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Synthetic studies towards furanocembrane diterpenes. A total synthesis of bis-deoxylophotoxin

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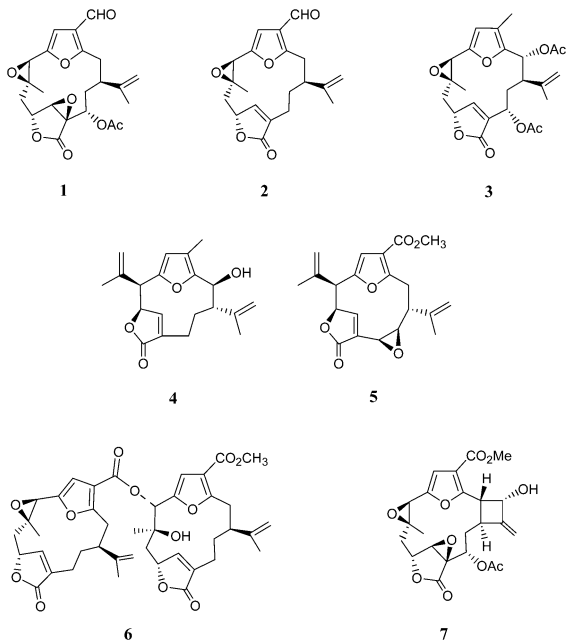
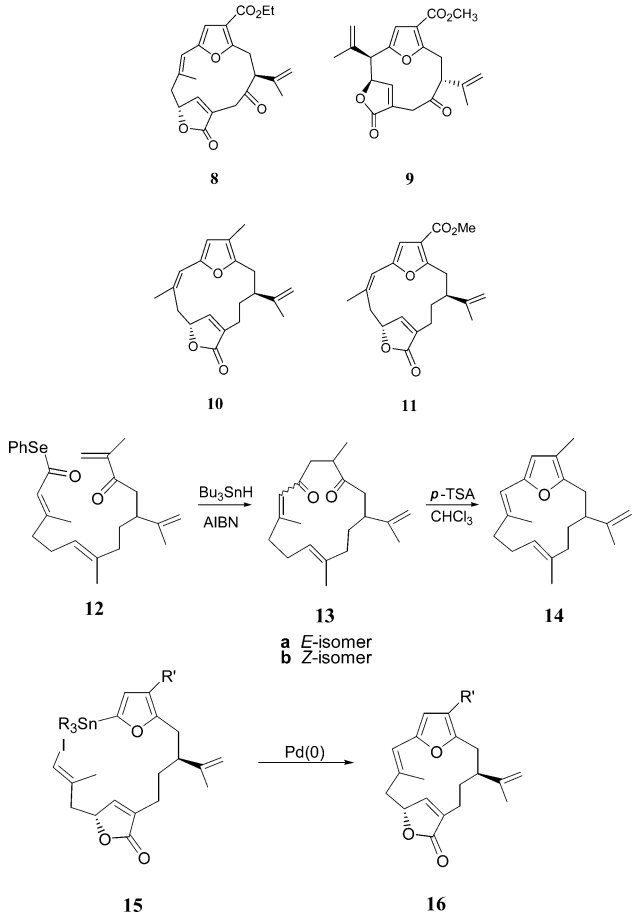
Synthetic approaches to the furanocembrane family of natural products, *e.g.* lophotoxins, pukalides, bipinnatins, based on: i) an intramolecular cyclisation of an α,β-unsaturated acyl radical intermediate into a conjugated enone, *viz.* **18** → **17**, and ii) an intramolecular Stille coupling reaction involving a 2-stannylfuran and a vinyl iodide, *i.e.* **67** → **68**, are described. A total synthesis of bis-deoxylophotoxin **71a**, the probable biological precursor to the neurotoxin lophotoxin **1**, isolated from species of the Pacific sea whip *Lophogorgia*, is then presented.

Introduction

Lophotoxin **1**, together with pukalide **2** and bipinnatin G (**3**), and their various oxygenated and deoxygenated congeners are representative of a novel family of furanocembrane natural products isolated from marine soft corals and sea whips.[1] Lophotoxin is a particularly potent neurotoxin that binds selectively and irreversibly to acetylcholine recognition sites in nicotine acetylcholine receptors, leading to paralysis and asphyxiation.[2] Another family of interesting furanoterpenoid natural products are the pseudopteranes, represented by kalloide A (**4**)[3] and pseudopterolide **5**,[4] which have 12-membered rings, instead of the 14-membered rings found in cembrane diterpenes. The range and variation in structure of furanoditerpenes found in soft corals increases annually, including the recent isolation of the dimer mayotolide A (**6**)[5] and the first α-ylidenecyclobutanol member providencin **7**.[6] With the plethora of interesting structural variations found within the furan-based diterpenes, alongside the novel biological properties found within their members, it is not surprising that synthetic chemists have been lured into studies of the total synthesis of these deceptively straightforward structures.[7] Paquette and co-workers[8] were the first to complete a synthesis of a furanocembrane, *i.e.* acerosolide **8**, and also a pseudopterane, *i.e.* gorgiacerone **9**, using a macrocyclisation strategy based on a Nozaki–Hiyama–Kishi protocol. More recently, Marshall *et al.*[9] have described total syntheses of kalloide A (**4**), rubifolide **10** and *Z*-deoxypukalide **11**, using an efficient intra-annular furan ring formation *via* either a conjugated allenone or an α-keto acetylene intermediate[10] in the latter two cases. In some earlier studies, published in 1991, we described an approach to the furanocembrane core in the lophotoxins, pukalides, and bipinnatins based on an intramolecular 14-*endo*-trig acyl radical cyclisation from the α,β-unsaturated phenyl seleno ester **12** in the presence of Bu_3SnH–AIBN leading to the macrocyclic 1,4-dione **13** in 40% yield.[11] Subsequent treatment of **13** with *p*-TSA in hot chloroform then resulted in furan ring formation, leading to the furanocembrane **14**. In later investigations we developed an alternative approach to the furanobutenolide cembrane core **16** in the same families of natural products using an intramolecular Stille reaction from the iodo-stannane **15** as the key stratagem.[12] In this paper we describe the outcome of our attempts to extend



1 **2** **3** **4** **5** **6** **7**



8 **9** **10** **11** **12** **13** **14** **15** **16**

a *E*-isomer
b *Z*-isomer

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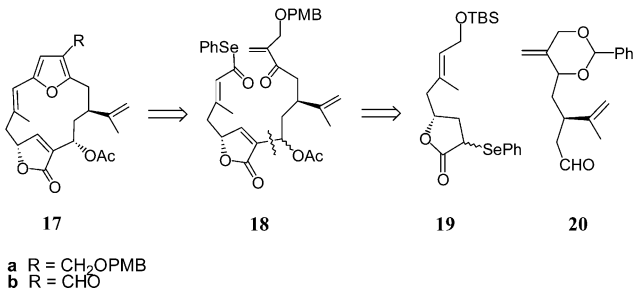
the radical macrocyclisation strategy, *viz.* **12** → **13**, to more oxygen-functionalised acyl radical precursors, and full details of a synthesis of deoxylophotoxin using the aforementioned intramolecular Stille reaction as the key reaction.

Results and discussion

The α,β-unsaturated acyl radical macrocyclisation approach

Over several years we have developed and tested the scope of a number of alkyl radical macrocyclisation reactions in the synthesis of natural products,[13] including the cembrane mukulol[14] and the oestrogenic mycotoxin zearalenone.[15] We have also used radical macrocyclisation reactions in tandem with radical transannulation reactions to synthesise a range of polycyclic constructs, especially steroids.[16] At the outset of our investigations into the scope of α,β-unsaturated acyl radical intermediates in the synthesis of furanocembranes, very little was known about the reactivity profile of these unusual species. Indeed, to our knowledge, the cyclisation **12** → **13** we had developed in 1991, *en route* to the furanocembrane core **14** in lophotoxin, was unprecedented.[11] The success of this model reaction gave us the confidence to develop a strategy to the more elaborate oxygen-substituted seleno ester **18**, and then to study its conversion into bis-deoxylophotoxin **17b**, as a precursor to lophotoxin **1** itself. Accordingly, we decided to prepare the selenoester **18** *via* an intermolecular alkylation reaction between the enantiopure phenylselenolactone **19** and the chiral γ-unsaturated aldehyde **20** (Scheme 1).

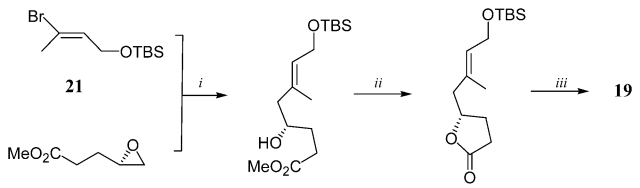


17 **18** **19** **20**

a R = CH_2OPMB
b R = CHO

Scheme 1

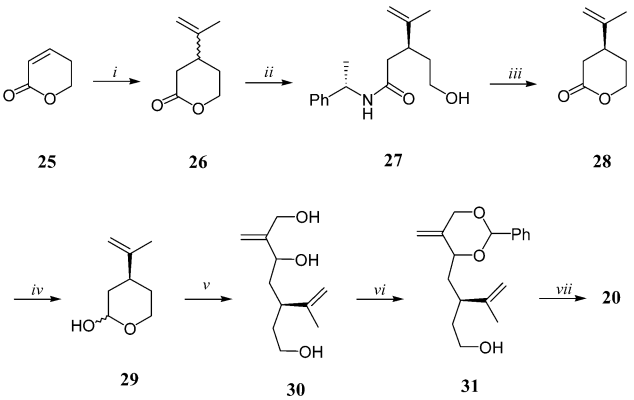
Thus, a regioselective ring opening of the epoxide **22** derived from (+)-glutamic acid[17] with the high-order cuprate prepared from the vinyl bromide **21**[18] first gave the α-hydroxy ester **23** in 70% yield (Scheme 2). Treatment of **23** with LDA in THF at −78 °C next gave the corresponding γ-lactone (**24**; 91%) which was then re-treated with LDA and quenched with phenylselenium bromide leading to the phenylselenolactone **19** as a 2 : 1 mixture of diastereoisomers.



21 **22** **23** **24**

Scheme 2 *Reagents and conditions*: (i) **21**, ^{t}BuLi, THF, −78 °C, 20 min, then CuCN, THF; $BF_3{\cdot}OEt_2$, THF, −60 °C, then **22**, 70%; (ii) LDA, THF, −78 °C, 91%; (iii) LDA, THF, −78 °C, then PhSeBr, −78 °C, 30 min, 50%.

The γδ-unsaturated aldehyde **20** was prepared in six straightforward steps starting from 5,6-dihydro-2*H*-pyran-2-one **25** (Scheme 3). Treatment of **25** with the high-order cuprate derived from 2-bromopropene first led to the racemic δ-lactone **26** which could be resolved *via* its 2-methylphenylamide derivative **27**[19] to provide the required *S*-enantiomer **28**. Reduction of the δ-lactone **28**, using DIBAL, next gave the corresponding lactol **29** which underwent smooth alkylation with the dianion produced from 2-bromopropen-1-ol[20] leading to the triol **30** as a 2 : 1 mixture of diastereoisomers. After protection of **30** as the corresponding benzylidene acetal **31**, oxidation under Swern conditions finally gave the γδ-unsaturated aldehyde **20**.



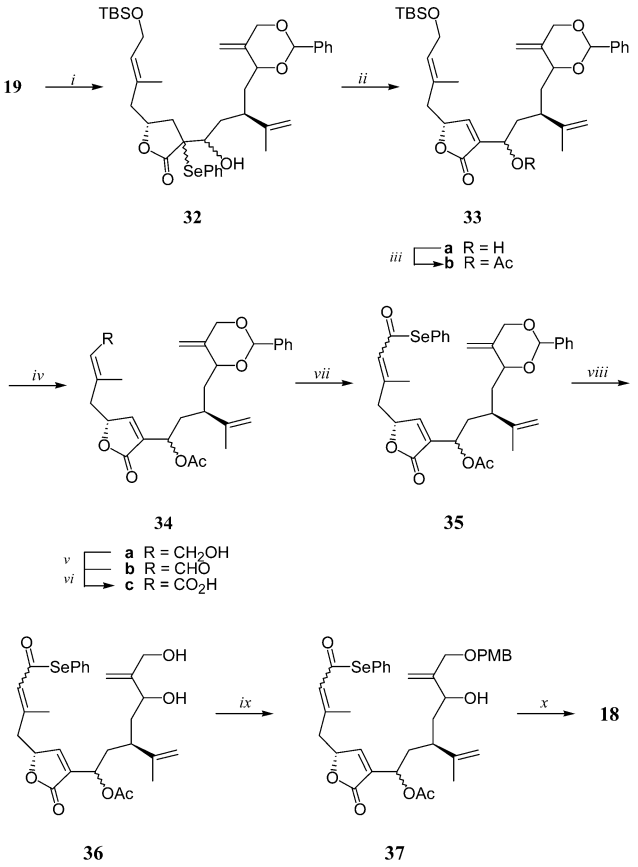
25 **26** **27** **28**

29 **30** **31**

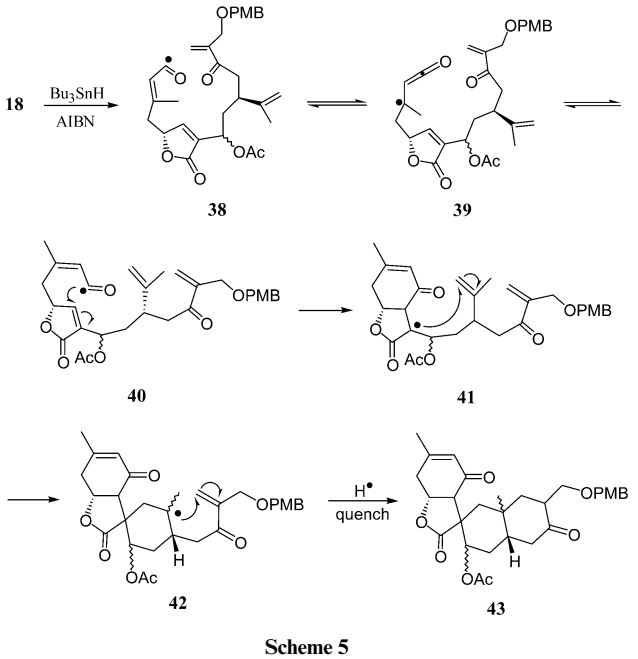
Scheme 3 *Reagents and conditions*: (i) $[CH_2{=}C[CH_3]]_2CuCNLi_2$, THF, −78 to 40 °C, 1 h, 58%; (ii) Me_3Al, (*S*)-(α)-$PhCH(CH_3)NH_2$, CH_2Cl_2, 0 °C, 15 min; r.t., 16 h; resolution, 39%; (iii) PPTS, PhMe, reflux, 16 h, 60%; (iv) DIBAL, THF, −78 °C, 30 min, 88%; (v) $CH_2{=}C(Li)CH_2OLi$, Et_2O, 0 °C, 2 h, 64%; (vi) $PhCH(OCH_3)_2$, PPTS, PhH, reflux, 2 h, 64%; (vii) Swern oxidation, 95%.

Treatment of the phenylselenolactone **19** with LDA at −78 °C followed by alkylation of the resulting carbanion with the aldehyde **20** led to the adduct **32** which was immediately subjected to oxidative dehydroselenylation, using H_2O_2 in aq. THF, resulting in the formation of a mixture of diastereoisomers of the unsaturated lactone **33a** (Scheme 4). The secondary hydroxyl group in **33a** was next protected as its acetate **33b** and then the silyl ether group was deprotected revealing the primary alcohol **34a**. Oxidation of **34a**, using Dess–Martin periodinane, followed by oxidation of the resulting α,β-unsaturated aldehyde **34b**, next gave the corresponding carboxylic acid **34c**.[21] Treatment of the acid **34c** with *N*-phenylselenophthalimide and Bu_3P[22] then produced the phenylselenoester **35** which, to our surprise, was found to be a 1 : 1 mixture of *Z*- and *E*-isomers. In pursuit of the key intermediate **18**, the benzylideneacetal group in **35** was removed using PPTS-MeOH, and the resulting doubly allylic alcohol **36** was converted, into the PMB ether **37**[23] and then into the conjugated enone **18** using standard reagents and conditions (Scheme 4).

Much to our chagrin, when the phenylselenoester **18** was treated under identical radical-initiating conditions to those used to convert **12** into **13** (*en route* to **14**) we were not able to detect the macrocylclic 1,4-dione corresponding to **13** amongst the mixture of products. Although the availability of material and spectroscopic data did not allow any unambiguous assignment, the dearth of olefinic proton signals in the NMR spectra in the products suggested that the unsaturated acyl radical **38** produced from the phenylselenoester **18** had most likely undergone a sequence of alternative radical cyclisation reactions leading to a polycyclic structure similar to the spirotetracycle **43**. The production of this unusual structure could be rationalised through isomerisation of the initially produced *E*-α,β-unsaturated acyl radical **38** into the corresponding *Z*-isomer **40** *via* the novel α-ketene alkyl radical species **39** followed by: (i) 6-*exo*-trig acyl radical cyclisation into the adjacent butenolide double bond, leading to **41**, (ii) 6-*endo*-trig cyclisation of **41** to **42**, and finally, (iii) 6-*endo*-trig cyclisation of the radical **42** into the proximate enone electrophore producing the tetracycle **43** (Scheme 5). Although this analysis is speculative and the structure of **43** is complete conjecture, precedent for the isomerisation of *E*- and *Z*-α,β-unsaturated acyl radicals *via* ketene alkyl radical species, *viz.* **39**, can be found in our contemporaneous studies directed towards a synthesis of the PAF antagonist phomactin



Scheme 4 *Reagents and conditions*: (i) LDA, −78 °C, then **20**, −78 °C, 55%; (ii) H_2O_2, THF (aq.), 90%; (iii) DMAP, Et_3N, Ac_2O, CH_2Cl_2, r.t., 88%; (iv) PhH, MeOH, PPTS, r.t., 70%; (v) Dess–Martin periodinane, CH_2Cl_2, 80%; (vi) $NaClO_2$, KH_2PO_4, ^{t}BuOH, 2-methyl-2-butene, r.t., 100%; (vii) NPSP, PBu_3, CH_2Cl_2, −30 °C to r.t., 80%; (viii) MeOH, PPTS, r.t., 90%; (ix) PMB-trichloroacetimidate, *p*-TSA, CH_2Cl_2–hexane (2 : 1), 0 °C; (x) Dess–Martin periodinane, CH_2Cl_2, r.t., 65%.

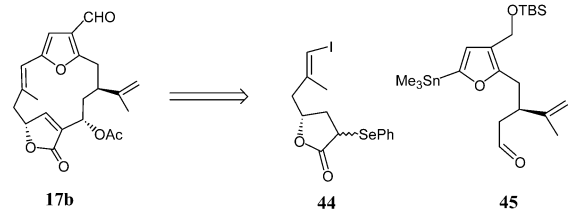


Scheme 5

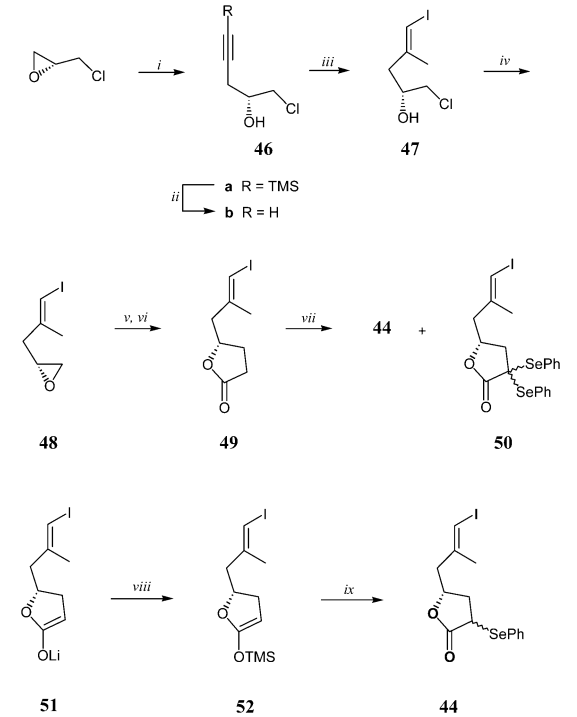
A.[24] Indeed, the scope for ketene alkyl radical species in synthesis has been subsequently developed by us and provided, *inter alia*, new syntheses of triquinanes *e.g.* pentalenene[25] and modhephene.[26] Notwithstanding these subsequent studies, it was clear that the proposed route to furanoterpenes *via* intramolecular cyclisation of α,β-unsaturated acyl radical intermediates into enone electrophores had limitations, and it was abandoned in favour of a Stille coupling approach, which is described below.

The Stille coupling reaction approach

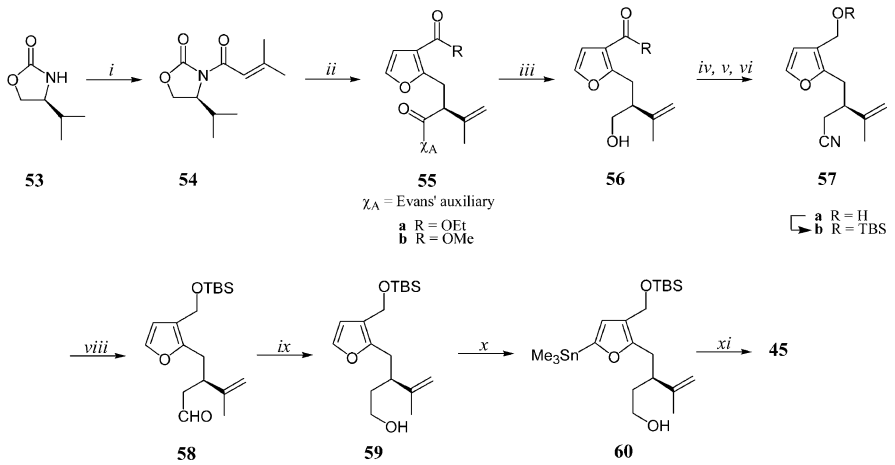
The Stille sp^2–sp^2 coupling reaction between alkene partners is one of the most revered contemporary synthetic methods.[27] The method has been applied widely in the synthesis of a range of target natural products including some from our own laboratory *e.g.* recently pateamine A, rhizoxin D, amphidinolide A.[28] Working alongside these contemporaneous investigations we designed a new approach to a synthesis of the bis-deoxylophotoxin **17b** based on sequential carbanion alkylation and Stille coupling between the enantiopure selenolactone-substituted vinyl iodide **44** and the enantiopure stannylfuran-substituted aldehyde **45**.[12]



The selenolactone **44** was synthesised from the (*R*)-epichlorohydrin[29] *via* the known (*R*)-chlorotrimethylsilylpent-4-yn-2-ol **46a**[30] in six straightforward steps as shown in Scheme 6. Thus, the silane **46a** was first deprotected to the monosubstituted acetylene **46b**. Carbometalation–iodination[31] of **46b** next gave the *E*-vinyl iodide **47**, which was smoothly converted into the corresponding epoxide **48** in the presence of NaOH. Treatment of **48** with the lithium salt of 1-ethoxyacetylene, followed by reaction with *p*-TSA, work up and chromatography next gave the enantiopure lactone **49** as an oil.[32] When the lactone **49** was deprotonated with LiHMDS and the resulting anion was quenched with phenylselenium bromide at −78 °C,[33] a 2 : 1 mixture of diastereoisomers of the α-phenylselenolactone **44** was obtained, but only in modest yield. A by-product from



Scheme 6 *Reagents and conditions*: (i) TMSC≡CH, *n*-BuLi, $BF_3{\cdot}OEt_2$, −78 °C; (ii) TBAF, HCl, THF, r.t., 42% over two steps; (iii) Me_3Al, Cp_2ZrCl_2, CH_2Cl_2, r.t., 3 days, then I_2/THF, −30 °C, 2 h, 60%; (iv) NaOH, Et_2O, r.t., 14 h, 84%; (v) 1-alkoxyacetylene, *n*-BuLi, $BF_3{\cdot}OEt_2$, 2 h; (vi) *p*-TSA, EtOH, 2 h, then $CHCl_3$, reflux, 14 h, 82% from **48**; (vii) LiHMDS, −78 °C; then PhSeBr; (viii) TMSCl, −78 °C; (ix) PhSeBr, 72% from **49**.



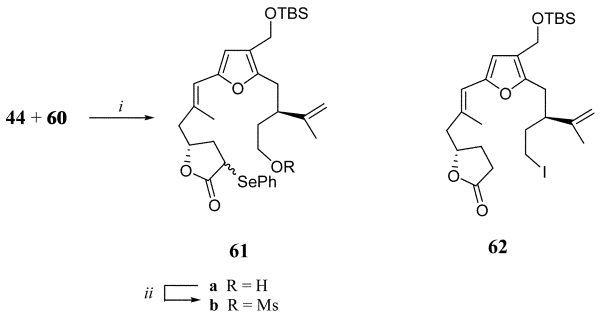
Scheme 7 *Reagents and conditions*: (i) *n*-BuLi, −78 °C, 20 min, then 3-methylbuten-2-oyl chloride, from −78 °C to r.t., 30 min, 75%; (ii) NaHMDS, 1 h, −78 °C, THF, then 1.2 equiv. of ethyl 2-bromomethyl-3-furoate, 65%; (iii) Super Hydride, toluene, −78 °C, 20 min, 80%; (iv) TsCl, Et_3N, DMAP, r.t., 75%; (v) DIBAL, CH_2Cl_2, −78 °C, 95%; (vi) *n*-Bu_4NCN, 3 equiv, DMSO, 60 °C, 90%; (vii) TBSCl, Et_3N, DMAP, r.t., 91%; (viii) DIBAL, 1.1 equiv., toluene, −78 °C to r.t., 85%; (ix) $NaBH_4$, MeOH, 0 °C, 70%; (x) *n*-BuLi, 20 min, then TMEDA for 6 h and *n*-BuLi for 20 min, r.t.; then Me_3SnCl, 0 °C to r.t. 16 h, 80%; (xi) TPAP, NMO, 4 Å molecular sieves, CH_2Cl_2, 1 h, 75%.

the reaction was the corresponding bis-selenated lactone **50**. The formation of this bis-selenated lactone **50** could be avoided completely, however, by trapping the intermediate lithium enolate **51** derived from **49** with trimethylsilyl chloride.[34] Subsequent treatment of the TMS ether **52** with phenylselenium bromide then gave the α-phenylselenolactone **44** as the sole product in 72% yield (Scheme 6).

