

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

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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 (3R,11R)- 3-methyl-11-(arylmethoxy)-11-phenylundeca-4,8-dienoates 30a,b stereoselectively. © 1999 Elsevier Science Ltd. All rights reserved.

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 rearrangement⁴ in order to migrate one of the stereogenic centres along the chain.

RESULTS AND DISCUSSION

The (6R)-6-hydroxynona-2,7-dienylstannane (6R)-10 was prepared, as a mixture of (2E)- and (2Z)isomers, ratio ca. 80 : 20, as outlined in Scheme 1. The key step in this synthesis is the regioselective, baseinduced 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 ¹⁹F NMR spectra of their (R)- and (S)-Mosher's derivatives 11 and 12. The racemic stannane (±)-10 was similarly prepared from the racemic ethyl ester⁶ corresponding to the methyl ester 4.



Scheme 1 Reagents and conditions: i, MgBr2, LiNPr¹2, crotonaldehyde; ii, NaOMe, MeOH; iii, Bu¹Me2SiCl, imidazole (85% from 3); iv, DIBAL-H (77%); v, I2, Ph3P, imidazole, THF (96%); vi, 13-Li, THF - HMPA, -78 °C (90%); vii, Bu3SnH, 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 reaction⁷ 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 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, SnBr4, -78 °C, 7.5 min, then PhCHO, -78 °C, 1 h (64%; 14 : 16 = 90 : 10); ii, Bu^tPh₂SiCl, imidazole (61% from 14); iii, EtO₂CN=NCO₂Et, Ph₃P, 4-NO₂C₆H₄CO₂H (76%); iv, NaOH, MeOH (83%); v, TBAF, THF (90%); vi, Ac₂O, Et₃N (80%); vii, O₃, Me₂S, NaBH₄ (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) : $10(\pm 5)$. 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 $1.^2$



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, PhCH2Br, NaH (70%) or p-MeOC6H4CH2Cl, NaH (68%); ii, TBAF (27a, 66%; 27b, 85%); iii, Ac2O, Et3N (28a, 96%; 28b, 98%); iv, LiNPr¹₂, Bu^tMe₂SiCl (29a, 68%; 29b, 60%); v, CH₂N₂ (30a, 58%; 30b, 88%).

Stereochemical assignments were made to the esters **30a,b** on the basis of the well precedented, 6membered, 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-2oxazolidinone¹⁰ 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'-CH₂'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 Nacyloxazolidinones 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 observed¹¹ is consistent with the (R)-configuration assigned to C(3').§



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

¹H and ¹³C 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 (40-60 μ , 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 (3R,4E)-3-(tert-butyldimethylsilyloxy)hex-4-enoate 5

