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Diastereoselectivity of the Thio-Claisen Rearrangement of Acyclic Precursors bearing a Chiral Centre Adjacent to Carbon 6

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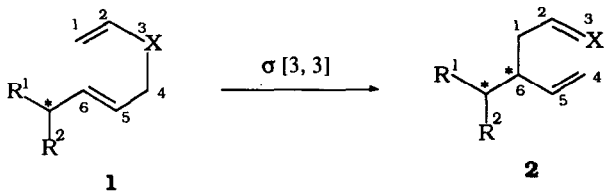
Abstract. *A number of chiral allylic alcohols have been prepared and submitted to a Mitsunobu reaction with dithioacetic acid. Allyl dithioesters were deprotonated by LDA at -30°C and resulting enethiolates were quenched with iodomethane to afford quantitatively S-allyl ketenedithioacetals. These precursors undergo a thio-Claisen rearrangement under smooth conditions: room temperature or heating at 101°C. The diastereoselectivity of this sigmatropic shift was examined with respect to the nature of the two substituents at the stereogenic centre. With a methyl and a tert-butyl group a 75 : 25 ratio was observed and interpreted by steric hindrance. With various alkoxy groups we have observed a very modest selectivity in favour of the* ***syn*** *diastereoisomer.*

The Claisen rearrangement is frequently used for the creation of carbon-carbon bonds (1-5). Its stereoselectivity led to many applications especially in natural product synthesis (5-10). Most of the examples reported in the acyclic series deal with stereochemical elements which are part of the pericyclic nucleus (1, 5, 8). We wished to study the rearrangement of precursors, such as **1**, bearing a chiral centre adjacent to carbon 6. Few examples have been reported so far (11-18). A model based on electronic effects has been proposed by Kahn and Hehre (19). We considered our study in the sulfur series (20-22) because:

i) neutral precursors are readily available by S-allylation of metallated dithioesters (20, 23-26).

ii) the thio-Claisen transposition occurs under mild conditions (22).



1 **2**

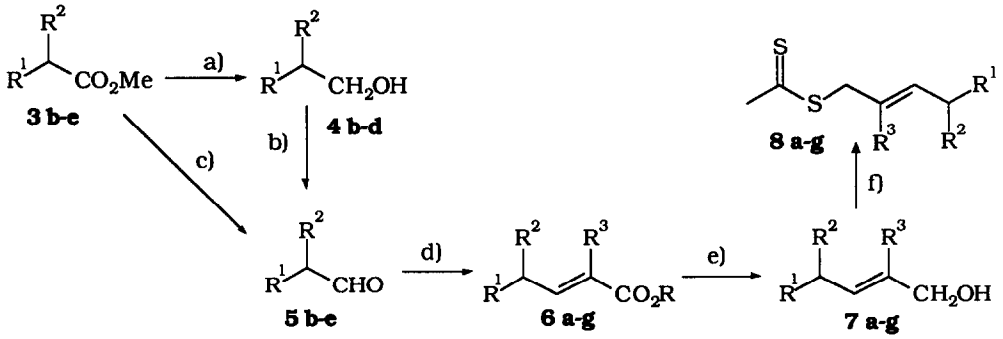
Scheme 1

During our recent work (26, 27) and a parallel study by Beslin and Perrio (25, 28), the behaviour of precursors bearing a stereogenic centre adjacent to carbon 1 was examined. It was shown that the sulfur rearrangement proceeds with diastereocontrol based either on steric or electronic effects.

We wish to report our results on compounds like **1** with alkyl, aryl or alkoxy groups as R^1 and R^2. Allylated dithioesters were obtained with various selectivities.

Results

The starting materials are esters **3** bearing two different R^1 and R^2 groups on the carbon α to the carbonyl. Racemic compounds were used when R^1 = Me and R^2 = Ph or *t*-Bu and enantiomerically pure materials were used when R^2 was alkoxy derivative.

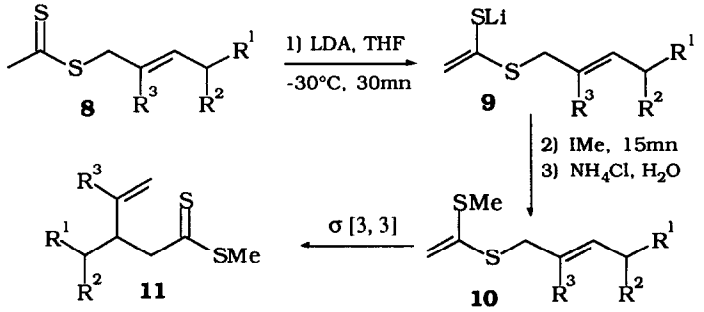


a) $LiAlH_4$, THF, RT. b) Swern oxydation. c) DIBALH, n-hexane, -78°C, 30 mn.
d) Wittig-Horner reaction. e) AlH_3, THF, 0°C, 3h.
f) PPh_3, $iPrCO_2N{=}NCO_2iPr$, $MeCS_2H$, THF, 0°C.

Scheme 2

Two routes provided aldehydes **5**. The first one involved reduction of esters into alcohols **4** with lithium aluminium hydride followed by Swern oxidation. In one case selective reduction of ester **3c** to aldehyde **5c** was achieved with DIBALH (29). Wittig-Horner type reactions of the sodium derivatives of phosphonoacetates or propionoate with aldehydes **5** led easily to unsaturated carboxylic esters **6**, mainly with *E* configuration. Selective 1,2-reduction was achieved (30) with AlH_3, prepared *in situ* by the reaction of $LiAlH_4$ with $AlCl_3$. Allylic alcohols **7** were converted to allyl dithioesters **8** with the aid of a Misunobu type reaction using dithioacetic acid. This method was recently reported by our group (31).

In connection with the high acidity of protons α to a thiocarbonyl group (32), dithioacetates **8** were easily deprotonated. LDA was used in THF at -30°C. Quenching the resulting mixture with iodomethane provided quantitatively S-allyl ketenedithioacetals **10**, arising from S-alkylation of enethiolates **9**.

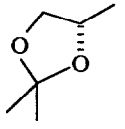


Scheme 3

^{1}H NMR reveals that ketenedithioacetals **10** are accompanied by a minor amount of dithioesters **11**. The [3,3] sigmatropic transposition was completed by letting the mixtures stand at room temperature for several days or by heating under reflux with methylcyclohexane (101°C) for some hours. Allyl dithioacetates **11** were obtained in modest to good yields (table 1).

Let us first examine the case of carbon chains as R^1 and R^2. When R^2 is a phenyl group and R^1 is a methyl (entry 1) the ratio of diastereoisomers is 70 : 30. With a *tertio*-butyl group as R^2 we obtained a 75 : 25 isomeric ratio. So, the selectivity increases with the hindrance of the R^2 group.

Table 1

Entry	R^1	R^2	R^3	C=C Configuration	Product **11**	Ratio of diastereoisomers	Yield %
1	Me	Ph	H	*E*	**11a**	70 : 30	30
2	Me	tBu	H	*E*	**11b**	75 : 25	45
3	Me	OMEM	H	*E*	**11c**	54 : 46	76
4	Me	OCH_2Ph	H	*E*	**11d**	53 : 47	66
5	Me	$OSiMe_2tBu$	H	*E*	**11e**	66 : 34	45
6			H	*E*	**11f**	65 : 35	65
7	Me	OCH_2Ph	Me	*E / Z = 50 : 50*	**11g**	61 : 39	84
8	Me	OCH_2Ph	Me	*E*	**11g**	61 : 39	53
9	Me	OCH_2Ph	Me	*Z*	**11g**	60 : 40	22

As a second series we examined homochiral examples bearing a heteroatomic group linked to carbon 1 of the pericyclic nucleus. Dithioesters **9c-9f** having an alkoxy or a silyloxy substituent as R^2 and generally a methyl group as R^1 were synthesized. We were surprised to observe that compounds **11c-11f**, obtained by rearrangement, exhibit very modest isomeric selectivities, generally around 60 : 40. Rather small variations of selectivity were attained by changing the nature of R^2: OMEM, $OSiMe_2tBu$, OCH_2Ph. We have assigned the ***syn*** relative configuration to the major isomer of dithioester **11f** by correlation with an analogous molecule (see below) and we propose that the preponderant isomers of similar compounds **11c 11g** have the same type of stereochemistry.

