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Vinylcyclopropylacyl and polyeneacyl radicals. Intramolecular ketene alkyl radical additions in ring synthesis

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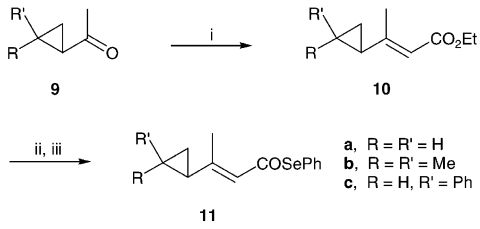
Treatment of a variety of substituted vinylcyclopropyl selenyl esters, *e.g.* **11**, with Bu_3SnH–AIBN in refluxing benzene leads to the corresponding acyl radical intermediates, which undergo rearrangement and intramolecular cyclisations *via* their ketene alkyl radical equivalents producing cyclohexenones in 50–60% yield. By contrast, treatment of conjugated triene selenyl esters, *e.g.* **32**, with Bu_3SnH–AIBN produces substituted 2-cyclopentenones *via* intramolecular cyclisations of their ketene alkyl radical intermediates. Under the same radical-initiating conditions the selenyl esters derived from *o*-vinylbenzoic acid and *o*-vinylcinnamic acid undergo intramolecular cyclisations producing 1-indanone and 5,6-dihydrobenzocyclohepten-7-one respectively in 60–70% yields. A tandem radical cyclisation from the α,β,γ,δ-diene selenyl ester **31** provides an expeditious synthesis of the diquinane **35** in 69% yield.

Introduction

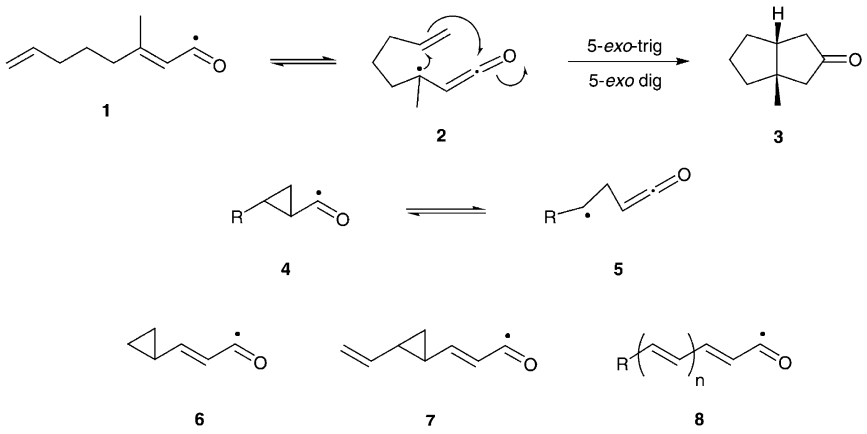
In the immediately preceding paper we demonstrated how α,β-unsaturated acyl radical intermediates **1** are able to react *via* their α-ketenyl alkyl radical equivalents, *viz.* **2**, in tandem cyclisation reactions involving proximate alkene bonds leading to a concise synthesis of diquinanes **3**.[1] We also demonstrated some scope for the corresponding cyclopropylacyl radicals **4** and their β-ketenyl alkyl radical counterparts **5** in ring synthesis. In this paper we describe our further studies of the scope for ketene alkyl radicals in synthesis by examining the chemistry of α,β-unsaturated acyl radicals containing additional cyclopropane and alkene unsaturation at their β-centres, *i.e.* vinylcyclopropylacyl **6**, **7** and polyeneacyl **8** radicals, respectively.[2]

Results and discussion

Acyl radical intermediates can be derived from a range of carboxylic acid derivatives.[3] We have found that treatment of phenyl selenyl esters with Bu_3SnH–AIBN in benzene under reflux is one of the most reliable and practical procedures.[4] Thus, we first synthesised a range of substituted vinylcyclopropane carboxylic acid esters **10** from the corresponding cyclopropyl methyl ketones (and aldehydes) using routine Wittig reactions as the key step, as shown in Scheme 1. Saponification of the esters **10** next led to the corresponding carboxylic acids, which were then converted into their phenyl selenyl esters, *e.g.* **11**, by reaction with *N*-(phenylseleno)phthalimide (NPSP) and tributylphosphine. When solutions of the 3-methyl-substituted vinylcyclopropyl selenyl esters **11a** and **11b** in benzene under reflux were treated separately with Bu_3SnH (dropwise over 2 h) in the presence of AIBN, work up and chromatography gave the 2-cyclohexenones **14a** and **14b**, respectively, in 50–60% yield. The cyclohexenones **14** are produced from the selenyl esters **11** as a result of intramolecular 6-*exo*/*endo*-dig cyclisations of the ketene radical intermediates **13** produced from delocalisation of the acyl radical precursors **12** through their conjugated vinylcyclopropane systems, *i.e.* **11**→**12**→**13**→**14** (Scheme 2). In a similar manner, the phenyl-substituted analogue **11c** led to the corresponding 6-phenyl-substituted cyclohexenone on treatment with Bu_3SnH–AIBN, but both the Δ^2 and Δ^3 isomers, *i.e.* **15**, **16**, were isolated. Interestingly, no cyclohexenone was produced when the vinylcyclopropane **17** lacking 3-methyl substitution was treated with Bu_3Sn–AIBN but the corresponding



Scheme 1 *Reagents*: i, $EtO_2CCH_2PO(OEt)_2$, NaH, THF, 80–90%; ii, LiOH, THF–H_2O, 90–99%; iii, NPSP, Bu_3P, CH_2Cl_2, 70–90%



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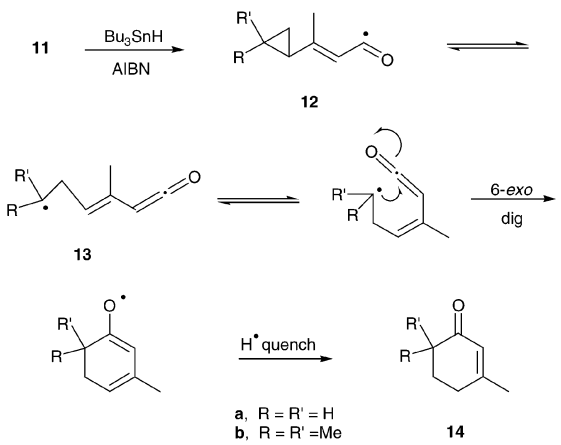
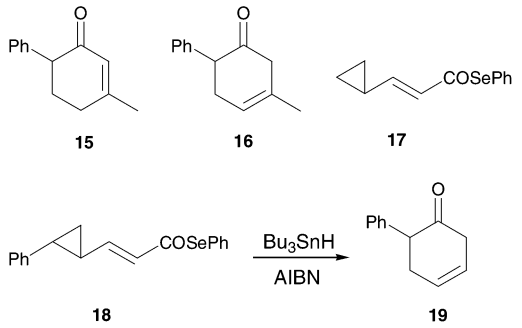
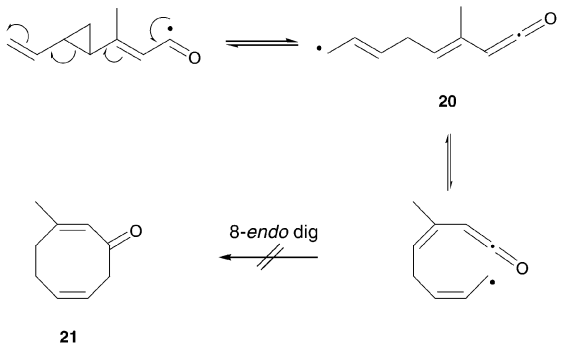


Scheme 2

phenylcyclopropane **18** gave the cyclohexenone **19** in 40% yield. These features clearly demonstrate the importance of substitution on the alkene and cyclopropane ring in determining the efficiency of the aforementioned vinylcyclopropane acyl radical-cyclohexenone interconversions.



We anticipated that including additional alkene unsaturation on the cyclopropane ring in the vinylcyclopropane selenyl esters **11** would provide us with an opportunity to examine the scope for extended ketene alkyl radicals, *viz.* **20**, in elaborating cyclooctadienones, *i.e.* **21**, as illustrated in Scheme 3. We therefore synthesised the 1,2-divinylcyclopropyl selenoesters **24a** and **24b** from the corresponding vinylcyclopropyl carbonyl precursors, *i.e.* **22**, using an identical sequence to that used to prepare **11** from **9**, as shown in Scheme 4. To our disappointment however, neither of the selenyl esters **24** led to a corresponding cyclooctenone product of type **21** on treatment with Bu_3SnH–AIBN. Instead, they produced the corresponding cyclohexenones **25** and **26**, respectively, by way of a sequence analogous to that shown in Scheme 2.



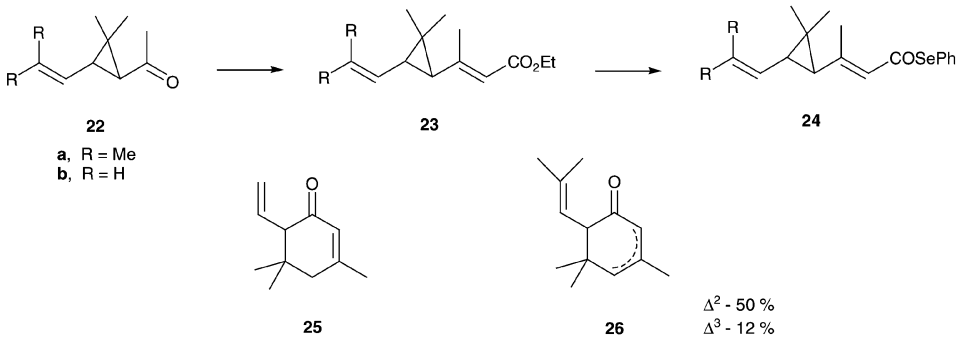
Scheme 3

Interestingly, however, when the substituted 1,2-divinylcyclopropane selenyl ester **27** lacking methyl group substitution at C-3, was treated with Bu_3SnH–AIBN in hot benzene in the presence of *methanol*, it gave the symmetrical dimeric tetraene diester **29** in 63% yield. This outcome clearly established the intermediacy of the delocalised ketene alkyl radical species **30**, analogous to **20**, and the counterpart of the acyl radical **28**, which in this reaction undergoes dimerisation and addition of methanol to the ketene unit, leading to the novel dimer **29**.

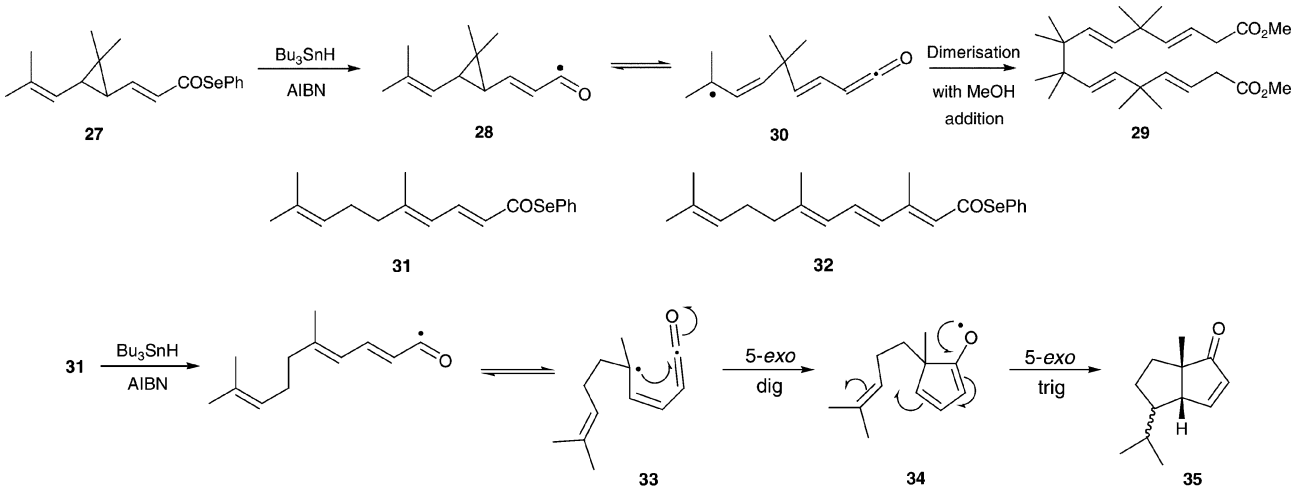
We next synthesised the conjugated diene and triene phenyl selenyl esters **31** and **32**, respectively, and examined their preferred modes of cyclisation under radical conditions. The selenyl esters were synthesised in the usual manner from the corresponding known carboxylic acids by treatment with *N*-(phenylseleno)phthalimide and tributylphosphine.[4] When a solution of the selenyl ester **31** in benzene was heated under reflux over 4.5 h in the presence of Bu_3SnH and AIBN, it underwent tandem radical cyclisation to produce a 1 : 1 mixture of diastereoisomers of the bicyclo[3.3.0]octenone **35** in 69% yield. The structures of the diastereoisomeric bicyclooctenones, which could be separated by chromatography, followed from examination of their NMR data and comparison with corresponding data for similar angular methyl-substituted bicyclo[3.3.0]octenones in the literature.[5,6] The bicyclooctenone **35** is produced from the selenyl ester **31** by way of: (i) 5-*exo*-dig cyclisation of the delocalised ketenyl alkyl radical equivalent, *i.e.* **33**, of the corresponding α,β,γ,δ-unsaturated acyl radical, leading to the dienolate radical **34**, followed by (ii) an intramolecular 5-*exo*-trig cyclisation of this delocalised radical into the non-conjugated alkene bond (Scheme 5).

