gem-Dimethylcyclopropanation Using Triisopropylsulfoxonium Tetrafluoroborate: Scope and Limitations

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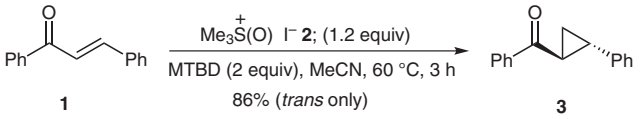
Abstract: A new nucleophilic isopropyl transfer reagent, triisopropylsulfoxonium tetrafluoroborate, has been prepared and evaluated. Thus, using this reagent and NaH in DMF, a range of electron deficient alkenes, including several chalcone analogues, α,β-unsaturated ketones, dienones and quinones, plus α,β-unsaturated esters, nitrile, sulfone and nitro examples, have been converted into the corresponding *gem*-dimethylcyclopropane compounds.

Key words: cyclopropanes, cyclopropanation, sulfoxonium salts, ruthenium tetraoxide

Classical procedures for the preparation of cyclopropanes from alkenes include Simmons–Smith methodology[1] and the addition of dihalocarbenes (generated from haloforms).[2] For the cyclopropanation of electron-deficient alkenes, Corey and Chaykovsky developed a methylene transfer process using sulfoxonium ylides.[3] This latter transformation has been widely used in organic synthesis,[4] and is the basis of a number of modern asymmetric cyclopropanation procedures.[4,5]

Our interest in new synthetic approaches to cyclopropanes[6,7] led to the recent development of an improved procedure for the cyclopropanation of α,β-unsaturated ketones (e.g., the conversion of chalcone **1** into cyclopropane **3**, Scheme 1) using trimethylsulfoxonium iodide (**2**) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD).[7]



Scheme 1

Although methylenecyclopropanes are present in many natural products, the *gem*-dimethylcyclopropane motif is even more prevalent. Figure 1 shows representative natural products possessing a *gem*-dimethylcyclopropane group: allethrin II (**4**) is a typical pyrethroid insecticide,[8] (–)-taylorione (**5**) was extracted from the liverwort *Mylia Taylorii* found in the Austrian alps,[9] and the novel cyclohexanone diterpenoid (+)-lathyranone A (**6**) was recently isolated from the seeds of *E. lathyris*.[10]

There are a number of procedures available for the preparation of *gem*-dimethylcyclopropanes from electron-rich alkenes,[11] but for a natural product target we required a nucleophilic isopropylidene transfer approach. The first such procedure was reported by Corey and Jautelat and utilised diphenylsulfonium isopropylide derived from salt **7**[12] (Figure 2). This reagent efficiently produces *gem*-dimethylcyclopropanes from unsaturated esters and amides, but with α,β-unsaturated ketones, epoxide formation can compete (e.g., 3-methylcyclohex-2-enone gives mainly the unsaturated epoxide[12a]). In addition, the use of a strong base and low temperature is required. In 1973, Johnson's group disclosed the use of (dimethylamino)isopropyl-*p*-tolyloxosulfonium tetrafluoroborate (**8**) for the *gem*-dimethylcyclopropanation of (*E*)-1,2-dibenzoylethene and (*E*)-chalcone.[13] However, the synthesis of salt **8** was difficult and low yielding, and the scope of the procedure has not been demonstrated. More recently, it has been shown that the cyclopropanation of unsaturated esters can be achieved using the isopropyl phosphorane **9**[14] and the nitro compound **10**,[15] but again the scope of these reagents has not been determined (e.g., there are no examples of their use with α,β-unsaturated ketones).

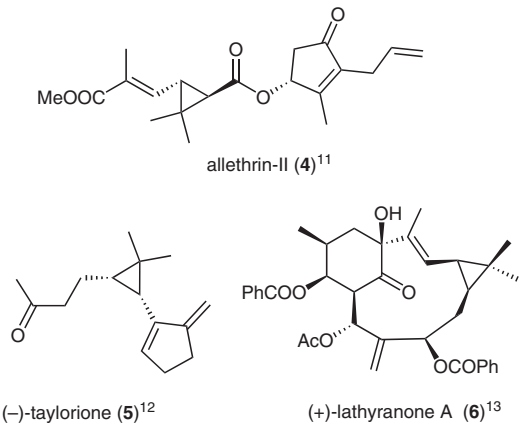


Figure 1 Some natural products containing *gem*-dimethylcyclopropyl group

We therefore decided to develop a new procedure for the nucleophilic *gem*-dimethylcyclopropanation of electron-deficient alkenes. Ideally, we required an isopropylidene transfer reagent that was readily available, would react under mild conditions, be applicable to a range of Michael acceptors, and would avoid competitive epoxide formation with α,β-unsaturated ketones.

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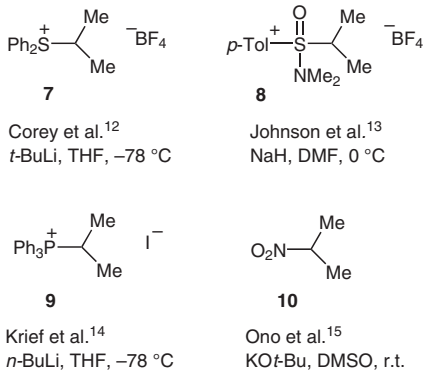
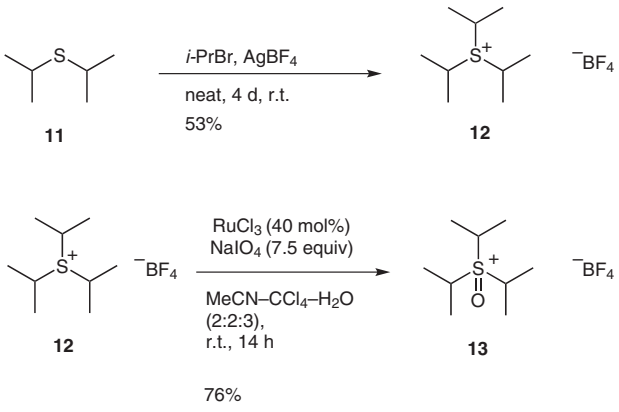


Figure 2 Reagents reported for *gem*-dimethylcyclopropanation

Sulfoxonium ylides favour 1,4-additon over 1,2-addition,[3,4,7] and we therefore decided to investigate the preparation and reactions of isopropylsulfoxonium salts. Given the availability of diphenylisopropylsulfonium tetrafluoroborate (**7**),[12] initial efforts involved the attempted oxidation of the corresponding sulfonium salt. This approach had the additional advantage that the phenyl substituents would be nontransferable groups derived from the inexpensive diphenyl sulfide. Unfortunately, all attempts to oxidise salt **7**, using either *m*-CPBA/Na_2CO_3[16] or RuO_2/$NaIO_4$,[17] gave none of the corresponding sulfoxonium salt and resulted only in degradation due to competing oxidation of the aryl rings.[18]

We therefore turned our attention to the preparation of the corresponding triisopropylsulfoxonium salt **13**.[19] As the S-alkylation of sulfoxides is successful only in the case of methylation,[20] it was necessary to carry out the oxidation of a triisopropylsulfonium salt. Badet and Julia[21] reported the preparation of triisopropylsulfonium tetrafluoroborate (**12**) from diisopropyl sulfide and isopropanol in the presence of methanesulfonic acid with subsequent anion exchange, but this procedure proved problematic in our hands. Instead, an alternative method using diisopropyl sulfide, 2-bromopropane, and silver tetrafluoroborate was developed to afford the desired salt **12** directly (Scheme 2).



