Tetrahedron 65 (2009) 10882–10892

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Manganese(III)-mediated oxidative free-radical cyclisations of allenyl malonates

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ARTICLE INFO

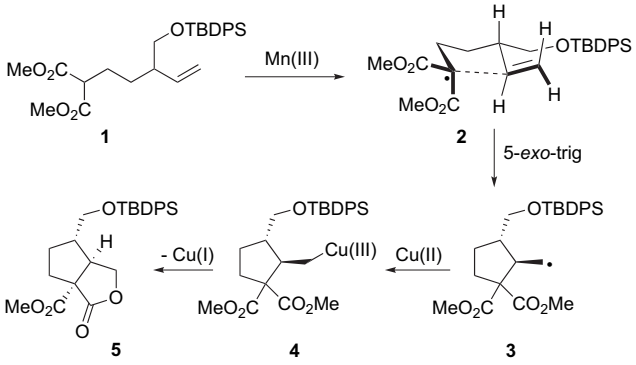
Article history:
Received 31 July 2009
Received in revised form 9 September 2009
Accepted 28 September 2009
Available online 1 October 2009

ABSTRACT

The regioselective synthesis of alkenylcyclanones by the oxidative radical cyclisation of malonyl radicals onto both allenes and an allylsilane is reported, along with the diastereoselective formation of [3.3.0]-bicyclic γ-lactones from two of these alkenylcyclanones. Furthermore, the cyclisation of 3-, 4- and 5-allenyl malonates on exposure to manganese(III) acetate under both oxidative and reductive termination conditions is reported.

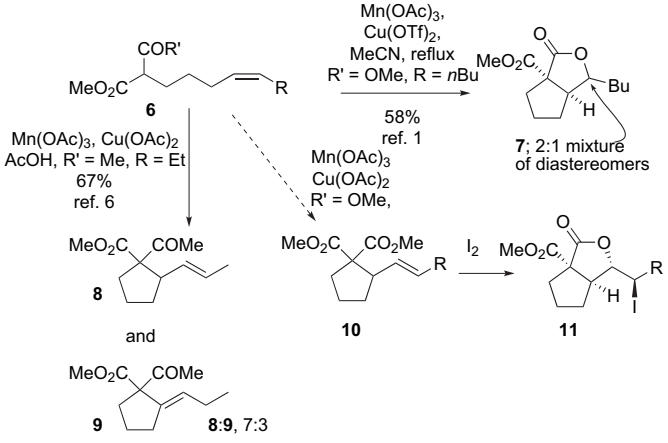
1. Introduction

We recently reported the diastereoselective formation of [3.3.0]-bicyclic γ-lactones from the cyclisation of 4-pentenyl malonates under oxidative radical conditions.[1,2] Treatment of the 4-pentenyl malonate **1** with manganese(III) acetate and copper(II) triflate in acetonitrile under reflux delivered the [3.3.0]-bicyclic γ-lactone **5** in 88% yield and with good diastereocontrol (>13:1 dr) (Scheme 1). The reaction most likely proceeds by generation of an electrophilic *C*-centred radical from the interaction of the substrate with manganese(III) acetate,[3] which undergoes 5-*exo*-*trig* cyclisation, via a chair-like transition state **2**,[4] to deliver the adduct radical **3**. Rapid reaction of the adduct radical with copper(II) gives a copper(III) intermediate **4** from which the γ-lactone product **5** is formed. These reaction conditions were applicable to the synthesis of a good number of substituted [3.3.0]-bicyclic γ-lactones.[1]



Scheme 1. Previous work on the synthesis of [3.3.0]-bicyclic γ-lactones.

Extension of the methodology to non-terminal alkenes was also possible; however, there was little control at the newly formed lactone stereocentre. For example, cyclisation of the 4-pentenyl malonate **6** (R′=OMe, R=*n*-butyl) gave the desired [3.3.0]-bicyclic γ-lactone **7** in 58% yield but as a 2:1 mixture of lactone diastereomers (Scheme 2).



Scheme 2. Cyclisations with non-terminal alkenes.

An indirect solution to the low diastereocontrol observed in the above reaction would be to synthesise the corresponding alkenyl-substituted cyclopentane e.g., **10**, which should then undergo a diastereocontrolled iodolactonisation, to give **11**, with good control over the lactone stereocentre.[5] The alkenyl-cyclopentane **10** would potentially be available by cyclisation of a 4-pentenyl malonate in the presence of manganese(III) acetate and copper(II) acetate[3]; however, Snider and co-workers have previously shown that cyclisation of methyl acetoacetate **6** (R′=Me, R=Et) using copper(II) acetate as the additive gave a 7:3 mixture of Hofmann–Saytzev alkenes (**8**:**9**).[6] We have similarly found that cyclisation of

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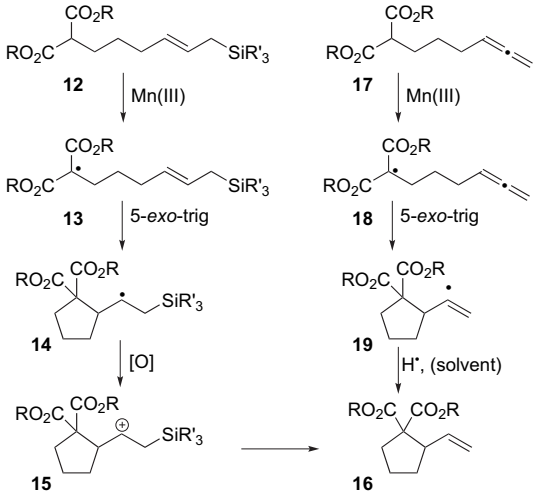
0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.09.112

5-pentenyl malonates in the presence of copper(II) acetate gives mixtures of olefin regioisomers.[7] The aim of this work was therefore to develop a regioselective synthesis of alkenyl-substituted cyclopentanes by the treatment of the appropriate malonate substrate with manganese(III) acetate. We envisaged two approaches to achieve this goal (Scheme 3). First, oxidative radical cyclisation of a malonate such as **12** would deliver the β-silyl adduct radical **14**, which would be readily oxidised to a β-silyl cation **15** in the presence of an appropriate metal oxidant. Electrofugal loss of the silyl group would deliver the desired vinylcyclopentane **16** (Hofmann alkene).[8] Alternatively treatment of the appropriately substituted allenyl malonate (e.g., **17**) under oxidative radical conditions could potentially yield the vinyl adduct radical **19**, which could undergo reduction by solvent to give the desired vinyl cyclopentane **16**.[9] In this article we describe the successful application of both strategies for the synthesis of alkenyl-cyclopentanes and more generally report an investigation into the manganese(III)-mediated oxidative free-radical cyclisations of allenyl malonates.

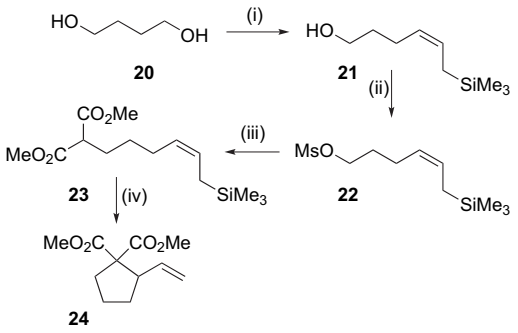


Scheme 3. Synthetic strategy for the formation of alkenyl-cyclopentanes.

2. Results and discussion

2.1. Allylsilane-substituted malonate

The allylsilane cyclisation substrate **23** was prepared from 1,4-butane diol **20** via the known alcohol **21**,[10] and was readily transformed into the desired cyclisation substrate **23** via the mesylate **22**[11] (Scheme 4). Treatment of the malonate **23** with 2 equiv of manganese(III) acetate in acetonitrile at reflux led to formation of the known desired vinylcyclopentane **24**[12] in only 30% yield. Copper(II) salts[3] are compatible with manganese(III) acetate and frequently give rise to higher yields of products arising from oxidation of adduct radicals formed during manganese(III)-mediated cyclisations. Treatment of the malonate **23** with 2 equiv of manganese(III) acetate and 1 equiv of copper(II) triflate[13] in acetonitrile at reflux returned the vinylcyclopentane **24** in excellent yield (96%). The formation of the vinylcyclopentane **24** most likely proceeds according to the mechanism outlined in Scheme 3. Thus, the malonate is oxidised in the presence of Mn(III) to give the corresponding educt radical **13** (R=R′=Me), which undergoes 5-*exo*-*trig* cyclisation to deliver the β-silyl adduct radical **14** (R=R′=Me). Oxidation of the β-silyl radical **14** (R=R′=Me) with copper(II) yields the corresponding β-silyl cation **15** (R=R′=Me), which gives the product on electrofugal loss of silicon. Although the cyclisation of the malonate **23** was efficient, the preparation of the substrate was lengthy, and, in our hands, low yielding. We therefore turned our attention to investigating the oxidative radical cyclisation of allenyl-substituted malonates.

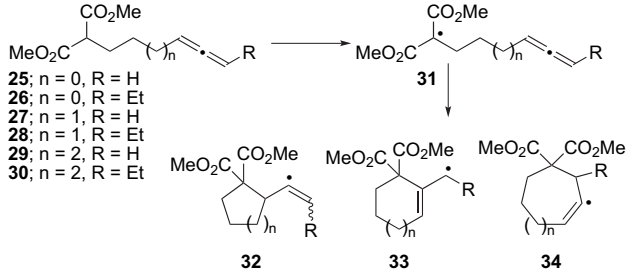


Scheme 4. Allylsilane preparation and cyclisation. (i) Ref. 10, 18%; (ii) MsCl, Et_3N, CH_2Cl_2, 99%; (iii) dimethyl malonate, NaH, KI, DMF, THF, 80%; (iv) $Mn(OAc)_3$, $Cu(OTf)_2$, MeCN, reflux, 96%.

2.2. Allenyl-substituted malonates

2.2.1. Introduction

The impetus for this research project was to develop a method for the synthesis of alkenyl-cyclopentanes by the oxidative radical cyclisation of appropriately substituted malonates. This presented us with the opportunity to investigate the cyclisation of various allenyl malonates under oxidative radical conditions. We elected to investigate the cyclisation of the six substrates **25**–**30** (Scheme 5) under two separate reaction conditions: Conditions **A** 2 equiv of manganese(III) acetate, 0.02 M substrate in ethanol conditions, which favour reduction of adduct radicals (e.g., **19**→**16**)[1,9]; Conditions **B** 2 equiv of manganese(III) acetate and 1 equiv of copper(II) triflate or acetate, 0.2 M substrate in acetonitrile conditions, which favour the formation of products arising from oxidation of adduct radicals.[1,7,9,14] The regiochemistry of the radical cyclisations onto allenes has been investigated both experimentally[15] and theoretically.[16] Guo et al.[16] have shown that the regiochemistry in the cyclisation of a range of allenyl-substituted alkyl radicals may be explained using Marcus theory, which provides excellent agreement with the experimental results of Crandall and co-workers.[15] On the basis of this prior art, cyclisation of the electrophilic *C*-centred radicals **31** derived from the malonates **25**–**30** would be expected to give the adduct radicals **32**, **33** and **34** in varying proportions depending on the value of *n*. The adduct radicals could then undergo various termination pathways depending on the reaction conditions.[9,14]

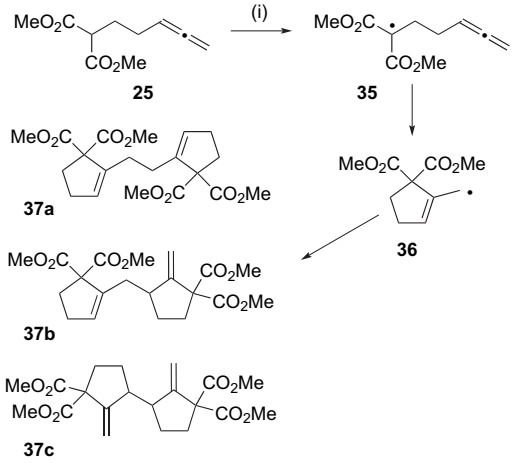


Scheme 5. Cyclisation substrates and possible adduct radicals.

