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Cascade radical cyclisations leading to steroid ring constructions. Regio- and stereo-chemical studies using ester- and fluoro-alkene substituted polyene acyl radical intermediates

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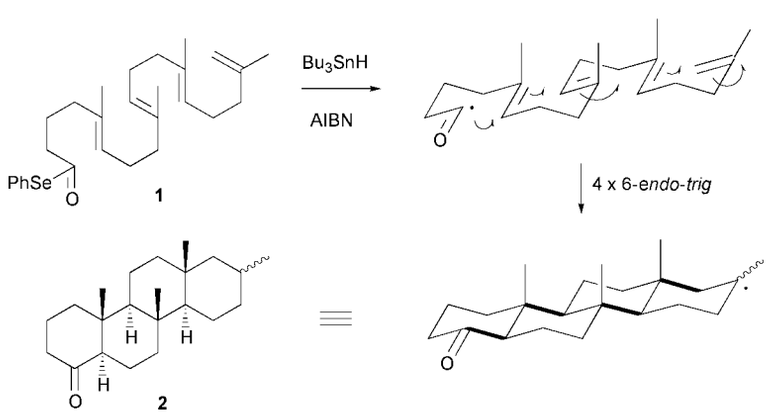
A study of the factors affecting the regio- and stereo-selective outcomes of consecutive 6-*endo-trig* cyclisations of polyene acyl-radical intermediates, leading to decalone, perhydrophenanthrone, and steroid ring constructions, has been carried out. Thus, whereas the *E*-substituted diene selenyl ester **7** underwent sequential cyclisations in the presence of Bu_3SnH-AIBN leading to the *trans*-decalone **8** exclusively, the corresponding *Z*- and *E*-isomers of the methoxycarbonyl-substituted diene **16**, under similar conditions, gave rise to a 2:1 mixture of the *trans*- and *cis*-decalones **17a** and **17b** respectively in 62–73% yield. Cyclisation of the triene selenoate **30** led to a single tricyclic product in 57% yield whose *cis*,*syn*,*trans* relative stereochemistry **32** was established by X-ray diffraction analysis. When solutions of the trienyne selenoates **41a**–**c** in benzene were treated with Bu_3SnH–AIBN they each underwent cascades of three 6-*endo-trig* followed by a 5-*exo-dig* cyclisation leading to the full steroid ring systems **42**, **45**, and **47** respectively in 20–40% yields. The stereochemistries of the major steroid diastereoisomers resulting from **41a** and **41c** were established as *trans*,*anti*,*trans*,*anti*,*cis*, *e.g.* **47**, following X-ray crystallographic analysis of the corresponding dione **44** produced from **42d** and **47** after ozonisation. In each of the cyclisations leading to **42** and **45** varying amounts of other bicyclic products tentatively assigned as **43** and **46** respectively, resulting from a competing radical pathway involving first a 10-*endo-trig* macrocyclisation of the corresponding acyl radical intermediate onto the C9–C10 olefin in **43/46**, followed by a 5-*exo-trig* cyclisation of the resulting radical intermediate onto the proximal C13–C14 double bond, were produced concurrently. Finally, when the fluoro-alkene selenoate **56** was treated with Bu_3SnH–AIBN, a complex mixture of polycyclic products resulted, from which only the indanone **57** could be separated and characterized. The origins of the differing regio- and stereo-selective outcomes in the aforementioned radical cascades are briefly considered.

In earlier, and extensive, investigations we have examined the scope for a wide range of free radical-mediated cascade processes involving polyene precursors in the elaboration of a variety of polycyclic ring systems.[1] Thus, more recently we have described serial 6-*endo-trig* cyclisations from polyene acyl precursors leading to steroid ring constructions (Scheme 1),[2] including the unique all-*trans* heptacycle **4** from the selenoate ester **3**.[3] We have also developed a second new approach to steroids based on the cascade of two 6-*endo-trig* cyclisations followed by a macrocyclisation–transannulation sequence, depicted in the conversion of **5** into **6**.[4]

In addition to their importance in synthesis, the aforementioned studies have revealed an interesting dependence on the nature of the substituents (H, Me, CO_2R) on the alkene bonds participating in the polycyclisations in determining the stereochemical outcomes of the various cascade processes we have evaluated. For example, the all-*trans* (*E*) methyl alkene-substituted polyenes **1** and **3** gave the corresponding all-*trans*-*anti* polycycles **2** and **4** respectively, on cascade cyclisation in the presence of Bu_3SnH–AIBN, whereas the ester alkene-substituted polyene selenoate ester **5** instead led to the *cis*-*anti*-*cis*-*anti*-*cis* tetracycle **6** under similar reaction conditions. We



Scheme 1

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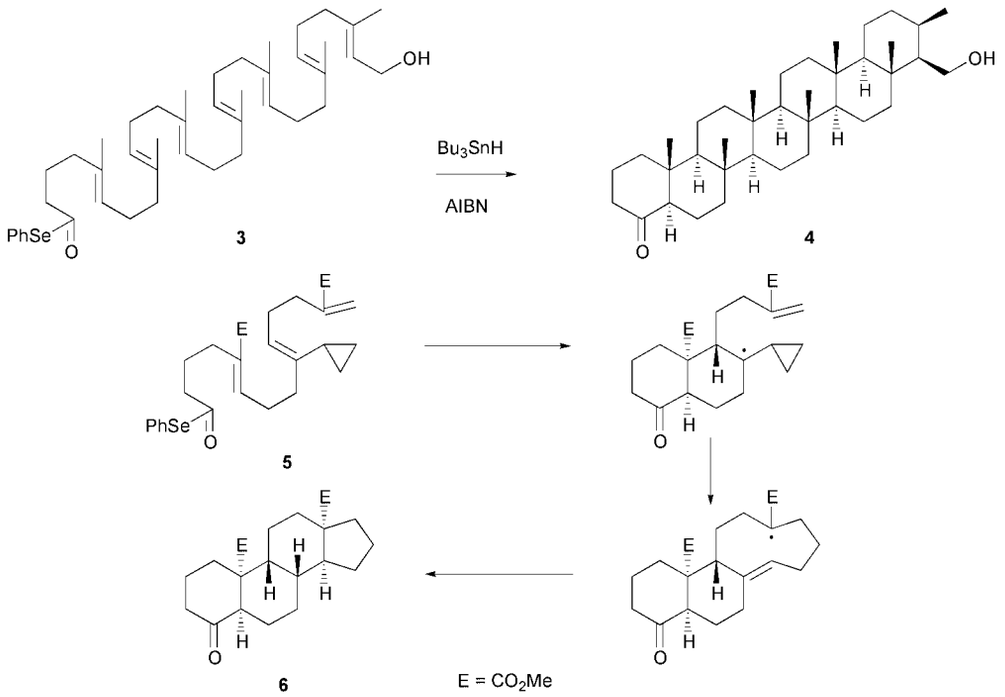
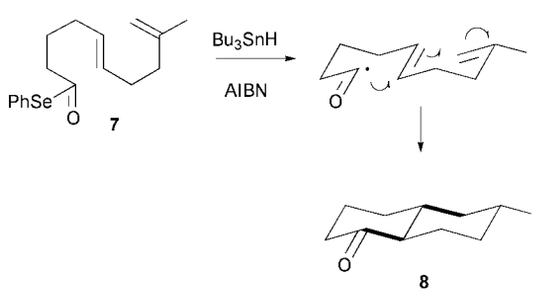


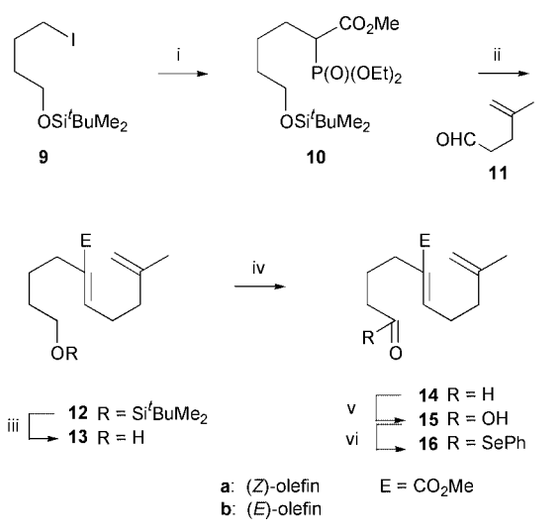
attributed these outcomes, and others, to a degree of pre-organisation in the polyene precursor molecules, and in the reaction intermediates, favouring the differential pathways followed in the polycycle constructions. In order to obtain greater insight with regard to the factors influencing the stereochemical outcomes of cascade processes involving polyene acyl radical precursors, we have carried out a systematic study of the effects of various ester and fluoro substituents on polyene precursors leading to decalins, perhydrophenanthrenes and steroid ring systems of varying stereochemistry.[5]

We first examined the radical cyclisation of the methoxycarbonyl-substituted diene **16** in order to compare the stereochemical outcome with the corresponding *E*-substituted diene **7** which had earlier been shown to lead to the *trans*-decalone **8** exclusively.[2] Both the *Z*-(**16a**) and the *E*-(**16b**)



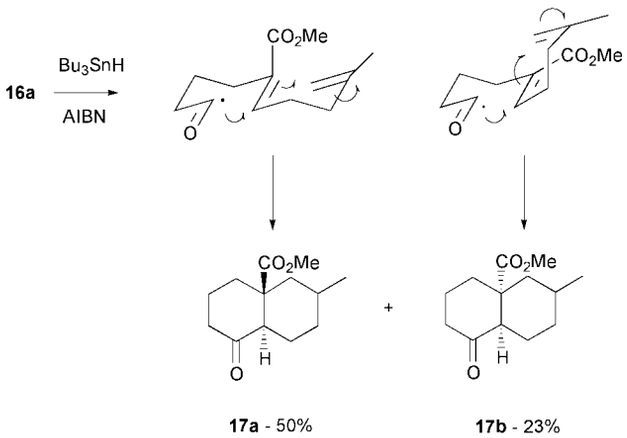
isomers of the diene selenoate were prepared, and the syntheses are shown in Scheme 2. Thus, alkylation of the anion of methyl diethylphosphonoacetate with the iodide **9**[6] first gave the substituted phosphonate **10**. A Horner–Wadsworth–Emmons (H–W–E) reaction between **10** and 4-methylpent-4-enal **11**[7] next produced a separable mixture of the (*Z*)- and (*E*)-dienes, **12a** and **12b** respectively, in 69% overall yield. For each diene in turn, deprotection of the silyl group to give the alcohols **13a** and **13b**, was followed by sequential oxidation using PCC and then sodium chlorite to give the two corresponding carboxylic acids (*viz.* **13a**,**b**→**14a**,**b**→**15a**,**b**), which were finally converted into the selenoates **16a**,**b** using *N*-(phenylseleno)phthalimide[8] and tributylphosphine.

When a 5 mM solution of the (*Z*)-selenoate **16a** in dry degassed benzene was heated to reflux and treated dropwise over 3 hours with a solution of Bu_3SnH and AIBN in benzene,[2]



Scheme 2 *Reagents and conditions*: i, $(EtO)_2(O)PCH_2CO_2Me$, NaH, DMSO; **9** (65%); ii, NaH, THF; **11** (**12a**, 23%; **12b**, 46%); iii, TBAF, THF, 0 °C (70–80%); iv, PCC, SiO_2, CH_2Cl_2 (71–82%); v, KH_2PO_4, ^{t}BuOH, H_2O, $NaClO_2$, 2-methylbut-2-ene (75–86%); vi, *N*-(phenylseleno)phthalimide, PBu_3, CH_2Cl_2, −30 °C (39–67%).

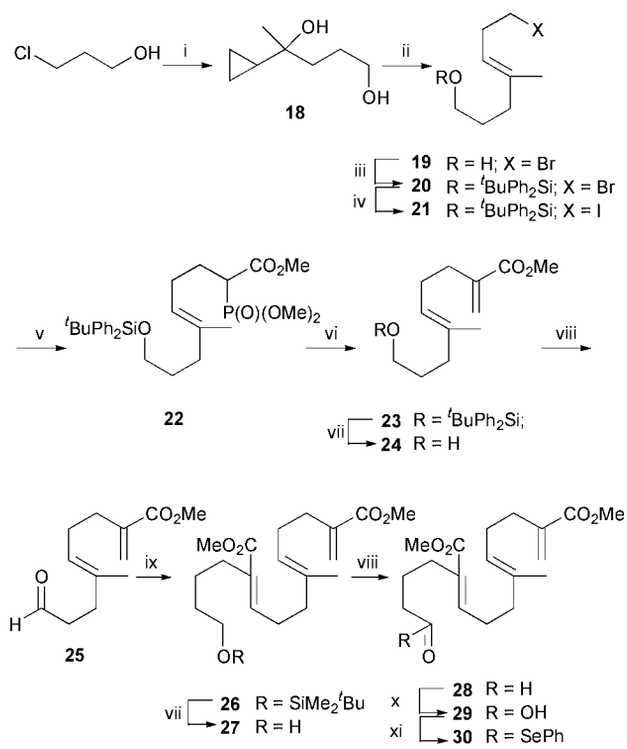
two products **17a** and **17b** (total mass recovery 73%) were isolated after chromatography (Scheme 3). Analysis of the ^{1}H NMR data for **17a** and **17b** indicated that they had the hoped for bicyclic structure resulting from two successive 6-*endo*-*trig* cyclisations of the acyl radical intermediate. A detailed analysis of the complete NMR data for **17a** and **17b** together with molecular modeling studies, encompassing global minimum and coupling constant calculations, demonstrated that they had the relative ring junction stereochemistries as shown in Scheme 3 (the relative stereochemistry of the methyl groups in both **17a** and **17b** could not be accurately determined). Thus, in comparison to our previously reported studies[2] that involved precursors analogous to **16a** and produced solely *trans*-decalones, the inclusion of the C-5 methoxycarbonyl substituent in **16a** can be seen to result in appreciable formation of the *cis*-stereoisomer **17b** together with the *trans*-decalone **17a**. Comparable results were also seen in the cyclisation of the (*E*)-selenoate **16b** which also produced **17a** (42%) and **17b**



Scheme 3

(20%), thereby confirming a previous observation[4] that the relative stereochemistry of the product polycycle is unaffected by the double bond geometry of the cyclisation precursor.

In light of the results obtained with **16a** and **16b**, we next turned our attention to investigating cascade 6-*endo*-*trig* tricycle formation where we could examine the effect of a methoxycarbonyl substituent on more than one ring junction stereochemistry and the stereochemistry between rings. In order to achieve this objective we prepared the triene selenoate **30** from commercially available 3-chloropropan-1-ol as outlined in Scheme 4. Thus, formation of the Normant[9] Grignard reagent



Scheme 4 *Reagents and conditions*: i, MeMgCl, THF, −78 °C; Mg; cyclopropyl methyl ketone, THF, −30 °C (71%); ii, 48% HBr, Et_2O, −30 °C (72%); iii, $^tBuPh_2SiCl$, NEt_3, DMAP, CH_2Cl_2, 0 °C (99%); iv, NaI, acetone (96%); v, $(MeO)_2(O)PCH_2CO_2Me$, NaH, DMSO; **21**, (81%); vi, NaH, THF; $(CH_2O)_n$ (89%); vii, TBAF, THF, 0 °C (96–99%); viii, Dess–Martin periodinane, CH_2Cl_2, 0 °C (87–91%); ix, $^tBuMe_2SiO(CH_2)_4CH(CO_2Me)P(O)(OMe)_2$ **31**, NaH, THF, 0 °C; **25** (54%, (*Z*,*E*)-isomer); x, KH_2PO_4, ^tBuOH, H_2O, $NaClO_2$, 2-methylbut-2-ene (99%); xi, *N*-(phenylseleno)phthalimide, PBu_3, CH_2Cl_2, −30 °C (79%).

from 3-chloropropan-1-ol was followed by reaction with cyclopropyl methyl ketone to give the diol **18**, which upon treatment with HBr, according to the procedure of Julia,[10] next generated

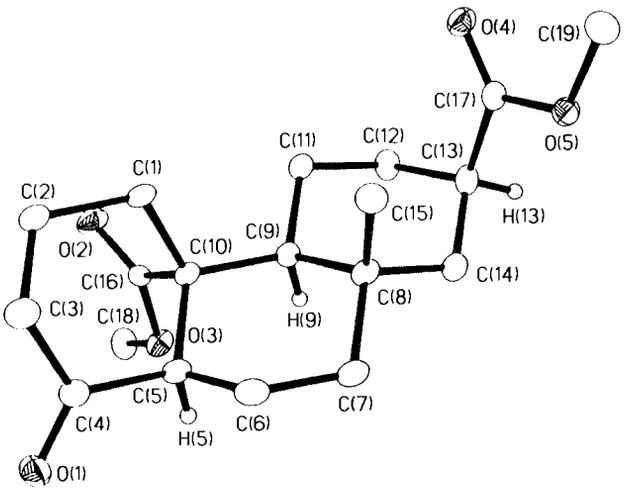
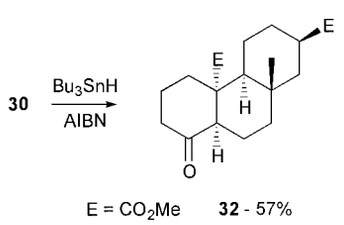


Fig. 1 X-Ray crystal structure of compound **32**.

the homoallylic bromide **19** in 51% overall yield. Protection of **19** as its silyl ether **20** and Finkelstein halide exchange then gave the corresponding iodide **21** which was used to alkylate the anion generated from trimethyl phosphonoacetate leading to the phosphonate **22**. A H–W–E coupling of the phosphonate **22** with paraformaldehyde next led to the methacrylate **23** in 89% yield. Removal of the silyl ether protection in **23**, followed by oxidation of the resulting alcohol **24** with Dess–Martin periodinane then produced the corresponding aldehyde **25**. The remainder of the acyclic carbon skeleton was installed by a further H–W–E coupling of **25** with the phosphonate **31** (produced by an analogous manner to **10**), to give the triene **26** as a mixture of geometric isomers about the newly formed alkene double bond, and from which the (*Z*,*E*)-isomer could be isolated in 54% yield. Finally, deprotection of the silyl group generated the alcohol **27** which was transformed into the corresponding selenoate (*viz.* **27**→**28**→**29**→**30**) as described previously.

Cyclisation of the triene selenoate **30** using our standard radical initiating conditions (4 mM solution of **30** in refluxing benzene, dropwise addition over 4 hours of Bu_3SnH and AIBN) led, after work-up and chromatography, to the isolation of a single identifiable product **32**, as a crystalline solid in 57% yield (Scheme 5). Whilst analysis of the NMR spectroscopic



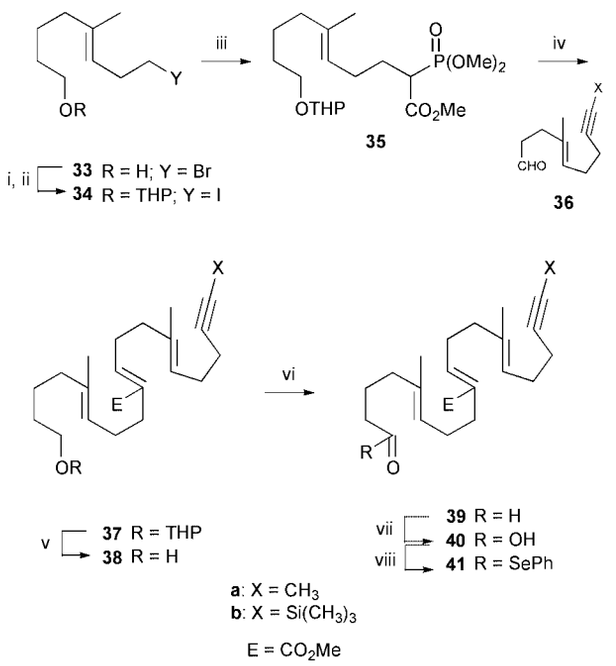
Scheme 5

data for **32** indicated that it had the expected tricyclic structure resulting from three consecutive 6-*endo*-*trig* cyclisations of the acyl radical, these data were not sufficient to determine the relative stereochemistry at the ring junctions. This was unequivocally determined by an X-ray diffraction analysis that showed **32** to have the *cis*,*syn*,*trans*-relative stereochemistry shown above (Fig. 1).

Thus, as with the dienes **16a** and **16b** the inclusion of a vinyl methoxycarbonyl group on the proximal olefin in the acyl radical precursor **30** produced a polycycle having the "unexpected" *cis*-stereochemistry about the newly formed AB ring junction. Additionally with this tricyclic system we now observed that the methoxycarbonyl substituent *also* affects the relative stereochemistry about the C5–C10 (steroid numbering) bond

promoting a *syn*-relationship in comparison to the *anti*-orientation seen in the majority of our previous studies.[2]

To complete our studies in this area we also examined the effect of a methoxycarbonyl substituent in the formation of a complete steroidal tetracyclic system. In order to achieve this objective we prepared the three polyene selenoates **41a**, **41b** and **41c**, each containing a methoxycarbonyl group on the internal olefin at C-9 and differing only in the substitution of the terminal acetylene. These syntheses are shown in Schemes 6 and 7.

