Tetrahedron 70 (2014) 7253–7267

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Open-chain remote stereocontrol using allylgermanes

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ARTICLE INFO

Article history:
Received 26 April 2014
Received in revised form 11 June 2014
Accepted 13 June 2014
Available online 25 June 2014

Keywords:
Allylgermane
Remote stereocontrol
Transmetallation
Stereoselective synthesis
Alcohol synthesis

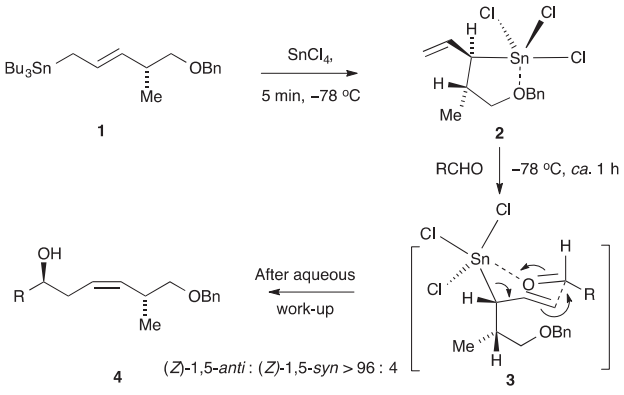
ABSTRACT

Alk-2-enyl(trialkyl- and -triaryl)germanes are transmetallated by tin(IV) halides at −78 °C with 15 min being sufficient for the transmetallation to proceed effectively to completion. Alk-2-enyl(trialkyl)germanes are transmetallated by both tin(IV) chloride and tin(IV) bromide under these conditions, but the corresponding triphenylgermanes are only transmetallated using tin(IV) chloride. These observations led to procedures for reactions of 5-substituted-pent-2-enyl- and -hex-2-enyl-germanes with aldehydes that proceed with useful levels of 1,5- and 1,6-stereocontrol in favour of the (*Z*)-1,5-*anti*- and (*Z*)-1,6-*syn*-alkenols, respectively. Slightly improved stereoselectivities were obtained using (*Z*)-alk-2-enylgermanes. The reaction of (*Z*)-6-hydroxyhept-2-enyl(triethyl)germane with benzaldehyde when promoted using tin(IV) bromide gave a 3-ethenyl-6-methyl-2-phenyltetrahydropyran rather than the expected homoallylic alcohol.

1. Introduction

Chiral alk-2-enylstannanes with heteroatom containing functionality are transmetallated stereoselectively by tin(IV) halides to generate alk-1-en-3-yltin trihalides that react with aldehydes with useful remote stereocontrol to give (*Z*)-alkenols.[1] For example, transmetallation of 5-benzyloxy-4-methylpent-2-enyl(tributyl)stannane **1** with tin(IV) chloride generates the (pent-1-en-3-yl)tin trichloride **2** that reacts with aldehydes to give the (*Z*)-1,5-*anti*-alkenols **4** typically with >96:4 1,5-*anti*/1,5-*syn* stereoselectivity possibly via the six-membered, chair-like, transition structure **3**. Slightly better stereoselectivity is observed using tin(IV) bromide to effect the transmetallation, whereas transmetallation using bismuth(III) iodide results in complementary stereocontrol in favour of the corresponding (*E*)-1,5-*anti*-alkenols.[2]

These reactions have been used in synthesis[3] but it was recognised that it would be useful to carry them out without employing organotin reagents that are toxic and which lead to the formation of tributyltin containing side-products. Allylsilanes are transmetallated by tin(IV) chloride but, in our hands, transmetallation of the pent-2-enylsilanes **5** [R^1=Me, Ph, also (*Z*)-isomers] was relatively slow taking 1–2 h at −78 °C in comparison to transmetallation of the pent-2-enylstannane **1** that was complete in less than 5 min. This led to the formation of (*Z*)-alkenols with aldehydes but with reduced overall 1,5-stereocontrol, 1,5-*anti*-**4**/1,5-*syn*-**6** ca. 75:25.[4] This loss of stereoselectivity was attributed to a slow equilibration of the intermediate allyltin trichlorides. Using the pentenylstannane **1**, the high stereoselectivity of the fast transmetallation is due to kinetic control, but under the conditions required for the transmetallation of the allylsilanes, the initially formed pent-1-en-3-yltin trichloride **2** has time to equilibrate with its 3-epimer **7** so leading to less useful overall 1,5-stereoselectivity.[5]



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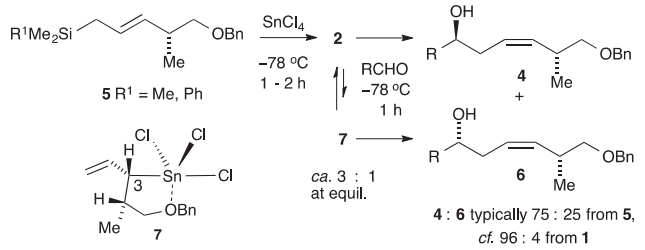
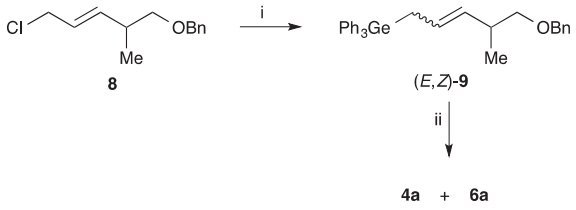


Allylgermanes are more reactive towards electrophilic attack than allylsilanes, but less reactive than the corresponding allylstannanes. It was therefore of interest to study transmetallation of allylgermanes with tin(IV) halides to see whether useful levels of 1,5-stereocontrol in reactions with aldehydes reminiscent of those obtained using allylstannanes could be achieved.[6]

2. Results and discussion

2.1. 1,5-Stereocontrol using pent-2-enylgermanes

The racemic pent-2-enyl chloride **8** was prepared from the corresponding alcohol[1] and coupled with triphenylgermanium bromide under Barbier conditions[7] to give the pent-2-enyl(triphenyl)germane **9** as a mixture of (*E*)- and (*Z*)-isomers. Tin(IV) halide promoted reactions of this mixture of germanes with benzaldehyde were carried out at −78 °C to establish the influence of the time allowed for transmetallation of the pentenylgermane on the overall 1,5-stereoselectivity, see Scheme 1 and Table 1. It was found that if the aldehyde was added to the reaction mixture 45 min after the tin(IV) chloride had been added to the germane, the (*Z*)-hex-3-enols **4a** and **6a** were formed (80% isolated) in a ratio of 82:18. However, if the transmetallation time was reduced to 15 min, the yield was more or less the same (77%), but the overall



Scheme 1. Preparation of (±)-(*E*,*Z*)-5-benzyloxy-4-methylpent-2-enyl(triphenyl)germane **9** and its reactions with benzaldehyde. Reagents and conditions: i, Ph_3GeBr, Mg, THF, 30 min, heat to 45 °C, 4 h [85%, (*E*)/(*Z*)=55:45]; ii, $SnCl_4$, DCM, −78 °C, then PhCHO, −78 °C, 45 min (77–83% see Table).

Table 1
Effect of transmetallation time on 1,5-stereoselectivity

Transmetallation time (min)	Yield[a] (%)	**4a**/**6a**[b]
45	80	82:18
30	83	88:12
15	77	94:6

[a] A 3-fold excess of benzaldehyde was used. Yields are based on the allylgermane.
[b] Both products are known. The ratios of the products were estimated by integration of the doublets due to the 4-Me peaks in ^{1}H NMR spectra.

stereoselectivity was significantly better being 96:4 in favour of the 1,5-*anti*-epimer **4a**. With a transmetallation time of 30 min, the 1,5-stereoselectivity was 88:12. If the transmetallation time was reduced significantly below 15 min, lower yields of the required products were obtained with increasing amounts of branched products indicative of incomplete transmetallation.[8] To a certain extent, this could be mitigated by using higher concentrations, with useful yields and stereoselectivities being obtained in some cases with transmetallation times as low as 7–8 min. However, a transmetallation time of 15 min proved reliable in terms of yield and stereoselectivity and was adopted for the standard procedure.

The stereoselectivity obtained in the reaction between the (*E*,*Z*)-pent-2-enylgermane **9** and benzaldehyde, 96:4, was similar to the stereocontrol observed for the reaction of the pent-2-enylstannane **1** with benzaldehyde[1] and so reactions of the germane (*E*,*Z*)-**9** with other aldehydes were investigated, see Table 2.

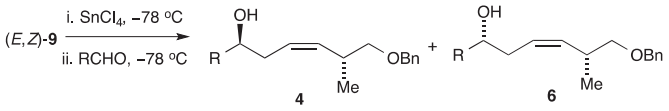
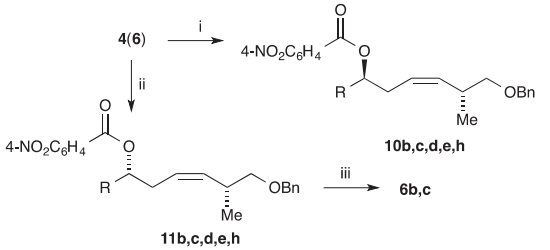


Table 2
Reactions of (±)-(*E*,*Z*)-pent-2-enylgermane **9** with aldehydes

Aldehyde (R)	Products[a]	Yield[b] (%)	1,5-*syn*/1,5-*anti*[c]
Ph	**4a**, **6a**	58 (77)	96:4
$(CH_3)_2CH$	**4b**, **6b**	66 (78)	99:1
$CH_3(CH_2)_2$	**4c**, **6c**	(67)	98:2
$BnOCH_2$	**4d**, **6d**	69	96:4
4-ClC_6H_4	**4e**, **6e**	56	99:1
3-ClC_6H_4	**4f**, **6f**	(34)	98:2
4-$MeOC_6H_4$	**4g**, **6g**	42	93:7
4-$NO_2C_6H_4$	**4h**, **6h**	88	94:6
(*E*)-CH_3CH=CH	**4i**, **6i**	(86)	97:3
(*E*)-PhCH=CH	**4j**, **6j**	(67)	95:5

[a] Products were identified by comparison with samples prepared earlier.[1]
[b] Using a 1.1 mol ratio of aldehyde/germane. For the reactions in parenthesis, 3 equiv of aldehyde were used. Transmetallation times were 15 min.
[c] Estimated by integration of the doublets attributed to the methyl or benzyl substituents in the ^{1}H NMR spectra of **4** or the corresponding 4-nitrobenzoates **10** and **11**.

Products **4a**,**b**,**e** and **g**, were known compounds.[1] The other products were identified by analogy, their (*Z*)-alkene geometry being confirmed by vinylic coupling constants of ca. 10 Hz in all cases. Product ratios were estimated by ^{1}H NMR using the methyl or benzyl peaks. For the products prepared from 2-methylpropanal, butanal, 2-benzyloxyacetaldehyde, 4-chlorobenzaldehyde and 4-nitrobenzaldehyde, the ^{1}H NMR spectra of the 4-nitrobenzoate esters **10** obtained by direct esterification were compared with those prepared with inversion of configuration using a Mitsunobu procedure, see Scheme 2 (and Experimental section). The inverted esters **11b** and **11c** were also saponified to prepare the 1,5-*syn*-alcohols **6b** and **6c**. This work confirmed that the 1,5-*anti*- and 1,5-*syn*-epimers could be distinguished by ^{1}H NMR and established which of the minor peaks in the ^{1}H NMR spectra of the products from the reactions of the pent-2-enylgermane **9** were due to the 1,5-*syn*-isomers **6**.

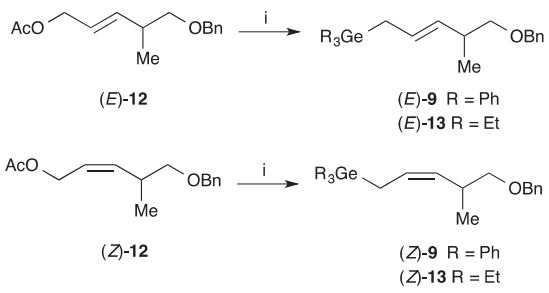


Scheme 2. Preparation of the 4-nitrobenzoates **10** and **11** and the 1,5-*syn*-alcohols **6**. Reagents and conditions: i, 4-nitrobenzoyl chloride, DMAP (cat.), Et_3N, THF, 0 °C to rt (**10b**, 59%; **10c**, 44%; **10d**, 66%; **10e**, 67%; **10h**, 85%); ii, DIAD, 4-nitrobenzoic acid, Ph_3P, THF, 0 °C, 7 h (**11b**, 54%; **11c**, 57%; **11d**, 68%; **11e**, 62%; **11h**, 79%), iii, NaOH, MeOH, rt, 2 h (**6b**, 60%; **6c**, 92%).

In all cases useful stereoselectivities in favour of the (*Z*)-1,5-*anti*-products **4** were obtained. The yields were generally good but were not optimised and so the modest yields obtained for 3-chloro- and 4-methoxy-benzaldehydes may not be definitive.

During the studies of reactions of the pent-2-enylstannane **1**, the influence of the geometry of the stannane on the overall stereoselectivity of reactions with aldehydes was not investigated, most results being obtained using mixtures of (*E*)- and (*Z*)-stannanes in which the (*E*)-isomer was the major component, typically 70:30. However, in the present work, since the pent-2-enylgermanes could be prepared as single geometrical isomers, it was decided to investigate the influence of pent-2-enylgermane geometry on the overall stereoselectivity.

Allylic acetates are known to react with lithium bis(-triethylgermyl)cuprate to give the corresponding allylgermanes.[10] Thus the (*E*)- and (*Z*)-pent-2-enyl acetates (*E*)-**12** and (*Z*)-**12** were prepared from the corresponding alcohols.[1,11,12] Initial studies were directed towards the preparation of the (*E*)- and (*Z*)-pent-2-enyl(triphenyl)germanes using lithium bis(triphenylgermyl)cuprate following the literature procedure for triethylgermanes. The required products (*E*)- and (*Z*)-**9** were obtained but only in modest yields. However, with the bis(triethylgermyl)cuprate, although the (*E*)-pent-2-enyl(triethyl)germane (*E*)-**13** was obtained again in only a modest yield, an excellent yield (96%) of the (*Z*)-pent-2-enyl(triethyl)germane (*Z*)-**13** was achieved, see Scheme 3.



Scheme 3. Preparation of the (*E*)- and (*Z*)-pent-2-enylgermanes **9** and **13**. Reagents and conditions: i, R_3GeH, TMEDA, THF, ^{t}BuLi, pentane, 30 min, 0 °C, CuI, 10 min, 0 °C, −23 °C, add (*E*)- or (*Z*)-**12**, 30 min [(*E*)-**9**, 17%; (*E*)-**13**, 29%; (*Z*)-**9**, 52%; (*Z*)-**13**, 96%).

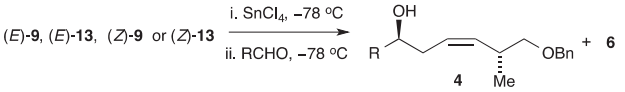


Table 3
Reactions of the (*E*)- and (*Z*)-pent-2-enylgermane with aldehydes

Aldehyde (R)	Germane	Products[a]	Yield[b] (%)	1,5-*syn*/1,5-*anti*[c]
Ph	(*E*)-**9**	**4a**, **6a**	86	90:10
	(*E*)-**13**		63	88:12
	(*Z*)-**9**		73	98:2
	(*Z*)-**13**		98	98:2
$(CH_3)_2CH$		**4b**, **6b**	57	99:1
$CH_3(CH_2)_2$		**4c**, **6c**	74	99:1
$BnOCH_2$		**4d**, **6d**	57	97:3
4-ClC_6H_4		**4e**, **6e**	84	99:1
4-$MeOC_6H_4$		**4g**, **6g**	81	96:4
4-$NO_2C_6H_4$		**4h**, **6h**	85	99:1

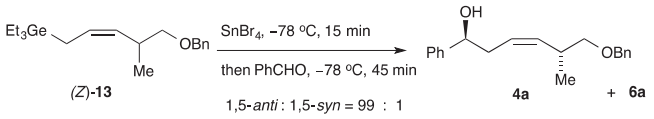
[a] The products were identified by comparison with samples prepared earlier.[1]
[b] Using 3 mol equiv of aldehyde relative to germane apart from the reactions of 4-methoxybenzaldehyde and benzyloxyacetaldehyde when 1.1 equiv of aldehyde were used. The transmetallation time was 15 min except for the reaction of the germane (*E*)-**9**, when only 7 min was allowed.
[c] Estimated by integration of the doublets attributed to the methyl or benzyl substituents in ^{1}H NMR spectra of **4** or the corresponding 4-nitrobenzoates **10** and **11**.

The reactions of the (*E*)- and (*Z*)-pent-2-enylgermanes (*E*)-**9**, (*E*)-**13**, (*Z*)-**9** and (*Z*)-**13** with benzaldehyde were investigated under the usual conditions, i.e., with 15 min for the transmetallation using tin(IV) chloride, see Table 3. Although only qualitative data were obtained, it did appear that the reactions using the (*Z*)-pent-2-enylgermanes were more stereoselective in favour of the (*Z*)-1,5-*anti*-product **4a**, compare 90:10 and 88:12 for the (*E*)-germanes, with 98:2 for both (*Z*)-isomers.

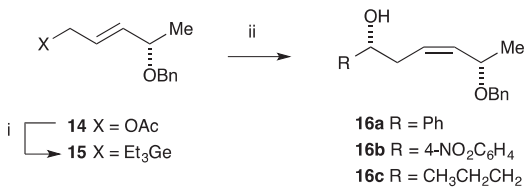
Tin(IV) chloride promoted reactions of the (*Z*)-pent-2-enyl(triethyl)germane (*Z*)-**13** with several aldehydes were then investigated and the results are summarised in Table 3. In all cases excellent stereoselectivities in favour of the (*Z*)-1,5-*anti*-alkenols **4** were obtained. Indeed, these results compare favourably to those obtained using the pent-2-enylstannane **1**.

During studies of remote stereocontrol using allylstannanes, improved stereoselectivities were observed using tin(IV) bromide rather than tin(IV) chloride for the transmetallation and so promotion of the reaction of the pent-2-enylgermanes **9** and **13** with benzaldehyde using tin(IV) bromide was briefly investigated.

Somewhat surprisingly, it was found that unchanged pent-2-enyl(triphenyl)germane was isolated during attempts to promote the reactions of either the (*E*)- or (*Z*)-pent-2-enyl(triphenyl)germanes (*E*)-**9** and (*Z*)-**9** with benzaldehyde under the usual conditions (−78 °C, 15 min transmetallation, 45 min for the reaction with the aldehyde). However the reaction using the (*Z*)-pent-2-enyl(triethyl)germane (*Z*)-**13** was successful and gave the (*Z*)-1,5-*anti*-product **4a** in a reasonable yield (67%) and with excellent stereoselectivity (99:1).



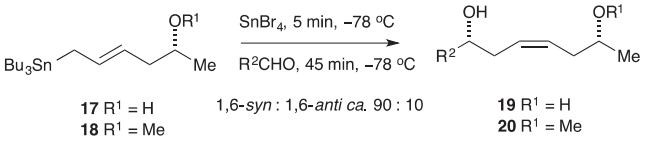
Tin(IV) chloride promoted reactions of 4-benzyloxypent-2-enylstannanes with aldehydes also proceed with excellent 1,5-stereocontrol,[13] and so it was of interest to investigate the analogous reactions of the corresponding triethylgermane **15**. The (*E*)-isomer of this germane (*E*)-**15** was prepared from the corresponding acetate **14**[14] using lithium bis(triethylgermyl)cuprate. 15 min were allowed for transmetallation with tin(IV) chloride at −78 °C before the addition of the aldehyde but only low to modest yields of the known[13] (*Z*)-1,5-*syn*-alkenols **16** were obtained, see Scheme 2. With benzaldehyde, the reaction proceeded with 89:11 stereoselectivity in favour of the (*Z*)-1,5-*syn*-product **16a** (40%). However, with 4-nitrobenzaldehyde and butanal, only 34% and 11% yields of the products **16b** and **16c** were obtained. Using tin(IV) bromide, only 26% of the (*Z*)-alkenol **16a**, 90:10 stereoselectivity, was obtained. The low yields in these reactions of the germane **15** were attributed to a competing 1,4-elimination process. In some cases, benzyl alcohol was detected in the product mixtures supporting this hypothesis (Scheme 4).



Scheme 4. Reactions of the 4-benzyloxypent-2-enylgermane **15**. Reagents and conditions: i, Et_3GeH, TMEDA, THF, ^{t}BuLi, pentane, 30 min, 0 °C, CuI, 10 min, 0 °C, −23 °C, add (*E*)-**14**, 30 min (83%); ii, $SnCl_4$, DCM, −78 °C, 15 min, then RCHO, −78 °C, 45 min (**16a**, 40%, 89:11; **16b**, 34%; **16c**, 11%).

