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Conformationally constrained 2-methylidene 1,3-oxathiane *S*-oxides: synthesis and nucleophilic additions

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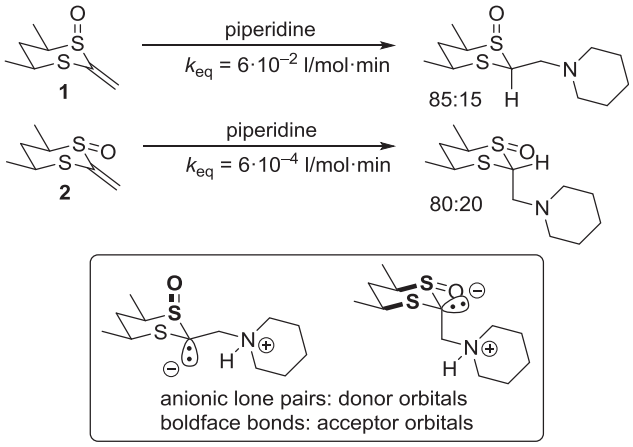
ABSTRACT

The properties of vinyl sulfoxides are significantly influenced by stereoelectronic effects, where the relative orientation of sulfoxide group and alkene moiety is responsible for reactivity and selectivity, e.g., in the addition of nucleophiles. Conformationally constrained derivatives of 2-methylidene 1,3-oxathiane *S*-oxides allow the quantification of stereoelectronic effects. Suitable substrates were prepared by oxidation of 2-hydroxymethyl-1,3-oxathianes and pyrolysis of the respective xanthogenates. Nucleophilic additions of ethyl thiolate, piperidine, and dimethyl malonate anion are over 100 times faster to axial sulfoxides than to the respective equatorial substrates. The oxathiane derivatives turned out to be about 1000 times less reactive than the respective 1,3-dithianes.

1. Introduction

Stereoelectronic effects have—together with charge, dipole, and steric effects—a significant influence on the structure, the physical properties, and the reactivity of chemical compounds.[1] We have investigated stereoelectronic interactions between anionic lone pairs at α-carbon atoms and S–C and S=O bonds in sulfides, sulfoxides, and sulfones.[2–4] Suitable substrates for the investigation of these effects turned out to be conformationally constrained dithianes due to their rigidity and the antiperiplanar orientation of bonds favoring possible stereoelectronic effects. In fact, a carbanion is best stabilized, when the lone pair is in an antiperiplanar orientation to an axial S=O bond of a sulfoxide. With NBO analysis we calculated that this interaction contributes with 111 kJ/mol to the total stabilization of the molecule.[3] In this context we investigated nucleophilic additions to vinyl sulfoxides derived from conformationally constrained 1,3-dithianes and found that the configuration of the sulfoxide has significant influence on selectivity and rate of the reaction. An axial S=O bond (as in **1**) leads to the preferential formation of an equatorially substituted product and the reaction is about 100 times faster than a reaction of the respective equatorial sulfoxide, where the selectivity is furthermore inverted toward an axially substituted product.[2] We reasoned that attack of the nucleophile from the top leads to an axial lone pair, perfectly stabilized by the antiperiplanar S=O bond. An attack from the bottom is preferred for the equatorial vinyl sulfoxide **2**; the equatorial lone pair is no longer stabilized by interaction with the S=O bond but benefits from a stereoelectronic effect with both of the S–C bonds (Scheme 1). These $n_C \rightarrow \sigma^*_{S-C}$ stereoelectronic effects contribute with 2×44.6 kJ/mol, which is thus of similar magnitude and of conflictive influence as the above mentioned $n_C \rightarrow \sigma^*_{S-O}$ interaction in axial sulfoxides (111 kJ/mol). To allow for a better analysis of the



Scheme 1. Nucleophilic addition to vinyl sulfoxides derived from dithianes.[2]

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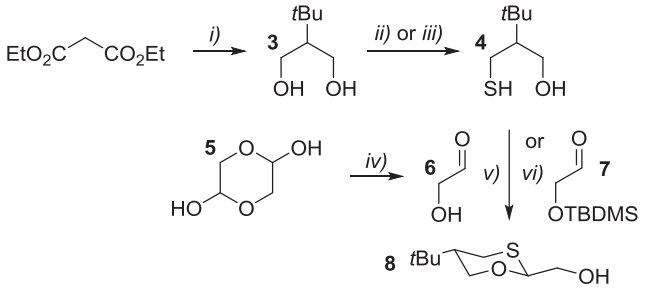
stereoelectronic effects we planned to investigate related reactions in sulfoxides derived from thianes or oxathianes. Here the competing $n_C \rightarrow \sigma^*_{S-C}$ interaction occurs only once; the related $n_C \rightarrow \sigma^*_{O-C}$ effect should be significantly smaller.

In this manuscript we present the synthesis of conformationally constrained 2-methylene 1,3-oxathiane *S*-oxides and their application in nucleophilic additions to investigate stereoelectronic and other effects.

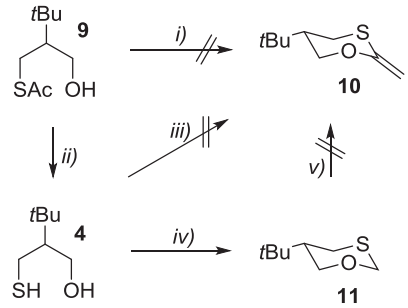
2. Synthesis of methylidene oxathiane *S*-oxides

A fixed conformation in six-membered rings avoiding a ring flip is usually achieved either by *tert*-butyl or by dimethyl substitution.[5] From a synthetic point of view we considered it advantageous to prepare 5-*tert*-butyl-1,3-oxathianes instead of the respective *cis*-4,6-dimethyl derivative (Scheme 2). Condensation of diethyl malonate with acetone in the presence of acetic anhydride and zinc chloride, conjugate addition of a methyl cuprate prepared from methyl magnesium bromide with copper(I) chloride,[6] and reduction with lithium aluminum hydride[7] yielded diol **3** with 31% yield. A published procedure[8] including benzylation, mesylation, S_N2 reaction with benzyl mercaptane, and debenzylation using Birch conditions furnished thiol **4** in a total yield of 22%. An alternate route consisting of tosylation, substitution with thioacetate, and hydrolysis of the thioester with methanolic hydrogen chloride gave a superior 34% yield.[9]



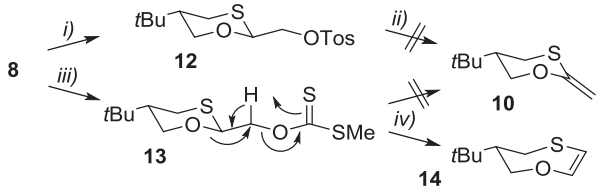
Scheme 2. Reaction conditions: (i) (a) acetone, $ZnCl_2$, Ac_2O, Δ (50%), (b) MeI, Mg, Et_2O, then CuCl (93%), (c) $LiAlH_4$, Et_2O (66%); (ii) (a) BnBr, NaH, THF, (b) MsCl, pyridine, CH_2Cl_2, (c) BnSH, NaH, DMF, (d) Na, NH_3(l), Et_2O (22%, four steps); (iii) (a) TsCl, pyridine, CH_2Cl_2, 0 °C to rt, 12 h (75%),[7] (b) KSAc, DMF, 80 °C, 40 min (45%), (c) HCl/MeOH, Δ, 4 h, (quant.); (iv) HCl/MeOH, rt, 12 h; (v) $BF_3{\cdot}OEt_2$, CH_2Cl_2, Δ (81%); (vi) $BF_3{\cdot}OEt_2$, CH_2Cl_2, Δ (70%).

We tested a direct approach toward the methylene oxathiane **10** (Scheme 3), which had been successful in the preparation of the respective dithiane derivatives.[2] Nevertheless, reaction of hydroxythiol **4** with acetyl chloride in the presence of perchloric acid and subsequent elimination with triethylamine[10] did not furnish the desired alkene **10**, which was detected only in trace amounts. Dehydration of the *S*-acetyl hydroxythiol **9** toward methylene oxathiane **10** could neither be achieved with trimethylaluminium,[11] borontrifluoride etherate, or titanium tetrachloride, nor with sodium hydride in the presence of borontrifluoride etherate. To take advantage of the higher nucleophilicity of sulfur we tried to synthesize the isomeric *O*-acetyl hydroxythiol: Nevertheless, disulfide formation from hydroxythiol with oxidative conditions,[12] O-acetylation, and reductive cleavage[13] of the disulfide function yielded the transacetylated,[14] i.e., the *S*-acetyl hydroxythiol **9**. 5-*tert*-Butyl-1,3-oxathiane **11** could be obtained from hydroxythiol **4** in quantitative yield by acetal formation with dimethoxymethane. We tested methylenation with various protocols including Peterson olefination,[15] Horner–Wadsworth–Emmons reaction,[16] or reaction with the Eschenmoser salt[17] (with an intended subsequent Hofmann elimination[18]). While deprotonation of oxathiane **11** with butyl lithium led to the lithiated substrate, neither of the performed further reactions was successful in the preparation of methylene derivative **10**.



