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Conformationally Constrained Oxides of 1,3-Dithiane: Synthesis and NMR Spectroscopic Investigations

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Dedicated to Professor Dr. Dieter Seebach on the occasion of his 75th birthday

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Conformationally constrained derivatives of 1,3-dithianes (5-*tert*-butyl- and 4,6-dimethyl-1,3-dithiane and dithiadecalin) have been oxidised with various oxidants to yield axial and equatorial sulfoxides, disulfoxides and sulfones. Axial sulfoxides were prepared by nucleophilic hydroxide addition to the corresponding 2-alkylidene derivatives with subsequent retro-aldol-type elimination. The reaction outcome is related to the relative energies of the derivatives, as demontstrated by DFT calculations. The NMR spectroscopic data of the compounds obtained were analysed to identify ^4J couplings. It was found that only ^4J W couplings can be observed regardless of whether there is an axial or an equatorial sulfoxide, sulfide or sulfone group present in between the respective C–H moieties. A previously postulated γ-*gauche* effect of axial sulfoxides (but not of equatorial sulfoxides or sulfones) leading to the shielding of carbon atoms is not unambiguously supported by the NMR spectroscopic data of conformationally fixed derivatives.

Introduction

Sulfides,[1] sulfoxides[2] and sulfones[3] are used as versatile building blocks in numerous named and unnamed reactions, for example, in the Julia reaction in all its variations,[4] the Ramberg–Bäcklund reaction[5] and the Pummerer rearrangement.[6] The special arrangement of atoms in 1,3-dithianes, in their corresponding oxidised derivatives and in related compounds like disulfoxides[7] has found significant interest in various transformations, for example, in the Corey–Seebach reaction[8] and in nucleophilic,[9,10] radical[11] and pericyclic[12] additions to alkylidene sulfoxides.

It turns out that not only is the constitution of these compounds essential for their stability and reactivity, but their configuration is as well, that is, the orientation of C–S and S=O bonds relative to the bonds of other functional groups (e.g., C–H, C–S, S=O bonds) or to (carbanionic) lone pairs. This has been attributed to stereoelectronic effects between donor orbitals (or bonds) and acceptor orbitals (or bonds), which are favourable when the corresponding groups adopt an antiperiplanar orientation.[13] These effects not only influence the stability, structure and reactivity of chemical compounds, but they also have an impact on spectroscopic data (NMR,[14] IR, UV spectroscopy[15]). Stereoelectronic effects in sulfides, sulfoxides and sulfones have been investigated repeatedly.[16]

The sulfur-containing compounds used to date for the elucidation of stereoelectronic effects were not in a fixed (or otherwise unambiguously known) conformation, thus precluding a concise treatment and thus hampering an independent examination of the effect of functional groups. Consequently, we have looked for conformationally constrained derivatives of 1,3-dithianes suitable for structural and mechanistic investigations (Figure 1). Herein we present the syntheses and spectroscopic data of such compounds.

A number of investigations (including theoretical work[17,18]) have been published on the syntheses, structural features, spectroscopic data and reactivities of most of the oxygenated 1,3-dithiane derivatives **1**–**10**[19] and their conformationally constrained derivatives (**11**–**13**, **16**, **17**, **21**, **23** and **31**).[20]

Results and Discussion

Synthesis of Oxygenated 1,3-Dithiane Derivatives

We studied 4,6-dimethyl- (**11**–**20**) and 5-*tert*-butyl-1,3-dithianes **21**–**30** as conformationally constrained substrates in which the dimethyl substrates should have (in comparison with the *tert*-butyl compounds) a somewhat higher preference for the conformation in which the methyl substituents adopt equatorial positions and are thus more useful in the

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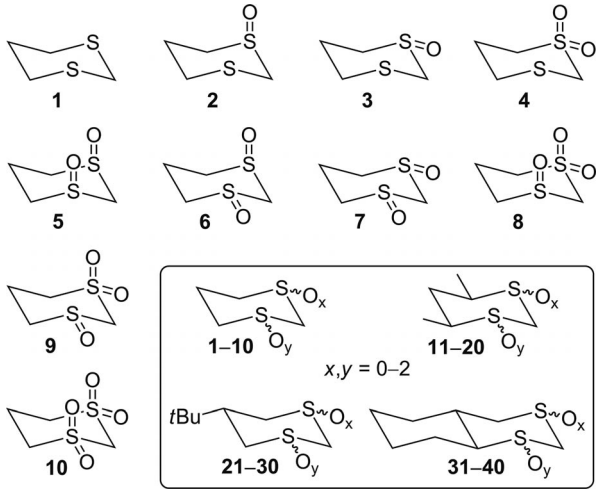


Figure 1. Oxygenated 1,3-dithianes **1**–**10** and their derivatives **11**–**40** (substituted compounds **11**–**40** have the same *S*-substituted pattern as the corresponding parent compounds **1**–**10**).

subsequent investigations.[21] The *trans*-1,3-dithiadecalin derivatives **31**–**40** can be expected to be highly constrained conformers, but the reduced symmetry of these compounds might lead to more laborious syntheses and purification procedures.

Most of the dimethyldithiane-derived oxidised compounds were accessible starting from the parent 4,6-dimethyl-1,3-dithiane (**11**), which was obtained from *meso*-pentane-2,4-diol according to published protocols.[22] It has already been noted that the oxidation of 1,3-dithiane and its derivatives preferentially leads to equatorial sulfoxides, for example, **11** → **13**.[23] This is in accordance with calculations on the stability of the monosulfoxides: equatorial sulfoxide **3** is 7.8 kJ/mol more stable than the axial sulfoxide **2** (cf. Table 2),[18] which has been attributed to a highly efficient $\sigma_{S-C} \rightarrow \sigma^*_{S-O}$ stereoelectronic interaction (Figure 2, top), possible only when the bonds involved adopt an antiperiplanar orientation. In contrast, oxygenated thianes show a different stability pattern;[24] the axial thiane 1-oxide is more stable than the equatorial substrate (ΔE = 1.3 kJ/mol[18]), most probably due to a somewhat less effective $\sigma_{H-C} \rightarrow \sigma^*_{S-O}$ interaction (Figure 2, bottom).

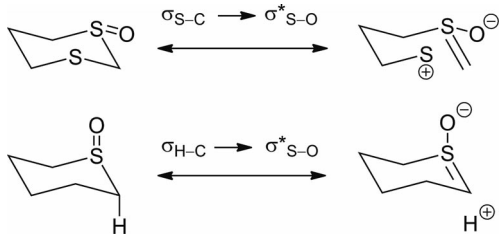


Figure 2. Stereoelectronic effects in sulfoxides.

The best results for the preparation of sulfoxide **13** were achieved with sodium periodate[25] or a hydrogen peroxide/urea complex (UHP) in the presence of acetic acid,[26] which gave sulfoxide **13** in yields of 74 and 70%, respectively (Table 1, entries 1 and 2). A minor product was the axial sulfoxide **12** (<10%), which could not be separated after purification of the crude material. When more than 1 equiv. of sodium periodate was employed, a mixture of disulfoxides **16** and **17** was obtained in addition to the mixed sulfoxide/sulfone **19** (entry 3). Compound **19** could be easily removed from the disulfoxides due to its considerably lower polarity. However, chromatographic separation of the disulfoxides **16** and **17**, which have quite similar polarities, turned out to be tedious; they could only be isolated in poor yields (19 and 7%, respectively), rendering this method only suitable for analytical purposes. The observation that more **16** than **17** is formed is in agreement with the investigations of Aggarwal et al., who found that **6** is thermodynamically more stable than **7**,[19a] and with calculations that showed that the energy difference between disulfoxides **6** and **7** is about 3.6 kJ/mol (see Table 2).[18] The disulfone **20** was obtained after the reaction of dithiane **11** with 30 equiv. of hydrogen peroxide in the presence of sodium tungstate as catalyst (entry 4).[27]

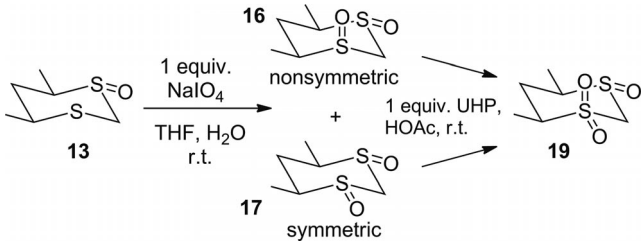
Table 1. Oxidation of 1,3-dithiane-derived substrates.

	Starting material	Conditions	Product	Yield [%][a]
1	**11**	1.2 equiv. $NaIO_4$, THF/H_2O 1:1, 24 h, room temp.	**13**	69[b,c]
			17	4
			16	12
2	**11**	1.2 equiv. UHP, AcOH, 24 h, room temp.	**13**	70[c]
			17	1
3	**11**	3 equiv. $NaIO_4$, THF/H_2O 1:1, 24 h, room temp.	**17**	7[d]
			16	19
			19	26
4	**11**	30 equiv. H_2O_2, cat. $Na_2WO_4 \cdot 2H_2O$, MeOH, 14 d, room temp	**20**	40
5	**13**	1 equiv. UHP, HOAc, 24 h, room temp.	**17**	28
			16	3
6	**13**	1 equiv. $KMnO_4$, acetone, cat. H_2O, 24 h, room temp.	**14**	86

[a] Yields of isolated and purified products. [b] Yield following purification by chromatography. Alternatively, pure **13** (74%) could be obtained when the crude product was purified by crystallisation. No disulfoxides were obtained by this protocol. [c] Axial sulfoxide (<10%) was observed in the crude product but could not be separated by chromatography. [d] The ratio of **17**/**16**/**19** in the crude reaction mixture was approx. 6:46:48.

