Tetrahedron: *Asymmetry* 20 (2009) 2097–2104

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

A study on the stereoselectivity of C,O bond formation in esterification of cyclic thiohydroxamic acids

Jens Hartung [a,*], Irina Kempter [a], Thomas Gottwald [b], Michaela Schwarz [b], Rainer Kneuer [b]

[a] *Fachbereich Chemie, Organische Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany*
[b] *Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*

ARTICLE INFO

Article history:
Received 25 May 2009
Accepted 6 August 2009
Available online 8 October 2009

ABSTRACT

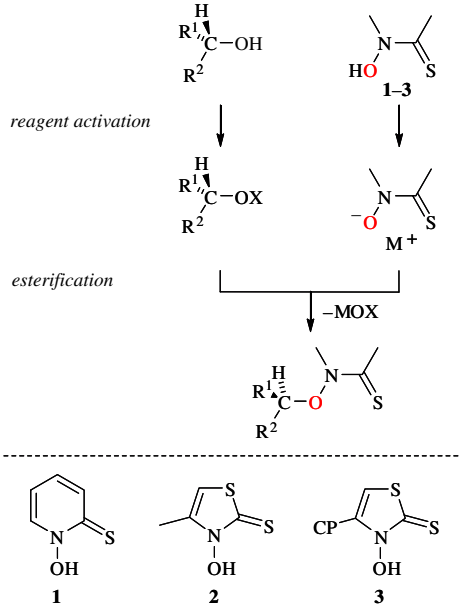
Esterification of cyclic thiohydroxamic acids, for example, *N*-hydroxypyridine-2(1*H*)-thione, *N*-hydroxy-4-methylthiazole-2(3*H*)-thione, and *N*-hydroxy-4-(*p*-chlorophenyl)-thiazole-2(3*H*)-thione, occurred with inversion of configuration at the attacked stereocenter, as evident from the use of chiral alcohols, alkyl *p*-toluene sulfonates, and cyclic sulfates. Stereochemical analysis of enantiomerically pure *O*-alkyl thiohydroxamates was performed on the basis of CD-spectroscopy and chemical derivatization. The assignment of the relative configuration in cyclic *O*-esters was feasible via NMR spectroscopy, whereas chiral aliphatic glycolato monoesters required hydroxyl group derivatization with chloro-(4*R*,5*R*)-bis[(1*R*,2*S*,5*R*)-menth-1-yloxycarbonyl)]-1,3,2-dioxaphospholane for this purpose.

1. Introduction

O-Alkyl thiohydroxamates[1,2] (Scheme 1) belong to a rare family of compounds that are able to liberate alkoxyl radicals[3] under pH neutral, non-oxidative conditions in radical chain reactions.[4] Alkoxyl radicals exhibit electrophilic properties in addition to olefins[5,6] and therefore pose useful complements to alcohols (nucleophilic oxygen) in synthesis.[7–10]

Unlike the diversity of methods developed for carboxylic acid ester synthesis,[11–16] thiohydroxamate esterification is restricted to *O*-alkylation.[2,17] In this step, the oxygen atom that upon *N*,*O*-homolysis becomes the radical center, is connected to the alkyl residue.

Since the use of achiral or racemic *O*-radicals has so far been adequate for addressing the majority of scientific problems, the issue of stereoselective thiohydroxamate *O*-alkylation was not yet a major concern.[18,19] The existing knowledge, however, is not sufficient for predicting the selectivity in asymmetric natural product synthesis via alkoxyl radical reactions using the thiohydroxamate method. In view of this background we have studied the systematics of the thiohydroxamate *O*-alkylation starting from substrates with one stereocenter and others with two vicinal asymmetrically substituted carbon atoms. The major results from this study clarified that *O*-alkylation of cyclic thiohydroxamates occurred with inversion of configuration at the attacked stereocenter. The use of cyclic sulfates[20] for *O*-alkyl thiohydroxamate synthesis has not previously been reported. It has the potential to significantly broaden the scope of this chemistry.

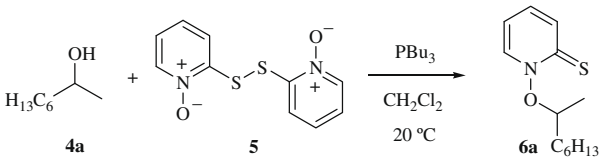


Scheme 1. Key steps in *O*-esterification of thiohydroxamic acids **1**–**3** with chiral alcohols (CP = *p*-ClC_6H_4; R^1, R^2 = alkyl; OX = leaving group; M^+ = e.g., NBu_4^+).

* Corresponding author. Tel.: +49 631 205 2431; fax: +49 631 205 3921.
E-mail address: hartung@chemie.uni-kl.de (J. Hartung).

0957-4166/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2009.08.020

Table 1
Synthesis of *N*-(oct-2-yloxy)-pyridinethione (±)-**6a**, (*R*)-**6a**, and (*S*)-**6a**

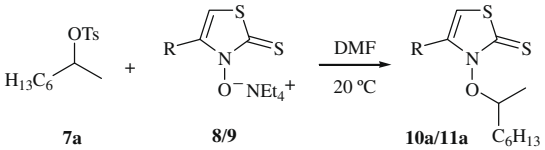


4a **5** **6a**

Entry	**4a**	**6**[a]/%
1	(±)-**4a**	(±)-**6a**/50
2	(*R*)-**4a** (>99% ee)	(*S*)-**6a**/43
3	(*S*)-**4a** (>99% ee)	(*R*)-**6a**/49

[a] For stereochemical analysis see Figure 1 and Table 3.

Table 2
Synthesis of *N*-(oct-2-yloxy)-thiazolethiones **10a**–**11a**



7a **8/9** **10a/11a**

Entry	**7a**	**8**/**9**/R	**10a**/**11a**[a]/%
1	(±)-**7a**	**8**/CH_3	(±)-**10a**/78
2	(*R*)-**7a** (>99% ee)	**8**/CH_3	(*S*)-**10a**/81
3	(*S*)-**7a** (>99% ee)	**8**/CH_3	(*R*)-**10a**/81
4	(±)-**7a**	**9**/*p*ClC_6H_4	(±)-**11a**/69
5	(*R*)-**7a** (>99% ee)	**9**/*p*ClC_6H_4	(*S*)-**11a**/61
6	(*S*)-**7a** (>99% ee)	**9**/*p*ClC_6H_4	(*R*)-**11a**/65

[a] For stereochemical analysis see Figure 1 and Table 3.

2. Results and discussion

2.1. Electrophiles with one stereocenter—enantioselectivity

The treatment of primary and secondary alcohols, for example, **4a**, with the combination of 1,2-bis-(1-oxidopyrid-2-yl)-disulfide **5**[21] and PBu_3 constitutes a versatile and convenient method for the synthesis of *N*-alkoxypyridine-2(1*H*)-thiones (Table 1).[22] This procedure circumvents the necessity to convert thiohydroxamic acid **1** into hygroscopic tetraalkylammonium salts that otherwise are required for *O*-selective alkylation in agreement with the principles of hard soft acids bases (HSAB).[23]

Octan-2-ol (**4a**) was selected as a reporter substrate for clarifying the stereochemical pathway of *O*-alkylation in the bispyridyldisulfane bis-*N*-oxide method because both enantiomers of the alcohol are commercially available in high enantiomeric purity (>99% ee). Conversion of racemic substrate (±)-**4a** with bispyridyldisulfane bis-*N*-oxide **5** and PBu_3 in a solution of CH_2Cl_2 provided octyl ester (±)-**6a** as a bright yellow oil in 50% yield. On a qualitative basis, a second, colorless, polar product was detected via TLC. Based on our knowledge from earlier investigations[24] and due to the fact that the pyridine-2(1*H*)-thione sulfur exhibits significant negative polarization,[25] this material was assumed to be 2-(2-octylsulfanyl)pyridine 1-oxide (not shown). The formation of such products was not pursued further because they provided no information for answering the question raised with the study. The use of enantiomerically pure octanols (*R*)-**4a** and (*S*)-**4a** gave octyl ester (*R*)-**6a** [starting from (*S*)-**4a**] and (*S*)-**6a** [starting from (*R*)-**4a**] in yields between 43% and 49% (Table 1). *N*-Alkoxypyridine-2(1*H*)-thiones decompose when exposed to daylight and should be immediately applied for the purpose they were prepared for.[4] CD spectra recorded from solutions of (*S*)-**6a** and (*R*)-**6a** in EtOH showed within first approximation mirror inverted curves (Fig. 1).

Photochemical conversion of octyl esters (*S*)-**6a** and (*R*)-**6a** with Bu_3SnH in solutions of C_6H_6[4] provided octanols (*S*)-**4a** [starting from (*S*)-**6a**] and (*R*)-**4a** [starting from (*R*)-**6a**] in quantitative yields (Table 3, entries 1 and 2). The configuration and enantiomeric purities (>96%) of the alcohols were determined via ^1H NMR spectroscopic analysis of derived Mosher's ester[26] in comparison with authentic samples. Bulb-to-bulb distillation was applied to the purification of (*R*)-**4a** and (*S*)-**4a**, since the fluoride method[27] was for unknown reasons inadequate for quantitatively removing tin residues after reductive cleavage of the octyl thiohydroxamates.

