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SILICA GEL-CATALYZED REGIO- AND STEREOSELECTIVE REACTIONS OF THIOCARBONYL COMPOUNDS WITH OPTICALLY ACTIVE MONOSUBSTITUTED OXIRANES

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(Dedicated to Professor A. I. Meyers on the occasion of his 70th birthday)

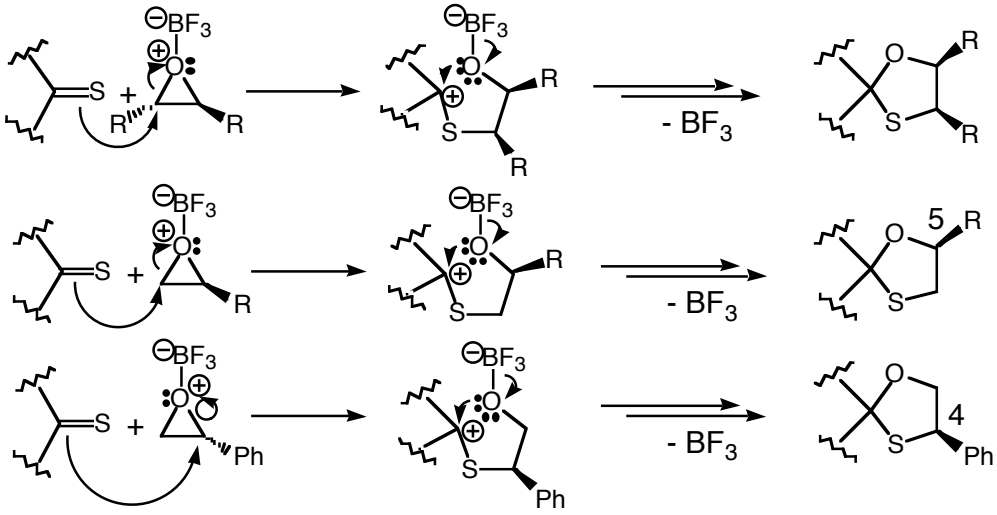
Abstract – The reactions of 1,1,3,3-tetramethylindane-2-thione (**1**) with (*S*)-2-methyloxirane ((*S*)-**2**) and (*R*)-2-phenyloxirane ((*R*)-**6**) in the presence of a *Lewis* acid such as $BF_3 \cdot Et_2O$, $SnCl_4$, $ZnCl_2$ or SiO_2 in dry CH_2Cl_2 led to the 1,3-oxathiolanes ((*S*)-**3**) and ((*R*)-**4**) with Me at C(5′) and C(4′), and to (*S*)-**7** with Ph at C(4′), respectively (*Schemes 2 and 3*). The SiO_2-catalyzed reaction of 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione (**8**) with (*R*)-**6** gave two diastereoisomers ((5*S*,8*S*)-**9**) and ((5*R*,8*S*)-**9**) (*Scheme 4*). In the case of adamantane-2-thione (**10**) and (*S*)-**2** or (*R*)-**6** with $ZnCl_2$ or SiO_2 as catalysts, (*S*)-**11** and (*R*)-**12** with Me at C(5′) and C(4′), respectively, and (*S*)-**13** with Ph at C(4′), were formed. In addition, an unexpected isomer ((*R*)-**14**) with Ph at C(5′) and 1,3-dioxolane ((*S*)-**15**) were isolated as minor products (*Schemes 5 and 6*). The structure of (*S*)-**13** was confirmed by X-Ray crystallography (*Figure 1*). These results show that the SiO_2-catalyzed addition of oxiranes to C=S bonds proceeds with high regio- and stereoselectivity *via* an S_N2-type mechanism.

INTRODUCTION

The reactions of thiocarbonyl compunds with 2-mono- and 2,3-disubstituted oxiranes in the presence of a *Lewis* acid to form 1,3-oxathiolanes have been investigated recently.[2-5] All of the

results described previously indicate an S_N2-type mechanism, involving the ring-opening of the activated oxiranes by the nucleophilic attack of the thiocarbonyl S-atom, *i.e.*, in the case of 2,3-disubstituted oxiranes, an inversion of the configuration of one oxirane C-atom occurred.[4] In the case of 2-monosubstituted oxiranes, the reactions proceeded with high regioselectivity[5] so that the preferred attack took place at C(3) of alkyl-substituted oxiranes (O-C(3) cleavage), but at C(2) of phenyloxirane (O-C(2) cleavage) with inversion of configuration. Therefore, for the formation of 1,3-oxathiolanes *via* the *Lewis* acid catalyzed reactions of oxiranes with thioketones, the following mechanisms were proposed (*Scheme 1*).

