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A convergent synthesis of γ-unsaturated thioaldehyde- and thioketone-*S*-oxides

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Summary — A general synthesis of the title compounds **4** is described, involving either treatment of vinylic or allenic sulfinates with allylic Grignard reagents, or allylic or allenic sulfinates with vinylic Grignard reagents. Some α,β-ethylenic thioaldehyde-*S*-oxides undergo a cycloaromatization to thiophenes **16**, **19**. Upon standing, the β,β-disubstituted γ-acetylenic thioaldehyde-*S*-oxides **21e–j** dimerize to the substituted 1,2-dithietane-1,1-dioxides **22a–f**. Treatment of *trans* **22b–e** with lithium cyanide in THF leads smoothly to the corresponding (*Z*)-alkenes **28a–d**.

unsaturated sulfinic ester / Grignard reaction / unsaturated sulfoxide / [3.3]-sigmatropic rearrangement / unsaturated thioketone-*S*-oxide / unsaturated thioaldehyde-*S*-oxide / 1,2-dithietane 1,1-dioxide / elimination / *Z*-alkene

Résumé — Synthèse convergente de *S*-oxydes de thioaldéhydes et thiocétones γ-insaturés. *Une synthèse générale des composés du titre* **4** *est réalisée par traitement de sulfinates vinyliques ou alléniques avec des réactifs de Grignard allyliques ou de sulfinates allyliques ou alléniques avec des réactifs de Grignard vinyliques. Quelques* S*-oxydes de thioaldéhydes* α,β*-éthyléniques subissent une cycloaromatisation facile en composés thiophéniques* **16**, **19**. *Après quelque temps à température ordinaire, les* S*-oxydes de thioaldéhydes* β,β*-disubstitués* γ*-acétyléniques* **21e–j** *sont dimérisés pour donner les 1,1-dioxydes des 1,2-dithiétanes substitués* **22a–f**. *Les composés* trans **22b–e** *sont transformés efficacement par le cyanure de lithium dans le THF en (Z)-alcènes* **28a–d**.

ester sulfinique insaturé / réaction de Grignard / sulfoxyde insaturé / transposition sigmatropique [3.3] / *S*-oxyde de thioaldéhyde insaturé / *S*-oxyde de thiocétone insaturée / 1,1-dioxyde de 1,2-dithiétane / élimination / (*Z*)-alcène

Introduction

Sulfines, with the general formula XYC=S=O are reactive heterocumulenic compounds and the occurrence of a sulfine in nature was established since propanethial *S*-oxide was found to be the principle lachrymatory factor in onions. They are accessible via a limited number of practicable procedures: 1,2-dehydrohalogenation of sulfinyl halides, oxidation of thiocarbonyl compounds, Wittig alkylidenation of sulfur dioxide, and alkylidenation of sulfur dioxide using α-silyl carbanions [1]. Recently a smooth preparation of thioaldehyde-*S*-oxides by base-induced elimination of chloroform from allylic and benzylic trichloromethyl sulfoxides under mild conditions was described [2].

However these preparations proceeded from substrates with the same number of carbon atoms and few convergent syntheses of sulfines were described, namely the β-addition of *n*- or *t*-butyllithium to vinylsilanes followed by reaction with sulfur dioxide [3] and the [2 + 3] cycloaddition of diazomethane or 2-diazopropane to thioketene-*S*-oxides [4]. A more versatile preparation of sulfines from easily-accessible starting materials is required if they are to be of real use as chemical intermediates. According to two known facile reactions, namely the efficient synthesis of sulfoxides from sulfinates and Grignard reagents and the oxidation of allyl vinyl sulfides to the corresponding sulfoxides which then undergo a [3.3]-sigmatropic rearrangement to thioaldehyde-*S*-oxides under exceptionally mild conditions [5, 6], it seemed very likely that the combination of the above two reactions could lead to a new general preparation of sulfines. In two preliminary communications [7, 8], we described a convergent synthesis of γ-unsaturated thioaldehyde- and thioketone-*S*-oxides by treatment of allylic or allenic sulfinates with vinylic Grignard reagents and vinylic or allenic sulfinates with allylic Grignard reagents. The corresponding details are now presented.

Reactions of substituted methyl alk-2-enesulfinates with vinylic Grignard derivatives

The methyl alk-2-enesulfinates **1a–f** were easily prepared by a previously described procedure in two steps from substituted allylic alcohols [9]. Reaction of these sulfinates with vinylic Grignard derivatives **2** in THF

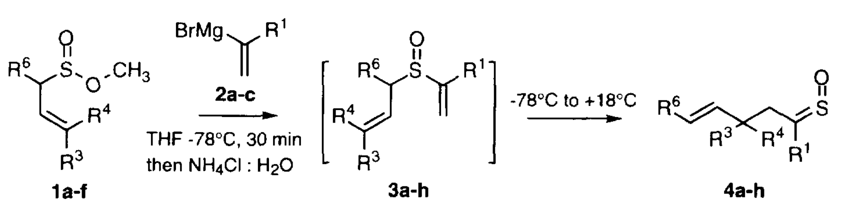

Fig 1

Table I. Reaction of β,γ-unsaturated methyl sulfinates with vinylic Grignard reagents.

Entry	*Grignard reagents*		*Substrates*				*Products*			
	2	R^1	**1**	R^3	R^4	R^6	**4**	*Yields (%)*	*Ratios (C=C)* E:Z	*(C=S)* E:Z
1	**2a**	H	**1a**	H	H	nC_4H_9	**4a**	45	[a]	5:95
2	**2a**	H	**1b**	$-(CH_2)_5-$		H	**4b**[b]	45[c]	–	5:95
3	**2a**	H	**1c**	nC_5H_{11}	H	H	**4c**	72	–	5:95
4	**2a**	H	**1d**	nC_7H_{15}	H	H	**4d**	53	–	5:95
5	**2b**	CH_3	**1e**	CH_3	CH_3	H	**4e**	50	–	60:40
6	**2b**	CH_3	**1d**	nC_7H_{15}	H	H	**4f**	90	–	65:35
7	**2b**	CH_3	**1f**	nC_7H_{15}	H	CH_3	**4g**	81	95:5	65:35
8	**2c**	C_6H_5	**1e**	CH_3	CH_3	H	**4h**	32[d]	–	90:10[e]

[a] Not determinable from ^1H NMR spectrum. [b] The [3.3]-sigmatropic rearrangement occurred during warming from −78 °C to room temperature over a period of 4 h. [c] Also compound **9** (22%); see text. [d] When this reaction was carried out at 0 °C for 1 h, the same yield was obtained. [e] For isomer *E*, the oxygen atom and phenyl group are *trans*.

at −78 °C for 30 min followed by hydrolysis with aqueous ammonium chloride at −78 °C*, warming to room temperature and usual work-up, afforded the β,γ-unsaturated sulfines **4a–h** (fig 1, table I). The yields were generally acceptable except for entries 1 and 8, probably on account of the presence of a bulky substituent R^1 or R^6. All the sulfines **4a–h** were purified by flash chromatography on silica gel.

The crude product obtained immediately after work-up (entry 2) showed (^1H NMR) the presence of sulfoxide **3b** and sulfine **4b** (33:67). After 4 h at room temperature a new ^1H NMR spectrum proved the presence of sulfine **4b** alone, but flash chromatography on silica gel produced pure sulfine **4b** (45%) and a new compound (22%). We tried, unsuccessfully, to increase the yield of this new product by prolonging the treatment of sulfine with silica gel. The ^1H, ^{13}C NMR and the mass spectrum indicated a molecular formula of $C_{20}H_{32}S$ which was confirmed by microanalysis. It should be noted that this formula represents two molecules of sulfine **4b** ($2 \times C_{10}H_{16}OS$) minus SO_2 and that the sulfine could have undergone an analogous dimerization to that previously reported for propanethial *S*-oxide **23** (fig 2) [10]. Employing similar conditions [10], we left a solution of sulfine **4b** in deuteriated benzene at −5 °C in the dark for 2–3 months and observed the formation of this same new product. We are led to suggest structure **9** for this product which is plausibly formed by the reaction sequence shown in figure 3. The dimerization of the sulfine **4b** leads to the first intermediate **5** which, due to the presence of the two cyclohexyl groups, does not turn into corresponding 3,4-disubstituted 1,2-dithietane 1,1-dioxide, analogous to that of Block [10] (see below our observations on dimers **22** of γ-acetylenic thioaldehyde-*S*-oxides **21**). A Thorpe–Ingold effect should facilitate the nucleophilic opening of the heterocycle **5** by the neighboring double bond to form the carbocation **6** and then the thiiranium salt **7** which extrudes sulfur dioxide and gives finally the thiiranes **9** (an inseparable isomeric mixture). In accord with their structure, treatment of the thiiranes **9** with triphenylphosphine gave a mixture of *Z* and *E* trienes **10**.

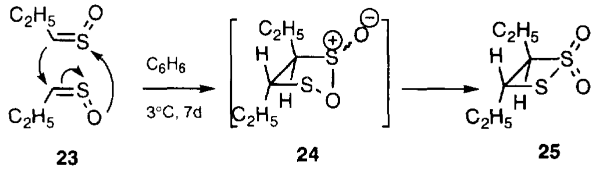

Fig 2

It is interesting to note that the reaction **7** → **9** is analogous to some previously reported eliminations [11, 12, 13] (fig 4). The results of Block [10] and our own (see below) suggest that the two substituents of the heterocyclic intermediate **5** should be *trans* and that the elimination of sulfur dioxide from **7** should have given stereoselectively the *Z* isomer **9**. No doubt due to steric congestion, the elimination is not concerted and the thiiranium salt **7** equilibrates with the thiirane-zwitterions **8** [13b,c] which finally undergo loss of sulfur dioxide to provide a mixture of *Z*- and *E*-**9**.

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* This point is essential for the success of the experiment. We also tried the following conditions: after the reaction of sulfinate **1c** with vinylmagnesium bromide at −78 °C for 30 min, the cooling bath was removed and the reaction mixture was left to warm to room temperature over 2.5 h. Subsequent hydrolysis with aqueous ammonium chloride and the usual work-up produced a very viscous resin which showed no typical signals for the thioaldehyde-*S*-oxide function by ^1H NMR. Our attempts at purification of the resin did not yield any products.

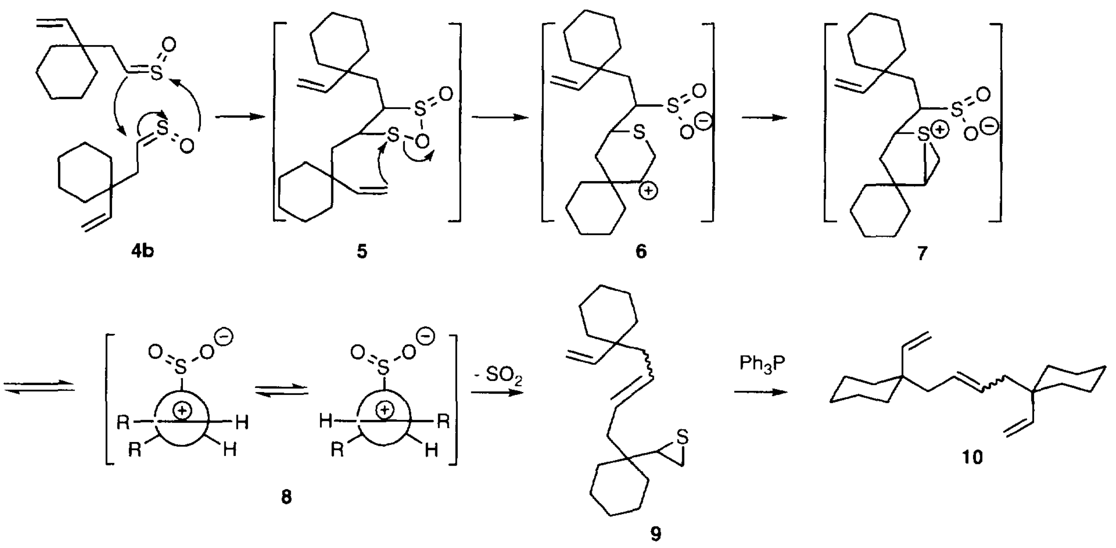


Fig 3

Table II. Reaction of α,β-unsaturated methyl sulfinates **11** with allylic Grignard reagents **12**.

