*-configuration of the 2,6-dimethylheptane **71** was confirmed by preparation of an authentic sample by an alternative route. Condensation of the (*S*)-ketophosphonate **73**[18] with the (*R*)-aldehyde (***R*)-72** gave the 2,6-*syn*-dimethylheptenone **74** that was reduced to give the saturated alcohol **75** as a mixture of epimers at C(3). Deoxygenation using the Barton procedure then gave the *syn*-2,6-dimethylhexane **71** so confirming the structure of the 2,6-dimethylheptane prepared by substitution of the sulfonate **70**.

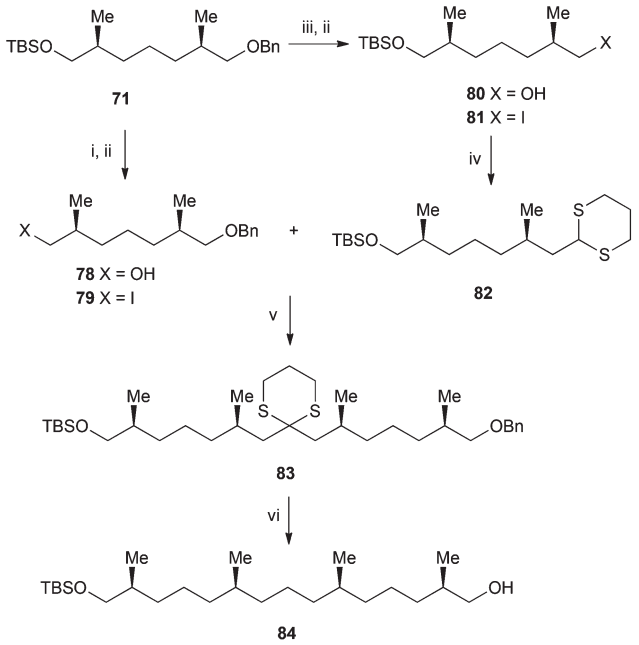
The spectroscopic data of the 2,6-*syn*-dimethylheptanes prepared by the two routes were identical and appeared to correspond to a single diastereoisomer. However to be certain of this it remained to show that the 2,6-*anti*- and 2,6-*syn*-dimethylheptanes could be distinguished. A mixture of the *syn*- and *anti*-2,6-dimethylheptanes **71** and **77** was therefore prepared using the racemic aldehyde (±)-**72** and the (*S*)-ketophosphonate **73**. A comparison of the ^{1}H NMR spectrum of the mixture of 2,6-*syn*- and 2,6-*anti*-dimethylheptanes **71** and **77** with that of the *syn*-2,6-dimethylheptane **71** showed that one each of the diastereotopic hydrogens at C(1) and C(7) was doubled up in the ^{1}H NMR spectrum of the mixture whereas clean double-doublets were observed for these hydrogens in the ^{1}H NMR of the single epimer **71**. It was confirmed that the *syn*-2,6-dimethylheptane **71** prepared from the toluene *p*-sulfonate **70** contained less than 5% of its 2,6-*anti*-epimer **77**, see Scheme 12.

The incorporation of the *syn*-2,6-dimethylheptane **71** into a synthesis of the all *syn*-2,6,10,14-tetramethylpentadecan-1-ol **84** is shown in Scheme 13. Selective deprotection gave the alcohols **78** and **80** that were converted into the iodides **79** and **81**. Alkylation of 1,3-dithiane with iodide **81** and then with the iodide **79** gave the bis-alkylated dithiane **83**. Desulfurisation using RANEY® nickel was accompanied by hydrogenolysis of the benzyl group and gave the all-*syn*-tetramethylpentadecanol **84**. This appeared to be essentially a single diastereoisomer, as indicated by the double-doublets observed for the diastereotopic hydrogens at C(1) and C(15) in the ^{1}H NMR spectra of the dialkylated dithiane **83** and the pentadecanol **84** (>10% of an epimer should have been detected by a doubling up of one or other of these peaks).

Compounds with methyl substituents at 1,3,5-positions along an aliphatic chain, *e.g.* the *syn*,*syn*- and *anti*,*anti*-isomers **85** and **86**, are of interest. Several iterative procedures that deliver excellent stereoselectivity involving conjugate addition,[19] displacement,[20] hydrogenation[21] and alkene methylation,[22] have been developed for the synthesis of these compounds. Although the 1,5-*anti*-stereocontrol observed for the reactions of the pent-2-enyl bromide **30** with aldehydes is less than the stereoselectivities of these iterative methods, the use of the products so obtained for the synthesis of compounds with 1,3,5-methyl substituents would provide a

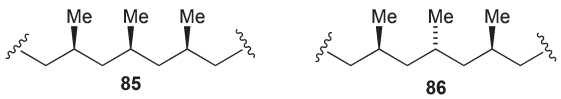


Scheme 12 Synthesis of (2*S*,6*R*)-1-*tert*-butyldimethylsilyloxy-7-benzyloxy-2,6-dimethylheptane **7l** and confirmation of its stereochemistry. Reagents and conditions: (i) NaOAc, $TsNHNH_2$, DME, H_2O, reflux, 16 h (92%); (ii) TsCl, DMAP, DCM, r. t., 16 h (90%); (iii) MeLi, CuCN, tol., ether, 0 °C, 15 min, **70**, 0 °C, 5 h; NMO, OsO_4, acetone, r.t., 16 h (73%); (iv) **73**, $Ba(OH)_2$, THF, r.t., 30 min, add **72**, r,t., 16 h (**74**, 84%; **74** + **76**, 82%); (v) $NaBH_4$, MeOH, 0 °C, 2 h (70%); (vi) (a) PhOC(SCl, py., DCM, r.t., 16 h) (b) Bu_3SnH, AIBN (cat.), reflux, 16 h (74%); (vii) (a) $NaBH_4$, MeOH, 2 h (68%) (b) PhOC(S)Cl, py., DCM, r.t., 16 h (c) Bu_3SnH, AIBN (cat.), reflux, 16 h (78% from **74** + **76**).



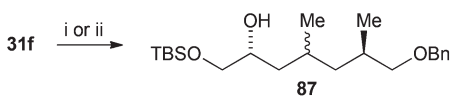
Scheme 13 Synthesis of the pentadecanol **84**. Reagents and conditions: (i) TBAF, THF, r.t., 16 h (98%); (ii) PPh_3, I_2, imid., THF, r.t., 2 h (**79**, 94%; **81**, 97%); (iii) 10% Pd/C, ethanol, H_2, r.t., 1 h (98%); (iv) ^{n}BuLi, 1,3-dithiane, THF −20 °C, 1 h, add **81**, 0 °C, 16 h (89%); (v) ^{n}BuLi, THF, HMPA, −78 °C, 30 min, add **79**, −78 °C, 1 h (88%); (vi) W-2 RANEY® nickel, THF, reflux, 16 h (95%).

conceptually different approach that may be useful.



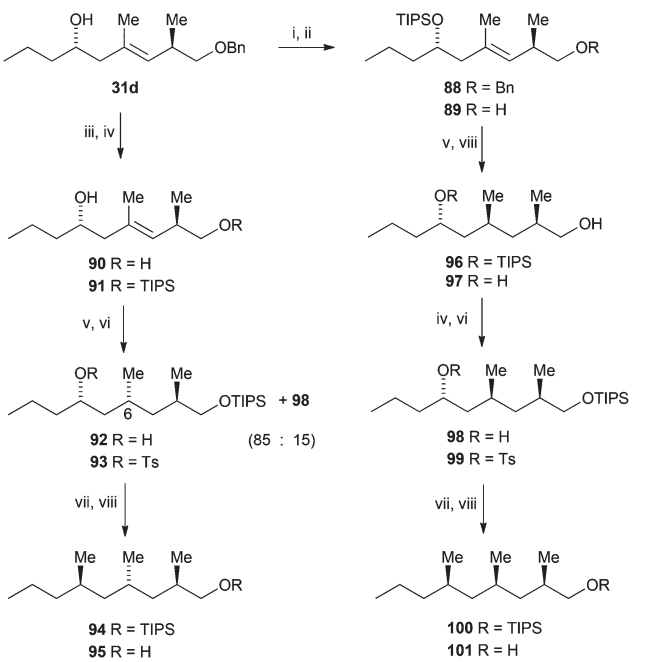
Preliminary studies of reduction of the 2,6-*anti*-4,6-dimethylheptenol **31f** using Pd/C catalysed hydrogenation or diimide were non-stereoselective, see Scheme 14. It was therefore decided to study the hydroxyl directed hydrogenation of homoallylic alcohols developed by Evans.[23,24]

Protection of the (*E*)-1,5-*anti*-product **31d** derived from butanal as its tri-isopropylsilyl ether **88** followed by removal of the benzyl group using lithium naphthalenide gave the primary alcohol **89**. Reversing these two steps, *i.e.* selective silylation of the diol **90** formed by removal of the benzyl ether under Birch conditions, gave the secondary alcohol **91**. Homogeneous hydrogenation of homoallylic alcohols using the achiral catalyst, [Rh(NBD)DIPHOS-4]BF_4 is known to be usefully stereoselective for primary alcohols.[23] Indeed, hydrogenation of the primary alcohol **89** gave the nonan-1-ol **96** in which the two methyl groups are *syn*-disposed with excellent stereoselectivity. The structure of this product was assigned by analogy with the literature.[23] The analogous hydrogenation of the secondary alcohol **91** was less stereoselective and gave a mixture of two epimeric products, ratio 85 : 15, although these were relatively easy to separate by chromatography. The minor product, isolated in a yield of 10%, was identified as the *syn*-dimethyl-epimer **98** by comparison with an authentic sample prepared from the nonan-1-ol **96** by desilylation and regioselective silylation of the resulting diol **97**. The major product, isolated in a yield of 56%, was therefore identified as the epimer **92** in which the two methyl groups are *anti*-disposed, see Scheme 15.

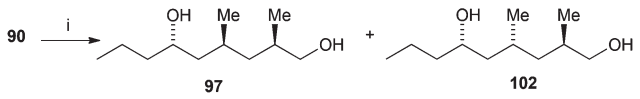


Scheme 14 Reduction of **31f**. Reagents and conditions: (i) NaOAc, $TsNHNH_2$, DME, reflux, 16 h (82%, 2 : 1); (ii) Pd/C, H_2, MeOH, r.t. 1 h (90%; 2 : 1).

To introduce the remaining methyl substituent to prepare open-chain compounds with either *syn*,*syn*- or *anti*,*anti*-1,3,5-disposed methyl substituents, it remained to substitute the secondary hydroxyl groups in the nonanols **92** and **98** by a methyl group with inversion of configuration. The toluene *p*-sulfonate **93** prepared from the alcohol **92** was converted into the *anti*,*anti*-2,4,6-trimethylnonane **94** using a higher order methyl cuprate.[17] This gave the required product **94** together with small amounts of elimination products that were removed by oxidation using osmium tetraoxide. Desilylation then gave the *anti*,*anti*-2,4,6-trimethylnonan-1-ol **95**. Similarly the alcohol **98** was converted to its toluene *p*-sulfonate **99** that gave the *syn*,*syn*-2,4,6-trimethylnonan-1-ol **101** on treatment



Scheme 15 Synthesis of the all-*anti*- and all *syn*-2,4,6-trimethylnonan-1-ols **95** and **101**. Reagents and conditions: (i) ^{i}Pr$_3$SiOTf, 2,6-lutidine, DCM, 0 °C to r.t., 16 h (89%); (ii) Li, naphthalene, THF, r.t. then −25 °C, add benzyl ether, −25 °C, 2 h (90%); (iii) Na, liq. NH_3, EtOH, NH_4Cl (75%); iv, ^{i}Pr$_3$SiCl, imid., DCM, r.t., 1 h (**91**, 90%; **98**, 90%); v, Rh(diphos-4), DCM, H_2, 950 psi, r.t., 5 h (**92**, 56% plus 10% of its C(6)-epimer **98**; **96**, 82%); (vi) TsCl, DMAP, DCM, r.t., 16 h (**93**, 91%; **99**, 91%); (vii) MeLi, CuCN, Et_2O, toluene, 0 °C, 15 min, add toluene *p*-sulfonate, 0 °C, 5 h (**94**, 48%; **100**, 45%); (viii) TBAF, THF, r.t., 16 h (**95**, 90%; **97**, 91%; **101**, 91%).



Scheme 16 Hydrogenation of diol **90**. Reagents and conditions: (i) Rh(diphos-4), DCM, H_2, 950 psi, r.t., 5 h (**97**, 48%; **102**, 10%).

with the higher order methyl cuprate followed by deprotection of the resulting product **100**, see Scheme 15.

Evans hydrogenation of the diol **90** was also investigated and found to give a mixture of two products, see Scheme 16. The major product was the *syn*-2,4-dimethylnonanediol **97**. The minor product was therefore the *anti*-dimethyl epimer **102**.

Summary and conclusions

This work has shown that bismuth(III) iodide mediated reactions of pent-2-enyl(tributyl)stannanes **1** and **16** with achiral aldehydes take place with useful levels of (*E*)-1,5-stereocontrol. This stereoselectivity is complementary to that observed for the analogous tin(IV) halide promoted processes.[2a,b] Moreover, the pent-2-enyl bromides **26**, **30** and **42** undergo reactions with aldehydes mediated by the low valency bismuth species generated from bismuth(III) iodide and activated zinc, a tin-free process, to give (*E*)-alk-3-enols with useful 1,5-stereoselectivity. However, only modest 1,6-*syn*-(*E*)-stereoselectivity was observed in the bismuth(III) iodide mediated reactions of the stannanes **43** and **44** with aldehydes and for the lower valency bismuth promoted reaction of the 5-methoxyhex-2-enyl bromide **48** with benzaldehyde.

These bismuth-mediated reactions were carried out in THF either at room temperature or under reflux. The stannane was added last in the bismuth(III) iodide-mediated reactions of the pent-2-enylstannanes. The pent-2-enyl bromide and the aldehyde were added simultaneously to the low valency bismuth species in the case of the tin-free procedure. Therefore, in these reactions the generation of any organobismuth species is taking place in the presence of the aldehyde under very different conditions from the tin(IV) halide mediated reactions of the pent-2-enylstannanes, where transmetallation of the stannane at −78 °C occurs before the addition of the aldehyde. Nevertheless, a transmetallation of the pent-2-enylstannanes by bismuth(III) iodide is believed to be taking place in these bismuth(III) iodide mediated reactions of the pentenylstannanes since the alternative process, involving the bismuth(III) iodide acting as a Lewis acid promoting the reactions by coordination to the aldehyde, would give rise to the regioisomeric products observed in the boron trifluoride etherate promoted reactions, see Scheme 1.[9] These products were either not observed at all or were only detected in trace amounts.

The formation of the same products in both the bismuth(III) iodide promoted reactions of the pent-2-enylstannanes and in the low valency bismuth induced reactions of the pent-2-enyl bromides, suggests that similar species may be involved in both processes. One possibility is that the transmetallation of the pent-2-enylstannanes, *e.g.* stannane **1**, is generating an allylic organobismuth species perhaps **104** (X = I) and that a similar species is being formed from the pent-2-enyl bromide **26** and the low-valency bismuth species formed from the bismuth(III) iodide and activated zinc. Reduction of bismuth(III) by zinc can give bismuth(0) although an alternative intermediate might be the zinc–bismuth(III) iodide insertion species **103**. Precisely what is coordinated to the bismuth in the allylic organobismuth intermediates is not known, the σ-bonded structure **104** is drawn for simplicity although there may be some Π-allyl character in the intermediate. However, once formed these intermediates could react with aldehydes either *via* an open-chain process or *via* the six-membered chair-like transition structure **105** to give the observed products.

Bismuth has a lone-pair and therefore the same coordination number as tin. Moreover carbon–tin and carbon–bismuth bond lengths are similar. So if similar σ-bonded allylic organic metallic species are involved why there are different stereochemical outcomes in the reactions with aldehydes of the allyltin trihalide **106** and the allylbismuth species **104** generated from the pent-2-enylstannane **1**? Typically the lone-pair and the bismuth–carbon bond are apical in pentacoordinated organobismuth compounds[25] and this is indicated in the structure **104**. If the bismuth–oxygen coordination is retained in the reaction with the aldehyde, then in the cyclic process **105** the bismuth would be octahedral. In the analogous reactions of allyltin trichlorides with aldehydes, it is believed that the tin is trigonal bypyramidal as indicated in transition structure **107**.[26] The different geometry around the metal in these transition structures may be responsible for their different stereochemical outcomes. However in the absence of clarification of the types of intermediates involved in the bismuth mediated processes, this dichotomy cannot really be resolved.

Indeed this mechanistic discussion is only speculative. In the case of the low-valency bismuth mediated reactions of the pent-2-enyl halides, the reactions fail if any of the components, *i.e.* the zinc powder or the bismuth(III) iodide, is omitted but full details of the nature of the participation of all of the components, *e.g.* the zinc, are not clear. The mechanism outlined in Fig. 1 is likely to be a significant oversimplification.

Under the reaction conditions, the reactive intermediates in the bismuth mediated reactions may be able to equilibrate unlike the kinetically controlled process believed to be involved in the tin(IV) halide mediated reactions.[26] The lower yields observed for reactions of the 4-alkoxypent-2-enylstannanes and the 4-alkoxypent-2-enyl bromides with aldehydes, may be due to a competing elimination, see structure **108** in Fig. 1.

The (*E*)-1,5-*anti*-stereoselectivity observed for the 5-alkoxypent-2-enylstannanes and the analogous pent-2-enyl bromides may be useful in synthesis. This is illustrated by the stereoselective syntheses of open-chain compounds with methyl groups at 1,3,5- and 1,5,9,13-positions along the aliphatic

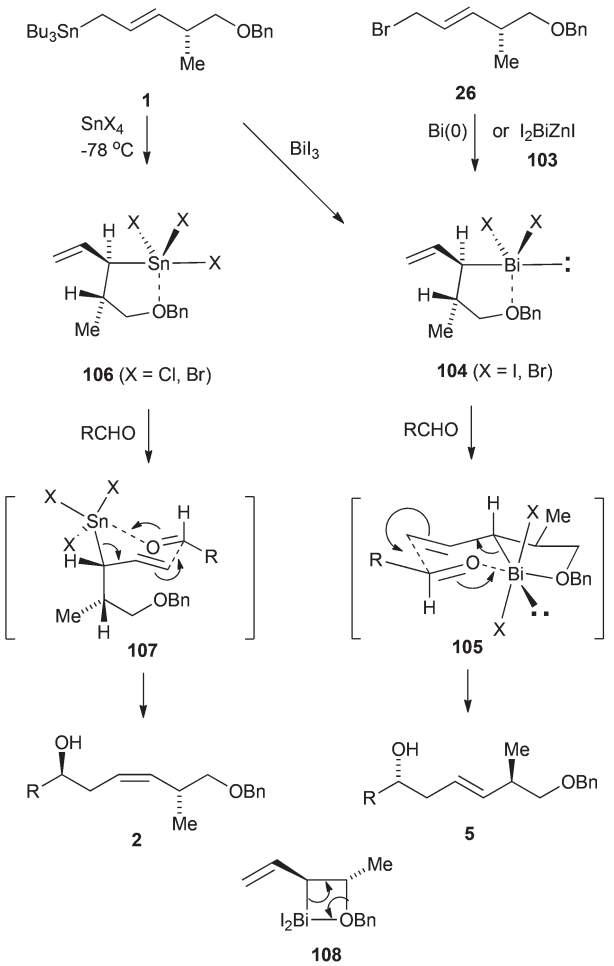


Fig. 1 Possible mechanisms for the bismuth-mediated reactions of allylstannanes and allyl bromides with aldehydes.

chain. The (*R*)-pentenyl bromide **(*R*)-26** was the only chiral starting material used in the synthesis of the pentadecanol **84**. Two of its stereogenic centres were derived directly from the pent-2-enyl bromide and the other two from its reaction with 2-*tert*-butyldimethylsilyloxyethanal. Similarly, the 2,4-dimethylpent-2-enyl bromide **30** was the only chiral starting material used in the synthesis of the *syn*,*syn*- and *anti*,*anti*-2,4,6-trimethylnonanols **95** and **101**. Although the (*R*)-enantiomer of the dimethylpent-2-enyl bromide **30** was used in this synthesis, the use of racemic bromide would have led to a diastereoselective synthesis of the racemic *syn*,*syn*- and *anti*,*anti*-trimethylnonanols. Stereoselective syntheses of racemic compounds of this type would be difficult by other routes and could be of interest. Finally this chemistry has since been applied to complete stereoselective syntheses of (4*S*,6*R*,8*R*,10*S*,16*S*)- and (4*S*,6*R*,8*R*,10*S*,16*R*)-pentamethyldocosanes so confirming the relative stereochemistry of the pentamethyldocosane isolated from the cuticular extract of the cane beetle *Antitrogus parvulus*.[27] The one-pot formation of allylic halides from the corresponding alcohols and their low valency bismuth induced reactions with aldehydes has been found to be useful[14c] and so it may be possible to use allylic alcohols, *e.g.* **25**, **29** and **41**, directly for remote stereocontrol, although this has yet to be confirmed. Alternatively the stereoselective generation of allylic organometallic intermediates by oxidation of suitable alkenes may be of interest and would be "atom efficient." These options have yet to be investigated.

Experimental

General experimental procedures

^{1}H and ^{13}C NMR spectra were recorded on Varian Unity 500, Varian Unity Inova 400 and Varian Unity Inova 300 spectrometers with residual non-deuterated solvent as the internal standard. Coupling constants are rounded to the nearest 0.5 Hz. IR spectra were recorded on an ATI Mattson Genesis FTIR as thin films produced by evaporation of a DCM solution on sodium chloride plates unless otherwise stated. Mass spectra were recorded on Fison VG Trio 2000 and Kratos Concept spectrometers. Chemical ionisation (CI) was performed using ammonia. Chromatography refers to flash column chromatography using Merck silica gel 60H (230–300 mesh).

Tetrahydrofuran (THF) was dried and distilled from sodium metal using benzophenone as an indicator under an atmosphere of nitrogen. Dichloromethane (DCM) was dried and distilled from calcium hydride under an atmosphere of nitrogen. Ether refers to diethyl ether, which was dried and distilled from sodium metal using benzophenone as an indicator under an atmosphere of nitrogen. Light petroleum refers to the fraction of petroleum ether distilled between 40–60 °C. Benzene and hexane were dried over sodium metal. Butyllithium (1.6 M in hexanes) was titrated against a solution of propan-2-ol in xylene with 2,2′-bipyridine as an indicator. Triethylamine and diisopropylamine were dried over potassium hydroxide pellets. Brine refers to saturated aqueous sodium chloride. Anhydrous cerium(III) chloride was prepared by heating the heptahydrate overnight at 80 °C under reduced pressure and was stored under an atmosphere of N_2.

2-(1-Benzyloxyprop-2-yl)-1-phenylbut-3-en-1-ols 3 and 4. Boron trifluoride diethyletherate (40 μL, 0.31 mmol) cooled to −78 °C was added to benzaldehyde (30 μL, 0.31 mmol) in DCM at −78 °C. After 10 min, stannane **1** (150 mg, 0.31 mmol) was added at −78 °C and the mixture was allowed to warm to 0 °C. Methanolic ammonium chloride (10 mL) was added and the aqueous phase extracted with DCM (3 × 10 mL). The organic extracts were washed with brine (30 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue (4 : 1 light petroleum–ether) afforded the title compounds **3** and **4** as a colourless oil (46 mg, 51%), a 70 : 30 mixture of epimers. These were separated by chromatography. The less polar isomer was the major product (21 mg, 23%); ν_{max}/cm^{-1} 3387, 3029, 2958, 2924, 2871, 1638, 1453, 1365, 1075, 1029, 1000 and 915; δ_H ($CDCl_3$, 300 MHz) 0.91 (3 H, d, *J* 7, 3′-H_3), 2.24 (1 H, m, 2′-H), 2.48 (1 H, m, 2-H), 3.32 (1 H, dd, *J* 7.5, 4, 1′-H), 3.48 (1 H, t, *J* 7.5, 1′-H′), 4.15 (1 H, d, *J* 6, OH), 4.60 (2 H, s, $PhCH_2O$), 4.80 (1 H, t, *J* 7, 1-H), 4.97

(1 H, dd, *J* 16 and 3, 4-H), 5.12 (1 H, dd, *J* 10 and 3, 4-H′), 5.77 (1 H, dt, *J* 17 and 10, 3-H) and 7.20–7.50 (10 H, m, ArH); *m*/*z* (CI) 314 (M^+ + 18, 5%), 296 (M^+, 3) and 279 (M^+ − 17, 100). The more polar isomer was the minor product; ν_{max}/cm^{-1} 3375, 2959, 2925, 2871, 1602, 1453, 1365, 1075, 1029, 916 and 736; δ_H ($CDCl_3$, 300 MHz) 0.84 (3 H, d, *J* 7, 3′-H_3), 2.13 (1 H, d, *J* 4, OH), 2.32 (1 H, m, 2′-H), 2.59 (1 H, dt, *J* 10 and 4, 2-H), 3.28 (2 H, m, 1′-H_2), 4.43 (2 H, s, $PhCH_2O$), 4.60 (1 H, m, 1-H), 4.69 (1 H, dd, *J* 17 and 2, 4-H), 4.84 (1 H, dd, *J* 10 and 2, 4-H′), 5.39 (1 H, dt, *J* 17 and 10, 3-H) and 7.25 (10 H, m, ArH); *m*/*z* (CI) 314 (M^+ + 18, 8%), 296 (M^+, 6), 279 (M^+ − 17, 100) and 111 (100).

Standard procedure for the bismuth(III) iodide promoted reactions of alk-2-enylstannanes with aldehydes. (3*E*,1*RS*,5*RS*)-6-benzyloxy-5-methyl-1-phenylhex-3-en-1-ol 5a. Benzaldehyde (0.1 mL, 0.93 mmol) was added to BiI_3 (182 mg, 0.31 mmol) in MeCN (2 mL) and the solution stirred for 15 min at room temperature. Racemic stannane **1** (150 mg, 0.31 mmol) in MeCN (0.5 mL) and DCM (0.3 mL) was added dropwise and the mixture stirred for 30 min. Saturated aqueous ammonium chloride (5 mL) was added and the aqueous phase extracted with DCM (3 × 15 mL). The organic extracts were washed with brine (40 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue (4 : 1, light petroleum–ether with 1% Et_3N) afforded the *title compound* **5a** as a colourless oil (67 mg, 72%) containing *ca.* 8% of its *syn*-epimer **6a** (^1H NMR) (Found: $M^+ + NH_4$, 314.2118. $C_{20}H_{28}NO_2$ requires *M*, 314.2120); ν_{max}/cm^{-1} 3424, 3029, 2857, 1494, 1453, 1361, 1201, 1091, 976 and 737; δ_H ($CDCl_3$, 300 MHz) major epimer **5a** 1.14 (3-H, d, *J* 7, 5-CH_3), 2.55 (3 H, m, 2-H_2 and 5-H), 3.34 (2 H, m, 6-H_2), 4.55 (2 H, s, $PhCH_2O$), 4.70 (1 H, dd, *J* 8 and 5, 1-H), 5.54 (2 H, m, 3-H and 4-H) and 7.36 (10 H, m, ArH); minor epimer **6a** 1.15 (3 H, d, *J* 7, 5-CH_3); (C_6D_6, 300 MHz) 1.09 (3-H, d, *J* 7, 5-CH_3 major) and 1.12 (3-H, d, *J* 7, 5-CH_3 minor); δ_C ($CDCl_3$, 75 MHz) 17.1, 32.3, 38.5, 73.0, 73.2, 74.6, 125.6, 126.1, 127.1, 127.6, 127.8, 128.2, 128.3, 136.7, 137.9 and 144.7; *m*/*z* (CI) 314 (M^+ + 18, 22%), 296 (M^+, 50), 279 (74), 261 (24), 173 (38) and 85 (100). Minor amounts of the (*Z*)-*anti*-isomer **2a** (<5 mg, <6%) were isolated.

The reactions using indium(III) halides were carried out using similar procedures except that equimolar amounts of the indium(III) halide, stannane **1** and benzaldehyde were used.

Standard procedure for the bismuth(III) iodide/zinc promoted reactions of allyl bromides with aldehydes: (3*E*,1*R*,5*R*)-6-benzyloxy-5-methyl-1-phenylhex-3-en-1-ol 5a. Activated zinc powder (31 mg, 0.48 mmol) was suspended in a solution of bismuth(III) iodide (248 mg, 0.42 mmol), in THF (1.5 mL) and the mixture stirred vigorously at room temperature for 1 h during which time the orange/grey suspension turned black. The (*R*)-bromide **26** (75 mg, 0.28 mmol) in THF (0.5 mL) and benzaldehyde (29 μL, 0.28 mmol) were added and the resulting mixture heated under reflux for 2 h. After cooling and concentration under reduced pressure, chromatography of the residue (4 : 1, light petroleum–ether) gave the (1*R*,5*R*)-enantiomer of the *title compound* **5a** as a colourless oil (69 mg, 83%) containing *ca.* 4% of its epimer **6a**, R_f = 0.25 (4 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +47.3 (*c* 1.8, $CHCl_3$) (Found: $M^+ + NH_4$, 314.2118. $C_{20}H_{28}NO_2$ requires *M*, 314.2120). Spectroscopic data were identical to those of the racemate.