Scheme 1



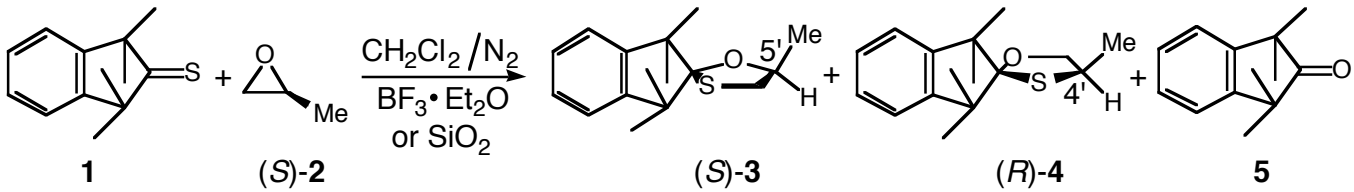
With the aim of getting more insight into the regioselectivity and the stereochemical course of the ring-opening of oxiranes in the formation of 1,3-oxathiolanes, the reactions of nonenolizable thiocarbonyl compounds with optically active oxiranes, *i.e.*, (*S*)-2-methyloxirane ((*S*)-**2**) and (*R*)-2-phenyloxirane ((*R*)-**6**) were carried out. For the first time, it was discovered that the reactions can be catalyzed by silica gel and take place with high regio- and stereoselectivity.

RESULTS AND DISCUSSION

Reactions of 1,1,3,3-tetramethylindane-2-thione (1) with oxiranes. – With (*S*)-2-methyloxirane ((*S*)-**2**). To a solution of **1** and 0.5 of equiv. of $BF_3{\cdot}Et_2O$ in dry CH_2Cl_2 at -60°C under N_2, 2 equiv. of (*S*)-**2** was added dropwise. The color of the mixture changed from orange to pale pink. After 25 min, the reaction was quenched by addition of H_2O. Chromatographic separation

gave two isomers ((*S*)-**3**) and ((*R*)-**4**), as well as **5** in 41, 2, and 9% yields, respectively. The starting material (**1**) was recovered in 46% yield (*Scheme 2*, *Table 1*). The reaction was repeated at room temperature for 2 days in the presence of silica gel, whereby only one isomer ((*S*)-**3**) and the ketone (**5**) were obtained in 2 and 3% yields, respectively. However, the starting material (**1**) was recovered in 85% yield (*Scheme 2*, *Table 1*).

Scheme 2



1 (*S*)-**2** (*S*)-**3** (*R*)-**4** **5**

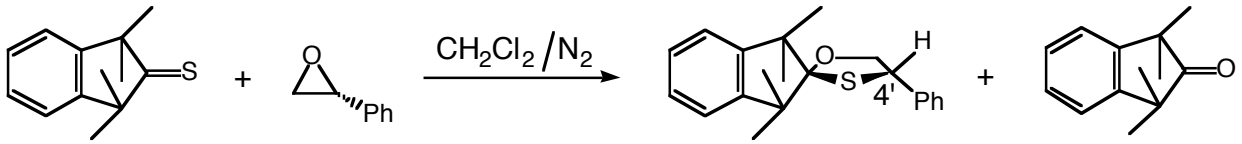
Table 1. *BF_3- and SiO_2-Catalyzed Reaction of* **1** *with* (*S*)-**2** *in CH_2Cl_2*

	Temp.	Reaction time	Yield [%] and specific rotation ($[\alpha]_D^{22}$) of products					
			(*S*)-**3**		(*R*)-**4**		**5**	**1**
BF_3·Et_2O	-60°C	25 min	41	(+12.9°)	2	(+26.5°)	9	46
SiO_2	rt	48 h	2	(+13.2°)	-		3	85

The structures of (*S*)-**3** and (*R*)-**4** were assigned by means of ^{1}H- and ^{13}C-NMR spectra and by comparison with those described previously.[5] The formation of (*S*)-**3** proceeded without change of configuration at C(5′) as the nucleophilic attack of the thiocarbonyl S-atom took place at C(3) of (*S*)-**2**. On the other hand, the formation of (*R*)-**4** occurred with inversion of configuration at C(4′) as a result of the nucleophilic attack of the thiocarbonyl S-atom at C(2) of (*S*)-**2** *via* an S_N2-type process, which led to the opening of the oxirane ring, and then, subsequent cyclization gave the product. The results are in accordance with the mechanism postulated in *Scheme 1*.

With (*R*)-2-phenyloxirane ((*R*)-**6**). The reaction of **1** with (*R*)-**6** in the presence of BF_3·Et_2O, $SnCl_4$, $ZnCl_2$ or silica gel at different temperatures gave only one isomer ((*S*)-**7**) in 8, 23, 6 and 3% yields, respectively. In the cases with $SnCl_4$ and $ZnCl_2$, as well as with BF_3·Et_2O after longer time, **5** was isolated as a by-product. The starting material (**1**) was recovered in a large amount (*Scheme 3*, *Table 2*).

