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# Expedient synthesis of highly substituted 3,4-dihydro-1,2-oxathiine 2,2-dioxides and 1,2-oxathiine 2,2-dioxides: revisiting sulfene additions to enaminoketones†

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Diversely substituted 1,2-oxathiine 2,2-dioxides, including 3,5,6-triaryl-, 3,6-diaryl-, 3,5-diaryl-, 5,6-diaryl- and selected fused heterocyclic analogues, have been efficiently obtained by the application of a mild Cope elimination of a 4-amino moiety from the requisite 4-amino-3,4-dihydro-1,2-oxathiine 2,2-dioxides, which themselves were readily obtained by the addition of sulfenes to enaminoketones.

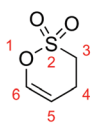


## Introduction

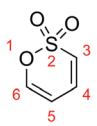
1,2-Oxathiine 2,2-dioxides (Fig. 1), historically referred to as δ-sultones, are the relatively scarcely studied isomers in the homologous series of sultones.[1] Indeed the 1,2-oxathiine ring is the lesser explored isomer of the six-membered heterocyclic systems which contain one sulfur and one oxygen atom.[2] However, there has been recent interest in the 1,2-oxathiine 2,2-dioxide unit in energy storage/battery technology[3] and as photoresists for high resolution lithography.[4]

There are relatively few synthetic routes to this fully unsaturated ring system, simple alkyl substituted analogues can be obtained by sulfonation of either α,β- or β,γ-unsaturated ketones.[5] 4,6-Diaryl substituted compounds result from either sulfonation of acetophenones[6] or arylacetylenes[7] though one drawback of this sulfonation approach is that the 4- and 6-aryl substituents are identical. Unexpected syntheses of the 1,2-oxathiine 2,2-dioxide ring have been noted from the sulfuric acid mediated acetolysis of methyl 5,6-di-*O*-acetyl-2,3-*O*-isopropylidene-β-L-gulofuranoside,[8] from the oxidative ring expansion of 2,5,9,12-tetra(*tert*-butyl)diacenaphtho[1,2-*b*:1′,2′-*d*]thiophene[9] and *via* tri-*n*-butylstannyl radical rearrangement of but-3-ynyl arenesulfonates.[10] Recent interest in the synthesis of benzofused δ-sultones has been stimulated by the Rh(III)-catalyzed oxidative coupling of arylsulfonic acids with internal alkynes.[11] In spite of the lack of general and versatile synthetic routes to 1,2-oxathiine 2,2-dioxides their chemistry offers potential with photolysis affording ketosulfonic esters[12] and thermolysis providing an efficient and frequently exploited route to 2,4-dimethylfuran[13] which serves as a useful building block for the A and C ring subunits of taxol[14] and the complex side chain of mycolactones A and B.[15] The addition of hydrazines to 1,2-oxathiine 2,2-dioxides affords both pyrroles and pyrazoles[16] and cycloaddition with acetylenes under forcing conditions results in overall expulsion of $SO_3$ to afford a useful array of terphenylene derivatives.[17]

A relatively scarcely explored route to the 1,2-oxathiine system involves the addition of sulfenes to enaminoketones.[18,19] Examination of the literature revealed that Schenone and co-workers had exploited the addition of sulfenes[20–24] to a selection of enaminoketones to afford 3,4-dihydro-1,2-oxathiine 2,2-dioxides. Interestingly, the amino function was retained in each of these sulfene addition reactions affording 3,4-dihydro-1,2-oxathiine 2,2-dioxide rather than undergoing a facile elimination to produce the conjugated 1,2-oxathiine 2,2-dioxide




3,4-dihydro-1,2-oxathiine 2,2-dioxide




1,2-oxathiine 2,2-dioxide

**Fig. 1** Structure and numbering for the 1,2-oxathiine 2,2-dioxide ring system.

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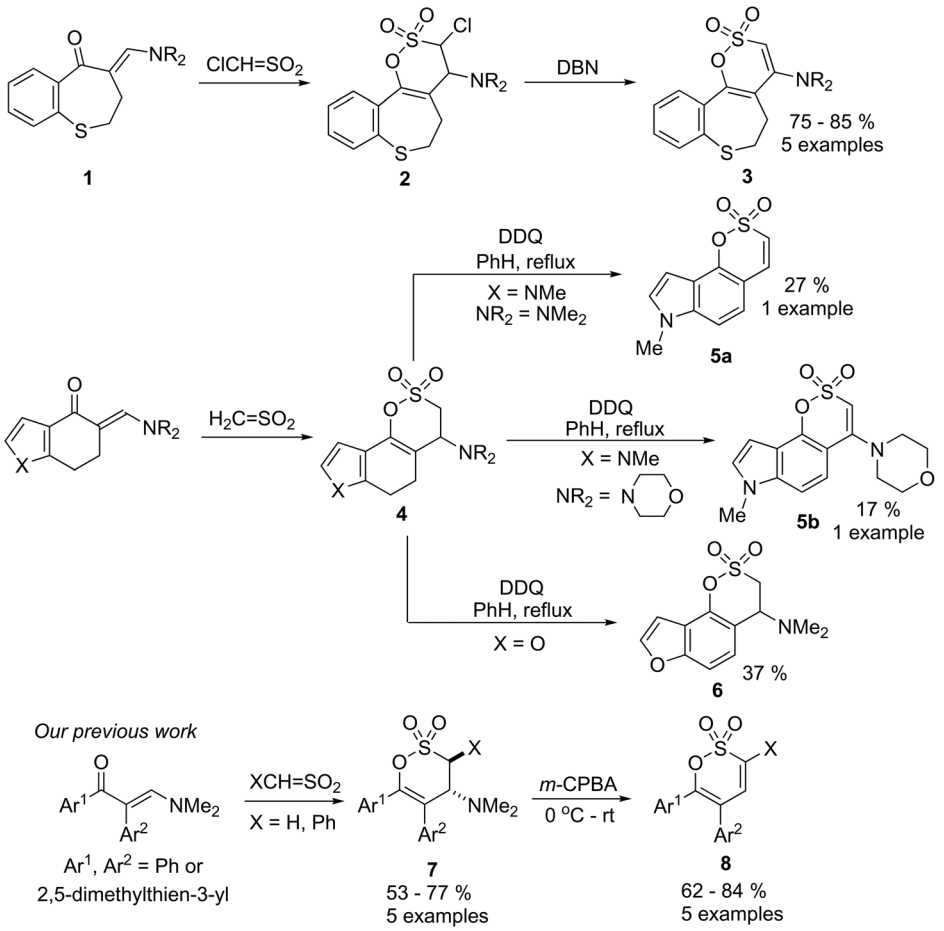



**Fig. 2** Previous attempts to obtain the 1,2-oxathiine 2,2-dioxide from substituted dihydro-1,2-oxathiine 2,2-dioxides.

system.[21–23] Notably, when chlorosulfene was added to a series of enaminoketones **1** the elimination of HCl was accomplished from the adducts **2** upon subsequent treatment with DBN to afford the substituted amino-1,2-oxathiine 2,2-dioxides **3**, but not the unsubstituted alkene, in good yield (Fig. 2).[24] In a related study the dehydrogenation of sulfene adduct **4** ($NR_2$ = $NMe_2$) with DDQ in refluxing benzene for 10 h gave the oxathiine **5a** in 27% yield and a similar treatment of **4** ($NR_2$ = morpholine) with a 24 h reflux gave **5b** in 17% yield (Fig. 2).[25] In the foregoing study the authors noted the variably of their DDQ aromatization protocol which failed to dehydrogenate the 1,2-oxathiine ring of the furan analogue **4** X = O and instead gave **6**.[26] We have previously examined the synthesis of a novel dithienylethene photochromic system in which the ethene bridge forms part of a 1,2-oxathiine 2,2-dioxide ring.[27] In the latter work the oxathiine unit was introduced by (phenyl) sulfene addition to a series of thienyl substituted enaminoketones with the intermediate 3,4-dihydro-1,2-oxathiine 2,2-dioxides **7** undergoing a facile, room temperature Cope elimination of the dimethylamine function to afford the unsaturated 1,2-oxathiine 2,2-dioxide moiety **8** in good yield (Fig. 2).

Given the success of our Cope elimination protocol coupled with the limited literature reports for the formation of 1,2-oxathiine 2,2-dioxides from preformed 3,4-dihydro analogues (Fig. 2) we commenced our exploration of the addition of arylsulfenes to a diverse series of enaminoketones with a view to widening access to 3,4-dihydro-1,2-oxathiine 2,2-dioxides and examining their transformation into new unsaturated 1,2-oxathiine 2,2-dioxides.

## Results and discussion

A range of enaminoketones **9a–k** were efficiently prepared by treatment of the requisite α-methylene ketones in *N*,*N*-dimethylformamide dimethylacetal (DMFDMA) according to literature procedures. Of note was the influence of the reaction medium and conditions on the outcome of the reaction of 3-oxo-3-phenylpropanenitrile (benzoylacetonitrile) with DMFDMA to afford **9f**; here crystalline salts **9f′** and **9f″** were isolated as minor by-products and have been characterised by X-ray crystallography (see ESI Fig. 1–3†).

Arylsulfenes, readily generated *in situ* from the base mediated elimination of HCl from the requisite arylmethanesulfonyl chlorides, underwent efficient addition to the acyclic enaminoketones **9a–d** to afford the 3,5,6-triaryl-4-amino-3,4-

dihydro-1,2-oxathiines 2,2-dioxides **10a–e** in generally high yield (48–96%). Enaminoketone **9d** which possesses an additional electron withdrawing group (X = Bz) required an extended reaction time in order to afford the desired oxathiine adduct **10e**. However, no oxathiines could be observed from the prolonged reaction of either **9e** or **9f** and the enaminoketone precursors were recovered (Scheme 1). The enaminoketones **9g–9k**, derived from 'acetophenones', similarly underwent smooth arylsulfene addition to afford 3,6-diaryl-4-amino-3,4-dihydro-1,2-oxathiines 2,2-dioxides **10f–j** in generally good yield (52–83%) with the exception of the pyridyl example **10i** (10%) where work-up was protracted due to the presence of the basic pyridyl function.

In a limited number of instances, the isolated crude 3,5,6-trisubstituted 4-dimethylamino-3,4-dihydro-1,2-oxathiines **10** were obtained as an unequal mixture of diastereoisomers as indicted from their NMR spectra. For example, the $^1$H NMR spectrum of crude **10a** revealed doublets at $\delta$ 4.96 (4-H) and $\delta$ 4.49 (3-H) with $J_{3,4}$ = 8.0 Hz for the major isomer and doublets at $\delta$ 4.89 (4-H) and $\delta$ 4.73 (3-H) with $J_{3,4}$ = 5.9 Hz for the minor isomer (Fig. 4), with the isomer ratio determined as 4 : 1. Similarly, crude **10d** displayed doublets at $\delta$ 4.76 (4-H) and $\delta$ 4.51 (3-H) with $J_{3,4}$ = 9.4 Hz for the major isomer (**10d1**) and doublets at $\delta$ 4.81 (4-H) and $\delta$ 4.69 (3-H) with $J_{3,4}$ = 6.3 Hz for the minor isomer (**10d2**), with an isomer ratio of 1.6 : 1. The major diastereoisomer **10d1** could be obtained in 48% yield by flash chromatography and crystallization. Additionally, a small amount of the minor isomer **10d2** was isolated (25%) and fully characterized. Interestingly, recording the $^1$H NMR spectrum of a $CDCl_3$ solution of **10d2** over 6 days revealed the gradual epimerisation of **10d2** into the original major isomer **10d1** (Fig. 3). We suspect that this epimerisation of **10d2** may be facilitated by protonation of the enol moiety (at C-5) which enables the 4-$NMe_2$ group to adopt a less hindered orientation that leads to a proposed *transoid* equatorial–equatorial arrangement of the 4-$NMe_2$ and 3-Ph substituents in the major isomer **10d1** (Scheme 5 insert).

The geometry of **10a** was established by X-ray crystallography (CCDC 1913655†), (Fig. 5 and ESI†) which revealed a *trans*-diaxial arrangement of 3-H and 4-H ($H_3$–$C_3$–$C_4$–$H_4$ torsion angle = 153°) in a half-chair conformation. The magnitude of $^1$H NMR coupling constant, $J_{3,4}$ = 8.0 Hz, in **10a** is somewhat diminished for such an arrangement *viz.* the typically larger *trans*-diaxial coupling in cyclohexane rings,[28] though in this instance the O–$C_6$–$C_5$–$C_4$–$C_3$ unit of the oxathiine ring is near planar. The $J_{3,4}$ coupling constants for the other 3,5,6-triaryl substituted dihydro-1,2-oxathiines are comparable with that of **10a** with **10b**, $J_{3,4}$ = 8.8 Hz and **10c**, $J_{3,4}$ = 7.6 Hz. Interestingly, the $J_{3,4}$ coupling constants for the remaining 3,5,6-trisubstituted oxathiines were larger with **10d1**, $J_{3,4}$ = 9.4 Hz and **10e**, $J_{3,4}$ = 10.3 Hz. For the minor isomer **10d2** the smaller $J_{3,4}$ coupling of 6.3 Hz results from the interaction between axial and equatorial disposed protons.

In contrast, $J_{3,4}$ for the 3,6-diaryl substituted oxathiines (unsubstituted at C-5) (**10f–10j**) were again larger for those of **10a–e** typically of the order of 11.2 Hz. Clearly the presence of an aryl ring at C-5 in **10a–e** modifies the conformation of the dihydro-1,2-oxathiine ring and thus the coupling constants (Fig. 4).

Examination of the $^1$H NMR spectra of the adducts **12a, b** which resulted from the addition of sulfene to enaminoketones **9a, b** (Scheme 3) revealed $J_{3,4}$ coupling constants of 7.4 Hz and 9.1 Hz (**12a**) and 6.3 Hz and 11.4 Hz (**12b**), respectively and which are indicative of the 4-dimethylamino substituent occupying an equatorial site of the half-chair conformer. Of note in the $^1$H NMR spectrum of **12b** was a long-range coupling of 1.0 Hz between 5-H and the equatorially disposed 3-H. Interestingly, a second component was isolated from the reaction between sulfene and **9b** which was characterized as the oxathiine-2,2-dioxide **13b** (50%) on the basis of the chemical shift of 3-H ($\delta$ 6.57, d, $J$ = 10.0 Hz), 4-H ($\delta$ 6.91, dd, $J$ = 10.0, 6.8 Hz) and 5-H ($\delta$ 6.30, d, $J$ = 6.8 Hz) and which presumably forms by the facile elimination of dimethylamine from the isomer in which the dimethylamine group and a 3-H are *trans*-disposed (*anti-peri*-planar arrangement). Selected $^1$H NMR data is presented in Fig. 4 for a series of 3,5,6-triphenyl-, 3,6-diphenyl- and 5,6-diphenyl-1,2-oxathiine 2,2-dioxides.

In order to extend the structural diversity of the dihydro-1,2-oxathiines, by substrate variation, sulfene additions to enaminoketones **15** and **18**, derived from arylmethyleneketone

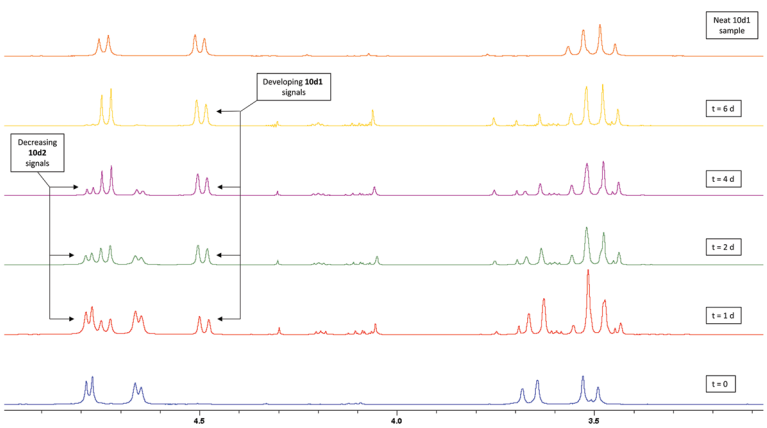



**Fig. 3** Time resolved $^1$H NMR spectra ($\delta$ 3.0–5.0) showing epimerisation of **10d2** into **10d1** over 6 days in $CDCl_3$ solution.

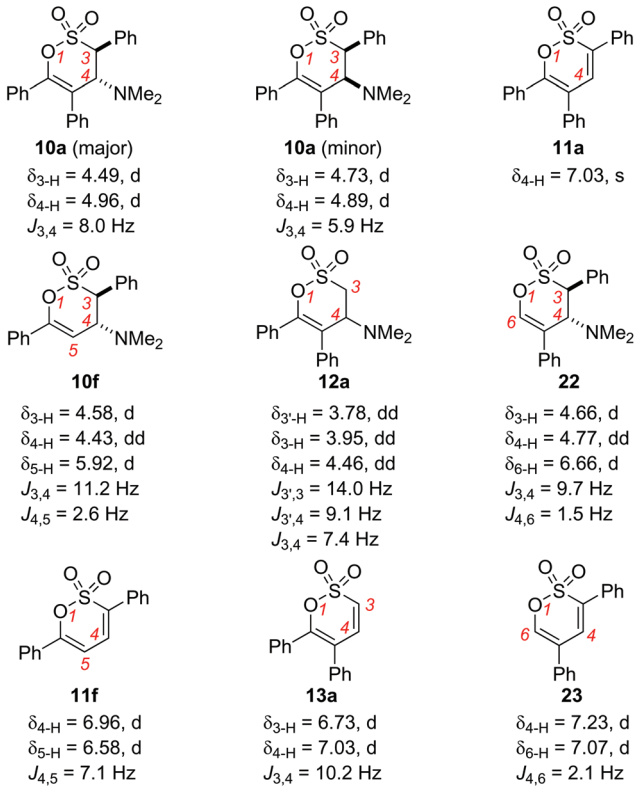



**Fig. 4** Selected $^1$H NMR data ($CDCl_3$) for 3,5,6-triphenyl-, 3,6-diphenyl-, 3,5-diphenyl- and 5,6-diphenyl- (3,4-dihydro) 1,2-oxathiine 2,2-dioxides.