Entry	*Substrates*			*Grignard reagents*					*Products*		
	11	R^1	R^2	***12***	R^5	R^6	R^7	X	**4**	*Yields (%)*	*Ratios (C=S)* E:Z
9	**11a**	H	nC_4H_9	**12a**	H	H	H	Br	**4i**	65	5:95
10	**11a**	H	nC_4H_9	**12b**	CH_3	H	H	Cl	**4j**	67	5:95
11	**11a**	H	nC_4H_9	**12c**	H	CH_3	CH_3	Cl	**4k**	73	5:95
12	**11b**	H	$CH_2{=}C(CH_3)$	**12c**	H	CH_3	CH_3	Cl	**4l**	51	5:95
13	**11c**	H	nC_6H_{13}	**12b**	CH_3	H	H	Cl	**4m**	65	5:95
14	**11c**	H	nC_6H_{13}	**12c**	H	CH_3	CH_3	Cl	**4n**	71	5:95
15	**11d**	C_6H_5	H	**12c**	H	CH_3	CH_3	Cl	**4o**	13[a]	[b]

[a] This reaction was run first at −78 °C for 15 min, then at 0 °C for 60 min before hydrolysis with aqueous ammonium chloride. [b] The ratio *E*:*Z* of the sulfine **4o** cannot be determined from its ^1H NMR spectrum.

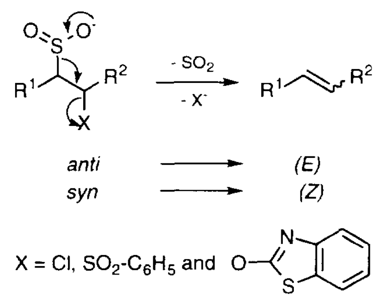


Fig 4

Reactions of substituted methyl alk-1-ene-sulfinates with allylic Grignard derivatives

The methyl alk-1-enesulfinates **11a–d** were prepared by a previously described procedure [14]. Reactions of these sulfinates with allylic Grignard derivatives **12** were carried out under the same conditions as those described in the previous paragraph (fig 5, table II). The structures of the four sulfines (**4k,l,n,o**) confirm that the reactions of (3-methylbut-2-enyl)magnesium chloride with sulfinates **11** are in agreement with earlier observations on similar systems [15]. The lavandulal-like skeleton of the thioaldehyde-*S*-oxide **4l** is remarkable. All the thioaldehyde-*S*-oxides obtained after purification on silica gel were found to be principally *Z*, like those obtained previously (entries 1–4, table I). Similarly to other thioaldehydes-*S*-oxides [1c, 16], the configurations of compounds (**4a–d,i–n**) were established to be *Z* by making use of the anisotropic deshielding effect of the CSO group on the C(1)-H. For the *Z*-isomers the characteristic proton signals are in the range 7.85–8.15 ppm whereas those of the *E*-isomers are shifted to lower fields 8.76–8.10 ppm. The configurational assignments of some sulfines **4m**, **15b** and **21a** were reliably made by using lanthanide-induced shift measurements [16b, 17]. The thermodynamically more stable (*Z*)-thioaldehyde-*S*-oxides were formed via the sulfoxides **3** with a pseudo-axial orientation of the sulfoxide oxygen in the chair-like transition state for rearrangement [5a]. The thioketone-*S*-oxides **4e–g** (table I) were formed by a less stereoselective process. The yields are generally acceptable but that of thioketone-*S*-oxide **4o** (entry 15) is poor, no doubt due to the styrenic structure of the sulfinate **11d** which should be sensitive to secondary reactions.

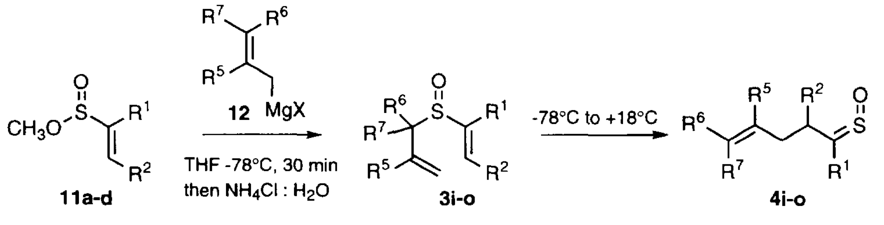


Fig 5

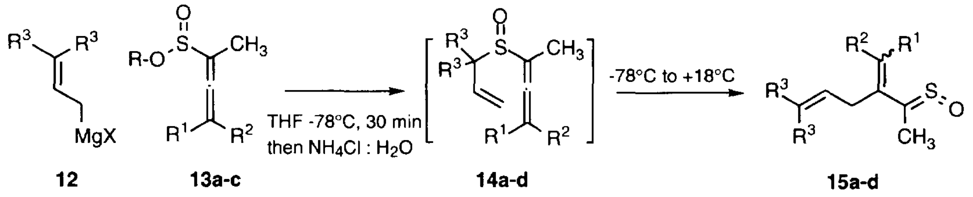


Fig 6

Table III. Reaction of α-allenic sulfinic esters **13** with allylic Grignard reagents.

Entry	*Substrates*				*Grignard reagents*				*Products*		
	13	*R*	*R^1*	*R^2*	*12*	*R^3*	*X*	*15*	*Yields (%)*	*Ratios (C=C)* E:Z	*(C=S)* E:Z
16	**13a**	C_2H_5	CH_3	CH_3	**12c**	CH_3	Cl	**15a**	80	–	100:0
17	**13b**	CH_3	$-(CH_2)_5-$		**12a**	H	Br	**15b**	62	–	100:0
18	**13c**	CH_3	H	$CH(CH_3)_2$	**12a**	H	Br	**15c**	10	100:0	100:0
19	**13c**	CH_3	H	$CH(CH_3)_2$	**12c**	CH_3	Cl	**15d**	46	[a]	100:0

[a] Precise ratio was not determinable from the ^{1}H NMR spectrum; the *trans* isomer being the major product.

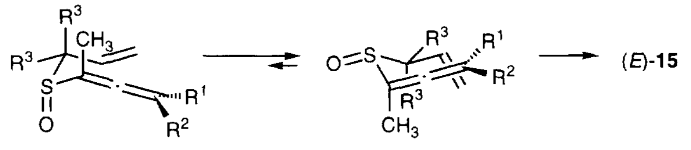


Fig 7

Reactions of substituted alka-1,2-dienesulfinic esters with allylic Grignard derivatives

Some α,β-ethylenic thioketone-*S*-oxides **15a–d** can be prepared from allenic sulfinates **13a–c** and allylic Grignard reagents (fig 6, table III). It seems that the presence of a bulky isopropyl group is responsible for the inferior yields observed for entries 18 and 19. All the methyl thioketone-*S*-oxides in table III possess an *E*-configuration for the sulfinyl oxygen, perhaps due to a repulsive interaction between the electronic clouds of the allene and the axial sulfinyl groups (fig 7).

When the allenic sulfinate **13d** was treated with allylic Grignard reagent **12c** under the same conditions as above, the usual work-up and purification by flash chromatography did not yield the corresponding thioaldehyde-*S*-oxide **15e**; instead the substituted thiophene **16** was obtained (fig 8). The reaction of the allenic sulfinate **13e** with prop-2-enylmagnesium chloride surprisingly gave a crude product of probable structure **18** (^{1}H NMR and MS). Purification of **18** by flash chromatography on silica gel yielded smoothly the thiophene compound **19** (45%). It is likely that the intermediate sulfine **15f** tautomerizes to the buta-1,3-dienylsulfenic acid **17** [18] which cyclizes to the 4,5-dihydrothiophene *S*-oxide **18** and this, in the presence of a weak acid or silica gel, undergoes an acid-catalyzed Pummerer reaction with the intermediate sulfur-stabilized carbocation losing a proton with concomitant aromatization [19]. Recently, a novel synthesis of thiophene derivatives, involving a rapid cycloaromatization of α,β-unsaturated sulfines, has been reported [20].

Reactions of substituted alka-1,2-dienesulfinic esters with vinylic Grignard derivatives

The results of Block [5a] and those shown above, clearly prove that the [3.3]-sigmatropic rearrangement of alk-1-enyl alk-2-enyl sulfoxides is substantially easier than that of the corresponding sulfides. Much less information is available on the behavior of alk-1-enyl alka-1,2-dienyl sulfides; in 1974, Brandsma and Verkruijsse [21] published a communication concerning the interesting

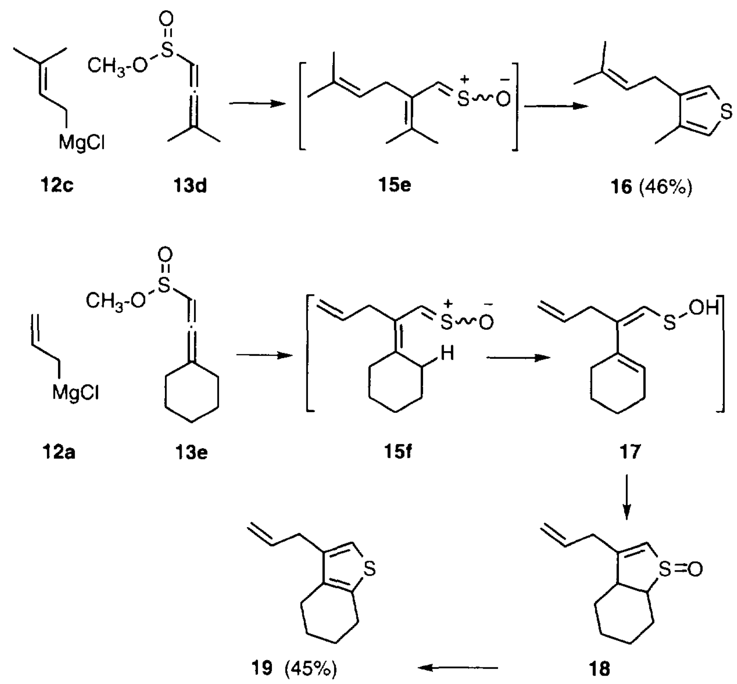


Fig 8

Table IV. Reaction of α-allenic sulfinic esters **13** with secondary vinylic Grignard derivatives.

Entry	*Grignard reagents* *2*	R^1	*13*	*Substrates* *R*	R^2,R^2	R^3	*Reaction time*	*Products* *21*	*Yields (%)*	*Ratios* E:Z
20	**2b**	CH_3	**13a**	C_2H_5	CH_3,CH_3	CH_3	30 min	**21a**	94	65:35
21	**2b**	CH_3	**13f**	CH_3	CH_3,CH_3	C_6H_5	60 min	**21b**	70	85:15
22	**2c**	C_6H_5	**13a′**	CH_3	CH_3,CH_3	CH_3	60 min	**21c**	96	92:8
23	**2c**	C_6H_5	**13b**	CH_3	$-(CH_2)_5-$	CH_3	60 min	**21d**	94	95:5

transformation of the vinyl allenyl sulfides shown in figure 9. The [3.3]-sigmatropic rearrangements were carried out under fairly vigorous conditions, which were also required for the hydrolysis of the intermediate thioketones.

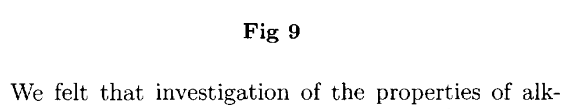


Fig 9

We felt that investigation of the properties of alk-1-enyl alka-1,2-dienyl sulfoxides **20** was mandated, since these sulfoxides could undergo [3.3]-sigmatropic rearrangement under milder conditions. The reactions of the alka-1,2-dienesulfinic esters (**13a,a′,b,f**) with secondary vinylic Grignard derivatives (fig 10) smoothly afforded the γ-acetylenic β,β-disubstituted thioketone-*S*-oxides **21a–d** (table IV). The success of these reactions seems due to the presence of *two* substituents R^2 on the carbon chain of intermediate sulfoxides **20a–d**. Indeed, reaction of methyl octa-1,2-dienesulfinate with propen-2-ylmagnesium bromide **2b** under the usual conditions was attempted, yielding firstly a crude product which was shown to be a α,β-allenic thioketone-*S*-oxide (^{1}H NMR) and subsequently, after chromatography, 4-(ethenylidene)nonan-2-one (19%). Obviously, the expected γ-acetylenic thioketone-*S*-oxide was converted into its allenic isomer and finally into the corresponding ketone [22].