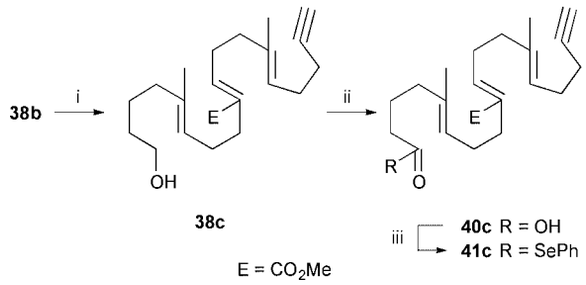


Scheme 6 *Reagents and conditions*: i, NaI, acetone (98%); ii, DHP, PPTS, CH_2Cl_2 (94%); iii, $(MeO)_2(O)PCH_2CO_2Me$, NaH, DMSO; **34** (84%); iv, KHMDS, 18-crown-6, −78 °C; **36a** or **36b**, −78 °C to 0 °C (84%); v, PPTS, EtOH, 55 °C (80%); vi, Dess–Martin periodinane, CH_2Cl_2, 0 °C (74–84%); vii, KH_2PO_4, ^tBuOH, H_2O, $NaClO_2$, 2-methylbut-2-ene (95%); viii, *N*-(phenylseleno)phthalimide, PBu_3, CH_2Cl_2, −30 °C (79–80%).

Thus conversion of the known bromo alcohol **33**[11] into the corresponding iodide under Finkelstein conditions was followed by protection of the hydroxy group as its tetrahydropyranyl (THP) ether **34**. Nucleophilic displacement of the resulting homoallylic iodide by the anion generated from trimethyl phosphonoacetate next gave the substituted phosphonate **35** in 77% overall yield (from **33**). Two separate H–W–E olefination reactions between the phosphonate **35** and each of the known aldehydes, (*E*)-4-methyldec-4-en-8-ynal **36a**[12] and (*E*)-4-methyl-9-trimethylsilylnon-4-en-8-ynal **36b**,[13] then generated the polyolefins **37a** and **37b** respectively in excellent yields. Whilst the reaction conditions employed in the H–W–E coupling were expected to produce selectively the (*Z*)-olefin,[14] the chemical shifts observed in the ^1H NMR spectra for both **37a** and **37b** indicated that the newly formed C9–C10 double bonds were in fact of (*E*)-stereochemistry. Deprotection of the acetal groups in **37** next gave the corresponding alcohols **38a** and **38b**, which were then converted into the selenoates **41a** and **41b** as previously described (*viz.* **38a**,**b**→**39a**,**b**→**40a**,**b**→**41a**,**b**).

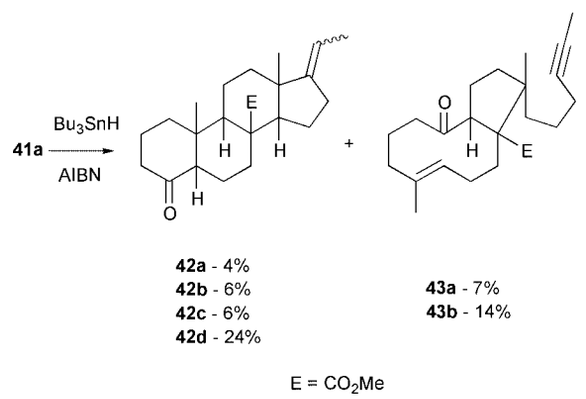
The third polyene selenoate, **41c**, was prepared from intermediate **38b** as shown in Scheme 7. Treatment of **38b** with tetrabutylammonium fluoride generated the corresponding desilylated alcohol **38c** in 86% yield. Subsequent oxidation with pyridinium dichromate next produced the carboxylic acid **40c**, which was then converted into the selenoester **41c** as before.

Cyclisation of **41a** under our standard radical initiating conditions (5 mM solution of **41a** in refluxing toluene, dropwise addition over 8 hours of Bu_3SnH and AIBN) led to a complex



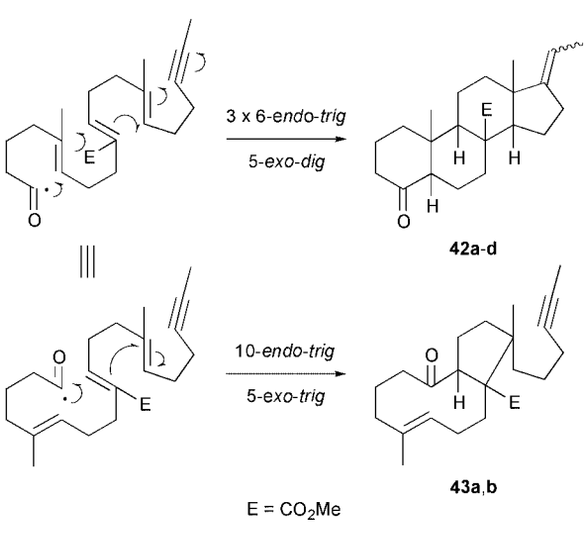
Scheme 7 *Reagents and conditions*: i, TBAF, THF, 0 °C (86%); ii, PDC, DMF (79%); iii, *N*-(phenylseleno)phthalimide, PBu_3, CH_2Cl_2, −30 °C (70%).

mixture of products from which six identifiable compounds (total mass recovery 61%) could be isolated after extensive chromatography (Scheme 8).



Scheme 8

NMR spectroscopic analysis of four of these components indicated that they had the tetracyclic steroidal structure, *i.e.* **42a**–**d**, resulting from three successive 6-*endo*-*trig* cyclisations of the corresponding acyl radical intermediate produced from **41a**, followed by a final 5-*exo*-*dig* cyclisation onto the acetylene functional group (Scheme 9). Detailed analysis of the spectro-



Scheme 9

scopic data for **42a**–**d** further indicated that they were in fact diastereoisomeric with respect to their ring junction stereochemistries; however their relative stereochemistries could not be accurately determined solely from these data. In addition all of the four tetracycles **42a**–**d** were isolated as mixtures of geometrical isomers about the exocyclic double bond, with isomeric ratios ranging from 1 : 1 to 2 : 1.

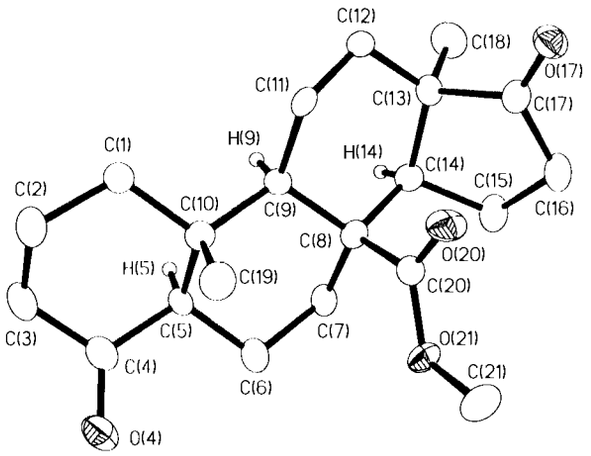
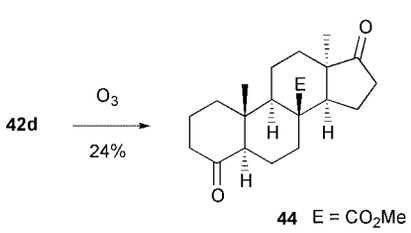


Fig. 2 X-Ray crystal structure of compound **44**.

The two remaining products isolated from the cyclisation of **41a** had spectroscopic data which were consistent with the 10,5-ring fused bicyclic structure **43a**,**b** (Scheme 8); once again NMR analysis indicated that **43a**,**b** were diastereoisomers and although their relative stereochemistries could not be firmly established, analysis of the signals in their ^{13}C NMR spectra suggested that they possessed the same relative stereochemistry about their ring junction and that they were epimeric at their methyl bearing quaternary carbon centre. The bicycles **43a**,**b** are produced from **41a** *via* a competing pathway involving first a 10-*endo*-*trig* macrocyclisation of the corresponding acyl radical intermediate onto the C9–C10 olefin, followed by a 5-*exo*-*trig* cyclisation of the resulting radical intermediate onto the proximal C13–C14 double bond (Scheme 9). The appreciable extent to which these bicycles are produced is most likely a consequence of the increased electrophilicity of the C9–C10 olefin (over that at C5–C6) in **41a** which would be expected to facilitate reaction with the nucleophilic acyl radical.[15]†

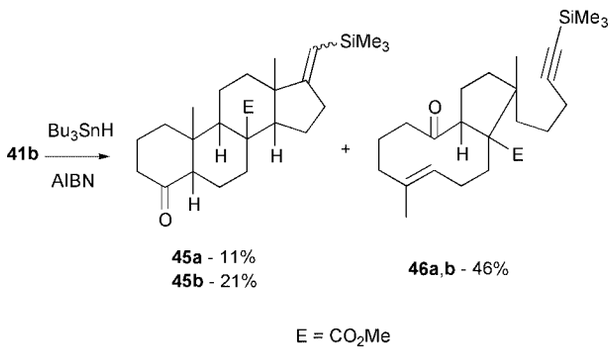
The relative stereochemistry at the ring junction in the major tetracyclic product resulting from cyclisation of **41a** came from X-ray diffraction analysis of the corresponding dione **44** (mp 56–58 °C, ethyl acetate–pentane) produced by ozonolysis (Scheme 10). The X-ray crystallographic results showed that **44**



Scheme 10

had the "unpredicted" *trans-anti-trans-anti-cis* relative stereochemistry between the ring junctions (Fig. 2). The interesting *cis*-stereochemistry at the CD ring junction in **44** has been observed in some of our earlier studies in this area.[16] A similar degradation approach to establish the stereochemistry of the minor isomers of **42** isolated from the cyclisation of **41a** was unfortunately unsuccessful.

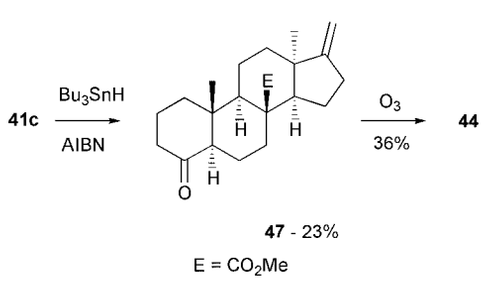
Cyclisation of the acetylene trimethylsilyl substituted selenoate **41b** under radical initiating conditions similar to those used for **41a** resulted in the isolation of two separate steroidal tetracyclic products *i.e.* **45**. Although one of the tetracycles was isolated as a single isomer, the second **45b** was a 1 : 1 mixture of isomers about the exocyclic olefin. A mixture of two isomeric bicyclic systems, *i.e.* **46**, was produced concurrently (Scheme 11).



Scheme 11

The major tetracyclic product **45b** isolated from the cascade cyclisation of **41b** was assigned the same *trans-anti-trans-anti-cis* relative stereochemistry as the tetracycle **42d**, based upon a detailed comparison of their respective ^{13}C NMR spectra. Additionally, the two bicycles **46a**,**b**, which now formed the majority of the material isolated from the cyclisation, could also be shown by ^{13}C NMR analysis to correlate with the two bicyclic products **43a**,**b** that had been isolated previously; again their relative stereochemistries could not be established with certainty but spectroscopic data suggested that the two products were epimeric at the methyl bearing quaternary carbon (*cf.* **43a**,**b**).

In the final reaction with polyene systems of this type we investigated, the selenoate **41c** was subjected to our standard radical initiating conditions, and produced the tetracycle **47** as the major product. Upon subsequent ozonolysis **47** gave the same dione **44** that was produced before with the same *trans-anti-trans-anti-cis* relative stereochemistry (Scheme 12).

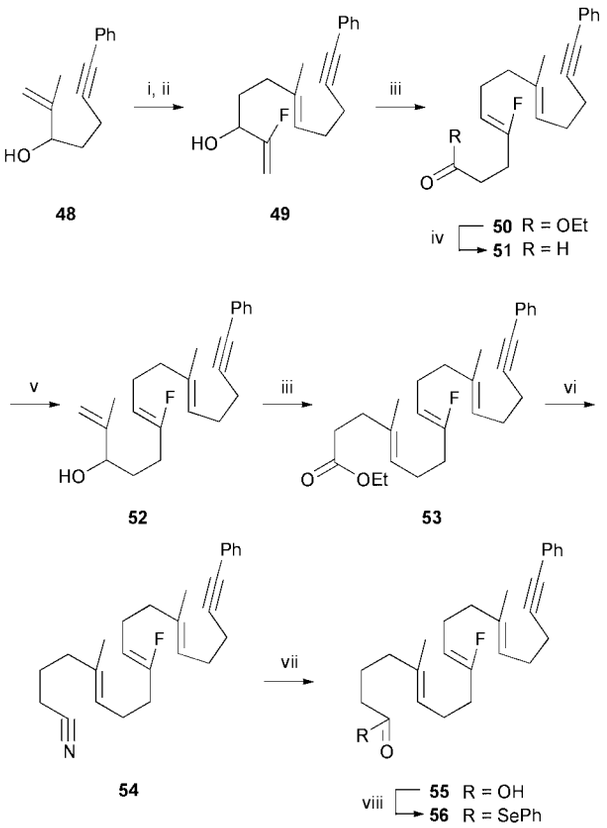


Scheme 12

Without doubt the somewhat unexpected stereochemistry seen in the aforementioned cyclisations is due wholly or in-part to the presence of the vinyl methoxycarbonyl substituents present in these systems. Whilst these preliminary findings are not sufficient to allow us to propose a working model to predict the stereochemical outcomes of these radical cascade reactions, we can be sure that they are due to the differing steric and electronic demands of the olefinic C-9 and C-5 methoxycarbonyl substituents present in the cyclisation precursors when compared to the methyl group substituents employed in previous studies.[1,2]

In a series of complementary radical cascade studies we sought to investigate the effect of olefin substituents other than the methoxycarbonyl group upon the cascade process. Initially, we chose the fluorine substituent due to its similar size but differing electronic properties to the hydrogen atom. The fluorinated polyolefin selenoate chosen for our studies, *i.e.* **56**,

† A referee pointed out that our spectroscopic data for **43** and **46** could also be consistent with the formation of a 6,5-ring fused bicycle, resulting from a tandem 6-*endo*,5-*exo*-*trig* cyclisation of **41**, *cf.* **57**. Although this goes against out instincts, and the electronics of the systems, indeed we cannot rule out this possibility in this instance. The assignments of **43** and **46** as 10,5-ring fused bicycles rather than 6,5-ring fused bicycles should therefore be regarded as tentative. We would like to thank the referees for their useful comments.

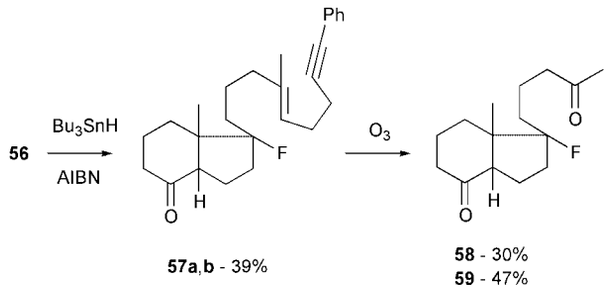


Scheme 13 *Reagents and conditions*: i, PPTS, 3-fluorobut-3-en-2-one, dipropyl ketal, 120 °C; ii, DIBAL-H, Et_2O, −78 °C (62%); iii, $CH(OEt)_3$, $CH_3CH_2CO_2H$, 140 °C (66–76%); iv, DIBAL-H, Et_2O, −78 °C (99%); v, 2-bromopropene, Mg, THF; **51**, 0 °C (99%); vi, $LiAlH_4$, THF; NEt_3, MsCl, CH_2Cl_2, 0 °C; NaCN, DMSO, 60 °C (86%); vii, KOH, EtOH–H_2O, 100 °C (83%); viii, Ph_2Se_2, PBu_3, C_6H_6 (74%).

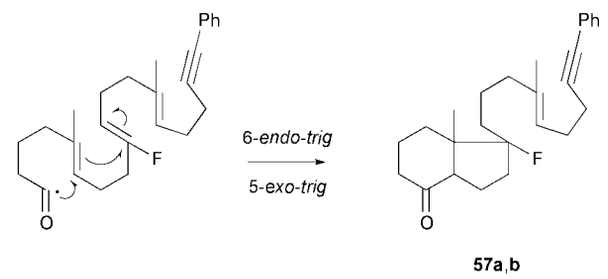
was produced from the allylic alcohol **48** as shown in Scheme 13.[17] Thus, treatment of **48** with 2-fluoro-3,3-dipropoxybut-1-ene and catalytic PPTS resulted in Claisen rearrangement to give a γδ-unsaturated ketone which was immediately reduced to the corresponding alcohol **49**. Further reaction of **49** under Claisen orthoester rearrangement conditions using triethyl orthoacetate and propionic acid next generated the ester **50** which upon treatment with DIBAL-H was reduced to the corresponding aldehyde **51**. Treatment of **51** with the Grignard reagent formed from 2-bromopropene produced the allylic alcohol **52** which was also subjected to a further Claisen orthoester rearrangement to give the ester **53**. A three step sequence, involving reduction of **53** to the corresponding alcohol, mesylation, and subsequent cyanide displacement next produced the nitrile **54** in 86% yield. Finally, hydrolysis of **54** to the carboxylic acid **55** followed by reaction with tributylphosphine and diphenyl diselenide gave the selenoate **56**.

When the selenoate **56** was subjected to our standard radical initiating conditions (8 mM solution of **56** in refluxing benzene, dropwise addition over 2 hours of Bu_3SnH and AIBN) an inseparable complex mixture of cyclised products was isolated in a combined 39% yield after work-up and chromatography (Scheme 14). Analysis of the NMR spectroscopic data for this mixture indicated that it consisted of the two major bicyclic products **57a**,**b** which was confirmed by isolation of the two isomeric indanones **58** and **59** after ozonolysis. Attempts to identify the relative stereochemistries of **58** and **59** from their NMR spectra however, proved inconclusive.

The bicyclic product **57** is produced from **56** by a 6-*endo-trig* cyclisation of the corresponding acyl radical intermediate followed by a further 5-*exo-trig* cyclisation as shown (Scheme 15). Thus our attempt to employ the fluorine substituent in order to "block" cyclisation at the C9 position in the polyene **56** proved



Scheme 14



Scheme 15

unsuccessful, thereby suggesting that it is most likely the size of the methyl groups on the alkenes used in our initial studies[1] that is the dominant factor in determining the outcome of these cascades of 6-*endo-trig* cyclisations leading to steroid ring systems.

Experimental

For general experimental details see reference 2.

Dess–Martin periodinane oxidations

General procedure. Dess–Martin periodinane (3.75 g, 8.73 mmol) was added portionwise over 10 min to a stirred solution of the alcohol (7.54 mmol) in dichloromethane (30 cm^3) at 0 °C. The reaction was stirred for 4 h, then diluted with diethyl ether (75 cm^3) and stirred with a solution of sodium bicarbonate (3.0 g) and sodium thiosulfate (7.5 g) in water (100 cm^3) for 30 min until two clear layers had formed. The organic layer was separated and the aqueous layer extracted with further diethyl ether (2 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using the eluent indicated in the experimental gave the aldehyde (74–91%).

Sodium chlorite oxidations

General procedure. A solution of sodium chlorite (8.8 g, 97.0 mmol, 80% tech) in water (35 cm^3) was added dropwise over 10 min to a vigorously stirred solution of the aldehyde (9.7 mmol), potassium dihydrogen phosphate (11.1 g, 77.0 mmol) and 2-methylbut-2-ene (45 cm^3) in *tert*-butyl alcohol (180 cm^3) and water (20 cm^3) at room temperature. The reaction was stirred at room temperature until TLC analysis indicated no remaining aldehyde, and the solvent evaporated *in vacuo*. The residue was partitioned between ethyl acetate (100 cm^3) and brine (75 cm^3), and then the aqueous layer was extracted with ethyl acetate (3 × 75 cm^3). The combined organic extracts were washed with brine (50 cm^3), dried ($MgSO_4$) and the solvent evaporated *in vacuo* to leave the acid (75–99%).

Preparation of *Se*-phenyl selenoates

General procedure. Tributylphosphine (134 μl, 108 mg, 0.536 mmol) was added dropwise over 5 min to a stirred solution of the acid (0.357 mmol) in dichloromethane (2 cm^3) at −30 °C. After 2 min *N*-(phenylseleno)phthalimide (162 mg, 0.536

mmol) was added in a single portion and the reaction then stirred at −30 °C for 20 min. The mixture was diluted with water (10 cm^3) and extracted with dichloromethane (3 × 20 cm^3). The combined organic extracts were washed with brine (20 cm^3), dried ($MgSO_4$) and then evaporated *in vacuo*. Chromatography of the residue on silica gel using the eluent indicated in the experimental gave the selenoester (39–80%).

