Pergamon

Tetrahedron 55 (1999) 3723–3734

TETRAHEDRON

# 1,9-Stereocontrol from 1,7-Induction using an Allylstannane followed by an Ireland-Claisen Rearrangement

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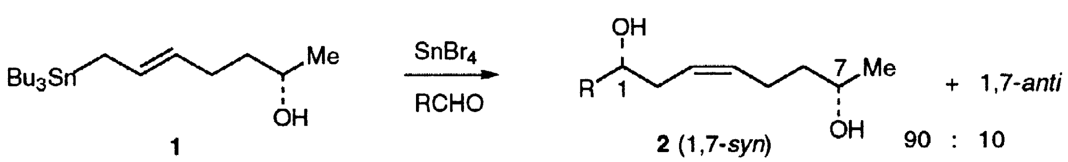
Received 24 September 1998; accepted 12 October 1998

***Abstract:*** The 6-hydroxynona-2,7-dienylstananne **10** reacts with aldehydes after transmetallation with tin(IV) bromide with *syn*-selective 1,7-induction (1,7-*syn* : 1,7-*anti* = *ca.* 90 : 10). Ireland-Claisen rearrangements of the acetates **28a,b** prepared from the *syn*-benzaldehyde product **14**, gave methyl (3*R*,11*R*)- 3-methyl-11-(arylmethoxy)-11-phenylundeca-4,8-dienoates **30a,b** stereoselectively.


Allyltin trihalides generated from alk-2-enylstannanes which have alkoxy-, hydroxy-, or amino-substituents at either the 4-, 5-, or 6-position react with aldehydes and imines with useful levels of 1,5-, 1,6- and 1,7-asymmetric induction.[1] For example, the 1,7-*syn*-products **2** were obtained using the 6-hydroxyhept-2-enoate **1** and tin(IV) bromide with both aliphatic and aromatic aldehydes (1,7-*syn* : 1,7-*anti* = *ca.* 90 : 10).[2]




Although this chemistry works well for 1,7-stereochemical control, initial studies into 1,8-asymmetric induction using 7-hydroxy-7-phenylhept-2-enylstannanes gave mixtures of *syn*- and *anti*-1,8-diols.[3] We now report investigations into the control of 1,9-stereogenic centres by combining the allylstannane - aldehyde reaction with an Ireland-Claisen rearrangement[4] in order to migrate one of the stereogenic centres along the chain.

## RESULTS AND DISCUSSION

The (6*R*)-6-hydroxynona-2,7-dienylstannane (6*R*)-**10** was prepared, as a mixture of (2*E*)- and (2*Z*)-isomers, ratio *ca.* 80 : 20, as outlined in Scheme 1. The key step in this synthesis is the regioselective, base-induced alkylation of the allylic sulfide **13**[5] using the iodide **7**. The stannanes **10** were found to have an e.e. of 60% by comparison of the $^{19}$F NMR spectra of their (*R*)- and (*S*)-Mosher's derivatives **11** and **12**. The racemic stannane (±)-**10** was similarly prepared from the racemic ethyl ester[6] corresponding to the methyl ester **4**.

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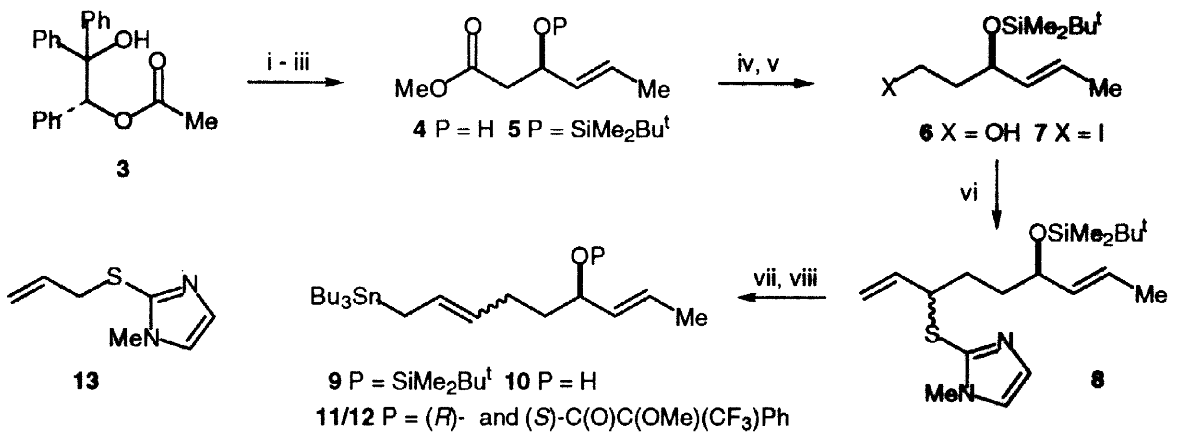
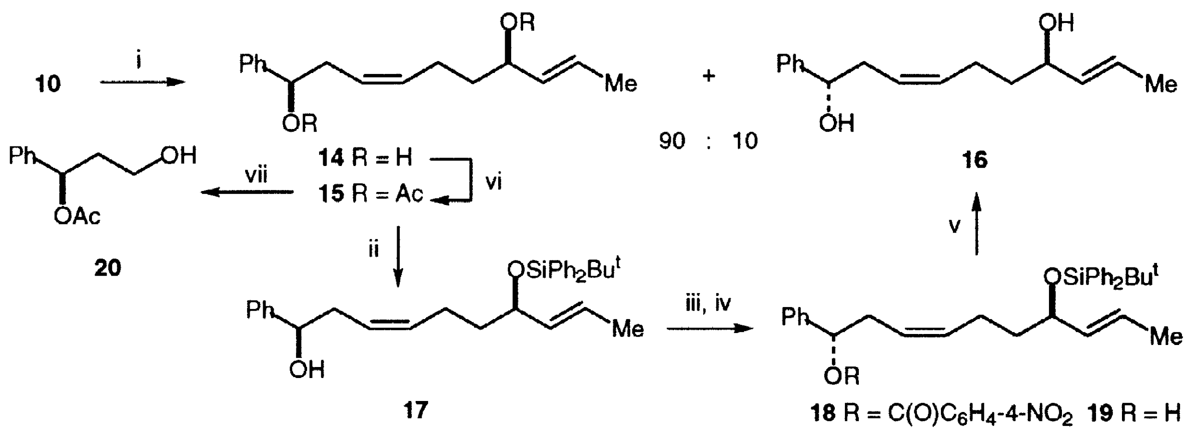
*PII:* S0040-4020(98)01179-X



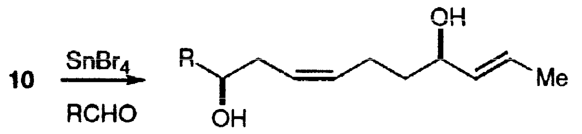

**Scheme 1** ***Reagents and conditions:*** i, $MgBr_2$, $LiNPr^i_2$, crotonaldehyde; ii, NaOMe, MeOH; iii, $Bu^tMe_2SiCl$, imidazole (85% from **3**); iv, DIBAL-H (77%); v, $I_2$, $Ph_3P$, imidazole, THF (96%); vi, **13**-Li, THF - HMPA, -78 °C (90%); vii, $Bu_3SnH$, AIBN, benzene, heat under reflux (70%; *E* : *Z* = 80 : 20); viii, TBAF, THF (55%: *E* : *Z* = 80 : 20).

Reactions between the stannane **10** and benzaldehyde were carried out by adding a solution of tin(IV) bromide in tetrahydrofuran to the stannane in tetrahydrofuran at -78 °C and stirring the mixture for 7.5 minutes before adding the aldehyde.[2] This procedure gave the 1,7-*syn*- and 1,7-*anti*-diols **14** and **16**, *syn* : *anti* = 90 : 10 (64%), see Scheme 2, which could be distinguished by $^1H$ NMR but not separated. Protection with *tert*-butyldiphenylsilyl chloride, which was more regioselective than with *tert*-butyldimethylsilyl chloride, gave the 7-silyloxydecadien-1-ol **17** (61%). Inversion using a Mitsunobu reaction[7] followed by saponification and desilylation then gave the 1,7-*anti*-diol **16** which corresponded to the minor product from the allylstannane - benzaldehyde reaction ($^1H$ NMR). Ozonolysis of the diacetate **15** (containing *ca.* 10% of the diacetate from **16**) gave the dextrorotatory enantiomer of 3-acetoxy-3-phenylpropanol **20** which is known to correspond to the (*R*)-enantiomer shown.[2,8] The optical purity of the 3-acetoxy-3-phenylpropanol corresponded to an e.e. of 56% which reflects the 60% e.e. of the allylstannane **10** and the 90 : 10 ratio of the *syn*- and *anti*-products **14** and **16**.



