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The direct preparation of functionalised cyclopropanes from allylic alcohols or α-hydroxyketones using tandem oxidation processes

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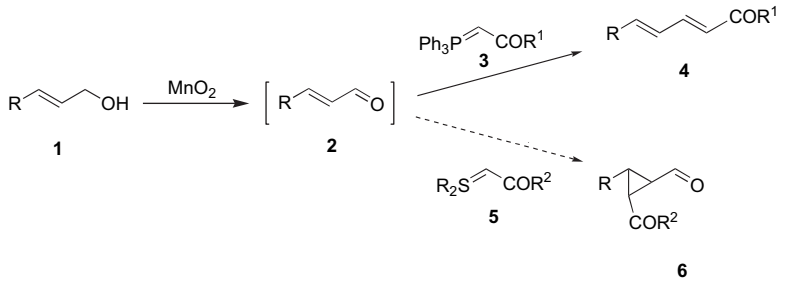
Abstract—New manganese dioxide-mediated tandem oxidation processes (TOPs) have been developed, which facilitate the direct conversion of allylic alcohols and α-hydroxyketones into polysubstituted functionalised cyclopropanes. In the simplest version, the oxidation of an allylic alcohol is carried out in the presence of a stabilised sulfurane, and the intermediate α,β-unsaturated carbonyl compound undergoes in situ cyclopropanation. By using a combination of stabilised phosphorane and sulfurane, the direct conversion of allylic alcohols or α-hydroxyketones into functionalised cyclopropanes is achieved, with in situ cyclopropanation being followed by Wittig olefination, or vice versa. The application of these methods to a formal synthesis of the lignan (±)-picropodophyllone, and to novel analogues of the insecticide allethrin II, is described.

1. Introduction

We have recently developed a range of manganese dioxide-mediated tandem oxidation processes (TOPs) in which primary alcohols are oxidised and the intermediate aldehydes are trapped in situ to give alkenes, imines, oximes, amines, nitriles, esters, amides and heterocyclic systems via one-pot procedures.[1] These TOP sequences offer a number of advantages to the organic chemist: they are operationally straightforward, the MnO_2 and its by-products being removed by a simple filtration; they result in a reduced number of operations, giving significant time–cost benefits; and they allow the use of 'difficult' carbonyl intermediates (i.e., those that are volatile, toxic or noxious) as they are prepared and elaborated in situ. The initial studies referred to above concentrated on 1,2-additions to the intermediate carbonyl compounds, as illustrated in Scheme 1 for the oxidation–Wittig reaction of allylic alcohols **1** in which the intermediate conjugated aldehydes **2** are trapped by a stabilised phosphorane **3** giving the product dienes **4**. However, since the seminal research of Corey and Chaykovsky and others,[2] it is well known that sulfuranes undergo 1,4-addition to α,β-unsaturated carbonyl compounds to produce the corresponding cyclopropanes. Cyclopropanes are widespread in natural products



Scheme 1.

Keywords: Oxidation; One-pot transformations; Tandem reactions; TOPs; Cyclopropanes; Picropodophyllone; Allethrin analogues.
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and biologically active analogues, and are valuable synthetic intermediates.[3] We therefore decided to investigate whether a manganese dioxide-mediated TOP sequence could be carried out using stabilised sulfuranes **5** to produce a one-pot procedure for converting allylic alcohols into polysubstituted cyclopropanes **6** (Scheme 1). Herein, we describe detailed results concerning TOP sequences involving oxidation–cyclopropanation and their applications in target molecule synthesis.[4]

2. Tandem oxidation–cyclopropanation reactions

In order to determine the viability of an oxidation–cyclopropanation sequence, we first examined the reaction of 2-methyl-2-propen-1-ol **1a** with activated MnO_2 in the presence of (carbethoxymethylene)dimethylsulfurane **5a**, prepared from the commercially available sulfonium salt,[2d] and powdered 4 Å molecular sieves in benzene at reflux (Scheme 2). We were delighted to observe the formation of the desired cyclopropanecarboxaldehyde **6a** in 37% yield, indicating that sulfurane **5a** is compatible with manganese dioxide. We quickly established that the use of dichloromethane as solvent gave the optimum yield of **6a**, 78% as a mixture of trans/cis-isomers (~2:1).

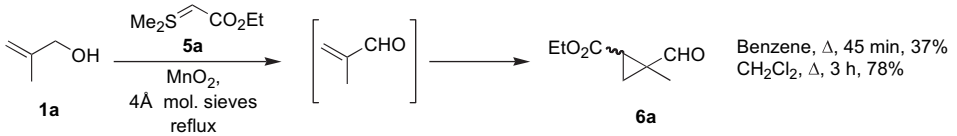
With this result in hand, we then moved on to establish the scope of the TOP–cyclopropanation methodology, with respect to the alcohol and sulfurane; the results are shown in Table 1. With 2-methyl-2-propen-1-ol **1a**, we first established that (benzoylmethylene)dimethylsulfurane **5b**, again prepared from the commercially available sulfonium salt,[2e] was also successful, producing cyclopropane **6b** in 53% yield (entry ii). Allyl alcohol **1b** also gave the desired cyclopropane **6c** on treatment with MnO_2 and sulfurane **5a** (entry iii), although the yield was low (36%), presumably due to the volatility of the product (bp 97 °C).[3q] By changing to sulfurane **5b**, however, adduct **6d** was obtained in an improved yield of 77% (entry iv).

Next we explored the use of the functionalised allylic alcohol **1c** (entries v and vi). This proved to be a viable substrate with both sulfuranes **5a** and **5b**, giving the expected cyclopropanes **6e** and **6f**, respectively. Cyclopropane **6e** (entry v) is a particularly interesting example as it is trisubstituted, with each substituent being in a different oxidation state (i.e., alkoxy, aldehyde and carboxylate), offering the possibility of further functionalisation in a selective manner. Cyclopropane **6f** (entry iv) has similar potential (i.e., alkoxy, aldehyde and ketone substituents).

We then proceeded to investigate the use of secondary alcohols with a range of 1-substituted propen-1-ols (entries vii–xi); these also gave good yields and complete trans-selectivity about the cyclopropane.

Divinylmethanol **1f** was studied next and, with both sulfuranes **5a** and **5b**, oxidation and double-cyclopropanation occurred, giving **6j** and **6k** in 60% and 69% yield, respectively; each product was obtained as a mixture of isomers (~1:1 as determined by ^{1}H NMR spectroscopy), but again with trans-orientation about the cyclopropanes (entries x and xi).

The trends in stereochemistry seen with 1- and 2-substituted propen-1-ols are consistent with the reaction mechanism proposed by Curley and DeLuca involving equilibration of initial adducts.[5] With 1-substituted propen-1-ols (entries vii–xi), the increased size of the substituent in the intermediate (ketone vs aldehyde) results in an equilibrium giving solely the trans-cyclopropane products. Thus (Fig. 1), the



Scheme 2.

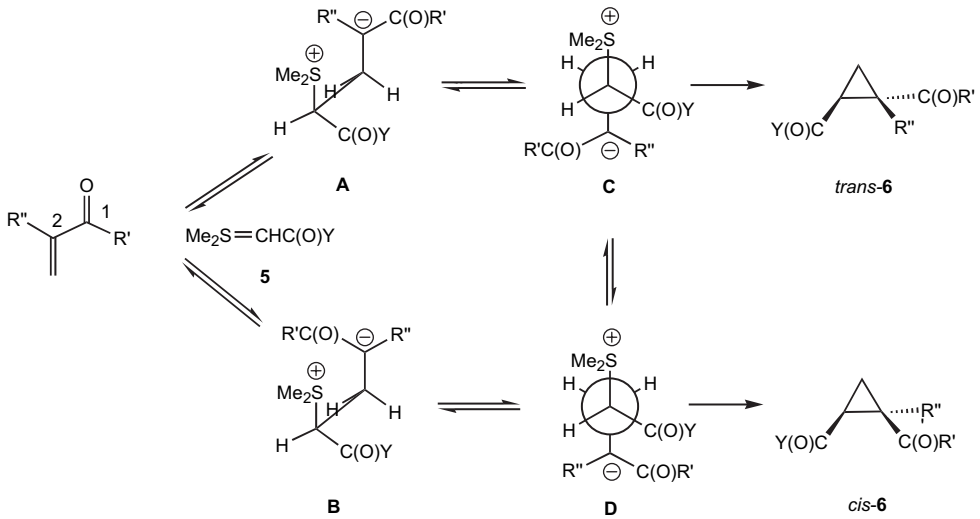
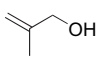
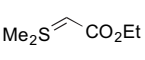
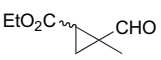
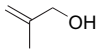
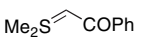
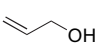
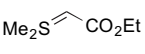
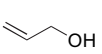
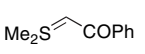
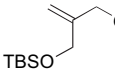
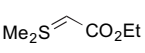
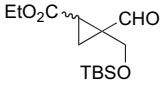
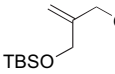
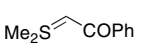
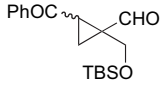
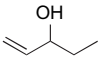
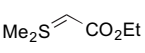
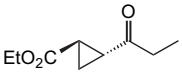
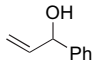
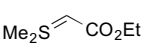
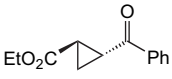
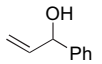
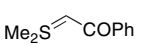
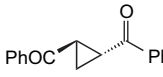
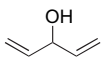
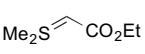
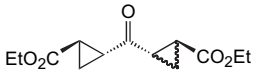
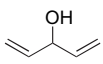
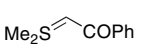
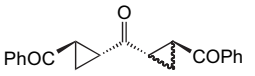
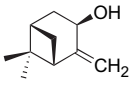
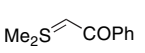
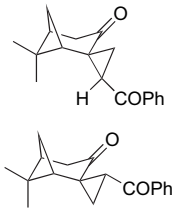
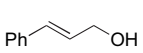
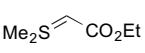
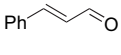
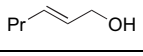


Figure 1.

Table 1. MnO_2-mediated TOP methodology for the preparation of cyclopropanes

Entry	Alcohol	Sulfurane	Product	Ratio (trans/cis)	Isolated yield (reaction time)
i	 **1a**	 **5a**	 **6a**	~2:1	78% (3 h)
ii	 **1a**	 **5b**	 **6b**	~4.2:1	53% (2 h)
iii	 **1b**	 **5a**	 **6c**	~3:1	36%[a] (6 h)
iv	 **1b**	 **5b**	 **6d**	~3:1	77% (3 h)
v	 **1c**	 **5a**	 **6e**	~3.6:1	74% (14 h)
vi	 **1c**	 **5b**	 **6f**	~2:1	73% (4.5 h)
vii	 **1d**	 **5a**	 **6g**	All trans	67% (18 h)
viii	 **1e**	 **5a**	 **6h**	All trans	100% (17 h)
ix	 **1e**	 **5b**	 **6i**	All trans	78% (2 h)
x	 **1f**	 **5a**	 **6j**	All trans	60% (4 h)
xi	 **1f**	 **5b**	 **6k**	All trans	69% (2 h)
xii	 **1g**	 **5b**	 **6l**	5:1[b]	76% (16 h)
xiii	 **1h**	 **5a**		—	(quant.)[c]
xiv	 **1i**	**5a**		—	(quant.)[c]

[a] It is probable that the low yield for this example is due in part to the volatility of **6c** (bp 97 °C).[3q]
[b] Of a possible four isomers, a mixture of just two (ca. 5:1) was isolated: the stereochemistry of these diastereoisomers has not been allocated with certainty.
[c] Based on ^{1}H NMR analysis of the unpurified reaction mixture, which showed only the aldehyde and sulfurane **5a**.

first 'kinetic' intermediates **A/B** (stabilised by electrostatic interactions) collapse to the cyclopropanes via the anti-conformers **C/D**. A solvent of low dielectric constant, such as CH_2Cl_2, retards this rotation and collapse due to the higher energy of the charge-separated intermediates. This allows greater equilibration of **A** and **B** and, hence, **C** and **D**, presumably driven by steric demands in the intermediates. In 2-substituted propen-1-ols, there is a balance between the aldehyde (R′=H) and R″ interacting with COY, resulting in isomeric mixtures. In 1-substituted propen-1-ols (R″=H), this is now a balance between a proton and a ketone (R′=alkyl, etc.) interacting with COY, making **A** and **C** highly favoured and resulting solely in trans-cyclopropane.

