Asymmetric Induction in Reductively Initiated [2,3]-Wittig and Retro [1,4]-Brook Rearrangements of Secondary Carbanions

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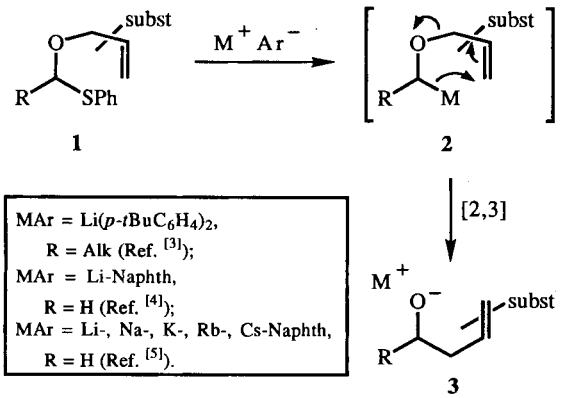
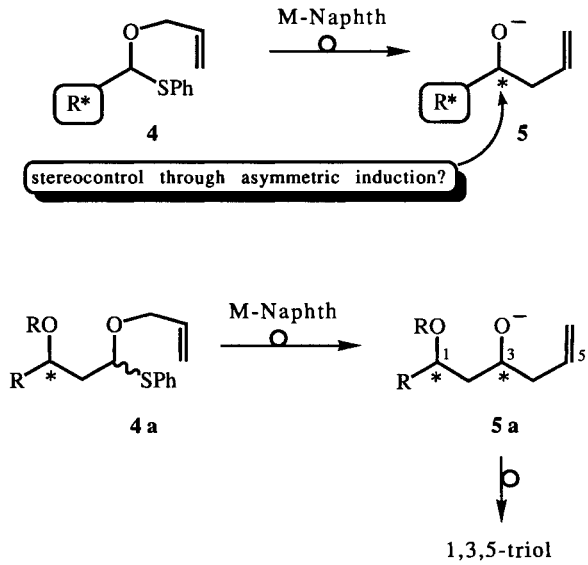
The synthesis of O,S-acetals and the lithium naphthalenide initiated rearrangement reactions thereof are described. O,S-Acetal **8a** resulted from trapping of the 1,4-dipole **7** with thiophenol. O,S-Acetals **16a** and **b** were obtained from aldehydes **14a/b** by a one-pot reaction with (trimethylsilyl)prenol, (trimethylsilyl)thiophenol, and trimethylsilyl triflate. Upon reduction with lithium naphthalenide all O,S-acetals delivered α-lithiated ethers. They rearranged either in a [2,3]-Wittig mode furnishing the 1,3-diol derivatives **20a–h/21** with moderate stereoselectivity (*syn*:*anti* = 35:65 to 78:22) or underwent retro [1,4]-Brook rearrangements yielding the α-silyl ethers **23i–k/24** with still less stereocontrol (*syn*:*anti* = 34:66 to 50:50). The mechanistic implications are discussed.

During the past decade, the [2,3]-Wittig rearrangement of metalated allyl ethers **2** giving homoallyl alcohols **3** has attracted considerable attention[1]. Such metalated ethers are obtained by deprotonation with LDA or KH or metalation with BuLi from compounds which are C-H acids due to the presence of a substituent R with −M effect. Alternatively, a tin/lithium exchange reaction between a stannylated ether and butyllithium provides non-conjugated metalated ethers **2**[2]; however, the substituent R therein is restricted to being hydrogen.

A third approach to Wittig rearrangement substrates **2** was described by Broka[3] and ourselves[4,5]. It starts from O,S-acetals **1**. In these the C–S bond is submitted to Cohen's reductive lithiation protocol[6]. Accordingly, treatment of **1** with ⩾2 equiv. of radical anion salts like lithium 4,4′-di-*tert*-butylbiphenylide ("LiDBB") or lithium naphthalenide ("Li-Naphth") liberates lithiated ethers **2** which subsequently undergo a [2,3] shift. So far, the latter approach has allowed non-conjugated organolithiums with OCH_2Li or OCH(*n*-alkyl)Li moieties to be involved in [2,3]-Wittig rearrangements.



The present paper decribes efforts to extend this method to O,S-acetals **4** *exhibiting a chiral substituent R**. We wondered whether such a substituent can enforce stereocontrol through asymmetric induction upon the Wittig rearrangement, i.e., whether it can determine the configuration of the new stereocenter which emerges in the course of the reaction. (Chiral substituents in the anion moiety of *conjugated* allyl ether anions are suitable for this type of stereocontrol[7].) Specifically, we chose to study O,S-acetals of substitution pattern **4a**. Their rearrangement products **5a** would be potential precursors of 1,3,5-triols with defined stereostructure. The latter compounds and their higher congeners, stereoregulated 1,3,5,7,...-polyols, are target molecules of current interest in natural-product synthesis[8].



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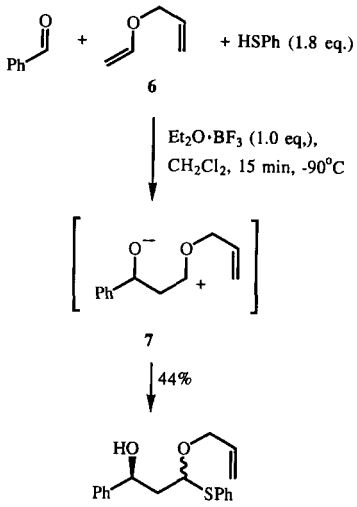
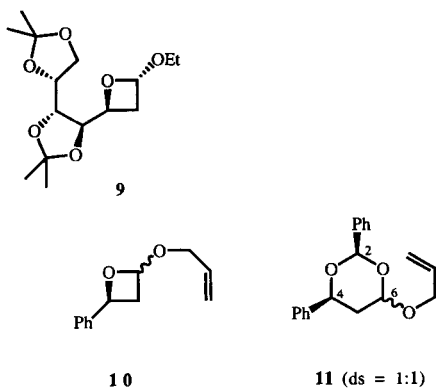
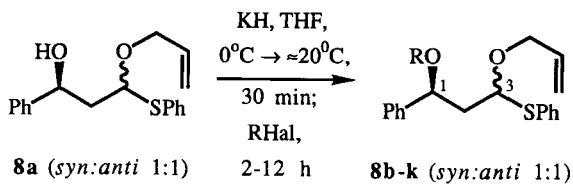
Synthesis of Functionalized O,S-Acetals

The main route to the O,S-acetals of the present study led via the hydroxylated O,S-acetal **8a**. Compound **8a** was obtained in a one-pot reaction from benzaldehyde, allyl vinyl ether[9] (**6**), and thiophenol. The reactants were treated with $Et_2O \cdot BF_3$ in CH_2Cl_2 at dry ice temperature. Presumably, the Lewis acid induces the formation of 1,4-dipole **7** from the aldehyde and the vinyl ether. Compound **7** is then trapped by thiophenol: The anionic center picks up the proton and the cationic center combines with the PhS moiety. O,S-Acetal **8a** resulted in 44% yield as an inseparable 1:1 mixture of diastereomers.



Initially, we had tried to synthesize **8a** in two steps via the oxetane **10**. Our lead was a recent report by Sugimura and Osumi[10] who had obtained oxetanes – for example **9** – by [2 + 2] cycloadditons of aldehydes to enol ethers *under the above-mentioned conditions but in the absence of thiophenol.* However, when we treated benzaldehyde with allyl vinyl ether and $Et_2O \cdot BF_3$ according to their procedure, we found none of the expected [2 + 2] cycloadduct **10**. Instead, we obtained 65% of the [2 + 2 + 2] adduct **11** (1:1 mixture of two of the four possible diastereomers). This indicates that the 1,4-dipole intermediate **7** had formed as expected. However, a 1,4-dipolar cycloaddition of **7** to a second equiv. of the aldehyde rather than ring closure of **7** to the oxetane occurred to afford the less strained six-membered ring **11**[11].

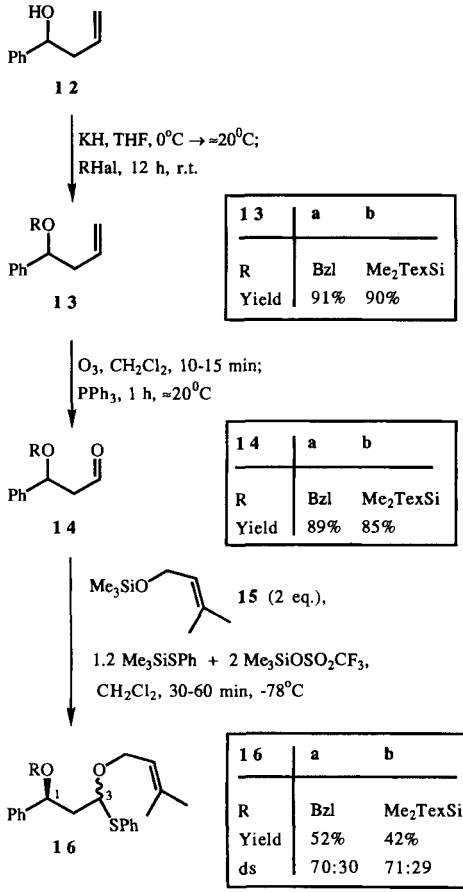




8	b	c	d	e	f	g
R	Me	Bzl	Ph_3C	MEM	BOM	Me_2TexSi
Yield	92%	87%	53%	79%	55%	86%

	h	i	j	k
R	iPr_3Si	Me_3Si	Et_3Si	$tBuPh_2Si$
Yield	74%	79%	93%	91%

The hydroxy group of O,S-acetal **8a** was protected under standard conditions to furnish the functionalized O,S-acetals **8b–k**[12]. The protective groups comprise alkyl ethers (**8b–d**), acetals (**8e,f**), and silyl ethers (**8g–k**). All derivatives were isolated as 1:1 mixtures of diastereomers. By flash chromatography[13], we could only separate the tritylated O,S-acetal **8d** into pure isomers.



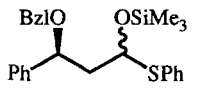
13	a	b
R	Bzl	Me_2TexSi
Yield	91%	90%

14	a	b
R	Bzl	Me_2TexSi
Yield	89%	85%

16	a	b
R	Bzl	Me_2TexSi
Yield	52%	42%
ds	70:30	71:29

Two more O,S-acetals of generic structure **4a** were prepared by a different strategy: **16a,b** with prenyloxy instead of hitherto used allyloxy residues were derived from the protected aldehydes **14a,b**. The latter compounds were readily available by protection/ozonolysis from the known[14] alcohol **12**. The thioacetalization of aldehydes **14** was achieved by using our recently published procedure[15]: **14**, (trimethylsilyl)prenol (**15**), (trimethylsilyl)thiophenol[16], and 2 equiv. of trimethylsilyl triflate were allowed to react at −78 °C in CH_2Cl_2 to give O,S-acetals **16a,b** in 52 and 42% yield, respectively.

The use of twice the stoichiometric rather than a catalytic amount of trimethylsilyl triflate in these reactions was mandatory. Otherwise – and worse so at −30 °C – side products like S,S-acetal **18** or sulfide **19** became more abundant. The annoying competing formation of the silylated O,S-acetal **17** ("Evans' product"[17]) was never entirely suppressed.



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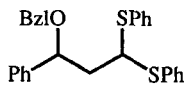

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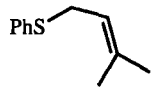

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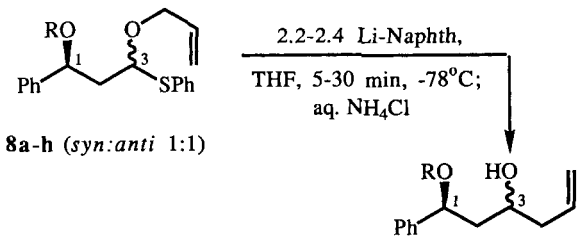
[2,3]-Wittig Rearrangements

The C–S bond of all O,S-acetals was cleaved at −78 °C in THF by the slow addition of 2.2–2.4 equiv.[18] of Li-Naphth (0.3–0.4 M in THF) *to* the substrate[19]. Li-Naphth rather than LiDBB was chosen since *both* reductants converted the dimethyl-*tert*-hexylsilyl ("Me_2TexSi-") O,S-acetal **8g** equally well (66% yield) into rearrangement product **20 g**.

The cleavage/rearrangement sequence O,S-acetal **8** → homoallyl alcohol **20** was generally very rapid. For instance,



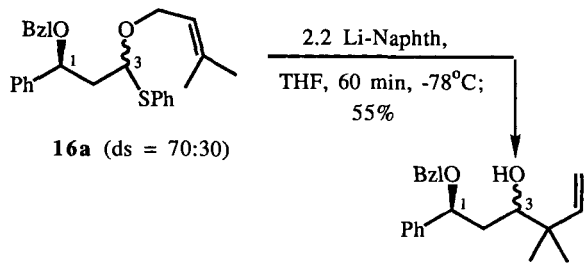
8a-h (*syn:anti* 1:1)

syn- and *anti*-**20a-h**

8→20	R	Yield	% *syn*-20
a	H	70%	50
b	Me	58%	56
c	Bzl	75%	64
d	Ph_3C	64%	35
e	MEM	78%	63
f	BOM	56%	57
g	Me_2TexSi	66%	76
h	iPr_3Si	59%	45 or 55

transformation of benzyl ether **8c** into the Wittig product **20c** was complete in THF at −90 °C after only 5 min. Yields were reliably 56–75%. Unfortunately, the extent of stereocontrol lagged behind our expectations: All products were isolated as *syn*:*anti* mixtures with *syn* contents up to 76% (**20g**) and a maximum value for the *anti* fraction of 65% (**20d**)[20].

The prenylated O,S-acetal **16a** was treated with Li-Naphth in the same fashion as the allylated counterparts **8a–g**. Homoallyl alcohol **21** formed with yield (55%) and selectivity (61% *syn* product) within the previously observed ranges. The location of the *gem*-dimethyl unit in the rearrangement product **21** – at an sp^3- and not an sp^2-carbon atom – proves unambiguously that *here* a [2,3]- and not a [1,2]-Wittig rearrangement had taken place. This finding suggests strongly that the allylated rearrangement products **20** are formed from **8** by [2,3] shifts, too, rather than by [1,2] shifts.



16a (ds = 70:30)

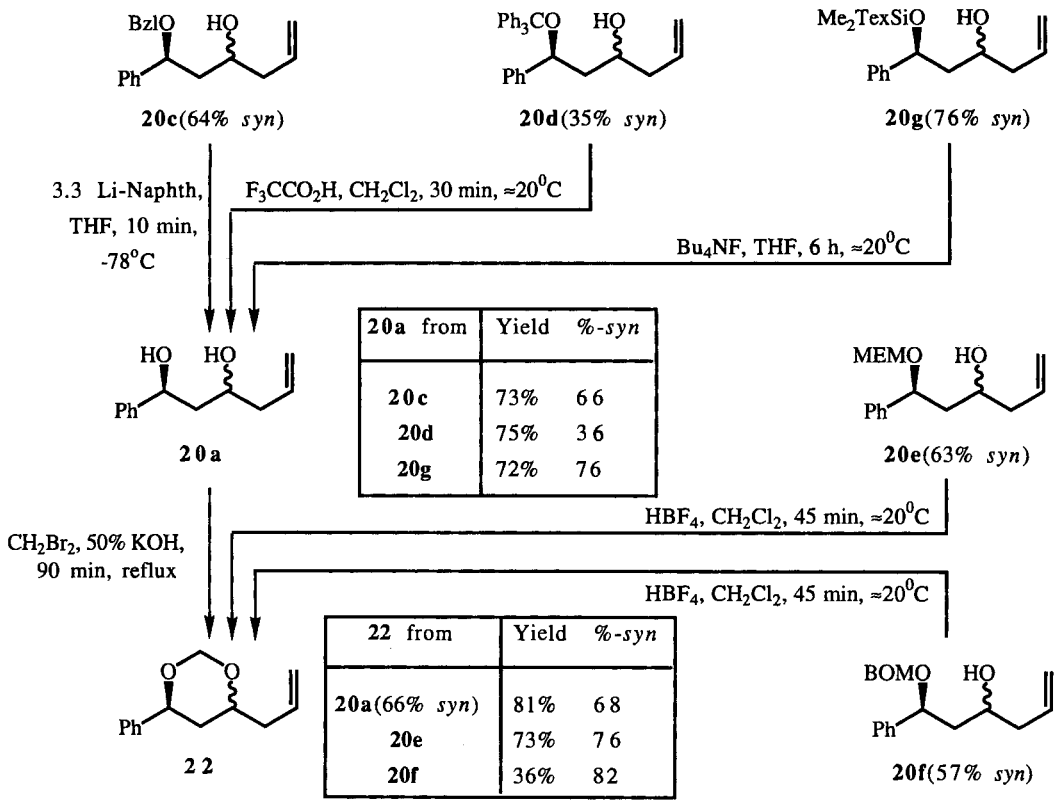
21 (61% *syn*)

The stereochemical assignments of rearrangement products **20** and **21** are based on chemical correlations (Scheme 1) and NMR data (vide infra).

The upper reaction triade of Scheme 1 allows the following conclusions: (1) The *major* diastereomers from the [2,3]-Wittig rearrangements of the Bzl-protected O,S-acetal **8c**[21] and the Me_2TexSi-protected O,S-acetal **8g** have the same configuration as the *major* product obtained from the unprotected **8a**. (2) The *minor* diastereomer of the tritylated rearrangement product **20d** has the same configuration as the three mentioned major diastereomers.