By contrast, and to our surprise, when the related α,β,γ,δ-unsaturated selenyl ester **38** prepared from *E*-8-methylnona-2,7-dien-4-one **36**, as shown in Scheme 6, was treated with Bu_3SnH–AIBN under similar conditions, the only product isolated was the substituted cyclopentenone **40** resulting from cyclisation of the ketene alkyl radical **39**. Neither of the anticipated bicyclooctenones **41** and **42**, resulting from further cyclisation of the intermediate, was isolated or detected in the crude product mixture. Also surprising was the finding that when the conjugated triene phenyl selenyl ester **32** was treated with Bu_3SnH–AIBN, the only product isolated was a mixture of *E*- and *Z*-isomers of the 3-methyl-5-substituted cyclopent-2-enone **47** in 76% yield. We believe that the acyl radical **43** produced from the selenyl ester **32** is fully delocalised through its triene system, but similar to the polyene systems already described, cyclisation at the δ-position into the extended ketene **44** is favoured over competing cyclisations leading to a 7-membered-ring system, *i.e.* **45** *via* **46**.

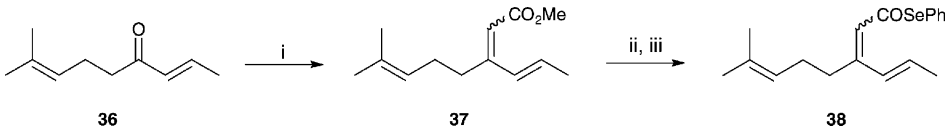
Finally, we also examined the propensity for acyl radicals associated with aromatic rings to undergo intramolecular cyclisation. Thus, when a solution of the phenyl selenyl ester **48** derived from 2-vinylbenzoic acid in benzene was treated with Bu_3SnH–AIBN under reflux, it underwent facile cyclisation producing indanone **51** in 56% yield. In a similar manner, under the same conditions, the corresponding cinnamyl selenyl ester **52** was converted into the benzene ring fused cycloheptenone **54** in 70% yield. Indanone has been produced previously by flash vacuum pyrolysis of *o*-vinylbenzaldehyde, where the mechanism was thought to involve a 5-*endo*-trig cyclisation from the intermediate acyl radical species **49**.[7] In keeping with our contemporaneous studies with acyclic conjugated polyene and cyclopropane acyl radical species, we favour mechanisms for the conversions **48**→**51** and **52**→**54** which involve the delocalised ketene alkyl radical species **50** and **53** respectively. It is a debatable point however, since although there is clear chemical and theoretical evidence which shows that α,β-unsaturated acyl radicals exist as α-ketene alkyl radical species, they do not all necessarily undergo cyclisations with proximate alkene bonds *via* an *exo*-dig pathway to the exclusion of the alternative *endo*-trig process. Nevertheless, whatever the precise reaction pathway, α,β-unsaturated acyl radicals and their α-ketene alkyl equivalents are clearly valuable and versatile intermediates in organic synthesis, as evidenced in this study and previous work. To reinforce this statement, in the following paper we describe



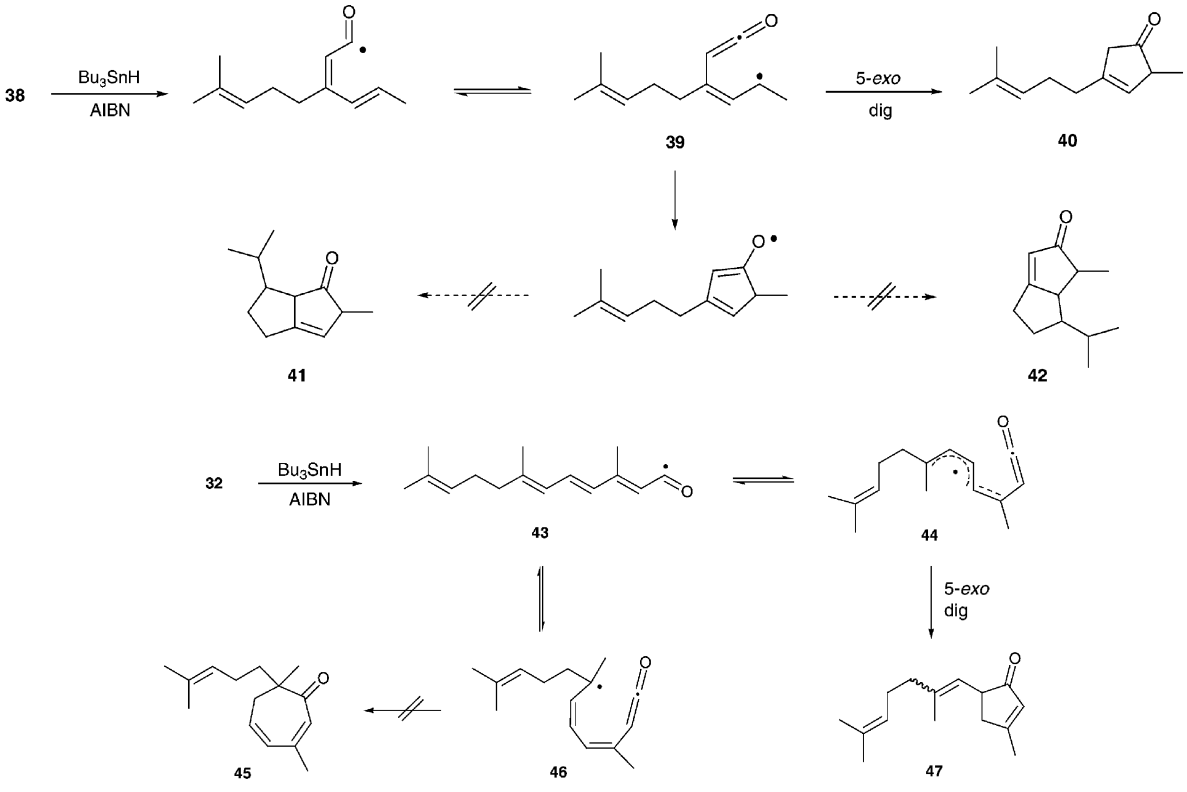
Scheme 4



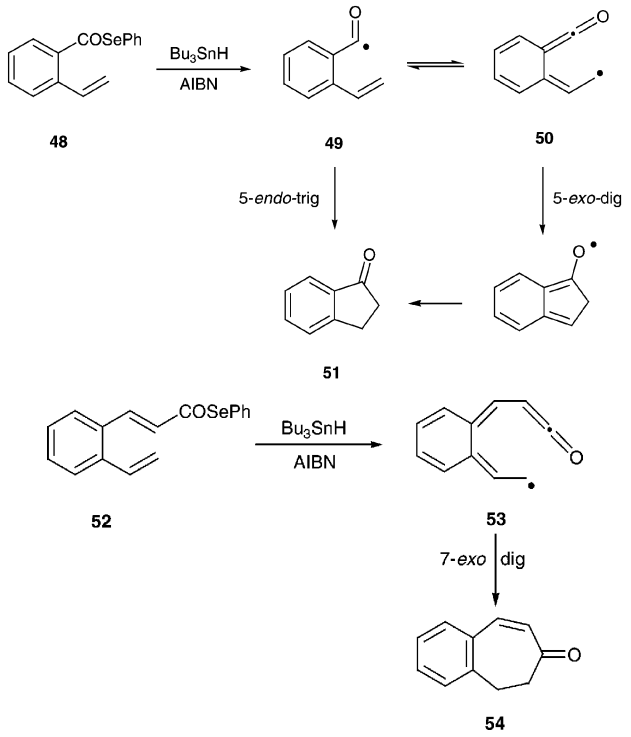
Scheme 5



Scheme 6 *Reagents*: i, $Me_3SiCH_2CO_2Me$, LDA, THF–H_2O, 94%; iii, NPSP, Bu_3P, CH_3Cl_2, 56%.



how we have applied α,β-unsaturated acyl radical species in the synthesis of the triquinane sesquiterpenes pentalenene and modhephene.



Experimental

For general experimental details see the preceding paper.[1]

General procedures

(i) Wadsworth–Emmons olefination reactions. Using a modification of the procedure described by Petter and co-workers,[8] a solution of triethyl phosphonoacetate (2.5 eq.) in THF (2.5 mol dm^{-3}) was added dropwise over 30 min to a stirred suspension of sodium hydride (2.4 eq.) in THF (5 mol dm^{-3}) at room temperature. The mixture was stirred at room temperature for 1 h and then a solution of the ketone/aldehyde (1 eq.) in THF (2.5 mol dm^{-3}) was added in one portion. The mixture was heated under reflux for 30 min, then stirred at room temperature overnight before saturated aqueous NH_4Cl solution was added. The mixture was evaporated *in vacuo* and the residue was then partitioned between water and diethyl ether. The separated aqueous layer was extracted with diethyl ether and the combined organic extracts were then washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure.

(ii) Saponifications of esters. (a) Lithium hydroxide (3 eq.) was added in one portion to a stirred solution of the saturated ester (1 eq.) in THF and water (1 : 1, 0.1 mol dm^{-3}) at room temperature and the mixture was then stirred at room temperature for 24 h. The mixture was evaporated *in vacuo* and the residue was then partitioned between water and diethyl ether. The separated aqueous layer was washed with diethyl ether, then acidified with HCl (2 mol dm^{-3}) and extracted with diethyl ether. The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to leave the crude carboxylic acid as a viscous oil.

(b) Sodium hydroxide was added in one portion to a stirred solution of the α,β-unsaturated ethyl ester (1 : 1 w/w) in ethanol and water (12 : 1, 0.4 mol dm^{-3}), and the mixture was heated under reflux for 1 h and then cooled to room temperature. The mixture was evaporated *in vacuo* and the residue was then diluted with water and washed with diethyl ether. The separated aqueous layer was acidified with HCl (2 mol dm^{-3}) and extracted with diethyl ether. The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to leave the crude α,β-unsaturated acid as a viscous oil.

(iii) α,β-Unsaturated selenyl esters. Using a modification of the literature procedure,[4] tributylphosphine (1.5 eq.) was added dropwise to a stirred solution of the α,β-unsaturated acid (1 eq.) in dichloromethane (0.8 mol dm^{-3}) at −30 °C. The mixture was stirred at −30 °C for 5 min and then solid *N*-phenylselenophthalimide (1.5 eq.) was added in one portion. The mixture was stirred and allowed to warm to room temperature over 10 min. The mixture was diluted with dichloromethane and washed with saturated $NaHCO_3$ solution and brine, dried ($MgSO_4$) and concentrated under reduced pressure to leave the crude selenyl ester as a yellow oil.

Phenyl 3-cyclopropylbut-2-enyl selenoate 11a

Following the general procedure, a solution of a 1 : 4 mixture of *Z*- and *E*-isomers of ethyl 3-cyclopropylbut-2-enoate[9] (1.5 g, 9.7 mmol) in ethanol (23 ml) and water (1.8 ml) was treated with sodium hydroxide (1.5 g) to give the corresponding acid (1.0 g, 94%), as a colourless solid. Recrystallisation from petrol–diethyl ether gave *E*-3-cyclopropylbut-2-enoic acid as needles, m.p. 59–63 °C; (found: C, 66.7; H, 8.1; $C_7H_{10}O_2$ requires C, 66.6; H, 8.0%); ν_{max}(soln. $CHCl_3$)/cm^{-1} 3169 (br), 2925 (br), 1682, 1622; major (*E*) isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.73 (1H, br. s, C*H*=C), 1.99 (3H, s, CH_3), 1.56 (1H, m, cyclopropyl C*H*), 0.93–0.67 (4H, m, 2 × cyclopropyl CH_2); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 172.4 (s), 164.9 (s), 112.8 (d), 20.4 (d), 15.2 (q), 7.2 (2 × t); minor (*Z*) isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.76 (1H, br. s, C*H*=C); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 172.8 (s), 164.2 (s), 115.7 (d), 18.6 (d), 14.2 (q), 5.9 (2 × t); *m*/*z* (EI) found 126.0684 (M^+), $C_7H_{10}O_2$ requires 126.0681.

Following the general procedure, a solution of 3-cyclopropylbut-2-enoic acid (100 mg, 0.8 mmol) in dichloromethane was treated with tributylphosphine (220 µl, 0.9 mmol) and *N*-phenylselenophthalimide (480 mg, 1.6 mmol). Chromatography on silica using petroleum ether–diethyl ether (10 : 1) as eluent gave a 1 : 4 mixture of *Z*- and *E*-siomers of the *selenyl ester* (140 mg, 67%) as a colourless oil; λ_{max}(EtOH)/nm 225 (10 610), 257 (14 440), 301 (6420); ν_{max}(film)/cm^{-1} 1693, 1592, 1476; major (*E*) isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.37 (5H, m, Ar*H*), 6.17 (1H, br. s, C*H*=C), 1.89 (3H, s, CH_3), 1.55 (1H, m, cyclopropyl C*H*), 0.95–0.76 (4H, m, 2 × cyclopropyl CH_2); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 188.5 (s), 160.2 (s), 135.8 (2 × d), 129.2 (2 × d), 128.2 (d), 127.4 (s), 122.3 (d), 20.3 (d), 16.0 (q), 7.6 (2 × t); minor (*Z*) isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (1H, br. s, C*H*=C); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 189.2 (s), 159.7 (s), 135.8 (2 × d), 129.2 (2 × d), 128.2 (d), 127.4 (s), 125.1 (d), 18.3 (q), 15.7 (d), 7.8 (2 × t).

