[2,3]-Thia-Wittig Rearrangements Proceeding with Complete Inversion or with Partial Loss of Configuration at the Carbanionic Center

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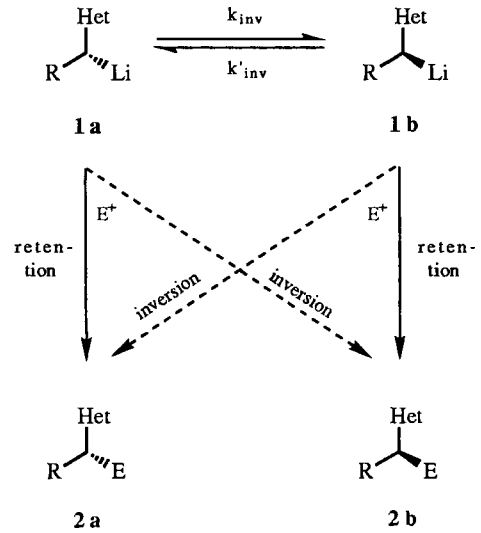
Two pairs of diastereomeric γ-(benzyloxy)-α-(tributylstannyl) sulfides (*anti*- and *syn*-**13**, *anti*- and *syn*-**30**) were prepared. *n*BuLi induced tin/lithium exchange in each of these compounds furnished α-lithiated sulfides which underwent [2,3]-thia-Wittig rearrangements in THF at −78°C within 30 min. Competing [1,2]-thia-Wittig rearrangements were not observed, not even starting from stannyl sulfides **30** where the [2,3] shift requires the intermediacy of lithium thiolates **32** in which the aromaticity of a benzene ring is given up. The homoallyl thiols *syn*- and *anti*-**19** were formed stereoselectively starting from the *allylthio* stannanes *anti*- and *syn*-**13**, respectively. This implies that the underlying thia-Wittig rearrangements are stereospecific and proceed with inversion of configuration at the carbanionic center, and that the lithio sulfides *anti*- and *syn*-**18** formed in the course of these reactions are configurationally stable until they rearrange. The *benzylthio* stannanes *anti*- and *syn*-**30** rearranged with low stereoselectivity. They furnished the benzyl thiols **33** as 71:29 and 28:72 mixtures of diastereomers, respectively. This means that the lithio sulfide intermediates involved in the latter rearrangements suffer some epimerization *anti*-**31** ⇄ *syn*-**31** prior to the sigmatropic bond shift.

α-Hetero-substituted organolithium compounds are important tools in organic synthesis[1]. Their carbanionic center is usually pyramidalized and often part of a C–Li bond[2]. In α-hetero-substituted organolithium compounds **1** (R ≠ H) which contain *four different ligands at the carbanionic center*, the latter becomes a stereogenic center („stereocenter"). Accordingly, the organolithium compounds **1a** and **1b** with opposite configurations at the carbanionic centers are stereoisomers, i.e., enantiomers, if R is achiral, or diastereomers, if R is chiral. These isomers can interconvert under appropriate conditions by inversion of configuration at the lithium bearing stereocenter in an equilibrium reaction **1a** ⇆ **1b**. Therefore, in order to convert *stereoselectively* – through reaction with an electrophile E^+ – *one* isomer of **1** into a single product **2a** or **2b** ***and*** the *other* isomer of **1** into the previous product's *stereoisomer*, **1** must be configurationally stable on the time scale of this trapping reaction: The rate constants k_{inv} and k'_{inv} for the isomerizations **1a** → **1b** and **1b** → **1a**, respectively, must be smaller than the trapping constants $k_{1\to 2}$.



This premise is particularly well fulfilled for α-lithio ethers **1** (Het = O) as first described by Still and Sreekumar[3] and often exploited thereafter[4]. It is fulfilled less reliably – if at all – in organolithium compounds **1** where the α-heteroatom is S[5–7], Se[6,8], N[9] or Br[10] as established in stereoselectivity studies of the mentioned or a conceptually different[11] type.

There is another way to look at such trapping reactions *provided that no stereomutation* **1a** ⇄ **1b** *competes*: If the configuration at the carbanionic center of the starting organolithium compound **1** *and* at the newly formed stereocenter of trapping product **2** are known, one can tell whether the C–Li bond of **1** is transformed into the C–E bond of **2** with retention (**1a** → **2a**, **1b** → **2b**) or inversion of configuration (**1a** → **2b**, **1b** → **2a**). For intermolecular trapping reactions, one has observed retention of configuration without exception. On the other hand, inversion of configuration was noticed recently in a number of intramolecular α-alkylations of α-lithio ethers by means of [1,2]-[12] and [2,3]-Wittig rearrangements[13].

In the present study we probed the configurational stability of α-lithio sulfides **1** (Het = S) on the time scale of [2,3]-thia-Wittig rearrangements **9** → **10**. While the lack of configurational stability of lithio sulfides with respect to the rate of an intermolecular attack of several electrophiles (**4**[6]; **5**[6]; **6**[5]; **7**[7]) was documented repeatedly (Table 1, lower

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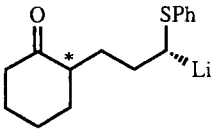
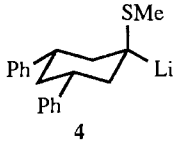
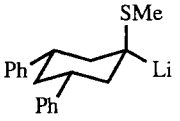
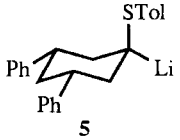
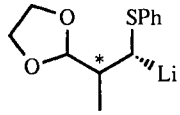
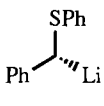
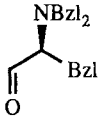
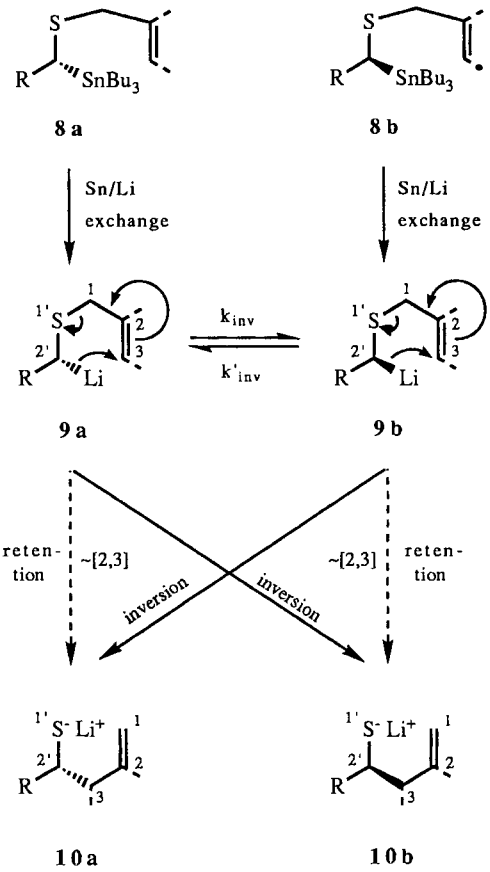
part), there are reports of established configurational stability, too (Table 1, upper part): Ritter and Cohen concluded that the diastereomeric forms of α-lithio sulfide **3** do not epimerize on the time scale of the intramolecular addition to the nearby carbonyl group[14]. In addition, Reich and Bowe were able to trap the equatorially lithiated sulfide **4** instead of its axial counterpart by Me_3SiCl (albeit only if this reagent was already present when **4** was generated)[6].

Table 1. Configurational stability of α-lithio sulfides estimated on various time scales

α-lithiosulfides *with* configurational stability ...	...on time-scale of reaction with:	Ref.
 **3** (both diastereomers)	ketone (intramolecular)	14
 **4**	Me_3SiCl (in-situ trapping)	6
α-lithiosulfides *without* configurational stability ...	**...on time-scale of reaction with:**	**Ref.**
 **4**	$EtCO_2H$, R_3SiCl, PhSeSePh, Me_2SO_4	6
 **5**	Me_3SiCl (in-situ trapping)	6
 **6** (both diastereomers)	Me_3SiCl	5
 **7**		7

The latter two findings made us hope that lithio sulfides like **9** might be configurationally stable until they undergo a [2,3]-thia-Wittig rearrangement giving **10**. This is because the trapping agent – the alkyl group of the alkylthio substituent – would be located within the same molecule, again, and would be present as soon as **9** would be formed, too. And if indeed configurational stability was found we would be able *concomitantly* to distinguish whether these rearrangements proceed with retention (**9a** → **10a**, **9b** → **10b**) or inversion of configuration (**9a** → **10b**, **9b** → **10a**) at the carbanionic center.

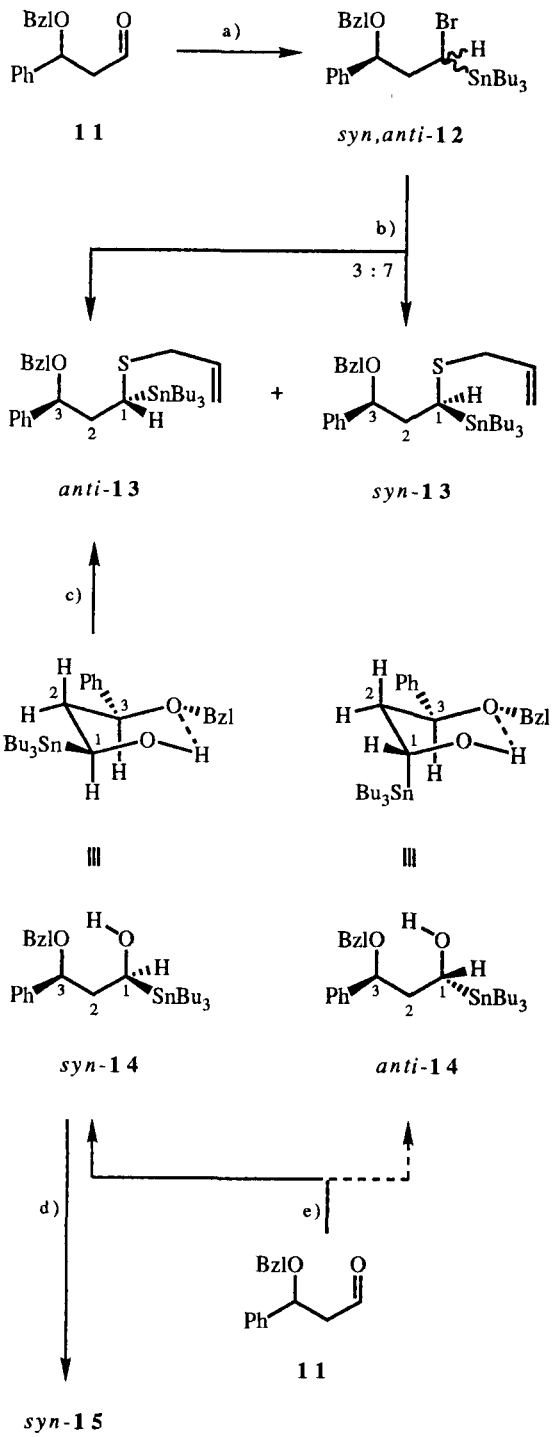


Lithio sulfides **9** (R = H, alkyl) in which R *cannot* stabilize the carbanionic center are easily obtained – and subject to [2,3]-thia-Wittig rearrangements subsequently[15] – by an *n*BuLi-induced Sn/Li exchange reaction of the corresponding α-stannylated sulfides[16] rather than by deprotonation of the tin-free sulfides themselves[17]. By all likelihood such Sn/Li exchanges proceed with retention of configuration as found for 1-propenylstannanes[18] or α-stannylated ethers[3]. Accordingly, our study began with the synthesis of appropriately stannylated sulfides of the **8a/b** class. In order to facilitate stereochemical analyses during our project we opted for *anti,syn*-**13** (Scheme 1) and *anti,syn*-**30** (Scheme 4) as model compounds; they possess the generic structure **8a/b** and are pairs of *diastereomers* and not of *enantiomers*.

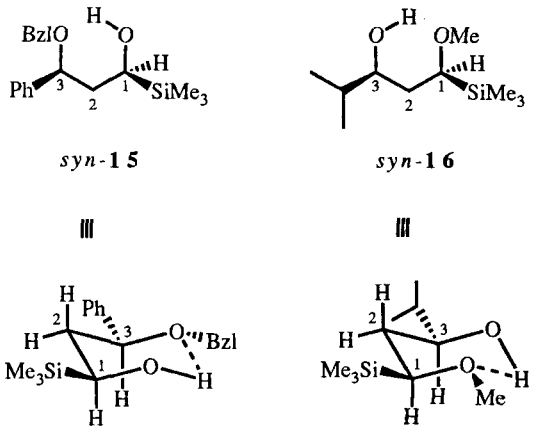
The synthesis of sulfides *anti,syn*-**13** started from the known aldehyde **11**[19] and $LiSnBu_3$[20] which furnished an α-stannylated alcohol after quenching with water. It was not purified but treated directly with CBr_4/PPh_3[21] to furnish the bromides *syn*- and *anti*-**12** as a 80:20 mixture of unassigned diastereomers. These bromides were stirred with a

suspension of $K^+ {}^-S{-}CH_2{-}CH{=}CH_2$ in THF to finally give the desired stannylated sulfides *anti*- and *syn*-**13** as a 7:3 mixture. It could be separated into the two stereochemically homogeneous constituents after several passages through a flash-chromatography column charged with silica gel[22].