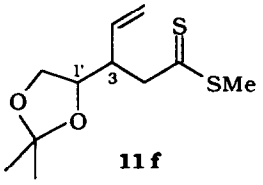
In order to enhance allylic strain and eventually increase the stereocontrol (33), a methyl group was placed as R^3 on the allylic double bond. For this series the starting unsaturated esters **6** could be isolated as pure ***E*** and ***Z*** isomers. The further reactions took place with retention of the allylic double bond configuration. Therefore we could submit pure ***E*** and ***Z*** ketenedithioacetals **10** separately. Unexpectedly, we observed that their thio-Claisen rearrangement proceeded with a very close stereochemical course, leading *ca* to 60 : 40 isomeric mixtures (Entry 7-9). This shows that the configuration of the carbon-carbon double bond has no influence on the stereoselectivity here.

Configurational Assignment

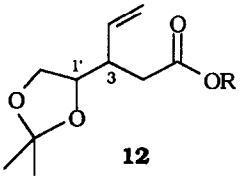
Isomeric dithioesters **11f** were correlated to two known molecules **12** in the oxygen series, having respectively 3*R*,1'*R* (*syn*) and 3*S*,1'*R* (*anti*) absolute configurations. Table 2 compares the ^{13}C NMR data reported for isomers **12** by Mulzer and co-workers (15) to our data.

Table 2

Entry	**12** (*syn*) 3*R*,1'*R*	**12** (*anti*) 3*S*,1'*R*	**11f** A major isomer	**11f** B minor isomer
1	25.3	25.0	25.1	24.7
2	26.6	26.1	26.3	25.8
3	44.8	42.6	49.2	47.4
4	60.1	60.3	52.5	52.4
5	67.8	66.5	67.2	66.3
6	77.4	77.1	77.0	76.7
7	109.2	109.0	109.0	108.6
8	117.5	117.5	117.8	118.0
9	136.4	136.0	135.1	134.5



11f



12

If we consider carbon shifts whose differences are superior to 0.2 ppm for the two isomers **12** we note that **12** ***syn*** values are all higher than **12** ***anti*** ones. Likewise all **11f** shifts of isomer **A** are higher than those of isomer **B**. Therefore we assign the ***syn*** relative configuration to the major isomer **A** of **11f**. Having started with an enantiomerically pure (4*S*)-ester **6** and assuming no change at this stereogenic centre, we assign a 3*S*,1'*S* structure to isomer **11f A**.

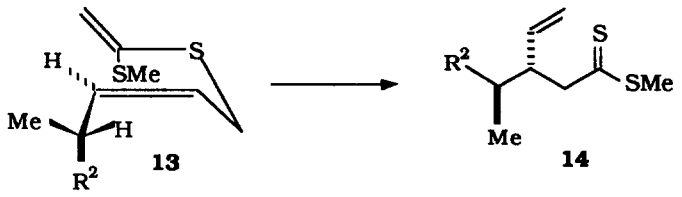
Discussion

The thio-Claisen rearrangement of ketenedithioacetals bearing substituted S-allyl groups has been achieved. For the first time in this sulfur series the sequence involves the use of unsaturated alcohols as a source of the allylic moiety. Deprotonation of allyl dithioesters and subsequent methylation provides requisite ketenedithioacetals under smooth conditions (-30°C). This stands in contrast with the reactions performed in the oxygen series: the orthoester method requires a temperature of at least 150°C for precursor synthesis.

Our first set of experiments carried out with R^1 = Me and R^2 = Ph, tBu shows us that the higher selectivity was observed with a *tert*-butyl group but that it is rather modest (75 : 25). We recently studied systems bearing the same substituents on a stereogenic centre adjacent to carbon 1 of the pericyclic nucleus. With a *tertio*-butyl and a methyl group (equivalent to **11b**) we reached a high degree of stereocontrol: 95 : 5.

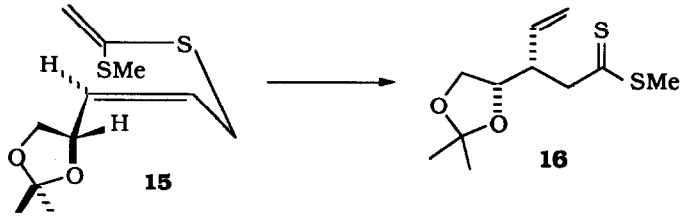
As a working hypothesis for our results we propose the following model (scheme 5) based on steric arguments. On the pseudo-cyclic chair transition state we place the substituents on the chiral centre as follows:

- the smallest group, hydrogen, is staggered with the C=C bond.
- the medium sized group, methyl, occupies the "outside" allylic staggered position.
- the largest group, *tertio*-butyl, is perpendicular to the C=C bond. The attack of the ketenedithioacetal moiety occurs antiperiplanear to this large R^2 group, thus leading to a predicted *anti* isomer **14**.



Scheme 4

The second series involved an alkoxy or silyloxy as R^2. Based on the configuration assignment of isomer **11f** and electrostatic arguments reported by Kahn and Hehre (19) we propose model **15**. The smallest group, hydrogen, is still located in a staggered position to the C-C double bond. The ketenedithioacetal moiety has a nucleophilic character. It will attack on the electronically deficient face of the allylic moiety. Therefore the OR group will occupy a position perpendicular to the C=C bond and delivery of the ketenedithioacetal part will occur on the side of the CH_2OR substituent of the stereogenic centre. Such a model leads to the formation of the ***syn*** isomer which was the major product experimentally observed.



Scheme 5

Despite the theoretical predictions of Kahn and Hehre which lead to the correct isomer, it must be stressed that the degree of control is not as high as expected. Variations of the nature of the alkoxy group did not lead to significant improvements. It is interesting to compare our observations with literature results in the oxygen series (table 3).

Table 3

Series	Method	C=C configuration	*syn* / *anti* ratio	References
Sulfur	-	*E*	65 : 35	This work
Oxygen	Orthoester	*E*	51 : 49	Mulzer (15)
-	-	*Z* or *E*	75 : 25	Suzuki (14)
-	-	*E*	68 : 32	Kametani (11)
-	-	*Z*	72 : 28	Kametani (11)
-	Ireland version	*Z* or *E*	58 : 42	Cha (12)

Various results have been reported, even for the same reaction conditions. The selection does not appear different in the sulfur series. Despite these modest selectivities this reaction is currently used for synthesis (11, 14, 15). A high stereocontrol has been attained only recently for a ketene Claisen rearrangement (18).

These results can also be compared to those of the thio-Claisen rearrangement of precursors bearing a stereogenic centre adjacent to carbon 1 of the pericyclic nucleus. Beslin and Perrio (25, 28) demonstrated that

introduction of a hydroxy group and a methyl leads to a high stereocontrol in favour of the *syn* isomer. The modest control in the carbon 6 substituted series let us think that electron donating groups are not suited for selectivity whereas electron withdrawing ones might be cooperative for this purpose.

Conclusion

We have reported the first study of steric effects of substituents of a chiral centre adjacent to carbon 6 of the pericyclic nucleus.

The selectivity of the thio-rearrangement of systems bearing various alkoxy groups was studied. Our results, as well as literature reports in the oxygen series, led to rather modest selectivities in favour of a *syn* isomer. Further series of compounds, for instance bearing electron withdrawing substituents, must now be tested.

EXPERIMENTAL SECTION

General

All reactions were run under a positive nitrogen pressure. THF was distilled over sodium benzophenone ketyl. Preparative liquid chromatographs were performed on a Jobin-Yvon Chromatospac Prep 10 chromatograph or by flash chromatography. The column was prepared with a suspension of silica gel in the eluting solvent: a mixture of cyclohexane and ethyl acetate in the ratio indicated below.