The synthesis of *N*-alkoxythiazole-2(3*H*)-thiones (Table 2), probably the most important group of thiohydroxamates relevant for alkoxyl radical chemistry,[28–30] is feasible starting from an appropriate thiohydroxamate salt and a hard alkylation reagent. Thus, treatment of octyl tosylate **7a** with *N*-hydroxythiazolethione tetraalkylammonium salts **8** and **9** afforded *N*-octylthiazolethiones (*R*)-**10a** and (*R*)-**11a** [from (*S*)-**7a**], and (*S*)-**10a** and (*S*)-**11a** [from (*R*)-**7a**] as tan oils. The yields of 4-methylthiazolethione-derived *O*-esters (*R*)- and (*S*)-**10a** (78–81%, Table 2, entries 2 and 3) were higher than those of the 4-(*p*-chlorophenyl) derivatives (*R*)- and (*S*)-**11a** (Table 2, entries 5 and 6). Reactions between racemic tosylate (±)-**7a** and salts **8**–**9** served as control and provided similar yields of products (±)-**10a** and (±)-**11a** (Table 2, entries 1 and 4). Products of competitive *S*-alkylation[31] were not observed (TLC, NMR) in these reactions.

Stereochemical analysis of esters **10a**–**11a** was performed via CD spectroscopy (Fig. 1) and after chemical derivatization via (i) photochemical reductive cleavage with Bu_3SnH, (ii) quantitative esterification of purified octanols (*S*)-**4a** and (*R*)-**4a** with Mosher's reagent, and (iii) ^1H NMR analysis of diastereomeric Mosher-esters in comparison with authentic samples (Table 3, entries 3–6).

2.2. Electrophiles with two stereocenters—diastereoselectivity

The effects of vicinal substituents on thiohydroxamate *O*-alkylation were probed with the aid of suitable cyclopentyl- and cyclohexyl-derived electrophiles, and cyclic sulfates.[20]

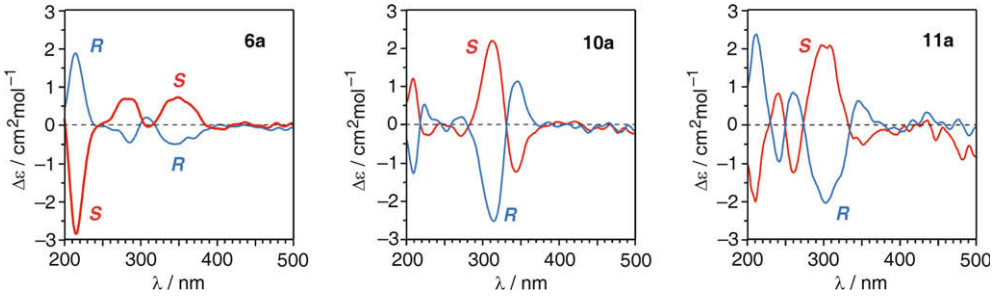
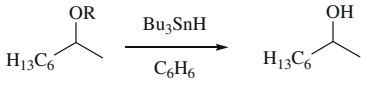


Figure 1. CD spectra of (*R*)- (figures in blue) and (*S*)-oct-2-yl thiohydroxamates (figures in red) **6a**, **10a**–**11a** (in EtOH, 25 °C).

Table 3
Determination of enantiomeric purity of octyl thiohydroxamates **6a**, **10a**–**11a**

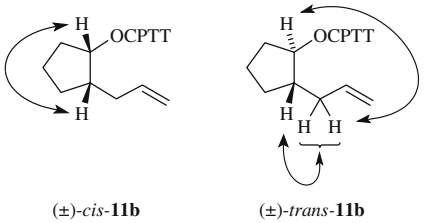


6a/10a/11a **4a**

Entry	**6a**/**10a**/**11a**	**4a**		
		Yield (GC)/%[a]	Yield/%[b]	ee/%[c]
1	(*R*)-**6a**	Quant.	53	(*R*)-**4a**/>96
2	(*S*)-**6a**	Quant.	59	(*S*)-**4a**/>96
3	(*R*)-**10a**	Quant.	54	(*R*)-**4a**/>96
4	(*S*)-**10a**	96	50	(*S*)-**4a**/>96
5	(*R*)-**11a**	Quant.	59	(*R*)-**4a**/>96
6	(*S*)-**11a**	Quant.	85	(*S*)-**4a**/>96

[a] From reaction mixture via internal standard.
[b] After bulb-to-bulb distillation.
[c] Via ^{1}H NMR of derived Mosher-ester.

Treatment of diastereomerically pure *cis*-(prop-2-en-1-yl)-cyclopentanol (±)-*cis*-**4b** with bispyridyldisulfane *N*-oxide **5**, and PBu_3 in a solution of CH_2Cl_2 furnished stereochemically pure (^{1}H and ^{13}C NMR) *N*-alkoxypyridinethione (±)-*trans*-**6b** as yellow oil (Table 4, entry 1). The stereochemical assignment was based on diagnostic NOEs (for representative example see Fig. 2) and ^{13}C NMR chemical shift homologies (Table 6). The reaction between alcohol (±)-*cis*-**4b** and *N*-hydroxy-4-methylthiazole-2(3*H*)-thione (**2**), diethyl azodicarboxylate, and PPh_3 in a solution of C_6H_6 (Mitsunobu-conditions)[11] afforded diastereomerically pure ester (±)-*trans*-**10b** as a tan colored oil in 60% yield (Table 4, entry 2). The ^{13}C NMR data for the cyclopentyl entity were virtually identical to those obtained for pyridinethione (±)-*trans*-**6b**. Subjecting *trans*-(2-allyl)-cyclopentanol (±)-*trans*-**4b** to a similar set of conversions gave *N*-alkoxy compounds (±)-*cis*-**6b** (yellow oil, from **5**, 47%) and (±)-*cis*-**10b** (tan oil, from **2**, 60%) as diastereomerically pure products. Efforts to prepare *N*-alkoxypridinethiones from *N*-hydroxypyridine-2(1*H*)-thione (**1**) and alcohols according to standard Mitsunobu-procedures[11,12] resulted in comparatively small yields (>10%, not shown) of target compounds (e.g., **6b**). Data from preliminary experiments suggested that the thione sulfur and not PPh_3 added in these reactions to diethyl azodicarboxylate, thus preventing selective *O*-alkylation. The fact that *N*-hydroxythiazole-2(3*H*)-thiones e.g. **2**, on the other hand, were useful substrates for Mitsunobu-reactions is explicable on the basis of significantly reduced negative polarization at the thione sulfur in these heterocycles compared to *N*-hydroxypyridine-2(1*H*)-thione (**1**).[25]



(±)-*cis*-**11b** (±)-*trans*-**11b**

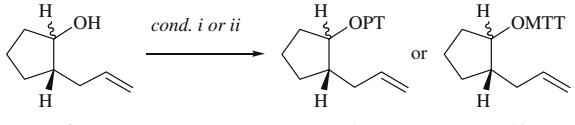
Figure 2. Visualization of diagnostic NOEs for distinguishing *cis*/*trans* isomers of cyclopentyl esters (±)-*cis*-**11b** and (±)-*trans*-**11b** as representative examples (arrows on one side refer to signal enhancement upon irradiation of the signal located at the opposite end).

The diastereoselectivity in the *O*-alkylation of thiohydroxamates **8**–**9** with hard electrophiles was investigated in reactions using 2-allylcycloalkyl tosylates (±)-**7b**–**c** in solutions of DMF (Table 5). The transformations of sterically demanding 4-(*p*-chlorophenyl)-thiazolethione **9** were restricted to reactions with more reactive[32] cyclopentyl tosylates *cis*/*trans*-(±)-**7b**, whereas the sterically less encroached 4-methyl analogue **8** was used in substitutions starting from less reactive[32] 2-allylcyclohexyl esters *cis*/*trans*-(±)-*cis*-**7c**. In all instances, diastereomerically pure products were formed (^{1}H and ^{13}C NMR; Table 5).

The relative configurations of chiral *O*-esters **10c** and **11b** were assigned on the basis of diagnostic NOEs and characteristic ^{1}H and ^{13}C NMR spectroscopic features of the compounds (Table 6, Fig. 2). In the cyclohexane series, for instance, a more pronounced shielding of C2 in *cis*-**10c** of 3.7 ppm in comparison *trans*-**10c** (Table 6, entries 3 and 4) was indicative of axial allyl substituent positioning in the *cis*-isomer.[33,34] For cyclopentane derivatives **6b**, **10b**, and **11b**, similar ^{13}C NMR trends were noted. This time, however, C1 was more shielded in the *cis*-isomers than C2. This finding suggested that the thiohydroxamate entity preferentially adopted an axial or a pseudoaxial position in *cis*-configured cyclopentyl esters of this type, thus directing the vicinal allyl group into equatorial or pseudo equatorial orientation.[35] In view of the well-known dynamic behavior of cyclopentane,[36,37] this aspect certainly merits future attention.

The feasibility of stereoselective *O*-alkyl thiohydroxamate synthesis from cyclic sulfates was explored starting from (4*R*,5*R*)-4,5-dibutyl-[1,3,2]-dioxathiolane-2,2-dioxide (*R*,*R*)-(**12d**)[38] and $MTTO^-$ NEt_4^+ **8**. The alkylation step was followed by acidic

Table 4
Formation of *O*-allylcyclopentyl thiohydroxamates **6b** and **10b**

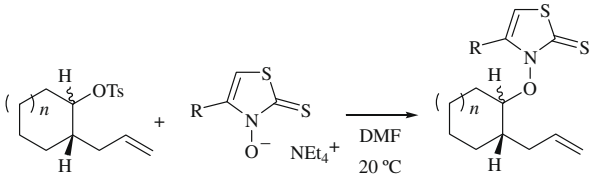


(±)-**4b** (±)-**6b** (±)-**10b**

Entry	(±)-**4b**/*cis*:*trans*[a]	Conditions[b]	(±)-**6b**/(±)-**10b**[c]	Yield/% (*cis*:*trans*)[d]
1	*cis*-**4b**/>99:1	i	*trans*-**6b**	28 (<5:95)
2	*cis*-**4b**/>99:1	i	*trans*-**10b**	60 (<5:95)
3	*trans*-**4b**/<1:99	ii	*cis*-**6b**	47 (>95:5)
4	*trans*-**4b**/<1:99	ii	*cis*-**10b**	60 (>95:5)

[a] GC.
[b] Reagents and conditions: (i) 1,2-bis-(1-oxidopyrid-2-yl)-disulfide **5**, PBu_3, CH_2Cl_2, 20 °C; (ii) *N*-hydroxythiazole-2(3*H*)-thione (**2**), diethylazodicarboxylate (DEAD), PPh_3, C_6H_6, 20 °C.
[c] PT = 2-thioxo-1,2-dihydropyrid-1-yl; MTT = 4-methyl-2-thioxo-2,3-dihydrothiaz-3-yl.
[d] ^{1}H NMR ($CDCl_3$, 20 °C).