**14** and 2-tetralone, respectively and sulfene addition to the enaminoaldehyde **21** were explored (Scheme 4). Phenylsulfene addition to **15** proceeded smoothly to afford **16** in 79% yield. As a consequence of restricted rotation of the *o*-fluorophenyl unit due to steric congestion with the adjacent methyl and dimethylamino groups the $^1$H NMR spectrum of **16** was complex. Indeed recording the spectrum at 233 K revealed a mixture of two rotamers (ESI) which coalesce upon recording the spectrum at 323 K. A small variation in $J_{3,4}$ was observed with the rotamers affording couplings of 9.7 and 9.9 Hz (233 K) and the thermally averaged compound giving $J_{3,4}$ = 9.5 Hz (323 K). The 1,2,5,6-tetrahydronaphtho[1,2-*e*][1,2]oxathiine 3,3-dioxide **19** (from **18**) was isolated in 65% yield and exhibited $J_{3,4}$ = 8.9 Hz. In contrast to the foregoing reactions of enaminoketones, the enaminoaldehyde derivative **21** afforded a complex crude product from which two new pure components **22** (5%) and **23** (2.9%) were isolated. The dihydro-1,2-oxathiine **22** exhibited a doublet with allylic coupling of 1.5 Hz, at $\delta$ 6.66 for 6-H and a doublet at $\delta$ 4.66 for 3-H with the typical $J_{3,4}$ value of 9.7 Hz. The introduction of the C=C bond in **23** resulted in the presence of a pair of doublets ($\delta$ 7.07, 7.03) in the $^1$H NMR spectrum with a coupling constant of 2.1 Hz (Fig. 4).

With a series of 4-dimethylamino-3,4-dihydro-1,2-oxathiine 2,2-dioxides to hand (**10a–j**, **12a**, **12b**, **16** and **19**) the introduction of the C-3–C-4 oxathiine ring double bond by the elimination of dimethylamine was examined. From our earlier observations it is clear that the elimination of dimethylamine can be facile *e.g.* **12b** → **13b** and **22** → **23**, presumably from an isomer where 3-H is suitably disposed to the 4-dimethylamino function. Thus, treatment of a PhMe solution of **10a** with a catalytic amount of 4-TsOH and stirring at either room temperature or under reflux failed to afford any **11a**. Indeed, increasing the amount of 4-TsOH up to a 10-fold molar excess of **10a** and heating the solution under reflux overnight resulted in darkening of the reaction mixture together with the formation of decomposition products as indicated by the presence of several very minor components observed by TLC together with some unchanged major component. Given the conformation depicted in Fig. 5, a Cope elimination protocol[29] was explored. Treatment of a cooled $CH_2Cl_2$ solution of **10a** with a slight excess of *m*-CPBA and stirring at room temperature for 18 h resulted in the efficient elimination of the dimethylamine unit to afford **11a** in 71% isolated yield. A singlet

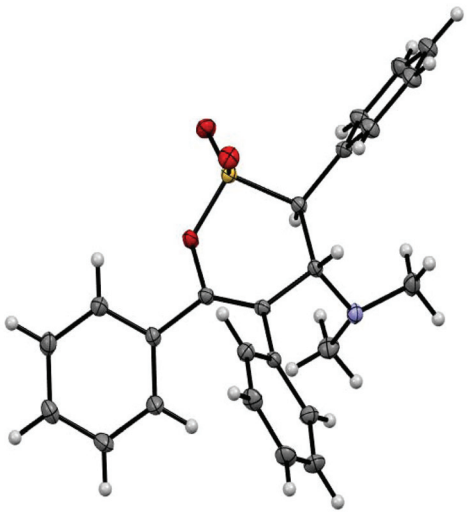


**Fig. 5** Crystal structure of **10a** (thermal ellipsoids shown at 50% probability level).

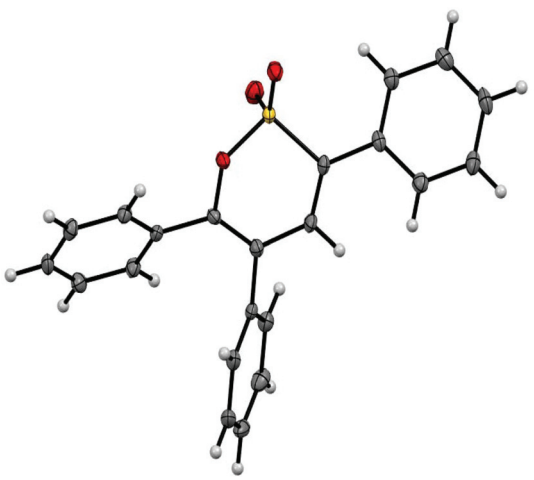
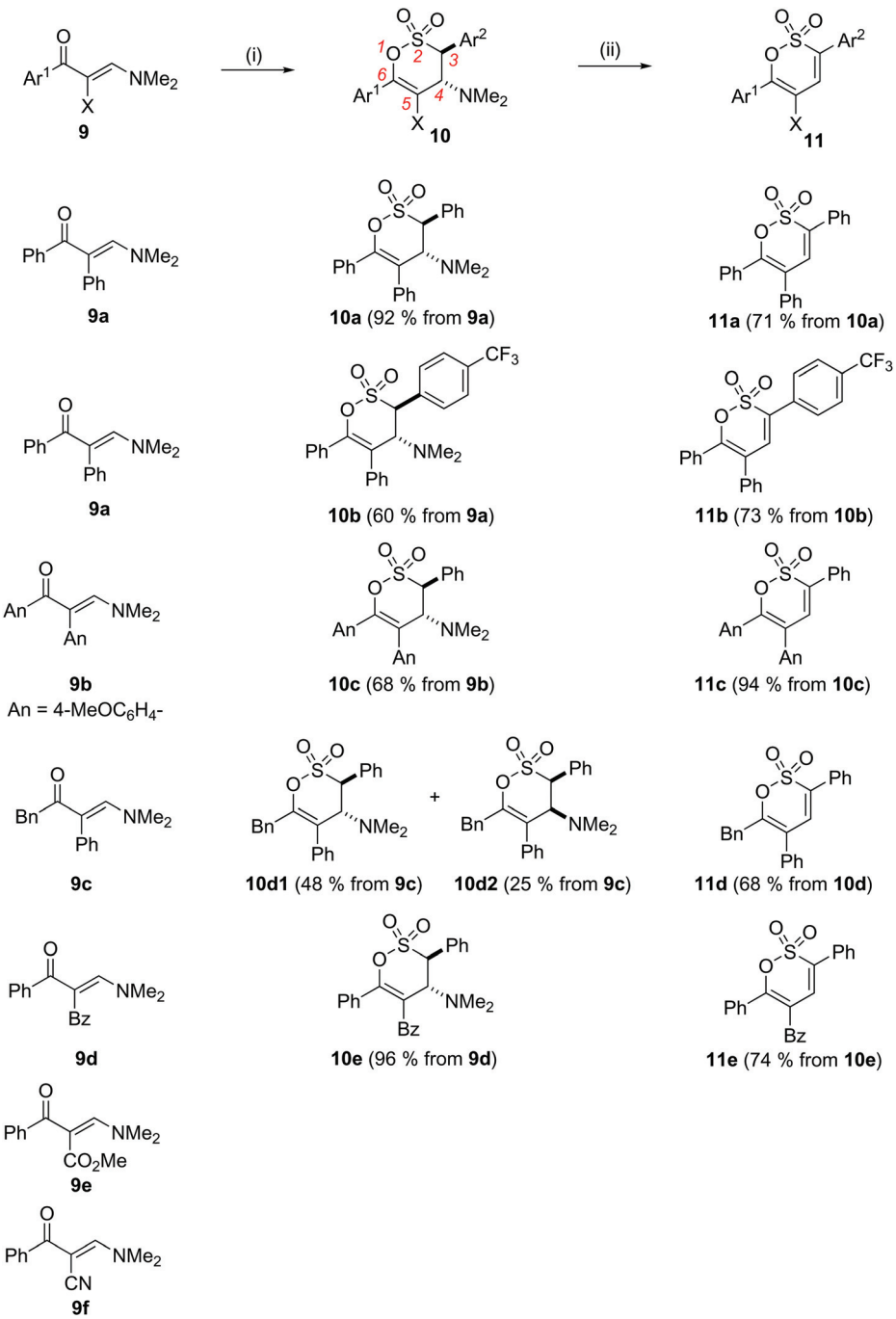


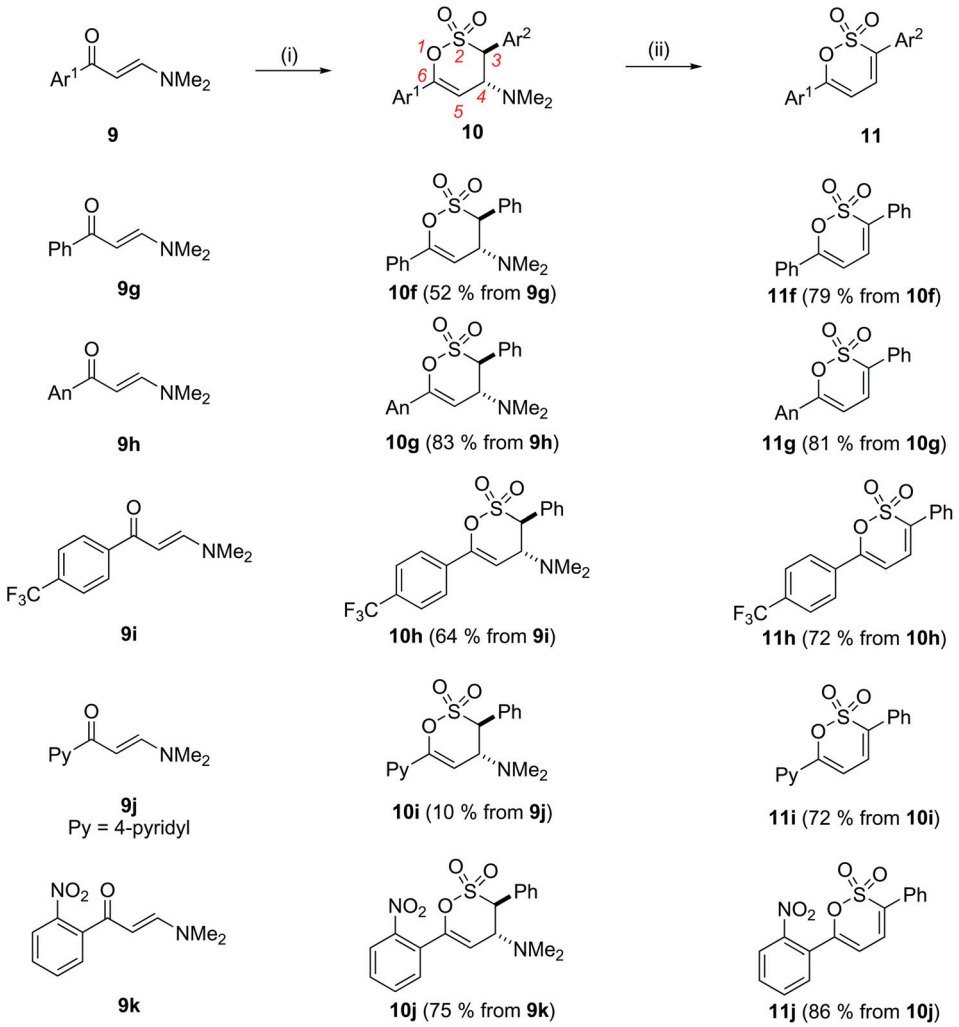
**Fig. 6** Crystal structure of **11a** (thermal ellipsoids shown at 50% probability level).

was observed at $\delta$ 7.03 for 4-H confirming the elimination of the amine and a single crystal structure (CCDC 1913656†), (Fig. 6) confirmed the successful elimination protocol. The Cope reaction sequence was then carried out on the remaining 4-dimethylamino substituted 1,2-oxathiine 2,2-dioxides to afford **11b–j**, **13a**, **13b**, **17** and **20** in good to excellent yields (68–96%) (Schemes 1 and 2). Interestingly for the 3,6-diaryl substituted 1,2-oxathiines (**11f–j**) $J_{4,5}$ was *ca.* 6.8–7.2 Hz, whereas $J_{3,4}$ = 10.2 Hz was typical of *cis*-alkene coupling for the 5,6-disubstituted analogue **13a** (Fig. 4). The foregoing trend in the magnitude of the coupling constants was consistent for the mono-aryl substituted oxathiine **13b** with $J_{3,4}$ = 10.0 Hz and $J_{4,5}$ = 6.8 Hz.

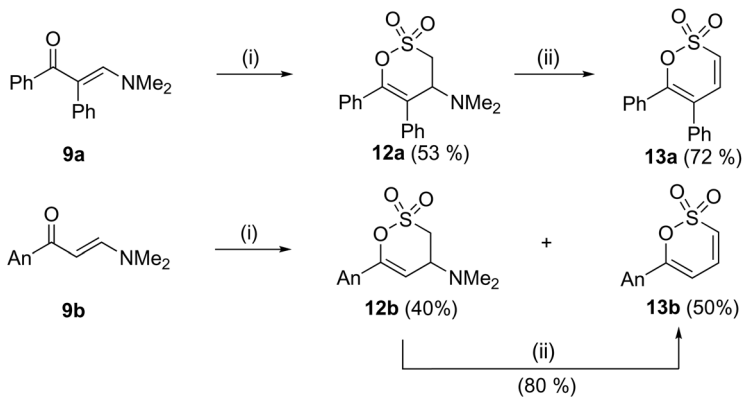
In an extension of the foregoing elimination study, we examined the acid-catalysed elimination of dimethylamine from the isolated minor isomer **10d2** in which 4-$NMe_2$ group is in an *anti-peri*-planar arrangement with 3-H. Thus, heating **10d2** in toluene containing 4-TsOH (20 mol%) gave a multi-




**Scheme 1** Synthesis of 3,5,6-trisubstituted 1,2-oxathiines 2,2-dioxides **11**. Reagents and conditions: (i) $Ar^2CH_2SO_2Cl$, $Et_3N$, THF 0 °C–rt; (ii) *m*-CPBA (1.2 eq), $CH_2Cl_2$, 0 °C–rt.




**Scheme 2** Synthesis of 3,6-disubstituted 1,2-oxathiine 2,2-dioxides **11**. Reagents and conditons: (i) $Ar^2CH_2SO_2Cl$, $Et_3N$, THF 0 °C–rt; (ii) *m*-CPBA (1.2 eq), $CH_2Cl_2$, 0 °C–rt.

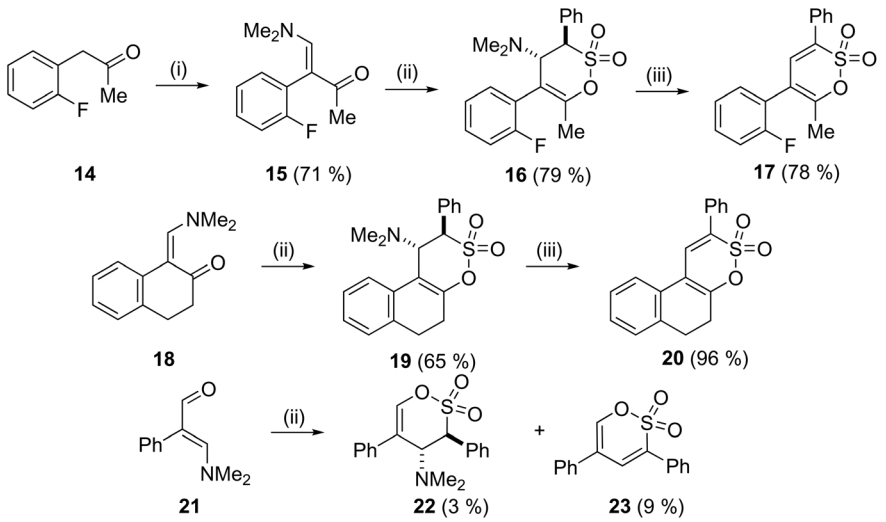



**Scheme 3** Synthesis of 5,6-diaryl- and 6-aryl-1,2-oxathiine 2,2-dioxides. Reagents and conditions: (i) $MeSO_2Cl$, $Et_3N$, THF 0 °C–rt; (ii) *m*-CPBA (1.2 eq.), $CH_2Cl_2$, 0 °C–rt.