2.2.2. Cyclisation studies

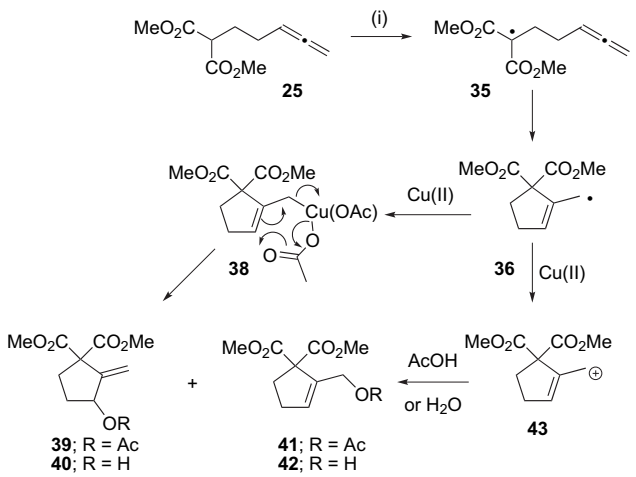
*2.2.2.1. Cyclisation of the allenyl malonate **25**.* Treatment of the known allenyl malonate **25**[12] with 2 equiv of manganese(III) acetate in ethanol at reflux (Conditions **A**) gave complete conversion of the starting material as indicted by crude ^{1}H NMR (Scheme 6). Purification of the reaction mixture allowed the isolation of a mixture of compounds, which were assigned as the isomeric cyclic dimers **37** (90%) for the following reasons. Mass spectrometry indicated that product had a molecular mass of 394 {ES *m*/*z* 395.1 [$(M+H)^+$, 61%], 412.2 [$(M+NH_4)^+$, 100%], 417.1 [$(M+Na)^+$, 89%], 806.3 [$(2M+NH_4)^+$, 60%] 811.3 [$(2M+Na)^+$, 63%]} demonstrating

that the product resulted from two molecules of starting material minus two hydrogen atoms. It was evident that cyclisation had occurred due to the absence of the malonate proton and the allene protons in the ^{1}H NMR. Furthermore, the ^{1}H NMR indicated the presence of a number of resonances in the olefinic region consistent with trisubstituted and 1,1-disubstituted alkenes. The fact that 4-allenyl radicals undergo cyclisation to form allyl adduct radicals[15,16] combined with the above data led us to assign the products as the isomeric dimers **37**. This assignment was confirmed by further purification to give the dimer **37a** in pure form, which was fully characterised. The likely mechanism for the formation of the dimers **37** involves conversion of substrate **25** into the electrophilic *C*-centred radical **35**, which undergoes exclusive five-membered ring formation to form the allyl radical **36** in accord with the work of Guo[16] and Crandall.[15] Allyl radicals are only slowly oxidised by manganese(III) acetate.[3b] The stability of the allyl radical results in slow hydrogen atom abstraction from the solvent and hence radical dimerisation occurs to give the products **37**.



Scheme 6. Cyclisation of the allene **25** in EtOH. (i) Conditions **A**, **37**, 90%.

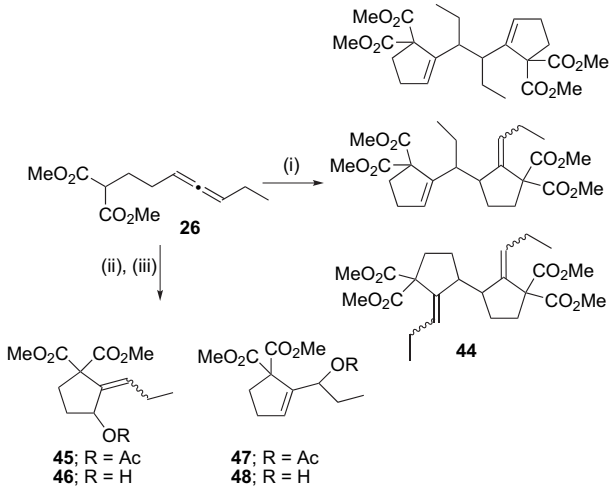
Treatment of the malonate **25** with manganese(III) acetate in acetonitrile (Scheme 7) using copper(II) acetate as a co-oxidant (Conditions **B**) gave the acetates **39**[17] and **41**[17] (71%, 8:1 inseparable mixture of **39**:**41**) also isolated were the alcohols **40**[17] and **42**[17] (10%, 4.5:1 inseparable mixture **40**:**42**). Using copper(II) triflate as additive gave similar results.[18]



Scheme 7. Cyclisation of the allene **25** in acetonitrile. (i) Conditions **B**, **39** and **41** (8:1 mixture), 71%, **40** and **42** (4.5:1 mixture), 10%.

As before, these reactions most likely proceed by the formation of an electrophilic *C*-centred radical **35**, which undergoes exclusive five-membered ring formation to give the allylic radical **36**.[15,16] In the absence of a copper(II) salt, the adduct radical **36** undergoes dimerisation giving **37**. In the presence of a copper(II) salt the adduct radical may be rapidly trapped at the primary carbon to give a copper(III) intermediate **38**, analogous to steps in the Kharasch–Sosnovsky reaction.[19] The copper(III) intermediate can then decompose via a pericyclic mechanism, as proposed by Beckwith,[20] to give the 1,1-disubstituted alkene **39** as the major regioisomeric product. Alternatively, the adduct radical may be oxidised by copper(II) to give the allylic cation **43**, which is trapped by acetic acid preferentially at the more electron deficient terminus, giving the same major product **39**. The alcohols **40** and **42** either arise from in situ hydrolysis of the acetates or from trapping of the allyl cation **43** with water.

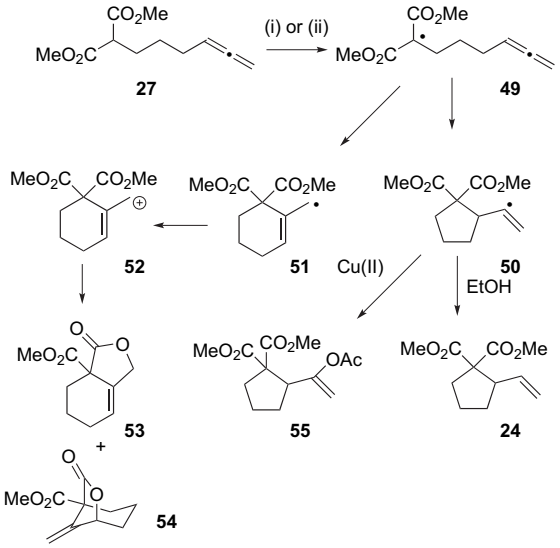
*2.2.2.2. Cyclisation of the allenyl malonate **26**.* Cyclisation of the non-terminal allene **26** under the two sets of reaction conditions gave products analogous to those formed in the cyclisation of the substrate **25** (Scheme 8). Analysis of the crude ^{1}H NMR from cyclisation of the allene **26** under reductive termination conditions (Conditions **A**) indicated the presence of a number of compounds. Mass spectrometry showed the presence of dimers **44** analogous to those formed in the cyclisation of substrate **25**; {ES *m*/*z* 451.25 [$(M+H)^+$, 23%], 468.3 [$(M+NH_4)^+$, 65%], 473.18 [$(M+Na)^+$, 98%], 918.52 [$(2M+NH_4)^+$, 18%], 923.4 [$(2M+Na)^+$, 95%], found [$M+Na]^+$ 437.2141; $C_{24}H_{34}NaO_8$ requires 473.2146}. However; it was not possible to isolate any of the pure isomers from the mixture. Exposure of the malonate **26** to manganese(III) acetate and copper(II) triflate (Conditions **B**) gave an impure component, which was tentatively assigned as the secondary allylic alcohols **48** and **46** as a 4:1 inseparable mixture of diastereomers (ca. 19%), and the corresponding acetates **47** and **45** as a 1:1.5 mixture of *endo*:*exo*-cyclic alkenes (50%); the *exo*-cyclic alkenes were formed as a 3:1 mixture of (unassigned) geometric isomers. In the presence of copper(II) acetate the acetates **47** and **45** were isolated in 76% yield as a 1.2:1 mixture of *endo*:*exo*-cyclic alkenes; the *exo*-cyclic alkenes were formed as a 1:1.5 mixture of unassigned geometric isomers. The formation of the products **44**–**48** is again in keeping with theoretical[16] and experimental work[15], which showed that hexa-4,5-dien-1-yl radicals undergo exclusive five-membered ring formation to give allyl radicals.



Scheme 8. Cyclisation of the allenyl malonate **26**. (i) Conditions **A**; (ii) Conditions **B**, copper(II) triflate **46** and **48**, 1:4, 19 %, **45** and **47**, 1.5:1, 50%; (iii) Conditions **B**, copper(II) acetate, **47** and **45**, 1.2:1, 76%.

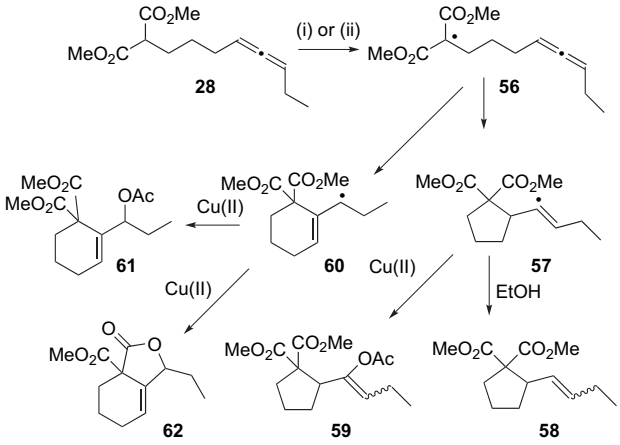
*2.2.2.3. Cyclisation of the allenyl malonate **27**.* Cyclisation of the malonyl radical derived from the substrate **27** was expected, on the

basis of precedent[15,16] to give rise predominantly to five-membered ring products with products containing six-membered rings being formed as minor components. To our delight, exposure of the malonate **27** to 2 equiv of manganese(III) acetate in ethanol (Conditions **A**) gave the desired known vinyl cyclopentane **24**[12] in 66% yield (Scheme 9). Additionally the γ-lactones **53** and **54** were isolated in 15% yield as an inseparable 7:1 mixture of isomers.[21] All of the products arise by cyclisation of the electrophilic *C*-centred radial **49** derived from the malonate **27** to give the five- and six-membered adduct radicals. The five-membered ring vinyl radical **50** undergoes H-atom abstraction from ethanol to give the desired vinylcyclopentane **24**.[9] The six-membered allylic radical **51** undergoes slow oxidation to give the corresponding allyl cation from which the γ-lactones are formed. It is not clear why the allylic radical **36** suffers dimerisation prior to oxidation whereas for the allylic radical **51** the reverse is true. Analysis of the crude ^{1}H NMR spectrum from the corresponding reaction conducted in the presence of copper(II) triflate (Conditions **B**) indicated the presence of two major products (**55**:**24**, 3:1 ratio) along with a trace amount of starting material. Purification by flash chromatography gave the vinylcyclopentane **24** (10%) and the vinyl acetate **55** (22%)—no products from six-ring formation were seen although there were a number of unidentifiable products in the crude ^{1}H NMR. Similar results were obtained using copper(II) acetate. The vinyl acetate **55** is derived from the vinyl radical **50**. Vinyl radicals are not oxidised by manganese(III)[3]; however, in the presence of copper(II) a vinyl copper(III) species may be formed from which on reductive elimination gives the vinyl acetate **55**. Alternatively, copper(II) may oxidise the vinyl radical to the corresponding vinyl cation, which is then trapped by acetic acid to give product **55**. The yield of the vinyl acetate **55** could be improved to 35% by slow addition (4 h) of the substrate **27** to the mixture of manganese(III) acetate and copper(II) triflate in acetonitrile at reflux. Keeping the substrate concentration low by slow addition reduces reduction of the vinyl radical **50** by H-atom abstraction from another molecule of starting material (**27**) thus maximising the likelihood of oxidation to the vinyl acetate **55**.



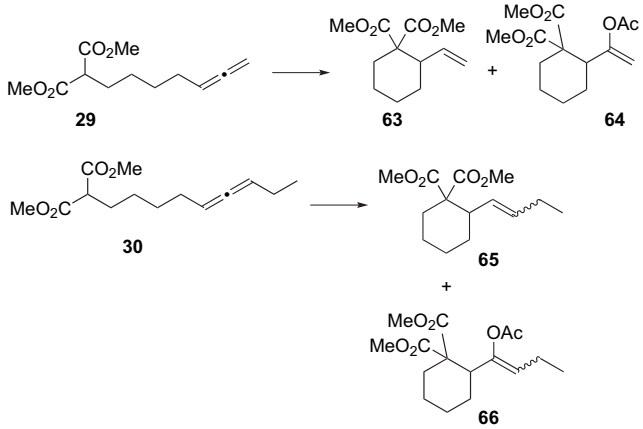
Scheme 9. Cyclisation of the allenyl malonate **27**. Conditions **A**, **24** 66%, **53** and **54** (7:1 mixture) 15%; (ii) Conditions **B**, **24** 10%, **55** 22%.

*2.2.2.4. Cyclisation of the allenyl malonate **28**.* Treatment of the non-terminal allene **28** with manganese(III) acetate in ethanol at reflux (Conditions **A**) resulted in complete conversion of the starting material to olefin-containing products and minor amounts of other products as judged by crude ^{1}H NMR (Scheme 10). Purification of the crude reaction mixture gave the alkenes **58** as a 1:1.5 mixture of (*Z*):(*E*)-diastereomers (56%) reflecting the configurational mobility of the intermediate alkenyl radical **57**.[22] Further purification by flash chromatography gave the allylic γ-lactones **62** as a 1:3.5 mixture of diastereomers (5%). These products arise by mechanisms analogous to those discussed in relation to Scheme 9. Changing the solvent to acetonitrile and addition of copper(II) triflate (Conditions **B**) again reduced the products arising from reductive termination, although a multitude of products were formed. The alkenes **58** were isolated in 25% yield along with the enol acetates **59**, the γ-lactones **62** and the allylic acetates **61**, which were formed as a 5.6:2:1 ratio in a combined yield of ca. 43%. These oxidative substitution products were partly separated by HPLC, which allowed characterisation and their structures were assigned by standard techniques. As with compound **27**, the cyclisation of **28** gave rise predominantly to five-membered ring products in keeping with the work of Guo[16] and Crandall.[15]



Scheme 10. Cyclisation of the allenyl malonate **28**. (i) Conditions **A**, **58**, 56%, **62**, 5%; (ii) Conditions **B**, **58**, 25%, **59**, **62**, **61**, combined yield of 43%.

