ARTICLE

OBC
www.rsc.org/obc

α,β-Unsaturated and cyclopropyl acyl radicals, and their ketene alkyl radical equivalents. Ring synthesis and tandem cyclisation reactions

Christopher J. Hayes, Nicola M. A. Herbert, Nicole M. Harrington-Frost and Gerald Pattenden*

School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK

Received 7th September 2004, Accepted 27th October 2004
First published as an Advance Article on the web 16th December 2004

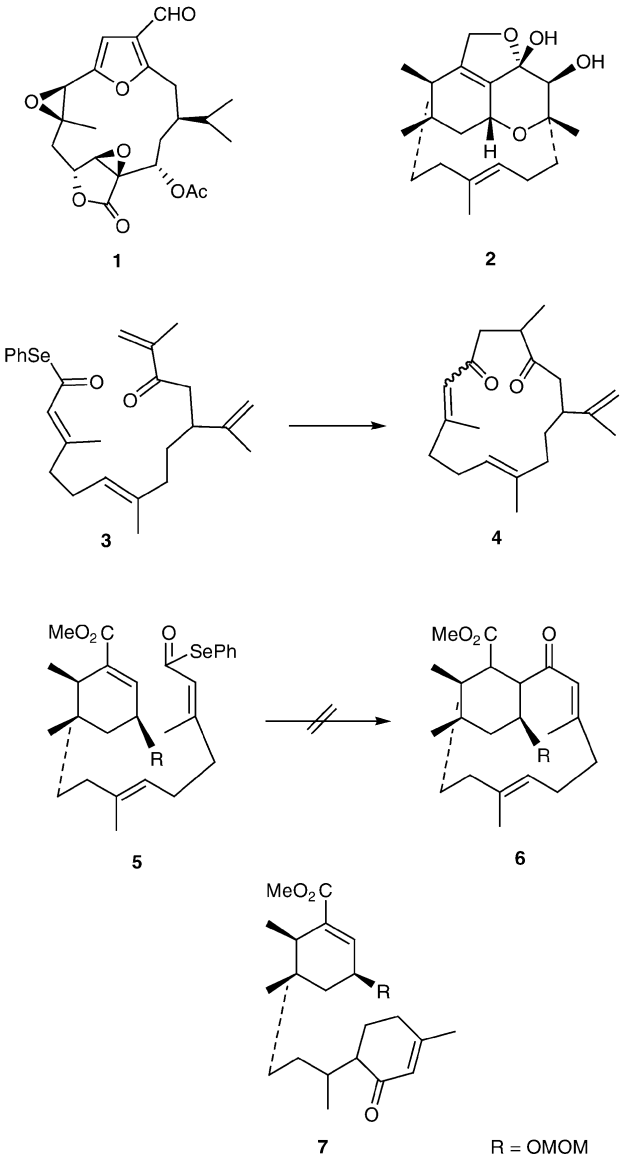
Treatment of the α,β-unsaturated selenyl esters **12** and **14** with Bu_3SnH–AIBN produces the corresponding 2-cyclohexenones **13** and **15** respectively *via* presumed α-ketene alkyl radical intermediates, *viz*. **10**. By contrast, the 2,7-diene esters **34** and **39** undergo tandem radical cyclisations producing diquinanes, *e.g.* **38** (76%), and the corresponding allene-substituted α,β-unsaturated selenyl ester **48** gives the cyclooctadienone **56** on treatment with Bu_3SnH–AIBN in refluxing benzene. The selenyl ester **19** derived from chrysanthemic acid produces a mixture of the γ,δ-unsaturated aldehyde **22** and the corresponding dimer **25a** on treatment with Bu_3SnH–AIBN. Furthermore, in the presence of methanol the only product from this reaction was the bis(methyl ester) dimer **25b**, thereby lending further credence to the involvement of ketene alkyl radical intermediates in these reactions, and in the aforementioned reactions involving 2,6- and 2,7-diene selenyl esters. Treatment of the cyclopropane selenyl esters **59** and **61**, containing keto- and oxy-group functionality in their side-chains, with Bu_3SnH–AIBN led to excellent syntheses of the enol lactone **66** (76%) and the *trans*-fused bicyclo[6.1.0]nonane **67** (80–95%) respectively.

Introduction

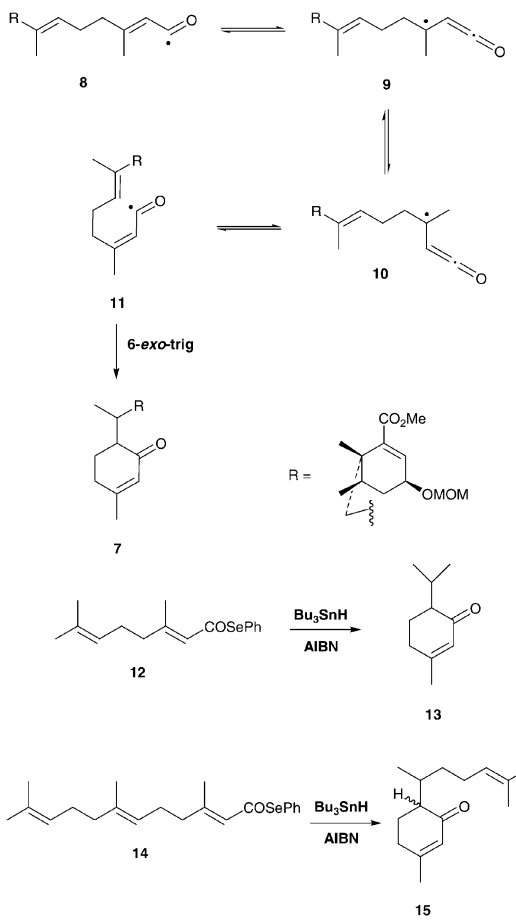
Acyl radicals are powerful reactive intermediates which are used widely in the synthesis of carbon-to-carbon bonds and, particularly, in the elaboration of carbo- and heterocyclic ring systems.[1] Our own group, for example, has used acyl radicals generated from polyolefinic phenyl selenyl esters to elaborate a range of interesting polycyclic ring systems, including steroids, *via* consecutive (cascade) 6-*endo*-trig cyclisations.[2] In contemporaneous studies, directed towards synthesis of the natural diterpenes lophotoxin A (**1**) and phomactin A (**2**), we evaluated the scope for macrocyclisation reactions from the α,β-unsaturated acyl radical precursors **3** and **5** as a route to the carbon frameworks in these natural products. In the event, treatment of the phenyl selenyl ester **3** with Bu_3SnH–AIBN led to the macrocyclic enone **4** as a 2 : 1 mixture of *E*- and *Z*-isomers[3] whereas, under similar reaction conditions, the selenyl ester **5** gave rise to the cyclohexenone **7** instead of the expected macrocyclic enone **6**.[4]

We reasoned that the cyclohexenone **7** was produced from **5** as a result of a 6-*exo*-trig cyclisation from the *Z*-2-unsaturated acyl radical intermediate **11** derived from the corresponding *E*-2-unsaturated acyl radical **8** by way of the interesting α-ketene alkyl radical species **9**/**10**.[5] In related studies the selenyl esters **12** and **14** derived from geranoic acid and 2*E*,6*E*-farnesoic acid, respectively, underwent similar cyclisations in the presence of Bu_3SnH–AIBN leading to (±)-piperitone **13**[5] (86%) and bisabolone **15** (74%; 1 : 1 mixture of diastereoisomers) respectively.[6]

Although α-ketene alkyl radical species have been recognised for some time, and their structures have been the subject of *ab initio* calculations,[7] investigations of their scope in synthesis have been limited. In this paper we have sought to vindicate the intermediacy of α-ketene radical species in the conversions of **5**→**7**, **12**→**13** and **14**→**15**, by studying the corresponding chemistry of cyclopropylacyl radical intermediates and the opportunity for α,β-unsaturated acyl radical species containing additional unsaturation in their structures to participate in tandem cyclisation processes.[8] In the accompanying papers we present our studies of the chemistry of vinylcyclopropylacyl radicals in the synthesis of cyclohexenones, and the applications of α-ketenyl radicals in the total synthesis of the triquinane natural products pentalenene and modhephene.



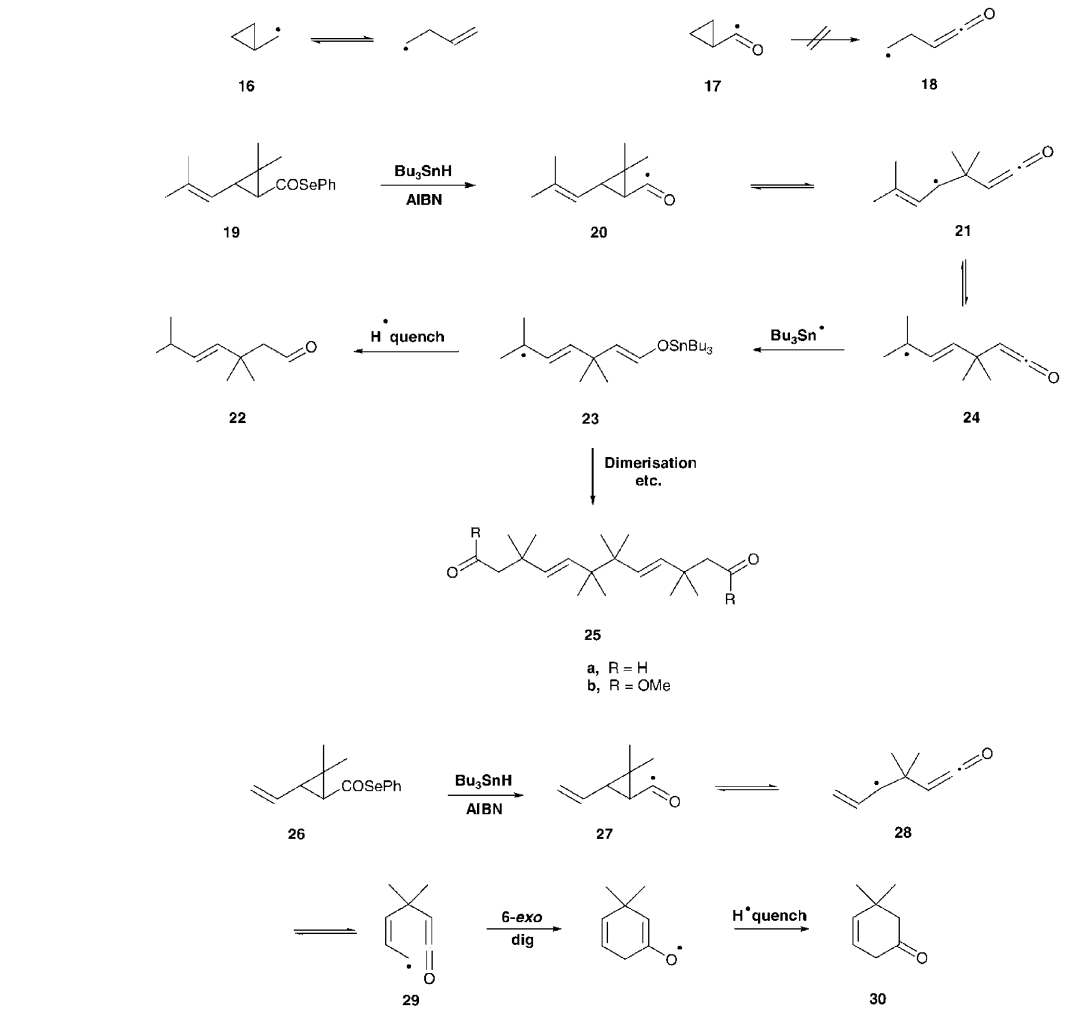
DOI: 10.1039/b413815p



Results and discussion

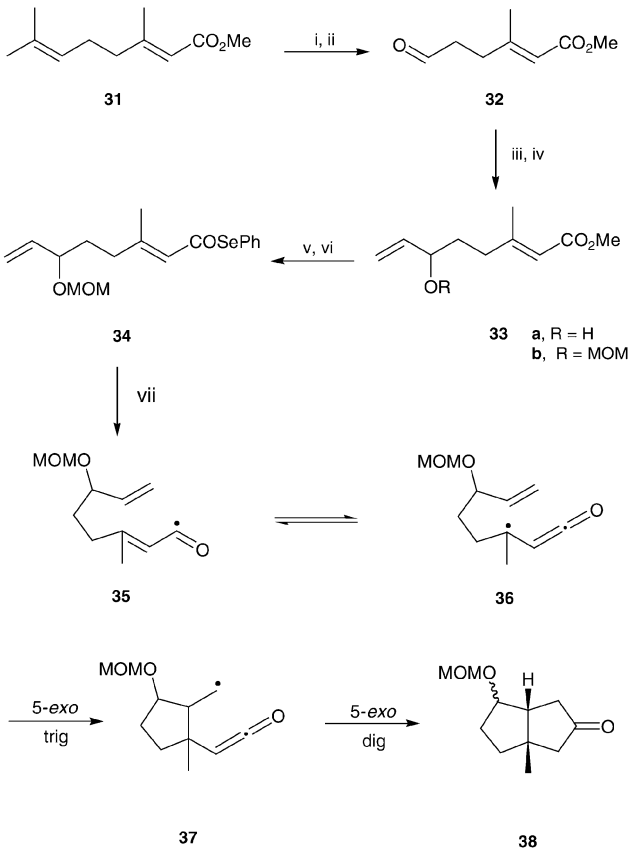
Although the cyclopropylmethyl radical **16** is well known to undergo exothermic ring opening (21 kJ mol^{-1}) and isomerisation to the corresponding but-3-enyl radical,[9] the cyclopropyl acyl radical **17** shows little propensity for similar ring opening leading to the corresponding ketene species, *viz.* **18**.[10] We reasoned, however, that the presence of additional unsaturation on the cyclopropane ring of an cyclopropyl acyl species would provide sufficient additional impetus for such species to undergo ring opening and the production of β-ketene radicals. Accordingly, we treated the selenyl ester **19**[11] derived from *trans*-chrysanthemic acid with Bu_3SnH–AIBN in hot benzene and found that the major product was the γ,δ-unsaturated aldehyde **22**, whose formation was accompanied by the corresponding dimer **25a**. The compounds **22** and **25a** are produced from **19** *via* the acyl radical **20**, which first undergoes ring opening to the β- and δ-ketene radicals **21** and **24**, respectively. Reduction of the ketene unit in **24**, preceded, or followed by H-abstraction, leads to the aldehyde **22**[12] whereas dimerisation and reduction of the enol stannane precursor **23** produces the corresponding dimer **25a**. When the same reaction between the selenyl ester **19** and Bu_3SnH–AIBN was carried out in the presence of methanol, as a ketene trap, the sole product isolated was the corresponding bis(ester) dimer **25b**.