^{1}H NMR 60 MHz spectra were run on a Varian EM 360 spectrometer. The products were dissolved in the mentioned solvent. Only assigned data are reported. They are in order: chemical shift in ppm, multiplicity (s, singulet; d, doublet; t, triplet; q, quartet, hept, heptuplet; m, multiplet), coupling constant in hertz, assignment. ^{13}C NMR spectra were determined at 20,15 MHz with a Bruker WP 80 spectrometer operating with broad band ^{1}H decoupling. The solvent used is indicated below. IR absorption spectra were run on Perkin-Elmer 257 and 684. The compound was dissolved in CCl_4 or $CDCl_3$. Mass spectra were obtained at 70 eV with Varian Mat CH5 or with Nermag spectrometers and the data tabulated as m/e and relative intensities in percent. Elemental analyses were performed by Service Central d'Analyse of CNRS at Vernaison. The results are described as percentages. The rotational measurement were obtained with Roussel-Jourdan 130 IF polarimeter.

Starting materials

Methyl 3,3-dimethylbutanoate, methyl (*S*)-lactate, 2-phenylpropanal and ethyl (*E*)-(*S*)-(+)-3-(2,2-dimethyl-1,3-dioxolane-4-yl)-2-propenoate are commercial products

Ethanedithioic acid was obtained (34) from the reaction of methylmagnesium iodide (150 mmol) with carbon disulfide (9 ml, 150 mmol) in THF (250 ml) at RT for 18 hours. The mixture was quenched with hydrochloric acid. The product (5.67 g, 61 mmol) was isolated by distillation (Eb_{12} = 35°C). Yield: 41%.

2,3,3-Trimethylbutanal 5b. Methyl 3,3-dimethylbutanoate (5.54 ml, 30.7 mmol) was deprotonated (35) by LDA (30.7 mmol) in presence of HMPA (26.6 ml, 153 mmol). The reaction with iodomethane (3.8 ml, 61 mmol) gave methyl 2,3,3-trimethylbutanoate **3b** (3.6 g, 25.2 mmol) after chromatogrophy with a mixture of cyclohexane and ethyl acetate 80 : 20. Yield: 82 %. The reduction (35) of ester **3b** (2.9 g, 20 mmol) by $LiAlH_4$ (788 mg, 20.8 mmol) afforded 2,3,3-trimethyl-1-butanol **4b** (1.48 g, 12.8 mmol). Yield: 64 %. Swern oxidation (36) of the alcohol **4b** (1.56 g, 13.5 mmol) provided **5b** (1.25 g, 11 mmol). Yield: 81 %.

(*S*)-2-(2-Methoxyethoxymethoxy)propanal 5c. The reaction (29, 37, 38) of methyl (*S*)-lactate (8.57 ml, 90 mmol) with 2-methoxyethoxymethyl chloride (15.3 ml, 135 mmol) in presence of diisopropylethylamine (31.5 ml, 180 mmol) furnished methyl (*S*)-2-(2-methoxyethoxymethoxy)propanoate **3c** (11.1 g, 57.8 mmol). Yield: 64 %. The reduction (37) of ester **3c** (10.9 g, 57 mmol) by $LiAlH_4$ (2.17 g, 57 mmol) conducted to (*S*)-2-(2-methoxyethoxymethoxy)-1-propanol **4c** (6.95 g, 42.4 mmol). Yield: 74 %. The alcohol **4c** (6.8 g, 41.8 mmol) gave **5c** (3.2 g, 19.8 mmol) by Swern oxidation (36). Yield: 47 %.

(*S*)-2-Phenylmethoxypropanal 5d. Methyl (*S*)-lactate (8 ml, 84 mmol) was deprotonated (39) by sodium hydride (84 mmol) in THF (130ml). Benzyl bromide (10 ml, 84 mmol) was added to the solution, in the presence of tetrabutylammonium iodide (310 mg, 0.84 mmol). Ethyl (*S*)-2-phenylmethoxypropanoate **3d** (16.3 g, 84 mmol) was isolated. Yield: 100 %. The reduction (40) of ester **3d** (4.94 g, 25.5 mmol) by $LiAlH_4$ (1.95 g, 51 mmol) afforded (*S*)-2-phenylmethoxy-1-propanol **4d** (4.1 g, 24.7 mmol). Yield: 97 %. Swern oxidation (36) of the alcohol **4d** (5 g, 30 mmol) conducted to **5d** (2.28 g, 14 mmol). Yield: 47 %.

(*S*)-2-(1,1-Dimethylethyldimethylsilyloxy)propanal 5e. The reaction (41) of methyl (*S*)-lactate (2.9 ml, 30 mmol) with 1,1-dimethylethyldimethylsilyl chloride (4.97 g, 33 mmol) in the presence of imidazole (4.7 g, 70 mmol) provided methyl (*S*)-2-(1,1-dimethylethyldimethylsilyloxy)propanoate **3e** (6.54 g, 30 mmol). Yield: 100 %. The reduction (29) of ester **3e** (4.58 g, 21 mmol) by DIBALH (63 mmol) gave **5e** (3.95 g, 21 mmol). Yield: 100 %.

Allylic esters 6

General procedure

To a solution of sodium hydride (3.3 mmol) in THF (5 ml) cooled to 0°C, the phosphonate (3.15 mmol) was added dropwise. The mixture was stirred for one hour at room temperature. The aldehyde (3 mmol) was added at 0°C. After stirring for one night, the solution was quenched with aqueous ammonium chloride. The extraction was executed by partition between ether and brine. The organic layers were dried on magnesium sulfate, and the solvents were evaporated.

Ethyl (*E*)-4-phenyl-2-pentenoate 6a. The reaction of 2-phenylpropanal (3.35 g, 25 mmol) with ethyl diethylphosphonoethanoate (5.3 ml, 26.7 mmol), followed by chromatography with a mixture of cyclohexane-ethyl acetate 95 : 5, gave **6a** (2.5 g, 12.3 mmol). Yield: 49 %. ^{1}H NMR (CCl_4): 1.13 (d, J = 7 Hz, 3H, $MeCH_2$), 1.38 (d, J = 6.8 Hz, 3H, MeCH), 3.50 (q, J = 6.8 Hz, 1H, CHMe), 4.10 (q, J = 7 Hz, 2H, CH_2O), 5.72 (dd, J = 16 Hz and J = 1.5 Hz, 1H, =CHMe), 6.95 (d, J = 6.6 Hz, 1H, =CH-CO_2Me), 7.18 (s, 5H, Ph).

Methyl 4,5,5-trimethyl-2-hexenoate 6b. The reaction of 2,3,3-trimethylbutanal **5b** (1.37 g, 12 mmol) with methyl dimethylphosphonoethanoate (2.04 ml, 12.6 mmol), furnished **6b** (1.16 g, 6.8 mmol). Ratio of *E*/*Z* isomers 90 : 10 from ^{13}C NMR. Yield: 57 %. ^{1}H NMR (CCl_4): 0.95 (s, tBu), 1.00 (d, J = 7 Hz, 3H, MeCH), 3.65 (s, 3H, OMe), 5.63 (d, J = 16 Hz, 1H, =CH-CO_2Me), 6.82 (dd, J = 16 Hz and J = 9 Hz, 1H, =CH-CH). ^{13}C NMR ($CDCl_3$): 14.6, 27.5, 33.2, 47.1, 51.2, 118.6 (*Z*), 120.8 (*E*), 152.6 (*E*), 153.6 (*Z*), 167.0.

Methyl (*S*)-4-(2-methoxyethoxymethoxy)-2-pentenoate 6c. The reaction of (*S*)-2-(2-methoxyethoxymethoxy)propanal **5c** (3.16 g, 19.5 mmol) with methyl dimethylphosphonoethanoate (3.3 ml, 20.5 mmol) afforded **6c** (2.97 g, 13.6 mmol). Ratio of *E*/*Z* isomers 77 : 23 from ^{13}C NMR. Yield: 70 %. ^{1}H NMR (CCl_4): 1.26 (d, J = 7 Hz, 3H, MeCH), 3.27 (s, 3H, OMe), 3.67 (s, 3H, CO_2Me), 4.59 (s, 2H, OCH_2O), 5.77 (d, J = 15.5 Hz, 1H, =CH-CO), 6.72 (d, J = 15.5 Hz and J = 5.5 Hz, 1H, =CH-CH). ^{13}C NMR ($CDCl_3$): 20.5, 51.2 (*Z*), 51.5 (*E*), 58.9, 67.0 (*Z*), 67.2 (*E*), 71.3, 71.9, 93.7, 119.2 (*Z*), 120.7 (*E*), 149.2 (*E*), 151.8 (*Z*), 166.1 (*Z*), 166.7 (*E*).

