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PAPER

Concerning the 1,5-stereocontrol in tin(IV) chloride promoted reactions of 4- and 5-alkoxyalk-2-enylstannanes: trapping intermediate allyltin trichlorides using phenyllithium†

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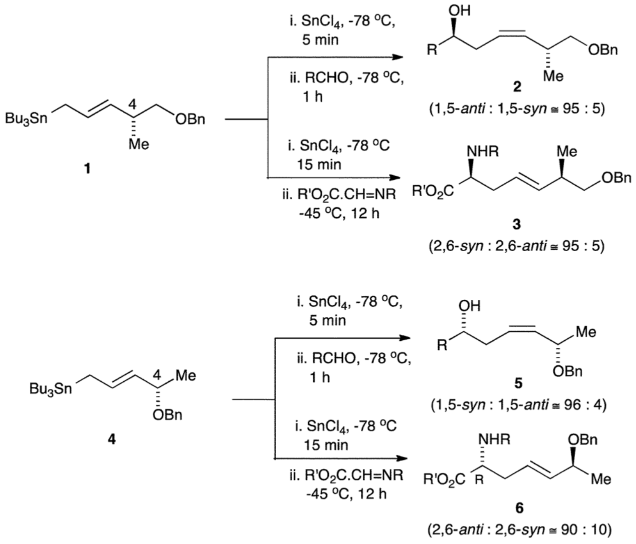
Transmetallation of the 5-benzyloxy-4-methylpent-2-en-1-yl(tributyl)- and -(triphenyl)stannanes **1** and **8** using tin(IV) chloride generates an allyltin trichloride that reacts with aldehydes to give (*Z*)-1,5-*anti*-6-benzyloxy-5-methylhex-3-en-1-ols **2**. The allyltin trichloride believed to be the key intermediate in these reactions has been trapped by phenyllithium to give *anti*-5-benzyloxy-4-methylpent-1-en-3-yl(triphenyl) stannane **9**. Transmetallation of this *anti*-5-benzyloxy-4-methylpent-1-en-3-yl(triphenyl)stannane **9** generated an allyltin trichloride that reacted with aldehydes to give the (*Z*)-1,5-*syn*-6-benzyloxy-5-methylhex-3-en-1-ols **23** and was trapped by phenyllithium to give *syn*-5-benzyloxy-4-methylpent-1-en-3-yl(triphenyl)stannane **24**. Similar stereoselectivity was observed for tin(IV) chloride promoted reactions of this *syn*-5-benzyloxy-4-methylpent-1-en-3-yl(triphenyl)stannane **24** with aldehydes and with phenyllithium. The allyltin trichlorides generated by transmetallation of 4-hydroxy- and 4-benzyloxy-pent-2-enyl(triphenyl)stannanes **34** and **35** were similarly trapped by phenyllithium to give 4-hydroxy- and 4-benzyloxy-pent-1-en-3-ylstannanes **36** and **37** whose configurations were established by correlation with known compounds. This work confirmed the configurations of the intermediate allyltin trichlorides involved in tin(IV) chloride promoted reactions of 4- and 5-alkoxypent-2-enylstannanes with aldehydes and showed that the high levels of remote stereocontrol were due mainly to kinetically controlled transmetallation. A fuller mechanistic scheme is proposed for the reactions in the 5-benzyloxy-4-methylpent-2-enylstannane series together with relevant ^{119}Sn NMR data.

Introduction

Tin(IV) halide promoted reactions of 4-, 5- and 6-alkoxy- and -hydroxy-alk-2-enylstannnanes with aldehydes give (*Z*)-alk-3-enols with useful levels of 1,5-, 1,6- and 1,7-stereocontrol.[1,2] For example, the (*Z*)-1,5-*anti*-alk-3-en-1-ols **2** were obtained from reactions of the 5-benzyloxy-4-methylpent-2-enyl(tributyl)stannane **1** and aldehydes[2a] and the 4-benzyloxypent-2-enylstannane **4** gave the (*Z*)-1,5-*syn*-products **5** with excellent stereoselectivity.[2b] N- and S-substituted pentenylstannanes show similar stereoselectivity[2c] and useful stereoselectivity, albeit in favour of the (*E*)-alkenes **3** and **6**, was observed for the reactions of alkoxyalk-2-enylstannanes **1** and **4** with 1-alkoxycarbonylimines.[3]



These reactions are believed to involve allyltin trichlorides formed stereoselectively from the alk-2-enylstannanes and tin(IV)

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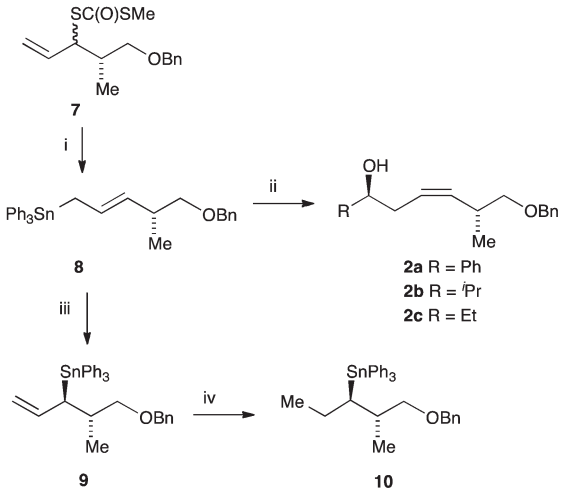
chloride before the addition of the aldehyde. The transmetallation step would appear to be complete in less than five minutes at −78 °C since no branched (SE′) product was ever obtained. To explain the high stereoselectivities, it was suggested that the transmetallation step must be highly stereoselective possibly due to delivery of the trichlorotin group to one face of the double-bond of the alk-2-enylstannanes after coordination of the tin(IV) chloride to the alkoxy substituent.[1,2] However, an alternative mechanism involving rapid equilibration of isomeric allyltin trichlorides with selective reaction of the more reactive isomer couldn't be ruled out. It was therefore decided to probe the mechanisms of these reactions by trapping the allyltin trichloride intermediates using reactions that retained the carbon–tin bond. We now report full details of reactions of allyltin trichlorides generated from 4- and 5-alkoxypent-2-enylstannanes with phenyllithium[4] together with relevant ^{119}Sn NMR data.

Results and discussion

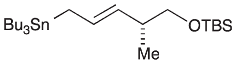
Trapping alkenyltin trichlorides in the 5-alkoxypent-2-enylstannane series

Studies were initiated using triphenylstannanes rather than the previously used tributylstannanes since preliminary studies using tributylstannanes led to some difficulties in purifying intermediates.[5] Thus the (*R*)-5-benzyloxypent-2-enyl(triphenyl)stannane **8** was prepared as an 80 : 20 mixture of (*E*)- and (*Z*)-isomers (^{1}H NMR) by reaction of the dithiocarbonate **7**[2a] with triphenyltin hydride under free radical conditions, see Scheme 1. The tin(IV) chloride mediated reactions of the pent-2-enyl(triphenyl)stannane **8** with benzaldehyde, 2-methylpropanal and propanal were then carried out under the usual conditions and gave the known[2a] (*Z*)-1,5-*anti*-alkenols **2a–c** with excellent stereoselectivity, *ca.* 95 : 5, in all cases, so showing that the change from tributylstannanes to triphenylstannanes had not had any effect on this chemistry. Attempts were now made to trap the allyltin trichloride believed to be an intermediate in these reactions. In the event, it was found that the addition of an excess of phenyllithium five minutes after the addition of tin(IV) chloride at −78 °C to the stannane **8** gave a new pentenylstannane identified as the *anti*-5-benzyloxy-4-methylpent-1-en-3-yl(triphenyl)stannane **9** together with a second minor product subsequently identified as the epimeric *syn*-stannane **24**, ratio **9** : **24** = 90 : 10. Since unsymmetric allylstannanes with the tin substituent at the more substituted end of the allyl fragment are prone to undergo 1,3-migration of the tin,[6] the pent-1-en-3-ylstannane **9** was reduced using diimide to give the *anti*-pent-3-yl(triphenyl)stannane **10** containing *ca.* 10% of its *syn*-epimer **25**, see Scheme 1.



Scheme 1 Tin(IV) chloride mediated reactions of the 5-benzyloxy-4-methylpentenyl(triphenyl)stannane **8**. Reagents and conditions: (i) Ph$_3$SnH, AIBN (cat.), benzene, heat under reflux, 3 h (86%); (ii) SnCl$_4$, DCM, −78 °C, 5 min, RCHO, −78 °C, 1 h (**2a**, 73%; **2b**, 72%; **2c**, 47%); (iii) SnCl$_4$, −78 °C, 5 min, PhLi, cyclohexane–ether, −78 °C, 2 h (64%; **9** : **24** = 90 : 10); (iv) NaOAc, H$_2$O, TsNHNH$_2$, DME, heat under reflux 4 h (72%; **10** : **25** = 90 :10).

The structures assigned to the products **9** and **10** were consistent with their spectroscopic data. Comparison with later spectra showed that the *anti*-pent-1-en-3-ylstannane **9** contained *ca.* 10% of its *syn*-epimer. It remained to establish the relative configuration of the stannanes **9** and **10** at their stereogenic centres, but attempts to prepare crystalline derivatives were thwarted as debenzylation of the benzyl ether **10** by hydrogenolysis or by using trimethyltin iodide gave either unchanged starting material or complex mixtures of products. The 5-*tert*-butyldimethylsilyloxy- and 5-hydroxy-pent-2-enylstannanes **11** and **12** are known to react with aldehydes with similar stereoselectivity to that observed for the 5-benzyloxystannane **1**,[7] and so it was decided to study reactions of the 5-silyloxy- and 5-hydroxy-pent-2-enyl(triphenyl)stannanes to access derivatives suitable for X-ray crystallography.



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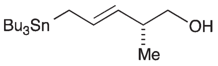

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The (±)-5-*tert*-butyldimethylsilyloxy-4-methylpent-2-enylstannane **14** was prepared by reaction of the dithiocarbonate **13**[2c] with triphenyltin hydride under free radical conditions and desilylation gave the 5-hydroxypent-2-enylstannane **15**. The pent-2-enylstannanes **14** and **15** were separately treated with tin(IV) chloride for 5 min at −78 °C before an excess of phenyllithium was added to trap any intermediate allyltin trichloride. Pent-1-en-3-yl(triphenyl)stannanes **16** and **17** (*anti* : *syn* = 85 : 15) were obtained and were reduced using diimide to give the pent-3-ylstannanes **18** and **19**. The 5-hydroxypent-3-ylstannane **19** was then esterified using 4-bromobenzoyl chloride to give the crystalline 4-bromobenzoate **20** whose structure was established by X-ray diffraction, see Fig. 1.[4a] This confirmed the *anti*-configuration indicated for the 5-hydroxypentylstannane **19**.

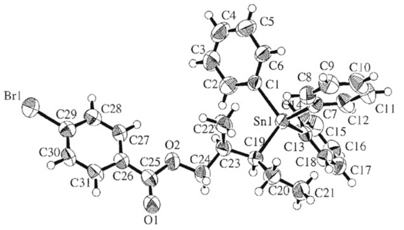
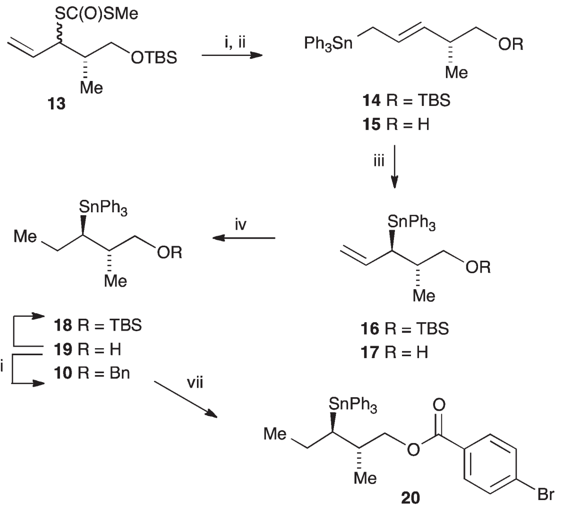


Fig. 1 The structure of the 4-bromobenzoate **20** as established by X-ray diffraction.[4a]



Scheme 2 Confirmation of the configurations of allyltin trichlorides generated by transmetallation of 5-substituted 4-methylpent-2-enyl(triphenyl)stannanes **14** and **15** by tin(IV) chloride. Reagents and conditions; (i) Ph$_3$SnH, AIBN (cat.), benzene, heat under reflux, 3 h (61%); (ii) TBAF, THF, 0 °C to r.t., 4 h (74%); (iii) SnCl$_4$, DCM, 5 min, −78 °C, then PhLi, −78 °C, 2 h (**16**, 61%; **17**, 42%; *anti* : *syn* = 85 : 15); (iv) NaOAc, H$_2$O, TsNHNH$_2$, DME, heat under reflux 4 h (**18**, 64%; **19**, 74%); (v) TBSCl, imid., DCM, r.t., 20 h (86%); (vi) KO^{t}Bu, THF, r.t., 15 min, BnBr, TBAI, r.t., 15 h (48%); (vii) Et$_3$N, DMAP (cat.), 4-BrC$_6$H$_4$COCl, r.t., 3 h (77%).

O-Benzylation of the hydroxypent-3-ylstannane **19** gave the benzyl ether **10** shown to be identical to the product prepared from the 5-benzyloxypentenylstannane **8**. *O*-Silylation of the alcohol **19** gave the TBS ether **18** prepared from the TBS-stannane **14**. These correlations established the structures of the triphenylstannanes **9**, **16** and **17** prepared from the allyltin trichlorides generated from the pent-2-enylstannanes **8**, **14** and **15**, see Scheme 2.

The stereoselective formation of the pent-1-en-3-ylstannanes **9**, **16** and **17** in these trapping experiments is consistent with stereoselective transmetallation of the 5-substituted pent-2-enylstannanes **8**, **14** and **15** by tin(IV) chloride to generate an allyltin trichloride, generic structure **21**, in which the vinyl and methyl substituents are *trans*-disposed about the 5-membered ring formed by coordination of the electron deficient tin by the alkoxy group, see Fig. 2. The allyltin trichloride **21** can then react with an aldehyde, possibly *via* the chair-like transition structure **22**, to give (3*Z*)-1,5-*anti*-alkenols **2** or be trapped by reaction with the phenyllithium, with retention of the pentenyl carbon–tin bond, to give the internal triphenylallylstannanes **9**, **16** and **17**.

These studies support the participation of the (3*RS*,4*SR*)-allyltin trichlorides **21** in the tin(IV) chloride promoted reactions of 5-substituted 4-methylpent-2-enylstannanes with aldehydes but at this stage it was not clear whether they were being formed stereoselectively by a kinetically controlled transmetallation or whether they were the more reactive components of mixtures of rapidly equilibrating allyltin trichlorides. However, the trapped products **9**, **16** and **17** are themselves allylstannanes and so it was decided to investigate transmetallation of the internal allylstannane **9** and reactions of the resulting allyltin trichloride.

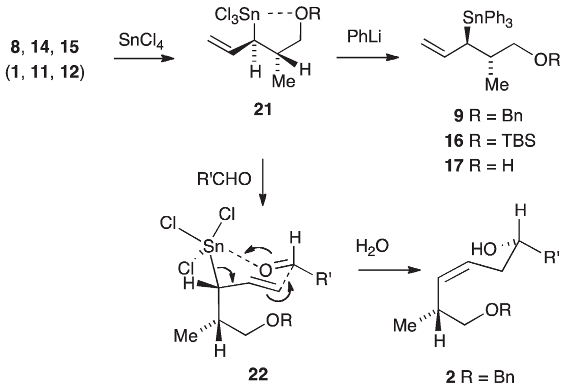
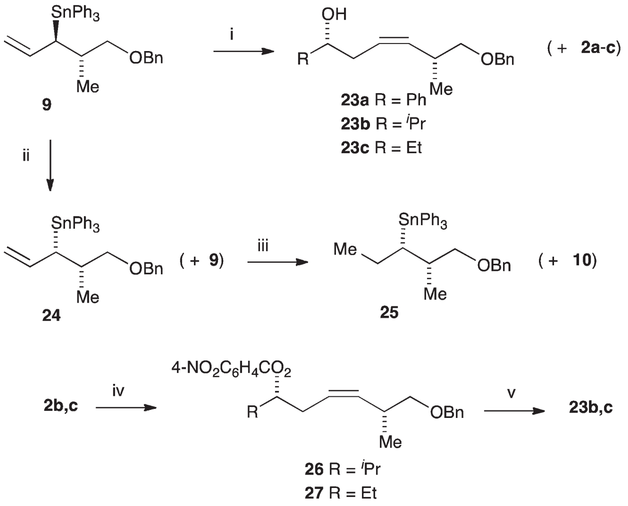


Fig. 2 The generation and reactions of allyltin trichlorides from 5-substituted-4-methylpent-2-enylstannanes.



