67. Investigation of the Chemo- and Stereoselectivity of the Ketene-*Claisen* Rearrangement

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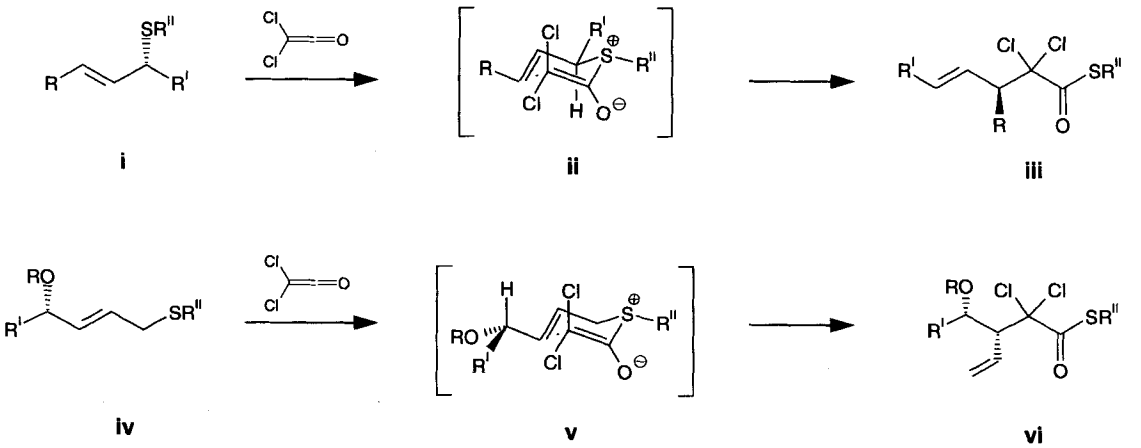
A novel type of ketene-*Claisen* rearrangement in which the precursor of the rearrangement is generated *in situ* by reaction of optically active allyl thioethers with dichloroketene is described. A characteristic feature of this rearrangement is the excellent chemoselectivity in favor of allyl thioethers *vs.* allyl ethers, *i.e.*, exclusive chirality transfer of the allylic sulfur moiety is observed with **12**, **13**, and **25**–**27**. The cyclic, optically active allyl thioethers (+)-(*R*)-**4** and (−)-(*S*)-**4** and the open-chain allyl thioethers **11**–**13** rearrange with *in situ* generated dichloroketene to the optically active thioesters (−)-(*S*)-**28**, (+)-(*R*)-**28**, and **31**–**33**, respectively. A chirality-transfer of > 99% in the cyclic cases (+)-(*R*)-**4** and (−)-(*S*)-**4**, and 96–98% in the open-chain cases **11**–**13** is observed. Furthermore, the dichloroketene-*Claisen* rearrangement is characterized by a high asymmetric 1,2-induction. The chiral allylic sulfides **25**–**27** give the optically active thioesters **36**–**38** with a 1,2-induction > 99% as determined by NMR-shift experiments.

Introduction. – The *Claisen* rearrangement [1] as well as the *Eschenmoser* [2a], *Johnson* [2b], and the *Ireland* variations [2c] thereof pass through a highly ordered transition state [3] which allows a very reliable prediction of the stereochemical course. This investigation is aimed at an intermolecular variant [4] of the [3,3]-sigmatropic rearrangement, in which the zwitterionic intermediates (such as **ii** or **v**) are generated *in situ* by reaction of the allyl thioethers **i** and **iv** with dichloroketene (*Scheme 1*). Firstly, the degree of the chirality transfer from the C–S to the C–C bond in the rearrangement of **i** *via* the zwitterionic intermediate **ii** containing a chiral center inside the pericyclic system to **iii** is analyzed [5]. Secondly, the chemoselectivity of this rearrangement is investigated by offering dichloroketene to a molecule containing an allylic oxygen- as well as an allylic sulfur-moiety [5]. Finally, the asymmetric 1,2-induction in the [3,3]-sigmatropic rearrangement of allyl thioethers (**iv** → **vi**) is examined [6].

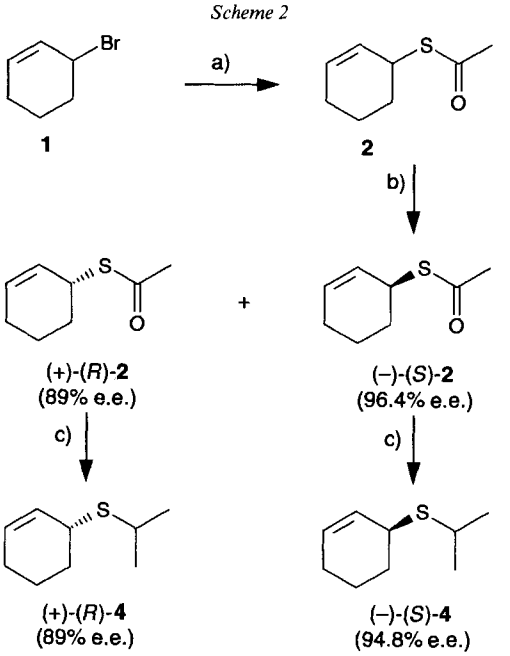
Results. – Synthesis of cyclic, optically active allyl thioethers. To analyze the chirality transfer in the rearrangement of **i** to **iii** the optically active thioethers (+)-(*R*)-**4** and (−)-(*S*)-**4** (*Scheme 2*) have been synthesized. For this purpose 3-bromocyclohexene (**1**) [7], was transferred into racemic *S*-cyclohexenyl thioacetate **2**. Using tri-*O*-acetylcellulose [8], **2** could be resolved chromatographically to (+)-(*R*)-**2** (89% e.e.) and (−)-(*S*)-**2** (96.4% e.e.) on gram scale[1]). Both thioesters (+)-(*R*)-**2** and (−)-(*S*)-**2** were deacetylated [9] to yield the thiols (+)-(*R*)-**3** and (−)-(*S*)-**3**, which were then alkylated with i-PrBr to

[1]) The acetate **2** was the only derivative of cyclohexenethiol that could be separated into its enantiomers. Several other esters resisted resolution. Neither could we achieve a resolution *via* diastereoisomeric thiocarbonates of cyclohexenethiol with (−)-menthol or (−)-borneol nor *via* cyclohexenyl camphanethioates.

Scheme 1



Scheme 2

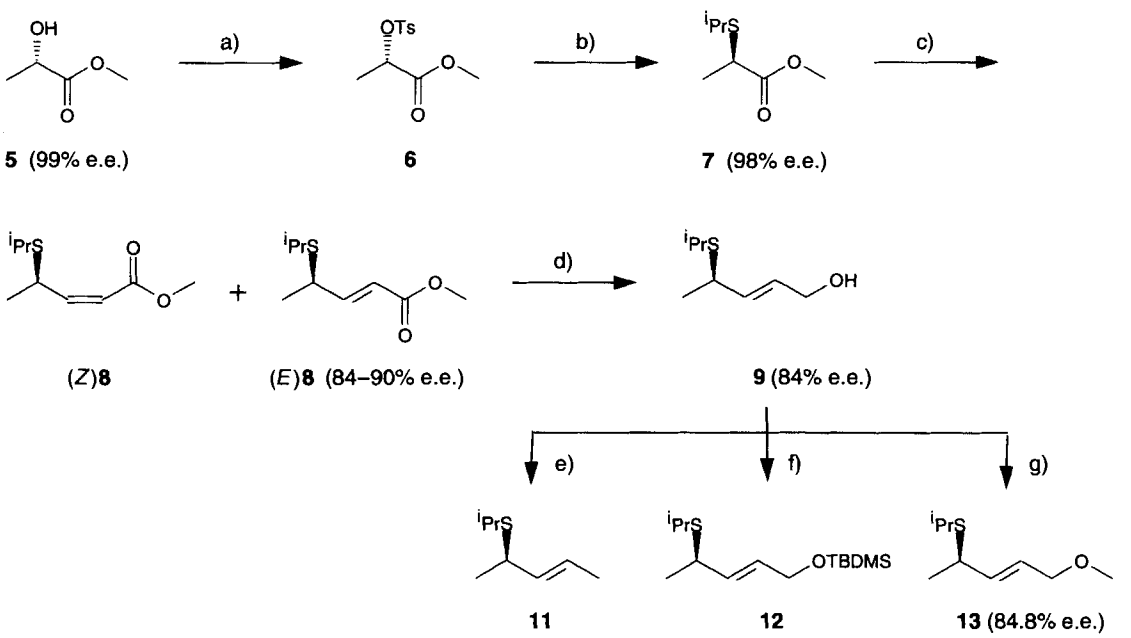


a) AcSH, Et_3N, Et_2O, r.t., 1 d (92%). b) Separation on Tri-*O*-acetylcellulose, eluent EtOH. c) 5% equiv. NaOH, 17 h (→ (+)-(*R*)-**3**: 59%; → (–)-(*S*)-**3**: 96%); i-PrBr, EtONa/EtOH, r.t. (→ (+)-(*R*)-**4**: 69%; → (–)-(*S*)-**4**: 53%).

form the thio ethers (+)-(*R*)-**4** and (−)-(*S*)-**4** [10]. NMR-Shift experiments with (−)-(*R*)-TFAE (= 1-(9-anthryl)-2,2,2-trifluoroethanol) [11] showed an e.e. of 89% for (+)-(*R*)-**4** and 94.4% for (−)-(*S*)-**4**. The absolute configuration of (−)-(*S*)-**4** was assigned by comparison of its TFAE-shifted ^{1}H-NMR spectrum and its optical rotation with the (−)-(*S*)-**4**-enantiomer [12] obtained by an independent synthesis starting from (−)-(*S*)-cyclohex-2-en-1-ol [13].

Synthesis of Open-Chain Chiral Allyl Thioethers. To investigate the chirality transfer in acyclic systems and to determine the chemoselectivity (S *vs.* O migration) [5] the allyl thioethers **11**–**13** have been synthesized starting from the commercially available methyl (−)-(*S*)-lactate **5** (e.e. ≥99%; *Scheme 3*). Ester **5** was first tosylated under carefully controlled conditions [14] to **6**. To avoid racemization of **6**, the reaction mixture was worked up below 5°, and the last traces of base were carefully removed at room temperature under high vacuum before the residue was purified by bulb-to-bulb distillation. Treatment with i-PrSH in MeCN and K_2CO_3 gave, after prolonged reaction time, the thioether **7** without any detectable racemization [15] as indicated in [Eu(hfc)$_3$]-NMR shift experiments (e.e. ≥ 98%). A similar result was obtained from the analysis of the ^{1}H-NMR of the *Mosher* ester (d.e. > 97.4%) obtained from **7** after $LiAlH_4$ reduction. DIBAH Reduction of **7** at low temperature generated the aldehyde, which was immediately quenched [16] with [(methoxycarbonyl)methylidene](triphenyl)phosphorane to give a mixture of the α,β-unsaturated ester (*E*)-**8** and traces of the corresponding (*Z*)-**8**.

Scheme 3

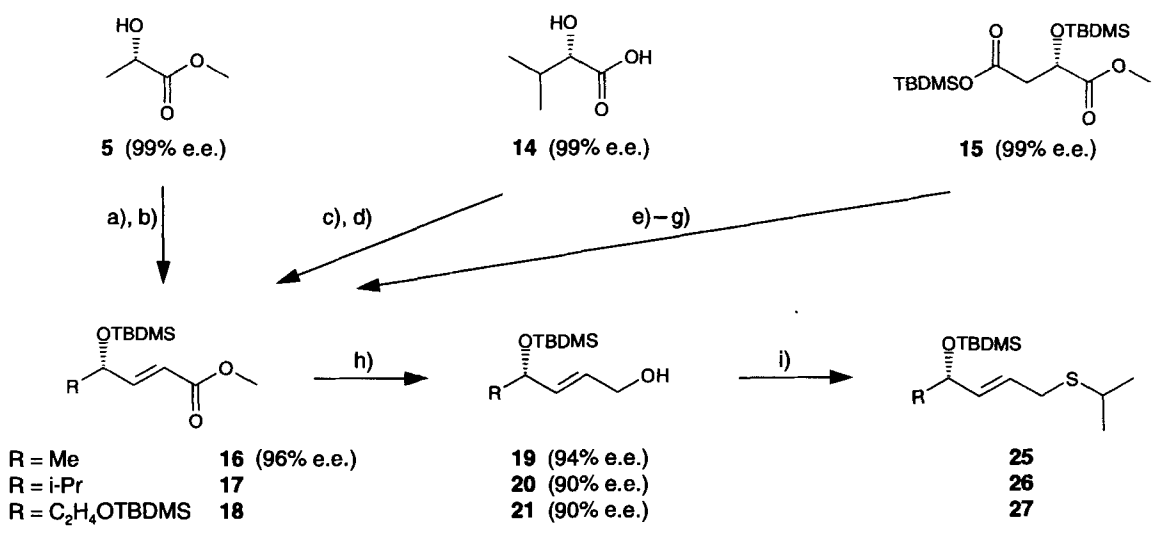


a) TsCl, pyridine, 0°, 6.5 h (69%). b) i-PrSH, K_2CO_3, MeCN, 0° → r.t., 5 d (91%). c) DIBAH, CH_2Cl_2, −78°, 90 min; then $Ph_3PCHCOOCH_3$, −78° → r.t., 12 h ((*E*)-**8**: 76%; (*Z*)-**8**: 1.5%). d) DIBAH, THF, 0°, 50 min (95%). e) Ph_3P, CBr_4, MeCN, r.t. (→ **10**, 81%); $LiAlH_4$, THF, reflux, 3 h (56%). f) (*t*-Bu)Me_2SiCl (TBDMSCl), imidazole, DMF, 16 h, r.t. (85%). g) MeI, NaH, THF (89%).