The reaction outcome of the oxidation of the equatorial sulfoxide **13** was strongly dependent on the oxidant used. It has already been noted by Ogura et al.[25,28] for related compounds that nucleophilic oxidants like permanganate attack the sulfur of the more electrophilic sulfoxide and not the sulfide in the molecule. Accordingly, when we exposed sulfoxide **13** to potassium permanganate we obtained the sulfone **14** in an excellent 86% yield (entry 6). The parent sulfone **4** is thermodynamically more stable than the disulfoxides **5**–**7**, as has been confirmed by calculations (see Table 2)[18] and the finding of Aggarwal et al. that a mixture of disulfoxides **6** and **7** disproportionates to **4** upon treat-

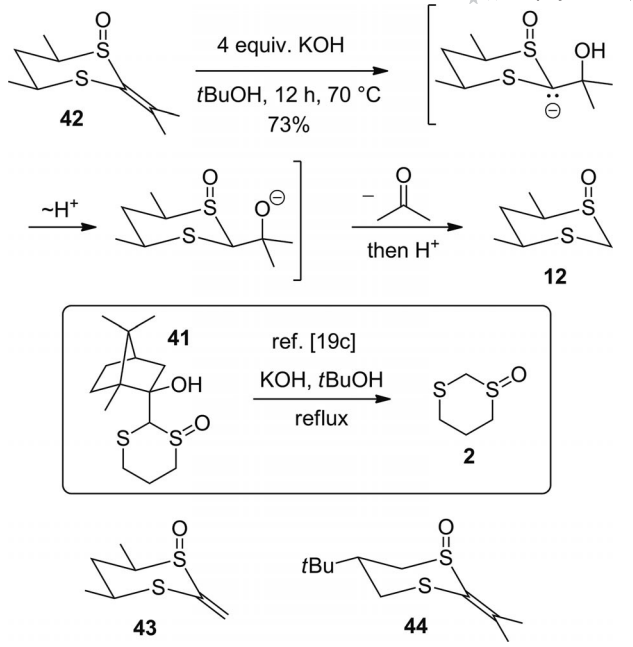
ment with N_2O_4.[19a,29] In contrast, the more electrophilic hydrogen peroxide/urea complex (which with acetic acid leads to a putative peracid as intermediate[26]) reacted at the nucleophilic sulfur of the sulfide to furnish a mixture of the disulfoxides **16** and **17**, albeit again in poor yield (entry 5). The identities of the disulfoxides **16** and **17** and the sulfoxide/sulfone **19** were unambiguously proven by comparison of the NMR spectra and by MS (Scheme 1). Oxidation of the monosulfoxide **13** with known configuration (X-ray crystal structure)[20c] furnished two disulfoxides, one symmetric and one non-symmetric (as is clear from the NMR spectra), which have necessarily been assigned the structures **16** and **17**, respectively. Because oxidation of these disulfoxides with UHP led to a single trioxide, this has to be the sulfoxide/sulfone **19** with the sulfoxide S=O bond in an equatorial position. This trioxide was also obtained in one pot starting from dithiane **11** (Table 1, entry 3).



Scheme 1. Structural elucidation of compounds **16**, **17** and **19**.

The axial sulfoxide **12** has already been obtained by Koskimies by *O*-methylation of the equatorial sulfoxide **13** and subsequent nucleophilic attack with hydroxide[20d] leading to a 9:1 mixture of **12** and **13**. We considered it useful to have a further method for the preparation of this compound in hand, for which we adapted the protocol of Bryan et al.[19c] used for the separation of enantiomers of sulfoxide **2**. They showed that hydroxyalkyl-substituted dithiane derivative **41** suffers a retro-aldol-type fragmentation upon deprotonation and heating (Scheme 2, bottom). Because we had previously synthesised alkylidenedithianes **42**–**44** bearing an axial oxygen,[15] we considered it possible that these could be used for a similar transformation upon the formal addition of water to the *exo* double bond. In fact, the 2-propylidene-substituted sulfoxide **42** is clearly attacked by hydroxide leading to a presumed hydroxyalkyl-substituted carbanion, which, after *trans*-protonation and fragmentation, leads to the desired axial sulfoxide **12**. Nevertheless, the harsh reaction conditions led to the formation of coloured side-products, which could be removed by crystallisation. The product was obtained in a satisfactory yield of 73%. Methylene-substituted sulfoxide **43** turned out to be stable when exposed to basic conditions, most probably due to the higher carbonyl activity and thus due to a lower elimination tendency of formaldehyde, shifting the equilibrium towards the starting materials.

tert-Butyl-substituted oxygenated 1,3-dithiane derivatives were prepared by essentially identical routes, with the parent dithiane **21** obtained by published protocols.[21,22a,30]



Scheme 2. Synthesis of an axial sulfoxide.

Oxidation with sodium periodate again led to the formation of the equatorial sulfoxide **23** (77%), whereas sulfone **24** was accessed in quantitative yield by the oxidation of sulfoxide **23** with permanganate. The oxidation of dithiane **21** with the hydrogen peroxide/urea complex (in the presence of tellurium oxide) led to a hardly separable mixture of disulfoxides **26** and **27** (10 and 30%). This protocol is a variation of a method published by Kim et al.,[31] who found that the oxidation of sulfoxide with hydrogen peroxide and tellurium oxide prevents overoxidation to sulfones. The oxidation of dithiane **21** with hydrogen peroxide furnished the mixed sulfoxide/sulfone **29** in 39% yield, whereas complete oxidation was again possible with sodium tungstate. A satisfactory 60% yield of disulfone **30** was obtained within only 15 h, whereas 2 weeks was necessary for the preparation of the dimethyl derivative **20**. The axial sulfoxide **22** was again accessible by a bypass reaction (cf. Scheme 2), the addition of hydroxide to the corresponding alkylidene-substituted derivative **44** with subsequent elimination of acetone (55%). The structure of sulfoxide **22** was unambiguously proven by X-ray crystallographic analysis (Figure 3).[32]

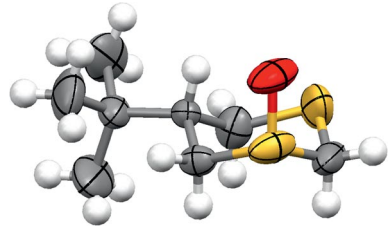
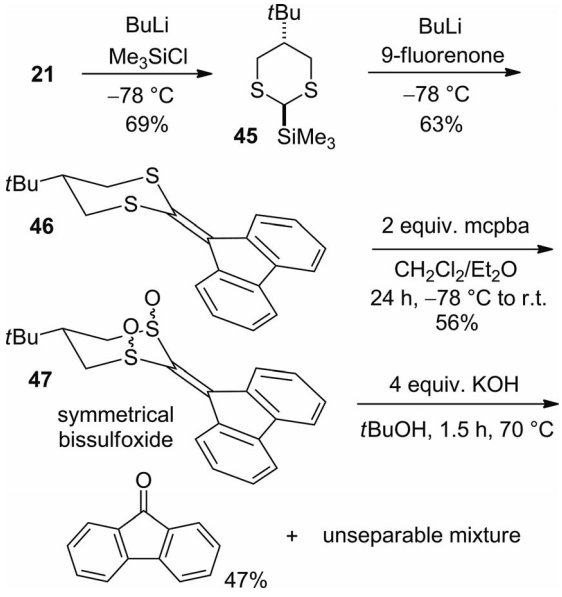


Figure 3. Structure of axial sulfoxide **22** in the crystal.[32]

We attempted the preparation of diaxial disulfoxide **25** by a similar strategy. We considered it likely that a 2-fluorenylidene-substituted 1,3-dithiane **46** (which was prepared

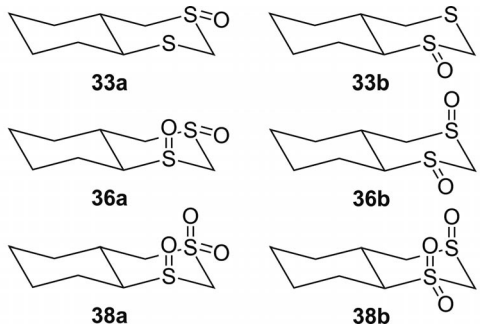
by Peterson olefination starting with dithiane **21**) could not be oxidised at the equatorial positions of the sulfur atoms because this would lead to considerable steric hindrance and therefore we expected instead an axial oxidation. In fact, oxidation of fluorenylidene-dithiane **46** with *m*-chloroperbenzoic acid[25] led to symmetrical disulfoxide **47** (proven by MS and NMR spectroscopy) in which it could not be decided whether its sulfoxide groups were diaxial or diequatorial (Scheme 3). Reaction with hydroxide led to the elimination of fluorenone, but unfortunately a dithiane derivative could neither be identified in the crude mixture nor be isolated. Consequently, the preparation of diaxial disulfoxides **15** and **25** remains a challenging task.