Methyl 2-(diethoxyphosphinyl)-6-{[dimethyl(1,1-dimethylethyl)-silyl]oxy}hexanoate 10

Methyl diethylphosphonoacetate (17.6 cm^3, 20.15 g, 94.4 mmol) was added dropwise over 30 min to a suspension of sodium hydride (3.8 g, 95.0 mmol, 60% oil dispersion) in DMSO (120 cm^3) at 0 °C. The mixture was stirred at 0 °C for 60 min and then a solution of 1-{[dimethyl(1,1-dimethylethyl)-silyl]oxy}-4-iodobutane[6] (10.0 g, 31.4 mmol) in DMSO (20 cm^3) was added. The mixture was allowed to warm to room temperature over 14 h, before being quenched with water (100 cm^3) and extracted with diethyl ether (3 × 100 cm^3). The combined organic extracts were dried ($MgSO_4$) and then evaporated *in vacuo*. Chromatography of the residue on silica gel using diethyl ether–light petroleum (bp 40–60 °C) (8:2) as eluent gave the *phosphonate* (8.08 g, 65%) as a pale yellow oil (Found: C, 51.3; H, 9.4. $C_{17}H_{37}O_6PSi$ requires C, 51.4; H, 9.4%); ν_{max}(film)/cm^{-1} 1739 and 1098; δ_H(360 MHz; $CDCl_3$) 4.12 (4H, q, *J* 7.1, 2 × O$CH_2$$CH_3$), 3.75 (3H, s, OCH_3), 3.57 (2H, t, *J* 6.4, CH_2O), 2.95 (1H, ddd, *J* 3.7 and 11.1, J_{HP} 22.5, CHP), 2.03–1.93 (1H, m, C*H*HCHP), 1.92–1.80 (1H, m, CH*H*CHP), 1.55–1.31 (4H, m), 1.31 (6H, t, *J* 7.1, 2 × OCH_2CH_3), 0.86 (9H, s, $C(CH_3)_3$) and 0.02 (6H, s, $Si(CH_3)_2$); δ_C(90.6 MHz; $CDCl_3$) 169.7 (s, J_{CP} 4.7), 62.8 (t, J_{CP} 6.6), 62.7 (t), 62.7 (t, J_{CP} 7.0), 52.3 (q), 45.7 (d, J_{CP} 131.6), 32.2 (2 × t), 25.8 (t, J_{CP} 4.8), 25.8 (3 × q), 18.2 (s), 16.3 (q), 16.2 (q) and −5.4 (2 × q).

(*Z*)- and (*E*)-5-Methoxycarbonyl-1-{[dimethyl(1,1-dimethyl-ethyl)silyl]oxy}-9-methyldeca-5,9-diene 12a and 12b

A solution of the phosphonate **10** (5.0 g, 12.6 mmol) in THF (30 cm^3) was added dropwise over 15 min to a stirred slurry of sodium hydride (1.0 g, 25.2 mmol, 60% oil dispersion) in THF (70 cm^3) at 0 °C. The mixture was stirred at 0 °C for 1 h and then a solution of 4-methylpent-4-enal **11**[7] (12.4 g, 63.0 mmol) in THF (30 cm^3) was added. The reaction was allowed to warm to room temperature over 4 h, quenched with water (100 cm^3) and extracted with diethyl ether (3 × 100 cm^3). The combined organic extracts were dried ($MgSO_4$) and then evaporated *in vacuo*. Chromatography of the residue on silica gel using diethyl ether–light petroleum (bp 40–60 °C) (3:7) as eluent gave both isomers of the *diene*.

The (*Z*)-isomer **12a** eluted first (0.98 g, 23%) as a yellow oil; λ_{max}(EtOH)/nm 219 (ε/dm^3 mol^{-1} cm^{-1} 6937); ν_{max}(film)/cm^{-1} 3073, 2929, 1718, 1649, 1103 and 888; δ_H(360 MHz; $CDCl_3$) 5.80 (1H, t, *J* 7.3, C*H*=$C(CO_2CH_3)$), 4.73 (1H, s, C*H*H=C), 4.69 (1H, s, CH*H*=C), 3.74 (3H, s, OCH_3), 3.60 (2H, t, *J* 7.4, CH_2O), 2.55 (2H, dt, *J* 7.3 and 7.5, CH_2CH=$C(CO_2CH_3)$), 2.25 (2H, t, *J* 7.1, $CH_2C(CO_2CH_3)$), 2.15 (2H, t, *J* 7.5, CH_2C=CH_2), 1.73 (3H, s, CH_2=$C(CH_3)$), 1.57–1.41 (4H, m), 0.89 (9H, s, $C(CH_3)_3$) and 0.05 (6H, s, $Si(CH_3)_2$); δ_C(90.6 MHz; $CDCl_3$) 168.5 (s), 144.9 (s), 141.3 (d), 131.9 (s), 110.3 (t), 62.9 (t), 51.1 (q), 37.3 (t), 34.2 (t), 32.2 (t), 27.5 (t), 25.9 (3 × q), 25.3 (t), 22.3 (q), 18.3 (s) and −5.4 (2 × q); *m*/*z* (EI) 283.1722 (M^+ − $C(CH_3)_3$, $C_{15}H_{27}OSi$ requires 283.1729).

The (*E*)-isomer **12b** eluted second (1.97 g, 46%) as a yellow oil; λ_{max}(EtOH)/nm 217 (ε/dm^3 mol^{-1} cm^{-1} 10 590); ν_{max}(film)/cm^{-1} 3074, 2950, 1716, 1649, 1192 and 889; δ_H(360 MHz; $CDCl_3$) 6.74 (1H, t, *J* 7.3, C*H*=$C(CO_2CH_3)$), 4.76 (1H, s, C*H*H=C), 4.71 (1H, s, CH*H*=C), 3.73 (3H, s, OCH_3), 3.61 (2H, t, *J* 7.4, CH_2O), 2.34 (4H, m, CH_2CH=$C(CO_2CH_3)$ and $CH_2C(CO_2CH_3)$), 2.13 (2H, t, *J* 7.5, CH_2C=CH_2), 1.74 (3H, s, CH_2=$C(CH_3)$), 1.58–1.41 (4H, m), 0.89 (9H, s, $C(CH_3)_3$) and 0.04 (6H, s, $Si(CH_3)_2$); δ_C(90.6 MHz; $CDCl_3$) 168.5 (s), 144.7 (s), 142.3 (d), 132.5 (s), 110.7 (t), 63.1 (t), 51.7 (q), 36.8 (t), 32.8 (t), 26.8 (2 × t), 26.0 (3 × q), 25.7 (t), 22.7 (q), 18.4 (s) and −5.2 (2 × q); *m*/*z* (EI) 283.1734 (M^+ − $C(CH_3)_3$, $C_{15}H_{27}O_3Si$ requires 283.1729).

(*Z*)-5-Methoxycarbonyl-9-methyldeca-5,9-dien-1-ol 13a

Tetrabutylammonium fluoride (21.8 cm^3, 21.8 mmol, 1 M in THF) was added dropwise over 2 min to a stirred solution of the silyl ether **12a** (2.47 g, 7.25 mmol) in THF (72 cm^3) at 0 °C. The mixture was stirred at 0 °C for 1 h and then allowed to reach room temperature over a further 22 h. The reaction was quenched with water (100 cm^3) and extracted with diethyl ether (3 × 70 cm^3). The combined organic extracts were dried ($MgSO_4$) and then evaporated *in vacuo*. Chromatography of the residue on silica gel using diethyl ether–light petroleum (bp 40–60 °C) (8:2) as eluent gave the *alcohol* (1.14 g, 70%) as a yellow oil (Found: C, 69.2; H, 10.0. $C_{13}H_{22}O_3$ requires C, 69.0; H, 9.8%); λ_{max}(EtOH)/nm 219 (ε/dm^3 mol^{-1} cm^{-1} 3767); ν_{max}(film)/cm^{-1} 3372, 1715, 1648, 1031 and 888; δ_H(360 MHz; $CDCl_3$) 5.87 (1H, t, *J* 7.3, C*H*=$C(CO_2CH_3)$), 4.71 (1H, s, C*H*H=C), 4.67 (1H, s, CH*H*=C), 3.73 (3H, s, OCH_3), 3.62 (2H, t, *J* 6.3, CH_2O), 2.55 (2H, dt, *J* 7.3 and 7.4, CH_2CH=$C(CO_2CH_3)$), 2.25 (2H, t, *J* 7.2, $CH_2C(CO_2CH_3)$), 2.10 (2H, t, *J* 7.4, CH_2C=CH_2), 1.73 (3H, s, CH_2=$C(CH_3)$) and 1.57–1.43 (4H, m); δ_C(90.6 MHz; $CDCl_3$) 168.6 (s), 144.9 (s), 141.9 (d), 131.8 (s), 110.5 (t), 62.7 (t), 51.3 (q), 37.4 (t), 34.2 (t), 32.4 (t), 27.7 (t), 25.3 (t) and 22.4 (q); *m*/*z* (EI) 226.1564 (M^+, $C_{13}H_{22}O_3$ requires 226.1571).

(*Z*)-5-Methoxycarbonyl-9-methyldeca-5,9-dienal 14a

A solution of the alcohol **13a** (1.14 g, 5.0 mmol) in dichloromethane (20 cm^3) was added dropwise over 10 min to a stirred suspension of PCC (2.69 g, 12.5 mmol) and silica (7 g) in dichloromethane (100 cm^3) at room temperature. The mixture was stirred for 22 h before being diluted with diethyl ether (50 cm^3), filtered through silica gel and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using diethyl ether–light petroleum (bp 40–60 °C) (4:6) as eluent gave the *aldehyde* (920 mg, 82%) as a yellow oil (Found: C, 69.0; H, 9.0. $C_{13}H_{20}O_3$ requires C, 69.5; H, 9.0%); λ_{max}(EtOH)/nm 219 (ε/dm^3 mol^{-1} cm^{-1} 2023); ν_{max}(film)/cm^{-1} 3073, 1718, 1647, 994 and 888; δ_H(360 MHz; $CDCl_3$) 9.75 (1H, t, *J* 1.5, CHO), 5.89 (1H, t, *J* 7.2, C*H*=$C(CO_2CH_3)$), 4.73 (1H, s, C*H*H=C), 4.68 (1H, s, CH*H*=C), 3.74 (3H, s, OCH_3), 2.59 (2H, dt, *J* 7.2 and 7.4, CH_2CH=$C(CO_2CH_3)$), 2.42 (2H, dt, *J* 1.5 and 7.3, CH_2CHO), 2.28 (2H, t, *J* 7.7, $CH_2C(CO_2CH_3)$), 2.12 (2H, t, *J* 7.4, CH_2C=CH_2), 1.76–1.72 (2H, m) and 1.74 (3H, s, CH_2=$C(CH_3)$); δ_C(90.6 MHz; $CDCl_3$) 202.4 (d), 168.2 (s), 144.9 (s), 143.1 (d), 130.9 (s), 110.6 (t), 51.4 (q), 43.4 (t), 37.3 (t), 33.9 (t), 27.7 (t), 22.3 (t) and 21.6 (q).

(*Z*)-5-Methoxycarbonyl-9-methyldeca-5,9-dienoic acid 15a

Oxidation of the aldehyde **14a** using sodium chlorite according to the general procedure gave the *acid* (76%) as a yellow oil (Found: C, 64.6; H, 8.3. $C_{13}H_{20}O_4$ requires C, 65.0; H, 8.4%); λ_{max}(EtOH)/nm 218 (ε/dm^3 mol^{-1} cm^{-1} 3572); ν_{max}(film)/cm^{-1} 3700–2700, 1711, 1649, 994 and 889; δ_H(360 MHz; $CDCl_3$) 5.91 (1H, t, *J* 7.2, C*H*=$C(CO_2CH_3)$), 4.73 (1H, s, C*H*H=C), 4.69 (1H, s, CH*H*=C), 3.74 (3H, s, OCH_3), 2.60 (2H, dt, *J* 7.2 and 7.4, CH_2CH=$C(CO_2CH_3)$), 2.39–2.28 (4H, m, CH_2CO_2H and $CH_2C(CO_2CH_3)$), 2.12 (2H, t, *J* 7.4, CH_2C=CH_2), 1.80–1.72 (2H, m) and 1.72 (3H, s, CH_2=$C(CH_3)$); δ_C(90.6 MHz; $CDCl_3$) 179.6 (s), 168.2 (s), 144.9 (s), 143.9 (d), 130.8 (s), 110.6 (t), 51.4 (q), 37.3 (t), 33.8 (t), 33.2 (t), 27.7 (t), 24.1 (t) and 22.6 (q); *m*/*z* (EI) 240.1363 (M^+, $C_{13}H_{20}O_4$ requires 240.1361).

Se-Phenyl (*Z*)-5-methoxycarbonyl-9-methyldeca-5,9-diene-selenoate 16a

Phenylselenylation of the acid **15a** according to the general

procedure and using diethyl ether–light petroleum (bp 40–60 °C) (0:100–1:9) as eluent gave the *selenoester* (39%) as a yellow oil; λ_{max}(EtOH)/nm 219 (ε/dm^3 mol^{-1} cm^{-1} 2066); ν_{max}(film)/cm^{-1} 3416, 1717, 1647, 910 and 880; δ_H(360 MHz; $CDCl_3$) 7.52–7.50 (2H, m, 2 × aryl-H), 7.39–7.36 (3H, m, 3 × aryl-H), 5.92 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 4.75 (1H, s, C*H*H=C), 4.71 (1H, s, CH*H*=C), 3.75 (3H, s, OCH_3), 2.70 (2H, t, *J* 7.4, CH_2COSePh), 2.62 (2H, dt, *J* 7.3 and 7.4, CH_2CH=C(CO_2CH_3)), 2.32 (2H, t, *J* 7.4, CH_2C(CO_2CH_3)), 2.14 (2H, t, *J* 7.4, CH_2C=CH_2), 1.83–1.77 (2H, app. quintet, *J* 7.4, CH_2-CH_2COSePh) and 1.74 (3H, s, CH_2=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 200.1 (s), 168.1 (s), 144.9 (s), 143.4 (d), 135.8 (2 × d), 130.6 (s), 129.4 (2 × d), 128.9 (d), 126.5 (s), 110.7 (t), 51.4 (q), 46.6 (t), 37.3 (t), 33.6 (t), 27.7 (t), 24.7 (t) and 22.4 (q), *m*/*z* (EI) 223.1331 ($M^+ - C_6H_5Se$, $C_{13}H_{19}O_3$ requires 223.1334).

trans- and *cis*-Methyl 6-methyl-1-oxodecahydronaphthalene-4a-carboxylate 17a and 17b

A solution of tributyltin hydride (60 µl, 65 mg, 0.23 mmol) and AIBN (3 mg) in benzene (2.5 cm^3) was added dropwise over 3 h to a refluxing solution of the phenyl selenoate **16a** (57 mg, 0.15 mmol) and AIBN (3 mg) in dry degassed benzene (30 cm^3). After the addition was complete the mixture was heated under reflux for a further 30 min, then cooled and the solvent removed *in vacuo*. Chromatography of the residue on silica gel using diethyl ether–light petroleum (bp 40–60 °C) (1:9) as eluent gave compounds **17a** and **17b**.

The *cis-decalone* **17b** (eluted first) (8 mg, 23%) as a yellow oil; ν_{max}(film)/cm^{-1} 1731; δ_H(360 MHz; $CDCl_3$) 3.73 (3H, s, OCH_3), 3.02 (1H, br s, C=OC*H*CH_2), 2.40–0.98 (13H, complex series of multiplets) and 0.85 (3H, d, *J* 6.3, CH(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 210.9 (s), 176.6 (s), 52.3 (q), 51.9 (s), 49.4 (d), 41.2 (t), 38.1 (t), 35.7 (t), 30.0 (d), 29.9 (t), 22.7 (q), 22.6 (t) and 21.9 (t).

The *trans-decalone* **17a** (eluted second) (17 mg, 50%) as a yellow oil (Found: C, 69.9; H, 8.5. $C_{13}H_{20}O_3$ requires C, 69.5; H, 8.9%); ν_{max}(film)/cm^{-1} 1727; δ_H(360 MHz; $CDCl_3$) 3.67 (3H, s, OCH_3), 2.66 (1H, dd, *J* 4.5 and 12.7, C=OC*H*CH_2), 2.47–1.00 (13H, complex series of multiplets) and 0.90 (3H, d, *J* 6.4, CH(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 212.9 (s), 177.1 (s), 52.9 (d), 52.2 (q), 49.8 (s), 42.2 (t), 36.4 (t), 33.7 (t), 27.4 (d), 27.0 (t), 26.9 (t), 22.4 (q) and 22.2 (t); *m*/*z* (EI) 224.1419 (M^+, $C_{13}H_{20}O_3$ requires 224.1412).

(*E*)-5-Methoxycarbonyl-9-methyldeca-5,9-dien-1-ol 13b

Deprotection of the silyl ether **12b** according to the same procedure used to deprotect **12a** gave the *alcohol* (80%) as a yellow oil (Found: C, 68.6; H, 9.8. $C_{13}H_{22}O_3$ requires C, 69.0; H, 9.8%); λ_{max}(EtOH)/nm 221 (ε/dm^3 mol^{-1} cm^{-1} 6799); ν_{max}(film)/cm^{-1} 3412, 3074, 1712, 1646, 1065 and 889; δ_H(360 MHz; $CDCl_3$) 6.74 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 4.75 (1H, s, C*H*H=C), 4.70 (1H, s, CH*H*=C), 3.72 (3H, s, OCH_3), 3.65 (2H, t, *J* 6.4, CH_2O), 2.33 (4H, m, CH_2CH=C(CO_2CH_3) and CH_2C(CO_2CH_3)), 2.13 (2H, t, *J* 7.5, CH_2C=CH_2), 1.70 (3H, s, CH_2=C(CH_3)), 1.64–1.55 (2H, m) and 1.50–1.39 (2H, m); δ_C(90.6 MHz; $CDCl_3$) 168.5 (s), 144.6 (s), 142.4 (d), 132.5 (s), 110.7 (t), 62.7 (t), 51.7 (q), 36.7 (t), 34.5 (t), 26.8 (t), 26.5 (t), 25.4 (t) and 22.5 (q); *m*/*z* (EI) 226.1569 (M^+, $C_{13}H_{22}O_3$ requires 226.1571).

(*E*)-5-Methoxycarbonyl-9-methyldeca-5,9-dienal 14b

Oxidation of the alcohol **13b** according to the procedure used to oxidise **13a** gave the *aldehyde* (71%) as a yellow oil (Found: C, 69.0; H, 9.0. $C_{13}H_{20}O_3$ requires C, 69.5; H, 9.0%); λ_{max}(EtOH)/nm 218 (ε/dm^3 mol^{-1} cm^{-1} 8283); ν_{max}(film)/cm^{-1} 3075, 1713, 1646 and 891; δ_H(360 MHz; $CDCl_3$) 9.76 (1H, t, *J* 1.3, CHO), 6.78 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 4.76 (1H, s, C*H*H=C), 4.70 (1H, s, CH*H*=C), 3.72 (3H, s, OCH_3), 2.44 (2H, dt, *J* 1.3 and 7.3, CH_2CHO), 2.31 (4H, m, CH_2CH=C(CO_2CH_3) and CH_2C(CO_2CH_3)), 2.13 (2H, t, *J* 7.3, CH_2C=CH_2), 1.81–1.69 (2H, m) and 1.73 (3H, s, CH_2=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 202.3 (d), 168.1 (s), 144.4 (s), 143.2 (d), 131.6 (s), 110.8 (t), 51.7 (q), 43.4 (t), 36.6 (t), 26.8 (t), 26.1 (t), 22.4 (q) and 21.6 (t).

(*E*)-5-Methoxycarbonyl-9-methyldeca-5,9-dienoic acid 15b

Oxidation of the aldehyde **14b** using sodium chlorite according to the general procedure gave the *acid* (85%) as a yellow oil (Found: C, 64.7; H, 8.5. $C_{13}H_{20}O_4$ requires C, 65.0; H, 8.4%); λ_{max}(EtOH)/nm 219 (ε/dm^3 mol^{-1} cm^{-1} 5320); ν_{max}(film)/cm^{-1} 3700–2700, 1710, 1646, 1095 and 890; δ_H(360 MHz; $CDCl_3$) 6.79 (1H, t, *J* 7.4, C*H*=C(CO_2CH_3)), 4.75 (1H, s, C*H*H=C), 4.70 (1H, s, CH*H*=C), 3.73 (3H, s, OCH_3), 2.39–2.30 (6H, m), 2.13 (2H, t, *J* 7.5, CH_2C=CH_2), 1.79–1.70 (2H, m) and 1.74 (3H, s, CH_2=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 179.4 (s), 168.2 (s), 144.6 (s), 131.6 (d), 131.6 (s), 110.8 (t), 51.8 (q), 36.7 (t), 33.5 (t), 26.9 (t), 26.0 (t), 24.1 (t) and 22.5 (q); *m*/*z* (EI) 240.1368 (M^+, $C_{13}H_{20}O_4$ requires 240.1361).