After chromatographic separation 76% of (*E*)-**8** were obtained. Reduction of (*E*)-**8** with DIBAH gave the alcohol **9** with a d.e. of 84% (determined by its *Mosher* ester). Its treatment with PPh_3/CBr_4 [17] resulted in the unstable allylic bromide **10**, which was immediately reduced with $LiAlH_4$ to yield the thioether **11**. In the ^{1}H-NMR, no chemical-shift differences with various amounts of (−)-(*R*)-TFAE could be observed. Silylation of **9** with (*t*-Bu)Me_2SiCl (TBDMSCl) in the presence of imidazole gave the allylic ether **12**. Methylation of **9** resulted in either **13** (84.8% e.e.) which, in contrast to **11** and **12**, displayed a signal splitting in the ^{1}H-NMR after addition of (−)-(*R*)-TFAE.

Synthesis of Open-Chain Allyl Thioethers. To study the 1,2-induction in the ketene-*Claisen* rearrangement [6], the optically active allyl thioethers **25**–**27** have been synthesized (*Scheme 4*). For this purpose, methyl (−)-L-lactate **5** (ee ≥ 99%) was first silylated [18][19], reduced to lactaldehyde with DIBAH [19], and elongated *in situ* to ester **16** by *Wittig* olefination [19]. The (*E*)/(*Z*) ratio varied between 7 and 9:1 depending on reaction conditions. (*E*)-ester **16** showed an e.e. > 96% according to ^{1}H-NMR experiments with (+)-(*S*)-TFAE. (+)-L-Hydroxyisovaleric acid **14** (e.e. ≥ 99%) was first disilylated, successively reduced to the aldehyde by DIBAH, and then elongated by *Wittig* olefination to yield the α,β-unsaturated ester **17**. Ester **15** was synthesized according to a known procedure [20] from (−)-L-malic acid (e.e. ≥ 99%). Compound **15** was then hydrolyzed selectively, and the resulting carboxylic acid was subsequently transformed to the corresponding alcohol by BH_3SMe_2 reduction [21]. After protection of the OH group as a silyl

Scheme 4



For **25**: a) TBDMSCl, imidazole, DMF, r.t. (98%). b) DIBAH, hexane, −78°, 1 h; then $Ph_3PCHCOOMe$, THF/CH_2Cl_2, −78° → 20°, 1 h ((*E*)-**16**: 51%; (*Z*)-**16**: 7%). h) DIBAH, THF, 0°, 30 min (92%). i) AcSH, Ph_3P, DEAD, THF, 0° (→ **22**, 95%); NaOEt/EtOH, r.t., 1 h, then i-PrBr, r.t. 12 h (92%).

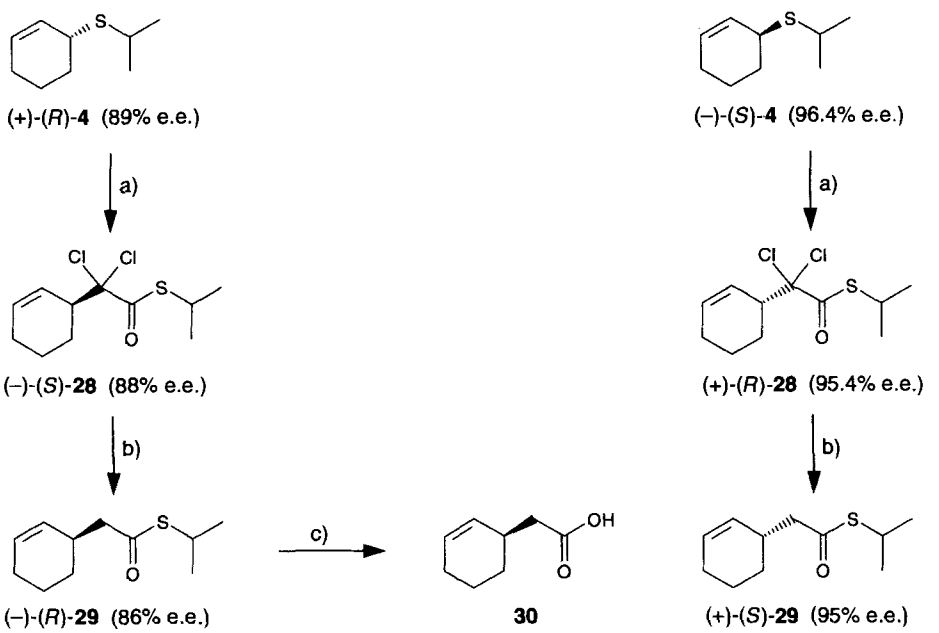
For **26**: c) TBDMSCl, imidazole, DMF, r.t. (quant.). d) DIBAH, THF, −78°, 1 h, then $Ph_3PCHCOOMe$, −78° → 20° ((*E*)-**17**: 81%; (*Z*)-**17**: 1%). h) 83%, i) → **23**: 81%, 82%.

For **27**: e) K_2CO_3, $MeOH/THF/H_2O$, then $KHSO_4$ until pH 4 to 5, 0° (52%). f) $Ph_3 \cdot SMe_2$, THF, 0°, 36 h, then TBDMSCl, imidazole, CH_2Cl_2 (56%). g) DIBAH, hexane, −78°, 1 h; then $Ph_3PCHCOOMe$, THF/CH_2Cl_2, −78° → 20°, 1 h ((*E*)-**18**: 44%; (*Z*)-**18**: 5%). h) 98%, i) → **24**: 79%, 84%.

ether, the chain elongation was processed as described above to yield the α,β-unsaturated ester **18**. The esters **16**–**18** were reduced with DIBAH to the allylic alcohols **19**–**21**. The S-atom was introduced *via* a *Mitsunobu* reaction using thioacetic *S*-acid. Saponification of the allylic thioacetates and alkylation of the resulting thiols with i-PrBr gave the compounds **25**–**27**. Their optical purity was checked *via Mosher* esters of the allyl alcohols **19**–**21**. Compound **19** showed a d.e. ≥ 94%, **20** and **21** a d.e. ≥ 90%.

Rearrangements with Dichloroketene. Dichloroketene [4] was generated *in situ* from Cl_3CCOCl by reductive elimination with activated Zn powder and reacted with (+)-(*R*)-**4** (89% e.e.) and (−)-(*S*)-**4** (96.4% e.e.) to the thioesters (−)-(*S*)-**28** and (+)-(*R*)-**28** (*Scheme 5*). Shift experiments with (−)-(*R*)-TFAE showed an e.e. of 88% for (−)-(*S*)-**28** and 95.4% for (+)-(*R*)-**28**. The two enantiomers could easily be dechlorinated with Zn in AcOH to yield the thioesters (+)-(*R*)-**29** and (−)-(*S*)-**29** in high yield. Furthermore, (−)-(*R*)-**29** could be saponified to the optically active carboxylic acid **30**.

Scheme 5

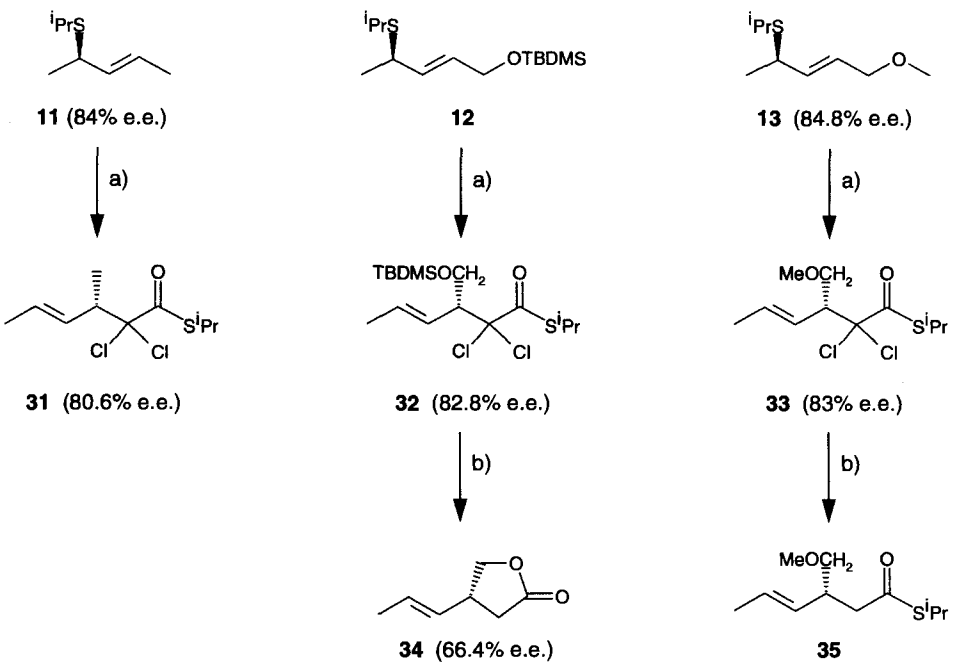


a) Zn/Cu, CCl_3COCl, reflux, Et_2O, 4 h ((−)-(*S*)-**28**: 60%; (+)-(*R*)-**28**: 83%). b) Zn, AcOH, 100°, 3 h ((−)-(*R*)-**29**: 86%; (+)-(*S*)-**29**: 92%). c) $AgNO_3$, dioxane/H_2O, reflux, 3 h (85%).

The open-chain allylic thioether **11** was rearranged under the same conditions to the thioester **31** (80.6% e.e., determined by shift experiments with (−)-(*R*)-TFAE) (*Scheme 6*). The substrates **12** and **13** also underwent a ketene-*Claisen* rearrangement. As determined by IR- and ^{1}H-NMR, exclusive S-migration took place. Only the IR absorption for a thioester (1680 cm^{-1}) and none for an ester (1740 cm^{-1}) could be detected. According to ^{1}H-NMR with TFAE shift reagent, **32** and **33** showed an e.e. of 82.8% and 83%, respectively. Reduction of the α,α-dichloro-thioester **33** with Zn in AcOH [4]

yielded the Cl-free thioester **35** without loss of optical activity, whereas the similar treatment of **32** initiated three simultaneous reactions: dechlorination, deprotection of the OH group, and ring closure to the lactone **34**.

Scheme 6

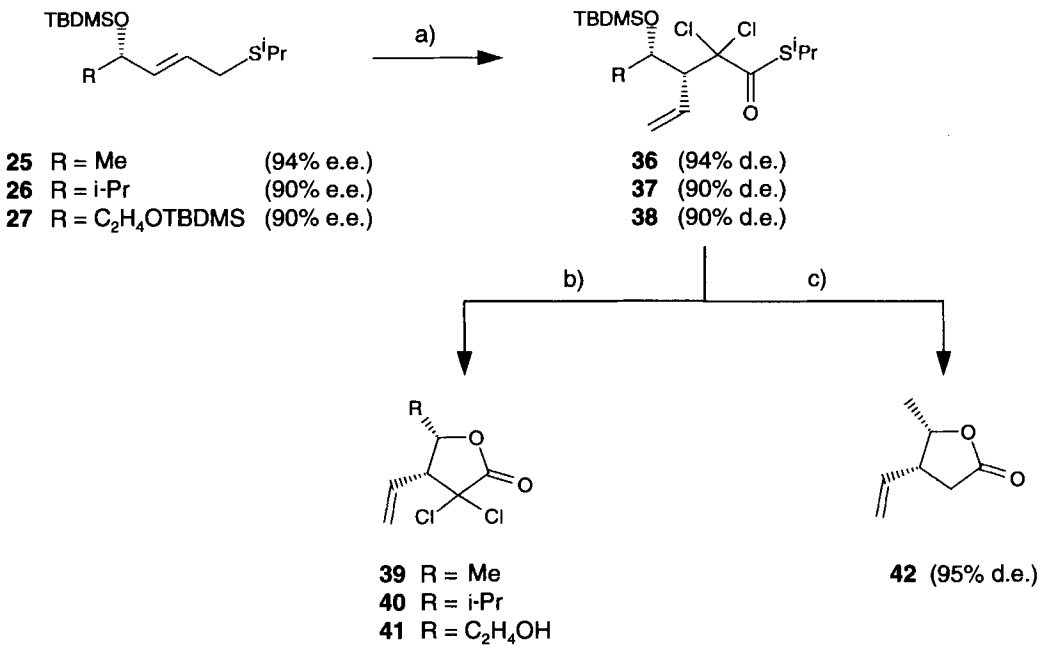


a) Zn/Cu, CCl_3COCl, reflux, 3–4 h (**31**: 71%; **32**: 89%; **33**: 77%). b) AcOH, Zn, reflux, 3 h (**34**: 86%; **35**: 91%).

The thioethers **25**–**27** were also rearranged under the same conditions yielding compounds with two adjacent stereogenic centers (*Scheme 7*). The chiral allylic sulfide **25** (e.e. ≥94%) gave the thioester **36** (d.e. ≥94%), **26** (e.e. ≥90%) the thioester **37** (d.e. ≥90%), and **27** (e.e. ≥90%) the thioester **38** (d.e. ≥90%) as single products each. The diastereoisomeric ratio of these thioesters could easily be deduced from ^{1}H-NMR analyses of the corresponding lactones **39**–**41**. NOE Measurements confirmed a *cis*-arrangement of the alkyl- and the 2-hydroxyethyl group, with respect to the vinyl group. Irradiation on H–C(2) of the vinyl group of **39**–**41** resulted in positive NOE effects on the protons of the Me, i-Pr, and 2-hydroxyethyl group. An additional stereochemical proof could be drawn from the lactone **39**, which was dechlorinated to the lactone **42**. Its spectroscopic data were in good agreement with published data of (4*R*,5*S*) 5-methyl-4-vinyldihydrofuran-2-one [22].