The stannylfuran-substituted aldehyde **45** was prepared starting with the oxazolidinone **54** derived from 3-methylbutan-2-oyl chloride and the chiral oxazolidinone **53**.[35] Deprotonation of the imide **54** with NaHMDS in THF at −78 °C, followed by addition of ethyl 2-bromomethyl-3-furoate[36] first gave the adduct **55a** resulting from deconjugative alkylation (Scheme 7). The relative stereochemistry of **55a** was established from X-ray measurements on the corresponding crystalline methyl ester **55b**, mp 59–61 °C.[37] Reduction of **55a**, using two equivalents of Super Hydride produced the alcohol **56**, which was then converted into the corresponding nitrile **57a** in three straightforward steps. After protection of the alcohol **57a** as its TBS ether **57b**, the nitrile group was reduced to the aldehyde **58**, which, on further reduction with $NaBH_4$, gave the alcohol **59**. Initial attempts to deprotonate the furan ring in **59** at the C-5 position were not successful.[38] We eventually achieved this objective, however, by treating **59** with an *excess* of *n*-BuLi in the presence of TMEDA at room temperature.[39] When the resulting furyllithium species was then quenched with Me_3SnCl, the desired stannylfuran **60** was isolated in 83% yield. Oxidation of the alcohol group in **60** using TPAP[40] finally gave the stannylfuran-substituted aldehyde **45**.

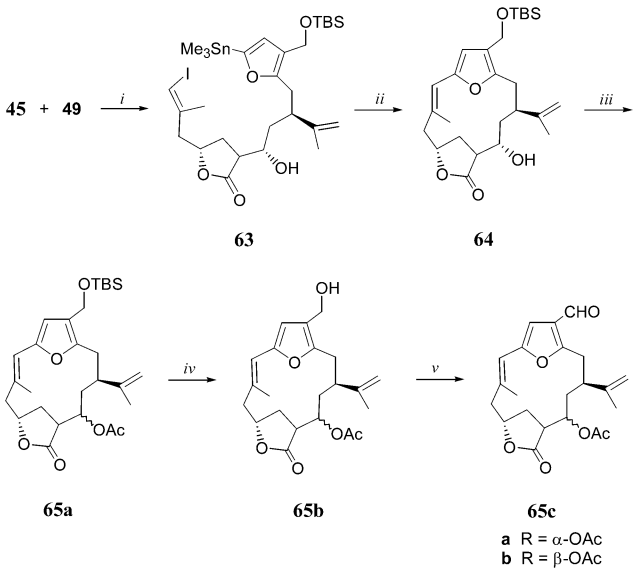
The proposed union of the stannylfuran **45** with the vinyl iodide **44** was first examined using an intermolecular Stille reaction between **60** and **44** in the presence of Pd_2dba_3–Ph_3As[41] which, gratifyingly, led to the coupled product **61a** in 55% yield (Scheme 8). With the aim of carrying out an intramolecular alkylation reaction, the alcohol **61a** was converted into the corresponding mesylate **61b**, but all attempts to induce macrocyclisation from this substrate under a variety of different conditions (solvent, base, temperature) met with failure. Similarly, we were also not able to effect macrocyclisation from the analogous lactone iodide **62** (prepared from **49** and **60**) under a variety of reaction conditions.

We then decided to combine **44** with **45** by carrying out the alkylation step first, followed by the Stille coupling reaction in an intramolecular fashion, as the final step.[42] This proposition was first modelled using the stannylfuran **45** and the lactone vinyl iodide **49** which was devoid of selenium substitution. Thus, alkylation of the anion derived from **49** using LiHMDS in THF



Scheme 8 *Reagents and conditions*: (i) $AsPh_3$, Pd_2dba_3, NMP, 40 °C, 16 h, 55%; (ii) MsCl, Et_3N, 3 h, 87%.

at −78 °C, with the aldehyde **45** gave the unstable secondary alcohol adduct **63** as an oil in 71% yield. An intramolecular Stille coupling reaction with **63**, under high dilution, then gave the furanocembrane **64** as a separable mixture of α- and β-OH epimers, in 41% yield (Scheme 9). The important feature of retention of the *E*-geometry of the trisubstituted double



Scheme 9 *Reagents and conditions*: (i) LiHMDS, −78 °C, 10 min; then **45**, 50 min, 93%; (ii) $AsPh_3$, Pd_2dba_3, 40 °C, 14 h, 10% from **64**; (iii) Ac_2O, Et_3N, DMAP, r.t., 4 h, 54%; (iv) CSA, MeOH, CH_2Cl_2, 3 h, 0 °C, 78%; (v) Dess–Martin periodinane, pyridine, CH_2Cl_2, 3 h, 0 °C, 61%.

bond in the vinyl iodide **63** during the Stille coupling was confirmed by carrying out detailed NOE experiments with the furanocembrane **64**.[43] Furthermore, acetylation of the major epimeric alcohol resulting from the macrocyclisation, followed by deprotection of the resulting TBS ether **65a** led to a single isomer of the furanylmethanol **65b**. Oxidation of the alcohol **65b** led to the corresponding aldehyde **65c**, which was obtained as a colourless crystalline solid. X-Ray crystallographic analysis of this cembrane then established its relative stereochemistry, which is shown in Fig. 1.[37]

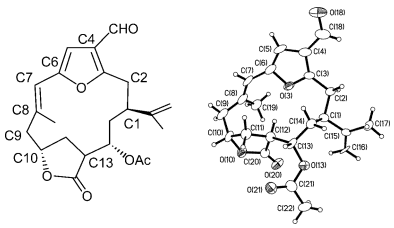
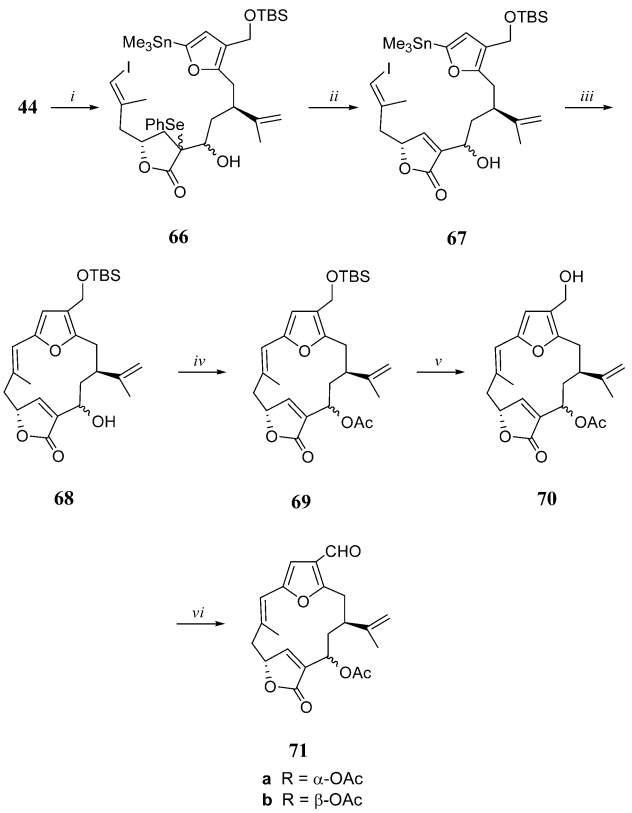


Fig. 1 X-Ray crystal structure of the furanocembrane **65c**.

With the aforementioned model studies, we next examined the same sequence of carbanion alkylation and Stille coupling reactions starting with the phenylselenyl-substituted lactone **44**. Deprotonation of the lactone **44**, using LiHMDS in THF at −78 °C, followed by addition of the aldehyde **45** gave the corresponding alkylated product **66** as a mixture of diastereoisomers in 93% yield (Scheme 10). After some optimisation of reaction conditions, to avoid significant destannylation of the sensitive stannylfuran unit in **66**/**67**, oxidative elimination of the phenylselenide residue in **66** using H_2O_2 in CH_2Cl_2–pyridine gave the butenolide **67**. An intramolecular Stille reaction with **67** under the conditions described by Farina *et al.*[41] then led to the furanocembrane **68**, which was obtained as a mixture of epimeric alcohols. Without purification, the labile furanocembrane **68** was acetylated *in situ* to give the corresponding acetate **69** as a 2.3 : 1 mixture of OAc epimers in 20% yield over two steps. Deprotection of the TBS group in **69** then gave the 3-furanylmethanol **70**, from which the major (presumed α-OAc) epimeric acetate could be separated by chromatography. Finally, oxidation of the α-acetate **70**, using Dess–Martin periodinane, gave bis-deoxylophotoxin **71a**. Corresponding oxidation of a 2 : 1 mixture of OAc epimers of **70** led to a mixture of OAc epimers of **71**. The structures of the α- and β-OAc epimers of bis-deoxylophotoxin followed from comparison of their NMR spectroscopic data with each other and with those of naturally occurring furanocembranes.



Scheme 10 *Reagents and conditions*: (i) LiHMDS, −78 °C, 10 min; then **45**, 50 min, 93%; (ii) H_2O_2, CH_2Cl_2/pyridine, 1 h; (iii) $AsPh_3$, Pd_2dba_3, 40 °C, 14 h, 20% from **66**; (iv) Ac_2O, Et_3N, DMAP, r.t., 4 h, 54%; (v) CSA, MeOH, CH_2Cl_2, 3 h, 0 °C, 78%; (vi) Dess–Martin periodinane, pyridine, CH_2Cl_2, 3 h, 0 °C, 61%.

The family of furanocembranes represented by lophotoxin **1**, pukalide **2** and bipinnatin G (**3**) are deceptively demanding targets for total synthesis. In this paper we have highlighted the scope for two quite different synthetic approaches to these targets which complement the contemporaneous synthetic work of others and notably the studies of Paquette and Marshall and their respective co-workers. Clearly there remains scope for further innovation in this area, and particularly when it comes to addressing the issue of introducing the epoxide functionalities in furanocembranes such as **1–3** in both a chemo- and stereoselective manner.

Experimental

General details

^{1}H NMR spectra were recorded on either a Varian 270 (270.13 MHz), a Bruker DPX 360 (360.13 MHz), a Bruker AV 400 (400.13 MHz), or a Bruker DRX 500 (500.12 MHz) spectrometer. Proton chemical shifts are quoted in parts per million (ppm), and spectra were referenced to residual protonated solvent (δ_H = 7.27 for $CDCl_3$). Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), bs (broad singlet) and bd (broad). Coupling constants (*J*) are quoted to the nearest 0.1 Hz. ^{13}C NMR spectra were recorded either on a Varian 270 (67.8 MHz), a Bruker DPX 360 (90.03 MHz) or a Bruker DRX 500 (125 MHz) spectrometer with complete proton decoupling. Carbon chemical shifts are quoted in parts per million (ppm) and spectra were referenced to residual protonated solvent (δ_C = 77.1 for $CDCl_3$). Assignments were made on the basis of chemical shift using the DEPT sequence with secondary pulses at 90° and 135°, where appropriate. In the spectroscopic data, C refers to quaternary carbon, CH to tertiary methine, CH_2 to secondary methylene and CH_3 to primary methyl.

Infra-red spectra were recorded using a Perkin–Elmer FT 1600 spectrometer as dilute solutions in spectroscopic grade chloroform or deuterated chloroform.

Mass spectra were recorded either on a VG Autospec, MM-701CF, or a Micromass LCT spectrometer using electro ionisation (EI), fast atom bombardment (FAB), or electrospray (ES) techniques. High-resolution mass spectra are calculated from the molecular formula corresponding to the observed signal using the most abundant isotopes of each element, to 4 decimal places.

Optical rotations were recorded on a JASCO DIP 370 polarimeter and melting points were recorded on a Stuart Scientific SMP3 melting point apparatus, and are uncorrected. Flash chromatography was carried out on Merck silica gel 60 (230–400 mesh ASTM) as the stationary phase or alumina Woelm basic (cationotropic), where indicated. Petroleum ether refers to the fraction b.p. 40–60 °C unless stated otherwise. All chemical reactions were monitored by thin layer chromatrography (TLC) using Merck silica gel 60 F_{254} precoated aluminium plates or Merck aluminium oxide F_{254} plates, which were visualised under

ultraviolet light and then developed with either basic potassium permanganate solution or acidic alcoholic vanillin solution.

Unless stated otherwise, reactions requiring anhydrous conditions were conducted under an inert atmosphere of nitrogen in flame-dried or oven-dried apparatus. When necessary, solvents were dried prior to use. Dichloromethane was either distilled from calcium hydride or was obtained in high-grade form from Fisher-Scientific. MeOH was distilled from magnesium methoxide, and ether and tetrahydrofuran from sodium metal and benzophenone ketyl. Anhydrous *N*,*N*-dimethylformamide (DMF) and 1-methyl-2-pyrrolidinone (NMP) were purchased from Aldrich.

2-Bromo-4-(*tert*-butyldimethylsilyloxy)but-2-ene 21. Imidazole (9.94 g, 146 mmol) and *tert*-butyldimethylchlorosilane (8.93 g, 59.5 mmol) were added sequentially to a stirred solution of *E*-3-bromobut-2-en-1ol (7.94 g, 52.5 mmol)[18] in dry DMF (15 mL) at room temperature. The resulting mixture was stirred at this temperature for 24 h and then poured into water (150 mL). The aqueous phase was extracted diethyl ether (3 × 150 mL) and the combined organic extracts were then washed with brine (150 mL), dried ($MgSO_4$) and evaporated *in vacuo* to leave an oil. Flash column chromatography with 1% diethyl ether in petroleum ether as eluant gave the silyl ether (13.1 g, 95%) as a colourless oil. (Found C, 45.6; H, 8.0 $C_{10}H_{21}BrOSi$ requires C, 45.4; H, 8.15); δ_H(270 MHz): 6.00 (tq, 1H, *J* 7.0 and 1.0, =C*H*CH_2OSi), 4.14 (dd, 2H, *J* 7.0 and 1.0, CH_2OSi), 2.29 (m, 3H, CH_3), 0.91 (s, 9H, SiC(CH_3)$_3$), 0.08 (s, 6H, Si(CH_3)$_2$); δ_C(67.8 MHz) 131.6 (CH), 121.7 (C), 60.2 (CH_2), 25.8 (3 × CH_3), 23.6 (CH_3), 18.2 (C), 5.3 (CH_3), −5.3 (CH_3); *m*/*z* (EI) found 208 (M^+, ^{81}Br − ^{t}Bu) (46), 206 (M^+, ^{79}Br − ^{t}Bu) (46), 185 (6), 139 (27), 137 (26), 75 (100).

(2*S*)-Methyl-4,5-epoxypentanoate 22. Potassium carbonate (11.56 g, 83.8 mmol) was added to a stirred suspension of (4*S*)-5-(*p*-toluenesufonyloxy)pent-4-olide (22.5 g, 83.8 mmol)[17] in dry methanol (200 mL) at room temperature. The mixture was stirred at this temperature for 20 h and then concentrated *in vacuo* to leave a colourless solid which was partitioned between water (150 mL) and diethyl ether (150 mL). The aqueous layer was further extracted with diethyl ether (2 × 150 mL), and the combined organic extracts were then washed in brine (100 mL), dried ($MgSO_4$) and evaporated *in vacuo* to leave a pale yellow oil. Flash chromotography with 30% diethyl ether in petroleum ether as eluent gave the *epoxide* (9.64 g, 89%) as a colourless oil. (Found C, 55.11, H, 7.90, $C_6H_{10}O_3$ requires C, 55.4; H, 7.8); $[\alpha]_D^{20}$ −16.6 (*c* 10.9 in CH_2Cl_2), lit.[17] $[\alpha]_D$ −16.3 (*c* 2.8 in CH_2Cl_2); ν_{max}/cm^{-1} (film) 1737, 1174; δ_H(270 MHz): 3.70 (s, 3H, CO_2CH_3), 3.03–2.96 (m, 1H, OC*H*CH_2CH_2), 2.79–2.76 (m, 1H, CH*H*COCH), 2.58–2.50 (m, 1H, CH*H*COCH), 2.48 (t, 2H, *J* 7.5 HZ, CH_2CO_2), 2.05–1.93 (m, 1H, CH*H*CH_2CO_2), 1.84–1.71 (m, 1H, CH*H*CH_2CO_2); δ_C(67.8 MHz): 173.2 (C), 51.6 (CH_3), 51.1 (CH), 46.9 (CH_2), 30.1 (CH_2), 27.5 (CH_2); *m*/*z* (EI) found 130.0618 (M^+), $C_6H_{10}O_3$ requires 130.0630.

(4*S*)-Methyl-4-hydoxy-6-methyl-8-(*tert*-butyldimethylsilyloxy)-oct-6-enoate 23. *t*-Butyllithium (4.52 mL, 7.70 mmol, 1.7 M in pentane) was added dropwise over 30 min to a stirred solution of the bromide **21** (1.00 g, 3.84 mmol) in dry THF (10 mL) at −78 °C. The yellow solution was stirred at −78 °C for 5 min and then added *via* cannula over 20 min to a stirred suspension of copper(I) cyanide (0.17 g, 1.93 mmol) in dry THF (10 mL) at −78 °C. The mixture was warmed to −60 °C, and boron trifluoride dietherate (0.71 mL, 11.5 mmol) was then added dropwise followed by the addition of a solution of the epoxide **22**[17] (0.75 g, 5.77 mmol) in dry THF (2 mL). The yellow solution was stirred at −60 °C for 1 h, then warmed slowly to −20 °C, and quenched with 10% ammonium hydroxide in saturated ammonium chloride solution (20 mL). The mixture was warmed to room temperature and then partitioned between water (40 mL) and diethyl ether (40 mL). The separated aqueous layer was extracted with diethyl ether (2 × 40 mL), and the combined organic extracts were then washed with brine (40 mL), dried ($MgSO_4$) and evaporated *in vacuo* to leave a yellow oil. Flash chromatography with 1% diethyl ether in CH_2Cl_2 as eluant gave the *γ-hydroxy ester* (0.5 g, 70%) as a colourless oil. (Found C, 60.7; H, 10.6, $C_{16}H_{32}O_4Si$ requires C, 60.7; H, 10.2); $[\alpha]_D^{20}$ −10.5 (*c* 1.02 in CH_2C1_2); ν_{max}/cm^{-1} (film) 3442, 2956, 2856, 1740, 776; δ_H(270 MHz): 5.48 (m, 1H, C*H*=C), 4.20 (d, 2H, *J* 6.2, CH_2OSi), 3.74 (s, 1H, C*H*OH), 3.68 (s, 3H, OCH_3), 2.49 (td, 2H, *J* 7.3 and 1.9 CH_2CO), 2.10 (m, 2H, CH_2CH_2CO), 1.66 (s, 3H, =CCH_3), 0.90 (s, 9H, SiC(CH_3)$_3$), 0.00 (s, 6H, Si(CH_3)$_2$); δ_C(67.8 MHz): 174.4 (C), 133.4 (C), 128.4 (CH), 68.0 (CH), 60.0 (CH), 51.6 (CH_3), 47.8 (CH_2), 31.8 (CH_2), 30.4 (CH_2), 25.9 (CH_3), 18.3 (CH_3), 16.4 (C), −5.2 (CH_3); *m*/*z* (EI) found 257 (M^+ − 59) (5), 243 (14), 197 (15), 185 (12), 131 (5), 117 (39), 115 (26), 101 (19), 75 (100), 55 (25), 45 (29).

(4*S*)-6-Methyl-8-(*tert*-butyldimethylsilyloxy)oct-6-en-4-olide 24. *n*-Butyllithium (0.59 mL, 0.95 mmol, 1.6 M in hexane) was added dropwise over 5 min to a stirred solution of diisopropylamine (0.12 mL, 0.95 mmol) in dry THF (5 mL) at 0 °C. The mixture was stirred at 0 °C for 20 min, then cooled to −78 °C and a solution of the hydroxy ester **23** (0.2 g, 0.63 mmol) in dry THF (1 mL) was added over 5 min. The mixture was stirred at −78 °C for 1 h and then quenched by the addition of saturated ammonium chloride solution (5 mL). The mixture was partitioned between water (10 mL) and diethyl ether (10 mL) and the aqueous layer was further extracted with diethyl ether (2 × 10 mL). The combined organic extracts were washed with brine (20 mL), dried ($MgSO_4$), and evaporated *in vacuo* to leave a yellow oil. Flash chromatography with 20% diethyl ether in petroleum ether as eluant gave the *lactone* (0.16 g, 91%) as a colourless oil. (Found C, 63.1; H, 10.0, $C_{15}H_{28}O_3Si$ requires C, 63.3, H, 9.9); $[\alpha]_D^{21}$ +33 (*c* 0.42 in CH_2Cl_2); ν_{max}/cm^{-1} (film) 1777, 836, 776; δ_H(270 MHz): 5.44–5.38 (m, 1H, C*H*=C), 4.69–4.58 (m, 1H, CO(O)C*H*), 4.21 (dd, 2H, *J* 6.0 and 1.0, CH_2OSi), 2.65–2.45 (m, 3H, CH(O)C*H*HC=C and COCH_2), 2.40–2.25 (m, 2H, CH*H*CH_2CO and CH(O)CH*H*C=C), 2.05–1.85 (m, 1H, C*H*HCH_2CO), 1.69 (d, 3H, *J* 1.0, CH_3), 0.91 (s, 9H, SiC(CH_3)$_3$), 0.08 (s, 6H, Si(CH_3)$_2$); δ_C(67.8 MHz): 177.2 (C), 131.8 (C), 128.5 (CH), 79.4 (CH), 60.1 (CH_2), 45.2 (CH_2), 28.7 (CH_2), 27.7 (CH_2), 26.0 (CH_3), 18.4 (C), 16.9 (CH_3), −5.1 (CH_3); *m*/*z* (EI) found 227 (M^+ − 57) (43), 197 (54), 181 (4), 143 (8), 85 (37), 75 (100).

(4*S*)-2-(Phenylselenyl)-6-methyl-8-(*tert*-butyldimethylsilyloxy)-oct-6-en-4-olide 19. For optimal yields, the reaction vessel was first filled with diisopropylamine and allowed to stand at room temperature for 16 h. The diisopropylamine was then poured off and the flask was washed with acetone before being oven and flame dried. *n*-Butyllithium (0.61 mL, 0.98 mmol, 1.6 M in hexane) was added dropwise over 5 min to a stirred solution of diisopropylamine (0.14 mL, 1.02 mmol) in dry THF (5 mL) at 0 °C. The solution was stirred at 0 °C for 20 min, then cooled to −78 °C and a solution of the lactone **24** (0.27 g, 0.93 mmol) in dry THF (5 mL) was added slowly, over 5 min. The mixture was stirred at −78 °C for 40 min and then a solution of phenylselenyl bromide was added *via* cannula, and the mixture was stirred at −78 °C for a further 1 h. The mixture was quenched with saturated ammonium chloride solution (10 mL) and then partitioned between water (10 mL) and diethyl ether (10 mL). The separated aqueous layer was further extracted with diethyl ether (2 × 10 mL) and the combined organic extracts were then washed with brine (20 mL), dried ($MgSO_4$), and evaporated *in vacuo* to leave a yellow oil. Chromatography with 30% diethyl ether in petroleum ether as eluant gave the *phenylselenide* (0.20 g, 50%; 92% based on recovered starting material) as a pale yellow oil, and as a 1 : 2 ratio of diastereoisomers. ν_{max}/cm^{-1} (film) 1772, 1176, 1064; δ_H(500 MHz) (minor diastereoisomer): 7.72 (m,

2H, Ar–*H*); 7.39 (m, 3H, Ar–*H*), 5.35 (t, 1H, *J* 5.8, C*H*=C), 4.57 (m, 1H, C*H*(O)), 4.20 (d, 2H, *J* 6.6, CH_2OSi), 4.05 (t, 1H, *J* 9.5, C*H*Se), 2.75 (m, 1H, CH*H*CHSe), 2.37 (m, 1H, CH*H*CHSe), 2.1 (dd, 1H, *J* 14.1 and 6.5, CH(O)C*H*HC=C), 2.02 (m, 1H, CH(O)C*H*HC=C), 1.66 (s, 3H, CH_3C=C), 0.95 (s, 9H, SiC(CH_3)$_3$), 0.11 (s, 6H, Si(CH_3)$_2$); δ_H(500 MHz) (major diastereoisomer): 7.72 (m, 2H, Ar–*H*), 7.39 (m, 3H, Ar–*H*), 5.39 (t, 1H, *J* 6.1, C*H*=C), 4.44 (m, 1H, C*H*(O)), 4.22 (d, 2H, *J* 6.2 CH_2OSi), 3.98 (dd, 1H, *J* 7.8 and 3.2, C*H*Se), 2.47 (dd, 1H, *J* 14.1 and 6.95 Hz, CH(O)CH*H*C=C), 2.37 (m, 2H, CH*H*CHSe), 2.26 (dd, 1H, *J* 14.1 and 6.3, CH(O)C*H*HC=C), 1.66 (s, 3H, CH_3C=C), 0.95 (s, 9H, SiC(CH_3)$_3$), 0.11 (s, 6H, Si(CH_3)$_2$); δ_C(125 MHz) (mixture of diastereoisomers): 175.6 (C), 136.0 (CH), 135.9 (CH), 131.3 (C), 129.5 (CH), 129.4 (CH), 129.3 (CH), 129.0 (CH), 128.8 (CH), 128.7 (CH), 126.9 (CH), 77.9 (CH_2), 60.0 (CH_2), 45.2 (CH_2), 44.9 (CH_2), 37.0 (CH), 36.6 (CH), 26.1 (CH_3), 18.5 (C), 16.9 (CH_3), −5.00 (CH_3); *m*/*z* (EI) found 383.0582 ($M^+ - {}^tBu$), $C_{17}H_{23}O_3SeSi$ requires 383.0555.

