Acid-promoted isomerisation of 1-acceptor-1-sulfenyl-substituted 2-vinylcyclopropanes with C^1–C^2 bond fission and novel 1,5-sulfenyl rearrangement

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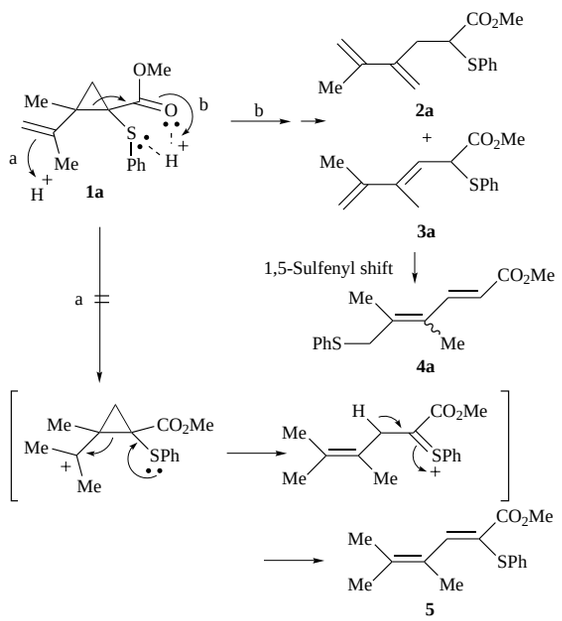
1-Acceptor-1-sulfenyl-substituted vinylcyclopropanes 1 undergo C^1–C^2 bond fission and 1,5-sulfenyl rearrangement to give 6-sulfenyl-α,β;γ,δ-unsaturated carboxylic esters and nitriles 4 by treatment with acid. The reactions proceed smoothly by use of a sulfonic acid such as *p*-TsOH·H_2O, CF_3SO_3H *etc.* in a non-polar solvent. The results, obtained from reactions of compounds 12 and 16, imply that the C^1–C^2 bond cleavage and deprotonation from the C^2-methyl group of substrates 1 occur *via* a concerted process. The cross-over experiment showed that the 1,5-sulfenyl shift proceeds intermolecularly. Addition of a catalytic amount of *m*-MeC_6H_4SH improves the yield of the rearranged product 4c.

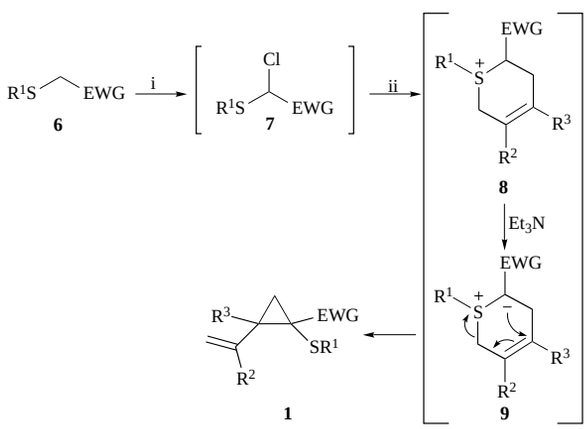
Introduction

The vinylcyclopropane unit, containing the cyclopropane ring[1] and its associated strain energy, is subject to a variety of chemical transformations.[2] Although various types of vinylcyclopropanes have been utilised for the synthesis of complex molecules, 1-acceptor-1-sulfenyl-substituted vinylcyclopropanes have received considerably less attention.[3] We therefore intended to explore the novel transformations of 1-acceptor-1-sulfenyl-substituted 2-vinylcyclopropanes. There are several reports of the transformations of 1-acceptor-substituted 2-vinylcyclopropanes, mainly chrysanthemic acid and its derivatives, with proton acids or Lewis acids.[4] These papers describe two types of reactions: (i) γ-lactonisation of vinylcyclopropanecarboxylic acids and its esters[4a–d] and (ii) diene formation following C^2–C^3 bond fission.[4d–h] In the latter case, reactions of chrysanthemic acid and its derivatives under acidic conditions proceed *via* protonation at the vinylic moiety. Recently we reported that C^1–C^2 bond fission and 1,5-sulfenyl rearrangement takes place on treatment of 1-acceptor-1-sulfenyl-substituted 2-vinylcyclopropanes with an acid.[5] In this study, dienes **2a** and **3a**, but not **5**, were obtained as minor products from compound **1a** *via* protonation at the carboxy group and subsequent C^1–C^2 bond fission (Scheme 1, route b). These types of dienes could not be formed from the similar mechanism described in previous papers,[4d–h] namely, route a in Scheme 1. This different protonation would be achieved with the aid of the electromeric effect of the sulfur atom. The 1,5-sulfenyl shift probably proceeds *via* the diene **3a**. There has only been one reported example of a 1,5-alkylthio shift catalysed by a base;[6] our finding, however, is the first example of an acid-promoted 1,5-sulfenyl shift. We now present a full account of our work in this area, including a mechanistic study of the C^1–C^2 bond cleavage and the 1,5-sulfenyl shift.

1-Acceptor-1-sulfenyl-substituted 2-vinylcyclopropanes **1** were synthesized as shown in Scheme 2. A sulfide **6** was chlorinated with *N*-chlorosuccinimide (NCS) in CCl_4. The resultant α-chloro sulfide **7** reacted with a diene in the presence of $SnCl_4$ to form a sulfonium salt intermediate **8**. The sulfonium salt **8**, without isolation, was subsequently treated with Et_3N to give a 1-acceptor-1-sulfenyl-substituted 2-vinylcyclopropane **1** *via* [2,3]sigmatropic rearrangement of the ylide **9**.[3] The relative configuration of compound **1a** as a representative for vinylcyclopropyl sulfides **1** was assigned by the nuclear Overhauser effect (NOE) technique.[5] It was revealed that the sulfenyl substituent and the vinyl group are in a *cis*-configuration. The stereochemistry agreed with the structure proposed from the mechanism of the vinylcyclopropanation reaction.



Scheme 1



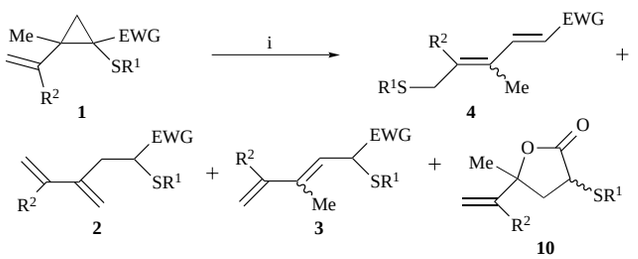
Scheme 2 *Reagents and conditions:* i, NCS, CCl_4; ii, diene and $SnCl_4$, CH_2Cl_2, then Et_3N

Firstly we investigated the effect of an acid catalyst on reactions of vinylcyclopropyl sulfide **1a** (Scheme 3, Table 1). The use of 42% HBF_4 and CF_3CO_2H as a proton acid gave γ-lactone **10a** as a diastereomeric mixture (~ 1 : 1, estimated by ^1H

Table 1 Acid-promoted isomerisation of vinylcyclopropyl sulfide **1a**

Entry	Conditions	Products (% yield)			
		4a (*Z*:*E*)[a]	**2a**[b]	**3a** (*E*)[b]	**10a**[c]
1	42% HBF_4 (1.0 equiv.), THF, room temp., 24 h				50
2	CF_3CO_2H (1.0 equiv.), benzene, room temp., 24 h				31
3	*p*-TsOH (0.1 equiv.), benzene, reflux, 18 h	49 (1:3)	24	10	8
4	PPTS (0.1 equiv.), benzene, reflux, 20 h	35 (1:1)	47		5
5	CSA (0.1 equiv.), benzene, reflux, 20 h	41 (1:1)	49		trace
6	CF_3SO_3H (0.1 equiv.), benzene, reflux, 20 h	41 (2:3)	trace	11	14
7	$BF_3{\cdot}Et_2O$ (1.0 equiv.), benzene, reflux, 14 h	4 (2:3)			31
8	*p*-TsOH (0.1 equiv.), EtOH, reflux, 9 h				60[d]
9	*p*-TsOH (0.1 equiv.), DMF, 80 °C, 9 h				15[d]
10	*p*-TsOH (0.1 equiv.), THF, reflux, 9 h	25 (1:1)	25		43
11	*p*-TsOH (0.1 equiv.), $(ClCH_2)_2$, reflux, 9 h				26[d]

[a] *Z*:*E* ratio was determined by ^{1}H NMR spectroscopy. [b] Isomers **2** and **3** were isolated as an inseparable mixture. Yields were estimated by ^{1}H NMR spectroscopy. [c] Diastereomeric mixture (~1:1, estimated by ^{1}H NMR spectroscopy). [d] A considerable amount of $(PhS)_2$ was obtained, in 36–41% yield.



a; EWG = CO_2Me, R^1 = Ph, R^2 = Me
b; EWG = CO_2Me, R^1 = *p*-MeC_6H_4, R^2 = Me
c; EWG = CO_2Me, R^1 = *m*-MeC_6H_4, R^2 = Me
d; EWG = CO_2Me, R^1 = *p*-ClC_6H_4, R^2 = Me
e; EWG = CO_2Me, R^1 = Ph, R^2 = H
f; EWG = CO_2Me, R^1 = R^2 = Me
g; EWG = CN, R^1 = Ph, R^2 = Me
h; EWG = CN, R^1 = *p*-ClC_6H_4, R^2 = Me
i; EWG = CN, R^1 = Ph, R^2 = H

Scheme 3 *Reagent:* i, acid

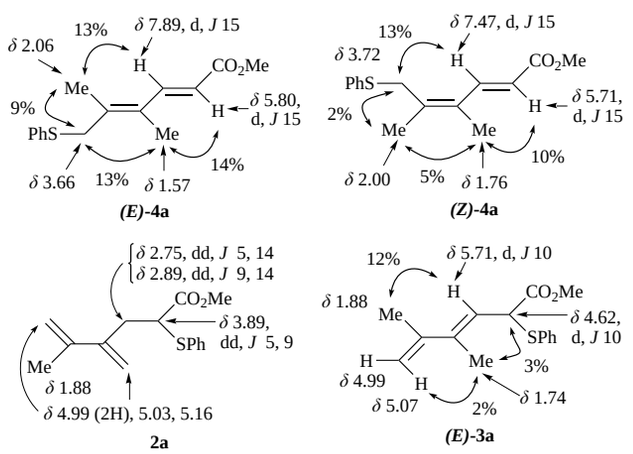


Fig. 1

NMR spectroscopy) (entries 1 and 2). The C^1–C^2 bond fission and 1,5-sulfenyl shift efficiently took place using a sulfonic acid such as toluene-*p*-sulfonic acid monohydrate (*p*-TsOH·H_2O), pyridinium toluene-*p*-sulfonate (PPTS), (+)-camphor-10-sulfonic acid (CSA) or CF_3SO_3H in benzene under reflux (entries 3–6). *p*-TsOH·H_2O was the most effective catalyst for the 1,5-sulfenyl shift (entry 3) and the rearranged diene **4a** was formed in 49% yield as a mixture of geometrical isomers accompanied by an inseparable mixture of the ring-opened dienes **2a** and (*E*)-**3a** (the yields were estimated from the intensities of the signals in the ^{1}H NMR spectrum). $BF_3{\cdot}Et_2O$ as a Lewis acid could not effect C^1–C^2 bond fission, and the 1,5-sulfenyl shift predominated giving lactone **10a** as the major product (entry 7). Next, we examined solvent effects on the acid-promoted C^1–C^2 bond fission and the 1,5-sulfenyl rearrangement of compound **1a** with 0.1 mol equiv. of *p*-TsOH·H_2O. The best result was obtained by use of benzene, a non-polar solvent, under reflux (entry 3). When the reaction was carried out in EtOH, a polar protic solvent, γ-lactone **10a** was formed in 60% yield and no ring-opened diene was obtained (entry 8). Polar aprotic solvents, especially dimethylformamide (DMF) and 1,2-dichloroethane, were ineffective for the C^1–C^2 bond fission and/or the 1,5-sulfenyl shift (entries 9 and 11). Tetrahydrofuran (THF) was less effective than benzene and compound **10a** was formed in 43% yield together with open-chain esters **4a** and **2a**, both in 25% yield (entry 10). A considerable amount of diphenyl disulfide was obtained (36–41%) when EtOH, DMF or 1,2-dichloroethane was used as the solvent. The structure of compounds (*E*)-**4a**, (*Z*)-**4a**, **2a** and (*E*)-**3a** were determined by ^{1}H NMR spectroscopy and NOE measurements (Fig. 1).