Scheme 3. Attempted synthesis of diaxial disulfoxide **25**.

trans-Dithiadecalins are conformationally constrained 1,3-dithianes in which the sulfur atoms are no longer equivalent. We therefore expected that the isolation and purification procedures could possibly be more difficult. The parent sulfide **31** was prepared according to a published protocol.[20e] Oxidation with 1 equiv. of sodium periodate led to a mixture (89%, 55:45) of two mono-oxygenated products (most probably a mixture of the equatorial sulfides **33a** and **33b**), which could not be separated by chromatography. The oxidation of **31** with 2 equiv. of the hydrogen peroxide/urea complex led to a mixture of three disulfoxides: one isomer could be separated and was obtained in pure form (25%), most likely compound **37**. A small fraction (4%), a mixture of two further isomers, could not be purified, but could be a mixture of isomers **36a** and **36b**. Exhaustive oxidation with hydrogen peroxide and catalytic amounts of sodium tungstate led to the disulfone **40** in 90% yield. Compared with compound **20**, its solubility in organic solvents turned out to be significantly higher.

We have thus accessed a range of conformationally constrained oxygenated 1,3-dithiane derivatives, for which we could determine most of the substitution patterns. Only two



derivatives could not be obtained in any of the parent dithiane systems, the diaxial disulfoxide **15** (or **25**/**35**) and the mixed sulfoxide/sulfone **18** (or **28**/**38**) with an axial sulfoxide group. Calculations[18] showed that these isomers have the highest energies within the respective group of isomers (Table 2), most probably because a favourable $\sigma_{S-C} \rightarrow \sigma^*_{S-O}$ stereoelectronic interaction requiring an equatorial S=O bond is not possible in these compounds. Their synthesis remains a challenge.

Table 2. Calculated stabilities of the oxygenated 1,3-dithianes **1**–**10**.[18]

	E_{el} [Hartree][a]	E_{rel} [kJ/mol]	μ [debye][b]
1	–953.6390	–	2.3
2	–1028.8196	7.8	4.7
3	–1028.8226	0.0	4.4
4	–1104.0324	0.0	5.3
5	–1103.9925	105.0	4.9
6	–1103.9985	89.1	7.0
7	–1103.9971	92.7	5.0
8	–1179.2060	10.3	6.5
9	–1179.2099	0.0	4.9
10	–1254.4167	–	5.9

[a] Electronic energies: B3LYP/6-31++G(d,p)//B3LYP/6-31++G(d,p), gas-phase calculation. Results of calculations with consideration of solvent effects are given in the Supporting Information of ref.[18]. [b] Electric dipole moment.

NMR Spectroscopic Investigations

It has been claimed by Tormena and co-workers[19b] for 1,3-dithiane and its oxidised derivatives that there is a long-range $^4J_{HH}$ coupling[33] between two axial hydrogen atoms when there is an axial S=O or sulfone group (similarly bearing an axial S=O group) in between (Figure 4, bottom) and between two equatorial hydrogen atoms if there is an equatorial S=O or sulfone group (similarly bearing an equatorial S=O group) in between (Figure 4, top). This was inferred from the spectra of **1**, **3**, **7**, **9** and **10** and from accompanying NBO calculations. We now had several conformationally constrained dithiane derivatives in hand that were perfectly suitable for NMR investigations and found that the above assumption is not supported by our analysis

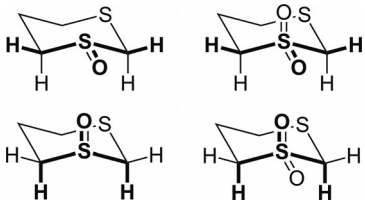


Figure 4. W coupling (top) and putative $^4J_{Hax–Hax}$ coupling (bottom) in dithiane derivatives.

(Table 3). We did not observe ^4J couplings ($^4J_{2\text{-Hax}–4\text{-Hax}}$ or $^4J_{2\text{-Heq}–4\text{-Hax}}$ coupling) in dithianes bearing equatorial substituents at C-4 and C-6 (i.e., in compounds **11**–**20**), but generally found a ^4J coupling in substrates bearing equatorial hydrogen atoms at C-4 and/or C-6 (numbering according to the numbering in the 1,3-dithiane), either as a doublet of doublets or pseudo-triplet, or as a doublet, depending on whether two (in *tert*-butyldithianes) or one (in dithiadecalins) equatorial hydrogen atom is available for W coupling. The data we have available neither support the presence of observable $^4J_{Hax–Hax}$ couplings nor a dependency of the configuration of the sulfoxide group between the respective hydrogen atoms. To assure these observations, the 2-H_{ax} and 2-H_{eq} atoms were unambiguously assigned by evaluation of NOESY spectra. The only unexpected observation was a ^5J coupling between the axial 2-H and 5-H atoms (1 Hz) in compound **17**, which was not observed or resolved in any of the other compounds.

Yet another trend in the NMR spectroscopic data, which has been claimed for similar substrates (e.g., for some of the parent dithiane derivatives **1**–**10**),[16b,38] is not clearly supported by the data obtained for the compounds with well-defined conformations. A γ-*gauche* effect had been postulated showing a dependency of the ^{13}C NMR shift of a carbon at the γ position on a sulfoxide's oxygen atom (Figure 5). The presence of an axial sulfoxide S=O group should therefore lead to a significant shielding effect (smaller ppm values). This has been attributed to the equatorial sulfur lone pair involved in a stereoelectronic effect ($n_S \rightarrow \sigma^*_{C–C}$), which should give rise to a higher electron density at the γ carbon (β to the sulfoxide group). Consequently, the presence of sulfones or of equatorial S=O groups should not have that effect because there is either no lone pair present or it is not in a suitable orientation.

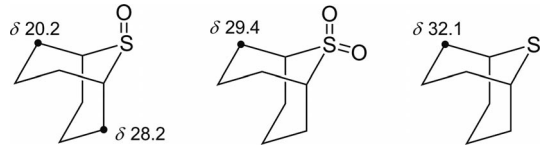
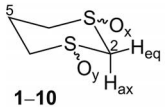
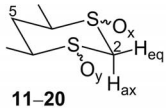


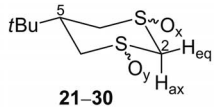
Figure 5. γ-*gauche* effect in sulfoxides.[39]

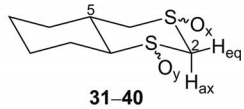
Nevertheless, in our investigations we have found no clear relationship between the constitution and configuration of dithiane derivatives and their spectroscopic data [given in Table 3 as δ(C-5) values]. Neither the number of axial (sulfoxide) S=O groups present in the respective com-

Table 3. Selected NMR spectroscopic data for the oxygenated 1,3-dithiane derivatives.









	δ(C-5) [ppm]		2-H	δ(2-H) [ppm]	^4J [Hz]	δ(C-5) [ppm]		2-H	δ(2-H) [ppm]	^4J [Hz]	δ(C-5) [ppm]		2-H	δ(2-H) [ppm]	^4J [Hz]	δ(C-5) [ppm]
1	26.6[34]	**11**	eq	3.56		44.6[33]	**21**	eq	3.35	1.8 (t)	47.5	**31**	eq	3.41	1.9 (d)	43.1[20e]
			ax	4.09				ax	4.00				ax	4.14		
2	[a]	**12**	eq	3.77		32.2	**22**	eq	3.65	1.9, 1.9 (dd)	34.4					
			ax	3.92				ax	3.72							
3	[a]	**13**	eq	3.99		45.4	**23**	eq	4.03	3.0, 1.4 (dd)	50.4					
			ax	3.78				ax	3.52							
		14	eq	3.70		44.8	**24**	eq	3.73	3.6, 1.3 (dd)	50.4					
			ax	4.13				ax	3.99							
6	14.6[35]	**16**	eq	4.67		31.1	**26**	eq	4.77	3.7, 2.0 (dd)	35.7					
			ax	3.55				ax	3.92							
7	[b]	**17**	eq	4.76		31.0	**27**	eq	4.79	2.5 (t)	34.8	**37**	eq	4.81	2.9 (d)	38.3
			ax	3.93	[c]			ax	3.70				ax	3.89		
		19	eq	4.78		33.3	**29**	eq	4.70	3.4, 2.4 (dd)	38.3					
			ax	4.00				ax	3.86							
10	17.6[36]	**20**	eq	5.51		32.8	**30**	eq	5.39	3.2 (t)	39.4	**40**	eq	5.47	3.7 (d)	32.8
			ax	5.23				ax	5.05				ax	5.13		

[a] The spectroscopic data for compound **2/3** (conformers) have been published previously:[19d,37] δ(C-5) = 27.1 ppm, δ(2-H) = 3.65, 4.01 ppm. This might suggest the presence of conformation **3** in solution. [b] An X-ray crystallographic analysis clearly proves the presence of conformation **5** in the crystal of compound **5/7**.[16b] This is not supported by calculated energies (for the compound in the gas phase and in solution, Table 2).[18] The presence of a diequatorial conformation in solution is mainly supported in the literature.[19b] δ(C-5) = 7.9 ppm.[16b] [c] ^5J coupling between the equatorial 2-H and the axial 5-H atom (d, 1 Hz).

pounds nor the number of equatorial lone pairs gives a clear correlation with the NMR spectroscopic data. Although the trend is clear for compounds **12**–**14** and **16** (and their respective derivatives **22**–**24** and **26**), in which one axial S=O group (**12** and **16**; **22** and **26**) leads to higher frequency shifts at C–5, it is not for compounds **11**, **17**, **19** and **20** (nor for **21**, **27**, **29** and **30**). Dithianes **11** and **21** should exhibit higher frequency shifts at C-5, whereas compounds **17**, **19**, **20**, **27**, **29** and **30** (no equatorial lone pairs) correspondingly should be deshielded and thus show higher frequency shifts. Once again, it seems necessary to have the reference compounds **15** and **18** (or **25** and **28**) in hand. A detailed investigation, including calculations and simulations of the NMR spectroscopic data for compounds **1**–**40**, is currently ongoing in our laboratories.