(3*RS*)-3-(Isopropenyl)pentanolide 26. *t*-Butyllithium (96.0 mL, 163 mmol) was added dropwise, over 10 min, to a stirred solution of 2-bromopropene (7.25 mL, 82.0 mmol) in dry THF (100 mL) at −78 °C, and the mixture was stirred at this temperature for 30 min. The solution was added *via* cannula over 20 min to a stirred suspension of copper(I) cyanide (3.66 g, 40.8 mmol) in dry THF (100 mL) at −78 °C. The mixture was warmed to −40 °C for 30 min and then recooled to −78 °C. A solution of commercially available 5,6-dihydro-2*H*-pyran-2-one (3.5 mL, 40.8 mmol) in dry THF (10 mL) was added dropwise *via* syringe, the mixture allowed to slowly reach −40 °C, and stirred at this temperature for a further 1 h. The mixture was warmed to 0 °C, then quenched with 10% ammonium hydroxide in saturated ammonium chloride solution (50 mL) and partitioned between water (50 mL) and diethyl ether (50 mL). The separated aqueous layer was extracted with diethyl ether (2 × 50 mL) and the combined organic extracts were then washed with brine (50 mL), dried ($MgSO_4$) and evaporated *in vacuo* to leave a yellow oil. Flash chromatography with 50% diethyl ether in petroleum ether as eluant gave the *lactone* (3.30 g, 58%) as a colourless oil. ν_{max}/cm^{-1} (film) 1736, 1646; δ_H(270 MHz): 4.84 (d, 1H, *J* 1.0, H*H*C=C), 4.75 (d, 1H, *J* 1, *H*HC=C), 4.42 (dt, 1H, *J* 4.5 and 11.0, OCH*H*), 4.27 (ddd, 1H, *J* 3.5, 10.0, and 11.5, OC*H*H), 2.71 (ddd, 1H, *J* 1.5, 5.5 and 16.5, C*H*HC=O), 2.63–2.53 (m, 1H, C*H*), 2.41 (dd, 1H, *J* 9.5 and 16.5, CH*H*C=O), 2.04–1.94 (m, 1H, CH_2CH*H*CH), 1.74 (s, 3H, CH_3), 1.85–1.60 (m, 1H, CH_2CH*H*CH); δ_C(67.8 MHz): 171.0 (C), 145.6 (C), 110.9 (CH_2), 68.4 (CH_2), 38.2 (CH), 35.2 (CH_2), 27.5 (CH_2), 20.4 (CH_3); *m*/*z* (EI) found 140.0841 (M^+), $C_8H_{12}O_2$ requires 140.0837.

(1*S*,3*R*)-*N*-(1-Methylbenzyl)-3-isopropenyl-5-hydroxypentamide and (1*S*,3*S*)-*N*-(1-methylbenzyl)-3-isopropenyl-5-hydroxypentamide 27. Trimethylaluminium (33.0 mL, 6 mmol, 2 M in hexane) was added dropwise over 5 min to a stirred solution of (*S*)-α-methylbenzylamine (8.0 mL, 62 mmol) in dry CH_2Cl_2 (250 mL) at 0 °C, and the mixture was stirred at 0 °C for 15 min and then warmed to room temperature. A solution of the lactone **26** (4.81 g, 34 mmol) in CH_2Cl_2 (20 mL) was added dropwise over 5 min and the mixture was stirred at room temperature for 16 h. The mixture was quenched by the careful addition of 2 N hydrochloric acid (25 mL), then diluted with water (200 mL) and extracted with CH_2Cl_2 (3 × 200 mL). The combined organic extracts were washed with water (150 mL), brine (150 mL), dried (MgSO4) and evaporated *in vacuo* to leave a brown oil. Flash chromatography with 40% ethyl acetate in diethyl ether as eluant gave (i) the (*S*,*R*)-diastereoisomer (3.8 g, 42%) (eluted first) as colourless needle-like crystals, mp 63–65 °C. (Found C, 73.1; H, 9.0; N, 5.5, $C_{16}H_{23}NO_2$ requires C, 73.5; H, 8.9; N, 5.4); $[\alpha]_D^{21}$ −69.2 (*c* 0.45 in CH_2Cl_2); ν_{max}/cm^{-1} (film) 3300, 1644; δ_H(270 MHz): 7.28–7.14 (m, 5H, Ar–*H*), 6.09 (d, 1H, *J* 6.5, N*H*), 5.02 (d, 1H, *J* 7, CH_3CH), 4.72 (s, 2H, H_2C=C), 3.48 (t, 2H, *J* 6.5, CH_2OH), 2.68 (d, 2H, *J* 7.5, CH_2CH$_2$OH), 2.19 (d, 2H, *J* 7.5, CH_2CO), 1.65–1.45 (m, 1H, CH$_2$C*H*CH$_2$), 1.61 (s, 3H, CH_3C=C), 1.37 (d, 3H, *J* 7.0, CH_3CH); δ_C(67.8 MHz): 171.3 (C), 146.7 (C), 143.1 (C), 128.5 (CH), 127.1 (CH), 126.1 (2 × CH), 112.1 (CH_2), 60.1 (CH_2), 48.6 (CH), 45.2 (CH_2), 40.5 (CH_2), 40.3 (CH), 35.7 (CH_2), 21.6 (CH_3), 19.0 (CH_3); *m*/*z* (ES) 261 (M^+) (26), 243 (72), 228 (100), 216 (14), 161 (23), 120 (30), 105 (83); and (ii) the (*S*,*S*)-diastereoismer (3.50 g, 39%) (eluted second) as a pale yellow oil. (Found C, 73.3; H, 9.2; N, 5.47); $[\alpha]_D^{21}$ −82.7 (*c* 0.36 in CH_2Cl_2); ν_{max}/cm^{-1} (film) 3300, 1645; δ_H(270 MHz): 7.28–7.14 (m, 5H, Ar–*H*), 6.09 (d, 1H, *J* 7.0, N*H*), 5.02 (d, 1H, *J* 7.0, CH_3CH), 4.71 (s, 2H, H_2C=C), 3.51 (t, 2H, *J* 6.5, CH_2OH), 2.67 (d, 2H, *J* 7.0, CH_2CH$_2$OH), 2.20 (d, 2H, *J* 7.5, CH_2CO), 1.70–1.45 (m, 1H, CH$_2$C*H*CH$_2$), 1.59 (s, 3H, CH_3C=C), 1.38 (d, 3H, *J* 7.0, CH_3CH); δ_C(67.8 MHz): 171.3 (C), 146.7 (C), 143.1 (C), 128.5 (CH), 127.1 (CH), 126.1 (2 × CH), 112.1 (CH_2), 60.1 (CH_2), 48.6 (CH), 45.2 (CH_2), 40.6 (CH_2), 40.3 (CH), 35.7 (CH_2), 21.6 (CH_3), 19.0 (CH_3); *m*/*z* (EI) found 261.1723 (M^+), $C_{16}H_{23}NO_2$ requires 261.1729.

(3*S*)-3-(Isopropenyl)pentan-5-olide 28. A solution of the amide **27** (2.55 g, 9.77 mmol) and pyridinium *p*-toluenesulfonate (2.00 g, 8.0 mmol) in dry toluene (75 mL) was heated under reflux for 16 h. The mixture was cooled to room temperature and the solvent was then removed *in vacuo*. The residue was purified by flash chromatography with 60% diethyl ether in petroleum ether as eluant to give the lactone (1.14 g, 85%) as a colourless oil. (Found C, 68.3; H, 8.9, $C_8H_{12}O_2$ requires: C, 68.5; H, 8.6); $[\alpha]_D^{21}$ −15.7 (*c* 1.5 in CH_2Cl_2); ν_{max}/cm^{-1} (film) 2969, 1738; δ_H(270 MHz): 4.87 (d, 1H, *J* 1.0, H*H*C=C), 4.77 (d, 1H, *J* 1.0, *H*HC=C), 4.44 (dt, 1H, *J* 4.5 and 11.0, OCH*H*), 4.29 (ddd, 1H, *J* 3.5, 10.0, and 11.5, OC*H*H), 2.73 (ddd, 1H, *J* 1.5, 5.5 and 16.5, C*H*HC=O), 2.65–2.54 (m, 1H, C*H*), 2.43 (dd, 1H, *J* 9.5 and 16.5, C*H*HC=O), 2.06–1.97 (m, 1H, CH_2CH*H*CH), 1.76 (s, 3H, CH_3), 1.85–1.71 (m, 1H, CH_2C*H*HCH); δ_C(67.8 MHz): 171.0 (C), 145.6 (C), 110.9 (CH_2), 68.4 (CH_2), 38.2 (CH), 35.2 (CH_2), 27.5 (CH_2), 20.4 (CH_3); *m*/*z* (EI) found 140.0846 (M^+), $C_8H_{12}O_2$ requires 140.0837.

3-(Isopropenyl)tetrahydropyran-2-ol 29. Diisobutylaluminium hydride (5.70 mL, 1.5 M in toluene, 8.57 mmol) was added dropwise over 5 min to a stirred solution of the lactone **28** (1.09 g, 7.77 mmol) in dry tetrahydrofuran (100 mL) at −78 °C, and the mixture was stirred at this temperature for 30 min. The mixture was warmed to room temperature and then quenched by the addition of methanol (40 mL). The resulting mixture was stirred at room temperature for 1 h, then magnesium sulfate (6.00 g), was added and the stirring was continued for a further 2 h. The mixture was filtered and the residue was washed with ethyl acetate (3 × 50 mL). The combined organic extracts were evaporated *in vacuo* to leave an oil. Flash chromatography with 10% ethyl acetate in CH_2Cl_2 as eluant gave the *lactol* (0.97 g, 88%) as a colourless oil consisting of a mixture of inseparable diastereoisomers. ν_{max}/cm^{-1} (film) 3387, 1645; δ_H(270 MHz): 5.30 (bd, 0.5H, *J* 2.5, OC*H*O); 4.76–4.71 (m, 2.5H, 2 × CH_2 =C and 0.5H × OC*H*O), 4.13–4.01 (m, 1H, OC*H*H), 3.67 (ddd, 0.5H, *J* 11, 4.5 and 2, OCH*H*), 3.54 (app. dt, *J* 9.0 and 2.5, OCH*H*), 3.44 (bs, 0.5H, CHO*H*), 2.85 (bs, 0.5H, CHO*H*), 2.55 (app. tt, 0.5H, *J* 12.0 and 3.5, CH$_2$C*H*CH$_2$), 2.20 (app. tt, 0.5H, *J* 12.0, and 3.5, CH$_2$C*H*CH$_2$), 1.99 (app. ddt, 0.5H, *J* 13.0, 3.5 and 2.0, OCH$_2$CH*H*), 1.85 (app. ddt, 0.5H, *J* 13, 3.5 and 2.0, OCH$_2$CH*H*), 1.73 (s, 3H, CH_3), 1.21–1.70 (m, 3H, CH$_2$CHC*H*H); δ_C(67.8 MHz): 148.6 (C), 147.6 (2 × C), 109.3 (CH_2), 108.8 (CH_2), 96.2 (CH), 91.3 (CH), 65.4 (CH_2), 59.5 (CH_2), 41.4 (CH), 37.8 (CH_2), 35.2 (CH), 35.1 (CH_2), 30.7 (CH_2), 30.1 (CH_2), 20.5 (CH_3), 20.4 (CH_3); *m*/*z* (%) 142 (M+, 2), 124 (95), 98 (32), 81 (100), 69 (88), 55 (69); *m*/*z* (EI) found 142.1023 (M^+), $C_8H_{14}O_2$ requires 142.0994.

(5*S*)-2-Methylene-5-(isopropenyl)hepta-1,3,7-triol 30. *t*-Butyllithium (23.5 mL, 40 mmol, 1.7 M in pentane) was added

dropwise, over 5 min, to a stirred solution of 2-bromoprop-2-en-1-ol (1.81 g, 13.2 mmol)[20] in diethyl ether (110 mL) at −78 °C and the mixture was warmed to 0 °C and then stirred at this temperature for a further 2 h. A solution of the lactol **29** (374 mg, 2.63 mmol) in diethyl ether (5 mL) was added dropwise over 2 min, and the mixture was stirred at 0 °C for 2 h, then warmed to room temperature and stirred for 24 h. The mixture was quenched with methanol (1 mL), followed by water (20 mL), and then extracted continuously with ethyl acetate for 72 h. The organic extract was dried ($MgSO_4$) and evaporated *in vacuo* to leave a pale yellow oil. Flash chromatography with 30% petroleum ether in ethyl acetate as eluant gave the *triol* (339 mg, 64%) as a colourless oil consisting of an inseparable mixture of diastereoisomers. ν_{max}/cm^{-1} (film) 3348, 1644; δ_H(270 MHz): 5.17–5.08 (m, 2H, H_2C=C), 4.85–4.77 (m, 2H, H_2C=CCH_3), 4.29–4.08 (m, 3H, =CCH_2OH and C*H*OH), 3.71–3.50 (m, 2H, CH_2OH), 3.40–2.70 (bs, 3H, 3 × O*H*), 2.66–2.53 (m, 0.4H, CH_2CHCH_2), 2.37–2.29 (m, 0.6H, CH_2CHCH_2), 1.80–1.59 (m, 7H, 2 × CH_2 and CH_3); δ_C(67.8 MHz): 150.6 (C), 149.1 (C), 147.4 (C), 146.7 (C), 113.2 (CH_2), 113.0 (CH_2), 112.3 (CH_2), 111.5 (CH_2), 72.6 (CH), 71.6 (CH), 63.7 (CH_2), 63.3 (CH_2), 60.6 (CH_2), 40.3 (CH), 40.2 (CH), 39.0 (CH_2), 38.7 (CH_2), 36.2 (CH_2), 35.3 (CH_2), 18.2 (CH_3), 17.8 (CH_3).

(3*S*)-Isopropenyl-5,7-0-benzylidene-6-methylene heptanol 31. Benzaldehyde acetal (0.19 mL, 1.2 mmol) and pyridinium *p*-toluene sulfonate (0.08 g, 0.32 mmol) were added to a stirred solution of the triol **30** (0.26 g, 1.31 mmol) in dry benzene (20 mL), and the mixture was heated under reflux for 2 h. The solvent was removed *in vacuo* to leave a pale yellow oil. Flash chromatography with 60% diethyl ether in petroleum ether as eluant gave the *acetal* (0.34 g, 64%) as a colourless oil consisting of a mixture of inseparable diastereoisomers. (Found C, 75.0; H, 8.4, $C_{18}H_{24}O_3$ requires C, 75.0; H, 8.4); ν_{max}/cm^{-1} (film) 3418, 1644; δ_H(270 MHz): 7.53–7.49 (m, 2H, Ar–*H*), 7.43–7.34 (m, 3H, Ar–*H*), 5.71 (s, 0.4H, C*H*Ph), 5.65 (s, 0.6H, C*H*Ph), 5.05–4.98 (m, 2H, H_2C=C), 4.92–4.82 (m, 2H, H_2C=CCH_3), 4.50 (s, 2H, CH_2OCHPh), 4.35 (t, 0.4 H, *J* 6.0, C*H*OCHPh), 4.26 (d, 0.6 H, *J* 10.0, C*H*OCHPh, one isomer), 3.68–3.52 (m, 2H, CH_2OH), 2.78–2.66 (m, 0.6 H, CH_2CHCH_2), 2.61–2.50 (m, 0.4 H, CH_2CHCH_2), 1.96–1.55 (m, 7H, 2 × CH_2 and CH_3); δ_C(67.8 MHz): 147.5 (C), 146.3 (C), 142.4 (C), 142.1 (C), 138.1 (C), 128.7 (CH), 128.2 (CH), 128.1 (2 × CH), 126.2 (CH), 126.0 (2 × CH), 125.9 (CH), 113.1 (CH_2), 112.0 (CH_2), 109.3 (CH_2), 108.7 (CH_2), 101.1 (CH), 101.0 (CH), 76.2 (CH), 75.5 (CH), 72.0 (CH_2), 71.8 (CH_2), 61.2 (CH_2), 61.1 (CH_2), 40.1 (CH), 39.2 (CH), 36.5 (CH_2), 35.2 (CH_2), 35.1 (CH_2), 34.2 (CH_2), 18.5 (CH_3), 17.7 (CH_3); *m*/*z* (%) 288 (M^+, 1), 257 (8), 188 (23), 182 (37), 175 (90), 105 (100); *m*/*z* (EI) found 288.1787 (M^+), $C_{18}H_{24}O_3$ requires 288.1726.

(3*S*)-3-Isopropenyl-5,7-*O*-benzylidene-6-(methylene)heptanal 20. Dimethyl sulfoxide (0.21 mL, 2.84 mmol) was added dropwise over 5 min to a stirred solution of oxalyl chloride (0.13 mL, 1.42 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C. The mixture was stirred at this temperature for a further 5 min before it was cooled to −78 °C and a solution of the alcohol **31** (0.21 g, 0.71 mmol) in dry CH_2Cl_2 (2 mL) was then added dropwise over 1 min. The mixture was stirred at −78 °C for 2 h and then quenched by the addition of triethylamine (0.96 mL, 9.28 mmol) at −78 °C and subsequently warmed to room temperature. The mixture was diluted with CH_2Cl_2 (30 mL) and washed with water (50 mL). The aqueous layer was further extracted with CH_2Cl_2 (2 × 30 mL) and the combined organic extracts were then washed with brine (30 mL), dried ($MgSO_4$), and evaporated *in vacuo* to leave a yellow-brown oil. Flash chromatography with 50% diethyl ether in petroleum ether as eluant gave the *aldehyde* (0.19 g, 95%) as a colourless oil, consisting of an inseparable mixture of diastereoisomers. (Found C, 75.4; H, 8.9, $C_{18}H_{22}O_3$ requires C, 75.5; H, 7.7); ν_{max}/cm^{-1} (film) 2836, 1723, 1645; δ_H(270 MHz): 9.68 (t, 0.5H, *J* 2.5, C*H*O), 9.65 (t, 0.5H, *J* 2.5, C*H*O), 7.51–7.48 (m, 2H, Ar–*H*), 7.41–7.35 (m, 3H, Ar–*H*), 5.66 (s, 0.5H, C*H*Ph), 5.65 (s, 0.5H, C*H*Ph), 5.07–499 (m, 2H, H_2C=C), 4.93–4.84 (m, 2H, H_2C=CCH_3), 4.49 (s, 2H, CH_2OCHPh), 4.35–4.27 (m, 1H, C*H*OCHPh), 3.29–3.15 (m, 0.5H, CH_2CHCH_2), 2.97–3.09 (m, 0.5H, CH_2CHCH_2), 2.60–2.48 (m, 2H, CH_2CHO), 2.01–1.71 (m, 5H, CH_2 and CH_3); δ_C(67.8 MHz): 202.2 (CH), 202.0 (CH), 146.6 (C), 144.9 (C), 142.0 (C), 141.7 (C), 138.1 (C), 138.0 (C), 128.8 (CH), 128.2 (2 × CH), 126.3 (2 × CH), 126.2 (CH), 126.1 (CH), 126.0 (CH), 113.6 (CH_2), 112.0 (CH_2), 109.4 (CH_2), 108.8 (CH_2), 101.2 (CH), 101.1 (CH), 75.5 (CH), 75.3 (CH), 71.9 (CH_2), 71.8 (CH_2), 47.7 (CH_2), 46.9 (CH_2), 37.0 (CH), 34.9 (CH_2), 34.3 (CH_2), 19.9 (CH_3), 18.4 (CH_3); *m*/*z* (%) 286 (M^+, 1), 243 (5), 188 (17), 180 (29), 175 (69), 137 (29), 105 (100), 91 (46), 77 (52); *m*/*z* (EI) found 286.1535 (M^+), $C_{18}H_{22}O_3$ requires 286.1569.

5-[(2*E*)-4-(*tert*-Butyldimethylsilyloxy)-2-methylbut-2-enyl]-3-{(3*S*)-1-hydroxy-4-methyl-3-[(5-methylene-2-phenyl-1,3-dioxan-4-yl)methyl]pent-4-enyl}-3-(phenylseleno)dihydrofuran-2(3*H*)-one 32. *n*-Butyllithium (0.45 mL, 0.72 mmol, 1.6 M in hexane) was added dropwise over 5 min to a stirred solution of diisopropylamine (0.1 mL, 0.75 mmol) in dry THF (10 mL) at −10 °C and the mixture was stirred at this temperature for 30 min, then cooled to −78 °C. A solution of the lactone **19** (0.3 g, 0.68 mmol) in dry THF (3 mL) was added dropwise over 5 min, and the mixture was stirred at −78 °C for 1 h before a solution of the aldehyde **20** (0.22 g, 0.75 mmol) in dry THF (3 mL) was added dropwise over 5 min. The solution was stirred at −78 °C for 1 h, then quenched at −78 °C by the addition of saturated ammonium chloride solution (2 mL). The mixture was warmed to room temperature and then partitioned between water (10 mL) and diethyl ether (10 mL). The aqueous layer was further extracted with diethyl ether (2 × 10 mL) and the combined organic extracts were dried ($MgSO_4$), and evaporated *in vacuo* to leave a pale yellow oil. Flash chromatography with 2.5% diethyl ether in CH_2Cl_2 as the eluant gave the *aldol* product (0.29 g, 60%) as a colourless oil consisting of an inseparable mixture of diastereoisomers. ν_{max}/cm^{-1} (film) 3470, 1757, 1644; δ_H(500 MHz): 7.67 (m, 2H, *H*–Ph), 7.49 (m, 2H, *H*–Ph), 7.38 (m, 1H, *H*–PhSe), 7.35 (m, 5H, 3 × *H*–Ph and 2 × *H*–PhSe), 5.70 (s, 0.35H, C*H*Ph), 5.69 (s, 0.07H, C*H*Ph), 5.64 (s, 0.64H, C*H*Ph), 5.64 (s, 0.07H, C*H*Ph), 5.30 (m, 0.41H, =$CHCH_20Si$), 5.23 (m, 0.59H, =$CHCH_20Si$), 5.04–4.80 (m, 4H, CH_2=C and CH_2=$C(CH_3)$), 4.49 (m, 3H, CH_2(O)CHPh and C*H*(O)CO), 4.39–4.33 (m, 0.37H, C*H*(O)CHPh), 4.25 (app. d, 0.63H, *J* 9.8, C*H*(O)CHPh), 4.19 (2 × d, 2H, *J* 5.9, CH_2OSi), 3.95 (m, 0.3H, C*H*OH), 3.77 (app. t, 0.7H, *J* 11.6, C*H*OH), 2.90 (m, 0.6H, CH_2CHCH_2), 2.81–2.53 (m, 2.4H, 2 × H, CH_2CHSe and 0.4 × H CH_2CHCH_2), 2.37–2.02 (m, 2H, $CH_2C(CH_3)$=C), 1.98–1.70 (m, 2H, HOCHCH*H* and CH*H*CH(O)CHPh), 1.63 (m, 2H, HOCHC*H*H and C*H*HCH(O)CHPh), 1.58 (s, 3H, CH_3C=C), 1.57 (s, 3H, CH_3C=C), 0.92 (s, 9H, $SiC(CH_3)_3$), 0.08 (s, 6H, $Si(CH_3)_2$); δc(67.8 MHz): 176.7 (C), 176.5 (C), 146.4 (C), 144.9 (C), 142.2 (C), 141.9 (C), 138.2 (C), 138.1 (C), 137.8 (CH), 131.2 (CH), 129.8 (CH), 129.2 (CH), 128.6 (CH), 128.5 (CH), 128.1 (CH), 126.1 (CH), 126.0 (CH), 114.3 (CH_2), 112.9 (CH_2), 109.3 (CH_2), 108.7 (CH_2), 101.1 (CH), 101.0 (CH), 76.3 (CH), 76.2 (CH), 75.7 (CH), 72.0 (CH), 71.9 (CH_2), 71.8 (CH_2), 71.6 (CH_2), 71.5 (CH), 59.9 (CH_2), 55.6 (C), 55.5 (C), 53.4 (C), 45.3 (CH_2), 39.9 (CH), 39.3 (CH), 36.1 (CH_2), 35.6 (CH_2), 35.4 (CH_2), 35.1 (CH_2), 34.7 (CH_2), 34.6 (CH_2), 25.8 (CH_3), 18.3 (CH_3), 18.2 (C), 17.2 (CH_3), 16.6 (CH_3), −0.5 (CH_3); *m*/*z* FAB found (%) 725 (M^+ + 1, 0.3), 579 (1.5), 526 (16), 490 (2), 489 (9), 487 (5), 313 (6), 181 (17), 137 (22), 73 (100), 55 (85); *m*/*z* (EI) found 725.2914 (M^+), $C_{35}H_{55}O_6SeSi$ requires 725.2941.

