Chiral methyl *trans*-2,2-dichloro-3-methylcyclopropanecarboxylate upon exposure to thiophenolate nucleophile

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Dedicated to Professor Pierre Vogel on the occasion of his 70th anniversary

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Abstract

Substitution of the β-halogen atoms in methyl (1*R*,3*S*)-2,2-dichloro-3-methylcyclopropanecarboxylate with sodium thiophenolate leads to the di(phenylthio) ester (1*RS*,3*S*)-**4** as a mixture of diastereomers. The c*is-trans* isomerisation of methyl (1*RS*,3*S*)-3-methyl-2,2-bis(phenylthio)-cyclopropanecarboxylate **4**, basic hydrolysis and subsequent crystallization gave the corresponding acid (1*R*,3*S*)-**5** in high diastereomeric and enantiomeric purity. On the other hand, ring opening of the ester (1*RS*,3*S*)-**4** under acidic conditions leads to methyl 3-methyl-4,4-di(phenylthio)prop-3-enoate (**8**) or the chiral *S*-phenyl thioester methyl (3*S*)-3-methyl-4-oxo-4-(phenylthio)butanoate (**7**).

Keywords: Halogenocyclopropanes, thiocyclopropanes, chiral acids, nucleophilic substitution, ring opening

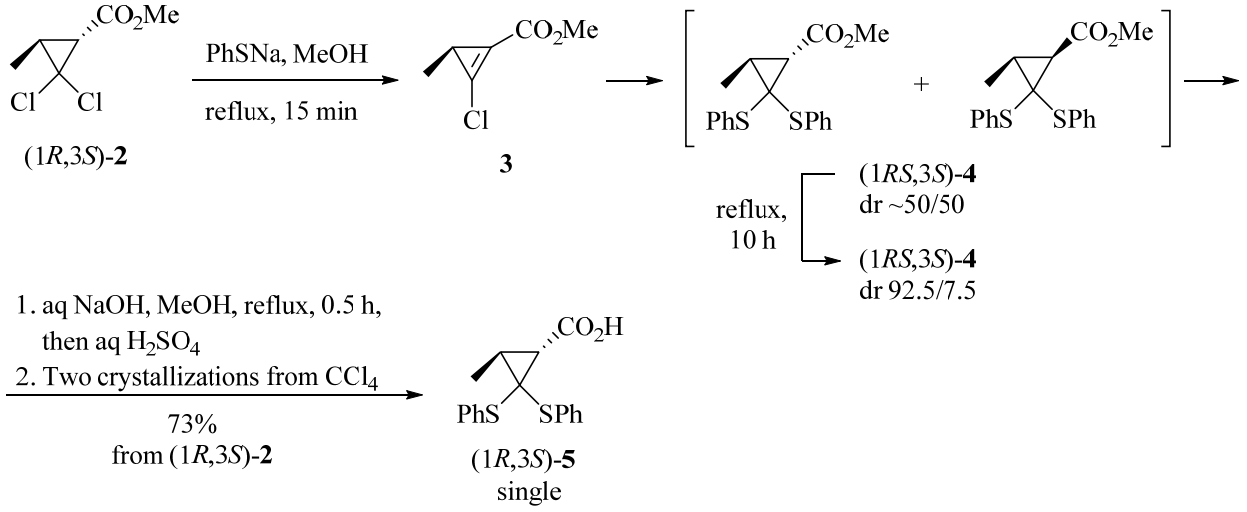
Introduction

Optically active halogenocyclopropanecarboxylic acids have been the object of a number of works in recent years.[1–11] These compounds are excellent building blocks due to their availability in high enantiomeric purity, simple techniques of preparation, and a substantial synthetic potential of the cyclopropane ring.[12-15] For example, they were utilized in the asymmetric synthesis of pyrethroids[1,2] and other natural products,[3,4] stereoregular oligocyclopropanes,[5] chiral biaryls,[6] and liquid crystals.[7] In a recent article we efficiently resolved racemic *trans*-2,2-dichloro-3-methylcyclopropanecarboxylic acid into enantiomers **1**.[10] Further, the chiral acid (1*R*,3*S*)-**1** was used in the construction of the methyl branched chain of the pine sawfly sex pheromone.[11]