Table V (fig 11) summarizes the results obtained upon reaction of alka-1,2-dienesulfinic esters **13** with vinylmagnesium bromide. The following features are particularly worthy of comment:

- The reaction mixture obtained by treatment of sulfinate **13d** with vinylmagnesium bromide at −78 °C for 30 min was quenched at −78 °C with saturated aqueous ammonium chloride. The usual work-up gave a crude product which was kept at −18 °C for 16 h before recording the ^{1}H NMR spectrum which showed the presence of sulfoxide **20e**, sulfine **21e** and a new compound **22a** in a ratio of 75:15:10 (entry 24). After standing in the dark under nitrogen at room temperature for the times mentioned in entries 24′ and 24″, the

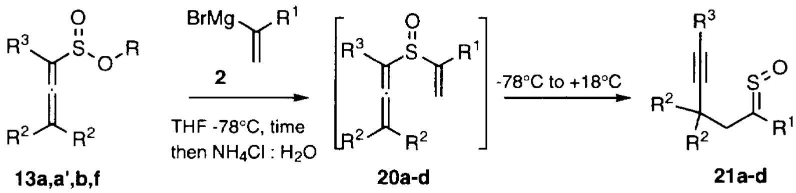


Fig 10

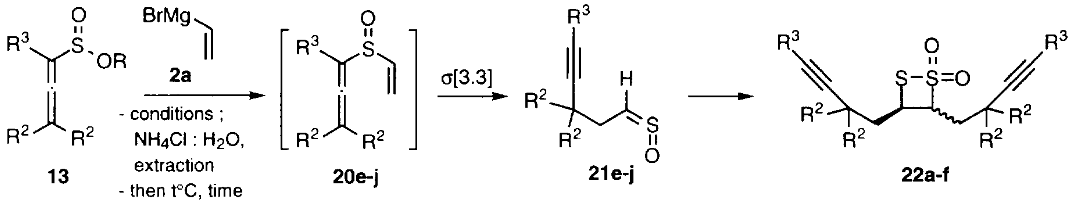


Fig 11

Table V. Reaction of α-allenic sulfinic esters **13** with vinylmagnesium bromide.

Entry	*Substrates*				*Conditions*	*Time*	*Products*	*Ratios**	*Total*
		R	*R²,R²*	*R³*		*t(°C)*		***20***: ***21*** :***22*** (E:Z) (cis/trans)	*yields* *(%)*
24	**13d**	CH_3	CH_3, CH_3	H	THF, −78 °C, 30 min then NH_4Cl, H_2O	−18 °C, 16 h	**20e**:**21e**:**22a**	75:15 (0/100):10	**
24′	**13d**					RT, 3 d		trace:23 (0/100):77	**
24″	**13d**					RT, 12 d		trace: 0 :100 (5/95)	33
25	**13a′**	CH_3	CH_3, CH_3	CH_3	idem	RT, 1 d	**20f**:**21f**:**22b**	0: 20 (5/95) :80	**
25′	**13a′**					RT, 2 d		0: 0 :100 (15/85)	86
26	**13g**	CH_3	CH_3, CH_3	C_2H_5	THF, −78 °C, 1 h then NH_4Cl, H_2O	RT, 5 h	**20g**:**21g**:**22c**	0: 13 (5/95) :87 (10/90)	71
27	**13e**	CH_3	$-(CH_2)_5-$	H	THF, −78 °C, 30 min then NH_4Cl, H_2O	RT, 2 h	**20h**:**21h**:**22d**	86: trace :14	**
27′	**13e**					RT, 11 d		trace: trace :100 (15/85)	67
28	**13b**	CH_3	$-(CH_2)_5-$	CH_3	idem	RT, 5 h	**20i**:**21i**:**22e**	0: 18 (5/95) :82 (15/85)	79
29	**13f**	CH_3	CH_3, CH_3	C_6H_5	Toluene: THF, −78 °C, 1 h; 0 °C, 2 h then NH_4Cl, H_2O	RT, 5 h	**20j**:**21j**:**22f**	0: 50 (5/95) :50 (15/85)	40

* The **20**:**21**:**22** ratios were estimated by ^1H NMR spectroscopy. ** The yields of the crude products were not determined.

^1H NMR spectra showed the disappearance of sulfoxide **20e**, an increase and then the disappearance of sulfine **21e** and, after 12 days, the formation of **22a** as the sole product.

– The sulfinate **13e** (entries 27, 27′) gave a similar result, ie, the initial formation of a mixture rich in sulfoxide **20h** which was completely converted into **22d** after 11 days at room temperature.

– The transformation of the sulfoxide **20f**, arising from sulfinate **13a′**, was more rapid and required only 2 days at room temperature in order to give the compound **22b** as the sole product (entry 25′).

– The transformations of the sulfoxides (**20g,i,j**) were faster and produced mixtures of the corresponding sulfines and the compounds **22c,e,f** which were often predominant (entries 26, 28 and 29).

Each of the resultant mixtures of compounds (**21**, **22**) was separated by flash chromatography; the new compounds **22** were purified by crystallization and their structures were not readily determinable from their IR, ^1H and ^{13}C NMR data. However the mass spectra led us to suppose that these products arose from a dimerization of the γ-acetylenic thioaldehyde-*S*-oxides **21**. Indeed Block et al [10] proved, by chemical methods, that the dimer of propanethial *S*-oxide **23** has the structure of the *trans* 3,4-diethyl-1,2-dithietane 1,1-dioxide **25**. Figure 2 rationalizes the stereospecific formation of *trans* **25** from (*Z*)-**23** via a [4 + 2] cycloaddition in which sulfine **23** functions as both a 1,3-dipole and a dipolarophile, followed by rearrangement of the unstable cyclic sulfenylsulfinate ester **24**. Similar dimerizations have been reported for (trimethylsilyl)methanethial *S*-oxide [23] and trifluoroethanethial *S*-oxide [24].

The dimers **22** gave a positive thiosulfonate test [25] and their ^1H and ^{13}C NMR data were consistent with the structure of 3,4-disubstituted-1,2-dithietane-1,1-dioxides **22a–f**. Final evidence for the *trans* structure of the major isomer of **22d** was obtained from a single crystal X-ray analysis [8].

In contrast to the γ-acetylenic thioaldehyde-*S*-oxides (**21e-j**) which undergo a facile dimerization, the γ-ethylenic substituted analogues **4** with the exception of **4b** do not produce any detectable dimer; the reasons for this difference in behavior are at present unclear.

Stereoselective conversion of 3,3-disubstituted-1,2-dithietane 1,1-dioxides 22 into symmetrical (*Z*)-alkenes 28

The presence of a reactive thiosulfonate group in the four-membered ring of compounds **22** prompted a search for appropriate nucleophilic reagents which could break open the ring and lead to an elimination to give the corresponding alkenes (fig 12). Similar eliminations have been reported for substituted sulfinic acid salts bearing different leaving groups (fig 4) [11–13].

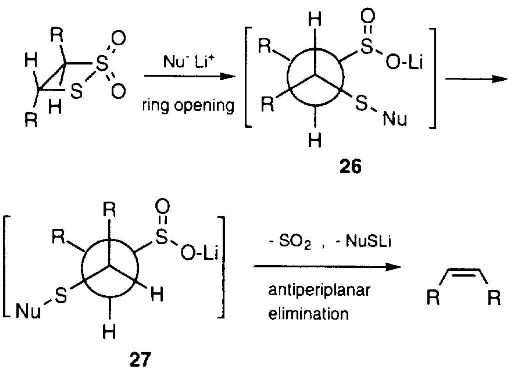
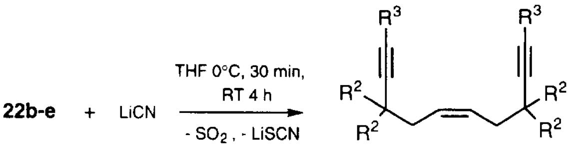


Fig 12

A first trial with a *cis/trans* (15:85) mixture of thiosulfonates **22b** and phenylethynyl lithium in THF at −78 °C for 30 min, followed by warming to room temperature over 2 h and finally addition of methyl iodide, gave a mixture ($E/Z = 62:38$) of olefins **28a** (36%). As some previous results [11–13] showed that eliminations were generally antiperiplanar for compounds carrying an R group with a small +M effect (fig 4), a ratio of $E/Z = 15:85$ should have been obtained for the olefins **28a**. The very poor stereoselectivity of this trial is perhaps due to the basicity of the nucleophile which can give rise to an equilibration via deprotonation of the intermediate **26** if the elimination of $C_6H_5C{\equiv}CSLi$ is slow.

Another experiment with 2-lithiobenzothiazole and pure *trans*-thiosulfonate **22b** at −78 °C for 1 h, then between −78 °C and +18 °C for 3 h, gave olefins **28a** in poor yield (13%) with an E/Z ratio of 82:18. This result is perhaps due to the combination of several factors: the steric crowding of thiosulfonate **22b**, the bulky nature of the nucleophile and the basicity of 2-lithiobenzothiazole.

As some simple cyclic thiosulfonates have been reported to react rapidly in aqueous dioxane with excess cyanide, undergoing opening of the thiosulfonate ring to form thiocyanates [26], it seemed interesting to examine the reaction of compounds **22** in THF with anhydrous lithium cyanide, a small and powerful nucleophile. A trial reaction of lithium cyanide (1 equiv) with *S*-phenylmethyl benzenethiosulfonate in THF at 0 °C for 30 min then at room temperature for 3 h, led to phenylmethyl thiocyanate (97%). Reaction of pure *trans* **22b** with LiCN (2 equiv) in THF under similar conditions gave the olefins **28a** (56%) with good stereoselectivity ($E/Z = 9:91$), but the reaction did not run to completion and a small amount of dimer **22b** was recovered. Employing 3 equiv of lithium cyanide, we obtained the results shown in figure 13 and table VI.



28a-d

Fig 13

Table VI. Reaction of substituted 1,2-dithietane-1,1-dioxides **22** with lithium cyanide (3 equiv).

Entry	*Substrates*	R^2,R^2	R^3	*Olefins*	*Yield* (%)	*Ratio* (E:Z)[a]
30	**22b**	CH_3,CH_3	CH_3	**28a**	90	8:92
31	**22c**	CH_3,CH_3	C_2H_5	**28b**	90	14:86
32	**22d**	$-(CH_2)_5-$	H	**28c**	89	6:94
33	**22e**	$-(CH_2)_5-$	CH_3	**28d**	93	7:93

[a] The ratios *E*:*Z* were determined using capillary gas chromatography, the *E*-isomers always having the lowest retention time.

Due to their symmetrical structure, the (*Z*) geometry of the alkenes **28a–d** could not be determined by ^1H NMR. When treated under the conditions summarized in figure 14, the bis-acetylenic compound **28c** afforded the mono-acylated product **29** with a *Z* olefinic structure ($J = 11$ Hz) ascertained by irradiation of the allylic hydrogens. Thus, the final elimination **26** → **28** is principally antiperiplanar, in agreement with some previously reported eliminations of both sulfur dioxide and a leaving group [11–13]. The above procedure, which gives the (*Z*)-olefins, may be considered as complementary to the reported photolysis of *trans*-3,4-bis(trimethylsilyl)-1,2-dithietane 1,1-dioxide, which gives the corresponding (*E*)-olefin [23].

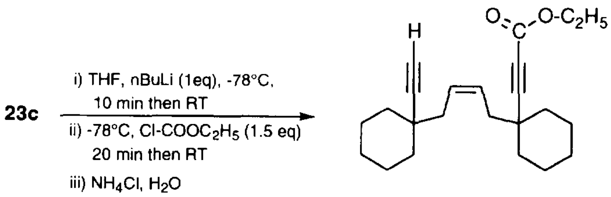
Conclusion

The above investigations have detailed:

– a facile and convergent synthesis of γ-ethylenic and γ-acetylenic thioketone- and thioaldehyde-*S*-oxides which should considerably extend the range of compounds available for the study of sulfine reactivity;

– the smooth dimerization of some γ-acetylenic β,β-disubstituted thioaldehyde-*S*-oxides and

– a new procedure for the stereoselective conversion of *trans*-3,4-disubstituted 1,2-dithietane 1,1-dioxides



29 (29%) + **28c** (30%)

Fig 14

into symmetrical (*Z*)-alkenes. It is conceivable that this transformation could be extended to other four-membered cyclic thiosulfonates bearing two different substituents. However, due to the lack of information concerning these compounds, their full synthetic potential remains to be determined.

Experimental section

For the general experimental conditions, see [27].

The unsaturated sulfinates **1** [9], **11** [14] and **13** [27] were prepared by previously-described procedures. All the purified sulfines below are fairly unstable compounds at room temperature; they can be stored at −18 °C for a few hours, and sometimes a few days.