5-[(2*E*)-4-(*tert*-Butyldimethylsilyloxy)-2-methylbut-2-enyl]-3-{(3*S*)-1-hydroxy-4-methyl-3-[(5-methylene-2-phenyl-1,3-dioxan-4-yl)methyl]pent-4-enyl}furan-2(5*H*)-one 33a. Hydrogen peroxide (1.08 mL, 100 vol.) was added dropwise over 5 min to a

stirred solution of the selenide **32** (0.6 g, 0.28 mmol) in THF (20 mL) containing water (1.4 mL), at 0 °C. The mixture was stirred at 0 °C for 30 min and then warmed to room temperature and stirred for 2 h. Saturated sodium hydrogen carbonate (10 mL) was added and the mixture was stirred vigorously for 30 min before being partitioned between water (30 mL) and diethyl ether (30 mL). The separated aqueous layer was extracted with diethyl ether (2 × 30 mL) and the combined organic extracts were dried ($MgSO_4$), and evaporated *in vacuo* to leave a pale yellow oil. Flash chromatography with 10% petroleum ether in diethyl ether as eluant gave the *butenolide* (0.45 g, 96%) as a colourless oil consisting of an inseparable mixture of diastereoisomers. ν_{max}/cm^{-1} (film) 3461, 1754, 1644; δ_H(500 MHz): 7.49 (m, 2H, Ar–*H*), 7.36 (m, 3H, Ar–*H*), 7.19 (m, 1H, C*H*=CCO(O)), 5.87 (s, 0.33H, CHPh), 5.70 (s, 0.11 H, CHPh), 5.69 (s, 0.44H, CHPh), 5.65 (s, 0.11H, C*H*Ph), 5.42 (app. t, 0.8H, *J* 5.8, =C*H*CH_2OSi), 5.38 (app. t, 0.2H, *J* 5.6, =C*H*CH_2OSi), 5.03–4.84 (m, 5H, CH_2C=C, CH_2C(CH_3)=C and C*H*(O)CO), 4.49 (m, 2H, CH_2(O)CHPh), 4.42 (m, 0.6H, C*H*(O)CHPh), 4.27 (app. d, 0.4H, *J* 10.6, C*H*(O)CHPh), 4.21 (app. d, 2H, *J* 6.1, CH_2OSi), 3.95 (m, 1H, C*H*OH), 2.93 (m, 0.67H, CH_2CHCH_2), 2.80 (m, 0.33H, CH_2CHCH_2), 2.32 (m, 2H, $CH_2C(CH_3)$=C), 1.93 (m, 2H, CH_2CHOH), 1.77 (m, 2H, CH_2CH(O)CHPh), 1.73 (s, 3H, CH_3C=C), 1.70 (s, 3H, CH_3C=C), 0.91 (s, 9H, SiC(CH_3)), 0.08 (s, 6H, Si(CH_3)$_2$); δ_C(67.8 MHz): 172.0 (C), 148.0 (CH), 147.1 (C), 145.2 (C), 142.2 (C), 141.9 (C), 138.2 (C), 138.1 (C), 137.1 (C), 137.0 (C), 130.9 (C), 130.8 (C), 128.9 (2 × CH), 128.6 (CH), 128.1 (CH), 128.0 (CH), 126.0 (CH), 125.9 (CH), 114.2 (CH_2), 112.8 (CH_2), 109.2 (CH_2), 108.7 (CH_2), 101.1 (CH), 100.9 (CH), 80.2 (CH), 75.9 (CH), 75.5 (CH), 71.8 (CH_2), 71.7 (CH_2), 65.2 (CH), 65.1 (CH), 59.9 (CH_2), 43.2 (CH_2), 42.9 (CH_2), 39.2 (CH), 39.1 (CH_2), 38.7 (CH), 37.3 (CH_2), 35.2 (CH_2), 35.1 (CH_2), 34.4 (CH_2), 25.9 (CH_3), 25.6 (CH_3), 18.4 (CH_3), 18.2 (C), 17.6 (CH_3), 17.4 (CH_3), 16.9 (CH_3), −5.2 (CH_3).

(3*R*)-1-{5-[(2*E*)-4-(*tert*-Butyldimethylsilyloxy)-2-methylbut-2-enyl]-2-oxo-2,5-dihydrofuran-3-yl}-4-methyl-3-[(5-methylene-2-phenyl-1,3-dioxan-4-yl)methyl]pent-4-enyl acetate 33b. Triethylamine (0.013 mL, 0.092 mmol), DMAP (1.0 mg, 8 × 10^{-3} mmol) and acetic anhydride (0.013 mL, 0.1 mmol) were added sequentially to a stirred solution of the alcohol **33a** (43.7 mg, 0.077 mmol) in dry CH_2Cl_2 (2 mL) at 0 °C, and the mixture was stirred at this temperature for 3 h. The solvent was removed *in vacuo* to leave a yellow-brown oil. Flash chromatography with 50% diethyl ether in petroleum ether as eluant gave the *acetate* (37.7 mg, 80%) as a colourless oil consisting of an inseparable mixture of diastereoisomers. ν_{max}/cm^{-1} (film) 1757, 1644; δ_H(500 MHz): 7.50 (m, 2H, Ar–*H*), 7.35 (m, 3H, Ar–*H*), 7.15 (app. dt, 0.22H, *J* 10.5 and 1.3, C*H*=CCO(O)), 7.09 (app. dt, 0.78H, *J* 11.3 and 1.4, C*H*=CCO(O)), 5.70 (s, 0.25H, C*H*Ph), 5.69 (s, 0.13H, C*H*Ph), 5.65 (s, 0.5H, C*H*Ph), 5.61 (s, 0.13H, C*H*Ph), 5.50 (m, 0.33H, C*H*(O)CO), 5.40 (m, 0.66H, C*H*(O)CO), 5.39 (m, 1H, =C*H*$CH_2$0Si), 5.02–4.71 (m, 5H, CH_2=CCH_3, CH_2=C and C*H*OAc), 4.48 (m, 2H, CH_2(O)CHPh), 4.35 (m, 0.33H, C*H*(O)CHPh), 4.25 (app. d, 0.66H, *J* 10.6, C*H*(O)CHPh), 4.20 (app. d, 2H, *J* 5.1, CH_2OSi), 2.79 (tt, 0.66H, *J* 11.2 and 7.3, CH_2CHCH_2), 2.77 (m, 0.33H, CH_2CHCH_2), 2.39–2.24 (m, 2H, $CH_2C(CH_3)$=), 2.03 (m, 1H, AcOCHCH*H*), 2.03 and 2.00 (2 × s (1:2), 3H, CH_3CO), 1.90 (m, 1H, CH*H*CH(O)CHPh), 1.75 (m, 2H, AcOCHC*H*H and C*H*HCH(O)CHPh), 1.73 (s, 3H, CH_3C=C), 1.67 (s, 3H, CH_3C=C), 0.90 (s, 9H, SiC(CH_3)$_3$), 0.08 (s, 6H, Si(CH_3)$_2$); δ_C(67.8 MHz): 170.7 (C), 169.7 (C), 149.1 (CH), 148.8 (CH), 146.1 (CH), 144.3 (C), 142.3 (C), 142.2 (C), 142.1 (C), 138.4 (C), 138.3 (C), 133.9 (C), 133.7 (C), 130.7 (2 × C), 129.1 (CH), 128.8 (CH), 128.6 (CH), 128.2 (CH), 128.1 (CH), 126.2 (CH), 126.1 (2 × CH), 126.0 (CH), 125.9 (CH), 114.7 (CH_2), 112.8 (CH_2), 109.2 (CH_2), 108.7 (CH_2), 101.1 (CH), 100.9 (CH), 79.9 (CH), 77.5 (CH), 75.4 (CH), 71.9 (CH_2), 71.8 (CH_2), 67.6 (CH), 67.5 (CH), 59.9 (CH_2), 42.0 (CH_2), 39.6 (CH), 39.5 (CH), 38.9 (2 × CH), 38.8 (CH), 36.4 (CH_2), 35.3 (CH_3), 35.1 (CH_2), 34.4 (CH_3), 34.3 (CH_2), 25.9 (CH_3), 25.6 (CH_3), 20.7 (CH_3), 18.6 (C), 18.3 (CH_3), 17.3 (CH_3), 17.0 (CH_3), −5.2 (CH_3); *m*/*z* (%) FAB 611 (M^+ + 1, 0.5), 553 (4), 505 (5), 373 (6), 313 (16), 295 (17), 227 (11), 175 (21), 154 (20), 145 (11), 136 (27), 105 (38), 73 (100); *m*/*z* (EI) found 611.3428 (M^+), $C_{35}H_{49}O_6Si$ requires 611.3404.

(3*R*)-1-{5-[(2*E*)-4-Hydroxy-2-methylbut-2-enyl]-2-oxo-2,5-dihydrofuran-3-yl}-4-methyl-3-[(5-methylene-2-phenyl-1,3-dioxan-4-yl)methyl]pent-4-enyl acetate 34a. Dry methanol (7.3 × 10^{-3} mL, 0.18 mmol) and pyridinium *p*-toluenesulfonate (4.1 × 10^{-3} g, 0.016 mmol) were added to a stirred solution of the silyl ether **33b** (0.1 g, 0.16 mmol) in dry benzene (0.5 mL) at room temperature and the mixture was stirred for three days and then evaporated to dryness *in vacuo*. The residue was purified by flash chromatography with 20% diethyl ether in CH_2Cl_2 as eluant to give the *alcohol* (41 mg, 50%; 84% based on recovered starting material) as a colourless oil consisting of an inseparable mixture of diastereoisomers. ν_{max}/cm^{-1} (film) 3478, 1747, 1731, 1643; δ_H(500 MHz): 7.50 (m, 2H, Ar–*H*), 7.35 (m, 3H, Ar–*H*), 7.04 (app. d, 1H, *J* 10.8, C*H*=CCO(O)), 5.70 (s, 0.22H, C*H*Ph), 5.69 (s, 0.11H, C*H*Ph), 5.65 (s, 0.56H, C*H*Ph), 5.62 (s, 0.11H, C*H*Ph), 5.40 (m, 2H, =C*H*CH_2OH and C*H*(O)CO), 5.06–4.76 (m, 5H, CH_2=CCH_3, CH_2=C and C*H*OAc), 4.49 (m, 2H, CH_2(O)CHPh), 4.36 (m, 0.25H, C*H*(O)CHPh), 4.25 (app. d, 0.75H, *J* 10.8, C*H*(O)CHPh), 4.12 (m, 2H, CH_2OH), 2.81 (tt, 0.7H, *J* 11.3 and 4.1, CH_2CHCH_2), 2.64 (m, 0.3H, CH_2CHCH_2), 2.38 (m, 2H, $CH_2C(CH_3)$=), 2.07 (m, 1H, AcOCHCH*H*), 2.07 and 2.05 (2 × s (1 : 2), 3H, CH_3CO), 1.91 (m, 1H, CH*H*CH(O)CHPh), 1.73 (m, 2H, AcOCHC*H*H and C*H*HCH(O)CHPh), 1.73 (s, 3H, CH_3C=C), 1.69 (s, 3H, CH_3C=C); δ_C(67.8 MHz): 170.7 (C), 170.2 (C), 148.5 (CH), 148.3 (CH), 146.0 (C), 144.3 (C), 142.3 (C), 138.4 (C), 134.2 (C), 132.5 (C), 128.7 (2 × CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 126.0 (CH), 125.9 (CH), 114.8 (CH_2), 113.1 (CH_2), 109.2 (CH_2), 108.8 (CH_2), 101.0 (CH), 80.1 (CH), 75.6 (CH), 75.4 (CH), 71.9 (CH_2), 71.8 (CH_2), 67.8 (CH), 59.0 (CH), 42.4 (CH_2), 39.0 (CH), 38.9 (CH), 36.4 (CH_2), 35.2 (CH_2), 34.2 (CH_2), 20.7 (CH_3), 18.5 (CH_3), 17.3 (CH_3), 17.2 (CH_3); *m*/*z* (%) FAB 497 (M^+ + 1, 9), 391 (26), 331 (3), 307 (24), 227 (8), 154 (100); *m*/*z* (EI) found 497.2577 (M^+), $C_{29}H_{37}O_7$ requires 497.2539.

(3*R*)-4-Methyl-3-[(5-methylene-2-phenyl-1,3-dioxan-4-yl)-methyl]-1-{5-[(2*E*)-2-methyl-4-oxobut-2-enyl]-2-oxo-2,5-dihydrofuran-3-yl}pent-4-enyl acetate 34b. Dess–Martin periodinane (0.162 g, 0.38 mmol) was added to a stirred solution of the allyl alcohol **34a**. (0.127 g, 0.26 mmol) in dry CH_2Cl_2 (2.5 mL) at 0 °C, and the mixture was stirred at 0 °C for 5 min, then warmed to room temperature and stirred for 1.5 h. The solvent was removed *in vacuo* to leave a colourless solid. Flash chromatography with 20% diethyl ether in CH_2Cl_2 as eluant gave the *aldehyde* (0.121 g, 93%) as a colourless, viscous oil consisting of an inseparable mixture of diastereoisomers. ν_{max}/cm^{-1} (film) 1755, 1673; δ_H(500 MHz): 9.99 (d, 0.4H, *J* 7.8, C*H*O), 9.98 (d, 0.6H, *J* 7.7, C*H*O), 7.49 (m, 2H, Ar–*H*), 7.34 (m, 3H, Ar–*H*), 7.15 (s, 0.11H, C*H*=CCO(O)), 7.11 (s, 0.11H, C*H*=CCO(O)), 7.07 (s, 0.22H, C*H*=CCO(O)), 7.05 (s, 0.55H, C*H*=CCO(O)), 5.88 (d, 0.9H, *J* 7.7, =C*H*CHO), 5.85 (d, 0.1H, *J* 7.4, =C*H*CHO), 5.70 (s, 0.22H, C*H*Ph), 5.68 (s, 0.11H, C*H*Ph), 5.64 (s, 0.56H, C*H*Ph), 5.61 (s, 0.11H, C*H*Ph), 5.48 (app. d, 0.35H, *J* 7.6, C*H*(O)CO), 5.41 (app. d, 0.65H, *J* 7.8, C*H*(O)CO), 5.07–4.76 (m, 5H, CH_2=CCH_3, CH_2=C and C*H*OAc), 4.46 (m, 2H, CH_2(O)CHPh), 4.35 (m, 0.23H, C*H*(O)CHPh), 4.22 (app. d, 0.77H, *J* 10.5, C*H*(O)CHPh), 2.78 (tt, 0.56H, *J* 11.3 and 3.9, CH_2CHCH_2), 2.56 (m, 1.44H, 1H × CH*H*C(CH_3)= and 0.44H CH_2CHCH_2), 2.42 (m, 1H, CH*H*C(CH_3)=), 2.19 (s, 3H, CH_3C=CHCO), 2.05 (m, 1H, AcOCHCH*H*), 2.05 and 2.03 (2 × s (1:2), 3H, CH_3CO), 1.87

(m, 1H, CH*H*CH(O)CHPh), 1.74 (m, 2H, AcOCHC*H*H and C*H*HCH(O)CHPh), 1.73 (s, 3H, CH_3C=C); δ_C(125 MHz): 190.5 (C), 170.1 (C), 169.8 (C), 169.7 (C), 156.1 (C), 147.8 (CH), 147.7 (CH), 146.1 (C), 144.3 (C), 142.2 (C), 142.0 (C), 138.4 (C), 138.3 (C), 134.8 (C), 129.8 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 126.0 (CH), 125.9 (CH), 114.8 (CH_2), 112.9 (CH_2), 109.2 (CH_2), 108.8 (CH_2), 101.2 (CH), 100.9 (CH), 78.6 (CH), 78.5 (CH), 75.6 (CH), 75.4 (CH), 71.9 (CH_2), 71.8 (CH_2), 67.5 (CH), 67.4 (CH), 43.6 (CH_2), 43.5 (CH_2), 39.4 (CH_2), 39.3 (CH_2), 38.8 (2 × CH_2), 35.3 (CH_2), 34.3 (CH_2), 34.2 (CH_2), 20.7 (CH_3), 20.6 (CH_3), 18.6 (CH_3), 18.1 (CH_3), 17.7 (CH_3), 17.3 (CH_3); *m*/*z* (FAB) found 495.2357 (M^+), $C_{29}H_{35}O_7$ requires 495.2383.

(3*R*)-5-Hydroxy-3-isopropenyl-6-{[(4-methoxybenzyl)oxy]-methyl}-1-{5-[(2*E*)-2-methyl-4-oxo-4-(phenylseleno)but-2-enyl]-2-oxo-2,5-dihydrofuran-3-yl}hept-6-enyl acetate 35. A solution of sodium chlorite (0.09 g, 0.98 mmol) and potassium dihydrogen ortho phosphate (0.1 g, 0.77 mmol)[21] in water (3.2 mL) was added to a stirred solution of the aldehyde **34b** (54 mg, 0.11 mmol) in *tert*-butanol (6 mL) and 2-methyl-2-butene (3 cm^3) at room temperature. The mixture was stirred for 7 h and then evaporated *in vacuo.* The aqueous residue was extracted with diethyl ether (3 × 10 mL) and the combined organic extracts were dried ($MgSO_4$), and evaporated *in vacuo* to leave the carboxylic acid **34c** (quantitative conversion) as a colourless oil.

Tri-*n*-butylphosphine (0.03 mL, 0.12 mmol) was added dropwise over 5 min to a stirred solution of the carboxylic acid (11.2 mg, 0.02 mmol) in dry CH_2Cl_2 (1.5 mL) at −30 °C. *N*-Phenylselenophthalimide (36 mg, 0.12 mmol) was added in one portion and the mixture was stirred at −30 °C for 2 min.[22] The cold bath was removed and the reaction immediately warmed to room temperature. The solution was stirred at room temperature for 25 min and then diluted with CH_2Cl_2 (5 mL) and extracted with 5% potassium carbonate solution (5 mL). The aqueous layer was further extracted with CH_2Cl_2 (2 × 5 mL) and the combined organic extracts were dried ($MgSO_4$), and evaporated *in vacuo* to leave a yellow oil. Flash chromatography with petroleum ether and then 20% diethyl ether in CH_2Cl_2 as eluant gave the *selenide* (11 mg, 80%) as a pale yellow oil consisting of an inseparable mixture of diastereoisomers. ν_{max}/cm^{-1} ($CDCl_3$ solution) 1760, 1691, 1617; δ_H(500 MHz): 7.52 (m, 2H, Ar–*H*), 7.34 (m, 3H, Ar–*H*), 7.10 (dt, 0.37H, *J* 15.8 and 1.5, C*H*=CCO(O)), 7.08 (dt, 0.63H, *J* 15 and 1.4, C*H*=CCO(O)), 6.26 (app. s, 0.5H, C*H*COSe), 6.15 (app. s, 0.5H, C*H*COSe), 5.71 (s, 0.16H, C*H*Ph), 5.70 (s, 0.16H, C*H*Ph), 5.65 (s, 0.34H, C*H*Ph), 5.64 (s, 0.34H, C*H*Ph), 5.52 (app. d, 0.18H, *J* 9.2, C*H*(O)CO), 5.45 (app. d, 0.47H, *J* 10.3, C*H*(O)CO), 5.39 (app. d, 0.35H, *J* 10.6, C*H*(O)CO), 5.07–4.75 (m, 5H, CH_2=CCH$_3$, CH_2=C and C*H*OAc), 4.49 (m, 2H, CH_2(O)CHPh), 4.36 (m, 0.35H, C*H*(O)CHPh), 4.24 (app. t, 0.65H, *J* 9.8, C*H*(O)CHPh), 3.12 (m, 0.57H, CH*H*C(CH$_3$)=), 2.78 (m, 0.62H, CH$_2$C*H*CH$_2$), 2.61 (m, 0.38H, CH$_2$C*H*CH$_2$), 2.48 (m, 0.43H, C*H*HC(CH$_3$)=), 2.40–2.35 (m, 1H, CH*H*C(CH$_3$)=), 2.12 and 2.09 (3 × s (1 : 2.5 : 4), 3H, CH_3C=CCHCO), 2.04 (m, 1H, AcOCHCH*H*), 2.01 and 1.99 (3 × s, (1 : 2.3 : 3), 3H, CH_3CO), 1.91 (m, 1H, CH*H*CH(O)CHPh), 1.76 (m, 2H, AcOCHCH*H* and C*H*HCH(O)CHPh), 1.74 and 1.71 (2 × s (1 : 1.4), 3H, CH_3C=C); δ_C(125 MHz): 190.7 (C), 189.8 (C), 170.8 (C), 170.2 (C), 169.9 (C), 169.8 (2 × C), 152.4 (C), 148.7 (CH), 148.1 (CH), 142 4 (2 × C), 138.5 (C), 135.8 (CH), 134.7 (C), 129.5 (2 × CH), 129.1 (CH), 129.0 (CH), 128.8 (2 × CH), 128.2 (CH), 127.6 (CH), 127.2 (CH), 126.2 (CH), 126.1 (CH), 126.0 (2 × CH), 114.9 (CH_2), 114.8 (CH_2), 108.9 (CH_2), 108.8 (CH_2), 101.1 (CH), 81.1 (CH), 78.6 (CH), 75.7 (CH), 75.6 (CH), 75.5 (CH), 72.0 (CH_2), 71.9 (CH_2), 67.7 (CH), 67.6 (2 × CH), 67.5 (CH), 44.1 (CH_2), 39.0 (2 × CH), 38.9 (CH), 38.3 (CH_2), 36.6 (CH_2), 36.4 (CH_2), 34.4 (CH_2), 34.3 (CH_2), 27.0 (CH_3), 20.9 (CH_3), 20.8 (2 × CH_3), 20.7 (CH_3), 20.6 (2 × CH_3), 17.5 (CH_3), 17.4 (CH_3),14.1 (CH_3); *m*/*z* (%) Cl 670 (23), 668 ($M^+ + (NH_4)^+$, ^{80}Se, 100), 666 (51), 65 (20), 664 (15), 608 (4), 562 (9), 542 (13), 485 (6), 452 (8), 346 (11), 327 (8); *m*/*z* (EI) found 668.2155 (M^+), $C_{35}H_{42}NO_7Se$ requires 668.2115.

(3*R*)-5-Hydroxy-6-(hydroxymethyl)-3-isopropenyl-1-{5-[(2*E*)-2-methyl-4-oxo-4-(phenylseleno)but-2-enyl]-2-oxo-2,5-dihydrofuran-3-yl}hept-6-enyl acetate 36. Pyridinium *p*-toluenesulfonate (3.7 mg, 0.015 mmol) was added to a stirred solution of the acetonide **35** (32 mg, 0.049 mmol) in dry methanol (1.5 mL) at room temperature and the mixture was stirred for 60 h and then evaporated *in vacuo* to leave an oil. Flash chromatography with ethyl acetate as eluant gave the *diol* (32 mg, 94%) as a colourless oil consisting of an inseparable mixture of diastereoisomers. ν_{max}/cm^{-1} ($CDCl_3$ solution) 3600, 1761, 1693, 1618; δ_H(500 MHz): 7.53 (m, 2H, Ar–*H*), 7.42 (m, 3H, Ar–*H*), 7.12 (app. s, 0.5H, C*H*=CCO(O)), 7.11 (app. s, 0.5H, C*H*=CCO(O)), 6.29 (s, 0.5H, C*H*COSe), 6.17 (s, 0.5H, C*H*COSe), 5.41 (m, 1H, C*H*(O)CO), 5.12 (m, 3H, CH_2=C and C*H*OAc), 4.86 (4 × d, 2H, *J* 14.2, CH_2=CCH$_3$), 4.27 (m, 0.3H, CH_2OH and CHOH), 3.12 (dt, 0.45H, *J* 9 and 3.9, C*H*HC(CH$_3$)=), 2.64 (m, 0.73H, CH$_2$C*H*CH$_2$), 2.53 (m, 0.55H, C*H*HC(CH$_3$)=), 2.45 (m, 1.27H, 1H × CH*H*C(CH$_3$)= and 0.27H × CH$_2$C*H*CH$_2$), 2.13, 2.12 and 2.04 (3 × s (1 : 2.5 : 4), 3H, CH_3C=CHCO), 1.96 (m, 1H, AcOCHCH*H*), 2.04, 2.03 and 1.95 (3 × s (1 : 1.7 : 2.7), 3H, CH_3CO), 1.82 (m, 1H, CH*H*CHOH), 1.75, 1.73, 1.71, 1.67 (4 × s (1 : 1 : 1.5 : 1.5), 3H, CH_3C=C), 1.65 (m, 2H, AcOCHC*H*H and CH*H*CHOH); δ_C(125 MHz): 190.8 (C) 189.8 (C), 170.8 (C), 170.3 (C), 169.9 (C), 169.8 (C), 152.3 (C), 150.5 (C), 149.4 (CH), 148.8 (CH), 148.1 (C), 147.9 (C), 144.9 (C), 135.8 (CH), 134.9 (C), 134.1 (C), 129.5 (2 × CH), 129.2 (CH), 129.0 (CH), 127.6 (CH), 127.2 (CH), 126.9 (CH), 126.8 (CH), 114.9 (CH_2), 114.8 (CH_2), 114.1 (CH_2), 113.2 (CH_2), 112.0 (CH_2), 111.9 (CH_2), 81.1 (CH), 78.6 (CH), 73.4 (CH), 73.3 (CH), 71.7 (CH), 67.6 (CH), 67.4 (CH), 67.2 (CH), 64.4 (CH_2), 64.1 (CH_2), 53.5 (CH_2), 44.2 (CH_2), 41.0 (2 × CH), 40.3 (CH), 40.2 (CH), 39.4 (CH), 38.3 (CH_2), 36.5 (CH_2), 36.3 (CH_2), 36.0 (CH_2), 35.8 (CH_2), 29.8 (CH_2), 26.9 (CH_3), 21.0 (CH_3), 20.9 (CH_3), 20.6 (CH_3), 17.9 (CH_3), 17.8 (CH_3), 17.4 (CH_3), 17.3 (CH_3); *m*/*z* (EI) found 580.1794 (M^+), $C_{25}H_{35}SNO_7Se$ requires 580.1804.