2.2. 1,6-Stereocontrol using hex-2-enylgermanes

1,6-Stereocontrol in favour of (*Z*)-1,6-*syn*-alkenols has been observed in reactions of 5-substituted hex-2-enyl(tributyl)stannanes with aldehydes but useful results required transmetallation of the 5-hydroxy- and 5-methoxyhex-2-enylstannanes **17** and **18** using tin(IV) bromide rather than tin(IV) chloride.[1] More bulky *O*-substituents resulted in lower 1,6-stereocontrol. It was therefore decided to see whether useful 1,6-stereocontrol could be achieved using hex-2-enylgermanes.



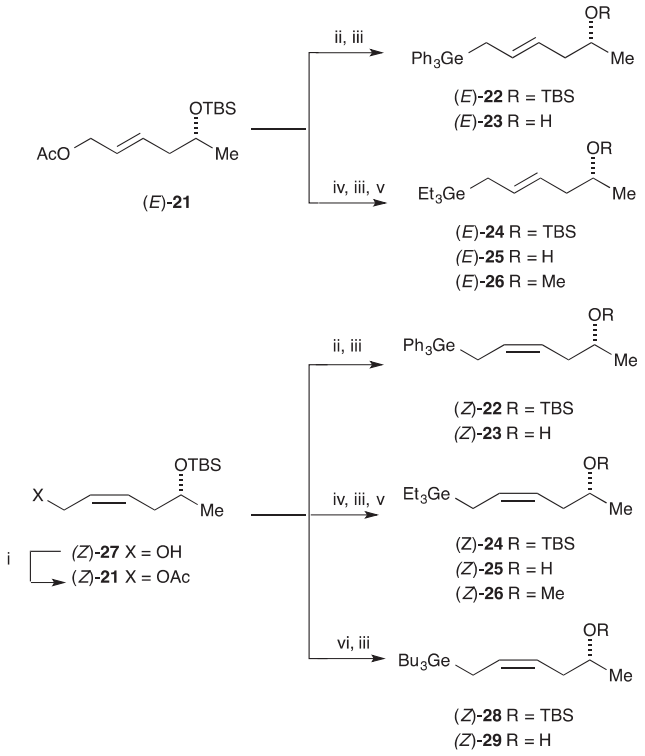
17 R^1 = H
18 R^1 = Me

1,6-*syn* : 1,6-*anti* *ca.* 90 : 10

19 R^1 = H
20 R^1 = Me

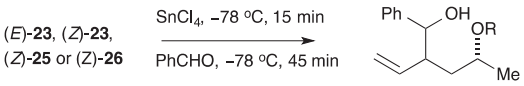
Although slightly enhanced 1,5-*anti*-stereoselectivities had been obtained using (*Z*)-pent-2-enylgermanes, with transmetallation using tin(IV) bromide limited to triethylgermanes, it was decided to check the use of both (*E*)- and (*Z*)-hex-2-enylgermanes, transmetallation using both tin(IV) chloride and bromide and the use of triphenyl- and trialkyl-germanes, for 1,6-stereocontrol.

The required (*E*)- and (*Z*)-hex-2-enylgermanes were prepared from the corresponding (*E*)- and (*Z*)-5-*tert*-butyldimethylsilyloxyhex-2-en-1-yl acetates (*E*)-[15] and (*Z*)-**21**, the latter being prepared by acetylation of the hex-2-en-1-ol (*Z*)-**27**,[16] see Scheme 5. Displacement of the acetoxy substituents using the corresponding bis-(triaryl- or -trialkyl-germyl)cuprate gave the 5-*tert*-butyldimethylsilyloxyhex-2-enylgermanes (*E*)- and (*Z*)-**22**, (*E*)-and (*Z*)-**24** and (*Z*)-**28**. These were desilylated to give the corresponding 5-hydroxyhex-2-enylgermanes (*E*)- and (*Z*)-**23**, (*E*)-and (*Z*)-**25** and (*Z*)-**29**. The 5-hydroxyhex-2-enyl(triethyl)germanes were also methylated to give the methyl ethers (*E*)- and (*Z*)-**26**, see Scheme 5.



Scheme 5. Synthesis of 5-substituted hex-2-enylgermanes for studies of 1,6-stereocontrol. Reagents and conditions: i, Ac_2O, py, rt, 16 h (97%); ii, Ph_3GeH, TMEDA, THF, ^{t}BuLi, pentane, 30 min, 0 °C, CuI, 10 min, 0 °C, −23 °C, add (*E*)- or (*Z*)-**21**, 30 min [(*E*)-**22**, 69%; (*Z*)-**22**, 44%]; iii, TBAF, THF, rt, 16 h [(*E*)-**23**, 93%; (*E*)-**25**, 97%); (*Z*)-**23**, 48%; (*Z*)-**25**, 95%; (*Z*)-**29**, 78% from (*Z*)-**21**]; iv, Et_3GeH, TMEDA, THF, ^{t}BuLi, pentane, 30 min, 0 °C, CuI, 10 min, 0 °C, −23 °C, add (*E*)- or (*Z*)-**21**, 30 min [(*E*)-**24**, 92%; (*Z*)-**24**, 93%]; v, NaH, MeI, rt [(*E*)-**26**, 84%; (*Z*)-**26**, 73%]; vi, Bu_3GeH, TMEDA, THF, ^{t}BuLi, pentane, 30 min, 0 °C, CuI, 10 min, 0 °C, −23 °C, add (*Z*)-**21**, 30 min.

Attempts to promote reactions between the 5-hydroxyhex-2-enyl(triphenyl)- and -(triethyl)gemanes (*E*)-**23**, (*Z*)-**23** and (*Z*)-**25**, and the (*Z*)-5-methoxyhex-2-enyl(triethyl)germane (*Z*)-**26**, with benzaldehyde using tin(IV) chloride, were not successful in that mixtures of products were formed that included significant amounts of products **30** and **31** formed by reaction of the hex-2-enylgermane at the 3-position.[2,8] These products may have been formed by the tin(IV) chloride promoting the reaction with the hex-2-enylgermanes by co-ordination to the aldehyde rather than by transmetallation, but this would require the transmetallation not to have taken place during the 15 min prior to the addition of the aldehyde. Alternatively perhaps the initially formed hex-1-en-3-yltin trichlorides undergo 1,3-migration of the trichlorotin moiety leading to the hex-3-en-1-yltin trichlorides that would be expected to give the branched products **30** and **31** on reaction with aldehydes.



30 R = H
31 R = Me

As before, transmetallation of the hex-2-enyl(triphenyl)germanes using tin(IV) bromide was unsuccessful, the germanes being recovered from the reaction mixtures. In contrast, when the reactions of the 5-hydroxy- and 5-methoxy-hex-2-enyl(triethyl)- and -(tributyl)germanes with aldehydes were promoted using tin(IV) bromide, good yields of products were obtained with useful levels of stereocontrol, see Tables 4 and 5. Products were identified from these reactions by comparison with samples prepared earlier,[1] with the structures of new compounds being assigned by analogy, see Experimental section. The product ratios were estimated by ^{1}H NMR using the doublets assigned to the terminal methyl groups and/or ^{13}C NMR (see Experimental section).

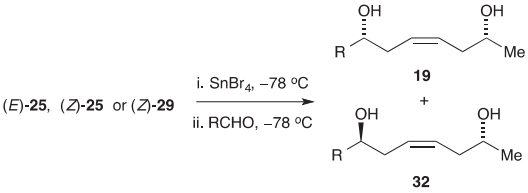


Table 4
Reactions of 5-hydroxyhex-2-enylgermanes with aldehydes

Aldehyde (R)	Germane	Products[a]	Yield[b] (%)	1,6-*syn*/1,6-*anti*[c]
Ph	(*E*)-**25**	**19a**, **32a**	63	89:11
$(CH_3)_2CH$	(*E*)-**25**	**19b**, **32b**	51	91:9
Ph	(*Z*)-**25**	**19a**, **32a**	80	94:6
$(CH_3)_2CH$		**19b**, **32b**	82	93:7
$CH_3(CH_2)_2$		**19c**, **32c**	75	93:7
4-ClC_6H_4		**19d**, **32d**	81	92:8
3-ClC_6H_4		**19e**, **32e**	83	93:7
4-$NO_2C_6H_4$		**19f**, **32f**	81	91:9
(*E*)-CH_3CH=CH		**19g**, **32g**	73	92:8
(*E*)-PhCH=CH		**19h**, **32 h**	81	91:9
Ph	(*Z*)-**29**	**19a**, **32a**	78	92:8
$CH_3(CH_2)_2$		**19c**, **32c**	68	90:10
4-ClC_6H_4		**19d**, **32d**	73	91:9

[a] The products were identified by comparison with samples prepared earlier.[1]
[b] Using 3 mol equiv of aldehyde relative to germane. The transmetallation time was 15 min.
[c] Estimated by ^{1}H NMR, integration of the doublets attributed to the $CHCH_3$ or by ^{13}C NMR.

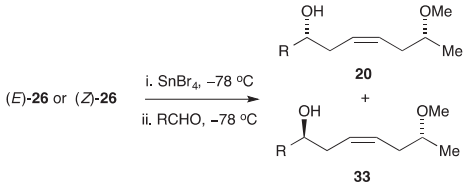


Table 5
Reactions of 5-methoxyhex-2-enylgermanes with aldehydes

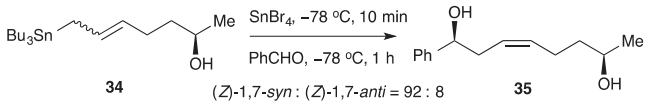
Aldehyde (R)	Germane	Products[a]	Yield[b] (%)	1,6-*syn*/1,6-*anti*[c]
Ph	(*E*)-**26**	**20a**, **33a**	83	86:14
Ph	(*Z*)-**26**	**20a**, **33a**	94	94:6
$CH_3(CH_2)_2$		**20b**, **33b**	86	95:5
4-ClC_6H_4		**20d**, **33d**	61	90:10

[a] The products were identified by comparison with samples prepared earlier.[1]
[b] Using 3 mol equiv of aldehyde relative to germane. The transmetallation time was 15 min.
[c] Estimated by ^{1}H NMR, integration of the doublets attributed to the CHCH_3 or by ^{13}C NMR.

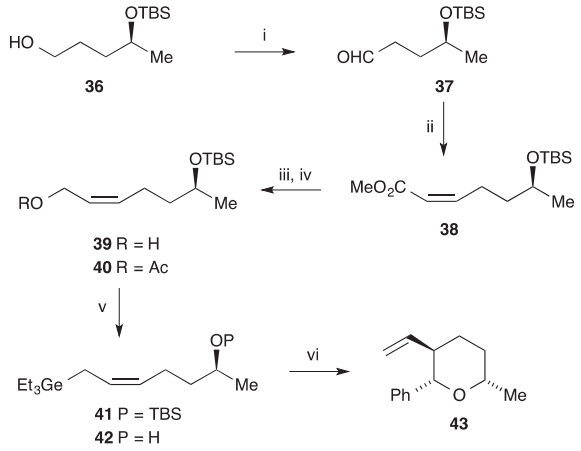
There would appear to be a slight improvement in 1,6-stereoselectivity if (*Z*)- rather than (*E*)-hex-2-enyl(triethyl)germanes were used. This was true for both the 5-methoxy- and 5-hydroxy-hexenylgermanes. The 1,6-stereoselectivities in favour of the (*Z*)-1,6-*syn*-products were 90:10 or better for both the (*Z*)-5-methoxy- and (*Z*)-5-hydroxyhex-2-enylgermanes with a range of aromatic and aliphatic aldehydes. These results, if anything, were better than those that had been obtained with the hex-2-enylstannanes **17** and **18**. Little difference was observed between the tin(IV) bromide promoted reactions of the triethyl- or tributylgermanes (*Z*)-**25** and (*Z*)-**29**.

2.3. Attempted 1,7-stereocontrol using hept-2-enylgermanes

Transmetallation of allylstannanes using tin(IV) bromide has also been used to provide 1,7-stereocontrol in reactions with aldehydes.[1] For example, the tin(IV) bromide promoted reaction of the 6-hydroxyhept-2-enyl(tributyl)stannane **34** with benzaldehyde proceeded with useful levels of stereoselectivity to give mainly the (*Z*)-1,7-*syn*-oct-3-ene-1,7-diol **35**. It was therefore of interest to see whether analogous 1,7-stereocontrol could be achieved using hept-2-enylgermanes.



(*S*,*Z*)-6-Hydroxyhept-2-enyl(triethyl)germane **42** was prepared from (*S*)-4-*tert*-butyldimethylsilyloxypentan-1-ol **36**,[17] see Scheme 6. Aldehyde **37**[18] was prepared by oxidation of the alcohol and was condensed with bis(trifluoroethyl) (methoxycarbonylmethyl) phosphonate giving the (*Z*)-unsaturated ester **38**, (*Z*)/(*E*)=20:1. Reduction using DIBAL-H and acetylation of the resulting alcohol **39** gave the hept-2-en-1-yl acetate **40**. This was taken through to the (*Z*)-hept-2-enyl(triethyl)germane **41** using the bis(-triethylgermyl)cuprate and desilylation gave the (*Z*)-6-hydroxyhept-2-enyl(triethyl)germane **42**. However, the reaction of this allylic germane with benzaldehyde when promoted by tin(IV) bromide under the standard conditions gave the tetrahydropyran **43** (55%) as the major product, see Scheme 6. The structure of this tetrahydropyran was established by spectroscopic methods with ^{1}H NMR, in particular NOEs, being used to confirm the configuration as shown. Tetrahydropyran **43** is a known compound having been prepared from the trimethylsilyl analogue of germane **42** via a Prins reaction.[19] A similar process would account for the formation of the tetrahydropyran from the hept-2-enylgermane **42**. This would appear to have competed with the expected transmetallation.



Scheme 6. Preparation and reaction with benzaldehyde of the 6-hydroxyhept-2-enylgermane **42**. Reagents and conditions: i, DMSO, DCM, $(COCl)_2$, −78 °C, 5 min, add **36**, 15 min, −78 °C, Et_3N (93%); ii, $MeO_2CCH_2P(O)(OCH_2CF_3)_2$, 18-*c*-6, THF, KHMDS, 5 min, −78 °C, add **37**, −60 to −78 °C, 30 min [70%; (*Z*)/(*E*)=20:1]; iii, DIBAL-H, hexanes, −78 °C, 45 min, −40 °C, 1 h (96%); iv, Ac_2O, py, rt, 16 h (89%); v, (a) Et_3GeH, TMEDA, THF, ^{t}BuLi, pentane, 30 min, 0 °C, CuI, 10 min, 0 °C, −23 °C, add **40**, 30 min; (b) TBAF, THF, rt, 16 h (73% from **40**); vi, $SnBr_4$, DCM, −78 °C, 15 min, then PhCHO, −78 °C, 45 min (55%).

3. Summary and conclusions

This work has shown that effective 1,5- and 1,6-open-chain stereocontrol can be achieved in reactions of allylgermanes with aldehydes promoted by tin(IV) halides. Indeed the yields and stereoselectivities in many cases are better than those that had been obtained using the corresponding allylstannanes.[1]

With the allylgermanes, slightly better stereoselectivities were observed for the (*Z*)-alkenylgermanes than for the (*E*)-isomers. This is consistent with the transmetallation processes discussed previously.[5] Transmetallation of the allylgermanes by tin(IV) halides would appear to be a finely balanced process. It is of interest that transmetallation using tin(IV) bromide was only successful for the alk-2-enyl(trialkyl)germanes and was not observed for the corresponding alk-2-enyl(triaryl)germanes. The formation of the branched products **30** and **31** from the tin(IV) chloride promoted reactions of the 5-hydroxy- and 5-methoxy-hex-2-enylgermanes is consistent with either the transmetallation not having occurred before the benzaldehyde was added[20] or a competing 1,3-isomerisation of the intermediate hex-1-en-3-yltin trichloride. Similarly the formation of the tetrahydropyran **43** during the tin(IV) bromide promoted reaction of the 6-hydroxyhept-2-enylgermane **42** with benzaldehyde is consistent with no reaction taking place until the aldehyde is added[20] or a 1,3-isomerisation of the intermediate hept-1-en-3-yltin tribromide. Just why these reactions are so dependent on the structure of the allylgermane is not clear. It may be that the rate of transmetallation and/or the stability of the co-ordinated intermediate tin trihalide is affected by the separation of the co-ordination site from the allylgermane moiety.

Notwithstanding this complication, the tin(IV) halide promoted reactions of 5-substituted pent-2-enyl- and hex-2-enyl-germanes with aldehydes were clean and reliable. They provide an organic-tin free process for useful 1,5- and 1,6-stereocontrol.

4. Experimental

4.1. General experimental procedures

^{1}H and ^{13}C NMR spectra were recorded on Varian Unity 500, Varian Unity Inova 400 and Varian Unity Inova 300 spectrometers with residual non-deuterated solvent as the internal standard. Coupling constants are rounded to the nearest 0.5 Hz. IR spectra were recorded on an ATI Mattson Genesis FTIR as thin films produced by evaporation of a DCM solution on sodium chloride plates unless otherwise stated. Mass spectra were recorded on Fison VG Trio 2000 and Kratos Concept spectrometers. Chemical ionisation (CI) was performed using ammonia. Characteristic clumps of peaks were observed for the alkenylgermanes due to the germanium isotopes, ^{74}Ge, ^{72}Ge and ^{70}Ge. Accurate mass measurements were taken for the major peaks corresponding to ^{74}Ge. Chromatography refers to flash column chromatography using Merck silica gel 60H (230–300 mesh). Tetrahydrofuran (THF) was dried and distilled from sodium metal using benzophenone as an indicator under an atmosphere of nitrogen. Dichloromethane (DCM) was dried and distilled from calcium hydride under an atmosphere of nitrogen. Ether refers to diethyl ether, which was dried and distilled from sodium metal using benzophenone as an indicator under an atmosphere of nitrogen. Light petroleum refers to the fraction of petroleum ether distilled between 40 and 60 °C. Benzene and hexane were dried over sodium metal. Butyllithium (1.6 M in hexanes) was titrated against a solution of propan-2-ol in xylene with 2,2′-bipyridine as an indicator. Triethylamine and diisopropylamine were dried over potassium hydroxide pellets. Brine refers to saturated aqueous sodium chloride.

Many of the products were known having been prepared using alkenylstannanes.[1] The structures of new compounds were assigned by analogy. The ratios of the products were estimated by ^{1}H and ^{13}C NMR. For the products prepared using aromatic aldehydes, the methyl doublets or the benzylic hydrogen peaks were most useful in this respect. It was more difficult to estimate accurately the ratios of products prepared using aliphatic aldehydes, and so, for example, the major products **4b**,**c** were converted into the minor products **6b**,**c** for direct comparison.[1]

4.2. Experimental procedures

*4.2.1. (2E,4RS)-5-Benzyloxy-1-chloro-4-methylpent-2-ene (**8**).* Triphenylphosphine (2.1 g, 8.24 mmol) was added to racemic (*E*)-5-benzyloxy-4-methylpent-2-en-1-ol[1] (1.0 g, 4.85 mmol) in carbon tetrachloride (10 mL) and the mixture was stirred at rt for 42 h. Ether (150 mL) was added and the organic extracts were washed with water (30 mL) and brine (30 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography using 5% ether in light petroleum as eluent gave the *title compound* **8** (0.8 g, 74%) as a colourless oil, R_f 0.42 in 9:1 light petroleum/ether; ν_{max}/cm^{-1} 3064, 2960, 2857, 1453, 1360, 1250, 1098, 969, 737 and 698; δ_H ($CDCl_3$, 300 MHz) 1.11 (3H, d, *J* 7.0, 4-CH_3), 2.59 (1H, hept, *J* 6.5, 4-H), 3.39 and 3.41 (each 1H, dd, *J* 14.0, 9.0, 1-H), 4.10 (2H, d, *J* 6.5, 5-H_2), 4.56 (2H, s, PhCH_2), 5.71 (1H, dt, *J* 15.5, 6.5, 2-H), 5.82 (1H, dd, *J* 15.5, 6.5, 3-H) and 7.30–7.45 (5H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 16.9, 36.8, 45.7, 73.3, 75.0, 126.0, 127.8, 127.9, 128.7, 138.5 and 138.7; *m*/*e* (CI) 244 (M^++18, 35%) and 242 (M^++18, 100); HRMS: M^+, found 224.0966. $C_{13}H_{17}{}^{35}ClO$ requires 224.0962.