β-Halogen atoms in esters, amides or nitriles of **1** may easily be substituted with nucleophiles and this property gives an additional method of functionalization of cyclopropane compounds.[16,17] These transformations could proceed with preservation or cleavage of the cyclopropane ring, depending on the nature of the nucleophilic reagent. The reactions of *gem*-dihalocyclopropanes with sulfur nucleophiles are known to give sufficiently stable dithiocyclopropanes.[16-20] Recently, numerous examples of stereoselective substitution in monobromocyclopropanes with heteroatomic nucleophiles have been described.[21,22] In continuation of our research,[10,11] the substitution of halogens by thiophenoxy groups in the chiral acids **1** has become the object of investigation. The stereochemistry of the dithiocyclopropanes obtained and the process of the cyclopropane ring opening were studied.

(1*S*,3*R*)-**1** (1*R*,3*S*)-**1**

Results and Discussion



(1*R*,3*S*)-**2** **3** (1*R*,3*S*)-**5**
single

Scheme 1. Synthesis of optically pure acid (1*R*,3*S*)-**5.**

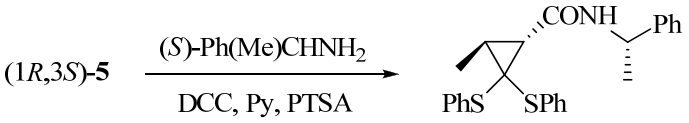
At first, the acid (1*R*,3*S*)-**1** (ee 99%) was converted in the usual way into the methyl ester (1*R*,3*S*)-**2**.[10] This last was reacted with a methanolic solution of sodium thiophenolate in accordance with prior procedure (Scheme 1).[20] This reaction proceeds quickly via an elimination-addition mechanism with formation of the proposed intermediate **3**.[16,17] After a short boiling time, complete substitution of the halogens and formation of an equimolar mixture of diastereomeric esters **4** was detected by TLC and NMR. However, continued heating under

reflux significantly decreased the amount of the *cis*-ester **4**. After 10 h, the ratio of diastereomers reached an equilibrium value 92.5/7.5 with a preference for the *trans*-ester **4** (established by ^{1}H NMR and GC). Basic hydrolysis of the resulting mixture led to the acid (1*R*,3*S*)-**5** containing the diastereomer (1*S*,3*S*)-**5** as the main impurity. In the final step, acid (1*R*,3*S*)-**5** was successfully separated from byproducts by a two-fold crystallization from CCl_4.

An assignment of the compounds to *cis*- and *trans*-isomer was in agreement with the values of vicinal coupling constants of cyclopropane protons in ^{1}H NMR (*J* 9.4 Hz and 6.7 Hz for *cis*- and *trans*-ester **4**, *J* 9.6 Hz and 7.0 Hz for *cis*- and *trans*-acid **5**). In GC analysis retention times were 38.3 min for *trans*-ester **4** and 38.8 min for *cis*-ester **4**.

Acid (1*R*,3*S*)-**5** is easily obtained as a single diastereomer and a stable crystalline compound. This short reaction sequence does not require the isolation of intermediate ester **4** and seems to be a convenient way for the modification of the readily available compounds **1**. Since the configuration of C-3 atom is not affected, the methyl substituent preserves the chirality of the initial compounds **1**.