*2.2.2.5. Cyclisation of the allenyl malonates **29** and **30**.* We were delighted to find that treatment of the malonate **29** under conditions **A** gave the known vinylcyclohexane **63**[23] (48%) and recovered starting material **29** (24%) (Scheme 11). By increasing the amount of manganese(III) acetate to 3 equiv and the reaction time to 45 h the yield of vinylcyclohexane could be raised to 65%. Under oxidative termination conditions using copper(II) triflate (Conditions **B**) the vinyl acetate **64** was isolated in 35% yield along with 11% of the vinylcyclohexane **63**; similar results were obtained with copper(II) acetate. With the non-terminal allene **30**, cyclisation under conditions **A** gave the alkylidene cyclohexane **65** (40%) along with

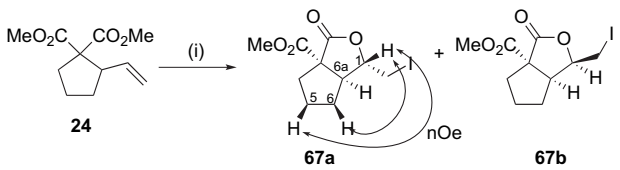


Scheme 11. Cyclisation of the allenyl malonates **29** and **30**. (i) Conditions **A** with 3 equiv of $Mn(OAc)_3$, **63**, 65%, **65**, 61%; (ii) Conditions **B** with copper(II) triflate, **63**, 11%, **64**, 35%; **65**, 9%, **66**, 25%.

recovered starting material **30** (22%). Again, changing the reaction conditions to 3 equiv of manganese(III) acetate and extending the reaction time to 45 h gave the desired product in an increased yield of 61% along with recovered starting material (8%); the olefins **65** were isolated as an inseparable 1:1.4 mixture of (*Z*):(*E*)-geometric isomers. Using conditions **B** with copper(II) triflate as additive gave the alkylidiene cyclohexane **65** (9%). It was clear that other components were present in the crude reaction mixture; however, complete purification was not possible. Nevertheless partial purification gave an impure oil, which appeared to be the enol acetate **66** in ca. 25% {ES *m*/*z* 330.20 [$(M+NH_4)^+$, 25%], 335.14 [$(M+Na)^+$, 80%], 647.24 [$(2M+Na)^+$, 100%], found $[M+Na]^+$ 335.1463; $C_{16}H_{24}NaO_6$ requires 335.1465}. Using copper(II) acetate did not give any of the enol acetate but rather the alkylidene cyclohexane **65** (27%). The exclusive formation of six-membered ring products from the cyclisation of the allenes **29** and **30** is in keeping with the experimental work of Crandall.[15]

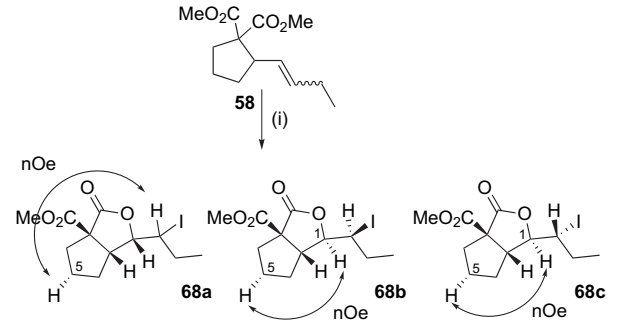
2.3. Iodolactonisation

The studies reported above indicate that it is indeed possible to form alkenylcyclonanes in synthetically useful yields by the cyclisation of electrophilic *C*-centred radicals onto allenes followed by reduction of the so-formed alkenyl radicals. The next step was to demonstrate a diastereoselective iodolactonisation for the formation of [3.3.0]-bicyclic γ-lactones. Treatment of the vinyl cyclopentane **24** with iodine in dichloromethane according to the procedure of Bian[5] gave the desired [3.3.0]-bicyclic γ-lactone **67** as a 7:1 mixture of diastereomers in 83% combined yield (Scheme 12). The relative configuration of the diastereomers was assigned on the basis of a ^{1}H NMR NOESY experiment. For the major diastereomer a diagnostic NOE was observed between the lactone proton H-1 and the ring protons H-5 and H-6. By contrast, in the minor diastereomer no NOEs were observed between H-1 and the cyclopentane protons; instead, one of the iodomethyl protons had an NOE to the cyclopentane protons.



Scheme 12. Iodocyclisation of the vinyl cyclopentane **24**. (i) I_2, CH_2Cl_2, 0 °C, **67**, (7:1 mixture) 83%.

Iodolactonisation of a 1.6:1 (*E*):(*Z*) mixture of alkenes **58** occurred analogously to give three separable iodolactone products with a diastereomeric ratio of 13:1 at the lactone stereocentre (Scheme 13). The relative configuration of the lactone stereocentre, *C*-1, was assigned on the basis of ^{1}H NMR NOESY experiments. A diagnostic NOE observed between H-1 and H-5 for both compounds **68b** and **68c** confirmed the lactone configuration. By contrast, the minor



Scheme 13. Iodocyclisation of the alkenyl-cyclopentane **58**. (i) I_2, CH_2Cl_2, 0 °C, **68a** 7%, **68b** 54%, **68c** 38%.

diastereomer **68a** showed no such NOE, and instead an NOE was observed between H-5 and the proton on the iodine-bearing carbon atom. The relative configuration of the iodine-bearing stereocentre in **68c** was established using X-ray crystallography (Fig. 1).[24] Interestingly, the racemic iodolactone **68c** crystallises with both enantiomers in the asymmetric unit forming a chiral racemate where the conformations of the two enantiomers in the unit cell are not related by a crystallographic inversion centre. This is a rare example of a racemic crystal, which belongs to an enantiomorphous class.[25]

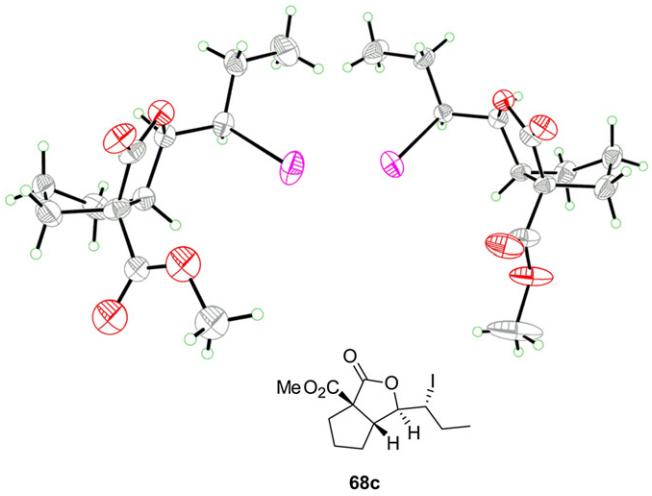
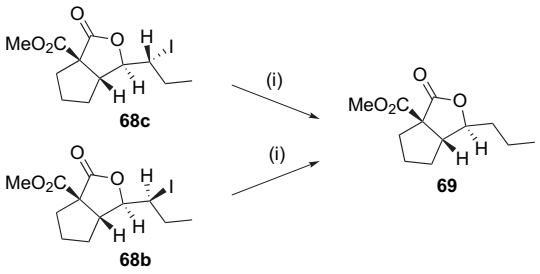


Figure 1. X-ray crystal structure of the iodolactone **68c** showing both enantiomers present in the asymmetric unit. Atomic displacement ellipsoids drawn at 50% probability; disorder omitted for clarity.

The final step in our proposed diastereoselective synthesis of [3.3.0]-bicyclic γ-lactones required removal of the iodine atom, this also served to verify that the γ-lactones **68b** and **68c** varied only in the configuration of the iodine-bearing stereocentre. Compounds **68b** and **68c** were individually reduced using tributyltin hydride giving the same bicyclic γ-lactone **69** (Scheme 14). This confirmed that iodolactonisation of disubstituted vinyl cyclopentanes had indeed given bicyclic γ-lactones with high diastereocontrol.



Scheme 14. Reduction of the iodolactones **68b**,**c**. (i) Bu_3SnH, AIBN, MeCN, reflux, 97% from **68c**, 63% from **68b**.

3. Conclusions

In conclusion, we have developed methodology for the regioselective synthesis of alkenylcyclanones by the oxidative radical cyclisation of malonyl radicals onto both allenes, and an allylsilane. Furthermore, we have demonstrated the diastereoselective formation of [3.3.0]-bicyclic γ-lactones from two of these alkenylcyclanone products. The cyclisation of 3-, 4- and 5-allenyl malonates on exposure to manganese(III) acetate under both oxidative and reductive termination conditions has also been studied. In keeping with previous theoretical and experimental work, the cyclisation of radicals derived from substrates **25** and **26** gives exclusively five-membered ring products. Under reductive termination conditions

(ethanol as solvent) the allylic adduct radicals dimerise, whereas under oxidative termination conditions (in the presence of a copper(II) additive) good yields of allylic acetates are formed. The substrates **27** and **28** gave predominantly five-membered ring products again in keeping with previous work, and the substrates **29** and **30** gave exclusively six-membered ring products. Under reductive termination conditions synthetically useful yields of alkenylcyclanones were formed from substrates **27**–**30**. Under oxidative termination conditions product yields were far lower, reflecting the difficulty in oxidising an alkenyl radical.

4. Experimental

4.1. General experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX-400, Bruker DQX-200, Bruker DRX-500, or Avance AVC-500 spectrometers, using $CDCl_3$ as reference or internal deuterium lock. Chemical shifts are quoted in parts per million relative to tetramethylsilane (δ=0 ppm) and referenced to the solvent residual. Multiplicities were assigned using DEPTQ or DEPT-135 sequence. The following abbreviations were used; s-singlet, d—doublet, t—triplet, q—quartet, m—multiplet, br—broad, dd—doublet of doublets (etc.). Coupling constants (*J*) are quoted in hertz. Infrared spectra were recorded on a Bruker Tensor 27 Fourier Transform spectrophotometer on a NaCl plate using a solution in the solvent indicated. The characteristic peaks are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the Mass Spectrometry Service of the Chemistry Research Laboratory, Oxford. Melting points were recorded on a Kofler hot block and are uncorrected. Flash chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Thin layer chromatography was carried out on Merck aluminium backed sheets coated with 60 F_{254} silica gel. Visualisation of the silica plates was achieved using a UV lamp (λ_{max}=254 or 365 nm), potassium permanganate or vanillin. High performance liquid chromatography was carried out using a Zorbax RX-SIL column with a pressure of 5 mL/min. Solvents were either used as commercially supplied, or as purified by standard techniques. Petroleum ether refers to the fraction boiling at 40–60 °C. Brine refers to a saturated aqueous solution of sodium chloride. Unless otherwise stated, reactions were carried out in oven-dried flasks under an atmosphere of dry nitrogen. Solvents were purified by standard techniques. The cyclisation substrates **25**–**30** were synthesised from the corresponding known allenyl mesylates, or from the known allenyl alcohols via the corresponding mesylates (vide infra).

4.1.1. General procedure for the preparation of the malonate cyclisation substrates. Sodium hydride (3 equiv of a 60% dispersion in mineral oil) was suspended in DMF (4 mL/mmol of mesylate) and cooled to 0 °C. Dimethyl malonate (3 equiv) was added over 10 min and the resulting mixture allowed to warm to room temperature. A solution of the primary mesylate (1 equiv) in THF (2 mL/mmol of mesylate) was added dropwise. Potassium iodide (1.5 equiv) was added and the reaction mixture was heated under reflux for 18 h and then allowed to cool. Water (5 mL/mmol mesylate) was added and the mixture extracted with diethyl ether (3×5 mL/mmol of mesylate). The combined organic layers were washed with brine (3×5 mL/mmol of mesylate), dried ($MgSO_4$) and the solvent removed in vacuo. Purification was achieved by flash chromatography.

*4.1.2. (Z)-Dimethyl 2-(6-(trimethylsilyl)hex-4-enyl)malonate **23**.* Prepared according to the general procedure from (*Z*)-6-(trimethylsilyl)hex-4-enyl methanesulfonate **22**[11] (187.5 mg, 0.75 mmol). Purification by flash column chromatography (gradient elution 5–10% diethyl ether/petroleum ether) to give the malonate **23** as a colourless oil (178.3 mg, 83%); R_f=0.56 (diethyl ether/hexane, 1:1); ν_{max} (film)/cm^{-1} 1739; δ_H (400 MHz, $CDCl_3$) 5.45–5.31 (1H, m, H-5′), 5.26–5.12 (1H, m, H-4′), 3.71 (6H, s, 2×OMe), 3.34 (1H, t, *J*=7.5, H-2), 1.99 (2H, q, *J*=7.3, H-3′, H-3″), 1.89 (2H, q, *J*=7.6, H-1′, H-1″), 1.43 (2H, d, *J*=8.7, H-6′, H-6″), 1.39–1.28 (2H, m, H-2′, H-2″), −0.03 (9H, s, $SiMe_3$); δ_C (50 MHz, $CDCl_3$) 171.6 (C-1), 128.2 (C-4′), 128.0 (C-5′), 54.2 (2×OMe), 53.4 (C-2), 30.1 (C-1′), 29.2 (C-2′), 28.4 (C-3′), 20.3 (C-6′), 0.0 (CH_3, $SiMe_3$); LRMS *m*/*z* (ESI$^+$) 350.3 (M+Na+MeCN$^+$, 100%); HRMS *m*/*z* (ESI$^+$) found [M+Na]$^+$, 309.1493; $C_{14}H_{26}O_4SiNa$ requires 309.1493.