In the lower set of reactions in Scheme 1 the dioxane **22** serves as a relay compound between the rearrangement products **20a,e**, and **f**. Compound **22** was obtained by treatment of the diol **20a** with CH_2Br_2 and base[22]. Methoxy-ethoxy-methyl (MEM) ether **20e** and benzyloxy-methyl (BOM) ether **20f** gave **22** by acid-catalyzed intramolecular transacetalization. On the way to **22**, *syn*:*anti* ratios changed. Therefore, a priori, one cannot even be sure that the major diastereomer of **22** originates indeed from the major diastereomer of the rearrangement product. Nonetheless, the *good* yields of the **20a** → **22** and **20e** → **22** conversions preclude a pitfall *there*. Hence, the major isomers of **20a**, **20e**, and **22** have the same relative configuration. On the other hand, the 36% yield for the **20f** → **22** conversion is too low to derive the configurational relationship.

Scheme 1. Stereochemical correlations between selected rearrangement products **20**



The main diastereomer of dioxane **22** was assigned the *syn* configuration. This is because one of its 5-H signals exhibits two large (11.0 Hz; cf. Figure 1) vicinal coupling constants and reveals thereby axial orientation of itself and the vicinal protons as well. Accordingly, the other 5-H signal exhibits two smaller (2.8 Hz) coupling constants with its neighbors underlining an equatorial/axial relation to them.

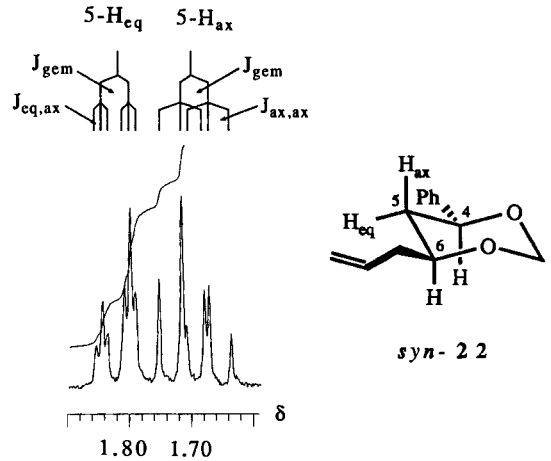
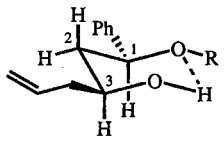


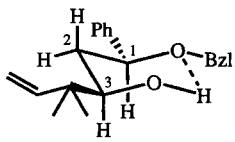
Figure 1. Section from the 300-MHz ^{1}H-NMR spectrum ($CDCl_3$) of the major dioxane isomer *syn*-**22**

The stereochemistry of **22** thus being established the *syn,anti* assignments of rearrangement products **2a,c–e**, and **g** follow because of the correlations in Scheme 1. A tabular survey of selected ^{1}H-NMR data of four of these plus three not yet assigned rearrangement products is given in Table 1 for the *syn* and in Table 2 for the *anti* isomers.

Table 1. Selected ^{1}H-NMR data (300 MHz, $CDCl_3$) of *syn*-configurated Wittig rearrangement products



syn- **20a-c, e-g**



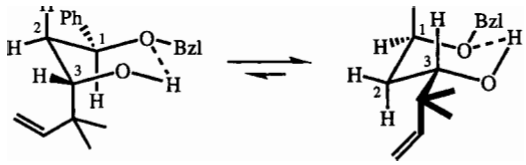
syn- **21**

20,21	R	δ(2-H_{ax})	$J_{ax,1}$ [Hz]	$J_{ax,3}$ [Hz]	δ(2-H_{eq})	$J_{eq,1}$ [Hz]	$J_{eq,3}$ [Hz]
20a	H	1.86	9.2	9.2	1.81	4.1	3.2
b	Me	1.89	9.8	9.8	1.75	3.8	2.2
c	Bzl	1.96	9.9	9.9	1.78	3.9	2.2
e	MEM	1.97	9.4	9.4	1.82	4.7	2.4
f	BOM	1.99	9.4	9.4	1.84	4.7	2.5
h	Me_2TexSi	1.87	9.2	9.2	1.75	4.5	2.4
21	-	1.85	9.9	9.0	1.79	4.8	2.6

Focusing on the entries for the already configurationally assigned compounds **20a,c,e**, and **g**, two patterns emerge. (1) In the *syn* series (Table 1), one 2-H signal exhibits two large vicinal coupling constants (9.2–9.9 Hz) while the other 2-H signal shows two considerably smaller J_{vic} values

(2.2–4.7 Hz). (2) In the *anti* series (Table 2), each of the observable 2-H signals couples with one large and one small J_{vic} value to the signals of the neighboring protons.

Table 2. Selected ^{1}H-NMR data (300 MHz, $CDCl_3$) of *anti*-configurated Wittig rearrangement products



20,21	R	δ(2-H_A)	$J_{A,1}$ [Hz]	$J_{A,3}$ [Hz]	δ(2-H_B)	$J_{B,1}$ [Hz]	$J_{B,3}$ [Hz]
20a	H	1.95	7.8	3.2	≈1.91	-	-
b	Me	1.90	8.8	2.6	1.78	3.4	10.1
c	Bzl	1.96	9.1	2.7	1.77	3.4	9.4
e	MEM	1.90	10.5	2.3	1.77	2.8	10.3
f	BOM	1.96	9.5	2.6	1.77	3.5	9.5
g	Me_2TexSi	≈1.62	-	-	≈1.81	-	
21		1.91	9.9	1.8	1.62	3.1	10.6

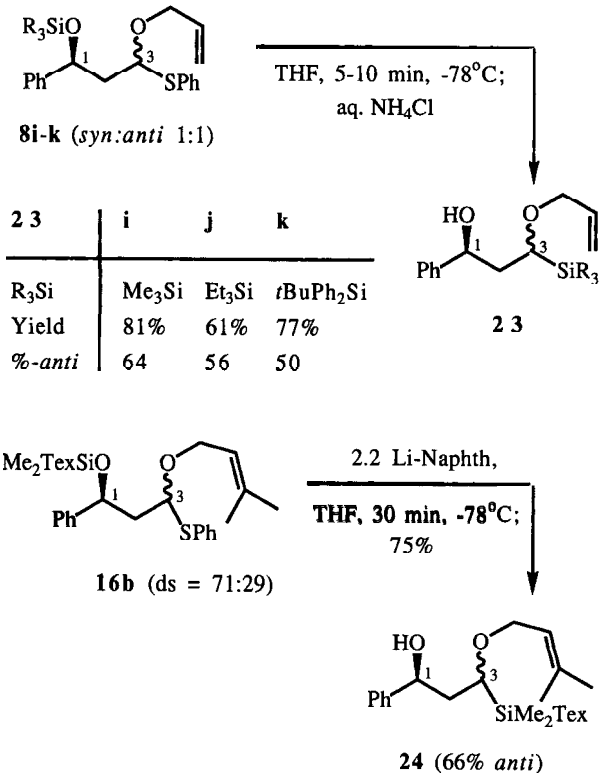
Such *J*-value patterns have been correlated with the stereochemistry of unprotected or monoprotected 1,3-diols[23]. These patterns arise when there is an intramolecular hydrogen bond between the proton of a hydroxy group and the oxygen atom of the nearby OH or OR group, respectively. Such hydrogen bonds give rise to chair-like six-membered rings. *syn* Products occur as *one* conformer (formulae in Table 1) with one clearly axial 2-H and one clearly equatorial 2-H. The former exhibits two large $J_{ax,ax}$ and the latter two small $J_{eq,ax}$ couplings. *anti* Products may consist of *two* equilibrating chair conformers (formulae in Table 2). The distinction between axial 2-H and equatorial 2-H is less pronounced; in essence, each 2-H signal is associated with one large and one small J_{vic} value.

Therefore, the configuration–J_{vic} relation which holds true for the stereochemically already assigned rearrangement products **20a,c,e**, and **g**, could be used by analogy as a *criterion* for the *syn/anti* assignments of **20b,f**, and **21** (Tables 1, 2).

On the other hand, the J_{vic} values of rearrangement product **20h** did not fit these patterns. Hence, we could not assign its stereochemistry. Seemingly, the ether oxygen atom of **20h** is too deeply buried in the iPr_3SiO group to form a chair through hydrogen bonding. For the same reason, the J_{vic} values of the tritylated rearrangement product **20d** do not conform to the trends of Tables 1 and 2 either. Fortunately, its stereochemistry was established by the correlations of Scheme 1.

Retro [1,4]-Brook Rearrangements

Upon treatment with Li-Naphth under the previous conditions (2.2 equiv., THF, –78 °C), the R_3Si-equipped O,S-



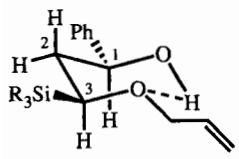
23	**i**	**j**	**k**
R_3Si	Me_3Si	Et_3Si	$tBuPh_2Si$
Yield	81%	61%	77%
%-*anti*	64	56	50

The chemoselectivity of the reductively initiated rearrangement ractions of functionalized O,S-acetals is noteworthy. The Me_3Si- and $tBuPh_2Si$-protected allyloxy sulfides **8i** and **k** underwent retro-Brook rearrangement only. Contrarily, their Me_2TexSi- and iPr_3Si-protected analogs **8g** and **h** were cleanly converted into Wittig products. The Et_3Si-protected **8j** reacted less selectively and with an 80:20 bias towards the retro-Brook process. Interestingly, the Me_2TexSi-protected prenyloxy sulfide **16b** followed the retro-Brook pathway exclusively whereas the Me_2TexSi-protected allyloxy sulfide **8g** showed an undivided inclination for the Wittig rearrangement. Obviously, [2,3]-Wittig and retro [1,4]-Brook rearrangements of secondary non-conju-

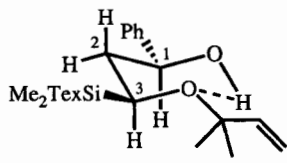
gated lithiated ethers proceed at similar rates. With small or medium-sized silyl groups, the retro-Brook rearrangement prevails. It does so, too, in the case of the bulky Me_2TexSi group when one starts from O,S-acetal **16b**; there, the prevalence is caused by hindrance of the [2,3]-Wittig rearrangement by the two methyl groups located at the carbon atom which would become part of the newly formed C–C bond.

In the three retro-Brook products with unequal isomer distributions (**23i,j,24**), the major diastereomer is *anti*. This follows from an analysis of the magnitude of the J_{vic} values of the central CH_2 unit (Tables 3, 4) on the assumption that bridged chair-like product structures are present. This analysis follows strictly the one given in the preceding section dealing with the sterochemical assignment of the Wittig rearrangement products.

Table 3. Selected ^{1}H-NMR data (300 MHz, $CDCl_3$) of *syn*-configurated retro-Brook rearrangement products



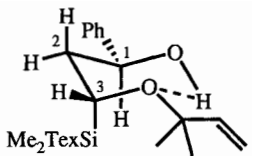
syn- **23i-j**



syn- **24**

23,24	R_3Si	δ(2-H_{ax})	$J_{ax,1}$ [Hz]	$J_{ax,3}$ [Hz]	δ(2-H_{eq})	$J_{eq,1}$ [Hz]	$J_{eq,3}$ [Hz]
23i	Me_3Si	2.03	9.1	11.8	1.75	3.0	3.0
j	Et_3Si	2.11	9.0	12.0	1.75	3.1	3.1
24	-	2.09	8.8	11.7	1.82	3.2	3.2

Table 4. Selected ^{1}H-NMR data (300 MHz, $CDCl_3$) of retro-Brook rearrangement product *anti*-**24**



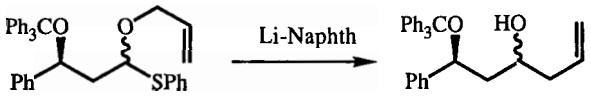
anti- **24**

δ(H_A)	$J_{A,1}$ [Hz]	$J_{A,3}$ [Hz]	δ(H_B)	$J_{B,1}$ [Hz]	$J_{B,3}$ [Hz]
2.09	9.9	3.7	1.89	2.5	7.4

Mechanistic Considerations

The rearrangements of this study occur after C–S bond cleavage through twofold single-electron transfer (SET) from Li-Naphth. Thermodynamic considerations led to the suggestion that this cleavage entails a dissociative SET on to the substrate which furnishes the PhS^- ion and a radical, and another SET which converts the radical into the alkyl lithium[25]. [That Li-Naphth induced [2,3]-Wittig rearrangements of (allyloxy)sulfides proceed indeed via a (formal) carbanion intermediate and not by an earlier radical cyclization, was made **plausible**[4].]

Since the presumed α-alkoxy radical intermediates are planar rather than pyramidal, they should have no memory of the orientation of the cleaved C–S bond. This implies that the diastereomeric composition of the starting O,S-acetal is unrelated to the stereochemical outcome of our reactions. We verified this implication for the [2,3]-Wittig rearrangement of the only O,S-acetal (**8d**) from which we could obtain *pure* diastereomers: Each pure diastereomer of **8d** gave homoallyl alcohol **20d** as the same 65:35 *anti*:*syn* mixture which was also obtained when **8d** was used as a 57:43 mixture of diastereomers.

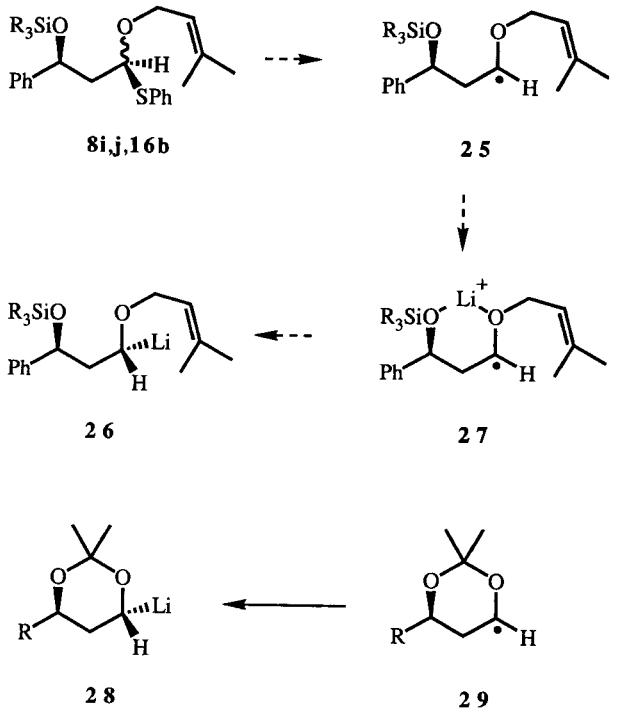


8d with ds	Yield	% *anti*-**20**	**20**
57:43	64%	65	
100:0	64%	65	
0:100	65%	65	

Different from α-alkoxy radicals, α-alkoxy organolithiums are pyramidal and configurationally stable up to temperatures of −20 °C and more[26]. Since the Wittig and retro-Brook rearrangements of the present study were performed at the far lower temperature of −78 °C, the organolithium intermediates *here* will not epimerize after being formed. If one knew how their configuration translates into the stereochemistry of the respective rearrangement product, one could deduce the former from the latter. Or, if one knew the preferred configuration of the intermediate one could conclude whether the ensuing rearrangement occurs with retention or inversion of configuration.

Retro [1,2]-Brook rearrangements of alkyl–CH(OSiR_3)Li or alkenyl–CH(OSiR_3)Li occur with *retention* of configuration at the lithiated carbon atom[27]. *Retention* of configuration is also highly probable for the retro [1,3]-Brook rearrangement of R–CH(OSiMe_3)CHLi(Oalkyl)[28]. It appears therefore likely that retro [1,4]-Brook rearrangements occur with *retention* of configuration as well. This would make the *anti*-configurated lithio ethers **26** the precursors of our major, i.e. *anti*-configurated, retro-Brook products **23i,j**, and **24**. (Our fourth retro-Brook product **23k** was formed unselectively.) Accordingly, **26** would have to form preferentially from the SET upon the α-alkoxy radical intermediates **25**. According to Rychnowsky the reaction of cyclic α-alkoxy radicals **29** with Li-Naphth affords stereoselectively α-alkoxy organolithiums **28**[29]. If our radicals **25** were associated with Li^+ in chair-like chelates **27**, reduction to **26** would be stereochemically analogous to the conversion **29** → **28**.

While our retro-Brook rearrangements were slightly *anti*-selective, the [2,3]-Wittig rearrangements gave mostly *syn*-



configurated products. If lithio ethers with the *same* preferred configuration were formed during both reactions and if our retro [1,4]-Brook rearrangements occurred indeed with *retention* of configuration, our Wittig rearrangements would show *inversion* of configuration. Such a course would agree with ab initio calculations[30] which have been supported experimentally very recently[31,32].

Support of this work by the *Deutsche Forschungsgemeinschaft* (SFB 260) and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

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[13] 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 300, WH 400; integrals in accord with assignments; coupling constants in Hz; resonances belonging to recognizable but configurationally unassigned diastereomers are labeled [isomer 1] or [isomer 2]; AB spectra: H_A refers to low- and H_B to high-field resonance.

