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1,5-Induction in Reactions of 4-Alkoxy-2-trimethylsilylalk-2-enyl(tributyl)stannanes with Aldehydes*

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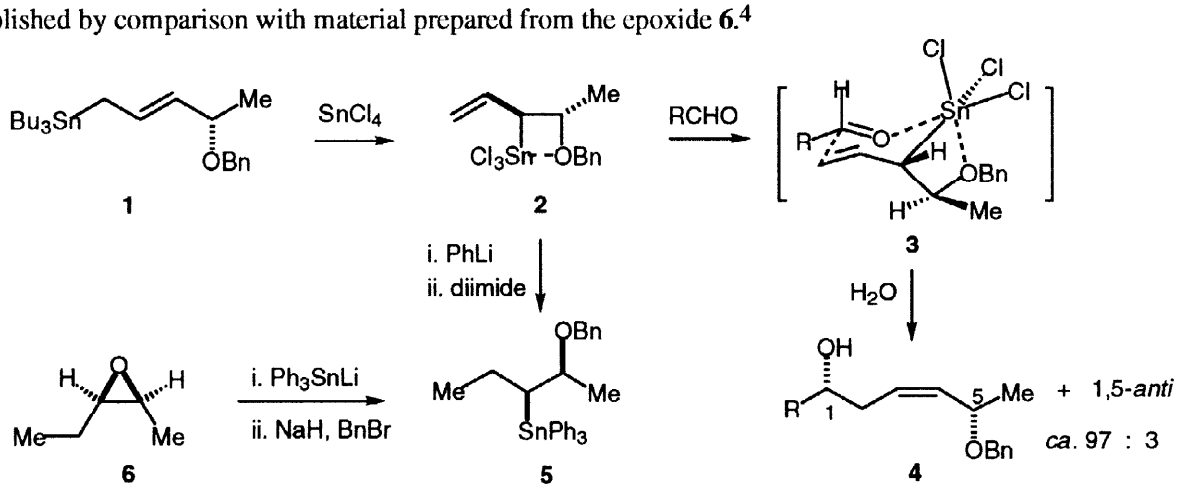
Abstract: 2-Trimethylsilylalk-2-enylstannanes undergo tin(IV) chloride promoted reactions with aldehydes to give homoallylic alcohols with retention of the 2-trimethylsilyl group. 4-Alkoxy-2-trimethylsilylalk-2-enyl(tributyl)stannane **31** reacts with aldehydes under these conditions with excellent stereoselectivity in favour of the 1,5-*syn*-(*E*)-products **32** - **35**. Preliminary studies into the chemistry of these vinylsilanes have been carried out.

Alk-2-enylstannanes with heteroatom substituents at the 4-, 5- and 6-positions undergo stereoselective transmetallation on treatment with tin(IV) halides to generate allyltin trihalides which react with aldehydes and imines with useful levels of 1,5-, 1,6- and 1,7-asymmetric induction.[1] For example, transmetallation of the 4-benzyloxypent-2-enylstannane **1** with tin(IV) chloride generates the allyltin trichloride **2** which reacts with aldehydes, *via* the transition structure **3**, to give the 1,5-*syn*-(*Z*)-products **4**.[2] The stereoselectivity of transmetallation is believed to be predominantly due to kinetic control.[3] The relative configuration of the two stereogenic centres in the allyltin trichloride **2** was confirmed by trapping using phenyllithium followed by reduction using diimide which gave the 4-benzyloxypent-3-yl(triphenyl)stannane **5** the structure of which was established by comparison with material prepared from the epoxide **6**.[4]



This paper is dedicated to Professor David Evans and Professor Teruaki Mukaiyama, worthy recipients of the 1998 Tetrahedron Prize, in appreciation of their seminal contributions to organic synthesis.

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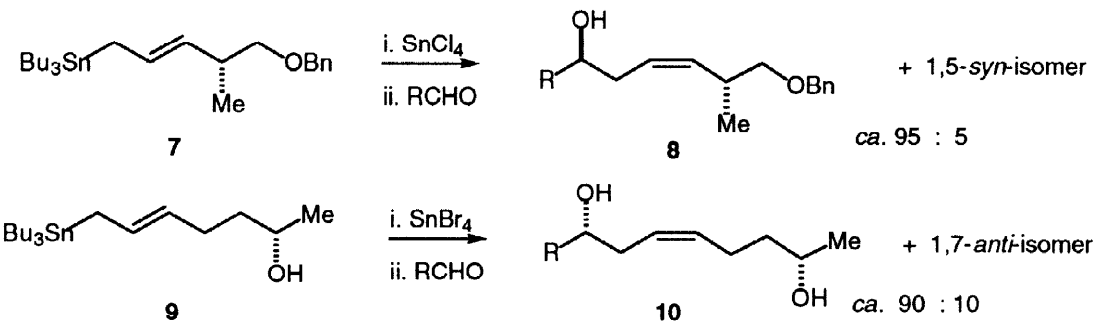
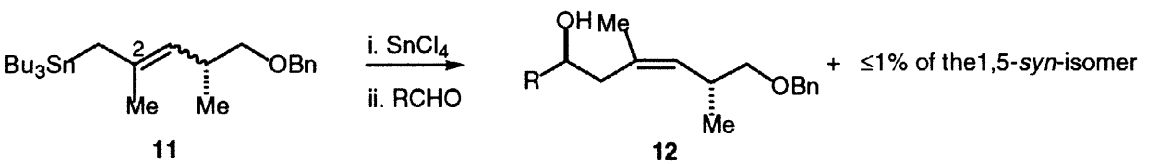
Other examples of remote induction using allylstannanes include reactions of the 5-alkoxy-4-methylpent-2-enylstannane **7** and the 6-hydroxyhept-2-enylstannane **9** which are transmetallated by tin(IV) halides to give allyltin trihalides which react with aldehydes to give the 1,5-*anti*- and 1,7-*syn*-products **8** and **10**, respectively.[5,6]



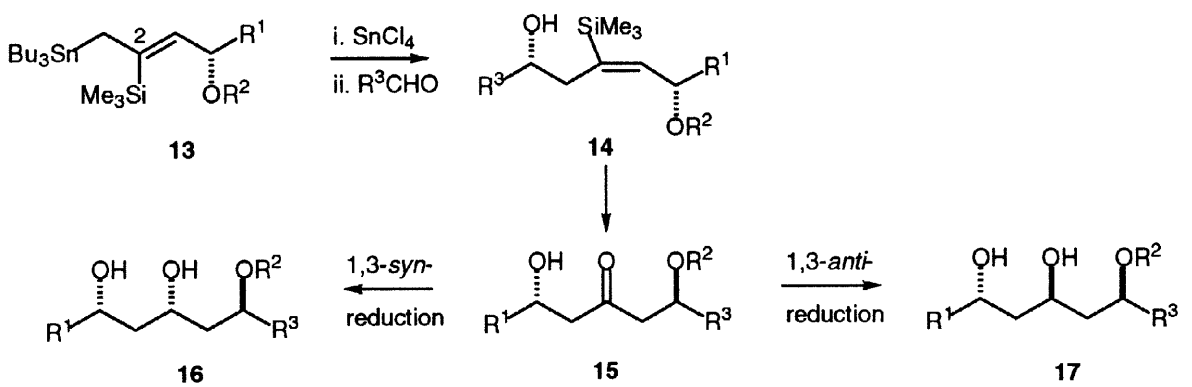
7 **8** **9** **10**

In order to delineate further the scope of these reactions, it is necessary to establish whether the chemistry is compatible with additional substituents in the alkenylstannane. An alkyl substituent at C(2) has been found not to interfere with the stereoselectivity of these reactions. Thus the 2-methylpent-2-enyl(tributyl)stannane **11**, as a mixture of (*E*)- and (*Z*)-geometrical isomers, gives rise to the 1,5-*anti*-(*Z*)-products **12**, which are analogous to the *anti*-products **8** obtained using the stannane **7**, with excellent stereoselectivity. Indeed the additional 2-methyl substituent appears to enhance the stereoselectivity.[7]