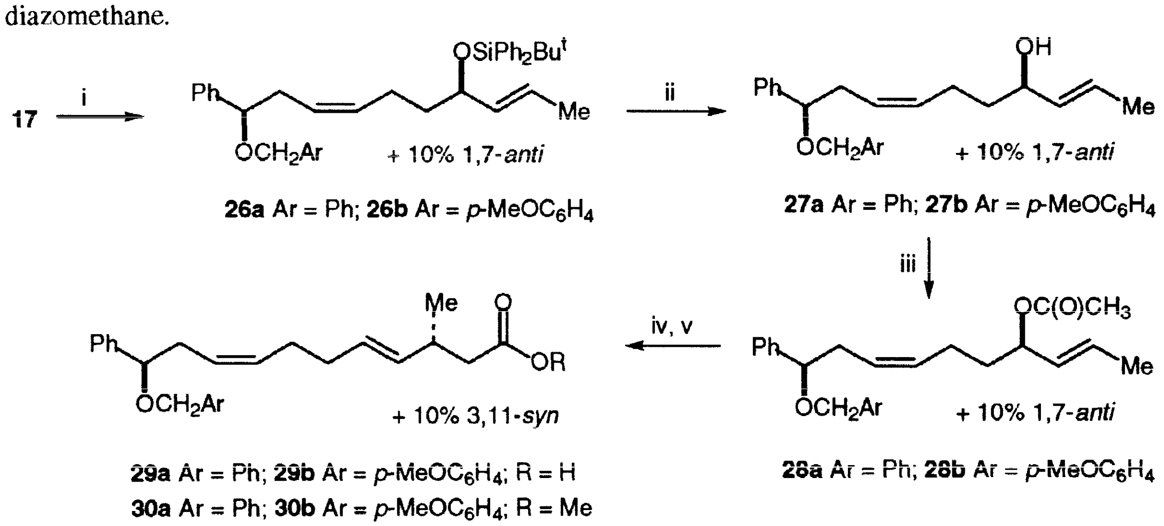

**Scheme 2** ***Reagents and conditions:*** i, $SnBr_4$, -78 °C, 7.5 min, then PhCHO, -78 °C, 1 h (64%; **14** : **16** = 90 : 10); ii, $Bu^tPh_2SiCl$, imidazole (61% from **14**); iii, $EtO_2CN{=}NCO_2Et$, $Ph_3P$, $4\text{-}NO_2C_6H_4CO_2H$ (76%); iv, NaOH, MeOH (83%); v, TBAF, THF (90%); vi, $Ac_2O$, $Et_3N$ (80%); vii, $O_3$, $Me_2S$, $NaBH_4$ (62%).

Other aldehydes reacted with the allylstannane **10** to give predominantly the 1,7-*syn*-products **21** - **25** together with their *anti*-diastereoisomers, 1,7-*syn* : 1,7-*anti* = 90(±5) : 10(±5). The 1,7-*syn*-configurations were assigned to the major products from these reactions by analogy with the *syn*-selective reaction of the stannane **10** with benzaldehyde and results obtained using stannane **1**.[2]




**21** R = $CH_3$ (59%) **22** R = $CH{=}CH_2$ (67%)
**23** R = $CH(CH_3)_2$ (62%) **24** R = 2-furyl (46%)
**25** R = 1,3-dithian-2-yl (51%)

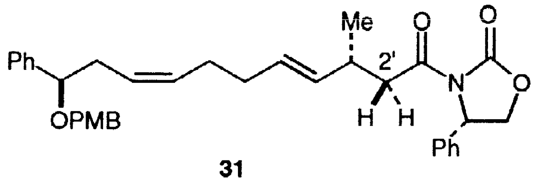
To prepare products with 1,9-stereogenic centres, the 7-silyloxydeca-3,8-dien-1-ol **17** (containing 10% of its *anti*-epimer) was converted into its benzyl and 4-methoxybenzyl ethers **26a,b** which were taken through to the acetates **28a,b** by desilylation and acetylation. Rearrangement of the acetates was effected by treatment with lithium diisopropylamide and *tert*-butyldimethylsilyl chloride in tetrahydrofuran - HMPA and gave the 3,11-*anti*-3-methyl-11-(arylmethoxy)undeca-4,8-dienoic acids **29a,b** which were converted into their methyl esters **30a,b** using diazomethane.



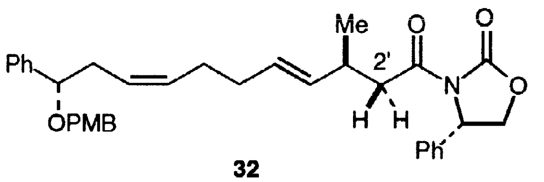

**Scheme 3** ***Reagents and conditions:*** i, $PhCH_2Br$, NaH (70%) or $p$-$MeOC_6H_4CH_2Cl$, NaH (68%); ii, TBAF (**27a**, 66%; **27b**, 85%); iii, $Ac_2O$, $Et_3N$ (**28a**, 96%; **28b**, 98%); iv, $LiNPr^i_2$, $Bu^tMe_2SiCl$ (**29a**, 68%; **29b**, 60%); v, $CH_2N_2$ (**30a**, 58%; **30b**, 88%).

Stereochemical assignments were made to the esters **30a,b** on the basis of the well precedented, 6-membered, chair-like, transition states usually invoked in Ireland-Claisen rearrangements.[4,9] The 90 : 10 mixture of the 1,7-*syn*- and *anti*-diols **14** and **16** obtained from the allylstannane - aldehyde reaction should therefore have given rise to 90 : 10 mixtures of the 3,11-*anti*-3-methyl-11-(arylmethoxy)undeca-4,8-dienoic acids **29a,b** and their 3,11-*syn*-diastereoisomers, although these could not be distinguished spectroscopically.

To provide evidence of the 1,9-stereoselectivity and configuration at C(3'), (*R*)-4-phenyl-2-oxazolidinone[10] was acylated using the racemic undecadienoic acid ±**29b**. This gave a 1:1 mixture of the diastereoisomeric *N*-acyloxazolidinones **31** and **32** which could be distinguished by $^1H$ NMR; for example the diasterotopic 2'-$CH_2$'s were clearly seen as two pairs of double-doublets.[11] When the undecadienoic acid **29b** prepared by rearrangement of the acetate **28b** of 60% e.e. was acylated by the (*R*)-4-phenyl-2-oxazolidinone, the $^1H$ NMR spectrum of the product showed the two pairs of double-doublets corresponding to the *N*-acyloxazolidinones **31** and **32** in a ratio of 74 : 26 with the (3'*R*)-diastereoisomer **31** predominating.[11] This correlates with the 56% e.e. observed for the ozonolysis product **20** and is entirely consistent with the rearrangement product **29b** consisting of a 90 : 10 mixture of the 3,11-*anti*- and *syn*-diastereoisomers each of 60% e.e. and the splitting patern observed[11] is consistent with the (*R*)-configuration assigned to C(3').§



**31**



**32**

This strategy of combining remote stereochemical control induced by an allylstannane - aldehyde reaction with 1,3-migration of chirality using an Ireland-Claisen rearrangement would appear to be useful for controlling the relative configurations of really remote chiral centres. This approach is not convergent, but enantiomerically enriched products with remote chiral centres can be accessed using just a single chiral starting material or reagent and *racemic* compounds with remote chiral centres can be prepared diastereoselectively.

## 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 (EI) or chemical ionisation (CI) modes. IR spectra were recorded on an ATI Mattson Genesis FTIR spectrometer as evaporated films on sodium chloride plates. 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.