Discussion. – One of the most striking features of the intermolecular variant of the *Claisen* rearrangement is its experimental simplicity and the high chirality transfer from a C–S to a C–C bond. With optically active allyl thioethers the chirality transfer is 99% in the cyclic case (*i.e.*, **4**) and 96–98% in the open-chain cases (*i.e.*, **11**–**13**).

Scheme 7



a) Zn/Cu, CCl_3COCl, Et_2O, reflux, 3–5 h (**36**: 87%; **37**: 71%; **38**: 76%). b) 48% HF in MeCN, 20°, 2 h (**39**: 90%; **40**: 61%; **41**: 46%). c) Zn/Cu, AcOH, 100–110°, 45 min (82%).

Interestingly, if both allylic S- and allylic O-atoms are present in the molecule, dichloroketene reacts with the more nucleophilic S-atom leading exclusively the thioester **32** and **33**, starting from **12** and **13**, respectively. Furthermore, the 1,2-induction in the ketene-*Claisen* rearrangement is close to 100% in the examined cases **25**–**27**. In contrast, diastereoisomeric excesses of only 50% and 13% are observed in the *Claisen* rearrangement of silylketene acetals of L-lactaldehyde [22] or D-glycerylaldehyde [23]. In our study as well as in the above cited examples [22][23], 1,2-*syn*-selectivity prevailed. This observation is in agreement with the models for the steric and electronic course of [3,3]-sigmatropic reactions proposed by *Felkin* and coworkers [24], *Houk et al.* [25], and *Kahn* and *Hehre* [26]. The rearrangement products **36**–**38** are expected to have *syn*-structure, because the reaction should occur *via* transition state **v** (*Scheme 1*) with the minimal 1,3-allylic strain as a stereochemical controlling factor [27]. The postulated selectivity was examined by ^{1}H-NMR spectroscopy of the corresponding butyrolactones **39**–**41** and confirmed to be *ca.* 20:1. A similar, highly prefered formation of the *syn*-diastereoisomers, involving the nucleophilic attacks *anti* with respect to the σ^*(C–O) bond on the chiral C-atom, was observed also in the mechanistically analogous [2,3]-sigmatropic *Wittig* rearrangement [28] and the aza-ketene-*Claisen* rearrangement [29].

Experimental Part

General. Reagents and solvents: purchased from *Fluka AG* in the highest obtainable purity, unless stated otherwise. $CHCl_3$ and $CDCl_3$ were passed through basic alumina (*Woelm*, act. 1) immediately before use. Optical

rotations: *Perkin-Elmer 241 MC*, rotation value at Na^D line was interpolated from the Hg lines 546 nm and 579 nm by the *Drude* equation. TLC: DC Alufolien Kieselgel 60_{F254} (*Merck*), detection UV (254 nm) and/or 0.1*m* $KMnO_4$ spray. Chromatography: Kieselgel 0.032–0.063 mesh (*Merck*). IR Spectra (2–3%) in $CHCl_3$ unless stated otherwise): *Perkin-Elmer 599* IR spectrometer; absorptions in cm^{-1}. NMR Spectra: δ in ppm relative to internal Me_4Si (= 0 ppm) in $CDCl_3$ at r.t. unless stated otherwise, *Varian EM 390* (90 MHz), *Bruker WM 360* (360.13 MHz, 90.56 MHz).

General Procedure A (GP-A): Activation of Zn Powder [30]. 50 ml of 2N HCl were deoxygenated for 20 min by vigorously bubbling Ar through with rapid magnetic stirring. 10 g Zn dust (*Riedel-de-Haen*) were added and the vigorous stirring continued for 30 min under Ar. The solvent was decanted and the moist Zn washed several times with freshly degassed H_2O. Under Ar, 1 g of $CuSO_4 \cdot 3H_2O$ and 40 ml of degassed H_2O were added, and the slurry was stirred overnight at r.t. The solvent was decanted and the activated Zn successively washed with 3×40 ml of degassed H_2O and degassed acteone (3×40 ml). The resulting Zn powder was further dried in high vacuum at r.t. for 4–6 h. The quality of the activated Zn could be maintained for a few months when traces of O_2 were carefully avoided.

General Procedure B (GP-B). Preparation of Mosher-*Ester Derivatives* [31]. 0.4 mmol of alcohol and 0.8 mmol of (+)-(*R*)-*Mosher*-ester chloride (MTPA-Cl) in 1 ml of CCl_4 and 1 ml of pyridine were stirred at r.t. After 1 d, 50 µl (0.4 mmol) *N,N*-dimethylpropanediamine were added, the mixture was stirred for 0.5 h and then poured into 20 ml of H_2O. The org. layer was washed successively with 2×10 ml of 2N HCl, 10 ml of sat. Na_2CO_3, 10 ml of H_2O and 10 ml of brine. After desiccation ($MgSO_4$) and concentration, a colorless oil was obtained, which was ready for NMR inspection. The required information was obtained by integrating the split signals that has been identified before by submitting the corresponding racemate to the same procedure.

General Procedure C (GP-C). Determination of Enantiomeric Excess [11]. The enantiomeric excess was determined by ^{1}H-NMR using (–)-(*R*)-TFAE (1-(9-anthryl)-2,2,2-trifluoroethanol) and (+)-(*S*)-TFAE as chiral shift reagents.

*Syntheses. (*R*)-*S*-(Cyclohex-2-en-1-yl) Thioacetate ((+)-(R)-2) and (*S*)-*S*-(Cyclohex-2-en-1-yl) Thioacetate ((–)-(S)-2).* MeCOSH (16.7 g, 0.22 mol) in 450 ml of Et_2O was treated at r.t. with 22.4 g (0.22 mol) of NEt_3. After 25 min, 32.2 g (0.20 mol) of *3-bromocyclohexene* (**1**) in 100 ml of Et_2O were added dropwise, and the mixture was stirred overnight. The org. layer was successively washed with 200 ml of H_2O, 100 ml of 2N HCl, 200 ml of sat. $NaHCO_3$, and 100 ml of brine. After drying ($MgSO_4$) and evaporation,a yellow liquid was obtained, which was distilled at 50–54°/0.01 mm to yield 28.7 g (92%) of **2**[2]). The enantiomers were separated on tri-*O*-acetylcellulose with EtOH as eluent: (+)-(*R*)-**2**: $[\alpha]_D = +261.8$ ($c = 0.6$, $CHCl_3$); 89% e.e. determined by chiral HPLC (on *Chiralcell CA-1, Daicel*, Jpn.). (–)-(*S*)-**2**: $[\alpha]_D = -267.50$ ($c = 0.5$, $CHCl_3$); 96.4% e.e. determined by chiral HPLC (on *Chiralcell CA-1, Daicel*, Jpn.). IR: 3040*m*, 2940*s*, 1690*s*, 1355*s*, 1115*s*, 755*s*, 645*s*, 635*s*. ^{1}H-NMR: 5.82 (*m*, 1 H); 5.62 (*m*, 1 H); 4.19 (*m*, 1 H); 3.30 (*s*, 3 H); 2.02 (*m*, 2 H); 1.70 (*m*, 4 H). ^{13}C-NMR: 195.46 (*s*); 130.70 (*d*); 126.20 (*d*); 30.44 (*q*); 29.55 (*t*); 24.69 (*t*); 20.05 (*t*). Anal. calc. for $C_8H_{12}OS$: C 61.50, H 7.74, S 20.52; found: C 61.51, H 7.83, S 20.36.

*(3*R*)-3-(Isopropylthio)cyclohexene ((+)-(R)-4) and (3*S*)-3-(Isopropylthio)cyclohexene ((–)-(S)-4).* 25 ml of 5% aq. NaOH were added to 1.56 g (10.0 mmol) of (–)-(*S*)-**2**. After stirring for 17 h at r.t., the mixture was neutralized with 30 ml of 1N HCl. Then, the aq. layer was extracted with Et_2O (3×20 ml), the combined org. layers were dried ($MgSO_4$) and concentrated. The residue was distilled at 90°/120 mm to give 1.1 g (96%) of (–)-(*S*)-**3** as a colorless liquid. By a similar procedure 1.57 g (10.0 mmol) of (+)-(*R*)-**2** were transferred into 0.67 g (59%) of volatile thiol (+)-(*R*)-**3**. The spectroscopic data of both enantiomers were identical. (+)-(*R*)-**3**: $[\alpha]_D = +300.5$ ($c = 0.7$, $CHCl_3$). (–)-(*S*)-**3**: $[\alpha]_D = -315.6$ ($c = 0.7$, $CHCl_3$). IR: 3020*s*, 2940*s*, 730*s*, 720*s*. ^{1}H-NMR: 5.71 (*m*, 2 H); 3.51 (*m*, 1 H); 1.4–2.2 (*m*, 7 H).

Both thiols were immediately alkylated [32]. To 3 ml of freshly prepared NaOEt soln. (1 mmolar in EtOH), 0.34 g (3 mmol) (+)-(*R*)-**3** were added. After 10 min, 0.37 g (3 mmol) of i-PrBr were injected, and the mixture was stirred for 1 d at r.t. Then, the mixture was diluted with 50 ml of Et_2O, dried ($MgSO_4$), and evaporated. After bulb-to-bulb distillation at 75–85°/14 mm, 0.32 g (69%) (+)-(*R*)-**4** were obtained as a colorless oil. Analogous treatment of (–)-(*S*)-**3** yielded 0.25 g (53%) of (–)-(*S*)-**4**. (+)-(*R*)-**4**: $[\alpha]_D = +212.5$ ($c = 0.8$, $CHCl_3$); optical purity determined by *GP-C*: 89% e.e. (–)-(*S*)-**4**: $[\alpha]_D = -215.7$ ($c = 0.9$, $CHCl_3$); optical purity determined by *GP-C*: 94.8% e.e. IR: 3025*s*, 2960*s*, 2930*s*, 2865*s*, 1455*s*, 755*s*, 725*s*. ^{1}H-NMR: 5.81 (*m*, 1 H); 5.62 (*m*, 1 H); 3.29 (*m*, 1 H); 2.76 (*sept.*, $J = 6.7$, 1 H); 1.81 (*m*, 5 H); 1.43 (*m*, 1 H); 1.16 (*d*, $J = 6.7$, 3 H); 1.14 (*d*, $J = 6.7$, 3 H). ^{13}C-NMR: 128.9 (*d*); 128.17 (*d*); 39.39 (*d*); 34.35 (*d*); 30.00 (*t*); 24.94 (*t*); 19.82 (*t*); 23.97 (*q*); 23.82 (*q*).

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[2]) The racemic acetate could also be obtained in 91% yield from acetylation of cyclohexenethiol with AcCl [30].

Methyl (2S)-2-(4-Tolylsulfonyloxy)propionate (**6**; *cf.* [14] for ethyl ester). TsCl (10.98 g, 110 mmol) was mixed with 100 ml of pyridine in an ice bath. Methyl (*S*)-lactate (**5**; 10.41 g, 100 mmol) was added keeping the temp. below 5°. After 6.5 h, the reaction was stopped by successive addition of 2.5 ml of ice-water and 10 ml of H_2O. After extraction with $CHCl_3$ (3 × 200 ml) the org. layer was successively washed with H_2O (3 × 150 ml), 1N HCl (3 × 150 ml), brine (150 ml), and H_2O (100 ml), and dried ($MgSO_4$). Filtration and evaporation at r.t. in high vacuum yielded 17.78 g (69%) **6** as an oily liquid, which crystallized at 6°. $[\alpha]_D = -36.6$ to -37.5 ($c = 1.9$, $CHCl_3$). IR: 3000*w*, 1860*s*, 1600*w*, 1195*s*, 1180*s*, 735*s*, 670*s*. ^{1}H-NMR: 7.86 (*m*, 2 H); 7.42 (*m*, 2 H); 5.01 (*q*, $J = 7$, 1 H); 3.72 (*s*, 3 H); 2.51 (*s*, 3 H); 1.48 (*d*, $J = 7.5$, 3 H). ^{13}C-NMR: 169.18 (*s*); 144.94 (*s*); 133.10 (*s*); 129.60 (*d*); 127.71 (*d*); 73.87 (*d*); 52.33 (*q*); 21.40 (*q*). Anal. calc. for $C_{14}H_{12}O_5S$: C 51.15, H 5.46, S 12.41; found: C 51.14, H 5.47, S 12.26.

Methyl (2R)-2-(Isopropylthio)propionate (**7**). Finely ground K_2CO_3 (18.19 g, 131 mmol) and i-PrSH (5.33 g, 70 mmol) were mixed in MeCN (100 ml). Within 1 h, 17.00 g (65.8 mmol) of **6** in 100 ml of MeCN were added dropwise. Then, the mixture was vigorously stirred for 5 d at r.t. After evaporation at 30°, the residue was dissolved in 300 ml of Et_2O. The org. layer was washed with 80 ml of H_2O, dried ($MgSO_4$), and evaporated. After bulb-to-bulb distillation at 110–115°/14 mm, 9.69 g (91%) of **7**, a pale yellow liquid, were obtained. $[\alpha]_D = +131.5$ ($c = 1.0$, $CHCl_3$); optical purity determined by *GP-C*: 98% e.e. IR: 2970*s*, 2940*s*, 1740*s*, 1450*s*, 1260*s*, 1160*s*, 1075*s*. ^{1}H-NMR: 3.74 (*s*, 3 H); 3.48 (*q*, $J = 7.5$, 1 H); 3.07 (*sept.*, $J = 7.5$, 1 H); 1.45 (*d*, $J = 7.5$, 3 H); 1.31 (*d*, $J = 7.5$, 3 H); 1.23 (*d*, $J = 7.5$, 3 H). ^{13}C-NMR: 174.14 (*s*); 52.14 (*q*); 40.29 (*d*); 35.42 (*d*); 23.57 (*q*); 23.18 (*q*); 17.64 (*q*). Anal. calc. for $C_7H_{13}O_2S$: C 51.82, H 8.70, S 19.76; found: C 51.41, H 8.62, S 19.46.

