A Stille cyclisation approach to (−)-periplanone-B: studies in alkene-selective ring-closing metathesis and an improved chromium(II)-mediated synthesis of (*E*)-alkenylstannanes from aldehydes

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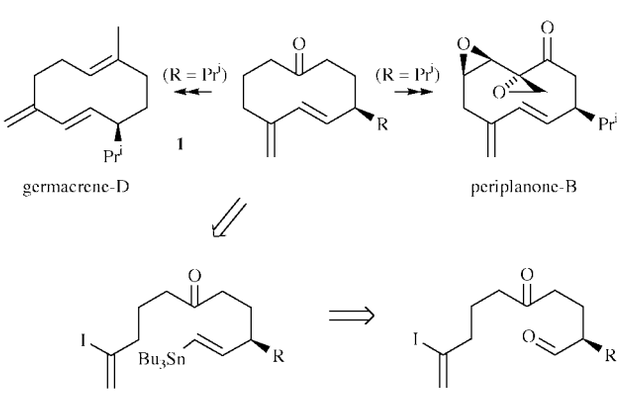
A synthesis of the dienone **7** *via* an efficient intramolecular Stille cross-coupling reaction, an improved chromium(II)-mediated synthesis of (*E*)-alkenylstannanes from aldehydes using Bu_3SnCHI_2 in DMF, and a synthesis of the substituted (−)-dienone **25** *via* ring-closing alkene metathesis to give dihydropyran **22** are described. The synthesis of (−)-dienone **25** constitutes a formal synthesis of (−)-periplanone-B.

Introduction

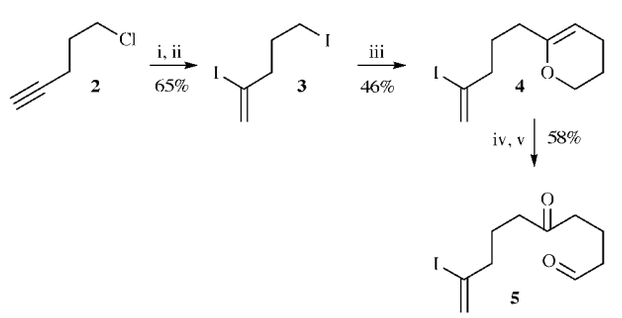
Intramolecular Pd-catalysed cross-coupling between alkenylstannane and alkenyl halide (or triflate) functionality is now firmly established as important methodology for the construction of unsaturated heterocycles and carbocycles.[1] However, there are only a limited number of efficient ways of introducing both stannane and halide (or triflate) groups into the same substrate. Structural and functional group constraints are particularly apparent for all-carbon backbone cases. We considered that our recently developed chromium(II)-based chemistry for preparing (*E*)-alkenylstannanes from aldehydes[2] could potentially provide, in certain cases, an attractive solution to the above problem. This process is highly chemoselective, complementing the Stille reaction, and any pre-existing alkenyl halide (or triflate) functionality should be unaffected by $CrCl_2$, in the absence of Ni or Pd salts.[3] To illustrate this approach we initially decided to examine a medium ring cyclisation strategy for generating the dienone **1** (Scheme 1, R = H),[4] with the subsequent aim of applying the methodology in a natural product synthesis by preparing the substituted (−)-dienone **1** (R = Pr^i).[5] An elegant related free-radical based cyclisation approach to the germacranes has been described by Parsons and co-workers.[6] The substituted dienone **1** (R = Pr^i), as the racemate, has been used by Schreiber and co-workers in syntheses of the potent sex attractant pheromone of the American cockroach (±)-periplanone-B[7] (first prepared by Still)[8] and (±)-germacrene-D.[9] Schreiber constructed the dienone **1** *via* anionic oxy-Cope rearrangement of a 1,2-divinylcyclohexanol. Mori and co-workers have prepared natural (−)-periplanone-B from substituted (−)-dienone **1** (R = Pr^i).[10] In this latter synthesis, (+)-limonene was elaborated *via* ozonolytic ring cleavage to an acyclic substituted α-phenylthioacrylate which underwent intramolecular alkylation to provide the ten-membered carbocycle.



Scheme 1

Results and discussion

To examine the viability of our strategy in the unsubstituted (nor-Pr^i) system, the ketoaldehyde **5** was prepared according to Scheme 2. Thus, 2,5-diiodopent-1-ene **3**[11] was conveniently



Scheme 2 *Reagents and conditions*: i, NaI, butan-2-one, reflux, 15 h; ii, TMSCl, NaI, H_2O, MeCN, 25 °C, 1 h; iii, dihydropyran (4.6 equiv.), Bu^tLi (4.5 equiv.), THF, −78 °C to 0 °C, then added to **3**, THF, 0 °C, 0.5 h; iv, 1 M HCl, THF, 25 °C, 1 h; v, PCC, SiO_2, CH_2Cl_2, 25 °C, 1 h.

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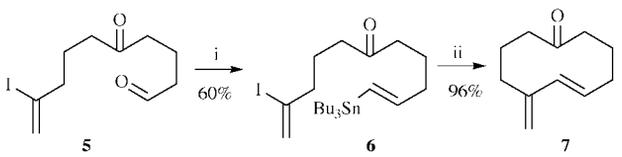
prepared from commercially available 5-chloropent-1-yne **2** *via* chlorine–iodine exchange[12] (77%) followed by addition of HI (85%).[13] It was important to limit the reaction time with HI to 1 h in order to minimize acid-catalysed isomerisation of 2,5-diiodopent-1-ene **3** to 2,5-diiodopent-2-ene. Addition of lithiated dihydropyran[14] to 2,5-diiodopent-1-ene **3** gave the substituted dihydropyran **4** (46%). The modest yield for the alkylation in this case stems from the basicity of lithiated dihydropyran which resulted in competing formation of the corresponding coupled material containing a triple bond instead of the alkenyl iodide unit present in **4**. Variation in either the quantity of lithiated dihydropyran used, the order of addition, the use of additives (HMPA or TMEDA) or reduced temperatures did not result in improved yields for this step. The substituted dihydropyran **4** was subjected to hydrolysis and then immediate oxidation using PCC in the presence of SiO_2[15] to give ketoaldehyde **5** (58%). PDC and Swern oxidations were also examined, but were found to give considerably lower yields of ketoaldehyde **5**.

Chemoselective conversion of ketoaldehyde **5** to stannane **6** (Scheme 3) proceeded smoothly (60%) using our original conditions,[2] although simple methylenation of the aldehyde (20%) and the stannane with the ketone methylenated (9%) were also observed (see Experimental section). Although we had previously found that bromostannane **6** (I = Br) was not a viable precursor to the dienone **7**,[16] we were pleased to observe that cyclisation of stannane **6** under Pd catalysis[1,17] reproducibly gave the dienone **7** in excellent yields which ranged from 82% for 0.04 M **6** in *N*-methylpyrrolidone (NMP) to 96% at 0.009 M.



Scheme 3 *Reagents and conditions*: i, $Bu_3SnCHBr_2$, LiI, $CrCl_2$, THF, DMF, 40 h; ii, cat. Pd_2dba_3, $AsPh_3$, NMP, 70 °C, 12 h.

The efficiency of the intramolecular Stille reaction may be partly due to the presence of the ketone and diene groups, which result in no serious transannular non-bonded interactions arising during formation of the ten-membered ring. This is evident from a conformational analysis of the dienone **7** using molecular models, and a crystal structure[18] and NOE studies[19] of **1** (R = Pr^i). In addition, models indicate that the Pd centre in the intermediate resulting from initial oxidative addition of Pd(0) into the C–I bond of the stannane **6** may be able to form a π-complex[17] with the ketone and then also with the stannyl-substituted alkene thus creating a favourable arrangement from which transmetallation could occur (Fig. 1).

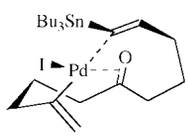
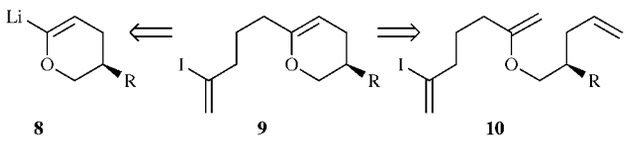


Fig. 1

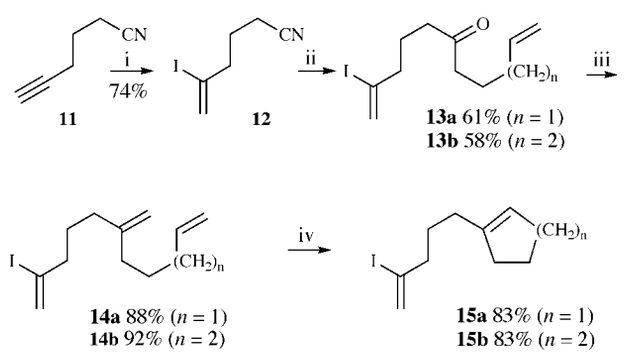
The above results encouraged us to pursue an enantioselective formal synthesis of natural (−)-periplanone-B by preparing the substituted (−)-dienone **1** (R = Pr^i). A strategy analogous to that carried out in the nor-Pr^i series would require an asymmetric synthesis of substituted lithiated dihydropyran **8** (R = Pr^i, Scheme 4). Although this appeared feasible,[20] the number of steps for its preparation together with the problems anticipated on the basis of our above study in its alkylation with 2,5-diiodopent-1-ene **3** to give **9** (R = Pr^i) combined to make this a potentially unattractive strategy towards



Scheme 4

(−)-periplanone-B. We considered that an attractive alternative would be to examine Grubbs' ring-closing metathesis (RCM) methodology for the synthesis of substituted dihydropyrans. RCM involving an enol ether to generate dihydropyrans usually requires $PhCMe_2CH{=}Mo{=}N(2,6\text{-}Pr^i_2C_6H_3)[OCMe(CF_3)_2]_2$ (Mo-F_6) as the metathesis catalyst.[21] Our strategy would require selective RCM in the presence of an alkenyl halide moiety (**10**→**9**).

Initial metathesis in a multiply unsaturated substrate usually occurs at the less substituted alkene,[21] suggesting that intermolecular alkylidene exchange should occur first at the terminal (monoalkyl-substituted) alkene in **10**, followed by RCM onto the proximal enol ether. Tolerance of alkenyl halide functionality during metathesis was unknown at the start of our work. During the course of our studies Kirkland and Grubbs reported that attempted RCM of a 2-bromohepta-1,6-diene using Mo-F_6 or $(PCy_3)_2Cl_2Ru{=}CHPh$ gave no cyclic product, only starting diene and alkylidene decomposition products were detected.[22] Also, Nicolaou and co-workers recently demonstrated that a 2,2-dialkyl-1-iodoalkene survived RCM using $(PCy_3)_2Cl_2Ru{=}CHPh$.[23] We first investigated RCM selectivity with trienes **14** (Scheme 5).

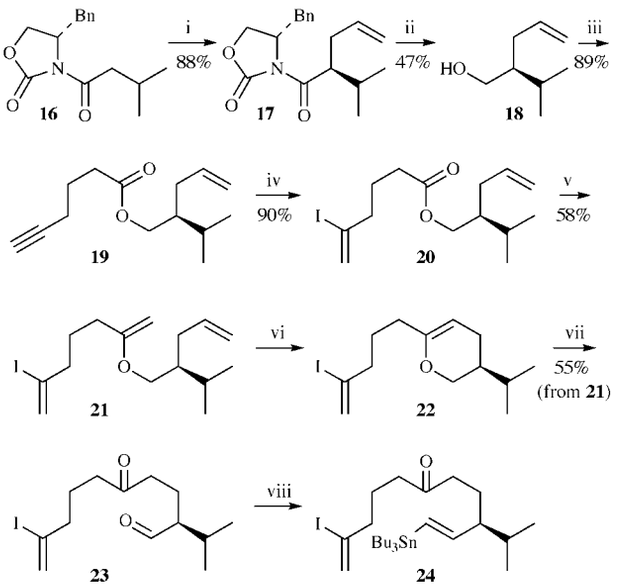


Scheme 5 *Reagents and conditions*: i, *B*-I-9-BBN, hexane–CH_2Cl_2, 0 °C, 18 h, then AcOH, 1 h; ii, pentenyl- or hexenylMgBr, Et_2O–benzene, 25 °C, 22 h, then 2 M HCl; iii, CH_2Br_2, Zn, cat. $PbCl_2$. $TiCl_4$, THF, 25 °C, 18 h; iv, Mo-F_6 (12 mol%), pentane, 25 °C, 5 h.

Trienes **14** were prepared in three steps from commercially available hex-5-ynenitrile **11** *via* iodoboration (74%),[24] reaction of the resultant alkenyl iodide **12** with either pent-4-enyl- or hex-5-enylmagnesium bromide (61% and 58%, respectively) and finally methylenation of the resulting ketones **13** under conditions described by Takai and co-workers (88% and 92%).[25] Reaction of triene **14b** with $(PCy_3)_2Cl_2Ru{=}CHPh$ under preferred conditions for RCM[22] resulted only in dimerisation [44% (*E*:*Z* = 73:27), 61% based on recovered triene **14b**, see Experimental section] arising from metathesis at the terminal (monoalkyl-substituted) alkene. Very recently, Grubbs has reported an imidazolinylidene-Ru catalyst which may be more effective.[26] However, using commercially available Mo-F_6 we were pleased to observe smooth RCM of trienes **14** to give cycloalkenes **15** (83%). Following the recent demonstration by Grigg and coworkers of RCM–intramolecular Heck reactions using aryl halides,[27] our results suggest that tandem RCM–intramolecular Heck reactions using tethered alkenyl halide functionality may also be possible.