Methyl (*S*)-4-phenylmethoxy-2-pentenoate 6d. The reaction of (*S*)-2-phenylmethoxypropanal **5d** (2.25 g, 13.7 mmol) with methyl dimethylphosphonoethanoate (2.38 ml, 14.7 mmol), followed by chromatography with a mixture of cyclohexane-ethyl acetate 90 : 10, conducted to the *E* isomer (1.56 g, 7.1 mmol) and the *Z* isomer (0.66 g, 3 mmol) of the ester **6d** (42) in the ratio *E*/*Z* = 70 : 30. Yield: 84 %.
***E* Isomer.** ^{1}H NMR (CCl_4): 1.20 (d, J = 6 Hz, 3H, MeCH), 3.60 (s, 3H, OMe), 3.98 (m, 1H, HCMe), 4.23 and 4.48 (AB, J = 15 Hz, 2H, CH_2Ph), 5.88 (d, J = 16 Hz, 1H, =CH-CO_2Me), 6.78 (d, J = 16 Hz, 1H, =CH-CHMe), 7.28 (m, 5H, Ph). IR= 1720 cm^{-1} (C=O). MS: 43 (48), 65 (46), 77 (30), 91 (100), 105 (15), 114 (31), 198 (6), 220 (1).
***Z* Isomer.** ^{1}H NMR (CCl_4): 1.20 (d, J = 6 Hz, 3H, MeCH), 3.55 (s, 3H, OMe), 4.34 (s, 2H, CH_2O), 5.50 (m, 1H, CHMe), 5.83 (m, J = 12 Hz, 1H, =CH-CHMe), 6.16 (d, J = 12 Hz, 1H, =CH-CO_2Me), 7.18 (m, 5H, Ph). IR: 1720 cm^{-1} (C=O).MS: 43 (27), 91 (100), 113 (85), 129 (9), 181 (4), 220 (43).

Methyl (*S*)-4-(1,1-dimethylethyldimethylsilyloxy)-2-pentenoate 6e. The reaction (43) of (*S*)-2-(1,1-dimethylethyldimethylsilyloxy)propanal **5e** (4.41 g, 24 mmol) with methyl dimethylphosphonoethanoate (4.1 ml, 25.2 mmol), provided **6e** (5.86 g, 24 mmol). Ratio of *E*/*Z* isomers 85 : 15 from ^{13}C NMR. Yield: 100 %. ^{1}H NMR (CCl_4): 0.05 (s, 6H, $(Me)_2Si$), 0.91 (s, 9H, tBuSi), 3.61 (s, 3H, OMe). IR (CCl_4): 1725 cm^{-1} (C=O). ^{13}C NMR: -4.7, 19.0, 23.6, 25.9, 51.4, 67.8, 116.5 (*Z*), 118.8 (*E*), 152.2 (*E*), 154.9 (*Z*), 167.2. MS: 57 (11), 59 (24), 75 (56), 89 (100), 109 (13), 151 (22), 187 (31), 213 (5), 229 (3), 244 (1).

Ethyl (*S*)-2-methyl-4-phenylmethoxy-2-pentenoate 6g. The reaction of (*S*)-2-phenylmethoxypropanal **5d** (3 g, 18.3 mmol) with ethyl 2-(diethylphosphono)propanoate (4.7 ml, 21.9 mmol), followed by chromatography with a mixture of cyclohexane-ethyl acetate 90 : 10, conducted to the *E* isomer (2.31 g, 9.3 mmol) and the *Z* isomer (1.44 g, 5.8 mmol) of the ester **6g** (42) in the ratio *E*/*Z* = 62 : 38. Yield: 83 %.
***E* Isomer.** ^{1}H NMR (CCl_4): 1.29 (t, J = 7 Hz, 3H, $MeCH_2$), 1.75 (d, J = 1.5 Hz, 3H, MeC=), 4.15 (q, J = 7 Hz, 2H, CH_2Me), 4.33 (s, 2H, CH_2Ph), 5.26 (dd, J = 8.5 Hz and J = 1.5 Hz, 1H, CH=), 7.23 (s, 5H, Ph). IR (CCl_4): 1710 cm^{-1} (C=O).

Z Isomer. ^{1}H NMR (CCl_4): 1.22 (t, J = 7 Hz, 3H, $MeCH_2$), 1.89 (d, J = 1.5 Hz, 3H, MeC=), 4.12 (q, J = 7 Hz, 2H, CH_2Me), 4.38 (s, 2H, CH_2Ph), 5.80 (dd, J = 8.5 Hz and J = 1.5 Hz, 1H, CH=), 7.21 (s, 5H, Ph). IR (CCl_4): 1710 cm^{-1} (C=O). ^{13}C NMR ($CDCl_3$): 14.2, 20.3, 20.8, 60.4, 70.8, 72.2, 127.4, 127.7, 128.3, 128.8, 139.0, 144.4, 167.5. MS: 91 (40), 111 (30), 118 (49), 142 (100), 192 (28), 248 (1).

Allylic alcohols 7

General procedure

To a solution of lithium aluminium hydride (52 mg, 1.35 mmol) dissolved in THF (5 ml) cooled to 0°C, aluminium chloride (60 mg, 0.4 mmol) was added. After stirring for one hour at RT, the allylic ester (0.3 mmol) was added (30) to the formed solution of aluminium hydride (1.8 mmol) cooled to 0°C. The mixture was stirred for 3 hours and then quenched with hydratised sodium sulfate. After the extraction by partition between ether and brine, the organic layers were dried on magnesium sulfate. The solvents were evaporated.

(*E*)-4-Phenyl-2-penten-1-ol 7a. Reduction of ethyl phenyl-2-pentenoate **6a** (2.1 g, 10.3 mmol), followed by chromatography with a mixture of cyclohexane-ethyl acetate 50 : 50, gave **7a** (1.45 g, 9 mmol). Yield: 88 %. ^{1}H NMR (CCl_4): 1.32 (d, J = 7 Hz, 3H, MeCH), 3.20-3.60 (m, 1H, CHMe), 3.85 (d, J = 5 Hz, 2H, CH_2O), 5.25-5.70 (m, 2H, CH=CH), 7.12 (s, 5H, Ph). IR: 3400 cm^{-1} (OH). ^{13}C NMR ($CDCl_3$): 21.1, 42.0, 63.0, 126.2, 127.2, 128.0, 128.5, 137.0. 145.6, MS: 51 (40), 65 (13), 77 (31), 91 (65), 105 (100), 117 (20), 129 (42), 131 (70), 162 (1).

(*E*)-4,5,5-Trimethyl-2-hexen-1-ol 7b. Reduction of methyl 4,5,5-trimethyl-2-hexenoate **6b** (1.28 g, 7.5 mmol), conducted to **7b** (637 mg, 4.49 mmol). Yield: 60 %. ^{1}H NMR (CCl_4): 0.87 (s, 9H, tBu), 3.97 (d, J = 4.5 Hz, 2H, CH_2OH). IR (CCl_4): 3450 cm^{-1} (OH). ^{13}C NMR ($CDCl_3$): 15.5, 27.5, 32.9, 46.9, 63.7, 129.0, 136.2. MS: 41 (23), 57 (61), 68 (100), 83 (5), 142 (1).

(*S*)-4-(2-Methoxyethoxymethoxy)-2-penten-1-ol 7c. Reduction of methyl (*S*)-4-(2-methoxyethoxymethoxy)-2-penten-1-oate **6c** (2.94 g, 13.5 mmol) furnished **7c** (1.31 g, 6.9 mmol). Ratio of *E*/*Z* isomers 65 : 35 from ^{13}C NMR. Yield: 51 %. ^{1}H NMR (CCl_4): 1.17 (d, J = 7 Hz, 3H, MeCH), 3.30 (s, 3H, OMe), 4.58 (s, 2H, OCH_2O). IR (CCl_4): 3456 and 3615 cm^{-1} (OH). ^{13}C NMR ($CDCl_3$): 21.3, 58.8, 62.5, 66.8 (*Z*), 66.9 (*E*), 71.9, 72.0, 92.7 (*Z*), 93.1 (*E*), 131.3 (*E*), 131.7 (*Z*), 132.5 (*E*), 132.9 (*Z*).