Methyl (4R,2E)-4-(Isopropylthio)pent-2-enoate ((*E*)-**8**) *and Methyl (4R,2Z)-4-(Isopropylthio)pent-2-enoate* ((*Z*)-**8**). Under Ar, 6.49 g (40 mmol) of **7** in 140 ml of dry CH_2Cl_2 were cooled to $-78°$; 45 ml (45 mmol; 1M in hexane) of DIBAL soln. were then added dropwise during 30 min. After further 45 min at $-78°$, 16.7 g (50 mmol) of (methoxycarbonyl)(methylidene)(triphenyl)phosphorane were added in one portion. The mixture was warmed to r.t. overnight with stirring. After addition of 100 ml of 30% aq. Na/K tartrate, the mixture was stirred for 1 h. The aq. layer was separated and washed with $CHCl_3$ (2 × 100 ml). The combined org. layers were dried ($MgSO_4$), concentrated, and the residue was purified by flash chromatography on silica gel with petroleum ether/AcOEt 85:15 yielding 5.71 g (76%) of (*E*)-**8** and 117 mg (1.5%) of (*Z*)-**8**.

Data of (E)-**8**: $[\alpha]_D = +112.6$ ($c = 1.3$, $CHCl_3$); optical purity determined by *GP-C*: 84–90% e.e. IR: 2970*s*, 2940*s*, 1740*s*, 1650*s*, 1440*s*, 1265*s*, 1220*s*, 1175*s*, 980*m*. ^{1}H-NMR: 6.78 (*dd*, $J = 15.5$, 9.3, 1 H); 5.79 (*dd*, $J = 15.5$, 0.7, 1 H); 3.74 (*s*, 3 H); 3.51 (*ddq*, $J = 9.3$, 6.9, 0.7, 1 H); 2.78 (*sept.*, $J = 6.7$, 1 H); 1.34 (*d*, $J = 6.9$, 3 H); 1.23 (*d*, $J = 6.7$, 3 H); 1.21 (*d*, $J = 6.7$, 3 H). ^{13}C-NMR: 166.67 (*s*); 150.05 (*d*); 119.11 (*d*); 51.52 (*q*); 39.85 (*d*); 34.10 (*d*); 23.73 (*q*); 23.05 (*q*); 19.76 (*q*). Anal. calc. for $C_9H_{16}O_2S$: C 57.41, H 8.57, S 17.03; found: C 57.03, H 8.61, S 16.20.

Data of (Z)-**8**: IR: 3030*w*, 2970*s*, 2940*s*, 1725*s*, 1640*s*, 1220*s*, 1200*s*, 1185*s*, 830*s*. ^{1}H-NMR: 6.04 (*dd*, $J = 11.3$, 10.8, 1 H); 5.73 (*dd*, $J = 11.3$, 0.8, 1 H); 4.87 (*ddq*, $J = 10.8$, 6.9, 0.8, 1 H); 3.71 (*s*, 3 H); 2.78 (*sept.*, $J = 6.7$, 1 H); 1.27 (*d*, $J = 6.7$, 3 H); 1.26 (*d*, $J = 6.7$, 3 H); 1.20 (*d*, $J = 6.9$, 3 H). ^{13}C-NMR: 166.67 (*s*); 152.16 (*d*); 117.01 (*d*); 51.16 (*q*); 42.30 (*d*); 34.62 (*d*); 24.26 (*q*); 23.25 (*q*); 20.24 (*q*).

(4R,2E)-4-(Isopropylthio)pent-2-en-1-ol (**9**). Under Ar, 0.63 g (3.3 mmol) of (*E*)-**8** in 10 ml THF were cooled to 0° and treated with 10 ml (10 mmol, 1M in hexane) of DIBAH soln. After 30 min, 1.5 ml of MeOH, 1 ml of H_2O, 1 ml of 5% aq. NaOH, and 10 ml of 30% aq. Na/K tartrate were added. The mixture was stirred for 2 h at r.t. and then extracted with Et_2O (3 × 20 ml). The combined org. layers were dried ($MgSO_4$), concentrated, and purified by bulb-to-bulb distillation at 90–100°/0.02 mm yielding 0.5 g (95%) of **9** as a colorless oil. $[\alpha]_D = +40.6$–42.6 ($c = 0.7$, $CHCl_3$); optical purity determined by *GP-B*: 84–88% e.e. IR: 3350*s*, 2970*s*, 2930*s*, 2870*s*, 1045*s*, 1005*s*, 970*s*. ^{1}H-NMR: 5.63 (*m*, 2 H); 4.12 (*d*, $J = 4.8$, 2 H); 3.43 (*dq*, $J = 8.1$, 6.9, 1 H); 2.84 (*sept.*, $J = 6.7$, 1 H); 2.43 (br. *d*, 1 H); 1.30 (*d*, $J = 6.9$, 3 H); 1.26 (*d*, $J = 8.1$, 3 H); 1.22 (*d*, $J = 8.1$, 2 H). ^{13}C-NMR: 134.78 (*d*); 128.52 (*d*); 62.81 (*t*); 40.41 (*d*); 33.79 (*d*); 23.73 (*q*); 23.14 (*q*); 20.76 (*q*). Anal. calc. for $C_8H_{16}OS$: C 59.95, H 10.06, S 20.00; found: C 60.37, H 10.24, S 18.90.

(4R,2E)-1-Bromo-4-(isopropylthio)pent-2-ene (**10**). At r.t. under Ar, 0.80 g (5 mmol) of **9** and 1.97 g (7.5 mmol) of PPh_3 in 20 ml of dry MeCN were treated with 2.49 g (7.5 mmol) of CBr_4 in 5 ml of MeCN. After 40 min, the mixture was diluted with 150 ml of Et_2O and filtered over 40 g of silica gel. The solvent was removed and the crude product immediately purified by flash chromatography on silica gel with petroleum ether/AcOEt 85:15 to give 0.90 g (81%) of the pale-yellow liquid **10**. Storage overnight at r.t. resulted in complete decomposition. IR: 3030*s*, 2960*s*, 2920*s*, 2860*s*, 1650*s*, 960*s*. ^{1}H-NMR: 5.67 (*m*, 2 H); 3.96 (*d*, $J = 14$, 2 H); 3.42 (*dq*, $J = 8.0$, 6.8, 1 H); 2.82 (*sept.*, $J = 8.1$, 1 H); 1.29 (*d*, $J = 6.8$, 3 H); 1.22 (*d*, $J = 8.1$, 3 H); 1.14 (*d*, $J = 8.1$, 3 H).

(4R,2E)-4-(Isopropylthio)pent-2-ene (**11**). Under Ar, 1.28 g (5.7 mmol) of **10** in 17 ml of dry THF were added to a suspension of 0.24 g (6.33 mmol) of $LiAlH_4$ in 5 ml of dry THF and refluxed of 3 h with vigorous stirring

[39]. After cooling to r.t. the excess hydride was destroyed by consecutive addition of 0.5 ml of H_2O, 0.5 ml of 2N NaOH, and again 0.5 ml of H_2O. The resulting slurry was stirred for 1.5 h and extracted with Et_2O (3 × 30). After drying ($MgSO_4$) and evaporation, the crude material was purified by bulb-to-bulb distillation at 90°/80–90 mm to yield 0.46 g (56%) of the colorless, volatile **11**. $[\alpha]_D = +19.6$ ($c = 0.7$, $CHCl_3$). IR: 3030*w*, 2980*s*, 1455*s*, 970*s*, 930*s*. ^{1}H-NMR (C_6D_6): 5.36 (*ddq*, $J = 15.1, 8.3, 1.2, 1$ H); 5.25 (*dq*, $J = 15.1, 6.6, 1$ H); 3.27 (*dq*, $J = 8.3, 6.9, 1$ H); 1.50 (*dd*, $J = 6.1, 1.2, 3$ H); 2.76 (*sept.*, $J = 6.7, 1$ H); 1.24 (*d*, $J = 6.9, 3$ H); 1.18 (*d*, $J = 6.7, 3$ H); 1.16 (*d*, $J = 6.7, 3$ H). ^{13}C-NMR: 134.40 (*d*); 124.53 (*d*); 41.11 (*d*); 33.67 (*d*); 23.78 (*q*); 23.18 (*q*); 21.02 (*q*); 17.50 (*q*).

*(4*R,*2*E*)-1-[(*tert-*Butyl)dimethylsilyloxy]-4-(isopropylthio)pent-2-ene* (**12**). Under Ar, 0.32 g (2 mmol) of **9** in 2 ml of dry DMF were treated at r.t. with 0.27 g (4 mmol) of imidazole and 0.33 g (2.2 mmol) of (*t*-Bu)Me_2SiCl (TBDMSCl) [19]. After 16 h, the mixture was poured on 10 ml ice-water and extracted with Et_2O (3 × 10 ml). The combined org. layers were dried ($MgSO_4$), concentrated, and purified by bulb-to-bulb distillation at 105–110°/0.05 mm to give 0.47 g (85%) of the colorless liquid **12**. $[\alpha]_D = +33.2$ ($c = 0.8$, $CHCl_3$). IR: 2980*s*, 2930*s*, 2860*s*, 1255*s*, 1110*s*, 1075*s*, 840*s*, 780*s*. ^{1}H-NMR: 5.55 (*m*, 2 H); 4.16 (*m*, 2 H); 3.42 (*dq*, $J = 6.9, 1.5, 1$ H); 2.83 (*sept.*, $J = 6.7, 1$ H); 1.30 (*d*, $J = 6.9, 3$ H); 1.25 (*d*, $J = 6.7, 3$ H); 1.21 (*d*, $J = 6.7, 3$ H); 0.91 (*s*, 9 H); 0.07 (*s*, 6 H). ^{13}C-NMR: 133.43 (*d*); 128.91 (*d*); 63.30 (*t*); 40.59 (*d*); 33.73 (*d*); 25.96 (*q*); 23.80 (*q*); 23.19 (*q*); 20.78 (*q*); 13.36 (*q*); −5.11 (*q*). Anal. calc. for $C_{14}H_{30}OSSi$: C 61.25, H 11.02, S 11.68; found: C 61.16, H 10.72, S 11.43.

*(4*R,*2*E*)-4-(Isopropylthio)-1-methoxypent-2-ene* (**13**). Compound **9** (0.48 g, 3 mmol) was added slowly to a suspension of 96 mg (4 mmol) of oil-free NaH in 12 ml of dry THF with vigorous stirring [38]. The deprotonation was completed by heating the mixture to reflux for 30 min. After cooling to r.t., 0.5 g (3.5 mmol) of MeI were injected, and the mixture was stirred overnight. For workup, the reaction was quenched with 10 ml of H_2O and extracted with Et_2O (3 × 20 ml). The org. layers were dried ($MgSO_4$) and concentrated. The residue was purified by bulb-to-bulb distillation at 120–125°/16 mm to yield 0.47 g (89%) **13**. Colorless oil. $[\alpha]_D = +34.3$ ($c = 0.8$, $CHCl_3$); optical purity determined by *GP-C*: 84.8% e.e. IR: 2980*s*, 2930*s*, 2870*s*, 1660*w*, 1120*s*, 970*s*. ^{1}H-NMR: 5.59 (*m*, 2 H); 4.44 (*dq*, $J = 6.8, 1.4, 2$ H); 3.91 (*d*, $J = 4.6, 1$ H); 3.32 (*s*, 3 H); 2.82 (*sept.*, $J = 6.7, 1$ H); 1.30 (*d*, $J = 6.8, 3$ H); 1.25 (*d*, $J = 6.7, 3$ H); 1.22 (*d*, $J = 6.7, 3$ H). ^{13}C-NMR: 136.48 (*d*); 125.68 (*d*); 72.52 (*t*); 57.75 (*q*); 40.54 (*d*); 33.75 (*d*); 23.76 (*q*); 23.14 (*q*); 20.73 (*q*).

*Methyl (4*S,*2*E*)-4-[(*tert-*Butyl)dimethylsilyloxy]pent-2-enoate* ((*E*)-**16**) *and Methyl (4*S,*2*Z*)-4-[(*tert-*Butyl)dimethylsilyloxy]pent-2-enoate* ((*Z*)-**16**). Compound **5** was transformed into the corresponding TBDMS derivative according to [18][19]. To 13.10 g (60 mmol) of methyl (2*S*)-2-[(*tert*-butyl)dimethylsilyloxy]propionate in 60 ml of dry hexane under Ar at −78°, 65 ml (1M in hexane; 65 mmol) of DIBAL soln. were added dropwise within 30 min. After 1 additional h of stirring 20.5 g (60 mmol) of (methoxycarbonyl)(methylidene)(triphenyl)phosphorane were added. The ylide was totally dissolved after further addition of 40 ml of THF and 50 ml of CH_2Cl_2. After 1 h, the mixture was warmed to r.t. and poured onto 60 ml ice-water. The org. layer was separated and the aq. layer extracted with Et_2O (3 × 100 ml). The combined org. layers were washed with brine (100 ml), dried ($MgSO_4$), and concentrated. The residue was purified by flash chromatography (petroleum ether/AcOEt 95:5) to give 7.48 g (51%) of (*E*)-**16** and 1.08 g (7%) of (*Z*)-**16**.