Se-Phenyl (*E*)-5-methoxycarbonyl-9-methyldeca-5,9-diene-selenoate 16b

Phenylselenylation of the acid **15b** according to the general procedure and using diethyl ether–light petroleum (bp 40–60 °C) (0:100–1:9) as eluent gave the *selenoester* (67%) as a yellow oil; λ_{max}(EtOH)/nm 219 (ε/dm^3 mol^{-1} cm^{-1} 4940); ν_{max}(film)/cm^{-1} 2947, 1717, 1646, 1081 and 890; δ_H(360 MHz; $CDCl_3$) 7.52–7.48 (2H, m, 2 × aryl-H), 7.40–7.36 (3H, m, 3 × aryl-H), 6.80 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 4.77 (1H, s, C*H*H=C), 4.72 (1H, s, CH*H*=C), 3.74 (3H, s, OCH_3), 2.73 (2H, t, *J* 7.3, CH_2COSePh), 2.41–2.30 (4H, m, CH_2CH=C(CO_2CH_3) and CH_2C(CO_2CH_3)), 2.14 (2H, t, *J* 7.5, CH_2C=CH_2), 1.83–1.77 (2H, m, CH_2CH_2-COSePh) and 1.74 (3H, s, CH_2=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 200.1 (s), 168.1 (s), 144.5 (s), 143.5 (d), 135.9 (2 × d), 131.2 (s), 129.4 (2 × d), 128.9 (d), 126.5 (s), 110.9 (t), 60.6 (q), 51.9 (t), 36.7 (t), 26.9 (t), 25.9 (t), 24.7 (t) and 22.5 (q); *m*/*z* (EI) 223.1323 ($M^+ - C_6H_5Se$, $C_{13}H_{19}O_3$ requires 223.1334).

trans- and *cis*-Methyl 6-methyl-1-oxodecahydronaphthalene-4a-carboxylate 17a and 17b

Reductive cyclisation of the selenoate **16b** according to the same procedure as used for **16a** gave: (i) the *cis-decalone* **17b** (20%)—analytical data exactly as before; and (ii) the *trans-decalone* **17a** (42%)—analytical data exactly as before.

4-Cyclopropylpentane-1,4-diol 18

Methylmagnesium chloride (13.9 cm^3, 41.7 mmol, 3 M in THF) was added dropwise over 15 min to a stirred solution of 3-chloropropan-1-ol (3.80 g, 40.2 mmol) in THF (40 cm^3) at −78 °C. The mixture was allowed to warm to room temperature over 2 h, before magnesium (1.07 g, 44.2 mmol) and 1,2-dibromoethane (100 µl) were added and the solution brought to reflux. The reaction was heated under reflux for 4 h, during which time further portions of 1,2-dibromoethane (50 µl) were added hourly, before being cooled to −30 °C. A solution of cyclopropyl methyl ketone (3.72 g, 44.2 mmol) in THF (5 cm^3) was added dropwise to the stirred mixture which was then allowed to warm to room temperature over 4 h, before being quenched with saturated aqueous ammonium chloride (30 cm^3) and then extracted with diethyl ether (3 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1:1 to 9:1) as eluent gave the diol (4.12 g, 71%) as a colourless oil; ν_{max}(film)/cm^{-1} 3394, 3084, 3005, 2946, 2873, 1644, 1455, 1373, 1056 and 1018; δ_H(360 MHz; $CDCl_3$) 3.62 (2H, t, *J* 6.0, CH_2O), 2.83 (2H, br s, 2 × OH), 1.72–1.65 (2H, m), 1.63–1.58 (2H, m), 1.09 (3H, s, CH_3), 0.91–0.84 (1H, m, cyclopropyl-CH) and 0.42–0.24 (4H, m, 2 × cyclopropyl-CH_2); δ_C(90.6 MHz; $CDCl_3$) 70.7 (s), 63.1 (t), 39.8 (t), 26.9 (t), 25.8 (d), 21.1 (q), 0.6 (t)

and 0.4 (t); *m/z* (EI) 126.1048 ($M^+ - H_2O$, $C_8H_{14}O$ requires 126.1045).

(*E*)-7-Bromo-4-methylhept-4-en-1-ol 19

A solution of the diol **18** (3.90 g, 27.0 mmol) in diethyl ether (2 cm^3) was added dropwise over 5 min to a stirred solution of 48% aqueous hydrobromic acid (8 cm^3) at −30 °C. The reaction was stirred at this temperature for 4 h, before being quenched by the addition of saturated aqueous sodium hydrogen carbonate (10 cm^3). The mixture was extracted with diethyl ether (3 × 30 cm^3), the combined organic extracts dried ($MgSO_4$) and then evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1 : 3 to 1 : 1) as eluent gave the *bromo alcohol* (4.05 g, 72%) as a colourless oil; ν_{max}(film)/cm^{-1} 3345, 2938, 2867, 1438, 1381, 1267, 1205 and 1051; δ_H(270 MHz; $CDCl_3$) 5.22 (1H, t, *J* 6.9, C*H*=C(CH_3)), 3.66 (2H, t, *J* 6.6, CH_2O), 3.40 (2H, t, *J* 6.9, CH_2Br), 2.62 (2H, app. q, *J* 6.9, C$H_2$$CH_2Br$), 2.48 (1H, br s, OH), 2.13 (2H, t, *J* 7.4, C$H_2$$CH_2CH_2O$), 1.78–1.72 (2H, m, C$H_2$$CH_2O$) and 1.69 (3H, s, CH_3); δ_C(67.5 MHz; $CDCl_3$) 138.0 (s), 121.1 (d), 62.2 (t), 35.7 (t), 32.9 (t), 31.4 (t), 30.4 (t) and 16.0 (q); *m/z* (EI) 126.1048 (M^+ − HBr, $C_8H_{14}O$ requires 126.1045).

(*E*)-7-Bromo-1-{[(1,1-dimethylethyl)diphenylsilyl]oxy}-4-methylhept-4-ene 20

4-Dimethylaminopyridine (221 mg, 1.81 mmol), triethylamine (3.03 cm^3, 2.20 g, 21.7 mmol) and *tert*-butylchlorodiphenylsilane (4.71 cm^3, 4.98 g, 18.1 mmol) were added sequentially to a stirred solution of the bromo alcohol **19** (3.75 g, 18.1 mmol) in dichloromethane (150 cm^3) at 0 °C. The mixture was allowed to warm to room temperature over 2 h and then stirred for a further 12 h before being diluted with brine (50 cm^3). The organic layer was separated and the aqueous layer extracted with dichloromethane (2 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated *in vacuo*. Chromatography of the residue on silica gel using diethyl ether–light petroleum (bp 40–60 °C) (1 : 19) as eluent gave the *silyl ether* (8.00 g, 99%) as a colourless oil; ν_{max}(film)/cm^{-1} 3069, 3048, 2930, 2857, 1589, 1472, 1427, 1388, 1361, 1267, 1205, 1188 and 1111; δ_H(360 MHz; $CDCl_3$) 7.69–7.67 (4H, m, 4 × aryl-H), 7.44–7.39 (6H, m, 6 × aryl-H), 5.12 (1H, t, *J* 7.2, C*H*=C(CH_3)), 3.66 (2H, t, *J* 6.4, CH_2O), 3.31 (2H, t, *J* 7.2, CH_2Br), 2.55 (2H, app. q, *J* 7.2, C$H_2$$CH_2Br$), 2.09 (2H, t, *J* 7.6, C$H_2$$CH_2CH_2O$), 1.73–1.67 (2H, m, C$H_2$$CH_2O$), 1.60 (3H, s, CH=C(C$H_3$)) and 1.06 (9H, s, C($CH_3$)$_3$); δ_C(90.6 MHz; $CDCl_3$) 138.2 (s), 135.5 (4 × d), 134.0 (2 × s), 129.5 (2 × d), 127.6 (4 × d), 120.9 (d), 63.3 (t), 35.7 (t), 32.7 (t), 31.7 (t), 30.6 (t), 26.9 (3 × q), 19.2 (s) and 16.2 (q); *m/z* (EI) 387.0762 (M^+ − C(CH_3)$_3$, $C_{20}H_{24}{}^{79}BrOSi$ requires 387.0780).

(*E*)-1-{[(1,1-Dimethylethyl)diphenylsilyl]oxy}-7-iodo-4-methylhept-4-ene 21

A solution of the bromo silyl ether **20** (6.5 g, 14.6 mmol), sodium iodide (6.57 g, 43.8 mmol) and potassium carbonate (200 mg, 1.46 mmol) in acetone (75 cm^3) was stirred at room temperature for 6 h. The mixture was then filtered, the solvent removed *in vacuo* and the residue partitioned between diethyl ether (50 cm^3) and water (50 cm^3). The organic layer was separated and the aqueous layer extracted with further diethyl ether (2 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$) and then evaporated *in vacuo*. Chromatography of the residue on silica gel using diethyl ether–light petroleum (bp 40–60 °C) (1 : 19) as eluent gave the *iodo silyl ether* (6.93 g, 96%) as a colourless oil; ν_{max}(film)/cm^{-1} 3068, 3047, 2930, 2856, 1588, 1472, 1427, 1387, 1360, 1246, 1166 and 1111; δ_H(360 MHz; $CDCl_3$) 7.70–7.67 (4H, m, 4 × aryl-H), 7.47–7.37 (6H, m, 6 × aryl-H), 5.08 (1H, t, *J* 7.1, C*H*=C(CH_3)), 3.68 (2H, t, *J* 6.4, CH_2O), 3.07 (2H, t, *J* 7.1, CH_2I), 2.57 (2H, app. q, *J* 7.1, C$H_2$$CH_2I$), 2.08 (2H, t, *J* 7.6, C$H_2$$CH_2CH_2O$), 1.72–1.64 (2H, m, C$H_2$$CH_2O$), 1.59 (3H, s, CH=C(C$H_3$)) and 1.07 (9H, s, C($CH_3$)$_3$); δ_C(90.6 MHz; $CDCl_3$) 137.8 (s), 135.6 (4 × d), 134.0 (2 × s), 129.5 (2 × d), 127.6 (4 × d), 123.0 (d), 63.4 (t), 35.7 (t), 32.4 (t), 30.6 (t), 26.9 (3 × q), 19.2 (s), 16.2 (q) and 6.0 (t); *m/z* (EI) 435.0632 (M^+ − C(CH_3)$_3$, $C_{20}H_{24}IOSi$ requires 435.0641).

Methyl (*E*)-2-(dimethoxyphosphinyl)-9-{[(1,1-dimethylethyl)-diphenylsilyl]oxy}-6-methylnon-5-enoate 22

Trimethyl phosphonoacetate (4.05 cm^3, 4.56 g, 25 mmol) was added dropwise over 10 min to a stirred slurry of sodium hydride (1.0 g, 25 mmol, 60% oil dispersion) in DMSO (40 cm^3). The mixture was stirred at room temperature for 1 h and then a solution of the iodo silyl ether **21** (6.16 g, 12.5 mmol) in THF (10 cm^3) was added. The reaction was stirred for 16 h, quenched with water (100 cm^3) and then extracted with diethyl ether (3 × 100 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1 : 4 to 3 : 1) as eluent gave the *phosphonate* (5.55 g, 81%) as a colourless oil; ν_{max}(film)/cm^{-1} 3070, 2954, 2858, 1738, 1589, 1472, 1429, 1388, 1360, 1336, 1259, 1187, 1147, 1111 and 1032; δ_H(360 MHz; $CDCl_3$) 7.68–7.66 (4H, m, 4 × aryl-H), 7.43–7.37 (6H, m, 6 × aryl-H), 5.05 (1H, t, *J* 6.4, C*H*=C(CH_3)), 3.80 (3H, d, J_{HP} 5.1, (CH_3O)P), 3.79 (3H, d, J_{HP} 5.3, (CH_3O)P), 3.76 (3H, s, OCH_3), 3.64 (2H, t, *J* 6.6, CH_2O), 3.05–2.95 (1H, m, CHP), 2.09–1.98 (6H, m), 1.68–1.62 (2H, m), 1.55 (3H, s, CH=C(CH_3)) and 1.05 (9H, s, C(CH_3)$_3$); δ_C(90.6 MHz; $CDCl_3$) 169.5 (s, J_{CP} 4.7), 139.6 (s), 135.5 (4 × d), 134.0 (2 × s), 129.4 (2 × d), 127.5 (4 × d), 122.1 (d), 63.4 (t), 53.3 (q, J_{CP} 6.5), 53.1 (q, J_{CP} 6.8), 52.4 (q), 44.3 (d, J_{CP} 130.4), 35.7 (t), 30.8 (t), 26.8 (3 × q), 26.6 (t), 26.4 (t, J_{CP} 15.2), 19.2 (s) and 15.9 (q); *m/z* (EI) 489.1864 (M^+ − C(CH_3)$_3$, $C_{25}H_{34}O_6PSi$ requires 489.1862).

(*E*)-8-Methoxycarbonyl-1-{[(1,1-dimethylethyl)diphenylsilyl]-oxy}-4-methylnona-4,8-diene 23

A solution of the phosphonate **22** (5.50 g, 10.1 mmol) in THF (5 cm^3) was added dropwise over 30 min to a stirred slurry of sodium hydride (424 mg, 10.6 mmol, 60% oil dispersion) in THF (15 cm^3). The mixture was stirred at room temperature for 1 h and then paraformaldehyde (450 mg) was added in a single portion. The reaction was stirred for 16 h, quenched with saturated aqueous ammonium chloride (20 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$) and then evaporated *in vacuo*. Chromatography of the residue on silica gel using diethyl ether–light petroleum (bp 40–60 °C) (1 : 9) as eluent gave the *methacrylate* (4.07 g, 89%) as a colourless oil; ν_{max}(film)/cm^{-1} 3070, 2930, 2857, 1722, 1630, 1589, 1472, 1428, 1388, 1305, 1195, 1169, 1134 and 1111; δ_H(360 MHz; $CDCl_3$) 7.71–7.69 (4H, m, 4 × aryl-H), 7.44–7.38 (6H, m, 6 × aryl-H), 6.14 (1H, d, *J* 1.4, C*H*H=C), 5.51 (1H, d, *J* 1.4, CH*H*=C), 5.13 (1H, t, *J* 7.3, C*H*=C(CH_3)), 3.77 (3H, s, OCH_3), 3.66 (2H, t, *J* 6.5, CH_2O), 2.34 (2H, t, *J* 7.5, C$H_2$$CH_2$-$CH_2O$), 2.17 (2H, app. q, *J* 7.3, CH_2CH=C(CH_3)), 2.08 (2H, t, *J* 7.3, CH_2C=CH_2), 1.72–1.63 (2H, m, C$H_2$$CH_2O$), 1.59 (3H, s, CH=C(C$H_3$)) and 1.08 (9H, s, C($CH_3$)$_3$); δ_C(90.6 MHz; $CDCl_3$) 167.7 (s), 140.2 (s), 135.7 (s), 135.5 (4 × d), 134.1 (2 × s), 129.5 (2 × d), 127.6 (4 × d), 124.9 (t), 123.3 (d), 63.5 (t), 51.7 (q), 35.7 (t), 32.0 (t), 30.9 (t), 26.8 (3 × q), 26.8 (t), 19.2 (s) and 15.9 (q); *m/z* (EI) 393.1878 (M^+ − C(CH_3)$_3$, $C_{24}H_{29}O_3Si$ requires 393.1886).

(*E*)-8-Methoxycarbonyl-4-methylnona-4,8-dien-1-ol 24

Tetrabutylammonium fluoride (10.2 cm^3, 10.2 mmol, 1 M in THF) was added dropwise over 5 min to a stirred solution of the methacrylate **23** (3.85 g, 8.54 mmol) in THF (20 cm^3) at 0 °C. The mixture was allowed to warm to room temperature

over 4 h, quenched with saturated aqueous ammonium chloride (20 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$) and then evaporated *in vacuo*. Chromatography of the residue on silica gel using diethyl ether–light petroleum (bp 40–60 °C) (1:1) as eluent gave the *alcohol* (1.79 g, 99%) as a colourless oil; ν_{max}(film)/cm^{-1} 3380, 2938, 2864, 1721, 1630, 1439, 1340, 1306, 1197, 1170, 1136 and 1058; δ_H(360 MHz; $CDCl_3$) 6.05 (1H, d, *J* 1.3, C*H*H=C), 5.44 (1H, d, *J* 1.3, CH*H*=C), 5.06 (1H, t, *J* 7.3, C*H*=C(CH_3)), 3.66 (3H, s, OCH_3), 3.50 (2H, t, *J* 6.6, CH_2O), 2.75–2.63 (1H, br s, OH), 2.48 (2H, t, *J* 7.4, $CH_2CH_2CH_2O$), 2.09 (2H, app. q, *J* 7.3, CH_2CH=C(CH_3)), 1.96 (2H, t, *J* 7.3, CH_2C=CH_2), 1.60–1.54 (2H, m, CH_2CH_2O) and 1.51 (3H, s, CH=C(C*H*$_3$)); δ_C(90.6 MHz; $CDCl_3$) 167.6 (s), 139.9 (s), 135.4 (s), 124.8 (t), 123.2 (d), 62.1 (t), 51.5 (q), 35.6 (t), 31.7 (t), 30.5 (t), 26.5 (t) and 15.6 (q); *m*/*z* (EI) 212.1418 (M^+, $C_{12}H_{20}O_3$ requires 212.1413).

(*E*)-8-Methoxycarbonyl-4-methylnona-4,8-dienal 25

Dess–Martin periodinane oxidation of the alcohol **24** according to the general procedure and using diethyl ether–light petroleum (bp 40–60 °C) (1:3) as eluent gave the *aldehyde* (91%) as a colourless oil; ν_{max}(film)/cm^{-1} 2951, 2722, 1722, 1631, 1440, 1389, 1306, 1248, 1197, 1170 and 1136; δ_H(360 MHz; $CDCl_3$) 9.73 (1H, t, *J* 1.9, CHO), 6.12 (1H, d, *J* 1.4, C*H*H=C), 5.50 (1H, d, *J* 1.4, CH*H*=C), 5.14 (1H, t, *J* 7.1, C*H*=C(CH_3)), 3.74 (3H, s, OCH_3), 2.52–2.48 (2H, m), 2.33–2.28 (4H, m), 2.18 (2H, app. q, *J* 7.1, CH_2CH=C(CH_3)) and 1.56 (3H, s, CH=C(C*H*$_3$)); δ_C(90.6 MHz; $CDCl_3$) 202.3 (d), 167.4 (s), 139.8 (s), 133.8 (s), 124.9 (t), 124.1 (d), 51.5 (q), 41.9 (t), 31.7 (t), 31.5 (t), 26.5 (t) and 15.9 (q).

Methyl 2-(dimethoxyphosphinyl)-6-{[dimethyl(1,1-dimethylethyl)silyl]oxy}hexanoate 31

Trimethyl phosphonoacetate (16.20 cm^3, 18.24 g, 100 mmol) was alkylated with 1-{[dimethyl(1,1-dimethylethyl)silyl]oxy}-4-iodobutane[6] (15.72 g, 25 mmol) according to the procedure used for the formation of **10**. Chromatography on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1:1 to 9:1) as eluent gave the *phosphonate* (7.91 g, 86%) as a colourless oil; ν_{max}(film)/cm^{-1} 3070, 3048, 2932, 2858, 1733, 1589, 1472, 1462, 1428, 1390, 1367, 1253, 1153, 1110, 1052 and 1028; δ_H(400 MHz; $CDCl_3$) 3.73 (3H, d, J_{HP} 6.7, (CH_3O)P), 3.71 (3H, d, J_{PH} 6.8, (CH_3O)P), 3.69 (3H, s, OCH_3), 3.52 (2H, t, *J* 6.3, CH_2O), 2.91 (1H, ddd, *J* 3.8 and 11.0, J_{HP} 22.6, CHP), 1.97–1.90 (1H, m, C*H*HCHP), 1.81–1.75 (1H, m, CH*H*CHP), 1.49–1.41 (2H, m), 1.39–1.28 (2H, m), 0.03 (9H, s, $C(CH_3)_3$) and −0.02 (6H, s, $Si(CH_3)_2$); δ_C(67.8 MHz; $CDCl_3$) 169.4 (s, J_{CP} 4.9), 62.5 (t), 53.2 (q, J_{CP} 6.1), 53.1 (q, J_{CP} 7.3), 52.4 (q), 45.0 (d, J_{CP} 131), 32.1 (t), 26.7 (3 × q), 25.8 (t), 24.7 (t, J_{CP} 14.6), 18.2 (s) and −5.5 (2 × q); *m*/*z* (EI) 353.1563 (M^+ − CH_3, $C_{14}H_{30}O_6PSi$ requires 353.1549).