Lithium diisopropylamide, from butyllithium (20.2 cm³; 1.6 M in hexanes; 33 mmol) and diisopropylamine (4.5 cm³, 33 mmol), was added to (S)-2-acetyl-1,1,2-triphenylethanol 3^{12} (5 g, 15 mmol) in THF (15 cm³) at -78 °C. The mixture was allowed to warm to room temperature then added to magnesium bromide, from 1,2-dibromoethane (3 cm³, 34.5 mmol) and magnesium turnings (1.1 g, 45 mmol), in THF (60 cm³) at -78 °C. After 1 h, crotonaldehyde (1.5 cm³, 18 mmol) was added and the solution stirred for 3 h at -78 °C. Satd. aq. NH4Cl 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 cm³) and sodium methoxide (2 g, 37 mmol) was added. After 2 h, satd. aq. NH4Cl 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 cm³) and light petroleum (500 cm³) 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 cm³) at 0 °C. After 16 h, satd. aq. NH₄Cl 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 CHCl₃); δ_H 0.04 and 0.06 (each 3 H, s, SiCH₃), 0.88 [9 H, s, SiC(CH₃)₃], 1.69 (3 H, d, J 6.5, 6-H₃), 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, CH₃O), 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); δ_C –4.8, –4.2, 17.5, 18.0, 25.7, 43.9, 51.4, 70.7, 126.1, 133.3 and 171.7; ν_{max}/cm^{-1} 1743, 1437, 1252, 1169, 1078, 835 and 777; *m/z* (CI) 259.1735 (MH⁺, 40%; C₁₃H₂₇O₃Si 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 cm³; 1 M in hexanes; 11.7 mmol) was added dropwise to the ester 5 (1 g, 3.9 mmol) in dichloromethane (40 cm³) 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. NH₄Cl 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%), [α]_D –19.3 (c 1.63 in CHCl₃); δ _H 0.07 and 0.10 (each 3 H, s, SiCH₃), 0.92 [9 H, s, SiC(CH₃)₃], 1.71 (3 H, d, J 6.5, 6-H₃), 1.83 (2 H, m, 2-H₂), 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); δ _C -4.9, -4.2, 17.6, 18.1, 25.9, 39.6, 60.4, 73.4, 125.7 and 133.7; ν_{max}/cm^{-1} 3362, 1472, 1360, 1255, 1080, 966, 835 and 775; *m/z* (CI) 231.1776 (MH⁺, 10%; C₁₂H₂₇O₂Si 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 cm³) at 0 °C. After 1 h at room temperature, satd. aq. NaHCO₃ (40 cm³) 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 CHCl₃); δ_H 0.07 and 0.12 (each 3 H, s, SiCH₃), 0.92 [9 H, s, SiC(CH₃)₃], 1.71 (3 H, d, *J* 7, 6-H₃), 1.98 (2 H, m, 2-H₂), 3.22 (2 H, m 1-H₂), 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); δ_C –4.6, –4.0, 3.1, 17.6, 18.2, 25.9, 42.0, 73.5, 126.3 and 133.5; ν_{max}/cm^{-1} 1471, 1254, 1085, 1038, 966, 940, 836 and 776; *m/z* (CI) 341.0803 (MH⁺, 10%; C₁₂H₂₆IOSi 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 cm³, 1.6 M in hexanes, 17 mmol) was added to the sulphide 13 (2.2 g, 14.2 mmol) in THF (100 cm³) at -78 °C. After 0.5 h, HMPA (5.2 cm³, 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. NH₄Cl 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); $\delta_{\rm H}$ 0.03 and 0.04 (each 3 H, s, SiCH₃), 0.89 [9 H, s, SiC(CH₃)₃], 1.59 (4 H, m, 4-H₂, 5-H₂), 1.68 (3 H, d, J 6, 9-H₃), 3.69 (1 H, s, NCH₃), 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-H₂), 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); $\delta_{\rm C}$ -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; $\nu_{\rm max}/\rm{cm}^{-1}$ 1455, 1253, 1079, 967, 836 and 775; *m/z* (EI) 367.2237 (M⁺, 5%; C_{19H35}N₂OSSi 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 cm³, 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 cm³) 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%) (2E : 2Z = 4 : 1); $\delta_{\rm H}$ 0.05 and 0.06 (each 3 H, s, SiCH₃), 0.91 [24 H, m, SiC(CH₃)₃, 3 × CH₃(CH₂)₂CH₂Sn], 1.3 - 1.8 [19 H, m, 3 × CH₃(CH₂)₂CH₂Sn, 1-H₂, 5-H₂, 9-H₃], 2.06 (2 H, m, 4-H₂), 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); $\delta_{\rm C}$ -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; $\upsilon_{\rm max}/cm^{-1}$ 1463, 1253, 1080, 965, 836 and 775; *m/z* (EI) 487.2419 (M⁺– C₄H₉, 90%; C₂₃H₄₇OSi¹²⁰Sn 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 cm³; 1 M in THF; 0.7 mmol) was added to the silyl ether **9** (0.2 g, 0.37 mmol) in THF (5 cm³). After 15 h, satd. aq. NH₄Cl 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%) (2E : 2Z = 4 : 1); $\delta_{\rm H}$ 0.85 [15 H, m, 3 x CH₃(CH₂)₂CH₂Sn], 1.2 - 1.8 [19 H, m, 3 × CH₃(CH₂)₂CH₂Sn), 1-H₂, 5-H₂, 9-H₃], 2.06 (2 H, q, J 7.5, 4-H₂), 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); $\delta_{\rm C}$ 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; $\nu_{\rm max}/{\rm cm^{-1}}$ 3347, 1455, 1071, 1051 and 963; *m/z* (CI) 373.1560 (M⁺- C₄H₉, 10%; C₁₇H₃₃O¹²⁰Sn 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 cm³; 1 M in dichloromethane; 6 mmol) was added to the stannane 10 (2.15 g, 5 mmol) in dichloromethane (50 cm³) at -78 °C. After 7.5 min, benzaldehyde (0.76 cm³; 1 M in dichloromethane; 0.76 mmol) was added and the mixture was stirred at -78 °C for 1 h. Satd. aq. NH4Cl 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 CHCl₃); δ_H (14) 1.42 and 1.53 (each 1 H, m, 6-H), 1.66 (3 H, d, J 7.5, 10-H₃), 2.10 (2 H, m, 5-H₂), 2.50 (2 H, m, 2-H₂), 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); δ_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; υ_{max}/cm^{-1} 3353, 3011, 1451, 1051, 966, 759 and 700; m/z (CI) 264.1970 (M⁺⁺ NH₄, C₁₆H₂₆NO₂ requires *M*, 264.1964), 246 (M⁺, 20) and 211 (100).