In order to examine the synthesis of the substituted (−)-dienone **1** (R = Pr^i) using the RCM step outlined in Scheme 4, the alcohol **18** was first prepared as a single enantiomer (by

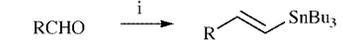
Mosher's ester analysis)[28] starting with allylation of the known *N*-isovaleryloxazolidinone **16**,[29] which gave a single alkene diastereomer **17** (88%) (Scheme 6).



Scheme 6 *Reagents and conditions*: i, LDA, allyl iodide, THF, −78 °C to 25 °C, 3 h; ii, H_2O_2, LiOH, THF, H_2O, 0 °C to 25 °C, 5 h, then Na_2SO_3; then $LiAlH_4$, Et_2O, 0 °C, 2 h; iii, hex-5-ynoic acid, DCC, cat. DMAP, CH_2Cl_2, 25 °C, 4 h: iv, *B*-I-9-BBN, pentane, −25 °C, 2 h, then AcOH, 1 h; v, CH_2Br_2, Zn, cat. $PbCl_2$, $TiCl_4$, TMEDA, THF, 25 °C, 3.5 h; vi, Mo-F_6 (12 mol%), pentane, 25 °C, 5 h; vii, 2 M HCl, THF, 25 °C, 2 h, then PCC, SiO_2, CH_2Cl_2, 25 °C, 3 h; viii, see text.

Alkene **17** was converted to the alcohol **18** by reaction with LiOOH–Na_2SO_3[30] to give the intermediate crude acid (96%) [with concomitant recovery (88%) of the chiral auxiliary] followed by reduction with $LiAlH_4$ (50%). Esterification of the alcohol **18** with commercially available hex-5-ynoic acid to give alkyne **19** (89%), was followed by chemoselective iodoboration[24] to give on protonolysis, the alkenyl iodide **20** (90%). Ester methylenation[25] of iodide **20** gave the desired substrate for RCM, triene **21** (58%). Pleasingly, RCM of triene **21** (0.06 M in pentane) using Mo-F_6 gave the desired dihydropyran **22** (44%). Due to its sensitive nature, the crude dihydropyran **22** was best converted directly into the aldehyde **23** (55% from triene **21**). Homologation of the aldehyde **23** using our original stannylation conditions[2] gave the stannane **24** (59%); terminal (monoalkyl-substituted) alkene signals could also be clearly observed in the crude ^{1}H NMR spectrum and were assigned to simple methylenation of the aldehyde (*ca.* 30%), as in the nor-Pr^i system.

Although our original method for preparing (*E*)-alkenylstannanes in one step from aldehydes using $Bu_3SnCHBr_2$ in THF with LiI and DMF as additives[2] has found utility in other syntheses,[31] it suffers from cogeneration of simple aldehyde methylenated product, as observed with aldehydes **5** and **23** above. As stated previously,[2] our initial studies with benzaldehyde originally led to the adoption of $CrCl_2$–$Bu_3SnCHBr_2$ in THF with LiI and DMF as additives as the preferred method for aldehyde homologation, since this led exclusively to the (*E*)-alkenylstannane, whereas $CrCl_2$–$Bu_3SnCHBr_2$ in DMF was less stereoselective (*E*:*Z* = 87:13, by ^{1}H NMR); however, styrene was *only* observed as a by-product in the former reaction. On further investigation we found that reaction of nonanal (as a representative aliphatic aldehyde) with $CrCl_2$–$Bu_3SnCHBr_2$ in DMF (25 °C, 2.5 h) gives *only* (*E*)-alkenylstannane[32] (78% *vs.* 60% reported[2] in our original study); addition of LiI did not lead to an improvement in yield (75%), however further improvement (85 and 89%, two runs) was observed using Bu_3SnCHI_2 in DMF (Scheme 7);[33] Bu_3SnCHI_2



Scheme 7 *Reagents and conditions*: i, Bu_3SnCHI_2, $CrCl_2$, DMF, 25 °C, 3 h.

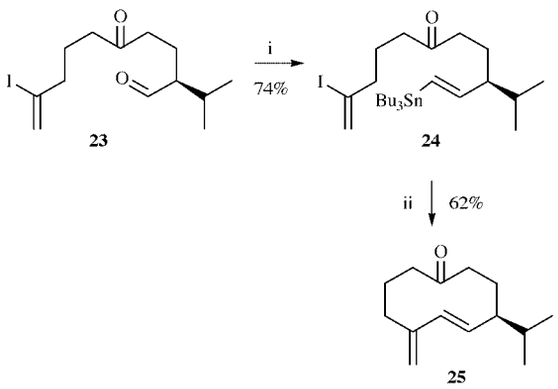
in THF or THF with DMF as an additive were less effective. Bu_3SnCHI_2 was prepared in quantitative yield from $Bu_3SnCHBr_2$[2] using NaI in acetone and was used directly without further purification and within one week of its preparation. It is important to minimize exposure of this reagent to light.[34]

Compared with our previous results,[2] the use of Bu_3SnCHI_2 in DMF also resulted in shorter reaction times and gave significantly improved yields of (*E*)-alkenylstannanes for cyclohexanecarbaldehyde (80% *vs.* 62%) and methyl 6-oxohexanoate (82% *vs.* 61%). However, the yield of stannnane from hex-5-ynal (59%) was essentially unchanged compared with that reported under the original conditions (60%);[2] the lack of improvement in yield in this case may suggest competing chromium(II)-mediated reduction of the triple bond in DMF ($CrCl_2$ is a stronger reducing agent in DMF compared to THF).[3] We had also found that hex-5-ynal gave a noticeably lower yield (38%) than most other aldehydes examined (64–94% yields) in our chromium(II)-mediated synthesis of 1,1-bis-(trimethylsilyl)alkenes in DMF.[35] Although aliphatic aldehydes gave only (*E*)-alkenylstannanes under the modified conditions, the erosion in stereoselectivity seen with benzaldehyde on moving from THF to DMF (*E*:*Z* = 76:24, with $CrCl_2$–Bu_3SnCHI_2 in DMF) was also paralleled with 3-methylbut-2-enal. Whilst 1,2-addition is observed with α,β-unsaturated aldehydes in chromium(II)-mediated olefinations, the stereoselectivity for the *E*-isomer is usually slightly lower than that seen with aliphatic (and aromatic) aldehydes.[3,36,37] We reported 3-methylbut-2-enal gave 1-(tributylstannyl)-3-methylpenta-1,3-diene (58%) as a mixture of geometrical isomers (*E*:*Z* = 83:17) under the original conditions;[2] using the modified conditions 77% yield of stannyldiene was obtained (*E*:*Z* = 58:42). Under the new conditions improved aldehyde selectivity was also apparent, as cyclododecanone was recovered unchanged after 5 h (96%), whereas we had previously found that it was partially methylenated (45%, 73% based on recovered ketone) using $Bu_3SnCHBr_2$ in THF with LiI and DMF as additives.[2]

Our present results together with our earlier studies indicate that revision is necessary of our suggestion[2] regarding the origin of the methylenated material observed in THF with DMF as an additive. Chromium(II)-mediated olefinations using *gem*-dihalides are generally accepted as proceeding *via gem*-dichromium species.[3] The present observations in preparing stannanes together with our earlier studies are consistent with the methylenated material observed (in THF with DMF as an additive) as arising from competitive formation of $CH_2(CrHal_2)_2$ [along with the desired $Bu_3SnCH(CrHal_2)_2$] during chromium(II)-mediated reduction of $Bu_3SnCHHal_2$. $CH_2(CrHal_2)_2$ would be anticipated to be a selective reagent for aldehydes, but also able to react with ketones. For example, reaction of dodecanal with CH_2I_2 using $CrCl_2$ in THF with DMF as an additive is known to give tridec-1-ene (73%),[37] and we find that cyclododecanone is similarly methylenated (59%, 85% based on recovered ketone). Although related chromium(II)-mediated alkylidenations of cyclododecanone have also been observed,[37] reaction with $Me_3SiCHBr_2$ under conditions ($CrCl_2$, THF) which produce (*E*)-alkenylsilanes from aldehydes [presumably *via* $Me_3SiCH(CrHal_2)_2$] is known to result in quantitative recovery of cyclododecanone;[38] the evidence brought together in the present paper suggests that $Bu_3SnCH(CrHal_2)_2$ is similarly aldehyde selective. Partial generation of $CH_2(CrHal_2)_2$ from $Bu_3SnCHBr_2$ using $CrCl_2$ would then explain why cyclododecanone is methylenated using $Bu_3SnCHBr_2$ in THF with DMF as an additive to approximately the same level as an aldehyde but with no alkenylstannane observed; it is possible that some $CH_2(CrHal_2)_2$ *is*

also formed from $Bu_3SnCHHal_2$ in DMF but has too short a lifetime in this solvent[3,37] to react with a carbonyl compound. Consistent with this last suggestion we find that attempted reaction of cyclododecanone with CH_2I_2 using $CrCl_2$ in DMF gives quantitative recovery of the ketone.

Application of the new stannylation conditions to aldehyde **23** gave the stannane **24** in improved yield (66%, Scheme 8);



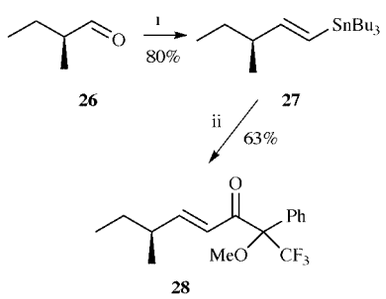
23 **24** **25**

Scheme 8 *Reagents and conditions*: i, Bu_3SnCHI_2, $CrCl_2$, DMF, 25 °C, 3.5 h; ii, cat. Pd_2dba_3, $AsPh_3$. NMP, 70 °C, 6 h.

no methylenated material was observed in the crude ^{1}H NMR. The yield of stannane **24** could be further improved to 74% by doubling the quantities of reagents used.

Intramolecular cross-coupling of stannane **24** under the conditions used for the nor-isopropyl substrate gave the substituted (−)-dienone **25** {62%, $[\alpha]_D^{25}$ −310 (*c* 1.22 in hexane), lit.,[10] $[\alpha]_D^{22}$ −362 (*c* 1.22 in hexane)}, which constitutes a formal synthesis of (−)-periplanone-B. The apparent optical purity (86%) of substituted (−)-dienone **25** led us to attempt to determine its enantiomeric purity with greater confidence using chiral chromatography. For this study a sample of aldehyde **23** was deliberately partially racemised [AcOH (2 mol dm^{-3} in H_2O), THF, 25 °C, 18 h] and carried through to dienone **25** {$[\alpha]_D^{25}$ −236 (*c* 1.22 in hexane)}. Accurate determination of the enantiomeric purity of germacrene-D (by derivatisation to an alcohol) was recently reported by HPLC analysis using a Daicel Chiralcel OD column.[39] However, we found that for dienone **25** no resolution whatsoever could be observed using a variety of chiral GC and HPLC columns and conditions. Resolution (close to baseline) was only achieved using a β-cyclodextrin (cyclobond I) HPLC column which gave the ee of the substituted (−)-dienone **25** to be 93% (the ee of the partially racemised material was 71%). Success with the β-cyclodextrin column may be due to the 6.0–8.0 Å internal diameter of β-cyclodextrin, which would be a suitable size for complexing the dienone **25**.[40]

As the dienone **25** was derived from the alcohol **18** which had been determined to be enantiomerically pure (by Mosher's ester analysis), we considered that slight reduction in enantiomeric purity of substituted (−)-dienone **25** compared with alcohol **18** could arise during preparation and/or Cr(II)-coupling of the aldehyde **23**. Oxidation of primary alcohols bearing an α-stereogenic centre with tetrapropylammonium perruthenate (TPAP) is known to give aldehydes without loss of enantiomeric purity.[41] Using 5 mol% TPAP (with NMO, 4 Å powdered molecular sieves in CH_2Cl_2–MeCN, 25 °C, 12 h) in the preparation of aldehyde **23**, though lower yielding [67% from crude (*ca.* 50% pure) dihydropyran **22**], resulted in a slight rise in specific rotation {from $[\alpha]_D^{25}$ +16.7 (*c* 1.0 in $CHCl_3$) to $[\alpha]_D^{26}$ +18.2 (*c* 0.5 in $CHCl_3$)}. However, given the uncertainty over drawing conclusions from small changes in low optical rotation values, we also focused on the possible reduction of enantiomeric purity in the chromium(II)-mediated olefination step (**23**→**24**). Under the original stannylation conditions we had previously established that (*R*)-glyceraldehyde acetonide could be converted into the corresponding stannane in ≥95% ee.[2] However, an α-alkyl-substituted aldehyde could potentially show reduced tolerence. For example, Burke *et al.* have observed partial epimerisation of such centres in chromium(II)-mediated syntheses of (*E*)-alkenylsilanes from aldehydes.[42] We first established that (*S*)-α-methylbutyraldehyde **26** (prepared from the corresponding commercially available alcohol by Swern oxidation)[43] could be converted without loss of enantiomeric purity to the corresponding stannane **27** {80%, $[\alpha]_D^{24}$ +14.7 (*c* 1.0 in $CHCl_3$)} under the new stannylation conditions (Scheme 9) {using the original

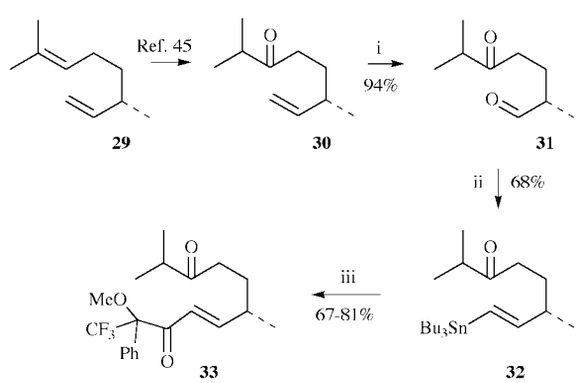


26 **27** **28**

Scheme 9 *Reagents and conditions*: i, Bu_3SnCHI_2, $CrCl_2$, DMF, 25 °C, 3 h; ii, MPTA-Cl, cat. Pd_2dba_3, P(2-furyl)$_3$, THF, 55 °C, 3 h.

stannylation conditions a similar specific rotation, $[\alpha]_D^{24}$ +14.0 (*c* 1.0 in $CHCl_3$), was observed but the yield was lower (50%)}. The enantiomeric purity was determined by Pd-catalysed cross-coupling of the stannane **27** with (*S*)-Mosher's acid chloride and inspection of the ^{1}H NMR alkenyl regions of the resulting enone **28**. Racemic stannane **27** gave a 1 : 1 diastereomeric mixture of enones **28** indicating that during the reactions there was no preference for the formation (or destruction) of a particular diastereomer.