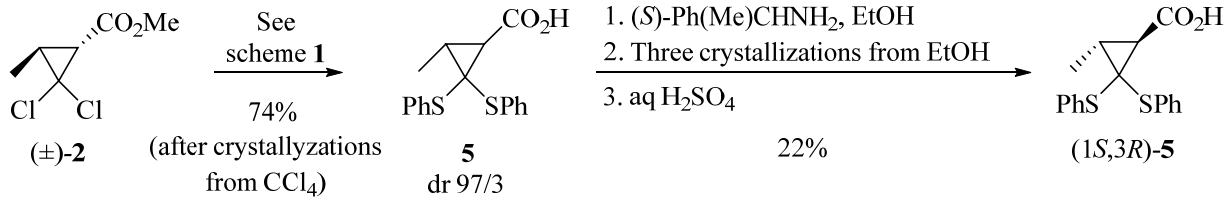
The enantiomeric purity of acid (1*R*,3*S*)-**5** was confirmed by its condensation with (*S*)-(–)-α-phenylethylamine into amide **6** (Scheme 2). The ^{1}H NMR spectrum of **6** was compared to that of the mixture of diastereomeric amides derived from acid (1*R*,3*S*)-**5** and (±)-α-phenylethylamine.



6

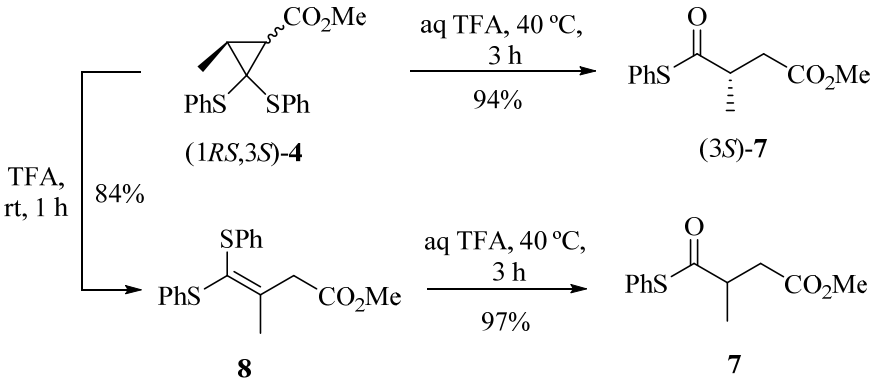
Scheme 2. Determination of the enantiomeric purity of acid (1*R*,3*S*)-**5**.

An alternative route to optically pure acids **5** could be realized via the resolution of the racemic acid but this attempt appeared to be less effective. In view of our previous results,[10] when individual enantiomers of acid **1** had been easily obtained from racemate by crystallization of the (*R*)- and (*S*)-α-phenylethylamine salts, the same procedure was applied to acid **5**. First, racemic acid **5** was obtained from correspondent ester (±)-**2**, as well as chiral (1*R*,3*S*)-**5** (Scheme 3). However, in contrast to chiral compound, crystallizations of racemic acid **5** from CCl_4 failed to isolate pure *trans*-isomer. Successive crystallization using (*S*)-(–)-α-phenylethylamine gave partially resolved *trans*-acid (1*S*,3*R*)-**5**. In the series of experiments the highest ee (~70%) was achieved after three crystallizations of the salt from EtOH (aqueous acetone also was used as solvent but this gave worse results). The configuration and ee of (1*S*,3*R*)-**5** were estimated by a comparison of its optical rotation with the value for pure (1*R*,3*S*)-**5**.



Scheme 3. Route to chiral acid **5** by resolution of racemate.

Finally, the process of the ring cleavage of dithiocyclopropanes obtained was investigated, because the derivatives of acids **5**, as well as acids **1**, could be the precursors of useful 1,4-bifunctional chiral compounds with an isopentane skeleton.[10,11] Ester (1*RS*,3*S*)-**4**, as described above, demonstrates high stability during long-term heating under basic conditions (Scheme 1), but similar *gem*-diphenylthiocyclopropyl ketones are known to be easily transformed into *S*-phenylalkanethioate or ketene diphenylthioacetals under acidic catalysis.[23,24] The experiments showed that ester (1*RS*,3*S*)-**4** was unreactive in aqueous formic acid and even in a refluxing mixture of acetone and hydrochloric acid. However, the ring-opening reaction proceeded easily upon the treatment of (1*RS*,3*S*)-**4** with aqueous TFA to give diester (3*S*)-**7** (Scheme 4). The ee for compound (3*S*)-**7** was at least 85% (see Experimental Section**)**. On the other hand, treatment of (1*RS*,3*S*)-**4** with anhydrous TFA caused isomerization to ketene dithioacetal **8**. The last was smoothly hydrolyzed to give racemic compound **7**. It should be noted that the formation of **8** was also detected by NMR and TLC in the reaction of (1*RS*,3*S*)-**4** with aqueous TFA, but then the final product **7** was not completely racemic. Thus, there are two competing pathways for the ring opening of dithiocyclopropane (1*RS*,3*S*)-**4**, and the formation of ketene dithioacetal **8** caused the decrease in optical purity of (3*S*)-**7**.