Table 5
Formation of *O*-allylcycloalkyl thiohydroxamates (±)-**10c** and (±)-**11b**

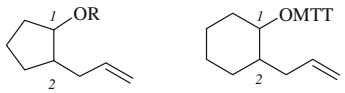


(±)-**7b–c** **8/9** (±)-**10c**/(±)-**11b**

Entry	(±)-**7b**–**c**/*cis*:*trans*[a]	**8**/**9**/R	(±)-**10c**/(±)-**11b**[b]	Yield/% (*cis*:*trans*)[a]
1	**7c** (*n* = 1)/>98:2	**8**/CH_3	*trans*-**10c**	42 (<2:98)
2	**7c** (*n* = 1)/>2:98	**8**/CH_3	*cis*-**10c**	11 (>98:2)
3	**7b** (*n* = 0)/>98:2	**9**/$pClC_6H_4$	*trans*-**11b**	54 (<2:98)
4	**7b** (*n* = 0)/<2:98	**9**/$pClC_6H_4$	*cis*-**11b**	52 (>98:2)

[a] NMR.
[b] R = CH_3 for **10c**; R = $pClC_6H_4$ for **11b**.

Table 6
Diagnostic ^{13}C NMR chemical shifts for distinguishing stereoisomers in *O*-(2-allylcycloalkoxy) thiohydroxamates **6** and **10–11**



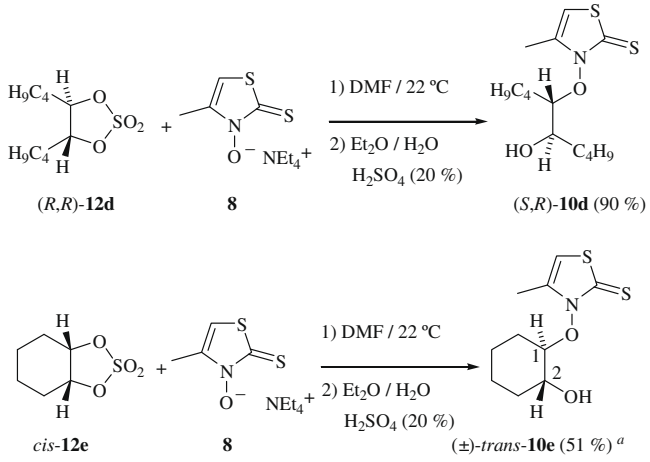
6b/10b/11b **10c**

Entry	Position	R = PT		R = MTT		R = CPTT	
		cis-**6**	*trans*-**6**	*cis*-**10**	*trans*-**10**	*cis*-**11**	*trans*-**11**
1	C1 (**b**)	87.9	91.5	88.3	92.1	87.9	93.1
2	C2 (**b**)	44.5	43.1	45.3	43.8	44.5	43.4
3	C1 (**c**)	—[a]	—[a]	85.2	86.0	—[a]	—[a]
4	C2 (**c**)	—[a]	—[a]	37.5	41.8	—[a]	—[a]

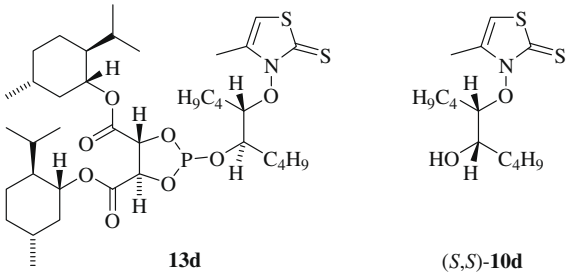
[a] Not available.

(H_2SO_4) hydrolysis of an intermediate sulfuric acid monoester[20] (not shown), to provide *O*-ester (*S*,*R*)-**10d** in a yield of 90% (Scheme 2, top).[39] TLC analysis of the crude reaction mixture provided no evidence for the formation of products originating from alkylation at thiohydroxamate sulfur. The stereochemical purity of product (*S*,*R*)-**10d** was verified by derivatization with 2-chloro-(4*R*,5*R*)-bis[(1*R*,2*S*,5*R*)-menth-1-yloxycarbonyl)]-1,3,2-dioxaphospholane[40] and the subsequent ^{31}P NMR analysis of derived phosphite **13d** (Fig. 3). A 97/3-ratio of diastereomers recorded for the sample of **13d** corresponded to the stereochemical purity of (*R*,*R*)-decane-5,6-diol (94% ee)[41] that was applied for the synthesis of cyclic sulfate (*R*,*R*)-**12d**. For the assignment of the major and the minor signals of the ^{31}P NMR spectrum (149.1 ppm/147.8 ppm = 97:3 in $CDCl_3$), stereoisomer (*S*,*S*)-**10d** was prepared from (*S*,*R*)-**10d** in a Mitsunobu-reaction[11] (39%, not shown). Treatment of (*S*,*S*)-**10d** with the phosphorous-based chiral derivatization reagent and the subsequent ^{31}P NMR analysis provided the phosphite as the major product (149.4 ppm/148.2 ppm = 3:97) which constituted the minor component in the sample of **13d**.

Bicyclic sulfate *cis*-**12e** afforded, upon treatment with thiohydroxamate salt **8** and the subsequent acid-catalyzed monoalkyl sulfate hydrolysis *O*-(2-hydroxycyclohexyl), thiohydroxamate (±)-*trans*-**10e** (Scheme 2, bottom). Product purification resulted in a minor loss of the material. Stereochemical analysis of the compound was attainable on the basis of NMR chemical shifts and $^3J_{H,H}$ coupling constants. The proton located in proximity to the thiohydroxamate O (δ = 4.73 for 1-H), for example, experienced stronger deshielding than 2-H (δ = 3.82) due to magnetic anisotropy[42] exerted by the thiocarbonyl group. Doublet coupling constants of $^3J_{H,H}$ = 9.1 and 11.4 Hz pointed to the axial positioning of 1-H. A third doublet coupling caused by *cis*-oriented 6-H ($^3J_{H,H}$ = 4.6 Hz) caused the resonance of 1-H to appear in the spectrum as a doublet of a double doublet. Although the signal of 2-H was not similarly well resolved, its axial orientation was evident from one of the large vicinal coupling constants associated with 1-H.



Scheme 2. Synthesis of chiral *N*-alkoxy-4-methylthiazolethiones **10d–e** from cyclic sulfates [[a]yield in the crude reaction mixture (^1H NMR); 36% after chromatography].



13d (*S*,*S*)-**10d**

Figure 3. Structure formulae of (*S*,*R*)-**10d**-derived chiral phosphite **13d** and thiazolethione (*S*,*S*)-**10d** (see text).

3. Conclusion

The results from the present study clarify that secondary *O*-esters of cyclic thiohydroxamic acids **1**–**3**, and probably of thiohydroxamates in general, occur with an inversion of configuration at the attacked electrophilic stereogenic center in alkyl *p*-toluenesulfonates, cyclic sulfates, and reagent activated alcohols. This observation correlates with the chemical behavior of other non-basic *O*-nucleophiles, such as carboxylates, hydroxamates, and oximates.[11,13,14]

The new information therefore is considered to serve as a guideline for devising new synthetic routes to natural products via *O*-radical reactions using the thiohydroxamate method. In view of the unique alkoxyl radical selectivities, this method will open up new perspectives for the synthesis of chiral target molecules, that otherwise are difficult to obtain, with similar ease and efficiency from ionic reactions. From the present results it is evident that the tertiary *O*-alkyl thiohydroxamate synthesis in combination with an appropriate stereochemical analysis will merit future attention, in order to continuously develop the alkoxyl radical method. This issue is currently being addressed in this laboratory.

4. Experimental

4.1. General

Melting points [°C] were determined on a Koffler hot-plate melting point microscope (*Reichert*). Differential Thermoanalyses (DTA) were recorded with a Thermal-Analyser 9000 (*Du Pont*). Melting points refer to endothermic signals, whereas exothermic signals are indicative of product decomposition. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded with FT-NMR DPX 200, DPX 400, and DMX 600 instruments (*Bruker*). Chemical shifts refer to the δ-scale. The resonances of residual protons and those of carbons in deuterated solvents $CDCl_3$ (δ_H 7.26, δ_C 77.0) were used as internal standards. The overlap of the two ^{13}C resonances in NMR spectra, as indicated by the information 2 C given in parentheses after the associated shift value, was verified via by HMQC-measurements. Mass spectra (EI, 70 eV) were recorded with a Mass Selective Detector HP 6890 (*Hewlett Packard*). IR spectra were measured either on NaCl plates or from KBr pellets using a Perkin Elmer

FT/IR 1600 spectrometer. UV/vis spectra were recorded in 1-cm quartz cuvettes with a Perkin Elmer UV/vis 330 spectrometer. CD spectra were recorded with a ISA/Jobin Yvon Dichrograph CD6 and were analyzed with the corresponding Dichrograph software. Photoreactions were carried out using a Southern New England Ultraviolet RPR-100 Rayonet® photoreactor, equipped with RPR 350 nm lamps [for *N*-alkoxythiazole-2(3*H*)-thiones **10**–**11**] or incandescent light [Philips 150 W Spotline® R80 for *N*-alkoxypyridine-2(1*H*)-thiones **6**]. Reaction progress was monitored via thin layer chromatography on aluminum sheets coated with silica gel (60 F_{254}, *Merck*). Compounds were visualized by UV-light (254 nm) or the use of Ekkert's reagent. Combustion analysis was performed with a Carlo Erba 1106 instrument (analytical laboratory of Universität Würzburg), a Perkin Elmer Elemental Analyzer 2400 CHN, or a Perkin Elmer Elemental Analyzer EA240 (the latter two at the analytical laboratory, Technische Universität Kaiserslautern).