As a structurally closer example to aldehyde **23**, ketoaldehyde **31** was also examined to see if the ketone group promoted racemisation (Scheme 10).



29 **30** **31** **32** **33**

Scheme 10 *Reagents and conditions*: i, O_3, MeOH, −65 °C, then Me_2S; ii, Bu_3SnCHI_2, $CrCl_2$, DMF, 3 h; iii, MPTA-Cl, cat. Pd_2dba_3, P(2-furyl)$_3$, THF, 55 °C, 3 h.

The starting material for the syntheis of ketoaldehyde **31** was commercially available (*S*)-(+)-β-citronellene **29**, whose ee was determined to be 90% following a literature procedure (hydroboration to give β-citronellol and chiral GC analysis of the corresponding trifluoroacetate).[44] Ozonolysis of the known ketoalkene **30**, derived in two steps from citronellene **29**,[45] gave the ketoaldehyde **31** (94%),[46] for which no loss of enantiomeric purity was observed [using the above cross-coupling method with racemic and (*S*)-Mosher's acid chlorides] on stannylation (68%). We conclude that α-alkyl-substituted aldehydes can be used in chromium(II)-mediated synthesis of (*E*)-alkenylstannanes without compromising enantiomeric purity (at

least within the limits of the detection methods used here), and that slight reduction in enantiomeric purity of substituted (−)-dienone **25** compared with alcohol **18** arises during the oxidation to aldehyde **23**.

In summary, we have demonstrated the tolerance of alkenyl halide functionality in RCM, developed a modified chromium(II)-mediated method for (*E*)-alkenylstannylation of aldehydes (which should be particularly useful with synthetically valuable aldehydes in complex molecule synthesis) and used this chemoselectivity in a Stille cyclisation strategy resulting in a formal synthesis of (−)-periplanone-B.

Experimental

General details

All reactions requiring anhydrous conditions were conducted in flame-dried apparatus under an atmosphere of argon. Syringes and needles for the transfer of reagents were dried at 140 °C and allowed to cool in a desiccator over P_2O_5 before use. Ethers were distilled from sodium benzophenone ketyl; (chlorinated) hydrocarbons, and amines from CaH_2. DMF was dried ($MgSO_4$) and then distilled under reduced pressure. Internal reaction temperatures are reported unless stated otherwise. Reactions were monitored by TLC using commercially available glass-backed plates, pre-coated with either a 0.25 mm layer of SiO_2 containing a fluorescent indicator (Merck), or a 0.2 mm layer of octadecylsilane bonded silica containing a fluorescent indicator (Whatman). Column chromatography was carried out either on Kieselgel 60 (40–63 μm), or on Preparative C-18 (55-105 μm, Millipore). Light petroleum refers to the fraction with bp 40–60 °C. $[a]_D$ Values are given in 10^{-1} deg cm^2 g^{-1}. IR spectra were recorded as thin films unless stated otherwise. Peak intensities are specified as strong (s), medium (m) or weak (w). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ unless stated otherwise with Varian Gemini 200, Bruker AC200, Bruker WM250, Bruker WH300, JEOL EX400, Bruker AM500 or Bruker AMX500 spectrometers. Chemical shifts are reported relative to $CHCl_3$ [δ_H 7.26, δ_C(central line of t) 77.0]. Coupling constants (J) are given in Hz. HPLC retention times for major ($t_R$mj) and minor ($t_R$mn) enantiomers are given in min.

6-(4-Iodopent-4-en-1-yl)-3,4-dihydro-2*H*-pyran 4

Bu^{t}Li (1.7 mol dm^{-3} in cyclohexane; 100 cm^3, 170 mmol] was added dropwise to a well-stirred solution of 3,4-dihydropyran (14.617 g, 174 mmol) in THF (25 cm^3) at −78 °C. The reaction mixture was allowed to warm to room temperature for 10 min, before being recooled to 0 °C. This solution was then added dropwise by cannula to a stirred solution of 2,5-diiodopentene **3** [11,47] (12.161 g, 38 mmol) in THF (20 cm^3) at 0 °C over a period of 30 min. Saturated aq. NH_4Cl (5 cm^3) was then added cautiously to the reaction. The solvents were removed by evaporation under reduced pressure and the resulting residue was extracted with Et_2O (3 × 100 cm^3). The combined organic layers were washed with brine (50 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure. Purification of the residue by bulb-to-bulb distillation, first at 70 °C/0.5 mmHg and then at 120 °C/0.5 mmHg afforded a colourless oil, the *dihydropyran* **4** (4.849 g, 46%): R_f 0.25 (light petroleum); ν_{max}(neat)/cm^{-1} 3310m, 2927s, 2852s, 1717m, 1674s, 1616m, 1086m, 1064s and 891m; δ_H(300 MHz) 6.01 (1H, s, C*H*=CI), 5.70 (1H, s, CH*H*=CI), 4.48 (1H, br t, *J* 3, CHCO), 3.97 (2H, dd, *J* 5 and 5, CH_2O), 2.41 (2H, t, *J* 7, =CICH_2), 2.02–1.98 (4H, m, CH_2CH$_2$O and CCH_2) and 1.82–1.63 (4H, m, CCH_2CH_2 and CH_2CHCO); δ_C(75 MHz) 153.4 (=CO), 125.4 (CH_2=), 112.8 (=CI), 95.8 (CH=), 66.0 (CH_2O), 44.5 (*C*H$_2$CI), 32.6 (OC*C*H$_2$), 26.2 (CH_2), 22.4 (CH_2) and 20.2 (CH_2); *m*/*z* (thermospray) 275 (100%), 211 (5), 195 (5) 168 (5) and 151 (10) (Found: (M + H$^+$, 279.0246. $C_{10}H_{16}IO$ requires *M*, 279.0246).

9-Iodo-5-oxodec-9-enal 5

Aq. HCl (1 mol dm^{-3}, 15 drops) was added to a stirred solution of dihydropyran **4** (4.849 g, 17.4 mmol) in wet THF (20 cm^3). After stirring for 1 h, $NaHCO_3$ (0.5 g) and $MgSO_4$ (2 g) were added and the reaction mixture was filtered and evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 cm^3) and added slowly dropwise to a stirred slurry of PCC (7.517 g, 34.9 mmol) and SiO_2 (7.5 g) in CH_2Cl_2 (15 cm^3). After 1 h, the reaction mixture was diluted with Et_2O (50 cm^3), filtered through a pad of Florisil® and evaporated under reduced pressure. Purification of the residue by column chromatography (50% Et_2O–light petroleum) gave a colourless oil, the *ketoaldehyde* **5** (3.137 g, 58%); R_f 0.23 (50% Et_2O–light petroleum); ν_{max}(neat)/cm^{-1} 2949s, 2895s, 1710s, 1615m, 1429m, 1409m, 1374m, 1198m, 1105m and 898m; δ_H(300 MHz) 9.75 (1H, s, CHO), 6.02 (1H, d, *J* 1, C*H*=CI), 5.72 (1H, s, CH*H*=CI), 2.46 [4H, t, *J* 7, $(CH_2)_2CO$], 2.42 (2H, t, *J* 7, CH_2CHO), 2.40 (2H, t, *J* 7, =CICH_2), 1.90 (2H, quintet, *J* 7, CH_2) and 1.80 (2H, quintet, *J* 7, CH_2); δ_C(75 MHz) 209.3 [$(CH_2)_2$*C*O], 201.7 (CHO), 126.1 (CH_2=), 111.2 (=CI), 44.1 (=CI*C*H$_2$), 42.8 (*C*H$_2$CO), 41.3 (*C*H$_2$CO), 40.5 (*C*H$_2$CO), 22.7 (CH_2) and 15.9 (CH_2); *m*/*z* (thermospray) 312 (100%), 259 (35), 278 (10), 196 (5) and 167 (10) (Found: M + NH_4^+, 312.0461. $C_{10}H_{19}INO_2$ requires *M*, 312.0461).

(*E*)-11-(Tributylstannyl)-2-iodoundeca-1,10-dien-6-one 6

Dry, deoxygenated DMF (0.78 ml, 10 mmol) was added dropwise to a well-stirred slurry of $CrCl_2$ (Aldrich, 95% w/w pure; 1.33 g, 10 mmol) in dry, deoxygenated THF (16 cm^3) under argon at room temperature. After 15 min a mixture of ketoaldehyde **5** (0.294 g, 1.0 mmol) and $Bu_3SnCHBr_2$ [2] (926 mg, 2 mmol) in dry, deoxygenated THF (4 cm^3) was added dropwise to the reaction mixture. The flask was covered with aluminium foil to exclude light and then anhydrous LiI (1 mol dm^{-3} in dry, deoxygenated THF; 4 cm^3, 4 mmol) was added dropwise. After 40 h at room temperature, water (30 cm^3) was added and the mixture was extracted with light petroleum (3 × 20 cm^3). The combined organic layers were washed with water (20 cm^3), brine (20 cm^3), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by reversed-phase flash chromatography (C-18, 5% CH_2Cl_2–MeCN). First to elute was a colourless oil, the *stannane* **6** (0.351 g, 60%); R_f 0.20 (C-18 reversed-phase, 5% CH_2Cl_2–MeCN); ν_{max}(neat)/cm^{-1} 2956s, 2925s, 2871s, 2851s, 1716s, 1616m, 1599m, 1415m, 1375m and 1072w; δ_H(300 MHz) 6.06 (1H, s, C*H*=CI), 5.93–5.92 (2H, m, CH=CHSn), 5.75 (1H, s, CH*H*=CI), 2.43 [6H, br, $(CH_2)_2C$=O and =CICH_2], 2.18–2.14 (2H, m, CH_2CH=CHSn), 1.82 (2H, quintet, *J* 7, CH_2), 1.69 (2H, quintet, *J* 7, CH_2), 1.58–1.42 [6H, m, Sn(CH$_2$CH_2)$_3$], 1.41–1.26 [6H, m, Sn(CH$_2$CH$_2$CH_2)$_3$] and 1.05–0.71 [15H, m, Sn(CH_2CH$_2$CH$_2$*Me*)$_3$, incl. at 0.92 (9H, t, *J* 7, 3 × Me)]; δ_C(75 MHz) 210.3 (C=O), 148.2 (*C*H=CHSn), 128.5 ($J_{119Sn-C}$ 386, $J_{117Sn-C}$ 375, =CHSn), 126.0 (CH_2=), 111.3 (=CI), 44.2 (CH_2), 41.9 (CH_2), 40.5 (CH_2), 37.0 (CH_2), 29.0 [J_{Sn-C} 19, Sn(CH$_2$CH_2)$_3$], 27.2 [J_{Sn-C} 52, Sn(CH$_2$CH$_2$CH_2)$_3$], 22.8 (CH_2), 22.6 (CH_2), 13.6 (3 × Me) and 9.4 [$J_{119Sn-C}$ 330, $J_{117Sn-C}$ 316, Sn$(CH_2)_3$]; *m*/*z* (thermospray) 582 (10%), 350 (10), 323 (40), 307 (45), 291 (100) and 287 (30) (Found: M + H$^+$, 583.1460. $C_{23}H_{44}IO^{120}Sn$ requires *M*, 583.1459].