Scheme 3



1 (*R*)-**6** (*S*)-**7** **5**

Table 2. *Lewis Acids Catalyzed Reaction of* **1** *with* (*R*)-**6** *in* CH_2Cl_2

	Temp.	Reaction time	Yield [%] and specific rotation ($[\alpha]_D^{22}$) of products		
			(*S*)-**7**	**5**	**1**
$BF_3 \cdot Et_2O$	rt	7 min	8 (-13.8°)	-	79
	-78°C	3.5 h	24 (+31.3°)[a]	4	72
$SnCl_4$	-78°C	5 min	23 (-42.9°)	26	44
$ZnCl_2$	-30°C	9 h	6 (-33.4°)	8	82
SiO_2	rt	48 h	3 (-36.5°)	-	93

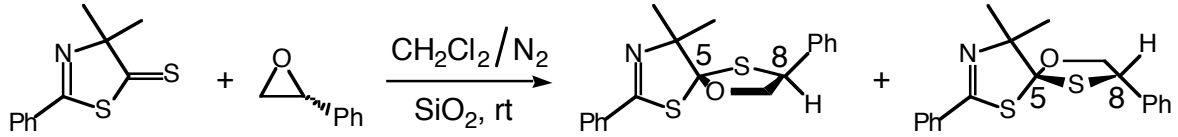
a) (*S*)-2-Phenyloxirane was used as reactant.

The structure of (*S*)-**7** was assigned on the basis of ^{1}H- and ^{13}C-NMR spectra and by comparison with those described previously.[5] The enantiomeric purity of (*S*)-**7** was determined with the help of the shift reagent (*R*)-(-)-1-(9-anthryl)-2,2,2-trifluoroethanol, and the results showed that (*S*)-**7** formed in the cases of $SnCl_4$ and silica gel was almost enantiomerically pure; however, the reactions with $BF_3 \cdot Et_2O$ or $ZnCl_2$ as a catalyst resulted in partial racemization depending largely on the temperatures at which the reactions were carried out. The determinations were in good agreement with the specific rotations shown in *Table 2*. It could be concluded that the higher the reaction temperature, or the stronger the *Lewis* acid was, the more racemization took place.

Reaction of 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione (8) with (*R*)-**6.** The reaction of **8** with (*R*)-**6** in the presence of silica gel at room temperature for 64 h and 72 h led to two diastereoisomers ((5*S*,8*S*)-**9**) and ((5*R*,8*S*)-**9**) as colorless oils in a ratio of 20:1 and 6:1, respectively. In addition, the starting material (**8**) was partially recovered (*Scheme 4*).

The reaction of **8** with (*RS*)-**6** in the presence of $BF_3 \cdot Et_2O$ at room temperature for 3 days, giving (*5RS*,*8RS*)-**9** and (*5RS*,*8SR*)-**9** in a ratio of 1:1.3, has been reported previously.[6] Therefore, with silica gel as the catalyst, the reaction proceeded with higher diastereoselectivity and, moreover, the sterically unfavorable (5*S*,8*S*)-**9** was the main product.

Scheme 4



8	(*R*)-**6**		(5*S*,8*S*)-**9**	(5*R*,8*S*)-**9**
		64 h	42%	2%
		72 h	23%	4%

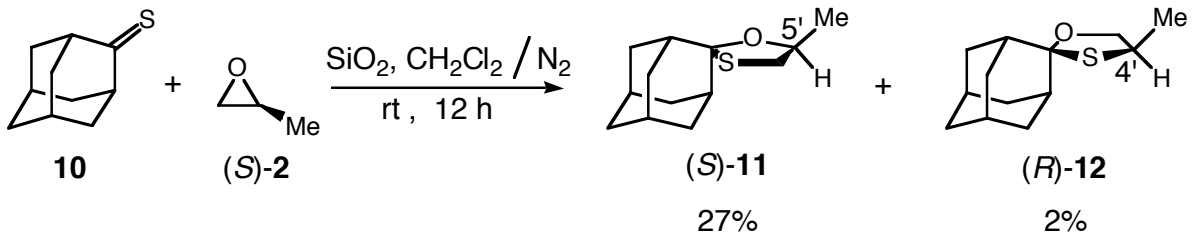
The structures of (5*S*,8*S*)-**9** and (5*R*,8*S*)-**9** were assigned by means of ^{1}H- and ^{13}C-NMR, CI-MS spectra and by comparison with those described previously.[6] The *Dreiding*-model examination of (5*S*,8*S*)-**9** shows that the spatial distances between the front Me-group and 2 H-atoms of the Ph-group at C(8) and 1 H-atom at C(7) are small, which corresponded well with the NOESY-spectrum (600 MHz, $CDCl_3$) of (5*S*,8*S*)-**9** that showed two relevant cross-signals between Me at 1.72 ppm and 2 H of Ph at 7.41-7.38 ppm as well as 1 H-C(7) at 4.55-4.53 ppm. The results were in accordance with the NOE-experiment described previously.[6] Similarly, the *Dreiding*-model of the diastereoisomer ((5*R*,8*S*)-**9**) shows that the distance between the front Me-group and the H-atom at C(8) is small, in accordance with the NOESY-spectrum (500 MHz, $CDCl_3$) of (5*R*,8*S*)-**9** that showed a relevant cross-signal between the front Me at 1.65 ppm and H-C(8) at 4.70 ppm.