*4.1.3. Dimethyl 2-vinylcyclopentane-1,1-dicarboxylate **24**[12].* Manganese(III) acetate (107.2 mg, 0.40 mmol) and copper(II) triflate (72.3 mg, 0.2 mmol) were added to a solution of the malonate **23** (57.2 mg, 1.0 mmol) in dry sparged acetonitrile (2 mL). The resulting suspension was heated to 80 °C for 24 h. Water (20 mL) and diethyl ether (20 mL) were added and the mixture was filtered and extracted with diethyl ether (3×100 mL). The combined organic layers were then dried ($MgSO_4$), filtered and then concentrated under vacuum. The resultant oil was purified by flash column chromatography (gradient elution 5–20% diethyl ether/petroleum ether) to yield the vinyl cyclopentane **24**[12] (40.8 mg, 96%) as a colourless oil; R_f=0.56 (diethyl ether/hexane, 1:1); δ_H (400 MHz, $CDCl_3$) 5.78 (1H, ddd, *J*=17.2, 10.3, 8.0, C*H*=CH$_2$), 5.12–5.06 (1H, m, CH=C*H*H), 5.03–4.99 (1H, m, CH=CH*H*), 3.73 (3H, s, OMe), 3.65 (3H, s, OMe), 3.24 (1H, q, *J*=7.7, H-2), 2.46 (1H, ddd, *J*=13.8, 8.4, 8.1, H-5), 2.08 (1H, ddd, *J*=13.5, 8.5, 4.9, H-5′), 1.99–1.91 (1H, m, H-3), 1.91–1.81 (1H, m, H-4), 1.73–1.55 (2H, m, H-3′, H-4′); δ_C (100 MHz, $CDCl_3$) 172.7, 171.2, 137.5 (*C*H=CH$_2$), 115.9 (CH=*C*H$_2$), 64.3 (C-1), 52.5 (OMe), 52.1 (OMe), 50.0 (C-2), 33.9 (C-5), 30.7 (C-3), 23.1 (C-4); ν_{max} (CH_2Cl_2/cm^{-1}) 2955, 1732, 1638; LRMS *m*/*z* (ESI$^+$) 235.1 (M+Na$^+$, 100%), 447.2 (2M+Na$^+$, 97%), 213.1 (M+H$^+$, 94%), 276.1 (M+Na+MeCN$^+$, 70%); HRMS *m*/*z* (ESI$^+$) found [M+Na]$^+$ 235.0944; $C_{11}H_{16}NaO_4$ requires 235.094; data consistent with literature.[12]

4.1.4. General procedures for manganese(III) acetate mediated reactions

4.1.4.1. Conditions A: reactions in ethanol. To a mixture of allenyl malonate (1 equiv) and manganese(III) acetate (2 equiv) was added degassed ethanol (50 mL/mmol of malonate). The reaction mixture was heated under reflux for 18 h before the solvent was removed in vacuo. The resulting mixture was diluted with water (60 mL/mmol of malonate), and extracted with ethyl acetate (3×80 mL/mmol of malonate). The combined organic layers were washed with brine (3×60 mL/mmol of malonate), dried ($MgSO_4$), filtered and the solvent removed in vacuo. The residue was purified by flash chromatography.

4.1.4.2. Conditions B: reactions in acetonitrile with copper(II) salt. To a mixture of allenyl malonate (1 equiv), manganese(III) acetate (2 equiv) and a copper additive (1 equiv) was added degassed acetonitrile (5 mL/mmol of malonate). The reaction mixture was heated under reflux for 18 h. The cooled reaction mixture was diluted with water (200 mL/mmol of malonate), and extracted with ethyl acetate (3×140 mL/mmol of malonate). The combined organic extracts were washed with brine (3×100 mL/mmol of malonate), dried ($MgSO_4$), filtered and the solvent removed in vacuo. The residue was purified by flash chromatography.

*4.1.5. Tetramethyl 2,2′-(ethane-1,2-diyl)dicyclopent-2-ene-1,1-dicarboxylate **37a**.* Synthesised from the known malonate **25**[12] (0.100 g, 0.505 mmol) using Conditions **A**. Purified by flash column chromatography (diethyl ether/petroleum ether, 1:2) to give a mixture of dimers **37** (0.457 mmol, 90%) from which **37a** could be isolated as a white crystalline solid after further chromatography (ethyl acetate/petroleum ether, 1:3) (16.8 mg, 42.6 μmol, 8%).

Dimer **37a**; R_f=0.26 (petroleum ether/ethyl acetate, 3:1); mp 93 °C; δ_H (500 MHz, $CDCl_3$) 5.73 (2H, br s, 2×H-3), 3.75 (12H, s,

OCH_3), 2.51 (4H, dd, J=7.1, 5.7, 2×H-5, 2×H-5′), 2.42–2.38 (8H, m, 2×H-4, 2×H-4′, CH_2CH_2); δ_C (125 MHz, $CDCl_3$) 171.8, 141.0 (C-2), 130.1 (C-3), 68.2 (C-1), 52.5 (OMe), 34.2 (C-5), 30.5 (C-4), 26.4 (CH_2CH_2); ν_{max} (CH_2Cl_2/cm^{-1}) 1731, 1646; LRMS m/z (ESI^+) 412.2 ($M+NH_4^+$, 100%), 417.1 ($M+Na^+$, 89%), 811.3 ($2M+Na^+$, 63%), 395.1 ($M+H^+$, 61%); HRMS m/z (ESI^+) found $[M+Na]^+$ 417.1514; $C_{20}H_{26}NaO_8$ requires 417.1520.

4.1.6. Dimethyl 3-acetoxy-2-methylenecyclopentane-1,1-dicarboxylate ***39****, dimethyl 2-(acetoxymethyl)cyclopent-2-ene-1,1-dicarboxylate* ***41****, dimethyl 3-hydroxy-2-methylenecyclopentane-1,1-dicarboxylate* ***40*** *and dimethyl 2-(hydroxymethyl)cyclopent-2-ene-1,1-dicarboxylate* ***42****.* Synthesised from the known malonate **25**[12] (0.100 g, 0.505 mmol) using Conditions **B** with copper(II) acetate. Purified by flash column chromatography (petroleum ether/ethyl acetate, 2:1) to give **39** and **41** as an inseparable 8:1 mixture of isomers as a colourless oil (94.6 mg, 0.369 mmol, 71%); characterisation is on the mixture of compounds. Further elution of the column gave the alcohols **40** and **42** as an inseparable 4.5:1 mixture (11 mg, 0.051 mmol, 10%); partial separation could be obtained by further chromatography.

Cyclopentane **39**; R_f=0.20 (petroleum ether/ethyl acetate, 3:1); δ_H (500 MHz, $CDCl_3$) 5.62 (1H, d, J=1.7, C=C*H*H), 5.61 (1H, d, J=1.7, C=CH*H*), 5.55 (1H, dddd, J=6.2, 4.9, 1.6, 1.6, H-3), 3.77 (3H, s, OMe), 3.75 (3H, s, OMe), 2.52 (1H, ddd, J=13.5, 8.0, 7.3, H-5), 2.34 (1H, ddd, J=13.5, 6.9, 6.5, H-5′), 2.10 (1H, dddd, J=13.2, 8.0, 6.9, 6.2, H-4), 2.06 (3H, s, $C(O)CH_3$), 1.81 (1H, dddd, J=13.2, 7.3, 6.5, 4.9, H-4′); δ_C (125 MHz, $CDCl_3$) 170.61, 170.59, 170.4, 145.7 (C-2), 118.3 ($C=CH_2$), 76.2 (C-3), 61.4 (C-1), 53.0 (OMe), 52.98 (OMe), 32.1 (C-5), 30.7 (C-4), 21.2 ($C(O)CH_3$); ν_{max} (CH_2Cl_2/cm^{-1}) 1735, 1659; LRMS m/z (ESI^+) 279.1 ($M+Na^+$, 100%), 274.1 ($M+NH_4^+$, 54%); HRMS m/z (ESI^+) found $[M+Na]^+$ 279.0841; $C_{12}H_{16}NaO_6$ requires 279.0839; Found C, 56.31; H, 6.22%; $C_{12}H_{16}O_6$ requires: C, 56.24; H, 6.29%.

Cyclopentane **41**, selected data; R_f=0.20 (petroleum ether/ethyl acetate, 3:1); δ_H (500 MHz, $CDCl_3$) 6.06–6.04 (1H, m, H-3), 4.82 (2H, q, J=1.8, CH_2O), 3.75 (6H, s, OMe), 2.59–2.56 (2H, m, H-5, H-5′), 2.48–2.44 (2H, m, H-4, H-4′), 2.05 (3H, s, $C(O)CH_3$); δ_C (125 MHz, $CDCl_3$) 171.1, 170.5, 136.1 (C-2), 135.3 (C-3), 61.9 (C-1), 61.4 (CH_2O), 33.8 (C-5), 305 (C-4), 20.9 ($C(O)CH_3$).

Alcohol **40**; R_f=0.37 (CH_2Cl_2/ethyl acetate, 5:1+1% IPA); δ_H (500 MHz, $CDCl_3$) 5.58 (1H, d, J=1.6, C=C*H*H), 5.54 (1H, d, J=1.6, C=CH*H*), 4.53 (1H, ddd, J=6.4, 5.8, 5.7, H-3), 3.77 (3H, s, OMe), 3.75 (3H, s, OMe), 2.50 (1H, dd, J=13.7, 6.9, H-5), 2.30 (1H, ddd, J=13.7, 7.4, 7.1, H-5′), 2.04 (1H, dddd, J=13.1, 7.1, 6.9, 6.4, H-4), 1.84 (1H, d, J=5.7, OH), 1.73 (1H, dddd, J=13.1, 7.4, 7.4, 5.8, H-4′); δ_C (125 MHz, $CDCl_3$) 171.2, 170.6, 150.4 (C-2), 115.3 ($C=CH_2$), 75.2 (C-3), 59.8 (*C*-1), 53.0 (OMe), 52.9 (OMe), 33.4 (C-4), 31.6 (C-5); ν_{max} (CH_2Cl_2/cm^{-1}) 3468, 1733, 1657; LRMS m/z (ESI^+) 451.1 ($2M+Na^+$, 100%), 237.1 ($M+Na^+$, 76%); HRMS m/z (ESI^+) found $[M+Na]^+$ 237.0733; $C_{10}H_{14}NaO_5$ requires 237.0733; Found C, 56.18; H, 6.56%; $C_{10}H_{14}O_5$ requires: C, 56.07; H, 6.59%.

Alcohol **42**; R_f=0.09 (CH_2Cl_2/ethyl acetate, 20:1); δ_H (500 MHz, $CDCl_3$) 6.06 (1H, tt, J=2.5, 1.3, H-3), 4.29 (2H, dtd, J=6.2, 1.5, 1.3, C*H*$_2$OH), 3.77 (6H, s, 2×OMe), 2.70 (1H, t, J=6.2, O*H*), 2.58–2.54 (2H, m, H-5, H-5′), 2.46 (2H, dddt, J=5.1, 3.5, 2.5, 1.5, H-4, H-4′); δ_C (125 MHz, $CDCl_3$) 172.0, 140.8 (C-2), 135.1 (C-3), 67.1 (C-1), 59.8 (CH_2OH), 52.9 (OMe), 34.2 (C-5), 30.4 (C-4); ν_{max} (CH_2Cl_2/cm^{-1}) 3458, 1731, 1651; LRMS m/z (ESI^+) 197.1 ($M-OH^+$, 100%), 237.1 ($M+Na^+$, 96%), 451.1 ($2M+Na^+$, 93%), 278.1 ($M+Na+MeCN^+$, 83%); HRMS m/z (ESI^+) found $[M+Na]^+$ 237.0745; $C_{10}H_{14}NaO_5$ requires 237.0733.

4.1.7. Hepta-3,4-dienyl methanesulfonate. To the known alcohol hepta-3,4-dien-1-ol[26–28] (1.27 g, 11.3 mmol) in DCM (30 mL) was added triethylamine (2.3 mL, 16.5 mmol) and the mixture was cooled to 0 °C. Methanesulfonyl chloride (1.05 mL, 13.5 mmol) was added and the reaction allowed to warm to room temperature and was stirred for 1.5 h. The reaction was quenched with 0.5 M aqueous HCl and extracted with DCM (3×50 mL). The organic layers were combined, dried (Na_2SO_4) and the solvent removed in vacuo to give crude hepta-3,4-dienyl methanesulfonate (2.07 g, 10.8 mmol, 96%) as an orange oil, which was used in the next reaction without further purification; δ_H (500 MHz, $CDCl_3$) 5.27–5.26 (1H, m, H-3 or H-5), 5.15–5.09 (1H, m, H-3 or H-5), 4.27 (2H, t, J=6.9, H-1, H-1′), 3.02 (3H, s, CH_3SO_2), 2.44 (2H, dq, J=3.0, 6.9, H-2, H-2′), 2.02 (2H, ddq, J=3.3, 6.2, 7.5, H-6, H-6′), 1.03 (3H, t, J=7.4, CH_2CH_3); δ_C (125 MHz, $CDCl_3$) 204.4 (C-4), 94.2, 86.1, 69.2 (C-1), 37.5 (CH_3SO_2), 28.8 (C-2), 21.7 (C-6), 9.3 (C-7); ν_{max} (film/cm^{-1}) 2967, 1965; HRMS m/z found M^+ 190.0661; $C_8H_{14}O_3S$ requires 190.0664.