Following our examinations of acid catalysts and solvents, several vinylcyclopropyl sulfides **1a**–**i** were treated with 0.1 or 1.0 mol equiv. of *p*-TsOH·H_2O in toluene under reflux (Table 2). Vinylcyclopropyl sulfides, **1a**–**e**,**g**–**i**, carrying an arylthio group, gave 6-sulfenyl-α,β;γ,δ-unsaturated carboxylic esters **4a**–**e** and nitriles **4g**–**i** in moderate to good yields, respectively. The rearranged dienes **4e** and **4i** were obtained as a single isomer. The rearranged products **4g**–**i** having a cyano group were less stable than those bearing an ester group. A slight substituent effect of an arylthio group was observed (entries 1–4). The yield of compound **4d** with an electron-withdrawing chloro substituent was lower than that of compound **4a** and a small amount of ring-opened diene **3d** was also obtained. In the reaction of compound **1b** bearing an electron-donating *para*-methyl group, product **3b** was not formed because the rate of the arylthio shift of **3b** was faster than those of **3a** and **3c**. A similar result was obtained from the reaction of compound **1c** with an electron-donating *meta*-methyl group. The methylthio group was ineffective for C^1–C^2 bond cleavage and for the 1,5-methylthio shift (entry 5), and consequently no rearranged diene was isolated. We investigated an improved method for the 1,5-sulfenyl shift (entry 10). In the reaction of compound **1c** bearing a *meta*-methylphenylthio group with 0.1 mol equiv. of *p*-TsOH·H_2O, addition of a catalytic amount of *m*-MeC_6H_4SH, corresponding to the sulfenyl group of substrate **1c**, and lowered reaction temperature (refluxing in benzene) as well as reaction time (8 h) increased the yield of the rearranged diene **4c** to 83% (compared with entry 3). This finding showed that a thiol catalysed the 1,5-sulfenyl rearrangement.

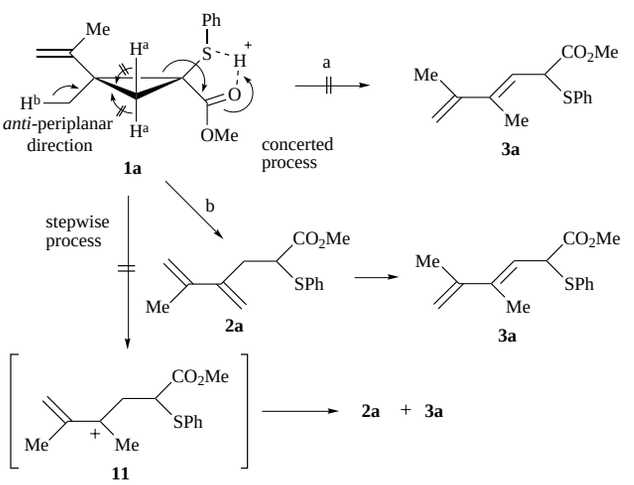
It is unreasonable that the C^1–C^2 bond is cleaved by protonation on the olefinic moiety because such a mechanism allows formation of a different type of diene as shown in Scheme 1.

Table 2 Reactions of vinylcyclopropyl sulfides **1** with *p*-TsOH·H_2O

Entry	Compd.	*p*-TsOH (mol equiv.)	Time (*t*/h)	Products (% yield) **4a** (*Z*:*E*)[a]	**2**[b]	**3** (*Z*:*E*)[b]	**10**[c]
1	**1a**	0.1	12	67 (1:3)	8	trace (*E*)	5
2	**1b**	0.1	12	75 (1:3)	5		8
3	**1c**	0.1	12	68 (1:3)	6		4
4	**1d**	0.1	12	63 (1:3)	8	3 (*E*)	2
5	**1e**	0.1	10	60 (*E*)	7	3 (1:2)	6
6	**1f**	1.0	20	complex mixture			
7	**1g**	1.0	3	60 (1:2)	4		
8	**1h**	1.0	3	55 (1:3)	3		
9	**1i**	1.0	3	42 (*E*)			
10[d]	**1c**	0.1	8	83 (1:4)	5		4

[a] *Z*:*E* ratio was determined by ^{1}H NMR spectroscopy. [b] Isomers **2** and **3** were isolated as an inseparable mixture. Yields and *Z*:*E* ratios were estimated by ^{1}H NMR spectroscopy. [c] Diastereomeric mixture (~1:1, estimated by ^{1}H NMR spectroscopy). [d] The reaction was carried out in benzene under reflux in the presence of 0.1 mol equiv. of *m*-MeC_6H_4SH.

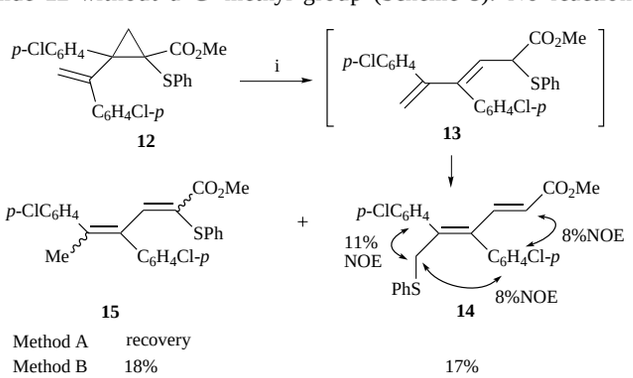
The C^1–C^2 bond fission would proceed by protonation on the carboxy group aided by the phenylthio substituent, *via* three possible pathways (Scheme 4). In the stepwise process, the



Scheme 4

thermodynamically more stable diene **3a** would be formed as a major product, rather than isomer **2a**, through a cationic intermediate **11**. The concerted process follows either or both of two plausible routes: one is deprotonation of H^a on the cyclopropane ring to give compound **3a** and the other is deprotonation of H^b of the C^2-methyl group to form product **2a**. Predominant formation of compound **2a** rather than isomer **3a** (see Tables 1 and 2) suggests that the concerted process with abstraction of the H^b proton is most likely.

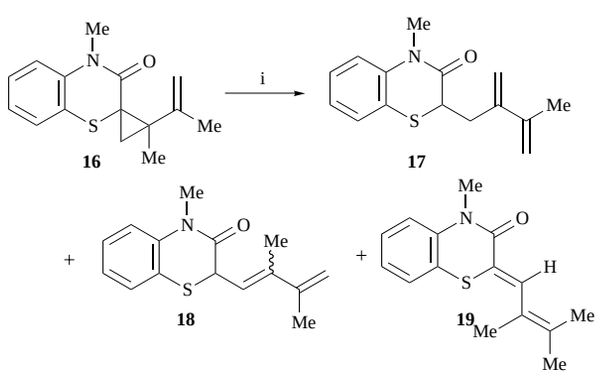
In order to confirm the mechanism of the C^1–C^2 bond cleavage, we carried out reactions of the vinylcyclopropyl sulfide **12** without a C^2-methyl group (Scheme 5). No reaction



Scheme 5 *Reagents and conditions:* i, Method A: *p*-TsOH·H_2O (0.1 mol equiv.), benzene, reflux, 20 h; Method B: *p*-TsOH·H_2O (1.0 mol equiv.), benzene, reflux, 21 h

occurred on treatment of compound **12** with 0.1 mol equiv. of *p*-TsOH·H_2O in benzene under reflux for 20 h, although the reaction of compound **1a** proceeded smoothly under similar conditions (see entry 3 in Table 1). The rearranged compound **14** was obtained in 18% yield accompanied by compound **15** (17%) when 1.0 mol equiv. of *p*-TsOH·H_2O in benzene was used under reflux for 21 h. Compound **15** would be formed by isomerisation of an intermediate diene **13** or by protonation on the vinyl group followed by ring-opening and removal of H^a in a similar way to the ring-opening of chrysanthemic acid derivatives.[4d–h] If the C^1–C^2 bond cleavage took place *via* the stepwise process, reactions of compound **12** should take place more easily than that of compound **1a** because of formation of a more stable carbocation intermediate than **11** in Scheme 4. However, reaction of compound **12** required vigorous conditions. This would exclude the stepwise process. The 2-methyl group is necessary for the smooth ring opening. One of the hydrogens (H^b) of the methyl group and C^1 of the cyclopropane ring are *anti*-planar (Scheme 4). This geometry works advantageously to effect the concerted process of ring-opening and deprotonation in vinylcyclopropanes **1**.

