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Catalytic cyclopropanation of electron deficient alkenes mediated by chiral and achiral sulfides: scope and limitations in reactions involving phenyldiazomethane and ethyl diazoacetate

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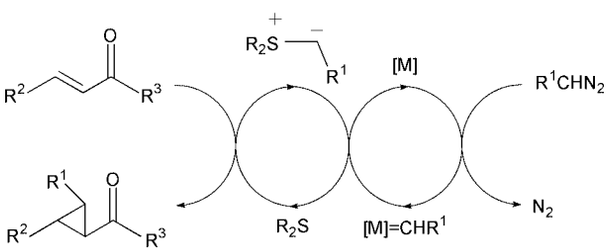
Phenyldiazomethane reacts with electron deficient alkenes in the presence of catalytic amounts of transition metal catalyst [$Rh_2(OAc)_4$ was better than $Cu(acac)_2$] and catalytic amounts of sulfide to give cyclopropanes. Pentamethylene sulfide was found to be superior to tetrahydrothiophene and the optimum solvent was toluene. Under these optimised conditions a range of enones were cyclopropanated in high yields. Cyclic enones and acrylates were not successful in this process. The use of the chiral 1,3-oxathiane derived from camphorsulfonyl chloride in 2 steps in this process furnished cyclopropanes in good yield and very high enantiomeric excess (>97% ee). The absolute stereochemistry of cyclopropane **10** was proven by X-ray analysis and the origin of the stereochemical induction has been rationalised. Extension of this work to include diazoesters was partially successful. Again pentamethylene sulfide was found to be superior to tetrahydrothiophene, but this time both $Rh_2(OAc)_4$ and $Cu(acac)_2$ were found to be equally effective. Enones, fumarates and unsaturated nitro compounds worked well but simple acrylates and unsaturated aldehydes were not effective substrates. Control experiments were conducted in which the stabilised ylide was isolated and reacted with the less successful substrates and, whilst unsaturated aldehydes still gave low yields, simple acrylates gave high yields of the corresponding cyclopropane. The use of the chiral 1,3-oxathiane was not successful with these more stable diazo compounds.

Introduction

Methods for the catalytic asymmetric synthesis of cyclopropanes from acyclic precursors have received considerable attention due to the prevalence of such motifs in biologically important molecules.[1] Towards this goal, high enantioselectivity has been achieved in reactions of diazo compounds with alkenes in the presence of chiral transition metal complexes (Cu–Schiff base,[2] Cu–semicorrin,[3] Cu–bis(oxazoline),[4] Cu–bipyridine,[5] Co–bis(dioxime),[6] Co–Salen,[7] $Rh_2(5S\text{-MEPY})_4$,[8] and Ru–Pybox[9]). Advances have also been made in asymmetric Simmons–Smith cyclopropanation of allylic alcohols using alkylborane complexes of tartaramides as promoters.[10] However, in all the above cases, the metal carbenoid only reacts efficiently with electron rich alkenes.[11] Methods are therefore required for the cyclopropanation of electron deficient alkenes. The asymmetric cyclopropanation of electron deficient alkenes has been achieved using stoichiometric amounts of sulfonium[12] and aminosulfoxonium ylides,[13] but in the latter case the reagent cannot be recycled.

We previously described a new catalytic process for recycling sulfur ylides and used this technology in catalytic asymmetric epoxidation[14] and aziridination[15] of carbonyl and imine compounds, respectively. We therefore considered the potential application of this chemistry to catalytic asymmetric cyclopropanation of electron deficient alkenes (Scheme 1). In this paper we describe the realisation of this process, and our results in full.[16]



Scheme 1

Results and discussion

We initially tested (*E*)-chalcone **1** and 4-phenylbut-3-en-2-one **2** with phenyldiazomethane (slow addition) using a stoichiometric amount of tetrahydrothiophene and catalytic amounts of $Cu(acac)_2$ under conditions that were similar to the successful epoxidation–aziridination process (Table 1, entries 1, 2), but were surprised at the lack of success in cyclopropanation. Only stilbenes and benzaldehyde azine were isolated, along with recovered enone and sulfide. However, a marked improvement was observed using $Rh_2(OAc)_4$ in place of $Cu(acac)_2$ (Table 1, entries 3, 4). Unlike epoxidation and aziridination where copper or rhodium based catalysts can be used, cyclopropanation seems to require rhodium. This observation may be due to the lower reactivity of enones coupled with the *ability of copper salts to react with sulfur ylides to give back metal carbenes*.[17] Indeed, this reaction has been utilised to cyclopropanate electron rich alkenes with sulfur ylides.[17] Thus, with $Cu(acac)_2$, a higher concentration of metal carbene can be expected based

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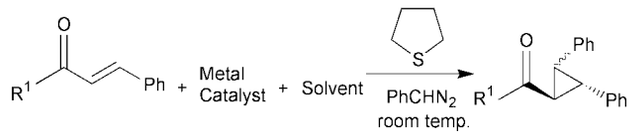
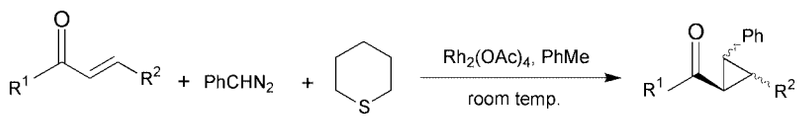
Table 1 Effect of metal catalyst and solvent on yield in enone cyclopropanation[a]



Entry	Enone	R^1	Metal catalyst	Solvent	Yield (%)[b]	Isomeric ratio[c]
1	**1**	Ph	$Cu(acac)_2$	CH_2Cl_2	0	—
2	**2**	Me	$Cu(acac)_2$	CH_2Cl_2	0	—
3	**1**	Ph	$Rh_2(OAc)_4$	CH_2Cl_2	40	1:1
4	**2**	Me	$Rh_2(OAc)_4$	CH_2Cl_2	41	1:1
5	**1**	Ph	$Rh_2(OAc)_4$	Toluene	40	1:1
6	**1**	Ph	$Rh_2(OAc)_4$	MeCN	30	1:1
7	**1**	Ph	$Rh_2(OAc)_4$	THF	41	1:1
8	**1**	Ph	$Rh_2(OAc)_4$	Hexane	17	1:1

[a] Phenyldiazomethane (1.5 eq.) added over 3 h to mixture of enone (1 eq.), tetrahydrothiophene (1 eq.), $Rh_2(OAc)_4$ (0.01 eq.) or $Cu(acac)_2$ (0.05 eq.) in appropriate solvent (1 M in enone). [b] Combined yield of *cis* and *trans* isomers. [c] Ratio determined by ^1H NMR spectroscopy.

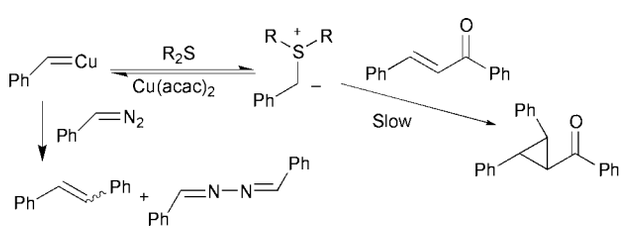
Table 2 Effect of solvent, stoichiometry and addition time on yield in enone cyclopropanation[a]



Entry	Enone	R^1	R^2	*t*/h	Sulfide (equiv.)	Yield (%)[b]	Isomeric ratio[c]
1	**1**	Ph	Ph	3	1.0	92	4:1
2	**2**	Me	Ph	3	1.0	80	4:1
3	**1**	Ph	Ph	3	0.2	20	4:1
4	**1**	Ph	Ph	12	0.2	70	4:1
5	**2**	Me	Ph	12	0.2	82	4:1
6	**5**	Ph	Me	12	0.2	50	1:1:1
7	**6**	Me	Me	12	0.2	30	1:1:1

[a] Phenyldiazomethane (1.5 eq.) added over 3 or 12 h to a mixture of enone (1 eq.), pentamethylene sulfide (1 eq./0.2 eq.), $Rh_2(OAc)_4$ (0.01 eq.) in toluene (1 M in enone). [b] Combined yield of diastereoisomers. [c] Ratio determined by ^1H NMR spectroscopy.

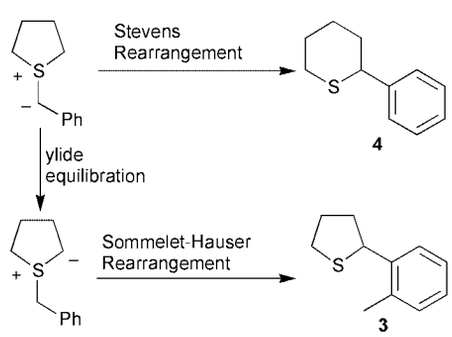
on the above precedent and this will lead to greater amount of stilbenes and benzaldehyde azine (Scheme 2).



Scheme 2

A brief survey of solvents (Table 1, entries 4–8) revealed that there was little influence on yield and diastereoselectivity, providing the reaction was homogeneous [the reaction was heterogeneous in hexane (Table 1, entry 8)]. Toluene became the solvent of choice as it gave comparable results to that obtained with dichloromethane and as phenyldiazomethane is prepared as a toluene solution,[18] this simplified the experimental procedure.