Conclusions

We have obtained oxidised derivatives of conformationally constrained 1,3-dithianes suitable for, for example, investigations of stereoelectronic effects. All oxidation states could be realised, except for derivatives of the diaxial disulfoxide **5** and the axial sulfoxide/sulfone **8**. An NMR analysis has shown that ^4J W couplings are observed when equatorial hydrogen atoms are present, regardless of whether there is an axial or equatorial sulfoxide, sulfide or sulfone group in between the respective C–H moieties; ^4J couplings between axial hydrogen atoms are not observed. A previously postulated γ-*gauche* effect of axial sulfoxides (but not of equatorial sulfoxides or sulfones) leading to a shielding of carbon atoms is not unambiguously supported by the NMR spectroscopic data available for these conformationally fixed derivatives.

Experimental Section

General: Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl radical and CH_2Cl_2 was distilled from CaH_2. Abbreviations and acronyms: mcpba, *m*-chloroperbenzoic acid; UHP, hydrogen peroxide/urea complex. All moisture-sensitive reactions were carried out under oxygen-free argon or N_2 using oven-dried glassware and a vacuum line. Flash column chromatography[40] was carried out by using Merck silica gel 60 (230–400 mesh) and TLC was carried out by using commercially available Merck F_{254} precoated sheets. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Cryospek WM-250, AM-400 or DRX 500 spectrometer. NOESY spectra were recorded with a Bruker DRX 500 or 600 MHz Avance III spectrometer. Chemical shifts are given in ppm downfield of tetramethylsilane. ^{13}C NMR spectra were recorded with broad-band proton decoupling and were assigned by means of DEPT-135 and DEPT-90 experiments. $^1J_{C,H}$ coupling constants were measured by means of coupled HMQC experiments[41,42] or coupled HSQC experiments (Bruker pulse program hsqcetgpi2; power level pl12 set to 120 dB to prevent decoupling).[42,43] Melting points were measured with a Büchi apparatus. IR spectra were recorded with a Bruker IFS-88 spectrometer. Elemental analyses were performed with a Heraeus, CHN-O-rapid or Elementar Vario MICRO spectrometer. Electrical ionisation and high-resolution mass spectra were recorded with a Finnigan MAT-90 spectrometer.

General Procedure (GP1) for Oxidation Reactions with $NaIO_4$: $NaIO_4$ in H_2O was added dropwise with stirring at 0 °C to a solution of the substrate in THF or MeOH and the mixture was stirred for 12–18 h at room temp. A white precipitate separated and the filtrate was extracted with EtOAc (3×). The organic layers were dried (Na_2SO_4) and concentrated.

General Procedure (GP2) for the Preparation of Axial Sulfoxides: Ground KOH (4 equiv.) was added with stirring at room temp. to a solution of the vinyl sulfoxide (1 equiv.) in *t*BuOH (4 mL/mmol). The mixture was heated for 12 h at 70 °C, cooled to room temp., poured into a saturated aqueous NH_4Cl solution and extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), concentrated and purified.

***cis*-4,6-Dimethyl-1,3-dithiane (11):** Dimethyldithiane **11** was prepared according to a published protocol.[21,22] ^{1}H NMR (250 MHz, [D$_6$]acetone): δ = 1.24 (d, ^3J = 6.9 Hz, 6 H, 2 Me), 1.35 (td, ^2J = 13.8, ^3J = 11.3 Hz, 1 H, 5-H$_{ax}$), 2.11 (tdd, ^2J = 13.8, ^3J = 2.3, ^5J = 0.9 Hz, 1 H, 5-H$_{eq}$), 2.84 (qdd, ^3J = 11.3, ^3J = 6.9, ^3J = 2.3 Hz, 2 H, 4-H$_{ax}$, 6-H$_{ax}$), 3.56 (d, ^2J = 14.1 Hz, 1 H, 2-H$_{eq}$), 4.13 (d, ^2J = 14.1 Hz, 1 H, 2-H$_{ax}$) ppm. ^{13}C NMR[34] (25 MHz, $CDCl_3$): δ = 21.9 (2 Me), 33.3 (C-2), 39.2 (C-4, C-6), 44.6 (C-5) ppm.

***rac*-(1*R*,4*S*,6*R*)-4,6-Dimethyl-1,3-dithiane 1-Oxide (12):** Sulfoxide **42**[15] (204 mg, 1.00 mmol) was reacted according to GP2 with KOH (224 mg, 4.00 mmol) to yield a crude brownish solid (181 mg), which was purified by chromatography (SiO_2, CH_2Cl_2/MeOH, 50:1) to furnish sulfoxide **12** (120 mg, 0.730 mmol, 73%) as a colourless solid, which was recrystallised (cyclohexane/CH_2Cl_2) if necessary; m.p. 128–130 °C (cyclohexane/CH_2Cl_2). R_f (CH_2Cl_2/MeOH, 20:1) = 0.37. IR (DRIFT): $\tilde{\nu}$ = 2963 (s), 1446 (m), 1375 (m), 1245 (m), 1043 (s), 1012 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.35 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.62 (dddd, ^2J = 14.8, ^3J = 2.4, ^3J = 2.4, ^5J = 0.8 Hz, 1 H, 5-H$_{eq}$), 2.09 (ddd, ^2J = 14.8, ^3J = 11.7, ^3J = 11.7 Hz, 1 H, 5-H$_{ax}$), 2.33–2.44 (m, 1 H, 6-H), 2.94 (dqd, ^3J = 11.7, ^3J = 6.8, ^3J = 2.4 Hz, 1 H, 4-H), 3.77 (d, ^2J = 14.3 Hz, 1 H, 2-H$_a$), 3.92 (d, ^2J = 14.3 Hz, 1 H, 2-H$_b$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.1 (CH_3), 21.1 (CH_3), 32.2 (CH_2, C-5), 37.8 (CH, C-4), 49.3 (CH_2, C-2), 52.0 (CH, C-6) ppm. MS (FAB): *m*/*z* (%) = 165 (100) [M + 1]$^+$. $C_6H_{12}OS_2$ (164.29): calcd. C 43.86, H 7.36, S 39.03; found C 43.98, H 6.96, S 39.11.

***rac*-(1*S*,4*S*,6*R*)-4,6-Dimethyl-1,3-dithiane 1-Oxide (13):** Dithiane **11** (593 mg, 4.00 mmol) and $NaIO_4$ (898 mg, 4.20 mmol) were reacted according to GP1 to give a crude product (575 mg), which was recrystallised (cyclohexane/CH_2Cl_2) to yield sulfoxide **13** (484 mg, 2.95 mmol, 74%) as colourless needles. If the crude product was purified by chromatography, **13** was obtained together with the disulfoxides given in Table 1; m.p. 155–157 °C (cyclohexane/CH_2Cl_2). R_f (CH_2Cl_2/MeOH, 20:1) = 0.29. IR (DRIFT): $\tilde{\nu}$ = 2960 (s), 2905 (s), 1453 (m), 1254 (m), 1034 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.46 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.93 (ddd, ^2J = 15.1, ^3J = 12.2, ^3J = 11.5 Hz, 1 H, 5-H$_{ax}$), 2.28 (dddd, ^2J = 15.1, ^3J = 2.5, ^3J = 2.5, ^5J = 0.5 Hz, 1 H, 5-H$_{eq}$), 2.69 (ddd, ^3J = 12.2, ^3J = 6.8, ^3J = 2.5 Hz, 1 H, 6-H), 3.06 (ddd, ^3J = 11.5, ^3J = 6.8, ^3J = 2.5 Hz, 1 H, 4-H), 3.78 (d, ^2J = 12.7 Hz, 1 H, 2-H$_{ax}$), 3.99 (d, ^2J = 12.7 Hz, 1 H, 2-H$_{eq}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.8 (CH_3), 20.0 (CH_3), 38.6 (CH, C-4), 45.4 (CH_2, C-5), 50.0 (CH_2, C-2), 60.4 (CH, C-6) ppm. MS (FAB): *m*/*z* (%) = 165 (100) [M + 1]$^+$. $C_6H_{12}OS_2$ (164.29): calcd. C 43.86, H 7.36; found C 43.81, H 7.34.