We also examined reactions of vinylcyclopropyl sulfide **16**,[7] lacking migratory capability by structural demand (Scheme 6,



Scheme 6 *Reagents and conditions:* i, *p*-TsOH·H_2O, benzene, reflux

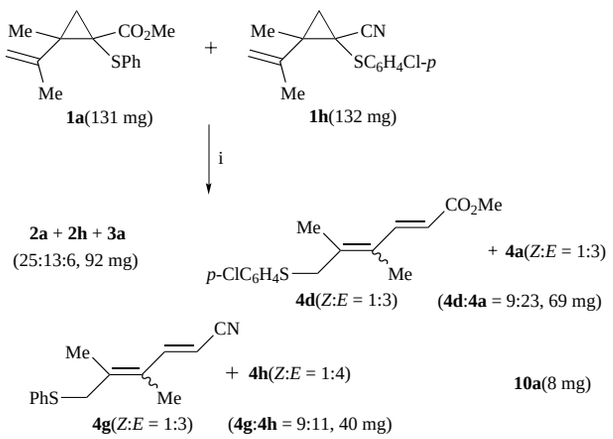
Table 3). Treatment of spirovinylcyclopropane **16** with 0.1 mol equiv. of *p*-TsOH·H_2O for 2 h gave dienes **17**, **18** and **19** in 51, 36 and 5% yield, respectively (entry 1). Although the diene **18** was obtained as a single isomer, the geometry has not been confirmed at present. The geometry of compound **19** was determined as being (*Z*) by applying the additivity rule in the ^{1}H NMR spectrum.[8] The olefinic proton of product **19** was observed at δ 7.53. Calculated chemical shifts for the (*Z*)- and (*E*)-isomers are δ 7.34 and 6.66, respectively. This result suggests that compound **19** exists as the (*Z*)-isomer. The yield of compound **17** decreased to 24% and that of isomer **18** increased to 52% when prolonged reaction conditions were used (5 h, entry 2). In the course of reactions with 1.0 mol equiv. of

Table 3 Acid-promoted isomerisation of spirovinylcyclopropane **16** with *p*-TsOH·H_2O

Entry	*p*-TsOH (mol equiv.)	Time (*t*/h)	Products (% yield) **17**	**18**	**19**
1	0.1	2	51	36	5
2	0.1	5	24	52	12
3	1.0	2	10	41	20
4	1.0	9	trace	25	33
5	1.0	18	trace	4	48

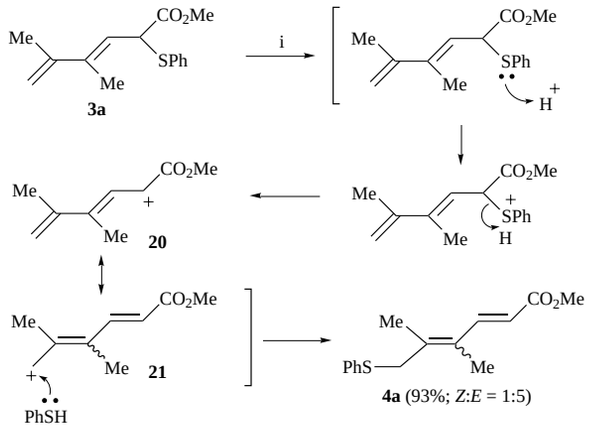
p-TsOH·H_2O, the yield of compound **19** increased with a decrease in the yield of compound **18** (entries 3–5). These results suggest that compound **17** is first formed by the concerted process with H^b abstraction, and that it then isomerises to compound **18** under acidic conditions, which is prevented from undergoing a 1,5-sulfenyl shift; subsequent isomerisation to the most stable diene **19** ensues.

To determine whether the rearranged dienes **4** were formed by an intermolecular or intramolecular 1,5-sulfenyl shift, we carried out the cross-over reaction of vinylcyclopropanes **1a** (131 mg, 0.5 mmol) and **1h** (132 mg, 0.5 mmol) with a catalytic amount of *p*-TsOH·H_2O (0.1 mmol) in 5 ml of benzene under reflux (Scheme 7). After the product was purified by preparative



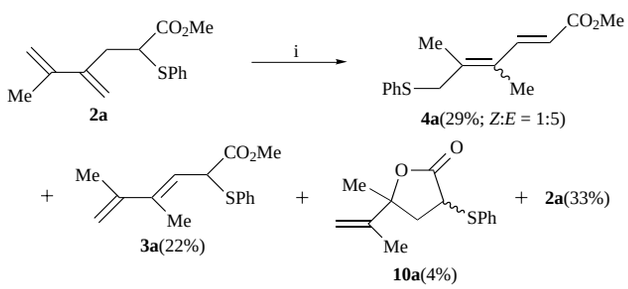
Scheme 7 *Reagents and conditions:* i, 0.1 mol equiv. of *p*-TsOH·H_2O, benzene, reflux, 20 h

TLC (PLC) on silica gel, an inseparable mixture (69 mg) of cross-coupled product **4d** and normally rearranged diene **4a**, and then (40 mg) of another cross-coupled diene **4g** and non-cross-coupled diene **4h** were isolated as the second and third fractions, respectively. Ring-opened dienes **2a**,**h** and **3a** were obtained as an inseparable mixture (92 mg) in the first fraction. All the structures of the products were identified in comparison with the ^{1}H NMR spectra of authentic samples, obtained from the reactions shown in Scheme 3. This experiment showed that the 1,5-sulfenyl shift proceeded intermolecularly. We also carried out the reaction of diene **3a** including a trace amount of isomer **2a** (obtained from the reaction of compound **1a** with CF_3SO_3H, Table 1, entry 6) with 0.1 mol equiv. of *p*-TsOH·H_2O to give the conjugated diene **4a** in 93% yield (Scheme 8). From these results, a plausible reaction mechanism for the 1,5-sulfenyl shift is assumed as shown in Scheme 8. Protonation on the sulfur atom of penta-2,4-dienyl sulfide **3a**, followed by elimination of thiophenol, gives a cationic intermediate **20**. Thiophenol then reacts with the cationic intermediate **21** at C–6 to provide compound **4a** as a mixture of geometrical isomers. The mechanism was supported by the results of a study into the substituent effects of arylthio groups (see entries 1–4 in Table 2) and by the additive effect of *m*-MeC_6H_4SH (entry 10 in Table 2).



Scheme 8 *Reagents and conditons:* i, 0.1 mol equiv. of *p*-TsOH·H_2O, benzene, reflux, 8 h

Treatment of the diene **2a** with 0.1 mol equiv. of *p*-TsOH·H_2O in benzene under reflux for 20 h afforded the rearranged diene **4a** in 29% yield together with 22% of isomerised diene **3a**, 4% of γ-lactone **10a** and 33% recovery of starting material (Scheme 9). From this result, the overall reaction



Scheme 9 *Reagents and conditions:* i, 0.1 mol equiv. of *p*-TsOH·H_2O, benzene, reflux, 20 h

pathway for acid-promoted isomerisation of 1-acceptor-1-sulfenyl-substituted 2-vinylcyclopropanes is proposed as follows. The diene **2a** is formed by C^1–C^2 bond fission and abstraction of a C^2-methyl proton followed by subsequent isomerisation to compound **3a** in acidic conditions. The 1,5-sulfenyl rearrangement then takes place to give 6-sulfenyl-α,β;γ,δ-unsaturated carboxylic ester **4a**. γ-Lactone **10a** would be formed by direct lactonisation of compound **1a** and by intramolecular 5-*exo-trig* lactonisation of diene **2a** *via* the corresponding carboxylic acids generated by hydrolysis with *p*-TsOH·H_2O. 5-*Endo-trig* lactonisation of compound **3a** is disfavoured according to Baldwin's rules,[9] and in fact the reaction of compound **3a** with *p*-TsOH·H_2O produced no γ-lactone (see Scheme 8).

In conclusion, treatment of 1-acceptor-1-sulfenyl-substituted 2-vinylcyclopropanes with an acid afforded 6-sulfenyl-α,β;γ,δ-unsaturated carboxylic esters and nitriles. Efficient C^1–C^2 bond fission and 1,5-sulfenyl shift occurred when a sulfonic acid such as *p*-TsOH·H_2O was used in a non-polar solvent. C^1–C^2 bond cleavage would proceed *via* a concerted process with abstraction of a C^2-methyl proton by protonation at the carboxy group with the aid of the sulfur atom. The 1,5-sulfenyl shift occurred intermolecularly and was accelerated by addition of a catalytic amount of thiol.

Experimental

Mps were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. IR Spectra of solids (KBr) and liquids (NaCl) were recorded on a JASCO IRA-100 spectrophotometer. ^{1}H NMR Spectra were obtained on a Hitachi

R-20B (60 MHz) or a JEOL GX-270 (270 MHz) or a JEOL EX-400 (400 MHz) spectrometer with tetramethylsilane as internal standard. ^{13}C NMR Spectra and NOE spectra were run on a JEOL EX-400 spectrometer. *J* Values are given in Hz. Mass spectra (EI) were measured on a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. Elemental analyses of new compounds were performed by a Yanaco CHN CORDER MT-5. All chromatographic isolations were accomplished either by Kieselgel 60 (70–230 mesh) for column chromatography or Kieselgel 60 PF_{254} containing gypsum for PLC.

Synthesis of 1-acceptor-1-sulfenyl-substituted 2-vinylcyclopropanes 1 and 12

General procedure. To a stirred solution of sulfide **6** (10 mmol) in CCl_4 (20 cm^3) was added NCS (1.335 g, 10 mmol) in portions at room temperature. After 2 h, the precipitate of succinimide was filtered off and the filtrate was evaporated under reduced pressure. $SnCl_4$ (1.35 cm^3, 11.5 mmol) was added to a solution of the resultant α-chloro sulfide in CH_2Cl_2 (30 cm^3) in the presence of a diene (12 mmol) at −20 °C under nitrogen. After 45 min, Et_3N (7.0 cm^3, 50 mmol) was added to the reaction mixture at −20 °C which was stirred for 30 min at room temperature. Et_2O (30 cm^3) was added and the precipitate was filtered through Celite. The filtrate was concentrated under reduced pressure (if needed, filtration was carried out two or three times) and the residue was purified by column chromatography on silica gel and eluted with hexane–EtOAc (20:1 ⟶ 5:1 v/v) to give a 1-acceptor-1-sulfenyl-substituted 2-vinylcyclopropane **1**.

Methyl 2-isopropenyl-2-methyl-1-(phenylthio)cyclopropane-1-carboxylate 1a

76%, *Oil* (Found: C, 68.45; H, 7.05. $C_{15}H_{18}O_2S$ requires C, 68.67; H, 6.92%); ν_{max}(NaCl)/cm^{-1} 3090 (cyclopropane), 1720 (C=O), 1645, 985 and 900 (vinyl) and 1250 (C–O); δ_H(400 MHz; $CDCl_3$) 1.30 (3 H, s, 2-Me), 1.45 and 2.01 (each 1 H, d, J_{AB} 5.4, 3-H), 1.88 (3 H, s, vinylic Me), 3.73 (3 H, s, OMe), 4.85 and 4.98 (each 1 H, s, C=CH_2) and 7.23–7.28 (5 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 19.7 (q), 21.1 (q), 28.7 (t), 37.4 (s), 39.6 (s), 52.8 (q), 114.2 (t), 125.7 (d), 127.7 (d), 128.8 (d), 128.9 (s), 145.1 (s) and 171.9 (s); *m*/*z* 262 (26%, M$^+$), 153 (17, M$^+$ − PhS) and 43 (100).

Methyl 2-isopropenyl-2-methyl-1-(4-methylphenylthio)cyclopropane-1-carboxylate 1b

78%, *Oil* (Found: C, 69.4; H, 7.4. $C_{16}H_{20}O_2S$ requires C, 69.53; H, 7.29%); ν_{max}(NaCl)/cm^{-1} 3090 (cyclopropane), 1720 (C=O), 1640, 985 and 900 (vinyl) and 1250 (C–O); δ_H(400 MHz; $CDCl_3$) 1.28 (3 H, s, 2-Me), 1.42 and 1.93 (each 1 H, d, J_{AB} 5, 3-H), 1.87 (3 H, s, vinylic Me), 2.29 (3 H, s, ArMe), 3.73 (3 H, s, OMe), 4.85 and 4.97 (each 1 H, s, C=CH_2), 7.06 and 7.18 (each 2 H, d, *J* 8, ArH); δ_C(400 MHz; $CDCl_3$) 20.1 (q), 21.2 (q), 21.4 (q), 28.8 (t), 38.4 (s), 39.8 (s), 53.0 (q), 114.4 (t), 129.0 (d), 129.9 (d), 133.1 (s), 136.3 (s), 145.4 (s) and 172 (s); *m*/*z* 276 (24%, M$^+$), 153 (54, M$^+$ − MeC_6H_4S) and 93 (100).