11 **12**

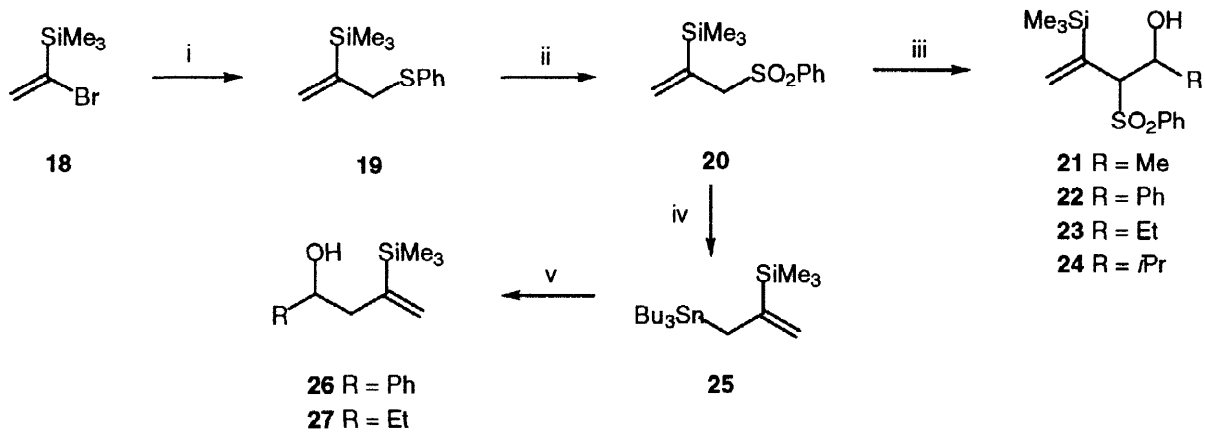
We here report the synthesis of 2-trimethylsilylalk-2-enylstannanes **13** and the results of a preliminary study of their tin(IV) chloride promoted reactions with aldehydes. The ultimate goal of this work is to provide stereoselective access to derivatives of 1,3,5-triols, e.g. **16** and **17**, by oxidation of the allylstannane - aldehyde products to the corresponding ketones followed by reduction. Indeed if both enantiomers of the allylstannane are available, with the option of either retaining or inverting the configuration of the 1,5-*syn*-product from the allylstannane - aldehyde reaction, it should be possible to access stereoselectively all possible 1,3,5-triol stereoisomers.



13 **14** **16** **15** **17**

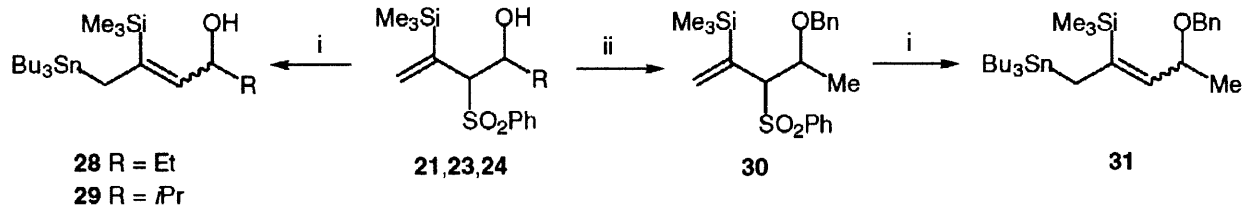
RESULTS AND DISCUSSION

The free-radical displacement of an allyl sulfone by tributyltin hydride was chosen as the method of synthesis of the allylstannanes.[8] Alkylation of the Grignard reagent derived from the vinyl bromide **18** using iodomethyl phenyl sulfide[9] gave the prop-2-enyl sulfide **19** and lithiation of the corresponding sulfone **20** using butyllithium followed by addition of an aldehyde gave the aldehyde adducts **21** - **24** as mixtures of diastereoisomers.[10] To check the viability of the proposed allyltin chemistry, the prop-2-enyl sulfone **20** was then treated with tributyltin hydride under free radical conditions to give the 2-trimethylsilylprop-2-enyl(tributyl)-stannane **25**. Reactions of this stannane with benzaldehyde and propanal were carried out by transmetallation using tin(IV) chloride at -78 °C followed by addition of the aldehyde. This procedure gave reasonable yields of the homoallylic alcohols **26** and **27** showing that the vinylsilane moiety is compatible with the conditions required for the stereoselective allylstannane - aldehyde reactions.



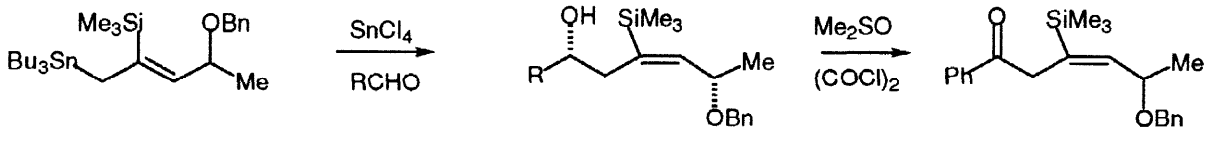
Scheme 1 i, Mg, $PhSCH_2I$ (65%); ii, Oxone (99%); iii, BuLi then RCHO (**21**, ratio 56 : 44, 93%; **22**, ratio 71 : 29, 81%; **23**, ratio 66 : 34, 91%; **24**, ratio 60 : 40, 95%); iv, Bu_3SnH, AIBN (90%); v, $SnCl_4$, RCHO (**26**, 70%; **27**, 68%).

Functionalized alk-2-enylstannanes were then prepared to study the stereoselectivity of the aldehyde - stannane reactions. The hydroxyalkyl sulfones **23** and **24** were converted directly into the (hydroxyalkenyl)-stannanes **28** and **29** by treatment with tributyltin hydride in the presence of a trace of azoisobutyronitrile. The sulfone **21** was converted into its benzyl ether **30** using benzyl trichloroacetimidate[11] and the benzyl ether taken through to the allylstannane **31** using the usual conditions. The stannanes **28**, **29** and **31** were obtained as mixtures of (*E*)- and (*Z*)-isomers, with ratios (*E*) : (*Z*) *ca.* 40 : 60. The major isomer in each case was assigned the (*Z*)-geometry, *i.e.* with the trimethylsilyl group *cis*- to the hydroxy- or alkoxyalkyl group, on the basis of the chemical shifts of the vinylic protons of the two isomers, e.g. δ 5.49 *vs.* 5.82 for the vinylic protons of the major (*Z*) and minor (*E*) isomers of the 4-benzyloxy-2-trimethylsilylpent-2-enylstannane **31**.



Scheme 2 i, Bu_3SnH, AIBN (**28**, 70%; **29**, 80%; **30**, 70%); ii, $Cl_3CC(=NH)OBn$, CF_3SO_3H (cat) (99%).

Reactions between 4-benzyloxy-2-trimethylsilylpent-2-enyl(tributyl)stannane 31 and aldehydes were carried out by adding tin(IV) chloride to a solution of the stannane in dichloromethane at -78 °C, stirring for five minutes and then adding the aldehyde. In all cases the 1,5-*syn*-(*E*)-stereoisomers **32** - **35** were obtained with excellent stereoselectivities and useful yields.