(3*E*,1*SR*,5*SR*)-6-Benzyloxy-5-methyl-1-(4-nitrophenyl)-hex-3-en-1-ol 5b. Following the standard procedure, 4-nitrobenzaldehyde (93 mg, 0.42 mmol), BiI_3 (120 mg, 0.21 mmol) in MeCN (2.0 mL) and the racemic stannane **1** (100 mg, 0.21 mmol) in MeCN (0.4 mL) and DCM (0.3 mL), after chromatography (3 : 1, light petroleum–ether with 1% Et_3N) afforded the *title compound* **5b** as a colourless oil (38 mg, 53%) containing *ca.* 5% of its (*E*)-1,5-*syn*-epimer **6b** (^1H NMR) (Found: $M^+ + NH_4$, 359.1975. $C_{20}H_{27}N_2O_4$ requires *M*, 359.1971); ν_{max}/cm^{-1} 3434, 2958, 2928, 2869, 1603, 1519, 1346, 1072 and 855, 749; δ_H ($CDCl_3$, 300 MHz) major 1,5-*anti*-epimer **5b** 1.03 (3 H, d, *J* 7, 5-CH_3), 2.36 (1 H, dt, *J* 13.5, 8, 2-H), 2.50–2.60 (2 H, m, 2-H′ and 5-H), 2.66 (1 H, d, *J* 3, OH), 3.25 (2 H, m, 6-H_2), 4.54 (2 H, s, $PhCH_2O$), 4.78 (1 H, m, 1-H), 5.48 (1 H, ddd, *J* 15.5, 7.5 and 5.5, 3-H), 5.56 (1 H, dd, *J* 15.5 and 6, 4-H), 7.36 (5 H, m, ArH), 7.54 (2 H, d, *J* 9, ArH) and 8.22 (2 H, d, *J* 9, ArH); minor 1,5-*syn*-epimer **6b** 1.05 (3 H, d, *J* 7, 5-CH_3); δ_C ($CDCl_3$, 75 MHz) 16.8, 37.2, 43.0, 71.9, 73.0, 74.7, 123.5, 124.5, 126.5, 127.6, 128.3, 138.2, 139.0, 147.1 and 151.3; *m*/*z* (CI) 359 (M^+ + 18, 100%), 342 (M^+ + 1, 4), 294 (60), 206 (24) and 108 (38).

(3*E*,1*SR*,5*SR*)-6-Benzyloxy-1-(4-methoxyphenyl)-5-methyl-hex-3-en-1-ol 5c. Following the standard procedure, 4-methoxybenzaldehyde (0.15 mL, 0.93 mmol), BiI_3 (243 mg, 0.41 mmol) in MeCN (3.0 mL) and the racemic stannane **1** (200 mg, 0.41 mmol) in MeCN (0.7 mL) and DCM (0.5 mL) after chromatography (3 : 1, light petroleum–ether with 1% Et_3N) afforded the *title compound* **5c** as a colourless oil (76 mg, 56%) containing about 8% of its 1,5-*syn*-epimer **6c** (^1H NMR) (Found: M^+ + H, 327.1965. $C_{21}H_{27}O_3$ requires *M*, 327.1962); ν_{max}/cm^{-1} 3426, 2956, 2928, 1612, 1513, 1454, 1247, 1094, 1036 and 832; δ_H ($CDCl_3$, 300 MHz) major 1,5-*anti*-epimer **5c** 0.95 (3 H, d, *J* 7, 5-CH_3), 2.07 (1 H, d, *J* 3, OH), 2.41 (3 H, m, 2-H_2 and 5-H), 3.13 (2 H, m, 6-H_2), 3.23 (3 H, s, OCH_3), 4.31 (2 H, s, $PhCH_2O$), 4.50 (1 H, td, *J* 6 and 3, 1-H), 5.44 (2 H, m, 3-H and 4-H), 6.81 (2 H, d, *J* 9, ArH) and 7.20 (7 H, m, ArH); minor 1,5-*syn*-epimer **6c** 0.98 (3 H, d, *J* 7, 5-CH_3); δ_C ($CDCl_3$, 75 MHz) 17.1, 36.7, 36.8, 41.7, 55.1, 72.8, 75.4, 77.9, 113.4, 126.3, 127.3, 127.4, 128.2, 134.3, 134.7, 138.6 and 158.8; *m*/*z* (CI) 327 (M^+ + 1, 14%), 326 (M^+, 30), 309 (100), 203 (48) and 137 (32). A sample of the (*Z*)-1,5-*anti*-isomer **2c** (R = 4-$MeOC_6H_4$) was also isolated (7 mg, 5%).

(2*E*,6*E*,4*SR*,8*SR*)-9-Benzyloxy-8-methylnona-2,6-dien-4-ol 5d. Following the standard procedure, crotonaldehyde (0.076 mL, 0.93 mmol), BiI_3 (182 mg, 0.31 mmol) in MeCN (2.0 mL) and the racemic stannane **1** (150 mg, 0.31 mmol) in MeCN (0.5 mL) and DCM (0.3 mL), after chromatography of the residue (3 : 1, light petroleum–ether with 1% Et_3N) afforded the *title compound* **5d** as a colourless oil (37 mg, 45%) containing *ca.* 10% of its *syn*-epimer **6d** (^1H NMR) (Found: $M^+ + NH_4$, 278.2123. $C_{17}H_{28}NO_2$ requires *M*, 278.2134); ν_{max}/cm^{-1} 3420, 2958, 2928, 2854, 1453, 1376, 1093, 1029, 966 and 736; δ_H ($CDCl_3$, 300 MHz) major *anti*-epimer **5d** 1.06 (3 H, d, *J* 7,

8-CH_3), 1.73 (3 H, d, *J* 7, 1-H_3), 2.26 (2 H, m, 5-H_2), 2.54 (1 H, m, 8-H), 3.35 (2 H, dd, *J* 7 and 3, 9-H_2), 4.07 (1 H, m, 4-H), 4.55 (2 H, s, $PhCH_2O$), 5.53 (3 H, m, 2-H, 6-H and 7-H), 5.71 (1 H, m, 3-H) and 7.35 (5 H, m, ArH); minor *syn*-epimer **6d** 1.08 (3 H, d, *J* 7, 8-CH_3); δ_C ($CDCl_3$, 75 MHz) 17.0, 17.6, 37.1, 41.0, 71.6, 72.9, 75.1, 125.5, 126.1, 126.6, 127.5, 128.3, 133.3, 137.1 and 138.4; *m*/*z* (CI) 278 (M^+ + 18, 36%), 260 (M^+, 64), 243 (100) and 225 (20).

Following the standard procedure, bromide **26** (100 mg, 0.374 mmol) and crotonaldehyde (31 μL, 0.374 mmol) afforded the (4*R*,8*R*)-enantiomer of the title compound **5d** as a colourless oil (84 mg, 86%) containing *ca.* 7% of its (4*S*)-epimer **6d**, R_f = 0.3 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +9 (*c* 1.7, $CHCl_3$) (Found: M^+ + NH_4, 278.2123. $C_{17}H_{28}NO_2$ requires *M*, 278.2134). Spectroscopic data were identical to those of the racemate.

(5*E*,3*SR*,7*SR*)-8-Benzyloxy-2,7-dimethyloct-5-en-3-ol 5e. Following the standard procedure, 2-methylpropanal (90 μL, 0.93 mmol), BiI_3 (182 mg, 0.31 mmol) in MeCN (2.0 mL) and the racemic stannane **1** (150 mg, 0.31 mmol) in MeCN (0.5 mL) and DCM (0.3 mL), after chromatography (3 : 1, light petroleum–ether with 1% Et_3N) afforded the *title compound* **5e** as a colourless oil (43 mg, 55%) containing 7% of its *syn*-epimer **6e** (^{1}H NMR) (Found: M^+ + NH_4, 280.2279. $C_{17}H_{30}NO_2$ requires *M*, 280.2290); ν_{max}/cm^{-1} 3443, 2958, 2930, 2872, 1454, 1365, 1094, 1029, 973 and 736; δ_H (C_6D_6, 300 MHz) major *anti*-epimer **5e** 0.89 (3 H, d, *J* 7, 7-CH_3), 0.97 (6 H, d, *J* 7, 1-H_3 and 2-CH_3), 1.60 (1 H, m, 2-H), 1.64 (1 H, d, *J* 4, OH), 1.98 (1 H, m, 4-H), 2.12 (1 H, m, 4-H′), 2.44 (1 H, m, 7-H), 3.13 (2 H, dd, *J* 7 and 3, 8-H_2), 3.18 (1 H, m, 3-H), 4.31 (2 H, s, $PhCH_2O$), 5.41 (2 H, m, 5-H and 6-H), 7.10 (1 H, m, ArH), 7.19 (2 H, m, ArH) and 7.29 (2 H, m, ArH); minor *syn*-epimer **6e** 1.41 (1 H, d, *J* 4, OH); *m*/*z* (CI) 280 (M^+ + 18, 100%), 263 (M^+ + 1, 45) and 245 (24). A small amount of the (*Z*)-*anti*-isomer **2e** (5 mg, 7%) was also isolated.

Following the standard procedure, the (*R*)-bromide **26** (100 mg, 0.374 mmol) and 2-methylpropanal (34 μL, 0.37 mmol) afforded the (3*R*,7*R*)-enantiomer of the title compound **5e** as a colourless oil (80 mg, 82%) containing *ca.* 5% of its 3-epimer **6e**, R_f = 0.3 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +14 (*c* 1.9, $CHCl_3$) (Found: M^+ + NH_4, 280.2279. $C_{17}H_{30}NO_2$ requires *M*, 280.2290); δ_C (C_6D_6, 75 MHz) 16.9, 17.2, 17.4, 18.6, 32.8, 37.0, 37.6, 72.7, 74.9, 127.3, 127.6, 127.9, 128.2, 136.5 and 138.4; *m*/*z* (CI) 280 (M^+ + 18, 100%), 263 (M^+ + 1, 45) and 245 (24).

(6*E*,4*RS*,8*SR*)-Benzyloxy-8-methylnon-6-en-4-ol 5f. Following the standard procedure, butanal (84 μL, 0.93 mmol), BiI_3 (182 mg, 0.31 mmol) in MeCN (2.0 mL) and the racemic stannane **1** (150 mg, 0.31 mmol) in MeCN (0.5 mL) and DCM (0.3 mL), after chromatography (3 : 1, light petroleum–ether with 1% Et_3N) afforded the *title compound* **5f** as a colourless oil (50 mg, 61%) containing about 7% of its *syn*-epimer **6f** (^{1}H NMR) (Found: M^+ + NH_4, 280.2280. $C_{17}H_{30}NO_2$ requires *M*, 280.2291); ν_{max}/cm^{-1} 3426, 2957, 2928, 2871, 1455, 1361, 1094, 1028, 973 and 736; δ_H ($CDCl_3$, 300 MHz) major *anti*-epimer **5f** 0.97 (3 H, t, *J* 7, 1-H_3), 1.06 (3 H, d, *J* 7, 8-CH_3), 1.35–1.60 (4 H, m, 2-H_2 and 3-H_2), 1.83 (1 H, m, OH), 2.09 (1 H, m, 5-H), 2.29 (1 H, m, 5-H′), 2.54 (1 H, m, 8-H), 3.35 (2 H, d, *J* 6, 9-H_2), 3.62 (1 H, m, 4-H), 4.55 (2 H, s, $PhCH_2O$), 5.52 (2 H, m, 6-H and 7-H) and 7.35 (5 H, m, ArH); minor *syn*-epimer **6f** 1.08 (3 H, d, *J* 7, 8-CH_3); δ_C (C_6D_6, 75 MHz) 13.9, 16.8, 18.9, 37.2, 39.0, 41.1, 69.9, 72.7, 74.9, 126.3, 127.2, 127.6, 128.1, 136.4 and 138.8; *m*/*z* (CI) 280 (M^+ + 18, 100%), 263 (M^+ + 1, 66), 245 (32), 174 (34) and 91 (44). A small amount of the (*Z*)-*anti*-isomer **2f** (R = ^{n}Pr) (5 mg, 6%) was also isolated.

Following the standard procedure, bromide **26** (100 mg, 0.374 mmol) and butanal (34 μL, 0.374 mmol) afforded the (4*S*,8*R*)-enantiomer of the *title compound* **5f** as a colourless oil (90 mg, 92%) containing *ca.* 7% of its 4-epimer **6f**, R_f = 0.3 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +9 (*c* 1.5, $CHCl_3$) (Found: M^+ + NH_4, 280.2279. $C_{17}H_{30}NO_2$ requires *M*, 280.2290). Spectroscopic data were identical to those of the racemate.

(4*E*,2*R*,6*R*)-1,7-Bis-benzyloxy-6-methylhept-4-en-2-ol 5g. Following the standard procedure, the (*R*)-bromide **26** (100 mg, 0.374 mmol) and benzyloxyacetaldehyde (53 μL, 0.374 mmol) afforded the *title compound* **5g** as a colourless oil (80 mg, 63%) containing *ca.* 13% of its (2*S*)-epimer **6g** (^{1}H NMR) R_f = 0.4 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +10 (*c* 0.9, $CHCl_3$) (Found: M^+ + NH_4, 358.2382. $C_{22}H_{32}NO_3$ requires *M*, 358.2377); ν_{max}/cm^{-1} 3445, 3028, 2856, 1602, 1453, 1363, 1204, 1092, 1028 and 973; δ_H ($CDCl_3$, 400 MHz) major *anti*-epimer **5g** 0.92 (3 H, d, *J* 7, 6-CH_3), 2.14 (2 H, m, 3-H_2), 2.31 (1 H, m, OH), 2.40 (1 H, m, 6-H), 3.20 and 3.24 (each 1 H, dd, *J* 9, 6.5, 7-H), 3.30 and 3.40 (each 1 H, dd, *J* 9.5, 7, 1-H), 3.74 (1 H, m, 2-H), 4.42 and 4.46 (each 2 H, s, OCH_2Ph), 5.39 (2 H, m, 4-H and 5-H) and 7.23 (10 H, m, ArH); minor *syn*-epimer **6g** 0.93 (3 H, d, *J* 7, 6-CH_3), 2.27 (1 H, m, OH) and 4.45 (2 H, s, OCH_2Ph); δ_C ($CDCl_3$, 100 MHz) 17.9, 37.7, 37.7, 70.7, 73.7, 74.1, 74.6, 76.0, 125.9, 128.3, 128.3, 128.5, 129.1, 129.2, 129.4, 137.3, 138.8 and 139.3; *m*/*z* (CI) 358 (M^+ + 18, 38%), 168 (66) and 108 (100).

(5*E*,3*R*,7*R*)-1,8-Bis-benzyloxy-7-methyloct-5-en-3-ol 5h. Following the standard procedure, the (*R*)-bromide **26** (100 mg, 0.374 mmol) and 3-benzyloxypropanal (61 mg, 0.374 mmol) afforded the *title compound* **5h** as a colourless oil (115 mg, 87%) containing *ca.* 5% of its (3*S*)-epimer **6h** (^{1}H NMR), R_f = 0.4 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +11 (*c* 0.9, $CHCl_3$) (Found: M^+, 355.2268. $C_{23}H_{31}O_3$ requires *M*, 355.2268); ν_{max}/cm^{-1} 3387, 3029, 2925, 2861, 1453, 1365, 1206, 1096 and 1027; δ_H ($CDCl_3$, 400 MHz) major *anti*-epimer **5h** 1.01 (3 H, d, *J* 7, 7-CH_3), 1.74 (2 H, m, 2-H_2), 2.19 (2 H, m, 4-H_2), 2.47 (1 H, m, 7-H), 2.77 (1 H, s, OH), 3.28 and 3.33 (each 1 H, dd, *J* 9, 8, 8-H), 3.60 3.70 (2 H, m, 1-H_2), 3.78 (1 H, m, 3-H), 4.50 and 4.51 (each 2 H, s, OCH_2Ph), 5.47 (2 H, m, 5-H and 6-H) and 7.31 (10 H, m, ArH); minor *syn*-epimer **6h** 1.02 (3 H, d, *J* 7, 7-CH_3); δ_C ($CDCl_3$, 100 MHz) 19.4, 38.1, 39.3, 43.1, 71.1, 72.5, 75.2, 75.6, 77.6, 128.2, 129.8, 129.9, 129.9, 130.0, 130.6, 130.7, 138.9, 140.4 and 140.9; *m*/*z* (CI) 372 (M^+ + 18, 4%), 354 (M^+, 8), 182 (6), 108 (64) and 91 (100).

(4*E*,2*R*,6*R*)-7-Benzyloxy-6-methyl-1-*tert*-butyldimethylsilyloxyhept-4-en-2-ol 5i. Following the standard procedure, the (*R*)-bromide **26** (100 mg, 0.374 mmol) and *tert*-butyldimethylsilyloxyacetaldehyde (71 μL, 0.374 mmol) afforded the *title*

compound **5i** as a colourless oil (90 mg, 66%) containing <5% of its (2*S*)-epimer **6i**, R_f = 0.4 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +4 (*c* 1.5, $CHCl_3$) (Found: M^+ + H, 365.2514. $C_{21}H_{37}O_3Si$ requires *M*, 365.2506); ν_{max}/cm^{-1} 3461, 2928, 2857, 1461, 1361, 1254, 1114, 1096, 972, 837 and 778; δ_H ($CDCl_3$, 400 MHz) 0.00 (6 H, s, 2 × $SiCH_3$), 0.83 [9 H, s, $SiC(CH_3)_3$], 0.96 (3 H, d, *J* 7, 6-CH_3), 2.11 (2 H, m, 3-H_2), 2.31 (1 H, d, *J* 4, OH), 2.42 (1 H, m, 6-H), 3.21 and 3.28 (each 1 H, dd, *J* 9 and 7, 7-H), 3.39 (1 H, dd, *J* 10 and 7, 1-H), 3.55 (2 H, m, 1-H′ and 2-H), 4.44 (2 H, s, OCH_2Ph), 5.41 (2 H, m, 4-H and 5-H) and 7.25 (5 H, m, ArH); δ_C ($CDCl_3$, 100 MHz) −5.1, 18.8, 20.0, 27.6, 38.2, 38.6, 68.2, 73.1, 74.6, 77.0, 127.2, 129.1, 129.2, 129.3, 137.8 and 140.3; *m*/*z* (CI) 382 (M^+ + 18, 6%), 365 (M^+ + 1, 6), 108 (46) and 91 (100).

(5*E*,3*R*,7*R*)-8-Benzyloxy-7-methyl-1-*tert*-butyldimethylsilyloxy-oct-5-en-3-ol 5j. Following the standard procedure, the (*R*)-bromide 26 (100 mg, 0.374 mmol) and 3-*tert*-butyldimethylsilyloxypropanal (70 mg, 0.374 mmol) afforded the *title compound* **5j** as a colourless oil (89 mg, 63%) containing <5% of its (3*S*)-epimer **6j**, R_f = 0.4 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +9 (*c* 1.7, $CHCl_3$) (Found: M+, 378.2577. $C_{22}H_{38}O_3Si$ requires *M*, 378.2585); ν_{max}/cm^{-1} 3445, 2930, 2857, 1455, 1361, 1255, 1092, 973, 836 and 777; δ_H ($CDCl_3$, 400 MHz) 0.00 (6 H, s, 2 × $SiCH_3$), 0.82 [9 H, s, $SiC(CH_3)_3$], 0.95 (3 H, d, *J* 7, 7-CH_3), 1.55 (2 H, m, 2-H_2), 2.12 (2 H, m, 4-H_2), 2.41 (1 H, m, 7-H_2), 3.21 and 3.27 (each 1 H, dd, *J* 9, 6.5, 8-H), 3.65–3.80 (3 H, m, 1-H_2 and 3-H), 4.43 (2 H, s, OCH_2Ph), 5.40 (2 H, m, 5-H and 6-H) and 7.24 (5 H, m, ArH); δ_C ($CDCl_3$, 100 MHz) −5.1, 18.7, 19.7, 27.4, 38.5, 39.4, 42.4, 63.9, 72.6, 74.4, 76.8, 127.6, 129.0, 129.1, 129.8, 137.6 and 140.1; *m*/*z* (CI) 396 (M^+ + 18, 6%), 379 (M^+ + 1, 18), 189 (16), 108 (22) and 91 (100).

(3*E*)-6-Benzyloxy-5-methyl-1-phenylhex-3-en-1-one 7. Alcohol **5a** (30 mg, 0.103 mmol containing *ca.* 30% of **6a**) in DCM (0.4 mL) was added dropwise to the Dess Martin periodinane (218 mg, 0.515 mmol) in DCM (0.8 mL) at room temperature. After 30 min, aqueous sodium hydroxide (1.3 M; 3 mL) was added and the aqueous layer was extracted with ether (2 × 15 mL). The combined organic extracts were washed with aqueous sodium hydroxide (1.3 M; 20 mL) and water (20 mL), dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography of the residue (6 : 1, light petroleum–ether) afforded the *title compound* **7** as a colourless oil (27 mg, 75%) (Found: M^+ + H, 295.1699. $C_{20}H_{23}O_2$ requires *M*, 295.1698); ν_{max}/cm^{-1} 3029, 2961, 2858, 1686, 1449, 1275, 1208, 1097, 973 and 746; δ_H ($CDCl_3$, 300 MHz) 0.97 (3 H, d, *J* 7, 5-CH_3), 2.46 (1 H, m, 5-H), 3.26 (2 H, m, 6-H_2), 3.63 (2 H, d, *J* 7, 2-H_2), 4.42 (2 H, s, $PhCH_2O$), 5.52 (1 H, dd, *J* 16 and 7, 4-H), 5.69 (1 H, dt, *J* 16 and 7, 3-H), 7.24 (5 H, m, ArH), 7.38 (2 H, m, ArH), 7.49 (1 H, m, ArH) and 7.88 (2 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 16.9, 36.9, 42.5, 72.9, 75.1, 122.2, 127.4, 127.5, 128.2, 128.5, 128.6, 133.0, 136.6, 137.1, 138.5 and 198.4; *m*/*z* (CI) 312 (M^+ + 18, 71%) and 295 (M^+ + 1, 100).

Standard procedure for Mitsunobu reactions: (3*E*,1*RS*,5*SR*)-6-benzyloxy-5-methyl-1-phenylhex-3-en-1-yl 4-nitrobenzoate 8. The alcohol **5a** [70 mg, 0.24 mmol containing *ca.* 30% of its (*E*)-1,5-*syn*-epimer **6a**], triphenylphosphine (240 mg, 0.94 mmol) and 4-nitrobenzoic acid (160 mg, 0.94 mmol) were dissolved in dry THF at 0 °C. DIAD (0.18 mL, 0.94 mmol) was added dropwise and, after 10 min, the mixture was allowed to warm to room temperature over 30 min. The solution was concentrated under reduced pressure and chromatography of the viscous yellow residue (30 : 1 then 15 : 1, light petroleum–ether) afforded the *title compound* **8** as a pale yellow oil (69 mg, 63%) containing *ca.* 30% of its 1,5-*anti*-epimer (Found: M^+, 445.1889. $C_{27}H_{27}NO_5$ requires *M*, 445.1889); ν_{max}/cm^{-1} 3032, 2855, 1725, 1607, 1529, 1454, 1346, 1272, 1102 and 973; δ_H ($CDCl_3$, 300 MHz) major 1,5-*syn*-epimer **8** 0.98 (3 H, d, *J* 7, 5-CH_3) 2.46 (1 H, m, 5-H), 2.75 (2 H, m, 2-H_2), 3.26 (2 H, m, 6-H_2), 4.47 (2 H, s, $PhCH_2O$), 5.51 (2 H, m, 3-H and 4-H), 6.06 (1 H, dd, *J* 7.5 and 6, 1-H), 7.36 (10 H, m, ArH) and 8.34 (4 H, m, ArH); minor 1,5-*anti*-epimer 0.95 (3 H, d, *J* 7, 5-H_3); δ_C ($CDCl_3$, 75 MHz) 17.0, 36.8, 39.8, 72.8, 75.1, 77.1, 123.4, 123.9, 126.4, 127.3, 128.2, 128.3, 128.5, 130.6, 135.8, 137.3, 138.4, 139.4 and 163.8; *m*/*z* (CI) 463 (M^+ + 18, 100%), 296 (50) and 279 (54).

Standard procedure for diimide reduction of alkenes; (1*RS*,5*SR*)-6-benzyloxy-5-methyl-1-phenylhex-1-yl 4-nitrobenzoate 9. Sodium acetate (370 mg, 2.64 mmol) in water (1.4 mL) was added dropwise to the alkene **8** (37 mg, 0.08 mmol) and toluene 4-sulfonylhydrazine (260 mg, 1.6 mmol) in DME (3.1 mL) heated under reflux over 2 h. The mixture was heated under reflux for a further 4 h then allowed to cool to room temperature. The aqueous phase was extracted with ether (2 × 10 mL) and the organic extracts were washed with water (15 mL), brine (15 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue (3 : 1, light petroleum–ether) afforded the *title compound* **9** as a colourless oil (25 mg, 68%) containing about 30% of its 1,5-*anti*-epimer **11** (^{1}H NMR) (Found: M^+ + NH_4, 465.2388. $C_{27}H_{33}N_2O_5$ requires *M*, 465.2389); ν_{max}/cm^{-1} 3031, 2927, 2855, 1723, 1528, 1453, 1347, 1270, 1100 and 1014; δ_H ($CDCl_3$, 300 MHz) major 1,5-*syn*-epimer **9** 0.81 (3 H, d, *J* 7, 5-CH_3), 1.05–1.50 (4 H, m, 3-H_2 and 4-H_2), 1.65 (1 H, m, 5-H), 1.86 (1 H, m, 2-H) 2.00 (1 H, m, 2-H′), 3.17 (2 H, m, 6-H_2), 4.39 (2 H, s, $PhCH_2O$), 5.92 (1 H, t, *J* 7, 1-H), 7.27 (5 H, m, ArH), 8.14 (2 H, d, *J* 9, ArH) and 8.19 (2 H, d, *J* 9, ArH); minor 1,5-*anti*-epimer **11** 0.82 (3 H, d, *J* 7, 5-CH_3); δ_C ($CDCl_3$, 75 MHz) both epimers (70 : 30) 16.9, 22.9, 23.0, 33.2, 33.3, 36.4, 36.5, 72.9, 75.7, 77.9, 123.5, 126.5, 127.4, 128.2, 128.5, 130.6, 135.8, 138.6, 140.0(2), 150.5 and 163.9; *m*/*z* (CI) 465 (M^+ + 18, 18%), 298 (100), 263 (56), 108 (38) and 91 (42).

(3*Z*,1*SR*,5*SR*)-6-Benzyloxy-5-methyl-1-phenylhex-3-en-1-yl 4-nitrobenzoate 10. Following the standard procedure, the alcohol **2a** (75 mg, 0.26 mmol), triphenylphosphine (260 mg, 1.02 mmol), 4-nitrobenzoic acid (170 mg, 0.96 mmol) and DIAD (0.2 mL, 1.02 mmol), after chromatography (30 : 1 then 15 : 1, light petroleum–ether), afforded the *title compound* **10** as a pale yellow oil (77 mg, 68%) (Found: M^+ + NH_4, 463.2226. $C_{27}H_{31}N_2O_5$ requires *M*, 463.2233); ν_{max}/cm^{-1} 3063, 3030, 2855, 1725, 1606, 1528, 1453, 1345, 1272, 1102, 1014 and 720; δ_H ($CDCl_3$, 200 MHz) 0.98 (3 H, d, *J* 7, 5-CH_3), 2.86 (3 H, m, 2-H_2 and 5-H), 3.24 (2 H, m, 6-H_2), 4.50 (2 H, s, $PhCH_2$), 5.41 (2 H, m, 3-H and 4-H), 6.07 (1 H, t, *J* 7, 1-H), 7.39 (10 H, m, ArH) and 8.29 (4 H,

m, ArH); δ_C ($CDCl_3$, 75 MHz) 17.6, 32.6, 34.6, 72.9, 74.9, 77.0, 123.5, 123.8, 126.5, 127.4, 128.2, 128.5, 130.7, 135.7, 136.1, 138.5, 139.5, 150.5 and 163.8; *m*/*z* (CI) 463 (M^+ + 18, 100%) and 279 (35).

(1*SR*,5*SR*)-6-Benzyloxy-5-methyl-1-phenylhex-1-yl 4-nitrobenzoate 11. Following the standard procedure, sodium acetate (190 mg, 1.35 mmol) in water (0.7 mL), the alkene **10** (30 mg, 0.06 mmol) and toluene 4-sulfonylhydrazine (130 mg, 0.8 mmol) in DME (1.6 mL), after chromatography (3 : 1, light petroleum–ether), afforded the *title compound* **11** as a colourless oil (23 mg, 62%) (Found: $M^+ + NH_4$, 465.2383. $C_{27}H_{33}N_2O_5$ requires *M*, 465.2389); ν_{max}/cm^{-1} 3031, 2927, 2855, 1723, 1606, 1528, 1453, 1347, 1270, 1100 and 1014; δ_H ($CDCl_3$, 300 MHz) 0.82 (3 H, d, *J* 7, 5-CH_3), 1.05–1.55 (4 H, m, 3-H_2 and 4-H_2), 1.67 (1 H, m, 5-H), 1.85 (1 H, m, 2-H) 2.02 (1 H, m, 2-H′), 3.17 (2 H, m, 6-H_2), 4.39 (2 H, s, $PhCH_2O$), 5.92 (1 H, t, *J* 7, 1-H), 7.27 (5 H, m, ArH), 8.14 (2 H, d, *J* 9, ArH) and 8.19 (2 H, d, *J* 9, ArH); δ_C ($CDCl_3$, 75 MHz) 17.3, 23.3, 33.6(2), 36.8, 73.2, 76.0, 78.2, 123.8, 126.8, 127.7, 128.5, 128.6, 128.9, 131.0, 136.1, 138.9, 140.4, 150.8 and 164.3; *m*/*z* (CI) 465 (M^+ + 18, 20%), 298 (100), 263 (52), 108 (34) and 91 (48).