***rac*-(4*S*,6*R*)-4,6-Dimethyl-1,3-dithiane 1,1-Dioxide (14):** $KMnO_4$ (553 mg, 3.50 mmol) dissolved in H_2O (10 mL) was added at 0 °C to a solution of sulfoxide **13** (575 mg, 3.50 mmol) in acetone (30 mL). After stirring for 24 h at room temp., the mixture was filtered to remove MnO_2 and the precipitate was washed with a small volume of acetone. The filtrate was concentrated, dissolved in CH_2Cl_2, dried (Na_2SO_4) and concentrated to yield a crude product (618 mg), which was purified by chromatography (SiO_2, CH_2Cl_2/MeOH, 50:1) to yield sulfone **14** (544 mg, 3.02 mmol, 86%) as a colourless solid and unreacted **13** (70 mg, 0.42 mmol, 12%). **14**: M.p. 198–200 °C. R_f (CH_2Cl_2/MeOH, 50:1) = 0.35 (staining: $KMnO_4$ soln.). IR (DRIFT): $\tilde{\nu}$ = 2968 (s), 1454 (m), 1321 (s), 1293 (s), 1144 (s), 1115 (s), 1035 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.29 (d, ^3J = 6.9 Hz, 3 H, CH_3), 1.38 (d, ^3J = 6.8 Hz, 3 H, CH_3), 2.25 (ddd, ^2J = 14.7, ^3J = 3.4, ^3J = 2.7 Hz, 1 H, 5-H_{eq}), 2.33 (m, 1 H, 5-H_{ax}), 3.05–3.14 (m, 1 H, 4-H or 6-H), 3.15–3.25 (m, 1 H, 4-H or 6-H), 3.70 (d, ^2J = 14.6 Hz, 1 H, 2-H_{eq}), 4.13 (d, ^2J = 14.6 Hz, 1 H, 2-H_{ax}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4 (CH_3), 20.0 (CH_3), 38.1 (CH), 44.8 (CH_2, C-5), 50.7 (CH_2, C-2), 57.1 (CH) ppm. MS (EI, 80 °C): *m*/*z* (%) = 180 (60) $[M]^+$, 101 (100). $C_6H_{12}O_2S_2$ (180.29): calcd. C 39.97, H 6.71, S 35.57; found C 39.94, H 6.40, S 35.53.

***rac*-(1*R*,3*R*,4*S*,6*R*)-4,6-Dimethyl-1,3-dithiane 1,3-Dioxide (16) and *meso*-(1*S*,3*R*,4*S*,6*R*)-4,6-Dimethyl-1,3-dithiane 1,3-Dioxide (17):** Freshly ground UHP (366 mg, 3.89 mmol) was added at room temp. to a solution of sulfoxide **13** (619 mg, 3.77 mmol) in HOAc (10 mL) and the mixture was stirred for 24 h, concentrated, neutralised with saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2 (4× 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated to yield a crude product (439 mg), which was purified by chromatography (SiO_2, CH_2Cl_2/MeOH, 50:1 to 20:1) to yield disulfoxides **17** (189 mg, 1.05 mmol, 28%) and **16** (21 mg, 0.12 mmol, 3%) as colourless solids together with a fraction containing both compounds (185 mg, **16**/**17**, ca. 70:30).

16: M.p. 196–200 °C. R_f (CH_2Cl_2/MeOH, 20:1) = 0.08. IR (DRIFT): $\tilde{\nu}$ = 2949 (m), 2891 (m), 1455 (m), 1032 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.40 (d, ^3J = 7.0 Hz, 3 H, CH_3), 1.53 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.99 (ddd, ^2J = 16.1, ^3J = 2.4, ^3J = 2.4 Hz, 1 H, 5-H_{eq}), 2.57 (ddd, ^2J = 16.1, ^3J = 12.1, ^3J = 12.1 Hz, 1 H, 5-H_{ax}), 2.86–2.96 (m, 1 H, 4-H or 6-H), 2.96–3.06 (m, 1 H, 4-H or 6-H), 3.55 (d, ^2J = 13.0 Hz, 1 H, 2-H_{ax}), 4.67 (d, ^2J = 13.0 Hz, 1 H, 2-H_{eq}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.2 (CH_3), 16.5 (CH_3), 31.1 (CH_2, C-5), 52.5 (CH), 59.9 (CH), 63.6 (CH_2, C-2) ppm. MS (FAB): *m*/*z* (%) = 181 (100) $[M + 1]^+$. $C_6H_{12}O_2S_2$ (180.29): calcd. C 39.97, H 6.71; found C 40.06, H 6.78.

17: M.p. 199–210 °C. R_f (CH_2Cl_2/MeOH, 20:1) = 0.13. IR (DRIFT): $\tilde{\nu}$ = 2962 (m), 2899 (m), 1458 (m), 1054 (s), 1032 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.49 (d, ^3J = 6.9 Hz, 6 H, 2 CH_3), 1.46–1.55 (m, 1 H, 5-H_{ax}), 2.21 (dtd, ^2J = 17.1, ^3J = 2.6, ^5J = 1.0 Hz, 1 H, 5-H_{eq}), 2.93 (dqd, ^3J = 12.4, ^3J = 6.9, ^3J = 2.6 Hz, 2 H, 4-H, 6-H), 3.93 (dd, ^2J = 10.8, ^5J = 1.0 Hz, 1 H, 2-H_{ax}), 4.76 (d, ^2J = 10.8 Hz, 1 H, 2-H_{eq}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.6 (2 CH_3), 31.0 (CH_2, C-5), 59.0 (2 CH), 67.6 (CH_2, C-2) ppm. MS (EI, 80 °C): *m*/*z* (%) = 180 (7) $[M]^+$, 131 (30), 69 (100). $C_6H_{12}O_2S_2$ (180.29): calcd. C 39.97, H 6.71, S 35.57; found C 39.90, H 6.44, S 36.11.

***rac*-(3*R*,4*S*,6*R*)-4,6-Dimethyl-1,3-dithiane 1,1,3-Trioxide (19):** Dithiane **11** (148 mg, 1.00 mmol) and $NaIO_4$ (642 mg, 3.00 mmol) were reacted according to GP1 to give a crude product (116 mg), which was purified by chromatography (SiO_2, CH_2Cl_2/MeOH) to yield trioxide **19** (50 mg, 0.26 mmol, 26%) and a mixture of disulfoxides **16** and **17** (55 mg, 0.31 mmol, 31%), which were separated as described above. **19**: M.p. 218–222 °C. R_f (CH_2Cl_2/MeOH, 20:1) = 0.40 (staining: $KMnO_4$ soln.). IR (DRIFT): $\tilde{\nu}$ = 2964 (m), 2906 (m), 1454 (m), 1316 (s), 1297 (s), 1054 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.42 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.56 (d, ^3J = 6.9 Hz, 3 H, CH_3), 1.98 (ddd, ^2J = 16.2, ^3J = 12.4, ^3J = 12.4 Hz, 1 H, 5-H_{ax}), 2.19 (ddd, ^2J = 16.2, ^3J = 2.8, ^3J = 2.8 Hz, 1 H, 5-H_{eq}), 2.88 (dqd, ^3J = 12.4, ^3J = 6.9, ^3J = 2.8 Hz, 1 H, 4-H or 6-H), 3.18 (dqd, ^3J = 12.4, ^3J = 6.8, ^3J = 2.8 Hz, 1 H, 4-H or 6-H), 4.00 (d, ^2J = 13.1 Hz, 1 H, 2-H_a), 4.78 (d, ^2J = 13.1 Hz, 1 H, 2-H_b) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.3 (CH_3), 15.7 (CH_3), 33.3 (CH_2, C-5), 56.8 (CH), 59.4 (CH), 68.5 (CH_2, C-2) ppm. MS (EI, 90 °C): *m*/*z* (%) = 196 (20) $[M]^+$, 134 (12), 69 (100). $C_6H_{12}O_3S_2$ (196.29): calcd. C 36.71, H 6.16, S 32.67; found C 36.64, H 5.96, S 32.78.

***meso*-(4*S*,6*R*)-4,6-Dimethyl-1,3-dithiane 1,1,3,3-Tetraoxide (20):** $Na_2WO_4{\cdot}2H_2O$ (33 mg, 0.10 mmol) was added to a solution of dithiane **11** (148 mg, 1.00 mmol) in MeOH (10 mL) and aqueous H_2O_2 (35%, 31 mmol) was added at 0 °C. After stirring for 14 d, aqueous 10% Na_2SO_3 solution was added and the mixture was extracted with CH_2Cl_2 (4× 20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed to yield a crude white solid (85 mg, 0.40 mmol, 40%). Chromatographic purification (SiO_2, CH_2Cl_2/MeOH, 50:1) was possible but complicated by the poor solubility of disulfone **20** in CH_2Cl_2; m.p. 270–280 °C (decomp.). R_f (CH_2Cl_2/MeOH, 20:1) = 0.40 (staining: I_2). ^1H NMR (400 MHz, [D_6]DMSO): δ = 1.24 (d, ^3J = 6.9 Hz, 6 H, 2 CH_3), 1.78 (td, ^2J = 15.6, ^3J = 12.1 Hz, 1 H, 5-H_{ax}), 2.28 (td, ^2J = 15.6, ^3J = 2.7 Hz, 1 H, 5-H_{eq}), 3.43–3.54 (m, 2 H, 4-H, 6-H), 5.23 (d, ^2J = 14.1 Hz, 1 H, 2-H_a), 5.51 (d, ^2J = 14.1 Hz, 1 H, 2-H_b) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 9.7 (2 CH_3), 32.8 (CH_2, C-5), 55.8 (2 CH), 68.0 (CH_2, C-2) ppm. MS (FAB): *m*/*z* (%) = 213 (90) $[M + 1]^+$.