The more complex (−)-trans-pinocarveol **1g** also worked well in this methodology, giving the spirocyclopropane **6l** in 76% yield (entry xii). This product was isolated as a mixture of just two of the four possible isomers (~5:1). We also

investigated the use of 3-substituted 2-propen-1-ols (entries xiii–xiv) but unfortunately no cyclopropanation was observed with **1h** and **1i**, despite complete oxidation occurring. The low reactivity of terminally substituted conjugated carbonyl compounds to stabilised sulfuranes has been well documented.[2]

Next, we went on to explore the use of disubstituted 2-propen-1-ols **1j–m** which, on oxidation, give chalcones which are known[6] to be good substrates for cyclopropanation with stabilised sulfuranes (Scheme 3). The results are summarised in Table 2 (no all-cis isomers were observed). For these alcohols, the choice of solvent was crucial, with each example being carried out in CH_2Cl_2, THF and 1,2-dichloroethane (DCE). The optimum solvent for each reaction is indicated in Table 2.

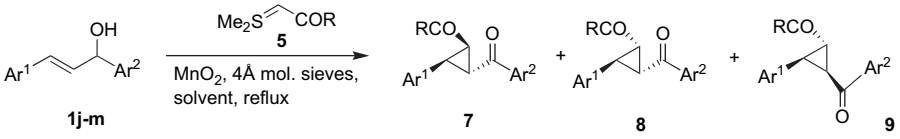
With sulfurane **5a** and electron-rich, electron-deficient, and 'electron-neutral' alcohols, the yields are good to excellent (entries i and iii–v, 51–90%). Sulfurane **5b** was also utilised in a reaction with alcohol **1j**, again in excellent yield (entry ii). The observed erosion of the original trans-double bond stereochemistry can be understood by the equilibration of reaction intermediates, as discussed earlier (Fig. 1).

3. Tandem oxidation–cyclopropanation–Wittig reactions

We were intrigued by the possibility that the cyclopropanecarboxaldehyde products **6** could be exploited in further in situ transformations. We decided to first examine the tandem oxidation–cyclopropanation–Wittig sequence, as we have already established the compatibility of phosphoranes with MnO_2.[1] We hoped to tune the reaction conditions so that both sulfuranes and phosphoranes could be used in situ, in the presence of MnO_2, to allow first oxidation, followed by sulfurane-mediated cyclopropanation, and finally phosphorane-induced olefination.

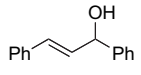
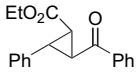
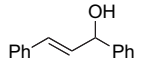
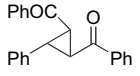
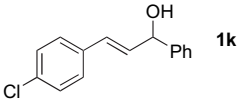
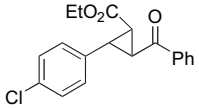
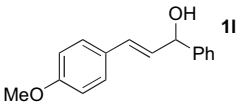
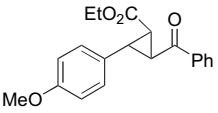
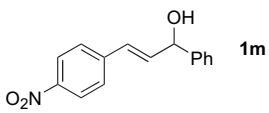
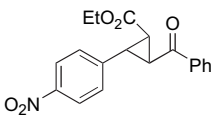
We first examined the reaction of 2-methylprop-2-en-1-ol **1a** with sulfurane **5a**, phosphorane **3a** and activated MnO_2. We were delighted to observe, in the first attempt, the formation of the desired cyclopropane **10a** as a ~1.4:1 mixture of cis/trans-isomers (about the cyclopropane) in a yield of 62% (Scheme 4). Cyclopropane **10a** was accompanied by a small amount (8%) of dienoate **11**. A brief optimisation study was then carried out, varying temperature and equivalents of ylides **3a** and **5a**. It was quickly established that use of a two-fold excess of sulfurane **5a** and carrying out the reaction at reflux gave the best yield of **10a**, 81%, with no dienoate **5a** being observed.

The optimum reaction stoichiometry indicates that the major reaction sequence involves oxidation, then cyclopropanation and then olefination. This is supported by the following observations: (i) TLC analysis indicates significant oxidation–cyclopropanation, giving cyclopropyl aldehyde **6a**, before major amounts of adduct **10a** are observed; (ii) when isolated dienoate **11** was exposed to sulfurane **5a** under similar conditions, only ~50% conversion to **10a** was observed after 16 h.

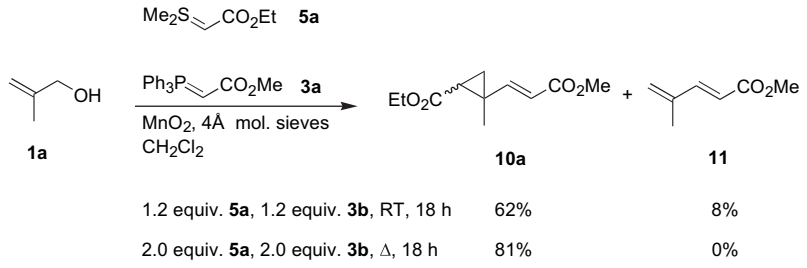


Scheme 3.

Table 2. Disubstituted 2-propen-1-ols in MnO_2-mediated TOP–cyclopropanation

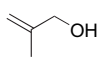
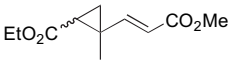
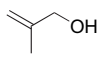
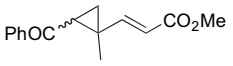
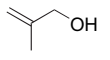
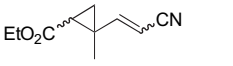
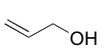
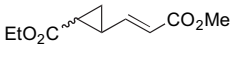
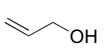
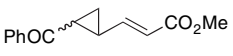
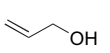
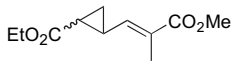
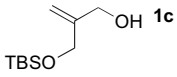
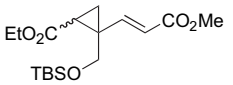
Entry	Alcohol	Ylide/solvent	Product	Ratio (**7**:**8**:**9**)	Yield (reaction time)
i	 **1j**	**5a** THF		**7a**:**8a**:**9a**=5.0:1.0:3.0	70% (10 h)
ii	 **1j**	**5b** THF		(**7b**+**9b**):**8b**=2.6:1[a]	75% (17 h)
iii	 **1k**	**5a** CH_2Cl_2		**7c**:**8c**:**9c**=3.9:1.0:2.8	80% (19 h)
iv	 **1l**	**5a** CH_2Cl_2		**7d**:**8d**:**9d**=4.5:1.0:2.8	51% (17 h)
v	 **1m**	**5a** CH_2Cl_2		**7e**:**8e**:**9e**=4.0:1.0:1.6	90% (14 h)

[a] Compounds **7b** and **9b** are enantiomers.



Scheme 4.

Table 3. TOP–cyclopropanation–olefination methodology

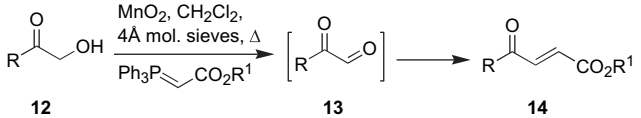
Entry	Alcohol	Sulfurane/phosphorane[a]	Product	2,3-*trans*/*cis*[b]	Yield (reaction time)
i	 **1a**	**5a**, **3a**	 **10a**	~3.5:1	81%[c] (18 h)
ii	 **1a**	**5b**, **3a**	 **10b**	~3.0:1	66% (14 h)
iii	 **1a**	**5a**, **3b**	 **10c**	—[d]	88% (23 h)
iv	 **1b**	**5a**, **3a**	 **10d**	~6.5:1	61% (5 h)
v	 **1b**	**5b**, **3a**	 **10e**	~3.5:1	74% (14 h)
vi	 **1b**	**5a**, **3c**	 **10f**	~7.0:1	56%[e] (18 h)
vii	 **1c**	**5a**, **3a**	 **10g**	~1.8:1	64% (18 h)

[a] **3a** = $Ph_3P{=}CHCO_2Me$; **3b** = $Ph_3P{=}CHCN$; **3c** = $Ph_3P{=}C(Me)CO_2Me$.
[b] Ratio determined by integration of ^1H NMR spectra.
[c] With $Ph_3P{=}CHCO_2Bu^t$ the corresponding *tert*-butyl ester was obtained in 56% yield (trans/cis = 1.8:1).
[d] Alkene also showed *E*- and *Z*-isomers. trans/*E*:cis/*E*:trans/*Z*:cis/*Z* ~8.5:4.4:3.6:1.0.
[e] The use of microwave irradiation reduced the reaction time to 1 h but the yield was reduced (45%); in both cases only the *E*-product was observed.

The optimum conditions illustrated in Scheme 4 were then applied to a range of alcohols **1**, sulfuranes **5** and phosphoranes **3**. The results are summarised in Table 3. As can be seen, good to excellent (56–88%) yields were obtained with the three allylic alcohols **1a–c** undergoing oxidation–elaboration with combinations of the sulfuranes **5a**,**b** and the phosphoranes **3a–c**, although the degree of stereocontrol in relation to the cis/trans-ratio of the 2,3-cyclopropane substituents was variable.

4. Tandem oxidation–Wittig–cyclopropanation reactions

We have previously described the manganese dioxide tandem oxidation–olefination of α-hydroxyketones **12** leading, by way of intermediate α-keto aldehydes **13**, to γ-ketocrotonates **14** in synthetically useful yields (Scheme 5).[7]

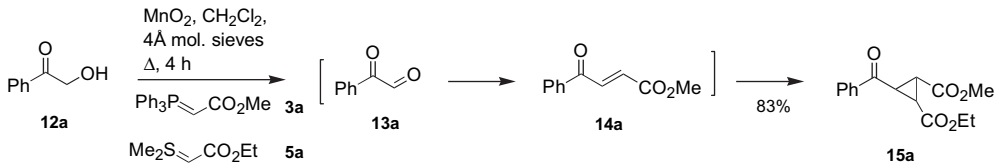


Scheme 5.

In the current study, we envisaged a complementary oxidation–olefination–cyclopropanation sequence, in which the alcohol is treated with MnO_2, phosphorane and sulfurane but, of course, in this case, olefination has to occur first, followed by in situ cyclopropanation of the intermediate γ-ketocrotonate (Scheme 6). As shown, this idea was tested out using hydroxyacetophenone **12a** and we were delighted to obtain an excellent 83% yield of the 1,2,3-trisubstituted cyclopropane **15a** from this one-pot, three-step tandem sequence.

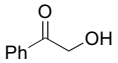
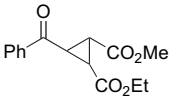
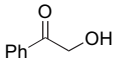
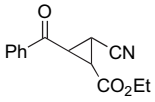
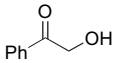
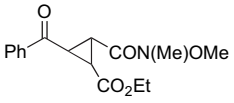
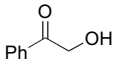
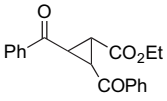
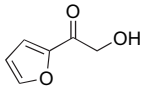
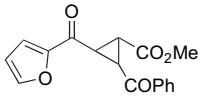
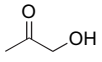
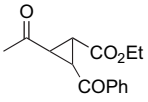
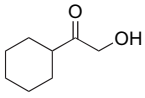
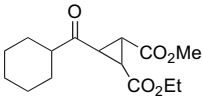
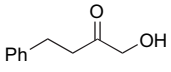
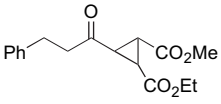
These conditions were then applied to a variety of α-hydroxyketones **12**, phosphoranes **3** and sulfuranes **5** to give substituted cyclopropanes **15b–h** in good to excellent (50–81%) yields (Table 4).