(*E*)-(*S*)-4-Phenylmethoxy-2-penten-1-ol 7d. Reduction of methyl (*S*)-4-phenylmethoxy-2-pentenoate **6d** (800 mg, 3.64 mmol), afforded **7d** (650 mg, 3.38 mmol). Yield: 93 %. ^{1}H NMR (CCl_4): 1.22 (d, J = 6 Hz, 3H, Me), 4.24 and 4.50 (AB, J = 16 Hz, 2H, CH_2Ph), 5.40-5.70 (m, 2H, CH=CH), 7.22 (s, Ph). IR: 3440 cm^{-1}(OH). MS 43 (49), 55 (38), 65 (53), 68 (73), 77 (40), 90 (100), 106 (14), 180 (5), 186 (6), 192 (2).

(*E*)-(*S*)-4-(1,1-Dimethylethyldimethylsilyloxy)-2-penten-1-ol 7e. Reduction (43) of methyl (*S*)-4-(1,1-dimethylethyldimethylsilyloxy)-2-pentenoate **6e** (4.56 g, 19.5 mmol) with aluminium hydride (246 mmol) provided **7e** (1.57 g, 7.3 mmol). Yield: 37 %. ^{1}H NMR (CCl_4): 0.05 (s, 6H, $(Me)_2Si$), 0.90 (s, 9H, tBuSi), 1.18 (d, J = 6 Hz, 3H, MeCH). IR (CCl_4): 3640 cm^{-1} and 3615 cm^{-1} (OH). ^{13}C NMR ($CDCl_3$): -4.7, -4.5, 18.9, 24.4, 26.7, 63.1, 68.7, 127.6, 136.4. MS: 41 (82), 45 (48), 57 (31), 75 (26), 142 (78), 160 (100), 186 (7), 200 (26), 201 (5), 216 (1).

(*E*)-(*S*)-3-(2,2-Dimethyl-1,3-dioxolane-4-yl)-2-propen-ol 7f. Reduction (14) of commercially available ethyl (*E*)-(*S*)-(+)-3-(2,2-dimethyl-1,3-dioxolane-4-yl)-2-propenoate (2.94 g, 15 mmol) gave **7f** (2.15 g, 13.6 mmol). Yield: 91 %. ^{1}H NMR (CCl_4): 1.32 (s, MeC), 1.35 (s, MeC). IR (CCl_4): 3430 cm^{-1} and 3610 cm^{-1} (OH).

(*E*) and (*Z*)-(*S*)-2-Methyl-4-phenylmethoxy-2-penten-1-ol 7g. Reduction of ethyl (*S*)-2-methyl-4 phenylmethoxy-2-pentenoate **6g** (*E*/*Z* = 50 : 50) (366 mg, 1.5 mmol) conducted to **7g** (156 mg, 0.76 mmol). Ratio of *E*/*Z* isomers 50 : 50 from ^{1}H NMR. Yield: 51 %.

(*E*)-(*S*)-2-Methyl-4-phenylmethoxy-2-penten-1-ol 7g. Reduction of ethyl (*E*)-(*S*)-2-methyl-4-phenylmethoxy-2-pentenoate **6g** (1.46 g, 6 mmol) afforded (*E*) **7g** (614 mg, 3 mmol). Yield: 50 %. ^{1}H NMR (CCl_4): 1.18 (d, J = 6 Hz, 3H, MeCH), 1.54 (s, 3H, MeC=), 3.79 (s, 2H, CH_2OH), 4.3 (d, J = 4.5 Hz, 2H, CH_2Ph), 5.26 (dd, J = 8.5 Hz and J = 1.5 Hz, 1H, CH=), 7.14 (s, 5H, Ph). ^{13}C NMR ($CDCl_3$): 13.9, 21.2, 67.9, 69.9, 70.9, 127.4, 127.7, 128.3, 137.7, 139.1. MS: 91 (100), 107 (38), 108 (47), 135 (12), 205 (7).

(*Z*)-(*S*)-2-Methyl-4-phenylmethoxy-2-penten-1-ol 7g. Reduction of ethyl (*Z*)-(*S*)-2-methyl-4-phenylmethoxy-2-pentenoate **6g**.(878 mg, 3.6 mmol) furnished (*Z*) **7g** (462 mg, 2.24 mmol). Yield: 62 %. ^{1}H NMR (CCl_4): 1.17 (d, J = 6 Hz, 3H, MeCH), 3.88 (s, 2H, CH_2OH), 4.33 (d, J = 3.5 Hz, 2H, CH_2Ph), 4.82 (dd, J = 8.5 Hz and J = 1.5 Hz, 1H, CH=), 7.20 (s, 2H, Ph). ^{13}C NMR ($CDCl_3$): 21.4, 21.7, 61.8, 69.9, 70.6, 127.6, 127.8, 128.4, 130.4, 138.0. MS: 91 (100), 107 (9), 108 (9), 132 (4), 205 (3).

Starting dithioesters 8

General procedure
To a solution of triphenylphosphine (1.03 g, 3.9 mmol) dissolved in THF (20 ml) and cooled to 0°C we added (31) isopropyl azodicarboxylate (0.77 ml, 3.9 mmol). A milky precipitate was formed. After 30 mn a mixture of ethanedithioic acid (0.335 ml, 4.5 mmol) and alcohol (3 mmol) in THF (3 ml) was added. The mixture turned dark brown and was stirred for 30 mn. THF was partially evaporated. We added cyclohexane. A precipitate appeared and we filtered it on Celite. We evaporated again the solvents. If a precipitate appeared, we repeated the operation until the disappearance of the precipitate.

(*E*)-4-Phenyl-2-pentenyl ethanedithioate 8a. Proceeded from the reaction of (*E*)-4-phenyl-2-penten-1-ol **7a** (538 mg, 3.3 mmol), followed by chromatography with a mixture of cyclohexane-ethyl acetate 95 : 5, conducted to **8a** (500 mg, 2.1 mmol). Yield: 64 %. ^{1}H NMR (CCl_4): 1.30 (d, J = 7 Hz, 2H, MeCH), 2.72 (s, 3H, MeC=S), 3.80 (d, J = 7 Hz, 2H, SCH_2), 3.40 (m, 1H, CHMe), 5.20-6.10 (m, 2H, CH=CH), 7.20 (s, 5H, Ph).

(*E*)-4,5,5-Trimethyl-2-hexenyl ethanedithioate 8b. Proceeded from the reaction of (*E*)-4,5,5-trimethyl-2-hexen-1-ol **7b** (682 mg, 4.8 mmol), followed by chromatography with a mixture of cyclohexane-ethyl acetate 95 : 5, gave **8b** (758 mg, 3.51 mmol). Yield: 73 %. ^{1}H NMR (CCl_4): 0.83 (s, 9H, tBu), 0.92 (d, J = 7 Hz, 3H, MeCH), 2.77 (s, 3H, MeC=S), 3.78 (d, J = 7 Hz, 2H, SCH_2) ^{13}C NMR ($CDCl_3$): 15.3, 27.4, 32.8, 39.0, 39.9, 47.1, 121.7, 139.6, 232.2. MS: 41 (36), 57 (100), 59 (66), 109 (11), 124 (11), 125 (4), 159 (68), 216 (7).