4.1.8. Dimethyl 2-(hepta-3,4-dienyl)malonate ***26****.* Synthesised from hepta-3,4-dienyl methanesulfonate (2.05 g, 10.7 mmol) according to the general procedure. Purification by flash column chromatography (gradient petroleum ether/ethyl acetate, 20:1→6:1) gave the malonate **26** (1.87 g, 8.27 mmol, 76%); R_f=0.58 (petroleum ether/ethyl acetate, 3:1); δ_H (500 MHz, $CDCl_3$) 5.20–5.15 (1H, m, H-3′ or H-5′), 5.08 (1H, tdt, J=6.1, 6.1, 3.3, H-3′ or H-5′), 3.74 (6H, s, 2×OMe), 3.49–3.40 (1H, m, H-1), 2.05–1.96 (6H, m, 2×H-1′, 2×H-2′, 2×H-6′), 1.00 (3H, t, J=7.4, CH_2CH_3); δ_C (125 MHz, $CDCl_3$) 203.7 (C-4′), 169.8, 93.6 (C-5′), 89.8 (C-3′), 52.4 (OMe), 52.4 (C-1), 50.7 (CH_2), 28.1 (CH_2), 26.5 (CH_2), 21.9 (C-6′), 13.4 (C-7′); ν_{max} (film)/cm^{-1} 2962, 1963, 1754, 1738; LRMS m/z (ESI^+) 475.2 ($2M+Na^+$, 100%), 249.1 ($M+Na^+$, 62%); HRMS m/z (ESI^+) found $[M+Na]^+$ 249.1091; $C_{12}H_{18}NaO_4$ requires 249.1097.

4.1.9. Dimethyl 3-acetoxy-2-propylidenecyclopentane-1,1-dicarboxylate ***45*** *and dimethyl 2-(1-acetoxypropyl)cyclopent-2-ene-1,1-dicarboxylate* ***47****.* Synthesised from the allene **26** (114 mg, 0.5 mmol) using Conditions **B** with copper(II) acetate. Purification by flash chromatography (gradient elution 30:1 petroleum ether/ethyl acetate→ethyl acetate) gave the acetates **45** and **47** as an inseparable 1:1.2 mixture (108 mg, 0.38 mmol, 76%); the *exo*-cyclic alkenes **45** were formed as a 1:1.5 mixture of geometric isomers and characterisation is on the mixture of compounds.

Acetates **45** and **47**; R_f=0.57 (petroleum ether/ethyl acetate, 3:1); δ_H (500 MHz, $CDCl_3$) 6.09–6.08 (1H, br, H-3$_{\mathbf{47}}$) 5.98 (1H, dt, J 1.6, 7.7, CH=C$_{\mathbf{45d1}}$), 5.92 (1H, t, J=7.6, CH=C$_{\mathbf{45d2}}$), 5.78 (1H, br d, J=5.6, H-3$_{\mathbf{45d1}}$), 5.56 (1H, t, J=7.4, H-3$_{\mathbf{47}}$), 5.52 (1H, t, J=4.2, H-3$_{\mathbf{45d2}}$), 3.77 (3H, s, OMe$_{\mathbf{45d1}}$), 3.77 (3H, s, OMe$_{\mathbf{47}}$), 3.74 (3H, s, OMe$_{\mathbf{47}}$), 3.737 (3H, s, OMe$_{\mathbf{45d2}}$), 3.731 (3H, s, OMe$_{\mathbf{45d1}}$), 3.72 (3H, s, OMe$_{\mathbf{45d2}}$), 2.65–2.34 (6H, m, H-5$_{\mathbf{45d1}}$, H-5′$_{\mathbf{45d1}}$, H-5$_{\mathbf{45d2}}$, H-5′$_{\mathbf{45d2}}$, H-4$_{\mathbf{47}}$, H-4′$_{\mathbf{47}}$), 2.24–2.08 (4H, m, allylicCH$_{\mathbf{245d1}}$, allylicCH$_{\mathbf{245d2}}$), 2.06–1.98 (3H, m, $CH_2OAc_{\mathbf{45d2}}$, C*H*HOAc$_{\mathbf{45d1}}$), 2.04 (3H, s, OAc$_{\mathbf{45d2}}$), 2.03 and 2.02 (2×3H, s, OAc$_{\mathbf{45d1}}$, OAc$_{\mathbf{47}}$), 1.88–1.81 (2H, m, CH*H*OAc$_{\mathbf{45d1}}$, C*H*HCH$_{\mathbf{347}}$), 1.78–1.69 (1H, m, CH*H*CH$_{\mathbf{347}}$), 1.01 (3H, t, J=7.7, $CH_2CH_{\mathbf{345d1}}$), 0.96 (3H, t, J=7.7, $CH_2CH_{\mathbf{345d2}}$), 0.91 (3H, t, J=7.7, $CH_2CH_{\mathbf{347}}$); δ_C (125 MHz, $CDCl_3$) 171.6, 171.5, 171.3, 171.2, 171.2, 171.0, 170.8, 170.5, 170.1, 140.5, 137.9, 136.3, 135.9, 134.8, 78.3, 73.6, 71.6, 67.0, 62.7, 61.0, 52.9, 52.8, 52.8, 52.6, 52.5, 34.6, 34.1, 32.9, 31.8, 31.1, 30.5, 27.4, 23.2, 23.2, 21.4, 21.3, 21.1, 13.6, 12.6, 9.9; ν_{max} (CH_2Cl_2)/cm^{-1} 2956, 1735; LRMS m/z (ESI^+) 307.1 ($M+Na^+$, 80%), 591.2 ($2M+Na^+$, 100%); HRMS m/z (ESI^+) found $[M+Na]^+$ 307.1151; $C_{14}H_{20}NaO_6$ requires 307.1152.

4.1.10. Dimethyl 2-vinylcyclopentane-1,1-dicarboxylate ***24****, methyl 3-oxo-1,3,3a,4,5,6-hexahydroisobenzofuran-3a-carboxylate* ***53*** *and (1S*,5R*)-methyl 8-methylene-7-oxo-6-oxabicyclo[3.2.1]octane-1-carboxylate* ***54****.* Synthesised from the known allene **27**[29,30] (106 mg, 0.5 mmol) using Conditions **A**. Purification by flash chromatography (petroleum ether/diethyl ether, 3:1) gave the vinylcyclopentane **24**[12] (70 mg, 0.33 mmol, 66%). Further elution of the column gave the lactones **53** and **54** as 7:1 inseparable mixture

(15 mg, 0.077 mmol, 15%); characterisation is on the mixture of compounds.

Lactone **53**; R_f=0.27 (CH_2Cl_2/IPA, 20:1); δ_H (500 MHz, $CDCl_3$) 5.90–5.87 (1H, m, H-7), 5.07 (1H, dddd, *J*=10.8, 3.3, 3.3, 2.0, H-1), 4.73 (1H, dddd, *J*=10.8, 1.5, 1.3, 1.3, H-1′), 3.78 (3H, s, OMe), 2.63 (1H, dt, *J*=13.2, 3.4, H-4), 2.22 (1H, dddd, *J*=6.7, 5.1, 3.3, 1.5, H-6), 2.16–2.06 (1H, m, H-6′), 1.95–1.82 (1H, m, H-5), 1.82–1.69 (1H, m, H-5′), 1.37 (1H, ddd, *J*=13.5, 13.2, 3.7, H-4′); δ_C (125 MHz, $CDCl_3$) 173.4, 168.3, 131.1 (C-7a), 125.2 (C-7), 72.1 (C-1), 62.3 (C-3a), 53.1 (OMe), 26.0 (C-4), 23.5 (C-6), 18.3 (C-5); ν_{max} (CH_2Cl_2/cm^{-1}) 2957, 1780, 1738; LRMS *m*/*z* (ESI^+) 415.1 ($2M+Na^+$, 100%), 219.0 ($M+Na^+$, 88%), 260.1 ($M+Na+MeCN^+$, 75%), 214.1 ($M+NH_4^+$, 63%); HRMS *m*/*z* (ESI^+) found $[M+Na]^+$ 219.0627; $C_{10}H_{12}NaO_4$ requires 219.0628.

Lactone **54**; R_f=0.27 (CH_2Cl_2:IPA, 20:1); δ_H (500 MHz, $CDCl_3$) 5.10–5.06 (2H, m, C*H*H=C, H-5), 4.87 (1H, t, *J*=1.0, CH*H*=C), 3.83 (3H, s, OMe), 2.39 (1H, ddt, *J*=12.6, 5.3, 1.4), 2.09 (1H, dt, *J*=5.8, 12.6), 2.24–2.18 (1H, m), 1.94–1.90 (2H, m), 1.76–1.68 (1H, m); δ_C (125 MHz, $CDCl_3$) 168.3, 168.0, 149.1 (C-8), 104.0 (CH_2=C), 81.3 (C-5), 72.9 (C-3a), 52.8 (OMe), 33.3, 31.4, 17.9.

4.1.11. Dimethyl 2-(1-acetoxyvinyl)cyclopentane-1,1,-dicarboxylate ***55***. Synthesised from the known allene **27**[29,30] (106 mg, 0.5 mmol) using Conditions **B** with copper(II) triflate. Purification by flash chromatography (petroleum ether/diethyl ether, 3:1) gave the vinylcyclopentane **24**[12] (11 mg, 0.05 mmol, 10%) and the enol acetate **55** (30 mg, 0.11 mmol, 22%).

Enol acetate **55**; R_f=0.14 (petroleum ether/ethyl acetate, 5:1); δ_H (500 MHz, $CDCl_3$) 4.89 (1H, dd, *J*=1.8, 0.8, C=C*H*H), 4.86 (1H, d, *J*=1.8, =CH*H*), 3.73 (3H, s, OMe), 3.68 (3H, s, OMe), 3.53 (1H, ddd, *J*=9.9, 7.2, 0.8, H-2), 2.55 (1H, ddd, *J*=13.8, 8.8, 8.6, H-5), 2.10 (3H, s, $C(O)CH_3$), 2.08–1.99 (2H, m, H-5′, H-3), 1.91–1.83 (1H, m, H-4), 1.74 (1H, dddd, *J*=12.8, 10.0, 9.9, 8.1, H-3′), 1.58 (1H, dtdd, *J*=12.5, 9.0, 8.8, 8.1, H-4′); δ_C (125 MHz, $CDCl_3$) 172.4, 170.9, 169.0, 154.4 (*C*=CH_2), 103.3 (C=*C*H_2), 63.3 (C-1), 52.7 (OMe), 52.4 (OMe), 49.7 (C-2), 34.9 (C-5), 29.4 (C-3), 23.1 (C-4), 21.1 ($C(O)CH_3$); ν_{max} (CH_2Cl_2/cm^{-1}) 2955, 1761, 1732, 1663; LRMS *m*/*z* (ESI^+) 288.1 ($M+NH_4^+$, 100%), 563.2 ($2M+Na^+$, 82%), 276.1 ($M+Na^+$, 81%); HRMS *m*/*z* (ESI^+) found $[M+Na]^+$ 293.0997; $C_{13}H_{18}NaO_6$ requires 293.0996. Found C, 57.81; H, 6.63%; $C_{13}H_{18}O_6$ requires: C, 57.77; H, 6.71%.

4.1.12. Dimethyl 2-(octa-4,5-dienyl)malonate ***28***. Synthesised from known octa-4,5-dienyl methanesulfonate[31] (1.12 g, 5.42 mmol) according to the general procedure but using THF in place of DMF. Purification by flash column chromatography (petroleum ether/diethyl ether, 10:1) gave the malonate **28** as a colourless oil (1.21 g, 5.04 mmol, 93%); R_f=0.13 (petroleum ether/diethyl ether, 10:1); δ_H (500 MHz, $CDCl_3$) 5.16 (1H, tq, *J*=3.0, 6.3, H-6′), 5.09 (1H, tq, *J*=3.2, 6.3, H-4′), 3.74 (6H, s, 2×OMe), 3.38 (1H, t, *J*=7.6, H-1), 2.05–1.92 (6H, m, 2×H-1′, 2×H-3′, 2×H-7′), 1.44 (2H, qn, *J*=7.7, 2×H-2′), 1.00 (3H, t, *J*=7.4, CH_2CH_3); δ_C (125 MHz, $CDCl_3$) 203.5 (C-5′), 169.9, 93.1 (C-6′), 90.7 (C-4′), 52.4 (OMe), 51.5 (C-1), 28.5 (C-3′), 28.2 (C-1′), 26.8, (C-2′), 21.9 (C-7′), 13.4 (C-8′); ν_{max} ($CDCl_3$/cm^{-1}) 1962, 1755, 1737; LRMS *m*/*z* (ESI^+) 503.2 ($2M+Na^+$, 100%), 241.1 ($M+H^+$, 65%), 258.2 ($M+NH_4^+$, 60%), 263.1 ($M+Na^+$, 52%); HRMS *m*/*z* (ESI^+) found $[M+Na]^+$ 263.1257; $C_{13}H_{20}NaO_4$ requires 263.1254; Found C, 64.90; H, 8.29%; $C_{13}H_{20}O_4$ requires: C, 64.98; H, 8.39%.

4.1.13. Dimethyl 2-(but-1-enyl)cyclopentane-1,1-dicarboxylate ***58*** *and methyl 1-ethyl-3-oxo-1,3,3a,4,5,6-hexahydroisobenzofuran-3a-carboxylate* ***62***. Synthesised from dimethyl 2-(octa-4,5-dienyl)malonate **28** (0.102 g, 0.424 mmol) using Conditions **A**. Purified by flash column chromatography (petroleum ether/ethyl acetate, 5:1) to give an inseparable mixture of alkenes **58** as a colourless oil (57.3 mg, 0.238 mmol, 56%, *E*:*Z* 1.5:1); characterisation is on the mixture. Further elution of the column gave a mixture of diastereoisomers of the lactones **62** (5 mg, 22.3 μmol, 5%); characterisation is on the mixture.