Preparation of O,S-Acetals

1-Phenyl-3-(phenylthio)-3[(2-propenyl)oxy]-1-propanol (**8a**; 1:1 mixture of diastereomers): At –78°C $Et_2O \cdot BF_3$ (0.58 ml, 670 mg, 4.7 mmol, 1.0 equiv.) in CH_2Cl_2 (10 ml) was added drowise to a cooled (–90°C) solution of benzaldehyde (0.48 ml, 500 mg, 4.7 mmol), allyl vinyl ether (595 mg, 7.07 mmol, 1.5 equiv.) and thiophenol (0.86 ml, 930 mg, 8.4 mmol, 1.8 equiv.) in CH_2Cl_2 (80 ml). After 15 min at –90°C, the reaction was quenched with pyridine (1 ml), the resulting mixture was washed with satd. aqueous $NaHCO_3$ solution (10 ml), and extracted with ether (3 × 50 ml); the crude product obtained by evaporation of the solvents from the combined extracts was purified by flash chromatography [petroleum ether/ether (15:1–5:1)] to yield **8a** (621 mg, 44%). – ^{1}H NMR: δ = 2.06 (ddd, J_{gem} = 14.5, J_1 = 5.3, J_2 = 4.0, 2-H^1*), 2.12–2.27 (m, 2-H^2*, 2-H$_2^*$), 2.5–3.0 (extremely br. s, OH), 4.00 (ddm$_c$, J_{gem} = 12.5, $J_{1',2'}$ = 6.3, 1'-H^1*), 4.06 (ddm$_c$, J_{gem} = 12.5, $J_{1',2'}$ = 6.4, 1'-H^1*), 4.42 (ddt, J_{gem} = 12.5, $J_{1',2'}$ = 5.2, J_{allyl} = 1.3, 1'-H^2*), 4.50 (ddt, J_{gem} = 12.5, $J_{1',2'}$ = 5.1, J_{allyl} = 1.5, 1'-H^2*), 4.83–4.95 (m, 1-H and 3-H), 5.18 and 5.22 (2 dm$_c$, $J_{cis\text{-}3'\text{-}H,2'} \approx 10$, 3'-H$^*_{cis}$), 5.26 and 5.29 (2 ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.2, J_{gem} = 1.5, $J_{allyl} \approx 1$, 3'-H$^*_{trans}$), 5.90 and 5.92 (dddd, $J_{2',trans\text{-}3'\text{-}H} \approx 16$–17, $J_{2',cis\text{-}3'\text{-}H} \approx 11$, $J_{2',1'\text{-}H^1} \approx J_{2',1'\text{-}H^2} \approx 5$–6, 2'-H*), 7.18–7.34 (m, 1-C$_6$H$_5$, *m*-, *p*-SPh), 7.39–7.47 (m, *o*-SPh); *resonance of a single but unidentified diastereomer.

$C_{18}H_{20}O_2S$ (300.4) Calcd. C 71.97 H 6.71
Found C 71.92 H 6.85

General Procedure for the Preparation of O,S-Acetals **8b,c,e–k**: Compounds **8b** (92%), **8c** (87%), **8e** (79%), **8f** (55%), **8g** (86%), **8h** (74%), **8i** (79%), **8j** (93%), and **8k** (91%) were obtained from **8a** as follows (for detailed conditions cf. individual descriptions): **8a** in THF was added dropwise to a suspension of KH (2.0–2.5 equiv.) in THF (0°C → room temp.). After 30 min, the derivatizing agent (1.2–1.8 equiv.) in THF was added at 0°C. Stirring for 2–12 h at room temp., quenching with satd. aqueous NH_4Cl solution (5 ml), washing of the resulting mixture with H_2O (10 ml) and extraction with Et_2O (3 × 30 ml), and flash chromatography of the residue obtained by evaporation of the solvents from the combined extracts yielded **8b, c, e–k**.

1-Methoxy-1-phenyl-3-(phenylthio)-3-[(2-propenyl)oxy]propane (**8b**): Compound **8a** (503 mg, 1.67 mmol) in THF (5 ml), KH (132 mg, 3.30 mmol, 2.0 equiv.) in THF (10 ml), methyl iodide (0.13 ml, 300 mg, 2.1 mmol, 1.2 equiv.) in THF (2 ml), 3 h at room temp.; flash chromatography [petroleum ether/ether (30:1)] yielded **8b** (486 mg, 92%). – ^{1}H NMR: δ = 1.90–2.03 (m, 2-H^1 [both isomers]), 2.20 (ddd, J_{gem} = 13.8, $J_{2\text{-}H^2,1}$ = 10.0, $J_{2\text{-}H^2,3}$ = 3.7, 2-H^2 [isomer 2]), 2.29 (ddd, J_{gem} = 14.7, $J_{2\text{-}H^2,1}$ = 8.2, $J_{2\text{-}H^2,3} \approx 6.8$, 2-H^2 [isomer 1]), 3.16 (s, OCH$_3^*$), 3.18 (s, OCH$_3^*$), 3.95 (dd, J_{gem} = 12.4, $J_{1'\text{-}H^1,2'}$ = 6.1, 1'-H^1), 4.12 (dd, J_{gem} = 12.6, $J_{1'\text{-}H^1,2'}$ = 6.3, 1'-H^1*), 4.31 (dd, $J_{1,2\text{-}H^2}$ = 9.9, $J_{1,2\text{-}H^1}$ = 3.6, 1-H [isomer 2]), 4.35–4.49 (m, 1'-H^2 [both isomers], 1-H [isomer 1]), 4.70 (dd, $J_{3,2\text{-}H^2} = J_{3,2\text{-}H^1}$ = 6.8, 3-H [isomer 1]), 5.02 (dd, $J_{3,2\text{-}H^1}$ = 9.8, $J_{3,2\text{-}H^2}$ = 3.6, 3-H [isomer 2]), 5.19 and 5.23 (2 dm$_c$, $J_{cis\text{-}3'\text{-}H,2'} \approx 10$–11, 3'-H$_{cis}$), 5.28 and 5.30 (2 dm$_c$, $J_{trans\text{-}3'\text{-}H,2'} \approx 16$–17, 3'-H$_{trans}$), 5.93 and 5.94 (2 dddd, $J_{2',trans\text{-}3'\text{-}H} \approx 16$–18, $J_{2',cis\text{-}3'\text{-}H} \approx 10$–12, $J_{2',1'\text{-}H^1} \approx J_{2',1'\text{-}H^2} \approx 5$–6, 2'-H), 7.20–7.36 (m, 1-C$_6$H$_5$, *m*-, *p*-SPh), 7.43–7.50 (m, *o*-SPh); *resonance of a single but unidentified diastereomer.

$C_{19}H_{22}O_2S$ (314.5) Calcd. C 72.57 H 7.05
Found C 72.79 H 7.33

1-(Benzyloxy)-1-phenyl-3-(phenylthio)-3-[(2-propenyl)oxy]propane (**8c**): Compound **8a** (283 mg, 0.943 mmol) in THF (3 ml), KH (94.4 mg, 2.35 mmol, 2.5 equiv.) in THF (5 ml), benzyl bromide (0.14 ml, 200 mg, 1.2 mmol, 1.2 equiv.) in THF (2 ml), 2 h at room temp.; flash chromatography [petroleum ether/ether (50:1–40:1)] yielded **8c** (321 mg, 87%). – ^{1}H NMR: AB signal (δ_A = 2.26, δ_B = 2.00, J_{AB} = 14.4, in addition split by $J_{A,1}$ = 10.1, $J_{A,3}$ = 3.4, $J_{B,3}$ = 9.7, $J_{B,1}$ = 3.5, 2-H$_2$ [isomer 2]), AB signal (δ_A = 2.37, δ_B = 2.00, J_{AB} = 14.2, in addition split by $J_{A,1}$ = 8.5, $J_{A,3}$ = 6.3, $J_{B,3}$ = 7.7, $J_{B,1}$ = 5.6, 2-H$_2$ [isomer 1]), 3.94 (ddt, J_{gem} = 12.5, $J_{1'\text{-}H^1,2'}$ = 6.1, J_{allyl} = 1.3, 1'-H^1*), 3.96 (ddt, J_{gem} = 12.3, $J_{1'\text{-}H^1,2'}$ = 6.2, J_{allyl} = 1.3,

1′-H[1]*), AB signal (δ_A = 4.37, δ_B = 4.20, J_{AB} = 11.5, 1″-H_2^*), AB signal (δ_A = 4.41, δ_B = 4.23, J_{AB} = 11.0, 1″-H_2^*), 4.38–4.47 (m, 1′-H[2]), 4.55 (dd, $J_{1,2\text{-}H^A}$ = 10.1, $J_{1,2\text{-}H^B}$ = 3.5, 1-H [isomer 2]), 4.65 (dd, $J_{1,2\text{-}H^A}$ = 8.5, $J_{1,2\text{-}H^B}$ = 5.6, 1-H [isomer 1]), 4.77 (dd, $J_{3,2\text{-}H^B}$ = 7.4, $J_{3,2\text{-}H^A}$ = 6.3, 3-H [isomer 1]), 5.02 (dd, $J_{3,2\text{-}H^B}$ = 9.8, $J_{3,2\text{-}H^A}$ = 3.4, 3-H [isomer 2]), 5.16 and 5.18 (2 ddt, $J_{cis\text{-}3'\text{-}H,2'} \approx 10$, $J_{gem} \approx J_{allyl} \approx 1.5$, 3′-$H^*_{cis}$), 5.26 and 5.27 (2 dm$_c$, $J_{trans\text{-}3'\text{-}H,2'} \approx 16-18$, 3′-$H^*_{trans}$), 5.85 and 5.91 (2 dm$_c$, $J_{2',trans\text{-}3'\text{-}H} \approx 16-18$, 2′-H*), 7.22–7.38 (m, 1-C_6H_5, 1′-C_6H_5, *m*-, *p*-SPh), 7.41–7.46 (m, *o*-SPh); *resonance of a single but unidentified diastereomer.

$C_{25}H_{26}O_2S$ (390.5) Calcd. C 76.89 H 6.71
Found C 76.72 H 6.57

1-Phenyl-3-(phenylthio)-3-[(2-propenyl)oxy]-1-[(triphenylmethyl)oxy]propane (**8d**): Compound **8a** (427 mg, 1.42 mmol) in CH_3CN (10 ml) was heated under reflux with Ph_3CBF_4[12] (563 mg, 1.71 mmol, 1.2 equiv.) and pyridine (0.3 ml, 2.0 equiv.). After 3 h, the reaction was quenched with satd. aqueous NH_4Cl solution (10 ml). Extraction of the mixture with Et_2O (3 × 30 ml) and flash chromatography [petroleum ether/ether (80:1–60:1)] of the crude product isolated from the combined extracts furnished **8d** (fast isomer) [248 mg (32%)] and **8d** (slow isomer) [162 mg (21%)] [combined yield 410 mg (53%)]. – ^{1}H NMR (fast isomer): δ = 2.09–2.15 (m, 2-H_2), AB signal (δ_A = 4.03, δ_B = 3.62, J_{AB} = 12.5, in addition split by $J_{A,2'}$ = 5.6, $J_{B,2'}$ = 5.8, 1′-H_2), 4.22 (dd, $J_{3,2}$ = 7.8, $J'_{3,2}$ = 6.0, 3-H*), 4.67 (dd, $J_{1,2}$ = 7.7, $J'_{1,2}$ = 6.3, 1-H*), 5.02 (dm$_c$, $J_{cis\text{-}3'\text{-}H,2'} \approx 10$, 3′-$H_{cis}$), 5.03 (dm$_c$, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.5, 3′-H_{trans}), 5.66 (ddt, $J_{2',trans\text{-}3'\text{-}H} \approx 17-18$, $J_{2',cis\text{-}3'\text{-}H} \approx 10-11$, $J_{2',1'\text{-}H^A} \approx J_{2',1'\text{-}H^B} \approx 5-6$, 2′-H), 7.01–7.42 (m, 1-C_6H_5, SPh, Ph_3C); *assignments interchangeable; (slow isomer): δ = 1.99 (dd, J_1 = 7.7, J_2 = 6.3, 2-H_2), 3.56 (ddm$_c$, J_{gem} = 12.7, $J_{1',2'}$ = 5.5, 1′-H[1]), 3.97 (dd, $J_{3,2}$ = 8.2, $J_{3,2}$ = 5.1, 3-H), 4.19 (ddm$_c$, $J_{gem} \approx 13$, $J_{1',2'} \approx 6$, 1′-H[2]), 4.59 (dd, $J_{1,2} \approx 7.1$, 3-H), 5.08 (dm$_c$, $J_{cis\text{-}3'\text{-}H,2'} \approx 11$, 3′-$H_{cis}$), 5.12 (dm$_c$, $J_{trans\text{-}3'\text{-}H,2'} \approx 16.5$, 3′-$H_{trans}$), 5.76 (ddt, $J_{2',trans\text{-}3'\text{-}H} \approx 16-17$, $J_{2',cis\text{-}3'\text{-}H} \approx 10-11$, $J_{2',1'\text{-}H^1} \approx J_{2',1'\text{-}H^2} \approx 5-6$, 2′-H), 6.97–7.42 (m, 1-C_6H_5, SPh, Ph_3C).

$C_{37}H_{34}O_2S$ (542.7) Calcd. C 81.88 H 6.31
Found C 81.81 H 6.39

1-[(2-Methoxyethoxy)methoxy]-1-phenyl-3-(phenylthio)-3-[(2-propenyl)oxy]propane (**8e**): Compound **8a** (250 mg, 0.831 mmol) in THF (3 ml), KH (66.5 mg, 1.66 mmol, 2.0 equiv.) in THF (5 ml), MEMCl (0.12 ml, 130 mg, 1.1 mmol, 1.3 equiv.) in THF (2 ml), 12 h at room temp.; flash chromatography [petroleum ether/ether (5:1–4:1)] yielded **8e** (256 mg, 79%). – ^{1}H NMR: AB signal (δ_A = 2.32, δ_B = 1.99, J_{AB} = 14.4, in addition split by $J_{A,3}$ = 8.2, $J_{A,1}$ = 6.7, $J_{B,1} \approx J_{B,3} \approx 6.5$, 2-$H_2$ [isomer 2]), AB signal (δ_A = 2.28, δ_B = 2.05, J_{AB} = 14.3, in addition split by $J_{A,1}$ = 9.6, $J_{A,3}$ = 4.1, $J_{B,3}$ = 9.3, $J_{B,1}$ = 4.3, 2-H_2 [isomer 1]), 3.33 and 3.34 (2 s, OCH_3^*), 3.36–3.53 (m, 2″-H_2, 3″-H[1]), 3.64–3.76 (m, 3″-H[2]), 3.96 (ddt, J_{gem} = 12.5, $J_{1',2'}$ = 6.0, J_{allyl} = 1.4, 1′-H[1]*), 4.02 (ddt, J_{gem} = 12.5, $J_{1',2'}$ = 5.9, $J_{allyl} \approx 1.5$, 1′-H[1]*), 4.44 (ddt, J_{gem} = 12.5, $J_{1',2'}$ = 5.2, $J_{allyl} \approx 1.5$, 1′-H[2]*), 4.50 (ddt, J_{gem} = 12.8, $J_{1',2'}$ = 5.3, J_{allyl} = 1.5, 1′-H[2]*), AB signal (δ_A = 4.62, δ_B = 4.56, J_{AB} = 6.9, 1″-H_2^*), AB signal (δ_A = 4.63, δ_B = 4.57, J_{AB} = 6.9, 1″-H_2^*), 4.67 (dd, $J_{1,2\text{-}H^A} = J_{1,2\text{-}H^B}$ = 6.8, 1-H [isomer 2]), 4.78 (dd, $J_{1,2\text{-}H^A}$ = 9.6, $J_{1,2\text{-}H^B}$ = 4.2, 1-H [isomer 1]), 4.85 (dd, $J_{3,2\text{-}H^A}$ = 8.2, $J_{3,2\text{-}H^B}$ = 6.1, 3-H [isomer 2]), 4.92 (dd, $J_{3,2\text{-}H^B}$ = 9.2, $J_{3,2\text{-}H^A}$ = 4.0, 3-H [isomer 1]), 5.20 (2 dm$_c$, $J_{cis\text{-}3'\text{-}H,2'} \approx 10.4$, 3′-$H^*_{cis}$), 5.30 (2 dm$_c$, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.2, 3′-H^*_{trans}), 5.86–6.02 (m, 2′-H [both isomers]), 7.20–7.33 (m, 1-C_6H_5, *m*-, *p*-SPh), 7.44–7.49 (m, *o*-SPh); *resonance of a single but unidentified diastereomer.

$C_{22}H_{28}O_4S$ (388.5) Calcd. C 68.01 H 7.26
Found C 67.80 H 7.01

1-[(Benzyloxy)methoxy]-1-phenyl-3-(phenylthio)-3-[(2-propenyl)oxy]propane (**8f**): Compound **8a** (272 mg, 0.907 mmol) in THF (3 ml), KH (72.6 mg, 1.81 mmol, 2.0 equiv.) in THF (5 ml), BOMCl (0.21 ml, 240 mg, 1.5 mmol, 1.7 equiv.) in THF (3 ml), 12 h at room temp.; flash chromatography [petroleum ether/ether (40:1)] yielded **8f** (210 mg, 55%). – ^{1}H NMR: AB signal (δ_A = 2.35, δ_B = 2.03, J_{AB} = 14.4, in addition split by $J_{A,3}$ = 8.2, $J_{A,1}$ = 6.8, $J_{B,1}$ = 6.9, $J_{B,3} \approx 6.5$, 2-H_2 [isomer 2]), AB signal (δ_A = 2.32, δ_B = 2.08, J_{AB} = 14.4, in addition split by $J_{A,1}$ = 9.6, $J_{A,3}$ = 4.0, $J_{B,1}$ = 9.2, $J_{B,3}$ = 4.2, 2-H_2 [isomer 1]), 3.97 (ddt, J_{gem} = 12.5, $J_{1',2'}$ = 6.0, $J_{allyl} \approx 1.5$, 1′-H[1]*), 4.01 (ddt, J_{gem} = 12.5, $J_{1',2'}$ = 6.0, J_{allyl} = 1.4, 1′-H[1]*), 4.44 (ddt, J_{gem} = 12.5, $J_{1',2'}$ = 5.2, J_{allyl} = 1.4, 1′-H[2]*), 4.49 (ddt, J_{gem} = 12.5, $J_{1',2'}$ = 5.3, $J_{allyl} \approx 1.5$, 1′-H[2]*), AB signal (δ_A = 4.58, δ_B = 4.41, J_{AB} = 11.7, 2″-H_2^*), AB signal (δ_A = 4.62, δ_B = 4.41, J_{AB} = 11.7, 2″-H_2^*), AB signal (δ_A = 4.67, δ_B = 4.59, J_{AB} = 6.9, 1″-H_2^*), AB signal (δ_A = 4.68, δ_B = 4.60, J_{AB} = 6.8, 1″-H_2^*), 4.71 (dd, $J_{1,2\text{-}H^A} = J_{1,2\text{-}H^B}$ = 6.8, 1-H [isomer 2]), 4.86 (dd, $J_{1,2\text{-}H^A}$ = 9.6, $J_{1,2\text{-}H^B}$ = 4.2, 1-H [isomer 1]), 4.92 (dd, $J_{3,2\text{-}H^A}$ = 8.1, $J_{3,2\text{-}H^B} \approx 6.5$, 3-H [isomer 2]), 4.96 (dd, $J_{3,2\text{-}H^B}$ = 9.2, $J_{3,2\text{-}H^A}$ = 4.1, 3-H [isomer 1]), 5.16 and 5.20 (2 ddt, $J_{cis\text{-}3'\text{-}H,2'} \approx 11$, $J_{gem} \approx J_{allyl} \approx 1.6$, 3′-$H^*_{cis}$), 5.26 and 5.30 (2 ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.2, $J_{gem} \approx J_{allyl} \approx 1.6$, 3′-$H^*_{trans}$), 5.91 and 5.93 (2 ddt, $J_{2',trans\text{-}3'\text{-}H} \approx 16-17$, $J_{2',cis\text{-}3'\text{-}H} \approx 10-11$, $J_{2',1'\text{-}H^1} \approx J_{2',1'\text{-}H^2} \approx 5-6$, 2′-H*), 7.18–7.37 (m, 1-C_6H_5, *m*-, *p*-SPh), 7.43–7.50 (m, *o*-SPh); *resonance of a single but unidentified diastereomer.