Scheme 3. Reaction conditions: (i) various basic and Lewis-acidic conditions (see text); (ii) HCl/MeOH, Δ, 4 h, (quant.); (iii) AcCl, $HClO_4$, then Et_3N; (iv) $CH_2(OMe)_2$, $BF_3{\cdot}OEt_2$, Δ, 30 min (quant.); (v) various protocols.

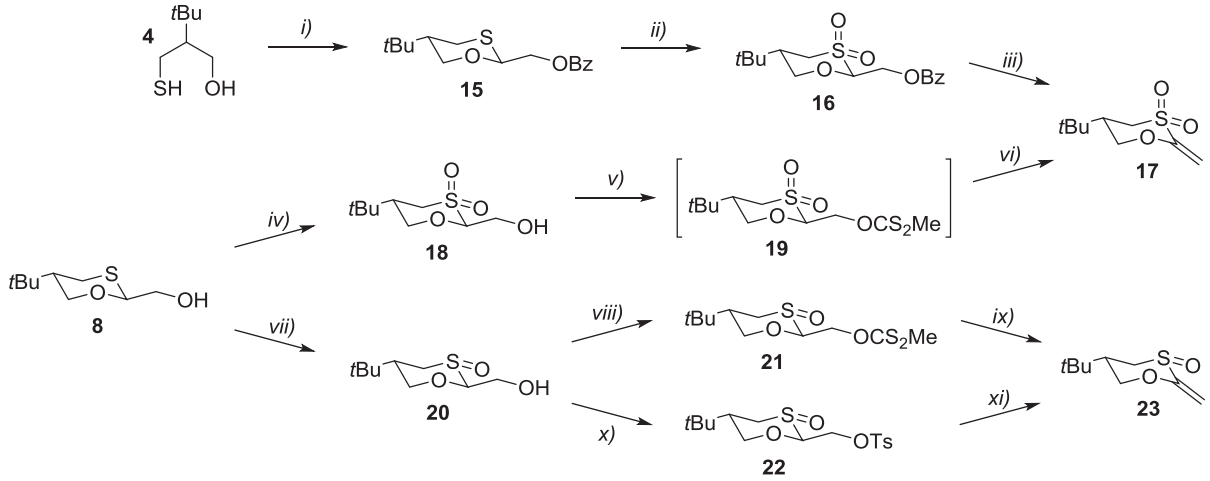
We thus aimed for a hydroxymethyl-substituted oxathiane **8** suitable for elimination. This derivative was easily prepared either by using in situ-prepared glycolaldehyde (**6**) for the acetal formation or by reaction with a silyl-protected glycolaldehyde **7** (Scheme 2). Both protocols furnished the product in good yields. For the elimination we considered a Chugaev reaction,[19] in which methyl xanthogenate **13** was pyrolyzed at 450 °C (Scheme 4). Nevertheless instead of methylene oxathiane **10** we isolated a rearranged oxathiepine **14** (35%). This is presumably formed in a concerted reaction with elimination of *S*-methyl dithiocarbonate and migration of either the S–C or the O–C (depicted) bond to the exocyclic carbon. A two-step mechanism either involving (hardly stabilized) carbene or carbenium species is possible but seems to be not very likely. Basic elimination of tosylate **12** at 180 °C was neither possible; decomposition of the material occurred.



Scheme 4. (i) TosCl, pyridine, CH_2Cl_2, 0 °C to rt (97%); (ii) KOH, triethylene glycol, 180 °C (decomp.); (iii) (a) NaH, THF, 0 °C, (b) CS_2, 60 °C, 5 h, (c) MeI, rt, 1 h (82%, three steps); (iv) pyrolysis, 450 °C (35%).

However, we were successful in preparing the methylene oxathianes by first oxidizing the sulfur to sulfoxides or sulfones, transferring the hydroxyl function into a leaving group, and subsequent elimination (Scheme 5). Sulfone **18**[20] could be obtained by oxidation with oxone at room temperature, while performing the reaction at 0 °C with a short reaction time furnished the respective equatorial sulfoxide **20**. A sulfone function (in **16**) could alternatively be prepared by oxidation of the benzoyl-protected oxathiane **15** with sodium periodate and then with potassium permanganate. Elimination was either achieved by Chugaev reaction of xanthogenates **19** or **21** or by elimination of tosylate **22** or benzoate **16**. The configuration of the equatorial sulfoxide was unambiguously elucidated by X-ray crystallographic analysis of tosylate **22** (Fig. 1).[20]

The axial vinyl sulfoxide **25** was synthesized in quantitative yield by elimination of tosylate **26** (not depicted) in analogy to the elimination of **22**, which furnished the equatorial vinyl sulfoxide **23** (Schemes 5 and 6). Nevertheless, no clean method could be developed for the synthesis of the axial sulfoxide **25**. Oxidation of alcohol **8** with various oxidation protocols including *tert*-butyl hydroperoxide,[21] hydrogen peroxide,[22,23] *meta*-chloroperbenzoic acid (*m*CPBA), and cumene hydroperoxide led to various amounts of



Scheme 5. (i) $BzOCH_2CHO$, TMSCl, Δ, 30 min (44%); (ii) (a) $NaIO_4$, THF/H_2O, rt, 23 h (77%), (b) $KMnO_4$, acetone/H_2O, 3 d (44%); (iii) DBU, *t*BuOH/CH_2Cl_2, rt (25%); (iv) oxone, THF/H_2O, rt (90%); (v) (a) NaH, THF, 0 °C, (b) CS_2, 60 °C, 5 h, (c) MeI, rt, 1 h; (vi) spontaneously (57% from **18**); (vii) oxone, THF/H_2O, 0 °C (66%); (viii) as in (v) (52%); (ix) NaH, THF, rt, 1 h (53%); (x) TsCl, Et_3N, CH_2Cl_2, rt, 24 h; (xi) as in (ix) (quant., two steps).

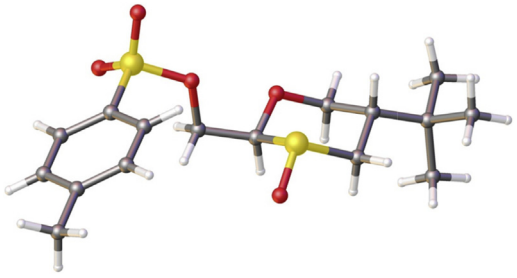
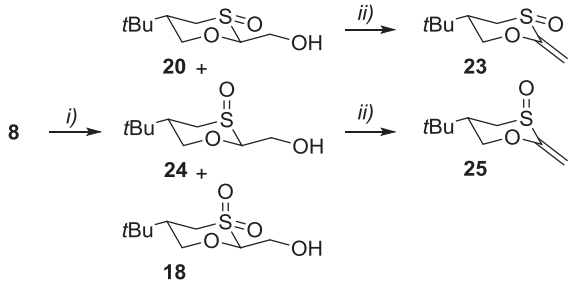


Fig. 1. Structure of **22** in the crystal.[20]



Scheme 6. (i) Conditions given in Table 1, separation; (ii) (a) TsCl, pyridine, CH_2Cl_2, rt, 12 h (→**26**), (b) NaH, THF, Δ, 12 h (quant., two steps).

equatorial and axial sulfoxides **20** and **24** together with sulfone **18** (Table 1). Best results were obtained with *tert*-butyl hydroperoxide together with titanium tetra(isopropoxide),[24] where an over-oxidation was avoided by utilization of only 0.5 equiv of the oxidant (entry 8). The sulfoxides could easily be separated by column chromatography. The configuration of **25** was determined by crystallographic analysis (Fig. 2).[20]

Table 1
Synthesis of methylidene oxathiane *S*-oxides (Scheme 6)

#	Conditions (equiv)	Products (%)
1	*t*BuOOH (1), CH_2Cl_2, rt, 2 d[21]	Undefined products
2	H_2O_2 (2), TMSCl (1), MeCN, rt, 2 h[22]	**20** (Traces)[a]
3	*m*CPBA (1), CH_2Cl_2, rt, 12 h[21]	**20**[a]
4	H_2O_2 (1), VCl_3 (0.05) THF, 0 °C, 5 min[23]	**20** (40), **18**[a]
5	Cumene hydroperoxide (1), $Ti(OiPr)_4$ (1) CH_2Cl_2, rt, 24 h	**18** (57)
6	*t*BuOOH (1), $Ti(OiPr)_4$ (1), CH_2Cl_2, 0 °C to rt, 18 h[24]	**18**[a]
7	*t*BuOOH (0.9), $Ti(OiPr)_4$ (1), CH_2Cl_2, 0 °C to rt, 12 h[24]	**20**/**24** (14), **18** (41)
8	*t*BuOOH (0.5), $Ti(OiPr)_4$ (1), CH_2Cl_2, −78 °C to rt, 12 h[24]	**20** (21), **24** (21)

[a] Not isolated. Detection by TLC.