Scheme 1



[a] $LiSnBu_3$, THF, −78 °C, 1 h; → 0 °C, aq. workup; CBr_4, PPh_3, CH_2Cl_2, room temp., 6 h; 60% over the 2 steps (80:20 mixture of unassigned diastereomers of *syn,anti*-**12**). — [b] $K^+ {}^-S{-}CH_2{-}CH{=}CH_2$ in THF, room temp., 12 h; 77%. — [c] MsCl, NEt_3, CH_2Cl_2, −20 °C, 2 h; addition to $K^+ {}^-S{-}CH_2{-}CH{=}CH_2$, THF, 0 °C, 5 h; 55%. — [d] $Me_3SiO{-}SO_2{-}CF_3$, 2,6-lutidine, CH_2Cl_2, −30 °C, 20 min; aq. workup; *n*BuLi (3 equiv.), THF, −78 °C, 20 min; 62% over the 2 steps. — [e] $LiSnBu_3$, THF, −78 °C, 20 min; 17%.



Our next task was to assign the stereochemistry of these sulfides. Unaware of spectroscopic means to do that, we resolved to prepare at least one of these compounds by a route with a *predictable* stereochemical outcome. It started from the *syn*-configuration γ-benzyloxy alcohol *syn*-**14**. In fact, we had already held *syn*-**14** in our hands on the way from aldehyde **11** to the bromides *syn,anti*-**12**. *There*, however, no attempt had been made to purify this compound, let alone to separate it from the minor diasteromer *anti*-**14**. Unfortunately, purification of crude *syn,anti*-**14** by flash chromatography was accompanied by substantial losses of material. Still, it provided us with the major product *as a single diastereomer*.

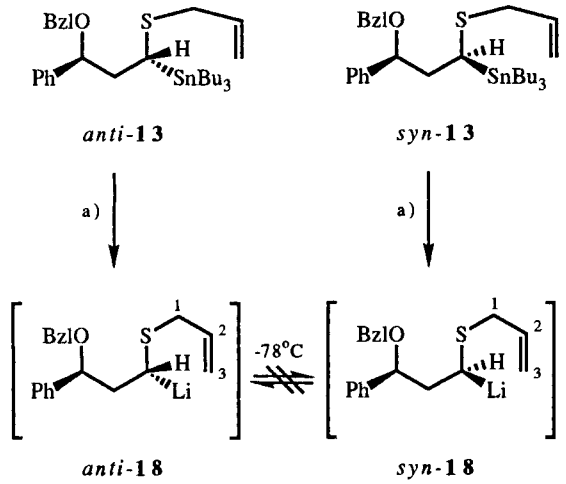
We felt safe to assign the *syn* configuration to this compound even though we lacked the diastereomer *anti*-**14** for comparisons. However, sufficient precedence has been collected in the literature showing that γ-benzyloxy alcohols like *syn*- and *anti*-**14** contain *reliably* an intramolecular hydrogen bond; it fixes them in six-membered chair-like rings as the ones depicted in Scheme 1[13b,19,23]. The stereostructure of the *isolated* diastereomer of **14** was then deduced from a comparison of its ^{1}H-NMR spectrum with characteristic reference data: The two large J_{vic} values displayed by one 2-H ($J_{2,1} = 11.5$ Hz, $J_{2,3} = 9.7$ Hz) in conjunction with the two small vicinal couplings displayed by the other ($J_{2,1} = 1.8$ Hz, $J_{2,3} = 3.9$ Hz) proves that the former 2-H is axially disposed and couples with two equally axially oriented vicinal protons. This proves the *syn*-configuration of **14**.

In an effort to corroborate this assignment we subjected the isolated diastereomer of **14** to the one-pot *O*-silylation/retro-[1,2]-Brook rearrangement sequence described by Linderman et al. for a similar system[24]. It led stereoselectively to the α-trimethylsilyl alcohol *syn*-**15**. The latter was labelled *syn* because its ^{1}H-NMR spectrum reveals a set of J_{vic} values which is very similar to that of the previous paragraph: The signal of one 2-H is split by $J_{2,1} = 11.2$ Hz and $J_{2,3} = 9.9$ Hz, that of the other by $J_{2,1} = 1.2$ Hz and $J_{2,3} = 3.8$ Hz. This order is again indicative for the $J_{ax,ax}/J_{ax,ax}$ and $J_{eq,ax}/J_{eq,ax}$ pattern expected in the *syn* diastereomer and disagrees with the J_{vic} values expected for the epimer *anti*-**15**. The implicit presupposition that *syn*-**15** has the hydrogen-

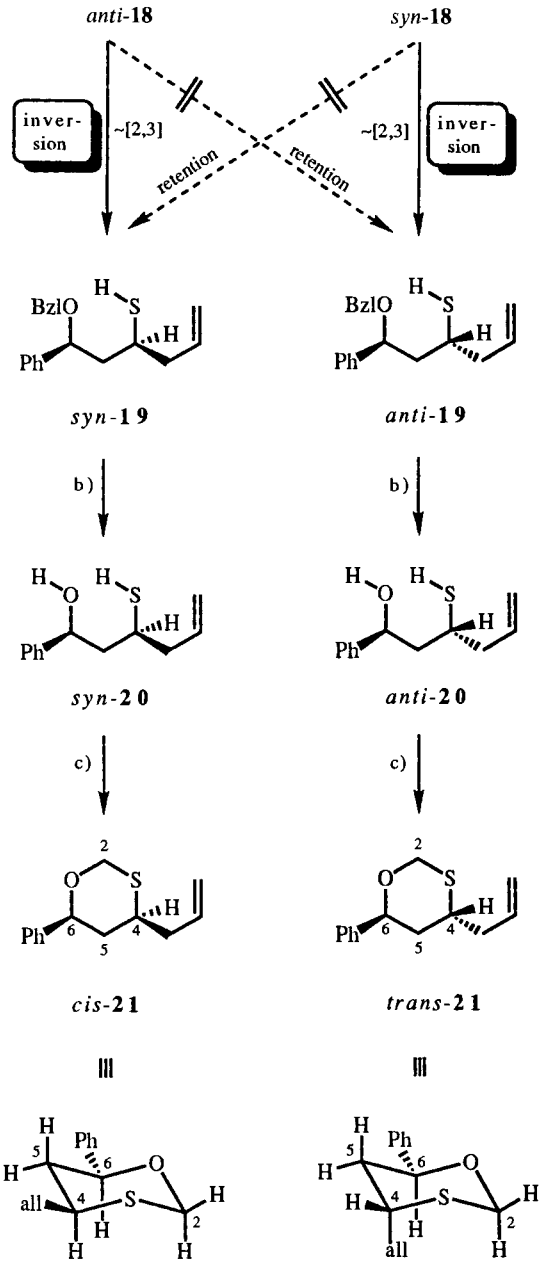
bridged ring structure depicted in Scheme 1 is well founded: For the closely related γ-alkoxy alcohol *syn*-**16** such bridging has been convincingly shown[23c]. Since the retro-Brook rearrangement **14**→**15** should proceed with retention of configuration at the carbanionic center[24], the obtention of *syn*-**15** constitutes the desired additional evidence for the *syn* configuration of the isolated diastereomer of **14**.

Having clarified their stereoformulae, we treated the stannylated sulfides *anti*- and *syn*-**13** in separate experiments at −78 °C in THF with excess *n*BuLi (Scheme 2, top half). They were presumably first converted by Sn/Li exchange with retention of configuration (*vide supra*) into the corresponding lithio sulfides *anti*- and *syn*-**18**, respectively. From **18**, thia-Wittig rearrangements ensued. They provided *isomerically pure* — upon aqueous quenching and a total reaction time of 30 min — the homoallyl thiol *syn*-**19** (79 %) starting from *anti*-**13** and the diastereomer *anti*-**19** (89 %) starting from *syn*-**13**. These rearrangements are therefore stereoselective and, in addition, stereospecific. The latter finding proves that the lithio sulfides *anti*- and *syn*-**18** are configurationally stable until they rearrange. Consequently, lithio sulfide *anti*-**18** reacts to thiol *syn*-**19** *directly* and not via the intermediacy of the epimer *syn*-**18**. Similarly, lithio sulfide *syn*-**18** furnishes thiol *anti*-**19** *directly* and not after epimerization. *Thus, the thia-Wittig rearrangements* **18** → **19** *occur with inversion of configuration at the carbanionic center.*

The configurational assignment of *syn*- vs. *anti*-**19** stemmed from the chemical correlations depicted in the bottom half of Scheme 2. Firstly, both diastereomers of thiol **19** were treated in separate experiments with excess lithium naphthalenide in order to cleave chemoselectively the primary in the presence of the secondary benzylic C—O bond[25]. Secondly, the resulting diastereomerically pure mercapto alcohols *syn*- and *anti*-**20** were incorporated into the oxathianes *cis*- and *trans*-**21**, respectively, by bisalkylation with CH_2Br_2 under phase-transfer catalysis[26]. The distinction of *cis*- vs. *trans*-**21** was readily accomplished by the comparison of pertinent ^{1}H-NMR data (Table 2) with the corresponding values of the structurally related oxathianes



Scheme 2



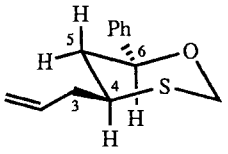
[a] *n*BuLi (2.5 equiv.), THF, −78 °C, 30 min; 79% *syn*-**19**, 89% *anti*-**19**. — [b] LiNaphth (4 equiv.), THF, −78 °C, 5 h; 51% *syn*-**20**, 53% *anti*-**20**. — [c] Slow addition to a refluxing 5:2 mixture of CH_2Br_2 and 50% aq. KOH containing $BnNEt_3^+Cl^-$ (0.4 equiv.), thereafter 1 h reflux; 53% *cis*-**21**, 49% *trans*-**21**.

cis- and *trans*-**22**[27]. Clearly, the shifts and J_{vic} values can be divided into two distinct sets. Each of them comprises a known (**22**) and a new compound (**21**). This circumstance shows unequivocally which configuration one has to attribute to both epimers of **21**.

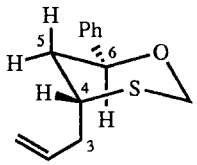
We realized that the homoallyl thiols **19** might result from the lithio sulfides **18** not only via the [2,3]-thia-Wittig rearrangement implied in Scheme 2 but also via a [1,2]-shift. We confirmed the first and ruled out the second possibility by repeating the rearrangement with a mixture of the deuterated α-stannyl sulfides 3-[D_2]-*anti*- and 3-[D_2]-*syn*-**13** (Scheme 3). The isotopic label of these compounds origi-

nated from the known[28] dideutero allyl alcohol **23**. The C–O bond of **23** was replaced regioselectively by a C–S bond after acylation with thiocarbonyl diimidazolide[29]. In refluxing acetonitrile the resulting ester **24** was isomerized via a [3,3] sigmatropic rearrangement to the allylically transposed ester **26**[30]. Treating **26** with NaOEt/EtOH liberated the deuterated sodium thiolate **25** within a few minutes (GLC analysis). **25** represented the best nucleophile in the resulting solution. Therefore, *it* reacted by a nucleophilic substitution with the diastereomeric stannyl bromides *syn,anti*-**12** which we added subsequently. The stannyl sulfides [D_2]-*anti,syn*-**13** resulted as a mixture of diastereomers. Unexpectedly, each of these diastereomers was also a mixture of isotopomers: While according to the 500-MHz ^{1}H-NMR spectrum 90% of the D_2 label was located as desired at C-3 (in 3-[D_2]-*syn,anti*-**13**), 10% were at C-1 (in 1-[D_2]-*syn,anti*-**13**). Hence, some [1,3] shift of the C–S bond must have happened in the course of this preparation.