*Methyl (3*R*,4*E*)-3-(*tert*-butyldimethylsilyloxy)hex-4-enoate* **5**

Lithium diisopropylamide, from butyllithium (20.2 cm$^3$; 1.6 M in hexanes; 33 mmol) and diisopropylamine (4.5 cm$^3$, 33 mmol), was added to (*S*)-2-acetyl-1,1,2-triphenylethanol **3**[12] (5 g, 15 mmol) in THF (15 cm$^3$) at –78 °C. The mixture was allowed to warm to room temperature then added to magnesium bromide, from 1,2-dibromoethane (3 cm$^3$, 34.5 mmol) and magnesium turnings (1.1 g, 45 mmol), in THF (60 cm$^3$) at –78 °C. After 1 h, crotonaldehyde (1.5 cm$^3$, 18 mmol) was added and the solution stirred for 3 h at –78 °C. Satd. aq. $NH_4Cl$ was added at –78 °C and the mixture allowed to warm to room temperature. The aqueous phase was extracted with ether and the organic extracts washed with brine, dried, and concentrated under reduced pressure to give a white solid (7.52 g). This was dissolved in methanol (140 cm$^3$) and sodium methoxide (2 g, 37 mmol) was added. After 2 h, satd. aq. $NH_4Cl$ was added and the aqueous phase was extracted with ether. The organic extracts were washed with brine, dried and concentrated under reduced pressure. The residue was dissolved in ethyl acetate (5 cm$^3$) and light petroleum (500 cm$^3$) was added slowly. After 16 h, the liquid was decanted and concentrated under reduced pressure to give the methyl ester **4** (3.53 g) as an orange solid. *tert*-Butyldimethylsilyl chloride (3.7 g, 24.4 mmol) and imidazole (2.5 g, 36.6 mmol) were added to the ester **4** (3.53 g, 24.4 mmol) in

§In this analysis, the chiral oxazolidinone is being used to distinguish between undecadienoic acids with opposite configurations at C(3) irrespective of the configurations at C(11).

dichloromethane (30 $cm^3$) at 0 °C. After 16 h, satd. aq. $NH_4Cl$ was added and the aqueous phase was extracted with dichloromethane. The organic extracts were washed with brine, dried and concentrated under reduced pressure. Chromatography of the residue using light petroleum – ether (20 : 1) gave the *title compound* **5** (3.3 g, 85%), $[\alpha]_D$ −12.5 (*c* 1.45 in $CHCl_3$); $\delta_H$ 0.04 and 0.06 (each 3 H, s, $SiCH_3$), 0.88 [9 H, s, $SiC(CH_3)_3$], 1.69 (3 H, d, *J* 6.5, 6-$H_3$), 2.43 (1 H, dd, *J* 5, 14, 2-H), 2.54 (1 H, dd, *J* 8.5, 14, 2-H'), 3.68 (3 H, s, $CH_3O$), 4.54 (1 H, q, *J* 7, 3-H), 5.46 (1 H, dd, *J* 7, 16, 4-H) and 5.65 (1 H, dq, *J* 16, 6.5, 5-H); $\delta_C$ −4.8, −4.2, 17.5, 18.0, 25.7, 43.9, 51.4, 70.7, 126.1, 133.3 and 171.7; $\upsilon_{max}/cm^{-1}$ 1743, 1437, 1252, 1169, 1078, 835 and 777; *m/z* (CI) 259.1735 ($MH^+$, 40%; $C_{13}H_{27}O_3Si$ requires *M*, 259.1729), 201 (30), 144 (70) and 127 (100).

*(3R,4E)-3-(tert-Butyldimethylsilyloxy)hex-4-en-1-ol* **6**

DIBAL-H (11.7 $cm^3$; 1 M in hexanes; 11.7 mmol) was added dropwise to the ester **5** (1 g, 3.9 mmol) in dichloromethane (40 $cm^3$) at −78 °C. After 1 h, the mixture was warmed to 0 °C and stirred for 2 h. The reaction mixture was then cooled to −78 °C, methanol was added and the mixture warmed to 0 °C before satd. aq. $NH_4Cl$ was added. After warming to room temperature, the mixture was stirred for 10 min, then filtered through Celite. The aqueous layer was extracted with dichloromethane/methanol (99:1) and the organic extracts were washed with brine, dried and concentrated. Chromatography using light petroleum – ether (5 : 1) gave the *title compound* **6** (0.6 g, 77%), $[\alpha]_D$ −19.3 (*c* 1.63 in $CHCl_3$); $\delta_H$ 0.07 and 0.10 (each 3 H, s, $SiCH_3$), 0.92 [9 H, s, $SiC(CH_3)_3$], 1.71 (3 H, d, *J* 6.5, 6-$H_3$), 1.83 (2 H, m, 2-$H_2$), 2.67 (1 H, br s, OH), 3.79 and 3.95 (each 1 H, m, 1-H), 4.38 (1 H, q, *J* 6, 3-H), 5.46 (1 H, dd, *J* 6, 15.5, 4-H) and 5.64 (1 H, dq, *J* 15.5, 6.5, 5-H); $\delta_C$ -4.9, -4.2, 17.6, 18.1, 25.9, 39.6, 60.4, 73.4, 125.7 and 133.7; $\upsilon_{max}/cm^{-1}$ 3362, 1472, 1360, 1255, 1080, 966, 835 and 775; *m/z* (CI) 231.1776 ($MH^+$, 10%; $C_{12}H_{27}O_2Si$ requires *M*, 231.1780), 183 (20) and 145 (20).

*(3R,4E)-3-(tert-Butyldimethylsilyloxy)-1-iodohex-4-ene* **7**

Iodine (5.5 g, 21.5 mmol), triphenylphosphine (5.6 g, 21.5 mmol) and imidazole (2.5 g, 36 mmol) were added to the alcohol **6** (3.3 g, 14.3 mmol) in THF (120 $cm^3$) at 0 °C. After 1 h at room temperature, satd. aq. $NaHCO_3$ (40 $cm^3$) was added and the solution stirred for 10 mins. Excess satd. aq. sodium thiosulphate was then added until the orange solution became colourless. The aqueous layer was extracted with ether and the organic extracts were washed with brine, dried and concentrated under reduced pressure. Chromatography of the resultant solid which was pre-absorbed on silica using light petroleum – ether (20 : 1) gave the *title compound* **7** (4.84 g, 96%), $[\alpha]_D$ −4.6 (*c* 1.22 in $CHCl_3$); $\delta_H$ 0.07 and 0.12 (each 3 H, s, $SiCH_3$), 0.92 [9 H, s, $SiC(CH_3)_3$], 1.71 (3 H, d, *J* 7, 6-$H_3$), 1.98 (2 H, m, 2-$H_2$), 3.22 (2 H, m 1-$H_2$), 4.16 (1 H, q, *J* 7, 3-H), 5.43 (1 H, dd, *J* 7, 15.5, 4-H) and 5.66 (1 H, dq, *J* 15.5, 7, 5-H); $\delta_C$ −4.6, −4.0, 3.1, 17.6, 18.2, 25.9, 42.0, 73.5, 126.3 and 133.5; $\upsilon_{max}/cm^{-1}$ 1471, 1254, 1085, 1038, 966, 940, 836 and 776; *m/z* (CI) 341.0803 ($MH^+$, 10%; $C_{12}H_{26}IOSi$ requires *M*, 341.0798), 300 (50), 283 (25), 255 (35), 226 (100) and 132 (80).

*(3RS,6R,7E)-6-(tert-Butyldimethylsilyloxy)-3-(1-methyl-2-thioimidazoyl)nona-1,7-diene* **8**

Butyllithium (10.7 $cm^3$, 1.6 M in hexanes, 17 mmol) was added to the sulphide **13** (2.2 g, 14.2 mmol) in THF (100 $cm^3$) at −78 °C. After 0.5 h, HMPA (5.2 $cm^3$, 42.6 mmol) was added and the stirring continued at −78 °C for a further 0.5 h. The iodide **7** (4.84 g, 14.2 mmol) was added and the mixture kept at −78 °C for 2.5 h. Satd. aq. $NH_4Cl$ was added and the mixture allowed to warm to room temperature. The aqueous phase was extracted with ether and the organic extracts were washed with brine, dried and concentrated under reduced pressure.

Chromatography of the residue using light petroleum – ethyl acetate (2 : 1) gave the *title compound* **8** (4.5 g, 90%) as a mixture of epimers at C(3); $\delta_H$ 0.03 and 0.04 (each 3 H, s, $SiCH_3$), 0.89 [9 H, s, $SiC(CH_3)_3$], 1.59 (4 H, m, 4-$H_2$, 5-$H_2$), 1.68 (3 H, d, *J* 6, 9-$H_3$), 3.69 (1 H, s, $NCH_3$), 3.81 (1 H, q, *J* 7.5, 3-H), 4.05 (1 H, q, *J* 6, 6-H), 4.89 (2 H, m, 1-$H_2$), 5.39 (1 H, dd, *J* 6, 15.5, 7-H), 5.55 (1 H, m, 8-H), 5.68 (1 H, m, 2-H) and 6.95 and 7.11 (each 1 H, br s, imid-H); $\delta_C$ –4.7, –4.2, 17.6, 18.2, 25.9, 30.0, 33.8, 35.8, 53.7, 73.4, 116.1, 122.5, 125.0, 129.7, 134.3, 138.6 and 140.0; $\upsilon_{max}/cm^{-1}$ 1455, 1253, 1079, 967, 836 and 775; *m/z* (EI) 367.2237 ($M^+$, 5%; $C_{19}H_{35}N_2OSSi$ requires *M*, 367.2239), 309 (20), 189 (30), 114 (60) and 75 (100).