(6*E*,4*SR*,8*SR*)-9-Benzyloxy-8-methylnon-6-en-4-yl 4-nitrobenzoate 12. Following the standard procedure, the alcohol **5f** (90 mg, 0.34 mmol), triphenylphosphine (350 mg, 1.37 mmol), 4-nitrobenzoic acid (270 mg, 1.37 mmol) and DIAD (0.26 mL, 1.37 mmol), after chromatography (30 : 1 then 15 : 1, light petroleum–ether), afforded the *title compound* **12** as a pale yellow oil (130 mg, 92%) (Found: $M^+ + NH_4$, 429.2393. $C_{24}H_{33}N_2O_5$ requires *M*, 429.2404); ν_{max}/cm^{-1} 2958, 2928, 2872, 1723, 1608, 1530, 1349, 1274, 1116, 1102 and 720; δ_H ($CDCl_3$, 300 MHz) 0.98 (6 H, m, 1-H_3 and 8-CH_3), 1.25–1.50 and 1.65–1.78 (each 2 H, m, 2-H_2 and 3-H_2), 2.40–2.55 (3 H, m, 5-H_2 and 8-H), 3.29 (2 H, m, 9-H_2), 4.50 (2 H, s, $PhCH_2O$), 5.24 (1 H, m, 4-H), 5.52 (2 H, m, 6-H and 7-H), 7.33 (5 H, m, ArH) and 8.23 and 8.29 (each 2 H, d, *J* 9, ArH); δ_C ($CDCl_3$, 75 MHz) 13.8, 17.0, 18.6, 35.7, 36.9, 37.6, 72.8, 75.1, 75.3, 123.4, 124.4, 127.3, 128.2, 130.5, 136.1, 136.8, 138.5, 150.3 and 164.2; *m*/*z* (CI) 429 (M^+ + 18, 100%), 412 (M^+ + 1, 18), 245 (16) and 106 (100).

(4*SR*,8*SR*)-9-Benzyloxy-8-methylnon-4-yl 4-nitrobenzoate 13. Following the standard procedure, sodium acetate (0.53 g, 3.8 mmol) in water (1.8 mL), the alkene **12** (81 mg, 0.19 mmol) and toluene 4-sulfonylhydrazine (0.42 g, 2.3 mmol) in DME (4.5 mL), after chromatography (3 : 1, light petroleum–ether), afforded the *title compound* **13** as a colourless oil (52 mg, 64%) (Found: $M^+ + NH_4$, 431.2552. $C_{24}H_{35}N_2O_5$ requires *M*, 431.2560); ν_{max}/cm^{-1} 2957, 2936, 2871, 1720, 1528, 1349, 1274, 1114, 1102 and 720; δ_H ($CDCl_3$, 300 MHz) 0.90 (6 H, m, 1-H_3 and 8-CH_3), 1.18–1.90 (11 H, m, 2-H_2, 3-H_2, 5-H_2, 6-H_2, 7-H_2 and 8-H), 3.28 (2 H, m, 9-H_2), 4.49 (2 H, s, $PhCH_2O$), 5.19 (1 H, m, 4-H), 7.32 (5 H, m, ArH) and 8.32 (4 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 14.2, 17.3, 18.9, 23.0, 33.6, 33.8, 34.6, 36.5, 73.2, 76.0, 76.5, 123.8, 127.7, 128.6, 130.9, 136.4, 139.0, 150.7 and 164.7; *m*/*z* (CI) 431 (M^+ + 18, 44%), 414 (M^+ + 1, 14), 247 (46), 108 (74) and 91 (100).

(6*Z*,4*RS*,8*SR*)-9-Benzyloxy-8-methylnon-6-en-4-yl 4-nitrobenzoate 14. Following the standard procedure, the alcohol **2f** (R = ^{n}Pr, 60 mg, 0.23 mmol), triphenylphosphine (230 mg, 0.92 mmol), 4-nitrobenzoic acid (178 mg, 0.92 mmol) and DIAD (0.17 mL, 0.92 mmol), after chromatography (30 : 1 then 15 : 1, light petroleum–ether), afforded the *title compound* **14** as a pale yellow oil (98 mg, 68%) (Found: $M^+ + NH_4$, 429.2388. $C_{24}H_{33}N_2O_5$ requires *M*, 429.2404); ν_{max}/cm^{-1} 2957, 2930, 2872, 1721, 1608, 1529, 1349, 1274, 1116, 1102 and 720; δ_H ($CDCl_3$, 300 MHz) 0.94 (6 H, m, 1-H_3 and 8-CH_3), 1.30–1.50 (2 H, m, 2-H_2), 1.60–1.80 (2 H, m, 3-H_2), 2.38–2.62 (2 H, m, 5-H_2), 2.81 (1 H, m, 8-H), 3.28 (2 H, dd, *J* 7 and 7, 9-H_2), 4.48 (2 H, s, $PhCH_2O$), 5.20 (1 H, pent, *J* 6.5, 4-H), 5.33 (1 H, t, *J* 10, 7-H), 5.44 (1 H, dt, *J* 11, 7, 6-H), 7.30 (5 H, m, ArH) and 8.19 and 8.28 (each 2 H, d, *J* 9, ArH); δ_C ($CDCl_3$, 75 MHz) 13.8, 17.7, 18.6, 32.3, 32.6, 35.8, 72.9, 75.0, 75.6, 123.4, 124.4, 127.3, 128.2, 130.6, 135.6, 136.0, 138.5 and 164.3; *m*/*z* (CI) 429 (M^+ + 18, 100%), 412 (M^+ + H, 36), 382 (68), 245 (100) and 91 (80).

(4*SR*,8*RS*)-9-Benzyloxy-8-methylnon-4-yl 4-nitrobenzoate 15. Following the standard procedure, sodium acetate (270 mg, 2.0 mmol) in water (0.9 mL), the alkene **14** (40 mg, 0.1 mmol) and toluene 4-sulfonylhydrazine (210 mg, 1.2 mmol) in DME (3 mL), after chromatography (3 : 1, light petroleum–ether), afforded the *title compound* **15** as a colourless oil (21 mg, 51%) (Found: $M^+ + NH_4$, 431.2550. $C_{24}H_{35}N_2O_5$ requires *M*, 431.2560); ν_{max}/cm^{-1} 2957, 2936, 2871, 1719, 1528, 1349, 1274, 1114, 1102 and 720; δ_H ($CDCl_3$, 300 MHz) 0.90 (6 H, m, 1-H_3 and 8-CH_3), 1.18–1.90 (11 H, m, 2-H_2, 3-H_2, 5-H_2, 6-H_2, 7-H_2 and 8-H), 3.28 (2 H, m, 9-H_2), 4.49 (2 H, s, $PhCH_2O$), 5.19 (1 H, m, 4-H), 7.32 (5 H, m, ArH) and 8.32 (4 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 14.2, 17.2, 18.9, 23.0, 33.6, 33.7, 34.6, 36.6, 73.2, 76.1, 76.4, 123.8, 127.7, 128.6, 130.9, 136.4, 139.0, 150.7 and 164.7; *m*/*z* (CI) 431 (M^+ + 18, 60%), 414 (M^+ + 1, 22), 247 (86), 108 (78) and 91 (100).

Samples of the nitrobenzoates **13** and **15** were mixed together: δ_C ($CDCl_3$, 75 MHz) mixture of **13** and **15** *17.249*/17.321, 22.982/*23.013*, *33.744*/33.786, 36.457/*36.560*, 76.041/*76.102* and *76.426*/76.484 (signals italicised assigned to isomer **15**).

(3*E*,1*RS*,5*RS*)-5-Benzyloxy-1-phenylhex-3-en-1-ol 18a. Following the standard procedure, benzaldehyde (63 μL, 0.63 mmol), BiI_3 (123 mg, 0.21 mmol) in MeCN (1 mL) and DCM (1 mL) and the racemic stannane **16** (100 mg, 0.21 mmol) in DCM (0.3 mL), after chromatography (3 : 1, light petroleum–ether with 1% Et_3N), gave the *title compound* **18a** as a colourless oil (33 mg, 56%) containing *ca.* 7% of the *anti*-epimer **19a**, R_f = 0.3 (3 : 1, light petroleum–ether) (Found: $M^+ + NH_4$, 300.1962. $C_{19}H_{26}NO_2$ requires *M*, 300.1963); ν_{max}/cm^{-1} 3397, 3028, 2974, 2863, 1602, 1494, 1453, 1370, 1069 and 735; δ_H ($CDCl_3$, 300 MHz) 1.27 (3 H, d, *J* 7, 6-H_3), 2.55 (2 H, m, 2-H_2), 3.90 (1 H, m, 5-H), 4.35 and 4.52 (each 1 H, d, *J* 12, OHC*H*Ph), 4.77 (1 H, t, *J* 6, 1-H), 5.51 (1 H, dd, *J* 16 and 6, 4-H), 5.61 (1 H, dt, *J* 16 and 6, 3-H) and 7.30 (10 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 21.9, 42.4, 70.1, 74.0, 75.7, 126.2, 127.7, 128.0, 128.1, 128.3, 128.6, 128.7, 136.1, 139.1 and 144.1; *m*/*z* (CI) 300 (M^+ + 18, 84%), 192 (96), 157 (100) and 124 (56). A less polar minor fraction was 2-(2-benzyloxyethyl)-1-phenylbut-3-en-1-ol **20**, R_f = 0.35 (3 : 1, light petroleum–ether) (Found: $M^+ + NH_4$, 300.1966.

$C_{19}H_{26}NO_2$ requires *M*, 300.1963); ν_{max}/cm^{-1} 3468, 2964, 2925, 1639, 1452, 1260, 1098, 1073, 1027 and 799; δ_H ($CDCl_3$, 300 MHz) 1.19 (3 H, d, *J* 6, 2′-H_3), 2.27 (1 H, m, 2-H), 3.20 (1 H, br. s, OH), 3.68 (1 H, m, 2′-H), 4.33 and 4.65 (each 1 H, d, *J* 12, OHC*H*Ph), 4.97 (1 H, d, *J* 6, 1-H), 5.05 (1 H, dd, *J* 17 and 2, 4-H), 5.32 (1 H, dd, *J* 10 and 2, 4-H′), 6.11 (1 H, dt, *J* 17 and 10, 3-H) and 7.34 (10 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 17.9, 59.2, 70.6, 76.0, 76.6, 121.0, 127.0, 127.8, 127.9, 127.9, 128.2, 129.0, 133.8, 138.7 and 142.8; *m*/*z* (CI) 281 ($M^+ - 1$, 6%), 265 (22), 108 (84) and 91 (100).

Following the standard procedure, the (*S*)-bromide **42** (100 mg, 0.394 mmol) and benzaldehyde (34 μL, 0.394 mmol) gave the (1*S*,5*S*)-enantiomer of the title compound **18a** as a colourless oil (51 mg, 46%) containing *ca.* 6% of its 1-epimer **19a**, R_f = 0.3 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +8 (*c* 1.4, $CHCl_3$) (Found: $M^+ + NH_4$, 300.1962. $C_{19}H_{26}NO_2$ requires *M*, 300.1963). Spectroscopic data were identical to those of the racemate.

(5*E*,3*RS*,7*RS*)-7-Benzyloxy-2-methyloct-5-en-3-ol 18b. Following the standard procedure, 2-methylpropanal (57 μL, 0.63 mmol), BiI_3 (123 mg, 0.21 mmol) in MeCN (1 mL) and DCM (1 mL) and the racemic stannane **16** (100 mg, 0.21 mmol) in DCM (0.3 mL), after chromatography (3 : 1, light petroleum–ether with 1% Et_3N), gave the *title compound* **18b** as a colourless oil (25 mg, 48%) containing *ca.* 7% of its epimer **19b** (^{13}C NMR), R_f = 0.3 (3 : 1, light petroleum–ether) (Found: $M^+ + NH_4$, 266.2113. $C_{16}H_{28}NO_2$ requires *M*, 266.2119); ν_{max}/cm^{-1} 3443, 2965, 2929, 2871, 1602, 1494, 1453, 1368, 1071, 975 and 732; δ_H ($CDCl_3$, 300 MHz) 0.96 and 0.98 (each 3 H, d, *J* 6.5, 1-H_3 or 2-CH_3), 1.32 (3 H, d, *J* 6.5, 8-H_3), 1.71 (1 H, m, 2-H), 2.10–2.40 (2 H, m, 4-H_2), 3.42 (1 H, m, 3-H), 3.96 (1 H, m, 7-H), 4.42 and 4.59 (each 1 H, d, *J* 12, OHC*H*Ph), 5.55 (1 H, dd, *J* 16 and 7, 6-H), 5.68 (1 H, dt, *J* 16 and 7, 5-H) and 7.26 (5 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) major *syn*-epimer **18b** 17.7, 19.0, 21.9, 33.4, 37.5, 70.1, 75.9, 76.0, 127.7, 127.9, 128.6, 129.4, 135.6 and 139.1; minor *anti*-epimer **19b** 32.8, 38.6 and 68.4; *m*/*z* (CI) 266 ($M^+ + 18$, 96%), 216 (24), 158 (100) and 123 (42).

(6*E*,4*SR*,4*RS*)-8-Benzyloxynon-6-en-4-ol 18c. Following the standard procedure, butanal (86 μL, 0.96 mmol), BiI_3 (185 mg, 0.32 mmol) in MeCN (1.25 mL) and DCM (1.25 mL) and the racemic stannane **16** (150 mg, 0.32 mmol) in DCM (0.4 mL), after chromatography (3 : 1, light petroleum–ether with 1% Et_3N), gave the *title compound* **18c** as a colourless oil (47 mg, 62%) containing *ca.* 8% of its epimer **19c**, R_f = 0.3 (3 : 1, light petroleum : ether) (Found: $M^+ + NH_4$, 266.2115. $C_{16}H_{28}NO_2$ requires *M*, 266.2119); ν_{max}/cm^{-1} 3403, 2958, 2929, 2870, 1602, 1494, 1453, 1370, 1071, 976 and 733; δ_H ($CDCl_3$, 300 MHz) 0.90 (3 H, m, 1-H_3), 1.34 (3 H, d, *J* 6, 9-H_3), 1.30–1.60 (4 H, m, 2-H_2 and 3-H_2), 2.00–2.40 (2 H, m, 5-H_2), 3.69 (1 H, m, 4-H), 3.98 (1 H, m, 8-H), 4.10 (1 H, d, *J* 4, OH), 4.60 and 4.69 (each 1 H, d, *J* 12, OHC*H*Ph), 5.56 (1 H, dd, *J* 15 and 7, 7-H), 5.66 (1 H, dt, *J* 15 and 7, 6-H) and 7.31 (5 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 14.4, 19.1, 21.9, 39.3, 40.6, 70.2, 71.1, 75.9, 127.8, 127.9, 128.7, 135.7 and 139.1; *m*/*z* (CI) 266 ($M^+ + 18$, 100%), 216 (36), 158 (98) and 123 (38).

(3*E*,1*SR*,1*RS*)-5-Benzyloxy-1-phenylhex-3-en-1-yl 4-nitrobenzoate 21. Following the standard procedure, the alcohol **18a** (100 mg, 0.35 mmol), triphenylphosphine (0.35 g, 1.38 mmol), 4-nitrobenzoic acid (0.23 g, 1.38 mmol) and DIAD (0.26 mL, 1.38 mmol), after chromatography (30 : 1 then 15 : 1, light petroleum–ether), afforded the *title compound* **21** as a pale yellow oil (74 mg, 49%), R_f = 0.4 (3 : 1, light petroleum–ether) (Found: $M^+ + NH_4$, 449.2071. $C_{26}H_{29}N_2O_5$ requires *M*, 449.2076); ν_{max}/cm^{-1} 2957, 2923, 2854, 1724, 1606, 1528, 1345, 1264, 1100 and 799; δ_H ($CDCl_3$, 300 MHz) 1.23 (3 H, d, *J* 6, 6-H_3), 2.86 (2 H, m, 2-H_2), 3.86 (1 H, m, 5-H), 4.24 and 4.42 (each 1 H, d, *J* 12, OHC*H*Ph), 5.50–5.70 (2 H, m, 3-H and 4-H), 6.16 (1 H, t, *J* 7, 1-H), 7.10–7.50 (10 H, m, ArH) and 8.28 (4 H, m, ArH); *m*/*z* (CI) 449 ($M^+ + 18$, 1%), 324 (2) and 157 (100).

(1*RS*,5*SR*)-5-Benzyloxy-1-phenylhex-1-yl 4-nitrobenzoate 22. Following the standard procedure, sodium acetate (0.44 g, 0.32 mmol) in water (1.5 mL), the alkene **21** (67 mg, 0.15 mmol) and toluene 4-sulfonylhydrazine (0.35 g, 1.90 mmol) in DME (4 mL) with heating under reflux for 16 h, after chromatography (3 : 1, light petroleum–ether), afforded the *title compound* **22** as a colourless oil (28 mg, 40%), R_f = 0.3 (3 : 1, light petroleum–ether) (Found: $M^+ + NH_4$, 451.2238. $C_{26}H_{31}N_2O_5$ requires *M*, 451.2233); ν_{max}/cm^{-1} 2963, 2929, 2863, 1723, 1606, 1528, 1346, 1270, 1100 and 719; δ_H ($CDCl_3$, 300 MHz) 1.21 (3 H, d, *J* 6.5, 6-H_3), 1.30–1.75 (4 H, m, 3-H_2 and 4-H_2), 1.98 and 2.13 (each 1 H, m, 2-H), 3.53 (1 H, m, 5-H), 4.43 and 4.60 (each 1 H, d, *J* 12, OHC*H*Ph), 6.04 (1 H, t, *J* 6, 1-H), 7.38 (10 H, m, ArH) and 8.30 (4 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 19.9, 21.9, 30.6, 36.6, 70.5, 74.6, 78.3, 123.8, 126.8, 127.7, 127.9, 128.5, 128.6, 128.9, 131.0, 136.1, 139.2, 140.3 and 164.3; *m*/*z* (CI) 451 ($M^+ + 18$, 6%), 391 (18), 284 (30), 175 (14) and 99 (100).

(3*Z*,1*RS*,5*RS*)-5-Benzyloxy-1-phenylhex-3-en-1-yl 4-nitrobenzoate 23. Following the standard procedure, the alcohol **17a** (80 mg, 0.28 mmol), triphenylphosphine (0.28 g, 1.10 mmol), 4-nitrobenzoic acid (0.19 g, 1.10 mmol) and DIAD (0.21 mL, 1.10 mmol), after chromatography (30 : 1 then 15 : 1, light petroleum–ether), afforded the *title compound* **23** as a pale yellow oil (77 mg, 63%). R_f = 0.4 (3 : 1, light petroleum–ether) (Found: $M^+ + NH_4$, 449.2080. $C_{26}H_{29}N_2O_5$ requires *M*, 449.2076); ν_{max}/cm^{-1} 3029, 2971, 2864, 1725, 1606, 1528, 1344, 1271, 1101 and 719; δ_H ($CDCl_3$, 300 MHz) 1.22 (3 H, d, *J* 6, 6-H_3), 2.70–2.95 (2 H, m, 2-H_2), 4.24 (1 H, d, *J* 12, OHC*H*Ph), 4.30 (1 H, m, 5-H), 4.41 (1 H, d, *J* 12, OHCHPh), 5.59 (2 H, m, 3-H and 4-H), 6.09 (1 H, t, *J* 7, 1-H), 7.30 (10 H, m, ArH) and 8.30 (4 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 21.7, 35.0, 70.1, 70.5, 77.4, 123.9, 126.0, 126.8, 127.9, 128.2, 128.7, 128.8, 129.0, 129.2, 131.0, 135.9, 138.9, 139.5, 150.9 and 164.1; *m*/*z* (CI) 449 ($M^+ + 18$, 4%), 324 (7), 265 (3) and 157 (100).

(1*RS*,5*RS*)-5-Benzyloxy-1-phenylhex-1-yl 4-nitrobenzoate 24. Following the standard procedure, sodium acetate (0.44 g, 0.32 mmol) in water (1.5 mL), the alkene **23** (70 mg, 0.16 mmol) and toluene 4-sulfonylhydrazine (0.35 g, 1.90 mmol) in DME (4 mL) with heating under reflux for 16 h, after chromatography (3 : 1, light petroleum–ether), afforded the *title compound* **24** as a colourless oil (28 mg, 48%), R_f = 0.3

(3 : 1, light petroleum–ether) (Found: $M^+ + NH_4$, 451.2237. $C_{26}H_{31}N_2O_5$ requires *M*, 451.2233); ν_{max}/cm^{-1} 2963, 2928, 2864, 1724, 1606, 1528, 1346, 1271, 1101 and 720; δ_H ($CDCl_3$, 300 MHz) 1.22 (3 H, d, *J* 6, 6-H_3), 1.30–1.75 (4 H, m, 3-H_2 and 4-H_2), 1.98 and 2.13 (each 1 H, m, 2-H), 3.54 (1 H, m, 5-H), 4.43 and 4.60 (each 1 H, d, *J* 12, OHC*H*Ph), 6.04 (1 H, t, *J* 6, 1-H), 7.38 (10 H, m, ArH) and 8.30 (4 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 19.9, 21.9, 30.6, 36.6, 70.6, 74.7, 78.2, 123.8, 126.8, 127.7, 127.9, 128.5, 128.6, 128.9, 131.0, 136.1, 139.2, 140.3 and 164.3; *m*/*z* (CI) 451 (M^+ + 18, 6%), 284 (14), 267 (19), 175 (16), 157 (16), 99 (68) and 59 (100).

(4*R*,2*E*)-5-Benzyloxy-1-bromo-4-methylpent-2-ene 26. Triphenylphosphine (0.42 g, 1.62 mmol) was added at room temperature in three portions over 30 min to the (*R*)-alcohol **25** (0.20 g, 0.98 mmol) and carbon tetrabromide (0.42 g, 1.27 mmol) in DCM (12 mL). The mixture was stirred for 2 h then concentrated under reduced pressure. Chromatography of the residue (15 : 1, light petroleum–ether) gave the *title compound* **26** as a colourless oil (242 mg, 92%), R_f = 0.25 (15 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +11.7 (*c* 2.5, $CHCl_3$) (Found: M^+, 268.0460. $C_{13}H_{17}O^{79}Br$ requires *M*, 268.0463); ν_{max}/cm^{-1} 3030, 2962, 2855, 1658, 1453, 1361, 1204, 1095, 967 and 736; δ_H ($CDCl_3$, 300 MHz) 1.10 (3 H, d, *J* 6, 4-CH_3), 2.60 (1 H, m, 4-H), 3.38 and 3.42 (each 1 H, dd, *J* 6 and 4, 5-H), 4.01 (2 H, m, 1-H_2), 4.57 (2 H, s, OCH_2Ph), 5.80 (2 H, m, 2-H and 3-H) and 7.38 (5 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 16.9, 33.7, 36.8, 73.3, 75.0, 126.4, 127.8, 128.7, 138.8 and 138.9; *m*/*z* (CI) 288, 286 (M^+ + 18, 100%).

Standard procedure for the preparation of *O*-acetyl mandelates from *O*-acetylmandelyl chlorides: (3*E*,1*R*,5*R*)-6-benzyloxy-5-methyl-1-phenylhex-3-en-1-yl (2*R*)-2-acetoxy-2-phenylacetate 27. Pyridine (0.27 mL, 3.9 mmol) and DMAP (cat.) were added to the alcohol **5a** (100 mg, 0.34 mmol) in DCM (0.9 mL) before cooling to 0 °C. A solution of (*R*)-*O*-acetylmandelyl chloride (212 mg, 1.01 mmol) in DCM (0.9 mL) was added dropwise before warming the mixture to room temperature and stirring for 2 h. Ether (2 mL) and saturated aqueous ammonium chloride (2 mL) were added and the aqueous phase extracted with ether (3 × 5 mL). The organic extracts were washed with brine (15 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (6 : 1, light petroleum–ether) of the residue gave the *title compound* **27** as a colourless oil (95 mg, 60%), R_f = 0.4 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −15.3 (*c* 2.2, $CHCl_3$) (Found: $M^+ + NH_4$, 490.2599. $C_{30}H_{36}NO_5$ requires *M*, 490.2593); ν_{max}/cm^{-1} 3032, 2926, 2853, 1746, 1454, 1371, 1231, 1173, 1084 and 1057; δ_H ($CDCl_3$, 300 MHz) 1.01 (3 H, d, *J* 7, 5-CH_3), 2.21 (3 H, s, CH_3), 2.40–2.70 (3 H, m, 2-H_2 and 5-H), 3.30 (2 H, m, 6-H_2), 3.53 (2 H, s, OCH_2Ph), 5.42 (2 H, m, 3-H and 4-H), 5.77 (1 H, t, *J* 7, 1-H), 6.04 (1 H, s, 2′-H), 6.99 (2 H, m, ArH), 7.20 (3 H, m, ArH) and 7.38 (10 H, m, ArH); *m*/*z* (CI) 490 (M^+ + 18, 6%), 174 (18), 157 (24) and 91 (100).

(3*E*,1*R*,5*R*)-6-Benzyloxy-5-methyl-1-phenylhex-3-en-1-yl (2*S*)-2-acetoxy-2-phenylacetate 28. Following the standard procedure, alcohol **5a** (100 mg, 0.34 mmol) and (*S*)-acetylmandelyl chloride gave the *title compound* **28** as a colourless oil (61 mg, 39%), R_f = 0.4 (3 : 1, light petroleum ether), $[\alpha]_D^{20}$ +50.2 (*c* 1.5, $CHCl_3$) (Found: $M^+ + NH_4$, 490.2597. $C_{30}H_{36}NO_5$ requires *M*, 490.2593); ν_{max}/cm^{-1} 3032, 2927, 2853, 1746, 1453, 1371, 1231, 1173, 1084 and 1057; δ_H ($CDCl_3$, 300 MHz) 0.87 (3 H, d, *J* 7, 5-CH_3), 2.19 (3 H, s, CH_3), 2.24 (1 H, m, 5-H), 2.46 (2 H, m, 2-H_2), 3.18 (2 H, m, 6-H_2), 3.47 (2 H, s, OCH_2Ph), 5.08 (1 H, dt, *J* 16 and 7, 3-H), 5.29 (1 H, dd, *J* 16 and 7, 4-H), 5.76 (1 H, t, *J* 7, 1-H), 6.01 (1 H, s, 2′-H), 7.35 (13 H, m, ArH) and 7.51 (2 H, m, ArH); *m*/*z* (CI) 490 (M^+ + 18, 4%), 174 (12), 157 (16) and 91 (100).

(2*E*,4*S*)-5-Benzyloxy-1-bromo-2,4-dimethylpent-2-ene 30. Triphenylphosphine (3.3 g, 12.74 mmol) was added at room temperature in three portions over 30 min to a solution of (*S*)-alcohol **(*S*)-29** (1.7 g, 7.72 mmol) and carbon tetrabromide (3.3 g, 10.04 mmol) in DCM (50 mL). The reaction mixture was stirred at this temperature for 2 h then concentrated under reduced pressure. Chromatography of the residue (15 : 1, light petroleum–ether) gave the *title compound* **(*S*)-30** as a colourless oil (2.0 g, 90%), R_f = 0.8 (2 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +11 (*c* 1.1, $CHCl_3$) (Found: $M^+ + NH_4$, 300.0959. $C_{14}H_{23}ON^{79}Br$ requires *M*, 300.0958); ν_{max}/cm^{-1} 2959, 2927, 2854, 1599, 1453, 1365, 1202, 1094, 1027 and 736; δ_H ($CDCl_3$, 300 MHz) 1.04 (3 H, d, *J* 7, 4-CH_3), 1.83 (3 H, s, 2-CH_3), 2.75 (1 H, m, 4-H), 3.35 (2 H, m, 5-H_2), 4.01 (2 H, s, 1-H_2), 4.55 (2 H, s, OCH_2Ph), 5.48 (1 H, d, *J* 9, 3-H) and 7.34 (5 H, m, ArH); δ_C ($CDCl_3$, 300 MHz) 15.2, 17.4, 33.8, 41.9, 73.2, 75.0, 127.8, 128.6, 132.7, 134.3 and 138.8; *m*/*z* (CI) 302, 300 (M^+ + 18, 72%), 205 (70), 130 (48), 108 (94) and 82 (100).

Following this procedure, the (*R*)-enantiomer **(*R*)-30**, $[\alpha]_D^{20}$ -15.1 (*c* 1.8, $CHCl_3$), was prepared from the (*R*)-alcohol **(*R*)-29**.

(3*E*,1*RS*,5*RS*)-6-Benzyloxy-3,5-dimethyl-1-phenylhex-3-en-1-ol 31a. Following the standard procedure, zinc powder (30 mg, 0.46 mmol), bismuth(III) iodide (234 mg, 0.4 mmol) in THF (1.65 mL), the racemic bromide **30** (75 mg, 0.26 mmol) and benzaldehyde (27 μL, 0.26 mmol), after chromatography (10 : 1, light petroleum–ether) gave the *title compound* **31a** (53 mg, 65%) as a colourless oil containing *ca.* 5% of its 1-epimer **32a** (^{1}H NMR), R_f = 0.25 (3 : 1, light petroleum–ether) (Found: $M^+ + NH_4$, 328.2273. $C_{21}H_{30}O_2N$ requires *M*, 328.2271); ν_{max}/cm^{-1} 3431, 3063, 3030, 2961, 2868, 1604, 1453, 1375, 1089 and 750; δ_H (300 MHz, $CDCl_3$) major isomer **31a** 0.98 (3 H, d, *J* 7, 5-CH_3), 1.77 (3 H, d, *J* 1, 3-CH_3), 2.33 (1 H, dd, *J* 13 and 9, 2-H), 2.44 (1 H, dd, *J* 13 and 4, 2-H′), 2.82 (1 H, m, 5-H), 3.30 (1 H, dd, *J* 9 and 8, 6-H), 3.34 (1 H, dd, *J* 9 and 6, 6-H′), 4.55 and 4.59 (each 1 H, d, *J* 12, OHC*H*Ph), 4.77 (1 H, dd, *J* 10 and 4, 1-H), 5.13 (1 H, dd, *J* 9 and 1, 4-H) and 7.39 (10 H, m, ArH); minor epimer **32a** 1.04 (3 H, d *J* 7, 5-CH_3); δ_C (75 MHz, $CDCl_3$) 16.6, 17.5, 33.5, 51.0, 71.0, 73.3, 75.4, 126.1, 127.5, 127.8, 127.9, 128.6, 128.6, 132.4, 133.1, 138.7 and 144.4; *m*/*z* (CI) 328 (M^+ + 18, 59%), 310 (M^+, 71), 293 (84), 275 (14) and 99 (100). A less polar fraction, R_f = 0.28 (3 : 1, light petroleum–ether), was the (*Z*)-isomer **33a** (8 mg, 10%), a colourless oil.