$C_{26}H_{28}O_3S$ (420.6) Calcd. C 74.25 H 6.71
Found C 74.02 H 6.85

1-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1-phenyl-3-(phenylthio)-3-[(2-propenyl)oxy]propane (**8g**): Compound **8a** (253 mg, 0.842 mmol) in THF (2 ml), KH (60.7 mg, 1.51 mmol, 1.8 equiv.) in THF (5 ml), chlorodimethyl(1,1,2-trimethylpropyl)silane (0.20 ml, 180 mg, 1.0 mmol, 1.2 equiv.) in THF (2 ml), 12 h at room temp.; flash chromatography [petroleum ether/ether (150:1)] yielded **8g** (321 mg, 86%). – ^{1}H NMR: δ = –0.33 and –0.24 [2 s, $(CH_3)_2$Si*], 0.04 and 0.08 [2 s, $(CH_3)_2$Si*], 0.788, 0.79, 0.81 and 0.82 [4 s, 1″-$(CH_3)_2^*$], 0.86 and 0.88 (2 d, $J_{3'',2''\text{-}H} = J_{2''\text{-}Me,2''\text{-}H}$ = 6.6, 2″-CH_3, 3″-H_3^*), 0.87 (d, $J_{3'',2''\text{-}H} = J_{2''\text{-}Me,2''\text{-}H}$ = 6.9, 2″-CH_3, 3″-H_3^*), 1.61 and 1.62 (2 qq, $J_{2''\text{-}H,3''\text{-}H} = J_{2''\text{-}H,2''\text{-}Me}$ = 6.9, 2″-H*), 1.89 (ddd, J_{gem} = 14.0, $J_{2,1}$ = 7.7, $J_{2,3}$ = 5.0, 2-H[1] [isomer 2]), 1.99 (ddd, J_{gem} = 14.2, $J_{2,3}$ = 9.6, $J_{2,1}$ = 3.5, 2-H[1] [isomer 1]), 2.15–2.25 (m, 2-H[2] [both isomers]), AB signal (δ_A = 4.56, δ_B = 3.95, J_{AB} = 12.2, in addition split by $J_{A,2'}$ = 5.6, $J_{B,2'}$ = 5.8, $J_{allyl} \approx 1$, 1′-H_2^*), AB signal (δ_A = 4.40, δ_B = 4.04, J_{AB} = 12.7, in addition split by $J_{A,2'}$ = 5.1, $J_{B,2'}$ = 6.0, $J_{allyl} \approx 1$, 1′-H_2^*), 4.75 (dd, $J_{1,2\text{-}H^1}$ = 7.7, $J_{1,2\text{-}H^2}$ = 6.0, 1-H [isomer 2]), 4.80 (dd, $J_{1,2\text{-}H^2}$ = 9.7, $J_{1,2\text{-}H^1}$ = 3.5, 1-H [isomer 1]), 4.86 (dd, $J_{3,2\text{-}H^2}$ = 8.3, $J_{3,2\text{-}H^1}$ = 5.0, 3-H [isomer 2]), 4.95 (dd, $J_{3,2\text{-}H^1}$ = 9.6, $J_{3,2\text{-}H^2}$ = 3.4, 3-H [isomer 1]), 5.20 and 5.22 (2 dm$_c$, $J_{cis\text{-}3'\text{-}H,2'}$ = 10.4, 3′-H^*_{cis}), 5.30 and 5.33 (ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.2, $J_{gem} \approx J_{allyl} \approx 1.7$, 3′-$H^*_{trans}$), 5.91 and 5.99 (2 ddt, $J_{2',trans\text{-}3'\text{-}H} \approx 15.5-17$, $J_{2',cis\text{-}3'\text{-}H} \approx 10-11$, $J_{2',1'\text{-}H^A} \approx J_{2',1'\text{-}H^B} \approx 5-6$, 2′-H*), 7.18–7.32 (m, 1-C_6H_5, *m*-, *p*-SPh), 7.41–7.49 (m, *o*-SPh); *no assignment to a single diastereomer was possible.

$C_{26}H_{38}O_2SSi$ (442.7) Calcd. C 70.54 H 8.65
Found C 70.58 H 8.57

1-Phenyl-3-(phenylthio)-3-[(2-propenyl)oxy]-1-[(triisopropylsilyl)oxy]propane (**8h**): Compound **8a** (168 mg, 0.558 mmol) in THF (2 ml), KH (55.9 mg, 1.39 mmol, 2.5 equiv.) in THF (5 ml), iPr_3SiCl (0.14 ml, 130 mg, 0.70 mmol, 1.3 equiv.) in THF (2 ml), 4 h at room temp.; flash chromatography [petroleum ether/ether (150:1)] yielded **8h** (189 mg, 74%). – ^{1}H NMR: δ = 0.85–0.97 (m, iPr_3Si), 0.97–1.16 (m, *i*Pr-H), 1.99 (ddd, J_{gem} = 13.8, $J_{2\text{-}H^1,3}$ = 8.1, $J_{2\text{-}H^1,1}$ = 4.7, 2-H[1] [isomer 2]), 2.07 (ddd, J_{gem} = 13.2, $J_{2\text{-}H^1,3}$ = 7.8, $J_{2\text{-}H^1,1}$ =

5.5, 2-H^1 [isomer 1]), 2.28–2.37 (m, 2-H^2 [both isomers]), 3.88 (ddt, J_{gem} = 12.6, $J_{1',2'}$ = 5.9, $J_{allyl} \approx$ 1, 1'-H^{1*}), superimposed by 3.90 (ddt, J_{gem} = 12.6, $J_{1',2'}$ = 5.8, $J_{allyl} \approx$ 1, 1'-H^{1*}), 4.37–4.50 (m, 1'-H^2 [both isomers]), 4.44 (dd, $J_{1,2\text{-}H^2}$ = 9.0, $J_{1,2\text{-}H^1}$ = 4.7, 1-H [isomer 2]), 4.76 (dd, $J_{1,2\text{-}H^2}$ = 7.7, $J_{1,2\text{-}H^1}$ = 5.5, 1-H [isomer 1]), 4.92 (dd, $J_{3,2\text{-}H^1}$ = 8.0, $J_{3,2\text{-}H^2}$ = 4.4, 3-H [isomer 2]), 4.94 (dd, $J_{3,2\text{-}H^1}$ = 8.0, $J_{3,2\text{-}H^2}$ = 4.4, 3-H [isomer 1]), 5.16 and 5.19 (2 dm$_c$, $J_{cis\text{-}3'\text{-}H,2'} \approx$ 10, 3'-H$^*_{cis}$), 5.25 and 5.30 (2 ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.3, $J_{gem} \approx J_{allyl} \approx$ 1.7, 3'-H$^*_{trans}$), 5.90 and 5.92 (2 ddt, $J_{2',trans\text{-}3'\text{-}H} \approx$ 16–17, $J_{2',cis\text{-}3'\text{-}H} \approx$ 10–11, $J_{2',1'} \approx$ 5–6, 2'-H*), 7.19–7.35 (m, 1-C$_6$H$_5$, *m*-, *p*-SPh), 7.37–7.46 (m, *o*-SPh); *resonance of a single but unidentified diastereomer.

C$_{27}$H$_{40}$O$_2$SSi (456.8) Calcd. C 71.00 H 8.83
Found C 70.91 H 8.72

1-Phenyl-3-(phenylthio)-3-[(2-propenyl)oxy]-1-[(trimethylsilyl)oxy]propane (**8i**): Compound **8a** (302 mg, 1.01 mmol) in THF (3 ml), KH (60.3 mg, 1.50 mmol, 1.5 equiv.) in THF (5 ml), Me$_3$SiCl (0.23 ml, 200 mg, 1.8 mmol, 1.8 equiv.) in THF (4 ml), 12 h at room temp.; flash chromatography [petroleum ether/ether (120:1)] yielded **8i** (295 mg, 79%). – ^{1}H NMR: δ = –0.03 and 0.00 [2 s, (CH$_3$)$_3$Si*], AB signal (δ$_A$ = 2.19, δ$_B$ = 1.93, J_{AB} = 14.0, in addition split by $J_{A,3}$ = 8.6, $J_{A,1}$ = 5.8, $J_{B,1}$ = 7.8, $J_{B,3}$ = 4.9, 2-H$_2$ [isomer 2]), AB signal (δ$_A$ = 2.15, δ$_B$ = 1.98, J_{AB} = 14.1, in addition split by $J_{A,3}$ = 9.6, $J_{A,1}$ = 3.3, $J_{B,1}$ = 9.8, $J_{B,3}$ = 3.4, 2-H$_2$ [isomer 1]), AB signal (δ$_A$ = 4.43, δ$_B$ = 4.01, J_{AB} = 12.6, in addition split by $J_{A,2'}$ = 5.2, J_{allyl} = 1.5, $J_{B,2'}$ = 6.1, 1'-H$^*_2$), AB signal (δ$_A$ = 4.55, δ$_B$ = 4.01, J_{AB} = 12.3, in addition split by $J_{A,2'}$ = 5.4, $J_{allyl} \approx$ 1.5, $J_{B,2'}$ = 6.1, 1'-H$^*_2$), 4.72 (dd, $J_{1,2\text{-}H^B}$ = 7.8, $J_{1,2\text{-}H^A}$ = 5.8, 1-H [isomer 2]), 4.82 (dd, $J_{1,2\text{-}H^B}$ = 9.9, $J_{1,2\text{-}H^A}$ = 3.3, 1-H [isomer 1]), 4.90 (dd, $J_{3,2\text{-}H^A}$ = 8.6, $J_{3,2\text{-}H^B}$ = 4.9, 3-H [isomer 2]), 4.95 (dd, $J_{3,2\text{-}H^B}$ = 9.8, $J_{3,2\text{-}H^A}$ = 3.3, 3-H [isomer 1]), 5.20 and 5.23 (2 dm$_c$, $J_{cis\text{-}3'\text{-}H,2'}$ = 10.4, 3'-H$^*_{cis}$), 5.30 and 5.34 (2 ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.2, $J_{gem} \approx J_{allyl} \approx$ 1.6, 3'-H$^*_{trans}$), 5.93 and 5.99 (2 ddt, $J_{2',trans\text{-}3'\text{-}H} \approx$ 16.5–18, $J_{2',cis\text{-}3'\text{-}H} \approx$ 10–11, $J_{2',1'\text{-}H^A} \approx J_{2',1'\text{-}H^B} \approx$ 5–6, 2'-H*), 7.17–7.34 (m, 1-C$_6$H$_5$, *m*-, *p*-SPh), 7.42–7.51 (m, *o*-SPh); *resonance of a single but unidentified diastereomer.

C$_{21}$H$_{28}$O$_2$SSi (372.6) Calcd. C 67.69 H 7.57
Found C 67.65 H 7.43

1-Phenyl-3-(phenylthio)-3-[(2-propenyl)oxy]-1-[(triethylsilyl)oxy]propane (**8j**): Compound **8a** (251 mg, 0.836 mmol) in THF (3 ml), KH (83.6 mg, 2.08 mmol, 2.5 equiv.) in THF (8 ml), Et$_3$SiCl (0.21 ml, 190 mg, 1.3 mmol, 1.5 equiv.) in THF (2 ml), 12 h at room temp.; flash chromatography [petroleum ether/ether (100:1)] yielded **8j** (321 mg, 93%). – ^{1}H NMR: δ = 0.40–0.56 (m, 3 CH$_3$C*H*$_2$Si), 0.82 and 0.83 (2 t, $J_{2',1'} \approx$ 7–8, 3 C*H*$_3$CH$_2$Si*), 1.91 (ddd, J_{gem} = 14.1, $J_{2\text{-}H^1,1}$ = 7.2, $J_{2\text{-}H^1,3}$ = 5.4, 2-H^1 [isomer 2]), 1.98 (ddd, J_{gem} = 14.2, $J_{2\text{-}H^1,3}$ = 9.4, $J_{2\text{-}H^1,1}$ = 3.6, 2-H^1 [isomer 1]), 2.15–2.25 (m, 2-H^2 [both isomers]), AB signal (δ$_A$ = 4.55, δ$_B$ = 3.98, J_{AB} = 12.3, in addition split by $J_{A,2'}$ = 5.5, $J_{B,2'}$ = 6.1, $J_{allyl} \approx$ 1, 1'-H$^*_2$), AB signal (δ$_A$ = 4.42, δ$_B$ = 4.00, J_{AB} = 12.6, in addition split by $J_{A,2'}$ = 5.2, $J_{B,2'}$ = 6.1, $J_{allyl} \approx$ 1, 1'-H$^*_2$), 4.70 (dd, $J_{1,2\text{-}H^1}$ = 7.3, $J_{1,2\text{-}H^2}$ = 6.3, 1-H [isomer 2]), 4.82 (dd, $J_{1,2\text{-}H^2}$ = 9.6, $J_{1,2\text{-}H^1}$ = 3.7, 1-H [isomer 1]), 4.88 (dd, $J_{3,2\text{-}H^2}$ = 8.1, $J_{3,2\text{-}H^1}$ = 5.4, 3-H [isomer 2]), 4.94 (dd, $J_{3,2\text{-}H^1}$ = 9.5, $J_{3,2\text{-}H^2}$ = 3.6, 3-H [isomer 1]), 5.20 (ddt, $J_{cis\text{-}3'\text{-}H,2'}$ = 10.4, J_{gem} = 1.6, $J_{allyl} \approx$ 1, 3'-H$^*_{cis}$), 5.21 (ddt, $J_{cis\text{-}3'\text{-}H,2'}$ = 10.3, J_{gem} = 1.7, $J_{allyl} \approx$ 1, 3'-H$^*_{cis}$), 5.30 and 5.32 (2 ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.2, J_{gem} = 1.6, $J_{allyl} \approx$ 1, 3'-H$^*_{trans}$), 5.92 and 5.98 (2 ddt, $J_{2',trans\text{-}3'\text{-}H}$ = 17.2, $J_{2',cis\text{-}3'\text{-}H} \approx$ 11–12, $J_{2',1'\text{-}H^A} \approx J_{2',1'\text{-}H^B} \approx$ 5–6, 2'-H*), 7.18–7.30 (m, 1-C$_6$H$_5$, *m*-, *p*-SPh), 7.42–7.49 (m, *o*-SPh); *resonance of a single but unidentified diastereomer.

C$_{24}$H$_{34}$O$_2$SSi (414.7) Calcd. C 69.51 H 8.26
Found C 69.12 H 8.33

1-[(tert-Butyldiphenylsilyl)oxy]-1-phenyl-3-(phenylthio)-3-[(2-propenyl)oxy]propane (**8k**): Compound **8a** (248 mg, 0.826 mmol) in THF (3 ml), KH (84.3 mg, 2.10 mmol, 2.5 equiv.) in THF (8 ml), *t*BuPh$_2$SiCl (0.26 ml, 270 mg, 0.99 mmol, 1.2 equiv.) in THF (3 ml), 12 h at room temp.; flash chromatography [petroleum ether/ether (150:1)] yielded **8k** (404 mg, 91%). – ^{1}H NMR: δ = 0.94 and 0.96 (2 s, *t*Bu*), AB signal (δ$_A$ = 2.33, δ$_B$ = 2.02, J_{AB} = 13.9, in addition split by $J_{A,1}$ = 8.5, $J_{A,3}$ = 6.1, $J_{B,3}$ = 7.6, $J_{B,1}$ = 5.0, 2-H$_2$ [isomer 2]), AB signal (δ$_A$ = 2.38, δ$_B$ = 2.08, J_{AB} = 13.8, in addition split by $J_{A,3}$ = 8.1, $J_{A,1}$ = 5.1, $J_{B,1}$ = 8.1, $J_{B,3}$ = 5.0, 2-H$_2$ [isomer 1]), 3.50 and 3.73 (2 ddt, J_{gem} = 12.7, $J_{1'\text{-}H^1,2'}$ = 5.7, $J_{allyl} \approx$ 1, 1'-H^{1*}), 4.11–4.20 (m, 1'-H^{2*}), 4.26 (ddt, J_{gem} = 12.3, $J_{1'\text{-}H^2,2'}$ = 5.6, $J_{allyl} \approx$ 1.5, 1'-H^{2*}), 4.40 (dd, $J_{1,2\text{-}H^A}$ = 8.6, $J_{1,2\text{-}H^B}$ = 5.0, 1-H [isomer 2]), 4.65 (dd, $J_{1,2\text{-}H^B}$ = 8.1, $J_{1,2\text{-}H^A}$ = 5.0, 1-H [isomer 1]), 4.81 (dd, $J_{3,2\text{-}H^B}$ = 7.5, $J_{3,2\text{-}H^A}$ = 6.3, 3-H [isomer 2]), 4.88 (dd, $J_{3,2\text{-}H^A}$ = 8.1, $J_{3,2\text{-}H^B}$ = 5.0, 3-H [isomer 1]), 5.07 (dm$_c$, $J_{cis\text{-}3'\text{-}H,2'} \approx$ 11–12, 3'-H$^*_{cis}$), 5.10 (ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.2, $J_{gem} \approx J_{allyl} \approx$ 1.5, 3'-H$^*_{trans}$), 5.12 (dm$_c$, $J_{trans\text{-}3'\text{-}H,2'} \approx$ 17–18, 3'-H$^*_{trans}$), 5.66–5.81 (m, 2'-H*), 7.11–7.68 (m, 1-C$_6$H$_5$, 2 PhSi, SPh); *resonance of a single but unidentified diastereomer.