Table 2. Selected ^{1}H-NMR shifts of the newly prepared (**21**; 400 MHz, $CDCl_3$) and known[27] 1,3-oxathianes (**22**; 60 MHz, CCl_4); *J* values in Hz

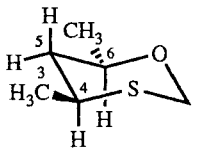


cis-**21**

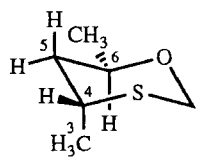


trans-**21**

Compound	$J_{6,5\text{-}H^{ax}}$	$J_{6,5\text{-}H^{eq}}$	$J_{4,5\text{-}H^{ax}}$	$J_{4,5\text{-}H^{eq}}$	$\delta_{3\text{-}H}$	$\delta_{6\text{-}H}$
cis-**21**	11.4	2.2	11.5	2.4	2.31	4.39
cis-**22**	10.4	2.0	11.2	2.7	1.22	3.44
trans-**21**	10.7	2.4	3.9	3.9	ca.2.73	4.73
trans-**22**	9.7	3.0	4.5	4.0	1.52	3.81



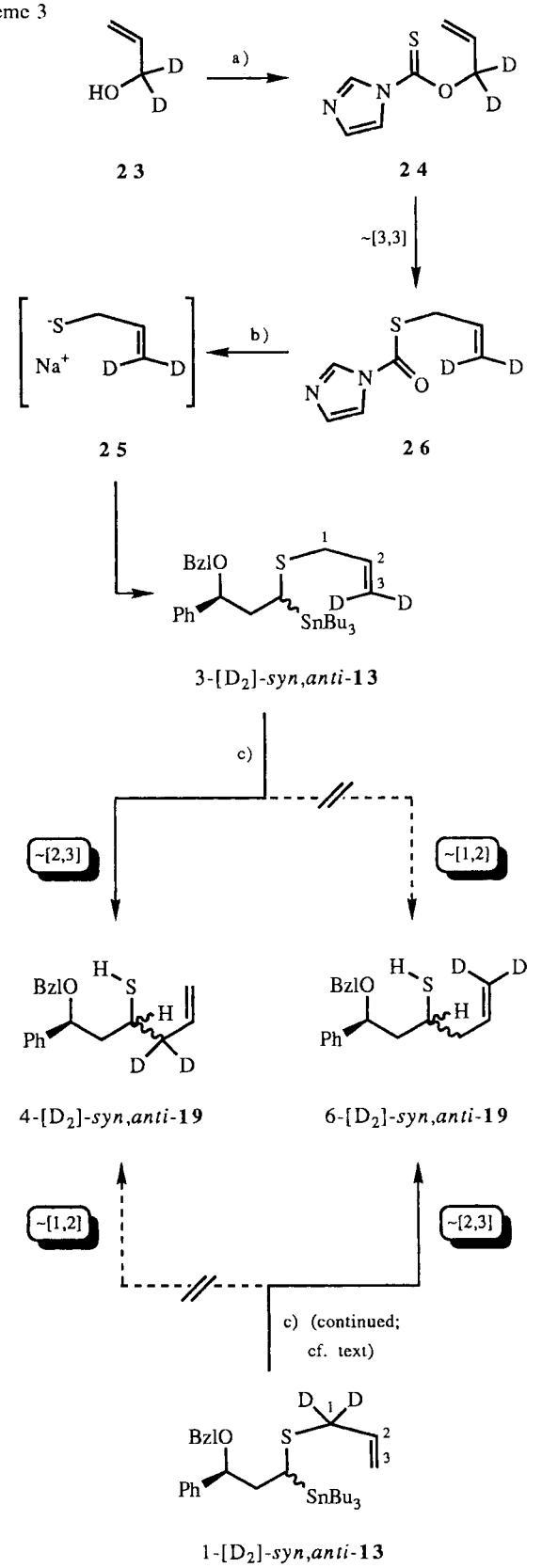
cis-**22**



trans-**22**

Nonetheless, our sample contained enough stannyl sulfide isotopomer 3-[D_2]-*anti,syn*-**13** for conducting a meaningful thia-Wittig rearrangement with it. Upon treatment with *n*BuLi it led through Sn/Li exchange and via [2,3] shift to the deuterated thiols [D_2]-*anti,syn*-**19** as a mixture of diastereomers (71%). As the 500 MHz ^{1}H-NMR spectrum revealed, these thiols constituted also a 94:6 mixture of isotopomers 4-[D_2]- and 6-[D_2]-*anti,syn*-**19**. Since this ratio is identical – within the error limits of the method – with the 90:10 isotopomer ratio of the starting materials 3-[D_2]- and 1-[D_2]-*anti,syn*-**13**, we conclude that the thia-Wittig rearrangements [D_2]-*anti,syn*-**13** → [D_2]-*anti,syn*-**19** and

Scheme 3

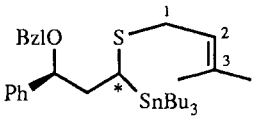


[a] S=C(imidazol)$_2$, acetonitrile, reflux, 3 h; 54% **26**. – [b] NaOEt, EtOH, then *syn,anti*-**12** (0.5 equiv.), room temp., 12 h; 59% of a 90:10 mixture of 3-[D_2]- and 1-[D_2]-*syn,anti*-**13**. – [c] *n*BuLi (3 equiv.), THF, –78°C, 30 min; 71% of a 94:6 mixture of 4-[D_2]- and 6-[D_2]-*syn,anti*-**19**.

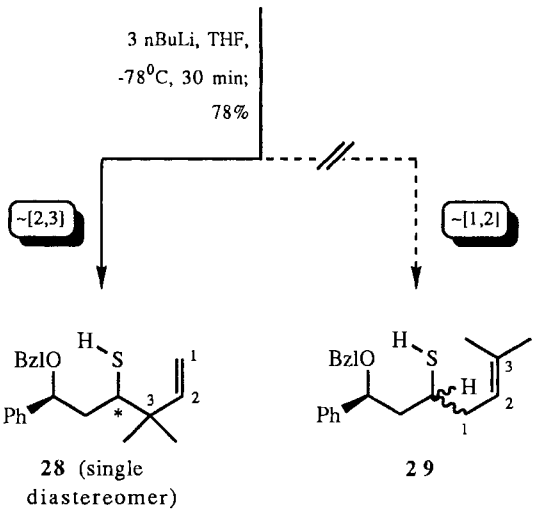
therefore *anti*-**13** → *syn*-**19** as well as *syn*-**13** → *anti*-**19**, too, belong to the [2,3] and not to the [1,2] type.

In summary, the results from Schemes 2 and 3 mean that the steric courses of thia- and oxa-[2,3]-Wittig rearrangements[13] are *identical* with respect to the geometry of the lithium-bearing carbon atom (if indeed it is bonded to lithium, cf. ref.[2a,b,f,g]): Its configuration is inverted.

Lithio sulfides with nonconjugated carbanionic moieties underwent [2,3]-thia-Wittig rearrangements at the expense of [1,2]-shifts in other cases, too. For example, the diastereomerically pure *prenyl* sulfide **27** gave only [2,3] rearrangement product **28**. The isomeric [1,2] rearrangement product **29** was not detected. It should be noted that **28** arose as a single though unassigned stereoisomer.



27 (single diastereomer)

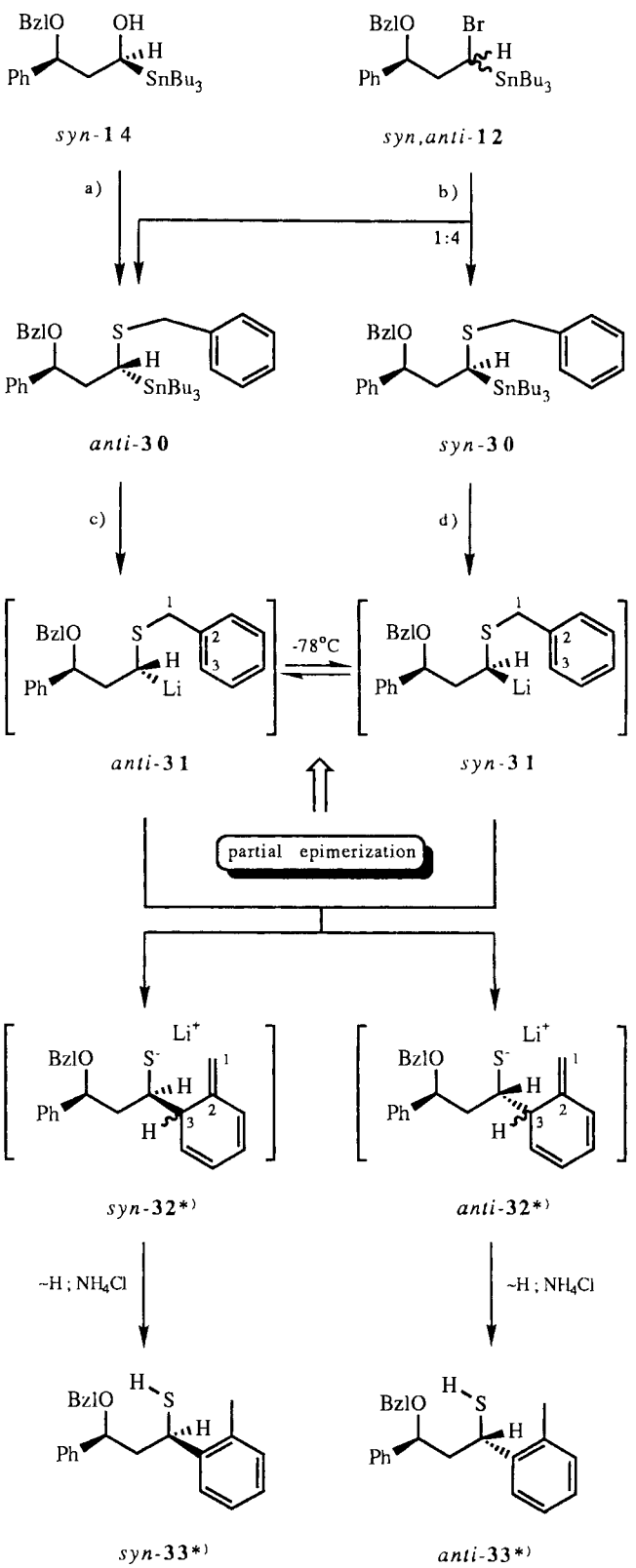


28 (single diastereomer) **29**

To our surprise the stannylated *benzyl* sulfides *anti*- and *syn*-**30** *also* turned out to be precursors for [2,3]- rather than [1,2]-thia-Wittig rearrangements (Scheme 4). These sulfides were obtained by an S_N reaction between $K^+-S-CH_2-C_6H_5$ and a mixture of the diastereomeric bromides *syn*- and *anti*-**12**. This preparation followed our protocol for the transformation $K^+-S-CH-CH=CH_2$ + **12** → **13** (Scheme 1); it provided **30** as a mixture of diastereomers. The *less abundant* of these diastereomers was identical with the *single* isomer of the same compound **30** obtained from a stereocontrolled route: it was accessible from the *syn*-configuration stannyl alcohol *syn*-**14** via the S_N displacement of the corresponding mesylate. Since this reaction should proceed with inversion of configuration at the Sn-bearing stereocenter the derived stannyl sulfide **30** must be *anti*-configurated.

The less laboriously obtained – and now configurationally assignable – 4:1 mixture of stannyl sulfides *syn*- and *anti*-**30** was parted into the pure diastereomers by repetitive

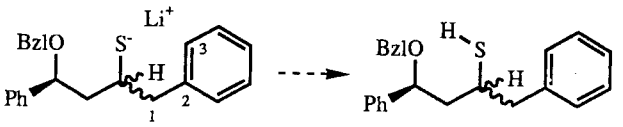
Scheme 4



[a] MsCl, NEt_3, CH_2Cl_2, −20°C, 2 h; addition to K^+-S-CH_2-Ph, 0°C, 5 h; 50%. – [b] K^+-S-CH_2-Ph in THF, room temp., *12 h*; 65%. – [c] *n*BuLi (3 equiv.), THF, −78°C, 30 min; 69% of a 71:29 mixture of *syn*- and *anti*-**33***. – [d] Same as[c]; 63% of a 72:28 mixture of *anti*- and *syn*-**33*** (*the configurational assignment is based on the assumption of inversion in the rearrangement step).

flash chromatography[22]. Thereafter, thia-Wittig rearrangements were performed. Within 30 min at −78°C in THF *anti*-**30** and *n*BuLi gave two thiols **33** as a 71:29 mixture of stereochemically unassigned diastereomers (69% yield). The same thiols were isolated in 63% yield but as a 28:72 mixture from the reaction between the isomeric stannyl sulfide *syn*-**30** and *n*BuLi. Obviously, the novel thia-Wittig rearrangements lack stereoselectivity.

The thiols **33** are substituted toluenes. This is unequivocally evidenced in their ^{1}H-NMR spectra by methyl singlets at $\delta = 2.32$ and 2.27. These singlets are incompatible with thiol structure **35**. Thiol **35** is the protonated form of **34**, the latter being the lithium thiolates which *would* have resulted from [1,2]-thia-Wittig rearrangements of the lithio sulfides **31** which themselves *were* formed by Sn/Li exchanges *anti*-**30** → *anti*-**31** and *syn*-**30** → *syn*-**31** from the stannylated sulfide. However, these lithio sulfides underwent [2,3]-thia-Wittig rearrangements giving the thiolates **32**. Tautomerization of **32** and protonation followed and led to the isolated rearrangement product **33**.

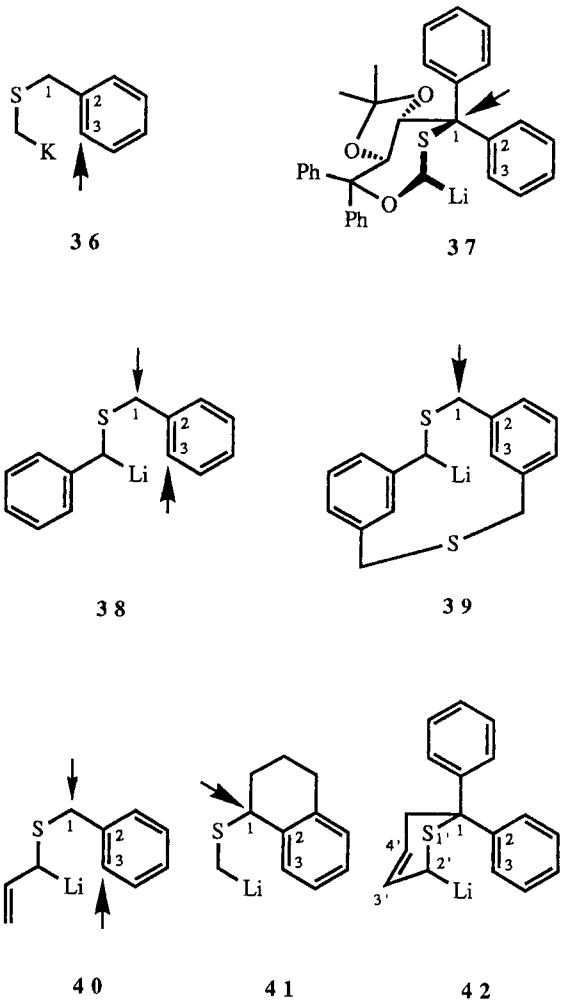


34 **35**

Remarkably, in the course of the rearrangements **31** → **32**, the aromaticity of one benzene ring is lost. This is a thermodynamic disadvantage from which the unobserved [1,2] shift would not suffer. The nonetheless observed dominance of the [2,3] shift indicates that the [1,2] rearrangement is kinetically hindered. If [1,2]-thia and [1,2]-oxa-Wittig rearrangement[31] adhered to the same mechanism, the rate determining step of the former would be the dissociation of the lithio sulfide R–CH(Li)–S–CH_2–C_6H_5 into the radical/radical anion pair R–C$^{\bullet}$H–S$^-$Li$^+$ + $H_2C^{\bullet}$–C_6H_5. This is obviously not easily possible.