Epimerization of (5*S*,8*S*)-9 with HCl. A solution of (5*S*,8*S*)-**9** in CH_2Cl_2 was treated with 3 drops of concentrated HCl at room temperature for 3 days. After usual workup, preparative TLC yielded 3% of (5*R*,8*S*)-**9**, and the starting material ((5*S*,8*S*)-**9**) was recovered in 25% yield.

Reactions of adamantane-2-thione (10) with oxiranes. – To a solution of **10** and 2 equiv. of (*S*)-**2** in dry CH_2Cl_2, silica gel was added at room temperature under N_2. After stirring the mixture for 12 h, the color of the suspension had changed very little. Chromatographic separation gave

two isomers ((*S*)-**11**) and ((*R*)-**12**) in 27 and 2% yields, respectively (ratio of 14:1). In addition, the starting material (**10**) was partly recovered (*Scheme 5*).

Scheme 5



The analogous $ZnCl_2$-catalyzed reaction of **10** with (*R*)-**6** at -30°C (8.5 h), led to only one isomer ((*S*)-**13**) in 28% yield, whereas in the presence of silica gel at room temperature (48 h), two isomers ((*S*)-**13**) and ((*R*)-**14**) were obtained in 29 and 2% yields, respectively (ratio of 15:1), as well as the un-expected product ((*S*)-**15**) in 23% yield.[7] After 10 h at room temperature, the SiO_2-catalyzed reaction gave only the two isomers ((*S*)-**13**) and ((*R*)-**14**) in 54 and 5% yields, respectively (ratio of 11:1); no (*S*)-**15** could be detected. In this case, 6% of the starting material (**10**) was recovered (*Scheme 6*, *Table 3*).

Scheme 6

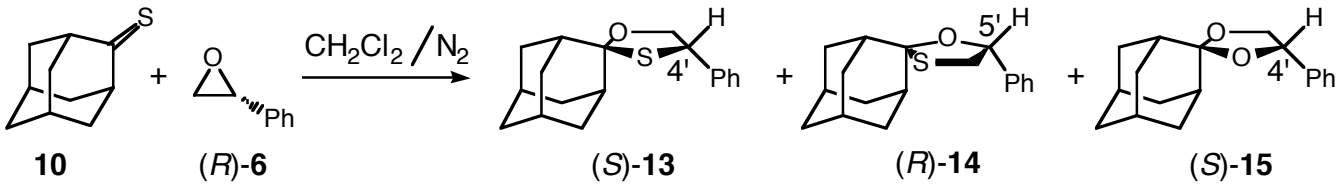


Table 3. *$ZnCl_2$- and SiO_2-Catalyzed Reaction of* **10** *with* (*R*)-**6** *in CH_2Cl_2*

	Temp.	Reaction time	Yield [%] and specific rotation ($[\alpha]_D^{24}$) of products			
		[h]	(*S*)-**13**	(*R*)-**14**	(*S*)-**15**	**10**
$ZnCl_2$	-30°C	8.5	28 (-66.5°)	-	-	-
SiO_2	rt	48	29 (-69.4°)	2	23 (+4.9°)	-
	rt	10	54 (-72.5°)	5 (-133.7°)	-	6

On the basis of ^{1}H- and ^{13}C-NMR spectra, elemental analyses, CI-MS, and comparison with the analogues described previously,[5] the structures of (*S*)-**11**, (*R*)-**12**, (*S*)-**13**, (*R*)-**14**, and (*S*)-**15** were assigned, and that of (*S*)-**13** was established by X-Ray crystallography (see *Figure 1*). The crystals are enantiomerically pure and the absolute configuration of the molecule has been confidently determined independently by the diffraction experiment. The compound has the expected 4′S configuration.

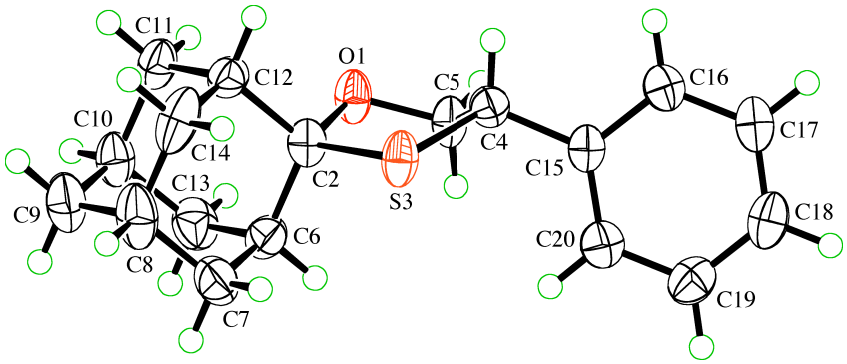


Figure 1. ORTEP Plot[8] of the molecular structure of (*S*)-**13** (arbitrary numbering of the atoms; 50% probability ellipsoids)