C$_{34}$H$_{38}$O$_2$SSi (538.8) Calcd. C 75.79 H 7.11
Found C 75.64 H 7.04

2,4-Diphenyl-6-[(2-propenyl)oxy]-1,3-dioxane (**11**): At –78°C Et$_2$O · BF$_3$ (60 µl, 69 mg, 0.49 mmol, 0.2 equiv.) in CH$_2$Cl$_2$ (3 ml) was added slowly to benzaldehyde (0.25 ml, 260 mg, 2.5 mmol) and allyl vinyl ether (222 mg, 2.63 mmol) in CH$_2$Cl$_2$ (20 ml). After 60 min, the reaction was quenched with pyridine (1 ml), and the resulting mixture was washed with satd. aqueous NaHCO$_3$ solution (10 ml) and extracted with CH$_2$Cl$_2$ (3 × 30 ml). Purification by flash chromatography [petroleum ether/ether (15:1)] of the crude product obtained by evaporation of the solvents from the combined extracts yielded two stereoisomers of **11** tentatively assigned as (2*R**,4*S**,6*R**)-**11** (119 mg, 33%) and (2*R**,4*S**,6*S**)-**11** (116 mg, 32%). – ^{1}H NMR: (2*R**,4*S**,6*R**)-**11**: AB signal (δ$_A$ = 2.12, δ$_B$ = 1.97, J_{AB} = 13.1, in addition split by $J_{A,4}$ = $J_{A,6}$ = 2.5, $J_{B,4}$ = 11.5, $J_{B,6}$ = 9.4, 5-H$_2$), AB signal (δ$_A$ = 4.48, δ$_B$ = 4.21, J_{AB} = 12.9, in addition split by $J_{A,2'}$ = 5.1 and small *J* values, $J_{B,2'}$ = 6.7, 1'-H$_2$), 4.90 (dd, $J_{4,5\text{-}H^B}$ = 11.5, $J_{4,5\text{-}H^A}$ = 2.5, 4-H), 5.07 (dd, $J_{6,5\text{-}H^B}$ = 9.5, $J_{6,5\text{-}H^A}$ = 2.4, 6-H), 5.23 (d, $J_{cis\text{-}3'\text{-}H,2'}$ = 10.4, 3'-H$_{cis}$), 5.34 (dm$_c$, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.3, 3'-H$_{trans}$), 5.76 (s, 2-H), 5.98 (br. dddd, $J_{2',trans\text{-}3'\text{-}H} \approx$ 16–18, $J_{2',cis\text{-}3'\text{-}H} \approx$ 10–12, $J_{2',1'} \approx$ 5–6, 2'-H), 7.26–7.45 (m, 4-C$_6$H$_5$, *m*-,*p*-2-C$_6$H$_5$), 7.56–7.62 (m, *o*-2-C$_6$H$_5$); (2*R**,4*S**,6*S**)-**11**: AB signal (δ$_A$ = 2.22, δ$_B$ = 2.01, J_{AB} = 13.5, in addition split by $J_{A,6}$ = 12.0, $J_{A,4}$ = 3.7, $J_{B,6}$ = 2.7, $J_{B,4}$ = 1.2, 5-H$_2$), AB signal (δ$_A$ = 4.40, δ$_B$ = 4.17, J_{AB} = 13.0, in addition split by $J_{A,2'}$ = 5.2, J_{allyl} = 1.5, $J_{B,2'}$ = 6.1, J_{allyl} = 1.3, 1'-H$_2$), 5.24 (m$_c$, 4-H), partly superimposed by 5.27 (dm$_c$, $J_{cis\text{-}3'\text{-}H,2'} \approx$ 10–12, 3'-H$_{cis}$), partly superimposed by 5.30 (dd, $J_{6,5\text{-}H^A} >$ 11, $J_{6,5\text{-}H^B}$ = 2.6, 6-H), 5.39 (ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.2, J_{gem} = 1.6, J_{allyl} = 1.7, 3'-H$_{trans}$), 6.03 (m$_c$, 2'-H), 6.20 (s, 2-H), 7.27–7.47 (m, 4-C$_6$H$_5$, *m*-, *p*-2-C$_6$H$_5$), 7.58 (dd, $J_{o,m}$ = 7.9, $J_{o,p}$ = 2.1, *o*-2-C$_6$H$_5$).

C$_{19}$H$_{20}$O$_3$ (296.4) Calcd. C 77.00 H 6.80
Found C 76.70 H 7.10

4-(Benzyloxy)-4-phenyl-1-butene (**13a**): At 0°C **12**[14] (1.80 g, 12.2 mmol) was added dropwise to a suspension of KH (0.876 g, 21.8 mmol, 1.8 equiv.) in THF (30 ml). After 30 min, benzyl bromide (2.17 ml, 3.12 g, 18.2 mmol, 1.5 equiv.) in THF (10 ml) was added, and the solution was stirred for ca. 12 h at room temp. The reaction was quenched at 0°C with satd. aqueous NH$_4$Cl solution (10 ml)/H$_2$O (10 ml) and the resulting mixture extracted with Et$_2$O (4 × 50 ml). Flash chromatography [petroleum ether/ether (50:1)] of the residue obtained by evaporation of the solvents from the combined

extracts furnished **13a** (2.63 g, 91%). – ^{1}H NMR: AB signal (δ_A = 2.63, δ_B = 2.44, J_{AB} = 14.2, in addition split by $J_{A,2} \approx J_{A,1} \approx 7$, $J_{B,2} \approx 7$, $J_{B,4} \approx 6$, 3-H$_2$), AB signal (δ_A = 4.47, δ_B = 4.27, J_{AB} = 11.9, 1′-H$_2$), 4.37 (dd, $J_{4,3\text{-}H^A}$ = 7.5, $J_{4,3\text{-}H^B}$ = 5.9, 4-H), 5.01 (dm$_c$, $J_{cis\text{-}1\text{-}H,2} \approx 10$, 1-H$_{cis}$), 5.04 (dm$_c$, $J_{trans\text{-}1\text{-}H,2} \approx 17$, 1-H$_{trans}$), 5.79 (dddd, $J_{2,trans\text{-}1\text{-}H}$ = 17.1, $J_{2,cis\text{-}1\text{-}H}$ = 10.2, $J_{2,3\text{-}H^A} = J_{2,3\text{-}H^B}$ = 6.9, 2-H), 7.24–7.40 (m, 4-C$_6$H$_5$, 1′-C$_6$H$_5$).

C$_{17}$H$_{18}$O (238.3) Calcd. C 85.67 H 7.61
Found C 85.59 H 7.76

4-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-4-phenyl-1-butene (**13b**) was prepared as described for **13a** from **12** (0.734 g, 4.95 mmol) in THF (5 ml), KH (0.297 g, 7.41 mmol, 1.5 equiv.) in THF (20 ml), and chlorodimethyl(1,1,2-trimethylpropyl)silane (0.98 ml, 0.89 g, 4.97 mmol, 1.0 equiv.) in THF (5 ml); flash chromatography [petroleum ether/ether (100:1)] yielded **13b** (1.298 g, 90%). – ^{1}H NMR: δ = –0.16 and 0.08 [2 s, (CH$_3$)$_2$Si], 0.83 and 0.85 (2 s, 2 1′-CH$_3$), 0.89 (d, $J_{2'\text{-}Me,2'\text{-}H} = J_{3'\text{-}H,2'\text{-}H}$ = 6.9, 2′-CH$_3$ and 3′-H$_3$), 1.64 (qq, $J_{2'\text{-}H,2'\text{-}Me} = J_{2'\text{-}H,3'\text{-}H}$ = 6.9, 2′-H), 2.32–2.56 (m, 3-H$_2$), 4.67 (dd, $J_{4,3}$ = 6.9, $J'_{4,3}$ = 5.4, 4-H), 4.99 (dm$_c$, 1-H$_{trans}$ and 1-H$_{cis}$ superimposed, $J \approx 13-14$), 5.76 (dddd, $J_{2,trans\text{-}1\text{-}H}$ = 17.8, $J_{2,cis\text{-}1\text{-}H}$ = 9.6, $J_{2,3}$ = 7.1, 2-H), 7.19–7.38 (m, 4-C$_6$H$_5$).

C$_{18}$H$_{30}$OSi (290.5) Calcd. C 74.42 H 10.41
Found C 74.32 H 10.35

3-(Benzyloxy)-3-phenylpropanal (**14a**): Compound **13a** (1.64 g, 6.89 mmol) was dissolved in CH_2Cl_2 (50 ml) and treated at –78°C with O_3 (7.0 g O_3/h) until the solution turned blue. Then triphenylphosphane (3.61 g, 13.8 mmol, 2.0 equiv.) was added. The solution was stirred at room temp. for 1 h. Most of the resulting Ph_3PO was removed by crystallization at –30°C. The crude product was purified by flash chromatography [petroleum ether/ether (5:1)] to yield **14a** (1.47 g, 89%). – ^{1}H NMR: AB signal (δ_A = 2.97, δ_B = 2.66, J_{AB} = 16.5, in addition split by $J_{A,3}$ = 9.2, $J_{A,1}$ = 2.6, $J_{B,3}$ = 4.2, $J_{B,1}$ = 1.6, 2-H$_2$), AB signal (δ_A = 4.47, δ_B = 4.30, J_{AB} = 11.6, 1′-H$_2$), 4.91 (dd, $J_{3,2\text{-}H^A}$ = 9.2, $J_{3,2\text{-}H^B}$ = 4.2, 3-H), 7.24–7.44 (m, 3-C$_6$H$_5$, 1′-C$_6$H$_5$), 9.78 (dd, $J_{1,2\text{-}H^A}$ = 2.5, $J_{1,2\text{-}H^B}$ = 1.6, 1-H).

C$_{16}$H$_{16}$O$_2$ (240.3) Calcd. C 79.97 H 6.71
Found C 79.81 H 6.75

3-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-3-phenylpropanal (**14b**) was obtained from **13b** (1.44 g, 4.95 mmol) in CH_2Cl_2 (45 ml) after flash chromatography [petroleum ether/ether (40:1)] (1.24 g, 85%) according to the procedure given for the ozonolysis **13a** → **14a**. – ^{1}H NMR: δ = –0.16 and 0.11 [2 s, (CH$_3$)$_2$Si], 0.82 and 0.83 (2 s, 2 1′-CH$_3$), 0.88 (2 d, $J_{2'\text{-}Me,2'\text{-}H} = J_{3'\text{-}H,2'\text{-}H}$ = 6.8, 2′-CH$_3$ and 3′-H$_3$), 1.62 (qq, $J_{2'\text{-}H,2'\text{-}Me} = J_{2'\text{-}H,3'\text{-}H}$ = 6.8, 2′-H), AB signal (δ_A = 2.85, δ_B = 2.63, J_{AB} = 15.6, in addition split by $J_{A,3}$ = 8.0, $J_{A,1}$ = 2.8, $J_{B,3}$ = 4.1, $J_{B,1}$ = 2.0, 2-H$_2$), 5.20 (dd, $J_{3,2\text{-}H^A}$ = 7.9, $J_{3,2\text{-}H^B}$ = 4.2, 3-H), 7.23–7.36 (m, 3-C$_6$H$_5$), 9.79 (dd, $J_{1,2\text{-}H^A} \approx J_{1,2\text{-}H^B} \approx$ 2.4, 1-H).

C$_{17}$H$_{28}$O$_2$Si (292.5) Calcd. C 69.81 H 9.65
Found C 69.02 H 9.52

3-Methyl-1-[(trimethylsilyl)oxy]-2-butene (**15**): 3-Methyl-2-buten-1-ol (20.0 ml, 17.1 g, 0.198 mol) was heated under reflux with *HN(SiMe$_3$)$_2$* (23.2 ml, 17.75 g, 0.110 mol) for 3 h. Distillation (b.p. 141–142°C) gave **15** (24.1 g, 77%). – ^{1}H NMR: δ = 0.07 [s, (CH$_3$)$_3$Si], 1.60 and 1.67 (2 br. s, 3-CH$_3$ and 4-H$_3$), 4.07 (d, $J_{1,2}$ = 6.8, 1-H$_2$), 5.27 (tqq, $J_{2,1}$ = 6.8, $J_{2,4} = J_{2,Me}$ = 1.4, 2-H).

1-(Benzyloxy)-3-[(3-methyl-2-butenyl)oxy]-1-phenyl-3-(phenylthio)propane (**16a**; 70:30 mixture of diastereomers): At –78°C trimethylsilyl triflate (1 M in CH_2Cl_2, 2.0 equiv.) was treated dropwise with a mixture of (trimethylsilyl)thiophenol (0.29 ml, 280 mg, 1.5 mmol, 1.2 equiv.) and alcohol **15** (397 mg, 2.51 mmol, 2.0 equiv.) in CH_2Cl_2 (3 ml). After 15 min, aldehyde **14a** (301 mg, 1.25 mmol) in CH_2Cl_2 (2 ml) was added. Stirring was continued for 60 min. After quenching the reaction with pyridine (1 ml), the obtained mixture was dissolved in Et_2O (30 ml), and the solution was washed with satd. aqueous $NaHCO_3$ solution (20 ml) and extracted with Et_2O (3 × 30 ml). Flash chromatography [petroleum ether/ether (50:1)] of the crude product obtained by evaporation of the solvents from the combined extracts provided **16a** (271 mg, 52%). – ^{1}H NMR: δ = 1.68 (s, CH$_3$), 1.71 (s, CH$_3$ [minor isomer]), 1.75 (s, CH$_3$ [major isomer]), 1.94–2.05 (m, 2-H^1), 2.26 (ddd, J_{gem} = 14.3, $J_{2,1}$ = 10.2, $J_{2,3}$ = 3.3, 2-H^2 [minor isomer]), 2.36 (ddd, J_{gem} = 14.2, $J_{2,1}$ = 8.1, $J_{2,3}$ = 6.7, 2-H^2 [major isomer]), 3.97 (dd, J_{gem} = 11.6, $J_{1',2'}$ = 7.5, 1′-H^1 [major isomer]), 4.02 (dd, 1′-H^1 [minor isomer] superimposed), AB signal (δ_A = 4.35, δ_B = 4.22, J_{AB} = 11.6, 1″-H$_2$ [minor isomer]), AB signal (δ_A = 4.35, δ_B = 4.23, J_{AB} = 11.3, 1″-H$_2$ [major isomer]), 4.37–4.46 (m, 1′-H^2), 4.55 (dd, $J_{1,2\text{-}H^2}$ = 10.2, $J_{1,2\text{-}H^1}$ = 3.5, 1-H [minor isomer]), 4.63 (dd, $J_{1,2\text{-}H^2}$ = 8.1, $J_{1,2\text{-}H^1}$ = 6.0, 1-H [major isomer]), 4.72 (dd, $J_{3,2\text{-}H^1} = J_{3,2\text{-}H^2}$ = 6.9, 3-H [major isomer]), 5.04 (dd, $J_{3,2\text{-}H^1}$ = 9.9, $J_{3,2\text{-}H^2}$ = 3.3, 3-H [minor isomer]), 5.27–5.38 (m, 2′-H), 7.21–7.38 (m, 1-C$_6$H$_5$, 1″-C$_6$H$_5$, *m*-, *p*-SPh), 7.41–7.48 (m, *o*-SPh).