*(6R,2EZ,7E)-6-tert-Butyldimethylsilyloxynona-2,7-dienyl(tributyl)stannane* **9**

Tributyltin hydride (0.2 $cm^3$, 0.75 mmol) was added to a degassed solution of the thioether **8** (0.2 g, 0.55 mmol) and AIBN (10 mg) in benzene (7 $cm^3$) and the mixture heated under reflux for 1.5 h then concentrated under reduced pressure. Chromatography of the residue using light petroleum – triethylamine (99 : 1) gave the *title compound* **9** (0.21 g, 70%) (2*E* : 2*Z* = 4 : 1); $\delta_H$ 0.05 and 0.06 (each 3 H, s, $SiCH_3$), 0.91 [24 H, m, $SiC(CH_3)_3$, 3 × $CH_3(CH_2)_2CH_2Sn$], 1.3 - 1.8 [19 H, m, 3 × $CH_3(CH_2)_2CH_2Sn$, 1-$H_2$, 5-$H_2$, 9-$H_3$], 2.06 (2 H, m, 4-$H_2$), 4.07 (1 H, q, *J* 6.5, 6-H), 5.19 (0.4 H, m, 2-$H^{cis}$, 3-$H^{cis}$) and 5.3 - 5.7 (3.6 H, m, 2-$H^{trans}$, 3-$H^{trans}$, 7-H, 8-H); $\delta_C$ –4.7, –4.1, 9.1, 13.8, 14.1, 17.6, 18.2, 26.0, 27.3, 28.6, 29.0, 38.5, 73.3, 124.8, 125.4, 128.3 and 134.9; $\upsilon_{max}/cm^{-1}$ 1463, 1253, 1080, 965, 836 and 775; *m/z* (EI) 487.2419 ($M^+$– $C_4H_9$, 90%; $C_{23}H_{47}OSi^{120}Sn$ requires *M*, 487.2418), 543 ($M^+$, 1), 365 (50) and 291 (100).

*(6R,2EZ,7E)-6-Hydroxynona-2,7-dienyl(tributyl)stannane* **10**

TBAF (0.7 $cm^3$; 1 M in THF; 0.7 mmol) was added to the silyl ether **9** (0.2 g, 0.37 mmol) in THF (5 $cm^3$). After 15 h, satd. aq. $NH_4Cl$ was added and the aqueous phase extracted with ether. The organic extracts were washed with brine, dried and concentrated under reduced pressure. Chromatography of the residue using light petroleum – ether – triethylamine (74 : 25 : 1) gave the *title compound* **10** (0.8 g, 55%) (2*E* : 2*Z* = 4 : 1); $\delta_H$ 0.85 [15 H, m, 3 x $CH_3(CH_2)_2CH_2Sn$], 1.2 - 1.8 [19 H, m, 3 × $CH_3(CH_2)_2CH_2Sn$), 1-$H_2$, 5-$H_2$, 9-$H_3$], 2.06 (2 H, q, *J* 7.5, 4-$H_2$), 4.08 (1 H, m, 6-H), 5.19 (0.4 H, m, 2-$H^{cis}$, 3-$H^{cis}$) and 5.4 - 5.7 (3.6 H, m, 2-$H^{trans}$, 3-$H^{trans}$, 7-H, 8-H); $\delta_C$ 7.1, 13.8, 14.1, 17.3, 27.3, 28.8, 29.3, 37.2, 72.7, 124.9, 126.7, 129.8 and 134.2; $\upsilon_{max}/cm^{-1}$ 3347, 1455, 1071, 1051 and 963; *m/z* (CI) 373.1560 ($M^+$– $C_4H_9$, 10%; $C_{17}H_{33}O^{120}Sn$ requires *M*, 373.1553), 429 (10) and 308 (100).

*General procedure for the allylstannane - aldehyde reactions:*

*(1R,7R,3Z,8E)-1-Phenyldeca-3,8-diene-1,7-diol* **14** Tin(IV) bromide (6 $cm^3$; 1 M in dichloromethane; 6 mmol) was added to the stannane **10** (2.15 g, 5 mmol) in dichloromethane (50 $cm^3$) at –78 °C. After 7.5 min, benzaldehyde (0.76 $cm^3$; 1 M in dichloromethane; 0.76 mmol) was added and the mixture was stirred at –78 °C for 1 h. Satd. aq. $NH_4Cl$ was added and the mixture allowed to warm to room temperature. Dichloromethane and water were added and the organic layer washed with brine, dried and concentrated under reduced pressure. Chromatography of the residue using light petroleum - ether – triethylamine (49 : 50 : 1) gave the *title compound* **14** (0.78 g, 64%) containing 10% of its 1,7-*anti*-isomer **16**, $[\alpha]_D$ –24.6 (*c* 1.34 in $CHCl_3$); $\delta_H$ (**14**) 1.42 and 1.53 (each 1 H, m, 6-H), 1.66 (3 H, d, *J* 7.5, 10-$H_3$), 2.10 (2 H, m, 5-$H_2$), 2.50 (2 H, m, 2-$H_2$), 4.00 (1 H, q, *J* 6.5, 7-H), 4.68 (1 H, t, *J* 6.5, 1-H), 4.8 (2 H, br s, 2 x OH), 5.1 - 5.5 (4 H, m, 3-H, 4-H, 8-H, 9-H) and 7.37 (5 H, m, ArH); $\delta_C$ 17.7, 23.6, 36.6, 37.2, 72.4, 73.8, 125.2, 125.9, 127.4, 128.3, 132.6, 132.8, 134.1

and 144.1; $\upsilon_{max}$/cm$^{-1}$ 3353, 3011, 1451, 1051, 966, 759 and 700; *m/z* (CI) 264.1970 ($M^+$+ $NH_4$, $C_{16}H_{26}NO_2$ requires *M*, 264.1964), 246 ($M^+$, 20) and 211 (100).

*(2S,8R,4Z,9E)-Undeca-4,9-diene-2,8-diol* **21** (25 mg, 59%) from acetaldehyde (1.5 cm$^3$; 2.3 mmol); $\delta_H$ 1.24 (3 H, d, *J* 6, 1-$H_3$), 1.58 (2 H, m, 7-$H_2$), 1.71 (3 H, d, *J* 6.5, 11-$H_3$), 1.75 (2 H, br s, 2 x OH), 2.18 (4 H, m, 3-$H_2$, 6-$H_2$), 3.86 (1 H, m, 2-H), 4.08 (1 H, q, *J* 6.5, 8-H) and 5.3 - 5.7 (4 H, m, 4-H, 5-H, 9-H, 10-H); $\delta_C$ 17.6, 22.7, 23.5, 36.8, 37.0, 67.5, 72.3, 125.5, 126.7, 132.5 and 134.0; $\upsilon_{max}$/cm$^{-1}$ 3343, 1671, 1449, 1121, 1065 and 966; *m/z* (CI) 202.1811 ($M^+$+ $NH_4$, 25%; $C_{11}H_{24}NO_2$ requires *M*, 202.1807), 184 (80), 167 (100) and 149 (100).

*(3R,9R,5Z,10E)-Dodeca-1,5,10-triene-3,9-diol* **22** (30 mg, 67%) from acrolein (0.023 cm$^3$; 0.23 mmol); $\delta_H$ 1.54 (2 H, m, 8-$H_2$), 1.67 (3 H, d, *J* 6, 12-$H_3$), 2.12 (2 H, m, 7-$H_2$), 2.29 (2 H, m, 4-$H_2$), 3.93 (1 H, q, *J* 7, 9-H), 4.12 (1 H, m, 3-H), 5.14 (1 H, d, *J* 10, 1-H), 5.22 (1 H, d, *J* 16.5, 1-H'), 5.42 (2 H, m, 5-H, 6-H), 5.54 (1 H, m, 10-H), 5.62 (1 H, m, 11-H) and 5.88 (1 H, ddd, *J* 5.5, 10, 16.5, 2-H); $\delta_C$ 17.7, 23.5, 34.9, 36.8, 72.3, 73.8, 114.7, 124.8, 126.9, 132.8, 134.0 and 140.4; $\upsilon_{max}$/cm$^{-1}$ 3367, 1261 and 1025; *m/z* (CI) 214.1813 ($M^+$+ $NH_4$, 10%; $C_{12}H_{24}NO_2$ requires *M*, 214.1807), 196 (40) and 161 (100).