A literature survey revealed that the rates of [2,3]-thia-Wittig rearrangements of other metalloalkyl benzyl sulfides are not always greater than those of alternative [1,2]-thia-Wittig rearrangements. For instance, the potassium sulfide **36** rearranges exclusively by the [2,3] mode[32]. The lithiated dibenzyl sulfide **38** – depending on the reaction conditions – undergoes either only a [2,3] rearrangement or is partitioned between the [2,3] and [1,2] rearrangement modes[32,33]. The lithio sulfide **40** prefers the [2,3]- over the [1,2]-thia-Wittig rearrangement route; moreover, some [4,5] rearrangement occurs[34,35]. On the other hand, *no* [2,3] rearrangements are observed when starting from the lithio sulfides **37**[36], **39**[37] or **41**[35]; these compounds undergo clean [1,2] shifts. Finally, lithio sulfide **42** evades both the [1,2] and [2,3] rearrangement pathways; it ring-contracts through a [1,4]-thia-Wittig rearrangement[38].

As expected, to break the aromatic sextet in the [2,3]-thia-Wittig rearrangements of the lithiated *benzyl* sulfides **31** (→ **32**; Scheme 4) slows down this reaction compared with the rearrangements of the lithiated *allyl* sulfides **18** (→ **19**; Scheme 1). To trespass the *increased* activation barrier costs the lithio sulfides *anti*- and *syn*-**30** so much time that they start to interconvert, i.e., to epimerize (*anti*-**31** ⇄ *syn*-**31**). However, epimerization remains incomplete. Otherwise, we would have found the *same* diastereoselectivity for *both* rearrangements *anti*-**31** → *anti*- + *syn*-**33** and *syn*-**31** → *anti*- + *syn*-**33**. The observed diastereoselectivities – 71:29 starting from *anti*-**31** and 28:72 starting from *syn*-**31** – differ from one another sufficiently to exclude a *full* equilibration *anti*-**31** ⇄ *syn*-**31** of the lithio sulfide intermediates. Clearly, the configurational stability of the lithioalkyl benzyl sulfides **31** is lost with nearly the same rate with which they rearrange.



36 **37**

38 **39**

40 **41** **42**

As already indicated, we could not elucidate the configurations of the diastereomeric rearrangement products *anti*- vs. *syn*-**33**. Therefore, the last set of experiments does not reveal whether the configuration of the carbanionic center is inverted or retained in the *rearrangement* step.

Financial support of this work by the *Deutsche Forschungsgemeinschaft* (SFB 347 „Selektive Reaktionen metallaktivierter Moleküle") is gratefully acknowledged. We thank *Chemetall GmbH* for donations of BuLi. Also, we are indebted to *C. Zolke* (Universität Göttingen) for measuring the 500-MHz ^{1}H-NMR spectra.

Experimental

All reactions were performed in oven-dried (100°C) glassware under dry nitrogen. During reductions with Li-Naphth, stirring bars with glass coating were used. THF was freshly distilled from K/Na. The molarity of THF solutions of Li-Naphth was determined by dropwise addition to 4-*tert*-butylcyclohexanol in THF until the green color persisted for ca. 10 s. Products were purified by flash chromatography[22] on Merck silica gel 60 (particle size 0.040–0.063 mm, 230–240 mesh ASTM; eluents given in brackets). Yields refer to analytically pure samples. Isomer ratios of diastereomeric mixtures were derived from suitable ^{1}H-NMR integrals. – ^{1}H and ^{13}C NMR (tetramethylsilane or $CHCl_3$ internal standard in $CDCl_3$): Bruker AC 200, AC 250, WH 400, Varian VXR/500S; integrals in accord with assignments; coupling constants in Hz; AB spectra: H_A refers to high- and H_B to low-field resonance; ^{13}C spectra: values refer to $\delta(^{13}CDCl_3) = 77.0$ ppm; ^{13}C-DEPT spectra: (+) for CH or CH_3, (–) for CH_2, (0) for C; ^{13}C-APT spectra: (+) for CH or CH_3, (–) for CH_2 or C. – MS: Finnigan MAT 95. – IR (film): Perkin-Elmer FT-IR 1600.

syn- and anti-1-(Benzyloxy)-3-bromo-1-phenyl-3-(tributylstannyl)propane (*syn,anti*-**12**): Diisopropylamine (4.3 g, 42 mmol, 1.2 equiv.) in THF (70 ml) was treated with *n*BuLi (1.50 mol/l in hexane; 25.9 ml, 39.0 mmol, 1.1 equiv.) for 10 min at –78°C. After 30 min tributyltin hydride (11.3 g, 39.0 mmol, 1.1 equiv.) was added followed 1 h later by 3-(benzyloxy)-3-phenylpropanal[19] (8.48 g, 35.3 mmol) in THF (20 ml). After another hour at –78°C the mixture was allowed to warm to room temp. and quenched with satd. aqueous NH_4Cl solution (200 ml). The organic layer was separated and washed with satd. aqueous NH_4Cl solution (200 ml), the aqueous layer was extracted with MTB (2 × 70 ml). The combined organic extracts were washed with satd. aqueous NaCl solution (250 ml), dried with Na_2SO_4 and liberated from solvent under reduced pressure. The residue (22.3 g), tetrabromomethane (11.7 g, 35.3 mmol, ⩾1 equiv.) and triphenylphosphane (9.25 g, 35.3 mmol, ⩾1 equiv.) were stirred in CH_2Cl_2 (200 ml) at room temp. for 6 h. The same aqueous workup as above (CH_2Cl_2 replacing MTB) delivered a crude product (36.9 g). Trituration with petroleum ether (3 × 50 ml) and flash chromatography [petroleum ether/MTB (petroleum ether → 10:1)] led to a configurationally unassigned 80:20 mixture of *syn,anti*-**12** (12.7 g, 60%). – *Major diastereomer:* ^{1}H NMR (400 MHz): δ = 0.83–1.07 (m, 3 × SnCH_2, 3 × CH_2CH_3), 1.18–1.56 (m, 3 × $CH_2CH_2CH_2$, 3 × $CH_2CH_2CH_3$), AB signal (δ_A = 2.11, δ_B = 2.24, J_{AB} = 15.2, in addition split by $J_{A,3}$ = 12.8, $J_{A,1}$ = 2.4, $J_{B,1}$ = 9.9, $J_{B,3}$ = 2.5, 2-H_2), 4.13 (dd topping a "mountain" of tin satellites, $J_{3,2\text{-}H^A}$ = 13.0, $J_{3,2\text{-}H^B}$ = 2.4, 3-H), AB signal (δ_A = 4.39, δ_B = 4.49, J_{AB} = 11.4, 1′-H_2), 4.78 (dd, $J_{1,2\text{-}H^B}$ = 10.1, $J_{1,2\text{-}H^A}$ = 2.3, 1-H), 7.26–7.45 (m, 1-C_6H_5, 1′-C_6H_5). – *Minor diastereomer* (superimposed in part by the major diastereomer): ^{1}H NMR (400 MHz): δ = 2.24–2.29 (m, 2-H^1), 2.66 (ddd, J_{gem} = 14.5, $J_{2,3}$ = 11.7, $J_{2,1}$ = 5.2, 2-H^2), 3.18 (dd, $J_{3,2\text{-}H^2}$ = 11.6, $J_{3,2\text{-}H^1}$ = 3.3, 3-H), AB signal (δ_A = 4.30, J_{AB} = 11.2, 1′-H_2), 4.71 (dd, $J_{1,2\text{-}H^1}$ = 8.6, $J_{1,2\text{-}H^2}$ = 5.1, 1-H). – IR (film): $\tilde{\nu}$ = 3065 cm^{-1}, 3030, 2955, 2930, 2870, 1495, 1455, 1415, 1375, 1340, 1085, 1075, 1025, 875, 760, 700, 670, 595.

$C_{28}H_{43}BrOSn$ (594.3) Calcd. C 56.59 H 7.29
Found C 56.37 H 7.46

syn- and anti-1-(Benzyloxy)-1-phenyl-3-[(2-propenyl)thio]-3-(tributylstannyl)propane (*syn,anti*-**13**): Allyl thiol (80%, 1.7 g, 19 mmol, 3 equiv.) was added at –78°C to KH (0.742 g, 18.5 mmol, 3 equiv.) in THF (5 ml). After 1 h the suspension was first warmed to room temp. and then recooled to 0°C. Under stirring a configurationally unassigned 80:20 mixture of *syn,anti*-**12** (3.67 g, 6.17 mmol) in THF (7 ml) was added. After 12 h at room temp. the reaction was quenched with satd. aqueous NH_4Cl solution (10 ml) and extracted with ether (2 × 40 ml). The crude product was flash-chromatographed once [petroleum ether/diethyl ether (300:1 → 150:1)] to give *syn,anti*-**13** as a 70:30 mixture (2.79 g, 77%) and subsequently several times [petroleum ether/diethyl ether (400:1)] to yield *syn*-**13** (0.825 g, 23%) in the early and *anti*-**13** (0.364 g, 10%) in the late fractions; the latter samples were *isomerically* entirely pure but contained small amounts of impurities. – *syn*-**13**: ^{1}H NMR (400 MHz): δ = 0.81–0.95 (m, 3 × SnCH_2, 3 × CH_2CH_3), 1.26 (tq, both *J* values ≈ 8, 3 × $CH_2CH_2CH_3$), 1.37–1.48 (m, 3 × $CH_2CH_2CH_2$), AB signal including tin satellites (δ_A = 2.05, δ_B = 2.30, J_{AB} = 14.7, in addition split by $J_{A,3}$ = 7.7, $J_{A,1}$ = 3.7, $J_{B,1}$ = 9.6, $J_{B,3}$ = 4.3, 2-H_2), 2.58 (dd including tin satellites, $J_{3,2\text{-}H^A}$ = 7.5, $J_{3,2\text{-}H^B}$ = 4.2, 3-H), AB signal (δ_A = 3.04, δ_B = 3.16, J_{AB} = 13.2, in addition split by $J_{A,2'}$ = 5.9, $J_{A,allyl}$ not resolved, $J_{B,2'}$ = 8.5, 1′-H_2), AB signal (δ_A = 4.25, δ_B = 4.40, J_{AB} = 11.4, 1″-H_2), 4.58 (dd, $J_{1,2\text{-}H^B}$ = 9.2, $J_{1,2\text{-}H^A}$ = 3.7, 1-H), 5.01 (dm_c, $J_{trans\text{-}3'\text{-}H,2'} \approx 17$, J_{gem} and J_{allyl} incompletely resolved, 3′-H_{trans}), 5.03 (dm_c, $J_{cis\text{-}3'\text{-}H,2'} \approx 9$, J_{gem} and J_{allyl} incompletely resolved, 3′-H_{cis}), 5.75 (dddd, $J_{2',trans\text{-}3'\text{-}H}$ = 16.7, $J_{2',cis\text{-}3'\text{-}H}$ = 10.2, $J_{2',1'\text{-}H^B}$ = 8.6, $J_{2',1'\text{-}H^A}$ = 6.0, 2′-H), 7.22–7.40 (m, 1-C_6H_5, 1″-C_6H_5). – ^{13}C NMR (100 MHz): δ = 9.97 (t including satellites for $^1J_{C,^{119}Sn}$ = 324.0 and $^1J_{C,^{117}Sn}$ = 309.9, 3 × SnCH_2), 13.68 (q, 3 × CH_2CH_3), 22.04 (d, C-3), 27.46 (t, including satellites for $^3J_{C,Sn}$ = 58.0, 3 × $CHCH_2CH_3$), 29.08 (t including satellites for $^2J_{C,Sn}$ = 19.8, 3 × $CH_2CH_2CH_2$), 35.30 (t including satellites for $^2J_{C,Sn}$ = 32.2, C-2), 42.38 (t, C-1′), 70.43 (t, C-1″), 80.15 (d, C-1), 116.94 (t, C-3′), 134.26 (d, C-2′), 126.79* (d), 127.32 (d), 127.62 (d), 127.68* (d), 128.12* (d), 128.52* (d), 138.55 (s), 142.67 (s) (2 × C_6H_5); * denotes *o*- or *m*- and not *p*-C (because of relatively high intensity). – IR (film): $\tilde{\nu}$ = 3065 cm^{-1}, 3030, 2955, 2920, 2870, 1635, 1490, 1455, 1425, 1375, 1345, 1215, 1090, 1050, 990, 915, 875, 760, 735, 700, 670, 595.