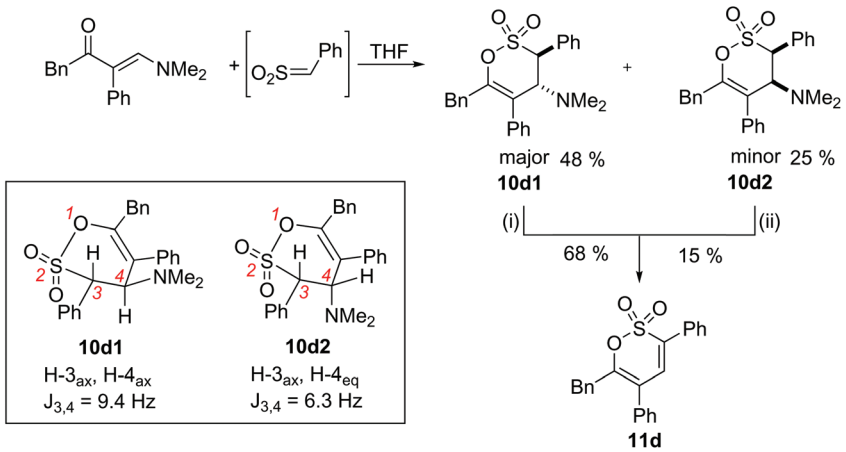
component reaction mixture from which the major component, the 1,2-oxathiine 2,2-dioxide **11d**, was isolated in low yield (15%) (Scheme 5).

With efficient methodology developed for the addition of sulfenes to the series of enaminoketones and the subsequent elimination of the dimethylamino function from the 3,4-



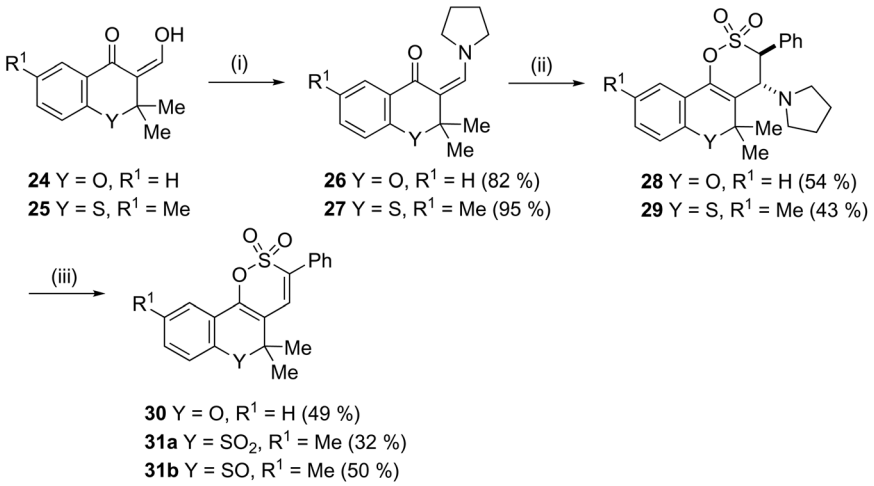

**Scheme 4** Synthesis of substituted 1,2-oxathiine 2,2-dioxides **17**, **20** and **23**. Reagents and conditions: (i) DMFDMA, reflux; (ii) $PhCH_2SO_2Cl$, $Et_3N$, THF 0 °C–rt; (iii) *m*-CPBA, $CH_2Cl_2$, 0 °C–rt.




**Scheme 5** Elimination reactions to afford **11d**. Reagents and conditions: (i) *m*-CPBA (1.2 eq.), $CH_2Cl_2$, 0 °C–rt; (ii) 4-TsOH (20 mol%), PhMe, reflux.

dihydro-1,2-oxathine 2,2-dioxides to afford a diverse series of novel 1,2-oxathine 2,2-dioxides the synthesis of some condensed heterocyclic ring systems was examined. 3-Hydroxymethylene substituted chroman-**24** and thiochroman-4-ones **25** were readily obtained by literature protocols.[30,31] Allowing a dry PhMe solution of either **24** or **25** containing pyrrolidine to stand overnight over anhyd. $Na_2SO_4$ resulted in the efficient formation of the enaminoketones **26** (82%) and **27** (95%), respectively. Using our standard procedure, the reaction of phenylsulfene, generated *in situ*, with **26** and **27** was undertaken and afforded the fused dihydro-1,2-oxathiines **28** (54%) and **29** (43%) (Scheme 6). The $^1$H NMR spectrum of crude **28** indicated the presence of a minor isomer (ratio minor : major = 3 : 20) with $J_{3,4}$ = 5.1 Hz ($\delta_{3\text{-H}}$ 4.65, $\delta_{4\text{-H}}$ 4.25) which was readily removed upon recrystallization to leave the major diastereoisomer which exhibited $\delta_{3\text{-H}}$ 4.94 and $\delta_{4\text{-H}}$ 4.61 with $J_{3,4}$ = 7.6 Hz. The X-ray crystal structure of **28** (CCDC 1913658†), (Fig. 7) revealed that the $C_3$–$C_4$–$C_5$–$C_6$–O is near planar with the $SO_2$ unit out of plane and that H-3 and H-4 are in a *trans*-diaxial arrangement with a $H_3$–$C_3$–$C_4$–$H_4$ torsion angle of *ca.* 162°. The $^1$H NMR spectrum of crude **29** also indicated the presence of a minor isomer (ratio minor : major = 3 : 50 with $J_{3,4}$ = 4.5 Hz). The $^1$H NMR spectrum of the major isomer showed similar features to that of **28** with $\delta_{3\text{-H}}$ 4.91 and $\delta_{4\text{-H}}$ 4.61, however $J_{3,4}$ is now smaller at 5.2 Hz which suggests that the presence of the larger sulfur atom exerts an influence on the geometry of the fused oxathiine dioxide ring.

The Cope elimination reaction proceeded smoothly with **28** to afford **30** in 49% yield. An excess of *m*-CPBA was used for the Cope reaction of **29**, as a consequence of the possibility of oxidation of the thiochroman ring heteroatom, and resulted in a mixture of the *S*-oxidised analogues **31a** (32%) and **31b** (50%) (Scheme 6). The chemical shift of the oxathiine ring proton (4-H) for the series **30**, **31a** and **31b** appeared in the narrow range $\delta$ 6.75–6.97 and the *gem*-methyl groups (C-5) are




**Scheme 6** Synthesis of fused benzo(thio)pyrano 1,2-oxathiines **30** and **31**. Reagents and conditions: (i) pyrrolidine, PhMe (anhyd.), rt; (ii) $PhCH_2SO_2Cl$, $Et_3N$, THF 0 °C–rt; (iii) *m*-CPBA (1.2–3.0 eq.), $CH_2Cl_2$, 0 °C–rt.

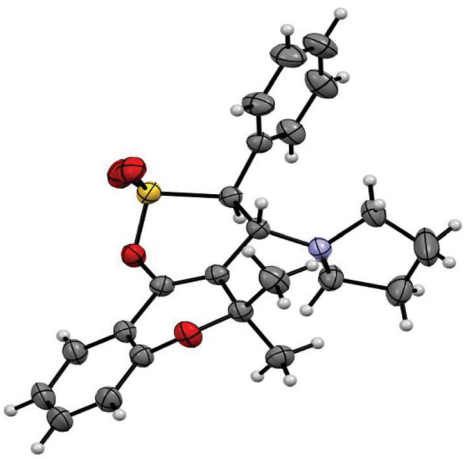
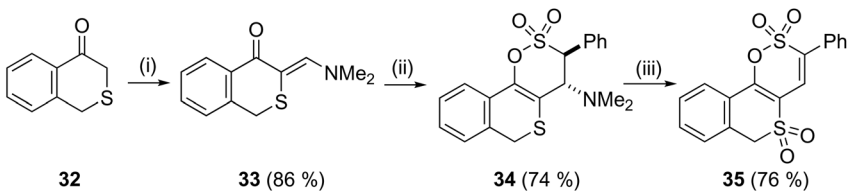


**Fig. 7** Crystal structure of **28** (thermal ellipsoids shown at 50% probability level).

non-equivalent in **31b** ($\delta_{Me}$ = 1.46, 1.71) and equivalent in **30** ($\delta_{Me}$ = 1.65) and **31a** ($\delta_{Me}$ = 1.68).

Isothiochromanone **32** was readily prepared by the Friedel–Crafts cyclisation of commercial *S*-benzylthioacetic acid according to the procedure described by Aiken *et al.*[32] Reaction of **32** with DMFDMA afforded the enaminoketone **33** ($\delta_{1\text{-H}}$ 3.75; $\delta_{=CH}$ 7.99) in 86% yield after crystallisation. Phenylsulfene addition proceeded smoothly to afford **34** in 74% yield, after routine flash column chromatography. Compound **34** was isolated as an inseparable mixture of diastereoisomers in a ratio 1.7 : 1.0 based on relative integrals of the $^1$H NMR signals for 3-H and for 4-H in each isomer which appear at (major)$\delta_{3\text{-H}}$ 4.79 ($J_{3,4}$ = 10.5 Hz) and (minor)$\delta_{3\text{-H}}$ 4.88 ($J_{3,4}$ = 6.4 Hz) and (major)$\delta_{4\text{-H}}$ 4.59 and (minor)$\delta_{4\text{-H}}$ 4.65. Cope elimination of the $NMe_2$ function using a 7.25-fold excess of *m*-CPBA afforded the tricyclic tetraoxide **35** in 76% yield (Scheme 7). In the $^1$H NMR spectrum of **35** 4-H and the 6-$CH_2$ unit appear as singlets at $\delta$ 7.54 and $\delta$ 5.00, respectively. Notably the signal for the equivalent 6-$CH_2$ protons in **35** is shifted downfield relative to that in **34**, in which the non-equivalent protons resonate as doublets [major diastereoisomer $\delta$ 3.56, $\delta$ 4.15 ($J$ = 14.2 Hz) and minor diastereoisomer $\delta$ 3.75, $\delta$ 4.07 ($J$ = 14.2 Hz)] as a consequence of the oxidation of the S atom during the Cope elimination protocol. The structure of **35** (Fig. 8) was confirmed by X-ray crystallography (CCDC 1913657†) which revealed that the $SO_2$ unit of each hetero-ring lies out of the main ring plane.

Given the preliminary success concerning the synthesis of the oxathiines **11a–j**, **13a**, **13b**, **17**, **20**, **23** and fused oxathiines **30**, **31a,b** and **35** we briefly examined the reaction of (*E*)-*N*-((dimethylamino)methylene)-4-methylbenzamide **36**, derived from




**Scheme 7** Preparation of 3-phenyl-6*H*-isothiochromeno[3,4-*e*][1,2]oxathiine 2,2,5,5-tetraoxide **35**. Reagents and conditions: (i) DMFDMA, reflux; (ii) $PhCH_2SO_2Cl$, $Et_3N$, THF 0 °C–rt; (iii) *m*-CPBA (7.25 eq.), $CH_2Cl_2$, 0 °C–rt.

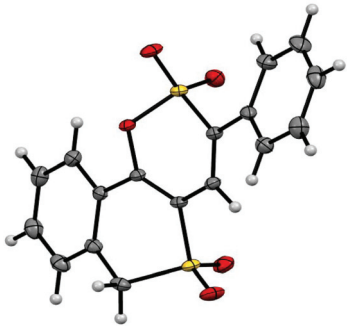


Fig. 8 Crystal structure of **35** (thermal ellipsoids shown at 50% probability level).

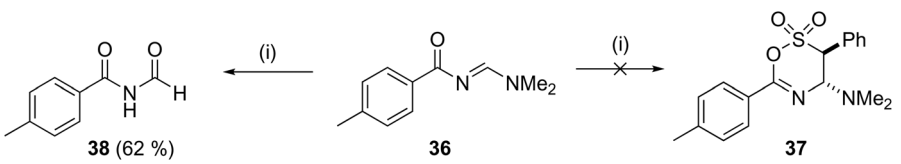
*p*-toluamide and DMFDMA, with a view to obtaining the 3,4-dihydro-1,2,5-oxathiazine 2,2-dioxide **37** (Scheme 8). Unfortunately, **37** could not be detected from the reaction of **36** with phenylsulfene and instead the *N*-formylbenzamide **38** (62%) was the major product isolated after aqueous work-up. The hydrolysis of *N*-((dimethylamino)methylene)benzamides has been previously reported as a useful route to *N*-formylbenzamides.[33]

We sought to capitalise on the foregoing observation and examined the reaction of the unsymmetrical bis-dimethylaminomethylene **39** with phenylsulfene in order to obtain the *N*-formyl protected 6-amino substituted 3,4-dihydrooxathiine dioxide **33** (Scheme 9). Our initial attempt to prepare precursor **39** upon refluxing a solution of 2-phenylacetamide was unsuccessful with the $^1$H NMR spectrum of the crude reaction product indicating two singlets at $\delta$ 3.02 and $\delta$ 2.95 each accounting for 6H and lower field singlet at $\delta$ 3.74 accounting for 3H. Column chromatography of the mixture gave the pure formimidate **41** (39%) as a consequence of adventitious addition of *in situ* produced MeOH to the formed **39**. Repeating the reaction with DMFDMA but with removal of the produced methanol from the reaction by distillation resulted in the smooth formation of **39**. Bis-dimethylaminomethylene **39** has been previously obtained in 90% yield by the reaction of bis(dimethylamino)-*t*-butoxymethane (Bredereck's reagent) with 2-phenylacetamide[34] though the present method affording **39** in 63% yield is advantageous as a consequence of the readily available and inexpensive DMFDMA. The generation of phenylsulfene in the presence of **39** unexpectedly afforded the oxathiine dioxide **42** directly in 9% yield after aqueous washings, column chromatography and recrystallizations; the anticipated 3,4-dihydro adduct **40** was not observed.

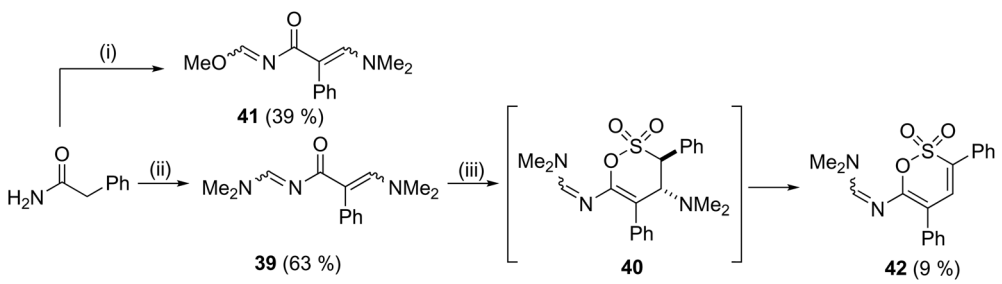
## Conclusions

(*E*)-2,4-Dicyano-1,5-dioxo-1,5-diphenylpent-3-en-2-ide, a new extensively delocalised carbanion, has been isolated and structurally characterised from the preparation of (*E*)-2-benzoyl-3-(dimethylamino)acrylonitrile from benzoylacetonitrile. The nature of the accompanying cation was dictated by the reaction conditions; with DMFDMA diluted with PhMe at RT the *N*-((dimethylamino)methylene)-*N*-methylmethanaminium counterion was preferred whereas neat DMFDMA favoured the formation of the tetramethylammonium counterion.

The addition of various sulfenes, generated *in situ* from the (aryl)alkylsulfonyl chlorides and $Et_3N$, to an extensive series of enaminoketones proceeded smoothly to afford diversely substituted 4-amino-3,4-dihydro-1,2-oxathiine 2,2-dioxides, including 3,5,6-triaryl-, 3,6-diaryl-, 3,5-diaryl- and 5,6-diaryl- analogues, in good yield. A *transoid* (di-equatorial) relationship between the 3-aryl substituent and the 4-amino function for the isolated major isomers was established by X-ray crystallo-




Scheme 8 Formation of *N*-formylbenzamide **38**. Reagents and conditions: (i) $PhCH_2SO_2Cl$, $Et_3N$, THF 0 °C–rt.




Scheme 9 Formation of *N*-protected 6-amino 1,2-oxathine **42**. Reagents and conditions: (i) DMFDMA, reflux; (ii) DMFDMA, reflux, MeOH removal; (iii) $PhCH_2SO_2Cl$, $Et_3N$, THF 0 °C–rt.

graphy and NMR spectroscopy for the adducts derived from an aryl methanesulfonyl chloride. In $CDCl_3$ solution, a sample of an isolated pure minor isomer (**10d2**) was observed by $^1$H NMR spectroscopy to epimerise to afford the major isomer in *ca*. 6 days.

The 4-amino-3-aryl-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**10a**) resisted attempts to effect an acid-catalysed elimination of the 4-amino function. However, the isolated minor isomer (**10d2**) underwent a reluctant acid acid-catalysed elimination to afford the 1,2-oxathiine 2,2-dioxide **11d**. Application of Cope methodology resulted in the efficient, smooth elimination of the 4-amino function from **10a–j** and **10d1** to afford the unsaturated 1,2-oxathiine 2,2-dioxides series **11** in high yield. This simple protocol constitutes an efficient route to a series of novel, structurally diverse 1,2-oxathiine 2,2-dioxides and in particular describes a new condensed heterocyclic ring system, the 6*H*-isothiochromeno[3,4-*e*][1,2]oxathiine. It is noteworthy that previously reported direct routes to 1,2-oxathiine 2,2-dioxides cannot provide the structural diversity afforded by the two-step protocol described herein. Attempts to extend our sulfene addition–elimination protocol to *N*-((dimethylamino) methylene)benzamides to obtain 1,2,5-oxathiazine 2,2-dioxides was unsuccessful and resulted in a new route to *N*-formylbenzamides.

Our studies concerning both the reactivity and the application of the 1,2-oxathiine 2,2-dioxide moiety as a scaffold for materials applications are ongoing.