C$_{27}$H$_{30}$O$_2$S (418.6) Calcd. C 77.47 H 7.22
Found C 77.66 H 7.18

1-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-3-[2-(3-methylbutenyl)oxy]-1-phenyl-3-(phenylthio)propane (**16b**; 71:29 mixture of diastereomers) was prepared as described for **16a** from trimethylsilyl triflate (1 M in CH_2Cl_2, 2.38 ml, 2.38 mmol, 2.0 equiv.), (trimethylsilyl)thiophenol (0.27 ml, 260 mg, 1.4 mmol, 1.2 equiv.), **15** (378 mg, 2.39 mmol, 2.0 equiv.) in CH_2Cl_2 (3 ml), and **14b** (349 mg, 1.19 mmol) in CH_2Cl_2 (2 ml). Flash chromatography [petroleum ether/ether (150:1)] yielded **16b** (234 mg, 42%). – ^{1}H NMR: δ = –0.38 and –0.05 {2 s, (CH$_3$)$_2$Si, [minor isomer]}, –0.30 and 0.03 {2 s, (CH$_3$)$_2$Si, [major isomer]}, 0.72–0.86 (m, 2 1″-CH$_3$, 3″-H$_3$), 1.55 (qq, $J_{2'',2''\text{-}Me} = J_{2'',3''\text{-}H}$ = 6.9, 2″-H [major isomer]), 1.56 (qq, $J_{2'',2''\text{-}Me} = J_{2'',3''\text{-}H}$ = 6.9, 2″-H, [minor isomer]), 1.65 and 1.71 (2 s, 3′-CH$_3$, 4′-H$_3$), AB signal (δ_A = 2.12, δ_B = 1.83, J_{AB} = 14.1, $J_{A,3}$ = 8.4, $J_{A,1}$ = 5.8, $J_{B,1}$ = 7.7, $J_{B,3}$ = 5.0, 2-H$_2$ [major isomer]), 1.93 (ddd, J_{gem} = 13.1, $J_{2,1} \approx$ 9.5, $J_{2,3}$ = 3.5, 2-H^1 [minor isomer]), 2.07–2.22 (m, 2-H^2 [minor isomer]), AB signal (δ_A = 4.53, δ_B = 3.89, J_{AB} = 10.9, in addition split by $J_{A,2'} = J_{B,2'}$ = 7.3, 1′-H$_2$ [minor isomer]), AB signal (δ_A = 4.27, δ_B = 4.06, J_{AB} = 11.7, in addition split by $J_{A,2'}$ = 6.3, $J_{B,2'}$ = 7.8, 1′-H$_2$ [major isomer]), 4.68 (dd, $J_{1,2\text{-}H^B}$ = 7.7, $J_{1,2\text{-}H^A}$ = 5.9, 1-H [major isomer]), 4.74 (dd, $J_{1,2\text{-}H^1}$ = 9.6, $J_{1,2\text{-}H^2}$ = 3.4, 1-H [minor isomer]), 4.79 (dd, $J_{3,2\text{-}H^A}$ = 8.4, $J_{3,2\text{-}H^B}$ = 5.0, 3-H [major isomer]), 4.87 (dd, $J_{3,2}$ = 9.5, $J'_{3,2}$ = 3.4, 3-H [minor isomer]), 5.28 (ddm$_c$, $J_{2',1'} \approx J'_{2',1'} \approx$ 7, 2′-H [major isomer]), 5.36 (ddm$_c$, $J_{2',1'} \approx J'_{2',1'} \approx$ 7, 2′-H [minor isomer]), 7.12–7.29 (m, 1-C$_6$H$_5$, *m*-, *p*-SPh), 7.37–7.44 (m, *o*-SPh).

C$_{28}$H$_{42}$O$_2$SSi (470.8) Calcd. C 71.43 H 8.99
Found C 71.48 H 9.02

1-(Benzyloxy)-1-phenyl-3-(phenylthio)-3-[(trimethylsilyl)oxy]propane (**17**; 74:26 mixture of diastereomers) accompanied the formation of **16a**. The maximum yield of **17** resulted from the reaction of **15** (225 mg, 1.42 mmol, 1.1 equiv.) in CH_2Cl_2 (3 ml), trimethylsilyl triflate (1 M in CH_2Cl_2, 0.13 ml, 0.13 mmol, 0.1 equiv.), and (trimethylsilyl)thiophenol (0.27 ml, 260 mg, 1.4 mmol) with **14a** (303 mg, 1.26 mmol) in CH_2Cl_2 (3 ml). Flash chromatography [petroleum ether/ether (40:1–30:1)] furnished **17** (199 mg, 37%). – ^{1}H NMR: δ = 0.05 {s, (CH$_3$)$_3$Si [minor isomer]}, 0.06 {s, (CH$_3$)$_3$Si [major isomer]}, AB signal (δ_A = 2.32, δ_A = 2.04, J_{AB} = 14.1, in addition split by $J_{A,1}$ = 9.5, $J_{A,3}$ = 3.9, $J_{B,3}$ = 9.1, $J_{B,1}$ = 4.0, 2-H$_2$ [major isomer]), AB signal (δ_A = 4.37, δ_B = 4.23, J_{AB} = 11.4, 1′-H$_2$ [major isomer]), AB signal (δ_A = 4.42, δ_B = 4.27, J_{AB} = 11.6,

1′-H_2 [minor isomer]), 4.51 (dd, $J_{1,2\text{-}H^A}$ = 9.6, $J_{1,2\text{-}H^B}$ = 4.0, 1-H [major isomer]), 4.61 (dd, $J_{1,2}$ = 8.9, $J'_{1,2}$ = 4.7, 1-H [minor isomer]), 5.22 (dd, $J_{3,2}$ = 8.1, $J'_{3,2}$ ≈ 5.4, 3-H [minor isomer]), 5.33 (dd, $J_{3,2\text{-}H^B}$ = 9.1, $J_{3,2\text{-}H^A}$ = 3.8, 3-H [major isomer]), 7.22–7.37 (m, 1-C_6H_5 and *m*-, *p*-SPh), 7.42–7.48 (m, *o*-SPh).

$C_{25}H_{30}O_2SiS$ (422.7) Calcd. C 71.04 H 7.15
Found C 70.85 H 6.89

1-(Benzyloxy)-3,3-[bis(phenylthio)]-1-phenylpropane (**18**): Trimethylsilyl triflate (1 M in CH_2Cl_2, 0.05 ml, 0.05 mmol, 0.05 equiv.) was treated at −78°C with a mixture of **15** (325 mg, 2.05 mmol, 2.0 equiv.) and (trimethylsilyl)thiophenol (0.39 ml, 380 mg, 2.1 mmol, 2.0 equiv.) in CH_2Cl_2 (3 ml). After 15 min, **14a** (246 mg, 1.03 mmol) in CH_2Cl_2 (2 ml) was added dropwise. After stirring for 30 min at −78°C, the solution was warmed to room temp. and quenched with pyridine (0.5 ml) and satd. aqueous $NaHCO_3$ solution. Extraction with Et_2O (3 × 30 ml) followed by flash chromatography [petroleum ether/ether (40:1)] of the crude product obtained by evaporation of the solvent from the combined extracts yielded **18** (219 mg, 48%). – ^{1}H NMR: AB signal (δ_A = 2.43, δ_B = 2.03, J_{AB} = 14.1, in addition split by $J_{A,3}$ = 9.1, $J_{A,1}$ = 5.2, $J_{B,1}$ = 9.2, $J_{B,3}$ = 4.5, 2-H_2), AB signal (δ_A = 4.41, δ_B = 4.21, J_{AB} = 11.5, 1′-H_2), 4.64 (dd, $J_{1,2\text{-}H^B}$ = 9.2, $J_{1,2\text{-}H^A}$ = 5.2, 1-H), 4.80 (dd, $J_{3,2\text{-}H^A}$ = 9.1, $J_{3,2\text{-}H^B}$ = 4.4, 3-H), 7.20–7.44 (m, 2 SPh and 1-C_6H_5).

1-Methyl-3-(phenylthio)-2-butene (**19**) was prepared as described for **16a** by treatment of **15** (203 mg, 1.28 mmol, 1.0 equiv.) with (trimethylsilyl)thiophenol (0.24 ml, 230 mg, 1.3 mmol, 1.0 equiv.), trimethylsilyl triflate (1 M in CH_2Cl_2, 0.64 ml, 0.64 mmol, 0.5 equiv.), and **14a** (304 mg, 1.27 mmol) with stirring at −30°C (30 min). Aqueous workup afforded after flash chromatography [petroleum ether/ether (80:1)] **19** (107 mg, 47%). – ^{1}H NMR: δ = 1.58 and 1.71 (2 s, 1-H_3 and 2-CH_3), 3.54 (d, $J_{4,3}$ = 7.6, 4-H_2), 5.30 (br. t, $J_{3,4}$ ≈ 7, 3-H), 7.13–7.37 (m, SPh).

[2,3]-Wittig Rearrangements

General Procedure for the Preparation of Homoallyl Alcohols **20a–f** *and* **21** (for detailed conditions cf. individual descriptions): At −78°C Li-Naphth (0.34–0.38 M in THF, 2.2–3.3 equiv.) was added dropwise through a cannula cooled with dry ice to the O,S-acetal in THF (5–10 ml). After stirring for 5–30 min, the reaction was quenched with satd. aqueous NH_4Cl solution and the mixture extracted with Et_2O (3 × 30 ml). Purification of the crude product obtained by evaporation of the solvents from the combined extracts was effected by flash chromatography.

1-Phenyl-5-hexen-1,3-diol (**20a**): Compound **8a** (148 mg, 0.494 mmol) in THF (5 ml), Li-Naphth (4.80 ml, 0.34 M in THF, 1.63 mmol, 3.3 equiv.); flash chromatography [petroleum ether/ether (1:1)] yielded **20a** (66.2 mg, 70%) as a 50:50 *syn:anti* mixture. – ^{1}H NMR ($CDCl_3$, 400 MHz): AB signal (δ_A = 1.86, δ_B = 1.81, J_{AB} = 14.5, in addition split by $J_{A,1}$ = $J_{A,3}$ = 9.2, $J_{B,1}$ = 4.1, $J_{B,3}$ = 3.2, 2-H_2 [*syn*]), 1.95 (ddd, J_{gem} = 14.6, $J_{2,1}$ = 7.8, $J_{2,3}$ = 3.2, 2-H^2 [*anti*]), 1.86–1.95 (m, 2-H^1 [*anti*]), 2.20–2.33 (m, 4-H_2), 2.93 and 3.32 (2 br. s, OH), 3.89–4.03 (m, 3-H), 4.95 (dd, $J_{1,2\text{-}H^A}$ = 9.2, $J_{1,2\text{-}H^B}$ = 3.9, 1-H [*syn*]), 5.07 (dd, $J_{1,2\text{-}H^2}$ = 7.9, $J_{1,2\text{-}H^1}$ = 3.5, 1-H [*anti*]), 5.10–5.17 (m, 6-H_{trans} and 6-H_{cis}), 5.73–5.86 (m, 5-H), 7.26–7.39 (m, 1-C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 41.91 (C-4 [*anti*]), 42.40 (C-4 [*syn*]), 44.05 (C-2 [*anti*]), 44.81 (C-2 [*syn*]), 67.99 (C-3 [*anti*]), 71.52 (C-3 [*syn*] and C-1 [*anti*]), 75.04 (C-1 [*syn*]), 118.28 (C-6 [*syn* + *anti*]), 125.51 (2 C-2′ [*anti*]), 125.66 (2 C-2′ [*syn*]), 127.25 (C-4′ [*anti*]), 127.55 (C-4′ [*syn*]), 128.39 (2 C-3′ [*anti*]), 128.45 (2 C-3′ [*syn*]), 134.10 (C-5 [*syn*]), 134.38 (C-5 [*anti*]), 144.37 (C-1′ [*syn*]), 144.48 (C-1′ [*anti*]).

$C_{12}H_{16}O_2$ (192.3) Calcd. C 74.97 H 8.39
Found C 75.21 H 8.64

1-Methoxy-1-phenyl-5-hexen-3-ol (**20b**): Compound **8b** (203 mg, 0.646 mmol) in THF (6 ml), Li-Naphth (3.78 ml, 0.38 M in THF, 1.44 mmol, 2.2 equiv.), 5 min; flash chromatography [petroleum ether/ether (5:1–4:1)] yielded 77.6 mg (58%) as a 56:44 *syn:anti* mixture. – ^{1}H NMR: AB signal (δ_A = 1.89, δ_B = 1.75, J_{AB} = 14.7, in addition split by $J_{A,1}$ = $J_{A,3}$ = 9.8, $J_{B,1}$ = 3.8, $J_{B,3}$ = 2.2, 2-H [*syn*]), superimposed by AB signal (δ_A = 1.90, δ_B = 1.77, $J_{A,B}$ = 14.6, in addition split by $J_{A,1}$ = 8.8, $J_{A,3}$ = 2.6, $J_{B,3}$ = 10.1, $J_{B,1}$ = 3.4, 2-H [*anti*]), 2.14–2.32 (m, 4-H_2), 2.61 (d, $J_{OH,3}$ = 4.2, OH [*syn*]), 3.22 (s, OCH_3 [*syn*]), 3.26 (s, OCH_3 [*anti*]), 3.74 (s, OH [*anti*]), 3.85–3.98 (m, 3-H [*syn* + *anti*]), 4.38 (dd, $J_{1,2\text{-}H^A}$ = 9.8, $J_{1,2\text{-}H^B}$ = 3.9, 1-H [*syn*]), 4.50 (dd, $J_{1,2\text{-}H^A}$ = 8.8, $J_{1,2\text{-}H^B}$ = 3.4, 1-H [*anti*]), 5.04–5.16 (m, 6-H_{cis} and 6-H_{trans} [*syn* + *anti*]), 5.75–5.89 (m, 5-H [*syn* + *anti*]), 7.28–7.40 (m, 1-C_6H_5).

$C_{13}H_{18}O_2$ (206.3) Calcd. C 75.69 H 8.79
Found C 75.21 H 8.93

1-(Benzyloxy)-1-phenyl-5-hexen-3-ol (**20c**): Compound **8c** (304 mg, 0.778 mmol) in THF (10 ml), Li-Naphth (5.56 ml, 0.34 M in THF, 1.89 mmol, 2.4 equiv.), 5 min; flash chromatography [petroleum ether/ether (5:1–4:1)] yielded 165 mg (75%) as a 64:36 *syn:anti* mixture. – ^{1}H NMR: AB signal (δ_A = 1.96, δ_B = 1.776, J_{AB} = 14.5, in addition split by $J_{A,1}$ = $J_{A,3}$ = 9.9, $J_{B,1}$ = 3.9, $J_{B,3}$ = 2.2, 2-H_2 [*syn*]), AB signal {δ_A = 1.96(!), δ_B = 1.774, J_{AB} = 14.5, in addition split by $J_{A,1}$ = 9.1, $J_{A,3}$ = 2.7, $J_{B,3}$ = 9.4, $J_{B,1}$ = 3.4, 2-H_2 [*anti*]}, 2.13–2.31 (m, 4-H_2 [*syn* + *anti*]), 2.48 (br. s, OH [*anti*]), 3.74 (br. s, OH [*syn*]), 3.84–3.92 (m, 3-H [*syn*]), 3.92–4.01 (m, 3-H [*anti*]), AB signal (δ_A = 4.46, δ_B = 4.26, J_{AB} = 11.5, 1′-H_2 [*syn*]), AB signal (δ_A = 4.51, δ_B = 4.29, J_{AB} = 11.6, 1′-H_2 [*anti*]), 4.60 (dd, $J_{1,2\text{-}H^A}$ = 10.0, $J_{1,2\text{-}H^B}$ = 3.9, 1-H [*syn*]), 4.70 (dd, $J_{1,2\text{-}H^A}$ = 9.0, $J_{1,2\text{-}H^B}$ = 3.4, 1-H [*anti*]), 5.01–5.13 (m, 6-H_{trans} and 6-H_{cis} [*syn* + *anti*]), 5.72–5.88 (m, 5-H [*syn* + *anti*]), 7.20–7.42 (m, 1-C_6H_5 and 1′-C_6H_5).

$C_{19}H_{22}O_2$ (282.4) Calcd. C 80.82 H 7.85
Found C 80.04 H 7.94

1-Phenyl-1-(triphenylmethoxy)-5-hexen-3-ol (**20d**): Compound **8d** (fast isomer) (241 mg, 0.445 mmol) in THF (10 ml), Li-Naphth (2.58 ml, 0.38 M in THF, 0.980 mmol, 2.2 equiv.), 5 min; flash chromatography [petroleum ether/ether (10:1)] yielded 124 mg (64%) as a 36:64 *syn:anti* mixture. Similarly, **8d** (slow isomer) (142 mg, 0.262 mmol) was converted into **20d** (74.1 mg, 65%) as a 35:65 *syn:anti* mixture. Alternatively, reaction of a 57:43 mixture of **8d** (slow isomer) and **8d** (fast isomer) (102 mg, 0.188 mmol) furnished **20d** (48.0 mg, 59%) as a 35:65 *syn:anti* mixture. – ^{1}H NMR: δ = 1.11 (d, $J_{OH,3}$ = 5.8, OH [*syn*]), 1.23–1.36 (m, 2-H^1 [*syn*] and 2-H_2 [*anti*]), 1.58 (partly superimposed by H_2O peak, ddd, J_{gem} ≈ 15, $J_{2,1}$ ≈ 9.5, $J_{2,3}$ ≈ 3, 2-H^2 [*syn*]), 1.81–2.00 (m, 4-H_2 [*syn* + *anti*]), 3.04–3.14 (m, 3-H [*syn*]), 3.37 (d, $J_{OH,3}$ ≈ 1.5, OH [*anti*]), 3.61 (tt, $J_{3,2}$ ≈ $J_{3,4}$ ≈ 8, 3-H [*anti*]), 4.74 (dd, $J_{1,2\text{-}H^A}$ = 9.5, $J_{1,2\text{-}H^B}$ = 4.4, 1-H [*syn*]), 4.85–5.01 (m, 1-H [*anti*], superimposed by 6-H_{trans}, 6-H_{cis} [*syn* + *anti*]), 5.50 (ddt, $J_{5,trans\text{-}6\text{-}H}$ = 17.3, $J_{5,cis\text{-}6\text{-}H}$ = 10.2, $J_{5,4}$ = 7.0, 5-H [*syn*]), 5.59 (ddt, $J_{5,trans\text{-}6\text{-}H}$ = 17.0, $J_{5,cis\text{-}6\text{-}H}$ = 10.4, $J_{5,4}$ = 7.0, 5-H [*anti*]), 7.12–7.25 (m, *m*-, *p*-Ph_3C and 1-C_6H_5), 7.45 (dd, $J_{o,m}$ = 8.1, $J_{o,p}$ = 1.6, *o*-Ph_3C). – Since residual amounts of petroleum ether could not be removed from the very viscous product no correct combustion analysis could be obtained.