*4.2.2. (2E,Z,4RS)-5-Benzyloxy-4-methylpent-2-enyl(triphenyl)germane (E,Z)-(**9**).* A mixture of magnesium turnings (0.38 g, oven dried, 15.6 mmol), iodine (1 crystal) and triphenylgermanium bromide (2.52 g, 6.57 mmol) in THF (15 mL) was placed in an ultrasonic bath. The chloride (*E*)-**8** (2.67 g, 11.9 mmol) in THF (15 mL) was added dropwise. After 30 min in the ultrasonic bath at rt, the flask was removed from the bath and heated to 45 °C for 4 h. Saturated aqueous ammonium chloride (60 mL) was added and the aqueous layer washed with ether (3×30 mL). The organic extracts were washed with water (30 mL) and brine (30 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography using light petroleum/ether (25:1) as eluent gave the *title compound* **9** (2.76 g, 85%), a 55:45 mixture of (*E*)-and (*Z*)-isomers as a colourless oil, R_f 0.58 in 10:1 light petroleum/ether; ν_{max}/cm^{-1} 3066, 2852, 2362, 1484, 1453, 1430, 1091 and 733; δ_H ($CDCl_3$, 300 MHz) 0.82 (1.35H, d, *J* 6.5, 4-CH_3), 0.94 (1.65H, d, *J* 6.5, 4-CH_3), 2.37–2.61 (2.45H, m, 1-H_2 and 4-H), 2.75 (0.55H, m, 4-H), 3.08–3.13 (0.9H, m, 5-H_2), 3.14 and 3.24 (each 0.55H, dd, *J* 7.0, 8.0, 5-H), 4.43 and 4.46 (each 0.55H, d, *J* 12.0, PhHC*H*), 4.48 and 4.50 (each 0.45H, d, *J* 12.0, PhHC*H*), 5.14 (0.45H, dd, *J* 10.5, 9.5, 3-H), 5.33 (0.55H, dd, *J* 15.5, 7.5, 3-H), 5.64 (1H, m, 2-H), 7.29–7.45 (15H, m, ArH) and 7.50–7.56 (5H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 15.8, 17.6, 17.7, 19.9, 32.4, 37.3, 73.1(2), 75.3, 75.8, 125.4, 125.7, 127.7, 127.8(2), 128.4(2) 128.6, 129.2, 129.3, 131.9, 133.2, 135.3(2), 136.9, 137.0 and 139.1; *m*/*z* (ESI) 517 (M^++23, 100%), 515 (M^++23, 80), 513 (M^++23, 60), 338 (30) and 242 (65); HRMS: M^++Na, found 517.1560. $C_{31}H_{32}{}^{74}GeNaO$ requires 517.1557.

*4.2.3. Syntheses of pent-2-enylgermanes **9** and **13** from acetates (E)- and (Z)-**12***

*4.2.3.1. (2E)-5-Benzyloxy-4-methylpent-2-enyl(triphenyl)germane (E)-(**9**); standard procedure.* To triphenylgermanium hydride (305 mg, 1.08 mmol) and TMEDA (170 μL, 1.19 mmol) in THF (2 mL) at 0 °C was added ^{t}BuLi (1.7 M in pentane, 0.70 mL, 1.19 mmol). After 30 min, copper(I) iodide (95 mg, oven dried, 0.54 mmol) was added. After a further 10 min, the solution was cooled to −23 °C and the acetate (*E*)-**12** (124 mg, 0.50 mmol) added in THF (1 mL). After 30 min at −23 °C, an aqueous phosphate buffer (pH 7, 5 mL) and aqueous ammonium chloride (4%, 10 mL) were added. The mixture was extracted with ether (3×15 mL) and the organic extracts washed with aqueous ammonium chloride (4%, 2 15 mL), water (15 mL) and brine (15 mL). After drying (Na_2SO_4) and concentration under reduced pressure, chromatography using light petroleum/ether (30:1) gave the *title compound* (*E*)-**9** (43 mg, 17%) as a colourless oil, R_f 0.40 in 9:1 light petroleum/ether; ν_{max}/cm^{-1} 3067, 3048, 2937, 2857, 1484, 1453, 1430, 1092, 1027 and 734; δ_H ($CDCl_3$, 300 MHz) 0.96 (3H, d, *J* 6.5, 4-CH_3), 2.45 (1H, m, 4-H), 2.48 (2H, d, *J* 8.0, 1-H_2), 3.16 (1H, dd, *J* 9.0, 7.0, 5-H), 3.26 (1H, dd, *J* 9.0, 6.5, 5-H′), 4.48 and 4.50 (each 1H, d, *J* 12.0, PhHC*H*), 5.34 (1H, dd, *J* 15.0, 7.5, 3-H), 5.64 (1H, dt, *J* 15.0, 7.5, 2-H), and 7.29–7.58 (20H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 17.6, 19.9, 37.3, 73.1, 75.8, 125.7, 127.7, 127.8, 128.4, 128.6, 129.2, 133.2, 135.3, 137.0 and 139.0; *m*/*z* (CI) 512 (M^++18, 28%), 510 (M^++18, 20), 508 (M^++18, 18), 322 (100), 320 (75), 318 (60) and 208 (37); HRMS: M^++NH_4, found 512.2002. $C_{31}H_{36}{}^{74}GeNaO$ requires 512.2003.

*4.2.3.2. (2Z)-5-Benzyloxy-4-methylpent-2-enyl(triphenyl)germane (Z)-(**9**).* Triphenylgermanium hydride (0.87 g, 2.82 mmol) and the acetate (*Z*)-**12** (350 mg, 1.41 mmol) after chromatography using light petroleum/ether (30:1) as eluent gave the *title compound* (*Z*)-**9** (363 mg, 52%) as a colourless oil, R_f 0.41 in 9:1 light petroleum/ether; ν_{max}/cm^{-1} 3067, 3048, 3006, 2957, 2925, 2853, 1484, 1430, 1092 and 734; δ_{3H} ($CDCl_3$, 300 MHz) 0.84 (3H, d, *J* 6.5, 4-CH_3), 2.40–2.65 (2H, m, 1-H_2), 2.76 (1H, m, 4-H), 3.13 (2H, d, *J* 7.0, 5-H_2), 4.43 and 4.50 (each 1H, d, *J* 12.5, PhHC*H*), 5.16 (1H, t, *J* 10.0, 3-H), 5.66 (1H, dt, *J* 10.0, 9.0, 2-H), 7.28–7.63 (20H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 15.9, 17.8, 32.4, 73.1, 75.3, 125.5, 127.8, 128.5, 128.6, 129.3, 131.9, 134.7, 135.3, 135.8 and 136.9; *m*/*z* (CI) 512 (M^++18, 25%), 510 (M^++18, 15), 508 (M^++18, 14), 322 (100), 320 (75), 318 (50) and 208 (40); HRMS: M^++NH_4, 512.1995. $C_{31}H_{36}{}^{74}GeNaO$ requires 512.2003.

*4.2.3.3. (2E)-5-Benzyloxy-4-methylpent-2-enyl(triethyl)germane (E)-(**13**).* The standard procedure but with addition of the solution of triethylgermanium hydride (0.25 mL, 1.55 mmol), TMEDA (0.26 mL, 1.70 mmol) in THF (2 mL) and ^{t}BuLi (1.7 M in pentane, 1.09 mL, 1.85 mmol) to the suspension of copper(I) iodide (147 mg, oven dried, 0.775 mmol) in THF (3 mL), followed by addition of the acetate (*E*)-**12** (192 mg, 0.78 mmol) in THF (2 mL), after chromatography using light petroleum/ether (60:1), gave the *title compound* (*E*)-**13** (151 mg, 29%) as a colourless oil, R_f 0.66 in 19:1 light petroleum/ether; ν_{max}/cm^{-1} 3414, 2963, 2916, 1719, 1655, 1364, 1260, 1018 and 799; δ_H ($CDCl_3$, 300 MHz) 0.76 (6H, q, *J* 8.0, 3× $GeCH_2$), 0.98–1.15 (12H, m, 3× $GeCH_2CH_3$ and 4-CH_3), 1.65 (2H, d, *J* 8.0, 1-H_2), 2.49 (1H, m, 4-H), 3.28 (1H, dd, *J* 9.0, 7.5, 5-H), 3.39 (1H, dd, *J* 9.0, 6.5, 5-H′), 4.56 (2H, s, $PhCH_2$), 5.25 (1H, dd, *J* 15.0, 7.0, 3-H), 5.55 (1H, dt, *J* 15.0, 7.0, 2-H) and 7.29–7.43 (5H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 4.1, 9.2, 17.3, 17.9, 37.3, 73.2, 76.2, 127.7, 127.8, 128.6, 130.5 and 139.0; *m*/*z* (EI) 350 (M^+, 10%), 348 (M^+, 9), 346 (M^+, 7), 321 (100), 319 (95), 317 (70) and 267 (70); HRMS: M^+, found 350.1659. $C_{19}H_{32}{}^{74}GeO$ requires 350.1659.

*4.2.3.4. (Z)-5-Benzyloxy-4-methylpent-2-enyl(triethyl)germane (Z)-(**13**).* The standard procedure with addition of the solution of triethylgermanium hydride, TMEDA and ^{t}BuLi to the copper(I) iodide, using triethylgermanium hydride (0.21 mL, 1.26 mmol) and the acetate (*Z*)-**12** (156 mg, 0.63 mmol), after chromatography using 2% ether in light petroleum as eluent gave the *title compound* (*Z*)-**13** (210 mg, 96%) as a colourless oil, R_f 0.74 in 9:1 light petroleum/ether; ν_{max}/cm^{-1} 2951, 2928, 2905, 2870, 1643, 1454, 1113, 1096, 1019 and 735; δ_H ($CDCl_3$, 300 MHz) 0.80 (6H, q, *J* 8.0, 3× $GeCH_2$), 1.02–1.13 (12H, m, 3× $GeCH_2CH_3$ and 4-CH_3), 1.67 and 1.76 (each 1H, ddd, *J* 14.0, 8.5, 1.5,1-H), 2.84 (1H, m, 4-H), 3.28 (1H, dd, *J* 9.0, 8.0, 5-H), 3.40 (1H, dd, *J* 9.0, 5.5, 5-H′), 4.55 and 4.61 (each 1H, d, *J* 14.5, PhHC*H*), 5.06 (1H, dd, *J* 10.5, 9.5, 3-H), 5.51 (1H, q, *J* 9.5, 2-H) and 7.30–7.42 (5H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 4.2, 9.2, 13.3, 18.2, 32.2, 73.2, 75.6, 127.5, 127.7, 127.8, 128.6, 129.4 and 139.1; *m*/*z* (CI) 368 (M^++18, 15%), 366 (M^++18, 13), 364 (M^++18, 10), 351 (M^++1, 5), 349 (M^++1, 4), 347 (M^++1, 3), 178 (100), 176 (70) and 174 (50): HRMS: M^++NH_4, 368.2005. $C_{19}H_{36}{}^{74}GeNO$ requires 368.2003.

*4.2.4. Synthesis of acetates (E)- and (Z)-**12***

*4.2.4.1. (2E,4RS)-5-Benzyloxy-4-methylpent-2-en-1-yl acetate (E)-(**12**); standard procedure.* Acetic anhydride (0.57 mL, 6.0 mmol) was added to (*E*)-5-benzyloxy-4-methylpent-2-en-1-ol[1,11] (1.13 g, 5.5 mmol) in pyridine (1.3 mL, 16.5 mmol) and the solution stirred at rt overnight. Ether (100 mL) was added and the organic extracts were washed with water (40 mL), aqueous hydrogen chloride (0.1 M, 40 mL) and saturated aqueous sodium bicarbonate (40 mL). After drying ($MgSO_4$) and concentration under reduced pressure, chromatography of the residue using light petroleum/ether (2:1) as eluent, gave the title compound[11] (*E*)-**12** (1.30 g, 95%) as a colourless oil, R_f 0.61 in 1:1 light petroleum/ether; ν_{max}/cm^{-1} 2961, 2858, 1739, 1453, 1364, 1235, 1097, 1027, 964 and 737; δ_H ($CDCl_3$, 300 MHz) 1.09 (3H, d, *J* 7.0, 4-CH_3), 2.10 (3H, s, CH_3CO), 2.58 (1H, m, 4-H), 3.38 (1H, dd, *J* 18.5 and 9.0, 5-H), 3.40 (1H, dd, *J* 18.5 and 9.0, 5-H′), 4.48–4.62 (4H, m, 1-H_2 and $PhCH_2$), 5.66 (1H, dt, *J* 15.5 and 6.0, 2-H), 5.80 (1H, dd, *J* 14.5 and 6.5, 3-H) and 7.29–7.42 (5H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 17.0, 21.3, 36.9, 65.5, 73.2, 75.1, 123.9, 127.8(2), 128.6, 138.8(2) and 171.1; *m*/*z* (CI) 266 (M^++18, 100%), 249 (M^++1, 10) and 189 (100); HRMS: M^++H, 249.1489. $C_{15}H_{21}O_3$ requires 249.1485.

*4.2.4.2. (2Z,4RS)-5-Benzyloxy-4-methylpent-2-en-1-yl acetate (Z)-(**12**).* Acetic anhydride (0.37 mL, 3.77 mmol), (*Z*)-5-benzyloxy-4-methylpent-2-en-1-ol[12] (0.71 g; 3.43 mmol) and pyridine (0.84 mL, 10.2 mmol), after chromatography using light petroleum/ether (5:1) as eluent gave the *title compound* (*Z*)-**12** (0.81 g, 95%) as a colourless oil, R_f 0.28 in 4:1 light petroleum/ether; ν_{max}/cm^{-1} 3027, 2960, 2929, 2857, 1739, 1454, 1372, 1232, 1099, 1027 and 738; δ_H ($CDCl_3$, 300 MHz) 1.07 (3H, d, *J* 6.5, 4-CH_3), 2.10 (3H, s, CH_3CO), 2.91 (1H, m, 4-H), 3.30–3.42 (2H, m, 5-H_2), 4.56 (2H, s, $PhCH_2$), 4.66 (1H, dd, *J* 12.5, 6.0, 1-H), 4.74 (1H, dd, *J* 12.5, 7.0, 1-H′), 5.54 (1H, dd, *J* 11.0, 9.5, 3-H), 5.63 (1H, dt, *J* 11.0, 6.5, 2-H) and 7.29–7.43 (5H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 17.9, 21.3, 33.1, 60.9, 73.2, 75.1, 124.2, 127.8, 128.6, 138.1, 138.8 and 171.2; *m*/*z* (CI) 266 (M^++18, 100%) and 249 (M^++1, 5); HRMS: M^++NH_4, found 266.1748. $C_{15}H_{24}NO_3$ requires 266.1751.

*4.2.5. Tin(IV) halide promoted reactions of pent-2-enylgermanes **9** and **13** with aldehydes*

*4.2.5.1. (1RS,5SR,3Z)-6-Benzyloxy-5-methyl-1-phenylhex-3-en-1-ol (**4a**); standard procedure.* Tin(IV) chloride (1 M in DCM, 0.22 mL, 0.22 mmol) in DCM (0.5 mL) cooled to −78 °C, was added to the (*E*,*Z*)-pent-2-enyl(triphenyl)germane (*E*,*Z*)-**9** (100 mg, 0.20 mmol) in DCM (0.8 mL) at −78 °C and the solution stirred at −78 °C for 15 min. Benzaldehyde (70 μL, 0.69 mmol) was added and the reaction mixture was stirred at −78 °C for 45 min. Saturated methanolic ammonium chloride (1 mL) was added followed by water (30 mL). The mixture was extracted using ether (3×20 mL) and the organic extracts were washed with water (20 mL) and brine (20 mL), then dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum/ether (4:1) as eluent gave the title compound **4a**[1] (46 mg, 77%) as a colourless oil, **4a**/**6a**=96:4 (^{1}H NMR; 5-CH_3 **4a**, δ 0.91, d; **6a**, δ 0.95, d), R_f 0.16 in 4:1 light petroleum/ether.

Tin(IV) chloride (1 M in DCM, 0.074 mL, 0.074 mmol) in DCM (0.3 mL), the (*E*)-pent-2-enyl(triphenyl)germane (*E*)-**9** (34 mg, 0.069 mmol) in DCM (0.5 mL) and benzaldehyde (27 μL, 0.26 mmol) gave the title compound **4a** (16 mg, 86%) as a colourless oil, **4a**/**6a**=90:10.

Tin(IV) chloride (1 M in DCM, 0.37 mL, 0.37 mmol) in DCM (0.5 mL), the (*E*)-pent-2-enyl(triethyl)germane (*E*)-**13** (120 mg, 0.34 mmol) in DCM (1.0 mL) and benzaldehyde (118 μL, 1.02 mmol) gave the title compound **4a** (64 mg, 63%) as a colourless oil, **4a**/**6a**=88:12.

Tin(IV) chloride (1 M in DCM, 0.18 mL, 0.18 mmol) in DCM (0.5 mL), the (*Z*)-pent-2-enyl(triphenyl)germane (*Z*)-**9** (84 mg, 0.203 mmol) in DCM (0.8 mL) and benzaldehyde (60 μL, 0.59 mmol) gave the title compound **4a** (37 mg, 73%) as a colourless oil, **4a**/**6a**=98:2.

Tin(IV) chloride (1 M in DCM, 0.18 mL, 0.18 mmol) in DCM (0.5 mL), the (*Z*)-pent-2-enyl(triethyl)germane (*Z*)-**13** (84 mg, 0.203 mmol) in DCM (0.8 mL) and benzaldehyde (60 μL, 0.59 mmol) gave the title compound **4a** (58 mg, 98%) as a colourless oil, **4a**/**6a**=98:2.

Tin(IV) bromide (84 mg, 0.12 mmol) in DCM (0.65 mL), the (*Z*)-pent-2-enyl(triethyl)germane (*Z*)-**13** (55 mg, 0.16 mmol) in DCM (0.8 mL) and benzaldehyde (58 μL, 0.57 mmol) gave the title compound **4a** (32 mg, 67%) as a colourless oil, **4a**/**6a**=99:1.

*4.2.5.2. (3RS,7SR,5Z)-8-Benzyloxy-2,7-dimethyloct-5-en-3-ol (**4b**).* Tin(IV) chloride (1 M in DCM, 0.22 mL, 0.22 mmol) in DCM (0.5 mL), the (*E*,*Z*)-pent-2-enyl(triphenyl)germane (*E*,*Z*)-**9** (100 mg, 0.203 mmol) in DCM (1.0 mL) and 2-methylpropanal (60 μL, 0.60 mmol), after chromatography using light petroleum/ether (5:1) as eluent, gave the title compound **4b**[1] (41 mg, 78%) as a colourless oil, **4b**/**6b**=99:1 (^{1}H NMR, $PhCH_2$), R_f 0.26 in 4:1 light petroleum/ether.

Tin(IV) chloride (1 M in DCM, 0.23 mL, 0.23 mmol) in DCM (0.5 mL), (*Z*)-pent-2-enyl(triethyl)germane (*Z*)-**13** (74 mg, 0.212 mmol) in DCM (1 mL) and 2-methylpropanal (58 μL, 0.60 mmol) gave the title compound **4b** (32 mg, 57%) as a colourless oil, **4b**/**6b**=99:1.

*4.2.5.3. (4RS,8RS,6Z)-9-Benzyloxy-8-methylnon-6-en-4-ol (**4c**).* Tin(IV) chloride (1 M in DCM, 0.22 mL, 0.22 mmol) in DCM (0.5 mL), the (*E*,*Z*)-pent-2-enyl(triphenyl)germane (*E*,*Z*)-**9** (100 mg, 0.203 mmol) in DCM (1.0 mL) and butanal (60 μL, 0.6 mmol), after chromatography using light petroleum/ether (5:1) as eluent, gave the title compound **4c**[3c] (36 mg, 67%) as a colourless oil, **4c**/**6c**=98:2 (^{1}H NMR, $PhCH_2$), R_f 0.21 in 4:1 light petroleum/ether.

Tin(IV) chloride (1 M in DCM, 0.26 mL, 0.26 mmol) in DCM (0.5 mL), the (*Z*)-pent-2-enyl(triethyl)germane (*Z*)-**13** (75 mg, 0.215 mmol) in DCM (1.0 mL) and butanal (59 mL, 0.64 mmol) after chromatography using light petroleum/ether (4:1) as eluent, gave the title compound **4c** (42 mg, 74%) as a colourless oil, **4c**/**6c**=99:1.

*4.2.5.4. (2RS,6SR,4Z)-1,7-Bis(benzyloxy)-6-methylhept-4-en-2-ol (**4d**).* Tin(IV) chloride (1 M in DCM, 0.22 mL, 0.22 mmol) in DCM (0.5 mL), the (*E*,*Z*)-pent-2-enyl(triphenyl)germane (*E*,*Z*)-**9** (100 mg, 0.203 mmol) in DCM (1.5 mL) and 2-benzyloxyethanal (31 μL, 1.1 0.22 mmol), after chromatography using light petroleum/ether (4:1) as eluent, gave the *title compound* **4d** (48 mg, 69%) as a colourless oil, **4d**/**6d**=96:4 (^{1}H NMR, 6-CH_3), R_f 0.35 in 1:1 light petroleum/ether.