## Equipment and materials

Unless otherwise stated, reagents and solvents were purchased from major chemical catalogue companies and were used as supplied. Routine $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a Bruker Avance DPX400 instrument in $CDCl_3$. Variable Temperature $^1$H NMR (500 MHz) and $^{13}$C NMR (125 MHz) spectra were recorded on a Bruker Avance I 500 MHz NMR instrument in $CDCl_3$. Chemical shifts are provided in parts per million (ppm) using either the residual solvent peak or TMS as the internal reference. Coupling constants (*J*) are provided in Hz and where applicable, in order to resolve close signals and extract valuable coupling information, the raw FID data was processed using a Gaussian multiplication in place of the more usual exponential multiplication. All FT-IR spectra were recorded on a Nicolet 380 FTIR spectrophotometer equipped with a diamond ATR attachment (neat sample). Flash column chromatography was performed on chromatography silica gel (Fluorochem, 40–63 micron particle size distribution). All final compounds were homogeneous by TLC using a range of eluent systems of differing polarity (Merck TLC aluminium sheets silica gel 60 F254 (Cat. No. 105554)) when visualised with a dual lamp (254 and 365 nm) Spectroline 8 W hand held TLC inspection lamp. High resolution mass spectra were recorded on an Agilent 6210 1200 SL TOF spectrometer within the IPOS centre at the University of Huddersfield. Single crystal X-ray diffraction data was collected on a Bruker Venture diffractometer equipped with a graphite monochromated Cu(Kα) radiation source and a cold stream of $N_2$ gas.

The following enamino-carbonyl compounds: (*E*)-3-(dimethylamino)-1,2-diphenylprop-2-en-1-one[35] (**9a**), (*E*)-3-(dimethylamino)-1,2-bis(4-methoxyphenyl)prop-2-en-1-one[36] (**9b**), (*E*)-3-(dimethylamino)-1-(4-methoxyphenyl)prop-2-en-1-one[37] (**9h**), (*E*)-3-(dimethylamino)-1-(2-nitrophenyl)prop-2-en-1-one[38] (**9k**), (*E*)-3-(dimethylamino)-1-(4-(trifluoromethyl)phenyl)-prop-2-en-1-one[39] (**9i**), 2-((dimethylamino)methylene)-1,3-diphenylpropane-1,3-dione[40] (**9d**), methyl 2-benzoyl-3-(dimethylamino) acrylate[41] (**9e**), 1-((dimethylamino)methylene)-3,4-dihydronaphthalen-2(1*H*)-one[42] (**18**), 3-(dimethylamino)-2-phenylacrylaldehyde[43] (**21**), (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one[44] (**9g**) and (*E*)-*N*-((dimethylamino)methylene)-4-methylbenzamide[45] (**36**) were obtained by refluxing the requisite α-methylene carbonyl compound or amide in neat *N*,*N*-dimethylformamide dimethylacetal (DMFDMA) (2.5 equivalents) until TLC examination of the reaction mixture indicated that no starting α-methylene carbonyl compound remained. (*Z*)-3-(Hydroxymethylene)-2,2-dimethylchroman-4-one[30] (**24**) and (*Z*)-3-(hydroxymethylene)-2,2,6-trimethylthiochroman-4-one[31] (**25**) and isothiochromanone[32] (**32**) were prepared according to previously reported procedures. 4-(Dimethylamino)-3-(2-fluorophenyl)but-3-en-2-one (**15**) was prepared according to the procedure described by Kozmin *et al.*, for the preparation of 4-(dimethylamino)-3-phenylbut-3-en-2-one.[46] (*E*)-4-(Dimethylamino)-1,3-diphenylbut-3-en-2-one[47] (**9c**) was prepared by heating 1,3-diphenylacetone in toluene containing DMFDMA. 3-(Dimethylamino)-1-(4-pyridyl)-2-propen-1-one (**9j**) was obtained by heating 4-acetylpyridine in DMFDMA containing 10 mol% L-proline.[44]

## Preparation of enaminoketones

### Preparation of (*E*)-2-benzoyl-3-(dimethylamino)acrylonitrile 9f

A solution of benzoylacetonitrile (12.0 g, 82.7 mmol) in *N*,*N*-dimethylformamide dimethylacetal (27.4 mL, 207 mmol, 2.5 eq.) under nitrogen was heated under reflux overnight. Upon cooling the excess *N*,*N*-dimethylformamide dimethylacetal and other volatiles were removed and the resulting crude product was eluted from silica using 4% to 10% MeOH in DCM to afford two fractions:

Fraction 1, (*E*)-2-Benzoyl-3-(dimethylamino)acrylonitrile **9f** as an off-white solid (9.36 g, 57%); mp 111–113 °C (lit. mp 113–114 °C (ref. 48)); $\nu_{max}$ (neat) 2924, 2191, 1640, 1586, 1568, 1444, 1426, 1412, 1318, 1300, 1229, 1180, 1135, 1095, 1070, 1056, 1027 cm$^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 3.38 (3H, s, NMe), 3.47 (3H, s, NMe), 7.45–7.41 (2H, m, Ar–H), 7.52–7.48 (1H, m, Ar–H), 7.69–7.67 (2H, m, Ar–H), 7.88 (s, 1H, alkene-H); $\delta_C$ ($CDCl_3$, 100 MHz) 39.0, 48.3, 79.7, 120.3, 128.1, 128.2, 131.5, 138.5, 159.4, 190.3; found $[M + H]^+$ = 201.1027, $C_{12}H_{12}N_2O$ requires $[M + H]^+$ = 201.1022.

Fraction 2, Tetramethylammonium (*E*)-2,4-dicyano-1,5-dioxo-1,5-diphenylpent-3-en-2-ide **9f′** as yellow crystals (2.15 g, 14%); mp 250 °C (decomp.); $\nu_{max}$ (neat) 3031, 2199, 2186, 1612, 1596,

1574, 1483, 1448, 1316, 1295, 1241, 1176, 1109, 1074, 1026, 1002 $cm^{-1}$; $\delta_H$ (DMSO-$d_6$, 400 MHz) 3.09 (12H, s, $N^+Me_4$), 7.51–7.39 (10H, m, Ar–H), 8.02 (1H, s, alkene-H); $\delta_C$ (DMSO-$d_6$, 100 MHz) 54.38 (t, $J$ = 4.0 Hz), 86.68, 118.62, 127.75, 127.96, 130.21, 139.76, 152.52, 190.04; found $[M - NMe_4]^-$ = 299.0825, $C_{23}H_{23}N_3O_2$ requires $[M - NMe_4]^-$ = 299.0821.

### Alternative preparation of (*E*)-2-benzoyl-3-(dimethylamino) acrylonitrile 9f

A solution of benzoylacetonitrile (2.00 g, 13.8 mmol) in PhMe (50 mL) containing *N*,*N*-dimethylformamide dimethylacetal (2.02 mL, 15.2 mmol, 1.1 eq.) was stirred overnight at room temperature whereupon the volatiles were removed *in vacuo*. Recrystallization from EtOH gave two fractions:

Fraction 1, (*E*)-2-Benzoyl-3-(dimethylamino)acrylonitrile **9f** from the room temperature crystallization as yellow filaments (2.34 g, 85%) mp 110–112 °C (lit. mp 113–114 °C (ref. 48)) with spectroscopic data identical to that obtained previously.

Fraction 2, *N*-((Dimethylamino)methylene)-*N*-methylmethanaminium (*E*)-2,4-dicyano-1,5-dioxo-1,5-diphenylpent-3-en-2-ide **9f″** from cooling the filtrate as an off-white solid (0.090 g, 3.5%); mp 146–147 °C; $\nu_{max}$ (neat) 3044, 2203, 2195, 1698, 1605, 1574, 1495, 1442, 1423, 1413, 1369, 1337, 1250, 1168, 1114, 1066, 1025, 1001 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 3.29 (6H, s, $NMe_2$), 3.32 (6H, s, $NMe_2$), 7.26–7.40 (6H, m, Ar–H), 7.56–7.58 (4H, m, Ar–H), 8.04 (1H, s, alkene-H), 8.16 (1H, s, $Me_2NCH$=); $\delta_C$ ($CDCl_3$, 100 MHz) 39.35, 46.51, 87.86, 120.09, 128.12, 128.32, 130.51, 139.77, 154.69, 157.49, 192.16; found $[M - Me_2N{=}CHNMe_2]^-$ = 299.0824, $C_{24}H_{24}N_4O_2$ requires $[M - Me_2N{=}CHNMe_2]^-$ = 299.0826.

### Preparation of 4-(dimethylamino)-3-(2-fluorophenyl)but-3-en-2-one 15

A solution of 1-(2-fluorophenyl)propan-2-one (5.0 g, 33 mmol) in *N*,*N*-dimethylformamide dimethylacetal (10.9 mL, 82.1 mmol) was heated under reflux for 48 h. Upon cooling the excess *N*,*N*-dimethylformamide dimethylacetal and other volatiles were removed by vacuum distillation to leave 4-(dimethylamino)-3-(2-fluorophenyl)but-3-en-2-one **15** as a pale brown viscous oil (4.80 g, 71%) which was used directly; $\nu_{max}$ (neat) 3034, 2923, 1651, 1614, 1557, 1492, 1423, 1384, 1351, 1288, 1213, 1087, 956, 754, 635 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 1.87 (3H, s, Me), 2.62 (6H, vbs, $NMe_2$), 6.92–6.97 (1H, m, Ar–H), 6.99–7.03 (1H, m, Ar–H), 7.06–7.10 (1H, m, Ar–H), 7.15–7.20 (1H, m, Ar–H), 7.58 (1H, s, alkene-H); $\delta_C$ ($CDCl_3$, 100 MHz) 26.89, 42.50 (broad), 103.34, 115.11 (d, $J$ = 22.8 Hz), 123.56 (d, $J$ = 3.6 Hz), 125.59 (d, $J$ = 17.3 Hz), 129.01 (d, $J$ = 7.9 Hz), 134.25 (d, $J$ = 2.8 Hz), 150.29, 161.02 (d, $J$ = 241.5 Hz), 195.33; found $[M + H]^+$ = 208.1132, $C_{12}H_{14}FNO$ requires $[M + H]^+$ = 208.1138. A sample of **15** was used directly for the preparation of the dihydro-1,2-oxathiine 2,2-dioxide **16**.

### Preparation of (*Z*)-2,2-dimethyl-3-(pyrrolidin-1-ylmethylene) chroman-4-one 26

Pyrrolidine (4.22 mL, 51.4 mmol) was added dropwise over 5 minutes to a stirred solution of (*Z*)-3-(hydroxymethylene)-2,2-dimethylchroman-4-one **24** (10.0 g, 49 mmol) in anhydrous toluene (150 mL) at room temperature. The resulting yellow solution was stirred at room temperature overnight and the resulting mixture was dried with anhydrous sodium sulphate and the toluene and excess pyrrolidine were removed by rotary evaporation to afford the crude product as a bright orange/yellow solid which was recrystallized from EtOAc/hexane to afford the pure pyrrolidinomethylene compound **26** as a bright yellow solid (10.40 g, 82%); mp 105–108 °C; $\nu_{max}$ (neat) 2976, 2844, 1652, 1589, 1538, 1455, 1250, 1212, 1177, 985, 837, 823, 758, 536 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 1.58 (6H, s, 2-Me), 1.90–1.93 (4H, m, $(CH_2)_2$), 3.36 (4H, bs, $N(CH_2)_2$), 6.82, (1H, s, alkene-H), 6.83 (1H, d, $J$ = 8.3 Hz, 8-H), 6.93 (1H, app. t, $J$ = 7.5 Hz, 6-H), 7.31–7.36 (1H, m, 7-H), 7.89 (1H, dd, $J$ = 7.8, 1.6 Hz, 5-H); $\delta_C$ ($CDCl_3$, 100 MHz) 25.5, 28.9, 53.7, 81.5, 107.0, 117.4, 120.3, 123.5, 126.2, 133.7, 144.3, 158.1, 179.1; found $[M + H]^+$ = 258.1485, $C_{16}H_{19}NO_2$ requires $[M + H]^+$ = 258.1489.

### Preparation of (*Z*)-2,2,6-trimethyl-3-(pyrrolidin-1-ylmethylene) thiochroman-4-one 27

Pyrrolidine (1.36 mL, 16.6 mmol) was added dropwise over 5 minutes to a stirred solution of (*Z*)-3-(hydroxymethylene)-2,2,6-trimethylthiochroman-4-one **25** (3.70 g, 16 mmol) in anhydrous toluene (70 mL) at room temperature. The resulting yellow solution was stirred at room temperature for 48 h and then the mixture was dried with anhydrous sodium sulfate and the toluene and excess pyrrolidine were removed by rotary evaporation to afford the crude product as a bright orange/yellow solid which was recrystallized from EtOAc/hexane to afford the pure pyrrolidinomethylene **27** as a bright yellow solid (4.38 g, 95%); mp 128–131 °C; $\nu_{max}$ (neat) 2944, 2866, 1625, 1598, 1538, 1463, 1372, 1335, 1266, 1215, 1159, 1133, 928, 827, 782, 671, 523 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 1.63 (6H, s, 2-Me), 1.89–1.92 (4H, m, $(CH_2)_2$), 2.35 (3H, s, 6-Me), 3.20 (4H, bs, $N(CH_2)_2$), 6.89 (1H, s, alkene-H), 7.09–7.16 (2H, m, 7-H, 8-H), 8.04 (1H, bs, 5-H); $\delta_C$ ($CDCl_3$, 100 MHz) 21.0, 25.5, 29.7, 47.5, 53.4, 109.7, 127.4, 128.6, 132.2, 132.7, 134.3, 135.9, 142.7, 182.4; found $[M + H]^+$ = 288.1412, $C_{17}H_{21}NOS$ requires $[M + H]^+$ = 288.1417.

### Preparation of (*Z*)-3-((dimethylamino)methylene) isothiochroman-4-one 33

A solution of isothiochroman-4-one **32** (5.0 g, 30 mmol) in *N*,*N*-dimethylformamide dimethylacetal (10.5 mL, 76 mmol) was heated under reflux for 18 h. Upon cooling the excess *N*,*N*-dimethylformamide dimethylacetal and other volatiles were removed by rotary evaporation to afford an orange-brown solid which was recrystallized from hexane/EtOAc to afford the title compound **33** as orange needles (5.75 g, 86%); mp 107–109 °C; $\nu_{max}$ (neat) 1633, 1595, 1539, 1402, 1319, 1293, 1255, 1131, 1092, 1051, 1031, 963, 946, 913, 896, 867, 780, 760, 728, 707, 685, 646, 573, 533, 484, 416 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 3.25 (6H, s, $N(CH_2)_2$), 3.75 (2H, s, 1-H), 7.10–7.12 (1H, m, 8-H), 7.32–7.39 (2H, m, 6-H, 7-H), 7.99 (1H, s, alkene-H), 8.00–8.02 (1H, m, 5-H); $\delta_C$ ($CDCl_3$, 100 MHz) 31.8, 43.6, 94.6, 125.8,

127.5, 128.8, 131.1, 134.7, 139.8, 149.7, 183.9; found $[M + H]^+$ = 220.0792, $C_{12}H_{13}NOS$ requires $[M + H]^+$ = 220.0791.

## Preparation of 1,2-oxathiine 2,2-dioxides

### General method for the preparation of dihydro-1,2-oxathiine 2,2-dioxides from arylmethanesulfonyl chlorides

A solution of the arylmethanesulfonyl chloride (1.1 eq.) [phenylmethanesulfonyl chloride unless otherwise indicated] in anhydrous THF (50 mL) under a nitrogen atmosphere was added dropwise over 15 minutes to an ice cold (0–5 °C) vigorously stirred solution of the enaminoketone (1.0 eq.) and triethylamine (1.125 eq.) in anhydrous THF (60 mL for a typical 20 mmol scale reaction) under nitrogen. Upon completion of the addition the ice-water bath was removed and the resulting solution was stirred until TLC examination of the reaction mixture indicated that no starting enaminoketone remained (typically stirred overnight). The reaction mixture was filtered through a sinter containing chromatography silica (*ca.* 20 mm depth) with further THF (*ca.* 200 mL) used to wash any remaining product from the silica. The THF and excess triethylamine were removed from the filtrate by rotary evaporation to afford the crude product which was then suspended in EtOAc (*ca.* 100 mL) and washed with water (3 × 50 mL) and brine (50 mL). The EtOAc layer was dried (anhyd. $Na_2SO_4$) and then evaporated to give the crude product which was purified by either column chromatography or crystallization. The following 3,4-dihydro-1,2-oxathiine 2,2-dioxides were obtained in this manner:

**4-(Dimethylamino)-3,5,6-triphenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide 10a** from **9a** (19.9 mmol) as off-white microcrystals (7.40 g, 92%) from EtOAc/hexane; mp = 152–154 °C; $\nu_{max}$ (neat) 3063, 2938, 1644, 1455, 1365 ($SO_2$–O), 1182 ($SO_2$–O), 1036, 925, 692, 508 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz)‡ 2.23 (6H, s, $NMe_2$), 4.49 (1H, d, $J$ = 8.0 Hz, 4-H), 4.96 (1H, d, $J$ = 8.0 Hz, 3-H), 7.15–7.32 (10H, m, Ar–H), 7.42–7.47 (3H, m, Ar–H), 7.60–7.62 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 40.64, 62.36, 71.75, 122.78, 127.72, 127.85, 128.22, 129.02, 129.14, 129.24, 129.49, 129.88, 129.95, 131.75, 132.84, 137.27, 148.30; found $[M + H]^+$ = 406.1471, $C_{24}H_{23}NO_3S$ requires $[M + H]^+$ = 406.1471. ‡The $^1H$ NMR spectrum of the crude isolated product indicated a mixture of diastereoisomers in a *ca.* 4 : 1 ratio (see ESI for spectrum†).