5-*tert*-Butyl-1,3-dithiane (21): *tert*-Butyldithiane **21** was prepared according to a published protocol.[21,22a,30] ^1H NMR (600 MHz, $CDCl_3$): δ = 0.93 (s, 9 H, *t*Bu), 1.73 (dtt, *J* = 11.3, *J* = 2.4, *J* = 1.0, $^1J_{C,H}$ = 131.1 Hz, 1 H, 5-H_{ax}), 2.61 (ddd, *J* = 13.8, *J* = 11.3, *J* = 1.0, $^1J_{C,H}$ = 137.2 Hz, 1 H, 4-H_{ax}, 6-H_{ax}), 2.82–2.85 (m, $^1J_{C,H} \approx$ 134 Hz, 2 H, 4-H_{eq}, 6-H_{eq}), 3.35 (dt, *J* = 13.8, *J* = 1.8, $^1J_{C,H}$ = 144.9 Hz, 1 H, 2-H_{eq}), 4.00 (d, *J* = 13.8, $^1J_{C,H}$ = 154.3 Hz, 1 H, 2-H_{ax}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.1 [C(*C*H_3)$_3$], 31.2 (CH_2, C-4, C-6), 31.4 (CH_2, C2), 34.2 [*C*(CH_3)$_3$], 47.5 (CH, C-5) ppm.

***rac*-(1*R*,5*S*)-5-*tert*-Butyl-1,3-dithiane 1-Oxide (22):** Vinyl sulfoxide **44**[15] (3.55 g, 15.3 mmol) was reacted according to GP2 with KOH (2.56 g, 45.8 mmol) to yield a crude brownish solid (3.65 g), which was purified by chromatography (SiO_2, CH_2Cl_2/MeOH, 50:1) to furnish a yellow solid (2.54 g), which was recrystallised (cyclohexane/CH_2Cl_2) to yield sulfoxide **22** (1.62 g, 8.46 mmol, 55%) as colourless needles; m.p. 169–171 °C (cyclohexane/CH_2Cl_2). R_f (CH_2Cl_2/MeOH, 50:1) = 0.11. IR (DRIFT): $\tilde{\nu}$ = 2959 (s), 1479 (m), 1367 (m), 1028 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.93 (s, 9 H, *t*Bu), 2.29 (dd, ^2J = 13.8, ^3J = 12.1 Hz, 1 H, 4-H_{ax} or 6-H_{ax}), 2.38–2.47 (m, 1 H, 5-H), 2.63 (dd, ^2J = 13.6, ^3J = 10.9 Hz, 1 H, 4-H_{ax} or 6-H_{ax}), 2.68–2.76 (m, 1 H, 4-H_{eq} or 6-H_{eq}), 3.12–3.20 (m, 1 H, 4-H_{eq} or 6-H_{eq}), 3.65 (ddd, ^2J = 14.1, ^4J = 1.9, ^4J = 1.9 Hz, 1 H, 2-H_{eq}), 3.72 (d, ^2J = 14.1 Hz, 1 H, 2-H_{ax}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.9 [C(*C*H_3)$_3$], 29.4 (CH_2), 33.4 [*C*(CH_3)$_3$], 34.4 (CH, C-5), 47.0 (CH_2, C-2), 47.4 (CH_2) ppm. MS (FAB): *m*/*z* (%) = 193 (100) $[M + 1]^+$. $C_8H_{16}OS_2$ (192.34): calcd. C 49.96, H 8.38, S 33.34; found C 50.25, H 7.97, S 32.69.

***rac*-(1*S*,5*S*)-5-*tert*-Butyl-1,3-dithiane 1-Oxide (23):** Dithiane **21** (3.81 g, 21.6 mmol) and $NaIO_4$ (4.75 g, 22.2 mmol) were reacted according to GP1 to give a crude product (4.38 g), which was purified by chromatography (SiO_2, cyclohexane/EtOAc) to yield sulfoxide **23** (3.21 g, 16.7 mmol, 77%) as a colourless solid. R_f (cyclohexane/EtOAc, 1:5) = 0.24. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.97 (s, 9 H, *t*Bu), 2.03 (dddd, ^3J = 12.3, ^3J = 11.3, ^3J = 2.9, ^3J = 2.0 Hz, 1 H, 5-H_{ax}), 2.37 (dd, ^2J = 12.3, ^3J = 12.3 Hz, 1 H, 4-H_{ax} or 6-H_{ax}), 2.39 (dd, ^2J = 13.7, ^3J = 11.3 Hz, 1 H, 4-H_{ax} or 6-H_{ax}), 2.57–2.66 (m, 1 H), 3.46–3.54 (m, 1 H), 3.52 (d, ^2J = 12.4 Hz, 1 H, 2-H_{ax}), 4.03 (ddd, ^2J = 12.4, ^4J = 3.0, ^4J = 1.4 Hz, 1 H, 2-H_{eq}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.1 [C(CH_3)$_3$], 29.8 (CH_2, C-4), 34.3 [C(CH_3)$_3$], 51.0 (CH_2, C-6), 50.4 (CH, C-5), 56.0 (CH_2, C-2) ppm.

***rac*-5-*tert*-Butyl-1,3-dithiane 1,1-Dioxide (24):** $KMnO_4$ (1.15 g, 7.28 mmol) dissolved in H_2O (20 mL) was added at 0 °C to a solution of sulfoxide **23** (1.40 g, 7.28 mmol) in acetone (60 mL). After stirring for 24 h at room temp., the mixture was filtered to remove MnO_2 and the precipitate was washed with a small volume of acetone. The filtrate was concentrated, dissolved in CH_2Cl_2, dried (Na_2SO_4) and concentrated to yield crude sulfone **24** (1.52 g, 7.28 mmol, quant.), which was essentially pure; m.p. 130–132 °C. R_f (CH_2Cl_2/MeOH, 50:1) = 0.80. IR (DRIFT): $\tilde{\nu}$ = 2963 (s), 1305 (s), 1159 (m), 1123 (s), 859 (s) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.96 (s, 9 H, *t*Bu), 2.44 (dddd, ^3J = 12.4, ^3J = 11.4, ^2J = 2.4, ^3J = 2.4, $^1J_{C,H}$ = 137.4 Hz, 1 H, 5-H_{ax}), 2.55 (dd, ^2J = 14.0, ^3J = 11.4, $^1J_{C,H}$ = 141.3 Hz, 1 H, 4-H_{ax}), 2.81 (dd, ^2J = 14.3, ^3J = 12.4, $^1J_{C,H}$ = 135.8 Hz, 1 H, 6-H_{ax}), 2.82 (dddd, ^2J = 14.0, ^3J = 2.4, ^4J = 1.9, ^4J = 1.3, $^1J_{C,H}$ = 139.0 Hz, 1 H, 4-H_{eq}), 3.26 (dddd, ^2J = 14.3, ^4J = 3.6, ^3J = 2.4, ^4J = 1.9, $^1J_{C,H}$ = 135.7 Hz, 1 H, 6-H_{eq}), 3.73 (ddd, ^2J = 14.4, ^4J = 3.6, ^4J = 1.3, $^1J_{C,H}$ = 145.4 Hz, 1 H, 2-H_{eq}), 3.99 (d, ^2J = 14.4, $^1J_{C,H}$ = 150.7 Hz, 1 H, 2-H_{ax}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.9 [C(CH_3)$_3$], 29.2 (CH_2), 33.9 [C(CH_3)$_3$], 50.3 (CH_2), 50.4 (CH, C-5), 54.7 (CH_2, C-2) ppm. MS (FAB): *m*/*z* (%) = 208 (38) [M]$^+$. HRMS (FAB): calcd. for $^{12}C_8{}^1H_{16}{}^{16}O_2{}^{32}S_2$ 208.0592; found 208.0590. $C_8H_{16}O_2S_2$ (208.34): calcd. C 46.12, H 7.74; found C 46.18, H 7.69.

***rac*-(1*R*,3*R*)-5-*tert*-Butyl-1,3-dithiane 1,3-Dioxide (26) and *rac*-(1*S*,3*R*,5*R*)-5-*tert*-Butyl-1,3-dithiane 1,3-Dioxide (27):** Dithiane **21** (176 mg, 1.00 mmol) was dissolved in MeCN (2 mL) and TeO_2 (16 mg, 0.10 mmol) and UHP (400 mg, 4.25 mmol) were added and the mixture was stirred for 24 h at room temp. Brine (10 mL) was added and the mixture was extracted with CH_2Cl_2 (3× 10 mL). The combined organic layers were dried (Na_2SO_4), concentrated and purified by chromatography (SiO_2, CH_2Cl_2/MeOH, 50:1 to 10:1) to yield **27** (62 mg, 0.30 mmol, 30%) and **26** (21 mg, 0.1 mmol, 10%) as essentially pure compounds.