Using the (*R*)-bromide **(*R*)-30**, the (1*R*,5*R*)-enantiomer of the title compound **31a** was obtained, $[\alpha]_D^{20}$ +48 (*c* 0.7, $CHCl_3$) (Found: $M^+ + NH_4$, 328.2273. $C_{21}H_{30}O_2N$ requires *M*, 328.2271). Using the (*S*)-bromide **(*S*)-30**, the (1*S*,5*S*)-

enantiomer of the title compound **31a** was obtained, $[\alpha]_D^{20}$ −50 (*c* 0.8, $CHCl_3$) (Found: $M^+ + NH_4 - H_2O$, 310.2162. $C_{21}H_{28}ON$ requires *M*, 310.2165).

(3*E*,1*SR*,5*RS*)-6-Benzyloxy-3,5-dimethyl-1-phenylhex-3-en-1-yl 4-nitrobenzoate 34. The racemic alcohol **31a** (90 mg, 0.29 mmol), triphenylphosphine (183 mg, 0.70 mmol) and 4-nitrobenzoic acid (58 mg, 0.35 mmol) were dissolved in THF at 0 °C. Di-isopropyl azodicarboxylate (0.14 mL, 0.7 mmol) was added dropwise and, after 10 min, the mixture was allowed to warm to room temperature for 30 min. After concentration under reduced pressure, chromatography of the residue (30 : 1 to 15 : 1, light petroleum–ether) gave the *title compound* **34** containing *ca.* 10% of its epimer (80 mg, 60%) as a pale yellow oil, R_f = 0.37 (2 : 1, light petroleum–ether) (Found: M^+, 459.2049 $C_{28}H_{29}O_5N$ requires *M*, 459.2046); ν_{max}/cm^{-1} 3033, 2858, 1728, 1608, 1532, 1455, 1348, 1273, 1102, 720 and 699; δ_H (500 MHz, $CDCl_3$) major epimer **34** 0.65 (3 H, d, *J* 7, 5-CH_3), 1.61 (3 H, s, 3-CH_3), 2.44 (1 H, dd, *J* 14 and 5, 2-H), 2.53 (1 H, m, 5-H), 2.66 (1 H, dd, *J* 14 and 9, 2-H′), 3.03 (1 H, dd, *J* 7 and 5, 6-H), 3.06 (1 H, dd, *J* 9 and 6, 6-H′), 4.34 (2 H, s, OCH_2Ph), 4.92 (1 H, d, *J* 9, 4-H), 6.06 (1 H, dd, *J* 9 and 5, 1-H), 7.18 (10 H, m, ArH) and 8.08 (4 H, m, ArH); minor 1-epimer 0.78 (3 H, d, *J* 7, 5-CH_3) and 4.90 (1 H, d, *J* 9, 4-H); δ_C (125 MHz, $CDCl_3$) 17.0, 17.9, 33.5, 47.6, 73.4, 75.4, 76.1, 123.9, 126.8, 127.9, 128.6, 128.7, 128.9, 131.1, 132.8, 136.3, 139.0, 140.3, 150.8 and 164.2; minor 1-epimer 47.5, 73.3 and 76.3 *m*/*z* (CI) 477 (M^+ + 18, 3%), 310 (16), 293 (18), 155 (30) and 199 (100).

(3*E*,1*SR*,5*RS*)-6-Benzyloxy-3,5-dimethyl-1-phenylhex-3-en-1-ol 32a. The nitrobenzoate **34** (80 mg, 0.17 mmol) and sodium hydroxide in methanol (1%, 3 mL) were stirred for 2 h then extracted with DCM (2 × 6 mL) and the extracts dried (Na_2SO_4). Chromatography of the residue (10 : 1, light petroleum–ether) gave the *title compound* **32a** as a pale yellow oil (23 mg, 43%) containing *ca.* 15% of the 1-epimer **31a** (^{1}H NMR), R_f = 0.28 (3 : 1, light petroleum–ether) (Found: $M^+ + NH_4$, 328.2273. $C_{21}H_{30}O_2N$ requires *M*, 328.2271); ν_{max}/cm^{-1} 3417, 3070, 2961, 2925, 2863, 1604, 1454, 1370, 1201, 1090, 753 and 699; δ_H (500 MHz, $CDCl_3$) major epimer **32a** 1.04 (3 H, d, *J* 7, 5-CH_3), 1.72 (3 H, d, *J* 1, 3-CH_3), 2.15 (1 H, br. s, OH), 2.35 (1 H, dd, *J* 14 and 9, 2-H), 2.44 (1 H, dd, *J* 14 and 4, 2-H′), 2.81 (1 H, m, 5-H), 3.31 (1 H, dd, *J* 9 and 7, 6-H), 3.34 (1 H, dd, *J* 9 and 6, 6-H′), 4.53 and 4.55 (each 1 H, d, *J* 12, OHC*H*Ph), 4.80 (1 H, dd, *J* 9 and 4, 1-H), 5.15 (1 H, d, *J* 9, 4-H) and 7.35 (10 H, m, ArH); minor epimer **31a** 0.98 (3 H, d, *J* 7, 5-CH_3), 1.75 (3 H, d, *J* 1, 3-CH_3) and 4.75 (1 H, dd, *J* 9 and 4, 1-H); δ_C (175 MHz, $CDCl_3$) 16.6, 17.5, 33.4, 51.0, 71.0, 73.3, 75.4, 126.1, 127.5, 127.8, 127.9, 128.6, 128.7, 132.4, 133.0, 138.7 and 144.4; minor epimer **37** 16.9, 18.2, 50.5 and 71.6; *m*/*z* (CI) 328 (M^+ + 18, 10%), 310 (M^+, 6), 293 (13) and 99 (100).

Standard procedure for the preparation of *O*-acetyl mandelates from *O*-acetylmandelic acid: (3*E*,1*R*,5*R*)-6-benzyloxy-3,5-dimethyl-1-phenylhex-3-en-1-yl (*R*)-2-acetoxy-2-phenylacetate 35. (*R*)-*O*-Acetylmandelic acid (24 mg, 0.12 mmol) and 4-dimethylaminopyridine (1 mg) were added to the alcohol **31a** (25 mg, 0.081 mmol, containing *ca.* 5% of its epimer **32a**) in DCM (0.5 mL) followed by a solution of *N*,*N*′-dicyclohexylcarbodiimide (25.1 mg, 0.12 mmol in DCM (0.5 mL)) at 0 °C. During the addition, a white precipitate was observed. The reaction mixture was allowed to warm to room temperature, stirred for 16 h, then diluted with ether (2 mL) and filtered through celite. The resulting solution was washed with aqueous hydrogen chloride (0.5 N, 2 × 5 mL), saturated aqueous sodium hydrogen carbonate (2 × 5 mL) and brine (5 mL), then dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue (10 : 1, light petroleum–ether) gave the *title compound* **35** as a colourless oil (31 mg, 78%), R_f = 0.42 (4 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −16.3 (*c* 0.5, $CHCl_3$) (Found: M^+ + 18, 504.2750. $C_{31}H_{38}O_5N$ requires *M*, 504.2744); ν_{max}/cm^{-1} 3065, 3033, 2958, 2927, 2856, 1744, 1605, 1454, 1372, 1232, 1208, 1175, 1084, 1058, 738 and 698; δ_H (500 MHz, $CDCl_3$) major isomer **35** 0.76 (3 H, d, *J* 7, 5-CH_3), 1.54 (3 H, s, $COCH_3$), 2.08 (3 H, d, *J* 1, 3-CH_3), 2.29 (1 H, dd, *J* 14 and 7, 2-H), 2.47 (1 H, dd, *J* 14 and 8, 2-H′), 2.56 (1 H, m, 5-H), 3.07 (1 H, dd, *J* 9 and 7, 6-H), 3.17 (1 H, dd, *J* 9 and 6, 6-H′), 4.38 and 4.42 (each 1 H, d, *J* 12, OHC*H*Ph), 4.77 (1 H, d, *J* 9, 4-H), 5.75 (1 H, t, *J* 7, 1-H), 5.90 (1 H, s, 2′-H), 6.84 (2 H, m, ArH), 7.05 (3 H, m, ArH) and 7.25 (10 H, m, ArH); δ_C (125 MHz, $CDCl_3$) 17.2, 17.9, 21.1, 33.4, 46.8, 73.2, 74.8, 75.5, 76.8, 126.4, 127.8, 128.1, 128.4, 128.6, 128.7, 129.0, 129.6, 130.7, 132.2, 134.1, 139.2, 140.0, 168.3 and 170.5; *m*/*z* (CI) 504 (M^+ + 18, 2%), 310 (19), 293 (14) and 99 (100).

(3*E*,1*R*,5*R*)-6-Benzyloxy-3,5-dimethyl-1-phenylhex-3-en-1-yl (*S*)-2-acetoxy-2-phenylacetate 36. Following the standard procedure for the synthesis of *O*-acetyl mandelates from *O*-acetylmandelic acid, alcohol **31a** (20 mg, 0.065 mmol) and (*S*)-*O*-acetylmandelic acid (19 mg, 0.098 mmol), after chromatography (10 : 1, light petroleum–ether), gave the *title compound* **36** as a colourless oil (24 mg, 75%), R_f = 0.42 (4 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +32.4 (*c* 0.5, $CHCl_3$) (Found: $M^+ + NH_4$, 504.2751. $C_{31}H_{38}O_5N$ requires *M*, 504.2744); ν_{max}/cm^{-1} 3065, 3033, 2959, 2927, 2856, 1749, 1605, 1454, 1372, 1056, 738 and 698; δ_H (500 MHz, $CDCl_3$) 0.67 (3 H, d, *J* 7, 5-CH_3), 1.35 (3 H, s, $COCH_3$), 2.07 (3 H, d, *J* 1, 3-CH_3), 2.19 (1 H, dd, *J* 14 and 7, 2-H), 2.36 (1 H, dd, *J* 14 and 8, 2-H′), 2.42 (1 H, m, 5-H), 2.94 (1 H, dd, *J* 9 and 7, 6-H), 3.03 (1 H, dd, *J* 9 and 6, 6-H′), 4.34 and 4.39 (each 1 H, d, *J* 12, OHC*H*Ph), 4.63 (1 H, d, *J* 9, 4-H), 5.73 (1 H, t, *J* 7, 1-H), 5.89 (1 H, s, 2′-H), 7.18 (13 H, m, ArH) and 7.38 (2 H, m, ArH); δ_C (125 MHz, $CDCl_3$) 17.0, 17.8, 21.1, 33.3, 46.5, 73.3, 74.8, 75.4, 126.8, 127.8, 127.9, 128.1, 128.4, 128.6, 128.7, 129.0, 129.6, 130.8, 131.9, 134.3, 139.1, 140.0, 168.5 and 170.4; *m*/*z* (CI) 504 (M^+ + 18, 16%), 310 (25), 293 (36), 171 (40) and 99 (100).

(2*E*,6*E*,4*RS*,8*RS*)-9-Benzyloxy-6,8-dimethylnona-2,6-dien-4-ol 31b. Following the standard procedure, racemic bromide **30** (75 mg, 0.26 mmol) and (*E*)-but-2-enal (22 μL, 0.26 mmol), after chromatography (10 : 1, light petroleum–ether) gave the *title compound* **31b** as a colourless oil (58 mg, 80%) containing *ca.* 9% of its 4-epimer **32b** (^{1}H NMR), R_f = 0.25 (3 : 1, light petroleum–ether) (Found: $M^+ + NH_4$, 292.2266. $C_{18}H_{30}O_2N$ requires *M*, 292.2271); ν_{max}/cm^{-1} 3429, 3030, 2960, 2927, 2855, 1453, 1377, 1092, 966, 737 and 698; δ_H (300 MHz, $CDCl_3$)

major isomer **31b** 1.00 (3 H, d, *J* 7, 8-CH_3), 1.75 (6 H, m, 1-H_3 and 6-CH_3), 2.15 (1 H, dd, *J* 13, 9, 5-H), 2.26 (1 H, dd, *J* 13, 6, 5-H′), 2.80 (1 H, m, 8-H), 3.30 (2 H, m, 9-H_2), 4.16 (1 H, m, 4-H), 4.50 and 4.56 (each 1 H, d, *J* 12, OHC*H*Ph), 5.10 (1 H, d, *J* 9, 7-H), 5.50 (1 H, ddd, *J* 17, 7 and 3, 3-H), 5.75 (1 H, m, 2-H) and 7.35 (5 H, m, ArH); minor epimer **32b** 1.04 (3 H, d, *J* 7, 8-CH_3); δ_C (75 MHz, $CDCl_3$) 16.7, 17.6, 18.0, 33.4, 48.7, 69.6, 73.3, 75.5, 126.8, 127.8, 127.9, 128.6, 132.3, 132.6, 133.7 and 138.8; *m*/*z* (CI) 292 (M^+ + 18, 7%), 274 (M^+, 10), 257 (20), 149 (10) and 99 (100). A less polar fraction was (2*E*,6*Z*,4*SR*,8*RS*)-9-benzyloxy-6,8-dimethylnona-2,6-dien-4-ol **33b** as a colourless oil (10 mg, 7%), R_f = 0.28 (3 : 1, light petroleum–ether) (Found: M^+ + NH_4, 292.2266. $C_{18}H_{30}O_2N$ requires *M*, 292.2271); ν_{max}/cm^{-1} 3439, 3031, 2960, 2927, 2855, 1454, 1376, 1090, 966, 737 and 698; δ_H (300 MHz, $CDCl_3$) 0.88 (3 H, d, *J* 7, 8-CH_3), 1.74 (3 H, d, *J* 7, 1-H_3), 1.81 (3 H, s, 6-CH_3), 2.04 (1 H, dd, *J* 13 and 2, 5-H), 2.55 (1 H, dd, *J* 13 and 6, 5-H′), 2.82 (1 H, m, 8-H), 3.12 (1 H, t, *J* 9, 9-H), 3.38 (1 H, dd, *J* 9 and 6, 9-H′), 3.43 (1 H, br. s, OH), 4.20 (1 H, m, 4-H), 4.53 and 4.59 (1 H, d, *J* 12, OHC*H*Ph), 5.11 (1 H, d, *J* 9, 7-H), 5.68 (1 H, ddd, *J* 17, 7 and 3, 3-H), 5.75 (1 H, m, 2-H) and 7.36 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 17.7, 18.0, 24.0, 33.2, 41.1, 70.0, 73.2, 75.1, 126.0, 127.9, 128.2, 128.6, 132.4, 132.6, 134.6 and 138.3; *m*/*z* (CI) 292 (M^+ + 18, 5%), 274 (M^+, 5), 257 (36), 151 (34) and 99 (100).

Following the standard procedure, the (*S*)-bromide **30** (75 mg, 0.265 mmol) and but-2-enal (22 μL, 0.265 mmol) afforded the (4*S*,8*S*)-enantiomer of the title compound **31b** as a colourless oil (57 mg, 78%) containing *ca.* 9% of its 4-epimer **32b**, R_f = 0.25 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −5 (*c* 0.8, $CHCl_3$) (Found: M^+, 274.1931. $C_{18}H_{26}O_2$ requires *M*, 274.1927).

(5*E*,3*R*,7*R*)-8-Benzyloxy-2,5,7-trimethyloct-5-en-3-ol 31c. Following the standard procedure, the (*R*)-bromide **30** (75 mg, 0.26 mmol) and 2-methylpropanal (24 μL, 0.26 mmol), after chromatography (10 : 1, light petroleum–ether), gave the *title compound* **31c** as a colourless oil (55 mg, 75%) containing *ca.* 10% of its 3-epimer **32c** (^{1}H NMR), R_f = 0.25 (3 : 1, light petroleum–ether) (Found: M^+ + NH_4, 294.2428. $C_{18}H_{32}O_2N$ requires *M*, 294.2428); ν_{max}/cm^{-1} 3487, 2961, 2929, 2871, 1454, 1365, 1092, 993, 735 and 697; δ_H (500 MHz, $CDCl_3$) major isomer **31c** 0.85 and 0.89 (each 3 H, d, *J* 7, 1-H_3 or 2-CH_3), 0.95 (3 H, d, *J* 7, 7-CH_3), 1.74 (3 H, d, *J* 1, 5-CH_3), 1.81 (1 H, m, 2-H), 2.01 (1 H, dd, *J* 13 and 10, 4-H), 2.43 (1 H, dd, *J* 13 and 3, 4-H′), 2.84 (1 H, m, 7-H), 3.16 (1 H, dd, *J* 9 and 8, 8-H), 3.40 (1 H, dd, *J* 9 and 7, 8-H′), 3.43 (1 H, m, 3-H), 4.55 and 4.58 (each 1 H, d, *J* 12, OHC*H*Ph), 5.16 (1 H, dd, *J* 9 and 1, 6-H) and 7.35 (5 H, m, ArH); minor epimer **32c** 0.98 (3 H, d, *J* 7, 7-CH_3); δ_C (125 MHz, $CDCl_3$) 16.3, 17.3, 18.0, 18.6, 33.2, 33.3, 44.8, 72.4, 73.0, 75.2, 127.5, 127.6, 128.3, 131.9, 132.9 and 138.5; *m*/*z* (CI) 294 (M^+ + 18, 21%), 277 (M^+ + 1, 31), 205 (100), 108 (44), 99 (37) and 91 (56). A less polar fraction was the (*Z*)-isomer **33c** (5 mg, 6%) as a colourless oil.

(6*E*,4*S*,8*R*)-9-Benzyloxy-6,8-dimethylnon-6-en-4-ol 31d. Following the standard procedure, (*R*)-bromide **30** (75 mg, 0.26 mmol) and butanal (24 μL, 0.26 mmol), after chromatography (10 : 1, light petroleum–ether), gave the *title compound* **31d** as a colourless oil (57 mg, 78%) containing <5% of its 4-epimer **32d** (^{1}H NMR), R_f = 0.25 (3 : 1, light petroleum–ether) (Found: M^+ + H, 277.2155. $C_{18}H_{29}O_2$ requires *M*, 277.2162); ν_{max}/cm^{-1} 3443, 3031, 2956, 2929, 2870, 1454, 1367, 1093, 1026, 737 and 698; δ_H (500 MHz, $CDCl_3$) major epimer **31d** 0.86 (3 H, t, *J* 6, 1-H_3), 0.88 (3 H, d, *J* 7, 8-CH_3), 1.25–1.45 (4 H, m, 2-H_2 and 3-H_2), 1.59 (3 H, d, *J* 1, 6-CH_3), 1.90 (1 H, dd, *J* 13 and 10, 5-H), 1.98 (1 H, br. s, OH), 2.11 (1 H, dd, *J* 13 and 3, 5-H′), 2.67 (1 H, m, 8-H), 3.15 (1 H, dd, *J* 9 and 8, 9-H), 3.22 (1 H, dd, *J* 9 and 7, 9-H′), 3.55 (1 H, m, 4-H), 4.41 and 4.44 (each 1 H, d, *J* 12, OHC*H*Ph), 4.98 (1 H, d, *J* 9, 7-H) and 7.35 (5 H, m, ArH); minor epimer **32d** 1.02 (3 H, d, *J* 7, 8-CH_3); δ_C (1255 MHz, $CDCl_3$) 14.2, 16.4, 17.3, 19.0, 33.1, 39.1, 48.2, 67.7, 73.0, 75.2, 127.5, 127.6, 128.4, 131.9, 132.6 and 138.5; *m*/*z* (ES) 299 (M^+ + 23, 100%), 294 (63), 277 (M^+ + 1, 8) and 205 (10). A less polar fraction was the (*Z*)-isomer **33d** isolated as a colourless oil (4 mg, 5%), R_f = 0.28 (3 : 1, light petroleum–ether); ν_{max}/cm^{-1} 3444, 3031, 2951, 2921, 2872, 1604, 1454, 1368, 1094 and 1028; δ_H (300 MHz, $CDCl_3$) 0.88 (3 H, d *J* 7, 8-CH_3), 0.98 (3 H, t, *J* 7, 1-H_3), 1.30–1.60 (4 H, m, 2-H_2 and 3-H_2), 1.78 (3 H, d, *J* 1, 6-CH_3), 1.99 (1 H, dd, *J* 14 and 2, 5-H), 2.45 (1 H, dd, *J* 14 and 10, 5-H′), 2.86 (1 H, m, 8-H), 3.16 (1 H, t, *J* 8, 9-H), 3.37 (1 H, dd, *J* 8 and 5, 9-H′), 3.75 (1 H, m, 4-H), 4.52 and 4.59 (each 1 H, d, *J* 12, OHC*H*Ph), 5.08 (1 H, d, *J* 9, 7-H) and 7.35 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 14.5, 17.7, 19.3, 24.1, 33.2, 40.4, 40.7, 68.8, 73.3, 75.2, 127.8, 128.1, 128.6, 132.3.

Following the standard procedure, (*S*)-bromide **30** (75 mg, 0.265 mmol) and butanal (24 μL, 0.265 mmol) gave the (4*R*,8*S*)-enantiomer of the title compound **31d** as a colourless oil (57 mg, 78%) containing *ca.* 7% of its 4-epimer **32d**, R_f = 0.25 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +9 (*c* 1.1, $CHCl_3$) (Found: M^+ + H, 277.2163. $C_{18}H_{29}O_2$ requires *M*, 277.2162).

(3*E*,1*RS*,5*RS*)-6-Benzyloxy-3,5-dimethyl-1-(4-nitrophenyl)hex-3-en-1-ol 31e. Following the standard procedure, racemic bromide **30** (75 mg, 0.26 mmol) and 4-nitrobenzaldehyde (40 mg, 0.26 mmol), after chromatography (10 : 1, light petroleum–ether), gave the *title compound* **31e** as a colourless oil (59 mg, 63%) containing *ca.* 5% of its 1-epimer **32e** (^{1}H NMR), R_f = 0.25 (3 : 1, light petroleum–ether) (Found: M^+ + NH_4, 373.2125. $C_{21}H_{29}O_4N_2$ requires *M*, 373.2122); ν_{max}/cm^{-1} 3426, 3066, 2928, 2871, 1605, 1520, 1455, 1348, 1198, 1072, 854, 750 and 699; δ_H (300 MHz, $CDCl_3$) major epimer **31e** 0.98 (3 H, d, *J* 7, 5-CH_3), 1.79 (3 H, s, 3-CH_3), 2.22 (1 H, dd, *J* 14 and 10, 2-H), 2.42 (1 H, dd, *J* 14 and 4, 2-H′), 2.85 (1 H, m, 5-H), 2.90 (1 H, br. s, OH), 3.26 (1 H, t, *J* 9, 6-H), 3.38 (1 H, dd, *J* 9 and 6, 6-H′), 4.50 and 4.54 (each 1 H, d, *J* 12, OHC*H*Ph), 4.80 (1 H, dd, *J* 10 and 6, 1-H), 5.17 (1 H, d, *J* 9, 4-H), 7.36 (5 H, m, ArH) and 7.53 and 8.18 (each 2 H, d, *J* 9, ArH); minor epimer **32e** 1.01 (3 H, d, *J* 7, 5-CH_3); δ_C (75 MHz, $CDCl_3$) 16.5, 17.2, 33.5, 51.1, 69.9, 73.3, 75.3, 123.8, 126.7, 127.9, 128.6, 131.5, 134.3, 138.5, 147.3 and 152.0; *m*/*z* (CI) 373 (M^+ + 18, 74%), 356 (M^+ + 1), 12), 338 (12), 308 (21), 205 (25), 108 (31) and 99 (100). A less polar fraction was (3*Z*,1*SR*,5*RS*)-6-benzyloxy-3,5-dimethyl-1-(4-nitrophenyl)hex-3-en-1-ol **33e** as a colourless oil (9 mg, 10%), R_f = 0.28 (3 : 1, light petroleum–ether) (Found: M^+ + NH_4, 373.2125. $C_{21}H_{29}O_4N_2$ requires *M*, 373.2122); ν_{max}/cm^{-1} 3411, 2960,

2873, 1602, 1520, 1455, 1347, 1074, 856, 749 and 698; δ_H (300 MHz, $CDCl_3$) 0.96 (3 H, d, *J* 7, 5-CH_3), 1.78 (3 H, s, 3-CH_3), 2.17 (1 H, dd, *J* 14 and 3, 2-H), 2.63 (1 H, dd, *J* 14 and 11, 2-H′), 2.83 (1 H, m, 5-H), 3.19 (1 H, dd, *J* 10 and 8, 6-H), 3.42 (1 H, dd, *J* 8 and 4, 6-H′), 4.58 (2 H, s, OCH_2Ph), 4.91 (1 H, dd, *J* 11 and 2, 1-H), 5.18 (1 H, d, *J* 10, 4-H), 7.36 (5 H, m, ArH) and 7.44 and 8.19 (each 2 H, d, *J* 9, ArH); δ_C (75 MHz, $CDCl_3$) 17.5, 23.6, 33.3, 43.4, 70.5, 73.5, 75.2, 123.8, 126.5, 128.2, 128.4, 128.7, 131.8, 133.8, 137.7, 147.2 and 153.6; *m*/*z* (CI) 373 (M^+ + 18, 21%), 356 (M^+ + 1, 53), 338 (14), 205 (30), 122 (30), 108 (51) and 99 (100).

(4*E*,2*S*,6*S*)- and (4*Z*,2*R*,6*S*)-7-(Benzyloxy)-1-*tert*-butyldimethylsilyloxy-4,6-dimethylhept-4-en-2-ols 31f and 33f. Following the standard procedure, the (*S*)-bromide **30** (75 mg, 0.265 mmol) and *tert*-butyldimethylsilyloxyethanal (56 μL, 0.265 mmol), after chromatography, afforded the *title compound* **33f** as a colourless oil (20 mg, 20%), R_f = 0.4 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +11 (*c* 0.8, $CHCl_3$) (Found: M^+ + H, 379.2660. $C_{22}H_{39}O_3Si$ requires *M*, 379.2663); ν_{max}/cm^{-1} 3443, 2954, 2928, 2857, 1586, 1456, 1362, 1254, 1118 and 837; δ_H (300 MHz, $CDCl_3$) 0.11 (6 H, s, 2 × $SiCH_3$), 0.92 (3 H, d, *J* 7, 6-CH_3), 0.95 [9 H, s, $SiC(CH_3)_3$], 1.80 (3 H, d, *J* 1, 4-CH_3), 2.21 (1 H, dd, *J* 13 and 4, 3-H), 2.39 (1 H, dd, *J* 13 and 9, 3-H′), 2.81 (1 H, m, 6-H), 3.19 (1 H, t, *J* 9, 7-H), 3.33 (1 H, dd, *J* 9 and 5, 7-H′), 3.54 (1 H, dd, *J* 10 and 6, 1-H), 3.64 (1 H, dd, 10 and 5, 1-H′), 3.78 (1 H, m, 2-H), 4.54 (2 H, s, OCH_2Ph), 5.08 (1 H, d, *J* 10, 5-H) and 7.34 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.0, 17.8, 18.6, 24.1, 26.2, 33.2, 36.8, 67.5, 70.0, 73.2, 75.2, 127.9, 128.0, 128.6, 131.9, 132.7 and 138.4; *m*/*z* (CI) 396 (M^+ + 18, 40%), 379 (M^+ + 1, 100) and 205 (72). Further chromatography afforded the *title compound* **31f** as a colourless oil (50 mg, 50%) containing *ca.* 5% of its 2-epimer **32f** (^1H NMR), R_f = 0.35 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +11 (*c* 1.2, $CHCl_3$) (Found: M^+ + H, 379.2663. $C_{22}H_{39}O_3Si$ requires *M*, 379.2663); ν_{max}/cm^{-1} 3468, 2956, 2857, 1455, 1362, 1254, 1121 and 838; δ_H (300 MHz, $CDCl_3$) major isomer **31f** 0.01 (6 H, s, 2 × $SiCH_3$), 0.94 [9 H, s, $SiC(CH_3)_3$], 1.01 (3 H, d, *J* 7, 6-CH_3), 1.74 (3 H, d, *J* 1, 4-CH_3), 2.15 (1 H, dd, *J* 13 and 8, 3-H), 2.23 (1 H, dd, *J* 13 and 6, 3-H′), 2.45 (1 H, br. s, OH), 2.78 (1 H, m, 6-H), 3.31 (2 H, m, 7-H_2), 3.52 (1 H, dd, *J* 10 and 6, 1-H), 3.62 (1 H, dd, *J* 10 and 4, 1-H′), 3.78 (1 H, m, 2-H), 4.52 and 4.57 (each 1 H, d, *J* 12, OHC*H*Ph), 5.08 (1 H, dd, *J* 9 and 1, 5-H) and 7.34 (5 H, m, ArH); minor 2-epimer **32f** 1.80 (3 H, d, *J* 1, 4-CH_3); δ_C (75 MHz, $CDCl_3$) −5.1, 16.8, 17.9, 18.6, 26.2, 33.4, 44.0, 67.0, 69.8, 73.2, 75.5, 127.7, 127.8, 128.6, 131.3, 132.5 and 138.9; *m*/*z* (CI) 396 (M^+ + 18, 12%), 379 (M^+ + 1, 14), 205 (100) and 123 (50).

(4*E*,2*S*,6*S*)-7-Benzyloxy-1-*tert*-butyldimethylsilyloxy-4,6-dimethylhept-4-en-2-yl (2*R*)-2-acetoxy-2-phenylacetate 37. Following the standard procedure, alcohol **31f** (20 mg, 0.053 mmol) in DCM (0.3 mL), pyridine (0.042 mL, 0.614 mmol), DMAP (cat.) and (*R*)-*O*-acetylmandelyl chloride (33 mg, 0.159 mmol) in DCM (0.3 mL), after chromatography (6 : 1, light petroleum–ether), gave the *title compound* **37** as a colourless oil (18 mg, 62%), R_f = 0.3 (6 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −60 (*c* 0.9, $CHCl_3$) (Found: M^+ + H, 555.3141. $C_{32}H_{47}O_6Si$ requires *M*, 555.3136); ν_{max}/cm^{-1} 2954, 2928, 2856, 1746, 1587, 1454, 1372, 1252, 1178, 1091, 1056 and 838; δ_H (300 MHz, $CDCl_3$) 0.08 (6 H, s, 2 × $SiCH_3$), 0.94 (12 H, m, $SiC(CH_3)_3$ and 6-CH_3), 1.52 (3 H, d, *J* 1, 4-CH_3), 2.10 (1 H, dd, *J* 10 and 7, 3-H), 2.22 (3 H, s, CH_3), 2.32 (1 H, dd, *J* 10 and 6, 3-H′), 2.62 (1 H, m, 6-H), 3.12 (1 H, dd, *J* 11 and 7, 7-H), 3.23 (1 H, dd, *J* 11 and 6, 7-H′), 3.68 (2 H, d, *J* 5, 1-H_2), 4.50 (2 H, s, OCH_2Ph), 5.02 (2 H, m, 2-H and 5-H), 5.96 (1 H, s, 2′-H) and 7.34 (10 H, m, ArH); *m*/*z* (CI) 572 (M^+ + 18, 6%), 272 (34), 229 (36) and 123 (100).