Second to elute was a colourless oil, *(E)-10-(tributylstannyl)-2-iodo-6-methyleneundeca-1,10-diene*, (0.047 g, 8%); R_f 0.16 (C-18 reversed-phase, 5% CH_2Cl_2–MeCN); ν_{max}(neat)/cm^{-1} 2955s, 2928s, 2871s, 2853s, 1642m, 1616m, 1598m, 1457m, 987m and 891m; δ_H(250 MHz) 6.02 (1H, d, *J* 1, C*H*H=CI), 5.95 (1H, t, *J* 5, C*H*=CHSn), 5.92 (1H, s, $J_{119Sn-H}$ 78, $J_{117Sn-H}$ 75, =CHSn), 5.71 (1H, s, CH*H*=CI), 4.75 [2H, d, *J* 3, $(CH_2)_2$C=CH_2], 2.40 (2H, t, *J* 7, =CICH_2), 2.15 (2H, td, *J* 7 and 5, CH_2CH=), 2.03 [4H, t, *J* 7, $(CH_2)_2$C=CH$_2$], 1.67 (2H, quintet, *J* 7, CH_2), 1.58–1.46 [8H, m, CH_2 and Sn$(CH_2CH_2)_3$], 1.39–1.26 (6H, m, 3 × CH_2Me) and 0.93–0.85 [15H, m, Sn(CH_2CH$_2$-

$CH_2Me)_3$, incl. at 0.90 (9H, t, *J* 7, 3 × Me)]; δ_C(100 MHz) 149.2 (*C*H=CHSn), 148.8 [$(CH_2)_2C$=CH_2], 127.5 ($J_{119Sn-C}$ 398, $J_{117Sn-C}$ 379, =CHSn), 125.4 (CH_2=CI), 112.3 (=CI), 109.4 [$(CH_2)_2C$=CH_2], 44.7 (CH_2), 37.4 (CH_2), 35.2 (CH_2), 34.2 (CH_2), 29.6 (CH_2), 29.0 [J_{Sn-C} 21, $Sn(CH_2CH_2)_3$], 27.2 (J_{Sn-C} 53, 3 × CH_2-Me), 26.9 (CH_2), 13.7 (3 × Me) and 9.3 [J_{119-C} 342, $J_{117Sn-C}$ 325, $Sn(CH_2)_3$]; *m*/*z* (EI) 483 (5%), 348 (20), 323 (60), 308 (70), 291 (100) and 165 (10) (Found: M − Bu^+, 523.0844. $C_{20}H_{36}I^{120}Sn$ requires *M*, 523.0884).

Fractions collected before elution of compound **6** were combined and evaporated under reduced pressure to give a residue which was purified by column chromatography (SiO_2, 15% Et_2O–light petroleum) to give a colourless oil, *2-iodoundeca-1,10-dien-6-one* (0.056 g, 19%); R_f 0.35 (15% Et_2O–light petroleum); ν_{max}(neat)/cm^{-1} 2929s, 2854m, 1712s, 1638m, 1616m, 1433m, 1410m, 1371m, 911m and 897m; δ_H(250 MHz) 6.02 (1H, t, *J* 1, C*H*H=CI), 5.80–5.73 (1H, m, C*H*=CH_2), 5.72 (1H, s, CH*H*=CI), 5.06 (1H, ddt, *J* 12, 1 and 1, CH=C*H*H), 4.99–4.96 (1H, m, CH=CH*H*), 2.42–2.38 [6H, m, $(CH_2)_2CO$ and CH_2=CICH_2], 2.06 (2H, dt, *J* 7 and 7, CH_2CH=CH_2), 1.80 (2H, quintet, *J* 7, CH_2) and 1.69 (2H, quintet, *J* 7, CH_2); δ_C(75 MHz) 210.2 (C=O), 137.8 (CH_2=*C*H), 126.1 (CH_2=CI), 115.2 (CH_2=CH), 111.3 (=CI), 44.1 (=CICH_2), 41.8 (CH_2CO), 40.5 (CH_2-CO), 33.0 (CH_2CH=), 29.6 (CH_2) and 22.8 (CH_2); *m*/*z* (thermospray) 310 (100%), 292 (15), 279 (10), 182 (5) and 151 (10) (Found: M + NH_4^+, 310.0668. $C_{11}H_{21}INO$ requires *M*, 310.0668).

(*E*)-5-Methylenecyclodec-6-en-1-one 7

Pd_2dba_3 (Aldrich, 7 mg, 0.01 mmol) was added to a stirred solution of the stannane **6** (200 mg, 0.34 mmol) and $AsPh_3$ (70 mg, 0.23 mmol) in degassed NMP (40 cm^3) at 25 °C under N_2. The reaction vessel was then wrapped in aluminium foil to exclude light, and heated to 70 °C. After 12 h the reaction mixture was cooled, diluted with water (50 cm^3) and extracted with Et_2O (3 × 30 cm^3). The combined organic layers were washed with aq. $CuSO_4$ (1 mol dm^{-3}; 2 × 20 cm^3), brine (20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The crude oil was diluted with 10% Et_2O–pentane (0.5 cm^3). DBN[48] (0.1 cm^3) was then added and the resultant mixture was purified by column chromatography (10% Et_2O–pentane) to give a colourless oil, the *dienone* **7** (0.054g, 96%); R_f 0.27 (10% Et_2O–pentane); δ_H(250 MHz) 6.10 (1H, d, *J* 16, CH=C*H*C), 5.36 (1H, dt, *J* 16 and 7, C*H*=CHC), 4.88 (1H, s, CC=*H*H), 4.86 (1H, s, CC=H*H*) and 2.51–1.95 (12H, m, 6 × CH_2); δ_C(75 MHz) 212.8 (C=O), 146.5 (*C*=CH_2), 133.9 (*C*H=CH), 132.7 (CH=*C*H), 113.2 (C=*C*H_2), 42.8 (CH_2CO), 42.2 (CH_2CO), 33.1 (CH_2), 30.4 (CH_2), 27.5 (CH_2) and 23.9 (CH_2). UV, IR, ^{1}H NMR and MS data were consistent with those previously reported.[49]

5-Iodohex-5-enenitrile 12

Hex-5-ynenitrile **11** (2.57 cm^3, 24.5 mmol) was added dropwise to a stirred solution of *B*-I-9-BBN [(Aldrich) 1 mol dm^{-3} in hexane; 54 cm^3, 54 mmol] in CH_2Cl_2 (100 cm^3) at 0 °C. The reaction mixture was then allowed to reach room temperature over 18 h, then cooled to 0 °C and glacial AcOH (30 cm^3) added slowly. After 1 h at 0 °C, NaOH (3 mol dm^{-3} in H_2O; 150 cm^3) and then H_2O_2 (30% w/w in H_2O, 45 cm^3) were carefully added and the reaction stirred for 30 min at room temperature. The organic layer was separated and the remaining aqueous layer was extracted with light petroleum (6 × 100 cm^3). The combined organic extracts were washed successively with H_2O (50 cm^3), saturated aq. $NaHCO_3$ (40 cm^3), saturated aq. Na_2SO_3 (25 cm^3), H_2O (40 cm^3) and brine (25 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by bulb-to-bulb distillation (75°C/1 mmHg) gave a light yellow oil, the *alkenyl iodide* **12** (3.99 g, 74%); R_f 0.56 (10% Et_2O–light petroleum); ν_{max}(neat)/cm^{-1} 2936s, 2247s, 1728m, 1618s, 1453m, 1428m, 1196s, 1185s, 1113s and 901s; δ_H(200 MHz) 6.16 (1H, d, *J* 1, C*H*H=CI), 5.79 (1H, d, *J* 1.5, CH*H*=CI), 2.54 (2H, t, *J* 7, =CICH_2), 2.35 (2H, t, *J* 7, CH_2CN) and 1.87 (2H, quintet, *J* 7.0, CH_2CH_2CN); δ_C(50 MHz) 127.9 (CH_2=CI), 119.0 (CN), 108.8 (CH_2=*C*I), 43.3 (=CI*C*H_2), 24.4 (CH_2CN) and 15.4 (CH_2CH_2-CH_2); *m*/*z* (EI) 221 (M^+, 50%), 127 (15) and 94 (52) (Found: M^+, 220.9702. C_6H_8IN requires *M*, 220.9702).

2-Iodoundeca-1,10-dien-6-one 13a

Alkenyl iodide **12** (1.00 g, 4.5 mmol) in Et_2O (3 cm^3) was added to a stirred solution of pent-4-enylmagnesium bromide [prepared from Mg (0.440 g, 18.1 mmol) and 5-bromopentene (2.70 g, 18.1 mmol) in Et_2O (15 cm^3), then diluted with C_6H_6 (14 cm^3)] at room temperature. After 22 h aq. HCl (2.0 mol dm^{-3}; 15 cm^3) was added and after a further 2 h at room temperature the organic layer was separated and the aqueous layer was extracted with Et_2O (6 × 20 cm^3). The combined organic layers were washed with H_2O (2 × 20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography (3% Et_2O–light petroleum) gave a colourless oil, the *ketone* **13a** (0.800 g, 61%); R_f 0.40 (10% Et_2O–light petroleum); ν_{max}(neat)/cm^{-1} 2932s, 2849w, 1714s, 1641m, 1618m, 1432m, 1410m, 1372m, 1198w, 1167w, 1111w, 998w and 912m; δ_H(200 MHz) 6.03 (1H, d, *J* 1, C*H*H=CI), 5.77 (1H, ddt, *J* 17, 10 and 7, C*H*=CHH), 5.72 (1H, d, *J* 1, CH*H*=CI), 5.07–4.96 (2H, m, CH=CH_2), 2.41 (2H, t, *J* 8, =CICH_2), 2.40 [4H, t, *J* 7, $(CH_2)C$=O], 2.06 (2H, q, *J* 7, CH_2CH=CH_2) and 1.86–1.61 (4H, 2 × quintet, *J* 7, 2 × $CH_2CH_2CH_2$); δ_C(50 MHz) 196.1 (C=O), 137.9 (*C*H=CH_2), 126.1 (CH_2=CI), 115.2 (CH=CH_2), 112.0 (*C*I=CH_2), 44.2 (CH_2CI=), 41.9 (CH_2C=O), 40.6 (CH_2C=O), 33.0 (CH_2CH=CH_2), 22.8 ($CH_2CH_2CH_2$) and 22.7 ($CH_2CH_2CH_2$); *m*/*z* (CI) 293 (M + H^+, 5%), 279 (15), 252 (7), 235 (10), 220 (100), 217 (20), 179 (10), 167 (45), 165 (10), 149 (95), 122 (50), 113 (60) and 109 (10) (Found: M + H^+, 293.0402. $C_{11}H_{18}OI$ requires *M*, 293.0402).

2-Iodododeca-1,11-dien-6-one 13b

Following the procedure for the preparation of ketone **13a**, but using alkenyl iodide **12** (0.988 g, 4.47 mmol) and 6-bromohexene (2.80 g, 17.2 mmol) gave, after purification by column chromatography (3% Et_2O–light petroleum), a colourless oil, the *ketone* **13b** (0.792 g, 58%); R_f 0.50 (10% Et_2O–light petroleum); ν_{max}(neat)/cm^{-1} 2932s, 2857m, 1714s, 1640m, 1617m, 1431m, 1410m, 1372m, 1202w, 1109w, 993m and 909m; δ_H(200 MHz) 6.03 (1H, d, *J* 1, C*H*H=CI), 5.79 (1H, ddt, *J* 17, 10 and 7, C*H*=CH_2), 5.73 (1H, d, *J* 1, CH*H*=CI), 5.04–4.93 (2H, m, CH=CH_2), 2.40 [6H, t, *J* 7, =CICH_2 and $(CH_2)C$=O], 2.06 (2H, q, *J* 7, CH_2CH=CH_2), 1.79 (2H, quintet, *J* 7, CH_2CH_2-IC=), 1.59 (2H, quintet, *J* 7, CH_2CH_2CH=CH_2) and 1.38 (2H, quintet, *J* 7, $CH_2CH_2CH_2CH$=CH_2); δ_C(50 MHz) 190.4 (C=O), 138.4 (*C*H=CH_2) 126.1 (CH_2=CI), 114.7 (CH=CH_2), 111.4 (*C*I=CH_2), 44.2 (=CICH_2), 42.6 (CH_2C=O), 40.5 (CH_2C=O), 33.5 (CH_2CH=CH_2), 28.4 ($CH_2CH_2CH_2$), 23.3 ($CH_2CH_2CH_2$) and 22.9 (CH_2CH_2CH=CH_2); *m*/*z* (EI) 179 (M − I^+, 100%), 123 (10), 109 (7), 95 (15), 83 (20) and 67 (50) (Found: M − I^+, 179.1436. $C_{12}H_{19}O$ requires *M*, 179.1436).

2-Iodo-6-(pent-4-en-1-yl)hepta-1,6-diene 14a

CH_2Br_2 (1.1 cm^3, 16 mmol) was added to a stirred suspension of zinc dust (1.86 g, 28.4 mmol) and $PbCl_2$ (0.40 g, 0.14 mmol) in THF (28 cm^3) at room temperature. After 30 min, $TiCl_4$ (1 mol dm^{-3} in CH_2Cl_2; 3.2 cm^3, 3.2 mmol) was added slowly to the reaction mixture at 0 °C and the resulting dark brown solution was stirred at room temperature. After 30 min a solution of ketone **13a** (0.900 g, 3.1 mmol) in THF (3 cm^3) was added dropwise to the reaction mixture. After 18 h the mixture was diluted with Et_2O (25 cm^3) and the organic layers was washed with aq. HCl (2 mol dm^{-3}; 15 cm^3), then brine (15 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Purification

of the residue by column chromatography (light petroleum) gave a colourless oil, the *triene* **14a** (0.785 g, 88%); R_f 0.82 (10% Et_2O–light petroleum); ν_{max}(neat)/cm^{-1} 3076m, 2978m, 2935s, 2860m, 1642m, 1618m, 1440m, 1173w, 1108w, 991w, 911m and 891s; δ_H(200 MHz) 6.04 (1H, d, *J* 1, C*H*H=CI), 5.84 (1H, ddt, *J* 17, 10 and 7, C*H*=CH_2), 5.72 (1H, s, CH*H*=CI), 5.08–4.95 (2H, m, CH=CH_2), 4.76 (2H, s, C=CH_2), 2.39 (2H, t, *J* 7, =$ClCH_2$), 2.13–2.00 (6H, m, 2 × CH_2C=CH_2 and CH_2CH=CH_2), 1.66 (2H, quintet, *J* 7, $CH_2CH_2CH_2$) and 1.54 (2H, quintet, *J* 7, $CH_2CH_2CH_2$); δ_C(50 MHz) 148.7 (*C*=CH_2), 138.7 (*C*H=CH_2), 125.5 (*C*H_2=CI), 114.5 (CH=*C*H_2), 112.3 (CH_2=*C*I), 109.6 (C=*C*H_2), 44.7 (=CI*C*H_2), 35.3 (*C*H_2C=CH_2), 34.3 (*C*H_2C=CH_2), 33.4 (*C*H_2CH=CH_2), 27.0 (=$ClCH_2$*C*H_2) and 26.9 (*C*H_2CH_2C=CH_2); *m*/*z* (CI) 308 (M + NH_4^+, 5%), 291 (5), 218 (100), 173 (12), 163 (25), 149 (20) and 122 (35) (Found: M + NH_4^+, 308.0875. $C_{12}H_{23}IN$ requires *M*, 308.0875).