Scheme 2

Oxidation of triisopropylsulfonium tetrafluoroborate (**12**) to give the triisopropylsulfoxonium salt **13** was the next issue to be addressed. The literature contains few reports on the oxidation of sulfonium salts to sulfoxonium salts, but the method reported by Kamigata and co-workers, using aqueous sodium *m*-chloroperbenzoate[16] seemed most appropriate. Unfortunately, when this procedure was applied to sulfonium salt **12** the reaction could not be driven to completion; at room temperature, only 36% conversion could be obtained and attempts to heat the reaction in the presence of a radical scavenger[22] proved futile. We reasoned that the use of a more powerful oxidant could overcome the slow oxidation of the sterically encumbered sulfonium salt **12**. RuO_4[17] has been applied to the oxidation of many organic functionalities, and optimisation studies were carried out to find the best conditions to oxidise the sulfonium salt **12** (Table 1).

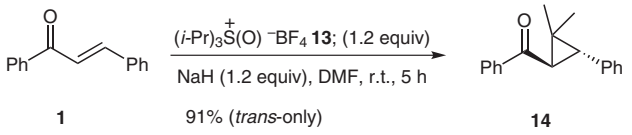
Table 1 Oxidation of Triisopropylsulfonium Tetrafluoroborate (**12**)[a]

Entry	Catalyst (mol%)	Oxidant (equiv)	Time (h)	Conversion to **13** (%)[b]
1	RuO_2 (20)	$NaIO_4$ (5)	16	63
2	RuO_2 (20)	$NaBrO_3$ (5)	16	59
3	RuO_2 (20)	NaOCl (5)	16	25
4	RuO_2 (20)	Oxone (5)	16	0
5	$RuCl_3$ (20)	$NaIO_4$ (5)	16	80
6	$RuCl_3$ (30)	$NaIO_4$ (7.5)	20	93
7	$RuCl_3$ (40)	$NaIO_4$ (5)	20	96

[a] Using triisopropylsulfonium tetrafluoroborate **12** (0.1 mmol) at 0.2 M concentration in MeCN–CCl_4–H_2O (2:2:3) with stirring at r.t.
[b] As determined by ^{1}H NMR spectroscopy.

As can be seen from the results presented in Table 1, the use of RuO_2 with a range of oxidants gave only moderate yields of sulfoxonium salt **13** at best (entries 1–4). However, use of the classic Sharpless conditions ($RuCl_3$/$NaIO_4$ in MeCN–CCl_4–H_2O)[23] gave much improved yields (entries 5–7), and with $RuCl_3$ (40 mol%) and $NaIO_4$ (5 equiv) the conversion was essentially quantitative (entry 7). Based on these results, triisopropylsulfonium tetrafluoroborate (**12**) was oxidised to the triisopropylsulfoxonium salt **13** on a 6 g scale in a 76%, recrystallised, yield (Scheme 2).

With the sulfoxonium salt **13** in hand, we explored its use as an isopropylidene transfer reagent with chalcone **1**. Several solvent/base combinations were investigated, but the use of NaH in DMF proved to be the best by far. Thus, after 5 hours at room temperature, the *gem*-dimethylcyclopropane adduct of chalcone **14** was obtained in 91% yield with no sign of any epoxide by-product (Scheme 3). Notably, only the *trans*-isomer was obtained, as shown by an H,H coupling constant of 6.0 Hz (which is consistent with the published value[24]).



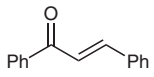
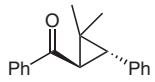
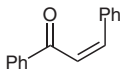
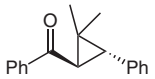
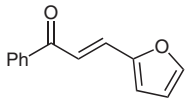
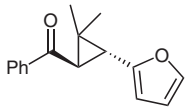
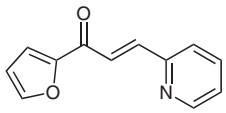
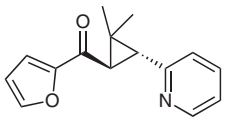
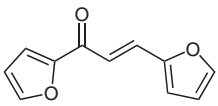
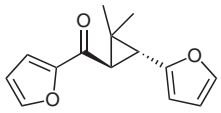
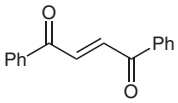
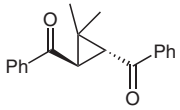
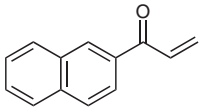
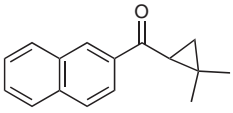
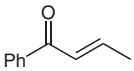
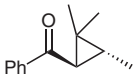
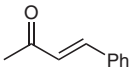
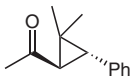
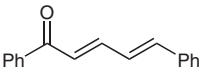
Scheme 3

Given the success of the chalcone reaction we moved on to examine a range of acyclic α,β-unsaturated ketones in the above dimethylcyclopropanation procedure (Table 2). With (*E*)-chalcone **1** giving only *trans*-cyclopropane **14** (entry 1), we first investigated the dimethylcyclopropanation of (*Z*)-chalcone **15**:[25] in this case (entry 2) the same *trans*-cyclopropane **14** was formed, as expected, indicating the potential for free rotation in the intermediate adduct.

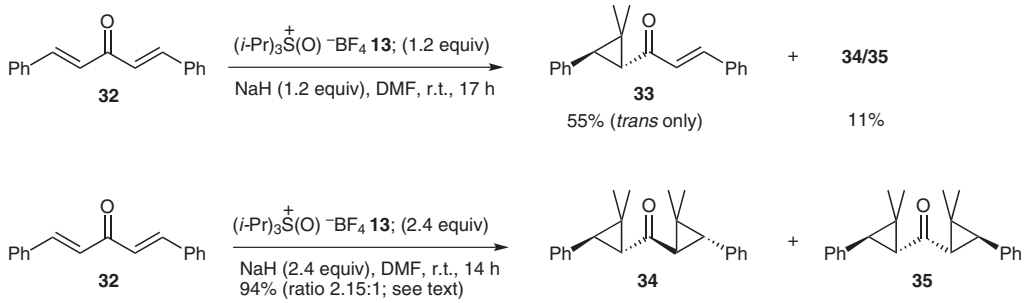
Heterocyclic chalcone analogues **16**, **18**, and **20**, and an enedione analogue **22** were studied next and in all cases fair to good yields of the corresponding dimethylcyclopropanes were obtained (entries 3–6). The simple acyclic enones **24**, **26**, and **28** were studied next (entries 7–9). Notably, the monosubstituted enone **24** underwent cyclopropanation giving adduct **25** in 53% yield, although the reaction was slow. The yields of the cyclopropanated products **27** and **29** were also modest (although in these cases the low yields could be attributed to the enolisable nature of the substrates **26** and **28**).