$C_{31}H_{48}OSSn$ (587.5) Calcd. C 63.38 H 8.24
Found C 63.20 H 8.43

anti-**13**: ^{1}H NMR (400 MHz): δ = 0.81–0.99 (m, 3 × SnCH_2, 3 × CH_2CH_3), 1.29 (tq, both *J* values 7.4, 3 × $CH_2CH_2CH_3$), 1.41–1.53 (m, 3 × $CH_2CH_2CH_2$), AB signal including tin satellites (δ_A = 2.05, δ_B = 2.26, J_{AB} = 14.4, in addition split by $J_{A,3}$ = 8.4, $J_{A,1}$ = 4.8, $J_{B,1}$ = 8.3, $J_{B,3}$ = 6.6, 2-H_2), 2.48 (dd including tin satellites, $J_{3,2\text{-}H^A}$ = 8.1, $J_{3,2\text{-}H^B}$ = 6.6, 3-H), 3.04 (d, $J_{1',2'}$ = 7.4, 1′-H_2), AB signal (δ_A = 4.23, δ_B = 4.41, J_{AB} = 11.6, 1″-H_2), 4.51 (dd, $J_{1,2\text{-}H^B}$ = 8.3, $J_{1,2\text{-}H^A}$ = 5.0, 1-H), 4.79 (ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 16.9, J_{gem} = J_{allyl} = 1.5, 3′-H_{trans}), 4.89 (dm_c, $J_{cis\text{-}3'\text{-}H,2'}$ = 9.9, J_{gem} and J_{allyl} incompletely resolved, 3′-H_{cis}), 5.68 (ddt, $J_{2',trans\text{-}3'\text{-}H}$ = 17.1, $J_{2',cis\text{-}3'\text{-}H}$ = 10.1, $J_{2',1'}$ = 7.3, 2′-H), 7.24–7.40 (m, 1-C_6H_5, 1″-C_6H_5). – ^{13}C NMR (100 MHz): δ = 9.65 (t including satellites for $^1J_{C,^{119}Sn}$ = 320.5 and $^1J_{C,^{117}Sn}$ = 306.4, 3 × SnCH_2), 13.66 (q, 3 × CH_2CH_3), 22.08 (d, C-3), 27.40 (t, including satellites for $^3J_{C,Sn}$ = 56.5, 3 × $CH_2CH_2CH_3$), 29.08 (t including satellites for $^2J_{C,Sn}$ = 19.8, 3 × $CH_2CH_2CH_2$), 37.07 (t including satellites for $^2J_{C,Sn}$ = 29.2, C-2), 44.61 (t, C-1′), 70.30 (t, C-1″), 80.19 (d, C-1), 116.56 (t, C-3′), 134.51 (d, C-2′), 126.86* (d), 127.43 (d), 127.62 (d), 127.73* (d), 128.23* (d), 128.53* (d), 138.44 (s), 142.55 (s) (2 × C_6H_5); * denotes *o*- or *m* and not *p*-C (because of relatively high intensity). – IR (film): $\tilde{\nu}$ = 3080 cm^{-1}, 3030, 2955, 2925, 2870, 2850, 1635, 1495, 1455, 1225, 1075, 990, 915, 735, 700, 595.

$C_{31}H_{48}OSSn$ (587.5) Calcd. C 63.38 H 8.24
Found C 63.41 H 8.38

Stereochemical Correlations

anti-1-(Benzyloxy)-1-phenyl-3-[(2-propenyl)thio]-3-(tributylstannyl)propane (*anti*-**13**): At –20°C methanesulfonyl chloride (0.02 ml, 0.03 g, 0.23 mmol, 1 equiv.) was added dropwise to *syn*-**14** (0.121

g, 0.228 mmol) and triethylamine (0.08 ml, 0.06 g, 0.6 mmol, 2.5 equiv.) in CH_2Cl_2 (3 ml). After 2 h at −20°C the mixture was transferred via cannula to a suspension of potassium allyl thiolate [prepared from allyl thiol (80%, 0.06 ml, 0.05 g, 0.6 mmol, 2.5 equiv.) and KH (0.018 g, 0.46 mmol, 2.0 equiv.) at −78°C] in THF (5 ml). After 5 h at 0°C the reaction was quenched with satd. aqueous NH_4Cl solution (3 ml) and the resulting mixture extracted with ether (4 × 15 ml). Purification by flash chromatography [petroleum ether/diethyl ether (300:1)] yielded *anti*-**13** (0.074 g, 55%) which was identified by its 200-MHz ^{1}H-NMR spectrum.

syn-3-(Benzyloxy)-3-phenyl-1-(tributylstannyl)-1-propanol (*syn*-**14**): A solution of diisopropylamine (0.13 g, 1.3 mmol, 1.2 equiv.) in THF (1 ml) was treated with *n*BuLi (1.21 mol/l in hexane; 0.99 ml, 1.2 mmol, 1.1 equiv.) at −78°C. After 30 min tributyltin hydride (0.35 g, 1.2 mmol, 1.1 equiv.) and after another 30 min, 3-(benzyloxy)-3-phenylpropanal[19] (**11**, 0.263 g, 1.09 mmol) was added. After 20 min the reaction was quenched with satd. aqueous NH_4Cl solution (3 ml) and extracted with H_2O and diethyl ether (3 × 20 ml). The crude product was purified by flash chromatography [petroleum ether/diethyl ether (50:1 → 10:1)] to yield *syn*-**14** (0.101 g, 17%). − ^{1}H NMR (400 MHz): δ = 0.77−0.96 (m, 3 $SnCH_2$, 3 CH_2CH_3), 1.23−1.33 and 1.43−1.52 (2 m, 3 $CH_2CH_2CH_2$, 3 $CH_2CH_2CH_3$), 1.87 (ddd, J_{gem} = 14.9, $J_{2,3}$ = 3.9, $J_{2,1}$ = 1.8, 2-H^1), 2.41 (ddd, J_{gem} = 14.9, $J_{2,1}$ = 11.5, $J_{2,3}$ = 9.7, 2-H^2), 3.40 (d including satellites for $^3J_{H,^{119}Sn} \approx 76$ and $^3J_{H,^{117}Sn} \approx 72$, $J_{OH,1}$ = 2.1, OH), AB signal (δ_A = 4.27, δ_B = 4.43, J_{AB} = 11.4, 1′-H$_2$), 4.28 (ddd, $J_{1,2\text{-}H^2}$ = 11.5, $J_{1,OH}$ = $J_{1,2\text{-}H^1}$ = 1.8, 1-H), 4.61 (dd, $J_{3,2\text{-}H^2}$ = 9.5, $J_{3,2\text{-}H^1}$ = 3.8, 3-H), 7.25−7.42 (m, 3-C_6H_5, 1′-C_6H_5). − ^{13}C NMR (50 MHz, impurities cause signals at δ ≈ 30 and 131.31): δ = 8.32 (t, 3 × $SnCH_2$), 13.66 (q, 3 × CH_2CH_3), 27.42 (t including satellites for $^3J_{C,Sn}$ = 36.6, 3 × $CH_2CH_2CH_3$), 29.15 (t, 3 × $CH_2CH_2CH_2$), 45.71 (t, C-2), 67.72 (d, C-1), 70.69 (t, C-1′), 85.94 (d, C-3), 126.61 (d), 127.91 (d), 128.46 (d), 128.64 (d), 137.89 (s), 141.62 (s) (2 × C_6H_5). − IR (film): $\tilde{\nu}$ = 3490 cm^{-1}, 3085, 3030, 2955, 2870, 1595, 1495, 1455, 1375, 1355, 1070, 760, 700.

$C_{28}H_{44}O_2Sn$ (531.4) Calcd. C 63.29 H 8.35
Found C 63.55 H 8.05

syn-3-(Benzyloxy)-3-phenyl-1-(trimethylsilyl)-1-propanol (*syn*-**15**): At −30°C trimethylsilyl triflate (0.51 ml, 0.59 g, 2.6 mmol, 1.5 equiv.) was added dropwise to a solution of *syn*-**14** (0.934 g, 1.76 mmol) and 2,6-lutidin (0.471 g, 4.39 mmol, 2.5 equiv.) in CH_2Cl_2 (5 ml). After 20 min the reaction mixture was poured into aqueous $NaHCO_3$ solution (25 ml) and extracted with diethyl ether (3 × 50 ml). The organic layer was dried with Na_2SO_4 and the solvents were removed under reduced pressure. The remaining silyl α-(tributylstannyl) ether was dissolved without purification in THF (10 ml) and treated with *n*BuLi (1.50 mol/l, 3.5 ml, 5.27 mmol, ⩾3 equiv.) at −78°C. After 20 min the reaction was quenched by the rapid addition of H_2O (5 ml). After dilution with petroleum ether (100 ml) and extraction with brine (50 ml), the organic layer was dried over Na_2SO_4 and liberated from solvent under reduced pressure. The residue was flash-chromatographed [petroleum ether/diethyl ether (100:1 → 10:1)] to yield *syn*-**15** (0.343 g, 62%). − ^{1}H NMR (200 MHz): δ = 0.00 [s, $Si(CH_3)_3$], 1.72 (ddd, J_{gem} = 14.8, $J_{2\text{-}H^1,3}$ = 3.8, $J_{2\text{-}H^1,1}$ = 1.2, 2-H^1), 2.07 (ddd, J_{gem} = 14.9, $J_{2\text{-}H^2,1}$ = 11.2, $J_{2\text{-}H^2,3}$ = 9.9, 2-H^2), 3.58 (br. d, $J_{1,2\text{-}H^2} \approx 13$, $J_{1,2\text{-}H^1}$ and $J_{1,OH}$ not resolved, 1-H), in part superimposed by 3.62 (br. s, OH), AB signal (δ_A = 4.28, δ_B = 4.44, J_{AB} = 11.4, 1′-H$_2$), 4.64 (dd, $J_{3,2\text{-}H^2}$ = 9.9, $J_{3,2\text{-}H^1}$ = 3.8, 3-H), 7.27−7.42 (m, 3-C_6H_5, 1′-C_6H_5). − ^{13}C NMR (50 MHz): δ = (+) −4.32 [$Si(CH_3)_3$], (−) 41.31 (C-2), (+) 66.24 (C-1), (−) 70.72 (C-1′), (+) 85.70 (C-3), (+) 126.64, (+) 127.76*, (+) 127.94**, (+) 128.49, (+) 128.67 [5 × Ar-CH; * denotes *p*-C (relatively low signal intensity), ** denotes superposition of *p*-C and another C (extra intensity)], (0) 137.76, (0) 141.68 (2 × Ar-C_{quat}). − IR (film): $\tilde{\nu}$ = 3485 cm^{-1}, 3065, 3030, 2955, 2870, 1680, 1625, 1605, 1495, 1455, 1395, 1360, 1245, 1055, 1030, 840, 750, 700.

$C_{19}H_{26}O_2Si$ (314.5) Calcd. C 72.56 H 8.33
Found C 72.64 H 8.50

syn-1-(Benzyloxy)-1-phenyl-5-hexene-3-thiol (*syn*-**19**): At −78°C *n*BuLi (1.32 mol/l in hexane; 2.0 ml, 2.68 mmol, 2.5 equiv.) was added dropwise to stannyl sulfide *anti*-**13** (0.629 g, 1.07 mmol) in THF (3 ml). After 30 min at −78°C the reaction was quenched with satd. aqueous NH_4Cl solution (2 ml) and extracted with ether (3 × 25 ml). Purification by flash chromatography [petroleum ether/diethyl ether (200:1)] yielded the thiol *syn*-**19** (0.252 g, 79%). − ^{1}H NMR (400 MHz): δ = 1.56 (d, $J_{SH,3}$ = 6.6, SH, exchangeable with D_2O), AB signal (δ_A = 1.98, δ_B = 2.12, J_{AB} = 14.2, in addition split by $J_{A,1}$ = $J_{A,3}$ = 6.8, $J_{B,1}$ = $J_{B,3}$ = 7.7, 2-H$_2$), AB signal (δ_A = 2.20, δ_B = 2.37, J_{AB} = 14.1, in addition split by $J_{A,3}$ = $J_{A,5}$ = 7.2, $J_{A,allyl}$ not resolved, $J_{B,5}$ = 6.4, $J_{B,3}$ = 5.1, $J_{B,allyl}$ = 1.3, 4-H$_2$), 2.79 (m$_c$, 3-H, signal form changes after exchanging the SH proton with D_2O), AB signal (δ_A = 4.24, δ_B = 4.42, J_{AB} = 11.6, 1′-H$_2$), 4.55 (dd, $J_{1,2\text{-}H^A}$ = $J_{1,2\text{-}H^B}$ = 7.0, 1-H), 5.04 (dm$_c$, $J_{trans\text{-}6\text{-}H,5} \approx 17$, J_{gem} and J_{allyl} incompletely resolved, 6-H_{trans}), 5.08 (dm$_c$, $J_{cis\text{-}6\text{-}H,5} \approx 10$, J_{gem} and J_{allyl} incompletely resolved, 6-H_{cis}), 5.71 (ddt, $J_{5,trans\text{-}6\text{-}H}$ = 17.0, $J_{5,cis\text{-}6\text{-}H}$ = 10.2, $J_{5,4}$ = 7.0, 5-H), 7.24−7.41 (m, 2 × C_6H_5). − ^{13}C NMR (100 MHz): δ = 36.42 (d, C-3), 42.80, 46.40 (2 t, C-2, C-4), 70.37 (t, C-1′), 79.21 (d, C-1), 117.89 (t, C-6), 134.81 (d, C-5), 126.96* (d), 127.61 (d), 127.87* (d), 127.94 (d), 128.37* (d), 128.61* (d), 138.30 (s), 141.44 (s) (2 × C_6H_5); * denotes *o*- or *m*- and not *p*-C (relatively high signal intensity). − IR (film): $\tilde{\nu}$ = 3065 cm^{-1}, 2930, 2865, 1640, 1495, 1455, 1205, 1095, 1070, 1025, 990, 915, 760, 735, 700.