(3*S*)-3-Isopropenyl-6-{[(4-methoxybenzyl)oxy]methyl}-1-{(5*R*)-5-[(2*E*)-2-methyl-4-oxo-4-(phenylseleno)but-2-enyl]-2-oxo-2,5-dihydrofuran-3-yl}-5-oxohept-6-enyl acetate 18. PMB-trichloroacetimidate (8.9 mg, 0.032 mmol) and *p*-toluenesulfonic acid (0.6 mg, 0.003 mmol) were added to a stirred solution of the diol **36** (16.9 mg, 0.03 mmol) in dry CH_2Cl_2 (0.8 mL) and hexane (0.4 mL) at 0 °C, and the mixture was stirred at this temperature for 70 h.[23] The mixture was warmed to room temperature and the solvent was then removed under reduced pressure to leave the PMB ether **37** as an oil. A solution of the PMB ether in dry CH_2Cl_2 (0.9 mL) was cooled to 0 °C, and then Dess–Martin periodinane (16.2 mg, 0.038 mmol) was added and the mixture was stirred at 0 °C for 5 min and then warmed to room temperature where it was stirred for a further 40 min. The solvent was removed under reduced pressure to leave a colourless oil. Flash chromatography, first with 20% diethyl ether in petroleum ether, then with 20% ethyl acetate in petroleum ether as eluant, gave the *enone* (9.2 mg, 50%) as a colourless oil. ν_{max}/cm^{-1} ($CDCl_3$ solution) 2957 1759, 1687, 1613; δ_H(500 MHz): 7.53 (m, 2H, 2H × PhSe), 7.41 (m, 3H, 3H × PhSe), 7.27 (m, 2H, 2H × $C_6H_4OCH_3$), 7.09 (d, 0.9H, *J* 12, C*H*=CCO(O)), 7.06 (d, 0.1H, *J* 11.7, C*H*=CCO(O)), 6.89 (m, 2H, 2H × C_6H_4–OCH$_3$), 6.26 (app. s, 0.6H, C*H*COSe), 6.16–6.01 (m, 2.4H, 2 × H, CH_2=C(CH$_3$), 0.4H C*H*COSe), 5.43 (app. d, 0.4H, *J* 9.5, C*H*(O)CO), 5.38 (app. d, 0.6H, *J* 10.5, C*H*(O)CO), 5.07 (m, 1H, C*H*OAc), 4.79 (2 × d, 2H, *J* 15.2, CH_2=C(CH$_3$)), 4.50 (app. d, 2H, *J* 7.1, $CH_2C_6H_4$–OCH$_3$), 4.20 (app. d, 2H, *J* 6.2, CH_2OPMB), 3.81 (s, 3H, OCH_3), 3.12 (m, 0.6H, CH*H*C(CH$_3$)=), 2.89 (m, 1H, CH$_2$C*H*CH$_2$), 2.81

(m, 0.4H, CH*H*C(CH_3)=), 2.70 (m, 1H, C*H*HCOC=C), 2.52 (m, 1H, CH*H*C(CH_3)=), 2.43 (m, 1H, CH*H*COC=C), 2.07 (m, 1H, AcOCHCH*H*), 2.13 and 2.05 (2 × s (1.7 : 2.7), 3H, CH_3CO), 1.94 (s, 3H, CH_3C=), 1.74, 1.73, 1.71 and 1.70 (4 × s (1 : 1 : 1.5 : 1.5), 3H, CH_3C=C), 1.63 (m, 1H, AcOCHCH*H*); δ_C(125 MHz): 199.6 (C), 193.9 (C), 190.7 (C), 189.8 (C), 170.7 (C), 169.9 (C), 169.8 (C), 152.3 (CH), 149.8 (CH), 148.7 (C), 147.8 (C), 145.3 (C), 144.8 (C), 135.8 (CH), 134.8 (C), 134.0 (C), 130.3 (CH), 130.2 (CH), 129.6 (CH), 129.5 (CH), 129.4 (CH), 129.1 (CH), 129.0 (CH), 127.2 (CH), 126.8 (CH), 126.7 (CH), 124.9 (CH_2), 124.7 (CH_2), 113.9 (CH), 113.8 (CH_2), 113.1 (CH_2), 81.1 (CH), 78.6 (CH), 72.7 (CH_2), 67.7 (CH), 67.4 (CH), 67.2 (CH), 55.4 (CH_3), 44.1 (CH_2), 42.2 (CH_2), 39.3 (CH), 39.1 (CH), 38.3 (CH_2), 35.7 (CH_2), 35.5 (CH_2), 29.8 (CH_2), 27.0 (CH_3), 22.8 (CH_3), 20.9 (CH_3), 20.8 (CH_3), 20.6 (CH_3), 18.8 (CH_3), 18.6 (CH_3), 14.2 (CH_3).

(*R*)-1-Chloropent-4-yn-2-ol 46b. 2 M Hydrochloric acid (12.7 mL, 25.3 mmol) was added to TBAF (1 M solution in THF, 13.2 g, 50.6 mmol), and the resulting yellow solution was added in one portion to (*R*)-1-chloro-5-(trimethylsilyl)pent-4-yn-2-ol **46a**[30] (4.88 g, 25.3 mmol). The mixture was stirred at room temperature for 40 h, and then diluted with Et_2O (100 mL) and water (50 mL). The separated aqueous layer was extracted with Et_2O (2 × 100 mL), and the combined organic extracts were then dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 1 : 1) followed by bulb-to-bulb distillation (water pump, 18 mmHg, 80 to 120 °C) gave the *acetylene* (1.5 g, 50%) as a colourless oil. $[\alpha]_D^{22}$ −15.1 (*c* 2.9 in CH_2Cl_2); ν_{max}/cm^{-1}: 3581, 3305, 2127; δ_H(360 MHz): 3.97–3.92 (m, 1H, C*H*OH), 3.65 (dd, 1H, *J* 11.1 and 4.5, C*H*HCl), 3.58 (dd, 1H, *J* 11.1 and 6.0, CH*H*Cl), 2.77 (m, 1H, O*H*), 2.49–2.46 (m, 2H, CH_2C≡), 2.04 (t, 1H, *J* 2.7, ≡C*H*); δ_C(90 MHz): 79.1 (C), 71.3 (CH), 69.5 (CH), 48.0 (CH_2), 24.1 (CH_2); *m*/*z* (EI) found 118.0183 (M^+), C_5H_7OCl requires 118.0185.

(*R*)-(*E*)-1-Chloro-5-iodo-4-methylpent-4-en-2-ol 47. A solution of trimethylaluminium (2 M) in hexanes (5.7 mL) was added dropwise over 5 min to a stirred solution of bis(cyclopentadienyl)zirconium dichloride (1.11 g, 3.8 mmol)[31] in anhydrous CH_2Cl_2 (15 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 15 min, then cooled to 0 °C. A solution of the acetylene **46b** (0.45 g, 3.8 mmol) in anhydrous CH_2Cl_2 (5 mL) was added dropwise *via* syringe over 5 min and the orange solution was stirred in the dark at room temperature for 72 h and then cooled to −30 °C. A solution of I_2 (2.41 g, 9.5 mmol) in THF (10 mL) was added dropwise *via* syringe over 5 min and the dark solution was stirred at −30 °C for 10 min and then allowed to warm to room temperature over 2 h. The mixture was carefully quenched by the addition of a saturated aqueous solution of K_2CO_3 (5 mL), then treated with $MgSO_4$ and stirred for 10 min. The mixture was filtered and the filtrate was concentrated *in vacuo*. The resulting heterogeneous residue was triturated with Et_2O (250 mL) and the combined organic extracts were then concentrated *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 2 : 1) gave the *vinyl iodide* (0.61 g, 60%) as a pale yellow oil. $[\alpha]_D^{22}$ −2.3 (*c* 3.3 in $CHCl_3$); ν_{max}/cm^{-1}: 3572, 1615; δ_H(360 MHz): 6.08–6.06 (m, 1H, =C*H*), 4.05–3.95 (m, 1H, C*H*OH), 3.59 (dd, 1H, *J* 11.3 and 3.9, C*H*HCl), 3.49 (dd, 1H, *J* 11.3 and 6.1, CH*H*Cl), 2.47–2.40 (m, 3H, CH_2C= and O*H*), 1.88 (s, 3H, =CCH_3); δ_C(90 MHz): 143.5 (C), 78.3 (CH), 68.9 (CH), 49.3 (CH_2), 43.9 (CH_2), 24.1 (CH_3); *m*/*z* (EI) found 259.9465 (M^+), $C_6H_{10}OClI$ requires 259.9465.

(*R*)-2-((*E*)-3-Iodo-2-methylallyl)oxirane 48. Powdered NaOH (0.73 g, 18.3 mmol) was added in one portion to a stirred solution of the chlorohydrin **47** (1.59 g, 6.1 mmol) in Et_2O (32 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 16 h and then filtered through Celite using Et_2O as eluent. The solvent was removed *in vacuo* to leave the *epoxide* (1.15 g, 84%) as a yellow oil which was used without purification in the next step. A small sample was purified by chromatography to leave the *epoxide* as a pale yellow oil. $[\alpha]_D^{22}$ +18.4 (*c* 0.3 in CH_2Cl_2); ν_{max}/cm^{-1}: 3057, 1618, 1277; δ_H(360 MHz): 6.10–6.09 (m, 1H, =C*H*), 3.05–3.00 (m, 1H, C*H*O), 2.82–2.80 (m, 1H, C*H*HO), 2.52 (dd, 1H, *J* 5.0 and 2.6, CH*H*O), 2.50–2.36 (m, 2H, CH_2), 1.94 (s, 3H, =CCH_3); δ_C(90 MHz): 143.9 (C), 77.1 (CH), 50.3 (CH), 46.5 (CH_2), 42.1 (CH_2), 24.4 (CH_3); *m*/*z* (EI) found 223.9694 (M^+), C_6H_9OI requires 223.9698.

(*S*)-5-((*E*)-3-Iodo-2-methylallyl)dihydrofuran-2-one 49. A solution of *n*-BuLi (2.5 M) in hexanes (2.2 mL) was added dropwise over 5 min to a stirred solution of ethoxyacetylene (50% solution w/w in hexanes, 1.3 mL, 6.7 mmol) in THF (7.4 mL) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 20 min and then freshly distilled $BF_3{\cdot}Et_2O$ (0.7 mL, 5.6 mmol) was added *via* syringe over 1 min. The mixture was stirred at −78 °C for 2 min and then a solution of the epoxide **48** (0.50 g, 2.2 mmol) in THF (3.7 mL) was added dropwise over 5 min. The reaction was stirred at −78 °C for 2 h and then quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (50 mL). The resulting mixture was diluted with Et_2O (50 mL) and water (40 mL), and the separated aqueous layer was then extracted with Et_2O (2 × 80 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. *p*-Toluenesulfonic acid (30 mg) was added to the residue and the mixture was dissolved in EtOH (10 mL) and stirred at room temperature for 2 h. The solvent was removed *in vacuo* and the residue was dissolved in $CHCl_3$ (20 mL) and heated under reflux for 16 h. The reaction was cooled to room temperature and then quenched with a saturated aqueous solution of $NaHCO_3$ (5 mL). The separated aqueous layer was extracted with $CHCl_3$ (3 × 30 mL) and the combined organic extracts were then dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 1 : 1) gave the *lactone* (0.49 g, 82%) as an oil. $[\alpha]_D^{22}$ +41.8 (*c* 3.5 in CH_2Cl_2);[32] ν_{max}/cm^{-1}: 1759; δ_H(360 MHz): 6.11–6.10 (m, 1H, =C*H*), 4.67–4.59 (m, 1H, C*H*O), 2.67 (dd, 1H, *J* 14.2 and 7.4, =CC*H*H), 2.57–2.48 (m, 3H, =CCH*H* and CH_2CO), 2.37–2.28 (m, 1H, C*H*HCH$_2$CO), 1.94–1.83 (m, 4H, =CCH_3 and CH*H*CH$_2$CO); δ_C(90 MHz): 176.5 (C), 142.6 (C), 78.5 (CH), 78.2 (CH), 44.8 (CH_2), 28.4 (CH_2), 27.5 (CH_2), 24.3 (CH_3); *m*/*z* (EI) found 265.9808 (M^+), $C_8H_{11}O_2I$ requires 265.9804.

(*R*)-5-((*E*)-3-Iodo-2-methylallyl)-3-phenylselanyldihydrofuran-2-one 44. A solution of the lactone **49** (100 mg, 0.40 mmol) in THF (2.0 mL) was added dropwise over 10 min *via* syringe to a stirred solution of LiHMDS (1.0 M in THF, 0.38 mL, 0.38 mmol) in THF (2.0 mL) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 10 min, and then a solution of PhSeBr (89 mg, 0.38 mmol) in THF (2 mL) was added *via* syringe over 1 min. This mixture was stirred at −78 °C for 50 min, then quenched by the addition of a saturated aqueous solution of NH_4Cl (15 mL) and allowed to warm to room temperature over 5 min. The resulting solution was diluted with water (20 mL) and Et_2O (50 mL), and the separated aqueous layer was then extracted with Et_2O (3 × 40 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 4 : 1) gave the *phenylselenolactone* (80 mg, 51%, 75% based on recovered starting material) separated as two diastereomers.

In an alternative procedure, a solution of the lactone **49** (400 mg, 1.50 mmol) in THF (3.0 mL) was added dropwise over 10 min *via* syringe to a stirred solution of LiHMDS (1.0 M in THF, 1.65 mL, 1.65 mmol) in THF (3.0 mL) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 15 min, and then TMSCl (0.21 mL, 1.65 mmol) was added dropwise over 1 minute. The mixture was stirred at −78 °C for 30 min and then a solution of PhSeBr (389 mg, 1.65 mmol) in

THF (3 mL) was added *via* syringe over 1 minute. The resulting mixture was stirred at −78 °C for 30 min, then allowed to warm to room temperature over 30 min and quenched by the addition of a saturated aqueous solution of NH_4Cl (15 mL). The solution was diluted with water (40 mL) and Et_2O (80 mL), and the separated aqueous layer was then extracted with Et_2O (3 × 80 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 4 : 1) separated the diastereoisomers of the *phenylselenolactone* (447 mg, 71%): (i) $[\alpha]_D^{22}$ +38.3 (*c* 0.2 in CH_2Cl_2); ν_{max}/cm^{-1}: 1765; δ_H(360 MHz): 7.72–7.69 (m, 2H, Ar*H*), 7.43–7.29 (m, 3H, Ar*H*), 6.06 (m, 1H, =C*H*), 4.43–4.35 (m, 1H, C*H*O), 3.96 (dd, 1H, *J* 5.1 and 5.1, C*H*Se), 2.61 (ddd, 1H, *J* 14.4, 7.3 and 0.6, =C*H*HCHO), 2.45 (ddd, 1H, *J* 14.4, 5.5 and 0.6, =CH*H*CHO), 2.37–2.33 (m, 2H, CH_2CHSe), 1.85 (m, 3H, =CCH_3); δ_C(90 MHz): 175.2 (C), 142.3 (C), 135.8 (CH), 129.4 (CH), 129.2 (CH), 126.4 (C), 78.6 (CH), 76.8 (CH), 44.4 (CH_2), 36.5 (CH), 36.2 (CH_2), 24.1 (CH_3); *m/z* (EI) 421.9289, (M^+, $C_{14}H_{15}O_2SeI$ requires 421.9282); (ii) $[\alpha]_D^{22}$ +48.0 (*c* 0.2 in CH_2Cl_2); ν_{max}/cm^{-1}: 1767; δ_H(360 MHz): 7.70–7.68 (m, 2H, Ar*H*), 7.42–7.35 (m, 3H, Ar*H*), 6.00 (m, 1H, =C*H*), 4.59–4.51 (m, 1H, C*H*O), 4.03 (dd, 1H, *J* 9.3 and 9.3, C*H*Se), 2.80–2.72 (m, 1H, C*H*HCHSe), 2.47 (ddd, 1H, *J* 14.4, 7.3 and 0.7, =C*H*HCHO), 2.32 (ddd, 1H, *J* 14.4, 5.7 and 0.7, =CH*H*CHO), 2.01–1.92 (m, 1H, C*H*HCHSe), 1.83 (m, 3H, =CCH_3); δ_C(90 MHz): 175.3 (C), 142.2 (C), 135.8 (CH), 129.4 (CH), 129.1 (CH), 126.7 (C), 78.8 (CH), 76.6 (CH), 44.8 (CH_2), 36.9 (CH), 35.1 (CH_2), 24.1 (CH_3); *m/z* (EI) found 421.9279 (M^+), $C_{14}H_{15}O_2SeI$ requires 421.9282.

2-{(*S*)-2-[1-((*S*)-4-Isopropyl-2-oxooxazolidin-3-yl)methanoyl]-3-methylbut-3-enyl}furan-3-carboxylic acid methyl ester 55b. A solution of the chiral imide **54**[35] (5 g, 23.7 mmol) in THF (60 mL) was added dropwise *via* cannula over 20 min to a stirred solution of NaHMDS (1 M solution in THF, 26.1 mL, 26.1 mmol) in THF (250 mL) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 1 h and then a solution of 2-bromomethylfuran-3-carboxylic acid methyl ester **44** (6.23 g, 28.4 mmol) in THF (60 mL) was added *via* cannula over 20 min. The solution was warmed from −78 °C to −20 °C over 4 h, then quenched by the addition of a saturated aqueous solution of NH_4Cl (100 mL) and finally diluted with Et_2O (100 mL) and water (100 mL). The separated aqueous layer was extracted with Et_2O (3 × 300 mL) and the combined organic extracts were then dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 5 : 1 to 3 : 1) gave the *substituted furan* (5.6 g, 61%) as a colourless solid, mp 59–61 °C. (Found: C, 61.9; H, 6.7; N, 4.0 $C_{18}H_{23}NO_6$ requires C, 61.9; H, 6.6; N, 4.0); $[\alpha]_D^{22}$ +76.5 (*c* 0.7 in CH_2Cl_2); ν_{max}/cm^{-1} ($CDCl_3$ solution): 1766, 1733, 1683; δ_H(360 MHz): 7.21 (d, 1H, *J* 1.9, OC*H*=CH), 6.63 (d, 1H, *J* 1.9, OCH=C*H*), 4.94–4.88 (m, 3H, =CH_2 and C*H*CON), 4.44–4.40 (m, 1H, C*H*N), 4.26–4.15 (m, 2H, OCH_2), 3.84 (s, 3H, OCH_3), 3.55 (dd, 1H, *J* 15.4 and 9.4, furan C*H*H), 3.38 (dd, 1H, *J* 15.4 and 5.3, furan CH*H*), 2.36–2.27 (m, 1H, C*H*(CH_3)$_2$), 1.84 (s, 3H, =CCH_3), 0.88 (d, 3H, *J* 7.0, CHCH_3), 0.80 (d, 3H, *J* 7.0, CHCH_3); δ_C(90 MHz) 171.2 (C), 163.1 (C), 159.2 (C), 152.9 (C), 141.9 (C), 140.3 (CH), 113.3 (C), 113.0 (CH_2), 110.2 (CH), 62.5 (CH_2), 58.1 (CH), 50.6 (CH_3), 47.7 (CH), 28.8 (CH_2), 27.7 (CH), 20.4 (CH_3), 17.0 (CH_3), 13.8 (CH_3); *m/z* (ES) found 372.1411 (M^+ + Na), $C_{18}H_{23}NO_6Na$ requires 372.1423.

X-Ray crystal structure of 55b. A crystal was encapsulated in a film of RS3000 perfluoropolyether oil and mounted on a dual-stage glass fibre before transfer to the diffractometer.

Crystal data. $C_{18}H_{23}NO_6$, M = 349.37, orthorhombic, a = 10.816(2), b = 16.904(3), c = 19.350(4) Å, U = 3538(2) Å^3, T = 150(2) K, space group $P2_12_12_1$ (No. 19), Z = 8, D_c = 1.312 g cm^{-3}, μ(Mo-Kα) = 0.099 mm^{-1}, 8076 unique reflections measured and used in all calculations. Final R_1 [5911 $F \geq 4\Phi(F)$] = 0.0400 and wR(all F^2) was 0.0789. No meaningful Flack parameter could be obtained for this experiment.†

2-{(*S*)-2-[1-((*S*)-4-Isopropyl-2-oxooxazolidin-3-yl)-methanoyl]-3-methylbut-3-enyl}furan-3-carboxylic acid ethyl ester 55a. A solution of the chiral imide **54**[35] (5 g, 23.7 mmol) in THF (60 mL) was added dropwise *via* cannula over 20 min to a stirred solution of NaHMDS (2 M solution in THF, 14.7 mL, 29.5 mmol) in THF (250 mL) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 1 h and then a solution of 2-bromomethylfuran-3-carboxylic acid ethyl ester[36] (8.9 g, 38.4 mmol) in THF (60 mL) was added *via* cannula over 20 min. The solution was warmed from −78 °C to −20 °C over 4 h, then quenched with a saturated aqueous solution of NH_4Cl (100 mL) and diluted with Et_2O (100 mL) and water (100 mL). The separated aqueous layer was extracted with Et_2O (3 × 300 mL) and the combined organic extracts were then dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 5 : 1 to 3 : 1) gave the *substituted furan* (5.9 g, 68%) as a colourless oil. (Found: C, 63.0; H, 7.0; N, 3.7 $C_{19}H_{25}NO_6$ requires C, 62.8; H, 6.9; N, 3.85); $[\alpha]_D^{22}$ +125.7 (*c* 2.9 in CH_2Cl_2); ν_{max}/cm^{-1} ($CDCl_3$ solution): 1781, 1707, 1600; δ_H(360 MHz): 7.22 (d, 1H, *J* 1.9, OC*H*=CH), 6.66 (d, 1H, *J* 1.9, OCH=C*H*), 4.96–4.90 (m, 3H, =CH_2 and C*H*CON), 4.45–4.41 (m, 1H, C*H*N), 4.32 (q, 2H, *J* 7.1, CH_3CH_2O), 4.27–4.16 (m, 2H, OCH_2), 3.56 (dd, 1H, *J* 15.3 and 9.3, furan C*H*H), 3.40 (dd, 1H, *J* 15.3 and 5.4, furan CH*H*), 2.38–2.29 (m, 1H, C*H*(CH_3)$_2$), 1.84 (s, 3H, =CCH_3), 1.37 (t, 3H, *J* 7.1, CH_3CH_2O), 0.89 (d, 3H, *J* 7.0, CHCH_3), 0.82 (d, 3H, *J* 7.0, CHCH_3); δ_C(90 MHz) 172.0 (C), 163.5 (C), 159.5 (C), 153.4 (C), 142.2 (C), 140.5 (CH), 114.1 (C), 113.8 (CH_2), 110.8 (CH), 62.9 (CH_2), 60.1 (CH_2), 58.6 (CH), 48.3 (CH), 29.3 (CH_2), 28.2 (CH), 21.0 (CH_3), 17.7 (CH_3), 14.3 (CH_3), 14.2 (CH_3); *m/z* (ES) found 364.1738 (M^+ + H), $C_{19}H_{26}NO_6$ requires 364.1760.

2-((*S*)-2-Hydroxymethyl-3-methylbut-3-enyl)furan-3-carboxylic acid ethyl ester 56. A solution of Super Hydride (1 M) in THF (29.7 mL) was added dropwise *via* syringe over 5 min to a stirred solution of the imide **55a** (4.9 g, 13.5 mmol) in anhydrous toluene (210 mL) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 30 min and then quenched by the careful addition of a saturated aqueous solution of NH_4Cl (80 mL). The resulting mixture was allowed to warm to room temperature over 10 min and then diluted with Et_2O (200 mL) and water (80 mL). The separated aqueous layer was extracted with Et_2O (3 × 250 mL) and the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 1 : 1) gave the *alcohol* (2.4 g, 75%) as a colourless oil. (Found C, 65.5; H, 7.7; $C_{13}H_{18}O_4$ requires C, 65.5; H, 7.6); $[\alpha]_D^{22}$ +1.9 (*c* 0.4 in EtOH); ν_{max}/cm^{-1} ($CDCl_3$ solution): 3418, 1713, 1646, 1599; δ_H(360 MHz): 7.26 (m, 1H, *J* 2.0, OC*H*=CH), 6.66 (d, 1H, *J* 2.0, OCH=C*H*), 4.91 (dd, 1H, *J* 1.3 and 1.3, =C*H*H), 4.81 (s, 1H, =CH*H*), 4.32 (q, 2H, *J* 7.1, CH_3CH_2O), 3.59 (d, 2H, *J* 5.9, CH_2OH), 3.23 (dd, 1H, *J* 14.4 and 8.2, furan C*H*H), 3.12 (dd, 1H, *J* 14.4 and 6.6, furan CH*H*), 2.73–2.69 (m, 1H, C*H*C=), 2.24–2.27 (m, 1H, O*H*), 1.80 (s, 3H, =CCH_3), 1.37 (t, 3H, *J* 7.1, CH_3CH$_2$O); δ_C(90 MHz): 164.3 (C), 160.9 (C), 144.6 (C), 140.7 (CH), 114.2 (C), 112.9 (CH_2), 110.4 (CH), 62.9 (CH_2), 60.3 (CH_2), 48.0 (CH), 27.8 (CH_2), 20.2 (CH_3), 14.2 (CH_3); *m/z* (ES) found 237.1108 (M^+ − H), $C_{13}H_{18}O_4Na$ requires 237.1126.

Reduction of **55b**, under the same conditions, gave the methyl ester analogous to **56**. (Found: C, 63.9; H, 7.2, $C_{12}H_{16}O_4$ requires C, 64.3; H, 7.2); $[\alpha]_D^{22}$ −4.2 (*c* 0.2 in CH_2Cl_2); ν_{max}/cm^{-1} ($CDCl_3$ solution): 3623, 3488, 1766, 1733, 1683; δ_H(360 MHz): 7.28 (d, 1H, *J* 2.0, OC*H*=CH), 6.65 (d, 1H, *J* 2.0, OCH=C*H*), 4.92–4.91 (m, 1H, =C*H*H), 4.82–4.81 (m, 1H, =CH*H*), 3.84 (s, 3H, OCH_3), 3.60 (d, 2H, *J* 5.9, CH_2OH), 3.23 (dd, 1H, *J* 14.5 and 8.0, furan C*H*H), 3.13 (dd, 1H, *J* 14.4 and 6.7 furan CH*H*), 2.75–2.67 (m, 1H, C*H*C=C), 1.80 (s, 3H, =CCH_3); δ_C(90 MHz): 164.9 (C), 161.2 (C), 144.7 (C), 141.0 (CH), 114.0 (C), 113.1 (CH_2),

110.5 (CH), 63.0 (CH_2), 51.6 (CH_3), 48.1 (CH), 28.0 (CH_2), 20.4 (CH_3).