Tri-*n*-butyltin hydride, (±)-2-octanol (±)-**4a**, (*R*)-2-octanol (*R*)-**4a** (>99% ee), and (*S*)-2-octanol (*S*)-**4a** (>99% ee), cyclopentene oxide, and cyclohexene oxide were obtained from commercial suppliers and used as received. *N*-Hydroxypyridine-2(1*H*)-thione **1**,[21] *N*-hydroxy-4-methylthiazole-2(3*H*)-thione **2**,[43] *N*-hydroxy-4-(*p*-chlorophenyl)-thiazole-2(3*H*)-thione **3**,[44] 1,2-[bis-(1-oxidopyrid-2-yl)]-disulfide **5**,[21] and tetraethylammonium salts **8**–**9**[23] were prepared according to the published procedures. *trans*-(Prop-2-en-1-yl)-cyclopentanol (±)-*trans*-**4b** and *trans*-(prop-2-en-1-yl)-cyclohexanol were prepared from cyclopentene oxide and cyclohexene oxide and allylmagnesium bromide.[45,46] *cis*-(Prop-2-en-1-yl)-cyclopentanol (±)-*cis*-**4b** and *cis*-(prop-2-en-1-yl)-cyclohexanol were synthesized from the corresponding trans stereoisomers via a Mitsunobu reaction.[47,48] Alkyl tosylates (±)-**7a**,[49,50] (*R*)-**7a**,[49,50] (*S*)-**7a**,[49,50] (±)-*cis*-**12b**–**c**,[51] and (±)-*trans*-**12b**–**c**,[51] were prepared from the corresponding alcohols by application of a method reported earlier from our laboratory.[52]

Petroleum ether refers to the fraction boiling between 40 and 55 °C. All solvents were purified according to standard procedures.[53]

4.2. Photoreactions of *O*-alkyl thiohydroxamates

A Schlenk flask was charged with a solution of *O*-alkyl thiohydroxamate **6**, **10**, or **11** in anhydrous CH_2Cl_2 in the dark. The flask was sealed with a rubber septum and cooled to liquid-nitrogen temperature. After thorough evacuation (10^{-2} mbar), the flask was flushed with argon and Bu_3SnH (2.5 equiv, c_0 = 0.18 M) was added. The reaction mixture was deaerated by means of two freeze–pump–thaw cycles using argon as the flushing gas and thermostated in a water bath to 18 °C. The solution was photolyzed [2 min incandescent light (150 W) for *N*-alkoxypyridine-2(1*H*)-thiones **6**; 25 min in a Rayonet® chamber photoreactor equipped with 350 nm light bulbs for *N*-alkoxythiazole-2(3*H*)-thiones **10**–**11**]. The solvent was removed under reduced pressure. The residue was purified by bulb-to-bulb distillation (80 °C, 12 mbar) to afford pure 2-octanols **4a** (GC, ^{1}H NMR). The enantiomeric purity was determined by ^{1}H NMR of derived (*R*)-Mosher-esters.[26]

4.3. Preparation of (*R*)-Mosher-esters from chiral alcohols

4.3.1. General procedure

A solution of purified alcohol (±)-**4a**, (*R*)-**4a**, or (*S*)-(**4a**) (70–100 μmol, 1 M) in anhydrous CH_2Cl_2 was treated with *N*,*N*-dimethylaminopyridine (2.0 equiv) at 0 °C. (*S*)-α-Methoxy-α-trifluoromethylphenylacetyl chloride[26,54] (1.5 equiv) was added in a dropwise manner to afford a mixture, which was stirred for 1 h at 20 °C. After dilution with Et_2O (2 mL) the organic layer was washed with 2 M aq HCl, satd aq $NaHCO_3$, brine (2 mL each), and dried ($MgSO_4$). The solvent was removed under reduced pressure to afford derived Mosher-ester in quantitative yield. Diastereomeric purity was checked by GC analysis and ^{1}H NMR (signal intensity of the OCH_3 group).

4.3.1.1. (*R*)-Mosher-ester of (*S*)-2-octanol (*S*)-4a. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.86 (t, 3H, *J* = 7.0 Hz), 1.11–1.28 (m, 8H), 1.33 (d, 3H, *J* = 6.4 Hz), 1.46–1.74 (m, 2H), 3.57 (q, 3H, *J* = 1.2 Hz, OCH_3), 5.15 (m_c, 1H), 7.37–7.42 (m, 3H), 7.52–7.56 (m, 2H).

4.3.1.2. (*R*)-Mosher-ester of (*R*)-2-octanol (*R*)-4a. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.88 (t, 3H, *J* = 7.0 Hz), 1.22–1.36 (m, 8H), 1.25 (d, 3H, *J* = 6.1 Hz), 1.48–1.79 (m, 2H), 3.55 (q, 3H, *J* = 1.2 Hz, OCH_3), 5.14 (m_c, 1H), 7.37–7.42 (m, 3H), 7.51–7.55 (m, 2H).

4.3.1.3. (*R*)-Mosher-ester of (±)-2-octanol (±)-4a. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.86 [t, 3H, *J* = 7.0 Hz, 8-H (*R*,*S*)], 0.88 [t, 3H, *J* = 7.0 Hz, 8-H (*R*,*R*)], 1.11–1.35 (m, 16H, CH_2), 1.25 [d, 3H, *J* = 6.3 Hz, 1-H (*R*,*R*)], 1.33 [d, 3H, *J* = 6.4 Hz, 1-H (*R*,*S*)], 1.46–1.79 (m, 4H, CH_2), 3.55 [q, 3H, *J* = 1.2 Hz, OCH_3 (*R*,*R*)], 3.57 [q, 3H, *J* = 1.2 Hz, OCH_3 (*R*,*S*)], 5.07–5.22 (m, 2H, 1-H), 7.36–7.43 (m, 3H, Ar-H), 7.50–7.57 (m, 2H, Ar-H).

4.4. Derivatization of chiral alcohols with 2-chloro-(4*R*,5*R*)-bis[1*R*,2*S*,5*R*)-menth-1-yloxycarbonyl)]-1,3,2-dioxaphospholane[55]

4.4.1. General procedure

In a NMR tube, purified thiazolethione (*S*,*R*)-**10d** or (*S*,*S*)-**10d** (5–10 mg) was treated with 2-chloro-(4*R*,5*R*)-bis[1*R*,2*S*,5*R*)-menth-1-yloxycarbonyl)]-1,3,2-dioxaphospholane (300 μL of a 0.2 M solution in THF). NEt_3 (5 μL). $CDCl_3$ (200 μL) was added to the solution and the diastereomeric purity was checked by ^{31}P NMR.

4.4.1.1. Derivatization of (*S*,*R*)-10d. ^{31}P NMR ($CDCl_3$, 242 MHz) δ 149.1 (97%), 147.8 (3%).

4.4.1.2. Derivatization of (*S*,*S*)-10d. ^{31}P NMR ($CDCl_3$, 242 MHz) δ 149.4 (3%), 148.2 (97%).

4.5. *N*-Alkoxypyridine-2(1*H*)-thiones

4.5.1. General method

A stirred slurry of 1,2-bis-(1-oxidopyrid-2-yl)-disulfide **5** (1.2 equiv) in anhydrous CH_2Cl_2 containing a substrate alcohol (*c* 0.18 M) was treated at a given temperature under an atmosphere of argon in a dropwise manner within 15 min with PBu_3 (1.2 equiv). Stirring of the resulting yellow solution was continued for 1 h at a given temperature. The mixture was washed with 0.1 M aq NaOH (10 mL). The organic phase was separated and kept. The aqueous layer was washed with methyl *tert*-butyl ether (2 × 10 mL). The combined organic phase and washings were extracted with satd aq $NaHCO_3$, H_2O, and brine (10 mL each) to afford a clear yellow solution, which was dried ($MgSO_4$) and concentrated under reduced pressure. The remaining yellow oil was purified by chromatography [SiO_2, petroleum ether/methyl *tert*-butyl ether 1:1 = (v/v)].

4.5.1.1. (±)-*N*-(Oct-2-yloxy)-pyridine-2(1*H*)-thione (±)-6a. From (±)-octan-2-ol (±)-**4a** (130 mg, 1.00 mmol), 1,2-bis-(1-oxidopyrid-2-yl)-disulfide **5** (278 mg, 1.10 mmol), and PBu_3 (223 mg, 1.10 mmol) in anhydrous CH_2Cl_2 (6 mL) at 20 °C. Yield: 120 mg (0.501 mmol, 50%); yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.79–0.94 (m, 3H), 1.15–1.46 (m, 11H), 1.59 (m_c, 1H, 3-H), 1.77 (m_c, 1H, 3-H), 5.17 (m_c, 1H, 2-H), 6.54 (dt, 1H, J_d = 1.8, J_t = 6.7 Hz, CH), 7.10 (ddd, 1H, *J* = 1.7, 6.7, 6.9 Hz, CH), 7.63 (m_c, 2H, CH). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.0, 17.5, 22.5, 24.7, 29.3, 31.7, 33.9, 81.0, 112.1, 132.5, 138.1, 139.8, 176.3. Anal. Calcd for $C_{13}H_{21}NOS$: C, 65.23; H, 8.84; N, 5.85; S, 13.40. Found: C, 65.24; H, 8.61; N, 5.83; S, 13.16.