Methyl 2-isopropenyl-2-methyl-1-(3-methylphenylthio)cyclopropane-1-carboxylate 1c

62%, Light yellow *oil* (Found: C, 69.4; H, 7.4%); ν_{max}(NaCl)/cm^{-1} 3090 (cyclopropane), 1720 (C=O), 1640, 985 and 900 (vinyl) and 1250 (C–O); δ_H(400 MHz; $CDCl_3$) 1.29 (3 H, s, 2-Me), 1.45 and 2.01 (each 1 H, d, J_{AB} 5.4, 3-H), 1.87 (3 H, s, vinylic Me), 2.29 (3 H, s, ArMe), 3.73 (3 H, s, OMe), 4.85 and 4.97 (each 1 H, s, C=CH_2), 6.94 (1 H, d, *J* 7, ArH), 7.07 (1 H, s, ArH), 7.08 (1 H, d, *J* 7, ArH) and 7.14 (1 H, t, *J* 7, ArH); δ_C(400 MHz; $CDCl_3$) 19.6 (q), 21.0 (q), 21.4 (q), 28.7 (t), 37.3 (s), 39.5 (s), 52.8 (q), 114.1 (t), 124.5 (d), 126.6 (d), 128.2 (d), 128.7 (d), 136.5 (s), 138.6 (s), 145.0 (s) and 171.9 (s); *m*/*z* 276 (22%, M$^+$), 153 (76, M$^+$ − MeC_6H_4S) and 93 (100).

Methyl 1-(4-chlorophenylthio)-2-isopropenyl-2-methylcyclopropane-1-carboxylate 1d

59%, Yellow *oil* (Found: C, 60.4; H, 5.8. $C_{15}H_{17}ClO_2S$ requires C, 60.70; H, 5.77%); ν_{max}(NaCl)/cm^{-1} 3090 (cyclopropane), 1725 (C=O), 1645, 995 and 905 (vinyl) and 1255 (C–O); δ_H(400 MHz; $CDCl_3$) 1.30 (3 H, s, 2-Me), 1.43 and 2.01 (each 1 H, d, J_{AB} 5.4, 3-H), 1.87 (3 H, s, vinylic Me), 3.73 (3 H, s, OMe), 4.85 and 4.98 (each 1 H, s, C=CH_2) and 7.20 (4 H, br s, ArH); δ_C(400 MHz; $CDCl_3$) 19.6 (q), 21.0 (q), 28.6 (t), 37.4 (s), 39.6 (s), 52.9 (q), 114.3 (t), 128.8 (d), 129.0 (d), 131.6 (s), 135.3 (s), 144.8 (s) and 171.5 (s); *m*/*z* 296 (10%, M$^+$), 153 (48, M$^+$ − ClC_6H_4S), 93 (79) and 43 (100).

Methyl 2-methyl-1-(phenylthio)-2-vinylcyclopropane-1-carboxylate 1e

75%, Light yellow *oil* (Found: C, 67.7; H, 6.6. $C_{14}H_{16}O_2S$ requires C, 67.70; H, 6.49%); ν_{max}(NaCl)/cm^{-1} 3100 (cyclopropane), 1725 (C=O), 1635, 995 and 915 (vinyl) and 1235 (C–O); δ_H(400 MHz; $CDCl_3$) 1.33 (3 H, s, 2-Me), 1.36 and 2.06 (each 1 H, d, J_{AB} 5, 3-H), 3.65 (3 H, s, OMe), 5.18 (1 H, d, J_{cis} 11, CH=C*H*$_2$), 5.19 (1 H, d, J_{trans} 17, CH=C*H*$_2$), 6.01 (1 H, dd, *J* 10 and 17, C*H*=CH_2), 7.11 (1 H, t, *J* 7, ArH) and 7.21–7.29 (4 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 17.2 (q), 28.8 (t), 33.6 (s), 38.6 (s), 52.5 (q), 115.8 (t), 125.5 (d), 127.4 (d), 128.6 (d), 136.1 (s), 139.4 (s) and 171.0 (s); *m*/*z* 248 (4%, M$^+$) and 43 (100).

Methyl 2-isopropenyl-2-methyl-1-(methylthio)cyclopropane-1-carboxylate 1f

62%, Oil, bp 90–100 °C/6 mmHg (Kugelrohr) (lit.,[3b] 65–66 °C/1 mmHg).

2-Isopropenyl-2-methyl-1-(phenylthio)cyclopropane-1-carbonitrile 1g

45%, Yellow *oil* (Found: C, 73.1; H, 6.7; N, 6.0. $C_{14}H_{15}NS$ requires C, 73.32; H, 6.59; N, 6.11%); ν_{max}(NaCl)/cm^{-1} 3090 (cyclopropane), 2225 (CN) and 1640, 1000 and 905 (vinyl); δ_H(270 MHz; $CDCl_3$) 1.54 (3 H, s, 2-Me), 1.59 and 1.62 (each 1 H, d, J_{AB} 5.9, 3-H), 1.82 (3 H, s, vinylic Me), 4.87 and 5.03 (each 1 H, s, C=CH_2), 7.28–7.37 (3 H, m, ArH) and 7.47 (2 H, dd, *J* 2 and 8, ArH); δ_C(400 MHz; $CDCl_3$) 20.9 (q), 22.2 (q), 23.7 (s), 31.0 (t), 39.8 (s), 115.6 (t), 120.5 (s), 127.7 (d), 129.1 (d), 130.6 (d), 133.5 (s) and 142.6 (s); *m*/*z* 229 (20%, M$^+$), 120 (73, M$^+$ − PhS) and 110 (100).

1-(4-Chlorophenylthio)-2-isopropenyl-2-methylcyclopropane-1-carbonitrile 1h

45%, Yellow *oil* (Found: C, 63.5; H, 5.3; N, 5.1. $C_{14}H_{14}ClNS$ requires C, 63.75; H, 5.35; N, 5.31%); ν_{max}(NaCl)/cm^{-1} 3100 (cyclopropane), 2240 (CN) and 1650, 960 and 915 (vinyl); δ_H(400 MHz; $CDCl_3$) 1.55 (3 H, s, 2-Me), 1.59 and 1.63 (each 1 H, d, J_{AB} 5.9, 3-H), 1.83 (3 H, s, vinylic Me), 4.89 and 5.04 (each 1 H, s, C=CH_2) and 7.33 and 7.42 (each 2 H, d, *J* 8, ArH); δ_C(400 MHz; $CDCl_3$) 21.1 (q), 22.3 (q), 24.0 (s), 31.1 (t), 40.1 (s), 115.8 (t), 120.4 (s), 129.5 (d), 132.0 (s), 132.2 (d), 134.2 (s) and 142.5 (s); *m*/*z* 263 (14%, M$^+$), 120 (43, M$^+$ − ClC_6H_4S) and 139 (100).

2-Methyl-1-(phenylthio)-2-vinylcyclopropane-1-carbonitrile 1i

32%, Yellow *oil* (Found: M$^+$, 215.0775. $C_{13}H_{13}NS$ requires *M*, 215.0769); ν_{max}(NaCl)/cm^{-1} 3090 (cyclopropane), 2240 (CN) and 1640, 995 and 925 (vinyl); δ_H(400 MHz; $CDCl_3$) 1.53 and 1.71 (each 1 H, d, J_{AB} 5.9, 3-H), 1.59 (3 H, s, 2-Me), 5.27 (1 H, d, J_{cis} 11, CH=C*H*$_2$), 5.28 (1 H, d, J_{trans} 17, CH=C*H*$_2$), 5.91 (1 H, dd, *J* 10 and 17, C*H*=CH_2) and 7.27–7.41 (5 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 20.1 (q), 25.0 (s), 29.9 (t), 33.9 (s), 117.7 (t), 119.9 (s), 127.5 (d), 129.2 (d), 129.5 (d), 133.1 (s) and 136.8 (s); *m*/*z* 215 (13%, M$^+$), 106 (19, M$^+$ − PhS) and 110 (100).

Methyl 2-(4-chlorophenyl)-2-[1-(4-chlorophenyl)vinyl]-1-(phenylthio)cyclopropane-1-carboxylate 12

72%, *Needles* (from CH_2Cl_2–hexane), mp 77–78 °C (Found: C, 65.7; H, 4.5. $C_{25}H_{20}Cl_2O_2S$ requires C, 65.94; H, 4.43%); ν_{max} (KBr)/cm^{-1} 3070 (cyclopropane), 1730 (C=O) and 1260 (C–O); δ_H(400 MHz; $CDCl_3$) 1.76 and 2.69 (each 1 H, d, J_{AB} 5, 3-H), 3.44 (3 H, s, OMe), 5.55 and 5.58 (each 1 H, s, C=CH_2) and 7.14–7.39 (13 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 27.6 (t), 41.0 (s), 46.1 (s), 52.8 (q), 118.5 (t), 126.5 (d), 128.2 (d), 128.3 (d), 128.8 (d), 128.9 (d), 129.0 (d), 130.4 (d), 133.2 (s), 133.7 (s), 135.5 (s), 137.7 (s), 137.8 (s), 146.0 (s) and 170.1 (s); *m*/*z* 454 (2%, M$^+$), 363 (79), 139 (100) and 123 (86).

Acid-promoted isomerisation of vinylcyclopropyl sulfides 1, 12 and 16

General procedure. A mixture of vinylcyclopropyl sulfide (1 mmol) and *p*-TsOH·H_2O (19 mg, 0.1 mmol) in an appropriate solvent (5 cm^3) was heated to reflux under nitrogen for an appropriate time. The cooled reaction mixture was poured into saturated aq. $NaHCO_3$ (10 cm^3) and the organic layer was separated. The water layer was extracted twice with EtOAc (10 cm^3). The organic layer and the extracts were combined, washed with water (15 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was separated by PLC on silica gel with hexane–EtOAc (10:1 ⟶ 5:1 v/v). Reaction conditions, products and their yields are summarised in Tables 1–3 and Scheme 5.

2(*E*,4*E*)- and (2*E*,4*Z*)-Methyl 4,5-dimethyl-6-(phenylthio)hexa-2,4-dienoate 4a

Yellow *oil* as a mixture of geometrical isomers (Found: C, 68.7; H, 7.1. $C_{15}H_{18}O_2S$ requires C, 68.67; H, 6.92%); ν_{max}(NaCl)/cm^{-1} 1710 (C=O), 1165 and 1285 (C–O); δ_H(400 MHz; $CDCl_3$) (4*E*)-isomer$_{major}$: 1.57 (3 H, s, 4-Me), 2.06 (3 H, s, 5-Me), 3.66 (2 H, s, 6-H), 3.75 (3 H, s, OMe), 5.80 (1 H, d, J_{trans} 15, 2-H), 7.23–7.39 (5 H, m, ArH) and 7.89 (1 H, d, J_{trans} 15, 3-H); (4*Z*)-isomer$_{minor}$: 1.76 (3 H, s, 4-Me), 2.00 (3 H, s, 5-Me), 3.72 (2 H, s, 6-H), 3.75 (3 H, s, OMe), 5.71 (1 H, d, J_{trans} 15, 2-H), 7.23–7.39 (5 H, m, ArH) and 7.47 (1 H, d, J_{trans} 15, 3-H); δ_C(400 MHz, $CDCl_3$) (4*E*)-isomer$_{major}$: 13.8 (q), 18.6 (q), 40.7 (t), 51.5 (q), 117.3 (d), 127.2 (d), 128.8 (d), 129.3 (s), 131.9 (d), 135.4 (s), 139.0 (s), 143.1 (d) and 168.0 (s); (4*Z*)-isomer$_{minor}$: 14.4 (q), 20.2 (q), 39.1 (t), 51.3 (q), 116.5 (d), 127.1 (d), 128.7 (d), 129.6 (s), 132.1 (d), 135.2 (s), 138.5 (s), 141.9 (d) and 167.9 (s); *m*/*z* 262 (12%, M$^+$), 139 (58) and 93 (100).