Intriguingly, when the vinylcyclopropyl selenyl ester **26** lacking *gem*-dimethyl substitution on the alkene bond was treated with Bu_3SnH–AIBN in an identical manner to **19**, the intermediate cyclopropyl acyl radical **27** underwent ring opening to the corresponding ketene alkyl radical **28**/**29**, which then underwent a 6-*exo*-dig cyclisation leading to the cyclohexenone **30** in 52% yield. This interesting outcome was developed further

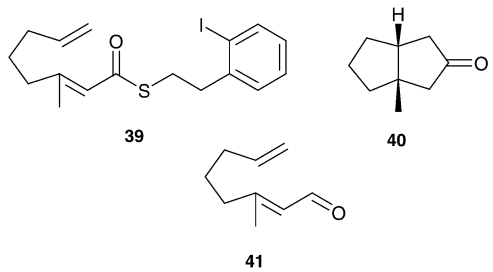


with other vinylcyclopropyl selenyl esters and led to a general synthesis of cyclohexenones, details of which are described in an accompanying paper.[13]

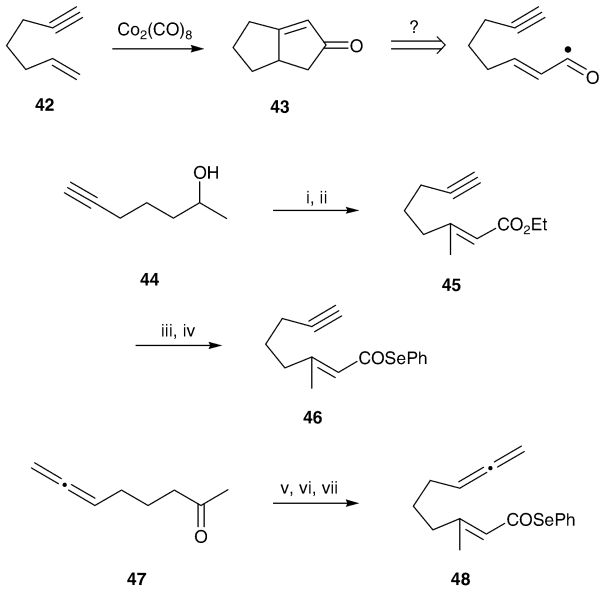
The aforementioned studies with cyclopropyl acyl radical intermediates clearly implicated β-ketene alkyl intermediates in their conversions to acyclic and cyclohexenone products and lent credence to the involvement of analogous α-ketene alkyl radical intermediates in the conversions **3**→**4**, **5**→**7** and **12**/**14**→**13**/**15**, described earlier. With a view to extending these intriguing transformations of ketene alkyl radical intermediates to the synthesis of diquinane products *via* tandem cyclisation processes we next synthesised the 2,7-octadienyl selenyl ester **34** in six short steps from methyl geranoate (Scheme 1). When the ester **34** was treated with Bu_3SnH–AIBN it underwent sequential 5-*exo*-trig and 5-*exo*-dig cyclisations *via* the intermediate α-ketene alkyl radical **36** and alkyl radical **37**, producing the diquinane **38** in a pleasing 76% yield.[5] In a similar manner, the α,β-unsaturated acyl radical intermediate derived from **39** underwent tandem cyclisation to the diquinane **40** (41%), whose formation was accompanied by that of the product of *in situ* reduction of the acyl radical intermediate, *viz.* **41** (46%).



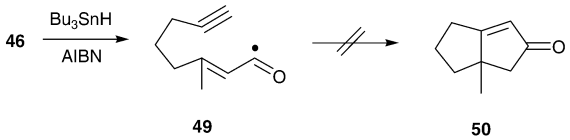
Scheme 1 *Reagents*: i, MCPBA, CH_2Cl_2, 90%; ii. $HClO_4$, THF–H_2O, then KIO_4, 92%; iii, CH_2=CHMgCl, THF, 64%; iv, MOMCl, $^iPr_2NEt$, CH_2Cl_2, 59%; v, LiOH, THF–H_2O, 93%; vi, NPSP, Bu_3P, CH_2Cl_2, −20 °C, 62%; vii, Bu_3SnH–AIBN, benzene, reflux, 76%.



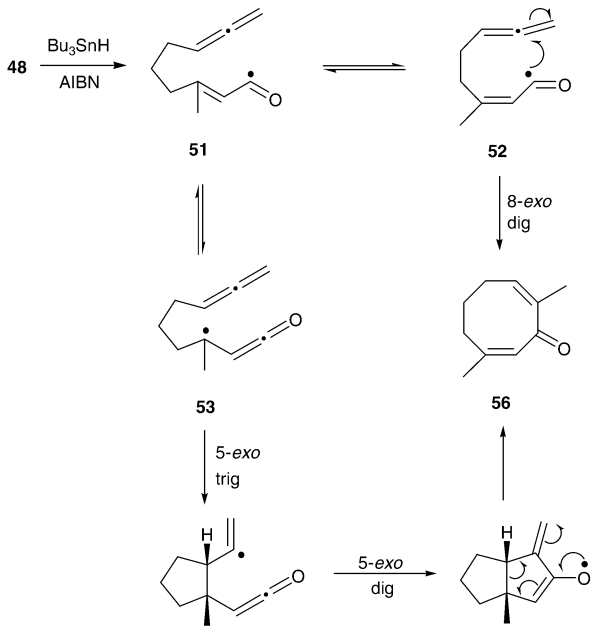
We next examined the scope for tandem radical cyclisations from the acetylene- and allene-substituted α,β-unsaturated selenyl esters **46** and **48**, with a view to replicating the more familiar Pauson–Khand method[14] of preparing diquinanes, *i.e.* **42**→**43**. The substituted selenyl esters **46** and **48** were both prepared from readily available starting materials as highlighted in Scheme 2. Disappointingly, however, when the acetylene **46** was treated with Bu_3SnH–AIBN, instead of leading to **50**, the only product isolated, in 46% yield, was the aldehyde resulting from reduction of the selenyl ester function in **46**. However, when the substituted allene selenyl ester **48** was reacted with Bu_3SnH–AIBN, the cyclooctadienone **56** was isolated in 25% yield, together with unreacted starting material (18%) and the corresponding aldehyde (8%). The cyclooctadienone **56** could result from an 8-*exo*-dig cyclisation of the *Z*-α,β-unsaturated acyl radical intermediate **52** produced from **48** or, alternatively, *via* an initial 5-*exo*-trig cyclisation of the allene **53**, leading to **54**, followed by a 5-*exo*-dig cyclisation to the diquinane **55** and fragmentation (Scheme 3).



Scheme 2 *Reagents*: i, PCC, CH_2Cl_2, silica; ii, $EtO_2CCH_2PO(OEt)_2$, NaH, THF, 44% over two steps; iii, NaOH, EtOH–H_2O, 90%; iv, NPSP, Bu_3P, CH_2Cl_2, 67%; v, $EtO_2C.CH_2PO(OEt)_2$, NaH, HF, 87%; vi, NaOH, EtOH–H_2O, 64%; vii, NPSP, Bu_3P, CH_2Cl_2, 82%.

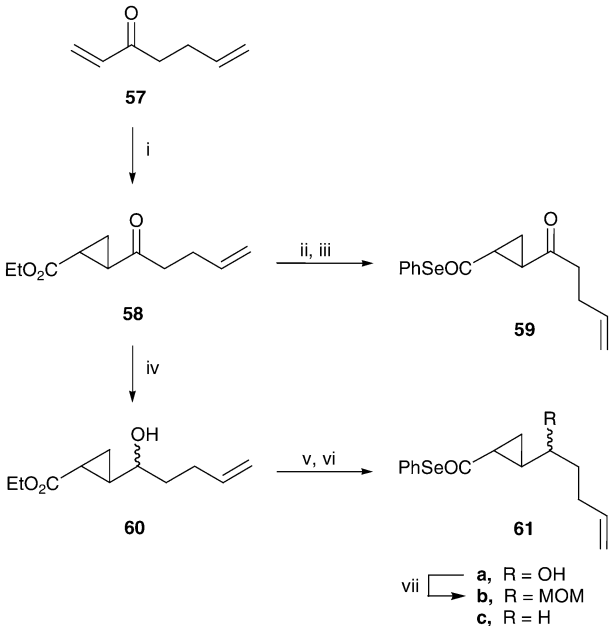


Finally, and in the context of assessing the potential for cyclopropylacyl radical intermediates in the synthesis of bicyclo[4.3.0]nonanes, *viz.* **65**, *via* tandem cyclisation processes, we prepared the substituted *trans*-cyclopropyl selenyl esters **59** and **61**, as shown in Scheme 4. Interestingly, when the keto-substituted cyclopropyl phenyl selenyl ester **59** was treated with Bu_3SnH–AIBN, the resulting acyl radical **62** underwent ring-opening leading to **63**, which then underwent cyclisation *via* the ketene enolate radical **64**, leading to the enol lactone **66** as the sole product in 76% yield; no evidence for the co-formation of the bicyclo[4.3.0]nonandione product **65** was obtained. By contrast, when a 1 : 1 mixture of epimeric alcohols of the *trans* cyclopropyl selenyl ester **61a** was treated with Bu_3SnH–AIBN, the *trans*-fused bicyclo [6.1.0]nonanone **67** (80–95%) was isolated as a mixture of epimeric alcohols. The α-epimer of **67** crystallised, and its structure and stereochemistry were confirmed by X-ray crystal analysis.[15] Likewise, the MOM ether



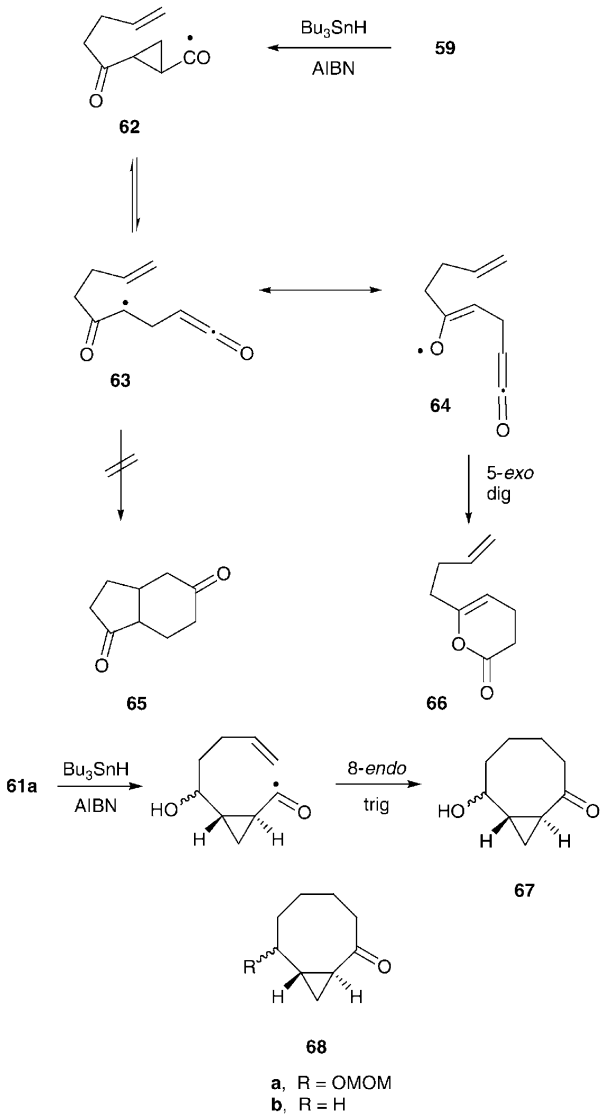
Scheme 3

61b and the desoxy analogue **61c** underwent identical 8-*endo*-trig cyclisation on treatment with Bu_3SnH–AIBN, leading to the corresponding bicyclononanes **68** in excellent yields (79%). The latter cyclisations, leading to bicyclo[6.1.0]nonanes, further emphasise the reluctance of cyclopropyl acyl radicals to undergo ring cleavage to β-ketene alkyl radicals, *i.e.* **18**, unless there is an additional radical-stabilising group (*e.g.* an alkene in the case of **20**, a carbonyl group in the case of **62**) attached to the cyclopropane ring.



Scheme 4 *Reagents*: i, $Me_2S.CHCO_2Et$, CH_2Cl_2, 77%; ii, LiOH, THF–H_2O, 93%; iii, NPSP, Bu_3P, CH_2Cl_2, 93%; iv, $NaBH_4$, EtOH, 98%; v, LiOH, THF–H_2O, 84%; vi, NPSP, Bu_3P, CH_2Cl_2, $^iPr_2NEt$, CH_2Cl_2, 78%.

The studies presented in this paper demonstrate the interesting and unusual reactivity of α,β-unsaturated and cyclopropyl acyl radicals and their ketene alkyl equivalents, particularly in the context of a synthesis of diquinanes, and for elaborating cyclohexenones and bicyclo[6.1.0]nonanes. In the accompanying papers we describe complementary studies of the chemistry of ketene alkyl radicals which contain additional alkene and



cyclopropane ring unsaturation, leading to alternative syntheses of a range of cyclohexenones and diquinanes,[13a] and also to new syntheses of the naturally occurring triquinanes pentalenene and modhephene.[13b]

Experimental

For general experimental details see ref. 4.

Se-Phenyl 3,7-dimethylocta-2*E*,6-dienselenoate 12

N-Phenylselenophthalimide (NPSP) (100 mg, 0.33 mmol) was added in one portion to a stirred solution of 3,7-dimethylocta-2*E*-6-dienoic acid[16] (40 mg, 0.24 mmol) and tributylphosphine (120 µl, 0.48 mmol) in dichloromethane (10 ml) at −20 °C, and the pale yellow mixture was stirred at −20 °C for 1.5 h. Water (5 ml) was added and the mixture was then allowed to warm to room temperature. The separated organic layer was washed successively with water (2 × 5 ml), aqueous potassium carbonate (2 × 5 ml, 10%) and brine (5 ml), and then dried ($MgSO_4$). The solvent was removed *in vacuo* to leave a yellow oil which was purified by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent to give the *selenyl ester* (60 mg, 82%) as a pale yellow oil; ν_{max}(soln. $CHCl_3$)/cm^{-1} 1695, 1614; ^{1}H NMR (270 MHz) δ 7.62–7.54 (2H, m, Ar), 7.42–7.37 (3H, m, Ar), 6.12 (1H, br s, MeC=C*H*COSe), 5.09 (1H, m, Me_2C=C*H*), 2.19–2.15 (4H, m, 2 × CH_2), 2.10 (3H, d, *J* 1 Hz, *Me*C=CHCOSe), 1.73 (3H, s, Me), 1.64 (3H, s, Me); ^{13}C NMR (100 MHz) δ 189.5 (s), 157.8 (s), 135.8 (2 × d), 132.8 (s), 129.2 (2 × d), 128.6 (d), 127.3 (s), 124.4 (d), 122.6 (d), 40.7 (t), 25.9 (t), 25.6 (q), 20.3 (q), 17.7

(q); *m/z* (FAB) found 309.0743 ($M^+ + H$), $C_{16}H_{21}OSe$ requires 309.0758.