We were surprised at the moderate yields obtained in the cyclopropanation reactions (Table 1), since the related epoxidation and aziridination reactions proceeded in much higher yield. Further examination of the reaction indicated that in addition to the cyclopropane, sulfide **3** had also been formed. This sulfide presumably results from ylide equilibration followed by a Sommelet–Hauser rearrangement (Scheme 3).[19] Sulfide **4** resulting from a Stevens rearrangement was not observed.[19] The rearranged sulfide **3** had not been previously observed in epoxidation and aziridination. We presume that the



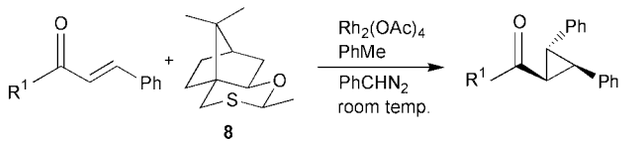
Scheme 3

slower reacting enones provided time for ylide equilibration and rearrangement to occur.

In an effort to reduce the extent of this side reaction we sought sulfides which had a lower propensity for ylide equilibration and were guided by Fava's studies on the rate of deuterium exchange of the α-protons of cyclic sulfonium salts.[20] He showed that the rate of exchange of the α-protons in a five membered ring was 4.3×10^{-5} M^{-1} s^{-1}, whilst in a six membered ring the rate was an order of magnitude slower at 6.3×10^{-6} M^{-1} s^{-1}. We therefore replaced tetrahydrothiophene with pentamethylene sulfide and observed a remarkable increase in yield of cyclopropanes (Table 2, entries 1, 2). In addition, a notable increase in diastereoselectivity was also observed.

We next explored the use of sub-stoichiometric quantities of sulfide. Initially, the same conditions employed for the stoichiometric reactions were used (Table 2, entry 1), but this led to low

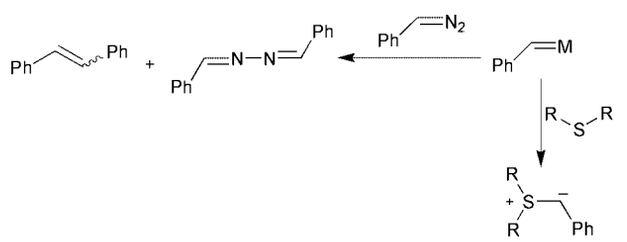
Table 3 Enantioselective cyclopropanation of enones[a]



Entry	Enone	R^1	Sulfide (equiv.)	Yield (%)[b]	Isomeric ratio[c]	Ee (%)[d]	$[\alpha]_D^{25}$[e]
1	**1**	Ph	1.0	60	4:1	97	−136
2	**1**	Ph	0.2	38	4:1	97	−136
3	**2**	Me	1.0	55	4:1	>98	−65
4	**2**	Me	0.2	14	4:1	>98	−65
5	**9**	*p*-BrC_6H_4	1.0	35	4:1	>98	−105

[a] Phenyldiazomethane (1.5 eq.) added over 12 h to mixture of enone (1 eq.), sulfide (0.2 or 1 eq.), $Rh_2(OAc)_4$ (0.01 eq.) in toluene (1 M in enone). [b] Combined yield of both diastereoisomers. [c] Ratio determined by ^1H NMR spectroscopy. [d] Determined using HPLC. [e] Conditions: $c = 1.0$, CH_2Cl_2.

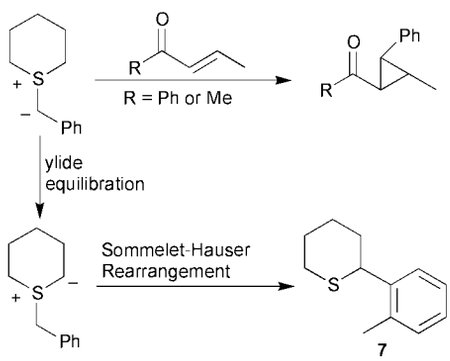
yields of cyclopropane (Table 2, entry 3) and large quantities of stilbenes and benzaldehyde azine. Sulfur ylide formation is dependent on sulfide concentration and as the concentration is reduced, side reactions of the metal carbenoid with phenyldiazomethane, to form stilbenes and benzaldehyde azine, begin to compete (Scheme 4). By increasing the addition time of



Scheme 4

the phenyldiazomethane, the concentration of phenyldiazomethane is reduced and more time is allowed for turnover of sulfide. Indeed, when longer addition times were employed a significant increase in yield of the cyclopropane was obtained, with a concomitant reduction in the quantity of stilbene and benzaldehyde azine (Table 2, entry 4).

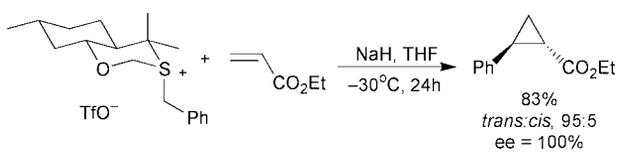
Having achieved cyclopropanation of (*E*)-chalcone **1** in high yields with catalytic quantities of sulfide we decided to extend the methodology to include other Michael acceptors and moderate to good yields were obtained (Table 2, entries 5–7). With enones **5** and **6** a small amount of the rearranged sulfide **7** was observed, indicating that these enones must be less electrophilic than **1** and **2** (Scheme 5). In all reactions, starting material



Scheme 5

was recovered and the yields of the cyclopropanes were quantitative when calculated by mass balance. Cyclopent-2-en-1-one, cyclohex-2-en-1-one, 4-methylpent-3-en-2-one, and several acrylates did not undergo cyclopropanation; only the rearranged sulfide **7** was isolated.

There is one example of the use of a benzylsulfonium ylide for the cyclopropanation of ethyl acrylate, in which a high yield and stereoselectivity were achieved.[12] In this example, ylide equilibration is blocked on one side of the sulfur moiety and significantly retarded by the oxygen on the other side (Scheme 6).



Scheme 6

These factors presumably contribute to the success of this reaction.

Having developed the catalytic cyclopropanation reaction of enones, we sought to render the process asymmetric through the use of chiral sulfides. The sulfide chosen was the 1,3-oxathiane **8**, which had been shown to be a very effective sulfide for asymmetric epoxidation[14] and aziridination.[15] Sulfide **8** was tested with (*E*)-chalcone **1** and enone **2** using stoichiometric and catalytic quantities of sulfide. Cyclopropanes were obtained in moderate to good yields, with the same diastereoselectivity as observed with pentamethylene sulfide and with excellent levels of enantioselectivity (Table 3). The yields were invariably lower when sub-stoichiometric amounts of sulfide were employed, but the enantioselectivities were identical, indicating that no background (non-sulfur ylide mediated) cyclopropanation was occurring. Indeed, in the absence of sulfide no cyclopropanation occurred, proving that all the cyclopropane is derived from the intermediacy of the sulfur ylide. The reduced yields with sub-stoichiometric amounts of sulfide indicate that the sulfide is not turning over efficiently and it is believed that some decomposition/alternative transformation of the sulfide also occurs. Indeed, although the sulfide **8** could be reisolated from the reaction in 80% using stoichiometric amounts of sulfide, it was only recovered in less than 5% yield when using 20 mol% sulfide. The use of the chiral sulfide with enones 1-phenylbut-2-en-1-one **5** and pent-3-en-2-one **6** was unsuccessful.

In order to determine the absolute stereochemistry of the cyclopropanes the *p*-bromo derivative of (*E*)-chalcone[21] was used, and treatment with phenyldiazomethane yielded the corresponding cyclopropanes (Table 3, entry 5). The major diastereomer (2*RS*,3*RS*)-**10** was then subjected to X-ray analysis and the absolute stereochemistry of the cyclopropane ring was determined to be (2*R*,3*R*) (Fig. 1).

To account for the excellent enantioselectivity the following model is proposed (Scheme 7). The sulfur ylide preferentially adopts conformations in which the filled orbital on carbon is orthogonal to the lone pair on sulfur and of these two conformers **11a** is preferred over **11b** due to 1,3-diaxial interactions. The ylide reacts with high face selectivity as a result of both

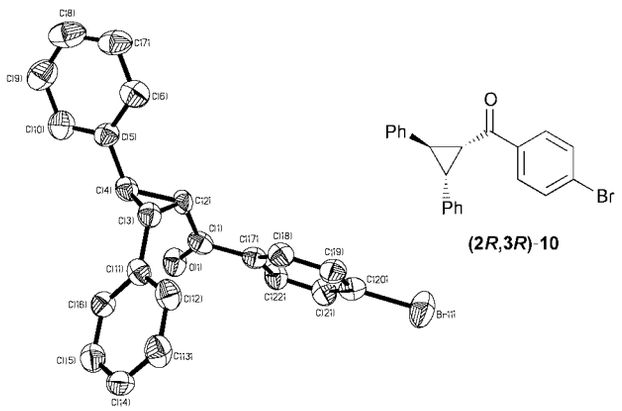
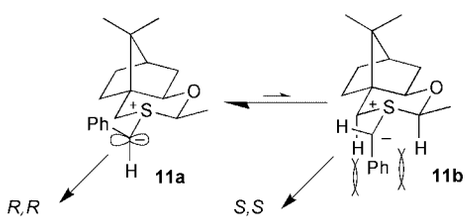


Fig. 1 ORTEP drawing of cyclopropane (2*R*,3*R*)-**10**.

steric and electronic control and indeed the face selectivity is believed to be complete. The minor enantiomer is believed to originate from the less favoured conformer **11b**, which again reacts with the same high face selectivity. The same model was used to rationalise the outcome of epoxidation reactions using the same sulfide.[14] The higher enantioselectivity observed in cyclopropanation compared to epoxidation must be due to a bigger difference in the rates of cyclopropanations of **11a** and **11b**, which in turn result from using less reactive electrophiles (enones being less reactive than aldehydes). To account for the diastereoselectivity we need to consider which face of the enone (*Re* or *Si* face) is preferentially attacked. Two possible approaches of the enone to the ylide are given in Scheme 8 and these lead to the two diastereomeric betaines which will then ring close to give the cyclopropane. Path A places the largest groups opposite each other and will therefore be preferred over path B. This accounts for the formation of the major diastereoisomer.