Phenyl 3-(2,2-dimethylcyclopropyl)but-2*E*-enyl selenoate 11b

Following the general procedure, 2-(2,2-dimethylcyclopropyl)-ethan-2-one[10] (560 mg, 5.0 mmol) was treated with sodium hydride (60% dispersion in oil, 360 mg, 15 mmol) and triethyl phosphonoacetate (3.4 g, 15 mmol) in THF (7 ml). The crude product was purified by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent to give ethyl 3-(2,2-dimethylcyclopropyl)but-2(*E*)-enoate (770 mg, 84%) as a colourless liquid; ν_{max}(film)/cm^{-1} 1716, 1645, 1448; ^{1}H NMR (250 MHz $CDCl_3$) δ 5.50 (1H, br. s, C*H*=C(CH$_3$)), 4.15 (2H, q, *J* 7.1 Hz, OCH_2CH$_3$), 2.23 (3H, br. s, CH=C(CH_3)), 1.34–1.22 (4H, m, OCH$_2$CH_3 + cyclopropyl C*H*), 1.19 (3H, s, CH_3), 0.94 (3H, s, CH_3), 0.69–0.6 (2H, m, cyclopropyl CH_2); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 166.9 (s), 159.0 (s), 114.9 (d), 59.4 (t), 34.8

(q), 21.0 (q), 20.2 (s), 19.1 (q), 18.5 (t), 14.4 (q); *m/z* (EI) found 136.0892 ($M^+ - HOEt$), $C_9H_{12}O$ requires 136.0888.

Following the general procedure, a solution of ethyl 3-(2,2-dimethylcyclopropyl)but-2(*E*)-enoate (0.7 g, 3.8 mmol) in ethanol (9.2 ml) and water (0.7 ml) was treated with sodium hydroxide (0.7 g) to give the crude acid as a solid. Recrystallisation from petroleum ether–diethyl ether gave the *E-carboxylic acid* (320 mg, 53%) as colourless crystals, m.p. 97–103 °C; (found: C, 70.4; H, 9.4; $C_9H_{14}O_2$ requires C, 70.1; H, 9.2%); λ_{max}(EtOH)/nm 234 (9260); ν_{max}(film)/cm^{-1} 3524 (br), 2991 (br), 1693, 1650; ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.17 (1H, br. s, C*H*=C(CH_3)), 1.89 (3H, s, CH=C(C*H*$_3$)), 1.02, (1H, t, *J* 7.3 Hz, cyclopropyl C*H*), 0.85 (3H, s, C*H*$_3$), 0.59 (3H, s, C*H*$_3$), 0.40–0.27 (2H, m, cyclopropyl C*H*$_2$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 172.7 (s), 162.4 (s), 114.3 (d), 35.2 (d), 27.5 (q), 21.4 (q), 20.8 (s), 19.1 (q), 18.8 (t); *m/z* found 154.0095 (M^+), $C_9H_{14}O_2$ requires 154.0094.

Following the general procedure, a solution of the *E*-carboxylic acid (100 mg, 0.7 mmol) in dichloromethane (6 ml) was treated with *N*-phenylselenophthalimide (390 mg, 1.3 mmol) and tributylphosphine (160 µl, 1.3 mmol). The crude product was purified by chromatography on silica using petroleum ether–diethyl ether (10 : 1) as eluent to give the *selenyl ester* (150 mg, 79%) as a pale yellow oil; (found: C, 61.5; H, 6.4; $C_{15}H_{18}OSe$ requires C, 61.4; 6.2%); λ_{max}(EtOH)/nm 224 (9350), 259 (12600), 302 (6200); ν_{max}(film)/cm^{-1} 1776, 1694, 1607; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.56–7.38 (5H, m, Ar*H*), 5.92 (1H, br. s, C*H*=C(CH_3)), 2.15 (3H, s, CH=C(C*H*$_3$)), 1.33 (1H, t, *J* 7.0 Hz, cyclopropyl C*H*), 1.21 (3H, s, C*H*$_3$), 0.97 (3H, s, C*H*$_3$), 0.71 (2H, m, cyclopropyl C*H*$_2$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 189.2 (s), 157.6 (s), 135.8 (2 × d), 129.2 (d), 128.6 (2 × d), 127.3 (s), 123.4 (d), 34.8 (d), 27.5 (q), 22.5 (q), 21.6 (s), 19.3 (q), 19.2 (t); *m/z* (FAB) found 295.0590 ($M^+ + H$), $C_{15}H_{19}O^{80}Se$ requires 295.0601.

Phenyl *trans*-3-(2-phenylcyclopropyl)but-2-enyl selenoate 11c

Following the general procedure, a solution of *trans*-1-(2-phenylcyclopropyl)ethan-1-one in THF (1.5 ml) was treated with sodium hydride (60% dispersion in oil, 520 mg, 13 mmol) and triethyl phosphonoacetate (2.2 ml, 11 mmol) in THF (4.5 ml). The crude product was purified by chromatography on silica using petroleum ether–diethyl ether (5 : 1) as eluent to give a 1 : 9 mixture of *Z*- and *E*-isomers of the corresponding *α,β-unsaturated ester* (770 mg, 77%), as a colourless oil; (found: C, 78.2; H, 8.1; $C_{15}H_{18}O_2$ requires C, 78.2; H, 7.9%); ν_{max}(film)/cm^{-1} 1710, 1604; major (*E*) isomer: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43–7.20 (5H, m, Ar*H*), 5.83 (1H, br. s, C*H*=C), 4.26 (2H, q, *J* 6.9 Hz, OC*H*$_2$CH$_3$), 2.29 (1H, m, cyclopropyl C*H*), 2.20 (3H, s, C*H*$_3$), 1.85 (1H, m, cyclopropyl C*H*), 1.50 (1H, m, cyclopropyl C*H*H), 1.41 (1H, m, cyclopropyl CH*H*), 1.40 (3H, t, *J* 6.9 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 166.7 (s), 159.3 (s), 141.5 (s), 128.4 (2 × d), 126.0 (d), 125.9 (2 × d), 113.8 (d), 59.4 (t), 32.4 (d), 25.5 (d), 16.1 (q), 15.8 (t), 14.3 (q); minor (*Z*) isomer: δ_H (270 MHz, $CDCl_3$) 5.89 (1H, br. s, C*H*=C); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 116.7 (d); *m/z* (EI) found 230.1324 (M^+), $C_{15}H_{18}O_2$ requires 230.1307.

Following the general procedure, a solution of ethyl *trans*-3-(2-phenylcyclopropyl)but-2 enoate (700 mg, 3 mmol) in ethanol (7.4 ml) and water (0.5 ml) was treated with sodium hydroxide (700 mg) to give the crude carboxylic acid as a viscous yellow oil which solidified on standing. Recrystallisation from petroleum ether–diethyl ether gave the *E*-carboxylic acid (620 mg, ~100%) as colourless plates, m.p. 89–91 °C; (found: C, 77.3; H, 7.1; $C_{13}H_{14}O_2$ requires C, 77.2; H, 7.0%); λ_{max}(EtOH)/nm 245 (11 970); ν_{max}(film)/cm^{-1} 3204, 1692, 1629; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.10 (5H, m, Ar*H*), 5.75 (1H, br. s, C*H*=C), 2.22 (1H, m, cyclopropyl C*H*), 2.14 (3H, s, C*H*$_3$), 1.44 (1H, m, cyclopropyl C*H*), 1.34 (1H, m, cyclopropyl C*H*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 172.0 (s), 162.7 (s), 141.2 (s), 128.5 (2 × d), 126.2 (d), 126.0 (2 × d), 113.3 (d), 32.7 (d), 25.8 (d), 16.3 (q), 16.1 (t); *m/z* (EI) found 202.0999 (M^+), $C_{13}H_{14}O_2$ requires 202.0994.

Following the general procedure, a solution of *trans*-3-(2-phenylcyclopropyl)-but-2-enoic acid (100 mg, 0.5 mmol) in dichloromethane (11 ml) was treated with *N*-phenylselenophthalimide (300 mg, 1.0 mmol) and tributylphosphine (250 µl, 1.0 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* (160 mg, 94%), as a pale yellow oil; λ_{max}(EtOH)/nm 222 (13 580), 267 (11 060); ν_{max}(film)/cm^{-1} 1693, 1682, 1592; major (*E*) isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.10 (10H, m, Ar*H*), 6.17 (1H, br. s, C*H*=C), 2.25 (1H, m, cyclopropyl C*H*), 2.02 (3H, s, CH_3), 1.77 (1H, m, cyclopropyl C*H*), 1.34 (2H, m, cyclopropyl C*H*$_2$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 189.1 (s), 158.2 (s), 141.3 (s), 136.2 (d), 129.6 (2 × d), 129.0 (d), 128.9 (2 × d), 127.6 (s), 126.7 (d), 126.5 (d), 126.3 (d), 123.2 (d), 33.0 (d), 26.4 (d), 19.5 (q), 16.7 (t); minor (*Z*) isomer (where observed): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (1H, br. s C*H*=C), 2.30 (1H, m, cyclopropyl C*H*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 27.7 (d), 26.0 (d), 17.6 (t), 17.3 (q); *m/z* (FAB) found 343.0633 ($M^+ + H$), $C_{19}H_{19}O^{80}Se$ requires 343.0601; found 341.0625, $C_{19}H_{19}O^{78}Se$ requires 341.0609.

3-Methylcyclohex-2-en-1-one 14a

A solution of tributyltin hydride (140 µl, 0.38 mmol) and catalytic AIBN (3 mg) in dry degassed benzene (2.0 ml) was added dropwise over 2 h, *via* syringe pump, to a solution of the selenyl ester **11a** (50 mg, 0.19 mmol) and AIBN (2 mg) in benzene (63 ml) under reflux in an atmosphere of argon. The mixture was stirred under reflux for a further 2 h, then cooled to room temperature and the solvent was evaporated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent to give the cyclohex-2-enone[11] (10 mg, 48%) as an oil; ν_{max}(film)/cm^{-1} 2928, 2854, 1659, 1456; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (1H, s, CH=), 2.32 (2H, t, *J* 6.4 Hz, $CH_2C(O)$), 2.26 (2H, t, *J* 6.4 Hz, CH_2CH_2C=), 1.97 (2H, app. qn, *J* 6.4 Hz, $CH_2CH_2CH_2$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 218.1 (s), 162.3 (s), 126.7 (d), 37.0 (t), 30.9 (t), 24.5 (q), 22.5 (t); *m/z* (EI) found 110.0732 (M^+), $C_7H_{10}O$ requires 110.0732.

3,6,6-Trimethylcyclohex-2-enone 14b

A solution of tributyltin hydride (120 µl, 0.34 mmol) and AIBN (3 mg) in dry degassed benzene (1 ml) was added dropwise over 1 h, *via* syringe pump, to a solution of the selenyl ester **11b** (50 mg, 0.17 mmol) and AIBN (2 mg) in dry degassed benzene (57 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*. The residue was purified by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent to give the cyclohexenone[12] (14 mg, 60%), as a colourless oil; ν_{max}(film)/cm^{-1} 1714, 1657; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.78 (1H, br. s, C*H*=C(CH_3)), 2.30 (2H, br. t, *J* 6.1 Hz, C*H*$_2$CH$_2$C(CH_3)=), 1.93 (3H, s, C*H*$_3$), 1.81 (2H, t, *J* 6.1 Hz, CH$_2$C*H*$_2$C(CH_3)=), 1.10 (6H, s, 2 × C*H*$_3$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 203.8 (s), 160.2 (s), 125.1 (d), 40.1 (s), 36.3 (t), 29.7 (t), 24.2 (2 × q), 24.0 (q); *m/z* (EI) found 138.1036 (M^+), $C_9H_{14}O$ requires 138.1045.