In the presence of silica gel, the results of the reactions of **10** with (*S*)-**2** and (*R*)-**6** showed that Me and Ph substituents have significant influence upon the regioselectivity of the ring opening of the oxirane by the nucleophilic attack of the thiocarbonyl S-atom. The ratio of 5′-Me substituted product ((*S*)-**11**) to 4′-Me substituted product ((*R*)-**12**) amounted to 14:1, whereas that of the corresponding Ph substituted products ((*R*)-**14**) to ((*S*)-**13**) was almost inverse, *i.e.*, 1:15 and 1:11, respectively, according to the reaction time of 48 h and 10 h (*Table 3*).

EXPERIMENTAL

General remarks. See ref.[9] IR spectra (film, cm^{-1}), NMR spectra at 300 (^{1}H) and 75.5 MHz (^{13}C) in $CDCl_3$, if not otherwise stated. Optical rotations were recorded on Perkin-Elmer-241 polarimeter (c = 1, in THF).

General procedures for the reactions of thiocarbonyl compounds (1, 8, and 10) with oxiranes ((*S*)-2) and ((*R*)-6). – Procedure 1: To the solution of thioketone (**1**) or (**10**) (*ca.* 1

mmol) in dry CH_2Cl_2 (10-15 mL) under N_2 atmosphere, 0.5 equiv. of a *Lewis* acid ($BF_3{\cdot}Et_2O$, $SnCl_4$ or $ZnCl_2$) was added at -78°C, -60°C, -30°C, and rt, respectively. In general, this led to a more or less pronounced change in the color of the solution. After stirring the mixture for 15 min at the selected temperature, *ca.* 2 equiv. of oxirane ((*S*)-**2**) or ((*R*)-**6**) was added dropwise, whereby the color of the solution changed rapidly in most cases. Then, the reaction was quenched by addition of H_2O and the mixture was washed with sat. aq. NaCl solution (3×). The combined organic layers were dried ($MgSO_4$) and evaporated *i.v.* The products were separated by chromatography (SiO_2, hexane/CH_2Cl_2; CC or prep. TLC (PLC)). Procedure 2: To the solution of **1**, **8** or **10** (*ca.* 1 mmol) and oxirane (*S*)-**2** or (*R*)-**6** (*ca.* 2 mmol) in dry CH_2Cl_2 (10-15 mL) under N_2 atmosphere, 4.5 g of silica gel were added at rt. After stirring the suspension for 10-72 h at rt, the mixture was filtered and the residue was washed with CH_2Cl_2 (4×). Then, the combined filtrate was evaporated *i.v.* The products were separated as described above.

Reactions of 1. – With (*S*)-2-methyloxirane ((*S*)-**2**). Reaction of **1** (204 mg, 1 mmol) with (*S*)-**2** (116 mg, 2 mmol) and 0.5 mmol of $BF_3{\cdot}Et_2O$ (or 4.5 g of SiO_2), at -60°C (or rt), and CC (hexane/CH_2Cl_2 10:1) yielded *(*S*)-1,1,3,3-tetramethyl-5′-methylspiro[indane-2,2′-[1,3]oxathiolane]* ((*S*)-**3**), *(*R*)-1,1,3,3-tetramethyl-4′-methylspiro[indane-2,2′-[1,3]oxathiolane]* ((*R*)-**4**), and *1,1,3,3-tetramethylindan-2-one* (**5**).[5] In addition, the starting material (**1**) was partly recovered (see *Table 1*).

With (*R*)-2-phenyloxirane ((*R*)-**6**). Reaction of **1** (204 mg, 1 mmol) with (*R*)-**6** (300 mg, 2.5 mmol) and 0.5 mmol of $BF_3{\cdot}Et_2O$ (or $SnCl_4$, $ZnCl_2$), or 4.5 g of SiO_2, at different temperatures, CC (hexane/CH_2Cl_2 10:1) and PLC yielded (*S*)-*1,1,3,3-tetramethyl-4′-phenylspiro[indane-2,2′-[1,3]oxathiolane]* ((*S*)-**7**) and **5**.[5] The starting material (**1**) was mainly recovered (see *Table 2*).