*(3RS,9RS,5Z,10E)-2-Methyldodeca-5,10-diene-3,9-diol* **23** (30 mg, 62%) from 2-methylpropanal (0.23 cm$^3$; 0.23 mmol) and racemic stannane; $\delta_H$ 0.90 and 0.91 (each 3 H, d, *J* 6, 1-$H_3$, 2-$CH_3$), 1.54 (1 H, m, 2-H), 1.62 (2 H, m, 8-$H_2$), 1.69 (3 H, d, *J* 6, 12-$H_3$), 2.10 (4 H, m, 4-$H_2$,, 7-$H_2$), 3.35 (1 H, q, *J* 6, 3-H), 4.40 (1 H, q, *J* 6.5, 9-H) and 5.4 - 5.7 (4 H, m, 5-H, 6-H, 10-H, 11-H); $\delta_C$ 17.6, 17.7, 18.8, 23.6, 32.0, 33.0, 36.9, 72.5, 76.2, 126.1, 126.9, 132.6 and 134.0; $\upsilon_{max}$/cm$^{-1}$ 3373, 1721, 1507, 1284, 1067, 1042 and 774; *m/z* (CI) 230.2123 ($M^+$+ $NH_4$, 10%; $C_{13}H_{28}NO_2$ requires *M*, 230.2120), 212 (20) and 182 (100).

*(1R,7R,3Z,8E)-1-(Fur-2-yl)-deca-3,8-diene-1,7-diol* **24** (25 mg, 46%) from furfural (19 µl; 0.23 mmol); $\delta_H$ 1.53 (2 H, m, 6-$H_2$), 1.66 (3 H, d, *J* 6.5, 10-$H_3$), 2.13 (2 H, m, 5-$H_2$), 2.60 (1 H, br, OH), 2.61 (2 H, t, *J* 6.5, 2-$H_2$), 4.02 (1 H, m, 7-H), 4.71 (1 H, t, *J* 6.5, 1-H), 5.37 (1 H, m, 4-H), 5.45 (1 H, m, 3-H), 5.54 (1 H, m, 8-H), 5.62 (1 H, m, 9-H), 6.22 (1 H, d, *J* 3, 3'-H), 6.31 (1 H, m, 4'-H) and 7.35 (1 H, s, 5'-H); $\delta_C$ 17.7, 23.5, 33.5, 36.7, 67.4, 72.5, 106.0, 110.1, 124.5, 126.9, 133.0, 133.9, 141.9 and 156.1; $\upsilon_{max}$/cm$^{-1}$ 3371, 1671, 1445, 1147, 1058, 1009, 967 and 736; *m/z* (CI) 254.1765 ($M^+$+ $NH_4$, 10%; $C_{14}H_{24}NO_3$ requires *M*, 254.1756), 236 (40) and 201 (100).

*(1RS,7RS,3Z,8E)-1-(1,3-Dithian-2-yl)-deca-3,8-diene-1,7-diol* **25** (34 mg, 51%) from 2-formyl-1,3-dithiane[13] (34 mg; 0.23 mmol) and racemic stannane; $\delta_H$ 1.58 (2 H, m, 6-$H_2$), 1.66 (3 H, d, *J* 6.5, 10-$H_3$), 1.95 - 2.15 (4 H, m), 2.41 and 2.60 (each 1 H, m), 2.72 and 2.92 (each 2 H, m), 3.88 (1 H, d, *J* 7, 2'-H), 3.90 (1 H, m, 1-H), 4.04 (1 H, q, *J* 6.5, 7-H), 5.44 (2 H, m, 3-H, 8-H), 5.55 (1 H, m, 4-H) and 5.64 (1 H, dq, *J* 12 and 6.5, 9-H); $\delta_C$ 17.6, 23.6, 25.6, 27.7, 28.3, 31.6, 36.8, 51.2, 71.9, 72.2, 124.6, 126.5, 132.9 and 134.0; $\upsilon_{max}$/cm$^{-1}$ 3397, 3009, 1656, 1423, 1277, 1069 and 967; *m/z* (CI) 288.1216 ($M^+$, 25%; $C_{14}H_{24}O_2S_2$ requires *M*, 288.1217), 271 (60) and 119 (100).

*(1*R*,7*R*,3*Z*,8*E*)-7-(*tert*-Butyldiphenylsilyloxy)-1-phenyldeca-3,8-dien-1-ol* **17**

*tert*-Butyldiphenylsilyl chloride (0.3 cm$^3$, 1.3 mmol) and imidazole (215 mg, 3 mmol) were added to the diol **14** (250 mg, 1 mmol) in DMF (2 cm$^3$). After 16 h water was added, the aqueous phase was extracted with dichloromethane and the organic extracts were washed with brine, dried and concentrated under reduced pressure. Chromatography using light petroleum – ether (10 : 1) gave *(1*R*,7*R*,3*Z*,8*E*)-1,7-bis-(*tert*-butyldiphenylsilyloxy)-1-phenyldeca-3,8-diene* (64 mg, 9%), $[\alpha]_D$ −16.2 (c 1.85 in $CHCl_3$); $\delta_H$ 0.94 [18 H, s, 2 × $SiC(CH_3)_3$], 1.18 (2 H, m, 6-$H_2$), 1.40 (3 H, d, *J* 6, 10-$H_3$), 1.55 (2 H, m, 5-$H_2$), 2.21 and 2.32 (each 1 H, m, 2-H), 3.86 (1 H, q, *J* 6.5, 7-H), 4.55 (1 H, dd, *J* 5.5, 7, 1-H), 5.0 (3 H, m, 3-H, 4-H, 9-H), 5.19 (1 H, dd, *J* 6.5, 15.5, 8-H), 7.21 (17 H, m, ArH) and 7.55 (8 H, m, ArH); $\upsilon_{max}$/cm$^{-1}$ 3048, 1427, 1110, 1068, 822, 739 and 701; *m/z* (CI) 740.4323 ($M^+$+ $NH_4$, 60%; $C_{48}H_{62}NO_2Si_2$ requires *M*, 740.4319) and 484 (100) and the *title compound* **17** (297 mg, 61%), $[\alpha]_D$ –26.2 (c 2.32 in $CHCl_3$); $\delta_H$ 1.00 [9 H, s, $SiC(CH_3)_3$], 1.35 (2 H, m, 6-$H_2$), 1.47 (3 H, d, *J* 6, 10-$H_3$), 2.05 (2 H, m, 5-$H_2$), 2.35 (2 H, m, 2-$H_2$), 4.00 (1 H, q, *J* 6.5, 7-H), 4.56 (1 H, t, *J* 5.5, 1-H), 5.35 (4 H, m, 3-H, 4-H, 8-H, 9-H), 7.25 (11 H, m) and 7.60 (4 H, m); $\upsilon_{max}$/cm$^{-1}$ 3377, 3048, 1427, 1111 and 701; *m/z* (CI) 485.2880 ($MH^+$, 5%; $C_{32}H_{41}O_2Si$ requires *M*, 485.2876), 427 (20), 377 (20) and 211 (100).

*(1S,7R,3Z,8E)-7-(*tert*-Butyldiphenylsilyloxy)-1-(4-nitrobenzoyloxy)-1-phenyldeca-3,8-diene* **18**

Diethyl azodicarboxylate (0.38 μl, 0.24 mmol) was added to a stirred solution of the alcohol **17** (77 mg, 0.16 mmol), triphenylphosphine (63 mg, 2.4 mmol) and *p*-nitrobenzoic acid (40 mg, 0.24 mmol) in toluene (3 cm$^3$) at –35 °C. After 2 h, the reaction mixture was concentrated under reduced pressure. Chromatography of the residue using light petroleum – ether (10 : 1) gave the *title compound* **18** (77 mg, 76%) as a colourless oil; $\delta_H$ 0.96 [9 H, s, $SiC(CH_3)_3$], 1.33 (2 H, m, 6-$H_2$), 1.44 (3 H, d, *J* 6.5, 10-$H_3$), 1.85 (2 H, m, 5-$H_2$), 2.52 and 2.67 (each 1 H, m, 2-H), 3.96 (1 H, q, *J* 6, 7-H), 5.2 (4 H, m, 3-H, 4-H, 8-H, 9-H), 5.80 (1 H, dd, *J* 7.5, 6.5, 1-H), 7.28 (11 H, m, ArH), 7.55 (4 H, m, ArH) and 8.15 (4 H, m, ArH); $\delta_C$ 17.4, 19.3, 22.9, 26.9, 34.2, 37.6, 74.1, 77.2, 123.4, 126.4, 127.2, 127.3, 128.2, 128.5, 129.3, 129.4, 130.6, 133.2, 133.6, 134.5, 135.8, 135.9, 150.4 and 163.7; $\upsilon_{max}$ /cm$^{-1}$ 3071, 1727, 1607, 1530, 1271, 1104 and 701; *m/z* (CI) 576.2209 ($M^+$– $C_4H_9$, 10%; $C_{35}H_{34}NO_5Si$ requires *M*, 576.2206), 498 (20), 409 (40), 348 (60) and 211 (100).