Non-4-enethial S*-oxide* **4a**

- *Typical procedure*

A 0.49 M solution of vinylmagnesium bromide in THF (6.8 mL, 3.3 mmol; 1.1 equiv) was slowly added to a solution of methyl 1-ethenylpentane-1-sulfinate **1a** (0.525 g; 3 mmol) in THF (12 mL) at −78 °C; the reaction mixture was then stirred at −78 °C for 30 min. A saturated aqueous ammonium chloride solution (20 mL) was then added, the cooling bath removed and after addition of ether (30 mL), the mixture was stirred whilst warming to room temperature. The aqueous layer was separated and extracted with ether (3 x 30 mL). The extracts were washed with aqueous ammonium chloride (3 x 6 mL), dried (MgSO$_4$), filtered and evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel, Merck) using pentane/ether 100:0 to 50:50, giving sulfine **4a** (0.232 g; 45%).

IR (film, cm^{-1}): 3 020, 1 460, 1 380, 1 140 (large), 975.

^{1}H NMR (250 MHz, CDCl$_3$) (two isomers E/Z = 5:95; the signals of the major isomer are given in italics) δ: 8.10 (t, J = 7.90 Hz, 1H); *8.09* (t, J = 7.85 Hz, 1H); 5.53-5.17 (m, 2H); 2.77 (q, J = 7.6 Hz, 2H); 2.24-2.07 (m, 2H); 2.07-1.83 (m, 2H); 1.39-1.13 (m, 4H); 0.83 (t, J = 7.4 Hz, 3H).

MS (CI, NH$_3$); m/z: 345 (2M$^+$ + 1, 15); 313 (4); 281 (29); 247 (14); 198 (M$^+$ + 18, 75); 173 (M$^+$ + 1, 100); 157 (83); 139 (12); 123 (18); 109 (10).

- *Reaction of methyl 2-cyclohexylideneethane-1-sulfinate* **1b** *with vinylmagnesium bromide*

Following the preceding typical procedure using sulfinate **1b** (0.566 g; 3 mmol) and 1.2 equiv of Grignard reagent, the work-up gave a crude product which was (^{1}H NMR) a mixture of sulfoxide **3b**:sulfine **4b** (33:67), from which the following data for sulfoxide **3b** were observed.

[2-(Ethenylsulfinyl)ethylidene]cyclohexane **3b**

^{1}H NMR (250 MHz, CDCl$_3$) δ: 6.60 (dd, J = 16.5 Hz and 9.8 Hz, 1H); 6.02 (d, J = 16.5 Hz, 1H); 5.89 (d, J = 9.8 Hz, 1H); 5.07 (t, J = 8.03 Hz, 1H); 3.58–3.33 (m, 2H); 2.20–2.03 (m, 2H); 1.64–1.16 (m, 8H).

After standing at room temperature for 4 h, the ^{1}H NMR spectrum of the crude product showed the presence of only the sulfine **4b**. Flash chromatography (silica gel; pentane:ether = 98:2 to 80:20) afforded first the thiirane **9** (0.100 g; 22%) and then sulfine **4b** (0.250 g, 45%).

(1-Ethenylcyclohexyl)ethanethial S*-oxide* **4b**

IR (film, cm^{-1}): 3 080, 1 640, 1 455, 1 135, 920.

^{1}H NMR (250 MHz, CDCl$_3$) (two isomers E/Z = 5:95; the signals of the major isomer are given in italics) δ: 8.64 (t, J = 8.01 Hz, 1H); *8.03* (t, J = 8 Hz, 1H); 5.59 (dd, J = 17.7 and 11 Hz, 1H); 5.11 (dd, J = 11 and 1 Hz, 1H); 4.96 (dd, J = 17.7 and 1 Hz, 1H); 2.73 (d, J = 8 Hz, 2H); 1,64–1,15 (m, 10H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 175.2 (d); 144.2 (d); 114.3 (t); 40.7 (t); 36.4 (s); 35.3 (t); 26.0 (t); 21.9 (t).

MS (CI, NH$_3$); m/z: 368 (2M$^+$, 1): 305 (100); 271 (39); 202 (M$^+$ + 18, 1); 109 (4).

2-{1-[4-(1-Ethenylcyclohexyl)but-2-enyl]cyclohexyl}-thiirane **9**

IR (film, cm^{-1}): 1 635, 1 455, 980, 915.

^{1}H NMR (250 MHz, CDCl$_3$) (two isomers; the signals of the major isomer are given in italics) δ: 5.66 (dd, J = 10.95 and 17.75 Hz, 1H) and *5.65* (dd, J = 10.94 and 17.75 Hz, *1H*); 5.56–5.48 (m, 2H) and *5.48–5.39* (m, *2H*); 5.095[*] (d, J = 10.97 Hz, 1H); *5.06*[*] (d, J = 10.97 Hz, *1H*); 4.96[*] (d, J = 17.72 Hz, 1H); *4.92*[*] (d, J = 17.7 Hz, *1H*); 2.97 (t, J = 6.41 and 6.56 Hz, 1H); 2.42–2.22 (m, 3H); 2.22–1.97 (m, 2H); 1.70–1.13 (m, 20H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: *146.5* and 146.1 (d); *129.7* and 128.2 (d); *127.6* and 126.1 (d); 112.8 and *112.5* (t); *46.5* and 46.4 (d); 44.3 (t); 40.0 (s) and *39.8* (s); 39.1 (t); 36.7 (s) and *36.4* (s); 35.4 (t); 35.3 (t); 34.7 (t); 34.4 (t); 33.2 (t); 29.5 (t); 29.4 (t); 26.4 (t); 26.0 (t); 25.9 (t); 22.2 (t); 22.1 (t); 21.7 (t); 21.5 (t); 21.2 (t).

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[*] On account of the presence of an asymmetric carbon on the thiirane function, the asterisked signals are doubled: for the major isomer, the signals at 5.06 and 4.92 are accompanied respectively by smaller signals at 5.07 (d, J = 10.9 Hz, 1H) and 4.91 (d, J = 17.8 Hz, 1H); for the minor isomer, the signals at 5.09 and 4.96 are accompanied respectively by smaller signals at 5.089 (d, J = 10.8 Hz) and 4.95 (d, J = 17.7 Hz, 1H).

MS (CI, NH$_3$); m/z: 322 (M$^+$ + 18, 1); 306 (M$^+$ + 2, 42); 305 (M$^+$ + 1, 100); 304 (M$^+$, 2); 271 (50); 195 (34); 109 (52).

Anal calc for $C_{20}H_{32}S$: C 78.95; H 10.53. Found: C 78.99; H 10.77.

3,3:8,8-Bis(pentane-1,5-diyl)deca-1,5,9-triene **10**

A solution of thiirane **9** (0.152 g; 0.5 mmol) and triphenylphosphine (0.132 g; 0.5 mmol, 1 equiv) in THF (5 mL) was refluxed for 10 h. As the reaction did not run to completion (^{1}H NMR and TLC), the solvent was evaporated and the residue heated at 90 °C for 15 h. Cooling to room temperature, addition of pentane, filtration and evaporation of the solvent afforded the crude triene **10** which was purified by chromatography (0.070 g; 51%).

^{1}H NMR (250 MHz, CDCl$_3$) δ: 5.66 (dd, J = 17.5 and 11 Hz, 1H); 5.65 (dd, J = 17.5 and 11 Hz, 1H); 5.4 (tt, J = 4.5 and 0.5 Hz, 1H); 5.31 (tt, J = 4 and 1.8 Hz, 1H); 5.06 (dd, J = 11 and 1.5 Hz, 1H); 5.04 (dd, J = 11 and 1.5 Hz, 1H); 4.91 (dd, J = 17.5 and 1.5 Hz, 1H); 4.89 (dd, J = 17.5 and 1.5 Hz, 1H); 2.01–1.95 (m, 8H); 1.6–1.2 (m, 40H)

^{13}C NMR (62 MHz, CDCl$_3$) δ: 146.9 (d); 146.5 (d); 128.7 (t); 127.1 (t); 112.7 (d); 112.4 (d); 44.3 (s); 40.2 (t); 39.9 (t); 39.0 (s); 35.5 (t); 35.4 (t); 26.6 (t); 26.5 (t); 22.4 (t); 22.2 (t).

GLC (capillary column, SGE BP 5; L = 50 m; D = 0.25 μm; P (He) = 1.5 bar): two isomers: 62:38.

GLC-MS coupling (CI, NH$_3$); m/z: first isomer: 290 (M$^+$ + 18, 100); 273 (M$^+$ + 2, 15); 272 (M$^+$ + 1, 5); 109 (35); second isomer: 290 (M$^+$ + 18, 56); 273 (M$^+$ + 2, 15); 272 (M$^+$ + 1, 13); 109 (100).

Anal calc for $C_{20}H_{32}$: C 88.16; H 11.84. Found: C 88.11; H 11.88.

3-(Ethenyl)octanethial S-*oxide* **4c**

^{1}H NMR (250 MHz, CDCl$_3$) (two isomers E/Z = 5:95) δ: 8.76 (t, J = 10.6 Hz, 1H); *8.15* (t, J = 7.92 Hz, 1H); 5.68–5.49 (m, 1H); 5.15–4.97 (m, 2H); 3.03–2.86 (m, 1H); 2.77–2.59 (m, 1H); 2.31–2.08 (m, 1H); 1.54–1.12 (m, 8H); 0.9 (t, J = 6.44 Hz, 3H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 176.5 (d); 140.6 (d); 115.9 (t); 43.2 (t); 34.4 (d); 31.7 (t); 30.9 (t); 26.6 (t); 22.5 (t); 14.0 (q).

MS (CI, NH$_3$); m/z: 309 (100); 326 (4); 275 (62); 204 (M$^+$ + 18, 3).

3-(Ethenyl)decanethial S-*oxide* **4d**

IR (film, cm^{-1}): 1 630, 1 460, 1 125, 910.

^{1}H NMR (250 MHz, CDCl$_3$) (two isomers E/Z = 5:*95*) δ: 8.77 (t, J = 9.5 Hz, 1H); *8.14* (t, J = 7.9 Hz, 1H); 5.59 (ddd, J = 16.7, 10.4 and 8.6 Hz, 1H); 5.12–4.98 (m, 2H); 2.93 (ddd, J = 15.4, 8.0 and 5.0 Hz, 1H); 2.68 (ddd, J = 15.4, 9.05 and 7.95 Hz, 1H); 2.29–2.12 (m, 1H); 1.53–1.14 (m, 12H); 0.88 (t, J = 6.5 Hz, 3H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 176.3 (d); 140.5 (d); 115.8 (t); 43.1 (d); 34.3 (t); 31.6 (t); 30.8 (t); 29.3 (t); 29.0 (t); 26.8 (t); 22.5 (t); 13.9 (q).

MS (CI, NH$_3$); m/z: 429 (2M$^+$ + 1, 2); 365 (80); 332 (38); 331 (56); 233 (M$^+$ + 19, 100); 215 (M$^+$ + 1, 5); 214 (M$^+$, 2).

4,4-Dimethylhex-5-ene-2-thione S-*oxide* **4e**

IR (film, cm^{-1}): 1 640, 1 385, 1 370, 1 120, 1 080, 1 010, 920.

^{1}H NMR (250 MHz, CDCl$_3$) (two isomers E/Z = 60:40) δ: 5.97–5.75 (m, 1H); 5.04–4.92 (m, 2H); 2.58 (s, 2H) and *2.41* (s, 2H); *2.29* (s, 3H); 2.20 (s, 3H); 1.14 (s, 6H) and *1.07* (s, 6H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 193.6 (s); *192.8* (s); 147.1 (d); *146.4* (d); *112.2* (t); 111.6 (t); 43.7 (t); *43.0* (t); 39.2 (s); *37.5* (s); 27.1 (q); *27.0* (q); *18.4* (q); 17.5 (q).

MS (CI, NH$_3$); m/z: 335 (2M$^+$ + 19, 1); 316 (2M$^+$, 6); 317 (2M$^+$ + 1, 35); 176 (M$^+$ + 18, 5); 159 (M$^+$ + 1, 100); 158 (M$^+$, 8) 143 (95); 127 (61); 109 (83).

4-Ethenylundecane-2-thione S-*oxide* **4f**

IR (film, cm^{-1}): 1 450, 1 085, 915.