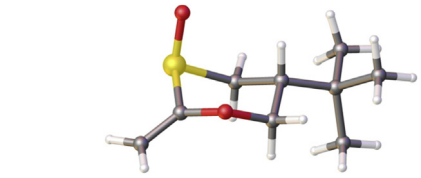
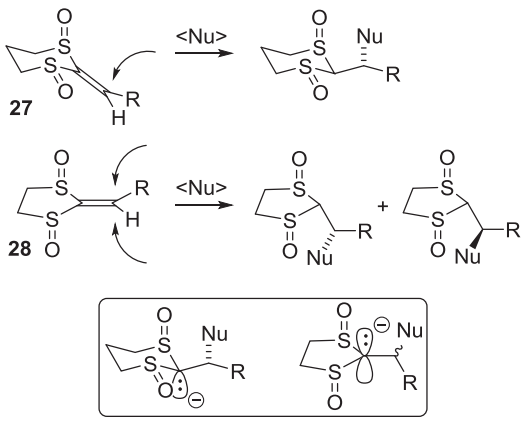


Fig. 2. Structure of **25** in the crystal.[20]

3. Nucleophilic additions to methylidene oxathiane *S*-oxides

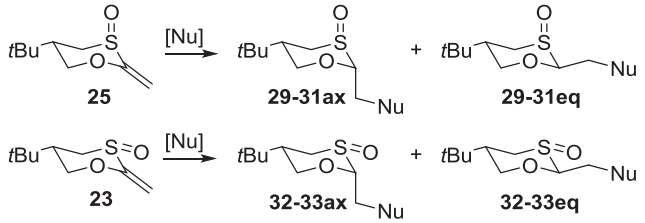
In prior work, we tested nucleophilic additions to vinyl sulfoxides and sulfones with different configurations and a variety of heteroatom patterns. Additions of enolates and other nucleophiles to alkylidene bissulfoxides **27** derived from 1,3-dithiane (one S=O bond equatorial, one axial) proceed slowly and with selectivities about 95:5 (Scheme 7).[25] Similar additions to 1,3-dithiolane-derived substrates **28** are significantly faster but show hardly any selectivity.[26] Here a stabilized carbanion is formed during the attack irrespective whether the nucleophile approaches from the top or the bottom of the molecule.



Scheme 7. Nucleophilic additions to alkylidene bissulfoxides.

When similar reactions were performed with conformationally constrained alkylidene dithiane monoxides, the rate of the nucleophilic attacks was not high[2] and selectivities were only moderate. The latter seemed to be due to a competing effect of different stereoelectronic interactions ($n_C \rightarrow \sigma^*_{S-C}$ vs $n_C \rightarrow \sigma^*_{S-O}$).

Significantly different results were obtained in nucleophilic additions to the corresponding oxathiane derivatives **23** and **25**. Results for a variety of additions are given in Scheme 8 and Table 2. Addition of sulfur, oxygen, and nitrogen nucleophiles (entries 1–5) exclusively yielded adducts with an equatorial substituent in position C-2. This supports the reasoning that the absence of one competing $n_C \rightarrow \sigma^*_{S-C}$ interaction puts forward other effects and favors an axial lone pair at C-2 (giving rise to equatorially substituted products). Yield and reaction rates were higher with good nucleophiles like ethanethiolate, piperidine (entries 1 and 3), but these criteria were especially influenced by the acceptors' configuration. The axial monosulfoxide reacted significantly faster than its equatorial analog (vide infra) and yields turned out to be significantly higher. Addition of the dimethyl malonate anion led to a mixture of both diastereoisomers with a slight preference for the axial product **31ax** (entry 6). A similar deviation with this nucleophile had already been observed with the corresponding dithiane analogs.[2b] Thermodynamic effects might be relevant in this case, but an unambiguous explanation for this observation is still missing. No reaction occurred, when equatorial sulfoxide **23** was reacted with the malonate anion (entry 7). Here a low nucleophilicity comes along with a significantly smaller reactivity of the equatorial sulfoxide.



Scheme 8. Nucleophilic additions to methylidene oxathiane *S*-oxides.

Table 2
Nucleophilic additions to methylidene oxathiane *S*-oxides

#	Sulfoxide	Nucleophile	Product	Yield [%]	Ratio
1	**25**	EtSH, NaH	**29eq**	86	0:100
2	**23**	EtSH, NaH	**32eq**	19	0:100
3	**25**	Piperidine	**30eq**	83	0:100
4	**23**	Piperidine		—[b]	
5	**23**	MeOH, NaH[a]	**33eq**	8	0:100
6	**25**	Dimethyl malonate, NaH	**31ax**/**31eq**	25	70:30
7	**23**	Dimethyl malonate, NaH		—[b]	

[a] **33eq** was obtained as a side product of entry 2.
[b] No conversion.

To allow for the comparison with dithiane derivatives we performed kinetic investigations and determined reaction rates for the addition of ethanethiol and piperidine. It already had turned out that the addition to 2-methylidene 1,3-oxathiane *S*-oxides is slower than addition to the respective dithianes; a quantitative determination of reaction rates in the addition of ethanethiol and piperidine, respectively, was possible with the help of ^{1}H NMR spectroscopy, where the conversion was monitored by integration of the vinylic signals. The analysis was made assuming a second order reaction, where details of the method had been described earlier.[2] A higher order reaction (e.g., with more than 1 equiv of the piperidine cannot be excluded, but would not alter the general validity of our analysis). Because of the low reactivity and thus too much side reactions, reaction rates of other addition reactions could not be determined properly (e.g., **23** with piperidine, **25** with the dimethyl malonate anion). It turned out that the addition of ethanethiolate to the axial vinyl sulfoxide **25** is over 100 times faster than that to the equatorial sulfoxide **23** (Table 3, entries 1 and 2). This is in line with our assumption that the intermediately formed carbanion is significantly stabilized by an $n_C \rightarrow \sigma^*_{S-O}$ interaction only possible in sulfoxide **29eq**. The addition of piperidine to 2-methylidene 1,3-oxathianes is about 1000 times slower than addition to the respective 1,3-dithiane derivatives (entries 3 and 4). The special ability of sulfur atoms to stabilize negative charges in α-position is well-known from various investigations.[27]

Table 3
Reaction rates[a]

#	Sulfoxide	Nucleophile	Time	Yield [%]	k [L mol^{-1} s^{-1}]
1	**25**	EtSH, NaH	6.5 h	85	1.8×10^{-4}
2	**23**	EtSH, NaH	27 d	50	1.3×10^{-6}
3	**25**	Piperidine	20 d	45	1.0×10^{-6}
4	**1**	Piperidine	5.5 h	62	1.0×10^{-3}
5	**2**	Piperidine	26 h	67	1.0×10^{-5}

[a] All reactions were performed in dimethyl sulfoxide-d_6 at room temperature.

4. Conclusion

Conformationally constrained 2-methylene 1,3-oxathiane *S*-oxides are suitable substrates for a nucleophilic addition of S-, N, and C-nucleophiles. It turned out that sulfoxides with an axial S—O bond are over 100 times more reactive than the respective equatorially oriented sulfoxides. Oxathianes are about 1000 times less reactive than the respective 1,3-dithiane derivatives.

5. Experimental section

5.1. General

Abbreviations: *m*CPBA, *meta*-chloroperbenzoic acid; NBO, natural bond orbital; TBDMS, *tert*-butyl-dimethylsilyl; DBU, 1,8-diazabicyclo[5.4.0]undec-7-en; Tos, *para*-toluenesulfonyl. Anhydrous solvents were used as purchased. All moisture-sensitive reactions were carried out under oxygen-free argon using oven-dried glassware and a vacuum line. Flash column chromatography[28] was carried out using Merck silica gel 60 (230–400 mesh) and thin layer chromatography (TLC) was carried out using commercially available Merck F_{254} pre-coated sheets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance AV 300, an AV-400 or a DRX 500. Chemical shifts are given in parts per million down field of tetramethylsilane. ^{13}C NMR spectra were recorded with broad band proton decoupling and were assigned using DEPT 135 and DEPT 90 experiments. IR spectra were recorded on a Bruker IFS-88 spectrometer. Electrical ionization and high-resolution mass spectra were recorded on a Finnigan MAT-95.