2-Iodo-6-(hex-5-en-1-yl)hepta-1,6-diene 14b

Following the procedure for the preparation of triene **14a**, but using ketone **13b** (2.93 g, 9.6 mmol) gave after purification by column chromatography (light petroleum) a colourless oil, the *triene* **14b** (2.67 g, 92%); R_f 0.83 (10% Et_2O–light petroleum); ν_{max}(neat)/cm^{-1} 3076m, 2977m, 2931s, 2857m, 1641m and 1618m, 1439w, 1173w, 1107w, 992w, 910m and 891s; δ_H(200 MHz) 6.03 (1H, d, *J* 1, C*H*H=CI), 5.82 (1H, ddt, *J* 17, 10 and 7, C*H*=CH_2), 5.71 (1H, s, CH*H*=CI), 5.07–4.92 (2H, m, CH=CH_2), 4.74 (2H, s, C=CH_2), 2.39 (2H, t, *J* 7, =$ClCH_2$), 2.12–1.98 [6H, m, (CH_2)$_2$C=CH_2 and CH_2CH=CH_2], 1.66 (2H, quintet, *J* 7, CH_2CH_2CH=CH_2) and 1.58–1.26 (4H, m, 2 × CH_2CH_2-CH_2); δ_C(50 MHz) 148.8 (*C*=CH_2), 138.9 (*C*H=CH_2), 125.5 (*C*H_2=CI), 114.3 (CH=*C*H_2), 112.4 (CH_2=*C*I), 109.4 (C=*C*H_2), 44.7 (=CI*C*H_2), 35.7 (*C*H_2C=CH_2), 34.3 (*C*H_2C(=CH_2), 33.6 (*C*H_2CH=CH_2), 28.6 (*C*H_2CH_2CH=CH_2), 27.2 (=$ClCH_2$*C*H_2) and 27.0 (CH_2*C*H_2CH_2); *m*/*z* (CI) 305 (M + H^+, 5%), 233 (15), 232 (100), 177 (25), 173 (30), 149 (20), 124 (35), 122 (100) and 102 (10) (Found: M^+, 304.0688. $C_{13}H_{21}I$ requires *M*, 304.0688).

Dimerisation of 2-iodo-6-(hex-5-en-1-yl)hepta-1,6-diene 14b

Triene **14b** (0.071 g, 0.23 mmol) in CH_2Cl_2 (5 cm^3) was added to a stirred solution of bis(tricyclohexylphosphine)benzylideneruthenium dichloride (Strem, 0.010 g, 5 mol%) in CH_2Cl_2 (15 cm^3) at room temperature. After 22 h the reaction mixture was exposed to air for 5 h and then evaporated under reduced pressure and the residue purified by column chromatography (light petroleum). First to elute was starting triene **14b** (0.020 g). Second to elute was a colourless oil, the *dimer* (0.030 g, 44%, 61% based on recovered triene **14b**) (*E*:*Z* = 2.7:1, by ^{1}H NMR analysis of the isomeric =CHs in the δ 5.40–5.37 region); R_f 0.35 (light petroleum); ν_{max}(neat)/cm^{-1} 2929s, 2855m, 1644s, 1617m, 1436m, 968m and 890s; *m*/*z* (CI) 598 (10%), 597 (15), 596 (30), 595 (60), 579 (25), 451 (60), 173 (70) and 149 (100) (Found: M + NH_4^+, 598.1407. $C_{24}H_{42}I_2N$ requires *M*, 598.1407); data for *E*-isomer: δ_H(400 MHz) 6.03 (1H, d, *J* 1, 2 × C*H*H=CI), 5.71 (1H, s, 2 × CH*H*=CI), 5.40 (2H, dt, *J* 4 and 2, CH=CH), 4.75 (2H, d, *J* 6, C=CH_2), 2.39 (2H, t, *J* 7, =$ClCH_2$), 2.01 (6H, t, *J* 7, 2 × CH_2C=CH_2 and CH_2CH=CH), 1.65 (2H, quintet, *J* 8, CH_2CH_2CH=CH) and 1.49–1.32 (4H, m, 2 × CH_2CH_2CH_2); δ_C(125 MHz) 149.0 (*C*=CH_2), 130.3 (*C*H=CH), 125.5 (*C*H_2=CI), 112.4 (CH_2=*C*I), 109.4 (C=*C*H_2), 44.8 (=CI*C*H_2), 35.8 (*C*H_2C=CH_2), 34.4 (*C*H_2C=CH_2), 32.4 (*C*H_2CH=CH), 29.4 (*C*H_2CH_2-CH=CH), 27.4 (=$ClCH_2$*C*H_2) and 27.1 (CH_2*C*H_2CH_2); discernible data for *Z*-isomer: δ_H(400 MHz) 5.37 (1H, t, *J* 5, CH=CH); δ_C(125 MHz) 149.0 (*C*=CH_2), 129.8 (*C*H=CH), 35.8 (*C*H_2C=CH_2), 29.3 (*C*H_2CH_2CH=CH) and 27.2 (=$ClCH_2$*C*H_2).

1-(4-Iodopent-4-en-1-yl)cyclopent-1-ene 15a

Triene **14a** (0.650 g, 2.24 mmol) in dry, degassed (freeze–pump–thawed) pentane (20 cm^3) was added to a stirred solution of 2,6-diisopropylphenylimidoneophylidenemolybdenum bis(hexafluoro-*tert*-butoxide) (Strem, 0.210 g, 0.27 mmol) in dry, degassed (freeze–pump–thawed) pentane (25 cm^3) at room temperature under a gentle flow of argon. The reaction flask was then wrapped in foil to exclude light. After 5 h the reaction mixture was exposed to air for 15 min and then evaporated under reduced pressure. Purification of the residue by column chromatography (light petroleum) gave a colourless oil, the *cycloalkene* **15a** (0.488 g, 83%); R_f 0.57 (light petroleum); ν_{max}(neat)/cm^{-1} 2937s, 2842s, 1618m, 1428m, 1172m, 1105m, 1040w, 945w, 891s and 816w; δ_H(200 MHz) 6.03 (1H, d, *J* 1, C*H*H=CI), 5.71 (1H, s, CH*H*=CI), 5.36 (1H, t, *J* 2, CH=C), 2.50–2.21 (6H, m, 2 × CH_2C= and =$ClCH_2$), 2.08 (2H, t, *J* 7, CH_2C=), 1.84–1.74 (2H, m, CH_2) and 1.67 (2H, quintet, *J* 7, CH_2); δ_C(50 MHz) 143.8 (CH_2*C*=CH), 125.4 (CI=*C*H_2), 123.9 (=CH), 112.5 (*C*I=CH_2), 44.9 (=CI*C*H_2), 35.0 (*C*H_2C=CH), 32.4 (*C*H_2C=CH), 29.5 (*C*H_2CH=C), 27.1 (CI*C*H_2*C*H_2CH_2) and 23.4 (CH_2*C*H_2CH_2); *m*/*z* (EI) 262 (10%), 261 (100), 259 (15), 175 (15), 151 (25), 149 (25), 134 (15), 133 (65), 122 (30) and 109 (55) (Found: M^+, 262.0219. $C_{10}H_{16}I$ requires *M*, 262.0219).

1-(4-Iodopent-4-en-1-yl)cyclohex-1-ene 15b

Following the procedure for the preparation of cycloalkene **15a**, but using triene **14b** (0.100 g, 0.33 mmol) gave, after purification by column chromatography (light petroleum), a colourless oil, the *cycloalkene* **15b** (0.075 g, 83%); R_f 0.65 (light petroleum); ν_{max}(neat)/cm^{-1} 2930s, 2856s, 2834s, 1617m, 1447m, 1437m, 1108m, 918w and 891s; δ_H(200 MHz) 6.02 (1H, d, *J* 1, C*H*H=CI), 5.70 (1H, d, *J* 1, CH*H*=CI), 5.41 (1H, s, CH=C), 2.37 (2H, t, *J* 7, =$ClCH_2$), 1.94 (6H, t, *J* 7, 3 × CH_2C=) and 1.72–1.50 (6H, m, 3 × CH_2); δ_C(50 MHz) 136.9 (CH_2*C*=CH), 125.3 (CI=*C*H_2), 121.5 (CH=), 112.7 (*C*I=CH_2), 44.8 (=CI*C*H_2), 36.4 (*C*H_2C=CH), 28.2 (*C*H_2C=CH), 27.0 (CICH_2*C*H_2CH_2), 25.2 (*C*H_2CH=C), 23.0 (CH_2) and 22.5 (CH_2); *m*/*z* (EI) 149 (M − I^+, 75%), 121 (5), 108 (35), 93 (57), 81 (100) and 67 (95) (Found: M − I^+, 149.1330. $C_{11}H_{17}$ requires *M*, 149.1330).

(4*S*)-3-[(2*S*)-2-(1-Methylethyl)pent-4-enoyl]-4-(phenylmethyl)-oxazolidin-2-one 17

Bu^{n}Li (2.5 mol dm^{-3} in hexanes; 142.0 cm^3, 354.8 mmol) was added dropwise to a stirred solution of diisopropylamine (48.4 cm^3, 369.0 mmol) in THF (160 cm^3) at 0 °C. After 15 min, the solution was cooled to −78 °C and *N*-isovaleryloxazolidinone **16**[29] (74.16 g, 283.8 mmol) in THF (100 cm^3) was added dropwise. After 1 h at −78 °C, allyl iodide (39.0 cm^3, 426 mmol) in THF (36 cm^3) was added dropwise, the cooling bath was then removed and the reaction mixture allowed to reach room temperature. After 3 h saturated aq. NH_4Cl (30 cm^3) was added cautiously to the reaction mixture, which was then evaporated under reduced pressure. The resulting concentrate was extracted with Et_2O (3 × 300 cm^3) and the combined organic layers were washed with H_2O (30 cm^3), brine (30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography (30% Et_2O–light petroleum) gave a light yellow oil, the *alkene* **17** (75.07 g, 88%); R_f 0.50 (35% Et_2O–light petroleum); $[\alpha]_D^{24}$ +67.6 (*c* 1.0 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 3029m, 2963s, 1781s, 1695s, 1641w, 1454m, 1386s, 1349s, 1291m, 1208s, 1100m, 1051m, 999m, 917m, 747m and 703s; δ_H(500 MHz) 7.35–7.23 [5H, m, Ar, incl. at 7.33 (2H, t, *J* 7, 2 × ArH)], 5.88–5.79 (1H, m, C*H*=CH_2), 5.10 (1H, dd, *J* 17 and 1, CH=CH*H*), 5.03 (1H, d, *J* 10, CH=C*H*H), 4.72–4.68 (1H, m, NCH), 4.16 (1H, d, *J* 9, NCHCH*H*O), 4.14 (1H, d, *J* 9 and 3, NCHC*H*HO), 3.87 (1H, ddd, *J* 11, 7 and 4, NC=OCH), 3.32 (1H, dd, *J* 13 and 3, C*H*HPh), 2.65 (1H, dd, *J* 13 and 10, CH*H*Ph), 2.52–2.38 (2H, m, CH_2CH=CH_2), 2.00 (1H, app. sextet, *J* 7, C*H*Me_2), 1.00 (3H, d, *J* 7, Me) and 0.98 (3H, d, *J* 7, Me); δ_C(125 MHz) 175.8 (OC=O), 153.2 (C=O), 135.6 (*C*H=CH_2), 135.5 (Ar, quat.), 129.4 (2 × Ar), 128.9 (2 × Ar), 127.3 (Ar), 116.9 (=CH_2), 65.9 (CH_2O), 55.6 (NCH),

48.2 (NC=O*C*H), 38.0 (*C*H_2Ar), 33.7 (*C*H_2CH=CH_2), 30.3 (*C*HMe$_2$), 20.9 (Me) and 19.2 (Me); *m*/*z* (EI) 301 (M^+, 35%), 259 (50), 178 (20), 170 (15), 125 (100), 117 (25), 97 (90) and 85 (60) (Found: M^+, 301.1678. $C_{18}H_{23}NO_3$ requires *M*, 301.1678).