Scheme 4. Ring cleavage of (1*RS*,3*S*)-**4**.

Conclusions

A new *trans*-3-methyl-2,2-bis(phenylthio)cyclopropanecarboxylic acid (1*R*,3*S*)-**5** was prepared from methyl *trans*-2,2-dichloro-3-methylcyclopropanecarboxylate (1*R*,3*S*)-**2** by a simple reaction sequence and with complete retention of the configuration of both stereocenters. The key steps included the substitution of halogens in ester (1*R*,3*S*)-**2** with thiophenoxy groups, the *cis*-*trans* isomerization of ester (1*RS*,3*S*)-**4** and an ordinary crystallization of the crude acid **5**. Decrease in the enantiomeric excess occurred in the course of the cleavage of ester (1*RS*,3*S*)-**4** into *S*-phenyl thioester (3*S*)-**7** under acidic conditions. This could be explained by the simultaneous formation of chiral thioester (3*S*)-**7** and ketene dithioacetal **8**. The last was the precursor of racemic **7**.

Supporting information available
NMR spectra are available free of charge via the Internet at http://www.arkat-usa.org.

Experimental Section

General. Melting points were determined with a capillary apparatus. Optical rotations were measured with a CM-3 polarimeter (scale factor: 0.05°) at rt. IR spectra were recorded on a Vertex 70 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 400 instrument at 400 and 100 MHz, respectively, $CHCl_3$ was used as internal standard (δ 7.26 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR). GC-MS analyses were performed using a Shimadzu GCMS-QP2010 instrument equipped with an Equity^{TM}-5 capillary column (30 m, 0.25 mm ID, 0.25 μm film thickness) in the electron impact ionization mode at 70 eV. The carrier gas helium was applied. Methanol was freshly distilled from magnesium methoxide, 96% ethanol was distilled without use of drying agents. Silica gel 60 F 254 plates were used for TLC analysis, column chromatography was performed on silica gel 70–230 mesh, 1–20% solutions of ethyl acetate in petroleum ether (bp 40–60 ºC) were used as eluent.

Methyl (1*RS*,3*S*)-3-methyl-2,2-bis(phenylthio)cyclopropanecarboxylate [(1*RS*,3*S*)-4]. Thiophenol (4.45 g, 40.4 mmol) and ester (1*R*,3*S*)-**2**[10] (3.20 g, 17.5 mmol) in MeOH (10 mL) were added to a stirred solution of MeONa (42 mmol) in MeOH (40 mL). The mixture obtained was slowly heated with stirring to a boiling point and then refluxed for 15 min. The reaction was cooled, quenched with water (200 ml) and extracted with Et_2O (5×50 mL). Combined organic extracts where washed with brine (50 mL), dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography to give compound **4** as a colorless liquid. Yield 5.55 g (96%), mixture of diastereomers ~1/1. IR (CCl_4, ν_{max}, cm^{-1}): 1743. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (d, *J* 6.4 Hz, 3H), 1.49 (d, *J* 6.4 Hz, 3H), 2.10–2.15 (m, 1H), 2.15 (d, *J* 6.7, 1H), 2.26 (app quin, *J* 6.5 Hz, 1H), 2.49 (d, *J* 9.4, 1H), 3.58 (s, 3H), 3.60 (s, 3H), 7.21–7.43 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.5, 14.0, 30.5, 31.2, 34.7, 38.2, 42.7, 44.9,