5.2. *S*-[2-(Hydroxymethyl)-3,3-dimethylbutyl] ethanethioate (9)

Potassium thioacetate (3.64 g, 31.8 mmol) was added to a solution of 2-(hydroxymethyl)-3-3-dimethylbutyl 4-methylbenzenesulfonate (7.60 g, 26.5 mmol) in DMF (20 mL) and the mixture was stirred for 40 min at 80 °C, cooled to rt, and concentrated. The precipitate was suspended with EtOAc and filtered. The filtrate was concentrated and purified by column chromatography (silica gel, cyclohexane/EtOAc, 20:1→10:1) to yield thioester **9** (2.27 g, 11.9 mmol, 45%) as yellow evil-smelling oil. R_f=0.52 (cyclohexane/

EtOAc, 2:1); IR (film): $\tilde{\nu}$ (cm^{-1})=3489 (m), 2961 (s), 1739 (s), 1690 (m), 1473 (m), 1367 (m), 1243 (s), 1040 (m), 960 (w), 634 (w); ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 9H, *t*Bu), 1.42 (dd, ^3J 8.1, 8.1 Hz, 1H, OH), 1.50 (dddd, ^3J 3.2, 4.6, 4.6, 7.8 Hz, 1H, CH), 2.02 (s, 3H, CH_3), 2.44 (ddd, ^3J 8.3, 9.6 Hz, ^2J 13.5 Hz, 1H, SCH_2), 2.74 (ddd, ^3J 3.2, 8.0 Hz, ^2J 13.5 Hz, 1H, SCH_2), 4.17 (dd, ^3J 4.7 Hz, ^2J 11.6 Hz, 1H, OCH_2), 4.36 (dd, ^3J 4.4 Hz, ^2J 11.6 Hz, 1H, OCH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0 (s), 22.6 (d), 28.1 (s), 33.3 (q), 51.1 (t), 63.0 (d), 170.9 (q); *m*/*z* (EI) 190 (M^+); HRMS (EI): M^+, found 190.1027. $C_9H_{18}O_2S$ requires 190.1028.

5.3. 2-(Mercaptomethyl)-3,3-dimethylbutan-1-ol (4)

HCl (1.4 M, 2 mL AcCl in 20 mL MeOH) was added to thioester **9** (2.27 g, 11.9 mmol) and the mixture was heated to reflux for 4 h, cooled to rt, and concentrated to yield thiol **4** (1.76 g, quant.) as a yellowish oil, which was used without further purification. ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (s, 9H, *t*Bu), 1.38 (m, 1H, 2-H), 1.49 (dd, ^3J 7.1, 8.9 Hz, 1H, SH), 2.10 (m, 1H, OH), 2.50 (ddd, ^3J 8.8, 9.8 Hz, ^2J 13.3 Hz, 1H, 1-H), 2.84 (ddd, ^3J 3.5, 7.0 Hz, ^2J 13.4 Hz, 1H, 1-H), 3.74 (dd, ^3J 5.6 Hz, ^2J 11.4 Hz, 1H, 3-H), 3.92 (ddd, ^3J 0.6, 3.8 Hz, ^2J 11.4 Hz, 1H, 3-H).

5.4. (*S*)-5-*tert*-Butyl-1,3-oxathiane (11)

A solution of thiol **4** (1.56 g, 10.5 mmol) in $CHCl_3$ (5 mL) was added dropwise via the reflux condenser to a boiling solution of $CH_2(OMe)_2$ (800 g, 10.5 mmol) and $BF_3{\cdot}OEt_2$ (2,66 mL, 21.0 mmol) in $CHCl_3$ (20 mL). The mixture was cooled and saturated aqueous $NaHCO_3$ solution (10 mL) was added. The organic layer was extracted with CH_2Cl_2 (3×5 mL) and the combined organic layers were dried (Na_2SO_4), concentrated to yield oxathiane **11** (1.70 g, 10.6 mmol, quant.) as a yellowish oil, which was used without further purification. R_f=0.30 (cyclohexane/EtOAc, 5:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=2955 (m), 2872 (w), 1736 (m), 1467 (m), 1365 (m), 1229 (m), 1033 (s), 918 (w), 736 (w); ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (s, 9H, *t*Bu), 1.74 (m, 1H, 5-H), 2.75 (dd, ^3J 11.9 Hz, ^2J 11.9 Hz, 1H, 6-H_{ax}), 2.78 (m, 1H, 6-H_{eq}), 3.32 (dd, ^3J 11.2 Hz, ^2J 11.6 Hz, 1H, 4-H_{ax}), 4.20 (dddd, ^4J 0.6, 1.6 Hz, ^3J 3.4 Hz, ^2J 11.6 Hz, 1H, 4-H_{eq}), 4.70 (d, ^2J 10.9 Hz, 1H, 2-H), 4.76 (ddd, ^4J 0.6, 1.6 Hz, ^2J 10.8 Hz, 1H, 2-H_{eq}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2 (s), 28.7 (t), 32.3 (q), 45.5 (d), 70.8 (d), 71.7 (d). The substance was too volatile for mass spectrometry.

5.5. (2*S*,5*S*)-(5-*tert*-Butyl-1,3-oxathian-2-yl)methanol (8)

A solution of thiol **4** (865 mg, 5.83 mmol) and TBDMSO-acetaldehyde (90%, 1.13 g, 5.83 mmol) in CH_2Cl_2 (8 mL) was added dropwise via the reflux condenser to a solution of $BF_3{\cdot}OEt_2$ (1.48 mL, 11.7 mmol) in CH_2Cl_2 (40 mL). Stirring was continued for further 10 min and saturated aqueous $NaHCO_3$ solution (20 mL) was added. The organic layer was extracted with EtOAc (3×15 mL) and the combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography (silica gel, cyclohexane/EtOAc, 5:1) to yield oxathiane **8** (784 mg, 4.11 mmol, 70%) as colorless oil, which solidified after a while.

Alternative preparation: Glycolaldehyde dimer (260 mg, 2.16 mmol) was added to a solution of acetyl chloride (1 mL) in MeOH (10 mL) and the mixture was stirred at rt overnight, concentrated, and dissolved in CH_2Cl_2 (15 mL). A solution of thiol **4** (520 mg, 3.51 mmol) and $BF_3{\cdot}OEt_2$ (0.89 mL, 7.01 mmol) in CH_2Cl_2 (3 mL) was added dropwise via a reflux condenser. Stirring was continued for further 10 min. Work-up was performed according to the protocol described above (519 mg, 2.73 mmol, 81%). R_f=0.42 (cyclohexane/EtOAc, 2:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=3227 (w), 2957 (m), 1469 (w), 1365 (m), 1256 (w), 1080 (m), 1033 (s), 995 (w), 840 (w), 776 (s). ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (s, 9H, *t*Bu), 1.68 (dddd, ^3J 3.4, 5.9, 8.2, 8.2 Hz, 1H, 5-H), 2.26 (br s, 1H, OH), 2.82 (m, 1H, 6-H), 2.84 (m, 1H, 6-H), 3.41 (t, ^3J 11.5 Hz, 1H, 2-H), 3.70 (dd, ^2J 1.0 Hz, ^3J 3.3 Hz, 1H, 4-H), 3.71 (m, 1H, 4-H), 4.28 (dd, ^2J 4.0 Hz, ^3J 11.6 Hz, 1H, 1′-H), 4.79 (dd, ^2J 4.0 Hz, ^3J 6.0 Hz, 1H, 1′-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3 (s), 28.7 (d), 32.1 (q), 44.9 (t), 64.8 (d), 71.8 (d), 83.0 (t); *m*/*z* (FAB) 191 (MH^+); HRMS (FAB): MH^+, found 191.1098. $C_9H_{19}O_2S$ requires 191.1100.