*Data of (*E*)-***16***: $[\alpha]_D = +5.3$ ($c = 1.0$, $CHCl_3$); optical purity determined by *GP-C*: 96% e.e. IR: 2965*s*, 2940*s*, 2860*s*, 1730*s*, 1660*m*, 1280*s*, 1155*s*, 970*s*, 840*s*, 780*s*. ^{1}H-NMR: 6.94 (*dd*, $J = 15.3, 4.2, 1$ H); 6.00 (*dd*, $J = 15.3, 1.8, 1$ H); 4.86 (*ddq*, $J = 6.5, 4.2, 1.8, 1$ H); 3.73 (*s*, 3 H); 1.25 (*d*, $J = 6.5, 3$ H); 0.91 (*s*, 9 H); 0.07 (*s*, 3 H); 0.06 (*s*, 3 H). ^{13}C-NMR: 167.13 (*s*); 152.13 (*d*); 113.57 (*d*); 67.70 (*d*); 51.45 (*q*); 25.83 (*q*); 23.54 (*q*); 13.22 (*s*); −4.83 (*q*).

*Data of (*Z*)-***16***: $[\alpha]_D = +57.4$ ($c = 1.0$, $CHCl_3$). IR: 2960*s*, 2935*s*, 2860*s*, 1725*s*, 1650*w*, 1200*s*, 1135*s*, 1080*s*, 835*s*, 780*s*. ^{1}H-NMR [23]: 6.21 (*dd*, $J = 11.6, 2.8, 1$ H); 5.65 (*dd*, $J = 11.6, 1.3, 1$ H); 5.55 (*ddq*, $J = 7.8, 6.4, 1.3, 1$ H); 3.71 (*s*, 3 H); 1.24 (*d*, $J = 6.4, 3$ H); 0.88 (*s*, 9 H); 0.06 (*s*, 3 H); 0.03 (*s*, 3 H). ^{13}C-NMR: 166.13 (*s*); 155.01 (*d*); 116.35 (*d*); 65.45 (*d*); 51.13 (*q*); 25.83 (*q*); 23.50 (*q*); 13.15(*s*); −4.73 (*q*); −4.77 (*q*).

*Methyl (4*S,*2*E*)-4-[(*tert-*Butyl)dimethylsilyloxy]-5-methylhex-2-enoate* ((*E*)-**17**) *and Methyl (4*S,*2*E*)-4-[(*tert-*Butyl)dimethylsilyloxy]-5-methylhex-2-enate* ((*Z*)-**17**): Under Ar at r.t., 5.0 g (42.3 mmol) *2-hydroxy-3-methylbutanoic acid* (**14**) in 80 ml of dry CH_2Cl_2 were treated successively with 11.8 g (173.1 mmol) of imidazole and 13.8 g (91.6 mmol) of TBDMSCl. After 24 h at r.t., additional portions of imidazole (3.52 g, 51.7 mmol) and TBDMSCl (4.1 g, 27.2 mmol) were added, and stirring was continued for further 15 h. The mixture was washed with sat. $NaHCO_3$ (2 × 25 ml), H_2O, and brine, and dried ($MgSO_4$). Evaporation gave 15 g of the crude silyl-ester which was used without further purification. $[\alpha]_D = -23.3$ ($c = 1.4$, $CHCl_3$). IR: 2950*s*, 2920*s*, 2850*s*, 1720*s*, 1250*s*, 1105*m*, 1065*m*, 835*s*. ^{1}H-NMR: 3.91 (*d*, $J = 4.5, 1$ H); 2.00 (*dsept.*, $J = 6.8, 4.5, 1$ H); 0.94 (*s*, 9 H); 0.93 (*d*, $J = 6.8, 3$ H); 0.91 (*s*, 9 H); 0.90 (*d*, $J = 6.8, 3$ H); 0.10 (*s*, 6 H); 0.06 (*s*, 3 H); 0.04 (*s*, 3 H). ^{13}C-NMR: 173.6 (*s*); 77.6 (*d*); 25.80 (*q*); 25.70 (*q*); 25.60 (*q*); 25.40 (*q*); 19.00 (*s*); 13.3 (*s*); 16.9 (*d*); −3.50 (*q*); −4.80 (*q*); −4.90 (*q*); −5.50 (*q*).

Under Ar, 15 g of crude silyl-ester (43.4 mmol) in 45 ml of dry hexane were cooled to −78° and reduced slowly by addition of 43.6 ml (43.6 mmol; 1M in hexane) of DIBAL soln. TLC showed complete consumption of the starting ester after 1 h at −78°. Then, 13.84 g (43.4 mmol) of (methoxycarbonyl)(methylidene)-(triphenyl)phosphorane were added, the resulting suspension was diluted with 30 ml of dry THF and 36 ml of dry CH_2Cl_2, and the reaction mixture warmed to r.t. within 4 h. For workup the reaction mixture was poured onto 45 ml of ice-water, the org. layer separated and the aq. layer extracted with Et_2O (3 × 40 ml). The combined org. layers were dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel (Et_2O/petroleum ether 1:25) to yield 9.107 g (81%) of (*E*)-**17** and 900 mg (8%) of (*Z*)-**17**.

Data of (E)-**17**: $[\alpha]_D$ = + 1.0 (*c* = 1.0, $CHCl_3$). IR: 2950*s*, 2925*s*, 2880*s*, 1705*s*, 1650*m*, 1280*s*, 1250*s*, 1165*m*, 1080*m*, 837*s*. ^{1}H-NMR: 6.90 (*dd*, *J* = 15.6, 4.9, 1 H); 5.95 (*dd*, *J* = 15.6, 1.6, 1 H); 4.04 (*dt*, *J* = 4.9, 1.6, 1 H); 3.71 (*s*, 3 H); 1.74 (*dsept.*, *J* = 6.8, 4.9, 1 H); 0.88 (*s*, 9 H); 0.85 (*d*, *J* = 6.8, 3 H); 0.83 (*d*, *J* = 6.8, 3 H); 0.01 (*s*, 3 H); −0.03 (*s*, 3 H). ^{13}C-NMR: 166.91 (*s*); 149.83 (*d*); 120.51 (*d*); 76.43 (*d*); 51.44 (*q*); 34.54 (*d*); 25.83 (*q*); 17.62 (*q*); 13.22 (*s*); 13.12 (*q*); −4.41 (*q*); −4.83 (*q*).

Data of (Z)−**17**: $[\alpha]_D$ = + 23.1 (*c* = 0.8, $CHCl_3$). IR: 2955*s*, 2925*s*, 2880*m*, 1712*s*, 1460*m*, 1250*s*, 1175*m*, 1055*s*, 970*s*, 835*s*. ^{1}H-NMR: 6.15 (*dd*, *J* = 11.8, 8.6, 1 H); 5.76 (*dd*, *J* = 11.8, 1.1, 1 H); 5.08 (*ddd*, *J* = 8.6, 5.4, 1.1, 1 H); 3.71 (*s*, 3 H); 1.62 (*m*, 1 H); 0.91 (*d*, *J* = 6.5, 3 H); 0.89 (*d*, *J* = 6.5, 3 H); 0.88 (*s*, 9 H); 0.06 (*s*, 3 H); 0.05 (*s*, 3 H). ^{13}C-NMR: 166.30 (*s*); 152.91 (*d*); 113.10 (*d*); 72.55 (*d*); 51.12 (*q*); 34.68 (*d*); 25.81 (*q*); 17.32 (*q*); 13.60 (*q*); 13.15 (*s*); −4.93 (*q*); −4.47 (*q*).

*Methyl (4S,2E)-4,6-Bis[(*tert*-Butyl)dimethylsilyloxy]hex-2-enoate* ((*E*)-**18**) *and Methyl (4S,2Z)-4,6-Bis-[(*tert*-butyl)dimethylsilyloxy]hex-2-enoate* ((*Z*)-**18**). 1. *Hydrolysis of the Silyl-ester:* Silyl-ester **15** (25.7 g, 70.29 mmol) in 160 ml of MeOH and 50 ml of THF were treated with 26.3 g (0.265 mmol) of K_2CO_3 dissolved in 250 ml of H_2O. After stirring at r.t. for 2 h, the mixture was concentrated to 25% of the original volume, 800 ml of brine were added, the soln. was cooled to 0°, and acidified to pH 4 to 5 with solid $KHSO_4$. After extraction with Et_2O (4 × 200 ml), the combined org. layers were dried (Na_2SO_4) and concentrated to yield 9.6 g (52%) of a pale-yellow oil.

2. *Borane Reduction.* The crude carboxylic acid in 60 ml of dry THF was cooled to 0° and 4.4 ml BH_3SMe_2 (10% in THF, 44 mmol) were injected slowly at 0°. After stirring overnight, the reaction was quenched by dropwise addition of 15 ml of H_2O. The mixture was extracted with Et_2O (4 × 20 ml). The combined org. layers were washed with sat. $NaHCO_3$ (3 × 20 ml) and brine (20 ml), dried ($MgSO_4$), and concentrated.

3. *Silylation.* The crude alcohol in 80 ml of CH_2Cl_2 was successively treated with 5.0 g (73.4 mmol) of imidazole and 5.6 g (37.15 mmol) of TBDMSCl. After stirring at r.t. overnight, the mixture was washed with H_2O (100 ml). The aq. layer was extracted with CH_2Cl_2 (3 × 20 ml), the combined org. layers were dried ($MgSO_4$), and the solvent was evaporated. Purification on silica gel (petroleum ether/Et_2O 1:3) yielded 7.43 g (56%) of the bis-silyl ether as a volatile liquid.

4. *Chain Elongation.* Under Ar, 7.38 g (20.35 mmol) of the bis-silyl ether in 25 ml of dry hexane were cooled to −78° and reduced by slow addition of 21 ml (1M in hexane; 21 mmol) DIBAL soln. TLC showed complete consumption of the ester after 90 min. Then, 7.1 g (21 mmol) of (methoxycarbonyl)(methylidene)(triphenyl)-phosphorane, 15 ml of THF, and 20 ml of CH_2Cl_2 were added, and the mixture was warmed to r.t. within 4 h. After pouring the mixture on ice-water, the org. layer was separated and the aq. layer extracted with Et_2O (3 × 30 ml). The combined org. layers were dried ($MgSO_4$) and concentrated to yield, after chromatographic separation on silica gel (petroleum ether/Et_2O 10:1), 3.48 g of (44%) (*E*)-**18** and 397 mg (5%) of (*Z*)-**18**.

Data of (E)-**18**: $[\alpha]_D$ = − 7.6 (*c* = 0.77, $CHCl_3$). IR: 2945*s*, 2920*s*, 2850*m*, 1710*s*, 1650*w*. ^{1}H-NMR: 6.97 (*dd*, *J* = 15.5, 4.6, 1 H); 5.98 (*dd*, *J* = 15.5, 1.6, 1 H); 4.50 (*qd*, *J* = 4.6, 1.6, 1 H); 3.74 (*s*, 3 H); 3.68 (*m*, 2 H); 1.72 (*m*, 2 H); 0.91 (*s*, 9 H); 0.89 (*s*, 9 H); 0.05 (*s*, 6 H); 0.01 (*s*, 6 H). ^{13}C-NMR: 186.24 (*s*); 151.33 (*d*); 119.19 (*d*); 68.71 (*d*); 58.86 (*t*); 51.40 (*q*); 40.60 (*t*); 25.85 (*q*); 18.19 (*s*); −4.58 (*q*); −4.99 (*q*); −5.33 (*q*).

Data of (Z)-**18**: $[\alpha]_D$ = −4.3 (*c* = 0.61, $CHCl_3$). IR: 2950*m*, 2920*m*, 2870*w*, 2850*m*, 1710*s*. ^{1}H-NMR: 6.19 (*dd*, *J* = 11.7, 8.2, 1 H); 5.68 (*dd*, *J* = 11.7, 1.2, 1 H); 5.40 (*m*, 1 H); 3.72 (*m*, 2 H); 3.71 (*s*, 3 H); 1.74 (*m*, 2 H); 0.89 (*s*, 9 H); 0.87 (*s*, 9 H); 0.05 (*s*, 6 H); 0.04 (*s*, 3 H); 0.01 (*s*, 3 H). ^{13}C-NMR: 166.28 (*s*); 153,73 (*d*); 117.16 (*d*); 66.27 (*d*); 59.48 (*t*); 51.20 (*q*); 40.54 (*t*); 25.99 (*q*); 25.84 (*q*); 18.31 (*s*); 18.10 (*s*); −4.58 (*q*); −4.96 (*q*); −5.31 (*q*).

*(4S,2E)-4-[(*tert*-Butyl)dimethylsilyloxy]pent-2-en-1-ol* (**19**). At 0°, 7.37 g (30 mmol) of **16** in 100 ml of dry THF were reduced within 20 min by careful addition of 95 ml (1M in hexane; 95 mmol) of DIBAL soln. After 30 min, the mixture was quenched by successive addition of 6 ml of MeOH, 6 ml of 2N NaOH, and 6 ml of H_2O with vigorous stirring. Na/K Tartrate (50 ml, 30%) was added and the org. layer separated. The aq. layer was further extracted with CH_2Cl_2 (3 × 100 ml). The combined org. layers were dried ($MgSO_4$) and concentrated leaving an oil, which was purified by bulb-to-bulb distillation at 115–120°/0.2 mm yielding 6.0 g (92%) of **19**.