(4*E*,2*S*,6*S*)-7-Benzyloxy-1-*tert*-butyldimethylsilyloxy-4,6-dimethylhept-4-en-2-yl (2*S*)-2-acetoxy-2-phenylacetate 38. Following the standard procedure, alcohol **31f** (20 mg, 0.053 mmol) and (*S*)-*O*-acetylmandelyl chloride gave the *title compound* **38** as a colourless oil (22 mg, 76%), R_f = 0.3 (6 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +65 (*c* 1.8, $CHCl_3$) (Found: M^+ + NH_4, 572.3403. $C_{32}H_{50}O_6NSi$ requires *M*, 572.3402); ν_{max}/cm^{-1} 2955, 2929, 2857, 1746, 1454, 1372, 1247, 1178, 1093, 1056 and 838; δ_H (300 MHz, $CDCl_3$) major isomer −0.08 (6 H, s, 2 × $SiCH_3$), 0.83 [9 H, s, $SiC(CH_3)_3$], 1.02 (3 H, d, *J* 7, 6-CH_3), 1.72 (3 H, d, *J* 1, 4-CH_3), 2.22 (3 H, s, CH_3), 2.35 (2 H, m, 3-H_2), 2.74 (1 H, m, 6-H), 3.25 (1 H, dd, *J* 11 and 7, 7-H), 3.37 (1 H, dd, *J* 11 and 6, 7-H′), 3.53 (2 H, d, *J* 5, 1-H_2), 4.54 and 4.56 (each 1 H, d, *J* 12, OHC*H*Ph), 5.03 (2 H, m, 2-H and 5-H), 5.94 (1 H, s, 2′-H) and 7.34 (10 H, m, ArH); *m*/*z* (CI) 572 (M^+ + 18, 8%), 271 (100) and 123 (70).

(4*Z*,2*R*,6*S*)-7-Benzyloxy-1-*tert*-butyldimethylsilyloxy-4,6-dimethylhept-4-en-2-yl (2*R*)-2-acetoxy-2-phenylacetate 39. Following the standard procedure, alcohol **33f** (20 mg, 0.053 mmol) and (*R*)-*O*-acetylmandelyl chloride gave the *title compound* **39** as a colourless oil (19 mg, 72%), R_f = 0.5 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −48 (*c* 0.6, $CHCl_3$) (Found: M^+ + NH_4, 572.3392. $C_{32}H_{50}O_6NSi$ requires *M*, 572.3402); ν_{max}/cm^{-1} 2956, 2928, 2857, 1746, 1595, 1455, 1372, 1231, 1120, 1090 and 838; δ_H (300 MHz, $CDCl_3$) −0.08 (6 H, s, 2 × $SiCH_3$), 0.80 [9 H, s, $SiC(CH_3)_3$], 1.02 (3 H, d, *J* 7, 6-CH_3), 1.77 (3 H, s, 4-CH_3), 2.22 (3 H, s, CH_3), 2.38 (1 H, dd, *J* 11 and 7, 3-H), 2.48 (1 H, dd, *J* 11 and 7, 3-H′), 2.80 (1 H, m, 6-H), 3.20–3.60 (4 H, m, 1-H_2 and 7-H_2), 4.54 (2 H, s, OCH_2Ph), 5.08 (2 H, m, 2-H and 5-H), 5.95 (1 H, s, 2′-H) and 7.34 (10 H, m, ArH); *m*/*z* (CI) 572 (M^+ + 18, 4%), 271 (56), 123 (96) and 108 (100).

(4*Z*,2*R*,6*S*)-7-Benzyloxy-1-*tert*-butyldimethylsilyloxy-4,6-dimethylhept-4-en-2-yl (2*S*)-2-acetoxy-2-phenylacetate 40. Following the standard procedure, alcohol **33f** (20 mg, 0.053 mmol) and (*S*)-*O*-acetylmandelyl chloride gave the *title compound* **40** as a colourless oil (23 mg, 80%), R_f = 0.5 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +67 (*c* 0.6, $CHCl_3$) (Found: M^+ + NH_4, 572.3394. $C_{32}H_{50}O_6NSi$ requires *M*, 572.3402); ν_{max}/cm^{-1} 2955, 2928, 2857, 1747, 1456, 1372, 1231, 1097, 1056 and 838; δ_H (300 MHz, $CDCl_3$) 0.10 (6 H, s, 2 × $SiCH_3$), 0.93 [9 H, s, $SiC(CH_3)_3$], 0.96 (3 H, d, 6-CH_3), 1.52 (3 H, s, 4-CH_3), 2.22 (3 H, s, CH_3), 2.38 (1 H, m, 6-H), 2.75 (2 H, m, 3-H_2), 3.10–3.60 (4 H, m, 1-H_2 and 7-H_2), 4.48 (2 H, s, OCH_2Ph), 5.04 (2 H, m, 2-H and 5-H), 5.93 (1 H, s, 2′-H) and 7.34 (10 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.1, 17.9, 18.1, 18.5, 21.0, 23.9, 26.1, 32.6, 33.0, 63.6, 73.1, 74.9, 75.4, 127.7, 127.8, 128.1, 128.6, 129.0, 129.0, 131.1, 131.5, 134.2, 139.0, 168.8 and 170.4; *m*/*z* (CI) 572 (M^+ + 18, 4%), 271 (54), 123 (94) and 108 (100).

(4*S*,2*E*)-4-Benzyloxy-1-bromopent-2-ene 42. Triphenylphosphine (1.76 g, 6.78 mmol) was added at room temperature in three portions over 30 min to the alcohol **41** (0.79 g, 4.11 mmol) and carbon tetrabromide (1.76 g, 5.34 mmol) in DCM (50 mL) and the mixture stirred at this temperature for 2 h. After concentration under reduced pressure, chromatography (15 : 1, light petroleum–ether) of the residue gave the *title compound* **42** as a colourless oil (936 mg, 90%), R_f = 0.3 (15 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −27.6 (*c* 4.6, $CHCl_3$) (Found: $M^+ - CH_3$, 239.0068. $C_{11}H_{12}O^{79}Br$ requires *M*, 239.0072); ν_{max}/cm^{-1} 2975, 2928, 2863, 1601, 1453, 1370, 1205, 1101, 1073 and 968; δ_H (300 MHz, $CDCl_3$) 1.32 (3 H, d, *J* 6, 5-H_3), 4.00 (3 H, m, 4-H and 1-H_2), 4.44 and 4.61 (each 1 H, d, *J* 12, OHC*H*Ph), 5.77 (1 H, dd, *J* 15 and 7, 3-H), 5.93 (1 H, dt, *J* 15 and 7, 2-H) and 7.36 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 21.5, 32.3, 70.4, 74.7, 127.9, 128.3, 128.7, 137.3, 138.7 and 138.8; *m*/*z* (CI) 274, 272 (M^+ + 18, 1%), 239 (M^+ − 15, 3), 108 (14) and 91 (100).

(5*R*,2*E*)-1-Bromo-5-methoxyhex-2-ene 48. Triphenylphosphine (130 mg, 0.51 mmol) was added at room temperature in three portions over 30 min to the alcohol **47** (40 mg, 0.31 mmol) and carbon tetrabromide (130 mg, 0.40 mmol) in DCM (4 mL) and the reaction mixture stirred at this temperature for 2 h. After concentration under reduced pressure, chromatography (15 : 1, light petroleum–ether) of the residue gave the *title compound* **48** as a colourless oil (55 mg, 92%), R_f = 0.9 (1 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +14 (*c* 2.1, $CHCl_3$); ν_{max}/cm^{-1} 2964, 2929, 1662, 1461, 1376, 1261, 1099, 1017 and 802; δ_H (300 MHz, $CDCl_3$) 1.14 (3 H, d, *J* 6, 6-H_3), 2.15–2.45 (2 H, m, 4-H_2), 3.33 (3 H, s, OCH_3), 3.38 (1 H, m, 5-H), 3.98 (2 H, m, 1-H_2) and 5.78 (2 H, m, 2-H and 3-H); δ_C (75 MHz, $CDCl_3$) 19.2, 33.5, 38.9, 56.3, 76.4, 128.9 and 132.6; *m*/*z* (CI) 212, 210 (M^+ + 18, 100%), 180 (32) and 98 (52).

(3*E*,1*S*,6*R*)-6-Methoxy-1-phenylhept-3-en-1-ol 49. Following the standard procedure, benzaldehyde (0.075 mL, 0.75 mmol), bismuth(III) iodide (144 mg, 0.25 mmol) in MeCN (1 mL) and DCM (1 mL) and stannane **44** (100 mg, 0.25 mmol) in DCM (0.3 mL), after chromatography (3 : 1, light petroleum–ether with 1% Et_3N), gave the *title compound* **49** as a colourless oil (44 mg, 80%) containing *ca.* 20% of its 1-epimer **50** (^1H and ^{13}C NMR), R_f = 0.3 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −24 (*c* 0.5, $CHCl_3$) (Found: $M^+ + NH_4$, 238.1812. $C_{14}H_{24}NO_2$ requires M, 238.1807); ν_{max}/cm^{-1} 3424, 2969, 2924, 1602, 1452, 1377, 1087, 1046, 971 and 756; δ_H (300 MHz, $CDCl_3$) major epimer **49** 1.13 (3 H, d, *J* 6, 7-H_3), 2.10–2.35 and 2.40–2.50 (each 2 H, m, 2-H_2 and 5-H_2), 3.34 (3 H, s, OCH_3), 3.35 (1 H, m, 6-H), 4.71 (1 H, m, 1-H), 5.40–5.55 (2 H, m, 3-H and 4-H) and 7.34 (5 H, m, ArH); minor epimer **50** 1.14 (3 H, d, *J* 6.5, 7-H_3); δ_H (300 MHz, C_6D_6) major epimer **49** 0.91 (3 H, d, *J* 6.5, 7-H_3); minor epimer **50** 0.93 (3 H, d, *J* 6.5, 7-H_3); δ_C (75 MHz, $CDCl_3$) major epimer **49** 19.0, 39.6, 43.1, 56.2, 73.4, 76.5, 126.0, 127.6, 128.4, 128.6, 131.1 and 144.1; minor epimer **50** 39.4, 43.0 and 73.6; *m*/*z* (CI) 238 (M^+ + 18, 100%), 220 (M^+, 98), 203 (60) and 117 (36).

Following the standard procedure, zinc powder (31 mg, 0.48 mmol), bismuth(III) iodide (248 mg, 0.42 mmol) in THF (1.5 mL), the bromide **48** (53 mg, 0.28 mmol) in THF (0.5 mL) and benzaldehyde (29 μL, 0.28 mmol), after chromatography (4 : 1, light petroleum–ether), gave the title compound **49** as a colourless oil (69 mg, 69%) containing *ca.* 26% of its 1-epimer **50**.

(3*E*,1*S*,6*R*)-6-Methoxy-1-phenylhept-3-en-1-yl(2*R*)-2-acetoxy-2-phenylacetate 51. Following the standard procedure, the alcohol **49** (40 mg, 0.18 mmol) in DCM (0.5 mL), pyridine (0.15 mL, 2.1 mmol), DMAP (cat.) and (*R*)-*O*-acetylmandelyl chloride (112 mg, 0.53 mmol) in DCM (0.9 mL), after chromatography (6 : 1, light petroleum–ether), afforded the *title compound* **51** as a colourless oil (48 mg, 59%), R_f = 0.3 (6 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −38 (*c* 1.1, $CHCl_3$) (Found: $M^+ + NH_4$, 414.2272. $C_{24}H_{32}NO_5$ requires *M*, 414.2280); ν_{max}/cm^{-1} 2971, 2929, 1747, 1455, 1373, 1231, 1175, 1085, 1056, 969 and 743; δ_H (300 MHz, $CDCl_3$) major isomer 1.00 (3 H, d, *J* 6, 7-H_3), 1.87 (1 H, m, 5-H), 2.06 (1 H, m, 5-H′), 2.18 (3 H, s, CH_3), 2.30–2.60 (2 H, m, 2-H_2), 3.16 (1 H, m, 6-H), 3.27 (3 H, s, OCH_3), 5.05 and 5.26 (each 1 H, dt, *J* 15, 7, 3-H or 4-H), 5.76 (1 H, t, *J* 7, 1-H), 6.00 (1 H, s, 2′-H), 7.19 (1 H, m, ArH), 7.36 (7 H, m, ArH) and 7.51 (2 H, m, ArH); *m*/*z* (CI) 414 (M^+ + 18, 48%), 220 (58) and 203 (100).

(3*E*,1*S*,6*R*)-6-Methoxy-1-phenylhept-3-en-1-yl (2*S*)-2-acetoxy-2-phenylacetate 52. Following the standard procedure, the alcohol **49** (40 mg, 0.18 mmol) and (*S*)-*O*-acetylmandelyl chloride gave the *title compound* **52** as a colourless oil (50 mg, 62%), R_f = 0.3 (6 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +36 (*c* 1.5, $CHCl_3$) (Found: $M^+ + NH_4$, 414.2286. $C_{24}H_{32}NO_5$ requires *M*, 414.2280); ν_{max}/cm^{-1} 2970, 2928, 1746, 1455, 1372, 1231, 1175, 1085, 1056, 971, 745 and 699; δ_H (300 MHz, $CDCl_3$) major isomer 1.07 (3 H, d, *J* 6, 7-H_3), 2.07 (1 H, m, 5-H), 2.19 (3 H, s, CH_3), 2.23 (1 H, m, 5-H′), 2.40–2.70 (2 H, m, 2-H_2), 3.22 (1 H, m, 6-H), 3.24 (3 H, s, OCH_3), 5.34 and 5.48 (each 1 H, dt, *J* 15, 7, 3-H or 4-H), 5.76 (1 H, t, *J* 7, 1-H), 6.00 (1 H, s, 2′-H), 6.98 (1 H, m, ArH), 7.19 (2 H, m, ArH) and 7.38 (7 H, m, ArH); *m*/*z* (CI) 414 (M^+ + 18, 1%), 259 (6) and 91 (100).

(3*E*,1*S*,6*R*)-1-Phenylhept-3-ene-1,6-diol 53a. Following the standard procedure, stannane **43** (30 mg, 0.077 mmol) and benzaldehyde (24 μL, 0.231 mmol) afforded the *title compound* **53a** as a colourless oil (10 mg, 63%) containing *ca.* 20% of its 1-epimer **54a** (^{13}C NMR), R_f = 0.3 (1 : 4, light petroleum–ether), $[\alpha]_D^{20}$ −18 (*c* 1.2, $CHCl_3$) (Found: $M^+ + NH_4$, 224.1651. $C_{13}H_{22}NO_2$ requires *M*, 224.1650); ν_{max}/cm^{-1} 3388, 2965, 2922, 1601, 1453, 1415, 1375, 1114, 1047, 972, 938 and 755; δ_H (300 MHz, $CDCl_3$) 1.13 (3 H, d, *J* 6, 7-H_3), 1.70 (2 H, br. s, OH), 2.10–2.40 and 2.52 (each 2 H, m, 2-H_2 or 5-H_2), 3.76 (1 H, m, 6-H), 4.71 (1 H, dd, *J* 8 and 6, 1-H), 5.49 (2 H, m, 3-H and 4-H) and 7.34 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) major epimer **53a** 23.0, 42.7, 42.9, 67.2, 73.7, 126.0, 127.8, 128.7, 129.9, 130.5 and 144.3; minor epimer **54a** 22.9, 42.9 and 73.6; *m*/*z* (CI) 224 (M^+ + 18, 54%), 206 (M^+, 26) and 117 (100).

(4*E*,2*R*,7*S*)-8,8-Dimethylnon-4-ene-2,7-diol 53b. Following the standard procedure, stannane **43** (60 mg, 0.154 mmol) and 2,2-dimethylpropanal (50 μL, 0.462 mmol) afforded the *title compound* **53b** as a colourless oil (20 mg, 71%) containing *ca.* 20% of its 7-epimer **54b** (^{13}C NMR), R_f = 0.2 (1 : 4, light

petroleum–ether), $[\alpha]_D^{20}$ −18 (*c* 1.1, $CHCl_3$) (Found: $M^+ + NH_4$, 204.1964. $C_{11}H_{26}NO_2$ requires *M*, 204.1963); ν_{max}/cm^{-1} 3368, 2963, 2913, 2871, 1479, 1428, 1364, 1304, 1127, 1069, 1040, 1014 and 967; δ_H (300 MHz, $CDCl_3$) 0.91 (9 H, s, 2 × 8-CH_3 and 9-H_3), 1.20 (3 H, d, *J* 6, 1-H_3), 1.80–2.40 (6 H, m, 3-H_2, 6-H_2 and 2 × OH), 3.22 (1 H, d, *J* 11, 7-H), 3.81 (1 H, m, 2-H) and 5.55 (2 H, m, 4-H and 5-H); δ_C (75 MHz, $CDCl_3$) major epimer **53b** 23.1, 26.0, 34.9, 35.4, 42.8, 67.3, 78.6, 129.8 and 131.9; minor epimer **54b** 23.0. 42.7, 67.4, 129.7 and 132.0; *m*/*z* (CI) 204 (M^+ + 18, 100%), 186 (M^+, 6) and 109 (12).

(4*E*,2*R*,7*S*)-8-Methylnon-4-ene-2,7-diol 53c. Following the standard procedure, stannane **43** (70 mg, 0.18 mmol) and 2-methylpropanal (50 μL, 0.72 mmol) afforded the *title compound* **53c** as a colourless oil (23 mg, 74%) containing *ca.* 32% of its 7-epimer **54c** (^{13}C NMR), R_f = 0.2 (1 : 4, light petroleum–ether), $[\alpha]_D^{20}$ −11 (*c* 1.1, $CHCl_3$) (Found: $M^+ + NH_4$, 190.1811. $C_{10}H_{24}NO_2$ requires *M*, 190.1806); ν_{max}/cm^{-1} 3368, 2976, 2927, 1600, 1465, 1370, 1260, 1118, 1040, 970, 940 and 801; δ_H (300 MHz, $CDCl_3$) 0.84 (3 H, d, *J* 7, 9-H_3), 0.86 (3 H, d, *J* 7, 8-CH_3), 1.22 (3 H, d, *J* 6, 1-H_3), 1.70 (1 H, m, 8-H), 1.80–2.00 (2 H, br. s, 2 × OH), 2.05–2.35 (4 H, m, 3-H_2 and 6-H_2), 3.38 (1 H, m, 7-H), 3.73 (1 H, m, 2-H) and 5.56 (2 H, m, 4-H and 5-H); δ_C (75 MHz, $CDCl_3$) major epimer **53c** 17.9, 19.0, 23.0, 33.5, 37.9, 42.7, 67.3, 75.9, 130.0 and 130.8; minor epimer **54c** 23.1, 33.4, 42.8, 67.4 and 129.9; *m*/*z* (CI) 190 (M^+ + 18, 100%), 172 (M^+ + 1, 8) and 137 (6).

(5*E*,2*R*,7*R*)- and (5*E*,2*R*,7*S*)-Dec-4-ene-2,7-diols 53d and 54d. Following the standard procedure, stannane **43** (70 mg, 0.18 mmol) and butanal (48 μL, 0.72 mmol) afforded the *title compounds* **53d** and **54d** as a colourless oil (24 mg, 78%) as a 50 : 50 mixture (^{13}C NMR), R_f = 0.2 (1 : 4, light petroleum–ether) (Found: $M^+ + NH_4$, 190.1799. $C_{10}H_{24}NO_2$ requires *M*, 190.1806); ν_{max}/cm^{-1} 3349, 2961, 2927, 1645, 1457, 1430, 1374, 1121, 1073, 1025, 972 and 940; δ_H (300 MHz, $CDCl_3$) both epimers 0.93 (3 H, t, *J* 7, 10-H_3), 1.20 (3 H, d, *J* 6, 1-H_3), 1.35–1.60 (4 H, m, 8-H_2 and 9-H_2), 1.90 (2 H, br. s, 2 × OH), 2.12 and 2.25 (each 2 H, m, 3-H_2 or 6-H_2), 3.63 (1 H, m, 7-H), 3.82 (1 H, m, 2-H) and 5.54 (2 H, m, 4-H and 5-H); δ_C (75 MHz, $CDCl_3$) both epimers **53d** and **54d** 14.3, 19.1, 23.0, 23.1, 39.2, 39.3, 40.9, 41.0, 42.7, 42.8, 67.3, 67.4, 70.8, 70.9, 130.0, 130.1 and 130.3(2); *m*/*z* (CI) 190 (M^+ + 18, 100%) and 172 (M^+, 6).

(3*E*,1*S*,6*R*)-1-(4-Nitrophenyl)hept-3-ene-1,6-diol 53e. Following the standard procedure, stannane **43** (60 mg, 0.154 mmol) and 4-nitrobenzaldehyde (46 mg, 0.462 mmol) afforded the *title compound* **53e** as a colourless oil (30 mg, 78%) containing *ca.* 28% of its 1-epimer **54e** (^{13}C NMR), R_f = 0.3 (1 : 4, light petroleum–ether), $[\alpha]_D^{20}$ −42 (*c* 1.6, $CHCl_3$) (Found: $M^+ + NH_4$, 269.1508. $C_{13}H_{21}N_2O_4$ requires *M*, 269.1501); ν_{max}/cm^{-1} 3387, 2967, 2921, 1603, 1518, 1347, 1109, 1057, 973 and 855; δ_H (300 MHz, $CDCl_3$) 1.16 (3 H, d, *J* 6, 7-H_3), 1.80 (1 H, br. s, OH), 2.12 (1 H, dt, *J* 14, 6.5, 5-H), 2.23 (1 H, dt, *J* 14, 4.5, 5-H′), 2.40 (1 H, dt, *J* 14, 8, 2-H), 2.52 (1 H, dt, *J* 14, 4, 2-H′), 2.85 (1 H, br. s, OH), 3.81 (1 H, m, 6-H), 4.82 (1 H, dd, *J* 4 and 8, 1-H), 5.54 (2 H, m, 3-H and 4-H) and 7.52 and 8.19 (each 2 H, d, *J* 9, ArH); δ_C (75 MHz, $CDCl_3$) major epimer **53e** 23.2, 42.6, 43.1, 67.3, 72.4, 123.9, 126.7, 128.5, 131.9, 147.4 and 151.7; major epimer **54e** 23.1, 42.5, 43.0, 128.4 and 131.8; *m*/*z* (CI) 269 (M^+ + 18, 100%) and 204 (56).

(6*E*,2*R*,4*R*,8*R*)-2,9-Bis-benzyloxy-8-methylnon-6-en-4-ol 56. Following the standard procedure, activated zinc powder (32 mg, 0.49 mmol), bismuth(III) iodide (258 mg, 0.44 mmol), in THF (1.5 mL), (*R*)-bromide **26** (60 mg, 0.29 mmol) in THF (0.5 mL) and aldehyde **(*R*)-55**[28] (70 mg, 0.39 mmol), after chromatography (4 : 1, light petroleum–ether), gave the *title compound* **56** as a colourless oil (56 mg, 53%), a 78 : 22 mixture of 4-epimers (^1H and ^{13}C NMR), R_f = 0.3 (4 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −27 (*c* 1.4, $CHCl_3$) (Found: M^+ + H, 369.2423. $C_{24}H_{33}O_3$ requires *M*, 369.2429); ν_{max}/cm^{-1} 3464, 2929, 2868, 1603, 1496, 1453, 1374, 1205, 1092 and 974; δ_H (300 MHz, $CDCl_3$) major epimer **56** 1.07 (3 H, d, *J* 7, 8-CH_3), 1.28 (3 H, d, *J* 6, 1-H_3), 1.68 (2 H, m, 5-H_2), 2.20 (2 H, m, 3-H_2), 2.54 (1 H, m, 8-H), 3.42 (2 H, m, 9-H_2), 3.78–4.03 (2 H, m, 2-H and 4-H), 4.51 (1 H, d, *J* 12, OHC*H*Ph), 4.56 (2 H, s, OCH_2Ph), 4.66 (1 H, d, *J* 12, OHC*H*Ph), 5.52 (2 H, m, 6-H and 7-H) and 7.38 (10 H, m, ArH); minor 4-epimer 1.06 (3 H, d, *J* 7, 8-CH_3) and 4.49 and 4.67 (each 1 H, d, *J* 12, OHC*H*Ph); δ_C (75 MHz, $CDCl_3$) major epimer **56** 17.4, 19.7, 37.3, 41.3, 42.9, 68.0, 70.6, 71.0, 73.2, 75.5, 126.4, 127.8, 127.9, 128.0, 128.1, 128.6, 128.7, 136.7 and 138.8; minor 4-epimer 19.9, 37.3, 41.2, 43.3 and 71.2; *m*/*z* (CI) 369 (M^+ + 1, 42%), 196 (34) and 106 (100).

(6*E*,2*S*,4*R*,8*R*)-2,9-Bis-benzyloxy-8-methylnon-6-en-4-ol 57. Following the standard procedure, (*R*)-bromide **26** (53 mg, 0.256 mmol) and aldehyde **(*S*)-55**[28] (35 mg, 0.197 mmol) afforded the *title compound* **57** as a colourless oil (90 mg, 63%), an 83 : 17 mixture of epimers (^1H and ^{13}C NMR), R_f = 0.3 (4 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +52 (*c* 1.9, $CHCl_3$) (Found: M^+ + 1, 369.2423. $C_{24}H_{33}O_3$ requires *M*, 369.2429); ν_{max}/cm^{-1} 3464, 2929, 2868, 1603, 1496, 1453, 1374, 1205, 1092, 974 and 736; δ_H (300 MHz, $CDCl_3$) major epimer **57** 1.04 (3 H, d, *J* 7, 8-CH_3), 1.26 (3 H, d, *J* 6, 1-H_3), 1.50–1.75 (2 H, m, 5-H_2), 2.27 (2 H, m, 3-H_2), 2.50 (1 H, m, 8-H), 3.29 (1 H, dd, *J* 9 and 7, 9-H), 3.37 (1 H, dd, *J* 9 and 7, 9-H′), 3.75–4.00 (2 H, m, 2-H and 4-H), 4.44 (1 H, d, *J* 12, OHC*H*Ph), 4.52 (2 H, s, OCH_2Ph), 4.67 (1 H, d, *J* 12, OHC*H*Ph), 5.47 (2 H, m, 6-H and 7-H) and 7.35 (10 H, m, ArH); minor 4-epimer 1.05 (3 H, d, *J* 7, 8-CH_3) and 4.46 and 4.63 (each 1 H, d, *J* 12, OHC*H*Ph); δ_C (75 MHz, $CDCl_3$) major epimer **57** 17.4, 19.9, 37.3, 41.3, 43.4, 70.6, 71.2, 73.1, 75.5, 76.0, 126.2, 127.7, 127.8, 127.9, 128.0, 128.6, 128.8, 136.3, 138.4 and 138.9; minor 4-epimer 19.7, 37.3, 42.9, 71.0 and 73.0 *m*/*z* (CI) 369 (M^+ + 1, 12%), 196 (40) and 106 (100).

(6*E*,2*S*,4*R*,8*R*)-2,9-Bis-benzyloxy-8-methylnon-6-en-4-yl (2*R*)-2-acetoxy-2-phenylacetate 58. Following the standard procedure, alcohol **57** (40 mg, 0.109 mmol) in DCM (0.7 mL), pyridine (88 μL, 1.26 mmol), DMAP (cat.) and (*R*)-*O*-acetylmandelyl chloride (68 mg, 0.327 mmol) in DCM (0.4 mL), after chromatography (6 : 1, light petroleum–ether), gave the *title compound* **58** as a colourless oil (40 mg, 68%), R_f = 0.3 (6 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −81 (*c* 1.9, $CHCl_3$) (Found: $M^+ + NH_4$, 562.3171. $C_{34}H_{44}NO_6$ requires *M*, 562.3168); ν_{max}/cm^{-1} 2964, 2925, 2853, 1744, 1603, 1453, 1373, 1232, 1210, 1178, 1091, 1058 and 737; δ_H (300 MHz, $CDCl_3$) major isomer 1.02 (3 H, d, *J* 6, 8-CH_3), 1.05 (3 H, d, *J* 7, 1-H_3), 1.58 (1 H, m, 3-H),

1.89 (1 H, m, 3-H′), 2.22 (3 H, s, CH_3), 2.34 (2 H, t, *J* 8, 5-H_2), 2.50 (1 H, m, 8-H), 3.12 (1 H, m, 2-H), 3.30 (1 H, dd, *J* 8 and 7, 9-H), 3.39 (1 H, dd, *J* 7 and 6, 9-H′), 4.21 and 4.32 (each 1 H, d, *J* 12, OHC*H*Ph), 4.55 (2 H, s, OCH_2Ph), 5.02 (1 H, m, 4-H), 5.35–5.53 (2 H, m, 6-H and 7-H), 5.92 (1 H, 2′-H), 7.34 (13 H, m, ArH) and 7.48 (2 H, m, ArH); δ_C (75 MHz, $CDCl_3$) major isomer 17.3, 19.4, 21.0, 37.1, 37.9, 40.2, 70.5, 72.0, 73.2, 74.9, 75.6, 124.2, 127.7, 127.8, 127.8, 127.9, 128.6, 129.0, 129.5, 134.3, 137.1, 138.9, 139.0, 168.7 and 170.5; *m*/*z* (CI) 562 (M^+ + 18, 16%), 206 (12), 150 (24) and 58 (100).