4.5.1.2. (*S*)-*N*-(Oct-2-yloxy)-pyridine-2(1*H*)-thione (*S*)-6a. From (*R*)-octan-2-ol (*R*)-**4a** (115 mg, 0.884 mmol), 1,2-bis-(1-oxidopyrid-2-yl)-disulfide **5** (245 mg, 0.972 mmol), and PBu_3 (197 mg, 0.972 mmol) in anhydrous CH_2Cl_2 (5 mL) at 20 °C. Yield: 91.1 mg (0.381 mmol, 43%); yellow oil. $[\alpha]_D^{25} = +28.3$ (*c* 1.27, EtOH). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.85–0.87 (m, 3H), 1.26–1.32 (m, 9H), 1.37–1.43 (m, 2H), 1.55–1.61 (m, 1H, 3-H), 1.78 (m_c, 1H, 3-H), 5.17 (sext, 1H, J = 6.2 Hz, 2-H), 6.54 (td, 1H, J_t = 6.8, J_d = 1.7 Hz, CH), 7.09–7.12 (m, 1H, CH), 7.60–7.65 (m, 2H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.0, 17.5, 22.5, 24.7, 29.3, 31.6, 33.9, 81.0, 112.2, 132.5, 138.0, 139.8, 176.2. UV/vis (EtOH) λ_{max} (lg ε) 362 nm (3.72). Anal. Calcd for $C_{13}H_{21}NOS$: C, 65.23; H, 8.84; N, 5.85; S, 13.40. Found: C, 64.79; H, 8.85; N, 5.82; S, 13.39.

4.5.1.3. (*R*)-*N*-(Oct-2-yloxy)-pyridine-2(1*H*)-thione (*R*)-6a. From (*S*)-octan-2-ol (*S*)-**4a** (125 mg, 0.958 mmol), 1,2-bis-(1-oxidopyrid-2-yl)-disulfide **5** (290 mg, 1.15 mmol), and PBu_3 (233 mg, 1.15 mmol) in anhydrous CH_2Cl_2 (6 mL) at 20 °C. Yield: 111 mg (0.465 mmol, 49%), yellow oil. $[\alpha]_D^{25} = -28.2$ (*c* 1.28, EtOH). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.86–0.89 (m, 3H), 1.28–1.33 (m, 9H), 1.38–1.45 (m, 2H), 1.56–1.60 (m, 1H, 3-H), 1.76–1.82 (m, 1H, 3-H), 5.17–5.20 (m, 1H, 2-H), 6.54 (bs, 1H, CH), 7.10–7.11 (m, 1H, CH), 7.61–7.67 (m, 2H, CH). For unknown reasons, the ^{1}H NMR spectrum of (*R*)-**6a** was less resolved than for (*S*)-**6a**. ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.0, 17.5, 22.5, 24.7, 29.3, 31.7, 33.9, 81.0, 112.2, 132.5, 138.1, 139.8, 176.2. UV/vis (EtOH) λ_{max} (lg ε) 363 nm (3.81). Anal. Calcd for $C_{13}H_{21}NOS$: C, 65.23; H, 8.84; N, 5.85; S, 13.40. Found: C, 64.40; H, 8.54; N, 5.42; S, 13.39.

4.5.1.4. (±)-*cis*-*N*-[2-(Prop-2-en-1-yl)-cyclopentoxy]-pyridine-2(1*H*)-thione (±)-*cis*-6b. From (±)-*trans*-2-(prop-2-en-1-yl)-cyclopentanol (±)-*trans*-**4b** (126 mg, 0.998 mmol), 1,2-bis-(1-oxidopyrid-2-yl)-disulfide **5** (313 mg, 1.24 mmol), and PBu_3 (315 mg, 1.20 mmol) in a solution of anhydrous CH_2Cl_2 (6 mL) at 41 °C. Yield: 66.6 mg (0.283 mmol, 28%); yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.59–2.21 (m, 7H), 2.25 (m_c, 1H), 2.72 (m_c, 1H), 4.99 (d, 1H, J = 10.1 Hz), 5.06 (d, 1H, J = 17.2 Hz), 5.53 (m_c, 1H), 5.98 (m_c, 1H), 6.56 (dt, 1H, J_d = 1.8 Hz, J_t = 6.9 Hz), 7.09 (ddd, 1H, J = 1.5, 6.9, 8.6 Hz), 7.57 (dd, 1H, J = 1.5, 6.9 Hz), 7.63 (dd, 1H, J = 1.8, 8.6 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.4, 28.7, 29.6, 33.2, 44.5, 87.9, 112.5, 115.2, 132.3, 138.0, 138.2, 139.2, 176.6. Anal. Calcd for $C_{13}H_{17}NOS$: C, 66.35; H, 7.28; N, 5.95; S, 13.62. Found: C, 65.64; H, 6.82; N, 5.85; S, 13.39.

4.5.1.5. (±)-*trans*-*N*-[2-(Prop-2-en-1-yl)-cyclopentoxy]-pyridine-2(1*H*)-thione (±)-*trans*-6b. From (±)-*cis*-2-(prop-2-en-1-yl)-cyclopentanol (±)-*cis*-**4b** (261 mg, 2.07 mmol), 1,2-bis-(1-oxidopyrid-2-yl)-disulfide **5** (574 mg, 2.27 mmol), and PBu_3 (459 mg, 2.27 mmol) in a solution of anhydrous CH_2Cl_2 (11 mL) at 20 °C. Yield: 228 mg (0.968 mmol, 47%); yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.23–1.42 (m, 1H), 1.69–2.15 (m, 6H), 2.19–2.35 (m, 2H), 4.96 (d, 1H, J = 10.1 Hz), 5.00 (d, 1H, J = 17.2 Hz), 5.29 (m_c, 1H), 5.74 (ddt, 1H, J_t = 7.1 Hz, J_d = 10.1, 17.2 Hz), 6.57 (m_c, 1H), 7.12 (m_c, 1H), 7.66 (m_c, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 22.8, 29.9, 37.6, 43.2, 91.5, 112.5, 116.3, 132.5, 136.3, 137.9, 139.3, 176.5. Anal. Calcd for $C_{13}H_{17}NOS$: C, 66.35; H, 7.28; N, 5.95; S, 13.62. Found: C, 66.49; H, 6.96; N, 5.81; S, 13.36.

4.6. *N*-Alkoxythiazole-2(3*H*)-thiones

4.6.1. From *N*-hydroxythiazole-2(3*H*)-thione tetraethylammonium salts and alkyl tosylates.

4.6.1.1. General method. A flame dried round-bottomed flask was charged with equimolar amounts of *N*-hydroxythiazole-2(3*H*)-thione tetraethylammmonium salt **8** or **9**, and an alkyl tosylate dissolved in a minimum amount of anhydrous DMF in an atmosphere of argon. The flask was closed with a drying tube ($CaCl_2$). The reaction mixture was stirred for 5 days at 20 °C in the dark and poured afterwards onto H_2O (40 mL). The mixture was extracted with Et_2O (2 × 40 mL). The combined organic extracts were washed with aq 2 M NaOH (30 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure to afford a brown oil, which was purified by column chromatography [R_f = 0.5–0.7, SiO_2, petroleum ether/Et_2O, or petroleum ether/methyl *tert*-butyl ether = 1:1 (v/v)].

4.6.1.2. (±)-*N*-(Oct-2-yloxy)-4-methylthiazole-2(3*H*)-thione (±)-10a. From (±)-oct-2-yl *p*-toluenesulfonate (±)-**7a** (300 mg, 1.06 mmol) and *N*-hydroxy-4-methylthiazole-2(3*H*)-thione tetraethylammonium salt **8** (321 mg, 1.16 mmol). Yield: 213 mg (0.823 mmol, 78%); tan oil. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.84–0.89 (m, 3H), 1.22–1.45 (m, 11H), 1.58 (m_c, 1H), 1.76 (m_c, 1H), 2.22 (d, 3H, J = 1.2 Hz, CH_3), 5.39 (m_c, 1H, 2-H), 6.16 (q, 1H, J = 1.2 Hz). ^{13}C NMR ($CDCl_3$, 63 MHz) δ 14.0, 18.1, 22.5, 25.1, 29.3, 31.7, 34.6, 81.6, 102.8, 139.1, 180.7. Anal. Calcd for $C_{12}H_{21}NOS_2$: C, 55.56; H, 8.16; N, 5.40; S, 24.72. Found: C, 55.83; H, 7.94; N, 5.38; S, 24.37.

4.6.1.3. (*S*)-*N*-(Oct-2-yloxy)-4-methylthiazole-2(3*H*)-thione (*S*)-10a. From (*R*)-oct-2-yl *p*-toluenesulfonate *R*-(**7a**) (570 mg, 2.00 mmol) and *N*-hydroxy-4-methylthiazole-2(3*H*)-thione tetraethylammonium salt **8** (680 mg, 2.46 mmol). Yield: 420 mg (1.62 mmol, 81%); tan oil. $[\alpha]_D^{25} = +34.7$ (*c* 1.47, EtOH). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86–0.89 (m, 3H), 1.24–1.36 (m, 9H), 1.39–1.45 (m, 2H), 1.53–1.64 (m, 1H), 1.72–1.80 (m, 1H), 2.22 (d, 3H, J = 1.7 Hz, CH_3), 5.40 (sext, 1H, J = 6.3 Hz, 2-H), 6.16 (m_c, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 18.2, 22.5, 25.1, 29.3, 31.7, 34.7, 81.7, 102.5, 139.1, 181.0. UV/vis (EtOH) λ_{max} (lg ε) 319 nm (4.01). Anal. Calcd for $C_{12}H_{21}NOS_2$: C, 55.56; H, 8.16; N, 5.40; S, 24.72. Found: C, 55.72; H, 8.29; N, 5.40; S, 24.50.