(2*S*)-2-(1-Methylethyl)pent-4-en-1-ol 18

H_2O_2 (35% w/w in H_2O, 66.4 cm^3, 684 mmol] was added dropwise to a stirred solution of alkene **17** (25.75 g, 85.4 mmol) in THF (800 cm^3) and H_2O (250 cm^3) at 0 °C. LiOH (4.1 g, 170 mmol] in H_2O (167 cm^3) was added portionwise to the reaction mixture which was then allowed to warm to room temperature. After 5 h the reaction mixture was recooled to 0 °C, and aq. Na_2SO_3 (1.5 mol dm^{-3}; 513 cm^3, 770 mmol) was added and the reaction mixture was then evaporated under reduced pressure. The resulting concentrate was adjusted to pH 12–13 using aq. NaOH (1.5 mol dm^{-3}) and extracted with CH_2Cl_2 (5 × 200 cm^3). The combined organic extracts were washed with brine (50 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give an off-white solid, the chiral auxiliary, (4*S*)-4-benzyloxazolidin-2-one (13.32 g, 88%). The combined aqueous layers were acidified to pH 1 at 0 °C with aq. HCl (5 mol dm^{-3}) and extracted with EtOAc (5 × 200 cm^3). The combined organic layers were washed with brine (50 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to give a light yellow oil, (2*S*)-2-(1-methylethyl)pent-4-enoic acid [50] (11.64 g, 96%) which was used in the next stage without further purification; R_f 0.20 (35% Et_2O–light petroleum); $[\alpha]_D^{24}$ +5.6 (*c* 1.0 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 3081m, 2965s, 1707s, 1643w, 1470w, 1440m, 1285m, 1244m, 1212m, 995w and 917m; δ_H(500 MHz) 5.79 (1H, ddt, *J* 17, 10 and 7, C*H*=CH_2), 5.09 (1H, dq, *J* 17 and 1, *cis*-CH*H*=CHCH$_2$), 5.03 (1H, dd, *J* 10 and 1, *trans*-CH*H*=CHCH$_2$), 2.39–2.24 (3H, m, CH_2CHC=O), 1.93 (1H, app. sextet, *J* 7, C*H*Me$_2$), 1.00 (3H, *J* 7, Me) and 0.99 (3H, *J* 7, Me); δ_C(125 MHz) 180.5 (C=O), 135.6 (*C*H=CH_2), 116.7 (=CH_2), 52.1 (*C*H_2CH=CH_2), 33.6 (*C*HC=O), 30.0 (*C*HMe$_2$), 20.2 (Me) and 20.1 (Me); *m*/*z* (EI) 143 (M + H^+, 40%), 125 (35), 100 (75), 99 (100), 97 (30), 55 (60), 43 (45), 41 (40) and 39 (30).

$LiAlH_4$ (2.76 g, 72.7 mmol) was added portionwise to a stirred solution of the above acid (10.36 g, 72.9 mmol) in Et_2O (520 cm^3) at 0 °C. After 2 h H_2O (2.76 cm^3), aq. NaOH (15% w/w, 2.76 cm^3) and H_2O (8.28 cm^3) were cautiously added successively to the reaction mixture. The resulting very thick white precipitate was slowly filtered on a sinter funnel and washed with Et_2O (250 cm^3). The filtrate was evaporated under reduced pressure to give a colourless oil, the *alcohol* **18** (4.70 g, 50%) which was used in the next stage without further purification; R_f 0.29 (35% Et_2O–light petroleum); $[\alpha]_D^{24}$ +10.1 (*c* 1.0 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 3340br, 2959s, 2874s, 1640w, 1467w, 1387w, 1368w, 1043m, 994w and 910m; δ_H(200 MHz) 5.92–5.71 (1H, m, C*H*=CH_2), 5.09–4.96 (2H, m, CH=C*H*$_2$), 3.62 (1H, d, *J* 6, C*H*HOH), 3.55 (1H, s, CH*H*OH), 2.22–1.94 (2H, m, CH_2CH=CH_2), 1.87–1.71 (1H, m, C*H*Me$_2$), 1.49–1.34 (1H, m, C*H*CHMe$_2$), 0.89 (3H, d, *J* 7, Me) and 0.88 (3H, d, *J* 7, Me); δ_C(50 MHz) 138.2 (*C*H=CH_2), 115.9 (CH=*C*H_2), 63.4 (CH_2-OH), 46.3 (*C*HCHMe$_2$), 32.7 (*C*H_2CH=CH_2), 27.6 (*C*HMe$_2$), 19.6 (Me) and 19.1 (Me); *m*/*z* (CI) 129 (10%), 111 (15), 57 (100) and 43 (15) (Found: M + H^+, 129.1280. $C_8H_{17}O$ requires *M*, 129.1279).

(2*S*)-2-(1-Methylethyl)pent-4-en-1-yl hex-5-ynoate 19

DMAP (0.98 g, 8.0 mmol) was added to a stirred solution of alcohol **18** (9.33 g, 72.8 mmol), hex-5-ynoic acid (8.97 g, 80.0 mmol) and DCC (16.5 g, 80.0 mmol) in CH_2Cl_2 (725 cm^3) at room temperature. After 4 h Et_2O (250 cm^3) was added and the reaction mixture was filtered through Celite and the precipitate washed with further Et_2O (200 cm^3). The combined organic filtrates were evaporated under reduced pressure and the residue was purified by column chromatography (5% Et_2O–light petroleum) to give a colourless oil, the *alkyne* **19** (14.42 g, 89%); R_f 0.64 (35% Et_2O–light petroleum); $[\alpha]_D^{22}$ +9.1 (*c* 1.0 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 3308m, 2961s, 2360w, 1735s, 1641w, 1467w, 1388w, 1370w, 1313w, 1161s, 996w and 915m; δ_H(200 MHz) 5.77 (1H, ddt, *J* 17, 10 and 7, C*H*=CH_2), 5.07–4.99 (2H, m, CH=C*H*$_2$), 4.05 (1H, d, *J* 6, C*H*HOC=O), 4.04 (1H, d, *J* 6, CH*H*OC=O), 2.45 (2H, t, *J* 7, CH_2C=O), 2.27 (2H, td, *J* 6 and 3, C≡CCH_2), 2.21–2.10 (2H, m, CH_2CH=CH_2), 1.98 (1H, t, *J* 3, C≡CH), 1.94–1.65 (3H, m, C$H_2$$CH_2$C=O and C*H*Me$_2$), 1.64–1.56 (1H, m, C*H*CHMe$_2$), 0.92 (3H, d, *J* 7, Me) and 0.90 (3H, d, *J* 7, Me); δ_C(50 MHz) 173.1 (C=O), 136.9 (*C*H=CH_2), 116.2 (CH=*C*H_2), 83.2 (*C*≡CH), 69.1 (C≡*C*H), 64.9 (OCH_2), 42.9 (*C*HCHMe$_2$), 32.9 (*C*H_2C=O), 32.8 (*C*H_2CH=CH_2), 28.0 (*C*HMe$_2$), 23.6 (≡C*C*H_2), 19.5 (Me), 19.4 (Me) and 17.8 (*C*$H_2$$CH_2$C=O); *m*/*z* (EI) 223 (10%), 111 (50), 95 (75), 81 (15), 69 (100), 55 (50) and 41 (65) (Found: M + H^+, 223.1698. $C_{14}H_{23}O_2$ requires *M*, 223.1698).

(2*S*)-2-(1-Methylethyl)pent-4-en-1-yl 5-iodohex-5-enoate 20

Alkyne **19** (7.40 g, 33.3 mmol) in pentane (25 cm^3) was added slowly to a stirred solution of *B*-I-9-BBN [(Aldrich) 1 mol dm^{-3} in hexanes; 73.2 cm^3, 73.2 mmol] in *n*-pentane (240 cm^3) at −25 °C. After 2 h glacial acetic acid (37 cm^3) was added to the reaction mixture which was then stirred at 0 °C. After 1 h aq. NaOH (3 mol dm^{-3}; 265 cm^3) and H_2O_2 (35% w/w in H_2O, 51 cm^3) were cautiously added to the reaction mixture which was then allowed to warm to room temperature. After 30 min the organic layer was separated and the aqueous layer further extracted with light petroleum (5 × 100 cm^3) and Et_2O (1 × 100 cm^3). The combined organic layers were washed with H_2O (20 cm^3), saturated aq. $NaHCO_3$ (20 cm^3), saturated aq. Na_2SO_3 (20 cm^3), H_2O (20 cm^3), brine (20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatgraphy (5% Et_2O–light petroleum) gave a light yellow oil, the *alkenyl iodide* **20** (10.48 g, 90%); R_f 0.65 (35% Et_2O–light petroleum); $[\alpha]_D^{24}$ +5.7 (*c* 1.0 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 2959s, 1735s, 1640w, 1617w, 1466w, 1388w, 1369w, 1167s, 1110w, 995w and 912w; δ_H(400 MHz) 6.05 (1H, q, *J* 1, C*H*H=CI), 5.76 (1H, ddt, *J* 17, 10 and 7, C*H*=CH_2), 5.74 (1H, d, *J* 1, CH*H*=CI), 5.07–5.01 (2H, m, CH=C*H*$_2$), 4.07 (1H, dd, *J* 11 and 6, OC*H*H), 4.02 (1H, dd, *J* 11 and 6, OCH*H*), 2.44 (2H, t, *J* 7, CH_2C=O), 2.32 (2H, t, *J* 7, CH_2CI=), 2.21–2.13 (1H, m, C*H*HCH=CH_2), 2.07–1.99 (1H, m, CH*H*CH=CH_2), 1.89–1.75 (3H, m, C$H_2$$CH_2$C=O and C*H*Me$_2$), 1.63–1.59 (1H, m, C*H*CHMe$_2$), 0.93 (3H, d, *J* 7, Me) and 0.92 (3H, d, *J* 7, Me); δ_C(100 MHz) 173.2 (C=O), 136.9 (*C*H=CH_2), 126.3 (*C*H_2=CI), 116.3 (CH=*C*H_2), 110.9 (CH_2=*C*I), 65.0 (OCH_2), 44.3 (=CI*C*H_2), 43.0 (*C*HCHMe$_2$), 32.8 (*C*H_2C=O), 32.5 (*C*H_2CH=CH_2), 28.1 (*C*HMe$_2$), 24.2 (*C*$H_2$$CH_2$C=O), 19.5 (Me) and 19.4 (Me); *m*/*z* (EI) 351 (M+H^+, 25%), 222 (15), 195 (10), 113 (80) and 69 (100) (Found: M + H^+, 351.0821. $C_{14}H_{24}IO_2$ requires *M*, 351.0821).

(2*S*)-[2-(1-Methylethyl)pent-4-en-1-yloxy]-6-iodohepta-1,6-diene 21

$TiCl_4$ (1 mol dm^{-3} in CH_2Cl_2; 3.9 cm^3, 3.9 mmol] and TMEDA (1.17 cm^3, 7.8 mmol) were successively added slowly dropwise to THF (2.5 cm^3) at 0 °C. After 20 min a mixture of zinc dust (0.572 g, 8.75 mmol) and $PbCl_2$ [(Aldrich) 0.013 g, 0.047 mmol] was added portionwise to the reaction mixture which was then allowed to warm to room temperature. After 30 min a solution of alkenyl iodide **20** (0.227 g, 0.65 mmol) and CH_2Br_2 (0.150 cm^3, 2.14 mmol) in THF (1.2 cm^3) was added dropwise to the reaction mixture over 10 min. After 3.5 h the reaction mixture was cooled to 0 °C then Et_3N (1.0 cm^3) and saturated aq. K_2CO_3 (1.3 cm^3) were added. After 15 min the reaction mixture was filtered through a pad of basic alumina (activity III, 40 g) using 1% Et_3N–Et_2O (100 cm^3) as eluent and then evaporated under reduced pressure. Purification of the residue by column chromatography (10% Et_2O–light petroleum) gave a clear col-

ourless oil, the *triene* **21** (0.131 g, 58%); R_f 0.78 (35% CH_2Cl_2–light petroleum with 1% Et_3N); $[a]_D^{24}$ +1.5 (*c* 1.0 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 2957s, 2929s, 2873m, 1652s, 1617m, 1466w, 1438w, 1282m, 1265m, 1174m, 1071m, 912w, 893w and 798m; δ_H(500 MHz) 6.08 (1H, d, *J* 1, C*H*H=CI), 5.84 (1H, ddt, *J* 17, 10 and 7, C*H*=CH_2), 5.76 (1H, d, *J* 1, CH*H*=CI), 5.10–5.04 (2H, m, CH=CH_2), 3.88 (1H, d, *J* 9, C=C*H*H), 3.89 (1H, s, C=CH*H*), 3.67–3.60 (2H, m, $COCH_2$), 2.45 [2H, t, *J* 7, CH_2C(=CH_2)], 2.26–2.08 [4H, m, CH_2CH=CH_2 and =$ClCH_2$, incl. at 2.15 (2H, t, *J* 7, =$ClCH_2$)], 1.93–1.87 (1H, m, C*H*Me_2), 1.77 (2H, quintet, *J* 7, =$ClCH_2$CH_2), 1.71–1.64 (1H, m, C*H*CHMe_2) and 0.97 (6H, t, *J* 6, 2 × Me); δ_C(125 MHz) 162.5 (*C*=CH_2), 137.5 (*C*H=CH_2), 125.6 (*C*H_2=CI), 115.9 (CH=*C*H_2), 112.2 (CH_2=*C*I), 80.9 (C=*C*H_2), 67.3 (OCH_2), 44.4 (=CI*C*H_2), 43.5 (OCH_2*C*H), 33.5 (*C*H_2C=CH_2), 33.0 (*C*H_2CH=CH_2), 28.3 (*C*HMe_2), 26.6 (=$ClCH_2$*C*H_2), 19.7 (Me), and 19.6 (Me); *m*/*z* (EI) 349 (M + H^+, 100%), 305 (15), 279 (35), 151 (10), 141 (30), 120 (30), 111 (70), 99 (40), 81 (55) and 70 (45) (Found: M + H^+, 349.1028. $C_{15}H_{26}IO$ requires *M*, 349.1028).