5.6. (2*S*,5*S*)-(5-*tert*-Butyl-1,3-oxathian-2-yl)methyl 4-methylbenzenesulfonate (12)

Et_3N (1 mL) and TosCl (392 mg, 2.06 mmol) were added to a solution of alcohol **8** (356 mg, 1.87 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred for 24 h at rt. H_2O (5 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3×3 mL). The combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography (silica gel, cyclohexane/EtOAc, 2:1) to yield tosylate **12** (628 mg, 1.82 mmol, 97%) as a colorless solid. R_f=0.60 (cyclohexane/EtOAc, 2:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=2952 (w), 2867 (w), 1367 (m), 1188 (s), 1083 (s), 1005 (s), 812 (m), 784 (m), 663 (m), 552 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (s, 9H, *t*Bu), 1.62 (m, 1H, 5-H), 2.45 (s, 3H, ArCH_3), 2.81 (m, 2H), 3.32 (dd, *J* 11.2, 11.8 Hz, 1H), 4.09 (m, 2H), 4.21 (ddd, ^4J 1.7 Hz, ^3J 3.3 Hz, ^2J 11.8 Hz, 1H), 4.90 (dd, ^4J 3.8 Hz, ^3J 6.7 Hz, 1H, 2-H), 7.34 (d, ^3J 8.3 Hz, 2H, Ar), 7.80 (d, ^3J 8.3 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 (s), 27.3 (s), 29.0 (d), 32.1 (q), 44.3 (t), 70.6 (d), 71.7 (d), 79.7 (t), 128.1 (t), 129.8 (t), 132.7 (q), 144.9 (q); *m*/*z* (EI) 344 (M^+); HRMS (EI): M^+, found 344.1113. $C_{16}H_{24}O_4S_2$ requires 344.1111.

5.7. (2*S*,5*S*)-*O*-[(5-*tert*-Butyl-1,3-oxathian-2-yl)methyl] *S*-methyl carbonodithioate (13)

A solution of alcohol **8** (1.61 g, 8.46 mmol) in THF (10 mL) was added dropwise at 0 °C to a suspension of NaH (305 mg, 12.7 mmol) in THF (15 mL). CS_2 (2.55 mL, 42.3 mmol) was added and the mixture was heated to 60 °C for 5 h and cooled to rt. MeI (3.16 mL, 50.8 mmol) was added and stirring was continued for 1 h. The reaction was stopped by addition of saturated aqueous NH_4Cl solution (5 mL), the aqueous layer was extracted with EtOAc (3×10 mL), and the combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography (silica gel, cyclohexane/EtOAc, 10:1) to yield xanthogenate **13** (1.95 g, 7.00 mmol, 82%) as dark yellow evil-smelling oil. R_f=0.69 (cyclohexane/EtOAc, 10:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=2957 (m), 2868 (w), 1647 (w), 1366 (w), 1078 (s), 865 (m), 698 (w); ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 9H, *t*Bu), 1.70 (m, 1H, 5-H), 2.56 (s, 3H, SCH_3), 2.85 (m, 2H), 2.75 (s, 1H), 3.42 (t, ^2J 11.5 Hz, 1H), 4.29 (m, 1H), 4.71 (d, ^3J 5.1 Hz, 2H, 1′-H), 5.08 (t, ^3J 5.1 Hz, 1H, 2-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2 (s), 27.3 (s), 29.0 (d), 32.1 (q), 44.4 (t), 71.9 (d), 73.8 (d), 79.7 (t), 215.5 (q); *m*/*z* (EI) 280 (M^+); HRMS (EI): M^+, found 280.0622. $C_{11}H_{20}O_2S_3$ requires 280.0620.

5.8. 6-*tert*-Butyl-6,7-dihydro-5*H*-1,4-oxathiepine (14)

Xanthogenate **13** (3.11 g, 11.1 mmol) was pyrolyzed at 450 °C in vacuo in a pyrolysis apparatus. Purification by column chromatography (silica gel, cyclohexane/EtOAc, 20:1) to yield olefin **14** (663 mg, 3.85 mmol, 35%) as smelly yellow oil. The xanthogenate could partially be recovered. R_f=0.84 (cyclohexane/EtOAc, 10:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=2958 (m), 2867 (w), 1601 (s), 1468 (w), 1366 (w), 1266 (m), 1231 (m), 1081 (s), 876 (m), 719 (m), 471 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 9H, *t*Bu), 1.85 (m, 1H, 5-H), 2.98 (tdd, ^4J 1.0 Hz, ^3J 5.8 Hz, ^2J 13.9 Hz, 1H, 6-H_{eq}), 3.30 (dd, ^3J 9.8 Hz, ^2J 14.0 Hz, 1H, 6-H_{ax}), 4.29 (ddd, ^4J 1.0 Hz, ^3J 3.3 Hz, ^2J 12.6 Hz, 1H, 4-H_{eq}), 4.79 (dd, ^3J 4.7 Hz, ^2J 12.7 Hz, 1H, 4-H_{ax}), 4.97 (ddd, ^4J 0.9, 0.9 Hz, ^3J 6.2 Hz, 1H, 2-H), 6.37 (d, ^3J 6.3 Hz, 1H, 3-H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 27.9 (s), 33.2 (q), 33.6 (t), 49.8 (d), 71.7 (d), 99.6 (t), 146.6 (t); *m*/*z* (EI) 172 (M^+); HRMS (EI): MH^+, found 172.0916. $C_9H_{16}OS$ requires 172.0916.

5.9. (2*S*,5*S*)-5-*tert*-Butyl-2-(hydroxymethyl)-1,3-oxathiane 3,3-dioxide (18)

Oxone (3.73 g, 6.07 mmol) was added to a solution of alcohol **8** (519 mg, 2.73 mmol) in THF/H_2O (1:1, 20 mL) and the mixture was stirred for 18 h at rt and filtered. The filtrate was concentrated to remove most of the THF and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL) and the combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography (silica gel, CH_2Cl_2/acetone, 5:1) to yield sulfone **18** (507 mg, 2.28 mmol, 90%) as a colorless solid. R_f=0.50 (CH_2Cl_2/acetone, 5:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=3304 (w), 2959 (w), 2877 (w), 1300 (s), 1098 (s), 870 (m), 519 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (s, 9H, *t*Bu), 2.38 (dddd, ^3J 3.3, 3.3, 11.2, 13.0 Hz, 1H, 5-H), 2.95 (dd, ^3J 12.9 Hz, ^2J 13.9 Hz, 1H, 4-H_{ax} or 6-H_{ax}), 3.27 (ddd, ^4J 2.2 Hz, ^3J 3.1 Hz, ^2J 13.8 Hz, 1H, 4-H_{eq} or 6-H_{eq}), 3.54 (dd, ^3J 11.1 Hz, ^2J 12.1 Hz, 1H, 6-H_{ax} or 4-H_{ax}), 4.06 (dd, ^3J 5.8 Hz, ^2J 12.7 Hz, 1H, 1′-H), 4.14 (dd, ^3J 4.1 Hz, *J* 12.7 Hz, 1H, 1-H′), 4.36 (ddd, ^4J 2.2 Hz, ^3J 3.5 Hz, ^2J 12.0 Hz, 1H, 6-H_{eq} or 4-H_{eq}), 4.40 (dd, ^3J 4.1, 5.8 Hz, 1H, 2-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2 (s), 31.9 (q), 46.0 (t), 53.2 (d), 58.0 (d), 71.3 (d), 92.1 (t); *m*/*z* (FAB) 223 (MH^+); HRMS (FAB): MH^+, found 223.0997. $C_9H_{19}O_4S$ requires 223.0999.

5.10. (*S*)-5-*tert*-Butyl-2-methylene-1,3-oxathiane 3,3-dioxide (17)

Sulfone **18** (507 mg, 2.28 mmol) was converted into the xanthogenate according to the procedure given for **13**. The elimination occurred during work-up. Purification by column chromatography (silica gel, cyclohexane/EtOAc, 2:1) yielded vinyl sulfone **17** (264 mg, 1.29 mmol, 57%) as a colorless solid. R_f=0.75 (cyclohexane/EtOAc, 1:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=2964 (w), 1643 (m), 1297 (s), 1095 (s), 1037 (m), 910 (m), 851 (m), 506 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (s, 9H, *t*Bu), 2.55 (m, 1H, 5-H), 2.96 (dd, ^3J 12.7 Hz, ^2J 13.6 Hz, 1H, 4-H_{ax} or 6-H_{ax}), 3.34 (dddd, ^4J 0.8, 2.3 Hz, ^3J 3.0 Hz, ^2J 13.7 Hz, 1H, 4-H_{eq} or 6-H_{eq}), 3.74 (dd, ^3J 11.4 Hz, ^2J 11.4 Hz, 1H, 6-H_{ax} or 4-H_{ax}), 4.44 (ddd, ^4J 2.2 Hz, ^3J 3.6 Hz, ^2J 11.5 Hz, 1H, 6-H_{eq} or 4-H_{eq}), 5.27 (d, ^2J 2.8 Hz, 1H), 5.63 (d, ^2J 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2 (s), 32.0 (q), 45.6 (t), 53.2 (d), 73.5 (d), 103.1 (d), 158.1 (q); *m*/*z* (FAB) 205 (MH^+); HRMS (FAB): MH^+, found 205.0891. $C_9H_{17}O_3S$ requires 205.083.