Scheme 3 Transmetallation of the (3*RS*,4*SR*)-5-benzyloxy-4-methylpent-1-en-3-yl(triphenyl)stannane **9**. Reagents and conditions: (i) SnCl$_4$, −78 °C, 2 min, then RCHO, −78 °C, 1 h (**23a**/**2a**, 44%, **23a** : **2a** = 75 : 25; **23b**/**2b**, 21%, **23b** : **2b** = 60 : 40; **23c**/**2c**, 60%, **23c** : **2c** = 82 : 18); (ii) SnCl$_4$, −78 °C, 2 min, then PhLi, −78 °C, 2 h (54%, **24** : **9** = 80 : 20); (iii) NaOAc, H$_2$O, TsNHNH$_2$, DME, heat under reflux 4 h (58%); (iv) DEAD, Ph$_3$P, 4-O$_2$NC$_6$H$_4$CO$_2$H, toluene, −60 °C to r.t., 20 h (**26**, 41%; **27**, 53%); (v) NaOH, MeOH, r.t., 3 h (**23b**, 64%; **23c**, 63%).

The stereoselectivity of the reaction of pentenylstannane **9** with tin(IV) chloride at −78 °C and benzaldehyde was found to depend on the time allowed before addition of the aldehyde. With a short transmetallation time of 2 or 5 min, the major product was the (3*Z*)-1,5-*syn*-isomer **23a**, ratio **23a** : **2a** = 80–70 : 20–30, see Scheme 3. If the reaction mixture was allowed to stand for longer at −78 °C before addition of the benzaldehyde, then the stereoselectivity was reversed, *e.g.* allowing 10 min at −78 °C before addition of the benzaldehyde led to selectivity for the 1,5-*anti*-epimer **2a**, ratio **23a** : **2a** = 20 : 80. This preference for formation of a (3*Z*)-1,5-*syn*-isomer when 2 min was allowed for the transmetallation, was also observed for reactions of the stannane **9** with 2-methylpropanal and propanal, see Scheme 3.

Structures were assigned to the major products **23b** and **23c** by comparison with samples prepared from the known (3*Z*)-1,5-*anti*-epimers **2b** and **2c**[2a] *via* saponification of the inverted 4-nitrobenzoates **26** and **27** prepared using Mitsunobu reactions; the (3*Z*)-1,5-*syn*-epimer **23a** was a known compound.[2a]

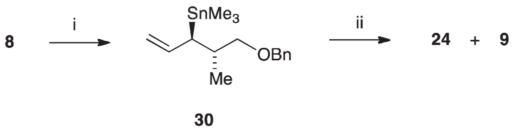
The formation of the 1,5-*syn*-epimers **23** in these reactions of the pentenylstannane **9** contrasts with the highly selective formation of the 1,5-*anti*-epimers **2a–c** from the terminal triphenylstannanes **1** and **8** and suggests that a diastereoisomeric allyltin trichloride is involved. This was investigated by treatment of the internal allylstannane **9** with tin(IV) chloride at −78 °C for 2 min followed by addition of an excess of phenyllithium. The major product from this reaction was the *syn*-3-(triphenylstannyl)pent-1-ene **24** together with the *anti*-epimer **9** as a minor component, ratio **24** : **9** = 80 : 20. These products could not be separated but were identified from spectroscopic data and by comparison of a sample of the *anti*-epimer **9** prepared earlier. Again to prevent 1,3-migration of the tin, the mixture of internal stannanes **24** and **9** was reduced using diimide to give the corresponding *syn*-pentylstannane **25** containing *ca.* 20% of its *anti*-epimer **10**, see Scheme 3.

This work showed that the *anti*- and *syn*-epimers **9** and **24** can be distinguished spectroscopically so confirming that the *anti*-epimer **9** had been obtained stereoselectively when the allyltin trichloride generated by transmetallation of the terminal pent-2-enylstannane **8** was trapped by phenyllithium. Moreover, the formation of the (3*Z*)-1,5-*syn*-products **23a–c** and the *syn*-triphenylstannane **24** from tin(IV) chloride mediated reactions of the *anti*-pentenylstannane **9** is consistent with the epimeric (3*SR*,4*SR*)-allyltin trichloride **28** being involved, the formation of the 1,5-*syn*-products **23** from reactions with aldehydes being compatible with participation of transition structure **29**, see Fig. 3. Since the epimeric allyltin trichlorides **21** and **28** give rise to different products, these allyltin trichlorides cannot be equilibrating substantially during their reactions with aldehydes at −78 °C unless the transmetallation time is prolonged. The high selectivity for formation of the (3*Z*)-1,5-*anti*-products **2** in the tin(IV) chloride mediated reactions of the 5-alkoxy-4-methylpent-2-enylstannanes **1** and **8** must therefore be due to kinetic control of the stereoselectivity of transmetallation.

To check that the phenyl substituents of the internal *syn*-triphenylstannane **24** prepared from the allyltin trichloride **28** and phenyllithium were derived from the phenyllithium and not from the *anti*-triphenylstannane **9**, the analogous *anti*-(trimethyl)stannane **30** was prepared from the 5-benzyloxypent-2-enylstannane **8** using methyllithium to intercept the allyltin trichloride. Only a modest yield of the *anti*-epimer **30** was isolated, its configuration being assigned by analogy with the formation of **9**. Transmetallation of the (trimethyl)stannane **30** using tin(IV) chloride with trapping using phenyllithium gave the *syn*-triphenylstannane **24** together with some of the *anti*-epimer **9**, so confirming that the phenyl moieties in stannane **24** were derived from the phenyllithium and not from the starting allylstannane, see Scheme 4.

Although the original objectives of this work had been achieved, there remained an explanation as to why transmetallation of the *anti*-pent-1-en-3-yl(triphenyl)stannane **9** gave rise predominantly to the *syn*-pent-1-en-3-yltin trichloride **28**, a reaction that is the equivalent of an *ipso* replacement of the tin with inversion of configuration at the more hindered end of the allyl moiety. It was therefore decided to study transmetallation of the third available isomeric allylstannane, the *syn*-pent-1-en-3-yl(triphenyl)stannane **24**.

In the event, the *syn*-pent-1-en-3-ylstannane **24**, after transmetallation using tin(IV) chloride for 5 min, gave the 1,5-*syn*-alkenol **23a** as the major product with benzaldehyde, ratio **23a** : **2a** = 80 : 20. Trapping the allyltin trichloride with phenyllithium in this case was a little capricious, but typically mixtures of the *syn*- and *anti*-pent-1-en-3-yl(triphenyl)stannanes **24** and **9** were obtained with the *syn*-epimer predominating, see Scheme 5. This suggests that the *syn*-allyltin trichloride **28** is the major product of transmetallation of both the *anti*- and *syn*-stannanes **9** and **24**. Both of these reactions correspond to an *ipso* substitution of the triphenylstannyl group, one with inversion, one with predominant retention.



Scheme 4 Trapping an allyltin trichloride using methyllithium. Reagents and conditions: (i) $SnCl_4$, −78 °C, 5 min, then MeLi, −78 °C, 2 h (20%); (ii) $SnCl_4$, −78 °C, 2 min, PhLi, −78 °C, 2 h (54%; **24** : **9** = 60 : 40).

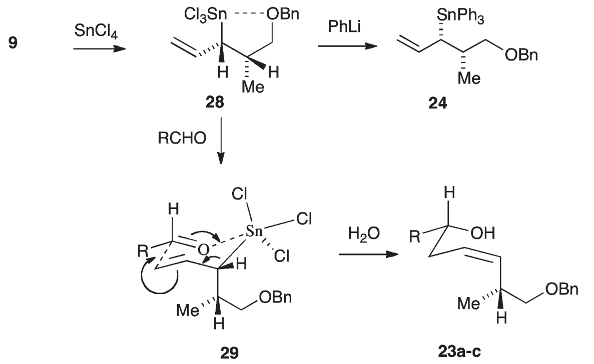
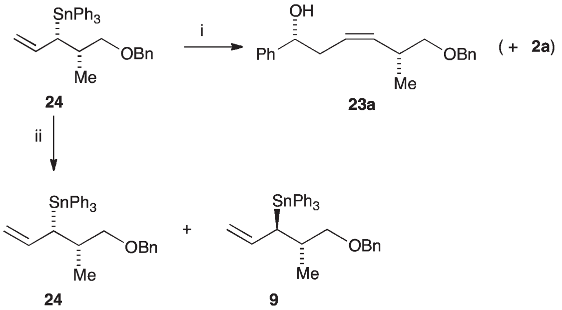


Fig. 3 The generation and reactions of the allyltin trichloride **28** derived from the *anti*-5-benzyloxy-4-methylpent-1-en-3-yl(triphenyl)stannane **9**.



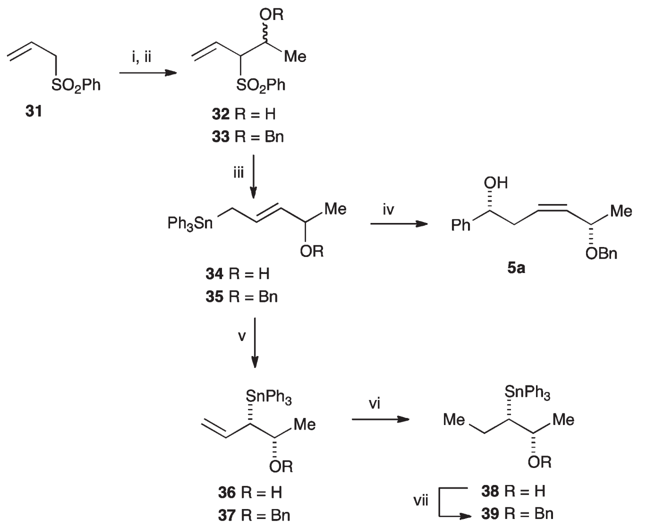
Scheme 5 Tin(IV) chloride mediated reactions of the (3*S*,4*S*)-pent-1-en-3-yl(triphenyl)stannane **24**. Reagents and conditions: (i) $SnCl_4$, DCM, −78 °C, 3 min, then PhCHO, −78 °C, 1 h (42%, **23a** : **2a** = 80 : 20); (ii) $SnCl_4$, −78 °C, 5 min, PhLi, −78 °C, 2 h (44%, **24** : **9** = 66 : 34).

Trapping alkenyltin trichlorides in the 4-alkoxypent-2-enylstannane series

The racemic hydroxy- and 4-benzyloxypent-2-enyl(triphenyl)stannanes **34** and **35** were prepared by reaction of the allylsulfones **32** and **33** with triphenyltin hydride under free radical conditions. The allylic sulfone **32** was prepared as a mixture of diastereoisomers by addition of lithiated propenyl phenyl sulfone **31** to ethanal. *O*-Benzylation gave the corresponding benzyl ether **33**. The tin(IV) chloride mediated reaction of the 4-benzyloxypentenylstannane **35** with benzaldehyde proceeded as expected to give the known[2b] (3*Z*)-1,5-*syn*-hex-3-enol **5a** with excellent stereoselectivity, 1,5-*syn* : 1,5-*anti* = 97 : 3 (^{1}H NMR), see Scheme 6.

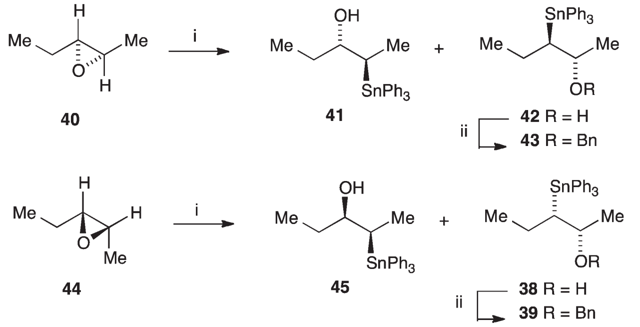
Trapping the allyltin trichlorides generated by treatment of both the 4-hydroxy- and 4-benzyloxy-pent-2-enylstannanes **34** and **35** with phenyllithium was highly stereoselective and gave the *syn*-pent-1-en-3-ylstannanes **36** and **37** containing less than 5% of any other isomer. Diimide reduction of these pentenylstannanes gave the pent-3-ylstannanes **38** and **39**, the 2-benzyloxypent-3-ylstannane **39** also being obtained by *O*-benzylation of the hydroxystannane **38**.

The structures of the products **36–39** were consistent with spectroscopic data but it remained to confirm their configurations. Attempts to prepare crystalline derivatives by esterification of the 2-hydroxypent-3-ylstannane **38** were unsuccessful. Recovered starting material was invariably obtained perhaps because of steric hindrance to functionalization of the alcohol. It was therefore decided to prepare authentic samples of the products **38** and **39** by a stereochemically defined path. Ring-opening of the epoxides **40** and **44**[8] prepared from (*E*)- and (*Z*)-pent-2-ene using triphenylstannyllithium gave mixtures of the regioisomeric hydroxypentylstannanes **41**/**42** and **45**/**38**. Their structures were assigned spectroscopically and their configurations on the basis that analogous epoxide ring openings are known to proceed with inversion of configuration.[9] The *syn*-2-hydroxypent-3-yl(triphenyl)stannane **38** obtained from the (*Z*)-pent-2-ene oxide **44** was identical to that obtained from the trapping of the allyltin trichloride generated from the 4-hydroxypent-3-enylstannane **34** after reduction using diimide. Moreover, *O*-benzylation gave the benzyl ether **39** identical to that obtained from the transmetallation and trapping using the 4-benzyloxypent-2-enylstannane **35**. The 2-hydroxy- and 2-benzyloxy-pent-3-enyl(triphenyl)stannanes **42** and **43** obtained from the epoxide derived from the (*E*)-pent-2-ene oxide **40** were significantly different spectroscopically from their isomers **38** and **39** (^{1}H NMR), see Scheme 7.



Scheme 6 Synthesis and tin(IV) chloride mediated reactions of the 4-hydroxy and 4-benzyloxypent-2-enylstannanes **34** and **35**. Reagents and conditions: (i) BuLi, −78 °C, 15 min, ethanal, −78 °C, 1 h (91%); (ii) BnOC(NH)CCl$_3$, TFA, r.t., 18 h (91%); (iii) Ph$_3$SnH, AIBN (cat.), benzene, heat under reflux, 3 h (**34**, 56%; **35**, 42%); (iv) SnCl$_4$, −78 °C, 5 min, then PhCHO, −78 °C, 1 h (66%; 1,5-*syn* : 1,5-*anti* = 97 : 3); (v) SnCl$_4$, −78 °C, 5 min, PhLi, −78 °C, 1 h (**36**, 35%; **37**, 54%); (vi) NaOAc, H$_2$O, TsNHNH$_2$, DME, heat under reflux (**38**, 69%; **39**, 68%); (vii) NaH, THF, r.t., 1 h, then BnBr, TBAI, r.t., 15 h (63%).

The stereoselective formation of the internal triphenylstannanes **36** and **37** from interception of the allyltin trichlorides generated from the 4-hydroxy- and 4-benzyloxypent-2-enylstannanes **34** and **35** on treatment with tin(IV) chloride is consistent with the allyltin trichlorides having the *syn*-configuration as indicated in structure **46**, see Fig. 4. Trapping the allyltin trichlorides **46** by phenyllithium with retention of configuration of the stereogenic tin-bearing centre would then give the observed *syn*-



Scheme 7 Stereoselective synthesis of 2-hydroxy- and 2-benzyloxy-pent-3-yl(triphenyl)stannanes. Reagents and conditions: (i) LiN^{i}Pr$_2$, THF, hexanes, −78 °C, add Ph$_3$SnH, −78 °C, 1 h, add epoxide, −10 °C to r.t., 4 h (**41**, 30%; **42**, 19%; **45**, 22%; **38**, 23%); (ii) NaH, THF, BnBr, TBAI, r.t., 15 h (**43**, 61%; **39**, 72%).