(25,88,4Z,9E)-Undeca-4,9-diene-2,8-diol **21** (25 mg, 59%) from acetaldehyde (1.5 cm³; 2.3 mmol); $\delta_{\rm H}$ 1.24 (3 H, d, J 6, 1-H₃), 1.58 (2 H, m, 7-H₂), 1.71 (3 H, d, J 6.5, 11-H₃), 1.75 (2 H, br s, 2 x OH), 2.18 (4 H, m, 3-H₂, 6-H₂), 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); $\delta_{\rm C}$ 17.6, 22.7, 23.5, 36.8, 37.0, 67.5, 72.3, 125.5, 126.7, 132.5 and 134.0; $\upsilon_{\rm max}/\rm{cm}^{-1}$ 3343, 1671, 1449, 1121, 1065 and 966; *m/z* (CI) 202.1811 (M⁺+ NH₄, 25%; C₁₁H₂₄NO₂ 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 cm³; 0.23 mmol); $\delta_{\rm H}$ 1.54 (2 H, m, 8-H₂), 1.67 (3 H, d, J 6, 12-H₃), 2.12 (2 H, m, 7-H₂), 2.29 (2 H, m, 4-H₂), 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); $\delta_{\rm C}$ 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; $\nu_{\rm max}$ /cm⁻¹ 3367, 1261 and 1025; *m*/z (CI) 214.1813 (M⁺+ NH₄, 10%; C₁₂H₂₄NO₂ 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 cm³; 0.23 mmol) and racemic stannane; $\delta_{\rm H}$ 0.90 and 0.91 (each 3 H, d, J 6, 1-H₃, 2-CH₃), 1.54 (1 H, m, 2-H), 1.62 (2 H, m, 8-H₂), 1.69 (3 H, d, J 6, 12-H₃), 2.10 (4 H, m, 4-H₂, 7-H₂), 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); $\delta_{\rm C}$ 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; $\nu_{\rm max}/{\rm cm}^{-1}$ 3373, 1721, 1507, 1284, 1067, 1042 and 774; m/z (CI) 230.2123 (M⁺+ NH₄, 10%; C₁₃H₂₈NO₂ 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); $\delta_{\rm H}$ 1.53 (2 H, m, 6-H₂), 1.66 (3 H, d, J 6.5, 10-H₃), 2.13 (2 H, m, 5-H₂), 2.60 (1 H, br, OH), 2.61 (2 H, t, J 6.5, 2-H₂), 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); $\delta_{\rm C}$ 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; $\upsilon_{\rm max}/\rm{cm}^{-1}$ 3371, 1671, 1445, 1147, 1058, 1009, 967 and 736; m/z (CI) 254.1765 (M⁺+ NH₄, 10%; C₁₄H₂₄NO₃ 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-dithiane¹³ (34 mg; 0.23 mmol) and racemic stannane; $\delta_{\rm H}$ 1.58 (2 H, m, 6-H₂), 1.66 (3 H, d, J 6.5, 10-H₃), 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); $\delta_{\rm C}$ 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; $\nu_{\rm max}$ /cm⁻¹ 3397, 3009, 1656, 1423, 1277, 1069 and 967; *m*/z (CI) 288.1216 (M⁺, 25%; C₁₄H₂₄O₂S₂ requires *M*, 288.1217), 271 (60) and 119 (100).