*(1S,7R,3Z,8E)-7-(*tert*-Butyldiphenylsilyloxy)-1-phenyldeca-3,8-dien-1-ol* **19**

The ester **18** (140 mg, 0.22 mmol) was added to sodium hydroxide (97 mg, 2.4 mmol) in methanol (10 cm$^3$). After 1 h, the solution was diluted with ether, washed with brine, dried and concentrated under reduced pressure. Chromatography of the residue using light petroleum – ether (20 : 1) gave the *title compound* **19** (80 mg, 45%); $\delta_H$ 0.97 [9 H, s, $SiC(CH_3)_3$], 1.38 (2 H, m, 6-$H_2$), 1.45 (3 H, d, *J* 6.5, 10-$H_3$), 1.86 (3 H, m, OH, 5-$H_2$), 2.43 (2 H, m, 2-$H_2$), 3.98 (1 H, q, *J* 6.5, 7-H), 4.56 (1 H, m, 1-H), 5.1 - 5.3 (4 H, m, 3-H, 4-H, 8-H, 9-H), 7.27 (11 H, m) and 7.58 (4 H, m); $\delta_C$ 17.4, 19.3, 22.9, 27.0, 37.2, 37.8, 73.8, 74.2, 124.6, 125.7, 127.2, 127.3, 129.3, 133.3, 133.6, 134.4, 135.8, 135.9 and 144.0; $\upsilon_{max}$/cm$^{-1}$ 3459, 3048, 1427, 1110, 966 and 701; *m/z* (CI) 502.3144 ($M^+$+ $NH_4$, 10%; $C_{32}H_{44}NO_2Si$ requires *M*, 502.3141), 467 (25), 274 (70) and 211 (100).

*(1S,7R,3Z,8E)-1-Phenyldeca-3,8-diene-1,7-diol* **16**

TBAF (0.2 cm$^3$, 1 M in THF; 0.2 mmol) was added to the ether **19** (40 mg, 0.11 mmol) in THF (3 cm$^3$). After 16 h, water was added and the aqueous layer was extracted with ether. The organic extracts were washed with brine, dried and concentrated under reduced pressure. Chromatography using light petroleum – ether (1 : 1) gave the *title compound* **16** (22 mg, 90%); $\delta_H$ 1.50 (2 H, m, 6-$H_2$), 1.60 (3 H, d, *J* 6.5, 10-$H_3$), 2.03 (1 H, sex, *J* 6.5, 5-H), 2.19 (2 H, m, OH, 5-H'), 2.37 and 2.58 (each 1 H, m, 2-H), 3.99 (1 H, m, 7-H), 4.68 (1 H, m, 1-H), 5.4 - 5.7 (4 H, m, 3-H, 4-H, 8-H, 9-H) and 7.33 (5 H, m, ArH); $\delta_C$ 17.6, 23.2, 36.5, 37.3. 71.7, 73.8, 125.6, 125.7, 126.5, 127.4, 128.3, 132.5, 134.0 and 144.2; $\upsilon_{max}$/cm$^{-1}$ 3353, 3009, 1672, 1451, 1052, 967 and 700; *m/z* (CI) 264.1963 ($M^+$+ $NH_4$, 5%; $C_{16}H_{26}NO_2$ requires *M*, 264.1963), 246 (20) and 211 (100).

*(4*R*,10*R*,2*E*,7*Z*)-Diacetoxy-10-phenyldeca-2,7-diene* **15**

Acetic anhydride (0.15 $cm^3$, 1.64 mmol), triethylamine (0.6 $cm^3$, 4.1 mmol) and DMAP (10 mg) were added to the diol **14** (100 mg, 0.41 mmol) in dichloromethane (3 $cm^3$) at 0 °C. After 2 h at room temperature, water was added and the aqueous phase was extracted with dichloromethane. The organic extracts were washed with brine, dried and concentrated under reduced pressure. Chromatography of the residue using light petroleum – ether (4 : 1) gave the *title compound* **15** (108 mg, 80%), $[\alpha]_D$ – 28.3 (*c* 21.3 in $CHCl_3$); $\delta_H$ 1.45 (2 H, m, 5-$H_2$), 1.73 (3 H, d, *J* 6.5, 1-$H_3$), 1.94 (2 H, m, 6-$H_2$), 2.06 (3 H, s, 4-$CH_3CO_2$), 2.11 (3 H, s, 10-$CH_3CO_2$), 2.61 (2 H, m, 9-$H_2$), 5.17 (1 H, q, *J* 7, 4-H), 5.2 -5.7 (5 H, m, 2-H, 3-H, 7-H, 8-H, 10-H) and 7.34 (5 H, m, ArH); $\delta_C$ 17.8, 21.3, 21.4, 23.2, 34.2, 34.3, 74.5, 75.4, 124.5, 126.5, 127.9, 128, 129.4, 129.5, 131.8, 140.2, 170.3 and 170.4; $\upsilon_{max}/cm^{-1}$ 1738, 1372, 1238, 1022 and 700; *m/z* (CI) 348.2173 ($M^+$+ $NH_4$, 80%; $C_{20}H_{30}NO_4$ requires *M*, 348.2173), 288 (40) and 211 (100). Ozonolysis of diacetate **15** (100 mg, 0.3 mmol) gave (*R*)-1-acetoxy-1-phenylpropanol **20** (36 mg, 62%) $[\alpha]_D$+36.2 (*c* 28.2 in $CHCl_3$) {lit.[8] $[\alpha]_D$ +72.4 (*c* 30.4 in $CHCl_3$)}.

*(4*RS*,10*RS*,4*E*,7*Z*)-10-Benzyloxy-4-(*tert*-butyldiphenylsilyloxy)-10-phenyldeca-2,11-diene* **26a**

Benzyl bromide (0.9 $cm^3$, 0.7 mmol), sodium hydride (28 mg, 0.7 mmol) and tetrabutylammonium iodide (2.5 mg) were added to the alcohol **17** (297 mg, 0.6 mmol) in THF (10 $cm^3$). After 16 h, water was added and the aqueous phase was extracted with ether. The organic extracts were washed with brine, dried and concentrated under reduced pressure. Chromatography of the residue using light petroleum gave the *title compound* **26a** (240 mg, 70%); $\delta_H$ 1.08 [9 H, s, $SiC(CH_3)_3$], 1.40 (2 H, m, 5-$H_2$), 1.56 (3 H, d, *J* 6, 1-$H_3$), 1.83 (2 H, m, 6-$H_2$), 2.42 and 2.57 (each 1 H, m, 9-H), 4.05 (1 H, m, 4-H), 4.30 (2 H, m, 10-H, C*H*HPh), 4.49 (1 H, d, *J* 12, C*H*HPh), 5.2 (4 H, m, 2-H, 3-H, 7-H, 8-H), 7.40 (16 H, m, ArH) and 7.70 (4 H, m, ArH); $\upsilon_{max}/cm^{-1}$ 3069, 3029, 1428, 1110, 1070, 823 and 701; *m/z* (CI) 592.3595 ($M^+$+ $NH_4$, 30%; $C_{39}H_{50}NO_2Si$ requires *M*, 592.3611), 336 (20) and 211 (100).

*(4*R*,10*R*,2*E*,7*Z*)-4-(*tert*-Butyldiphenylsilyloxy)-10-(4-methoxybenzyloxy)-10-phenyldeca-2,7-diene* **26b**

*p*-Methoxybenzyl chloride (61 µl, 0.35 mmol) was added to sodium hydride (12.6 mg, 0.31 mmol), tetrabutylammonium iodide (3 mg) and the alcohol **17** (69 mg, 0.14 mmol) in DMF (0.5 $cm^3$). After 16 h, water was added and the organic extract washed with brine, dried and concentrated under reduced pressure. Chromatography of the residue using light petroleum – ether (10 : 1) gave the *title compound* **26b** (60 mg, 68%), $[\alpha]_D$ – 16.2 (*c* 2.34 in $CHCl_3$); $\delta_H$ 1.13 [9 H, s, $SiC(CH_3)_3$], 1.44 (2 H, m, 5-$H_2$), 1.58 (3 H, d, *J* 6, 1-$H_3$), 1.92 (2 H, m, 6-$H_2$), 2.42 and 2.58 (each 1 H, m, 9-H), 3.86 (3 H, s, $OCH_3$), 4.10 (1 H, q, *J* 6.5, 4-H), 4.26 (1 H, d, *J* 11.5, OC*H*HAr), 4.32 (1 H, t, *J* 6.5, 10-H), 4.46 (1 H, d, *J* 11.5, OCH*H*'Ar), 5.35 (4 H, m, 2-H, 3-H, 7-H, 8-H), 6.94 and 7.29 (each 2 H, d, *J* 8.5, ArH), 7.42 (11 H, m, ArH) and 7.73 (4 H, m, ArH); $\upsilon_{max}/cm^{-1}$ 3025, 1611, 1513, 1247, 1108, 1077 and 702; *m/z* (CI) 622.3715 ($M^+$+ $NH_4$, 40%; $C_{40}H_{52}NO_3Si$ requires *M*, 622.3716), 441 (10) and 331 (20).