(*S*)-3-(3-Hydroxymethylfuran-2-ylmethyl)-4-methylpent-4-enenitrile 57a. Triethylamine (2.2 mL, 16.1 mmol), DMAP (0.20 g, 1.7 mmol) and tosyl chloride (1.84 g, 9.6 mmol) were added sequentially to a stirred solution of the alcohol **56** (1.80 g, 8.6 mmol) in CH_2Cl_2 (45 mL) at room temperature under a nitrogen atmosphere The reaction was stirred at room temperature for 16 h, then diluted with CH_2Cl_2 (40 mL) and washed successively with aqueous citric acid (10% w/w, 80 mL) and a saturated aqueous solution of $NaHCO_3$ (50 mL). The separated organic layer was dried ($MgSO_4$) and concentrated *in vacuo* to leave the corresponding *tosylate* (2.2 g, 75%) as a brown oil, which was used without purification in the next step. A sample was purified by chromatography to leave the corresponding *tosylate* as a pale yellow oil. (Found C, 61.15; H, 6.1, $C_{20}H_{24}O_6S$ requires C, 61.2; H, 6.2); $[\alpha]_D^{22}$ −2.7 (*c* 3.8 in CH_2Cl_2); ν_{max}/cm^{-1}: 1698, 1595; δ_H(360 MHz): 7.77 (d, 2H, *J* 8.4, Ar*H*), 7.34 (d, 2H, *J* 8.4, Ar*H*), 7.23 (d, 1H, *J* 2.0, OC*H*=CH), 6.63 (d, 1H, *J* 2.0, OCH=C*H*), 4.81–4.80 (m, 1H, =C*H*H), 4.71–4.70 (m, 1H, =CH*H*), 4.29 (q, 2H, *J* 7.1, CH_3CH_2O), 4.02–3.98 (m, 2H, CH_2OTs), 3.13–3.11 (m, 2H, furan CH_2), 2.94–2.88 (m, 1H, C*H*C=), 2.47 (s, 3H, ArCH_3), 1.64 (s, 3H, =CCH_3), 1.35 (t, 3H, *J* 7.1, CH_3CH_2O); δ_C(90 MHz): 163.6 (C), 159.3 (C), 144.7 (C), 142.3 (C), 140.8 (CH), 132.8 (C), 129.7 (CH), 127.9 (CH), 114.5 (C), 113.9 (CH_2), 110.6 (CH), 70.9 (CH_2), 60.2 (CH_2), 44.8 (CH), 28.2 (CH_2), 21.6 (CH_3), 19.6 (CH_3), 14.2 (CH_3); *m*/*z* (ES) found 415.1222 (M^+ + Na), $C_{20}H_{24}O_6SNa$ requires 415.1191.

A solution of DIBAL (1.5 M) in toluene (28.6 mL) was added dropwise over 5 min to a stirred solution of the furanyl ester tosylate (5.4 g, 14.3 mmol) in anhydrous CH_2Cl_2 (175 mL) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 1 h and then quenched by the careful addition of a saturated aqueous solution of NH_4Cl (50 mL). The mixture was warmed to room temperature, and then filtered through a pad of Celite. The residual cake was washed with CH_2Cl_2 (3 × 150 mL) and the combined organic extracts were then dried ($MgSO_4$) and concentrated *in vacuo* to leave toluene-4-sulfonic acid (*S*)-2-[3-(hydroxymethyl)furan-2-ylmethyl]-3-methylbut-3-enyl ester (3.9 g, 78%) as a yellow oil, which was used without further purification. A sample was purified by chromatography to leave the corresponding furanylmethanol as a colourless oil. (Found C, 61.6; H, 6.4; $C_{18}H_{22}O_5S$ requires C, 61.7; H, 6.3); $[\alpha]_D^{22}$ +1.9 (*c* 0.4 in EtOH); ν_{max}/cm^{-1}: 3672, 3609, 1598; δ_H(360 MHz): 7.78 (d, 2H, *J* 8.3, Ar*H*), 7.36 (d, 2H, *J* 8.3, Ar*H*), 7.24 (d, 1H, *J* 1.8, OC*H*=CH), 6.37 (d, 1H, *J* 1.8, OCH=C*H*), 4.85 (dd, 1H, *J* 1.3 and 1.3, =C*H*H), 4.69 (s, 1H, =CH*H*), 4.48–4.39 (m, 2H, CH_2OH), 4.03–3.99 (m, 2H, CH_2OTs), 2.88–2.70 (m, 3H, furan CH_2 and C*H*C=), 2.47 (s, 3H, ArCH_3), 1.64 (s, 3H, =CCH_3); δ_C(90 MHz): 149.3 (C), 144.8(C), 143.0 (C), 141.0 (CH), 132.6 (C), 129.7 (CH), 127.8 (CH), 120.7 (C), 113.3 (CH_2), 110.8 (CH), 70.7 (CH_2), 56.1 (CH_2), 44.6 (CH), 26.7 (CH_2), 21.5 (CH_3), 20.5 (CH_3); *m*/*z* (ES) found 373.1080 (M^+ + Na), $C_{18}H_{22}O_5SNa$ requires 373.1086.

Tetra-*n*-ethylammonium cyanide (3.33 g, 21.4 mmol) was added portionwise over 5 min to a stirred solution of the above tosylate (2.49 g, 7.1 mmol) in anhydrous DMSO (40 mL) at room temperature under a nitrogen atmosphere. The mixture was warmed to 60 °C, stirred for 1 h at this temperature, and then recooled to room temperature and diluted with Et_2O (300 mL) and water (40 mL). The separated aqueous layer was extracted with ethyl acetate (3 × 100 mL) and the combined organic extracts were then washed successively with water (50 mL) and brine (50 mL). The organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to leave the *nitrile* as a pale yellow oil (1.0 g, 69%) which was used without further purification. A sample was purified by chromatography to leave the *nitrile* as a colourless oil. $[\alpha]_D^{22}$ −7.6 (*c* 2.1 in CH_2Cl_2); ν_{max}/cm^{-1}: 3611, 3493, 1621; δ_H(360 MHz): 7.29 (d, 1H, *J* 1.8, OC*H*=CH), 6.37 (d, 1H, *J* 1.8, OCH=C*H*), 4.94 (dd, 1H, *J* 1.4 and 1.4, =C*H*H), 4.86 (s, 1H, =C*H*H), 4.41 (s, 2H, CH_2OH), 2.89–2.79 (m, 3H, furan CH_2 and C*H*C=), 2.49–2.38 (m, 3H, CH_2CN and O*H*), 1.78–1.77 (m, 3H, =CCH_3); δ_C(90 MHz): 148.9 (C), 143.8 (C), 141.2 (CH), 120.9 (C), 118.4 (C), 113.1 (CH_2), 110.7 (CH), 55.8 (CH_2), 41.9 (CH), 29.3 (CH_2), 20.8 (CH_2), 19.9 (CH_3); *m*/*z* (ES) found 269.1261 (M^+ + CH_3CN + Na), $C_{14}H_{18}O_2N_2Na$ requires 269.1265.

(*S*)-3-[3-(*tert*-Butyldimethylsilyloxymethyl)furan-2-ylmethyl]-4-methylpent-4-enenitrile 57b. Triethylamine (3.0 mL, 21.4 mmol), DMAP (0.26 g, 2.1 mmol) and TBSCl (1.94 g, 11.7 mmol) were added sequentially to a stirred solution of the furanyl alcohol **57a** (2.20 g, 10.7 mmol) in anhydrous CH_2Cl_2 (80 mL) at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 20 h and then diluted with CH_2Cl_2 (100 mL) and water (80 mL). The separated aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL) and the combined organic extracts were washed with $NaHCO_3$ (100 mL), dried ($MgSO_4$) and concentrated *in vacuo* to leave the silyl ether (3.1 g, 91%) as an oil, which was used without further purification. A sample was purified by chromatography to leave the *silyl ether* as a colourless oil. (Found: C, 67.6; H, 9.2; N, 4.2 $C_{18}H_{29}NO_2Si$ requires C, 67.7; H, 9.1; N, 4.4); $[\alpha]_D^{22}$ −2.2 (*c* 2.7 in CH_2Cl_2); ν_{max}/cm^{-1}: 1649; δ_H(360 MHz): 7.30 (d, 1H, *J* 1.8, OC*H*=CH), 6.34 (d, 1H, *J* 1.8, OCH=C*H*), 4.98 (dd, 1H, *J* 1.3 and 1.3, =C*H*H), 4.91 (s, 1H, =CH*H*), 4.54 (s, 2H, CH_2OH), 2.92–2.81 (m, 3H, furan CH_2 and C*H*C=), 2.53–2.38 (m, 2H, CH_2CN), 1.80 (s, 3H, =CCH_3); 0.94 (s, 9H, SiC(CH_3)$_3$), 0.12 (s, 6H, Si(CH_3)$_2$); δ_C(90 MHz): 148.3 (C), 143.8(C), 140.9 (CH), 121.1 (C), 118.3 (C), 113.2 (CH_2), 110.9 (CH), 56.9 (CH_2), 42.3 (CH), 29.7 (CH_2), 25.8 (CH_3), 20.9 (CH_2), 19.9 (CH_3), 18.2 (C), −5.2 (CH_3); *m*/*z* (EI) found 262.1257 (M^+ − C_4H_9), $C_{15}H_{23}O_2SiN$ requires: 262.1263.

(*R*)-3-[3-(*tert*-Butyldimethylsilyloxymethyl)furan-2-ylmethyl]-4-methylpent-4-enal 58. A solution of DIBAL in toluene (1.5 M, 3.8 mL) was added dropwise over 5 min *via* syringe to a stirred solution of the nitrile **57b** (1.50 g, 4.7 mmol) in dry toluene (32 mL) at −78 °C under a nitrogen atmosphere. The mixture was allowed to warm to 0 °C over 4 h, then treated with MeOH (2 mL) and stirred at 0 °C for 10 min. A suspension of silica (37.5 g) in ethyl acetate (100 mL) was added to the mixture and the resulting suspension was stirred at room temperature for 1 h. The mixture was filtered and then water (20 mL) was added to the filtrate. The separated aqueous layer was extracted with Et_2O (3 × 100 mL) and the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to leave the *aldehyde* (1.35 g, 89%) as a pale yellow oil which was used without purification. A sample was purified by chromatography to leave the *aldehyde* as a colourless oil. $[\alpha]_D^{22}$ +11.2 (*c* 1.1 in CH_2Cl_2); ν_{max}/cm^{-1}: 1722, 1647; δ_H(360 MHz): 9.57 (dd, 1H, *J* 2.2 and 2.2, *CH*O), 7.28 (d, 1H, *J* 1.8, OC*H*=CH), 6.33 (d, 1H, *J* 1.8, OCH=C*H*), 4.83 (dd, 1H, *J* 1.3 and 1.3, =CH*H*), 4.80 (s, 1H, =C*H*H), 4.51 (s, 2H, CH_2OTBS), 3.13–3.05 (m, 1H, C*H*C=), 2.84 (dd, 1H, *J* 14.6 and 6.1, furan C*H*H), 2.72 (dd, 1H, *J* 14.6 and 8.7, furan CH*H*), 2.49 (dd, 2H, *J* 7.3 and 2.1, CH_2CHO), 1.76 (s, 3H, =CCH_3), 0.94 (s, 9H, SiC(CH_3)$_3$), 0.12 (s, 6H, Si(CH_3)$_2$); δ_C(90 MHz): 201.7 (CH), 149.3 (C), 145.9 (C), 140.7 (CH), 120.8 (C), 112.1 (CH_2), 111.0 (CH), 57.0 (CH_2), 46.5 (CH_2), 40.8 (CH), 30.8 (CH_2), 25.9 (CH_3), 19.9 (CH_3), 18.4 (C), −5.2 (CH_3); *m*/*z* (EI) found 322.1955 (M^+), $C_{18}H_{30}O_3Si$ requires 322.1964.

(*S*)-3-[3-(*tert*-Butyldimethylsilyloxymethyl)furan-2-ylmethyl]-4-methylpent-4-en-1-ol 59. Sodium borohydride (65 mg, 1.7 mmol) was added portionwise over 1 min to a stirred solution of the aldehyde **58** (1.10 g, 3.4 mmol) in MeOH (30 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h, and then quenched by the addition of an aqueous solution

of citric acid (10% w/w, 6 mL). The resulting suspension was concentrated *in vacuo*, and the residue was diluted with Et_2O (30 mL). The separated organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 4 : 1, 3 : 1) gave the *alcohol* (0.67 g, 61%) as a colourless oil. $[\alpha]_D^{22}$ +11.2 (*c* 1.1 in CH_2Cl_2); ν_{max}/cm^{-1}: 3623, 3074, 1644; δ_H(360 MHz): 7.28 (d, 1H, *J* 1.8, OC*H*=CH), 6.33 (d, 1H, *J* 1.8, OCH=C*H*), 4.84 (dd, 1H, *J* 1.3 and 1.3, =C*H*H), 4.80 (s, 1H, =CH*H*), 4.51 (s, 2H, CH_2OTBS), 3.58–3.50 (m, 2H, CH_2OH), 2.80–2.65 (m, 3H, furan CH_2 and C*H*C=), 1.76 (s, 3H,=CCH_3), 1.75–1.65 (m, 2H, CH_2CH$_2$OH), 0.94 (s, 9H, SiC(CH_3)$_3$), 0.12 (s, 6H, Si(CH_3)$_2$); δ_C(90 MHz): 150.4 (C), 147.1 (C), 140.4 (CH), 120.0 (C), 112.0 (CH_2), 110.9 (CH), 61.3 (CH_2), 57.1 (CH_2), 43.5 (CH), 35.2 (CH_2), 31.2 (CH_2), 25.9 (CH_3), 18.7 (CH_3), 18.4 (C), −5.2 (CH_3); *m*/*z* (EI) found 324.2119 (M^+), $C_{18}H_{32}O_3Si$ requires: 324.2121.

(*S*)-4-Methyl-3-(3-trimethylsilyloxymethyl-5-trimethylstannanylfuran-2-ylmethyl)pent-4-en-1-ol 60. A solution of *n*-BuLi in hexanes (2.5 M, 0.54 mL) was added dropwise over 1 min to a stirred solution of the furanyl alcohol **59** (220 mg, 0.7 mmol) in dry Et_2O (5 mL), and the resulting yellow solution was stirred at room temperature for 20 min under a nitrogen atmosphere. Freshly distilled TMEDA (0.19 mL, 1.4 mmol) was added over 1 min, and the resulting yellow solution was stirred at room temperature for 6 h. The mixture was treated with a solution of *n*-BuLi (2.5 M) in hexanes (4.3 mL) and was then stirred at room temperature for 20 min. The solution was cooled to 0 °C and then treated with a solution of trimethyltin chloride (2.7 g, 13.6 mmol) in Et_2O (3 mL). The solution was stirred at room temperature for 12 h, and then diluted with water (40 mL) and Et_2O (40 mL). The separated aqueous layer was extracted with Et_2O (3 × 70 mL) and the combined organic extracts were then washed successively with $NaHCO_3$ (75 mL) and brine (50 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography of the residue over basic alumina (petroleum ether–Et_2O 3 : 1) gave the *furanostannane* (274 mg, 83%) as a pale yellow oil. $[\alpha]_D^{22}$ +3.9 (*c* 2.1 in CH_2Cl_2); ν_{max}/cm^{-1}: 3620, 1645; δ_H(360 MHz): 6.50–6.46 (m, 1H, OCSn=C*H*), 4.75 (d, 2H, *J* 1.1, =CH_2), 4.48 (s, 2H, CH_2OTBS), 3.60–3.55 (m, 2H, CH_2OH), 2.77–2.64 (m, 3H, furan CH_2 and C*H*C=), 1.70 (s, 3H, =CCH_3), 1.69–1.60 (m, 2H, CH_2CH$_2$OH), 1.48 (bs, 1H, O*H*), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.37–0.22 (m, 9H, Sn(CH_3)$_3$), 0.11 (s, 6H, Si(CH_3)$_2$); δ_C(125 MHz): 158.0 (C), 155.4 (C), 147.6 (C), 122.5 (CH), 119.8 (C), 111.9 (CH_2), 61.5 (CH_2), 57.3 (CH_2), 43.6 (CH), 35.5 (CH_2), 31.6 (CH_2), 26.0 (CH_3), 18.8 (CH_3), 18.6 (C), 1.1 (CH_3), −5.1 (CH_3), −9.2 (CH_3); *m*/*z* (EI) found 356.0793 (M^+ − H − OTBS), $C_{15}H_{24}O_2Sn$ requires 356.0806.

(*R*)-3-[(*tert*-Butyldimethylsilyloxymethyl)trimethylstannanylfuran-2-ylmethyl]-4-methylpent-4-enal 45. TPAP (10 mg) was added in one portion to a suspension of the alcohol **60** (260 mg, 0.53 mmol), NMO (99.8 mg, 0.8 mmol) and powdered 4 Å molecular sieves (284 mg) in anhydrous CH_2Cl_2 under a nitrogen atmosphere. The mixture was stirred at room temperature for 1 h and then filtered through a pad of alumina, eluting with Et_2O. The solvent was dried (Na_2SO_4) and concentrated *in vacuo* to leave the aldehyde (220 mg, 85%) as a colourless oil. $[\alpha]_D^{22}$ +2.7 (*c* 1.6 in CH_2Cl_2); ν_{max}/cm^{-1}: 1722; δ_H(360 MHz) 9.51 (dd, 1H, *J* 2.1, C*H*O), 6.50–6.44 (m, 1H, OCSn=C*H*), 4.79 (dd, 1H, *J* 1.5 and 1.5, =C*H*H), 4.76 (s, 1H, =CH*H*), 4.48 (s, 2H, CH_2OTBS), 3.11–3.01 (m, 1H, C*H*C=), 2.84 (dd, 1H, *J* 14.7 and 6.1, furan C*H*H), 2.71 (dd, 1H, *J* 14.7 and 8.7, furan CH*H*), 2.45 (dd, 2H, *J* 7.3 and 2.1, CH_2CHO), 1.73 (s, 3H, =CCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.38–0.13 (m, 9H, Sn(CH_3)$_3$), 0.10 (s, 6H, (Si(CH$_3$)$_2$); δ_C(90 MHz): 201.9 (CH), 158.6 (C), 154.2 (C), 146.2 (C), 122.3 (CH), 120.7 (C), 112.0 (CH_2), 57.2 (CH_2), 46.6 (CH_2), 41.0 (CH), 31.1 (CH_2), 26.5 (CH_3), 20.0 (CH_3), 18.5 (C), 1.1 (CH_3), −5.1 (CH_3), −9.2 (CH_3); *m*/*z* (ES) found 509.1507 (M^+ + Na), $C_{21}H_{38}O_3SiSnNa$ requires 509.1510.

(*R*)-5-(3-{4-*tert*-Butyldimethylsilyloxymethyl)-5-[(*S*)-2-(2-hydroxyethyl)-3-methylbut-3-enyl]furan-2-yl}-2-methylallyl)-3-phenylselanyldihydrofuran-2-one 61a. Triphenylarsine (22 mg, 0.08 mmol, 80%mol) and Pd_2dba_3 (18 mg, 0.02 mmol, 20% mol) were added sequentially to a stirred solution of the furanostannane **44** (70 mg, 0.14 mmol) and the phenylselenolactone **60** (40 mg, 0.10 mmol) in degassed NMP (3 mL) under an argon atmosphere. The resulting dark solution was stirred at 45 °C for 6 h and then cooled to room temperature and diluted with water (20 mL) and Et_2O (40 mL). The separated aqueous layer was extracted with Et_2O (2 × 40 mL), and the combined organic extracts were washed successively with a saturated aqueous solution of $NaHCO_3$ (12 mL) and brine (12 mL), then dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 5 : 1 to 2 : 1) gave the *furanolactone* (28 mg, 55%) as a separable mixture of two diastereoisomers: (i) $[\alpha]_D^{22}$ +46.0 (*c* 0.2 in CH_2Cl_2); ν_{max}/cm^{-1}: 3690, 1766, 1602; δ_H(500 MHz): 7.70–7.68 (m, 2H, Ar*H*), 7.39–7.33 (m, 3H, Ar*H*), 6.14 (s, 1H, OC=C*H*), 6.00 (s, 1H, C*H*=CCH$_3$), 4.77 (bs, 2H, =CH_2), 4.49–4.45 (m, 3H, CH_2OTBS and C*H*O), 3.95 (dd, 1H, *J* 8.0 and 2.9, C*H*Se), 3.62–3.55 (m, 2H, CH_2OH), 2.71–2.62 (m, 3H, furan CH_2 and C*H*C=CH$_2$), 2.56 (dd, 1H, *J* 14.0 and 6.5, =CC*H*HCHO), 2.41–2.32 (m, 3H, CH_2CHSe and =CCH*H*CHO), 1.94 (s, 3H, CH=CCH_3), 1.71 (s, 3H, CH$_2$=CCH_3), 1.66 (q, 2H, *J* 6.8, CHCH_2CH$_2$), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.10 (s, 6H, Si(CH_3)$_2$),δ_C (90 MHz): 175.7 (C), 150.7 (C), 149.3 (C), 147.1 (C), 136.0 (CH), 130.6 (C), 129.5 (CH), 129.3 (CH), 126.8 (C), 121.8 (C), 117.6 (CH), 112.2 (CH_2), 110.3 (CH), 77.9 (CH), 61.4 (CH_2), 57.2 (CH_2), 46.0 (CH_2), 43.6 (CH), 37.0 (CH), 36.4 (CH_2), 35.3 (CH_2), 31.4 (CH_2), 26.0 (CH_3), 18.9 (CH_3), 18.8 (CH_3), 18.5 (C), − 5.1 (CH_3); *m*/*z* (ES) 641.2129, (M^+ + Na, $C_{32}H_{46}O_5SiSeNa$ requires 641.2177); (ii) $[\alpha]_D^{22}$ +37.5 (*c* 0.2 in CH_2Cl_2), ν_{max}/cm^{-1}: 1766; δ_H(500 MHz): 7.70–7.67 (m, 2H, Ar*H*), 7.39–7.31 (m, 3H, Ar*H*), 6.13 (s, 1H, OC=C*H*), 5.95 (s, 1H, C*H*=CCH$_3$), 4.77 (bs, 2H, =CH_2), 4.62–4.55 (m, 1H, C*H*O), 4.48 (s, 2H, CH_2OTBS), 4.02 (dd, 1H, *J* 9.4 and 9.4, C*H*Se), 3.61–3.55 (m, 2H, CH_2OH), 2.77–2.62 (m, 4H, C*H*C=CH$_2$, furan CH_2 and C*H*HCHSe), 2.48 (dd, 1H, *J* 14.0 and 6.4, =CC*H*HCHO), 2.22 (dd, 1H, *J* 14.0 and 6.4, =CCH*H*CHO), 2.05–1.99 (m, 1H, CH*H*CHSe), 1.94 (s, 3H, CH=CCH_3), 1.72 (s, 3H, CH$_2$=CCH_3), 1.66 (q, 2H *J* 6.6, CH_2CH$_2$OH), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.10 (s, 6H, Si(CH_3)$_2$); δ_C (90 MHz): 175.8 (C), 150.7 (C), 149.3 (C), 147.1 (C), 135.8 (CH), 130.5 (C), 129.5 (CH), 129.0 (CH), 126.7 (C), 121.8 (C), 117.7 (CH), 112.2 (CH_2), 110.3 (CH), 77.7 (CH), 61.4 (CH_2), 57.2 (CH_2), 46.3 (CH_2), 43.6 (CH), 37.4 (CH), 35.4 (CH_2), 35.3 (CH_2), 31.4 (CH_2), 26.0 (CH_3), 18.9 (CH_3), 18.8 (CH_3), 18.5 (C), −5.1 (CH_3); *m*/*z* (ES) found 641.2129 (M^+ + Na), $C_{32}H_{46}O_5SiSeNa$ requires 641.2177.

Methanesulfonic acid (*S*)-3-{3-(*tert*-butyldimethylsilyloxymethyl)-5-[(*E*)-2-methyl-3-((*R*)-5-oxo-4-phenylselanyl)tetrahydrofuran-2-yl)propenyl]furan-2-ylmethyl}-4-methylpent-4-enyl ester 61b. Triethylamine (8 μL, 0.04 mmol) and mesyl chloride (4 μL, 0.02 mmol) were added sequentially to a stirred solution of the diastereoisomer of the **61a** (eluting first) (18 mg, 0.02 mmol) in anhydrous CH_2Cl_2 (1.5 mL) at room temperature under a nitrogen atmosphere. The resulting solution was stirred at room temperature for 4 h and then diluted with CH_2Cl_2 (16 mL) and water (8 mL). The separated aqueous layer was extracted with CH_2Cl_2 (2 × 16 mL) and the combined organic extracts were washed successively with citric acid (10% w/w, 4 mL) and a saturated aqueous solution of $NaHCO_3$ (5 mL), then dried ($MgSO_4$) and evaporated in *vacuo* to leave the *mesylate* (17 mg, 87%) as a yellow oil. ν_{max}/cm^{-1}: 1770, 1606; δ_H(500 MHz): 7.70–7.68 (m, 2H, Ar*H*), 7.40–7.32 (m, 3H, Ar*H*), 6.14 (s, 1H, OC=C*H*), 6.00 (s, 1H, C*H*=CCH$_3$), 4.83 (bs, 1H, =C*H*H), 4.76 (s, 1H, =CH*H*), 4.48–4.46 (m, 3H, C*H*O and CH_2OTBS), 4.20–4.16 (s, 1H, C*H*HOMs),

4.11–4.07 (s, 1H, CH*H*OMs), 3.96 (dd, 1H, *J* 8.0 and 2.9, C*H*Se), 2.96 (s, 3H, SO_2CH_3), 2.76–2.62 (m, 4H, furan CH_2, C*H*C=CH_2 and =CC*H*HCHO), 2.56 (dd, 1H, *J* 14.0 and 6.5, =CC*H*HCHO), 2.39–2.32 (m, 2H, CH_2CHSe), 1.95 (s, 3H, CH=CCH_3),1.91–1.78 (m, 2H, CH_2CH_2OMs), 1.70 (s, 3H, CH_2=CCH_3), 0.93 (s, 9H, SiC(CH_3)$_3$), 0.10 (s, 6H, Si(CH_3)$_2$); δ_C(90 MHz): 175.6 (C), 150.9 (C), 148.5 (C), 145.2 (C), 135.9 (CH), 130.9 (C), 129.5 (CH), 129.2 (CH), 126.8 (C), 122.2 (C), 117.5 (CH), 113.2 (CH_2), 110.2 (CH), 77.9 (CH), 68.4 (CH_2), 57.1 (CH_2), 46.0 (CH_2), 42.8 (CH), 37.4 (CH_3), 36.9 (CH), 36.4 (CH_2), 31.4 (CH_2), 31.2 (CH_2), 26.0 (CH_3), 18.9 (CH_3), 18.7 (CH_3), 18.4 (C), −5.1 (CH_3); *m*/*z* (ES) found 719.1985 (M^+ + Na), $C_{33}H_{48}O_7SiSeSNa$ requires 719.1953.