Finally in this group, dienones **30** and **32** were studied. With dienone **30**, only the alkene adjacent to the carbonyl group underwent dimethylcyclopropanation affording *trans*-cyclopropane **31** in excellent yield (entry 10). In contrast, under the standard conditions, dibenzylideneacetone (**32**) gave a mixture of the expected dimethylcyclopropane **33** together with two inseparable diastereomers of the bis-cyclopropyl adducts **34** and **35** (Scheme 4). With excess sulfoxonium salt, the bis-ad-

Table 2 Cyclopropanation of Acyclic Enones Using Triisopropylsulfoxonium Tetrafluoroborate (**13**) and NaH in DMF[a]

Entry	Substrate		Product		Time (h)	Yield (%)[b]
1	**1**		**14**		5	91
2	**15**		**14**		2	76
3	**16**		**17**		2	52
4	**18**		**19**		2	71
5	**20**		**21**		1	71
6	**22**		**23**		23	68
7	**24**		**25**		24	53
8	**26**		**27**		1.5	53
9	**28**		**29**		2	33
10	**30**		**31**		4	85

[a] Using *i*-$Pr_3S(O)BF_4$ (1.2 equiv) in DMF at r.t.
[b] Isolated yield of chromatographically homogeneous material; >95% *trans*-isomers by ^1H NMR spectroscopy.



Scheme 4

ducts **34** and **35** were formed in 94% yield as an inseparable mixture of diastereomers (2.15:1; we were unable to assign the structure of the major diastereomer).

The dimethylcyclopropanatations of cyclic enones were studied next (Table 3). Indenone polymerised under the reaction conditions and cyclohexenone (**36**) produced the known[3a] adduct **37** in extremely low yield (entry 1). However, naphthoquinone (**38**) and chromone (**40**) produced the expected adducts, **39** and **41**, in excellent yields (entries 2 and 3).

Interestingly, with benzoquinone, only a low yield of the monocyclopropane **43** was observed and double addition was preferred even using sulfoxonium salt **13** in approximately stoichiometric quantities (1.2 equiv, entry 4). With excess sulfoxonium salt, the biscyclopropane was observed as the only product and as a single diasteromer; X-ray crystallography confirmed this product to be the *trans*-diastereomer **44** (Figure 3).

Non-ketone Michael acceptors were also examined (Table 4). Under the standard conditions, methyl cin-

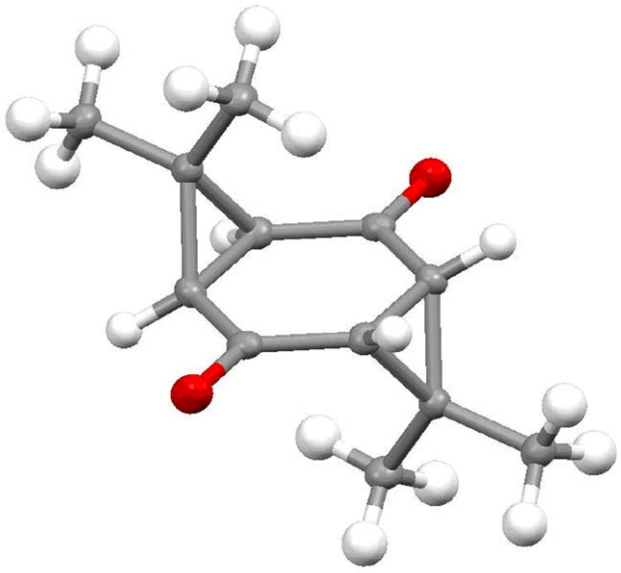
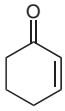
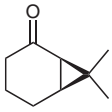
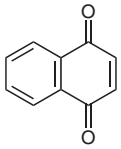
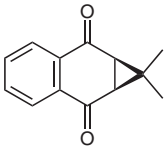
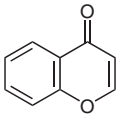
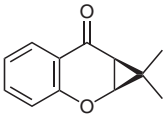
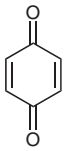
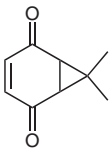
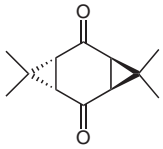


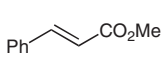
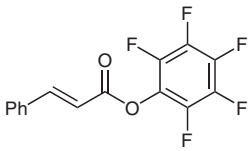
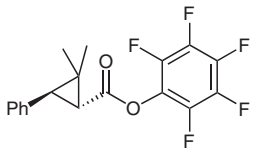
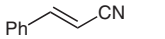
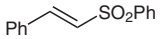
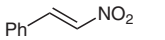
Figure 3 X-ray crystal structure of bis-cyclopropane **44** (depicted in Mercury 1.4.2)

Table 3 Cyclopropanation of Cyclic Enones Using Triisopropylsulfoxonium Tetrafluoroborate (**13**) and NaH in DMF[a]

Entry	Substrate	Product	Time (h)	Yield (%)[b]
1	**36** 	**37** 	4	4
2	**38** 	**39** 	3	92
3	**40** 	**41** 	3	95
4[c]	**42** 	**43**  **44** 	3	**43**: 7 **44**: 36

[a] Using *i*-$Pr_3S(O)BF_4$ (1.2 equiv) in DMF at r.t.
[b] Isolated yield of chromatographically homogeneous material; >95% *trans*-isomers by ^1H NMR spectroscopy.
[c] Use of *i*-$Pr_3S(O)BF_4$ (2.4 equiv) in DMF at r.t. for 6 h gave only **44** (67%).

Table 4 Cyclopropanation of Non-ketone Acceptors Using Triisopropylsulfoxonium Tetrafluoroborate (**13**) and NaH in DMF[a]

Entry	Substrate		Product		Time (h)	Yield (%)[b]
1	**45**		**46**		40	52[c]
2	**47**		**48**		30	49[c]
3	**49**		**50**		16	51
4	**51**		**52**		24	45
5	**53**		**54**		17	93

[a] Using *i*-$Pr_3S(O)BF_4$ (1.2 equiv) in DMF at r.t.
[b] Isolated yield of chromatographically homogeneous material; >95% *trans*-isomers by ^1H NMR spectroscopy.
[c] Using *i*-$Pr_3S(O)BF_4$ (2.0 equiv).

namate (**45**) and pentafluorophenyl cinnamate (**47**) produced adducts **46** and **48** in around 50% yield (entries 1 and 2). Similar yields were obtained using cinnamonitrile (**49**) and 2-phenylsulfonylstyrene (**51**) producing dimethylcyclopropanes **50** and **52**, respectively, whereas nitrostyrene (**53**) underwent an extremely successful transformation giving adduct **54** in 93% yield (entries 3–5).