31

32 R = Ph (90%)
33 R = Me (72%)
34 R = Et (64%)
35 R = *i*Pr (79%)

36

$NaBH_4$

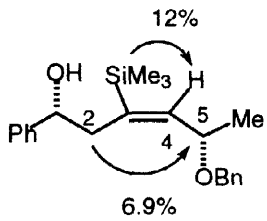
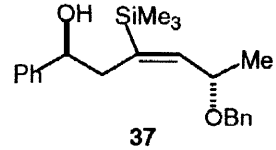


Figure 1 nOe's observed for **32**



37
(+32)

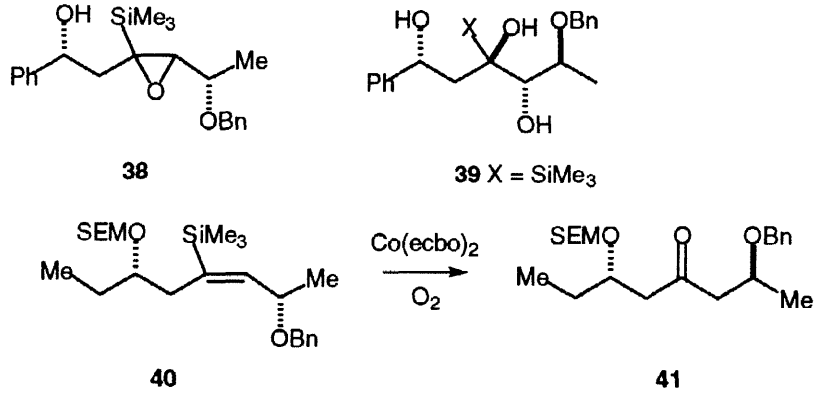
By both ^1H and ^{13}C NMR the products from these allylstannane - aldehyde reactions appeared to consist essentially (>98%) of a single diastereoisomer. To check that the 1,5-stereoisomers could be distinguished by NMR, the product **32** derived from benzaldehyde was oxidized to the ketone **36** using a Swern oxidation and the ketone reduced non-stereoselectively using sodium borohydride. This gave a mixture of the 1,5-*syn*-alcohol **32** and its 1,5-*anti*-epimer **37** which could just about be separated by careful chromatography and which could be clearly distinguished by ^1H NMR. Examination of the product mixture from the reaction between benzaldehyde and the stannane **31** showed that the reaction had been extremely stereoselective with less than 2% of the 1,5-*anti*-epimer **37** being formed.

The geometry of the double-bonds in the adducts **32** - **35** was confirmed by nOe studies. For example, for **32** on irradiation of the allylic protons, 2-H_2, an enhancement of 5-H (6.9%) was observed whereas there was neglible enhancement of the vinylic proton, 4-H. Conversely, irradiation of the trimethylsilyl group enhanced the peak due to 4-H (12%) but had no effect on 5-H, see Figure 1.

The 1,5-*syn*-stereoselectivity was assigned by analogy with the stereoselectivity observed for the 4-benzyloxypent-2-enylstannane **1**, and the correspondence in stereoselectivity observed for the reactions of the 5-benzyloxypent-2-enylstannane **7** and its 2-methylated homologue **11**. The regioselectivity observed in these reactions is consistent with the mechanism outlined for the tin(IV) chloride promoted reactions of the allylstannane **1** with aldehydes and is believed to involve participation of an allyltin trichloride analogous to **2** which reacts with aldehydes *via* six-membered chair-like transition states analogous to **3**. Of note is the high overall stereoselectivity despite the use of mixtures of (*E*)- and (*Z*)-isomers of the stannane **31**. This double-bond geometry is lost in the reaction between the allylstannane and the tin(IV) chloride and does not appear to affect the stereoselectivity of the transmetallation step.

Having prepared the 1,5-*syn*-products **32** - **35**, preliminary investigations into the oxidation of the vinyl silane components of these products were undertaken. Epoxidation using *m*-chloropeoxybenzoic acid gave the epoxide **38** as a mixture of stereoisomers but attempts to hydrolyse the epoxide **39** were unsuccessful, with mild conditions returning the epoxide and more vigorous conditions leading to decomposition. Hydroxylation, which

required a stoichiometric amount of osmium tetroxide, was more stereoselective and gave an 85 : 15 mixture of diastereoisomers. The major diastereoisomer was identified as the triol **39** on the basis of the diastereofacial selectivity usually observed on hydroxylation of (*Z*)-allylic ethers.[12] Finally, the alcohol **34** was protected as its (2-trimethylsilylethoxy)methyl (SEM) ether **40** and this was oxidized directly to the ketone **41** using oxygen and bis(2-ethoxycarbonyl-3-oxobutanalato)cobalt(II) [Co(ecbo)$_2$][13] albeit in only modest yield (23%).



CONCLUSIONS

This work has shown that a 2-trimethylsilyl substituent is compatible with the conditions required for tin(IV) chloride promoted reactions of alkoxyalk-2-enylstannanes and aldehydes which proceed with remote asymmetric induction. Useful yields of the 1,5-*syn*-products were obtained for a range of aliphatic and aromatic aldehydes using the 5-benzyloxypent-2-enylstannane **31**. The next phase of this programme, which is aimed at the stereoselective synthesis of 1,3,5-triols, will focus on the development of an asymmetric synthesis of the (2-trialkylsilylalk-2-enyl)stannanes, improved procedures, perhaps involving aryldimethylsilanes, for the conversion of the vinylsilanes into ketones[14] and stereoselective reduction of the β-hydroxyketones.[15,16]

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on Varian Unity 500, Bruker AC300 and Varian XL300 spectrometers in chloroform-d_1. Mass spectra were recorded on Kratos Concept and Fisons VG Trio 2000 mass spectrometers using electron impact (E.I.) or chemical ionisation (C.I.) modes. IR spectra were recorded on an ATI Mattson Genesis FTIR spectrometer as evaporated films on sodium chloride plates unless otherwise stated. Flash column chromatography was carried out using Merck silica gel 60H (40-60μ, 230-300 mesh) as the stationary phase. Melting points were recorded on a Köfler heated stage microscope and are uncorrected. Optical rotations were measured on an Optical Activity AA-100 polarimeter operating at 589 nm. Light petroleum refers to the fraction with b.p. 40 °C - 60 °C and was redistilled before use. Ether refers to diethyl ether. All solvents were distilled and purified by standard procedures. All products were obtained as colourless oils after chromatography.

Phenyl 2-trimethylsilylprop-2-enyl sulfide **19**

(1-Bromoethenyl)trimethylsilane **18** (3.43 cm^3, 27.9 mmol) in tetrahydrofuran (50 cm^3) was added to magnesium (887 mg, 36.3 mmol) and a few grains of iodine in tetrahydrofuran (5 cm^3) at a rate maintaining

gentle reflux. The solution was heated under reflux for 30 min then cooled to 0 °C and copper(I) iodide (1.06 g, 5.58 mmol) added. Iodomethyl phenyl sulfide (8 g) in THF(50 cm^3)was added dropwise at 0 °C and the mixture stirred at 0 °C for 1 h. Saturated aqueous ammonium chloride (10 cm^3) was added and the mixture allowed to warm to room temperature and extracted with ether (2 x 100 cm^3). The organic extracts were washed with brine (50 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum as eluent gave the *title compound* **19** (4.05 g, 65 %) as a pale yellow oil (Found: M^+, 222.0898. $C_{12}H_{18}SSi$ requires *M*, 222.0898); υ_{max} /cm^{-1} 3057, 1584, 1479, 1249, 840, 738 and 690; δ_H 0.21 [9 H, s, $Si(CH_3)_3$], 3.74 (2 H, s, 1-H_2), 5.46 (1 H, d, *J* 2, 3-H), 5.80 (1 H, d, *J* 2, 3-H') and 7.28 (5 H, m, ArH); δ_C -1.2, 39.9, 125.7, 127.4, 128.8, 129.2, 137.0 and 146.4; *m/z* (C.I.) 223 (M^+ + 1, 100 %), 207 (10) and 90 (87).