(6*E*,2*S*,4*R*,8*R*)-2,9-Bis-benzyloxy-8-methylnon-6-en-4-yl(2*S*)-2-acetoxy-2-phenylacetate 59. Following the standard procedure, alcohol **57** (40 mg, 0.109 mmol) and (*S*)-*O*-acetylmandelyl chloride gave the *title compound* **59** as a colourless oil (45 mg, 76%), R_f = 0.3 (6 : 1, light petroleum–ether); δ_H (300 MHz, $CDCl_3$) major isomer 0.92 (3 H, d, *J* 6, 8-CH_3), 1.25 (3 H, d, *J* 7, 1-H_3), 1.67 (1 H, m, 3-H), 2.04 (1 H, m, 3-H′), 2.18 (2 H, m, 5-H_2), 2.24 (3 H, s, CH_3), 2.25 (1 H, m, 8-H), 3.18 (1 H, dd, *J* 8 and 7, 9-H), 3.27 (1 H, dd, *J* 7 and 6, 9-H′), 3.63 (1 H, m, 2-H), 4.45 (1 H, d, *J* 12, OHC*H*Ph), 4.51 (1 H, s, OCH_2Ph), 4.60 (1 H, d, *J* 12, OHC*H*Ph), 5.06 (2 H, m, 4-H and 6-H), 5.28 (1 H, dd, *J* 16 and 7, 7-H), 5.88 (1 H, s, 2′-H), 7.35 (13 H, m, ArH) and 7.50 (2 H, m, ArH); δ_C (75 MHz, $CDCl_3$) major isomer 17.1, 19.7, 21.0, 36.9, 37.4, 40.6, 70.5, 72.0, 73.1, 73.3, 75.0, 75.5, 124.1, 127.7, 127.8, 127.8, 127.9, 128.1, 128.6, 129.0, 129.4, 134.2, 136.7, 138.9, 139.1, 168.6 and 170.6.

(5*E*,2*R*,3*RS*,7*R*)- and (5*E*,2*S*,3*RS*,7*R*)-2,8-Bis-benzyloxy-7-methyloct-5-en-3-ols 61 and 62. Following the standard procedure, the (*R*)-bromide **26** (44 mg, 0.214 mmol) and the aldehyde **(*R*)-60**[2a] (35 mg, 0.214 mmol) afforded the *title compound* **61** as a colourless oil (45 mg, 60%), a 60 : 40 mixture of 3-epimers (^{1}H NMR), R_f = 0.4 (3 : 1, light petroleum–ether) (Found: M^+ + NH_4, 372.2547. $C_{23}H_{34}NO_3$ requires *M*, 372.2539); ν_{max}/cm^{-1} 3424, 3029, 2870, 1495, 1453, 1370, 1093 and 736; δ_H (300 MHz, $CDCl_3$) major epimer **61** 1.05 (3 H, d, *J* 7, 7-CH_3), 1.22 (3 H, d, *J* 6, 1-H_3), 2.20 (1 H, m, 4-H), 2.34 (1 H, m, 4-H′), 2.56 (1 H, m, 7-H), 3.37 (2 H, m, 8-H_2), 3.50 (2 H, m, 2-H and 3-H), 4.43 (1 H, d, *J* 12, OHC*H*Ph), 4.54 (2 H, s, OCH_2Ph), 4.68 (1 H, d, *J* 12, OHC*H*Ph), 5.52 (2 H, m, 5-H and 6-H) and 7.34 (10 H, m, ArH); minor 3-epimer 1.06 (3 H, d, *J* 7, 7-CH_3); *m*/*z* (CI) 372 (M^+ + 18, 88%) and 106 (100).

Following the standard procedure, the (*R*)-bromide **26** (44 mg, 0.214 mmol) and the aldehyde **(*S*)-60** (35 mg, 0.214 mmol) afforded the *title compound* **62** as a colourless oil (45 mg, 67%), a 60 : 40 mixture of 3-epimers (^{1}H NMR), R_f = 0.4 (3 : 1, light petroleum–ether); δ_H (300 MHz, $CDCl_3$) major isomer **62** 1.05 (3 H, d, *J* 7, 7-CH_3), 1.24 (3 H, d, *J* 6, 1-H_3), 2.15–2.60 (3 H, m, 4-H_2 and 7-H), 3.25–3.60 (3 H, m, 2-H and 8-H_2), 3.75 (1 H, m, 3-H), 4.54 (1 H, d, *J* 12, OHC*H*Ph), 4.55 (2 H, s, OCH_2Ph), 4.65 (1 H, d, *J* 12, OHC*H*Ph), 5.53 (2 H, m, 5-H and 6-H) and 7.34 (10 H, m, ArH); minor 3-epimer 1.06 (3 H, d, *J* 7, 7-CH_3) and 4.50 and 4.68 (each 1 H, d, *J* 12, OHC*H*Ph); *m*/*z* (CI) 372 (M^+ + 18, 78), 182 (22) and 106 (100).

(6*E*,2*R*,4*R*,8*R*)-9-Benzyloxy-2-*tert*-butyldimethylsilyloxy-8-methylnon-6-en-4-ol 64. Following the standard procedure, the (*R*)-bromide **26** (68 mg, 0.327 mmol) and the aldehyde **(*R*)-63**[29] (50 mg, 0.25 mmol) afforded the *title compound* **64** as a colourless oil (45 mg, 51%), a 78 : 22 *anti* : *syn* mixture of 4-epimers (^{1}H and ^{13}C NMR), R_f = 0.3 (3 : 1, light petroleum–ether) (Found: M^+ + H, 393.2820. $C_{23}H_{41}O_3Si$ requires *M*, 393.2825); ν_{max}/cm^{-1} 3462, 2956, 2930, 2856, 1455, 1374, 1255, 1093, 836 and 775; δ_H (300 MHz, $CDCl_3$) major epimer **64** 0.12 (6 H, s, 2 × $SiCH_3$), 0.93 [9 H, s, $SiC(CH_3)_3$], 1.06 (3 H, d, *J* 7, 8-CH_3), 1.24 (3 H, d, *J* 7, 1-H_3), 1.59 (2 H, m, 3-H_2), 2.21 (2 H, m, 5-H_2), 2.54 (1 H, m, 8-H), 3.32 (1 H, dd, *J* 9 and 7, 9-H), 3.38 (1 H, dd, *J* 9 and 7, 9-H′), 3.97 (1 H, m, 4-H), 4.22 (1 H, m, 2-H), 4.56 (2 H, s, OCH_2Ph), 5.52 (2 H, m, 6-H and 7-H) and 7.36 (5 H, m, ArH); minor 4-epimer 0.15 and 0.16 (each 3 H, s, $SiCH_3$), 1.21 (3 H, d, *J* 7, 1-H_3), 3.8 (1 H, m, 4-H) and 4.10 (1 H, m, 2-H); δ_C (75 MHz, $CDCl_3$) major epimer **64** −4.7, −4.3, 17.5, 18.2, 23.3, 26.1, 37.3, 41.5, 44.2, 67.6, 68.1, 73.2, 75.6, 126.4, 127.8, 127.8, 128.6, 136.4 and 138.9; minor 4-epimer −4.5, −3.6, 24.7, 41.2 and 45.3; *m*/*z* (CI) 410 (M^+ + 18, 64), 393 (M^+ + 1, 32%), 132 (68) and 106 (100).

(6*E*,2*R*,4*R*,8*R*)-9-Benzyloxy-2-*tert*-butyldimethylsilyloxy-8-methylnon-6-en-4-yl (2*R*)-2-acetoxy-2-phenylacetate 65. Following the standard procedure, alcohol **64** (30 mg, 0.077 mmol) and (*R*)-*O*-acetylmandelyl chloride afforded the *title compound* **65** as a colourless oil (25 mg, 58%), R_f = 0.3 (6 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −74 (*c* 1.8, $CHCl_3$) (Found: M^+ + NH_4, 586.3556. $C_{33}H_{52}NO_6Si$ requires *M*, 586.3563); ν_{max}/cm^{-1} 2928, 2855, 1746, 1603, 1454, 1373, 1233, 1096, 1058, 836, 776 and 736; δ_H (300 MHz, $CDCl_3$) major isomer −0.19 and −0.11 (each 3 H, s, $SiCH_3$), 0.84 [9 H, s, $SiC(CH_3)_3$], 0.97 (3 H, d, *J* 6, 8-CH_3), 1.05 (3 H, d, *J* 7, 1-H_3), 1.56 (2 H, m, 3-H_2), 2.24 (3 H, s, CH_3), 2.35 (2 H, t, *J* 6, 5-H_2), 2.50 (1 H, m, 8-H), 3.30 (1 H, dd, *J* 10 and 7, 9-H), 3.40 (2 H, m, 2-H and 9-H′), 4.55 (2 H, s, OCH_2Ph), 4.97 (1 H, m, 4-H), 5.47 (2 H, m, 6-H and 7-H), 5.91 (1 H, s, 2′-H), 7.37 (8 H, m, ArH) and 7.51 (2 H, m, ArH); *m*/*z* (CI) 586 (M^+ + 18, 34%), 152 (32) and 106 (100).

(6*E*,2*R*,4*R*,8*R*)-9-Benzyloxy-2-*tert*-butyldimethylsilyloxy-8-methylnon-6-en-4-yl (2*S*)-2-acetoxy-2-phenylacetate 66. Following the standard procedure, alcohol **64** (30 mg, 0.077 mmol) and (*S*)-*O*-acetylmandelyl chloride afforded the *title compound* **66** as a colourless oil (31 mg, 69%), R_f = 0.3 (6 : 1, light petroleum–ether); δ_H (300 MHz, $CDCl_3$) major isomer 0.02 and 0.06 (each 3 H, s, $SiCH_3$), 0.91 [9 H, s, $SiC(CH_3)_3$], 0.93 (3 H, d, *J* 6, 8-CH_3), 1.16 (3 H, d, *J* 7, 1-H_3), 1.64 (2 H, m, 3-H_2), 2.16 (2 H, m, 5-H_2), 2.24 (3 H, s, CH_3), 2.32 (1 H, m, 8-H), 3.19 (1 H, dd, *J* 9 and 7, 9-H), 3.28 (1 H, dd, *J* 9 and 6, 9-H′), 3.87 (1 H, m, 2-H), 4.52 (2 H, s, OCH_2Ph), 5.00–5.15 (2 H, m, 4-H and 6-H), 5.29 (1 H, dd, *J* 16 and 7, 7-H), 5.94 (1 H, s, 2′-H), 7.37 (8 H, m, ArH) and 7.51 (2 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −4.8, −4.0, 17.2, 18.2, 21.0, 24.8, 26.1, 26.2, 36.9, 37.8, 43.9, 65.5, 73.1, 73.6, 74.9, 75.5, 124.2, 127.7, 127.8, 127.9, 128.6, 129.0, 129.4, 134.3, 136.4, 138.9, 168.6 and 170.4.

(6*E*,2*R*,8*R*)-2,9-Bis-benzyloxy-8-methylnon-6-en-4-one 67. Dess–Martin periodinane (38 mg, 0.088 mmol) was added portionwise to the alcohol **56** containing *ca.* 22% of its 4-epimer (25 mg, 0.068 mmol) in DCM (1 mL) and the resulting suspension stirred at room temperature for 2 h before addition of aqueous sodium hydroxide (2 mL, 1.3 M). The aqueous phase

was extracted with ether (2 × 5 mL) and the organic extracts washed with aqueous sodium hydroxide (10 mL, 1.3 M) and water (10 mL), then dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (15 : 1, light petroleum–ether) of the residue afforded the *title compound* **67** as a pale yellow oil (19 mg, 74%), R_f = 0.7 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −18 (*c* 1.0, $CHCl_3$) (Found: M^+ + 1, 367.2267. $C_{24}H_{31}O_3$ requires *M*, 367.2270); ν_{max}/cm^{-1} 3062, 3029, 2966, 2928, 2870, 1714, 1602, 1453, 1372, 1261, 1092, 971, 876 and 801; δ_H (300 MHz, $CDCl_3$) 1.05 (3 H, d, *J* 7, 8-CH_3), 1.25 (3 H, d, *J* 6, 1-H_3), 2.49 (1 H, dd, *J* 15 and 5, 3-H), 2.50 (1 H, m, 8-H), 2.83 (1 H, dd, *J* 15 and 7, 3-H′), 3.16 (2 H, d, *J* 6, 5-H), 3.32 (1 H, dd, *J* 10 and 5, 9-H), 3.39 (1 H, dd, *J* 10 and 7, 9-H′), 4.46 (1 H, d, *J* 12, OHC*H*Ph), 4.53 (2 H, s, OCH_2Ph), 4.58 (1 H, d, *J* 12, OHC*H*Ph) 5.52 (1 H, dd, *J* 16 and 6, 7-H), 5.62 (1 H, dt, *J* 16 and 7, 6-H) and 7.32 (10 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 17.2, 20.1, 37.1, 48.1, 49.5, 71.1, 71.9, 73.1, 75.3, 121.8, 127.7, 127.8, 127.9, 128.5, 128.5, 137.7, 138.7 and 208.0; *m*/*z* (CI) 384 (M^+ + 18, 68%), 367 (M^+ + 1, 4) and 276 (100).

(2*R*,6*R*)-7-Benzyloxy-1-*tert*-butyldimethylsilyloxy-6-methylheptan-2-ol 69. Sodium acetate (462 mg, 3.3 mmol), in water (1.1 mL) was added dropwise to a solution of alkene **5i** (100 mg, 0.28 mmol) and toluene *p*-sulfonylhydrazine (303 mg, 1.65 mmol) in DME (3.5 mL) under reflux over 30 min. The solution was then heated under reflux for a further 16 h and allowed to cool to room temperature. The aqueous phase was extracted with ether (2 × 15 mL) and the organic extracts were washed with water (20 mL) and brine (20 mL) then dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue (3 : 1, light petroleum–ether) afforded the *title compound* **69** as a colourless oil (92 mg, 92%), R_f = 0.3 (3–1, light petroleum–ether), $[\alpha]_D^{20}$ +3 (*c* 1.1, $CHCl_3$) (Found: M^+ + 1, 367.2668. $C_{21}H_{39}O_3Si$ requires *M*, 367.2663); ν_{max}/cm^{-1} 3465, 2929, 2857, 1587, 1462, 1362, 1255, 1099, 837 and 778; δ_H (300 MHz, $CDCl_3$) 0.09 (6 H, s, 2 × $SiCH_3$), 0.92 [9 H, s, $SiC(CH_3)_3$], 0.96 (3 H, d, *J* 7, 6-CH_3), 1.10–1.60 (6 H, m, 3-H_2, 4-H_2 and 5-H_2), 1.79 (1 H, m, 6-H), 2.46 (1 H, br. s, OH), 3.26 (1 H, dd, *J* 9 and 7, 7-H), 3.35 (1 H, dd, *J* 9 and 6, 7-H′), 4.10 (1 H, m), 3.63 (2 H, m), 4.52 (2 H, s, OCH_2Ph) and 7.34 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.1, 17.3, 18.5, 23.2, 26.1, 33.3, 33.7, 33.9, 67.5, 72.0, 73.2, 76.2, 127.7, 127.8, 128.6 and 139.0; *m*/*z* (CI) 384 (M^+ + 18, 12%), 367 (M^+ + 1, 50) and 108 (100).

(2*R*,6*R*)-7-Benzyloxy-1-*tert*-butyldimethylsilyloxy-6-methylheptan-2-yl 4-methylbenzenesulfonate 70. Toluene *p*-sulfonyl chloride (96 mg, 4.89 mmol) and DMAP (101 mg, 0.83 mmol) were added to the alcohol **69** (75 mg, 0.21 mmol) in DCM (2 mL) at room temperature and the mixture stirred for 16 h. After concentration under reduced pressure, chromatography (6 : 1, light petroleum–ether) of the residue gave the *title compound* **70** as a colourless oil (97 mg, 90%), R_f = 0.3 (5 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +6 (*c* 0.8, $CHCl_3$) (Found: M^+ + 1, 521.2750. $C_{28}H_{45}O_5SiS$ requires *M*, 521.2751); ν_{max}/cm^{-1} 2928, 2855, 1598, 1461, 1363, 1255, 1177, 1098, 907, 836 and 778; δ_H (300 MHz, $CDCl_3$) −0.06 (6 H, s, 2 × $SiCH_3$), 0.79 (3 H, d, *J* 7, 6-CH_3), 0.80 [9 H, m, $SiC(CH_3)_3$], 0.90–1.40 (4 H, m, 4-H_2 and 5-H_2), 1.58 (3 H, m, 3-H_2 and 6-H), 2.37 (3 H, s, $ArCH_3$), 3.17 (2 H, m, 7-H_2), 3.60 (2 H, m, 1-H_2), 4.41 (1 H, m, 2-H), 4.42 (2 H, s, OCH_2Ph), 7.26 (7 H, m, ArH) and 7.75 (2 H, d, *J* 8, ArH); δ_C (75 MHz, $CDCl_3$) −5.4, 17.0, 18.4, 21.7, 22.2, 25.9, 31.4, 33.3, 33.4, 64.2, 73.1, 75.8, 83.4, 127.6, 127.6, 127.9, 128.4, 129.8, 134.5, 138.8 and 144.6; *m*/*z* (CI) 538 (M^+ + 18, 2%), 521 (M^+ + 1, 1), 259 (14), 201 (16) and 91 (100).

(2*S*,6*R*)-7-Benzyloxy-1-*tert*-butyldimethylsilyloxy-2,6-dimethylheptane 71. Methyllithium (1.44 mL, 1.6 M in ether, 2.31 mmol) was added dropwise to copper(I) cyanide (103 mg, 1.15 mmol) in toluene (3 mL) at 0 °C and the mixture stirred at this temperature for 15 min. The toluene *p*-sulfonate **70** (120 mg, 0.23 mmol) in toluene (2 mL) was added and the mixture stirred at 0 °C for 5 h. The mixture was then filtered through celite® that was washed with DCM (50 mL) and ether (50 mL). The extracts were concentrated and the residue was dissolved in acetone (1.5 mL) and water (0.3 mL). *N*-Methylmorpholine *N*-oxide (34 mg, 0.29 mmol) and osmium(IV) oxide (1 crystal, cat.) were added at room temperature and the solution stirred for 16 h. Saturated aqueous sodium sulfite (4 mL) was added and the mixture was stirred for 1 h before being extracted with ether (3 × 5 mL). The organic extracts were washed with brine (15 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (10 : 1, light petroleum–ether) of the residue gave the *title compound* **71** as a colourless oil (61 mg, 73%), R_f = 0.8 (10 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +4 (*c* 1.7, $CHCl_3$) (Found: M^+ + 1, 365.2873. $C_{22}H_{41}O_2Si$ requires *M*, 365.2870); ν_{max}/cm^{-1} 2928, 2855, 1589, 1462, 1362, 1257, 1098, 1028, 836 and 775; δ_H (300 MHz, $CDCl_3$) 0.08 (6 H, s, 2 × $SiCH_3$), 0.91 (3 H, d, *J* 7, 2-CH_3), 0.93 [9 H, s, $SiC(CH_3)_3$], 0.97 (3 H, d, *J* 7, 6-CH_3), 1.10–1.55 (6 H, m, 3-H_2, 4-H_2 and 5-H_2), 1.61 (1 H, m, 2-H), 1.80 (1 H, m, 6-H), 3.26 (1 H, dd, *J* 9 and 7, 1-H), 3.34 (1 H, dd, *J* 9 and 6, 1-H′), 3.37 (1 H, dd, *J* 10 and 6, 7-H), 3.45 (1 H, dd, *J* 10 and 6, 7-H′), 4.55 (2 H, s, OCH_2Ph) and 7.35 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.1, 17.1, 17.5, 18.6, 24.6, 26.2, 33.7, 34.3, 36.0, 68.7, 73.2, 76.3, 127.7, 127.8 and 128.6; *m*/*z* (CI) 382 (M^+ + 18, 54%), 366 (30), 365 (M^+ + 1, 22), 217 (38), 132 (52) and 108 (100).

Phenyl chlorothionoformate (65 μL, 0.473 mmol) was added to the alcohol **75** (150 mg, 0.394 mmol) and pyridine (127 μL, 1.576 mmol) in DCM (1.3 mL) at room temperature and the solution stirred at for 16 h. Water (2 mL) and ethyl acetate (2 mL) were added and the organic phase was washed with saturated aqueous sodium hydrogen carbonate (4 mL) and brine (2 mL) then dried ($MgSO_4$). After concentration under reduced pressure, the residue was dissolved in toluene (8 mL). AIBN (cat.) and tributyltin hydride (0.38 mL) were added at room temperature and the solution was then heated under reflux for 16 h. After concentration under reduced pressure, chromatography (30 : 1, light petroleum–ether, eluting with 1% TEA by volume) of the residue gave the title compound **71** as a colourless oil (98 mg, 74%), R_f = 0.8 (10 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +4 (*c* 1.5, $CHCl_3$) (Found: M^+ + 1, 365.2871. $C_{22}H_{41}O_2Si$ requires *M*, 365.2870) with spectroscopic data identical with those of the sample prepared from the toluene *p*-sulfonate **70**.

(*S*)-Dimethyl 4-benzyloxy-3-methyl-2-oxobutylphosphonate 73.[18] ^{n}Butyllithium (12.33 mL, 1.7 M hexanes, 20.96 mmol) was added to dimethyl methylphosphonate (2.92 g, 23.56 mmol) in THF (48 mL) at −78 °C and the solution stirred at this temperature for 20 min. Methyl (*S*)-3-benzyloxy-2-methylpropanoate (2.45 g, 11.78 mmol) in THF (4 mL) was added and the solution was stirred at −78 °C for 15 min and then allowed to warm to room temperature and stirred for 1 h. Saturated aqueous oxalic acid (25 mL) and ether (50 mL) were added and the organic layer was washed with brine (50 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (ether) of the residue gave the *title compound* **73** as a colourless oil (3.11 g, 88%), R_f = 0.2 (ether) (Found: M^+, 300.1113. $C_{14}H_{21}O_5P$ requires *M*, 300.1121); ν_{max}/cm^{-1} 2955, 2855, 1713, 1454, 1366, 1259, 1185, 1032, 877, 810 and 742; δ_H (300 MHz, $CDCl_3$) 1.13 (3 H, d, *J* 7, 3-CH_3), 3.12 (1 H, m, 3-H), 3.13 (1 H, dd, *J* 22 and 14, 1-H), 3.30 (1 H, dd, *J* 22.5 and 14, 1-H′), 3.56 (1 H, dd, *J* 9 and 6, 4-H), 3.61 (1 H, dd, *J* 9 and 8, 4-H′), 3.77 and 3.81 (each 3 H, d, *J* 5, OCH_3), 4.52 (2 H, s, OCH_2Ph) and 7.34 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 13.3, 40.4, 42.1, 47.4, 53.2, 72.6, 73.5, 127.9, 128.0, 128.7, 138.1 and 205.0; *m*/*z* (CI) 318 (M^+ + 18, 34%) and 301 (M^+ + 1, 100).

(4*E*,2*S*,6*S*)-1-Benzyloxy-7-*tert*-butyldimethylsilyloxy-2,6-dimethylhept-4-en-3-one 74.[18] The ketophosphonate **73** (207 mg, 0.69 mmol) and barium hydroxide hexahydrate (activated by heating at 110 °C for 2 h; 178 mg, 0.55 mmol) in THF (4 mL) were stirred at room temperature for 30 min. (*R*)-3-*tert*-Butyldimethylsilyloxy-2-methylpropanal **(*R*)-72** (130 mg, 0.69 mmol) in THF (2 mL) and water (0.05 mL) was added and the solution was stirred for 16 h. DCM (60 mL) was added and the mixture filtered through celite® before being washed with saturated aqueous sodium hydrogen carbonate (50 mL) and brine (50 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (5 : 1, light petroleum–ether) of the residue gave the title compound **74** as a pale yellow oil (217 mg, 84%), R_f = 0.3 (5 : 1, light petroleum–ether) (Found: M^+ + 1, 377.2502. $C_{22}H_{37}O_3Si$ requires *M*, 377.2506); ν_{max}/cm^{-1} 2930, 2857, 1695, 1671, 1627, 1455, 1362, 1254, 1099, 838 and 777; δ_H (300 MHz, $CDCl_3$) 0.08 (6 H, s, 2 × $SiCH_3$), 0.93 [9 H, s, $SiC(CH_3)_3$], 1.10 (3 H, d, *J* 6, 6-CH_3), 1.16 (3 H, d, *J* 7, 2-CH_3), 2.55 (1 H, m, 6-H), 3.19 (1 H, m, 2-H), 3.50 (1 H, dd, *J* 9 and 6, 1-H), 3.58 (2 H, d, *J* 6, 7-H_2), 3.75 (1 H, dd, *J* 9 and 7, 1-H′), 4.51 and 4.56 (each 1 H, d, *J* 12, OHC*H*Ph), 6.24 (1 H, d, *J* 16, 4-H), 6.90 (1 H, dd, *J* 16 and 7, 5-H) and 7.34 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.1, 14.4, 15.9, 18.5, 26.1, 39.7, 44.2, 67.2, 72.4, 73.5, 127.8, 128.6, 129.0, 138.5, 150.2 and 202.5; *m*/*z* (CI) 377 (M^+ + 1, 100%).

(2*S*,3*RS*,6*S*)-1-Benzyloxy-7-*tert*-butyldimethylsilyloxy-2,6-dimethylheptan-3-ol 75. Sodium borohydride (30 mg, 0.79 mmol) was added to the ketone **74** (30 mg, 0.079 mmol) in methanol (1 mL) at 0 °C over 5 min and the mixture allowed to warm to room temperature and then stirred for 2 h. After concentration under reduced pressure, chromatography (4 : 1, light petroleum–ether) afforded the *title compound* **75** as a colourless oil (21 mg, 70%), R_f = 0.3 (3 : 1, light petroleum–ether) (Found: M^+ + 1, 381.2818. $C_{22}H_{41}O_3Si$ requires *M*, 381.2819); ν_{max}/cm^{-1} 2954, 2929, 2856, 1461, 1362, 1253, 1093, 837, 775 and 736; δ_H (300 MHz, $CDCl_3$) −0.04 (6 H, s, 2 × $SiCH_3$), 0.84 [15 H, m, $SiC(CH_3)_2$, 2-CH_3 and 6-CH_3], 1.00–1.62 (5 H, m, 4-H_2, 5-H_2 and 6-H), 1.80 (1 H, m, 2-H), 2.53 (0.5 H, d, *J* 4, OH), 3.20–3.60 (4.5 H, m, 1-H_2, 3-H and 7-H_2), 3.65 (0.5 H, m, 3-H), 4.45 (2 H, s, OCH_2Ph) and 7.24 (5 H, m, ArH); *m*/*z* (CI) 381 (M^+ + 1, 100%).

(4*E*,2*S*,6*S*)- and (4*E*,2*S*,6*R*)-1-Benzyloxy-7-*tert*-butyldimethylsilyloxy-2,6-dimethylhept-4-en-3-one 74 and 76. A solution of the ketophosphonate **73** (750 mg, 2.50 mmol) and barium hydroxide hexahydrate (activated by heating to 110 °C for 2 h) (1.18 g, 3.75 mmol) in THF (20 mL) was stirred at room temperature for 30 min. Racemic 3-*tert*-butyldimethylsilyloxy-2-methylpropanal (±)-**72** (505 mg, 2.50 mmol) in THF (10 mL) and water (0.75 mL) was added and the mixture stirred at room temperature for 16 h. DCM (100 mL) was added and the mixture filtered through celite® before being washed with saturated aqueous sodium hydrogen carbonate (100 mL) and brine (100 mL) then dried ($MgSO_4$). The organic layer was concentrated under reduced pressure and chromatography (5 : 1, light petroleum–ether) of the residue gave a mixture of the title compound **74** and **76** as a pale yellow oil (771 mg, 82%) as a 50 : 50 mixture of epimers (^1H and ^{13}C NMR), R_f = 0.3 (5 : 1, light petroleum–ether); δ_H (300 MHz, $CDCl_3$) both epimers 0.08 (6 H, s, 2 × $SiCH_3$), 0.93 [9 H, s, $SiC(CH_3)_3$], 1.09 and 1.10 (each 1.5 H, d, *J* 6, 6-CH_3), 1.16 (3 H, d, *J* 7, 2-CH_3), 2.55 (1 H, m, 6-H), 3.19 (1 H, m, 2-H), 3.50 (1 H, dd, *J* 9 and 6, 1-H), 3.58 (2 H, d, *J* 6, 7-H_2), 3.75 (1 H, dd, *J* 9 and 7, 1-H′), 4.51 and 4.56 (each 1 H, d, *J* 12, OHC*H*Ph), 6.24 (1 H, d, *J* 16, 4-H), 6.88 and 6.90 (each 0.5 H, dd, *J* 16 and 7, 5-H) and 7.34 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) both epimers −5.1, 14.4, 15.9(2), 18.5, 26.1, 39.7, 44.2, 44.3, 67.2, 72.4, 73.5, 127.8, 128.6, 129.0(2), 138.5, 150.1, 150.2 and 202.5.

(2*S*,6*R*)- and (2*R*,6*R*)-7-Benzyloxy-1-*tert*-butyldimethylsilyloxy-2,6-dimethylhexane 71 and 77. Sodium borohydride (60 mg, 1.58 mmol) was added to a mixture of the ketones **74** and **76** (60 mg, 0.158 mmol) in methanol (2 mL) at 0 °C and the mixture allowed to warm to room temperature then stirred for 2 h. After concentration under reduced pressure, chromatography (4 : 1, light petroleum–ether) of the residue gave the corresponding 2,6-dimethylheptan-3-ol as a colourless oil (40 mg, 68%), a mixture of diastereoisomers, R_f = 0.3 (3 : 1, light petroleum–ether).