In summary, we have described the preparation of triisopropylsulfoxonium tetrafluoroborate (**13**) and its use as an isopropylidene transfer reagent for the *gem*-dimethylcyclopropanation of electron-deficient alkenes. Good to excellent yields were obtained with a range of cyclic and acyclic α,β-unsaturated ketones, quinones, a dienone, chromone, and with nitrostyrene. In addition, modest yields were obtained from unsaturated esters, nitriles, and sulfones; it should be noted that all of these processes have been carried out using the standard conditions (NaH, DMF) derived for chalcone and so higher yields may be possible with further optimisation. In the ketone examples, epoxide formation was never observed as a side reaction. However, enolisable substrates do present a problem with reagent **13**; this contrasts to the use of dimethylsulfoxonium methylide[3a,c] and diphenylsulfonium isopropylide[12a] [e.g., the latter reagent effects the conversion of cyclohexenone (**36**) into adduct **37** in 74% yield].[12a] These facts suggest that with reagent **13**, steric effects may slow down the initial addition process, or may favour reversible addition, resulting in side reactions with enolisable substrates. We are currently examining the use of triisopropylsulfoxonium tetrafluoroborate (**13**) in natural product synthesis.

PE refers to light petroleum ether; bp 40–60 °C. All reagents were used as supplied by the manufacturers, or prepared by literature methods. Flash column chromatography was performed using Fluka silica gel 60 at a low positive pressure. Analytical TLC was performed on aluminum sheets pre-coated with Merck silica gel 60 F_{254}, and visualised with ultraviolet light (254 nm), alcoholic *p*-anisaldehyde, aq $KMnO_4$, or alcoholic vanillin solutions, as appropriate. All melting points were taken on a Gallenkamp apparatus. ^1H NMR spectra were recorded at 400 MHz on a Jeol ECX400 spectrometer and are reported as follows: chemical shift δ (ppm) [multiplicity, coupling constant *J* (Hz), number of protons, assignment]. The coupling constants are quoted to the nearest 0.1 Hz and are reported as measured splittings on each individual resonance. The residual protic solvent $CHCl_3$ ($\delta_H = 7.26$) or acetone ($\delta_H = 2.05$) was used as an internal reference. ^{13}C NMR spectra were recorded at 100 MHz on a Jeol ECX400 spectrometer or at 125 MHz on a Bruker AV500 spectrometer. The central reference of $CDCl_3$ ($\delta_C = 77.0$) or acetone ($\delta_C = 29.8$) was used as an internal reference. ^{19}F spectra were recorded at 376 MHz on a Jeol ECX400 spectrometer or at 254 MHz on a Jeol EX270 spectrometer. ^{11}B spectra were recorded at 87 MHz on a Jeol EX270 spectrometer. Chemical shifts are reported in parts per million (ppm) to the nearest 0.01 ppm for ^1H, or to 0.1 ppm for ^{13}C, ^{19}F, and ^{11}B. IR spectra were recorded on a ThermoNicolet IR100 spectrometer between NaCl disks. Absorption maxima are reported in wavenumbers (cm^{-1}) and only selected absorbencies are reported. Mass spectra and accurate mass measurements were recorded on a Micromass Autospec spectrometer. All known products were characterised by NMR spectroscopy and comparison of key data with those published; new products were fully characterised.

Triisopropylsulfonium Tetrafluoroborate (12)

A 250 mL pear-shaped flask with a stirrer bar, was charged with diisopropyl sulfide (12.65 g, 107 mmol, 2.0 equiv) and 2-bromopropane (26.32 g, 214 mmol, 4 equiv) and cooled to 0 °C (ice-bath). The mixture was stirred vigorously and $AgBF_4$ (10.41 g, 53.5 mmol, 1 equiv) added in small portions. On complete addition the flask was fitted with a rubber septum and balloon of argon, the ice-bath was removed and the reaction allowed to warm to r.t. with continuous stirring. After 4 d, the mixture was passed through a pre-

packed silica column (60 g, 50 mm diam.) topped with Celite and eluted with acetone (1 L) to give a cloudy white filtrate, which was concentrated in vacuo. The residue was suspended in Et_2O (100 mL), filtered, washed with Et_2O (3 × 25 mL) to give a silver-coloured precipitate. The solid was left to stand overnight in the light, before being suspended in hot MeOH (100 mL) and filtered through a pad of Celite to remove residual silver, washed with further MeOH (150 mL) and concentrated in vacuo to give a yellow/brown solid that was recrystallised from MeOH–Et_2O. The product was collected by filtration, washed with Et_2O (50 mL), and dried in vacuo to give the title compound **12**; yield: 7.1 g (53%); mp 167–170 °C; cream-coloured plates.

IR (NaCl): 2972, 1464, 1388, 1259, 1163, 1046 cm^{-1}.

^1H NMR (400 MHz, acetone- d_6): δ = 1.66 (d, J = 7.0 Hz, 18 H, CH_3), 4.14 (sept, J = 7.0 Hz, 3 H, CH).

^{13}C NMR (100 MHz, acetone-d_6): δ = 20.8 (CH_3), 44.4 (CH).

^{19}F NMR (254 MHz, acetone-d_6): δ = –151.8.

^{11}B NMR (87 MHz, acetone-d_6): δ = –1.8.

MS (FAB): m/z = 161 [$(i\text{-Pr})_3S^+$].

HRMS-FAB: m/z calcd for $C_9H_{21}S$: 161.1364; found: 161.1360 (2.5 ppm error).

Anal. Calcd for $C_9H_{21}BF_4S$: C, 43.56; H, 8.53. Found: C, 43.85; H, 8.06.

Triisopropylsulfoxonium Tetrafluoroborate (13)

A 250 mL round-bottomed flask with stirrer bar was charged with triisopropylsulfonium tetrafluoroborate (**12**; 6.20 g, 25.0 mmol, 1.0 equiv) and then MeCN (36 mL), CCl_4 (36 mL), and H_2O (54 mL) were added via a syringe. The resulting biphasic solution was stirred vigorously and $RuCl_3$ (2.07 g, 10.0 mmol, 0.40 equiv) was added in a single portion. The mixture was stirred for 10 min and then $NaIO_4$ (40.10 g, 187.5 mmol, 7.5 equiv) was added in 5 portions over ~5 min to the brown-coloured solution. The flask was loosely stoppered with a cork and the mixture stirred vigorously overnight at r.t. (14 h). The resulting grey-brown heterogeneous suspension was filtered through a Celite pad (3 cm × 70 mm diam.) and washed with H_2O (400 mL). The yellow filtrate was stirred vigorously and MeOH (50 mL) was added to quench the residual RuO_4. The green suspension was concentrated under reduced pressure to remove the H_2O present (60 °C) and the grey solid residue suspended in acetone (400 mL). The mixture was stirred for a further 10 min and filtered to remove the residual inorganic solids. Concentration of the filtrate under reduced pressure afforded a yellow-orange powder that was recrystallised from MeOH–Et_2O giving the title compound **13**; yield: 5.6 g (76%); mp 108–109 °C; colourless plates.

IR (NaCl): 3427, 1699, 1642, 1462, 1369, 1235, 1198, 1049 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 1.79 (d, J = 7.0 Hz, 18 H, CH_3), 4.73 (sept, J = 7.0 Hz, 3 H, CH).