Phenyl 2-trimethylsilylprop-2-enyl sulfone **20**

To a solution of $KHSO_5$ (Oxone®, 33 g, 53.61 mmol) in water (70 cm^3) was added a solution of sulfide **19** (4 g, 17.87 mmol) in methanol (70 cm^3) and the solution stirred overnight then diluted with water (50 cm^3) and extracted with dichloromethane (5 x 50 cm^3). The organic extracts were washed with water (40 cm^3), then brine (40 cm^3), and concentrated under reduced pressure. Chromatography of the residue using 20 % ether in light petrol as eluent gave the *title compound* **20** (4.47 g, 99 %) as a pale yellow oil (Found: $M^+ + NH_4$, 272.1139. $C_{12}H_{22}NO_2SSi$ requires *M* 272.1140); υ_{max}/cm^{-1} 3066, 1447, 1317, 1248, 1152, 1086, 842 and 689; δ_H 0.16 [9 H, s, $Si(CH_3)_3$], 3.90 (2 H, s, 1-H_2), 5.75 (2 H, m, 3-H_2), 7.57 (2 H, m, ArH), 7.68 (1 H, m, ArH) and 7.88 (2 H, m, ArH); δ_C -1.3, 62.2, 128.7, 129.1, 133.7, 135.6, 138.7 and 139.1; *m/z* (C.I.) 272 (M^+ + 18, 100%) and 239 (20).

General procedure for the preparation of hydroxysulfones

Butyllithium in hexanes was added to phenyl 2-trimethylsilylprop-2-enyl sulfone **20** in dichloromethane at -78 °C and the solution stirred for 30 min, warmed to -35 °C and stirred for a further hour. The aldehyde was then added and temperature maintained at -35 °C for 1 h. Saturated methanolic ammonium chloride was added and the mixture allowed to warm to room temperature. Water was added, the mixture extracted into ether, and the organic phase washed with brine and dried ($MgSO_4$). After concentration under reduced pressure, flash chromatography of the residue gave the products as follows.

3-phenylsulfonyl-4-trimethylsilylpent-4-en-2-ol **21**; from butyllithium (1.42 M; 7.1 cm^3, 12.8 mmol), prop-2-enyl sulfone **20** (3.1 g, 12.2 mmol) in tetrahydrofuran (50 cm^3) and ethanal (1.38 cm^3, 24.4 mmol). Chromatography using 15 % ethyl acetate in light petroleum as the eluent gave the *title compound* **21** (3.37 g, 93 %) as a pale yellow oil, a mixture of diastereoisomers, ratio 56 : 44 (^{1}H NMR) (Found: $M^+ + NH_4$, 316.1392. $C_{14}H_{26}NO_3SSi$ requires *M* 316.1403); υ_{max} /cm^{-1} 3499, 3067, 1447, 1304, 1145, 1081, 841 and 689; δ_H 0.04 and 0.07 [each 4.5 H, s, $Si(CH_3)_3$], 1.21 and 1.26 (each 1.5 H, d, *J* 6, 1-H_3), 3.30 (0.5 H, d, *J* 3, OH), 3.75 (0.5 H, d, *J* 2, 3-H), 3.81 (0.5 H, d, *J* 9, 3-H), 4.24 (0.5 H, s, OH), 4.64 (1 H, m, 2-H), 5.76, 5.88, 5.98 and 6.7 (each 0.5 H, s, 5-H), 7.58 (2 H, m, ArH), 7.68 (1 H, m, ArH) and 7.86 (2 H, m, ArH); *m/z* (C.I.) 316 (M^+ + 18, 100 %), 281 (16) and 90 (23).

1-Phenyl-2-phenylsulfonyl-3-trimethylsilylbut-3-en-1-ol **22**; from butyllithium (1.56 M; 630 µl, 1.03 mmol), prop-2-enyl sulfone **20** (250 mg, 0.98 mmol) in tetrahydrofuran (2 cm^3) and benzaldehyde (124 µl, 1.18 mmol). Chromatography using 15 % ethyl acetate in light petroleum as the eluent gave the major diastereomer of the *title*

compound **22** (200 mg, 57 %) as a white solid (Found: C, 63.55; H, 6.75; S, 8.7; $M^+ + NH_4$, 378.1566. $C_{19}H_{28}NO_3SSi$ requires C, 63.3; H, 6.7; S, 8.9 %; *M*, 378.1559); υ_{max} /cm^{-1} 3495, 3061, 1448, 1291, 1248, 1145, 1085, 1060 and 841; δ_H -0.52 [9 H, s, $Si(CH_3)_3$], 3.61 (1 H, d, *J* 2, OH), 3.97 (1 H, d, *J* 2, 2-H), 5.82 (1 H, t, *J* 2, 1-H), 5.98 (1 H, d, *J* 2, 4-H), 6.88 (1 H, d, *J* 2, 4-H'), 7.28 (5 H, m, ArH), 7.59 (2 H, m, ArH), 7.69 (1 H, m, ArH) and 7.90 (2 H, m, ArH); δ_C -2.3, 70.7, 70.9, 126.6, 128.0, 128.3, 129.1, 129.5, 133.9, 136.2, 138.3, 138.5 and 139.8; *m/z* (C.I.) 378 (M^+ + 18, 75 %), 360 (M^+ + 1, 3), 343 (20), 272 (100) and 203 (39). The minor diastereomer of the *title compound* **22** (86 mg, 42 %) was isolated as a white solid; υ_{max} /cm^{-1} 3482, 3063, 1585, 1302, 1249, 1141, 1084, 840 and 756; δ_H 0.53 [9 H, s, $Si(CH_3)_3$], 4.20 (1 H, d, *J* 10, 2-H), 5.41 (1 H, d, *J* 2, OH), 5.43 (1 H, dd, *J* 2, 10, 1-H), 5.74 (1 H, s, 4-H), 5.88 (1 H, s, 4-H'), 7.30 (5 H, m, ArH), 7.59 (2 H, m, ArH), 7.69 (1 H, m, ArH) and 7.91 (2 H, m, ArH); δ_C -2.0, 73.0, 75.0, 126.8, 128.3, 128.4, 129.1, 123.0, 134.0, 134.7, 138.7, 139.9 and 142.7; *m/z* (C.I.) 378 (M^+ + 18, 80%), 360 (5), 343 (90) and 272 (100).

***4-Phenylsulfonyl-5-trimethylsilylhex-5-en-3-ol* 23**; from prop-2-enyl sulfone **20** (1.28 g, 5.05 mmol), butyllithium (3.31 cm^3, 5.3 mmol) and propanal (437 µl, 6.05 mmol). Chromatography using 15% ethyl acetate and light petroleum gave the *title compound* **23** (1.43 g, 91%) as a pale yellow oil, a mixture of two diastereoisomers, ratio 2 : 1 (^{1}H NMR); δ_H -0.12 (3 H, s, $SiCH_3$), -0.05 (6 H, s, 2 x $SiCH_3$), 0.97 (2 H, t, *J* 8, 1-H_3), 1.42 (3 H, m, 2-H_2 and 1-H_3), 3.15 (0.7 H, d, *J* 1, OH), 3.77 (0.3 H, d, *J* 3, OH), 3.81 (0.7 H, d, *J* 12, 4-H), 4.06 (0.3 H, m, 3-H), 4.12 (0.3 H, d, *J* 9, 4-H), 4.33 (0.7 H, m, 3-H), 5.71 (0.7 H, d, *J* 1, 6-H), 5.78 (0.7 H, d, *J* 1, 6-H), 5.92 (0.3 H, d, *J* 1, 6-H), 6.66 (0.3 H, d, *J* 1, 6-H), 7.59 (3 H, m, ArH) and 7.82 (2 H, m, ArH).