To demonstrate the applicability of this technology to complex, multifunctional substrates, hydrocortisone **12f** was employed as the α-hydroxyketone, giving the desired cyclopropane **15i** in 78% yield (Scheme 7). Moreover, NMR spectroscopy indicates that just one diastereoisomer (yet to be determined) of the product **15i** greatly predominates,

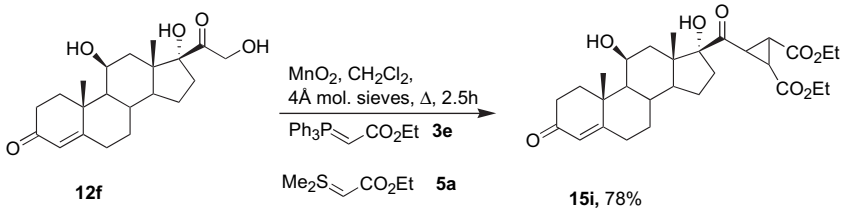


Scheme 6.

Table 4. TOP–olefination–cyclopropanation methodology[a]

Entry	Alcohol		Phosphorane/sulfurane[b]	Product[c]		Yield (diastereoisomer ratio)
i		**12a**	**3a**, **5a**		**15a**	83% (3.2:1)
ii		**12a**	**3b**, **5a**		**15b**	80% (3.8:1)
iii		**12a**	**3d**, **5a**		**15c**	50% (2.2:1)
iv		**12a**	**3e**, **5b**		**15d**	81% (1.2:1)
v		**12b**	**3a**, **5b**		**15e**	70%[d]
vi		**12c**	**3e**, **5b**		**15f**	60%[e] (2.7:1)
vii		**12d**	**3a**, **5a**		**15g**	78%[f]
viii		**12e**	**3a**, **5a**		**15h**	51%[g]

[a] Reaction times 1.5–15 h (see Section 6 for exact time); traces of a third diastereoisomer were observed (NMR) in entries i–iii.
[b] **3a** = $Ph_3P{=}CHCO_2Me$; **3b** = $Ph_3P{=}CHCN$; **3d** = $Ph_3P{=}CHCON(Me)OMe$; **3e** = $Ph_3P{=}CHCO_2Et$.
[c] Isolated as a mixture of isomers about the cyclopropane.
[d] The structures of individual diastereoisomers were not assigned.
[e] When sulfurane **5a** was used, the corresponding cyclopropane was isolated in 54% yield.
[f] When sulfurane **5a** was used, the corresponding cyclopropane was isolated in 55% yield.
[g] One major diastereoisomer with only traces of minor isomers.



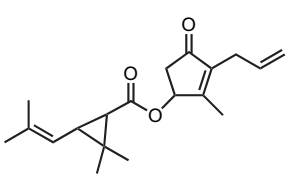
Scheme 7.

implying substrate-induced regio- and stereoselectivity in the in situ cyclopropanation step.

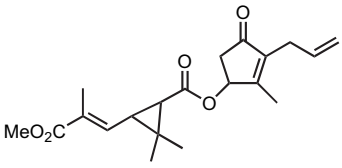
5. Applications in target molecule synthesis

In order to validate the TOP–cyclopropanation methodology, we decided to examine applications in target molecule synthesis. In the first example (Scheme 8), we prepared cyclopropane **17**, which was utilised by Murphy and Wattanasin as a late-stage intermediate in their synthesis of (±)-picropodophyllone[8] which, along with related lignan lactones, is of interest as a cancer chemotherapeutic agent. Allylic alcohol **16** was treated with MnO_2 and sulfurane **5a** in DCE at reflux. We were delighted to find that this procedure produced cyclopropane **17** as a mixture of three diastereoisomers (ca. 3.6:2.9:1.0) in 80% combined yield. This result is noteworthy as allylic alcohol **16** is particularly electron-rich, and in our experience, this slows oxidation by MnO_2. Cyclopropane **17**, also as a mixture of diastereoisomers,[8] has been converted into (±)-picropodophyllone in four steps;[8] the sequence shown in Scheme 8 therefore represents a formal synthesis of this simple natural product.

Pyrethroids have proved extremely valuable as naturally occurring, non-toxic and biodegradable insecticides and insect repellants.[9] Allethrin **18** and allethrin II **19** are typical synthetic pyrethroids, and **18** is widely used against houseflies and mosquitoes.[3e,10] In order to showcase the TOP–cyclopropanation methodology, we prepared novel allethrin analogues as shown in Scheme 9. Cyclopentenone **20** is commercially available (Salor) and readily prepared.[11] Conversion into the ester **21**, salt **22** and then to sulfurane **22** was straightforward (although attempts to go directly from the bromide corresponding to **21** to a sulfonium salt such as **22** by treatment with dimethyl sulfide were unsuccessful). Then, treatment of allyl alcohol **1b**, sulfurane **22** and phosphorane **3c** with MnO_2 gave allethrin II analogue **24** in 57% yield via the one-pot TOP sequence illustrated in Scheme 9. Examination of the ^1H and ^{13}C NMR spectra of **24** indicated that only two diastereoisomers were present (ca. 3:1 as an inseparable mixture). Extensive NOE studies indicated that both diastereoisomers possessed *E*-configured trisubstituted alkenes. Coupling constant analysis showed that both major and minor components are trans-cyclopropane isomers, with no cis-isomers observed. Thus, coupling constants across the cyclopropane ring (J 8.5 Hz in both diastereomers) are in accordance with literature values.[13] Also, in the ^{13}C NMR spectrum, the chemical shifts of the ring carbons [δ_C 16.7 (CH_2), 22.3 (CH) and 22.4 (CH) ppm] are consistent with those of closely related *trans*-disubstituted cyclopropanes.[14] Other allethrin analogues should be readily available by similar processes.



Allethrin **18**



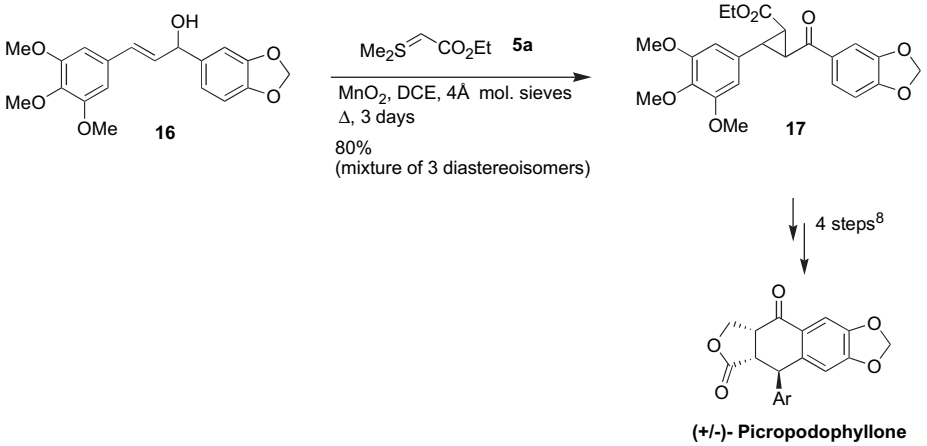
Allethrin II **19**

In summary, a number of different one-pot MnO_2-mediated TOP methodologies have been developed, which allow straightforward access to a range of functionalised cyclopropanes. Applications of the methodology in target molecule synthesis have been described, and further examples are currently under investigation.

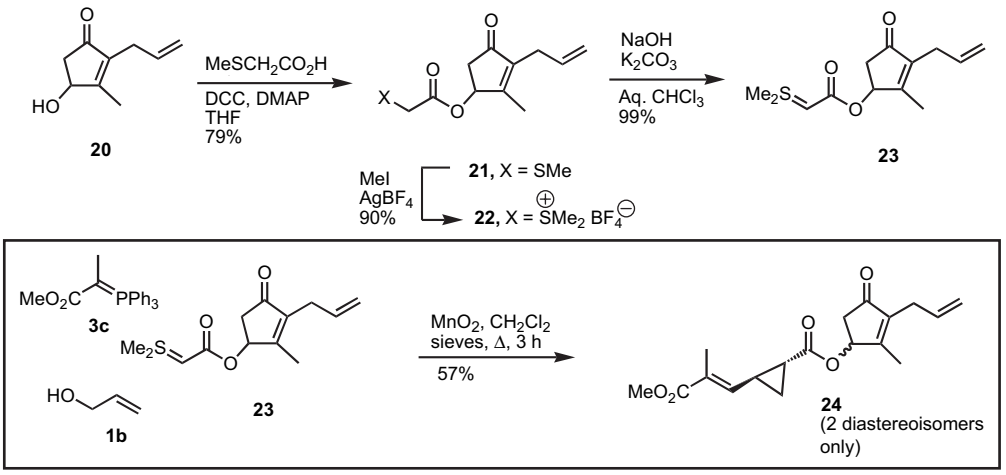
6. Experimental

6.1. General details

NMR spectra were recorded on Jeol EX-270 and ECX-400 spectrometers. Diastereomer ratios were obtained by ^1H NMR integration. Chemical shifts (δ) are given in parts per million (ppm), using the residual solvent as reference ($CDCl_3$ unless otherwise stated), and coupling constants are given in Hertz (Hz). IR spectra were recorded on ThermoNicolet IR100 or ATI Mattson Genesis FTIR spectrometers, as thin films between NaCl plates. Mass spectra were recorded on a Fisons analytical autospec instrument in either chemical ionisation (CI), electron ionisation (EI), or fast atom bombardment (FAB) modes. Melting points were measured on a Gallenkamp instrument in open capillary tubes, and are uncorrected. Flash chromatography was performed on Fluorochem silica gel (35–70 μm) using the eluent specified. Thin layer chromatography (TLC) was



Scheme 8.



Scheme 9.

carried out using Merck silica gel $60F_{254}$ pre-coated aluminium foil plates with a thickness of 250 μm, and visualised with UV light (254 nm), and $KMnO_4$/vanillin solutions. All reagents were purchased from commercial sources, and used without further purification, unless specified. Activated manganese(IV) dioxide was purchased from Aldrich (cat. no. 21,764; <5 μm, activated, 85%). Tetrahydrofuran, diethyl ether and dichloromethane were either dried using standard distillation procedures, or with an MBraun Solvent Purification System (SPS), immediately prior to use. Petrol is the fraction with boiling range 40–60 °C. Alcohol **16** was obtained from the corresponding ketone[12] by standard reduction with $NaBH_4$/CsBr. Sulfuranes **5a** and **5b** were prepared from the commercially available (Aldrich) sulfonium salts using published procedures.[2d,e]

Compounds **6a**,[3n,q] **6c**,[3m] **6d**,[3i] **6g**,[3r] **6h**,[3p] **6i**,[3o] **7a**,[2g] **7b**,[3h] **7d**[3k] and **17**[8] are known compounds and the data correspond with those reported in the literature.

6.2. Tandem oxidation–cyclopropanation reactions

6.2.1. 2-Benzoyl-1-methylcyclopropanecarboxaldehyde 6b: representative procedure. To a solution of 2-methyl-2-propen-1-ol **1a** (36 mg, 0.50 mmol) in dichloromethane (5 mL) was added powdered 4 Å molecular sieves (0.50 g), (benzoylmethylene)dimethylsulfurane **5b** (108 mg, 0.60 mmol) and manganese dioxide (435 mg, 5.0 mmol). The mixture was heated at reflux for 2 h, and then cooled to rt. The crude mixture was then filtered through Celite® and the residue washed with dichloromethane (50 mL) giving a pale yellow solution. After removal of the solvent in vacuo, the residue was purified by flash column chromatography (petrol–EtOAc, 19:1 to 4:1) to give the *title compound* **6b** (50 mg, 53%) as an inseparable mixture (~4.2:1 trans/cis) as a colourless oil, R_f 0.31 (petrol–EtOAc, 4:1); ν_{max} (film) 2935, 1712, 1665, 1596, 1449, 1379, 1305, 1225 cm^{-1}; δ_H (400 MHz, $CDCl_3$) *trans*: 1.26 (3H, s), 1.59 (1H, dd, *J* 4.9 and 8.2 Hz), 1.91 (1H, dd, *J* 4.9 and 7.0 Hz), 3.20 (1H, dd, *J* 8.2 and 7.0 Hz), 7.47 (2H, dd (app t), *J* 7.6 Hz), 7.58 (1H, dd (app t), *J* 7.6 Hz), 7.90 (2H, d, *J* 7.6 Hz), 9.09 (1H, s); cis: δ_H 1.44 (3H, s), 1.54 (1H, dd, *J* 4.9 and 7.6 Hz), 2.39 (1H, dd, *J* 4.9 and 7.0 Hz), 3.01 (1H, dd, *J* 7.6 and 7.0 Hz), 7.47 (2H, dd (app t), *J* 7.6 Hz), 7.58 (1H, dd (app t), *J* 7.6 Hz), 7.93 (2H, d, *J* 7.6 Hz), 9.11 (1H, s); δ_C (100 MHz, $CDCl_3$) *trans*: 10.3 (CH_3), 18.6 (CH_2), 29.9 (CH), 37.4 (C), 128.3 (CH), 128.9 (CH), 133.6 (CH), 137.8 (C), 194.9 (C), 200.0 (C); *cis*: 17.5 (CH_3), 21.2 (CH_2), 35.0 (CH), 37.8 (C), 128.4 (CH), 128.9 (CH), 133.7 (CH), 137.2 (C), 195.6 (C), 200.4 (C); *m/z* (CI) 189 (MH^+); HRMS (CI) [MH^+], found 189.0912. $C_{12}H_{13}O_2$ requires 189.0916 (2.1 ppm error).