26: R_f (CH_2Cl_2/MeOH, 20:1) = 0.10. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.04 (s, 9 H, *t*Bu), 2.08 (dddd, ^3J = 12.7, ^3J = 12.6, ^3J = 2.9, ^3J = 1.9 Hz, 1 H, 5-H), 2.61 (dd, ^2J = 12.8, ^3J = 12.7 Hz, 1 H, 4-H_{ax} or 6-H_{ax}), 2.91 (dd, ^2J = 14.3, ^3J = 12.6 Hz, 1 H, 4-H_{ax} or 6-H_{ax}), 3.22 (dddd, ^2J = 14.3, ^4J = 3.1, ^3J = 2.9, ^4J = 2.0 Hz, 1 H, 4-H_{eq} or 6-H_{eq}), 3.70 (ddd, ^2J = 12.8, ^4J = 3.7, ^3J = 1.9 Hz, 1 H, 4-H_{eq} or 6-H_{eq}), 3.92 (d, ^2J = 12.8 Hz, 1 H, 2-H_{ax}), 4.77 (ddd, ^2J = 12.8, ^4J = 3.7, ^4J = 2.0 Hz, 1 H, 2-H_{eq}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.2 [C(CH_3)$_3$], 33.7[C(CH_3)$_3$], 35.7 (CH, C-5), 47.4. 54.8 (CH_2, C-4, C-6), 63.3 (CH_2, C-2) ppm.

27: R_f (CH_2Cl_2/MeOH, 20:1) = 0.15. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (s, 9 H, *t*Bu), 1.46 (tt, ^3J = 12.5, ^3J = 1.8, $^1J_{C,H}$ = 127.1 Hz, 1 H, 5-H_{ax}), 2.56 (dd, ^2J = 12.5, ^3J = 12.5, $^1J_{C,H}$ = 141.0 Hz, 2 H, 4-H_{ax}), 3.50 (ddd, ^2J = 12.5, ^4J = 2.5, ^3J = 1.8, $^1J_{C,H}$ = 139.5 Hz, 2 H, 4-H_{eq}), 3.70 (d, ^2J = 10.6, $^1J_{C,H}$ = 150.9 Hz, 1 H, 2-H_{ax}), 4.79 (dt, ^2J = 10.6, ^4J = 2.5, $^1J_{C,H}$ = 149.4 Hz, 2-H_{eq}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.2 [C(CH_3)$_3$], 34.1 [C(CH_3)$_3$], 34.8 (CH, C-5), 53.4 (CH_2, C-4, C-6), 69.1 (CH_2, C-2) ppm.

***rac*-(3*R*,5*R*)-5-*tert*-Butyl-1,3-dithiane 1,1,3-Trioxide (29):** Aqueous H_2O_2 (30%, 450 mL) was added to a solution of dithiane **21** (176 mg, 1 mmol) in PhOH (1.13 g) and the mixture was stirred for 10 min. A saturated $NaHSO_3$ solution (1 mL) and NaOH solution (10%, 4.35 mL) were added. The mixture was extracted (3× CH_2Cl_2) and the organic layers were dried, concentrated and the residue purified by chromatography (SiO_2, hexanes/ethyl acetate, 1:2 to 0:1) to yield **29** (87 mg, 39%). R_f = 0.32 (EtOAc/hexanes, 2:1). IR (DRIFT): $\tilde{\nu}$ = 2966 (m), 1310 (s), 1154 (m), 1123 (m), 1059 (m), 857 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (s, 9 H, *t*Bu), 2.01 (dddd, ^3J = 12.7, ^3J = 12.6, ^3J = 2.6, ^3J = 1.8, $^1J_{C,H}$ = 129.4 Hz, 1 H, 5-H_{ax}), 2.54 (dd, ^2J = 12.8, ^3J = 12.7, $^1J_{C,H}$ = 139.2 Hz, 1 H, 4-H_{ax}), 2.84 (dd, ^2J = 14.3, ^3J = 12.6, $^1J_{C,H}$ = 137.6 Hz, 1 H, 6-H_{ax}), 3.15 (dddd, ^2J = 14.3, ^4J = 3.4, ^3J = 2.6, ^4J = 1.5, $^1J_{C,H}$ = 140.0 Hz, 1 H, 6-H_{eq}), 3.63 (dddd, ^2J = 12.8, ^4J = 2.4, ^3J = 1.8, ^4J = 1.5, $^1J_{C,H}$ = 139.6 Hz, 1 H, 4-H_{eq}), 3.86 (d, ^2J = 12.8, $^1J_{C,H}$ = 149.1 Hz, 1 H, 2-H_{ax}), 4.70 (ddd, ^2J = 12.8, ^4J = 3.4, ^4J = 2.4, $^1J_{C,H}$ = 148.8 Hz, 1 H, 2-H_{eq}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.1 [C(CH_3)$_3$], 33.7 [C(CH_3)$_3$], 38.3 (CH, C-5), 52.7 (CH_2, C-6), 54.2 (CH_2, C-4), 69.3 (CH_2, C2) ppm. MS (EI): *m*/*z* (%) = 224 (25) [M]$^+$. HRMS (EI): calcd. for $^{12}C_8{}^1H_{16}{}^{16}O_3{}^{32}S_2$ 224.0541; found 224.0539. $C_8H_{16}O_3S_2$ (224.34): calcd. C 42.83, H 7.19; found C 43.13, H 7.21.

5-*tert*-Butyl-1,3-dithiane 1,1,3,3-Tetraoxide (30): $Na_2WO_4{\cdot}2H_2O$ (33 mg, 0.10 mmol) was added to a solution of dithiane **21** (176 mg, 1.00 mmol) in MeOH (7 mL). The mixture was cooled to 0 °C, aqueous H_2O_2 (35%, 3 mL, 30 mmol) was added dropwise and the mixture was stirred at room temp. for 15 h whereupon the formation of a white precipitate was observed. CH_2Cl_2 (5 mL) and aqueous Na_2SO_3 solution (10%, 5 mL) were added and the mixture was extracted with CH_2Cl_2 (20× 10 mL). The combined organic layers were dried (Na_2SO_4), concentrated and purified by chromatography (SiO_2, CH_2Cl_2/MeOH, 40:1 to 10:1) to yield disulfone **30** (145 mg, 0.60 mmol, 60%) as a colourless solid. The product has a very low solubility in common organic solvents like MeOH, acetone and CH_2Cl_2. R_f = 0.25 (CH_2Cl_2/MeOH, 40:1). IR (DRIFT): $\tilde{\nu}$ = 2982 (wm), 1322 (s), 1154 (m), 1118 (m), 886 (m), 870 (m), 846 (m) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 0.90 (s, 9 H, *t*Bu), 2.09 (tt, ^3J = 12.0, ^3J = 2.2, $^1J_{C,H}$ = 134.0 Hz, 1 H, 5-H_{eq}), 3.33 (dd, ^2J = 14.2, ^3J = 12.0, $^1J_{C,H}$ = 139.5 Hz, 2 H, 4-H_{ax}, 6-H_{ax}), 3.44 (ddd, ^2J = 14.2, ^4J = 3.2, ^3J = 2.2, $^1J_{C,H}$ = 137.7 Hz, 2 H, 4-H_{eq}, 6-H_{eq}), 5.05 (d, ^2J = 13.8, $^1J_{C,H}$ = 148.5 Hz, 1 H, 2-H_{ax}), 5.39 (dt, ^2J = 13.8, ^4J = 3.2, $^1J_{C,H}$ = 147.9 Hz, 1 H, 2-H_{eq}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.7 [C(CH_3)$_3$], 33.1 [C(CH_3)$_3$], 39.4 (CH, C-5), 52.4 (2 CH_2, C-4, C-6), 68.3 (CH_2, C-2), 130.2 (2 CH), 132.1 (2 CH), 135.8 (2 CH), 137.3 (C), 142.8 (2 C), 152.2 (C) ppm. MS (FAB): *m*/*z* (%) = 224 (13) [M – 16]$^+$. $C_8H_{16}O_4S_2$ (240.34): calcd. C 39.98, H 6.71; found C 40.29, H 6.73.

(1*S*,3*R*,4a*S*,8a*R*)-4a,5,6,7,8,8a-Hexahydro-2*H*,4*H*-1,3-benzodithiine 1,3-Dioxide (37): Freshly ground UHP (1.25 g, 12.9 mmol) was added at room temp. to a solution of dithiadecalin **31** (1.12 g, 6.44 mmol) in HOAc (10 mL) and CH_2Cl_2 (20 mL), and the mixture was stirred at that temperature for 5 d, concentrated, neutralised with a saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2 (4× 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated to a crude colourless solid (609 mg), which was purified by chromatography (SiO_2, CH_2Cl_2/MeOH, 50:1 to 20:1) to yield compound **37** (330 mg, 1.60 mmol, 25%) as a white solid together with a fraction (50 mg) that is most probably a mix-

ture of isomers **33a** and **33b**. **37**: M.p. 210–220 °C (decomp.). R_f = 0.24 (CH_2Cl_2/MeOH, 20:1). IR (DRIFT): $\tilde{\nu}$ = 2965 (m), 2944 (m), 2901 (m), 1037 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26–1.44 (m, 4 H), 1.58–1.72 (m, 1 H), 1.84–1.92 (m, 1 H), 1.93–2.05 (m, 2 H), 2.48–2.60 (m, 2 H), 2.72 (dd, ^2J = 12.6, ^3J = 12.5 Hz, 1 H, 4-H_{ax}), 3.33 (ddd, ^2J = 12.6, ^3J = 2.7, ^4J = 2.9 Hz, 1 H, 4-H_{eq}), 3.89 (d, ^2J = 10.5 Hz, 1 H, 2-H_{ax}), 4.81 (dd, ^2J = 10.5, ^4J = 2.9 Hz, 1 H, 2-H_{eq}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8 (CH_2), 25.2 (CH_2), 26.6 (CH_2), 29.7 (CH), 33.0 (CH_2), 58.6 (CH_2), 66.1 (CH), 68.6 (CH_2) ppm. MS (EI, 140 °C): *m*/*z* (%) = 206 (8) $[M]^+$, 157 (23), 95 (100). HRMS (FAB): calcd. for $^{12}C_8{}^1H_{14}{}^{16}O_2{}^{32}S_2$ 206.0435; found 206.0432. $C_8H_{14}O_2S_2$ (206.33): calcd. C 46.57, H 6.84, S 31.08; found C 46.59, H 7.48, S 31.35.