Reaction of 8 with (*R*)-6. Reaction of **8** (50 mg, 0.23 mmol) with (*R*)-**6** (54 mg, 0.45 mmol) and 2.26 g of SiO_2 at rt and PLC (hexane/ether 20:1) yielded *(5*S*,8*S*)-4,4-dimethyl-2,8-diphenyl-6-oxa-1,9-dithia-3-azaspiro[4.4]non-2-ene* ((5*S*,8*S*)-**9**, $[\alpha]_D^{23}$ = +26.7°), and *(5*R*,8*S*)-4,4-dimethyl-2,8-diphenyl-6-oxa-1,9-dithia-3-azaspiro[4.4]non-2-ene* ((5*R*,8*S*)-**9**) (see ref.[6]). In addition, 26 and 30%, respectively, of the starting material (**8**) were recovered (see *Scheme 4*).

Epimerization of (5*S*,8*S*)-9 to (5*R*,8*S*)-9. Treatment of (5*S*,8*S*)-**9** (32 mg, 0.09 mmol) with 3 drops of conc. HCl in CH_2Cl_2 (3 mL) at rt, 3 days, and prep. TLC (hexane/Et_2O 20:1) yielded 1 mg (3%) of (5*R*,8*S*)-**9**, and 8 mg (25%) of (5*S*,8*S*)-**9** was recovered.

Reactions of 10. – With (*S*)-**2**. Reaction of **10** (166 mg, 1 mmol) with (*S*)-**2** (116 mg, 2 mmol) in the presence of 4.5 g of SiO_2 at rt, 12 h, and CC (hexane/CH_2Cl_2 10:1) yielded 61 mg (27%) of (*S*)-**11** and 4 mg (2%) of (*R*)-**12**, and 47 mg (28%) of the starting material (**10**) was recovered (see *Scheme 5*).

*(*S*)-5′-Methylspiro[tricyclo[3.3.1.1^{3,7}]decane-2,2′-[1,3]oxathiolane]* ((*S*)-**11**). Colorless oil. $[\alpha]_D^{23}$ = +37.7°. IR: 2974*m*, 2909*s*, 2855*s*, 1470*m*, 1452*s*, 1379*m*, 1359*m*, 1351*m*, 1334*m*, 1309*w*, 1278*w*, 1230*w*, 1220*w*, 1174*m*, 1159*w*, 1138*s*, 1095*s*, 1066*s*, 1050*m*, 1027*s*, 1017*m*, 995*w*, 965*m*, 950*w*, 919*w*, 898*s*, 880*w*, 867*m*, 838*m*, 802*w*, 773*w*, 759*w*, 689*w*, 664*m*. ^{1}H-NMR: 4.31-4.21 (*m*, 1 H-C(5′)); 2.95 (*dd*, *J* = 10.0, 4.5, 1 H-C(4′)); 2.61 (*t*, *J* = 9.9, 1 H-C(4′)); 2.23-2.11 (br *m*, 3 H); 1.98-1.70 (br *m*, 9 H); 1.66-1.56 (*m*, 2 H); 1.38 (*d*, *J* = 6.0, Me). ^{13}C-NMR: 101.1 (*s*, C(2)); 76.9 (*d*, C(5′)); 41.5, 39.6 (2*d*, C(1), C(3)); 39.5 (*t*, C(6)); 37.5, 34.5, 34.3 (3*t*, C(4), C(8), C(9), C(10)); 35.4 (*t*, C(4′)); 27.0, 26.3 (2*d*, C(5), C(7)); 19.5 (*q*, Me). CI-MS (NH_3): 226 (15), 225 (100, [*M*+H]$^+$), 169 (10), 168 (93). Anal. Calcd for $C_{13}H_{20}OS$: C, 69.59; H, 8.98; S, 14.29. Found: C, 69.80; H, 8.93; S, 14.17.

*(*R*)-4′-Methylspiro[tricyclo[3.3.1.1^{3,7}]decane-2,2′-[1,3]oxathiolane]* ((*R*)-**12**). Colorless oil. IR: 2910*s*, 2855*s*, 1469*w*, 1452*m*, 1375*w*, 1358*w*, 1351*w*, 1310w, 1278*w*, 1262*w*, 1227*w*, 1193*w*, 1132*w*, 1103*m*, 1091*m*, 1079*m*, 1062*w*, 1050*w*, 1031*w*, 1009*m*, 994*w*, 982*w*, 968*w*, 937*w*, 891*m*, 879*w*, 850*w*, 834*w*, 802*w*, 658*w*. ^{1}H-NMR: 4.16 (*dd*, *J* = 9.2, 5.2, 1 H-C(5′)); 3.76 (*dd*, *J* = 9.3, 5.7, 1 H-C(5′)); 3.60-3.50 (*m*, H-C(4′)); 2.21-2.04 (br *m*, 4 H); 1.85-1.63 (br *m*, 8 H); 1.62-1.57 (*m*, 2 H); 1.31 (*d*, *J* = 6.6, Me). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 102.6 (*s*, C(2)); 75.6 (*t*, C(5′)); 44.0 (*d*, C(4′)); 40.8, 40.0 (2*d*, C(1), C(3)); 37.4 (*t*, C(6)); 36.6, 36.5, 34.3, 34.2 (4*t*, C(4), C(8), C(9), C(10)); 26.9, 26.2 (2*d*, C(5), C(7)); 20.2 (*q*, Me). CI-MS (NH_3): 227 (6), 226 (15), 225 (100, [*M*+H]$^+$), 222 (7), 169 (11), 168 (98).