*(4*RS*,10*RS*,2*E*,7*Z*)-10-Benzyloxy-10-phenyldeca-2,7-dien-4-ol* **27a** *and (4*R*,10*R*,2*E*,7*Z*)-10-(4-methoxy-benzyloxy)-10-phenyldeca-2,7-dien-4-ol* **27b**

TBAF (0.72 $cm^3$, 1 M in THF, 0.72 mmol) was added to the silyl ether **26a** (224 mg, 0.4 mmol) in THF (20 $cm^3$). After 16 h water was added and the aqueous phase extracted with ether. The organic extracts were washed with brine, dried and concentrated under reduced pressure. Chromatography of the residue using light petroleum – ether (10 : 1) gave the *title compound* **27a** (88 mg, 66%); $\delta_H$ 1.49 (2 H, m, 5-$H_2$), 1.75 (3 H, d, *J* 6.5, 1-$H_3$), 2.06 (2 H, m, 6-$H_2$), 2.55 and 2.64 (each 1 H, m, 9-H), 4.00 (1 H, q, *J* 6.5, 4-H), 4.33 (1 H, d, *J* 12, C*H*HPh), 4.42 (1 H, t, *J* 6.5, 10-H), 4.55 (1 H, d, *J* 12, CH*H'*Ph), 5.48 (3 H, m, 3-H, 7-H, 8-H), 5.66 (1 H, m, 2-H) and 7.40 (10 H, m, ArH); $\upsilon_{max}$/cm$^{-1}$ 3424, 1494, 1453, 1069, 966 and 699; *m/z* (CI) 354.2427 ($M^+$+ $NH_4$, $C_{23}H_{32}NO_2$ requires *M*, 354.2433), 336 (25), 301 (20) and 211 (100).

Following the same procedure, the silyl ether **26b** (238 mg, 0.385 mmol) gave, after chromatography using light petroleum – ether (3 : 1), the *title compound* **27b** (120 mg, 85%), $[\alpha]_D$ – 21.5 (*c* 2.21 in $CHCl_3$); $\delta_H$1.40 (2 H, m, 5-$H_2$), 1.73 (3 H, d, *J* 6.5, 1-$H_3$), 2.04 (2 H, q, *J* 7.5, 6-$H_2$), 2.50 and 2.62 (each 1 H, m, 9-H), 3.85 (3 H, s, $OCH_3$), 3.97 (1 H, m, 4-H), 4.25 (1 H, d, *J* 11.5, OC*H*HAr), 4.36 (1 H, t, *J* 6.5, 10-H), 4.46 (1 H, d, *J* 11.5, OCH*H'*Ar), 5.44 (3 H, m, 3-H, 7-H, 8-H), 5.63 (1 H, dq, *J* 15, 6.5, 2-H), 6.92 and 7.27 (each 2 H, d, *J* 8.5, ArH) and 7.35 (5-H, m, ArH); $\upsilon_{max}$/cm$^{-1}$ 3429, 3001, 1612, 1513, 1452, 1247, 1175, 1083, 1036, 967, 822 and 702; *m/z* (CI) 384.2541 ($M^+$+ $NH_4$, 5%; $C_{24}H_{34}NO_3$ requires *M*, 384.2539), 366 (10), 331 (90) and 121 (100).

*(4RS,10RS,2E,7Z)-4-Acetoxy-10-benzyloxy-10-phenyldeca-2,7-diene* **28a** *and (4R,10R,2E,7Z)-4-acetoxy-10-(4-methoxybenzyloxy)-10-phenyldeca-2,7-diene* **28b**

Acetic anhydride (0.05 cm$^3$, 0.52 cm$^3$), triethylamine (0.22 cm$^3$, 1.56 mmol) and DMAP (10 mg) were added to the alcohol **27a** (88 mg, 0.26 mmol) in dichloromethane (5 cm$^3$) at 0 °C. After 2 h at room temperature, water was added and the aqueous phase extracted with dichloromethane. The organic extracts were washed with brine, dried and concentrated under reduced pressure. Chromatography of the residue using light petroleum – ether (10 : 1) gave the *title compound* **28a** (94 mg, 96%); $\delta_H$ 1.54 (2 H, m, 5-$H_2$), 1.71 (3 H, d, *J* 6.5, 1-$H_3$), 1.97 (2 H, m, 6-$H_2$), 2.05 (3 H, s, $CH_3CO_2$), 2.48 and 2.62 (each 1 H, m, 9-H), 4.31 (1 H, d, *J* 12, C*H*HPh), 4.36 (1 H, t, *J* 6.5, 10-H), 4.51 (1 H, d, *J* 12, CH*H'*Ph), 5.15 (1 H, q, *J* 7, 4-H), 5.42 (3 H, m, 3-H, 7-H, 8-H), 5.73 (1 H, m, 2-H) and 7.37 (10 H, m, ArH); $\upsilon_{max}$/cm$^{-1}$ 3028, 1735, 1241, 700; *m/z* (CI) 396.2549 ($M^+$+ $NH_4$, 30%, $C_{25}H_{34}NO_3$ requires *M*, 396.2539), 336 (10) and 211 (100).

Following the same procedure, the alcohol **27b** (117 mg, 0.32 mmol) gave, after chromatography using light petroleum – ether (3 : 1), the *title compound* **28b** (130 mg, 98%); $[\alpha]_D$ – 33.7 (*c* 2.63 in $CHCl_3$); $\delta_H$ 1.44 and 1.61 (each 1 H, m, 5-H), 1.73 (3 H, d, *J* 6.5, 1-$H_3$), 1.96 (2 H, m, 6-$H_2$), 2.05 (3 H, s, $CH_3CO_2$), 2.45 and 2.61 (each 1 H, m, 9-H), 3.85 (3 H, s, $OCH_3$), 4.25 (1 H, d, *J* 11.5, OC*H*HAr), 4.34 (1 H, t, *J* 6.5, 10-H), 4.44 (1 H, d, *J* 11.5, OCH*H'*Ar), 5.15 (1 H, q, *J* 6.5, 4-H), 5.40 (3 H, m, 3-H, 7-H, 8-H), 5.71 (1 H, m, 2-H), 6.91and 7.27 (each 2 H, d, *J* 8, ArH) and 7.37 (5 H, m, ArH); $\upsilon_{max}$/cm$^{-1}$ 1734, 1612, 1513 and 1244; *m/z* (CI) 426.2655 ($M^+$+ $NH_4$, 20%; $C_{26}H_{36}NO_4$ requires *M*, 426.2644), 366 (5), 331 (20) and 121 (100).

*(3RS,11RS,4E,8Z)-11-Benzyloxy-3-methyl-11-phenylundeca-4,8-dienoic acid* **29a** *and (3R,11R,4E,8Z)-11-(4-methoxybenzyloxy)-3-methyl-11-phenylundeca-4,8-dienoic acid* **29b**

Butyllithium (0.36 mmol, 1.6 M in hexanes) was added to diisopropylamine (0.05 cm$^3$, 0.36 mmol) in THF (2.5 cm$^3$) at 0 °C and, after 10 min at room temperature, the solution was cooled to –78 °C. The ester **28a** (110 mg, 0.3 mmol) was added in THF (1 cm$^3$) followed, after 20 min, by *tert*-butyldimethylsilyl chloride (136 mg, 0.9 mmol) in HMPA (1 cm$^3$). After 16 h at room temperature, aqueous sodium hydroxide (5%) was added and the aqueous phase was extracted with ether then acidified with conc. aq. hydrogen chloride. The aqueous phase was extracted with dichloromethane, and the organic extracts were washed with brine, dried and concentrated under reduced pressure. Chromatography of the residue using light petroleum - ether gave the *title compound* **29a** (77 mg, 68%); $\delta_H$ 1.09 (3 H, d, *J* 6.5, 3-$CH_3$), 2.00 (4 H, m, 6-$H_2$, 7-$H_2$), 2.48 (2 H, m, 2-$H_2$), 2.66 (3 H, m, 10-$H_2$, 3-H), 4.33 (1 H, d, *J* 12, C*H*HPh), 4.39 (1 H, t, *J* 6.5, 11-H), 4.54 (1 H, d, *J* 12, CH*H*'Ph), 5.25 (4 H, m, 4-H, 5-H, 8-H, 9-H) and 7.38 (10 H, m, ArH); *m/z* (CI) 396.2544 ($M^+$+ $NH_4$, 5%; $C_{25}H_{34}NO_3$ requires *M*, 396.2539), 379 (5), 288 (30) and 91 (100).