**4-(Dimethylamino)-5,6-diphenyl-3-(4-(trifluoromethyl) phenyl)-3,4-dihydro-1,2-oxathiine 2,2 dioxide 10b** from **9a** (15.5 mmol) and 4-trifluoromethylphenylmethanesulfonyl chloride (4.50 g, 17.4 mmol) as colourless microcrystals (4.40 g, 60%) from EtOAc/hexane; mp = 125–128 °C; $\nu_{max}$ (neat) 2833, 2794, 2248, 2222, 2179, 2159, 2041, 2028, 2005, 1978, 1955, 1662, 1620, 1491, 1446, 1421, 1371, 1364 ($SO_2$–O), 1323, 1223, 1186, 1162 ($SO_2$–O), 1114, 1098, 1069, 1049, 1035, 1018, 1000 $cm^{-1}$; $\delta_H$ ($(CD_3)_2CO$, 400 MHz) 2.22 (6H, s, $NMe_2$), 4.79 (1H, d, $J$ = 8.8 Hz, 4-H), 5.42 (1H, d, $J$ = 8.8 Hz, 3-H), 7.22–7.27 (8H, m, Ar–H), 7.35–7.38 (2H, m, Ar–H), 7.86 (2H, app. d, $J$ = 8.2 Hz, Ar–H), 8.06 (2H, app. d, $J$ = 8.2 Hz, (Ar–H); $\delta_C$ ($(CD_3)_2CO$, 100 MHz) 40.13, 61.90, 70.88, 124.2 (q, $J$ = 270.0 Hz, $CF_3$), 123.58, 125.84 (q, $J$ = 4.0 Hz, *o*-Ar*C*-$CF_3$), 127.65, 127.97, 128.07, 129.04, 130.06, 130.76 (q, $J$ = 32.0 Hz, Ar*C*-$CF_3$), 131.05, 133.29, 136.66, 137.03, 147.83; $\delta_F$ ($(CD_3)_2CO$, 376 MHz) −63.13; found $[M + H]^+$ = 473.1260, $C_{25}H_{22}F_3NO_3S$ requires $[M + H]^+$ = 473.1272.

**4-(Dimethylamino)-5,6-bis(4-methoxyphenyl)-3-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide 10c** from **9b** (16.1 mmol) as off-white microcrystals (5.10 g, 68%) from EtOAc/hexane; mp = 120–121 °C; $\nu_{max}$ (neat) 2945, 2836, 2793, 1604, 1509, 1371, 1354 ($SO_2$–O), 1240, 1171 ($SO_2$–O), 1063, 965, 839, 728 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz)‡ 2.23 (6H, s, $NMe_2$), 3.76 (3H, s, OMe), 3.79 (3H, s, OMe), 4.39 (1H, d, $J$ = 7.6 Hz, 4-H), 4.92 (1H, d, $J$ = 7.6 Hz, 3-H), 6.67–6.72 (2H, m, Ar–H), 6.77–6.80 (2H, m, Ar–H), 7.14–7.17 (2H, m, Ar–H), 7.21–7.25 (2H, m, Ar–H), 7.40–7.45 (3H, m, Ar–H), 7.57–7.59 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 40.59, 55.16, 55.26, 62.23, 71.93, 113.29, 113.70, 120.79, 125.31, 127.10, 128.06, 129.20, 129.39, 129.76, 129.89, 130.57, 130.82, 131.14, 132.03, 148.01, 158.98, 159.84; found $[M + H]^+$ = 466.1684, $C_{26}H_{27}NO_5S$ requires $[M + H]^+$ = 466.1688. ‡The $^1H$ NMR spectrum of the crude isolated product indicated a mixture of diastereoisomers in a *ca.* 5 : 1 ratio.

**6-Benzyl-4-(dimethylamino)-3,5-diphenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide 10d1** and **10d2** from **9c** (18.8 mmol) after elution from silica using 10% to 30% EtOAc/hexane and crystallization from EtOAc/hexane. Fraction 1: **10d1** as colourless microcrystals (3.78 g, 48%), mp = 133–136 °C; $\nu_{max}$ (neat) 2935, 2834, 2788, 2010, 1667, 1600, 1495, 1454, 1442, 1428, 1361 ($SO_2$–O), 1313, 1223, 1182 ($SO_2$–O), 1119, 1091, 1067, 1031 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz)‡ 2.07 (6H, s, $NMe_2$), 3.48 (1H, d, $J$ = 15.3 Hz, PhCH), 3.56 (1H, d, $J$ = 15.3 Hz, PhCH), 4.51 (1H, d, $J$ = 9.4 Hz, 4-H), 4.76 (1H, d, $J$ = 9.4 Hz, 3-H), 7.18–7.45 (13H, m, Ar–H), 7.57–7.60 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 30.97, 37.89, 40.82, 62.59, 70.51, 122.86, 126.84, 127.88, 128.42, 128.57, 128.69, 129.06, 129.18, 129.53, 129.80, 131.03, 135.84, 137.10, 148.67; found $[M + H]^+$ = 420.1627, $C_{25}H_{25}NO_3S$ requires $[M + H]^+$ = 420.1628.

Fraction 2: **10d2** as a white solid (1.94 g, 25%), mp = 101–102 °C; $\nu_{max}$ (neat) 2863, 2796, 1657, 1600, 1493, 1453, 1362 (O–$SO_2$), 1290, 1247, 1187, 1163 (O–$SO_2$), 1102, 1071, 1041 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.06 (6H, s, N($CH_3$)$_2$), 3.52 (1H, d, $J$ = 15.3 Hz, PhC*H*), 3.68 (1H, d, $J$ = 15.3 Hz, PhC*H*), 4.67 (1H, d, $J$ = 6.3 Hz, 4-H), 4.79 (1H, d, $J$ = 6.3 Hz, 3-H), 7.21–7.41 (13H, m, ArH), 7.55–7.57 (2H, m, ArH); $\delta_C$ ($CDCl_3$, 100 MHz) 37.80, 42.03, 64.76, 68.09, 120.74, 126.88, 127.89, 128.29, 128.61, 128.64, 128.78, 129.33, 129.44, 129.79, 130.58, 136.18, 136.90, 148.37; found $[M + H]^+$ = 420.1627, $C_{25}H_{25}NO_3S$ requires $[M + H]^+$ = 420.1631.

‡The $^1H$ NMR spectrum of the crude isolated product indicated a mixture of diastereoisomers in a *ca.* 1.6 : 1 ratio.

**(4-(Dimethylamino)-2,2-dioxido-3,6-diphenyl-3,4-dihydro-1,2-oxathiin-5-yl)(phenyl)methanone 10e** from **9d** (17.9 mmol) as a waxy solid (7.40 g, 96%) after filtration through silica using $CH_2Cl_2$ as eluent. Crystallization of a small sample from

EtOAc/hexane gave off-white microcrystals; mp = 146–148 °C; $\nu_{max}$ (neat) 1655, 1613, 1596, 1448, 1371 ($SO_2$–O), 1242, 1185, 1160 ($SO_2$–O), 1072, 883, 711, 670, 684, 513 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.06 (6H, s, $NMe_2$), 4.83 (1H, d, $J$ = 10.3 Hz, 4-H), 4.87 (1H, d, $J$ = 10.3 Hz, 3-H), 7.27–7.31 (3H, m, Ar–H), 7.43–7.48 (5H, m, Ar–H), 7.52–7.56 (3H, m, Ar–H), 7.60–7.62 (2H, m, Ar–H), 7.94 (2H, app. d, $J$ = 7.3 Hz, Bz–H); $\delta_C$ ($CDCl_3$, 100 MHz) 40.68, 62.14, 69.03, 123.01, 128.29, 128.65, 128.83, 128.87, 129.41, 129.65, 129.74, 130.01, 130.35, 131.39, 133.29, 136.45, 149.84, 193.25; found $[M + H]^+$ = 434.1428, $C_{25}H_{23}NO_4S$ requires $[M + H]^+$ = 434.1421.

**4-(Dimethylamino)-3,6-diphenyl-3,4-dihydro-1,2-oxathiine 2,2 dioxide 10f** from **9g** (28.5 mmol) as colourless microcrystals (4.96 g, 52%) from EtOH; mp = 144–146 °C; $\nu_{max}$ (neat) 3388, 2831, 2783, 1659, 1575, 1494, 1469, 1452, 1367 ($SO_2$–O), 1313, 1272, 1222, 1178 ($SO_2$–O), 1117, 1105, 1072, 1039 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.29 (6H, s, $NMe_2$), 4.43 (1H, dd, $J$ = 11.2, 2.6 Hz, 4-H), 4.58 (1H, d, $J$ = 11.2 Hz, 3-H), 5.92 (1H, d, $J$ = 2.6 Hz, 5-H), 7.51–7.37 (6H, m, Ar–H), 7.60–7.51 (2H, m, Ar–H), 7.69–7.60 (2H, m, Ar–H); $\delta_C$ ($(CD_3)_2CO$, 100 MHz) 41.27, 63.08, 64.60, 104.38, 125.02, 128.69, 129.24, 129.36, 129.76 (×2), 129.86, 131.81, 150.51; found $[M + H]^+$ = 330.1140, $C_{18}H_{19}NO_3S$ requires $[M + H]^+$ = 330.1158.

**4-(Dimethylamino)-6-(4-methoxyphenyl)-3-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide 10g** from **9h** (24.4 mmol) as off-white microcrystals (7.30 g, 83%) from EtOAc/hexane; mp = 123–124 °C; $\nu_{max}$ (neat) 2943, 2798, 1662, 1606, 1509, 1359 ($SO_2$–O), 1250, 1172 ($SO_2$–O), 1045, 984, 903, 818, 790, 698, 592 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.28 (6H, s, $NMe_2$), 3.85 (3H, s, OMe), 4.41 (1H, dd, $J$ = 11.1, 2.6 Hz, 4-H), 4.55 (1H, d, $J$ = 11.1 Hz, 3-H), 5.79 (1H, d, $J$ = 2.5 Hz, 5-H), 6.92 (2H, app. d, $J$ = 8.9 Hz, Ar–H), 7.44–7.46 (3H, m, Ar–H), 7.54–7.57 (4H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 41.24, 55.42, 63.04, 64.60, 102.36, 114.04, 124.36, 126.54, 129.21, 129.49, 129.70, 129.76, 150.37, 160.86; found $[M + H]^+$ = 360.1264, $C_{19}H_{21}NO_4S$ requires $[M + H]^+$ = 360.1264.

**4-(Dimethylamino)-6-(4-trifluoromethylphenyl)-3-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide 10h** from **9i** (14.4 mmol) as off-white microcrystals (3.67 g, 64%) from EtOAc/hexane; mp = 125–127 °C; $\nu_{max}$ (neat) 2981, 1615, 1497, 1455, 1375 ($SO_2$–O), 1322, 1167 ($SO_2$–O), 1114, 1066, 990, 903, 785, 733, 698, 566, 500 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.29 (6H, s, $NMe_2$), 4.46 (1H, dd, $J$ = 11.2, 2.4 Hz, 4-H), 4.62 (1H, d, $J$ = 11.2 Hz, 3-H), 6.06 (1H, d, $J$ = 2.4 Hz, 5-H), 7.45–7.47 (3H, Ar–H), 7.54–7.57 (2H, m, Ar–H), 7.67 (2H, app d, $J$ = 8.4 Hz, Ar–H), 7.75 (2H, app d, $J$ = 8.4 Hz, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 41.29, 63.05, 64.67, 106.77, 123.77 (q, $J$ = 272 Hz), 125.31, 125.74 (q, $J$ = 3.8 Hz), 128.99, 129.33, 129.73, 129.94, 131.66 (q, $J$ = 32.9 Hz), 135.09, 149.23; $\delta_F$ ($CDCl_3$, 376 MHz) −62.80; found $[M + H]^+$ = 398.1033, $C_{19}H_{18}F_3NO_3S$ requires $[M + H]^+$ = 398.1032.

**4-(Dimethylamino)-3-phenyl-6-(pyridin-4-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide 10i** from **9j** (29 mmol) as orange-yellow microcrystals (0.95 g, 10%) from 2 × EtOAc; mp = 124–126 °C; $\nu_{max}$ (neat) 3046, 2979, 2942, 2800, 2359, 1651, 1594, 1548, 1495, 1474, 1454, 1410, 1368 ($SO_2$–O), 1315, 1278, 1220, 1178 ($SO_2$–O), 1117, 1099, 1072, 1056, 1040 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.29 (6H, s, $NMe_2$), 4.45 (1H, dd, $J$ = 11.2, 2.6 Hz, 4-H), 4.61 (1H, d, $J$ = 11.2 Hz, 3-H), 6.17 (1H, d, $J$ = 2.6 Hz, 5-H), 7.46–7.51 (5H, m, Ar–H), 7.54–7.56 (2H, m, Py–H), 8.68–8.70 (2H, m, Py–H); $\delta_C$ ($CDCl_3$, 100 MHz) 41.35, 63.20, 64.62, 108.46, 118.70, 128.82, 129.34, 129.71, 129.97, 138.99, 148.14, 150.49; found $[M + H]^+$ = 331.1117, $C_{17}H_{18}N_2O_3S$ requires $[M + H]^+$ = 331.1111.

**4-(Dimethylamino)-6-(2-nitrophenyl)-3-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide 10j** from **9k** (22.7 mmol) as off-white microcrystals (6.40 g, 75%) from EtOAc/hexane; mp = 125–127 °C; $\nu_{max}$ (neat) 2950, 2835, 2778, 1530, 1471, 1356 ($SO_2$–O), 1182 ($SO_2$–O), 1109, 1034, 985, 902, 848, 805, 705, 569 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.28 (6H, s, $NMe_2$), 4.40 (1H, dd, $J$ = 11.3, 2.1 Hz, 4-H), 4.63 (1H, d, $J$ = 11.3 Hz, 3-H), 5.63 (1H, d, $J$ = 2.1 Hz, 5-H), 7.45–7.47 (3H, m, Ar–H), 7.55–7.57 (2H, m, Ar–H), 7.60–7.63 (2H, m, Ar–H), 7.67–7.70 (1H, m, Ar–H), 7.98 (1H, d, $J$ = 7.9 Hz, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 41.24, 63.29, 64.54, 109.08, 124.55, 127.68, 128.90, 129.27, 129.77, 129.85, 130.94, 131.39, 133.13, 147.39, 148.04; found $[M + H]^+$ = 375.1008, $C_{18}H_{18}N_2O_5S$ requires $[M + H]^+$ = 375.1015.

**4-(Dimethylamino)-5-(2-fluorophenyl)-6-methyl-3-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide 16** from **15** (23.1 mmol) as off-white microcrystals (6.62 g, 79%) from EtOAc/hexane; mp = 130–132 °C; $\nu_{max}$ (neat) 2919, 2833, 2785, 1612, 1487, 1359 ($SO_2$–O), 1230, 1159 ($SO_2$–O), 1143, 1106, 1037, 934, 853, 829, 742, 618, 553 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz, 295 K) 1.92 (3H, s, 6-Me), 2.04 (6H, s, $NMe_2$), 4.61 (1H, bs, 4-H), 4.78 (1H, d, $J$ = 9.5 Hz, 3-H), 7.10–7.20 (2H, m, Ar–H), 7.28–7.36 (2H, m, Ar–H), 7.44–7.49 (3H, m, Ar–H), 7.62–7.64 (2H, m, Ar–H); $\delta_F$ ($CDCl_3$, 376 MHz) −114.5 to −112.7; $\delta_C$ ($CDCl_3$, 100 MHz) 18.58, 40.69, 62.47, 68.93, 69.59, 115.66, 115.89, 116.19,† 123.99, 124.66, 124.81, 127.26, 128.14, 129.30, 129.35, 129.43, 129.58, 129.89, 130.08, 130.57, 130.80, 131.04,† 133.75, 148.32, 158.94, 161.38.

**1-(Dimethylamino)-2-phenyl-1,2,5,6-tetrahydronaphtho[1,2-*e*][1,2]oxathiine 3,3-dioxide 19** from **18** (61.4 mmol) as off-white microcrystals (14.18 g, 65%) from EtOAc/hexane; mp = 154–156 °C; $\nu_{max}$ (neat) 2946, 2832, 2788, 1666, 1467, 1363 ($SO_2$–O), 1169 ($SO_2$–O), 1139, 1026, 937, 829, 805, 765, 698, 571 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.14 (6H, s, $NMe_2$), 2.48 (1H, ddd, $J$ = 2.4, 7.0, 17.1, 5-H), 2.65–2.75 (1H, m, 5-H), 2.86 (1H, ddd, $J$ = 2.5, 6.3, 17.1 Hz, 6-H), 3.00–3.09 (1H, m, 6-H), 4.80 (1H, dd, $J$ = 3.0, 8.9 Hz, 1-H), 4.90 (1H, d, $J$ = 8.9 Hz, 2-H), 7.16–7.27 (4H, m, Ar–H), 7.43–7.50 (3H, m, Ar–H), 7.62–7.65 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 27.71, 28.26, 40.10, 61.34, 65.47, 115.60, 125.17, 126.34, 126.80, 127.34, 129.35, 129.71, 129.98, 131.32, 132.00, 133.88, 151.02; found $[M + H]^+$ = 356.1314, $C_{20}H_{21}NO_3S$ requires $[M + H]^+$ = 356.1320.