^{13}C NMR (100 MHz, acetone-d_6): δ = 15.7 (CH_3), 53.0 (CH).

^{19}F NMR (254 MHz, acetone-d_6): δ = –151.6.

^{11}B NMR (87 MHz, acetone-d_6): δ = –1.9.

MS (ESI): m/z = 177 [$(i\text{-Pr})_3SO^+$].

HRMS-FAB: m/z calcd for $C_9H_{21}OS$: 177.1308; found: 177.1308 (0.4 ppm error).

Anal. Calcd for $C_9H_{21}BF_4OS$: C, 40.93; H, 8.01. Found: C, 40.76; H, 7.85.

Cyclopropanation of α,β-Unsaturated Carbonyl Compounds; [(1*RS*,3*RS*)-2,2-Dimethyl-3-phenylcyclopropyl](phenyl)methanone (14); Typical Procedure (Table 2, Entry 1)

A 25 mL round-bottomed flask with stirrer bar was charged with NaH (60% dispersion in mineral oil, 23 mg, 0.57 mmol, 1.2 equiv), sealed with a rubber septum, and purged with argon. The flask was maintained under argon and anhyd DMF (4 mL) was added. The stirred suspension was cooled to 0 °C, the septum briefly removed and triisopropylsulfoxonium tetrafluoroborate (**13**; 152 mg, 0.57 mmol, 1.2 equiv) was added in a single portion. The mixture was stirred for 5 min before the addition of a solution of (*E*)-chalcone (**1**; 100 mg, 0.48 mmol) in DMF (1 mL) dropwise by a cannula. The cooling bath was removed and the brown-coloured solution allowed to stir at r.t. until the reaction was deemed to be complete by TLC (5 h). The reaction was quenched by the addition of sat. aq NH_4Cl (5 mL), diluted with H_2O (20 mL), and extracted with Et_2O (3 × 15 mL). The combined organic extracts were dried (Na_2SO_4) and the solvent removed in vacuo. The residue was purified by column chromatography (PE–Et_2O, 19:1) to afford **14** as a cream-coloured solid; yield: 109 mg (91%); mp 63–64 °C (Lit.[13] mp 65–66 °C); R_f = 0.39 (PE–EtOAc, 3:1).

^1H NMR (400 MHz, $CDCl_3$): δ = 1.12 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 2.91 (d, J = 6.0 Hz, 1 H, CH), 3.12 (d, J = 6.0 Hz, 1 H, CH), 7.20–7.24 (m, 3 H, ArH), 7.28–7.32 (m, 2 H, ArH), 7.49–7.53 (m, 2 H, ArH), 7.57–7.61 (m, 1 H, ArH), 7.99–8.02 (m, 2 H, ArH).

Data in accord with reported values.[24]

A similar procedure was followed for all other examples (which were carried out on a scale of 0.24–1.34 mmol).

[(1*RS*,3*RS*)-2,2-Dimethyl-3-(furan-2-yl)cyclopropyl](phenyl)methanone (17)

Yield: 15 mg (52%); colourless oil; R_f = 0.51 (PE–EtOAc, 3:1).

IR (film): 2925, 1670, 1449, 1241, 909, 733, 689 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.19 (s, 3 H, CH_3), 1.26 (s, 3 H, CH_3), 2.91–2.95 (m, 2 H, CH), 6.08 (d, J = 3.0 Hz, 1 H, ArH), 6.30 (dd, J = 3.0, 2.0 Hz, 1 H, ArH), 7.30 (dd, J = 0.5, 2.0 Hz, 1 H, ArH), 7.47–7.51 (m, 2 H, ArH), 7.55–7.60 (m, 1 H, ArH), 7.97–7.99 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3 (CH_3), 21.5 (CH_3), 29.4 (CH), 32.4 (C), 37.7 (CH), 107.0 (ArCH), 110.4 (ArCH), 128.3 (ArCH), 128.8 (ArCH), 133.1 (ArCH), 138.9 (ArC), 141.5 (ArCH), 153.2 (ArC), 197.7 (C=O).

MS (ESI): m/z = 263 [M + Na]$^+$, 241 [M + H]$^+$.

HRMS-ESI: m/z calcd for $C_{16}H_{17}O_2$ [M + H]$^+$: 241.1229; found: 241.1223 (3.2 ppm error).

[(1*RS*,3*RS*)-2,2-Dimethyl-3-(pyridin-2-yl)cyclopropyl](furan-2-yl)methanone (19)

Yield: 41 mg (71%); yellow solid; mp 64–65 °C; R_f = 0.19 (PE–EtOAc, 3:1).

IR (NaCl): 2924, 1657, 1591, 1568, 1468, 1415, 1261, 909, 733 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.20 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 3.10 (d, J = 6.0 Hz, 1 H, CH), 3.46 (d, J = 6.0 Hz, 1 H, CH), 6.57 (dd, J = 3.5, 1.5 Hz, 1 H, ArH), 7.12 (ddd, J = 7.5, 5.0, 1.0 Hz, 1 H, ArH), 7.27 (dd, J = 3.5, 1.0 Hz, 1 H, ArH), 7.28 (dt, J = 8.0, 1.0 Hz, 1 H, ArH), 7.57 (dd, J = 7.5, 2.0 Hz, 1 H, ArH), 7.60 (dd, J = 1.5, 1.0 Hz, 1 H, ArH), 8.53 (ddd, J = 5.0, 1.5, 1.0 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1 (CH_3), 20.2 (CH_3), 34.6 (CH), 36.4 (CH), 38.3 (C), 112.3 (ArCH), 116.9 (ArCH), 121.3 (ArCH), 124.7 (ArCH), 136.2 (ArCH), 146.5 (ArCH), 149.1 (ArCH), 154.5 (ArC), 157.9 (ArC), 187.0 (C=O).

MS (ESI): m/z = 242 $[M + H]^+$.

HRMS-ESI: m/z calcd for $C_{15}H_{16}NO_2$ $[M + H]^+$: 242.1103; found: 242.1176 (1.8 ppm error).

[(1*RS*,3*RS*)-2,2-Dimethyl-3-(furan-2-yl)cyclopropyl](furan-2-yl)methanone (21)
Yield: 89 mg (71%); colourless oil; R_f = 0.44 (PE–EtOAc, 3:1).

IR (film): 3134, 2954, 2874, 1661, 1569, 1469, 1415, 1378, 1257, 1098, 1035, 1015, 761 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.19 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 2.86–2.91 (m, 2 H, CH), 6.09 (d, J = 3.0 Hz, 1 H, ArH), 6.27 (dd, J = 3.0, 2.0 Hz, 1 H, ArH), 6.55 (dd, J = 3.5, 1.5 Hz, 1 H, ArH), 7.21 (dd, J = 3.5, 0.5 Hz, 1 H, ArH), 7.30 (dd, J = 2.0, 1.0 Hz, 1 H, ArH), 7.60 (dd, J = 1.5, 0.5 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0 (CH_3), 21.7 (CH_3), 29.9 (CH), 32.9 (C), 36.7 (CH), 107.0 (ArCH), 110.4 (ArCH), 112.4 (ArCH), 116.7 (ArCH), 141.5 (ArCH), 146.5 (ArCH), 153.0 (ArC), 154.3 (ArC), 186.2 (C=O).