51.7, 52.0, 126.2, 126.6, 126.8, 127.0, 128.5 (4C), 128.7 (2C), 128.8 (2C), 129.5 (2C), 129.7 (2C), 130.1 (2C), 130.4 (2C), 134.0, 134.1, 134.2, 134.4, 168.1, 168.8. MS for *trans*-ester (1*R*,3*S*)-**4**, *m*/*z* (%) = 299 (1.2, $[M - 31]^+$), 271 (2.8), 255 (1.3), 221(46.8), 161 (100); MS for *cis*-ester (1*S*,3*S*)-**4**, *m*/*z* (%) = 299 (1.1, $[M - 31]^+$), 271 (2.7), 255 (1.2), 221(41.7), 161 (100). Anal. Calcd for $C_{18}H_{18}O_2S_2$ (330.46): C 65.42, H 5.49%. Found: C 65.60, H 5.44%.

(1*R*,3*S*)-3-Methyl-2,2-bis(phenylthio)cyclopropanecarboxylic acid [(1*R*,3*S*)-5].

Thiophenol (4.75 g, 43.1 mmol) and ester (1*R*,3*S*)-**2**[10] (3.40 g, 18.6 mmol) in MeOH (10 mL) were subsequently added to a stirred solution of MeONa (45 mmol) in MeOH (40 mL). The mixture obtained was slowly heated with stirring to a boiling point and then refluxed for 10 h. After this time, solution of NaOH (4.0 g, 100 mmol) in water (10 ml) was added and the reflux was continued for 0.5 h. Then, the reaction was cooled and evaporated under reduced pressure. The residue was quenched with water (120 mL) and extracted with Et_2O (30 mL). The ethereal phase was removed, and the water phase was acidified with 20% H_2SO_4 (100 mL) and extracted with Et_2O (5×50 mL). Combined organic extracts where washed with brine (30 mL), dried with Na_2SO_4 and concentrated under reduced pressure. The residue was two times recrystallized from CCl_4 (40 and 30 mL) to give acid (1*R*,3*S*)-**5** as white crystals. Yield 4.30 g, 73%, mp 138–139 ºC, $[\alpha]_D$ +121.9 (*c* 0.8, acetone). IR (KBr, ν_{max}, cm^{-1}): 3186, 1731. ^1H NMR (400 MHz, $CDCl_3$): δ 1.46 (d, *J* 6.1 Hz, 3H), 2.19 (d, *J* 7.0 Hz, 1H), 2.27 (app quin, *J* 6.5 Hz, 1H), 7.21–7.43 (m, 10H), 10.50 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 31.1, 38.6, 46.3, 126.9, 127.3, 128.7 (2C), 128.9 (2C), 130.0 (2C), 131.3 (2C), 133.8, 133.9, 174.4. MS (DIP), *m*/*z* (%) = 316 (1.1, $[M]^+$), 271 (2.5), 255 (1.0), 239 (0.8), 207 (66.3), 161 (100). Anal. Calcd for $C_{17}H_{16}O_2S_2$ (316.44): C 64.53, H 5.10%. Found: C 64.31, H 5.08%.

Determination of the enantiomeric purity of acid (1*R*,3*S*)-5

Amide of acid (1*R*,3*S*)-5 with (*S*)-(–)-α-phenylethylamine (**6**). Acid (1*R*,3*S*)-**5** (0.10 g, 0.32 mmol), PTSA (0.05 g, 0.3 mmol), and DCC (0.16 g, 0.78 mmol) were added to a solution of (*S*)-(–)-α-phenylethylamine (0.10 g, 0.83 mmol) in pyridine (1 mL). The reaction was left at rt for 12 h and then, quenched with 10% aq H_2SO_4 (10 mL). After stirring for 0.5 h, the mixture was filtered and extracted with ether (3 × 5 mL). The extracts were washed with water (5 ml), brine (5 mL), dried with Na_2SO_4 and evaporated under reduced pressure. The crude amide was analyzed without purification. ^1H NMR (400 MHz, $CDCl_3$): δ 1.38 (d, *J* 6.8 Hz, 3H), 1.46 (d, *J* 6.3 Hz, 3H), 1.94 (d, *J* 7.1 Hz, 1H), 2.21 (app quin, *J* 6.6 Hz, 1H), 5.10 (app quin, *J* 7.1 Hz, 1H), 5.86 (br d, *J* 7.4 Hz, 1H); 7.20–7.44 (m, 15H).