$\delta_H$ ($CDCl_3$, 500 MHz, 233 K)* 1.89 (3H, app. t, $J$ = 1.5 Hz, 6-Me), 1.97 (3H, d, $J$ = 1.7 Hz, 6-Me), 2.01 (12H, bs, $NMe_2$), 4.52 (1H, ddd, $J$ = 1.5, 3.5, 9.7 Hz, 4-H), 4.76 (1H, ddd, $J$ = 1.7, 3.5, 9.9 Hz, 4-H), 4.80 (1H, d, $J$ = 9.7 Hz, 3-H), 4.87 (1H, d, $J$ = 9.9 Hz, 3-H), 7.07–7.39 (8H, m, Ar–H), 7.43–7.52 (6H, m, Ar–H), 7.60–7.68 (4H, m, Ar–H); $\delta_C$ ($CDCl_3$, 126 MHz) 18.84, 19.07, 40.62, 61.55, 61.84, 67.69, 69.73, 114.63, 115.71, 115.88,

115.98, 116.16, 117.39, 124.03, 124.05, 124.30, 124.33, 124.45, 124.65, 124.78, 129.46, 129.52, 129.61, 129.67, 129.90, 129.97, 130.33, 131.92, 148.24, 148.53, 158.77, 159.32, 160.71, 161.28.

$\delta_H$ ($CDCl_3$, 500 MHz, 323 K) 1.89 (3H, dd, $J$ = 0.8, 1.8 Hz, 6-Me), 2.04 (6H, s, $NMe_2$), 4.55 (1H, app. d, $J$ = 9.5 Hz, 4-H), 4.73 (1H, d, $J$ = 9.5 Hz, 3-H), 7.05–7.17 (2H, m, Ar–H), 7.22–7.32 (2H, m, Ar–H), 7.37–7.45 (3H, m, Ar–H), 7.56–7.63 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 126 MHz) 18.43, 40.58, 62.80, 69.30, 115.64, 115.82, 123.91, 123.94, 124.78, 124.90, 129.08, 129.46, 129.50, 129.56, 129.87, 131.01, 148.35, 159.25, 161.21; found $[M + H]^+$ = 362.1215, $C_{19}H_{20}FNO_3S$ requires $[M + H]^+$ = 362.1226.

*At this temperature there are two rotamers present in solution. †Very broad signal and approximate position is given.

### General method for the preparation of dihydro-1,2-oxathiine 2,2-dioxides from methanesulfonyl chloride

A solution of methanesulfonyl chloride (1.1 eq.) in anhydrous THF (50 mL) under a nitrogen atmosphere was added dropwise over 15 minutes to an ice cold (0–5 °C) vigorously stirred solution of the enaminoketone (1.0 eq.) and triethylamine (1.125 eq.) in anhydrous THF (60 mL for a typical 20 mmol scale reaction) under nitrogen. Upon completion of the addition the ice-water bath was removed and the resulting solution was stirred until TLC examination of the reaction mixture indicated that no starting enaminoketone remained (typically stirred overnight). The reaction mixture was filtered through a sinter containing chromatography silica (*ca.* 20 mm depth) with further THF (*ca.* 200 mL) used to wash any remaining product from the silica. The THF and excess triethylamine were removed from the filtrate by rotary evaporation to afford the crude product which was then suspended in EtOAc (*ca.* 100 mL) and washed with water (3 × 50 mL) and brine (50 mL). The EtOAc layer was dried (anhyd. $Na_2SO_4$) and then evaporated to give the crude product which was purified by either column chromatography or crystallization. The following dihydro-1,2-oxathiine 2,2-dioxides were obtained in this manner:

**4-(Dimethylamino)-5,6-diphenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide 12a** from **9a** (27.4 mmol) as off-white microcrystals (10.03 g, 53%) from EtOAc/hexane; mp = 157–159 °C; $\nu_{max}$ (neat) 3398, 2830, 2781, 1658, 1493, 1443, 1370 ($SO_2$–O), 1339, 1280, 1260, 1225, 1192, 1173 ($SO_2$–O), 1149, 1114, 1101, 1072, 1045, 1004 $cm^{-1}$; $\delta_H$ ($(CD_3)_2CO$, 400 MHz) 2.30 (6H, s, $NMe_2$), 3.78 (1H, dd, $J$ = 9.1, 14.0 Hz, 3-H), 3.95 (1H, dd, $J$ = 7.4, 14.0 Hz, 3-H), 4.46 (1H, dd, $J$ = 7.4, 9.1 Hz, 4-H), 7.14–7.23 (10H, m, ArH); $\delta_C$ ($CDCl_3$, 100 MHz) 40.13, 42.63, 63.92, 121.71, 127.66, 127.82, 128.14, 128.99, 129.15, 129.90, 132.94, 136.38, 148.47; found $[M + H]^+$ = 330.1155, $C_{18}H_{19}NO_3S$ requires $[M + H]^+$ = 330.1158.

**6-(4-Methoxyphenyl)-1,2-oxathiine 2,2-dioxide 13b and 4-(dimethylamino)-6-(4-methoxyphenyl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide 12b** from **9b** (19.9 mmol) after elution from silica with 50% EtOAc in hexanes increasing to 80% EtOAc in hexanes after elution of fraction 1.

Fraction 1: **6-(4-Methoxyphenyl)-1,2-oxathiine 2,2-dioxide 13b** as off-white microneedles (2.38 g, 50%) from EtOAc/hexane, mp = 86–88 °C; $\nu_{max}$ (neat) 1603, 1547, 1507, 1345 ($SO_2$–O), 1173 ($SO_2$–O), 1022, 920, 759, 708, 646, 530 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 3.86 (3H, s, MeO), 6.31 (1H, d, $J$ = 6.8 Hz, 5-H), 6.58 (1H, d, $J$ = 10.0 Hz, 3-H), 6.91 (1H, dd, $J$ = 10.0, 6.8 Hz, 4-H), 6.93–6.96 (2H, m, Ar–H), 7.64–7.67 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 55.52, 98.43, 114.45, 117.60, 123.11, 127.52, 134.87, 157.58, 162.18; found $[M + H]^+$ = 239.0375, $C_{11}H_{10}O_4S$ requires $[M + H]^+$ = 239.0373.

Fraction 2: **4-(dimethylamino)-6-(4-methoxyphenyl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide 12b** as off-white microcrystals (2.28 g, 40%) from EtOAc/hexane, mp = 104–105 °C; $\nu_{max}$ (neat) 2928, 2831, 2780, 1613, 1486, 1355 ($SO_2$–O), 1317, 1259, 1246, 1171 ($SO_2$–O), 1110, 1028, 989, 967, 843, 831, 818, 766, 570, 549 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.37 (6H, s, $NMe_2$), 3.25 (1H, dd, $J$ = 13.3, 11.4 Hz, 3-H), 3.50 (1H, ddd, $J$ = 13.3, 6.3, 1.0 Hz, 3-H), 3.83 (3H, s, OMe), 4.15 (1H, ddd, $J$ = 11.4, 6.3, 2.6 Hz, 4-H), 5.65 (1H, dd, $J$ = 2.6, 1.0 Hz, 5-H), 6.88–6.92 (2H, m, Ar–H), 7.48–7.52 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 40.64, 42.75, 55.40, 59.46, 103.00, 114.02, 124.30, 126.45, 150.45, 160.85; found $[M + H]^+$ = 284.0956, $C_{13}H_{17}NO_4S$ requires $[M + H]^+$ = 284.0951.

### Method for the addition of phenylsulfene to 3-(dimethylamino)-2-phenylacrylaldehyde 21

A solution of phenylmethanesulfonyl chloride (7.07 g, 37.1 mmol) in anhydrous THF (70 mL) under a nitrogen atmosphere was added dropwise over 15 minutes to an ice cold (0–5 °C) vigorously stirred solution of the crude 3-(dimethylamino)-2-phenylacrylaldehyde **21** (5.0 g, 28 mmol) and triethylamine (5.4 mL, 38 mmol) in anhydrous THF (100 mL) under nitrogen. Upon completion of the addition the ice-water bath was removed and the resulting solution was stirred until TLC examination of the reaction mixture indicated that no starting enaminoketone remained (30 h). The reaction mixture was filtered through a sinter containing chromatography silica (*ca.* 20 mm depth) with further THF (*ca.* 100 mL) used to wash any remaining product from the silica. The THF and excess triethylamine were removed from the filtrate by rotary evaporation to give the crude product as a multicomponent viscous brown sludge which was chromatographed on silica using $CH_2Cl_2$ (5–100% in hexanes) to MeOH (2% in $CH_2Cl_2$) gradient as eluent. The fractions eluting at $R_f$ values of 0.15 and 0.38 (TLC eluent $CH_2Cl_2$ 40% in hexanes) were collected. The band with $R_f$ = 0.38 was further chromatographed on silica using $CH_2Cl_2$ (40% in hexanes) as eluent and the solvent removed under reduced pressure. The residue was crystallised from hot toluene/hexanes to give **3,5-diphenyl-1,2-oxathiine 2,2-dioxide 23** (0.71 g, 9%) as a cream powder. The solvent was reduced to give a second crop (0.24 g, 3%) as a pale-yellow powder; mp = 90–91 °C; $\nu_{max}$ (neat) 2989, 2932, 2850, 1634, 1496, 1454, 1362 ($SO_2$–O), 1174 ($SO_2$–O), 1108, 1082, 1048, 955, 841, 765, 759, 732, 697, 620, 570, 540, 474 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 7.07 (1H, d, $J$ = 2.1 Hz, 6-H‡), 7.23 (1H, d, $J$ = 2.1 Hz, 4-H‡), 7.54–7.40 (8H, m, Ar–H), 7.70–7.63 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 122.37, 126.43, 127.95, 128.89, 129.11, 129.26, 129.95, 130.25, 130.34, 133.45, 136.07, 142.11; found

$[M + NH_4]^+$ = 302.0850, $C_{16}H_{12}O_3S$ requires $[M + NH_4]^+$ = 302.0845.

‡ $^1$H NMR assignments may be reversed.

The fraction with $R_f$ = 0.15 was crystallised from chloroform/hexanes to give **4-(dimethylamino)-3,5-diphenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide 22** (0.27 g, 3%) as a cream powder. The solvent was reduced to give a second crop (0.20 g, 2%) as a pale orange powder; mp = 145–150 °C (dec.); $\nu_{max}$ (neat) 2953, 2839, 1556, 1494, 1449, 1359 ($SO_2$–O), 1285, 1175 ($SO_2$–O), 1131, 1002, 974, 688, 664, 643, 622, 595, 582, 560, 512, 459 cm$^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.08 (6H, s, $NMe_2$), 4.77 (1H, dd, $J$ = 9.7, 1.5 Hz, 4-H), 4.66 (1H, d, $J$ = 9.7 Hz, 3-H), 6.66 (1H, d, $J$ = 1.5 Hz, 6-H), 7.32–7.42 (5H, m, Ar–H), 7.45–7.52 (3H, m, Ar–H), 7.62–7.69 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 40.55, 62.52, 67.44, 127.11, 127.52, 128.09, 128.38, 129.30, 129.76, 129.90, 130.63, 135.48, 138.12; found $[M + H]^+$ = 330.1178, $C_{18}H_{19}NO_3S$ requires $[M + H]^+$ = 330.1158.

### General method for the preparation of 1,2-oxathiine 2,2-dioxides

A solution of 3-chloroperoxybenzoic acid (1.2 eq., *ca.* 77%) in dichloromethane (40 mL) was added dropwise over 15 minutes to an ice cold (*ca.* 0–5 °C) vigorously stirred solution of the 3,4-dihydro-1,2-oxathiine 2,2-dioxide (1.0 eq.) in dichloromethane (70 mL for a typical 12 mmol scale reaction). Upon completion of the addition the cooling bath was removed and the resulting solution was stirred until TLC indicated that no starting 3,4-dihydro-1,2-oxathiine 2,2-dioxide remained (*ca.* 24 h). The mixture was transferred into a separating funnel and diluted with dichloromethane (50 mL). The mixture was washed with aq. sodium thiosulfate solution (5 × 100 mL, 10% aq.) followed by washing with dilute NaOH (3 × 50 mL, 1 M aq.) solution and finally with water (100 mL). The dichloromethane solution was dried with anhydrous $Na_2SO_4$ and then the solvent was removed by rotary evaporation to afford the crude product which was further purified by crystallization from EtOAc/hexane. The following compounds were obtained by this protocol:

**3,5,6-Triphenyl-1,2-oxathiine 2,2-dioxide 11a** from **10a** (12.3 mmol) as pale yellow microcrystals (3.15 g, 71%) from EtOAc/hexane; mp = 159–160 °C; $\nu_{max}$ (neat) 3060, 1621, 1540, 1444, 1368 ($SO_2$–O), 1349, 1186 ($SO_2$–O), 1130, 1011, 972, 851, 771, 697, 605, 524 cm$^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 7.03 (1H, s, 4-H), 7.25–7.39 (10H, m, Ar–H), 7.46–7.50 (3H, m, Ar–H), 7.67–7.71 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 118.99, 127.74, 128.21, 128.35, 129.05, 129.13, 129.20, 129.28, 129.90, 129.95, 130.27, 131.11, 133.99, 134.11, 135.80, 152.14; found $[M + NH_4]^+$ = 378.1158, $C_{22}H_{16}O_3S$ requires $[M + NH_4]^+$ = 378.1158.

**5,6-Diphenyl-3-(4-(trifluoromethyl)phenyl)-1,2-oxathiine 2,2-dioxide 11b** from **10b** (4.2 mmol) as pale yellow microcrystals (1.38 g, 73%) from EtOH; mp = 161–163 °C; $\nu_{max}$ (neat) 3060, 1617, 1576, 1557, 1488, 1446, 1415, 1365 ($SO_2$–O), 1350, 1324, 1275, 1170 ($SO_2$–O), 1116, 1068, 1035, 1016, 1008 cm$^{-1}$; $\delta_H$ ($(CD_3)_2CO$, 400 MHz) 7.32–7.44 (10H, m, Ar–H), 7.54 (1H, s, 4-H), 7.89 (2H, app. d, $J$ = 8 Hz, Ar–H), 8.02 (2H, app. d, $J$ = 8 Hz, Ar–H); $\delta_C$ ($(CD_3)_2CO$, 100 MHz) 118.99, 123.74 (q, $J$ = 270.0 Hz), 126.02 (q, $J$ = 3.7 Hz), 128.07, 128.30, 128.55, 129.08, 129.32, 130.60, 130.82, 131.68 (q, $J$ = 33 Hz), 132.62, 133.44, 135.41, 135.61, 153.03; $\delta_F$ ($CDCl_3$, 376 MHz) −63.32; found $[M + NH_4]^+$ = 428.0707, $C_{23}H_{15}F_3O_3S$ requires $[M + NH_4]^+$ = 428.0694.

**5,6-Bis(4-methoxyphenyl)-3-phenyl-1,2-oxathiine 2,2-dioxide 11c** from **10c** (9.13 mmol) as bright yellow microcrystals (3.60 g, 94%) from EtOAc/hexane; mp = 129–131 °C; $\nu_{max}$ (neat) 3006, 2935, 2838, 1604, 1506, 1462, 1354 ($SO_2$–O), 1256, 1243, 1171 ($SO_2$–O), 1130, 1106, 1032, 972, 835, 788, 697, 589 cm$^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 3.80 (3H, s, OMe), 3.82 (3H, s, OMe), 6.75–6.77 (2H, m, Ar–H), 6.87–6.89 (2H, m, Ar–H), 6.98 (1H, s, 4-H), 7.18–7.21 (2H, m, Ar–H), 7.29–7.31 (2H, s, Ar–H), 7.43–7.46 (3H, m, Ar–H), 7.64–7.67 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 55.32, 55.34, 113.68, 114.65, 117.22, 123.60, 127.64, 128.21, 129.00, 129.71, 130.11, 130.28, 130.57, 130.88, 133.08, 134.56, 151.92, 159.45, 160.94; found $[M + NH_4]^+$ = 438.1370, $C_{24}H_{20}O_5S$ requires $[M + NH_4]^+$ = 438.1370.

**(6-Benzyl-3,5-diphenyl-1,2-oxathiine 2,2-dioxide 11d** from **10d1** (4.8 mmol) as colourless microcrystals (1.21 g, 68%) from EtOAc/hexane; mp = 110–111 °C; $\nu_{max}$ (neat) 3062, 3026, 1634, 1601, 1576, 1557, 1493, 1454, 1444, 1421, 1365 ($SO_2$–O), 1349, 1286, 1264, 1224, 1175 ($SO_2$–O), 1155, 1105, 1072, 1031, 1002 cm$^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 3.78 (2H, s, $CH_2$), 6.85 (1H, s, 4-H), 7.21–7.47 (13H, m, Ar–H), 7.59–7.62 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 37.52, 119.73, 127.18, 127.74, 128.59, 128.68, 128.82, 128.88, 129.00, 129.07, 129.88, 129.91, 132.65, 133.89, 135.11, 135.32, 154.48; found $[M + NH_4]^+$ = 392.1315, $C_{23}H_{18}O_3S$ requires $[M + NH_4]^+$ = 392.1315.

**(2,2-Dioxido-3,6-diphenyl-1,2-oxathiin-5-yl)(phenyl)methanone 11e** from **10e** (9.2 mmol) as pale yellow microcrystals (2.64 g, 74%) after elution from silica $CH_2Cl_2$ (60–100% gradient) in hexanes and crystallization from EtOAc/hexanes; mp = 129–130 °C; $\nu_{max}$ (neat) 1655, 1612, 1558, 1369 ($SO_2$–O), 1256, 1242, 1175 ($SO_2$–O), 1090, 922, 882, 711, 684, 544 cm$^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 7.21–7.31 (6H, m, Ar–H, s, 4-H), 7.35–7.39 (1H, m, Ar–H), 7.48–7.49 (5H, m, Ar–H), 7.68–7.71 (2H, m, Ar–H), 7.73–7.76 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 117.60, 127.88, 128.51, 128.54, 129.13, 129.42, 129.64, 129.68, 130.23, 130.44, 132.03, 133.75, 134.78, 136.03, 157.77, 193.27; found $[M + NH_4]^+$ = 406.1112, $C_{23}H_{16}O_4S$ requires $[M + NH_4]^+$ = 406.1108.