Repetition of this experiment with the diastereoisomer of the **61a** (eluting second), on the same scale and under the same conditions, gave the corresponding *mesylate* (16 mg, 82%) as a yellow oil. ν_{max}/cm^{-1}: 1766; δ_H(360 MHz) 7.69–7.66 (m, 2H, Ar*H*), 7.40–7.31 (m, 3H, Ar*H*), 6.13 (s, 1H, OC=C*H*), 5.96 (s, 1H, C*H*=CCH$_3$), 4.83 (s, 1H, =C*H*H), 4.76 (s, 1H, =CH*H*), 4.63–4.56 (m, 1H, C*H*O), 4.47 (s, 2H, CH_2OTBS), 4.21–4.15 (s, 1H, C*H*HOMs), 4.12–4.08 (s, 1H, CH*H*OMs), 4.02 (dd, 1H, *J* 9.4 and 9.4, C*H*Se), 2.95 (s, 3H, SO_2CH_3), 2.80–2.61 (m, 4H, C*H*C=CH_2, furan CH_2 and C*H*HCHSe), 2.47 (dd, 1H, *J* 14.0 and 6.4, =CC*H*HCHO), 2.23 (dd, 1H, *J* 14.0 and 6.4, =CCH*H*CHO), 2.05–1.97 (m, 1H, CH*H*CHSe), 1.90–1.78 (m, 2H, CH_2CH_2OMs), 1.95 (s, 3H, CH=CCH_3), 1.70 (s, 3H, CH_2=CCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.10 (s, 6H, Si(CH_3)$_2$); δ_C(90 MHz): 175.8 (C), 150.9 (C), 148.5 (C), 145.2 (C), 135.8 (CH), 130.9 (C), 129.5 (CH), 129.1 (CH), 127.1 (C), 122.2 (C), 117.6 (CH), 113.3 (CH_2), 110.2 (CH), 77.7 (CH), 68.4 (CH_2), 57.1 (CH_2), 46.4 (CH_2), 42.8 (CH), 37.4 (CH), 37.3 (CH_3), 35.5 (CH_2), 31.4 (CH_2), 31.3 (CH_2), 26.0 (CH_3), 19.0 (CH_3), 18.7 (CH_3), 18.5 (C), −5.1 (CH_3); *m*/*z* (ES) found 719.1985 (M^+ + Na), $C_{33}H_{48}O_7SiSeSNa$ requires 719.1953.

(*S*)-5-((*E*)-3-{4-(*tert*-Butyldimethylsilyloxymethyl)-5-[2-(2-iodoethyl)-3-methylbut-3-enyl]furan-2-yl}-2-methylallyl)dihydrofuran-2-one 62. Triphenylarsine (60 mg, 0.20 mmol, 80%mol) and Pd_2dba_3 (44 mg, 0.05 mmol, 20%mol) were added sequentially to a stirred solution of the furanostannane **60** (150 mg, 0.31 mmol) and the lactone **49** (65 mg, 0.24 mmol) in degassed NMP (3 mL) under an argon atmosphere. The resulting dark solution was stirred at 45 °C for 16 h and then cooled to room temperature and diluted with Et_2O (40 mL) and water (30 mL). The separated aqueous layer was extracted with Et_2O (2 × 40 mL) and the combined organic extracts were washed successively with a saturated aqueous solution of $NaHCO_3$ (20 mL) and brine (20 mL), then dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 4 : 1 to 2 : 1) gave (*S*)-5-(3-{4-(*tert*-butyldimethylsilyloxymethyl)-5-[(*S*)-2-(2-hydroxyethyl)-3-methylbut-3-enyl]furan-2-yl}-2-ethylallyl)dihydrofuran-2-one (55 mg, 50%) as a yellow oil. $[\alpha]_D^{22}$ +34.8 (*c* 1.1 in CH_2Cl_2); ν_{max}/cm^{-1}: 3616, 1770, 1645; δ_H(360 MHz): 6.15 (s, 1H, OC=C*H*), 6.06 (s, 1H, C*H*=CCH$_3$), 4.76 (bs, 2H, =CH_2), 4.72–4.65 (m, 1H, C*H*O), 4.47 (s, 2H, CH_2OTBS), 3.63–3.51 (m, 2H, CH_2OH), 2.70–2.25, 2.05–1.90, 1.70–1.60, 0.90–0.80 (m, 11H, C*H*C= and 5 × CH_2), 2.02 (s, 3H, CH=CCH_3), 1.70 (s, 3H, CH_2=CCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.08 (s, 6H, Si(CH_3)$_2$); δ_C(90 MHz): 177.1 (C), 150.8 (C), 149.3 (C), 147.1 (C), 131.0 (C), 121.8 (C), 117.6 (CH), 112.2 (CH_2), 110.2 (CH), 79.5 (CH), 61.4 (CH_2), 57.2 (CH_2), 46.3 (CH_2), 43.6 (CH), 35.3 (CH_2), 31.4 (CH_2), 28.7 (CH_2), 27.7 (CH_2), 26.0 (CH_3), 19.1 (CH_3), 18.8 (CH_3), 18.5 (C), −5.1 (CH_3); *m*/*z* (ES) found 485.2668 (M^+ + Na), $C_{26}H_{42}O_5SiNa$ requires 485.2699.

Triethylamine (38 μL, 0.29 mmol) and mesyl chloride (12 μL, 0.16 mmol) were added sequentially to a stirred solution of the above alcohol (67 mg, 0.14 mmol) in anhydrous CH_2Cl_2 (2 mL) at room temperature under a nitrogen atmosphere. The resulting solution was stirred at room temperature for 3 h and then diluted with CH_2Cl_2 (15 mL) and water (10 mL). The separated aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL) and the combined organic extracts were washed successively with aqueous citric acid (10% w/w, 10 mL) and a saturated aqueous solution of $NaHCO_3$ (20 mL), dried ($MgSO_4$) and concentrated in *vacuo* to leave the corresponding *mesylate* (69 mg, 93%) as a yellow oil. $[\alpha]_D^{22}$ +14.5 (*c* 1.1 in CH_2Cl_2); ν_{max}/cm^{-1}: 1773, 1604; δ_H(360 MHz): 6.15 (s, 1H, OC=C*H*), 6.07 (s, 1H, C*H*=CCH$_3$), 4.83 (bs, 1H, =C*H*H), 4.76 (s, 1H, =CH*H*), 4.73–4.66 (m, 1H, C*H*O), 4.47 (s, 2H, CH_2OTBS), 4.20–4.15 (m, 1H, C*H*HOMs), 4.12–4.07 (m, 1H, CH*H*OMs), 2.95 (s, 3H, OSO_2CH_3), 2.75–2.31, 1.98–1.75 (m, 11H, C*H*C= and 5 × CH_2), 2.02 (s, 3H, CH=CCH_3), 1.69 (s, 3H, CH_2=CCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.09 (s, 6H, Si(CH_3)$_2$); δ_C(90 MHz): 177.1 (C), 151.0 (C), 148.4 (C), 145.2 (C), 131.3 (C), 122.2 (C), 117.4 (CH), 113.2 (CH_2), 110.1 (CH), 79.4 (CH), 68.5 (CH_2), 57.1 (CH_2), 46.3 (CH_2), 42.8 (CH), 37.3 (CH_3), 31.4 (CH_2), 31.2 (CH_2), 28.7 (CH_2), 27.7 (CH_2), 26.0 (CH_3), 19.1 (CH_3), 18.7 (CH_3), 18.5 (C), −5.1 (CH_3); *m*/*z* (ES) found 563.2499 (M^+ + Na), $C_{27}H_{44}O_7SiSNa$ requires 563.2475.

A solution of the above mesylate (69 mg, 0.13 mmol) in THF (1 mL) was added to a stirred suspension of sodium iodide (20 mg, 0.13 mmol) in dry THF (1.5 mL) under a nitrogen atmosphere. The resulting suspension was heated under reflux for 2 h and then treated with more NaI (20 mg, 0.13 mmol) and stirred further under reflux for 1 h. The reaction was cooled to room temperature, then diluted with Et_2O (30 mL) and washed successively with a saturated aqueous solution of NH_4Cl (10 mL) and water (10 mL). The separated aqueous layer was extracted with Et_2O (2 × 20 mL) and the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to leave the *iodide* (73 mg, 100%) as a yellow oil. $[\alpha]_D^{22}$ +5.0 (*c* 0.2 in CH_2Cl_2); ν_{max}/cm^{-1}: 1772, 1725, 1606; δ_H(360 MHz): 6.16 (s, 1H, OC=C*H*), 6.07 (s, 1H, C*H*=CCH$_3$), 4.82 (app. s, 1H, =C*H*H), 4.78 (app. s, 1H, =CH*H*), 4.73–4.66 (m, 1H, C*H*O), 4.47 (s, 2H, CH_2OTBS), 3.19–3.13 (m, 1H, C*H*HI), 3.03–2.95 (m, 1H, CH*H*I), 2.76–2.28, 2.00–1.87, 0.89–0.84 (m, 11H, C*H*C= and 5 × CH_2), 2.04 (s, 3H, CH=CCH_3), 1.68 (s, 3H, CH_2=CCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.09 (s, 6H, Si(CH_3)$_2$); δ_C(90 MHz): 177.1 (C), 150.9 (C), 148.7 (C), 144.9 (C), 131.1 (C), 122.0 (C), 117.5 (CH), 113.3 (CH_2), 110.2 (CH), 79.5 (CH), 57.2 (CH_2), 47.2 (CH), 46.4 (CH_2), 36.3 (CH_2), 32.0 (CH_2), 29.8 (CH_2), 29.0 (CH_2), 27.7 (CH_2), 26.0 (CH_3), 19.1 (CH_3), 18.7 (CH_3), 18.5 (C), −5.1 (CH_3); *m*/*z* (ES) found 595.1689 (M^+ + Na), $C_{26}H_{41}O_4SiINa$ requires 595.1717.

{(*S*)-3-[(*tert*-Butyldimethylsilyloxymethyl)trimethylstannyl-furan-2-ylmethyl]-1-hydroxy-4-methylpent-4-enyl}-5-((*E*)-3-iodo-2-methylallyl)dihydrofuran-2-one 63. A solution of the lactone **49** (119 mg, 0.45 mmol) in dry THF (2.0 mL) at −78 °C was added dropwise over 10 min to a stirred solution of LiHMDS (1.0 M in THF, 0.49 mL, 0.49 mmol) in THF (1.7 mL) under a nitrogen atmosphere. The mixture was stirred at −78 °C for 15 min and then a solution of the aldehyde **45** (209 mg, 0.43 mmol) in THF (2.5 mL) was added dropwise over 10 min. The mixture was stirred at −78 °C for 50 min and then quenched with saturated aqueous NH_4Cl (30 mL). The solution was allowed to warm to room temperature for 10 min and then diluted with water (30 mL) and Et_2O (50 mL). The separated aqueous layer was extracted with Et_2O (3 × 70 mL) and the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to leave the *furanolactone* (265 mg, 71%) as a yellow oil, which was used without purification. $[\alpha]_D^{22}$ +16.6 (*c* 1.0 in CH_2Cl_2), ν_{max}/cm^{-1}: 3529, 1756, 1645, 1628; δ_H(360 MHz): 6.48 (1H, s, OC=C*H*), 6.10–6.06 (1H, bs, =C*H*I), 4.81–4.73 (2H, s, =CH_2), 4.72–4.59 (m, 1H, C*H*O), 4.48 (s, 2H, CH_2OTBS), 4.00–3.41 (m, 1H, C*H*OH), 3.18–2.00 (m, 10H, C*H*C=CH_2, furan CH_2, C*H*C=CH_2, CH_2CHO, CH_2CHCH(OH), CHOHCH_2, CH_2C*H*CH(OH)), 1.85, 1.78 (s, 6H, CH=CCH_3 and CH_2=CCH_3), 0.90 (s, 9H, SiC(CH_3)$_3$),

0.38–0.21(m, 9H, Sn(CH_3)$_3$), 0.10 (s, 6H, (Si(CH_3)$_2$); δ_C (90 MHz) (two main isomers): 178.1 (C), 178.0 (C), 158.2 (C), 157.9 (C), 154.9 (2 × C), 147.8 (C), 146.1 (C), 142.9(C), 142.7 (C), 122.6 (CH), 122.3 (CH), 120.0 (C), 119.8 (C), 112.7 (CH_2), 112.3 (CH_2), 78.8 (CH), 78.7 (CH), 77.2 (CH), 76.6 (CH), 70.0 (CH_2), 69.1 (CH_2), 46.3 (CH), 45.5 (CH), 45.3 (CH_2), 44.9 (CH_2), 44.4 (CH), 44.1 (CH), 43.0 (CH), 42.5 (CH), 37.9 (CH_2), 37.6 (CH_2), 31.7 (CH_2), 31.3 (CH_2), 30.3 (CH_2), 29.7 (CH_2), 26.0 (CH_3), 25.9 (CH_3), 24.4 (CH_3), 18.9 (CH_3), 18.8 (CH_3), 18.5 (C), 1.00 (CH_3), −5.1 (CH_3), −11.2 (CH_3); *m/z* (ES) found 775.1304, (M^+ + Na), $C_{29}H_{49}O_5SnSiINa$ requires 775.1314.

(5*S*,11*S*)-14-(*tert*-Butyldimethylsilyloxymethyl)-9-hydroxy-11-isopropenyl-3-methyl-6,16-dioxatricyclo[11.2.1.1^{5,8}]heptadeca-1(15),2,13-trien-7-one 64. Triphenylarsine (53 mg, 80% mol) and Pd_2dba_3 (21 mg, 10%mol) were added sequentially to a degassed solution of NMP (40 mL) under an argon atmosphere. The resulting yellow solution was stirred at room temperature for 10 min and then a solution of the furanolactone **63** (150 mg, 0.20 mmol) in degassed NMP (40 mL) was added *via* syringe over 2 min. The resulting yellow solution was stirred at 40 °C under argon for 16 h, then cooled to room temperature and diluted with water (50 mL) and Et_2O (60 mL). The separated aqueous layer was extracted with Et_2O (3 × 70 mL) and the combined organic extracts were washed with water (60 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 3 : 1) gave the *furanocembrane* (38 mg, 41%) which could be separated into three diastereoisomers: (i) eluted first (traces), ν_{max}/cm^{-1}: 3516, 1743; δ_H(360 MHz): 6.17 (s, 1H, OC=C*H*), 6.10 (s, 1H, C*H*=CCH$_3$), 5.05–5.01 (m, 1H, C*H*O), 4.75 (bs, 1H, =C*H*H), 4.64 (s, 1H, =CH*H*), 4.52–4.50 (m, 1H, C*H*OH), 4.48 (s, 2H, CH_2OTBS), 4.07 (bs, 1H, CHO*H*), 3.38–3.35, 3.00–1.95 (m, 10H, 4 × CH_2, 2 × C*H*), 1.84 (s, 3H, CH=CCH_3), 1.80 (s, 3H, CH$_2$=CCH_3), 0.95 (s, 9H, SiC(CH_3)$_3$), 0.11 (s, 6H, Si(CH_3)$_2$); *m/z* (ES) 483.2512 (M^+ + Na, $C_{26}H_{40}O_3SiNa$ requires 483.2543); (ii) β-OH diastereomer, eluted second (14 mg), $[\alpha]_D^{22}$ +20.0 (*c* 0.1 in CH_2Cl_2); ν_{max}/cm^{-1}: 1746; δ_H(360 MHz): 6.19 (s, 1H, OC=C*H*), 6.10 (s, 1H, C*H*=CCH$_3$), 5.06 (s, 1H, =C*H*H), 4.94–4.92 (m, 1H, CH$_2$C*H*O), 4.86 (dd, 1H, *J* 1.5 and 1.5, =CH*H*), 4.48 (s, 2H, CH_2OTBS), 4.22 (d, 1H, *J* 6.9, CHO*H*), 3.96–3.88 (m, 1H, C*H*OH), 3.47–3.38 (m, 1H, C*H*CHOH), 3.01 (app. q, 1H, *J* 8.0, C*H*C=CH$_2$), 2.82 (dd, 1H, *J* 13.8 and 2.4, =CC*H*HCHO), 2.66 (d, 2H, *J* 8.0, furan CH_2), 2.31 (dd, 1H, *J* 14.0 and 4.0, =CCH*H*CHO), 2.28–1.80 (m, 4H, CHOCH_2CH and CHOHCH_2), 2.02 (d, 3H, *J* 1.2, CH=CCH_3), 1.84 (s, 3H, CH$_2$=CCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.08 (s, 6H, Si(CH_3)$_2$); δ_C(90 MHz): 179.6 (C), 150.4 (C), 150.1 (C), 149.4 (C), 138.1 (C), 122.4 (C), 119.1 (CH), 111.1 (CH_2), 110.6 (CH), 79.5 (CH), 71.9 (CH), 57.1 (CH_2), 44.2 (CH_2), 39.8 (CH), 39.7 (CH), 37.1 (CH_2), 32.4 (CH_2), 31.9 (CH_2), 26.0 (CH_3), 22.4 (CH_3), 20.2 (CH_3), 18.5 (C), −5.1 (CH_3); *m/z* (ES) 483.2544 (M^+ + Na, $C_{26}H_{40}O_3SiNa$ requires 483.2543); iii) α-OH diastereoisomer,eluted third (13 mg), ν_{max}/cm^{-1}: 3610, 1763, 1602; δ_H(360 MHz): 6.18 (s, 1H, OC=C*H*), 6.10 (s, 1H, C*H*=CCH$_3$), 4.96 (s, 1H, =C*H*H), 4.96–4.91 (m, 1H, CH$_2$C*H*O), 4.88 (dd, 1H, *J* 1.5 and 1.5, =CH*H*), 4.49 (s, 2H, CH_2OTBS), 4.23–4.19 (m, 1H, C*H*OH), 3.27 (dd, 1H, *J* 13.3 and 8.5, C*H*CHOH), 2.80 (dd, 1H, *J* 13.8 and 2.4, =CC*H*HCHO), 2.70 (d, 2H, *J* 8.0, furan CH_2), 2.59–2.44 (m, 2H, CHOC*H*HCH and C*H*C=CH$_2$), 2.35 (dd, 1H, *J* 13.9 and 4.5, =CCH*H*CHO), 2.10 (dd, 1H, *J* 12.3 and 8.5, CHOCH*H*CH), 1.95 (d, 3H, *J* 1.3, CH=CCH_3), 1.79 (s, 3H, CH$_2$=CCH_3), 1.52–1.43 (m, 2H, CHOHCH_2), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.09 (s, 6H, Si(CH_3)$_2$); δ_C(90 MHz): 179.0 (C), 149.2 (C), 149.1 (C), 146.3 (C), 138.5 (C), 121.9 (C), 119.5 (CH), 113.1 (CH_2), 110.4 (CH), 79.1 (CH), 67.2 (CH), 57.2 (CH_2), 44.3 (CH_2), 42.1 (CH), 41.9 (CH), 38.7 (CH_2), 30.5 (CH_2), 26.0 (CH_3), 24.0 (CH_2), 21.9 (CH_3), 19.0 (CH_3), 18.5 (C), −5.1 (CH_3); *m/z* (ES) found 483.2504 (M^+ + Na), $C_{26}H_{40}O_5SiNa$ requires 483.2543.

Acetic acid (5*S*,11*S*)-14-(*tert*-butyldimethylsilyloxymethyl)-11-isopropenyl-3-methyl-7-oxo-6,16-dioxatricyclo[11.2.1.1^{5,8}]heptadeca-1(15),2,13-trien-9-yl ester 65a (β-OAc). Triethylamine (8 μL, 60.8 μmol), DMAP (1 mg, cat.) and acetic anhydride (3.44 μL, 36.5 μmol) were added sequentially to a stirred solution of the alcohol **64** (β-OH) (14 mg, 30.4 μmol) in anhydrous CH_2Cl_2 (1 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 2 h, then allowed to warm to room temperature and treated with more triethylamine (8 μL, 60.8 μmol), DMAP (1 mg, cat.) and acetic anhydride (3.44 μL, 36.5 μmol). The mixture was stirred for a further 2 h and then the solvent was partially removed *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 2 : 1) gave the *acetylated furanocembrane* (8 mg, 52%) as a colourless oil. $[\alpha]_D^{22}$ +20.5 (*c* 0.4 in CH_2Cl_2); ν_{max}/cm^{-1}: 2953, 1767, 1727; δ_H(360 MHz): 6.19 (s, 1H, OC=C*H*), 6.08 (s, 1H, C*H*=CCH$_3$), 4.92 (s, 1H, =C*H*H), 4.88–4.82 (m, 2H, =CH*H* and CH$_2$C*H*O), 4.71 (ddd, 1H, *J* 4.9, 4.9 and 1.8, C*H*OAc), 4.49 (s, 2H, CH_2OTBS), 3.52–3.45 (m, 1H, C*H*CHOAc), 2.99–2.91 (m, 1H, C*H*C=CH$_2$), 2.77 (dd, 1H, *J* 13.6 and 2.2, =CC*H*HCHO), 2.24 (dd, 1H, *J* 13.6 and 3.5, =CCH*H*CHO), 2.75–2.40, 2.18–1.80 (m, 6H, furan CH_2, CHOCH_2CH and CH(OAc)CH_2), 2.00 (s, 6H, CH=CCH_3), 1.87 (s, 3H, CH$_2$=CCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.10 (s, 6H, Si(CH_3)$_2$); δ_C (90 MHz): 175.3 (C), 171.8 (C), 149.7 (2 × C), 149.6 (C), 138.2 (C), 122.5 (C), 118.7 (CH), 110.8 (CH_2), 110.7 (CH), 78.5 (CH), 73.0 (CH), 57.1 (CH_2), 44.4 (CH_2), 39.7 (CH), 38.4 (CH), 35.2 (CH_2), 32.5 (CH_2), 31.9 (CH_2), 26.0 (CH_3), 22.3 (CH_3), 21.3 (CH_3), 20.8 (CH_3), 18.5 (C), −5.1 (CH_3); *m/z* (ES) found 525.2610 (M^+ + Na), $C_{28}H_{42}O_6SiNa$ requires 525.2648.

Acetic acid (5*S*,11*S*)-14-hydroxymethyl-11-isopropenyl-3-methyl-7-oxo-6,16-dioxatricyclo[11.2.1.1^{5,8}]heptadeca-1(15),2,13-trien-9-yl ester 65b (β-OAc). A solution of 10-camphorsulfonic acid (1.5 mg, 6.4 μmol) in CH_2Cl_2–MeOH (0.1 mL : 0.1 mL) was added to a stirred solution of the furanocembrane **65a** (β-OAc) (8 mg, 15.9 μmol) in CH_2Cl_2–MeOH (0.5 mL : 0.5 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h and then treated with more 10-camphorsulfonic acid (1.5 mg, 6.4 μmol). The mixture was further stirred at 0 °C for 2 h and then the solvent was partially removed *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 1 : 1) gave the *alcohol* (4 mg, 65%) as a colourless solid. $[\alpha]_D^{22}$ +21.0 (*c* 0.4 in CH_2Cl_2); ν_{max}/cm^{-1}: 3679, 1774, 1728, 1606; δ_H(360 MHz): 6.25 (s, 1H, OC=C*H*), 6.08 (s, 1H, C*H*=CCH$_3$), 4.92 (s, 1H, =C*H*H), 4.90–4.85 (m, 2H, =CH*H* and CH$_2$C*H*O), 4.70 (ddd, 1H, *J* 5.0, 5.0 and 1.9, CHC*H*OAc), 4.47 (s, 2H, CH_2OH), 3.49–3.42 (m, 1H, C*H*CHOAc), 2.99–2.95 (m, 1H, C*H*C=CH$_2$), 2.81–2.09 (m, 8H, =CCH_2CHO, furan CH_2, CHOCH_2CH and CH(OAc)CH_2), 2.01 (d, 3H, *J* 1.2, CH=CCH_3), 2.00 (s, 3H, COCH_3), 1.87 (s, 3H, CH$_2$=CCH_3); δ_C(90 MHz): 175.2 (C), 171.8 (C), 150.9 (C), 150.1 (C), 149.5 (C), 138.7 (C), 122.1 (C), 118.5 (CH), 110.9 (CH_2), 110.6 (CH), 78.3 (CH), 72.7 (CH), 56.3 (CH_2), 44.4 (CH_2), 39.7 (CH), 38.3 (CH), 35.2 (CH_2), 32.2 (CH_2), 31.8 (CH_2), 22.3 (CH_3), 21.6 (CH_3), 20.8 (CH_3); *m/z* (ES) found 411.1773 (M^+ + Na), $C_{22}H_{28}O_6Na$ requires 411.1783.