With (*R*)-**6**. Reaction of **10** (166 mg, 1 mmol) with (*R*)-**6** (240 mg, 2 mmol) and 0.5 mmol of $ZnCl_2$ or 4.5 g of SiO_2, at -30°C or rt, CC (hexane/CH_2Cl_2 10:1) and PLC yielded (*S*)-**13**, (*R*)-**14** and (*S*)-**15**. In addition, the starting material (**10**) was partly recovered (see *Scheme 6*, *Table 3*).

*(*S*)-4′-Phenylspiro[tricyclo[3.3.1.1^{3,7}]decane-2,2′-[1,3]oxathiolane]* ((*S*)-**13**). Colorless crystals, mp 44.3-46.6°C. IR (KBr): 3081*w*, 3059*w*, 3024*w*, 2912*s*, 2855*s*, 1600*w*, 1492*m*, 1469*w*, 1452*s*,

1372*w*, 1351*m*, 1277*w*, 1269*w*, 1246*w*, 1226*w*, 1212*w*, 1104*s*, 1084*s*, 1047*w*, 1036*w*, 1026*w*, 997*m*, 979*m*, 962*m*, 937*w*, 892*s*, 861*m*, 850*m*, 833*w*, 803*w*, 761*s*, 708*m*. ^{1}H-NMR: 7.43-7.40 (*m*, 2 arom. H); 7.39-7.20 (*m*, 3 arom. H); 4.61 (*t*, *J* = 6.1, H-C(4′)); 4.41 (*dd*, *J* = 9.5, 5.8, 1 H-C(5′)); 4.10 (*dd*, *J* = 9.5, 6.3, 1 H-C(5′)); 2.32-2.17 (br *m*, 4 H); 1.91-1.74 (br *m*, 6 H); 1.70-1.63 (*m*, 4 H). ^{13}C-NMR: 140.6 (*s*, 1 arom. C); 128.5, 127.8, 127.3 (3*d*, 5 arom. CH); 103.4 (*s*, C(2)); 75.9 (*t*, C(5′)); 53.5 (*d*, C(4′)); 40.1 (*d*, C(1), C(3)); 37.4 (*t*, C(6)); 36.8, 36.6, 34.4, 34.2 (4*t*, C(4), C(8), C(9), C(10)); 27.0, 26.2 (2*d*, C(5), C(7)). CI-MS (NH_3): 289 (6), 288 (20), 287 (100, [*M*+H]$^+$), 168 (42), 151 (7). Anal. Calcd for $C_{18}H_{22}OS$: C, 75.48; H, 7.74; S, 11.19. Found: C, 75.48; H, 7.71; S, 10.91. Crystals of (*S*)-**13** suitable for an X-Ray crystal structure determination were grown from CH_2Cl_2/i-PrOH.

*(*R*)-5′-Phenylspiro[tricyclo[3.3.1.1^{3,7}]decane-2,2′-[1,3]oxathiolane]* ((*R*)-**14**). Colorless oil. IR: 3088*w*, 3064*w*, 3030*w*, 2908*s*, 2855*m*, 1605*w*, 1498*w*, 1469*w*, 1452*m*, 1351*w*, 1304*w*, 1277*w*, 1209*w*, 1144*w*, 1103*m*, 1082*m*, 1070*m*, 1052*w*, 1034*w*, 1014*w*, 966*w*, 941*w*, 917*w*, 897*w*, 880*w*, 864*w*, 833*w*, 802*w*, 767*w*, 740*w*, 698*m*, 666*w*. ^{1}H-NMR: 7.45-7.27 (*m*, 5 arom. H); 5.15 (*dd*, *J* = 10.2, 4.6, H-C(5′)); 3.23 (*dd*, *J* = 10.3, 4.6, 1 H-C(4′)); 2.90 (*t*, *J* = 10.3, 1 H-C(4′)); 2.31-2.19 (br *m*, 3 H); 2.10 (br *s*, 1 H); 1.95-1.72 (br *m*, 6 H); 1.70-1.59 (*m*, 4 H). ^{13}C-NMR: 140.0 (*s*, 1 arom. C); 128.4, 127.9, 126.0 (3*d*, 5 arom. CH); 101.1 (*s*, C(2)); 82.6 (*d*, C(5′)); 41.5, 39.8 (2*d*, C(1), C(3)); 40.2 (*t*, C(6)); 37.7, 37.5, 34.6, 34.4 (4*t*, C(4), C(8), C(9), C(10)); 35.3 (*t*, C(4′)); 27.0, 26.3 (2*d*, C(5), C(7)). CI-MS (NH_3): 288 (9), 287 (45, [*M*+H]$^+$), 169 (11), 168 (100), 136 (5). Anal. Calcd for $C_{18}H_{22}OS$: C, 75.48; H, 7.74; S, 11.19. Found: C, 75.29; H, 7.63; S, 11.06.