5.11. (2*S*,3*S*,5*S*)- and (2*S*,3*R*,5*S*)-5-*tert*-Butyl-2-(hydroxymethyl)-1,3-oxathiane 3-oxide (20 and 24)

Oxone (315 mg, 0.51 mmol) was added at 0 °C to a solution of alcohol **72** (195 mg, 1.02 mmol) in THF/H_2O (1:1, 10 mL) and the mixture was stirred at rt for 1 h and filtered. The filtrate was concentrated to remove most of the THF and the aqueous layer was extracted with CH_2Cl_2 (3×8 mL) and the combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography (silica gel, CH_2Cl_2/acetone, 3:2) to yield sulfoxide **20** (135 mg, 0.65 mmol, 64%) as a colorless solid.

Alternative protocol: Ti(O*i*Pr)$_4$ (909 μL, 3.04 mmol) was added under Ar to a solution of alcohol **8** (578 mg, 3.04 mmol) in CH_2Cl_2 (10 mL). After 10 min the solution was cooled to −78 °C and *t*BuOOH (6 M, 254 μL, 1.52 mmol) was added dropwise within 10 min. The mixture was allowed to warm to rt within 2 h and H_2O (5 mL) was added. After vigorous stirring for 5 min, the mixture was filtered and the aqueous layer of the filtrate was extracted with CH_2Cl_2 (2×3 mL). The combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography (silica gel, CH_2Cl_2/acetone, 3:2) to yield a mixture of sulfoxides **20** and **24** (1:1.1, 266 mg, 1.29 mmol, 42%), which could not be separated. Not converted alcohol was recovered. Both isomers: R_f=0.30 (CH_2Cl_2/acetone, 2:1). *Compound* **20**: IR (ATR): $\tilde{\nu}$ (cm^{-1})=3324 (w), 2956 (w), 2868 (w), 1366 (w), 1082 (m), 1010 (s), 607 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 9H, *t*Bu), 1.83 (dddd, ^3J 2.4, 3.9, 11.2, 12.9 Hz, 1H, 5-H), 2.59 (dd, ^2J 11.8 Hz, ^3J 12.7 Hz, 1H, 6-H_{ax}), 3.48 (dd, ^3J 11.3 Hz, ^2J 11.3 Hz, 1H, 4-H_{ax}), 3.67 (ddd, ^4J 2.3 Hz, ^3J 2.3 Hz, ^2J 11.6 Hz, 1H, 6-H_{eq}), 4.06 (dd, ^3J 3.7 Hz, 1H, 2-H), 4.12 (d, ^3J 3.7 Hz, 2H, 1′-H), 4.20 (ddd, ^4J 2.1 Hz, ^3J 3.9 Hz, ^2J 11.5 Hz, 1H, 4-H_{eq}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5 (s), 32.1 (q), 44.7 (d), 52.3 (t), 60.4 (t), 71.5 (t), 97.3 (d); *m*/*z* (EI) 206 (M^+); HRMS (EI): M^+, found 206.0970. $C_9H_{18}O_3S$ requires 206.0971.

5.12. (2*S*,3*S*,5*S*)-*O*-[(5-*tert*-Butyl-3-oxido-1,3-oxathian-2-yl)-methyl] *S*-methyl carbonodithioate (21)

Sulfoxide **20** (134 mg, 0.650 mmol) was reacted according to the procedure given for **13** to yield xanthogenate **21** (100 mg, 0.337 mmol, 52%) as a yellow oil. R_f=0.35 (cyclohexane/EtOAc, 1:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=2961 (w), 2871 (w), 1368 (m), 1201 (s), 1075 (s), 1036 (s), 729 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 9H, *t*Bu), 1.87 (dddd, ^3J 2.2, 3.8, 11.4, 11.4 Hz, 1H, 5-H), 2.58 (s, 3H, SCH_3), 2.60 (m, 1H, 6-H_{ax}), 3.49 (ddd, ^4J 1.6 Hz, ^3J 11.4 Hz, ^2J 11.5 Hz, 1H, 4-H_{ax}), 3.70 (ddd, ^4J 2.2 Hz, ^3J 2.2 Hz, ^2J 11.8 Hz, 1H, 6-H_{eq}), 4.21 (ddd, ^4J 1.9 Hz, ^3J 3.8 Hz, ^2J 11.5 Hz, 1H, 4-H_{eq}), 4.31 (dd, ^3J 1.9, 5.3 Hz, 1H, 2-H), 4.99 (dd, ^3J 5.4 Hz, ^2J 12.3 Hz, 1H, 1′-H), 5.13 (dd, ^3J 1.9 Hz, ^2J 12.2 Hz, 1H, 1′-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3 (s), 27.4 (s), 32.1 (q), 44.6 (t), 53.0 (d), 69.5 (d), 71.7 (d), 95.1 (t), 215.3 (q); *m*/*z* (FAB) 297 (MH^+); HRMS (FAB): MH^+, found 297.0647. $C_{11}H_{21}O_3S_3$ requires 297.0647.

5.13. (3*S*,5*S*)- and (3*R*,5*S*)-5-*tert*-Butyl-2-methylene-1,3-oxathiane 3-oxide (23 and 25)

(A) NaH (7.92 mg, 0.330 mmol) was added under Ar to a solution of xanthogenate **20** (98.0 mg, 0.330 mmol) in THF (10 mL). The suspension was heated to reflux for 1 h, cooled to rt, and saturated aqueous NH_4Cl solution was added. Most of the THF was removed at reduced pressure and the remnant was dissolved in CH_2Cl_2/H_2O (1:1, 10 mL). The aqueous layer was extracted with CH_2Cl_2 (3×5 mL), and the combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography (silica gel, cyclohexane/EtOAc, 2:1) yielding vinyl sulfoxide **23** (33 mg, 0.175 mmol, 53%) as a colorless solid.

(B) NaH (100 mg, 4.17 mmol) was added to a solution of tosylate **22** (1.05 g, 2.92 mmol) in THF (30 mL) and the suspension was heated to reflux for 12 h. Work-up as given under (A) yielded vinyl sulfoxide **23** (558 mg, 2.92 mmol, quant.) as a beige solid.

(C) A mixture of **22** and **25** (1:1, 1.64 g, 4.55 mmol) was reacted according to the protocol (A) to yield vinyl sulfoxides **23** (304 mg, 1.62 mmol, 36%) and **25** (294 mg, 1.56 mmol, 34%) as colorless solids. *Compound* **23**: R_f=0.44 (cyclohexane/EtOAc, 1:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=2962 (w), 2877 (w), 1637 (m), 1160 (m), 1047 (s), 897 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (s, 9H, *t*Bu), 2.01 (dddd, ^3J 3.3, 3.3, 11.6, 13.0 Hz, 1H, 5-H), 2.63 (dd, ^2J 11.3 Hz, ^3J 12.7 Hz, 1H, 4-H_{ax}), 3.56 (m, 1H, 4-H_{eq}), 3.59 (ddd, ^4J 1.0 Hz, ^3J 11.1 Hz, ^2J 11.1 Hz, 1H, 6-H_{ax}), 4.27 (ddd, ^4J 2.5 Hz, ^3J 3.7 Hz, ^2J 11.0 Hz, 1H, 6-H_{eq}), 5.27 (ddd, *J* 1.0, 1.0 Hz, ^2J 2.6 Hz, 1H, =C$H_a$$H_b$), 5.34 (dd, *J* 1.0 Hz, ^2J 2.7 Hz, 1H, =C$H_a$$H_b$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4 (s), 32.2 (q), 44.5 (t), 53.5 (d), 73.9 (d), 99.7 (d), 164.2 (q); *m*/*z* (FAB) 189 [MH^+]; HRMS (FAB): MH^+, found 189.0945. $C_9H_{17}O_2S$ requires 189.0944. *Compound* **25**: R_f=0.23 (cyclohexane/EtOAc, 1:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=2964 (w) 2875 (w), 1622 (m), 1169 (m), 1034 (s), 893 (m), 563 (m), 452 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (s, 9H, *t*Bu), 2.63 (m, 2H), 3.21 (m, 1H), 3.80 (m, 1H), 4.45 (m, 1H), 5.10 (dd, ^4J 0.7 Hz, ^3J

2.1 Hz, 1H, =CH_aH$_b$), 5.13 (d, ^3J 2.0 Hz, 1H, =CH$_a$$H_b$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3 (s), 31.8 (q), 33.9 (t), 47.9 (d), 72.8 (d), 104.1 (d), 160.3 (q); *m*/*z* (FAB) 189 (MH^+); HRMS (FAB): MH^+, found 189.0946. $C_9H_{17}O_2S$ requires 189.0944.