(*E*)-(*S*)-4-(2-Methoxyethoxymethoxy)-2-pentenyl ethanedithioate 8c. Proceeded from the reaction of (*S*)-4-(2-methoxyethoxymethoxy)-2-penten-1-ol **7c** (1.71 g, 9 mmol), followed by chromatography with a mixture of cyclohexane-ethyl acetate 90 : 10, afforded **8c** (1.02 g, 3.9 mmol). Yield: 43 %. ^{1}H NMR (CCl_4): 1.19 (d, J = 6.5 Hz, 3H, MeCH), 2.79 (s, 3H, MeCH), 2.79 (s, 3H, MeC=S), 3.31 (s, 3H, OMe), 4.55 (s, 2H, OCH_2O). ^{13}C NMR ($CDCl_3$): 21.2, 38.6, 58.9, 66.9, 71.9, 93.0, 124.3, 136.7, 231.8. MS: 45 (20), 59 (100), 89 (7), 100 (2), 144 (8), 159 (28), 249 (1), 264 (1).

(*E*)-(*S*)-4-Phenylmethoxy-2-pentenyl ethanedithioate 8d. Proceeded from the reaction of (*E*)-4-phenylmethoxy-2-penten-1-ol **7d** (5.29 mg, 2.76 mmol), followed by chromatography with a mixture of cyclohexane-ethyl acetate 95 : 5, provided **8d** (300 mg, 1.13 mmol). Yield: 41 %. ^{1}H NMR (CCl_4): 1.18 (d, J = 6 Hz, 3H, MeCH), 3.82 (d, J = 6 Hz, 2H, SCH_2), 4.20 and 4.50 (AB, J = 16 Hz, 2H, CH_2Ph), 5.48-5.70 (m, 2H, CH=CH), 7.20 (s, 5H, Ph). MS: 51 (66), 65 (100), 92 (84), 100 (54), 117 (30), 131 (66), 143 (35), 174 (14), 243 (2), 266 (1). Anal. calcd. for $C_{14}H_{18}S_2O$: C, 63.16 ; H, 6.76 ; S, 24.06. Found: C, 61.54 ; H, 6.62 ; S, 25.25.

(*E*)-(*S*)-4-(1,1-Dimethylethyldimethylsilyloxy)-2-pentenyl ethanedithioate 8e. Proceeded from the reaction of (*E*)-(*S*)-4-(1,1-dimethylethyldimethylsilyloxy)-2-penten-1-ol **7e** (842 mg, 3.9 mmol), followed by chromatography with a mixture of cyclohexane-ethyl acetate 90 : 10, furnished **8e** (760 mg, 2.62 mmol). Yield: 67 %. ^{1}H NMR: 60 MHz (CCl_4): 0.05 (s, 4H, $(CH_2)_2Si$), 0.90 (s, 9H, tBuSi), 1.17 (d, J = 6 Hz, 3H, MeCH), 2.80 (s, 3H, MeC=S), 3.76 (d, J = 6 Hz, 2H, CH_2S). ^{13}C NMR ($CDCl_3$): -4.7, -4.6, 18.2, 24.3, 25.9, 39.0, 39.1, 68.6, 120.8, 140.0, 231.9. MS: 59 (100), 75 (27), 141 (21), 159 (16), 175 (28), 198 (70), 233 (19), 275 (2), 290 (2).

(*E*)-(*S*)-3-(2,2-Dimethyl-1,3-dioxolane-4-yl)-2-propenyl ethanedithioate 8f. Proceeded from the reaction of (*E*)-(*S*)-3-(2,2-dimethyl-1,3-dioxolane-4-yl)-2-propen-1-ol **7f** (1.19 g, 7.5 mmol), followed by chromatography with a mixture of cyclohexane-ethyl acetate 90 : 10, conducted to **8f** (730 mg, 3.15 mmol). Yield: 42 %. ^{1}H NMR (CCl_4): 1.28 (s, 3H, MeC), 1.33 (s, 3H, MeC), 2.82 (s, 3H, MeC=S). ^{13}C NMR ($CDCl_3$): 25.8, 26.7, 38.6, 38.9, 69.4, 76.3, 109.4, 126.4, 132.9, 231.5. MS: 43 (74), 59 (100), 72 (16), 83 (25), 91 (12), 99 (19), 140 (51), 141 (10), 217 (6), 232 (1).

(*E*) and (*Z*)-(*S*)-2-Methyl-4-phenylmethoxy-2-pentenyl ethanedithioate 8g. Proceeded from the reaction of (*S*)-2-methyl-4-phenylmethoxy-2-penten-1-ol **7g** (*E*/*Z* = 50 : 50) (247 mg, 1.2 mmol), followed by chromatography with a mixture of cyclohexane-ethyl acetate 95 : 5, afforded **8g** (89 mg, 0.32 mmol). Ratio of *E*/*Z* isomers 50 : 50 from ^{1}H NMR. Yield: 27 %.

(*E*)-(*S*)-2-Methyl-4-phenylmethoxy-2-pentenyl ethanedithioate 8g. Proceeded from the reaction of (*E*)-(*S*)-2-methyl-4-phenylmethoxy-2-penten-1-ol **7g** (494 mg, 2.4 mmol), followed by chromatography with a mixture of cyclohexane-ethyl acetate 95 : 5, gave (*E*) **8g** (593 mg, 2.1 mmol). Rdt = 87 %. ^{1}H NMR (CCl_4): 1.19 (d, J = 6.5 Hz, 3H, MeCH), 1.61 (s, 3H, MeC=C), 2.79 (s, 3H, MeC=S), 3.86 (s, 2H, CH_2S), 4.4 (s, 2H, CH_2Ph), 5.41 (d, J = 8 Hz, 1H, CH=), 7.28 (s, 5H, Ph). ^{13}C NMR ($CDCl_3$): 16.7, 21.2, 39.1, 46.2, 70.0, 71.0, 127.4, 127.7, 128.4, 131.6, 132.7, 232.5. MS: 59 (38), 91 (100), 113 (18), 145 (12), 173 (16), 205 (1), 241 (1), 263 (1), 265 (1), 280 (1).

(*Z*)-(*S*)-2-Methyl-4-phenylmethoxy-2-pentenyl ethanedithioate 8g. Proceeded from the reaction of (*Z*)-(*S*)-2-methyl-4-phenylmethoxy-2-penten-1-ol **7g** (371 mg, 1.8 mmol), followed by chromatography

with a mixture of cyclohexane-ethyl acetate 95 : 5, provided (Z) **8g** (242 mg, 0.86 mmol). Yield: 48 %. ^{1}H NMR 60 MHz (CCl_4): 1.20 (d, J = 6.5 Hz, 3H, MeCH), 1.78 (s, 3H, MeC=C), 2.78 (s, 3H, MeC=S), 3.81 (s, 2H, CH_2S), 4.36 (d, J = 4.5 Hz, 2H, CH_2Ph), 5.28 (d, J = 8 Hz, 1H, CH=), 7.2 (s, 5H, Ph). ^{13}C NMR ($CDCl_3$): 21.6, 23.2, 38.9, 39.7, 70.1, 71.1, 127.4, 127.6, 128.3, 131.4, 133.5, 232.6. MS: 59 (43), 91 (100), 113 (21), 145 (14), 173 (49), 188 (20), 205 (1), 241 (1), 263 (4), 265 (1), 280 (1).

Synthesis of Ketenedithioacetals and Thio-Claisen Rearrangement

General procedure

To a solution of LDA (3 mmol for compounds **10a-d, 10f-g** and 6 mmol for the compound **10e**) cooled to -30°C in THF (10 ml), we added dropwise the dithioester (3 mmol). The mixture was stirred for 30 mn. The iodomethane (3 mmol) was added to the solution. After 15 mn, we quenched with aqueous ammonium chloride and extracted by partition between ether and brine. The organic layers were dried over magnesium sulfate. The solvents were evaporated. The ketenedithioacetals and the dithioesters are very fragile, thus we could not generally obtain correct elemental analyses.

(*E*)-1-(4-Phenyl-2-pentenylthio)-1-methylthioethene 10a. Proceeded from the reaction of (*E*)-4-phenyl-2-pentenyl ethanedithioate **8a** (972 mg, 4.12 mmol). One hour after hydrolysis, an ^{1}H NMR spectrum of the crude product was run. We observed a mixture of ketene dithioacetal **10a** and dithioester **11a** (83 : 17). ^{1}H NMR (CCl_4): 1.30 (d, J = 7 Hz, 3H, MeCH), 2.15 (s, 3H, SMe), 3.35 (d, J = 7 Hz, 2H, SCH_2), 5.15 and 5.35 (2s, 2H, H_2C=), 5.45-5.75 (m, 2H, CH=CH), 7.20 (s, 5H, Ph).