Acetic acid (5*S*,11*S*)-(*E*)-14-formyl-11-isopropenyl-3-methyl-7-oxo-6,16-dioxatricyclo[11.2.1.1^{5,8}]heptadeca-1(15),2,13-trien-9-yl ester 65c (β-OAc). Dess–Martin periodinane (15% w/w solution in CH_2Cl_2, 35 μL, 12.4 μmol) was added to a stirred solution of the alcohol **65b** (β-OAc) (4 mg, 10.4 μmol) and pyridine (1 drop) in anhydrous CH_2Cl_2 (1 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 2 h and then the solvent was partially removed *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 1 : 1) gave the *aldehyde* (3.5 mg, 87%) as a colourless solid. $[\alpha]_D^{22}$ −9.8 (*c* 0.9 in CH_2Cl_2); ν_{max}/cm^{-1}: 1775, 1733, 1679; δ_H(360 MHz): 9.90 (s, 1H, C*H*O), 6.55 (s, 1H, OC=C*H*), 6.10 (s, 1H, C*H*=CCH$_3$), 4.95 (s, 1H, =C*H*H), 4.90–4.85 (m, 2H, =CH*H* and CH$_2$C*H*O), 4.82–4.80 (m, 1H, CHC*H*OAc), 3.33 (m, 1H, C*H*CHOAc), 3.10–2.85 (m, 3H, furan CH_2 and

C*H*C=CH_2), 2.82 (dd, 1H, *J* 13.6 and 2.3, =CC*H*HCHO), 2.52–2.44 (m, 1H, CHOC*H*HCH), 2.32 (dd, 1H, *J* 13.6 and 4.0, =CC*H*HCHO), 2.20–1.80 (m, 3H, CHOCH*H*CH and CH(OAc)CH_2), 2.02 (s, 3H, COCH_3), 1.98 (s, 3H, CH=CCH_3), 1.89 (s, 3H, CH_2=CCH_3); δ_C(90 MHz): 184.4 (CH), 174.7 (C), 171.6 (C), 163.0 (C), 151.0 (C), 148.6 (C), 142.6 (C), 124.8 (C), 117.6 (CH), 111.6 (CH_2), 106.9 (CH), 77.4 (CH), 72.3 (CH), 44.2 (CH_2), 39.7 (CH), 38.4 (CH), 35.4 (CH_2), 33.2 (CH_2), 31.6 (CH_2), 22.1 (CH_3), 21.1 (CH_3), 20.7 (CH_3); *m*/*z* (ES) found 409.1601 (M^+ + Na), $C_{22}H_{26}O_6Na$ requires 409.1627.

Acetic acid (5*S*,8*S*,9*S*,11*S*)-14-(*tert*-butyldimethylsilyloxymethyl)-11-isopropenyl-3-methyl-7-oxo-6,16-dioxatricyclo[11.2.1.1^{5,8}]-heptadeca-1(15),2,13-trien-9-yl ester 65a (α-OAc). Triethylamine (7.4 μL, 56.5 μmol), DMAP (1 mg, cat.) and acetic anhydride (3.4 mg, 33.9 μmol) were added sequentially to a stirred solution of the alcohol **64** (α-OAc) (13 mg, 28.3 μmol) in anhydrous CH_2Cl_2 at 0 °C under a nitrogen atmosphere. The solution was stirred at 0 °C for 1 h and then the solvent partially removed *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 2 : 1) gave the *aceylated furanocembrane* (7 mg, 49%) as a colourless oil. $[\alpha]_D^{22}$ +50.9 (*c* 0.7 in CH_2Cl_2); ν_{max}/cm^{-1}: 1768, 1735; δ_H(360 MHz): 6.20 (s, 1H, OC=C*H*), 6.09 (s, 1H, C*H*=CCH$_3$), 5.06–5.03 (m, 2H, =C*H*H and C*H*OAc), 4.94 (s, 1H, =CH*H*), 4.91–4.88 (m, 1H, CH_2C*H*O), 4.49 (s, 2H, CH_2OTBS), 3.46 (dd, 1H, *J* 12.9 and 9.6, C*H*CHOAc), 2.80 (dd, 1H, *J* 13.8 and 1.9, =CC*H*HCHO), 2.72–2.65 (m, 3H, furan CH_2, C*H*C=CH_2), 2.30 (dd, 1H, *J* 14.0 and 4.0, =CCH*H*CHO), 2.22–1.80 (m, 4H, CHOCH_2CH, CH(OAc)CH_2), 2.00 (s, 3H, CH=CCH_3), 1.98 (s, 3H, COCH_3), 1.79 (s, 3H, CH_2=CCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.10 (s, 6H, Si(CH_3)$_2$); δ_C (90 MHz): 177.6 (C), 169.8 (C), 149.4 (C), 149.1 (C), 145.3 (C), 137.6 (C), 122.5 (C), 119.1 (CH), 113.9 (CH_2), 110.7 (CH), 78.6 (CH), 70.1 (CH), 57.1 (CH_2), 44.6 (CH_2), 40.9 (CH), 40.3(CH), 35.1 (CH_2), 30.6 (CH_2), 26.0 (CH_3), 25.6 (CH_2), 22.2 (CH_3), 20.9 (CH_3), 18.8 (CH_3), 18.5 (C), −5.1 (CH_3); *m*/*z* (ES) found 525.2609 (M^+ + Na), $C_{28}H_{42}O_6SiNa$ requires 525.2648.

Acetic acid (5*S*,8*S*,9*S*,11*S*)-14-hydroxymethyl-11-isopropenyl-3-methyl-7-oxo-6,16-dioxatricyclo[11.2.1.1^{5,8}]heptadeca-1(15),2,13-trien-9-yl ester 65b (α-OAc). A solution of 10-camphorsulfonic acid (1.3 mg, 5.6 μmol) in CH_2Cl_2–MeOH (0.1 mL : 0.1 mL) was added to a stirred solution of the furanocembrane **65a** (α-OAc) (7 mg, 13.9 μmol) in CH_2Cl_2–MeOH (0.5 mL : 0.5 mL) at 0 °C. The solution was stirred at 0 °C for 1 h and then treated with more 10-camphorsulfonic acid (1.3 mg, 5.6 μmol). The reaction was stirred for 2 h and then the solvent was partially removed *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 1 : 1) gave the *alcohol* (4 mg, 75%) as a colourless solid. ν_{max}/cm^{-1}: 3854, 1773, 1734; δ_H(360 MHz): 6.27 (s, 1H, OC=C*H*), 6.10 (s, 1H, C*H*=CCH$_3$), 5.07–5.04 (m, 2H, CHC*H*OAc and =C*H*H), 4.95 (s, 1H, =CH*H*), 4.92–4.88 (m, 1H, CH_2C*H*O), 4.47 (s, 2H, CH_2OTBS), 3.44 (dd, 1H, *J* 13.0 and 9.1, C*H*CHOAc), 2.82 (dd, 1H, *J* 13.8 and 2.0, =CC*H*HCHO), 2.75–2.62 (m, 3H, furan CH_2 and C*H*=CCH$_3$), 2.31 (dd, 1H, *J* 13.8 and 4.0, =CCH*H*CHO), 2.28–1.85 (m, 4H, CHOCH_2CH, CH(OAc)CH_2), 2.01 (d, 3H, *J* 1.2, CH=CCH_3), 1.98 (s, 3H, COCH_3), 1.81 (s, 3H, CH_2=CCH_3); δ_C (90 MHz): 177.5 (C), 169.8 (C), 150.3 (C), 149.9 (C), 145.1 (C), 138.1 (C), 122.1 (C), 118.9 (CH), 114.0 (CH_2), 110.7 (CH), 78.6 (CH), 70.1 (CH), 56.3 (CH_2), 44.6 (CH_2), 40.9 (CH), 40.3 (CH), 35.2 (CH_2), 30.4 (CH_2), 25.6 (CH_2), 22.2 (CH_3), 21.0 (CH_3), 18.8 (CH_3); *m*/*z* (ES) found 411.1750 (M^+ + Na), $C_{22}H_{28}O_6Na$ requires 411.1783.

Acetic acid (5*S*,8*S*,9*S*,11*S*)-(*E*)-14-formyl-11-isopropenyl-3-methyl-7-oxo-6,16-dioxatricyclo[11.2.1.1^{5,8}]heptadeca-1(15),2,13-trien-9-yl ester 65c (α-OAc). Dess–Martin periodinane (15% w/w solution in CH_2Cl_2, 35 μL, 12.4 μmol) was added to a stirred solution of the alcohol **65b** (4 mg, 10.4 μmol) and pyridine (1 drop) in CH_2Cl_2 at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 2 h and then the solvent was partially removed *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 1 : 1) gave the *aldehyde* (3.5 mg, 74%) as a colourless solid. $[\alpha]_D^{22}$ +26.0 (*c* 0.9 in CH_2Cl_2); ν_{max}/cm^{-1}: 1734, 1678, 1602; δ_H(360 MHz): 9.90 (s, 1H, C*H*O), 6.56 (s, 1H, OC=C*H*), 6.12 (s, 1H, C*H*=CCH$_3$), 5.09–5.06 (m, 2H, CHC*H*OAc and =C*H*H), 4.99 (s, 1H, =CH*H*), 4.95–4.93 (bs, 1H, CH_2C*H*O), 3.33 (dd, 1H, *J* 13.0 and 8.5, C*H*CHOAc), 3.12–3.07 (m, 2H, furan CH_2), 2.86 (dd, 1H, *J* 13.7 and 1.9, =CC*H*HCHO), 2.65 (ddd, 1H, *J* 10.0, 10.0 and 3.6, C*H*C=CH_2), 2.37 (dd, 1H, *J* 13.7 and 4.0, =CCH*H*CHO), 2.20–1.80 (m, 4H, CHOCH_2CH, CH(OAc)CH_2), 2.00 (s, 6H, CH=CCH_3 and COCH_3), 1.84 (s, 3H, CH_2=CCH_3); δ_C (90 MHz): 184.5 (CH), 177.0 (C), 169.8 (C), 162.4 (C), 150.9 (C), 144.4 (C), 141.8 (C), 124.9 (C), 117.9 (CH), 114.5 (CH_2), 107.2 (CH), 78.3 (CH), 69.7 (CH), 44.4 (CH_2), 40.9 (CH), 40.4 (CH), 35.6 (CH_2), 31.6 (CH_2), 25.4 (CH_2), 22.2 (CH_3), 20.9 (CH_3), 18.7 (CH_3); *m*/*z* (ES) found 409.1591 $C_{22}H_{26}O_6Na$ (M^+ + Na), $C_{22}H_{26}O_6Na$ requires 409.1627.

X-Ray crystal structure of 65c. A crystal was encapsulated in a film of RS3000 perfluoropolyether oil and mounted on a dual-stage glass fibre before transfer to a SMART1k diffractometer on Station 9.8 of the Synchrotron Radiation Source at CCLRC Daresbury Laboratory.

Crystal data. $C_{22}H_{26}O_6$, M = 386.43, orthorhombic, a = 6.565(4), b = 8.698(5), c = 34.72(2) Å, U = 1983(3) Å^3, T = 150(2) K, space group $P2_12_12_1$ (No. 19), Z = 4, D_c = 1.295 g cm^{-3}, μ(Mo-Kα) = 0.094 mm^{-1}, 1680 unique reflections measured were used in all calculations. Final R_1 [1651 $F \geq 4\Phi(F)$] = 0.0878 and wR(all F^2) was 0.222. No meaningful Flack parameters could be obtained for this experiment.†

(*R*)-3-{(*S*)-3-[(*tert*-Butyldimethylsilyloxymethyl)trimethylstannanylfuran-2-ylmethyl]-1-hydroxy-4-methylpent-4-enyl}-5-(3-iodo-2-methylallyl)-3-phenylselanyldihydrofuran-2-one 66. A solution of the phenylselenolactone **44** (127 mg, 0.30 mmol) in THF (2.0 mL) was added dropwise over 10 min to a stirred solution of LiHMDS (0.33 mL, 0.33 mmol) in THF (2.5 mL) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 15 min and then a solution of the aldehyde **45** (146 mg, 0.30 mmol) in THF (2.0 mL) was added dropwise over 10 min. The mixture was stirred at −78 °C for 50 min and then quenched by the addition of a saturated solution of aqueous NH_4Cl (10 mL). The resulting mixture was allowed warm to room temperature for 10 min and then diluted with water (30 mL) and Et_2O (50 mL). The separated aqueous layer was extracted with Et_2O (2 × 40 mL) and the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to leave the *furanolactone* (254 mg, 93%) as a mixture of diastereoisomers. $[\alpha]_D^{22}$ +12.9 (*c* 0.7 in CH_2Cl_2); ν_{max}/cm^{-1}: 3593, 1755, 1644, 1618; δ_H(360 MHz): 7.69–7.55 (m, 2H, Ar*H*), 7.46–7.31 (m, 3H, Ar*H*), 6.52, 6.48 (s, 1H, OCSn=C*H*), 5.98, 5.92, 5.86 (s, 1H, =C*H*I), 4.80–4.68 (m, 2H, =CH_2), 4.52–4.48 (m, 3H, C*H*O and CH_2OTBS), 3.76 (d, 1H, *J* 3.5, C*H*OH), 2.80–2.15 (m, 9H, C*H*C=CH_2, furan CH_2, CHOCH_2CSe, =CCH_2CHO and CHOHCH_2), 1.83, 1.81, 1.79, 1.76, 1.58 (s, 6H, CH=CCH_3 and CH_2=CCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.37–0.21 (m, 9H, Sn(CH_3)$_3$), 0.09 (s, 6H, Si(CH_3)$_2$); δ_C(90 MHz) (main isomer): 176.4 (C), 158.1 (C), 155.0 (C), 145.8 (C), 142.5 (C), 138.0 (CH), 130.0 (CH), 129.4 (CH), 126.3 (C), 122.4 (CH), 119.9 (C), 113.2 (CH_2), 78.7 (CH), 75.5 (CH), 71.8 (CH), 57.3 (C), 55.5 (CH_2), 45.3 (CH_2), 43.4 (CH), 35.6 (CH_2), 35.1 (CH_2), 33.4 (CH_2), 26.1 (CH_3), 18.5 (C), 18.1 (CH_3), 1.1 (CH_3), −5.1 (CH_3), −9.1 (CH_3).

† CCDC reference numbers 270128 and 270127. See http://dx.doi.org/10.1039/b504545b for crystallographic data in CIF or other electronic format.

(*R*)-3-{(*S*)-3-[3-(*tert*-Butyldimethylsilyloxymethyl)-5-trimethylstannanylfuran-2-ylmethyl]-1-hydroxy-4-methylpent-4-enyl}-5-((*E*)-3-iodo-2-methylallyl)-5*H*-furan-2-one 67. Hydrogen peroxide (30% w/w in water, 0.05 mL) was added dropwise over 1 min to a stirred solution of the phenylselenolactone **66** (150 mg, 0.16 mmol) in anhydrous CH_2Cl_2–pyridine (5 mL : 5 mL). The solution was stirred at room temperature for 1 h and then treated with a saturated aqueous solution of $NaHCO_3$ (15 mL). The separated aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL) and the combined organic layers were then dried (Na_2SO_4) and concentrated *in vacuo*. Chloroform was added to the residue and the solution was concentrated *in* vacuo to leave a 2 : 1 mixture of diastereoisomers of the butenolide (150 mg) which was used without purification. δ_H(360 MHz) (main isomer): 7.22–7.19 (bs, 1H, CHOC*H*=C), 6.52–6.48 (bs, 1H, OC=C*H*), 6.05–5.95 (bs, 1H, =C*H*I), 5.00–4.90 (m, 1H, C*H*OCH=C), 4.82–4.77 (m, 2H, =CH_2), 4.51 (s, 2H, CH_2OTBS), 4.45–4.35 (m, 1H, =CC*H*OH), 2.90–2.50, 1.75–1.60 (m, 7H, C*H*C=CH$_2$, furan CH_2, =CCH_2CHO and CHOHCH_2), 1.93, 1.73 (s, 6H, CH=CCH_3 and CH$_2$=CCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.37–0.21 (m, 9H, Sn(CH_3)$_3$), 0.09 (s, 6H, Si(CH_3)$_2$); δ_C(90 MHz) (main isomer): 171.8 (C), 154.8 (C), 146.2 (C), 145.3 (C), 141.9 (C), 140.6 (CH), 137.9 (C), 122.4 (CH), 120.2 (C), 113.2 (CH$_2$), 111.1 (CH), 79.5 (CH), 65.3 (CH), 57.3 (CH$_2$), 42.9 (CH$_2$), 42.8 (CH), 37.9 (CH$_2$), 29.5 (CH$_2$), 26.0 (CH$_3$), 24.5 (CH$_3$), 18.5 (C), 1.1 (CH$_3$), −5.1 (CH$_3$), −9.1 (CH$_3$); *m*/*z* (ES) found 773.1119 (M$^+$ + Na), $C_{29}H_{47}O_5SiSnINa$ requires 773.1157. Approximately 20% destannylated material was also obtained, which could not be completely removed from the product.

Acetic acid (5*R*,11*S*)-14-(*tert*-butyldimethylsilyloxymethyl)-11-isopropenyl-3-methyl-7-oxo-6,16-dioxatricyclo[11.2.1.1^{5,8}]heptadeca-1(15),2,8(17),13-tetraen-9-yl ester 69. Triphenylarsine (49 mg, 80% mol) and Pd_2dba_3 (18 mg, 10% mol) were added sequentially to a degassed solution of NMP (40 mL) under an argon atmosphere. The resulting yellow solution was stirred at room temperature for 10 min and then a solution of the crude furanolactone **67** (150 mg, 0.20 mmol) in degassed NMP (40 mL) was added dropwise *via* syringe over 2 min. The resulting yellow mixture was stirred at 40 °C for 16 h under an argon atmosphere and then diluted with water (40 mL) and Et_2O (50 mL). The separated aqueous layer was extracted with Et_2O (3 × 100 mL) and the combined organic extracts were then washed with water (4 × 70 mL), dried ($MgSO_4$) and evaporated *in vacuo*. The residue was quickly forced through a pad of silica (petroleum ether–Et_2O 3 : 1) to leave the impure *furanocembrane* **68** as a mixture of two diastereoisomers. The reaction was repeated with the furanolactone **67** (150 mg, 0.20 mmol) and the combined products were used in the next step (17 mg, 10% from **66**).

Triethylamine (10 μL, 74.2 μmol), DMAP (1 mg, cat.) and acetic anhydride (4 μL, 44.5 μmol) were added sequentially to a stirred solution of the secondary alcohol **68** (17 mg, 37.1 μmol) in anhydrous CH_2Cl_2 (1.5 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 2 h, then warmed to room temperature and further treated with triethylamine (5 μL, 37.1 μmol), DMAP (1 mg, cat.) and acetic anhydride (2 μL, 22.2 μmol). The mixture was stirred at room temperature for 3 h and the solvent was then partially removed *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 2 : 1) gave the *acetylated furanocembrane* (10 mg, 54%) as a 2.3 : 1 mixture of diastereoisomers, which could not be separated. *Major isomer*: δ_H(400 MHz, 318 K): 7.34 (d, 1H, *J* 1.2, CHOC*H*=), 6.04 (s, 1H, OC=C*H*), 5.90 (bs, 1H, C*H*=CCH$_3$), 5.74 (dd, 1H, *J* 6.3 and 2.5, C*H*OAc), 5.24 (bs, 1H, CH$_2$C*H*O), 4.86 (bs, 1H, =C*H*H), 4.82 (bs, 1H, =CH*H*), 4.47 (s, 2H, CH_2OTBS), 2.91 (dd, 1H, *J* 13.6 and 3.6, =CC*H*HCHO), 2.80–2.00 (m, 6H, furan CH_2, C*H*C=CH$_2$, =CCH*H*CHO and CH(OAc)CH_2), 1.94 (s, 3H, OCOCH_3), 1.85 (s, 3H, CH$_2$=CCH_3), 1.73 (s, 3H, CH=CCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.09 (s, 6H, Si(CH_3)$_2$); *m*/*z* (ES) 523.2484 (M$^+$ + Na, $C_{28}H_{40}O_6SiNa$ requires 523.2492). *Minor isomer*: δ_H(400 MHz, 318 K): 7.13 (bs, 1H, CHOC*H*=), 6.07 (s, 1H, OC=C*H*), 5.97 (bs, 1H, C*H*=CCH$_3$), 5.43 (d, 1H, *J* 12, C*H*OAc), 5.24 (bs, 1H, CH$_2$C*H*O), 5.12 (bs, 1H, =C*H*H), 4.97 (bs, 1H, =CH*H*), 4.46 (s, 2H, CH_2OTBS), 2.98 (dd, 1H, *J* 13.4 and 3.1, C*H*HCHO), 2.8–2.05 (m, 6H, furan CH_2, C*H*C=CH$_2$, CH*H*CHO and CH(OAc)CH_2), 2.02 (s, 3H, OCOCH_3), 1.85 (s, 3H, CH$_2$=CCH_3), 1.81 (s, 3H, CH=CCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.09 (s, 6H, Si(CH_3)$_2$); *m*/*z* (ES) found 523.2484 (M$^+$ + Na), $C_{28}H_{40}O_6SiNa$ requires 523.2492.

Acetic acid (5*R*,11*S*)-14-hydroxymethyl-11-isopropenyl-3-methyl-7-oxo-6,16-dioxatricyclo[11.2.1.1^{5,8}]heptadeca-1(15),2,8(17),13-tetraen-9-yl ester 70. A solution of 10-camphorsulfonic acid (6.0 μmol) in anhydrous CH_2Cl_2–MeOH (0.5 mL : 0.5 mL) was added over 1 min to a stirred solution of the silyl ether **69** (2.3 : 1 mixture of OAc epimers) (7 mg, 15.0 μmol) in anhydrous CH_2Cl_2–MeOH (0.5 mL : 0.5 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h, then treated with more 10-camphorsulfonic acid (6.0 μmol, 0.4 eq.) and stirred for 2 h. The solvent was partially removed *in vacuo* to leave a residue which was purified by chromatography (petroleum ether–Et_2O 1 : 1) to leave the *alcohol* (4.5 mg, 78%) as a 2.3 : 1 mixture of diastereoisomers. Further chromatography gave: (i) the major OAc-epimer, δ_H(400 MHz, 318 K): 7.34 (d, 1H, *J* 1.4, CHOC*H*=), 6.12 (s, 1H, OC=C*H*), 5.92 (bs, 1H, C*H*=CCH$_3$), 5.73 (dd, 1H, *J* 5.8 and 2.6, C*H*OAc), 5.25 (bs, 1H, CH$_2$C*H*O), 4.87 (s, 1H, =C*H*H), 4.83 (s, 1H, =CH*H*), 4.44 (d, 2H, *J* 5.2, CH_2OH), 2.92 (dd, 1H, *J* 13.6 and 3.5, =CC*H*HCHO), 2.8–2.00 (m, 6H, furan CH_2, C*H*C=CH$_2$, =CCH*H*CHO and CH(OAc)CH_2), 1.95 (s, 3H, OCOCH_3), 1.85 (s, 3H, CH$_2$=CCH_3), 1.74 (s, 3H, CH=CCH_3); *m*/*z* (ES) found 409.1605 (M$^+$ + Na) $C_{22}H_{26}O_6Na$ requires 409.1627; (ii) a 2 : 1 mixture of diastereoisomers of the acetate, from which the ^{1}H NMR data for the minor epimeric acetate were deduced. δ_H(400 MHz, 318 K): 7.13 (bs, 1H, CHOC*H*=), 6.14 (s, 1H, OC=C*H*), 5.98 (bs, 1H, C*H*=CCH$_3$), 5.42 (bd, 1H, *J* 12, C*H*OAc), 5.25 (bs, 1H, CH$_2$C*H*O), 5.16 (bs, 1H, =C*H*H), 4.98 (bs, 1H, =CH*H*), 4.44 (s, 2H, CH_2OH), 2.98 (dd, 1H, *J* 13.7 and 3.6, =CC*H*HCHO), 2.8–2.05 (m, 6H, furan CH_2, C*H*C=CH$_2$, =CCH*H*CHO and CH(OAc)CH_2), 2.02 (s, 3H, COCH_3), 1.85 (s, 3H, CH=CH_3), 1.81 (s, 3H, CH$_2$=CH_3).

Acetic acid (5*R*,11*S*)-14-formyl-11-isopropenyl-3-methyl-7-oxo-6,16-dioxatricyclo[11.2.1.1^{5,8}]heptadeca-1(15),2,8(17),13-tetraen-9-yl ester 71. Dess–Martin periodinane (35% w/w in CH_2Cl_2, 34 μL, 12.5 μmol) was added in one portion to a stirred solution of the major, pure diastereoisomer of the alcohol **70a** (4 mg, 10.4 μmol) in anhydrous CH_2Cl_2 (1 mL) and pyridine (1 drop) at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 2 h and then the solvent was partially removed *in vacuo*. Chromatography of the residue (petroleum ether–Et_2O 1 : 1) gave the α-OAc *bis-deoxylophotoxin* (2.5 mg, 61%) as an oil. δ_H(400 MHz, 318 K): 9.86 (s, 1H, C*H*O), 7.31 (bs, 1H, CHOC*H*=), 6.44 (s, 1H, OC=C*H*), 5.95 (bs, 1H, C*H*=CCH$_3$), 5.77 (dd, 1H, *J* 4.3 and 4.3, C*H*OAc), 5.27 (bs, 1H, CH$_2$C*H*O), 4.91 (s, 1H, =C*H*H), 4.88 (s, 1H, =CH*H*), 2.92 (dd, 1H, *J* 13.6 and 3.6, =CC*H*HCHO), 2.8–2.5 (m, 6H, furan CH_2, C*H*C=CH$_2$, =CCH*H*CHO and CH(OAc)CH_2), 1.95 (s, 3H, OCOCH_3), 1.85 (s, 3H, CH=CCH_3), 1.74 (s, 3H, CH$_2$=CCH_3); *m*/*z* (ES) 407.1444, (M$^+$ + Na, $C_{22}H_{24}O_6Na$ requires 407.1470). Oxidation of a 2 : 1 mixture of diastereoisomers of **70**, under the same conditions, gave a 2 : 1 mixture of diastereoisomers of **71**, from which the ^{1}H NMR data for the minor β-OAc epimer were deduced. δ_H(400 MHz, 318 K): 9.84 (s, 1H, C*H*O), 7.16 (s, 1H, CHOC*H*=), 6.44 (s, 1H, OC=C*H*), 5.95 (bs, 1H, C*H*=CCH$_3$), 5.46 (bd, 1H, *J* 11.0, C*H*OAc), 5.27 (bs, 1H, CH$_2$C*H*O), 5.21 (s, 1H, =C*H*H), 5.02 (s, 1H, =CH*H*), 2.98 (dd, 1H, *J* 13.6 and 3.6, =CC*H*HCHO), 2.80–2.00 (m, 6H, 2 × CH$_2$, C*H*C=CH$_2$ and =CCH*H*CHO), 2.03 (s, 3H, OCOCH_3),

1.87 (s, 3H, CH_2=CCH_3), 1.84 (s, 3H, CH=CCH_3); *m/z* (ES) found 407.1441 (M^+ + Na), $C_{22}H_{24}O_6Na$ requires 407.1470.

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