Phenyl chlorothionoformate (65 μL, 0.473 mmol) was added to this alcohol (150 mg, 0.394 mmol) and pyridine (127 μL, 1.576 mmol) in DCM (1.3 mL) at room temperature and the solution stirred at room temperature for 16 h. Water (2 mL) and ethyl acetate (2 mL) were added and the organic phase washed with saturated aqueous sodium hydrogen carbonate (4 mL) and brine (2 mL) then dried ($MgSO_4$). The organic phase was then concentrated under reduced pressure to leave a residue that was dissolved in toluene (8 mL). AIBN (cat) and tributyltin hydride (0.38 mL) were added at room temperature and the solution heated under reflux for 16 h. After concentration under reduced pressure, chromatography (30 : 1, light petroleum–ether containing 1% Et_3N) gave a

mixture of the title compounds **71** and **77** as a colourless oil (98 mg, 78%), a 50 : 50 mixture of 2-epimers (^{1}H and ^{13}C NMR), R_f = 0.8 (10 : 1, light petroleum–ether); δ_H (300 MHz, $CDCl_3$) both epimers 0.08 (6 H, s, 2 × $SiCH_3$), 0.91 (3 H, d, *J* 7, 2-CH_3), 0.93 [9 H, s, $SiC(CH_3)_3$], 0.98 and 0.99 (each 1.5 H, d, *J* 7, 6-CH_3), 1.00–1.90 (8 H, m, 2-H, 3-H_2, 4-H_2, 5-H_2 and 6-H), 3.28 (1 H, dd, *J* 9 and 7, 1-H), 3.37 and 3.38 (each 0.5 H, dd, *J* 9 and 6, 1-H′), 3.40 (1 H, dd, *J* 10 and 6, 7-H), 3.48 and 3.49 (each 0.5 H, dd, *J* 10 and 6, 7-H′), 4.55 (2 H, s, OCH_2Ph) and 7.35 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) both epimers −5.1, 17.0, 17.4, 17.8, 18.6, 24.6, 26.3, 27.1, 28.1, 33.7, 34.2, 34.3, 36.0, 68.7, 73.2, 76.3(2), 127.7, 127.8, 128.6 and 139.1.

(2*S*,6*R*)-7-Benzyloxy-2,6-dimethylheptan-1-ol 78. Tetra-*n*-butylammonium fluoride (1 M in THF, 2.47 mL, 2.47 mmol) was added to the silyl ether **71** (600 mg, 1.47 mmol) in THF (2 mL) and the solution was stirred at room temperature for 16 h. Water (4 mL) was added and the mixture was stirred for 1 h then extracted with ether (3 × 8 mL). The organic extracts were washed with brine (20 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (3 : 1, light petroleum–ether) of the residue gave the *title compound* **78** as a colourless oil (403 mg, 98%), R_f = 0.3 (1 : 1, light petroleum–ether); $[\alpha]_D^{20}$ +2 (*c* 2.2, $CHCl_3$) (Found: M^+ + H, 251.2001. $C_{16}H_{27}O_2$ requires *M*, 251.2006); ν_{max}/cm^{-1} 3385, 2928, 2857, 1454, 1364, 1100, 1030 and 736; δ_H (300 MHz, $CDCl_3$) 0.95 (3 H, d, *J* 7, 6-CH_3), 0.98 (3 H, d, *J* 7, 2-CH_3), 1.00–1.55 (6 H, m, 3-H_2, 4-H_2 and 5-H_2), 1.64 (1 H, m, 6-H), 1.82 (1 H, m, 2-H), 1.95 (1 H, br. s, OH), 3.28 (1 H, dd, *J* 9 and 7, 7-H), 3.37 (1 H, dd, *J* 9 and 6, 7-H′), 3.44 (1 H, dd, *J* 11 and 7, 1-H), 3.52 (1 H, dd, *J*, 11 and 6, 1-H′), 4.54 (2 H, s, OCH_2Ph) and 7.35 (5 H, m, ArH); *m*/*z* (CI) 251 (M^+ + 1, 8%), 107 (26) and 91 (100). Minor splitting of the dds at *δ*3.37 and *δ*3.52 indicated that *ca.* 15% of the 2-epimer was present, *cf.* ^{1}H NMR data for **71** and **77**. This was not observed for any other compound along this series, *i.e.* intermediates **79–84**.

(2*R*,6*S*)-7-Iodo-1-benzyloxy-2,6-dimethylheptane 79. Imidazole (259 mg, 3.80 mmol), triphenylphosphine (496 mg, 1.90 mmol) and iodine (500 mg, 1.98 mmol) were added to the alcohol **78** (190 mg, 0.76 mmol) in THF (8 mL) at room temperature and the solution stirred at room temperature for 2 h. Saturated aqueous sodium thiosulfate (10 mL) was added and the mixture stirred until the colour of iodine disappeared. Ether was added, the layers were separated and the aqueous phase was extracted with ether (3 × 10 mL). The organic extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (15 : 1, light petroleum–ether) of the residue gave the *title compound* **79** as a colourless oil (257 mg, 94%), R_f = 0.8 (15 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +3 (*c* 2.8, $CHCl_3$) (Found: M^+ + NH_4, 378.1285. $C_{16}H_{29}ONI$ requires *M*, 378.1288); ν_{max}/cm^{-1} 2956, 2927, 2853, 1453, 1376, 1363, 1256, 1195, 1099, 1028 and 735; δ_H (300 MHz, $CDCl_3$) 0.99 (3 H, d, *J* 7, 2-CH_3), 1.02 (3 H, d, *J* 6, 6-CH_3), 1.10–1.60 (7 H, m, 3-H_2, 4-H_2, 5-H_2 and 6-H), 1.83 (1 H, m, 2-H), 3.20 (1 H, dd, *J* 10 and 6, 7-H), 3.29 (2 H, m, 7-H′ and 1-H), 3.37 (1 H, dd, *J* 9 and 6, 1-H′), 4.57 (2 H, s, OCH_2Ph) and 7.36 (5 H, m, ArH); δ_C (300 MHz, $CDCl_3$) 17.5, 18.3, 21.0, 24.5, 33.7, 33.9, 35.0, 37.0, 73.3, 76.2, 127.7, 127.8, 128.6 and 139.1; *m*/*z* (CI) 378 (M^+ + 18, 100%), 361 (M^+ + 1, 8) and 108 (56).

(2*R*,6*S*)-7-*tert*-Butyldimethylsilyloxy-2,6-dimethylheptan-1-ol 80. Palladium (10% on carbon, 70 mg, 0.066 mmol) was added to the benzyl ether **71** (155 mg, 0.46 mmol) in ethanol (5 mL) at room temperature. The mixture was stirred under an atmosphere of hydrogen for 1 h then filtered through celite®. The filtrate was washed with DCM (50 mL) and concentrated under reduced pressure to afford the *title compound* **80** as a colourless oil (123 mg, 98%), R_f = 0.8 (15 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +5 (*c* 1.4, $CHCl_3$) (Found: M^+ + 1, 275.2406. $C_{15}H_{35}O_2Si$ requires *M*, 275.2401); ν_{max}/cm^{-1} 3351, 2954, 2928, 2857, 1463, 1388, 1254, 1098, 1038, 837 and 775; δ_H (300 MHz, $CDCl_3$) 0.03 (6 H, s, 2 × $SiCH_3$), 0.85 (3 H, d, *J* 7, 6-CH_3), 0.89 [9 H, s, $SiC(CH_3)_3$], 0.91 (3 H, d, *J* 7, 2-CH_3), 1.06 (2 H, m), 1.15–1.50 and 1.60 (each 3 H, m), 3.34 (1 H, dd, *J* 10 and 7), 3.39 (1 H, dd, *J* 10.5 and 6.5) and 3.43 and 3.49 (each 1 H, dd, *J* 10 and 6); δ_C (75 MHz, $CDCl_3$) −5.1, 16.9, 17.0, 18.6, 24.6, 26.2, 33.6, 33.7, 33.7, 36.0, 68.5 and 68.6; *m*/*z* (CI) 292 (M^+ + 18, 2%), 275 (M^+ + 1, 100).

(2*R*,6*S*)-1-Iodo-7-*tert*-butyldimethylsilyloxy-2,6-dimethylheptane 81. Imidazole (149 mg, 2.19 mmol), triphenylphosphine (285 mg, 1.09 mmol) and iodine (289 mg, 1.14 mmol) were added to the alcohol **80** (120 mg, 0.44 mmol) in THF (4 mL) at room temperature and the solution stirred at room temperature for 2 h. Saturated aqueous sodium thiosulfate (5 mL) was added and the mixture stirred until the colour of iodine disappeared. Ether (10 mL) was added and the aqueous phase was extracted with ether (3 × 5 mL). The organic extracts were washed with brine, dried ($MgSO_4$), concentrated under reduced pressure. Chromatography (15 : 1, light petroleum–ether) of the residue gave the *title compound* **81** as a colourless oil (178 mg, 97%), R_f = 0.8 (15 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +4 (*c* 0.9, $CHCl_3$) (Found: M^+ + 1, 385.1418. $C_{15}H_{34}OSiI$ requires *M*, 385.1418); ν_{max}/cm^{-1} 2954, 2928, 2855, 1462, 1377, 1254, 1193, 1094, 837 and 775; δ_H (300 MHz, $CDCl_3$) 0.08 (6 H, s, 2 × $SiCH_3$), 0.90 (3 H, *J* 7, 2-CH_3), 0.93 [9 H, $SiC(CH_3)_3$], 1.01 (3 H, d, *J* 7, 6-CH_3), 1.00–1.55 (7 H, m, 2-H, 3-H_2, 4-H_2 and 5-H_2), 1.62 (1 H, m, 6-H), 3.19 (1 H, dd, *J* 10 and 6, 1-H), 3.27 (1 H, dd, *J* 10 and 5, 1-H′), 3.40 (1 H, dd, *J* 10 and 7, 7-H) and 3.47 (1 H, dd, *J* 10 and 6, 7-H′); δ_C (75 MHz, $CDCl_3$) −5.1, 17.0, 18.2, 18.6, 20.9, 24.6, 26.3, 33.4, 35.0, 35.9, 37.0 and 68.6; *m*/*z* (CI) 402 (M^+ + 18, 24%), 385 (M^+ + 1, 100) and 132 (80). Slight splitting of the dd at *δ*3.27 indicated a small amount, <5% of an epimer was present.

2-[(2*R*,6*S*)-7-*tert*-Butyldimethylsilyloxy-2,6-dimethylhept-1-yl]-1,3-dithiane 82. ^{n}Butyllithium (1.7 M in hexanes, 10.4 mL, 0.63 mmol) was added dropwise to recrystallised (methanol) dithiane (87 mg, 0.78 mmol), in THF (1 mL) at −20 °C. The solution was stirred at −20 °C for 1 h then allowed to warm to 0 °C. Iodide 81 (120 mg, 0.31 mmol) in THF (1 mL) was added and the mixture was stirred at 0 °C for 16 h. Water (2 mL) and ether (2 mL) were added and the aqueous phase was extracted with ether (3 × 3 mL). The organic extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (20 : 1, light petroleum–ether) of

the residue gave the *title compound* **82** as a colourless oil (100 mg, 89%), R_f = 0.8 (10 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +7 (*c* 2.3, $CHCl_3$) (Found: M^+ + 1, 377.2360. $C_{19}H_{41}OS_2Si$ requires *M*, 377.2363); ν_{max}/cm^{-1} 2952, 2928, 2855, 1592, 1462, 1252, 1094, 836 and 774; δ_H (300 MHz, $CDCl_3$) 0.06 (6 H, s, 2 × $SiCH_3$), 0.89 (3 H, d, *J* 7, 2′-CH_3), 0.95 [12 H, m, $SiC(CH_3)_3$ and 6′-CH_3], 1.00–2.00 (11 H, m, 5-H_2, 2′-H, 3′-H_2, 4′-H_2, 5′-H_2 and 1′-H_2), 2.13 (1 H, m, 6′-H), 2.87 (4 H, m, 4-CH_2 and 6-CH_2), 3.38 (1 H, dd, *J* 10 and 7, 7′-H), 3.47 (1 H, dd, *J* 10 and 6, 7′-H′) and 4.13 (1 H, dd, *J* 8 and 6, 2-H); δ_C (75 MHz, $CDCl_3$) −5.1, 17.1, 18.6, 19.7, 24.4, 26.2, 26.4, 29.9, 30.7, 30.9, 33.6, 36.0, 37.4, 42.8, 45.8 and 68.6; *m*/*z* (CI) 394 (M^+ + 18, 32%), 377 (M^+ + 1, 100), 245 (40) and 132 (48). Less than 5% of any epimer was present, *cf.* the dd at δ3.47.

(2*R*,6*S*,10*R*,14*S*)-1-Benzyloxy-15-*tert*-butyldimethylsilyloxy-8,8-(1,5-dithiatrimethylene)-2,6,10,14-tetramethylpentadecane 83. ^{n}Butyllithium (1.7 M in hexanes, 0.19 mL, 0.113 mmol) was added dropwise to the 1,3-dithiane **82** (43 mg, 0.119 mmol), in THF (1 mL) and HMPA (0.1 mL) at −78 °C. After 30 min, the iodide **79** in THF (0.5 mL) was added and the mixture was stirred at −78 °C for 1 h. Saturated aqueous ammonium chloride (4 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 5 mL). The organic extracts were washed with brine (15 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (30 : 1, light petroleum–ether) of the residue gave the *title compound* **83** as a colourless oil (60 mg, 88%), R_f = 0.7 (10 : 1, light petroleum–ether); $[\alpha]_D^{20}$ +5 (*c* 1.5, $CHCl_3$) (Found: M^+ + H, 610.4263. $C_{34}{}^{13}CH_{65}O_2S_2Si$ requires *M*, 609.4258); ν_{max}/cm^{-1} 2927, 2854, 1598, 1460, 1297, 1251, 1210, 1097, 985, 836, 775 and 738; δ_H (300 MHz, $CDCl_3$) 0.07 (6 H, s, 2 × $SiCH_3$), 0.91 (3 H, d, *J* 7, 10-CH_3), 0.93 [9 H, s, $SiC(CH_3)_3$], 0.97 (3 H, d, *J* 7, 6-CH_3), 1.05 (6 H, d, *J* 6, 2-CH_3 and 14-CH_3), 1.00–2.00 (22 H, m), 2.84 (4 H, t, *J* 6, 2′-H_2 and 4′-H_2), 3.27 (1 H, dd, *J* 9 and 7, 15-H), 3.36 (1 H, dd, *J* 9 and 6, 15-H′), 3.39 (1 H, dd, *J* 10.5 and 6.5, 1-H), 3.48 (1 H, dd, *J* 9 and 6, 1-H′), 4.54 (2 H, s, OCH_2Ph) and 7.34 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.0, 17.1, 17.4, 17.5, 18.6, 22.3, 22.4, 24.6, 24.7, 25.4, 26.3, 26.9, 30.0, 33.7, 33.8, 34.2, 36.0, 39.7, 39.8, 47.2, 55.4, 68.7, 73.2, 76.3, 127.7, 127.8, 128.6 and 139.1; *m*/*z* (CI) 610 (M^+ + 2, 12%), 377 (12), 351 (16) and 180 (100).

(2*R*,6*R*,10*S*,14*S*)-15-*tert*-Butyldimethylsilyloxy-2,6,10,14-tetramethylpentadecan-1-ol 84. Freshly activated (by washing with deionised water under an inert atmosphere) W-2 RANEY® nickel (500 mg, 8.5 mmol) was added to the dithiane **83** (20 mg, 0.033 mmol) in THF (2.5 mL) and the suspension was stirred under reflux for 16 h. After cooling to room temperature, the mixture was filtered through celite® to afford the *title compound* **84** as a colourless oil (13 mg, 95%), R_f = 0.8 (10 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +4 (*c* 1.0, $CHCl_3$) (Found: M^+ + 1, 415.3966. $C_{25}H_{55}O_2Si$ requires *M*, 415.3966); ν_{max}/cm^{-1} 2954, 2927, 2856, 1463, 1377, 1257, 1095, 1034, 836 and 775; δ_H (300 MHz, $CDCl_3$) 0.07 (6 H, s, 2 × $SiCH_3$), 0.80 (6 H, d, *J* 6, 6-CH_3 and 10-CH_3), 0.93 [12 H, m, $SiC(CH_3)_3$ and 14-CH_3], 0.96 (3 H, d, *J* 7, 2-CH_3), 1.00–1.75 (22 H, m), 3.38 (1 H, dd, *J* 10 and 7, 15-H), 3.46 (2 H, m, 1-H and 15-H′) and 3.55 (1 H, dd, *J* 11 and 6, 1-H′); δ_C (75 MHz, $CDCl_3$) −5.1, 1.30, 16.9, 17.1, 18.6, 20.0, 20.0, 24.7, 26.2, 30.0(2), 33.7, 33.8, 36.0, 37.6 and 68.7; *m*/*z* (CI) 432 (M^+ + 18, 2%), 415 (M^+ + 1, 100), 132 (46) and 92 (54).

(2*R*,4*SR*,6*R*)-7-Benzyloxy-1-*tert*-butyldimethylsilyloxy-4,6-dimethylheptan-2-ols 87. Following the standard procedure, sodium acetate (302 mg, 2.2 mmol) in water (0.8 mL), the alkene **31f** (70 mg, 0.19 mmol) and toluene *p*-sulfonylhydrazine (207 mg, 1.1 mmol) in DME (3 mL), after heating under reflux for 16 h and chromatography (10 : 1, light petroleum–ether) gave the *title compounds* **87** as a colourless oil (48 mg, 82%), a 2 : 1 mixture of epimers (^{1}H and ^{13}C NMR), R_f = 0.48 (2 : 1, light petroleum–ether); ν_{max}/cm^{-1} 3471, 3031, 2935, 2859, 1462, 1255, 1103, 840, 779 and 697; δ_H (300 MHz, $CDCl_3$) major 4-epimer 0.12 (6 H, s, 2 × $SiCH_3$), 0.83 [9 H, s, $SiC(CH_3)_3$], 0.85 (3 H, d, *J* 7, 4-CH_3), 0.87 (3 H, d, *J* 7, 6-CH_3), 1.10–2.00 (6 H, m, 3-H_2, 4-H, 5-H_2 and 6-H), 2.50 (1 H, br. s, OH), 3.28 (1 H, dd, *J* 9 and 7, 7-H), 3.35 (1 H, dd, *J* 9 and 7, 7-H′), 3.39 (1 H, dd, *J* 10 and 7, 1-H), 3.60 (1 H, dd, *J* 10 and 4, 1-H′), 3.80 (1 H, m, 2-H), 4.58 (2 H, s, OCH_2Ph) and 7.35 (5 H, m, ArH); minor 4-epimer 2.41 (1 H, br. s, OH), 3.23 (1 H, dd, *J* 9 and 7, 7-H), 3.40 (1 H, dd, *J* 10 and 7, 1-H) and 3.62 (1 H, dd, *J* 10 and 4, 1-H′); δ_C (75 MHz, $CDCl_3$) major 4-epimer −5.1, 17.1, 18.3, 20.5, 26.3, 27.1, 31.3, 41.0, 42.6, 67.9, 70.3, 73.4, 76.5, 127.8, 127.9, 128.7 and 139.1; minor 4-epimer 18.7, 26.9, 31.1, 40.0 and 69.9; *m*/*z* (CI) 398 (M^+ + 18, 3%), 381 M^+ + 1, 52), 108 (51) and 91 (100).

Palladium (11 mg, 10% on activated carbon, 0.01 mmol) was added to the alkene **31f** (20 mg, 0.053 mmol) in MeOH (1 mL) at room temperature. The mixture was stirred under an atmosphere of hydrogen for 1 h then filtered through celite. The filtrate was washed with DCM (5 mL) and concentrated under reduced pressure. Chromatography (10 : 1, light petroleum–ether) also gave a 2 : 1 mixture of the 4-epimers of the title compound **87** (18 mg, 90%) as a colourless oil.

(3*E*,2*R*,6*S*)-1-Benzyloxy-6-tri-isopropylsilyloxy-2,4-dimethylnon-3-ene 88. 2,6-Lutidine (0.76 mL, 6.51 mmol) and tri-isopropylsilyl trifluoromethanesulfonate (0.70 mL, 2.60 mmol) were added to the alcohol **31d** (600 mg, 2.17 mmol) in DCM (5 mL) at 0 °C. The solution was allowed to warm to ambient temperature and was stirred for 16 h. Saturated aqueous ammonium chloride (20 mL) was added and the mixture was extracted with DCM (3 × 20 mL). The organic extracts were washed with brine (20 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (10 : 1, light petroleum–ether) of the residue gave the *title compound* **88** as a colourless oil (834 mg, 89%), R_f = 0.73 (3 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −6.4 (*c* 0.3, $CHCl_3$) (Found: M^+ + NH_4, 450.3766. $C_{27}H_{52}O_2NSi$ requires *M*, 450.3762); ν_{max}/cm^{-1} 2958, 2941, 2863, 1459, 1366, 1096, 1043, 883, 732 and 677; δ_H (500 MHz, $CDCl_3$) 0.79 (3 H, t, *J* 7, 9-H_3), 0.89 (3 H, d, *J* 7, 2-CH_3), 0.99 [21 H, m, 3 × $SiCH(CH_3)_2$], 1.25–1.39 (4 H, m, 7-H_2 and 8-H_2), 1.57 (3 H, d, *J* 1, 4-CH_3), 2.04 (1 H, dd, *J* 13 and 9, 5-H), 2.16 (1 H, dd, *J* 13 and 5, 5-H′), 2.63 (1 H, m, 2-H), 3.13 (1 H, dd, *J* 9 and 8, 1-H), 3.23 (1 H, dd, *J* 9 and 6, 1-H′), 3.87 (1 H, m, 6-H), 4.41 and 4.44 (each 1 H, d, *J* 12, OHC*H*Ph), 4.89 (1 H, d, *J* 9,

3-H) and 7.26 (5 H, m, ArH); δ_C (125 MHz, $CDCl_3$) 12.7, 14.4, 16.9, 17.7, 17.8, 18.2, 33.0, 38.4, 47.6, 70.8, 72.9, 75.3, 127.4, 127.5, 128.3, 130.1, 133.0 and 138.7; *m*/*z* (ES+) 455 (M^+ + 23, 95%), 450 (M^+ + 18, 100%) and 433 (M^+ + 1, 3).

(3*E*,2*R*,6*S*)-6-Tri-isopropylsilyloxy-2,4-dimethylnon-3-en-1-ol 89. Lithium metal (88 mg, 12.50 mmol) was added in small portions to naphthalene (2.13 g, 16.64 mmol) in THF (30 mL). The reaction mixture was stirred at room temperature under an argon atmosphere until the lithium metal had completely dissolved. The resulting dark green solution of lithium naphthalenide was then cooled to −25 °C and the alkene **88** (900 mg, 2.08 mmol) in THF (15 mL) was added dropwise. The mixture was stirred at −25 °C for 2 h and then saturated aqueous ammonium chloride (30 mL) and water (30 mL) were added. The mixture was extracted with ether (3 × 40 mL) and the organic extracts were washed with water and brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (4 : 1, light petroleum–ether) of the residue gave the *title compound* **89** (642 mg, 90% yield) as a light yellow oil, R_f = 0.32 (2 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −3.0 (*c* 0.3, $CHCl_3$) (Found: M^+ + NH_4, 360.3301. $C_{20}H_{46}O_2NSi$ requires *M*, 360.3292); ν_{max}/cm^{-1} 3339, 2956, 2946, 2868, 1462, 1383, 1108, 1040, 883 and 677; δ_H (500 MHz, $CDCl_3$) 0.80 (3 H, t, *J* 6, 9-H_3), 0.85 (3 H, d, *J* 7, 2-CH_3), 0.99 [21 H, m, 3 × $SiCH(CH_3)_2$], 1.28–1.39 (4 H, m, 7-H_2 and 8-H_2), 1.61 (3 H, d *J* 0.5, 4-CH_3), 2.09 (1 H, dd, *J* 13 and 8, 5-H), 2.19 (1 H, dd, *J* 13 and 5, 5-H′), 2.55 (1 H, m, 2-H), 3.25 (1 H, t, *J* 9, 1-H), 3.39 (1 H, m, 1-H′), 3.90 (1 H, m, 6-H) and 4.85 (1 H, d, *J* 9, 3-H); δ_C (125 MHz, $CDCl_3$) 12.7, 14.4, 17.0, 17.1, 17.8, 18.3, 35.4, 38.5, 47.6, 67.9, 70.7, 129.7 and 135.2; *m*/*z* (ES+) 365 (M^+ + 23, 100%) and 343 (M^+ + 1, 10). No minor isomer detected, *i.e.* <2%.

(3*E*,2*R*,6*S*)-2,4-Dimethylnon-3-ene-1,6-diol 90. The alcohol **31d** (200 mg, 0.72 mmol) in ethanol (8 mL) was added to a 50 mL, three-necked flask equipped with a stirrer, Dewar condenser, and an ammonia inlet. The flask was cooled to −78 °C and ammonia was condensed until a final volume of 15 mL was achieved. Small pieces of sodium wire were added to the solution until a characteristic deep blue colour persisted. Solid ammonium chloride was added in portions until the mixture was white. The mixture was allowed to warm to room temperature over a period of 1 h and ethyl acetate (30 mL) was added. Water (30 mL) was added and the aqueous layer extracted with ethyl acetate (3 × 30 mL). The organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography (1 : 1, light petroleum–ether) of the residue gave the *title compound* **90** as a colourless oil (101 mg, 75%), R_f = 0.17 (1 : 2, light petroleum–ether), $[\alpha]_D^{20}$ +2.7 (*c* 0.3, $CHCl_3$) (Found: M^+ + Na, 209.1505. $C_{11}H_{22}O_2Na$ requires *M*, 209.1512); ν_{max}/cm^{-1} 3338, 2957, 2929, 2872, 1455, 1124, 1073, 1036 and 830; δ_H (500 MHz, $CDCl_3$) 0.83 (3 H, d, *J* 7, 2-CH_3), 0.85 (3 H, t, *J* 7, 9-H_3), 1.28–1.43 (4 H, m, 7-H_2 and 8-H_2), 1.59 (3 H, s, 4-CH_3), 1.90 (1 H, dd, *J* 13 and 10, 5-H), 2.09 (1 H, d, *J* 13, 5-H′), 2.55 (1 H, m, 2-H), 2.82 (1 H, br. s, 1-OH), 3.15 (1 H, br. s, 6-OH), 3.17 (1 H, t, *J* 10, 1-H), 3.42 (1 H, m, 1-H′), 3.61 (1 H, m, 6-H) and 4.89 (1 H, d, *J* 10, 3-H); δ_C (125 MHz, $CDCl_3$) 14.1, 16.2, 16.8, 19.0, 34.2, 39.6, 48.3, 67.6, 67.8, 131.5 and 133.7; *m*/*z* (ES+) 209 (M^+ + 23, 100%). No minor isomer detected.

(6*E*,4*S*,8*R*)-9-Tri-isopropylsilyloxy-6,8-dimethylnon-6-en-4-ol 91. Imidazole (274 mg, 4.03 mmol) and tri-isopropylsilyl chloride (0.45 mL, 2.097 mmol) were added to the diol **90** (300 mg, 1.61 mmol) in DCM (8 mL) at 0 °C and the solution was stirred for 1 h at room temperature. Water was added (15 mL) and the mixture extracted using DCM (3 × 15 mL). The organic extracts were washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (10 : 1, light petroleum–ether) of the residue gave the *title compound* **91** as a colourless oil (495 mg, 90%), R_f = 0.70 (1 : 1, light petroleum–ether), $[\alpha]_D^{20}$ −6.3 (*c* 0.3, $CHCl_3$) (Found: M^+ + NH_4, 360.3294. $C_{20}H_{46}O_2NSi$ requires *M*, 360.3292); ν_{max}/cm^{-1} 3435, 2961, 2941, 2867, 1462, 1385, 1093, 882 and 787; δ_H (500 MHz, $CDCl_3$) 0.86 and 0.87 (each 3 H, d, *J* 7, 1-H_3 and 8-CH_3), 0.98 [21 H, m, 3 × $SiCH(CH_3)_2$], 1.25–1.45 (4 H, m, 2-H_2 and 3-H_2), 1.59 (3 H, s, 6-CH_3), 1.87 (1 H, br. s, 6-OH), 1.90 (1 H, dd, *J* 13 and 10, 5-H), 2.09 (1 H, dd, *J* 13 and 3, 5-H′), 2.53 (1 H, m, 8-H), 3.36 (1 H, dd, *J* 10 and 7, 9-H), 3.41 (1 H, dd, *J* 10 and 7, 9-H′), 3.56 (1 H, m, 4-H) and 4.96 (1 H, d, *J* 10, 7-H); δ_C (125 MHz, $CDCl_3$) 12.0, 14.2, 16.5, 17.1, 18.0, 19.0, 35.8, 39.0, 48.2, 67.7, 68.4, 132.1 and 132.4; *m*/*z* (ES+) 365 (M^+ + 23, 100%).