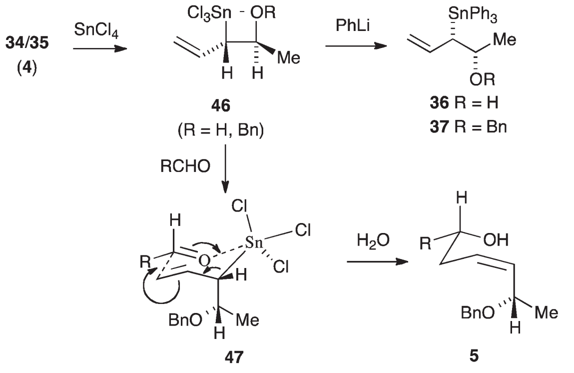
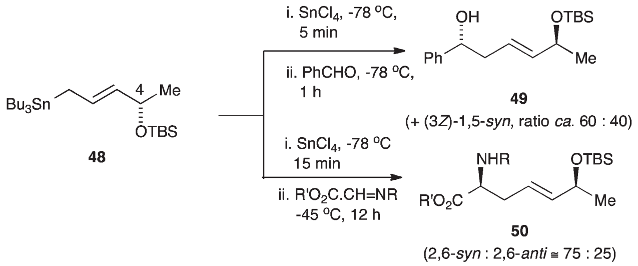


Fig. 4 Outline mechanism for the generation and reactions of allyltin trichlorides from 4-hydroxy- and 4-benzyloxypent-2-enyl(triphenyl)stannanes **34** and **35**.

triphenylstannanes **36** and **37**, and reaction with an aldehyde, possibly *via* the chair-like transition structure **47**, would give rise to the observed (3*Z*)-1,5-*syn*-products **5**.

In the 4-alkoxypent-2-enylstannane series, reactions of the 4-*tert*-butyldimethylsilyloxypent-2-enylstannane **48** with benzaldehyde and imines differed from the analogous reactions of the 4-benzyloxypentenylstannane **4** in that the (3*E*)-1,5-*anti*-isomer **49** was the major product with benzaldehyde[10] and the (4*E*)-2,6-*syn*-epimers **50** predominated with imines,[3] albeit in pretty non-stereoselective reactions. It was therefore decided to attempt to trap the allyltin trichlorides generated from a 4-silyloxypent-2-enylstannane.

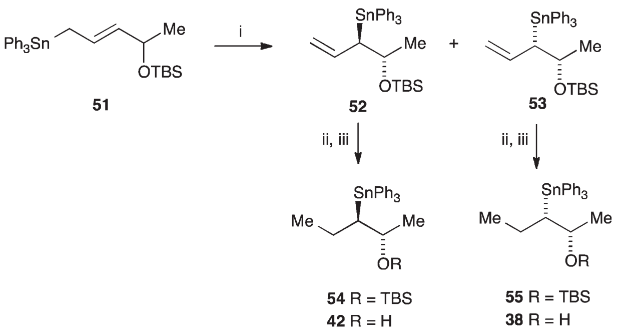


O-Silylation of the 4-hydroxypent-2-enyl(triphenyl)stannane **34** gave the *tert*-butyldimethylsilyl ether **51**. Following transmetallation using tin(IV) chloride and subsequent addition of phenyllithium, an approximately 50 : 50 mixture of the two internal pent-1-en-3-yl(triphenyl)stannanes **52** and **53** was obtained, see Scheme 8. The structures of these products were confirmed by hydrogenation using diimide and desilylation of the resulting pent-3-ylstannanes **54** and **55** which gave the known 2-hydroxypent-3-ylstannanes **42** and **38**. This shows that in the case of 4-(*tert*-butyldimethylsilyloxy)pent-2-enylstannanes the initial transmetallation is pretty non-stereoselective perhaps because the *O*-silyloxy substituent is not involved directly in delivering the trichlorotin substituent to the double-bond of the pent-2-enylstannane.

^{119}Tin NMR studies

^{119}Tin chemical shifts are very sensitive to the environment of the tin.[11] It was therefore of interest to study the ^{119}tin chemical shifts of the allyltin trichlorides generated by transmetallation of the alkoxypent-2-enylstannanes to see whether they were consistent with co-ordination of the tin by the alkoxy groups.[12,13] Transmetallation of prop-2-enyl(tributyl)- and -(triphenyl)-stannanes **56** and **59** gave prop-2-enyltin trichloride **57** and either tributyltin chloride **58** or triphenyltin chloride **60** with ^{119}Sn chemical shifts similar to those in the literature,[12,14,15] see Fig. 5. The ^{119}Sn chemical shifts observed for the 5-benzyloxy-4-methylpent-2-enyl(tributyl)- and -(triphenyl)-stannanes **1** and **8** were similar to those of the prop-2-enylstannanes **56** and **59**, respectively, indicating that, as would be expected, no significant co-ordination of the benzyloxy group to the tin in these benzyloxypentenylstannanes. The two peaks observed for the pentenylstannanes **1** and **8** were attributed to the presence of both (*E*)- and (*Z*)-isomers, (*E*) : (*Z*) *ca.* 70 : 30 and the shielding effect of the phenyl groups over the butyl groups is consistent with that observed for the simple prop-2-enyl(triphenyl)- and -(tributyl)-stannanes **56** and **59**. However, transmetallation of the 5-benzyloxypent-2-enyl(tributyl)- and (triphenyl)-stannanes **1** and **8** using tin(IV) chloride gave rise to a new ^{119}Sn peak at δ −197 that was assigned to the intermediate allyltin trichloride **21a**. The significant shielding observed for this intermediate relative to that of prop-2-enyltin trichloride **57**, δ −36, was attributed to co-ordination of the electron deficient tin by the benzyloxy-substituent.[11] Similarly transmetallation of the 4-benzyloxypent-2-enyl (triphenyl)stannane **35** gave rise to an intermediate with a ^{119}Sn chemical shift of δ −149 attributed to the co-ordinated allyltin trichloride **46a**.

These ^{1}H NMR studies are consistent with pentaco-ordinated tin trichlorides being involved in the reactions of the benzyloxypent-2-enylstannanes **1**, **8** and **35**.[11,16] The tin in the proposed four-membered ring intermediate **46a**, δ −149, is deshielded



Scheme 8 Trapping the allyltin trichlorides formed from the 4-(*tert*-butyldimethylsilyloxy)pent-2-enyl(triphenyl)stannane **51**. Reagents and conditions: (i) SnCl$_4$, −78 °C, 5 min, PhLi, −78 °C, 1 h (80%; **52** : **53** = 50 : 50); (ii) NaOAc, H$_2$O, TsNHNH$_2$, DME, heat under reflux 4 h (77%); (iii) TBAF, THF, r.t., 3 h (**42**, 12%; **38**, 26%).

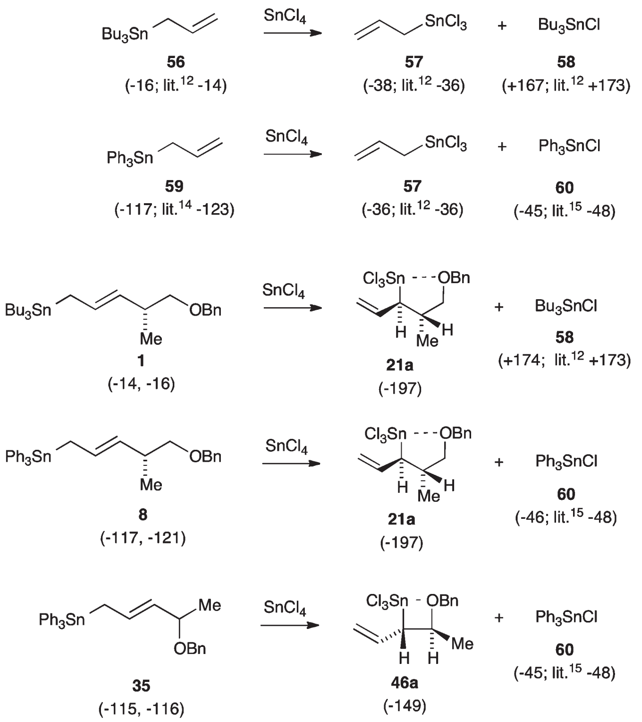


Fig. 5 ^{119}Tin NMR studies (chemical shifts in parentheses).

relative to that in the proposed five-membered ring intermediate **21a**, δ −197, consistent with the effect of ring size on ^{119}Sn chemical shifts.[11]

Summary and conclusions

The reactions of the intermediate allyltin trichlorides prepared from 5- and 4-benzyloxypent-2-enylstannanes **8** and **35** with phenyllithium gave the pent-1-en-3-yl(triphenyl)stannanes **9** and **37** stereoselectively. Since the pentenyl carbon–tin bond in the allyltin trichlorides is retained in these reactions, this work confirmed the configurations of the intermediate allyltin trichlorides shown in structures **21a** and **46a** that had been postulated on the basis of the stereoselectivities of their reactions with aldehydes. Moreover, since the pent-1-en-3-yltin trichloride **28**, generated from the internal pent-1-en-3-ylstannanes **9** and **24** gave different products with both aldehydes and phenyllithium from those obtained from the pent-1-en-3-yltin trichloride **21a**, the stereoselectivity of the initial transmetallation of the 5-alkoxypent-2-enylstannanes **8** must be due primarily to kinetic control, and the same is inferred for the stannane **35**, see Fig. 6.

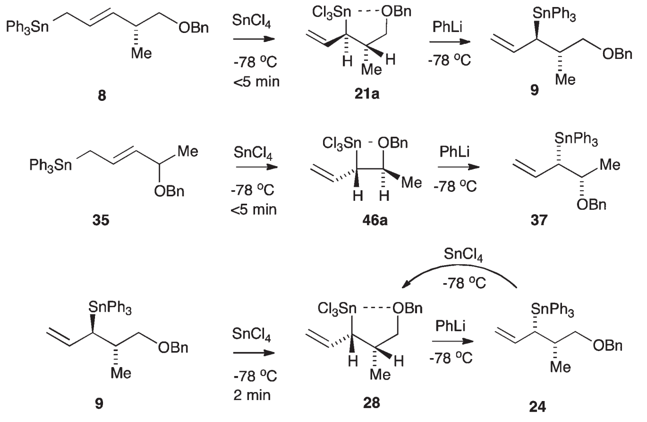


Fig. 6 Summary of trapping allyltin trihalides.

The co-ordinated structures with trigonal bipyramidal tin indicated in structures **21** and **46** are consistent with the ^{119}Sn NMR data.[11] Although dimeric structures that would avoid the formation of the four-membered ring shown in structure **21** can also be envisaged, the phenyllithium trapping experiments establish the configuration of the tin-bearing carbon in the intermediate allyltin trichlorides and it is the configuration at this centre that determines the stereoselectivity of reactions with aldehydes (and imines).

The generation of the (3*RS*,4*RS*)-5-benzyloxy-4-methylpent-1-enyltin trichloride **28** from both epimers **9** and **24** of 5-benzyoxy-4-methylpent-1-enyl(triphenyl)stannane was unexpected since these reactions involve *ipso* electrophilic substitutions, one with inversion and one with retention, at the more hindered end of an allylic system. It is possible that both of these reactions are SE′ type processes that generate a terminal allyltin trichloride that rapidly undergoes an allylic rearrangement to give the internal (3*RS*,4*RS*)-pent-1-enyltin trichloride **28**. With this in mind an outline summarising all of the transmetallations in the 5-benzyloxypentenylstannane series is suggested in Fig. 7. The initial transmetallation of the 5-benzyloxy-4-methylpent-2-enylstannane **8** gives the (3*RS*,4*SR*)-pent-1-en-3-yltin trichloride **21a** with excellent stereoselectivity by a kinetically controlled process. This then reacts with aldehydes to give the (3*Z*)-1,5-*anti*-products **2** with good overall stereoselectivity possibly by the transition structure **22** shown in Fig. 2. Trapping the tin trichloride **21a** using phenyllithium gives the *anti*-pent-1-en-3-yl-(triphenyl)stannane **9**. This may be transmetallated by tin(IV) chloride *via* an SE′ process to give the unstable 5-benzyloxypent-2-enyltin trichloride **61** which rapidly rearranges, with reasonable stereoselectivity, to give the (3*RS*,4*RS*)-pent-1-en-3-yltin trichloride **28**. In turn, this reacts with aldehydes to give the (3*Z*)-1,5-*syn*-products **23**, possibly *via* transition structure **29**, see Fig. 3, or is trapped by phenyllithium to give the *syn*-pent-1-en-3-ylstannane **24**. Transmetallation of this *syn*-pent-1-en-3-

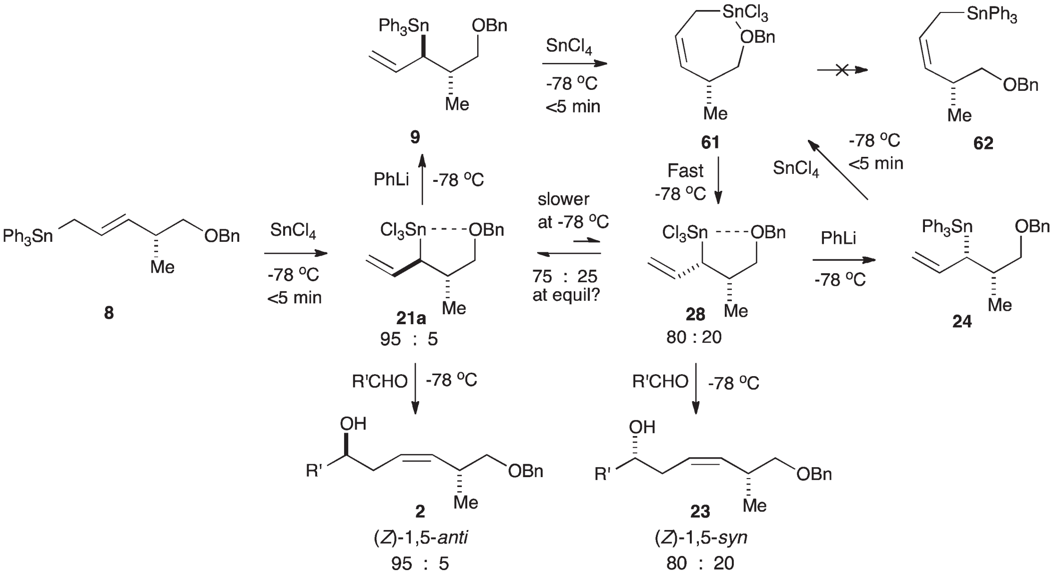


Fig. 7 Outline scheme for tin(IV) chloride promoted reactions in the 5-pentenyl(triphenyl)stannane series.

ylstannane again delivers the unstable primary allyltin trichloride **61** which rearranges into the (3*S*,4*S*)-pent-1-en-3-yltin trichloride **28** hence providing moderately stereoselective access to the (*Z*)-1,5-*syn*-products **23** on reaction with aldehydes and returning the *syn*-pent-1-en-3-ylstannane **24** when trapped by phenyllithium.[17]

In Fig. 7 it is suggested that the primary allyltin trichloride **61** isomerises to the (3*RS*,4*RS*)-pent-1-en-3-yltin trichloride **28** relatively rapidly but that equilibration of the (3*RS*,4*SR*)- and (3*RS*,4*RS*)-pent-1-en-3-intermediates **21a** and **28** is relatively slow. The evidence for this is that no 5-benzyloxy-4-methylpent-2-enyl(triphenyl)stannane **62** was isolated on trapping the intermediates from the transmetallation of the internal triphenylstannanes **9** and **24** and that the epimeric allyltin trichlorides **21a** and **28** give rise to substantially different products. However, there would appear to be some leakage from the (3*RS*,4*RS*)-epimer **28** to the (3*RS*,4*SR*)-epimer **21a** on standing as indicated by the reversal in stereoselectivity with aldehydes when the transmetallation time for the reaction of the *anti*-pentenylstannane **9** was increased. Indeed it looks as if an equilibrium mixture is *ca.* 75 : 25 in favour of the (3*RS*,4*SR*)-epimer **21a**, but this is only an estimate.[17,18]

Both antarafacial and suprafacial processes can be envisaged for the transmetallation of allylstannanes with tin(IV) chloride. However, the selective formation of the (3*RS*,4*SR*)-epimer **21a** from the pent-2-enylstannane **8** is consistent with the preferred reaction taking place *via* either the antarafacial transition structure **63**, in which the 4-methyl substituent is in the less hindered exo-position, or the suprafacial transition structure **64** with the 4-methyl in the preferred pseudo-equatorial position. For the alternative transition structures **65** and **66** that would give the (3*RS*,4*RS*)-allyltin trichloride **28**, the 4-methyl group is in either the more hindered endo or the pseudo-axial position, see Fig. 8.[19,20]

The selective isomerisation of the terminal allyltin trichloride **61** into the (3*RS*,4*RS*)-pent-1-en-3-yltin trichloride **28** is consistent with approach of the tin(IV) chloride on the opposite face of the 7-membered ring present in the co-ordinated allyltin trichloride **61** to the allylic methyl substituent. A suprafacial process *via* transition structure **67** for this is outlined in Fig. 9.[22]

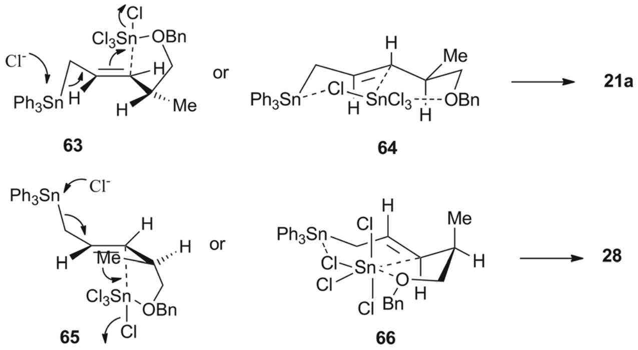


Fig. 8 Possible transition structures for transmetallation of the 5-benzyloxypent-2-enylstannane **8**.