2-Methyl-4-phenylsulfonyl-5-trimethylsilylhex-5-en-3-ol **24**; from prop-2-enyl sulfone **20** (1.48 g, 5.61 mmol), butyllithium (3.67 cm^3, 5.87 mmol) and propanone (609 µl, 6.71 mmol). Chromatography using 11% ethyl acetate and light petroleum as eluent gave the *title compound* **24** (1.73 g, 95%) as a pale yellow oil, a mixture of two diastereoisomers, ratio 60 : 40 (^{1}H NMR); δ_H -0.03 (3.6 H, s, $SiCH_3$), 0.06 (5.4 H, s, $SiCH_3$), 0.80 and 1.03 (each 3 H, m, CH_3), 1.77 (1 H, m, 2-H), 3.91 (1 H, m, 3-H), 4.03 (0.6 H, m, 4-H), 4.28 (0.4 H, m, 4-H), 5.59 (0.4 H, d, *J* 1, 6-H), 5.67 (0.4 H, d, *J* 1, 6-H), 5.95 (0.6 H, d, *J* 1, 6-H), 6.61 (0.6 H, d, *J* 1, 6-H), 7.59 (3 H, m, ArH) and 7.82 (2 H, m, ArH).

General procedure for the preparation of the alk-2-enylstannanes

Tributyltin hydride was added to a degassed, stirred solution of the alkenyl sulfone and a trace of AIBN in benzene and the mixture heated to 65 °C for 2 h. After concentration under reduced pressure, chromatography of the residue gave the alk-2-enylstannane as a colourless oil.

(2-Trimethylsilylprop-2-en-1-yl)tributylstannane **25**; from the sulfone **20** (100 mg, 0.39 mmol), tributyltin hydride (200 µl, 0.79 mmol) and AIBN (5 mg) in benzene (2 cm^3). Chromatography using 1% triethylamine and light petroleum as eluent gave the *title compound* **25** (144 mg, 90%) as a colourless oil; δ_H 0.08 (9 H, s, 3 x $SiCH_3$), 0.90 (9 H, m, 3 x CH_3), 1.39 (18 H, m, 6 x CH_2), 1.90 (2 H, s, 1-H_2), 5.07 (1 H, d, *J* 2, 3-H), 5.34 (1 H, d, *J* 2, 3-H').

(4-Hydroxy-2-trimethylsilylhex-2-en-1-yl)tributylstannane **28**; from the hexenyl sulfone **23** (1.68 g, 5.39 mmol), tributyltin hydride (2.86 cm^3, 10.78 mmol) and AIBN (85 mg) in benzene (7 cm^3). Chromatography using 1% triethylamine and light petroleum as eluent gave the *title compound* **28** (5.06 g, 70%), as a colourless oil, a 60 : 40 mixture of diastereoisomers (Found: M^+ - C_4H_9, 405.1638. $C_{17}H_{37}OSiSn$ requires *M*, 405.1634); ν_{max}/cm^{-1} 3430 br, 1463, 1247 and 836; δ_H 0.10 (6 H, s, 2 x $SiCH_3$), 0.21 (3 H, s, $SiCH_3$), 0.97 (12 H, m),

1.12 (0.4 H, d, *J* 2, OH), 1.19 (0.6 H, d, *J* 2, OH), 1.42 (20 H, m), 1.73 (2 H, m, 1-H_2), 3.98 (0.4 H, m, 4-H), 4.09 (0.6 H, m, 4-H), 5.47 (0.6 H, d, *J* 8, 3-H) and 5.86 (0.4 H, d, *J* 10, 3-H); δ_C -1.6, 0.9, 9.7, 10.1, 12.9, 13.7, 17.8, 18.3, 18.7, 18.9, 19.8, 27.1, 27.5, 27.8, 29.0, 29.2, 29.3, 34.3, 73.1, 134.3, 138.3, 144.5; *m/z* (E.I.) 405 (M^+ - 57, 11%) and 387 (38).

(4-Hydroxy-5-methyl-2-trimethylsilylhex-2-en-1-yl)tributylstannane **29**; from hexenyl sulfone **24** (1.73 g, 5.30 mmol), tributyltin hydride (2.81 cm^3, 10.6 mmol) and AIBN (90 mg) in benzene (10 cm^3). Chromatography with 1% triethylamine and light petroleum as eluent gave the *title compound* **29** (2.01 g, 80%) as a colourless oil, (Found: M^+ - C_4H_9, 419.1770. $C_{18}H_{39}OSiSn$ requires *M*, 419.1791); ν_{max}/cm^{-1} 3398 br, 1462, 1247 and 836; δ_H 0.10 (6 H, s, $SiCH_3$), 0.20 (3 H, s, $SiCH_3$), 0.97 (15 H, m), 1.42 (19 H, m), 1.87 (0.6 H, d, *J* 16, 1-H), 1.97 (0.6 H, d, *J* 16, 1-H), 2.55 (0.4 H, d, *J* 10, 1-H), 2.60 (0.4 H, d, *J* 10, 1-H), 4.23 (0.4 H, m, 4-H), 4.27 (0.6 H, m, 4-H), 5.43 (0.6 H, d, *J* 8, 3-H) and 5.78 (0.4 H, d, *J* 10, 3-H); δ_C -1.5, 0.7, 8.0, 9.7, 9.9, 10.1, 12.8, 13.7, 19.6, 27.0, 27.4, 27.8, 29.0, 29.2, 29.3, 30.1, 30.5, 46.3, 69.7, 72.7, 135.6, 139.6, 143.9, 144.5; *m/z* (E.I.) 419 (M^+ - 57, 27%), 401 (29), 361 (35) and 251 (85).

(4-Benzyloxy-2-trimethylsilylpent-2-en-1-yl)tributylstannane **31**; from the sulfone **30** (4.53 g, 13.39 mmol), tributyltin hydride, and AIBN (230 mg) in benzene (20 cm^3). Chromatography using 1% triethylamine in light petroleum as the eluent gave the *title compound* **31** (5.06 g, 70 %) as a pale yellow oil, a 60 : 40 mixture of diastereoisomers (^1H NMR) (Found: M^+ - C_4H_9, 481.1945. $C_{23}H_{41}O_1SiSn$ requires *M*, 481.1948); υ_{max}/cm^{-1} 1454, 1247, 1071, 836 and 695; δ_H 0.12 (5.4 H, s, $SiCH_3$), 0.17 (3.6 H, s, $SiCH_3$), 0.90 (9 H, m), 1.42 (18 H, m), 1.75 (0.6 H, d, *J* 11, 1-H), 1.90 and 1.96 (each 0.4 H, d, *J* 11, 1-H), 2.0 (0.6 H, d, *J* 11, 1-H'), 4.28 (1 H, m, 4-H), 4.40 (0.4 H, d, *J* 12, *H*CHAr), 4.41 (0.6 H, d, *J* 12, *H*CHAr), 4.58 (0.6 H, d, *J* 12, *H*CHAr), 4.59 (0.4 H, d, *J* 12, *H*CHAr), 5.49 (0.6 H, d, *J* 8, 3-H), 5.82 (0.6 H, d, *J* 10, 2-H) and 7.37 (5 H, m, ArH); δ_C -1.5, 0.6, 5.6, 6.2, 6.9, 9.7, 10.2, 12.8, 13.8, 19.5, 20.8, 22.4, 27.5, 27.5, 27.8, 29.1, 29.3, 69.7, 70.8, 74.5, 127.2, 127.4, 127.6, 127.6, 127.7, 128.3, 135.2, 139.3, 140.3 and 143.7; *m/z* (C.I.) 397 (M^+ - 57, 72%), 341 (68), 235 (71) and 179 (78).