Tin(IV) chloride (1 M in DCM, 0.20 mL, 0.2 mmol) in DCM (0.5 mL), the (*Z*)-pent-2-enyl(triethyl)germane (*Z*)-**13** (65 mg, 0.186 mmol) in DCM (1.0 mL) and 2-benzyloxyethanal (29 μL, 0.2 mmol), after chromatography using light petroleum/ether (3:1) as eluent, gave the *title compound* **4d** (36 mg, 57%) as a colourless oil, **4d**/**6d**=97:3; ν_{max}/cm^{-1} 3426, 2954, 2925, 2859, 1453, 1094, 1075, 1028 and 735; δ_H ($CDCl_3$, 300 MHz) 0.98 (3H, d, *J* 6.5, 6-CH_3), 2.20–2.45 (2H, m, 3-H_2), 2.90 (1H, m, 6-H), 3.18 (1H, s, OH), 3.26 (1H, t, *J* 8.5, 7-H), 3.36 (1H, dd, *J* 8.5, 6.0, 7-H′), 3.51 (2H, m, 1-H_2), 3.87 (1H, m, 2-H), 4.56 and 4.61 (each 2H, s, $PhCH_2$), 5.37 (1H, t, *J* 11.0, 6-H), 5.53 (1H, td, *J* 11.0, 7.0, 5-H) and 7.30–7.50 (10H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 17.6, 32.5, 32.6, 70.3, 73.2, 73.7, 74.5, 75.0, 126.0, 127.9, 128.0, 128.6, 128.7, 128.8, 134.4, 136.3 and 138.5; *m*/*z* (CI) 358 (M^++18, 100%) and 341 (M^++1, 30); HRMS: M^++H, found 341.2123. $C_{22}H_{29}O_3$ requires 341.2111.

*4.2.5.5. (1RS,5SR,3Z)-6-Benzyloxy-1-(4-chlorophenyl)-5-methylhex-3-en-1-ol (**4e**).* Tin(IV) chloride (1 M in DCM, 0.18 mL, 0.18 mmol) in DCM (0.5 mL), the (*E*,*Z*)-pent-2-enyl(triphenyl)germane (*E*,*Z*)-**9** (80 mg, 0.162 mmol) in DCM (1.3 mL) and 4-chlorobenzaldehyde (68 mg, 0.49 mmol) in DCM (0.3 mL), after chromatography using light petroleum/ether (4:1) as eluent, gave the title compound **4e**[1] (30 mg, 56%) as a colourless oil, **4e**/**6e**=99:1 (^{1}H NMR), R_f 0.13 in 4:1 light petroleum/ether.

Tin(IV) chloride (1 M in DCM, 0.20 mL, 0.2 mmol) in DCM (0.5 mL), the (*Z*)-pent-2-enyl(triethyl)germane (*Z*)-**13** (58 mg, 0.166 mmol) in DCM (1.0 mL) and 4-chlorobenzaldehyde (70 mg, 0.5 mmol) in DCM (0.3 mL), after chromatography using light petroleum/ether (4:1) as eluent, gave the title compound **4e** (46 mg, 84%) as a colourless oil, **4e**/**6e**=99:1.

*4.2.5.6. (1RS,5SR,3Z)-6-Benzyloxy-1-(3-chlorophenyl)-5-methylhex-3-en-1-ol (**4f**).* Tin(IV) chloride (1 M in DCM, 0.18 mL, 0.18 mmol) in DCM (0.5 mL), the (*E*,*Z*)-pent-2-enyl(triphenyl)germane (*E*,*Z*)-**9** (80 mg, 0.162 mmol) in DCM (1.3 mL) and 3-chlorobenzaldehyde (55 mL, 0.49 mmol), after chromatography using light petroleum/ether (4:1) as eluent, gave the *title compound* **4f** (18 mg, 34%) as a colourless oil, **4f**/**6f**=98:2 (^{1}H NMR, 5-CH_3), R_f 0.15 in 4:1 light petroleum/ether; ν_{max}/cm^{-1} 3426, 2957, 2925, 2862, 1598, 1573, 1476, 1454, 1198, 1094, 1073 and 786; δ_H ($CDCl_3$, 300 MHz) 0.93 (3H, d, *J* 6.5, 5-CH_3), 2.38 (1H, m, 2-H), 2.60 (1H, dt, *J* 13.5, 10.5, 2-H′), 2.91 (1H, m, 5-H), 3.22 (1H, t, *J* 9.5, 6-H), 3.78 (1H, br s, OH), 3.41 (1H, dd, *J* 8.5, 5.0, 6-H′), 4.60 (2H, s, $PhCH_2$), 4.67 (1H, dd, *J* 10.0, 3.5, 1-H), 5.41 (1H, t, *J* 10.0, 4-H), 5.60 (1H, td, *J* 10.5, 6.0, 3-H) and 7.22–7.44 (9H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 17.3, 32.6, 38.9, 72.8, 73.4, 74.9, 124.1, 126.1, 127.5, 128.0, 128.2, 128.7, 129.8, 134.4, 137.5, 138.0 and 147.3; *m*/*z* (CI) 350 (M^++18, 10%), 348 (M^++18, 25), 332 (M^+, 5), 330 (M^+, 10), 102 (90) and 85 (100); HRMS: M^++NH_4 found 348.1726. $C_{20}H_{27}{}^{35}ClNO_2$ requires 348.1725.

*4.2.5.7. (1RS,5SR,3Z)-6-Benzyloxy-1-(4-methoxyphenyl)-5-methylhex-3-en-1-ol (**4g**).* Tin(IV) chloride (1 M in DCM, 0.44 mL, 0.44 mmol) in DCM (0.5 mL), the (*E*,*Z*)-pent-2-enyl(triphenyl)germane (*E*,*Z*)-**9** (200 mg, 0.406 mmol) in DCM (2.0 mL) and 4-methoxybenzaldehyde (54 mL, 0.45 mmol), after chromatography using light petroleum/ether (2:1), gave the title compound **4g**[1] (56 mg, 42%) as a colourless oil, **4g**/**6g**=93:7 (^{1}H NMR), R_f 0.17 in 2:1 light petroleum/ether.

Tin(IV) chloride (1 M in DCM, 0.24 mL, 0.24 mmol) in DCM (0.5 mL), the (*Z*)-pent-2-enyl(triethyl)germane (*Z*)-**13** (70 mg, 0.20 mmol) in DCM (1.0 mL) and 4-methoxybenzaldehyde (27 μL, 2.2 mmol) after chromatography using light petroleum/ether (2:1) as eluent gave the title compound **4g** (53 mg, 81%) as a colourless oil, **4g**/**6g**=96:4.

*4.2.5.8. (1RS,5SR,3Z)-6-Benzyloxy-5-methyl-1-(4-nitrophenyl) hex-3-en-1-ol (**4h**).* Tin(IV) chloride (1 M in DCM, 0.18 mL, 0.18 mmol) in DCM (0.5 mL), the (*E*,*Z*)-pent-2-enyl(triphenyl)germane (*E*,*Z*)-**9** (80 mg, 0.162 mmol) in DCM (1.3 mL) and 4-nitrobenzaldehyde (74 mg, 0.49 mmol) in DCM (0.3 mL), after chromatography using light petroleum/ether (3:1), gave the *title compound* **4h** (49 mg, 88%) as a colourless oil **4h**/**6h**=94:6, R_f 0.18 in 2:1 light petroleum/ether.

Tin(IV) chloride (1 M in DCM, 0.22 mL, 0.22 mmol) in DCM (0.5 mL), the (*Z*)-pent-2-enyl(triethyl)germane (*Z*)-**13** (70 mg, 0.20 mmol) in DCM (1.0 mL) and 4-nitrobenzaldehyde (65 mg, 0.60 mmol) in DCM (0.3 mL), after chromatography using light petroleum/ether (3:1), gave the *title compound* **4h** (58 mg, 85%) as a colourless oil, **4h**/**6h**=99:1 (^{1}H NMR); ν_{max}/cm^{-1} 3424, 2925, 2858, 1602, 1520, 1454, 1345, 1073, 855 and 744; δ_H ($CDCl_3$, 300 MHz) 0.93 (3H, d, *J* 7.0, 5-CH_3), 2.70 (1H, m, 2-H), 2.59 (1H, dt, *J* 14.0, 10.0, 2-H′), 2.92 (1H, m, 5-H), 3.20 (1H, t, *J* 8.5, 6-H), 3.46 (1H, dd, *J* 8.5, 4.5, 6-H′), 4.16 (1H, br s, OH), 4.61 (2H, s, $PhCH_2$), 4.80 (1H, dd, *J* 10.0, 3.0, 1-H), 5.46 (1H, t, *J* 11.0, 4-H), 5.63 (1H, dt, *J* 5.5, 11.0, 3-H), 7.30–7.49 (5H, m, ArH) and 7.53 and 8.21 (each 2H, d, *J* 9.0, ArH); δ_C ($CDCl_3$, 75 MHz) 17.3, 32.6, 39.0, 72.5, 73.5, 75.0, 123.8, 125.8, 126.7, 128.2, 128.4, 128.8, 134.4, 137.9, 138.0, 147.3 and 152.9; *m*/*z* (CI) 359 (M^++18, 50%), 342 (M^++1, 10), 294 (100) and 106 (95); HRMS: M^++NH_4, found 359.1962. $C_{20}H_{27}N_2O_4$ requires 359.1965.

*4.2.5.9. (4RS,8SR,2E,6Z)-9-Benzyloxy-8-methylnona-2,6-dien-4-ol (**4i**).* Tin(IV) chloride (1 M in DCM, 0.22 mL, 0.22 mmol) in DCM (0.5 mL), the (*E*,*Z*)-pent-2-enyl(triphenyl)germane (*E*,*Z*)-**9** (100 mg, 0.203 mmol) in DCM (1.0 mL) and (*E*)-but-2-enal (60 mL, 0.60 mmol), after chromatography using light petroleum/ether (5:1) gave the *title compound* **4i** (46 mg, 86%) as a colourless oil, **4i**/**6i**=97:3 (^{1}H NMR, 8-CH_3), R_f 0.19 in 4:1 light petroleum/ether; ν_{max}/cm^{-1} 3426, 3004, 2959, 2927, 2855, 1453, 1434, 1094, 966 and 737; δ_H ($CDCl_3$, 300 MHz) 0.97 (3H, d, *J* 6.5, 8-CH_3), 1.75 (3H, d, *J* 7.0, 1-H_3), 2.27 (2H, dt, *J* 14.0, 5.5, 5-H), 2.42 (1H, dt, *J* 14.0, 9.0, 5-H′), 2.87–2.98 (2H, m, OH and 8-H), 3.23 (1H, t, *J* 9.0, 9-H), 3.37 (1H, dd, *J* 9.0, 5.5, 9-H′), 4.09 (1H, m, 4-H), 4.57 (2H, s, $PhCH_2$), 5.38 (1H, dd, *J* 11.0, 10.0, 7-H), 5.48–5.62 (2H, m, 3-H and 6-H), 5.74 (1H, dq, *J* 15.0, 6.5, 2-H) and 7.28–7.54 (5H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 17.6, 18.0, 32.6, 36.5, 72.1, 73.3, 75.0, 126.2, 126.5, 127.9, 128.1, 128.3, 134.2, 136.6 and 138.4; *m*/*z* (CI) 278 (M^++18, 7%), 260 (M^+, 15), 243 (M^+−17, 90), 225 (40) and 137 (100); HRMS: M^++NH_4, 278.2116. $C_{17}H_{28}NO_2$ requires 278.2115.

*4.2.5.10. (3RS,7SR,1E,5Z)-8-Benzyloxy-7-methyl-1-phenylocta-1,5-dien-3-ol (**4j**).* Tin(IV) chloride (1 M in DCM, 0.33 mL, 0.33 mmol) in DCM (0.5 mL), the (*E*,*Z*)-pent-2-enyl(triphenyl)

germane (*E,Z*)-**9** (150 mg, 0.304 mmol) in DCM (2 mL) and (*E*)-cinnamaldehyde (120 μL, 0.90 mmol), after chromatography using light petroleum/ether (3:1) as eluent gave the *title compound* **4j** (66 mg, 67%) as a colourless oil, **4j**/**6j**=95:5 (^{1}H NMR, 7-CH_3), R_f 0.11 in 4:1 light petroleum/ether; ν_{max}/cm^{-1} 3417, 3026, 2960, 2926, 2858, 1453, 1432, 1095, 967 and 738; δ_H ($CDCl_3$, 300 MHz) 0.96 (3H, d, *J* 6.5, 7-CH_3), 2.36 (1H, dt, *J* 14.0, 4.5, 4-H), 2.52 (1H, dt, *J* 14.0, 9.0, 4-H′), 2.93 (1H, m, 7-H), 3.23 (1H, t, *J* 9.0, 8-H), 3.38 (1H, dd, *J* 9.0, 5.5, 8-H′), 4.32 (1H, m, 3-H), 4.57 (2H, s, $PhCH_2$), 5.41 (1H, t, *J* 11.0, 6-H), 5.57 (1H, dt, *J* 6.5, 10.5, 5-H), 6.28 (1H, dd, *J* 16.0, 6.0, 2-H), 6.65 (1H, d, *J* 16.0, 1-H) and 7.20–7.52 (10H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 17.5, 32.6, 36.5, 71.9, 73.3, 75.0, 125.9, 126.7, 127.9, 128.1, 128.6, 128.7, 129.8, 130.3, 132.6, 134.3, 137.0 and 138.3; *m*/*z* (CI) 340 (M^++18, 5%), 322 (M^+, 20), 305 (100), 287 (30) and 199 (45).

4.2.6. Synthesis of 4-nitrobenzoates by esterification using 4-nitrobenzoyl chloride

*4.2.6.1. (3RS,7SR,5Z)-8-Benzyloxy-2,7-dimethyloct-5-en-3-yl 4-nitrobenzoate (**10b**); standard procedure.* A solution of alcohol **4b** (16 mg, 0.061 mmol), triethylamine (20 μL, 0.12 mmol) and DMAP (2/3 crystals) in THF (0.6 mL) was cooled to 0 °C. After 10 min, 4-nitrobenzoyl chloride (17 mg, 0.91 mmol) in THF (0.4 mL) was added and the solution stirred at rt for 4.5 h. More DMAP (2/3 crystals) was added and the reaction mixture stirred at rt overnight. Saturated aqueous sodium hydrogen carbonate (1 mL) and water (10 mL) were added and the mixture extracted with ether (3×15 mL). The organic extracts were washed with water (15 mL) and brine (15 mL) before drying (Na_2SO_4) and concentration under reduced pressure. Chromatography of the residue using light petroleum/ether (10:1) as eluent gave the *title compound* **10b** (15 mg, 59%) as a yellow oil containing ca. 1% of its *syn*-epimer **11b**, R_f 0.28 in 9:1 light petroleum/ether; ν_{max}/cm^{-1} 2963, 2930, 2874, 1723, 1529, 1348, 1274, 1115, 1102 and 720; δ_H ($CDCl_3$, 300 MHz) major **10b** 1.03 (6H, d, *J* 6.5, 1-H_3 and 2-CH_3), 1.06 (3H, d, *J* 7.0, 7-CH_3), 2.07 (1H, m, 2-H), 2.45–2.65 (2H, m, 4-H_2), 2.85 (1H, m, 7-H), 3.36 (2H, dd, *J* 6.5, 2.0, 8-H_2), 4.46 (2H, s, $PhCH_2$), 5.10 (1H, dt, *J* 7.5, 5.5, 3-H), 5.34 (1H, dd, *J* 11.0, 9.5, 6-H), 5.46 (1H, dt, *J* 11.0, 7.5, 5-H), 7.25–7.40 (5H, m, ArH) and 8.24 and 8.32 (each 2H, d, *J* 9.0, ArH); minor **11b** 4.52 and 4.53 (each 1H, d, *J* 12.0, PhHC*H*); δ_C ($CDCl_3$, 75 MHz) 17.8, 18.0, 19.0, 29.8, 31.4, 32.9, 73.1, 75.3, 80.2, 123.7, 124.8, 127.6, 127.7, 128.2, 128.5, 130.9, 134.6, 135.6, 138.7 and 164.6; *m*/*z* (ESI) 434 (M^++23, 12%), 412 (M^++1, 5), 337 (30) and 305 (100); HRMS: M^++Na, found 434.1937. $C_{24}H_{29}NNaO_5$ requires 434.1938.

*4.2.6.2. (4SR,8SR,6Z)-9-Benzyloxy-8-methylnon-6-en-4-yl 4-nitrobenzoate (**10c**).* The alcohol **4c** (25 mg, 0.095 mmol), triethylamine (31 mL, 0.19 mmol), DMAP (a few crystals) in THF (1 mL) and 4-nitrobenzoyl chloride (27 mg, 0.13 mmol) in THF (0.5 mL) with stirring overnight, after chromatography using light petroleum/ether (10:1) as eluent, gave the *title compound* **10c** (17 mg, 44%) as a yellow oil containing ca. 2% of its *syn*-epimer **11c**, R_f 0.22 in 9:1 light petroleum/ether; ν_{max}/cm^{-1} 2960, 2931, 2872, 1723, 1529, 1349, 1274, 1116, 1102 and 720; δ_H ($CDCl_3$, 300 MHz) major **10c** 0.97 (3H, t, *J* 7.5, 1-H_3), 1.02 (3H, d, *J* 6.5, 8-CH_3), 1.30–1.55 and 1.60–1.87 (each 2H, m, 2-H_2 or 3-H_2), 2.53 (2H, m, 5-H_2), 2.86 (1H, m, 8-H), 3.29 (2H, m, 9-H_2), 4.49 (2H, s, $PhCH_2$), 5.25 (1H, quin, *J* 6.5, 4-H), 5.37 (1H, dd, *J* 11.0, 9.5, 7-H), 5.48 (1H, dt, *J* 11.0, 7.0, 6-H), 7.27–7.40 (5H, m, ArH) and 8.26 and 8.32 (each 2H, d, *J* 9.0, ArH); minor **11c** 4.52 (2H, s, $PhCH_2$); δ_C ($CDCl_3$, 75 MHz) 14.2, 18.0, 19.0, 32.5, 32.9, 36.1, 73.2, 75.3, 75.9, 123.7, 124.5, 127.7(2), 128.6, 130.9, 135.9, 136.3, 138.8, 150.7 and 164.6; *m*/*z* (CI) 429 (M^++18, 100%), 412 (M^++1, 10) and 245 (40); HRMS: M^++H, found 412.2114. $C_{24}H_{30}NO_5$ requires 412.2118.

*4.2.6.3. (2RS,6SR,4Z)-1,7-Bis(benzyloxy)-6-methylhept-4-en-2-yl 4-nitrobenzoate (**10d**).* The alcohol **4d** (40 mg, 0.12 mmol), triethylamine (39 μL, 0.24 mmol), DMAP (a few crystals) in THF (1 mL) and 4-nitrobenzoyl chloride (33 mg, 0.18 mmol) in THF (0.5 mL) with stirring overnight, after chromatography using light petroleum/ether (7:1) as eluent, gave the *title compound* **10d** (38 mg, 66%) as a yellow oil containing about 4% of its *syn*-epimer **11d**, R_f 0.27 in 4:1 light petroleum/ether; ν_{max}/cm^{-1} 2860, 2361, 1724, 1527, 1349, 1269, 1103, 720 and 698; δ_H ($CDCl_3$, 300 MHz) major **10d** 1.02 (3H, d, *J* 6.5, 6-CH_3), 2.62 (2H, t, *J* 6.5, 3-H_2), 2.89 (1H, m, 6-H), 3.30 (2H, d, *J* 6.5, 7-H_2), 3.70 (2H, m, 1-H_2), 4.49 (2H, s, $PhCH_2$), 4.55 and 4.63 (each 1H, d, *J* 12.0, PhHC*H*), 5.36–5.53 (3H, m, 2-H, 4-H and 5-H), 7.25–7.40 (5H, m, ArH) and 8.22 and 8.30 (each 2H, d, *J* 9.0, ArH); minor **11d** 0.98 (3H, d, *J* 6.5, 6-CH_3); δ_C ($CDCl_3$, 75 MHz) 17.9, 29.4, 32.9, 70.7, 73.2, 73.5, 74.5, 75.3, 123.7, 123.9, 127.7(2), 127.9, 128.0, 128.6, 128.7, 131.1, 136.1, 136.6, 138.2, 138.8, 150.8 and 164.5; *m*/*z* (CI) 490 (M^++1, 100%), 489 (M^+, 60), 473 (40) and 459 (40); HRMS: M^++NH_4, found 507.2488. $C_{29}H_{35}N_2O_6$ requires 507.2490.