*(*S*)-4′-Phenylspiro[tricyclo[3.3.1.1^{3,7}]decane-2,2′-[1,3]dioxolane]* ((*S*)-**15**). Colorless oil. IR: 3088*w*, 3065*w*, 3031*w*, 2933*s*, 2905*s*, 2857*m*, 1605*w*, 1495w, 1469*w*, 1452*m*, 1385*w*, 1362*w*, 1351*w*, 1320*w*, 1306*w*, 1249*w*, 1220*m*, 1129*s*, 1097*m*, 1063*w*, 1047*m*, 999*m*, 944*w*, 924*m*, 882*w*, 842*w*, 802*w*, 784*w*, 763*w*, 752*w*, 698*s*, 669*w*. ^{1}H-NMR: 7.40-7.27 (*m*, 5 arom. H); 5.06 (*dd*, *J* = 8.1, 6.2, H-C(4′)); 4.29 (*dd*, *J* = 8.1, 6.2, 1 H-C(5′)); 3.67 (*t*, *J* = 8.1, 1 H-C(5′)); 2.18-1.99 (br *m*, 6 H); 1.84-1.69 (br *m*, 8 H). ^{13}C-NMR: 139.8 (*s*, 1 arom. C); 128.4, 127.8, 126.2 (3*d*, 5 arom. CH); 112.7 (*s*, C(2)); 77.7 (*d*, C(4′)); 71.5 (*t*, C(5′)); 37.5, 36.9 (2*d*, C(1), C(3)); 37.2 (*t*, C(6)); 35.2, 35.0, 34.7, 34.6 (4*t*, C(4), C(8), C(9), C(10)); 27.0, 26.9 (2*d*, C(5), C(7)). CI-MS (NH_3): 277 (7), 271 (35, [*M*+H]$^+$), 169 (11), 168 (100), 164 (6). Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.77; H, 8.17.

X-Ray Crystal Structure Determination of (*S*)-**13** (see *Table 4* and *Figure 1*).[10] All measurements were made on a *Nonius KappaCCD* diffractometer[11] using graphite-monochromated MoK_α

Table 4. *Crystallographic Data of Compound* ((*S*)-**13**)

Crystallised from		CH_2Cl_2 / i-PrOH
Empirical formula		$C_{18}H_{22}OS$
Formula weight [g mol^{-1}]		286.43
Crystal color, habit		colorless, needle
Crystal dimensions [mm]		0.02 × 0.10 × 0.20
Temperature [K]		160(1)
Crystal system		orthorhombic
Space group		$P2_12_12_1$
Z		4
Reflections for cell determination		1550
2θ range for cell determination [°]		4-50
Unit cell parameters	a [Å]	8.7970(3)
	b [Å]	10.6973(3)
	c [Å]	15.8944(6)
	V [Å^3]	1495.73(9)
D_x [g cm^{-3}]		1.272
μ(MoK_α) [mm^{-1}]		0.210
$2\theta_{(max)}$ [°]		50
Total reflections measured		20980
Symmetry independent reflections		2642
Reflections used [$I > 2\sigma(I)$]		2372
Parameters refined		183
Final R, wR		0.0387, 0.0369
Weights: p in $w = [\sigma^2 (F_O) + (pF_O)^2]^{-1}$		0.005
Goodness of fit		2.152
Secondary extinction coefficient		2.2(2) × 10^{-6}
Final Δ_{max}/σ		0.0006
$\Delta\rho$ (max; min) [e Å^{-3}]		0.21; -0.20

radiation (λ 0.71073 Å) and with an *Oxford Cryosystems Cryostream 700* cooler. The data collection and refinement parameters are given in *Table 4*, and a view of the molecule is shown in *Figure 1*. Data reduction was performed with *HKL Denzo* and *Scalepack*.[12] The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods using SIR92,[13] which revealed the positions of all non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. All of the H-atoms were fixed in geometrically calculated positions [d(C–H) = 0.95 Å] and each was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom. Refinement of the structure was carried out on F using full-matrix least-squares procedures, which minimised the function $\Sigma w(|F_o| - |F_c|)^2$. A correction for secondary extinction was applied. Refinement of the absolute structure parameter[14] yielded a value of 0.01(5), which confidently confirms that the refined coordinates represent the true enantiomorph. Neutral atom scattering factors for non-hydrogen atoms were taken from ref.,[15a] and the scattering factors for H-atoms were taken from ref.[16] Anomalous dispersion effects were included in F_c;[17] the values for f' and f'' were those of ref.[15b] The values of the mass attenuation coefficients are those of ref.[15c] All calculations were performed using the *teXsan* crystallographic software package.[18]

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