4-Benzyloxy-3-phenylsulfonyl-2-trimethylsilylpent-1-ene **30**

Benzyl 2,2,2-trichloroacetimidate (3.08 cm^3, 16.56 mmol) was added to a solution of the sulfone **21** (4.11 g, 13.79 mmol) in hexane (30 cm^3), a few drops of trifluoromethane sulfonic acid (*ca.* 5 µl) were added and the solution stirred overnight. Saturated aqueous ammonium chloride (10 cm^3) was added, the solution diluted with water (20 cm^3) and ether (20 cm^3), and the aqueous layer extracted with ether (3 x 30 cm^3). The organic extracts were washed with brine (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using 15 % ether in light petroleum as eluent gave the *title compound* **30** (4.61 g, 99 %) as a pale yellow oil (Found: M^+ + NH_4, 406.1879. $C_{21}H_{32}NO_3SSi$ requires *M*, 406.1872); υ_{max}/cm^{-1} 3347 br, 3063, 3030, 1714, 1447, 1305, 1249, 1145, 1082, 841 and 689; δ_H 0.07 and 0.13 (each 4.5 H, s, 3 x $SiCH_3$), 1.22 and 1.32 (each 1.5 H, d, *J* 6, 5-H_3), 3.86 (0.5 H, d, *J* 4, 3-H), 4.11 (0.5 H, d, *J* 9, 3-H), 4.35 (0.5 H, dq, *J* 6, 9, 4-H), 4.58 (2.5 H, m, 4-H and CH_2Ar), 5.91 (0.5 H, d, *J* 2, 1-H), 5.96 (0.5 H, d, *J* 1, 1-H), 6.35 (0.5 H, d, *J* 2, 1-H'), 6.48 (0.5 H, d, *J* 1, 1-H'), 7.32 (5 H, m, ArH), 7.47 (3 H, m, ArH) and 7.83 (2 H, m, ArH); δ_C -1.4, 18.0, 18.8, 71.1, 71.6, 71.7, 71.8, 74.1, 75.9, 77.3, 127.5, 127.8, 128.2, 128.2, 128.4, 128.5, 129.0, 130.0, 132.7, 133.3, 133.5, 136.5, 137.8, 138.2, 139.3, 140.8, 141.9 and 142.7; *m/z* (C.I.) 406 (M^+ + 18, 100 %).

General procedure for the Lewis acid promoted stannane - aldehyde reaction

Tin(IV) chloride (1 M in dichloromethane) was added to a solution of the alk-2-enylstannane in dichloromethane at -78 °C. After 5 min, the aldehyde was added dropwise and the mixture stirred at -78 °C for 30 min. Saturated methanolic ammonium chloride was then added and the mixture allowed to warm to room temperature. Dichloromethane and water were added and the aqueous phase extracted with dichloromethane. The organic extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue gave the coupled products as colourless oils as follows.

1-Phenyl-3-trimethylsilylbut-3-en-1-ol **26**; from stannane **25** (90 mg, 0.22 mmol), tin(IV) chloride (260 μl, 0.26 mmol), and benzaldehyde (28 μl, 0.26 mmol). Chromatography using 1% triethylamine, 10% ethyl acetate and light petroleum as eluent gave the *title compound* **26** (33 mg, 70%) as a colourless oil (Found: M^+, 220.1283. $C_{13}H_{20}OSi$ requires *M*, 220.1283); ν_{max}/cm^{-1} 3423, 3032, 1248, 838, 757 and 699; δ_H 0.16 (9 H, s, 3 x $SiCH_3$), 2.14 (1 H, s, OH), 2.47 (1 H, dd, *J* 12, 16, 2-H), 2.68 (1 H, dd, *J* 5, 16, 2-H'), 4.78 (1 H, dd, *J* 12, 5, 1-H), 5.59 (1 H, d, *J* 2, 4-H), 5.76 (1 H, s, 4-H') and 7.34 (5 H, m, ArH); δ_C -1.4, 46.9, 72.2, 125.7, 127.4, 128.2, 128.3, 144.1 and 149.1; *m/z* (C.I.) 238 (M^+ + 18, 20%) and 220 (M^+, 100).

5-Trimethylsilylhex-5-en-3-ol **27**; from stannane **25** (100 mg, 0.25 mmol), tin(IV) chloride (300 μl, 0.30 mmol), and propanal (21 μl, 0.26 mmol). Chromatography using 1% triethylamine, 11% ethyl acetate and light petroleum gave the *title compound* **27** (29 mg, 68%) as a colourless oil (Found: $M^+ + NH_4$, 190.1632. $C_9H_{24}NOSi$ requires *M*, 190.1627); ν_{max}/cm^{-1} 3351 br, 1729, 1626, 1411, 1277, 1120 and 1071; δ_H 0.06 (9 H, s, 3 x $SiCH_3$), 0.94 (3 H, t, *J* 7, 1-H_3), 1.54 (2 H, m, 2-H_2), 1.65 (1 H, d, *J* 2, OH), 2.07 (1 H, m, 4-H), 2.43 (1 H, m, 4-H'), 3.53 (1 H, m, 3-H), 5.45 (1 H, dd, *J* 4, 1, 6-H) and 5.63 (1 H, m, 6-H'); δ_C -1.2, 10.1, 29.9, 44.5, 70.9, 127.7, 149.5; *m/z* (C.I.) 190 (M^+ + 18, 68%) and 170 (41).

(1RS,5SR,3E)-5-Benzyloxy-1-phenyl-3-trimethylsilylhex-3-en-1-ol **32**; from tin(IV) chloride (4.47 cm^3, 4.47 mmol), the stannane **31** (2 g, 3.72 mmol) and benzaldehyde (467 μl, 4.47 mmol). Chromatography using 1 % triethylamine and 6 % ethyl acetate in light petroleum as eluent gave the *title compound* **32** (1.19 g, 90 %) as a colourless oil (Found: M^+ + H, 355.2086. $C_{22}H_{31}O_2Si$ requires *M*, 355.2094); υ_{max} /cm^{-1} 3434 br, 3063, 3029, 1453, 1248, 1070, 836, 751 and 698; δ_H 0.22 (9 H, s, 3 x $SiCH_3$), 1.15 (3 H, d, *J* 6, 6-H_3), 2.56 (1 H, dd, *J* 6, 13, 2-H), 2.73 (1 H, dd, *J* 10, 13, 2-H'), 2.82 (1 H, br s, OH), 4.38 (1 H, m, 5-H), 4.54 (1 H, d, *J* 15, *H*CHAr), 4.58 (1 H, d, *J* 15, *H*CHAr), 4.70 (1 H, dd, *J* 6, 10, 1-H), 5.95 (1 H, d, *J* 8, 4-H) and 7.37 (10 H, m, ArH); δ_C -0.8, 20.3, 41.1, 70.1, 70.7, 73.2, 125.8, 127.4, 127.7, 128.1, 128.5, 128.6, 138.5, 140.9, 144.8 and 145.1; *m/z* (C.I.) 355 (M^+ + 1, 2 %), 264 (2) and 229 (100).