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

tert-Butyldiphenylsilyl chloride (0.3 cm³, 1.3 mmol) and imidazole (215 mg, 3 mmol) were added to the diol 14 (250 mg, 1 mmol) in DMF (2 cm³). 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,7R,3Z,8E)-1,7-bis-(tertbutyldiphenylsilyloxy)-1-phenyldeca-3,8-diene (64 mg, 9%), $[\alpha]_D$ –16.2 (c 1.85 in CHCl₃); δ_H 0.94 [18 H, s, $2 \times SiC(CH_3)_3$], 1.18 (2 H, m, 6-H₂), 1.40 (3 H, d, J 6, 10-H₃), 1.55 (2 H, m, 5-H₂), 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); v_{max}/cm^{-1} 3048, 1427, 1110, 1068, 822, 739 and 701; m/z (CI) 740.4323 (M⁺⁺ NH₄, 60%; C₄₈H₆₂NO₂Si₂ requires *M*, 740.4319) and 484 (100) and the *title compound* 17 (297 mg, 61%), [α]_D -26.2 (c 2.32 in CHCl₃); $\delta_{\rm H}$ 1.00 [9 H, s, SiC(CH₃)₃], 1.35 (2 H, m, 6-H₂), 1.47 (3 H, d, J 6, 10-H₃), 2.05 (2 H, m, 5-H₂), 2.35 (2 H, m, 2-H₂), 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); v_{max}/cm^{-1} 3377, 3048, 1427, 1111 and 701; m/z (CI) 485.2880 (MH⁺, 5%; C₃₂H₄₁O₂Si 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 cm³) 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; $\delta_{\rm H}$ 0.96 [9 H, s, SiC(CH₃)₃], 1.33 (2 H, m, 6-H₂), 1.44 (3 H, d, J 6.5, 10-H₃), 1.85 (2 H, m, 5-H₂), 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); $\delta_{\rm C}$ 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; $\nu_{\rm max}$ /cm⁻¹ 3071, 1727, 1607, 1530, 1271, 1104 and 701; *m*/z (CI) 576.2209 (M⁺- C₄H₉, 10%; C₃₅H₃₄NO₅Si 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 cm³). 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%); $\delta_{\rm H}$ 0.97 [9 H, s, SiC(CH₃)₃], 1.38 (2 H, m, 6-H₂), 1.45 (3 H, d, J 6.5, 10-H₃), 1.86 (3 H, m, OH, 5-H₂), 2.43 (2 H, m, 2-H₂), 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); $\delta_{\rm C}$ 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; $\nu_{\rm max}/{\rm cm}^{-1}$ 3459, 3048, 1427, 1110, 966 and 701; m/z (CI) 502.3144 (M⁺+ NH₄, 10%; C₃₂H₄₄NO₂Si 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 cm³, 1 M in THF; 0.2 mmol) was added to the ether **19** (40 mg, 0.11 mmol) in THF (3 cm³). 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%); $\delta_{\rm H}$ 1.50 (2 H, m, 6-H₂), 1.60 (3 H, d, J 6.5, 10-H₃), 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); $\delta_{\rm C}$ 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; $\nu_{\rm max}/{\rm cm}^{-1}$ 3353, 3009, 1672, 1451, 1052, 967 and 700; *m*/z (CI) 264.1963 (M⁺+ NH₄, 5%; C₁₆H₂₆NO₂ requires *M*, 264.1963), 246 (20) and 211 (100).

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

Acetic anhydride (0.15 cm³, 1.64 mmol), triethylamine (0.6 cm³, 4.1 mmol) and DMAP (10 mg) were added to the diol **14** (100 mg, 0.41 mmol) in dichloromethane (3 cm³) 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 CHCl₃); δ_H 1.45 (2 H, m, 5-H₂), 1.73 (3 H, d, J 6.5, 1-H₃), 1.94 (2 H, m, 6-H₂), 2.06 (3 H, s, 4-CH₃CO₂), 2.11 (3 H, s, 10-CH₃CO₂), 2.61 (2 H, m, 9-H₂), 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); δ_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; ν_{max}/cm^{-1} 1738, 1372, 1238, 1022 and 700; *m/z* (CI) 348.2173 (M⁺⁺ NH₄, 80%; C₂₀H₃₀NO₄ 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%) [α]_D+36.2 (*c* 28.2 in CHCl₃) {lit.⁸ [α]_D +72.4 (*c* 30.4 in CHCl₃)}.

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

Benzyl bromide (0.9 cm³, 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 cm³). 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%); $\delta_{\rm H}$ 1.08 [9 H, s, SiC(CH₃)₃], 1.40 (2 H, m, 5-H₂), 1.56 (3 H, d, J 6, 1-H₃), 1.83 (2 H, m, 6-H₂), 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, CHHPh), 4.49 (1 H, d, J 12, CHHPh), 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); υ_{max}/cm^{-1} 3069, 3029, 1428, 1110, 1070, 823 and 701; m/z (CI) 592.3595 (M⁺+ NH₄, 30%; C₃₉H₅₀NO₂Si requires *M*, 592.3611), 336 (20) and 211 (100).