4.6.1.4. (*R*)-*N*-(Oct-2-yloxy)-4-methylthiazole-2(3*H*)-thione (*R*)-10a. From (*S*)-oct-2-yl *p*-toluenesulfonate (*S*)-**7a** (314 mg, 1.10 mmol) and *N*-hydroxy-4-methylthiazole-2(3*H*)-thione tetraethylammonium salt **8** (337 mg, 1.22 mmol). Yield: 231 mg (0.891 mmol, 81%); tan oil; $[\alpha]_D^{25} = -34.9$ (*c* 1.46, EtOH). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86–0.89 (m, 3H), 1.24–1.34 (m, 9H), 1.39–1.45 (m, 2H), 1.53–1.60 (m, 1H), 1.72–1.80 (m, 1H), 2.23 (s, 3H, CH_3), 5.40 (sext, 1H, J = 6.3 Hz, 2-H), 6.16 (s, 1H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.0, 18.1, 22.5, 25.1, 29.3, 31.6, 34.6, 81.6, 102.7, 139.1, 180.7. UV/vis (EtOH) λ_{max} (lg ε) 319 nm (4.00). $C_{12}H_{21}NOS_2$: C, 55.56; H, 8.16; N, 5.40; S, 24.72. Found: C, 55.61; H, 8.14; N, 5.64; S, 24.43.

4.6.1.5. (±)-*N*-(Oct-2-yloxy)-4-(*p*-chlorophenyl)-thiazole-2(3*H*)-thione (±)-11a. From (±)-oct-2-yl *p*-toluenesulfonate (±)-**7a** (411 mg, 1.45 mmol) and *N*-hydroxy-4-(*p*-chlorophenyl)-thiazole-2(3*H*)-thione tetraethylammonium salt **9** (582 mg, 1.56 mmol). Yield: 358 mg (1.01 mmol, 69%); tan oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.86 (t, 3H, J = 6 Hz), 1.93 (d, 3H, J = 6 Hz), 1.09–1.34 (m, 8H), 1.57–1.63 (m, 2H), 4.98 (m_c, 1H), 6.50 (s, 1H), 7.47 (m_c, 4H). ^{13}C NMR ($CDCl_3$, 63 MHz) δ 14.1, 17.8, 22. 5, 24.8, 29.2, 31.6, 34.3, 82.7, 105.2, 127.4, 129.0, 129.9, 135.9, 141.6, 181.1. Anal. Calcd for $C_{17}H_{22}ClNOS_2$: C, 57.36; H, 6.23; N, 3.94; S, 18.02. Found: C, 57.43; H, 5.97; N, 3.99; S, 18.19.

4.6.1.6. (*S*)-*N*-(Oct-2-yloxy)-4-(*p*-chlorophenyl)-thiazole-2(3*H*)-thione (*S*)-11a. From (*R*)-oct-2-yl *p*-toluenesulfonate (*R*)-**7a** (570 mg, 2.00 mmol) and *N*-hydroxy-4-(*p*-chlorophenyl)-thiazole-2(3*H*)-thione tetraethylammonium salt **9** (917 mg, 2.46 mmol). Yield: 435 mg (1.22 mmol, 61%); tan oil. $[\alpha]_D^{25} = +30.5$ (*c* 0.93, $CHCl_3$). UV/vis (EtOH) λ_{max} (lg ε) = 318 nm (4.14). ^{1}H and ^{13}C NMR spectroscopic data matched with those of the racemate.

4.6.1.7. (*R*)-*N*-(Oct-2-yloxy)-4-(*p*-chlorophenyl)-thiazole-2(3*H*)-thione (*R*)-11a. From (*S*)-oct-2-yl *p*-toluenesulfonate (*S*)-**7a** (314 mg, 1.10 mmol) and *N*-hydroxy-4-(*p*-chlorophenyl)-thiazole-2(3*H*)-thione tetraethylammonium salt **9** (455 mg, 1.22 mmol). Yield: 256 mg (0.718 mmol, 65%); tan oil. $[\alpha]_D^{25} = -32.6$ (*c* 0.93, $CHCl_3$); UV/vis (EtOH) λ_{max} (lg ε) 317 nm (4.14). ^1H and ^{13}C NMR spectroscopic data matched with those of the racemate.

4.6.1.8. (±)-*cis*-*N*-[2-(Prop-2-en-1-yl)-cyclohexyloxy]-4-methylthiazole-2(3*H*)-thione (±)-*cis*-10c. From (±)-*trans*-2-(prop-2-en-1-yl)-cyclohexyl *p*-toluenesulfonate (±)-*trans*-**7c** (1.19 g, 4.04 mmol) and *N*-hydroxy-4-methylthiazole-2(3*H*)-thione tetraethylammonium salt **8** (2.22 g, 8.03 mmol). Yield: 119 mg (0.441 mmol, 11%); tan oil. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.24–1.47 (m, 4H), 1.62–1.80 (m, 4H), 2.14–2.43 (m, 2H), 2.25 (d, 3H, J = 1.2 Hz, CH_3), 2.50–2.58 (m, 1H), 5.03 (d, 1H, J = 10.1 Hz), 5.05 (d, 1H, J = 17.4 Hz), 5.29 (m_c, 1H), 5.78 (m_c, 1H), 6.16 (q, 1H, J = 1.2 Hz). ^{13}C NMR ($CDCl_3$, 63 MHz) δ 14.2, 20.4, 23.8, 26.1, 26.7, 30.5, 37.5, 9.2, 102.8, 116.1, 137.2, 139.1, 180.6. Anal. Calcd for $C_{13}H_{19}NOS_2$: C, 57.95; H, 7.11; N, 5.20; S, 23.28. Found: C, 58.37; H, 6.61; N, 5.05; S, 23.04.

4.6.1.9. (±)-*trans*-*N*-[2-(Prop-2-en-1-yl)-cyclohexyloxy]-4-methylthiazole-2(3*H*)-thione (±)-trans-10c. From (±)-*cis*-[2-(prop-1-en-1-yl)cyclohexyl] *p*-toluenesulfonate (±)-*cis*-**7c** (486 mg, 1.65 mmol) and *N*-hydroxy-4-methylthiazole-2(3*H*)-thione tetraethylammonium salt **8** (592 mg, 2.14 mmol). Yield: 185 mg (0.686 mmol, 42%); tan oil. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.17–1.49 (m, 4H), 1.62–1.94 (m, 5H), 2.13 (dt, 1H, J_d = 14.0 J_t = 7.9 Hz), 2.24 (d, 3H, J = 1.2 Hz, CH_3), 2.83 (m_c, 1H), 4.99–5.02 (m, 1H), 5.05 (d, 1H, J = 17.1 Hz), 5.06 (d, 1H, J = 10.4 Hz), 5.88 (m_c, 1H), 6.15 (q, 1H, J = 1.2 Hz). ^{13}C NMR ($CDCl_3$, 63 MHz) δ 14.2, 24.3 25.0, 30.2, 30.3, 36.4, 41.8, 86.0, 102.8, 116.3, 136.8, 139.2, 180.7. Anal. Calcd for $C_{13}H_{19}NOS_2$: C, 57.95; H, 7.11; N, 5.20; S, 23.28. Found: C, 58.07; H, 6.82; N, 5.03; S, 23.46.

4.6.1.10. (±)-*cis*-*N*-[2-(Prop-2-en-1-yl)-cyclopentoxy]-4-(p-chlorophenyl)-thiazole-2(3*H*)-thione (±)-*cis*-11b. From (±)-*trans*-[2-(prop-2-en-1-yl)]-cyclopentyl *p*-toluenesulfonate (±)-*trans*-**7b** (1.03 g, 3.68 mmol) and *N*-hydroxy-4-(*p*-chlorophenyl)thiazole-2(3*H*)-thione tetraethylammonium salt **9** (1.30 g, 3.70 mmol). Yield: 673 mg (1.91 mmol, 52%); colorless solid, mp 125 °C. ^1H NMR ($CDCl_3$, 250 MHz) δ 0.65–0.79 (m, 1H), 1.10–1.45 (m, 3H), 1.65–1.72 (m, 1H), 1.80–1.91 (m, 1H), 2.20 (m_c, 1H), 2.62 (m_c, 1H), 4.97 (d, 1H, J = 10.1 Hz), 5.05 (d, 1H, J = 17.1 Hz), 5.50 (s, 1H), 5.97 (m_c, 1H), 6.49 (s, 1H), 7.43 (d, 2H, J = 8.9 Hz), 7.49 (d, 2H, J = 8.9 Hz). ^{13}C NMR ($CDCl_3$, 63 MHz) δ 20.8, 29.0, 29.1, 32.2, 45.3, 88.7, 105.4, 115.3, 127.3, 128.9, 129.9, 135.9, 137.8, 141.7, 180.9. Anal. Calcd for $C_{17}H_{18}ClNOS_2$: C, 58.02; H, 5.16; N, 3.98; S, 18.22. Found: C, 57.63; H, 5.19; N, 3.92; S, 17.98.