1-[(2-Methoxyethoxy)methoxy]-1-phenyl-5-hexen-3-ol (**20e**): Compound **8e** (241 mg, 0.620 mmol) in THF (8 ml), Li-Naphth (4.02 ml, 0.34 M in THF, 1.37 mmol, 2.2 equiv.), 5 min; flash chromatography [petroleum ether/ether (2:1–1:1)] yielded 135 mg (78%) as a 63:37 *syn:anti* mixture. – ^{1}H NMR: AB signal (δ_A = 1.90, δ_B = 1.67, J_{AB} = 14.5, in addition split by $J_{A,1}$ = 10.5, $J_{A,3}$ = 2.3, $J_{B,3}$ = 10.3, $J_{B,1}$ = 2.8, 2-H_2 [*anti*]), AB signal (δ_A = 1.97, δ_B =

1.82, J_{AB} = 14.6, in addition split by $J_{A,1}$ = $J_{A,3}$ = 9.4, $J_{B,1}$ = 4.7, $J_{B,3}$ = 2.4, 2-H_2 [*syn*]), 2.18–2.32 (m, 4-H_2 [*syn* + *anti*]), 3.26 (br. d, $J_{OH,3} \approx 2$, OH [*syn*]), 3.38 (s, OCH_3 [*syn*]), 3.42 (s, OCH_3 [*anti*]), 3.46–3.61 (m, 2′-H_2 and 3′-H_2 [*syn* + *anti*]), 3.78–3.90 (m, 3-H [*syn*]), 3.91–4.05 (m, 3-H [*anti*]), AB signal (δ_A = 4.64, δ_B = 4.58, J_{AB} = 7.0, 1′-H_2 [*syn*]), AB signal (δ_A = 4.62, δ_B = 4.59, J_{AB} = 7.1, 1′-H_2 [*anti*]), 4.88 (dd, $J_{1,2\text{-}H^A}$ = 9.5, $J_{1,2\text{-}H^B}$ = 4.7, 1-H [*syn*]), 5.00 (dd, $J_{1,2\text{-}H^A}$ = 10.5, $J_{1,2\text{-}H^B}$ = 2.8, 1-H [*anti*]), 5.08 (dm_c, $J_{cis\text{-}6\text{-}H,5} \approx 11.5$, 6-$H_{cis}$ [*syn* + *anti*]), 5.09 (dm_c, $J_{trans\text{-}6\text{-}H,5} \approx 17$, 6-$H_{trans}$ [*syn* + *anti*]), 5.75–5.94 (m, 5-H [*syn* + *anti*]), 7.27–7.35 (m, 1-C_6H_5).

$C_{16}H_{24}O_4$ (280.4) Calcd. C 68.55 H 8.63
Found C 68.39 H 8.60

1-[(Benzyloxy)methoxy]-1-phenyl-5-hexen-3-ol (**20f**): Compound **8f** (184 mg, 0.437 mmol) in THF (5 ml), Li-Naphth (2.53 ml, 0.38 M in THF, 0.961 mmol, 2.2 equiv.), 5 min; flash chromatography [petroleum ether/ether (5:1–4:1)] yielded 76.7 mg (56%) as a 57:43 *syn:anti* mixture. – ^{1}H NMR: AB signal (δ_A = 1.96, δ_B = 1.77, J_{AB} = 14.6, in addition split by $J_{A,1}$ = 9.5, $J_{A,3}$ = 2.6, $J_{B,3} \approx 9.5$, $J_{B,1} \approx 3.5$, 2-H_2 [*anti*]), AB signal (δ_A = 1.99, δ_B = 1.84, J_{AB} = 14.6, in addition split by $J_{A,1}$ = $J_{A,3}$ = 9.4, $J_{B,1}$ = 4.7, $J_{B,3}$ = 2.5, 2-H_2 [*syn*]), 2.17–2.34 (m, 4-H_2 [*syn* + *anti*]), 2.39 (d, $J_{OH,3}$ = 4.0, OH [*anti*]*), 3.24 (d, $J_{OH,3}$ = 1.9, OH [*syn*]*), 3.79–3.91 (m, 3-H [*syn*]), 3.93–4.03 (m, 3-H [*anti*]), AB signal (δ_A = 4.74, δ_B = 4.51, J_{AB} = 11.8, 2′-H_2 [*syn*]), AB signal (δ_A = 4.73, δ_B = 4.52, J_{AB} = 11.7, 2′-H_2 [*anti*]), AB signal (δ_A = 4.69, δ_B = 4.60, J_{AB} = 7.0, 1′-H_2 [*syn*]), AB signal (δ_A = 4.75, δ_B = 4.64, J_{AB} = 6.8, 1′-H_2 [*anti*]), 4.92 (dd, $J_{1,2\text{-}H^A}$ = 9.5, $J_{1,2\text{-}H^B}$ = 4.7, 1-H [*syn*]), 5.01 (dd, $J_{1,2\text{-}H^A}$ = 9.5, $J_{1,2\text{-}H^B}$ = 3.4, 1-H [*anti*]), 5.05–5.16 (m, 6-H_{trans}, 6-H_{cis} [*syn* + *anti*]), 5.75–5.89 (m, 5-H [*syn* + *anti*]), 7.25–7.39 (m, 1-C_6H_5 and 2′-C_6H_5 [*syn* + *anti*]); *assignments interchangeable.

$C_{20}H_{24}O_3$ (312.4) Calcd. C 76.89 H 7.74
Found C 76.74 H 7.84

1-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1-phenyl-5-hexen-3-ol (**20g**): Compound **8g** (298 mg, 0.674 mmol) in THF (10 ml), Li-Naphth (3.91 ml, 0.38 M in THF, 1.49 mmol, 2.2 equiv.), 5 min; flash chromatography [petroleum ether/ether (12:1)] yielded 150 mg (66%) as a 76:24 *syn:anti* mixture. Under identical conditions the use of LiDBB furnished **20g** in 66% yield. – ^{1}H NMR: δ = –0.26 and 0.12 and 0.14 {3 s, $(CH_3)_2Si$ [*syn* and silicon grease]}, –0.13 and 0.13 {2 s, $(CH_3)_2Si$ [*anti*]}, 0.82 (s, 1′-CH_3 [*anti*]), 0.86 (s, 1′-CH_3 [*syn*]), 0.84–0.92 (m, 3′-H_3 and 2′-CH_3 [*syn* + *anti*]), 1.56–1.70 (m, 2-H^1 [*anti*], 3′-H [*syn* + *anti*]), AB signal (δ_A = 1.87, δ_B = 1.75, J_{AB} = 14.4, in addition split by $J_{A,1}$ = $J_{A,3}$ = 9.2, $J_{B,1}$ = 4.5, $J_{B,3}$ = 2.4, 2-H_2 [*syn*]), superimposed by 1.78 to 1.83 (m, 2-H^2, [*anti*]), 2.14–2.31 (m, 4-H_2 [*syn* + *anti*]), 3.08 (d, $J_{OH,3} \approx 2.2$, OH [*anti*]), 3.33 (s, OH [*syn*]), 3.78–3.87 (m, 3-H [*syn* + *anti*]), 4.86 (dd, $J_{1,2\text{-}H^A}$ = 9.2, $J_{1,2\text{-}H^B}$ = 4.5, 1-H [*syn*]), 5.02–5.12 (m, 1-H [*anti*], 6-H_{cis}, 6-H_{trans} [*syn* + *anti*]), 5.69–5.88 (m, 5-H [*syn* + *anti*]), 7.22–7.33 (m, 1-C_6H_5).

$C_{20}H_{34}O_2Si$ (334.6) Calcd. C 71.80 H 10.24
Found C 71.76 H 9.99

1-Phenyl-1-[(triisopropylsilyl)oxy]-5-hexen-3-ol (**20h**): Compound **8h** (169 mg, 0.369 mmol) in THF (6 ml), Li-Naphth (2.14 ml, 0.38 M in THF, 0.813 mmol, 2.2 equiv.), 5 min; flash chromatography [petroleum ether/ether (18:1)] yielded 75.5 mg (59%) as a 55:45 mixture of isomers. – ^{1}H NMR: δ = 0.91–1.15 (m, *i*Pr_3Si [major + minor]), AB signal (δ_A = 1.99, δ_B = 1.77, J_{AB} = 14.3, in addition split by $J_{A,3}$ = 10.0, $J_{A,1}$ = 4.3, $J_{B,1}$ = 4.5, $J_{B,3}$ = 2.3, 2-H_2 [minor]), superimposed by AB signal (δ_A = 1.94, δ_B = 1.78, J_{AB} = 14.2, in addition split by $J_{A,1}$ = 9.9, $J_{A,3}$ = 7.4, $J_{B,3}$ = 6.4, $J_{B,1}$ = 2.2, 2-H_2 [major]), 2.08–2.24 (m, 4-H_2 [major + minor]), 2.73 and 3.61 (2 s, OH), 3.64–3.72 (m, 3-H [major]), 3.74–3.83 (m, 3-H [minor]), 4.97–5.10 (m, 1-H [major], 6-H_{trans} and 6-H_{cis} [major + minor]), 5.22 (dd, $J_{1,2\text{-}H^A}$ = $J_{1,2\text{-}H^B}$ = 4.3, 1-H [minor]), 5.73 and 5.76 (2 m_c, 5-H [major + minor]), 7.22–7.38 (m, 1-C_6H_5).

$C_{21}H_{36}O_2Si$ (348.6) Calcd. C 72.36 H 10.41
Found C 72.13 H 10.40

1-(Benzyloxy)-4,4-dimethyl-1-phenyl-5-hexen-3-ol (**21**): Compound **16a** (235 mg, 0.561 mmol) in THF (8 ml), Li-Naphth (3.63 ml, 0.34 M in THF, 1.23 mmol, 2.2 equiv.), 60 min; flash chromatography [petroleum ether/ether (9:1)] yielded *syn*-**21** (58.2 mg, 33%) and *anti*-**21** (37.6 mg, 22%). – ^{1}H NMR: *syn*-**21**: δ = 0.98 and 0.99 [2 s, 4-$(CH_3)_2$], AB signal (δ_A = 1.85, δ_B = 1.79, J_{AB} = 14.6, in addition split by $J_{A,3} \approx J_{A,1} \approx 9.0$, $J_{B,1}$ = 4.8, $J_{B,3} \approx 2.6$, 2-H_2), 3.50 (dm_c, $J_{3,2\text{-}H^A} \approx 10$, 3-H), 3.72 (d, $J_{OH,3}$ = 1.4, OH), AB signal (δ_A = 4.41, δ_B = 4.28, J_{AB} = 11.3, 1′-H_2), 4.58 (dd, $J_{1,2\text{-}H^A}$ = 8.9, $J_{1,2\text{-}H^B}$ = 4.7, 1-H), 4.96 (dd, $J_{trans\text{-}6\text{-}H,5}$ = 17.5, J_{gem} = 1.4, 6-H_{trans}), 4.99 (dd, $J_{cis\text{-}6\text{-}H,5}$ = 10.8, J_{gem} = 1.3, 6-H_{cis}), 5.83 (dd, $J_{5,trans\text{-}6\text{-}H}$ = 17.4, $J_{5,cis\text{-}6\text{-}H}$ = 10.9, 5-H), 7.24–7.42 (m, 1-C_6H_5, 1′-C_6H_5); *anti*-**21**: δ = 0.96 and 0.99 [2 s, 4-$(CH_3)_2$], AB signal (δ_A = 1.91, δ_B = 1.62, J_{AB} = 14.4, in addition split by $J_{A,1}$ = 9.0, $J_{A,3}$ = 1.8, $J_{B,3}$ = 10.6, $J_{B,1}$ = 3.1, 2-H_2), 2.02 (br. d, $J_{OH,3} \approx 3$, OH), 3.67 (dm_c, $J_{3,2\text{-}H^A} \approx 10$, 3-H), AB signal ($\delta_A$ = 4.51, δ_B = 4.30, J_{AB} = 11.8, 1′-H_2), 4.68 (dd, $J_{1,2\text{-}H^A}$ = 9.0, $J_{1,2\text{-}H^B}$ = 3.1, 1-H), 5.00 (dd, $J_{trans\text{-}6\text{-}H,5}$ = 17.4, J_{gem} = 1.4, 6-H_{trans}), 5.03 (dd, $J_{cis\text{-}6\text{-}H,5}$ = 10.8, J_{gem} = 1.4, 6-H_{cis}), 5.80 (dd, $J_{5,trans\text{-}6\text{-}H}$ = 17.5, $J_{5,cis\text{-}6\text{-}H}$ = 10.9, 5-H), 7.24–7.42 (m, 1-C_6H_5, 1′-C_6H_5).

$C_{21}H_{26}O_2$ (310.4) Calcd. C 81.25 H 8.44
Found C 81.17 H 8.21

Stereochemical Correlations

1-Phenyl-5-hexen-1,3-diol (**20a**). – a) *From* **20g**: Compound **20g** (95.2 mg, 0.285 mmol, 76:24 *syn:anti* mixture) was stirred with $Bu_4NF \cdot 3\ H_2O$ (286 mg, 0.856 mmol, 3.0 equiv.) in THF (2 ml) at room temp. for 6 h. Removal of the solvent followed by flash chromatography [petroleum ether/ether (1:2)] of the residue furnished 39.5 mg (72%) as a 76:24 *syn:anti* mixture.

b) *From* **20c**: Compound **20c** (157 mg, 0.555 mmol, 64:36 *syn:anti* mixture) in THF (10 ml) was treated at –78°C with Li-Naphth (5.62 ml, 0.38 M in THF, 2.14 mmol, 3.8 equiv.) for 10 min. Satd. aqueous NH_4Cl solution (5 ml) and H_2O (10 ml) were added. Extraction with ether (3 × 30 ml) and flash chromatography [petroleum ether/ether (1:2)] of the crude product obtained by evaporation of the solvent from the combined extracts yielded 77.8 mg (73%) as a 66:34 *syn:anti* mixture.

c) *From* **20d**: Compound **20d** (124 mg, 0.286 mmol, 36:64 *syn:anti* mixture) and F_3CCO_2H (0.05 ml, 0.65 mmol, 2.3 equiv.) in CH_2Cl_2 (2 ml) were stirred at room temp. for 30 min. Addition of aqueous $NaHCO_3$ solution, extraction with ether, and flash chromatography [petroleum ether/ether (1:2)] of the residue obtained by evaporation of the solvent from the extract furnished 41.3 mg (75%) as a 36:64 *syn:anti* mixture.

4-Phenyl-6-(2-propenyl)-1,3-dioxan (**22**). – a) *From* **20e**: Compound **20e** (122 mg, 0.434 mmol, 63:37 *syn:anti* mixture) in CH_2Cl_2 (4 ml) was treated at room temp. for 45 min with a catalytic amount of HBF_4 (30% in Et_2O). Addition of solid Na_2CO_3 (0.2 g) and filtration of the mixture followed by flash chromatography [petroleum ether/ether (40:1–25:1)] of the concentrated filtrate furnished 64.5 mg (73%) as a 76:24 *syn:anti* mixture. – ^{1}H NMR: AB signal (δ_A = 1.82, δ_B = 1.70, J_{AB} = 13.3, in addition split by $J_{A,4}$ = $J_{A,6}$ = 2.8, $J_{B,4}$ = $J_{B,6}$ = 11.0, 5-H_2 [*syn*]), 1.98 (ddd, J_{gem} = 14.0, J_1 = 6.5, J_2 = 4.5, 5-H^1 [*anti*]), 2.22–2.48 (m, 5-H^2 [*anti*], 1′-H^1 [*syn* + *anti*], 1′-H^2 [*syn*]), 2.61 (br. ddd, $J_{gem} \approx 14$, $J_{1',6} \approx J_{1',2'} \approx 7$, 1′-$H^2$ [*anti*]), 3.74–3.86 (m, 6-H [*syn*]), 3.92–4.02 (m, 6-

H [*anti*]), 4.63 (dd, $J_{4,5\text{-}H^B}$ = 11.1, $J_{4,5\text{-}H^A}$ = 2.7, 4-H [*syn*]), AB signal (δ_A = 5.03, δ_B = 4.91, J_{AB} = 6.6, 2-H_2 [*anti*]), AB signal {δ_A = 5.26, δ_B = 4.91(!), J_{AB} = 6.4, 2-H_2 [*syn*]}, 5.04–5.20 (m, 3′-H_{trans}, 3′-H_{cis}, 4-H [*anti*]), 5.76–5.92 (m, 2′-H), 7.27–7.40 (m, 4-C_6H_5).

$C_{13}H_{16}O_2$ (204.3) Calcd. C 76.44 H 7.89
Found C 76.51 H 7.68

b) *From* **20a**: During 60 min, **20a** (73.4 mg, 0.382 mmol, 68:34 *syn:anti* mixture) in CH_2Br_2 (10 ml) was added dropwise to a refluxing solution of benzyltriethylammonium chloride (26.2 mg, 0.115 mmol, 0.3 equiv.) in 50% aqueous KOH solution (15 ml). After 30 min, the organic layer was separated and dried with $MgSO_4$. Flash chromatography [petroleum ether/ether (40:1–1:1)] of the residue obtained by evaporation of the solvent furnished 63.2 mg (81%) as a 68:32 *syn:anti* mixture along with recovered **20a** (10.1 mg, 13%).

c) *From* **20f**: Under the conditions described for **20a** → **22**, **20f** (52.6 mg, 0.168 mmol, 57:43 *syn:anti* mixture) yielded 13.2 mg (38%) as a 82:18 *syn:anti* mixture.