Methyl 5-methyl-4-methylene-2-(phenylthio)hex-5-enoate 2a and (3*E*)-methyl 4,5-dimethyl-2-(phenylthio)hexa-3,5-dienoate 3a

Yellow *oil* as a mixture of regioisomers (Found: C, 68.8; H, 7.1. $C_{15}H_{18}O_2S$ requires C, 68.67; H, 6.92%); ν_{max}(NaCl)/cm^{-1} 1740 (C=O), 1155 (C–O), 995 and 900 (vinyl); δ_H(400 MHz; $CDCl_3$) **2a**$_{major}$: 1.88 (3 H, s, 5-Me), 2.75 (1 H, dd, *J* 5 and 14, 3-H), 2.89 (1 H, dd, *J* 9 and 14, 3-H), 3.62 (3 H, s, OMe), 3.89 (1 H, dd, *J* 5 and 9, 2-H), 4.99 (2 H, s, olefinic H), 5.03 and 5.16 (each 1 H, s, olefinic H), 7.28–7.32 (3 H, m, ArH) and 7.44–7.47 (2 H, m, ArH); **3a**$_{minor}$: 1.74 (3 H, s, 4-Me), 1.88 (3 H, s, 5-Me), 3.66 (3 H, s, OMe), 4.62 (1 H, d, *J* 10, 2-H), 4.99 and 5.07 (each 1 H, s, 6-H), 5.71 (1 H, d, *J* 10, 3-H), 7.28–7.32 (3 H, m, ArH) and 7.44–7.47 (2 H, m, ArH); δ_C(400 MHz; $CDCl_3$) **2a**$_{major}$: 21.0 (q), 36.2 (t), 49.9 (d), 52.0(d), 113.0 (t), 115.1 (t), 128.0 (d), 128.9 (d), 133.1 (d), 133.2 (s), 141.7 (s), 143.6 (s) and 172.2 (s); **3a**$_{minor}$: 14.1 (q), 20.7 (q), 50.1 (d), 52.5 (q), 114.1 (t), 120.2 (d), 129.0 (d), 129.4 (d), 130.7 (d), 135.9 (s), 139.9 (s), 143.5 (s) and 170.9 (s); *m*/*z* 262 (62%, M$^+$), 93 (72) and 43 (100).

4-Isopropenyl-4-methyl-2-phenylthio-γ-butyrolactone 10a

Oil as a 1:1 mixture of diastereoisomers (Found: C, 67.55; H, 6.6. $C_{14}H_{16}O_2S$ requires C, 67.70; H, 6.49%); ν_{max}(NaCl)/cm^{-1} 1765 (C=O) and 1230 (C–O); δ_H(400 MHz; $CDCl_3$) 1.44 and 1.48 (each 3 H, s, 4-Me × 2), 1.66 and 1.76 (each 3 H, s, vinylic Me × 2), 2.01 (1 H, dd, *J* 10 and 13, 3-H), 2.26 (1 H, dd, *J* 9 and 13, 3-H), 2.52 (1 H, dd, *J* 9 and 13, 3-H), 2.72 (1 H, dd, *J* 9 and 13, 3-H), 3.92 (1 H, dd, *J* 9 and 10, 2-H), 4.04 (1 H, t, *J* 9, 2-H), 4.83, 4.87, 4.98 and 5.01 (each 1 H, s, C=CH_2 × 2), 7.29–7.35 (total 6 H, m, ArH) and 7.51–7.55 (total 4 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 18.1 and 18.7 (q), 25.6 and 26.2 (q), 39.6 and 40.2 (t), 45.7 and 45.9 (d), 83.5 and 85.4 (s), 111.0 and 111.1 (t), 128.2 and 128.4 (d), 128.8 and 129.1 (d), 129.2 and 132.3 (s), 132.4 and 133.0 (d), 145.1 and 146.0 (s) and 174.0 and 174.3 (s); *m*/*z* 248 (74%, M$^+$) and 95 (100).

(2*E*,4*E*)- and (2*E*,4*Z*)-Methyl 4,5-dimethyl-6-(4-methylphenylthio)hexa-2,4-dienoate 4b

Yellow *oil* as a mixture of geometrical isomers (Found: C, 69.7; H, 7.4. $C_{16}H_{20}O_2S$ requires C, 69.53; H, 7.29%); ν_{max}(NaCl)/cm^{-1} 1715 (C=O), 1165 and 1285 (C–O); δ_H(270 MHz; $CDCl_3$) (4*E*)-isomer$_{major}$: 1.53 (3 H, s, 4-Me), 2.05 (3 H, s, 5-Me), 2.31 (3 H, s, ArMe), 3.60 (2 H, s, 6-H), 3.75 (3 H, s, OMe), 5.79 (1 H, d, J_{trans} 16, 2-H), 7.05 and 7.27 (each 2 H, d, *J* 8, ArH) and 7.79 (1 H, d, J_{trans} 16, 3-H); (4*Z*)-isomer$_{minor}$: 1.74 (3 H, s, 4-Me), 1.98 (3 H, s, 5-Me), 2.28 (3 H, s, ArMe), 3.68 (2 H, s, 6-H_2), 3.71 (3 H, s, OMe), 5.65 (1 H, d, J_{trans} 15, 2-H), 7.03 and 7.24 (each 2 H, d, *J* 8, ArH) and 7.36 (1 H, d, J_{trans} 15, 3-H); δ_C(400 MHz; $CDCl_3$) (4*E*)-isomer$_{major}$: 13.8 (q), 18.7 (q), 21.1 (q), 41.3 (t), 51.5 (q), 117.2 (d), 129.1 (s), 129.6 (d), 129.9 (s), 132.7 (d), 137.5 (s), 139.5 (s), 142.0 (d) and 167.9 (s); (4*Z*)-isomer$_{minor}$: 14.4 (q), 20.2 (q), 21.0 (q), 39.8 (t), 51.3 (q), 116.2 (d), 129.7 (s), 129.5 (d), 131.6 (s), 133.1 (d), 137.6 (s), 138.8 (s), 143.3 (d) and 168.1 (s); *m*/*z* 276 (25%, M$^+$) and 93 (100).

Methyl 5-methyl-4-methylene-2-(4-methylphenylthio)hex-5-enoate 2b

Yellow *oil* (Found: C, 69.7; H, 7.4%); ν_{max}(NaCl)/cm^{-1} 1735 (C=O), 1155 (C–O), 995 and 900 (vinyl); δ_H(270 MHz; $CDCl_3$) 1.87 (3 H, s, 5-Me), 2.33 (3 H, s, ArH), 2.73 (1 H, dd, *J* 5 and 14, 3-H), 2.85 (1 H, dd, *J* 9 and 14, 3-H), 3.62 (3 H, s, OMe), 3.82 (1 H, dd, *J* 5 and 9, 2-H), 4.99 (2 H, s, olefinic H), 5.02 and 5.15 (each 1 H, s, olefinic H) and 7.11 and 7.35 (each 2 H, d, *J* 8, ArH); δ_C(400 MHz; $CDCl_3$) 21.0 (q), 21.1 (q), 36.2 (t), 50.2 (d), 52.0 (q), 113.0 (t), 115.0 (t), 129.2 (s), 129.7 (d), 133.8 (d), 138.4 (s), 141.7 (s), 143.8 (s) and 172.2 (s); *m*/*z* 276 (68%, M$^+$) and 190 (100).

4-Isopropenyl-4-methyl-2-(4-methylphenylthio)-γ-butyrolactone 10b

Light yellow *oil* as a 1:1 mixture of diastereoisomers (Found: C, 68.6; H, 7.0. $C_{15}H_{18}O_2S$ requires C, 68.67; H, 6.92%); ν_{max} (NaCl)/cm^{-1} 1765 (C=O) and 1230 (C–O); δ_H(400 MHz; $CDCl_3$) 1.43 and 1.48 (each 3 H, s, 4-Me × 2), 1.59 and 1.66 (each 3 H, s, vinylic Me × 2), 2.06 (1 H, dd, *J* 10 and 13, 3-H), 2.27 (1 H, dd, *J* 9 and 13, 3-H), 2.34 (total 6 H, s, ArMe × 2), 2.49 (1 H, dd, *J* 9 and 13, 3-H), 2.74 (1 H, dd, *J* 9 and 13, 3-H), 3.90 (1 H, dd, *J* 9 and 10, 2-H), 3.97 (1 H, t, *J* 9, 2-H), 4.83, 4.92, 4.98 and 5.03 (each 1 H, s, C=CH_2 × 2) and 7.14 and 7.44 (each total 4 H, d, *J* 8, ArH); δ_C(400 MHz; $CDCl_3$) 18.2 and 18.8 (q), 21.2 and 21.1 (q), 25.8 and 26.3 (q), 39.7 and 40.3 (t), 46.1 and 46.4 (d), 85.3 and 85.4 (s), 111.1 and 111.1 (t), 128.4 and 128.6 (s), 129.9 and 130.0 (d), 133.8 and 133.9 (d), 138.8 and 138.9 (s), 145.3 and 146.1 (s) and 174.2 and 174.5 (s); *m*/*z* 262 (52%, M$^+$) and 95 (100).

(2*E*,4*E*)- and (2*E*,4*Z*)-Methyl 4,5-dimethyl-6-(3-methylphenylthio)hexa-2,4-dienoate 4c

Yellow *oil* as a mixture of geometrical isomers (Found: C, 69.8; H, 7.5. $C_{16}H_{20}O_2S$ requires C, 69.53; H, 7.29%); ν_{max}(NaCl)/cm^{-1} 1715 (C=O), 1165 and 1285 (C–O); δ_H(400 MHz; $CDCl_3$) (4*E*)-isomer$_{major}$: 1.60 (3 H, s, 4-Me), 2.06 (3 H, s, 5-Me), 2.29 (3 H, s, ArMe), 3.64 (2 H, s, 6-H), 3.74 (3 H, s, OMe), 5.81 (1 H, d, J_{trans} 16, 2-H), 7.01–7.26 (4 H, m, ArH) and 7.80 (1 H, d, J_{trans} 16, 3-H); (4*Z*)-isomer$_{minor}$: 1.75 (3 H, s, 4-Me), 1.99 (3 H, s,

5-Me), 2.27 (3 H, s, ArMe), 3.71 (2 H, s, 6-H_2), 3.74 (3 H, s, OMe), 5.76 (1 H, d, J_{trans} 15, 2-H), 7.01–7.26 (4 H, m, ArH) and 7.49 (1 H, d, J_{trans} 15, 3-H); δ_C(400 MHz; $CDCl_3$) (4*E*)-isomer$_{major}$: 14.1 (q), 18.9 (q), 21.5 (q), 40.8 (t), 51.7 (q), 117.6 (d), 128.2 (d), 128.8 (d), 128.9 (d), 129.0 (s), 129.8 (s), 132.5 (d), 138.8 (s), 138.9 (s), 143.4 (d) and 168.3 (s); (4*Z*)-isomer$_{minor}$: 14.7 (q), 20.4 (q), 21.3 (q), 39.2 (t), 51.6 (q), 116.6 (d), 128.2 (d), 129.4 (d), 129.5 (d), 129.9 (s), 133.0 (d), 135.2 (s), 135.6 (s), 138.9 (s), 142.2 (d) and 168.1 (s); *m*/*z* 276 (22%, M^+), 139 (79) and 93 (100).