3-Methyl-6-isopropylcyclohex-2-en-1-one (piperitone) 13

AIBN (2 mg, 0.1 eq.) was added in one portion, under an atmosphere of argon, to a stirred solution of the selenyl ester **12** (40 mg, 0.13 mmol) in dry, degassed (using argon) benzene (44 ml), and the resulting solution was then heated to the point of reflux. Tributyltin hydride (40 µl, 0.15 mmol) was added in one portion and the mixture was heated under reflux for 1.5 h and then cooled to room temperature. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica using petroleum ether–diethyl ether (2 : 1) as eluent to give the *cyclohexenone* (17 mg, 86%) as a colourless oil; ν_{max}(soln. $CHCl_3$)/cm^{-1} 2931, 2871, 1658, 1464, 1380, 1314, 989, 892; ^{1}H NMR (250 MHz) δ 5.83 (1H, q, *J* 1 Hz, MeC=C*H*CO), 2.36 (1H, sept d, *J* 7, 4.8 Hz, Me_2CH), 2.30 (2H, m), 2.07–1.95 (2H, m), 1.93 (3H, d, *J* 1 Hz, *Me*C=CHCO), 1.81 (1H, ddd, *J* 11.6, 8.2, 4.1, 2.2 Hz, CH_2CHHCH), 0.94 (3H, d, *J* 7 Hz, Me), 0.85 (3H, d, *J* 7 Hz, Me); ^{13}C NMR (67.8 MHz) δ 201.3 (s), 161.1 (s), 126.8 (d), 51.6 (d), 30.4 (t), 27.8 (d), 24.1 (q), 22.9 (t), 20.6 (q), 18.5 (q); *m/z* (EI) found 110.0730 ($M^+ - C_3H_6$), $C_7H_{10}O$ requires 110.0732.

Se-Phenyl 3,7,11-trimethyldodecatri-2*E*,6*E*,10-trienselenoate 14

The selenyl ester was prepared in an identical procedure to that described for the synthesis of *Se*-phenyl 3,7-dimethylocta-2,6-dienselenoate **12**, using 2*E*,6*E*-farnesoic acid (100 mg, 0.42 mmol), NPSP (192 mg, 0.64 mmol), tributylphosphine (211 µl, 0.84 mmol) and dichloromethane (5 ml). Purification by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent gave the *selenyl ester* (92 mg, 58%) as a pale yellow oil; ν_{max}(soln. $CHCl_3$)/cm^{-1} 1695, 1614; ^{1}H NMR (270 MHz) δ 7.57–7.54 (2H, m, Ar), 7.41–7.39 (3H, m, Ar), 6.12 (1H, s, MeC=C*H*COSePh), 5.12 (2H, m, 2 × MeC=C*H*), 2.22–2.16 (4H, m, 2 × CH_2), 2.11 (3H, s, *Me*C=CHCOSePh), 2.07–2.02 (4H, m 2 × CH_2), 1.71 (3H, s, Me), 1.64 (6H, s, 2 × Me); ^{13}C NMR (67.8 MHz) δ 189.5 (s), 157.9 (s), 136.5 (s), 135.8 (2 × d), 131.4 (s), 129.2 (2 × d), 128.6 (d), 127.4 (s), 124.4 (d), 124.1 (d), 122.5 (d), 40.7 (t), 39.6 (t), 26.7 (t), 25.8 (t), 25.7 (q), 20.3 (q), 17.7 (q), 16.0 (q); *m/z* (CI, methane) found 377.1356 ($M^+ + H$), $C_{21}H_{29}OSe$ requires 377.1384.

6-(1,5-Dimethylhex-4-enyl)-3-methylcyclohex-2-en-1-one (bisabolone) 15

The cyclohexenone was prepared from *Se*-phenyl-3,7,11-trimethyldodecatri-2*E*,6*E*,10-trienselenoate **14** (58 mg, 0.15 mmol) using an identical procedure to that described for the preparation of piperitone **13**. Purification by chromatography on silica using petroleum ether–diethyl ether (2 : 1) as eluent gave a 1 : 1 mixture of diastereoisomers of the cyclohexenone (24 mg, 71%) as an oil; ν_{max}(soln. $CHCl_3$)/cm^{-1} 1659, 1456; ^{1}H NMR (250 MHz) δ 5.86/5.83 (1H, s, MeC=C*H*CO), 5.10 (1H, m, Me_2C=C*H*), 2.30–2.28 (2H, m), 2.20–1.76 (6H, complex m), 1.93 (3H, s, *Me*C=CHCO), 1.67 (3H, s, *Me*MeC=CH), 1.59 (3H, s, Me*Me*C=CH), 1.33–1.21 (2H, m), 0.93 (1.5H, d, *J* 6.9 Hz, Me), 0.80 (1.5H, d, *J* 6.8 Hz, Me); ^{13}C NMR (100 MHz) δ 201.1 (s), 161.1/160.9 (s), 131.4/131.2 (s), 127.1/127.0 (d), 124.7/124.5 (d), 51.2/49.8 (d), 34.7/33.3 (t), 30.9/30.6 (t), 30.9/30.2 (d), 26.1/26.0 (t), 25.7 (q), 24.0 (q), 23.4/22.3 (t), 17.6/17.3 (q), 15.6 (q); *m/z* (EI) found 220.1826 (M^+), $C_{15}H_{24}O$ requires 220.1827.

Phenyl *trans*-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropane selenoate 19

Tributylphosphine (1.5 ml, 6.0 mmol) was added dropwise over 10 min to a stirred solution of (±)-*trans*-chrysanthemic acid[17] (0.5 g, 3.0 mmol) and diphenyl diselenide (1.9 g, 6.0 mmol) in benzene (12 ml) at room temperature. The resulting mixture was stirred at room temperature for 24 h and then the solvent was evaporated *in vacuo* to leave an orange residue. The residue was purified by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent to give the *selenyl ester* (770 mg, 83%) as a pale yellow oil; (found C, 62.4, H, 6.8. $C_{16}H_{21}OSe$ requires C, 62.5, H, 6.6%); ν_{max}(film)/cm^{-1} 1711, 1580; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.56–7.37 (5H, m, Ar*H*), 4.91 (1H, br. d, *J* 7.9 Hz, CHC*H*=C), 2.34 (1H, dd, *J* 5.1, 7.9 Hz, cyclopropyl C*H*CH=C), 1.93 (1H, d, *J* 5.1 Hz, cyclopropyl CHC*H*COSePh), 1.73 (3H, s, CH_3C=), 1.69 (3H, s, CH_3C=), 1.26 (3H, s, CH_3), 1.17 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 196.4 (s), 136.0 (s), 135.6 (2 × d), 129.1 (2 × d), 128.5 (d), 127.2 (s), 120.3 (d), 47.1 (d), 35.6 (d), 33.1 (s), 25.5 (q), 21.8 (q), 20.3 (q), 18.4 (q); *m/z* (FAB) found 309.0760 ($M^+ + H$), $C_{16}H_{21}O^{80}Se$ requires 309.0758; found 307.0749, $C_{16}H_{21}O^{78}Se$ requires 307.0765 ($M + H^+$).

6,6-Bis(3,3,6-trimethylhept-4-enal) 25a

Using an identical procedure to that described for the conversion of the selenyl ester **12** into piperitone **13**, the bis(aldehyde) was prepared from the selenyl ester **19** (50 mg, 0.16 mmol), tributyltin hydride (48 µl, 0.18 mmol), AIBN (1 mg) and benzene (54 ml). Purification by chromatography on silica using petroleum ether–diethyl ether (1 : 1) as eluent gave the *dial* (5 mg, 55% (based on secovered selenyl ester)) as a colourless oil; ν_{max}(soln. $CHCl_3$)/cm^{-1} 2855, 1715, 1602; ^{1}H NMR (250 MHz) δ 9.71 (2H, t, *J* 3.2 Hz, 2 × Me_2CH_2CHO), 5.51 (2H, d, *J* 16.2 Hz, Me_2CCH=CHCMe_2), 5.38 (2H, d, *J* 16.2 Hz, Me_2CCH=C*H*CMe_2), 2.34 (4H, d, *J* 3.2 Hz, 2 × Me_2CH_2CHO), 1.15 (12H, s, 4 × Me), 0.93 (12H, s, 4 × Me); ^{13}C NMR (67.8 MHz) δ 203 (2 × d), 135.1 (2 × d), 135.0 (2 × d), 55.3 (2 × t), 40.5 (2 × s), 35.0 (2 × s), 28.2 (4 × q), 23.1 (4 × q); *m/z* (EI) found 153.1258 ($M^+/2$), $C_{10}H_{17}O$ requires 153.1279.

Dimethyl bis(3,3,6,6-tetramethylhex-4-en-6-yloate) 25b

A solution of tributyltin hydride (110 µl, 0.4 mmol) and AIBN (0.15 mmol) in dry degassed benzene (2.2 ml) and methanol (0.3 ml) was added dropwise over 2 h, *via* syringe pump, to a stirred solution of the selenyl ester **19** (100 mg, 0.33 mmol) in dry degassed benzene (120 ml) and methanol (11 ml), under reflux in an atmosphere of argon. The mixture was stirred under reflux overnight, then cooled to room temperature and the solvent was evaporated *in vacuo* to leave a pale yellow oil. The residue was purified by chromatography on silica gel using petroleum ether–diethyl ether (10 : 1) as eluent to give the *dimeric ester* (34 mg, 78% (based on recovered starting material)) as a colourless oil; ν_{max}(film)/cm^{-1} 1738; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (2H, d, *J* 16.1 Hz, 2 × C*H*=CH), 5.33 (2H, d, *J* 16.1 Hz, 2 × CH=C*H*), 3.62 (6H, s, 2 × CO_2CH_3), 2.30 (4H, s, 2 × CH_2CO_2Me), 1.13 (12H, s, 4 × CH_3), 0.91 (12H, s, 4 × CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 172.3 (2 × s), 135.3 (2 × d), 134.1 (2 × d), 51.1 (2 × q), 47.2 (2 × t), 40.2 (2 × s), 35.4 (2 × s), 27.8 (4 × q), 23.0 (4 × q); *m/z* (EI) found 335.2613 ($M^+ - OMe$), $C_{21}H_{35}O_3$ requires 335.2586).

Phenyl 2,2-dimethyl-3-(eth-1-enyl)cyclopropyl selenoate 26

Tributylphosphine (700 µl, 2.8 mmol) was added dropwise over 10 min to a stirred solution of 2,2-dimethyl-3(eth-1-enyl)cyclopropanecarboxylic acid[18] (200 mg, 14 mmol) and diphenyl diselenide (890 mg, 2.8 mmol) in benzene (6 ml) and the mixture was then stirred at room temperature overnight. The solvent was evaporated *in vacuo* and the residue was purified by chromatography using petroleum ether–diethyl ether (10 : 1) as eluent to give the *trans-selenyl ester* (216 mg, 55%) as a pale yellow oil; λ_{max}(EtOH)/nm 245 (1600); ν_{max}(film)/cm^{-1} 1709, 1636; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.60–7.38 (5H, m, Ar*H*), 5.56 (1H, m, C*H*=CH_2), 5.17 (2H, m, CH=CH_2), 2.32 (1H, dd, *J* 5.1, 8.6 Hz, cyclopropyl C*H*), 2.14 (1H, d, *J* 5.1 Hz, cyclopropyl C*H*), 1.27 (3H, s, CH_3), 1.20 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 196.4 (s), 135.7 (2 × d), 134.4 (d), 129.3

(2 × d), 128.8 (d), 127.1 (s), 117.1 (t), 45.9 (d), 39.5 (d), 33.1 (s), 21.6 (q), 20.3 (q); *m/z* (EI) found 280.0365 (M^{++}), $C_{14}H_{16}O^{80}Se$ requires 280.0366; found 123.0821 (M–$SePh^+$, 100%), $C_8H_{11}O$ requires 123.0810.

5,5,-Dimethylcyclohex-3-en-1-one 30

A solution of tributyltin hydride (100 µl, 0.3 mmol) and AIBN (2 mg) in dry degassed benzene (2 ml) was added over 4 h *via* syringe pump to a stirred solution of the selenyl ester **26** (50 mg, 0.18 mmol) and AIBN (2 mg) in benzene (60 ml) under reflux in an atmosphere of argon. The mixture was stirred under reflux for 12 h then cooled to room temperature and the solvent was evaporated *in vacuo*. The residue was purified by chromatography using petroleum ether–diethyl ether (9 : 1 to 5 : 1) as eluent to give the *cyclohexenone* (12 mg, 52%) as a colourless oil; ν_{max}(film)/cm^{-1} 1699; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74–5.62 (2H, m, C*H*=C*H*), 2.83 (2H, m, C(O)CH_2CH=), 2.39 (2H, s, CH_2C(O)), 1.04 (3H, s, CH_3), 0.98 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 209.1 (s), 141.7 (d), 121.4 (d), 48.1 (t), 27.9 (t), 29.8 (s), 18.0 (2 × q).

(±)-Methyl 6-hydroxy-3-methylocta-2*E*,7-dienoate 33a

Vinylmagnesium chloride (900 µl, 15 wt.% in THF) was added dropwise over 10 min to a stirred solution of the aldehyde **32**[19] (200 mg, 1.28 mmol) in THF (10 ml) at 0 °C, and the resulting brown solution was then stirred at this temperature for 1 h. Aqueous saturated ammonium chloride (1 ml) was added carefully and the mixture was then allowed to warm to room temperature. Ether (20 ml) and water (10 ml) were added and the separated aqueous layer was extracted with ether (3 × 20 ml). The combined organic extracts were washed with brine (10 ml) and then dried ($MgSO_4$). The solvent was removed *in vacuo* to leave a brown oil which was purified by chromatography on silica using petroleum ether–diethyl ether (1 : 1) as eluent to give the *alcohol* (150 mg, 64%) as a colourless oil; ν_{max}(soln. $CHCl_3$)/cm^{-1} 3380, 1713, 1650; ^{1}H NMR (250 MHz) δ 5.84 (1H, ddd, *J* 17.3, 10.4, 6.3 Hz, CH_2=C*H*CH(O)), 5.67 (1H, q, *J* 1.2 Hz, MeC=C*H*CO_2), 5.21 (1H, br. d, *J* 17.3 Hz, C*H*H=CHCH(O)), 5.11 (1H, br. d, *J* 10.4 Hz, CH*H*=CHCH(O)), 4.07 (1H, m, CH_2=CHC*H*(O)), 3.66 (3H, s, *Me*O), 2.22 (2H, m, CH_2MeC=CH), 2.14 (3H, d, *J* 1.2 Hz, *Me*C=CHCO_2), 2.04 (1H, br s, O*H*), 1.67 (2H, m, CH_2CH(OH)); ^{13}C NMR (67.8 MHz) δ 167.1 (s), 159.8 (s), 140.6 (d), 115.1 (d), 114.7 (t), 72.0 (d), 50.6 (q), 36.4 (t), 34.3 (t), 18.6 (q); *m/z* (EI) found 169.0864 (M^+ − Me), $C_9H_{13}O_3$ requires 169.0865.