(*Z*,*E*)-5,13-Bis(methoxycarbonyl)-1-{[dimethyl(1,1-dimethylethyl)silyl]oxy}-9-methyltetradeca-5,9,13-triene 26

A solution of the phosphonate **31** (2.58 g, 7.01 mmol) in THF (5 cm^3) was added dropwise over 10 min to a stirred slurry of sodium hydride (280 mg, 7.0 mmol, 60% oil dispersion) in THF (10 cm^3) at 0 °C. The mixture was stirred at 0 °C for 1 h and then a solution of the aldehyde **25** (1.34 g, 6.37 mmol) in THF (10 cm^3) was added dropwise. The reaction was stirred at 0 °C for 6 h, quenched with saturated aqueous ammonium chloride (20 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$) and then evaporated *in vacuo*. Chromatography of the residue on silica gel using diethyl ether–light petroleum (bp 40–60 °C) (1:49 to 1:9) as eluent gave both isomers of the *triene*.

The (*Z*,*E*)-isomer **26** eluted first (1.56 g, 54%) as a colourless oil; ν_{max}(film)/cm^{-1} 2950, 2929, 2857, 1721, 1631, 1460, 1437, 1284, 1255, 1196, 1170, 1130 and 1101; δ_H(360 MHz; $CDCl_3$) 6.12 (1H, d, *J* 1.4, C*H*H=C), 5.82 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 5.51 (1H, d, *J* 1.4, CH*H*=C), 5.12 (1H, t, *J* 7.2, C*H*=C(CH_3)), 3.74 (3H, s, OCH_3), 3.72 (3H, s, OCH_3), 3.58 (2H, t, *J* 6.2, CH_2O), 2.49 (2H, app. q, *J* 7.3, CH_2CH=C(CO_2CH_3)), 2.32 (2H, t, *J* 7.3, $CH_2C(CH_3)$=CH), 2.23 (2H, t, *J* 7.2, CH_2C-(CO_2CH_3)=CH_2), 2.15 (2H, app. q, *J* 7.2, CH_2CH=C(CH_3)), 2.06 (2H, t, *J* 7.6, $CH_2C(CO_2CH_3)$=CH), 1.57 (3H, s, CH=C(C*H*$_3$)), 1.51–1.40 (4H, m), 0.87 (9H, s, $C(CH_3)_3$) and 0.03 (6H, s, $Si(CH_3)_2$); δ_C(90.6 MHz; $CDCl_3$) 168.5 (s), 167.6 (s), 141.5 (d), 140.2 (s), 135.2 (s), 131.8 (s), 124.8 (t), 123.8 (d), 62.9 (t), 51.7 (q), 51.1 (q), 39.1 (t), 34.2 (t), 32.3 (t), 32.0 (t), 27.9 (t), 26.7 (t), 25.9 (3 × q), 25.3 (t), 18.3 (s), 15.9 (q) and −5.3 (2 × q); *m*/*z* (EI) 395.2264 (M^+ − $C(CH_3)_3$, $C_{21}H_{35}O_5Si$ requires 395.2254).

The (*E*,*E*)-isomer eluted second (892 mg, 31%) as a colourless oil; ν_{max}(film)/cm^{-1} 2951, 2929, 2857, 1719, 1632, 1461, 1436, 1283, 1256, 1195, 1171, 1128 and 1101; δ_H(360 MHz; $CDCl_3$) 6.66 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 6.07 (1H, d, *J* 1.4, C*H*H=C), 5.46 (1H, d, *J* 1.4, CH*H*=C), 5.09 (1H, t, *J* 7.2, C*H*=C(CH_3)), 3.68 (3H, s, OCH_3), 3.65 (3H, s, OCH_3), 3.55 (2H, t, *J* 6.3, CH_2O), 2.29–2.20 (6H, m), 2.14 (2H, app. q, *J* 7.2, CH_2CH=C(CH_3)), 2.03 (2H, t, *J* 7.8), 1.54 (3H, s, CH=C(C*H*$_3$)), 1.49–1.35 (4H, m), 0.82 (9H, s, $C(CH_3)_3$) and −0.02 (6H, s, $Si(CH_3)_2$); δ_C(90.6 MHz; $CDCl_3$) 167.4 (s), 165.6 (s), 142.1 (d), 139.9 (s), 134.6 (s), 132.1 (s), 124.7 (t), 124.0 (d), 62.8 (t), 51.5 (q), 51.3 (q), 38.4 (t), 32.5 (t), 31.8 (t), 26.9 (t), 26.6 (t), 26.4 (t), 25.8 (3 × q), 25.4 (t), 18.1 (s), 15.8 (q) and −5.5 (2 × q).

(*Z*,*E*)-5,13-Bis(methoxycarbonyl)-9-methyltetradeca-5,9,13-trien-1-ol 27

Tetrabutylammonium fluoride (3.5 cm^3, 3.5 mmol, 1 M in THF) was added dropwise over 5 min to a stirred solution of the triene **26** (1.43 g, 3.16 mmol) in THF (15 cm^3) at 0 °C. The mixture was allowed to reach room temperature over 6 h, quenched with saturated aqueous ammonium chloride (10 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$) and then evaporated *in vacuo*. Chromatography of the residue on silica gel using diethyl ether–light petroleum (bp 40–60 °C) (3:2) as eluent gave the *alcohol* (1.03 g, 96%) as a colourless oil; ν_{max}(film)/cm^{-1} 3425, 2948, 2861, 1714, 1631, 1438, 1377, 1306, 1198, 1170, 1133, 1060 and 1031; δ_H(360 MHz; $CDCl_3$) 6.14 (1H, d, *J* 0.9, C*H*H=C), 5.85 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 5.52 (1H, d, *J* 0.9, CH*H*=C), 5.13 (1 H, t, *J* 7.1, C*H*=C(CH_3)), 3.75 (3H, s, OCH_3), 3.73 (3H, s, OCH_3), 3.64 (2H, t, *J* 6.3, CH_2O), 2.50 (2H, app. q, *J* 7.3, CH_2CH=C(CO_2CH_3)), 2.33 (2H, t, *J* 7.3, CH_2-$C(CH_3)$=CH), 2.26 (2H, t, *J* 7.1, $CH_2C(CO_2CH_3)$=CH_2), 2.16 (2H, app. q, *J* 7.1, CH_2CH=C(CH_3)), 2.07 (2H, t, *J* 7.5, CH_2-$C(CO_2CH_3)$=CH), 1.59 (3H, s, CH=C(C*H*$_3$)) and 1.55–1.45 (4H, m); δ_C(90.6 MHz; $CDCl_3$) 168.5 (s), 167.8 (s), 141.9 (d), 140.1 (s), 135.1 (s), 131.6 (s), 124.9 (t), 123.9 (d), 62.6 (t), 51.8 (q), 51.2 (q), 39.1 (t), 34.2 (t), 32.1 (t), 32.0 (t), 27.9 (t), 26.7 (t), 25.3 (t) and 15.8 (q); *m*/*z* (EI) 306.1834 (M^+ − CH_3OH, $C_{18}H_{26}O_4$ requires 306.1831).

(*Z*,*E*)-5,13-Bis(methoxycarbonyl)-9-methyltetradeca-5,9,13-trienal 28

Dess–Martin periodinane oxidation of the alcohol **27** according to the general procedure and using diethyl ether–light petroleum (bp 40–60 °C) (1:3) as eluent gave the *aldehyde* (87%) as a colourless oil; ν_{max}(film)/cm^{-1} 2955, 2712, 1716, 1629, 1436, 1381, 1194, 1174 and 1129; δ_H(360 MHz; $CDCl_3$) 9.76 (1H, t, *J* 1.6, CHO), 6.13 (1H, d, *J* 1.3, C*H*H=C), 5.87 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 5.52 (1H, d, *J* 1.3, CH*H*=C), 5.13 (1 H, t, *J* 7.1, C*H*=C(CH_3)), 3.75 (3H, s, OCH_3), 3.74 (3H, s, OCH_3), 2.53 (2H, app. q, *J* 7.3, CH_2CH=C(CO_2CH_3)), 2.42 (2H, dt, *J* 1.6 and 7.4, CH_2CHO), 2.38–2.23 (4H, m), 2.16 (2H, app. q, *J* 7.1, CH_2CH=C(CH_3)), 2.07 (2H, t, *J* 7.4, $CH_2C(CO_2CH_3)$=

CH), 1.75 (2H, app. quintet, J 7.4, CH_2CH_2CHO) and 1.59 (3H, s, CH=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 202.3 (d), 168.1 (s), 167.7 (s), 143.1 (d), 140.2 (s), 135.1 (s), 130.7 (s), 124.9 (t), 124.0 (d), 51.7 (q), 51.3 (q), 43.0 (t), 39.0 (t), 33.8 (t), 32.2 (t), 27.9 (t), 26.7 (t), 21.5 (t) and 15.8 (q); *m/z* (EI) 304.1688 ($M^+ - CH_3OH$, $C_{18}H_{24}O_4$ requires 304.1675).

(*Z*,*E*)-5,13-Bis(methoxycarbonyl)-9-methyltetradeca-5,9,13-trienoic acid 29

Oxidation of the aldehyde **28** using sodium chlorite according to the general procedure gave the *acid* (quantitative) as a colourless oil; ν_{max}(film)/cm^{-1} 3600–3100, 2950, 1714, 1632, 1435, 1379 and 1197; δ_H(360 MHz; $CDCl_3$) 6.14 (1H, d, J 0.9, C*H*=C), 5.89 (1H, t, J 7.3, C*H*=C(CO_2CH_3)), 5.52 (1H, d, J 0.9, CH*H*=C), 5.13 (1 H, t, J 7.0, C*H*=C(CH_3)), 3.75 (3H, s, OCH_3), 3.74 (3H, s, OCH_3), 2.53 (2H, app. q, J 7.3, CH_2CH=C(CO_2CH_3)), 2.36–2.28 (6H, m), 2.15 (2H, app. q, J 7.0, CH_2CH=C(CH_3)), 2.07 (2H, t, J 7.4), 1.76 (2H, app. quintet, J 7.4, $CH_2CH_2CO_2H$) and 1.59 (3H, s, CH=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 179.0 (s), 168.1 (s), 167.8 (s), 143.2 (d), 140.1 (s), 135.0 (s), 130.5 (s), 124.9 (t), 124.0 (d), 51.8 (q), 51.3 (q), 39.0 (t), 33.7 (t), 33.0 (t), 31.9 (t), 27.9 (t), 26.7 (t), 24.0 (t) and 15.8 (q); *m/z* (EI) 320.1640 ($M^+ - CH_3OH$, $C_{18}H_{24}O_5$ requires 320.1624).

Se-Phenyl (*Z*,*E*)-5,13-bis(methoxycarbonyl)-9-methyltetradeca-5,9,13-trieneselenoate 30

Phenylselenylation of the acid **29** according to the general procedure and using diethyl ether–light petroleum (bp 40–60 °C) (1 : 99 to 1 : 3) as eluent gave the *selenoester* (79%) as a colourless oil; ν_{max}(film)/cm^{-1} 2949, 2856, 1714, 1631, 1579, 1478, 1438, 1379, 1304, 1242, 1197, 1170 and 1134; δ_H(360 MHz; $CDCl_3$) 7.52–7.49 (2H, m, 2 × aryl-H), 7.40–7.36 (3H, m, 3 × aryl-H), 6.14 (1H, d, J 1.4, C*H*=C), 5.90 (1H, t, J 7.3, C*H*=C(CO_2CH_3)), 5.52 (1H, d, J 1.4, CH*H*=C), 5.15 (1 H, m, C*H*=C(CH_3)), 3.76 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 2.70 (2H, t, J 7.4, CH_2COSe), 2.54 (2H, app. q, J 7.3, CH_2CH=C(CO_2CH_3)), 2.39–2.29 (4H, m), 2.18 (2H, app. q, J 7.2, CH_2CH=C(CH_3)), 2.09 (2H, t, J 7.4, CH_2C(CO_2CH_3)=CH), 1.82 (2H, app. quintet, J 7.4, CH_2CH_2COSe) and 1.60 (3H, s, CH=C(C*H*$_3$)); δ_C(90.6 MHz; $CDCl_3$) 200.0 (s), 168.0 (s), 167.7 (s), 143.5 (d), 140.2 (s), 135.8 (2 × d), 135.1 (s), 130.4 (s), 129.3 (2 × d), 128.8 (d), 126.4 (s), 124.9 (t), 124.0 (d), 51.8 (q), 51.3 (q), 46.6 (t), 39.0 (t), 33.5 (t), 32.0 (t), 28.0 (t), 26.8 (t), 24.7 (t) and 15.9 (q); *m/z* (EI) 335.1852 ($M^+ - C_6H_5Se$, $C_{19}H_{27}O_5$ requires 335.1856).

4a,7-Bis(methoxycarbony)-8a-methyltetradecahydrophenanthren-1-one 32

A solution of tributyltin hydride (54 μl, 58 mg, 0.201 mmol) and AIBN (10 mg) in benzene (4 cm^3) was added dropwise over 4 h to a refluxing solution of the phenyl selenoate **30** (82 mg, 0.167 mmol) and AIBN (5 mg) in dry degassed benzene (38 cm^3). After the addition was complete the mixture was heated under reflux for a further 8 h, then cooled and the solvent removed *in vacuo*. Chromatography of the residue on silica gel using diethyl ether–light petroleum (bp 40–60 °C) (1 : 4 to 4 : 1) as eluent gave the *tricycle* (32 mg, 57%) as a white crystalline solid; mp 105–107 °C (from diethyl ether–pentane); ν_{max}($CHCl_3$)/cm^{-1} 3011, 2951, 2854, 1723, 1450, 1435, 1376, 1344, 1281, 1264, 1101, 1072 and 1025; δ_H(500 MHz; $CDCl_3$) 3.69 (3H, s, CO_2CH_3), 3.67 (3H, s, CO_2CH_3), 2.94 (1H, dd, J 4.3 and 13.2), 2.59 (1H, t, J 5.8), 2.42 (1H, dt, J 6.8 and 14.5), 2.33–2.30 (1H, m), 2.20–2.17 (1H, m), 2.04 (2H, dt, J 13.6 and 1.9), 1.95–1.91 (1H, m), 1.90–1.83 (1H, m), 1.80 (1H, dd, J 3.3 and 13.4), 1.77–1.66 (2H, m), 1.63–1.54 (3H, m), 1.48 (1H, dd, J 6.6 and 13.6), 1.41 (1H, dd, J 2.3 and 13.0), 1.38–1.30 (2H, m) and 0.98 (3H, s, CH_3); δ_C(125.8 MHz; $CDCl_3$) 213.5 (s), 176.4 (s), 175.6 (s), 55.9 (d), 54.3 (s), 52.1 (q), 51.5 (q), 50.0 (d), 46.2 (t), 40.0 (t), 37.4 (t), 37.3 (d), 34.6 (s), 27.3 (t), 22.9 (t), 22.7 (t), 22.5 (t), 20.2 (t) and 19.4 (q); *m/z* (EI) 336.1936 (M^+, $C_{19}H_{28}O_5$ requires 336.1937).

X-Ray structure determination of 32

A crystal was mounted in a film of RS3000 perfluoropolyether on a duel-stage glass fibre and transferred to the diffractometer.

Crystal data. $C_{19}H_{28}O_5$ $M = 336.41$, monoclinic, $a = 11.865(7)$, $b = 11.890(7)$, $c = 12.306(12)$ Å, $\beta = 94.22(12)°$, $U = 1731(2)$ $Å^3$, $T = 150(2)$ K, space group $P2_1/c$ (No. 14), $Z = 4$, $D_c = 1.291$ g cm^{-3}, μ(Mo-$K\alpha$) = 0.092 mm^{-1}, 3085 unique reflections (R_{int} 0.098) used in all calculations. Final R_1 [2060 $F \geq 4\sigma(F)$] = 0.0630 and wR (all F^{-2}) was 0.145.‡

(*E*)-2-[(8-Iodo-5-methyloct-5-enyl)oxy]tetrahydro-2*H*-pyran 34

A mixture of (*E*)-8-bromo-5-methyloct-5-en-1-ol **33**[11] (2.30 g, 10.4 mmol) and sodium iodide (3.90 g, 26.0 mmol) in acetone (25 cm^3) was stirred at room temperature for 48 h. The solvent was removed *in vacuo* and the residue was then partitioned between diethyl ether (100 cm^3) and water (50 cm^3). The separated ether layer was washed with 10% sodium thiosulfate solution (50 cm^3) and brine (50 cm^3) and then each of the aqueous layers was extracted with diethyl ether (75 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated *in vacuo* to give the corresponding iodide (2.73 g, 98%) as a pale yellow oil. A solution of the crude iodide (2.73 g, 10.2 mmol), dihydropyran (DHP) (1.40 cm^3, 1.29 g, 15.3 mmol) and pyridinium toluene-*p*-sulfonate (256 mg, 1.02 mmol) in dichloromethane (25 cm^3) was stirred at room temperature for 15 h. The reaction was diluted with diethyl ether (100 cm^3) and then washed with half saturated brine (75 cm^3). The separated aqueous layer was washed with diethyl ether (75 cm^3), the combined organic extracts dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1 : 19) as eluent gave the *iodide* (3.39 g, 94%) as a colourless oil (Found: C, 45.7; H, 7.0. $C_{14}H_{25}IO_2$ requires C, 47.7; H, 7.15%); ν_{max}(film)/cm^{-1} 2938 and 1440; δ_H(250 MHz; $CDCl_3$) 5.10 (1H, dt, J 1.2, 7.2, C*H*=C(CH_3)), 4.59 (1H, t, J 3.4, CH_2C*H*O), 3.90–3.38 (4H, m, 2 × CH_2O), 3.12 (2H, t, J 7.4, CH_2I), 2.58 (2H, app. q, J 7.4, CH_2CH_2I), 2.07–1.45 (12H, m) and 1.58 (3H, s, CH=C(C*H*$_3$)); δ_C(90.6 MHz; $CDCl_3$) 137.9 (s), 123.0 (d), 98.7 (d), 67.3 (t), 62.2 (t), 39.2 (t), 32.2 (t), 30.7 (t), 29.1 (t), 25.4 (t), 24.2 (t), 19.6 (t), 16.0 (q) and 6.0 (t); *m/z* (EI) 352.0900 (M^+, $C_{14}H_{25}IO_2$ requires 352.0899).

Methyl (*E*)-2-(dimethoxyphosphinyl)-6-methyl-10-[(tetrahydro-2*H*-pyran-2-yl)oxy]dec-5-enoate 35

Trimethyl phosphonoacetate (2.61 cm^3, 2.93 g, 16.1 mmol) was added dropwise over 10 min to a slurry of sodium hydride (644 mg, 16.1 mmol, 60% oil dispersion) in DMSO (18 cm^3) at room temperature. The resultant solution was stirred for 30 min and then a solution of the iodide **34** (3.10 g, 8.80 mmol) in DMSO (7 cm^3) was added. The reaction was stirred for 15 h, quenched with water (100 cm^3) and extracted with diethyl ether (2 × 100 cm^3), dichloromethane (100 cm^3) and ethyl acetate (100 cm^3). The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (3 : 1) as eluent gave the *phosphonate* (3.00 g, 84%) as a colourless oil (Found: C, 56.1; H, 9.1. $C_{19}H_{35}O_7P$ requires C, 56.15; H, 8.7%); ν_{max}(film)/cm^{-1} 1737 and 1646; δ_H(270 MHz; $CDCl_3$) 5.03 (1H, t, J 6.3, C*H*=C(CH_3)), 4.55 (1H, t, J 3.3, CH_2C*H*O) 3.87–3.37 (4H, m, 2 × CH_2O), 3.78 (3H, d, J_{HP} 3.6, (CH_3O)P), 3.75 (3H, d, J_{HP} 3.6, (CH_3O)P), 3.73 (3H, s, CO_2CH_3), 3.04–2.91 (1H, m, C*H*P), 2.04–1.35 (16H, m) and 1.53 (3H, s,

‡ CCDC reference number 207/464. See http://www.rsc.org/suppdata/p1/b0/b002999h/ for crystallographic files in .cif format.

CH=C(CH_3)); δ_C(67.8 MHz; $CDCl_3$) 168.9 (s), 137.2 (s), 122.2 (d), 98.8 (d), 67.4 (t), 62.3 (t), 53.3 (q, J_{CP} 6.1), 53.2 (q, J_{CP} 7.3), 51.2 (q), 44.3 (d, J_{CP} 30.6), 39.3 (t), 30.7 (t), 29.2 (t), 26.8 (t, J_{CP} 4.9), 26.4 (t, J_{CP} 5.8), 25.4 (t), 24.4 (t), 19.6 (t) and 15.8 (q); *m/z* (EI) 322.1540 ($M^+ - C_5H_8O$ (THP), $C_{14}H_{27}O_6P$ requires 322.1545).