*4.2.6.4. (1RS,5SR,3Z)-6-Benzyloxy-1-(4-chlorophenyl)-5-methylhex-3-enyl 4-nitrobenzoate (**10e**).* The alcohol **4e** (36 mg, 0.11 mmol), triethylamine (36 μL, 0.22 mmol), DMAP (a few crystals) in THF (1 mL) and 4-nitrobenzoyl chloride (30 mg, 0.16 mmol) in THF (0.5 mL), after chromatography using light petroleum/ether (8:1) as eluent, gave the *title compound* **10e** (35 mg, 67%) as a yellow oil containing about 1% of its *syn*-epimer **11e**, R_f 0.16 in 9:1 light petroleum/ether; ν_{max}/cm^{-1} 2958, 2923, 2852, 1726, 1528, 1345, 1271, 1101, 1014 and 720; δ_H ($CDCl_3$, 300 MHz) major **10e** 0.91 (3H, d, *J* 6.5, 5-CH_3), 2.68–2.86 (2H, m, 2-H_2), 2.92 (1H, m, 5-H), 3.20–3.35 (2H, m, 6-H_2), 4.52 (2H, s, $PhCH_2$), 5.35–5.42 (2H, m, 3-H and 4-H), 6.02 (1H, t, *J* 7.0, 1-H), 7.28–7.41 (9H, m, ArH) and 8.24 and 8.30 (each 2H, d, *J* 9.0, ArH); minor **11e** 0.97 (3H, d, *J* 6.5, 5-CH_3); δ_C ($CDCl_3$, 75 MHz) 17.9, 33.0, 34.8, 73.3, 75.2, 76.9, 123.8, 123.9, 127.8(2), 128.5, 128.6, 129.1, 131.0, 134.4, 135.8, 136.7, 138.3, 138.8, 150.9 and 164.1; *m*/*z* (CI) 497 (M^++18, 50%), 467 (25), 330 (40) and 106 (100); HRMS: M^++NH_4, found 497.1848. $C_{27}H_{30}{}^{35}ClN_2O_5$ requires 497.1838.

*4.2.6.5. (1RS,5SR,3Z)-6-Benzyloxy-5-methyl-1-(4-nitrophenyl) hex-3-enyl 4-nitrobenzoate (**10h**).* The alcohol **4h** (31 mg, 0.09 mmol), triethylamine (30 μL, 0.18 mmol), DMAP (a few crystals) in THF (1 mL) and 4-nitrobenzoyl chloride (25 mg, 0.14 mmol) in THF (0.5 mL), after chromatography using light petroleum/ether (3:1) as eluent, gave the *title compound* **10h** (38 mg, 85%) as a yellow oil containing ca. 10% of its *syn*-epimer **11h**, R_f 0.41 in 4:1 light petroleum/ether; ν_{max}/cm^{-1} 2958, 2927, 2855, 1727, 1606, 1525, 1347, 1270, 1101 and 720; δ_H ($CDCl_3$, 300 MHz) major **10h** 0.92 (3H, d, *J* 7.0, 5-CH_3), 2.80 (2H, m, 2-H and 5-H), 2.97 (1H, dt, *J* 14.5, 6.5, 2-H′), 3.20–3.40 (2H, m, 6-H_2), 4.54 (2H, s, $PhCH_2$), 5.32–5.49 (2H, m, 3-H and 4-H), 6.13 (1H, t, *J* 7.0, 1-H), 7.28–7.42 (5H, m, ArH), 7.60 (2H, d, *J* 9.0, ArH) and 8.23–8.36 (6H, m, ArH); minor **11h** 0.98 (3H, d, *J* 6.5, 5-CH_3) and 4.50 and 4.51 (each 1H, d *J* 12.0, PhHC*H*); δ_C ($CDCl_3$, 75 MHz) 17.7, 33.1, 34.6, 73.4, 75.3, 76.5, 122.8, 123.9, 124.1, 127.7, 127.8, 127.9, 128.7, 131.1, 135.3, 137.7, 138.7, 146.9, 148.0, 151.0 and 164.0; *m*/*z* (CI) 508 (M^++18, 30%), 294 (100) and 155 (40); HRMS: M^++NH_4, found 508.2094. $C_{27}H_{30}N_3O_7$ requires 508.2078.

4.2.7. Synthesis of 4-nitrobenzoates via a Mitsunobu reaction

*4.2.7.1. (3RS,7RS,5Z)-8-Benzyloxy-2,7-dimethyloct-5-en-3-yl 4-nitrobenzoate (**11b**); standard procedure.* Di-isopropyl azodicarboxylate (216 μL, 1.09 mmol) was added dropwise to the alcohol **4b** (225 mg, 0.456 mmol), 4-nitrobenzoic acid (92 mg, 0.50 mmol) and triphenylphosphine (288 mg, 1.09 mmol) in THF (4 mL) at 0 °C and the solution stirred at rt for 7 h. After concentration under reduced pressure, chromatography of the residue using light petroleum/ether (15:1) as eluent gave the *title compound* **11b** (101 mg, 54%) as a yellow oil containing ca. 3% of its *anti*-epimer **10b**, R_f 0.26

in 9:1 light petroleum/ether; ν_{max}/cm^{-1} 2964, 2930, 2874, 1723, 1608, 1529, 1348, 1274, 1116, 1102 and 720; δ_H ($CDCl_3$, 300 MHz) major **11b** 0.93 (3H, d, *J* 7.0, 7-CH_3), 1.02 and 1.04 (each 3H, d, *J* 5.0, 1-H_3 or 2-CH_3), 2.10 (1H, m, 2-H), 2.46 (1H, dt, *J* 15.0, 5.0, 4-H), 2.60 (1H, dt, *J* 8.0, 7.0, 4-H′), 2.84 (1H, m, 7-H), 3.26–3.35 (2H, m, 8-H_2), 4.52 and 4.53 (each 1H, d, *J* 12.0, PhHC*H*), 5.10 (1H, dt, *J* 8.0, 5.0, 3-H), 5.32 (1H, dd, *J* 11.0, 9.5, 6-H), 5.49 (1H, dt, *J* 11.0, 7.5, 5-H), 7.27–7.42 (5H, m, ArH) and 8.24 and 8.32 (each 2H, d, *J* 9.0, ArH); minor **10b** 4.46 (2H, s, $PhCH_2$); δ_C ($CDCl_3$, 75 MHz) 17.9, 18.0, 19.1, 30.0, 31.6, 32.9, 73.3, 75.4, 80.3, 123.8, 125.1, 127.7, 128.6, 130.9, 134.7, 135.7, 136.3, 138.8, 150.7 and 164.6; *m*/*z* (ESI) 434 (M^++23, 100%), 393 (40) and 288 (80); HRMS: M^++Na, found 434.1941. $C_{24}H_{29}NNaO_5$ requires 434.1938.

Sodium hydroxide (69 mg, 3.8 mmol) was added to a suspension of the ester **11b** (90 mg, 0.218 mmol) in methanol (1 mL) and the mixture stirred at rt for 2 h. After concentration under reduced pressure, ether (15 mL) and saturated aqueous ammonium hydroxide (7 mL) were added. The aqueous layer was washed with ether (2×15 mL) and the ether extracts dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography of the residue using light petroleum/ether (4:1) as eluent gave the *alcohol* **6b** (35 mg, 60%) as a colourless oil containing ca. 1% of its *anti*-epimer **4b**, R_f 0.15 in 4:1 light petroleum/ether; ν_{max}/cm^{-1} 3427, 3004, 2957, 2928, 2871, 1453, 1366, 1096 and 736; δ_H ($CDCl_3$, 300 MHz) 0.94 and 0.98 (each 3H, d, *J* 4.5, 1-H_3 or 2-CH_3), 1.01 (3H, d, *J* 6.5, 7-CH_3), 1.70 (1H, m, 2-H), 2.12 (1H, s, OH), 2.27 (1H, dt, *J* 14.0, 7.0, 4-H), 2.34 (1H, m, 4-H′), 2.91 (1H, m, 7-H), 3.27–3.42 (3H, m, 3-H and 8-H_2), 4.56 (2H, s, $PhCH_2$), 5.44 (1H, dd, *J* 11.0, 9.5, 6-H), 5.53 (1H, dt, *J* 11.0, 7.5, 5-H), and 7.30–7.42 (5H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 17.9, 18.4, 19.2, 32.6, 32.7, 33.3 73.3, 75.3, 76.5, 126.1, 127.8, 127.9, 128.6, 136.6 and 138.6; *m*/*z* (CI) 280 (M^++18, 100%) and 263 (30); HRMS: M^++NH_4, found 280.2272. $C_{17}H_{30}NO_2$ requires 280.2271.

*4.2.7.2. (4RS,8SR,6Z)-9-Benzyloxy-8-methylnon-6-en-4-yl 4-nitrobenzoate (**11c**).* Di-isopropyl azodicarboxylate (54 μL, 0.27 mmol), the alcohol **4c** (60 mg, 0.23 mmol), 4-nitrobenzoic acid (46 mg, 0.27 mmol) and triphenylphosphine (72 mg, 0.27) in THF (4 mL), after stirring for 4 h and chromatography using light petroleum/ether (15:1) gave the *title compound* **11c** (54 mg, 57%) as a yellow oil containing ca. 2% of its *anti*-epimer **10c**, R_f 0.27 in 9:1 light petroleum/ether; ν_{max}/cm^{-1} 2960, 2928, 2871, 1722, 1529, 1349, 1274, 1115, 1102 and 720; δ_H ($CDCl_3$, 300 MHz) major **11c** 0.94–1.02 (6H, m, 1-H_3, and 8-CH_3), 1.35–1.55 and 1.65–1.85 (each 2H, m, 2-H_2 or 3-H_2), 2.49 (1H, dt, *J* 15.0, 6.0, 5-H), 2.60 (1H, dt, *J* 14.5, 7.5, 5-H′), 2.85 (1H, m, 8-H), 3.32 (2H, d, *J*7.5, 9-H_2), 4.52 (2H, s, $PhCH_2$), 5.24 (1H, pent, *J* 6.0, 4-H), 5.37 (1H, dd, *J* 11.0, 9.5, 6-H), 5.48 (1H, dt, *J* 11.0, 7.0, 5-H), 7.28–7.40 (5H, m, ArH) and 8.23 and 8.31 (each 2H, d, *J* 9.0, ArH); minor **10c** 4.49 (2H, s, $PhCH_2$); δ_C ($CDCl_3$, 75 MHz) 14.2, 18.0, 19.0, 32.7, 32.9, 36.1, 73.2, 75.4, 76.0, 123.8, 124.7, 127.7, 127.8, 128.6, 130.9, 136.0, 136.3, 138.8, 150.7 and 164.6; *m*/*z* (CI) 429 (M^++18, 15%) and 106 (100); HRMS: M^++NH_4, found 429.2376. $C_{24}H_{33}N_2O_5$ requires 429.2384.

Sodium hydroxide (33 mg, 1.74 mmol) and the ester **11c** (43 mg, 0.218 mmol) in methanol (1 mL), after chromatography using light petroleum/ether (4:1) gave the *alcohol* **6c** (25 mg, 92%) as a colourless oil containing ca. 2% of its *anti*-epimer **4c**, R_f 0.09 in 4:1 light petroleum/ether; ν_{max}/cm^{-1} 3414, 2957, 2928, 2871, 1454, 1096, 1075 and 737; δ_H ($CDCl_3$, 300 MHz) 0.98 (3H, t, *J* 6.5, 1-H_3), 1.03 (3H, d, *J* 6.5, 8-CH_3), 1.35–1.54 (4H, m, 2-H_2 and 3-H_2), 2.18–2.31 (2H, m, 5-H and OH), 2.40 (1H, m, 5-H′), 2.92 (1H, m, 8-H), 3.31 (1H, dd, *J* 9.0, 6.0, 9-H), 3.39 (1H, dd, *J* 9.0, 7.5, 9-H′), 3.70 (1H, m, 4-H), 4.56 (2H, s, $PhCH_2$), 5.43 (1H, dd, *J* 11.0, 9.5, 7-H), 5.53 (1H, dt, *J* 11.0, 7.5, 6-H) and 7.30–7.43 (5H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 14.4, 17.9, 19.4, 32.7, 35.4, 39.1, 71.2, 73.3, 75.3, 125.6, 127.8, 127.9, 128.6, 136.7 and 138.6; *m*/*z* (CI) 280 (M^++18, 100%) and 263 (M^++1, 25); HRMS: M^++H, found 263.2006. $C_{17}H_{27}O_2$ requires 263.2006.

*4.2.7.3. (2SR,6SR,4Z)-1,7-Bis(benzyloxy)-6-methylhept-4-en-2-yl 4-nitrobenzoate (**11d**).* Di-isopropyl azodicarboxylate (23 μL, 0.14 mmol), the alcohol **4d** (31 mg, 0.091 mmol), 4-nitrobenzoic acid (20 mg, 0.11 mmol) and triphenylphosphine (31 mg, 0.11 mmol) in THF (2.5 mL), after stirring at rt for 4 h and chromatography using light petroleum/ether (8:1), gave the *title compound* **11d** (33 mg, 68%) as a yellow oil containing about 4% of its *anti*-epimer **10d**, R_f 0.35 in 4:1 light petroleum/ether; ν_{max}/cm^{-1} 2959, 2924, 2857, 1724, 1528, 1454, 1349, 1275, 1103 and 720; δ_H ($CDCl_3$, 300 MHz) major **11d** 0.98 (3H, d, *J* 6.5, 6-CH_3), 2.50–2.75 (2H, m, 3-H_2), 2.87 (1H, m, 6-H), 3.32 (2H, d, *J* 6.5, 7-H_2), 3.71 (2H, d, *J* 5.0, 1-H_2), 4.52, 4.53, 4.56 and 4.59 (each 1H, d, *J* 12.0, PhHC*H*), 5.35–5.43 (3H, m, 2-H, 4-H and 5-H), 5.48 (1H, dt, *J* 11.0, 7.0, 4-H), 7.30–7.39 (10H, m, ArH) and 8.24 and 8.32 (each 2H, d, *J* 9.0, ArH); minor **10d** 1.02 (3H, d, *J* 6.5, 6-CH_3); δ_C ($CDCl_3$, 75 MHz) 18.0, 29.5, 32.8, 70.8, 73.2, 73.4, 74.5, 75.3, 123.7, 124.1, 127.7, 127.8, 128.0, 128.6, 128.7, 131.1, 136.1, 136.6, 138.2, 138.8, 150.8 and 164.5; *m*/*z* (CI) 507 (M^++18, 13%) and 108 (100); HRMS: M^++NH_4, found 507.2510. $C_{29}H_{35}N_2O_6$ requires 507.2490.

*4.2.7.4. (1SR,5SR,3Z)-6-Benzyloxy-1-(4-chlorophenyl)-5-methylhex-3-enyl 4-nitrobenzoate (**11e**).* Di-isopropyl azodicarboxylate (32 μL, 0.16 mmol), the alcohol **4e** (45 mg, 0.136 mmol), 4-nitrobenzoic acid (27 mg, 0.16 mmol) and triphenylphosphine (42 mg, 0.16 mmol) in THF (2 mL) after stirring at rt for 4 h and chromatography using light petroleum/ether (8:1) gave the *title compound* **11e** (41 mg, 62%) as a yellow oil containing ca. 1% of its *anti*-epimer **10e**, R_f 0.34 in 4:1 light petroleum/ether; ν_{max}/cm^{-1} 2959, 2927, 2856, 1727, 1529, 1346, 1271, 1102, 1014 and 720; δ_H ($CDCl_3$, 300 MHz) major **11e** 0.97 (3H, d, *J* 6.5, 5-CH_3), 2.68–2.85 (2H, m, 2-H and 5-H), 2.92 (1H, m, 2-H′), 3.18 (1H, dd, *J* 10.0, 6.5, 6-H), 3.25 (1H, dd, *J* 9.0, 7.0, 6-H′), 4.49 and 4.51 (each H, d, *J* 12.0, PhHC*H*), 5.33–5.47 (2H, m, 3-H and 4-H), 6.02 (1H, dd, *J* 7.5, 6.5, 1-H), 7.28–7.40 (9H, m, ArH) and 8.26 and 8.33 (each 2H, d, *J* 9.0, ArH); minor **10e** 0.91 (3H, d, *J* 6.5, 5-CH_3) δ_C ($CDCl_3$, 75 MHz) 17.8, 33.1, 34.6, 73.3, 75.3, 76.9, 123.5, 123.8, 127.7, 127.8, 128.3, 128.6, 129.1, 131.0, 134.4, 135.8, 136.9, 138.3, 138.8, 150.8 and 164.1; *m*/*z* (CI) 497 (M^++18, 6%) and 330 (100); HRMS: M^++NH_4, found 497.1848. $C_{27}H_{30}{}^{35}ClN_2O_5$ requires 497.1838.

*4.2.7.5. (1SR,5SR,3Z)-6-Benzyloxy-5-methyl-1-(4-nitrophenyl) hex-3-enyl 4-nitrobenzoate (**11h**).* Di-isopropyl azodicarboxylate (23 mL, 0.14 mmol), the alcohol **4h** (40 mg, 0.117 mmol), 4-nitrobenzoic acid (23 mg, 0.14 mmol) and triphenylphosphine (37 mg, 0.14 mmol) in THF (2 mL), after stirring at rt for 4 h and chromatography using light petroleum/ether (4:1) as eluent, gave the *title compound* **11h** (46 mg, 79%) as a yellow oil containing ca. 10% of its *anti*-epimer **10h**, R_f 0.28 in 2:1 light petroleum/ether; ν_{max}/cm^{-1} 2957, 2924, 2853, 1728, 1606, 1525, 1348, 1271, 1102 and 720; δ_H ($CDCl_3$, 300 MHz) major **11h** 0.98 (3H, d, *J* 6.5, 5-CH_3), 2.71–2.87 (2H, m, 2-H and 5-H), 2.94 (1H, m, 2-H′), 3.22 (1H, dd, *J* 9.0, 7.0, 6-H), 3.31 (1H, dd, *J* 9.0, 6.5, 6-H′), 4.50 and 4.51 (each 1H, d, *J* 12.0, PhHC*H*), 5.35–5.52 (2H, m, 3-H and 4-H), 6.14 (1H, dd, *J* 7.5, 6.0, 1-H), 7.28–7.45 (5H, m, ArH), 7.58 (2H, d, *J* 8.5, ArH) and 8.22–8.40 (6H, m, ArH); minor **10h** 0.92 (3H, d, *J* 7.0, 5-CH_3) and 4.54 (2H, s, $PhCH_2$); δ_C ($CDCl_3$, 75 MHz) 17.9, 33.1, 34.8, 73.4, 75.3, 76.7, 123.2, 124.0, 124.2, 127.5, 127.7, 127.8, 128.7, 131.1, 135.4, 137.4, 138.7, 147.1, 148.0, 151.0 and 164.0; *m*/*z* (CI) 508 (M^++18, 6%) and 294 (100); HRMS: M^++NH_4, found 508.2085. $C_{27}H_{30}N_3O_7$ requires 508.2078.

*4.2.8. (4S,2E)-4-Benzyloxypent-2-enyl(triethyl)germane (**15**) and its reactions with aldehydes.* The standard procedure using triethylgermanium hydride (0.16 mL, 1.0 mmol) and TMEDA (0.17 mL,

1.1 mmol) in THF (1 mL), ^{t}BuLi (1.7 M in pentane, 0.70 mL, 1.2 mmol), and copper(I) iodide (95 mg, 0.50 mmol) in THF (2 mL) and acetate **14** (117 mg, 0.50 mmol) in THF (1 mL), after chromatography using light petroleum/ether (60:1) as eluent, gave the *title compound* **15** (139 mg, 83%) as a colourless oil, R_f 0.63 in 9:1 light petroleum/ether, $[\alpha]_D^{24}$ −59 (*c* 1.16 in $CHCl_3$); ν_{max}/cm^{-1} 2951, 2905, 2870, 2267, 1655, 1366, 1096, 1069, 1025 and 734; δ_H ($CDCl_3$, 300 MHz) 0.81 (6H, q, *J* 8.0, 3× $GeCH_2$), 1.08 (9H, t, *J* 8.0, 3× $GeCH_2CH_3$), 1.31 (3H, d, *J* 6.5, 5-H_3), 1.72 (2H, d, *J* 8.5, 1-H_2), 3.90 (1H, dq, *J* 8.0, 6.5, 4-H), 4.38 and 4.61 (each 1H, d, *J* 12.0, PhHC*H*), 5.30 (1H, dd, *J* 15.0, 8.0, 3-H), 5.55 (1H, dt, *J* 15.0, 8.5, 2-H) and 7.27–7.42 (5H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 4.2, 9.2, 17.2, 22.4, 69.7, 76.5, 127.5, 127.9, 128.6, 129.9, 131.4 and 139.4; *m*/*z* (ESI) 359 (M^++23, 50%), 357 (M^++23, 35) and 355 (M^++23, 30); HRMS: M^++Na, found 359.1406. $C_{15}H_{30}{}^{74}GeNaO$ requires 359.1401.