(*Z*)-Dimethyl 2-(but-1-enyl)cyclopentane-1,1-dicarboxylate (*Z*)-**58**; R_f=0.16 (petroleum ether/ethyl acetate, 20:1); δ_H (500 MHz, $CDCl_3$) 5.40 (1H, dtd, *J*=10.8, 7.4, 0.8, =C*H*CH_2), 5.15 (1H, ddt, *J*=10.8, 10.7, 1.6, CHC*H*=), 3.72 (3H, s, OMe), 3.66 (3H, s, OMe), 3.65–3.64 (1H, m, H-2), 2.21–2.03 (4H, m, C*H*$_2$$CH_3$, H-4, H-4′), 2.02–1.94 (1H, m, H-3), 1.89–1.80 (1H, m, H-5), 1.63–1.48 (2H, m, H-3′, H-5′), 0.96 (3H, t, *J*=7.5 z, CH_2C*H*$_3$); δ_C (125 MHz, $CDCl_3$) 172.8, 171.3, 133.3, 128.3, 64.6 (C-1), 52.5 (OMe), 52.1 (OMe), 43.3 (C-2), 34.1 (C-4), 32.9 (C-3), 23.4 (C-5), 20.7 (*C*H_2CH_3), 14.3 (CH_2CH_3); ν_{max} (CH_2Cl_2/cm^{-1}) 2958 (=CH), 1733 (C=O ester); LRMS *m*/*z* (ESI^+) 241.1 ($M+H^+$, 100%), 263.1 ($M+Na^+$, 94%), 503.2 ($2M+Na^+$, 93%); HRMS *m*/*z* (ESI^+) found $[M+Na]^+$ 263.1253; $C_{13}H_{20}NaO_4$ requires 263.1254.

(*E*)-Dimethyl 2-(but-1-enyl)cyclopentane-1,1-dicarboxylate (*E*)-**58**; R_f=0.16 (petroleum ether/ethyl acetate, 20:1); δ_H (500 MHz, $CDCl_3$) 5.55 (1H, dtd, *J*=15.3, 6.4, 1.0, =C*H*CH_2), 5.34 (1H, ddt, *J*=15.3, 8.0, 1.5, CHC*H*=), 3.73 (3H, s, OMe), 3.64 (3H, s, OMe), 3.23 (1H, br dt, *J*=8.0, 7.6, H-2), 2.51–2.43 (2H, m, H-4, H-4′), 2.21–2.14 (2H, m, H-5, H-5′), 2.02–1.90 (3H, m, C*H*$_2$$CH_3$, H-3), 1.67–1.60 (1H, m, H-3′), 0.94 (3H, t, *J*=7.5, CH_2C*H*$_3$); δ_C (125 MHz, $CDCl_3$) 172.9, 171.33, 133.8, 128.0, 64.5 (C-1), 52.4 (OMe), 51.9 (OMe), 48.9 (C-2), 33.8 (C-4), 31.3 (C-3), 25.5 (*C*H_2CH_3), 23.2 (C-5), 13.8 (CH_2CH_3).

Lactones **62**; R_f=0.13 (petroleum ether/CH_2Cl_2, 1:3 with 1% IPA); δ_H (500 MHz, $CDCl_3$) 5.86–5.83 (1H, m, H-7$_{\mathbf{d1}}$), 5.82 (1H, ddd, *J*=3.7, 3.5, 2.1, H-7$_{\mathbf{d2}}$), 5.19–5.15 (1H, m, H-1$_{\mathbf{d2}}$), 4.77 (1H, ttd, *J*=7.7, 1.5, 1.4, H-1$_{\mathbf{d1}}$), 3.78 (6H, s, OMe$_{\mathbf{d1\ and\ d2}}$), 2.61 (1H, dt, *J*=13.2, 3.4, H-4$_{\mathbf{d2}}$), 2.52 (1H, dt, *J*=13.0, 3.4, H-4$_{\mathbf{d1}}$), 2.31–2.27 (1H, m, H-6$_{\mathbf{d1}}$), 2.23 (1H, ddddd, *J*=19.1, 6.9, 3.5, 3.4, 1.4, H-6$_{\mathbf{d2}}$), 2.15–2.05 (2H, m, H-6′$_{\mathbf{d1\ and\ d2}}$), 2.05–1.96 (1H, m, C*H*HCH$_{3\mathbf{d2}}$), 1.94–1.80 (4H, m, H-5$_{\mathbf{d1\ and\ d2}}$, H-5′, C*H*HCH$_{3\mathbf{d1}}$), 1.78–1.70 (1H, m, H-5′$_{\mathbf{d2}}$), 1.70–1.63 (1H, m, CH*H*CH$_{3\mathbf{d1}}$), 1.69–1.62 (1H, m, CH*H*CH$_{3\mathbf{d2}}$), 1.50–1.43 (1H, m, H-4′$_{\mathbf{d1}}$), 1.38 (1H, ddd, *J*=13.5, 13.2, 3.7, H-4′$_{\mathbf{d2}}$), 1.09 (3H, t, *J*=7.4, CH_2C*H*$_{3\mathbf{d2}}$), 1.02 (3H, t, *J*=7.4, CH_2C*H*$_{3\mathbf{d1}}$); δ_C (125 MHz, $CDCl_3$) 173.0, 168.5, 134.9 (C-7a$_{\mathbf{d1\ and\ d2}}$), 125.9 (C-7$_{\mathbf{d1}}$), 123.2 (C-7$_{\mathbf{d2}}$), 85.5 (C-1$_{\mathbf{d1}}$), 84.0 (C-1$_{\mathbf{d2}}$), 62.32 (C-3a$_{\mathbf{d1\ or\ d2}}$), 60.4 (C-3a$_{\mathbf{d1\ or\ d2}}$), 53.2 (OMe$_{\mathbf{d1}}$), 53.1 (OMe$_{\mathbf{d2}}$), 27.9 (C-4$_{\mathbf{d1}}$), 27.6 (*C*H_2CH$_{3\mathbf{d1}}$), 26.3 (C-4$_{\mathbf{d2}}$), 25.3 (*C*H_2CH$_{3\mathbf{d2}}$), 23.6 (*C*-6$_{\mathbf{d2}}$), 23.3 (*C*-6$_{\mathbf{d1}}$), 18.1 (*C*-5$_{\mathbf{d2}}$), 17.8 (*C*-5$_{\mathbf{d1}}$), 9.7 (CH_2*C*H$_{3\mathbf{d1}}$), 9.6 (CH_2*C*H$_{3\mathbf{d2}}$); ν_{max} (CH_2Cl_2/cm^{-1}) 1780 (C=O γ-lactone), 1738 (C=O ester), 1692 (C=C); LRMS *m*/*z* (ESI^+) 471.2 ($2M+Na^+$, 100%), 247.1 ($M+Na^+$, 82%), 225.1 ($M+H^+$, 56%), 279.1 ($M+Na+MeOH^+$, 48%); HRMS *m*/*z* (ESI^+) found $[M+Na]^+$ 247.0944; $C_{12}H_{16}NaO_4$ requires 247.0941.

4.1.14. Dimethyl 2-(1-acetoxybut-1-enyl)cyclopentane-1,1-dicarboxylate ***59*** *and dimethyl 2-(1-acetoxypropyl)cyclohex-2-ene-1,1-dicarboxylate* ***61***. Synthesised from dimethyl 2-(octa-4,5-dienyl)malonate **28** (0.116 g, 0.481 mmol) using Conditions **B** with copper(II) triflate. Purified by flash column chromatography (petroleum ether/ethyl acetate, 5:1) to give the alkenes **58** (0.0285 g, 0.119 mmol, 25% yield, *E*:*Z* 1.7:1) and a 5.6:2:1 mixture of **59**:**62**:**61** (50 mg, ca. 43%); the enol acetates **59** were formed as an inseparable mixture of geometric isomers. This mixture was further purified by semi-preparative HPLC (hexane with 1% IPA).

Enol acetate **59a**; R_f=0.18 (petroleum ether/ethyl acetate, 5:1); δ_H (500 MHz, $CDCl_3$) 5.22 (1H, t, *J*=7.7, C=CH), 3.95 (1H, t, *J*=8.2, H-2), 3.73 (3H, s, OMe), 3.68 (3H, s, OMe), 2.55 (1H, ddd, *J*=13.2, 9.6, 8.0, H-5), 2.29–2.20 (2H, m, C*H*$_2$$CH_3$), 2.08 (3H, s, $C(O)CH_3$), 2.07 (1H, ddd, *J*=13.2, 7.7, 3.2, H-5′), 1.99 (1H, ddd, *J*=12.6, 8.2, 4.5, H-3), 1.94–1.85 (1H, m, H-4), 1.75–1.65 (1H, m, H-3′), 1.60–1.48 (1H, m, H-4′), 1.02 (3H, t, *J*=7.5, CH_2C*H*$_3$); δ_C (125 MHz, $CDCl_3$) 172.6, 170.9, 169.4 (*C*$(O)CH_3$), 145.1 (*C*=CH), 123.0 (C=*C*H), 63.3 (C-1), 52.7 (OMe), 52.5 (OMe), 45.0 (C-2), 34.8 (C-5), 29.6 (C-3), 23.8 (C-4), 21.1 ($C(O)CH_3$), 20.1 (*C*H_2CH_3), 14.2 (CH_2*C*H$_3$); ν_{max} (CH_2Cl_2/cm^{-1}), 1756, 1732, 1642; LRMS *m*/*z* (ESI^+) 321.1 ($M+Na^+$, 100%); HRMS *m*/*z* (ESI^+) found $[M+Na]^+$ 321.1310; $C_{15}H_{22}NaO_6$ requires 321.1309.

Enol acetate **59b**; R_f=0.17 (petroleum ether/ethyl acetate, 5:1); δ_H (500 MHz, $CDCl_3$) 5.19 (1H, t, J=7.3, =C*H*), 3.73 (3H, s, OMe), 3.68 (3H, s, OMe), 3.50 (1H, dd, J=10.4, 7.1, H-2), 2.55 (1H, ddd, J=13.7, 8.7, 8.6, H-5), 2.13 (3H, s, C(O)CH_3), 2.05–1.94 (2H, m, H-3, H-5′), 1.94–1.81 (3H, m, C$H_2$$CH_3$, H-4), 1.73–1.64 (1H, m, H-3′), 1.62–1.52 (1H, m, H-4′), 0.94 (3H, t, J=7.5, CH_2CH_3); δ_C (125 MHz, $CDCl_3$) 172.6, 171.2, 170.0, 145.9 (*C*=CH), 120.5 (C=*C*H), 63.3 (*C*-1), 52.6 (OMe), 52.2 (OMe), 49.8 (C-2), 34.8 (C-5), 29.0 (C-3), 23.1 (C-4), 20.7 (C(O)*C*H_3), 19.0 (*C*H_2CH_3), 13.5 (CH_2*C*H_3); ν_{max} (CH_2Cl_2/cm^{-1}) 1753, 1731, 1699, 1685; LRMS m/z (ESI$^+$) 321.1 (M+Na$^+$, 100%), 316.2 (M+NH_4^+, 77%), 619.2 (2M+Na$^+$, 70%), 299.1 (M+H$^+$, 64%); HRMS m/z (ESI$^+$) found [M+Na]$^+$ 321.1309; $C_{15}H_{22}NaO_6$ requires 321.1309.

Allylic acetate **61**; R_f=0.13 (petroleum ether/ethyl acetate, 5:1); δ_H (500 MHz, $CDCl_3$) 6.17 (1H, t, J=3.9, H-3), 5.41 (1H, dd, J=8.1, 5.3, C*H*OC(O)CH_3), 3.75 (3H, s, OMe), 3.70 (3H, s, OMe), 2.29 (1H, ddd, J=13.1, 7.8, 3.1, H-6), 2.21–2.15 (3H, m, H-4, H-4′, H-6′), 2.02 (3H, s, C(O)CH_3), 1.82–1.64 (3H, m, C$H_2$$CH_3$, H-5), 1.53 (1H, dddd, J=13.9, 13.5, 6.9, 3.1, H-5′), 0.89 (3H, t, J=7.4, CH_2*C*H_3); δ_C (125 MHz, $CDCl_3$) 171.6, 171.4, 170.2, 133.2 (C-2), 131.4 (C-3), 75.0 (*C*HOC(O)CH_3), 58.0 (C-1), 52.7 (OMe), 52.5 (OMe), 31.4 (C-6), 28.1 (*C*H_2CH_3), 24.9 (C-4), 21.3 (C(O)*C*H_3), 18.6 (C-5), 10.4 (CH_2*C*H_3); ν_{max} (CH_2Cl_2/cm^{-1}) 1732, 1659; LRMS m/z (ESI$^+$) 619.2 (2M+Na$^+$, 100%), 614.3 (2M+NH_4, 86%), 316.2 (M+NH_4^+, 86%), 321.1 (M+Na$^+$, 66%); HRMS m/z (ESI$^+$) found [M+Na]$^+$ 321.1305; $C_{15}H_{22}NaO_6$ requires 321.1309.