$C_{19}H_{22}OS$ (298.4) Calcd. C 76.47 H 7.43
Found C 76.09 H 7.54

anti-1-(Benzyloxy)-1-phenyl-5-hexene-3-thiol (*anti*-**19**): At −78°C *n*BuLi (1.40 mol/l in hexane; 1.4 ml, 2.0 mmol, 2.5 equiv.) was added dropwise to stannyl sulfide *syn*-**13** (0.458 g, 0.779 mmol) in THF (3 ml). After 30 min the reaction was quenched with satd. aqueous NH_4Cl solution (2 ml) and extracted with diethyl ether (3 × 25 ml). Purification by flash chromatography (petroleum ether/diethyl ether (200:1)] yielded the thiol *anti*-**19** (0.208 g, 89%). − ^{1}H NMR (400 MHz): δ = 1.41 (d, $J_{SH,3}$ = 7.3, SH, exchangeable with D_2O), 1.57 (ddd, J_{gem} = 14.2, $J_{2\text{-}H^1,3}$ = 11.1, $J_{2\text{-}H^1,1}$ = 2.9, 2-H^1), 2.17 (ddd, J_{gem} = 14.2, $J_{2\text{-}H^2,1}$ = 10.7, $J_{2\text{-}H^2,3}$ = 3.3, 2-H^2), AB signal (δ_A = 2.30, δ_B = 2.41, $J_{AB} \approx 14$, in addition split by $J_{A,3}$ = $J_{A,5} \approx 7$, $J_{A,allyl}$ not resolved, $J_{B,3}$ = $J_{B,5} \approx 7$, $J_{B,allyl}$ incompletely resolved, 4-H$_2$), 3.27 (m$_c$, 3-H, signal form changes after exchanging the SH proton with D_2O), AB signal (δ_A = 4.27, δ_B = 4.47, J_{AB} = 11.6, 1′-H$_2$), 4.69 (dd, $J_{1,2\text{-}H^2}$ = 10.5, $J_{1,2\text{-}H^1}$ = 2.9, 1-H), 5.08 (dm$_c$, $J_{trans\text{-}6\text{-}H,5} \approx 17$, J_{gem} and J_{allyl} incompletely resolved, 6-H_{trans}), 5.09 (dm$_c$, $J_{cis\text{-}6\text{-}H,5} \approx 10$, J_{gem} and J_{allyl} incompletely resolved, 6-H_{cis}), 5.80 (ddt, $J_{5,trans\text{-}6\text{-}H}$ = 16.9, $J_{5,cis\text{-}6\text{-}H}$ = 10.2, $J_{5,4}$ = 6.9, 5-H), 7.27−7.41 (m, 1-C_6H_5, 1′-C_6H_5). − H,H-decoupling experiments for the assignments of the couplings between 1-H, 2-H$_2$ and 3-H: Irradiation at δ = 4.69 (1-H) converted the ddd at δ = 1.57 (2-H^1) into a dd (J_{gem} = 14.2 and $J_{2\text{-}H^1,3}$ = 11.1, i.e., $J_{2\text{-}H^1,1}$ vanished) and the ddd at δ = 2.17 (2-H^2) into a dd (J_{gem} = 14.2 and $J_{2\text{-}H^2,3}$ = 3.3, i.e., $J_{2\text{-}H^2,1}$ vanished). Irradiation at δ = 3.27 (3-H) simplified the ddd δ = 1.57 (2-H^1), where $J_{2\text{-}H^1,3}$ vanished, converted the ddd at δ = 2.17 (2-H^2) into a dd (J_{gem} = 14.2 and $J_{2\text{-}H^2,1}$ = 10.7, i.e., $J_{2\text{-}H^2,3}$ vanished), simplified the AB signal δ = 2.30/2.41 (4-H$_2$), where $J_{4,3}$ vanished, and removed the doublet splitting of δ = 1.41 (SH). − ^{13}C NMR (100 MHz): δ = 36.99 (d, C-3), 43.74, 47.47 (2 t, C-2, C-4), 70.78 (t, C-1′), 78.73 (d, C-1), 117.77 (t, C-6), 135.04 (d, C-5), 126.59* (d), 127.68* (d), 128.03 (d), 128.41* (d), 128.58* (d), 138.35 (s), 142.33 (s)

(2 × C_6H_5); * denotes *o*- or *m*- and not *p*-C (relatively high signal intensity). – IR (film): $\tilde{\nu}$ = 3065 cm^{-1}, 3030, 2905, 2890, 2570, 1640, 1605, 1495, 1455, 1350, 1205, 1100, 1065, 1025, 995, 915, 760, 736, 700, 610.

$C_{19}H_{22}OS$ (298.4) Calcd. C 76.47 H 7.43
Found C 76.73 H 7.50

syn-3-Mercapto-1-phenyl-5-hexene-1-ol (*syn*-**20**): At −78 °C lithium naphthalenide (0.85 mol/l in THF; 1.2 ml, 1.1 mmol, 4.0 equiv.) was added dropwise to the thiol *syn*-**19** (0.079 g, 0.265 mmol) in THF (1 ml). After 5 h at −78 °C the reaction was quenched with satd. aqueous NH_4Cl solution (3 ml) and extracted with ether (2 × 30 ml). Purification by flash chromatography [petroleum ether/diethyl ether (100:1 → 5:1)] yielded alcohol *syn*-**20** (0.028 g, 51%). – ^{1}H NMR (400 MHz): δ = 1.62 (d, $J_{SH,3}$ = 7.4, SH), AB signal (δ_A = 2.00, δ_B = 2.05, J_{AB} = 14.1, in addition split by $J_{A,3}$ = 8.7, $J_{A,1}$ = 7.3, $J_{B,1}$ = 6.5, $J_{B,3}$ = 5.4, 2-H_2), 2.23 (br. s, OH), AB signal (δ_A = 2.32, δ_B = 2.45, J_{AB} ≈ 14, in addition split by $J_{A,3}$ = $J_{A,5}$ ≈ 7, $J_{A,allyl}$ not resolved, $J_{B,5}$ ≈ 7, $J_{B,3}$ ≈ 5–6, $J_{B,allyl}$ = 1.3, 4-H_2), 2.78 (ddddd, $J_{3,2\text{-}H^A}$ = $J_{3,4\text{-}H^A}$ = 8.8, $J_{3,SH}$ = 7.2, $J_{3,2\text{-}H^B}$ = $J_{3,4\text{-}H^B}$ = 5.3, 3-H), 4.92 (t, $J_{1,2}$ = 6.9, 1-H), 5.10 (dm_c, $J_{trans\text{-}6\text{-}H,5}$ ≈ 16–17, J_{gem} and J_{allyl} incompletely resolved, 6-H_{trans}), 5.12 (dm_c, $J_{cis\text{-}6\text{-}H,5}$ ≈ 11, J_{gem} and J_{allyl} incompletely resolved, 6-H_{cis}), 5.76 (this signal was only expanded and hence only interpreted at a field strength of 200 MHz; essentially ddt, but transition to higher order spectrum, $J_{5,trans\text{-}6\text{-}H}$ = 16.2, $J_{5,cis\text{-}6\text{-}H}$ = 11.0, $J_{5,4}$ = 7.0, 5-H), 7.27–7.40 (m, C_6H_5). – Homodecoupling experiments for the assignments of SH and OH: Irradiation at δ = 2.78 (3-H) simplified the two AB signals δ = 2.00/2.05 (2-H_2) where $J_{2,3}$ vanished, and δ = 2.32/2.45 (4-H_2) where $J_{4,3}$ vanished, and removed the doublet splitting of δ = 1.62 (SH). Irradiation at δ = 4.92 (1-H) simplified one AB signal δ = 2.00/2.05 (2-H_2) where $J_{2,1}$ vanished. – ^{13}C NMR (50 MHz): δ = (+) 37.19 (C-3), (−) 43.52, (−) 47.01 (C-2, C-4), (+) 73.09 (C-1), (−) 118.09 (C-6), (+) 126.03, (+) 127.91*, (+) 128.64 [3 × Ar-*C*H; * denotes *p*-C (relatively low intensity)], (+) 134.67 (C-5), (0) 143.83 (Ar-C_{quat}). – IR (film): $\tilde{\nu}$ = 3390 cm^{-1}, 3065, 3030, 2930, 1640, 1495, 1455, 1435, 1280, 1200, 1030, 1000, 915, 760, 700, 555.

$C_{12}H_{16}OS$ (208.3) Calcd. C 69.19 H 7.74
Found C 69.09 H 7.79

anti-3-Mercapto-1-phenyl-5-hexene-1-ol (*anti*-**20**): At −78 °C lithium naphthalenide (0.85 mol/l in THF; 2.5 ml, 2.1 mmol, 3.9 equiv.) was added dropwise to the thiol *anti*-**19** (0.164 g, 0.550 mmol) in THF (2 ml). After 5 h at −78 °C the reaction was quenched with satd. aqueous NH_4Cl solution (5 ml) and extracted with diethyl ether (2 × 50 ml). Purification by flash chromatography [petroleum ether/diethyl ether (100:1 → 5:1)] yielded alcohol *anti*-**20** (0.061 g, 53%). – ^{1}H NMR (250 MHz): δ = 1.59 (d, $J_{SH,3}$ = 7.2, SH), 1.67 (ddd, J_{gem} = 14.2, $J_{2\text{-}H^1,3}$ = 11.0, $J_{2\text{-}H^1,1}$ = 3.1, 2-H^1), 2.04 (br. s, OH), 2.12 (ddd, J_{gem} = 14.2, $J_{2\text{-}H^2,1}$ = 10.3, $J_{2\text{-}H^2,3}$ = 3.7, 2-H^2), 2.27–2.52 (m, 4-H_2), 3.13–3.31 (m, 3-H), 5.02 (dd, $J_{1,2\text{-}H^2}$ = 10.1, $J_{1,2\text{-}H^1}$ = 2.7, 1-H), 5.11 (dm_c, $J_{trans\text{-}6\text{-}H,5}$ ≈ 18, J_{gem} and J_{allyl} incompletely resolved, 6-H_{trans}), 5.12 (dm_c, $J_{cis\text{-}6\text{-}H,5}$ ≈ 10, J_{gem} and J_{allyl} incompletely resolved, 6-H_{cis}), 5.82 (ddt with extra peaks indicating transition to higher order spectrum, $J_{5,trans\text{-}6\text{-}H}$ = 18.3, $J_{5,cis\text{-}6\text{-}H}$ = 8.9, $J_{5,4}$ = 7.0, 5-H), 7.23–7.41 (m, C_6H_5). – ^{13}C NMR (50 MHz): δ = (+) 37.04 (C-3), (−) 44.01, (−) 47.38 (C-2, C-4), (+) 71.85 (C-1), (−) 117.93 (C-6), (+) 125.61, (+) 127.61*, (+) 128.55 [3 × Ar-*C*H; * denotes *p*-C (relatively low intensity)], (+) 134.94 (C-5), (0) 144.62 (Ar-C_{quat}). – IR (film): $\tilde{\nu}$ = 3410 cm^{-1}, 2930, 1640, 1600, 1495, 1455, 1280, 1055, 915.

$C_{12}H_{16}OS$ (208.3) Calcd. C 69.19 H 7.74
Found C 68.95 H 8.16

cis-6-Phenyl-4-(2-propenyl)-1,3-oxathian (*cis*-**21**): Alcohol *syn*-**20** (0.025 g, 0.12 mmol) in CH_2Br_2 (10 ml) was added very slowly (50 min with help of a syringe pump) under vigorous stirring to a refluxed mixture of CH_2Br_2 (15 ml), 50% aqueous KOH solution (10 ml), and benzyltriethylammonium chloride (0.011 g, 0.048 mmol, 0.4 equiv.). After refluxing for 1 h the recooled solution was extracted with diethyl ether (2 × 100 ml). The combined extracts were dried with Na_2SO_4 and liberated from the solvent in vacuo. Purification by flash chromatography [petroleum ether/diethyl ether (200:1 → 10:1)] yielded O,S-acetal *cis*-**21** (0.014 g, 53%). – ^{1}H NMR (400 MHz): δ = 1.69 (ddd, J_{gem} = 13.9, $J_{5\text{-}H^1,4}$ = $J_{5\text{-}H^1,6}$ = 11.4, 5-H^1), 2.06 (ddd, J_{gem} = 13.8, $J_{5\text{-}H^2,4}$ = $J_{5\text{-}H^2,6}$ = 2.3, 5-H^2), 2.31 (dd, $J_{1',2'}$ = $J_{1',4}$ = 6.9, 1′-H_2), 3.24 (dtd, $J_{4,5\text{-}H^1}$ = 11.6, $J_{4,1'}$ = 6.9, $J_{4,5\text{-}H^2}$ = 2.5, 4-H), 4.39 (dd, $J_{6,5\text{-}H^1}$ = 11.4, $J_{6,5\text{-}H^2}$ = 2.0, 6-H), AB signal (δ_A = 5.01, δ_B = 5.05, J_{AB} = 11.3, B part broadened, 2-H_2), 5.10 (dm_c, $J_{cis\text{-}3'\text{-}H,2'}$ ≈ 10, J_{gem} and J_{allyl} incompletely resolved, 3′-H_{cis}), 5.11 (dm_c, $J_{trans\text{-}3'\text{-}H,2'}$ ≈ 17, J_{gem} and J_{allyl} incompletely resolved, 3′-H_{trans}), 5.81 (ddt, $J_{2',trans\text{-}3'\text{-}H}$ = 16.7, $J_{2',cis\text{-}3'\text{-}H}$ = 10.3, $J_{2',1'}$ = 7.0, 2′-H), 7.25–7.36 (m, C_6H_5). – ^{13}C NMR (125 MHz): δ = (−) 40.45, (−) 41.09 (C-1′, C-5), (+) 42.21 (C-4), (−) 71.38 (C-2), (+) 81.79 (C-6), (−) 117.88 (C-3′), (+) 125.88, (+) 127.84, (+) 128.48 (3 × Ar-*C*H), (+) 134.03 (C-2′), (−) 141.85 (Ar-C_{quat}). – IR (film): $\tilde{\nu}$ = 2920 cm^{-1}, 2850, 1730, 1455, 1245, 1060, 995, 915, 755, 700.