Retro-Brook Rearrangements

1-Phenyl-3-[(2-propenyl)oxy]-3-(trimethylsilyl)-1-propanol (**23i**): Compound **8i** (255 mg, 0.684 mmol) in THF (8 ml), Li-Naphth (4.42 ml, 0.34 M in THF, 1.50 mmol, 2.2 equiv.), 5 min; flash chromatography [petroleum ether/ether (8:1)] yielded 94.9 mg (52%) of *anti*-**23i** and 52.4 mg (29%) of *syn*-**23i**. – ^{1}H NMR: *syn*-**23i**: δ = 0.06 [s, $(CH_3)_3Si$], AB signal (δ_A = 2.03, δ_B = 1.75, J_{AB} = 14.8, in addition split by $J_{A,3}$ = 11.8, $J_{A,1}$ = 9.1, $J_{B,3}$ = $J_{B,1}$ = 3.0, 2-H_2), 3.42 (dd, $J_{3,2\text{-}H^A}$ = 11.8, $J_{3,2\text{-}H^B}$ = 2.9, 3-H), 3.96 (d, $J_{OH,1}$ = 1.2, OH), 4.01 (ddm$_c$, J_{gem} ≈ 12, $J_{1'\text{-}H^1,2'}$ ≈ 6, J_{allyl} ≈ 1–2, 1′-H^1), 4.09 (ddm$_c$, J_{gem} ≈ 12, $J_{1'\text{-}H^2,2'}$ ≈ 5, J_{allyl} ≈ 1–2, 1′-H^2), 4.92 (br. dd, $J_{1,2\text{-}H^A}$ = 9.0, $J_{1,2\text{-}H^B}$ ≈ 3, 1-H), 5.21 (dm$_c$, $J_{cis\text{-}3'\text{-}H,2'}$ ≈ 10, 3′-H_{cis}), 5.31 (ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.2, J_{gem} = J_{allyl} = 1.6, 3′-H_{trans}), 5.96 (dddd, $J_{2',trans\text{-}3'\text{-}H}$ = 17.2, $J_{2',cis\text{-}3'\text{-}H}$ = 10.4, $J_{2',1'\text{-}H^1}$ ≈ $J_{2',1'\text{-}H^2}$ ≈ 5–6, 2′-H), 7.24–7.41 (m, 1-C_6H_5); *anti*-**23i**: δ = 0.11 [s, $(CH_3)_3Si$], 1.86–2.03 (m, 2-H_2), 3.37 (d, $J_{OH,1}$ = 3.1, OH), 3.40 (dd, $J_{3,2}$ = 8.1, $J'_{3,2}$ = 4.1, 3-H), AB signal (δ_A = 4.09, δ_B = 4.00, J_{AB} = 12.4, in addition split by $J_{A,2'}$ = 5.7, J_{allyl} ≈ 1.5, $J_{B,2'}$ = 5.7, J_{allyl} ≈ 1.5, 1′-H_2), 5.00 (ddd, $J_{1,2}$ = 8.8, $J_{1,OH}$ = $J_{1,2}$ = 3.3, 1-H), 5.19 (ddt, $J_{cis\text{-}3'\text{-}H,2'}$ = 10.4, J_{gem} = 1.6, J_{allyl} ≈ 1, 3′-H_{cis}), 5.29 (ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.2, J_{gem} = 1.6, J_{allyl} ≈ 1, 3′-H_{trans}), 5.94 (dddd, $J_{2',trans\text{-}3'\text{-}H}$ = 17.2, $J_{2',cis\text{-}3'\text{-}H}$ = 10.3, $J_{2',1'\text{-}H^A}$ = $J_{2',1'\text{-}H^B}$ = 5.7, 2′-H), 7.23–7.40 (m, 1-C_6H_5).

$C_{15}H_{24}O_2Si$ (264.4) Calcd. C 68.13 H 9.15
Found C 68.14 H 8.97

1-Phenyl-3-[(2-propenyl)oxy]-3-(triethylsilyl)-1-propanol (**23j**) *and Wittig Rearrangement Product 1-Phenyl-1-[(triethylsilyl)oxy]-5-hexen-3-ol:* **8j** (222 mg, 0.536 mmol) in THF (8 ml), Li-Naphth (3.47 ml, 0.34 M in THF, 1.18 mmol, 2.2 equiv.), 5 min; flash chromatography [petroleum ether/ether (11:1–8:1)] furnished *syn*-**23j** (44.1 mg, 27%) and a mixture of *anti*-**23j** (55.5 mg, 34%) and 1-phenyl-1-[(triethylsilyl)oxy]-5-hexen-3-ol (25.0 mg, 15%). – ^{1}H NMR: *syn*-**23j**: δ = 0.56–0.64 (m, 3 CH_3CH_2Si), 0.97 (t, $J_{2'',1''}$ = 7.9, 3 CH_3CH_2Si), AB signal (δ_A = 2.11, δ_B = 1.75, J_{AB} = 14.8, in addition split by $J_{A,3}$ = 12.0, $J_{A,1}$ = 9.0, $J_{B,3}$ = $J_{B,1}$ = 3.1, 2-H_2), 3.54 (dd, $J_{3,2\text{-}H^A}$ = 12.0, $J_{3,2\text{-}H^B}$ = 2.9, 3-H), 3.97 (br. s, OH), AB signal (δ_A = 4.08, δ_B = 4.02, J_{AB} = 12.2, in addition split by $J_{A,2'}$ = 5.1, $J_{A,allyl}$ = 1.4, $J_{B,2'}$ = 5.8, $J_{B,allyl}$ ≈ 1.5, 1′-H_2), 4.91 (dd, $J_{1,2\text{-}H^A}$ = 8.9, $J_{1,2\text{-}H^B}$ = 3.3, 1-H), 5.19 (ddt, $J_{cis\text{-}3'\text{-}H,2'}$ = 10.5, J_{gem} = 1.6, J_{allyl} = 1.4, 3′-H_{cis}), 5.31 (ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.2, J_{gem} = 1.6, J_{allyl} = 1.7, 3′-H_{trans}), 5.95 (dddd, $J_{2',trans\text{-}3'\text{-}H}$ ≈ 16–17, $J_{2',cis\text{-}3'\text{-}H}$ = 10.6, $J_{2',1'\text{-}H^A}$ ≈ $J_{2',1'\text{-}H^B}$ ≈ 5–6, 2′-H), 7.23–7.40 (m, 1-C_6H_5); *anti*-**23j**: δ = 0.61–0.72 (m, 3 CH_3CH_2Si), 0.99 (t, $J_{2',1''}$ = 7.9, 3 CH_3CH_2Si), 1.75–2.06 (m, 2-H_2), 3.41 (s, OH), 3.55 (dd, $J_{3,2}$ = 7.8, $J'_{3,2}$ = 4.0, 3-H), AB signal (δ_A = 4.10, δ_B = 3.97, J_{AB} = 12.5, in addition split by $J_{A,2'}$ = 5.6, $J_{B,2'}$ = 5.5, J_{allyl} ≈ 1.5, 1′-H_2), 4.88 (dd, $J_{1,2}$ = 9.6, $J'_{1,2}$ = 4.2, 1-H), 5.18 (ddt, $J_{cis\text{-}3'\text{-}H,2'}$ = 10.4, J_{gem} ≈ J_{allyl} ≈ 1.6, 3′-H_{cis}), 5.29 (ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.2, J_{gem} = 1.7, J_{allyl} ≈ 1.5, 3′-H_{trans}), 5.94 (ddt, $J_{2',trans\text{-}3'\text{-}H}$ = 17.2, $J_{2',cis\text{-}3'\text{-}H}$ = 10.4, $J_{2',1'\text{-}H^A}$ = $J_{2',1'\text{-}H^B}$ = 5.6, 2′-H), 7.22–7.40 (m, 1-C_6H_5); 1-Phenyl-1-[(triethylsilyl)oxy]-5-hexen-3-ol: δ = 0.40–0.60 (m, 3 CH_3CH_2Si), 0.87 and 0.90 (2 t, $J_{2',1'}$ = 7.9, 3 CH_3CH_2Si), 1.75–2.06 (m, 2-H_2), 2.15–2.29 (m, 4-H_2), 3.70 (s, OH), 3.83–3.92 (m, 3-H), 3.19–4.25 (m, 1-H), 4.96–5.12 (m, 6-H_{cis}, 6-H_{trans}), 5.74–5.87 (m, 2-H), resonances of C_6H_5 superimposed by *anti*-**23j**.

$C_{18}H_{30}O_2Si$ (306.5) Calcd. C 70.53 H 9.86
Found C 70.59 H 9.91

3-(tert-Butyldiphenylsilyl)-1-phenyl-[(2-propenyl)oxy]-1-propanol (**23k**): Compound **8k** (367 mg, 0.681 mmol) in THF (10 ml), Li-Naphth (4.30 ml, 0.38 M in THF, 1.63 mmol, 2.4 equiv.), 10 min; flash chromatography [petroleum ether/ether (10:1)] yielded 226 mg (77%) as a 50:50 *syn:anti* mixture. – ^{1}H NMR: δ = 1.11 and 1.13 (2 s, 2 *t*-C_4H_9*), 1.92–2.28 (m, 2-H_2*), 2.43 and 2.61 (2 m$_c$, 2 OH*), 3.86–3.99 (m, 1′-H^1), 4.14–4.33 (m, 1′-H^2, 3-H), 4.75 (dm$_c$, $J_{1,2}$ ≈ 11, 1-H*), 5.15 and 5.16 (2 ddt, $J_{cis\text{-}3'\text{-}H,2'}$ = 10.6, J_{gem} ≈ J_{allyl} ≈ 1.6, 3′-H^*_{cis}), 5.27 and 5.28 (2 ddt, $J_{trans\text{-}3'\text{-}H,2'}$ = 17.3, J_{gem} ≈ J_{allyl} ≈ 1.6, 3′-H^*_{trans}), 5.93 (2 m$_c$, 2′-H*), 7.03–7.44 (m, 1-C_6H_5, 2 *m*-, *p*-Ph_2Si), 7.58–7.80 (m, 2 *o*-Ph_2Si); *resonance of a single but unidentified diastereomer.

$C_{28}H_{34}O_2Si$ (430.7) Calcd. C 78.09 H 7.96
Found C 77.93 H 8.22

3-[Dimethyl(1,1,2-trimethylpropyl)silyl]-3-[(3-methyl)-2-butenyl)oxy]-1-phenylpropanol (**24**): Compound **16b** 8223 mg, 0.474 mmol) in THF (5 ml), Li-Naphth (2.98 ml, 0.35 M in THF, 1.04 mmol, 2.2 equiv.), 30 min; flash chromatography [petroleum ether/ether (20:1)] yielded *anti*-**24** (84.9 mg, 49%) and *syn*-**24** (44.1 mg, 26%). – ^{1}H NMR: *syn*-**24**: δ = 0.05 and 0.11 [2 s, $(CH_3)_2Si$], 0.80–0.87 [m, 1″-$(CH_3)_2$, 2″-CH_3, 3″-H_3), 1.62 (qq, $J_{2'',H,3'',H}$ = $J_{2'',H,2'',Me}$ = 6.8, 2″-H), 1.70 and 1.75 (2 s, 3′-CH_3, 4′-H_3), AB signal (δ_A = 2.09, δ_B = 1.82, J_{AB} = 15.0, in addition split by $J_{A,3}$ = 11.7, $J_{A,1}$ = 8.8, $J_{B,1}$ = $J_{B,3}$ = 3.2, 2-H_2), 3.48 (dd, $J_{3,2\text{-}H^A}$ = 11.5, $J_{3,2\text{-}H^B}$ = 3.0, 3-H), 4.03 (d, $J_{1',2'}$ = 7.0, 1′-H_2), 4.91 (dd, $J_{1,2\text{-}H^A}$ = 8.7, $J_{1,2\text{-}H^B}$ = 3.5, 1-H), 5.39 (tm$_c$, $J_{2',1'}$ = 7.0, 2′-H), 7.23–7.39 (m, 1-C_6H_5); *anti*-**24**: δ = 0.11 and 0.19 [2 s, $(CH_3)_2Si$], 0.81–1.00 (m, 1″-$(CH_3)_2$, 2″-CH_3, 3″-H_3), 1.67 (qq, $J_{2'',H,3'',H}$ = $J_{2'',H,2'',Me}$ = 6.9, 2″-H), 1.71 and 1.76 (2 s, 3-CH_3, 4-CH_3), AB signal (δ_A = 2.09, δ_B = 1.89, J_{AB} = 15.1, in addition split by $J_{A,1}$ = 9.9, $J_{A,3}$ = 3.7, $J_{B,3}$ = 7.4, $J_{B,1}$ = 2.5, 2-H_2), 3.56 (dd, $J_{3,2\text{-}H^B}$ = 7.4, $J_{3,2\text{-}H^A}$ = 3.7, 3-H), AB signal (δ_A = 4.14, δ_B = 3.95, J_{AB} = 11.2, in addition split by $J_{A,2'}$ = 7.2, $J_{B,2'}$ = 6.8, 1′-H_2), 5.03 (dd, $J_{1,2\text{-}H^A}$ = 9.9, $J_{1,2\text{-}H^B}$ = 2.2, 1-H), 5.38 (tm$_c$, $J_{2',1'}$ = 7.1, 2′-H), 7.22–7.60 (m, 1-C_6H_5).

$C_{22}H_{38}O_2Si$ (362.6) Calcd. C 72.87 H 10.56
Found C 72.40 H 9.77

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[18] In the case of O,S-acetal **8a** 3.3 eq. of Li-Naphth were used in order to deprotonate also the OH group.

[19] When we added the O,S-acetal to Li-Naphth, rearrangement products **20c,d**, and **f** lost their Bzl, Ph_3C, and BOM protecting groups to some extent to deliver **20a** as a side product. Combining the reagents in the opposite order minimized the concurrent formation of **20a** (<5%, <5%, and <10% yield, respectively).

[20] Accordingly, in a preparative manner, one would convert aldehydes of type **14** into *syn*- or *anti*-configurated homoallylic alcohols of type **20** rather by reagent-controlled [cf., for instance, U. S. Racherla, H. C. Brown, *J. Org. Chem.* **1991**, *56*, 401–404 and work by the Hoffmann, Reetz, Roush, Masamune, and Corey groups cited therein] or – into *anti* alcohols of type **20** – by chelation-controlled [cf. M. T. Reetz, *Angew. Chem.* **1984**, *96*, 542–555; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 556–569] addition of allyl nucleophiles.

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[32] *Note added in proof:* For experimental evidence which appeared after submission of our manuscript, see: E. J. Verner und T. Cohen, *J. Am. Chem. Soc.* **1992**, *114*, 375–377.

[16/92]

CAS Registry Numbers

8a (*syn* isomer): 140854-33-7 / **8a** (*anti* isomer): 140854-32-6 / **8b** (*syn* isomer): 140854-34-8 / **8b** (*anti* isomer): 140854-35-9 / **8c** (*syn* isomer): 140854-36-0 / **8c** (*anti* isomer): 140854-37-1 / **8d** (*syn* isomer): 140854-38-2 / **8d** (*anti* isomer): 140854-39-3 / **8e** (*syn* isomer): 140854-40-6 / **8e** (*anti* isomer): 140854-41-7 / **8f** (*syn* isomer): 140854-42-8 / **8f** (*anti* isomer): 140854-43-9 / **8g** (*syn* isomer): 140854-44-0 / **8g** (*anti* isomer): 140854-45-1 / **8h** (*syn* isomer): 140854-46-2 / **8h** (*anti* isomer): 140854-47-3 / **8i** (*syn* isomer): 140854-48-4 / **8i** (*anti* isomer): 140854-49-5 / **8j** (*syn* isomer): 140854-50-8 / **8j** (*anti* isomer): 140854-51-9 / **8k** (*syn* isomer): 140854-52-0 / **8k** (*anti* isomer): 140854-53-1 / **11** (2*R**,4*S**,6*R**): 140854-54-2 / **11** (2*R**,4*S**,6*S*): 140924-56-7 / **12**: 936-58-3 / **13a**: 137438-51-8 / **13b**: 140854-55-3 / **14a**: 132816-01-4 / **14b**: 140854-56-4 / **15**: 71821-61-9 / **16a** (*syn* isomer): 132816-14-9 / **16a** (*anti* isomer): 132816-15-0 / **16b** (*syn* isomer): 140854-57-5 / **16b** (*anti* isomer): 140854-58-6 / **17** (*syn* isomer): 140854-59-7 / **17** (*anti* isomer): 140854-60-0 / **18**: 140854-61-1 / **19**: 10276-04-7 / **20a** (*syn* isomer): 140854-62-2 / **20a** (*anti* isomer): 140854-63-3 / **20b** (*syn* isomer): 140854-64-4 / **20b** (*anti* isomer): 140854-65-5 / **20c** (*syn* isomer): 140854-66-6 / **20c** (*anti* isomer): 140854-67-7 / **20d** (*syn* isomer): 140854-68-8 / **20d** (*anti* isomer): 140854-69-9 / **20e** (*syn* isomer): 140854-70-2 / **20e** (*anti* isomer): 140854-71-3 / **20f** (*syn* isomer): 140854-72-4 / **20f** (*anti* isomer): 140854-73-5 / **20g** (*syn* isomer): 140854-74-6 / **20g** (*anti* isomer): 140854-75-7 / **20h** (*syn* isomer): 140854-76-8 / **20h** (*anti* isomer): 140854-77-9 / **21** (*syn* isomer): 140854-78-0 / **21** (*anti* isomer): 140854-79-1 / **22a** (*syn* isomer): 140854-80-4 / **22a** (*anti* isomer): 140854-81-5 / **23i** (*syn* isomer): 140854-83-7 / **23i** (*anti* isomer): 140854-82-6 / **23j** (*syn* isomer): 140854-84-8 / **23j** (*anti* isomer): 140854-85-9 / **23k** (*syn* isomer): 140854-86-0 / **23k** (*anti* isomer): 140854-87-1 / **24** (*syn* isomer): 140854-88-2 / **24** (*anti* isomer): 140854-89-3 / MEM-Cl: 3970-21-6 / BOM-Cl: 3587-60-8 / Li-Naphth: 7308-67-0 / *t*$BuPh_2SiCl$: 58479-61-1 / Me_3SiSph: 4551-15-9 / Ph_3CBF_4: 341-02-6 / *i*Pr_3SiCl: 13154-24-0 / Et_3SiCl: 994-30-9 / benzaldehyde: 100-52-7 / thiophenol: 108-98-5 / chlorodimethyl(1,1,2-trimethylpropyl)silane: 67373-56-2 / 3-methyl-2-buten-1-ol: 556-82-1 / trimethylsilyl triflate: 27607-77-8 / allyl vinyl ether: 3917-15-5