6-Phenyl-3-methylcyclohex-2-en-1-one 15 and 6-phenyl-3-methylcyclohex-3-en-1-one 16

A solution of tributyltin hydride (110 µl, 0.3 mmol) and AIBN (2 mg) in dry degassed benzene (1 ml) was added over 2 h *via* syringe pump to a stirred solution of the selenyl ester **11c** (50 mg,

0.15 mmol) and AIBN (2 mg) under reflux in an atmosphere of argon. The mixture was allowed to stir at reflux for 4 h then cooled to room temperature and the solvent was evaporated *in vacuo*. The residue was purified by chromatography on silica using petroleum ether–diethyl ether (10 : 1 then 5 : 1) as eluent to give: (i), *6-phenyl-3-methylcyclohex-3-en-1-one* (4 mg, 15%) (eluted first) as a pale yellow oil; ν_{max}(film)/cm^{-1} 1716, 1674; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.39–7.16 (5H, m, Ar*H*), 5.69 (1H, br. s, C*H*=C), 3.78 (1H, t, *J* 8.3 Hz, PhC*H*C(O)), 2.91 (2H, app. d, *J* 8.3 Hz, CH_2CHPh), 2.76 (2H, m, CH_2C(O)), 1.79 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 209.3 (s), 138.7 (s), 128.5 (d), 128.3 (2 × d), 127.1 (2 × d), 120.6 (d), 53.9 (d), 44.5 (t), 32.8 (t), 22.6 (q); (ii), a 1 : 4 mixture of the *Z*- and *E*-isomers of *6-phenyl-3-methylhex-3-en-1-al* (3 mg, 11%), (eluted second) as a viscous yellow oil; ν_{max}(film)/cm^{-1} 1722, 1673, 1602; major isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.60 (1H, t, *J* 2.5 Hz, C*H*O), 7.35–7.16 (5H, m, Ar*H*), 5.38 (1H, br. t, *J* 5.0 Hz, CH_2C*H*=C), 3.06 (2H, br. s, CH_2CHO), 2.57 (2H, m, CH_2CH=C), 2.41 (2H, m, CH_2Ph), 1.58 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 201.8 (s), 130.8 (s), 130.3 (d), 129.7 (s), 128.9 (2 × d), 128.8 (d), 126.4 (2 × d), 54.7 (t), 36.1 (2 × t), 30.5 (q); minor isomer (when not obscured by major isomer): ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.35 (1H, t, *J* 2.5 Hz, C*H*O), 5.53 (1H, br. t, *J* 5.0 Hz, CH_2C*H*=C), 1.61 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 202.5 (s), 53.7 (t), 36.2 (2 × t), 30.9 (q); (iii), *6-phenyl-3-methylcyclohex-2-en-1-one* (14 mg, 51%) (eluted last) as a colourless oil; ν_{max}(film)/cm^{-1} 1661 (lit.[12] ν_{max}(CCl_4)/cm^{-1} 1675); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.29–7.07 (5H, m, Ar*H*), 5.96 (1H, br. s, C*H*=C), 3.45 (1H, app. t, *J* 8.6 Hz, PhC*H*C(O)), 2.41–2.15 (4H, m, 2 × CH_2), 1.93 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 199.5 (s), 162.6 (s), 141.2 (s), 128.9 (d), 128.7 (d), 127.5 (d), 127.3 (d), 52.7 (d), 31.1 (t), 24.8 (q); *m*/*z* (EI) found 186.1035 (M$^+$), $C_{13}H_{14}O$ requires 186.1045.

Phenyl 3-cyclopropylprop-2*E*-enyl selenoate 17

Following the general procedure, a solution of 3-cyclopropylprop-2(*E*)-enoic acid[13] (80 mg, 0.7 mmol) in dichloromethane (15 ml) was treated with *N*-phenylselenophthalimide (430 mg, 1.4 mmol) and tributylphosphine (360 µl, 1.4 mmol). The crude product was purified by chromatography on silica using petroleum ether–diethyl ether (10 : 1) as eluent to give the *selenyl ester* (75 mg, 42%) as a pale yellow oil; ν_{max}(film)/cm^{-1} 1693, 1614; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.67–7.32 (5H, m, Ar*H*), 6.47–6.27 (2H, m, C*H*=C*H*), 1.61 (1H, m, cyclopropyl C*H*), 1.09 (2H, m, cyclopropyl CH_2), 0.78 (2H, m, cyclopropyl CH_2); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 191.4 (s), 152.8 (d), 136.8 (2 × d), 130.1 (2 × d), 129.7 (d), 128.0 (d), 127.2 (s), 15.8 (d), 10.2 (2 × t); *m*/*z* (FAB) found 253.0110 (M$^+$ + H), $C_{12}H_{13}O^{80}Se$ requires 253.0132; found 251.0113, $C_{12}H_{13}O^{78}Se$ requires 251.0139.

Phenyl *trans*-3-(2-phenylcyclopropyl)-prop-2*E*-enyl selenoate 18

Following the general procedure, a solution of *trans*-2-phenylcyclopropyl carboxaldehyde[14] (1.0 g, 6.8 mmol) in THF (3.6 ml) was treated with sodium hydride (60% dispersion in oil, 550 mg, 14 mmol) and triethyl phosphonoacetate (2.9 ml, 15 mmol) in THF (7.2 ml). The crude product was purified by chromatography on silica using petroleum ether–diethyl ether (5 : 1) as eluent to give the *E*-isomer of the *(phenylcyclopropyl)prop-2-enoate* (1.2 g, 84%), as a colourless oil; (found: C, 77.8; H, 7.6; $C_{14}H_{16}O_2$ requires C, 77.7; H, 7.5%); λ_{max}(EtOH)/nm 247 (11 400); ν_{max}(film)/cm^{-1} 1713, 1644, 1604; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.54–7.16 (5H, m, Ar*H*), 6.66 (1H, dd, *J* 9.6, 15.2 Hz, C*H*=CHCO$_2$Et), 5.96 (1H, d, *J* 15.2 Hz, CH=C*H*CO$_2$Et), 4.26 (2H, q, *J* 6.9 Hz, OCH_2CH$_3$), 2.21 (1H, m, cyclopropyl C*H*), 1.86 (1H, m, cyclopropyl C*H*), 1.50 (1H, m, cyclopropyl C*H*), 1.35 (4H, t, *J* 6.9 Hz, OCH$_2$CH_3 + obs. cyclopropyl C*H*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 166.9 (s), 151.9 (d), 141.1 (s), 128.8 (2 × d), 126.5 (d), 126.2 (2 × d), 119.2 (d), 60.4 (t), 27.17 (2 × d), 18.1 (t), 14.6 (q); *m*/*z* (EI) found 216.1153 (M$^+$), $C_{14}H_{16}O_2$ requires 216.1150.

Following the general procedure, a solution of the (phenylcyclopropyl)prop-2(*E*)-enoate (500 mg, 2.3 mmol) in ethanol (5 ml) and water (0.5 ml), was treated with sodium hydroxide (500 mg) to give the corresponding *carboxylic acid* (410 mg, 95%) as a viscous oil; (found: C, 76.7; H, 6.4; $C_{12}H_{12}O_2$ requires C, 76.6; H, 6.4%); λ_{max}(EtOH)/nm 244 (7150); ν_{max}(soln. $CHCl_3$)/cm^{-1} 3178 (br), 2826 (br), 2677 (br), 1694, 1644; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.09 (5H, m, Ar*H*), 6.72 (1H, dd, *J* 15.0 and 9.0 Hz, C*H*=CHCO$_2$H), 5.81 (1H, d, *J* 15 Hz, CH=C*H*CO$_2$H), 2.24 (1H, m, cyclopropyl C*H*), 1.85 (1H, m, cyclopropyl C*H*), 1.51 (1H, m, cyclopropyl C*H*H), 1.32 (1H, m, cyclopropyl CH*H*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 172.0 (s), 154.7 (d), 140.4 (s), 128.5 (2 × d), 126.3 (d), 125.8 (2 × d), 118.0 (d), 27.2 (d), 26.9 (d), 18.0 (t); *m*/*z* (EI) found 188.0838 (M$^+$), $C_{12}H_{12}O_2$ requires 188.0837.

Following the general procedure, a solution of the *trans*-phenylcyclopropylprop-2(*E*)-enoic acid (200 mg, 1.1 mmol) in dichloromethane (15 ml) was treated with tributylphosphine (400 µl, 1.6 mmol) and *N*-phenylselenophthalimide (480 mg, 1.6 mmol). The crude product was purified by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent to give the *selenyl ester* (140 mg, 40%) as a pale yellow oil; ν_{max}(film)/cm^{-1} 1692, 1613, 1580, 1496; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73–7.11 (10H, m, Ar*H*), 6.61 (1H, dd, *J* 9.1 and 14.3 Hz, CHC*H*=CH), 6.30 (1H, d, *J* 14.3 Hz, CH=C*H*COSePh), 2.27 (1H, m, cyclopropyl C*H*), 1.92 (1H, m, cyclopropyl C*H*), 1.54 (1H, m, cyclopropyl C*H*H), 1.39 (1H, m, cyclopropyl CH*H*); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 189.3 (s), 149.1 (d), 140.2 (s), 135.9 (2 × d), 129.2 (2 × d), 129.1 (s), 128.9 (2 × d), 127.4 (d), 126.3 (d), 125.7 (2 × d), 27.5 (d), 27.2 (d), 18.2 (t); *m*/*z* (FAB) found 329.0435 (M$^+$ + H), $C_{18}H_{16}O^{80}Se$ requires 329.0445; found 327.0448, $C_{18}H_{16}O^{78}Se$ requires 327.0452.

6-Phenylcyclohex-3-en-1-one 19

A solution of tributyltin hydride (72 µl, 0.2 mmol) and AIBN (2 mg) in dry degassed benzene (2 ml) was added over 8 h *via* syringe pump to a stirred solution of the selenyl ester **18** (60 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 4 h, then cooled to room temperature and the solvent was evaporated *in vacuo*. The residue was purified by chromatography on silica using petroleum ether–diethyl ether (10 : 1 then 5 : 1) as eluent to give: (i), *6-phenylhex-2-en-1-al* (14 mg, 45%) (eluted first) as a pale yellow oil; ν_{max}(film)/cm^{-1} 1692; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (1H, d, *J* 7.9 Hz, C*H*O), 7.32–7.18 (5H, m, Ar*H*), 6.85 (1H, dt, *J* 6.8, 15.6 Hz, C*H*=CHCHO), 6.14 (1H, dd, *J* 7.9, 15.6 Hz, CH=C*H*CHO), 2.69 (2H, t, *J* 7.3 Hz, PhCH_2CH$_2$), 2.37 (2H, app. q, *J* 7.3 Hz, CH$_2$CH_2CH=), 1.87 (2H, app. qn, *J* 7.3 Hz, CH$_2$CH_2CH$_2$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 198.6 (d), 162.7 (d), 137.7 (d), 132.9 (2 × d), 132.8 (2 × d), 131.2 (s), 130.5 (d), 39.7 (t), 36.6 (t), 33.9 (t); (ii), *6-phenylcyclohex-3-en-1-one* (6 mg, 20%) (eluted second) as a colourless oil; ν_{max}(film)/cm^{-1} 1716, 1680; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.49–7.17 (5H, m, Ar*H*), 6.04–5.95 (1H, m, C(O)CH$_2$C*H*=CH), 5.84–5.77 (1H, m, CH=C*H*CH$_2$CH), 3.85 (1H, t, *J* 7.8 Hz, PhC*H*C(O)), 2.99 (2H, br. AB, app. q, *J* 21.7 Hz, CH_2C(O)), 2.84–2.79 (2H, m, CHCH_2CH=); *m*/*z* (EI) found 172.0894 (M$^+$), $C_{12}H_{12}O$ requires 172.0888.

Ethyl *trans*-3-[2,2-dimethyl-3-(2-methylprop-1-enyl)-cyclopropyl]but-2*E*-enoate 23a

Following the modified general procedure, a solution of the cyclopropyl ketone[15] (1.5 g, 9.0 mmol) in THF (3.2 ml), was

treated with sodium hydride (60% dispersion in oil, 1.1 g, 27 mmol) and triethyl phosphonoacetate (4.5 ml, 25.0 mmol) in THF (9.5 ml) and the mixture was heated at reflux overnight. The crude product was purified by chromatography on silica using petroleum ether–diethyl ether (20 : 1) as eluent to give the *E-α,β-unsaturated ester* (1.0 g, 47%) as a colourless oil; (found: C. 76.1; H, 10.3; $C_{15}H_{24}O_2$ requires C, 76.2; H, 10.3%); ν_{max}(film)/cm^{-1} 1714, 1643; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.60 (1H, br. s, =C*H*CO_2Et), 4.90 (1H, d, *J* 7.6 Hz, =C*H*CH), 4.15 (2H, q, *J* 7.2 Hz, OCH_2CH$_3$), 2.21 (3H, s, CH_3C=), 1.72 (6H, s, 2 × CH_3C=), 1.61 (1H, m, cyclopropyl C*H*), 1.29 (4H, m, OCH_2CH_3 + cyclopropyl C*H*), 1.15 (3H, s, CH_3), 0.99 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 166.8 (s), 158.5 (s), 133.9 (s), 122.4 (d), 114.8 (d), 59.3 (t), 42.8 (d), 28.4 (d), 26.1 (s), 25.4 (q), 22.7 (q), 20.7 (2 × q), 18.4 (q), 14.2 (q); *m/z* (EI) found 235.1684 (M^+ − H), $C_{15}H_{23}O_2$ requires 235.1698.

Phenyl *trans*-3-[2,2-dimethyl-3-(2-methylprop-1-enyl)-cyclopropyl]but-2*E*-enyl selenoate 24a

Following the general procedure, a solution of the ester **23a** (170 mg, 0.7 mmol) in refluxing EtOH (5.0 ml) and water (0.5 ml) was treated with sodium hydroxide (170 mg) to give the corresponding carboxylic acid (130 mg, 89%) as a pale yellow oil; ν_{max}(film)/cm^{-1} 3439, 2919, 1713, 1682, 1632; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.61 (1H, br. s, =C*H*CO_2H), 4.89 (1H, app. d, *J* 7.6 Hz, C*H*=C), 2.21 (3H, s, CH_3C(O)), 1.73 (6H, s, 2 × CH_3C=), 1.69 (1H, m, cyclopropyl C*H*), 1.33 (1H, d, *J* 7.0 Hz, cyclopropyl C*H*), 1.17 (3H, s, CH_3), 0.99 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 172.5 (s), 162.4 (s), 134.2 (s), 122.2 (d), 114.0 (d), 43.1 (d), 28.7 (d), 26.8 (s), 25.4 (q), 22.5 (q), 20.7 (2 × q), 18.3 (q); *m/z* (EI) found 195.1225 (M^+ − CH_3), $C_{12}H_{17}O_2$ requires 193.1229.