^{1}H NMR (250 MHz, CDCl$_3$) (two isomers E/Z ≈ 65:35) δ: 5.65–5.55 (m, 1H); *5.51–5.41* (m, 1H); 5.10–4.98 (m, 2H); 3.01 (dd,J = 13.5 and 9.7 Hz, 1H); 2.71 (dd, J = 13.5 and 5.5 Hz, 1H); 2.47–2,25 (m, 1H and *2H*); *2.28* (s, 3H); 2.02 (s, 3H); 1.51–1.21 (m, 12H); 0.91 (t, J = 6.5 Hz, 3H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 193.5 and *193.1* (s); 140.6 and *140.2* (d); *116.2* and 115.5 (t); 42.4 and *42.0* (d); *36.5* and 36.1 (t); 34.9 and *34.5* (t); 31.7 (t); 29.5 and *29.4* (t); 29.1 (t); 27.0 and *26.9* (t); 22.6 (t); *16.1* and 15.7 (q); 14.0 (q).

MS (CI, NH$_3$); m/z: 246 (M$^+$ + 18, 1); 229 (M$^+$ + 1, 34); 113 (100).

Anal calc for $C_{13}H_{24}OS$: C 68.37; H 10.59. Found: C 68.58; H 10.70.

(Z)- and (E)-4-(Prop-1-enyl)undecane-2-thione S-*oxide* **4g**

IR (film, cm^{-1}): 1 460–1 430, 1 370, 1 360, 1 110, 1 075, 960.

^{1}H NMR (400 MHz, CDCl$_3$) (four isomers: sulfines E/Z ≈ 65:35, double bond E/Z ≈ 95:5; the signals for the Z double bond are neglected) δ: 5.47–5.30 (m, 1H); 5.22–5.10 (m, 1H; ZE); 5.08–4.92 (m, 1H, EE); 2.91 (dd, J = 13.5and 9.7 Hz, 1H); 2.66 (dd, J = 13.5 and 5.5 Hz, 1H); *2.37* (dd, J = 13.5 and 5.5 Hz, 1H); 2.31–2.13 (m, 1H and 1H); *2.24* (s, 3H); 1.98 (s, 3H); 1.67–1.63 (m 3H); 1.40–1.18 (m, 12H); 0.88 (t, J = 6.7 Hz, 3H).

^{13}C NMR (62 MHz, CDCl$_3$) (in italics: EE isomer) δ: 194.0 and *193.4* (s); 133.3 and *132.9* (d); *126.7* and 125.9 (d); 41.1 and *40.8* (d); *36.9* and 36.4 (t); 35.3 and 35.0 (t); 31.7 (t); 29.42 and *29.38* (t); 29.1 (t); 27.0 and *26.9* (t); 22.5 (t); *17.7* and 17.6 (q); *16.1* and 15.9 (q); 14.0 (q).

MS (CI, NH$_3$); m/z: 260 (M$^+$ + 18, 3); 243 (M$^+$ + 1, 100); 153 (53); 127 (46).

1-Phenyl-3,3-dimethylpent-4-ene-1-thione S-*oxide* **4h**

IR (film, cm^{-1}): 1 680, 1 635, 1 440, 1 380, 1 360, 1 125, 1 090, 1 070, 915.

^{1}H NMR (250 MHz, CDCl$_3$) (two isomers E/Z = 90:10) δ: 7.54–7.25 (m, 5H); 5.77 (dd, J = 16.5 and 10.11 Hz, 1H); 4.78–4.82 (m, 2H); *3.26* (s, 2H); 2.75 (s, 2H); *1.00* (s, 6H); 0.95 (s, 6H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 196.5 (s); *146.4* (d); 146.2 (d); 133.1 (s); 130.6 (d); 129.1 (d); 125.8 (d); 111.8 (t); *111.2* (t); *41.6* (t); 40.4 (t); *39.9* (s); 37.8 (s); *27.1* (q); 27.1 (q).

MS (CI, NH$_3$); m/z: 386 (100); 372 (83); 344 (23); 221 (M$^+$ + 1; 23); 220 (M$^+$; 4); 205 (43); 138 (45).

2-(Prop-2-enyl)hexanethial S-*oxide* **4i**

IR (film, cm^{-1}): 1 640, 1 450, 1 375, 1 120, 920.

^{1}H NMR (250 MHz, $CDCl_3$) (two isomers $E/Z \approx 5{:}95$) δ: 8.52 (d, J = 11.8 Hz, 1H E); 7.85 (d, J = 10.5 Hz, 1H Z); 5.79–5.60 (m, 1H); 5.08–4.94 (m, 2H); 3.73–3.57 (m, 1H); 2.26 (dtm, J = 13.8 and 6.4 Hz, 1H); 2.09 (dtm, J = 13.8 and 7.4 Hz, 1H); 1.67–1.42 (m, 2H); 1.42–1.16 (m, 4H); 0.82 (t, J = 6.9 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 181.4 (s); 134.6 (d); 117.3 (t); 38.4 (t); 36.3 (d); 33.3 (t); 29.2 (t); 22.4 (t); 13.8 (q).

MS (CI, NH_3); m/z: 209 (100); 190 (M^+ + 18, 68); 173 (M^+ + 1, 59).

2-(2-Methylprop-2-enyl)hexanethial S-*oxide* **4j**

IR (film, cm^{-1}): 1 645, 1 450, 1 370, 1 120, 890.

^{1}H NMR (250 MHz, $CDCl_3$) (two isomers $E/Z = 5{:}95$) δ: 8.53 (d, J = 11.9 Hz, 1H E); 7.85 (d, J = 10.4 Hz, 1H Z); 4.82–4.77 (m, 1H); 4.73–4.68 (m, 1H); 3.93–3.76 (m, 1H); 2.27 (dd, J = 13.8 and 5.7 Hz, 1H); 2.09 (dd, J = 13.8 and 9.2 Hz, 1H); 1.75 (br s, 3H); 1.49–1.21 (m, 6H); 0.90 (t, J = 6.9 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 181.8 (d); 142.6 (s); 112.6 (t); 43.0 (t); 35.0 (d); 34.0 (t); 29.4 (t); 22.6 (t); 22.0 (q); 13.9 (q).

MS (CI, NH_3); m/z: 204 (M^+ + 18, 45); 187 (M^+ + 1, 56); 169 (100).

Anal calc for $C_{10}H_{18}OS$: C 64.47; H 9.74. Found: C 64.74; H 9,80.

2-Butyl-5-methylhex-4-enethial S-*oxide* **4k**

IR (film, cm^{-1}): 1 450, 1 375, 1 120.

^{1}H NMR (250 MHz, $CDCl_3$) (two isomers $E/Z = 5{:}95$) δ: 8.57 (d, J = 11.9 Hz, 1H E); 7.92 (d, J = 10.4 Hz, 1H Z); 5.12 (th, J = 14.4 and 7.4 Hz, 1H); 3.74–3.59 (m, 1H); 2.23 (td, J = 14.4 and 7.4 Hz, 1H); 2.12 (td, J = 14.4 and 7.4 Hz, 1H); 1.71 (d, J = 1.4 Hz, 3H); 1.61 (broad s, 3H); 1.44–1.21 (m, 6H); 0.89 (t, J = 6.9 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 182.1 (d); 134.0 (s); 120.3 (d); 37.2 (d); 33.2 (t); 32.5 (t); 29.3 (t); 25.6 (q); 22.4 (t); 17.8 (q); 13.8 (q).

MS (CI, NH_3); m/z: 418 ($2M^+$ + 18, 15); 401 ($2M^+$ + 1, 100); 218 (M^+ + 18, 6); 201 (M^+ + 1, 3).

5-Methyl-2-(1-methylethenyl)hex-4-enethial S-*oxide* **4l**

IR (film, cm^{-1}): 1 640, 1 440, 1 370, 1 130, 890.

^{1}H NMR (250 MHz, $CDCl_3$) (two isomers $E/Z = 5{:}95$) δ: 8.68 (d, J = 11.4 Hz, 1H E); 8.06 (d, J = 10.3 Hz, 1H Z); 5.08 (th, d, J = 7 and 1.4 Hz, 1H); 4.92–4.86 (m, 2H); 4.27 (dt, J = 10.3 and 7.2 Hz, 1H); 2.43–2.21 (m, 2H); 1.79 (t, J = 1 Hz, 3H); 1.70 (t, J = 1 Hz, 3H); 1.63 (broad s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 178.9 (d); 143.2 (s); 134.2 (s); 120.0 (d); 112.7 (t); 43.3 (d); 31.1 (t); 25.6 (q); 20.6 (q); 17.9 (q).

MS (CI, NH_3); m/z: 205 (100); 185 (M^+ + 1, 4); 169 (29); 135 (28).

2-(2-Methylprop-2-enyl)octanethial S-*oxide* **4m**

IR (film, cm^{-1}): 1 645, 1 450, 1 370, 1 120, 890.

^{1}H NMR (250 MHz, $CDCl_3$) (two isomers $E/Z = 5{:}95$) δ: 8.53 (d, J = 11.9 Hz, 1H E); 7.85 (d, J = 10.5 Hz, 1H Z); 4.81–4.78 (m, 1H); 4.72–4.69 (m, 1H); 3.92–3.76 (m, 1H); 2.27 (dd, J = 13.8 and 6 Hz, 1H); 2.08 (ddm, J = 13.8 and 9.8 Hz, 1H); 1.75 (s, 3H); 1.42–1.22 (m, 10H); 0.83 (t, J = 6.9 Hz, 3H).

Δ_{EuFOD}: 8.53 → 8.83 (0.30); 7.85 → 7.88 (0.03).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 181.6 (d); 142.4 (s); 112.5 (t); 42.9 (t); 34.9 (d); 34.2 (t); 31.5 (t); 29.0 (t); 27.1 (t); 22.4 (t); 21.9 (q); 13.9 (q).

MS (CI, NH_3); m/z: 232 (M^+ + 18; 36); 215 (M^+ + 1; 100); 197 (62); 165 (39).

2-(3-Methylbut-2-enyl)octanethial S-*oxide* **4n**

IR (film, cm^{-1}): 1 450, 1 375, 1 120.

^{1}H NMR (250 MHz, $CDCl_3$) (two isomers $E/Z = 5{:}95$) δ: 8.57 (d, J = 12 Hz, 1H E); 7.92 (d, J = 10.3 Hz, 1H Z); 5.12 (th, J = 7.4 and 1.4 Hz, 1H); 3.74–3.59 (m, 1H); 2.23 (td, J = 14.4 and 7.4 Hz, 1H); 2.12 (td, J = 14.4 and 7.4 Hz, 1H); 1.71 (d, J = 1.4 Hz, 3H); 1.61 (br s, 3H); 1.46–1.21 (m, 10H); 0.89 (t, J = 6.7 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 182.1 (d); 134.0 (s); 120.3 (d); 37.2 (d); 33.6 (t); 32.5 (t); 31.5 (t); 29.0 (t); 27.1 (t); 25.6 (q); 22.4 (t); 17.8 (q); 13.9 (q).

MS (CI, NH_3); m/z: 229 (M^+ + 1, 2); 213 (100); 179 (15).

1-Phenyl-5-methylhex-4-ene-1-thione S-*oxide* **4o**

IR (film, cm^{-1}): 1 680, 1 600, 1 445, 1 375, 110.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.56–7.09 (m, 5H); 4.92–4.80 (m, 1H); 3.46–3.38 (m, 2H); 2.53–2.33 (m, 2H); 1.48 (s, 3H); 1.40 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 194.2 (s); 132.1 (s); 128.8 (d); 128.5 (d); 127.2 (d); 123.4 (d); 91.0 (s); 47.1 (t); 25.5 (t); 24.9 (q); 17.7 (q).

3-(1-Methylethylidene)-6-methylhept-5-ene-2-thione S-*oxide* **15a**

IR (film, cm^{-1}): 1 440, 1 370, 1 075.

^{1}H NMR (250 MHz, $CDCl_3$) (one single isomer E) δ: 4.92 (tm, J = 7.1 Hz, 1H); 2.84 (broad d, J = 7.1 Hz, 2H); 2.32 (s, 3H); 1.82 (s, 3H); 1.77 (s, 3H); 1.70 (broad s, 3H); 1.61 (broad s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 193.7 (s); 134.8 (s); 133.3 (s); 125.3 (s); 120.0 (d); 30.2 (t); 25.4 (q); 22.4 (q); 20.4 (q); 17.7 (q); 16.9 (q).

MS (CI, NH_3); m/z: 213 (100); 199 (M^+ + 1, 70); 181 (79).

Anal calc for $C_{11}H_{18}OS$: C 66.62; H 9.15. Found: C 66.51; H 9.14.