(3*S*)-6-(4-Iodopent-4-en-1-yl)-3-(1-methylethyl)-3,4-dihydro-2*H*-pyran 22

A solution of triene **21** (0.123 g, 0.35 mmol) in dry, degassed pentane (3.5 cm^3) was added dropwise to a stirred solution of 2,6-diisopropylphenylimidoneophylidenemolybdenum bis-(hexafluoro-*tert*-butoxide) [(Strem) 0.037 g, 0.05 mmol] in dry, degassed pentane (4 cm^3) at 25 °C under a gentle flow of Ar. The reaction vessel was wrapped in aluminium foil to exclude light and after 5 h the reaction mixture was exposed to air. After 15 min the reaction was diluted with 1% Et_3N–Et_2O (10 cm^3), filtered through a pad of basic alumina (activity III, 10 g) and evaporated under reduced pressure. Purification of the residue by column chromatography (1% Et_2O–light petroleum with 1% Et_3N) gave a light yellow oil, the *dihydropyran* **22** (0.050 g, 44%); R_f 0.64 (5% Et_2O–light petroleum with 1% Et_3N); $[a]_D^{23}$ −28.3 (*c* 1.0 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 2963s, 2928s, 2872s, 1679m, 1618w, 1464w, 1386w, 1368w, 1314w, 1173m, 1056m, 1032w, 923w, 882m and 754w; δ_H(500 MHz) 6.03 (1H, d, *J* 1, C*H*H=CI), 5.70 (1H, d, *J* 1, CH*H*=CI), 4.49 (1H, dd, *J* 5 and 2, CH=CO), 4.12 (1H, dq, *J* 10 and 2, C*H*HO), 3.54 (1H, t, *J* 10, CH*H*O), 2.39 (2H, t, *J* 7, CH_2CI), 2.00 (2H, t, *J* 7, CH=CCH_2), 1.80–1.74 (1H, m, C*H*Me_2), 1.72–1.65 (2H, m, CH_2CH=CO), 1.58–1.44 (3H, m, CH_2 and C*H*CHMe_2), 0.94 (3H, d, *J* 7, Me) and 0.92 (3H, d, *J* 7, Me); δ_C(100 MHz) 153.3 (=CO), 125.5 (=CH_2), 112.2 (=CI), 95.5 (CH=), 69.2 (CH_2O), 44.6 (*C*H_2CI), 38.7 (*C*HCHMe_2), 32.3 (*C*H_2C=CH), 29.6 (*C*HMe_2), 26.3 (*C*H_2CH=CO), 24.6 (CH_2), 20.3 (Me) and 19.7 (Me); *m*/*z* (CI) 339 (15%), 321 (M + H^+, 100%), 211 (45), 207 (40), 193 (M − I, 30), 175 (20), 153 (80), 135 (15), 107 (15) and 102 (20) (Found: M + H^+, 321.0715. $C_{13}H_{22}IO$ requires *M*, 321.0715).

(2*S*)-9-Iodo-2-(1-methylethyl)-5-oxodec-9-enal 23

Following the procedure for the preparation of dihydropyran **22**, but using triene **21** (0.758 g, 2.18 mmol) and 2,6-diisopropylphenylimidoneophylidenemolybdenum bis(hexafluoro-*tert*-butoxide) [(Strem) 0.200 g, 0.26 mmol] in dry, degassed pentane (220 cm^3), gave crude dihydropyran which was immediately dissolved in THF (12 cm^3) and HCl (2 mol dm^{-3} in H_2O, 24 drops) added. After 2 h, $NaHCO_3$ (2.3 g) was added and the reaction mixture was filtered and evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (12 cm^3) and PCC (2.10 g, 9.74 mmol) and SiO_2 (2.10 g) added to the stirred solution. After 3 h, the reaction mixture was diluted with Et_2O (20 cm^3), filtered through a pad of Florisil® (Aldrich) and evaporated under reduced pressure. Purification of the residue by column chromatography (20% Et_2O–light petroleum) gave a colourless oil, the *aldehyde* **23** (0.400 g, 55% from **21**): R_f 0.15 (20% Et_2O–light petroleum); $[a]_D^{25}$ +16.7 (*c* 1.0 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 3429s, 2960s, 2931m, 1716s, 1618m, 1371w, 1166w and 896w; δ_H(500 MHz) 9.61 (1H, d, *J* 3, CHO), 6.04 (1H, d, *J* 1, C*H*H=CI), 5.73 (1H, d, *J* 1, CH*H*=CI), 2.51–2.27 [7H, m, =$ClCH_2$, $(CH_2)_2CO$ and C*H*CHO], 2.10–2.00 (1H, m, C*H*Me_2), 1.89–1.75 (4H, m, 2 × CH_2), 1.01 (3H, d, *J* 7, Me) and 0.98 (3H, d, *J* 7, Me); δ_C(125 MHz) 209.5 (CO), 205.3 (CHO), 126.2 (CH_2=), 111.3 (=CI), 57.6 (*C*HCHO), 44.2 (=CI*C*H_2), 40.7 (*C*H_2CO), 40.4 (*C*H_2CO), 28.4 (*C*HMe_2), 22.8 (CH_2), 20.3 (Me), 19.5 (Me) and 19.4 (CH_2); *m*/*z* (CI, NH_3) 337 (5%), 319 (25), 301 (15), 223 (45), 209 (90), 191 (35), 173 (20), 151 (50) and 113 (100) (Found: M + H^+, 337.0665. $C_{13}H_{22}IO_2$ requires *M*, 337.0665).

Tributyl(diiodomethyl)stannane

Dry NaI (0.78 g, 5.2 mmol) was added to a stirred solution of $Bu_3SnCHBr_2$[2] (0.600 g, 1.30 mmol) in acetone (7.7 cm^3) at room temperature and the reaction flask was then wrapped in foil to exclude light. After 18 h the reaction mixture was evaporated under reduced pressure. The residue was diluted with hexane (20 cm^3), filtered, concentrated under reduced pressure, diluted with $CHCl_3$ (20 cm^3), filtered and further concentrated under reduced pressure to afford a yellow oil, *Bu_3SnCHI_2* (0.720 g, quant.); R_f 0.5 (100% light petroleum) (Found: C, 28.4; H, 5.4. $C_{13}H_{28}I_2Sn$ requires C, 28.0, H, 5.1%); ν_{max}(neat)/cm^{-1} 2956s, 2926s, 2851m, 1463w, 1375w, 1071w and 875w; δ_H(400 MHz) 4.27 (1H, s, CHI_2), 1.71–1.55 [6H, m, $Sn(CH_2CH_2)_3$], 1.33 (6H, sextet, *J* 7, 3 × $MeCH_2$), 1.16–1.08 [6H, m, $Sn(CH_2)_3$] and 0.94 (9H, t, *J* 7, 3 × Me); δ_C(125 MHz) 28.4 [$Sn(CH_2CH_2)_3$], 27.3 (J_{Sn-C} 60, 3 × $MeCH_2$), 16.4 (CHI_2), 13.7 (3 × Me) and 12.9 [$Sn(CH_2)_3$]; *m*/*z* (CI) 557 (M^+, 20%), 536 (30), 291 (40), 289 (30), 287 (15), 235 (30), 233 (25), 231 (15), 172.7 (100), 124 (30) and 122 (95).

Typical procedure for the preparation of (*E*)-alkenylstannanes using Bu_3SnCHI_2

Dry, deoxygenated DMF (7 cm^3) was added dropwise to well-stirred $CrCl_2$ (0.527 g, Aldrich 99.9% w/w pure, 4.3 mmol) in a flask under argon in an ice-bath. After allowing the flask to warm to room temperature over 15 min it was surrounded by aluminium foil to exclude light and then a mixture of nonanal (0.061 g, 0.43 mmol) and Bu_3SnCHI_2 (0.478 g, 0.86 mmol) in dry, deoxygenated DMF (2 cm^3) was added dropwise to the reaction mixture. After 2.5 h at 25 °C, H_2O (14 cm^3) was added and the mixture extracted with Et_2O (3 × 10 cm^3). The combined organic layers were washed with H_2O (10 cm^3) and brine (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Purification by reversed-phase column chromatography[51] (C-18, 30% CH_2Cl_2–MeCN) gave a colourless oil, (*E*)-tributyl-(dec-1-enyl)stannane (0.157 g, 85%); spectral data as lit.[2]

(9*S*,10*E*)-11-(Tributylstannyl)-2-iodo-9-(1-methylethyl)undec-1-en-6-one 24

Following the typical procedure for the preparation of (*E*)-alkenylstannanes, but using double the relative quantities of reagents [$CrCl_2$ (0.300 g, 2.4 mmol) and Bu_3SnCHI_2 (0.265 mg, 0.48 mmol)] with aldehyde **23** (0.040 g, 0.119 mmol) in DMF (3.7 cm^3) gave, after purification by reversed-phase column chromatography (C-18, 5% CH_2Cl_2–MeCN), a colourless oil, the *stannane* **24** (0.055 g, 74%); R_f 0.24 (10% CH_2Cl_2–MeCN); $[a]_D^{24}$ −11.4 (*c* 1.0 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 2956s, 2926s, 2871m, 1716m, 1617w, 1596w, 1464w, 1376w, 997w and 893w; δ_H(500 MHz) 6.03 (1H, d, *J* 1, C*H*H=CI), 5.79 (1H, d, *J* 19, $J_{119Sn-H}$ 81 and $J_{117Sn-H}$ 78, =CHSn), 5.72 (1H, s, CH*H*=CI), 5.60 (1H, dd, *J* 19 and 8, C*H*=CHSn), 2.48–2.29 [7H, m, =$ClCH_2$, $(CH_2)_2CO$ and C*H*CH=], 1.81–1.69 (4H, m, 2 × CH_2), 1.60–1.42 [7H, m, C*H*Me_2, and $Sn(CH_2CH_2)_3$] 1.37–1.26 (6H, m, 3 × CH_2Me) and 0.94–0.82 [21H, m, $Sn(CH_2CH_2CH_2Me)_3$ and 2 × Me, incl. at 0.87 (3H, d, *J* 8, Me) and 0.85 (3H, d, *J* 7, Me)];

δ_C(125 MHz) 210.7 (CO), 150.8 (*C*H=CHSn), 129.5 (J_{Sn-C} 432, =CHSn), 126.1 (=CI), 111.4 (CH_2=), 54.5 (*C*HCH=), 44.3 (=CI*C*H_2), 41.2 (*C*H_2CO), 40.7 (*C*H_2CO), 31.8 (*C*HMe_2), 29.2 [Sn($CH_2C H_2$)$_3$], 27.2 (J_{Sn-C} 52, 3 × *C*H_2Me), 25.6 (CH_2), 22.9 (CH_2), 20.6 (Me), 19.2 (Me), 13.8 (3 × CH_2*Me*) and 9.5 [J_{Sn-C} 325, Sn(CH_2)$_3$]; *m*/*z* (CI) 625 (M + H^+, 35%), 567 (100), 441 (55), 360 (65), 308 (80) and 123 (25) (Found: M + H^+, 625.1948. $C_{26}H_{50}IO^{120}Sn$ requires *M*, 625.1928).

(4*S*,5*E*)-7–Methylene-4-(1-methylethyl)cyclodec-5-en-1-one 25

Following the procedure for the preparation of dienone **7**, but using stannane **24** (0.307 g, 0.49 mmol), $Pd_2(dba)_3$ (0.027 g, 0.029 mmol) and $AsPh_3$ (0.091 g, 0.30 mmol) in NMP (49 cm^3) gave, after column chromatography (10% Et_2O–pentane), a colourless oil, the *substituted (−)-dienone* **25** (0.063 g, 62%); R_f 0.24 (10% Et_2O–pentane); $[\alpha]_D^{25}$ −310 (*c* 1.22 in hexane) [lit.,[10] $[\alpha]_D^{22}$ −362 (*c* 1.22 in hexane)]; δ_H(500 MHz; C_6D_6; C_6H_6) 5.89 (1H, d, *J* 16, CH_2=CC*H*=CH), 5.24 (1H, dd, *J* 16 and 10, CH=C*H*CH), 4.85 (1H, br s, C=CH*H*), 4.81 (1H, d, *J* 2, C=C*H*H), 2.55 (1H, dt, *J* 13 and 5, CH*H*C=CH_2), 2.32–2.23 (2H, m, CH_2CO), 2.09 (1H, app. dq, *J* 12 and 3, CH*H*CH-$CHMe_2$), 1.99 (1H, ddd, *J* 13, 7 and 2, C*H*HC=CH_2), 1.89–1.79 (3H, m, CH_2CO and C*H*HCH_2C=CH_2), 1.59–1.53 (1H, m, C*H*HCHCHMe_2), 1.47–1.38 (1H, m, C*H*CHMe_2), 1.35–1.25 (1H, m, C*H*Me_2), 1.22–1.11 (1H, m, C*H*HCH_2C=CH_2), 0.79 (3H, d, *J* 7, Me) and 0.77 (3H, m, *J* 7, Me); δ_C(125 MHz; C_6D_6; C_6H_6) 210.6 (C=O), 146.9 (*C*=CH_2), 136.9 (CH=*C*HC=CH_2), 132.6 (CH=*C*HCH), 113.4 (C=*C*H_2), 52.8 (*C*HCH=), 42.4 (*C*H_2C=O), 42.0 (*C*H_2C=O), 31.9 (*C*HMe_2), 31.7 (*C*H_2C=CH_2), 30.2 (*C*H_2CHCH), 24.5 ($CH_2C H_2CH_2$), 20.9 (Me) and 20.8 (Me). UV, IR, ^{1}H NMR data were consistent with those previously reported.[10] The ee was determined to be 93% by chiral HPLC [Cyclobond I (β-cyclodextrin) column (4.6 mm × 250 mm), 42 : 58 MeOH–H_2O, 1 cm^3min^{-1}], $t_R$mj, 36.2 min; $t_R$mn, 40.9 min.