(4R,10R,2E,7Z)-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 cm³). 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 CHCl₃); δ_H 1.13 [9 H, s, SiC(CH₃)₃], 1.44 (2 H, m, 5-H₂), 1.58 (3 H, d, J 6, 1-H₃), 1.92 (2 H, m, 6-H₂), 2.42 and 2.58 (each 1 H, m, 9-H), 3.86 (3 H, s, OCH₃), 4.10 (1 H, q, J 6.5, 4-H), 4.26 (1 H, d, J 11.5, OCHHAr), 4.32 (1 H, t, J 6.5, 10-H), 4.46 (1 H, d, J 11.5, OCHH'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); ν_{max}/cm^{-1} 3025, 1611, 1513, 1247, 1108, 1077 and 702; *m/z* (CI) 622.3715 (M⁺+ NH₄, 40%; C₄₀H₅₂NO₃Si requires *M*, 622.3716), 441 (10) and 331 (20).

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

TBAF (0.72 cm³, 1 M in THF, 0.72 mmol) was added to the silyl ether **26a** (224 mg, 0.4 mmol) in THF (20 cm³). 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%); δ_H 1.49 (2 H, m, 5-H₂), 1.75 (3 H, d, J 6.5, 1-H₃), 2.06 (2 H, m, 6-H₂), 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, CHHPh), 4.42 (1 H, t, J 6.5, 10-H), 4.55 (1 H, d, J 12, CHH'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); ν_{max}/cm^{-1} 3424, 1494, 1453, 1069, 966 and 699; *m/z* (CI) 354.2427 (M⁺+ NH₄, C₂₃H₃₂NO₂ 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 CHCl₃); $\delta_H 1.40$ (2 H, m, 5-H₂), 1.73 (3 H, d, *J* 6.5, 1-H₃), 2.04 (2 H, q, *J* 7.5, 6-H₂), 2.50 and 2.62 (each 1 H, m, 9-H), 3.85 (3 H, s, OCH₃), 3.97 (1 H, m, 4-H), 4.25 (1 H, d, *J* 11.5, OCHHAr), 4.36 (1 H, t, *J* 6.5, 10-H), 4.46 (1 H, d, *J* 11.5, OCHH'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); υ_{max}/cm^{-1} 3429, 3001, 1612, 1513, 1452, 1247, 1175, 1083, 1036, 967, 822 and 702; *m*/z (CI) 384.2541 (M⁺+ NH₄, 5%; C₂₄H₃₄NO₃ 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 cm³, 0.52 cm³), triethylamine (0.22 cm³, 1.56 mmol) and DMAP (10 mg) were added to the alcohol **27a** (88 mg, 0.26 mmol) in dichloromethane (5 cm³) 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%); $\delta_{\rm H}$ 1.54 (2 H, m, 5-H₂), 1.71 (3 H, d, J 6.5, 1-H₃), 1.97 (2 H, m, 6-H₂), 2.05 (3 H, s, CH₃CO₂), 2.48 and 2.62 (each 1 H, m, 9-H), 4.31 (1 H, d, J 12, CHHPh), 4.36 (1 H, t, J 6.5, 10-H), 4.51 (1 H, d, J 12, CHH'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); υ_{max}/cm^{-1} 3028, 1735, 1241, 700; *m*/z (CI) 396.2549 (M⁺⁺ NH₄, 30%, C₂₅H₃₄NO₃ 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 CHCl₃); δ_H 1.44 and 1.61 (each 1 H, m, 5-H), 1.73 (3 H, d, J 6.5, 1-H₃), 1.96 (2 H, m, 6-H₂), 2.05 (3 H, s, CH₃CO₂), 2.45 and 2.61 (each 1 H, m, 9-H), 3.85 (3 H, s, OCH₃), 4.25 (1 H, d, J 11.5, OCHHAr), 4.34 (1 H, t, J 6.5, 10-H), 4.44 (1 H, d, J 11.5, OCHH'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); υ_{max}/cm^{-1} 1734, 1612, 1513 and 1244; *m/z* (CI) 426.2655 (M⁺⁺ NH₄, 20%; C₂₆H₃₆NO₄ 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-(4methoxybenzyloxy)-3-methyl-11-phenylundeca-4,8-dienoic acid **29b**