Colorless liquid. $[\alpha]_D = +5.0$ ($c = 0.8$, $CHCl_3$); optical purity determined by *GP-B*: ≥ 94% e.e. IR: 3340*s*, 2970*s*, 2940*s*, 2870*s*, 2800*s*, 1260*s*, 1155*s*, 1090*s*, 970*s*, 840*s*, 780*s*. ^{1}H-NMR: 5.73 (*m*, 2 H); 4.32 (*m*, 1 H); 4.12 (*m*, 2 H); 1.84 (br. *s*, OH); 1.22 (*d*, $J = 6.6$, 3 H); 0.90 (*s*, 9 H); 0.07 (*s*, 3 H); 0.06 (*s*, 3 H). ^{13}C-NMR: 136.23 (*d*); 127.36 (*d*); 68.53 (*d*); 63.06 (*t*); 25.90 (*q*); 24.35 (*q*); 13.29 (*s*); −4.59 (*q*); −4.73 (*q*). Anal. calc. for $C_{11}H_{24}O_2Si$: C 61.05, H 11.13; found: C 61.13, H 11.22.

*(4S,2E)-4-[(*tert*-Butyl)dimethylsilyloxy]-5-methylhex-2-en-1-ol* (**20**). Reaction of 1.96 g (7.2 mmol) of **17** following the procedure for the preparation of **19** gave, after bulb-to-bulb distillation at 135°/0.5 mm, 1.45 g (83%) of the colorless **20**. $[\alpha]_D = +1.2$ ($c = 0.8$, $CHCl_3$); optical purity determined by *GP-B*: ≥ 90% e.e. IR: 3600*s*, 2955*s*, 2925*s*, 2850*s*, 2800*s*, 1382*s*, 1360*s*, 1250*s*, 1080*s*, 1055*s*, 975*s*, 855*s*, 838*s*. ^{1}H-NMR: 5.75 (*ddt*, $J = 15.5$, 5.4, 0.8, 1 H); 5.65 (*ddt*, $J = 15.5$, 5.4, 1.2, 1 H); 4.14 (*ddd*, $J = 5.4$, 1.2, 0.8, 2 H); 3.62 (*dt*, $J = 5.4$, 0.8, 1 H); 1.67 (*dsept.*, $J = 6.9$, 5.4, 1 H); 0.90 (*s*, 9 H); 0.87 (*d*, $J = 6.9$, 3 H); 0.85 (*d*, $J = 6.9$, 3 H); 0.04 (*s*, 3 H); 0.01 (*s*, 3 H). ^{13}C-NMR: 133.53 (*d*); 129.51 (*d*); 77.74 (*d*); 63.23 (*t*); 34.73 (*d*); 25.90 (*q*); 17.83 (*q*); 13.22 (*q*); 13.09 (*s*); −4.12 (*q*); −4.83 (*q*).

*(4S,2E)-4,6-Bis[(*tert*-Butyl)dimethylsilyloxy]hex-2-en-1-ol* (**21**). Reaction of 3.5 g (9 mmol) of **18** following the procedure for the preparation of **19** gave, after purification by flash chromatography on silica gel (petroleum ether/Et_2O 3:1), 3.2 g (98%) of **21**. $[\alpha]_D = -7.5$ ($c = 0.8$, $CHCl_3$); optical purity determined by *GP-B*: ≥ 90% e.e. IR: 3600*s*, 2950*s*, 2920*s*, 2850*s*, 2800*s*, 1386*m*, 1360*m*, 1250*s*, 1085*s*, 970*s*, 832*s*. ^{1}H-NMR: 5.78 (*dt*, $J = 15.5$, 5.0, 1 H); 5.70 (*dd*, $J = 15.5$, 5.5, 1 H); 4.33 (br. *q*, $J = 5.7$, 1 H); 4.14 (*d*, $J = 5.0$, 2 H); 3.66 (*m*, 2 H); 1.69 (*m*, 2 H); 0.90 (*s*, 9 H); 0.89 (*s*, 9 H); 0.06 (*s*, 3 H); 0.04 (*s*, 6 H); 0.03 (*s*, 3 H). ^{13}C-NMR: 135.33 (*d*); 128.61 (*d*); 69.82 (*d*); 63.24 (*t*); 59.53 (*t*); 41.43 (*t*); 25.90 (*q*); 13.32 (*s*); −4.21 (*q*); −4.81 (*q*); −5.34 (*q*).

S-*(4S,2E)-4-[(tert-Butyl)dimethylsilyloxy]pent-2-enyl Thioacetate* (**22**). Under Ar at 0°, 5.25 g (20 mmol) of PPh_3 in 20 ml of dry THF were treated with 3.52 g (20 mmol) of freshly distilled diethyl azodicarboxylate (DEAD). After 10 min of vigorous stirring, a white precipitate formed. After further 30 min, 2.16 g (10 mmol) of **19** dissolved in 5 ml of THF and 1.42 ml (20 mmol) of freshly distilled AcSH dissolved in 5 ml of THF were successively added. Then, the mixture was stirred at 0°, until the precipitate was completely dissolved. TLC showed the complete consumption of **19** after 1 h. For workup, 0.3 ml of H_2O and 50 ml of pentane were added to precipitate the major amount of $Ph_3P{=}O$ which was removed by filtration over silica gel (150 ml of pentane/Et_2O 3:2). The solvent was evaporated to give 3.11 g of a pink oil. Further purification by MPLC (petroleum ether/AcOEt 95:5) and bulb-to-bulb distillation at 105°/0.03 mm yielded 2.60 g (95%) of **22**. Colorless oil. This ester has previously been prepared [19], but no optical rotation and ^{13}C-NMR data were given. $[\alpha]_D = +5.9$ ($c = 0.9$, $CHCl_3$). IR: 2970*s*, 2940*s*, 2800*s*, 2775*s*, 1695*s*, 1260*s*, 1140*s*, 1085*s*, 970*m*, 840*s*, 740*s*. ^{1}H-NMR: 5.66 (*ddt*, $J = 15.1$, 5.8, 0.7, 1 H); 5.55 (*ddt*, $J = 15.1$, 6.8, 1.0, 1 H); 4.25 (*ddq*, $J = 6.3$, 5.8, 0.7, 1 H); 3.50 (*d*, $J = 6.8$, 2 H); 2.32 (*s*, 3 H); 1.13 (*d*, $J = 6.3$, 3 H); 0.88 (*s*, 9 H); 0.04 (*s*, 3 H); 0.03 (*s*, 3 H). ^{13}C-NMR: 192.92 (*s*); 137.37 (*d*); 123.05 (*d*); 69.54 (*d*); 30.87 (*t*); 30.36 (*q*); 25.86 (*q*); 24.27 (*q*); 13.21 (*s*); −4.59 (*q*); −4.79 (*q*).

S-*(4S,2E)-4-[(*tert*-Butyl)dimethylsilyloxy]-5-methylhex-2-enyl Thioacetate* (**23**). Reaction of 1.3 g (5.3 mmol) of **20** following the procedure for the preparation of **22** gave, after bulb-to-bulb distillation at 150°/0.4 mm, 1.3 g (81%) of **23**. $[\alpha]_D = +4.9$ ($c = 0.6$, $CHCl_3$). IR: 2970*s*, 2955*s*, 2800*s*, 1685*s*, 1460*s*, 1250*s*, 1108*s*, 1070*s*, 970*m*, 836*s*. ^{1}H-NMR: 5.62 (*ddt*, $J = 15.3$, 6.5, 0.7, 1 H); 5.52 (*ddt*, $J = 15.3$, 7.0, 0.8, 1 H); 3.78 (*t*, $J = 6.1$, 1 H); 3.52 (*d*, $J = 6.8$, 2 H); 2.32 (*s*, 3 H); 1.62 (*dsept.*, $J = 6.8$, 5.7, 1 H); 0.88 (*s*, 9 H); 0.85 (*d*, $J = 6.8$, 3 H); 0.82 (*d*, $J = 6.8$, 3 H); 0.02 (*s*, 3 H); −0.02 (*s*, 3 H). ^{13}C-NMR: 194.91 (*s*); 135.84 (*d*); 125.03 (*d*); 77.81 (*d*); 34.73 (*d*); 31.03 (*t*); 30.36 (*q*); 25.92 (*q*); 17.94 (*q*); 13.21 (*s*); 13.03 (*q*); −4.12 (*q*); −4.89 (*q*).

S-*(4S,2E)-4,6-Bis[(*tert*-butyl)dimethylsilyloxy]hex-2-enyl Thioacetate* (**24**). Reaction of 1.37 g (5 mmol) of **21** following the procedure for the preparation of **22** gave, after purification by flash chromatography (ether/petroleum ether 1:25) 2.73 g (79%) of **24**. $[\alpha]_D = -6.4$ ($c = 1.0$, $CHCl_3$). IR: 2950*s*, 2920*s*, 2800*s*, 1680*s*, 1460*s*, 1250*s*, 1090*s*, 965*m*, 830*s*. ^{1}H-NMR: 5.65 (*ddd*, $J = 15.3$, 6.2, 0.8, 1 H); 5.54 (*ddt*, $J = 15.3$, 6.6, 0.6, 1 H); 4.26 (*q*, $J = 6.2$, 1 H); 3.66 (*dt*, $J = 10.2$, 6.7, 1 H); 3.60 (*dt*, $J = 10.2$, 6.2, 1 H); 3.51 (*d*, $J = 6.6$, 2 H); 2.32 (*s*, 3 H); 1.65 (*m*, 2 H); 0.89 (*s*, 9 H); 0.88 (*s*, 9 H); 0.03 (*s*, 6 H); 0.01 (*s*, 6 H). ^{13}C-NMR: 194.91 (*s*); 137.34 (*d*); 124.19 (*d*); 69.68 (*d*); 59.32 (*t*); 41.33 (*t*); 30.87 (*t*); 30.38 (*q*); 25.90 (*q*); 13.21 (*s*); −4.13 (*q*); −4.88 (*q*); −5.28 (*q*).

*(4S,2E)-4-[(*tert*-Butyl)dimethylsilyloxy]-1-(isopropylthio)pent-2-ene* (**25**). Compound **22** (1.37 g, 5 mmol) in 5 ml of EtOH was added to 7 mmol of freshly prepared NaOEt in 1 ml of EtOH. After stirring at r.t. for 1 h, the mixture was treated with 0.62 g (5 mmol) of 2-bromopropane. After 12 h, the mixture was diluted with 50 ml of Et_2O and washed with H_2O (2 × 15 ml), brine (10 ml), and dried ($MgSO_4$). Evaporation and final bulb-to-bulb distillation at 105°/0.1 mm yielded 1.26 g (92%) of **25**. Colorless liquid. $[\alpha]_D = -4.0$ ($c = 0.9$, $CHCl_3$). IR: 2970*s*, 2940*s*, 2800*s*, 2775*s*, 1480*m*, 1460*m*, 1260*s*, 1145*s*, 1085*s*, 975*m*, 840*s*, 740*s*. ^{1}H-NMR: 5.57 (*m*, 2H); 4.29 (*m*, 1H); 3.14 (*m*, 2 H); 2.87 (*sept.*, $J = 6.3$, 1 H); 1.24 (*d*, $J = 6.3$, 1 H); 1.20 (*d*, $J = 6.3$, 3 H); 0.89 (*s*, 9 H); 0.06 (*s*, 3 H);

0.05 (*s*, 3 H). ^{13}C-NMR: 137.10 (*d*); 123.03 (*d*); 68.79 (*d*); 33.69 (*d*); 32.42 (*t*); 25.89 (*q*); 24.60 (*q*); 23.27 (*q*); 13.27 (*s*); −4.58 (*q*); −4.73 (*q*).

*(4S,2E)-4-[(*tert*-Butyl)dimethylsilyloxy]-1-(isopropylthio)-5-methylhex-2-ene* (**26**). According to the procedure for the preparation of **25**, 1.1 g (3.63 mmol) of **23** gave, after bulb-to-bulb distillation at 130°/0.4 mm, 0.9 g (82%) of **26**. $[\alpha]_D = -3.7$ ($c = 0.8$, $CHCl_3$). IR: 2950*s*, 2920*s*, 2845*s*, 1460*m*, 1250*s*, 1050*s*, 970*m*, 855*s*, 830*s*. ^{1}H-NMR: 5.53 (*m*, 2 H); 3.82 (*t*, $J = 5.4$, 1 H); 3.16 (*d*, $J = 6.2$, 2 H); 2.89 (*sept.*, $J = 6.8$, 1 H); 1.65 (*dsept.*, $J = 6.9$, 5.4, 1 H); 1.25 (*d*, $J = 6.8$, 6 H); 0.89 (*s*, 9 H); 0.86 (*d*, $J = 6.9$, 3 H); 0.84 (*d*, $J = 6.9$, 3 H); 0.03 (*s*, 3 H); 0.01 (*s*, 3 H). ^{13}C-NMR: 134.29 (*d*); 127.10 (*d*); 77.89 (*d*); 34.78 (*d*); 33.60 (*d*); 32.51 (*t*); 25.89 (*q*); 17.96 (*q*); 13.25 (*s*); −4.85 (*q*); −4.73 (*q*).

*(4S,2E)-4,6-Bis[(*tert*-butyl)dimethylsilyloxy]-1-(isopropylthio)hex-2-ene* (**27**). According to the procedure for the preparation of **25**, 2.7 g (6.5 mmol) of **24** gave, after flash chromatography, 2.27 g (84%) of **27**. $[\alpha]_D = -7.6$ ($c = 1.0$, $CHCl_3$). IR: 2950*s*, 2920*s*, 2880*s*, 2850*s*, 1460*m*, 1250*s*, 1090*s*, 970*m*, 830*s*. ^{1}H-NMR: 5.57 (*m*, 2 H); 4.30 (*dq*, $J = 5.4$, 1.4, 1 H); 3.65 (*m*, 2 H); 3.14 (*d*, $J = 6.3$, 2 H); 2.89 (*sept.*, $J = 6.7$, 1 H); 1.63 (*m*, 2 H); 1.25 (*d*, $J = 6.7$, 6 H); 0.89 (*s*, 18 H); 0.06 (*s*, 6 H); 0.05 (*s*, 3 H); 0.04 (*s*, 3 H). ^{13}C-NMR: 136.17 (*d*); 126.38 (*d*); 70.02 (*d*); 59.46 (*t*); 41.56 (*t*); 33.68 (*d*); 32.53 (*t*); 25.99 (*q*); 23.17 (*q*); 13.21 (*s*); −4.28 (*q*); −4.76 (*q*); −5.27 (*q*).