**3,6-Diphenyl-1,2-oxathiine 2,2-dioxide 11f** from **10f** (1.52 mmol) as pale yellow microcrystals (0.34 g, 79%) from $CH_2Cl_2$; mp = 130–132 °C; $\nu_{max}$ (neat) 3063, 1633, 1559, 1493, 1447, 1353 ($SO_2$–O), 1336, 1264, 1173 ($SO_2$–O), 1071, 1031, 1010 cm$^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 6.58 (1H, d, $J$ = 7.1 Hz, 5-H), 6.96 (1H, d, $J$ = 7.1 Hz, 4-H), 7.50–7.47 (6H, m, Ar–H), 7.67–7.64 (2H, m, Ar–H), 7.83–7.77 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 101.60, 125.49, 127.66, 128.98, 129.01, 129.05, 129.87, 130.12, 130.65, 131.13, 134.48, 156.02; found $[M + H]^+$ = 284.0511, $C_{16}H_{12}O_3S$ requires $[M + H]^+$ = 284.0507.

**6-(4-Methoxyphenyl)-3-phenyl-1,2-oxathiine 2,2-dioxide 11g** from **10g** (11.8 mmol) as yellow microcrystals (3.00 g, 81%) from EtOAc/hexane; mp = 173–174 °C; $\nu_{max}$ (neat) 2984, 2939, 2842, 1626, 1604, 1547, 1507, 1456, 1361 ($SO_2$–O), 1253, 1182,

1168 ($SO_2$–O), 1117, 999, 815, 787, 695, 569 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 3.89 (3H, s, OMe), 6.44 (1H, d, $J$ = 7.2 Hz, 5-H), 6.93 (1H, d, $J$ = 7.2 Hz, 4-H), 6.97–7.01 (2H, m, Ar–H), 7.44–7.50 (3H, m, Ar–H), 7.652–7.65 (2H, m, Ar–H), 7.71–7.74 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 55.52, 99.88, 114.47, 123.17, 127.31, 127.56, 129.00, 129.41, 129.62, 130.31, 133.21, 156.19, 162.03; found $[M + NH_4]^+$ = 332.0953, $C_{17}H_{14}O_4S$ requires $[M + NH_4]^+$ = 332.0951.

**6-(4-Trifluoromethylphenyl)-3-phenyl-1,2-oxathiine 2,2-dioxide 11h** from **10h** (4.3 mmol) as yellow microcrystals (1.09 g, 72%) from EtOAc/hexane; mp = 139–140 °C; $\nu_{max}$ (neat) 3049, 1629, 1615, 1366 ($SO_2$–O), 1328, 1301, 1177 ($SO_2$–O), 1116, 1065, 957, 870, 757, 690, 581 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 6.64 (1H, d, $J$ = 7.1 Hz, 5-H), 6.95 (1H, d, $J$ = 7.1 Hz, 4-H), 7.46–7.49 (3H, m, Ar–H), 7.61–7.66 (2H, m, Ar–H), 7.72 (2H, app d, $J$ = 8.3 Hz, Ar–H), 7.87 (2H, app d, $J$ = 8.3 Hz, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 103.36, 123.61 (q, $J$ = 272 Hz), 125.65, 126.02 (q, $J$ = 3.8 Hz), 127.72, 128.40, 129.13, 129.76, 130.21, 132.54 (q, $J$ = 33 Hz), 133.93 (q, $J$ = 1.4 Hz), 135.82, 154.23; $\delta_F$ ($CDCl_3$, 376 MHz) −62.96; found $[M + NH_4]^+$ = 370.0723, $C_{17}H_{11}F_3O_3S$ requires $[M + NH_4]^+$ = 370.0719.

**3-Phenyl-6-(pyridin-4-yl)-1,2-oxathiine 2,2-dioxide 11i** from **10i** (1.82 mmol) as pale-yellow microcrystals (0.37 g, 72%) from EtOAc/hexane; mp = 141–143 °C; $\nu_{max}$ (neat) 3053, 1637, 1594, 1550, 1492, 1447, 1410, 1352 ($SO_2$–O), 1326, 1267, 1250, 1222, 1175 ($SO_2$–O), 1067, 1023 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 6.74 (1H, d, $J$ = 6.9 Hz, 4-H), 6.95 (1H, d, $J$ = 6.9 Hz, 5-H), 7.48–7.63 (7H, m, Ar–H, Py–H), 8.74–8.76 (2H, m, Py–H); $\delta_C$ ($CDCl_3$, 100 MHz) 104.47, 118.63, 127.79, 127.91, 129.18, 129.59, 130.43, 136.99, 137.81, 150.74, 153.14; found $[M + H]^+$ = 286.0533, $C_{15}H_{11}NO_3S$ requires $[M + H]^+$ = 286.0532.

**6-(2-Nitrophenyl)-3-phenyl-1,2-oxathiine 2,2-dioxide 11j** from **10j** (2.67 mmol) as pale-yellow microcrystals (0.76 g, 86%) from EtOAc/hexane; mp = 208–210 °C; $\nu_{max}$ (neat) 2914, 2842, 1642, 1568, 1519, 1368 ($SO_2$–O), 1178 ($SO_2$–O), 1061, 1030, 788, 550 $cm^{-1}$; $\delta_H$ (DMSO-$d_6$, 400 MHz) 6.86 (1H, d, $J$ = 7.2 Hz, 5-H), 7.41 (1H, d, $J$ = 7.2 Hz, 4-H), 7.51–7.55 (3H, m, Ar–H), 7.62–7.67 (2H, m, Ar–H), 7.80–7.90 (3H, m, Ar–H), 8.10 (1H, d, $J$ = 7.9 Hz, Ar–H); $\delta_C$ (DMSO-$d_6$, 100 MHz) 106.99, 125.02, 128.00, 129.67, 129.71, 130.64, 131.83, 133.07, 134.11, 134.14, 147.86, 152.65; found $[M + NH_4]^+$ = 347.0693, $C_{16}H_{11}NO_5S$ requires $[M + NH_4]^+$ = 347.0696.

**5-(2-Fluorophenyl)-6-methyl-3-phenyl-1,2-oxathiine 2,2-dioxide 17** from **16** (5.1 mmol†) as colourless needles (1.25 g, 78%) from EtOAc/hexane; mp = 98–99 °C; $\nu_{max}$ (neat) 1651, 1579, 1491, 1359 ($SO_2$–O), 1264, 1155 ($SO_2$–O), 971, 782, 719, 568 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.15 (3H, s, 6-Me), 6.76 (1H, s, 4-H), 7.15–7.31 (3H, m, Ar–H), 7.37–7.43 (4H, m, Ar–H), 7.59–7.62 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 18.65, 112.69, 116.30 (d, $J$ = 21.7 Hz), 122.82 (d, $J$ = 15.2 Hz), 124.63 (d, $J$ = 3.7 Hz), 127.73, 128.99, 129.83, 129.87, 130.68 (d, $J$ = 8.1 Hz), 131.25 (d, $J$ = 2.6 Hz), 132.21, 133.26, 155.18, 159.67 (d, $J$ = 246.6 Hz); found $[M + NH_4]^+$ = 334.0911, $C_{17}H_{13}FO_3S$ requires $[M + NH_4]^+$ = 334.0908. †An additional 0.2 eq. of *m*-CPBA with an additional 24 h reaction time was required.

**2-Phenyl-5,6-dihydronaphtho[1,2-*e*][1,2]oxathiine 3,3-dioxide 20** from **19** (14.1 mmol) as off-white microcrystals (4.20 g, 96%) from EtOAc/hexane; mp = 126–128 °C; $\nu_{max}$ (neat) 2889, 1634, 1583, 1364 ($SO_2$–O), 1184, 1171 ($SO_2$–O), 1158, 1090, 973, 925, 778, 755, 734, 690, 557 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.81 (2H, t, $J$ = 8.0 Hz, 6-H), 3.06 (2H, t, $J$ = 8.0 Hz, 5-H), 7.21–7.34 (5H, m, Ar–H, 1-H), 7.45–7.48 (3H, m, Ar–H), 7.63–7.65 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 26.82, 27.88, 113.35, 122.87, 127.34, 127.75, 127.86, 127.89, 128.25, 129.07, 129.91, 130.37, 130.49, 132.99, 135.00, 155.91; found $[M + NH_4]^+$ = 328.1002, $C_{18}H_{14}O_3S$ requires $[M + NH_4]^+$ = 328.1002.

**5,6-Diphenyl-1,2-oxathiine 2,2-dioxide 13a** from **12a** (6.6 mmol) as off-white microcrystals (1.87 g, 72%) from EtOAc/hexane; mp = 154–155 °C; $\nu_{max}$ (neat) 3079, 1616, 1574, 1545, 1487, 1444, 1372, 1356 ($SO_2$–O), 1294, 1237, 1182 ($SO_2$–O), 1164, 1149, 1093, 1069, 1033, 1005 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 6.73 (1H, d, $J$ = 10.2 Hz, 3-H), 7.03 (1H, d, $J$ = 10.2 Hz, 1H, 4-H), 7.18–7.34 (10H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 117.49, 118.83, 128.20, 128.33, 129.00, 129.18, 129.46, 130.45, 131.10, 135.29, 139.32, 153.63; found $[M + H]^+$ = 285.0587, $C_{16}H_{12}O_3S$ requires $[M + H]^+$ = 285.0580.

**6-(4-Methoxyphenyl)-1,2-oxathiine 2,2-dioxide 13b** from **12b** (10.6 mmol) as pale fawn microneedles (2.02 g, 80%) by trituration from $Et_2O$; mp = 86–88 °C; $\nu_{max}$ (neat) 1603, 1547, 1507, 1345 ($SO_2$–O), 1173 ($SO_2$–O), 1022, 920, 759, 708, 646, 530 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 3.86 (3H, s, MeO), 6.31 (1H, d, $J$ = 6.8 Hz, 5-H), 6.58 (1H, d, $J$ = 10.0 Hz, 3-H), 6.91 (1H, dd, $J$ = 10.0, 6.8 Hz, 4-H), 6.93–6.96 (2H, m, Ar–H), 7.64–7.67 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 55.52, 98.43, 114.45, 117.60, 123.11, 127.52, 134.87, 157.58, 162.18; found $[M + H]^+$ = 239.0375 $C_{11}H_{10}O_4S$ requires $[M + H]^+$ = 239.0373.

### Acid-catalysed dehydration of 10d2: alternative preparation of (6-benzyl-3,5-diphenyl-1,2-oxathiine 2,2-dioxide 11d

4-(Dimethylamino)-3,5,6-triphenyl-3,4-dihydro-1,2-oxathiine 2,2 dioxide **10d2** (0.50 g, 1.2 mmol) was dissolved in PhMe (60 mL) and mixed with 4-TsOH (0.046 g, 0.24 mmol, 20 mol%) at room temperature. The reaction mixture was heated under reflux overnight, with the colour of the mixture gradually turning orange. Upon full consumption of the starting material, as confirmed by TLC, the solvent was removed under reduced pressure. Purification of the crude product by column chromatography (neutral alumina, dry loading, 10% EtOAc in petroleum ether (bp 60–80 °C)) gave 6-benzyl-3,5-diphenyl-1,2-oxathiine 2,2-dioxide **11d** as colourless microcrystals in 15% yield which was identical to material previously obtained by the Cope elimination reaction on **10d1**.

### Addition of phenylsulfene to (*Z*)-2,2-dimethyl-3-(pyrrolidin-1-ylmethylene)chroman-4-one 26

A solution of phenylmethanesulfonyl chloride (1.17 g, 6.12 mmol) in anhydrous THF (15 mL) under a nitrogen atmosphere was added dropwise over 10 minutes to an ice cold (−10 to 0 °C) vigorously stirred solution of the pyrrolidinomethylenechromanone **26** (1.5 g, 5.8 mmol) and triethylamine (0.90 mL, 6.4 mmol) in anhydrous THF (25 mL) under nitrogen. The resulting solution was stirred and allowed to warm room temperature over *ca.* 4 hours. The mixture was filtered

through a sinter containing a little chromatography silica (1 cm depth) and then the THF and excess $Et_3N$ were removed by rotary evaporation to afford the crude product which was further purified by recrystallization from ethyl acetate and hexane to afford 5,5-dimethyl-3-phenyl-4-(pyrrolidin-1-yl)-4,5-dihydro-3*H*-[1,2]oxathiino[5,6-*c*]chromene 2,2-dioxide **28** as a yellow solid (1.29 g, 54%); mp 134–136 °C; $\nu_{max}$ (neat) 2980, 2932, 2823, 1660, 1485, 1456, 1372 ($SO_2$–O), 1184 ($SO_2$–O), 1034, 935, 880, 830, 768, 702, 516, 508 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz)‡ 1.46 (3H, s, 5-Me), 1.56–1.70 (7H, m, $(CH_2)_2$, s, 5-Me), 2.47 (2H, bs, $NCH_2$), 2.59–2.64 (2H, m, $NCH_2$), 4.61 (1H, d, $J$ = 7.6 Hz, 4-H), 4.94 (1H, d, $J$ = 7.6 Hz, 3-H), 6.86 (1H, d, $J$ = 8.1 Hz, 7-H), 6.95–6.99 (1H, m, 9-H), 7.22–7.27 (1H, m, 8-H), 7.40 (1H, dd, $J$ = 7.7, 1.4 Hz, 10-H), 7.42–7.48 (3H, m, Ar–H), 7.53–7.56 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 23.6, 25.4, 26.4, 47.6, 61.9, 62.0, 79.8, 116.6, 117.9, 121.2, 122.3, 129.4, 129.69, 129.73, 131.0, 131.7, 153.4; found $[M + H]^+$ 412.1575, $C_{23}H_{25}NO_4S$ requires $[M + H]^+$ 412.1577. ‡The $^1H$ NMR spectrum of the crude isolated product indicated a mixture of diastereoisomers in a *ca.* 20 : 3 ratio.

### Addition of phenylsulfene to (*Z*)-2,2,6-trimethyl-3-(pyrrolidin-1-ylmethylene)thiochroman-4-one 27

A solution of phenylmethanesulfonyl chloride (1.14 g, 5.98 mmol) in anhydrous THF (15 mL) under a nitrogen atmosphere was added dropwise over 10 minutes to an ice cold (−10 to 0 °C) vigorously stirred solution of the pyrrolidinomethylenethiochromanone **27** (1.53 g, 5.32 mmol) and excess $Et_3N$ (0.87 mL, 6.2 mmol) in anhydrous THF (25 mL) under nitrogen. The resulting yellow solution was then allowed to warm to room temperature and stirred. After the reaction was judged to be complete by TLC examination (5 h) the mixture was filtered through a sinter containing chromatography silica (1 cm depth) and the THF and triethylamine were removed by rotary evaporation to afford the crude product which was further purified by elution from silica with 20% EtOAc in *n*-hexanes to afford the 5,5,9-trimethyl-3-phenyl-4-(pyrrolidin-1-yl)-4,5-dihydro-3*H*-thiochromeno[3,4-*e*][1,2]oxathiine 2,2-dioxide **29** as a yellow solid (1.00 g, 43%); mp 146–148 °C; $\nu_{max}$ (neat) 2939, 2865, 1626, 1598, 1537, 1462, 1372 ($SO_2$–O), 1266, 1160 ($SO_2$–O), 1133, 827, 782, 403 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 1.55 (3H, s, 5-Me), 1.62 (3H, s, 5-Me), 1.68–1.75 (4H, m, $(CH_2)_2$), 2.35 (3H, s, 9-Me), 2.61–2.65 (4H, m, $N(CH_2)_2$), 4.61 (1H, d, $J$ = 5.2 Hz, 4-H), 4.91 (1H, d, $J$ = 5.2 Hz, 3-H), 7.08 (1H, dd, $J$ = 7.9, 1.0 Hz, 8-H), 7.19 (1H, d, $J$ = 7.9 Hz, 7-H), 7.42–7.47 (4H, m, Ar–H, 10-H), 7.52–7.54 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 21.2, 23.8, 26.9, 27.5, 43.9, 47.0, 62.4, 63.2, 122.2, 124.9, 126.9, 127.4, 129.37, 129.39, 129.8, 130.4, 133.2, 135.4, 145.6; found $[M + H]^+$ 442.1500, $C_{24}H_{27}NO_3S_2$ requires $[M + H]^+$ 442.1505.