Amide of acid (1*R*,3*S*)-5 with (±)-α-phenylethylamine. This compound was formed in the reaction of acid (1*R*,3*S*)-**5** with (±)-α-phenylethylamine as described above for amide **6**. Mixture of diastereomers ~1/1. ^1H NMR (400 MHz, $CDCl_3$): δ 1.36 (d, *J* 6.9 Hz, 3H), 1.38 (d, *J* 6.8 Hz, 3H), 1.43 (d, *J* 6.3 Hz, 3H), 1.46 (d, *J* 6.3 Hz, 3H), 1.92 (d, *J* 6.8 Hz, 1H), 1.94 (d, *J* 7.1 Hz, 1H), 2.18–2.28 (m, 2H), 5.04 (app quin, *J* 7.1 Hz, 1H), 5.10 (app quin, *J* 7.1 Hz, 1H), 5.75 (br d, *J* 7.4 Hz, 1H); 5.86 (br d, *J* 7.4 Hz, 1H); 7.20–7.48 (m, 30H).

Racemic 3-methyl-2,2-bis(phenylthio)cyclopropanecarboxylic acid (**5**). Methyl ester (±)-**2** (prepared by esterification of racemic acid **1** as described in ref. 10) was converted into racemic

acid **5** using the procedure for (1*R*,3*S*)-**5**. White crystals, yield 74%, mp 136–138 ºC, mixture of diastereomers ~97/3 (based on ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): signals of predominant *tans*-isomer corresponded to those of acid (1*R*,3*S*)-**5**, individual signals of minor *cis*-isomer were detected at δ 1.52 (d, *J* 6.5 Hz, 3H), 2.13–2.17 (m, 1H), and 2.54 (d, *J* 9.6 Hz, 1H). The IR and ^{13}C NMR spectra were similar to those for acid (1*R*,3*S*)-**5**.

(1*S*,3*R*)-3-Methyl-2,2-bis(phenylthio)cyclopropanecarboxylic acid [(**1*S*,3*R*)-5**]. To a solution of racemic acid **5** (1.00 g, 3.16 mmoL) in 96% ethanol (10 mL) (*S*)-(–)-α-phenylethylamine (0.22 g, 1.8 mmol) was added. The resulting mixture was heated to reflux and then cooled to –10 ºC. After standing at this temperature for 24 h, the crystals formed were separated by filtration and additionally twice recrystallized from 96% ethanol. The salt obtained was treated with 10% H_2SO_4 (10 mL), and the resulting mixture was extracted with Et_2O (3×10 mL). The combined organic phases where washed with brine (10 mL), dried with Na_2SO_4. After removal of the solvent under reduced pressure, acid (1*S*,3*R*)-**5** was obtained as white crystals. Yield 0.22 g (22%), mp 132–133 ºC, $[\alpha]_D$ –88.0 (*c* 0.8, acetone), ee ~70%. The IR and NMR spectra were in accordance to those for acid (1*R*,3*S*)-**5**.