(*E*,*E*,*E*)-2-[(9-Methoxycarbonyl-5,13-dimethylnonadeca-5,9,13-trien-17-ynyl)oxy]tetrahydro-2*H*-pyran 37a

KHMDS (916 mg, 4.57 mmol) was added to a stirred solution of the phosphonate **35** (1.69 g, 4.16 mmol) and 18-crown-6 (5.51 g, 20.8 mmol) in THF (24 cm^3) at −78 °C. After 30 min a solution of (*E*)-4-methyldec-4-en-8-ynal **36a**[12] (1.20 g, 7.31 mmol) in THF (3 cm^3) was added and the reaction stirred for 18 h warming to room temperature in the process. The reaction was quenched with water (50 cm^3) and extracted with diethyl ether (2 × 50 cm^3). Both ethereal layers were washed with brine (50 cm^3), the combined extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1:9) as eluent gave the *trienyne* (1.55 g, 84%) as a colourless oil; ν_{max}(film)/cm^{-1} 1715 and 1643; δ_H(360 MHz; $CDCl_3$) 6.71 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 5.19–5.12 (2H, m, 2 × C*H*=C(CH_3)), 4.55 (1H, br s, CH_2CHO), 3.87–3.33 (4H, m, 2 × CH_2O), 3.71 (3H, s, OCH_3), 2.53–1.94 (14H, m), 1.82–1.38 (10H, m), 1.75 (3H, t, *J* 2.2, C≡C(CH_3)), 1.61 (3H, s, CH=C(CH_3)) and 1.56 (3H, s, CH=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 168.3 (s), 142.5 (d), 135.7 (s), 135.1 (s), 131.8 (s), 123.8 (d), 123.5 (d), 98.8 (d), 79.0 (s), 75.4 (s), 67.4 (t), 62.3 (t), 51.5 (q), 39.4 (t), 38.5 (t), 30.7 (t), 29.3 (t), 27.7 (t), 27.6 (t), 27.1 (t), 25.4 (t), 24.4 (t), 19.6 (t), 19.1 (t), 19.0 (t), 16.0 (q), 15.7 (q) and 3.4 (q).

(*E*,*E*,*E*)-9-Methoxycarbonyl-5,13-dimethylnonadeca-5,9,13-trien-17-yn-1-ol 38a

A solution of the trienyne **37a** (1.50 g, 3.37 mmol) and pyridinium toluene-*p*-sulfonate (85 mg, 0.34 mmol) in ethanol (27 cm^3) was warmed to 55 °C for 15 h. The mixture was allowed to cool and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1:3) as eluent gave the *trienynol* (975 mg, 80%) as a colourless oil (Found: C, 76.6; H, 10.1. $C_{23}H_{36}O_3$ requires C, 76.6; H, 10.1%); ν_{max}(film)/cm^{-1} 3382 and 1714; δ_H(360 MHz; $CDCl_3$) 6.72 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 5.21–5.11 (2H, m, 2 × C*H*=C(CH_3)), 3.72 (3H, s, OCH_3), 3.62 (2H, t, *J* 6.4, CH_2OH), 2.33–1.97 (14H, m), 1.76 (3H, t, *J* 2.2, C≡C(CH_3)), 1.66–1.41 (4H, m), 1.61 (3H, s, CH=C(CH_3)) and 1.57 (3H, s, CH=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 168.4 (s), 142.6 (d), 135.6 (s), 135.1 (s), 131.8 (s), 123.8 (d), 123.6 (d), 79.0 (s), 75.5 (s), 62.9 (t), 51.6 (q), 39.3 (t), 38.5 (t), 32.3 (t), 27.7 (t), 27.5 (t), 27.2 (t), 26.9 (t), 23.9 (t), 19.1 (t), 16.0 (q), 15.7 (q) and 3.4 (q); *m/z* (EI) 360.2679 (M^+, $C_{23}H_{36}O_3$ requires 360.2665).

(*E*,*E*,*E*)-9-Methoxycarbonyl-5,13-dimethylnonadeca-5,9,13-trien-17-ynal 39a

Dess–Martin periodinane oxidation of the alcohol **38a** according to the general procedure and using ethyl acetate–light petroleum (bp 40–60 °C) (1:9) as eluent gave the *aldehyde* (74%) as a colourless oil (Found: C, 77.05; H, 9.60. $C_{23}H_{34}O_3$ requires C, 77.05; H, 9.55%); ν_{max}(film)/cm^{-1} 1713 and 1643; δ_H(360 MHz; $CDCl_3$) 9.75 (1H, t, *J* 1.7, CHO), 6.72 (1H, t, *J* 7.4, C*H*=C(CO_2CH_3)), 5.20–5.12 (2H, m, 2 × C*H*=C(CH_3)), 3.72 (3H, s, OCH_3), 2.38 (2H, dt, *J* 1.7 and 7.3, CH_2CHO), 2.33–1.97 (14H, m), 1.76 (3H, t, *J* 2.3, C≡C(CH_3)), 1.72 (2H, app. quintet, *J* 7.3, CH_2CH_2CHO), 1.61 (3H, s, CH=C(CH_3)) and 1.57 (3H, s, CH=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 202.7 (d), 168.3 (s), 142.6 (d), 135.1 (s), 134.7 (s), 131.7 (s), 124.6 (d), 123.8 (d), 79.0 (s), 75.5 (s), 51.6 (q), 43.2 (t), 38.8 (t), 38.5 (t), 27.7 (t), 27.6 (t), 27.2 (t), 26.9 (t), 20.1 (t), 19.1 (t), 16.0 (q), 15.6 (q) and 3.5 (q); *m/z* (EI) 358.2521 (M^+, $C_{23}H_{34}O_3$ requires 358.2508).

(*E*,*E*,*E*)-9-Methoxycarbonyl-5,13-dimethylnonadeca-5,9,13-trien-17-ynoic acid 40a

Oxidation of the aldehyde **39a** using sodium chlorite according to the general procedure gave the *acid* (95%) as a colourless oil; ν_{max}(film)/cm^{-1} 3700–2700, 1711 and 1643; δ_H(360 MHz; $CDCl_3$) 6.72 (1H, t, *J* 7.4, C*H*=C(CO_2CH_3)), 5.21–5.15 (2H, m, 2 × C*H*=C(CH_3)), 3.71 (3H, s, OCH_3), 2.32–1.98 (16H, m), 1.76 (3H, t, *J* 2.3, C≡C(CH_3)), 1.72 (2H, app. quintet, *J* 7.4, $CH_2CH_2CO_2H$), 1.61 (3H, s, CH=C(CH_3)) and 1.57 (3H, s, CH=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 179.8 (s), 168.4 (s), 142.6 (d), 135.1 (s), 134.6 (s), 131.7 (s), 124.5 (d), 123.8 (d), 79.0 (s), 75.5 (s), 51.6 (q), 38.7 (t), 38.5 (t), 33.3 (t), 27.7 (t), 27.6 (t), 27.1 (t), 26.9 (t), 22.6 (t), 19.1 (t), 16.0 (q), 15.6 (q) and 3.4 (q).

Se-Phenyl (*E*,*E*,*E*)-9-methoxycarbonyl-5,13-dimethylnonadeca-5,9,13-trien-17-yneselenoate 41a

Phenylselenylation of the acid **40a** according to the general procedure and using ethyl acetate–light petroleum (bp 40–60 °C) (0:100 to 1:19) as eluent gave the *selenoester* (79%) as a colourless oil (Found: C, 67.8; H, 7.2. $C_{29}H_{38}O_3Se$ requires C, 67.8; H, 7.2%); ν_{max}(film)/cm^{-1} 1713 and 1643; δ_H(250 MHz; $CDCl_3$) 7.53–7.49 (2H, m, 2 × aryl-H), 7.40–7.37 (3H, m, 3 × aryl-H), 6.74 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 5.21–5.14 (2H, m, 2 × C*H*=C(CH_3)), 3.73 (3H, s, OCH_3), 2.71–2.64 (2H, m), 2.38–2.01 (14H, m), 1.85–1.79 (2H, m), 1.78 (3H, t, *J* 2.3, C≡C(CH_3)), 1.61 (3H, s, CH=C(CH_3)) and 1.57 (3H, s, CH=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 200.2 (s), 168.3 (s), 142.5 (d), 135.7 (2 × d), 135.1 (s), 134.4 (s), 131.7 (s), 129.3 (2 × d), 128.8 (d), 126.5 (s), 124.8 (d), 123.9 (d), 79.0 (s), 75.4 (s), 51.6 (q), 46.8 (t), 38.5 (2 × t), 27.7 (t), 27.6 (t), 27.2 (t), 26.9 (t), 23.3 (t), 19.1 (t), 16.0 (q), 15.6 (q) and 3.4 (q); *m/z* (EI) 357.2423 ($M^+ - C_6H_5Se$, $C_{23}H_{33}O_3$ requires 357.2430).

(*E*,*E*,*E*)-2-[(9-Methoxycarbonyl-5,13-dimethyl-18-trimethylsilyloctadeca-5,9,13-trien-17-ynyl)oxy]tetrahydro-2*H*-pyran 37b

Reaction of the phosphonate **35** with (*E*)-4-methyl-9-trimethylsilylnon-4-en-8-ynal **36b**[13] according to the same procedure used in the formation of **37a** and using ethyl acetate–light petroleum (bp 40–60 °C) (1:32 to 1:9) as eluent gave the *trienyne* (84%) as a colourless oil; ν_{max}(film)/cm^{-1} 2173, 1714 and 1643; δ_H(360 MHz; $CDCl_3$) 6.71 (1H, t, *J* 7.4, C*H*=C(CO_2CH_3)), 5.17–5.10 (2H, m, 2 × C*H*=C(CH_3)), 4.56 (1H, br s, CH_2CHO), 4.13–3.35 (4H, m, 2 × CH_2O), 3.71 (3H, s, OCH_3), 2.31–1.11 (24H, m), 1.62 (3H, s, CH=C(CH_3)), 1.56 (3H, s, CH=C(CH_3)) and 0.13 (9H, s, Si(CH_3)$_3$); δ_C(90.6 MHz; $CDCl_3$) 167.1 (s), 142.4 (d), 135.8 (s), 135.4 (s), 131.8 (s), 123.5 (d), 123.4 (d), 107.2 (s), 98.8 (d), 88.6 (s), 67.5 (t), 62.3 (t), 51.6 (q), 39.4 (t), 30.7 (t), 27.6 (t), 27.6 (t), 27.3 (t), 25.4 (t), 24.4 (t), 22.6 (t), 20.4 (t), 20.2 (t), 19.6 (t), 19.4 (t), 16.1 (q), 15.7 (q) and 0.1 (3 × q); *m/z* (EI) 502.3473 (M^+, $C_{30}H_{50}O_4Si$ requires 502.3478).

(*E*,*E*,*E*)-9-Methoxycarbonyl-5,13-dimethyl-18-trimethylsilyloctadeca-5,9,13-trien-17-yn-1-ol 38b

Reaction of the trienyne **37b** with pyridinium toluene-*p*-sulfonate according to the same procedure as used for the formation of **38a** and using ethyl acetate–light petroleum (bp 40–60 °C) (1:3) as eluent gave the *trienynol* (80%) as a colourless oil (Found: C, 71.5; H, 10.5. $C_{25}H_{42}O_3Si$ requires C, 71.7; H, 10.1%); ν_{max}(film)/cm^{-1} 3406, 2173, 1714 and 1642; δ_H(250 MHz; $CDCl_3$) 6.72 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 5.24–5.17 (2H, m, 2 × C*H*=C(CH_3)), 3.72 (3H, s, OCH_3), 3.62 (2H, t, *J* 6.7, CH_2OH), 2.57–1.93 (14H, m), 1.68–1.41 (4H, m), 1.57 (6H, s, 2 × CH=C(CH_3)) and 0.15 (9H, s, Si(CH_3)$_3$); δ_C(67.8 MHz; $CDCl_3$) 168.3 (s), 142.4 (d), 135.5 (s), 135.4 (s), 131.8 (s), 123.6 (d), 123.3 (d), 107.2 (s), 84.3 (s), 62.8 (t), 51.5 (q), 39.2 (t), 38.4 (t), 32.2 (t), 27.5 (t), 27.2 (t), 27.1 (t), 26.8 (t), 23.8 (t), 20.1

(t), 16.0 (q), 15.7 (q) and 0.0 (3 × q); *m/z* (EI) 418.2860 (M^+, $C_{25}H_{42}O_3Si$ requires 418.2903).

(*E*,*E*,*E*)-9-Methoxycarbonyl-5,13-dimethyl-18-trimethylsilyl-octadeca-5,9,13-trien-17-ynal 39b

Dess–Martin periodinane oxidation of the alcohol **38b** according to the general procedure and using ethyl acetate–light petroleum (bp 40–60 °C) (1 : 9) as eluent gave the *aldehyde* (84%) as a colourless oil (Found: C, 72.1; H, 10.0. $C_{25}H_{40}O_3Si$ requires C, 72.1; H, 9.7); ν_{max}(film)/cm^{-1} 2173, 1716 and 1644; δ_H(360 MHz; $CDCl_3$) 9.76 (1H, t, *J* 1.6, CHO), 6.73 (1H, t, *J* 7.4, C*H*=C(CO_2CH_3)), 5.19–5.10 (2H, m, 2 × C*H*=C(CH_3)), 3.73 (3H, s, OCH_3), 2.41–2.22 (10H, m), 2.12–1.98 (6H, m), 1.75–1.56 (2H, m), 1.64 (3H, s, CH=C(C*H*$_3$)), 1.58 (3H, s, CH=C(C*H*$_3$)), and 0.14 (9H, s, Si(CH_3)$_3$); δ_C(90.6 MHz; $CDCl_3$) 202.7 (d), 168.3 (s), 142.5 (d), 135.4 (s), 134.7 (s), 131.7 (s), 124.6 (d), 123.4 (d), 107.2 (s), 84.3 (s), 51.6 (q), 43.2 (t), 38.8 (t), 38.5 (t), 27.6 (t), 27.3 (t), 27.2 (t), 26.9 (t), 20.2 (t), 20.1 (t), 16.1 (q), 15.6 (q) and 0.1 (3 × q).

(*E*,*E*,*E*)-9-Methoxycarbonyl-5,13-dimethyl-18-trimethylsilyl-octadeca-5,9,13-trien-17-ynoic acid 40b

Oxidation of the aldehyde **39b** using sodium chlorite according to the general procedure gave the *acid* (95%) as a colourless oil; ν_{max}(film)/cm^{-1} 3700–2900, 2173 and 1717; δ_H(360 MHz; $CDCl_3$) 6.73 (1H, t, *J* 7.4, C*H*=C(CO_2CH_3)), 5.19–5.10 (2H, m, 2 × C*H*=C(CH_3)), 3.73 (3H, s, OCH_3), 2.55–1.40 (18H, m), 1.63 (3H, s, CH=C(C*H*$_3$)), 1.57 (3H, s, CH=C(C*H*$_3$)) and 0.13 (9H, s, Si(CH_3)$_3$); δ_C(90.6 MHz; $CDCl_3$) 179.3 (s), 168.3 (s), 142.6 (d), 135.5 (s), 135.4 (s), 131.6 (s), 124.8 (d), 123.6 (d), 107.2 (s), 84.3 (s), 51.7 (q), 42.6 (t), 38.9 (t), 38.5 (t), 27.3 (t), 27.1 (t), 26.4 (t), 24.4 (t), 20.2 (t), 20.1 (t), 16.1 (q), 15.7 (q) and 0.1 (3 × q); *m/z* (EI) 417.2443 ($M^+ - CH_3$, $C_{24}H_{37}O_4Si$ requires 417.2461).

Se-Phenyl (*E*,*E*,*E*)-9-methoxycarbonyl-5,13-dimethyl-18-trimethylsilyloctadeca-5,9,13-trien-17-yneselenoate 41b

Phenylselenylation of the acid **40b** according to the general procedure and using ethyl acetate–light petroleum (bp 40–60 °C) (0 : 100 to 1 : 32) as eluent gave the *selenoester* (80%) as a colourless oil (Found: C, 65.0; H, 7.8. $C_{31}H_{44}O_3SeSi$ requires C, 65.1; H, 7.8%); ν_{max}(film)/cm^{-1} 2173, 1714 and 1643; δ_H(250 MHz; $CDCl_3$) 7.55–7.49 (2H, m, 2 × aryl-H), 7.42–7.38 (3H, m, 3 × aryl-H), 6.73 (1H, t, *J* 7.4, C*H*=C(CO_2CH_3)), 5.19–5.10 (2H, m, 2 × C*H*=C(CH_3)), 3.72 (3H, s, OCH_3), 2.68 (2H, t, *J* 7.0, CH_2COSe), 2.39–1.98 (10H, m), 1.84–1.50 (6H, m), 1.59 (6H, s, 2 × CH=C(C*H*$_3$)) and 0.15 (9H, s, Si(CH_3)$_3$); δ_C(90.6 MHz; $CDCl_3$) 200.2 (s), 168.3 (s), 142.5 (d), 135.8 (2 × d), 135.4 (s), 134.4 (s), 131.8 (s), 129.3 (2 × d), 128.8 (d), 126.1 (s), 124.8 (d), 123.5 (d), 107.2 (s), 84.3 (s), 51.6 (q), 46.8 (t), 38.5 (2 × t), 27.6 (t), 27.3 (t), 27.2 (t), 26.9 (t), 23.3 (t), 20.2 (t), 16.1 (q), 15.6 (q) and 0.1 (3 × q); *m/z* (EI) 415.2662 ($M^+ - C_6H_5Se$, $C_{25}H_{39}O_3Si$ requires 415.2668).

(*E*,*E*,*E*)-9-Methoxycarbonyl-5,13-dimethyloctadeca-5,9,13-trien-17-yn-1-ol 38c

Tetrabutylammonium fluoride (2.2 cm^3, 2.20 mmol, 1 M in THF) was added dropwise over 2 min to a stirred solution of the trienyne **38b** (461 mg, 1.10 mmol) in THF (11 cm^3) at 0 °C. The reaction was stirred for 4 h, quenched with saturated aqueous ammonium chloride (25 cm^3) and extracted with diethyl ether (2 × 50 cm^3). The combined organic extracts were washed with brine (25 cm^3), dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1 : 9) as eluent gave the *trienynol* (443 mg, 86%) as a colourless oil (Found: C, 76.2; H, 9.7. $C_{22}H_{34}O_3$ requires C, 76.3; H, 9.9%); ν_{max}(film)/cm^{-1} 3400, 3303, 2117 and 1712; δ_H(400 MHz; $CDCl_3$) 6.74 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 5.22–5.15 (2H, m, 2 × C*H*=C(CH_3)), 3.74 (3H, s, OCH_3), 3.62–3.64 (3H, m, CH_2OH and CH_2O*H*), 2.34–2.01 (14H, m), 1.95 (1H, t, *J* 2.5, C≡CH), 1.63–1.43 (4H, m), 1.61 (3H, s, CH=C(C*H*$_3$)) and 1.59 (3H, s, CH=C(C*H*$_3$)); δ_C(67.8 MHz; $CDCl_3$) 168.4 (s), 142.5 (d), 135.6 (s), 135.5 (s), 131.8 (s), 123.6 (d), 123.3 (d), 84.3 (s), 68.2 (d), 62.8 (t), 51.5 (q), 39.3 (t), 38.4 (t), 32.3 (t), 27.5 (t), 27.0 (2 × t), 26.9 (t), 23.9 (t), 18.7 (t), 16.0 (q) and 15.7 (q).

(*E*,*E*,*E*)-9-Methoxycarbonyl-5,13-dimethyloctadeca-5,9,13-trien-17-ynoic acid 40c

Pyridinium dichromate (2.35 g, 3.61 mmol) was added portionwise to a solution of the alcohol **38c** (360 mg, 1.04 mmol) in DMF (10 cm^3) and the reaction stirred at room temperature for 24 h. The reaction was diluted with water (25 cm^3) and extracted with ethyl acetate (3 × 50 cm^3). Each organic extract was washed with water (25 cm^3) and then brine (25 cm^3). The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1 : 3) as eluent gave the *acid* (295 mg, 79%) as a colourless oil; ν_{max}(film)/cm^{-1} 3700–2700, 3305, 1709 and 1642; δ_H(250 MHz; $CDCl_3$) 6.73 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 5.21–5.15 (2H, m, 2 × C*H*=C(CH_3)), 3.73 (3H, s, OCH_3), 2.35–2.00 (16H, m), 1.95 (1H, t, *J* 2.4, C≡CH), 1.73 (2H, app. quintet, *J* 7.6, C$H_2$$CH_2$-$CO_2H$), 1.64 (3H, s, CH=C(C*H*$_3$)) and 1.59 (3H, s, CH=C(C*H*$_3$)); δ_C(90.6 MHz; $CDCl_3$) 179.1 (s), 168.4 (s), 142.5 (d), 135.6 (s), 135.5 (s), 131.5 (s), 124.5 (d), 123.3 (d), 84.3 (s), 68.2 (d), 51.6 (q), 38.7 (t), 38.5 (t), 33.2 (t), 27.6 (t), 27.1 (2 × t), 26.9 (t), 22.7 (t), 18.8 (t), 16.1 (q) and 15.6 (q); *m/z* (EI) 300.2102 ($M^+ - CH_3CO_2H$, $C_{20}H_{28}O_2$ requires 300.2089).