(±)-Methyl 3-methyl-6-methoxymethyloxyocta-2*E*,7-dienoate 33b

Chloromethyl methyl ether (70 µl, 0.92 mmol) was added in one portion to a stirred solution of the alcohol **33a** (150 mg, 0.82 mmol) and diisopropylethylamine (150 µl, 0.86 mmol) in dichloromethane (5 ml), and the resulting solution was stirred at room temperature for 18 h. Water (2 ml) was added and the mixture was stirred vigorously for 30 min. Dichloromethane (10 ml) and water (5 ml) were added and the separated aqueous layer was extracted with dichloromethane (3 × 10 ml). The combined organic extracts were washed with brine, dried ($MgSO_4$) and then concentrated *in vacuo* to leave a pale yellow oil. Purification by chromatography on silica using petroleum ether–diethyl ether (3 : 1) as eluent gave the *ether* (110 mg, 59%) as a colourless oil; ν_{max}(soln. $CHCl_3$)/cm^{-1} 1711, 1649; ^{1}H NMR (400 MHz) δ 5.63 (1H, ddd, *J* 17, 10, 7 Hz, CH_2=C*H*CH(O)), 5.65 (1H, br s, MeC=C*H*CO_2), 5.18 (1H, br. d, *J* 17 Hz, C*H*H=CHCH(O)), 5.17 (1H, br. d, *J* 10 Hz, CH*H*=CHCH(O)), 4.65 (1H, d, *J* 6.8 Hz, MeOC*H*HO), 4.48 (1H, d, *J* 6.8 Hz, MeOCH*H*O), 3.94 (1H, m, CH_2=CHC*H*(O)), 3.63 (3H, s, *Me*O), 3.33 (3H, s, *Me*O), 2.24–2.17 (2H, m, CH_2MeC=CH), 2.13 (3H, s, *Me*C=CHCO_2), 1.75–1.60 (2H, m, CH_2CH(OH)); ^{13}C NMR (100 MHz) δ 167.0 (s), 159.5 (s), 137.8 (d), 117.5 (t), 115.2 (d), 93.7 (t), 76.6 (d), 55.4 (q), 50.6 (q), 36.4 (t), 33.0 (t), 18.7 (q); *m/z* (EI) found 197.1180 (M^+ − OMe), $C_{11}H_{17}O_3$ requires 197.1178.

(±)-*Se*-Phenyl 3-methyl-6-methoxymethyloxyocta-2*E*,7-dienselenoate 34

Lithium hydroxide monohydrate (35 mg, 0.83 mmol) was added in one portion to a stirred solution of the ester **33b** (80 mg, 0.35 mmol) in THF (2.5 ml) and water (2.5 ml), and the mixture was stirred at room temperature for 36 h. The mixture was acidified to pH ~2 with hydrochloric acid (*ca.* 2 ml, 2 M) and then diluted with water (2 ml) and ether (10 ml). The separated aqueous phase was extracted with ether (3 × 10 ml), and the combined organic layers were washed with brine (10 ml) and then dried ($MgSO_4$). The solvent was removed *in vacuo* to leave a colourless oil which was purified by chromatography on silica using petroleum ether–diethyl ether (1 : 1) as eluent to give the corresponding *carboxylic acid* (70 mg, 93%) as a colourless oil; ν_{max}(soln. $CHCl_3$)/cm^{-1} 3200 (br), 1693, 1644; ^{1}H NMR (270 MHz) δ 5.71 (1H, ddd, *J* 17.5, 9.9, 7.6 Hz, CH_2=C*H*CH(O)), 5.72 (1H, br s, MeC=C*H*CO_2), 5.23 (1H, br. d, *J* 17.5 Hz, C*H*H=CHCH(O)), 5.22 (1H, br. d, *J* 9.9 Hz, CH*H*=CHCH(O)), 4.71 (1H, d, *J* 6.8 Hz, MeOC*H*HO), 4.54 (1H, d, *J* 6.8, MeOCH*H*O), 3.99 (1H, m, CH_2=CHC*H*(O)), 3.38 (3H, s, *Me*O), 2.37–2.21 (2H, m, CH_2MeC=CH), 2.18 (3H, d, *J* 1.3 Hz, *Me*C=CHCO_2), 1.86–1.62 (2H, m, CH_2CH(OH)); ^{13}C NMR (67.8 MHz) δ 172.0 (s), 162.5 (s), 137.7 (d), 117.8 (t), 115.3 (d), 93.7 (t), 76.7 (d), 55.5 (q), 36.8 (t), 33.0 (t), 19.1 (q); *m/z* (EI) found 169.0866 (M^+ − CH_2OMe), $C_9H_{13}O_3$ requires 169.0865.

The selenyl ester was prepared from the carboxylic acid (70 mg, 0.33 mmol) in an identical procedure to that described for the preparation of *Se*-phenyl 3,7-dimethylocta-2,6-dienselenoate **12**, using NPSP (148 mg, 0.49 mmol), tributylphosphine (163 µl, 0.65 mmol) and dichloromethane (5 ml). Purification by chromatography on silica using petroleum ether–diethyl ether (3 : 1) as eluent gave the *selenyl ester* (72 mg, 62%) as a 2 : 1 mixture of 2*E* and 2*Z* geometric isomers. Data for 2*E* isomer only: ν_{max}(soln. $CHCl_3$)/cm^{-1} 1696, 1615; ^{1}H NMR (270 MHz) δ 7.67–7.52 (2H, m, Ar), 7.42–7.33 (3H, m, Ar), 6.14 (1H, q, *J* 1.3 Hz, MeC=C*H*COSe), 5.69 (1H, ddd, *J* 17.5, 9.9, 7.6 Hz, CH_2=C*H*CH(O)), 5.23 (1H, br. d, *J* 17.5 Hz, C*H*H=CHCH(O)), 5.22 (1H, br. d, *J* 9.9 Hz, CH*H*=CHCH(O)), 4.72 (1H, d, *J* 6.8 Hz, MeOC*H*HO), 4.56 (1H, d *J* 6.8 Hz, MeOCH*H*O), 4.01 (1H, m, CH_2=CHC*H*(O)), 3.41 (3H, s, *Me*O), 2.31–2.17 (2H, m, CH_2MeC=CH), 2.10 (3H, d, *J* 1.3 Hz, *Me*C=CHCOSe), 1.85–1.62 (2H, m, CH_2CH(OH)); ^{13}C NMR (67.8 MHz) δ 189.5 (s), 157.5 (s), 137.7 (d), 135.8 (2 × d), 129.2 (2 × d), 128.7 (d), 127.1 (s), 124.5 (d), 117.9 (t), 93.8 (t), 76.5 (d), 55.6 (q), 36.4 (t), 32.9 (t), 20.3 (q); *m/z* (EI) found 197.1170 (M^+ − SePh), $C_{11}H_{17}O_3$ requires 197.1178.

6aβ-Methyl-4β-methoxymethyloxy-1,2,3,3aβ,4α,5,6,6a-hexahydropentalen-2-one and 6aβ-methyl-4α-methoxymethyloxy-1,2,3,3aβ,4β,5,6,6a-hexahydropentalen-2-one 38

A solution of tributyltin hydride (60 µl, 0.22 mmol) in dry, degassed (using argon) benzene (5 ml) was added *via* syringe pump, over 2 h, to a refluxing solution of the selenyl ester **34** (70 mg, 0.20 mmol) and AIBN (3 mg) in dry, degasssed (using argon) benzene (60 ml). The solution was heasted under reflux for 1 h and then cooled to room temperature. The solvent was removed *in vacuo* to leave a residue which was purified by chromatography on silica using petroleum ether–diethyl ether (3 : 1) as eluent to give a 2 : 1 mixture of diastereoisomers of the *diquinane* (26 mg, 76%) as an oil; ν_{max}(soln. $CHCl_3$)/cm^{-1} 1732, 1668; ^{1}H NMR (400 MHz) data for major isomer: δ 4.65 (1H, d, *J* 6.8 Hz, MeOC*H*HO), 4.62 (1H, d, *J* 6.8 Hz, MeOCH*H*O), 3.85 (1H, m, CH_2C*H*(O)), 3.36 (3H, s, *Me*O), 2.60 (1H, dd, *J* 18.8,

9.8 Hz, COC*H*HCH), 2.50 (1H, d, *J* 14.5 Hz, C*H*HCOCH$_2$CH), 2.34–1.61 (7H, complex m), 1.27 (3H, s, Me); data for minor isomer (where not obscured by major isomer): δ 4.63 (1H, d, *J* 6.7 Hz, MeOC*H*HO), 4.54 (1H, d, *J* 6.7 Hz, MeOCH*H*O), 4.18 (1H, m, CH$_2$C*H*(O)), 3.35 (3H, s, *Me*O), 1.19 (3H, s, Me); ^{13}C NMR (67.8 MHz) data for major isomer: δ 219.0 (s), 95.4 (t), 85.0 (d), 55.3 (q), 53.0 (d), 52.5 (t), 45.3 (s), 42.7 (t), 37.8 (t), 31.4 (t), 28.6 (q); data for minor isomer (where not obscured by major isomer) 219.9 (s), 80.0 (d), 55.5 (q), 53.3 (t), 51.0 (d), 45.5 (s), 38.3 (t), 37.7 (t), 28.9 (q); *m*/*z* (EI) found 198.1263 (M$^+$), $C_{11}H_{18}O_3$ requires 198.1256.

S-[2-(2-Iodophenyl)ethyl] thio-3-methylocta-2,7-dienoate 39

Following the general procedures described in the accompanying paper,[13a] a solution of hept-6-en-2-one[20] (200 mg, 1.8 mol) in THF (1 ml) was treated with sodium hydride (60% dispersion, 170 mg, 4.3 mmol) and triethylphosphonoacetate (0.9 ml, 4.5 mmol) in THF (3 ml). Sodium hydroxide (200 mg) was added in one portion to a solution of the crude α,β-unsaturated ester in refluxing ethanol (3.0 ml) and water (0.3 ml). The mixture was stirred under reflux for 1 h, then cooled to room temperature and evaporated *in vacuo*. The residue was washed with diethyl ether (20 ml), and the separated aqueous layer was acidified with HCl (2 mol dm^{-3}) and extracted with diethyl ether (3 × 20 ml). The combined organic extracts were dried (MgSO$_4$) and concentrated *in vacuo* to leave a 1 : 4 mixture of the *Z*- and *E*-isomers of 3-methylocta-2,7-dienoic acid (219 mg, 94%), as a clear colourless viscous oil; ν_{max}(film)/cm^{-1} 2936 (br), 1690, 1639; ^{1}H NMR (250 MHz, CDCl$_3$) δ 5.79 (1H, ddt, *J* 6.7, 10.3, 17.0 Hz, C*H*=CH$_2$), 5.71 (1H, br s, C*H*=C(CH$_3$)), 5.08–4.95 (2H, m, CH=C*H*$_2$), 2.17 (3H, s, CH=C(C*H*$_3$)), 2.16 (2H, t, *J* 7.5 Hz, CH$_2$C*H*$_2$C(CH$_3$)=), 2.06 (2H, app. q, *J* 7.5 Hz, CH$_2$C*H*$_2$CH=), 1.60 (2H, app. qn, *J* 7.5 Hz, CH$_2$C*H*$_2$CH$_2$); ^{13}C NMR (67.8 MHz, CDCl$_3$) major (*E*) isomer: δ 172.5 (s), 163.2 (s), 137.9 (d), 115.3 (d), 115.1 (t), 40.5 (t), 33.2 (t), 26.5 (t), 19.0 (q); minor (*Z*) isomer: δ 172.0 (s), 163.7 (s), 138.3 (d), 115.8 (d), 114.2 (t), 41.8 (t), 33.7 (t), 27.4 (t), 25.5 (q); *m*/*z* (EI) found 154.099 (M$^+$), $C_9H_{14}O_2$ requires 154.0994.

DCC (63 mg, 0.3 mmol) and DMAP (63 mg, 0.5 mmol) were added in one portion to a stirred solution of the carboxylic acid (40 mg, 0.26 mmol) in dichloromethane (4 ml) at room temperature. The mixture was stirred at room temperature for 5 min, and then a solution of 2-(2-iodophenyl)ethanethiol[21] (82 mg, 0.3 mmol) in dichloromethane (0.5 ml) was added in one portion. The mixture was stirred at room temperature for 3 h, and the solvent was then evaporated *in vacuo* to leave a residue. Purification by chromatography on silica using petroleum ether–diethyl ether (10 : 1) as eluent gave a 1 : 4 mixture of *Z*- and *E*-isomers of the *thiol ester* (93 mg, 89%) as a colourless oil; ν_{max}(film)/cm^{-1} 1673, 1622; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.82 (1H, d, *J* 8.1 Hz, Ar*H*), 7.32–7.27 (2H, m, Ar*H*), 6.91 (1H, m, Ar*H*), 5.99 (1H, br s, C*H*=C(CH$_3$)), 5.80 (1H, ddt, *J* 6.7, 10.4, 17.1 Hz, C*H*=CH$_2$), 5.06–4.97 (2H, m, CH=C*H*$_2$), 3.15 (2H, t, *J* 8.4 Hz, CH$_2$C*H*$_2$S), 3.02 (2H, t, *J* 8.4 Hz, C*H*$_2$CH$_2$S), 2.17 (3H, s, CH$_3$), 2.12 (2H, t, *J* 7.5 Hz, CH$_2$C*H*$_2$C(CH$_3$)=), 2.07 (2H, app. q, *J* 7.5 Hz, CH$_2$C*H*$_2$CH=), 1.55 (2H, app qn, *J* 7.5 Hz, CH$_2$C*H*$_2$CH$_2$); ^{13}C NMR (100.6 MHz, CDCl$_3$) major isomer: δ 188.9 (s), 157.0 (s), 142.8 (s), 139.5 (d), 137.9 (d), 130.0 (d), 128.3 (d), 128.2 (d), 100.4 (s), 40.7 (t), 40.0 (t), 33.1 (t), 28.7 (t), 26.5 (t), 19.7 (q); minor isomer: δ 188.3 (s), 156.4 (s), 142.8 (s), 139.5 (d), 138.4 (d), 130.0 (d), 128.3 (d), 128.2 (d), 123.4 (d), 114.7 (t), 100.4 (s), 40.7 (t), 40.6 (t), 33.8 (t), 28.7 (t), 27.4 (t), 24.9 (q); *m*/*z* (CI) found 401.0436 (M$^+$ + H), $C_{17}H_{21}IOS$ requires 401.0436.

cis-Hexahydro-3a-methylpentalen-2(1*H*)-one 40 and 3-methylocta-2,7-dien-1-al 41

Tributyltin hydride (60 µl, 0.16 mmol) was added in one portion to a stirred solution of the thiol ester **39** (50 mg, 0.13 mmol) and AIBN (2 mg) in dry degassed benzene (42 ml), under an atmosphere of argon, and the mixture was then heated under reflux for 1 h. The mixture was cooled to room temperature and the benzene was then evaporated *in vacuo*. The residue was purified by chromatography on silica using petroleum ether–diethyl ether as eluent to give: (i), the *aldehyde* **41** (8 mg, 46%) (eluted first) as a colourless oil; ν_{max}(soln. CHCl$_3$)/cm^{-1} 1731, 1666; ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 191.0 (d), 171.2 (s), 138.7 (d), 137.8 (d), 127.4 (t), 39.9 (t), 33.1 (t), 26.3 (q), 23.0 (t); *m*/*z* (EI) (found 109.1018. C_8H_{13} requires 109.1017 (M$^+$ − CHO, 4%), and (ii), the *diquinane* **40** (7 mg, 41%) (eluted second) as an oil; ν_{max}(soln. CHCl$_3$)/cm^{-1} 2850, 1731 (lit.[22] (soln. CHCl$_3$)/cm^{-1} 2861, 1737); ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.54 (2H, dd, *J* 9.1, 18.6 Hz, CHC*H*$_2$C(O)), 2.25 (1H, d, *J* 18.6 Hz, C*H*HC(O)), 2.15 (1H, d, *J* 18.6 Hz, CH*H*C(O)), 2.11–1.98 (3H, m, C*H* + C*H*$_2$), 1.75 (2H, app. qn, *J* 7.6 Hz, CH$_2$C*H*$_2$CH$_2$), 1.66–1.58 (2H, m, C*H*$_2$), 1.18 (3H, s, C*H*$_3$); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 217.0 (s), 51.7 (t), 46.9 (s), 46.8 (d), 5.0 (t), 39.9 (t), 32.9 (t), 27.8 (s), 27.5 (q), 24.3 (t); *m*/*z* (EI) found 138.1056 (M$^+$), $C_9H_{14}O$ requires 138.1045.