(2*R*,4*S*,6*S*)-6-Tri-isopropylsilyloxy-2,4-dimethylnonan-1-ol 96. To a steel screw-cap high-pressure bomb was added alcohol **89** (50 mg, 0.15 mmol) followed by [Rh(NBD)Diphos-4]BF_4 (5 mg, 0.0073 mmol, 5 mol%) and DCM (2.5 mL). The pressure gauge block was attached, and the bomb was flushed three times with hydrogen and then filled with hydrogen to a pressure of to 950 psi. After being stirred for 5 h at room temperature, the solution was filtered through silica gel and concentrated under reduced pressure. Chromatography (10 : 1, light petroleum–ether) of the residue gave the *title compound* **96** as a colourless oil (41 mg, 82%), R_f = 0.35 (2 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +4.8 (*c* 0.3, $CHCl_3$) (Found: M^+ + Na, 367.2987. $C_{20}H_{44}O_2NaSi$ requires *M*, 367.3003); ν_{max}/cm^{-1} 3340, 2956, 2868, 1462, 1380, 1126, 1089, 1040, 883, 718 and 675; δ_H (500 MHz, $CDCl_3$) 0.83 (3 H, t, *J* 7, 9-H_3), 0.83 (3 H, d, *J* 7, 4-CH_3), 0.85 (3 H, d, *J* 7, 2-CH_3), 0.89 (1 H, dd, *J* 14 and 7, 3-H), 0.99 (21 H, m, 3 × $SiCH(CH_3)_2$], 1.05 (1 H, m, 3-H′), 1.17 (2 H, m, 8-H_2), 1.26 (1 H, m, 7-H), 1.32–1.46 (3 H, m, 5-H_2 and 7-H′), 1.62–1.70 (2 H, m, 2-H and 4-H), 3.27 (1 H, dd, *J* 10 and 7, 1-H), 3.44 (1 H, dd, *J* 10 and 5, 1-H′) and 3.82 (1 H, m, 6-H); δ_C (125 MHz, $CDCl_3$) 12.9, 14.4, 17.4, 17.7, 18.2, 20.7, 26.4, 33.0, 40.3, 41.8, 44.2, 68.2 and 70.4; *m*/*z* (ES+) 367 (M^+ + 23, 100%).

(2*R*,4*S*,6*S*)- and (2*R*,4*R*,6*S*)-2,4-Dimethylnonane-1,6-diols 97 and 102. To a steel screw-cap high-pressure bomb was added diol **90** (70 mg, 0.37 mmol) and [Rh(NBD)Diphos-4]BF_4 (13 mg, 0.019 mmol, 5 mol%) and DCM (2.5 mL). The pressure gauge block was attached, and the bomb was flushed three times with hydrogen and then was filled with hydrogen to a pressure of to 950 psi. After being stirred for 5 h at room temperature, the solution was filtered through silica gel and concentrated under reduced pressure. Chromatography (5 : 1, light

petroleum–ether) of the residue gave the *title compound* **102** (7 mg, 10%) as a colourless oil, R_f = 0.19 (1 : 2, light petroleum–ether), $[\alpha]_D^{20}$ +4.8 (*c* 0.3, $CHCl_3$) (Found: $M^+ - H$, 187.1687. $C_{11}H_{23}O_2$ requires *M*, 187.1693); ν_{max}/cm^{-1} 3336, 2958, 2925, 2873, 1462, 1379, 1124 and 1037; δ_H (500 MHz, $CDCl_3$) 0.83 (6 H, d, *J* 7, 2-CH_3 and 4-CH_3), 0.86 (3 H, t, *J* 7, 9-H_3), 1.04–1.06 (2 H, m, 3-H_2), 1.26–1.43 (6 H, m, 5-H_2, 7-H_2 and 8-H_2), 1.65–1.70 (2 H, m, 2-H and 4-H), 3.37 (1 H, dd, *J* 10 and 6, 1-H), 3.40 (1 H, dd, *J* 10 and 6, 1-H′) and 3.65 (1 H, m, 6-H); δ_C (125 MHz, $CDCl_3$) 14.1, 16.2, 18.8, 20.4, 26.6, 33.2, 40.1, 46.1, 69.1 and 69.5; *m*/*z* (ES−) 188 (M^+, 14%) and 187 ($M^+ - 1$, 100). The second fraction was the *title compound* **97** (34 mg, 48%) as a colourless oil, R_f = 0.17 (1 : 2, light petroleum–ether), $[\alpha]_D^{20}$ +7.6 (*c* 0.2, $CHCl_3$) (Found: $M^+ - H$, 187.1687. $C_{11}H_{23}O_2$ requires *M*, 187.1693); ν_{max}/cm^{-1} 3339, 2957, 2923, 2872, 1461, 1378, 1123 and 1037; δ_H (500 MHz, $CDCl_3$) 0.84 (3 H, d, *J* 7, 2- or 4-CH_3), 0.85 (3 H, t, *J* 7, 9-H_3), 0.86 (3 H, d, *J* 7, 4- or 2-CH_3), 0.91 (1 H, m, 3-H), 1.01 (1 H, m, 3-H′), 1.24–1.39 (6 H, m, 5-H_2, 7-H_2, 8-H_2), 1.62–1.73 (2 H, m, 2-H and 4-H), 1.84 (1 H, br. s, OH), 2.10 (1 H, br. s, OH), 3.37 (1 H, dd, *J* 10 and 6, 1-H), 3.41 (1 H, dd, *J* 10 and 5, 1-H′) and 3.62 (1 H, m, 6-H); δ_C (125 MHz, $CDCl_3$) 14.1, 17.5, 18.9, 20.1, 26.7, 32.9, 40.7, 41.9, 44.8, 67.8 and 69.5; *m*/*z* (ES−) 188 (M^+, 14%) and 187 ($M^+ - 1$, 100).

Tetrabutylammonium fluoride (1.0 M in THF, 0.12 mL, 0.41 mmol) was added to the silyl ether **96** (70 mg, 0.20 mmol) in THF (1 mL) and the mixture left to stir at room temperature for 16 h. Water (2 mL) was added and the mixture stirred for a further 1 h. The mixture was then extracted with ether (3 × 3 mL) and the organic extracts washed with brine (5 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (1 : 2, light petroleum–ether to ether) of the residue gave the diol **97** as a colourless oil (35 mg, 91%).

(4*S*,6*R*,8*R*)- and (4*S*,6*S*,8*R*)-9-Tri-isopropylsilyloxy-6,8-dimethylnonan-4-ols 92 and 98. To a steel screw-cap high-pressure bomb was added alcohol **91** (50 mg, 0.15 mmol) and [Rh(NBD)Diphos-4]BF_4 (5 mg, 0.0073 mmol, 5 mol%) and DCM (2.5 mL). The pressure gauge block was attached, and the bomb was flushed three times with hydrogen and then was filled with hydrogen to a pressure of 950 psi. After being stirred for 5 h at room temperature, the solution was filtered through silica gel and concentrated under reduced pressure. Chromatography (10 : 1, light petroleum–ether) gave the *title compound* **98** (5 mg, 10%) as a colourless oil, R_f = 0.70 (1 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +7.6 (*c* 1.1, $CHCl_3$) (Found: M^+ + Na, 367.2999. $C_{20}H_{44}O_2NaSi$ requires *M*, 367.3003); ν_{max}/cm^{-1} 3351, 2967, 2925, 2867, 1462, 1381, 1257, 1103, 1017, 883 and 791; δ_H (500 MHz, $CDCl_3$) 0.84 and 0.85 (each 3 H, d, *J* 7, 6-CH_3 or 8-CH_3), 0.86 (3 H, t, *J* 7, 1-H_3), 0.88 (1 H, dd, *J* 14 and 7, 7-H), 0.99 [21 H, m, 3 × $SiCH(CH_3)_2$], 1.02 (1 H, m, 7-H′), 1.25–1.39 (6 H, m, 2-H_2, 3-H_2 and 5-H_2), 1.62–1.72 (2 H, m, 6-H and 8-H), 3.37 (1 H, dd, *J* 10 and 6, 9-H), 3.46 (1 H, dd, *J* 10 and 6, 9-H′) and 3.64 (1 H, m, 4-H); δ_C (125 MHz, $CDCl_3$) 12.0, 14.1, 17.5, 18.0, 18.9, 20.2, 26.6, 33.3, 40.6, 41.9, 44.8, 68.7 and 69.3; *m*/*z* (ES−) 367 (M^+ + Na, 100%). The more polar product was the *title compound* **92** (28 mg, 56%) as a colourless oil, R_f = 0.68 (1 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +7.8 (*c* 1.5, $CHCl_3$) (Found: M^+ + Na, 367.3011. $C_{20}H_{44}O_2NaSi$ requires *M*, 367.3003); ν_{max}/cm^{-1} 3346, 2956, 2927, 2867, 1462, 1382, 1103, 1068, 997, 882, 787 and 681; δ_H (500 MHz, $CDCl_3$) 0.80 (3 H, d, *J* 7, 8-CH_3), 0.81 (3 H, d, *J* 7, 6-CH_3), 0.85 (3 H, t, *J* 7, 1-H_3), 0.99 [21 H, m, 3 × $SiCH(CH_3)_2$], 1.02–1.10 (2 H, m, 7-H_2), 1.26–1.42 (6 H, m, 2-H_2, 3-H_2 and 5-H_2), 1.63–1.67 (2 H, m, 6-H and 8-H), 3.36 (1 H, dd, *J* 10 and 7, 9-H), 3.41 (1 H, dd, *J* 10 and 6, 9-H′) and 3.64 (1 H, m, 4-H); δ_C (125 MHz, $CDCl_3$) 12.0, 14.1, 16.5, 18.0, 18.8, 20.3, 26.8, 33.5, 40.1, 40.3, 46.2, 69.3 and 69.6; *m*/*z* (ES−) 367 (M^+ + Na, 100%).

Imidazole (27 mg, 0.39 mmol) and tri-isopropylsilyl chloride (40 μL, 0.21 mmol) were added to the diol **97** (30 mg, 0.16 mmol) in DCM (1 mL) at 0 °C and the solution was stirred for 1 h at room temperature. Water was added (3 mL) and the mixture extracted into DCM (3 × 5 mL). The organic extracts were washed with water (5 mL) and brine (5 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (20 : 1, light petroleum–ether) of the residue gave the alcohol **98** as a colourless oil (49 mg, 90%).

(2*R*,4*R*,6*S*)-1-Tri-isopropylsilyloxy-2,4-dimethylnonan-6-yl 4-methylbenzenesulfonate 93. Toluene *p*-sulfonyl chloride (512 mg, 2.69 mmol) and 4-dimethylaminopyridine (460 mg, 3.77 mmol) were added to the alcohol **92** (370 mg, 1.08 mmol) in DCM (10 mL) at room temperature and the mixture was stirred for 16 h. The solution was concentrated under reduced pressure and chromatography (6 : 1, light petroleum–ether) of the white solid residue gave the *title compound* **93** as a colourless oil (474 mg, 91%), R_f = 0.67 (2 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +3.0 (*c* 1.5, $CHCl_3$) (Found: M^+ + H, 499.3278. $C_{27}H_{51}O_4SSi$ requires *M*, 499.3272); ν_{max}/cm^{-1} 2961, 2867, 1600, 1463, 1363, 1177, 1099, 885 and 665; δ_H (500 MHz, $CDCl_3$) 0.73 and 0.74 (each 3 H, d, *J* 7, 2- or 4-CH_3), 0.75 (3 H, t, *J* 7.5, 9-H_3), 0.98 [21 H, s, 3 × $SiCH(CH_3)_2$], 1.05–1.28 (4 H, m, 3-H_2 and 8-H_2), 1.39–1.45 (5 H, m, 4-H, 5-H_2 and 7-H_2), 1.56 (1 H, m, 2-H), 2.37 (3 H, s, CH_3Ar), 3.33 (1 H, dd, *J* 3 and 1, 1-H), 3.35 (1 H, dd, *J* 3 and 1, 1-H′), 4.59 (1 H, m, 6-H) and 7.24 and 7.71 (each 2 H, d, *J* 9, ArH); δ_C (125 MHz, $CDCl_3$) 12.0, 13.8, 16.3, 17.8, 18.1, 19.4, 21.6, 26.7, 33.3, 36.5, 40.7, 42.7, 69.1, 82.9, 127.7, 129.6, 135.0 and 144.3; *m*/*z* (CI) 499 (M^+ + 1, 28%), 327 (100), 326 (24) and 283 (30).

(2*R*,4*S*,6*R*)-1-Tri-isopropylsilyloxy-2,4,6-trimethylnonane 94. Methyllithium (1.6 M in Et_2O, 3.14 mL, 5.02 mmol) was added dropwise to copper(I) cyanide (225 mg, 2.51 mmol) in toluene (6.5 mL) at 0 °C and the mixture was stirred at this temperature for 15 min. Toluene *p*-sulfonate **93** (250 mg, 0.50 mmol) in toluene (4.5 mL) was added dropwise and the mixture was stirred at 0 °C for a further 5 h. The mixture was filtered through celite, washing the celite with DCM (10 mL) and Et_2O (10 mL). The organic extracts were concentrated under reduced pressure and the yellow residue was dissolved in acetone (7.5 mL) and water (1.5 mL). *N*-Methylmorpholine *N*-oxide (75 mg, 0.20 mmol, 1.2 equiv.) and OsO_4 (1 crystal, cat.) were added at room temperature and the solution was stirred for 16 h. Saturated aqueous sodium sulfite (20 mL) was added and the mixture was stirred for 1 h before being extracted with ether (3 × 30 mL). The organic extracts were washed with brine

(30 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography (10 : 1, light petroleum–ether) of the residue gave the *title compound* **94** (82 mg, 48%) as a colourless oil, R_f = 0.43 (100% light petroleum), $[\alpha]_D^{20}$ +3.8 (*c* 1.0, $CHCl_3$) (Found: $M^+ + NH_4$, 360.3648. $C_{21}H_{50}ONSi$ requires *M*, 360.3656); ν_{max}/cm^{-1} 2956, 2927, 2868, 1464, 1380, 1247, 1107, 1068, 1013, 996, 918, 883, 787 and 681; δ_H (500 MHz, $CDCl_3$) 0.72 (3 H, d, *J* 7, 6-CH_3), 0.74 (3 H, d, *J* 7, 4-CH_3), 0.79 (3 H, t, *J* 7, 9-H_3), 0.80 (3 H, d, *J* 7, 2-CH_3), 0.88 (1 H, m, 3-H), 0.99 [21 H, m, 3 × $SiCH(CH_3)_2$], 1.04 (1 H, m, 3-H′), 1.07–1.28 (6 H, m, 5-H_2, 7-H_2 and 8-H_2), 1.39–1.53 (2 H, m, 4-H and 6-H), 1.65 (1 H, m, 2-H), 3.32 (1 H, dd, *J* 9 and 7, 1-H) and 3.43 (1 H, dd, *J* 9 and 6, 1-H′); δ_C (125 MHz, $CDCl_3$) 12.0, 14.4, 16.8, 18.1, 19.4, 19.5, 20.1, 27.3, 29.7, 33.5, 40.2, 41.6, 45.7 and 69.2; *m*/*z* (CI) 343 (M^+ + 1, 100%), 342 (M^+, 77) and 316 (20).

(2*R*,4*S*,6*R*)-2,4,6-Trimethylnonan-1-ol 95. Tetra-*n*-butylammonium fluoride (1.0 M in THF, 0.29 mL, 0.29 mmol) was added to the silyl ether **94** (50 mg, 0.15 mmol) in THF (1 mL) and the mixture was stirred at room temperature for 16 h. Water (2 mL) was added and the mixture was stirred for a further 1 h then extracted with ether (3 × 3 mL). The organic extracts were washed with brine (5 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (10 : 1 to 5 : 1, light petroleum–ether) of the residue gave the *title compound* **95** as a colourless oil (25 mg, 90%), R_f = 0.33 (1 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +4.1 (*c* 0.3, $CHCl_3$) (Found: $M^+ - H_2O$, 168.1881. $C_{12}H_{24}$ requires *M*, 168.1873); ν_{max}/cm^{-1} 3325, 2956, 2916, 2872, 2845, 1460, 1378 and 1040; δ_H (400 MHz, $CDCl_3$) 0.74 (3 H, d, *J* 6.5, 6-CH_3), 0.75 (3 H, d, *J* 6.5, 4-CH_3), 0.83 (3 H, t, *J* 7, 9-H_3), 0.83 (3 H, d, *J* 6.5, 2-CH_3), 0.93–1.33 (8 H, m, 3-H_2, 5-H_2, 7-H_2 and 8-H_2), 1.39–1.55 (2 H, m, 4-H and 6-H), 1.66 (1 H, m, 2-H), 3.33 (1 H, m, 1-H) and 3.41 (1 H, m, 1-H′); δ_C (125 MHz, $CDCl_3$) 14.4, 16.4, 19.2, 19.5, 19.9, 27.2, 29.7, 33.2, 40.1, 41.5, 45.7 and 69.0; *m*/*z* (CI) 204 (M^+ + 18, 15%), 186 (M^+, 9), 137 (92) and 57 (100).

(2*R*,4*S*,6*S*,)-1-Tri-isopropylsilyloxy-2,4-dimethylnonan-6-yl 4-methylbenzenesulfonate 99. Following the standard procedure, toluene *p*-sulfonyl chloride (104 mg, 0.55 mmol), 4-dimethylaminopyridine (101 mg, 0.83 mmol) and the alcohol **98** (75 mg, 0.22 mmol), after chromatography (6 : 1, light petroleum–ether) afforded the *title compound* **99** as a colourless oil (99 mg, 91%), R_f = 0.67 (2 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +4.7 (*c* 1.7, $CHCl_3$) (Found: M^+ + H, 499.3273. $C_{27}H_{51}O_4SSi$ requires *M*, 499.3272); ν_{max}/cm^{-1} 2961, 2867, 1600, 1463, 1364, 1177, 1098, 897, 683 and 665; δ_H (500 MHz, $CDCl_3$) 0.70 (3 H, d, *J* 7, 4-CH_3), 0.74 (3 H, d, *J* 7, 2-CH_3), 0.77 (3 H, t, *J* 7, 9-H_3), 0.98 [21 H, s, 3 × $SiCH(CH_3)_2$], 1.05 (1 H, m, 3-H), 1.15–1.26 (3 H, m, 3-H′ and 8-H_2), 1.39 (1 H, m, 4-H), 1.48–1.62 (5 H, m, 2-H, 5-H_2 and 7-H_2), 2.36 (3 H, s, CH_3Ar), 3.31 (1 H, dd, *J* 10 and 6, 1-H), 3.38 (1 H, dd, *J* 10 and 6, 1-H′), 4.60 (1 H, m, 6-H) and 7.23 and 7.71 (each 2 H, d, *J* 8, ArH); δ_C (125 MHz, $CDCl_3$) 11.8, 12.2, 13.8, 17.3, 18.0, 20.3, 21.6, 26.3, 33.3, 37.3, 41.2, 41.4, 68.5, 82.6, 127.7, 129.6, 134.9 and 144.2; *m*/*z* (CI) 499 (M^+ + 1, 27%), 327 (100) and 283 (27).

(2*R*,4*R*,6*R*)-1-(Tri-isopropylsilyloxy)-2,4,6-trimethylnonane 100. Following the standard procedure, methyllithium (1.6 M in Et_2O, 3.14 mL, 5.02 mmol), copper(I) cyanide (225 mg, 2.51 mmol) and the toluene *p*-sulfonate **99** (250 mg, 0.50 mmol), after chromatography (10 : 1, light petroleum–ether), afforded the *title compound* **100** (77 mg, 45%) as a colourless oil, R_f = 0.41 (100% light petroleum), $[\alpha]_D^{20}$ +3.1 (*c* 0.3, $CHCl_3$) (Found: M^+, 342.3311. $C_{21}H_{46}OSi$ requires *M*, 342.3312); ν_{max}/cm^{-1} 2956, 2925, 2868, 1462, 1380, 1104, 882 and 682; δ_H (500 MHz, $CDCl_3$) 0.76 (3 H, d, *J* 6.5, 6-CH_3), 0.78 (3 H, d, *J* 6.5, 4-CH_3), 0.81 (3 H, t, *J* 7, 9-H_3), 0.84 (3 H, d, *J* 6.5, 2-CH_3), 0.92 (1 H, m, 3-H), 0.99 [21 H, m, 3 × $SiCH(CH_3)_2$], 1.02 (1 H, m, 3-H′), 1.10–1.31 (6 H, m, 5-H_2, 7-H_2 and 8-H_2), 1.40–1.53 (2 H, m, 4-H and 6-H), 1.60 (1 H, m, 2-H), 3.36 (1 H, dd, *J* 10 and 6, 1-H) and 3.47 (1 H, dd, *J* 10 and 5, 1-H′); δ_C (125 MHz, $CDCl_3$) 12.1, 14.1, 14.4, 18.0, 20.0, 20.5, 21.0, 27.7, 29.8, 33.5, 38.9, 41.4, 45.5 and 68.4; *m*/*z* (CI) 343 (M^+ + 1, 81%), 316 (28), 110 (100), 83 (87) and 58 (76).

(2*R*,4*R*,6*R*)-2,4,6-Trimethylnonan-1-ol 101. Following the standard procedure, tetra-*n*-butylammonium fluoride (1.0 M in THF, 0.29 mL, 0.29 mmol) and the silyl ether **100** (50 mg, 0.15 mmol), after chromatography (10 : 1 to 5 : 1, light petroleum–ether), afforded the *title compound* **101** (25 mg, 91%) as a colourless oil, R_f = 0.33 (1 : 1, light petroleum–ether), $[\alpha]_D^{20}$ +7.3 (*c* 1.1, $CHCl_3$) (Found: $M^+ - H_2O$, 168.1867. $C_{12}H_{24}$ requires *M*, 168.1873); ν_{max}/cm^{-1} 3326, 2956, 2916, 2872, 2845, 1460, 1378 and 1040; δ_H (400 MHz, $CDCl_3$) 0.77 (3 H, d, *J* 6.5, 6-CH_3), 0.80 (3 H, d, *J* 6.5, 4-CH_3), 0.81 (3 H, t, *J* 7, 9-H_3), 0.86 (3 H, d, *J* 6.5, 2-CH_3), 0.91 (1 H, m, 3-H), 1.11–1.31 (7 H, m, 3-H′, 5-H_2, 7-H_2 and 8-H_2), 1.41–1.55 (2 H, m, 4-H and 6-H), 1.65 (1 H, m, 2-H), 3.31 (1 H, dd, *J* 10 and 7, 1-H) and 3.47 (1 H, dd, *J* 10 and 5, 1-H′); δ_C (125 MHz, $CDCl_3$) 14.4, 17.5, 19.9, 20.4, 20.9, 27.5, 29.7, 33.1, 38.8, 41.3, 45.2 and 68.3; *m*/*z* (CI) 204 (M^+ + 18, 18%), 186 (M^+, 4), 137 (23), 83 (41) and 58 (100).

Notes and references

1 E. J. Thomas, *Chem. Rec.*, 2007, **7**, 115.
2 (*a*) A. H. MacNeill and E. J. Thomas, *Synthesis*, 1994, 322; (*b*) J. S. Carey, S. MacCormick, S. J. Stanway, A. Teerawutgulrag and E. J. Thomas, *Org. Biomol. Chem.*, 2011, **9**, 3896; (*c*) D. J. Hallett, N. Tanikkul and E. J. Thomas, *Org. Biomol. Chem.*, 2012, **10**, 6130; (*d*) S. J. Stanway and E. J. Thomas, *Tetrahedron*, 2012, **68**, 5998.
3 K. Dorling and E. J. Thomas, *Org. Biomol. Chem.*, 2012, **10**, 6995.
4 N. Martin and E. J. Thomas, *Org. Biomol. Chem.*, 2012, **10**, 7952.
5 O. Germay, N. Kumar, C. Moore and E. J. Thomas, *Org. Biomol. Chem.*, 2012, **10**, 9709.
6 (*a*) P. Casteno, E. J. Thomas and A. Weston, *Tetrahedron Lett.*, 2007, **48**, 337; (*b*) E. J. Thomas and A. Weston, *Tetrahedron Lett.*, 2007, **48**, 341.

7 For a preliminary communication of the bismuth(III) iodide promoted reactions of the allylstannanes see: S. Donnelly, E. J. Thomas and E. A. Arnott, *J. Chem. Soc., Chem. Commun.*, 2003, 1460.
8 For preliminary communications on the low valency bismuth initiated reactions of the pent-2-enyl bromides and the stereoselective synthesis of the 2,4,6-trimethylnonanols see: (*a*) S. Donnelly, M. Fielding and E. J. Thomas, *Tetrahedron Lett.*, 2004, **45**, 6779; (*b*) N. Basar, S. Donnelly, H. Liu and E. J. Thomas, *Synlett*, 2010, 575.
9 Y. Yamamoto, H. Yatagai, Y. Ishihara, N. Maeda and K. Maruyama, *Tetrahedron*, 1984, **40**, 2239.
10 S. C. Archibald, D. J. Barden, J. F. Y. Bazin, I. Fleming, C. F. Foster, A. K. Mandal, A. K. Mandal, D. Parker, K. Takaki, A. C. Ware, A. R. B. Williams and A. B. Zwicky, *Org. Biomol. Chem.*, 2004, **2**, 1051.
11 (*a*) J. A. Marshall and K. W. Hinkle, *J. Org. Chem.*, 1995, **60**, 1920; (*b*) J. A. Marshall and K. W. Hinkle, *J. Org. Chem.*, 1996, **61**, 105; (*c*) J. A. Marshall and K. W. Hinkle, *J. Org. Chem.*, 1997, **62**, 5989; (*d*) J. A. Marshall and M. Chen, *J. Org. Chem.*, 1997, **62**, 5996; (*e*) J. A. Marshall and M. R. Palovich, *J. Org. Chem.*, 1997, **62**, 6001; (*f*) J. A. Marshall and A. W. Garofalo, *J. Org. Chem.*, 1996, **61**, 8732; (*g*) M. Yasuda, T. Miya, I. Shibata, A. Baba, R. Nomura and H. Matsuda, *Tetrahedron Lett.*, 1995, **36**, 9497; (*h*) D. Behnke, S. Hamm and P. Welzel, *Tetrahedron Lett.*, 1997, **38**, 7059; (*i*) T. Miyai, K. Inoue, M. Yasuda and A. Baba, *Synlett*, 1997, 699; (*j*) J. Cossy, C. Rasamison, D. G. Pardo and J. A. Marshall, *Synlett*, 2001, 629; (*k*) J. Cossy, M. Defosseux and C. Meyer, *Synlett*, 2001, 815; (*l*) W. Miao, W. Lu and T. H. Chan, *J. Am. Chem. Soc.*, 2003, **125**, 2412.
12 (*a*) J. A. Marshall and C. M. Grant, *J. Org. Chem.*, 1999, **64**, 8214; (*b*) B. M. Choudary, S. Chidara and Cc. V. R. Sekhar, *Synlett*, 2002, 1694.
13 O. Mitsunobu, *Synthesis*, 1981, 1.
14 (*a*) M. Wada, H. Ohki and K.-Y. Akiba, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1738; (*b*) M. Wada, H. Ohki and K. Akiba, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1738; (*c*) N. Miyoshi, M. Nishio, S. Murakami, T. Fukuma and M. Wada, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 689; (*d*) M. Wada, M. Honna, Y. Kuramoto and N. Miyoshi, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 2265; (*e*) P. J. Bhuyan, D. Prajapati and J. S. Sandhu, *Tetrahedron Lett.*, 1993, **34**, 7975; (*f*) M. Wada, H. Ohki and K. Akiba, *Tetrahedron Lett.*, 1986, **27**, 4771; (*g*) M. Wada and K. Akiba, *Tetrahedron Lett.*, 1985, **26**, 4211.
15 B. M. Trost, J. L. Belletire, S. Godleski, P. G. McDougal, J. M. Balkovec, J. L. Baldwin, M. E. Christy, G. S. Ponticello, S. L. Varga and J. P. Springer, *J. Org. Chem.*, 1986, **51**, 2370.
16 T. Eguchi, K. Ibaragi and K. Kakinuma, *J. Org. Chem.*, 1998, **63**, 2689.
17 B. H. Lipshutz, R. S. Wilhelm and J. A. Kozlowski, *Tetrahedron*, 1984, **40**, 5005.
18 F. Godin, I. Katsoulis, E. Fiola-Masson, S. Dhambri, P. Mochirian and Y. Guindon, *Synthesis*, 2012, 474.
19 (*a*) B. ter Horst, B. L. Feringa and A. J. Minnaard, *Chem. Commun.*, 2010, **46**, 2535; (*b*) T. den Hartog, D. J. van Dijken, A. J. Minnaard and B. L. Feringa, *Tetrahedron: Asymmetry*, 2010, **21**, 1574.
20 C. Herber and B. Breit, *Eur. J. Org. Chem.*, 2007, 3512.
21 (*a*) J. Zhou, J. W. Ogle, Y. Fan, V. Banphavichit, Y. Zhu and K. Burgess, *Chem.–Eur. J.*, 2007, **13**, 7162; (*b*) J. Zhou, Y. Zhu and K. Burgess, *Org. Lett.*, 2007, **9**, 1391.
22 (*a*) B. Liang, T. Novak, Z. Tan and E.-i. Negishi, *J. Am. Chem. Soc.*, 2006, **128**, 2770; (*b*) G. Zhu, B. Liang and E.-i. Negishi, *Org. Lett.*, 2008, **10**, 1099.
23 (*a*) D. A. Evans and M. M. Morrissey, *Tetrahedron Lett.*, 1985, **26**, 6005; (*b*) D. A. Evans and M. M. Morrissey, *J. Am. Chem. Soc.*, 1984, **106**, 3866.
24 J. M. Brown, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 190.
25 (*a*) S. Wang, D. B. Mitzi, G. A. Landrum, H. Genin and R. Hoffmann, *J. Am. Chem. Soc.*, 1997, **119**, 724; (*b*) S. C. James, N. C. Norman and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1999, 2837; (*c*) P. Hodge, S. C. James, N. C. Norman and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1998, 4049; (*d*) C. J. Carmalt, A. H. Cowley, A. Decken and N. C. Norman, *J. Organomet. Chem.*, 1995, **496**, 59.
26 L. A. Hobson and E. J. Thomas, *Org. Biomol. Chem.*, 2012, **10**, 7510.
27 N. Basar, H. Liu, G. A. Morris, H. M. Sirat and E. J. Thomas, *Org. Biomol. Chem.*, 2012, 1743.
28 (*a*) I. Paterson, M. J. Coster, D. Y.-K. Chen, K. R. Gibson and D. J. Wallace, *Org. Biomol. Chem.*, 2005, **3**, 2410; (*b*) M. T. Reetz and A. Jung, *J. Am. Chem. Soc.*, 1983, **105**, 4833.
29 (*a*) K. Marukawa and K. Mori, *Eur. J. Org. Chem.*, 2002, 3974; (*b*) G. Solladié, F. Somny and F. Colobert, *Tetrahedron: Asymmetry*, 1997, **8**, 801.