We also considered the possibility of extending the process to include diazoesters as there were numerous examples of the reactions of ester-stabilised sulfonium ylides with electron deficient alkenes.[22] Furthermore, as a large number of biologically important cyclopropanes have acid functional groups directly attached to them (Fig. 2), we were particularly keen to explore this chemistry. Although the formation of stabilised ylides from the reaction of ethyl diazoacetate with a sulfide is well documented and the reaction of the corresponding ylide with Michael acceptors reported, the compatibility of the two processes in the same reaction remained to be established.



Scheme 7

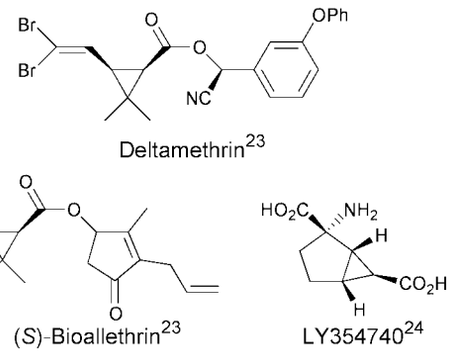
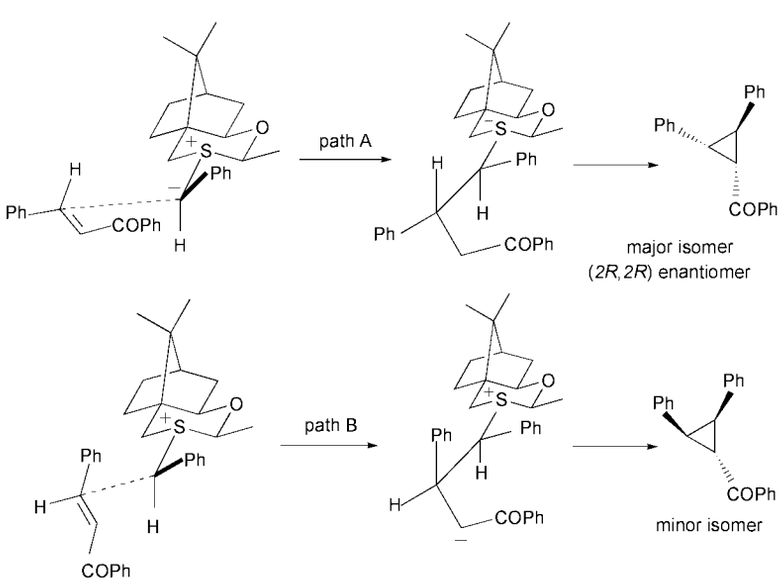


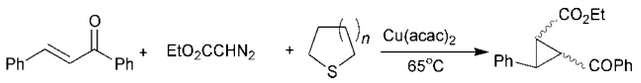
Fig. 2

(*E*)-Chalcone **1** was selected as our test substrate using ethyl diazoacetate. Reactions had to be performed at 60 °C as no decomposition of ethyl diazoacetate occurred at lower temperatures with either $Cu(acac)_2$ or $Rh_2(OAc)_4$. In contrast to the use of phenyldiazomethane, ethyl diazoacetate gave similar results for the cyclopropanation of (*E*)-chalcone **1** with $Rh_2(OAc)_4$ and $Cu(acac)_2$ and so further studies were conducted with $Cu(acac)_2$. In order to find the optimum conditions for cyclopropanation, sulfide structure, solvents and the period of addition of ethyl diazoacetate were varied (Table 4). As with phenyldiazomethane, pentamethylene sulfide was found to be superior to tetrahydrothiophene but the difference was not as marked (compare entries 1, 2 with 3, 4). Longer addition times of ethyl diazoacetate were found to increase yields presumably because this led to a lower concentration of ethyl diazoacetate and higher concentration of sulfide (allowing time for the sulfide to turnover) (Table 4, entries 5–8). Both of these factors would increase the likelihood of ylide formation and reduce the likelihood of fumarate/maleate formation (Scheme 9). Indeed when the yields were low, large quantities of diethyl fumarate and diethyl maleate were formed.



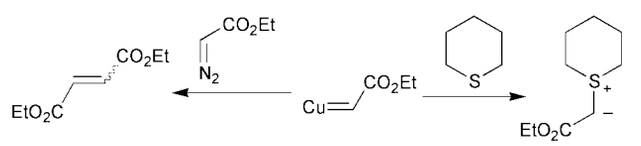
Scheme 8

Table 4 Effect of addition time and solvent on yield in cyclopropanation of chalcone[a]



Entry	Sulfide (*n*)	*t*/h	Solvent	Yield (%)[b]	Isomeric ratio[c]
1	**1**	3	THF	12	4:2:1
2	**1**	6	THF	20	4:2:1
3	**2**	3	THF	15	4:2:1
4	**2**	6	THF	38	4:2:1
5	**2**	3	THF	10	4:2:1
6	**2**	6	THF	38	4:2:1
7	**2**	16	THF	70	4:2:1
8	**2**	24	THF	71	4:2:1
9	**2**	24	MeCN	70	4:2:1
10	**2**	24	1,2-DCE	72	4:2:1

[a] Ethyl diazoacetate (1 eq.) added to mixture of enone (1 eq.), sulfide (1 eq.) and $Cu(acac)_2$ (0.05 eq.) in the appropriate solvent (1 M in enone). [b] Combined yield of all isomers. [c] Ratio determined by ^1H NMR spectroscopy.



Scheme 9

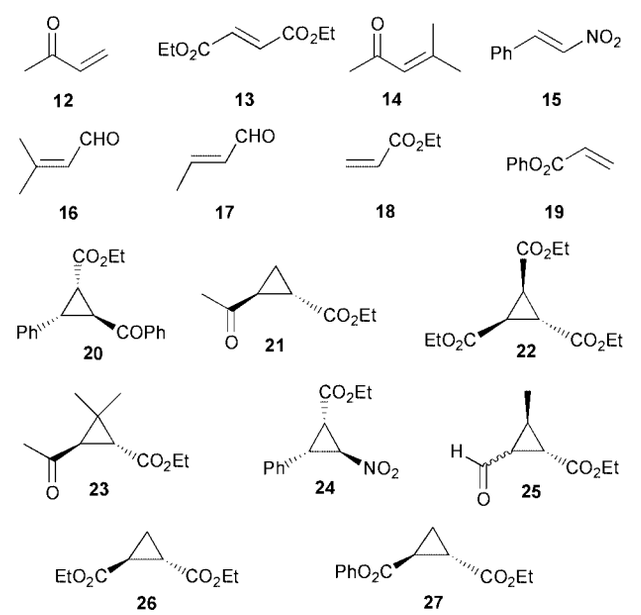
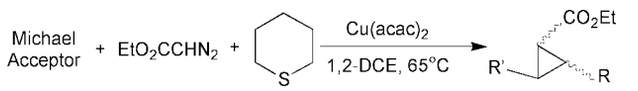


Fig. 3

As with phenyldiazomethane, the choice of solvent did not influence the yield or diastereoselectivities of the process significantly and 1,2-dichloroethane was chosen for further studies. Having found conditions that gave high yields for cyclopropanation, we tested a range of Michael acceptors with stoichiometric and catalytic loadings of sulfide (Table 5). Substrates that worked well with stoichiometric amounts of sulfide (**1**, **12**, **13**, Fig. 3) also worked well under catalytic conditions. Unsaturated ketone **14** and nitrostyrene **15** also gave the corresponding cyclopropane, but in low yields. However, unsaturated aldehydes **16**, **17** and acrylates **18**, **19** did not give any cyclopropane. With substrates which were ineffective in our catalytic process, control experiments were conducted to test the efficiency of the final step of the process (ylide formation was

Table 5 Cyclopropanation of Michael acceptors with ethyl diazoacetate[a]



Entry	Michael acceptor	Sulfide (eq.)	Product	Yield (%)[b]	Isomeric ratio[c]
1	**1**	1.0	**20**	72	4:2:1
2	**1**	0.2	**20**	77	4:2:1
3	**12**	1.0	**21**	64	>95:5
4	**12**	0.2	**21**	43	>95:5
5	**13**	1.0	**22**	68	>95:5
6	**13**	0.2	**22**	68	>95:5
7	**14**	1.0	**23**	5	>95:5
8	**15**	1.0	**24**	38	5:4:2

[a] Ethyl diazoacetate (1 eq.) added to mixture of enone (1 eq.), sulfide (1 eq.), $Cu(acac)_2$ (0.05 eq.) in 1,2-dichloroethane (1 M in enone). [b] Combined yield of all isomers. [c] Ratio determined by ^1H NMR spectroscopy.