4.6.1.11. (±)-*trans*-*N*-[2-(Prop-2-en-1-yl)-cyclopentoxy]-4-(*p*-chlorophenyl)-thiazole-2(3*H*)-thione (±)-*trans*-11b. From (±)-*cis*-[2-(prop-2-en-1-yl)cyclopentyl] *p*-toluenesulfonate (±)-*cis*-**7b** (279 mg, 0.995 mmol) and *N*-hydroxy-4-(*p*-chlorophenyl)-thiazole-2(3*H*)-thione tetraethylammonium salt **9** (559 mg, 1.50 mmol). Yield: 188 mg (0.534 mmol, 54%); tan oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.05–1.14 (m, 1H), 1.20–1.32 (m, 1H), 1.39–1.66 (m, 4H), 1.88 (m_c, 1H), 2.05 (m_c, 2H), 4.91 (d, 1H, J = 16.9 Hz), 4.93 (d, 1H, J = 10.3 Hz), 5.05 (m_c, 1H), 5.97 (ddt, 1H, J_t = 5.9 Hz, J_d = 10.1, 16.9 Hz), 6.49 (s, 1H), 7.44 (d, 2H, J = 8.7 Hz), 7.49 (d, 2H, J = 8.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.8, 30.1, 30.4, 37.5, 43.4, 93.1, 105.2, 116.2, 127.5, 129,1, 129.8, 136.1, 136.2, 141.3, 181.3. Anal. Calcd for $C_{17}H_{18}ClNOS_2$: C, 58.02; H, 5.16; N, 3.98; S, 18.22. Found: C, 58.12; H, 5.15; N, 3.89; S, 18.45.

4.6.2. From *N*-hydroxy-4-methylthiazole-2(3*H*)-thione (2) via Mitsunobu-reaction

4.6.2.1. General method. A flame dried Schlenk flask was charged with *N*-hydroxy-4-methylthiazole-2(3*H*)-thione (**2**) (1.5 equiv), PPh_3 (2 equiv), and a substrate alcohol (1 equiv) dissolved in anhydrous C_6H_6. The solution was treated in a dropwise manner at 0 °C with DEAD (2.1 equiv). Stirring was continued for 36 h at 20 °C. The reaction mixture was subsequently washed with aq NaOH (2 M, 10 mL). The organic layer was separated and kept. The aq phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer and washings were dried ($MgSO_4$) and concentrated under reduced pressure to afford a brown oil, which was purified by chromatography [SiO_2, petroleum ether/Et_2O = 2:1 (v/v)].

4.6.2.2. (±)-*cis*-*N*-[2-(Prop-2-en-1-yl)-cyclopentoxy]-4-methylthiazole-2(3*H*)-thione (±)-*cis*-10b. From (±)-*trans*-[2-(prop-2-en-1-yl)]-cyclopentanol (±)-*trans*-**4b** (125 mg, 1.00 mmol), PPh_3 (525 mg, 2.00 mmol), DEAD (366 mg, 2.10 mmol, 0.33 mL) and *N*-hydroxy-4-methylthiazole-2(3*H*)-thione (**2**) (221 mg, 1.50 mmol). Yield: 174 mg (0.681 mmol, 68%); tan oil. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.23–1.35 (m, 1H), 1.65–2.15 (m, 6H), 2.42 (d, 3H, J = 1.2 Hz), 2.45–2.58 (m, 1H), 2.62–2.77 (m, 1H), 4.98–5.15 (m, 2H), 5.75–5.81 (m, 1H), 6.03 (m_c, 1H), 6.16 (q, 1H, J = 1.2 Hz). ^{13}C NMR ($CDCl_3$, 63 MHz) δ 13.9, 21.9, 29.3, 29.3, 33.1, 45.3, 88.3, 102.9, 115.4, 137.9, 139.2, 171.4. Anal. Calcd for $C_{12}H_{17}NOS_2$: C, 56.44; H, 6.71; N, 5.48; S, 25.11. Found: C, 56.72; H, 6.86; N, 5.42; S, 24.82.

4.6.2.3. (±)-*trans*-*N*-[2-(2-Propenyl)cyclopentoxy)]-4-methylthiazole-2(3*H*)-thione (±)-*trans*-10b. From (±)-*cis*-[2-(prop-2-en-1-yl)]cyclopentanol (±)-*cis*-**4b** (125 mg, 1.00 mmol), PPh_3 (525 mg, 2.00 mmol), DEAD (366 mg, 2.10 mmol, 0.33 mL) and *N*-hydroxy-4-methylthiazole-2(3*H*)-thione (**2**) (221 mg, 1.50 mmol). Yield: 143 mg (0.560 mmol, 56%); tan oil. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.30–1.37 (m, 1H), 1.65–1.97 (m, 4H), 1.97–2.15 (m, 2H), 2.25 (m, 2H), 2.25 (d, 3H, J = 1.2 Hz), 5.02 (m_c, 2H), 5.47 (m_c, 1H), 5.80 (m_c, 1H), 6.16 (q, 1H, J = 1.2 Hz). ^{13}C NMR ($CDCl_3$, 63 MHz) δ 14.1, 23.3, 30.4, 30.7, 37.7, 43.8, 92.1, 102.9, 116.4, 136.4, 138.8, 181.1.

4.7. From *N*-hydroxythiazole-2(3*H*)-thione tetraethylammonium salt 8 and cyclic sulfates

4.7.1. General method

A solution of *N*-hydroxythiazole-2(3*H*)-thione tetraethylammonium salt **8** and a cyclic sulfate in anhydrous DMF were stirred for 5 days in the dark. The solvent was removed afterwards under reduced pressure. The remaining red oil was dissolved in Et_2O and treated for 21 h at 22 °C with aq H_2SO_4 [20% (w/w)]. The mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with H_2O (3 × 20 mL), brine (30 mL), and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified by column chromatography.

4.7.1.1. *N*-[(5*S*,6*R*)-6-Hydroxydecyl-5-oxy]-4-methylthiazole-2(3*H*)-thione (*S*,*R*)-10d. From *N*-hydroxy-4-methylthiazole-2(3*H*)-thione tetraethylammonium salt **8** (2.10 g, 7.2 mmol), and (4*R*,5*R*)-4,5-dibutyl-[1,3,2]-dioxathiolane-2,2-dioxide (*R*,*R*)-**12d** (1.20 mg, 5.10 mmol) in DMF (50 mL). The crude product was purified by column chromatography [R_f = 0.49, SiO_2, Et_2O/pentane = 5:1 (v/v)]. Yield: 1.40 g (4.61 mmol, 90%); orange solid; $[\alpha]_D^{25} = -26.8$ (*c* 1.01, EtOH). ^1H NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, 3H, ^3J = 7.2 Hz), 0.93 (t, 3H, ^3J = 7.2 Hz), 1.22–2.00 (m, 12H), 2.34 (d, 3H, ^4J = 1.2 Hz), 3.82–3.85 (m, 1H), 4.16 (d, 1H, ^3J = 9.1 Hz), 4.39 (d, 1H, ^4J = 3.5 Hz, OH), 6.26 (m, 1H, ^4J = 0.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.8, 13.9 (2C), 14.0, 22.6, 22.9, 26.6, 28.5, 28.7, 31.6, 68.5, 92.8, 104.2, 138.8,

183.2. Anal. Calcd for $C_{14}H_{25}O_2NS_2$: C, 55.41; H, 8.30; N, 4.62. Found: C, 55.60; H, 8.23; N, 4.64.

4.7.1.2. (±)-*trans*-*N*-(2-Hydroxycyclohexyloxy)-4-methylthiazole-2(3*H*)-thione (±)-*trans*-10e. From *N*-hydroxy-4-methylthiazole-2(3*H*)-thione tetraethylammonium salt **8** (912 mg, 3.30 mmol) and *cis*-hexahydro-benz-[1,3,2]-dioxathiolane-2,2-dioxide *cis*-**12e** (588 mg, 3.30 mmol) in DMF (30 mL). The crude product was purified by column chromatography [R_f = 0.26, SiO_2, Et_2O/pentane = 2:1 (v/v)]. Yield: 290 mg (1.18 mmol, 36%); colorless solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.25–1.81 (m, 6H), 2.08–2.20 (m, 2H), 2.32 (d, 3H, ^4J = 0.9 Hz, CH_3), 3.79–3.86 (m, 1H), 4.32 (s, 1H, OH), 4.70–4.76 (m, 1H), 6.24 (m, 1H, ^4J = 0.9 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.1, 23.4, 24.2, 30.1, 33.6, 72.2, 90.5, 103.1, 139.0, 181.0. Anal. Calcd for $C_{10}H_{15}NO_2S_2$: C, 48.95; H, 6.16; N, 5.71. Found: C, 49.06; H, 6.31; N, 5.71.