Se-Phenyl (*E*,*E*,*E*)-9-methoxycarbonyl-5,13-dimethyloctadeca-5,9,13-trien-17-yneselenoate 41c

Phenylselenylation of the acid **40c** according to the general procedure and using ethyl acetate–light petroleum (bp 40–60 °C) (0 : 100 to 1 : 19) as eluent gave the *selenoester* (70%) as a colourless oil; ν_{max}(film)/cm^{-1} 3298, 2116, 1715 and 1643; δ_H(270 MHz; $CDCl_3$) 7.52–7.49 (2H, m, 2 × aryl-H), 7.39–7.36 (3H, m, 3 × aryl-H), 6.74 (1H, t, *J* 7.3, C*H*=C(CO_2CH_3)), 5.24–5.17 (2H, m, 2 × C*H*=C(CH_3)), 3.73 (3H, s, OCH_3), 2.66 (2H, t, *J* 7.3, CH_2COSe), 2.35–2.02 (14H, m), 1.94 (1H, t, *J* 2.5, C≡CH), 1.78 (2H, app. quintet, *J* 7.3, C$H_2$$CH_2$COSe), 1.63 (3H, s, CH=C(C*H*$_3$)) and 1.57 (3H, s, CH=C(C*H*$_3$)); δ_C(90.6 MHz; $CDCl_3$) 200.2 (s), 168.2 (s), 142.5 (d), 135.7 (2 × d), 135.5 (s), 134.4 (s), 131.7 (s), 129.2 (2 × d), 128.7 (d), 126.4 (s), 124.8 (d), 123.3 (d), 84.2 (s), 68.2 (d), 51.6 (q), 46.8 (t), 38.7 (t), 38.4 (t), 27.5 (t), 27.1 (t), 27.0 (t), 26.9 (t), 23.3 (t), 18.7 (t), 16.1 (q), and 15.6 (q).

4-Oxopregn-17(20)-ene-8-carboxylic acid, methyl ester 42a–d and 5,13-dimethyl-9-oxo-13-(hex-4-ynyl)bicyclo[8.3.0]tridec-4-ene-1-carboxylic acid, methyl ester 43a,b

A solution of tributyltin hydride (262 µl, 283 mg, 0.973 mmol) and AIBN (11 mg) in toluene (9 cm^3) was added dropwise over 8 h to a refluxing solution of the phenyl selenoester **41a** (333 mg, 0.648 mmol) and AIBN (11 mg) in dry degassed toluene (121 cm^3) under argon. The reaction was heated under reflux for a further 8 h, then cooled and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using first ethyl acetate–light petroleum (bp 40–60 °C) (1 : 9) then ethyl acetate–dichloromethane (1 : 99) as eluent gave the following products.

(i) *Pregnene* **42a** (eluted first) (8 mg, 4%, 2 : 1 mixture of olefin isomers) as a colourless oil; δ_H(360 MHz; $CDCl_3$)—data for the *isomeric* mixture—5.15–5.01 (1H, m, CH=), 3.58 (1H, s, OCH_3), 3.51 (2H, s, OCH_3), 2.41–1.04 (24H, complex series of multiplets), 1.15 (1H, s, CH_3), 0.92 (1H, s, CH_3), 0.88 (2H, s, CH_3) and 0.85 (2H, s, CH_3); δ_C(125.8 MHz; $CDCl_3$)—data for the *major isomer*—212.7 (s), 176.0 (s), 148.6 (s), 109.4 (d), 61.0 (d),

59.0 (d), 56.7 (d), 50.5 (q), 47.6 (s), 44.8 (s), 43.9 (s), 41.5 (t), 37.9 (t), 35.1 (t), 34.2 (t), 33.9 (q), 26.8 (t), 23.0 (q), 22.3 (t), 20.1 (t), 18.8 (t), 18.4 (t) and 14.4 (q).

(ii) *Pregnene* **42b** (eluted second) (14 mg, 6%, 1:1 mixture of olefin isomers) as a thick colourless oil—data for the *isomeric* mixture; δ_H(360 MHz; $CDCl_3$) 5.18–5.09 (1H, m, CH=), 3.62 (3H, s, OCH_3), 2.32–0.85 (24H, complex series of multiplets), 0.87 (3H, s, CH_3), 0.77 (1.5H, s, CH_3) and 0.73 (1.5H, s, CH_3); δ_C(125.8 MHz; $CDCl_3$) 213.2 (2 × s), 176.0 (s), 175.3 (s), 152.8 (s), 150.1 (s), 113.1 (d), 110.0 (d), 61.0 (d), 60.4 (d), 60.3 (d), 59.8 (d), 59.6 (d), 59.1 (d), 50.9 (2 × q), 48.7 (2 × s), 44.5 (s), 43.6 (s), 43.5 (s), 43.4 (s), 40.5 (2 × t), 39.1 (t), 38.1 (t), 38.1 (t), 38.0 (t), 37.3 (2 × t), 30.4 (t), 29.3 (t), 27.4 (t), 25.5 (t), 22.3 (2 × t), 21.8 (q), 19.8 (t), 19.6 (t), 19.4 (q), 18.6 (2 × t), 14.5 (q), 14.4 (q), 13.8 (q) and 13.6 (q).

(iii) *Pregnene* **42c** (eluted third) (14 mg, 6%, 1:1 mixture of olefin isomers) as a colourless oil—data for the *isomeric* mixture; δ_H(360 MHz; $CDCl_3$) 5.20–5.04 (1H, m CH=), 3.68 (1.5H, s, OCH_3), 3.67 (1.5H, s, OCH_3), 2.58–0.81 (24H, complex series of multiplets), 0.96 (1.5H, s, CH_3), 0.90 (1.5H, s, CH_3), 0.86 (1.5H, s, CH_3) and 0.74 (1.5H, s, CH_3); δ_C(125.8 MHz; $CDCl_3$) 216.5 (s), 216.3 (s), 176.2 (s), 175.9 (s), 152.6 (s), 149.9 (s), 113.3 (d), 110.2 (d), 61.8 (d), 60.9 (d), 59.6 (d), 59.2 (d), 58.8 (d), 58.3 (d), 51.6 (q), 51.0 (q), 48.8 (2 × s), 44.5 (s), 44.3 (s), 43.7 (s), 41.5 (s), 39.7 (t), 38.3 (t), 37.6 (t), 36.7 (t), 36.3 (t), 29.4 (t), 29.3 (q), 28.0 (t), 27.4 (t), 27.1 (t), 25.6 (q), 24.9 (t), 22.4 (t), 22.1 (t), 21.9 (t), 21.9 (t), 19.4 (t), 19.3 (t), 19.2 (q), 19.1 (t), 18.7 (t), 17.3 (q), 13.8 (q) and 13.6 (q).

(iv) *Pregnene* **42d** (eluted fourth) (55 mg, 24%, 2:1 mixture of olefin isomers) as a colourless oil; ν_{max}(film)/cm^{-1} 1724 and 1714; δ_H(360 MHz; $CDCl_3$) *major isomer* 5.17–5.13 (1H, m, CH=), 3.50 (3H, s, OCH_3), 2.62 (1H, dt, *J* 13.2, 3.2), 2.40–0.65 (23H, complex series of multiplets), 0.92 (3H, s, CH_3) and 0.49 (3H, s, CH_3); *minor isomer* 5.09–5.03 (1H, m, CH=), 3.56 (3H, s, OCH_3), 2.66 (1H, dt, *J* 13.2, 3.2), 2.40–0.65 (23H, complex series of multiplets), 1.22 (3H, s, CH_3) and 0.56 (3H, s, CH_3); δ_C(90.6 MHz; $CDCl_3$) *major isomer* 212.8 (s), 175.2 (s), 148.4 (s), 109.7 (d), 59.8 (d), 59.3 (d), 55.9 (d), 50.7 (q), 47.3 (s), 44.7 (s), 43.7 (s), 40.7 (t), 38.4 (t), 37.1 (t), 34.3 (q), 34.1 (t), 26.7 (t), 22.6 (t), 22.3 (t), 18.8 (t), 18.5 (t), 14.4 (q) and 13.5 (q); *minor isomer* 212.7 (s), 175.4 (s), 150.3 (s), 113.4 (d), 61.2 (d), 59.9 (d), 51.1 (d), 50.6 (q), 48.1 (s), 43.8 (s), 43.7 (s), 40.7 (t), 39.5 (t), 37.0 (t), 34.0 (t), 30.4 (t), 29.8 (q), 25.9 (t), 22.4 (t), 19.4 (t), 19.1 (t), 13.5 (q) and 13.1 (q); *m/z* (EI) 358.2501 (M^+, $C_{23}H_{34}O_3$ requires 358.2508).

(v) *Bicyclotridecenone* **43a** (eluted fifth) (17 mg, 7%) as a colourless oil; δ_H(360 MHz; $CDCl_3$) 5.17–5.13 (1H, m, C*H*=C(CH_3)), 3.68 (3H, s, OCH_3), 2.67–2.45 (3H, m), 2.21–1.58 (14H, m), 1.77 (3H, t, *J* 2.0, C≡C(CH_3)), 1.56 (3H, s, CH_3), 1.43–1.01 (4H, m) and 1.11 (3H, s, CH_3); δ_C(90.6 MHz; $CDCl_3$) 214.1 (s), 175.2 (s), 135.6 (s), 123.4 (d), 79.0 (s), 75.4 (s), 60.8 (s), 59.2 (d), 52.3 (s), 51.4 (q), 39.1 (t), 36.7 (t), 32.0 (t), 30.2 (q), 29.5 (t), 28.9 (t), 26.8 (q), 25.6 (t), 23.2 (t), 22.4 (t), 19.2 (t), 18.7 (t) and 3.5 (q).

(vi) *Bicyclotridecenone* **43b** (eluted sixth) (32 mg, 14%) as a colourless oil; ν_{max}(film)/cm^{-1} 1722 and 1712; δ_H(360 MHz; $CDCl_3$) 5.16–5.13 (1H, m, C*H*=C(CH_3)), 3.64 (3H, s, OCH_3), 2.54 (1H, t, *J* 9.6), 2.47 (1H, ddd, *J* 15.1, 13.3, 6.7), 2.36–2.28 (1H, m), 2.22–1.44 (14H, m), 1.77 (3H, t, *J* 2.2, C≡C(CH_3)), 1.57 (3H, s, CH_3), 1.32–1.12 (4H, m) and 0.92 (3H, s, CH_3); δ_C(125.8 MHz; $CDCl_3$) 214.3 (s), 175.9 (s), 135.9 (s), 123.3 (d), 79.2 (s), 75.4 (s), 61.9 (s), 59.4 (d), 52.2 (s), 51.3 (q), 40.1 (t), 37.0 (t), 31.7 (t), 31.4 (t), 29.2 (t), 27.7 (t), 25.9 (t), 24.2 (t), 22.1 (t), 21.3 (q), 19.2 (t), 15.8 (q) and 3.5 (q); *m/z* (EI) 358.2508 (M^+, $C_{23}H_{34}O_3$ requires 358.2508).

4,17-Dioxoandrostane-8-carboxylic acid, methyl ester 44

(i) From 42d. A solution of the ketone **42d** (35 mg, 0.0976 mmol) in dichloromethane (3 cm^3) was cooled to −78 °C and ozone (50 cm^3 min^{-1}) bubbled through the solution until a blue colour persisted (5 min). The colour was discharged by passing a stream of oxygen and then nitrogen through the solution before dimethyl sulfide (100 µl, 1.36 mmol) was added dropwise and the reaction warmed to room temperature overnight. Volatiles were removed *in vacuo*, the residue dissolved in diethyl ether (50 cm^3) and then washed with water (25 cm^3) and brine (25 cm^3). The aqueous layers were extracted with diethyl ether (25 cm^3) and the combined organic extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using first, ethyl acetate–light petroleum (bp 40–60 °C) (1:4) and secondly, ethyl acetate–dichloromethane (1:19) as eluent gave the *androstanedione* (8 mg, 24%) as white needles; mp 56–58 °C (from ethyl acetate–pentane); ν_{max}(film)/cm^{-1} 1728 and 1715; δ_H(360 MHz; $CDCl_3$) 3.54 (3H, s, OCH_3), 2.58 (1H, dt, *J* 13.3, 3.2), 2.50–0.85 (20H, complex series of multiplets), 1.00 (3H, s, CH_3) and 0.47 (3H, s, CH_3); δ_C(90.6 MHz; $CDCl_3$) 218.4 (s), 212.2 (s), 175.0 (s), 59.3 (d), 55.5 (d), 55.3 (d), 50.7 (q), 48.3 (s), 46.9 (s), 43.3 (s), 40.6 (t), 37.1 (t), 36.5 (t), 32.7 (t), 30.8 (t), 29.0 (q), 22.2 (t), 18.6 (t), 18.4 (2 × t) and 12.8 (q); *m/z* (EI) 346.2143 (M^+, $C_{21}H_{30}O_4$ requires 346.2144).

(ii) From 47. Reaction of the ketone **47** with ozone according to the same procedure as for **42d** gave the *androstanedione* **44** (36%) with analytical data exactly as above.

X-Ray structure determination of 44

A crystal was mounted in a film of silicone grease on a glass fibre and transferred to the diffractometer.

Crystal data. $C_{21}H_{30}O_4$ $M = 346.45$, orthorhombic, $a = 8.567(3)$, $b = 12.272(14)$, $c = 16.895(3)$ Å, $U = 1776(2)$ Å^3, $T = 150(2)$ K, space group $P2_12_12_1$ (No. 19), $Z = 4$, $D_c = 1.296$ g cm^{-3}, μ(Mo-Kα) = 0.088 mm^{-1}, 2769 unique reflections (R_{int} 0.158) used in all calculations. Final R_1 [884 $F \geq 4\sigma(F)$] = 0.0354 and wR(all F^{-2}) was 0.0821.‡

17-[(Trimethylsilyl)methylene]-4-oxoandrostane-8-carboxylic acid, methyl ester 45a,b and 5,13-dimethyl-9-oxo-13-(5-trimethylsilylpent-4-ynyl)bicyclo[8.3.0]tridec-4-ene-1-carboxylic acid, methyl ester 46a,b

A solution of tributyltin hydride (282 µl, 306 mg, 1.05 mmol) and AIBN (12 mg) in benzene (8 cm^3) was added dropwise over 8 h to a refluxing solution of the phenyl selenoester **41b** (400 mg, 0.700 mmol) and AIBN (12 mg) in dry degassed benzene (142 cm^3) under argon. The reaction was heated under reflux for a further 8 h, then cooled and the solvent removed *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1:9) as eluent gave:

(i) The *androstanone* **45a** (eluted first) (33 mg, 11%) as a colourless oil; δ_H(400 MHz; $CDCl_3$) 5.21 (1H, m, CH=C), 3.71 (3H, s, OCH_3), 2.60–0.90 (21H, complex series of multiplets), 1.06 (3H, s, CH_3), 0.84 (3H, s, CH_3) and 0.16 (9H, s, $Si(CH_3)_3$); δ_C(67.8 MHz; $CDCl_3$) 212.0, 177.5, 169.4, 115.8, 56.2, 53.2, 52.3, 51.7, 46.0, 45.6, 41.4, 36.2, 32.3, 27.0, 23.5, 22.9, 22.8, 22.5, 21.1, 20.7, 20.0, 17.8 and 1.5.

(ii) The *androstanone* **45b** (eluted second) (63 mg, 21%, 1:1 mixture of olefin isomers) as a colourless oil—data for *isomeric* mixture; ν_{max}(film)/cm^{-1} 1730 and 1714; δ_H(400 MHz; $CDCl_3$) 5.21 (0.5H, br s, CH=C), 5.08 (0.5H, br s, CH=C), 3.62 (1.5H, s, OCH_3), 3.53 (1.5H, s, OCH_3), 2.64–0.80 (21H, complex series of multiplets), 1.06 (1.5H, s, CH_3), 0.83 (1.5H, s, CH_3), 0.77 (1.5H, s, CH_3), 0.54 (1.5H, s, CH_3), 0.15 (4.5H, s, $Si(CH_3)_3$) and 0.11 (4.5H, s, $Si(CH_3)_3$); δ_C(67.8 MHz; $CDCl_3$) 212.6 (s), 212.5 (s), 175.1 (s), 175.0 (s), 171.5 (s), 169.2 (s), 115.6 (d), 113.9 (d), 60.6 (d), 60.3 (d), 59.6 (d), 59.5 (d), 58.9 (d), 54.7 (d), 50.1 (q), 49.9 (q), 48.7 (s), 47.3 (s), 45.9 (s), 45.3 (s), 43.4 (s), 43.3 (s), 40.5 (t), 40.3 (t), 38.7 (t), 37.2 (t), 36.9 (t), 35.6 (t), 34.0 (t), 33.9

(t), 33.4 (t), 23.3 (q), 22.3 (t), 22.2 (t), 21.6 (t), 21.4 (t), 19.6 (t), 19.0 (t), 18.6 (t), 18.5 (t), 17.8 (q), 14.4 (q), 13.2 (q), 1.9 (3 × q) and 1.6 (3 × q); *m*/*z* (EI) 416.2735 (M^+, $C_{25}H_{40}O_3Si$ requires 416.2747).

(iii) *Bicyclotridecenone* **46a**,**b** (eluted third) (134 mg, 46%, 2:1 mixture of isomers) as a colourless oil—data for *major isomer* only; ν_{max}(film)/cm^{-1} 1731 and 1714; δ_H(400 MHz; $CDCl_3$) 5.15 (1H, m, C*H*=C(CH_3)), 3.65 (3H, s, OCH_3), 2.55–0.84 (21H, complex series of multiplets), 1.64 (3H, s, CH_3), 0.97 (3H, s, CH_3) and 0.15 (9H, s, Si(CH_3)$_3$); δ_C(67.8 MHz; $CDCl_3$) 213.2 (s), 175.3 (s), 135.8 (s), 122.8 (d), 107.1 (s), 84.5 (s), 61.9 (s), 59.3 (d), 52.2 (s), 51.3 (q), 40.0 (t), 36.8 (t), 31.3 (t), 29.1 (t), 27.2 (t), 25.8 (t), 24.1 (t), 23.3 (t), 22.0 (t), 21.1 (q), 20.2 (t), 15.8 (q) and 0.1 (3 × q); *m*/*z* (EI) 416.2743 (M^+, $C_{25}H_{40}O_3Si$ requires 416.2747).

17-Methylene-4-oxoandrostane-8-carboxylic acid, methyl ester 47

A solution of tributyltin hydride (108 μl, 116 mg, 0.400 mmol) and AIBN (10 mg) in benzene (3 cm^3) was added dropwise over 2 h to a refluxing solution of the phenyl selenoester **41c** (100 mg, 0.200 mmol) and AIBN (5 mg) in dry degassed benzene (20 cm^3) under argon. The reaction was heated under reflux for a further 14 h, then cooled and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1:9) as eluent gave the *androstanone* (20 mg, 29%, 7:2 mixture of isomers) as a colourless oil—data for the *major isomer*; ν_{max}(film)/cm^{-1} 1712 and 1650; δ_H(500 MHz; $CDCl_3$) 4.68 (2H, m, CH_2=C), 3.53 (3H, s, OCH_3), 2.61 (1H, dt *J* 13.2 and 3.3), 2.41–0.81 (20H, complex series of multiplets), 1.00 (3H, s, CH_3) and 0.52 (3H, s, CH_3); δ_C(125.6 MHz; $CDCl_3$) 212.7 (s), 175.5 (s), 158.8 (s), 100.5 (t), 59.8 (d), 59.1 (d), 55.1 (d), 50.3 (q), 47.4 (s), 44.9 (s), 43.7 (s), 40.7 (t), 38.5 (t), 37.1 (t), 34.1 (q), 33.6 (t), 30.2 (t), 23.0 (t), 22.3 (t), 18.9 (t), 18.6 (t) and 13.4 (q); *m*/*z* (EI) 344.2341 (M^+, $C_{22}H_{32}O_3$ requires 344.2351).