Following the standard procedure, tin(IV) chloride (1 M in DCM, 0.42 mL, 0.42 mmol) in DCM (0.5 mL), the pent-2-enylgermane **15** (116 mg, 0.35 mmol) in DCM (1.0 mL) and benzaldehyde (106 mL, 1.0 mmol), after chromatography using light petroleum/ether (3:1) as eluent, gave the *syn*-5-benzyloxy-1-phenylhex-3-en-1-ol **16a**[13] (39 mg, 40%) as a colourless oil containing ca. 11% of its 1,5-*anti*-epimer, R_f 0.15 in 4:1 light petroleum/ether.

Tin(IV) bromide (64 mg, 1.4 mmol) in DCM (0.47 mL), the pent-2-enylgermane **15** (40 mg, 0.12 mmol) in DCM (0.53 mL) and benzaldehyde (43 μL, 0.36 mmol) gave the alcohol **16a** (9 mg, 26%) as a colourless oil containing ca. 10% of its 1,5-*anti*-epimer, $[\alpha]_D^{23}$ +52 (*c* 0.77 in $CHCl_3$).

Tin(IV) chloride (1 M in DCM, 0.27 mL, 0.27 mmol) in DCM (0.5 mL), the pent-2-enylgermane **15** (75 mg, 0.22 mmol) in DCM (1.0 mL) and 4-nitrobenzaldehyde (41 mg, 0.24 mmol) in DCM (0.5 mL), after chromatography using light petroleum/ether (2:1) as eluent, gave the *syn*-5-benzyloxy-1-(4-nitrophenyl)hex-3-en-1-ol **16b**[13] (25 mg, 34%) as a yellow oil, R_f 0.07 in 4:1 light petroleum/ether, $[\alpha]_D^{23}$ +65 (*c* 0.97 in $CHCl_3$); HRMS: M^++NH_4, found 345.1815. $C_{19}H_{25}N_2O_4$ requires 345.1809.

Tin(IV) chloride (1 M in DCM, 0.69 mL, 0.69 mmol) in DCM (1.0 mL), the pent-2-enylgermane **15** (192 mg, 0.57 mmol) in DCM (2.0 mL) and butanal (110 μL, 0.63 mmol) after chromatography using light petroleum/ether (4:1) as eluent gave the *syn*-8-benzyloxy-4-hydroxynon-6-en-4-ol **16c**[13] (15 mg, 11%) as a yellow oil, R_f 0.10 in 4:1 light petroleum/ether, $[\alpha]_D^{23}$ +23 (*c* 1.03 in $CHCl_3$).

*4.2.9. (5R,2Z)-5-tert-Butyldimethylsilyloxyhex-2-enyl acetate [(Z)-**21**].* The standard procedure using acetic anhydride (1.2 mL, 12.3 mmol), the (*Z*)-5-*tert*-butyldimethylsilyloxyhex-2-enol (*Z*)-**27** (2.58 g, 11.2 mmol) and pyridine (2.8 mL, 33.6 mmol), after chromatography using light petroleum/ether (20:1), gave the *title compound* (*Z*)-**21** (2.96 mg, 97%) as a colourless oil, R_f 0.28 in 9:1 light petroleum/ether, $[\alpha]_D^{23}$ −11.5 (*c* 1.34 in $CHCl_3$); ν_{max}/cm^{-1} 2957, 2930, 2894, 2858, 1743, 1374, 1250, 1231, 1007, 836 and 775; δ_H ($CDCl_3$, 300 MHz) 0.06 and 0.07 (each 3H, s, $SiCH_3$), 0.89 [9H, s, $SiC(CH_3)_3$], 1.14 (3H, d, *J* 6.0, 6-H_3), 2.07 (3H, s, CH_3CO), 2.25 (2H, m, 4-H_2), 3.92 (1H, hex, *J* 6.0, 5-H), 4.63 (2H, m, 1-H_2) and 5.58–5.76 (2H, m, 2-H and 3-H); δ_C ($CDCl_3$, 75 MHz) −4.5, −4.3, 18.3, 21.2, 23.8, 26.1, 37.8, 60.7, 68.4, 125.1, 131.9 and 171.2; *m*/*z* (CI) 290 (M^++18, 25%) and 273 (M^++1, 100); HRMS: M^++NH_4, found 290.2147. $C_{14}H_{32}NO_3Si$ requires 290.2146.

*4.2.10. Syntheses of hex-2-enylgermanes **22**–**26**, **28** and **29***

*4.2.10.1. (5R,2E)-5-tert-Butyldimethylsilyloxyhex-2-enyl(triphenyl)germane [(E)-**22**].* The standard procedure using triphenylgermanium hydride (530 mg, 1.74 mmol) and TMEDA (0.29 mL, 1.9 mmol) in THF (2.5 mL), ^{t}BuLi (1.7 M in pentane, 1.20 mL, 2.04 mmol), copper iodide (164 mg, 0.87 mmol) and the (*E*)-acetate (*E*)-**21** (237 mg, 0.87 mmol) in THF (2 mL), after chromatography using 2% ether in light petroleum as eluent, gave the *title compound* (*E*)-**22** (309 mg, 69%) as a colourless oil, R_f 0.20 in 1% ether in light petroleum, $[\alpha]_D^{23}$ +0.33 (*c* 0.59 in $CHCl_3$); ν_{max}/cm^{-1} 3068, 2955, 2928, 2892, 2856, 1430, 1253, 1092, 834, 744 and 733; δ_H ($CDCl_3$, 300 MHz) 0.04 and 0.05 (each 3H, s, $SiCH_3$), 0.90 [9H, s, $SiC(CH_3)_3$], 1.00 (3H, d, *J* 6.0, 6-H_3), 2.03 (1H, dt, *J* 13.5, 7.0, 4-H), 2.14 (1H, dt, *J* 13.5, 6.5, 4-H′), 2.46 (2H, d, *J* 8.0, 1-H_2), 3.67 (1H, sext, *J* 6.0, 5-H), 5.38 (1H, dt, *J* 15.0, 6.5, 2-H), 5.59 (1H, dt, *J* 15.0, 8.0, 3-H), 7.39–7.44 (9H, m, ArH) and 7.49–7.54 (6H, m, ArH); δ_C ($CDCl_3$, 75 MHz) −4.5, −4.3, 18.5, 19.9, 23.3, 26.2, 43.4, 69.2, 127.3, 128.0, 128.4, 129.2, 135.3 and 137.0; *m*/*z* (CI) 536 (M^++18, 2%), 322 (100), 320 (80) and 318 (60); HRMS: M^++NH_4, found 536.2396. $C_{30}H_{44}{}^{74}GeNOSi$ requires 536.2398.

*4.2.10.2. (5R,2E)-5-Hydroxyhex-2-enyl(triphenyl)germane [(E)-**23**]; standard procedure.* Tetra-*n*-butylammonium fluoride (1 M in THF, 0.9 mL, 0.9 mmol) was added to the (*E*)-5-*tert*-butyldimethylsilyloxyhex-2-enylgermane (*E*)-**22** (309 mg, 1.6 mmol) in THF (5 mL) and the reaction mixture stirred at rt overnight. Water was added (15 mL) and the mixture extracted with ether (3×20 mL). The organic extracts were washed with water (20 mL) and brine (20 mL), dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography of the residue using light petroleum/ether (3:1) gave the *title compound* (*E*)-**23** (223 mg, 93%) as a white crystalline solid, mp 86.4–87.2 °C, R_f 0.20 in 2:1 light petroleum/ether, $[\alpha]_D^{23}$ −7.6 (*c* 1.62 in $CHCl_3$); ν_{max}/cm^{-1} 3384, 3067, 3048, 2967, 2902, 1484, 1430, 1091, 965 and 734; δ_H ($CDCl_3$, 300 MHz) 1.08 (3H, d, *J* 6.0, 6-H_3), 1.26 (1H, m, OH), 2.02 (1H, dt, *J* 14.0, 7.5, 4-H), 2.16 (1H, dt, *J* 14.0, 4.5, 4-H′), 2.50 (2H, d, *J* 8.0, 1-H_2), 3.61 (1H, m, 5-H), 5.34 (1H, dt, *J* 15.0, 6.5, 2-H), 5.71 (1H, dt, *J* 15.0, 8.0, 3-H), 7.40–7.46 (9H, m, ArH) and 7.50–7.55 (6H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 20.1, 22.7, 42.9, 67.4, 126.4, 128.5, 129.4, 130.1, 135.2 and 136.7; *m*/*z* (CI) 422 (M^++18, 70%), 420 (M^++18, 60), 418 (M^++18, 50), 322 (100), 320 (80) and 318 (50) HRMS: M^++NH_4, found 422.1534. $C_{24}H_{30}{}^{74}GeNO$ requires 422.1534.

*4.2.10.3. (5R,2Z)-5-Hydroxyhex-2-enyl(triphenyl)germane [(Z)-**23**].* Triphenylgermanium hydride (1.02 g, 3.3 mmol) and TMEDA (0.56 mL, 3.63 mmol) in THF (5 mL), ^{t}BuLi (1.7 M in pentane, 2.31 mL, 3.63 mmol), copper iodide (313 mg, 1.65 mmol) and the (*Z*)-acetate (*Z*)-**21** (450 mg, 1.65 mmol), after chromatography using 1% ether in light petroleum as eluent, gave the hex-2-enylgermane (*Z*)-**22** (379 mg, 44%) as a colourless oil, R_f 0.13 in 1% ether in petrol, $[\alpha]_D^{23}$ +2.4 (*c* 1.22 in $CHCl_3$); ν_{max}/cm^{-1} 3069, 2957, 2929, 2856, 1431, 1256, 1091, 1027, 734 and 698; δ_H ($CDCl_3$, 300 MHz) 0.04 (6H, s, 2× $SiCH_3$), 0.91 [9H, s, $SiC(CH_3)_3$], 1.05 (3H, d, *J* 6.0, 6-H_3), 2.00–2.08 (2H, m, 4-H_2), 2.50 (2H, d, *J* 8.5, 1-H_2), 3.63 (1H, sext, *J* 5.5, 5-H), 4.95 (1H, m, 2-H), 5.37 (1H, m, 3-H), 7.35–7.48 (9H, m, ArH) and 7.50–7.62 (6H, m, ArH); *m*/*z* (CI) 536 (M^++18, 3%), 534 (M^++18, 2), 532 (M^++18, 1.5), 519 (M^++1, 3) and 322 (100); HRMS: M^+−C_6H_5, found 441.1663. $C_{24}H_{35}{}^{74}GeOSi$ requires 441.1663.

The standard procedure using tetra-*n*-butylammonium fluoride (1 M in THF, 1.26 mL, 1.26 mmol) and the (*Z*)-5-*tert*-butyldimethylsilyloxyhex-2-enylgermane (*Z*)-**22** (331 mg, 0.640 mmol) in THF (5 mL), after chromatography using light petroleum/ether (3:1) as eluent, gave the *title compound* (*Z*)-**23** (124 mg, 48%) as a colourless oil containing about 10% of its (*E*)-isomer (*E*)-23, R_f 0.25 in 1:1 light petroleum/ether, $[\alpha]_D^{21}$ +10.8 (*c* 0.74 in $CHCl_3$); ν_{max}/cm^{-1} 3352, 3068, 3048, 2966, 1485, 1431, 1092, 734 and 699; δ_H ($CDCl_3$, 300 MHz) 1.12 (3H, d, *J* 6.0, 6-H_3), 1.32 (1H, br s, OH), 1.96–2.16 (2H, m, 4-H_2), 2.45–2.60 (2H, m, 1-H_2), 3.61 (1H, m, 5-H), 5.34 and 5.82 (each 1H, m, 2-H or 3-H), 7.38–7.46 (9H, m, ArH) and 7.52–7.58 (6H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 15.8, 23.0, 37.1, 67.9, 124.8, 128.2, 128.5, 129.3, 135.2 and 136.7; *m*/*z* (CI) 422 (M^++18, 100%), 420 (M^++18, 75), 418 (M^++18, 60), 404 (M^++1, 4), 322 (96), 320 (80) and 318 (50); HRMS: M^+, found 404.1197. $C_{24}H_{26}{}^{74}GeO$ requires 404.1190.

*4.2.10.4. (5R,2E)-5-tert-Butyldimethylsilyloxyhex-2-enyl(triethyl) germane [(E)-**24**].* Triethylgermanium hydride (0.16 mL, 1.0 mmol) and TMEDA (0.17 mL, 1.1 mmol) in THF (1 mL), ^{t}BuLi (1.7 M in pentane, 0.70 mL, 1.2 mol), copper iodide (95 mg, 0.50 mmol) in THF (2 mL) and the (*E*)-acetate (*E*)-**21** (137 mg, 0.50 mmol), after chromatography using 1% ether in light petroleum as eluent, gave the *title compound* (*E*)-**24** (172 mg, 92%) as a colourless oil, R_f 0.63 in 9:1 light petroleum/ether, $[\alpha]_D^{21}$ −2.6 (*c* 1.65 in $CHCl_3$); ν_{max}/cm^{-1} 2952, 2929, 2905, 2857, 1462, 1256, 1095, 1017, 834 and 774; δ_H ($CDCl_3$, 300 MHz) 0.09 (6H, s, 2× $SiCH_3$), 0.77 (6H, q, *J* 7.5, 3× $GeCH_2$), 0.93 [9H, s, $SiC(CH_3)_3$], 1.05 (9H, t, *J* 7.5, 3× $GeCH_2CH_3$), 1.14 (3H, d, *J* 6.0, 6-H_3), 1.64 (2H, d, *J* 8.0, 2-H_2), 2.09 (1H, dt, *J* 13.5, 7.0, 4-H), 2.20 (1H, dt, *J* 13.5, 6.0, 4-H′), 3.80 (1H, sext, *J* 6.0, 5-H), 5.28 (1H, dt, *J* 15.0, 7.0, 2-H) and 5.55 (1H, dt, *J* 15.0, 8.0, 3-H); δ_C ($CDCl_3$, 75 MHz) −4.4, −4.3, 4.1, 9.1, 17.3, 18.5, 23.4, 26.2, 43.5, 69.5, 124.5 and 130.0; *m*/*z* (ESI) 317 (M^+−57, 7%) and 159 (60); HRMS: $M^+-C_4H_9$, found 317.1356. $C_{14}H_{31}{}^{74}GeOSi$ requires 317.1350.

*4.2.10.5. (5R,2Z)-5-tert-Butyldimethylsilyloxyhex-2-enyl(triethyl) germane [(Z)-**24**].* Triethylgermanium hydride (0.53 mL, 3.3 mmol) and TMEDA (0.56 mL, 3.63 mmol) in THF (5 mL), ^{t}BuLi (1.7 M in pentane, 2.31 mL, 3.93 mmol), copper iodide (313 mg, 1.65 mmol) and the (*Z*)-acetate (*Z*)-**21** (450 mg, 1.65 mmol), after chromatography using 2% ether in petrol as eluent, gave the *title compound* (*Z*)-**24** (575 mg, 93%) as a colourless oil, R_f 0.69 in light petroleum, $[\alpha]_D^{23}$ +2.89 (*c* 1.06 in $CHCl_3$); ν_{max}/cm^{-1} 2960, 2931, 2905, 2872, 1644, 1462, 1256, 1129, 1089, 834 and 774; δ_H ($CDCl_3$, 300 MHz) 0.10 (6H, s, 2× $SiCH_3$), 0.78 (6H, q, *J* 8.0, 3× $GeCH_2$), 0.93 [9H, s, $SiC(CH_3)_3$], 1.06 (9H, t, *J* 8.0, 3× $GeCH_2CH_3$), 1.17 (3H, d, *J* 6.0, 6-H_3), 1.67 (2H, d, *J* 8.0, 1-H_2), 2.10–2.29 (2H, m, 4-H_2), 3.84 (1H, sext, *J* 6.0, 5-H), 5.25 (1H, dt, *J* 10.5, 7.0, 2-H), 5.55 (1H, dt, *J* 11.0, 10.5, 3-H); δ_C ($CDCl_3$, 75 MHz) −4.4, −4.3, 4.3, 9.2, 13.3, 18.5, 23.8, 26.2, 37.5, 69.2, 123.1 and 128.4; *m*/*z* (CI) 375 (M^++1, 5%), 373 (M^++1, 3), 371 (M^++1, 2), 178 (90), 176 (100) and 174 (60); HRMS: $M^+-C_2H_5$, 345.1668. $C_{16}H_{35}{}^{74}GeOSi$ requires 345.1663.

*4.2.10.6. (5R,2E)-5-Hydroxyhex-2-enyl(triethyl)germane [(E)-**25**].* The standard procedure using tetra-*n*-butylammonium fluoride (1 M in THF, 3.9 mL, 3.9 mmol) and the silyl ether (*E*)-**24** (0.94 g, 2.52 mmol) in THF (15 mL), after chromatography using light petroleum/ether (4:1) as eluent, gave the *title compound* (*E*)-**25** (630 mg, 97%) as a colourless oil, R_f 0.25 in 4:1 light petroleum/ether, $[\alpha]_D^{23}$ −8.0 (*c* 0.35 in $CHCl_3$); ν_{max}/cm^{-1} 3404, 2950, 2905, 2872, 1655, 1460, 1374, 1326, 1017 and 964; δ_H ($CDCl_3$, 300 MHz) 0.78 (6H, q, *J* 7.5, 3× $GeCH_2$), 1.06 (9H, t, *J* 7.5, 3× $GeCH_2CH_3$), 1.21 (3H, d, *J* 6.0, 6-H_3), 1.64 (2H, d, *J* 8.0, 1-H_2), 2.05 (1H, dt, *J* 14.0, 7.5, 4-H), 2.23 (1H, dt, *J* 14.0, 6.5, 4-H′), 3.78 (1H, m, 5-H), 5.29 (1H, dt, *J* 15.0, 7.0, 2-H) and 5.57 (1H, dt, *J* 15.0, 8.0, 3-H); δ_C ($CDCl_3$, 75 MHz) 4.1, 9.1, 17.5, 22.8, 43.0, 67.6, 123.4 and 132.4; *m*/*z* (APCI) 260 (M^+, 10%), 258 (M^+, 8), 256 (M^+, 5), 239 (40), 100 (50) and 79 (100); HRMS: M^++H, found 261.1286. $C_{12}H_{27}{}^{74}GeO$ requires 261.1268.

*4.2.10.7. (5R,2Z)-5-Hydroxyhex-2-enyl(triethyl)germane [(Z)-**25**].* Tetra-*n*-butylammonium fluoride (1 M in THF, 2.2 mL, 2.2 mmol) and the silyl ether (*Z*)-**24** (533 mg, 1.428 mmol) in THF (9 mL), after chromatography using light petroleum/ether (3:1) as eluent, gave the *title compound* (*Z*)-**25** (350 mg, 95%) as a colourless oil, R_f 0.46 in 1:1 light petroleum/ether, $[\alpha]_D^{23}$ +21.1 (*c* 1.18 in $CHCl_3$); ν_{max}/cm^{-1} 3350, 2949, 2906, 2872, 1641, 1460, 1260, 1116, 1078, 1020 and 773; δ_H ($CDCl_3$, 300 MHz) 0.79 (6H, q, *J* 8.5, 3× $GeCH_2$), 1.07 (9H, t, *J* 7.5, 3× $GeCH_2CH_3$), 1.26 (3H, d, *J* 6.5, 6-H_3), 1.63–1.80 (3H, m, 1-H_2 and OH), 2.14–2.34 (2H, m, 4-H_2), 3.87 (1H, sext, *J* 6.5, 5-H), 5.28 (1H, dt, *J* 10.0, 7.5, 2-H) and 5.70 (1H, q, *J* 9.0, 3-H); δ_C ($CDCl_3$, 75 MHz) 4.3, 9.2, 13.4, 23.1, 37.1, 68.2, 122.0 and 130.7; *m*/*z* (CI) 261 (M^++1, 6%), 259 (M^++1, 5), 257 (M^++1, 4), 178 (100) and 176 (80); HRMS: M^++H, found 261.1271. $C_{12}H_{27}{}^{74}GeO$ requires 261.1268.