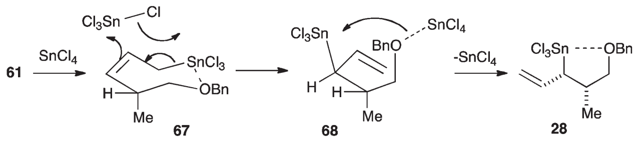


Fig. 9 Stereoselective isomerisation of the primary tin trichloride **61** into the secondary tin trichloride **28**.

The effect of an OTBS substituent on the stereoselectivity of transmetallation appears to vary according to its position in the pent-2-enylstannane. In the 5-position, there is a small attenuation on the 1,5-*anti*-stereocontrol,[7] whereas in the 4-position, an OTBS group delivers low stereoselectivity that if anything is reversed from that observed for 4-*O*-alkoxypent-2-enylstannanes.[10] It would appear that the bulky OTBS group is less effective at co-ordinating to the electron deficient tin in the allyltin trichloride intermediates and that this is more pronounced in the more compact 4-alkoxy series.

The mechanism of the reactions of allyltin trichlorides with aldehydes has not been studied. However, the high preference for *cis*-alkenol formation observed for tin(IV) halide mediated reactions of 4-, 5- and 6-substituted alk-2-enylstannnanes with aldehydes shows that the length of the tether connecting the alkoxy group does not appear to be critical in establishing *cis*-alkenol formation.[1] Thermal reactions of 1-substituted but-2-enylstannanes with aldehydes are known to give (*Z*)-alk-3-enols, and six-membered chair-like transition structures in which the group next to tin is axial have been postulated to rationalise this stereoselectivity.[23] For this reason, transition structures with penta-co-ordinated tin have been postulated for the reactions of the allyltin trichlorides **21**, **28** and **46** with aldehydes, see Fig. 2–4. However, the formation of *cis*-hex-3-enols from 4-alkoxypent-2-enylstannanes is also consistent with participation of a transition structure with octahedral tin[24,25] so this question remains to be resolved.

Experimental

General experimental procedures

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC-300, Varian Inova or Varian Gemini 200 spectrometers. Coupling constants are given in Hz. ^{119}Sn NMR spectra (112 MHz) were recorded at −80 °C in a 5 mm NMR tube using 0.15 mmol of substrate in 0.7 mL CD_2Cl_2. Chemical shifts are relative to TMS.

IR spectra were recorded on an ATI Mattson Genesis Series FTIR spectrometer as a thin film produced by evaporation of a chloroform solution on a sodium chloride plate. Low resolution chemical ionisation (C.I.) and electron impact (E.I.) mass spectra were recorded on a Fisons TRIO 2000 quadrupole mass spectrometer. High resolution mass spectra were recorded on a Kratos Concept-1S mass spectrometer coupled to a Mach 3 data system. Compounds containing tin showed characteristic clusters of peaks in their mass spectra, only those corresponding to ^{120}Sn are quoted.

All optical rotations were recorded at ambient temperature on an Optical Activity AA-100 polarimeter at 589 nm, using chloroform as the solvent.

Capillary gas chromatography was carried out on a Perkin-Elmer 8320 using a 25 m × 0.32 mm (ID) of CP-Sil-cB (OV-1), carrier gas He, split injection technique at 700 : 1 split ratio and FID detection. Chromatography refers to flash chromatography and was performed using Merck silica gel 60H (40–63 m, 230–300 mesh) as the stationary phase. Thin layer chromatography was performed using Machery Nagel DC-Fertigplatten SIL G-25 UV_{254} silica gel glass plates. Visualisation was by ultraviolet absorption at 254 nm and by treatment with 10% w/v methanolic dodecamolybdophosphoric acid followed by heating.

Light petroleum refers to the fraction of petroleum ether which boils between 40 °C and 60 °C and was redistilled prior to use. Tetrahydrofuran was dried over sodium–benzophenone and distilled under an atmosphere of nitrogen. DCM was dried over calcium hydride and distilled under an atmosphere of nitrogen. Ether refers to diethyl ether and was dried over sodium wire. Benzene and toluene were dried over sodium wire. Triethylamine and diisopropylamine were dried over potassium hydroxide pellets. All other commercially available reagents were purified following standard procedures.

General procedure for the tin(IV) halide promoted reactions of allylstannanes with aldehydes: (1*S*,5*R*,3*Z*)-6-benzyloxy-5-methyl-l-phenylhex-3-en-l-ol 2a[2a]

Tin(IV) chloride (0.185 mL, 1.0 M in DCM, 0.185 mmol) cooled to −78 °C was added to the stannane **8** (0.10 g, 0.185 mmol) in DCM (2 mL) at −78 °C. After 5 min, benzaldehyde (0.20 mL, 1.0 M in DCM, 0.20 mmol) cooled to −78 °C was added and the mixture stirred at −78 °C for 1 h. Saturated aqueous sodium hydrogen carbonate (2 mL) was added and the mixture allowed to warm to room temperature then partitioned between DCM (25 mL) and water (25 mL). The organic phase was washed with water (15 mL) and brine (15 mL) then dried ($MgSO_4$). After concentration under reduced pressure, chromatography of the residue using hexane : ether, (3 : 1) as eluent gave the title compound **2a**[2a] (40 mg, 73%) as a colourless oil (Found: M^+, 296.1781. $C_{20}H_{24}O_2$ requires *M*, 296.1776).

(3*R*,7*S*,5*Z*)-8-Benzyloxy-2,7-dimethyloct-5-en-3-ol 2b.[2a] Following the general procedure, stannane **8** (0.10 g, 0.185 mmol), tin(IV) chloride (0.185 mL, 0.185 mmol) and 2-methylpropanal (0.20 mL, 0.20 mmol), after chromatography using hexane : ether (3 : 1) as eluent gave the title compound **2b**[2a] (35 mg, 72%), as a colourless oil (Found: M^+, 263.2007. $C_{17}H_{26}O_2$ requires *M*, 263.2011).

(2*RS*,6*SR*,5*Z*)-8-Benzyloxy-7-methyloct-5-en-3-ol 2c.[2a] Following the general procedure, stannane **8** (0.416 g, 0.77 mmol), tin(IV) chloride (0.77 mL, 0.77 mmol) and propanal (0.92 mL, 0.92 mmol), after chromatography using hexane : ether (3 : 1) as eluent gave the title compound **2c**[2a] (90 mg, 47%), as a colourless oil (Found: $M^+ + NH_4$, 266.2119. $C_{16}H_{28}NO_2$ requires *M*, 266.2119).

(4*R*,2*E*)-5-Benzyloxy-4-methylpent-2-enyl(triphenyl)stannane 8

Triphenyltin hydride (4.17 g, 11.88 mmol) and α-azo-bis-isobutyronitrile (5 mg, cat.) were added to a thoroughly degassed solution of the dithiocarbonate **7**[2a] (2.9 g, 9.78 mmol) in benzene (150 mL) and the solution heated under reflux for 3 h. After concentration under reduced pressure, chromatography of the residue using light petroleum : ether (50 : 1) and triethylamine (1%) as eluent gave the *title compound* **8** (4.52 g, 86%) as a colourless oil, (*E*) : (*Z*) = 85 : 15 (^{1}H NMR) $[\alpha]_D$ +3.8 (*c* 0.73, $CHCl_3$) (Found: M^+, 540.1479. $C_{31}H_{32}O^{120}Sn$ requires *M*, 540.1475); ν_{max}/cm^{-1} 2924, 1480, 1453, 1428, 1094, 1075, 727 and 697; δ_H (300 MHz, $CDCl_3$) (*E*)-isomer 1.05 (3 H, d, *J* 7, 4-CH_3), 2.54 (3 H, m, 1-H_2 and 4-H), 3.24 (1 H, dd, *J* 7, 10, 5-H), 3.35 (1 H, dd, *J* 7, 10, 5-H), 4.54 and 4.60 (each 1 H, d, *J* 11, HC*H*Ph), 5.46 (1 H, dd, *J* 7, 15, 3-H), 5.86 (1 H, dt, *J* 15, 8, 2-H) and 7.35–7.72 (20 H, m, ArH); (*Z*)-isomer 0.93 (3 H, d, *J* 7, 4-CH_3), 2.88 (1 H, m, 4-H), 4.46 and 4.50 (each 1 H, d, *J* 11, HC*H*Ph) and 5.15 (1 H, t, *J* 10.5, 3-H); δ_C (75 MHz, $CDCl_3$) (*E*)-isomer 16.3, 17.5, 37.0, 72.9, 75.7, 127.2, 128.5, 128.6, 129.1, 131.0, 137.2, and 138.8; *m*/*z* (E.I.) 540 (30%), 463 (50), 351 (90) and 49 (100).

General procedure for trapping the intermediate allyltin trichlorides: (3*R*,4*S*)-5-benzyloxy-4-methylpent-1-en-3-yl-(triphenyl)stannane 9

Tin(IV) chloride (1.85 mL, 1.0 M in DCM, 1.85 mmol) was added to the stannane **8** (1.0 g, 1.85 mmol) in DCM (10 mL) at −78 °C. After 5 min, phenyllithium (6.16 mL, 1.8 M in cyc1ohexane : ether, 11.1 mmol) was added and the solution stirred at −78 °C for 2 h. Saturated ammonium chloride was added at −78 °C and the mixture allowed to warm to room temperature. After extraction with ether, the extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using hexane : ether (50 : 1) and triethylamine (1%) as eluent afforded the *title compound* **9** (0.64 g, 64%), as a colourless oil, containing *ca.* 10% of its *syn*-epimer **24** (^{1}H NMR) $[\alpha]_D$ −3.7 (*c* 1.17, $CHCl_3$) (Found: M^+, 540.1473. $C_{31}H_{32}O^{120}Sn$ requires *M*, 540.1475); ν_{max}/cm^{-1} 2922, 1480, 1453, 1428, 1092, 1074, 997, 841, 728 and 692; δ_H (300 MHz, $CDCl_3$) major *anti*-epimer **9** 1.12 (3 H, d, *J* 7, 4-CH_3), 2.46 (1 H, septet, *J* 7, 4-H), 3.15 (1 H, dd, *J* 6, 11, 3-H), 3.40 (2 H, d, *J* 6, 5-H_2), 4.25 and 4.32 (each 1 H, d, *J* 11, HC*H*Ph), 4.96 (2 H, m, 1-H_2), 6.14 (1 H, dt, *J* 10, 16, 2-H) and 7.21–7.66 (20 H, m, ArH); minor *syn*-epimer **24** 3.03 (1 H, m, 3-H) and 4.30 (2 H, s, CH_2Ph); δ_C (75 MHz, $CDCl_3$) 17.6, 35.5, 40.0, 72.8, 75.0, 112.8, 127.5, 127.7, 128.3, 128.4, 128.7, 137.3, and 139.6; *m*/*z* (E.I.) 540 (20%), 351 (60) and 91 (100).

General procedure for reduction of pent-1-en-3-ylstannanes: (2*S*,3*R*)-1-benzyloxy-2-methylpent-3-yl(triphenyl)stannane 10

Sodium acetate (1.73 g, 20.60 mmol) in water (12 mL) was added to the pent-1-enylstannane **9** (0.56 g, 1.03 mmol) and toluene 4-sulfonylhydrazide (2.30 g, 12.36 mmol) in DME (40 mL) under reflux over a period of 2 h. The solution was heated under reflux for a further 2 h and then allowed to cool to room temperature. The reaction mixture was extracted with ether, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum : ether (50 : 1) and triethylamine (1%) as eluent yielded the *title compound* **10** (0.40 g, 72%), as a colourless oil, as a 90 : 10 mixture of **10** and **25** (^{1}H NMR) $[\alpha]_D$ −9.3 (*c* 0.56, $CHCl_3$) (Found: $M^+ - Ph$, 465.1245. $C_{25}H_{29}O^{120}Sn$ requires *M*, 465.1240); ν_{max}/cm^{-1} 2924, 1480, 1453, 1427, 1073, 1022, 997, 728 and 698; δ_H

(300 MHz, $CDCl_3$) *anti*-epimer **10** 1.09 (6 H, m, 5-H_3, 2-CH_3), 1.95 (2 H, m, 4-H_2), 2.28 (1 H, dd, *J* 7, 3, 3-H), 2.47 (1 H, m, 2-H), 3.44 (2 H, d, *J* 6, 1-H_2), 4.30 (2 H, s, CH_2Ph), and 7.20–7.73 (20 H, m, ArH); *syn*-epimer **25** 3.31 (2 H, d, *J* 6, 1-H_2); δ_C (75 MHz, $CDCl_3$) 15.2, 17.9, 22.3, 35.3, 36.6, 72.7, 74.5, 127.5, 127.8, 128.3, 128.4, 137.5 and 141.0; *m/z* (C.I.) 465 (70%) and 78 (100).

5-*tert*-Butyldimethylsilyloxy-4-methylpent-2-enyl(triphenyl)stannane 14

Triphenyltin hydride (21.92 g, 62.4 mmol) and α-azo-bis-isobutyronitrile (50 mg) were added to a thoroughly degassed solution of the dithiocarbonate **13**[2c] (16.46 g, 51.4 mmol) in benzene (250 cm^3) and the solution heated under reflux for 3 h. After concentration under reduced pressure, chromatography of the residue using light petroleum : ether (50 : 1) and triethylamine (1%) as eluent gave the *title compound* **14** (17.79 g, 61%) as a colourless oil, (*E*) : (*Z*) = 85 : 15 (^{1}H NMR), (Found: $M^+ - Ph$, 487.1489. $C_{24}H_{35}OSi^{120}Sn$ requires *M*, 487.1478); ν_{max}/cm^{-1} 2955, 2928, 2855, 1470, 1428, 1254, 1076, 837, 776, 727, 698; δ_H (300 MHz, $CDCl_3$) (*E*)-isomer 0.10 (6 H, s, 2 × $SiCH_3$), 0.96 [12 H, m, $Si(CH_3)_3$ and 4-CH_3], 2.28 (1 H, m, 4-H), 2.46 (2 H, d, *J* 7, 1-H_2), 3.24 (1 H, dd, *J* 8, 9, 5-H), 3.45 (1 H, dd, *J* 5, 9, 5-H), 5.37 (1 H, dd, *J* 5, 7, 3-H), 5.78 (1 H dt, *J* 15, 7, 2-H) and 7.40–7.63 (15 H, m, ArH); (*Z*)-isomer 0.83 (3 H, d, *J* 7, 4-CH_3), 2.63 (1 H, m, 4-H), 3.39 (1 H, dd, *J* 5, 9, 5-H), 5.08 (1 H, t, *J* 10, 3-H); δ_C (75 MHz, $CDCl_3$) (*E*)-isomer −5.2(2), 16.3, 17.0, 18.5, 26.1, 39.5, 68.4, 128.8, 129.0, 130.9, 137.1 and 138.6; (*Z*)-isomer 12.7, 17.1, 34.6, 67.7; *m/z* (C.I.) 565 (2%), 487 (32) and 368 (100).