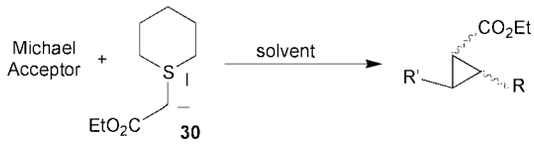
clearly efficient): the ylide **30** was formed from (ethoxycarbonylmethyl)pentamethylenesulfonium bromide by conventional chemistry, isolated, and reacted with Michael acceptors at both room temperature and at 65 °C (which is the temperature of the catalytic process) (Table 6). Although unsaturated aldehyde **17** and ketone **14** gave a low yield in cyclopropanation, mirroring their ineffectiveness in our catalytic system, unsaturated ketone **12**, fumarate **13** and acrylates **18**, **19** gave good yields at both room and elevated temperatures. Payne[25] has similarly shown that dimethyl-λ^4-sulfanylideneacetate reacts efficiently with ethyl acrylate although lower yields were observed with unsaturated aldehydes. Although it may seem that substrates which are particularly prone to polymerisation (unsaturated aldehydes **16**, **17** and acrylates **18**, **19**) are not compatible with our catalytic process, other substrates, for example methyl vinyl ketone **12** are compatible. It is therefore difficult to generalise which substrates are compatible with our *in situ* generated sulfur ylide process. The relative stereochemistry of the adducts derived from (*E*)-chalcone **1** and nitrostyrene **15** was determined by NOE (Fig. 4).

The application of oxathiane **8** to asymmetric cyclopropanation of (*E*)-chalcone using ethyl diazoacetate under our optimised conditions was not successful: only a small amount of product was obtained and the sulfide was not recovered. This suggested that the intermediate stabilised ylide, which clearly has lower reactivity than that derived from phenyldiazomethane, undergoes competitive rearrangement–hydrolysis reactions faster than reaction with (*E*)-chalcone. More stable chiral sulfides are therefore required to promote this asymmetric process.

Conclusion

Cyclopropanation of enones using phenyldiazomethane and catalytic quantities of sulfide has been achieved and the use of the chiral sulfide **8** furnishes products with high enantioselectivity. Reactions are limited to relatively reactive enones as with less reactive Michael acceptors, ylide equilibration and rearrangement occurs. Cyclopropanation of a broader range of Michael acceptors using ethyl diazoacetate and catalytic quantities of sulfides has also been achieved, although the reaction is limited to enones, fumarates and nitrostyrenes; simple acrylates and unsaturated aldehydes were not compatible with our process. 1,3-Oxathiane **8** derived from camphorsulfonyl chloride was not a suitable chiral sulfide for use with ethyl diazoacetate and more stable sulfides are currently being sought.

Table 6 Cyclopropanation of Michael acceptors using preformed ylide



Entry	Michael acceptor	Solvent	*T*/°C	Product	Yield (%)[a]	Isomeric ratio[b]
1	**12**	1,2-DCE	20	**21**	99	>95:5
2	**17**	MeCN	20	**25**	17	1:1
3	**18**	1,2-DCE	20	**26**	99	>95:5
4	**19**	1,2-DCE	20	**27**	99	>95:5
5	**12**	1,2-DCE	65	**21**	83	>95:5
6	**13**	1,2-DCE	65	**22**	99	>95:5
7	**14**	1,2-DCE	65	**23**	Trace	—
8	**17**	MeCN	65	**25**	28	1:1
9	**18**	1,2-DCE	65	**26**	99	>95:5
10	**19**	1,2-DCE	65	**27**	69	>95:5

[a] Combined yield of all isomers. [b] Ratio determined by ^{1}H NMR spectroscopy.

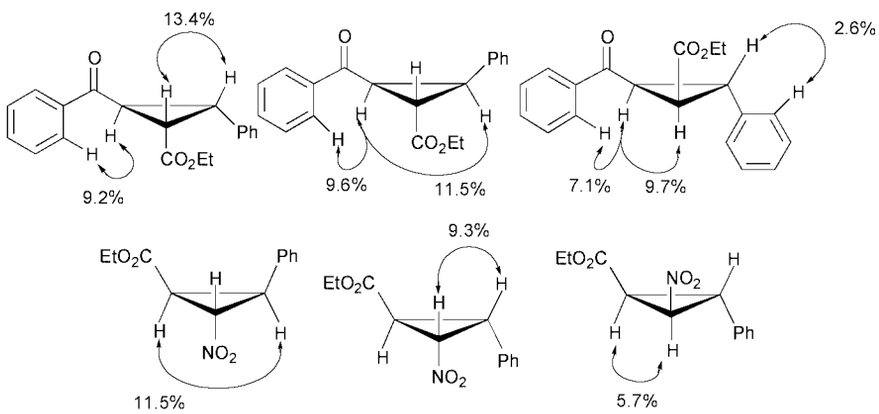


Fig. 4

Experimental

General

^{1}H and ^{13}C magnetic resonance spectra were recorded using a Bruker ACS-250 and a Bruker AMX-2 400 spectrometer supported by an Aspect 2000 data system. The chemical shifts are reported in ppm. All coupling constants are measured in hertz and rounded to one decimal place. ^{1}H chemical shifts were measured relative to the residual signal of chloroform at 7.25 ppm. ^{13}C chemical shifts were measured from the central peak of chloroform at 77.0 ppm. Mass spectra were obtained using either a Kratos MS 25 or MS 80 instrument supported by a DS 55 data system operating in EI, CI and +ve FAB mode. Melting points (mp) were determined using a Kofler Hot Stage Micro Melting Point Apparatus and stand uncorrected. Elemental micro analyses were carried out using a Perkin-Elmer 2400 Elemental Analyser CHN, involving classical wet analysis for anions (Br, Cl, I, S). Infrared spectra were recorded in the 4000–600 cm^{-1} range using a Perkin-Elmer 157G Grating Infra Red FT Spectrophotometer. Optical rotations ($[\alpha]_D^{20}$) were measured using a Perkin-Elmer 141 Polarimeter. $[\alpha]_D^{20}$ values are given in 10^{-1} deg cm^2 g^{-1}. Enantiomeric excesses (ee) were determined by chiral HPLC using a Highchrom D-phenylglycine column with a detector wavelength of 240 nm. Gas chromatography was performed using a Perkin-Elmer Autosystem XL supported by a Turbochrom 4.0 data system. Solvents and reagents were dried and purified prior to use according to standard procedures. TLC plates were visualised when possible by ultraviolet light, wavelength 254 nm, and by treatment with a solution of phosphomolybdic acid (5.0 g in 100 mL 95% absolute alcohol), 0.5% (w/v) aqueous solution of potassium permanganate or anisaldehyde (9.2 mL of anisaldehyde, 3.7 mL of acetic acid, 12.5 mL of concentrated sulfuric acid dissolved in 340 mL of 95% ethanol), followed by warming of the TLC plate with a heat gun. Chromatographic purification of compounds was achieved by flash chromatography using Kieselgel 60 F_{254}. All reagents used were commercially available unless otherwise stated.

The following starting materials were made according to literature procedures: 4-phenylbut-3-en-2-one **2**,[26] *trans*-2-nitrostyrene **14**[27] and phenyldiazomethane.[18]

General procedure for the synthesis of 3 and 7

For characterisation purposes, sulfides **3** and **7** were prepared independently by the following method. NaH (60% dispersion in mineral oil) (80 mg, 2 mmol) was washed with hexane (2 × 0.5 mL) and dried under vacuum. The NaH was flushed with N_2 and dimethyl sulfoxide (5 mL) added. Upon completion of the evolution of gas the benzylsulfonium salt, 1-benzyltetrahydrothiophenium perchlorate or 1-benzyltetrahydro-2*H*-thiopyranium perchlorate (0.5 mmol) was added and stirred for 20 min. The reaction was quenched with water (10 mL) and extracted with hexane (3 × 5 mL). The combined organics were washed with water (2 × 5 mL), dried (Na_2SO_4) and reduced *in vacuo* to furnish the desired *sulfide* as a clear oil.