Following the general procedure, a solution of the carboxylic acid (77 mg, 0.37 mmol) in dichloromethane (8 ml) was treated with tributylphosphine (100 µl, 0.41 mmol) and *N*-phenylselenophthalimide (220 mg, 0.74 mmol). The crude product was purified by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent to give the *selenyl ester* (92 mg, 72%) as a pale yellow oil; ν_{max}(film)/cm^{-1} 1697, 1605, 1580; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.57–7.38 (5H, m, Ar*H*), 5.99 (1H, s, =C*H*COSePh), 4.92 (1H, d, *J* 7.6 Hz, CHC*H*=C), 2.16 (3H, s, CH_3C=), 1.74 (3H, s, CH_3C=), 1.71 (3H, s, CH_3C=), 1.62 (1H, m, cyclopropyl C*H*), 1.23 (1H, d, *J* 7.0 Hz, cyclopropyl C*H*), 1.18 (3H, s, CH_3), 1.03 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 189.3 (s), 157.4 (s), 135.7 (2 × d), 134.7 (s), 129.2 (2 × d), 128.7 (d), 127.4 (s), 123.3 (d), 122.0 (d), 42.8 (d), 29.1 (d), 27.6 (s), 25.5 (q), 22.7 (q), 22.3 (q), 20.9 (q), 18.6 (q).

Phenyl *trans*-3-[2,2-dimethyl-3-(eth-1-enyl)-cyclopropyl]but-2-enyl selenoate 24b

Methyllithium (1.5 mol dm^{-3} in THF, 6.2 ml, 9.3 mmol) was added dropwise over 10 min to a stirred solution of 2,2-dimethyl-3-(eth-1-enyl)cyclopropylcarboxylic acid[16] (1 : 9 *cis* : *trans*, 500 mg, 3.6 mmol) in diethyl ether (1 ml) at 0 °C. The mixture was stirred at room temperature for 5 h then poured onto ice–water and the separated aqueous layer was then extracted with diethyl ether (3 × 10 ml). The combined organic layers were washed with water (1 × 10 ml) and brine (1 × 10 ml), then dried ($MgSO_4$) and the volume of the solution was reduced to provide a 5 ml solution of the corresponding methyl ketone. A solution of triethyl phosphonoacetate (3.2 ml, 16 mmol) in THF (2 ml) was added dropwise over 30 min to a stirred suspension of sodium hydride (60% dispersion in oil, 720 mg, 18 mmol) in THF (4 ml) at room temperature. The mixture was stirred at room temperature for 1 h, then a solution of the methyl ketone (3.6 mmol) in diethyl ether (5 ml) was added in one portion. The mixture was heated to reflux for 30 min then allowed to stir at room temperature overnight before saturated NH_4Cl solution was added. The mixture was concentrated *in vacuo* and the residue was then partitioned between water (25 ml) and diethyl ether (25 ml). The separated aqueous layer was extracted with diethyl ether (3 × 25 ml) and the combined organic extracts were washed with brine (25 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent to give the *E-α,β-unsaturated ester* **23b** (500 mg, 67%) as a colourless oil; ν_{max}(film)/cm^{-1} 1718, 1645; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.67–5.53 (2H, m, CH_3C=C*H* + C*H*=CH_2), 5.13 (1H, d, *J* 18.8 Hz, CH=C*H*H), 5.00 (1H, d, *J* 10.3 Hz, CH=CH*H*), 4.15 (2H, q, *J* 7.0 Hz, OCH_2CH$_3$), 2.22 (3H, s, CH=C(CH_3)), 1.63 (1H, app. t, *J* 6.2 Hz, cyclopropyl C*H*CH=), 1.43 (1H, d, *J* 6.2 Hz, cyclopropyl C*H*), 1.29 (3H, t, *J* 7.0 Hz, OCH_2CH_3), 1.18 (3H, s, CH_3), 0.99 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 167.2 (s), 157.9 (s), 136.9 (d), 115.4 (d), 114.9 (t), 55.5 (t), 41.5 (d), 33.2 (d), 26.4 (s), 22.2 (q), 20.7 (q), 14.3 (q); *m/z* (EI) found 208.1473 (M^+), $C_{13}H_{20}O_2$ requires 208.1463.

Following the general procedure, a solution of the α,β-unsaturated ester **23b** (900 mg, 4.3 mmol) in ethanol (10 ml) and water (1 ml) was treated with sodium hydroxide (900 mg) to give a 1 : 4 mixture of *Z*- and *E*-isomers of the corresponding carboxylic acid (600 mg, 77%) as a pale yellow oil; ν_{max}(film)/cm^{-1} 3174 (br), 2640, 1694, 1642; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.88–5.53 (2H, m, CH_3C=C*H* + C*H*=CH_2), 5.15 (1H, d, *J* 17.1 Hz, CH=C*H*H), 5.05 (1H, d, *J* 10.1 Hz, CH=CH*H*), 2.23 (3H, s, CH=C(CH_3)), 1.68 (1H, app. t, *J* 6.0 Hz, cyclopropyl C*H*CH=), 1.46 (1H, d, *J* 6.0 Hz, cyclopropyl C*H*), 1.19 (3H, s, CH_3), 0.99 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) major isomer: δ 172.4 (s), 161.1 (s), 136.6 (d), 115.2 (t), 114.8 (d), 41.8 (d), 33.5 (d), 26.9 (s), 22.2 (q), 21.1 (q), 20.5 (q); minor isomer: δ 177.2 (s), 161.1 (s), 137.5 (d), 114.7 (d), 114.5 (t), 37.4 (d), 33.0 (d), 25.4 (s), 21.9 (q), 21.1 (q), 20.5 (q); *m/z* (EI) found 180.1150 (M^+), $C_{11}H_{16}O_2$ requires 180.1150.

Following the general procedure, a solution of the *trans*-cyclopropyl-but-2-enoic acid (250 mg) in dichloromethane (30 ml) was treated with *N*-phenylselenophthalimide (840 mg, 2.8 mmol) and tributylphosphine (690 µl, 2.8 mmol). The crude product was purified by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent to give the *selenyl ester* (310 mg, 70%) as a pale yellow oil; (found: C, 63.9, H, 6.5; $C_{17}H_{21}$OSe requires C, 63.9, H, 6.3%); λ_{max}(EtOH)/nm 224 (8190), 260 (5280) 300 (2430); ν_{max}(film)/cm^{-1} 1704, 1634, 1607; major (*E*) isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.34 (5H, m, Ar*H*), 6.00 (1H, br. s, C*H*=C), 5.63 (1H, m, C*H*=CH_2), 5.24 (2H, m, CH=CH_2), 2.14 (3H, s, CH=C(CH_3)), 1.65 (1H, dd, *J* 6.2, 6.4 Hz, cyclopropyl C*H*CH=), 1.42 (1H, d, *J* 6.2 Hz, cyclopropyl C*H*), 1.19 (3H, s, CH_3), 1.02 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 189.3 (s), 156.2 (s), 136.3 (d), 135.8 (2 × d), 129.3 (2 × d), 128.8 (d), 127.3 (s), 123.7 (d), 115.7 (t), 41.4 (d), 33.7 (d), 27.5 (s), 22.3 (q), 21.9 (q), 120.8 (q); minor (*Z*) isomer (where observed): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (3H, s, CH_3), 1.00 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 197.3 (s), 139.3 (s), 137.3 (d), 135.8 (2 × d), 129.3 (2 × d), 128.8 (d), 128.6 (d), 127.3 (s), 114.6 (t), 37.4 (d), 33.2 (d), 25.5 (s), 22.3 (q), 21.9 (q), 20.8 (q); *m/z* (FAB) found 321.0745 (M^+ + H), $C_{17}H_{21}O^{80}Se$ requires 321.0758; found 319.0719; $C_{17}H_{21}O^{78}Se$ requires 319.0765.

3,5,5-Trimethyl-6-ethenylcyclohex-2-en-1-one 25

A solution of tributyltin hydride (64 µl, 0.17 mmol) and AIBN (2 mg) in dry degassed benzene (2 ml) was added over 2 h *via* syringe pump to a stirred solution of the selenyl ester **24b** (50 mg, 0.15 mmol) and AIBN (2 mg) in benzene (60 ml) under reflux in an atmosphere of argon. The mixture was stirred under reflux for 2 h then cooled to room temperature and the solvent was evaporated *in vacuo*. The residue was purified by chromatography on silica using petroleum ether–diethyl ether (5 : 1) as eluent to give the *cyclohex-2-en-1-one*

(14 mg, 55%) as a colourless oil; ν_{max}(film)/cm^{-1} 1661; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (1H, br. s, C(O)C*H*=C), 5.73 (1H, dt, *J* 7.0, 10.9 Hz, C*H*=CH$_2$), 5.26 (1H, d, *J* 7.0 Hz, CH=C*H*H), 5.18 (1H, d, *J* 10.9 Hz, CH=CH*H*), 2.72 (1H, d, *J* 7.0 Hz, C(O)C*H*CH=), 2.21 (2H, app. d, *J* 6.3 Hz, CH_2), 1.96 (3H, s, CHC=(CH_3)), 1.04 (3H, s, CH_3), 0.98 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 201.8 (s), 158.6 (s), 133.8 (d), 125.9 (d), 120.3 (t), 62.5 (d), 30.2 (t), 29.5 (s), 28.8 (q), 24.8 (q), 23.1 (q).

6-(2-Methylprop-2-enyl)-3,5,5-trimethylcyclohex-2-en-1-one and 6-(2-methylprop-2-enyl)-3,5,5-trimethylcyclohex-3-en-1-one 26

A solution of tributyltin hydride (60 µl, 0.17 mmol) in dry degassed benzene (1.0 ml) was added over 2 h *via* syringe pump to a stirred solution of the selenyl ester **24c** (30 mg, 0.82 mmol) and AIBN (14 mg, 0.08 mmol) in benzene (28 ml) under reflux in an atmosphere of argon. The mixture was stirred under reflux for a further 2 h, then cooled to room temperature and the solvent was evaporated *in vacuo*. The residue was purified by chromatography on silica using petroleum ether–diethyl ether (5 : 1) as eluent to give: (i), the *cyclohex-3-enone* (2 mg, 12%) (eluted first); ν_{max}(film)/cm^{-1} 1709; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (1H, br. s, C*H*=C), 5.26 (1H, br. d, *J* ~10 Hz, C*H*C=), 3.15 (1H, d, *J* ~10 Hz, C*H*C(O)), 2.81 (1H, d, *J* 16.0 Hz, =CC*H*H), 2.71 (1H, d, *J* 16.0 Hz, =CCH*H*), 1.78 (3H, s, CH_3C=), 1.72 (3H, s, CH_3C=), 1.66 (3H, s, CH_3C=), 1.03 (3H, s, CH_3C=), 0.92 (3H, s, CH_3C=); (ii), the *cyclohex-2-enone* (9 mg, 52%) (eluted second); ν_{max}(film)/cm^{-1} 1656; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (1H, br. s, =C*H*C(O)), 5.08 (1H, d, *J* 9.9 Hz, CHC*H*=), 2.96 (1H, d, *J* 9.9 Hz, C(O)C*H*CH=), 2.28 (1H, d, *J* 18.5 Hz, =CC*H*H), 2.12 (1H, d, *J* 18.5 Hz, =CCH*H*), 1.93 (3H, s, CH_3C=), 1.78 (3H, s, CH_3C=), 1.69 (3H, s, CH_3C=), 1.02 (3H, s, CH_3CCH$_2$), 0.97 (3H, s, CH_3CCH$_2$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 202.1 (s), 136.9 (s), 128.5 (s), 125.1 (d), 118.6 (d), 56.8 (d), 36.9 (s), 29.7 (t), 28.1 (q), 26.2 (q), 24.6 (q), 24.3 (q), 18.6 (q); *m*/*z* (EI) found 192.1507 (M$^+$), $C_{13}H_{20}O$ requires 192.1514.

Phenyl *trans*-3-[2,2-dimethyl-3-(2-methylprop-1-enyl)-cyclopropyl]prop-2*E*-enyl selenoate 27

Following the general procedure, *trans*-2,2-dimethyl-3(2-methylprop-1-enyl)cyclopropyl carboxaldehyde[17] (400 mg, 2.6 mmol) was treated with sodium hydride (60% dispersion in oil, 170 mg, 4.2 mmol) and triethyl phosphonoacetate (590 mg, 2.6 mmol) in THF (4 ml). Purification by chromatography on silica using petroleum ether–diethyl ether (5 : 1) as eluent gave a 1 : 3 mixture of *Z*- and *E*-isomers of ethyl 3-(2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropyl)prop-2-enoate (380 mg, 65%), as a colourless oil; (found: C, 76.0; H, 10.4; $C_{14}H_{22}O_2$ requires C, 75.6; H, 10.0%); λ_{max}(EtOH)/nm 254 (6030); ν_{max}(film)/cm^{-1} 1714, 1638, 1449; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.75 (1H, dd, *J* 10.5, 15.3 Hz, C*H*=CHCO$_2$Et), 5.87 (1H, d, *J* 15.3 Hz, CH=C*H*CO$_2$Et), 4.92 (1H, br. d, *J* 8.1 Hz, C*H*=C), 4.17 (2H, q, *J* 7.2 Hz, OCH_2CH$_3$), 1.72 (3H, s, CH_3C=), 1.68 (3H, s, CH_3C=), 1.62 (1H, m, cyclopropyl C*H*), 1.31 (1H, m, cyclopropyl C*H*), 1.28 (3H, t, *J* 7.2 Hz, OCH$_2$CH_3), 1.21 (3H, s, CH_3), 1.12 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 166.1 (s), 150.4 (d), 134.5 (s), 121.7 (d), 119.4 (d), 59.8 (t), 37.3 (d), 35.0 (d), 27.7 (s), 25.6 (q), 22.5 (q), 22.0 (q), 18.3 (q), 14.2 (q); *m*/*z* (EI) found 222.1630 (M$^+$), $C_{14}H_{22}O_2$ requires 222.1620.