Ethyl 3-methyloct-2-en-7-yn-1-oate 45

Dichloromethane (30 ml) was added in one portion to a vigorously stirred mixture of pyridinium chlorochromate (4.9 g, 22.5 mmol) and silica (4.9 g) at room temperature, and the mixture was stirred for 5 min. A solution of hept-6-yn-2-ol **44** (1.7 g, 15 mmol) in dichloromethane (1 ml) was added in one portion and the mixture was stirred at room temperature for 2 h and then filtered through a short column of silica using dichloromethane as eluent. The filtrate was evaporated to leave a solution of 6-heptyn-2-one[23] in CH_2Cl_2 which was used directly in the next stage.

A solution of triethylphosphonoacetate (9.3 ml, 47 mmol) in THF (16 ml) was added dropwise over 15 min to a stirred suspension of sodium hydride (1.1 g, 45 mmol) in THF (8 ml) at room temperature. The mixture was stirred at room temperature for 30 min and then the solution of the 6-heptyn-2-one[23] in dichloromethane (5 ml) and THF (8 ml) was added dropwise *via* cannula, over 5 min. The mixture was stirred for 2 h, then saturated NH_4Cl solution (10 ml) was added dropwise over 10 min, and the mixture was evaporated *in vacuo*. The residue was partitioned between water (50 ml) and diethyl ether (50 ml) and the separated aqueous layer was then extracted with diethyl ether (3 × 30 ml). The combined organic extracts were washed with water (30 ml) and brine (30 ml), dried (MgSO$_4$) and concentrated under reduced pressure to leave a yellow oil. The residue was purified by chromatography on silica using petroleum ether–diethyl ether as eluent to give a 1 : 4 mixture of *Z*- and *E*-isomers of the *α,β-unsaturated ester* (1.2 g, 44%) as a colourless oil; ν_{max}(film)/cm^{-1} 1716, 1650; ^{1}H NMR (250 MHz, CDCl$_3$) δ 5.70 (1H, s, C*H*=C), 4.18–4.11 (2H, m, OC*H*$_2$CH$_3$), 2.29–2.24 (2H, m, C*H*$_2$C=), 2.21 (2H, dt, *J* 2.6, 7.0 Hz, C*H*$_2$C≡), 2.17 (3H, s, CH=C(C*H*$_3$)), 1.99 (1H, t, *J* 2.6 Hz, C*H*≡C), 1.72 (2H, m, CH$_2$C*H*$_2$CH$_2$), 1.30–1.22 (3H, m, OCH$_2$C*H*$_3$); ^{13}C NMR (100.6 MHz, CDCl$_3$) major (*E*) isomer: δ 201.2 (s), 158.6 (s), 116.2 (d), 83.6 (s), 68.9 (d), 59.5 (t), 29.7 (t), 26.2 (t), 18.7 (q), 17.9 (t), 14.3 (q); minor (*Z*) isomer: δ 201.2 (s), 157.6 (s), 116.9 (d), 84.5 (s), 68.5 (d), 59.5 (t), 32.6 (t), 27.1 (t), 18.5 (q), 17.9 (t), 14.1 (q); *m*/*z* (EI) found 135.0824 (M$^+$ − OEt), $C_9H_{11}O$ requires 135.0810.

Phenyl 3-methyloct-2-en-7-ynyl selenoate 46

Following the general procedures described in the accompanying paper,[13a] a solution of the ester **45** (400 mg, 2.2 mmol) in ethanol (5 ml) and water (0.5 ml) was treated with sodium hydroxide (400 mg) to give a 1 : 4 mixture of *Z*- and *E*-isomers of 3-methyloct-2-en-7-yn-1-oic acid (300 mg, 90%), as a yellow oil; ν_{max}(film)/cm^{-1} 3302 (br), 2963 (br), 1693, 1643; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.69 (1H, br s, CH=C(CH$_3$)), 2.25 (2H, app. q, *J* 7.1 Hz, C*H*$_2$C(CH$_3$)), 2.18 (2H, dt, *J* 7.1,

2.9 Hz, $CH_2C{\equiv}CH$), 2.14 (3H, s, CH_3), 1.93 (1H, t, *J* 2.9 Hz, $CH_2C{\equiv}CH$), 1.69 (2H, app. qn, *J* 7.1 Hz, $CH_2CH_2CH_2$); ^{13}C NMR (67.8 MHz, $CDCl_3$) major (*E*) isomer: δ 172.1 (s), 162.6 (s), 115.6 (d), 83.7 (s), 69.1 (d), 39.8 (t), 26.0 (t), 19.0 (q), 17.9 (t); minor (*Z*) isomer: δ 171.5 (s), 163.2 (s), 115.9 (d), 84.2 (s), 68.7 (d), 42.3 (t), 28.7 (t), 24.6 (q), 18.6 (t); *m/z* (EI) found 152.0837 (M^+), $C_9H_{12}O_2$ requires 152.0837.

A solution of the carboxylic acid (200 mg, 1.3 mmol) in dichloromethane (18 ml) was then treated with tributylphosphine (500 µl, 2.0 mmol) and *N*-phenylselenophthalimide (600 mg, 2.0 mmol). The crude product was purified by chromatography on silica using petroleum ether–diethyl ether (10 : 1) as eluent to give a 1 : 4 mixture of *Z*- and *E* -isomers of the *selenyl ester* (250 mg, 67%) as a pale yellow oil; ν_{max}(film)/cm^{-1} 1951, 1875, 1698, 1614; major (*E*) isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.38 (5H, m, Ar*H*), 6.14 (1H, s, $CH{=}C(CH_3)$), 2.60 (2H, t, *J* 7.2 Hz, $CH_2C(CH_3)$), 2.20 (2H, dt, *J* 2.5, 7.2 Hz, $CH_2C{\equiv}CH$), 1.95 (1H, t, *J* 2.5 Hz, $CH_2C{\equiv}CH$), 1.89 (3H, s, CH_3), 1.69 (2H, m, $CH_2CH_2CH_2$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 189.8 (s), 157.3 (s), 135.8 (2 × d), 129.3 (2 × d), 128.9 (s), 128.8 (d), 125.5 (d), 83.4 (s), 68.7 (d), 34.0 (t), 26.9 (t), 24.2 (q), 18.5 (t); minor (*Z*) isomer (where observed): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99 (1H, t, *J* 2.5 Hz, $CH_2C{\equiv}CH$), 1.86 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 126.4 (d), 22.3 (q); *m/z* (FAB) found 293.0439 ($M^+ + H$), $C_{15}H_{17}O^{80}Se$ requires 293.0445; found 291.0500, $C_{15}H_{17}O^{78}Se$ requires 291.0452.

3-Methyloct-2-en-7-yn-1-al

A solution of tributyltin hydride (110 µl, 0.3 mmol) and AIBN (2 mg) in dry degassed benzene (2 ml) was added dropwise over 5 h, *via* syringe pump, to a stirred solution of the selenyl ester **46** (80 mg, 0.27 mmol) and AIBN (3 mg), in benzene (90 ml) under reflux in an atmosphere of argon. The mixture was stirred under reflux for 6 h, then cooled to room temperature and the benzene was evaporated *in vacuo* to leave a colourless oil. The oil was purified by chromatography on silica using petroleum ether–diethyl ether (5 : 1) as eluent to give the *aldehyde* (17 mg, 46%) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (1H, d, *J* 8.0 Hz, C*H*O), 5.91 (1H, br. d, *J* 8.0 Hz, C=C*H*CHO), 2.35 (2H, t, *J* 6.9 Hz, $CH_2CH_2C(CH_3)$=), 2.23 (2H, dt, *J* 2.5, 6.9 Hz, $CH_2C{\equiv}CH$), 2.18 (3H, s, CH_3), 2.00 (1H, t, *J* 2.5 Hz, $CH_2C{\equiv}CH$), 1.8–1.68 (2H, m, $CH_2CH_2CH_2$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 191.2 (d), 162.2 (s), 127.6 (d), 83.4 (s), 69.2 (d), 39.3 (t), 25.8 (t), 23.4 (t), 17.9 (q); *m/z* (EI) found 121.0651($M^+ - CH_3$), C_8H_9O requires 121.0653.

Se-Phenyl (*E*,*Z*)-3-methyl-2,7,8-nonatrieneselenoate 48

Triethyl phosphonoacetate (1.10 ml, 5.54 mmol) was added to a stirred suspension of sodium hydride (60% dispersion in mineral oil; 210 mg, 5.25 mmol), previously washed with dry THF, in dry THF (6 ml) at 0 °C under a nitrogen atmosphere. The resulting colourless solution was stirred at room temperature for 30 min, then a solution of octa-6,7-dien-2-one (451 mg, 3.63 mmol)[24] in THF (1 ml) was added, and the mixture was stirred at room temperature for 4 h. Saturated aqueous NH_4Cl was added, then water, and the mixture was extracted with ether. The combined organic extracts were washed with brine, dried and evaporated *in vacuo*. The residue was purified by chromatography on silica using petroleum ether as eluent to give a 7 : 2 mixture of *E*- and *Z*-isomers of ethyl 3-methyl-2,7,8-nonatrienoate (610 mg, 87%) as a colourless liquid (found, C, 74.4%; H, 9.3%. $C_{12}H_{18}O_2$ requires C, 74.2%; H, 9.3%); ν_{max}(film)/cm^{-1} 1956, 1715, 1648; ^{1}H NMR 2*E* isomer: (360 MHz, $CDCl_3$) δ 1.27 (3H, t, *J* 7.1 Hz, $CO_2CH_2CH_3$), 1.56–1.64 (2H, m, $=CHCH_2CH_2$), 1.96–2.03 (2H, m, $=CHCH_2$), 2.15 (3H, d, *J* 1.3 Hz, $=CCH_3$), 2.15–2.21 (2H, m, $=C(CH_3)CH_2$), 4.13 (2H, q, *J* 7.1 Hz, $CO_2CH_2CH_3$), 4.67 (2H, dt, *J* 6.7, 3.3 Hz, $=CH_2$), 5.08 (1H, app. qn, *J* 6.7 Hz, $=CHCH_2$), 5.65–5.67 (1H, m, $=CHCO_2Et$); 2*Z* isomer: (360 MHz, $CDCl_3$) δ 1.27 (3H, t, *J* 7.1 Hz, $CO_2CH_2CH_3$), 1.55–1.64 (2H, m, $=CHCH_2CH_2$), 1.89 (3H, d, *J* 1.4 Hz, $=CCH_3$), 2.02–2.10 (2H, m, $=CHCH_2$), 2.64–2.68 (2H, m, $=C(CH_3)CH_2$), 4.14 (2H, q, *J* 7.1 Hz, $CO_2CH_2CH_3$), 4.66 (2H, dt, *J* 6.7, 3.3 Hz, $=CH_2$), 5.13 (1H, app. qn, *J* 6.7 Hz, $=CHCH_2$), 5.65–5.68 (1H, m, $=CHCO_2Et$); ^{13}C NMR (125 MHz) 2*E* isomer: δ 14.3 (q), 18.7 (q), 26.6 (t), 27.5 (t), 40.2 (t), 59.4 (t), 75.0 (t), 89.3 (d), 115.8 (d), 159.6 (s), 166.8 (s), 208.6 (s); 2*Z* isomer: δ 14.3 (q), 25.1 (q), 27.6 (t), 28.2 (t), 32.8 (t), 59.4 (t), 74.8 (t), 89.7 (d), 116.3 (d), 160.1 (s), 166.3 (s), 208.6 (s); *m/z* (EI) found 194.1298 (M^+), $C_{12}H_{18}O_2$ requires 194.1307.

A solution of the mixture of isomers of ethyl 3-methyl-2,7,8-nonatrienoate (315 mg, 1.62 mmol) in methanol (7.5 ml) and water (6 ml) was heated with sodium hydroxide (128 mg, 3.20 mmol) at 70 °C for 2 h. The methanol was removed under reduced pressure and the residue was then extracted into ether. Saturated aqueous NH_4Cl was added to the aqueous phase, and the product was extracted twice into ether. The combined ether extracts were dried and the solvents were evaporated to leave a 7 : 2 mixture of *E*- and *Z*-isomers of the corresponding carboxylic acid (170 mg, 64%) as a colourless oil. No satisfactory microanalytical data could be obtained; ν_{max}(film)/cm^{-1} 3500–2500 (br), 1956, 1692, 1639; ^{1}H NMR 2*E* isomer: (360 MHz, $CDCl_3$) δ 1.59–1.67 (2H, m, $=CHCH_2CH_2$), 1.98–2.06 (2H, m, $=CHCH_2$), 2.18 (3H, d, *J* 1.2 Hz, CH_3), 2.20–2.24 (2H, m, $=C(CH_3)CH_2$), 4.69 (2H, dt, *J* 6.7, 3.3 Hz, $=CH_2$), 5.10 (1H, app. qn, *J* 6.7 Hz, $=CHCH_2$), 5.69–5.72 (1H, m, $=CHCO_2H$); 2*Z* isomer: 1.57–1.67 (2H, m, $=CHCH_2CH_2$), 1.94 (3H, d, *J* 1.3 Hz, CH_3), 2.02–2.09 (2H, m, $=CHCH_2$), 2.67–2.70 (2H, m, $=C(CH_3)CH_2$), 4.68 (2H, dt, *J* 6.6, 3.3 Hz, $=CH_2$), 5.10–5.16 (1H, m, $=CHCH_2$), 5.71 (1H, br. s, $=CHCO_2H$); ^{13}C NMR (125 MHz) 2*E* isomer: 19.0 (q), 26.6 (t), 27.5 (t), 40.4 (t), 75.1 (t), 89.3 (d), 115.3 (d), 163.0 (s), 172.3 (s), 208.6 (s); 2*Z* isomer: δ 25.5 (q), 27.5 (t), 28.1 (t), 32.9 (t), 74.9 (t), 89.6 (d), 115.6 (d), 163.5 (s), 170.7 (s), 208.6 (s); *m/z* (EI) found 166.0985 (M^+), $C_{10}H_{14}O_2$ requires 166.0994, 148.0888 ($M^+ - H_2O$), $C_{10}H_{14}O_2$ requires 148.0888.