3-(Cyclohexylidene)hex-5-ene-2-thione S-*oxide* **15b**

IR (film, cm^{-1}): 1 630, 1 440, 1 070, 990, 910.

^{1}H NMR (250 MHz, $CDCl_3$) (one single isomer E) δ: 5.64 (ddt, J = 16.8, 10.3 and 6.3 Hz, 1H); 5.10–4.94 (m, 2H); 2,89 (dm, J = 6.3 Hz, 2H); 2.32 (s, 3H); 2,31–2.13 (m, 4H); 1.66–1.47 (m, 6H).

Δ_{EuFOD}: 2.32 → 2.71 (0.39); 2.89 → 3.02 (0.13).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 193.5 (s); 145.2 (s); 134.1 (d); 120.1 (s); 116.3 (t); 35.0 (t); 32.7 (t); 31.0 (t); 29.4 (t); 28.1 (t); 26.3 (t); 17.4 (q).

MS (CI, NH_3); m/z: 211 (M^+ + 1, 54); 195 (56); 155 (100); 116 (84).

Anal calc for $C_{12}H_{18}OS$: C 68.53; H 8.63. Found: C 68.79; H 8.65.

5-Methyl-3-(prop-2-enyl)hex-3-ene-2-thione S-*oxide* **15c**

IR (film, cm^{-1}): 1 690, 1 640, 1 470, 1 365, 1 085, 920.

^{1}H NMR (250 MHz, CDCl$_3$) (E-sulfine with E-double bond as major isomer) δ: 5.76–5.56 (m, 1H); 5.45 (d, $J = 8.3$ Hz, 1H); 5.13–4.97 (m, 2H); 2,87 (dd, $J = 0.99$ and 6.7 Hz, 2H); 2.63–2.45 (m, 1H); 2,33 (s, 3H); 0,96 (d, $J = 7.5$ Hz, 6H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 191.7 (s); 141.7 (d); 134.6 (d); 127.5 (s); 117.4 (t); 40.5 (t); 28.8 (d); 23.8 (q); 16.8 (q).

MS (CI, NH$_3$); m/z: 202 (M$^+$ + 18, 100); 185 (M$^+$ + 1, 36); 169 (57); 153 (54); 135 (37).

6-Methyl-3-(2-methylpropylidene)hept-5-ene-2-thione S-*oxide* **15d**

IR (film, cm^{-1}): 1 666, 1 450, 1 375, 1 080.

^{1}H NMR (250 MHz, CDCl$_3$) (E-sulfine with E-double bond as major isomer) δ: 5.65 (d, $J = 9.7$ Hz, 1H); *5.39* (d, $J = 8.3$ Hz, 1H); *5.04–4.94* (m, 1H); 4.94–4.83 (m, 1H); 3.01 (d, $J = 6.57$ Hz, 2H); *2.80* (d, $J = 12.35$ Hz, 2H); 2.72–2.42 (m, 1H); 2.35 (s, 3H); *2.32* (s, 3H); 1.73–1.68 (m, 3H); 1.6–1.55 (m, 3H); 1.03 (d, $J = 7.5$ Hz, 6H); *0.95* (d, $J = 7.5$ Hz, 6H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 191,6 (s); 140.5 (d); 134.5 (s); 128.4 (s); 120.3 (d); 35.1 (t); 28.6 (d); 25.6 (q); 23,8 (q); 22.5 (q); 16,8 (q).

MS (CI, NH$_3$); m/z: 230 (M$^+$ + 18, 20); 213 (M$^+$ + 1, 100); 197 (29); 181 (5); 163 (22).

3-Methyl-4-(3-methylbut-2-enyl)thiophene **16**

The reaction of sulfinate **13d** (0.226 g, 1.55 mmol) with (3-methylbut-2-enyl)magnesium chloride **12c** (1.7 mmol) was run in THF following the typical procedure. Flash chromatography of the crude product (silica gel, pentane/ether 100:0 to 70:30) afforded compound **16** (0.110 g; 46%).

IR (film, cm^{-1}): 1 435, 1 370, 1 100, 1 025.

^{1}H NMR (250 MHz, CDCl$_3$) δ: 6.91–6.86 (m, 2H); 5.31 (th, $J = 7.2$ and 1.4 Hz, 1H); 3.20 (dd, $J = 7.2$ and 0.7 Hz, 2H); 2.17 (d, $J = 0.9$ Hz, 3H); 1.76 (d, $J = 1.4$ Hz, 3H); 1.69 (broad s, 3H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 140.9 (s); 136.7 (s); 132.5 (s); 121.8 (d); 120.8 (d); 120.3 (d); 27.9 (t); 25.5 (q); 17.6 (q); 14.3 (q).

MS (CI, NH$_3$); m/z: 167 (M$^+$ + 1, 51); 166 (M$^+$, 100); 151 (52).

Anal calc for C$_{10}$H$_{14}$S: C 72.23; H 8.49. Found: C 72.35; H 8.39.

3-(Prop-2-enyl)-4,5,6,7-tetrahydrobenzothiophene **19**

Following the preceding typical procedure using sulfinate **13e** and 2-propenylmagnesium chloride (1.1 equiv), the work-up gave a crude compound **18** with the following spectral data:

^{1}H NMR (80 MHz, CDCl$_3$) δ: 6.23–5.86 (m, 2H); 5.46 (s, 1H); 5.41–4.90 (m, 2H); 3.53 (broad d, $J = 6.5$ Hz, 2H); 2.56–1.98 (m, 3H); 1.98–1.38 (m, 6H).

MS (CI, NH$_3$); m/z: 197 (M$^+$ + 1, 100); 179 (93).

Purification by a flash chromatography on silica gel (pentane/ether) gave the thiophene compound **19** (45%).

IR (film, cm^{-1}): 3 060, 1 630, 1 435, 930, 910.

^{1}H NMR (250 MHz, CDCl$_3$) δ: 6.62–6.58 (m, 1H); 5.96–5.76 (m, 1H); 5.03–4.90 (m, 2H); 3.13 (dq, $J = 6.6$ and 1.2 Hz, 1H); 2.71–2.62 (m, 2H); 2.43–2.33 (m, 2H); 1.80–1.64 (m, 4H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 138.6 (s); 136.1 (d); 136.0 (s); 134.3 (s); 117.0 (d); 115.7 (t); 33.3 (t); 25.2 (t); 24.2 (t); 23.3 (t); 22.5 (t).

MS (CI, NH$_3$); m/z: 179 (M$^+$ + 1, 100).

Anal calc for C$_{11}$H$_{14}$S: C 74.10; H 7.91. Found: C 73.98; H 8.05.

4,4-Dimethylhept-5-yne-2-thione S-*oxide* **21a**

IR (film, cm^{-1}): 1 430, 1 360, 1 265, 1 110, 1 070, 1 060, 1 050.

^{1}H NMR (250 MHz, CDCl$_3$) (two isomers E/Z = 65:35) δ: 2.92 (s, 2H, Z); 2.47 (s, 3H + 2H, E); 2.25 (s, 3H, Z); 1.78 and 1.78 (2s, 3H); 1.30 (s, 6H, Z); 1.22 (s, 6H, E).

Δ_{EuFOD}: 2.47 (s, 5H) → 2.62 (s, 3H) ($\Delta = 0.15$) and 2.53 (s, 2H) ($\Delta = 0.06$).

After standing at −18 °C for 3 weeks, the ^{1}H NMR spectrum showed the presence of only E-isomer.

^{13}C NMR (62 MHz, CDCl$_3$) δ: 192.9 and 192.5 (s); 85.6 and 84.6 (s); 77.8 and 76.7 (s); 43.7 and 42.6 (t); 31.5 and 31.0 (s); 29.73 and 29.68 (q); 17.6 (q); 16.7 (q); 3.2 and 3.1 (q).

MS (CI, NH$_3$); m/z: 171 (M$^+$ + 1; 43); 155 (16); 139 (28); 121 (20); 81 (100).

Anal calc for C$_9$H$_{14}$OS: C 63.49; H 8.29. Found: C 63.61; H 8.13.

4,4-Dimethyl-6-phenylhex-5-yne-2-thione S-*oxide* **21b**

IR (film, cm^{-1}): 2 240, 1 700, 1 595, 1 440, 1 360, 1 110, 1 070, 910.

^{1}H NMR (250 MHz, CDCl$_3$) (two isomers E/Z = 85:15) δ: 7.42–7.32 (m, 5H); 7.32–7.24 (m, 5H, E); 3.05 (s, 2H); 2.57 (s, 2H, E); 2.52 (s, 3H, E); 2.28 (s, 3H); 1.41 (s, 6H); 1.33 (s, 6H, E).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 192.7 (s); 131.4 (d); 128.3 (d); 128.0 (d); 123.0 (s); 95.0 (s); 82.7 (s); 43.8 (t); 32.2 (s); 29.6 (q); 17.8 (q).

MS (CI, NH$_3$); m/z: 218 (42); 201 (100); 185 (14); 143 (52). (There were no peak at M$^+$, M$^+$ + 1, or M$^+$ + 18).

3,3-Dimethyl-1-phenylhex-4-yne-1-thione S-*oxide* **21c**

IR (film, cm^{-1}): 2 220, 1 675, 1 445, 1 380, 1 360, 1 115, 1 080, 1 075.

^{1}H NMR (250 MHz, CDCl$_3$) (two isomers E/Z = 92:8) δ: 7.54–7.36 (m, 5H); 2.83 (s, 2H, E); 2.6 (s, 2H, Z); 1,57 (s, 3H); 1,14 (s, 6H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 184.4 (s); 133.5 (s); 130.5 (d); 128.3 (d); 127.8 (d); 84.5 (s); 79.0 (s); 40.9 (t); 32.4 (s); 29.9 (q); 3.2 (q).

MS (CI, NH$_3$); m/z: 250 (M$^+$ + 18, 45); 233 (M$^+$ + 1, 100); 217 (46); 138 (30).

Anal calc for C$_{14}$H$_{16}$OS: C 72.37; H 6.94. Found: C 72.29; H 7.03.

1-Phenyl-2-[1-(prop-1-ynyl)cyclohexyl]ethane-1-thione S-*oxide* **21d**

IR (film, cm^{-1}): 2 220, 1 680, 1 600, 1 450, 1 090, 1 070.

^{1}H NMR (250 MHz, CDCl$_3$) (two isomers E/Z = 95:5) δ: 7.52–7.38 (m, 5H); 2.81 (s, 2H, E); 2.63 (s, 2H, Z); 1.68–1.48 (m, 8H); 1.62 (s, 3H); 1.24–1.10 (m, 2H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 183.9 (s); 133.9 (s); 130.4 (d); 128.2 (d); 127.8 (d); 82.3 (s); 81.7 (s); 41.1 (t); 38.4 (t); 38.2 (s); 25.7 (t); 23.0 (t); 3.2 (q).

MS (CI, NH_3); m/z: 290 (M^+ + 18; 23); 273 (M^+ + 1; 83); 257 (100); 241 (27); 225 (29).

Anal calc for $C_{17}H_{20}OS$: C 74.96; H 7.40. Found: C 75.04; H 7.31.

4-(Ethenylidene)nonane-2-thione S-*oxide*

The reaction of methyl octa-1,2-dienesulfinate with prop-2-enylmagnesium bromide was carried out following the general procedure and after the usual work-up gave a crude product with the following data:

IR (film, cm^{-1}): 1 950, 1 450–1 425, 1 080, 850.

^1H NMR (80 MHz, $CDCl_3$) (two isomers $E/Z \approx 75{:}25$) δ: 4.90–4.63 (m, 2H); 3.54–3.35 and 3.08–2.94 (2m, 2H); 2.26 and 2.01 (2s, 3H); 2.15–1.70 (m, 2H); 1.58–1.10 (m, 6H); 1.03–0.78 (m, 3H).

Purification by flash chromatography on silica gel (pentane/ether) gave *4-(ethenylidenyl)nonan-2-one* (19%).

IR (film, cm^{-1}): 1 950, 1 710, 1 350, 1 160, 950.

^1H NMR (250 MHz, $CDCl_3$) δ: 4.78–4.71 (m, 2H); 3.03 (t, J = 2.3 Hz, 2H); 2.18 (s, 3H); 1.94 (tt, J = 7 and 3.5 Hz, 2H); 1.5–1.18 (m, 6H); 0.88 (t, J = 6.8 Hz, 3H)

^{13}C NMR (62 MHz, $CDCl_3$) δ: 207.1 (s); 206.6 (s); 97.6 (s); 75.8 (t); 48.1 (t); 31.8 (t); 31.4 (t); 29.1 (q); 27.0 (t); 22.5 (t); 14.0 (q).