Methyl 5-methyl-4-methylene-2-(3-methylphenylthio)hex-5-enoate 2c

Yellow *oil* (Found: C, 69.7; H, 7.5%) ν_{max}(NaCl)/cm^{-1} 1735 (C=O), 1155 (C–O) and 995 and 900 (vinyl); δ_H(270 MHz; $CDCl_3$) 1.87 (3 H, s, 5-Me), 2.32 (3 H, s, ArH), 2.74 (1 H, dd, *J* 5 and 14, 3-H), 2.88 (1 H, dd, *J* 9 and 14, 3-H), 3.62 (3 H, s, OMe), 3.89 (1 H, dd, *J* 5 and 9, 2-H), 4.99 (2 H, s, olefinic H), 5.03 and 5.15 (each 1 H, s, olefinic H) and 7.03–7.34 (4 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 21.0 (q), 21.1 (q), 36.3 (t), 49.9 (d), 52.0 (q), 113.0 (t), 115.1 (t), 128.7 (d), 128.8 (d), 129.9 (d), 132.9 (s), 133.5 (d), 138.6 (s), 141.7 (s), 143.6 (s) and 172.3 (s); *m*/*z* 276 (74%, M^+), 175 (92) and 190 (100).

4-Isopropenyl-4-methyl-2-(3-methylphenylthio)-γ-butyrolactone 10c

Light yellow *oil* as a 1:1 mixture of diastereoisomers (Found: C, 68.7; H, 7.1. $C_{15}H_{18}O_2S$ require C, 68.67; H, 6.92%); ν_{max} (NaCl)/cm^{-1} 1765 (C=O) and 1230 (C–O); δ_H(400 MHz; $CDCl_3$) 1.45 and 1.48 (each 3 H, s, 4-Me × 2), 1.67 and 1.77 (each 3 H, s, vinylic Me × 2), 2.02 (1 H, dd, *J* 9 and 13, 3-H), 2.28 (1 H, dd, *J* 9 and 13, 3-H), 2.33 and 2.34 (each 3 H, s, ArMe × 2), 2.52 (1 H, dd, *J* 9 and 13, 3-H), 2.71 (1 H, dd, *J* 9 and 13, 3-H), 3.90 (1 H, t, *J* 9, 2-H), 4.04 (1 H, t, *J* 9, 2-H), 4.83, 4.87, 5.00 and 5.02 (each 1 H, s, C=CH_2 × 2) and 7.12–7.34 (total 8 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 18.1 and 18.7 (q), 21.1 and 21.1 (q), 25.6 and 26.2 (q), 39.6 and 40.2 (t), 45.8 and 45.9 (d), 85.3 and 85.4 (s), 111.0 and 111.0 (t), 128.9 and 129.0 (d), 129.0 and 129.1 (d), 129.9 and 129.9 (d), 132.0 and 132.2 (s), 133.4 and 133.5 (d), 138.9 and 138.9 (s), 145.1 and 146.0 (s) and 174.2 and 174.4 (s); *m*/*z* 262 (57%, M^+), 95 (100).

(2*E*,4*E*)- and (2*E*,4*Z*)-Methyl 6-(4-chlorophenylthio)-4,5-dimethylhexa-2,4-dienoate 4d

Yellow *oil* as a mixture of geometrical isomers (Found: C, 60.7; H, 5.8. $C_{15}H_{17}ClO_2S$ requires C, 60.70; H, 5.77%); ν_{max}(NaCl)/cm^{-1} 1710 (C=O), 1165 and 1280 (C–O); δ_H(400 MHz; $CDCl_3$) (4*E*)-isomer$_{major}$: 1.58 (3 H, s, 4-Me), 2.06 (3 H, s, 5-Me), 3.63 (2 H, s, 6-H_2), 3.76 (3 H, s, OMe), 5.82 (1 H, d, J_{trans} 15, 2-H), 7.23 and 7.29 (each 2 H, d, *J* 8, ArH) and 7.78 (1 H, d, J_{trans} 15, 3-H); (4*Z*)-isomer$_{minor}$: 1.76 (3 H, s, 4-Me), 1.99 (3 H, s, 5-Me), 3.70 (2 H, s, 6-H), 3.73 (3 H, s, OMe), 5.70 (1 H, d, J_{trans} 15, 2-H), 7.19 and 7.27 (each 2 H, d, *J* 8, ArH) and 7.35 (1 H, d, J_{trans} 15, 3-H); δ_C(400 MHz; $CDCl_3$) (4*E*)-isomer$_{major}$: 13.8 (q), 18.5 (q), 40.8 (t), 51.5 (q), 117.5 (d), 128.9 (d), 129.4 (s), 133.2 (d), 133.3 (s), 133.8 (s), 138.5 (s), 142.9 (d) and 167.9 (s); (4*Z*)-isomer$_{minor}$: 14.4 (q), 20.1 (q), 39.3 (t), 51.4 (q), 116.5 (d), 128.8 (d), 129.8 (s), 133.6 (s), 133.9 (d), 135.7 (s), 138.1 (s), 141.5 (d) and 167.7 (s); *m*/*z* 296 (9%, M^+), 93 (95) and 43 (100).

Methyl 2-(4-chlorophenylthio)-5-methyl-4-methylenehex-5-enoate 2d and (3*E*)-methyl 2-(chlorophenylthio)-4,5-dimethylhexa-3,5-dienoate 3d

Yellow *oil* as a mixture of regioisomers (Found: C, 60.6; H, 5.8%); ν_{max}(NaCl)/cm^{-1} 1735 (C=O), 1155 (C–O) and 900 (vinyl); δ_H(270 MHz; $CDCl_3$) **2d**$_{major}$: 1.88 (3 H, s, 5-Me), 2.73 (1 H, dd, *J* 6 and 14, 3-H), 2.86 (1 H, dd, *J* 9 and 14, 3-H), 3.63 (3 H, s, OMe), 3.85 (1 H, dd, *J* 6 and 9, 2-H), 5.00 (2 H, s, olefinic H), 5.02 and 5.17 (each 1 H, s, olefinic H) and 7.27 and 7.37 (each 2 H, d, *J* 8, ArH); **3d**$_{minor}$: 1.76 (3 H, s, 4-Me), 1.88 (3 H, s, 5-Me), 3.69 (3 H, s, OMe), 4.58 (1 H, d, *J* 10, 2-H), 5.02 and 5.09 (each 1 H, s, 6-H), 5.67 (1 H, d, *J* 10, 3-H) and 7.27 and 7.37 (each 2 H, d, *J* 8, ArH); δ_C(400 MHz; $CDCl_3$) **2d**$_{major}$: 21.0 (q), 36.1 (t), 49.9 (d), 52.1 (q), 113.1 (t), 115.4 (t), 129.1 (d), 131.6 (s), 134.4 (d), 135.0 (s), 141.6 (s), 143.4 (s) and 172.2 (s); **3d**$_{minor}$: 14.1 (q), 20.7 (q), 50.1 (d), 52.5 (q), 114.1 (t), 120.2 (d), 129.0 (d), 129.4 (s), 130.7 (s), 135.9 (s), 139.9 (s), 143.5 (s) and 170.9 (s); *m*/*z* 296 (15%, M^+) and 93 (100).

2-(4-Chlorophenylthio)-4-isopropenyl-4-methyl-γ-butyrolactone 10d

Yellow *oil* as a 1:1 mixture of diastereoisomers (Found: M^+, 282.0461. $C_{14}H_{15}ClO_2S$ requires *M*, 282.0481); ν_{max}(NaCl)/cm^{-1} 1765 (C=O) and 1235 (C–O); δ_H(400 MHz; $CDCl_3$) 1.48 and 1.49 (each 3 H, s, 4-Me × 2), 1.70 and 1.78 (each 3 H, s, vinylic Me × 2), 2.01 (1 H, dd, *J* 9 and 13, 3-H), 2.26 (1 H, dd, *J* 9 and 13, 3-H), 2.54 (1 H, dd, *J* 9 and 13, 3-H), 2.74 (1 H, dd, *J* 9 and 13, 3-H), 3.87 (1 H, t, *J* 9, 2-H), 3.99 (1 H, t, *J* 9, 2-H), 4.86, 4.89, 5.00 and 5.02 (each 1 H, s, C=CH_2 × 2) and 7.30 and 7.49 (each total 4 H, d, *J* 8, ArH); δ_C(400 MHz; $CDCl_3$) 18.3 and 18.8 (q), 25.8 and 26.3 (q), 39.6 and 40.2 (t), 45.8 and 46.1 (d), 85.6 and 91.1 (s), 111.2 and 111.3 (t), 128.7 and 129.2 (d), 129.3 and 130.0 (d), 130.8 and 131.0 (s), 134.6 and 134.7 (s), 145.0 and 145.9 (s) and 174.0 and 174.2 (s); *m*/*z* 282 (52%, M^+) and 95 (100).

(2*E*,4*E*)-Methyl 4-methyl-6-(phenylthio)hexa-2,4-dienoate 4e

Yellow *oil* (Found: C, 67.8; H, 6.7. $C_{14}H_{16}O_2S$ requires C, 67.71; H, 6.49%); ν_{max}(NaCl)/cm^{-1} 1720 (C=O), 1170 and 1270 (C–O); δ_H(400 MHz; $CDCl_3$) 1.62 (3 H, s, 4-Me), 3.64 (2 H, d, *J* 8, 6-H), 3.73 (3 H, s, OMe), 5.80 (1 H, d, J_{trans} 15, 2-H), 5.96 (1 H, t, *J* 8, 5-H), 7.21–7.36 (5 H, m, ArH) and 7.28 (1 H, d, J_{trans} 15, 3-H); δ_C(400 MHz; $CDCl_3$) 11.9 (q), 32.8 (t), 51.4 (q), 116.9 (d), 126.9 (d), 128.8 (d), 131.1 (d), 135.0 (s), 135.1 (s), 135.2 (d), 148.5 (d) and 167.5 (s); *m*/*z* 248 (49%, M^+) and 79 (100).