6.2.2. Ethyl 2-(*tert*-butyldimethylsilanyloxymethyl)-2-formyl-cyclopropanecarboxylate 6e. Using the above procedure for **6b** (but with sulfurane **5a** and for 14 h), the *title compound* **6e** was prepared in 74% yield as an inseparable mixture (trans/cis ~3.6:1) as a colourless oil, R_f 0.33 (petrol–EtOAc, 12:1); ν_{max} (film) 2953, 2931, 2856, 1732, 1704, 1257, 1176, 1097, 839, 779 cm^{-1}; δ_H (270 MHz, $CDCl_3$) *trans*: δ_H 0.02 (3H, s), 0.05 (3H, s); 0.84 (9H, s), 1.23–1.28 (3H, m), 1.45 (1H, dd, *J* 4.5 and 8.5 Hz), 1.53 (1H, dd, *J* 4.5 and 6.7 Hz), 2.31 (1H, dd, *J* 8.5 and 6.7 Hz), 3.86 (1H, d, *J* 11.1 Hz), 4.03–4.20 (2H, m), 4.32 (1H, d, *J* 11.1 Hz), 9.52 (1H, s); *cis*: δ_H 0.02 (3H, s), 0.05 (3H, s); 0.84 (9H, s), 1.23–1.28 (3H, m), 1.63 (1H, dd, *J* 4.8 and 8.2 Hz), 1.91 (1H, dd, *J* 4.8 and 6.7 Hz), 2.33 (1H, dd, *J* 8.2 and 6.7 Hz), 3.93 (2H, s), 4.03–4.20 (2H, m), 9.38 (1H, s); δ_C (67.5 MHz, $CDCl_3$) *trans*: −5.5 (CH_3), −5.4 (CH_3), 14.3 (CH_3), 18.3 (C), 18.9 (CH), 25.8 (CH_3), 26.4 (CH), 40.6 (C), 59.4 (CH_2), 61.3 (CH_2), 170.1 (C), 200.2 (C); *cis*: δ_C −5.5 (CH_3), −5.4 (CH_3), 14.3 (CH_3), 16.1 (CH_2), 18.3 (C), 25.2 (CH), 25.8 (CH_3), 40.3 (C), 59.1 (CH_2), 61.5 (CH_2), 171.0 (C), 200.4 (C); *m/z* (CI) 287 (MH^+); HRMS (CI) [MH^+], found: 287.1681. $C_{14}H_{27}O_4Si$ requires 287.1679 (0.2 ppm error).

6.2.3. 2-Benzoyl-1-(*tert*-butyldimethylsilanyloxymethyl)-cyclopropanecarboxaldehyde 6f. Using the above procedure for **6b** (for 14 h), the *title compound* **6f** was prepared in 73% yield as an inseparable mixture (trans/cis ~2:1) as a colourless oil, R_f 0.51 (petrol–EtOAc, 4:1); ν_{max} (film) 2954, 2929, 2857, 1716, 1675, 1451, 1255, 1223, 1090 cm^{-1}; δ_H (400 MHz, $CDCl_3$) *trans*: −0.29 (3H, s), −0.09 (3H, s), 0.62 (9H, s), 1.49 (1H, dd, *J* 4.1 and 7.9 Hz), 1.91 (1H, dd, *J* 4.1 and 6.7 Hz), 3.35 (1H, dd, *J* 7.9 and 6.7 Hz), 3.58 (1H, d, *J* 11.3 Hz), 4.35 (1H, d, *J* 11.3 Hz), 7.39–7.49 (2H, m), 7.50–7.62 (2H, m), 7.94 (1H,

d, *J* 7.3 Hz), 9.76 (1H, s); *cis*: 0.11 (3H, s), 0.12 (3H, s), 0.92 (9H, s), 1.68 (1H, dd, *J* 4.6 and 7.6 Hz), 2.27 (1H, dd, *J* 4.6 and 6.7 Hz), 3.35 (1H, dd, *J* 7.6 and 6.7 Hz), 3.79 (1H, d, *J* 10.8 Hz), 4.30 (1H, d, *J* 10.8 Hz), 7.39–7.49 (2H, m), 7.50–7.62 (2H, m), 8.03 (1H, d, *J* 7.6 Hz), 9.12 (1H, s); δ_C (100 MHz, $CDCl_3$) *trans*: −6.0 (CH_3), −5.8 (CH_3), 18.1 (C), 18.6 (CH_2), 25.6 (CH_3), 30.2 (CH), 43.7 (C), 59.2 (CH_2), 128.5 (CH), 128.6 (CH), 133.2 (CH), 137.7 (C), 194.9 (C), 200.7 (C); *cis*: −5.4 (CH_3), −5.3 (CH_3), 16.6 (CH_2), 18.4 (C), 25.9 (CH_3), 30.1 (CH), 42.8 (C), 60.3 (CH_2), 128.6 (CH), 128.8 (CH), 133.6 (CH), 137.3 (C), 195.9 (C), 199.4 (C); *m/z* (CI) 319 (MH^+); HRMS (CI) [MH^+], found: 319.1730. $C_{18}H_{27}O_3Si$ requires 319.1729 (0.1 ppm error).

6.2.4. Diethyl 2,2′-carbonyldicyclopropanecarboxylate 6j. Using the above procedure for **6b** (but with sulfurane **5a** and for 4 h), the *title compound* **6j** was prepared in 60% yield as a wax: R_f 0.32 (petrol–EtOAc, 4:1); ν_{max} (film) 2983, 1731, 1692, 1369, 1334, 1186 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.26 (6H, t, *J* 7.0 Hz), 1.40–1.46 (4H, m), 2.16–2.23 (2H, m), 2.58–2.65 (2H, m), 4.14 (4H, q, *J* 7.0 Hz); δ_C (67.5 MHz, $CDCl_3$) 14.3 (CH_3), 17.8 (CH), 24.9 (CH), 29.9 (CH_2), 61.3 (CH_2), 171.9 (C), 204.7 (C); *m/z* (CI) 255 (MH^+) 272 (MNH_4^+); HRMS (CI) [MNH_4^+], found: 272.1500. $C_{13}H_{22}NO_5$ requires 272.1498 (0.7 ppm error).

6.2.5. {2-[(2-Benzoylcyclopropyl)carbonyl]cyclopropyl}(phenyl)methan-one 6k. Using the above procedure for **6b** (also for 2 h), the *title compound* **6k** was prepared in 69% yield as a white solid, mp 148–150 °C; R_f 0.35 (petrol–EtOAc, 4:1); ν_{max} (film) 1660, 1349, 1225 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.58–1.78 (4H, m), 2.84–2.97 (2H, m), 3.23–3.38 (2H, m), 7.38–7.51 (4H, m), 7.52–7.64 (2H, m), 7.91–8.06 (4H, m); δ_C (100 MHz, $CDCl_3$) 20.2/20.3 (CH_2), 28.4/28.5 (CH), 32.3/32.4 (CH), 128.3/128.4 (CH), 128.7/128.8 (CH), 133.4/133.5 (CH), 136.9 (C), 196.9 (C), 205.8 (C); *m/z* (CI) 319 (MH^+) 336 (MNH_4^+); HRMS (CI) [MH^+], found: 319.1330. $C_{21}H_{19}O_3$ requires 319.1334 (1.3 ppm error).

6.2.6. (1*R*,3*R*,6*S*,8*S*)-1-Benzoyl-7,7-dimethyl-6,8-methylene-spiro[2.5]octan-4-one and (1*S*,3*S*,6*S*,8*S*)-isomer 6l. Using the above procedure for **6b** (but for 16 h), the *title compound* **6l** was prepared in 76% yield as an inseparable mixture (trans/cis ~5:1) as a colourless oil, R_f 0.54 (petrol–EtOAc, 4:1); ν_{max} (film) 2924, 1703, 1664, 1597, 1449, 1385, 1326, 1289, 1220, 1033 cm^{-1}; δ_C (400 MHz, $CDCl_3$) *major*: 0.94 (3H, s), 1.01 (1H, d, *J* 10.7 Hz), 1.28 (3H, s), 1.65 (1H, dd, *J* 6.4 and 3.4 Hz), 1.72 (1H, dd, *J* 7.9 and 3.4 Hz), 1.93 (1H, t, *J* 6.7 Hz), 2.10–2.19 (1H, m), 2.30–2.39 (1H, m), 2.56 (1H, dd, *J* 19.2 and 2.5 Hz), 2.71 (1H, dt, *J* 19.2 and 2.5 Hz), 3.27 (1H, t, *J* 7.3 Hz), 7.39–7.45 (2H, m), 7.49–7.55 (2H, m), 7.91 (1H, d, *J* 7.6 Hz); *minor*: δ_H 0.56 (3H, s), 1.13 (3H, s), 1.37 (1H, d, *J* 10.5 Hz), 1.52–1.59 (2H, m), 1.93 (1H, obscured), 2.10–2.19 (2H, m), 2.54 (1H, dd, *J* 19.3 and 2.8 Hz), 2.65 (1H, dt, *J* 19.3 and 2.8 Hz), 3.56 (1H, t, *J* 7.3 Hz), 7.39–7.45 (2H, m), 7.49–7.55 (2H, m), 7.93 (1H, d, *J* 7.3 Hz); δ_C (100 MHz, $CDCl_3$) *major*: 21.1 (CH_3), 22.5 (CH_2), 26.2 (CH_3), 32.2 (CH), 32.6 (CH_2), 38.6 (CH), 40.3 (CH), 40.4 (C), 43.5 (CH_2), 45.3 (CH), 128.2 (CH), 128.6 (CH), 133.2 (CH), 137.9 (C), 195.8 (C), 210.5 (C); *minor*: 21.4 (CH_3), 22.1 (CH_2), 25.9 (CH_3), 32.6 (CH_2), 33.4 (CH), 38.7 (CH), 39.5 (C), 40.0 (CH), 43.4 (CH_2), 45.6 (C), 128.4 (CH), 128.6 (CH), 133.1 (CH), 137.8 (C), 195.8 (C), 210.4 (C); *m/z* (CI) 269 (MH^+); HRMS (CI) [MH^+], found: 269.1537. $C_{18}H_{21}O_2$ requires 269.1542 (1.7 ppm error).