(4a*S*,8a*R*)-4a,5,6,7,8,8a-Hexahydro-2*H*,4*H*-1,3-benzodithiine 1,1,3,3-Tetraoxide (40): $Na_2WO_4{\cdot}2H_2O$ (33 mg, 0.10 mmol) was added to a solution of dithiadecalin **31** (174 mg, 1.00 mmol) in MeOH (15 mL). The mixture was cooled to 0 °C, aqueous H_2O_2 (35%, 3 mL, 31 mmol) was added dropwise and the mixture was stirred at room temp. for 3 weeks. An aqueous Na_2SO_3 solution (10%, 5 mL) and H_2O (30 mL) were added and the mixture was extracted with CH_2Cl_2 (4× 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated to yield essentially pure **40** (216 mg, 0.91 mmol, 91%) as a colourless solid; m.p. 270–280 (decomp.). R_f = 0.40 (CH_2Cl_2/MeOH, 50:1). ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 1.05–1.18 (m, 1 H), 1.20–1.48 (m, 3 H), 1.66–1.75 (m, 1 H), 1.82–1.91 (m, 2 H), 2.01–2.13 (m, 2 H), 3.20 (ddd, ^3J = 12.2, ^3J = 11.2, ^3J = 3.5 Hz, 1 H, 8a-H), 3.32 (dd, ^2J = 14.4, ^3J = 11.8 Hz, 1 H, 4-H_{ax}), 3.43 (ddd, ^2J = 14.4, ^3J = 2.9, ^4J = 3.7 Hz, 1 H, 4-H_{eq}), 5.13 (d, ^2J = 14.0 Hz, 1 H, 2-H_{ax}), 5.47 (dd, ^2J = 14.0, ^4J = 3.7 Hz, 1 H, 2-H_{eq}) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 19.8 (CH_2), 23.8 (CH_2), 24.4 (CH_2), 30.8 (CH_2), 32.8 (CH), 56.0 (CH_2), 62.5 (CH), 68.9 (CH_2) ppm. MS (FAB): *m*/*z* (%) = 239 (22) $[M + 1]^+$. $C_8H_{14}O_4S_2$ (238.32): calcd. C 40.32, H 5.92, S 26.91; found C 40.45, H 5.70, S 26.90.

***trans*-5-*tert*-Butyl-2-trimethylsilyl-1,3-dithiane (45):** In analogy to a published procedure,[44] *n*BuLi (14.4 mmol) was added with stirring at –78 °C to a solution of dithiane **21** (2.53 g, 14.3 mmol) in anhydrous THF (20 mL) and stirring was continued for 1 h at –78 °C and for 30 min at 0 °C. The mixture obtained was transferred portionwise through a syringe to a cooled (–78 °C) solution of TMSCl (2.19 mL, 17.2 mmol) in anhydrous THF (10 mL). The mixture was warmed to room temp. overnight, poured into H_2O (100 mL) and extracted with cyclohexane (3× 50 mL). The combined organic layers were extracted with H_2O (4× 30 mL), dried (K_2CO_3) and concentrated to yield a pale-yellow crude solid, which was immediately purified by distillation (bulb-to-bulb distillation, 130 °C/130 Pa) to furnish silane **45** (2.47 g, 9.94 mmol, 69%) as a colourless solid, which is stable at 7 °C for several months; m.p. 110–116 °C. IR (DRIFT): $\tilde{\nu}$ = 2960 (s), 1477 (m), 1365 (s), 1248 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.17 (s, 9 H, $SiMe_3$), 0.89 (s, 9 H, *t*Bu), 1.67–1.76 (m, 1 H, 5-H), 2.52–2.61 (m, 2 H), 2.80–2.88 (m, 2 H), 3.56 (s, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –3.06 ($SiMe_3$), 27.0 [C(CH_3)$_3$], 32.4 (2 CH_2), 33.5 (CH), 34.1 [C(CH_3)$_3$], 47.1 (CH) ppm. MS (EI, 25 °C): *m*/*z* (%) = 248 (42) $[M]^+$, 175 (20) $[C_8H_{15}S_2]^+$, 143 (100).

5-*tert*-Butyl-2-(9*H*-fluoren-9-ylidene)-1,3-dithiane (46): *n*BuLi (7.52 mmol) was added at –78 °C to a solution of dithiane **45** (1.70 g, 6.84 mmol) in anhydrous THF (10 mL). The mixture was stirred for 1 h at –78 °C and for 30 min at 0 °C and again cooled to –78 °C. A precooled solution of 9-fluorenone (1.23 g, 6.84 mmol) in anhydrous THF (10 mL) was added through a cannula and the mixture was warmed to room temp. within 12 h, poured into a saturated aqueous solution of NH_4Cl and extracted with EtOAc (3× 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated to yield a crude oil (2.85 g), which was purified by recrystallisation (EtOH/cyclohexane) to yield ketene *S*,*S*-acetal **46** (1.46 g, 4.31 mmol, 63%) as a yellow solid; m.p. 139–142 °C (EtOH/CH_2Cl_2). R_f = 0.43 (cyclohexane/EtOAc, 10:1). IR (ATR): $\tilde{\nu}$ = 3051 (w), 2952 (m), 1519 (s), 1439 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.01 (s, 9 H, *t*Bu), 2.11–2.20 (m, 1 H, 5-H), 3.09–3.21 (m, 4 H, 4-H_2, 6-H_2), 7.26–7.34 (m, 4 H, Ar), 7.73–7.77 (m, 2 H, Ar), 8.51–8.55 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.1 [C(CH_3)$_3$], 31.7 (2 CH_2), 34.4 [C(CH_3)$_3$], 45.4 (CH), 119.1 (2 CH_{Ar}), 125.4 (2 CH_{Ar}), 126.1 (2 CH_{Ar}), 126.7 (2 CH_{Ar}), 130.3 (C), 138.0 (2 C), 138.8 (2 C), 143.6 (C) ppm. MS (FAB): *m*/*z* (%) = 338 (100) $[M]^+$. HRMS (FAB): calcd. for $^{12}C_{21}{}^1H_{22}{}^{32}S_2$ 338.1163; found 338.1160. $C_{21}H_{22}S_2$ (338.53): calcd. C 74.51, H 6.55, S 18.94; found C 74.46, H 6.49, S 18.83.

***meso*-5-*tert*-Butyl-2-(9*H*-fluoren-9-ylidene)-1,3-dithiane 1,3-Dioxide (47):** mcpba (70%, 910 mg, 3.70 mmol) dissolved in Et_2O (11 mL) was added slowly at –78 °C to a solution of the ketene *S*,*S*-acetal **46** (624 mg, 1.85 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 24 h after warming to room temp., diluted with CH_2Cl_2 (20 mL) and poured into a saturated aqueous $NaHCO_3$ solution. The phases were separated and the organic layer extracted with $NaHCO_3$ solution (3×), dried (Na_2SO_4) and concentrated to yield a crude yellow solid (696 mg), which was purified by chromatography (SiO_2, CH_2Cl_2/MeOH, 100:0 to 50:1) and recrystallisation (CH_2Cl_2/cyclohexane) at room temp. to yield disulfoxide **47** (382 mg, 1.03 mmol, 56%) as a yellow solid; m.p. 180–190 °C (decomp.). R_f = 0.33 (CH_2Cl_2/MeOH, 20:1). IR (ATR): $\tilde{\nu}$ = 2951 (w), 1444 (m), 1060 (s), 1033 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.08 (s, 9 H, *t*Bu), 2.85–2.95 (m, 2 H, 4-H_{ax}, 6-H_{ax}), 3.55–3.64 (m, 1 H, 5-H), 3.71–3.78 (m, 2 H, 4-H_{eq}, 6-H_{eq}), 7.20–7.28 (m, 2 H, Ar), 7.37–7.43 (m, 2 H, Ar), 7.55–7.60 (m, 2 H, Ar), 8.18–8.22 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4 (CH), 27.2 [C(CH_3)$_3$], 33.0 [C(CH_3)$_3$], 50.9 (2 CH_2), 120.1 (2 CH), 128.1 (2 CH), 130.2 (2 CH), 132.1 (2 CH), 135.8 (2 CH), 137.3 (C), 142.8 (2 C), 152.2 (C) ppm. MS (FAB): *m*/*z* (%) = 371 (100) $[M + 1]^+$.

Supporting Information (see footnote on the first page of this article): Spectra of compounds **12**–**17**, **19**, **20**, **22**, **23**, **26**, **27**, **29**, **30**, **37**, **46** and **47**.

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