4.8. From other *N*-alkoxythiazole-2(3*H*)-thiones via chemical transformation

4.8.1. *N*-[(5*S*,6*S*)-6-Hydroxydecyl-5-oxy]-4-methylthiazole-2(3*H*)-thione (*S*,*S*)-10d

A flame dried Schlenk flask was charged with *N*-alkoxythiazole-2(3*H*)-thione (*S*,*R*)-**10d** (480 mg, 1.60 mmol), PPh_3 (1.68 g, 6.40 mmol), *p*-nitrobenzoic acid (1.07 g, 6.40 mmol) and toluene (25 mL). At 0 °C DEAD (1.12 g, 6.40 mmol) was added in a dropwise manner. The resulting reaction mixture was stirred in the dark for 94 h at 22 °C. Thereafter the solution was washed with satd aq K_2CO_3 (3 × 50 mL) and H_2O (2 × 50 mL). The combined aq layers were extracted with Et_2O (3 × 50 mL). Combined organic layer and washings were dried ($MgSO_4$), the solvent was removed under reduced pressure. The remaining residue was purified by column chromatography [R_f = 0.25, SiO_2, Et_2O/pentane = 1:2 (v/v)] to afford 330 mg (0.73 mmol, 46%) of *N*-[(5*S*,6*S*)-6-sulfooxydecyl-5-oxy]-4-methylthiazole-2(3*H*)-thione as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.85 (t, 3H, *J* = 7.2 Hz), 0.90 (t, 3H, *J* = 7.0 Hz), 1.18–1.61 (m, 12H), 2.24 (s, 3H), 5.44–5.47 (m, 1H), 5.76–5.79 (m, 1H), 6.13 (m, 1H, *J* = 1.0 Hz), 8.22–8.32 (m, 4H, Ar-H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 13.8, 13.9 (2C), 14.0, 22.5, 22.7, 26.9, 27.6, 28.0, 30.5, 74.8, 83.0, 103.1, 123.6, 130.8, 135.2, 138.8, 150.7, 164.1, 183.2. A solution of *N*-[(5*S*,6*S*)-6-sulfooxydecyl-5-oxy]-4-methylthiazole-2(3*H*)-thione (0.73 mmol) in MeOH (15 mL) was added in a dropwise manner with a solution of NaOH (117 mg, 2.92 mmol) in MeOH (15 mL). The reaction mixture was stirred in the dark at 22 °C for 22 h. Next, Et_2O (60 mL) and H_2O (60 mL) were added. The organic layer was separated and kept. The aq layer was extracted with Et_2O (3 × 30 mL). The combined organic layer and washings were dried ($MgSO_4$). The solvent was removed under reduced pressure to afford a residue, which was purified by column chromatography [R_f = 0.24, SiO_2, Et_2O/pentane = 1:1 (v/v)]. Yield: 190 mg (0.63 mmol, 86%); yellow oil; $[\alpha]_D^{25} = +92.2$ (*c* 1.46, EtOH). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89 (t, 3H, *J* = 7.0 Hz), 0.92 (t, 3H, *J* = 7.2 Hz), 1.22–1.85 (m, 12H), 2.28 (d, 3H, *J* = 1.2 Hz), 3.20 (d, 1H, *J* = 1.2 Hz, OH), 3.75–3.82 (m, 1H), 4.99–5.03 (m, 1H), 6.20 (m, 1H, ^4J = 1.2 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 13.8, 13.9 (2C), 14.0, 22.6, 22.8, 26.9, 28.0, 28.4, 33.4, 71.3, 88.4, 103.1, 139.2, 181.2. Anal. Calcd for $C_{14}H_{25}NO_2S_2$: C, 55.41; H, 8.30; N, 4.62. Found: C, 55.90; H, 8.34; N, 4.46.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (Grants Ha1705/3–3 and 5–2).

References

1. Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1988**, *110*, 4115–4116.
2. Walter, W.; Schaumann, E. *Synthesis* **1971**, 111–130.
3. Hartung, J.; Gottwald, T.; Špehar, K. *Synthesis* **2002**, 1469–1498.
4. Hartung, J. *Eur. J. Org. Chem.* **2001**, 619–632.
5. Jones, M. J.; Moad, G.; Rizzardo, E.; Solomon, D. H. *J. Org. Chem.* **1989**, *54*, 1607–1611.
6. Elson, I. H.; Mao, S. W.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 335–341.
7. Gottwald, T.; Greb, M.; Hartung, J. *Synlett* **2004**, 65–68.
8. Hartung, J.; Kneuer, R. *Tetrahedron: Asymmetry* **2003**, *14*, 3019–3031.
9. Haramange, J.-C.; Figadère, B. *Tetrahedron: Asymmetry* **1993**, *4*, 1711–1774.
10. Wolfe, J. P.; Hay, M. B. *Tetrahedron* **2007**, *63*, 261–290.
11. Mitsunobu, O. *Synthesis* **1981**, 1–28.
12. But, T. Y. S.; Toy, P. H. *Chem. Asian J.* **2007**, *2*, 1340–1355.
13. Haslam, E. *Tetrahedron* **1980**, *36*, 2409–2433.
14. Makosza, M.; Fedorynski, M. *Adv. Catal.* **1987**, *35*, 375–422.
15. Kocieński, P. J. *Protecting Groups*; Thieme: Stuttgart, 1994.
16. Salomon, C. J.; Mata, E. G.; Mascaretti, O. A. *Tetrahedron* **1993**, *49*, 3691–3734.
17. Chmiak, A.; Przychodzen, R. *J. Heteroatom Chem.* **2002**, *13*, 169–194.
18. Hartung, J.; Schneiders, N.; Gottwald, T. *Tetrahedron Lett.* **2007**, *48*, 6027–6030.
19. Hartung, J.; Daniel, K.; Rummey, C.; Bringmann, G. *Org. Biomol. Chem.* **2006**, *4*, 4089–4100.
20. Gao, Y.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 7538–7539.
21. Barton, D. H. R.; Samadi, M. *Tetrahedron* **1992**, *48*, 7083–7090.
22. Hartung, J. *Synlett* **1996**, 1206–1209.
23. Hartung, J.; Kneuer, R.; Schwarz, M.; Svoboda, I.; Fueß, H. *Eur. J. Org. Chem.* **1999**, 97–106.
24. Hartung, J.; Kneuer, R.; Laug, S.; Schmidt, P.; Špehar, K.; Svoboda, I.; Fuess, H. *Eur. J. Org. Chem.* **2003**, 4033–4052.
25. Hartung, J.; Bergsträßer, U.; Daniel, K.; Schneiders, N.; Svoboda, I.; Fuess, H. *Tetrahedron* **2009**, *65*, 2567–2573.
26. Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543–2549.
27. Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 553–565.
28. Hartung, J.; Schwarz, M.. In *Organic Syntheses*; Freeman, J. P., Ed.; Wiley: New York, 2004; Coll. Vol. 10, pp 437–441.
29. Gross, A.; Schneiders, N.; Daniel, K.; Gottwald, T.; Hartung, J. *Tetrahedron* **2008**, *64*, 10882–10889.
30. Hartung, J. In *Handbook of Reagents for Organic Synthesis—Reagents for Radical and Radical Ion Chemistry*; Crich, D., Ed.; Wiley: Chichester, 2008; pp 175–179.
31. Hartung, J.; Daniel, K.; Bergsträßer, U.; Kempter, I.; Schneiders, N.; Danner, S.; Schmidt, P.; Svoboda, I.; Fuess, H.; *Eur. J. Org. Chem*. doi: 10.1002/ejoc.200900069.
32. Isaacs, N. *Physical Organic Chemistry*, 2nd ed.; Longman: Burnt Mill, Harlow, 1995. Chapter 10.
33. Damm, W.; Giese, B.; Hartung, J.; Hasskerl, T.; Houk, K. N.; Hüter, O.; Zipse, H. *J. Am. Chem. Soc.* **1992**, *114*, 4067–4079.
34. Kalinowski, H. O.; Berger, S.; Braun, S. *^{13}C NMR-Spektroskopie*; Thieme: Stuttgart, 1984. pp 102–106.
35. Testa, B. *Grundlagen der Organischen Stereochemie*; VCH: Weinheim, 1983. p 103.
36. Fuchs, B. *Top. Stereochem.* **1978**, *10*, 1–94.
37. Eliel, E. L.; Wilen, S. H.; Mander, L. N. In *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, NY, 1993; pp 686–754.
38. Kolb, H. C.; van Nieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483–2547.
39. Lohray, B. B. *Synthesis* **1992**, 1035–1052.
40. Amberg, M.; Bergsträßer, U.; Stapf, G.; Hartung, J. *J. Org. Chem.* **2008**, *73*, 3907–3910; Amberg, M.; Bergsträßer, U.; Stapf, G.; Hartung, J. *J. Org. Chem.* **2008**, *73*, 6052.
41. Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Chadha, R. J.; Crispino, G. A.; Davis, W. D.; Hartung, J.; Ogino, Y.; Shibata, T. *J. Org. Chem.* **1993**, *58*, 844–849.
42. Walter, W.; Schaumann, E.; Paulsen, H. *Liebigs Ann. Chem.* **1969**, *727*, 61–70.
43. Barton, D. H. R.; Crich, D.; Kretzschmar, G. *J. Chem. Soc., Perkin Trans. 1* **1986**, 39–53.
44. Hartung, J.; Schwarz, M.. In *Organic Syntheses*; Freeman, J. P., Ed.; Wiley: New York, 2004; Coll. Vol. 10, pp 437–441.
45. Hegedus, L. S.; McKearin, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 2444–2451.
46. Letsinger, R. L.; Traynham, J. G.; Bobko, E. *J. Am. Chem. Soc.* **1952**, *74*, 399–401.
47. (a) Mitsunobu, O. *Synthesis* **1981**, 1–28; (b) Martin, S. F.; Dodge, J. A. *Tetrahedron Lett.* **1991**, *32*, 3017–3020.
48. Mori, K.; Otsuka, T.; Oda, M. *Tetrahedron* **1984**, *40*, 2929–2934.
49. Streitwieser, A.; Waiss, A. C. *J. Org. Chem.* **1962**, *27*, 290–292.
50. Neubert, M. E.; Keast, S. S.; Ezenyilimba, M. C.; Hanlon, C. A.; Jones, W. C. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1993**, *237*, 193–206.
51. Michel, T.; Kirschning, A.; Beier, Ch.; Bräuer, N.; Schaumann, E.; Adiwidjaja, G. *Liebigs Ann. Org. Bioorg. Chem.* **1996**, *11*, 1811–1822.
52. Hartung, J.; Hünig, S.; Kneuer, R.; Schwarz, M.; Wenner, H. *Synthesis* **1997**, 1433–1438.
53. Perrin, D. D.; Armarego, W. L. F.; Perin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, 1980.
54. Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512–519.
55. Amberg, M.; Bergsträßer, U.; Stapf, G.; Hartung, J. *J. Org. Chem.* **2008**, *73*, 3907–3910; Amberg, M.; Bergsträßer, U.; Stapf, G.; Hartung, J. *J. Org. Chem* **2008**, *73*, 6052.