6.2.7. Ethyl 2-benzoyl-3-(4-chlorophenyl)cyclopropanecarboxylate 7c. Using the above procedure for **6b** (but with sulfurane **5a** and for 10 h), the *title compound* **7c** was prepared in 80% yield as a mixture of isomers, partially separable by chromatography (petrol–EtOAc, 10:1). The first eluting and major product **7c** was obtained as a colourless oil, R_f 0.52 (petrol–EtOAc, 10:1); ν_{max} (film) 2980, 1730, 1680, 1494, 1450, 1372, 1191, 1014 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.11 (3H, t, *J* 7.2 Hz), 2.82 (1H, dd, *J* 4.8 and 10.0 Hz), 3.21 (1H, dd, *J* 6.3 and 10.0 Hz), 3.80 (1H, dd, *J* 4.8 and 6.3 Hz), 4.01 (2H, q, *J* 7.2 Hz), 7.27 (4H, br s), 7.48–7.56 (2H, m), 7.61–7.67 (1H, m), 8.10 (2H, d, *J* 7.2 Hz); δ_C (67.5 MHz, $CDCl_3$) 14.3 (CH_3), 29.8 (CH), 32.3 (CH), 34.3 (CH), 61.3 (CH_2), 128.6 (CH), 128.7 (CH), 130.4 (CH), 132.2 (CH), 133.3 (CH), 133.4 (C), 133.8 (C), 137.0 (C), 168.8 (C), 196.5 (C); *m/z* (CI) 328 (MH^+); HRMS (CI) [MH^+], found 329.0947. $C_{19}H_{18}O_3^{35}Cl$ requires 329.0944 (0.8 ppm error).

6.2.8. Ethyl 2-benzoyl-3-(4-nitrophenyl)cyclopropanecarboxylate 7e. Using the above procedure for **6b** (but for 17 h), the *title compound* **7e** was prepared in 90% yield as a mixture of isomers, partially separable by chromatography (petrol–EtOAc, 5:1). The first eluting and major product **7e** was obtained as a pale yellow oil, R_f 0.54 (petrol–EtOAc, 5:1); ν_{max} (film) 3390, 2923, 2852, 1597, 1515, 1344, 1010 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.12 (3H, t, *J* 7.1 Hz), 2.88 (1H, dd, *J* 4.8 and 10.0 Hz), 3.32 (1H, dd, *J* 6.3 and 9.7 Hz), 3.88 (1H, dd, *J* 4.8 and 6.3 Hz), 4.02 (2H, q, *J* 7.1 Hz), 7.45–7.58 (4H, m), 7.60–7.69 (1H, m), 8.07–8.12 (2H, m), 8.13–8.20 (2H, m); δ_C (67.5 MHz, $CDCl_3$) 14.2 (CH_3), 29.9 (CH), 32.4 (CH), 33.9 (CH), 61.5 (CH_2), 123.5 (CH), 128.5 (CH), 129.0 (CH), 130.0 (CH), 134.0 (CH), 136.7 (C), 142.5 (C), 147.3 (C), 168.5 (C), 195.9 (C); *m/z* (CI) 240 (MH^+) 257 (MNH_4^+); HRMS (CI) [MNH_4^+], found: 357.1448. $C_{19}H_{21}N_2O_5$ requires 357.1450 (0.2 ppm error).

6.3. Tandem oxidation–cyclopropanation–Wittig reactions

6.3.1. Ethyl 2-(2-cyanoethenyl)-2-methyl-cyclopropanecarboxylate 10c: representative procedure. To a solution of 2-methyl-2-propen-1-ol **1a** (36 μL, 0.50 mmol) in CH_2Cl_2 (5.0 mL) was added powdered 4 Å molecular sieves (0.50 g), (carbethoxymethylene)dimethylsulfurane **5a** (0.148 g, 1.00 mmol), (cyanomethylene)triphenylphosphorane **3b** (0.181 g, 0.60 mmol) and manganese dioxide (0.435 g, 5.0 mmol). The mixture was heated at reflux for 23 h, and then cooled to rt. The crude mixture was filtered through Celite® and the residue washed with CH_2Cl_2. After removal of the solvent, the resulting yellow oil was purified by flash column chromatography (petrol–EtOAc, 19:1 to 4:1) to give the *title compound* **10c** (0.079 g, 88%) as an inseparable mixture of cis/trans cyclopropane isomers and *E*/*Z* alkene isomers (trans/*E*:cis/*E*:trans/*Z*:cis/*Z* ~8.5:4.4:3.6:1) as a colourless oil, R_f 0.35 (petrol–EtOAc, 4:1); ν_{max} (film) 2983,

2222, 1726, 1626, 1448, 1406, 1383, 1223, 1184, 1097, 1073, 1024, 980 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.20–1.28 (m, $CO_2CH_2CH_3$, all isomers), 1.30 (s, Me, *trans*-cyclopropanes), 1.33–1.39 (m), 1.42–1.50 (m), 1.51 (s, Me, *cis*-cyclopropanes), 1.56 (dd (app t), *J* 5.5 Hz, trans/*E*), 1.66–1.76 (m), 1.86–1.98 (m), 4.04–4.22 (m, $CO_2CH_2CH_3$, all isomers), 5.27 (d, *J* 11.9 Hz, trans/*Z*), 5.31 (d, *J* 16.2 Hz, trans/*E*), 5.33 (d, *J* 16.5 Hz, cis/*E*), 5.35 (d, *J* 11.6 Hz, cis/*Z*), 5.98 (d, *J* 11.9 Hz, trans/*Z*), 6.14 (d, *J* 16.2 Hz, trans/*E*) 6.44 (d, *J* 11.6 Hz, cis/*Z*), 6.85 (d, *J* 16.5 Hz, cis/*E*); δ_C (100 MHz, $CDCl_3$) [though it was not possible to assign signals to a given isomer, all are cited] 13.3 (CH_3), 14.1 (CH_3), 14.2 (CH_3), 14.2 (CH_3), 14.3 (CH_3), 14.3 (CH_3), 14.3 (CH_3), 15.4 (CH_3), 21.6 (CH_2), 21.9 (CH_2), 23.6 (CH_2), 23.8 (CH_2), 27.8 (C), 27.9 (C), 28.1 (CH), 28.4 (CH), 28.6 (CH), 30.0 (C), 30.5 (CH), 31.7 (C), 61.0 (CH_2), 61.1 (CH_2), 61.4 (CH_2), 61.5 (CH_2), 97.3 (CH), 97.4 (CH), 98.1 (CH), 99.2 (CH), 116.1 (C), 117.5 (C), 117.5 (C), 117.8 (C), 153.9 (CH), 156.3 (CH), 157.3 (CH), 160.4 (CH), 170.1 (C), 170.4 (C), 170.7 (C), 170.8 (C); *m/z* (CI) 197 (MNH_4^+); HRMS (CI) [MNH_4^+], found: 197.1291. $C_{10}H_{17}N_2O_2$ requires 197.1290 (0.6 ppm error).

6.3.2. 2-((*E*)-2-Methoxycarbonyl-vinyl)-2-methyl-cyclopropanecarboxylic acid ethyl ester 10a. Using the above procedure for **10c** (but with phosphorane **3a** for 18 h), the *title compound* **10a** was prepared in 81% yield as a colourless oil as a mixture (trans/cis ~3.5:1), which was separated by column chromatography (petrol–EtOAc, 19:1 to 4:1): *major isomer*: R_f 0.41 (petrol–EtOAc, 4:1); ν_{max} (film) 2934, 1723, 1646, 1437, 1405, 1384, 1317, 1272, 1228, 1172, 1019 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.22–1.26 (4H, m), 1.33 (3H, s), 1.46 (1H, dd, *J* 5.2 and 6.4 Hz), 1.90 (1H, dd, *J* 6.4 and 8.5 Hz), 3.70 (3H, s), 4.12 (2H, q, *J* 7.0 Hz), 5.83 (1H, d, *J* 15.6 Hz), 6.43 (1H, d, *J* 15.6 Hz); δ_C (100 MHz, $CDCl_3$) 14.1 (CH_3), 14.4 (CH_3), 21.8 (CH_2), 27.2 (C), 28.7 (CH), 51.6 (CH_3), 60.9 (CH_2), 118.4 (CH), 154.7 (CH), 167.1 (C), 170.7 (C); *m/z* (CI) 213 (MH^+) 230 (MNH_4^+); HRMS (CI) [MH^+], found: 213.1125. $C_{11}H_{17}O_4$ requires 213.1127 (0.9 ppm error). *Minor isomer*: R_f 0.35 (petrol–EtOAc, 3:1); ν_{max} (film) 2951, 1727, 1644, 1437, 1407, 1382, 1304, 1273, 1228, 1170, 1019 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.23–1.26 (4H, m), 1.30 (3H, s), 1.60 (1H, dd, *J* 4.9 and 76.59 Hz), 1.92 (1H, dd, *J* 6.5 and 7.9 Hz), 3.71 (3H, s), 4.12 (2H, m), 5.88 (1H, d, *J* 15.9 Hz), 7.08 (1H, d, *J* 15.9 Hz); δ_C (100 MHz, $CDCl_3$) 14.3 (CH_3), 21.8 (CH_3), 23.5 (CH_2), 27.6 (C), 30.5 (CH), 51.6 (CH_3), 61.0 (CH_2), 120.0 (CH), 150.3 (CH), 167.0 (C), 171.0 (C); *m/z* (CI) 213 (MH^+) 230 (MNH_4^+); HRMS (CI) [MH^+], found: 213.1125. $C_{11}H_{17}O_4$ requires 213.1127 (0.9 ppm error).

6.3.3. (*E*)-3-(2-Benzoyl-1-methyl-cyclopropyl)-acrylic acid methyl ester 10b. Using the above procedure for **10c** (but with sulfurane **5b** and phosphorane **3a** for 14 h), the *title compound* **10b** was prepared in 66% yield as a pale yellow oil as a mixture (trans/cis ~3:1), which was separated by column chromatography (petrol–EtOAc, 19:1 to 9:1): *major isomer*: R_f 0.34 (petrol–EtOAc, 9:1); ν_{max} (film) 2950, 1721, 1673, 1643, 1450, 1386, 1317, 1273, 1225, 1173, 987 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.18 (3H, s), 1.33 (1H, dd, *J* 4.8 and 8.0 Hz), 1.87 (1H, dd, *J* 4.8 and 6.5 Hz), 2.85 (1H, dd, *J* 6.5 and 8.0 Hz), 3.75 (3H, s), 5.92 (1H, d, *J* 15.6 Hz), 6.68 (1H, d, *J* 15.6 Hz), 7.41–7.57 (3H, m), 7.85–7.88 (2H, m); δ_C (100 MHz, $CDCl_3$) 13.6 (CH_3), 21.3 (CH_2), 30.1 (CH), 33.5 (CH), 51.6 (CH_3), 118.6 (CH), 128.0 (CH), 128.6 (CH), 133.0 (CH), 138.1 (C), 154.6 (CH), 167.0 (C), 195.9 (C); *m/z* (CI) 245 (MH^+) 262 (MNH_4^+); HRMS (CI) [MH^+], found: 245.1178. $C_{15}H_{17}O_3$ requires 245.1174 (1.4 ppm error). *Minor isomer*: R_f 0.22 (petrol–EtOAc, 9:1); ν_{max} (film) 2950, 1721, 1669, 1643, 1449, 1395, 1326, 1273, 1222, 1172, 992 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.25 (3H, s), 1.38 (1H, dd, *J* 4.5 and 7.4 Hz), 2.02 (1H, dd, *J* 4.5 and 6.3 Hz), 2.92 (1H, dd, *J* 6.3 and 7.4 Hz), 3.66 (3H, s), 5.86 (1H, d, *J* 15.6 Hz), 6.85 (1H, d, *J* 15.6 Hz), 7.92–8.12 (3H, m), 8.13–8.15 (2H, m); δ_C (125 MHz, $CDCl_3$) 21.9 (CH_3), 23.3 (CH_2), 30.7 (C), 35.4 (CH), 51.4 (CH_3), 120.0 (CH), 128.1 (CH), 128.5 (CH), 132.9 (CH), 138.0 (C), 149.1 (CH), 166.6 (C), 196.0 (C); *m/z* (CI) 245 (MH^+), 262 (MNH_4^+); HRMS (CI) [MH^+], found: 245.1178. $C_{15}H_{17}O_3$ requires 245.1174 (1.4 ppm error).