Methyl 4-methylene-2-(phenylthio)hex-5-enoate 2e and (3*E*)- and (3*Z*)-methyl 4-methyl-2-(phenylthio)hexa-3,5-dienoate 3e

Light yellow *oil* as a mixture of isomers (Found: C, 67.8; H, 6.7%); ν_{max}(NaCl)/cm^{-1} 1740 (C=O), 1155 (C–O) and 995 and 915 (vinyl); δ_H(270 MHz; $CDCl_3$) **2e**: 2.67 (1 H, dd, *J* 5 and 15, 3-H), 2.83 (1 H, dd, *J* 10 and 15, 3-H), 3.62 (3 H, s, OMe), 3.88 (1 H, dd, *J* 5 and 10, 2-H), 5.06 and 5.09 (each 1 H, s, 4-methylene), 5.07 (1 H, d, J_{cis} 10, 6-H), 5.15 (1 H, d, J_{trans} 17, 6-H), 6.53 (1 H, dd, *J* 10 and 17, 5-H), 7.25–7.30 (3 H, m, ArH) and 7.44–7.47 (2 H, m, ArH); (*E*)-**3e**: 1.65 (3 H, s, 4-Me), 3.66 (3 H, s, OMe), 4.61 (1 H, d, *J* 10, 2-H), 5.07 (1 H, d, J_{cis} 10, 6-H), 5.18 (1 H, d, J_{trans} 17, 6-H), 5.63 (1 H, d, *J* 10, 3-H), 6.33 (1 H, dd, *J* 10 and 17, 5-H), 7.25–7.30 (3 H, m, ArH) and 7.44–7.47 (2 H, m, ArH); (*Z*)-**3e**: 1.85 (3 H, s, 4-Me), 3.64 (3 H, s, OMe), 4.74 (1 H, d, *J* 10, 2-H), 5.16 (1 H, d, J_{cis} 10, 6-H), 5.29 (1 H, d, J_{trans} 17, 6-H), 5.53 (1 H, d, *J* 10, 3-H), 6.67 (1 H, dd, *J* 10 and 17, 5-H), 7.25–7.30 (3 H, m, ArH) and 7.44–7.47 (2 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 11.9 (q), 19.7 (q), 33.8 (t), 48.6 (d), 49.4 (d), 49.9 (d), 52.0 (q), 52.3 (q), 52.4 (q), 113.8 (t), 113.9 (t), 116.7 (t), 118.4 (t), 122.5 (d), 124.8 (d), 127.6 (d), 128.1 (d), 128.3 (d), 128.4 (s), 128.5 (d), 128.8 (d), 128.9 (d), 132.2 (d), 132.3 (s), 132.9 (s), 133.2 (d), 134.1 (d), 134.4 (d), 136.9 (s), 137.8 (d), 138.2 (s), 140.0 (d), 142.0 (s), 170.7 (s), 170.8 (s) and 172.1 (s); *m*/*z* 248 (48%, M^+) and 79 (100).

4-Methyl-2-phenylthio-4-vinyl-γ-butyrolactone 10e

Light yellow *oil* as a 1:1 mixture of diastereoisomers (Found: C, 66.85; H, 6.25. $C_{13}H_{14}O_2S$ requires C, 66.64; H, 6.02%); ν_{max} (NaCl)/cm^{-1} 1770 (C=O) and 1225 (C–O); δ_H(400 MHz; $CDCl_3$) 1.45 and 1.49 (each 3 H, s, 4–Me × 2), 2.08 (1 H, dd, *J* 11 and 13, 3-H), 2.25 (1 H, dd, *J* 9 and 13, 3-H), 2.55 (1 H, dd, *J* 9 and 13, 3-H), 2.61 (1 H, dd, *J* 9 and 13, 3-H), 3.95 (1 H, dd, *J* 9 and 11, 2-H), 4.03 (1 H, t, *J* 9, 2-H), 5.13 and 5.15 (each 1 H, d, J_{cis} 11, CH=CH_2 × 2), 5.26 and 5.29 (each 1 H, d, J_{trans} 17,

CH=CH_2 × 2), 5.84 and 5.89 (each 1 H, dd, *J* 11 and 17, C*H*=CH_2 × 2), 7.27–7.34 (total 6 H, m, ArH) and 7.53–7.56 (total 4 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 26.6 and 26.9 (q), 41.0 and 41.4 (t), 45.8 and 45.9 (d), 83.2 and 83.4 (s), 114.1 and 114.5 (t), 128.3 and 128.4 (d), 129.2 and 129.2 (d), 132.2 and 132.7 (s), 133.0 and 133.2 (d), 139.5 and 140.1 (d) and 174.4 and 174.4 (s); *m*/*z* 234 (33%, M^+) and 43 (100).

(2*E*,4*E*)- and (2*E*,4*Z*)-4,5-Dimethyl-6-(phenylthio)hexa-2,4-dienonitrile 4g

Yellow *oil* as a mixture of geometric isomers (Found: C, 73.2; H, 6.7; N, 6.05. $C_{14}H_{15}NS$ requires C, 73.32; H, 6.59; N, 6.11%); ν_{max}(NaCl)/cm^{-1} 2220 (CN); δ_H(270 MHz; $CDCl_3$) (4*E*)-isomer$_{major}$: 1.51 (3 H, s, 4-Me), 2.03 (3 H, s, 5-Me), 3.64 (2 H, s, 6-H_2), 5.20 (1 H, d, J_{trans} 16, 2-H), 7.26–7.39 (5 H, m, ArH) and 7.49 (1 H, d, J_{trans} 16, 3-H); (4*Z*)-isomer$_{minor}$: 1.71 (3 H, s, 4-Me), 2.02 (3 H, s, 5-Me), 3.64 (2 H, s, 6-H), 5.06 (1 H, d, J_{trans} 16, 2-H), 6.99 (1 H, d, J_{trans} 16, 3-H) and 7.26–7.39 (5 H, m, ArH); δ_C(400 MHz; $CDCl_3$) (4*E*)-isomer$_{major}$: 13.0 (q), 20.3 (q), 39.4 (t), 95.4 (d), 118.9 (s), 127.5 (d), 128.9 (d), 129.1 (s), 133.0 (d), 135.0 (s), 139.9 (s) and 148.7 (d); (4*Z*)-isomer$_{minor}$: 13.6 (q), 18.6 (q), 40.7 (t), 94.3 (d), 119.0 (s), 128.0 (d), 128.8 (s), 132.2 (d), 134.4 (s), 138.9 (d), 140.4 (s) and 147.3 (d); *m*/*z* 229 (62%, M^+), 120 (78, M^+ − SPh), 110 (100) and 93 (92).

5-Methyl-4-methylene-2-(phenylthio)hex-5-enonitrile 2g

Light yellow *oil* (Found: C, 73.2; H, 6.7; N, 6.05%); ν_{max} (NaCl)/cm^{-1} 2235 (CN) and 900 (vinyl); δ_H(270 MHz; $CDCl_3$) 1.91 (3 H, s, 5-Me), 2.70 (1 H, dd, *J* 10 and 14, 3-H), 2.86 (1 H, dd, *J* 5 and 14, 3-H), 3.90 (1 H, dd, *J* 5 and 10, 2-H), 4.95, 5.04, 5.17 and 5.30 (each 1 H, s, olefinic H), 7.36–7.42 (3 H, m, ArH) and 7.60–7.63 (2 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 20.8 (q), 36.2 (d), 37.1 (t), 113.0 (t), 116.9 (t), 118.7 (s), 129.2 (d), 129.4 (d), 130.3 (s), 134.5 (d), 141.0 (s) and 141.6 (s); *m*/*z* 229 (33%, M^+) and 43 (100).

(2*E*,4*E*)- and (2*E*,4*Z*)-6-(4-Chlorophenylthio)-4,5-dimethylhexa-2,4-dienonitrile 4h

Yellow *oil* as a mixture of geometric isomers (Found: M^+, 263.0521. $C_{14}H_{14}ClNs$ requires *M*, 263.0535); ν_{max}(NaCl)/cm^{-1} 2225 (CN); δ_H(270 MHz, $CDCl_3$) (4*E*)-isomer$_{major}$: 1.54 (3 H, s, 4-Me), 2.02 (3 H, s, 5-Me), 3.62 (2 H, s, 6-H_2), 5.24 (1 H, d, J_{trans} 16, 2-H), 7.25 and 7.28 (each 2 H, d, *J* 8, ArH) and 7.48 (1 H, d, J_{trans} 16, 3-H); (4*Z*)-isomer$_{minor}$: 1.72 (3 H, s, 4-Me), 2.00 (3 H, s, 5-Me), 3.62 (2 H, s, 6-H), 5.12 (1 H, d, J_{trans} 16, 2-H), 7.04 (1 H, d, J_{trans} 16, 3-H) and 7.25 and 7.30 (each 2 H, d, *J* 8, ArH); δ_C(400 MHz; $CDCl_3$) (4*E*)-isomer$_{major}$: 13.1 (q), 18.6 (q), 40.8 (t), 95.7 (d), 118.9 (s), 129.0 (d), 129.4 (s), 133.4 (d), 133.5 (s), 133.7 (s), 139.9 (s) and 148.4 (d); (4*Z*)-isomer$_{minor}$: 13.6 (q), 20.03 (q), 39.3 (t), 94.7 (d), 118.7 (s), 129.0 (d), 130.9 (s), 132.9 (s), 134.1 (d), 134.2 (s), 139.4 (s) and 147.0 (d); *m*/*z* 263 (22%, M^+), 120 (33, M^+ − ClC_6H_4S) and 43 (100).

2-(Chlorophenylthio)-5-methyl-4-methylenehex-5-enonitrile 2h

Light yellow *oil* (Found: M^+, 263.0557); ν_{max}(NaCl)/cm^{-1} 2245 (CN) and 900 (vinyl); δ_H(270 MHz; $CDCl_3$) 1.92 (3 H, s, 5-Me), 2.70 (1 H, dd, *J* 10 and 14, 3-H), 2.84 (1 H, dd, *J* 6 and 14, 3-H), 3.88 (1 H, dd, *J* 6 and 10, 2-H), 4.97, 5.06, 5.17 and 5.31 (each 1 H, s, olefinic H) and 7.36 and 7.55 (each 2 H, d, *J* 8, ArH); δ_C(400 MHz; $CDCl_3$) 20.9 (q), 36.4 (d), 37.2 (t), 113.2 (t), 117.2 (t), 118.6 (s), 128.8 (s), 129.6 (d), 136.1 (d), 136.2 (s), 141.2 (s) and 141.6 (s); *m*/*z* 263 (38%, M^+) and 43 (100).

(2*E*,4*E*)-4-Methyl-6-(phenylthio)hexa-2,4-dienonitrile 4i

Yellow *oil* (Found: M^+ 215.0751. $C_{13}H_{13}NS$ requires *M*, 215.0769); ν_{max}(NaCl)/cm^{-1} 2215 (CN); δ_H(400 MHz; $CDCl_3$) 1.57 (3 H, s, 4-Me), 3.64 (2 H, d, *J* 8, 6-H_2), 5.23 (1 H, d, J_{trans} 17, 2-H), 5.94 (1 H, t, *J* 8, 5-H), 6.99 (1 H, d, J_{trans} 17, 3-H) and 7.25–7.38 (5 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 11.2 (q), 32.9 (t), 95.2 (d), 118.3 (s), 127.2 (d), 129.0 (d), 129.5 (s), 131.5 (d), 134.6 (s), 136.3 (d) and 153.9 (d); *m*/*z* 215 (76%, M^+), 106 (33, M^+ − PhS), 110 (93) and 79 (100).