Following the general procedure, a solution of the α,β-unsaturated ester (370 mg, 1.7 mmol) in ethanol (4.1 ml) and water (0.3 ml) was treated with sodium hydroxide (370 mg) to give the corresponding *carboxylic acid* (280 mg, 86%), as a yellow oil; λ_{max}(EtOH) 250 (10 500) nm; ν_{max}(film)/cm^{-1} 3363 (br), 1708, 1650; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (1H, dd, *J* 10.7, 15.3 Hz, C*H*=CHCO$_2$H), 5.88 (1H, d, *J* 15.3 Hz, C*H*=C*H*CO$_2$H), 4.93 (1H, br. d, *J* 8.0 Hz, C*H*=C), 1.73 (3H, s, CH_3C=), 1.69 (3H, s, CH_3C=), 1.73–1.69 (1H, obs. cyclopropyl C*H*), 1.36 (1H, dd, *J* 4.9, 10.7 Hz, cyclopropyl C*H*), 1.22 (3H, s, CH_3), 1.14 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 177.7 (s), 154.0 (d), 134.4 (s), 121.4 (d), 118.3 (d), 37.6 (d), 35.7 (d), 28.4 (s), 22.4 (q), 21.9 (q), 20.8 (2 × q); *m*/*z* (EI) found 194.1309 (M$^+$), $C_{12}H_{18}O_2$ requires 194.1307.

Following the general procedure, a solution of the carboxylic acid (100 mg, 0.5 mmol) in dichloromethane (6 ml) was treated with *N*-phenylselenophthalimide (230 mg, 7.6 mmol) and tributylphosphine (200 µl, 7.6 mmol). The crude product was purified by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent, to give the *selenyl ester* (100 mg, 60%) as a colourless oil; λ_{max}(EtOH)/nm 205 (8060), 250 (4050); ν_{max}(film)/cm^{-1} 1693, 1603; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.57–7.37 (5H, m, Ar*H*), 6.73 (1H, dd, *J* 10.6, 15.0 Hz, C*H*=CHCOSePh), 6.26 (1H, d, *J* 15.0 Hz, CH=C*H*COSePh), 4.92 (1H, br. d, *J* 8.0 Hz, C*H*=C), 1.73 (3H, s, CH_3C=), 1.69 (3H, s, CH_3C=), 1.73–1.69 (1H, obs. cyclopropyl C*H*), 1.32 (1H, dd, *J* 4.8, 10.6 Hz, cyclopropyl C*H*), 1.23 (3H, s, CH_3), 1.15 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 188.7 (s), 148.6 (d), 135.9 (2 × d), 134.3 (s), 129.2 (2 × d), 128.9 (d), 128.7 (d), 128.1 (s), 121.3 (d), 38.0 (d), 36.2 (d), 29.0 (s), 25.6 (q), 22.7 (q), 22.1 (q), 18.5 (q); *m*/*z* (FAB) found 335.0919 (M$^+$ + H), $C_{18}H_{23}O^{80}Se$ requires 335.0914; found 333.0888, $C_{18}H_{23}O^{78}Se$ requires 333.0922 (M + H$^+$).

Bis(methyl 5,5,8-trimethylnona-3,6-dien-8-yloate) 29

A solution of tributyltin hydride (81 µl, 0.3 mmol) and AIBN (25 mg) in dry degassed benzene (1 ml) and methanol (0.1 ml) was added over 1.5 h *via* syringe pump to a stirred solution of the selenyl ester **27** (58 mg, 0.17 mmol) and AIBN (3 mg) in dry degassed benzene (90 ml) and methanol (9 ml), under reflux in an atmosphere of argon. The mixture was stirred under reflux for 4 h then cooled to room temperature and the solvent was evaporated *in vacuo*. The residue was purified by chromatography on silica using petroleum ether–diethyl ether (10 : 1 then 3 : 1), as eluent to give the *dimeric ester* (20 mg, 63%) as a colourless oil; ν_{max}(film)/cm^{-1} 1731, 1601; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.56–5.32 (4H, m, 2 × C*H*=C*H*), 5.43 (2H, d, *J* 17.5 Hz, 2 × CC*H*=CHC), 5.25 (2H, d, *J* 17.5 Hz, 2 × CCH=C*H*C), 3.69 (6H, s, 2 × CH_3), 3.03 (4H, d, *J* 6.3 Hz, 2 × =CHCH_2CO$_2$Me), 1.08 (12H, s, 4 × CH_3), 0.91 (12H, s, 4 × CH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 173.7 (2 × s), 144.3 (2 × d), 135.8 (2 × d), 134.8 (2 × d), 128.4 (2 × d), 118.1 (2 × d), 52.2 (2 × q), 40.8 (2 × s), 38.9 (2 × s), 38.5 (2 × t), 28.1 (4 × q), 23.5 (4 × q); *m*/*z* (FAB) found 209.1558 (M$^+$), $C_{13}H_{21}O_2$ requires 209.1542.

Se-Phenyl (2*E*,4*E*,*Z*)-5,9-dimethyl-2,4,8-decatrieneselenoate 31

Tri-*n*-butylphosphine (0.4 ml, 1.65 mmol) was added dropwise over 3 min to a stirred solution of (2*E*,4*E*)-5,9-dimethyl-2,4,8-decatrienoic acid[18] (212 mg, 1.09 mmol) in dry CH_2Cl_2 (5.2 ml) at −30 °C under a nitrogen atmosphere. The mixture was stirred at −30 °C for 20 min and then NPSP (495 mg, 1.6 mmol) was added. The mixture turned yellow, and it was stirred at −28 °C to −35 °C for 1.75 h, and then allowed to warm to room temperature. Diethyl ether (25 ml) was added and the mixture was then washed with water (2 × 12 ml). The separated aqueous phase was extracted with ether (15 ml) and the combined organic extracts were then washed with brine and dried. Evaporation of the solvents, followed by chromatography on silica using petroleum ether–diethyl ether (99 : 1) as eluent gave a 2 : 1 mixture of *E*- and *Z*- C-4 isomers of the *seleno ester* (274 mg, 75%) as a yellow oil. No satisfactory microanalytical data could be obtained; λ_{max}(EtOH)/nm 293 (8000); ν_{max}(film)/cm^{-1} 1691, 1623, 1581; ^{1}H NMR (2*E*,4*E*) isomer: (360 MHz, $CDCl_3$) δ 1.61 (3H, s, =C(CH$_3$)CH_3), 1.69 (3H, s, =C(CH$_3$)CH_3), 1.90 (3H, s, =C(CH_3)CH$_2$), 2.15–2.20 (4H, m, CH_2CH_2), 5.05–5.15 (1H, m, =C*H*CH$_2$), 5.97 (1H, d, *J* 11.6 Hz, CH$_2$(CH$_3$)C=C*H*), 6.13 (1H,

d, *J* 14.8 Hz, =C*H*COSePh), 7.35–7.40 (3H, m, 3 × Ar*H*), 7.53 (1H, dd, *J* 14.8, 11.6 Hz, C*H*=CHCOSePh), 7.50–7.55 (2H, m, 2 × Ar*H*); (2*E*,4*Z*) isomer: 1.61 (3H, s, =C(CH_3)CH_3), 1.68 (3H, s, =C(CH_3)CH_3), 1.90 (3H, s, =C(CH_3)CH_2), 2.10–2.20 (2H, m, =CHCH_2), 2.30–2.35 (2H, m, =C(CH_3)CH_2), 5.05–5.15 (1H, m, =C*H*CH_2), 5.97 (1H, d, *J* 11.6 Hz, CH_2(CH_3)C=C*H*), 6.10 (1H, d, *J* 14.8 Hz, =C*H*COSePh), 7.35–7.40 (3H, m, 3 × Ar*H*), 7.51 (1H, dd, *J* 14.8, 11.6 Hz, C*H*=CHCOSePh), 7.50–7.55 (2H, m, 2 × Ar*H*); ^{13}C NMR (2*E*,4*E*) isomer δ 17.6 (q), 25.6 (q), 26.1 (t), 40.5 (t), 123.0 (d), 123.1 (d), 126.5 (s), 127.0 (d), 128.6 (d), 129.1 (2 × d), 132.3 (s), 135.7 (2 × d), 137.5 (d), 153.3 (s), 190.5 (s); (2*E*,4*Z*) isomer δ 17.6 (q), 24.7 (q), 25.6 (q), 26.7 (q), 33.1 (t), 122.9 (d), 124.0 (d), 126.5 (s), 126.7 (d), 128.6 (d), 129.1 (2 × d), 132.8 (s), 135.8 (2 × d), 137.5 (d), 153.4 (s), 190.6 (s); *m*/*z* (ES) found 335.0893 (M^+ + H), $C_{18}H_{22}$OSe requires 335.0914.

Se-Phenyl (2*E*,4*E*/*Z*,6*E*)-3,7,11-trimethyldodeca-2,4,6,10-tetraeneselenoate 32

Tri-*n*-butylphosphine (0.40 ml, 1.61 mmol) was added dropwise over 3 min to a stirred solution of (2*E*,4*E*/*Z*,6*E*)-trimethyldodeca-2,4,6,10-tetraenoic acid[19] (2*E*,4*E*,6*E* : 2*E*,4*Z*, 6*E*, 5 : 3; 253 mg, 1.08 mmol) in dry CH_2Cl_2 (5 ml) at −30 °C under a nitrogen atmosphere. After 5 min, NPSP (490 mg, 1.62 mmol) was added in one portion, and the mixture was stirred at −30 °C for a further 20 min. Ether (10 ml) was added, and the mixture was washed with water (12 ml), then dried, and the solvents were removed under reduced pressure. Chromatography on silica using graduated petroleum ether–diethyl ether as eluent gave a complex mixture of double bond isomers of the *selenyl ester* (400 mg, 97%) as a yellow oil; (found, C, 67.3%; H, 7.1%; $C_{21}H_{26}$OSe requires C, 67.6%; H, 7.0%); ν_{max}(film)/cm^{-1} 1692, 1629, 1588, 1557; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.58–2.29 (m, 16H, 4 × CH_3, CH_2CH_2), 5.01–5.17 (m, 1H, =C*H*CH_2), 5.93–6.15 (m, 3H), 6.90–7.04 (1H, m, =CHC*H*=CH), 7.33–7.43 (3H, m, 3 × Ar*H*), 7.50–7.60 (2H, m, 2 × Ar*H*); ^{13}C NMR δ 15.0 (q), 17.2 (q), 17.6 (q), 20.4 (q), 24.4 (q), 25.6 (q), 26.2 (t), 26.3 (t), 26.7 (t), 32.9 (t), 40.2 (t), 123.3 (d), 123.4 (2 × d), 123.8 (2 × d), 125.0 (d), 125.6 (2 × d), 125.7 (d), 125.9 (d), 126.5 (d), 127.4 (s), 127.6 (d), 128.2 (d), 128.5 (2 × d), 129.1 (d), 131.3 (d), 131.9 (s), 132.2 (d), 132.3 (s), 132.4 (s), 132.5 (d), 133.8 (d), 134.0 (d), 134.9 (d), 135.0 (d), 135.6 (d), 145.5 (s), 145.7 (s), 145.9 (s), 146.1 (s), 148.7 (s), 150.1 (s), 150.2 (s), 188.5 (s), 188.6 (s), 189.3 (s); *m*/*z* (EI) found 374.1154 (M^+), $C_{21}H_{26}$OSe requires 374.1149.