6.3.4. 2-((*E*)-2-Methoxycarbonyl-vinyl)-cyclopropanecarboxylic acid ethyl ester 10d. Using the above procedure for **10c** (but with phosphorane **3a** for 5 h), the *title compound* **10d** was prepared in 61% yield as a colourless oil as a mixture (trans/cis ~6.5:1), which was not separated: ν_{max} (film) 2978, 2950, 1721, 1655, 1438, 1410, 1261, 1197, 1180, 1148, 1032 cm^{-1}; *major isomer*: R_f 0.36 (petrol–EtOAc, 3:1); δ_H (400 MHz, $CDCl_3$) 1.11 (1H, ddd, *J* 4.3, 5.8 and 10.4 Hz), 1.24 (3H, t, *J* 7.0 Hz), 1.51 (1H, app td, *J* 5.5 and 10.4 Hz), 1.82 (1H, ddd, *J* 4.3, 5.5 and 8.9 Hz), 2.12 (1 H, m), 3.69 (3 H, s), 4.12 (2 H, q, *J* 7.0 Hz), 5.94 (1H, d, *J* 15.6 Hz), 6.39 (1H, dd, *J* 10.1 and 15.6 Hz); δ_C (100 MHz, $CDCl_3$) 14.3 (CH_3), 16.5 (CH_2), 23.0 (CH), 24.4 (CH), 51.6 (CH_3), 61.0 (CH_2), 120.7 (CH), 149.0 (CH), 166.7 (C), 172.5 (C). *Minor isomer*: R_f 0.33 (petrol–EtOAc, 3:1); δ_H (400 MHz, $CDCl_3$) 1.31–1.44 (1H, m), 1.95–2.06 (1H, m), 3.68 (3H, s), 5.98 (1H, d, *J* 15.0 Hz), 6.91 (1H, dd, *J* 9.8 and 15.0 Hz) (*the remaining signals were obscured by the major isomer)*; δ_C (100 MHz, $CDCl_3$) 14.3 (CH_3), 15.4 (CH_2), 22.3 (CH), 23.4 (CH), 51.5 (CH_3), 61.0 (CH_2), 120.0 (CH), 146.6 (CH), 166.5 (C), 171.2 (C); *m/z* (CI) 199 (MH^+), 216 (MNH_4^+); HRMS (CI) [MNH_4^+], found: 216.1236. $C_{10}H_{18}NO_4$ requires 216.1235 (0.2 ppm error).

6.3.5. (*E*)-3-(2-Benzoyl-cyclopropyl)-acrylic acid methyl ester 10e. Using the above procedure for **10c** (but with sulfurane **5a** and phosphorane **3a** for 14 h), the *title compound* **10e** was prepared in 74% yield as an off-white solid as a mixture (trans/cis ~3.5:1), which was separated by column chromatography (petrol–EtOAc, 19:1 to 9:1): *major isomer*: mp 85–87 °C; R_f 0.15 (petrol–EtOAc, 9:1); ν_{max} (film) 2960, 1710, 1661, 1580, 1450, 1434, 1399, 1261, 1211, 1152, 1023, 919 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.31 (1H, ddd, *J* 4.3, 5.8 and 10.0 Hz), 1.82 (1H, ddd, *J* 4.3, 6.0 and 9.0 Hz), 2.30 (1H, ddd, *J* 3.7, 6.0 and 10.0 Hz), 2.88 (1H, ddd, *J* 3.7, 5.8 and 9.0 Hz), 3.71 (3H, s), 5.98 (1H, d, *J* 15.6 Hz), 6.56 (1H, dd, *J* 10.0 and 15.6 Hz), 7.43–7.59 (3H, m), 7.95–7.97 (2H, m); δ_C (100 MHz, $CDCl_3$) 18.7 (CH_2), 26.9 (CH), 27.6 (CH), 51.5 (CH_3), 120.5 (CH), 128.0 (CH), 128.6 (CH), 133.1 (CH), 137.2 (CH), 149.2 (CH), 166.6 (C), 197.4 (C); *m/z* (CI) 231 (MH^+) 248 (MNH_4^+); HRMS (CI) [MH^+], found: 231.1018. $C_{14}H_{15}O_3$ requires 231.1021 (1.2 ppm error). *Minor isomer*: mp 86–87 °C; R_f 0.10 (petrol–EtOAc, 9:1); ν_{max} (film) 2955, 1708, 1661, 1646, 1450, 1432, 1258, 1195, 1150, 1016, 985 cm^{-1}; δ_H (400 MHz,

$CDCl_3$) 1.49 (1H, app dt, *J* 4.5 and 8.2 Hz), 1.83 (1H, app dt, *J* 4.5 and 7.0 Hz), 2.30 (1H, dddd, *J* 7.0, 8.2, 10.4 and 11.0 Hz), 3.13 (1H, ddd, *J* 4.5, 7.0 and 11.0 Hz), 3.66 (3H, s), 5.98 (1H, d, *J* 15.6 Hz), 6.79 (1H, dd, *J* 10.4 and 15.6 Hz), 7.42–7.59 (3H, m), 7.95–7.99 (2H, m); δ_C (100 MHz, $CDCl_3$) 15.6 (CH_2), 26.5 (CH), 26.6 (CH), 51.4 (CH_3), 121.9 (CH), 128.1 (CH), 128.6 (CH), 133.0 (CH), 138.0 (CH), 146.0 (CH), 166.1 (C), 196.0 (C); *m/z* (CI) 231 (MH^+) 248 (MNH_4^+); HRMS (CI) [MH^+], found: 231.1016. $C_{14}H_{15}O_3$ requires 231.1021 (1.6 ppm error).

6.3.6. 2-((*E*)-2-Methoxycarbonyl-propenyl)-cyclopropanecarboxylic acid ethyl 10f. Using the above procedure for **10c** (but with phosphorane **3c** for 18 h), the *title compound* **10f** was prepared in 56% yield as a colourless oil as an inseparable mixture (trans/cis ~7:1), R_f 0.34 (petrol–Et_2O, 3:1); ν_{max} (film) 2950, 1719, 1710, 1648, 1437, 1412, 1349, 1311, 1263, 1252, 1200, 1180, 1104, 1037 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.05 (1H, ddd, *J* 4.3, 5.8 and 9.0 Hz), 1.22 (3H, d, *J* 7.0 Hz), 1.49 (1H, ddd, *J* 4.3, 5.5 and 9.4 Hz), 1.77 (1H, ddd, *J* 3.7, 5.5 and 9.0 Hz), 1.90 (3H, d, *J* 1.5 Hz), 2.15 (1H, dddd, *J* 3.7, 5.8, 9.4 and 11.0 Hz), 3.67 (3H, s), 4.10 (2H, *J* 7.0 Hz), 6.06 (1H, dd, *J* 1.5 and 11.0 Hz); δ_C (100 MHz, $CDCl_3$) 12.6 (CH_3), 14.1 (CH_3), 16.3 (CH_2), 21.9 (CH), 22.6 (CH), 51.6 (CH_3), 60.8 (CH_2), 127.8 (C), 142.0 (CH), 168.0 (C), 172.7 (C); *m/z* (CI) 213 (MH^+) 230 (MNH_4^+); HRMS (CI) [MH^+], found: 230.1392. $C_{11}H_{20}NO_4$ requires 230.1391 (0.2 ppm error).

6.3.7. Ethyl 2-(*tert*-butyldimethylsilanyloxymethyl)-2-(2-methoxycarbonylethenyl)-cyclopropanecarboxylate 10g. Using the above procedure for **10c** (but with phosphorane **3a** for 18 h), the *title compound* **10g** was prepared in 64% yield as a colourless oil as an inseparable mixture of cis/trans cyclopropane isomers (trans/*E*:cis/*E* ~1.8:1), R_f 0.40 (petrol–EtOAc, 4:1); ν_{max} (film) 2954, 2931, 2858, 1727, 1650, 1259, 1213, 1178, 1094, 838, 778 cm^{-1}; δ_H (400 MHz, $CDCl_3$) *trans*: 0.00 (3H, s, SiMe), 0.04 (3H, s, SiMe), 0.83 (9H, s, $SiCMe_3$), 1.21–1.26 (3H, m, $CO_2CH_2CH_3$), 1.26–1.30 (1H, m), 1.48–1.53 (1H, m), 1.94 (1H, dd, *J* 8.0 and 6.4 Hz), 3.71 (3H, s, OMe), 3.75 (1H, d, *J* 11.0 Hz), 4.02 (1H, d, *J* 11.0 Hz), 4.04–4.20 (2H, m, $CO_2CH_2CH_3$), 5.97 (1H, d, *J* 15.6 Hz), 6.63 (1H, d, *J* 15.6 Hz); *cis*: 0.04 (3H, s, SiMe), 0.05 (3H, s, SiMe), 0.85 (9H, s, $SiCMe_3$), 1.26–1.30 (3H, m, $CO_2CH_2CH_3$), 1.42 (1H, dd, *J* 4.0 and 8.2 Hz), 1.41–1.50 (1 H, m), 2.14 (1 H, dd, *J* 8.2 and 5.2 Hz), 3.70 (3H, s, OMe), 3.72 (1H, d, *J* 10.4 Hz), 3.82 (1H, d, *J* 10.4 Hz), 4.04–4.20 (2H, m, $CO_2CH_2CH_3$), 5.89 (1H, d, *J* 16.5 Hz), 6.63 (1 H, d, *J* 16.5 Hz); δ_C (100 MHz, $CDCl_3$) *trans*: −5.4 (CH_3), 14.3 (CH_3), 18.2 (C), 18.3 (CH), 25.9 (CH_3), 26.0 (CH), 33.6 (C), 51.6 (CH_3), 61.0 (CH_2), 61.6 (CH_2), 119.3 (CH), 151.2 (CH), 167.2 (C), 170.6 (C); *cis*: −5.4 (CH_3), −5.3 (CH_3), 14.3 (CH_3), 18.3 (C), 19.9 (CH_2), 25.8 (CH), 25.9 (CH_3), 32.3 (C), 51.6 (CH_3), 61.0 (CH_2), 63.4 (CH_2), 120.5 (CH), 147.2 (CH), 166.9 (C), 171.2 (C); *m/z* (CI) 343 (MH^+); HRMS (CI) [MH^+], found: 343.1940. $C_{17}H_{31}O_5Si$ requires 343.1941 (0.1 ppm error).

6.3.8. 3-Benzoyl-cyclopropane-1,2-dicarboxylic acid 1-ethyl ester 2-methyl ester 15a. Using the above procedure for **10c** (but with phosphorane **3a** for 4 h), the *title compound* **15a** was prepared in 83% yield as a colourless oil as an inseparable mixture of cyclopropane isomers (3.2:1), R_f 0.21 (petrol–EtOAc, 6:1); ν_{max} (film) 2980, 2954, 1735, 1679, 1597, 1449, 1372, 1353, 1302, 1211, 1175, 1059, 1020 cm^{-1}; *major isomer*: δ_H (400 MHz, $CDCl_3$) 1.28 (3H, t, *J* 7.3 Hz), 1.30–1.32 (1H, m), 2.72 (1H, d, *J* 5.8 Hz), 3.75 (3H, s), 3.77–3.78 (1H, m), 4.19–4.24 (2H, m), 7.48–7.53 (3H, m), 8.09–8.12 (2H, m); *minor isomer*: δ_H (400 MHz, $CDCl_3$) 2.78 (1H, dd, *J* 5.2 and 9.8 Hz), 3.00 (1H, app t, *J* 5.5 Hz), 3.28 (1H, dd, *J* 5.5 and 9.8 Hz), 3.58 (3H, s), 7.51–7.60 (3H, m), 7.92–7.97 (2H, m) (*the remaining signals were obscured by the major isomer*); δ_C (100 MHz, $CDCl_3$) 14.1 (CH_3), 29.1 (CH), 29.9 (CH), 30.0 (CH), 52.5 (CH_3), 61.6 (CH_2), 128.4 (CH), 128.7 (CH), 133.8 (CH), 136.3 (C), 168.0 (C), 168.4 (C), 194.9 (C); *m/z* (CI) 277 (MH^+); HRMS (CI) [MH^+], found: 277.1077. $C_{15}H_{17}O_5$ requires 277.1076 (−0.5 ppm error).