Methyl 3-(1-phenylethyl)-4-pentenedithioate 11a. Thermolysis of **10a** under reflux in methylcyclohexane for 4 hours, followed by chromatography with a mixture of cyclohexane and ethyl acetate 99 : 1, furnished **11a** (307 mg, 1.23 mmol). Ratio of A/B diastereoisomers 70 : 30 from ^{1}H NMR 400 MHz (SMe signals). Yield: 30 %. ^{1}H NMR 400 MHz (CCl_4): 1.23 (d, J = 7 Hz, 3H, Me de A), 1.25 (d, J = 7 Hz, 3H, Me de B), 2.51 (s, 3H, SMe de A), 2.57 (s, 3H, SMe de B), 4.85-5.00 (m, 2H, CH_2=C), 5.35-5.55 (m, 1H, CH=), 7.13-7.30 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): 18.8 (B), 19.5 (A), 19.7, 43.2, 43.6 (A), 45.1, 51.6 (B), 52.3 (A), 54.5 (B), 55.3 (A), 117.0, 126.3, 127.6, 128.5, 137.5 (B), 138.2 (A), 145.0, 237.4. MS: 59 (33), 77 (45), 91 (59), 105 (100), 129 (61), 145 (54), 203 (13), 221 (8), 235 (4), 250 (4). Anal. calcd. for $C_{14}H_{18}S_2$: C, 67.20 ; H, 7.20 ; S, 25.6. Found: C, 67.01 ; H, 7.07 ; S, 25.84.

(*E*)-1-(4,5,5-Trimethyl-2-hexenylthio)-1-methylthioethene 10b. Proceeded from the reaction of (*E*)-4,5,5-trimethyl-2-hexenyl ethanedithioate **8b** (648 mg, 3 mmol). 3 Hours after hydrolysis, an ^{1}H NMR spectrum of the crude product was run. We observed a mixture of ketene dithioacetal **10b** and dithioester **11b** (94 : 6). ^{1}H NMR 60 MHz (CCl_4): 0.86 (s, 9H, tBu), 0.90 (d, J = 8 Hz, 3H, MeCH), 2.25 (s, 3H, SMe), 3.31 (d, J = 7 Hz, 2H, SCH_2), 5.25 (d, J = 9 Hz, 2H, CH_2=).

Methyl 3-(1,2,2-trimethylpropyl)-4-pentenedithioate 11b. Rearrangement of **10b** at RT for 10 days, followed by chromatography with a mixture of cyclohexane and ethyl acetate 99 : 1, provided **11b** (312 mg, 1.35 mmol). Ratio of A/B diastereoisomers 75 : 25 from ^{13}C NMR. Yield: 45 %. ^{1}H NMR (CCl_4): 0.86 (s, 9H, tBu), 0.90 (d, J = 8 Hz, 3H, MeCH), 2.55 (s, 3H, SMe). ^{13}C NMR ($CDCl_3$): 15.3 (B), 19.8 (A), 27.4 (B), 27.5 (A), 28.3, 32.6 (B), 34.0 (A), 45.1, 46.2 (A), 47.1 (B), 57.3, 116.2 (A), 121.7 (B), 138.5 (A), 139.7 (B), 237.4. MS: 57 (100), 69 (25), 91 (18), 109 (44), 124 (10), 145 (43), 159 (17), 173 (43), 215 (2), 230 (1).

(*E*)-(*S*)-1-Methylthio-1-[4-(2-methoxyethoxymethoxy)-2-pentenylthio]ethene 10c. Proceeded from the reaction of (*E*)-(*S*)-4-(2-methoxy-ethoxymethoxy)-2-pentenyl ethanedithioate **8c** (792 mg, 3 mmol). One hour and half after hydrolysis, an ^{1}H NMR spectrum of the crude product was run. We observed a mixture of ketene dithioacetal **10c** and dithioester **11c** (93 : 7). ^{1}H NMR (CCl_4): 1.18 (d, J = 6 Hz, 3H, MeCH), 2.26 (s, 3H, SMe), 3.32 (s, 3H, OMe), 4.53 (s, 2H, OCH_2O), 5.29 (d, J = 10 Hz, 2H, CH_2=).

Methyl (3*S*,1'*S*) and (3*R*,1'*S*)-3-[1-(2-methoxyethoxymethoxy)ethyl]-4-pentenedithioate 11c. Thermolysis of **10c** under reflux in methylcyclohexane for 6 hours, followed by chromatography with a mixture of cyclohexane and ethyl acetate 80 : 20, afforded **11c** (633 mg, 2.28 mmol). Ratio of A/B diastereoisomers 54 : 46 from ^{13}C NMR. Yield: 76 %. ^{1}H NMR (CCl_4): 2.56 (s, 3H, SMe), 3.30 (s, 3H, OMe), 4.66 (s, 2H, OCH_2O). ^{13}C NMR ($CDCl_3$): 17.5 (B), 17.7 (A), 19.8, 51.0 (B), 51.1 (A), 52.5 (A), 52.6 (B), 58.9, 67.2, 71.9, 75.0 (B), 75.1 (A), 94.2 (A), 94.5 (B), 117.1 (B), 117.6 (A), 136.2 (A), 136.9 (B), 237.2 (A), 237.3 (B). MS: 45 (41), 59 (100), 89 (23), 91 (8), 157 (3), 172 (4), 202 (19), 230 (3), 278 (1). Anal. calcd for $C_{12}H_{22}O_3S_2$: C, 51,77 ; H, 7.96 ; S, 23.3. Found: C, 55.34 ; H, 9.08 ; S, 21.12. $[\alpha]^{20}_D$ = -15° (c = 30 g/l, $CHCl_3$).

(*E*)-(*S*)-1-(4-Phenylmethoxy-2-pentenylthio)-1-methylthioethene 10d. Proceeded from the reaction of (*E*)-(*S*)-4-phenylmethoxy-2-pentenyl ethanedithioate **8d** (228 mg, 0.857 mmol). One hour after hydrolysis, an ^{1}H NMR spectrum of the crude product was run. We observed a mixture of ketene dithioacetal **10d** and dithioester **11d** (90 : 10). ^{1}H NMR (CCl_4): 1.22 (d, J = 6 Hz, 3H, MeCH), 2.20 (s, 3H, SMe),

3.35 (d, J = 6 Hz, 2H, SCH_2), 4.20 and 4.50 (AB, J = 16 Hz, 2H, OCH_2), 5.20 and 5.40 (2s, 2H, CH_2C=), 5.40-5.65 (m, 2H, CH=CH), 7.25 (s, Ph).

Methyl (3*S*,1'*S*) and (3*R*,1'*S*)-3-(1-phenylmethoxyethyl)-4-pentenedithioate 11d. Thermolysis of **10d** under reflux in methylcyclohexane for 4 hours, followed by chromatography with a mixture of cyclohexane and ethyl acetate 99 : 1, gave **11d** (155 mg, 0.554 mmol). Ratio of A/B diastereoisomers 53 : 47 from ^{1}H NMR 400 MHz (SMe signals). Yield: 64 %. ^{1}H NMR 400 MHz (CCl_4): 1.15 (d, J = 5 Hz, 3H, Me de B), 1.17 (d, J = 5 Hz, Me 3H, de A), 2.51 (s, 3H, SMe de A), 2.53 (s, 3H, SMe de B), 5.10-5.40 (m, CH_2C=), 5.58-5.75 (m, 1H, HC=), 7.20-7.35 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): 16.9, 19.9, 50.8, 52.6 (A), 52.8 (B), 70.8, 76.2, 117.1 (B), 117.5 (A), 127.4, 127.6, 128.3, 136.6 (A), 137.0 (B), 138.9, 237.6 (B), 237.9 (A). MS: 45 (61), 59 (72), 92 (36), 125 (46), 141 (40), 172 (100), 221 (2), 233 (8), 247 (1), 263 (5), 280 (1).