4-Isopropyl-6a-methyl-4,5,6,6a-tetrahydro-3a*H*-pentalen-1-one 34

A solution of tributyltin hydride (245 µl, 0.91 mmol) and AIBN (6 mg, 37 µmol) in dry benzene (5 ml), was added dropwise over 4.5 h *via* syringe pump to a stirred, refluxing solution of the phenyl selenyl ester **31** (2*E*,4*E* : 2*E*,4*Z*, 2 : 1; 253 mg, 0.76 mmol) and AIBN (6 mg, 37 µmol) in dry, degassed benzene (210 ml), under an argon atmosphere. The mixture was heated for a further 6 h, then allowed to cool to room temperature. The solvent was evaporated under reduced pressure to leave an oil, which was purified by column chromatography on silica using graduated petroleum ether–diethyl ether as eluent to give an approximately 1 : 1 mixture of the diastereoisomers of the *diquinane* (93 mg, 69%), as a pale yellow oil. Repeated chromatography gave clean samples of each compound; ν_{max}(film)/cm^{-1} 1710, 1586; ^{1}H NMR (360 MHz, $CDCl_3$) α-epimer: δ 0.92 (3H, d, *J* 6.6 Hz, CHCH_3), 1.02 (3H, d, *J* 6.6 Hz, CHCH_3), 1.19 (3H, s, CH_3), 1.35–1.45 (1H, m, C*H*$CHMe_2$), 1.50–1.80 (5H, m, MeCCH_2CH_2, MeCCH_2, C*H*Me_2), 2.65 (1H, dm, *J* 5.7 Hz, =CHC*H*), 5.96 (1H, dd, *J* 5.7, 1.7 Hz, =C*H*CO), 7.52 (1H, dd, *J* 5.7, 2.8 Hz, C*H*=CHCO); β-epimer: δ 0.90 (3H, d, *J* 6.5 Hz, CHCH_3), 0.90–0.96 (1H, m, MeCCH_2CH*H*), 1.08 (3H, d, *J* 6.5 Hz, CHCH_3), 1.17 (3H, s, CH_3), 1.32 (1H, dd, *J* 13.0, 6.0 Hz, MeCCH*H*), 1.35–1.45 (1H, m, C*H*Me_2), 1.60–1.70 (2H, m, C*H*$CHMe_2$, MeCCH_2CH*H*), 1.92 (1H, dd, *J* 13.0, 6.4 Hz, MeCCH*H*), 2.93 (1H, dm, *J* 6.7 Hz, =CHC*H*), 6.22 (1H, dd, *J* 5.8 and 1.7 Hz, =C*H*CO), 7.61 (1H, dd, *J* 5.8 and 2.6 Hz, C*H*=CHCO); ^{13}C NMR α-epimer: δ 21.3 (q), 21.6 (q), 22.6 (q), 31.3 (t), 32.4 (d), 34.9 (t), 51.6 (d), 54.6 (s), 60.0 (d), 130.5 (d), 166.4 (d), 215.1 (s); β-epimer: δ 22.0 (q), 22.2 (q), 22.5 (q), 28.8 (t), 30.2 (d), 37.0 (t), 50.5 (d), 54.1 (s), 56.4 (d), 134.9 (d), 163.9 (d), 215.7 (s); *m*/*z* (EI) found 178.1360 (M^+), $C_{12}H_{18}$O requires 178.1358.

Methyl (*E*,*Z*)-7-methyl-3*E*-propenylocta-2,6-dienoate 37

Diisopropylamine (3.15 ml, 22.5 mmol) was added dropwise over 10 min to a stirred solution of *n*-butyllithium (1.6 M in hexanes; 11.5 ml, 18.4 mmol) in dry THF (45 ml), at 0 °C under a nitrogen atmosphere, and the mixture was stirred at 0 °C for 30 min, then at room temperature for 30 min. The mixture was cooled to −78 °C and methyl (trimethylsilyl)acetate (3.30 ml, 20.1 mmol) was added dropwise over 10 min. The resulting mixture was stirred at −78 °C for 1 h, and then a solution of (*E*)-8-methylnona-2,7-dien-4-one[20] (1.25 g, 8.2 mmol) in THF (9 ml) was added dropwise over 15 min. The mixture was stirred at −78 °C for a further 1.75 h then quenched with water, and extracted with ether. The combined organic extracts were washed with brine and dried. The solvents were evaporated and the residue was purified by chromatography on silica using petroleum ether–diethyl ether as eluent to give: (i), the *E-methyl ester* (230 mg) as a colourless oil, and (ii), an 8 : 5 mixture of 2*E*- and 2*Z*-isomers (1.18 g); (found, C, 75.2%; H, 9.7%; $C_{13}H_{20}O_2$ requires C, 75.0%; H, 9.7%); ν_{max}(film)/cm^{-1} 1715, 1640, 1604; ^{1}H NMR 2*E* isomer: (360 MHz, $CDCl_3$) δ 1.62 (3H, s, =C(CH_3)CH_3), 1.69 (3H, s, =C(CH_3)CH_3), 1.86 (3H, d, *J* 6.6 Hz, =CHCH_3), 2.11–2.18 (2H, m, =CHCH_2), 2.76–2.80 (2H, m, =CHCH_2CH_2), 3.70 (3H, s, CO_2CH_3), 5.20 (1H, tm, *J* 7.3 Hz, =C*H*CH_2), 5.65 (1H, s, =C*H*CO_2Me), 6.03 (1H, d, *J* 15.6 Hz, CH_3CH=C*H*), 6.18 (1H, dq, *J* 15.6, 6.6 Hz, =C*H*CH_3); 2*Z* isomer: 1.60 (3H, s, =C(CH_3)CH_3), 1.69 (3H, s, =C(CH_3)CH_3), 1.90 (3H, d, *J* 6.7 Hz, =CHCH_3), 2.13–2.21 (2H, m, =CHCH_2), 2.32–2.36 (2H, m, =CHCH_2CH_2), 3.70 (3H, s, CO_2CH_3), 5.12 (1H, tm, *J* 7.1 Hz, =C*H*CH_2), 5.59 (1H, s, =C*H*CO_2Me), 6.15–6.26 (1H, m, =C*H*CH_3), 7.50 (1H, d, *J* 16.0 Hz, CH_3CH=C*H*); ^{13}C NMR 2*E* isomer: δ 17.5 (q), 18.6 (q), 25.6 (q), 27.8 (t), 28.2 (t), 50.8 (q), 116.4 (d), 123.9 (d), 131.7 (d), 131.9 (s), 133.7 (d), 157.1 (s), 167.1 (s); 2*Z* isomer: δ 17.6 (q), 19.0 (q), 25.6 (q), 27.8 (t), 34.4 (t), 50.8 (q), 114.3 (d), 123.2 (d), 128.0 (d), 132.4 (s), 133.2 (d), 155.3 (s), 167.0 (s); *m*/*z* (EI) found 208.1457 (M^+), $C_{13}H_{20}O_2$ requires 208.1463.

Se-Phenyl (*E*,*Z*)-7-methyl-3*E*-propenylocta-2,6-dieneselenoate 38

A solution of the ester **37** (2*E* : 2*Z*, 1.6 : 1; 1.18 g, 5.7 mmol) in THF–water (3 : 1; 24 ml) was heated under reflux with lithium hydroxide monohydrate (490 mg, 11.7 mmol) for 43 h. 2 N HCl was added to acidify the mixture, and it was then extracted with ether. The combined extracts were washed with water and brine, then dried. The solvents were evaporated to leave an oil, which was again heated under reflux in THF–water (3 : 1; 24 ml) with lithium hydroxide monohydrate (490 mg, 11.7 mmol) for a further 43 h. The mixture was acidified with 2 N HCl, and then extracted with ether. The combined organic extracts were washed with brine and dried. Evaporation of the solvents left an 8 : 5 mixture of 2*E*- and 2*Z*-isomers of the corresponding carboxylic acid (1.04 g, 94%) as a colourless solid. No satisfactory microanalytical data could be obtained; ν_{max}(film)/cm^{-1} (nujol) 3500–2300 (br), 1685, 1637, 1600; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.63 (3H, s, =C(CH_3)CH_3, 2*Z*),

1.65 (3H, s, =C(CH_3)CH_3, 2*E*), 1.73 (3H, s, =C(CH_3)CH_3, 2*E* and 3H, =C(CH_3)CH_3, 2*Z*), 1.91 (3H, dm, *J* 6.7 Hz, =CHCH_3, 2*E*), 1.94 (3H, dm, *J* 6.8 Hz, =CHCH_3, 2*Z*), 2.12–2.26 (2H, m, =CHCH_2, 2*E* and 2H, =CHCH_2, 2*Z*), 2.36–2.43 (2H, m, =CHCH_2CH_2, 2*Z*), 2.78–2.84 (2H, m, =CHCH_2CH_2, 2*E*), 5.13 (1H, tm, *J* 7.0 Hz, =C*H*CH_2, 2*Z*), 5.20 (1H, tm, *J* 7.4 Hz, =C*H*CH_2, 2*E*), 5.61 (1H, s, =C*H*CO_2H, 2*Z*), 5.68 (1H, s, =C*H*CO_2H, 2*E*), 6.07 (1H, dm, *J* 15.6 Hz, CH_3CH=C*H*, 2*E*), 6.19–6.32 (1H, m, =C*H*CH_3, 2*E* and 1H, =C*H*CH_3, 2*Z*), 7.48 (1H, dm, *J* 16.0 Hz, CH_3CH=C*H*, 2*Z*); ^{13}C NMR 2*E* isomer: δ 17.5 (q), 18.7 (q), 25.7 (q), 28.1 (t), 28.3 (t), 116.3 (d), 123.8 (d), 132.2 (s), 132.8 (d), 133.7 (d), 159.5 (s), 172.5 (s); 2*Z* isomer: δ 17.7 (q), 19.1 (q), 25.6 (q), 27.9 (t), 34.6 (t), 114.1 (d), 123.1 (d), 128.0 (d), 132.6 (s), 134.1 (d), 157.6 (s), 171.5 (s); *m*/*z* (EI) found 194.1307 (M^+), $C_{12}H_{18}O_2$ requires 194.1307.

Tri-*n*-butylphosphine (0.20 ml, 0.80 mmol) was added to a stirred solution of the propenylocta-2,6-dienoic acid (2*E* : 2*Z*, 8 : 5; 105 mg, 0.54 mmol) in dry CH_2Cl_2 (2.2 ml) at −30 °C under a nitrogen atmosphere. The mixture was stirred at *ca.* −30 °C for 15 min, and then NPSP (230 mg, 0.76 mmol) was added in one portion. The resulting bright yellow mixture was stirred at −30 °C for a further 30 min, then the cooling bath was removed and ether (25 ml) was added. The mixture was washed with water, then brine, and dried. The solvents were removed under reduced pressure to leave a residue which was purified by chromatography on silica using petroleum ether–diethyl ether as eluent to give a 3 : 2 mixture of 2*E*- and 2*Z*-isomers of the *selenyl ester* (100 mg, 56%) as a bright yellow oil; (found, C, 65.0%; H, 6.8%; $C_{18}H_{22}$OSe requires C, 64.9%; H, 6.7%); ν_{max}(film)/cm^{-1} 1693, 1633, 1570; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.58 (3H, s, =C(CH_3)CH_3, 2*E*), 1.62 (3H, s, =C(CH_3)CH_3, 2*Z*), 1.67 (3H, s, =C(CH_3)CH_3, 2*E*), 1.73 (3H, s, =C(CH_3)CH_3, 2*Z*), 1.83 (3H, dm, *J* 6.8 Hz, =CHCH_3, 2*Z*), 1.88 (3H, dd, *J* 6.8, 1.5 Hz, =CHCH_3, 2*E*), 2.07–2.16 (2H, m, =CHCH_2, 2*E*), 2.16–2.24 (2H, m, =CHCH_2, 2*Z*), 2.28–2.35 (2H, m, =CHCH_2CH_2, 2*Z*), 2.64–2.71 (2H, m, =CHCH_2CH_2, 2*E*), 5.09–5.17 (1H, m, =C*H*CH_2, 2*E* and 1H, =C*H*CH_2, 2*Z*), 5.95 (1H, s, =C*H*COSePh, 2*Z*), 5.99 (1H, dm, *J* 15.6 Hz, CH_3CH=C*H*, 2*E*), 6.04 (1H, s, =C*H*COSePh, 2*E*), 6.27–6.39 (1H, m, =C*H*CH_3, 2*E* and 1H, =C*H*CH_3, 2*Z*), 7.31 (1H, dm, *J* 15.9 Hz, CH_3CH=C*H*, 2*Z*), 7.37–7.43 (3H, m, 3 × Ar*H*, 2*E* and 3H, 3 × Ar*H*, 2*Z*), 7.52–7.58 (2H, m, 2 × Ar*H*, 2*E* and 2H, 2 × Ar*H*, 2*Z*); ^{13}C NMR δ 17.7 (q), 17.8 (q), 19.0 (q), 19.1 (q), 25.6 (q), 25.7 (q), 27.8 (t), 28.1 (t), 29.0 (t), 34.0 (t), 122.9 (d), 123.6 (d), 124.9 (d), 127.4 (s), 128.6 (d), 128.7 (d), 129.1 (d), 129.2 (4 × d), 132.1 (s), 132.8 (s), 133.2 (d), 135.2 (d), 135.7 (2 × d), 135.8 (2 × d), 136.2 (d), 152.1 (s), 154.0 (s), 188.9 (s), 189.4 (s); *m*/*z* (EI) found 177.1270 (M^+ − SePh), $C_{18}H_{22}$OSe requires 177.1279.