S-Isopropyl 2,2-Dichloro-2-[(1R)-cyclohex-2-enyl]thioacetate ((+)-(*R*)-**28**) *and S-Isopropyl 2,2-Dichloro-2-[(1S)-cyclohex-2-enyl] thioacetate* ((−)-(*S*)-**28**). Thioether (+)-(*R*)-**4** (0.16 g, 1.0 mmol) was added to 0.61 g (9.3 mmol) of activated Zn/Cu couple (see *GP-A*) in 15 ml of dry Et_2O. To the refluxing suspension, 0.36 g (2.0 mmol) of CCl_3COCl in 5 ml of Et_2O were added with a syringe pump within 4 h. After cooling, 15 ml of hexane were added to precipitate the Zn salts. The org. layer was decanted and the solvent evaporated. The residue was purified by flash chromatography (petroleum ether/AcOEt 85:15) to yield, after bulb-to-bulb distillation at 85–90°/0.08 mm, 0.16 g (60%) of (−)-(*S*)-**28** as a colorless oil. By the same procedure, starting from 0.16 g (1 mmol) of (−)-(*S*)-**4** 0.38 g (83%) of (+)-(*R*)-**28** were obtained.

Data of (−)-(*S*)-**28**: $[\alpha]_D = -3.7$ ($c = 0.5$, $CHCl_3$); optical purity determined by *GP-C*: 88% e.e. IR: 3040*m*, 2980*s*, 2940*s*, 2870*s*, 2850*s*, 1680*s*, 1450*s*, 875*s*, 710*s*, 555*s*, 540*s*. ^{1}H-NMR: 5.86 (*m*, 1 H); 5.74 (*m*, 1 H); 3.46 (*m*, 2 H); 1.89–1.26 (*m*, 6 H); 1.02 (*d*, $J = 6.8$, 3 H); 1.01 (*d*, $J = 6.8$, 3 H). ^{13}C-NMR: 194.34 (*s*); 131.56 (*d*); 124.15 (*d*); 93.85 (*s*); 48.08 (*d*); 36.82 (*d*); 24.70 (*t*); 22.34 (*q*); 21.26 (*t*). Anal. calc. for $C_{11}H_{16}Cl_2OS$: C 49.44, H 6.04, S 12.00, Cl 26.54; found: C 49.45, H 6.07, S 12.09, Cl 26.92.

Data of (+)-(*R*)-**28**: $[\alpha]_D = 5.8$ ($c = 1.0$, $CHCl_3$); optical purity determined by *GP-C*: 95.4% e.e. Spectroscopic data as above.

S-Isopropyl 2-[(1R)-Cyclohex-2-enyl]thioacetate ((−)-(*R*)-**29**) *and S-Isopropyl 2-[(1S)-Cyclohex-2-enyl]-thioacetate* ((+)-(*S*)-**29**). Thioester (−)-(*S*)-**28** (0.22 g, 0.82 mmol) in 3.5 ml of AcOH was heated to 80–100° and treated, under vigorous stirring, wtih 0.5 g (7.5 mmol) of Zn powder in portions during 4 h. Then, the mixture was cooled to r.t., poured on ice, treated with 15 ml of 2N NaOH, and extracted with Et_2O (20 ml). The Et_2O layer was washed with sat. $NaHCO_3$ (2 × 20 ml), dried, and concentrated. The residue was purified by buld-to-bulb distillation at 80–90°/0.03 mm yielding 0.14 g (86%) of (−)-(*R*)-**29** as an oil. Starting from (−)-(*S*)-**28**, (+)-(*S*)-**29** was obtained in 86% yield following the same procedure.

Data of (−)-(*R*)-**29**: $[\alpha]_D = -38.1$ ($c = 0.8$, $CHCl_3$); optical purity determined by *GP-C*: 86% e.e. IR: 3020*m*, 2970*s*, 2930*s*, 2860*s*, 1685*s*, 1450*s*, 680*s*, 560*s*, 505*s*. ^{1}H-NMR: 5.71 (*m*, 1 H); 5.52 (*m*, 1 H); 3.66 (*sept.*, $J = 6.8$, 1 H); 2.64 (*m*, 1 H); 2.50 (*dd*, $J = 14.5$, 6.6, 1 H); 2.45 (*dd*, $J = 14.5$, 8.1, 1 H); 1.97–1.29 (*m*, 6 H); 1.29 (*d*, $J = 6.8$, 6 H). ^{13}C-NMR: 198.56 (*s*); 129.81 (*d*); 128.17 (*d*); 50.25 (*t*); 34.57 (*d*); 31.97 (*d*); 28.59 (*t*); 25.01 (*t*); 22.97 (*q*); 20.92 (*t*). Anal. calc. for $C_{11}H_{13}OS$: C 66.62, H 9.15, S 16.17; found: C 66.82, H 9.24, S 15.75.

Data of (+)-(*S*)-**29**: $[\alpha]_D = +38.9$ ($c = 1.0$, $CHCl_3$); optical purity determined by *GP-C*: 95% e.e. Spectroscopic data as above.

2-[(1R)-Cyclohex-2-enyl]acetic Acid (**30**). Thioester (−)-(*R*)-**29** (0.12 g, 0.61 mmol) in 1 ml of dioxane and 1 ml of H_2O was treated with 1 g of $AgNO_3$ and heated to reflux. After 3 h, the mixture was cooled to r.t. and extracted with Et_2O (3 × 5 ml). The combined Et_2O layers were dried and evaporated. After purification by bulb-to-bulb distillation at 95°/0.03 mm, 70 mg (85%) of **30** were obtained as an oil. $[\alpha]_D = -46.9$ ($c = 0.9$, $CHCl_3$). IR: 3400 – 2500*m* (br.), 3020*s*, 2940*s*, 1750*s*, 1435*s*, 1415*s*, 1290*s*. ^{1}H-NMR: 11.00 (br. *s*, 1 H); 5.73 (*m*, 1 H); 5.56 (*m*, 1 H); 2.61 (*m*, 1 H); 2.36 (*dd*, $J = 15.3$, 6.9, 1 H); 2.32 (*dd*, $J = 15.3$, 8.1, 1 H); 1.98 (*m*, 2 H); 1.86 (*m*, 1 H); 1.71 (*m*, 1 H); 1.57 (*m*, 1 H); 1.31 (*m*, 1 H). ^{13}C-NMR: 179.36 (*s*); 129.76 (*d*); 128.32 (*d*); 40.61 (*t*); 32.02 (*d*); 28.76 (*t*); 24.98 (*t*); 20.92 (*t*). Anal. calc. for $C_8H_{12}O_2$: C 68.55, H 8.63; found: C 67.83, H 8.67.

S-Isopropyl (3S,4E)-2,2-Dichloro-3-methylthiohex-4-enoate (**31**). Thioether **11** (120 mg, 0.82 mmol) was rearranged following the procedure for the preparation of **28**: 150 mg (67%) of **31** after purification by bulb-to-bulb distillation at 50–55°/0.05 mm. $[\alpha]_D = -25.6$ ($c = 0.8$, $CHCl_3$); optical purity determined by *GP-C*: 80.6% e.e. IR: 3030*m*, 2970*s*, 2940*s*, 2870*s*, 1680*s*, 1450*s*, 970*s*, 775*s*, 755*s*, 560*s*, 550*s*. ^{1}H-NMR (C_6D_6): 5.41 (*m*, 2 H);

3.43 (*sept.*, J = 6.9, 1 H); 3.33 (*m*, 1 H); 1.45 (*dd*, J = 6.4, 1.2, 3 H); 1.19 (*d*, J = 6.6, 3 H); 0.99 (*d*, J = 6.9, 6 H). ^{13}C-NMR (D_6D_6): 194.76 (*s*); 130.17 (*d*); 128.48 (*d*); 94.36 (*s*); 49.12 (*d*); 36.75 (*d*); 22.42 (*q*); 22.29 (*q*); 17.98 (*q*); 16.12 (*q*). Anal. calc. for $C_{10}H_{16}Cl_2OS$: C 47.06, H 6.32, Cl 27.78, S 12.57; found: C 46.92, H 6.32, Cl 28.13, S 12.43.

S-*Isopropyl (3*R,*4*E*)-3-[(*tert-*Butyl)dimethylsilyloxy]-2,2-dichlorothiohex-4-enoate* (**32**). Thioether **12** (0.68 g, 2.5 mmol) was rearranged following the procedure for the preparation of **28**: 85 mg (85%) of **32** after flash chromatography. $[\alpha]_D = -4.3$ (c = 0.6, $CHCl_3$); optical purity determined by *GP-C*: 80.6% e.e. IR: 2980*s*, 2940*s*, 2890*s*, 1680*s*, 1465*s*, 1115*s*, 970*s*, 840*s*, 780*s*, 560*s*. ^{1}H-NMR: 5.63 (*ddq*, J = 15.2, 6.4, 0.5, 1 H); 5.30 (*ddq*, J = 15.2, 9.0, 1.7, 1 H); 3.92 (*dd*, J = 5.2, 5.2, 1 H); 3.66 (*dd*, J = 5.2, 7.1, 1 H); 3.54 (*sept.*, J = 6.8, 1 H); 3.24 (*ddd*, J = 9.0, 7.7, 5.2, 1 H); 1.68 (*dd*, J = 6.4, 1.7, 3 H); 1.31 (*d*, J = 6.8, 3 H); 1.30 (*d*, J = 6.8, 3 H); 0.85 (*s*, 9 H); 0.02 (*s*, 3 H); 0.01 (*s*, 3 H). ^{13}C-NMR: 193.87 (*s*); 132.78 (*d*); 125.40 (*d*); 91.63 (*s*); 63.67 (*t*); 56.36 (*d*); 36.71 (*d*); 25.86 (*q*); 22.55 (*q*); 22.17 (*q*); 13.33 (*s*); 13.13 (*q*); −5.12 (*q*). Anal. calc. for $C_{16}H_{30}Cl_2O_2SSi$: C 49.86, H 7.85, Cl 13.40, S 8.32; found: C 50.83, H 7.97, Cl 17.66, S 8.05.

S-*Isopropyl (3*R,*4*E*)-2,2-Dichloro-3-(methoxymethyl)thiohex-4-enoate* (**33**). Thioether **13** (172 mg, 1.0 mmol) was rearranged following the procedure for the preparation of **28**: 0.22 g (77%) of **33** after flash chromatography (petroleum ether/AcOEt 85:15). $[\alpha]_D = -16.9$ (c = 0.6, $CHCl_3$); optical purity determined by *GP-C*: 82.8% e.e. IR: 3030*m*, 2970*s*, 2930*s*, 2890*s*, 1680*s*, 1450*s*, 1120*s*, 560*s*, 550*s*, 970*s*, 755*s*. ^{1}H-NMR: 5.70 (*ddq*, J = 15.2, 6.6, 0.5, 1H); 5.36 (*ddq*, J = 15.2, 8.6, 1.6, 1 H); 3.66 (*dd*, J = 9.7, 5.9, 1 H); 3.57 (*sept.*, J = 6.8, 1 H); 3.50 (*dd*, J = 9.7, 7.1, 1 H); 3.42 (*m*, 1 H); 3.29 (*s*, 3 H); 1.72 (*d*, J = 6.8, 6 H); 1.34 (*d*, J = 6.8, 3 H). ^{13}C-NMR: 194.00 (*s*); 133.02 (*d*); 124.83 (*d*); 91.70 (*s*); 72.68 (*t*); 58.80 (*q*); 53.84 (*d*); 36.75 (*d*); 22.34 (*q*); 22.32 (*q*); 13.13 (*q*). Anal. calc. for $C_{11}H_{13}Cl_2O_2S$: C 46.32, H 6.36, Cl 24.86, S 11.24; found: C 46.57, H 6.43, Cl 24.75, S 11.06.

*(4*R*)-4-[(*E*)-Prop-1-enyl]tetrahydrofuran-2-one* (**34**). Thioester **32** (300 mg, 0.77 mmol) in 3 ml of AcOH was heated to 100° and treated with 500 mg of Zn/Cu couple (see *GP-A*) in five portions during 45 min with stirring. The mixture was cooled to r.t., poured onto 10 ml of ice-water, and diluted with 30 ml of Et_2O. The org. layer was successively washed with 2N NaOH (20 ml) and sat. $NaHCO_3$ (2 × 30 ml), dried ($MgSO_4$), and concentrated. The residue was purified by bulb-to-bulb distillation at 95–105°/14 mm to yield 84 mg (86%) of **34**. Colorless liquid. $[\alpha]_D = -2.8$ (c = 0.8, $CHCl_3$) optical purity determined by *GP-C*: 66.4% e.e. IR: 3030*w*, 2970*m*, 2930*m*, 1760*s*, 1140*s*, 1030*s*, 880*m*. ^{1}H-NMR: 5.01 (*dq*, J = 12.6, 5.6, 1 H); 4.70 (*ddq*, J = 12.6, 6.4, 1.4, 1 H); 3.62 (*t*, J = 8.3, 1 H); 3.24 (*t*, J = 8.3, 1 H); 2.18 (*m*, 1 H); 1.96 (*dd*, J = 16.9, 8.2, 1 H); 1.66 (*dd*, J = 16.9, 8.2, 1 H); 1.34 (*dd*, J = 6.2, 1.4, 3 H). ^{13}C-NMR: 176.8 (*s*); 128.6 (*d*); 128.4 (*d*); 72.7 (*t*); 39.1 (*d*); 34.5 (*d*); 34.65 (*t*); 17.8 (*q*).