(*E*)-2-Fluoro-6-methyl-11-phenylundeca-1,6-dien-10-yn-3-ol 49

3-Fluorobut-3-en-2-one, dipropyl ketal (2.42 g, 12.7 mmol), catalytic hydroquinone and pyridinium toluene-*p*-sulfonate were added to a solution of 2-methyl-7-phenylhept-1-en-6-yn-3-ol **48**[17] (2.40 g, 12.0 mmol) in toluene (16 cm^3). The solution was heated for 16 h so that propanol–toluene was distilled from the mixture. The cooled mixture was diluted with diethyl ether (150 cm^3) and then washed with saturated aqueous sodium bicarbonate (50 cm^3) and brine (50 cm^3). The separated aqueous layers were extracted with diethyl ether (100 cm^3) and the combined organic extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1:9) as eluent gave (*E*)-2-fluoro-6-methyl-3-oxo-11-phenylundeca-1,6-dien-10-yne (2.66 g, 82%) as a colourless oil. This unstable ketone (2.61 g, 9.65 mmol) was dissolved in diethyl ether (34 cm^3) the solution cooled to −78 °C and treated dropwise over 10 min with diisobutylaluminium hydride (11.6 cm^3, 11.6 mmol, 1 M in hexane). The reaction was stirred for a further 10 min and then methanol (2 cm^3) was added in a single portion. The resulting mixture was warmed to room temperature, 2 M H_2SO_4 (100 cm^3) added and the mixture shaken vigourously for 10 min in a separatory funnel. The separated organic layer was then washed with saturated aqueous sodium bicarbonate (50 cm^3) and brine (50 cm^3). The aqueous layers were extracted with diethyl ether (100 cm^3) and the combined organic extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (3:17) as eluent gave the *alcohol* (1.98 g, 76%) as a colourless oil; ν_{max}(film)/cm^{-1} 3418, 1719 and 1676; δ_H(270 MHz; $CDCl_3$) 7.30–7.14 (5H, m, 5 × aryl-H), 5.24–5.18 (1H, m, C*H*=C(CH_3)), 4.54 (1H, dd, *J* 3.3, J_{HF} 17.2, C*H*H=CF), 4.43 (1H, dd, *J*, 3.3, J_{HF} 48.8, CH*H*=CF), 4.22 (1H, app. q, *J* 7.0, C*H*OH), 2.54 (2H, t, *J* 6.6), 2.22 (2H, t, *J* 6.6), 2.05 (2H, t, *J* 7.4), 1.80–1.61 (2H, m) and 1.58 (3H, s, CH=C(CH_3)); δ_C(67.8 MHz; $CDCl_3$) 166.6 (s, J_{CF} 250), 135.8 (s), 131.5 (2 × d), 128.1 (2 × d), 127.5 (d), 123.8 (s), 123.7 (d), 90.1 (d, J_{CF} 17.0), 90.0 (s), 80.6 (s), 69.7 (t, J_{CF} 30.5), 35.1 (t), 31.8 (t), 27.3 (t), 19.8 (t) and 16.0 (q); *m*/*z* (EI) 272.1573 (M^+, $C_{18}H_{21}FO$ requires 272.1577).

Ethyl (4*Z*,8*E*)-4-fluoro-8-methyl-13-phenyltrideca-4,8-dien-12-ynoate 50

A solution of the alcohol **49** (3.80 g, 14.0 mmol) and propionic acid (0.5 cm^3) in triethyl orthoacetate (38 cm^3, 33.6 g, 0.207 mol) was heated at 140 °C with continuous removal of ethanol for 4 h. The reaction was cooled and the volatiles removed *in vacuo* at 60 °C. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1:19) as eluent gave the *ester* (3.14 g, 66%) as a colourless oil; ν_{max}(film)/cm^{-1} 1732; δ_H(360 MHz; $CDCl_3$) 7.30–7.14 (5H, m, 5 × aryl-H), 5.29–5.21 (1H, m, C*H*=C(CH_3)), 4.53 (1H, dt, J_{HF} 37.8, *J* 7.3, CH=CF), 4.13 (2H, q, *J* 7.1, CH_3CH_2O), 2.51–2.39 (6H, m), 2.30 (2H, app. q, *J* 7.3, CH_2CH=CF), 2.17 (2H, q, *J* 7.2), 2.05 (2H, q, *J* 7.6), 1.64 (3H, s, CH=C(CH_3)) and 1.25 (3H, t, *J* 7.1, CH_3CH$_2$O); δ_C(67.8 MHz; $CDCl_3$) 173.2 (s), 159.1 (s, J_{CF} 253), 135.8 (s), 131.5 (2 × d), 128.2 (2 × d), 127.5 (d), 123.7 (s), 123.2 (d), 105.3 (d, J_{CF} 15.9), 90.1 (s), 80.6 (s), 60.5 (t), 39.2 (t), 31.3 (t), 27.4 (t), 27.3 (t, J_{CF} 29.3), 21.9 (t, J_{CF} 4.9), 19.9 (t), 15.9 (q) and 14.2 (q); *m*/*z* (EI) 342.1991 (M^+, $C_{22}H_{27}FO_2$ requires 342.1995).

(6*Z*,10*E*)-6-Fluoro-2,10-dimethyl-15-phenylpentadeca-1,6,10-trien-14-yn-3-ol 52

Diisobutylaluminium hydride (9.63 cm^3, 9.63 mmol, 1 M in dichloromethane) was added dropwise over 10 min to a solution of the ester **50** (3.14 g, 9.17 mmol) in dry diethyl ether (35 cm^3) at −78 °C. The mixture was stirred at this temperature for an additional 10 min, quenched with methanol (2.5 cm^3) and then stirred vigorously with cold 2 M H_2SO_4 (50 cm^3) for 10 min. Diethyl ether (100 cm^3) was added and the separated organic layer washed with saturated aqueous sodium bicarbonate (50 cm^3) and then brine (50 cm^3). The aqueous layers were extracted with diethyl ether (100 cm^3), the combined organic extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo* to give (4*Z*,8*E*)-4-fluoro-8-methyl-13-phenyltrideca-4,8-dien-12-ynal **51** (2.74 g, 99%) as a colourless oil which was used immediately. 2-Bromopropene (1.22 cm^3, 1.66 g, 13.7 mmol) was added to a suspension of magnesium chips (333 mg, 13.7 mmol) in THF (18 cm^3). The reaction was stirred allowing the magnesium to disappear and then cooled to 0 °C before a solution of the aforementioned aldehyde **51** (2.73 g, 9.15 mmol) in THF (7 cm^3) was added dropwise over 10 min. The mixture was stirred for an additional 30 min and quenched with saturated aqueous ammonium chloride (50 cm^3). The mixture was extracted with diethyl ether (100 cm^3) and the organic layer washed with water (50 cm^3) and then brine (50 cm^3). The aqueous layers were extracted with diethyl ether (100 cm^3), the combined organic extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo* to give the *alcohol* (3.09 g, 99%) as a colourless oil; ν_{max}(film)/cm^{-1} 3423, 1708 and 1652; δ_H(360 MHz; $CDCl_3$) 7.30–7.14 (5H, m, 5 × aryl-H), 5.27–5.24 (1H, m, C*H*=C(CH_3)), 4.95 (1H, br s, C*H*H=C), 4.86 (1H, br s, CH*H*=C), 4.47 (1H, dt, J_{HF} 38.1, *J* 7.2, CH=CF), 4.03 (1H, t, *J* 6.4, C*H*OH), 2.45–2.03 (10H, m), 1.73 (3H, s, CH_2=C(CH_3)), 1.70–1.62 (2H, m) and 1.66 (3H, s, CH=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 159.1 (s, J_{CF} 252), 147.0 (s), 136.0 (s), 131.5 (2 × d), 128.2 (2 × d), 127.5 (d), 124.0 (s), 123.2 (d), 111.3 (t), 104.8 (d, J_{CF} 15.7), 90.2 (s), 80.5 (s), 74.8 (d), 39.3 (t), 31.4 (t), 28.2 (t, J_{CF} 28.2), 27.4 (t), 21.9 (t, J_{CF} 4.7), 19.9 (t), 17.6 (q) and 15.9 (q); *m*/*z* (EI) 340.2200 (M^+, $C_{23}H_{29}FO$ requires 340.2203).

Ethyl (4*E*,8*Z*,12*E*)-8-fluoro-4,12-dimethyl-17-phenylheptadeca-4,8,12-trien-16-ynoate 53

Reaction of the alcohol **52** and propionic acid in triethyl orthoacetate according to the same procedure used for the formation of **50** gave the *ester* (76%) as a colourless oil (Found: C, 78.5; H, 8.3. $C_{27}H_{35}FO_2$ requires C, 78.9; H, 8.6%); ν_{max}(film)/cm^{-1} 1736 and 1701; δ_H(360 MHz; $CDCl_3$) 7.39–7.25 (5H, m, 5 × aryl-H), 5.26–5.23 (1H, m, C*H*=C(CH_3)), 5.14–5.10 (1H, m, C*H*=C(CH_3)), 4.46 (1H, dt, J_{HF} 38.2, J 7.2, CH=CF), 4.11 (2H, q, J 7.1, CH_3CH_2O), 2.42–2.03 (16H, m), 1.65 (3H, s, CH=C(CH_3)), 1.61 (3H, s, CH=C(CH_3)) and 1.24 (3H, t, J 7.1, CH_3CH_2O); δ_C(90.6 MHz; $CDCl_3$) 173.4 (s), 159.0 (s, J_{CF} 253), 136.1 (s), 134.4 (s), 131.5 (2 × d), 128.2 (2 × d), 127.4 (d), 124.0 (s), 123.6 (d), 123.1 (d), 104.6 (d, J_{CF} 15.6), 90.1 (s), 80.6 (s), 60.2 (t), 39.3 (t), 34.6 (t), 33.2 (t), 32.0 (t, J_{CF} 27.6), 27.4 (t), 24.8 (t), 21.9 (t, J_{CF} 4.9), 19.9 (t), 15.9 (q), 15.9 (q) and 14.2 (q); *m*/*z* (EI) 410.2603 (M^+, $C_{27}H_{35}FO_2$ requires 410.2610).

(5*E*,9*Z*,13*E*)-9-Fluoro-5,13-dimethyl-18-phenyloctadeca-5,9,13-trien-17-ynenitrile 54

A solution of the ester **53** (2.50 g, 6.09 mmol) in THF (38 cm^3) was added dropwise over 20 min to a slurry of lithium aluminium hydride (693 mg, 18.3 mmol) in THF (13 cm^3). The mixture was stirred at room temperature for 16 h and then warmed to reflux for 1 h before being cooled to 0 °C. Water (10 cm^3) was carefully added to the mixture which was then stirred with aqueous 1 M H_2SO_4 (25 cm^3) for 10 min. The resulting mixture was diluted with water (30 cm^3) and then extracted with diethyl ether (75 cm^3). The organic layer was washed with saturated aqueous sodium bicarbonate (50 cm^3) and then brine (50 cm^3). The aqueous layers were extracted with diethyl ether (75 cm^3) and the combined organic extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo* to give (4*E*,8*Z*,12*E*)-8-fluoro-4,12-dimethyl-17-phenylheptadeca-4,8,12-trien-16-yn-1-ol. A solution of this alcohol and triethylamine (1.27 cm^3, 923 mg, 9.12 mmol) in dichloromethane (28 cm^3) at 0 °C was treated with methanesulfonyl chloride (518 μl, 766 mg, 6.69 mmol). After 90 min, the solvent was removed *in vacuo* and the resulting crude mesylate dissolved in DMSO (28 cm^3), treated with sodium cyanide (914 mg, 18.2 mmol) and stirred at 60 °C for 15 h. The mixture was allowed to cool, poured into diethyl ether (150 cm^3) and washed with water (2 × 50 cm^3) then brine (50 cm^3). The aqueous layers were extracted with diethyl ether (2 × 75 cm^3), the combined organic extracts dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1:9) as eluent gave the *nitrile* (1.98 g, 86%) as a colourless oil; ν_{max}(film)/cm^{-1} 2245 and 1707; δ_H(360 MHz; $CDCl_3$) 7.39–7.25 (5H, m, 5 × aryl-H), 5.26–5.22 (1H, m, C*H*=C(CH_3)), 5.17–5.13 (1H, m, C*H*=C(CH_3)), 4.47 (1H, dt, J_{HF} 38.1, J 7.2, CH=CF), 2.42 (2H, t, J 7.1, CH_2CN), 2.34–2.01 (14H, m), 1.74 (2H, app. quintet, J 7.1, CH_2CH_2CN), 1.65 (3H, s, CH=C(CH_3)) and 1.58 (3H, s, CH=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 159.0 (s, J_{CF} 253), 136.0 (s), 133.4 (s), 131.4 (2 × d), 128.1 (2 × d), 127.4 (d), 125.1 (d), 123.9 (s), 123.1 (d), 119.7 (s), 104.7 (d, J_{CF} 15.5), 90.1 (s), 80.6 (s), 39.3 (t), 38.1 (t), 31.9 (t, J_{CF} 27.6), 27.3 (t), 24.8 (t), 23.2 (t), 21.9 (t, J_{CF} 4.9), 19.9 (t), 16.1 (t), 15.9 (q) and 15.5 (q); *m*/*z* (EI) 377.2505 (M^+, $C_{26}H_{32}FN$ requires 377.2519).

(5*E*,9*Z*,13*E*)-9-Fluoro-5,13-dimethyl-18-phenyloctadeca-5,9,13-trien-17-ynoic acid 55

A solution of the nitrile **54** (1.78 g, 4.71 mmol) and KOH (2.87 g, 51.1 mmol) in water (30 cm^3) and ethanol (100 cm^3) was heated at reflux for 24 h. After this time a further amount of KOH (1.40 g, 26.0 mmol) in water (2 cm^3) was added and the reaction heated at reflux for a further 12 h. The mixture was allowed to cool and the ethanol evaporated *in vacuo*. The resulting aqueous solution was acidified to pH 1 with 2 M HCl (60 cm^3) and extracted with ethyl acetate (3 × 100 cm^3). The combined organic extracts were washed with brine (50 cm^3), dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1:4) as eluent gave the *acid* (1.55 g, 83%) as a colourless oil; ν_{max}(film)/cm^{-1} 3500–2700 and 1708; δ_H(400 MHz; $CDCl_3$) 7.38–7.24 (5H, m, 5 × aryl-H), 5.25–5.21 (1H, m, C*H*=C(CH_3)), 5.17–5.13 (1H, m, C*H*=C(CH_3)), 4.46 (1H, dt, J_{HF} 38.5, J 7.3, CH=CF), 2.40 (2H, t, J 7.3, CH_2CO_2H), 2.32–1.99 (14H, m), 1.72 (2H, app. quintet, J 7.3, $CH_2CH_2CO_2H$), 1.64 (3H, s, CH=C(CH_3)) and 1.57 (3H, s, CH=C(CH_3)); δ_C(67.8 MHz; $CDCl_3$) 180.1 (s), 159.1 (s, J_{CF} 253), 136.1 (s), 134.8 (s), 131.5 (2 × d), 128.1 (2 × d), 127.5 (d), 124.0 (s), 124.0 (d), 123.1 (d), 104.6 (d, J_{CF} 15.7), 90.2 (s), 80.5 (s), 39.3 (t), 38.7 (t), 33.3 (t), 32.0 (t, J_{CF} 28.1), 27.4 (t), 24.8 (t), 22.6 (t), 21.9 (t, J_{CF} 4.9), 19.9 (t), 15.9 (q) and 15.7 (q); *m*/*z* (EI) 396.2479 (M^+, $C_{26}H_{33}FO_2$ requires 396.2465).

***Se*-Phenyl (5*E*,9*Z*,13*E*)-9-fluoro-5,13-dimethyl-18-phenyloctadeca-5,9,13-trien-17-yneselenoate 56**

Tributylphosphine (1.31 cm^3, 1.06 g, 5.25 mmol) was added dropwise over 2 min to a solution of the acid **55** (1.04 g, 2.62 mmol) and diphenyl diselenide (1.64 g, 5.25 mmol) in benzene (20 cm^3) and the reaction stirred at room temperature for 20 h. The reaction was diluted with diethyl ether (150 cm^3), washed with water (50 cm^3) and then brine (50 cm^3). The aqueous layers were extracted with diethyl ether (100 cm^3) and the combined organic extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (0 to 1:19) as eluent gave the *selenoester* (1.04 g, 74%) as a colourless oil (Found: C, 71.6; H, 6.9. $C_{32}H_{37}FO_2Se$ requires C, 71.7; H, 7.0%); ν_{max}(film)/cm^{-1} 1723; δ_H(360 MHz; $CDCl_3$) 7.51–7.25 (10H, m, 10 × aryl-H), 5.27–5.23 (1H, m, C*H*=C(CH_3)), 5.13–5.09 (1H, m, C*H*=C(CH_3)), 4.48 (1H, dt, J_{HF} 38.2, J 7.2, CH=CF), 2.65 (2H, t, J 7.4, CH_2COSe), 2.42 (2H, t, J 7.1), 2.30 (2H, q, J 7.1), 2.21–2.01 (10H, m), 1.79 (2H, app. quintet, J 7.3, CH_2CH_2COSe), 1.65 (3H, s, C*H*=C(CH_3)) and 1.58 (3H, s, C*H*=C(CH_3)); δ_C(90.6 MHz; $CDCl_3$) 200.3 (s), 159.1 (s, J_{CF} 253), 136.1 (s), 135.7 (2 × d), 134.6 (s), 131.5 (2 × d), 129.3 (2 × d), 128.8 (d), 128.2 (2 × d), 127.5 (d), 126.5 (s), 124.3 (d), 124.0 (s), 123.1 (d), 104.6 (d, J_{CF} 15.6), 90.2 (s), 80.5 (s), 46.7 (t), 39.4 (t), 38.5 (t), 32.0 (t, J_{CF} 27.8), 27.4 (t), 24.8 (t), 23.3 (t), 22.0 (t, J_{CF} 5.0), 19.9 (t), 15.9 (q) and 15.6 (q); *m*/*z* (EI) 379.2437 ($M^+ - C_6H_5Se$, $C_{26}H_{32}FO$ requires 379.2437).

Octahydro-1-fluoro-7a-methyl-1-(4-oxopentyl)-4*H*-inden-4-one 58 and 59

A solution of tributyltin hydride (1.01 cm^3, 1.09 g, 3.74 mmol) and AIBN (50 mg) in benzene (30 cm^3) was added dropwise over 2 h to a refluxing solution of the phenyl selenoester **56** (1.00 g, 1.87 mmol) and AIBN (50 mg) in dry degassed benzene (190 cm^3) under argon. The reaction was heated under reflux for a further 2 h, then cooled and the solvent removed *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (bp 40–60 °C) (1:19 to 1:9) as eluent gave a complex mixture of cyclised products including the bicycles **57a**,**b** (272 mg, 39%). This mixture (250 mg, 0.657 mmol) was dissolved in dichloromethane (20 cm^3), cooled to −78 °C and ozone (50 cm^3 min^{-1}) was bubbled through the solution until a blue colour persisted (10 min). The colour was discharged by passing a stream of oxygen and then nitrogen through the solution before dimethyl sulfide (750 μl, 10.2 mmol) was added dropwise and the reaction warmed to room temperature overnight. The mixture was then washed with water (25 cm^3) and brine (25 cm^3). The aqueous layers were extracted with dichloromethane (25 cm^3) and the combined organic extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue on silica gel using ethyl acetate–

light petroleum (bp 40–60 °C) (3:7 to 1:1) as eluent gave the following products:

(i) *Indenone* **58** (eluted first) (49 mg, 30%) as a colourless oil; ν_{max}(film)/cm^{-1} 1713; δ_H(270 MHz; $CDCl_3$) 2.77–0.84 (17H, complex series of multiplets), 2.12 (3H, s, CH_3CO) and 1.03 (3H, s, CH_3); δ_C(67.8 MHz; $CDCl_3$) 211.9 (s), 208.7 (s), 109.4 (s, J_{CF} 176), 57.4 (d), 51.8 (s, J_{CF} 19.6), 43.6 (t), 39.2 (t), 33.2 (t, J_{CF} 23.2), 31.5 (t, J_{CF} 23.2), 29.8 (q), 29.6 (t, J_{CF} 4.9), 26.6 (q, J_{CF} 8.7), 21.4 (t, J_{CF} 3.7) and 18.2 (2 × t); *m/z* (EI) 234.1616 ($M^+ - HF$, $C_{15}H_{22}O_2$ requires 234.1620).

(ii) *Indenone* **59** (eluted second) (78 mg, 47%) as a colourless oil; ν_{max}(film)/cm^{-1} 1704; δ_H(270 MHz; $CDCl_3$) 2.74–0.85 (17H, m), 2.15 (3H, s, CH_3CO) and 1.02 (3H, s, CH_3); δ_C(67.8 MHz; $CDCl_3$) 213.9 (s), 208.7 (s), 109.1 (s, J_{CF} 178), 58.2 (d), 53.4 (s, J_{CF} 19.5), 43.6 (t), 36.5 (t), 33.5 (t, J_{CF} 24.4), 31.4 (t, J_{CF} 24.4), 29.9 (q), 29.2 (t, J_{CF} 4.9), 25.1 (t), 22.3 (t), 18.1 (t, J_{CF} 3.7) and 16.5 (q, J_{CF} 8.5); *m/z* (EI) 234.1625 ($M^+ - HF$, $C_{15}H_{22}O_2$ requires 234.1620).

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