5-Methyl-3-(4-methylpent-3-enyl)cyclopent-2-enone 40

A solution of tributyltin hydride (75 µl, 0.28 mmol) and AIBN (6 mg, 37 µmol) in dry, degrassed benzene (6 ml) was added dropwise over 6 h *via* syringe pump to a stirred, refluxing solution of the selenyl ester **38** (77 mg, 0.23 mmol) and AIBN (4 mg, 24 µmol) in dry, degassed benzene (70 ml) under an argon atmosphere. The mixture was heated under reflux for a further 3 h and then evaporated to dryness. The residue was purified by chromatography on silica using 0–10% petroleum ether–diethyl ether as eluent to give the *cyclopentenone* (23 mg, 70%), based on unreacted starting material (11 mg), as a colourless oil; ν_{max}(film)/cm^{-1} 1704, 1616; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.17 (3H, d, *J* 7.5 Hz, CH_3CH), 1.62 (3H, s, C(CH_3)CH_3), 1.69 (3H, s, C(CH_3)CH_3), 2.18 (1H, dm, *J* 18.4 Hz, CH*H*CHCH_3), 2.27 (2H, app. q, *J* 7.0 Hz, =CHCH_2), 2.37–2.47 (3H, m, CH_3C*H*, =CHCH_2CH_2), 2.82 (1H, ddm, *J* 18.4, 6.7 Hz, CH*H*CHCH_3), 5.09 (1H, tm, *J* 7.0 Hz, =CHCH_2), 5.89–5.93 (1H, m =C*H*CO); ^{13}C NMR δ 16.4 (q), 17.7 (q), 25.6 (q), 25.6 (t), 33.5 (t), 40.4 (t), 40.7 (d), 122.7 (d), 128.3 (d), 132.9 (s), 180.9 (s), 212.8 (s); M^+ not observed in EI or FAB.

(*E*,*Z*)-5-(2,6-Dimethylhepta-1,5-dienyl)-3-methylcyclopent-2-enone 47

A solution of tributyltin hydride (90 µl, 0.33 mmol) and AIBN (cat.) in dry, degassed benzene (3.5 ml) was added dropwise over 5.25 h *via* syringe pump to a stirred, refluxing solution of the phenyl selenyl ester **32** (100 mg, 0.27 mmol) and AIBN (cat.) in dry, degassed benzene (85 ml) under an argon atmosphere. The mixture was heated for an additional 3.5 h, and then allowed to cool to room temperature. The benzene was evaporated under reduced pressure, and the residue was purified by chromatography on silica using petroleum ether–diethyl ether as eluent to give the *Z*- and the *E*-isomers of the *cyclopentenone* (each 23 mg, 38%), as pale yellow oils; *E*-isomer: λ_{max}(EtOH)/nm 223 (13 200); ν_{max}(film)/cm^{-1} 1704, 1625; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60 (3H, s, =C(CH_3)CH_3), 1.68 (3H, s, =C(CH_3)CH_3), 1.72 (3H, s, =C(CH_3)CH$_2$), 1.98–2.15 (4H, m, CH_2CH_2), 2.12 (3H, s, CH_3C=CHCO), 2.30 (1H, d, *J* 18.5 Hz, CH*H*CHCO), 2.90 (1H, dd, *J* 18.5, 6.9 Hz, CH*H*CHCO), 3.27–3.34 (1H, m, CH$_2$C*H*CO), 5.00 (1H, d, *J* 8.7 Hz, =C*H*CHCO), 5.05–5.12 (1H, m, =C*H*CH$_2$), 5.93 (1H, s, =C*H*CO); ^{13}C NMR δ 16.9 (q), 17.7 (q), 19.3 (q), 25.7 (q), 26.5 (t), 39.4 (t), 41.5 (t), 46.6 (d), 121.7 (d), 124.0 (d), 129.7 (d), 139.6 (s), 151.6 (s), 177.1 (s), 210.6 (s); *m*/*z* found 218.1676 (M^+), $C_{15}H_{22}$O requires M^+, 218.1671). *Z*-isomer: λ_{max}(EtOH)/nm 223 (7700); ν_{max}(film)/cm^{-1} 1704, 1625; ^{1}H NMR δ 1.63 (3H, s, =C(CH_3)CH_3), 1.70 (3H, s, =C(CH_3)CH_3), 1.76 (3H, d, *J* 1.3 Hz, =C(CH_3)CH$_2$), 2.05–2.21 (4H, m, CH_2CH_2), 2.12 (3H, s, CH_3C=CHCO), 2.30 (1H, dm, *J* 18.5 Hz, CH*H*CHCO), 2.86 (1H, dd, *J* 18.5, 7.0 Hz, CH*H*CHCO), 3.32 (1H, ddd, *J* 9.2, 7.0, 2.7 Hz, CH$_2$C*H*CO), 5.00 (1H, dd, *J* 9.2, 1.3 Hz, =C*H*CHCO), 5.10–5.18 (1H, m, =C*H*CH$_2$), 5.90–5.92 (1H, m, =C*H*CO); ^{13}C NMR δ 17.7 (q), 19.3 (q), 23.3 (q), 25.7 (q), 26.7 (t), 32.5 (t), 41.5 (t), 46.6 (d), 122.4 (d), 124.1 (d), 129.7 (d), 131.8 (s), 139.7 (s), 177.1 (s), 210.5 (s); *m*/*z* found 218.1666 (M^+), $C_{15}H_{22}$O requires 218.1671.

Phenyl *o*-vinylbenzoselenoate 48

N-Phenylselenophthalimide (1.6 g, 5.4 mmol) was added in one portion to a stirred solution of tributylphosphine (0.6 g, 3 mmol) and *o*-vinylbenzoic acid[21] (0.4 g, 2.7 mmol) in dichloromethane (30 ml) at −30 °C, and the bright yellow mixture was then stirred at −30 °C for 4 h. The mixture was diluted with dichloromethane, and then washed successively with water, 5% $NaHCO_3$ and brine. The separated organic extract was dried and concentrated under reduced pressure to leave an oil which was purified by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent to give the *selenyl ester* (430 mg, 56%) as a pale yellow oil; ν_{max}(film)/cm^{-1} 1694; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.38 (1H, dd, *J* 11.0, 1.1 Hz, CH=C*H*), 5.75 (1H, dd, *J* 17.4, 1.1 Hz, CH=CH*H*), 7.20 (1H, dd, *J* 17.4, 11.0 Hz, C*H*=CH$_2$), 7.41–7.47 (4H, m, arom. C*H*), 7.4–7.5 (1H, m, arom. C*H*), 7.62–7.67 (3H, m, arom. C*H*), 7.90 (1 H, dd, *J* 7.8, 1.2 Hz, arom. C*H*); ^{13}C NMR δ 117.4 (t), 126.9 (s), 127.1 (d), 127.7 (d), 128.4 (d), 129.0 (d), 129.0 (d), 129.4 (d), 132.3 (d), 134.5 (d), 135.7 (s), 136.0 (d), 137.5 (s), 195.4 (s).

Phenyl 3-(*o*-vinylphenyl)-2*E*-propeneselenoate 52

A mixture of methyltriphenylphosphonium bromide (0.72 g, 2 mmol) and potassium *t*-butoxide (0.22 g, 2 mmol) in benzene (40 ml) was stirred at room temperature for 1 h, then cooled to 0 °C and a solution of ethyl *o*-formylcinnamate[22] (0.2 g, 1 mmol) in dry benzene (5 ml) was added dropwise over 30 min. The mixture was heated at 45–50 °C for 1 h, then cooled, diluted with water (50 ml) and extracted with ether. The

combined organic extracts were washed with brine, then dried and evaporated under reduced pressure. The residue was purified by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent to give ethyl *o*-vinyl-*E*-cinnamate (96 mg, 47%) as a pale yellow oil; ν_{max}(film)/cm^{-1} 1713, 1633; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.32 (3H, t, *J* 7.1 Hz, OCH_2CH_3), 4.25 (2H, q, *J* 7.1 Hz, OCH_2CH_3), 5.41 (1H, dd, *J* 11.0, 1.3 Hz, *H*HC=), 5.62 (1H, dd, *J* 17.1, 1.3 Hz, H*H*C), 6.33 (1H, d, *J* 15.8 Hz, C*H*CO_2Et), 7.05 (1H, dd, *J* 17.1, 11.0 Hz, ArC*H*=CH_2), 7.26–7.37 (2H, m, arom. C*H*), 7.47 (1H, dd, *J* 7.7, 1.5 Hz, arom. C*H*), 7.51 (1H, dd, *J* 7.6, 1.3 Hz, arom. C*H*), 8.01 (1H, d, *J* 15.8 Hz, ArC*H*=CHCO_2Et); ^{13}C NMR δ 14.3 (q), 60.4 (t), 117.9 (t), 120.2 (d), 126.8 (d), 126.9 (d), 127.8 (d), 129.9 (d), 132.4 (s), 134.1 (d), 137.9 (s), 142.2 (d), 166.7 (s).

A solution of the cinnamate ester (40 mg, 0.2 mmol), and potassium carbonate (138 mg, 1.0 mmol) in water (460 mg, 25 mmol) and ethanol (7 ml) was heated under reflux for 14 h, then cooled and evaporated under reduced pressure. Water (50 ml) was added to the residue followed by concentrated HCl (2 ml), and the mixture was then extracted with ether. The combined organic extracts were treated with 5% NaOH (50 ml), and the separated aqueous layer was then treated with concentrated HCl (2 ml) and extracted with ether. Evaporation of the dried ether extracts under reduced pressure left the corresponding *cinnamic acid* (30 mg, 86%) which recrystallised from ethanol–water 1 : 1) as colourless needles; ν_{max}(film)/cm^{-1} 3168, 1692, 1631; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.38 (1H, d, *J* 10.9 Hz, *H*HC), 5.56 (1H, d, *J* 17.0 Hz, H*H*C), 6.30 (1H, d, *J* 15.8 Hz, C*H*CO_2H), 6.99 (1H, dd, *J* 17.0, 10.9 Hz, ArC*H*=CH_2), 7.17–7.33 (2H, m, arom. C*H*), 7.42 (1H, d, *J* 7.6 Hz, arom. C*H*), 7.49 (1H, d, *J* 7.6 Hz, arom. C*H*), 8.09 (1H, d, *J* 15.8 Hz, ArC*H*=CHCO_2H); ^{13}C NMR δ 118.8 (t), 119.5 (d), 127.5 (d), 128.3 (d), 130.8 (d), 132.3 (s), 134.4 (d), 138.6 (s), 145.2 (d), 172.8 (s); *m*/*z* (EI) found 174.0680 (M^+), $C_{11}H_{10}O_2$ requires 174.0681.

Triethylamine (35 mg, 0.34 mmol) was added to a solution of the cinnamic acid (60 mg, 0.34 mmol) in dry dichloromethane (2 ml) at −35 °C and the mixture was stirred at room temperature for 5 min under a nitrogen atmosphere. The solvent was evaporated under reduced pressure and the oily residue was dried under vacuum for 30 min, and then dissolved in tetrahydrofuran (2 ml). Tributylphosphine (0.14 g, 0.7 mmol) was added to the cooled solution at −35 °C under a nitrogen atmosphere followed, after 10 min, by phenylselenyl chloride (0.13 g, 0.69 mmol). The mixture was allowed to warm to room temperature, then stirred at this temperature for a further 1.5 h, diluted with ether (30 ml) and washed with 5% $NaHCO_3$ (20 ml). The separated organic layer was dried and evaporated under reduced pressure to leave a residue which was purified by chromatography on silica using petroleum ether–diethyl ether (9 : 1) as eluent to give the *selenyl ester* (60 mg 56%) as a pale yellow oil; ν_{max}($CHCl_3$)/cm^{-1} 1692, 1605; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.52 (1H, dd, *J* 11.0, 1.1 Hz, C*H*H=CHAr), 5.70 (1H, dd, *J* 17.3, 1.1 Hz, CH*H*=CHAr), 6.74 (1H, d, *J* 15.6 Hz, ArCH=C*H*COSe), 7.09 (1H, dd, *J*, 17.3, 11.0 Hz, ArC*H*=CH_2), 7.3–7.4 (2H, m, arom. C*H*), 7.40–7.50 (3H, m, arom. C*H*), 7.53 (1H, d, *J* 7.7 Hz, arom. C*H*), 7.61 (1H, d, *J* 7.8 Hz, arom. C*H*), 7.64 (1H, d, *J* 7.1 Hz, arom. C*H*), 7.65 (1H, d, *J* 7.9 Hz, arom. C*H*), 8.03 (1H, d, *J* 15.6 Hz, ArC*H*=CHCOSe); ^{13}C NMR δ 118.8 (t), 126.3 (s), 127.1 (d), 127.3 (d), 128.0 (d), 129.0 (d), 129.4 (d), 130.6, (2 × d), 131.9 (s), 134.0 (d), 135.7 (s), 135.9 (d), 138.9 (d), 190.8 (s).

1-Indanone 51

A solution of tributyltin hydride (244.5 mg, 0.84 mmol) in dry degassed benzene (8 ml) was added dropwise *via* syringe pump over 6 h, under an argon atmosphere, to a refluxing solution of the selenyl ester **48** (172.3 mg, 0.60 mmol) and AIBN (4.9 mg, 0.03 mmol) in argon-degassed benzene (60 ml). The mixture was heated under reflux for a further 10 h, then cooled and evaporated to dryness under reduced pressure. The residue was purified by chromatography on silica using petroleum ether–diethyl ether (95 : 5) as eluent to give 1-indanone (44 mg, 56%), which was identical with a commercial sample.

5,6-Dihydrobenzocyclohepten-7-one 54

Phenyl 3-(*o*-vinylphenyl)-2-propeneselenoate **52** (60 mg, 0.19 mmol) was treated with Bu_3SnH–AIBN and AIBN according to the usual procedure and gave the benzocyclohepten-7-one (21 mg, 70%) as a pale yellow oil, which displayed spectroscopic data identical with those previously reported.[23]

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