(*Z*)-(*S*)-1-[4-(1,1-Dimethylethyldimethylsiloxy)-2-pentenylthio]-1-methylthioethene 10e. Proceeded from the reaction of (*Z*)-(*S*)-4-(1,1-dimethylethyldimethylsiloxy)-2-pentenyl ethanedithioate **8e** (870 mg, 3 mmol). Two hours after hydrolysis, an ^{1}H NMR spectrum of the crude product was run. We observed a mixture of ketene dithioacetal **10e** and dithioester **11e** (80 : 20). ^{1}H NMR (CCl_4): 0.05 (s, 6H, Me_2Si), 0.90 (s, 9H, tBuSi), 2.28 (s, 3H, SMe), 5.33 (d, J = 9 Hz, 2H, CH_2=).

Methyl (3*S*,1'*S*) and (3*R*,1'*S*)-3-[1-(1,1-dimethylethyldimethylsiloxy)ethyl]-4-pentenedithioate 11e. Rearrangement of **10e** at RT for one day, followed by chromatography with a mixture of cyclohexane and ethyl acetate 99 : 1, conducted to **11e** (405 mg, 1.33 mmol). Ratio of A/B diastereoisomers 66 : 34 from ^{13}C NMR. Yield: 44 %. ^{1}H NMR: 0.05 (s, 4H, $(Me)_2Si$), 0.90 (s, 9H, tBu), 2.53 (s, 3H, SMe). ^{13}C NMR: -4.7, -4.2, 18.1 (A), 18.2 (B), 19.8, 20.9 (A), 21.2 (B), 25.9, 52.6 (B), 53.0 (A), 53.1 (A), 53.3 (B), 70.4 (A), 70.7 (B), 116.7 (B), 117.3 (A), 136.6 (A), 137.6 (B), 237.9. MS: 75 (12), 159 (13), 172 (100), 198 (68), 247 (87), 304 (2). Anal. calcd for $C_{14}H_{28}S_2OSi$: C, 55.21, H 9.27, S 21.05. Found: C 55.34, H 9.08, S 21.12. $[\alpha]^{20}_D$= -19.7° (c = 30 g/l, $CHCl_3$).

(*E*)-(*S*)-1-[3-(2,2-Dimethyl-1,3-dioxolane-4-yl)-2-propenylthio]-1-methylthioethene 10f. Proceeded from the reaction of (*E*)-(*S*)-3-(2,2-dimethyl-1,3-dioxolane-4-yl)-2-propenyl ethanedithioate **8f** (5.56 mg, 2.4 mmol). Two hours after hydrolysis, an ^{1}H NMR spectrum of the crude product was run. We observed a mixture of ketene dithioacetal **10f** and dithioester **11f** (58 : 42). ^{1}H NMR (CCl_4): 1.28 (s, 3H, MeC), 1.32 (s, 3H, MeC), 2.25 (s, 3H, SMe), 5.32 (d, J = 9 Hz, 2H, CH_2=).

Methyl (3*S*,1'*S*) and (3*R*,1'*S*)-3-(2,2-dimethyl-1,3-dioxolanne-4-yl)-4-pentenedithioate 11f. Rearrangement of **10f** at RT for 5 days, followed by chromatography with a mixture of cyclohexane and ethyl acetate 99 : 1, furnished **11f** (381 mg, 1.55 mmol). Ratio of A/B diastereoisomers 68 : 32 from ^{13}C NMR. A and B were assigned respectively to (3*S*,1'*S*) and (3*R*,1'*S*) isomers (see thereotical part). Yield: 65 %. ^{1}H NMR 60 MHz (CCl_4): 1.27 (s, 3H, MeC), 1.32 (s, 3H, MeC), 2.58 (s, 3H, SMe). ^{13}C NMR (68 MHz) ($CDCl_3$): 19.4 (A), 19.5 (B), 24.7 (B), 25.1 (A), 25.8 (B), 26.3 (A), 47.4 (B), 49.2 (A), 52.4 (B), 52.5 (A), 66.3 (B), 67.2 (A), 76.7 (B), 77.0 (A), 108.6 (B), 109.0 (A), 117.8 (A), 118.0 (B), 134.5 (B), 135.1 (A), 235.8. MS: 41 (42), 43 (100), 59 (32), 82 (36), 91 (73), 101 (41), 123 (20), 140 (64), 145 (23), 189 (16), 231 (11), 246 (3). $[\alpha]^{20}_D$= - 12.5° (c = 30 g/l, $CHCl_3$).

(*E*) and (*Z*)-(*S*)-1-(2-Methyl-4-phenylmethoxy-2-pentenylthio)-1-methylthioethene 10g. Proceeded from the reaction of (*S*)-2-methyl-4-phenylmethoxy-2-pentenyl ethanedithioate **8g** (*E*/*Z* = 50 : 50) (840 mg, 3 mmol). Two hours after hydrolysis, an ^{1}H NMR spectrum of the crude product was run. We observed a mixture of ketene dithioacetal **10g** and dithioester **11g** (93 : 7).

(*E*)-(*S*)-1-(2-Methyl-4-phenylmethoxy-2-pentenylthio)-1-methylthioethene 10g. Proceeded from the reaction of (*E*)-(*S*)-2-methyl-4-phenylmethoxy-2-pentenyl ethanedithioate **8g** (420 mg, 1.5 mmol). ^{1}H NMR (CCl_4): 1.20 (d, J = 6 Hz, 3H, MeCH), 1.85 (s, 3H, MeCH), 1.85 (s, 3H, MeC=C), 2.20 (s, 3H, MeS), 3.63 (s, 2H, CH_2S), 4.40 (s, 2H, CH_2Ph), 5.23 (d, J = 10 Hz, CH_2=C), 7.11 (s, Ph).

(*Z*)-(*S*)-1-(2-Methyl-4-phenylmethoxy-2-pentenylthio)-1-methylthioethene 10g. Proceeded from the reaction of (*Z*)-(*S*)-2-methyl-4-phenylmethoxy-2-pentenyl ethanedithioate **8g** (420 mg, 1.5 mmol). ^{1}H NMR (CCl_4): 1.20 (d, J = 6 Hz, 3H, MeCH), 1.85 (s, 3H, MeCH), 1.85 (s, 3H, MeC=C), 2.20 (s, 3H, MeS), 3.63 (s, 2H, CH_2S), 4.40 (s, 2H, CH_2Ph), 5.23 (d, J = 10 Hz, 2H, CH_2=C), 7.11 (s, 5H, Ph).

Methyl (3*S*,1'*S*) and (3*R*,1'*S*)-3-(1-phenylmethoxyethyl)-4-pentenedithioate 11g.
Rearrangement of **10g** at RT for 12 days, followed by chromatography with a mixture of cyclohexane and ethyl acetate 99 : 1, furnished **11g** (743 mg, 2.53 mmol). Ratio of A/B diastereoisomers 61 : 39 from ^{13}C NMR. Yield: 84 %.
Thermolysis of **10g** (*E*) afforded **11g** (92 mg, 0.33 mmol). Ratio of A/B diastereoisomers 61 : 39 from ^{13}C NMR. Yield: 53 %.
Thermolysis of **10g** (*Z*) conducted to **11g** (92 mg, 0.33 mmol). Ratio of A/B diastereoisomers 60 : 40 from ^{13}C NMR. Yield: 22 %.

^{1}H NMR (CCl_4): 1.18 (d, J = 6.5 Hz, 3H, MeCH), 1.65 (s, 3H, MeC=), 2.52 (s, 3H, SMe), 7.26 (s, 5H, Ph). ^{13}C NMR ($CDCl_3$): 16.9 (B), 17.4 (A), 19.4 (B), 19.7 (A), 20.4 (A), 21.9 (B), 52.3 (B), 54.9 (A), 70.6 (B), 70.9 (A), 74.1 (B), 76.5 (A), 112.7 (B), 114.4 (A), 127.4, 127.6, 128.2, 138.7 (B), 138.8 (A), 143.6, 238.0. MS: 91 (100), 105 (5), 107 (6), 135 (3), 159 (11), 279 (1), 294 (1). $[\alpha]^{20}_D$= + 4.7° (c = 30 g/l, $CHCl_3$).

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