2-(2-Methylphenyl)tetrahydrothiophene 3. Using 1-benzyltetrahydrothiophenium perchlorate (0.14 g, 0.5 mmol) the *title compound* was obtained as a clear oil (88 mg, 99%), R_f 0.2

(petrol); ν_{max} (thin film)/cm^{-1} 3028–2824 (CH), 1603, 1461 (ArH); ^{1}H (250 MHz; $CDCl_3$) 1.88–2.12 (2 H, m, CH_2), 2.16–2.35 (2 H, m, CH_2), 2.37 (1 H, s, CH_3), 2.95–3.05 (1 H, m, SCH), 3.09–3.20 (1 H, m, SCH), 4.73 (1 H, dd, *J* 8.0, 6.0, SCHAr), 7.08–7.25 (3 H, m, ArH), 7.60 (1 H, d, *J* 7.0, ArH); ^{13}C (63 MHz; $CDCl_3$) 19.7, 29.7, 30.8, 38.6, 48.6, 126.3, 126.7, 126.8, 130.3, 135.8, 140.8; *m/z* (EI) 178 (M^+, 100%), 163 (48), 135 (55), 131 (64), 117 (20), 115 (25), 91 (27) (Found: M^+, 178.0816. $C_{11}H_{14}S$ requires M^+, 178.0816).

2-(2-Methylphenyl)tetrahydro-2*H*-thiopyran 7. Using 1-benzyltetrahydro-2*H*-thiopyranium perchlorate (0.15 g, 0.5 mmol) the *title compound* was obtained as a clear oil (95 mg, 99%), R_f 0.3 (petrol); ν_{max} (thin film)/cm^{-1} 3023–2924 (CH), 1601 (ArH); ^{1}H (250 MHz; $CDCl_3$) 1.50–1.80 (2 H, m, CH_2), 2.00–2.15 (4 H, m, CH_2), 2.50 (3 H, s, CH_3), 2.65–2.76 (1 H, m, SCH_{eq}), 2.93 (1 H, ddd, *J* 13.0, 11.7, 2.2, SCH_{ax}), 4.05 (1 H, dd, *J* 10.5, 3.3, SCHAr), 7.15–7.27 (3 H, m, ArH), 7.44 (1 H, d, *J* 7.0, *ortho*-ArH); ^{13}C (63 MHz; $CDCl_3$) 19.3, 27.1, 27.5, 31.1, 34.5, 43.5, 126.4, 126.7, 127.0, 130.4, 135.5, 140.9; *m/z* (CI) 193 (MH^+, 78%), 159 (27), 105 (8), 101 (100), 87 (13) (Found: M^+, 192.0967. $C_{12}H_{16}S$ requires M^+, 192.0973).

(*E*)-1-(4-Bromophenyl)-3-phenylprop-2-en-1-one 9.[21] Aqueous NaOH (2.5 M, 8.0 mL, 20 mmol) was added dropwise to a stirred solution of 4-bromoacetophenone (0.60 g, 3.0 mmol), benzaldehyde (0.30 mL, 3.0 mmol) and absolute EtOH (8 mL) at 0 °C, under N_2 and stirred for 1 h. The precipitate was collected, washed with ice cold water and dried to yield the crude product as a pale yellow solid (0.83 g, 97%) which was recrystallised (hexane–EtOAc, 19 : 1) to furnish the *title compound* as off-white needles (0.71 g, 82%), mp 96 °C (hexane–EtOAc, 19 : 1) [lit.,[21] 101–102 °C (hexane–EtOAc, 20 : 1)]; R_f 0.6 (CH_2Cl_2–petrol, 1 : 1); ^{1}H (250 MHz; $CDCl_3$) 7.41–7.44 (5 H, m, ArH), 7.47 (1 H, d, *J* 15.5, CHPh), 7.64 (2 H, d, *J* 8.5, *meta*-ArHBr), 7.82 (1 H, d, *J* 15.5, C*H*COPh), 7.89 (2 H, d, *ortho*-ArHBr); ^{13}C (101 MHz; $CDCl_3$) 121.4, 127.9, 128.5, 129.0, 130.0, 130.8, 131.9, 134.7, 136.9, 145.4, 189.4.

General procedure for the optimised reaction used in Tables 2 and 3, with phenyldiazomethane

$Rh_2(OAc)_4$ (1 mol%), sulfide (1.0 mmol or 0.2 mmol) and substrate (1.0 mmol) were stirred in toluene (1 mL), under N_2, at room temperature. Phenyldiazomethane (1.5 mmol in 1 mL toluene) was added *via* an inverted syringe pump over the time period indicated in Tables 2 or 3 and the reaction stirred for a further hour. The crude mixture was then purified by flash column chromatography.

General procedure for the optimised reaction used in Tables 4 and 5 with ethyl diazoacetate

$Cu(acac)_2$ (5 mol%), sulfide (1.0 mmol or 0.2 mmol) and substrate (1.0 mmol) were stirred in 1,2-DCE (0.5 mL) under N_2 and warmed to 65 °C. Ethyl diazoacetate (1 mmol in 0.5 mL 1,2-DCE) was added *via* a syringe pump over the time period indicated in Tables 4 or 5 and the reaction stirred for a further hour. After cooling the mixture was purified by flash column chromatography.

(Ethoxycarbonylmethyl)pentamethylenesulfonium bromide

Pentamethylene sulfide (4.2 mL, 40 mmol) and ethyl bromoacetate (4.5 mL, 40 mmol) were stirred in acetone (5 mL), under N_2 for 18 h. The resulting solid was collected and washed with cold acetone (5 mL) to yield the *title compound* as a white powder (8.2 g, 77%), mp 140–142 °C (Found: C, 40.24; H, 6.46; S, 11.91; Br, 29.94. $C_9H_{17}SO_2Br$ requires C, 40.16; H, 6.32; S, 11.90; Br, 29.71%); ν_{max} (KBr disc)/cm^{-1} 2982–2890 (CH), 1717 (C=O); ^{1}H (250 MHz; DMSO-d_6) 1.26 (3 H, t, *J* 7.0, CH_3), 1.53–1.62 (2 H, m, CH_2), 1.76–1.92 (2 H, m, 2 × CH), 2.00–2.15 (2 H, m, 2 × CH), 3.40 (2 H, ddd, *J* 12.0, 7.5, 3.5, SCH_{eq}), 3.59 (2 H, ddd, *J* 12.0, 8.5, 3.5, SCH_{ax}), 4.24 (2 H, q, *J* 7.0, CO_2CH_2), 4.74 (2 H, s, SCH_2CO_2Et); ^{13}C (63 MHz; DMSO-d_6) 14.3, 20.3, 24.5, 27.8, 28.5, 63.2, 165.2; *m/z* (EI) 268 (M^+, 1%), 189 (49), 102 (100), 87 (93) (Found: M^+, 268.0132. $C_9H_{17}SO_2Br$ requires M^+, 268.0133).

Ethyl pentamethylene-λ^4-sulfanylideneacetate 30

(Ethoxycarbonylmethyl)pentamethylenesulfonium bromide (0.54 g, 2.0 mmol) was stirred in $CHCl_3$ (1.6 mL) under N_2 at 0 °C. A solution of saturated K_2CO_3 (1.2 mL) and NaOH (0.16 mL, 50% w/v) was added and the resulting suspension stirred at room temperature for 20 min. The mixture was then filtered through Celite and the filtrate dried (K_2CO_3) and concentrated *in vacuo* to give *title compound* as a white crystalline solid (0.37 g, 99%), mp 40–41 °C; ν_{max} (KBr disc)/cm^{-1} 2970–2924 (CH), 1623 (C=O); ^{1}H (250 MHz; $CDCl_3$) 1.20 (3 H, t, *J* 7.0, CH_3), 1.35–1.51 (2 H, m, CH_2), 1.63–1.79 (2 H, m, 2 × CH), 2.03–2.17 (2 H, m, 2 × CH), 2.64–2.78 (2 H, m, 2 × CHS), 3.21 (1 H, s, C*H*CO_2Et), 3.56–3.72 (2 H, m, 2 × CHS), 4.00 (2 H, q, *J* 7.0, CO_2CH_2); ^{13}C (63 MHz; $CDCl_3$) 15.0, 23.6, 24.2, 36.9, 42.1, 57.8, 170.2; *m/z* (CI) 189 (MH^+, 100%), 143 (8), 52 (36) (Found: MH^+, 189.0951. $C_9H_{17}SO_2$ requires MH^+, 189.0949).

General procedure for neutral ylide reactions (Table 6)

Ethyl pentamethylene-λ^4-sulfanylideneacetate **30** (0.10 g, 0.55 mmol) was stirred in solvent (0.5 mL) under N_2. Substrate (0.5 mmol) was added dropwise and the reaction stirred at 20 or 65 °C for 30 min. The reaction was then purified by flash column chromatography.