5.14. (2*S*,3*S*,5*S*)- and (2*S*,3*R*,5*S*)-(5-*tert*-Butyl-3-oxido-1,3-oxathian-2-yl)methyl 4-methylbenzenesulfonate (22 and 26)

Alcohols **20** and **24** (1:1, 780 mg, 3.79 mmol) were reacted according to the procedure given for tosylate **12** to yield a mixture of tosylates **22** und **26** (1.05 g, 2.92 mmol, 98%) as a viscous oil, which solidified after a while. *Compound* **22**: R_f=0.47 (CH_2Cl_2/acetone, 5:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=3226 (w), 2957 (w), 2872 (w), 1365 (m), 1180 (m), 1032 (s), 970 (m), 551 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (s, 9H, *t*Bu), 1.72 (m, 1H, 5-H), 2.38 (s, 3H, $ArCH_3$), 2.47 (dd, *J* 11.8, 12.6 Hz, 1H, 4-H$_{ax}$ or 6-H$_{ax}$), 3.33 (t, ^3J 11.5 Hz, 1H, 2-H), 3.58 (m, 1H, 6-H$_{ax}$ or 4-H$_{ax}$), 4.08 (m, 2H, 1′-H), 4.36 (ddd, ^4J 0.7 Hz, ^3J 5.9 Hz, ^2J 11.4 Hz, 1H, 4-H$_{eq}$ or 6-H$_{eq}$), 4.45 (ddd, *J* 1.1, 2.1 Hz, ^2J 11.6 Hz, 1H, 6-H$_{eq}$ or 4-H$_{eq}$), 7.29 (d, ^3J 8.1 Hz, 2H, Ar), 7.74 (d, ^3J 8.2 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6 (s), 27.4 (s), 32.1 (q), 44.5 (t), 53.0 (d), 66.5 (d), 71.5 (d), 94.9 (t), 128.1 (t), 129.9 (t), 132.4 (q), 145.2 (q); *m*/*z* (FAB) 361 (MH^+); HRMS (FAB): MH^+, found 361.1136. $C_{16}H_{25}O_5S_2$ requires 361.1138. *Compound* **26**: R_f=0.69 (CH_2Cl_2/acetone, 5:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=3326 (m), 2959 (m), 1472 (w), 1367 (w), 1075 (s), 1010 (s), 971 (s), 848 (m), 582 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, 9H, *t*Bu), 2.32 (m, 1H, 5-H), 2.45 (dd, ^3J 12.5 Hz, ^2J 13.9 Hz, 1H, 6-H$_{ax}$), 2.44 (s, 3H, $ArCH_3$), 3.28 (ddd, ^3J 2.5 Hz, ^4J 2.5 Hz, ^2J 13.8 Hz, 1H, 6-H$_{eq}$), 3.50 (dd, ^3J 11.4 Hz, ^2J 11.4 Hz, 1H, 4-H$_{ax}$), 4.20 (dd, ^3J 6.6 Hz, ^2J 11.0 Hz, 1H, CH_aH$_b$OTs), 4.26 (ddd, ^4J 2.7 Hz, ^3J 3.6 Hz, ^2J 11.8 Hz, 1H, 4-H$_{eq}$), 4.28 (dd, ^3J 6.2 Hz, ^2J 11.0 Hz, 1H, CH$_a$$H_b$OTs), 4.40 (dd, ^3J 6.4 Hz, 1H, 2-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 (s), 27.2 (s), 31.4 (q), 32.2 (t), 46.2 (d), 66.3 (d), 71.4 (d), 87.9 (t), 128.1 (t), 130.0 (t), 132.0 (q), 135.4 (q).

5.15. (2*S*,3*R*,5*S*)-5-*tert*-Butyl-2-(ethylthiomethyl)-1,3-oxathiane 3-oxide (29eq)

NaH (44.8 mg, 1.87 mmol) was added to a solution of vinyl sulfoxide **25** (87.8 mg, 0.47 mmol) and ethanethiol (172 μL, 2.34 mmol) in MeOH (5 mL). After stirring for 24 h at rt saturated aqueous NH_4Cl solution (1 mL) was added and most of the MeOH was removed in vacuo. The remnant was dissolved in CH_2Cl_2/H_2O (1:1, 10 mL) and the aqueous layer was extracted with CH_2Cl_2 (2×3 mL). The combined organic layers were dried (Na_2SO_4), concentrated, and purified by columns chromatography (silica gel, CH_2Cl_2/acetone, 5:1) to yield adduct **29eq** (101 mg, 0.403 mmol, 86%) as a colorless solid. R_f=0.24 (cyclohexane/EtOAc, 1:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=2958 (w), 2872 (w), 1374 (w), 1080 (s), 1022 (s), 1009 (s), 972 (m), 602 (m), 452 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (s, 9H, *t*Bu), 1.27 (t, ^3J 7.4 Hz, 3H, CH_2CH_3), 2.35 (m, 1H, 5-H), 2.46 (dd, ^3J 13.0 Hz, ^2J 13.0 Hz, 1H, 6-H$_{ax}$), 2.65 (q, ^3J 7.4 Hz, 2H, CH_2CH_3), 2.95 (dd, ^2J 1.9 Hz, 1H, ^3J 6.9 Hz, CH_2SEt), 3.32 (m, 1H, 6-H$_{eq}$), 3.53 (dd, ^3J 10.9 Hz, ^2J 11.6 Hz, 1H, 4-H$_{ax}$), 4.13 (t, *J* 6.9 Hz, 1H, 2-H), 4.31 (ddd, ^4J 2.6 Hz, ^3J 3.4 Hz, ^2J 11.6 Hz, 1H, 4-H$_{eq}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7 (s), 27.2 (s), 27.2 (d), 31.3 (q), 31.7 (d), 32.3 (t), 46.4 (d), 71.8 (d), 91.3 (t); *m*/*z* (FAB) 251 (MH^+); HRMS (FAB): MH^+, found 251.1135. $C_9H_{17}O_2S$ requires 251.1135.

5.16. (2*S*,3*S*,5*S*)-5-*tert*-Butyl-2-(ethylthiomethyl)-1,3-oxathiane 3-oxide (32eq) and (2*S*,3*S*,5*S*)-5-*tert*-butyl-2-(methoxymethyl)-1,3-oxathiane 3-oxide (33eq)

NaH (25.8 mg, 1.07 mmol) was added to a solution of vinyl sulfoxide **23** (101 mg, 0.54 mmol) and ethanethiol (79.3 μL, 1.07 mmol) in MeOH (10 mL). After stirring for 23 d at 50 °C saturated aqueous NH_4Cl solution (1 mL) was added and most of the MeOH was removed in vacuo. The remnant was dissolved in CH_2Cl_2/H_2O (1:1, 10 mL) and the aqueous layer was extracted with CH_2Cl_2 (2×3 mL). The combined organic layers were dried (Na_2SO_4), concentrated, and purified by columns chromatography (silica gel, CH_2Cl_2/acetone, 10:1→5:1) to yield adduct **32eq** (25 mg, 0.100 mmol, 19%) as a colorless solid together with MeOH adduct **33eq** (10 mg, 0.045 mmol, 3%) and starting material **23** (3 mg, 0.016 mmol, 3%). *Compound* **32eq**: R_f=0.77 (CH_2Cl_2/acetone, 5:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=2960 (m), 2870 (w), 1469 (w), 1368 (m), 1107 (m) 1036 (s), 978 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 9H, *t*Bu), 1.25 (t, ^3J 7.4 Hz, 3H, CH_2CH_3), 1.83 (dddd, ^3J 2.4, 3.9, 11.2, 13.1 Hz, 1H, 5-H), 2.53 (dd, ^2J 11.8 Hz, ^3J 12.8 Hz, 1H, 6-H$_{ax}$), 2.65 (q, ^3J 7.4 Hz, 2H, CH_2CH_3), 2.95 (dd, ^3J 8.6 Hz, ^2J 14.3 Hz, 1H, CH_aH$_b$SEt), 3.24 (dd, ^3J 2.2 Hz, ^2J 14.3 Hz, 1H, CH$_a$$H_b$SEt), 3.44 (dd, ^3J 11.4, 11.4 Hz, 1H, 4-H$_{ax}$), 3.62 (ddd, ^4J 2.3 Hz, ^3J 2.3 Hz, ^2J 11.7 Hz, 1H, 6-H$_{eq}$), 4.09 (dd, ^3J 2.2, 8.6 Hz, 1H, 2-H), 4.18 (ddd, ^4J 2.2 Hz, ^3J 3.9 Hz, ^2J 11.5 Hz, 1H, 4-H$_{eq}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6 (s), 27.3 (d), 27.4 (s), 31.7 (d), 32.1 (q), 44.8 (t), 52.5 (d), 71.7 (d), 98.2 (t); *m*/*z* (FAB) 251 (MH^+); HRMS (FAB): MH^+, found 251.1133. $C_{11}H_{23}O_2S_2$ requires 251.1134. *Compound* **33eq**: R_f=0.57 (CH_2Cl_2/acetone, 5:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})= 2958 (w), 2874 (w), 1469 (w), 1093 (s), 1036 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 9H, *t*Bu), 1.84 (dddd, ^3J 2.3, 3.8, 11.1, 12.2 Hz, 1H, 5-H), 2.53 (dd, ^3J 11.9 Hz, ^2J 12.7 Hz, 1H, 6-H$_{ax}$), 3.44 (dd, ^3J 11.3 Hz, ^2J 11.3 Hz, 1H, 4-H$_{ax}$), 3.45 (s, 3H, OCH_3), 3.65 (ddd, ^4J 2.2 Hz, ^3J 2.2 Hz, ^2J 11.6 Hz, 1H, 6-H$_{eq}$), 3.87 (dd, ^3J 2.3 Hz, ^2J 11.2 Hz, 1H, CH_aH$_b$OCH$_3$), 3.92 (dd, *J* 4.4 Hz, ^2J 11.2 Hz, 1H, CH$_a$$H_bOCH_3$), 4.07 (dd, ^3J 2.2, 4.4 Hz, 1H, 2-H), 4.19 (ddd, ^4J 2.2 Hz, ^3J 3.9 Hz, ^2J 11.5 Hz, 1H, 4-H$_{eq}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4 (s), 32.1 (q), 44.7 (t), 52.6 (d), 59.7 (s), 69.1 (d), 71.7 (d), 96.7 (t); *m*/*z* (FAB) 220 (M^+); HRMS (EI): M^+, found 220.1126. $C_{10}H_{22}O_3S$ requires 220.1128.