### Addition of phenylsulfene to (*Z*)-3-((dimethylamino) methylene)isothiochroman-4-one 33

A solution of phenylmethanesulfonyl chloride (2.80 g, 14.7 mmol) in anhydrous THF (50 mL) under a nitrogen atmosphere was added dropwise over 10 minutes to a cold (~0 °C) vigorously stirred solution of (*Z*)-3-((dimethylamino)methylene)isothiochroman-4-one **33** (2.80 g, 12.8 mmol) and excess $Et_3N$ (2.14 mL, 15.3 mmol) in anhydrous THF (50 mL) under nitrogen. The resulting yellow suspension was then allowed to warm to room temperature and stirred. After the reaction was judged to be complete by TLC examination (7 h) the mixture was filtered through a sinter containing chromatography silica (30 mm depth) and the volatiles were removed by rotary evaporation to afford the crude product as a yellow solid which was recrystallized from EtOAc/hexanes to afford the 4-(dimethylamino)-3-phenyl-4,6-dihydro-3*H*-isothiochromeno[3,4-*e*][1,2]oxathiine 2,2-dioxide **34** as yellow microcrystals (3.55 g, 74.4%); mp 173–176 °C; $\nu_{max}$ (neat) 2981, 2875, 2796, 1490, 1448, 1364 ($SO_2$–O), 1183 ($SO_2$–O), 1161, 1008, 983, 947, 839, 792, 776, 697, 573, 533 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz)† 2.16 (6H, s, $NMe_2$(maj)), 2.18 (6H, s, $NMe_2$(min)), 3.56 (1H, d, $J$ = 14.2 Hz, 6-H (maj)), 3.75 (1H, d, $J$ = 14.2 Hz, 6-H(min)), 4.07 (1H, d, $J$ = 14.2 Hz, 6-H(min)), 4.15 (1H, d, $J$ = 14.2 Hz, 6-H(maj)), 4.59 (1H, d, $J$ = 10.5 Hz, 4-H(maj)), 4.65 (1H, d, $J$ = 6.4, 4-H(min)), 4.79 (1H, d, $J$ = 10.5 Hz, 3-H(maj)), 4.88 (1H, d, $J$ = 6.4, 3-H (min)), 7.15–7.21 (2H, m, Ar–H), 7.29–7.49 (11H, m, Ar–H), 7.57–7.63 (4H, m, Ar–H), 7.64–7.69 (1H, m, Ar–H(min)); $\delta_C$ ($CDCl_3$, 100 MHz) 30.71, 30.85, 40.99, 41.57, 62.67, 63.49, 66.53, 68.74, 118.74, 120.18, 122.51, 122.58, 126.56, 126.58, 127.52, 127.79, 128.33, 128.53, 129.17, 129.41, 129.75, 129.79, 129.89, 129.98, 130.01, 130.44, 130.65, 131.11, 140.60, 141.28; found $[M + H]^+$ 374.0876, $C_{19}H_{19}NO_3S_2$ requires $[M + H]^+$ 374.0879. †Sample present as an inseparable mixture of diastereoisomers by routine flash chromatography (ratio 1.7 : 1.0 based on relative integrals of $^1H$ NMR signals) where possible signals from the major (maj) and minor (min) isomer have been identified.

### Preparation of 5,5-dimethyl-3-phenyl-5*H*-[1,2]oxathiino[5,6-*c*] chromene 2,2-dioxide 30

A solution of 3-chloroperoxybenzoic acid (*ca.* 77%, 1.64 g, 6.69 mmol) in dichloromethane (20 mL) was added dropwise over 15 minutes to an ice cold vigorously stirred solution of 5,5-dimethyl-3-phenyl-4-(pyrrolidin-1-yl)-4,5-dihydro-3*H*-[1,2]oxathiino[5,6-*c*]chromene 2,2-dioxide **20** (2.5 g, 6.1 mmol) in dichloromethane (50 mL). The orange solution was allowed to warm to room temperature and stirred for 48 hours. The mixture was then diluted with water and the $CH_2Cl_2$ layer was separated. The $CH_2Cl_2$ layer was washed with aqueous sodium thiosulfate (2 × 50 mL), washed with dilute aqueous sodium bicarbonate (4 × 50 mL) and then with water (50 mL). The orange solution was then dried with anhydrous sodium sulphate and the solvent was removed by rotary evaporation to afford the crude product which was further purified by column chromatography with 25% EtOAc in *n*-hexanes to afford the title product **30** as a pale yellow solid (1.02 g, 49%); mp 98–100 °C; $\nu_{max}$ (neat) 2976, 1633, 1549, 1482, 1362 ($SO_2$–O), 1352, 1170 ($SO_2$–O), 1053, 950, 833, 778, 695, 682, 563, 525 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 1.65 (6H, s, 5-Me), 6.75 (1H, s, 4-H), 6.88 (1H, dd, $J$ = 8.2, 0.4 Hz, 7-H), 7.00–7.04 (1H, m, 9-H), 7.30–7.35 (1H, m, 8-H), 7.44–7.48 (3H, m, Ar–H), 7.55 (1H, dd,

$J$ = 7.7, 1.5 Hz, 10-H), 7.62–7.64 (2H, m, Ar–H); $\delta_C$ ($CDCl_3$, 100 MHz) 27.3, 78.6, 114.7, 115.8, 117.1, 121.8, 122.9, 127.3, 127.7, 129.1, 130.0, 130.3, 132.9, 134.8, 146.9, 154.0; found $[M + H]^+$ 341.0843, $C_{19}H_{16}O_4S$ requires $[M + H]^+$ 341.0842.

### Oxidation of 5,5,9-trimethyl-3-phenyl-4-(pyrrolidin-1-yl)-4,5-dihydro-3*H*-thiochromeno[3,4-*e*][1,2]oxathiine 2,2-dioxide 29

A solution of 3-chloroperoxybenzoic acid (*ca.* 77%, 4.59 g, 18.7 mmol) in dichloromethane (35 mL) was added dropwise over 15 minutes to an ice cold vigorously stirred solution of 5,5,9-trimethyl-3-phenyl-4-(pyrrolidin-1-yl)-4,5-dihydro-3*H*-thiochromeno[3,4-*e*][1,2]oxathiine 2,2-dioxide **29** (2.5 g, 5.7 mmol) in dichloromethane (50 mL). The cloudy orange/yellow solution was allowed to warm to room temperature and stirred until TLC examination of the reaction mixture indicated that no starting material remained (*ca.* 48 hours). The mixture was then diluted with water (200 mL) and the dichloromethane layer was separated. The $CH_2Cl_2$ layer was washed with aqueous sodium thiosulfate solution (2 × 50 mL), washed with dilute aqueous sodium bicarbonate solution (3 × 50 mL) and finally with water (100 mL). The orange/yellow solution was then dried with anhydrous sodium sulfate and solvent was removed by rotary evaporation to afford the crude product which was further purified by column chromatography using 40% EtOAc in *n*-hexanes to afford two fractions. Fraction 1, 5,5,9-trimethyl-3-phenyl-5*H*-thiochromeno[3,4-*e*][1,2]oxathiine 2,2,6,6-tetraoxide **31a** as a yellow solid (0.79 g, 32%); mp 161–163 °C; $\nu_{max}$ (neat) 2973, 1633, 1549, 1481, 1455, 1362 ($SO_2$–O), 1267 ($SO_2$), 1168 ($SO_2$–O), 1138 ($SO_2$), 946, 760, 697, 562 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 1.68 (6H, s, 5-Me), 2.53 (3H, s, 9-Me), 6.95 (1H, s, 4-H), 7.48–7.50 (4H, m, Ar–H, 8-H), 7.61–7.64 (2H, m, Ar–H), 7.76 (1H, s, 10-H), 7.96 (1H, d, $J$ = 7.9 Hz, 7-H); $\delta_C$ ($CDCl_3$, 100 MHz) 20.1, 21.8, 58.1, 119.8, 125.5, 126.6, 126.7, 127.0, 127.8, 129.3, 129.5, 130.4, 130.7, 132.6, 137.3, 145.2, 146.5; found $[M + H]^+$ 403.0669, $C_{20}H_{18}O_5S_2$ requires $[M + H]^+$ 403.0668.

Fraction 2, 5,5,9-trimethyl-3-phenyl-5*H*-thiochromeno[3,4-r*e*][1,2]oxathiine 2,2,6-trioxide **31b** as a yellow solid (1.19 g, 50%); mp 70–73 °C; $\nu_{max}$ (neat) 2976, 1633, 1548, 1455, 1363 ($SO_2$–O), 1172 ($SO_2$–O), 1298, 1267, 1124, 1083, 1036 (SO), 953, 901, 759, 734, 696, 564 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 1.46 (3H, s, 5-Me), 1.71 (3H, s, 5-Me), 2.49 (3H, s, 9-Me), 6.97 (1H, s, 4-H), 7.44 (1H, d, $J$ = 7.9 Hz, 8-H), 7.48–7.51 (3H, m, Ar–H), 7.61–7.64 (2H, m, Ar–H), 7.70–7.72 (2H, app. d, $J$ = 7.6 Hz, 7-H, 10-H); $\delta_C$ ($CDCl_3$, 100 MHz) 20.03, 21.62, 22.49, 55.27, 116.07, 124.53, 126.51, 127.78, 127.91, 129.20, 129.77, 129.81, 130.40, 132.74, 132.91, 136.61, 143.51, 148.28; found $[M + H]^+$ 387.0716, $C_{20}H_{18}O_4S_2$ requires $[M + H]^+$ 387.0719.

### Preparation of 3-phenyl-6*H*-isothiochromeno[3,4-*e*][1,2]oxathiine 2,2,5,5-tetraoxide 35

A solution of 3-chloroperoxybenzoic acid (*ca.* 77%, 13.05 g, 58.23 mmol) was added portionwise over 15 minutes to an ice cold vigorously stirred solution of 4-(dimethylamino)-3-phenyl-4,6-dihydro-3*H*-isothiochromeno[3,4-*e*][1,2]oxathiine 2,2-dioxide **34** (3.0 g, 8.0 mmol) in dichloromethane (150 mL). The yellow suspension was allowed to warm to room temperature and stirred for 6 days. The mixture was then diluted with water (200 mL) and the $CH_2Cl_2$ layer was separated. The $CH_2Cl_2$ layer was washed with aqueous sodium sulfite solution (6 × 50 mL), washed with dilute aqueous sodium bicarbonate (5 × 50 mL) and then with water (100 mL). The yellow solution was then dried with anhydrous sodium sulphate and the solvent was removed by rotary evaporation to afford the crude product which was recrystallized from acetone/MeOH to afford the title product **35** as a pale yellow solid (2.21 g, 76%); mp 215–216 °C; $\nu_{max}$ (neat) 1610, 1381 ($SO_2$–O), 1307, 1155 ($SO_2$–O), 1053, 752, 684, 612, 543, 442 $cm^{-1}$; $^1H$ NMR ($(CD_3)_2CO$, 400 MHz) 5.00 (2H, s, 6-H), 7.54 (1H, s, 4-H), 7.61–7.63 (3H, m, Ar–H), 7.70–7.77 (3H, m, Ar–H), 7.79–7.83 (2H, m, Ar–H), 8.03–8.07 (1H, m, 10-H); $^{13}C$ NMR ($(CD_3)_2CO$, 100 MHz) 54.3, 118.7, 122.4, 124.8, 126.3, 128.0, 129.1, 129.3, 129.7, 130.2, 130.6, 130.8, 133.4, 136.0, 154.6; found $[M + K]^+$ = 398.9771 $C_{17}H_{12}O_5S_2$ requires $[M + K]^+$ = 398.9758.

### Attempted preparation of 4-(dimethylamino)-3-phenyl-6-(*p*-tolyl)-3,4-dihydro-1,2,5-oxathiazine 2,2-dioxide 37 (Preparation of *N*-formyl-4-methylbenzamide 38)

A solution of phenylmethanesulfonyl chloride (3.98 g, 20.9 mmol) in anhydrous THF (40 mL) was added dropwise to a cold (−5 °C) stirred solution of (*E*)-*N*-((dimethylamino) methylene)-4-methylbenzamide (3.79 g, 19.9 mmol) and triethylamine (3.05 mL, 21.9 mmol) in anhydrous THF (50 mL) under nitrogen. The solution was allowed to warm to room temperature and stirred for 24 hours. Following TLC analysis, further triethylamine (3.05 mL, 21.9 mmol) was added to the reaction mixture which was cooled to −5 °C and a solution of phenylmethanesulfonyl chloride (3.98 g, 20.9 mL) in anhydrous THF (40 mL) was added dropwise to the reaction mixture. The reaction mixture was allowed to warm to room temperature stirred for 6 days. The reaction mixture was filtered through Celite and the solvent removed under vacuum. The resulting residue was purified by column chromatography (1% methanol in dichloromethane) to afford *N*-formyl-4-methylbenzamide **38** as the major fraction (2.00 g, 62%) as colourless needles; mp = 128–130 °C (lit. mp = 130–132 °C[49]); $\nu_{max}$ 1668, 1609, 1443, 1363, 1204, 1182, 11223, 1067, 1036, 834, 726, 677, 640, 608, 563, 471 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta_H$ 10.1 (1H, bd, $J$ = 8.2 Hz, NH), 9.38 (1H, d, $J$ = 9.7 Hz, CHO), 7.89–7.87 (2H, m, Ar–H), 7.35–7.26 (2H, m Ar–H), 2.44 (3H, s, Ar–Me).

### Preparation of (*E*)-3-(dimethylamino)-*N*-((*E*)-(dimethylamino) methylene)-2-phenylacrylamide 39

A stirred solution of 2-phenylacetamide (2.0 g, 15 mmol) in DMF·DMA (10 mL, 83 mmol) was heated in a distillation set up such that the produced MeOH was removed. After 4 h the reaction mixture was cooled to room temperature and the volume reduced under pressure. The crude yellow product was washed with hexane containing a little EtOAc and filtered to yield the title compound **39** (2.3 g, 63%) as pale yellow crystals;

mp 115–116 °C (lit. mp 112 °C[37]); $\nu_{max}$ (neat) 1601, 1553, 1495, 1435, 1421, 1384, 1328, 1283, 1266, 1204, 1172, 1087, 1063, 981, 947, 920, 890, 798, 738, 728, 700, 634, 568, 546 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.69 (6H, s, =CH-N$\underline{Me}_2$), 3.02 (3H, s, NMe), 3.05 (3H, s, NMe), 7.15–7.28 (5H, m, Ar–H), 8.13 (1H, s, =C$\underline{H}$-$NMe_2$), 8.42 (1H, s, N=C$\underline{H}$-$NMe_2$); $\delta_C$ ($CDCl_3$, 100 MHz) 34.77, 40.90, 43.22, 107.60, 125.69, 127.12, 132.17, 138.28, 150.28, 158.39, 179.26; found $[M + H]^+$ = 246.1604 $C_{14}H_{19}N_3O$ requires $[M + H]^+$ = 246.1601.

### Preparation of methyl *N*-((*E*)-3-(dimethylamino)-2-phenylacryloyl)formimidate 41

A stirred solution of 2-phenylacetamide (10.1 g, 75 mmol) in DMF·DMA (35 mL, 262 mmol) was heated at reflux for 24 h. The reaction mixture was cooled to room temperature and the volatiles removed under reduced under pressure. The resulting dark red oil was purified by column chromatography (1% methanol in dichloromethane) to afford the title compound **41** (6.8 g, 39%) as a pale-yellow powder; mp 65–66 °C; $\nu_{max}$ (neat) 1537, 1414, 1395, 1221, 1185, 1118, 1046, 1024, 770, 695 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.96 (3H, s, NMe), 3.02 (3H, s, NMe), 3.74 (3H, s, OMe), 7.22–7.18 (1H, m, Ar–H), 7.33–7.29 (2H, m, Ar–H), 7.48–7.45 (2H, m, Ar–H), 7.70 (1H, s, =C$\underline{H}$-$NMe_2$), 8.04 (1H, s, N=C$\underline{H}$-OMe); $\delta_C$ ($CDCl_3$, 100 MHz) 169.72, 160.72, 152.78, 135.43, 130.97, 127.14, 126.14, 117.16, 51.41, 40.48, 35.08; found $[M + H]^+$ = 233.1287 $C_{13}H_{16}N_2O_2$ requires $[M + H]^+$ = 233.1290.

### Preparation of (*E*)-*N*'-(2,2-dioxido-3,5-diphenyl-1,2-oxathiin-6-yl)-*N*,*N*-dimethylformimidamide 42

A solution of phenylmethanesulfonyl chloride (3.03 g, 1.3 eq.) in THF (30 mL) was added dropwise over 10 min to a cold (0–5 °C) stirred solution of (*E*)-3-(dimethylamino)-*N*-((*E*)-(dimethylamino)methylene)-2-phenylacrylamide **39** (3.00 g, 12.2 mmol) in THF (35 mL) containing $Et_3N$ (2.22 mL, 15.9 mmol, 1.3 eq.) under $N_2$. Additional amounts of phenylmethanesulfonyl chloride (0.3 eq.) and $Et_3N$ (0.3 eq.) were added as required to ensure reaction completion. The resulting mixture was filtered through a layer of alumina (5 mm) and the THF was removed by rotary evaporation. The crude mixture was chromatographed on an alumina column (40% DCM in hexane) and the fractions containing the main component of the mixture were combined, washed with aq. sat. $Na_2CO_3$ (25 mL) and $H_2O$ (2 × 25 mL) and dried over anhyd. $Na_2SO_4$. Recrystallization of the obtained solid from EtOAc/petroleum spirit (bp 40–60 °C) gave the title compound **42** (0.38 g, 9%) as yellow crystals; mp 145–147 °C; $\nu_{max}$ (neat) 3041, 2929, 1631, 1614, 1595, 1574, 1519, 1445, 1406, 1372, 1342 (O–$SO_2$), 1294, 1272, 1258, 1211, 1175 (O–$SO_2$), 1100, 1076, 1031 $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 3.04 (3H, s, $NCH_3$), 3.15 (3H, s, $NCH_3$), 7.15 (1H, s, 4-H), 7.22–7.44 (6H, m, Ar–H), 7.57–7.60 (4H, m, Ar–H), 8.20 (1H, s, HC=N); $\delta_C$ ($CDCl_3$, 100 MHz) 35.44, 41.34, 104.76, 126.81, 127.17, 128.14, 128.59, 128.82, 129.12, 129.62, 131.49, 136.09, 136.80, 152.75, 153.42; found $[M + H]^+$ = 355.1111, $C_{19}H_{18}N_2O_3S$ requires $[M + H]^+$ = 355.1117.

## Conflicts of interest

There are no conflicts to declare.

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