5-Hydroxy-4-methylpent-2-enyl(triphenyl)stannane 15

TBAF (93.5 mL, 1 M in THF, 93.5 mmol) was added to the stannane **14** (17.6 g, 31.19 mmol) in THF (150 mL) at 0 °C. After 4 h at room temperature, water (200 mL) was added and the mixture was extracted with ether, washed with water (100 mL) and brine (100 mL) then dried ($MgSO_4$). After concentration under reduced pressure, chromatography of the residue using light petroleum : ether (3 : 1) and triethylamine (1%) as eluent gave the *title compound* **15** (10.33 g, 74%) as a yellow oil (Found: $M^+ - C_6H_5$, 373.0612. $C_{15}H_{21}O^{120}Sn$ requires *M*, 373.0613); ν_{max}/cm^{-1} 3370, 3063, 2957, 2870, 1480, 1428, 1075, 1024, 971, 965, 728 and 699; δ_H (300 MHz, $CDCl_3$) (*E*)-isomer 0.94 (3 H, d, *J* 7, 4-CH_3), 2.29 (1 H, m, 4-H), 2.50 (2 H, d, *J* 8, 1-H_2), 3.25 (1 H, dd, *J* 8, 11, 5-H), 3.37 (1 H, dd, *J* 6, 11, 5-H), 5.27 (1 H, dd, *J* 8, 15, 3-H), 5.86 (1 H, dt, *J* 16, 8, 2-H) and 7.42–7.67 (15 H, m, ArH); (*Z*)-isomer 0.80 (3 H, d, *J* 7, 4-CH_3) and 5.05 (1 H, t, *J* 10, 3-H); δ_C (75 MHz, $CDCl_3$) 11.5, 16.3, 39.9, 46.2, 67.5, 128.7, 129.4, 130.6, 137.1 and 138.3; *m/z* (C.I.) 450 (M^+, 1%) and 373 (100).

[(3*RS*,4*SR*)-5-*tert*-Butyldimethylsilyloxy-4-methylpent-1-en-3-yl]-(triphenyl)stannane 16

The general procedure using stannane **14** (1.14 g, 2.02 mmol), tin(IV) chloride (2.02 mL, 1 M in DCM, 2.02 mmol) and phenyllithium (6.73 mL, 1.8 M, in cyclohexane–ether, 12.12 mmol), after chromatography using light petroleum : ether (50 : 1) and triethylamine (1%) as eluent, gave the *title compound* **16** (0.69 g, 61%) as a yellow oil (Found: $M^+ - C_6H_5$, 487.1476. $C_{24}H_{35}OSi^{120}Sn$ requires *M*, 487.1478); ν_{max}/cm^{-1} 3063, 2955, 2928, 2856, 1481, 1428, 1255, 1093, 1075, 838, 728 and 699; δ_H (300 MHz, $CDCl_3$) 0.03 and 0.05 (each 3 H, s, $SiCH_3$), 0.96 [9 H, s, $SiC(CH_3)_3$], 1.08 (3 H, d, *J* 7, 4-CH_3), 2.31 (1 H, m, 4-H), 3.38 (1 H, dd, *J* 5, 11, 3-H), 3.44 and 3.59 (each 1 H, dd, *J* 6, 8, 5-H), 4.99 (2 H, m, 1-H_2), 6.15 (1 H, dt, *J* 10, 16, 2-H) and 7.40–7.74 (15 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.3, −5.2, 16.6, 18.4, 26.0, 37.7, 39.1, 68.2, 112.9, 127.2, 128.4, 128.8, 137.3 and 139.1; *m/z* (C.I.) 487 (22%) and 318 (100).

[(3*RS*,4*SR*)-2-Methyl-1-hydroxypent-4-en-3-yl](triphenyl)-stannane 17

The general procedure using stannane **15** (1.0 g, 2.22 mmol), tin (IV) chloride (2.22 mL, 1 M in DCM, 2.22 mmol), and phenyllithium (7.41 mL, 1.8 M in cyclohexane–ether, 13.32 mmol), after chromatography using light petroleum : ether (3 : 1) and triethylamine (1%), gave the *title compound* **17** (0.42 g, 42%) as a yellow oil containing *ca.* 15% of its *syn*-epimer (^{1}H NMR) (Found: $M^+ - C_6H_5$, 373.0617. $C_{15}H_{21}O^{120}Sn$ requires *M*, 373.0613); ν_{max}/cm^{-1} 3386, 3063, 2959, 2833, 1480, 1428, 1073, 1024, 997, 895, 729 and 699; δ_H (300 MHz, $CDCl_3$) major *anti*-epimer **17** 0.91 (3 H, d, *J* 7, 2-CH_3), 2.27 (1 H, m, 2-H), 3.04 (1 H, dd, *J* 6, 11, 3-H), 3.57 (2 H, m, 1-H_2), 4.95 (2 H, m, 5-H_2), 6.13 (1 H, dt, *J* 11, 16, 4-H) and 7.36–7.64 (15 H, m, ArH); minor *syn*-epimer 3.16 (1 H, dd, *J* 6, 11, 3-H); δ_C (75 MHz, $CDCl_3$) 11.5, 39.7, 46.2, 67.7, 112.7, 128.4, 128.7, 137.3 and 139.6; *m/z* (C.I.) 373 (100%).

[(3*RS*,4*SR*)-1-*tert*-Butyldimethylsilyloxy-2-methylpent-3-yl]-(triphenyl)stannane 18

The general procedure using pentenylstannane **16** (0.57 g, 1.01 mmol), toluene 4-sulfonylhydrazide (2.25 g, 12.12 mmol), DME (50 mL) and sodium acetate (1.69 g, 20.2 mmol in water, 16 mL), after chromatography using light petroleum : ether, (50 : 1) and triethylamine (1%) gave the *title compound* **18** (0.36 g, 64%) as a colourless oil (Found: $M^+ - C_6H_5$, 489.1639. $C_{24}H_{37}OSi^{120}Sn$ requires *M*, 489.1635); ν_{max}/cm^{-1} 3063, 2955, 2856, 1428, 1255, 1097, 1074, 837, 776, 728 and 699; δ_H (300 MHz, $CDCl_3$) 0.05 and 0.07 (each 3 H, s, $SiCH_3$), 0.97 [9 H, s, $SiC(CH_3)_3$], 1.09 (6 H, m, 2-CH_3 and 5-H_3), 1.94 (2 H, m, 4-H_2), 2.40 (2 H, m, 3-H and 2-H), 3.50 (1 H, dd, *J* 7, 10, 1-H), 3.74 (1 H, dd, *J* 6, 10, 1-H) and 7.40–7.76 (15 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.4, −5.3, 15.6, 16.6, 18.4, 21.7, 26.1, 36.2, 37.9, 68.1, 127.2, 128.4, 128.8, 137.3 and 140.2; *m/z* (C.I.) 489 (100%).

[(3*RS*,4*SR*)-1-Hydroxy-2-methylpent-3-yl](triphenyl)stannane 19

The general procedure using pentenylstannane **17** (0.22 g, 0.48 mmol), toluene 4-sulfonylhydrazide (1.09 g, 5.86 mmol), DME (40 mL) and sodium acetate (0.82 g, 9.6 mmol in water, 10 mL), after chromatography using light petroleum : ether (3 : 1) and triethylamine (l%) as eluent, gave the *title compound* **19** (0.16 g, 74%) as a yellow oil (Found: $M^+ - C_6H_5$, 375.0766. $C_{15}H_{23}O^{120}Sn$ requires *M*, 375.0770); ν_{max}/cm^{-1} 3569, 3393, 3063, 2955, 2870, 1480, 1428, 1073, 1022, 997, 728 and 699; δ_H (300 MHz, $CDCl_3$) 0.91 (3 H, t, *J* 6, 5-H_3), 1.06 (3 H, d, *J* 6, 2-CH_3), 1.92 (2 H, m, 4-H_2), 2.14 (1 H, q, *J* 6, 3-H), 2.29 (1 H, m, 2-H), 3.63 (2 H, m, 1-H_2) and 7.35–7.67 (15 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 15.1, 17.6, 22.7, 36.1, 37.2, 66.8, 128.3, 137.2 and 141.1; *m*/*z* (C.I.) 375 (100%).

The hydroxypentylstannane **19** (134 mg, 0297 mmol) in THF (1 mL) was added to potassium *tert*-butoxide (38 mg, 0.342 mmol) in THF (1 mL) at ambient temperature. After 15 min, benzyl bromide (0.042 mL, 0.357 mmol) and TBAI (5 mg) in THF (1 mL) were added and the suspension stirred at room temperature for 15 h. Water (3 mL) was added and the mixture extracted with ether, washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum : ether (30 : 1) and triethylamine (1%) gave the benzyl ether **10** (77 mg, 48%) as a colourless oil (Found: $M^+ - C_6H_5$, 465.1234. $C_{25}H_{29}O^{120}Sn$ requires *M*, 465.1239); spectroscopic data were identical to those of a sample prepared by hydrogenation of pentenylstannane **9**.

The hydroxypentylstannane **19** (0.195 g, 0.432 mmol) in DCM (1 mL) was added to *tert*-butyldimethylsilyl chloride (0.072 g, 0.476 mmol) and imidazole (0.195 g, 0.865 mmol) in DCM (2 mL). After stirring at room temperature for 20 h, water (5 mL) was added and the mixture extracted with DCM and dried ($MgSO_4$). After concentration under reduced pressure chromatography of the residue using light petroleum : ether (5 : 1) and triethylamine (1%) as eluent gave the silyl ether **18** (0.21 g, 86%) as a colourless oil (Found: $M^+ - C_6H_5$, 489.1640. $C_{24}H_{37}OSi^{120}Sn$ requires *M*, 489.1635); spectroscopic data were identical to those of a sample prepared by hydrogenation of pentenylstannane **16**.

[(3*RS*,4*SR*)-1-(4-Bromobenzoyloxy)-2-methylpent-3-yl](triphenyl)stannane 20

Triethylamine (0.16 mL, 1.15 mmol) was added to the hydroxypentylstannane **19** (0.13 g, 0.287 mmol) and DMAP (cat.) in DCM (2.8 mL) at 0 °C. After 5 min, 4-bromobenzoyl chloride (0.126 g, 0.575 mmol) was added and the solution stirred for 3 h at room temperature. Saturated aqueous sodium carbonate (10 mL) was added and the mixture extracted with DCM, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum : ether (5 : 1) and triethylamine (l%) as eluent gave the *title compound* **20** (0.139 g, 77%) as a white solid which was recrystallised from hexane, mp 92–94 °C (Found: $M^+ - C_6H_5$, 557.0134. $C_{25}H_{26}{}^{79}BrO_2{}^{120}Sn$ requires *M*, 557.0138); ν_{max}/cm^{-1} 3425, 3063, 2959, 1720, 1590, 1428, 1397, 1269, 1173, 1102, 1072, 1012, 847, 757, 728 and 699; δ_H (300 MHz, $CDCl_3$) 1.04 (3 H, t, *J* 7, 5-H_3), 1.14 (3 H, d, *J* 7, 2-CH_3), 1.95 (2 H, m, 4-H_2), 2.35 (1 H, m, 3-H), 2.61 (1 H, m, 2-H), 4.20 (1 H, dd, *J* 7, 11, 1-H), 4.42 (1 H, dd, *J* 6, 10, 1-H), 7.36–7.70 (17 H, m, ArH) and 7.88 (2 H, d, *J* 8, ArH); δ_C (75 MHz, $CDCl_3$) 15.6, 17.0, 21.7, 34.9, 36.5, 65.9, 69.9, 128.7, 128.8, 131.1, 131.7, 137.2, 139.4 and 165.8; *m*/*z* (C.I.) 557 (68%) and 479 (100).

(1*RS*,5*RS*,3*Z*)-6-Benzyloxy-5-methyl-1-phenylhex-3-en-1-ol 23a

The general procedure with transmetallation using tin(IV) chloride (0.389 mL, 1.0 M in DCM, 0.389 mmol) and penten-3-ylstannane **9** (0.21 g, 0.389 mmol) in DCM (5 mL) for 2 min at −78 °C followed by addition of benzaldehyde (0.467 mL, 1.0 M in DCM, 0.467 mmol) after chromatography using hexane : ether, (3 : 1) as eluent gave a mixture of the 1,5-*syn*-hexenol **23a** (51 mg, 44%) containing *ca.* 25% of its 1,5-*anti*-epimer **2a** (^{1}H NMR) as a colourless oil. HPLC gave the *title compound* **23a** (Found: $M^+ + NH_4$, 314.2125. $C_{20}H_{28}NO_2$ requires *M*, 314.2120); ν_{max}/cm^{-1} 3432, 2925, 2872, 1453, 1090, 1073 and 738; δ_H (300 MHz, $CDCl_3$) 0.98 (3 H, d, *J* 7, 5-CH_3), 2.58 and 2.72 (each 1 H, m, 2-H), 2.90 (1 H, m, 5-H), 2.99 (1 H, br d, *J* 4, OH), 3.21 (1 H, t, *J* 8, 6-H), 3.35 (1 H, dd, *J* 6, 8, 6-H), 4.55 (2 H, s, CH_2Ph), 4.85 (1 H, m, 1-H), 5.36 (2 H, m, 3-H and 4-H) and 7.28–7.41 (10 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 17.5, 32.5, 36.9, 73.1, 74.9, 124.6, 125.7, 127.1, 127.7, 127.8, 128.2, 128.4, 136.8, 138.2 and 144.2; *m*/*z* (C.I.) 296 (10%), 279 (80) and 85 (100). The 1,5-*anti*-epimer **2a** (Found: $M^+ + NH_4$, 314.2131. $C_{20}H_{28}NO_2$ requires *M*, 314.2120) had spectroscopic data identical to those of samples prepared using the stannane **1**.

(3*RS*,7*RS*,5*Z*)-8-Benzyloxy-2,7-dimethyloct-5-en-3-ol 23b

The general procedure with 2 min for transmetallation using stannane **9** (0.108 g, 0.20 mmol), tin(IV) chloride (0.20 mL, 0.20 mmol) and 2-methylpropanal (0.22 mL, 0.22 mmol), after chromatography using hexane : ether (3 : 1) as eluent gave the *title compound* **23b** (11 mg, 21%) as a colourless oil (Found: $M^+ + NH_4$, 280.2272. $C_{17}H_{30}NO_2$ requires *M*, 280.2276); ν_{max}/cm^{-1} 3442, 2958, 2871, 1454, 1366, 1096, 1029 737 and 698; δ_H (300 MHz, $CDCl_3$) 0.96, 0.97 and 1.01 (each 3 H, d, *J* 7, CH_3), 1.68 (1 H, m, 2-H), 2.04 (1 H, d, *J* 5, OH), 2.33 (2 H, m, 4-H_2), 2.90 (1 H, m, 7-H), 3.35 (3 H, m, 3-H, 8-H_2), 4.52 (2 H, s, CH_2Ph), 5.47 (2 H, m, 5-H and 6-H) and 7.36 (5 H, s, ArH); δ_C (75 MHz, $CDCl_3$) 17.6, 18.1, 19.0, 32.3, 32.5, 33.0, 73.0, 75.1, 76.3, 125.8, 127.6, 127.6, 128.4, 136.4 and 138.4; *m*/*z* (C.I.) 280 (40%) and 263 (100). The minor product was the 1,5-*anti*-epimer **2b** (7 mg, 13%) (Found: $M^+ + NH_4$, 280.2277. $C_{17}H_{30}NO_2$ requires *M*, 280.2276) with spectroscopic data identical to those of an authentic sample prepared using stannane **1**.