5.17. (2*S*,3*R*,5*S*)-5-*tert*-Butyl-2-(piperidin-1-ylmethyl)-1,3-oxathiane 3-oxide (30eq)

Piperidine (195 μL, 1.98 mmol) and DBU (1 drop) were added to a solution of vinyl sulfoxide **25** (93.0 mg, 0.49 mmol) in MeOH (5 mL). The solution was heated for 5 d at 60 °C and cooled to rt. H_2O (5 mL) and CH_2Cl_2 (20 mL) were added, the aqueous layer was extracted with CH_2Cl_2 (2×2 mL), the combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography (silica gel, CH_2Cl_2/acetone, 2:1) to yield adduct **30eq** (112 mg, 0.410 mmol, 83%) as a colorless solid. R_f=0.16 (CH_2Cl_2/acetone, 2:1); IR (ATR): $\tilde{\nu}$ (cm^{-1})=3505 (w), 2936 (m), 2799 (w), 1467 (w), 1304 (w), 1100 (s), 1023 (s), 781 (m), 616 (m), 460 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 9H, *t*Bu), 1.41 (m, 2H, piperidine), 1.57 (m, 4H, piperidine), 2.35 (m, 2H, 5-H, 6-H$_{ax}$), 2.50 (m, 4H, piperidine), 2.68 (ddd, ^4J 0.6 Hz, ^3J 6.2 Hz, ^2J 13.6 Hz, 1H, CH_aH$_b$NR$_2$), 2.87 (ddd, ^4J 1.0 Hz, ^3J 6.7 Hz, ^2J 13.6 Hz, 1H, CH$_a$$H_bNR_2$), 3.26 (dd, ^3J 2.3 Hz, ^2J 11.3 Hz, 1H, 6-H$_{eq}$), 3.49 (dd, ^3J 10.9 Hz, ^2J 11.6 Hz, 1H, 4-H$_{ax}$), 4.22 (ddt, ^4J 0.9, 1.6 Hz, ^3J 6.4 Hz, 1H, 2-H), 4.29 (ddd, ^4J 3.0 Hz, ^3J 3.0 Hz, ^2J 11.5 Hz, 1H, 4-H$_{eq}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9 (d), 25.6 (d), 27.2 (s), 31.4 (q), 32.5 (t), 46.2 (d), 55.3 (d), 58.3 (d), 71.4 (d), 89.0 (t); *m*/*z* (FAB) 274 (MH^+); HRMS (FAB): MH^+, found 274.1836. $C_{14}H_{28}NO_2S$ requires 276.1835.

5.18. (2*R*,3*R*,5*S*) and (2*S*,3*R*,5*S*) Dimethyl 2-[(5-*tert*-butyl-3-oxido-1,3-oxathian-2-yl)methyl]malonate (31ax and 31eq)

NaH (38.6 mg, 1.61 mmol) was added to a solution of vinyl sulfoxide **25** (75.6 mg, 0.40 mmol) and dimethyl malonate (185 μL, 1.61 mmol) in THF (6 mL) and the suspension was stirred for 22 d at 50 °C. Saturated aqueous NH_4Cl solution (1 mL) was added and most of the THF was removed in vacuo. The remnant was dissolved in CH_2Cl_2/H_2O (1:1, 10 mL) and the aqueous layer was extracted with CH_2Cl_2 (2×3 mL). The combined organic layers were dried

(Na_2SO_4), concentrated, and purified by columns chromatography (silica gel, cyclohexane/EtOAc, 1:1) to yield adducts **31ax** (18.3 mg, 0.057 mmol, 14%) and **31eq** (13.7, 0.043 mmol, 11%) as colorless solids. *Compound* **31ax**: R_f=0.31 (cyclohexane/EtOAc, 1:2); IR (ATR): $\tilde{\nu}$ (cm^{-1})=2954 (m), 1732 (s), 1435 (m) 1154 (m), 1031 (s), 909 (w), 831 (w), 729 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (d, ^4J 1.5 Hz, 9H, *t*Bu), 2.44 (m, 4H, 5-H, 6-H_{ax}, 2′-H), 3.27 (dddd, ^4J 1.3, 2.5 Hz, ^3J 2.6 Hz, ^2J 13.6 Hz, 1H, 6-H_{eq}), 3.44 (ddd, ^4J 1.1 Hz, ^3J 11.5 Hz, ^2J 11.6 Hz, 1H, 4-H_{ax}), 3.72 (d, ^4J 1.4 Hz, 3H, OCH_3), 3.72 (m, 1H, 1′-H), 3.76 (d, ^4J 1.5 Hz, 3H, OCH_3), 4.23 (m, 1H, 2-H), 4.27 (m, 1H, 4-H_{eq}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2 (q), 30.1 (d), 31.3 (q), 32.2 (t), 46.5 (d), 46.8 (t), 52.7 (s), 52.7 (s), 71.6 (d), 87.6 (t), 169.2 (q); *m*/*z* (EI) 320 (M^+); HRMS (EI): M^+, found 320.1287. $C_{14}H_{24}O_6S$ requires 320.1288. *Compound* **31eq**: R_f=0.25 (cyclohexane/EtOAc, 1:2); IR (ATR): $\tilde{\nu}$ (cm^{-1})=2954 (m), 1732 (s), 1435 (m), 1154 (m), 1032 (s), 910 (w), 832 (w), 729 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 9H, *t*Bu), 2.19 (m, 1H, 5-H), 2.46 (m, 1H, 2′-H), 2.67 (ddd, ^4J 3.6 Hz, ^3J 7.9 Hz, ^2J 14.6 Hz, 1H, 2′-H), 2.86 (m, 2H, H-6), 3.62 (dd, *J* 6.6, 7.8 Hz, 1H, 1′-H), 3.85 (ddd, ^4J 0.8 Hz, ^3J 6.3 Hz, ^2J 11.7 Hz, 1H, 4-H), 3.91 (ddd, ^4J 0.7 Hz, ^3J 7.2 Hz, ^2J 11.7 Hz, 1H, 4-H), 4.01 (ddd, ^4J 0.7 Hz, ^3J 3.5, 9.4 Hz, 1H, 2-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6 (s), 30.1 (d), 31.3 (q), 36.7 (t), 46.1 (d), 48.1 (t), 52.8 (s), 52.8 (s), 68.2 (d), 94.2 (t), 168.6 (q), 169.0 (q); *m*/*z* (EI) 320 (M^+); HRMS (EI): M^+, found 320.1287. $C_{14}H_{24}O_6S$ requires 320.1288.

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