1-Benzoyl-2,3-diphenylcyclopropane[28]

(Table 3, entries 1, 2) Using (*E*)-chalcone (0.208 g, 1.0 mmol) the reaction mixture was purified by flash column chromatography (eluent CH_2Cl_2–petrol, 4 : 6) to furnish the *title compound* as a white solid, which was a mixture of two diastereoisomers (4 : 1, 2*R*,3*R* : *meso*) (0.18 g, 60%), mp 144–146 °C (EtOH) [lit. 2*RS*,3*RS*,[28] 148–149 °C (EtOH)]; $[a]_D^{25}$ −136 (*c*, 1.0, CH_2Cl_2); R_f 0.6 (CH_2Cl_2–petrol, 1 : 1); ^{1}H (250 MHz; $CDCl_3$) 2*R*,3*R* 3.28 (1 H, dd, *J* 7.0, 5.5, CHPh), 3.38 (1 H, dd, *J* 9.5, 7.0, CHPh), 3.65 (1 H, dd, *J* 9.5, 5.5, CHCOPh), 7.00–7.65 (13 H, m, ArH), 7.95 (2 H, dd, *ortho*-ArHCO); *meso* 3.33 (2 H, d, *J* 5.5, C*H*Ph), 3.55 (1 H, t, *J* 5.5, C*H*COPh), 7.00–7.65 (13 H, m, ArH), 8.20 (2 H, dd, *ortho*-ArHCO); ^{13}C (63 MHz; $CDCl_3$) 30.0, 32.4, 36.3, 36.6, 37.9, 126.6, 126.7, 126.9, 127.0, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 128.8, 129.0, 132.8, 133.2, 135.6, 136.2, 137.8, 138.4, 140.0, 195.0, 198.6; Chiracel OD, *i*-PrOH–light petroleum (0.7 : 99.3), flow rate of 2 mL min^{-1}. Retention times: *meso* isomer 5.4 min, *trans* isomer (2*R*,3*R*) enantiomer, 6.1 min; (2*S*,3*S*) 6.7 min, separations performed at 10 °C.

1-Acetyl-2,3-diphenylcyclopropane

(Table 3, entries 3, 4) Using 4-phenylbut-3-en-2-one, the reaction mixture was purified by flash column chromatography (eluent CH_2Cl_2–petrol, 3 : 7) to furnish the *title compound* as a white solid, which was a mixture of two diastereoisomers (4 : 1, 2*R*,3*R* : *meso*), mp 78–80 °C (EtOH); R_f 0.4 (CH_2Cl_2–petrol, 3 : 7) (Found: C, 86.42; H, 6.85. $C_{17}H_{16}O$ requires C, 86.44; H, 6.78%); $[a]_D^{25}$ −65 (*c*, 1.0, CH_2Cl_2); ν_{max} (KBr disc)/cm^{-1} 3087–3032 (CH), 1694 (C=O), 1602, 1582 (ArH); ^{1}H (250 MHz; $CDCl_3$) 2*R*,3*R* 2.12 (3 H, s, CH_3), 2.72 (1 H, dd, *J* 9.5, 5.5, C*H*$COCH_3$), 3.08 (1 H, dd, *J* 9.5, 7.5, CHPh), 3.32 (1 H, dd, *J* 7.5, 5.5, CHPh), 7.15–7.40 (10 H, m, ArH); *meso* 2.47 (3 H, s, CH_3), 2.86 (1 H, t, *J* 5.5, C*H*$COCH_3$), 3.12 (2 H, d, *J* 5.5, CHPh), 7.15–7.40 (10 H, m, ArH); ^{13}C (63 MHz; $CDCl_3$) 2*R*,3*R* 29.9, 31.6, 37.1, 39.8, 126.6, 126.7, 127.0, 128.2, 128.6, 129.1, 135.5, 139.8, 203.0; *meso* 31.2, 35.8, 35.9, 127.6, 128.0, 128.9,

131.3, 135.9, 206.7; *m*/*z* (EI) 236 (M^+, 14%), 193 (100), 178 (33), 115 (75) (Found: M^+, 236.1196. $C_{17}H_{16}O$ requires M^+, 236.1201); Chiracel OD, *i*-PrOH–light petroleum (0.7 : 99.3), flow rate of 2 mL min^{-1}. Retention times: *meso* isomer 3.9 min, *trans* isomer (2*R*,3*R*) enantiomer, 8.6 min; (2*S*,3*S*) 9.1 min, separations performed at 10 °C.

1-Benzoyl-2-phenyl-3-methylcyclopropane [29]

(Table 2, entry 6) Using 1-phenylbut-2-en-1-one (0.15 g, 1.0 mmol), the reaction was purified by flash column chromatography (eluent EtOAc–petrol, 5 : 95) to furnish the *title compound* as a white solid which was a mixture of three diastereoisomers [eluting **a** and **b** followed by **b** and **c** (1 : 1 : 1, **a** : **b** : **c**)], (0.14 g, 50%), mp 42–44 °C (EtOH); R_f 0.4, 0.5 (EtOAc–petrol, 1 : 9); ν_{max} (KBr disc)/cm^{-1} 3059–2868 (CH), 1665 (C=O), 1598–1448 (aromatic); ^1H (250 MHz; $CDCl_3$) **a** 1.35 (3 H, d, *J* 6.0, CH_3), 2.06 (1 H, dqd, *J* 9.5, 6.0, 4.3, C*H*CH_3), 2.88 (1 H, dd, *J* 4.8, 4.3, CHPh), 3.04 (1 H, dd, *J* 9.5, 4.8, CHCOPh), 7.10–7.60 (8 H, m, ArH), 7.88 (2 H, dd, *J* 8.0, 2.0, *ortho*-ArHCO); **b** 1.05 (3 H, d, *J* 6.0, CH_3), 2.46 (1 H, dqd, *J* 7.0, 6.0, 5.0, C*H*CH_3), 2.67 (1 H, dd, *J* 9.0, 7.0, CHPh), 2.83 (1 H, dd, *J* 9.0, 5.0, CHCOPh), 7.10–7.60 (8 H, m, ArH), 8.05 (2 H, dd, *J* 2.0, 8.0, *ortho*-ArHCO); **c** 1.28 (3 H, d, *J* 6.5, CH_3), 2.05 (1 H, dqd, *J* 9.3, 6.5, 6.5, C*H*CH_3), 2.82 (1 H, dd, *J* 6.5, 5.0, CHCOPh), 2.99 (1 H, dd, *J* 9.3, 5.0, C*H*Ph), 7.10–7.60 (8 H, m, ArH), 7.88 (2 H, dd, *J* 8.0, 2.0, *ortho*-ArHCO); ^{13}C (101 MHz; $CDCl_3$) **a** and **b** 12.9, 17.6, 20.4, 26.9, 31.8, 35.3, 35.7, 38.5, 126.5, 127.8, 127.9, 128.0, 128.2, 128.4, 128.5, 128.6, 128.9, 129.0, 132.4, 132.8, 136.2, 136.8, 138.0, 138.7, 196.2, 199.4; **c** 11.6, 28.9, 32.9, 34.8, 126.2, 126.3, 128.0, 128.5, 128.6, 132.7, 138.7, 140.9, 197.4; *m*/*z* (EI) 236 (M^+, 35%), 221 (34), 131 (19), 105 (100), 91 (16), 77 (42), 51 (11) (Found: M^+, 236.1203. $C_{17}H_{16}O$ requires M^+, 236.1201).

1-Acetyl-2-phenyl-3-methylcyclopropane [30]

(Table 2, entry 7) Using pent-3-en-2-one (97 μL, 1.0 mmol), the reaction was purified by flash column chromatography (eluent EtOAc–petrol, 5 : 95) to furnish the *title compound* as a pale yellow oil, which was a mixture of three diastereoisomers [eluting **a** and **b** followed by **b** and **c** (1 : 1 : 1, **a** : **b** : **c**)] (95 mg, 30%), bp 200 °C (20 mmHg) (Kugelrohr); R_f **a** 0.6, **b** and **c** 0.5 (EtOAc–petrol, 1 : 9); ν_{max} (thin film)/cm^{-1} 3027–2869 (CH), 1697 (C=O), 1498–1357 (Ar); ^1H (250 MHz; $CDCl_3$) **a** 1.25 (3 H, d, *J* 6.5, CH_3), 1.85 (1 H, dqd, *J* 9.0, 6.5, 6.5 C*H*CH_3), 2.29 (3 H, s, $COCH_3$), 2.34 (1 H, dd, *J* 9.0, 5.0, CHPh), 2.54 (1 H, dd, *J* 6.5, 5.0, C*H*$COCH_3$), 7.16–7.30 (5 H, m, ArH); **b** 0.94 (3 H, d, *J* 6.5, CH_3), 1.86 (1 H, dqd, *J* 9.5, 6.5, 4.8, C*H*CH_3), 2.34 (3 H, s, $COCH_3$), 2.17 (1 H, m, CHPh), 2.81 (1 H, dd, *J* 9.5, 4.8, C*H*$COCH_3$), 7.16–7.34 (5 H, m, ArH); **c** 1.25 (3 H, d, *J* 5.5, CH_3), 2.0 (3 H, s, $COCH_3$), 2.17 (2 H, m, C*H*CH_3 CHPh), 2.47 (1 H, dd, *J* 8.5, 7.5, C*H*$COCH_3$), 7.16–7.34 (5 H, m, ArH); ^{13}C (63 MHz; $CDCl_3$) **a** 11.4, 28.5, 32.3, 33.5, 37.9, 126.0, 126.2, 128.6, 131.3, 205.6; **b** 12.7, 26.1, 30.9, 34.7, 35.6, 126.6, 128.2, 128.9, 136.5, 207.6; **c** 17.8, 20.4, 31.4, 37.3, 39.0, 126.5, 128.0, 129.0, 136.2, 204.3; *m*/*z* (EI) 174 (M^+, 32%), 159 (21), 131 (100), 91 (46), 77 (9) (Found: M^+, 174.1045 $C_{12}H_{14}O$ requires M^+, 174.1046).