MS (CI): m/z = 284 $[M + NH_4]^+$, 231 $[M + H]^+$, 135.

HRMS-CI: m/z calcd for $C_{14}H_{15}O_3$ $[M + H]^+$: 231.1021; found: 231.1014 (2.9 ppm error).

[(1*RS*,2*RS*)-3,3-Dimethylcyclopropane-1,2-diyl]bis(phenylmethanone) (23)
Yield: 78 mg (68%); colourless solid; mp 70–71 °C; R_f = 0.45 (PE–EtOAc, 3:1).

IR (NaCl): 2887, 2254, 1662, 1449, 1346, 1254, 909, 731, 650 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.35 (s, 6 H, CH_3), 3.54 (s, 2 H, CH), 7.49–7.53 (m, 4 H, ArH), 7.58–7.62 (m, 2 H, ArH), 8.01–8.03 (m, 4 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.8 (CH_3), 35.6 (C), 38.3 (CH), 128.5 (ArCH), 128.9 (ArCH), 133.4 (ArCH), 138.5 (ArC), 197.0 (C=O).

MS (ESI): m/z = 301 $[M + Na]^+$.

HRMS-ESI: m/z calcd for $C_{19}H_{18}O_2$ + Na $[M + Na]^+$: 301.1205; found: 301.1199 (3.15 ppm error).

(2,2-Dimethylcyclopropyl)(naphthalen-2-yl)methanone (25)
Yield: 38 mg (53%); colourless oil; R_f = 0.53 (PE–EtOAc, 3:1).

IR (film): 3059, 2924, 2870, 1666, 1627, 1465, 1394, 1376, 1275, 1180, 1117, 1000, 808 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.02 (dd, J = 7.5, 4.0 Hz, 1 H, CH), 1.14 (s, 3 H, CH_3), 1.43 (s, 3 H, CH_3), 1.59 (dd, J = 5.5, 4.0 Hz, 1 H, CH), 2.65 (dd, J = 7.5, 5.5 Hz, 1 H, CH), 7.55–7.63 (m, 2 H, ArH), 7.92 (t, J = 8.0 Hz, 2 H, ArH), 8.01 (d, J = 7.5 Hz, 1 H, ArH), 8.05 (dd, J = 8.5, 1.5 Hz, 1 H, ArH), 8.48 (s, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.2 (CH_3), 21.8 (CH_2), 28.7 (C), 28.8 (CH_3), 32.7 (CH), 124.3 (ArCH), 126.9 (ArCH), 128.0 (ArCH), 128.4 (ArCH), 128.5 (ArCH), 129.6 (ArCH), 129.8 (ArCH), 132.8 (ArC), 135.6 (ArC), 136.7 (ArC), 199.0 (C=O).

MS (ESI): m/z = 225 $[M + H]^+$.

HRMS-ESI: m/z calcd for $C_{16}H_{17}O$ $[M + H]^+$: 225.1279; found: 225.1274 (2.75 ppm error).

[(1*RS*,3*RS*)-2,2,3-Trimethylcyclopropyl)phenylmethanone (27)
Yield: 20 mg (53%); colourless oil; R_f = 0.52 (PE–EtOAc, 3:1).

IR (film): 2920, 1665, 1449, 1378, 1344, 1243, 1214, 1090, 1025, 910 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.10 (s, 3 H, CH_3), 1.16 (d, J = 6.5 Hz, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.81 (m, 1 H, CH), 2.11 (d, J = 5.5 Hz, 1 H, CH), 7.44–7.47 (m, 2 H, ArH), 7.52–7.56 (m, 1 H, ArH), 7.90–7.92 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7 (CH_3), 19.9 (CH_3), 20.8 (CH_3), 27.5 (CH), 31.9 (C), 40.2 (CH), 128.1 (ArCH), 128.7 (ArCH), 132.6 (ArCH), 139.6 (ArC), 199.7 (C=O).

MS (ESI): m/z = 189 $[M + H]^+$.

HRMS-ESI: m/z calcd for $C_{13}H_{17}O$ $[M + H]^+$: 189.1279; found: 189.1274 (2.6 ppm error).

1-[(1*RS*,3*RS*)-2,2-Dimethyl-3-phenylcyclopropyl]ethanone (29)
Yield: 44 mg (33%); colourless oil; R_f = 0.53 (PE–EtOAc, 3:1).

^1H NMR (400 MHz, $CDCl_3$): δ = 0.97 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 2.29 (d, J = 6.0 Hz, 1 H, CH), 2.33 (s, 3 H, CH_3), 2.85 (d, J = 6.0 Hz, 1 H, CH), 7.13–7.16 (m, 2 H, ArH), 7.19–7.22 (m, 1 H, ArH), 7.26–7.30 (m, 2 H, ArH).

Data in accord with reported values.[26]

[(1*RS*,3*RS*)-2,2-Dimethyl-(3*E*)-styrylcyclopropyl](phenyl)methanone (31)
Yield: 117 mg (85%); colourless solid; mp 66–69 °C; R_f = 0.54 (PE–Et_2O, 9:1).

IR (NaCl): 3059, 3027, 2947, 2923, 2781, 1664, 1597, 1579, 1494, 1449, 1413, 1378, 1353, 1278, 1227, 1178, 1111, 1053, 1022, 961, 862, 822, 767, 716, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.22 (s, 3 H, CH_3), 1.43 (s, 3 H, CH_3), 2.62–2.66 (m, 2 H, CH, CH), 6.08 (dd, J = 15.9, 4.0 Hz, 1 H, CH), 6.61 (d, J = 15.9 Hz, 1 H, CH), 7.21 (tt, J = 7.3, 1.5 Hz, 1 H, ArH), 7.28–7.36 (m, 4 H, ArH), 7.48 (t, J = 7.3 Hz, 2 H, ArH), 7.57 (tt, J = 7.3, 1.3 Hz, 1 H, ArH), 7.95 (dd, J = 7.3, 1.3 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0 (CH_3), 22.2 (CH_3), 33.1 (C), 36.7 (CH), 40.3 (CH), 125.8 (ArCH), 127.0 (ArCH), 127.5 (CH), 127.9 (ArCH), 128.5 (ArCH), 128.5 (ArCH), 131.7 (CH), 132.5 (ArCH), 137.3 (ArC), 138.8 (ArC), 197.5 (C=O).

MS (ESI): m/z = 299 $[M + Na]^+$, 277 $[M + H]^+$.

HRMS-ESI: m/z calcd for $C_{20}H_{21}O$ $[M + H]^+$: 277.1587; found: 277.1591 (1.5 ppm error).

(*E*)-1-[(1*RS*,3*RS*)-2,2-Dimethyl-3-phenylcyclopropyl]-3-phenylprop-2-en-1-one (33)
Yield: 65 mg (55%); colourless solid; 75–76 °C; R_f = 0.52 (PE–EtOAc, 3:1).