*4.2.10.8. (5R,2E)-5-Methoxyhex-2-enyl(triethyl)germane [(E)-**26**]; standard procedure.* The (*E*)-5-hydroxyhex-2-enylgermane (*E*)-**25** (233 mg, 0.90 mmol) in THF (3.5 mL) was added to a suspension of sodium hydride (60% dispersion in mineral oil, 78 mg, 1.1 mmol) in THF (2 mL) and the reaction mixture stirred at 35 °C for 2 h. Methyl iodide (0.3 mL, 4.5 mmol) was added. After stirring at rt overnight, water was added (4 mL) and the mixture extracted with ether (3×25 mL). The organic extracts were washed with water (25 mL) and brine (25 mL), then dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum/ether (30:1) gave the *title compound* (*E*)-**26** (206 mg, 84%) as a colourless oil, R_f 0.46 in 9:1 light petroleum/ether, $[\alpha]_D^{23}$ +8.8 (*c* 0.77 in $CHCl_3$); ν_{max}/cm^{-1} 2951, 2930, 2907, 2872, 1459, 1374, 1260, 1099, 1017, 963 and 805; δ_H ($CDCl_3$, 300 MHz) 0.76 (6H, q, *J* 8.0, 3× $GeCH_2$), 1.05 (9H, t, *J* 8.0, 3× $GeCH_2CH_3$), 1.15 (3H, d, *J* 6.0, 6-H_3), 1.64 (2H, d, *J* 8.0, 1-H_2), 2.10 (1H, dt, *J* 14.0, 6.5, 4-H), 2.29 (1H, dt, *J* 14.0, 7.0, 4-H′), 3.30 (1H, m, 5-H), 3.36 (3H, s, OCH_3) and 5.28 and 5.53 (each 1H, dt, *J* 15.0, 7.0, 2-H or 3-H); δ_C ($CDCl_3$, 75 MHz) 4.1, 9.2, 17.3, 19.1, 39.7, 56.2, 76.9, 123.8 and 130.3; *m*/*z* (CI) 275 (M^++1, 1.5%), 273 (M^++1, 1.5), 271 (M^++1, 1), 178 (100), 176 (75) and 174 (50); HRMS: M^+, found 274.1344. $C_{13}H_{28}{}^{74}GeO$ requires 274.1346.

*4.2.10.9. (5R,2Z)-5-Methoxyhex-2-enyl(triethyl)germane [(Z)-**26**].* The (*Z*)-5-hydroxyhex-2-enylgermane (*Z*)-**25** (147 mg, 0.57 mmol) in THF (2 mL) and sodium hydride (60% dispersion in mineral oil, 45 mg, 0.68 mmol) in THF (1 mL), and methyl iodide (177 μL, 2.85 mmol), after chromatography using light petroleum/ether (60:1) as eluent, gave the *title compound* (*Z*)-**26** (133 mg, 73%) as a colourless oil, R_f 0.52 in 9:1 light petroleum/ether, $[\alpha]_D^{23}$ +15.9 (*c* 0.96 in $CHCl_3$); ν_{max}/cm^{-1} 2949, 2925, 2909, 2865, 1460, 1378, 1259, 1098, 1016 and 799; δ_H ($CDCl_3$, 300 MHz) 0.74 (6H, q, *J* 8.0, 3× $GeCH_2$), 1.03 (9H, t, *J* 8.0, 3× $GeCH_2CH_3$), 1.15 (3H, d, *J* 6.0, 6-H_3), 1.60 (2H, m, 1-H_2), 2.13 (1H, dt, *J* 10.0, 6.5, 4-H), 2.31 (1H, dt, *J* 10.0, 7.0, 4-H′), 3.22 (1H, m, 5-H), 3.36 (3H, s, OCH_3) and 5.29 and 5.55 (each 1H, dt, *J* 10.0, 7.0, 2-H or 3-H); δ_C ($CDCl_3$, 75 MHz) 4.3, 9.2, 17.4, 19.2, 39.7, 56.3, 77.0, 123.7 and 130.2; *m*/*z* (CI) 275 (M^++1, 40%), 273 (M^++1, 30), 271 (M^++1, 20), 178 (100), 176 (75) and 174 (50); HRMS: M^+, found 274.1347. $C_{13}H_{28}{}^{74}GeO$ requires 274.1346.

*4.2.10.10. (5R,2Z)-5-Hydroxyhex-2-enyl(tributyl)germane [(Z)-**29**].* The standard procedure using tributylgermanium hydride (0.53 mL, 1.98 mmol) and TMEDA (0.34 mL, 2.2 mmol) in THF (3 mL), ^{t}BuLi (1.7 M in pentane, 1.39 mL, 2.4 mmol), copper(I) iodide (188 mg, 0.99 mmol) and the acetate (*Z*)-**21** (270 mg, 0.99 mmol) THF (2.5 mL) gave the 5-*tert*-butyldimethylsilyloxyhex-2-enyl(tributyl)germane (*Z*)-**28** as an oil used immediately without chromatography, R_f 0.69 in 2% ether in light petroleum, $[\alpha]_D^{21}$ +8.0 (*c* 1.10 in $CHCl_3$); ν_{max}/cm^{-1} 2958, 2926, 2857, 2007, 1462, 1376, 1254, 1129, 1084, 1002, 835 and 775; δ_H ($CDCl_3$, 500 MHz) 0.01 (6H, s, 2× $SiCH_3$), 0.84 (9H, t, *J* 8.0, 3× CH_2CH_3), 0.93 [9H, s, $SiC(CH_3)_3$], 1.07 (3H, d, *J* 6.5, 6-H_3), 1.20-1.36 (18H, m, 9× CH_2), 1.56 (2H, d, *J* 9.0, 1-H_2), 2.02–2.16 (2H, m, 4-H_2), 3.76 (1H, sext, *J* 6.0, 5-H) and 5.15 and 5.44 (each 1H, m, 2-H or 3-H); δ_C ($CDCl_3$, 125 MHz) −4.7, −4.5, 12.1, 12.6, 13.8, 25.9, 26.1, 26.7, 27.6, 28.6, 37.3, 69.0, 122.8 and 128.3; *m*/*z* (EI) 401 (M^+−57, 20%) and 262 (100); HRMS: $M^+-C_4H_9$, found 401.2287. $C_{20}H_{43}{}^{74}GeOSi$ requires 401.2289.

The standard procedure using tetra-*n*-butylammonium fluoride (1 M in THF, 1.95 mL, 1.95 mmol) and the crude silyl ether (*Z*)-**28** in THF (8 mL), after chromatography using light petroleum/ether (9:1), gave the *title compound* (*Z*)-**29** (235 mg, 78% over the two steps) as a colourless oil, R_f 0.17 in 9:1 light petroleum/ether, $[\alpha]_D^{23}$ +17.5 (*c* 1.14 in $CHCl_3$); ν_{max}/cm^{-1} 3340, 2958, 2938, 2872, 2856, 1643, 1461,

1376, 1260, 1118, 1081, 1027 and 881; δ_H ($CDCl_3$, 400 MHz) 0.73 (6H, m, 3× CH_2), 0.89 (9H, t, *J* 7.0, 3× CH_3), 1.19 (3H, d, *J* 7.0, 6-H_3), 1.25–1.49 (12H, m, 6× CH_2), 1.57 (1H, br s, OH), 1.62 (1H, dd, *J* 12.0, 8.0, 1-H), 1.70 (1H, dd, *J* 12.0, 9.0, 1-H′), 2.10–2.28 (2H, m, 4-H_2), 3.80 (1H, m, 5-H), 5.23 (1H, dt, *J* 9.5, 8.0, 2-H) and 5.64 (1H, dt, *J* 10.0, 9.0, 3-H); δ_C ($CDCl_3$, 100 MHz) 12.5, 13.7, 14.2, 22.8, 26.5, 27.4, 36.8, 67.8, 121.6 and 130.5; *m*/*z* (CI) 345 (M^++1, 5%) and 260 (100): HRMS: M^+, found 344.2125. $C_{18}H_{38}{}^{74}GeO$ requires 344.2129.

4.2.11. Tin(IV) halide promoted reactions of hex-2-enylgermanes with aldehydes

*4.2.11.1. (1R,6R,3Z)-1-Phenylhept-3-ene-1,6-diol (**19a**).* The standard procedure using tin(IV) bromide (89 mg, 0.2 mmol) in DCM (0.65 mL), the (*Z*)-hex-2-enyl(triethyl)germane (*Z*)-**25** (44 mg, 0.17 mmol) in DCM (0.8 mL) and benzaldehyde (58 μL, 0.5 mmol), after chromatography using ether/light petroleum (3:1) as eluent, gave the title compound **19a**[1] (28 mg, 80%) as a colourless oil, **19a**/**32a**=94:6 (^{1}H NMR; **19a**, 1-H, 4.68; **32a**, 1-H, 4.77[1]), R_f 0.46 in ether.

Similarly the (*Z*)-hex-2-enyl(tributyl)germane (*Z*)-**29** (52 mg, 0.17 mmol) in DCM (0.8 cm) gave the title compound **19a** (27 mg, 78%) as a colourless oil, **19a**/**32a**=92:8.

Similarly the (*E*)-hex-2-enyl(triethyl)germane (*E*)-**25** (44 mg, 0.17 mmol) in DCM (0.8 mL) gave the title compound **19a** (22 mg, 63%) as a colourless oil, **19a**/**32a**=89:11, R_f 0.46 in ether, $[\alpha]_D^{22}$ +65 (*c* 1.15 in $CHCl_3$), lit.[1] $[\alpha]_D^{20}$ +75 (*c* 1.26 in $CHCl_3$).

*4.2.11.2. (2R,7R,4Z)-8-Methylnon-4-ene-2,7–diol (**19b**).* Tin(IV) bromide (89 mg, 0.2 mmol) in DCM (0.65 mL), (*Z*)-hex-2-enyl(triethyl)germane (*Z*)-**25** (44 mg, 0.17 mmol) in DCM (0.8 mL) and 2-methylpropanal (50 μL, distilled, 0.5 mmol), after chromatography using ether/light petroleum (3:1) as eluent, gave the title compound **19b**[1] (24 mg, 82%) as a colourless oil, **19b**/**32b**=93:7 (^{13}C NMR), R_f 0.41 in ether.

Similarly the (*E*)-hex-2-enyl(triethyl)germane (*E*)-**25** (44 mg, 0.17 mmol) in DCM (0.8 mL) gave the title compound **19b** (15 mg, 51%) as a colourless oil, **19b**/**32b**=91:9, $[\alpha]_D^{23}$ +10.2 (*c* 0.90 in $CHCl_3$).

*4.2.11.3. (2R,7S,4Z)-Dec-4-ene-2,7-diol (**19c**).* Tin(IV) bromide (89 mg, 0.2 mmol) in DCM (0.65 mL), the (*Z*)-hex-2-enyl(triethyl) germane (*Z*)-**25** (44 mg, 0.17 mmol) in DCM (0.8 mL) and butanal (45 μL, 0.45 mol), after chromatography using ether/light petroleum (3:1) as eluent, gave the *title compound* **19c** (22 mg, 75%) as a colourless oil, **19c**/**32c**=93:7 (^{13}C NMR), R_f 0.45 in ether.

Similarly the (*Z*)-hex-2-enyl(tributyl)germane (*Z*)-**29** (52 mg, 0.17 mmol) in DCM (0.8 mL) gave the *title compound* **19c** (20 mg, 68%) as a colourless oil, **19c**/**32c**=90:10, $[\alpha]_D^{23}$ +7.2 (*c* 1.34 in $CHCl_3$); ν_{max}/cm^{-1} 3349, 2961, 2931, 2873, 1459, 1374, 1122, 1075, 1023, 943, 846 and 714; δ_H ($CDCl_3$, 500 MHz) 0.96 (3H, t, *J* 7.0, 10-H_3), 1.25 (3H, d, *J* 6.0, 1-H_3), 1.36–1.56 (4H, m, 2× CH_2), 2.18 and 2.30 (each 2H, m, 3-H_2 or 6-H_2), 2.50 (2H, br s, 2× OH), 3.67 (1H, m, 7-H), 3.87 (1H, m, 2-H) and 5.61–5.66 (2H, m, 4-H and 5-H); δ_C ($CDCl_3$, 75 MHz) major **19c** 14.3, 19.2, 23.6, 35.5, 37.2, 39.8, 67.8, 71.2, 129.1 and 129.3; minor **32c** 23.2, 35.2, 36.9, 39.3, 125.8 and 128.8; *m*/*z* (CI) 190 (M^++18, 100%); HRMS: M^++NH_4, found 190.1800. $C_{10}H_{24}NO_2$ requires 190.1802.

*4.2.11.4. (1R,6R,3Z)-1-(4-Chlorophenyl)hept-3-ene-1,6-diol (**19d**).* Tin(IV) bromide (89 mg, 0.2 mmol) in DCM (0.6 mL), (*Z*)-hex-2-enyl(triethyl)germane (*Z*)-**25** (44 mg, 0.17 mmol) in DCM (0.7 mL) and 4-chlorobenzaldehyde (72 mg, 0.5 mmol) in DCM (0.3 mL), after chromatography using ether/light petroleum (3:1) as eluent, gave the *title compound* **19d** (33 mg, 81%) as a colourless oil, **19d**/**32d**=92:8 (^{1}H NMR), R_f 0.34 in ether.

Similarly the (*Z*)-hex-2-enyl(tributyl)germane (*Z*)-**29** (52 mg, 0.17 mmol) in DCM (0.7 mL) gave the *title compound* **19d** (30 mg, 73%) as a colourless oil, **19d**/**32d**=91:9, $[\alpha]_D^{21}$ +91.7 (*c* 1.44 in $CHCl_3$); ν_{max}/cm^{-1} 3350, 3015, 2968, 2926, 1491, 1406, 1090, 1067, 1013 and 830; δ_H ($CDCl_3$, 300 MHz) major **19d** 1.23 (3H, d, *J* 6.0, 7-H_3), 1.23 (1H, dt, *J* 13.5, 3.5, 2-H or 5-H), 2.26–2.40 (2H, m, 2× 2-H or 5-H), 2.60 (1H, dt, *J* 14.0, 8.5, 2-H or 5-H), 3.85 (1H, m, 6-H), 4.68 (1H, dd, *J* 9.0, 4.0, 1-H), 5.56–5.72 (2H, m, 3-H and 4-H) and 7.33 (4H, m ArH); minor **32d** 4.79 (1H, dd, *J* 6.5, 4.5, 1-H); δ_C ($CDCl_3$, 75 MHz) 23.5, 36.8, 37.5, 67.4, 72.8, 127.2, 128.1, 128.4, 129.6, 133.0 and 143.0; *m*/*z* (CI) 260 (M^++18, 33%) and 258 (M^++18, 100); HRMS: M^++NH_4, found 258.1263. $C_{13}H_{21}{}^{35}ClNO_2$ requires 258.1255.

*4.2.11.5. (1R,6R,3Z)-1-(3-Chlorophenyl)hept-3-ene-1,6-diol (**19e**).* Tin(IV) bromide (89 mg, 0.2 mmol) in DCM (0.65 mL), (*Z*)-hex-2-enyl(triethyl)germane (*Z*)-**25** (44 mg, 0.17 mmol) in DCM (0.8 mL) and 3-chlorobenzaldehyde (58 μL, 0.35 mmol), after chromatography using ether/light petroleum (3:1) as eluent gave the *title compound* **19e** (34 mg, 83%) as a pale yellow oil, **19e**/**32e**=93:7 (^{1}H and ^{13}C NMR), R_f 0.55 in ether, $[\alpha]_D^{21}$ +68 (*c* 1.33 in $CHCl_3$); ν_{max}/cm^{-1} 3351, 3015, 2968, 2925, 1598, 1574, 1432, 1063, 885, 844, 787 and 697; δ_H ($CDCl_3$, 300 MHz) major **19e** 1.23 (3H, d, *J* 6.0, 7-H_3), 2.13 (1H, dt, *J* 13.0, 3.5, 2-H or 5-H), 2.25–2.42 (2H, m, 2× 2-H or 5-H), 2.60 (1H, dt, *J* 14.5, 8.5, 2-H or 5-H), 3.00–3.27 (2H, br s, 2× OH), 3.85 (1H, m, 6-H), 4.67 (1H, m, 1-H), 5.59–5.71 (2H, m, 3-H and 4-H), 7.21–7.36 (3H, m, ArH) and 7.40 (1H, s, ArH); minor **32e** 4.79 (1H, m, 1-H); δ_C ($CDCl_3$, 75 MHz) major **19e** 23.7, 37.0, 37.8, 67.6, 73.0, 124.2, 126.2, 127.7, 128.3, 129.9, 134.5 and 147.0; minor **32e** 23.2, 36.6 and 72.7; *m*/*z* (CI) 260 (M^++18, 30%), 258 (M^++18, 100), 242 (M^+, 40), 240 (M^+, 76) and 223 (70); HRMS: M^+, found 240.0908. $C_{13}H_{17}{}^{35}ClO_2$ requires 240.0912.

*4.2.11.6. (1R,6R,3Z)-1-(4-Nitrophenyl)hept-3-ene-1,6-diol (**19f**).* Tin(IV) bromide (89 mg, 0.2 mmol) in DCM (0.6 mL), (*Z*)-hex-2-enyl(triethyl)germane (*Z*)-**25** (44 mg, 0.17 mmol) and 4-nitrobenzaldehyde (77 mg, 0.5 mmol) in DCM (0.3 mL), after chromatography using ether/light petroleum (3:1) as eluent gave title compound **19f**[1] (35 mg, 81%) as a yellow oil, **19f**/**32f**=91:9 (^{1}H NMR), R_f 0.32 in ether, $[\alpha]_D^{23}$ +84 (*c* 1.57 in $CHCl_3$), lit.[1] $[\alpha]_D^{20}$ +94 (*c* 0.8 in $CHCl_3$); HRMS: M^+, found 251.1152. $C_{13}H_{17}NO_4$ requires 251.1152.

*4.2.11.7. (2R,7R,4Z,8E)-Deca-4,8-diene-2,7-diol (**19g**).* Tin(IV) bromide (89 mg, 0.2 mmol) in DCM (0.65 mL), (*Z*)-hex-2-enyl(triethyl)germane (*Z*)-**25** (44 mg, 0.17 mmol) in DCM (0.8 mL) and (*E*)-but-2-enal (42 μL, 0.5 mmol), after chromatography using ether/light petroleum (3:1) as eluent, gave the *title compound* **19g** (21 mg, 73%) as a colourless oil, **19g**/**32g**=92:8 (^{13}C NMR), R_f 0.47 in ether, $[\alpha]_D^{22}$ +12.8 (*c* 1.54 in $CHCl_3$); ν_{max}/cm^{-1} 3350, 3015, 2967, 2919, 1673, 1451, 1316, 1077, 1120, 1045, 966 and 722; δ_H ($CDCl_3$, 300 MHz) 1.22 (3H, d, *J* 6.5, 1-H_3), 1.73 (3H, d, *J* 6.0, 10-H_3), 2.10–2.49 (6H, m, 3-H_2, 6-H_2 and 2× OH), 3.83 (1H, m, 2-H), 4.12 (1H, m, 7-H) and 5.45–5.77 (4H, m, 4-H, 5-H, 8-H and 9-H); δ_C ($CDCl_3$, 75 MHz) major **19g** 17.9, 23.5, 35.6, 37.3, 67.7, 72.4, 127.0, 128.8, 129.0 and 134.0; minor **32g** 37.0; *m*/*z* (CI) 188 (M^++18, 20%), 170 (M^+, 38) and 153 (100): HRMS: M^+, found 170.1298. $C_{10}H_{18}O_2$ requires 170.1301.

*4.2.11.8. (2R,7R,4Z,8E)-9-Phenylnona-4,8-diene-2,7-diol (**19h**).* Tin(IV) bromide (89 mg, 0.2 mmol) in DCM (0.65 mL), (*Z*)-hex-2-enyl(triethyl)germane (*Z*)-**25** (44 mg, 0.17 mmol) in DCM (0.8 mL) and *trans*-cinnamaldehyde (64 mL, 0.5 mmol), after chromatography using ether/light petroleum (3:1) gave the *title compound* **19h** (32 mg, 81%) as a colourless oil, **19h**/**32h**=91:9 (^{1}H and ^{13}C NMR), R_f 0.42 in ether, $[\alpha]_D^{21}$ +41.5 (*c* 1.36 in $CHCl_3$); ν_{max}/cm^{-1} 3351, 3024, 2967, 2927, 1657, 1450, 1071, 1046, 967 and 750; δ_H ($CDCl_3$, 300 MHz) major **19h** 1.27 (3H, d, *J* 6.5, 1-H_3), 2.10 (1H, m, 3-H or 6-H), 2.25–2.42 (2H, m, 2× 3-H or 6-H), 2.52 (1H, dt, *J* 14.0, 8.5,

3-H′ or 6-H′), 2.85 (2H, br s, 2× OH), 3.90 (1H, m, 2-H), 4.38 (1H, m, 7-H), 5.63 (2H, m, 4-H and 5-H), 6.29 (1H, dd, *J* 16.0, 6.0, 8-H), 6.29 (1H, d, *J* 16.0, 9-H) and 7.23–7.44 (5H, m, ArH); minor **32h** 4.43 (1H, m, 7-H); δ_C ($CDCl_3$, 75 MHz) major **19h** 23.6, 35.7, 37.2, 67.7, 72.3, 126.7, 127.9, 128.5, 128.8, 129.5, 130.3, 132.3 and 137.0; minor **32h** 23.2, 35.4, 36.9 and 72.1; *m*/*z* (CI) 250 (M^++18, 25%), 232 (M^+, 24%) and 215 (100); HRMS: M^+, 232.1454. $C_{15}H_{20}O_2$ requires 232.1458.