MS (CI, NH_3); m/z: 183 (M^+ + 17; 100); 181 (84); 167 (M^+ + 1; 41).

1-(Ethenylsulfinyl)-3-methylbuta-1,2-diene **20e**

This compound, present in the mixture **20e**:**21e**:**22a** (entry 24), showed the following characteristic data:

^1H NMR (250 MHz, $CDCl_3$) δ: 6.67 (dd, J = 16.5 and 9.5 Hz, 1H); 6.10 (d, J = 16.5 Hz, 1H); 5.93 (d, J = 9.5 Hz, 1H); 5.88–5.73 (m, 1H).

[(2-Ethenylsulfinyl)ethenylidene]cyclohexane **20h**

This compound, present in the mixture **20h**:**22d** (entry 27), showed the following characteristic data:

^1H NMR (250 MHz, $CDCl_3$) δ: 6.68 (dd, J = 16 and 10 Hz, 1H); 6.10 (d, J = 16 Hz, 1H); 5.94 (d, J = 10 Hz, 1H); 5.87–5.80 (m, 1H); 2.40–2.10 (m, 4H); 1.84–1.40 (m, 6H).

3,3-Dimethylpent-4-ynethial S-*oxide* **21e**

This compound, present in the mixture **21e**:**22a** (entry 24′), showed the following characteristic data:

^1H NMR (250 MHz, $CDCl_3$) δ: 8.39 (t, J = 7.94 Hz, 1H); 2.90 (d, J = 7.94 Hz, 2H); 1.25 (s, 6H).

3,3-Dimethylhex-4-ynethial S-*oxide* **21f**

The crude mixture obtained (entry 25) was separated by flash chromatography affording the pure sulfine **21f**:

IR (film, cm^{-1}): 1 450, 1 385, 1 365, 1 135, 1 070, 1 050, 960.

^1H NMR (250 MHz, $CDCl_3$) δ: 8.36 (t, J = 7.85 Hz, 1H); 2.84 (d, J = 7.85 Hz, 2H); 1.78 (s, 3H); 1.25 (s, 6H).

Data for the E isomer δ: 8.9 (t, J = 8 Hz, 1H); 2.42 (d, J = 8 Hz, 2H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 175.3 (d); 93.9 (s); 84.2 (s); 39.1 (t); 34.9 (s); 29.2 (q); 3.5 (q).

3,3-Dimethylhept-4-ynethial S-*oxide* **21g**

The crude mixture (entry 26) was separated by flash chromatography affording the pure sulfine **21g**:

IR (film, cm^{-1}): 1 450, 1 385, 1 365, 1 320, 1 135, 1 050, 950.

^1H NMR (250 MHz, $CDCl_3$) δ: 8.34 (t, J = 7.9 Hz, 1H); 2.84 (d, J = 7.9 Hz, 2H); 2.16 (q, J = 7.4 Hz, 2H); 1.24 (s, 6H); 1.1 (t, J = 7.4 Hz, 3H).

Data for the E isomer δ: 8.91 (t, J = 8 Hz, 1H); 2.41 (d, J = 8 Hz, 2H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 175.4 (d); 94.0 (s); 84.4 (s); 39.2 (t); 34.9 (s); 29.6 (q); 13.7 (t); 12.2 (q).

3,3-(Pentane-1,5-diyl)pent-4-ynethial S-*oxide* **21h**

The crude mixture (entry 27′) was separated by flash chromatography affording the pure sulfine **21h**.

IR (film, cm^{-1}): 2 200, 1 450, 1 140, 1 090, 1 075, 950.

^1H NMR (250 MHz, $CDCl_3$) δ: 8.40 (t, J = 7.92 Hz, 1H); 2.87 (d, J = 7.92 Hz, 2H); 2.24 (s, 1H); 1.87–1.42 (m, 4H); 1.42–1.00 (m, 6H).

Data for the E isomer δ: 8.88 (t, J = 8 Hz, 1H); 2.55 (d, J = 8 Hz, 2H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 174. 3 (d); 93.7 (s); 87.4 (d); 38.3 (t); 37.3 (s); 25.5 (t); 22.7 (t).

MS (CI, NH_3); m/z: 382 ($2M^+$ + 18, 100); 364 ($2M^+$, 1); 200 (M^+ + 18, 7); 183 (M^+ + 1, 2).

3,3-(Pentane-1,5-diyl)hex-4-ynethial S-*oxide* **21i**

The crude mixture (entry 28) was separated by flash chromatography affording the pure sulfine **21i**.

IR (film, cm^{-1}): 2 240, 1 450, 1 140, 1 090, 1 075, 950.

^1H NMR (250 MHz, $CDCl_3$) δ: 8.42 (t, J = 7.89 Hz, 1H); 2.85 (d, J = 7.89 Hz, 2H); 1.84 (s, 3H); 1.78–1.48 (m, 8H); 1.32–1.02 (m, 2H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 175.3 (d); 82.3 (s); 79.0 (s); 38.7 (t); 36.9 (s); 25.7 (t); 22.6 (t); 3.4 (q).

3,3-Dimethyl-5-phenylpent-4-ynethial S-*oxide* **21j**

The crude mixture (entry 29) was separated by flash chromatography affording the pure sulfine **21j**.

IR (film, cm^{-1}): 2 240, 1 720, 1 600, 1 440, 1 360, 1 130, 920.

^1H NMR (250 MHz, $CDCl_3$) δ: 8.43 (t, J = 7.94 Hz, 1H); 7.47–7.36 (m, 2H); 7.36–7.27 (m, 3H); 2.99 (d, J = 7.94 Hz, 2H); 1.40 (s, 6H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 174.7 (d); 131.6 (d); 128.3 (d); 128.0 (d); 123.1 (s); 94.5 (s); 81.7 (s); 43.2 (t); 35.0 (s); 29.0 (q).

MS (CI, NH_3); m/z: 236 (M^+ + 18; 17); 219 (M^+ + 1; 2); 204 (100); 187 (9).

3,4-Bis-(2,2-dimethylbut-3-ynyl)-1,2-dithietane 1,1-dioxide **22a**

The flash chromatography (entry 24″) gave a fraction containing a mixture (*cis*/*trans* 5:95) of the two isomers of compound **22a**. Crystallization from ether/pentane gave the pure *trans* isomer; mp = 104.5–105 °C.

IR (KBr, cm^{-1}): 3 300, 3 280, 1 385, 1 365, 1 315, 1 135, 870, 570, 530, 460.

^1H NMR (250 MHz, $CDCl_3$) δ: (*trans* isomer): 5.21 (ddd, J = 9.3, 9.3 and 1.5 Hz, 1H); 3.64 (ddd, J = 9, 9 and 2 Hz, 1H); 2.57 (dd, J = 15.3 and 9.3 Hz, 1H); 2.23 (s, 1H); 2.22 (s, 1H); 2.18–1.94 (m, 2H); 1.78 (dd, J = 15.3 and 1.83 Hz, 1H); 1.32 (s, 3H); 1.30 (s, 3H); 1.28 (s, 3H); 1.23 (s, 3H).

Data for *cis* isomer δ: 5.87 (ddd, J = 6.5, 6.5 and 2.8 Hz, 1H); 4.01 (ddd, J = 6.5, 6.5 and 2.8 Hz, 1H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 94.2 (d); 89.3 (s); 88.8 (s); 71.6 (d); 70.2 (d); 47.4 (t); 42.7 (t); 34.4 (d); 30.6 (s); 30.1 (s); 29.8 (q); 29.1 (q); 28.7 (q); 27.8 (q).

MS (CI, NH$_3$); *m/z*: 302 (M$^+$ + 18, 100); 286 (M$^+$ + 2, 1); 223 (47); 218 (42); 191 (44).

Anal calc for $C_{14}H_{20}O_2S_2$: C 59.16; H 7.04. Found: C 59.29; H 7.06.

3,4-Bis-(2,2-dimethylpent-3-ynyl)-1,2-dithietane 1,1-dioxide **22b**

Flash chromatography (entry 25′) gave a fraction containing a mixture of the two isomers (*cis/trans* = 15:85) of compound **22b**, which was crystallized from ether/pentane affording pure *trans* compound mp = 94–95.5 °C.

IR (KBr, cm^{-1}): 2 240, 1 315, 1 305, 1 140, 720, 565.

^{1}H NMR (250 MHz, CDCl$_3$) δ: (*trans* isomer): 5.16 (ddd, J = 9.35, 9.35 and 1.8 Hz, 1H); 3.54 (ddd, J = 9.35, 9.35 and 2.5 Hz, 1H); 2.55 (dd, J = 15.2 and 9.35 Hz, 1H); 2.10–1.86 (m, 2H); 1.80 (s, 3H); 1.77 (s, 3H); 1.67 (dd, J = 15.2 and 2.5 Hz, 1H); 1.27 (s, 3H); 1.26 (s, 3H); 1.23 (s, 3H); 1.22 (s, 3H).

Data for *cis* isomer δ: 5.83 (ddd, J = 9, 9 and 3.5 Hz, 1H); 3.96 (ddd, J = 9, 9 and 3.5 Hz, 1H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 94.4 (d); 84.2 (s); 80.0 (s); 77.9 (s); 47.7 (t); 43.7 (t); 35.1 (d); 30.7 (s); 30.3 (s); 30.2 (q); 29.9 (q); 28.8 (q); 28.3 (q); 3.3 (q).

MS (CI, NH$_3$); *m/z*: 330 (M$^+$ + 18, 100); 313 (M$^+$ + 1, 3); 251 (8); 234 (25); 217 (5); 81 (33).

Anal calc for $C_{16}H_{24}O_2S_2$: C 61.54; H 7.69. Found: C 61.39; H 7.78.

3,4-Bis-(2,2-dimethylhex-3-ynyl)-1,2-dithietane 1,1-dioxide **22c**

Obtained as a mixture (*cis/trans* 10:90) after flash chromatography (entry 26) and purified by crystallization from ether/pentane, mp = 73–73.5 °C.

IR (KBr, cm^{-1}): 2 215, 1 450, 1 390, 1 370, 1 315, 1 295, 1 140, 720, 580.

^{1}H NMR (250 MHz, CDCl$_3$) δ; (*trans* isomer): 5.17 (ddd, J = 9, 9 and 2.4 Hz, 1H); 3.54 (ddd, J = 9, 9 and 2.4 Hz, 1H); 2.54 (dd, J = 15.25 and 9.3 Hz, 1H); 2.24–2.07 (m, 4H); 2.06–1.85 (m, 2H); 1.73–1.58 (m, 1H); 1.25 (s, 3H); 1.23 (s, 3H); 1.20 (s, 6H); 1.12 (t, J = 7.5 Hz, 3H); 1.11 (t, J = 7.5 Hz, 3H).

Data for *cis* isomer δ: 5.82 (ddd, J = 9, 9 and 3.5 Hz, 1H); 3.95 (ddd, J = 9, 9 and 2 Hz, 1H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 94.0 (d); 85.7 (s); 84.5 (s); 83.9 (s); 83.6 (s); 47.8 (t); 43.3 (t); 34.9 (d); 30.6 (s); 30.3 (s); 30.2 (q); 30.0 (q); 28.5 (q); 28.4 (q); 14.2 (t); 13.7 (t); 12.4 (q); 12.2 (q).

Data for *cis* isomer δ: 91.3 (d); 43.9 (t); 40.0 (t); 33.5 (d).

MS (CI NH$_3$); *m/z*: 358 (M$^+$ + 18, 100); 341 (M$^+$ + 1, 3); 277 (4); 262 (37).

Anal calc for $C_{18}H_{28}O_2S_2$: C 63.53; H 8.23. Found: C 63.44; H 8.25.

3,4-Bis-([2,2-(pentane-1,5-diyl)but-3-ynyl]-1,2-dithietane 1,1-dioxide **22d**

Obtained as a mixture (*cis/trans* 15:85) after flash chromatography (entry 27′) and purified by crystallization from ether/pentane, mp = 126–128 °C.

IR (KBr, cm^{-1}): 2 100, 1 445, 1 315, 1 305, 1 140, 1 130, 710, 570.