Tri-*n*-butylphosphine (0.40 ml, 1.61 mmol) was added to a solution of the above carboxylic acid (180 mg, 1.08 mmol) in dry CH_2Cl_2 (5 ml) at −35 °C under a nitrogen atmosphere, and the mixture was stirred at −30 °C for 20 min. NPSP (492 mg, 1.63 mmol) was added in one portion, and the resulting yellow mixture was stirred at −30 °C for 15 min. The cooling bath was removed, and the mixture was diluted with ether (40 ml). The solution was washed with water (2 × 20 ml), then brine, and dried. The solvents were removed under reduced pressure to leave a residue which was purified by chromatography on silica using 0–1% diethyl ether–petroleum ether as eluent to give an 8 : 3 mixture of *E*- and *Z*-isomers of the *selenyl ester* (270 mg, 82%) as a pale yellow oil. No satisfactory microanalytical data could be obtained; λ_{max}(EtOH)/nm 2*Z* isomer: 299 (5400); ν_{max}(film)/cm^{-1} 1954, 1700, 1615, 1578; ^{1}H NMR 2*E* isomer: (360 MHz, $CDCl_3$) δ 1.62–1.68 (2H, m, $=CHCH_2CH_2$), 2.01–2.06 (2H, m, $=CHCH_2$), 2.10 (3H, d, *J* 1.2 Hz, CH_3), 2.15–2.19 (2H, m, $=C(CH_3)CH_2$), 4.73 (2H, dt, *J* 6.7, 3.3 Hz, $=CH_2$), 5.11 (1H, app. qn, *J* 6.7 Hz, $=CHCH_2$), 6.11–6.14 (1H, m, $=CHCOSePh$), 7.36–7.42 (3H, m, 3 × Ar*H*), 7.52–7.57 (2H, m, 2 × Ar*H*); 2*Z* isomer: δ 1.53–1.62 (2H, m, $=CHCH_2CH_2$), 1.88 (3H, d, *J* 1.3 Hz, CH_3), 1.99–2.07 (2H, m, $=CHCH_2$), 2.54–2.58 (2H, m, $=C(CH_3)CH_2$), 4.66 (2H, dt, *J* 6.7, 3.3 Hz, $=CH_2$), 5.09 (1H, app. qn, *J* 6.7 Hz, $=CHCH_2$), 6.10–6.12 (1H, m, $=CHCOSePh$), 7.38–7.43 (3H, m, 3 × Ar*H*), 7.50–7.58 (2H, m, 2 × Ar*H*); ^{13}C NMR 2*E* isomer: δ 20.2 (q), 26.5 (t), 27.5 (t), 40.0 (t), 75.2 (t), 89.2 (d), 124.6 (d), 127.2 (s), 128.7 (d), 129.2 (2 × d), 135.8 (2 × d), 157.9 (q), 189.5 (s), 208.6 (s); 2*Z* isomer: δ 24.5 (q), 27.4 (t), 28.1 (t), 34.3 (t), 74.9 (t), 89.5 (d), 125.1 (d), 127.2 (s), 128.7 (d), 129.2 (2 × d), 135.7 (2 × d), 158.4 (s), 188.9 (s), 208.5 (s); *m/z* (ES) found 307.0612 ($M^+ + H$), $C_{16}H_{18}OSe$ requires 307.0601.

2,7-Dimethylcycloocta-2,7-dienone 56

A solution of tributyltin hydride (0.28 ml, 1.04 mmol) and AIBN (22 mg, 0.13 mmol) in dry, degassed benzene (5 ml) was added dropwise (*via* syringe pump) over 6.5 h to a stirred, refluxing solution of a 2 : 1 mixture of *E*- and *Z*-isomers of the selenyl ester **48** (245 mg, 0.80 mmol) and AIBN (17 mg, 0.10 mmol) in dry, degassed benzene (285 ml), under an argon atmosphere. The mixture was heated under reflux for a further 8.5 h, then allowed to cool to room temperature and evaporated under reduced pressure. The residue was purified by chromatography on silica using 0.3% diethyl ether–petroleum ether as eluent to give: (i), the *cyclooctadienone* (30 mg, 25%), as a colourless oil; λ_{max}(EtOH)/nm 254 (7100); ν_{max}(film)/cm^{-1} 1673; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.67–1.76 (2H, m, =CCH$_2$CH_2), 1.94–1.95 (6H, m, 2 × CH_3), 2.23–2.32 (2H, m, =CHCH_2), 2.36–2.39 (2H, m, =C(CH$_3$)CH_2), 6.16 (1H, tq, *J* 9.0, 1.4 Hz, =C*H*CH$_2$), 6.24 (1H, q, *J* 1.3 Hz, =C*H*CO); ^{13}C NMR 20.4 (q), 25.0 (t), 26.3 (q), 27.0 (t), 30.4 (t), 132.2 (d), 135.6 (d), 140.9 (s), 152.5 (s), 194.6 (s); *m*/*z* (EI) 150.1047 (M$^+$), $C_{10}H_{14}O$ requires 150.1045, and (ii), unreacted starting material (44 mg, 18%).

Ethyl *trans*-2-(1-oxo-4-pentenyl)cyclopropanoate 58

Ethyl(sulfuranylidene) acetate[25] (4.7 g, 32 mmol) was added dropwise over 5 min to a stirred solution of hepta-1,6-dien-3-one **57** (3.3 g, 30 mmol) in dichloromethane (60 ml) at room temperature, and the mixture was then stirred at room temperature for 24 h. The mixture was evaporated under reduced pressure to leave a pale yellow oil which was purified by chromatography on silica using petroleum ether–diethyl ether (5 : 1) as eluent to give the *cyclopropyl ester* (4.5 g, 77%) as a colourless, sweet smelling oil; (found C, 67.0; H, 8.4. $C_{11}H_{16}O_3$ requires C, 67.3; H, 8.2%); ν_{max}(film)/cm^{-1} 1734, 1704, 1642; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (1H, ddt, *J* 6.5, 10.6, 17.5 Hz, CH$_2$C*H*=CH$_2$), 5.04 (1H, dd, *J* 1.5, 17.5 Hz, CH=C*H*H), 4.98 (1H, dd, *J* 1.5, 10.6 Hz, CH=CH*H*), 4.14 (2H, q, *J* 7.1 Hz, OCH_2CH$_3$) δ 2.71 (2H, t, *J* 7.2 Hz, C(O)CH_2CH$_2$), 2.45 (1H, m, C(O)C*H*), 2.35 (2H, app.q, *J* 7.2 Hz, CH$_2$CH_2CH=), 2.15 (1H, m, C*H*CO$_2$Et), 1.42 (2H, app. t, *J* 7.2 Hz, cyclopropyl CH_2), 1.26 (3H, t, *J* 7 Hz, OCH$_2$CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 206.6 (s), 171.9 (s), 136.7 (d), 115.3 (t), 60.9 (t), 42.9 (t), 28.9 (d), 27.6 (t), 23.9 (d), 16.9 (t), 14.1 (q); *m*/*z* (EI) found 196.1093 (M$^+$), $C_{11}H_{16}O_3$ requires 196.1099.

Phenyl *trans*-2-(1-oxo-4-pentenyl)cyclopropylselenoate 59

Following the general procedures described in the accompanying paper,[13a] a solution of the cyclopropyl ester **58** (1.0 g, 5.0 mmol) in THF (25 ml) and water (25 ml) was treated with lithium hydroxide (350 mg, 15 mmol) to give the corresponding acid as an oil which solidified on standing. Recrystallisation from petroleum ether–diethyl ether gave the *cyclopropyl acid* (0.8 g, 93%) as needles, m.p. 39–42 °C; (found C, 64.2; H, 7.3. $C_9H_{12}O_3$ requires C, 64.3; H, 7.2%); ν_{max}(film)/cm^{-1} 2922, 1697, 1642; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.99 (1H, s, CO$_2$*H*), 5.72 (1H, ddt, *J* 6.5, 10.2, 17.2 Hz, CH$_2$C*H*=CH$_2$), 4.97 (1H, dd, *J* 2.0, 17.2 Hz, CH=C*H*H), 4.93 (1H, dd, *J* 2.0, 10.2 Hz, CH=CH*H*), 2.65 (2H, t, *J* 6.5 Hz, C(O)CH_2CH$_2$), 2.44 (1H, m, cyclopropyl C(O)C*H*), 2.27 (2H, app. q, *J* 6.5 Hz, CH$_2$CH_2CH=CH$_2$), 2.07 (1H, m, cyclopropyl C*H*CO$_2$H), 1.38 (2H, t, *J* 7.3 Hz, cyclopropyl CH_2); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 206.8 (s), 176.7 (s), 136.4 (d), 115.2 (t), 42.9 (t), 29.9 (d), 27.6 (t), 23.5 (d), 17.1 (t); *m*/*z* (EI) found 168.0788 (M$^+$), $C_9H_{12}O_3$ requires 168.0786.

A solution of the cyclopropyl carboxylic acid (200 mg, 1.2 mmol) in CH_2Cl_2 (27 ml) was treated with tributylphosphine (360 mg, 1.8 mmol) and *N*-phenylselenophthalimide (540 mg, 1.8 mmol). The crude product was purified by chromatography on silica using petroleum ether–diethyl ether (10 : 1) as eluent to give the *selenyl ester* (340 mg, 93%) as a pale yellow oil; (found C, 58.3; H, 6.0. $C_{15}H_{16}O_2Se$ requires C, 58.3; H, 5.9%); λ_{max}(EtOH)/nm 260 (5570); ν_{max}(film)/cm^{-1} 1694, 1641, 1579; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.37 (5H, m, Ar*H*), 5.81 (1H, ddt, *J* 6.5, 10.2, 17.1 Hz, CH$_2$C*H*=CH$_2$), 5.07 (1H, dd, *J* 2.0, 17.1 Hz, CH=C*H*H), 5.02 (1H, dd, *J* 2.0, 10.2 Hz, CH=CH*H*), 2.74–2.62 (4H, m, CH_2C(O) and 2 × cyclopropyl C*H*), 2.36 (2H, app. q, *J* 6.5 Hz, CH$_2$CH_2CH=), 1.57 (2H, m, cyclopropyl CH_2); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 205.9 (s), 197.7 (s), 136.5 (2 × d), 135.6 (d), 129.3 (2 × d), 129.0 (d), 115.5 (t), 43.8 (t), 35.1 (d), 30.9 (d), 27.5 (t), 18.6 (t); *m*/*z* (CI) found 309.04079 (M$^+$ + H), $C_{15}H_{16}O_2{}^{80}Se$ requires 309.0394.

6-(3-Butenyl)-3,4-dihydro-2-pyrone 66

A solution of tributyltin hydride (150 μg, 0.42 mmol) and AIBN (4 mg) in dry degassed benzene (2 ml) was added dropwise over 2 h *via* syringe pump, to a stirred solution of the selenyl ester **59** (100 mg, 0.33 mmol) and AIBN (4 mg) in dry degassed benzene (106 ml) under reflux in an atmosphere of argon. The mixture was stirred under reflux for a further 2 h and then cooled to room temperature. The solvent was removed *in vacuo* to leave a residue which was purified by chromatography on silica using petroleum ether–diethyl ether (5 : 1) as eluent to give the *enol lactone* (37 mg, 76%) as a colourless oil; ν_{max}(film)/cm^{-1} 3076, 1764, 1641; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (1H, ddt, *J* 6.5, 10.2, 16.9 Hz, CH$_2$C*H*=CH$_2$), 5.08–4.98 (3H, m, =C*H* + CH=CH_2), 2.57 (2H, t, *J* 7.6 Hz, C(O)CH_2), 2.30–2.20 (6H, m, 3 × CH_2); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 169.3 (s), 152.8 (s), 137.0 (d), 115.4 (t), 99.9 (d), 32.3 (t), 30.4 (t), 28.7 (t), 18.6 (t); *m*/*z* (EI) found 152.08343 (M$^+$), $C_9H_{12}O_2$ requires 152.08372.

Ethyl *trans*-2-(1-hydroxy-4-pentenyl)cyclopropanoate 60

A solution of the cyclopropyl ester **58** (500 mg, 2.5 mmol) in ethanol (5 ml) was added dropwise over 10 min to a stirred solution of sodium borohydride (120 mg, 3 mmol) in ethanol (50 ml) at 0 °C. The mixture was allowed to warm to room temperature over 1 h, and was then diluted with water (20 ml) and reduced *in vacuo*. The residue was partitioned between water (10 ml) and diethyl ether (40 ml) and the separated aqueous layer was extracted with diethyl ether (3 × 50 ml). The combined organic extracts were washed with water (20 ml) and brine (20 ml), dried ($MgSO_4$) and evaporated *in vacuo* to leave a colourless oil. Chromatography on silica gel using petroleum ether–diethyl ether (5 : 3) as eluent gave a 1 : 1 mixture of diastereoisomers of the *alcohol* (495 mg, 98%), as a colourless oil; (found C, 66.5; H, 9.6. $C_{11}H_{18}O_3$ requires C 66.6; H 9.2%.); ν_{max}(film)/cm^{-1} 3434, 3076, 1726, 1641; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (1H, ddt, *J* 6.7, 10.3, 17.1 Hz, C*H*=CH$_2$), 5.06 (1H, d, *J* 17.1 Hz, CH=C*H*H), 4.99 (1H, d, *J* 10.2 Hz, CH=CH*H*), 4.16–4.10 (2H, m, OCH_2CH$_3$), 3.26 (0.5 H, br m, C*H*OH), 3.14 (0.5 H, br m, C*H*OH), 2.25–2.19 (2H, m, CH_2CH=CH$_2$), 1.73–1.54 (4H, m, CH_2 + 2 × cyclopropyl C*H*), 1.27 (3H, s, OCH$_2$CH_3), 1.23–1.15 (1H, m, cyclopropyl C*H*H), 0.97–0.84 (1H, m, cyclopropyl CH*H*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 174.3 (s), 138.2 (d), 114.9 (t), 73.0 (d), 72.1 (d), 67.8 (t), 36.2 (t), 29.8 (t), 28.6 (d), 27.9 (d), 17.8 (d), 14.1 (q), 12.5 (t), 11.9 (t); *m*/*z* (EI) found 198.1252 (M$^+$), $C_{11}H_{18}O_3$ requires 198.1256.

Phenyl *trans*-2-(1-hydroxy-4-pentenyl)cyclopropyl selenoate 61a

Following the general procedures described in the accompanying paper,[13a] a solution of the cyclopropyl ester **60** (500 mg, 2.5 mmol) in THF (10 ml) and water (10 ml) was treated with lithium hydroxide (10 mg, 3.8 mmol) to give a 1 : 1 mixture of diastereoisomers of *trans*-2-(1-hydroxy-4-pentenyl)cyclopropyl carboxylic acid (370 mg, 2.1 mmol, 84%), as a pale yellow oil; ν_{max}(film)/cm^{-1} 3461, 2923, 1713, 1643, 1442; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.11 (1H, ddt, *J* 6.6, 10.2, 17.1 Hz, CH$_2$C*H*=CH$_2$), 5.1 (1H, dd, *J* 2.0, 10.2 Hz, CH=C*H*H), 5.05 (1H, d, *J* 10.2 Hz, CH=CH*H*), 3.35 (0.5H, br. app. q, *J* 6.6 Hz,

$CH_2CH(OH)CH$), 3.15 (0.5 H, br. app. q, J 6.6 Hz, $CH_2CH(OH)CH$), 2.26 (2H, m, $CH_2CH_2CH(OH)$) 1.80–1.59 (4H, m, 2 × CH_2) 1.35–1.25 (2H, m, cyclopropyl CH_2) 1.11–0.93 (2H, m, 2 × cyclopropyl CH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 178.9 (s), 178.8 (s), 138.0 (d), 115.0 (t), 73.5 (d), 72.0 (d), 35.9 (t), 29.6 (t), 29.2 (d), 28.4 (d), 18.1 (d), 17.6 (d), 13.3 (t), 12.6 (t); m/z (EI) found 152.08367 ($M^+ - H_2O$), $C_9H_{12}O_2$ requires 152.08372.