2,3-Diphenylcyclopropyl(4-bromophenyl)methanone 10

(Table 3, entry 5) Using 1-(4-bromophenyl)-3-phenylpropan-1-one (0.29 g, 1.0 mmol) and sulfide **8** (0.21 g, 1.0 mmol), the reaction was purified by flash column chromatography, eluent (CH_2Cl_2–petrol, 1 : 4) to furnish the *title compound* as pale yellow needles which was a mixture of two diastereoisomers (4 : 1, 2*R*,3*R* : *meso*) (0.11 g, 35%), mp 102–104 °C (EtOH) [lit. 2*RS*,3*RS*,[31] 113–115 °C (hexane–benzene)]; $[\alpha]_D^{25}$ −105 (*c*, 1.0, $CHCl_3$); R_f 0.6 (CH_2Cl_2–petrol, 1 : 1) (Found: C, 68.40; H, 4.68; Br, 20.70. $C_{22}H_{17}OBr \cdot 1/2H_2O$ requires C, 68.41; H, 4.66; Br, 20.70%); ν_{max}/cm^{-1} 3062–2921 (CH), 1666 (C=O), 1495–1364 (ArH); ^1H (250 MHz; $CDCl_3$) 2*R*,3*R* 3.30 (2 H, d, *J* 6.0, 2 × CHPh), 3.61 (1 H, d, *J* 6.0, CHCOPh), 7.13–7.97 (15 H, m, ArH); *meso* 3.31 (2 H, d, *J* 5.0, 2 × CHPh), 3.45 (1 H, d, *J* 5.0, CHCOPh), 7.13–7.97 (15 H, m, ArH); ^{13}C (101 MHz; $CDCl_3$) 29.9, 32.3, 36.4, 36.5, 37.9, 126.6, 126.8, 127.0, 127.9, 128.1, 128.3, 128.5, 128.6, 128.9, 129.0, 129.4, 129.5, 129.6, 130.0, 132.0, 135.2, 135.9, 137.0, 139.7, 145.4, 193.9, 197.5; *m*/*z* (EI) 376 (M^+, 5%), 287 (89), 207 (47), 193 (100), 185 (49), 178 (35), 131 (34), 115 (33), 77 (33) (Found: M^+, 376.0453. $C_{22}H_{17}OBr$ requires M^+, 376.0463); Chiracel OD, *i*-PrOH–light petroleum (0.7 : 99.3), flow rate of 2 mL min^{-1}. Retention times: *meso* isomer 7.4 min, *trans* isomer (2*R*,3*R*) enantiomer, 8.6 min; (2*S*,3*S*) 9.1 min, separations performed at 10°C.

Crystal structure of (2*R*,3*R*)-10 ‡

Crystal data for $C_{22.5}H_{19}BrO_{1.5}$ (including a half occupancy CH_3OH); $M = 393.29$, crystallises from acetone–*n*-pentane–methanol as colourless blocks; crystal dimensions 0.30 × 0.20 × 0.10 mm^3. Monoclinic, $a = 24.604(8)$, $b = 5.8049(18)$, $c = 14.597(4)$ Å, $\beta = 111.784(6)°$, $U = 1935.9(10)$ $Å^3$, $Z = 4$, $D_c = 1.349$ Mg m^{-3}, space group *C*2, Mo-Kα radiation (λ = 0.71073 Å), μ(Mo-K_α) = 2.132 mm^{-1}, $F(000) = 804$.

Ethyl 2-benzoyl-3-phenylcyclopropane-1-carboxylate 20 [32]

(Table 5, entries 1, 2) Using (*E*)-chalcone **1** (0.208 g, 1.0 mmol), the reaction mixture was purified by flash column chromatography (eluent EtOAc–petrol, 5 : 95) to yield the *title compound* as a white solid, which was a mixture of three diastereoisomers (**20a** : **20b** : **20c**, 4 : 1 : 2) (0.22 g, 72%) mp 90–91 °C (EtOH); R_f 0.2 (petrol–EtOAc, 9 : 1) (Found: C, 77.27; H, 6.39. $C_{19}H_{18}O_3$ requires C, 77.55; H, 6.12%); ν_{max} (KBr disc)/cm^{-1} 3056–2898 (CH), 1722, 1683 (C=O), 1460–1431 (Ar); ^1H (250 MHz; $CDCl_3$) **20a** 1.32 (3 H, t, *J* 7.0, CH_3), 3.22 (1 H, dd, *J* 6.0, 5.0, CHPh), 3.35 (1 H, dd, *J* 10.0, 6.0, $CHCO_2Et$), 3.57 (1 H, dd, *J* 10.0, 5.0, CHCOPh), 4.23 (2 H, q, *J* 7.0, CO_2CH_2), 7.18–7.37 (5 H, m, Ar), 7.39–7.67 (3 H, m, *meta* and *para*-ArHCO), 7.95 (2 H, dd, *J* 8.0, 1.5, *ortho*-ArHCO); **20b** 1.07 (3 H, t, *J* 7.0, CH_3), 2.86 (1 H, dd, *J* 10.0, 5.0, $CHCO_2Et$), 3.26 (1 H, dd, *J* 10.0, 6.0, CHPh), 3.85 (1 H, dd, *J* 6.0, 5.0, CHCOPh), 3.99 (2 H, 2 × q, *J* 7.0, 2 × CO_2CH), 7.18–7.37 (5 H, m, Ar), 7.39–7.67 (3 H, m, *meta* and *para*-ArHCO), 8.12 (2 H, dd, *J* 8.0, 1.5, *ortho*-ArHCO); **20c** 1.13 (3 H, t, *J* 7.0, CH_3), 2.64 (1 H, dd, *J* 10.0, 6.0, $CHCO_2Et$), 3.09 (1 H, dd, *J* 10.0, 6.5, CHCOPh), 3.36 (1 H, dd, *J* 6.5, 6.0, CHPh), 4.09 (2 H, q, *J* 7.0, CH_2), 7.20–7.39 (5 H, m, Ar), 7.42–7.60 (3 H, m, *meta* and *para*-ArHCO), 8.02 (2 H, dd, *J* 8.0, 1.5, *ortho*-ArHCO); ^{13}C (101 MHz; $CDCl_3$) **20a** and **20b** 14.0, 14.2, 25.9, 29.6, 32.1, 35.0, 35.0, 35.8, 60.9, 61.3, 127.2, 127.3, 128.0, 128.1, 128.2, 128.3, 128.6, 128.8, 128.9, 133.1, 133.5, 133.7, 134.7, 137.0, 137.4, 168.7, 172.2, 193.2, 196.7; **20c** 14.0, 29.7, 31.6, 35.1, 61.1, 126.5, 127.1, 128.4, 128.6, 128.7, 133.3, 136.9, 138.0, 169.2, 193.7; *m*/*z* (EI) 294 (M^+, 6%), 249 (8), 221 (100), 189 (12), 115 (19), 105 (51), 77 (25) (Found: M^+, 294.1256 $C_{19}H_{18}O_3$ requires M^+, 294.1244).

Ethyl (1*RS*,2*RS*)-2-acetylcyclopropanecarboxylate 21 [25]

(Table 5, entries 3, 4; Table 6, entries 1, 5) Using methyl vinyl ketone (83 μL, 1.0 mmol) the reaction mixture was purified by flash column chromatography (eluent EtOAc–petrol, 5 : 95) to yield the *title compound* as a colourless oil (0.10 g, 64%), R_f 0.5 (EtOAc–petrol, 4 : 1) (Found: C, 61.09; H, 7.65. $C_8H_{12}O_3$ requires C, 61.54; H, 7.69%); ν_{max} (thin film)/cm^{-1} 3621–2984 (CH), 1707, 1730 (C=O); ^1H (250 MHz; $CDCl_3$) 1.26 (3 H, t, *J* 7.0, CH_3), 1.35–1.44 (2 H, m, 2 × CH), 2.16 (1 H, ddd, *J* 8.3, 6.0, 3.8, $CHCO_2Et$), 2.30 (3 H, s, CH_3), 2.45 (1 H, ddd, *J* 8.3,

‡ CCDC reference number 207/467. See http://www.rsc.org/suppdata/p1/b0/b004367m/ for crystallographic files in .cif format.