6.3.9. 2-Benzoyl-3-cyano-cyclopropanecarboxylic acid ethyl ester 15b. Using the above procedure for **10c** (but for 3 h), the *title compound* **15b** was prepared in 80% yield as a yellow oil as a mixture of cyclopropane isomers (3.8:1), *m/z* (CI) 261 (MNH_4^+); HRMS (CI) [MH^+], found: 261.1240. $C_{14}H_{17}N_2O_3$ requires 261.1239 (−0.1 ppm error). These isomers could be partially separated by chromatography (petrol–EtOAc, 4:1) giving *major isomer*: R_f 0.21 (petrol–EtOAc, 4:1); ν_{max} (film) 3062, 2984, 2247, 1734, 1678, 1597, 1450, 1372, 1346, 1295, 1201, 1186, 1014 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.33 (3H, t, *J* 7.0 Hz), 2.56 (1H, dd, *J* 5.5 and 8.9 Hz), 2.66 (1H, dd, *J* 5.5 and 8.9 Hz), 3.74 (1H, app t, *J* 5.5 Hz), 4.30 (2H, q, *J* 7.0 Hz), 7.51–7.55 (2H, m), 7.65–7.68 (1H, m), 8.01–8.03 (2H, m); δ_C (100 MHz, $CDCl_3$) 14.1 (CH_3), 28.4 (CH), 28.5 (CH), 29.3 (CH), 62.4 (CH_2), 115.8 (C), 128.6 (CH), 129.0 (CH), 134.5 (CH), 135.5 (C), 167.0 (C), 192.6 (C); *minor isomer*: R_f 0.18 (petrol–EtOAc, 4:1); ν_{max} (film) 3050, 2983, 2246, 1729, 1672, 1596, 1449, 1368, 1350, 1296, 1199, 1180, 1011 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.32 (3H, t, *J* 7.3 Hz), 2.55 (1H, dd, *J* 5.5 and 8.8 Hz), 3.03 (1H, app t, *J* 5.5 Hz), 3.52 (1H, dd, *J* 5.5 and 8.8 Hz), 4.22–4.29 (2H, m), 7.52–7.66 (3H, m), 8.04–8.05 (2H, m); δ_C (100 MHz, $CDCl_3$) 14.0 (CH_3), 27.4 (CH), 29.2 (CH), 29.3 (CH), 62.4 (CH_2), 115.3 (C), 128.6 (CH), 129.1 (CH), 134.3 (CH), 135.9 (C), 168.7 (C), 190.9 (C).

6.3.10. 2-Benzoyl-3-(methoxy-methyl-carbamoyl)-cyclopropanecarboxylic acid ethyl ester 15c. Using the above procedure for **10c** (but with phosphorane **3d** for 4 h), the *title compound* **15c** was prepared in 50% yield as a yellow oil as an inseparable mixture of cyclopropane isomers (2.2:1), R_f 0.26 (petrol–EtOAc, 3:2); ν_{max} (film) 2980, 2940, 1732, 1686, 1655, 1597, 1449, 1411, 1381, 1335, 1277, 1220, 1183, 1010 cm^{-1}; δ_H (400 MHz, $CDCl_3$) *major isomer*: 1.07 (3H, t, *J* 7.0 Hz), 2.79 (1H, dd, *J* 5.5 and 10.0 Hz), 3.03 (1H, app t, *J* 5.5 Hz), 3.25 (3H, s), 3.29 (1H, dd, *J* 5.5 and 10.0 Hz), 3.83 (3H, s), 4.02 (2H, q, *J* 7.0 Hz), 7.45–7.50 (3H, m), 7.95–8.00 (2H, m); *minor isomer*: 1.30 (3H, t, *J* 7.0 Hz), 3.21 (3H, s), 3.71 (3H, s), 4.22 (2H, q, *J* 7.0 Hz), 7.56–7.58 (3H, m), 8.06–8.11 (2H, m) (*the remaining signals were obscured by the major isomer*); δ_C (100 MHz, $CDCl_3$) *major isomer* 13.9 (CH_3), 23.2 (CH), 29.9 (CH), 32.6 (CH), 32.7 (CH_3), 61.2 (CH_2), 62.1 (CH_3), 128.4 (CH), 128.7 (CH), 133.5 (CH), 136.4 (C), 168.2 (C), 169.7 (C), 192.8 (C); *minor isomer* 14.1 (CH_3), 25.4 (CH),

30.3 (CH), 30.4 (CH), 32.6 (CH_3), 61.5 (CH_2), 62.1 (CH_3), 128.4 (CH), 128.7 (CH), 133.3 (CH), 136.6 (C), 170.4 (C), 171.4 (C), 192.6 (C); *m/z* (CI) 306 (MH^+); HRMS (CI) [MH^+], found: 306.1342. $C_{16}H_{20}NO_5$ requires 306.1341 (−0.1 ppm error).

6.3.11. Ethyl 2,3-dibenzoylcyclopropanecarboxylate 15d. Using the above procedure for **10c** (but with sulfurane **5b** and phosphorane **3e** for 1.5 h), the *title compound* **15d** was prepared in 81% yield as a colourless oil as a mixture of cyclopropane isomers (1.2:1), which were not separated, R_f 0.30/0.25 (petrol–EtOAc, 4:1); ν_{max} (film) 3062, 2984, 1731, 1673, 1449, 1326, 1216, 1020, 738 cm^{-1}; δ_H *major (2,3-trans)*: 1.07 (3H, t, *J* 7.3 Hz), 2.98 (1H, dd, *J* 9.8 and 5.2 Hz), 3.43 (1 H, dd, *J* 9.8 and 5.8 Hz), 3.98–4.15 (3H, m), 7.35–7.60 (6H, m), 8.04 (2H, d, *J* 7.3 Hz), 8.12 (2H, d, *J* 7.3 Hz); *minor (2,3-cis)*: 1.30 (3H, t, *J* 7.0 Hz), 3.22 (1H, t, *J* 5.5 Hz), 3.56 (1H, d, *J* 5.5 Hz), 4.23 (2H, q, *J* 7.0 Hz), 7.35–7.60 (6H, m), 8.04 (4H, d, *J* 7.3 Hz); δ_C (100 MHz, $CDCl_3$) *major (2,3-trans)*: 13.9 (CH_3), 29.1 (CH), 31.6 (CH), 34.8 (CH), 61.4 (CH_2), 128.5 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 133.7 (CH), 133.8 (CH), 136.3 (C), 136.5 (C), 168.0 (C), 192.5 (C), 195.4 (C); *minor (2,3-cis)*: 14.2 (CH_3), 26.6 (CH), 34.6 (CH), 61.7 (CH_2), 128.4 (CH), 128.6 (CH), 133.5 (CH), 136.5 (C), 171.1 (C), 192.4 (C); (*no all-syn-isomer was detected*); *m/z* (CI) 323 (MH^+); HRMS (CI) [MH^+], found: 323.1280. $C_{20}H_{19}O_4$ requires 323.1283 (1.2 ppm error).

6.3.12. 2-Benzoyl-3-(furan-2-carbonyl)-cyclopropanecarboxylic acid ethyl ester 15e. Using the above procedure for **10c** (but with sulfurane **5b** and phosphorane **3a** for 15 h), the *title compound* **15e** was prepared in 70% yield as an orange oil as an inseparable mixture of cyclopropane isomers (1.2:1), R_f 0.14 (petrol–EtOAc, 3:1); ν_{max} (film) 2950, 1735, 1667, 1468, 1323, 1207, 1015, 731 cm^{-1}; *major isomer*: δ_H (400 MHz, $CDCl_3$) 2.92 (1H, dd, *J* 5.5 and 9.5 Hz), 3.44 (1H, dd, *J* 5.8 and 9.5 Hz), 3.69 (3H, s), 3.98 (1H, dd, *J* 5.5 and 5.8 Hz), 6.56–6.57 (1H, m), 7.30 (1H, d, *J* 3.6 Hz), 7.45–7.52 (3H, m), 7.63 (1H, br s), 8.10 (2H, d, *J* 8.0 Hz); *minor isomer*: δ_H (400 MHz, $CDCl_3$) 2.96 (1H, dd, *J* 5.5 and 9.5 Hz), 3.46 (1H, dd, *J* 5.5 and 9.5 Hz), 3.61 (3H, s), 3.86 (1H, t, *J* 5.5 Hz), 6.60–6.61 (1H, m), 7.43 (1H, d, *J* 3.4 Hz), 7.57–7.61 (3H, m), 7.69 (1H, br s), 8.02 (2H, d, *J* 7.9 Hz); δ_C (100 MHz, $CDCl_3$) (there was difficulty in assigning signals to a given isomer, but the following were observed) 28.5 (CH), 28.7 (CH), 30.6 (CH), 31.1 (CH), 32.8 (CH), 33.5 (CH), 51.9 (CH_3), 52.0 (CH_3), 112.3 (CH), 112.5 (CH), 128.3 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 133.6 (CH), 133.8 (CH), 136.1 (C), 136.2 (C), 147.2 (CH), 147.2 (CH), 147.7 (CH), 147.7 (CH), 152.1 (C), 152.3 (C), 168.2 (C), 168.4 (C), 181.6 (C), 183.7 (C), 192.6 (C), 195.5 (C); *m/z* (CI) 299 (MH^+); HRMS (CI) [MH^+], found: 299.0917. $C_{17}H_{15}O_5$ requires 299.0919 (0.7 ppm error).

6.3.13. 2-Acetyl-3-benzoyl-cyclopropanecarboxylic acid ethyl ester 15f. Using the above procedure for **10c** (but with sulfurane **5b** and phosphorane **3e** for 2.5 h), the *title compound* **15f** was prepared in 60% yield as an orange oil as a mixture of cyclopropane isomers (2.7:1), ν_{max} (film) 2955, 1735, 1709, 1685, 1597, 1450, 1372, 1359, 1301, 1191, 1003 cm^{-1}; *m/z* (CI) 261 (MH^+); HRMS (CI) [MH^+], found: 261.1127. $C_{15}H_{17}O_4$ requires 261.1125 (0.7 ppm error). This mixture could be partially separated by chromatography (petrol–EtOAc, 4:1) giving *major isomer*: R_f 0.16 (petrol–EtOAc, 4:1); δ_H (400 MHz, $CDCl_3$) 1.03 (3H, t, *J* 7.0 Hz), 1.22–1.29 (1H, m), 2.40 (3H, s), 2.72–2.76 (1H, m), 3.21–3.28 (1H, m), 3.97 (2H, q, *J* 7.0 Hz), 7.39–7.55 (3H, m), 7.89–7.96 (2H, m); δ_C (100 MHz, $CDCl_3$) 13.8 (CH_3), 31.2 (CH_3), 31.6 (CH), 31.9 (CH), 34.5 (CH), 61.2 (CH_2), 128.3 (CH), 128.6 (CH), 133.5 (CH), 136.0 (C), 167.7 (C), 192.0 (C), 204.1 (C); *minor isomer*: R_f 0.11 (petrol–EtOAc, 4:1); δ_H (400 MHz, $CDCl_3$) 2.31 (3H, s), 2.93–2.98 (1H, m), 3.33 (1H, d, *J* 5.5 and 10.0 Hz), 3.78 (1H, dd, J 4.3 and 5.5 Hz), 4.13–4.21 (2H, m), 7.97–8.03 (2H, m) (*the remaining signals were obscured by the major isomer*); δ_C (100 MHz, $CDCl_3$) 14.1 (CH_3), 29.3 (CH_3), 30.6 (CH), 34.2 (CH), 36.9 (CH), 61.5 (CH_2), 128.6 (CH), 128.7 (CH), 136.2 (CH), 136.3 (C), 1707.7 (C), 195.1 (C), 201.2 (C).

6.3.14. Cyclopropane-3-(cyclohexanecarbonyl)-1,2-dicarboxylic acid 1-ethyl ester 2-methyl ester 15g. Using the above procedure for **10c** (but with phosphorane **3a** for 15 h), the *title compound* **15g** was prepared in 78% yield as essentially a single diastereomer as a clear oil; R_f 0.28 (petrol–EtOAc, 3:1); ν_{max} (film) 2934, 2854, 1735, 1703, 1450, 1373, 1294, 1174 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.24 (3H, t, *J* 7.0 Hz), 1.28–1.34 (4H, m), 1.63–1.78 (4H, m), 1.93–1.95 (2H, m), 2.46 (2H, d, *J* 5.5 Hz), 2.52–2.58 (1H, m), 3.07 (1H, t, *J* 5.5 Hz), 3.70 (3H, s), 4.15 (2H, q, *J* 7.0 Hz); δ_C (100 MHz, $CDCl_3$) 13.7 (CH_3), 25.2 (CH_2), 25.5 (CH_2), 27.5 (CH_2), 29.2 (CH), 29.4 (CH), 30.2 (CH), 51.5 (CH), 52.3 (CH_3), 61.4 (CH_2), 168.5 (C), 168.9 (C), 209.0 (C); *m/z* (CI) 283 (MH^+); HRMS (CI) [MH^+], found: 283.1546. $C_{15}H_{23}O_5$ requires 283.1545 (−0.4 ppm error).