*4.1.15. Dimethyl 2-(hepta-5,6-dienyl)malonate **29**.* Synthesised from known hepta-5,6-dienyl methanesulfonate[29,30,32] (1.40 g, 7.35 mmol) using the general procedure. Purification by flash column chromatography (gradient petroleum ether/ethyl acetate, 40:1→30:1) gave the allene **29** as a colourless oil (1.26 g, 5.04 mmol, 76%); R_f=0.30 (petroleum ether/ethyl acetate, 9:1); δ_H (500 MHz, $CDCl_3$) 5.07 (1H, tt, J=6.7, 6.7, H-5′), 4.65 (2H, dt, J=6.7, 3.2, 2×H-7′), 3.74 (6H, s, 2×OMe), 3.36 (1H, t, J=7.5, H-1), 2.00 (2H, dtt, J=7.2, 6.7, 3.3, 2×H-4′), 1.93–1.89 (2H, m, 2×H-1′), 1.48–1.41 (2H, m, H-3′), 1.38–1.32 (2H, m, 2×H-2′); δ_C (125 MHz, $CDCl_3$) 208.5 (C-6′), 169.8 (CO), 89.6 (C-5′), 74.8 (C-7′), 52.4 (OMe), 51.6 (C-1), 28.6 (CH_2), 28.5 (CH_2), 27.8 (C-4′), 26.7 (C-2′); ν_{max} (film)/cm^{-1} 2953, 1956, 1753, 1737; LRMS m/z (ESI$^+$) 475.2 (2M+Na$^+$, 100%), 249.1 (M+Na$^+$, 59%); HRMS m/z (ESI$^+$) found [M+Na]$^+$ 249.1091; $C_{12}H_{18}NaO_4$ requires 249.1097.

*4.1.16. Dimethyl 2-vinylcyclohexane-1,1-dicarboxylate **63**.* Synthesised from allene **29** (0.114 g, 0.5 mmol) using Conditions **A** with 3 equiv of manganese(III) acetate for 45 h. Purification by flash chromatography (gradient elution petroleum ether/ethyl acetate, 40:1→20:1) gave the known olefin **63**[23] as a colourless oil (0.074 g, 65%); R_f=0.37 (petroleum ether/ethyl acetate, 9:1); δ_H (500 MHz, $CDCl_3$) 6.09 (1H, ddd, J=17.5, 10.1, 9.3, CH=C), 5.00 (1H, ddd, J=17.5, 2.0, 0.9, =C*H*H), 4.98 (1H, ddd, J=10.1, 2.0, 0.6, =CH*H*), 3.70 (3H, s, OMe), 3.69 (3H, s, OMe), 2.76 (1H, td, J=8.4, 4.1, H-2), 2.16 (1H, ddd, J=13.7, 7.9, 3.3, H-6), 1.99 (1H, ddd, J=13.7, 8.0, 4.0, H-6′), 1.82 (1H, ddt, J=16.2, 8.0, 4.0, H-3), 1.69–1.56 (2H, m, H-3′, H-4), 1.47–1.37 (3H, m, H-4′, H-5, H-5′); δ_C (125 MHz, $CDCl_3$) 172.0, 171.0, 138.7 (*C*H=C), 115.8 (=*C*H_2), 59.2 (C-1), 52.2 (OMe), 52.0 (OMe), 45.9 (C-2), 30.2 (C-6), 28.4 (C-3), 22.9 (C-4), 22.4 (C-5); ν_{max} (film/cm^{-1}) 2952, 1750, 1732; LRMS m/z (ESI$^+$) 475.2 (2M+Na$^+$, 100%), 249.1 (M+Na$^+$, 52%); HRMS m/z (ESI$^+$) found [M+Na]$^+$ 249.1093; $C_{12}H_{18}NaO_4$ requires 249.1097. Data in accord with the literature.[23]

*4.1.17. Dimethyl 2-(1-acetoxyvinyl)cyclohexane-1,1-dicarboxylate **64**.* Synthesised from allene **29** (0.114 g, 0.5 mmol) using Conditions **B** with copper(II) triflate. Purification by flash chromatography (gradient elution petroleum ether/ethyl acetate, 40:1→0:1) gave starting material **29** (13 mg, 0.057 mmol, 11%). Further elution of the column gave the enol acetate **64** as a colourless oil (0.049 g, 35%); R_f=0.42 (petroleum ether/ethyl acetate, 3:1); δ_H (500 MHz, $CDCl_3$) 4.96 (1H, dd, J=2.0, 1.0, C=C*H*H), 4.89 (1H, d, J=2.0, C=CH*H*), 3.75 (3H, s, OMe), 3.72 (3H, s, OMe), 2.92 (1H, dd, J=9.1, 3.9, H-2), 2.29 (1H, ddd, J=13.0, 5.4, 2.6, H-6), 2.11 (3H, s, OAc) 1.98–1.94 (1H, m, H-3), 1.93–1.87 (1H, m, H-6′), 1.74–1.67 (2H, m), 1.52–1.41 (3H, m); δ_C (125 MHz, $CDCl_3$) 172.2, 170.5, 169.0, 156.0 (*C*=CH_2), 104.0 (C=*C*H_2), 57.9 (C-1), 52.6 (OMe), 52.0 (OMe), 44.7 (C-2), 32.2, 26.2, 23.9, 22.3, 21.2; ν_{max} (film/cm^{-1}) 2949, 1733; LRMS m/z (ESI$^+$) 307.1 (M+Na$^+$, 98%), 591.2 (2M+Na$^+$, 100%); HRMS m/z (ESI$^+$) found [M+Na]$^+$ 307.1153; $C_{14}H_{20}NaO_6$ requires 307.1152.

4.1.18. Nona-5,6-dienyl methanesulfonate. The known alcohol nona-5,6-dien-1-ol[33] (1.34 g, 9.97 mmol) in DCM (30 mL) was added triethylamine (1.95 mL, 14.0 mmol) and the mixture was cooled to 0 °C. Methanesulfonyl chloride (0.93 mL, 12.0 mmol) was added and the reaction allowed to warm to room temperature and was stirred for 1.5 h. The reaction was quenched with 1.0 M aqueous HCl (60 mL) and extracted with DCM (3×50 mL). The organic layers were combined and dried ($MgSO_4$) and the solvent removed in vacuo to give crude hepta-3,4-dienyl methanesulfonate (2.08 g, 9.56 mmol, 96%) as an orange oil, which was used in the next reaction without further purification; δ_H (500 MHz, $CDCl_3$) 5.19–5.14 (1H, m, H-3 or H-5), 5.12–5.07 (1H, m, H-3 or H-5), 4.24 (2H, t, J=6.5, H-1, H-1′), 3.00 (3H, s, CH_3SO_2), 2.06–1.96 (4H, m, H-4, H-4′, H-8, H-8′), 1.84–1.78 (2H, m, H-2, H-2′), 1.53 (2H, qn, J=7.6, H-3, H-3′), 1.00 (3H, t, J=7.6, CH_2*C*H_3); δ_C (125 MHz, $CDCl_3$) 203.6 (C-6), 93.4, 90.6, 69.8 (C-1), 37.4 (CH_3SO_2), 28.5 (C-3), 28.2, 24.8 (C-3), 21.9, 13.4 (C-9); ν_{max} (film)/cm^{-1} 2965, 2937, 1961; HRMS m/z (EI) found M$^+$ 218.0973; $C_{10}H_{18}O_3S$ requires 218.0977.

*4.1.19. Dimethyl 2-(nona-5,6-dienyl)malonate **30**.* Synthesised from nona-5,6-dienyl methanesulfonate (2.09 g, 9.26 mmol) according to the general procedure. Purification by flash column chromatography (gradient elution petroleum ether/ethyl acetate, 40:1→30:1) gave the malonate **30** as a colourless oil (1.41 g, 5.54 mmol, 59%); R_f=0.3 (petroleum ether/ethyl acetate, 9:1); δ_H (500 MHz, $CDCl_3$) 5.13 (1H, tdt, J=6.1, 6.1, 3.0, H-5′), 5.08 (1H, tdt, J=6.4, 6.4, 3.3, H-7′), 3.74 (6H, s, 2×OMe), 3.36 (1H, t, J=7.5, H-1), 2.01–1.94 (4H, m, 2×H-4′ 2×H-8′), 1.93–1.88 (2H, m, 2×H-1′), 1.46–1.39 (2H, m, 2×H-3′), 1.38–1.31 (2H, m, 2×H-2′), 0.99 (3H, t, J=7.4, CH_2*C*H_3); δ_C (125 MHz, $CDCl_3$) 203.4 (C-6′), 169.9 (CO), 92.8 (C-5′), 91.1 (C-7′), 52.4 (OMe), 51.6 (C-1), 30.9 (CH_2), 28.7 (CH_2), 28.6 (CH_2), 28.5 (CH_2), 26.7 (C-2′), 22.0, 13.4 (C-9′); ν_{max} (film)/cm^{-1} 2950, 1735; LRMS m/z (ESI$^+$) 531.2 (2M+Na$^+$, 100%), 277.1 (M+Na$^+$, 87%); HRMS m/z (ESI$^+$) found [M+Na]$^+$ 277.1413; $C_{14}H_{22}NaO_4$ requires 277.1410.

*4.1.20. Dimethyl 2-(but-1-enyl)cyclohexane-1,1-dicarboxylate **65**.* Syncthesised from allene **30** (0.128 g, 0.5 mmol) using Conditions **A** with 3 equiv of manganese(III) acetate for 45 h. Purification by flash chromatography (gradient elution petroleum ether/ethyl acetate, 40:1→20:1) gave the olefins **65** as an inseparable 1.4:1 mixture of (*E*):(*Z*) geometric isomers a colourless oil (0.077 g, 0.03 mmol, 61%); characterisation is on the mixture; R_f=0.42 (petroleum ether/ethyl acetate, 9:1); δ_H (500 MHz, $CDCl_3$) 5.68 (1H, ddt, J=15.2, 9.4, 1.5, *C*H=CHCH$_{2}$**65*E***), 5.68 (1H, ddt, J=12.5, 10.8, 1.6, *C*H=CHCH$_{2}$**65*Z***), 5.45 (1H, dt, J=15.2, 6.4, CH=C*H*CH$_{2}$**65*E***), 5.40 (1H, dt, J=10.8, 7.3, CH=C*H*CH$_{2}$**65*Z***), 3.70 (3H, s, OMe$_{Z}$), 3.69 (3H, s, OMe$_{E}$), 3.67 (3H, s, OMe$_{E}$), 3.66 (3H, s, OMe$_{Z}$), 3.21–3.17 (1H, m, H-2$_{Z}$), 2.75–2.71 (1H, m, H-2$_{E}$), 2.17–1.94 (8H, m), 1.84–1.77 (2H, m, H-3$_{Z}$, H-3$_{E}$), 1.66–1.30 (10H, m), 0.94 (2H, t, J=7.5, CH_2*C*H$_{3Z}$), 0.93 (2H, t, J=7.2, CH_2*C*H$_{3E}$); δ_C (125 MHz, $CDCl_3$) 172.1, 172.1, 171.3, 171.1, 134.0, 133.1, 128.8, 128.0, 59.4 and 58.3 (C-1$_{E}$ and C-1$_{Z}$), 52.3, 52.1, 52.1, 51.9, 44.7 (C-2$_{E}$), 38.0 (C-2$_{Z}$), 29.9, 29.3, 29.2, 25.6, 22.8, 22.5, 22.4, 20.4, 14.3, 14.0; ν_{max} (CH_2Cl_2)/cm^{-1} 1735; LRMS m/z (ESI$^+$) 531.2 (2M+Na$^+$, 100%), 277.1 (M+Na$^+$, 40%); HRMS m/z (ESI$^+$) found [M+Na]$^+$ 277.4106; $C_{14}H_{22}NaO_4$ requires 277.1410.

4.1.21. (1S,3aR*,6aS*)-Methyl 1-(iodomethyl)-3-oxohexahydro-1H-cyclopenta[c]furan-3a-carboxylate **67a** and (1R*,3aR*,6aS*)-methyl*

1-(iodomethyl)-3-oxohexahydro-1H-cyclopenta[c]furan-3a-carboxylate ***67b***. According to the procedure of Bian[5]: iodine (0.144 g, 0.565 mmol) was added to a solution of alkene **24** (0.040 g, 0.189 mmol) in CH_2Cl_2 (2 mL) at 0 °C, and stirring was continued until the iodine had completely dissolved. The reaction was incubated at 4 °C for 15 h and was then quenched with saturated aqueous sodium thiosulfate solution (15 mL), and further diluted with water (50 mL). The aqueous layer was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were washed with brine (60 mL), dried ($MgSO_4$), filtered and the solvent removed in vacuo. The resulting crude compound was then absorbed onto silica and purified by flash column chromatography (petroleum ether/diethyl ether, 3:1) to give an inseparable 7:1 mixture of lactones **67a**:**67b** mixture of (47.9 mg, 0.148 mmol, 83%); characterisation is on the mixture.