IR (NaCl): 3082, 3058, 3027, 2975, 2945, 2921, 2869, 1672, 1647, 1606, 1576, 1495, 1448, 1418, 1377,1342, 1304, 1282, 1234, 1202, 1179, 1107, 1055, 1029, 976, 913, 860, 801, 767 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 2.56 (d, J = 5.9 Hz, 1 H, CH), 3.02 (d, J = 5.9 Hz, 1 H, CH), 6.96 (d, J = 16.2 Hz, 1 H, CH) 7.18–7.24 (m, 3 H, ArH), 7.26–7.32 (m, 2 H, ArH), 7.38–7.45 (m, 3 H, ArH), 7.57–7.62 (m, 2 H, ArH), 7.59 (d, J = 16.2 Hz, 1 H, CH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.2 (CH_3), 22.4 (CH_3), 33.3 (C), 38.1 (CH), 39.3 (CH), 126.4 (ArCH), 128.1 (ArCH), 128.2 (ArCH), 128.4 (ArCH), 129.0 (ArCH), 129.0 (ArCH), 130.4 (ArCH), 134.7 (ArC), 137.9 (ArC), 141.9 (ArCH), 197.3 (C=O).

MS (ESI): m/z = 299 $[M + Na]^+$.

HRMS-ESI: m/z calcd for $C_{20}H_{20}O$ + Na $[M + Na]^+$: 299.1406; found: 299.1411 (1.7 ppm error).

Bis[(1*RS*,3*RS*)-2,2-dimethyl-3-phenylcyclopropyl]methanone (34) and [(1*RS*,3*RS*)-2,2-dimethyl-3-phenylcyclopropyl][(1*S*,3*S*)-2,2-dimethyl-3-phenylcyclopropyl]methanone (35)
Yield: 350 mg (94%); colourless solid; inseparable mixture of diastereoisomers (2.15:1); mp 58–60 °C; R_f = 0.63 (PE–EtOAc, 3:1; no separation).

IR (NaCl): 3027, 2972, 2950, 2919, 2871, 2361, 2338, 1666, 1602, 1579, 1497, 1443, 1422, 1375, 1278, 1103, 1070, 770 cm^{-1}.

MS (ESI): *m*/*z* = 341 $[M + Na]^+$.

HRMS-ESI: *m*/*z* calcd for $C_{23}H_{26}O$ + Na $[M + Na]^+$: 341.1876; found: 341.1882 (1.82 ppm error).

Major Diastereoisomer
^1H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 6 H, CH_3), 1.29 (s, 6 H, CH_3), 2.54 (d, *J* = 6.1 Hz, 2 H, CH), 2.93 (d, *J* = 6.1 Hz, 2 H, CH), 7.17–7.32 (m, 10 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.6 (CH_3), 22.6 (CH_3), 33.7 (C), 38.6 (CH), 42.0 (CH), 126.3 (ArCH), 128.1 (ArCH), 128.9 (ArCH), 138.0 (ArC), 205.2 (C=O).

Minor Diastereoisomer
^1H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, 6 H, CH_3), 1.32 (s, 6 H, CH_3), 2.50 (d, *J* = 6.1 Hz, 2 H, CH), 2.92 (d, *J* = 6.1 Hz, 2 H, CH), 7.17–7.32 (m, 10 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3 (CH_3), 22.4 (CH_3), 32.6 (C), 38.2 (CH), 41.9 (CH), 126.3 (ArCH), 128.1 (ArCH), 128.8 (ArCH), 137.9 (ArC), 205.0 (C=O).

(1*RS*,6*SR*)-7,7-Dimethylbicyclo[4.1.0]heptan-2-one (37)
Yield: 3 mg (4%); colourless oil; R_f = 0.68 (PE–EtOAc, 3:1)

^1H NMR (400 MHz, $CDCl_3$): δ = 1.16 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.40–1.85 (m, 6 H), 1.95–2.00 (m, 1 H), 2.15–2.20 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.7 (CH_3), 18.8 (CH_2), 25.8 (CH_2), 27.6 (C), 29.3 (CH_3), 30.9 (CH), 34.6 (CH), 40.0 (CH_2), 210.0 (C=O).

Data in accord with reported values.[27]

1,1a-Dihydro-1,1-dimethyl-7a*H*-cyclopropa[*b*]naphthalene-2,7-dione (39)
Yield: 92 mg (92%); beige solid; mp 109–111 °C; R_f = 0.32 (PE–EtOAc, 9:1).

IR (NaCl): 3041, 2949, 2924, 1675, 1592, 1361, 1325, 1297 (s), 1189, 1117, 1039, 1019, 996, 912, 849, 813, 749 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.09 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 2.54 (s, 2 H, CH), 7.68–7.72 (m, 2 H, ArH), 8.02–8.05 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.0 (CH_3), 29.4 (CH_3), 33.4 (CH), 40.3 (CH), 126.5 (ArCH), 134.1 (ArCH), 134.6 (ArC), 192.9 (C=O).

MS (ESI): *m*/*z* = 223 $[M + Na]^+$, 201 $[M + H]^+$.

HRMS-ESI: *m*/*z* calcd for $C_{13}H_{13}O_2$ $[M + H]^+$: 201.0910; found: 201.0908 (1.0 ppm error).

(1a*SR*,7a*SR*)-1,1-Dimethyl-1,1a-dihydrocyclopropa[*b*]chromen-7(7a*H*)-one (41)
Yield: 89 mg (95%); colourless solid; mp 96–98 °C; R_f = 0.26 (PE–Et_2O, 9:1).

IR (NaCl): 3036, 2996, 2959, 2927, 1658, 1606, 1578, 1462, 1337, 1231, 1126, 1055, 994, 887, 763 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 1.91 (d, *J* = 6.4 Hz, 1 H, CH), 4.19 (d, *J* = 6.4 Hz, 1 H, CH), 6.89 (d, *J* = 8.5 Hz, 1 H, ArH), 6.95 (ddd, *J* = 8.0, 7.5, 1.0 Hz, 1 H, ArH), 7.43 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1 H, ArH), 7.88 (dd, *J* = 8.0, 1.5 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.2 (C), 25.3 (CH_3), 33.8 (CH), 66.6 (CH), 116.8 (ArCH), 119.7 (ArC), 120.9 (ArCH), 126.2 (ArCH), 135.8 (ArCH), 159.9 (ArC), 188.4 (C=O).

MS (ESI): *m*/*z* = 211 $[M + Na]^+$, 189 $[M + H]^+$.

HRMS-ESI: *m*/*z* calcd for $C_{12}H_{13}O_2$ $[M + H]^+$: 189.0919; found: 189.0910 (4.6 ppm error).

7,7-Dimethylbicyclo[4.1.0]hept-3-ene-2,5-dione (43)
Yield: 9 mg (7%); brown-coloured needles; mp 60–62 °C; R_f = 0.39 (PE–EtOAc, 3:1).

IR (NaCl): 1673, 1653, 1458, 1380, 1304, 1117, 1050 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 2.33 (s, 2 H, CH) 6.61 (s, 2 H, CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.6 (CH_3), 29.2 (CH_3), 39.4 (C), 140.7 (CH), 194.7 (C=O).

MS (EI): *m*/*z* = 150 $[M]^+$.