6.3.15. 2-Benzoyl-3-(3-phenyl-propionyl)-cyclopropanecarboxylic acid ethyl ester 15h. Using the above procedure for **10c** (but with phosphorane **3a** for 15 h), the *title compound* **15h** was prepared as essentially a single diastereomer in 51% yield as a colourless oil; R_f 0.24 (petrol–EtOAc, 3:1); ν_{max} (film) 2909, 1735, 1710, 1454, 1373, 1304, 1197, 912, 732 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.24 (3 H, t, *J* 7.0 Hz), 2.49 (2H, d, *J* 5.5 Hz), 2.92–2.94 (3H, m), 3.00 (2H, d, *J* 5.5 Hz), 3.69 (3H, s), 4.14 (2H, q, *J* 7.0 Hz), 7.16–7.17 (1H, m), 7.19–7.20 (2H, m), 7.26–7.27 (1H, m), 7.28–7.29 (1H, m); δ_C (100 MHz, $CDCl_3$) 13.4 (CH_3), 28.9 (CH_2), 29.1 (CH), 29.3 (CH), 31.1 (CH), 45.2 (CH_2), 52.0 (CH_3), 61.1 (CH_2), 126.2 (CH), 128.2 (CH), 128.5 (CH), 140.3 (C), 167.9 (C), 168.4 (C), 205.1 (C); *m/z* (CI) 305 (MH^+); HRMS (CI) [MH^+], found: 305.1386. $C_{17}H_{21}O_5$ requires 305.1389 (1.0 ppm error).

6.3.16. Diethyl 3-(11,17-dihydroxy-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene-17-carbonyl)-cyclopropane-1,2-dicarboxylate 15i. Using the above procedure for **10c** (but with phosphorane **3e** for 2.5 h), the *title compound* **15i** was prepared in 78% yield as a colourless oil as an inseparable mixture (5:1) of cyclopropane isomers with one major, R_f 0.34 (petrol–EtOAc, 4:1); ν_{max} (film) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.91 (3H, s), 0.95–1.02 (1H, m), 1.17–1.31 (7H, m), 1.32–1.55 (5H, m), 1.66–1.88 (4H, m), 1.92–2.37 (4H, m), 1.98 (3H, s), 2.37–2.51 (3H, m),

2.68–2.84 (2H, m), 3.43 (1H, dd (app t), *J* 5.5 Hz), 4.03–4.15 (5H, m), 4.41 (1H, br s), 5.62 (1H, s); δ_C (100 MHz, $CDCl_3$) 14.1 (CH_3), 14.2 (CH_3), 18.0 (CH_3), 21.0 (CH_3), 23.9 (CH_2), 29.2 (CH), 30.0 (CH), 31.4 (CH), 31.7 (CH), 32.1 (CH_2), 32.8 (CH_2), 33.1 (CH_2), 33.8 (CH_2), 34.9 (CH_2), 39.3 (C), 40.0 (CH_2), 47.6 (C), 51.8 (CH), 56.0 (CH), 61.6 (CH_2), 61.7 (CH_2), 68.3 (CH), 90.0 (C), 122.3 (CH), 167.8 (C), 168.3 (C), 172.7 (C), 199.9 (C), 207.4; *m/z* (CI) 517 (MH^+); HRMS (CI) [MH^+], found: 517.2794. $C_{29}H_{41}O_8$ requires 517.2801 (1.5 ppm error).

6.3.17. Methylsulfanyl-acetic acid 3-allyl-2-methyl-4-oxo-cyclopent-2-enyl ester 21. Dicyclohexylcarbodiimide (3.31 g, 16.0 mmol) in THF (20 mL) was added to a solution of alcohol **20**[11] (2.03 g, 13.4 mmol), (methylthio)acetic acid (1.28 mL, 14.7 mmol), and DMAP (163 mg, 1.3 mmol) in THF (90 mL) at rt under a nitrogen atmosphere. Precipitation of DCU was observed after a few minutes. After 2 h, the reaction was filtered through Celite® washing with EtOAc, and then the filtrate concentrated in vacuo. Purification by flash column chromatography (petrol–EtOAc, 4:1) gave the *title compound* **21** (2.52 g, 79%) as a yellow oil; R_f 0.48 (petrol–EtOAc, 3:1); ν_{max} (film) 2953, 1734, 1710, 1655, 1638, 1385, 1268, 1130, 1001 cm^{-1}; δ_H (400 MHz, C_6D_6) 1.57 (3H, s), 1.81 (3H, s), 2.07 (1H, dd, *J* 1.9 and 18.5 Hz), 2.49 (1H, dd, *J* 6.0 and 18.5 Hz), 2.66 (2H, s), 2.80 (2H, t, *J* 5.6 Hz), 4.88–4.97 (2H, m), 5.34 (1H, br d, *J* 6.0 Hz), 5.70 (1H, ddt, *J* 6.3, 10.0 and 16.7 Hz); δ_C (100 MHz, C_6D_6) 12.8 (CH_3), 15.4 (CH_3), 30.3 (CH_2), 34.6 (CH_2), 40.7 (CH_2), 73.0 (CH), 115.2 (CH_2), 127.6 (C), 133.4 (CH), 141.1 (C), 163.2 (C), 169.0 (C); *m/z* (CI) 241 (MH^+), 258 (MNH_4^+); HRMS (CI) [MNH_4^+], found: 241.0894. $C_{12}H_{17}O_3S$ requires 241.0898 (2.0 ppm error).

6.3.18. (3-Allyl-2-methyl-4-oxo-cyclopent-2-enyloxycarbonylmethyl)-dimethylsulfonium tetrafluoroborate 22. Ester **21** (661 mg, 2.75 mmol) was dissolved in iodomethane (15 mL). Silver tetrafluoroborate (574 mg, 2.95 mmol) was added in one portion and the reaction stirred in the dark for 3 h at rt, after which time stirring was stopped and the precipitate allowed to settle. The supernatant was decanted carefully and the residue dried in vacuo before being extracted with MeOH (three times). Filtration and removal of the MeOH in vacuo (water bath <35 °C) gave the *title compound* **22** (848 mg, 90%) as a yellow oil; ν_{max} (film) 3033, 2944, 1736, 1709, 1655, 1638, 1432, 1388, 1312, 1194, 1064, 922 cm^{-1}; δ_H (400 MHz, CD_3OD) 2.10 (3H, s), 2.44 (1H, dd, *J* 1.6 and 18.6 Hz), 2.91 (1H, dd, *J* 6.1 and 18.6 Hz), 2.99–3.02 (8H, m), 4.50 and 4.57 (2H, AB q, *J* 16.5 Hz), 4.98–5.04 (2H, m), 5.77 (1H, ddt, *J* 6.3, 10.0 and 16.7 Hz), 5.86 (1H, d, *J* 6.1 Hz); δ_C (100 MHz, CD_3OD) 14.0 (CH_3), 25.7 (CH_3), 27.8 (CH_2), 41.9 (CH_2), 46.4 (CH_2), 77.6 (CH), 116.4 (CH_2), 134.7 (CH), 143.2 (C), 166.0 (C), 166.7 (C), 205.3 (C); *m/z* (FAB) 255 (M^+), 597 (2 M^++BF_4^-); HRMS (FAB) [M^+], found: 255.1062. $C_{13}H_{19}O_3S$ requires 255.1055 (−3.0 ppm error).

6.3.19. (Dimethyl-λ⁴-sulfanylidene)-acetic acid 3-allyl-2-methyl-4-oxo-cyclopent-2-enyl ester 23. Salt **22** (836 mg, 2.44 mmol) was suspended in $CHCl_3$ (4 mL), and to this was added a suspension of powdered NaOH (98 mg, 2.44 mmol) in satd aq K_2CO_3 (2 mL). The biphasic solution was stirred at rt for 20 min before being filtered through Celite®, and washed with CH_2Cl_2. The filtrate was dried ($MgSO_4$) and concentrated in vacuo to give the title compound **23** (617 mg, 99%) as a pale yellow oil, which was used immediately; ν_{max} (film) 2981, 2923, 1703, 1647, 1636, 1616, 1431, 1383, 1366, 1317, 1190, 1129, 1055, 1031, 996, 916 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.99 (3H, s), 2.26 (1H, dd, *J* 1.8 and 18.6 Hz), 2.73 (6H, s), 2.76 (1H, dd, *J* 6.1 and 18.6 Hz), 2.92 (2H, d, *J* 6.4 Hz), 2.95 (1H, br s), 4.93–4.99 (2H, m), 5.66–5.78 (2H, m); δ_C (100 MHz, $CDCl_3$) 14.0 (CH_3), 27.0 (CH_2), 30.5 (CH_3), 30.6 (CH_3), 32.8 (CH), 42.3 (CH_2), 70.2 (CH), 115.5 (CH_2), 133.9 (CH), 140.0 (C), 168.5 (C), 169.3 (C), 205.1 (C).

6.3.20. 2-((*E*)-2-Methoxycarbonyl-propenyl)-cyclopropanecarboxylic acid 3-allyl-2-methyl-4-oxo-cyclopent-2-enyl ester 24. To a solution of allyl alcohol **1b** (77 μL, 1.13 mmol) in CH_2Cl_2 (7 mL) was added powdered 4 Å molecular sieves (1.13 g), dimethylsulfurane **23** (573 mg, 2.26 mmol) in CH_2Cl_2 (3 mL), (carbomethoxyethylene)triphenylphosphorane **3c** (471 mg, 1.35 mmol) and manganese dioxide (981 mg, 11.3 mmol). The mixture was heated at reflux for 3 h, and then cooled to rt. The crude mixture was filtered through Celite® and the residue washed with CH_2Cl_2. After removal of the solvent, the resulting yellow oil was purified by flash column chromatography (petrol–Et_2O, 2:1) to give the *title compound* **24** (206 mg, 57%) as a mixture of cyclopropane isomers (~3.1:1) as a colourless oil, R_f 0.21 (petrol–Et_2O, 2:1); ν_{max} (film) 2922, 1716, 1655, 1437, 1409, 1386, 1255, 1173, 916, 734 cm^{-1}; *m/z* (CI) 319 (MH^+), 336 (MNH_4^+); HRMS (CI) [MH^+], found 319.1545. $C_{18}H_{23}O_5$ requires 319.1546 (0.2 ppm error). *NMR data for major isomer only*: δ_H (500 MHz, $CDCl_3$) 1.12–1.15 (1H, m), 1.57 (1H, ddd, *J* 5.1, 10.1, 14.5 Hz), 1.83 (1H, dd, *J* 5.1, 8.5 Hz), 1.94 (3H, d, *J* 5.0Hz), 2.01 (3H, s), 2.19–2.29 (2H, m), 2.85 (1H, dd, *J* 6.3, 18.6 Hz), 2.97 (2H, d, *J* 6.3 Hz), 3.70 (3H, s), 4.98–5.01 (2H, m), 5.70–5.73 (1H, m), 5.76 (1H, tdd, *J* 6.3, 9.5, 13.0 Hz), 6.09 (1H, app t, *J* 9.0 Hz); δ_C (125 MHz, $CDCl_3$) 12.7 (CH_3), 13.8 (CH_3), 16.7 (CH_2), 22.3 (CH), 22.4 (CH), 27.1 (CH_2), 41.5 (CH_2), 51.8 (CH_3), 73.4 (CH), 116.0 (CH_2), 128.4 (C), 133.4 (CH), 141.3 (CH), 141.7 (C), 165.2 (C), 168.0 (C), 172.6 (C), 203.3 (C).

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