Lactone **67a**; R_f=0.14 (petroleum ether/diethyl ether, 3:1); δ_H (500 MHz, $CDCl_3$) 4.31 (1H, ddd, *J*=9.1, 4.9, 3.2, H-1), 3.80 (3H, s, OMe), 3.45 (1H, dd, *J*=10.0, 4.9, C*H*HI), 3.30 (1H, dd, *J*=10.0, 9.1, CH*H*I), 3.01 (1H, ddd, *J*=8.4, 3.2, 3.0, H-6a), 2.37 (1H, ddd, *J*=13.5, 10.9, 6.5, H-4), 2.30 (1H, ddd, *J*=13.5, 6.6, 3.6, H-4′), 2.08 (1H, dddd, *J*=13.2, 10.5, 8.4, 6.3, H-6), 1.88 (1H, dddd, *J*=12.9, 10.5, 6.5, 3.6, H-5), 1.84–1.77 (1H, m, H-6′), 1.63–1.53 (1H, m, H-5′); δ_C (125 MHz, $CDCl_3$) 175.1, 170.4, 84.7 (C-1), 62.6 (C-3a), 53.4 (OMe), 50.7 (C-6a), 35.6 (C-4), 34.8 (C-6), 25.7 (C-5), 6.2 (CH_2I); ν_{max} (CH_2Cl_2/cm^{-1}) 1778, 1742; LRMS *m*/*z* (ESI^+) 342.0 ($M+NH_4^+$, 84%), 357.0 ($M+H+MeOH^+$, 79%), 325.0 ($M+H^+$, 73%), 379.0 ($M+Na+MeOH^+$, 67%); HRMS *m*/*z* (ESI^+) found $[M+Na]^+$ 346.9747; $C_{10}H_{13}INaO_4$ requires 346.9751. Found C, 37.13; H, 3.98%; $C_{10}H_{13}IO_4$ requires: C, 37.06; H, 4.04%.

Lactone **67b**; R_f=0.14 (petroleum ether/diethyl ether, 3:1); δ_H (500 MHz, $CDCl_3$) 4.93 (1H, ddd, *J*=9.9, 5.8, 5.8, H-1), 3.80 (3H, s, OMe), 3.48 (1H, dd, *J*=10.0, 5.8, C*H*HI), 3.16 (1H, ddd, *J*=8.2, 8.2, 5.8, H-6a), 3.13 (1H, dd, *J*=10.0, 9.9, CH*H*I), 2.46 (1H, dddd, *J*=14.0, 7.9, 6.1, H-4), 2.32–2.23 (1H, m, H-4′), 2.00 (1H, ddt, *J*=12.3, 8.2, 5.8,, H-6), 1.92–1.84 (1H, m, H-5), 1.79–1.69 (1H, m, H-6′), 1.67–1.60 (1H, m, H-5′); δ_C (125 MHz, $CDCl_3$) 175.2, 170.0, 79.8 (C-1), 64.0 (C-3a), 53.3 (OMe), 49.8 (C-6a), 34.2 (C-4), 26.24 (C-6), 26.17 (C-5), 0.2 (CH_2I).

4.1.22. (1S,3aS*,6aR*)-Methyl 1-(1-iodopropyl-3-oxohexahydro)-1H-cyclopenta[c]furan-3a-carboxylate* ***68a****, (1R*,3aS*,6aR*)-methyl 1-((S*)-1-iodopropyl)-3-oxohexahydro-1H-cyclopenta[c]furan-3a-carboxylate* ***68b*** *and (1R*,3aS*,6aR*)-methyl 1-((R*)-1-iodopropyl)-3-oxohexahydro-1H-cyclopenta[c]furan-3a-carboxylate* ***68c***. According to the procedure of Bian[5]: iodine (0.29 g, 1.14 mmol) was added to a solution dimethyl 2-(but-1-enyl)cyclopentane-1,1-dicarboxylate (91.5 mg, 0.381 mmol, approximate ratio *E*:*Z*, 1.6:1) in CH_2Cl_2 (4.6 mL) at 0 °C. The resulting mixture was stirred at 0 °C until the iodine had completely dissolved. The reaction was incubated at 4 °C for 15 h was then quenched with saturated aqueous sodium thiosulfate solution (15 mL), and diluted with water (30 mL). The aqueous layer was extracted with CH_2Cl_2 (3×30 mL), the combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), filtered and the solvent removed in vacuo. The resulting crude compound was purified by flash column chromatography to give lactone **68a** as a colourless oil (9.5 mg, 27.0 μmol, 7%), lactone **68b** as a colourless oil (72.4 mg, 0.206 mol, 54%) and lactone **68c** as a white crystalline solid (51.3 mg, 0.146 mmol, 38%), which was recrystallised using diethyl ether.

Lactone **68a**; R_f=0.24 (petroleum ether/ethyl acetate, 3:1); δ_H (500 MHz, $CDCl_3$) 4.84 (1H, dd, *J*=11.6, 5.4, H-1), 3.92 (1H, ddd, *J*=11.6, 9.1, 2.9, C*H*I), 3.82 (3H, s, OMe), 3.22 (1H, ddd, *J*=8.6, 8.4, 5.4, H-6a), 2.48 (1H, dddd, *J*=13.7, 7.8, 5.9, 0.8, H-4), 2.28 (1H, ddd, *J*=13.7, 7.5, 7.4, H-4′), 2.18–2.08 (2H, m, H-6, CH*H*CH_3), 1.85 (1H, ddq, *J*=14.4, 9.1, 7.2, C*H*HCH_3), 1.81–1.69 (2H, m, H-5, H-5′), 1.60 (1H, dddd, *J*=12.9, 8.9, 8.6, 7.1, H-6), 1.10 (3H, t, *J*=7.2, CH_2CH_3); δ_C (125 MHz, $CDCl_3$) 175.6, 170.1, 82.5 (C-1), 63.8 (C-3a), 53.3 (OMe), 51.6 (C-6a), 34.8 (CHI), 34.1 (C-4), 30.1 (CH_2CH_3), 26.6 (C-6), 25.9 (C-5), 13.4 (CH_2CH_3); ν_{max} (CH_2Cl_2/cm^{-1}) 1783, 1743; LRMS *m*/*z* (ESI^+) 370.0 ($M+NH_4^+$, 100%), 727.0 ($2M+Na^+$, 84%), 375.0 ($M+Na^+$, 76%), 353.0 ($M+H^+$, 66%); HRMS *m*/*z* (ESI^+) found $[M+Na]^+$ 375.0056; $C_{12}H_{17}NaIO_4$ requires 375.0064; Found C, 40.93; H, 4.91%; $C_{12}H_{17}IO_4$ requires: C, 40.93; H, 4.87%.

Lactone **68b**; R_f=0.19 (petroleum ether/ethyl acetate, 3:1); δ_H (500 MHz, $CDCl_3$) 4.22 (1H, dd, *J*=10.0, 3.4, H-1), 4.11 (1H, ddd, *J*=10.0, 9.0, 3.1, C*H*I), 3.79 (3H, s, OMe), 3.12 (1H, ddd, *J*=8.2, 3.4, 3.1, H-6a), 2.37 (1H, ddd, *J*=13.4, 10.9, 6.4, H-4), 2.29 (1H, dddd, *J*=13.4, 6.5, 3.4, 0.9, H-4′), 2.13–2.00 (2H, m, H-6, C*H*HCH$_3$), 1.90–1.76 (3H, m, H-5, H-6′, C*H*HCH$_3$), 1.62–1.52 (1H, m, H-5′), 1.08 (3H, t, *J*=7.2, CH_2CH_3); δ_C (125 MHz, $CDCl_3$) 175.3, 170.5, 87.4 (C-1), 62.2 (C-3a), 53.3 (OMe), 51.9 (C-6a), 41.4 (CHI), 35.8 (C-4), 35.1 (C-6), 28.9 (CH_2CH_3), 25.7 (C-5), 13.4 (CH_2CH_3); ν_{max} (CH_2Cl_2/cm^{-1}) 1779, 1743; LRMS *m*/*z* (ESI^+) 726.9 ($2M+Na^+$, 100%), 370.0 ($M+NH_4^+$, 96%), 353.0 ($M+H^+$, 79%), 385.0 ($M+H+MeOH^+$, 71%); HRMS *m*/*z* (ESI^+) found $[M+Na]^+$ 375.0063; $C_{12}H_{17}NaIO_4$ requires 375.0064; Found C, 41.06; H, 4.83%; $C_{12}H_{17}IO_4$ requires: C, 40.93; H, 4.87%.

Lactone **68c**; R_f=0.09 (petroleum ether/ethyl acetate, 3:1); mp 80.0–82.6 °C; δ_H (500 MHz, $CDCl_3$) 4.15–4.09 (2H, m, CHI, H-1), 3.79 (3H, s, OMe), 3.15 (1H, ddd, *J*=6.8, 4.5, 1.6, H-6a), 2.40–2.31 (2H, m, H-4, H-4′), 2.04 (1H, dddd, *J*=13.1, 11.8, 7.8, 6.8, H-6), 1.97–1.90 (1H, m, H-5), 1.89–1.74 (3H, m, H-6′, CH_2CH_3), 1.65–1.54 (1H, m, H-5′), 1.09 (3H, t, *J*=7.2, CH_2CH_3); δ_C (125 MHz, $CDCl_3$) 174.9, 170.6, 87.2 (C-1), 62.4 (C-3a), 53.1 (M), 49.1 (C-6a), 38.9 (CHI), 36.8 (C-4), 35.0 (C-6), 27.4 (CH_2CH_3), 25.8 (C-5), 14.4 (CH_2CH_3); ν_{max} (CH_2Cl_2/cm^{-1}) 1774, 1737; LRMS *m*/*z* (ESI^+) 726.9 ($2M+Na^+$, 100%), 370.0 ($M+NH_4^+$, 94%), 722.0 ($2M+NH_4$, 78%), 353.0 ($M+H^+$, 76%), 385.0 ($M+H+MeOH^+$, 53%); HRMS *m*/*z* (ESI^+) found $[M+Na]^+$ 375.0061; $C_{12}H_{17}NaIO_4$ requires 375.0064; Found C, 40.95; H, 4.85%; $C_{12}H_{17}IO_4$ requires: C, 40.93; H, 4.87%.

4.1.23. (1S,3aS*,6aR*)-Methyl 3-oxo-1-propylhexahydro-1H-cyclopenta[c]furan-3a-carboxylate* ***69***. To a stirring solution of lactone **68b** (32 mg, 91.7 μmol) and AIBN (0.2 mg, 1.38 μmol) was added tributyltin hydride (34 μL, 128 μmol) followed quickly by degassed acetonitrile (1.5 mL). The reaction mixture was heated under reflux for 1 h, then allowed to cool. The resulting solution was diluted with water (30 mL) and extracted with ethyl acetate (3×30 mL). The combined organic layers were washed with brine (3×30 mL), dried ($MgSO_4$), filtered and the solvent removed in vacuo. The resulting crude compound was purified by flash column chromatography with KF silica[34] (petroleum ether/ethyl acetate, 5:1) to give lactone **69** as a colourless oil (20.1 mg, 88.8 μmol, 97%); To a stirring solution of lactone **68c** (30 mg, 85.2 μmol) and AIBN (0.2 mg, 1.38 μmol) was added tributyltin hydride (34 μL, 128 μmol) followed quickly by degassed acetonitrile (1.5 mL). The reaction mixture was heated under reflux for 2 h, then allowed to cool. The resulting solution was diluted with water (30 mL) and extracted with ethyl acetate (3×30 mL). The combined organic layers were washed with brine (3×30 mL), dried ($MgSO_4$), filtered and the solvent removed in vacuo. The resulting crude compound was purified by flash column chromatography with KF silica[34] (petroleum ether/ethyl acetate, 5:1) to give lactone **60** as a colourless oil (12.2 mg, 53.9 μmol, 63%); R_f=0.14 (petroleum ether/ethyl acetate, 5:1); δ_H (500 MHz, $CDCl_3$) 4.07 (1H, ddd, *J*=8.1, 5.4, 3.8, H-1), 3.78 (3H, s, OMe), 2.81 (1H, ddd, *J*=7.9, 3.8, 2.8, H-6a), 2.34 (1H, ddd, *J*=13.4, 11.0, 6.4, H-4), 2.26 (1H, ddd, *J*=13.4, 6.8, 3.1, *H*-4′), 1.95 (1H, dddd, *J*=12.9, 11.0, 7.9, 6.6, H-6), 1.85 (1H, ddddd, *J*=12.6, 6.6, 6.4, 3.2, 3.1, H-5), 1.78 (1H, dddd, *J*=13.7, 10.0, 8.1, 5.1, CH*H*CH_2CH_3), 1.72–1.66 (1H, m, H-6′), 1.65–1.53 (2H, m, H-5′, C*HH*CH_2CH_3), 1.53–1.36 (2H, m, CH_2CH_3), 1.25 (3H, t, *J*=7.2, CH_2CH_3); δ_C (125 MHz, $CDCl_3$) 175.9, 171.1, 85.9 (C-1), 62.3 (C-3a), 53.1 (OMe), 50.8 (C-6a), 38.3 ($CH_2CH_2CH_3$), 35.5 (C-4), 34.0 (C-6), 25.7 (C-5), 18.6 (CH_2CH_3), 13.7 (CH_2CH_3); ν_{max} (CH_2Cl_2/cm^{-1}) 1772, 1742; LRMS *m*/*z* (ESI^+) 475.2 ($2M+Na^+$, 100%), 227.1 ($M+H^+$, 67%), 244.1 ($M+NH_4^+$, 63%),

470.3 ($2M+NH_4^+$, 48%); HRMS m/z (ESI^+) found $[M+Na]^+$ 249.1098; $C_{12}H_{18}NaO_4$ requires 249.1097; Found C, 63.60; H, 7.97%; $C_{12}H_{18}O_4$ requires: C, 63.70; H, 8.02%.

Acknowledgements

We thank the EPSRC for funding part of this work and the Oxford Chemical Crystallography Service for the use of the instruments.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.09.112.

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