Methyl (3*S*)-3-methyl-4-oxo-4-(phenylthio)butanoate [(**3*S*)-7**]. Compound (1*RS*,3*S*)-**4** (2.00 g, 6.05 mmol) was added to a mixture of trifluororacetic acid (10 mL) and water (2 mL). The reaction was heated to 40 ºC and stand at this temperature for 3 h. Then, toluene (30 mL) was added and the mixture was evaporated under reduced pressure. The residue was purified by column chromatography to give compound (3*S*)-**7** as a light yellow liquid, yield 1.35 g, (94%). $[\alpha]_D$ +18.3 (*c* 7.0, ethyl acetate). IR (CCl_4, ν_{max}, cm^{-1}): 1744, 1710. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (d, *J* 7.2 Hz, 3H), 2.44 (dd, *J* 16.6, 6.4 Hz, 1H), 2.84 (dd, *J* 16.6, 7.8 Hz, 1H), 3.12–3.29 (m, 1H), 3.69 (s, 3H), 7.38–7.43 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.8, 37.4, 44.0, 51.7, 127.3, 129.1 (2C), 129.3, 134.5 (2C), 171.7, 200.2. MS, *m*/*z* (%) = 207 (2.2, $[M - 31]^+$), 129 (37.7), 109 (12.8), 101 (15.1), 59 (100). Anal. Calcd for $C_{12}H_{14}O_3S$ (238.30): C 60.48, H 5.92%. Found: C 60.65, H 5.88%.

Determination of the enantiomeric purity of compound (3*S*)-7. For the determination of ee, diester (3*S*)-**7** was exhaustively reduced with $LiAlH_4$ into (2*S*)-2-methylbutane-1,4-diol which was then acylated with chloride of (*R*)-(+)-Mosher acid.[10,25]

A solution of thioester (3*S*)-**7** (0.36 g, 1.5 mmol) in THF (3 mL) was added under argon to a stirred and ice cooled solution of $LiAlH_4$ (0.12 g, 3.2 mmol) in THF (10 mL). The mixture was warmed to rt and then stirring was continued for 1 h. After this time, the reaction was cooled to 0 ºC, quenched with 15% aq NaOH (0.2 ml) and filtrated. The filtrate was dried with K_2CO_3, and evaporated under reduced pressure. The residue was purified by column chromatography to give (2*S*)-2-methylbutane-1,4-diol as a colorless liquid. Yield 63%, 0.10 g, $[\alpha]_D$ –10.5 (*c* 1.0, MeOH), lit.[26] $[\alpha]^{20}_D$ = –13.1 (*c* 3.3, MeOH). The ^{1}H NMR and ^{13}C spectral data corresponded to those reported in the literature.[26] Determination of the enantiomeric excess of (2*S*)-2-methylbutane-1,4-diol based on ^{1}H NMR spectra of Mosher acid derivatives was described previously,[10] see also Supplementary Material. The ee more than 85% was established at present.

Methyl 3-methyl-4,4-bis(phenylthio)but-3-enoate (**8**). Compound (1*RS*,3*S*)-**4** (0.50 g, 1.51 mmol) was added to anhydrous trifluororacetic acid (3 mL) and the reaction was stirred at rt for 1 h. Then, toluene (10 mL) was added and the mixture was evaporated under reduced pressure. The residue was purified by chromatography on a short pad of silica gel to give compound **8** as a light yellow liquid. Yield 0.42 g (84%). IR (CCl_4 ν_{max}, cm^{-1}): 1742, 1583. ^1H NMR (400 MHz, $CDCl_3$): δ 2.24 (br s, 3H), 3.71 (s, 3H), 3.75 (br s, 2H), 7.13–7.25 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.8, 42.4, 52.0, 126.3, 126.5, 126.8, 128.6 (4C), 129.5 (2C), 129.9 (2C), 134.8, 135.0, 146.3, 170.7. MS, *m*/*z* (%) = 330 (13.3, $[M]^+$), 271 (4.3), 256 (13.5), 221 (55.9), 193 (89.9), 45.1 (100). Anal. Calcd for $C_{18}H_{18}O_2S_2$ (330.46): C 65.42, H 5.49%. Found: C 65.48, H 5.42%.

Racemic methyl 3-methyl-4-oxo-4-(phenylthio)butanoate (**7**). Compound **8** (0.100 g, 0.30 mmol) was added to a mixture of trifluororacetic acid (1 mL) and water (0.2 mL). The reaction was heated to 40 ºC and maintained at this temperature for 3 h. Then, toluene (5 mL) was added and the mixture was evaporated under reduced pressure. The residue was purified by column chromatography to give compound **7** as a light yellow liquid. Yield 0.070 g (97%). Spectroscopic data corresponded to those of (3*S*)-**7**.

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