(3*RS*,7*SR*,5*Z*)-8-Benzyloxy-7-methyloct-5-en-3-ol 23c

The general procedure with 2 min for transmetallation using, stannane **9** (0.11 g, 0.205 mmol), tin(IV) chloride (0.205 mL, 0.205 mmol) and propanal (0.247 mL, 0.247 mmol), after chromatography using hexane : ether (3 : 1) as eluent gave the *title compound* **23c** (30 mg, 60%) as a colourless oil containing its 1,5-*anti*-epimer **2c**, ratio **23c** : **2c** = 82 : 18 (^{1}H NMR) (Found: $M^+ + NH_4$, 266.2119. $C_{16}H_{28}NO_2$ requires *M*, 266.2120); ν_{max}/cm^{-1} 3419, 2960, 2927, 2858, 1454, 1095, 737 and 697; δ_H (300 MHz, $CDCl_3$) 0.95 (3 H, t, *J* 7, 1-H_3), 1.00 (3 H, d, *J* 7, 7-CH_3), 1.51 (2 H, m, 2-H_2), 2.24 (2 H, m, OH and 4-H), 2.39

(1 H, m, 4-H), 2.90 (1 H, m, 7-H), 3.32 (2 H, m, 8-H_2), 3.57 (1 H, m, 3-H), 4.54 (2 H, s, CH_2Ph), 5.47 (2 H, m, 5-H and 6-H) and 7.36 (5 H, s, ArH); δ_C (75 MHz, $CDCl_3$) 10.2, 17.6, 29.4, 32.5, 34.6, 72.6, 73.0, 75.0, 125.3, 127.6, 127.7, 127.6, 128.3, 136.5 and 138.4; *m/z* (C.I.) 266 (100%) and 249 (70).

[(3*RS*,4*RS*)-5-Benzyloxy-4-methylpent-l-en-3-yl](triphenyl)-stannane 24

Tin(IV) chloride (0.33 mL, 1.0 M in DCM, 0.33 mmol) was added to the pentenylstannane **9** (0.178 g, 0.33 mmol) in DCM (5 mL) at −78 °C. After 2 min, phenyllithium (1.10 mL, 1.8 M in cyclohexane : ether, 1.98 mmol) was added and the solution stirred at −78 °C for 2 h. Saturated ammonium chloride was added at −78 °C and the mixture allowed to warm to room temperature then extracted with ether. The ethereal extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using hexane : ether (50 : 1) and triethylamine (1%) as eluent afforded a mixture of the *title compound* **24** and its epimer **9** (96 mg, 54%) as a yellow oil, **24** : **9** = 80 : 20 (^1H NMR) (Found: $M^+ - C_6H_5$, 463.1083. $C_{25}H_{27}O^{120}Sn$ requires *M*, 463.1083); ν_{max}/cm^{-1} 3063, 3046, 1428, 1074, 728 and 699; δ_H (300 MHz, $CDCl_3$) major epimer **24** 1.05 (3 H, d, *J* 7, 4-CH_3), 2.46 (1 H, m, 4-H), 2.99 (1 H, dd, *J* 5, 11, 3-H), 3.36 (2 H, m, 5-H_2), 4.29 (2 H, s, CH_2Ph), 4.94 (2 H, m, 1-H_2), 6.12 (1 H, m, 2-H) and 7.30–7.75 (20 H, m, ArH); minor epimer **9** 1.10 (3 H, d, *J* 7, 4-CH_3), 3.13 (1 H, dd, *J* 6, 11, 3-H), 4.25 and 4.32 (each 1 H, *J* 11, HC*H*Ph); δ_C (75 MHz, $CDCl_3$) major epimer **24** 19.0, 35.4, 40.5, 72.9, 73.5, 112.6, 128.2, 128.5, 128.6, 137.2 and 140.1; *m/z* (C.I.) 541 (15), 463 (20) and 208 (100).

[(2*RS*,3*RS*)-1-Benzyloxy-2-methylpent-3-yl](triphenyl)stannane 25

The general procedure using pentenylstannane **24** (64 mg, 0.118 mmol), toluene 4-sulfonylhydrazide (0.265 g, 1.424 mmol), DME (5 mL) and sodium acetate (0.199 g, 2.37 mmol in water 2 mL), after chromatography using light petroleum : ether (50 : 1) and triethylamine (1%) as eluent, gave the *title compound* **25** (37 mg, 58%) as a colourless oil (Found: $M^+ - C_6H_5$, 465.1242. $C_{25}H_{29}O^{120}Sn$ requires *M*, 465.1239); ν_{max}/cm^{-1} 3062, 2955, 2857, 1428, 1073, 728 and 699; δ_H (300 MHz, $CDCl_3$) major *syn*-epimer **25** 1.08 (6 H, m, 2-CH_3, 5-H_3), 1.92 (2 H, m, 4-H_2), 2.37 (1 H, m, 3-H), 2.50 (1 H, m, 2-H), 3.31 (2 H, d, *J* 7, 1-H_2), 4.25 and 4.32 (each 1 H, d, *J* 12, HC*H*Ph) and 7.18–7.75 (20 H, m, ArH); minor *anti*-epimer **10** 3.44 (2 H, d, *J* 7, 1-H_2); δ_C (75 MHz, $CDCl_3$) 15.4, 18.2, 23.0, 35.7, 37.8, 72.9, 74.5, 127.8, 128.3, 137.3 and 140.9; *m/z* (C.I.) 465 (100%).

(3*RS*,7*RS*,5*Z*)-8-Benzyloxy-2,7-dimethyl-3-(4-nitrobenzoyloxy)-oct-5-ene 26

DEAD (0.053 mL, 0.338 mmol) was added to the 3,7-*anti*-7-methyloctenol **2b** (0.059 g, 0.225 mmol), triphenylphosphine (0.088 g, 0.338 mmol) and 4-nitrobenzoic acid (0.057 g, 0.338 mmol) in toluene (3 mL) at −60 °C and the solution allowed to warm to room temperature. After 20 h, water (5 mL) was added and the mixture was extracted with ether. The extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum : ether (3 : 1) as eluent gave the *title compound* **26** (38 mg, 41%) as a yellow oil (Found: $M^+ + NH_4$, 429.2383. $C_{24}H_{33}N_2O_5$ requires *M*, 429.2389); ν_{max}/cm^{-1} 2963, 2873, 1723, 1529, 1347, 1274, 1101 and 720; δ_H (300 MHz, $CDCl_3$) 0.83, 0.94 and 0.96 (each 3 H, d, *J* 6, CH_3), 1.98 (1 H, m, 2-H), 2.40 and 2.50 (each 1 H, m, 4-H), 2.75 (1 H, m, 7-H), 3.21 (2 H, m, 8-H_2), 4.25 and 4.35 (each 1 H, d, *J* 11, HC*H*Ph), 5.02 (1 H, dt, *J* 8, 5, 3-H), 5.23 (1 H, t, *J* 10, 6-H), 5.35 (1 H, dt, *J* 10, 7, 5-H), 7.26 (5 H, m, ArH) and 8.14 and 8.23 (each 2 H, d, *J* 9, ArH); δ_C (75 MHz, $CDCl_3$) 17.4, 17.5, 18.6, 29.5, 31.1, 32.4, 72.6, 74.8, 79.7, 123.1, 124.4, 127.0, 127.9, 130.2, 135.0, 137.8, 138.3 and 163.9; *m/z* (C.I.) 429 (35%), 412 (10) and 382 (100).

Sodium hydroxide (10 mg, 0.25 mmol) was added to the ester **26** (25 mg, 0.06 mmol) in methanol (3 mL) and the solution stirred at room temperature for 3 h. Water (10 mL) was added and the reaction mixture extracted with ether. The ethereal extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum : ether, (3 : 1) as eluent gave the 3,7-*syn*-alkenol **23b** (10 mg, 64%) as a colourless oil (Found: $M^+ + H$, 263.2008. $C_{17}H_{27}O_2$ requires *M*, 263.2010); spectroscopic data were identical to those of the alkenol **23b** prepared from the stannane **9**.

(3*RS*,7*SR*,5*Z*)-8-Benzyloxy-7-methyl-3-(4-nitrobenzoyloxy)oct-5-ene 27

DEAD (0.053 mL, 0.342 mmol) was added to the alcohol **2c** (0.056 g, 0.228 mmol), triphenylphosphine (0.0898 g, 0.342 mmol) and 4-nitrobenzoic acid (0.0573 g, 0.342 mmol) in toluene (3 mL) at −60 °C and the mixture allowed to warm to room temperature. After 20 h, water (5 mL) was added and the mixture was extracted with ether. The ethereal extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum : ether (3 : 1) as eluent yielded the *title compound* **27** (48 mg, 53%) as a yellow oil (Found: $M^+ + NH_4$, 415.2227. $C_{23}H_{31}N_2O_5$ requires *M*, 415.2233); ν_{max}/cm^{-1} 2967, 1722, 1529, 1349, 1275, 1102 and 720; δ_H (300 MHz, $CDCl_3$) 0.78 (3 H, d, *J* 7, 7-CH_3), 0.82 (3 H, t, *J* 7, 1-H_3), 1.70 (2 H, m, 2-H_2), 2.48 (2 H, m, 4-H_2), 2.77 (1 H, m, 7-H), 3.24 (2 H, m, 8-H_2), 4.45 (2 H, s, CH_2Ph), 5.08 (1 H, m, 3-H), 5.33 (2 H, m, 5-H and 6-H), 7.25 (5 H, m, ArH) and 8.15 and 8.25 (each 2 H, d, *J* 8, ArH); δ_C (75 MHz, $CDCl_3$) 9.6, 17.6, 26.5, 31.7, 32.4, 72.8, 74.9, 76.9, 123.2, 124.1, 127.1(2), 128.0, 130.3, 135.4, 135.7, 138.2 and 163.9; *m/z* (C.I.) 415 (88%), 398 (22) and 368 (100).

Sodium hydroxide (10 mg, 0.25 mmol) was added to the ester **27** (38 mg, 0.095 mol) in methanol (3 mL) and the solution stirred at room temperature for 3 h. Water (10 mL) was added and the mixture extracted with ether. The ethereal extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum : ether, (3 : 1) as eluent afforded the 3,7-*syn*-alkenol **23c** (15 mg, 63%) as a colourless oil (Found: $M^+ + H$, 249.1854. $C_{16}H_{25}O_2$ requires *M*, 249.1854); spectroscopic data were identical to those of the alkenol **23c** prepared from the stannane **9**.

(3*RS*,4*SR*)-5-Benzyloxy-4-methylpent-1-en-3-yl(trimethyl)-stannane 30

Tin(IV) chloride (0.285 mL, 1.0 M in DCM, 0.285 mmol) was added to the stannane **8** (0.154 g, 0.285 mmol) in DCM (2 mL) at −78 °C. After 5 min, methyllithium (1.22 mL, 1.4 M in ether, 1.71 mmol) was added and the solution stirred at −78 °C for 2 h. Saturated aqueous ammonium chloride was added at −78 °C and the mixture allowed to warm to room temperature then extracted with ether. The ethereal extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using hexane : ether (50 : 1) and triethylamine (1%) as eluent afforded the *title compound* **30** (20 mg, 20%) as a colourless oil (Found: ($M^+ - CH_3$, 339.0775. $C_{15}H_{23}O^{120}Sn$ requires *M*, 339.0770); ν_{max}/cm^{-1} 2961, 2858, 1619, 1454, 1095, 886, 765 and 697; δ_H (300 MHz, $CDCl_3$) 0.10 (9 H, s, 3 × $SnCH_3$), 1.04 (3 H, d, *J* 6, 4-CH_3), 2.16 (1 H, m, 4-H), 2.26 (1 H, dd *J* 6, 9, 3-H), 3.32 and 3.39 (each 1 H, dd *J* 8, 6, 5-H), 4.52 (2 H, s, CH_2Ph), 4.80 (2 H, m, 1-H_2), 5.89 (1 H, dt, *J* 9, 17, 2-H) and 7.37 (5 H, s, ArH); δ_C (75 MHz, $CDCl_3$) −9.6, 17.2, 35.5, 37.9, 65.9, 73.1, 109.7, 127.5, 127.7, 128.3, 138.6 and 139.5; *m/z* (C.I.) 339 (12%) and 182 (100).

Tin(IV) chloride (0.338 mL, 1.0 M in DCM, 0.338 mmol) was added to the stannane **30** (0.120 g, 0.338 mmol) in DCM (4 mL) at −78 °C. After 2 min, phenyllithium (1.13 mL, 1.8 M in cyclohexane : ether, 2.03 mmol) was added and the solution stirred at −78 °C for 2 h. Saturated aqueous ammonium chloride was added at −78 °C and the mixture allowed to warm to room temperature then extracted with ether. The ethereal extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using hexane : ether (50 : 1) and triethylamine (1%) as eluent afforded the *syn*- and *anti*-pent-1-en-3-yl (triphenyl)stannanes **24** and **9**, ratio **24** : **9** = 60 : 40 (^1H NMR) (96 mg, 54%) as a yellow oil (Found: M^+, 540.1470. $C_{31}H_{32}O^{120}Sn$ requires *M*, 540.1474); spectroscopic data were identical to those of the stannanes **24** and **9** prepared earlier.

Transmetallation and trapping the tin(IV) chloride from the [(3*RS*,4*RS*)-5-benzyloxy-4-methylpent-l-en-3-yl](triphenyl)-stannane 24

A cooled solution of tin(IV) chloride (0.268 mL, 1.0 M in dichloromethane, 0.268 mmol) was added to the stannane **24** (0.145 g, 0.268 mmol) in DCM (3 mL) at −78 °C. After 3 min, benzaldehyde (0.322 mL, 1.0 M in DCM, 0.322 mmol) was added and the mixture stirred at −78 °C for 1 h. Saturated aqueous sodium hydrogen carbonate (2 mL) was added at −78 °C and the mixture allowed to warm to room temperature then partitioned between DCM (25 cm^3) and water (25 cm^3). The organic phase was washed with water (15 mL) and brine (15 mL) then dried ($MgSO_4$). After concentration under reduced pressure, chromatography using hexane : ether (3 : 1) gave a mixture of the 1,5-*syn*- and 1,5-*anti*-hex-3-enols **23a** and **2a** (33 mg, 42%) as a colourless oil, **23a** : **2a** = 80 : 20 (^1H NMR) (Found: $M^+ + NH_4$, 314.2126. $C_{20}H_{28}NO_2$ requires *M*, 314.2119); spectroscopic data were identical to those of earlier samples.

Tin(IV) chloride (0.370 mL, 1.0 M in DCM, 0.370 mmol) was added to a cooled solution of stannane **24** (0.200 g, 0.370 mmol) in DCM (2 mL) at −78 °C. After 5 min, phenyllithium (1.23 mL, 1.8 M in cyclohexane : ether, 2.22 mmol) was added and the suspension stirred at −78 °C for 2 h. Saturated ammonium chloride (3 mL) was added at −78 °C and the mixture allowed to warm to room temperature then extracted with ether. The ethereal extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using hexane : ether (50 : 1) and triethylamine (1%) as eluent afforded a mixture of the stannanes **24** and **9** (87 mg, 44%) as a yellow oil, **24** : **9** = 66 : 34 (^1H NMR) (Found: $M^+ - C_6H_5$, 463.1075. $C_{25}H_{27}O^{120}Sn$ requires *M*, 463.1082); spectroscopic data were identical to those of earlier samples.

2-Hydroxypent-4-en-3-yl phenyl sulfone 32

^{n}Butyllithium (31.7 mL, 1.6 M in hexanes, 50.72 mmol) was added to phenyl (prop-2-en-1-yl) sulfone **31** (7.4 mL, 48.0 mmol) in THF (45 mL) at −78 °C. After 15 min, ethanal (3.3 mL, 59.04 mmol) in THF (45 mL) was added and the solution stirred at −78 °C for 1 h. Water (50 mL) was added and the mixture allowed to warm to room temperature then extracted with ether. The organic extracts were washed with brine (100 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue using light petroleum : ether (1 : 1) as eluent gave the *title compound* **32** (9.93 g, 91%) as a colourless oil, a 60 : 40 mixture of diastereoisomers (Found: $M^+ + NH_4$, 244.1011. $C_{11}H_{18}NO_3S$ requires *M*, 244.1007); ν_{max}/cm^{-1} 3513, 1447, 1305, 1288, 1146, 1082, 937, 756, 722 and 689; δ_H (500 MHz, $CDCl_3$) 1.16 (3 H, m, 1-H_3), 3.13 (0.6 H, s, OH), 3.38 (0.6 H, d, *J* 10, 3-H), 3.52 (0.4 H, dd, *J* 8.5, 10, 3-H), 4.00 (0.4 H, s, OH), 4.42 (0.4 H, m, 2-H), 4.65 (0.6 H, m, 2-H), 4.92 (0.4 H, d, *J* 17.1, 5-H), 4.98 (0.6 H, d, *J* 17.3, 5-H), 5.21 (0.4 H, d, *J* 10.3, 5-H), 5.35 (0.6 H, d, *J* 10.3, 5-H), 5.46 (0.4 H, dt, *J* 10.3, 17, 4-H), 5.97 (0.6 H, m, 4-H) and 7.48–7.82 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 20.7, 21.0, 64.4, 65.3, 74.7, 76.6, 124.4, 125.5, 126.0, 127.6, 128.9, 129.0, 129.2, 134.0, 134.1, 137.0 and 137; *m/z* (C.I.) 244 (M^+ + 18, 100%), 227 (M^+ + 1, 8) and 209 (10).