(2SR,6SR,4E)-6-Benzyloxy-4-trimethylsilylhept-4-en-2-ol **33**; from tin(IV) chloride (368 μl, 0.37 mmol), stannane **31** (165 mg, 0.31 mmol) and ethanal (21 μl, 0.37 mmol). Chromatography using 1 % triethylamine and 11 % ethyl acetate in light petroleum as eluent gave the *title compound* **33** (65 mg, 72 %) as a colourless oil (Found: M^+ + H, 293.1934. $C_{18}H_{29}O_2Si$ requires *M*, 293.1937); υ_{max} /cm^{-1} 3443 br, 1454, 1369, 1248, 1070, 837, 752 and 696; δ_H 0.16 (9 H, s, 3 x $SiCH_3$), 1.22 (3 H, d, *J* 6, 7-H_3), 1.32 (3 H, d, *J* 6, 1-H_3), 2.26 (1 H, br s, OH), 2.29 (1 H, ddd, *J* 1, 4, 13, 3-H), 2.43 (1 H, ddd, *J* 1, 9, 13, 3-H'), 3.84 (1 H, m, 6-H), 4.48 (3 H, m, 2-H and CH_2Ar), 5.94 (1 H, d, *J* 8, 5-H) and 7.37 (5 H, m, ArH); δ_C -1.0, 20.6, 23.5, 40.2, 66.9, 70.2, 70.8, 127.6, 128.0, 128.4, 138.6, 141.1 and 144.8; *m/z* (C.I.) 293 (M^+ + 1, 3%) and 226 (100).

(3SR,7SR,5E)-7-Benzyloxy-5-trimethylsilyloct-5-en-3-ol **34**; from tin(IV) chloride (225 μl, 0.22 mmol), the stannane **31** (100 mg, 0.17 mmol) and propanal (16 μl, 0.22 mmol). Chromatography using 1 % triethylamine and 5 % ethyl acetate in light petroleum petrol as eluent gave the *title compound* **34** (36 mg, 64 %) as a colourless oil (Found: M^+ + H, 307.2095. $C_{18}H_{31}O_2Si$ requires *M*, 307.2093); υ_{max} /cm^{-1} 3458 br, 1453, 1369, 1248,

1070, 836, 751 and 696; δ_H 0.15 (9 H, s, 3 x $SiCH_3$), 0.99 (3 H, t, *J* 4.5, 1-H_3), 1.32 (3 H, d, *J* 6, 8-H_3), 1.52 (2 H, m, 2-H_2), 2.17 (1 H, br s, OH), 2.36 (2 H, m, 4-H_2), 3.54 (1 H, m, 3-H), 4.50 (3 H, m, 7-H and CH_2Ar), 5.95 (1 H, d, *J* 8, 6-H) and 7.36 (5 H, m, ArH); δ_C -0.9, 10.1, 20.6, 30.5, 38.0, 70.1, 70.8, 72.2, 127.7, 128.0, 128.5, 138.5, 141.0 and 145.0; *m/z* (C.I.) 324 (M^+ + 18, 40%), 307 (M^+ + 1, 100), 216 (68) and 199 (32).

(3RS,7SR,5E)-7-Benzyloxy-2-methyl-5-trimethylsilyloct-5-en-3-ol **35**; from tin(IV) chloride (225 µl, 0.22 mmol), the stannane **31** (100 mg, 0.17 mmol) and 2-methylpropanal (21 µl, 0.22 mmol). Chromatography using 1 % triethylamine and 6 % ethyl acetate in light petroleum as eluent gave the *title compound* **35** (47 mg, 79 %) as a colourless oil (Found: M^+ + H, 321.2250. $C_{19}H_{33}O_2Si$ requires *M*, 321.2250); υ_{max} /cm^{-1} 3490 br, 1454, 1368, 1248, 1071, 836, 751 and 697; δ_H 0.16 (9 H, s, 3 x $SiCH_3$), 0.97 (3 H, d, *J* 7, 1-H_3), 0.99 (3 H, d, *J* 7, 2-CH_3), 1.33 (3 H, d, *J* 6, 8-H_3), 1.72 (1 H, m, 2-H), 2.22 (1 H, br s, OH), 2.30 (1 H, ddd, *J* 1, 3, 13, 4-H), 2.38 (1 H, dd, *J* 10, 13, 4-H'), 3.38 (1 H, ddd, *J* 3, 6, 10, 3-H), 4.51 (3 H, m, 7-H and CH_2Ar), 5.97 (1 H, d, *J* 8, 6-H) and 7.38 (5 H, m, ArH); δ_C -0.9, 17.9, 18.5, 20.6, 34.0, 34.7, 70.2, 70.9, 75.1, 127.6, 128.0, 128.5, 138.5, 141.6 and 144.9; *m/z* (C.I.) 338 (M^+ + 18, 40%), 321 (M^+ + 1, 100), 230 (59) and 213 (40).

(E)-5-Benzyloxy-1-phenyl-3-trimethylsilylhex-3-en-1-one **36**

Dimethyl sulfoxide (48 µl, 0.34 mmol) in dichloromethane (500 µl) was added to oxalyl chloride (29 µl, 0.34 mmol) in dichloromethane (500 µl) and the solution stirred at -78 °C for 5 min. The alcohol **32** (100 mg, 0.31 mmol) in dichloromethane (500 µl) was added and the mixture stirred at -78 °C for 20 min. Triethylamine (216 µl, 1.55 mmol) was added and the mixture stirred at -78 °C for 10 min, then allowed to warm to 0 °C. Water was added and the mixture allowed to warm to room temperature. Dichloromethane was added and the organic layer washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using 5 % ethyl acetate in light petroleum as eluent gave the *title compound* **36** (75 mg, 69 %) as a colourless oil (Found: M^+ + H, 353.1934. $C_{22}H_{29}O_2Si$ requires *M*, 353.1938); υ_{max} /cm^{-1} 1688, 1597, 1580, 1449, 1324, 1248, 1207, 1073, 832, 753 and 691; δ_H 0.13 (9 H, s, 3 x $SiCH_3$), 1.31 (3 H, d, *J* 6, 6-H_3), 3.84 (2 H, m, 2-H_2), 4.21 (1 H, dq, *J* 6, 8, 5-H), 4.41 (1 H, d, *J* 14, *H*CHAr), 4.60 (1 H, d, *J* 14, *H*CHAr), 6.02 (1 H, d, *J* 8, 4-H), 7.33 (5 H, m, ArH), 7.50 (2 H, m, ArH), 7.61 (1 H, m, ArH) and 7.93 (2 H, m, ArH); δ_C -1.5, 6.3, 21.0, 39.1, 70.1, 70.9, 127.4, 127.8, 128.1, 128.6, 133.1, 136.9, 137.2, 139.0, 145.0 and 197.5; *m/z* (C.I.) 353 (M^+ + 1, 3 %) and 245 (100).

(1SR,5SR,3E)-5-Benzyloxy-1-phenyl-3-trimethylsilylhex-3-en-1-ol **37**

Sodium borohydride (10 mg, 0.28 mmol) was added in one portion to the ketone **36** (64 mg, 0.18 mmol) in ethanol (1 cm^3) at 0 °C and the resulting mixture allowed to warm to room temperature and stirred for 4 h. Saturated aqueous ammonium chloride (1 cm^3) was added and the organic layer diluted with ether (10 cm^3) then washed with brine (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using 10% ether in light petroleum as eluent gave the alcohol **32** (32 mg, 49%) followed by the *title compound* **37** (32 mg, 49 %), a colourless oil (Found: M^+ + H, 355.2084. $C_{22}H_{31}O_2Si$ requires *M*, 355.2094); υ_{max} /cm^{-1} 3432 br, 1453, 1247, 1071, 836, 751 and 698; δ_H 0.20 (9 H, s, 3 x $SiCH_3$), 1.36 (3 H, d, *J* 6, 6-H_3), 1.99 (1 H, s, OH), 2.51 (1 H, dd, *J* 4, 13, 2-H), 2.72 (1 H, dd, *J* 10, 13, 2-H'), 4.26 (1 H, d, *J* 12, *H*CHAr), 4.43 (1 H, d, *J* 12, *H*CHAr), 4.44 (1 H, m, 5-H), 4.68 (1 H, dd, *J* 4, 10, 1-H), 5.96 (1 H, d, *J* 8.5, 4-H) and 7.34 (10 H, m, ArH); δ_C -0.9, 21.2, 40.7, 70.1, 70.9, 73.2, 125.8, 127.5, 127.6, 127.7, 128.5, 128.5, 138.8, 140.2, 144.4 and 145.8; *m/z* (C.I.) 355 (M^+ + 1, 1 %), 264 (36) and 229 (100).