^{1}H NMR (250 MHz, CDCl$_3$) δ: (*trans* isomer): 5.25 (ddd, J = 9.5, 9.5 and 1.7 Hz, 1H); 3.68 (ddd, J = 9.5, 9.5 and 2.2 Hz, 1H); 2.54 (dd, J = 15.4 and 9.5 Hz, 1H); 2.28 (s, 1H); 2.26 (s, 1H); 2.20–1.89 (m, 2H); 1.89–1.33 (m, 14H); 1.33–0,92 (m, 7H).

Data for *cis* isomer δ: 5.73 (ddd, J = 9, 9 and 4 Hz; 1H); 4.07 (ddd, J = 9, 9 and 2.2 Hz, 1H);

^{13}C NMR (62 MHz, CDCl$_3$) δ: 93.7 (d); 87.5 (s); 87.1 (s); 73.7 (d); 72.4 (d); 47.4 (t); 42.7 (t); 38.1 (t); 37.4 (t); 36.1 (s); 36.0 (s); 35.7 (t); 33.7 (d); 25.7 (t); 25.4 (t); 22.8 (t); 22.6 (t); 22.5 (t).

MS (CI NH$_3$); *m/z*: 382 (M$^+$ + 18, 100); 301 (3); 261 (1).

Anal calc for $C_{20}H_{28}O_2S_2$: C 65.93; H 7.69. Found: C 65.98; H 7.75.

3,4-Bis-[2,2-(pentane-1,5-diyl)pent-3-ynyl]-1,2-dithietane 1,1-dioxide **22e**

Obtained as a mixture (*cis/trans* 15:85) after flash chromatography (entry 28) and purified by crystallization from ether/pentane, mp = 141–142 °C.

IR (KBr, cm^{-1}): 2 100, 1 445, 1 310, 1 300, 1 130, 945, 580.

^{1}H NMR (250 MHz, CDCl$_3$) δ: (*trans* isomer): 5.2 (ddd, J = 9, 9 and 1.7 Hz, 1H); 3.58 (ddd, J = 9, 9 and 1.7 Hz, 1H); 2.33 (dd, J = 15.3 and 9.2 Hz, 1H); 2.11–1.86 (m, 2H); 1.86–1.45 (m, 14H); 1.83 (s, 3H); 1.79 (s, 3H); 1.29–1.00 (m, 7H).

Data for *cis* isomer δ: 5.85 (ddd, J = 9, 9 and 3.15 Hz, 1H); 3.99 (ddd, J = 9, 9 and 2.1 Hz, 1H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 93.4 (d); 82.3 (s); 82.0 (s); 81.96 (s); 79.6 (s); 47.6 (t); 43.3 (t); 38.6 (t); 38.3 (t); 37.2 (t); 36.8 (t); 36.0 (s); 35.7 (s); 34.1 (d); 25.9 (t); 25.6 (t); 22.9 (t); 22.8 (t); 22.7 (t); 3.6 (q); 3.5 (q).

MS (CI, NH$_3$); *m/z*: 391 (M$^+$ − 1; 1); 329 (21); 314 (100); 281 (20); 121 (53).

Anal calc for $C_{22}H_{32}O_2S_2$: C 67.30; H 8.22. Found: C 67.37; H 8.09.

3,4-Bis-(2,2-dimethyl-4-phenylbut-3-ynyl)]-1,2-dithietane 1,1-dioxide **22f**

Obtained as a mixture (*cis/trans* 15:85) after flash chromatography (entry 29).

^{1}H NMR (250 MHz, CDCl$_3$) δ: (*trans* isomer): 7.51–7.34 (m, 4H); 7.33–7.22 (m, 6H); 5.26 (ddd, J = 9, 9 and 1.6 Hz, 1H); 3.66 (ddd, J = 9, 9 and 2.2 Hz, 1H); 2.66 (dd, J = 15.4 and 9 Hz, 1H); 2.5 (d, J = 3 Hz, 1H); 2.4–2.22 (m, 2H); 1.90 (dd, J = 15.42 and 1.4 Hz; 1H); 1.41 (s, 3H); 1.40 (s, 3H); 1.31 (s, 3H); 1.30 (s, 3H).

Data for *cis* isomer δ: 5.91 (ddd, J = 9, 9 and 3 Hz, 1H) 4.08 (ddd, J = 9, 9 and 2.5 Hz, 1H).

^{13}C NMR (62 MHz, CDCl$_3$) δ: 131.6 (d); 131.5 (d); 128.3 (d); 128.2 (d); 128.1 (s); 94.5 (s); 94.1 (d); 93.7 (s); 84.0 (s); 82.3 (s); 47.7 (t); 43.1 (t); 35.1 (d); 31.3 (q); 30.9 (s); 30.1 (s); 29.8 (q); 29.6 (q); 28.2 (q).

MS (CI, NH$_3$); *m/z*: 454 (M$^+$ + 18, 100); 437 (M$^+$ + 1, 2); 371 (1); 358 (11); 143 (16).

Phenylmethyl thiocyanate

A solution of *S*-phenylmethyl benzenethiosulfonate [28] (0.528 g, 2 mmol) in THF (10 mL) was added to a solution of lithium cyanide [29] (0.066 g, 2 mmol) in THF (15 mL) at 0 °C. A white precipitate was formed and the resulting suspension was stirred at 0 °C for 30 min then at room temperature for 3.5 h. The usual work-up gave phenylmethyl thiocyanate (0.289 g, 97%).

^{1}H NMR (80 MHz, CDCl$_3$) δ: 7.36 (s, 5H); 4.15 (s, 2H).

4,4,9,9-Tetramethyldodec-6-ene-2,10-diyne **28a**

A solution of pure *trans* compound **22b** (0.156 g, 0.5 mmol) in THF (2.5 mL) was added to a 0.5 M solution of lithium cyanide (3 mL, 1.5 mmol) at 0 °C and the mixture stirred at 0 °C for 30 min then at room temperature for 4 h. Water (10 mL) was then added, the aqueous layer was extracted with ether (3 × 40 mL), and the extracts were washed with water (5 mL). The usual work-up gave a crude product with was purified by flash chromatography (silica gel, pentane/ether, 100:0 to 50:50), affording the compound **28a** (0.097 g, 90%) with E/Z ratio 8:92 (capillary gas chromatography, the E isomer having the lowest retention time).

IR (film, cm^{-1}): 2 050, 1 450, 1 470, 1 380, 1 360, 1 050, 855.

^1H NMR (250 MHz, $CDCl_3$) δ: 5.75–5.65 (m, 2H); 2.14 (d, J = 5 Hz, 4H); 1.78 (s, 6H); 1.16 (s, 12H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: (Z isomer): 128.1 (d); 86.5 (s); 75.1 (s); 40.9 (t); 31.2 (s); 29.1 (q); 29.0 (q); 3.42 (q).

Data for E isomer δ: 129.6 (d); 46.7 (t); 31.1 (s).

MS (CI, NH_3); m/z: 234 (M^+ + 18, 100); 217 (M^+ + 1, 13); 201 (11); 160 (8); 135 (7).

Anal calc for $C_{16}H_{24}$: C 88.88; H 11.11. Found: C 88.71; H 11.29.

5,5,10,10-Tetramethyltetradec-7-ene-3,11-diyne **28b**

IR (film, cm^{-1}): 1 450, 1 380, 1 360, 1 320 (s), 1 050, 840.

^1H NMR (250 MHz, $CDCl_3$) δ: *5.75–5.65* (m, 2H); 5.59–5.53 (m, 2H); 2.22–2.09 (m, 8H); 1.15 (s, 12H); 1.1 (t, J = 7 Hz, 6H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 129.6 (d); *128.1* (d); 86.8 (s); *86.7* (s); 81.3 (s); 46.7 (t); *41.0* (t); *31.1* (s); 31.0 (s); *29.2* (q); 29.1 (q); 14.4 (t); 12.3 (q).

MS (CI NH_3); m/z: 262 (M^+ + 18, 33); 244 (M^+, 2); 243 (M^+ + 1, 3); 229 (33); 215 (100); 159 (44); 185 (53).

Anal calc for $C_{18}H_{28}$: C 88.52; H 11.47. Found: C 87.96; H 11.72.

3,3:8,8-Bis(pentane-1,5-diyl)dec-5-ene-1,9-diyne **28c**

IR (film, cm^{-1}): 3 300, 2 100, 1 450, 625 (s).

^1H NMR (250 MHz, $CDCl_3$) δ: *5.83–5.70* (m, 2H); 5.66–5.58 (m, 2H); 2.19 (d, J = 5 Hz, 4H); 2.16 (s, 2H); 1.84–1.50 (m, 12H); 1.29–1.03 (m, 8H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 128.8 (d); *127.4* (d); 89.6 (s); *70.4* (d); 70.2 (d); 46.0 (t); *40.5* (t); 37.3 (t); 36.7 (s); 26.0 (t); 22.9 (t).

MS (CI NH_3); m/z: 286 (M^+ + 18, 5); 269 (M^+ + 1, 100).

Anal calc for $C_{20}H_{28}$: C 89.55; H 10.45. Found: C 89.42; H 10.55.

4,4:9,9-Bis(pentane-1,5-diyl)dodec-6-ene-2,10-diyne **28d**

Mp = 73,5–74 °C (ether/pentane).

IR (KBr, cm^{-1}): 1 440, 1 340, 1 320, 630 (s).

^1H NMR (250 MHz, $CDCl_3$) δ: *5.79–5.68* (m, 2H); 5.63–5.54 (m, 2H); 2.14 (d, J = 4.8 Hz, 4H); 1.83 (s, 6H); 1.76–1.47 (m, 16H); 1.23–1.02 (m, 4H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 127.6 (d); 84.3 (s); 77.6 (s); 40.9 (t); 37.7 (t); 36.8 (s); 26.2 (t); 23.1 (t); 3.54 (q).

MS (CI, NH_3); m/z: 314 (M^+ + 18, 100); 297 (M^+ + 1, 9); 121 (11).

Anal calc for $C_{22}H_{32}$: C 89.19; H 10.81. Found: C 89.25; H 10.72.

Ethyl 3-{1-[4-(1-ethynylcyclohexyl)but-2-enyl]cyclohexyl} prop-2-ynoate **29**

A 0.95 M solution of n-butyllithium (1.05 mL, 1 mmol) was slowly added to a solution of compound **28c** (0.268 g, 1 mmol) in THF at −78 °C. After stirring at −78 °C for 10 min, the cooling bath was removed and the mixture warmed to room temperature. After cooling at −78 °C, ethyl chloroformate (0.162 g, 0.14 mL, 1.5 mmol) was added then the cooling bath removed and the mixture stirred while warming to room temperature. Water (2 mL) was added; extraction with ether (3 × 15 mL) and the usual work-up gave a mixture which was separated by flash chromatography (silica gel, pentane/ether = 100:0 to 98:2). Starting compound **28c** (0.080 g, 30%) and ester **29** (0.098 g, 29%) were obtained.

IR (film, cm^{-1}): 3 020, 2 220, 1 710, 1 450, 1 360.

^1H NMR (250 MHz, $CDCl_3$) δ: 5.85–5.60 (m, 2H); 4.23 (q, J = 7.21 Hz, 2H); 2.26 (d, J = 6.67 Hz, 2H); 2.20 (d, J = 6.53 Hz, 2H); 2.16 (s, 1H); 1.91–1.50 (m, 16H); 1.30–1.08 (m, 4H); 1.33 (t, J = 7.21 Hz, 3H).

^1H NMR (400 MHz, $CDCl_3$) δ: with irradiation of the allylic hydrogens (2.26 and 2.20): 5.81 (dtt, J = 11, 7 and 1 Hz, 1H); 5.72 (dtt, J = 11, 7 and 1 Hz, 1H); 4.22 (q, J = 7 Hz, 2H); 2.28 (dd, J = 7 and 1 Hz, 2H); 2.22 (dd, J = 7 and 1 Hz, 2H); 2.19 (s, 1H); 1.90–1.70 (m, 4H); 1.70–1.50 (m, 10H); 1.32 (t, J = 7 Hz, 3H); 1.30–1.10 (m, 6H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 158.9 (s); 128.2 (d); 126.4 (d); 93.8 (s); 89.4 (s); 76.9 (s); 70.5 (d); 61.6 (t); 40.4 (t); 39.7 (t); 37.3 (t); 37.2 (s); 36.7 (t); 25.7 (t); 25.6 (t); 22.9 (t); 22.8 (t); 14.0 (q).

MS (CI, NH_3); m/z: 358 (M^+ + 18, 12); 341 (M^+ + 1, 11); 295 (53); 267 (100); 161 (47); 105 (23).

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