*4.2.11.9. (1R,6R,3Z)-6-Methoxy-1-phenylhept-3-en-1-ol (**20a**).* Tin(IV) bromide (89 mg, 0.2 mmol) in DCM (0.65 mL), (*Z*)-hex-2-enyl(triethyl)germane (*Z*)-**26** (46 mg, 0.17 mmol) in DCM (0.8 mL) and benzaldehyde (60 μL, 0.5 mmol), after chromatography using light petroleum/ether (2:1), gave the title compound **20a**[1] (35 mg, 94%) as a pale yellow oil, **20a**/**33a**=94:6 (^{1}H NMR; **20a**, 1-H, 4.76, dd; **33a**, 1-H, 4.82, t[1]), R_f 0.33 in 1:1 ether/light petroleum.

Similarly, the (*E*)-hex-2-enyl(triethyl)germane (*E*)-**26** (46 mg, 0.17 mmol) in DCM (0.8 mL) gave the title compound **20a** (31 mg, 83%) as a pale yellow oil, **20a**/**33a**=86:14, $[\alpha]_D^{21}$ +88 (*c* 0.96 in $CHCl_3$), lit.[1] $[\alpha]_D^{20}$ +95 (*c* 0.9 in $CHCl_3$).

*4.2.11.10. (4S,9R,6Z)-9-Methoxydec-6-en-4-ol (**20b**).* Tin(IV) bromide (107 mg, 0.24 mmol) in DCM (0.8 mL), (*Z*)-hex-2-enyl(triethyl)germane (*Z*)-**26** (56 mg, 0.205 mmol) in DCM (0.9 mL) and butanal (55 μL, 0.6 mmol), after chromatography using light petroleum/ether (2:1) as eluent, gave the *title compound* **20b** (23 mg, 61%) as a pale yellow oil, **20b**/**33b**=90:10 (^{13}C NMR), R_f 0.33 in 1:1 ether/light petroleum, $[\alpha]_D^{21}$ +12.9 (*c* 1.55 in $CHCl_3$); ν_{max}/cm^{-1} 3417, 2960, 2928, 2872, 1463, 1376, 1262, 1094, 1024 and 807; δ_H ($CDCl_3$, 500 MHz) 0.87 (3H, t, *J* 7.0, 1-H_3), 1.09 (3H, d, *J* 6.0, 10-H_3), 1.27–1.50 (4H, m, 2-H_2 and 3-H_2), 2.03–2.13 (2H, m, 2× 5-H or 8-H), 2.15–2.23 (2H, m, 5-H or 8-H and OH), 2.31 (1H, dt, *J* 14.0, 7.5, 5-H or 8-H), 3.25 (3H, s, OCH_3), 3.29 (1H, m, 4-H), 3.53 (1H, m, 9-H) and 5.45–5.55 (2H, m, 6-H and 7-H); δ_C ($CDCl_3$, 125 MHz) major **20b** 13.1, 17.9, 18.0, 33.6, 34.4, 38.4, 55.1, 69.8, 75.4, 126.9 and 128.08; minor **33b** 32.9, 34.2, 38.1, 126.6 and 127.5; *m*/*z* (CI) 206 (M^++18, 6%) and 187 (M^++1, 100); HRMS: M^++H, found 187.1695. $C_{11}H_{23}O_2$ requires 187.1698.

*4.2.11.11. (1R,6R,3Z)-1-(4-Chlorophenyl)-6-methoxyhept-3-en-1-ol (**20d**).* Tin(IV) bromide (67 mg, 0.14 mmol) in DCM (0.5 mL), (*Z*)-hex-2-enyl(triethyl)germane (*Z*)-**26** (31 mg, 0.11 mmol) in DCM (0.6 mL) and 4-chlorobenzaldehyde (54 mg, 0.33 mmol) in DCM (0.3 mL), after chromatography using ether/light petroleum (3:10) as eluent, gave the *title compound* **20d** (25 mg, 86%) as a yellow oil, **20d**/**33d**=95:5 (^{13}C NMR), R_f 0.32 in ether, $[\alpha]_D^{21}$ +91 (*c* 1.38, $CHCl_3$); ν_{max}/cm^{-1} 3410, 2972, 2930, 2825, 1491, 1377, 1135, 1089, 1014, 877, 830 and 724; δ_H ($CDCl_3$, 500 MHz) 1.09 (3H, d, *J* 6.5, 7-H_3), 2.03 (1H, dt, *J* 14.0, 6.0, 2-H or 5-H), 2.25–2.33 (2H, m, 2× 2-H or 5-H), 2.45 (1H, dt, *J* 14.0, 9.0, 2-H or 5-H), 3.25 (3H, OCH_3), 3.29 (1H, m, 6-H), 4.60 (1H, dd, *J* 9.5, 4.0, 1-H), 5.45–5.59 (2H, m, 3-H and 4-H) and 7.21–7.27 (4H, m, ArH); δ_C ($CDCl_3$, 125 MHz) major **20d** 18.8, 34.6, 37.9, 56.1, 72.6, 76.4, 127.2, 128.4, 129.8, 132.7 and 143.1; minor **33d** 128.1; *m*/*z* (CI) 274 (M^++18, 4%), 272 (M^++18, 13), 256 (M^+, 6), 254 (M^+, 18), 239 (35) and 237 (100); HRMS: M^+, found 254.1065. $C_{14}H_{19}{}^{35}ClO_2$ requires 254.1068.

*4.2.12. Methyl (6S,2Z)-6-tert-butyldimethylsilyloxyhept-2-enoate (**38**).* Dimethyl sulfoxide (0.89 mL, 12.3 mmol) in DCM (3 mL) was added to oxalyl chloride (0.84 mL, 9.3 mmol) in DCM (3 mL) at −78 °C and the solution was stirred for 3 min at −78 °C before the addition of the 4-*tert*-butyldimethylsilyloxypentanol **36** (1.35 g, 6.19 mmol) in DCM (6 mL). The solution was stirred for 15 min at −78 °C before the addition of triethylamine (4.4 mL, 16.0 mmol). The reaction mixture was allowed to warm to rt and stirred for 30 min. Saturated aqueous ammonium chloride (5 mL) and water (40 mL) were added and the mixture extracted using ether (3×30 mL). The organic extracts were washed with water (30 mL) and brine (30 mL), then dried ($MgSO_4$) before concentration under reduced pressure. Chromatography of the residue using light petroleum/ether (9:1) yielded 4-*tert*-butyldimethylsilyloxypentanal **37** (1.24 g, 93%) as a colourless oil, R_f 0.41 in 9:1 light petroleum/ether, $[\alpha]_D^{23}$ +13.5 (*c* 1.42 in $CHCl_3$); ν_{max}/cm^{-1} 2957, 2937, 2858, 2361, 1728, 1257, 1097, 1045, 835 and 774; δ_H ($CDCl_3$, 300 MHz) 0.06 and 0.08 (each 3H, s, $SiCH_3$), 0.92 [9H, s, $SiC(CH_3)_3$], 1.18 (3H, d, *J* 6.0, 5-H_3), 1.66–1.89 (2H, m, 3-H_2), 2.48–2.56 (2H, m, 2-H_2), 3.90 (1H, m, 4-H) and 9.81 (1H, t, *J* 2.0, CHO); δ_C ($CDCl_3$, 75 MHz) −4.6, −4.1, 18.3, 23.9, 26.1, 31.9, 40.4, 67.7 and 203.1; *m*/*z* (CI) 233 (42%) and 217 (M^++1, 100).

A solution of bis(2,2,2-trifluoroethyl) (methoxycarbonylmethyl) phosphonate (95%, 1.25 mL, 11.1 mmol) and 18-crown-6 (7.23 g, 22.2 mmol) in THF (100 mL) was cooled to −78 °C. Potassium hexamethyldisilazide (0.5 M in toluene, 10.9 mL, 5.5 mmol) was added. After 5 min, the aldehyde **37** (1.2 g, 5.55 mmol) in THF (19 mL) was added dropwise so that the temperature remained below −60 °C. The reaction mixture was stirred for 30 min at −78 °C before saturated aqueous ammonium chloride (18 mL) and water (50 cm) were added. The mixture was extracted using ether (3×50 mL) and the organic extracts were washed with water (50 mL) and brine (50 mL) then dried ($MgSO_4$). After concentration under reduced pressure, chromatography of the residue using 2% ether in light petroleum gave the *title compound* **38** (1.06 g, 70%), R_f 0.16 in 2% ether in light petroleum, $[\alpha]_D^{23}$ +14.9 (*c* 1.37 in $CHCl_3$); ν_{max}/cm^{-1} 2956, 2931, 2858, 1730, 1647, 1439, 1257, 1174, 1092, 1041, 1007, 835 and 775; δ_H ($CDCl_3$, 300 MHz) 0.08 (6H, s, 2× $SiCH_3$), 0.91 [9H, s, $SiC(CH_3)_3$], 1.18 (3H, d, *J* 6.0, 7-H_3), 1.51–1.66 (2H, m, 5-H_2), 2.68–2.78 (2H, m, 4-H_2), 3.74 (3H, s, OCH_3), 3.87 (1H, sext, *J* 6.0, 6-H), 5.80 (1H, dt, *J* 11.5, 2.0, 2-H) and 6.28 (1H, dt, *J* 11.5, 7.5, 3-H); δ_C ($CDCl_3$, 75 MHz) −4.5, −4.1, 18.4, 24.0, 26.0, 26.1, 39.1, 51.3, 68.5, 119.4, 151.0 and 167.1; *m*/*z* (CI) 290 (M^++18, 10%) and 273 (M^++1, 100); HRMS: M^++NH_4, found 290.2149. $C_{14}H_{32}NO_3Si$ requires 290.2146. The second fraction was the (*E*)-isomer of the title compound (52 mg, 3%), R_f 0.10 in 2% ether in light petroleum.

*4.2.13. (6S,2Z)-6-tert-Butyldimethylsilyloxyhept-2-en-1-ol (**39**).* Diisobutylaluminium hydride (1 M in hexanes, 9 mL, 9.0 mmol) was added to the ester **38** (1.01 g, 3.71 mmol) in DCM (11 mL) at −78 °C and the solution stirred at −78 °C for 45 min then at −40 °C for 1 h. Saturated aqueous potassium/sodium tartrate (8 mL) and ether (25 mL) were added and the solution stirred at rt overnight. The organic extracts were washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum/ether (4:1) as eluent gave the *title compound* **39** (0.87 g, 96%) as a colourless oil, R_f 0.46 in 2:1 light petroleum/ether, $[\alpha]_D^{21}$ +13.3 (*c* 1.41 in $CHCl_3$); ν_{max}/cm^{-1} 3340, 3016, 2957, 2938, 2858, 1657, 1462, 1375, 1255, 1137, 1093, 1053, 1004, 835 and 775; δ_H ($CDCl_3$, 300 MHz) 0.08 (6H, s, 2× $SiCH_3$), 0.92 [9H, s, $SiC(CH_3)_3$], 1.18 (3H, d, *J* 6.0, 7-H_3), 1.44–1.56 (2H, m, 4-H_2) 1.63 (1H, br s, OH), 2.02–2.26 (2H, m, 5-H_2), 3.85 (1H, sext, *J* 6.0, 6-H), 4.22 (2H, d, *J* 6.0, 1-H_2) and 5.54–5.68 (2H, m, 2-H and 3-H); δ_C ($CDCl_3$, 75 MHz) −4.5, −4.1, 18.4, 24.0(2), 26.1, 39.8, 58.8, 68.4, 128.7 and 133.1; *m*/*z* (CI) 245 (M^++1, 100%) and 227 (M^+−17, 43); HRMS: M^+−OH, found 227.1826. $C_{13}H_{27}OSi$ requires 227.1826.

*4.2.14. (6S,2Z)-6-tert-Butyldimethylsilyloxyhept-2-en-1-yl acetate (**40**).* Acetic anhydride (0.38 mL, 3.9 mmol) was added to the alcohol **39** (0.87 g, 3.57 mmol) in pyridine (0.9 mL, 10.7 mmol) and the solution stirred at rt overnight. Ether (30 mL) was added and the organic extract washed with water (20 mL), aqueous hydrogen chloride (0.1 M, 20 mL) and saturated aqueous sodium bicarbonate (20 mL), then dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum/

ether (9:1) as eluent gave the *title compound* **40** (0.91 mg, 89%) as a colourless oil, R_f 0.35 in 9:1 light petroleum/ether, $[\alpha]_D^{23}$ +17.5 (*c* 1.20 in $CHCl_3$); ν_{max}/cm^{-1} 2955, 2932, 2889, 2858, 1731, 1664, 1257, 1162, 1093, 836 and 777; δ_H ($CDCl_3$, 300 MHz) 0.06 and 0.07 (each 3H, s, $SiCH_3$), 0.92 [9H, s, $SiC(CH_3)_3$], 1.17 (3H, d, *J* 6.0, 7-H_3), 1.45–1.57 (2H, m, 4-H_2), 2.10 (1H, s, CH_3CO) 2.10–2.30 (2H, m, 5-H_2), 3.84 (1H, sext, *J* 6.0, 6-H), 4.65 (2H, d, *J* 6.5, 1-H_2), 5.56 (1H, dt, *J* 11.0, 7.0, 3-H) and 5.68 (1H, dt, *J* 11.0, 7.5, 2-H); δ_C ($CDCl_3$, 75 MHz) −4.5, −4.1, 18.4, 21.3, 24.0, 24.2, 26.1, 39.6, 60.6, 68.3, 123.6, 135.5 and 171.3; *m*/*z* (CI) 287 (M^++1, 100%); HRMS: M^+, found 286.1963. $C_{15}H_{30}O_3Si$ requires 286.1959.

*4.2.15. (6S,2Z)-6-Hydroxyhept-2-en-1-yl(triethyl)germane (**42**).* The standard procedure using triethylgermanium hydride (0.53 mL, 3.3 mmol), TMEDA (0.56 mL, 3.63 mmol) in THF (5 mL), ^{t}BuLi (1.7 M in pentane, 2.31 mL, 3.93 mmol), copper(I) iodide (313 mg, 1.65 mmol) and the acetate **40** (473 mg 1.65 mmol) in THF (4 mL), after concentration under reduced pressure, gave the 6-*tert*-butyldimethylsilyloxyhept-2-en-1-yl(triethyl)germane **41** (754 mg) as an oil, used without further purification, R_f 0.5 in light petroleum, $[\alpha]_D^{23}$ +13.2 (*c* 1.16 in $CHCl_3$); δ_H ($CDCl_3$, 300 MHz) 0.09 (6H, s, 2× $SiCH_3$), 0.77 (6H, q, *J* 8.0, 3× $GeCH_2$), 0.93 [9H, s, $SiC(CH_3)_3$], 1.06 (9H, t, *J* 8.0, 3× $GeCH_2CH_3$), 1.17 (3H, d, *J* 6.0, 7-H_3), 1.38–1.57 (2H, m, 4-H_2), 1.67 (2H, d, *J* 8.0, 1-H_2), 2.00 and 2.15 (each 1H, m, 5-H), 3.83 (1H, sext, *J* 6.0, 6-H), 5.22 (1H, dt, *J* 10.5, 7.0, 2-H or 3-H) and 5.47 (1H, dt, *J* 10.5, 9.0, 3-H or 2-H); *m*/*z* (CI) 389 (M^++1, 40%), 387 (M^++1, 30), 385 (M^++1, 25), 178 (100), 176 (60) and 174 (40); HRMS: M^+, found 388.2222. $C_{19}H_{42}{}^{74}GeOSi$ requires 388.2211.

Following the standard procedure, tetra-*n*-butylammonium fluoride (1 M in THF, 4.0 mL, 4.0 mmol) and the silyl ether **41** (754 mg, 1.95 mmol) in THF (9 mL), after chromatography using light petroleum/ether (4:1) as eluent, gave the *title compound* **42** (331 mg, 73% over the two steps) as a colourless oil, R_f 0.22 in 4:1 light petroleum/ether, $[\alpha]_D^{23}$ +3.06 (*c* 1.08 in $CHCl_3$); ν_{max}/cm^{-1} 3340, 2960, 2871, 1642, 1460, 1424, 1129, 1078, 1019, 962 and 703; δ_H ($CDCl_3$, 500 MHz) 0.67 (6H, q, *J* 8.5, 3× $GeCH_2$), 0.95 (9H, t, *J* 7.5, 3× $GeCH_2CH_3$), 1.13 (3H, d, *J* 6.5, 7-H_3), 1.40–1.48 (2H, m, 5-H_2), 1.48–1.56 (1H, br s, OH), 1.58 (2H, d, *J* 8.0, 1-H_2), 1.97–2.12 (2H, m, 4-H_2), 3.77 (1H, sext, *J* 6.5, 6-H), 5.13 (1H, dt, *J* 10.5, 7.0, 2-H or 3-H) and 5.41 (1H, q, *J* 9.0, 3-H or 2-H); δ_C ($CDCl_3$, 75 MHz) 4.3, 9.2, 13.1, 23.7(2), 39.4, 68.3, 126.1 and 127.7; *m*/*z* (CI) 178 (100%), 176 (75) and 174 (60); HRMS: M^+, 274.1351. $C_{13}H_{25}{}^{74}GeO$ requires 274.1346.

*4.2.16. (2S,3R,6S)-3-Ethenyl-6-methyl-2-phenyltetrahydro-2H-pyran (**43**).* A cooled solution of tin(IV) bromide (89 mg, 0.2 mmol) in DCM (0.65 mL) was added to the 6-hydroxyhept-2-enylgermane **42** (46 mg, 0.169 mmol) in DCM (0.80 mL) at −78 °C and the solution stirred at −78 °C for 15 min before the addition of benzaldehyde (60 μL, 0.5 mmol). The reaction mixture was stirred at −78 °C for 45 min before the addition of saturated methanolic ammonium chloride (1 mL) and water (30 mL). The mixture was extracted using ether (3×20 mL) and the organic extracts were washed with water (20 mL) and brine (20 mL), then dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum/ether (12:1) as eluent gave the title compound **43**[19] (19 mg, 55%) as a pale yellow oil, R_f 0.47 in 9:1 light petroleum/ether, $[\alpha]_D^{23}$ +20.3 (*c* 1.54 in $CHCl_3$); ν_{max}/cm^{-1} 2970, 2930, 2851, 1640, 1452, 1117, 1069, 912, 756 and 698; δ_H ($CDCl_3$, 500 MHz) 1.75 (3H, d, *J* 6.0, 6-CH_3), 1.39 and 1.52 (each 1H, m, 4-H), 1.67 (1H, ddt, *J* 13.5, 3.5, 2.5, 5-H), 1.88 (1H, dtd, *J* 13.5, 3.5, 3.0, 5-H′), 2.25 (1H, m, 3-H), 3.59 (1H, dqd, *J* 11.0, 6.0, 2.0, 6-H), 4.02 (1H, d, *J* 10.0, 2-H), 4.73–4.78 (2H, m, 2′-H_2), 5.38 (1H, ddd, *J* 17.0, 11.0, 7.5, 1′-H) and 7.15–7.24 (5H, m, ArH); δ_C ($CDCl_3$, 125 MHz) 22.2, 30.0, 33.1, 46.3, 74.2, 84.9, 115.3, 127.6(2), 128.1, 139.0 and 141.3; *m*/*z* (CI) 220 (M^++18, 100%) and 203 (M^++1, 15); HRMS: M^++NH_4, found 220.1701. $C_{14}H_{22}NO$ requires 220.1696.

Acknowledgements

We thank the Engineering and Physical Sciences Research Council for a studentship (to A.W.) and P. Casteno for preliminary studies.

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20. 1,3-Isomerisations of alk-3-en-1-yltin trihalides to alk-1-en-3-yltin trihalides at −78 °C have been postulated to account for the chemistry of 5-alkoxypent-1-en-3-ylstannanes on transmetallation using tin(IV) chloride; see Ref. 5. In the present work, the increased time allowed for the transmetallation may allow the reverse 1,3-isomerisation to take place under conditions for the more remote 1,6- and 1,7-stereocontrol. The positions of equilibrium of these isomerisations may depend on the relative positions of the tin trihalide and coordinating moieties