The *trans*-2-(1-hydroxy-4-pentenyl)cyclopropyl carboxylic acid (100 mg, 0.6 mmol) then gave the *selenyl ester* (107 mg, 59%), as a 1 : 1 mixture of diastereoisomers which could be separated by chromatography on silica using petroleum ether–diethyl ether (3 : 1) as eluent. First eluted isomer: (found C, 58.3; H, 6.0. $C_{15}H_{19}O_2Se$ requires C, 58.3; H, 5.9%); ν_{max}(film)/cm^{-1} 3408, 1704, 1640; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.36 (5H, m, ArH), 5.83 (1H, ddt, J 6.7, 10.3, 16.9 Hz, CH=CH_2), 5.07 (1H, dd, J 1.6, 16.9 Hz, CH=CHH), 5.01 (1H, dd, J 1.6, 10.3 Hz, CH=CHH), 3.29 (1H, br. app. q, J 6.4 Hz, CHOH), 2.28–2.17 (3H, m, CH_2 + cyclopropyl CH), 1.81–1.75 (1H, m, cyclopropyl CH), 1.69 (2H, app. q, J 7.5 Hz, CH(OH)CH_2CH$_2$), 1.48–1.43 (1H, m, cyclopropyl CHH) 1.10–1.06 (1H, cyclopropyl CHH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 198.9 (s), 138.0 (d), 135.8 (2 × d), 129.3 (2 × d), 126.4 (s), 115.2 (t), 72.1 (d), 36.1 (t), 31.6 (d), 29.8 (d), 29.7 (t), 15.3 (t). Second eluted isomer: ν_{max}(film)/cm^{-1} 3411, 3074, 2923, 1704, 1640, 1580; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6–7.5 (2H, m, ArH), 7.4–7.3 (3H, m, ArH), 5.8 (1H, ddt, J 6.8, 10.2, 17.0 Hz, CH_2CH=CH_2), 5.1 (1H, dd, J 1.6, 17.0 Hz, CH=CHH), 5.0 (1H, d, J 10.2 Hz, CH=CHH), 3.4 (1H, dt, J 6.5 Hz, CH_2CH(OH)CH), 2.3–2.2 (3H, m, CH_2 + cyclopropyl CH), 1.8–1.62 (3H, m, CH_2 + cyclopropyl CH), 1.4–1.1 (2H, m, cyclopropyl CH_2); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 199.3 (s), 138.3 (d), 136.1 (2 × d) 129.6 (2 × d), 129.2 (d), 126.7 (s), 115.6 (t), 71.9 (d), 36.5 (t), 31.1 (d), 30.4 (d), 30.1 (t), 15.1 (t); m/z (FAB) found 311.0537 (M^+ + H), $C_{15}H_{19}O_2{}^{80}Se$ requires 311.0550.

trans-7-Hydroxybicyclo[6.1.0]nona-2-one 67

A solution of tributyltin hydride (84 µl, 0.24 mmol) and AIBN (2 mg) in dry degassed benzene (2 ml) was added dropwise over 2 h, *via* syringe pump, to a stirred solution of the selenyl ester **61a** (50 mg, 0.16 mmol) and AIBN (2 mg) in dry degassed benzene (60 ml) under reflux in an atmosphere of argon. The mixture was stirred under reflux for a further 2 h and then cooled to room temperature. The solvent was removed *in vacuo* to leave a yellow residue which was purified by chromatography on silica using petroleum ether–diethyl ether (1 : 1) then diethyl ether as eluents to give: (i), the *bicyclic nonanone* (10 mg, 38%) (eluted first) as a colourless oil; ν_{max}(film)/cm^{-1} 3408, 2930, 1682; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.3 (1H, m, CH_2CH(OH)CH), 2.6 (1H, dt, J 3, 13.1 Hz, cyclopropyl CH), 2.5 (1H, q, J 6.5 Hz, CH_2CHCH), 2.38–0.83 (11H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 212.9 (s), 65.1 (d), 46.5 (t), 40.4 (t), 31.1 (t), 30.2 (d), 21.4 (d), 21.42 (t), 6.1 (t); m/z (EI) found 154.09963, $C_9H_{14}O_2$ requires 154.09938 (M^+ 13%); and (ii), the diastereoisomeric bicyclic compound (10 mg, 38%) (eluted second) as a colourless oil; ν_{max}(film)/cm^{-1} 3409, 2926, 1694; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.1 (1H, dt, J 4.8, 7.2 Hz, CH_2CH(OH)CH), 2.61–2.17 (5H, m), 1.91 (1H, app. q, J 7.2 Hz), 1.63–1.45 (4H, m), 0.88 (2H, m, cyclopropyl CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.0 (s), 77.4 (d), 46.5 (t), 40.8 (t), 30.4 (d), 29.3 (t), 26.0 (d), 25.1 (t), 8.8 (t); m/z (EI) found 136.0893 ($M^+ - H_2O$), $C_9H_{12}O$ requires 136.0888.

Phenyl *trans*-2-(1-methoxymethyloxy-4-pentenyl)cyclopropylselenoate 61b

Methoxymethyl chloride (80 mg, 1.0 mmol) was added in one portion to a stirred solution of the cyclopropyl ester **60** (100 mg, 0.5 mmol) and diisopropylethylamine (260 µl, 1.5 mmol) in CH_2Cl_2 (3 ml) at room temperature and the mixture was then stirred at this temperature for 24 h. Water (1 ml) was added and the mixture was stirred vigorously for 0.5 h and then diluted with CH_2Cl_2 (10 ml) and water (10 ml). The separated aqueous layer was extracted with CH_2Cl_2 (3 × 10 ml) and the combined organic extracts were washed with brine (10 ml), dried ($MgSO_4$) and concentrated *in vacuo* to leave a colourless oil. Column chromatography on silica, using petroleum ether–diethyl ether (5 : 1) as eluent gave an inseparable 1 : 1 mixture of diastereoisomers of the corresponding *MOM ether* (95 mg, 78%) as a colourless oil; (found C, 64.5; H, 9.4, $C_{13}H_{22}O_4$ requires C, 64.4; H, 9.2%); ν_{max}(film)/cm^{-1} 1727; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (1H, ddt, J 6.6, 10.2, 16.9 Hz, CH=CH_2), 5.04 (1H, d, J 16.9 Hz, CH=CHH), 5.00 (1H, d, J 10.2 Hz, CH=CHH), 4.78 (0.5H, d, J 6.9 Hz, d, CH_3OCHHO), 4.73 (0.5H, d, J 6.9 Hz, CH_3OCHHO), 4.61 (0.5H, d, J 6.9 Hz, CH_3OCH_2O), 4.59 (0.5H, d, J 6.9 Hz, CH_3OCH_2O), 4.13 (2H, q, J 7.1 Hz, OCH_2CH_3), 3.37 (3H, s, CH_3OCH_2O), 3.12 (1H, br. app. q, J 5.1 Hz, CHOMOM), 3.04 (0.5H, br. app. q, J 5.1 Hz, CHOMOM), 2.20 (2H, m, CH_2CH=), 1.76–1.67 (2H, m, CH_2CH_2CHOH), 1.52–1.4 (2H, m, 2 × cyclopropyl CH), 1.29–0.74 (5H, m, CH_3 + cyclopropyl CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 173.8 (s), 138.2 (d), 114.8 (t), 94.9 (t), 95.1 (t), 78.2 (d), 77.4 (d), 60.5 (t), 55.3 (d), 34.5 (t), 29.4 (t), 26.1 (d), 25.6 (d), 19.3 (d), 17.2 (d), 14.2 (q), 13.6 (t), 11.9 (t); m/z (FAB) found 243.1594 (M^+), $C_{13}H_{22}O_4$ requires 243.1596.

The ethyl ester (90 mg, 0.4 mmol), from the above procedure, was treated with lithium hydroxide (20 mg, 0.7 mmol) in THF (1 ml) and water (1 ml) using the general procedure[15] to give the corresponding *carboxylic acid* (60 mg, 78%) as an oil; ν_{max}(film)/cm^{-1} 3190 (br), 1697, 1640; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (1H, ddt, J 6.5, 10.2, 17.1 Hz, CH=CH_2) 5.04 (1H, d, J 17.1 Hz, CH=CHH), 4.98 (1H, d, J 10.2 Hz, CH=CHH), 4.77 (0.5H, d, J 6.9 Hz, CH_3OCHHO), 4.73 (0.5H, d, J 6.9 Hz, CH_3OCHHO), 4.61 (0.5H, d, J 6.9 Hz, CH_3OCH_2O), 4.60 (0.5H, d, J 6.9 Hz, CH_3OCH_2O), 3.38 (1.5H, s, CH_3OCH_2O), 3.37 (1.5H, s, CH_3OCH_2O), 3.15 (0.5H, br. app. q, J 7.4 Hz, CHOMOM), 3.05 (0.5H, br. app. q, J 7.4 Hz, CHOMOM), 2.19 (2H, m, CH_2CH_2CH=), 1.78–0.82 (6H, m, CH_2 + cyclopropyl CH_2 and 2 × CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0 (s), 138.1 (d), 114.9 (t), 95.4 (t), 95.1 (t), 78.2 (d), 77.5 (d), 55.5 (q), 34.6 (t), 32.7 (t), 27.2 (d), 26.8 (d), 19.2 (d), 17.2 (d), 14.6 (t), 12.9 (t); m/z (EI) found 159.0640 (M^+), $C_7H_{11}O_4$ requires 159.0657.

Following the general procedure,[13a] the *trans*-cyclopropyl carboxylic acid (50 mg, 0.2 mmol) was treated with *N*-phenylselenophthalimide (110 mg, 0.35 mmol) and tributylphosphine (70 mg, 0.35 mmol) in CH_2Cl_2 (5 ml). The crude product was purified by chromatography on silica using petroleum ether–diethyl ether (3 : 1) as eluent to give a 1 : 1 mixture of diastereoisomers of the *selenyl ester* (74 mg, 89%) as a pale yellow viscous oil; ν_{max}(film)/cm^{-1} 1707, 1640; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (2H, m, ArH), 7.38 (3H, m, ArH), 5.82 (1H, m, CH=CH_2) 5.05 (1H, m, CH=CH_2), 4.77 (0.5H, d, J 6.9 Hz, CH_3OCHHO), 4.73 (0.5H, d, J 6.9 Hz, CH_3OCHHO), 4.62 (0.5H, d, J 6.9 Hz, CH_3OCH_2O), 4.58 (0.5H, d, J 6.9 Hz, CH_3OCH_2O), 3.42 (3H, s, CH_3OCH_2O), 3.37 (3H, s, CH_3OCH_2O), 3.20 (0.5H, br. app. q, J 7.1 Hz, CHOMOM), 3.15 (0.5H, br. app. q, J 7.1 Hz, CHOMOM), 2.34–2.05 (3H, m, CH_2 + cyclopropyl CH), 1.79 (3H, m, CH_2 + cyclopropyl CH), 1.51–0.97 (2H, m, cyclopropyl CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 198.9 (s), 138.1 (d), 135.8 (d), 134.4 (d), 129.3 (d), 126.4 (s), 115.0 (t), 95.2 (t), 95.0 (t), 77.4 (d), 77.3 (d), 55.7 (q), 55.5 (q), 34.4 (t), 31.4 (d), 29.6 (t), 29.5 (d), 29.2 (d), 28.9 (d), 16.5 (t), 14.9 (t); m/z (FAB) found 355.0826 (M^+ + H), $C_{17}H_{22}O_3$ requires 355.0824.

trans-7-(Methoxymethyloxy)bicyclo[6.1.0]nona-2-one 68a

A solution of tributyltin hydride (66 µl, 0.18 mmol) and AIBN (2 mg) in dry degassed benzene (2 ml) was added dropwise over 2 h, *via* syringe pump, to a stirred solution of a 1 : 1 mixture of diastereoisomers of the selenyl ester **61b** (50 mg, 0.14 mmol) and

AIBN (2 mg) in dry degassed benzene (47 ml) under reflux in an atmosphere of argon. The mixture was stirred under reflux for a further 2 h and then cooled to room temperature. The benzene was removed *in vacuo* to leave a residue which was purified by chromatography on silica using petroleum ether–diethyl ether (5 : 3) as eluent to give a 2 : 3 mixture of diastereoisomers of the *bicyclic ketone* (26 mg, 0.13 mmol, 93%) as an oil. Minor isomer: ν_{max}(film)/cm^{-1} 1692; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61 (1H, d, *J* 7.0 Hz, OC*H*HOCH$_3$), 4.52 (1H, *J* 7.0 Hz, OC*H*HOCH$_3$), 3.31 (3H, s, C*H*$_3$), 2.61 (1H, dt, *J* 3.1, 13.1 Hz, C*H*OMOM), 2.43–2.15 (4H, m), 1.94 (2H, m), 1.58–1.34 (2H, m), 0.93–0.82 (2H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 212.4 (s), 95.1 (t), 70.9 (d), 55.4 (q), 46.6 (t), 37.5 (t), 31.2 (t), 29.1 (d), 22.2 (d), 21.9 (t), 6.2 (t); *m*/*z* (EI) found 198.1257 (M$^+$, 0.5%), $C_{11}H_{18}O_3$ requires 198.1256; found 153.0909, $C_9H_{13}O_2$ requires 153.0916 (M$^+$). Major isomer: ν_{max}(film)/cm^{-1} 1704; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (1H, d, *J* 7.0 Hz, OC*H*HOCH$_3$), 4.57 (1H, d, *J* 7.0 Hz, OCH*H*OCH$_3$), 3.35 (3H, s, OCH$_2$OC*H*$_3$), 3.09 (1H, m, C*H*OCH$_2$OCH$_3$), 2.65–2.20 (5H, m), 1.88 (1H, app. q, *J* 7 Hz), 1.67–1.49 (4H, m), 0.89 (2H, m, cyclopropyl C*H*$_2$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 210.1 (s), 93.9 (t), 80.4 (d), 55.1 (q), 46.6 (t), 38.8 (t), 29.3 (t), 28.1 (d), 25.3 (d), 25.2 (t), 9.7 (t); *m*/*z* (EI) found 198.1265 (M$^+$), $C_{11}H_{18}O_3$ requires 198.1256.

Phenyl 2-(4-pentenyl)cyclopropyl selenoate 61c

Following the general procedures described in the accompanying paper,[13a] a solution of a 1 : 1 mixture of *cis*- and *trans*-isomers of ethyl 2-(4-pentenyl)cyclopropanoate[26] (100 mg, 0.6 mmol) in ethanol (1.5 ml) and water (two drops) was treated with sodium hydroxide (100 mg) to give a 1 : 1 mixture of *cis*- and *trans*-isomers of the corresponding *carboxylic acid* (93 mg, ~100%) as an oil; ν_{max}(film)/cm^{-1} 2926 (br), 1694, 1642; ^{1}H NMR (270 MHz, $CDCl_3$) δ 11.20 (1H, br. s, CO_2H), 5.87–6.73 (1H, m, C*H*=CH$_2$), 5.03–4.92 (2H, m, CH=C*H*$_2$), 2.07 (2H, q, *J* 6.9 Hz, C*H*$_2$CH=CH$_2$), 1.70–0.74 (8H, complex m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 181.2 (s), 180.0 (s), 138.7 (d), 138.5 (d), 114.6 (t), 114.4 (t), 33.3 (t), 33.2 (t), 32.3 (t), 28.7 (t), 28.2 (t), 26.3 (t), 23.9 (d), 22.9 (d), 20.1 (d), 18.0 (d), 16.3 (t), 14.4 (t); *m*/*z* (EI) found 154.0988 (M$^+$), $C_9H_{14}O_2$ requires 154.0994.