2-Benzyloxypent-4-en-3-yl phenyl sulfone 33

Benzyl trichloroacetimidate (13.6 mL, 73.12 mmol) in cyclohexane (20 mL) was added to the sulfone **32** (5.51 g, 24.37 mmol) in cyclohexane : DCM (120 mL, 5 : 1) at room temperature. Trifluoromethanesulfonic acid (10 drops) was added and the suspension stirred at room temperature for 16 h. Water (100 mL) was added and the suspension stirred for a further 1 h. The mixture was filtered through Celite and the precipitate washed with cyclohexane (2 × 50 mL). The filtrate and washings were washed with saturated aqueous sodium hydrogen carbonate (100 mL) and brine (100 mL) then dried ($MgSO_4$). After concentration under reduced pressure, chromatography of the residue using light petroleum : ether (3 : 1) as eluent gave the *title compound* **33** (8.32 g, 91%) as an orange oil, a 60 : 40 mixture of diastereoisomers (Found: M^+ + NH_4, 334.1471. $C_{18}H_{24}NO_3S$ requires *M*, 334.1477); ν_{max}/cm^{-1} 3062, 3028, 2980, 2930, 1495, 1447, 1306, 1146, 1083, 1027, 998, 936, 723 and 691; δ_H (300 MHz, $CDCl_3$) 1.24 (1.8 H, d, *J* 6, 1-H_3), 1.40 (1.2 H, d, *J* 6, 1-H_3), 3.50 (0.6 H, d, *J* 10, 3-H), 3.86 (0.4 H, dd, *J* 10, 5, 3-H), 4.36 (0.4 H, m, 2-H), 4.49–4.74 (2.6 H, m, $PhCH_2O$ and 2-H), 5.08 (0.4 H, d, *J* 17 5-H), 5.16 (0.6 H, d, *J* 17, 5-H), 5.39 (0.4 H, d, *J* 10, 5-H), 5.44 (0.6 H, d, *J* 10, 5-H), 5.93 (1 H, m, 4-H) and 7.20–7.86 (10 H, m, ArH); *m*/*z* (C.I.) 334 (M^+ + 18, 100%) and 317 (M^+ + 1, 5).

4-Hydroxypent-2-en-1-yl(triphenyl)stannane 34

Triphenyltin hydride (8.98 g, 25.5 mmol) and α-azo-bis-isobutyronitrile (0.42 g, 10 mol%) were added to a degassed solution of the sulfones **32** (5.26 g, 23.2 mmol) in benzene (100 mL) and the solution heated under reflux for 3 h. After concentration under reduced pressure, chromatography of the residue using light petroleum : ether (1 : 1) and triethylamine (1%) as eluent gave the *title compound* **34** (5.72 g, 56%) as a colourless oil, a 67 : 33 mixture of (*E*)- and (*Z*)-isomers, ν_{max}/cm^{-1} 3420, 3063, 2970, 1652, 1480, 1447, 1428, 1318, 1306, 1147, 1075, 997, 965, 935, 867, 728 and 699; δ_H (300 MHz, $CDCl_3$) (*E*)-isomer 1.16 (3 H, d, *J* 6.3, 5-H_3), 2.44 (2 H, d, *J* 8.7, 1-H_2), 4.17 (1 H, m, 4-H), 5.46 (1 H, dd, *J* 7.3, 15.1, 3-H), 5.88 (1 H, m, 2-H) and 7.32–7.72 (15 H, m, ArH); (*Z*)-isomer 1.04 (3 H, d, *J* 6.3, 5-H_3), 4.47 (1 H, m, 4-H) and 5.24 (1 H, t *J* 9, 3-H); *m*/*z* (C.I.) 418 (60%), 368 (100) and 78 (43).

4-Benzyloxypent-2-en-1-yl(triphenyl)stannane 35

Triphenyltin hydride (10.99 g, 31.3 mmol) and α-azo-bis-isobutyronitrile (0.51 g, 10 mol%) were added to a degassed solution of sulfone **33** (8.25 g, 26.1 mmol) in benzene (150 mL) and the solution was heated under reflux for 3 h. After concentration under reduced pressure, chromatography of the residue using light petroleum : ether (30 : 1) and triethylamine (1%) as eluent gave the *title compound* **35** (5.74 g, 42%) as a colourless oil; ν_{max}/cm^{-1} 3063, 2973, 2860, 1480, 1453, 1428, 1073, 1023, 997, 965, 728 and 699; δ_H (300 MHz, $CDCl_3$) 1.21 (3 H, d, *J* 6.3, 5-H_3), 2.51 (2 H, d, *J* 8.4, 1-H_2), 3.82 (1 H, m, 4-H), 4.17 and 4.39 (each 1 H, d, *J* 12, HC*H*Ph), 5.41 (1 H, dd, *J* 8.3, 15.3, 3-H), 5.85 (1 H, dt, *J* 15, 7, 2-H) and 7.20–7.70 (20 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 15.9, 21.9, 69.2, 75.7, 127.1, 127.5, 128.1, 128.5, 129.0, 130.0, 130.3, 136.9, 138.1 and 138.9; *m*/*z* (C.I.) 368 (100%), 326 (28) and 292 (30).

A cooled solution of tin(IV) chloride (0.203 mL, 1.0 M in DCM, 0.203 mmol) was added to the stannane **35** (0.107 g, 0.203 mmol) in DCM (2 mL) at −78 °C. After 5 min, a cooled solution of benzaldehyde (0.244 mL, 1.0 M in DCM, 0.244 mmol) was added and the mixture stirred at −78 °C for 1 h. Saturated aqueous sodium hydrogen carbonate (2 mL) was added. The mixture allowed to warm to room temperature then partitioned between DCM (25 mL) and water (25 mL). The organic phase was washed with water (15 mL) and brine (15 mL) then dried ($MgSO_4$). After concentration under reduced pressure, chromatography of the residue using hexane : ether (3 : 1) as eluent gave the (*Z*)-1,5-*syn*-5-benzyloxy-1-phenylhex-3-en-1-ol **5a** (38 mg, 66%) as a colourless oil (Found: M^+ + NH_4, 300.1966. $C_{19}H_{26}NO_2$ requires *M*, 300.1963); spectroscopic data were identical to those of an authentic sample.

(2*RS*,3*RS*)-2-Hydroxypent-4-en-3-yl(triphenyl)stannane 36

The general procedure with a 5 min transmetallation time using stannane **34** (1.07 g, 2.45 mmol), tin(IV) chloride (2.45 mL, 2.45 mmol) and phenyllithium (8.17 mL, 1.8 M in cyclohexane–ether, 14.72 mmol), after chromatography using light petroleum : ether (3 : 1) and triethylamine (1%) as eluent gave the *title compound* **36** (0.37 g, 35%) as a colourless oil; ν_{max}/cm^{-1} 3568, 3048, 2969, 1623, 1480, 1428, 1110, 1074, 908, 730 and 700; δ_H (300 MHz, $CDCl_3$) 1.34 (3 H, d, *J* 6, 1-H_3), 1.89 (1 H, d, *J* 5, OH), 3.09 (1 H, dd, *J* 6, 5, 3-H), 4.28 (1 H, m, 2-H), 4.91 (1 H, d, *J* 10, 5-H), 4.97 (1 H, d, *J* 17, 5-H), 6.10 (1 H, dt, *J* 17, 10, 4-H) and 7.36–7.77 (15 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 24.3, 48.3, 69.7, 112.5, 128.7, 128.9, 137.4, 137.9 and 139.6; *m*/*z* (C.I.) 368 (99%), 152 (100), 135 (40) and 78 (53).

(2*RS*,3*RS*)-2-Benzyloxypent-4-en-3-yl(triphenyl)stannane 37

Tin(IV) chloride (0.95 mL, 1.0 M in DCM, 0.95 mmol) was added to the stannane **35** (0.50 g, 0.950 mmol) in DCM (8 mL) at −78 °C. After 5 min, phenyllithium (3.2 mL, 1.8 M in cyclohexane : ether, 5.76 mmol) was added and the solution stirred at −78 °C for 1 h. Saturated aqueous ammonium chloride (10 mL) was added at −78 °C and the mixture allowed to warm to room temperature. The mixture was extracted with ether (3 × 10 mL) and the ethereal extracts dried ($MgSO_4$). After concentration under reduced pressure, chromatography of the residue using hexane : ether (50 : 1) and triethylamine (1%) as eluent afforded the *title compound* **37** (0.27 g, 54%) as a colourless oil; ν_{max}/cm^{-1} 3062, 2969, 2863, 1623, 1480, 1428, 1073, 1024, 997, 894, 729 and 699; δ_H (300 MHz, $CDCl_3$) 1.31 (3 H, d, *J* 6, 1-H_3), 3.12 (1 H, dd, *J* 7, 10, 3-H), 3.98 (1 H, m, 2-H), 4.18 and 4.56 (each 1 H, d, *J* 11, PhHC*H*), 4.87 (1 H, d, *J* 10, 5-H), 4.95 (1 H, d, *J* 17, 5-H), 6.12 (1 H, dt, *J* 10, 17, 4-H) and 7.03–7.76 (20 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 19.7, 47.0, 70.5, 76.7, 111.7, 128.2, 128.3, 128.4, 137.5 and 139.8; *m*/*z* (C.I.) 373 (5%), 368 (80) and 78 (100).

(2*RS*,3*RS*)-2-Hydroxypent-3-yl(triphenyl)stannane 38

The general procedure using stannane **36** (0.45 g, 1.03 mmol), toluene 4-sulfonylhydrazide (2.30 g, 12.35 mmol), DME (40 mL) and sodium acetate (1.69 g, 20.61 mmol in water, 14 mL), after chromatography using light petroleum : ether (3 : 1) and triethylamine (1%) as eluent, afforded the *title compound* **38** (0.31 g, 69%) as a colourless oil; ν_{max}/cm^{-1} 3400, 3063, 2959, 1428, 1073, 782 and 699; δ_H (300 MHz, $CDCl_3$) 1.11 (3 H, t, *J* 7, 5-H_3), 1.30 (3 H, d, *J* 7, 1-H_3), 1.94 (3 H, m, 4-H_2 and OH), 2.24 (1 H, q, *J* 7, 3-H), 4.29 (1 H, quin, *J* 6, 2-H) and 7.37–7.76 (15 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 14.8, 23.8, 24.6, 44.8, 70.0, 128.0, 128.4, 128.5, 137.3 and 140.5; *m*/*z* (C.I.) 368 (86%), 152 (60), 94 (70) and 78 (100).

(2*RS*,3*RS*)-2-Benzyloxypent-3-yl(triphenyl)stannane 39

The general procedure using stannane **37** (0.107 g, 0.203 mmol), toluene 4-sulfonylhydrazide (0.45 g, 2.436 mmol), DME (10 mL) and sodium acetate (0.34 g, 0.414 mmol in water, 2 mL), after chromatography using light petroleum : ether (50 : 1) and triethylamine (1%) as eluent, gave the *title compound* **39** (0.073 g, 68%) as a colourless oil; ν_{max}/cm^{-1} 3063, 2960, 2868, 1480, 1428, 1073, 728 and 699; δ_H (300 MHz, $CDCl_3$) 1.02 (3 H, t, *J* 8, 5-H_3), 1.29 (3 H, d, *J* 6, 1-H_3), 1.96 (2 H, m, 4-H_2), 2.26 (1 H, m, 3-H), 4.01 (1 H, quint, *J* 6, 2-H), 4.32 and 4.64 (each 1 H, d, *J* 11, PhHC*H*) and 7.12–7.80 (20 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 15.0, 20.1, 24.2, 43.5, 70.6, 77.3, 127.8, 128.2, 128.4, 129.2, 136.8, 137.2 and 140.7; *m/z* (C.I.) 444 (7%), 427 (17), 368 (100) and 78 (79).

The hydroxypentylstannane **38** (0.20 g, 0.456 mmol) in THF (2 mL) was added to a stirred suspension of sodium hydride (55 mg, 1.36 mmol, 60% dispersion) in THF (2 mL) at 0 °C. After 1 h at room temperature, benzyl bromide (0.108 mL, 0.91 mmol) and TBAI (5 mg) were added and the mixture stirred at room temperature overnight. Water (5 mL) was added and the mixture was extracted with ether (3 × 5 mL). The ethereal extracts were washed with brine (10 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum : ether (50 : 1) and triethylamine (1%) as eluent gave the benzyloxypentylstannane **39** (151 mg, 63%) as a colourless oil with spectroscopic data identical to those of the sample prepared by reduction of stannane **37**.

(2*RS*,3*RS*)-2-Ethyl-3-methyloxirane 40[8]

N-Bromosuccinimide (15.81 g, 88.82 mmol) was added portionwise to (*E*)-pent-2-ene (9.6 mL, 88.82 mmol) in water (25 mL) such that the temperature remained below 45 °C. The mixture was stirred at room temperature for 18 h. Two layers formed and the lower layer was separated. This layer was slowly added to a solution of potassium hydroxide (13.45 g, 0.239 mol) in water (30 mL). During the course of the addition (~1 h) a lighter yellow layer separated. The solution was saturated with sodium chloride and the layers separated. The top layer was dried ($MgSO_4$) and then fractionally distilled, bp 80 °C/760 mm (lit.[8] bp 80.2 °C/750 ± 15 mm) to afford the title compound **40** (2.27 g, 30%) as a colourless liquid; δ_H (300 MHz, $CDCl_3$) 1.20 (3 H, t, *J* 7.5, CH_3CH_2), 1.33 (3 H, d, *J* 5.21, CH_3CH), 1.59 (2 H, m, CH_2CH_3), 2.65 (1 H, dt, *J* 2, 5, 2-H) and 2.80 (1 H, dq, *J* 2, 5, 3-H); δ_C (75 MHz, $CDCl_3$) 9.8, 17.6, 25.0, 54.2 and 60.8; *m/z* (C.I.) 87 (M^+ + 1, 70%), 86 (30), 69 (88) and 45 (100).

(2*RS*,3*SR*)-3-Hydroxypent-2-yl(triphenyl)stannane 41 and (2*RS*,3*SR*)-2-hydroxypent-3-yl(triphenyl)stannane 42

^{n}Butyllithium (1.91 mL, 1.58 M in hexanes, 3.02 mmol) was added to di-isopropylamine (0.425 mL, 3.02 mmol) in THF (2 mL) at 0 °C. After 5 min, the solution was cooled to −78 °C and triphenyltin hydride (1.06 g, 3.02 mmol) in THF (2 mL) was added. The yellow suspension was stirred at −78 °C for 1 h, warmed to −10 °C and epoxide **40** (0.130 g, 1.51 mmol) in THF (1 mL) was added. The solution was stirred at room temperature for 4 h then saturated aqueous ammonium chloride (3 mL) was added. The mixture was extracted with ether (3 × 5 mL) and the organic extracts were washed with brine (10 mL) then dried ($MgSO_4$). After concentration under reduced pressure, chromatography of the residue using light petroleum : ether (5 : 1) and triethylamine (1%) as eluent gave the *title compound* **41** (0.20 g, 30%) as a colourless oil; ν_{max}/cm^{-1} 3570, 3434, 3062, 2960, 2868, 1578, 1480, 1428, 1073, 971, 913, 728 and 700; δ_H (300 MHz, $CDCl_3$) 0.98 (3 H, t, *J* 7, 5-H_3), 1.45 (3 H, d, *J* 7, 1-H_3), 1.54–1.78 (2 H, m, 4-H_2), 1.81 (1 H, d, *J* 5, OH), 2.43 (1 H, dq, *J* 4, 7, 2-H), 3.98 (1 H, m, 3-H) and 7.38–7.80 (15 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 10.7, 11.9, 28.6, 30.1, 75.9, 128.3, 128.6, 137.2 and 139.3; *m/z* (C.I.) 368 (100%) and 78 (33%). The second fraction contained the *title compound* **42** (0.128 g, 19%) as a colourless oil; ν_{max}/cm^{-1} 3569, 3432, 3062, 2959, 2869, 1480, 1428, 1073, 998, 728 and 699; δ_H (300 MHz, $CDCl_3$) 0.91 (3 H, t, *J* 7, 5-H_3), 1.19 (3 H, d, *J* 6, 1-H_3), 1.53 (1 H, d, *J* 5, OH), 1.79 (2 H, m, 4-H_2), 2.23 (1 H, m, 3-H), 4.25 (1 H, m, 2-H) and 7.24–7.62 (15 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 15.3, 21.0, 23.2, 43.4, 69.6, 128.3, 128.5, 137.2 and 139.9; *m/z* (C.I.) 368 (100%), 94 (49) and 78 (88).