(3*S*,1*E*)-Tributyl(3-methylpent-1-enyl)stannane 27

Following the typical procedure for the preparation of (*E*)-alkenylstannanes using Bu_3SnCHI_2 with (*S*)-α-methylbutyraldehyde **26**[43] (0.066 g, 0.77 mmol) gave, after purification by reversed-phase column chromatography (C-18, 10% CH_2Cl_2–MeCN), a colourless oil, *stannane* **27** (0.230 g, 80%); R_f 0.22 (10% CH_2Cl_2–MeCN); $[\alpha]_D^{24}$ +14.7 (*c* 1.0 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 2958s, 2925s, 2872m, 2854m, 1597w, 1463m, 1376w, 1071w, 990w and 874w; δ_H(400 MHz) 5.80 (1H, s, C*H*=CHSn) 5.80 (1H, d, *J* 2, $J_{119Sn-H}$ 75, $J_{117Sn-H}$ 72, =C*H*Sn), 2.04 (1H, m, C*H*Me), 1.56–1.26 [14H, m, Sn($CH_2C H_2CH_2$)$_3$ and Me*C*H_2] and 0.99–0.78 [21H, m, CH*Me*, CH_2*Me* and Sn(*C*$H_2$$CH_2$$CH_2$*Me*)$_3$, incl. at 0.98 (3H, d, *J* 7, CH*Me*) and 0.89 (9H, t, *J* 7, 3 × Me)]; δ_C(125 MHz) 155.3 (*C*H=CHSn), 124.6 (=CHSn), 43.2 (*C*HMe), 29.3 (Me*C*H_2), 29.1 [J_{Sn-C} 20, Sn($CH_2C H_2$)$_3$], 27.2 (J_{Sn-C} 52, 3 × *C*H_2Me), 19.8 (CH*Me*), 13.7 (3 × Me), 11.7 (*Me*CH_2) and 9.4 [J_{Sn-C} 330, Sn(CH_2)$_3$]; *m*/*z* (EI) 317 (M − Bu^+, 80%), 291 (100), 269 (80), 235 (40), 205 (40) and 177 (50) (Found: M − Bu^+, 317.1291. $C_{14}H_{29}{}^{120}Sn$ requires *M*, 317.1291).

(2*R*,6*S*,4*E*)-1,1,1-Trifluoro-2-methoxy-6-methyl-2-phenyloct-4-en-3-one 28

Pd_2dba_3 (1.5 mg, 1.6×10^{-3} mmol) and tri(2-furyl)phosphine (1.5 mg, 6.5×10^{-3} mmol) were added to a stirred solution of (*S*)-MPTA-Cl (34 μl, 0.18 mmol) in THF (1.5 cm^3). After 10 min a solution of (*S*)-stannane **27** (0.061 g, 0.16 mmol) in THF (0.5 cm^3) was added, the reaction vessel was wrapped in foil to exclude light and then heated at 55 °C. After 3 h the reaction mixture was cooled to room temperature, then Et_2O (15 cm^3) was added, the mixture filtered through a pad of Florisil® (Aldrich, 10 g) and concentrated under reduced pressure. The residue was diluted with 5% Et_2O–pentane, DBN[48] (1 drop) was then added and the resultant mixture was purified by column chromatography (5% Et_2O–light petroleum) to give a light yellow oil, the *enone* **28** [0.031 g, 63%, diastereomerically pure (by ^{1}H NMR comparison with a diastereomeric mixture of similarly prepared enones in the δ 7.1–6.2 region)]; R_f 0.50 (5% Et_2O–light petroleum); $[\alpha]_D^{24}$ −173.0 (*c* 0.15 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 3411br, 2968s, 1707s, 1626s, 1495w, 1452m, 1354w, 1271s, 1226m, 1166s, 1107m, 1079m, 1005m, 948w, 914w, 857w, 762w and 705s; δ_H(500 MHz) 7.50–7.29 (5H, m, Ar), 7.01 (1H, dd, *J* 16 and 8, C*H*=CHCO), 6.21 (1H, dd, *J* 16 and 1, =CHCO), 3.61 (3H, q, J_{H-F} 2, OMe), 2.15 (1H, quintet, *J* 7, C*H*Me), 1.42–1.20 (2H, m, CH_2), 0.97 (3H, d, *J* 7, CH*Me*) and 0.81 (3H, t, *J* 7, CH_2*Me*); δ_C(125 MHz) 192.6 (C=O), 156.8 (*C*H=CHCO), 133.2 (Ar, quat.), 129.9 (Ar), 128.9 (2 × Ar), 127.8 (2 × Ar), 123.4 (Q, J_{C-F} 290, CF_3), 121.5 (=*C*HCO), 86.0 (*C*CF_3), 56.3 (OMe), 39.0 (*C*HMe), 29.2 (CH_2), 19.3 (CH*Me*) and 11.9 (CH_2*Me*); δ_F(235 MHz; ref. $CFCl_3$) −70.17; *m*/*z* (CI) 323 (M + Na, 80%), 301 (M + H^+, 25), 273 (65), 269 (90), 251 (100), 227 (35), 199 (25), 197 (25), 157 (25), 156 (70), 139 (30), 124 (15) and 102 (15) (Found: M + H^+, 301.1415. $C_{16}H_{20}F_3O_2$ requires *M*, 301.1415).

(2*S*)-2,6-Dimethyl-5-oxoheptanal 31

A mixture of O_2 and O_3 was bubbled through a stirred mixture of (6*S*)-2,6-dimethyloct-7-en-3-one[45] (0.757 g, 4.9 mmol) and $NaHCO_3$ (0.023 g) in MeOH (10.3 cm^3) at −65 °C until the appearance of O_3 at the outlet (starch–iodide test). The reaction mixture was then purged with argon until no more O_3 expelled, Me_2S (0.915 g, 14.7 mmol) was added and the reaction was allowed to warm to room temperature. After 16 h the reaction mixture was filtered and concentrated under reduced pressure. H_2O (10 cm^3) was added to the residue which was then extracted with Et_2O (3 × 20 cm^3). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the residue by column chromatography (20% Et_2O–light petroleum) gave a colourless oil, the *ketoaldehyde* **31** (0.720 g, 94%); R_f 0.15 (15% Et_2O–light petroleum); $[\alpha]_D^{23}$ +18.0 (*c* 0.3 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 2973s, 2937m, 1709s, 1467m, 1411w, 1384w, 1213w, 1099w and 928w; δ_H(200 MHz); 9.51 (1H, d, *J* 2, CHO), 2.58–2.23 [4H, m, CH_2C=O and CH_2CHMe, incl. at 2.43 (2H, t, *J* 7, CH_2C=O)], 1.87 (1H, septet, *J* 7, C*H*Me_2), 1.56 (1H, sextet, *J* 7, C*H*Me), 1.02 (3H, d, *J* 7, Me) and 0.99 (6H, d, *J* 7, 2 × Me); δ_C(50 MHz) 204.5 (C=O), 192.9 (CHO), 45.5 (*C*HMe), 40.7 (*C*HMe_2), 37.0 (*C*H_2C=O), 24.0 (*C*H_2CHMe), 18.1 (2 × Me) and 13.3 (Me); *m*/*z* (CI) 157 (M + H^+, 10%), 155 (11), 141 (100), 139 (30), 123 (5) and 111 (10) (Found: M + H^+, 157.1229. $C_9H_{17}O_2$ requires *M*, 157.1229).

(6*S*,7*E*)-8-Tributylstannyl-2,6-dimethyloct-7-en-3-one 32

Following the typical procedure for the preparation of (*E*)-alkenylstannanes using Bu_3SnCHI_2 with ketoaldehyde **31** (0.078 g, 0.50 mmol) gave, after purification by column chromatography (2% Et_2O–light petroleum), a colourless oil, *stannane* **32** (0.150 g, 68%); R_f 0.25 (15% Et_2O–light petroleum); $[\alpha]_D^{23}$ +14.5 (*c* 1.0 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 2958s, 2926s, 2872m, 1715m, 1597w, 1464m, 1376w, 992w and 874w; δ_H(500 MHz) 5.83 (1H, d, *J* 19, CHSn), 5.72 (1H, dd, *J* 19 and 7, C*H*=CHSn), 2.58 (1H, septet, *J* 7, C*H*Me_2), 2.43 (2H, t, *J* 8, CH_2C=O), 2.11 (1H, sextet, *J* 7, C*H*Me), 1.66–1.58 (2H, m, CH_2CHMe), 1.55–1.43 [6H, quintet, *J* 8, Sn($CH_2C H_2$)$_3$], 1.36–1.26 (6H, m, 3 × CH_2Me), 1.08 (6H, d, *J* 7, CHMe_2), 1.01 (3H, d, *J* 7, CH*Me*) and 0.93–0.82 [15H, m, Sn(C$H_2$$CH_2$$CH_2$*Me*)$_3$, incl. at 0.89 (9H, t, *J* 7, 3 × Me)]; δ_C(125 MHz) 215.1 (C=O), 154.3 (*C*H=CHSn), 126.1 (CH=*C*HSn), 41.4 (*C*HMe), 40.9 (*C*HMe_2), 38.2 (*C*H_2C=O), 30.0 (*C*H_2CHMe), 29.1 (Sn($CH_2C H_2$), 27.2 (3 × *C*H_2Me), 20.5 (CH*Me*), 18.3 (CHMe_2), 13.7 (3 × Me) and 9.4 (Sn(CH_2)$_3$); *m*/*z* (EI) 443 (M − H^+, 20%), 387 (M − Bu^+,

100), 331 (10), 175 (15), 121 (10), 71 (15), 43 (40) and 29 (20) (Found: M − Bu^+, 387.1710. $C_{18}H_{35}O^{120}Sn$ requires *M*, 387.1710).

(2*R*,6*S*,4*E*)-1,1,1-Trifluoro-2-methoxy-6,10-dimethyl-2-phenyl-undec-4-ene-3,9-dione 33

Following the procedure for the preparation of enone **28**, but using stannane **32** (0.019 g, 0.04 mmol), $Pd_2(dba)_3$ (0.4 mg, 4.4×10^{-4} mmol), tri(2-furyl)phosphine (0.4 mg, 1.7×10^{-3} mmol) and (*S*)-MPTA-Cl (8.9 μl, 0.048 mmol) in THF (0.3 cm^3) gave, after column chromatography (5% Et_2O–pentane), a light, yellow oil, the *enone* **33** [0.013 g, 81%, diastereomerically pure (by ^1H NMR comparison with a diastereomeric mixture of similarly prepared enones in the δ 7.0–6.2 region)]; R_f 0.10 (5% Et_2O–light petroleum); $[\alpha]_D^{23}$ +54.0 (*c* 0.1 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 2970m, 2360m, 1708s, 1626m, 1272m, 1166s, 1005w and 708m; δ_H(500 MHz) 7.78–7.32 (5H, m, Ar), 6.95 (1H, dd, *J* 16 and 9, C*H*=CHCO), 6.19 (1H, dd, *J* 16 and 1, CH=C*H*CO), 3.61 (3H, q, $J_{H\text{-}F}$ 1.5, OMe), 2.35 (1H, septet, *J* 8, C*H*Me_2), 2.22 (2H, t, *J* 7, CH_2C=O), 1.56–1.43 (2H, m, CH_2CHMe), 1.39–1.26 (1H, m, C*H*Me), 1.02 (3H, d, *J* 7, CH*Me*) and 1.00–0.93 (6H, m, CHMe_2); δ_C(125 MHz) 213.9 (CH_2CO), 192.4 (CH*C*O), 155.2 (*C*H=CHCO), 132.5 (Ar, quat.), 129.4 (Ar), 128.4 (2 × Ar), 127.2 (2 × Ar), 123.4 (=*C*HCO), 122.1 (CF_3), 86.0 (CCF_3), 55.8 (OMe), 40.8 (*C*Me_2), 37.4 (CH_2CO), 36.4 (*C*HMe), 29.3 (CH_2CHMe), 19.6 (CH*Me*), 18.2 (Me) and 18.1 (Me); δ_F(235 MHz; ref. $CFCl_3$) −70.07; *m*/*z* (CI) 393 (M + Na, 20%), 371 (M + H^+, 80%), 339 (100), 319 (60), 253 (50), 235 (10), 149 (10), 124 (15) and 122 (45) (Found: M + H^+, 371.1834. $C_{20}H_{26}F_3O_3$ requires *M*, 371.1834).

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