$C_{13}H_{16}OS$ (220.3) Calcd. C 70.87 H 7.32
Found C 70.94 H 7.33

trans-6-Phenyl-4-(2-propenyl)-1,3-oxathian (*trans*-**21**): Alcohol *anti*-**20** (0.071 g, 0.34 mmol) in CH_2Br_2 (10 ml) was added very slowly (50 min with help of a syringe pump) under vigorous stirring to a refluxed mixture of CH_2Br_2 (15 ml), 50% aqueous KOH solution (10 ml), and benzyltriethylammonium chloride (0.031 g, 0.14 mmol, 0.4 equiv.). After refluxing for 1 h the recooled solution was extracted with diethyl ether (2 × 100 ml). The combined extracts were dried with Na_2SO_4 and liberated from the solvent in vacuo. Purification by flash chromatography [petroleum ether/diethyl ether (200:1 → 10:1)] yielded O,S-acetal *trans*-**21** (0.037 g, 49%). – ^{1}H NMR (400 MHz): δ = AB signal (δ_A = 1.97, δ_B = 2.29, J_{AB} = 14.3, in addition split by $J_{A,4}$ = 3.8, $J_{A,6}$ = 2.5, $J_{B,6}$ = 10.5, $J_{B,4}$ = 4.2, 5-H_2), AB signal (δ_A = 2.71, δ_B = 2.80, J_{AB} = 14.2, in addition split by $J_{A,2'}$ = $J_{A,4}$ = 7.5, $J_{B,4}$ = 7.7, $J_{B,2'}$ = 6.4, $J_{B,allyl}$ not resolved, 1′-H_2), 3.10 (dddd, $J_{4,1'\text{-}H^A}$ = $J_{4,1'\text{-}H^B}$ = 7.8, $J_{4,5\text{-}H^A}$ = $J_{4,5\text{-}H^B}$ = 4.0, 4-H), 4.73 (dd, $J_{6,5\text{-}H^B}$ = 10.8, $J_{6,5\text{-}H^A}$ = 2.2, 6-H), 4.87 (d, J_{gem} = 11.3, 2-H^1), 5.15 (dm_c, $J_{cis\text{-}3'\text{-}H,2'}$ ≈ 10, J_{gem} and J_{allyl} not resolved, 3′-H_{cis}), in part superimposed by 5.18 (dm_c, $J_{trans\text{-}3'\text{-}H,2'}$ ≈ 17, J_{gem} and J_{allyl} incompletely resolved, 3′-H_{trans}), superimposed by 5.19 (d, J_{gem} = 11.6, 2-H^2), 5.88 (dddd, $J_{2',trans\text{-}3'\text{-}H}$ = 16.8, $J_{2',cis\text{-}3'\text{-}H}$ = 10.4, $J_{2',1'\text{-}H^A}$ = 7.6, $J_{2',1'\text{-}H^B}$ = 6.6, 2′-H), 7.25–7.38 (m, C_6H_5). – ^{13}C NMR [50 MHz, small impurity at δ = 30.22 (+)]: δ = (−) 29.70, (−) 36.82 (C-1′, C-5), (+) 37.52 (C-4), (−) 66.36 (C-2), (+) 75.42 (C-6), (−) 117.30 (C-3′), (+) 125.91, (+) 127.70*, (+) 128.49 [3 × Ar-*C*H; * denotes *p*-C (relatively low intensity)], (+) 135.73 (C-2′), (0) 141.68 (Ar-C_{quat}). – IR (film): $\tilde{\nu}$ = 2920 cm^{-1}, 2850, 1730, 1455, 1365, 1245, 1060, 995, 915, 755, 700. – $C_{13}H_{16}OS$: calcd. 220.0921; the molecular mass (±2 ppm; *R* = 10000) was checked by EI HRMS of the exact mass.

1-[(3,3-Dideuterio-2-propenyl)thiocarbonyl]imidazol (**26**): The yellow solution of 3,3-dideuterioallyl alcohol[28] (**23**, 1.20 ml, 1.00 g, 16.6 mmol) and thiocarbonyl diimidazolide (3.56 g, 19.9 mmol, 1.2 equiv.) in CH_3CN (40 ml) was refluxed for 3 h. The reaction was quenched with H_2O (40 ml) and extracted with Et_2O (5 × 50 ml). Purification by flash chromatography [petroleum ether/diethyl ether (3:1)] gave a slightly contaminated sample of **26** (1.52 g, ≤54%). – ^{1}H NMR (250 MHz): δ = 3.79 (d, $J_{1',2'}$ = 7.0, 1′-H_2), 5.90 (m_c, 2′-H), 7.10 and 7.47 (2 m_c, 4-H, 5-H), 8.20 (s, 2-H).

syn- and anti-1-(Benzyloxy)-3-[(3,3-dideuterio-2-propenyl)thio]-1-phenyl-3-(tributylstannyl)propane (3-[D_2]-*syn,anti*-**13**) in a 90:10

mixture with *syn- and anti-1-(Benzyloxy)-3-[(1,1-dideuterio-2-propenyl)thio]-1-phenyl-3-(tributylstannyl)propane* (1-[D_2]-*syn,anti*-**13**): NaOEt (1.0 mol/l in EtOH; 6.7 ml, 6.7 mmol, 1.2 equiv.) was added to thio ester **26** (0.948 g, 5.57 mmol) in EtOH (5 ml) at room temp. After 10 min a configurationally unassigned 80:20 mixture of *syn,anti*-**12** (1.65 g, 2.78 mmol, 0.5 equiv.) was added to the reaction mixture. After 12 h at room temp. the reaction was quenched with satd. aqueous NH_4Cl solution (20 ml) and extracted with diethyl ether (5 × 40 ml). Purification by flash chromatography [petroleum ether/diethyl ether (100:1)] furnished a 90:10 mixture (0.968 g, 59%) of 3-[D_2]-**13** and 1-[D_2]-**13**; therein, 3-[D_2]-**13** was a 67:33 *syn,anti* mixture. – ^{1}H NMR (500 MHz): $\delta_{olefinic}$ = 4.80 (dd, $J_{trans\text{-}3'\text{-}H,2'}$ = 16.9, J_{gem} = 1.6, 3'-H_{trans} of 1-[D_2]-*anti*-**13**), 4.90 (dd, $J_{cis\text{-}3'\text{-}H,2'}$ = 10.0, J_{gem} = 1.8, 3'-H_{cis} of 1-[D_2]-*anti*-**13**), 5.01 (dd, $J_{trans\text{-}3'\text{-}H,2'} \approx 17$, J_{gem} = 1.6, 3'-H_{trans} of 1-[D_2]-*syn*-**13**), 5.04 (dd, $J_{cis\text{-}3'\text{-}H,2'} \approx 10$, J_{gem} = 1.7, 3'-H_{cis} of 1-[D_2]-*syn*-**13**), 5.67 (br. t, $J_{2',1'} \approx 3$, $J_{2',3'\text{-}D}$ not resolved, 2'-H of 3-[D_2]-*anti*-**13**), 5.74 (br. t, $J_{2',1'} \approx 4$, $J_{2',3'\text{-}D}$ not resolved, 2'-H of 3-[D_2]-*syn*-**13**).

syn- and anti-1-(Benzyloxy)-4,4-dideuterio-1-phenyl-5-hexene-3-thiol (4-[D_2]-*syn,anti*-**19**), *mixed in a 94:6 ratio with anti-1-(Benzyloxy)-6,6-dideuterio-1-phenyl-5-hexene-3-thiol* (6-[D_2]-*anti*-**19**): At –78°C *n*BuLi (1.32 mol/l in hexane; 1.10 ml, 1.51 mmol, 3.0 equiv.) was added dropwise to a 90:10 mixture (0.297 g, 0.504 mmol) of stannyl sulfides 3-[D_2]-*syn,anti*-**13** (which itself was a 67:33 *syn,anti* mixture) and 1-[D_2]-*syn,anti*-**13** in THF (2 ml). After 30 min the reaction was quenched with satd. aqueous NH_4Cl solution (2 ml) and extracted with diethyl ether (3 × 25 ml). Purification by flash chromatography [petroleum ether/diethyl ether (200:1)] yielded a 94:6 mixture (0.082 g, 71%) of the thiols 4-[D_2]-**19** (which itself was a 13:87 *syn,anti* mixture) and 6-[D_2]-*anti*-**19**. – ^{1}H NMR (500 MHz): $\delta_{allylic}$ = 2.29–2.33 and 2.38–2.41 (2 m, 4-H_2 of 6-[D_2]-*anti*-**19**); $\delta_{olefinic}$ = 5.02–5.12 (m, 6-H_2 of 4-[D_2]-*syn,anti*-**19**), 5.70 (dd, $J_{5,trans\text{-}6\text{-}H}$ = 17.0, $J_{5,cis\text{-}6\text{-}H}$ = 10.2, 5-H of 4-[D_2]-*syn*-**19**), 5.80 (dd, $J_{5,trans\text{-}6\text{-}H}$ = 16.9, $J_{5,cis\text{-}6\text{-}H}$ = 10.4, 5-H of 4-[D_2]-*anti*-**19**).

1-(Benzyloxy)-3-[(3-methyl-2-butenyl)thio]-1-phenyl-3-(tributylstannyl)propane (**27**, single diastereomer): Prenyl thiol (0.607 g, 5.95 mmol, 3 equiv.) was added at –78°C to KH (0.238 g, 5.95 mmol, 3 equiv.) in THF (5 ml). After 1 h the suspension was first warmed to room temp. and then recooled to 0°C. A configurationally unassigned 80:20 mixture of *syn,anti*-**12** (1.18 g, 1.98 mmol) in THF (5 ml) was added. After stirring for 12 h at room temp. the reaction was quenched with satd. aqueous NH_4Cl solution (10 ml) and extracted with diethyl ether (2 × 30 ml). The crude product was flash-chromatographed [petroleum ether/diethyl ether (200:1)] to give a mixture containing **27** (62:38 mixture of diastereomers, 0.541 g, 44%) and 1-(benzyloxy)-1-phenyl-1-propene (single isomer, 0.171 g, 39%). After two more flash chromatographies [petroleum ether/diethyl ether (300:1)] we isolated *that* diastereomer of **27** isomerically pure which had constituted the major diastereomer after the first of the three mentioned chromatographies (0.064 g, configuration unknown). – **27**: ^{1}H NMR (250 MHz): δ = 0.81–1.01 (m, 3 × $SnCH_2$, 3 × CH_2CH_3), 1.18–1.54 (m, 3 × $CH_2CH_2CH_2$, 3 × $CH_2CH_2CH_3$), 1.63 and 1.71 (2 s, 4'-H_3 and 3'-CH_3), AB signal (δ_A = 2.06, δ_B = 2.35, $J_{AB} \approx 15$, in addition split by $J_{A,3}$ = 8.0, $J_{A,1}$ = 4.0, $J_{B,1}$ = 9.0, $J_{B,3}$ = 5.0, 2-H_2), 2.52 (dd, $J_{3,2\text{-}H^A}$ = 7.4, $J_{3,2\text{-}H^B}$ = 5.0, 3-H), AB signal (δ_A = 3.03, δ_B = 3.21, $J_{AB} \approx 14$, in addition split by $J_{A,2'}$ = 7.0, $J_{B,2'}$ = 8.4, 1'-H_2), AB signal (δ_A = 4.25, δ_B = 4.39, J_{AB} = 11.5, 1''-H_2), 4.61 (dd, $J_{1,2\text{-}H^B}$ = 9.0, $J_{1,2\text{-}H^A}$ = 3.8, 1-H), 5.22 (m_c, 2'-H), 7.23–7.40 (m, 1-C_6H_5, 1''-C_6H_5).