(2*RS*,3*SR*)-2-Benzyloxypent-3-yl(triphenyl)stannane 43

The hydroxypentylstannane **42** (0.206 g, 0.470 mmol) in THF (2 mL) was added to a suspension of sodium hydride (56 mg, 1.41 mmol, 60% dispersion) in THF (2 mL) at 0 °C. After 1 h at room temperature, benzyl bromide (0.111 mL, 0.94 mmol) and TBAI (5 mg) were added and the mixture was stirred at room temperature overnight. Water (5 mL) was added and the reaction mixture was extracted with ether (3 × 5 mL). The organic extracts were washed with brine (10 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum : ether (50 : 1) and triethylamine (1%) as eluent gave the *title compound* **43** (151 mg, 61%) as a colourless oil; ν_{max}/cm^{-1} 3062, 2960, 2868, 1480, 1455, 1428, 1073, 728 and 698; δ_H (300 MHz, $CDCl_3$) 1.13 (3 H, t, *J* 7, 5-H_3), 1.35 (3 H, d, *J* 6, 1-H_3), 1.97 (2 H, m, 4-H_2), 2.49 (1 H, dt, *J* 4, 7, 3-H), 4.09 (1 H, m, 2-H), 4.16 and 4.53 (each 1 H, d, *J* 11, PhHC*H*) and 7.16–7.70 (20 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 15.4, 18.6, 21.3, 42.2, 70.2, 76.5, 127.1, 127.7, 128.0, 128.2, 128.4, 137.3, 138.7 and 140.1; *m/z* (C.I.) 368 (100%) and 94 (56).

(2*RS*,3*SR*)-2-Ethyl-3-methyloxirane 44[8]

N-Bromosuccinimide (8.34 g, 46.83 mmol) was added portionwise to (*Z*)-2-pentene (5.0 mL, 46.83 mmol) in water (20 mL) such that the temperature remained below 45 °C. The mixture was stirred at room temperature for 18 h. During the reaction two layers formed and the lower layer was separated and slowly added to potassium hydroxide (7.09 g, 0.126 mol) in water (15 mL). During the course of the addition (~2 h) a lighter yellow layer separated. The mixture was saturated with sodium chloride and the layers separated. The top layer was dried ($MgSO_4$) and fractionally distilled, bp 84–85 °C/760 mm (lit.[8] bp 85.4 °C/750 ± 15 mm) to afford the title compound **44** (0.50 g, 13%) as a colourless liquid; δ_H (300 MHz, $CDCl_3$) 1.07 (3 H, t, *J* 7.5, CH_3CH_2), 1.31 (3 H, d, *J* 5.63, CH_3CH), 1.58

(2 H, m, $\mathrm{C}H_2\mathrm{CH}_3$), 2.91 (1 H, dt, *J* 4, 6, 2-H) and 3.09 (1 H, m, 3-H); δ_C (75 MHz, CDCl$_3$) 10.3, 12.9, 20.8, 52.6 and 58.2; *m*/*z* (C.I.) 87 (M$^+$ + 1, 72%), 86 (25), 69 (80) and 45 (100).

(2*RS*,3*RS*)-3-Hydroxypent-2-yl(triphenyl)stannane 45 and (2*RS*,3*RS*)-2-hydroxypent-3-yl(triphenyl)stannane 38

^{n}Butyllithium (2.18 mL, 1.28 M in hexanes, 2.79 mmol) was added to di-isopropylamine (0.39 mL, 2.79 mmol) in THF (2 mL) at 0 °C. After 5 min, the solution was cooled to −78 °C and a triphenyltin hydride (0.979 g, 2.79 mmol) in THF (2 mL) was added. The yellow suspension was stirred at −78 °C for 1 h, warmed to −10 °C and the epoxide **44** (0.12 g, 1.39 mmol) in THF (1 mL) was added. The solution was stirred at room temperature for 4 h and saturated aqueous ammonium chloride (3 mL) was added. The mixture was extracted with ether (3 × 5 mL) and the organic extracts washed with brine (10 mL), dried (MgSO$_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum : ether (5 : 1) and triethylamine (1%) gave the *title compound* **45** (0.132 g, 22%) as a colourless oil; ν_{max}/cm^{-1} 3578, 3062, 2961, 2931, 2860, 1480, 1428, 1073, 961, 728 and 699; δ_H (300 MHz, CDCl$_3$) 0.97 (3 H, t, *J* 7, 5-H$_3$), 1.45 (3 H, d, *J* 7, 1-H$_3$), 1.72 (2 H, m, 4-H$_2$), 1.94 (1 H, d, *J* 4, OH), 2.29 (1 H, quint, *J* 7, 2-H), 3.77 (1 H, m, 3-H) and 7.30–7.74 (15 H, m, ArH); δ_C (75 MHz, CDCl$_3$) 10.1, 16.5, 30.0, 33.2, 78.3, 128.2, 128.5, 137.4 and 140.0; *m*/*z* (C.I.) 368 (100%) and 78 (12). The second fraction was the title compound **38** (0.138 g, 23%), a colourless oil with spectroscopic data identical to those of a sample prepared by reduction of the penten-3-ylstannane **36**.

Alcohol **38** (88 mg, 0.20 mmol) in THF (1 mL) was added to a suspension of sodium hydride (24 mg, 0.602 mmol, 60% dispersion) in THF (1 mL) at 0 °C. After 1 h at room temperature, benzyl bromide (47 µl, 0.402 mmol) and TBAI (5 mg) were added and the mixture was stirred at room temperature overnight. Water (3 mL) was added and the mixture was extracted with ether (3 × 3 mL). The ether extracts were washed with brine (5 mL), dried (MgSO$_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum : ether (50 : 1) and triethylamine (1%) as eluent gave the 2-benzyloxypent-3-ylstannane **39** (76 mg, 72%), a colourless oil with spectroscopic data identical to those of a sample prepared by reduction of penten-3-ylstannane **37**.

4-*tert*-Butyldimethylsilyloxypent-2-enyl(triphenyl)stannane 51

The 4-hydroxypent-2-enylstannane **34** (9.42 g, 21.6 mmol) in DCM (150 mL) was added to a suspension of *tert*-butyldimethylsilyl chloride (3.58 g, 23.8 mmol) and imidazole (2.94 g, 43.2 mmol) in DCM (150 mL) and the mixture stirred at room temperature for 24 h. Water (100 mL) was added and the organic phase washed with brine (100 mL), dried (MgSO$_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum : ether (10 : 1) and triethylamine (1%) gave the *title compound* **51** (6.86 g, 55%) as a colourless oil; ν_{max}/cm^{-1} 3064, 2955, 2856, 1471, 1428, 1365, 1254, 1075, 996, 960, 834, 776, 727 and 699; δ_H (300 MHz, CDCl$_3$) 0.03 and 0.06 (each 3 H, s, SiCH$_3$), 0.93 [9 H, s, SiC(CH$_3$)$_3$], 1.17 (3 H, d, *J* 6, 5-H$_3$), 2.48 (2 H, d, *J* 8, 1-H$_2$), 4.26 (1 H, quin, *J* 5.5, 4-H), 5.52 (1 H, dd, *J* 8, 15, 3-H), 5.90 (1 H, dt, *J* 15, 8, 2-H) and 7.40–7.70 (15 H, m, ArH); δ_C (75 MHz, CDCl$_3$) −4.7, −4.5, 15.8, 18.3, 24.8, 26.0, 69.3, 125.8, 128.9, 129.0, 133.1, 136.9 and 138.5; *m*/*z* (C.I.) 473 (M$^+$ − 77, 2%) and 368 (100).

[(3*RS*,4*SR*)- and (3*RS*,4*RS*)-4-*tert*-Butyldimethylsilyloxypent-1-en-3-yl](triphenyl)stannane 52 and 53

The general procedure using pentenylstannane **51** (0.74 g, 1.35 mmol), tin(IV) chloride (1.35 mL, 1 M in DCM, 1.35 mmol) and phenyllithium (4.48 mL, 1.8 M in cyclohexane–ether, 8.07 mmol) in DCM (13 mL), after chromatography using light petroleum and triethylamine (1%) as eluent, gave the *title compounds* **52** and **53** (0.60 g, 80%) as a yellow oil, **52** : **53** = 50 : 50; ν_{max}/cm^{-1} 3063, 2956, 2981, 2855, 1428, 1255, 1074, 996, 834, 777, 728 and 699; δ_H (300 MHz, CDCl$_3$) 0.00, 0.03, 0.10 and 0.14 (each 1.5 H, s, SiCH$_3$), 0.90 [9 H, s, SiC(CH$_3$)$_3$], 1.31 (1.5 H, d, *J* 6.1, 5-H$_3$), 1.39 (1.5 H, d, *J* 8.0, 5-H$_3$), 3.18 (0.5 H, d, *J* 10.5, 3-H), 3.31 (0.5 H, dd, *J* 4.9, 11.1, 3-H), 4.47 (1 H, m, 4-H), 5.00 (2 H, m, 1-H$_2$), 6.19 and 6.36 (each 0.5 H, dt, *J* 15, 10, 2-H) and 7.10–7.80 (15 H, m, ArH); δ_C (75 MHz, CDCl$_3$) −4.3, 18.0, 24.5, 24.8, 26.0(2), 48.9, 49.1, 71.0, 71.5, 112.0, 113.0, 128.2, 128.4, 128.5, 137.5 and 139.7; *m*/*z* (C.I.) 425 (10%), 368 (45), 351 (52) and 78 (100).

[(2*RS*,3*SR*)- and (2*RS*,3*RS*)-2-*tert*-Butyldimethylsilyloxypent-3-yl](triphenyl)stannane 54 and 55

The general procedure using a mixture of the stannanes **52** and **53** (0.48 g, 0.872 mmol), toluene 4-sulfonylhydrazide (1.94 g, 10.46 mmol), DME (35 mL) and sodium acetate (1.46 g in 17.80 mmol in water, 10 mL), after chromatography using light petroleum and triethylamine (1%) afforded the *title compounds* **54** and **55** (0.37 g, 77%) as a colourless oil, **64** : **55** = 50 : 50 (Found: M$^+$ − C$_6$H$_5$, 475.1482. C$_{23}$H$_{35}$OSi^{120}Sn requires *M*, 475.1478); ν_{max}/cm^{-1} 3063, 2956, 2928, 2856, 1428, 1255, 1073, 1043, 968, 833, 776, 728 and 699; δ_H (300 MHz, CDCl$_3$) 0.00, 0.03, 0.08 and 0.10 (each 1.5 H, s, CH$_3$Si), 0.86 and 0.89 [each 4.5 H, s, SiC(CH$_3$)$_3$], 1.01 (1.5 H, t, *J* 7.1, 5-H$_3$), 1.06 (1.5 H, t, *J* 7.2, 5-H$_3$), 1.23 (1.5 H, d, *J* 6.1, 1-H$_3$), 1.30 (1.5 H, d, *J* 6.0, 1-H$_3$), 1.70–2.50 (3 H, m, 3-H and 4-H$_2$), 4.45 (1 H, m, 2-H) and 7.20–7.70 (15 H, m, ArH); δ_C (75 MHz, CDCl$_3$) −4.8, −4.7, 14.9, 15.2, 18.2, 23.5, 23.9, 24.4, 25.3, 25.9, 26.0, 46.2, 46.4, 70.9, 71.0, 127.8, 128.1, 128.2, 136.9, 137.4 and 140.4; *m*/*z* (C.I.) 475 (2%), 425 (11) and 368 (100).

TBAF (0.39 mL, 1.0 M in THF, 0.39 mmol) was added to a mixture of the stannanes **54** and **55** (72 mg, 0.130 mmol) in tetrahydrofuran (1 mL) at 0 °C. After 3 h at room temperature, water (3 mL) was added and the mixture extracted with ether (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 of the residue using light petroleum : ether (3 : 1) and triethylamine (1%) as eluent gave the (2*RS*,3*RS*)-2-hydroxypent-3-ylstannane **38** (15 mg, 26%) and the (2*RS*,3*SR*)-2-hydroxypent-3-ylstannane **42** (7 mg, 12%) both as colourless oils with spectroscopic data identical to those obtained earlier.

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Notes and references

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17 Our results are qualitative rather than quantitative and the reaction scheme shown in Fig. 7 is certainly an oversimplification of the processes that may be involved. The reactions postulated to proceed *via* the *anti*-allyltin trichloride **21a** are reliably stereoselective showing that the *anti*-allyltin trichloride **21a** has little tendency to epimerise into its *syn*-epimer **28**. However although fast reactions postulated to involve the *syn*-allyltin trichloride **28** proceed with stereoselectivity that is markedly different from those that involve the *anti*-allyltin trichloride **21a**, slower processes proceed with reduced stereoselectivity showing that equilibration of **28** and **21a** can occur. Indeed reactions of analogous allylsilanes require transmetallation times of *ca.* 1.5 h and with aldehydes typically give mixtures of the 1,5-*anti* and 1,5-*syn*-products **2** and **23** with stereoselectivities of **2** : **23** = 75 : 25. These reactions may well proceed *via* mixtures of **21a** and **28** that have effectively reached equilibrium (see ref. 18). The same may be true of some of the slower reactions with imines, see ref. 3.

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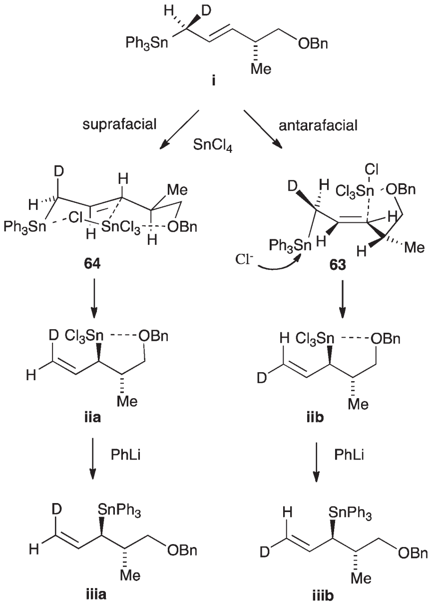

20 In this work using allylstannanes, mixtures of (*E*)- and (*Z*)-isomers of the allylstannanes were usually used with (*E*) : (*Z*) ratios of typically 85 : 15. It might be expected that (*Z*)-allylstannanes would undergo transmetallation with higher stereoselectivities that their (*E*)-isomers and so react, *e.g.* with aldehydes, with higher overall stereoselectivity. This has not been studied using allylstannanes but analogous reactions using allylgermanesdo show better stereoselectivities for the (*Z*)-isomers – see ref. 21.

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24 A transition structure with an octahedral tin must be involved if the alkoxy group remains co-ordinated to the tin during the reaction with an aldehyde. For allyltin trichlorides with four-membered oxastannane rings, *e.g.* **46**, such processes would be expected to give rise to (*Z*)-alkenes, see ref. 25. However for reactions of allylstannanes with substituents in more remote positions that are believed to involve reactions of allyltin trichlorides with five- and six-membered oxastannane rings, the high selectivity for (*Z*)-alkene formation is more difficult to explain. If a trigonal bipyramidal tin is involved in the transition structure of the reaction with an aldehyde as indicated in Fig. 2–4, the prefence for formation of (*Z*)-alkenes is disconnected from the length of the tether and has analogy in the thermal reactions discussed in ref. 23.

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