HRMS-EI: *m*/*z* calcd for $C_9H_{10}O_2$ $[M]^+$: 150.0681; found: 150.0675 (4.0 ppm error).

(2*RS*,4*SR*,6*SR*,8*RS*)-4,4,8,8-Tetramethyltricyclo[5.1.0.$0^{0,0}$]octane-2,6-dione (44)
Yield: 64 mg (67%); cream-coloured solid; mp 155–158 °C; R_f = 0.22 (PE–EtOAc, 4:1).

IR (NaCl): 2990, 2959, 2931, 1672, 1453, 1366, 1344, 1303, 1276, 1123, 1044, 904, 885, 851, 731 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.21 (s, 6 H, CH_3), 1.32 (s, 6 H, CH_3), 1.91 (s, 4 H, CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.7 (CH_3), 28.7 (CH_3), 31.6 (C), 39.7 (CH), 201.6 (C=O).

MS (ESI): *m*/*z* = 215 $[M + Na]^+$, 193 $[M + H]^+$.

HRMS-ESI: *m*/*z* calcd for $C_{12}H_{17}O_2$ $[M + H]^+$: 193.1223; found: 193.1226 (1.8 ppm error).

Crystals suitable for X-ray diffraction were obtained by dissolving **44** in a minimal volume of CH_2Cl_2 and layering with hexane.[28]

Methyl (1*RS*,3*RS*)-2,2-Dimethyl-3-phenylcyclopropanecarboxylate (46)
Yield: 70 mg (52%); colourless oil; R_f = 0.41 (PE–EtOAc, 9:1).

^1H NMR (400 MHz, $CDCl_3$): δ = 0.93 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.96 (d, *J* = 6.0 Hz, 1 H, CH), 2.70 (d, *J* = 6.0 Hz, 1 H, CH), 3.73 (s, 3 H, OCH_3), 7.12–7.24 (m, 3 H, ArH), 7.27–7.32 (m, 2 H, ArH).

Data in accord with reported values.[29]

Pentafluorophenyl (1*RS*,3*RS*)-2,2-Dimethyl-3-phenylcyclopropanecarboxylate (48)
Yield: 55 mg (49%); colourless oil; R_f = 0.51 (PE–EtOAc, 3:1).

IR (film): 3062, 3031, 2956, 2925, 2876, 1773, 1521, 1452, 1421, 1381, 1340, 1311, 1281, 1233, 1192, 1106, 1057, 1021, 999, 906, 862, 821, 765 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 2.28 (d, *J* = 5.8 Hz, 1 H, CH), 2.87 (d, *J* = 5.8 Hz, 1 H, CH), 7.20–7.23 (m, 2 H, ArH), 7.25–7.28 (m, 1 H, ArH), 7.30–7.35 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6 (CH_3), 21.8 (CH_3), 30.5 (CH), 31.8 (C), 39.2 (CH), 125.3 (m, C), 126.8 (ArCH), 128.4 (ArCH), 128.7 (ArCH), 136.2 (ArC), 137.8 (dm, *J* = 249 Hz,

ArCF), 139.3 (dm, J = 253 Hz, ArCF), 141.2 (dm, J = 267 Hz, ArCF), 168.3 (C=O).

^{19}F NMR (254 MHz, acetone-d_6): δ = –162.4, –158.3, –152.4.

MS (EI): m/z = 356 $[M]^+$.

HRMS-EI: m/z calcd for $C_{18}H_{13}F_5O_2$ $[M]^+$: 356.0836; found: 356.0824 (3.4 ppm error).

(1*RS*,3*RS*)-2,2-Dimethyl-3-phenylcyclopropanecarbonitrile (50)

Yield: 71 mg (51%); pale yellow oil; R_f = 0.61 (PE–EtOAc, 3:1).

IR (film): 3032, 2961, 2926, 2234, 1603, 1497, 1451, 1382, 1270, 1195, 1117, 1061, 1029, 971, 850, 800, 742, 702 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3), 1.63 (d, J = 5.6 Hz, 1 H, CH), 2.52 (d, J = 5.6 Hz, 1 H, CH), 7.12–7.16 (m, 2 H, ArH), 7.23–7.34 (m, 3 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.1 (CH_3), 20.2 (CH_3), 23.8 (C), 26.5 (CH), 37.7 (CH), 120.5 (CN), 127.1 (ArCH), 128.4 (ArCH), 128.5 (ArCH), 135.2 (ArC).

MS (CI): m/z = 189 $[M + NH_4]^+$.

HRMS-CI: m/z calcd for $C_{12}H_{17}N_2$ $[M + NH_4]^+$: 189.1392; found: 189.1387 (2.6 ppm error).

[(1*SR*,3*RS*)-2,2-Dimethyl-3-(phenylsulfonyl)cyclopropyl]benzene (52)

Yield: 63 mg (45%); colourless solid; mp 88–90 °C; R_f = 0.35 (PE–EtOAc, 3:1).

IR (NaCl): 3429, 3062, 3028, 2958, 2923, 1447, 1306, 1148, 1087, 702, 689, 608 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3), 2.60 (d, J = 6.0 Hz, 1 H, CH), 3.09 (d, J = 6.0 Hz, 1 H, CH), 7.00–7.02 (m, 2 H, ArH), 7.22–7.26 (m, 3 H, ArH), 7.57–7.61 (m, 2 H, ArH), 7.65–7.69 (m, 1 H, ArH), 7.98–8.00 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2 (CH_3), 21.9 (CH_3), 29.4 (C), 36.3 (CH), 49.7 (CH), 127.3 (ArCH), 127.5 (ArCH), 128.6 (ArCH), 128.7 (ArC), 128.8 (ArCH), 129.5 (ArCH), 133.6 (ArCH), 135.6 (ArC).

MS (ESI): m/z = 287 $[M + H]^+$.

HRMS-ESI: m/z calcd for $C_{17}H_{19}O_2S$ $[M + H]^+$: 287.1106; found: 287.1100 (1.2 ppm error).

[(1*SR*,3*RS*)-2,2-Dimethyl-3-nitrocyclopropyl]benzene (54)

Yield: 123 mg (93%); pale yellow oil; R_f = 0.60 (PE–EtOAc, 3:1).

IR (film): 3064, 3031, 2960, 2927, 2879, 2359, 1603, 1536, 1500, 1451, 1361, 1268, 1113, 1055, 1029, 952, 930, 862, 828, 770, 716, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 3.36 (d, J = 4.6 Hz, 1 H, CH), 4.47 (d, J = 4.6 Hz, 1 H, CH), 7.14–7.19 (m, 2 H, ArH), 7.25–7.35 (m, 3 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.6 (CH_3), 20.7 (CH_3), 33.0 (C), 38.9 (CH), 70.3 (CH), 127.3 (ArCH), 128.4 (ArCH), 128.6 (ArCH), 134.1 (ArC).

MS (CI): m/z = 209 $[M + NH_4]^+$, 145.

HRMS-CI: m/z calcd for $C_{11}H_{17}N_2O_2$ $[M + NH_4]^+$: 209.1290; found: 209.1288 (1.1 ppm error).

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