$C_{33}H_{52}OSSn$ (615.6) Calcd. C 64.39 H 8.52
Found C 64.73 H 8.30

1-(Benzyloxy)-4,4-dimethyl-1-phenyl-5-hexane-3-thiol (**28**): At –78°C *n*BuLi (1.50 mol/l in hexane; 0.17 ml, 0.249 mmol, 3.0 equiv.) was added dropwise to stannyl sulfide **27** (0.051 g, 0.083 mmol) in THF (1 ml). After 30 min the reaction was quenched with satd. aqueous NH_4Cl solution (2 ml) and extracted with diethyl ether (3 × 15 ml). Purification by flash chromatography [petroleum ether/diethyl ether (200:1)] yielded the thiol **28** (0.021 g, 78%). – ^{1}H NMR (250 MHz): δ = 1.06 and 1.10 [2 s, 4-$(CH_3)_2$], 1.19 (d, $J_{SH,3}$ = 8.2, SH), 1.37 (ddd, J_{gem} = 14.4, $J_{2\text{-}H^1,1}$ = 11.7, $J_{2\text{-}H^1,3}$ = 2.3, 2-H^1), 2.21 (ddd, J_{gem} = 14.5, $J_{2\text{-}H^2,3}$ = 10.7, $J_{2\text{-}H^2,1}$ = 1.9, 2-H^2), 3.12 (ddd, $J_{3,2\text{-}H^2}$ = 10.3, $J_{3,SH}$ = 8.1, $J_{3,2\text{-}H^1}$ = 2.1, 3-H), AB signal (δ_A = 4.29, δ_B = 4.49, J_{AB} = 11.8, 1'-H_2), 4.75 (dd, $J_{1,2\text{-}H^1}$ = 10.7, $J_{1,2\text{-}H^2}$ = 2.3, 1-H), 4.98 (dd, $J_{trans\text{-}6\text{-}H,5}$ = 17.4, J_{gem} = 1.3, 6-H_{trans}), 5.03 (dd, $J_{cis\text{-}6\text{-}H,5}$ = 10.8, J_{gem} = 1.3, 6-H_{cis}), 5.81 (dd, $J_{5,trans\text{-}6\text{-}H}$ = 17.4, $J_{5,cis\text{-}6\text{-}H}$ = 10.8, 5-H), 7.26–7.42 (m, 1-C_6H_5, 1'-C_6H_5); alternative assignment: 1.37 (ddd, J_{gem} = 14.4, $J_{2\text{-}H^1,3}$ = 11.7, $J_{2\text{-}H^1,1}$ = 2.3, 2-H^1), 2.21 (ddd, J_{gem} = 14.5, $J_{2\text{-}H^2,1}$ = 10.7, $J_{2\text{-}H^2,3}$ = 1.9, 2-H^2), 3.12 (ddd, $J_{3,2\text{-}H^1}$ = 10.3, $J_{3,SH}$ = 8.1, $J_{3,2\text{-}H^2}$ = 2.3, 3-H), 4.75 (dd, $J_{1,2\text{-}H^2}$ = 10.7, $J_{1,2\text{-}H^1}$ = 2.3, 1-H). – ^{13}C NMR (63 MHz): δ = 23.05, 25.56 [4-$(CH_3)_2$], 41.20, 43.43, 47.54 (C-2, C-3, C-4), 70.69 (C-1'), 78.98 (C-1), 112.60 (C-6), 126.52, 127.52, 127.76, 128.32, 128.51 (5 × Ar-C*H*), 138.64 (C-5), 142.79, 146.14 (2 × Ar-C_{quat}). – IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 3030, 2970, 2930, 2870, 1690, 1600, 1495, 1455, 1220, 1070, 1025, 915, 735, 700.

$C_{21}H_{26}OS$ (326.5) Calcd. C 77.25 H 8.03
Found C 76.94 H 7.84

syn- and anti-1-(Benzyloxy)-3-(benzylthio)-1-phenyl-3-(tributylstannyl)propane (*syn,anti*-**30**): Benzyl mercaptane (3.60 g, 29.0 mmol, 2.5 equiv.) was added at –78°C to KH (1.07 g, 26.7 mmol, 2.3 equiv.) in THF (60 ml). After 1 h the suspension was first warmed to room temp. and then recooled to 0°C. A configurationally unassigned 80:20 mixture of stannyl bromides *syn,anti*-**12** (6.93 g, 11.6 mmol) in THF (50 ml) was added. After stirring for 12 h at room temp. the reaction was quenched with satd. aqueous NH_4Cl solution (30 ml) and the resulting mixture extracted with diethyl ether (2 × 100 ml). The crude product was flash-chromatographed once [petroleum ether/diethyl ether (petroleum ether → 30:1)] to give **30** as a 80:20 *syn,anti* mixture (4.81 g, 65%) and subsequently several times [petroleum ether/diethyl ether (100:1)] to yield – besides still unseparated material – isomerically pure *syn*-**30** (1.32 g, 18%) in the early and pure *anti*-**30** (0.236 g, 3%) in the late fractions.

$C_{35}H_{50}OSSn$ (637.6) Calcd. C 65.94 H 7.91
Found C 65.65 H 7.99

syn-**30**: ^{1}H NMR (400 MHz, $CDCl_3$, contains a small amount of impurity, but no *anti*-**30**): δ = 0.73–0.94 (m, 3 × $SnCH_2$, 3 × CH_2CH_3), 1.16–1.41 (m, 3 × $CH_2CH_2CH_2CH_3$), 2.08 (ddd, J_{gem} = 14.3, $J_{2\text{-}H^1,3}$ = 7.7, $J_{2\text{-}H^1,1}$ = 3.5, 2-H^1), 2.36 (ddd, J_{gem} = 14.3, $J_{2\text{-}H^2,1}$ = 9.3, $J_{2\text{-}H^2,3}$ = 4.2, 2-H^2), 2.45 (dd including tin satellites, $J_{3,2\text{-}H^1}$ = 7.8, $J_{3,2\text{-}H^2}$ = 4.2, 3-H), AB signal (δ_A = 3.61, δ_B = 3.71, J_{AB} = 13.0, SCH_2Ph), AB signal (δ_A = 4.22, δ_B = 4.40, J_{AB} = 11.5, OCH_2Ph), 4.55 (dd, $J_{1,2\text{-}H^2}$ = 9.4, $J_{1,2\text{-}H^1}$ = 3.5, 1-H), 7.17–7.41 (m, 3 × C_6H_5). – The 300-MHz ^{1}H-NMR spectrum in C_6D_6 served for the distinction from the diastereomer by resonances at δ = 2.68 (dd, $J_{3,2\text{-}H^1}$ = 7.6, $J_{3,2\text{-}H^2}$ = 3.4, 3-H) and 4.76 (dd, $J_{1,2\text{-}H^2}$ = 9.8, $J_{1,2\text{-}H^1}$ = 2.8, 1-H). – IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 3030, 2920, 2850, 1600, 1495, 1460, 1345, 1070, 1025, 875, 760, 700.

anti-**30**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.76–0.93 (m, 3 × $SnCH_2$), superimposed by 0.85 (t, *J* = 7.4, 3 × CH_2CH_3), 1.20–1.45 (m, 3 × $CH_2CH_2CH_2CH_3$), AB signal including tin satellites (δ_A = 2.11, δ_B = 2.30, J_{AB} = 14.3, in addition split by $J_{A,3}$ = 8.4, $J_{A,1}$ = 4.9, $J_{B,1}$ = 8.2, $J_{B,3}$ = 6.3, 2-H_2), 2.44 (dd including tin satellites, $J_{3,2\text{-}H^A}$ = 8.5, $J_{3,2\text{-}H^B}$ = 6.3, 3-H), AB signal (δ_A = 3.56, δ_B = 3.64,

J_{AB} = 12.9, SCH_2Ph), AB signal (δ_A = 4.22, δ_B = 4.42, J_{AB} = 11.7, OCH_2Ph), 4.52 (dd, $J_{1,2\text{-}H^B}$ = 8.0, $J_{1,2\text{-}H^A}$ = 4.9, 1-H), 7.09–7.47 (m, 3 × C_6H_5). – The 300-MHz ^{1}H-NMR spectrum in C_6D_6 served for the distinction from the diastereomer by resonances at δ = 2.75 (dd, $J_{3,2\text{-}H^A}$ = 8.4, $J_{3,2\text{-}H^B}$ = 6.0, 3-H) and 4.68 (dd, $J_{1,2\text{-}H^B}$ = 8.6, $J_{1,2\text{-}H^A}$ = 4.3, 1-H). – ^{13}C NMR [125 MHz; impurity at δ = 29.70 (–)]: δ = (–) 9.57 (3 × $SnCH_2$), (+) 13.67 (3 × CH_2CH_3), (+) 22.75 (C-3), (–) 27.38, (–) 29.01 (3 × $CH_2CH_2CH_3$), (–) 38.60, (–) 44.64 (C-2, SCH_2Ph), (–) 70.33 (OCH_2Ph), (+) 80.20 (C-1), (+) 126.56, (+) 126.88, (+) 127.46, (+) 127.64, (+) 127.77, (+) 128.26, (+) 128.58, (+) 128.95 (3 × C_6H_5), (–) 138.45, (–) 138.77, (–) 142.55 (3 × Ar-C_{quat}). – IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 3030, 2925, 2870, 1600, 1495, 1455, 1070, 1030, 760, 735, 700.

syn- and anti-3-(Benzyloxy)-1-(2-methylphenyl)-3-phenylpropanethiol (*syn,anti-***33**): a) At –78°C *n*BuLi (1.39 mol/l in hexane; 0.23 ml, 0.32 mmol, 2.5 equiv.) was added dropwise to stannyl sulfide *syn-***30** (0.081 g, 0.127 mmol) in THF (1.5 ml). After 30 min the reaction was quenched with satd. aqueous NH_4Cl solution (2 ml) and the resulting mixture extracted with diethyl ether (3 × 20 ml). Purification by flash chromatography [petroleum ether/diethyl ether (200:1 → 75:1)] yielded the thiols **33** (0.028 g, 63%) as a 72:28 mixture of diastereomers; the major diastereomer is tentatively assigned the *anti* configuration.

b) At –78°C *n*BuLi (1.30 mol/l in hexane; 0.55 ml, 0.72 mmol, 3.0 equiv.) was added dropwise to stannyl sulfide *anti-***30** (0.152 g, 0.238 mmol) in THF (2.0 ml). After 30 min the reaction was quenched with satd. aqueous NH_4Cl solution (2 ml) and the resulting mixture extracted with diethyl ether (3 × 20 ml). Purification by flash chromatography [petroleum ether/diethyl ether (200:1 → 75:1)] provided the thiol **33** (0.057 g, 69%) as a 71:29 mixture of diastereomers; the major product is tentatively assigned the *syn* configuration. – IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 3030, 2920, 2865, 1600, 1490, 1455, 1390, 1345, 1310, 1210, 1095, 1025, 910, 745, 700.

$C_{23}H_{24}OS$ (348.5) Calcd. C 79.27 H 6.94
Found C 79.56 H 6.92

*syn-***33**: ^{1}H NMR (500 MHz, signals in part superimposed by those of *anti-***33**): δ = 1.87 (d, $J_{SH,1}$ = 6.4, SH), 2.27 (s, C_6H_4-CH_3), AB signal (δ_A = 2.37, δ_B = 2.53, J_{AB} = 14.1, in addition split by $J_{A,1}$ = 9.3, $J_{A,3}$ = 4.5, $J_{B,3}$ = 9.2, $J_{B,1}$ = 6.2, 2-H_2), AB signal (δ_A = 4.05, δ_B = 4.31, J_{AB} = 11.3, 1′-H_2), 4.20 (dd, $J_{3,2\text{-}H^B}$ = 9.2, $J_{3,2\text{-}H^A}$ = 4.4, 3-H), 4.43 (ddd, $J_{1,2\text{-}H^A}$ = 9.3, $J_{1,SH}$ = $J_{1,2\text{-}H^B}$ = 6.3, 1-H), 7.10–7.41 (m, H_3C-C_6H_4, 3-C_6H_5, 1′-C_6H_5).

*anti-***33**: ^{1}H NMR (500 MHz, signals in part superimposed by those of *syn-***33**): δ = 1.69 (d, $J_{SH,1}$ = 7.1, SH), AB signal (δ_A = 2.20, δ_B = 2.46, J_{AB} = 14.1, in addition split by $J_{A,1(*)}$ = 9.8, $J_{A,3(*)}$ = 4.2, $J_{B,3(*)}$ = 9.4, $J_{B,1(*)}$ = 4.8, 2-H_2), 2.31 (s, C_6H_4-CH_3), AB signal (δ_A = 4.28, δ_B = 4.49, J_{AB} = 11.9, 1′-H_2), 4.36 (ddd, $J_{1,2\text{-}H^{A(*)}}$ = 9.9, $J_{1,SH}$ = 7.0, $J_{1,2\text{-}H^{B(*)}}$ = 4.8, 1-H), 4.60 (dd, $J_{3,2\text{-}H^{B(*)}}$ = 9.4, $J_{3,2\text{-}H^{A(*)}}$ = 4.2, 3-H); assignments marked with an asterisk are interchangeable.

Stereochemical Correlation

anti-1-(Benzyloxy)-3-(benzylthio)-1-phenyl-3-(tributylstannyl)-propane (*anti-***30**): At –20°C methanesulfonyl chloride (0.04 ml, 0.06 g, 0.5 mmol, 1 equiv.) was added dropwise to *syn-***14** (0.271 g, 0.510 mmol) and triethylamine (0.21 ml, 0.15 g, 1.5 mmol, 3.0 equiv.) in CH_2Cl_2 (5 ml). After 2 h at –20°C the mixture was transferred via cannula to a suspension of potassium benzyl thiolate [prepared from benzyl mercaptane (0.18 ml, 0.19 g, 1.5 mmol, 3.0 equiv.) and KH (0.057 g, 1.4 mmol, 2.8 equiv.) at –78°C] in THF (5 ml). After 5 h at 0°C the reaction was quenched with satd. aqueous NH_4Cl (5 ml) and the resulting mixture extracted with diethyl ether (4 × 20 ml). Purification by flash chromatography [petroleum ether/diethyl ether (200:1)] yielded *anti-***30** (0.163 g, 50%) as evidenced by its 500-MHz ^{1}H-NMR spectrum in $CDCl_3$ and its 300-MHz ^{1}H-NMR spectrum in C_6D_6.

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