Butyllithium (0.36 mmol, 1.6 M in hexanes) was added to diisopropylamine (0.05 cm³, 0.36 mmol) in THF (2.5 cm³) 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 cm³) followed, after 20 min, by *tert*-butyldimethylsilyl chloride (136 mg, 0.9 mmol) in HMPA (1 cm³). 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%); $\delta_{\rm H}$ 1.09 (3 H, d, J 6.5, 3-CH₃), 2.00 (4 H, m, 6-H₂, 7-H₂), 2.48 (2 H, m, 2-H₂), 2.66 (3 H, m, 10-H₂, 3-H), 4.33 (1 H, d, J 12, CHHPh), 4.39 (1 H, t, J 6.5, 11-H), 4.54 (1 H, d, J 12, CHHPh), 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⁺⁺ NH₄, 5%; C₂₅H₃₄NO₃ 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 CHCl₃); δ_H 1.09 (3 H, d, *J* 6.5, 3-CH₃), 1.98 (4 H, m, 6-H₂, 7-H₂), 2.34 (2 H, m, 2-H₂), 2.46 (1 H, m, 10-H), 2.66 (2 H, m, 3-H, 10-H'), 3.85 (3 H, s, OCH₃), 4.25 (1 H, d, *J* 11.5, CHHPh), 4.36 (1 H, t, *J* 6.5, 11-H), 4.48 (1 H, d, *J* 11.5, CHH'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); δ_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; ν_{max}/cm^{-1} 1708, 1513, 1247 and 701; *m*/z (CI) 408.2304 (M⁺, 20%; C₂₆H₃₂O₄ 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 cm³) 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%); $\delta_{\rm H}$ 0.93 (3 H, d, J 6.5, 3-CH₃), 1.86 (4 H, m, 6-H₂, 7-H₂), 2.37 (2 H, m, 2-H₂), 2.52 (3 H, m, 10-H₂, 3-H), 3.55 (3 H, s, CO₂CH₃), 4.20 (1 H, d, J 12, CHHPh), 4.25 (1 H, t, J 6.5, 11-H), 4.39 (1 H, d, J 12, CHH'Ph), 5.25 (4 H, m, 4-H, 5-H, 8-H, 9-H) and 7.25 (10 H, m, ArH); υ_{max}/cm^{-1} 1738, 1452, 1092, 1070 and 699; *m/z* (CI) 410.2702 (M⁺+ NH₄, 100%, C₂₆H₃₆NO₃ 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 CHCl₃); δ_H 1.06 (3 H, d, *J* 6.5, 3-CH₃), 1.98 (4 H, m, 6-H₂, 7-H₂), 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, OCH₃), 4.25 (1 H, d, *J* 11.5, CHHPh), 4.35 (1 H, t, *J* 7, 11-H), 4.46 (1 H, d, *J* 11.5, CHH'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); δ_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; ν_{max}/cm^{-1} 1738, 1612, 1513, 1247, 1173, 1085 and 702; *m*/z (CI) 422.2451 (M⁺, 10%, C₂₇H₃₄O₄ requires *M*, 422.2457), 440 (70), 405 (20) and 121 (100).

3-[(3[°]R,4[°]R,11[°]R,4[°]E,8[°]Z)- and (3[°]S,4[°]R,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 μ l, 0.05 mmol) and triethylamine (8 μ l, 0.06 mmol) were added to the acid **29b** (16 mg, 0.04 mmol) in THF (0.5 cm³) at -78 °C. The reaction mixture was kept at -78 °C for 15 min and warmed to room temperature for 45 min. Butyllithium (25 μ l, 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 cm³) 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. NH₄Cl was added and the solution was concentrated under reduced pressure. Dichloromethane was added and the organic phase washed with satd. aq. NaHCO₃, dried and concentrated under reduced pressure. Chromatography of the residue using dichloromethane gave the *title compound* **31** (16 mg, 78%); $\delta_{\rm H}$ 0.97 (3 H, d, J 6.5, 3'-CH₃), 1.83 (2 H, m, 6'-H₂), 1.90 (2 H, m, 7'-H₂), 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, OCH₃), 4.19 (1 H, d, J 11.5, OCHHAr), 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, OCHHAr), 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); v_{max}/cm^{-1} 1782, 1721, 1610, 1513, 1457, 1249, 1284 and 1071; *m/z* (CI) 571.3172 (M⁺+ NH₄, 5%, C₃₅H₄₃N₂O₅ requires *M*, 571.3172), 331 (15) and 181 (100).

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