Following the same procedure, the ester **28b** (150 mg, 0.36 mmol) gave, after chromatography using light petroleum – ether (4 : 1), the *title compound* **29b** (90 mg, 60%), $[\alpha]_D$ – 34.5 (*c* 1.52 in $CHCl_3$); $\delta_H$ 1.09 (3 H, d, *J* 6.5, 3-$CH_3$), 1.98 (4 H, m, 6-$H_2$, 7-$H_2$), 2.34 (2 H, m, 2-$H_2$), 2.46 (1 H, m, 10-H), 2.66 (2 H, m, 3-H, 10-H'), 3.85 (3 H, s, $OCH_3$), 4.25 (1 H, d, *J* 11.5, C*H*HPh), 4.36 (1 H, t, *J* 6.5, 11-H), 4.48 (1 H, d, *J* 11.5, CH*H*'Ph), 5.4 (4 H, m, 4-H, 5-H, 8-H, 9-H), 6.92 and 7.28 (each 2 H, d, *J* 7, ArH), and 7.39 (5 H, m, ArH); $\delta_C$ 20.4, 27.3, 32.2, 33.4, 36.0, 41.6, 55.2, 69.9, 80.9, 113.7, 125.6, 126.9, 127.6, 128.3, 129.0, 129.3, 130.3, 130.9, 134.1, 141.9, 159.0 and 178.1; $\upsilon_{max}/cm^{-1}$ 1708, 1513, 1247 and 701; *m/z* (CI) 408.2304 ($M^+$, 20%; $C_{26}H_{32}O_4$ requires *M*, 408.2304), 426 (20), 391 (50), 290 (30) and 121 (100).

*Methyl (3RS,11RS,4E,8Z)-11-Benzyloxy-3-methyl-11-phenylundeca-4,8-dienoate* **30a** *and (3R,11R,4E,8Z)-11-(4-methoxybenzyloxy)-3-methyl-11-phenylundeca-4,8-dienoate* **30b**

An excess of diazomethane was added dropwise to the acid **29a** (70 mg, 0.19 mmol) in dichloromethane (2 $cm^3$) untill the solution remained yellow, then acetic acid was added to quench the excess of diazomethane. After concentration under reduced pressure, chromatography using light petroleum – ether (10 : 1) gave the *title compound* **30a** (42 mg, 58%); $\delta_H$ 0.93 (3 H, d, *J* 6.5, 3-$CH_3$), 1.86 (4 H, m, 6-$H_2$, 7-$H_2$), 2.37 (2 H, m, 2-$H_2$), 2.52 (3 H, m, 10-$H_2$, 3-H), 3.55 (3 H, s, $CO_2CH_3$), 4.20 (1 H, d, *J* 12, C*H*HPh), 4.25 (1 H, t, *J* 6.5, 11-H), 4.39 (1 H, d, *J* 12, CH*H*'Ph), 5.25 (4 H, m, 4-H, 5-H, 8-H, 9-H) and 7.25 (10 H, m, ArH); $\upsilon_{max}/cm^{-1}$ 1738, 1452, 1092, 1070 and 699; *m/z* (CI) 410.2702 ($M^+$+ $NH_4$, 100%, $C_{26}H_{36}NO_3$ requires *M*, 410.2695).

Following the same procedure, the acid **29b** (85 mg, 0.21 mmol) gave, after chromatography using petroleum – ether (4 : 1), the *title compound* **30b** (77 mg, 88%); $[\alpha]_D$ – 38.5 (*c* 2.22 in $CHCl_3$); $\delta_H$ 1.06 (3 H, d, *J* 6.5, 3-$CH_3$), 1.98 (4 H, m, 6-$H_2$, 7-$H_2$), 2.27 and 2.36 (each 1 H, dd, *J* 7.5, 14.5, 2-H), 2.49 (1 H, m, 10-H), 2.65 (2 H, m, 3-H, 10-H'), 3.69 and 3.85 (each 3 H, s, $OCH_3$), 4.25 (1 H, d, *J* 11.5, C*H*HPh), 4.35 (1 H, t, *J* 7, 11-H), 4.46 (1 H, d, *J* 11.5, CH*H*'Ph), 5.4 (4 H, m, 4-H, 5-H, 8-H, 9-H), 6.92 and 7.28 (each 2 H, d, *J* 8.5, ArH), and 7.25 (5 H, m, ArH); $\delta_C$ 20.3, 27.3, 32.2, 33.5, 36.4, 41.7, 51.3, 55.2, 69.9, 80.9, 113.7, 125.4, 126.9, 127.5, 128.3, 128.7, 129.2, 130.6, 130.9, 134.3, 142.1, 159.0 and 173.0; $\upsilon_{max}/cm^{-1}$ 1738, 1612, 1513, 1247, 1173, 1085 and 702; *m/z* (CI) 422.2451 ($M^+$, 10%, $C_{27}H_{34}O_4$ requires *M*, 422.2457), 440 (70), 405 (20) and 121 (100).

*3-[(3'R,4R,11'R,4'E,8'Z)- and (3'S,4R,11'S,4'E,8'Z)-11-(4-Methoxybenzyloxy)-3-methyl-11-phenylundeca-4,8-dienoyl]-4-phenyl-1,3-oxazolan-2-one* **31** *and* **32**

Pivaloyl chloride (6 µl, 0.05 mmol) and triethylamine (8 µl, 0.06 mmol) were added to the acid **29b** (16 mg, 0.04 mmol) in THF (0.5 $cm^3$) at –78 °C. The reaction mixture was kept at –78 °C for 15 min and warmed to room temperature for 45 min. Butyllithium (25 µl, 1.6 M solution in hexanes, 0.04 mmol) was added to (*R*)-4-phenyl-2-oxazolidinone (6 mg, 0.04 mmol) in THF (0.5 $cm^3$) at –78 °C and the mixture stirred for 20 min. The mixed anhydride solution was then added *via* a canula and the mixture stirred at –78 °C for 30 min then at room temperature for 2 h. Satd. aq. $NH_4Cl$ was added and the solution was concentrated under reduced pressure. Dichloromethane was added and the organic phase washed with satd. aq. $NaHCO_3$, dried and concentrated under reduced pressure. Chromatography of the residue using dichloromethane gave the ***title compound*** **31** (16 mg, 78%); $\delta_H$ 0.97 (3 H, d, *J* 6.5, 3'-$CH_3$), 1.83 (2 H, m, 6'-$H_2$), 1.90 (2 H, m, 7'-$H_2$), 2.44 and 2.56 (each 1 H, m, 10'-H), 2.64 (1 H, m, 3'-H), 2.80 (0.74 H, dd, *J* 8, 16, 2'-$H^R$), 2.88 (0.26 H, dd, *J* 6.5, 16, 2'-$H^S$), 2.93 (0.26 H, dd, *J* 8, 16, 2'-$H^S$), 3.02 (0.74 H, dd, *J* 6.5, 16, 2'-$H^R$), 3.80 (3 H, s, $OCH_3$), 4.19 (1 H, d, *J* 11.5, OC*H*HAr), 4.24 and 4.26 (each 1 H, dd, *J* 4, 7.5, 5-H), 4.30 (1 H, t, *J* 7, 11'-H), 4.39 (1 H, d, *J* 11.5, OCH*H*Ar), 4.64 (0.26 H, t, *J* 7.5, 4-H), 4.67 (0.74 H, t, *J* 7.5, 4-H), 5.25 - 5.43 (4 H, m, 4'-H, 5'-H, 8'-H, 9'-H), 6.87 and 7.22 (each 2 H, d, *J* 8.5, ArH) and 7.32 (10 H, m, ArH); $\upsilon_{max}$/$cm^{-1}$ 1782, 1721, 1610, 1513, 1457, 1249, 1284 and 1071; *m/z* (CI) 571.3172 ($M^+$+ $NH_4$, 5%, $C_{35}H_{43}N_2O_5$ requires *M*, 571.3172), 331 (15) and 181 (100).

## ACKNOWLEDGEMENTS

We thank the EPSRC and Rhone Poulenc Rorer for a CASE Award (to E-M.M.) and Dr. C. McCarthy of Rhone Poulenc Rorer for helpful discussions.

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