6.0, 3.8, C*H*COCH$_3$), 4.14 (2 H, q, *J* 7.0, CO$_2$CH$_2$); ^{13}C (63 MHz; CDCl$_3$) 14.1, 17.1, 24.2, 29.5, 30.8, 61.0, 172.0, 205.3; *m*/*z* (EI) 156 (M$^+$, 21%), 141 (100), 113 (23), 111 (57), 85 (61), 82 (42), 68 (41), 57 (39), 55 (74) (Found: M$^+$, 156.0779. $C_8H_{12}O_3$ requires M$^+$, 156.0786).

trans,meso-1,2,3-Triethyl cyclopropanetricarboxylate 22[25]

(Table 5, entries 5, 6; Table 6, entry 6) Using diethyl fumarate (0.16 mL, 1.0 mmol), the reaction was purified by flash column chromatography (eluent EtOAc–petrol, 5:95) to yield the *title compound* as a colourless oil (0.18 g, 68%), R_f 0.4 (EtOAc–petrol, 4:1) (Found: C, 55.78; H, 6.93. $C_{12}H_{18}O_6$ requires C, 55.81; H, 6.98%); ν_{max} (thin film)/cm^{-1} 3450–2984 (CH), 1728 (C=O); ^{1}H (250 MHz; CDCl$_3$) 1.24 (6 H, t, *J* 7.0, 2 × CH$_3$), 1.27 (3 H, t, *J* 7.0, CH$_3$), 2.52 (2 H, d, *J* 5.5, 2 × CH), 2.75 (1 H, t, *J* 5.5, CH), 4.14 (4 H, q, *J* 7.0, 2 × CO$_2$CH$_2$), 4.16 (2 H, q, *J* 7.0, CH$_2$); ^{13}C (63 MHz; CDCl$_3$) 14.1, 25.7, 28.5, 61.5, 61.6, 167.6; *m*/*z* (EI) 258 (M$^+$, 29%), 213 (100), 185 (95), 157 (44), 140 (38), 112 (38), 84 (39) (Found: M$^+$, 258.1101 $C_{12}H_{18}O_6$ requires M$^+$, 258.1103).

Ethyl 2-nitro-3-phenylcyclopropane-1-carboxylate 24

(Table 5, entry 8) Using *trans*-2-nitrostyrene (0.15 g, 1.0 mmol), the reaction was purified by flash column chromatography (eluent EtOAc–petrol, 5:95) to furnish the *title compound* as a pale yellow oil which was a mixture of three diastereoisomers (**24a**:**24b**:**24c**, 5:2:4) (94 mg, 38%), bp 150 °C (0.01 mmHg); R_f **24a** and **24b** 0.4, **24c** 0.3 (EtOAc–petrol, 1:9) (Found: C, 61.17; H, 5.78; N, 5.66. $C_{12}H_{13}O_4N$ requires C, 61.28; H, 5.53; N, 5.96%); ν_{max} (thin film)/cm^{-1} 2985 (CH), 1732 (C=O), 1550, 1368 (NO$_2$), 1428 (ArH); ^{1}H (250 MHz; CDCl$_3$) **24a** 1.02 (3 H, t, *J* 7.0, CH$_3$), 3.21 (1 H, dd, *J* 11.0, 3.5, CHCO$_2$Et), 3.66 (1 H, dd, *J* 11.0, 4.8, CHPh), 3.97 (1 H, q, *J* 7.0, CO$_2$CH), 3.98 (1 H, q, *J* 7.0, CO$_2$CH), 5.18 (1 H, dd, *J* 4.8, 3.5, CHNO$_2$), 7.16–7.24 (5 H, m, ArH); **24b** 1.34 (3 H, t, *J* 7.0, CH$_3$), 3.33 (1 H, dd, *J* 9.0, 8.0, CHPh), 3.40 (1 H, dd, *J* 8.0, 4.0, CHCO$_2$Et), 4.25 (1 H, q, *J* 7.0, CO$_2$CH), 4.26 (1 H, q, *J* 7.0, CO$_2$CH), 4.92 (1 H, dd, *J* 9.0, 4.0, CHNO$_2$), 7.16–7.24 (5 H, m, ArH); **24c** 1.29 (3 H, t, *J* 7.0, CH$_3$), 2.70 (1 H, dd, *J* 8.5, 8.0, CHCO$_2$Et), 3.73 (1 H, dd, *J* 8.0, 4.5, CHPh), 4.24 (2 H, q, *J* 7.0, CO$_2$CH$_2$), 4.60 (1 H, dd, *J* 8.5, 4.5, CHNO$_2$), 7.24–7.37 (5 H, m, ArH); ^{13}C (101 MHz; CDCl$_3$) **24a** and **24b** 13.8, 14.1, 27.6, 32.2, 34.4, 34.7, 61.6, 62.1, 62.7, 64.7, 128.2, 128.5, 128.6, 128.7, 128.8, 128.9, 130.2, 131.2, 129.7, 168.7; **24c** 14.0, 32.0, 34.7, 62.2, 64.9, 126.8, 128.2, 128.6, 134.2, 165.8; *m*/*z* (CI) 236 (MH$^+$, 66%), 190 (70), 146 (38), 128 (100), 105 (43) (Found: MH$^+$, 236.0931. $C_{12}H_{14}NO_2$ requires MH$^+$, 236.0923).

Ethyl 2-formyl-3-methylcyclopropane-1-carboxylate 25[25]

(Table 6, entries 2, 8) Using crotonaldehyde (83 μL, 1 mmol) the reaction mixture was purified by flash column chromatography (eluent EtOAc–petrol, 5:95) to furnish the *title compound* as a pale yellow oil which was a mixture of two diastereoisomers (1:1, 1*RS*,2*RS*,3*SR*:1*SR*,2*RS*,3*RS*) (45 mg, 28%), R_f 0.3 (EtOAc–petrol, 1:4); ν_{max} (thin film)/cm^{-1} 2982–2936 (CH), 1726, 1712 (C=O); ^{1}H (250 MHz; CDCl$_3$) 1.23 (3 H, d, *J* 6.5, CHC*H*$_3$), 1.25 (3 H, t, *J* 7.0, CH$_2$C*H*$_3$), 1.26 (3 H, t, *J* 7.0, CH$_2$C*H*$_3$), 1.28 (3 H, d, *J* 6.5, CHC*H*$_3$), 1.78–1.95 (1 H, m, C*H*CHO), 1.99 (1 H, dd, *J* 8.5, 6.5, C*H*CO$_2$Et), 4.14 (2 H, q, *J* 7.0, CO$_2$C*H*$_2$CH$_3$), 4.15 (2 H, 2 q, *J* 7.0, 2 × CO$_2$C*H*), 9.35 (1 H, d, *J* 3.8, CHO), 9.58 (1 H, d, *J* 3.8, CHO); ^{13}C (63 MHz; CDCl$_3$) 11.1, 14.2, 14.3, 16.6, 22.5, 24.1, 28.3, 30.8, 37.1, 38.7, 61.1, 61.3, 169.4, 169.5, 198.7, 199.5.

Diethyl *trans*-cyclopropane-1,2-dicarboxylate 26[33]

(Table 6, entries 3, 9) Using ethyl acrylate (54 μL, 0.5 mmol) the reaction was purified by flash column chromatography (eluent EtOAc–petrol, 5:95) to yield the *title compound* as a colourless oil (0.18 g, 99%), R_f 0.6 (EtOAc–petrol, 4:1) (Found: C, 57.83; H, 7.14. $C_9H_{14}O_4$ requires C, 58.06; H, 7.53%); ν_{max} (thin film)/cm^{-1} 2984 (CH), 1725 (C=O); ^{1}H (250 MHz; CDCl$_3$) 1.25 (6 H, t, *J* 7.0, 2 × CH$_3$), 1.41 (2 H, dd, *J* 8.8, 6.8, 2 × CH), 2.14 (2 H, dd, *J* 8.8, 6.8, 2 × CHCO$_2$Et), 4.14 (4 H, 2 q, *J* 7.0, 2 × CO$_2$CH$_2$); ^{13}C (63 MHz; CDCl$_3$) 14.2, 15.3, 22.4, 61.2, 171.8; *m*/*z* (EI) 186 (M$^+$, 11%), 159 (8), 141 (100), 113 (29), 85 (36), 68 (18), 55 (14) (Found: M$^+$, 186.0892 $C_9H_{14}O_4$ requires M$^+$, 186.0892).

Phenyl 2-ethyl *trans*-cyclopropane-1,2-dicarboxylate 27

(Table 6, entries 4, 10) Using phenyl acrylate (80 μL, 0.5 mmol), the reaction was purified by flash column chromatography (eluent EtOAc–petrol, 5:95) to yield the *title compound* as a white solid (0.16 g, 69%), mp 48–49 °C (EtOH); R_f 0.4 (EtOAc–petrol, 1:4) (Found: C, 66.37; H, 6.11. $C_{13}H_{14}O_4$ requires C, 66.67; H, 5.98%); ν_{max} (KBr disc)/cm^{-1} 3099–2874 (CH), 1750, 1720 (C=O), 1599, 1494, 1479 (ArH); ^{1}H (250 MHz; CDCl$_3$) 1.30 (3 H, t, *J* 7.0, CH$_3$), 1.54–1.62 (2 H, m, 2 × CH), 2.28–2.44 (2 H, m, C*H*CO$_2$Ph and C*H*CO$_2$Et), 4.19 (2 H, q, *J* 7.0, CH$_2$), 7.09 (2 H, dd, *J* 1.5, 8.0, *ortho*-ArH), 7.23 (1 H, m, *para*-ArH), 7.38 (2 H, m, *meta*-ArH); ^{13}C (63 MHz; CDCl$_3$) 14.2, 15.9, 22.2, 23.0, 61.2, 121.3, 125.9, 129.4, 150.4, 170.4, 171.5; *m*/*z* (EI) 234 (M$^+$, 44%), 189 (20), 141 (100), 113 (16), 94 (10), 85 (23) (Found: M$^+$, 234.0898. $C_{13}H_{14}O_4$ requires M$^+$, 234.0892).

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