(2*E*,4*E*)-4-Methyl-6-(phenylthio)hexa-2,4-dienonitrile 4i

Yellow *oil* (Found: M^+, 215.0751. $C_{13}H_{13}NS$ requires *M*, 215.0769); ν_{max}(NaCl)/cm^{-1} 2215 (CN); δ_H(400 MHz; $CDCl_3$) 1.57 (3 H, s, 4-Me), 3.64 (2 H, d, *J* 8, 6-H_2), 5.23 (1 H, d, J_{trans} 17, 2-H), 5.94 (1 H, t, *J* 8, 5-H), 6.99 (1 H, d, J_{trans} 17, 3-H) and 7.25–7.38 (5 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 11.2 (q), 32.9 (t), 95.2 (d), 118.3 (s), 127.2 (d), 129.0 (d), 129.5 (s), 131.5 (d), 134.6 (s), 136.3 (d) and 153.9 (d); *m*/*z* 215 (76%, M^+), 106 (33, M^+ − PhS), 110 (93) and 79 (100).

(2*E*,4*Z*)-Methyl 4,5-bis(4-chlorophenyl)-6-(phenylthio)hexa-2,4-dienoate 14

Pale yellow *oil* (Found: C, 65.7; H, 4.6. $C_{25}H_{20}Cl_2O_2S$ requires C, 65.94; H, 4.43%); ν_{max}(NaCl)/cm^{-1} 1720 (C=O), 1170 and 1285 (C–O); δ_H(400 MHz; $CDCl_3$) 3.62 (3 H, s, OMe), 3.70 (2 H, s, 6-H), 5.28 (1 H, d, J_{trans} 16, 2-H), 6.96 and 7.38 (each 2 H, d, *J* 8, 4-ArH), 7.07–7.10 (2 H, m, SPh), 7.17–7.19 (3 H, m, SPh), 7.25 and 7.32 (each 2 H, d, *J* 8, 5-ArH) and 7.42 (1 H, d, J_{trans} 16, 3-H); δ_C(400 MHz; $CDCl_3$) 41.2 (t), 51.5 (q), 122.7 (d), 127.1 (d), 128.7 (d), 128.8 (d), 128.9 (d), 130.7 (d), 130.9 (d), 131.4 (d), 133.8 (s), 134.4 (s), 135.1 (s), 135.4 (s), 137.0 (s), 137.7 (s), 143.9 (d), 144.2 (s) and 167.2 (s); *m*/*z* 454 (41%, M^+), 346 (76), 345 (66, M^+ − PhS), 285 (77) and 215 (100).

Methyl 4,5-bis(4-chlorophenyl)-2-(phenylthio)hexa-2,4-dienoate 15

Yellow *oil* (Found, 65.7; H, 4.55. $C_{25}H_{20}Cl_2O_2S$ requires C, 65.94; H, 4.43%); ν_{max}(NaCl)/cm^{-1} 1735 (C=O) and 1235 (C–O); δ_H(400 MHz; $CDCl_3$) 2.05 (3 H, s, 6-H_3), 3.49 (3 H, s, OMe), 6.87 (2 H, d, *J* 16, ArH), 7.14–7.36 (11 H, m, ArH) and 7.62 (1 H, s, 3-H); δ_C(400 MHz; $CDCl_3$) 22.5 (q), 52.6 (q), 126.0 (d), 126.4 (s), 128.0 (d), 128.4 (d), 128.5 (d), 128.6 (d), 130.2 (d), 131.2 (d), 133.0 (s), 134.0 (s), 134.1 (s), 136.0 (s), 138.1 (s), 140.4 (s), 144.7 (s), 146.3 (d) and 166.6 (s); *m*/*z* 454 (47%, M^+), 422 (66), 285 (67), 250 (69) and 215 (100).

4-Methyl-2-(3-methyl-2-methylenebut-3-enyl)-2*H*-1,4-benzothiazin-3(4*H*)-one 17 and 2-(2,3-dimethylbuta-1,3-dienyl)-4-methyl-2*H*-1,4-benzothiazin-3(4*H*)-one 18

Yellow *oil* as a mixture of compound **17** and **18** (Found: C, 69.5; H, 6.7; N, 5.4. $C_{15}H_{17}NOS$ requires C, 69.46; H, 6.61; N, 5.40%); ν_{max}(NaCl)/cm^{-1} 1665 (C=O) and 900 (vinyl); δ_H(270 MHz; $CDCl_3$) **17**: 1.91 (3 H, s, 4′-H_3), 2.37 (1 H, dd, *J* 9 and 14, 1′-H), 2.98 (1 H, dd, *J* 5 and 14, 1′-H), 3.45 (3 H, s, 4-Me), 3.61 (1 H, dd, *J* 5 and 9, 2-H), 4.92, 5.01 and 5.20 (each 1 H, s, olefinic H), 7.02–7.10 (2 H, m, ArH) and 7.25–7.38 (2 H, m, ArH); **18**: 1.84 and 1.94 (each 3 H, s, Me × 2), 3.47 (3 H, s, 4-Me), 4.30 (1 H, d, *J* 9, 2-H), 4.98 and 5.11 (each 1 H, s, 4′-H), 5.73 (1 H, d, *J* 9, 1′-H). 7.02–7.10 (2 H, m, ArH) and 7.25–7.38 (2 H, m, ArH); δ_C(400 MHz; $CDCl_3$) **17**: 21.1 (q), 32.4 (q), 33.8 (t), 42.3 (d), 113.3 (t), 115.8 (t), 117.1 (d), 117.3 (d), 121.6 (s), 127.1 (d), 128.9 (d), 138.3 (s), 141.6 (s), 143.2 (s) and 167.2 (s); **18**: 14.5 (q), 20.7 (q), 32.6 (q), 41.4 (d), 113.8 (t), 117.5 (d), 119.1 (d), 122.7 (s), 123.4 (d), 127.2 (d), 128.6 (d), 139.9 (s), 140.7 (s), 143.8 (s) and 166.6 (s); *m*/*z* 259 (100%, M^+).

2-(2,3-Dimethylbut-2-enylidene)-4-methyl-2*H*-1,4-benzothiazin-3(4*H*)-one 19

Yellow oil (Found: C, 69.55; H, 6.7; N, 5.5%); ν_{max}(NaCl)/cm^{-1} 1665 (C=O); δ_H(270 MHz; $CDCl_3$) 1.72, 1.81 and 1.87 (each 3 H, s, Me × 3), 3.50 (3 H, s, 4-Me), 7.00–7.04 (2 H, m, ArH), 7.17–7.26 (2 H, m, ArH) and 7.53 (1 H, s, 1′-H); δ_C(400 MHz; $CDCl_3$) 17.3 (q), 20.7 (q), 22.1 (q), 32.5 (q), 116.5 (d), 119.3 (s), 120.7 (s), 123.1 (d), 124.7 (s), 126.2 (d), 126.6 (d), 135.3 (s), 137.8 (s), 138.3 (d) and 162.8 (s); *m*/*z* 259 (42%, M^+) and 202 (100).

Reaction of alicyclic ester 1c with *p*-TsOH·H_2O in the presence of *m*-MeC_6H_4SH (see Entry 10, Table 2)

A mixture of cyclopropanecarboxylate **1c** (111 mg, 0.4 mmol), *p*-TsOH·H_2O (8 mg, 0.04 mmol) and *m*-MeC_6H_4SH (5 mg, 0.04 mmol) in benzene (2 cm^3) was refluxed under nitrogen for 8 h. The cooled reaction mixture was poured into saturated aq. $NaHCO_3$ (5 cm^3) and the organic layer was separated. The water layer was extracted twice with EtOAc (5 cm^3). The organic layer and the extracts were combined, washed with water (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was separated by PLC on silica gel with hexane–EtOAc (10:1 v/v) to give 6 mg (5%) of open-chain ester **2c** as the first fraction, 92 mg (83%) of isomer **4c** as the second fraction and 4 mg (4%) of lactone **10c** as the third fraction.

Cross-over experiment of compounds 1a and 1h with *p*-TsOH·H_2O (see Scheme 7)

A mixture of vinylcyclopropyl sulfides **1a** (131 mg, 0.5 mmol) and **1h** (132 mg, 0.5 mmol) and *p*-TsOH·H_2O (19 mg, 0.1 mmol) in benzene (5 cm^3) was refluxed under nitrogen for 20 h. The cooled reaction mixture was poured into saturated aq. $NaHCO_3$ (10 cm^3) and the organic layer was separated. The water layer was extracted twice with EtOAc (10 cm^3). The organic layer and the extracts were combined, washed with water (15 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was separated by PLC on silica gel with hexane–EtOAc (10:1 v/v) to give a mixture of products **2a**, **2h** and **3a** (92 mg) (**2a**:**2h**:**3a** = 25:13:6 estimated by ^{1}H NMR spectroscopy) as the first fraction, a mixture of esters **4a** and **4d** (69 mg) (**4a**:**4d** = 23:9 estimated by ^{1}H NMR spectroscopy) as the second fraction, a mixture of nitriles **4g** and **4h** (40 mg) (**4g**:**4h** = 9:11 estimated by ^{1}H NMR spectroscopy) as the third fraction and 8 mg of lactone **10a** as the fourth fraction.

Reaction of acyclic sulfide 3a with *p*-TsOH·H_2O (see Scheme 8)

A mixture of sulfide **3a** including a trace amount of isomer **2a** (14 mg, 0.053 mmol, obtained from the reaction of cyclopropanecarboxylate **1a** with CF_3SO_3H, entry 6 in Table 1) and *p*-TsOH·H_2O (1 mg) in benzene (1.5 cm^3) was refluxed under nitrogen for 8 h. The cooled reaction mixture was poured into saturated aq. $NaHCO_3$ (5 cm^3) and the organic layer was separated. The water layer was extracted twice with EtOAc (6 cm^3). The organic layer and the extracts were combined, washed with water (8 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was separated by PLC on silica gel with hexane–EtOAc (10:1 v/v) to give 13 mg of rearrangement product **4a** (93%) and a trace amount of starting material **3a**.

Reaction of compound 2a with *p*-TsOH·H_2O (see Scheme 9)

A mixture of sulfide **2a** (131 mg, 0.5 mmol) and *p*-TsOH·H_2O (10 mg, 0.05 mmol) in benzene (2,5 cm^3) was refluxed under nitrogen for 20 h. The cooled reaction mixture was poured into saturated aq. $NaHCO_3$ (5 cm^3) and the organic layer was separated. The water layer was extracted twice with EtOAc (5 cm^3). The organic layer and the extracts were combined, washed with water (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was separated by PLC on silica gel with hexane–EtOAc (10:1 v/v) to give 72 mg (55%) of a mixture of isomers **2a** and **3a** (3:2, estimated by ^{1}H NMR spectroscopy) as the first fraction, 38 mg (29%) of rearrangement product **4a** as the second fraction and 5 mg (4%) of lactone **10a** as the third fraction.

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