S-*Isopropyl (3*R,*4*E*)-3-(Methoxymethyl)thiohex-4-enoate* (**35**). By the procedure described for the preparation of **29**, 90 mg (0.3 mmol) of **33** were dechlorinated, yielding, after bulb-to-bulb distillation at 75–85°/0.03 mm, 71 mg (98%) of **35**. Colorless liquid. $[\alpha]_D = -26.7$ (c = 0.7, $CHCl_3$); optical purity determined by *GP-C*: 83% e.e. IR: 3030*m*, 2970*s*, 2930*s*, 2870*s*, 1685*s*, 1450*s*, 1125*s*, 965*s*, 500*s*. ^{1}H-NMR: 5.53 (*ddq*, J = 15.2, 6.4, 0.7, 1 H); 5.30 (*ddq*, J = 15.2, 7.9, 1.4, 1 H); 3.32 (*dd*, J = 9.3, 5.8, 1 H); 3.63 (*sept.*, J = 6.9, 1 H); 3.26 (*dd*, J = 9.3, 6.7, 1 H); 2.84 (*m*, 1 H); 3.31 (*s*, 3 H); 2.68 (*dd*, J = 14.7, 6.0, 1 H); 2.47 (*dd*, J = 14.7, 8.1, 1 H); 1.65 (*dd*, J = 6.4, 1.2, 3 H); 1.28 (*d*, J = 6.9, 3 H); 1.27 (*d*, J = 6.9, 3 H). ^{13}C-NMR: 198.35 (*s*); 130.19 (*d*); 127.09 (*d*); 75.55 (*t*); 58.73 (*q*); 46.27 (*t*); 39.90 (*d*); 34.54 (*d*); 22.95 (*q*); 13.01 (*q*). Anal. calc. for $C_{11}H_{20}O_2S$: C 61.07, H 9.32, S 14.82; found: C 61.09, H 9.35, S 14.67.

*(*S*-Isopropyl (3*R*)-{(*S*)-1-[(*tert-*Butyl)dimethylsilyloxy]ethyl}2,2-dichlorothiopent-4-enoate* (**36**). Following the procedure described for the preparation of **28**, 0.41 g (1.5 mmol) of **25** were rearranged to yield, after purification by MPLC (petroleum ether/AcOEt 95:5) followed by bulb-to-bulb distillation at 130°/0.5 mm, 0.5 g (87%) of **36**. Colorless oil. $[\alpha]_D = -27.4$ (c = 0.9, $CHCl_3$). IR: 3080*w*, 2970*s*, 2940*s*, 1680*s*, 1260*s*, 1140*s*, 835*s*, 815*s*, 780*s*, 560*s*. ^{1}H-NMR: 5.94 (*ddd*, J = 17.4, 5.2, 9.4, 1 H); 5.33 (*dd*, J = 5.2, 2.0, 1 H); 5.13 (*dd*, J = 17.4, 2.0, 1 H); 4.46 (*dq*, J = 6.2, 1.5, 1 H); 3.57 (*sept.*, J = 6.7, 1 H); 2.93 (*dd*, J = 9.4, 1.5, 1 H); 1.35 (*d*, J = 6.7, 3 H); 1.32 (*d*, J = 6.7, 3 H); 1.15 (*d*, J = 6.2, 3 H); 0.89 (*s*, 9 H); 0.11 (*s*, 3 H); 0.07 (*s*, 3 H). ^{13}C-NMR: 194.77 (*s*); 131.26 (*d*); 122.12 (*t*); 91.59 (*s*); 67.06 (*d*); 60.78 (*d*); 36.82 (*d*); 25.97 (*q*); 23.91 (*q*); 22.36 (*q*); 17.98 (*s*); −3.59 (*q*); −4.33 (*q*).

S-*Isopropyl (3*R,*4*S*)-4[(*tert-*Butyl)dimethylsilyloxy]-2,2-dichloro-3-ethenyl-5-methylthiothexanoate* (**37**). Following the procedure described for the preparation of **28**, 0.30 g (1 mmol) of **26** were rearranged to yield, after flash chromatography on silica gel (petroleum ether/AcOEt 9:1), 0.31 g (76%) of **37**. Colorless oil. $[\alpha]_D = -27.4$ (c = 0.9, $CHCl_3$). IR: 2955*s*, 2925*s*, 1665*s*, 1250*s*, 1155*s*, 830*s*, 570*s*. ^{1}H-NMR: 5.95 (*ddd*, J = 17.4, 5.3, 9.2, 1 H); 5.24 (*dd*, J = 5.3, 1.8, 1 H); 5.08 (*dd*, J = 17.4, 1.8, 1 H); 4.21 (*dd*, J = 3.4, 1.5, 1 H); 3.55 (*sept.*, J = 6.8, 1 H); 3.24 (*dd*, J = 9.2, 1.5, 1 H); 1.90 (*dsept.*, J = 7.0, 3.4, 1 H); 1.34 (*d*, J = 6.8, 3 H); 1.32 (*d*, J = 6.8, 3 H); 0.94 (*d*, J = 7.0, 3 H); 0.91 (*s*, 9 H); 0.88 (*d*, J = 7.0, 3 H); 0.14 (*s*, 3 H); 0.10 (*s*, 3 H). ^{13}C-NMR: 194.73 (*s*); 133.36 (*d*); 121.39 (*t*); 93.16 (*s*); 74.52 (*d*); 55.77 (*d*); 36.98 (*d*); 36.28 (*d*); 26.21 (*q*); 22.31 (*q*); 13.52 (*s*); 13.03 (*q*); −3.59 (*q*); −4.23 (*q*).

*S-Isopropyl (3R,4S)-4,6-Bis[(*tert*-Butyl)dimethylsilyloxy]-2,2-dichloro-3-ethenylthiohexanoate* (**38**). Following the procedure described for the preparation of **28**, 0.30 g (0.7 mmol) of **27** were rearranged to yield, after flash chromatography on silica gel (petroleum ether/AcOEt 9:1), 0.28 g (71%) **38**. Colorless oil. $[\alpha]_D = -7.6$ ($c = 1.2$, $CHCl_3$). IR: 2950*s*, 2920*s*, 1670*s*, 1250*s*, 1150*s*, 830*s*, 550*s*. ^{1}H-NMR: 5.95 (*ddd*, $J = 17.3, 9.4, 5.2, 1$ H); 5.32 (*dd*, $J = 5.2, 1.9, 1$ H); 5.11 (*dd*, $J = 17.3, 1.9, 1$ H); 4.53 (*ddd*, $J = 8.6, 7.7, 0.9, 1$ H); 3.61 (*m*, 3 H); 3.17 (*dd*, $J = 9.4, 0.9, 1$ H); 1.75 (*m*, 2 H); 1.34 (*d*, $J = 6.3$, 3 H); 1.32 (*d*, $J = 6.3$, 3 H); 0.90 (*s*, 9 H); 0.89 (*s*, 9 H); 0.13 (*s*, 3 H); 0.12 (*s*, 3 H); 0.06 (*s*, 3 H); 0.05 (*s*, 3 H). ^{13}C-NMR: 194.99 (*s*); 131.74 (*d*); 122.28 (*t*); 92.09 (*s*); 68.78 (*d*); 59.33 (*t*); 57.84 (*d*); 40.01 (*t*); 36.92 (*d*); 26.21 (*q*); 26.04 (*q*); 22.43 (*q*); 22.31 (*q*); 13.26 (*s*); 13.12 (*s*); 3.59 (*q*); −4.08 (*q*); −5.43 (*q*).

(4R,5S)-3,3-Dichloro-4-ethenyl-5-methyltetrahydrofuran-2-one (**39**). Thioester **36** (1.00 g, 2.6 mmol) in 60 ml of MeCN was treated slowly with 4 ml of 48% HF in MeCN with stirring at r.t. After 2.5 h, the mixture was poured on ice/solid $NaHCO_3$ and extracted with CH_2Cl_2 (5 × 25 ml). The org. layer was dried ($MgSO_4$) and concentrated to give a yellow oil. Rapid chromatography on silica gel (ether/petroleum ether 1:3) followed by bulb-to-bulb distillation at 55°/0.2 mm yielded 0.46 g (90%) of **39**. $[\alpha]_D = -41.5$ ($c = 0.8$, $CHCl_3$). IR: 3500*w*, 3030*w*, 2945*w*, 1300*s*, 1200*s*, 975*s*, 915*s*, 560*s*. ^{1}H-NMR: 5.72 (*dt*, $J = 16.8, 5.0, 1$ H); 5.50 (*d*, $J = 5.0, 1$ H); 5.41 (*d*, $J = 16.8, 1$ H); 4.94 (*quint.*, $J = 6.7, 1$ H); 3.53 (*dd*, $J = 5.9, 6.7, 1$ H); 1.43 (*d*, $J = 6.7$, 3 H). ^{13}C-NMR: 167.83 (*s*); 128.44 (*d*); 123.68 (*t*); 80.84 (*s*); 77.56 (*d*); 60.09 (*d*); 16.17 (*q*).

(4R,5S)-3-3-Dichloro-4-ethenyl-5-isopropyltetrahydrofuran-2-one (**40**). Following the procedure described for the preparation of **39**, 0.54 g (1.3 mmol) of **37**, gave after chromatography on silica gel (ether/petroleum ether 1:5), 0.33 g (61%) of **40**. $[\alpha]_D = -59.4$ ($c = 0.7$, $CHCl_3$). IR: 3080*w*, 3020*w*, 2960*m*, 1790*s*, 1175*s*, 870*s*. ^{1}H-NMR: 5.45 (*m*, 3 H); 4.34 (*dd*, $J = 5.9, 4.1, 1$ H); 3.46 (*dd*, $J = 5.0, 4.1, 1$ H); 1.87 (*m*, 1 H); 1.14 (*d*, $J = 6.5$, 3 H); 0.87 (*d*, $J = 6.6$, 3 H). ^{13}C-NMR: 167.32 (*s*); 128.51 (*d*); 122.88 (*t*); 86.5 (*d*); 81.44 (*s*); 60.49 (*d*); 28.45 (*d*); 19.67 (*q*); 6.17 (*q*).

(4R,5S)-3,3-Dichloro-4-ethenyl-5-(2-hydroxyethyl)tetrahydrofuran-2-one (**41**). Following the procedure described for the preparation of **39**, 0.84 g (1.6 mmol) of **38** gave, after chromatography on silica gel (ether/petroleum ether 3:2), 0.16 g (46%) of **41**. $[\alpha]_D = -77.8$ ($c = 0.4$, $CHCl_3$). IR: 3600*m* (br.), 3080*w*, 3020*w*, 2960*m*, 1795*s*, 1130*s*, 970*s*. ^{1}H-NMR: 5.67 (*dt*, $J = 16.7, 5.1, 1$ H); 5.49 (*dd*, $J = 5.1, 1.3, 1$ H); 5.41 (*ddd*, $J = 16.7, 1.3, 0.4, 1$ H); 5.05 (*ddd*, $J = 5.0, 5.8, 3.7, 1$ H); 3.84 (*m*, 2 H); 3.58 (*dd*, $J = 5.1, 5.8, 1$ H); 2.03 (*ddt*, $J = 14.7, 5.0, 4.7, 1$ H); 1.83 (*dddd*, $J = 14.7, 7.6, 6.8, 3.7, 1$ H); 1.65 (br. *s*, 1 H). ^{13}C-NMR: 167.52 (*s*); 128.32 (*d*); 125.58 (*t*); 80.04 (*s*); 78.30 (*d*); 59.90 (*d*); 58.55 (*t*); 33.33 (*t*).

(4R,5S)-4-Ethenyl-5-methyltetrahydrofuran-2-one (**42**). Thioester **36** (1.5 g, 4.0 mmol) in 15 ml of AcOH at 100–110° was treated with 2.6 g Zn powder in portions. The mixture was cooled to r.t., poured onto 50 ml ice-water and 30 ml of 2N NaOH, and extracted with Et_2O (5 × 50 ml). The combined org. layers were successively washed with 2N NaOH (50 ml) and sat. $NaHCO_3$ (2 × 50 ml), dried ($MgSO_4$), and concentrated. The residue was purified by bulb-to-bulb distillation at 75°/20 mm to yield 0.41 g (82%) of **42**. Colorless liquid. $[\alpha]_D = -60.6$ ($c = 0.6$, $CHCl_3$). IR: 3040*m*, 3000*m*, 2950*m*, 1775*s*, 1135*s*, 950*s*, 935*s*, 555*s*. ^{1}H-NMR: 5.75 (*ddd*, $J = 17.1, 8.6, 5.4, 1$ H); 5.22 (*dd*, $J = 5.4, 1.0, 1$ H); 5.13 (*dd*, $J = 17.1, 1.0, 1$ H); 4.72 (*quint.*, $J = 6.6, 1$ H); 3.19 (*m*, 1 H); 2.68 (*dd*, $J = 17.2, 8.0, 1$ H); 2.48 (*dd*, $J = 17.2, 7.1, 1$ H); 1.27 (*d*, $J = 6.6$, 3 H). ^{13}C-NMR: 176.07 (*s*); 123.97 (*d*); 113.17 (*t*); 79.5 (*d*); 43.34 (*d*); 33.92 (*t*); 16.36 (*q*).

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