A solution of the carboxylic acid (50 mg, 0.3 mmol) in dichloromethane (7 ml) was treated with *N*-phenylselenophthalimide (147 mg, 0.5 mmol) and tributylphosphine (123 µl, 0.5 mmol). The crude product was purified by chromatography on silica using petroleum ether then petroleum ether–diethyl ether (10 : 1) as eluent, to give a 1 : 1 mixure of *cis*- and *trans*-isomers of the *selenyl ester* (61 mg, 88%) as a pale yellow oil; (found C, 61.7; H, 6.4. $C_{15}H_{18}$OSe requires C, 61.4; H, 6.2%); λ_{max} (EtOH)/nm 220.7 (124400), 260 (34500); ν_{max}(film)/cm^{-1} 1710, 1640; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.48–7.27 (5H, m, Ar*H*), 5.81–5.64 (1H, m, C*H*=CH$_2$) 4.98–4.84 (2H, m, CH=C*H*$_2$), 2.24–1.84 (3H, m, C*H*$_2$CH= + cyclopropyl C*H*), 1.58–1.05 (6H, m, 2 × C*H*$_2$ + 2 × cyclopropyl C*H*), 0.87–0.77 (1H, m, cyclopropyl C*H*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 198.6 (s), 197.3 (s), 138.7 (d), 138.4 (d), 135.8 (4 × d), 129.2 (4 × d), 128.7 (2 × d), 126.7 (s), 126.0 (s), 114.7 (t), 114.4 (t), 33.3 (t), 33.2 (t), 32.9 (d), 32.8 (t), 30.7 (d), 28.9 (t), 28.1 (t), 26.5 (t), 26.4 (d), 26.2 (d), 18.8 (t), 16.3 (t); *m*/*z* (FAB) found 295.0600 (M$^+$ + H), $C_{15}H_{19}O^{80}$Se requires 295.0601.

trans-Bicyclo[6.1.0]nona-2-one 68b

A solution of tributyltin hydride (92 µl, 0.26 mmol) and AIBN (2 mg) in dry degassed benzene (2 ml) was added dropwise over 2 h, *via* syringe pump, to a stirred solution of the selenyl ester **58c** (50 mg, 0.17 mmol) and AIBN (3 mg) in dry degassed benzene (57 ml) under reflux in an atmosphere of argon. The mixture was stirred under reflux for a further 3 h and then cooled to room temperature. The solvent was removed *in vacuo* to leave a residue which was purified by chromatography on silica using petroleum ether–diethyl ether (5 : 3) as eluent to give: (i), a 3 : 1 mixture of *cis*- and *trans*-isomers of the corresponding aldehyde (16 mg, 33%) (eluted first); ^{1}H NMR (400 MHz, $CDCl_3$) (major isomer) δ 9.02 (1H, d, *J* 6 Hz, C*H*O), 5.78 (1H, m, C*H*=CH$_2$), 4.99 (2H, m, CH=C*H*$_2$), 2.65 (1H, m, cyclopropyl C*H*CHO), 2.24–0.61 (9H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 202.1 (s), 138.7 (d), 115.3 (t), 33.7 (t), 32.5 (t), 31.3 (d), 27.5 (d), 16.0 (t); ^{1}H NMR (400 MHz, $CDCl_3$) (minor isomer) δ 9.38 (1H, d, *J* 7.3 Hz, C*H*CHO); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 201.4 (s), 139.2 (d), 114.8 (t), 33.3 (t), 31.9 (t), 30.9 (d), 27.0 (d), 18.1 (t), and (ii), the *bicyclo[6.1.0]nonanone* (10 mg, 41%)[27] eluted second; as an oil ν_{max}(film)/cm^{-1} 1698, 1455; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (1H, dt, *J* 2.2, 13.1 Hz, C(O)C*H*(CH$_2$)CH), 2.39 (13H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 211.6 (s), 46.9 (t), 34.3 (t), 32.2 (t), 31.2 (t), 29.8 (d), 28.0 (t), 27.5 (d), 10.1 (t); *m*/*z* (EI) found 138.1047 (M$^+$), $C_9H_{14}O$ requires 138.1045.

References

1 For a recent review on acyl radical chemistry, see: C. Chatgilialoglu, D. Crich, M. Komatsu and I. Ryu, *Chem. Rev.*, 1999, **99**, 1991–2070.

2 (*a*) See, for example: G. Pattenden, L. Roberts and A. J. Blake, *J. Chem. Soc., Perkin Trans. 1*, 1998, 863–869; (*b*) S. Handa, G. Pattenden and W.-S. Li, *Chem. Commun.*, 1998, 311–313; (*c*) A. Batsanov, L. Chen, G. B. Gill and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, 1996, 45–55; (*d*) L. Chen, G. B. Gill, G. Pattenden and H. Simonian, *J. Chem. Soc., Perkin Trans. 1*, 1996, 31–43; (*e*) S. Handa and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, 1999, 843–845; (*f*) H. M. Boehm, S. Handa, G. Pattenden, L. Roberts, A. J. Blake and W-S. Li, *J. Chem. Soc., Perkin Trans. 1*, 2000, 3522–3538; (*g*) S. Handa, P. S. Nair and G. Pattenden, *Helv. Chim. Acta*, 2000, **83**, 2629–2643, and references cited therein..

3 (*a*) M. P. Astley and G. Pattenden, *Synthesis*, 1992, 101–106; (*b*) M. Cases, G. Pattenden and F. G.-L. de Turiso, *Synlett*, 2001, 1869–1872.

4 K. M. Foote, C. J. Hayes, M. P. John and G. Pattenden, *Org. Biomol. Chem.*, 2003, **1**, 3917–3948.

5 (*a*) Preliminary communication: C. J. Hayes and G. Pattenden, *Tetrahedron Lett.*, 1996, **37**, 271–274; (*b*) For a comprehensive bibliography of the generation of α-ketenyl radicals under a variety of circumstances see: T. T. Tidwell, *Ketenes*, Wiley, New York, 1995.

6 For the conversion of citral into piperitone in the presence of di-*t*-butylperoxide, see: J.-P. Montheard, *C.R. Acad. Sci., Se. Paris*, 1965, **260**, 577.

7 (*a*) L. Salem, *J. Am. Chem. Soc.*, 1974, **96**, 3486–3501; (*b*) Y. Yamamoto, M. Ohno and S. Eguchi, *J. Org. Chem.*, 1996, **61**, 9264–9271; (*c*) *cf.*C. E. Brown, A. G. Neville, D. M. Rayner, K. U. Ingold and J. Lusztyk, *Aust. J. Chem.*, 1995, **48**, 363–379; (*d*) P. J. Krusic and T. A. Rettig, *J. Am. Chem. Soc.*, 1970, **92**, 722–724.

8 Preliminary communications; see: (*a*) ref. 5; (*b*) N. M. A. Herbert and G. Pattenden, *Synlett*, 1997, 69–70; (*c*) B. De Boeck, N. M. A. Herbert and G. Pattenden, *Tetrahedron Lett.*, 1998, **39**, 6971–6974and; (*d*) N. M. Harrington-Frost and G. Pattenden, *Synlett*, 1999, 1917–1918.

9 (*a*) D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 317–323; (*b*) A. Effio, D. Griller, K. U. Ingold, A. L. J. Beckwith and A. K. Serelis, *J. Am. Chem. Soc.*, 1980, **102**, 1734–1736; (*c*) B. Maillard, D. Forrest and K. U. Ingold, *J. Am. Chem. Soc.*, 1976, **98**, 7024–7026.

10 (*a*) A. G. Davies and R. Sutcliffe, *J. Chem. Soc., Perkin Trans. 2*, 1982, **11**, 1483–1488; (*b*) A. G. Davies, J.-Y. Godet, B. Muggleton and M. Pereyre, *J. Chem. Soc. Chem. Commun.*, 1976, **20**, 813–814; (*c*) A. G. Davies, B. Muggleton, J.-Y. Godet, M. Pereyre and J.-C. Pommier, *J. Chem. Soc., Perkin Trans. 2*, 1976, **14**, 1719–1724; (*d*) Y. Zelechonok and R. B. Silverman, *J. Org. Chem.*, 1992, **57**, 5785–5787.

11 (*a*) For the use of phenyl selenyl esters and other methods of producing acyl radical intermediates, see: D. L. Boger and R. J. Mathvink, *J. Org. Chem.*, 1988, **53**, 3377–3379; (*b*) J. Pfenninger, C. Heuberger and W. Graf, *Helv. Chim. Acta*, 1980, **63**, 2328–2337; (*c*) M. Ballestri, C. Chatgilialoglu, N. Cardi and A. Sommazzi, *Tetrahedron Lett.*, 1992, **33**, 1787–1790; (*d*) G. Pattenden and S. J. Reynolds, *Tetrahedron Lett.*, 1991, **32**, 259–262; (*e*) V. F. Patel, G. Pattenden and D. M. Thompson, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2729–2734; (*f*) G. B. Gill, G. Pattenden and S. J. Reynolds, *Tetrahedron Lett.*, 1989, **30**, 3229–3232; (*g*) V. F. Patel and G. Pattenden, *Tetrahedron Lett.*, 1988, **29**, 707–710; (*h*) D. J. Coveney, V. F. Patel and G. Pattenden, *Tetrahedron Lett.*, 1987, **28**, 5949–5952; (*i*) D. Crich, C. Chen, J.-T. Hwang, H. Yuan, A. Papadatos and R. I. Walter, *J. Am. Chem. Soc.*, 1994, **116**, 8937–8951; (*j*) C. Chen and D. Crich, *Tetrahedron Lett.*, 1993, **34**, 1545–1548; (*k*) C. Chen, D. Crich and A. Papadatos, *J. Am. Chem. Soc.*, 1992, **114**, 8313–8314; (*l*) S. Z.

Zard, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 672–685; (*m*) P. Delduc, C. Tailhan and S. Z. Zard, *J. Chem. Soc., Chem. Commun.*, 1988, 308–310; (*n*) D. H. R. Barton, M. V. George and M. Tomoeda, *J. Chem. Soc.*, 1962, 1967–1974; (*o*) J. H. Penn and F. Liu, *J. Org. Chem.*, 1994, **59**, 2608–2612; (*p*) D. Crich and S. M. Fortt, *Tetrahedron*, 1989, **45**, 6581–6598; (*q*) D. Crich and X. Hao, *J. Org. Chem.*, 1997, **62**, 5982–5988; (*r*) D. Crich and Q. Yao, *J. Org. Chem.*, 1996, **61**, 3566–3570; See also:; (*s*) I. Ryu and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1050–1066; (*t*) I. Ryu, T. Niguma, S. Minakata, M. Komatsu, S. Hadida and D. P. Curran, *Tetrahedron Lett.*, 1997, **38**, 7883–7886; (*u*) D. P. Curran, J. Sisko, A. Balog, N. Sonoda, K. Nagahara and I. Ryu, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1591–1593.

12 (*a*) *Cf.* E. J. Enholm, Y. Xie and K. A. Abboud, *J. Org. Chem.*, 1995, **60**, 1112–1113; (*b*) E. J. Enholm and Z. J. Jia, *Tetrahedron Lett.*, 1995, **36**, 6819–6822.

13 (*a*) B. De Boeck, N. M. A. Herbert, N. M. Harrington-Frost and G. Pattenden, *Org. Biomol. Chem.*, 2004, DOI: 10.1039/b413816n; (*b*) B. De Boeck, N. M. Harrington-Frost and G. Pattenden, *Org. Biomol. Chem.*, 2004, DOI: 10.1039/b413817c.

14 (*a*) I. U. Khand, G. R. Knox, P. L. Pauson and W. E. Watts, *J. Chem. Soc., Chem. Commun.*, 1971, 36; (*b*) I. U. Khand, G. R. Knox, P. L. Pauson and W. E. Watts, *J. Chem. Soc., Perkin Trans. 1*, 1973, 975–977; (*c*) C. Exon and P. Magnus, *J. Am. Chem. Soc.*, 1983, **105**, 2477–2478; (*d*) E. Carceller, V. Centellas, A. Moyano, M. A. Pericas and F. Serratosa, *Tetrahedron Lett.*, 1985, **26**, 2475–2476; (*e*) N. E. Schore and M. J. Knudsen, *J. Org. Chem*, 1987, **52**, 569–580; (*f*) N. E. Schore and E. G. Rowley, *J. Am. Chem. Soc.*, 1988, **110**, 5224–5225.

15 We thank Dr A. J. Blake (University of Nottingham) for determining this X-ray structure. CCDC reference number 253408. See http://www.rsc.org/suppdata/ob/b4/b413815p/ for crystallographic data in .cif format..

16 R. V. M. Campbell, L. Crombie, D. A. R. Findley, R. W. King, G. Pattenden and D. A. Whiting, *J. Chem. Soc., Perkin 1*, 1975, 897–913.

17 D. Arlt, M. Jautelat and R. Lantzsch, *Angew. Chem., Int. Ed. Rngl.*, 1981, **20**, 703–722.

18 (*a*) L. Crombie, C. F. Doherty and G. Pattenden, *J. Chem. Soc. C*, 1970, 1076–1080; (*b*) *cf.* P. A. Wender, S. McN. Sieburth, J. J. Petraitis and J. J. Singh, *Tetrahedron*, 1981, **37**, 3967–3975.

19 B. H. Braun, M. Jacobson, M. Schwarz, P. E. Sonnet, N. Wakabayashi and R. M. Waters, *J. Econ. Etomol.*, 1968, **61**, 861–869.

20 B. Kongkathip, R. Sookkho and N. Kongkathip, *Chem. Lett.*, 1985, 1849–1850.

21 (*a*) D. Crich and Q. Yao, *J. Org. Chem.*, 1996, **61**, 3566–3570; (*b*) R. K. Howe and F. M. Schleppnik, *J. Heterocycl. Chem.*, 1982, **19**, 721–726.

22 P. Müller and P. Polleux, *Helv. Chim. Acta*, 1994, **77**, 645–654.

23 J. Schreiber, D. Felix, A. Eschenmoser, M. Winter, F. Gautschi, K. H. Schulteelte, E. Sundt, G. Ohloff, J. Kalvoda, H. Kaufmann, P. Wieland and G. Anner, *Helv. Chim. Acta*, 1967, **50**, 2101–2108.

24 P. Audin, A. Doutheau and J. Gore, *Bull. Soc. Chim. Fr.*, 1984, **11**, 297–306.

25 G. B. Payne, *J. Org. Chem.*, 1967, **32**, 3351–3355.

26 M. P. Doyle, R. L. Dorow, W. E. Buhro, J. H. Griffin, W. H. Tamblyn and M. L. Trudell, *Organometallics*, 1984, **3**, 44–52.

27 C. H. DePuy and J. L. Marshall, *J. Org. Chem.*, 1968, **44**, 3326–3327.