5-Benzyloxy-1-phenyl-3-trimethylsilylhexane-1,3,4-triol **39**

Pyridine (1 cm^3) and osmium tetroxide (173 mg, 0.68 mmol) were added to a solution of the vinylsilane **32** (220 mg, 0.62 mmol) in benzene (2 cm^3) at room temperature. The mixture was stirred at room temperature for 18 h then concentrated under reduced pressure. Tetrahydrofuran (1 cm^3) was added and the mixture cooled to -78 °C. A solution of lithium aluminium hydride (1 M in tetrahydrofuran; 3.1 cm^3, 3.10 mmol) was added dropwise to the solution which, after warming, was stirred for 1 h at room temperature. The mixture was cooled to -78 °C and ethyl acetate (1 cm^3) and water were added dropwise. The mixture was warmed to room temperature and filtered through celite. The filter cake was washed several times with ethyl acetate, the aqueous layer was extracted with ethyl acetate (5 x 5 cm^3) and the organic extracts were washed with brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using 50 % ethyl acetate in light petroleum as eluent gave the *title compound* **39** (194 mg, 79 %) as a colourless oil, an 85 : 15 mixture of diastereoisomers (Found: M^+ + H, 389.2154. $C_{22}H_{33}O_4Si$ requires *M*, 389.2148); υ_{max} /cm^{-1} 3413 br, 3062, 3030, 1453, 1248, 1069, 841, 749 and 699; δ_H (major diastereoisomer) 0.15 (9 H, s, 3 x $SiCH_3$), 1.49 (3 H, d, *J* 6, 6-H_3), 2.01 (2 H, m, 2-H_2), 2.56 (1 H, b s, OH), 3.98 (1 H, m, 5-H), 4.08 (2 H, m, 4-H and OH), 4.46 (1 H, d, *J* 11, *H*CHAr), 4.62 (1 H, b s, OH), 4.74 (1 H, d, *J* 11, *H*CHAr), 5.21 (1 H, dd, *J* 4, 10, 1-H) and 7.37 (10 H, m, ArH); δ_H (minor diastereoisomer) 4.57 and 4.72 (each 1 H, d, *J* 11, HC*H*Ar); δ_C -1.9, 16.6, 43.4, 70.0, 71.9, 73.7, 125.6, 127.2, 127.8, 127.9, 128.0, 128.4, 128.5, 128.7, 137.4 and 145.3; *m/z* (C.I.) 389 (M^+ + 1, 12%), 284 (47), 263 (48) and 190 (62).

(2SR,6SR,3E)-2-Benzyloxy-4-trimethylsilyl-6-(2-trimethylsilylethoxymethyloxy)oct-3-ene **40**

Diisopropylethylamine (9.93 g, 79.83 mmol) and (2-trimethylsilylethoxy)methyl chloride (5.12 g, 30.73 mmol) were added to a solution of the alcohol **34** (2 g, 15.37 mmol) in dichloromethane (40 cm^3) at 0 °C and the solution allowed to warm to room temperature and stirred for 18 h. Saturated aqueous ammonium chloride (10 cm^3) was added and the organic layer washed with dichloromethane (40 cm^3). The organic extracts were washed with water (40 cm^3), brine (40 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using 2 % ether in light petroleum as eluent gave the *title compound* **40** (3.56 g, 93 %) as a colourless oil (Found: M^+ + NH_4, 454.3180. $C_{24}H_{48}NO_3Si_2$ requires *M*, 454.3173); υ_{max} /cm^{-1} 1455, 1369, 1249, 1049, 1032, 923, 855, 836, 752 and 694; δ_H -0.02 (9 H, s, 3 x $SiCH_3$), 0.09 (9 H, s, 3 x $SiCH_3$), 0.87 (5 H, m, CH_2Si and 8-H_3), 1.23 (3 H, d, *J* 6, 1-H_3), 1.33 (1 H, m, 7-H), 1.43 (1 H, m, 7-H'), 2.28 (1 H, dd, *J* 7, 14, 5-H), 2.37 (1 H, ddd, *J* 1, 7, 14, 5-H'), 3.55 (3 H, m, C*H*$_2$CH_2Si and 6-H), 4.32 (1 H, d, *J* 12 *H*CHAr), 4.38 (1 H, dq, *J* 9, 6, 2-H), 4.47 (1 H, d, *J* 12 *H*CHAr), 4.62 (1 H, d, *J* 7, O*H*CHO), 4.65 (1 H, d, *J* 7, O*H*CHO), 5.73 (1 H, d, *J* 9, 3-H) and 7.26 (5 H, m, ArH); δ_C -0.3, 0.3, 10.8, 19.2, 22.1, 28.2, 36.4, 66.2, 71.1, 71.8, 79.3, 94.8, 128.5, 128.8, 129.4, 140.1, 141.8 and 145.2; *m/z* (C.I.) 454 (M^+ + 18, 31 %).

2-Benzyloxy-6-(2-trimethylsilylethoxymethoxy)octan-4-one **41**

Activated 4 Å sieves (100 mg) were added to a solution of the vinyl silane **40** (68 mg, 0.16 mmol) in propan-2-ol (1 cm^3) under an atmosphere of oxygen. Bis(2-ethoxycarbonyl-3-oxobutanalato)cobalt(II) (6 mg, 0.02 mmol) was added and the mixture heated to 75 °C and stirred for 4 h. The mixture was filtered and concentrated under reduced pressure. Chromatography of the residue using 8 % ethyl acetate in light petroleum as eluent gave the *title compound* **41** (11 mg, 23 %) as a colourless oil (Found: M^+ + NH_4, 398.2725. $C_{21}H_{40}NO_4Si$ requires *M*, 398.2726); υ_{max} /cm^{-1} 1717, 1458, 1375, 1249, 1098, 1055, 1029, 859, 836, 735 and 697; δ_H 0.04 (9 H, s, 3

x $SiCH_3$), 0.86 (5 H, m, 8-H_3 and CH_2Si), 1.19 (3 H, d, *J* 6, 1-H_3), 1.51 (2 H, m, 7-H_2), 2.43 and 2.46 (each 1 H, dd, *J*, 16, 5), 2.69 and 2.76 (each 1 H, dd, *J* 7, 16), 3.55 (2 H, m, CH_2CH_2Si), 3.99 (2 H, m, 2-H and 6-H), 4.41 (1 H, d, *J* 11, *H*CHAr), 4.52 (1 H, d, *J* 11, *H*CHAr), 4.62 (1 H, *J* 7, OCH_2O), 4.67 (1 H, d, *J* 7, OCH_2O) and 7.26 (5 H, m, ArH); δ_C -0.3, 10.5, 19.2, 21.0, 28.7, 49.8, 52.1, 66.3, 72.1, 72.7, 76.0, 95.3, 128.6, 128.8, 129.4, 139.7 and 208.8; *m/z* (C.I.) 398 (M^+ + 18, 4 %), 305 (17), 263 (100), 249 (51), 233 (94) and 215 (22).

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